

Supporting Information

Functionalization of α -hydroxyphosphonates as a convenient route to *N*-tosyl- α -aminophosphonates

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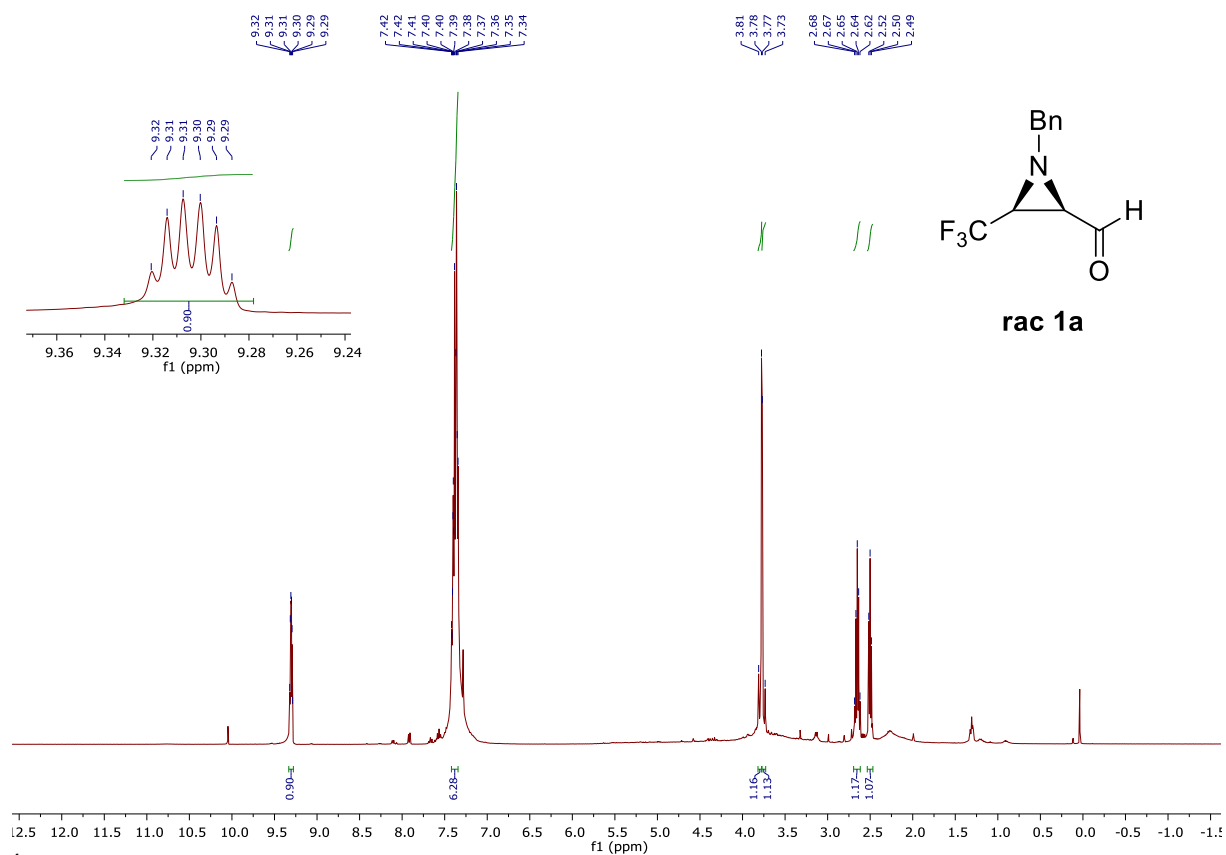
^b Centre for Advanced Technologies, Adam Mickiewicz University in Poznań, Umultowska 89c, 61-614 Poznań, Poland

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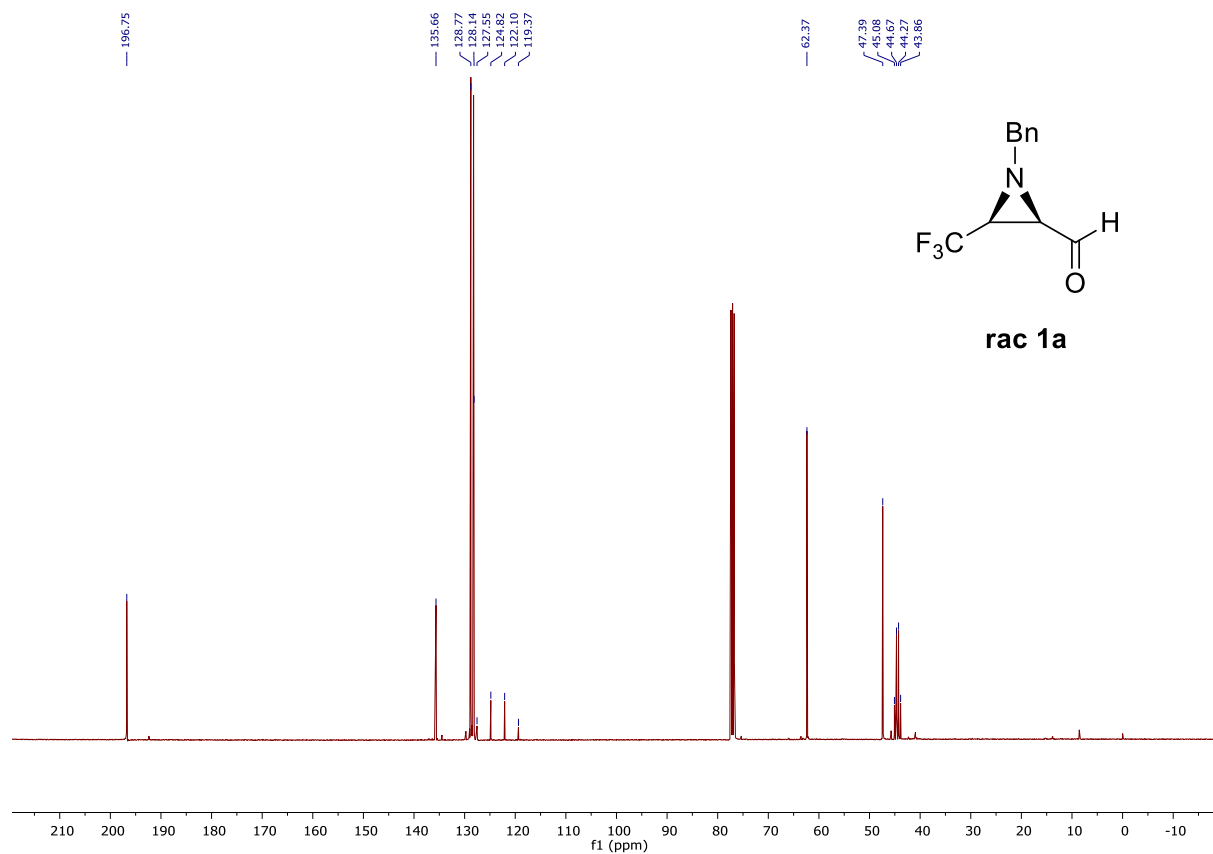
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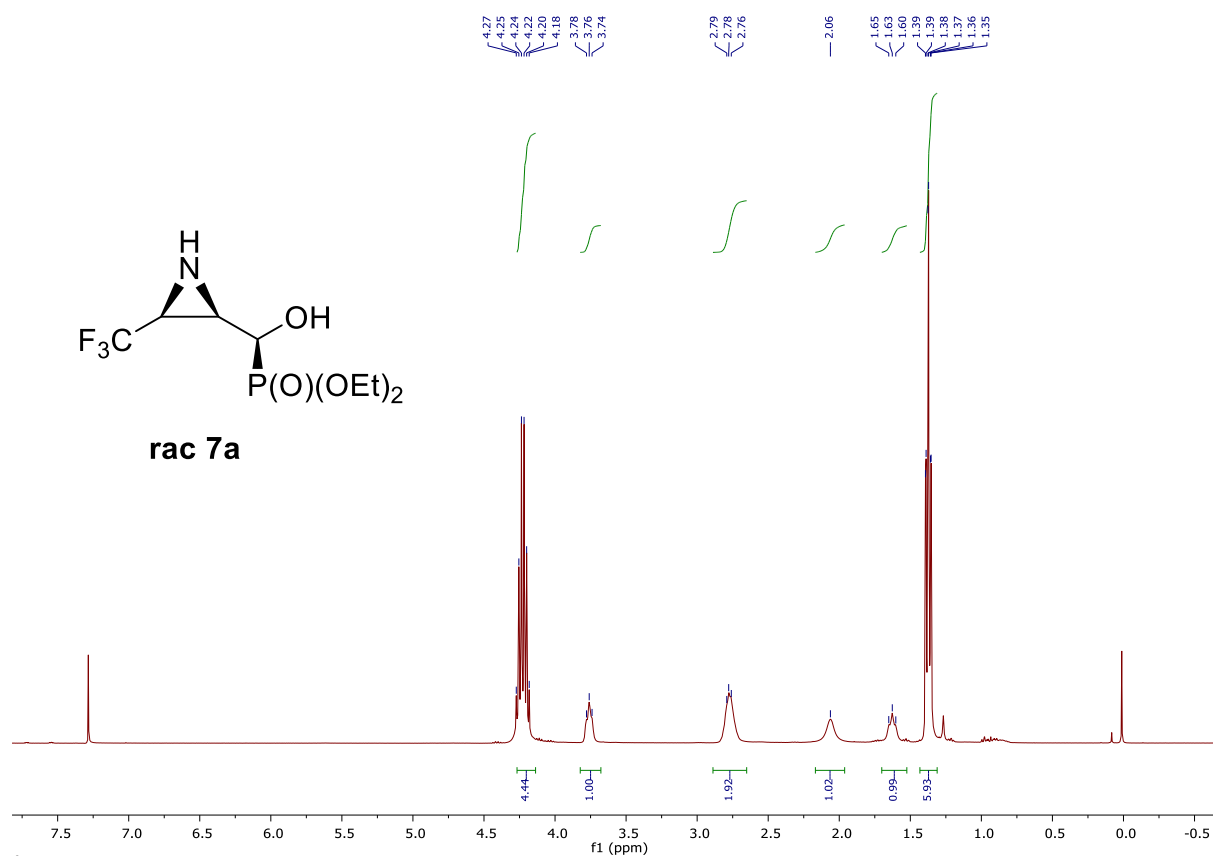
1. ^1H , ^{13}C , ^{19}F , ^{31}P and 2D NMR Spectra of Compounds



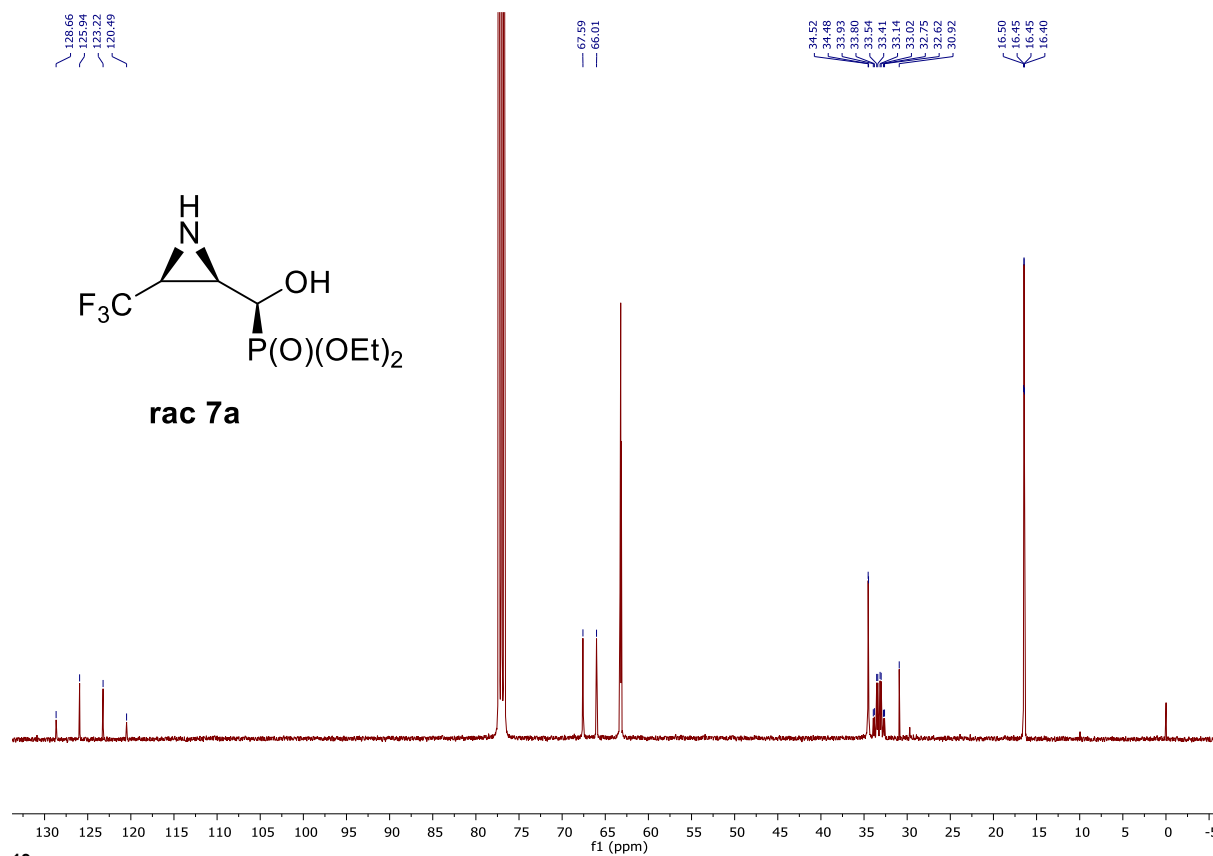
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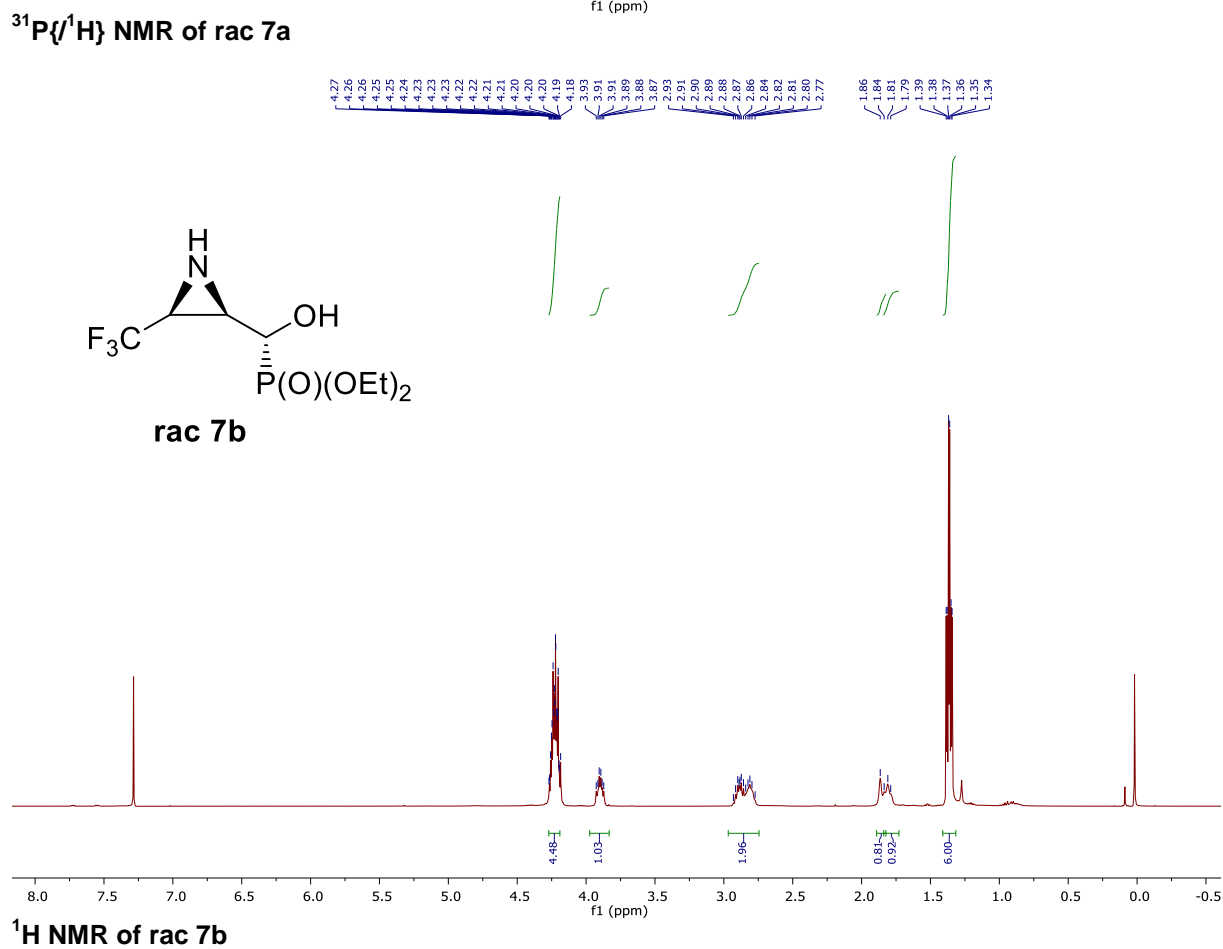
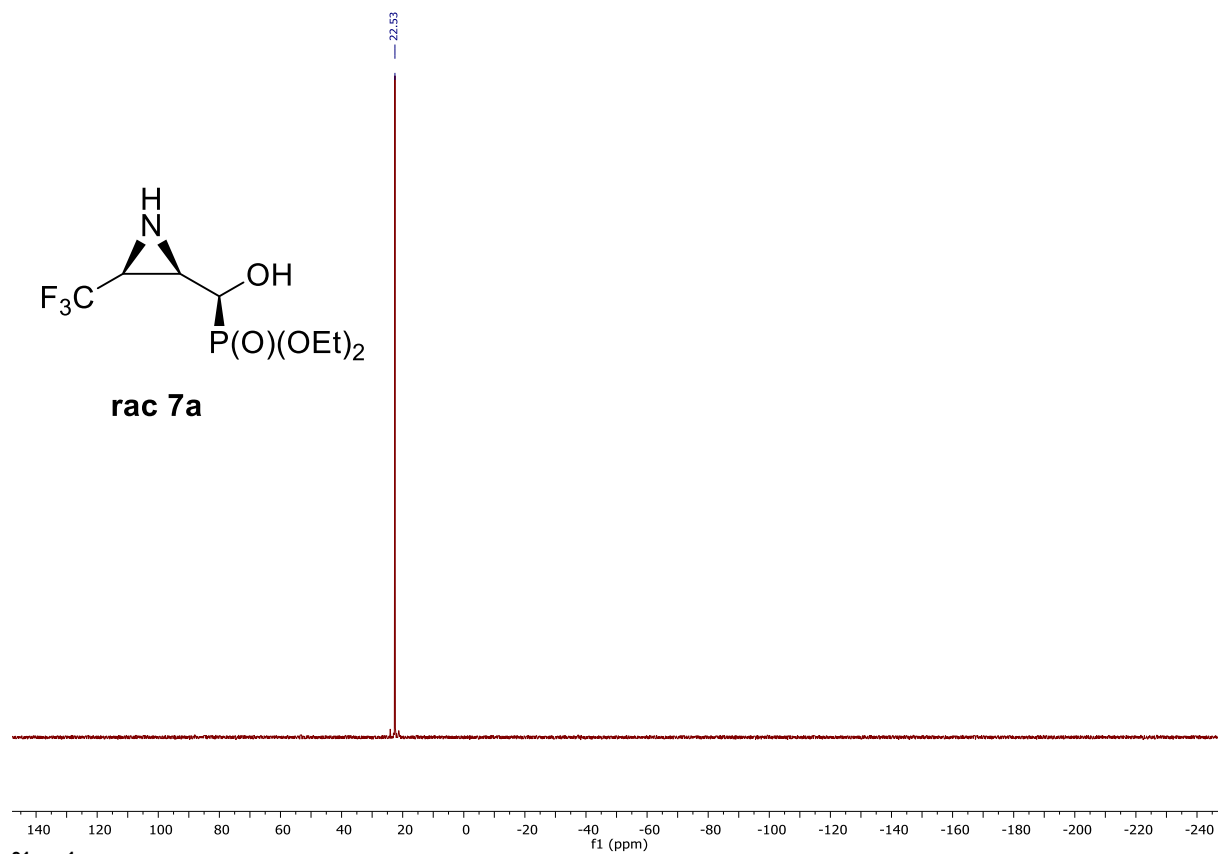
¹³C NMR of rac 1a

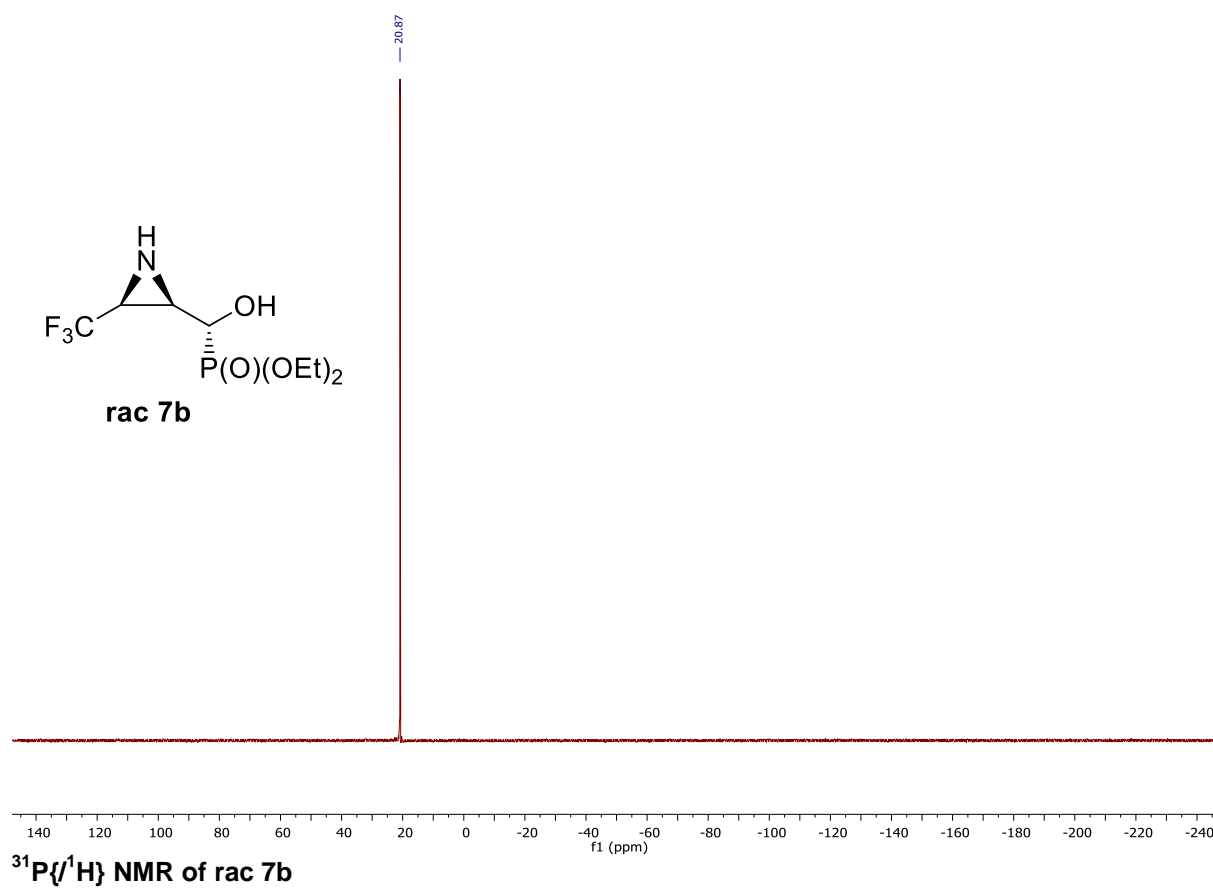
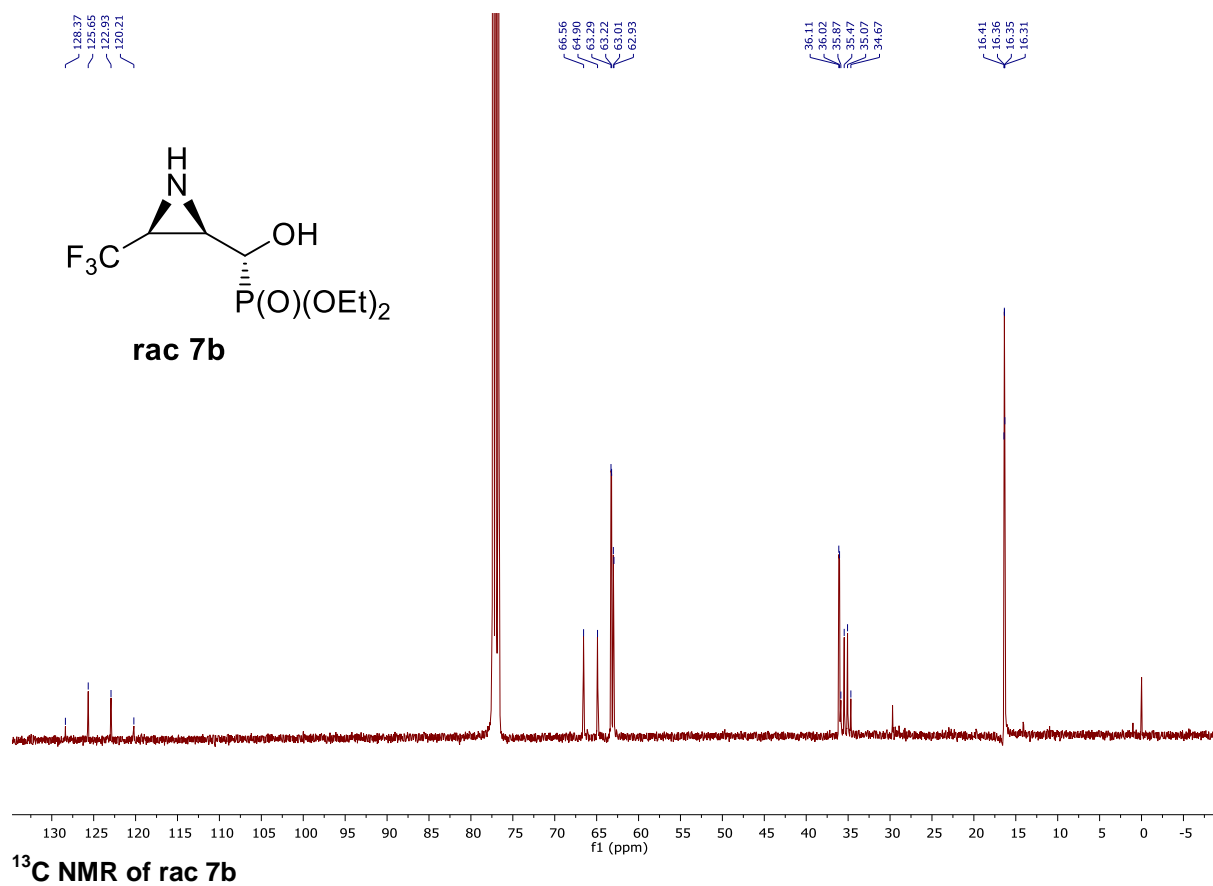


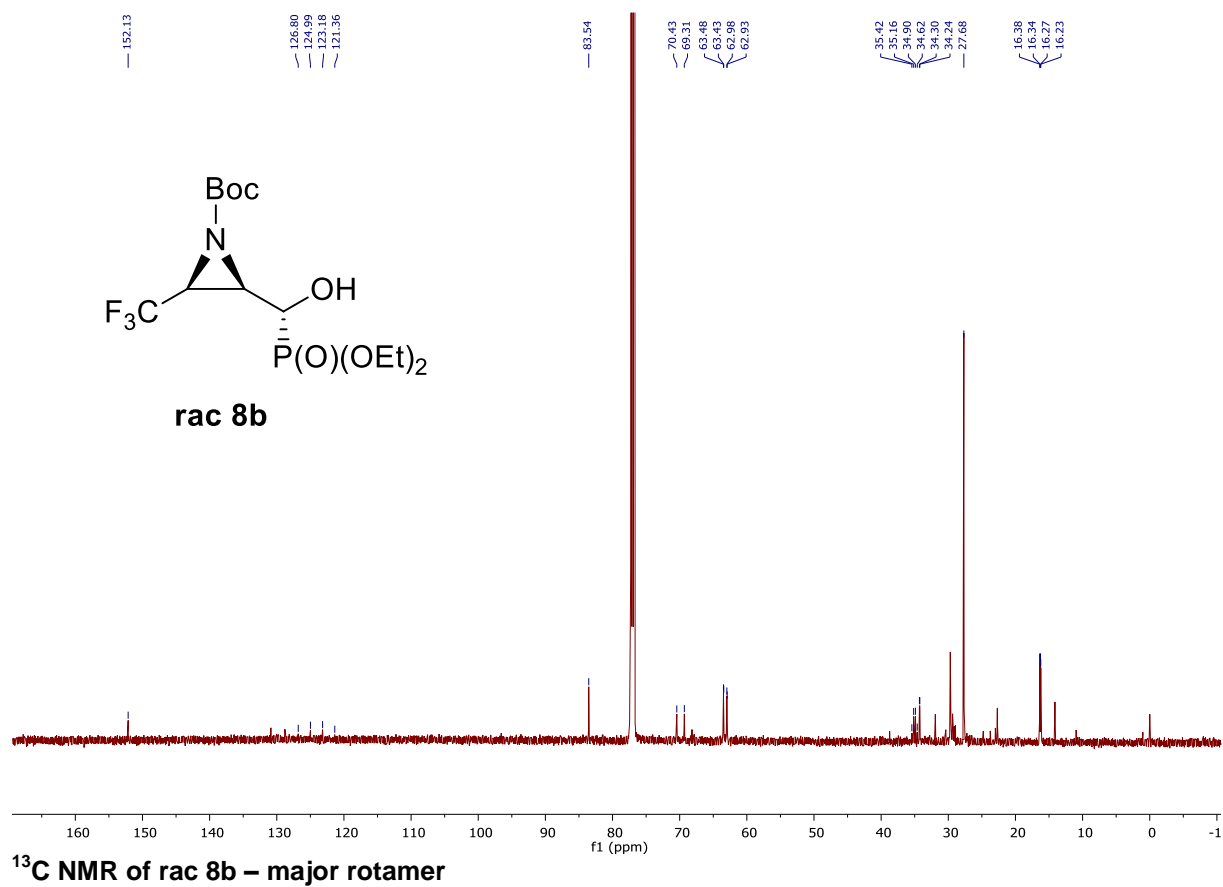
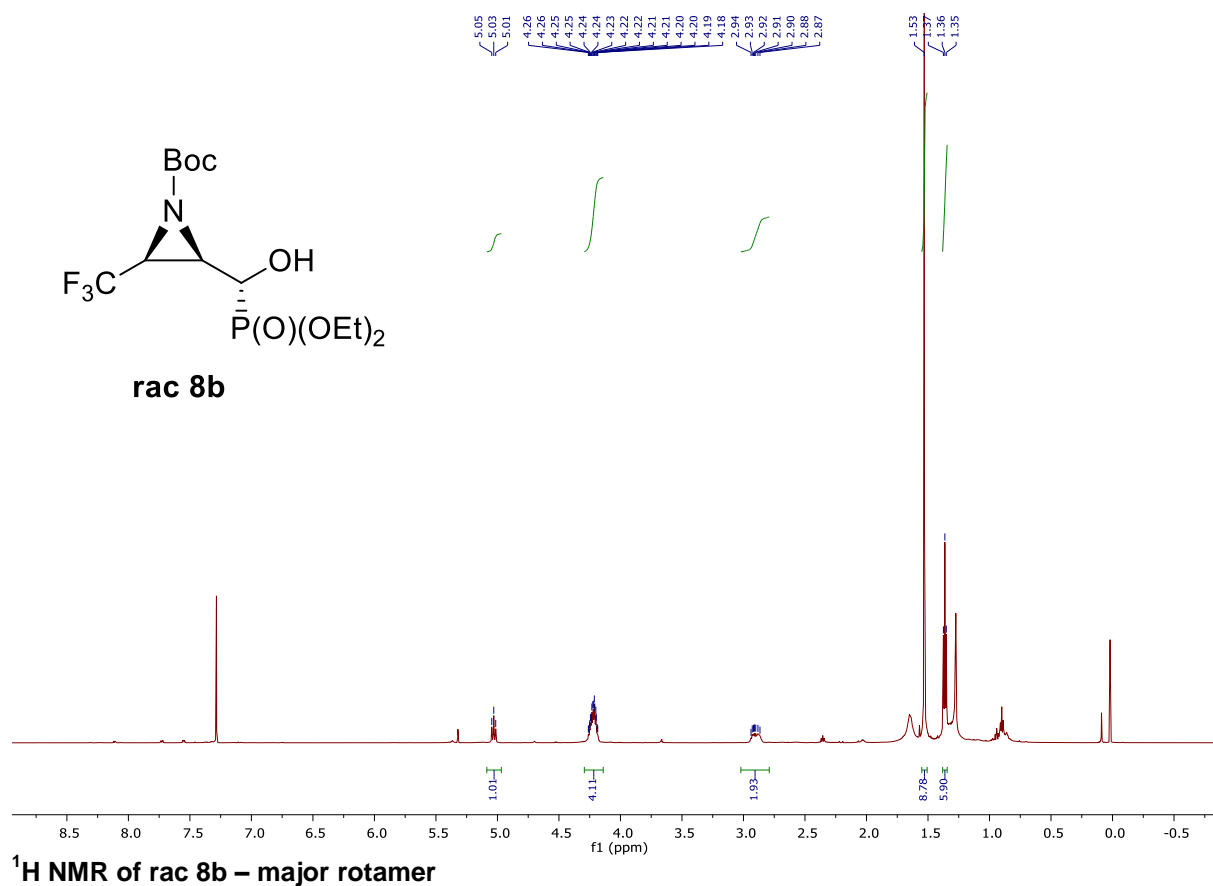
¹H NMR of rac 7a



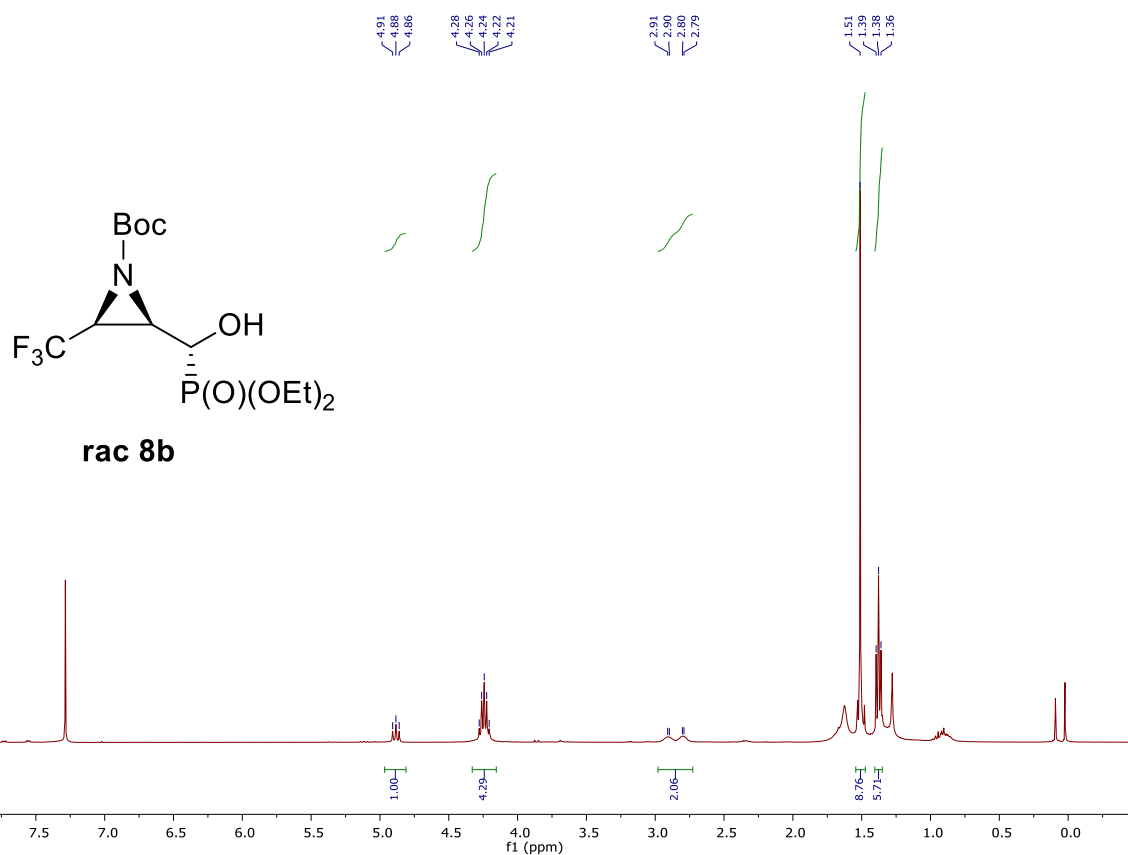
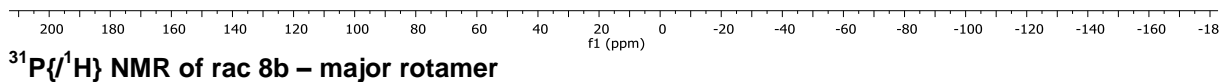
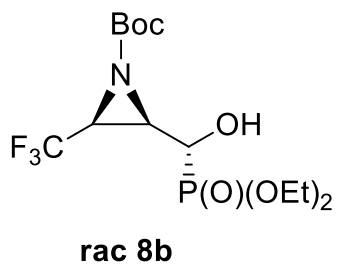
¹³C NMR of rac 7a

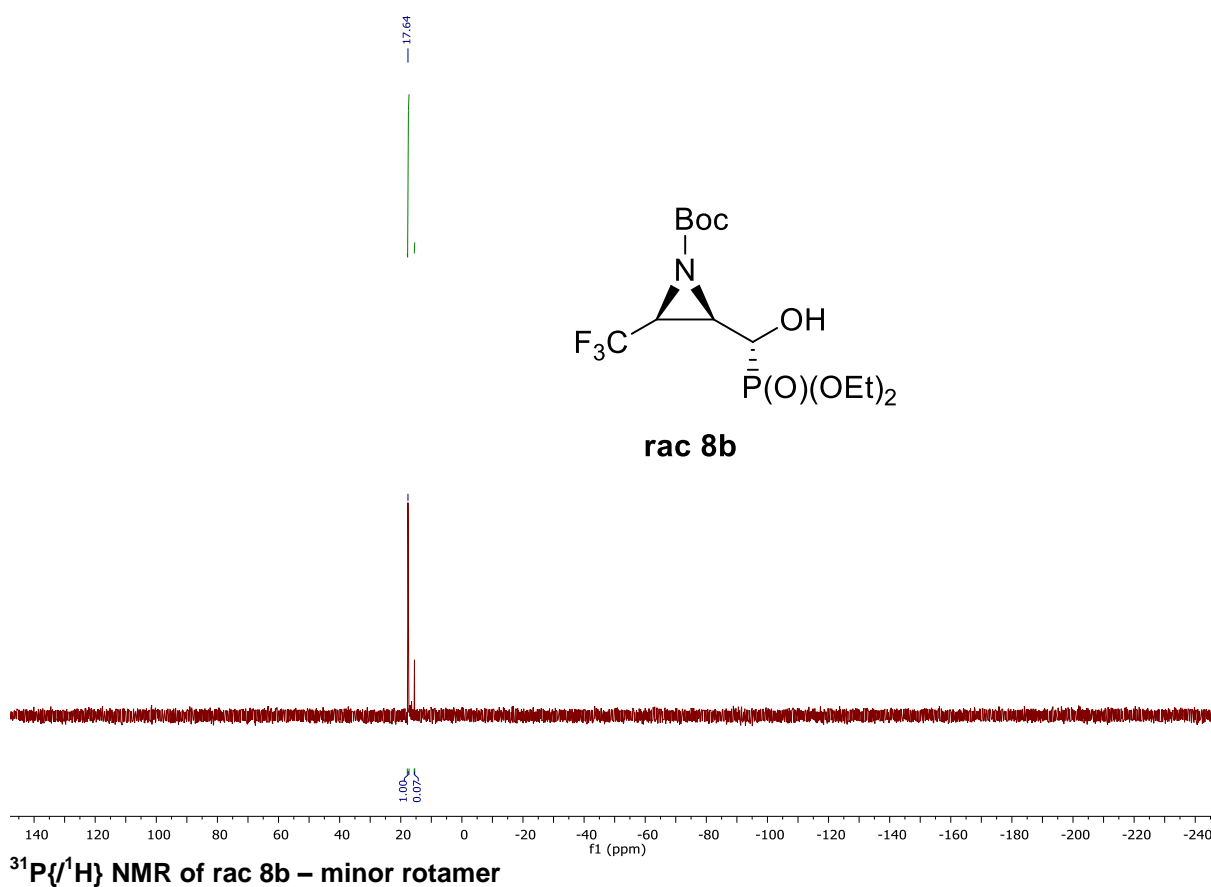
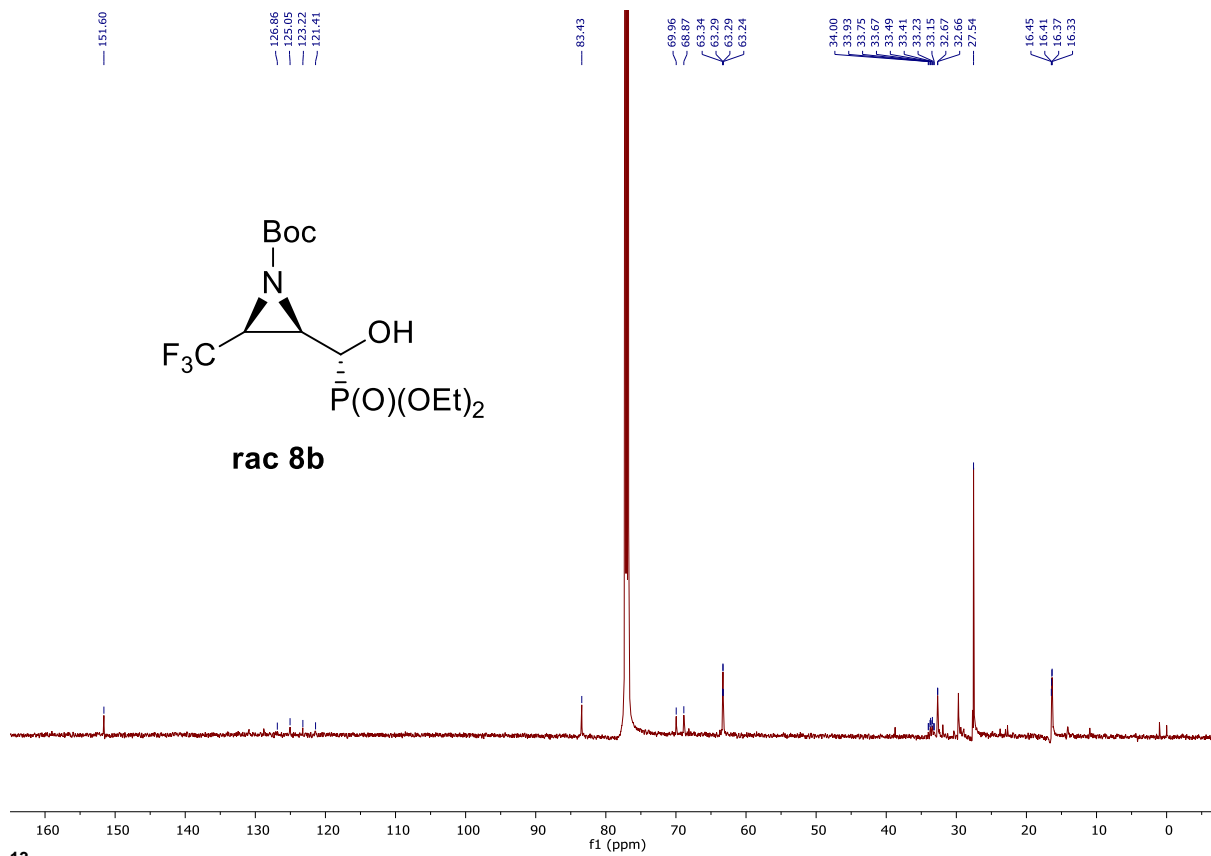


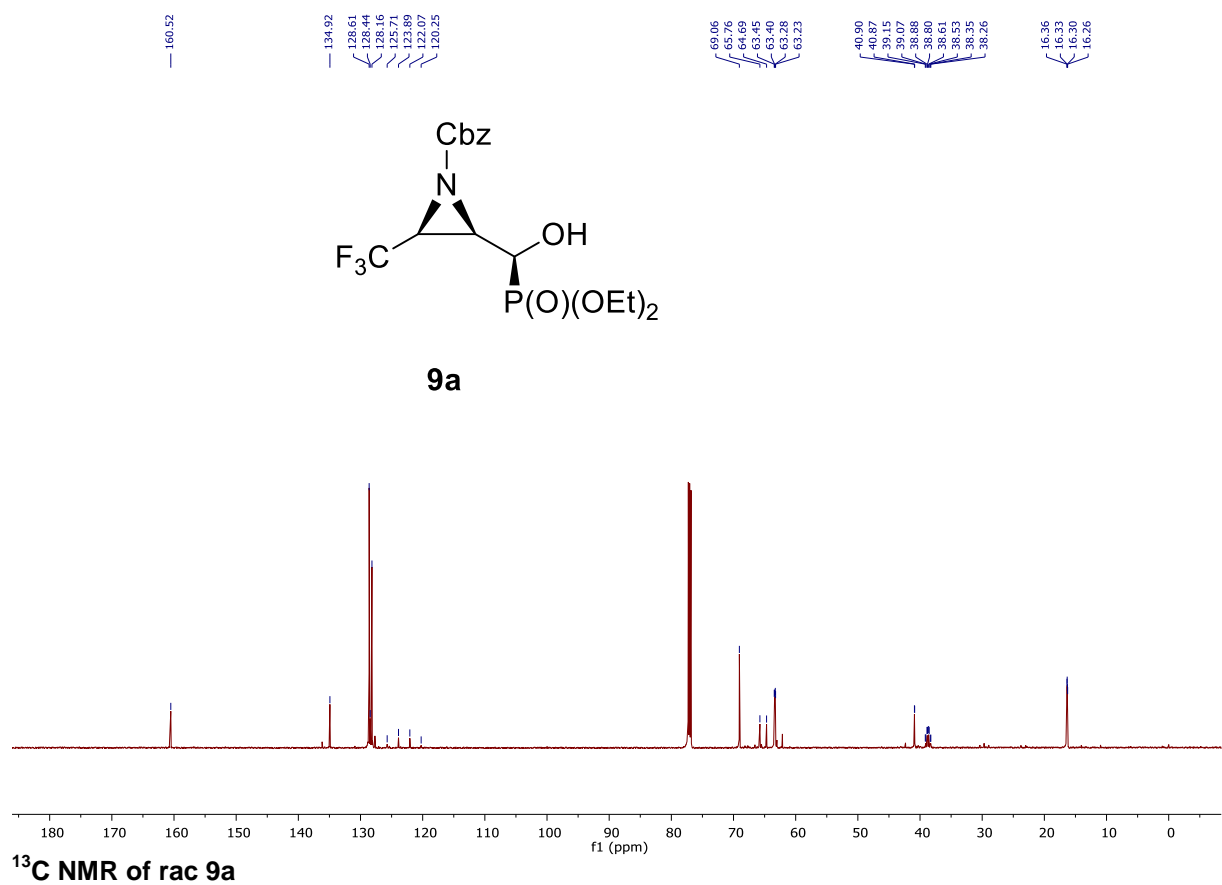
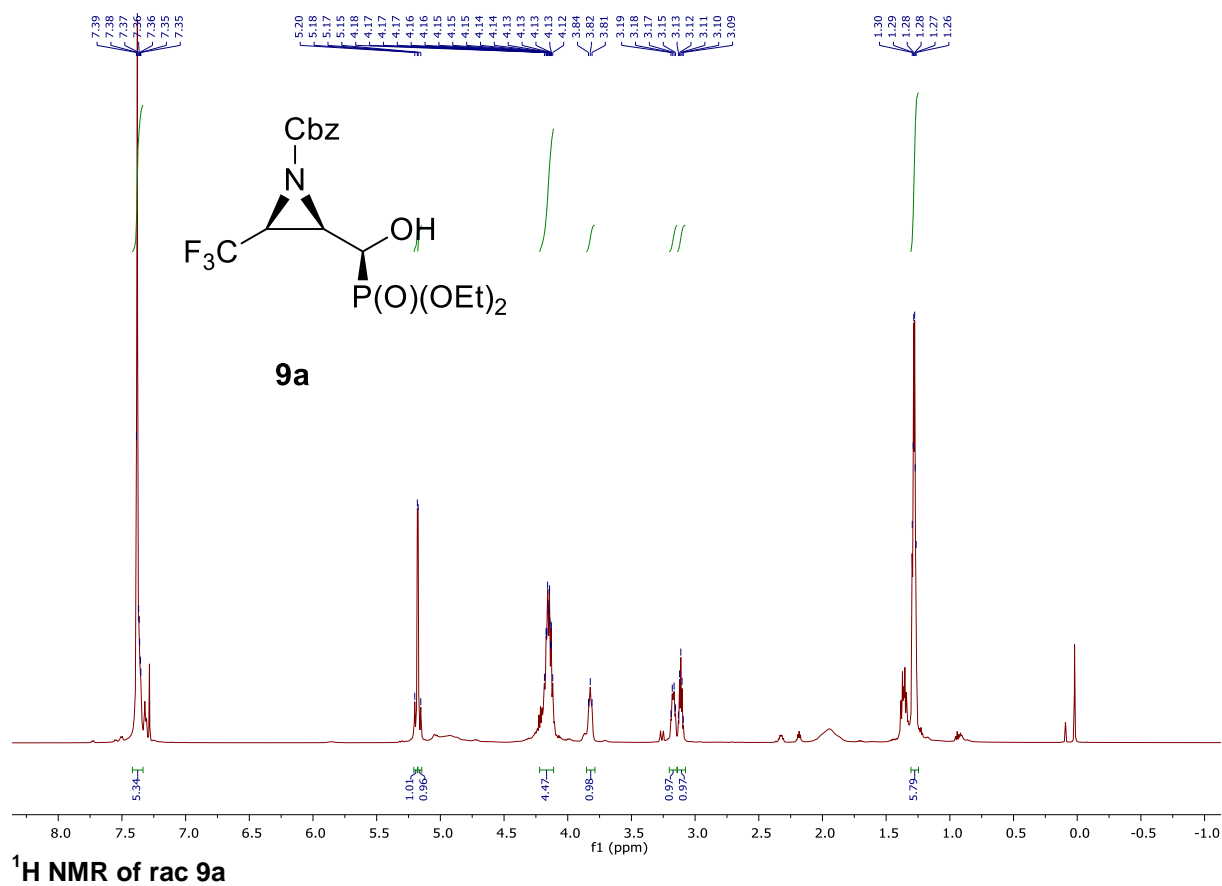


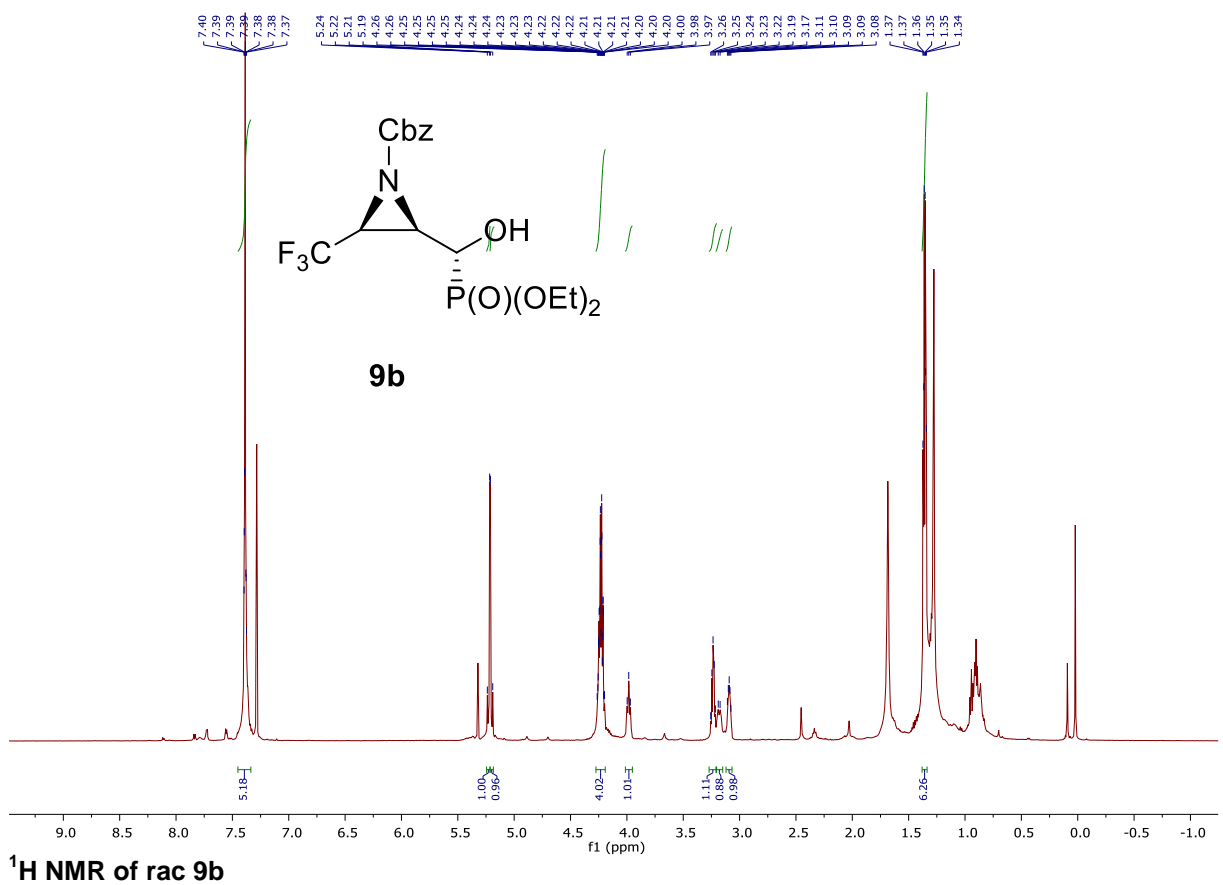
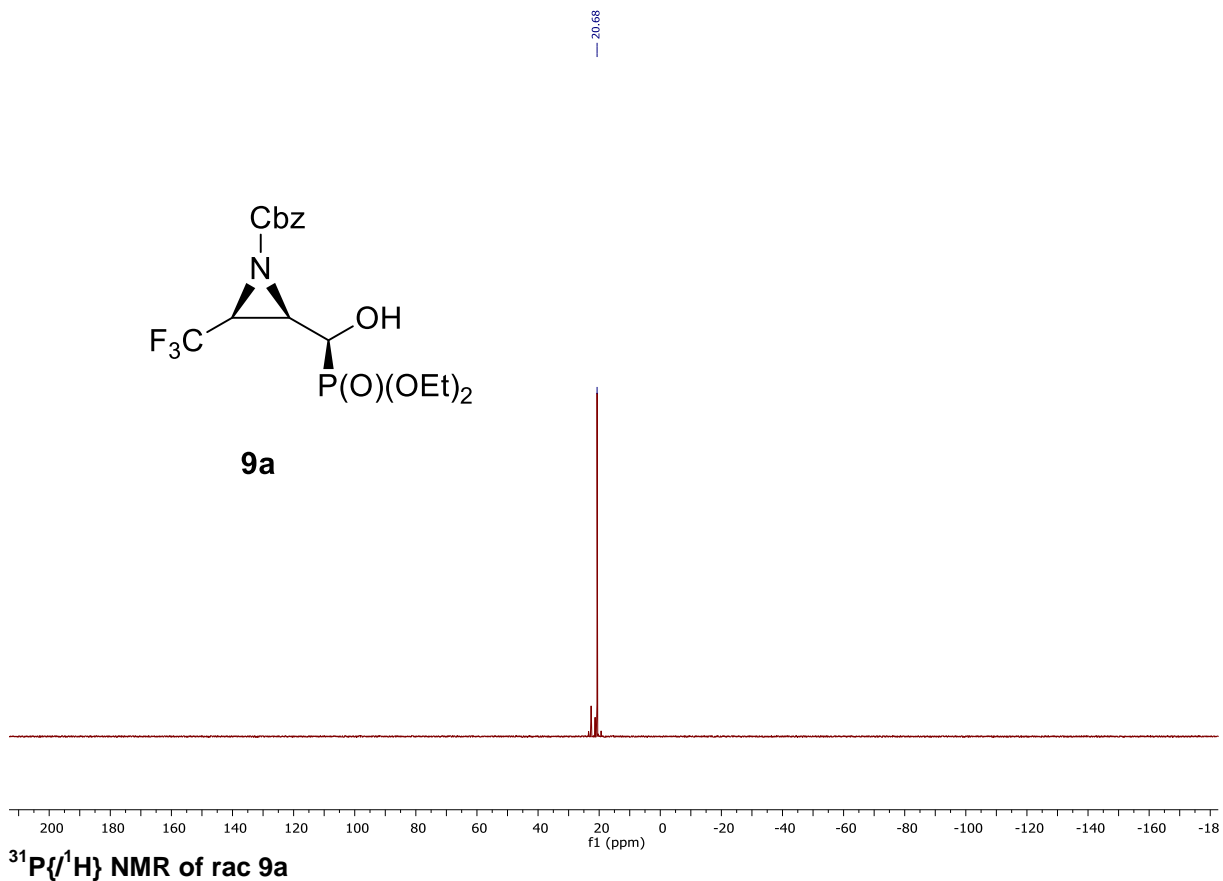


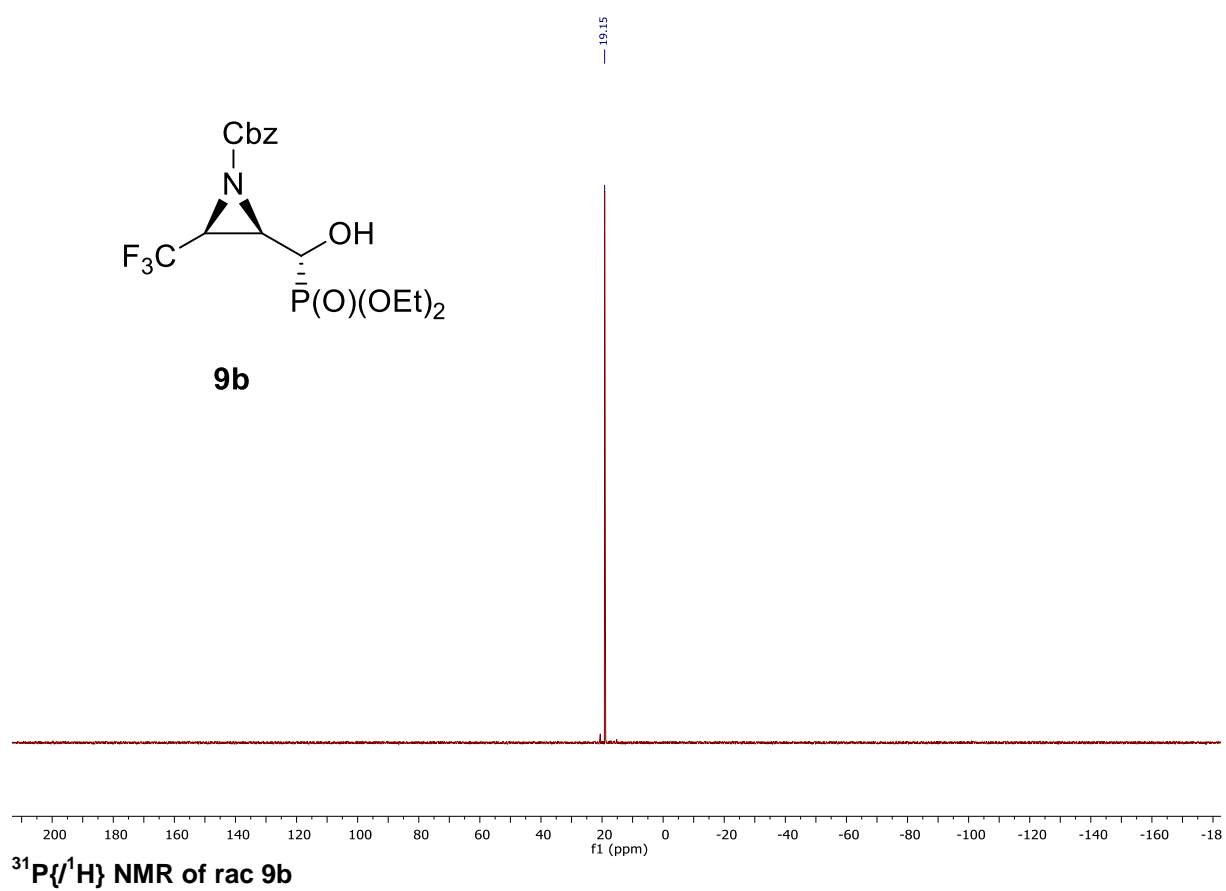
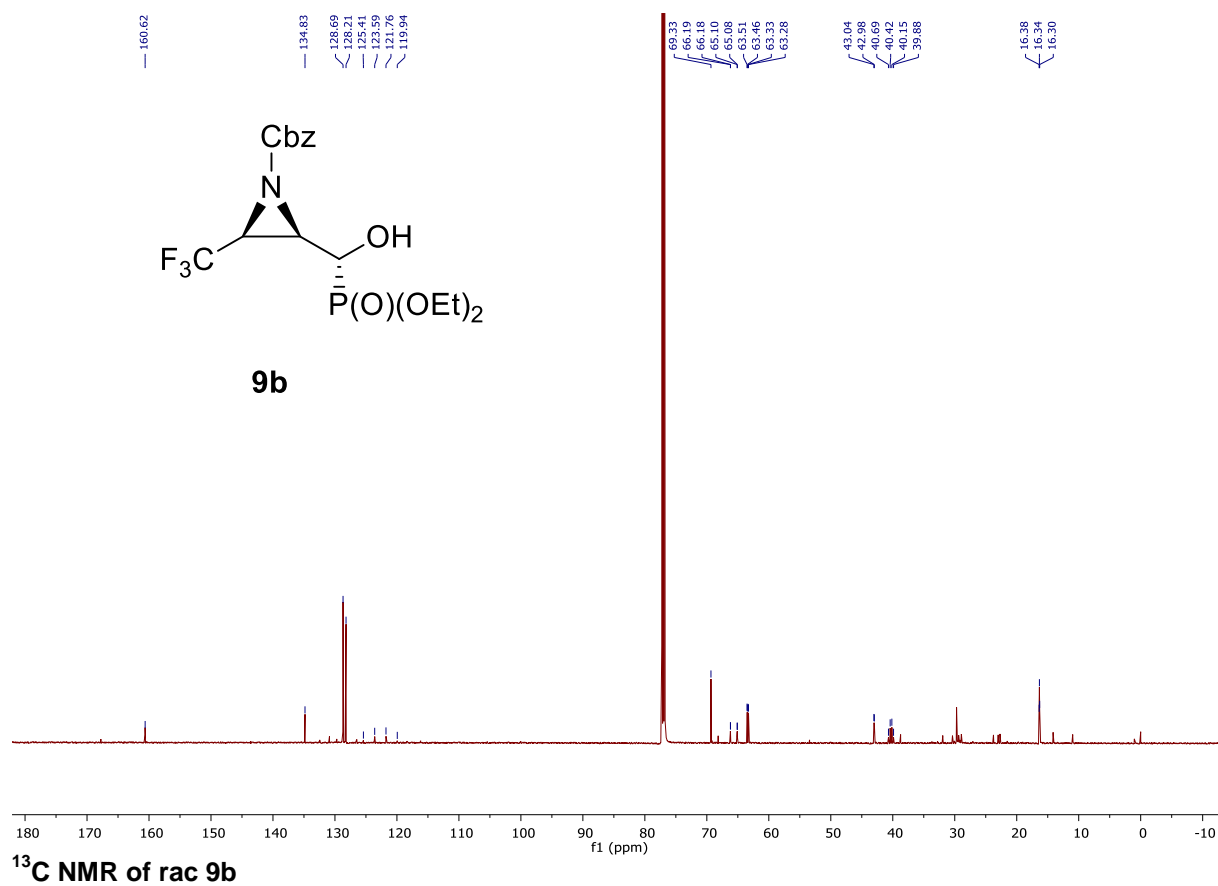
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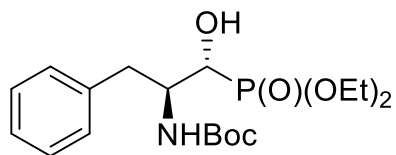




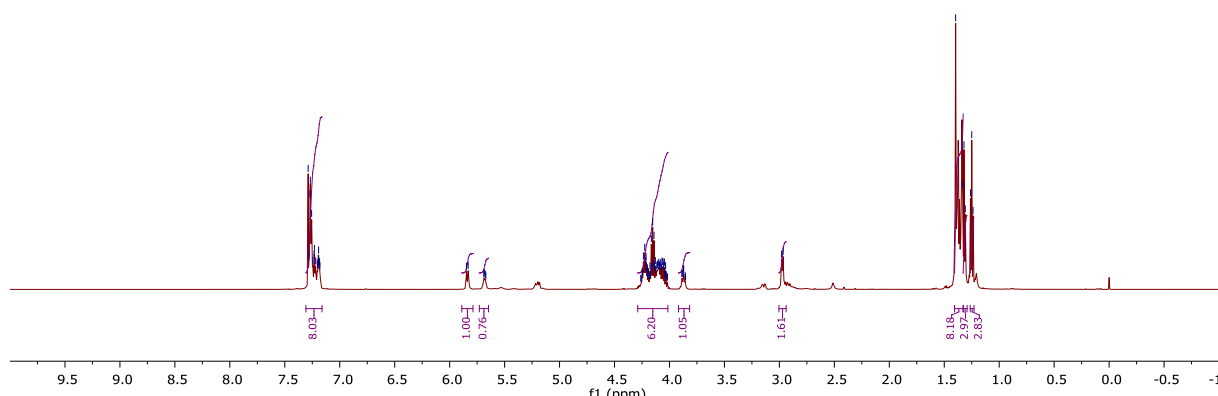




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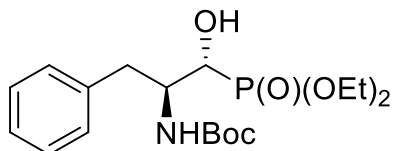


11a

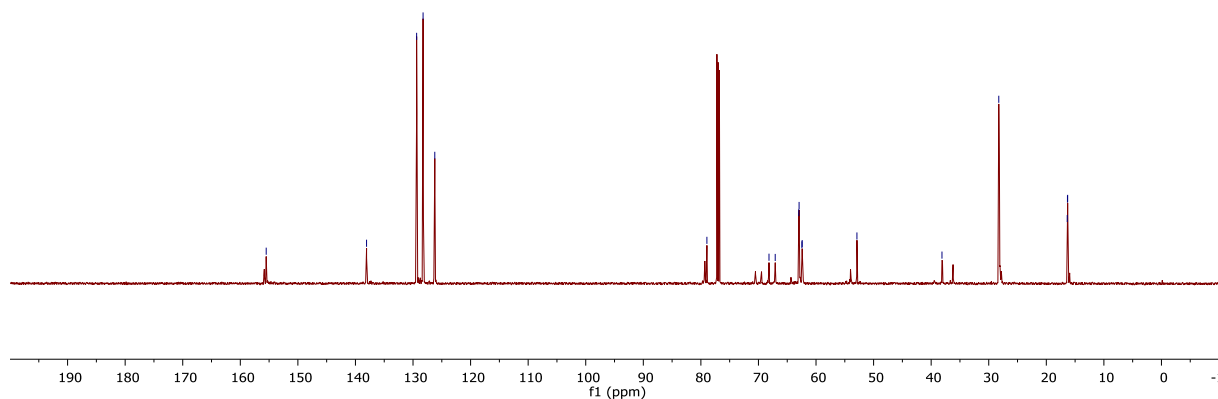


¹H NMR of 11a. Mixture of 11a and 11b [1.9:1, d.r.]

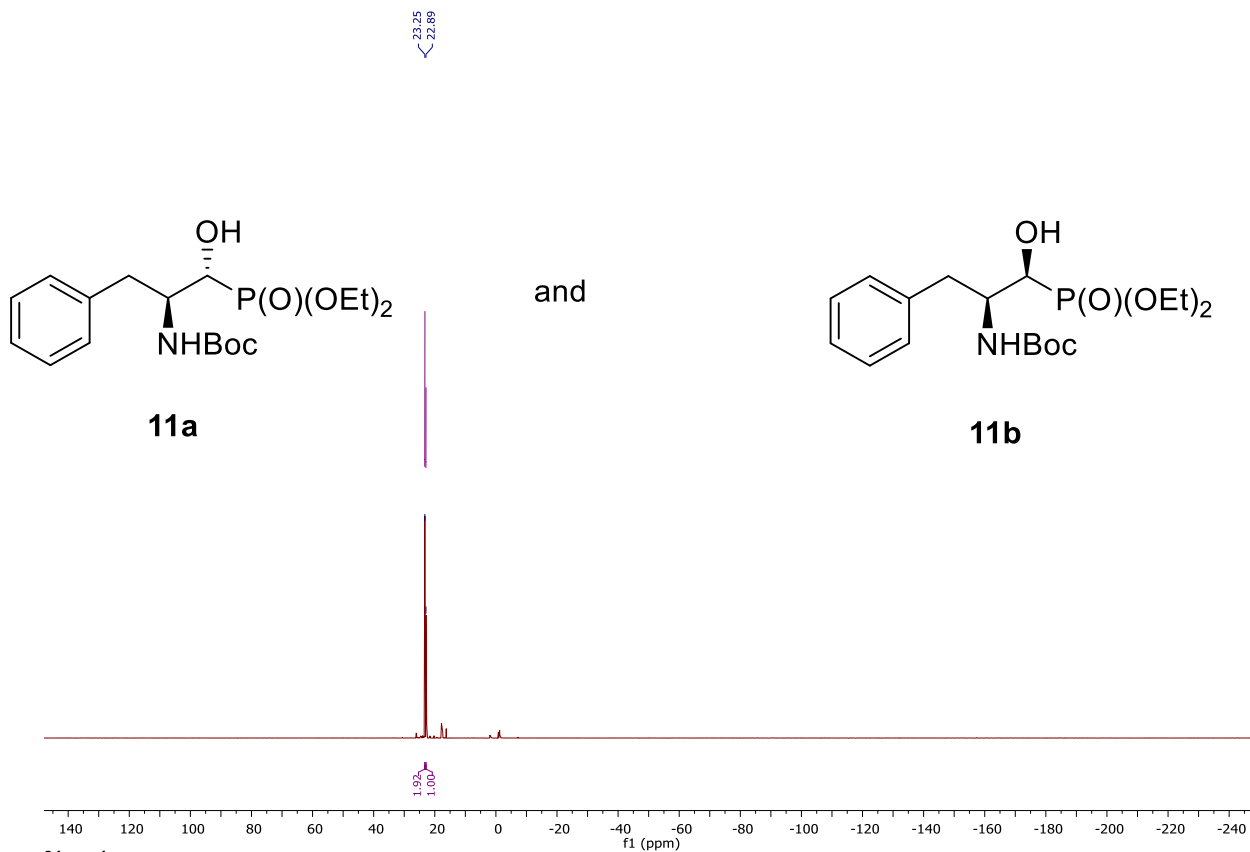
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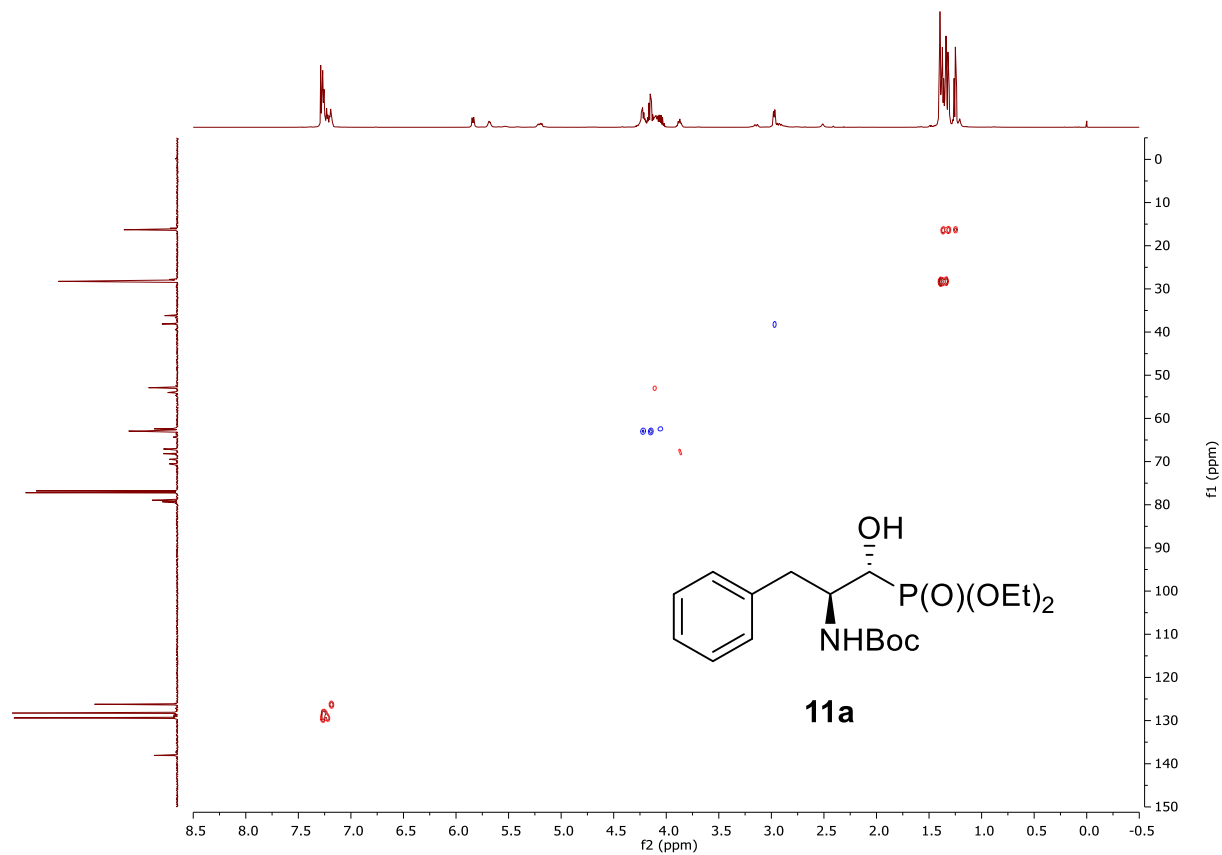
11a



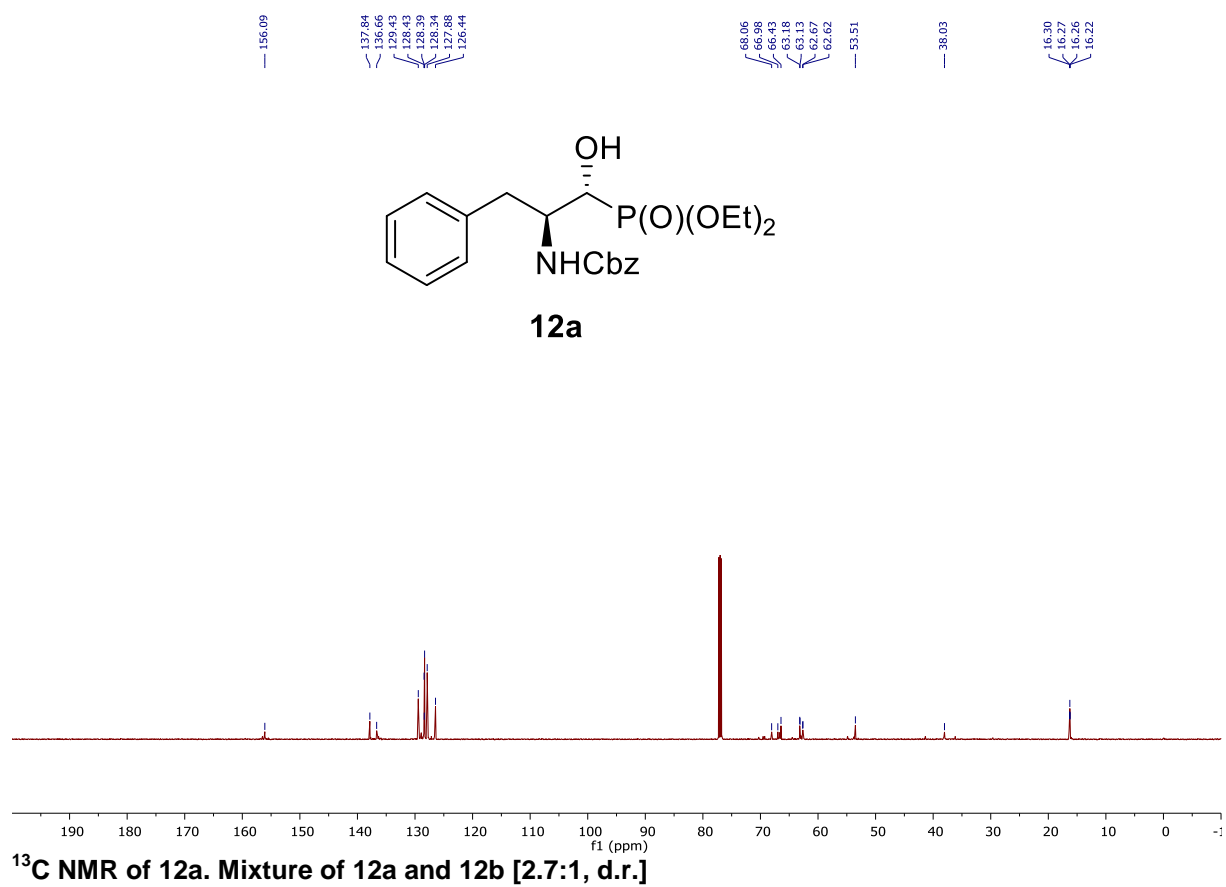
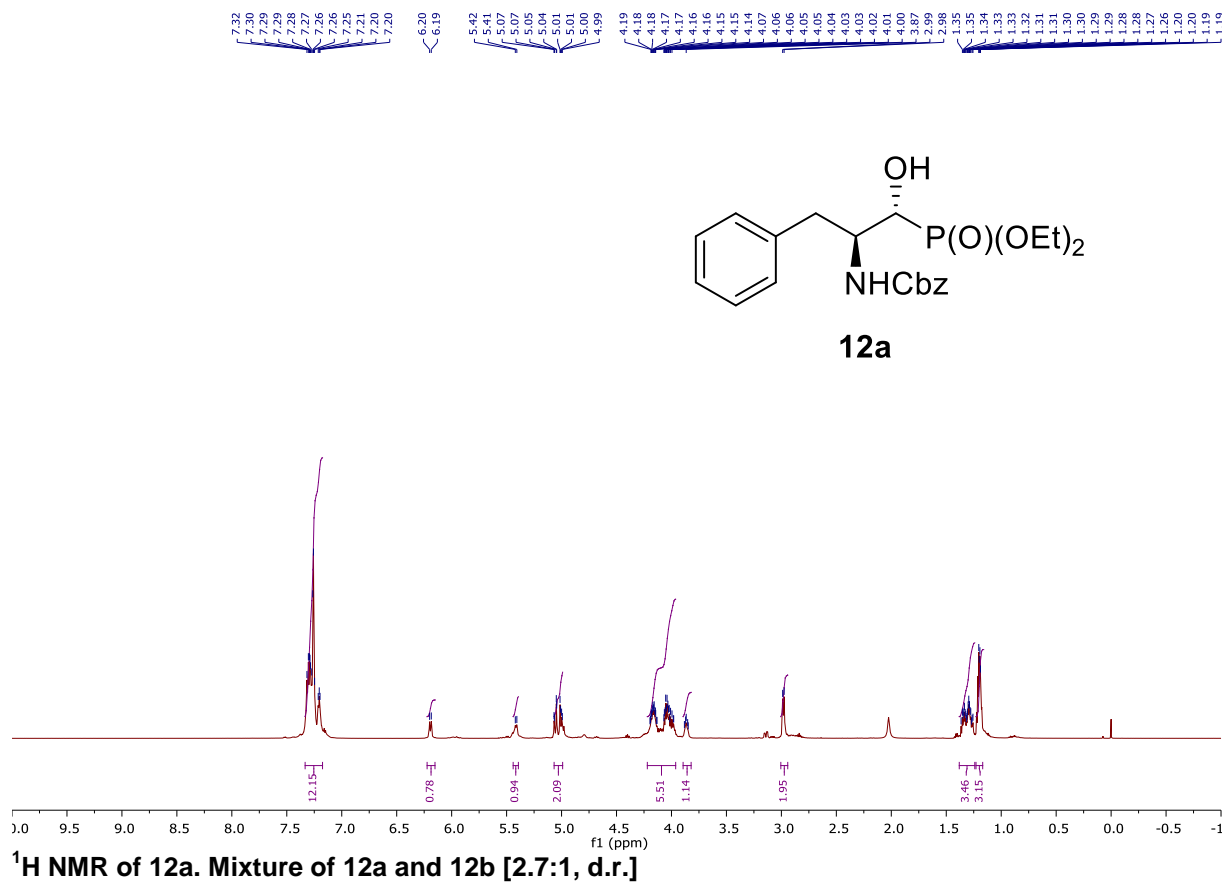
¹³C NMR of 11a. Mixture of 11a and 11b [1.9:1, d.r.]

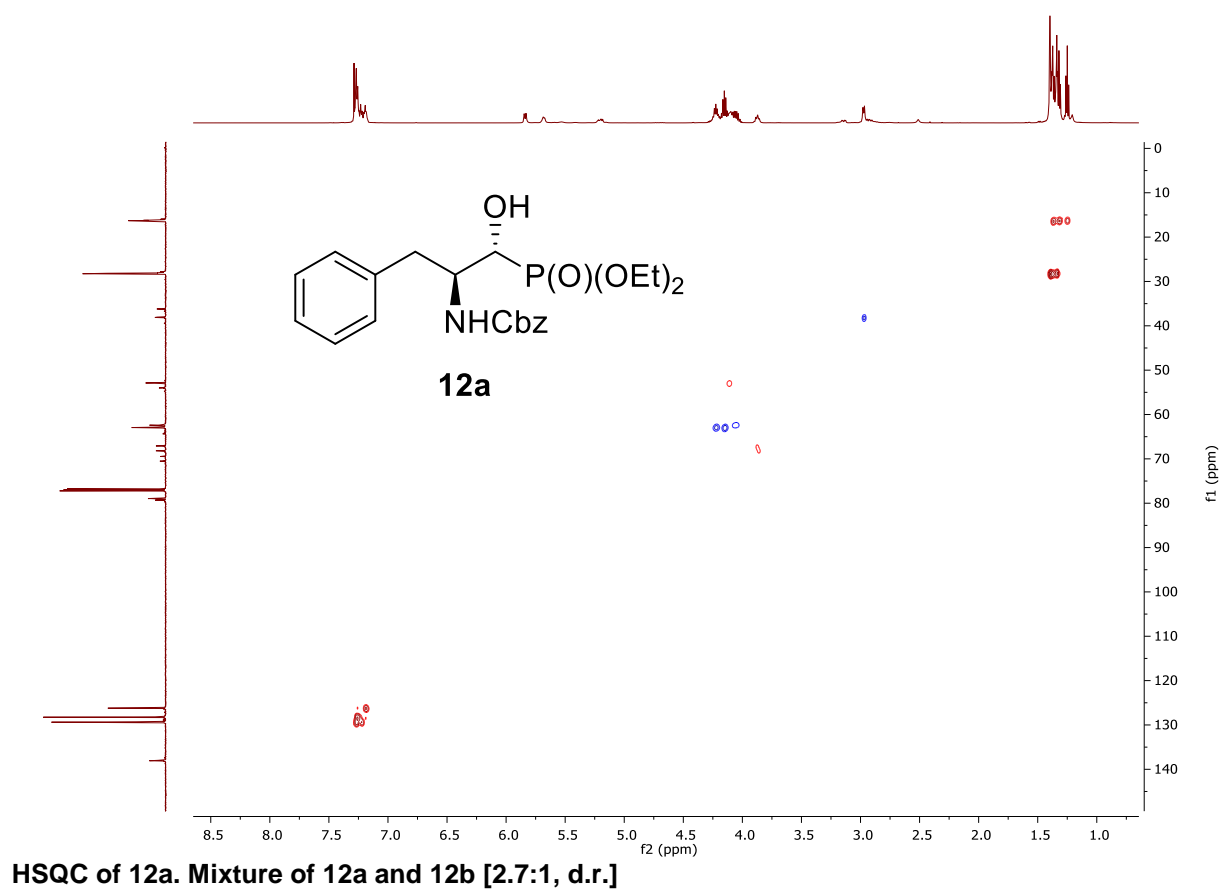
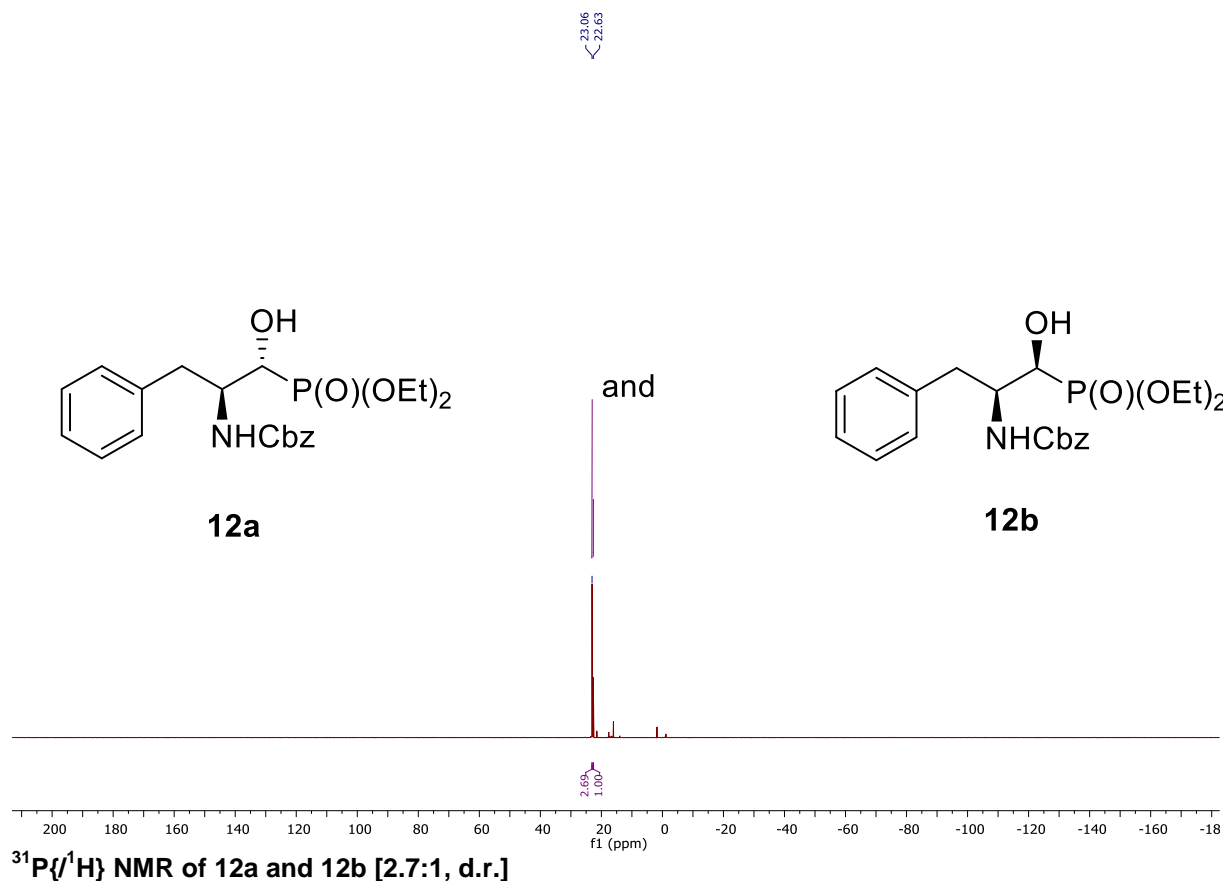


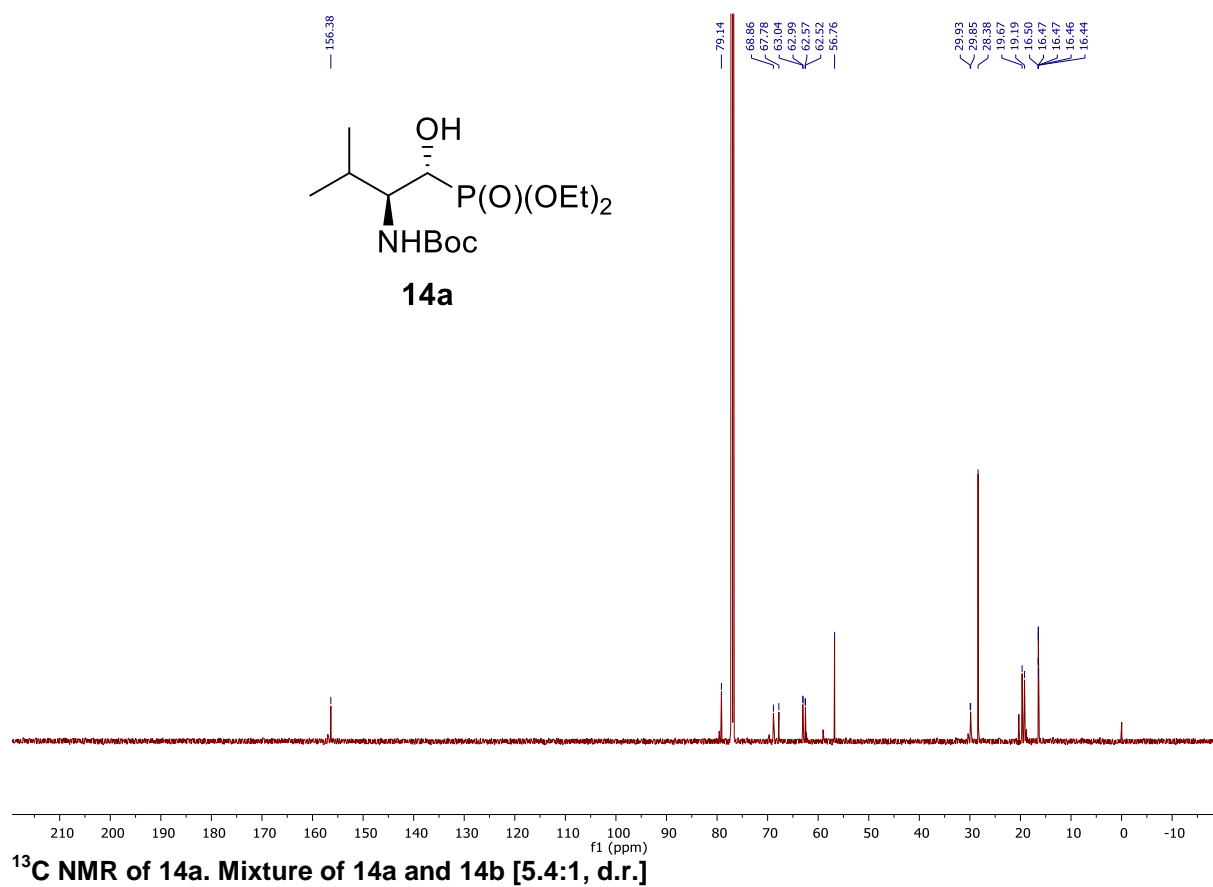
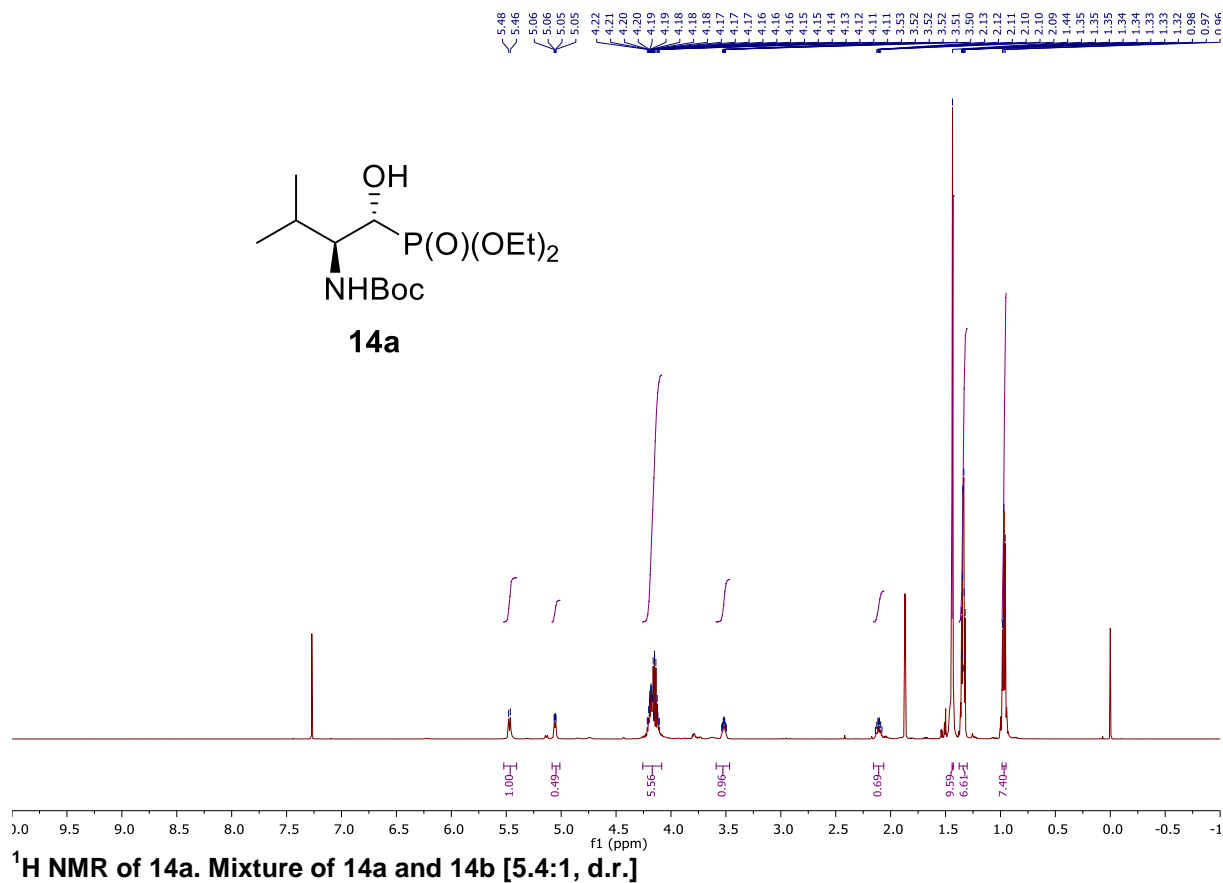
$^{31}\text{P}\{^1\text{H}\}$ NMR of 11a and 11b [1.9:1, d.r.]

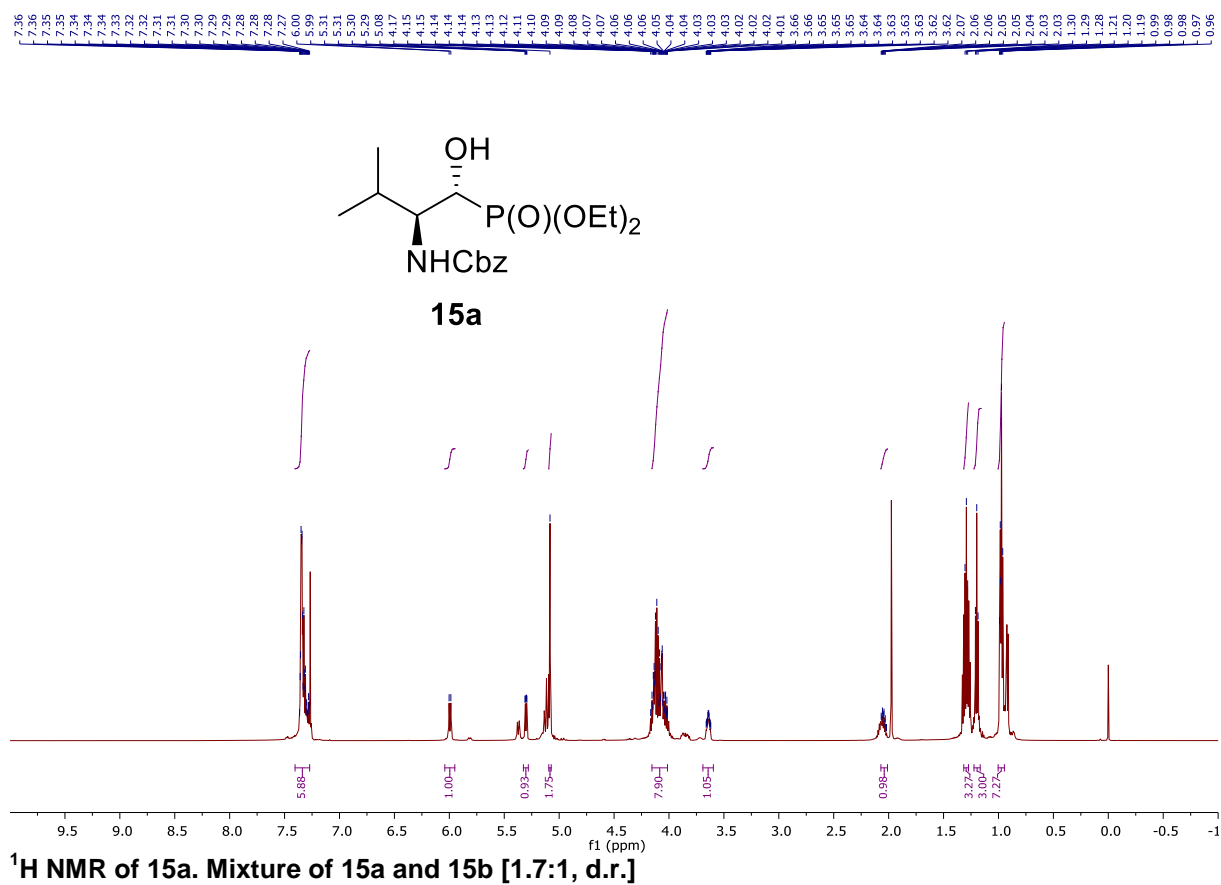
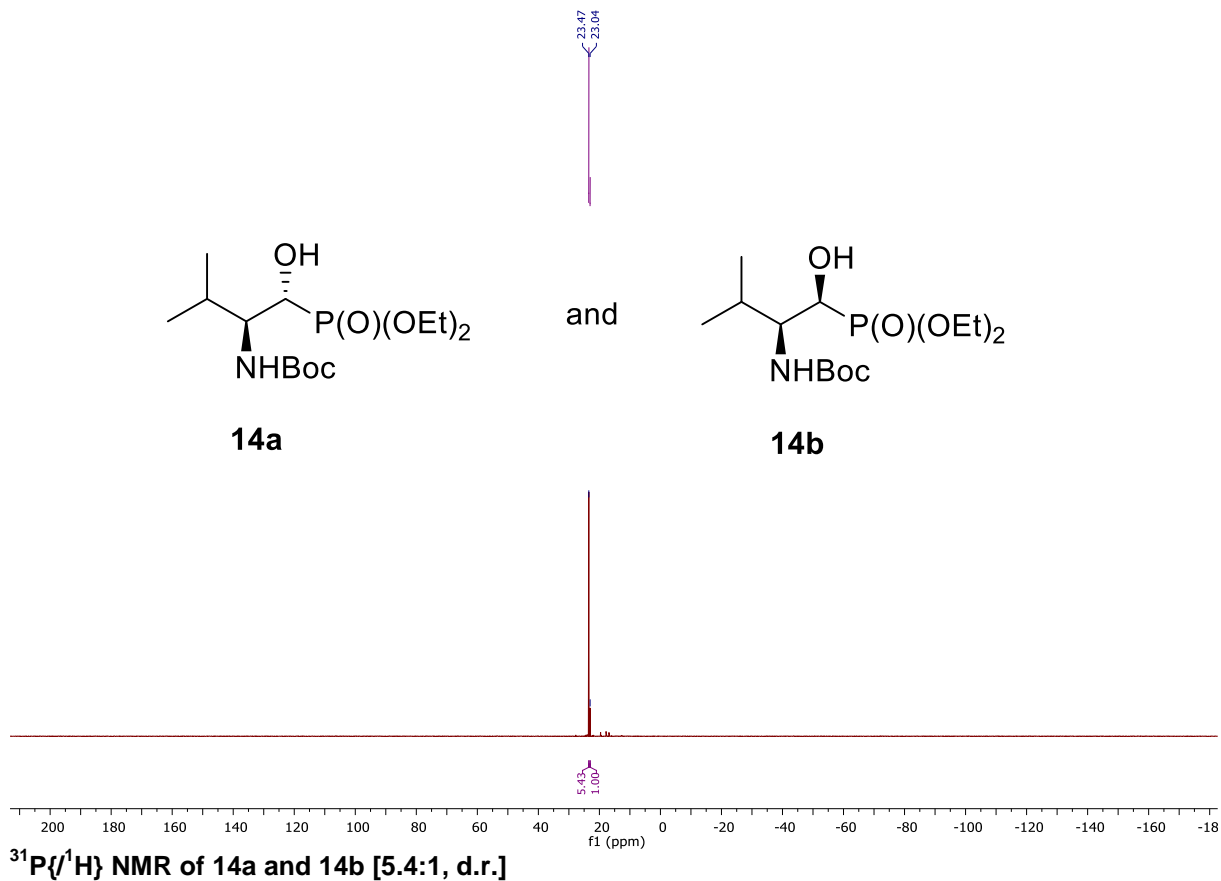


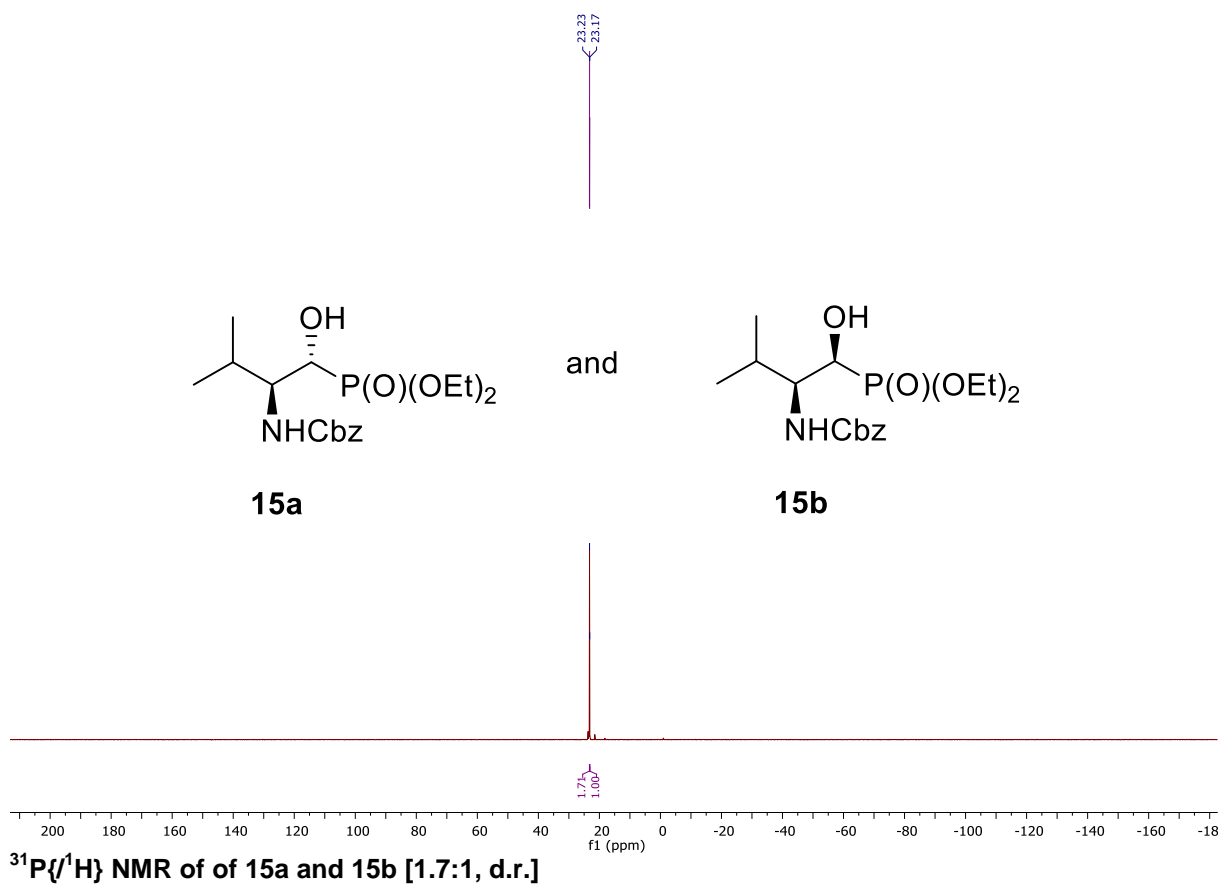
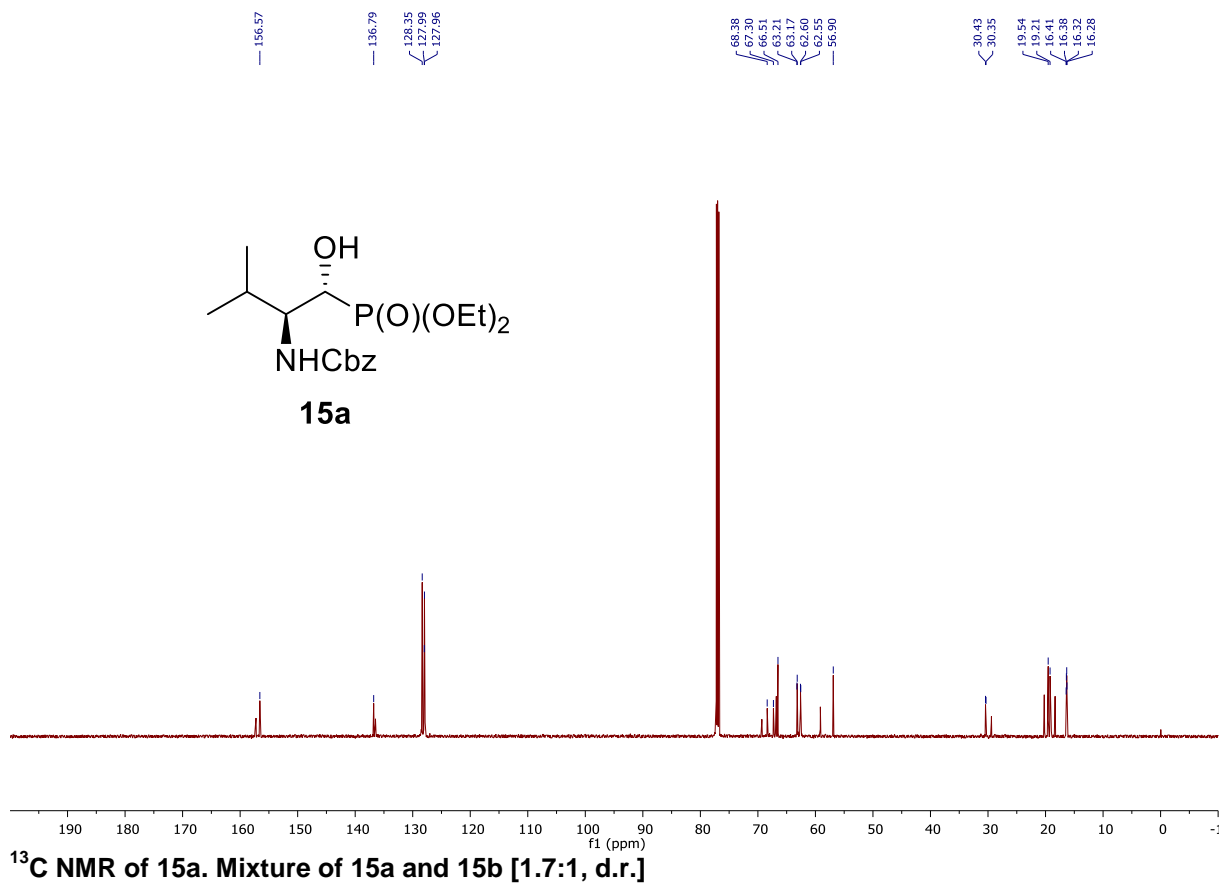
HSQC of 11a. Mixture of 11a and 11b [1.9:1, d.r.]

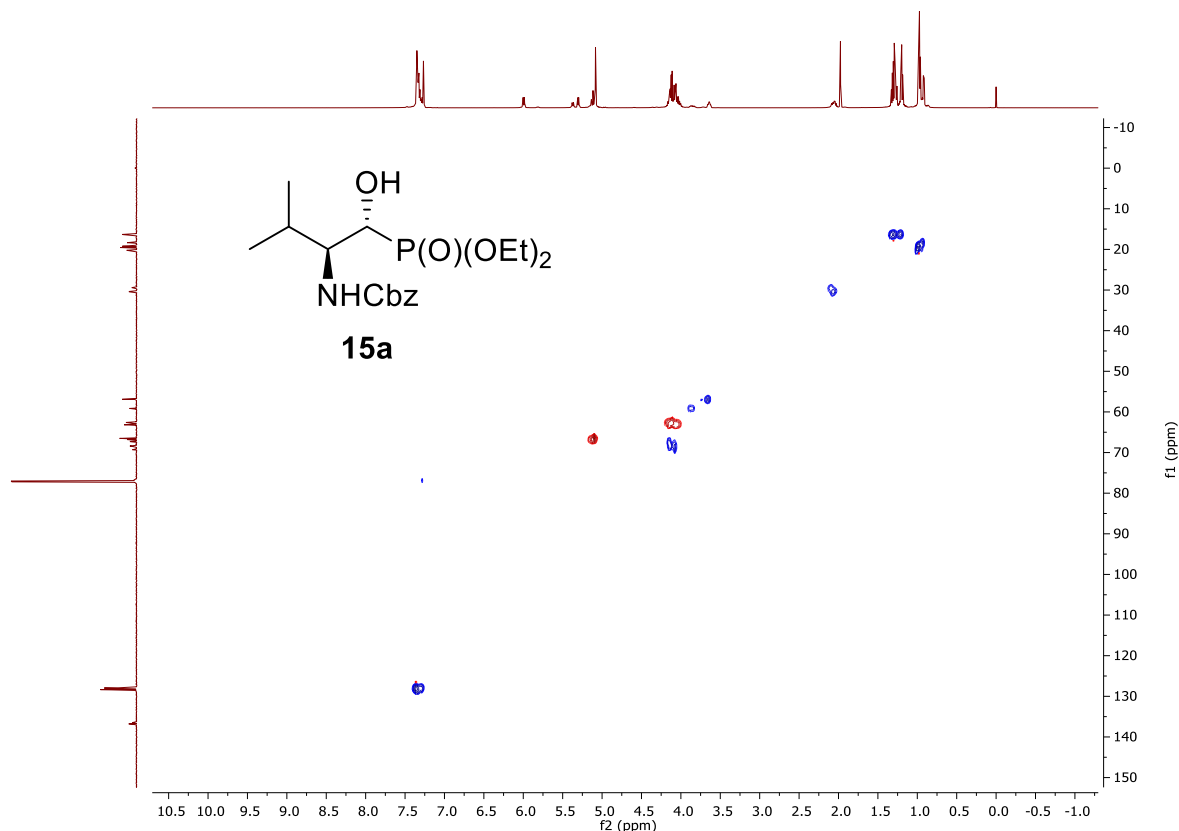




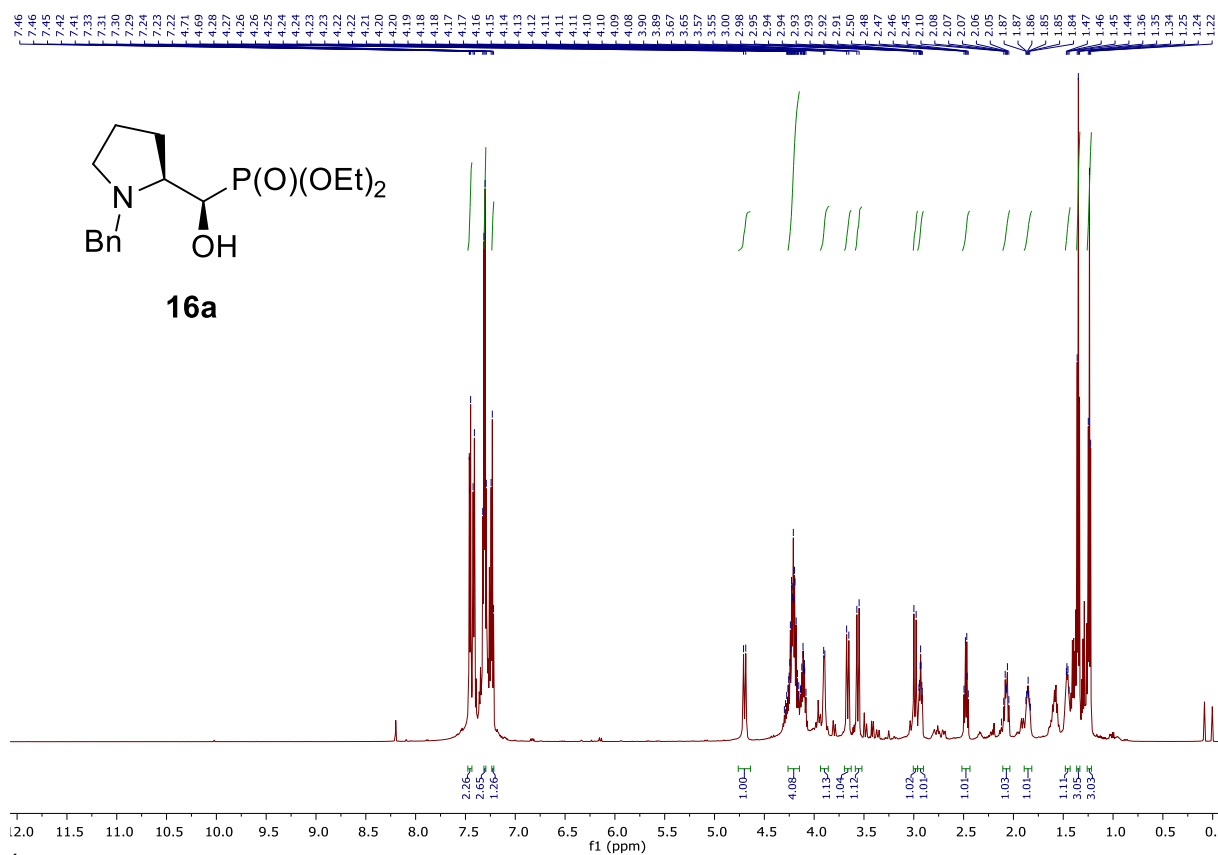


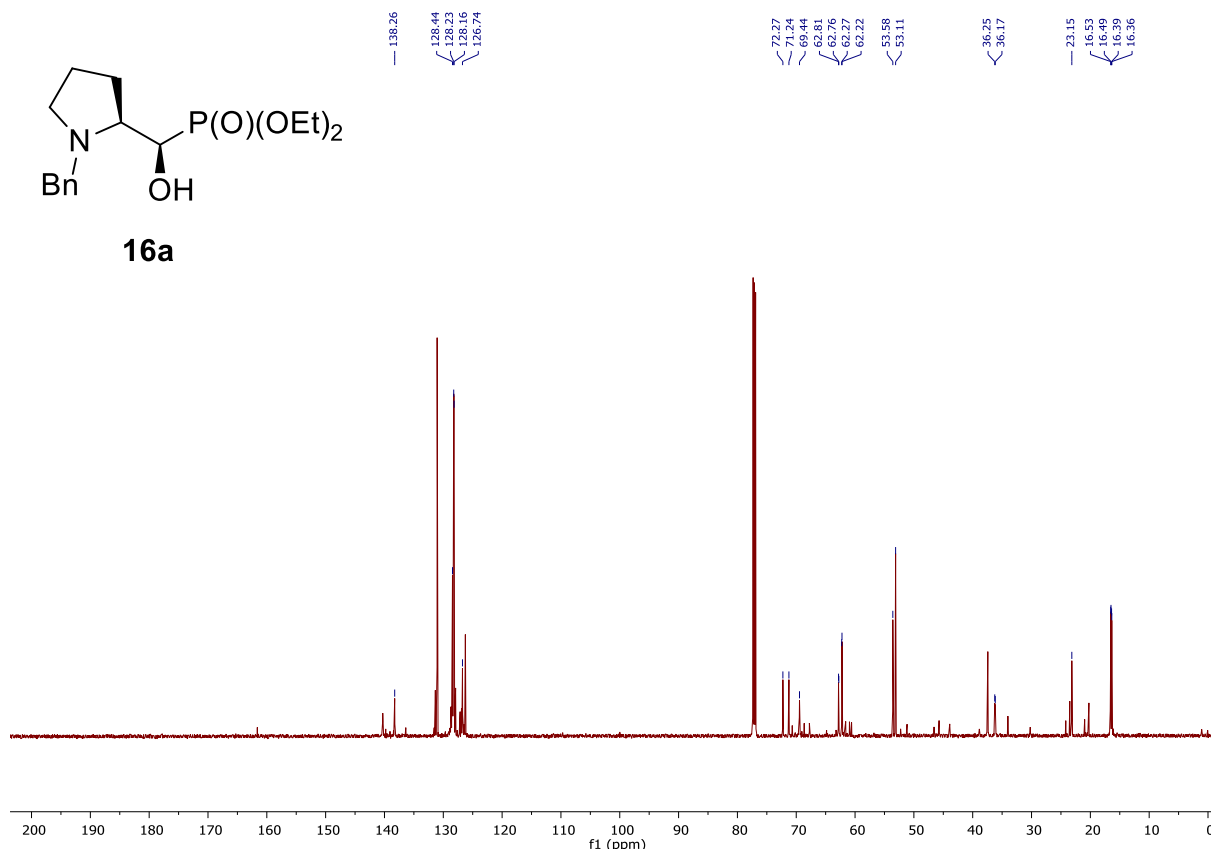
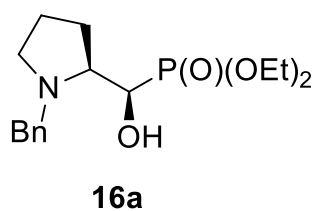




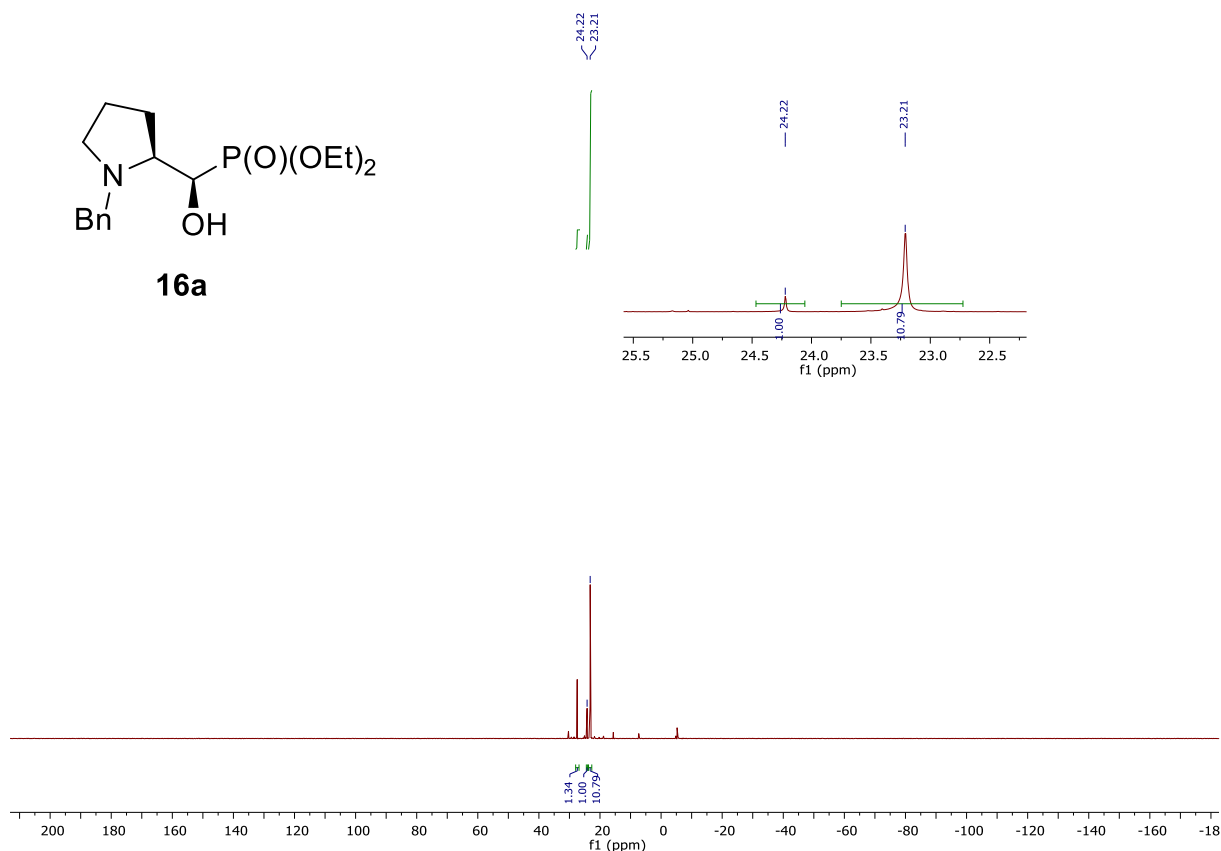
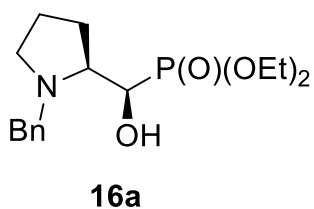


HSQC of 15a. Mixture of 15a and 15b [1.7:1, d.r.]

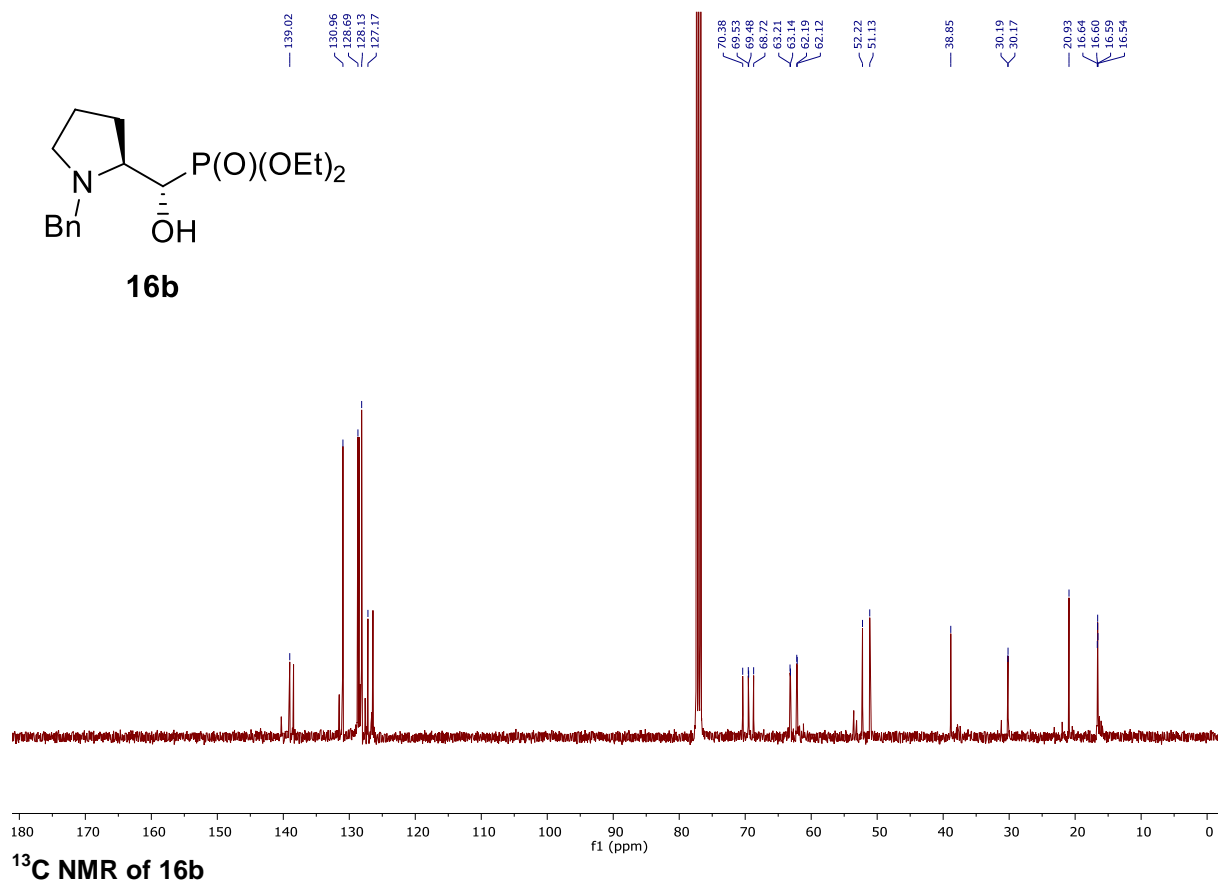
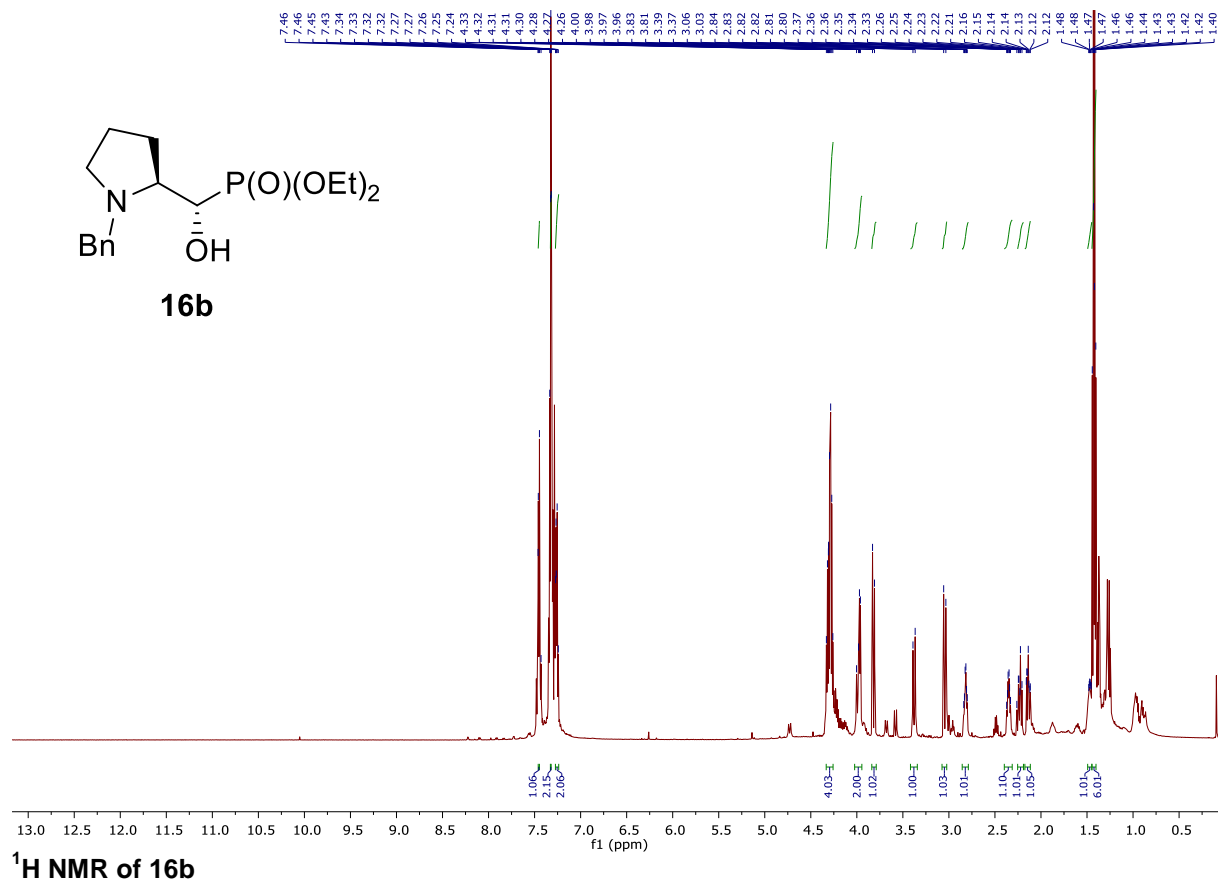


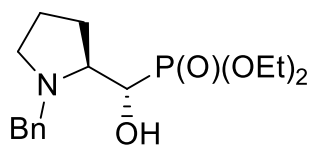


¹³C NMR of 16a. Mixture of 16a and 16b [10.8:1, d.r.]

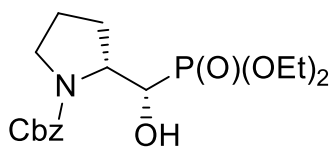
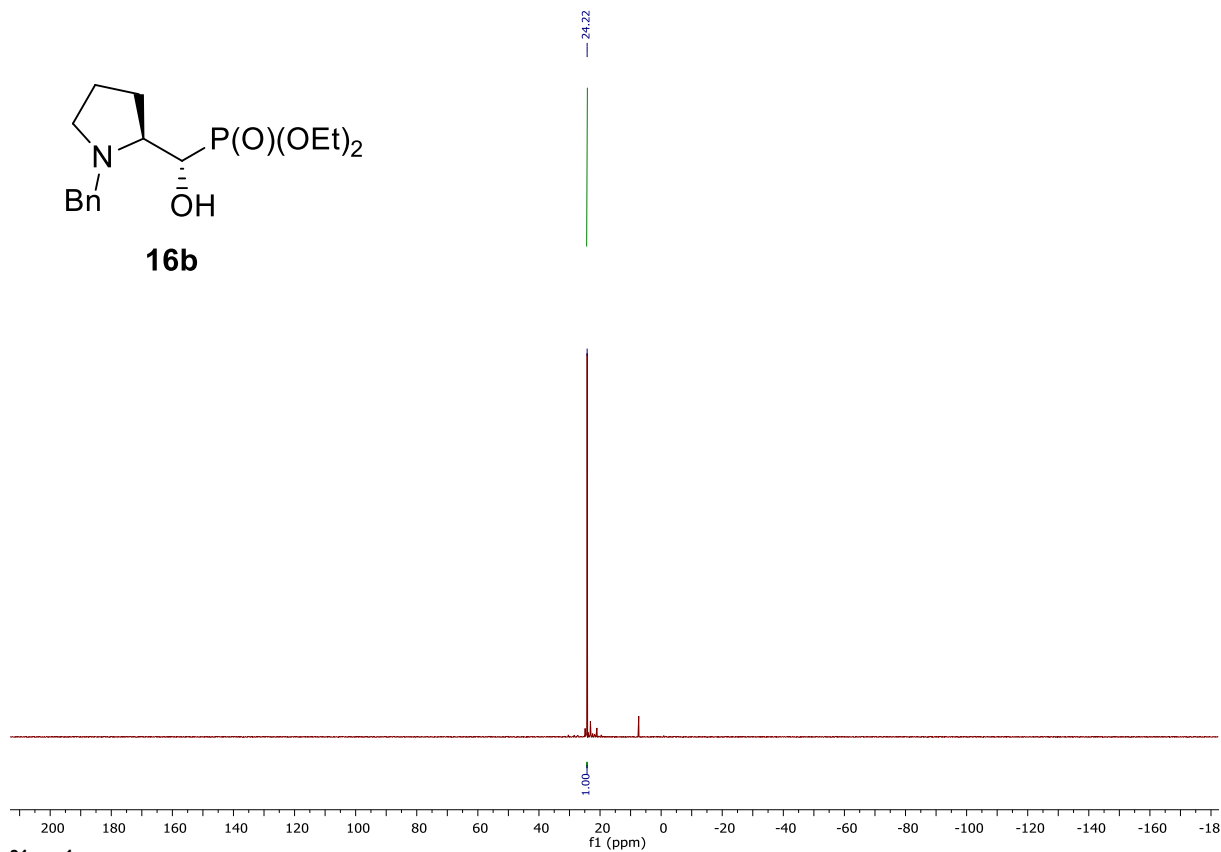


³¹P{¹H} NMR of 16a. Mixture of 16a and 16b [10.8:1, d.r.]

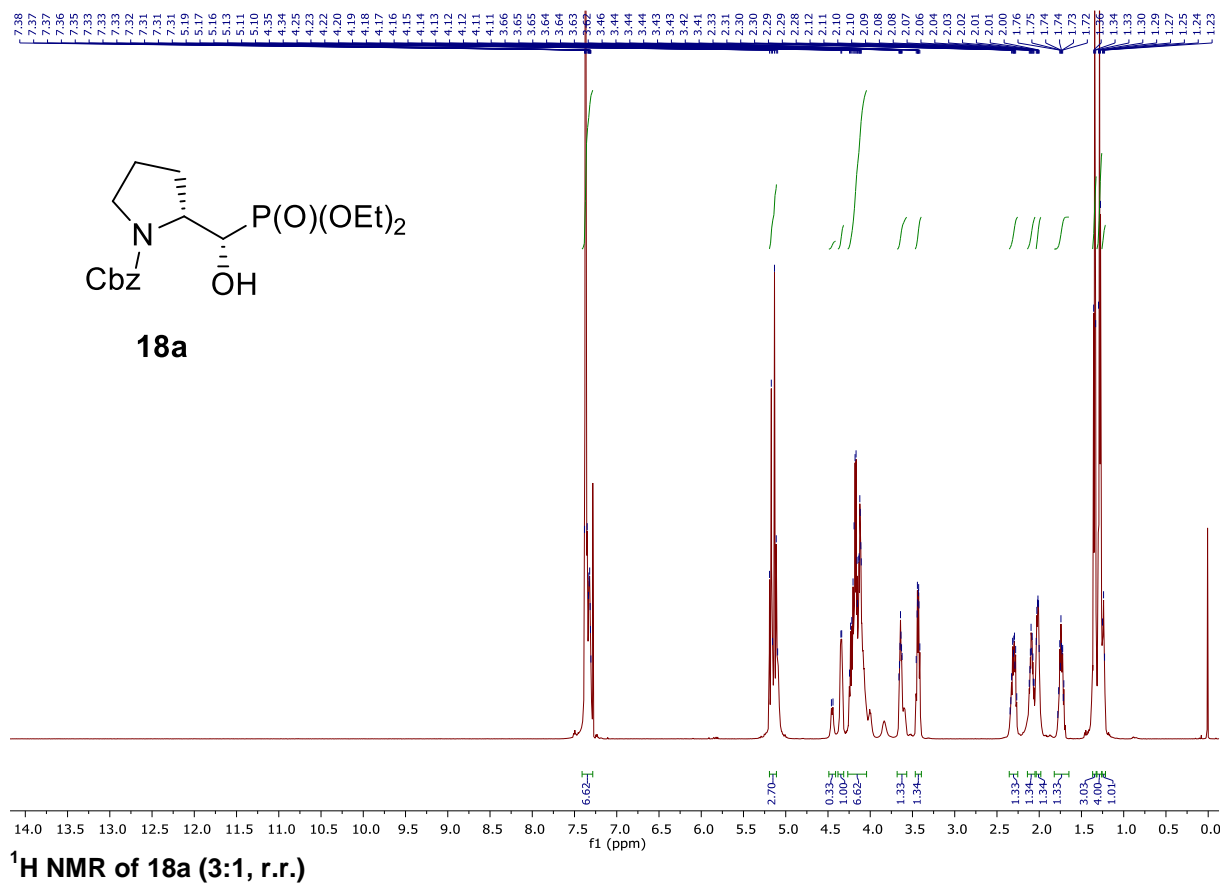


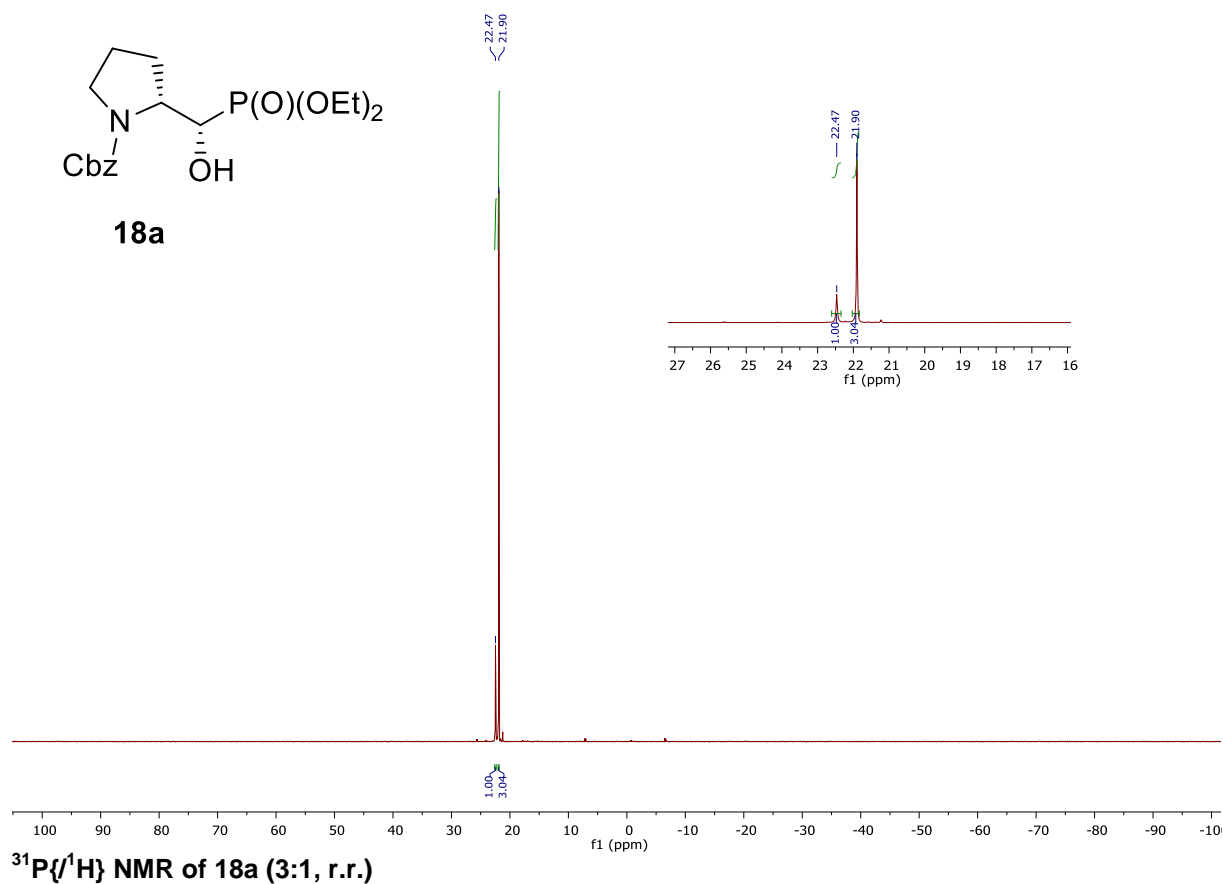
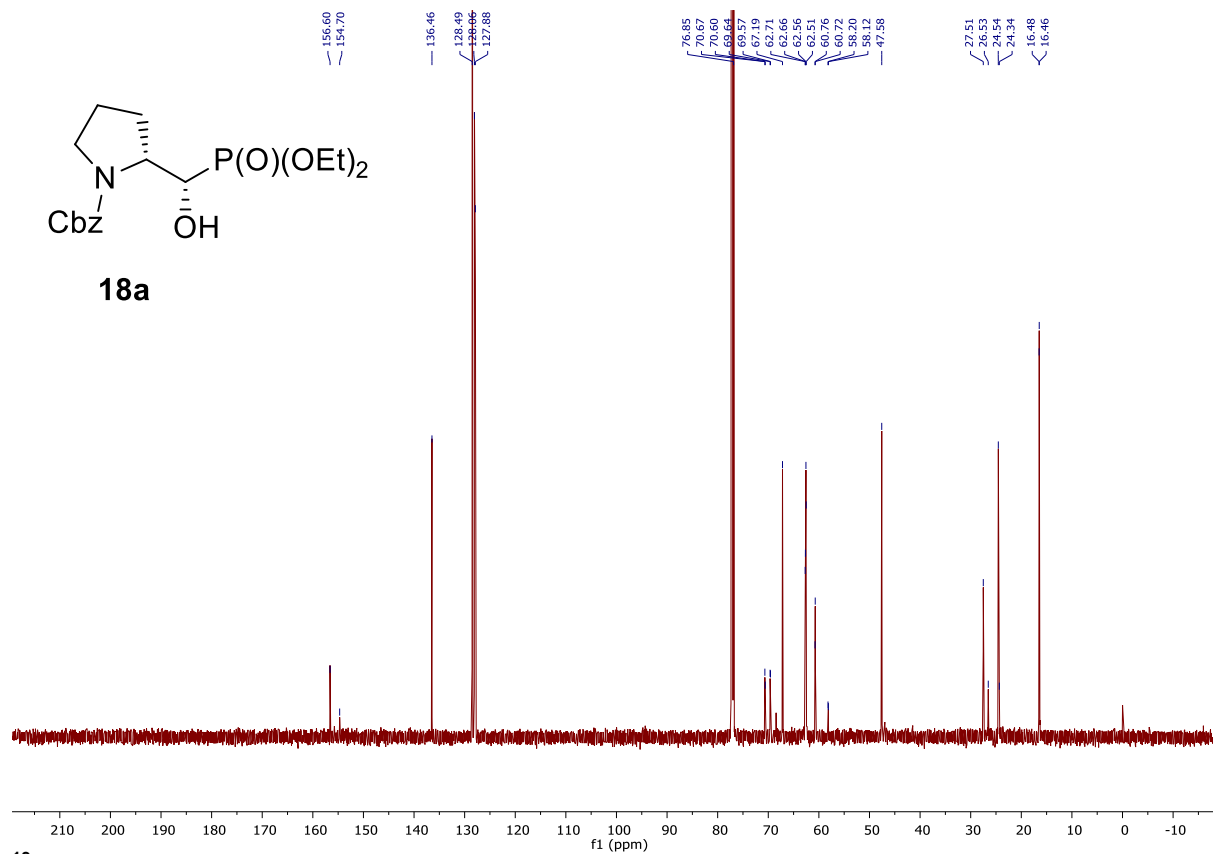


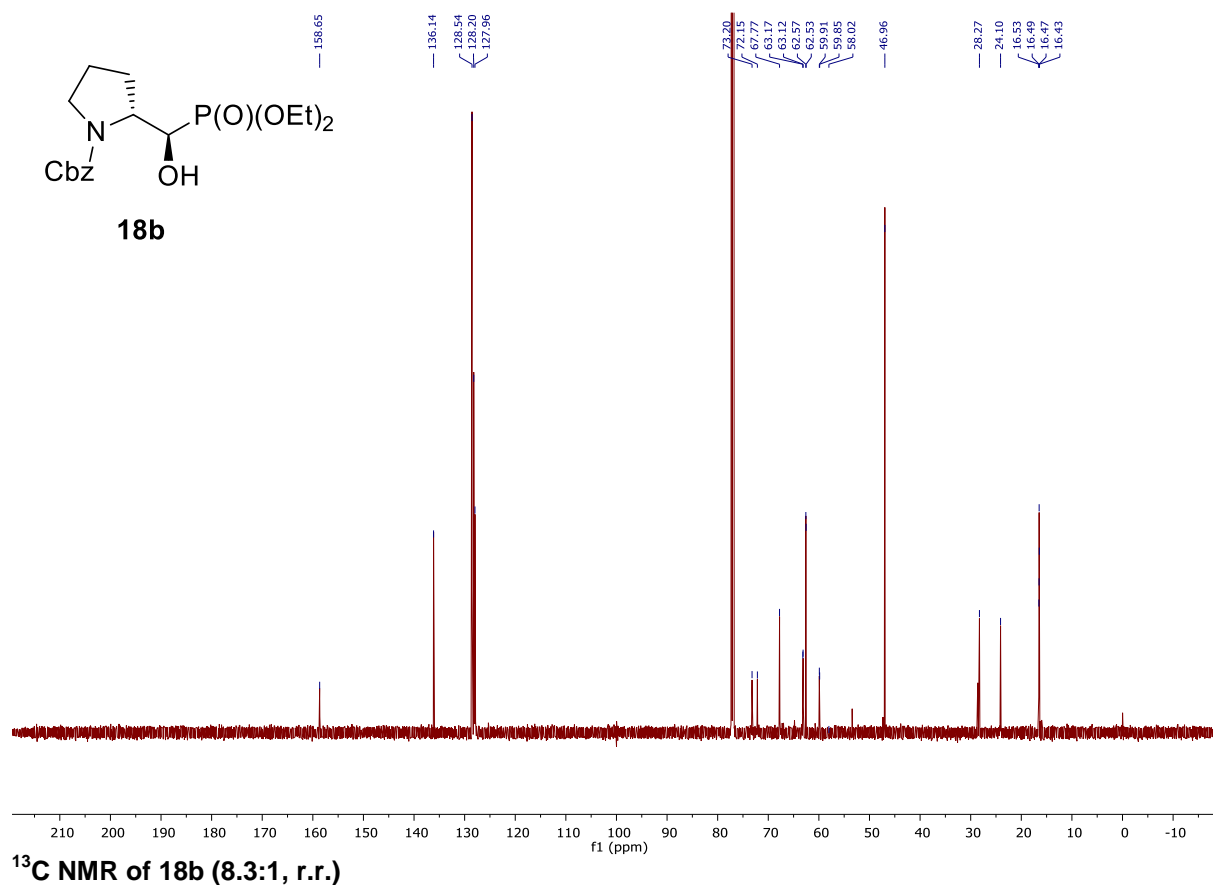
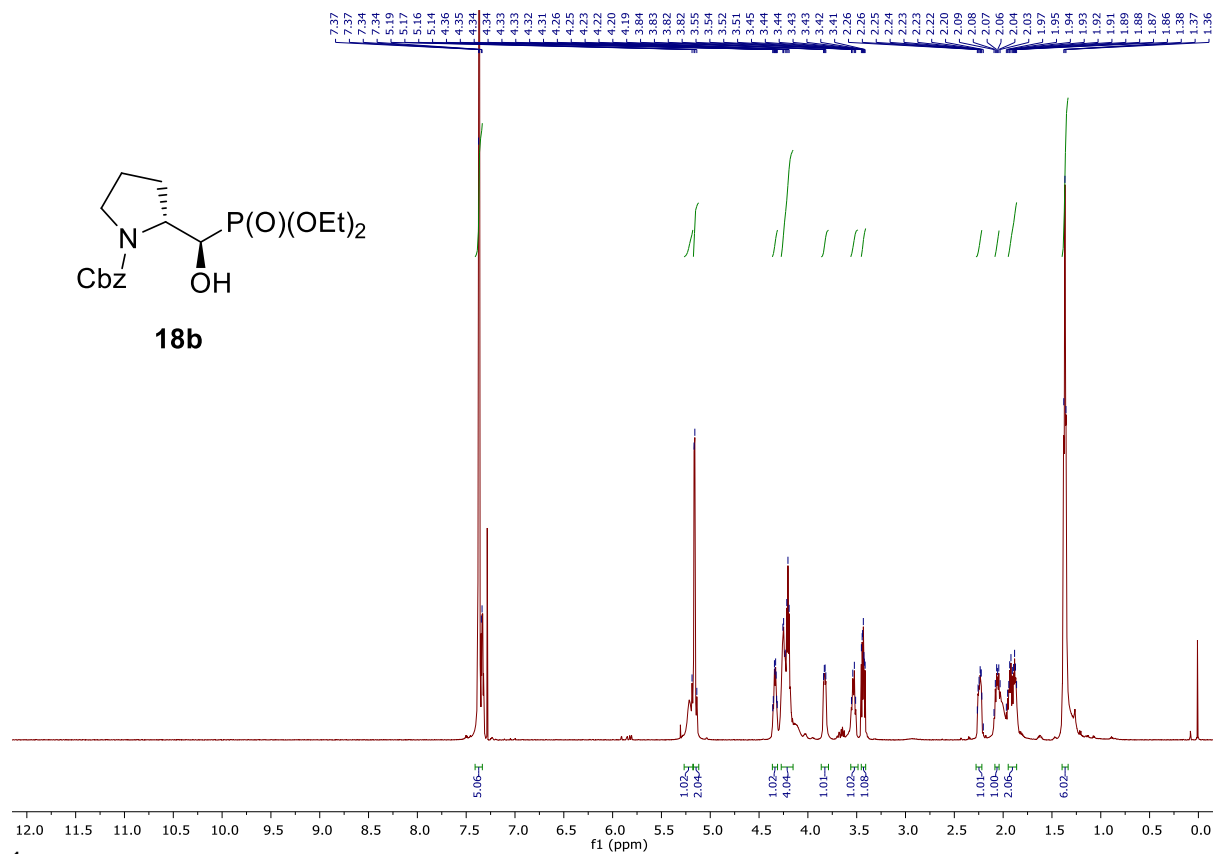
16b

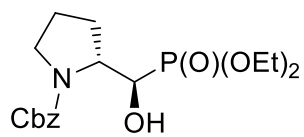


18a

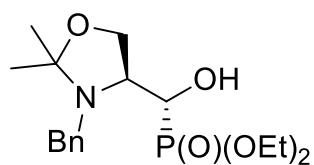
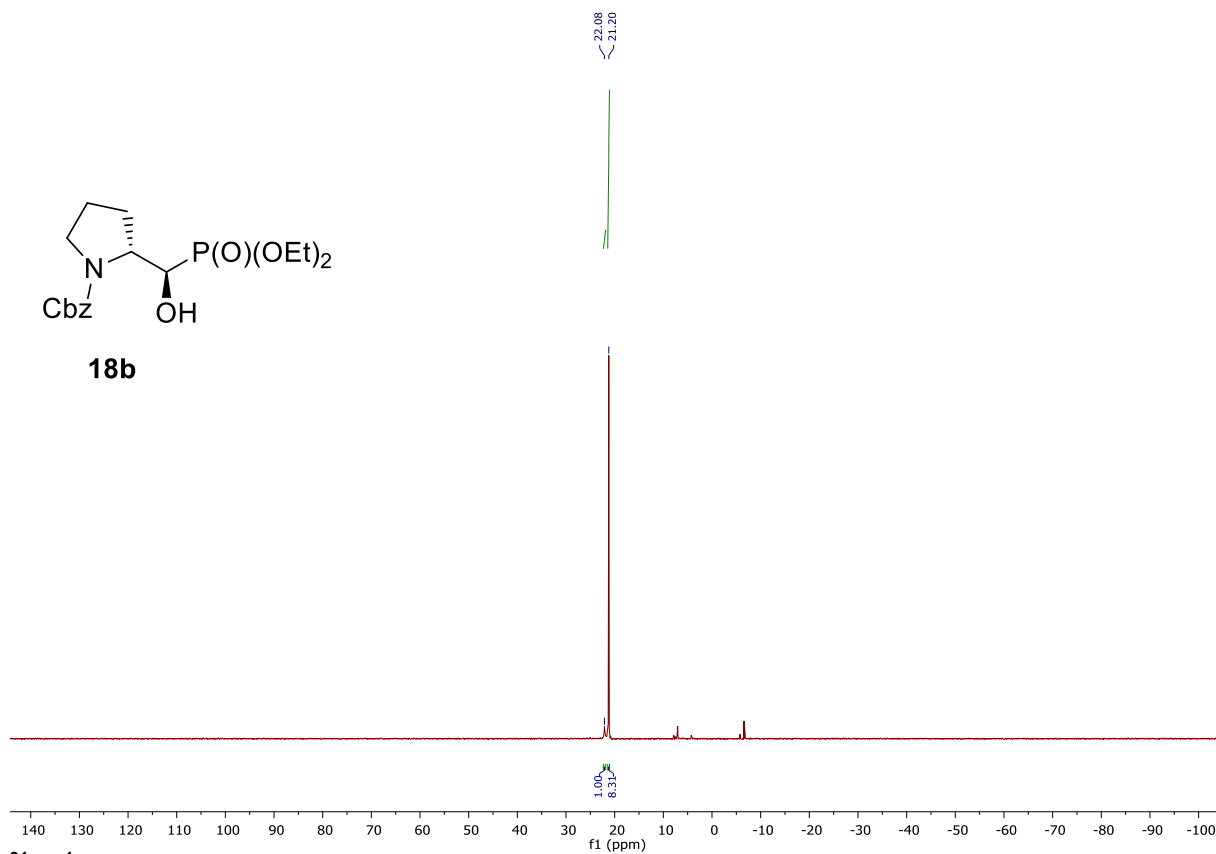




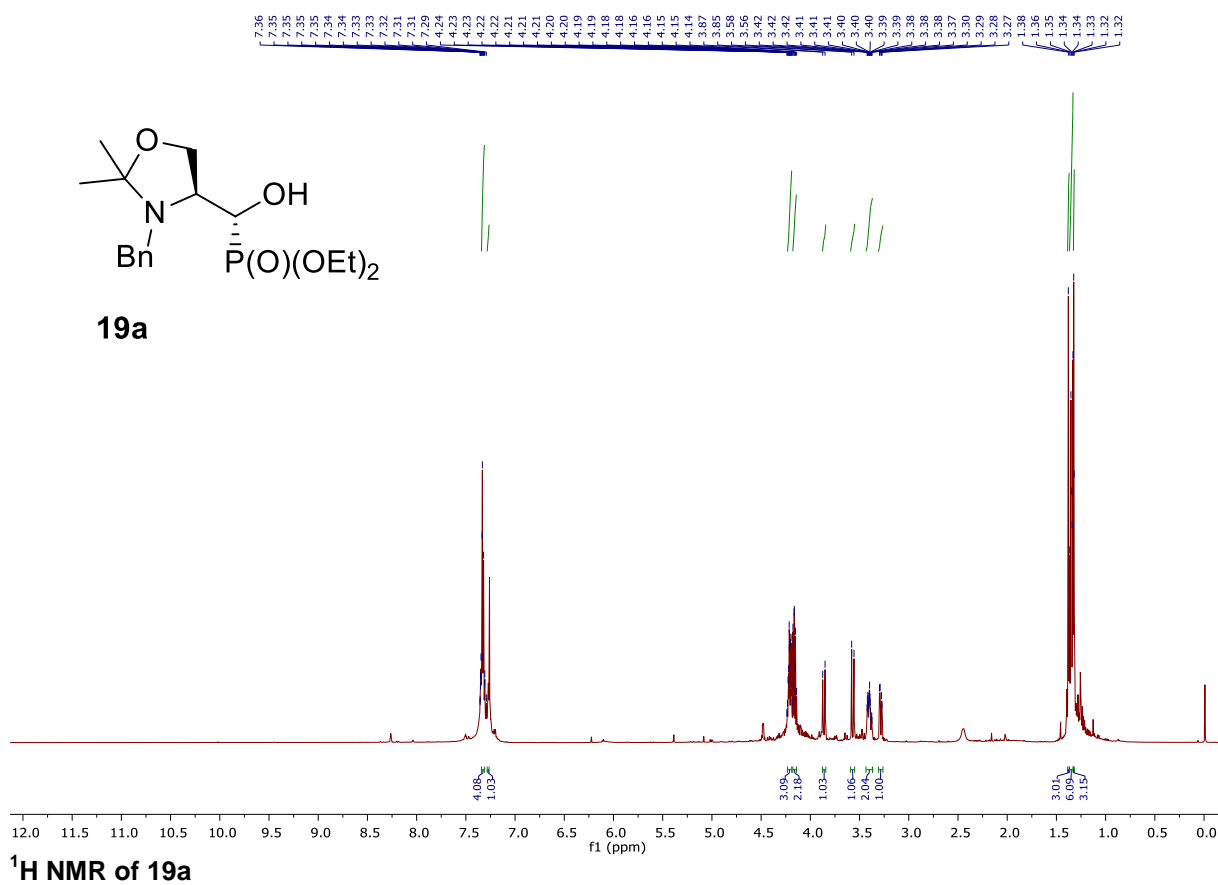


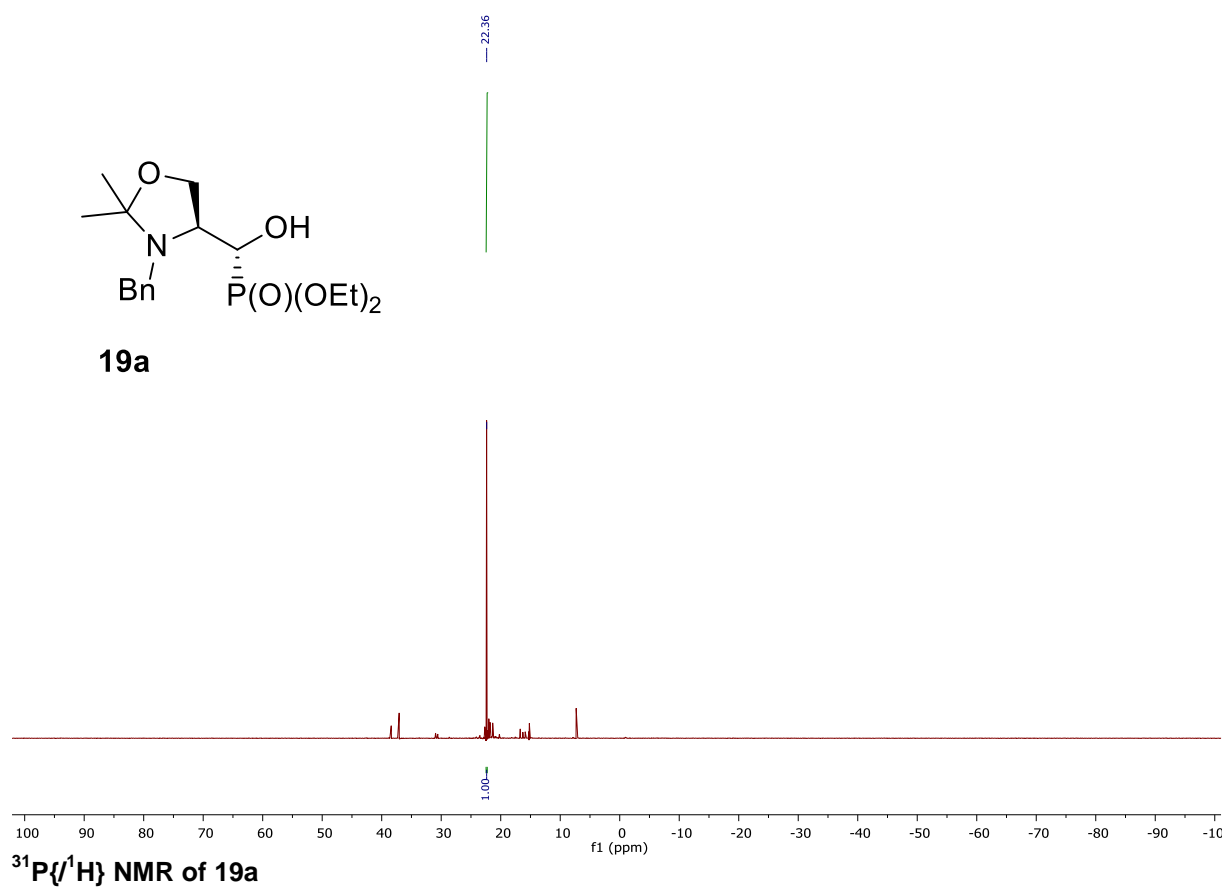
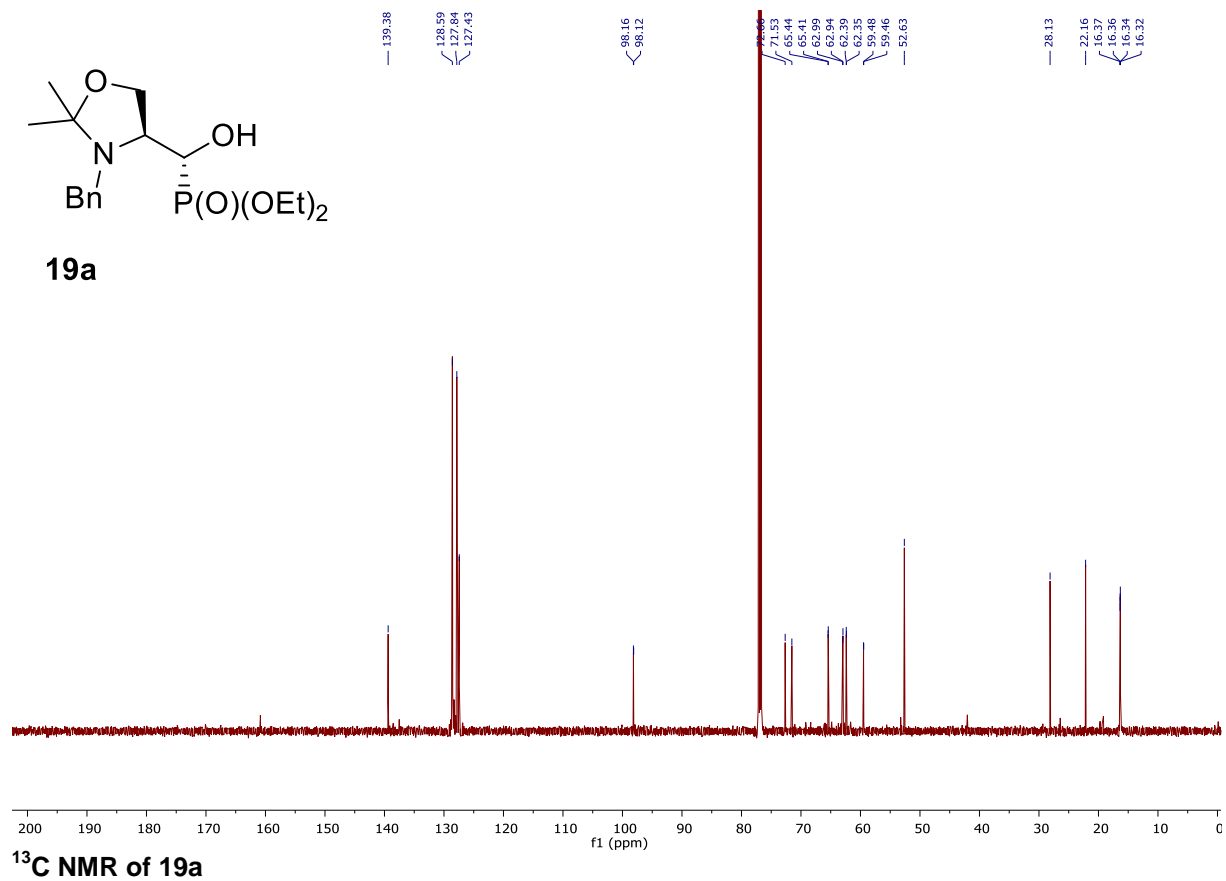


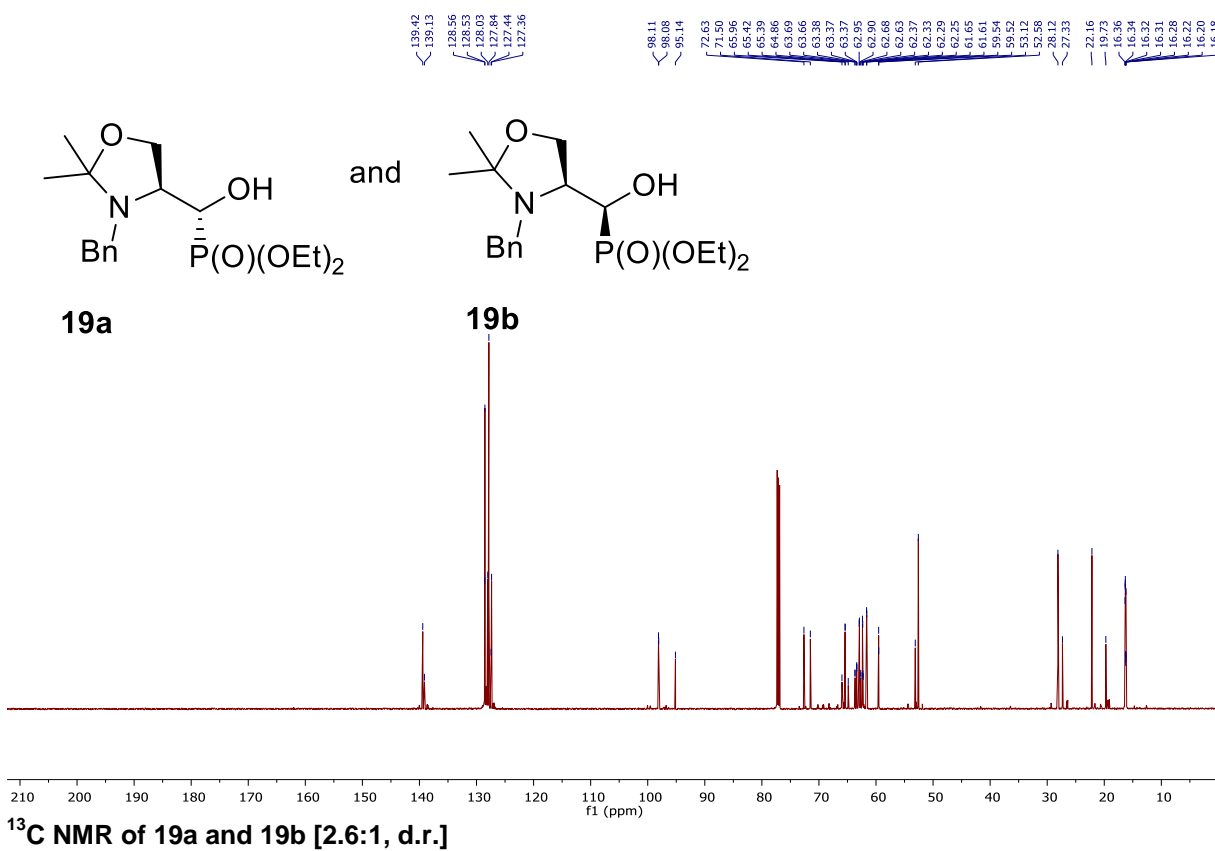
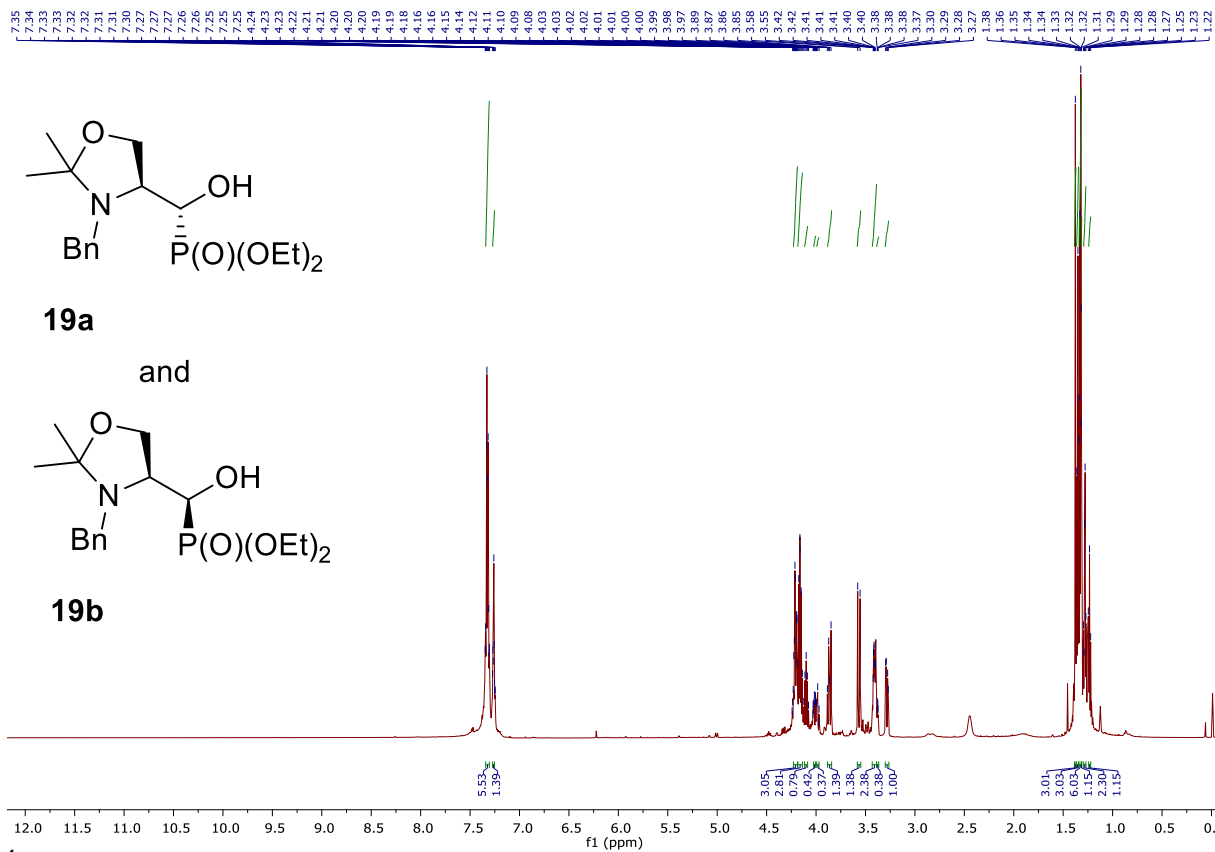
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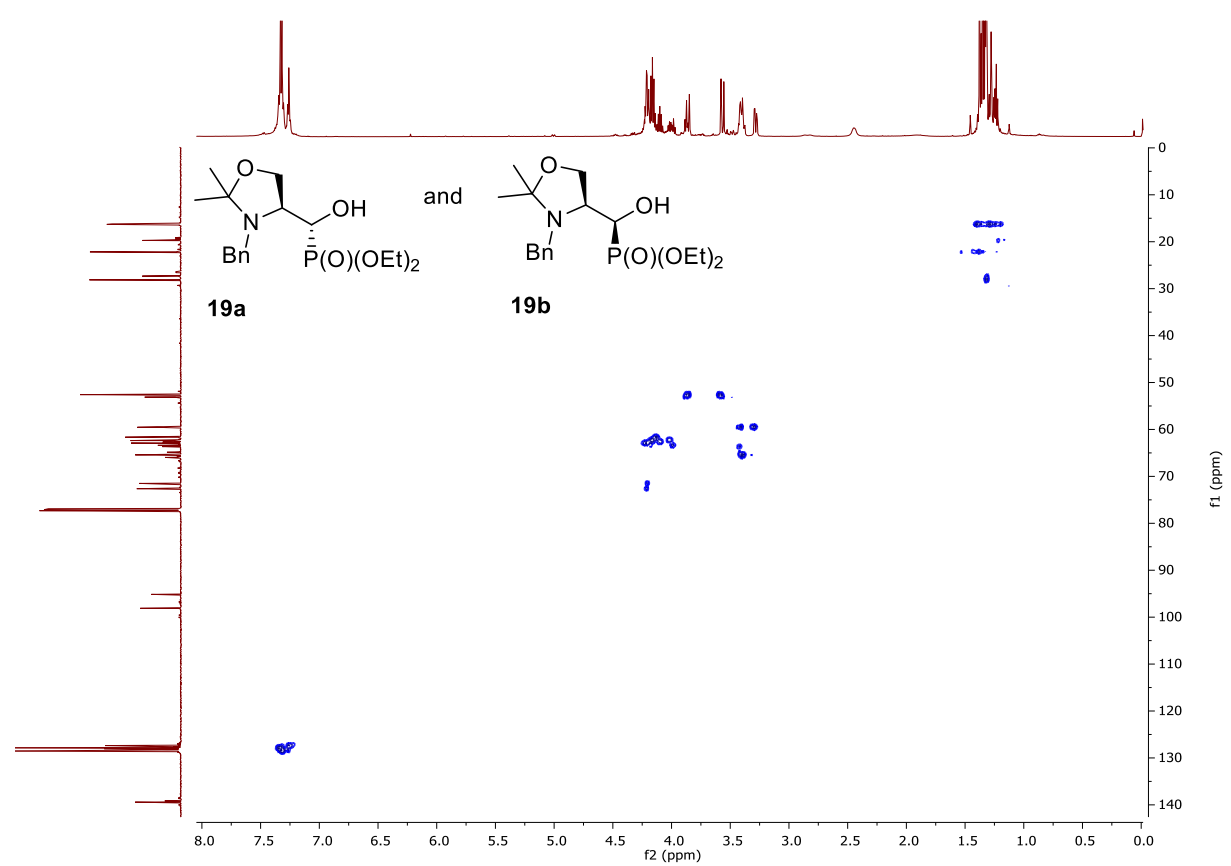
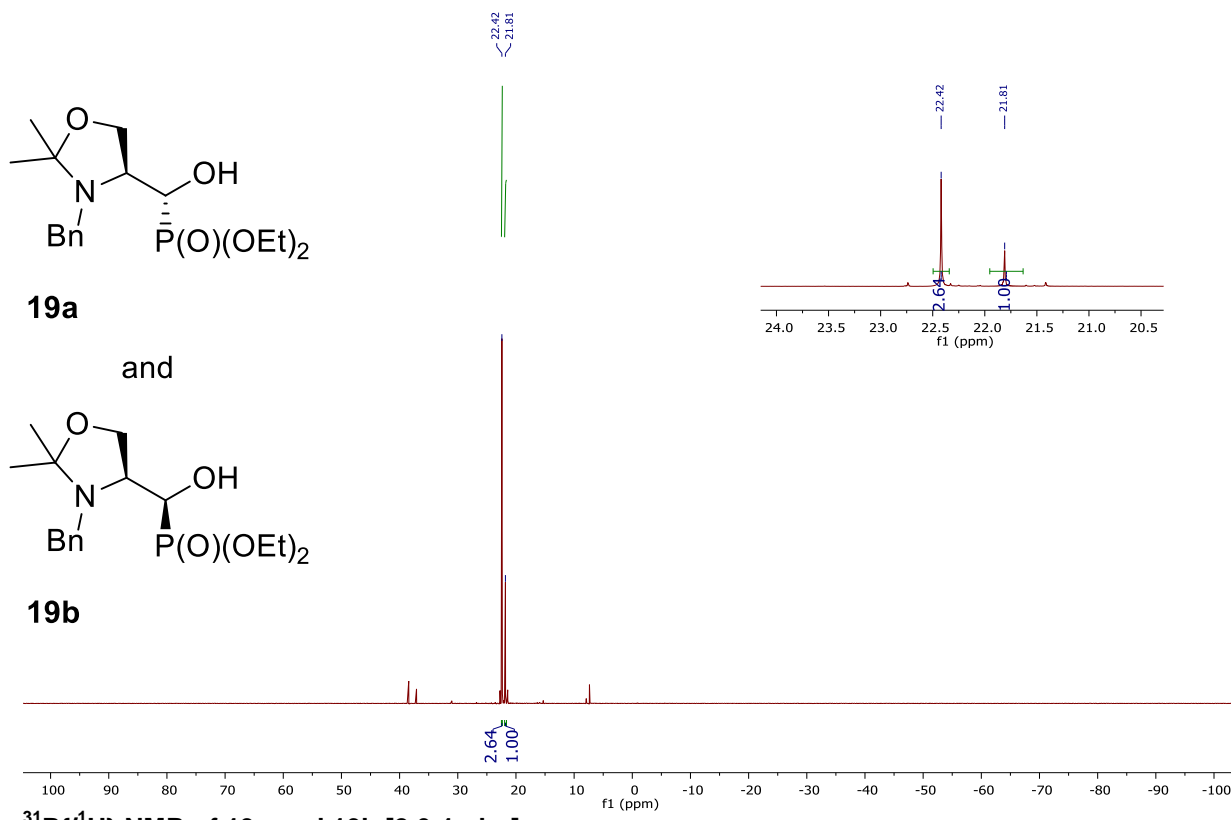


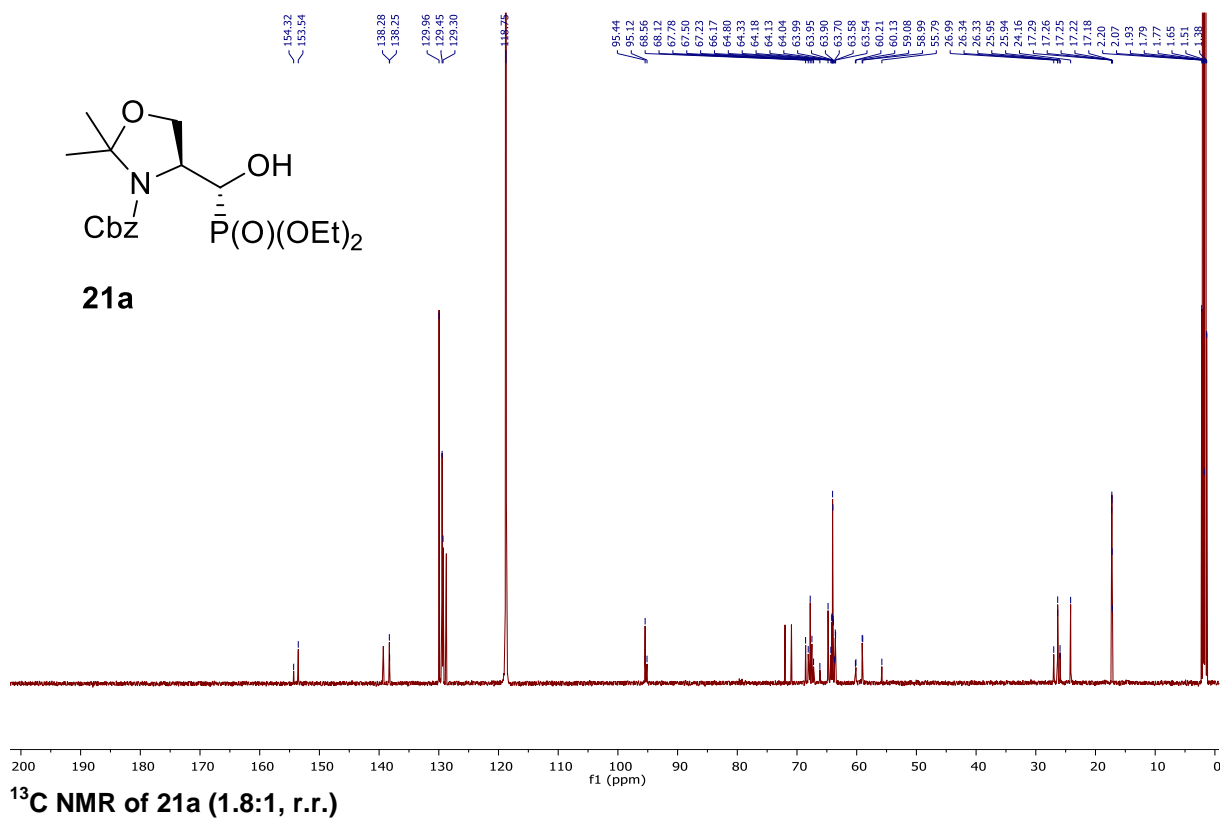
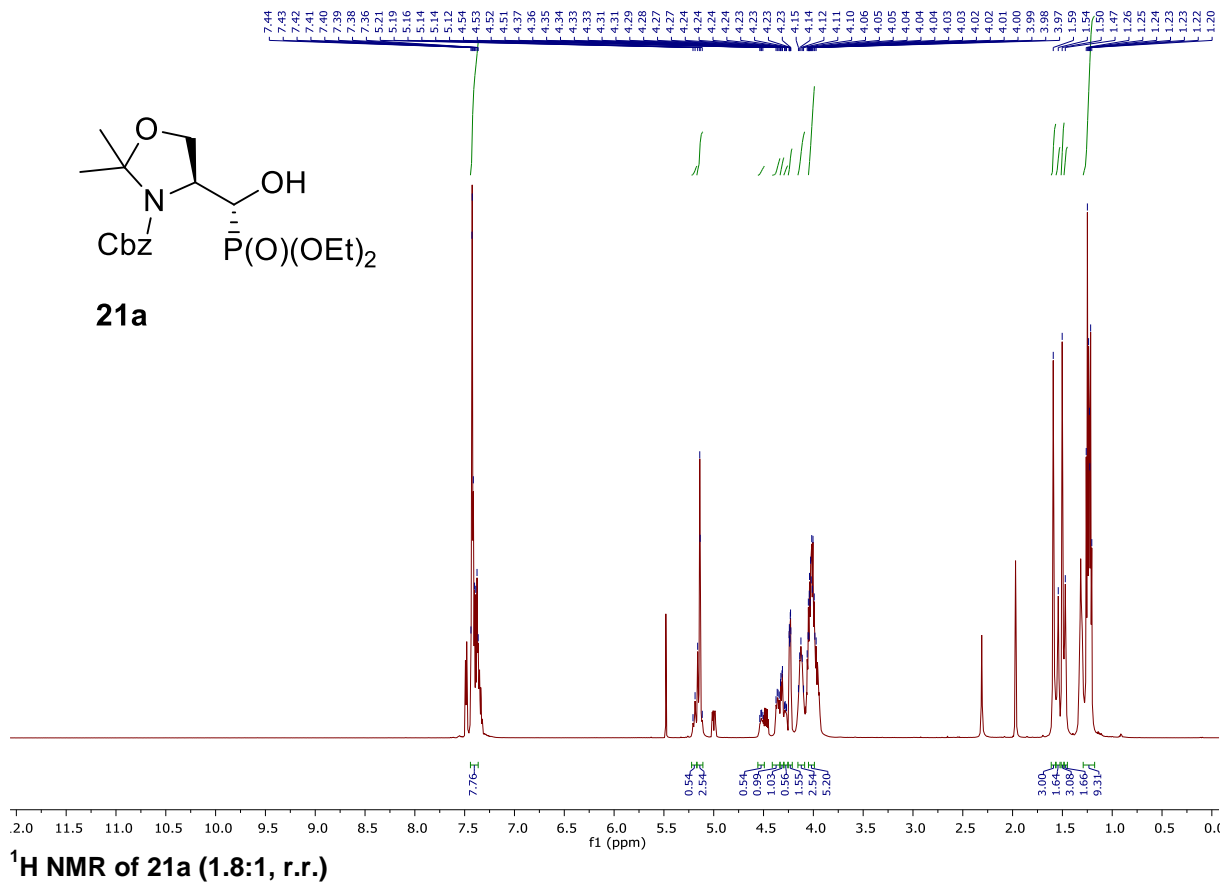
19a

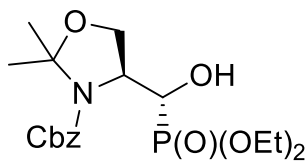




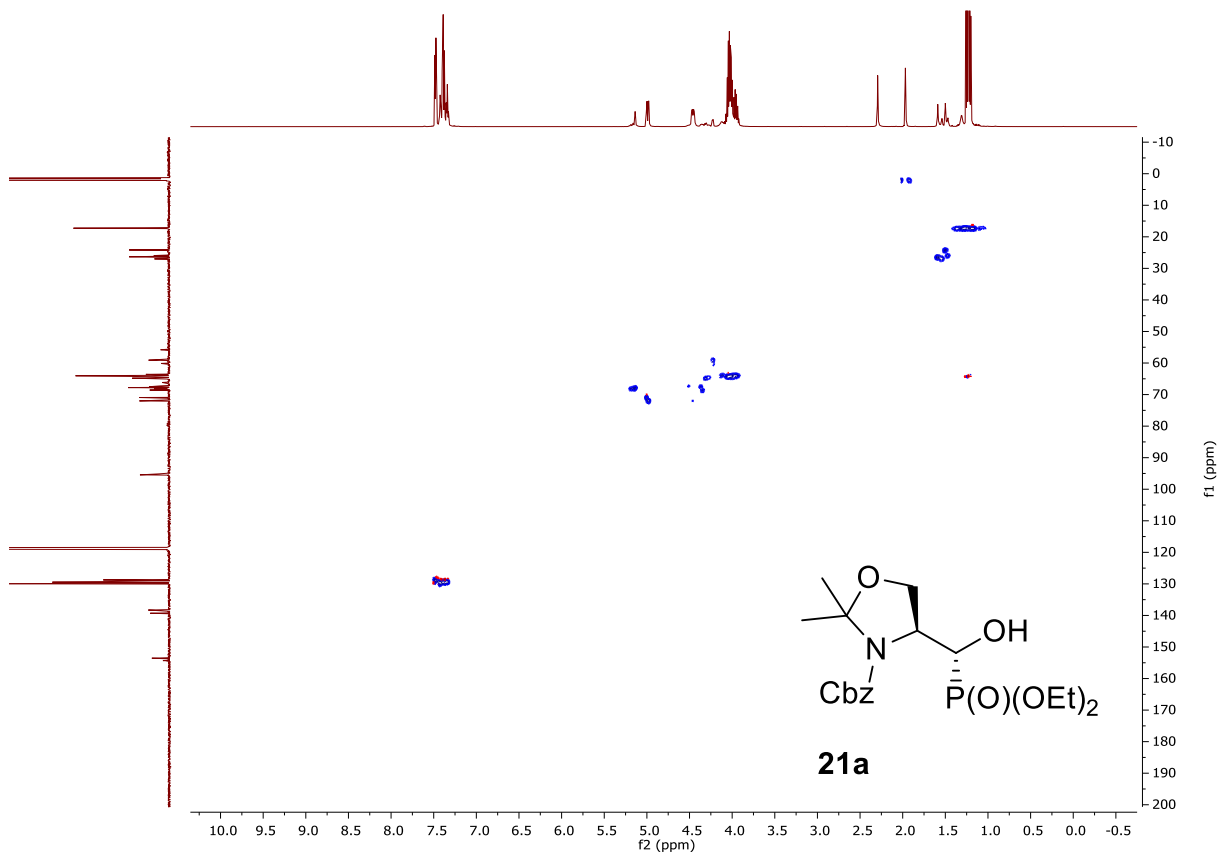
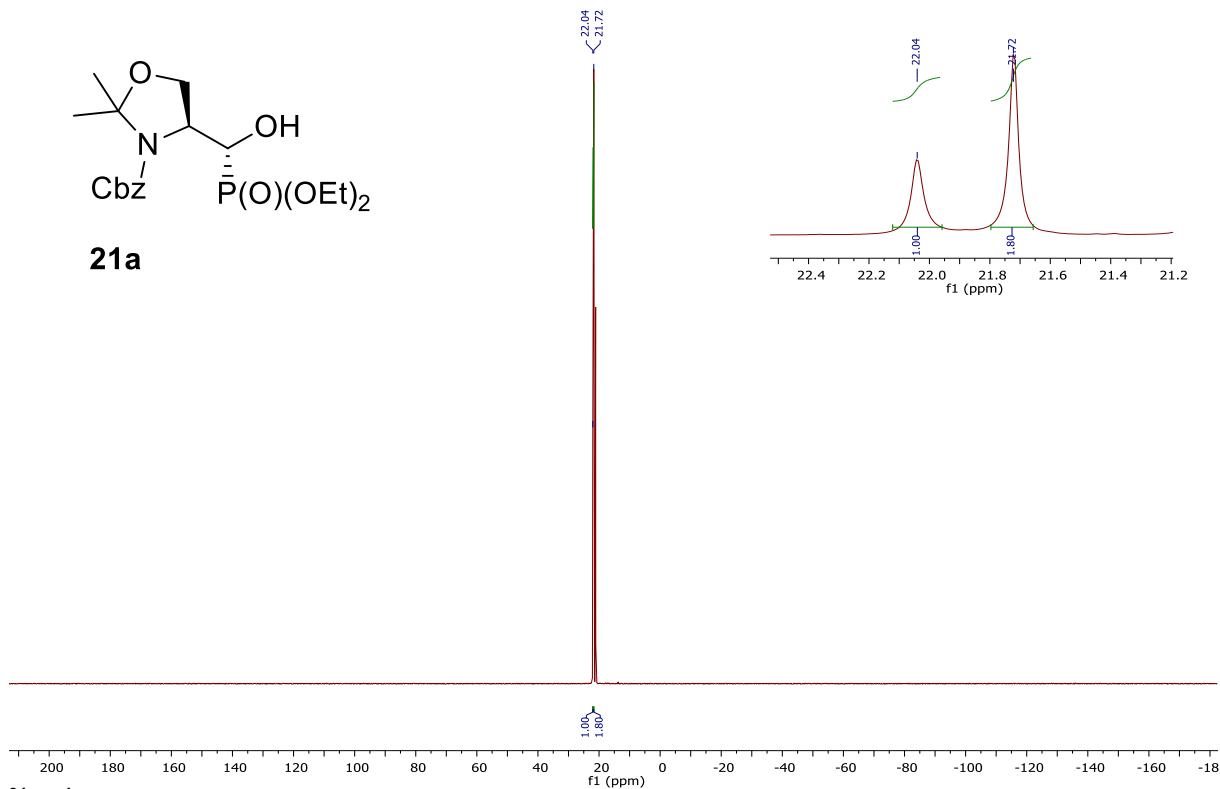


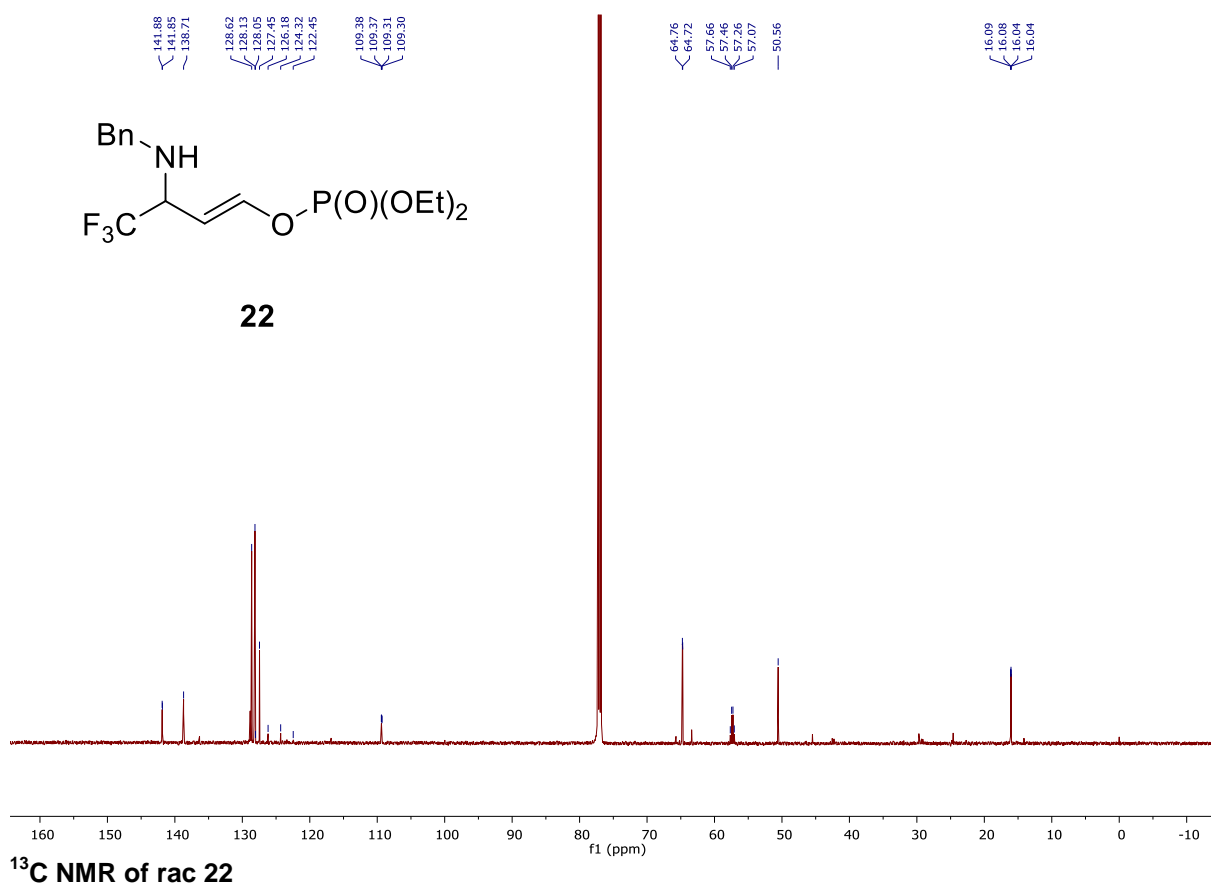
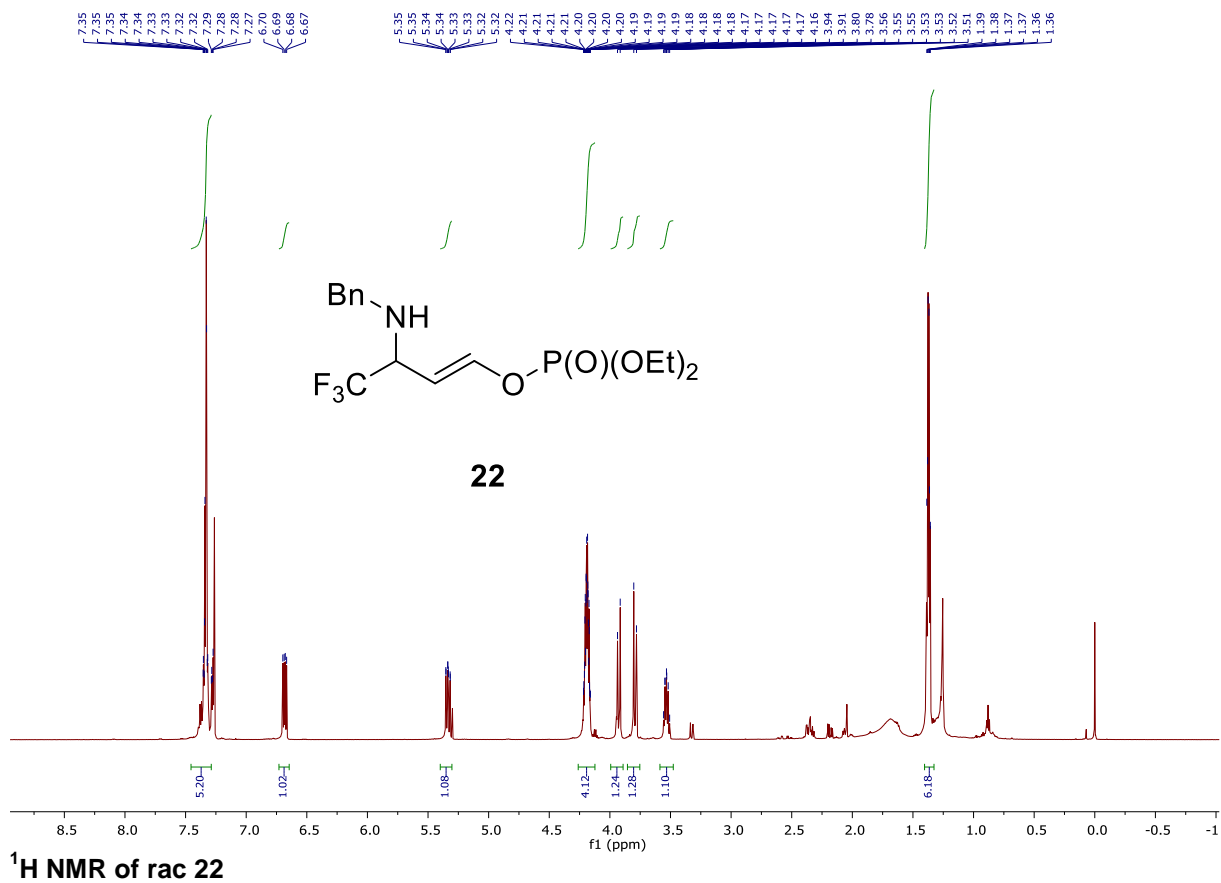


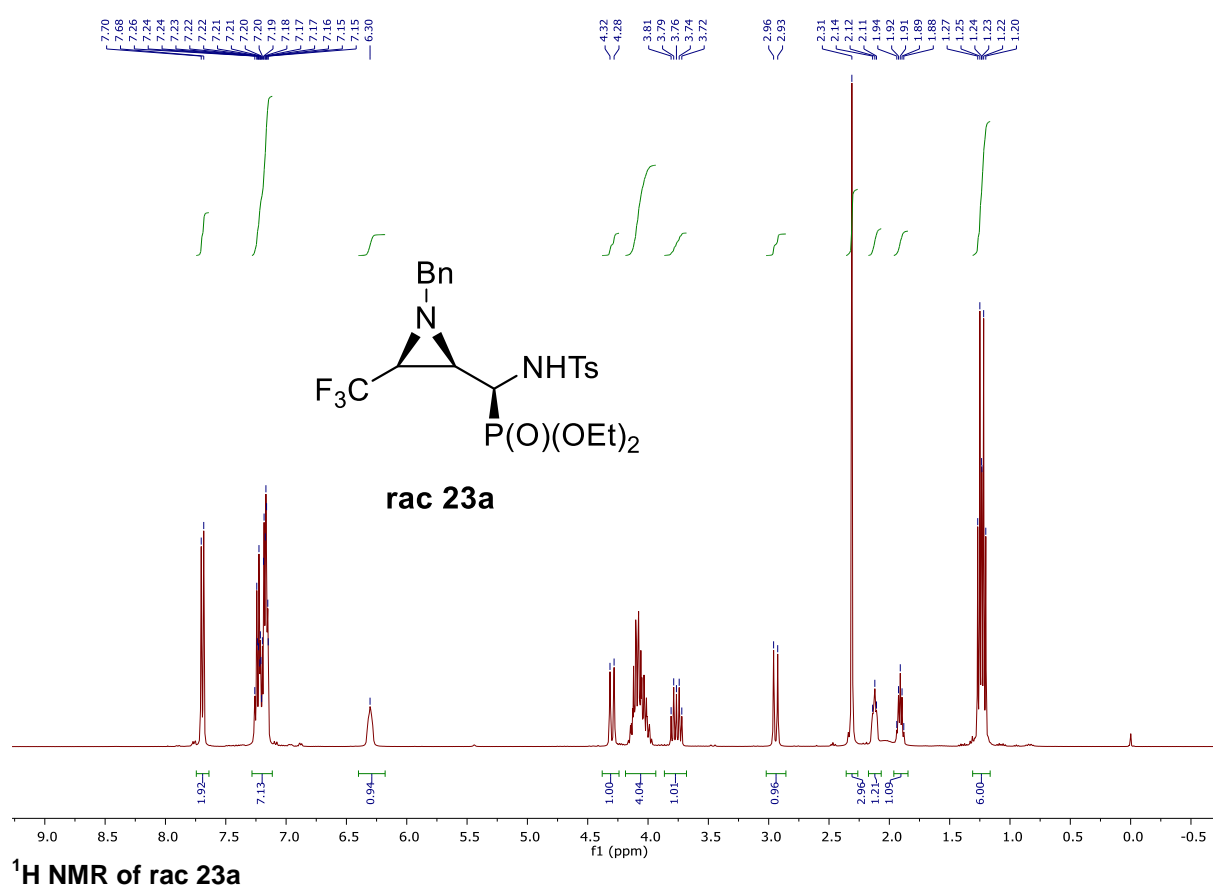
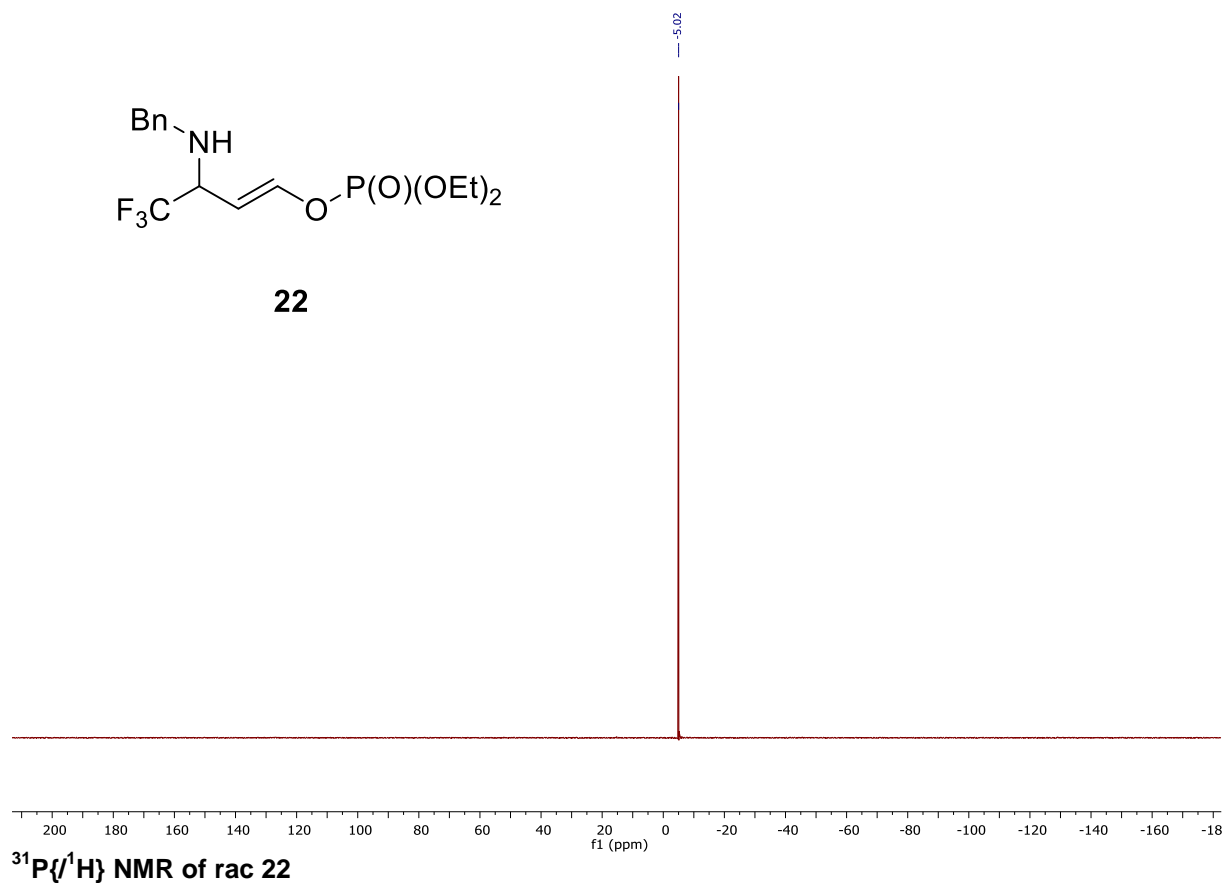


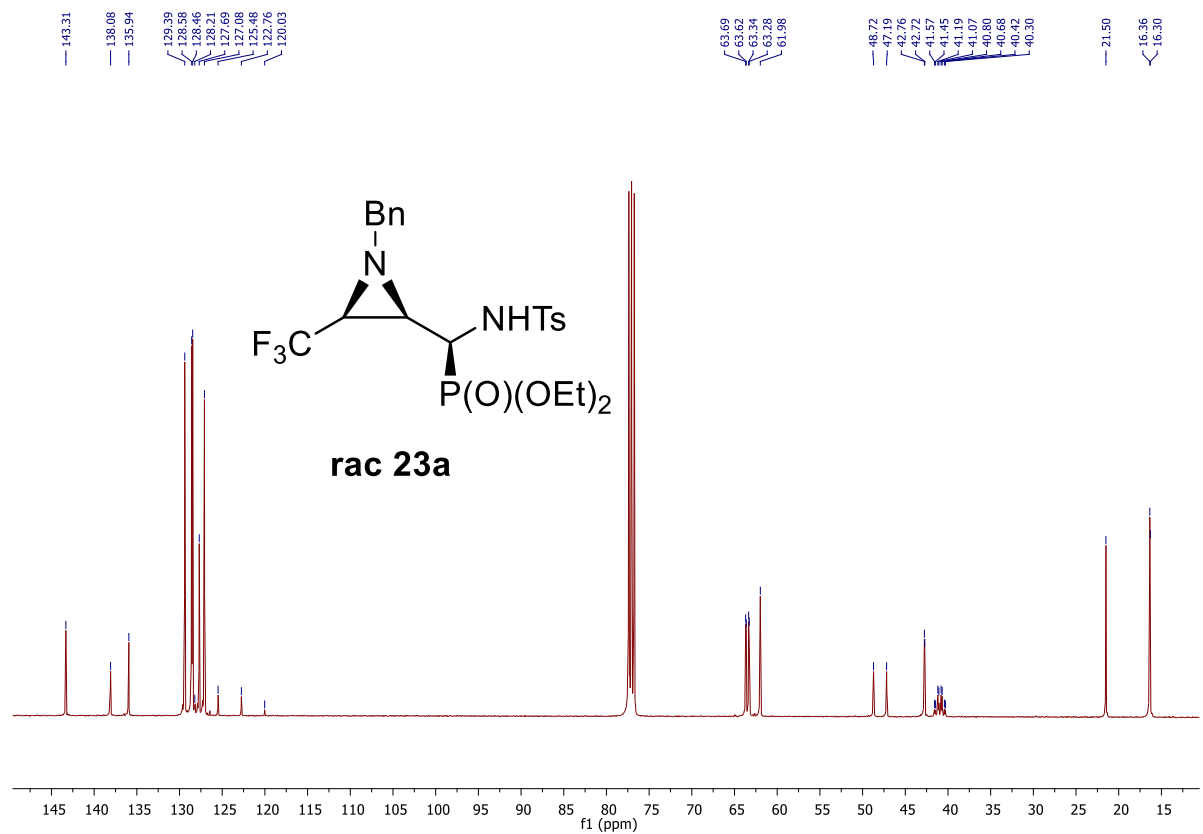


21a

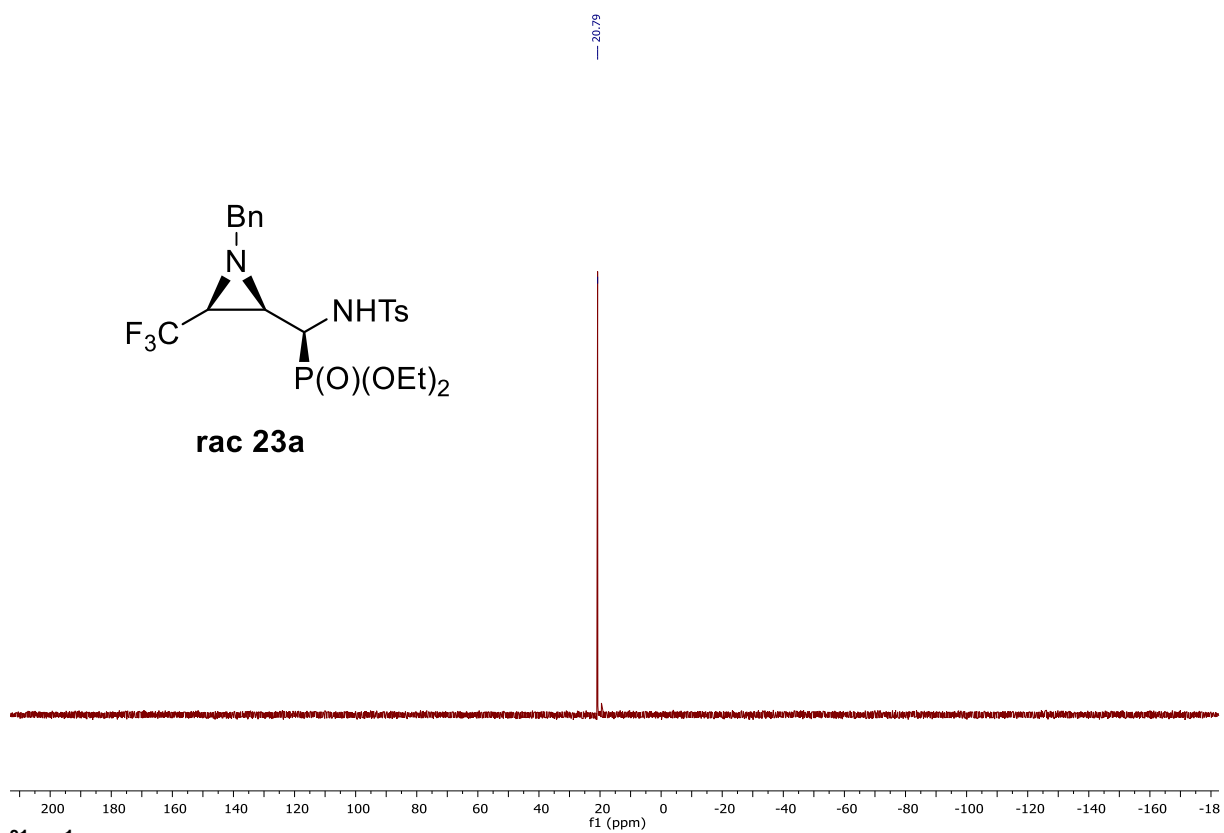




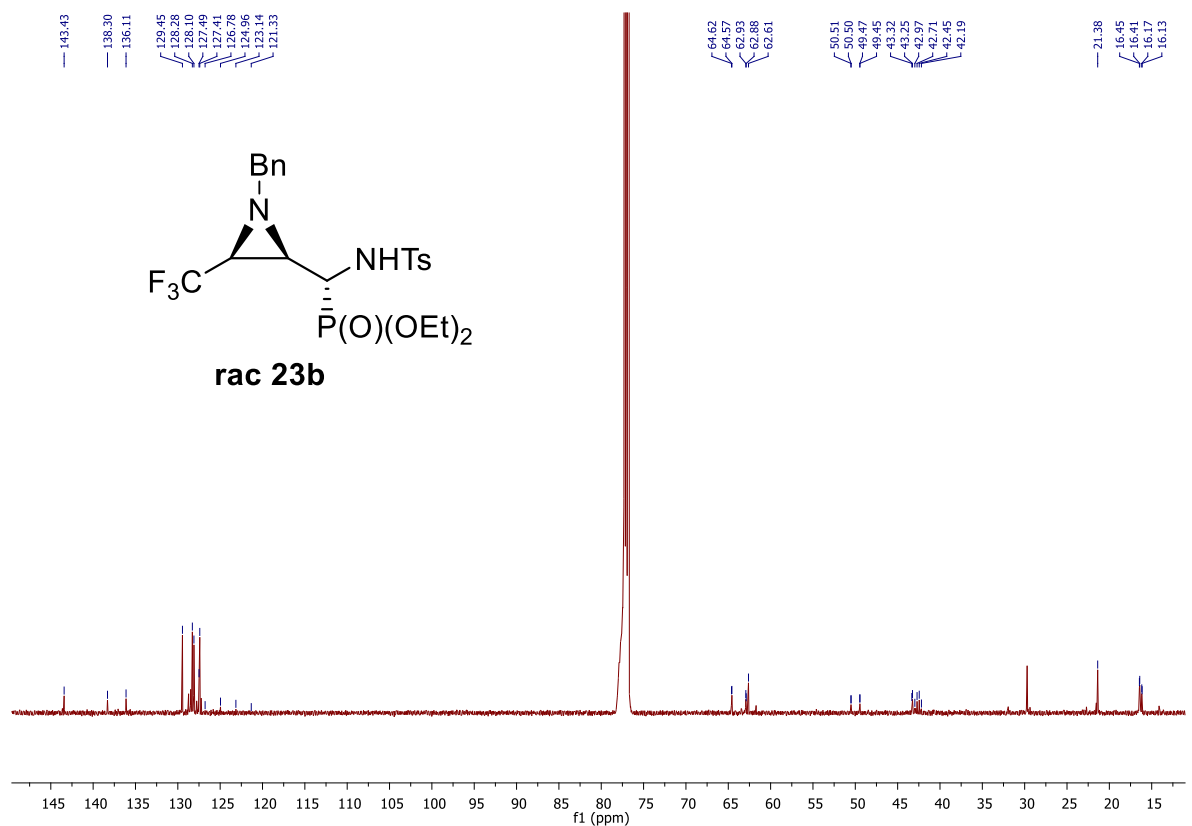
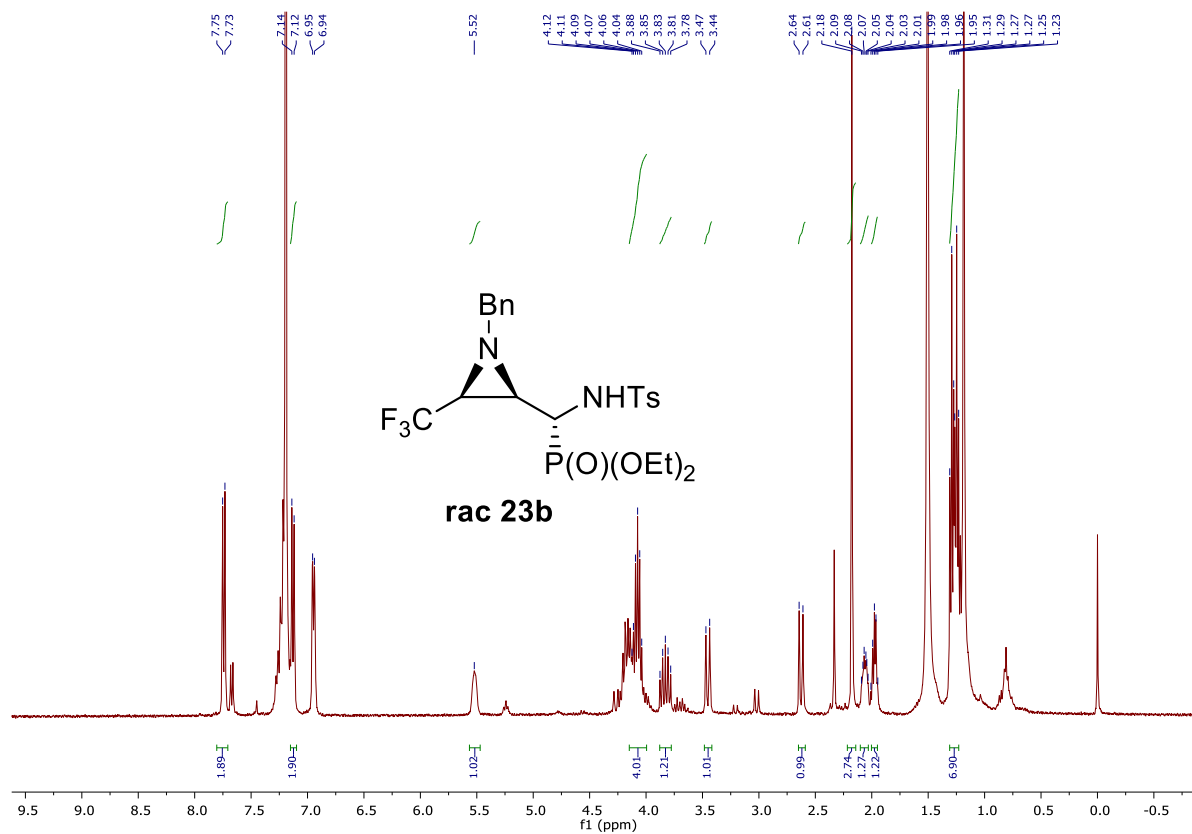


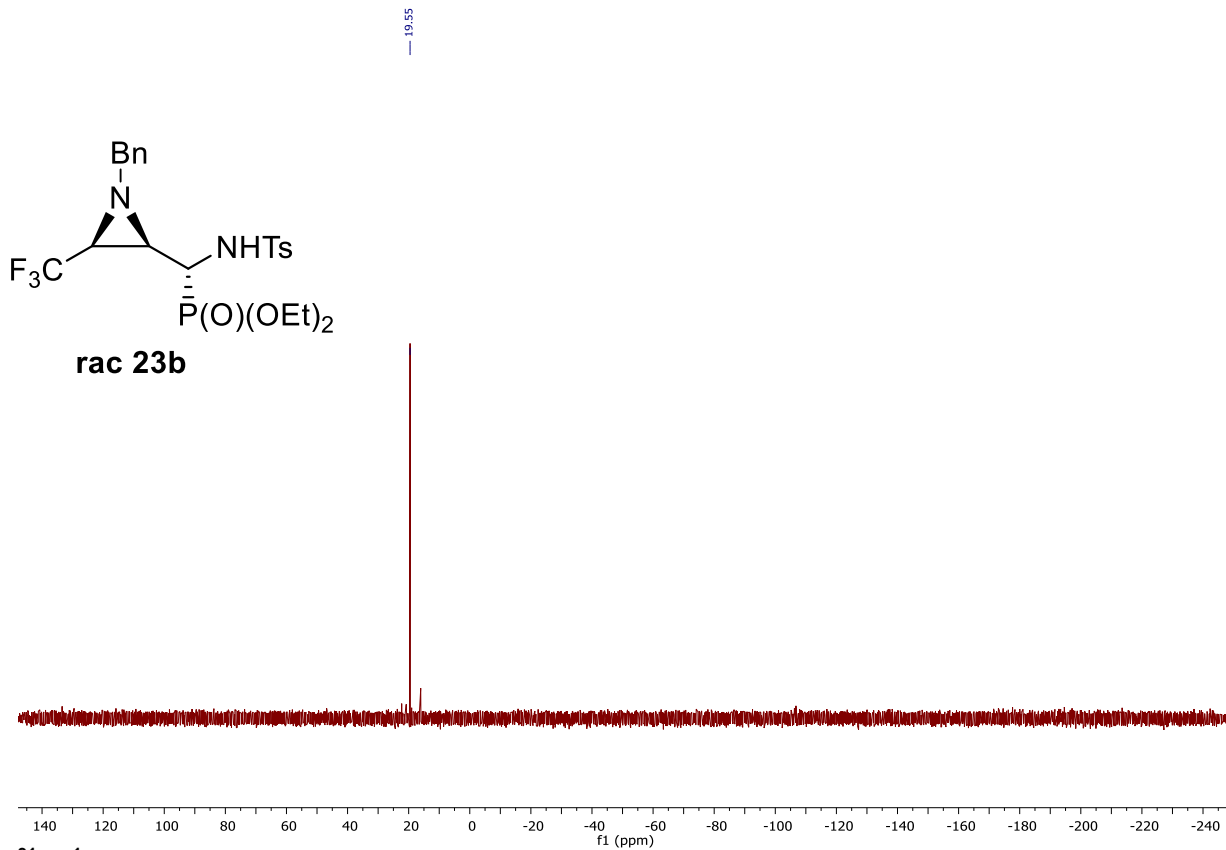


¹³C NMR of rac 23a

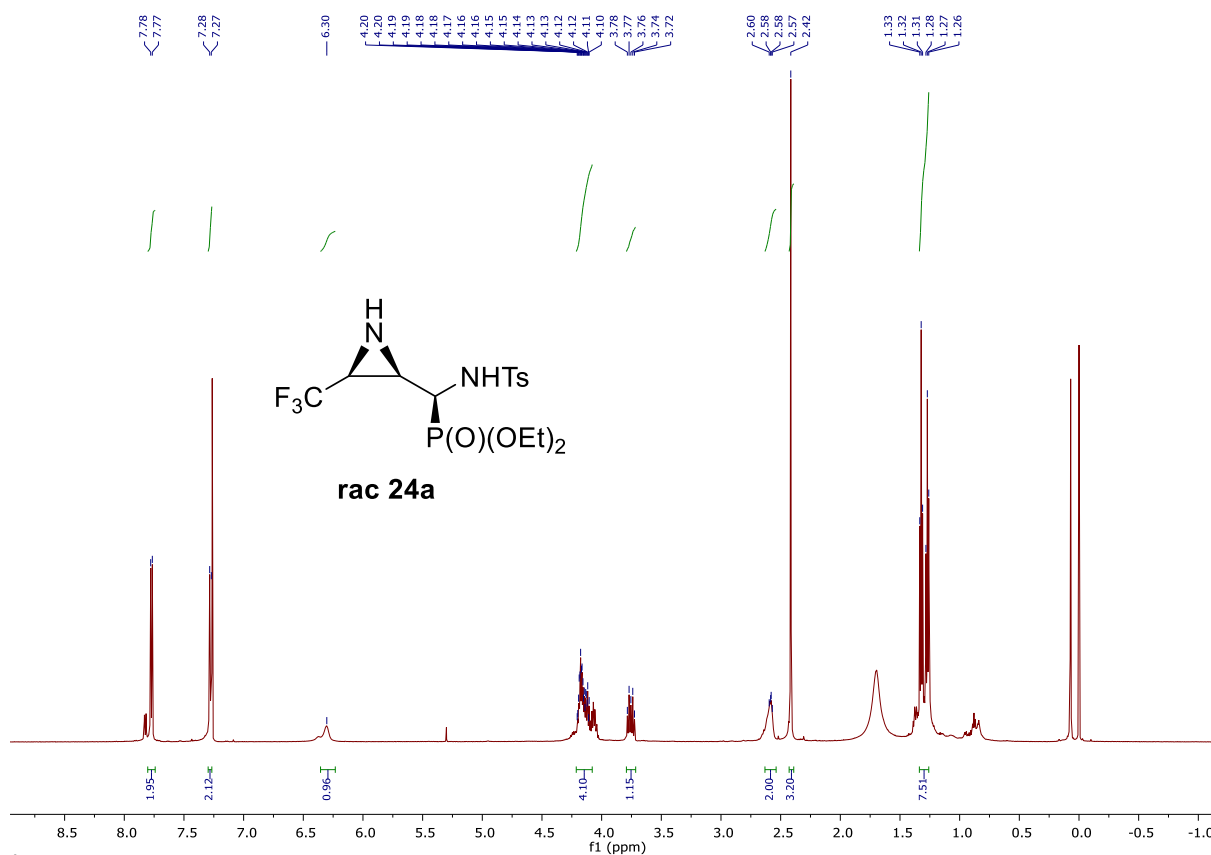


³¹P{¹H} NMR of rac 23a

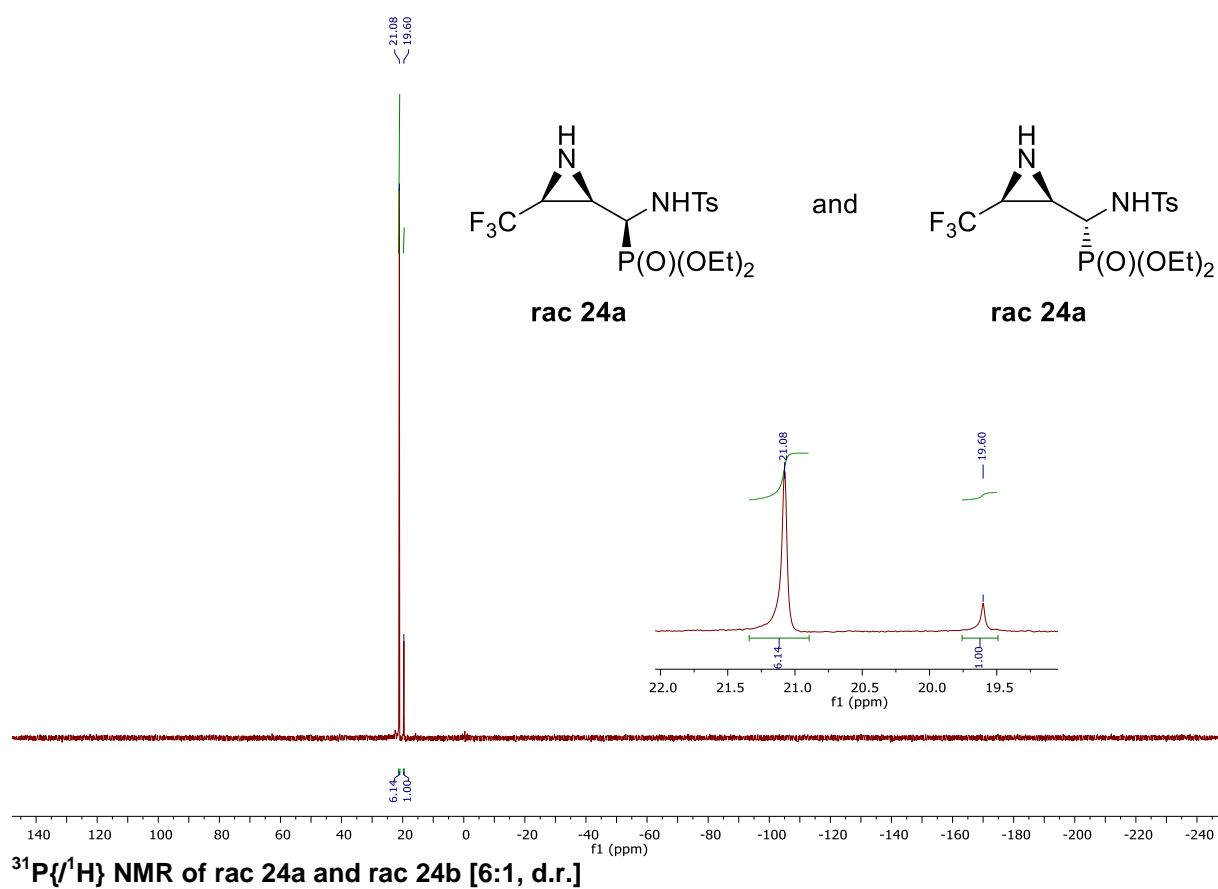
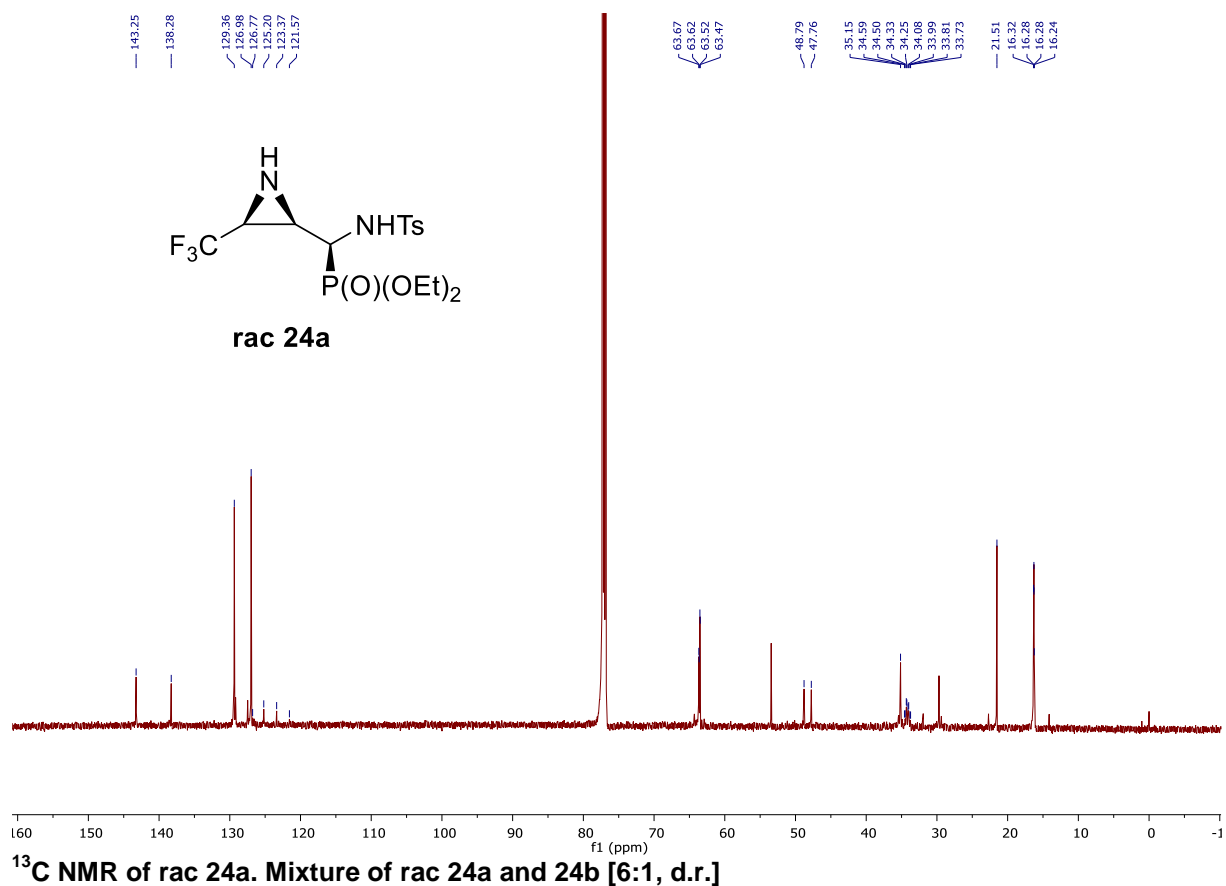




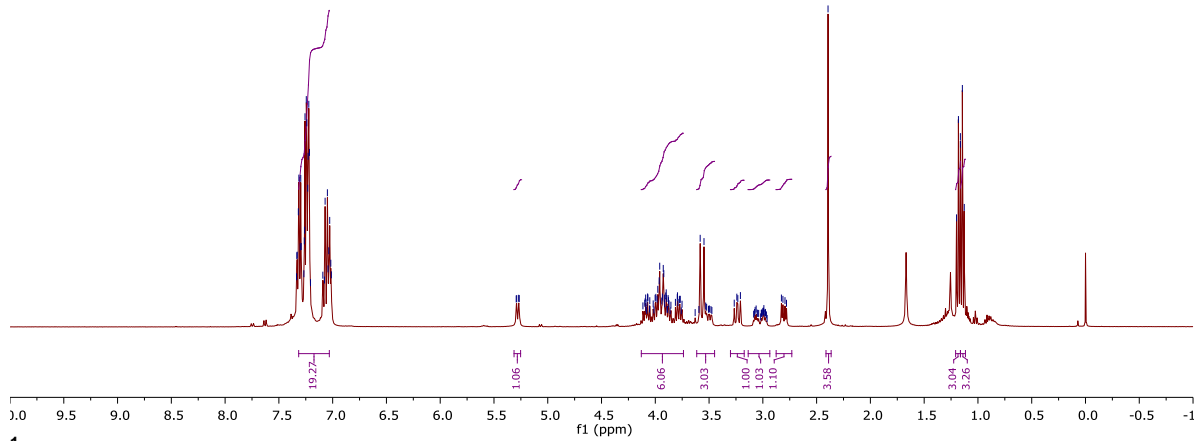
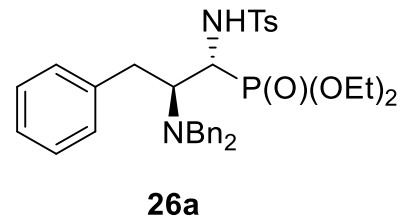
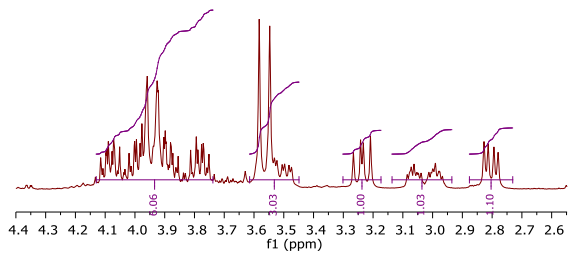
³¹P{¹H} NMR of rac 23b



¹H NMR of rac 24a. Mixture of rac 24a and 24b [6:1, d.r.]



7.34
7.33
7.33
7.31
7.31
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7.07
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7.04
7.04
7.03
7.02
7.01
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5.29
5.29
5.27
5.27
4.12
4.10
4.09
4.09
4.08
4.07
4.07
4.05
4.05
4.02
4.00
3.99
3.98
3.98
3.96
3.96
3.94
3.93
3.92
3.91
3.91
3.90
3.90
3.88
3.88
3.85
3.85
3.81
3.80
3.79
3.79
3.77
3.77
3.75
3.58
3.55
3.53
3.52
3.52
3.24
3.24
3.23
3.21
3.21
2.83
2.81
2.79
2.79
2.39
1.20
1.18
1.16
1.14
1.14
1.13



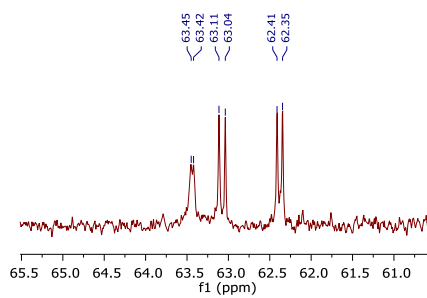
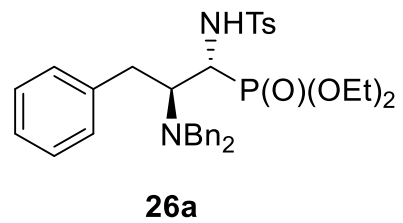
¹H NMR of 26a

142.89
139.09
138.84
136.84
129.51
129.51
128.87
128.87
128.40
128.31
127.18
127.11
126.17

63.45
63.42
63.11
63.04
62.41
62.35
54.50
49.43
47.90

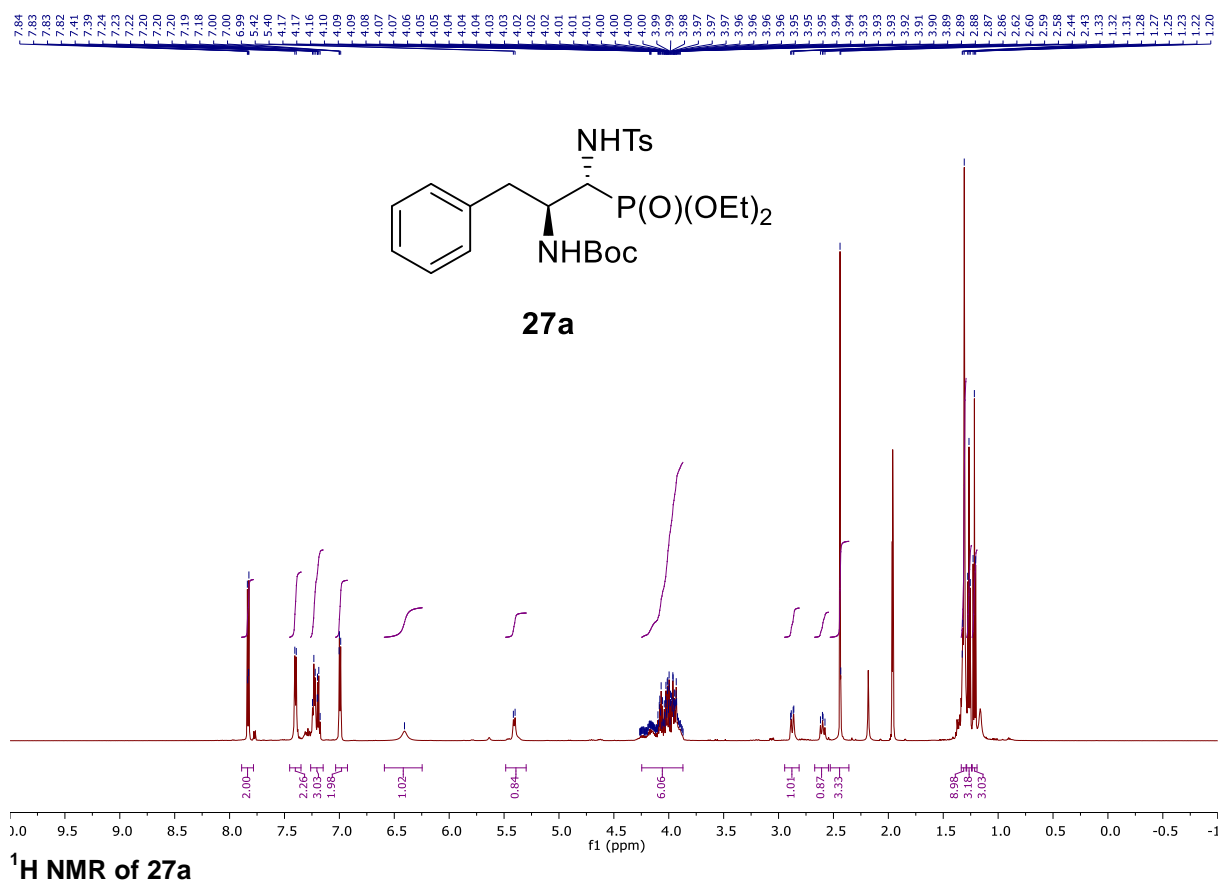
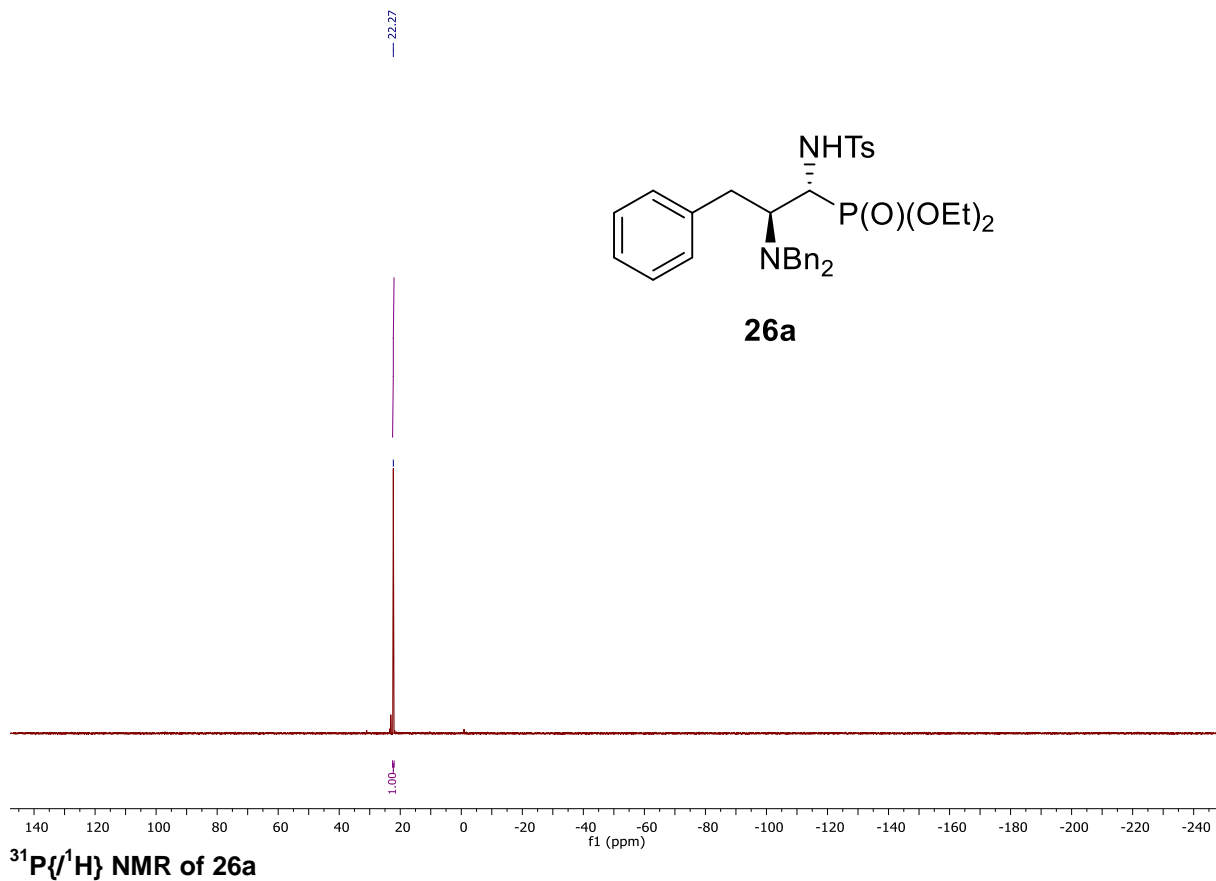
31.46

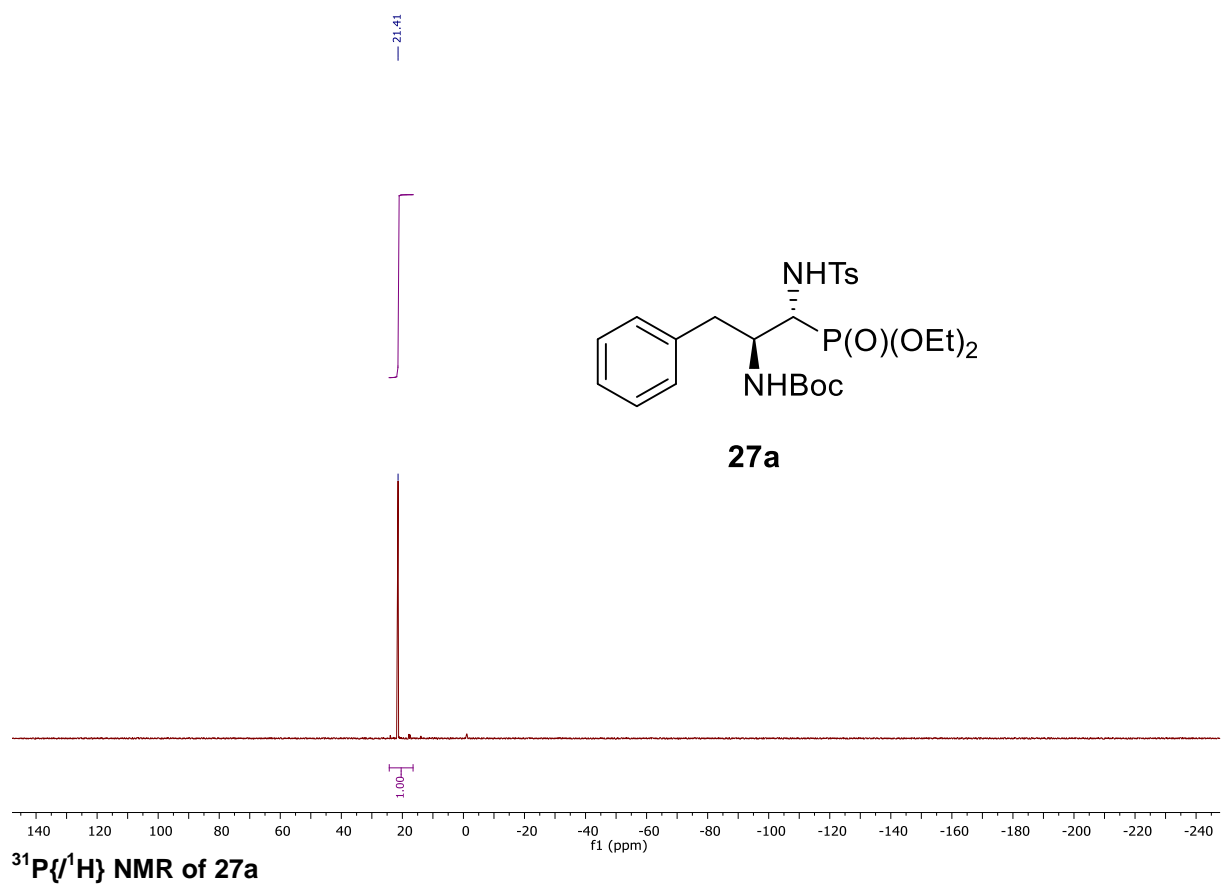
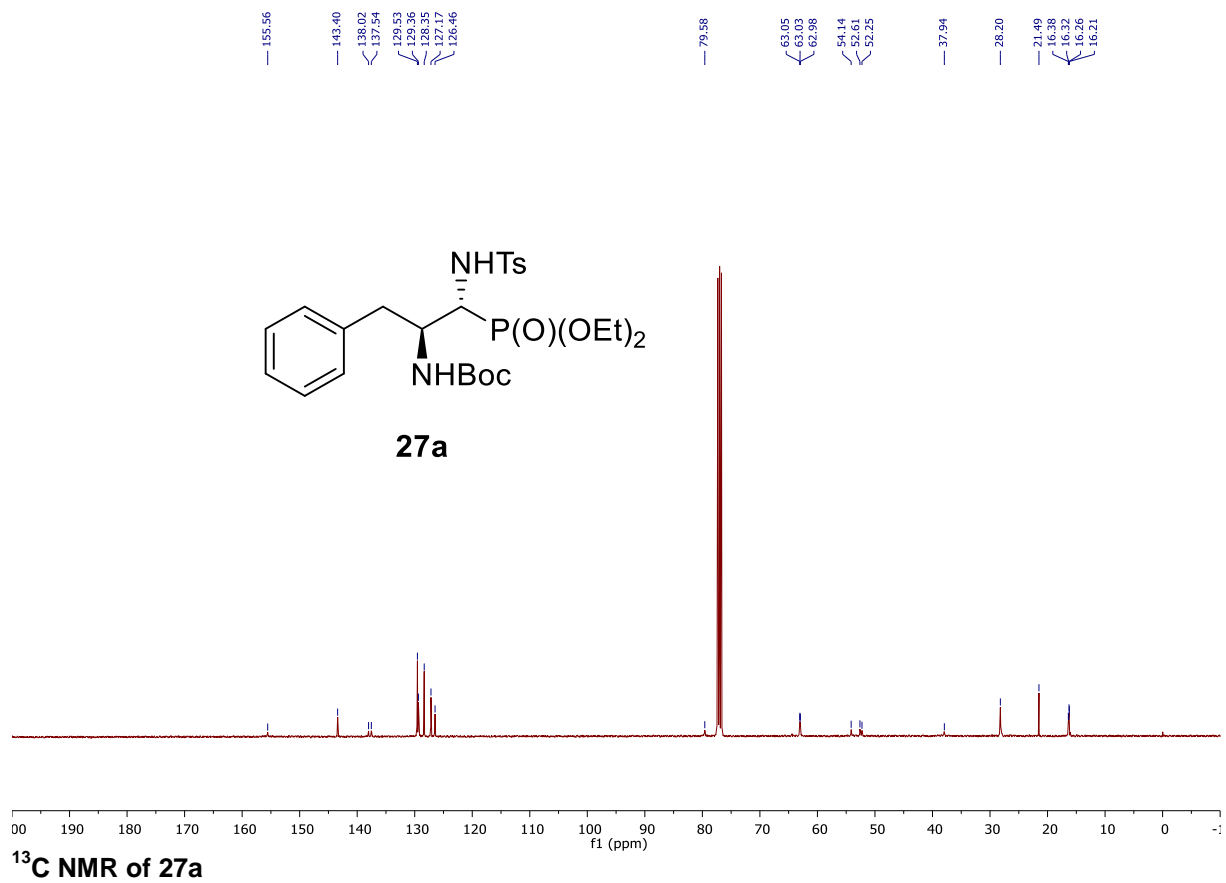
21.50
16.23
16.22
16.21
16.15
16.15

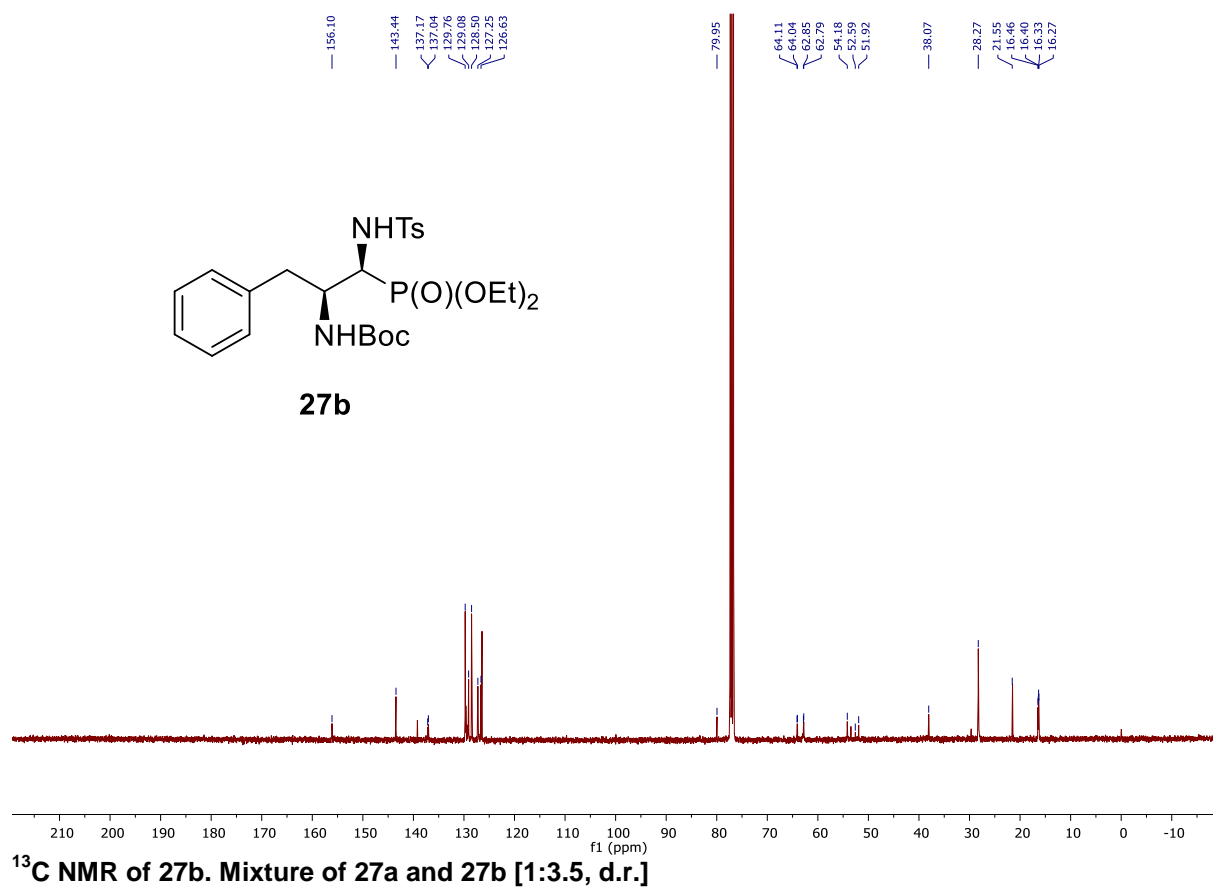
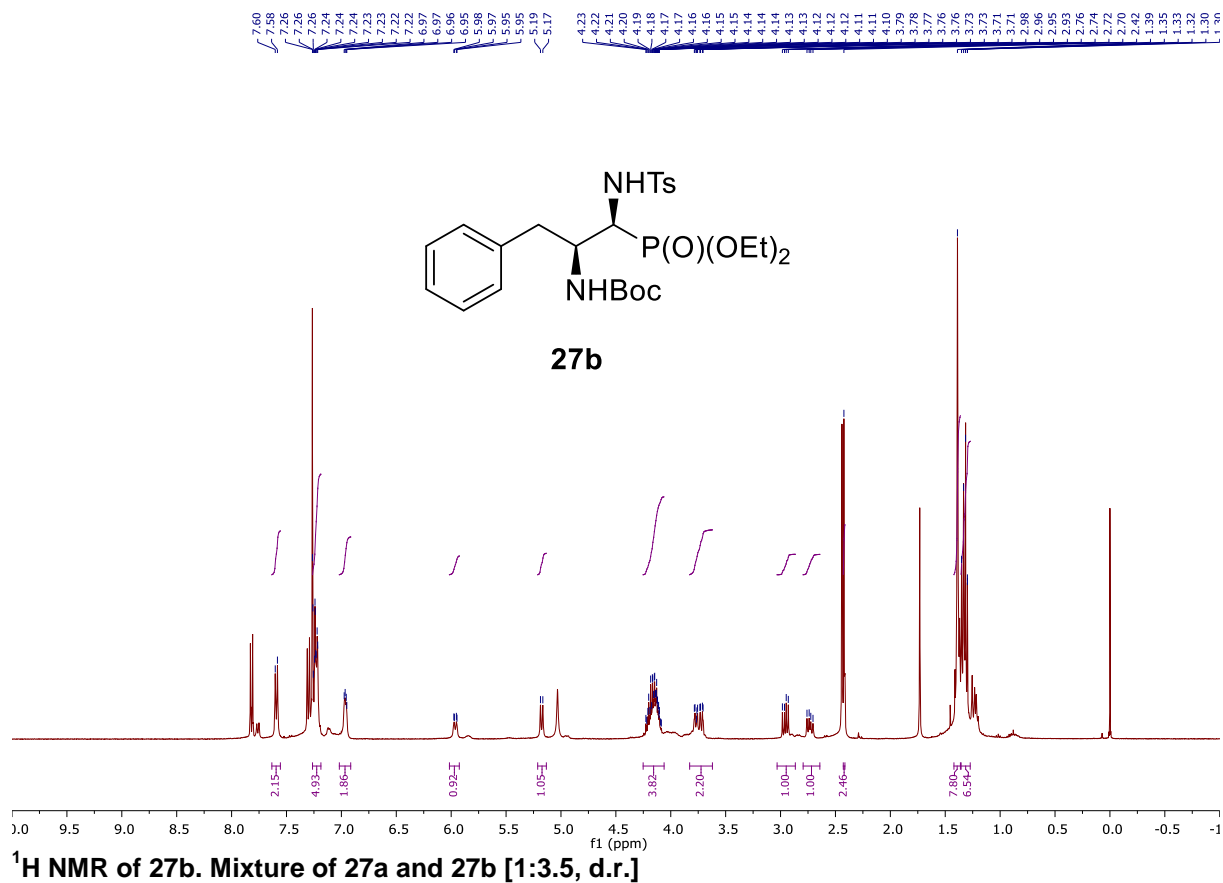


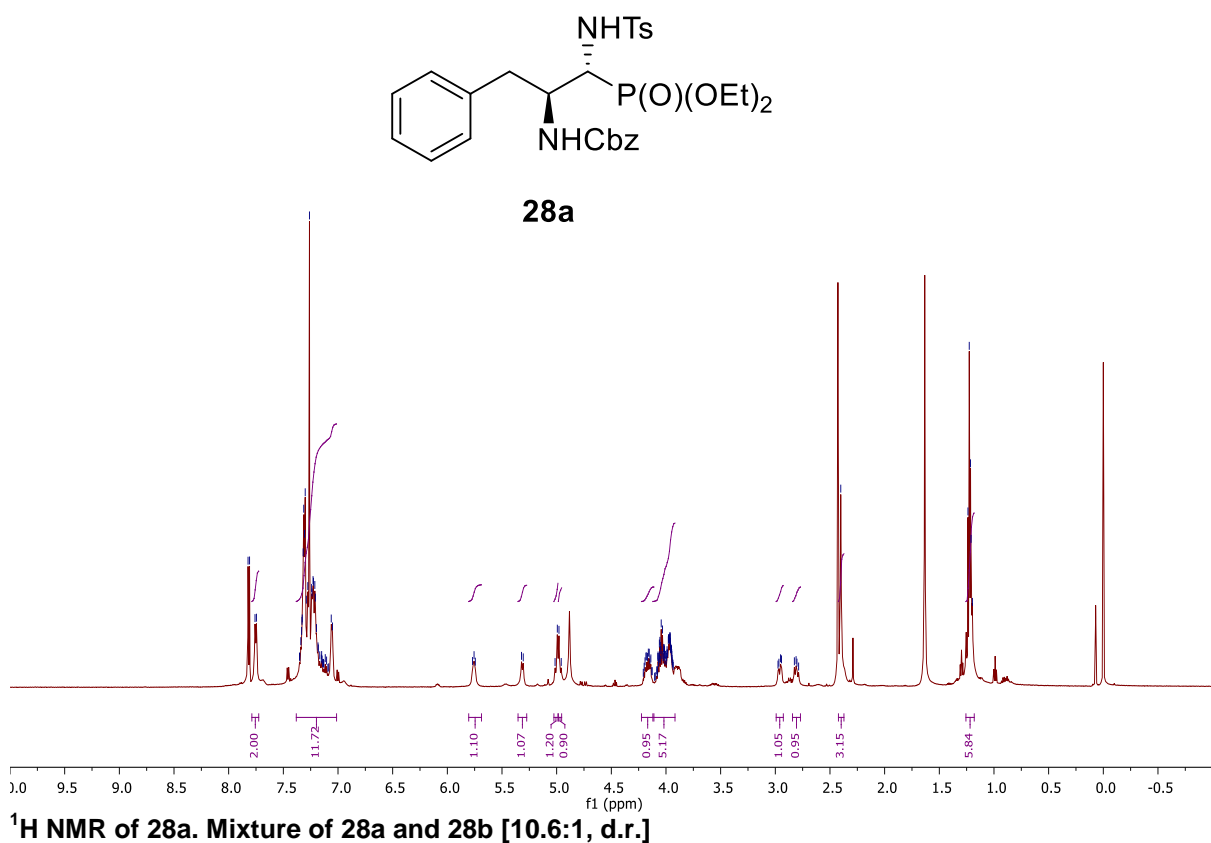
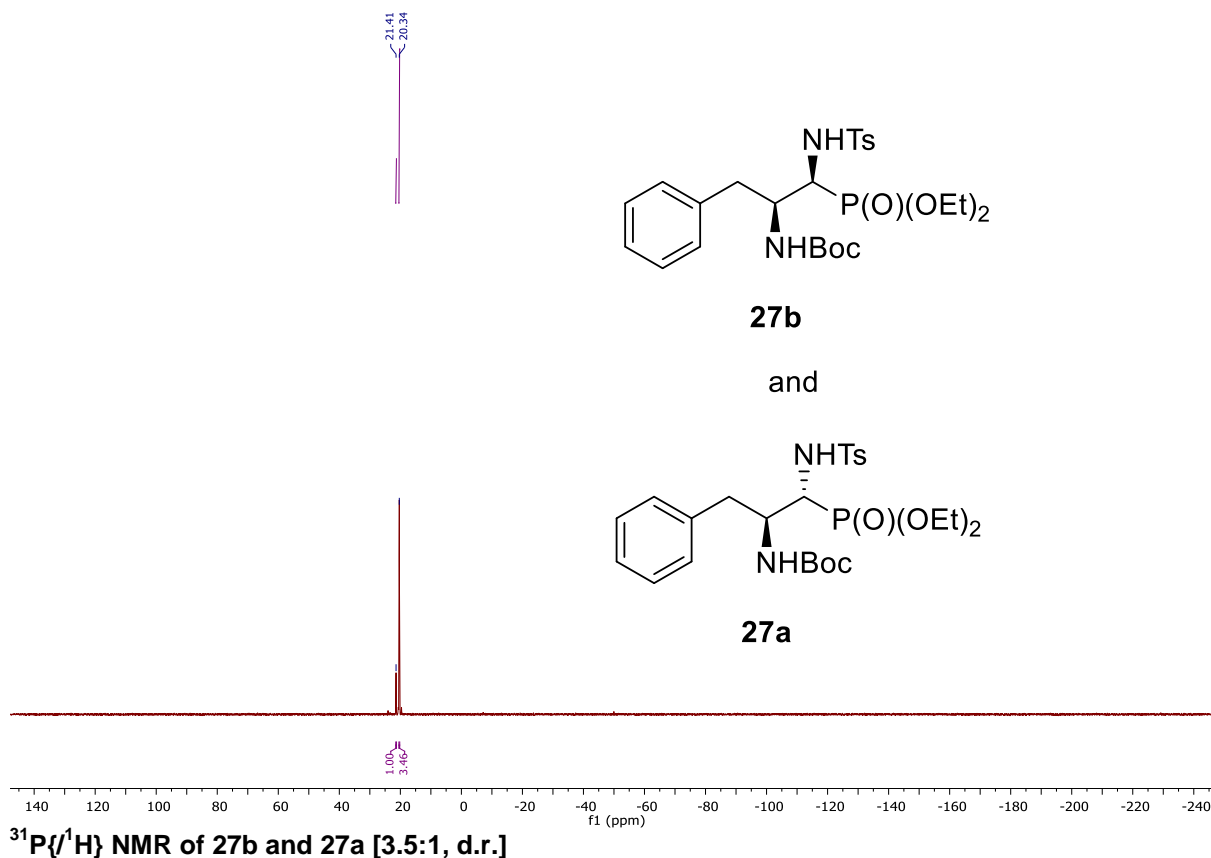
¹³C NMR of 26a

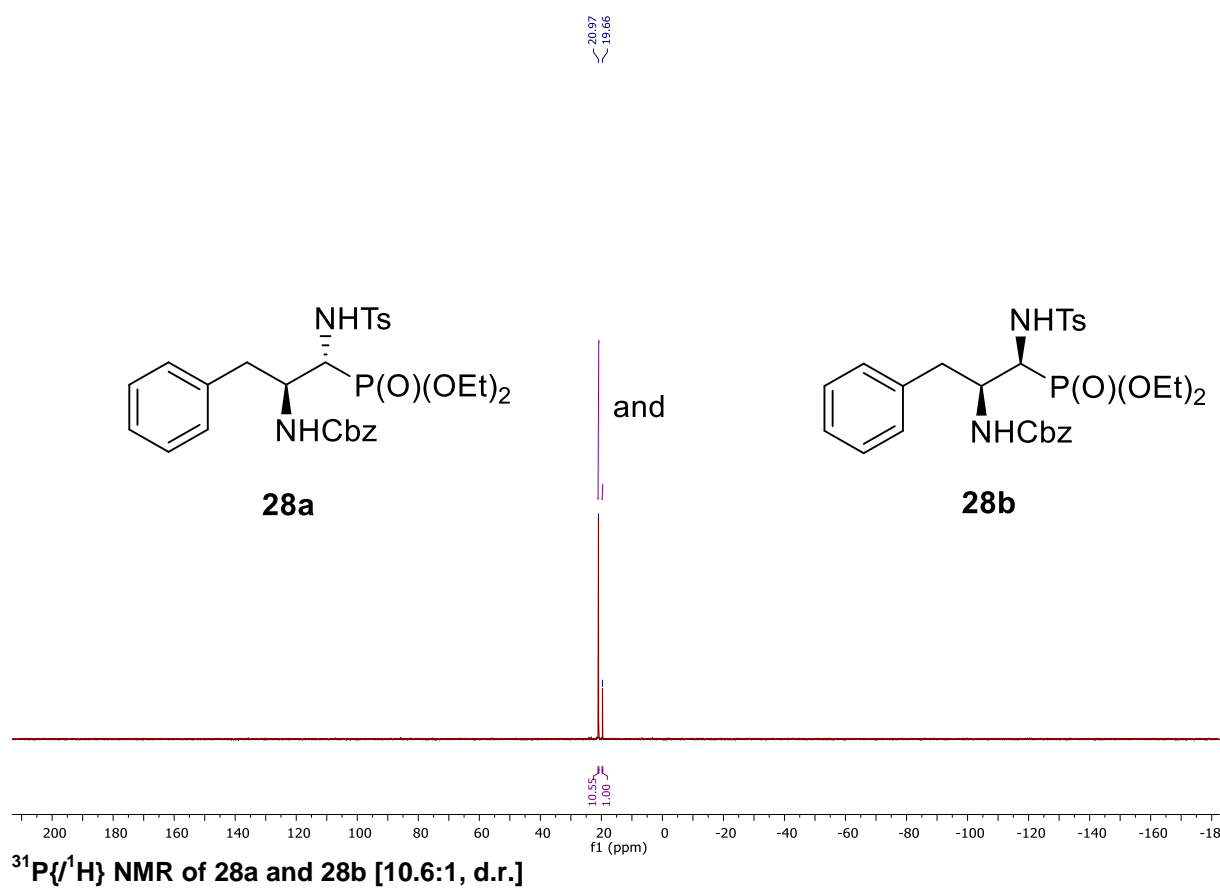
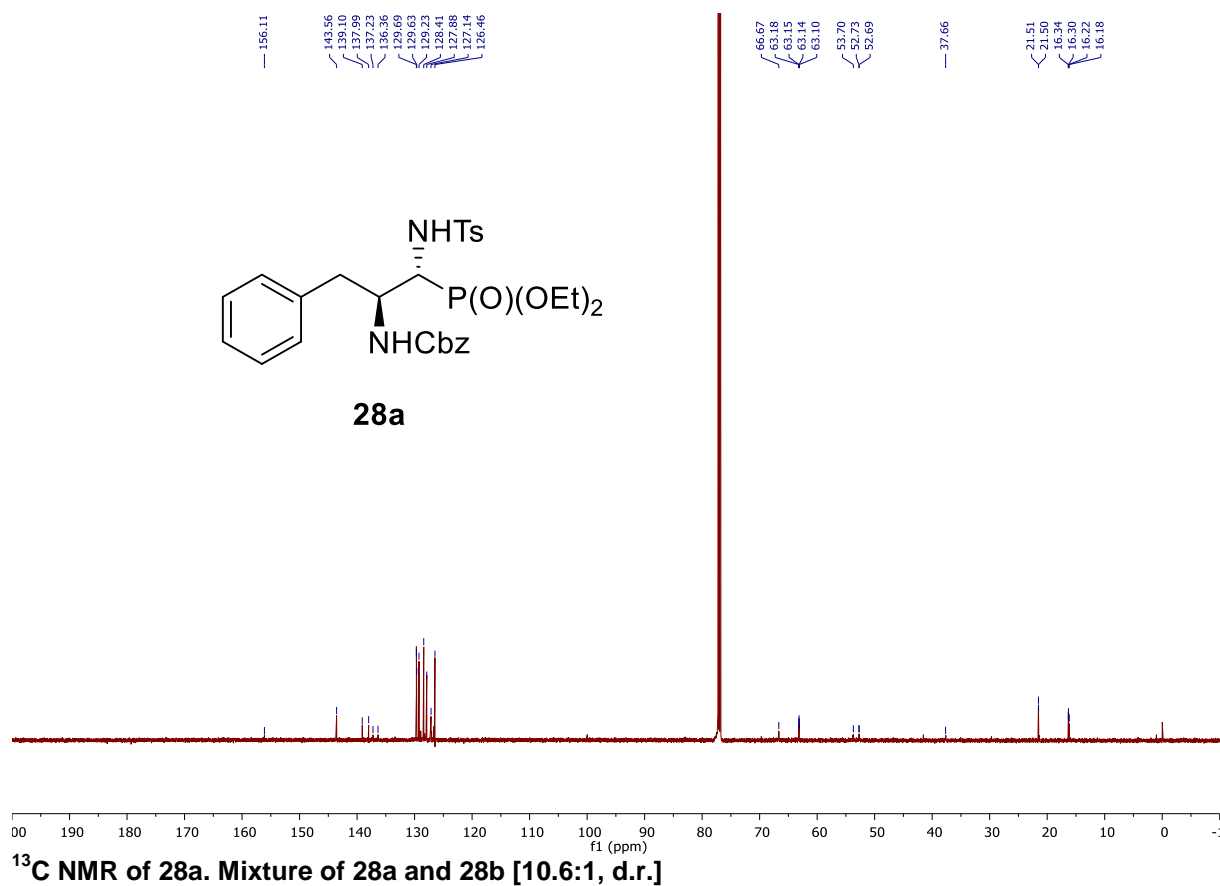
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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30
20
10
0

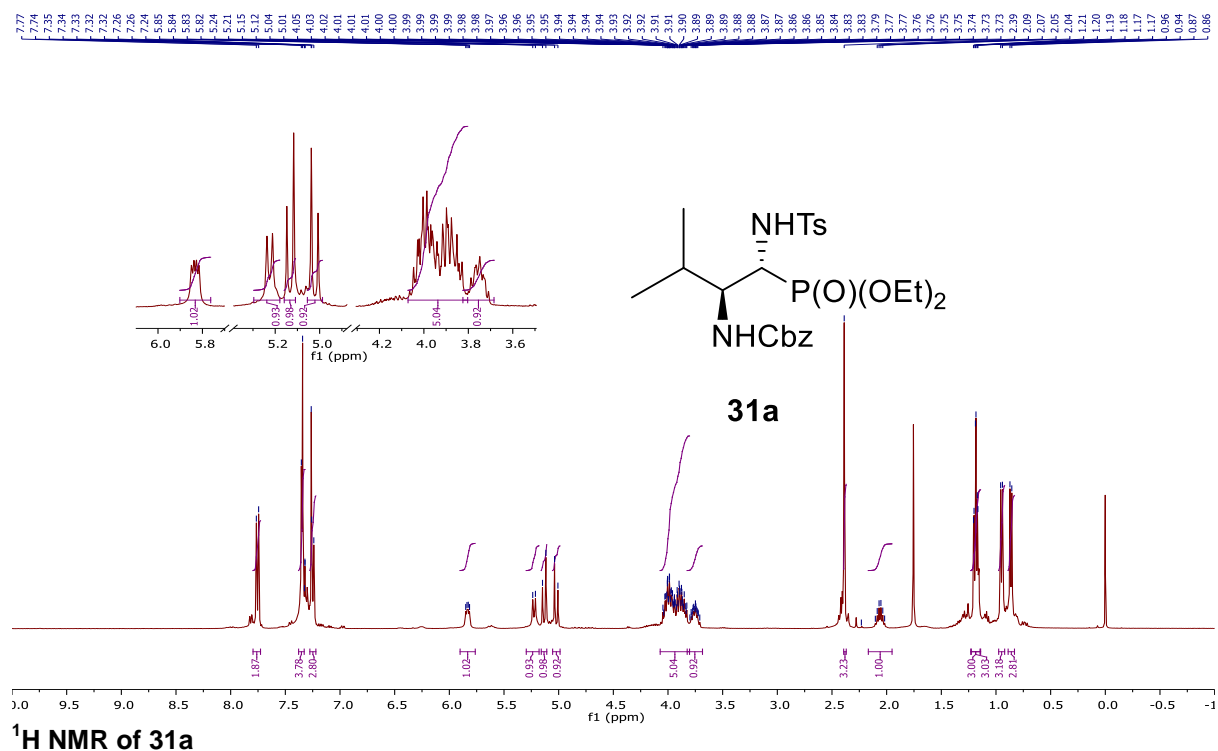
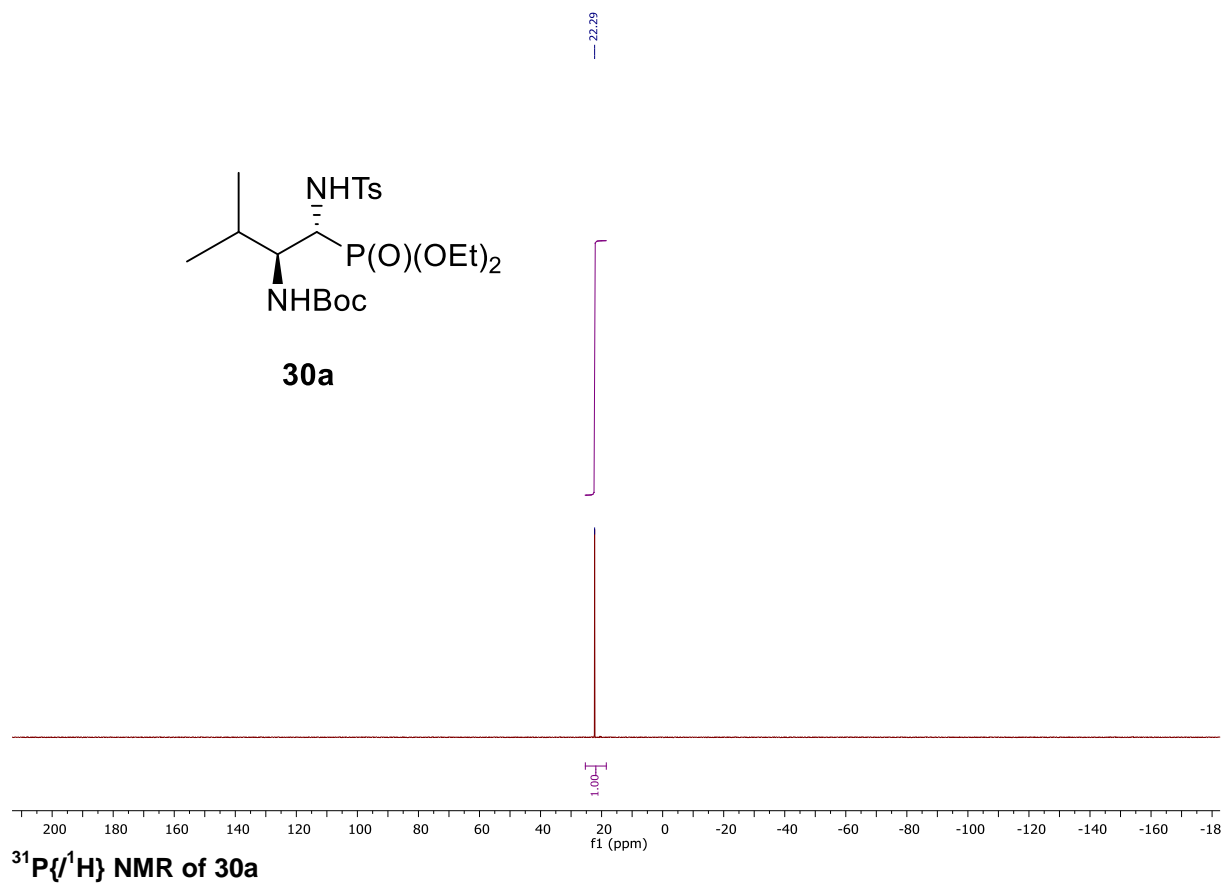


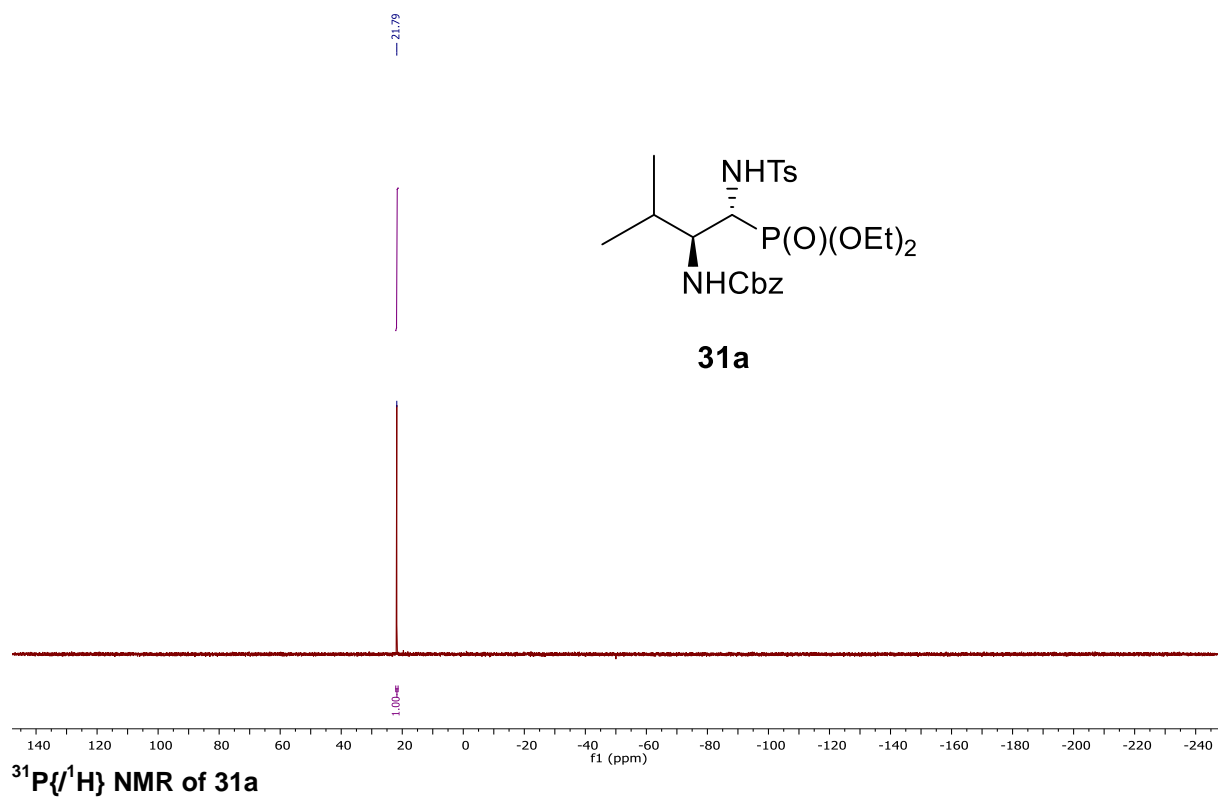
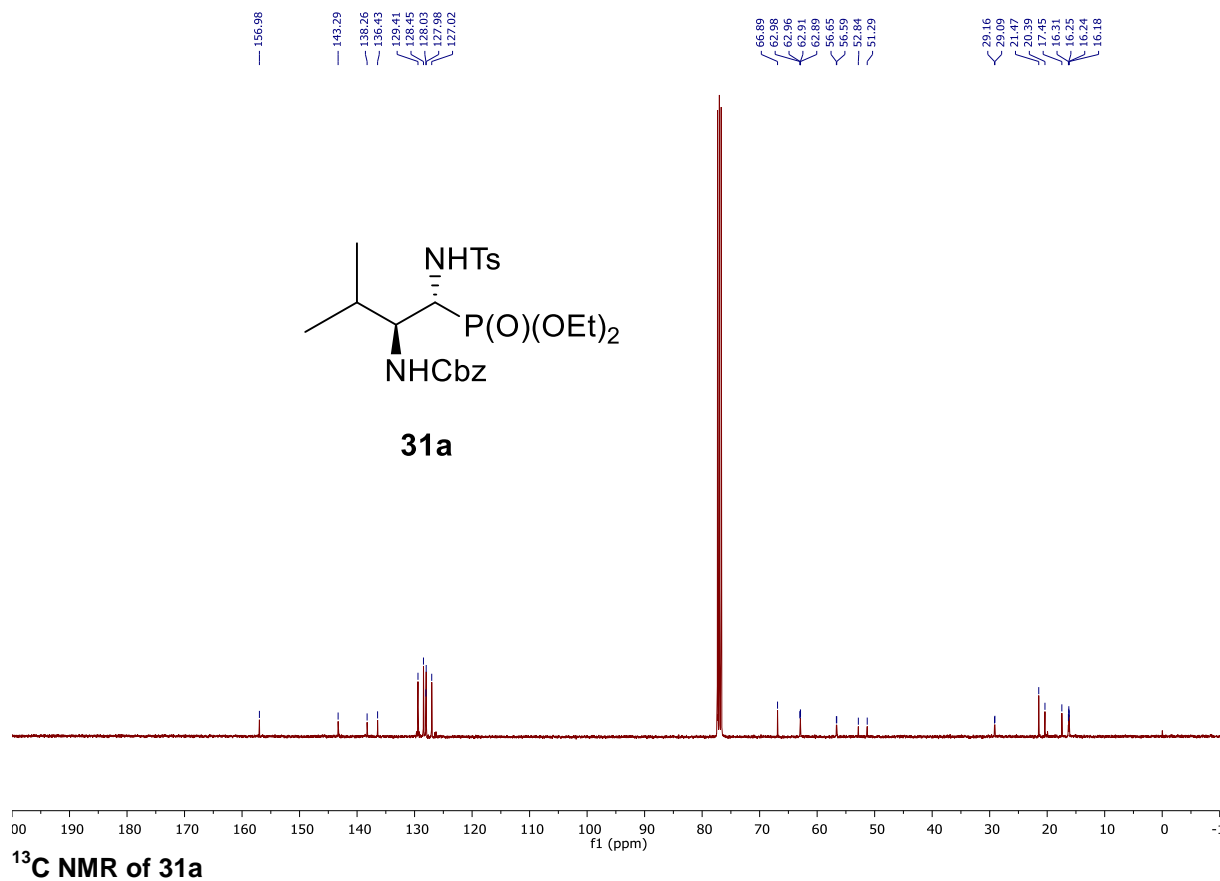


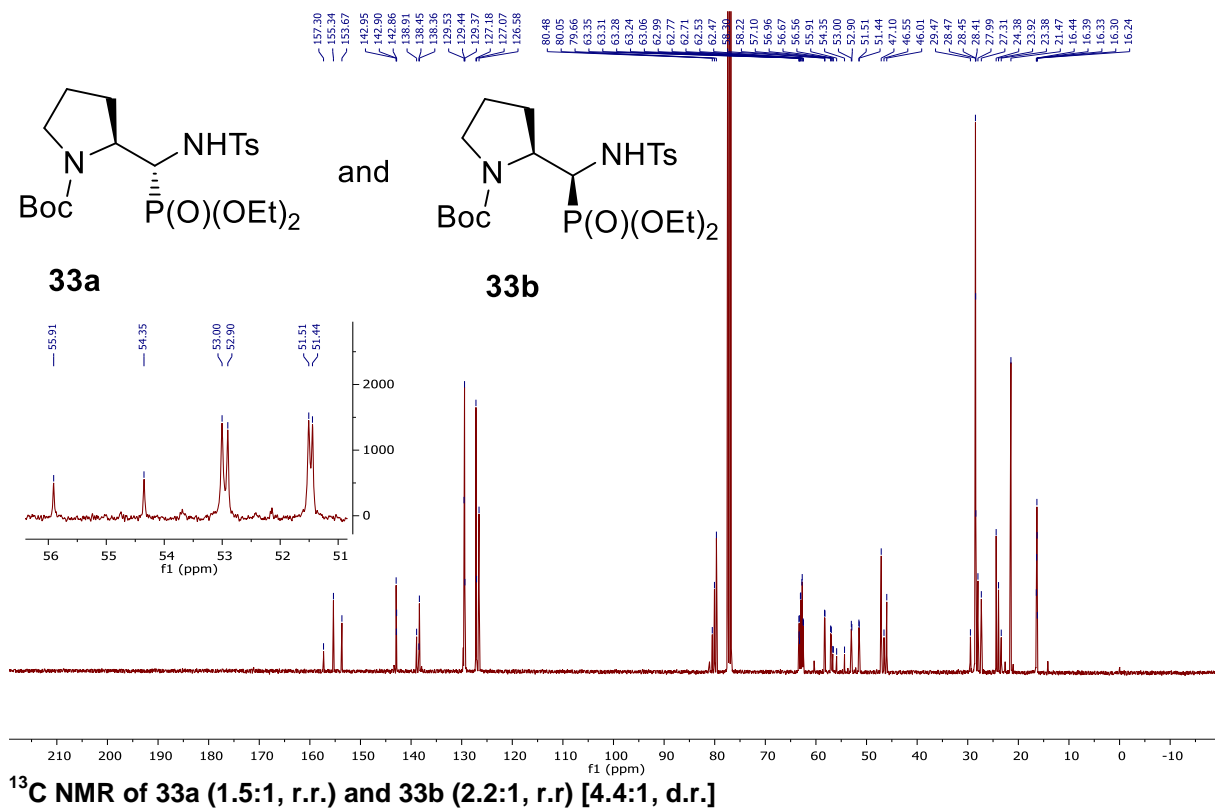
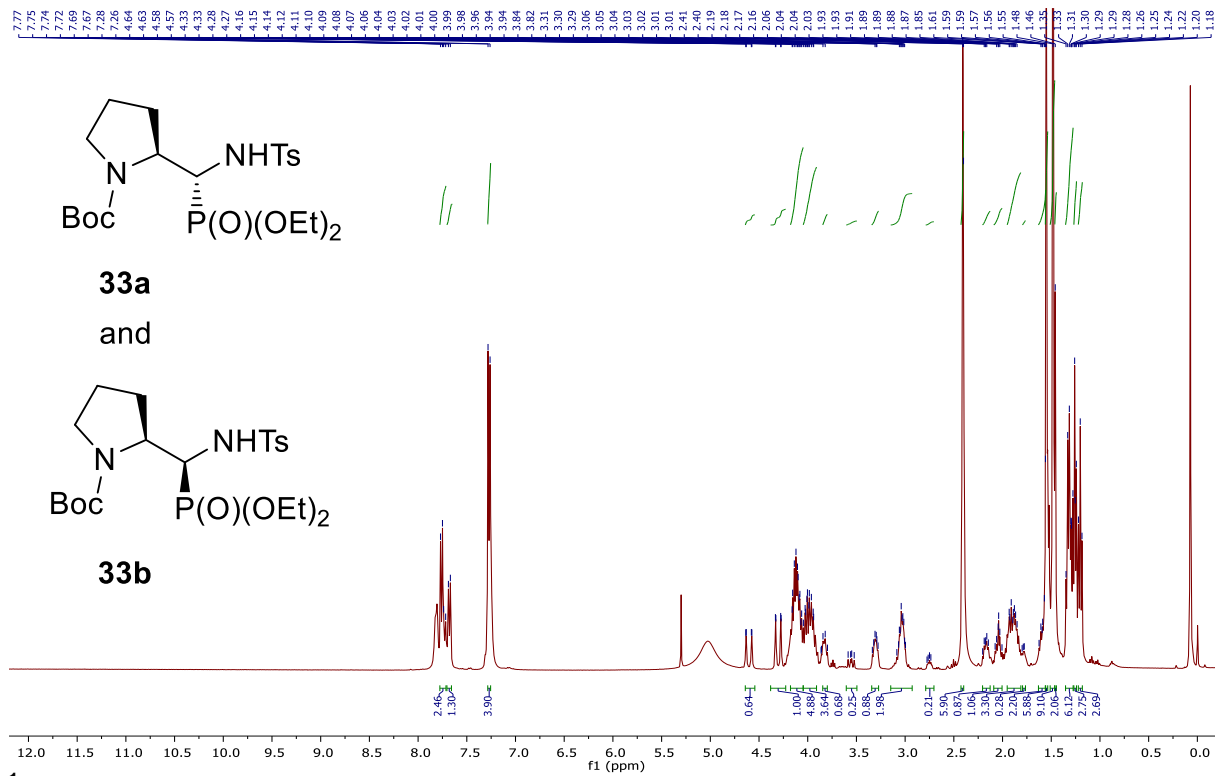


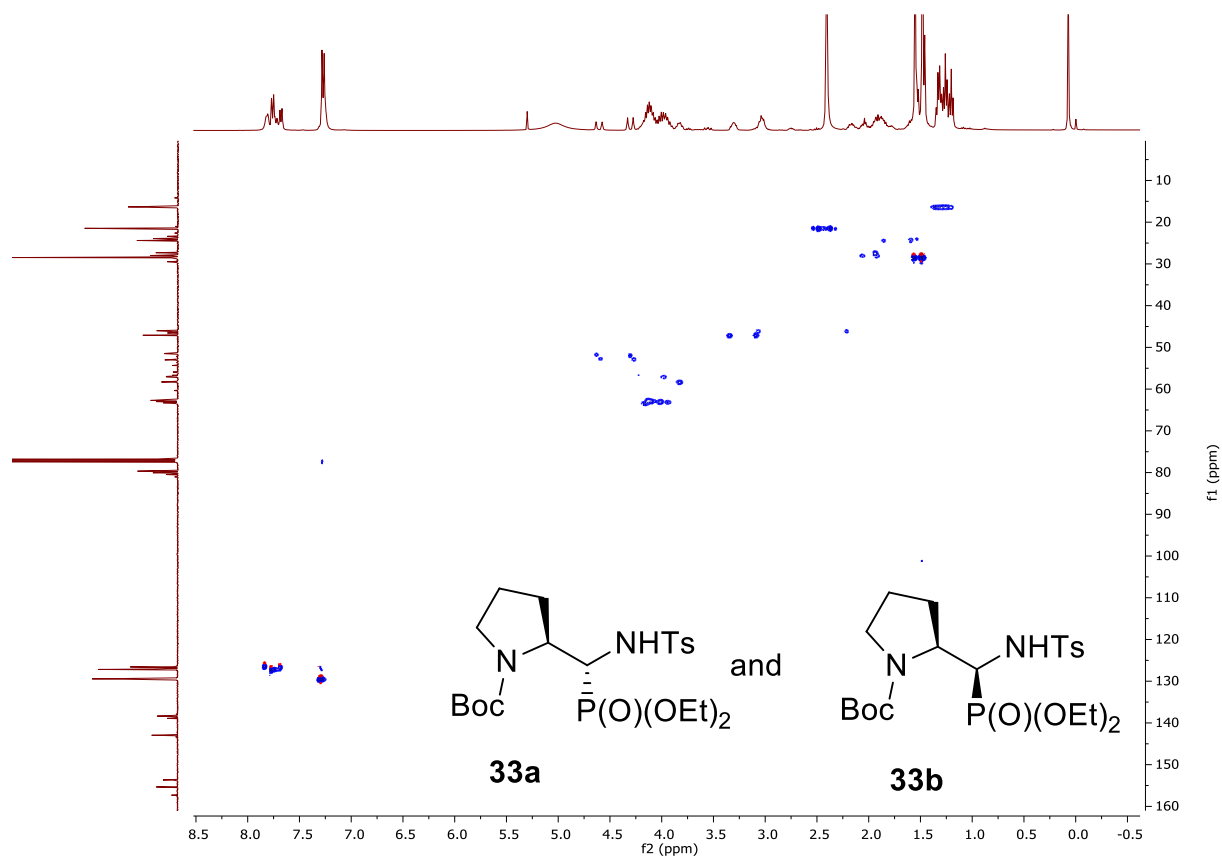
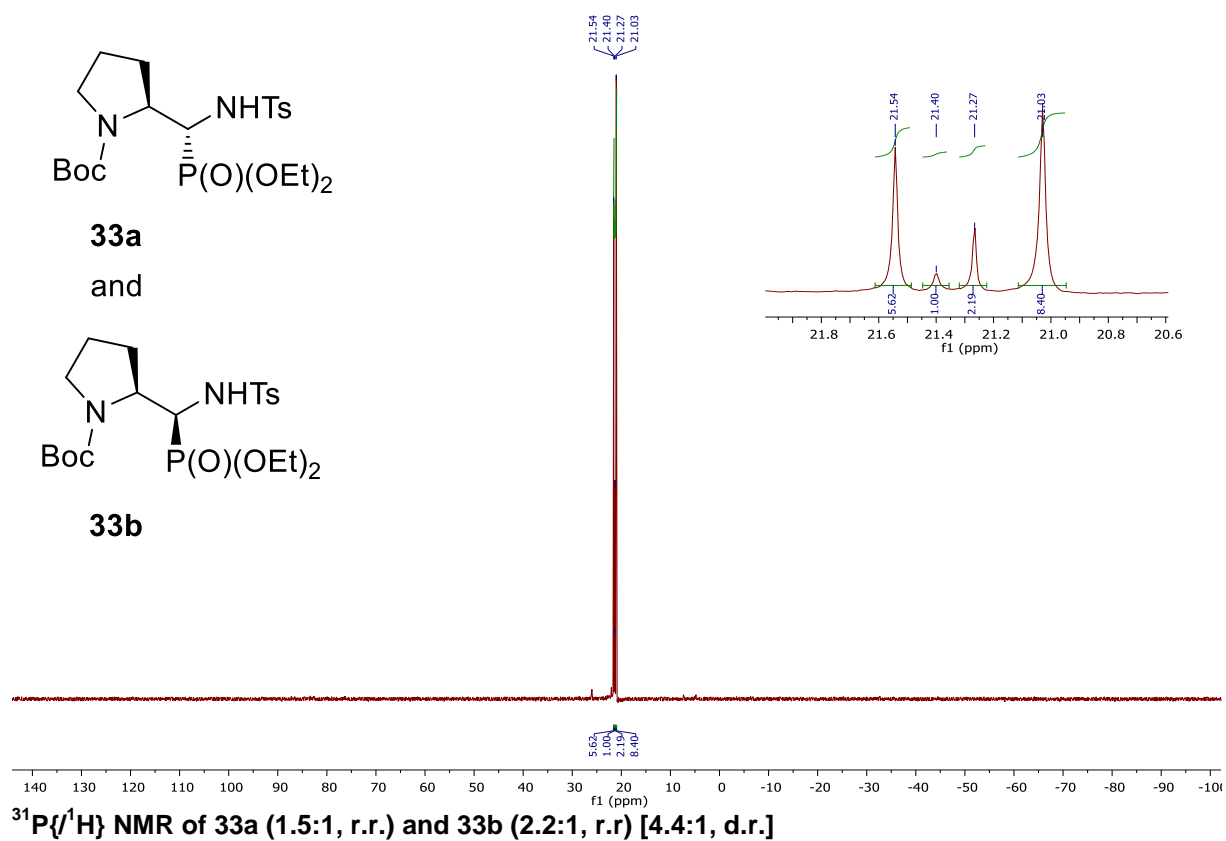


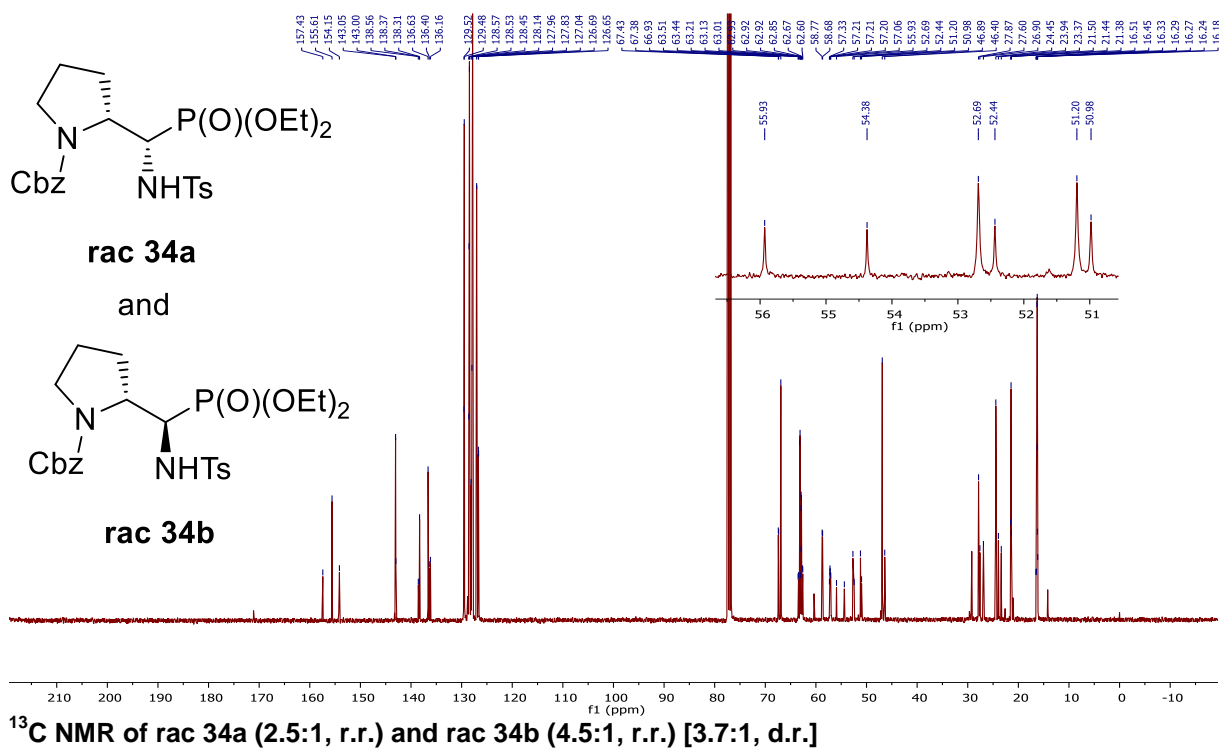
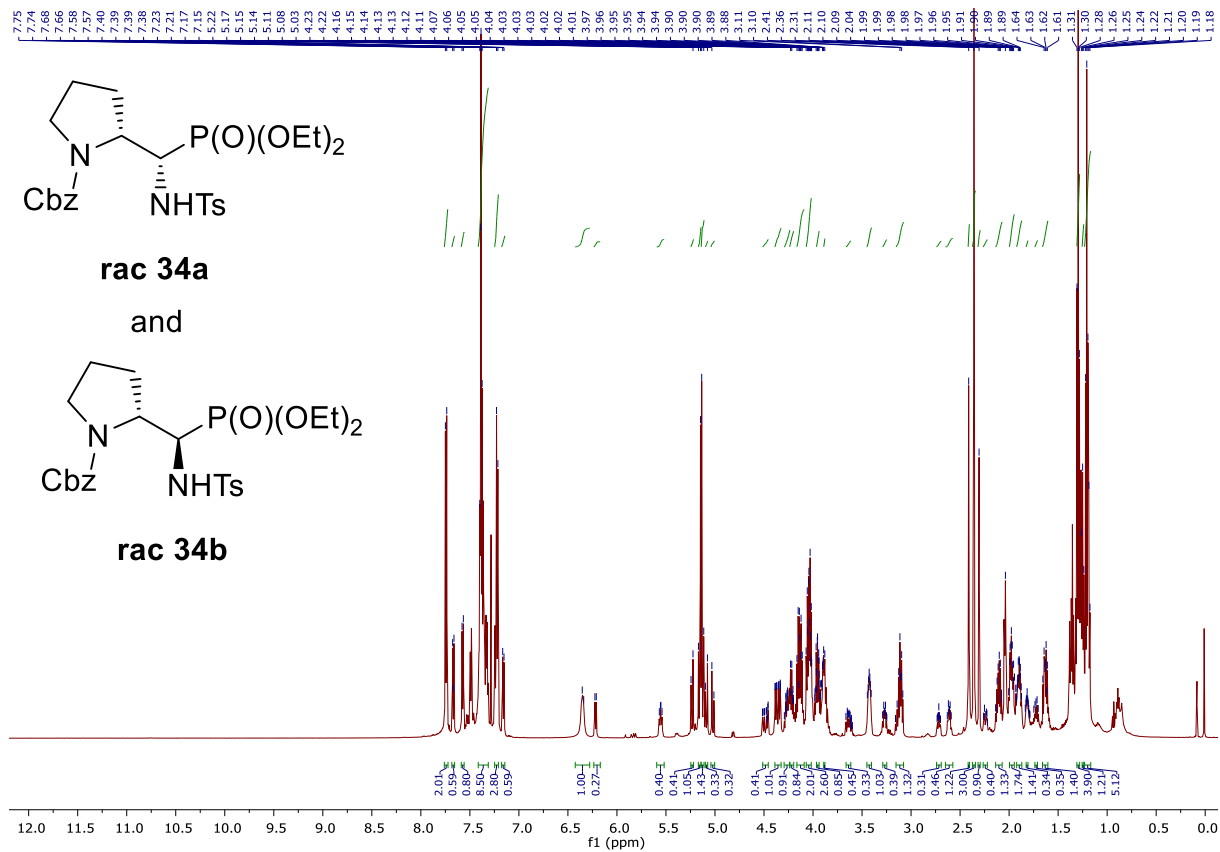


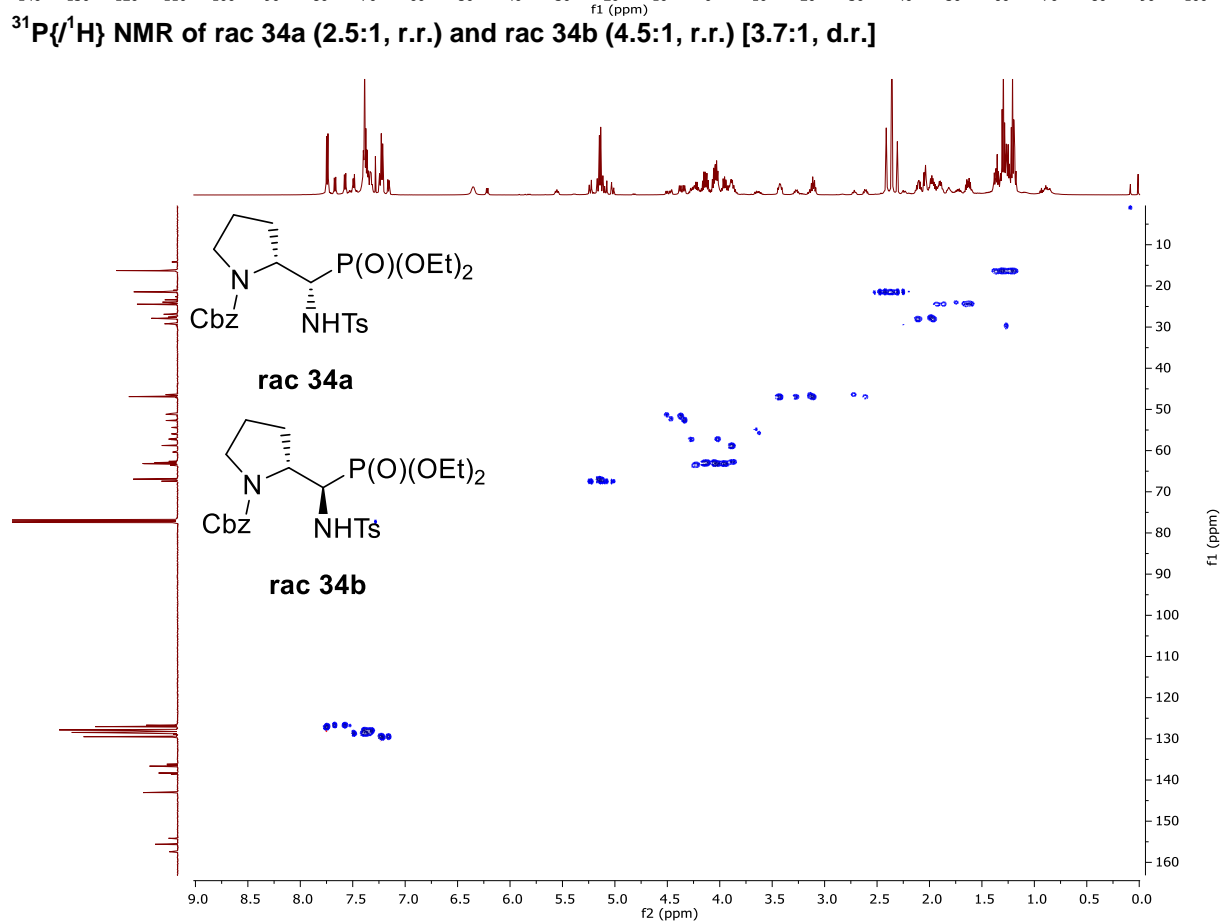
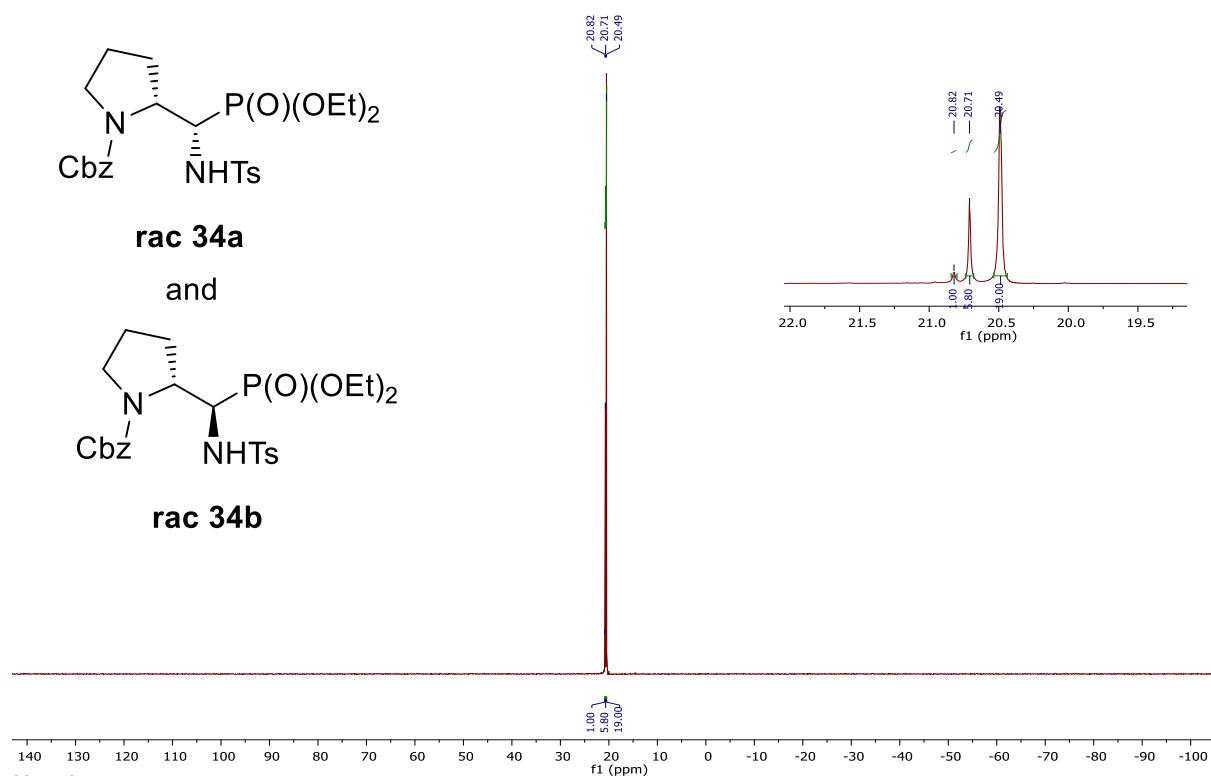


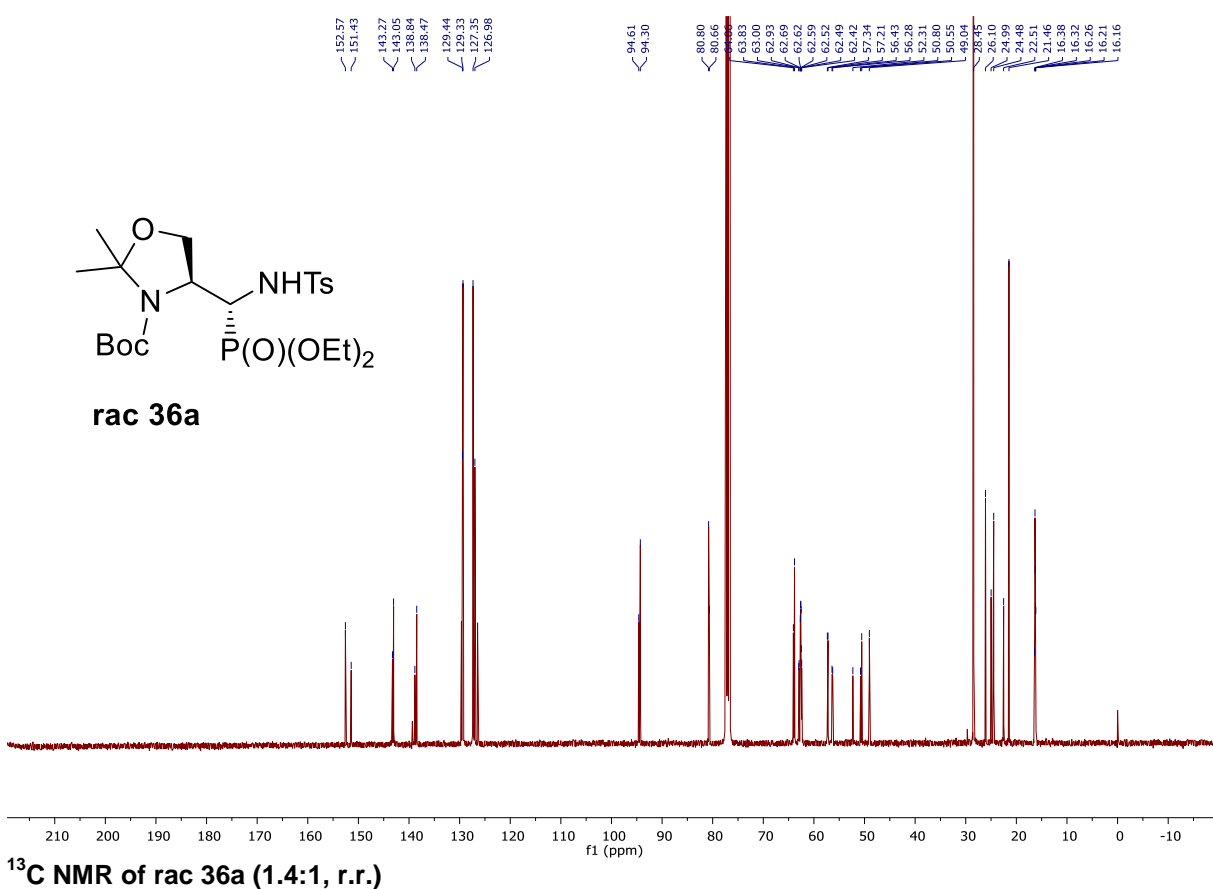
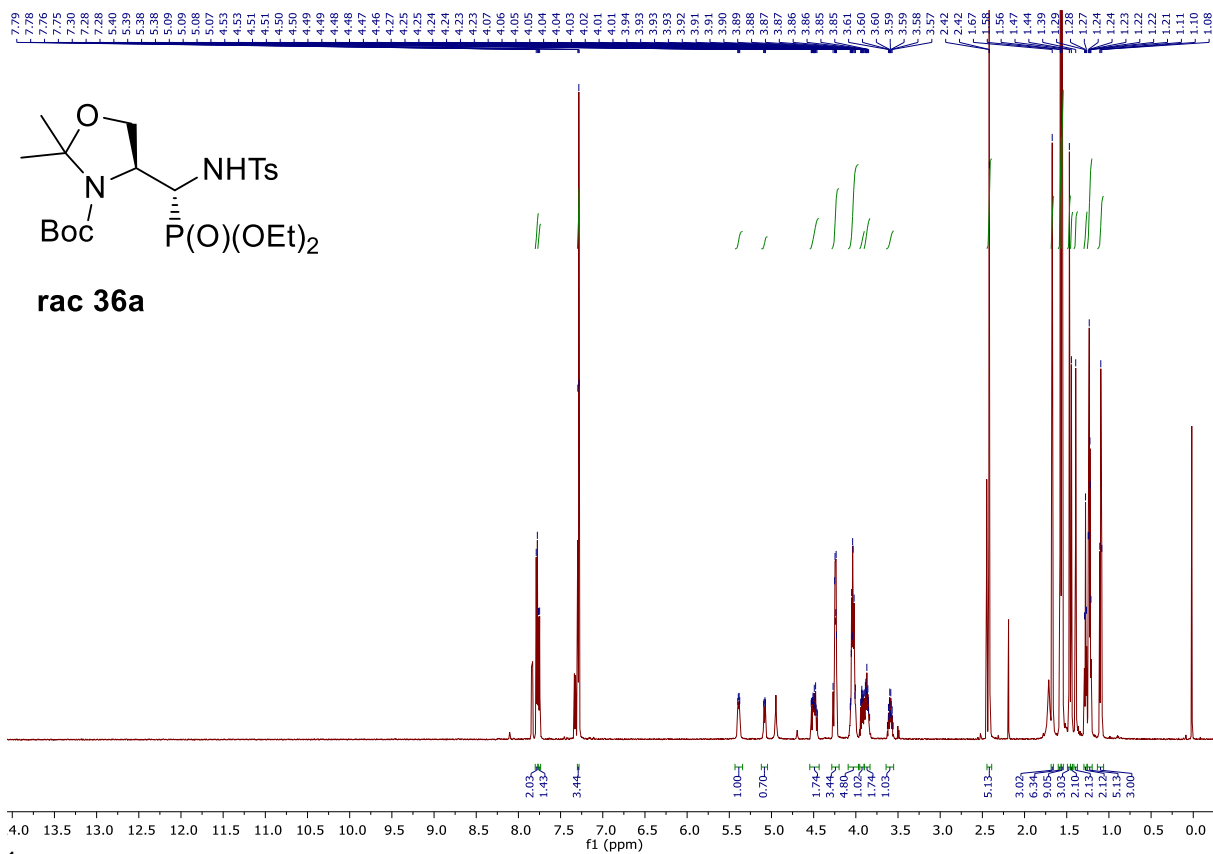


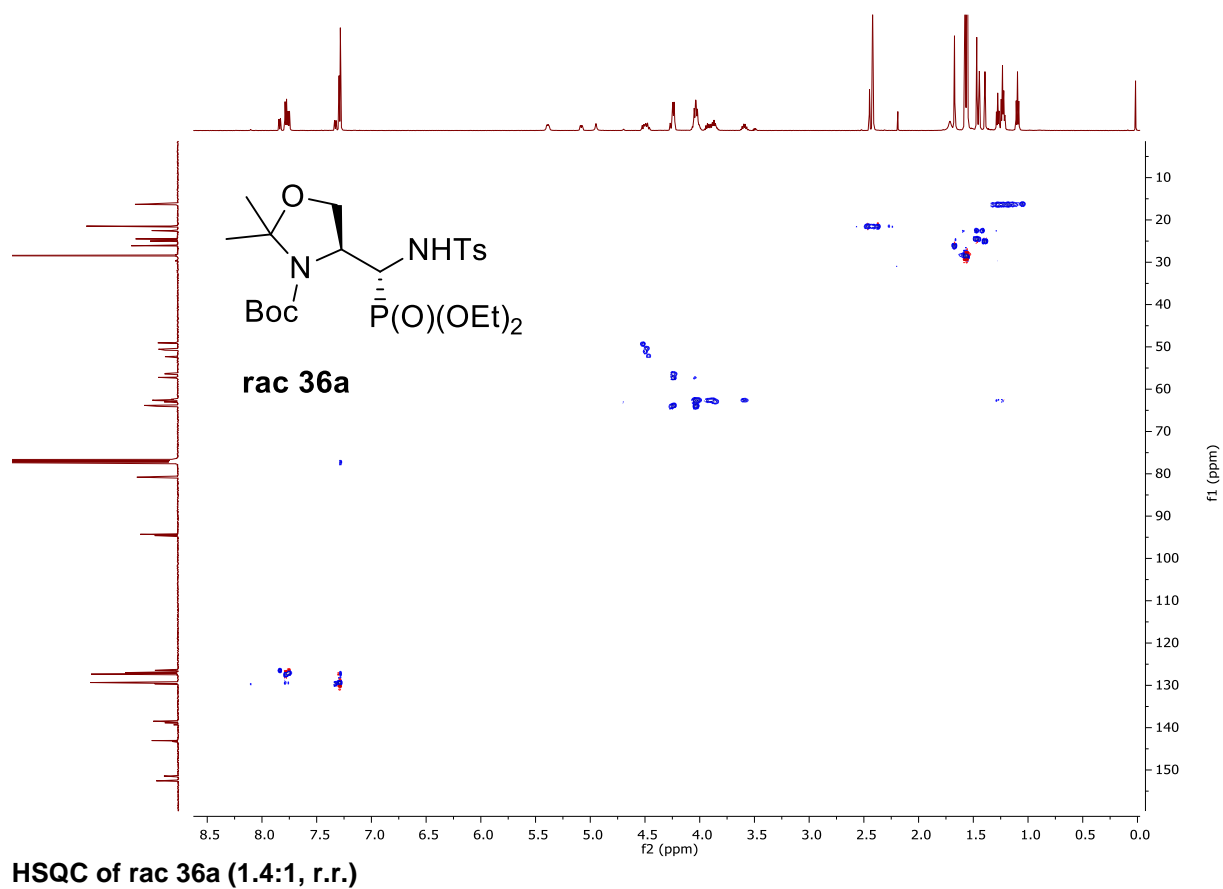
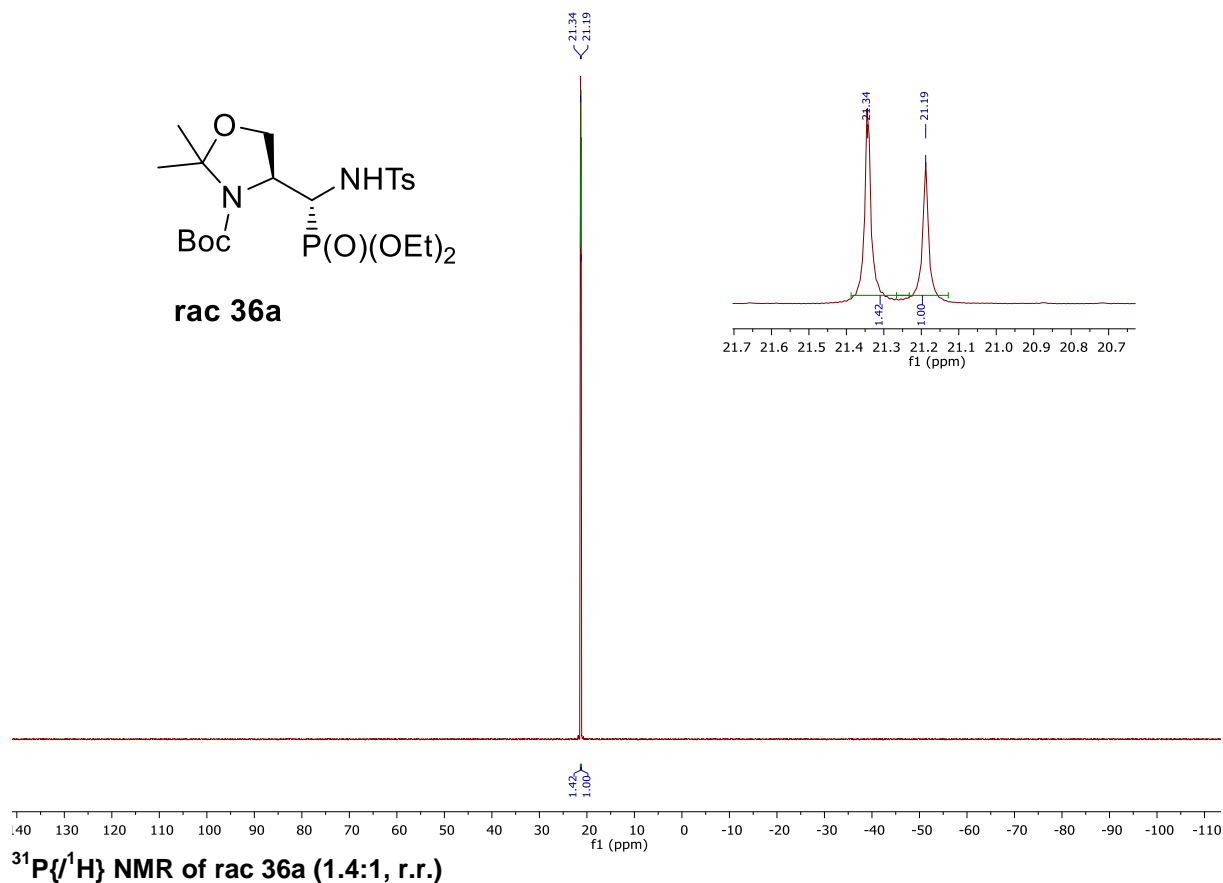


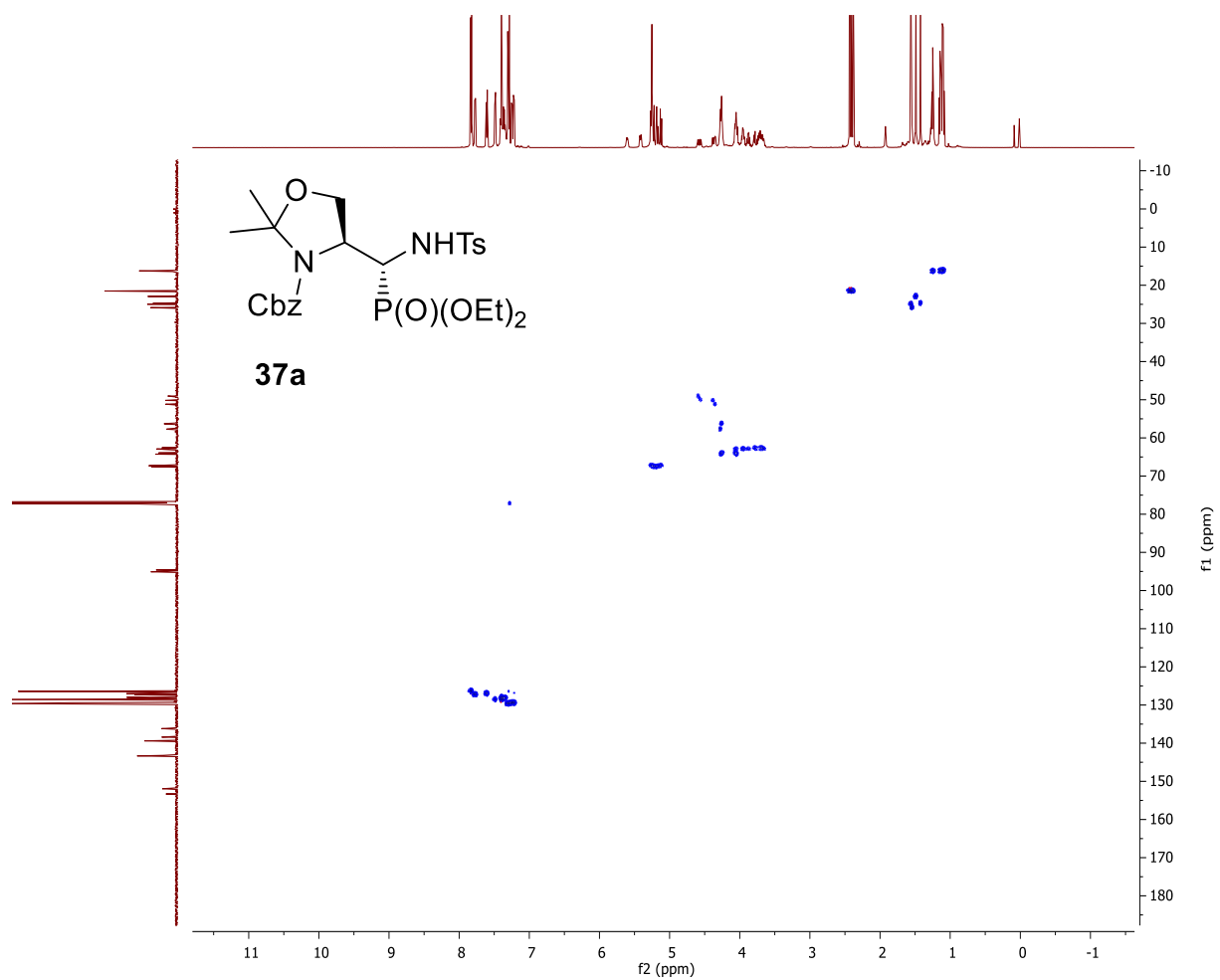
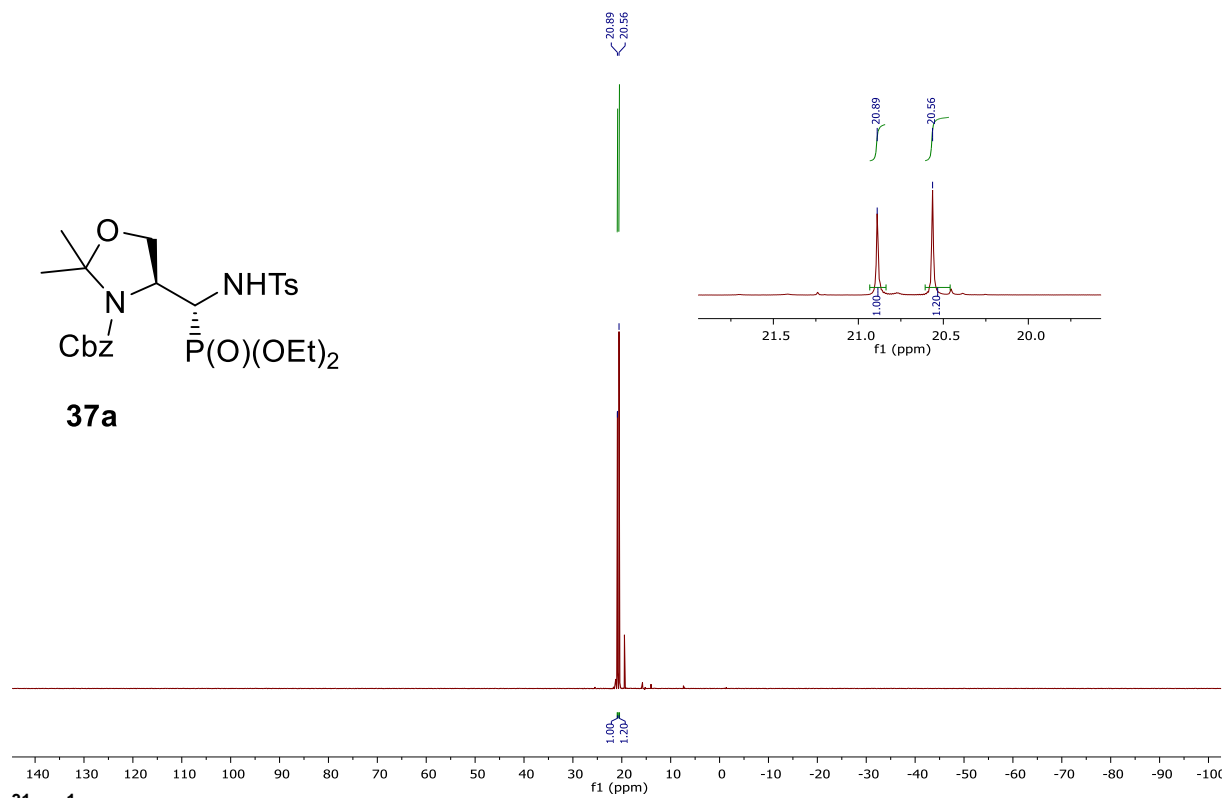


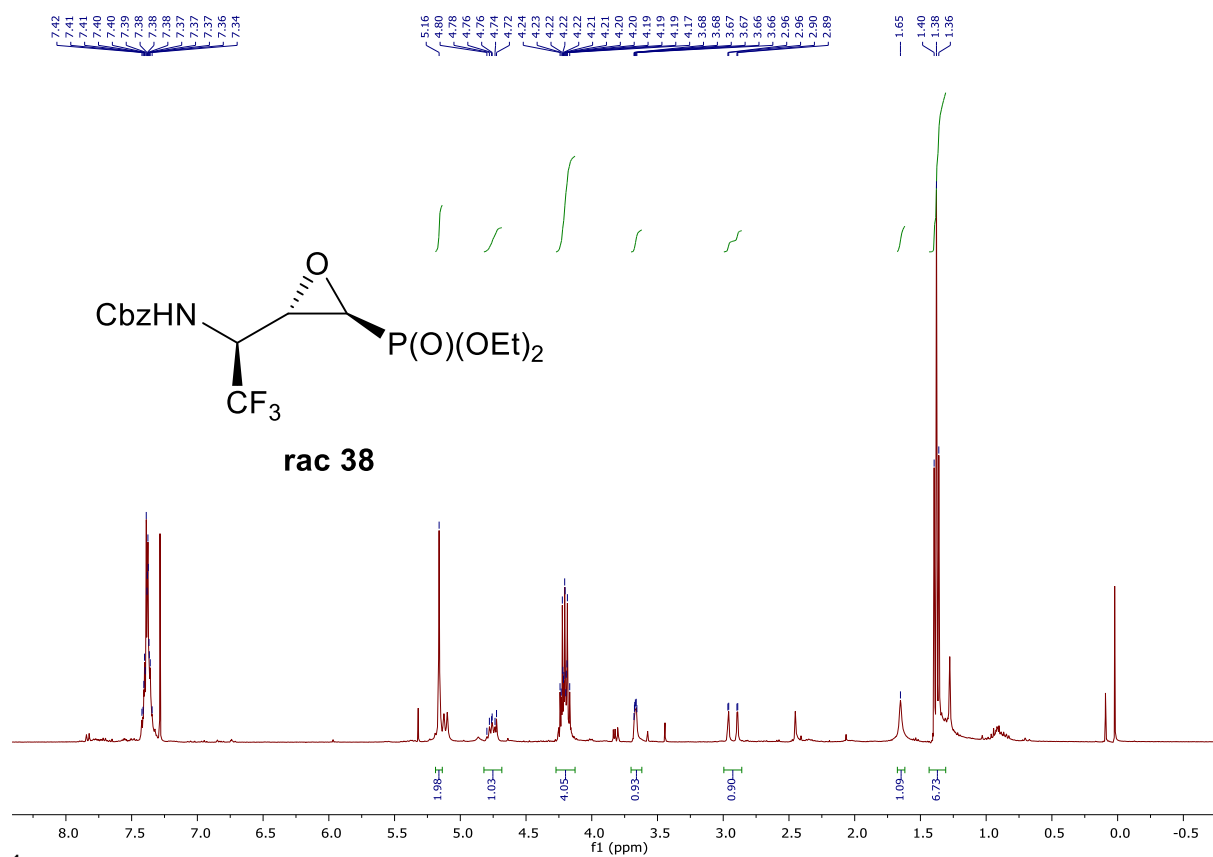




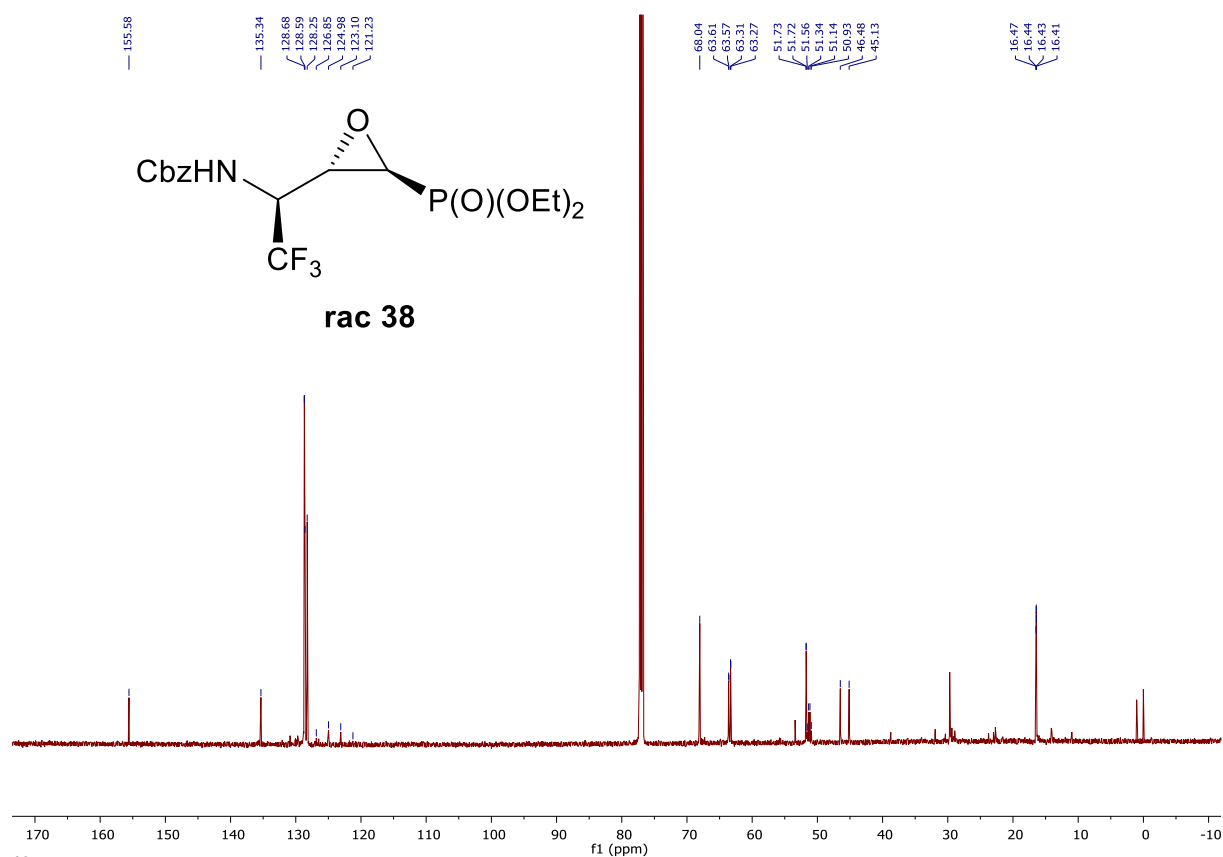




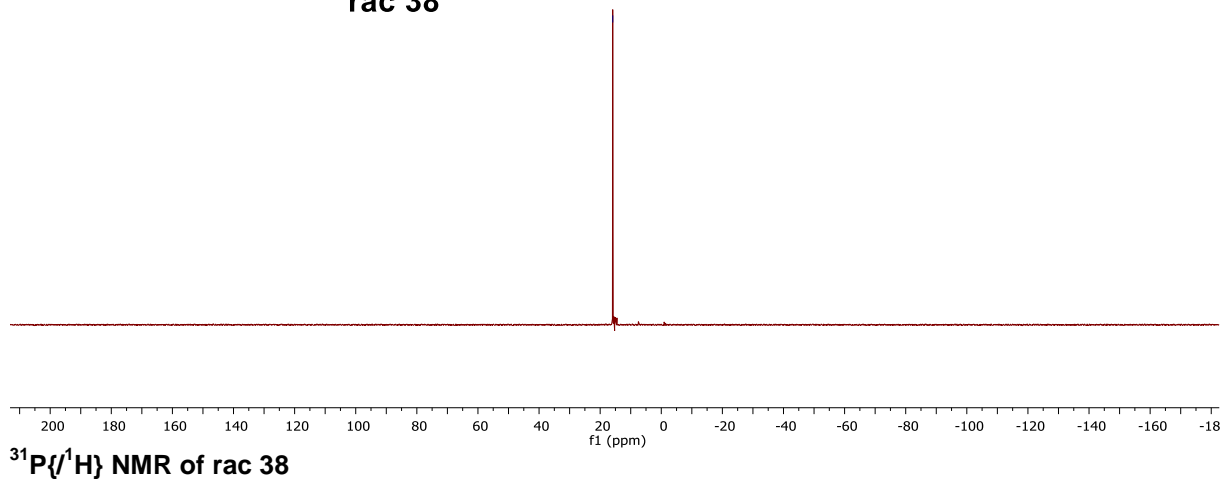
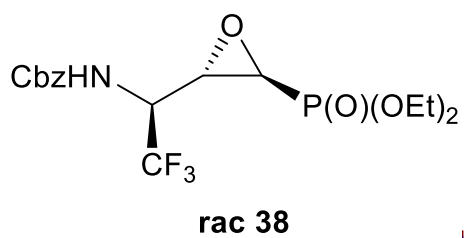




¹H NMR of rac 38



¹³C NMR of rac 38



2. Crystallographic Data

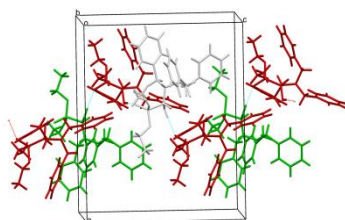


Figure 1. Chain of hydrogen-bonded 4-fold screw related molecules of **10a**, as seen approximately along y-direction. Hydrogen bonds are shown as thin blue lines.

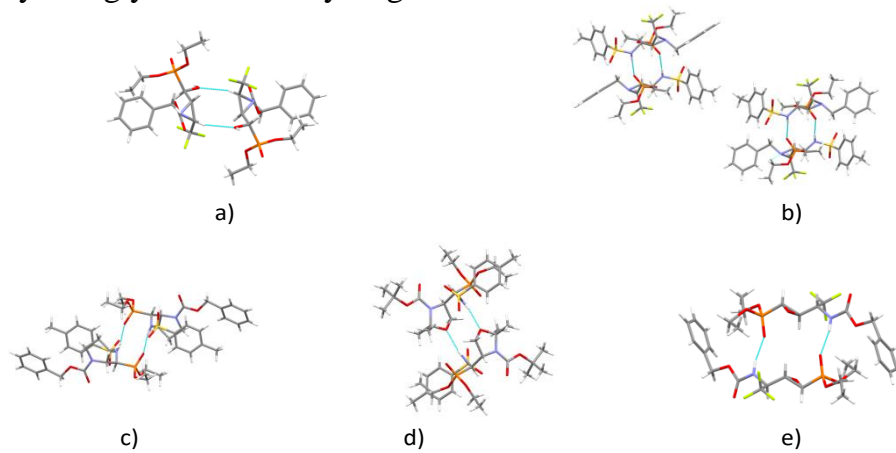


Figure 2. Centrosymmetric, hydrogen-bonded dimers observed in the crystal structures of a) **9a**, b) **23a**, c) **34a**, d) **36a**, e) **38**. Hydrogen bonds are shown as dashed blue lines; for **23a** the dimers created by both symmetry-independent molecules are shown.

Table 1. Crystal data and refinement details

Compound	9a	10a	23a	34a	36a	38
Formula	C ₁₆ H ₂₁ F ₃	C ₂₇ H ₃₄ NO	C ₂₂ H ₂₈ F ₃ N	C ₂₄ H ₃₃ N ₂	C ₂₂ H ₃₇ N ₂ O ₈	C ₁₆ H ₂₁ F ₃ N
Formula	411.31	467.52	520.49	524.55	520.56	411.31
Crystal	triclinic	Tetragonal	triclinic	triclinic	triclinic	triclinic
Space	P-1	P4 ₁ 2 ₁ 2	P-1	P-1	P-1	P-1
a(Å)	9.2602(5)	18.3893(4)	9.4187(3)	9.1196(7)	11.2960(6)	10.1589(16)
b(Å)	9.4720(4)	18.3893(4)	11.5503(5)	11.0522(9)	12.0965(6)	10.3309(11)
c(Å)	11.9414(4)	15.9702(8)	25.4175(1)	13.6480(1)	12.4628(6)	10.8732(11)
α(°)	107.154(4)	90	90.406(3)	71.568(8)	112.998(5)	108.225(10)
β(°)	96.395(3)	90	99.189(3)	77.690(7)	110.653(4)	112.480(12)
γ(°)	95.550(4)	90	113.524(4)	87.393(6)	98.152(4)	90.483(10)
V(Å ³)	985.29(8)	5400.6(4)	2495.13(1)	1274.7(2)	1387.41(16)	990.8(2)
Z	2	8	4	2	2	2
d _x (g cm ⁻³)	1.39	1.15	1.39	1.37	1.25	1.38
F(000)	428	2000	1088	556	556	428
μ(mm ⁻¹)	0.198	0.132	0.251	0.236	0.219	0.197
Θ range (°)	3.27 –	3.38 –	3.22 –	3.31 –	3.37 –	3.64 –
Reflections						
collected	17923	14476	18335	8392	16691	6885
unique	3448	5216	9637	4881	5328	3461
with	2844	4155	7875	3446	4503	1499
R(F)	0.074	0.044	0.041	0.085	0.059	0.118
wR(F ²)	0.212	0.103	0.099	0.191	0.173	0.306
R(F) [all]	0.084	0.061	0.053	0.117	0.068	0.222
wR(F ²) [all]	0.220	0.114	0.106	0.205	0.181	0.366
Goodness	1.14	1.03	1.04	1.02	1.08	1.03
max/min	0.68/-0.32	0.14/-0.17	0.55/-0.45	1.80/-1.03	0.70/-0.48	0.71/-0.35

Table 2. Hydrogen bond data (Å, °) with s.u.'s in parentheses

D	H	A	D-H	H···A	D···A	D-H···A
8a						
O10	H10	O2 ⁱ	0.82	1.85	2.665(4)	173
10a						
O10	H10	O2 ⁱⁱ	0.82	1.95	2.764(3)=	175
23a						
N10A	H10A	O2A ⁱⁱⁱ	0.80(2)	1.99(2)	2.783(2)	175(2)
N10B	H10B	O2B ^{iv}	0.78(2)	2.02(2)	2.800(2)	173(2)
N3	H3N	O11 ⁱⁱⁱ	0.87(2)	2.32(2)	3.1049(17)	151.5(19)
C3	H3	O13	1.00	2.29	3.0590(19)	133
34a						
N10	H10	O2 ^v	0.88	1.94	2.801(6)	166
36a						
N10	H10	O24 ^{vi}	0.86	2.12	2.956(3)	163
38						

N17	H17	O2 ^{vii}	0.88	1.92	2.778(6)	166

Symmetry codes: ⁱ 1-x,1-y,-z; ⁱⁱ 3/2-y,1/2+x,1/4+z; ⁱⁱⁱ 2-x,1-y,-z; ^{iv} -x,2-y,1-z; ^v 1-x,1-y,2-z; ^{vi} 1-x,-y,-z; ^{vii} 1-x,1-y,1-z.