Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis of trifluoromethyl *γ*-aminophosphonates by nucleophilic aziridine ring opening

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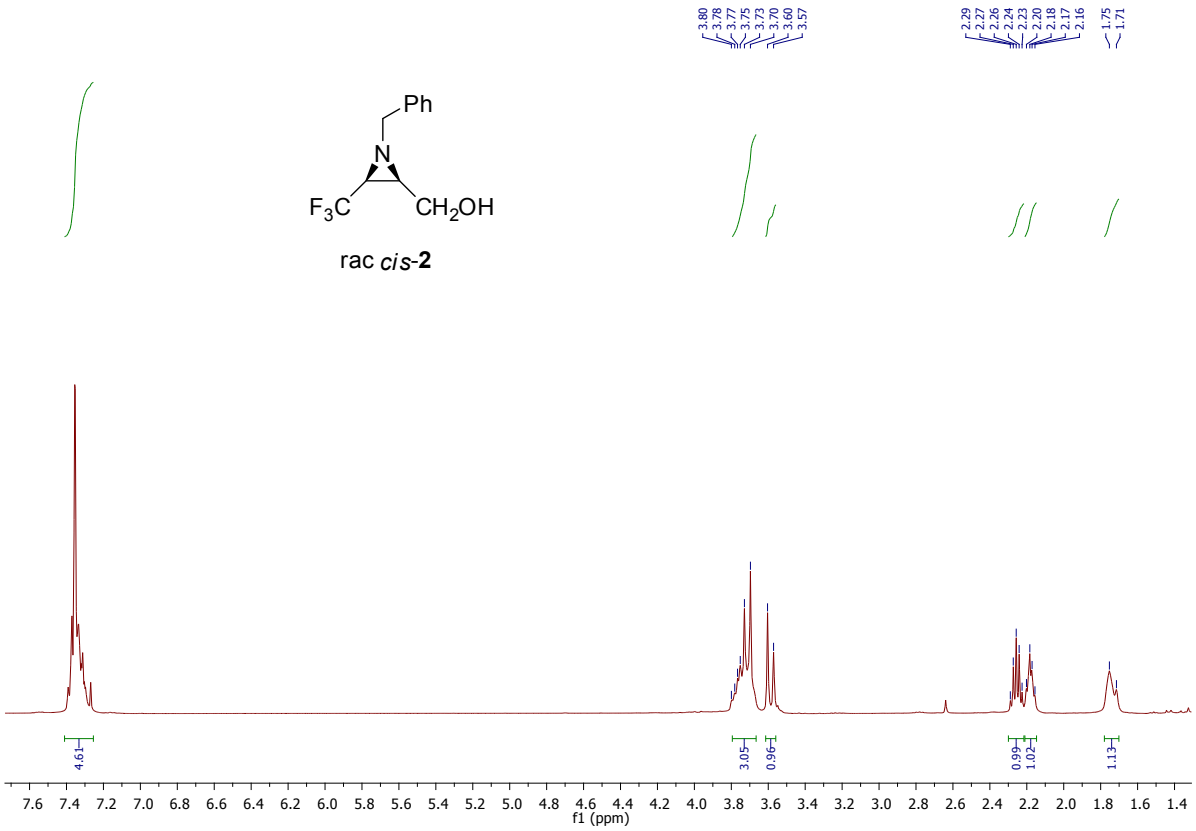
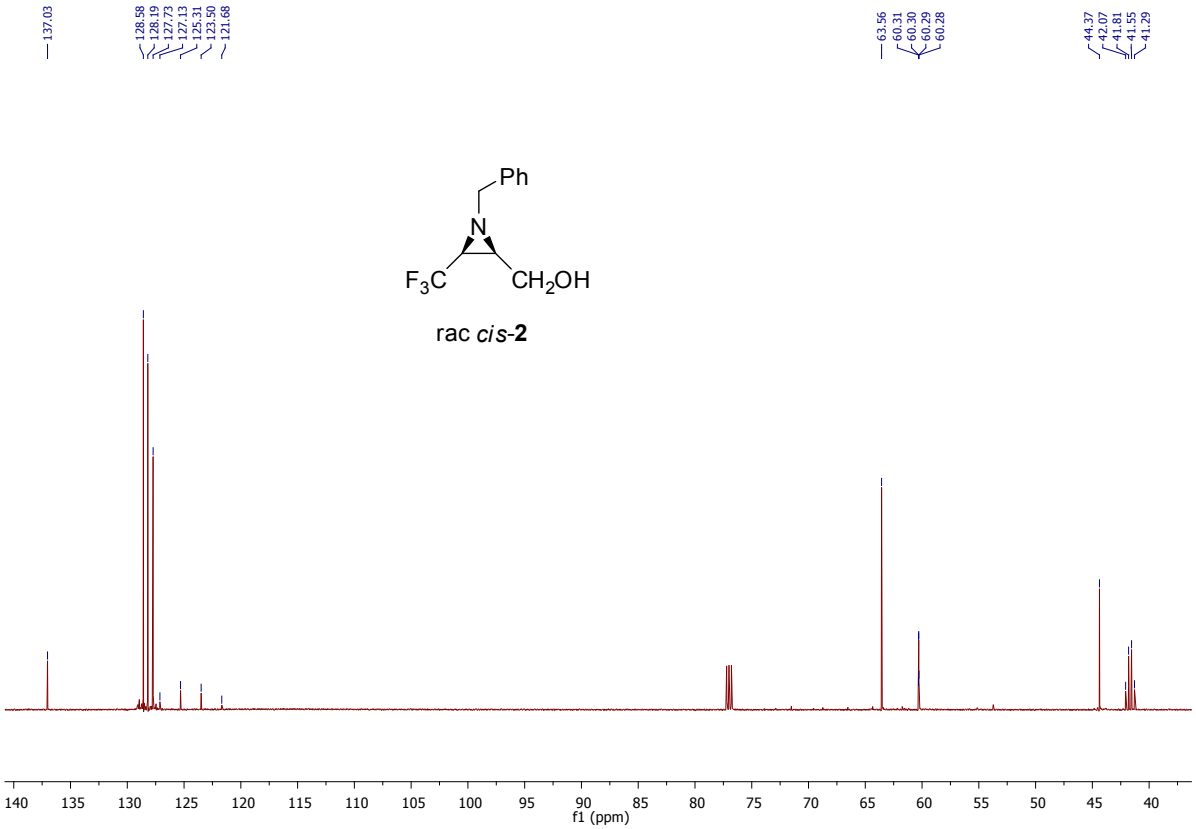
I) ^{1}H, ^{13}C and ^{31}P NMR Spectra of Compounds

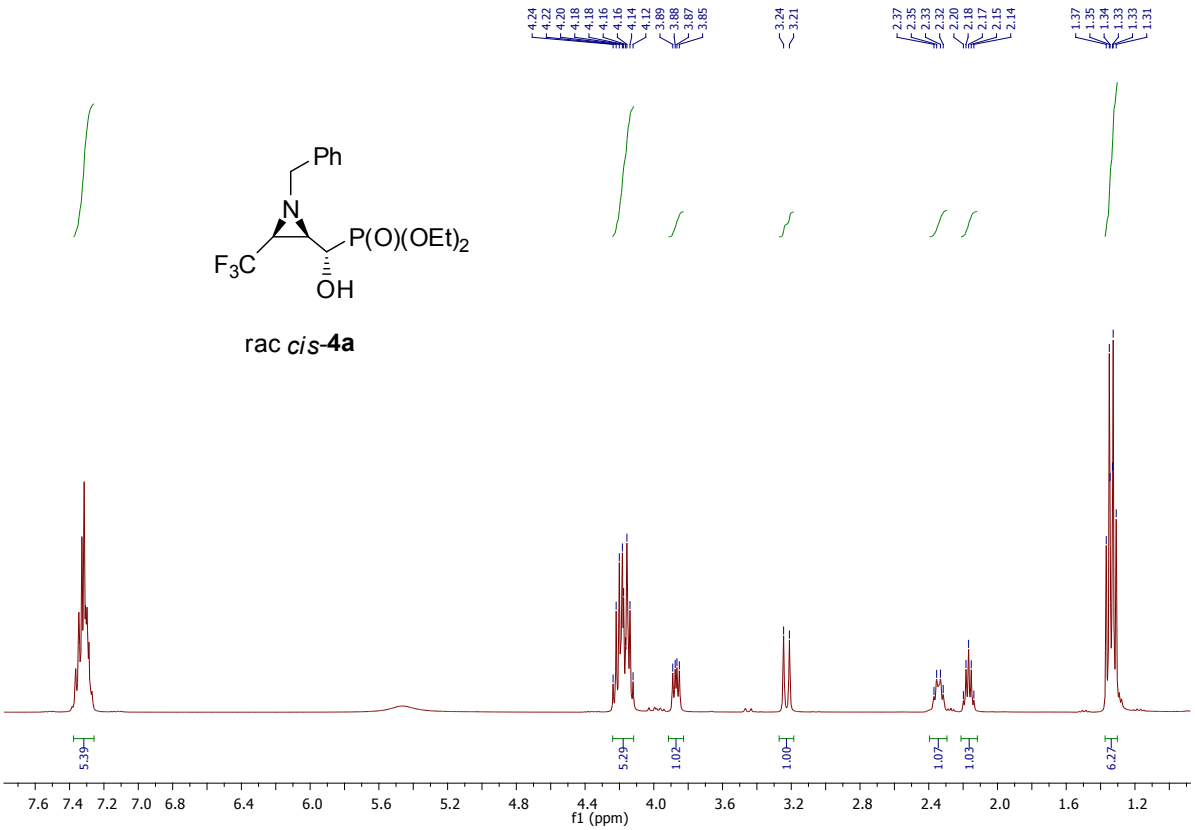
II) Crystallographic Data



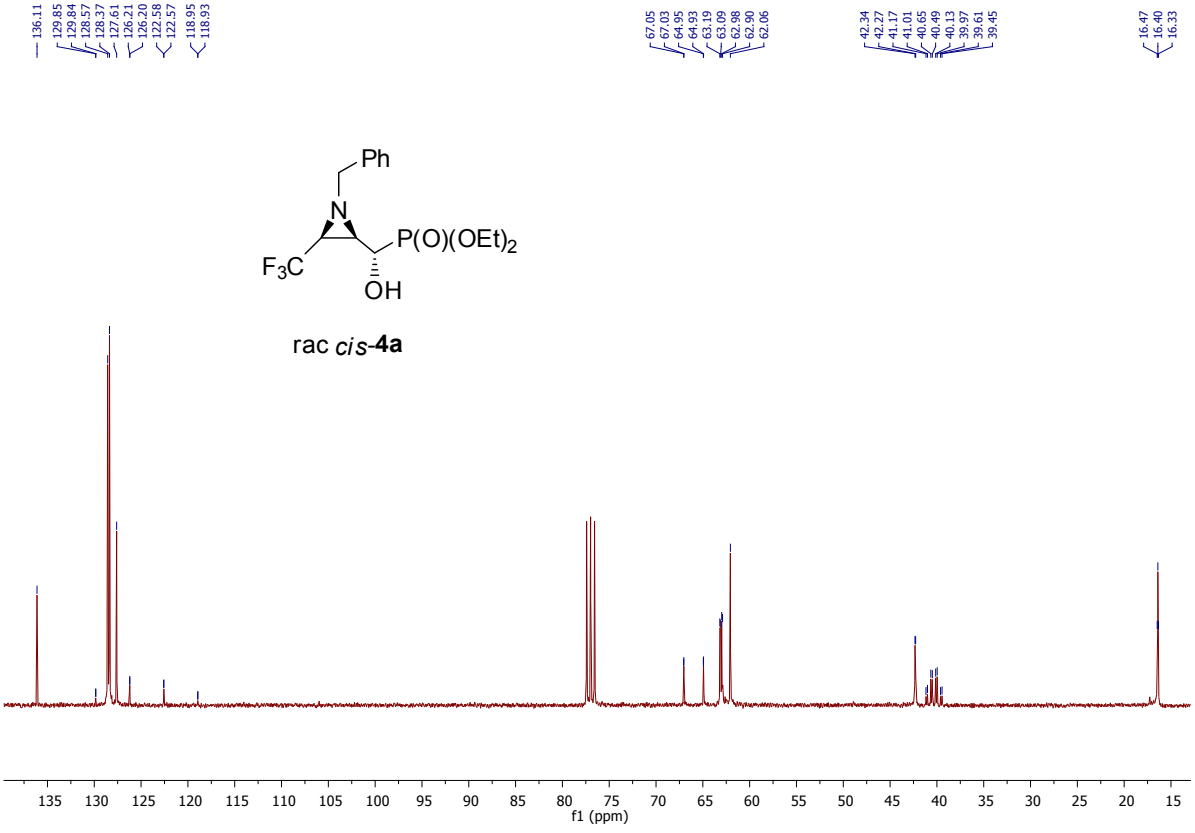
^{1}H NMR of (1-benzyl-3-(trifluoromethyl)aziridin-2-yl)methanol (rac *cis*-2)



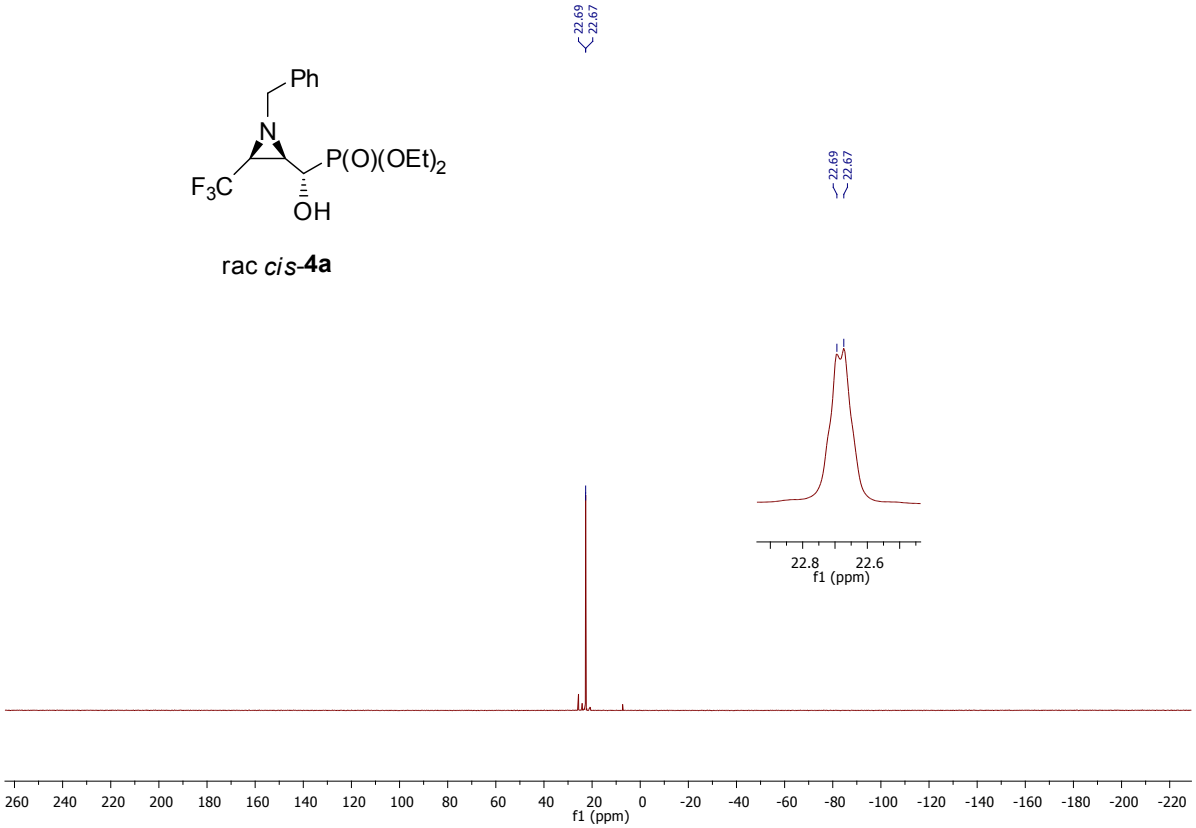
^{13}C NMR of 1-benzyl-3-(trifluoromethyl)aziridin-2-yl)methanol (rac *cis*-2)



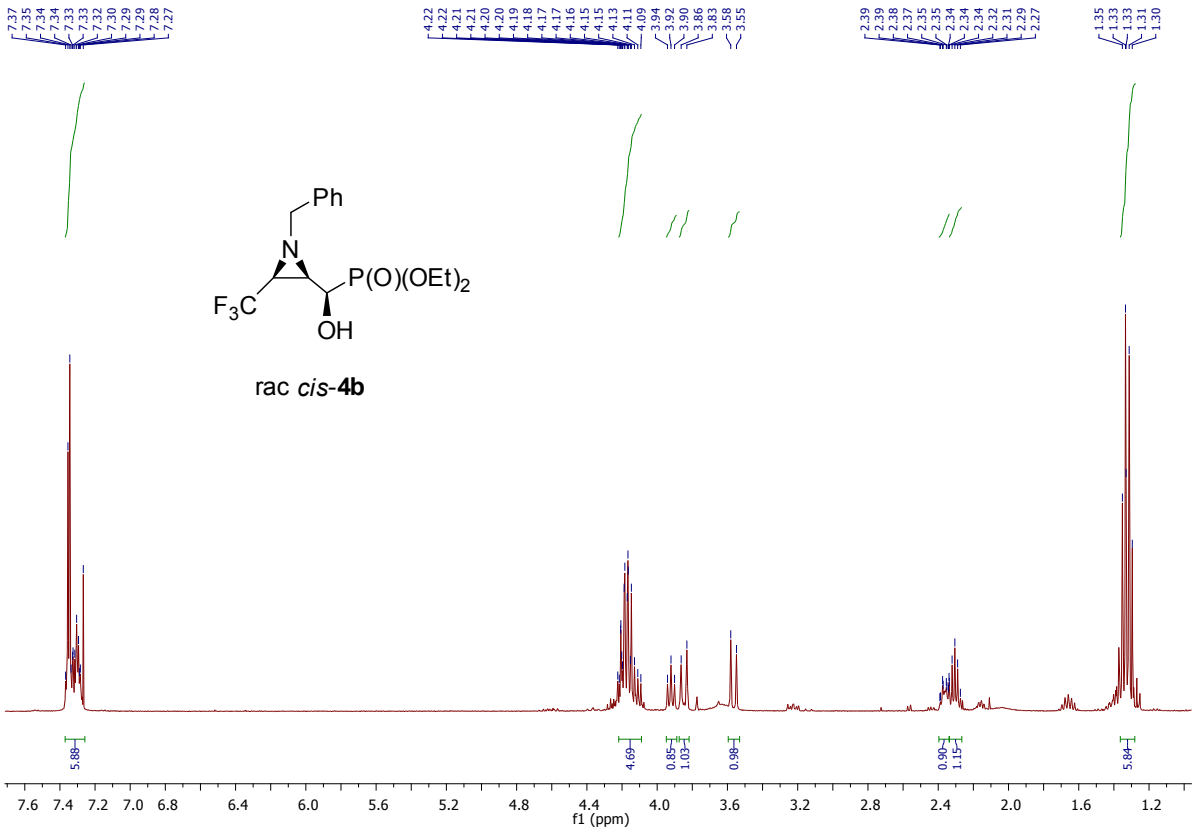
^{1}H NMR of diethyl 1-benzyl-3-(trifluoromethyl)aziridin-2-yl)(hydroxy)methylphosphonate (rac cis-4a)



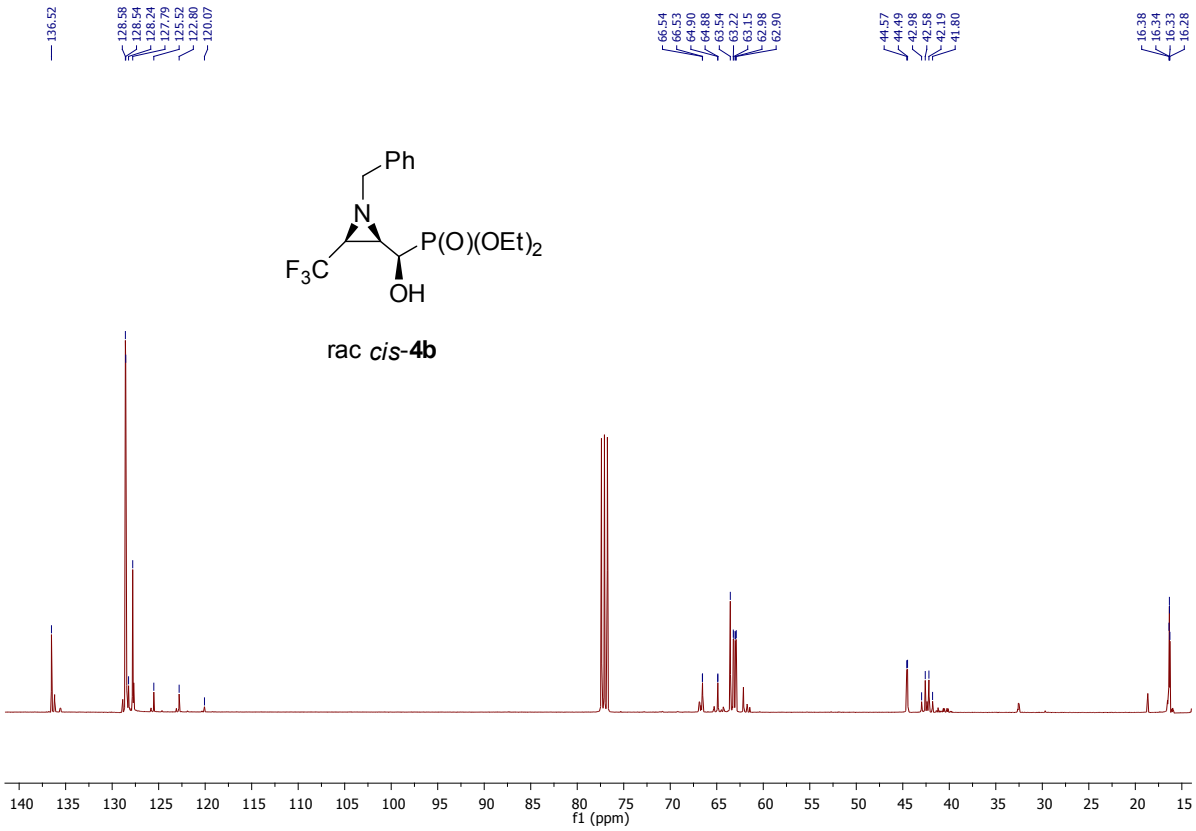
^{13}C NMR of diethyl 1-benzyl-3-(trifluoromethyl)aziridin-2-yl)(hydroxy)methylphosphonate (rac cis-4a)



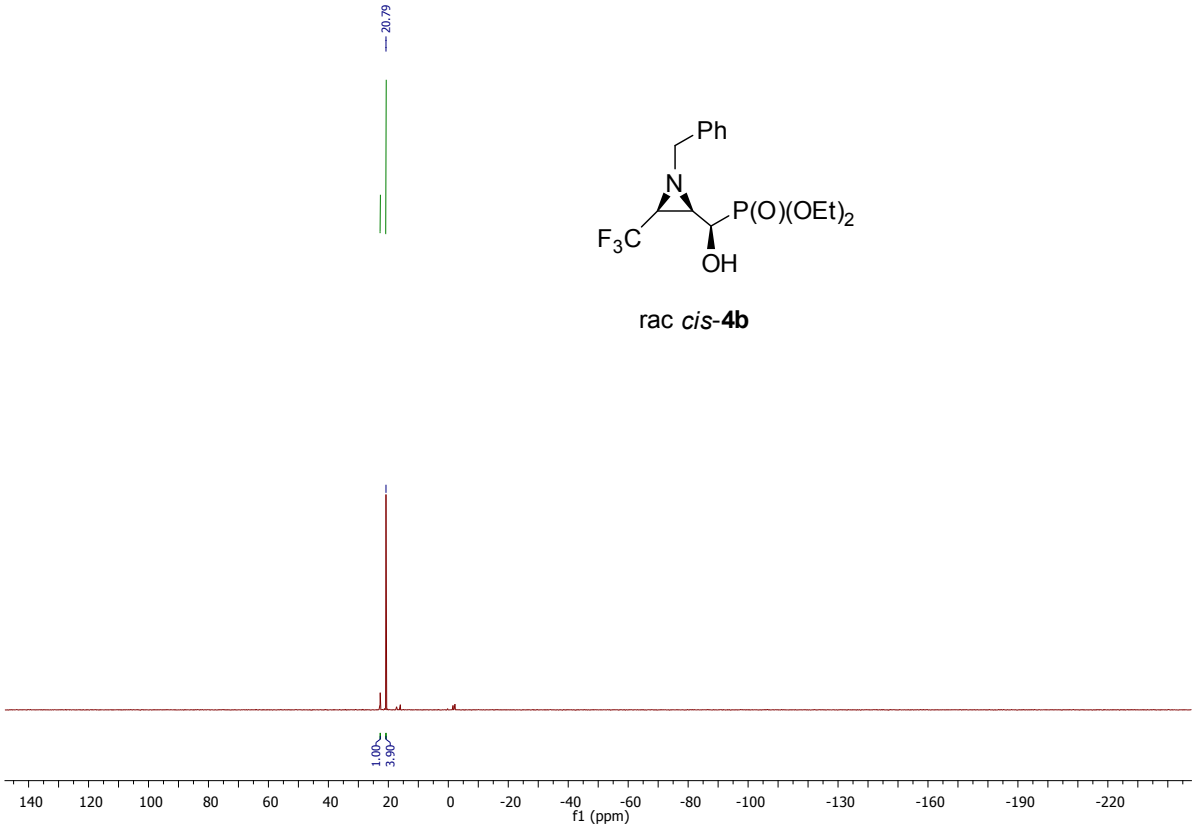
^{31}P NMR of diethyl 1-benzyl-3-(trifluoromethyl)aziridin-2-yl)(hydroxy)methylphosphonate (rac cis-4a)



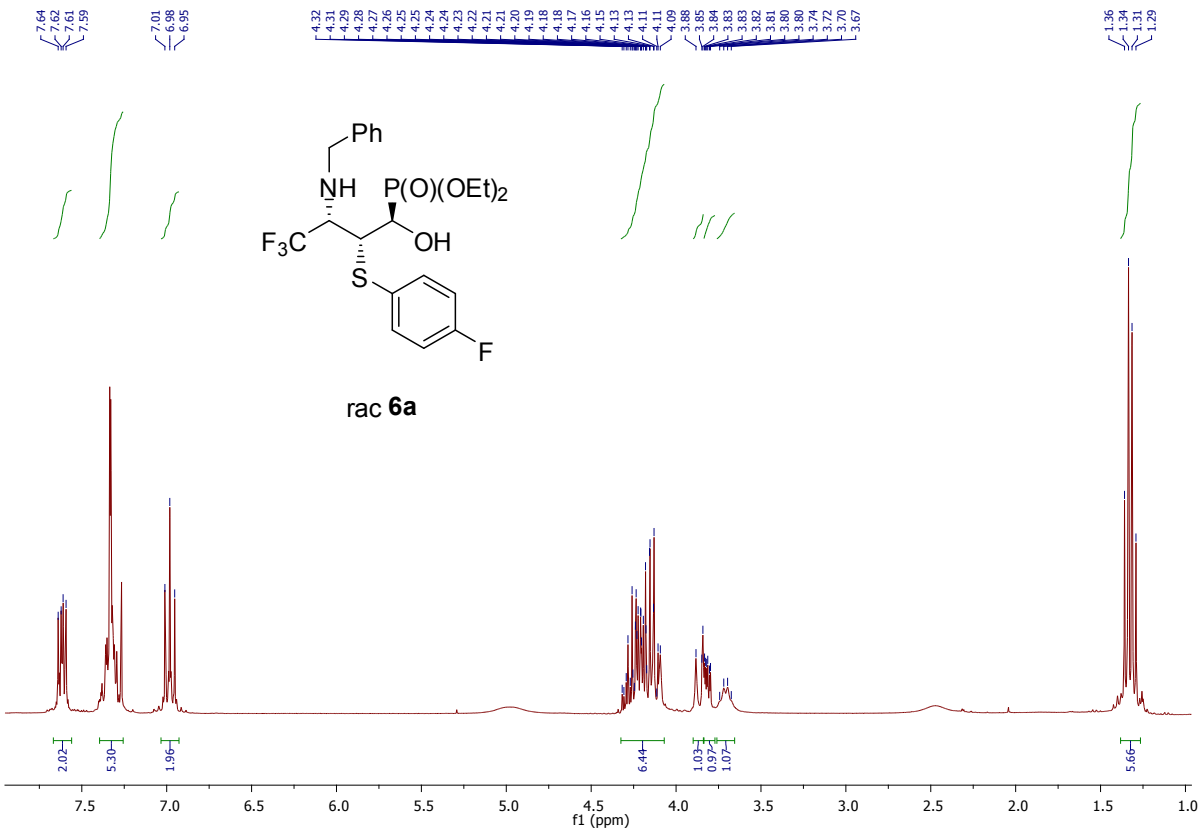
^{1}H NMR of diethyl 1-benzyl-3-(trifluoromethyl)aziridin-2-yl)(hydroxy)methylphosphonate (rac cis-4b)



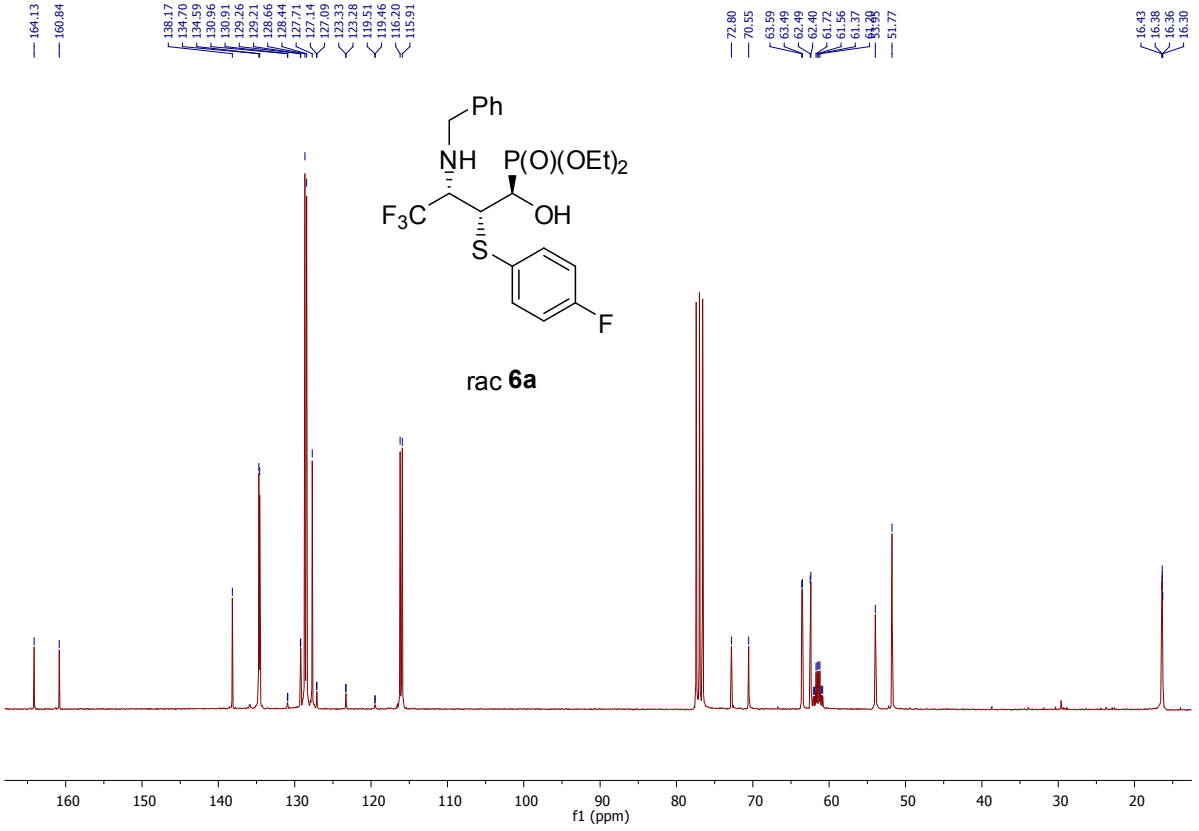
^{13}C NMR of diethyl 1-benzyl-3-(trifluoromethyl)aziridin-2-yl)(hydroxy)methylphosphonate (rac cis-4b)



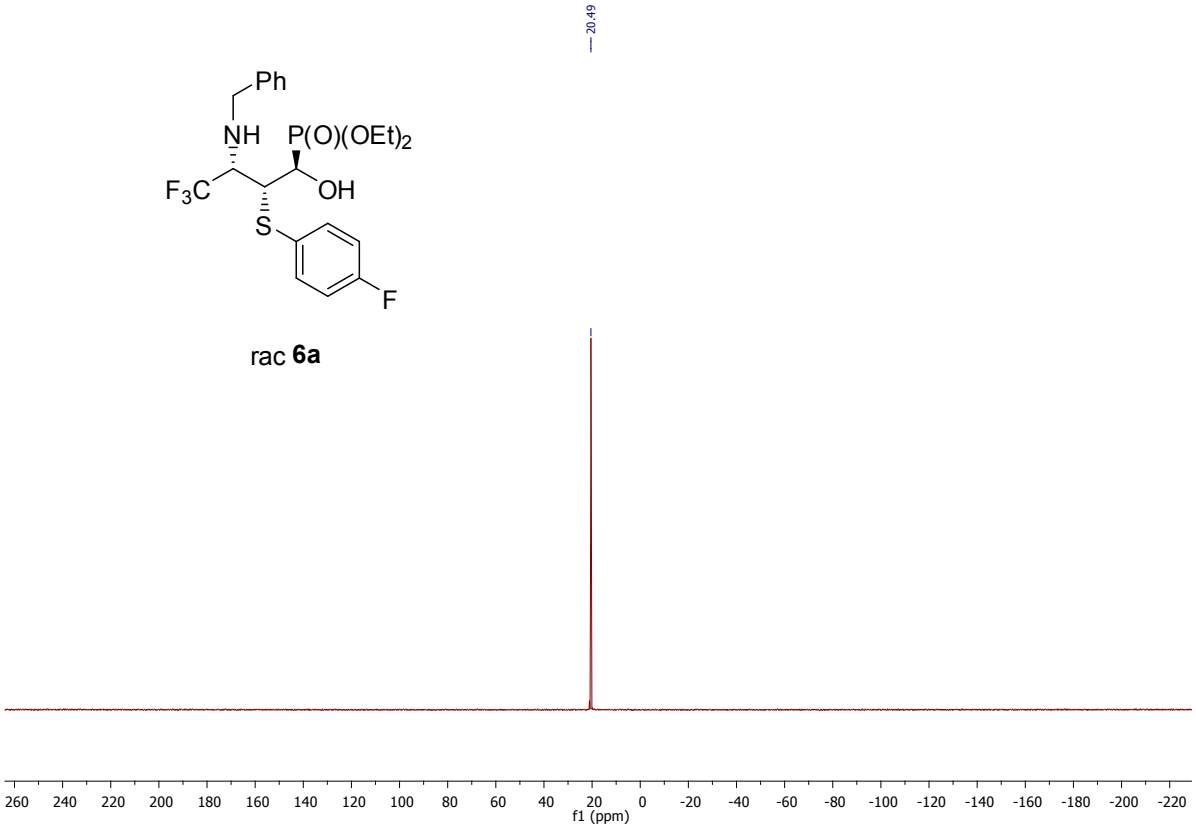
^{31}P NMR of diethyl 1-benzyl-3-(trifluoromethyl)aziridin-2-yl)(hydroxy)methylphosphonate (rac cis-4b)



^{1}H NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-2-(4-fluorophenylthio)-1-hydroxybutylphosphonate (rac 6a)

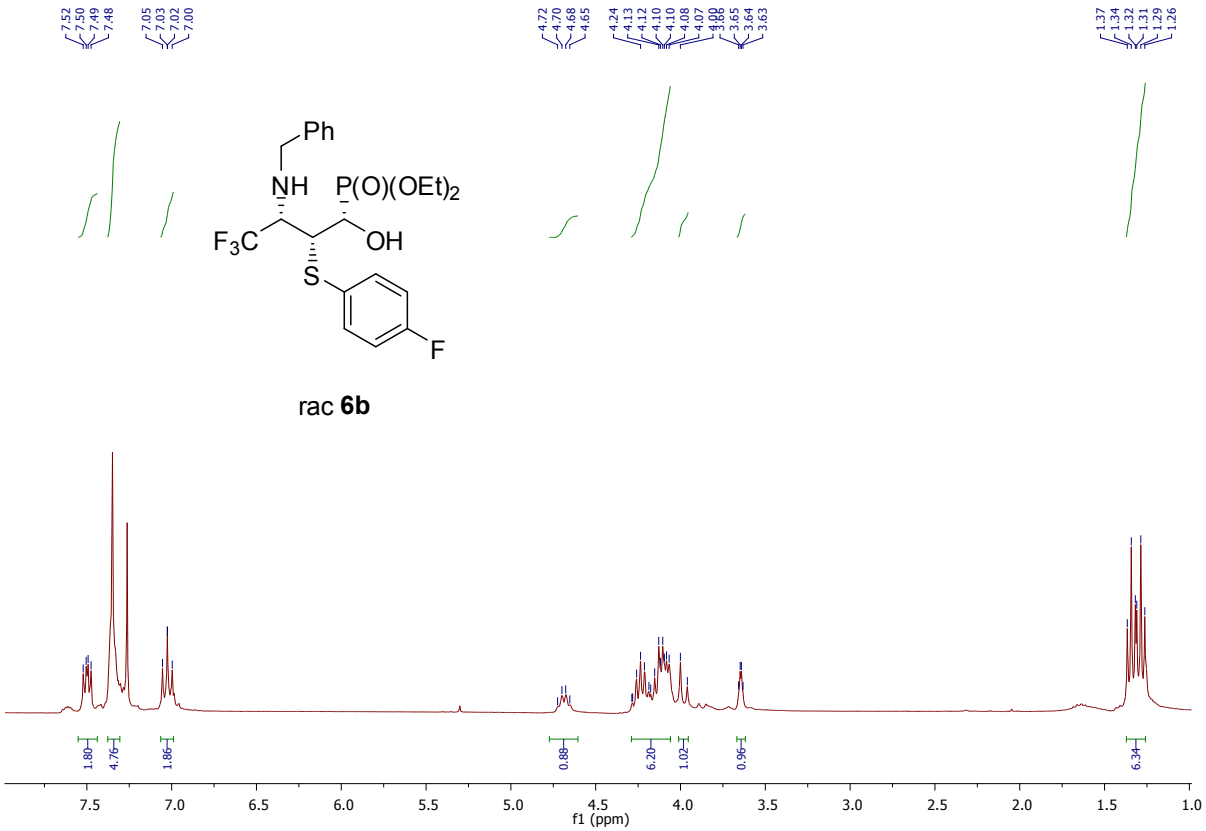


^{13}C NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-2-(4-fluorophenylthio)-1-hydroxybutylphosphonate (rac 6a)



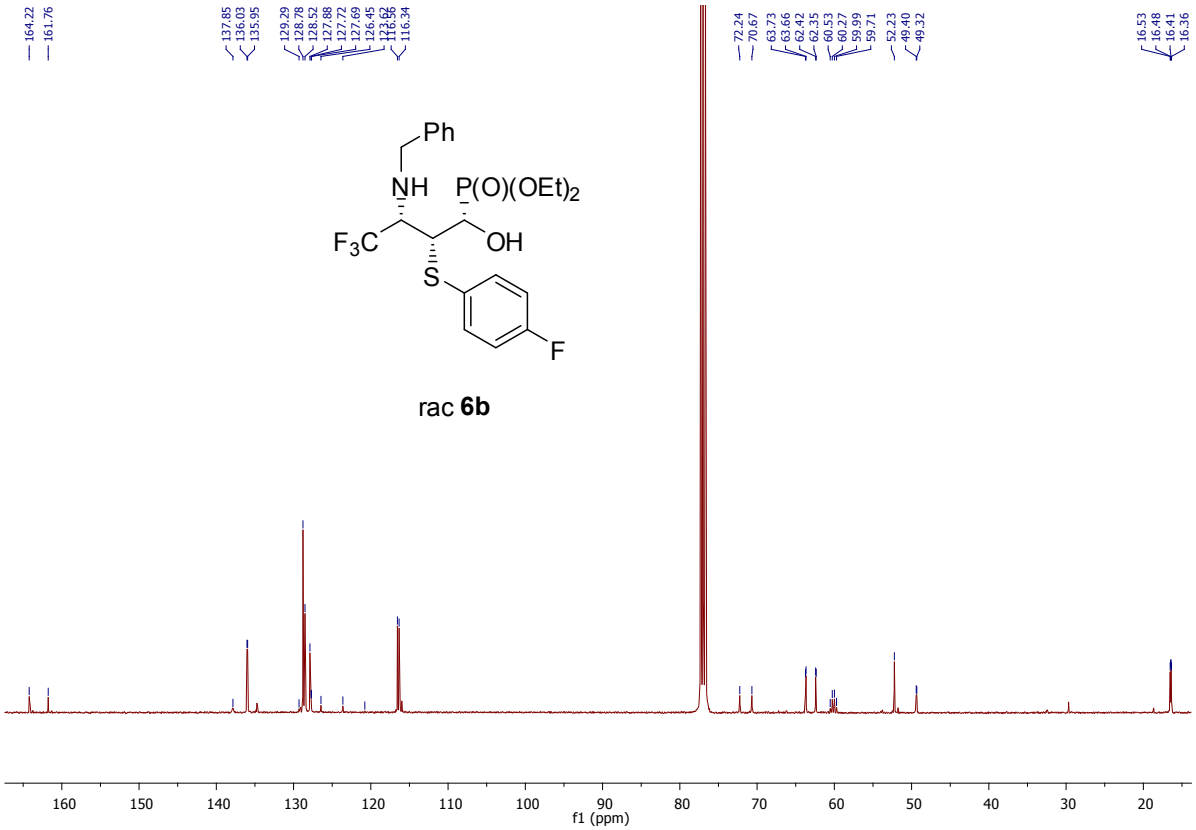
rac **6a**

^{31}P NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-2-(4-fluorophenylthio)-1-hydroxybutylphosphonate (rac 6a)



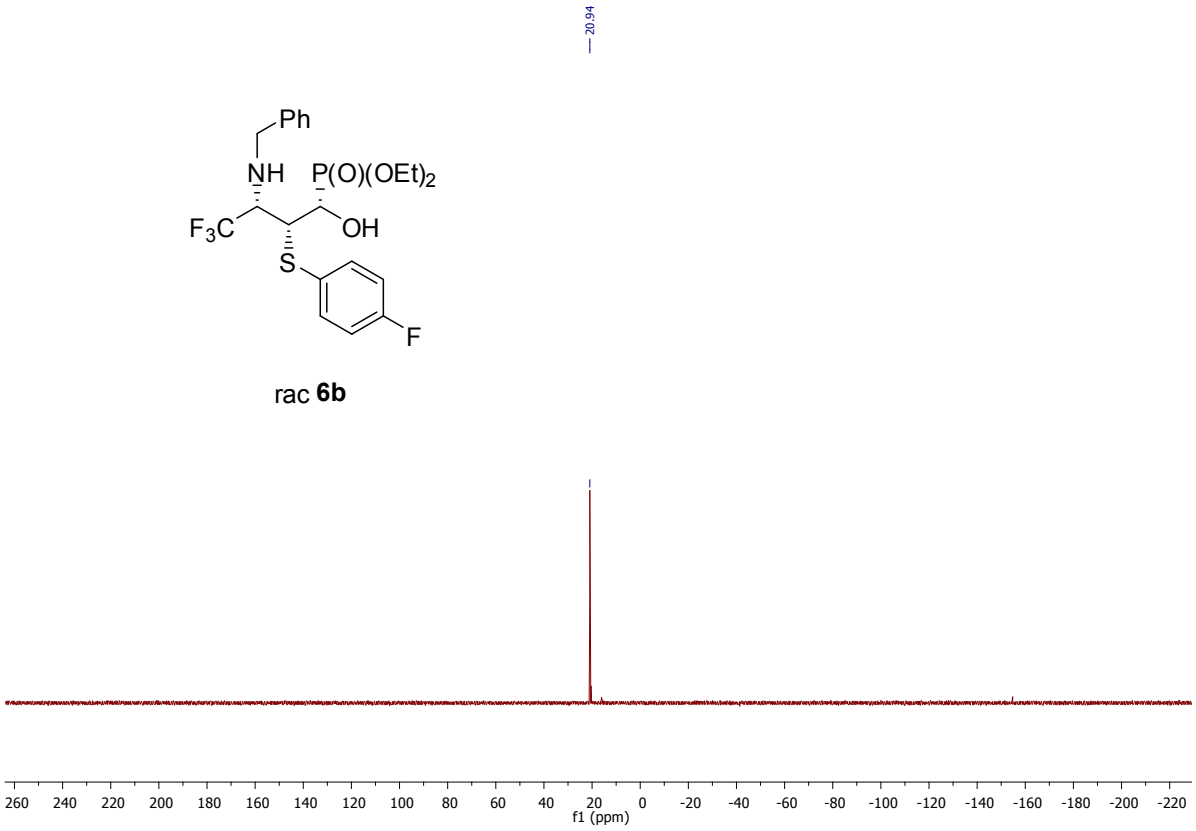
rac **6b**

^{1}H NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-2-(4-fluorophenylthio)-1-hydroxybutylphosphonate (rac 6b)



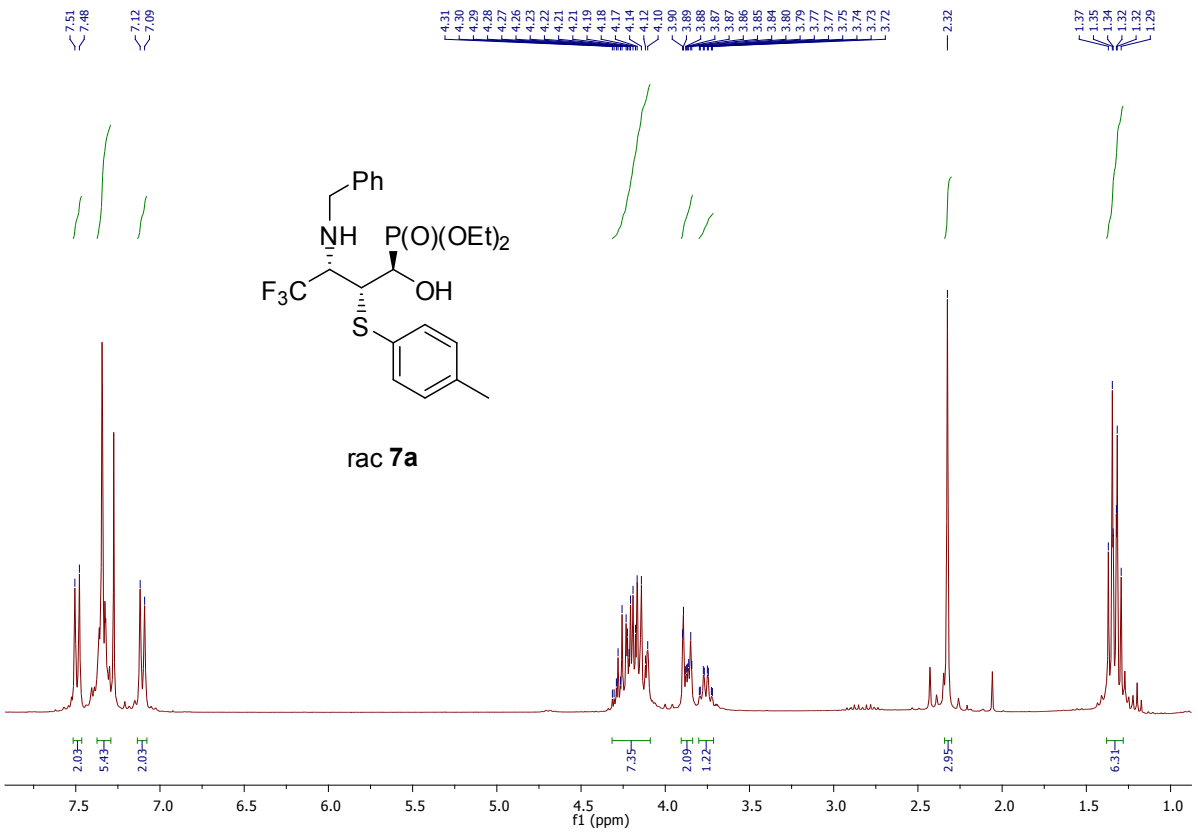
rac **6b**

^{13}C NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-2-(4-fluorophenylthio)-1-hydroxybutylphosphonate (rac 6b)

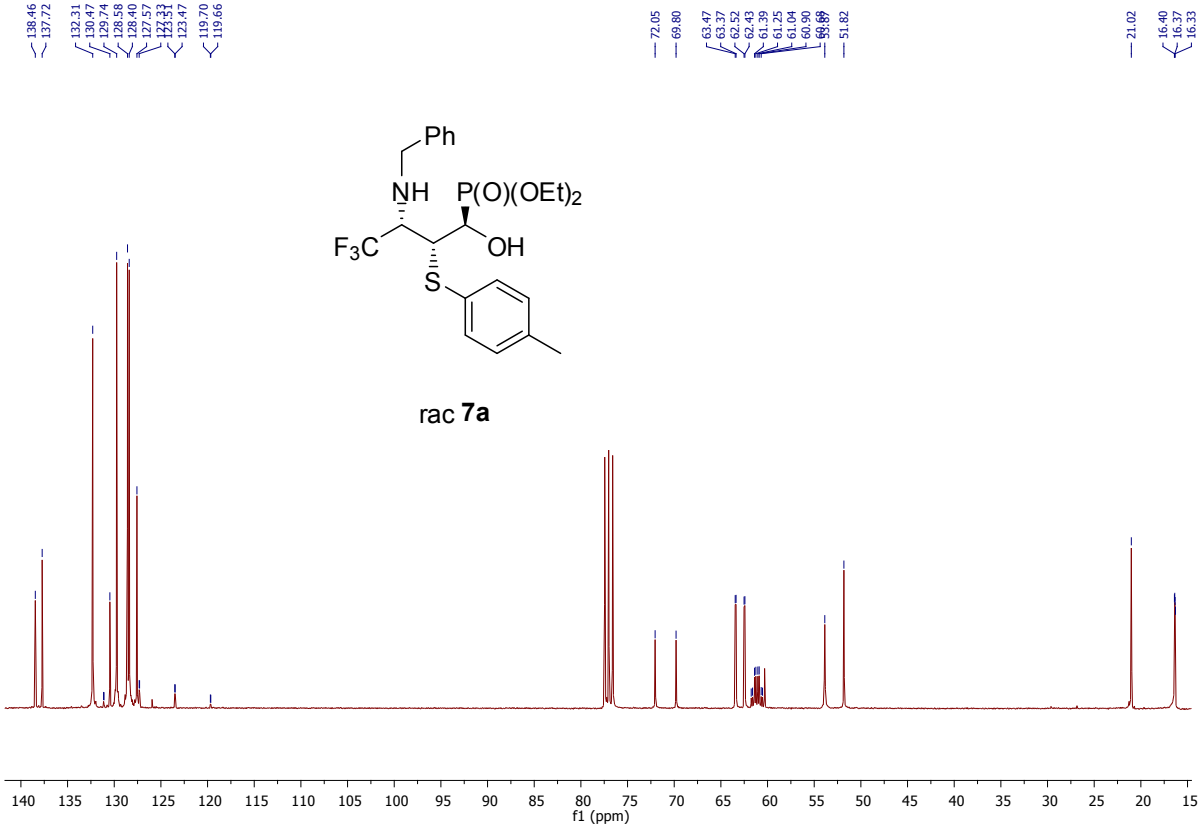


rac **6b**

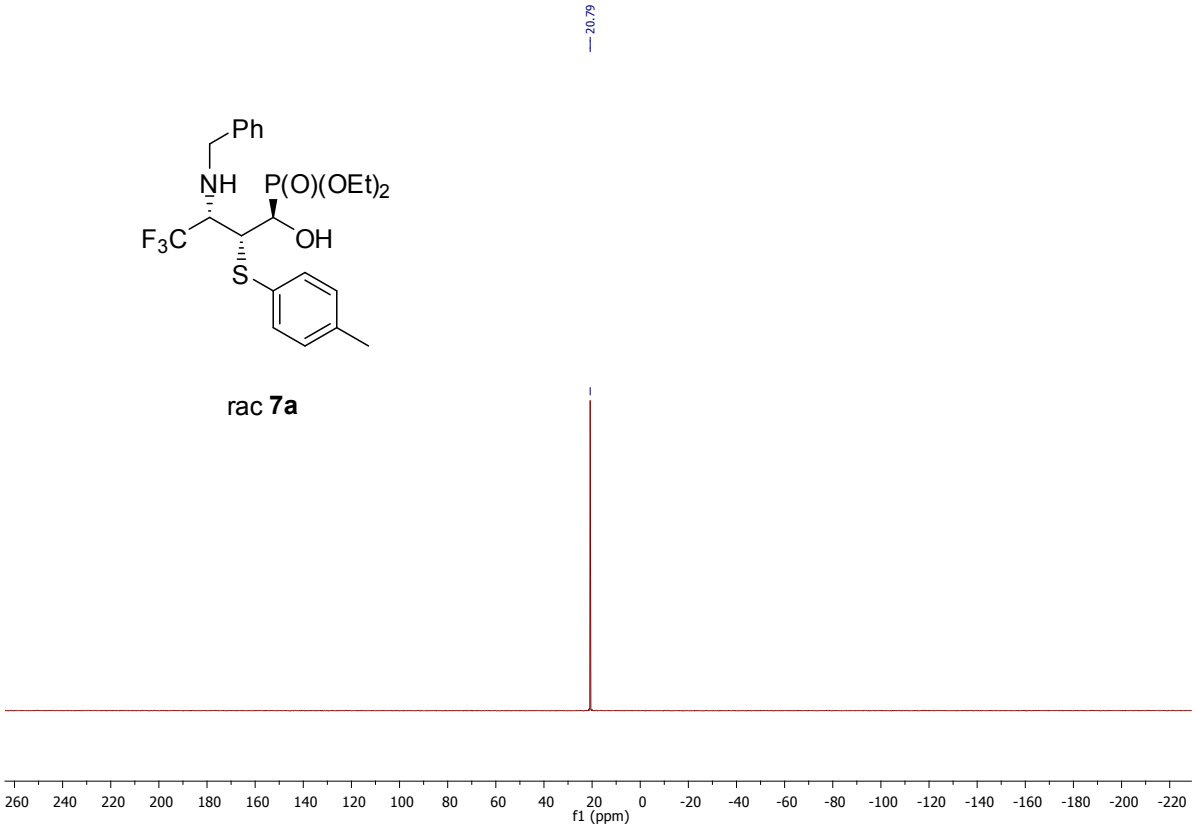
^{31}P NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-2-(4-fluorophenylthio)-1-hydroxybutylphosphonate (rac 6b)



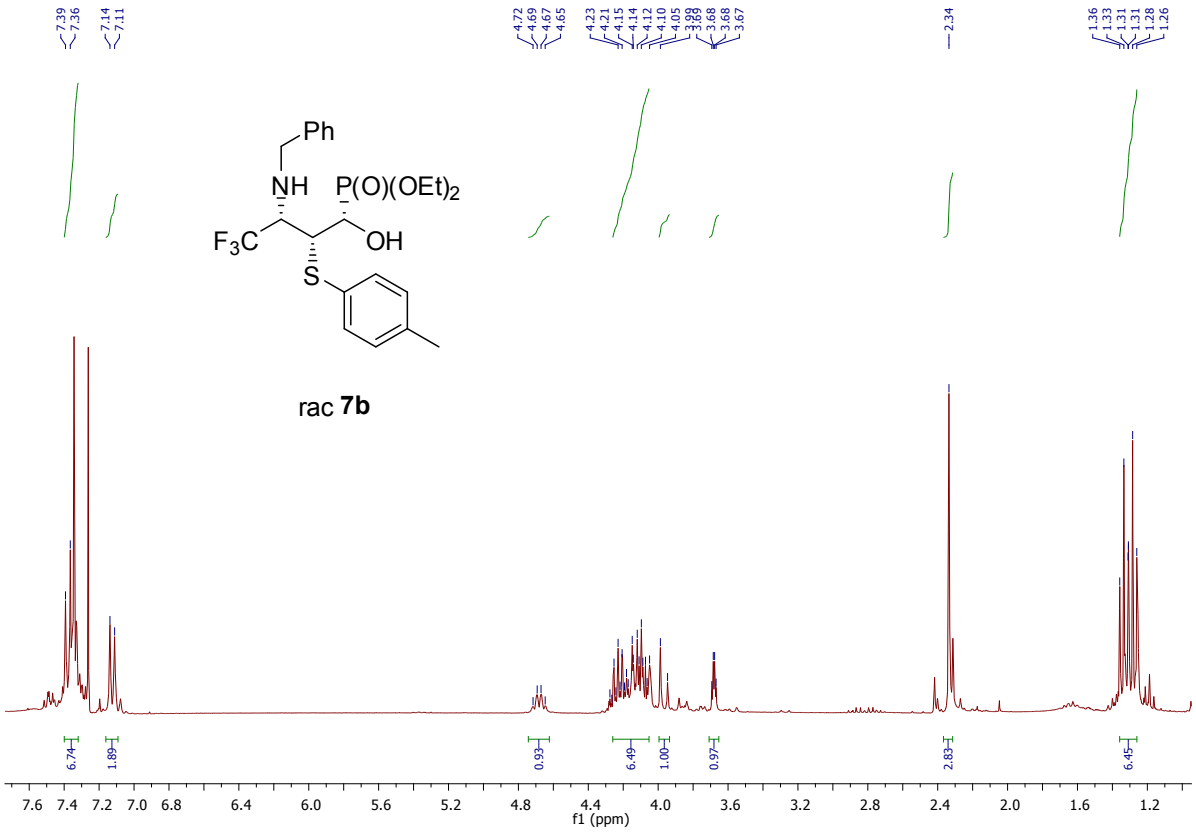
^{1}H NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(*p*-tolylthio)butylphosphonate (rac 7a)



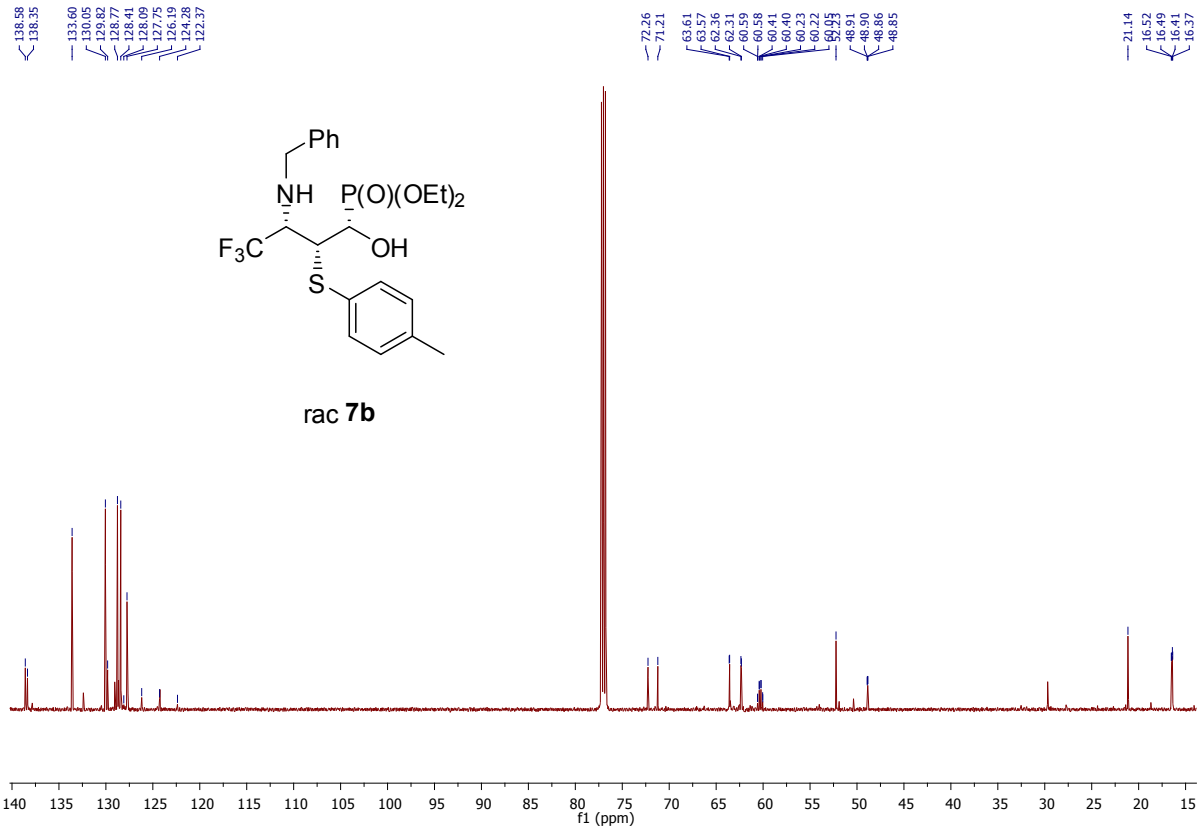
^{13}C NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(*p*-tolylthio)butylphosphonate (rac 7a)



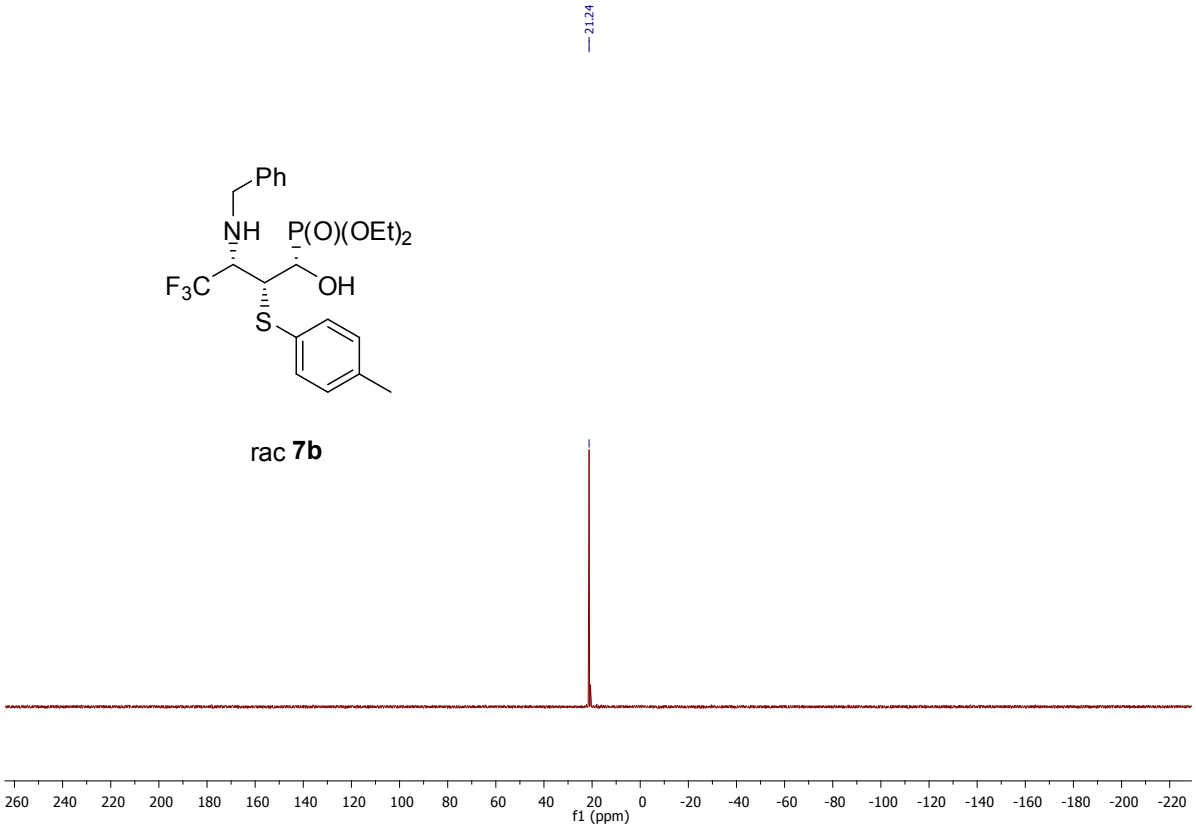
^{31}P NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(*p*-tolylthio)butylphosphonate (rac 7a)



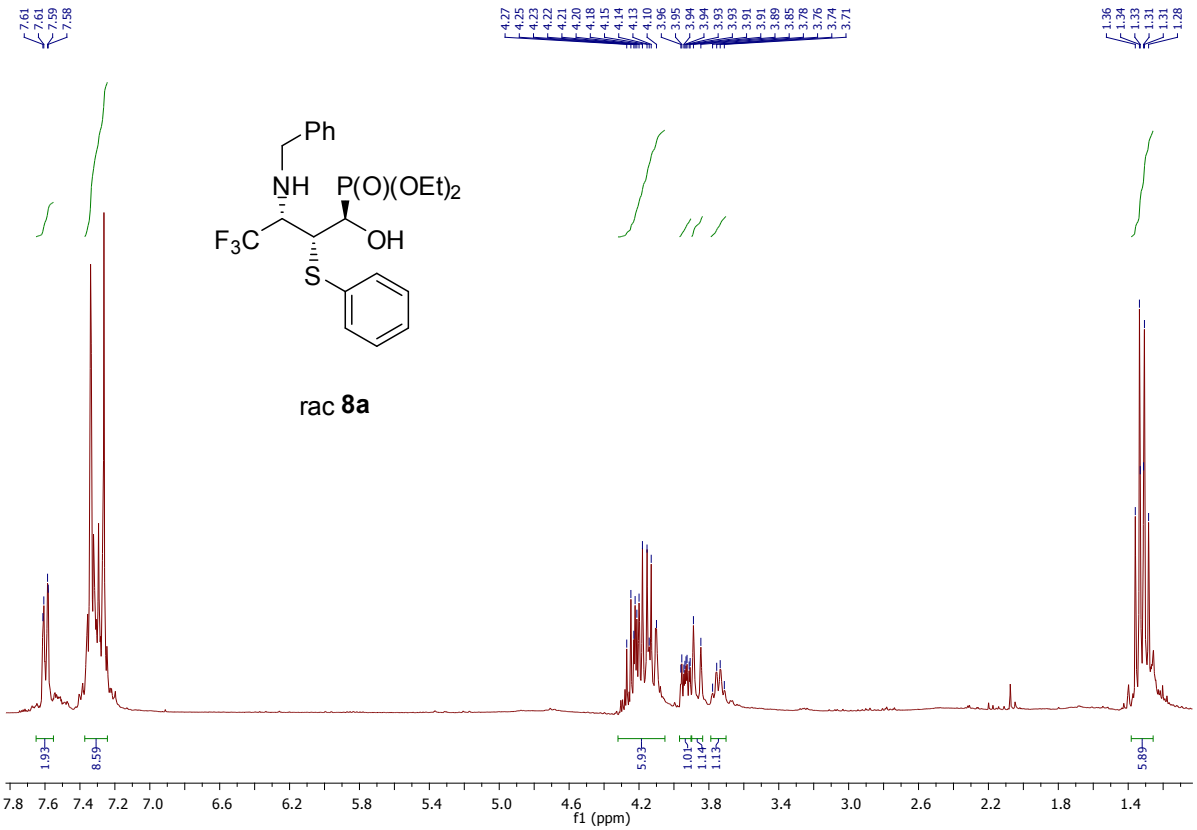
^{1}H NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(*p*-tolylthio)butylphosphonate (rac 7b)



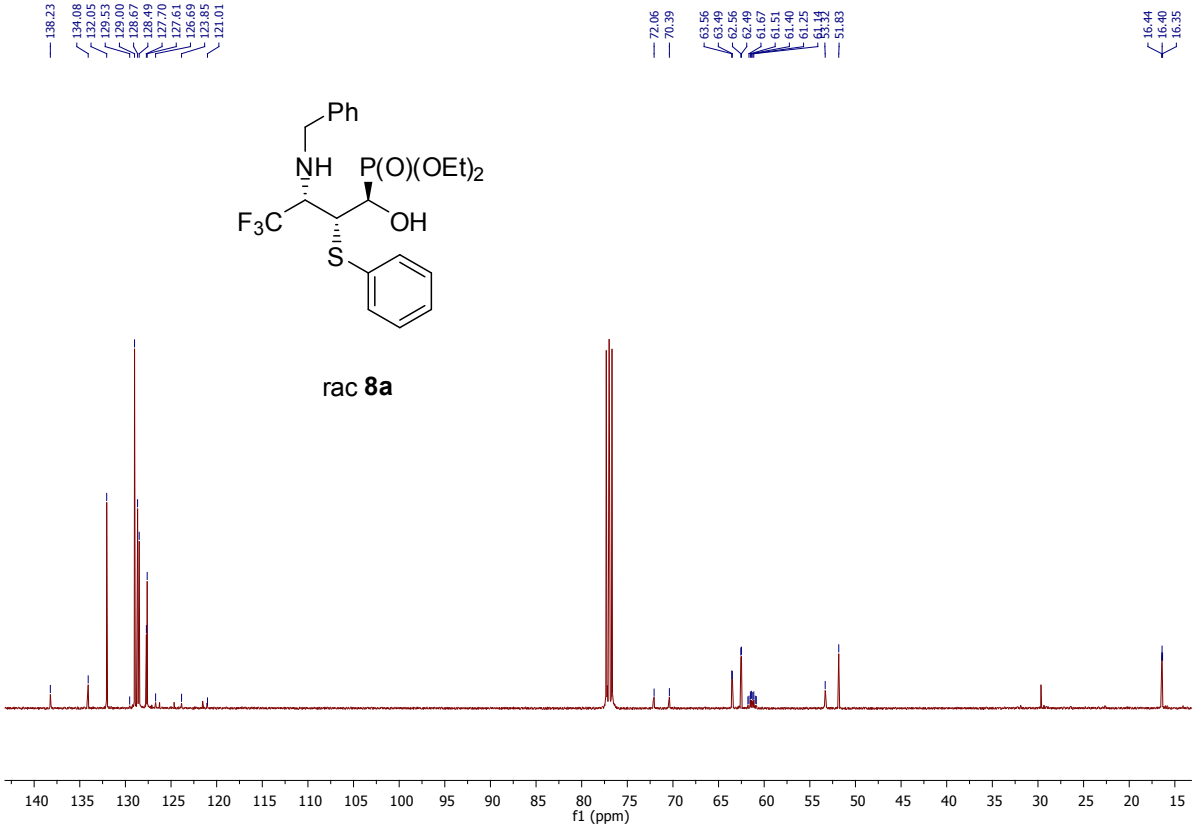
^{13}C NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(*p*-tolylthio)butylphosphonate (rac 7b)



^{31}P NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(*p*-tolylthio)butylphosphonate (rac 7b)



^{1}H NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(phenylthio)butylphosphonate (rac 8a)



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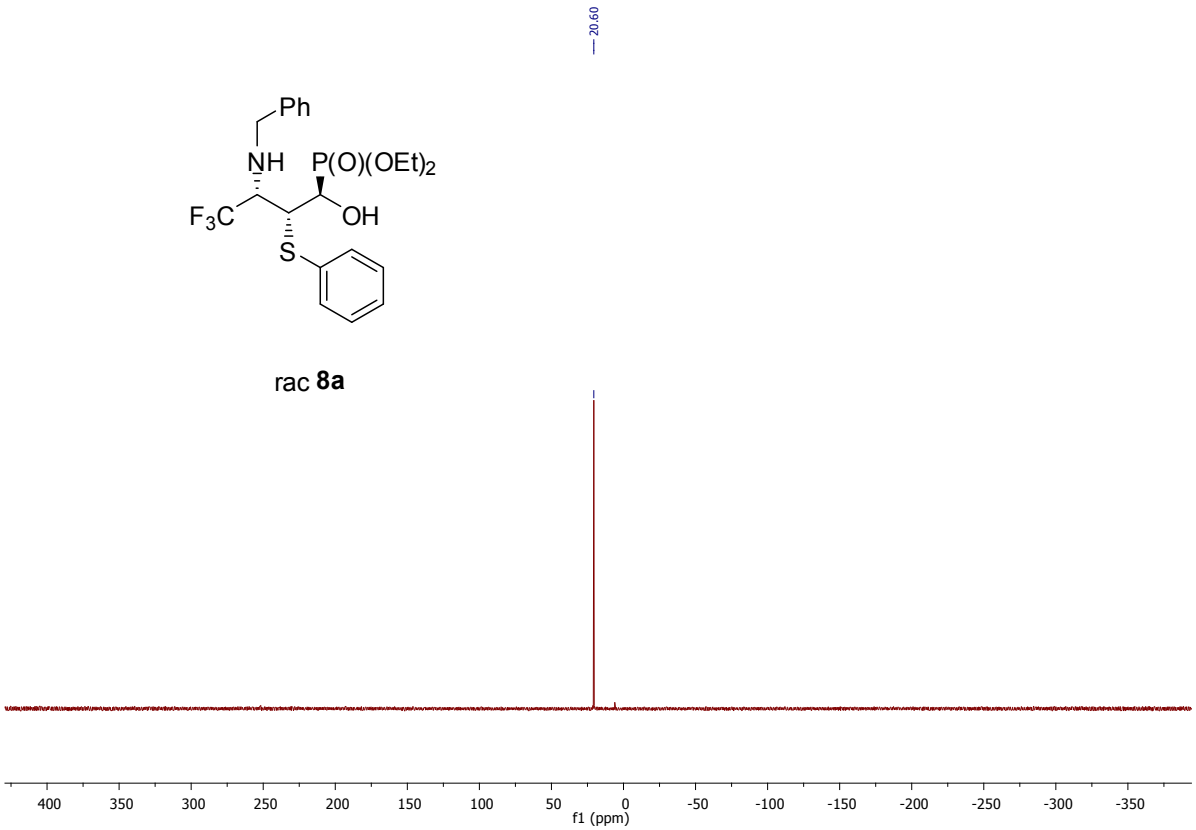
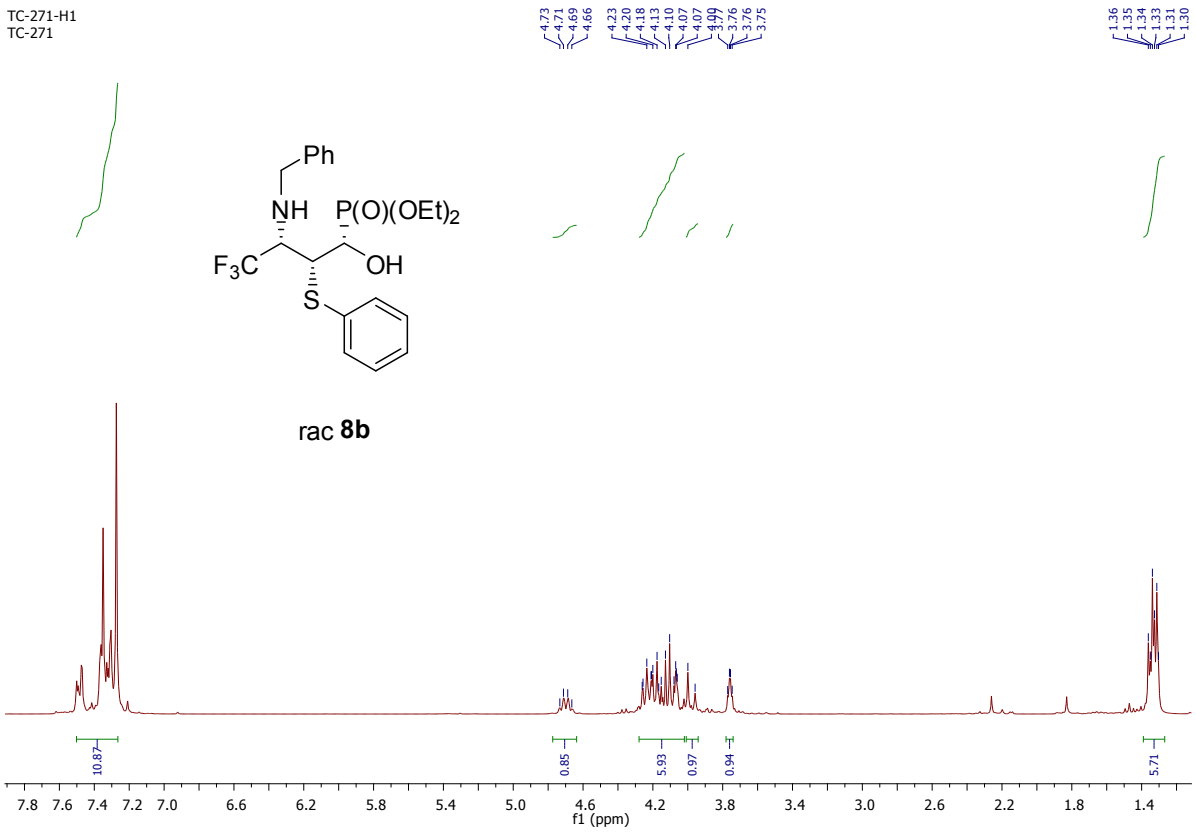


rac **8a**

^{31}P NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(phenylthio)butylphosphonate (rac 8a)



rac **8b**

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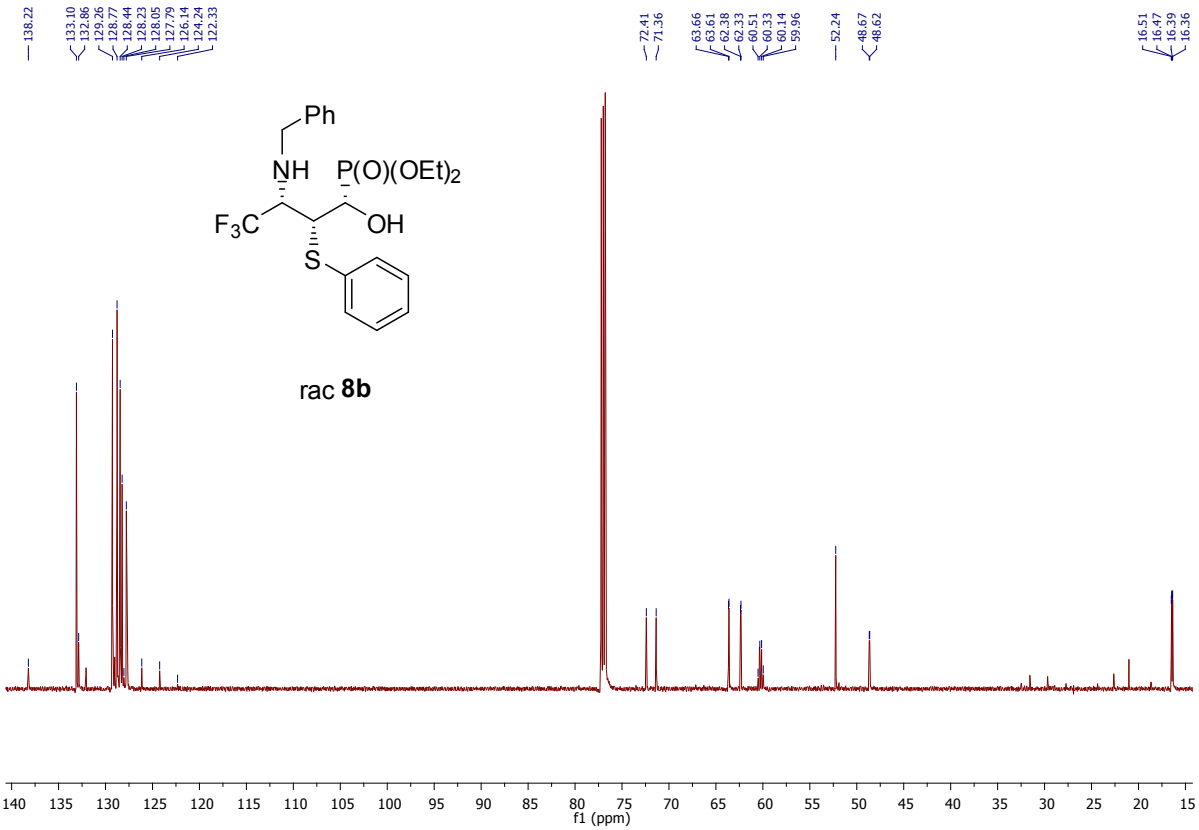
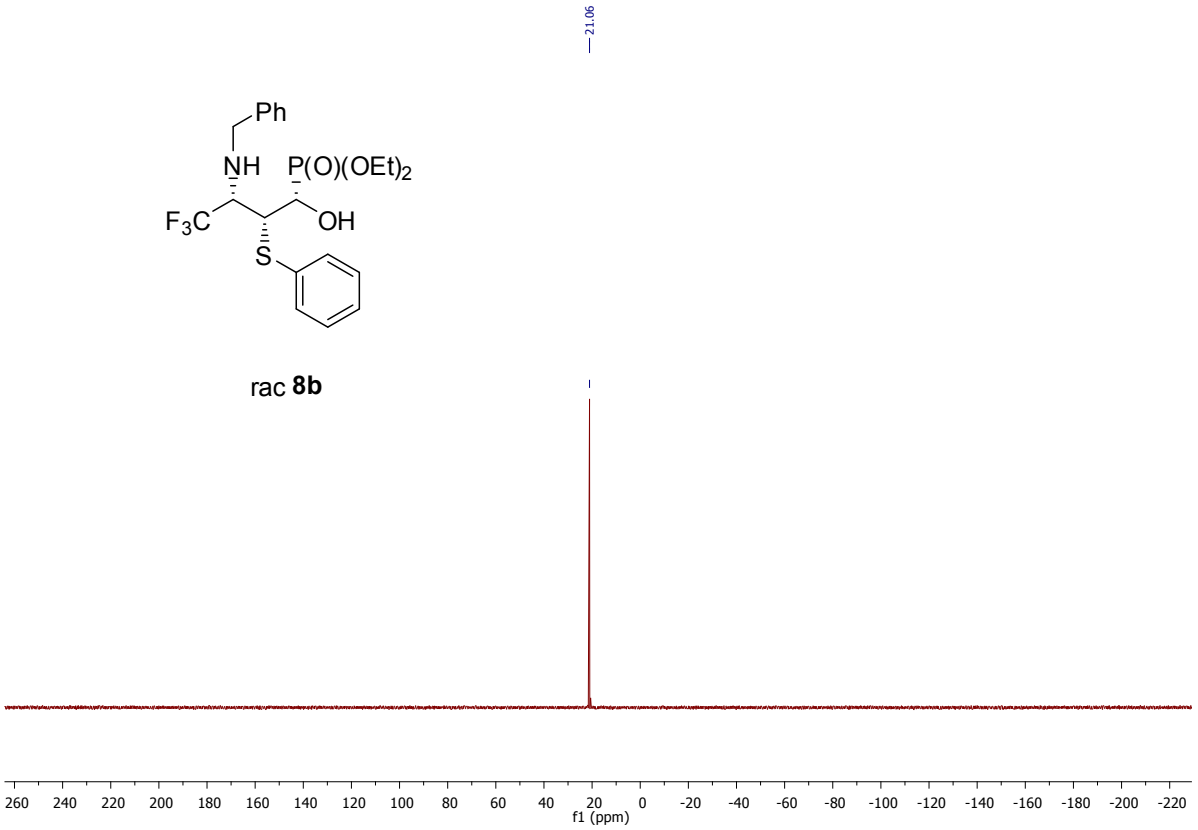


^{13}C NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(phenylthio)butylphosphonate (rac 8b)



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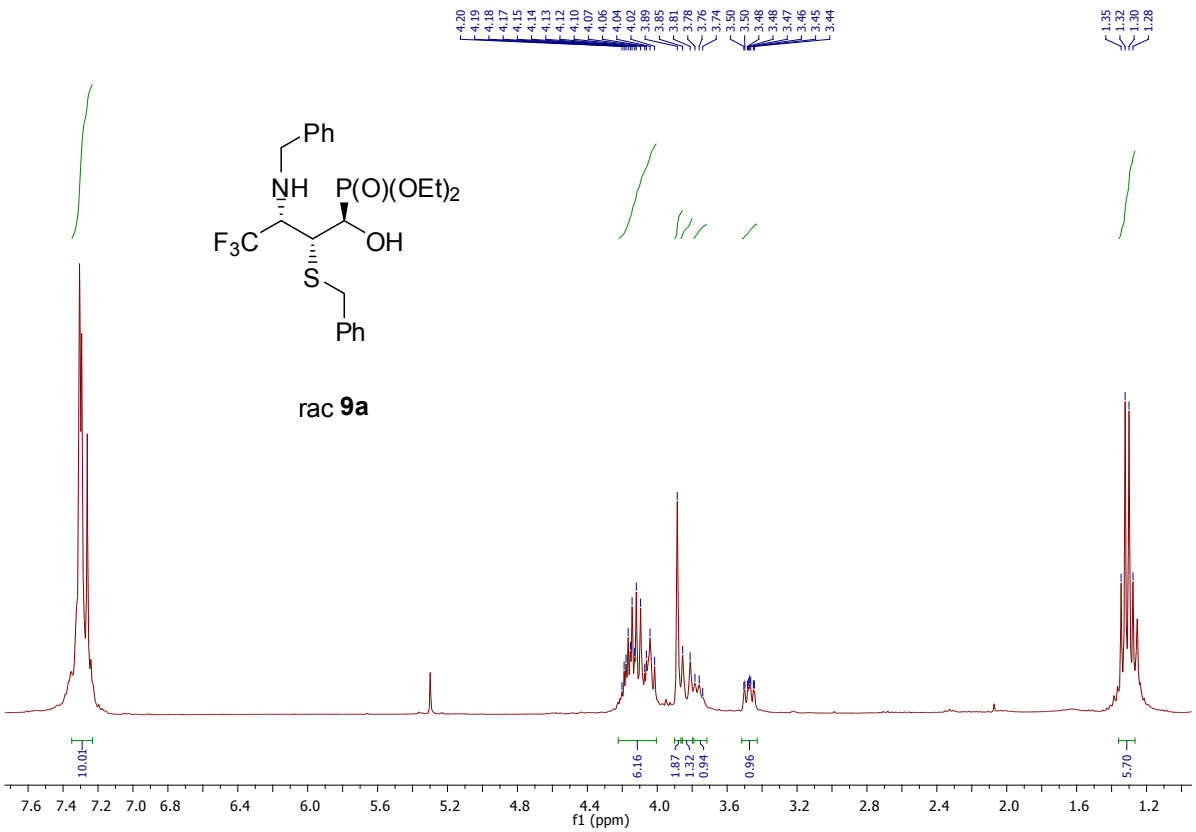
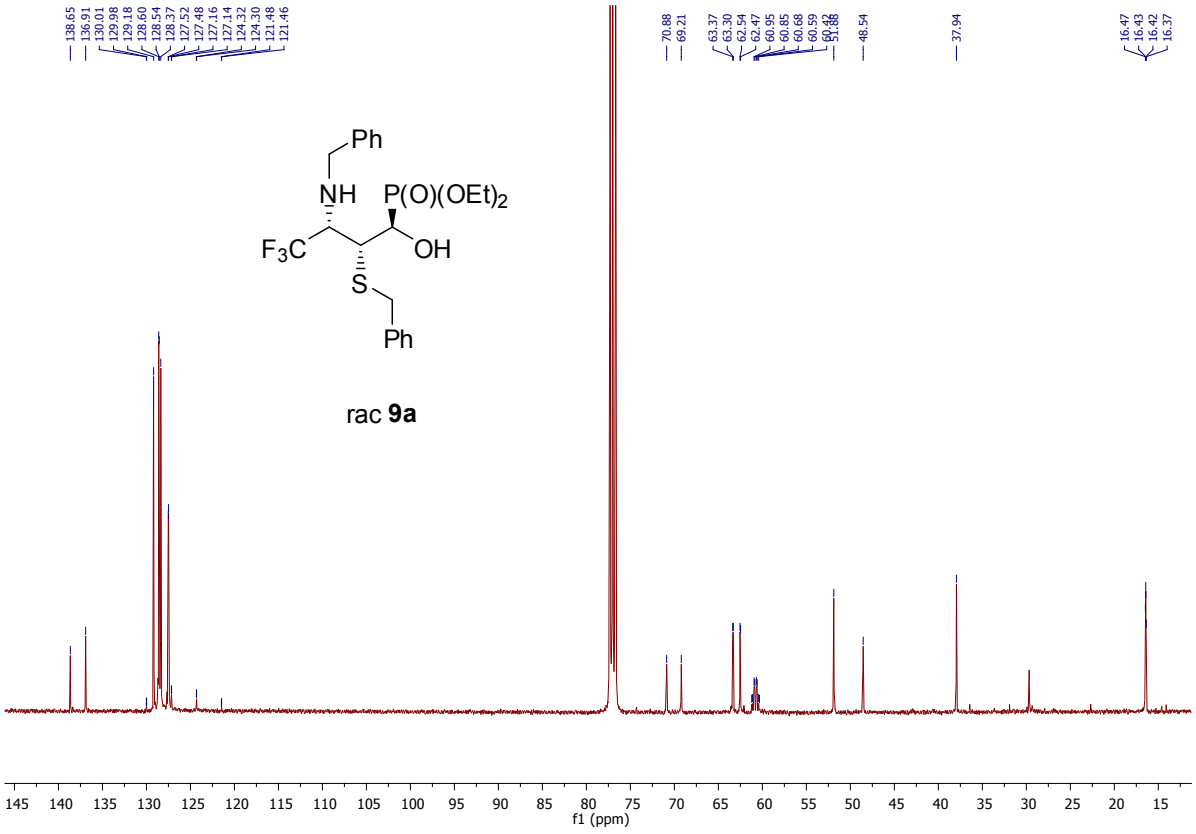


^{1}H NMR of diethyl 3-(benzylamino)-2-(benzylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 9a)



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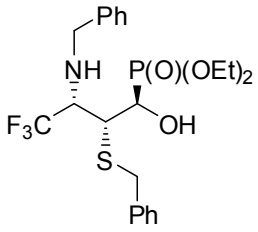

rac **9a**

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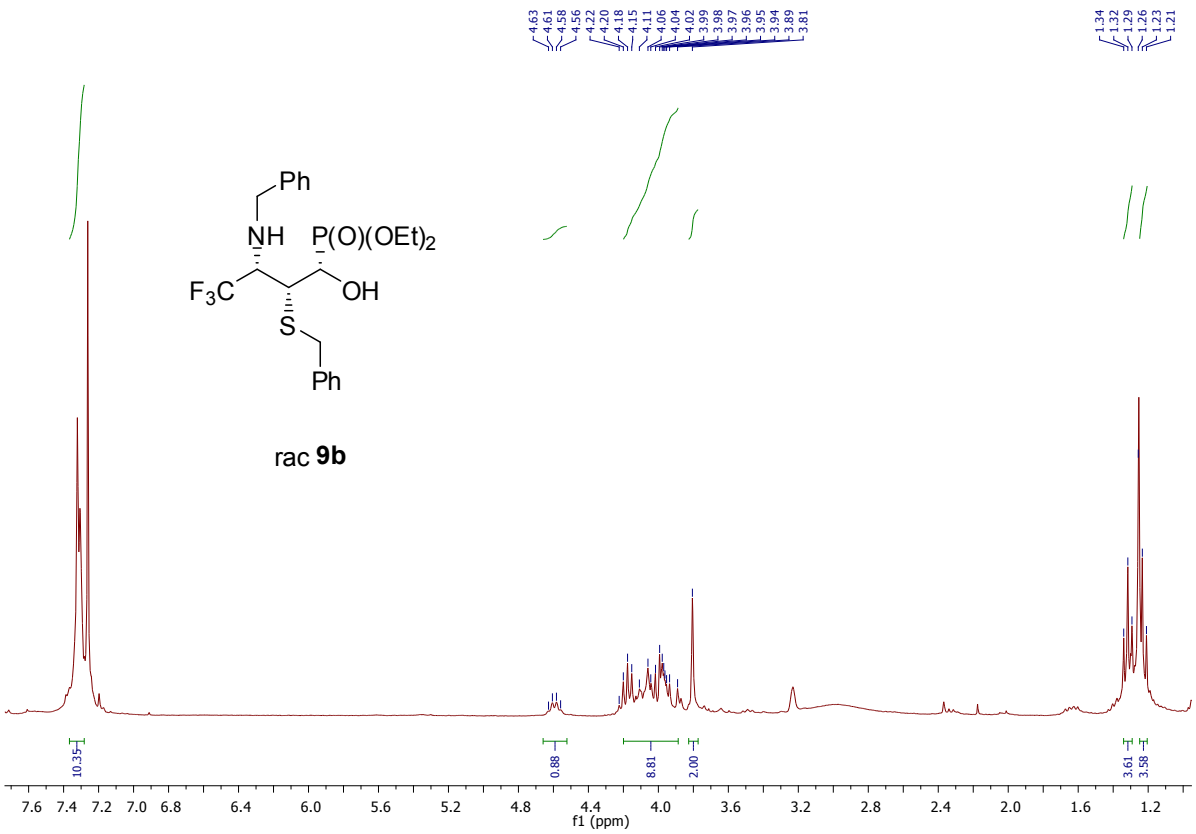

rac **9b**

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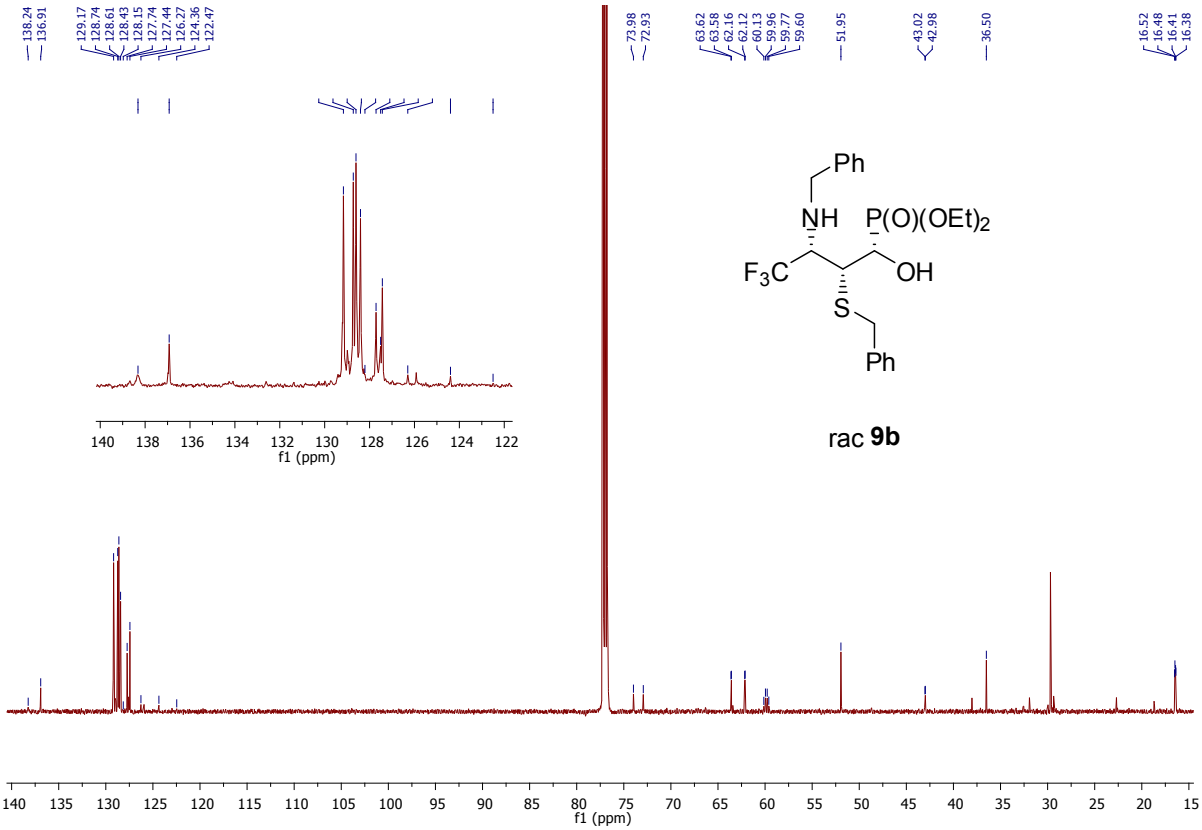
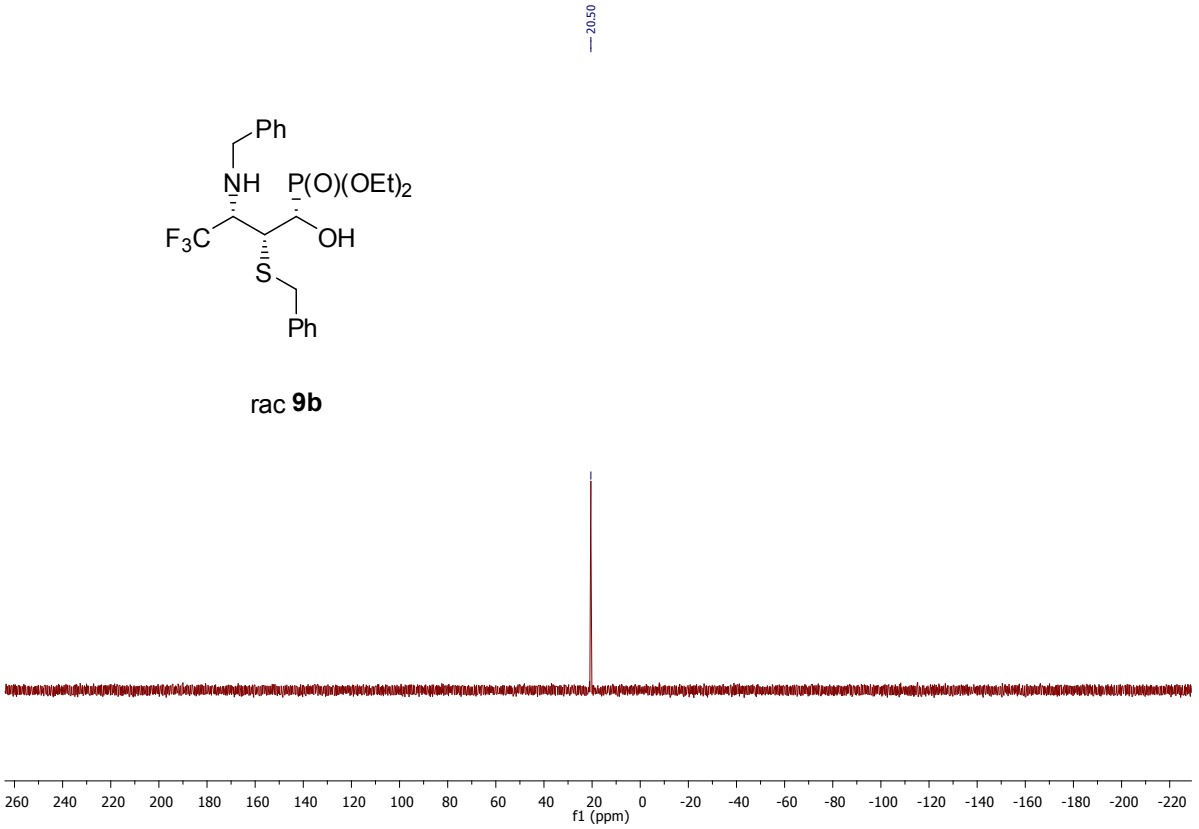


^{13}C NMR of diethyl 3-(benzylamino)-2-(benzylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 9b)



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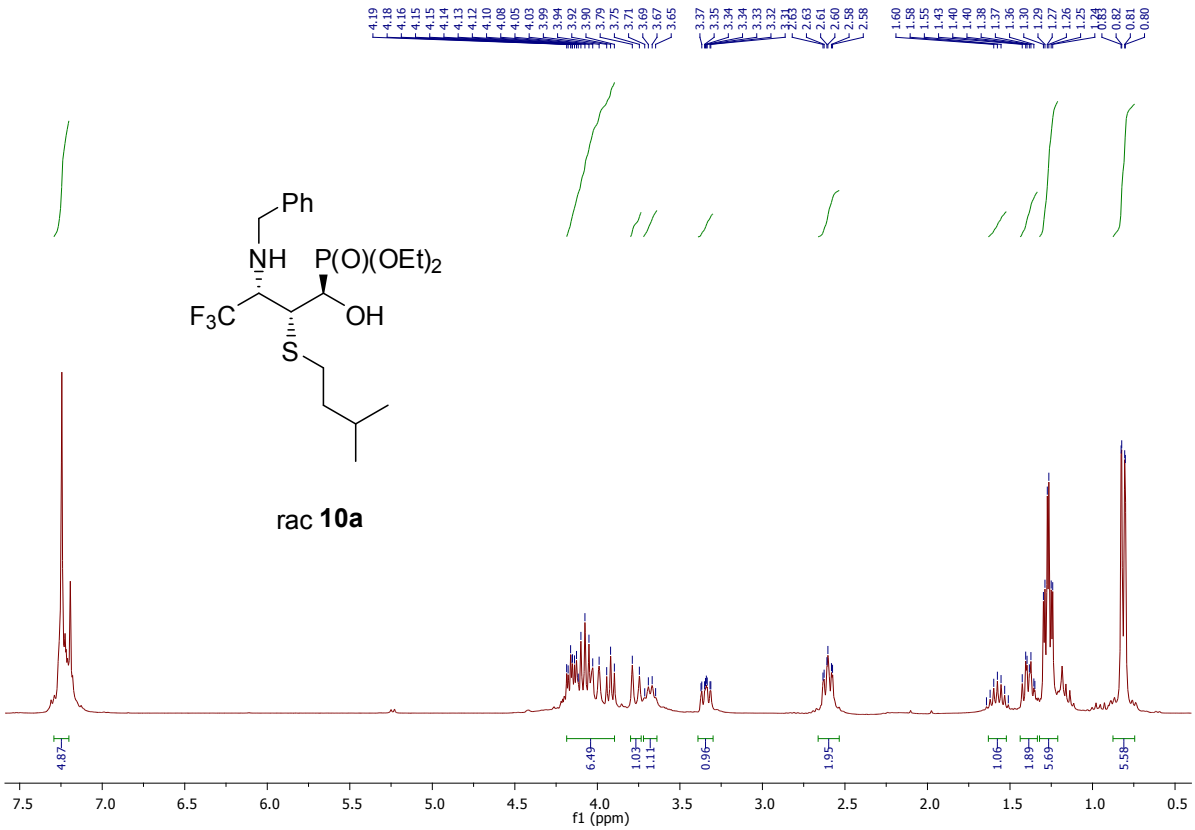
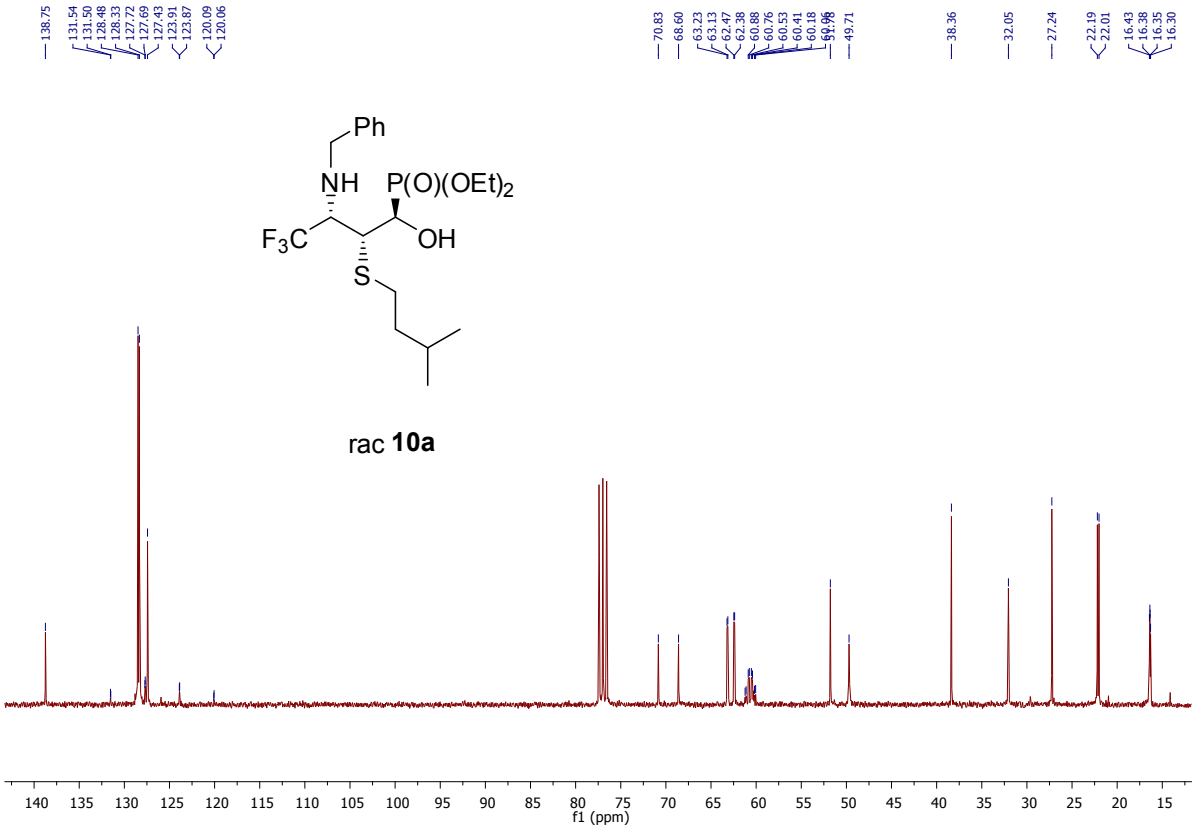
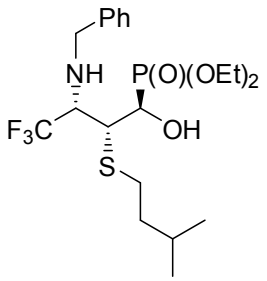


^{1}H NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(isopentylthio)butylphosphonate (rac-10a)

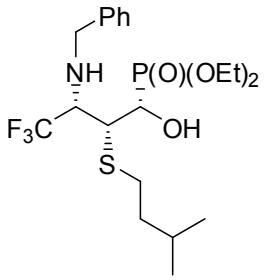


^{13}C NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(isopentylthio)butylphosphonate (rac-10a)



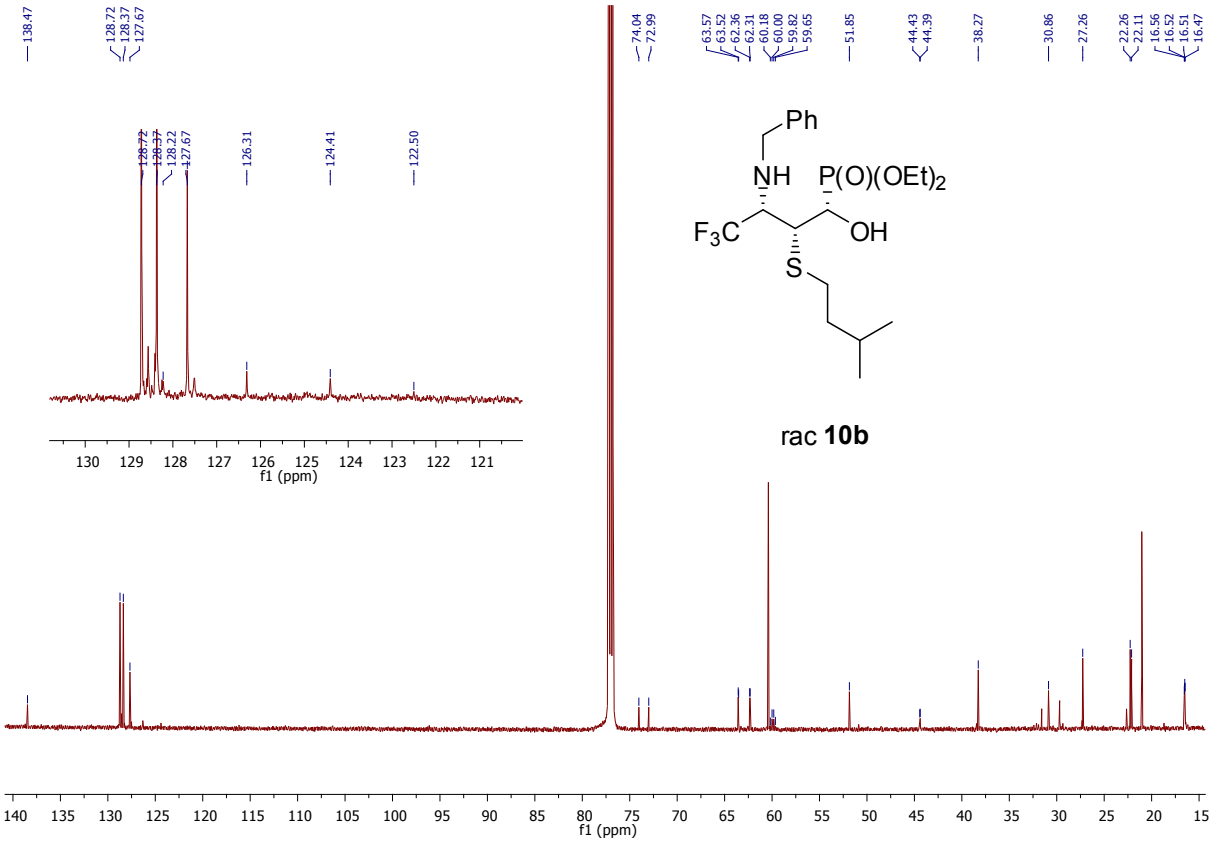
rac **10a**

^{31}P NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(isopentylthio)butylphosphonate (rac-10a)

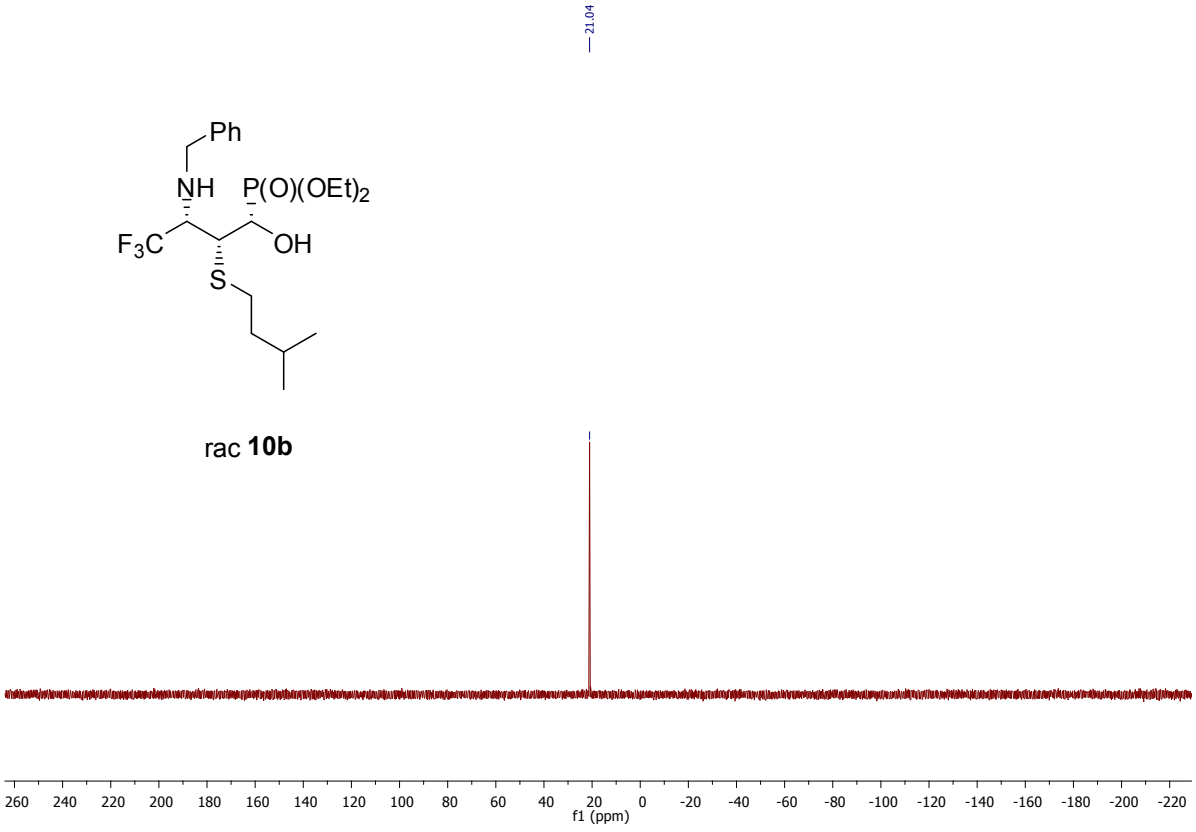


rac **10b**

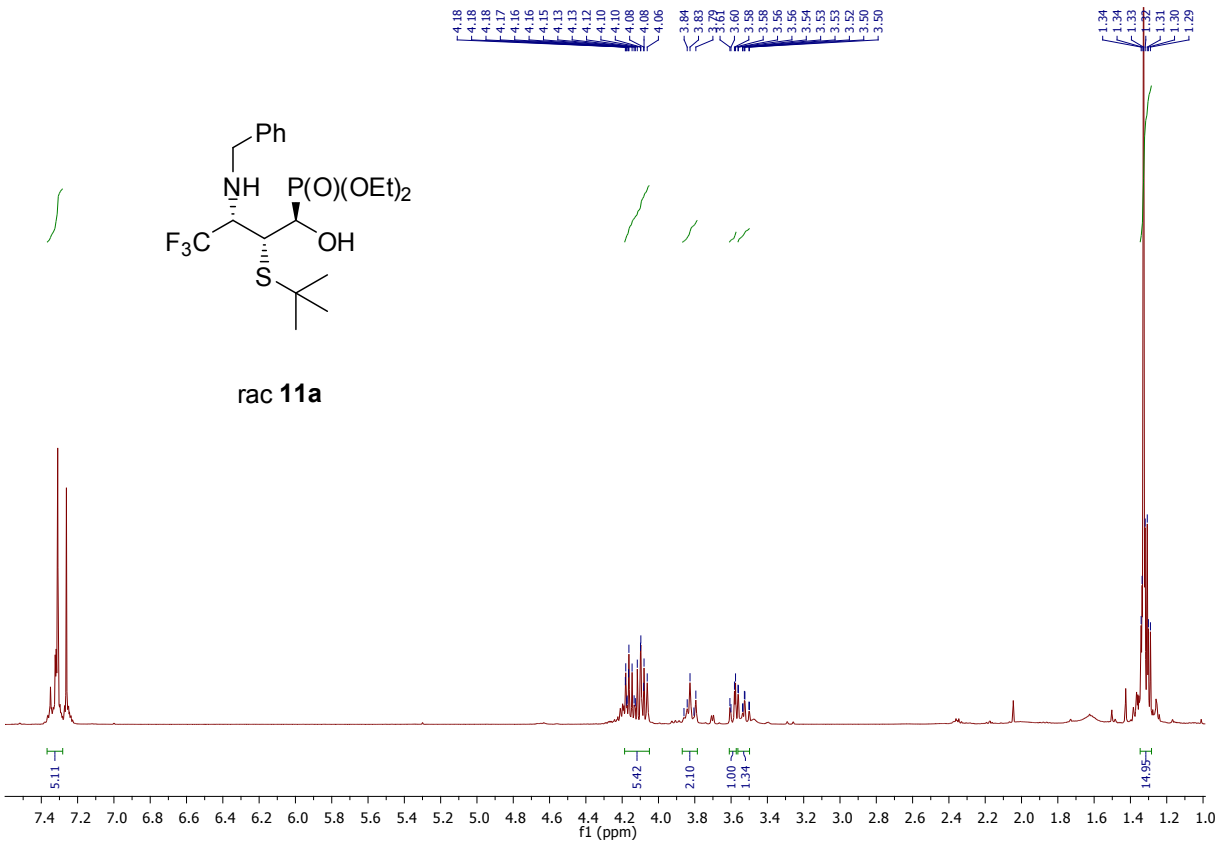
^{1}H NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(isopentylthio)butylphosphonate (rac-10b)



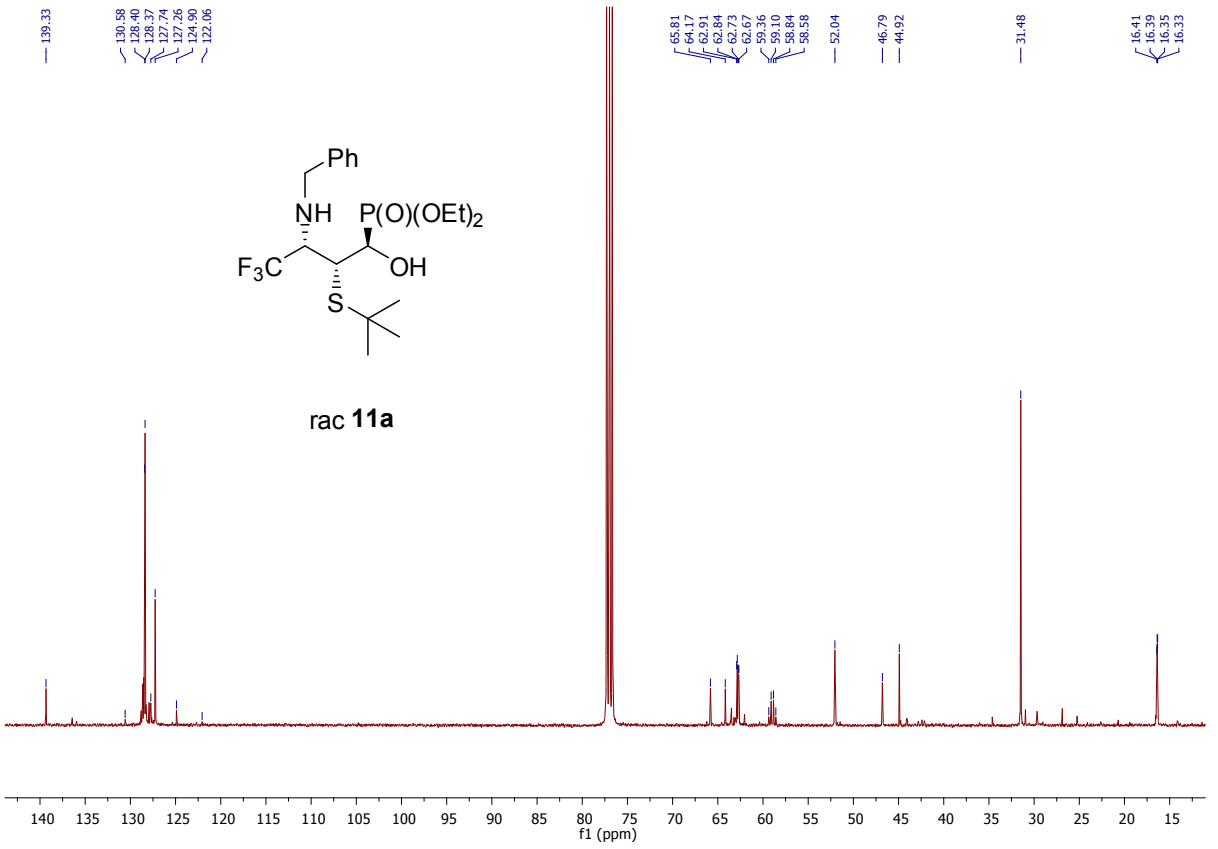
^{13}C NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(isopentylthio)butylphosphonate (rac-10b)



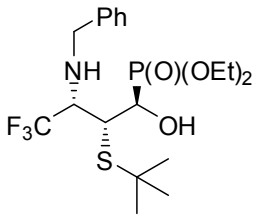
^{31}P NMR of diethyl 3-(benzylamino)-4,4,4-trifluoro-1-hydroxy-2-(isopentylthio)butylphosphonate (rac-10b)



^{1}H NMR of diethyl 3-(benzylamino)-2-(tert-butylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 11a)

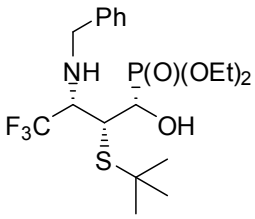


^{13}C NMR of diethyl 3-(benzylamino)-2-(tert-butylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 11a)



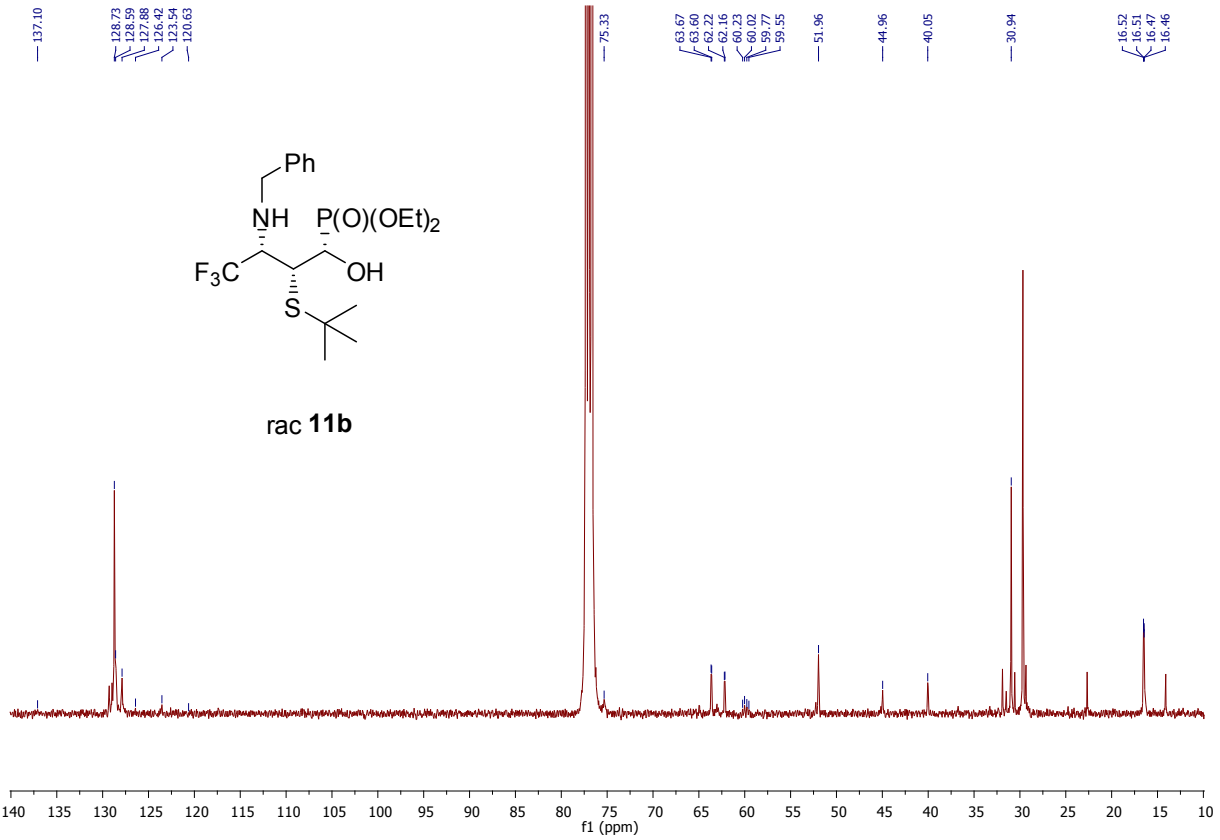
rac **11a**

31P NMR of diethyl 3-(benzylamino)-2-(tert-butylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 11a)

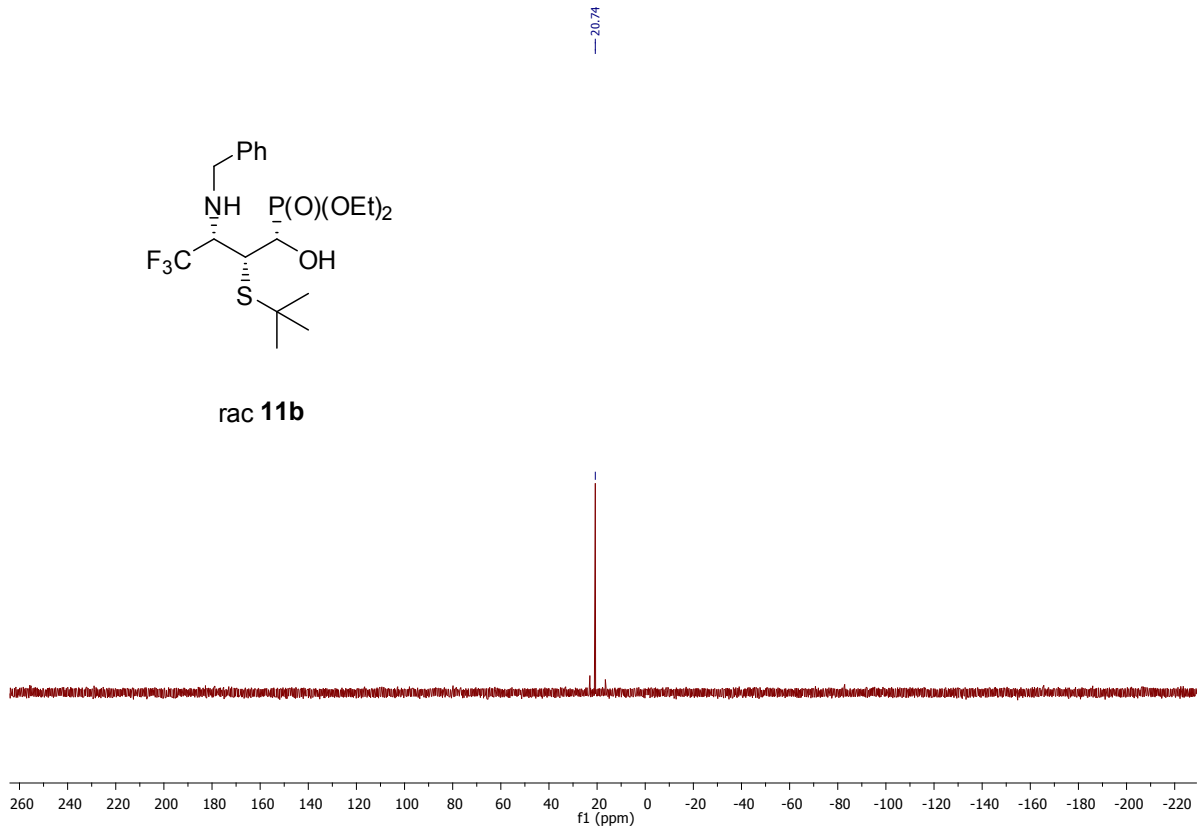


rac **11b**

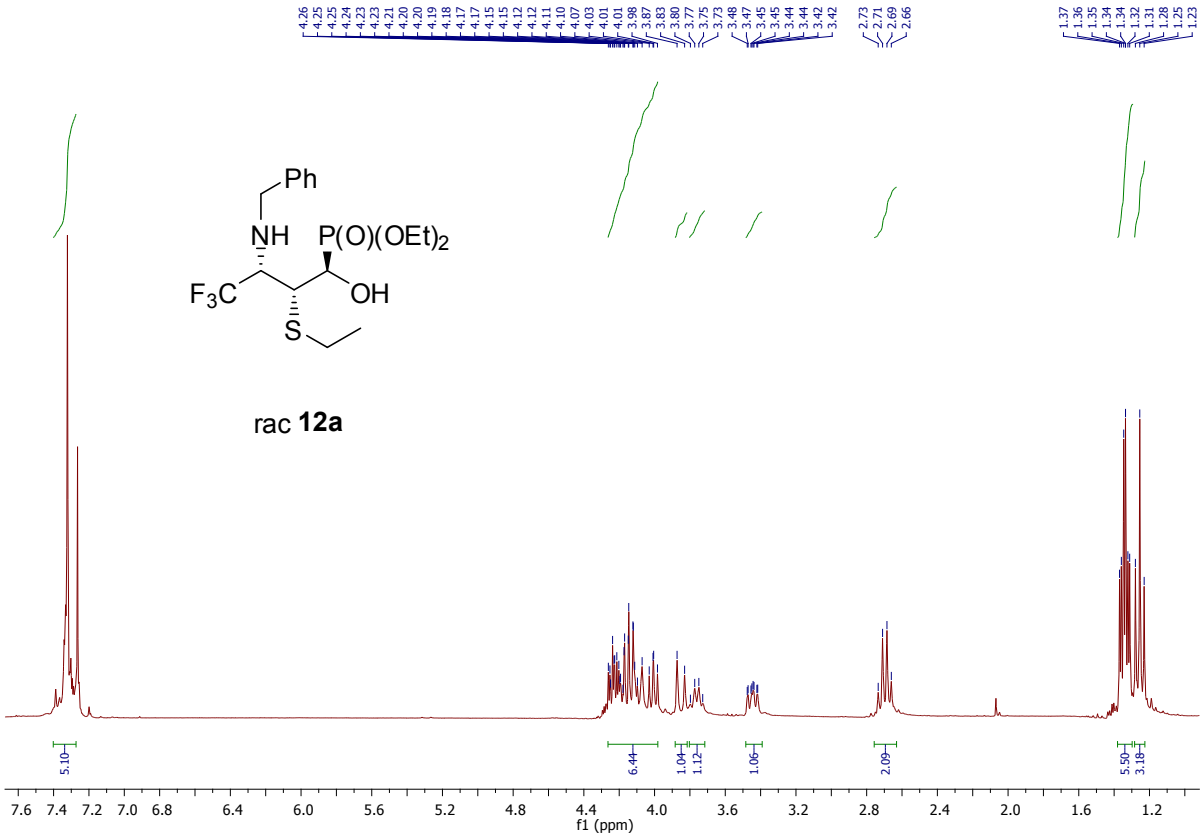
^{1}H NMR of diethyl 3-(benzylamino)-2-(tert-butylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 11b)



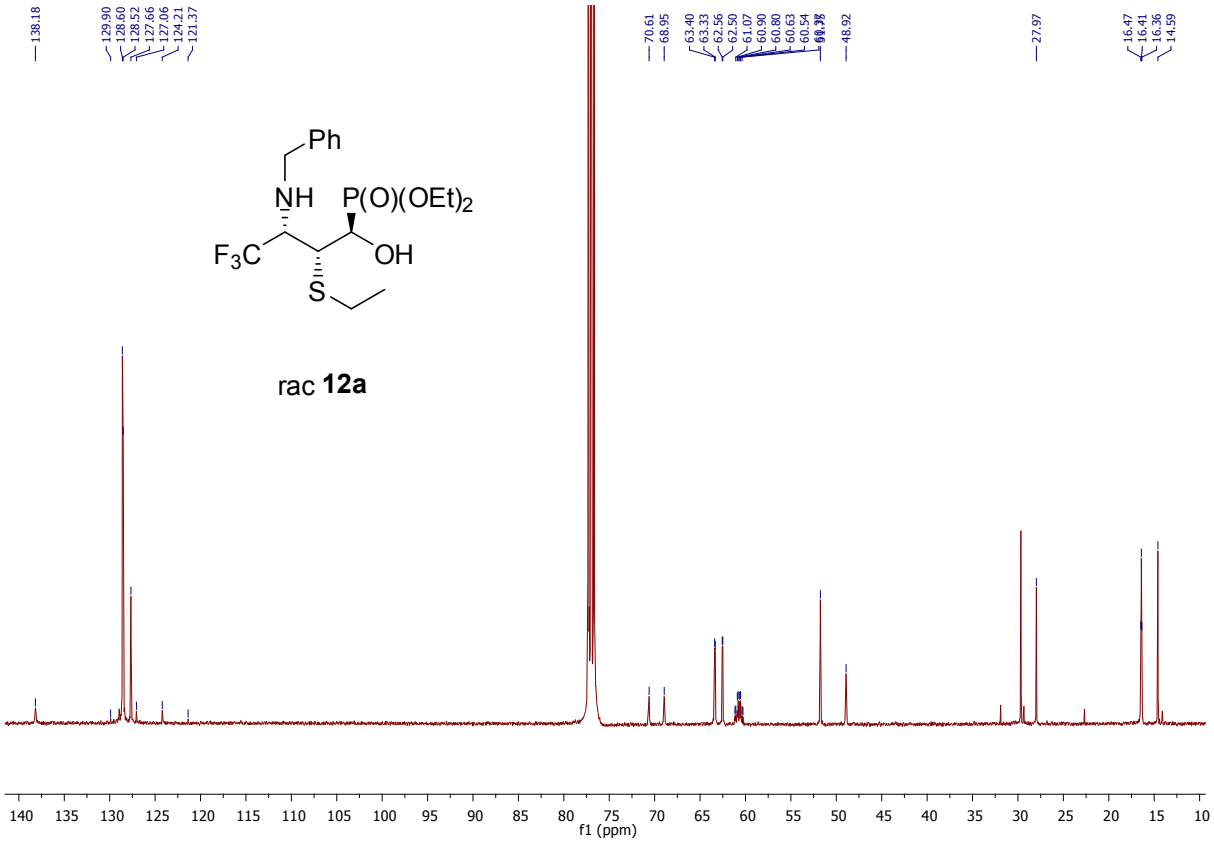
^{13}C NMR of diethyl 3-(benzylamino)-2-(tert-butylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 11b)



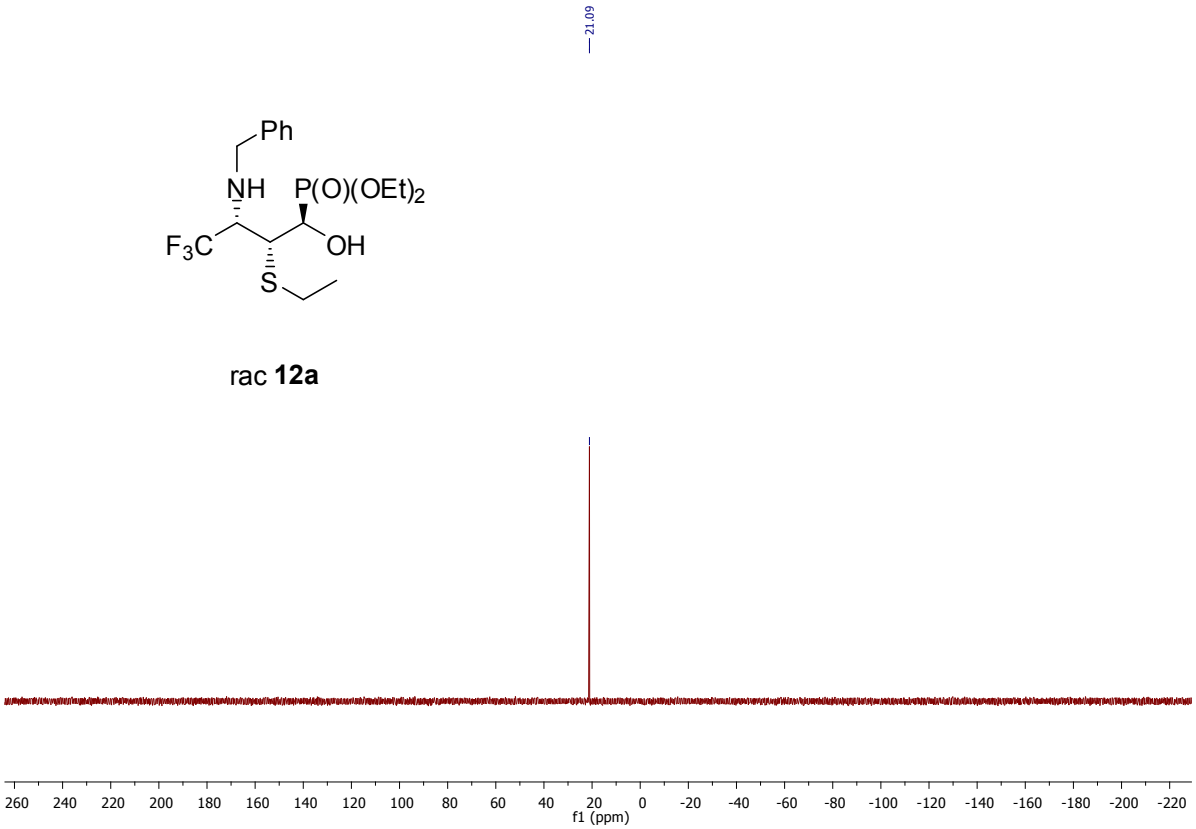
^{31}P NMR of diethyl 3-(benzylamino)-2-(tert-butylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 11b)



^{1}H NMR of diethyl 3-(benzylamino)-2-(ethylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 12a)

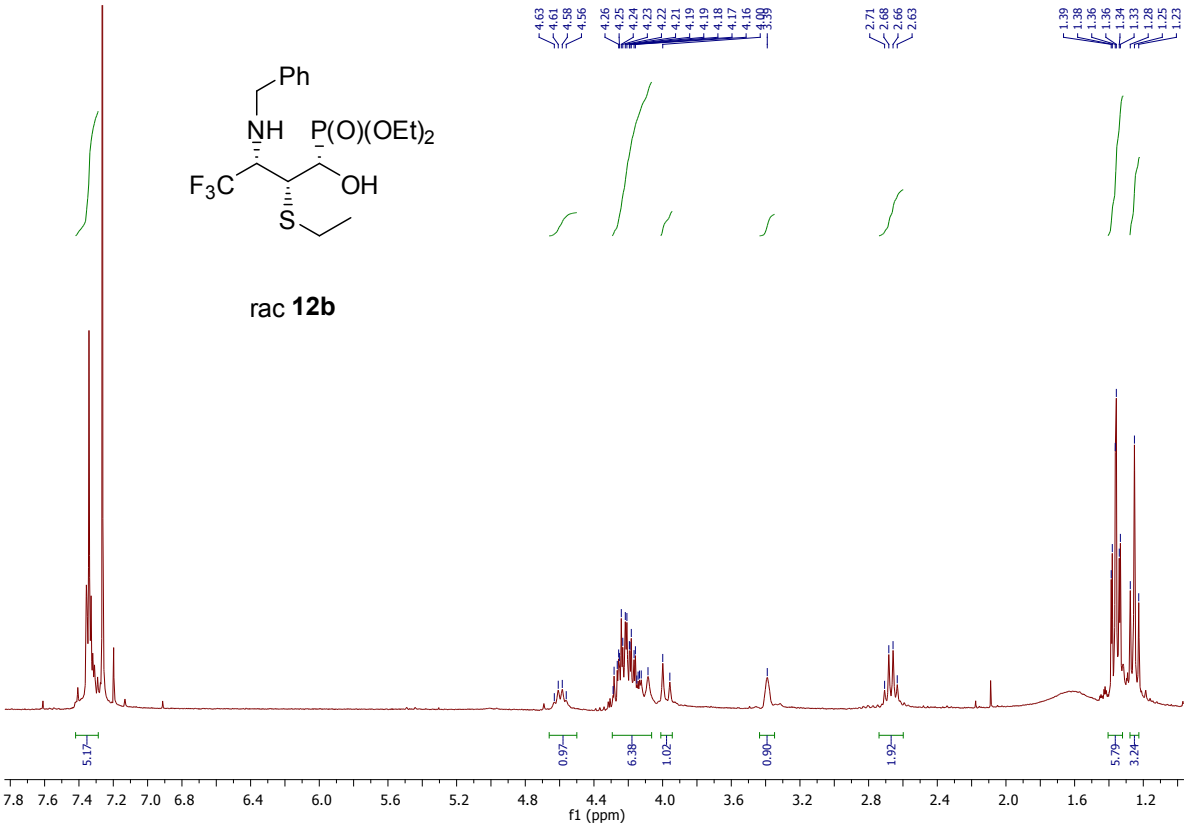


^{13}C NMR of diethyl 3-(benzylamino)-2-(ethylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 12a)



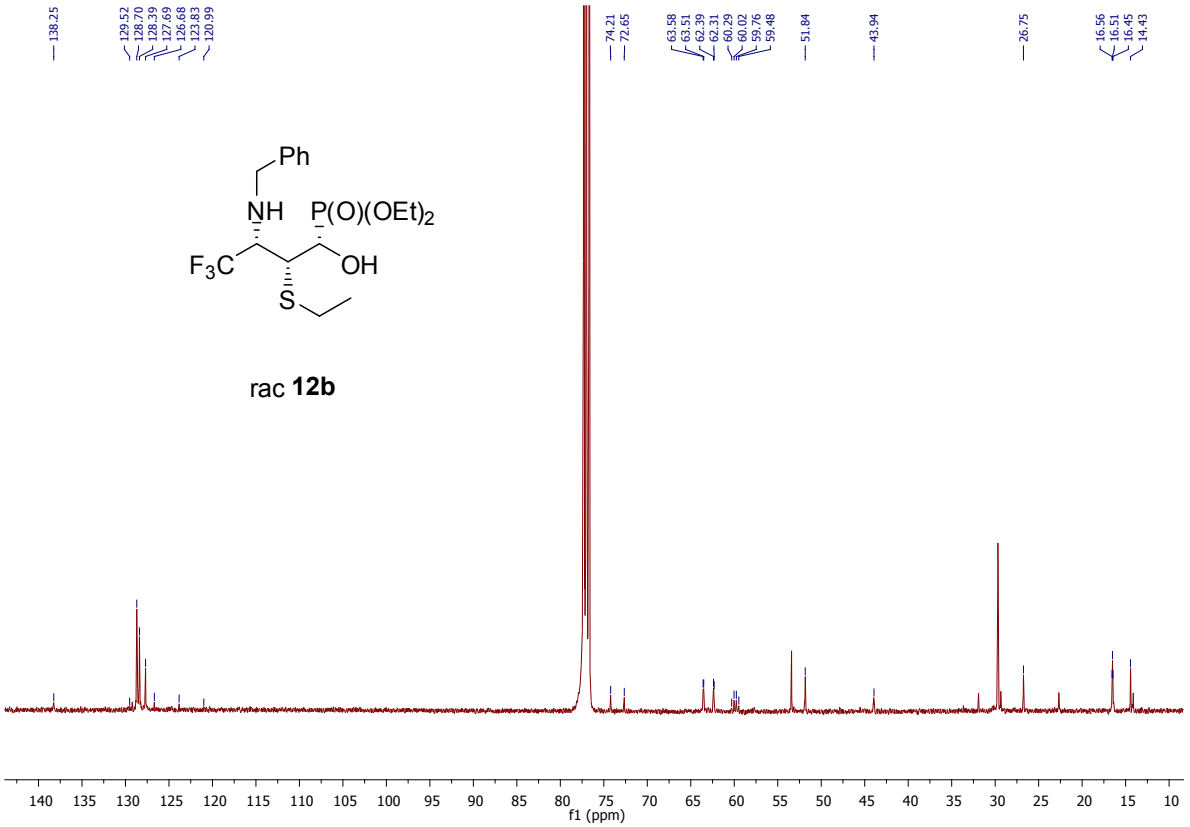
rac **12a**

31P NMR of diethyl 3-(benzylamino)-2-(ethylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 12a)

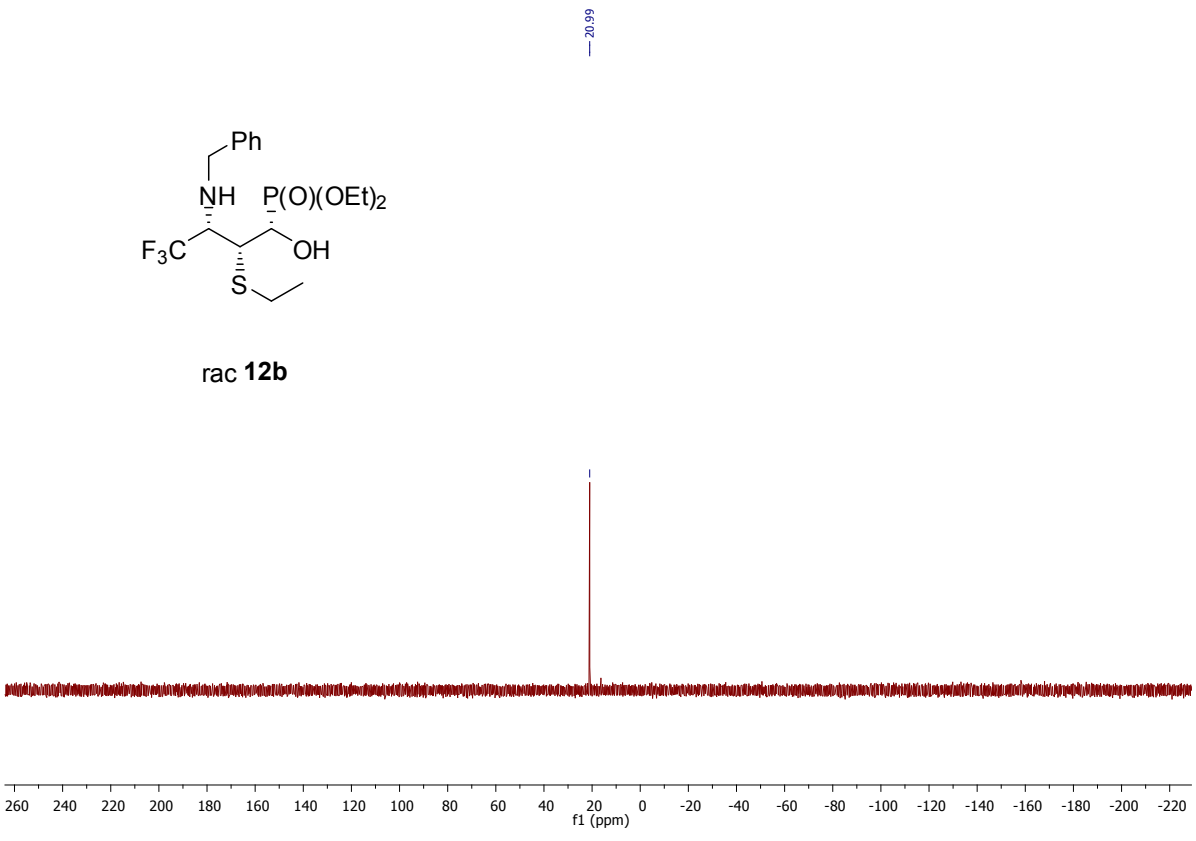


rac **12b**

^{1}H NMR of diethyl 3-(benzylamino)-2-(ethylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 12b)



^{13}C NMR of diethyl 3-(benzylamino)-2-(ethylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 12b)



31P NMR of diethyl 3-(benzylamino)-2-(ethylthio)-4,4,4-trifluoro-1-hydroxybutylphosphonate (rac 12b)

Table 1. Crystal data and refinement details

Compound	**4a**	**4b**	**6a**	**8a**
Formula	$C_{15}H_{21}F_3NO_4P$	$C_{15}H_{21}F_3NO_4P$	$C_{21}H_{26}F_4NO_4PS$	$C_{21}H_{27}F_3NO_4PS$
Formula weight	367.30	367.30	495.46	477.46
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	P-1	$P2_1/c$	P-1	$P2_1/n$
a(Å)	8.4461(6)	16.654(4)	8.5249(3)	8.5794(6)
b(Å)	10.0719(7)	5.0589(13)	12.2868(6)	12.6291(16)
c(Å)	12.0079(8)	21.395(6)	12.5737(11)	22.1208(17)
α(°)	113.979(6)	90	105.079(6)	90
β(º)	92.730(5)	94.15(2)	91.166(5)	91.615(7)
γ(°)	92.505(5)	90	110.256(4)	90
V(Å^3)	930.04(12)	1797.8(8)	1184.13(13)	2395.8(4)
Z	2	4	2	4
d_x(g cm^{-3})	1.31	1.36	1.39	1.32
F(000)	384	768	516	1000
μ(mm^{-1})	0.19	0.20	2.39	2.28
Θ range (^{0})	3.16 – 25.00	3.00 – 25.00	3.67 – 75.74	4.00 – 75.84
hkl range	-9≤h≤10	-19≤h≤19	-10≤h≤7	-10≤h≤10
	-11≤k≤11	-5≤k≤6	-14≤k≤15	-15≤k≤15
	-14≤l≤14	-25≤l≤22	-15≤l≤15	-26≤l≤27
Reflections:				
collected	6013	10939	9046	19491
unique (R_{int})	3258 (0.035)	3136 (0.181)	4747 (0.027)	4918 (0.022)
with I>2σ(I)	2126	1151	4376	4091
No. of pars.	223	220	299	290
R(F) [I>2σ(I)]	0.081	0.081	0.037	0.049
wR(F^2) [I>2σ(I)]	0.237	0.173	0.094	0.137
R(F) [all data]	0.116	0.234	0.040	0.059
wR(F^2) [all data]	0.267	0.221	0.097	0.145
Goodness of fit	1.07	0.88	1.05	1.03
max/min $\Delta\rho$ (e Å^{-3})	0.52/-0.43	0.36/-0.31	0.34/-0.44	0.41/-0.34

Table 2. Relevant torsion angles (°) with s.u.'s in parentheses.

	4a	**4b**	**6a**	**8a**
C2-C1-P1-O11	-62.1(3)	49.9(5)	-179.78(10)	-179.76(14)
P1-C1-C2-C3	-152.5(4)	89.1(6)	85.09(13)	83.84(18)
C1-C2-C3-N3	103.7(4)	103.8(6)	80.06(15)	79.1(2)
C2-C3-N3-C4	107.4(4)	107.5(5)	-153.06(13)	-151.77(19)
C3-N3-C4-C41	88.1(5)	-169.7(5)	61.14(18)	61.5(3)
C1-C2-C3-C31	-0.6(7)	3.8(10)	-150.86(13)	-151.86(18)

Table 3. Hydrogen bond data (Å, °) with s.u.'s in parentheses

D	H	A	D-H	H···A	D···A	D-H···A
6a						
O1	H1	O11^{iii}	0.80(2)	1.93(2)	2.7254(18)	176(2)
N3	H3N	O11^{ii}	0.87(2)	2.32(2)	3.1049(17)	151.5(19)
C3	H3	O13	1.00	2.29	3.0590(19)	133
8a						
O1	H1	O11^{i}	0.77(3)	1.98(3)	2.736(3)	169(3)
N3	H3N	O11^{ii}	0.95(3)	2.34(3)	3.204(2)	151(2)
C3	H3	O12	0.98	2.28	3.054(2)	135
4a						
O1	H1	O11^{v}	0.96(5)	1.73(5)	2.682(4)	170(4)
4b						
O1	H1	O11^{iv}	0.82	1.85	2.655(5)	167

Symmetry codes: ^{i} 2-x,1-y,1-z; ^{ii} x-1,y,z; ^{iii} 1-x,1-y,2-z; ^{iv} x,1+y,z; ^{v} –x,-y,1-z.