Supporting Information

Efficient and Convenient Access to Optically Active Tetrafluoroethylenated Amines Based on [1,3]-Proton Shift Reaction

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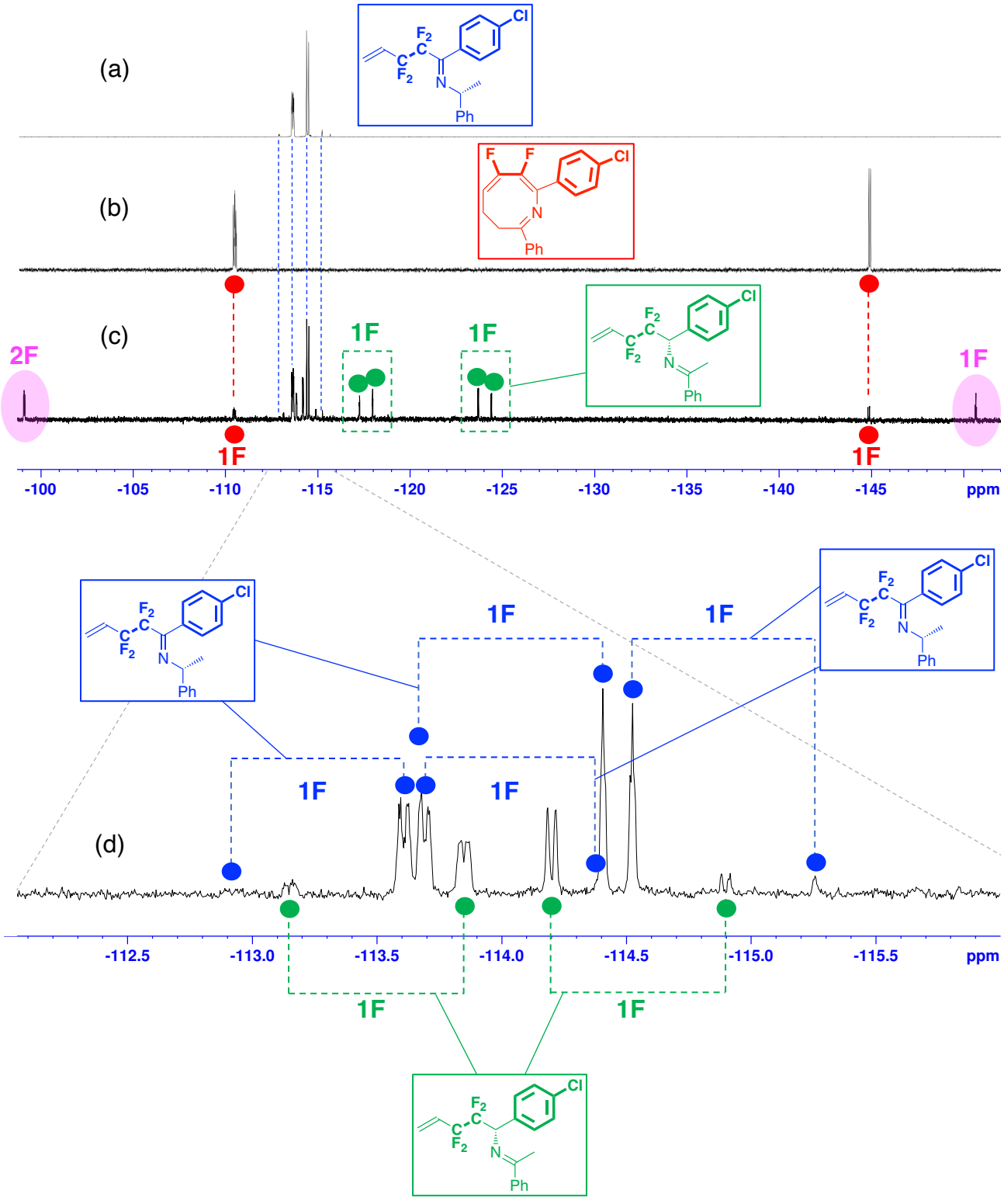
Structural assignment of **21b**

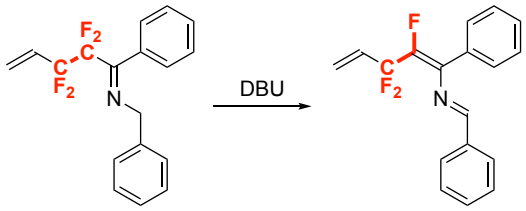
Spectra (a) and (b), shown below, are the ^{19}F NMR ones of **(*R*)-16b** and **22b**, respectively. A spectrum (c) is the ^{19}F NMR one immediately after the reaction finished when diethyl ether was used as a solvent (Table 2 Entry 3) in the investigation of the reaction conditions, and (d) is an expanded spectrum from -112 ppm to -116 ppm in (c).



As can be seen from the ^{19}F NMR spectra, all signals except those marked in pink in the spectrum (c) can be attributed to **(*R*)-16b**, **20b**, and **22b**.
The signals marked in pink were analyzed as follows.

^{19}F NMR ($CDCl_3$, $CFCl_3$): δ -99.10 to -99.00 (m, 1F), -150.66 (t, J = 15.43 Hz, 2F).

This compound was found to be difficult to be isolated, and ^{1}H NMR and ^{13}C NMR measurements were not available.
On the other hand, it was possible to isolate *N*-benzylidene-1-phenyl-2,3,3-trifluoro-1,4-pentadienylamine, which was obtained *via* the reaction of *N*-(2,2,3,3-tetrafluoro-1-phenyl-4-pentenylidene)benzylamine with DBU. The structure of this compound could be unambiguously identified based on ^{1}H NMR and ^{13}C NMR spectra, as shown below.



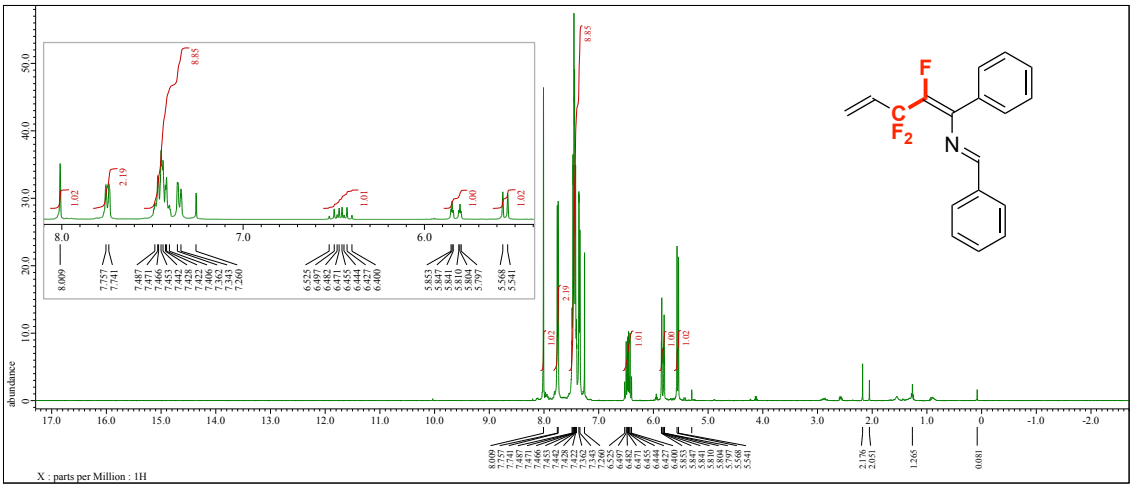
^{1}H NMR ($CDCl_3$): δ 8.01 (s, 1H), 7.75 (d, J = 6.39 Hz, 2H), 7.34-7.49 (m, 8H), 6.46 (tdd, J = 17.38, 11.19, 10.79 Hz, 1H), 5.83 (td, J = 17.38, 2.40 Hz, 1H), 5.55 (d, J = 10.79 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 137.3 (dt, J = 27.3, 4.1 Hz), 135.9, 132.1 (t, J = 25.7 Hz), 131.7, 131.0, 129.7, 129.3 (d, J = 3.3 Hz), 129.0, 128.9, 128.7, 128.7, 118.8 (t, J = 9. Hz), 115.2 (dt, J = 29.8, 239.7 Hz).

The ^{19}F NMR was also analyzed as follows.

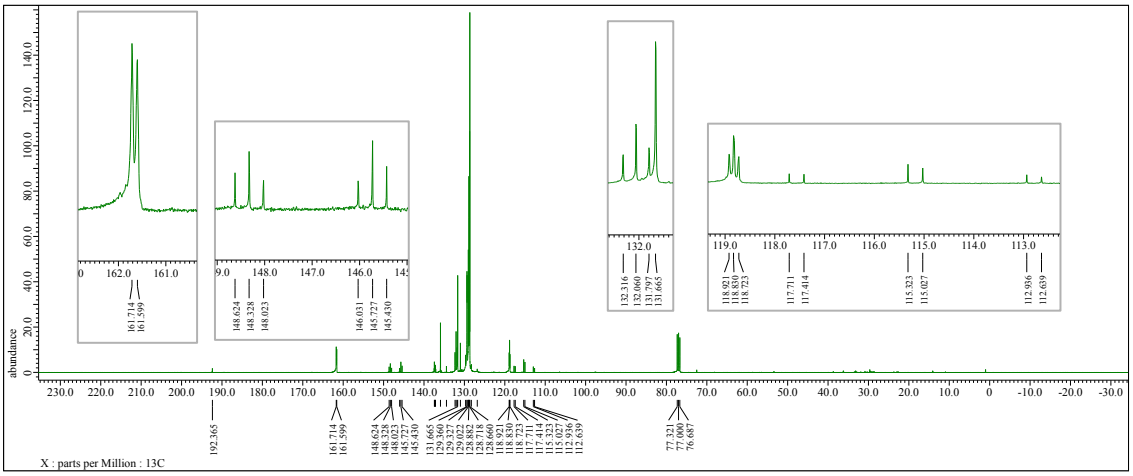
^{19}F NMR ($CDCl_3$, $CFCl_3$): δ -96.56 (t, J = 14.67 Hz, 1F), -134.17 (t, J = 14.67 Hz, 2F).

Despite some differences in chemical shifts, the ^{19}F NMR spectrum of *N*-benzylidene-1-phenyl-2,3,3-trifluoro-1,4-pentadienylamine is quite similar to the one marked in pink in spectrum (c).
Based on these results, the spectrum marked in pink in spectrum (c) was determined to be the HF eliminated product **21b**.

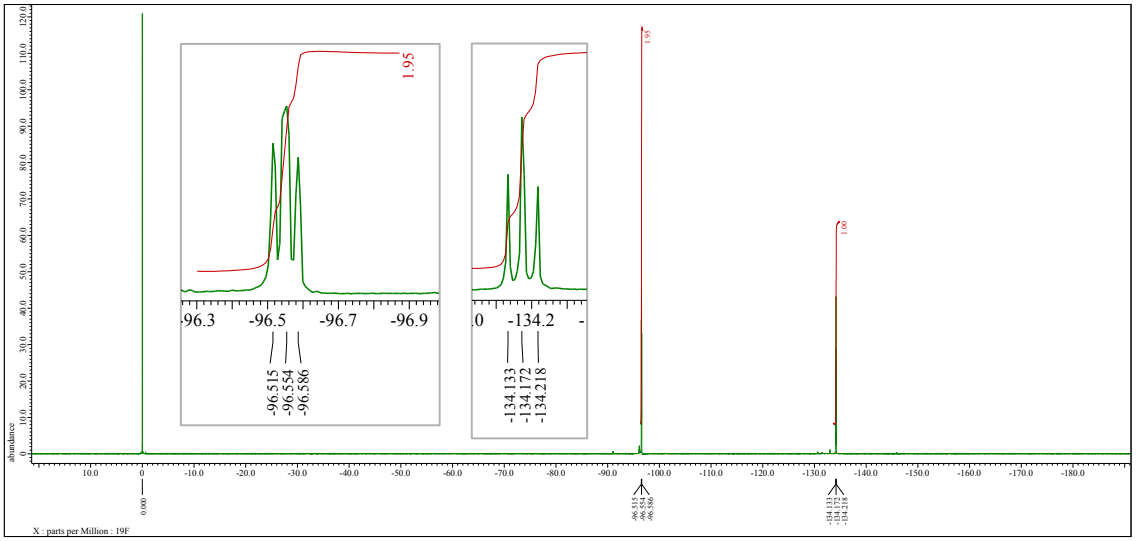
^{1}H NMR Spectrum of *N*-(2,3,3-trifluoro-1-phenylpenta-1,4-dien-1-yl)benzylideneamine



^{13}C NMR Spectrum of *N*-(2,3,3-trifluoro-1-phenylpenta-1,4-dien-1-yl)benzylideneamine



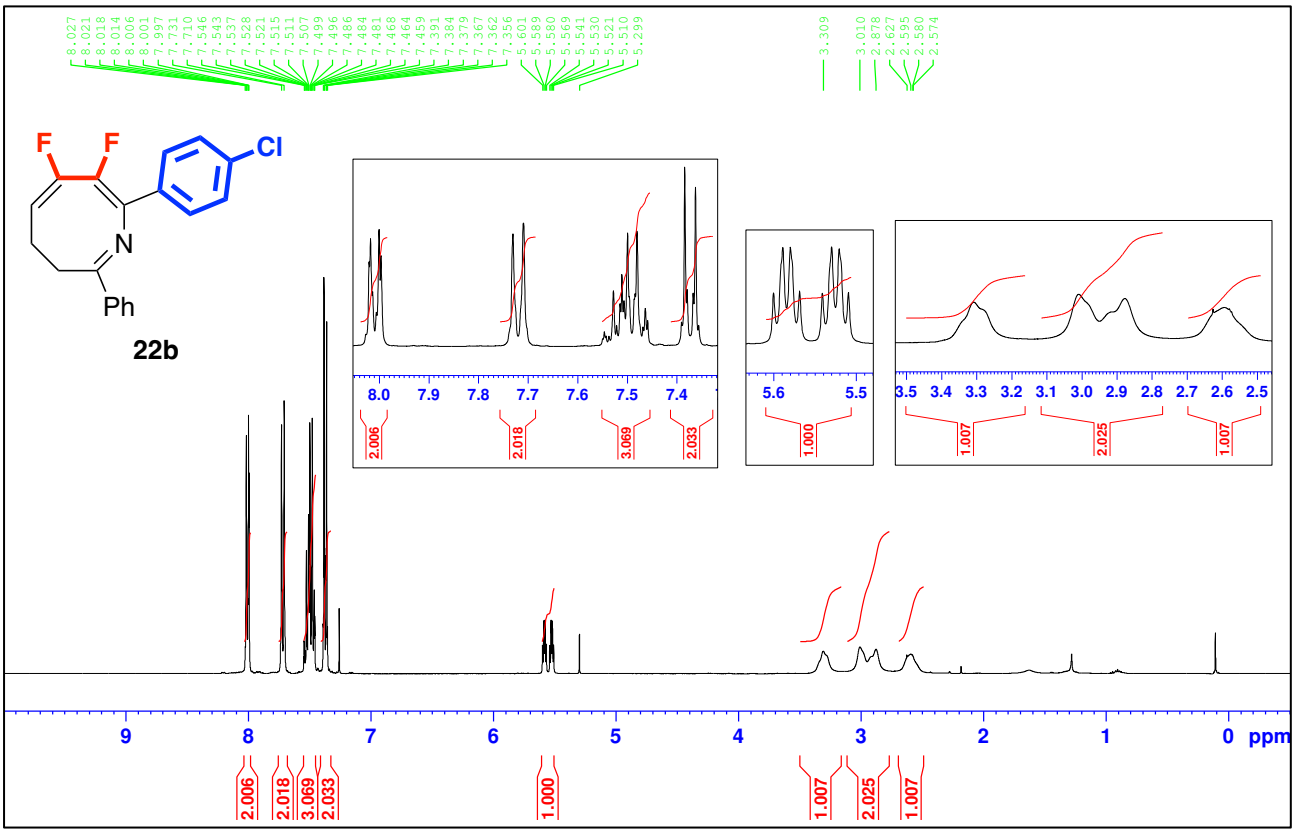
^{19}F NMR Spectrum of *N*-(2,3,3-trifluoro-1-phenylpenta-1,4-dien-1-yl)benzylideneamine



Structural assignment of **22b**

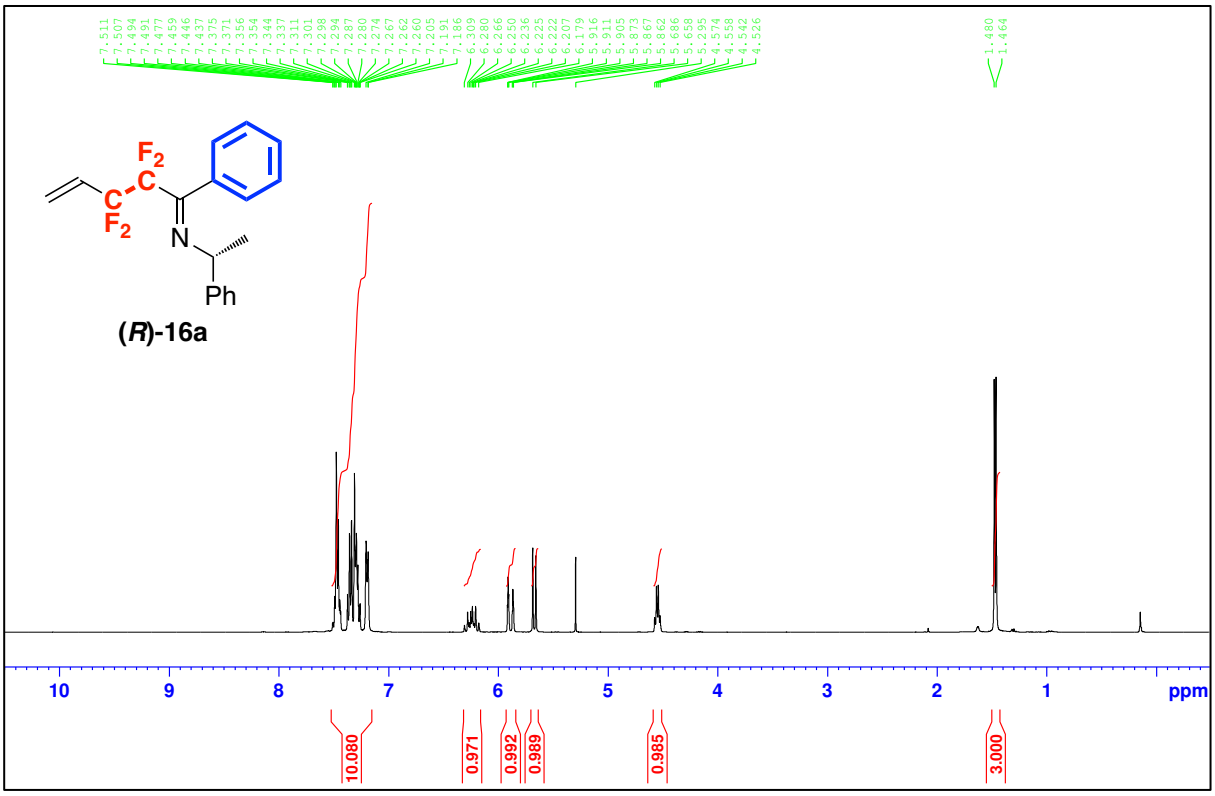
^{1}HNMR of azocine derivative **22b** and its analysis data are as follows.

^{1}H NMR Spectrum of 2-(4-Chlorophenyl)-3,4-difluoro-6,7-dihydro-8-phenylazocine (**22b**)

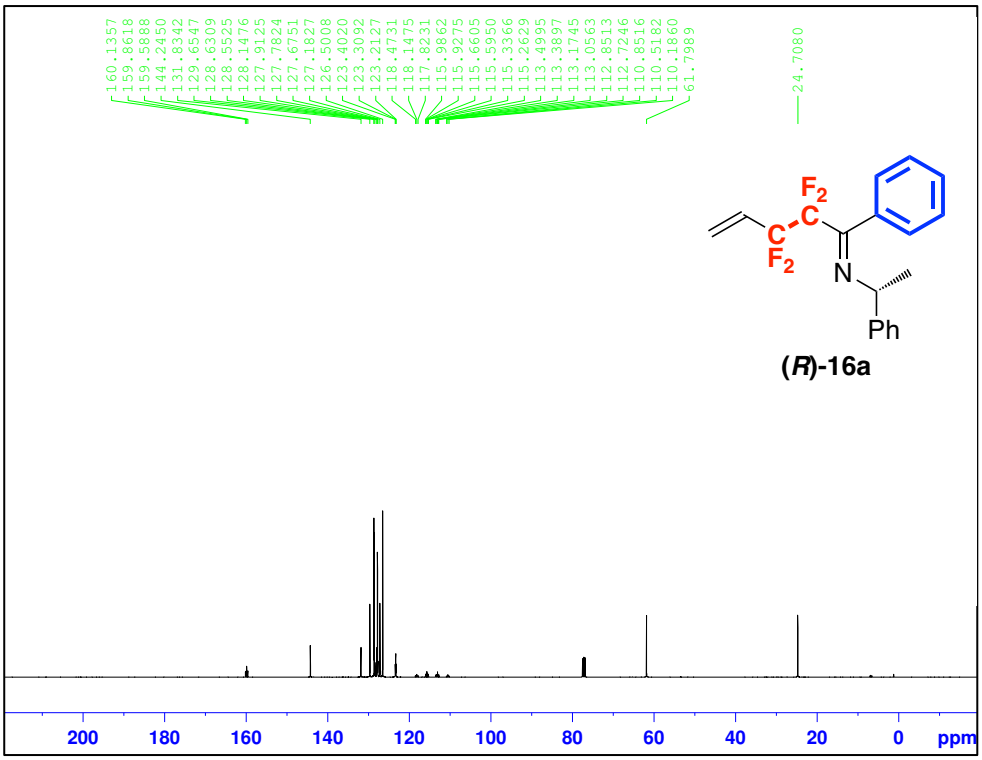


Yellow solid; M.P.: 114.0–114.3 ºC (Hexane/AcOEt = 20/1, R_f = 0.19); ^{1}H NMR ($CDCl_3$): δ 7.99–8.02 (m, 2H, Ar–*H*), 7.70–7.72 (m, 2H, Ar–*H*), 7.48–7.52 (m, 3H, Ar–*H*), 7.36–7.38 (m, 2H, Ar–*H*), 5.56 (dtd, *J* = 23.69, 4.48, 3.64 Hz, 1H, CF=C*H*), 3.31 (brs, 1H, CH_2), 3.01 (brs, 1H, CH_2), 2.88 (brs, 1H, CH_2), 2.59 (brs, 1H, CH_2).

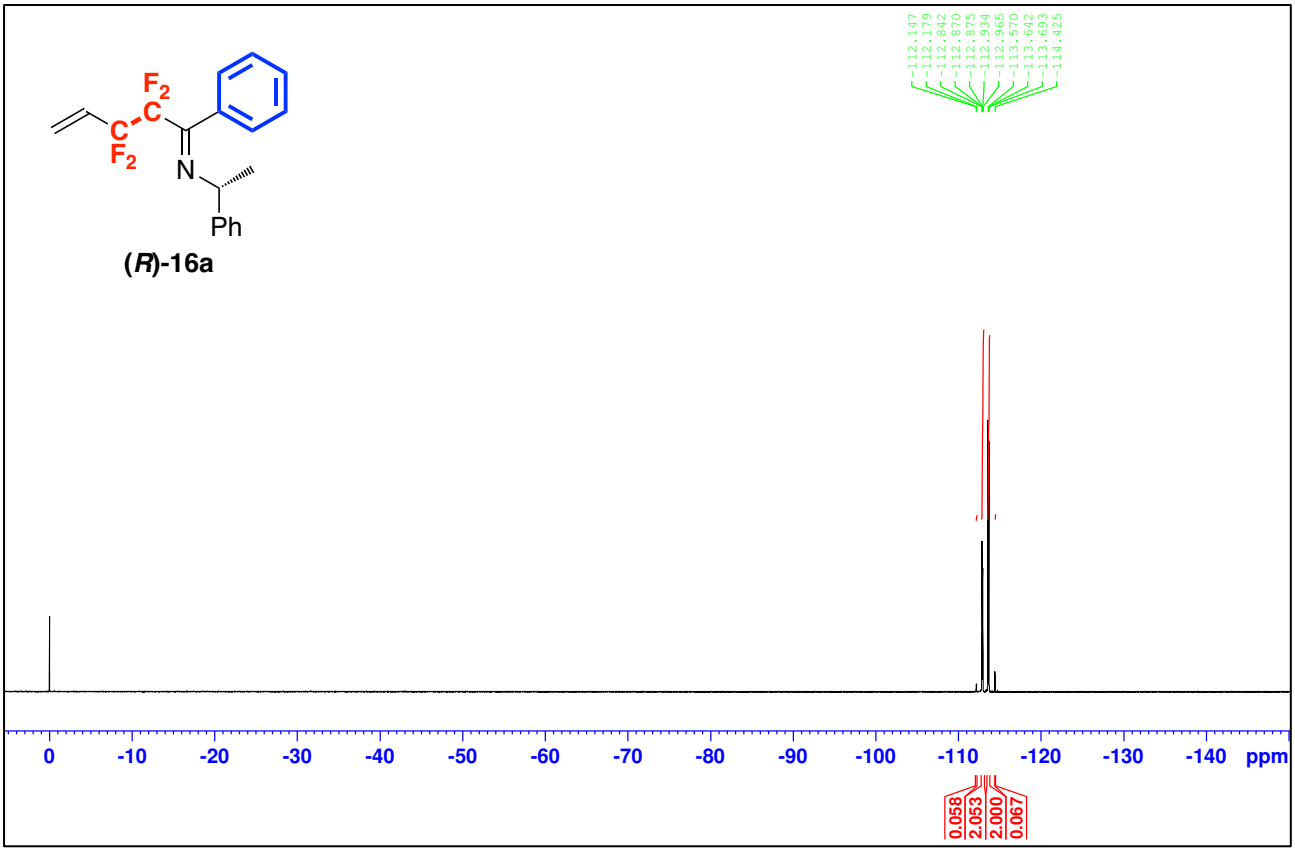
^{1}H NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-phenylpent-4-en-1-ylidene)-1-phenylethylamine (**(*R*)-16a**)



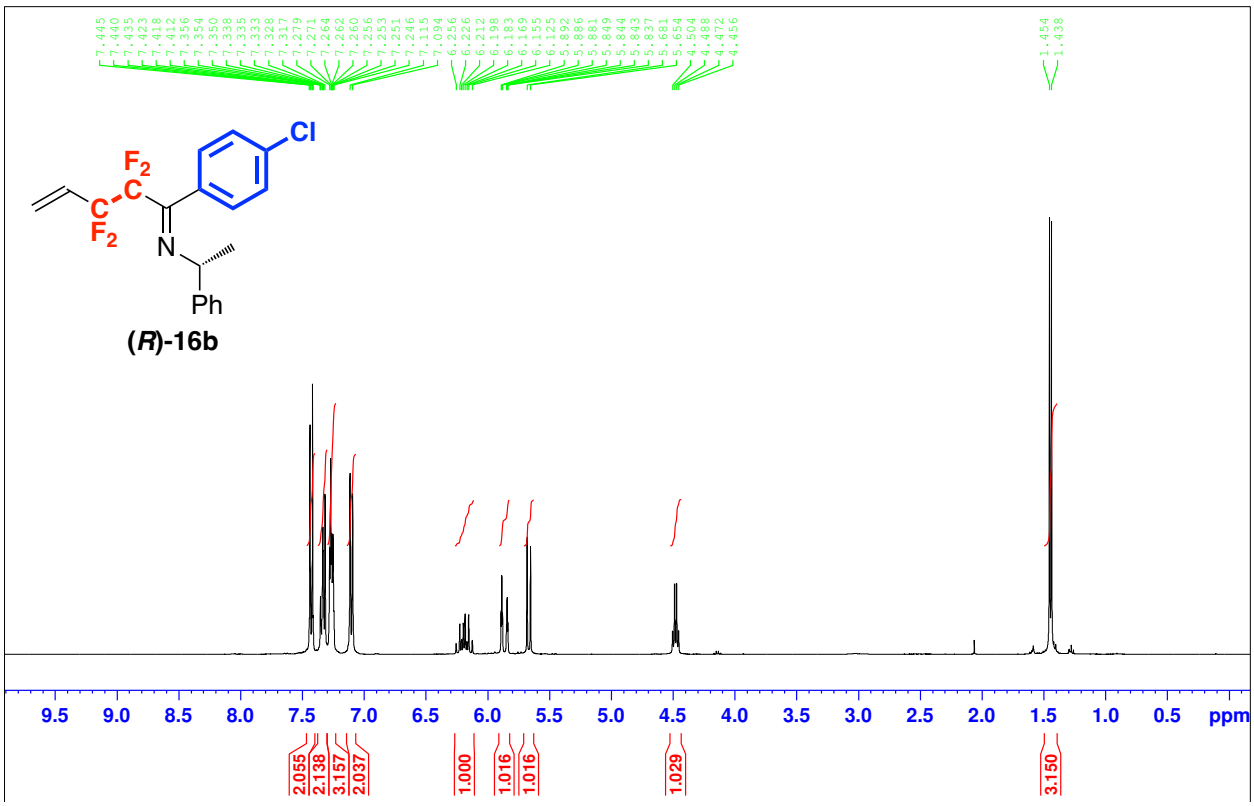
^{13}C NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-phenylpent-4-en-1-ylidene)-1-phenylethylamine (**(*R*)-16a**)



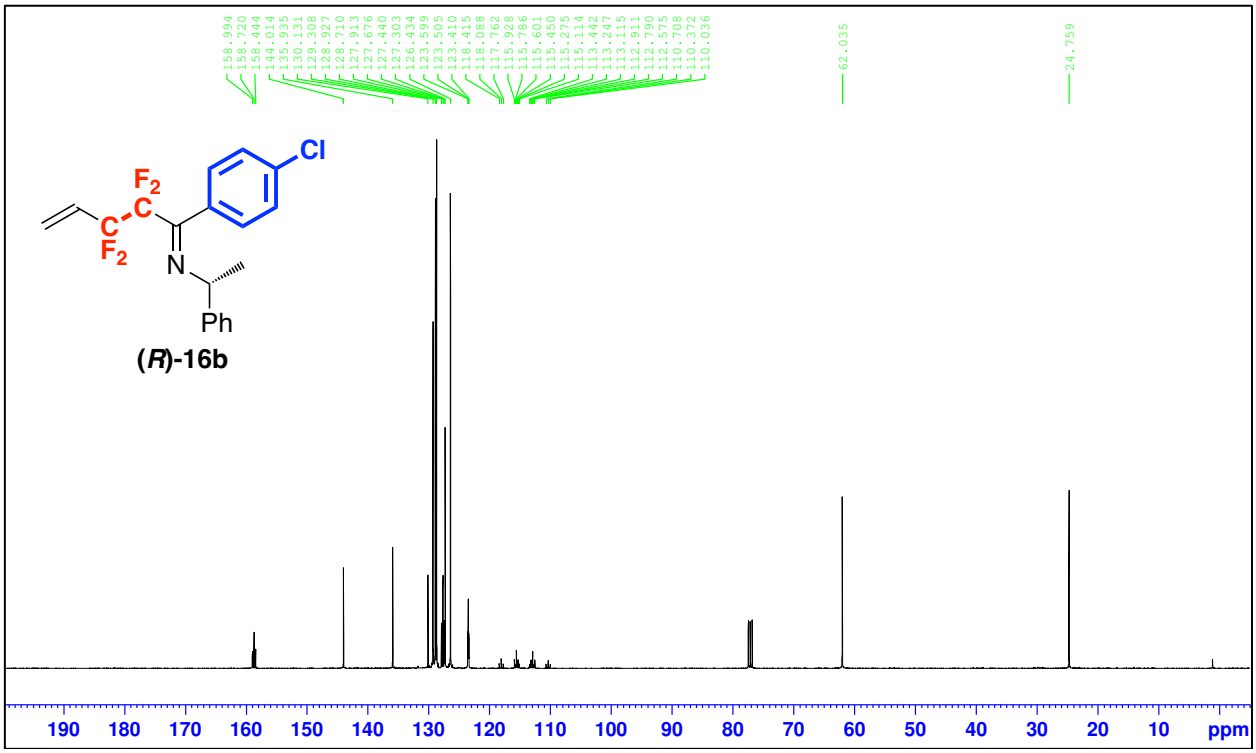
^{19}F NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-phenylpent-4-en-1-ylidene)-1-phenylethylamine (**(*R*)-16a**)



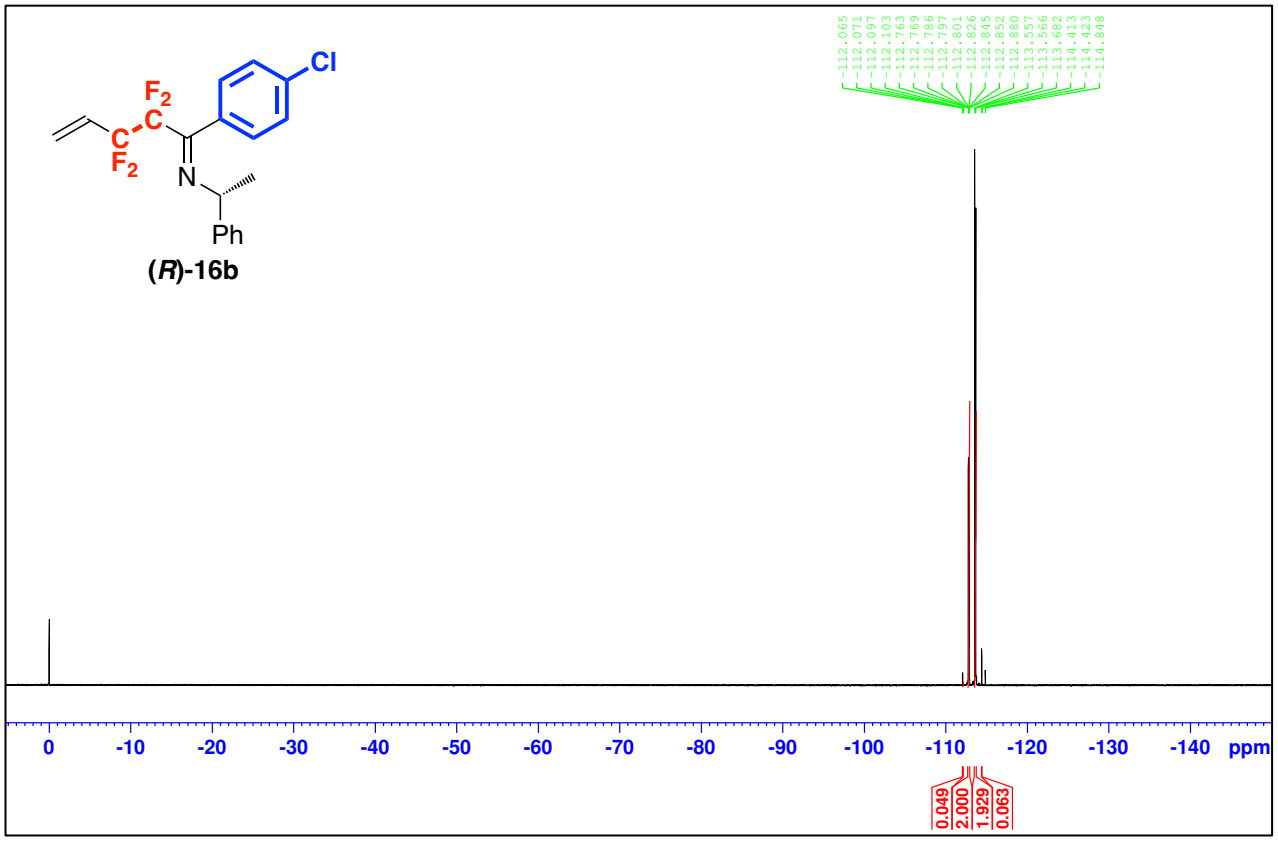
^{1}H NMR Spectrum of (*R*)-*N*-(1-(4-chlorophenyl)-2,2,3,3-tetrafluoropent-4-en-1-ylidene)-1-phenyethylamine (**(*R*)-16b**)



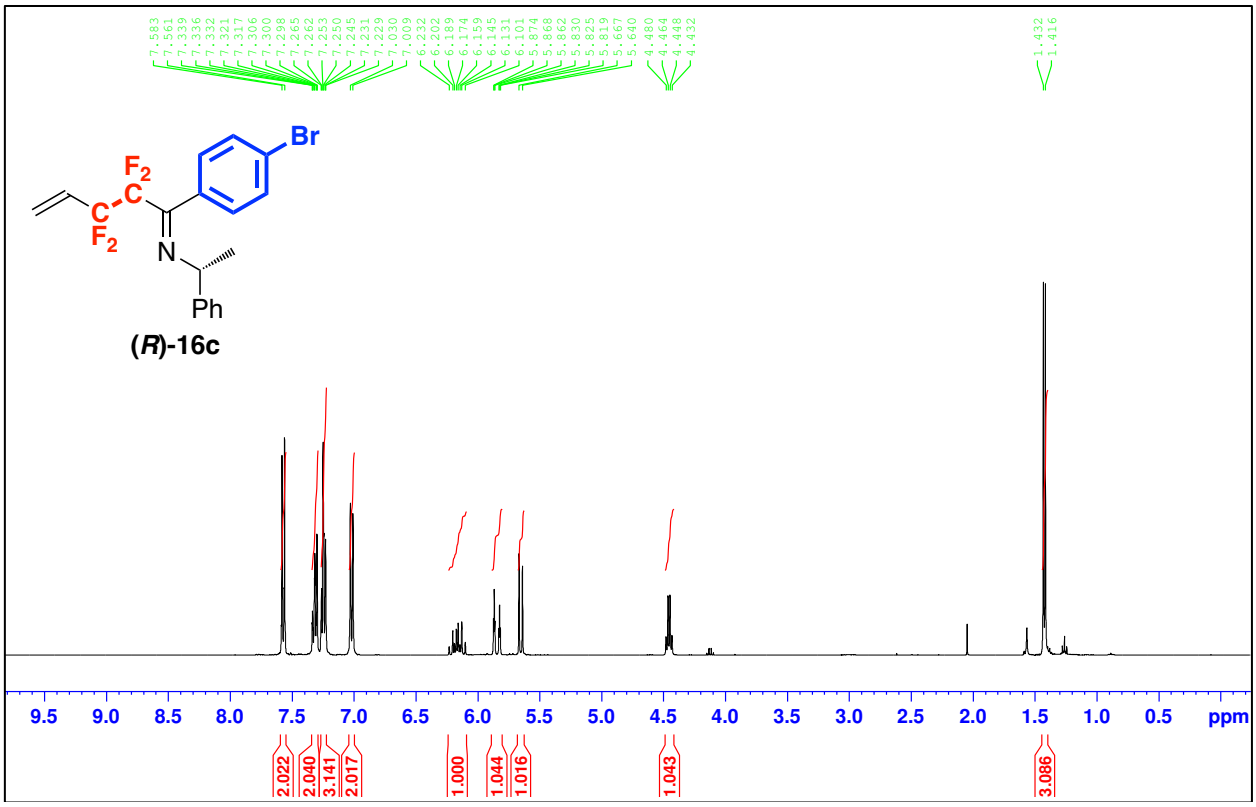
^{13}C NMR Spectrum of (*R*)-*N*-(1-(4-chlorophenyl)-2,2,3,3-tetrafluoropent-4-en-1-ylidene)-1-phenyethylamine (**(*R*)-16b**)



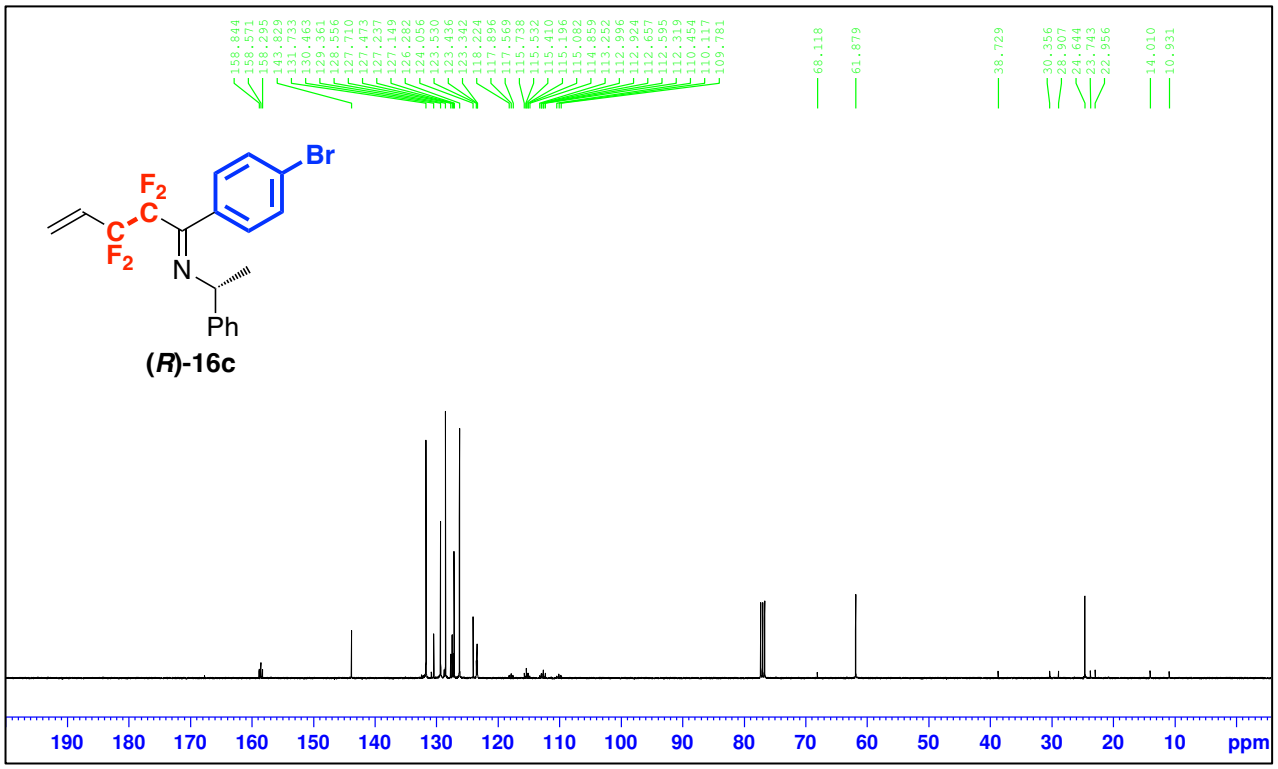
^{19}F NMR Spectrum of (*R*)-*N*-(1-(4-chlorophenyl)-2,2,3,3-tetrafluoropent-4-en-1-ylidene)-1-phenyethylamine (**(*R*)-16b**)



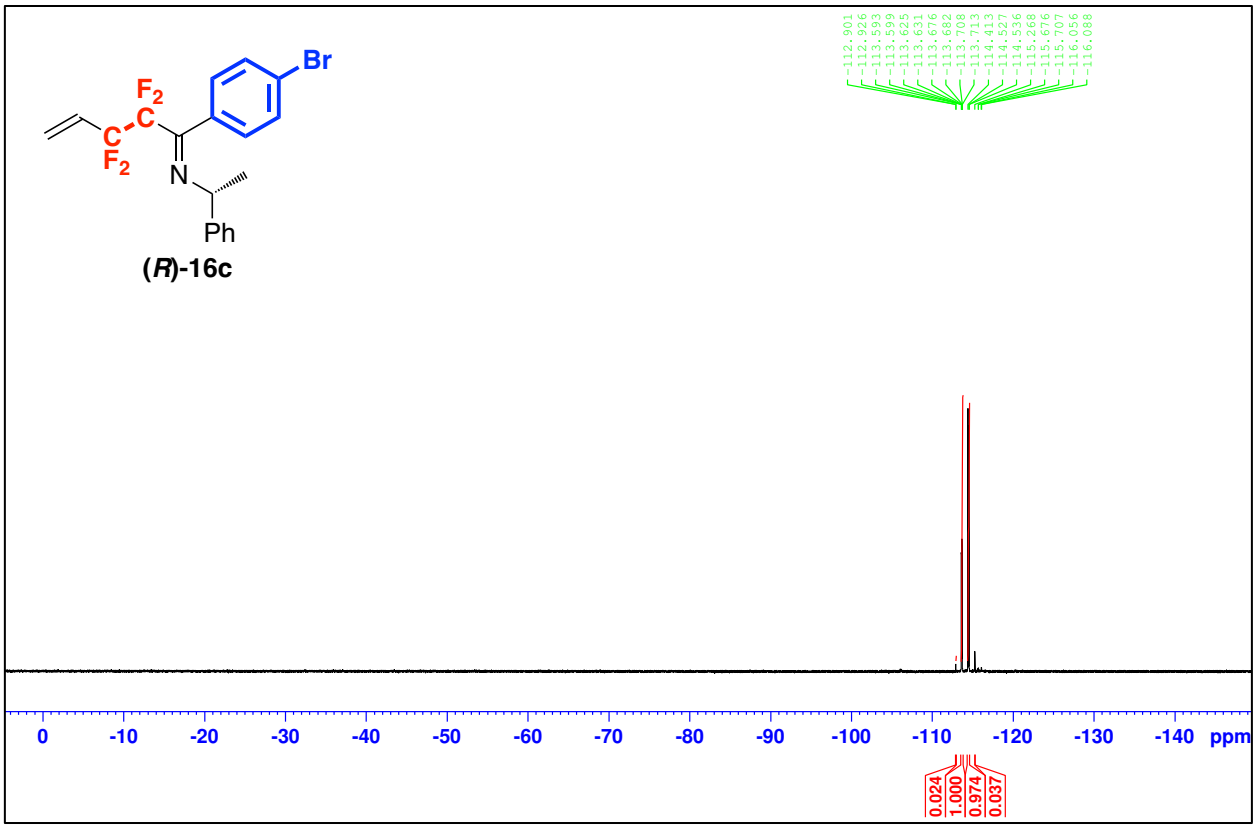
^{1}H NMR Spectrum of (*R*)-*N*-(1-(4-bromophenyl)-2,2,3,3-tetrafluoropent-4-en-1-ylidene)-1-phenyethylamine (**(*R*)-16c**)



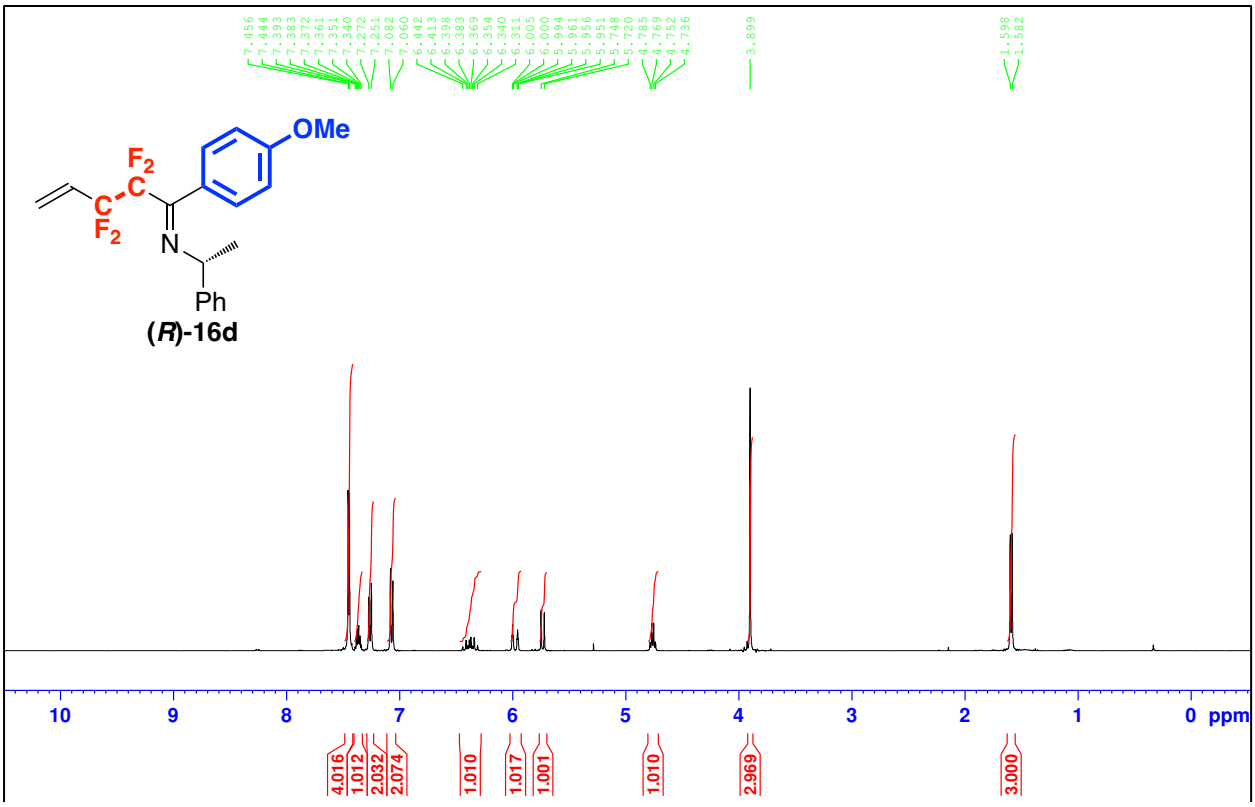
^{13}C NMR Spectrum of (*R*)-*N*-(1-(4-bromophenyl)-2,2,3,3-tetrafluoropent-4-en-1-ylidene)-1-phenyethylamine (**(*R*)-16c**)



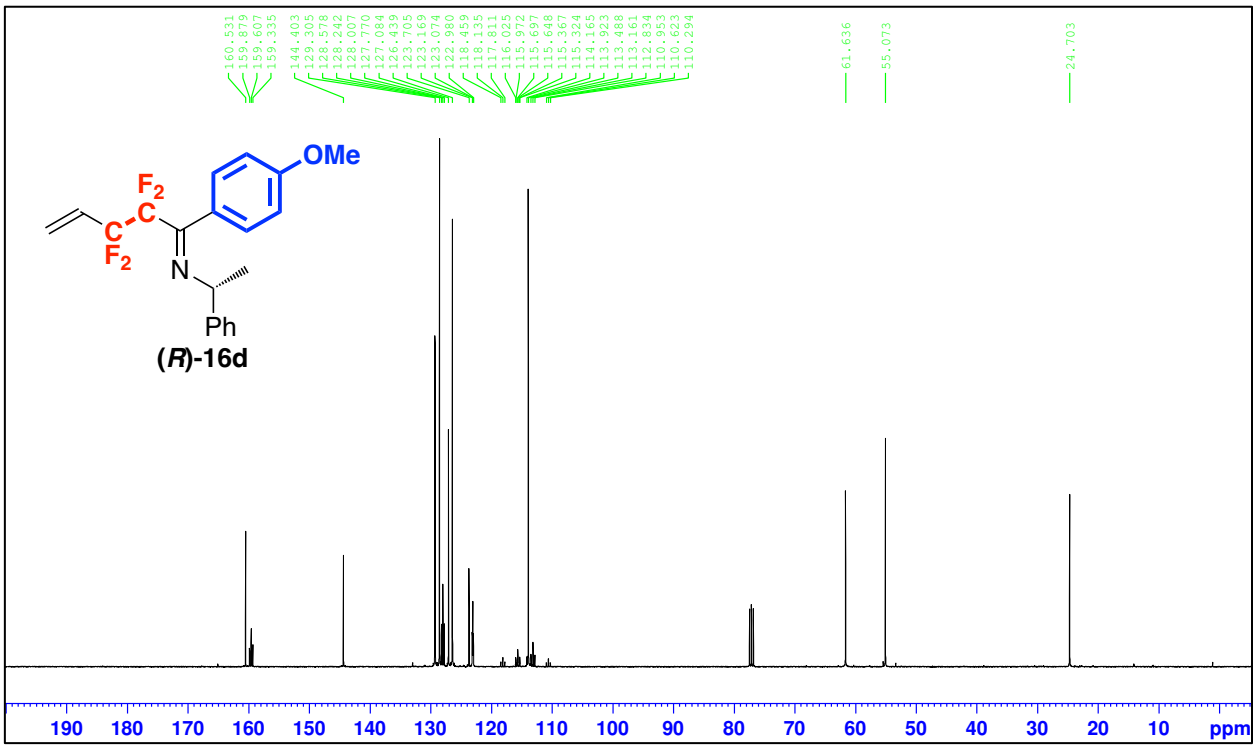
^{19}F NMR Spectrum of (*R*)-*N*-(1-(4-bromophenyl)-2,2,3,3-tetrafluoropent-4-en-1-ylidene)-1-phenyethylamine (**(*R*)-16c**)



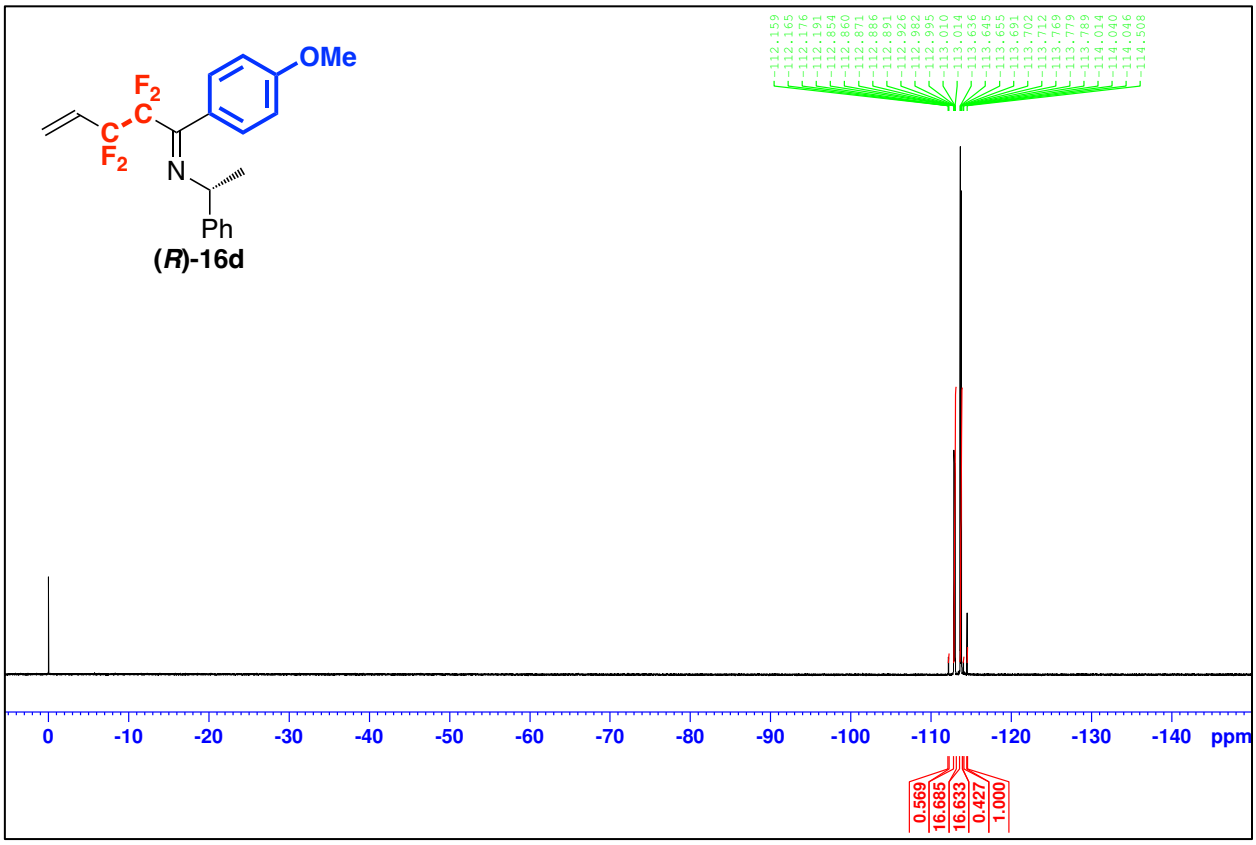
^{1}H NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(4-methoxyphenyl)pent-4-en-1-ylidene)-1-phenylethylamine ((***R*)-16d**)



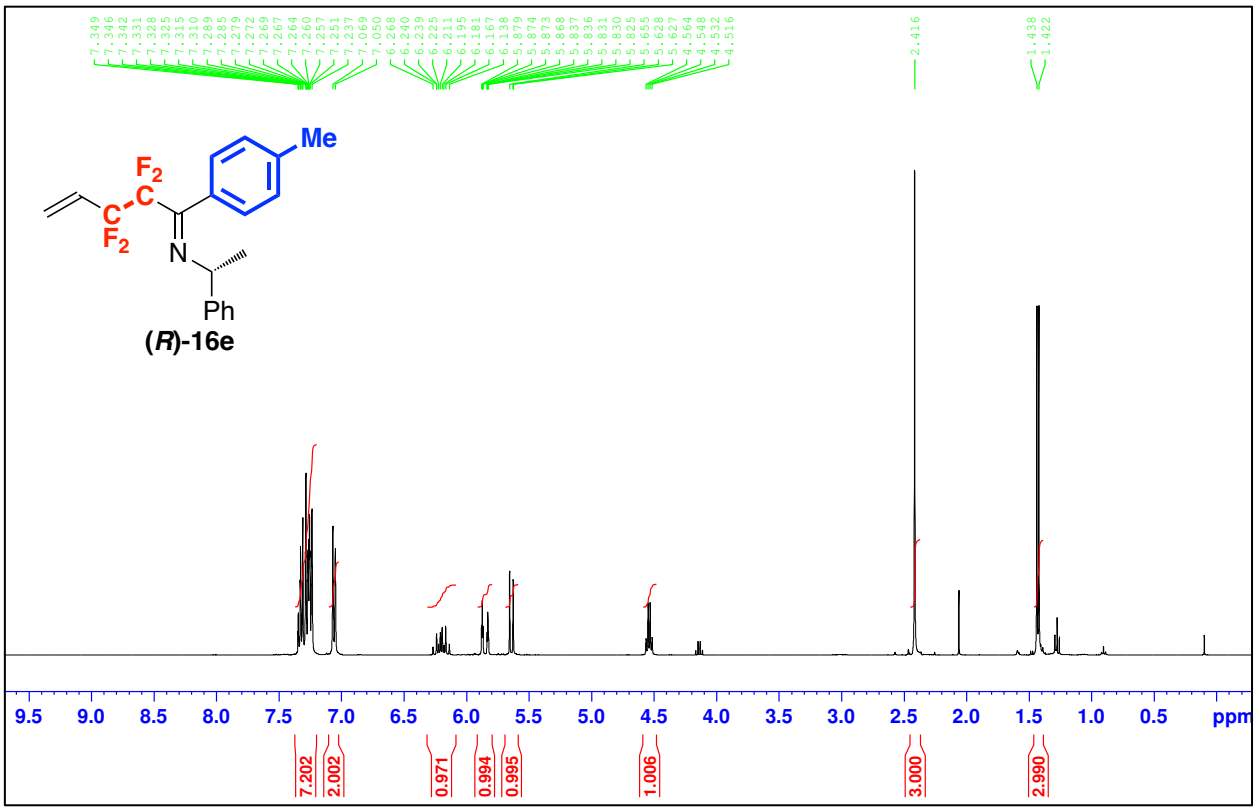
^{13}C NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(4-methoxyphenyl)pent-4-en-1-ylidene)-1-phenylethylamine ((***R*)-16d**)



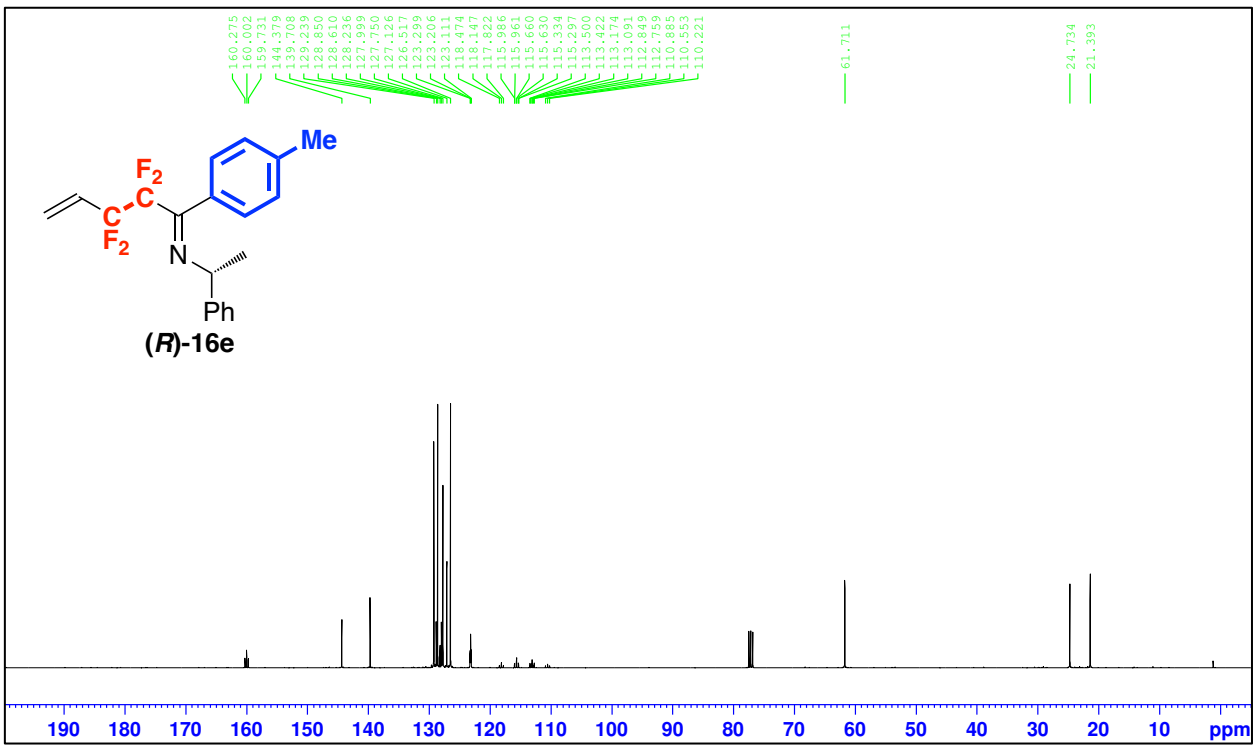
^{19}F NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(4-methoxyphenyl)pent-4-en-1-ylidene)-1-phenylethylamine (**(*R*)-16d**)



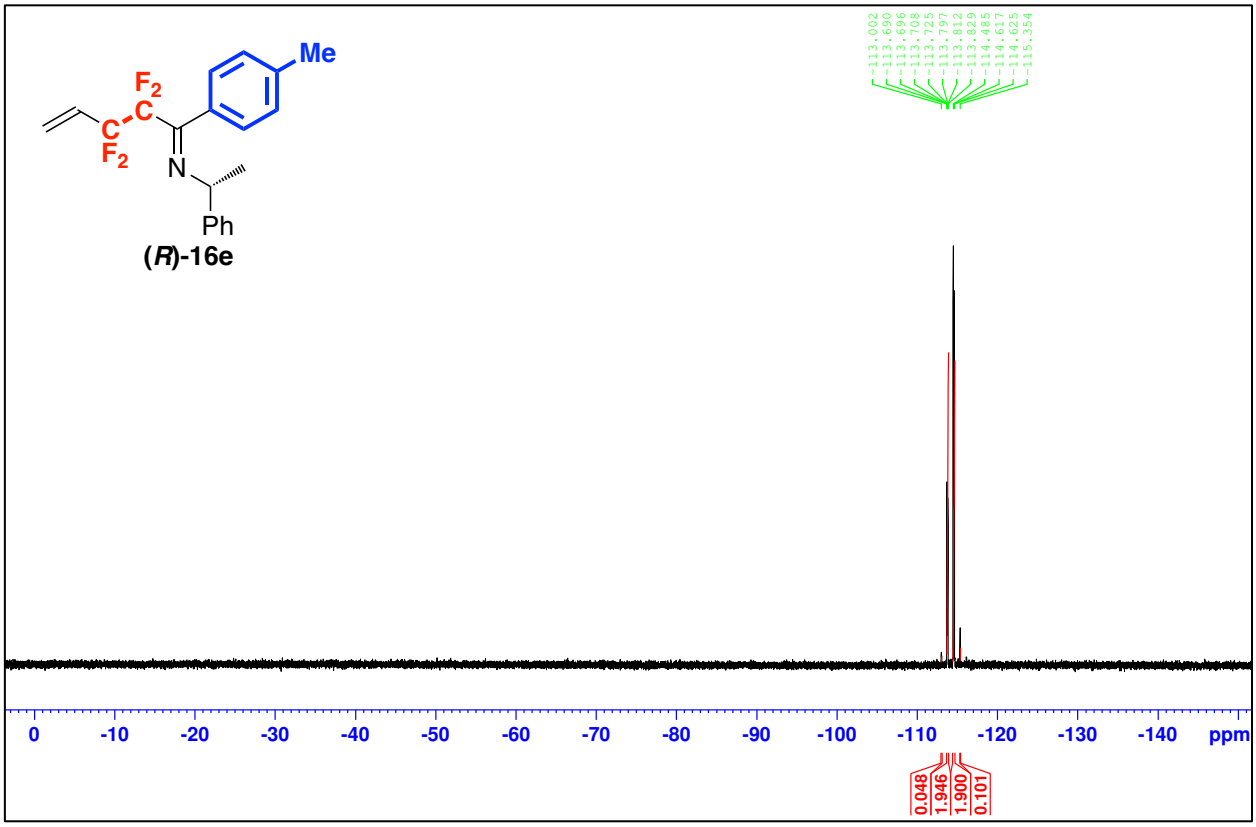
^{1}H NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(4-methylphenyl)pent-4-en-1-ylidene)-1-phenylethylamine (**(*R*)-16e**)



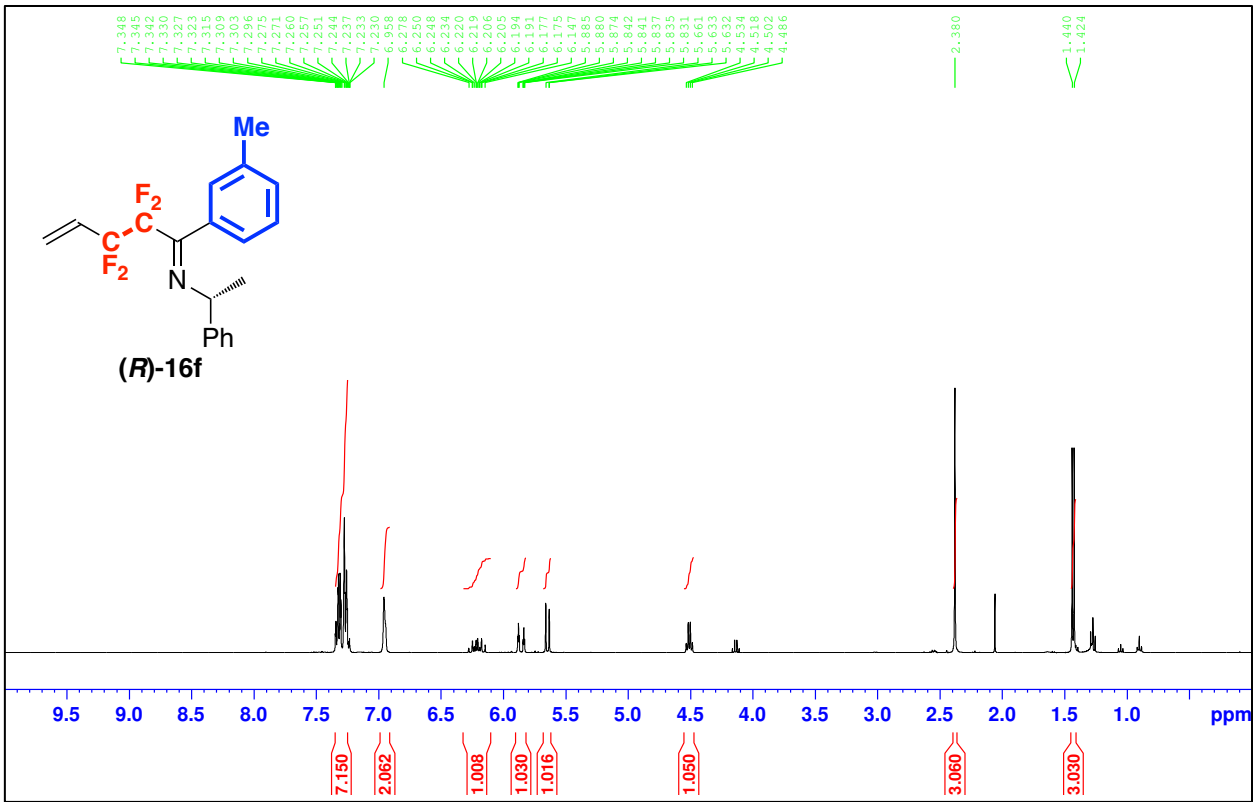
^{13}C NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(4-methylphenyl)pent-4-en-1-ylidene)-1-phenylethylamine (**(*R*)-16e**)



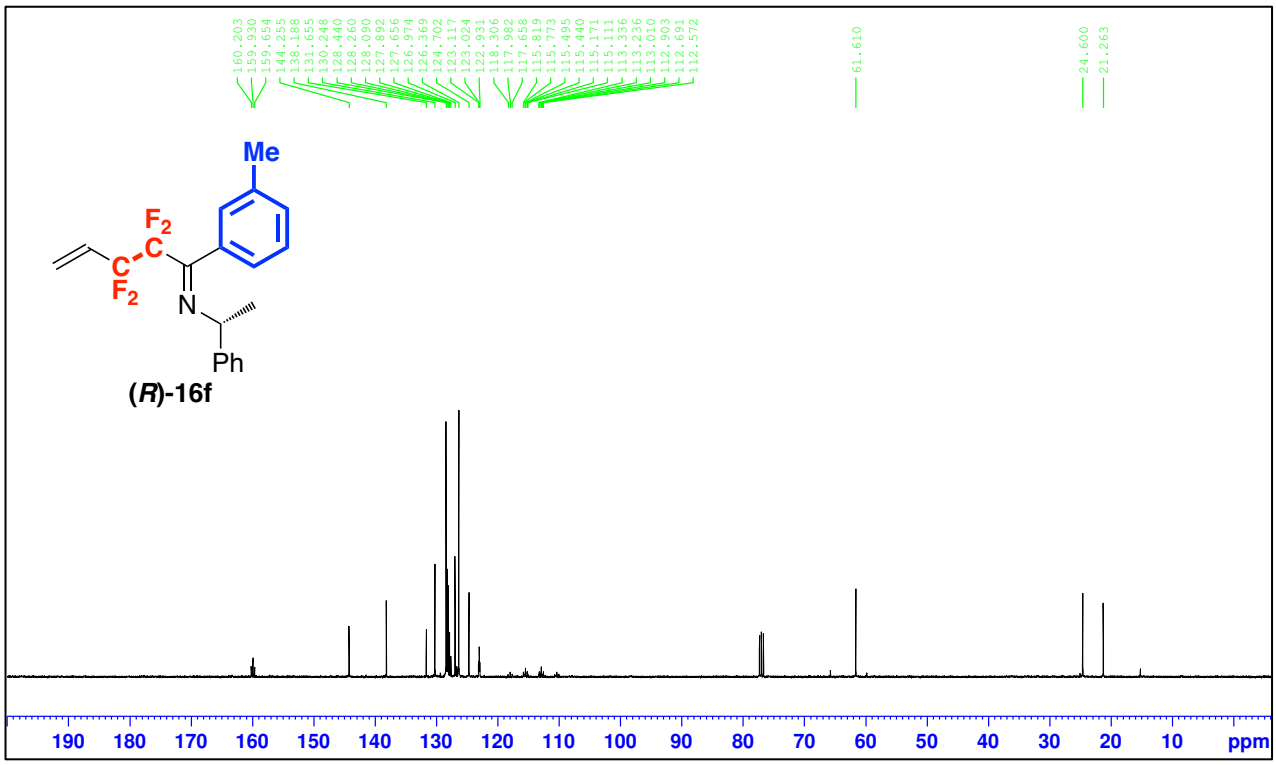
^{19}F NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(4-methylphenyl)pent-4-en-1-ylidene)-1-phenylethylamine (**(*R*)-16e**)



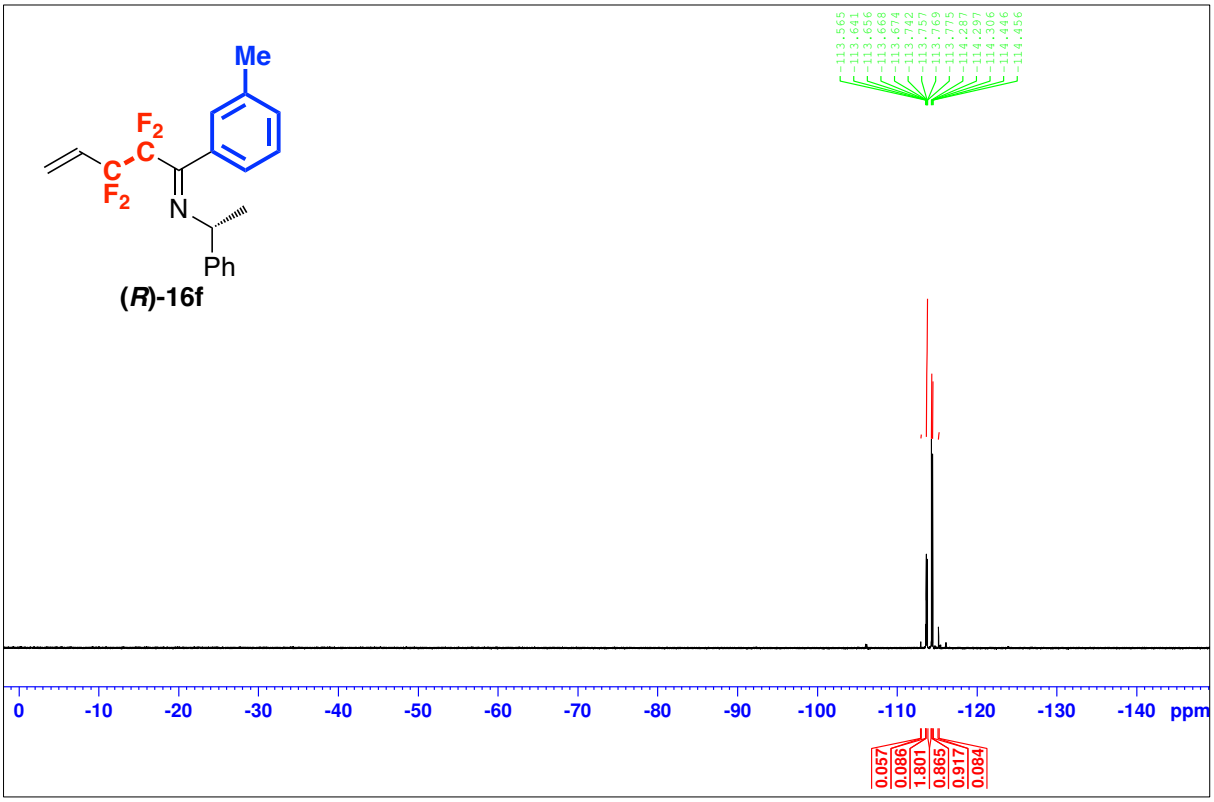
^{1}H NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(3-methylphenyl)pent-4-en-1-ylidene)-1-phenylethylamine ((***R*)-16f**)



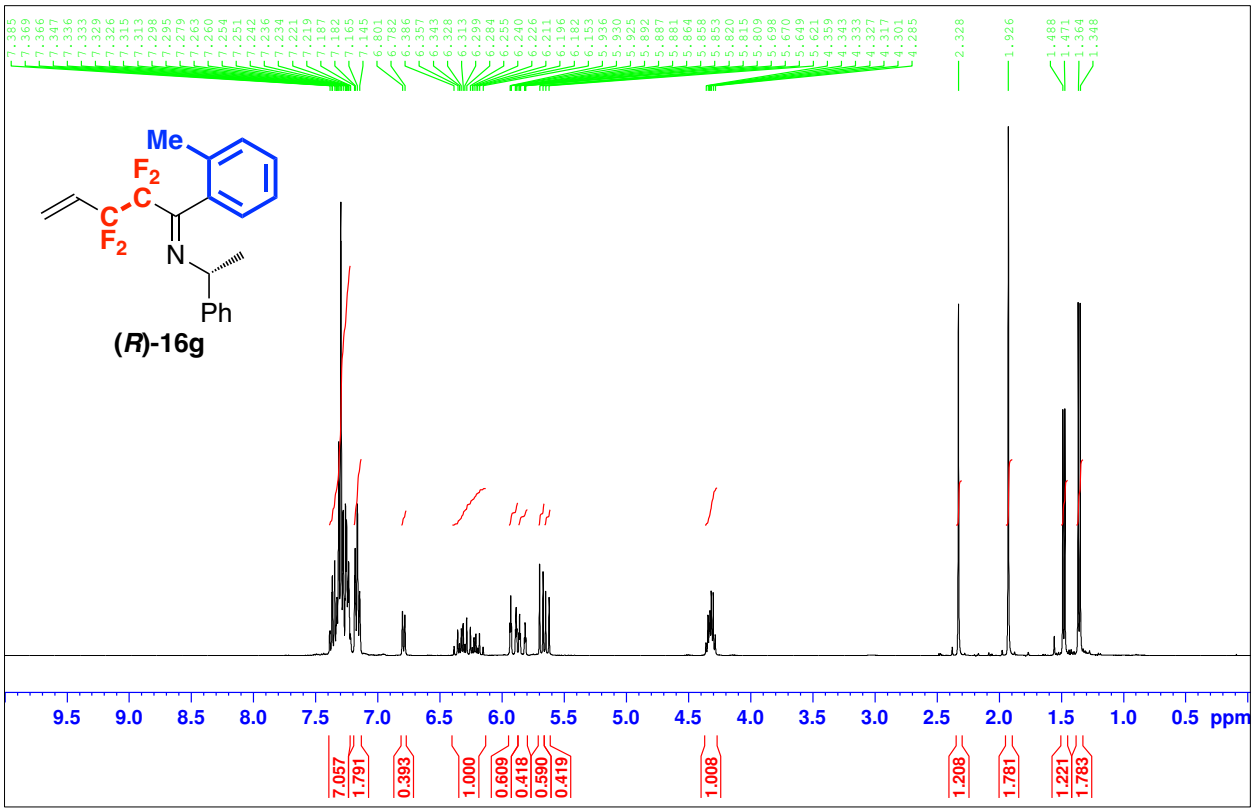
^{13}C NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(3-methylphenyl)pent-4-en-1-ylidene)-1-phenylethylamine ((***R*)-16f**)



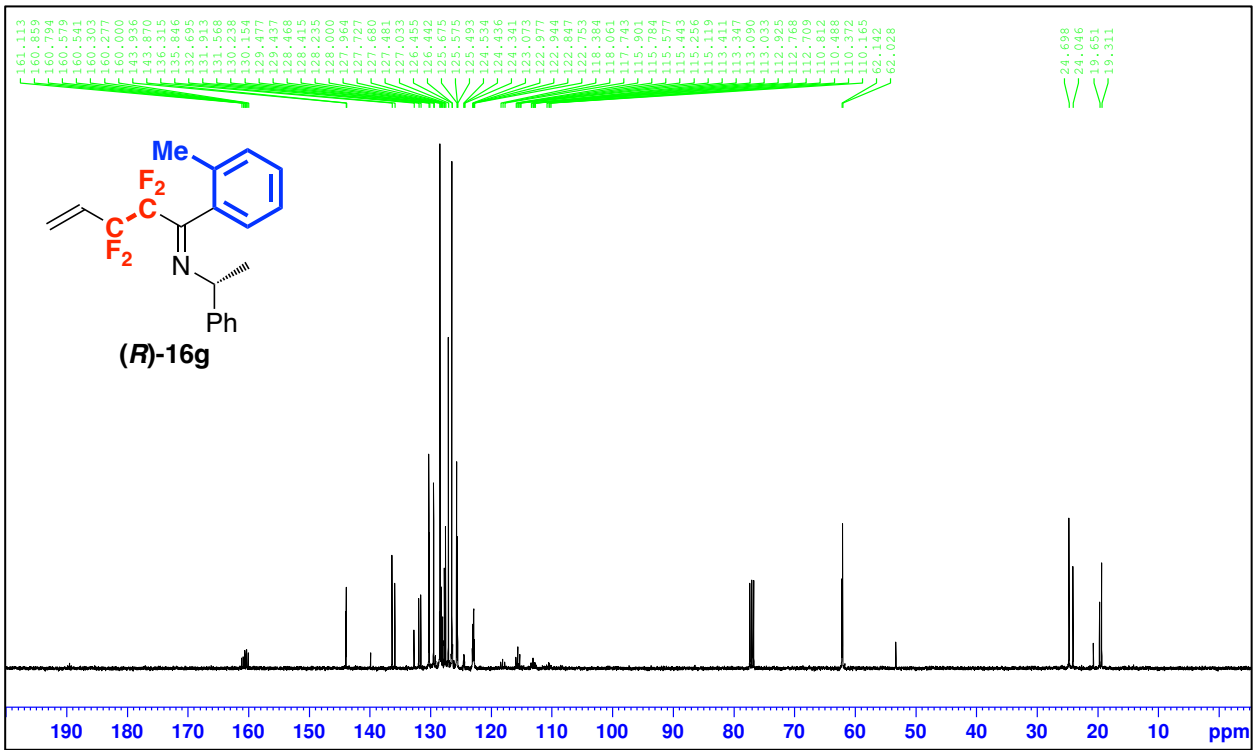
^{19}F NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(3-methylphenyl)pent-4-en-1-ylidene)-1-phenylethylamine (**(*R*)-16f**)



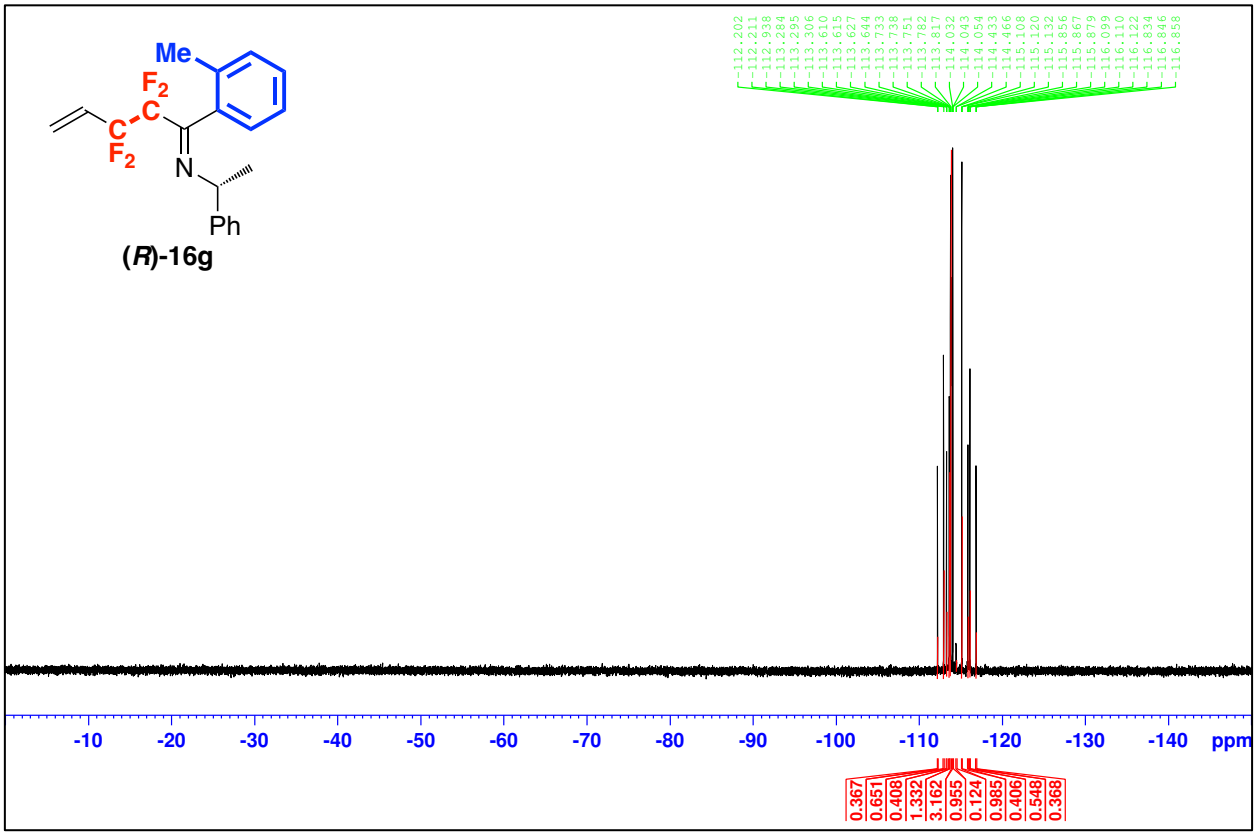
^{1}H NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(2-methylphenyl)pent-4-en-1-ylidene)-1-phenylethylamine ((***R*)-16g**)



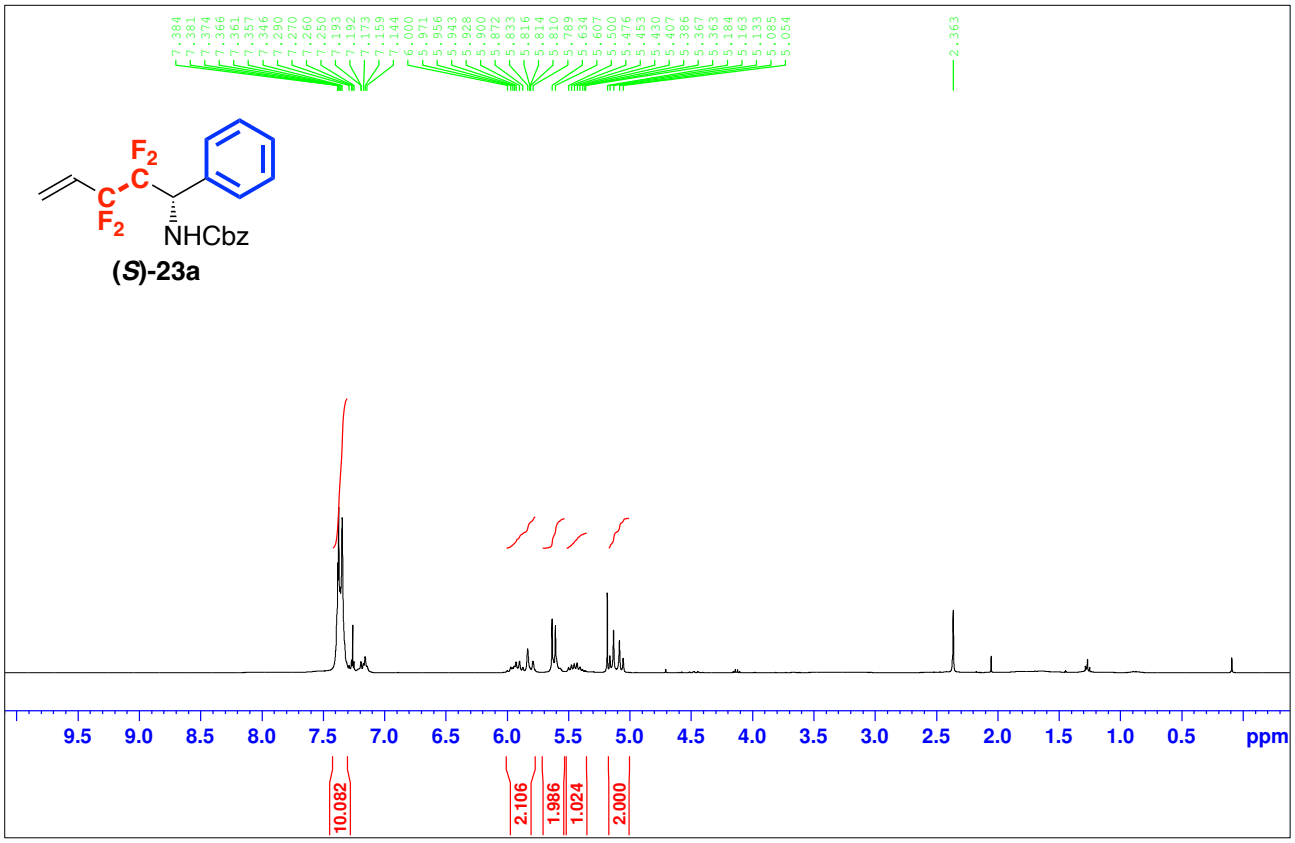
^{13}C NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(2-methylphenyl)pent-4-en-1-ylidene)-1-phenylethylamine ((***R*)-16g**)



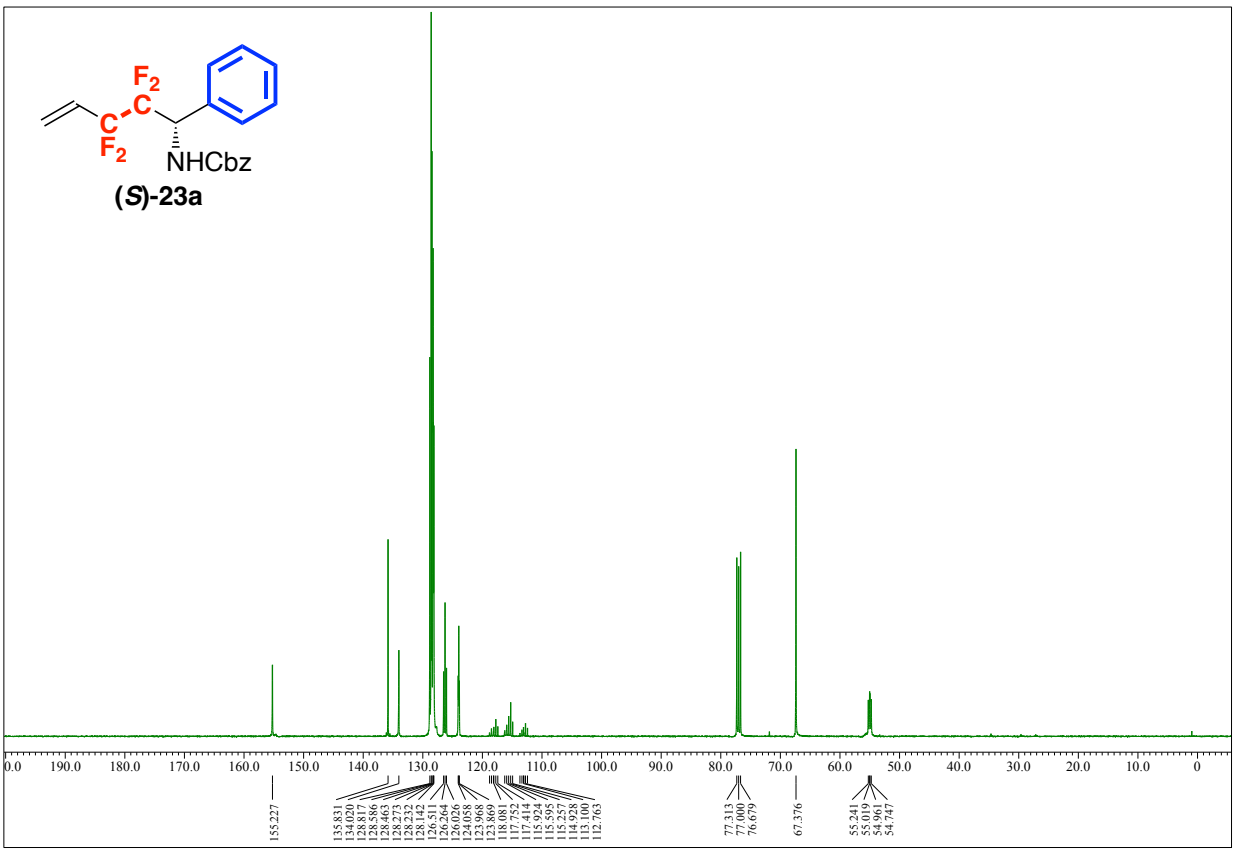
^{19}F NMR Spectrum of (*R*)-*N*-(2,2,3,3-tetrafluoro-1-(2-methylphenyl)pent-4-en-1-ylidene)-1-phenylethylamine (**(*R*)-16g**)



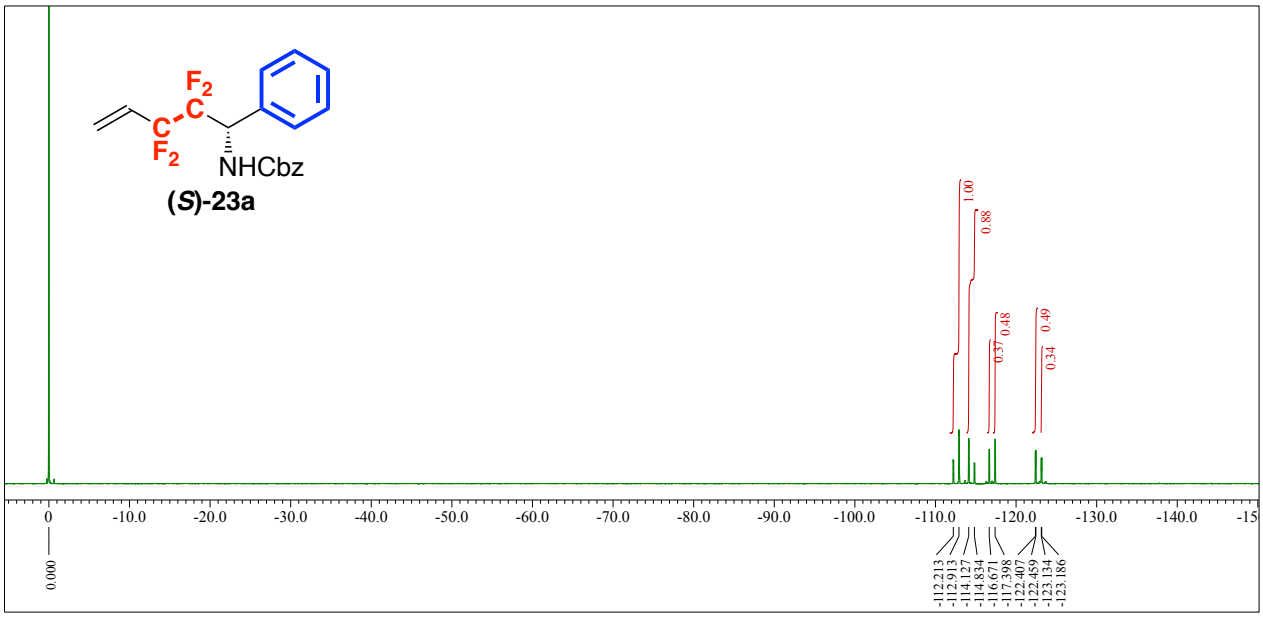
^{1}H NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-phenylpent-4-en-1-yl)carbamate (**(*S*)-23a**)



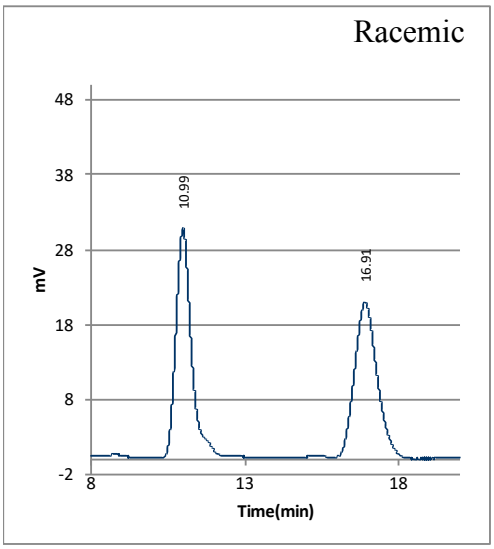
^{13}C NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-phenylpent-4-en-1-yl)carbamate (**(*S*)-23a**)



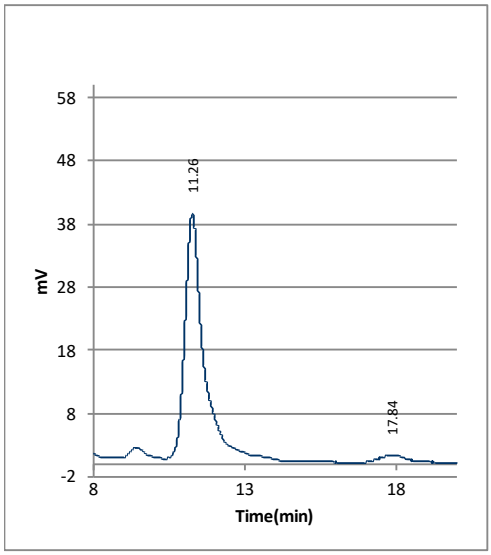
^{19}F NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-phenylpent-4-en-1-yl)carbamate (**(*S*)-23a**)



Chromatograph in HPLC for **(*S*)-23a**

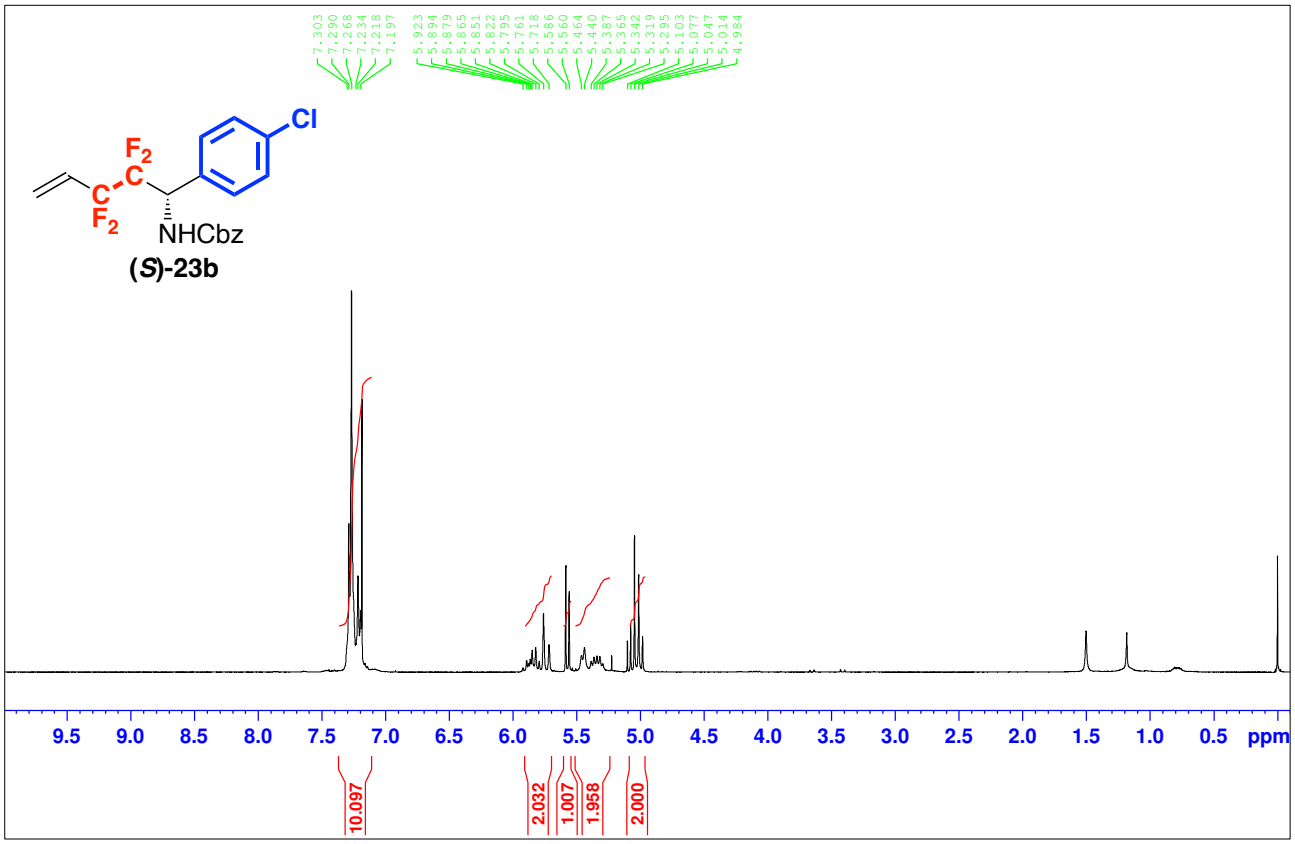


No.	Rt	Area(%)
1	10.99	50.019
2	16.91	49.981
		100

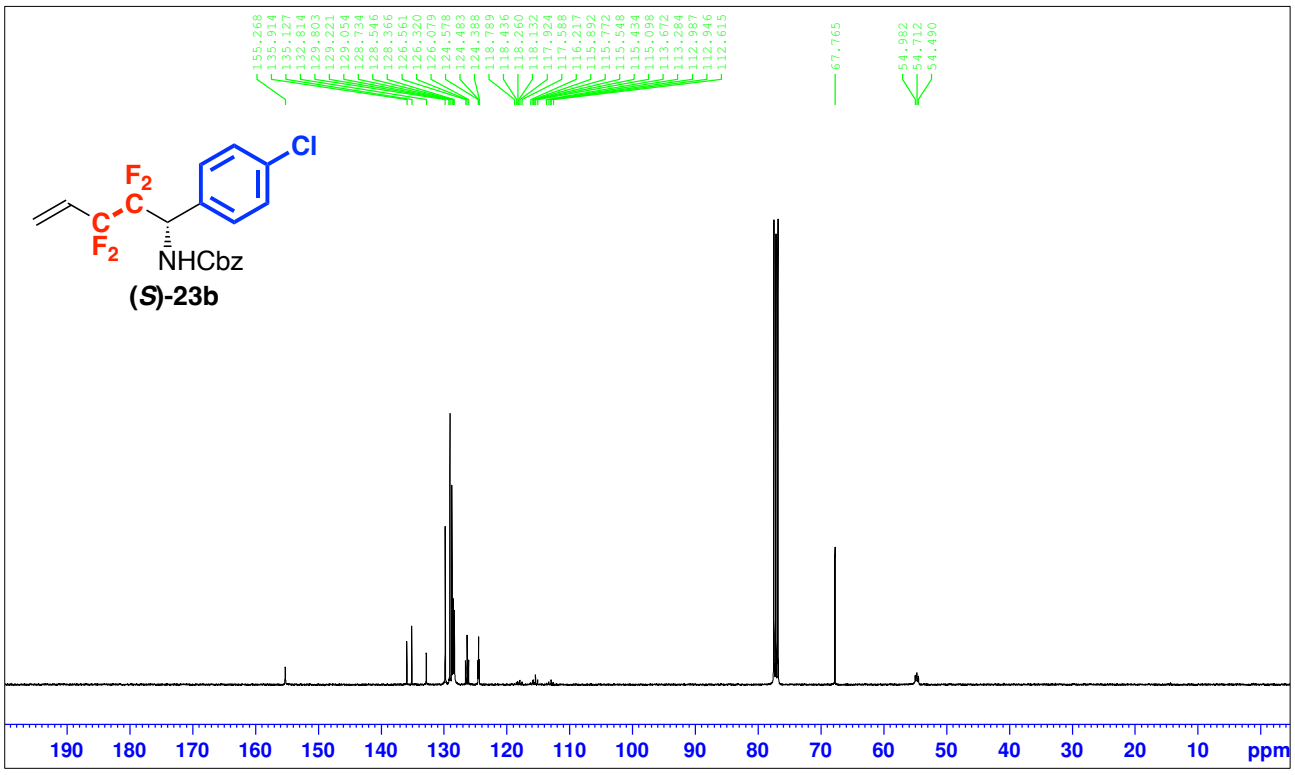


No.	Rt	Area(%)
1	11.26	96.085
2	17.84	3.915
		100

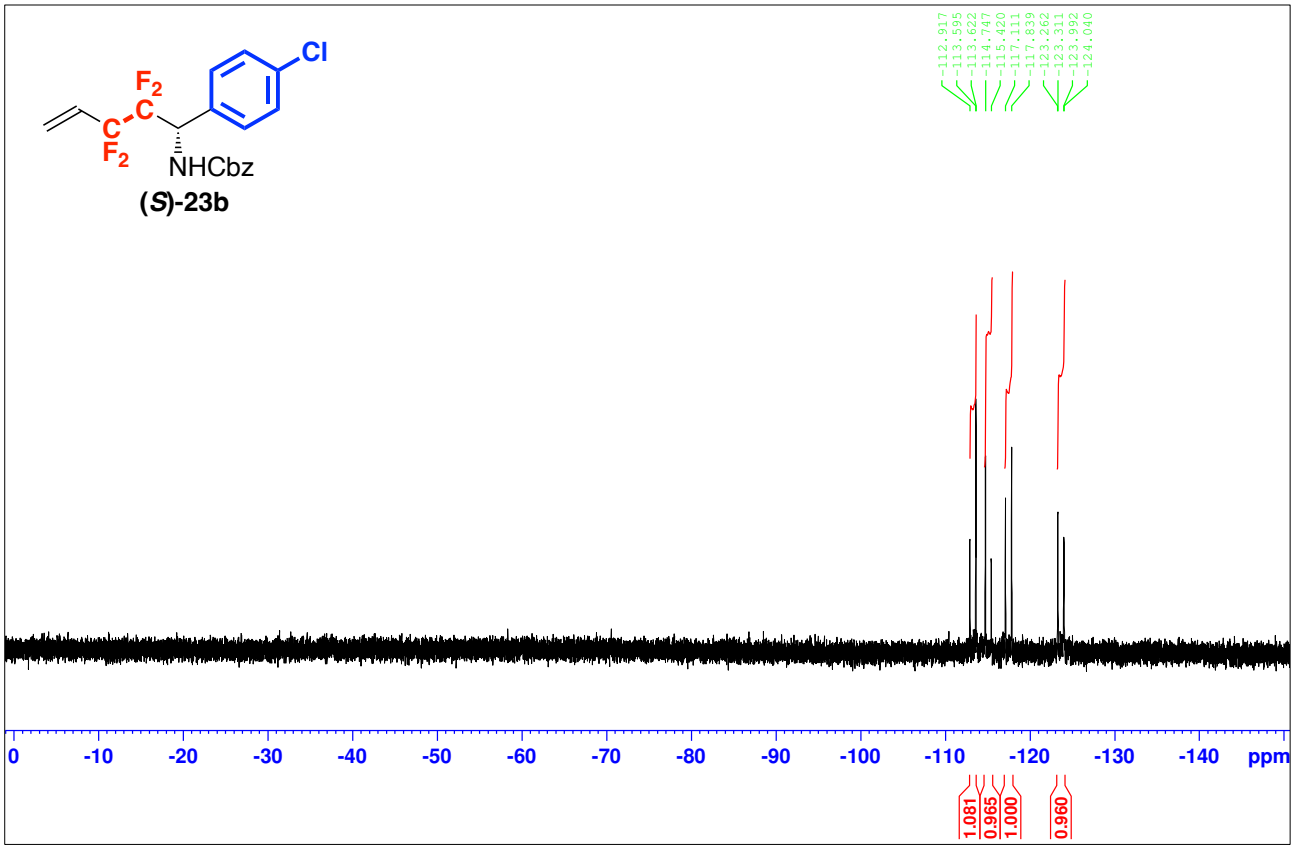
^{1}H NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-chlorophenylpent-4-en-1-yl)carbamate (**(*S*)-23b**)



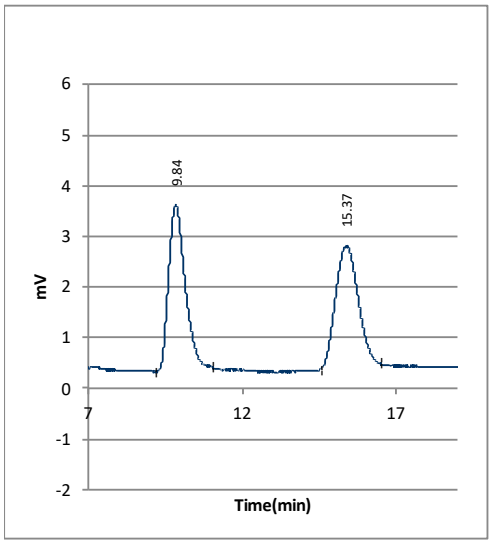
^{13}C NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-chlorophenylpent-4-en-1-yl)carbamate (**(*S*)-23b**)



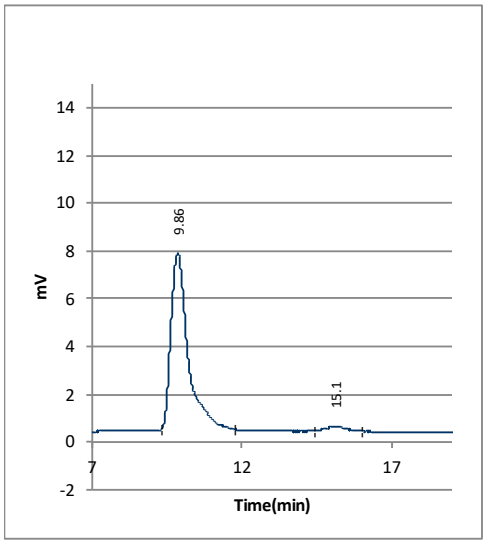
^{19}F NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-chlorophenylpent-4-en-1-yl)carbamate (**(*S*)-23b**)



Chromatograph in HPLC for **(*S*)-23b**

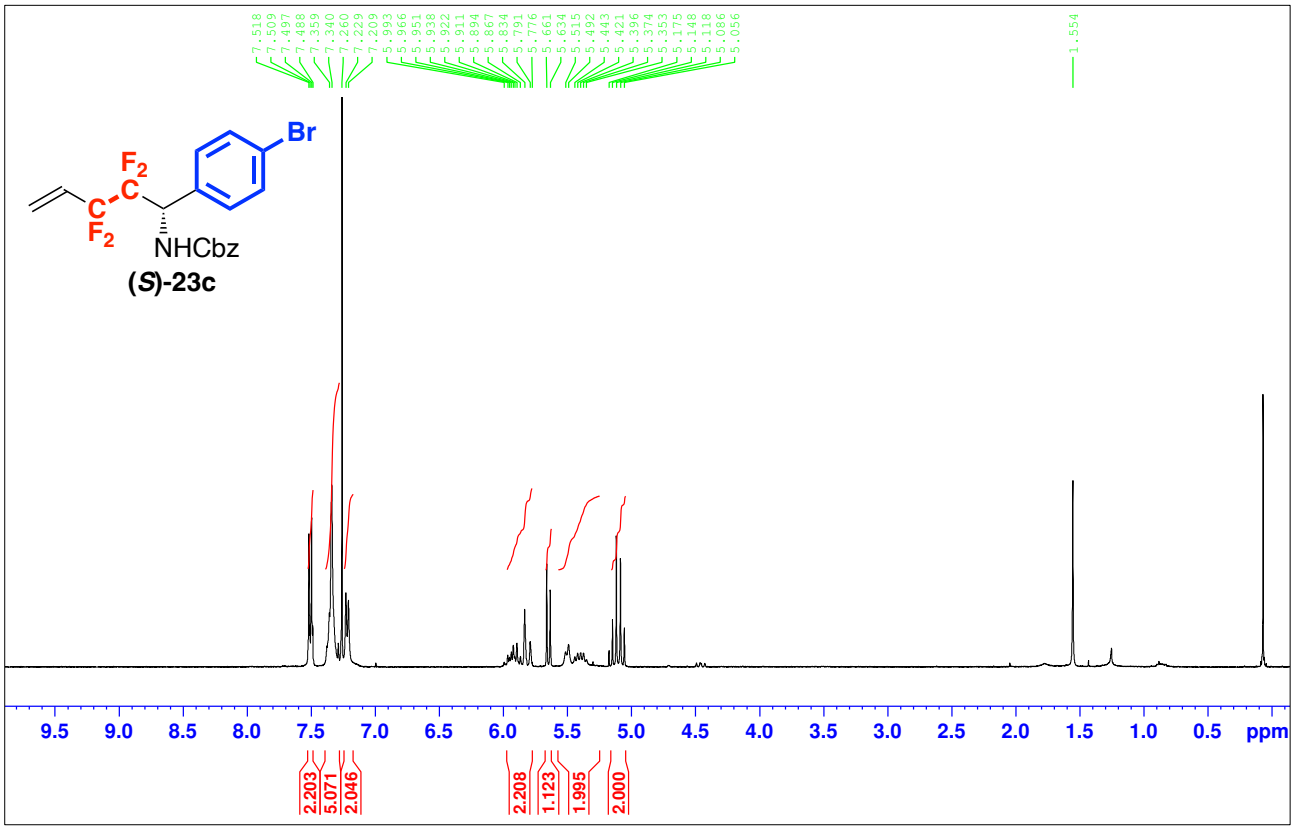


No.	Rt	Area(%)
1	9.84	49.966
2	15.37	50.034
		100

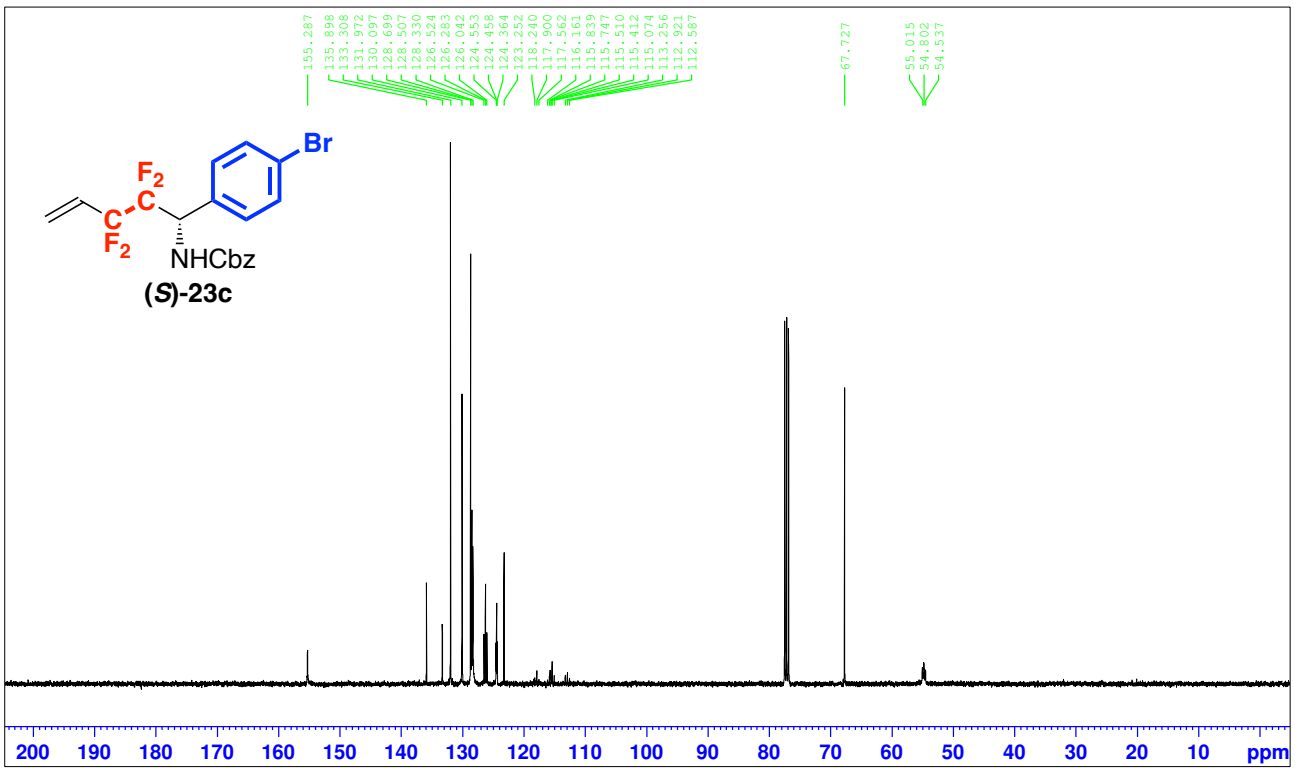


No.	Rt	Area(%)
1	9.86	97.352
2	15.1	2.648
		100

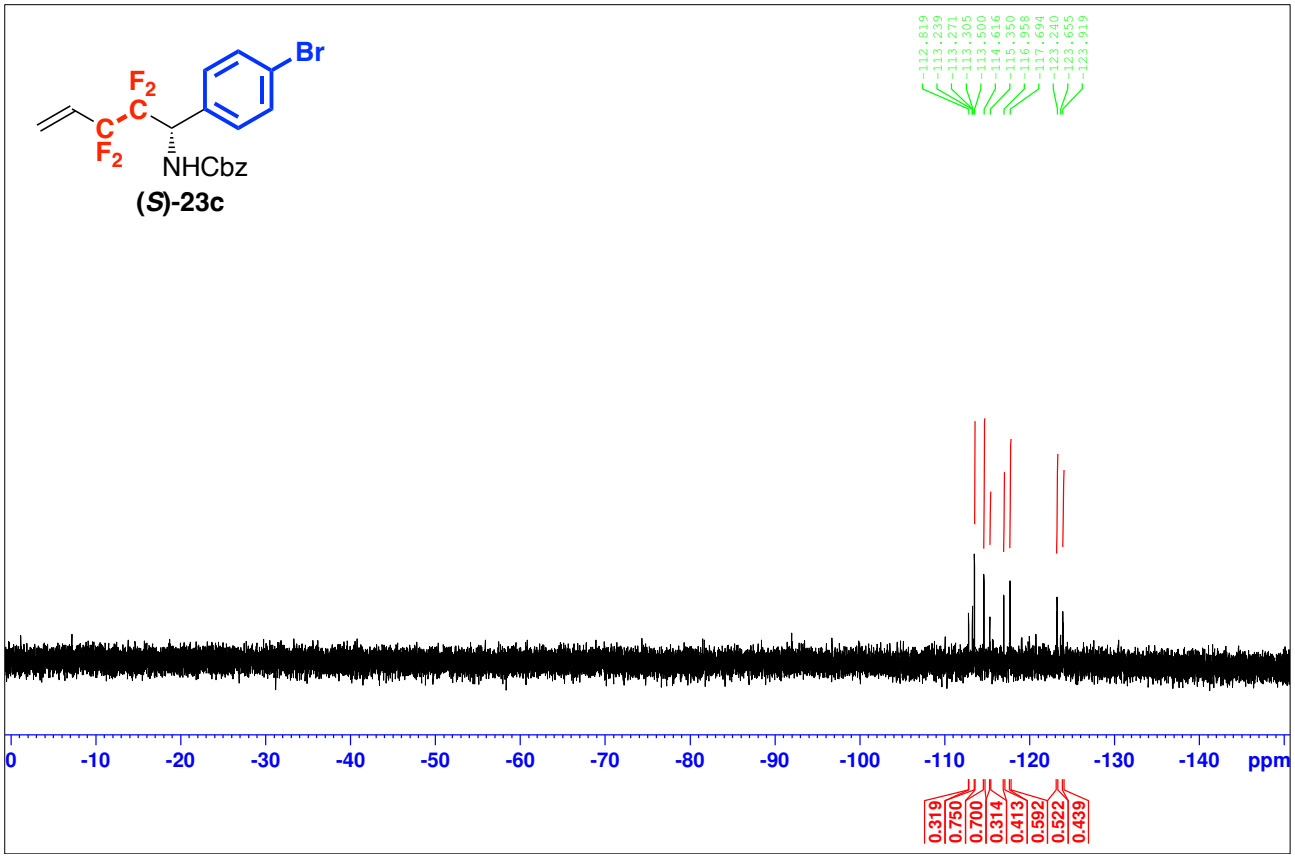
^{1}H NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-bromophenylpent-4-en-1-yl)carbamate ((***S***)-**23c**)



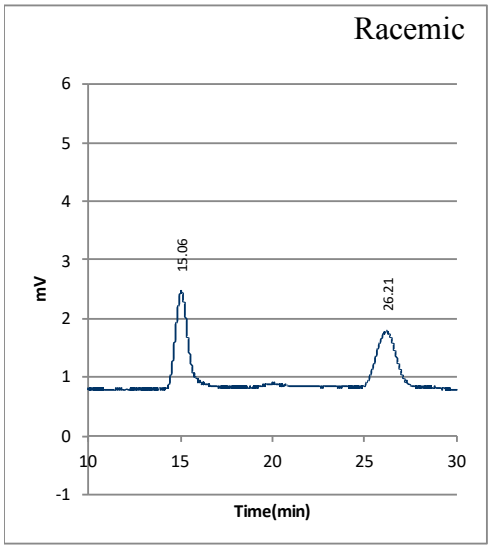
^{13}C NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-bromophenylpent-4-en-1-yl)carbamate ((***S***)-**23c**)



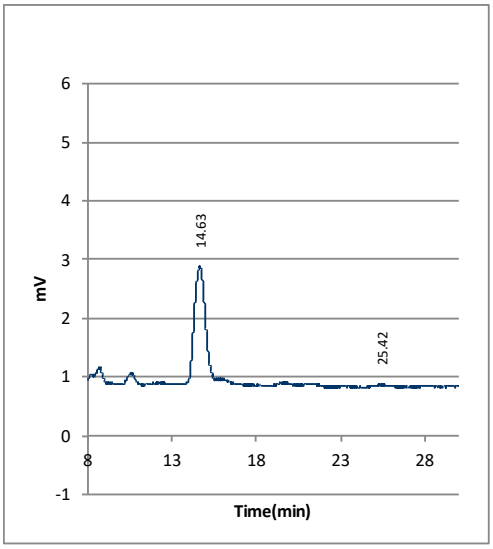
^{19}F NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-bromophenylpent-4-en-1-yl)carbamate ((***S*)-23c**)



Chromatograph in HPLC for **(*S*)-23c**

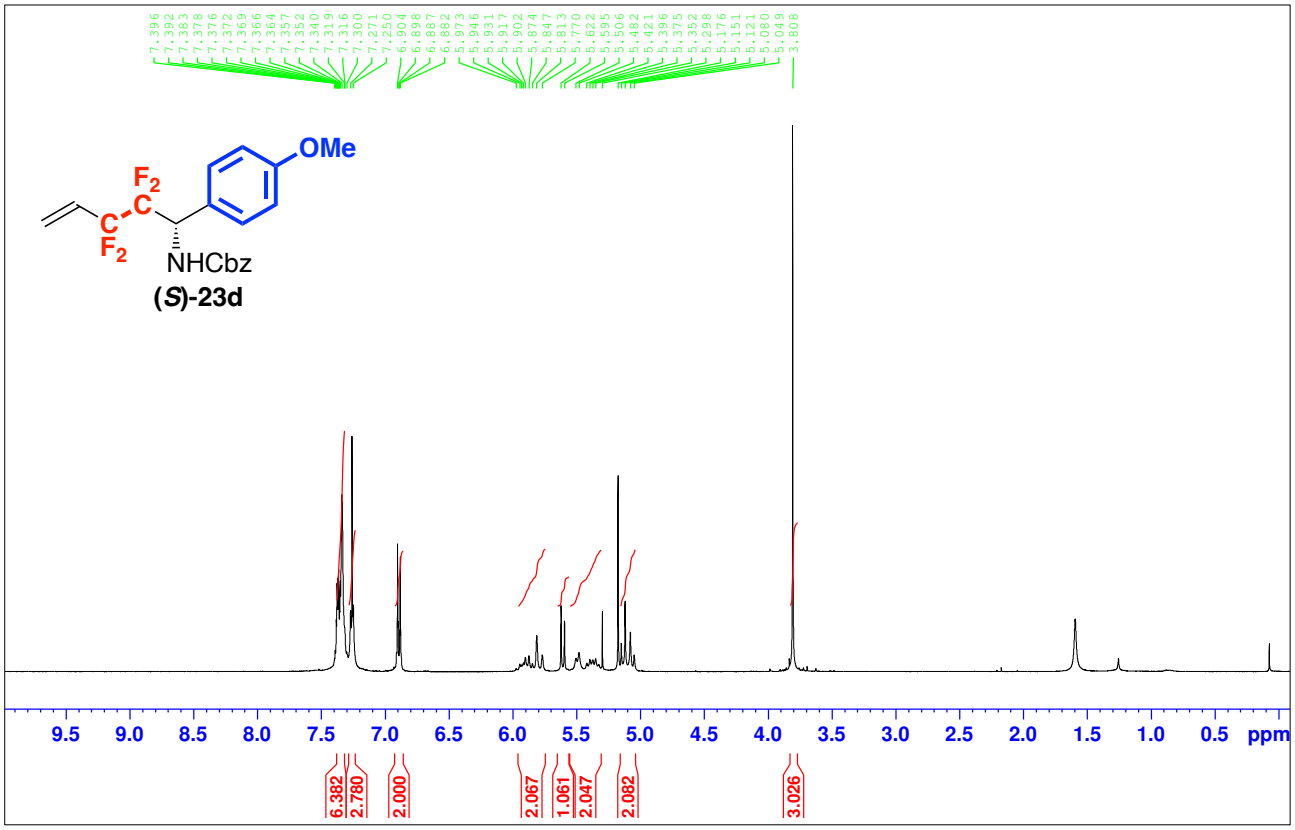


No.	Rt	Area(%)
1	15.06	49.901
2	26.21	50.099
		100

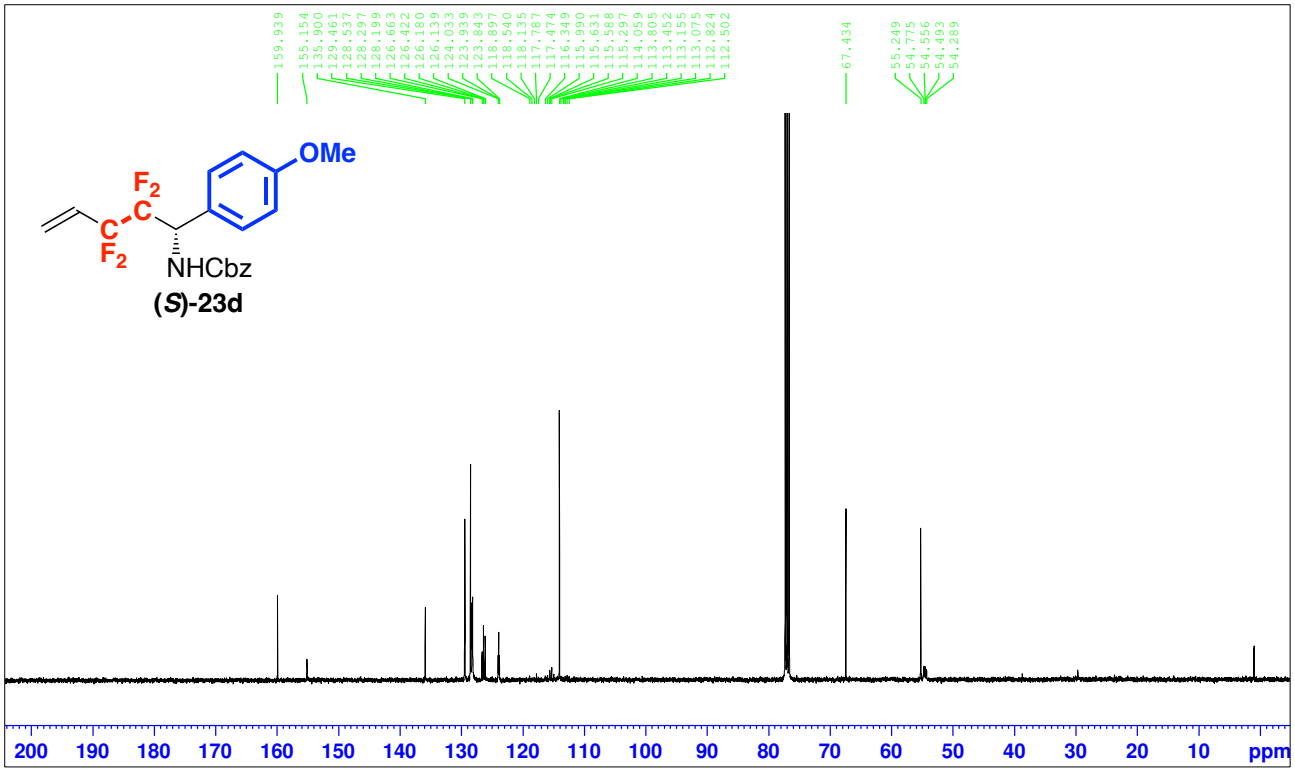


No.	Rt	Area(%)
1	14.63	98.824
2	25.42	1.176
		100

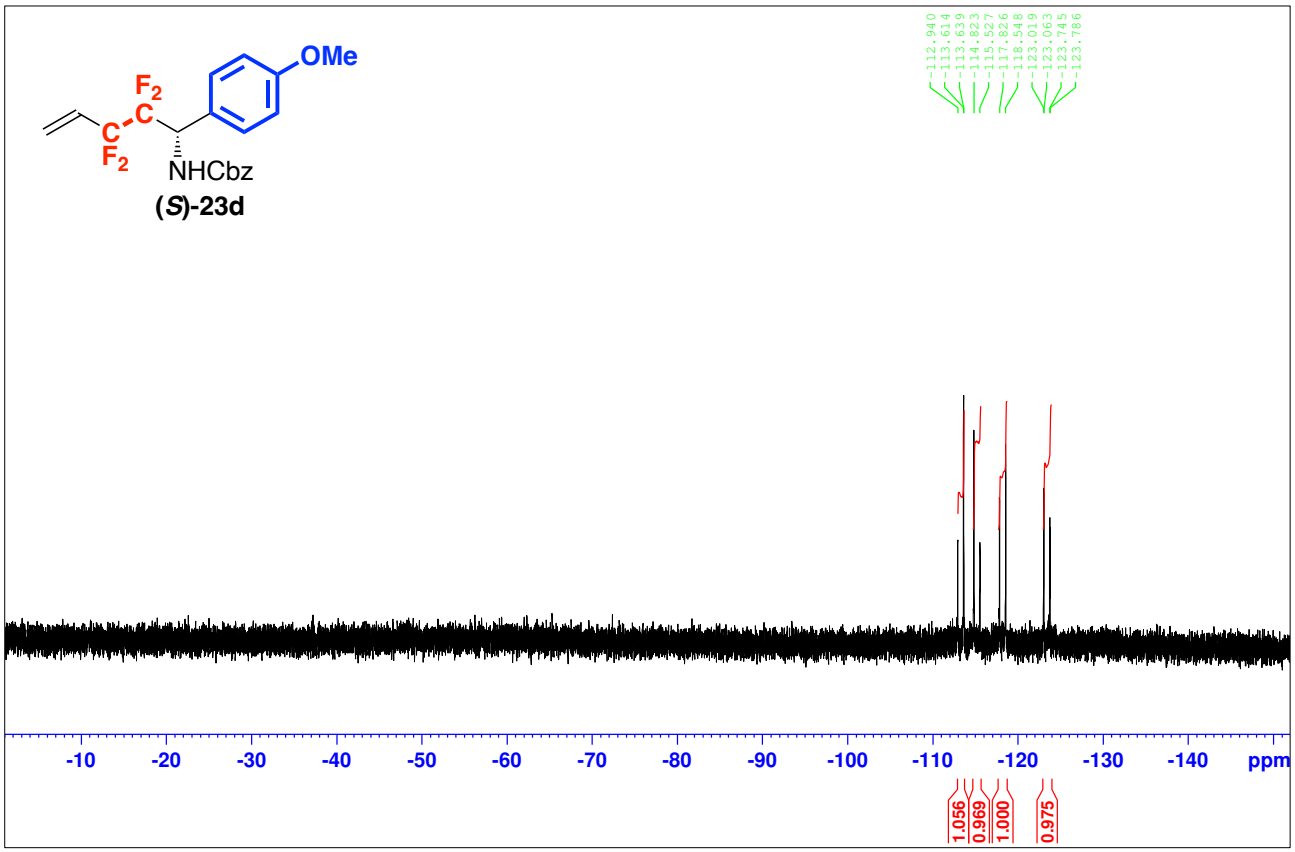
^{1}H NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-methoxyphenylpent-4-en-1-yl)carbamate (**(*S*)-23d**)



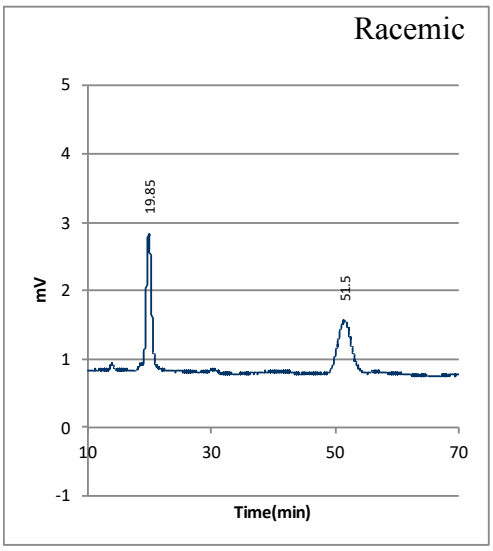
^{13}C NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-methoxyphenylpent-4-en-1-yl)carbamate (**(*S*)-23d**))



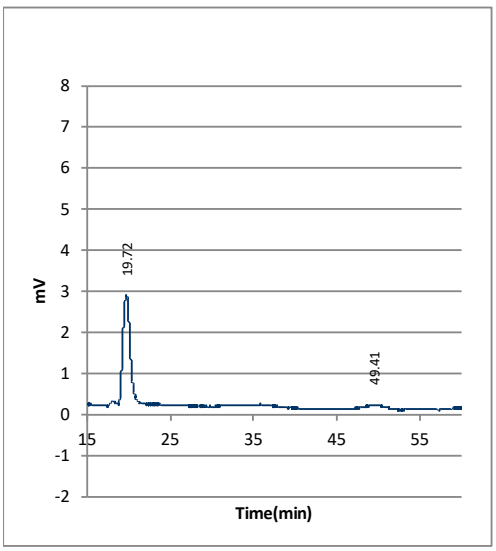
^{19}F NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-methoxyphenylpent-4-en-1-yl)carbamate (**(*S*)-23d**)



Chromatograph in HPLC for **(*S*)-23d**

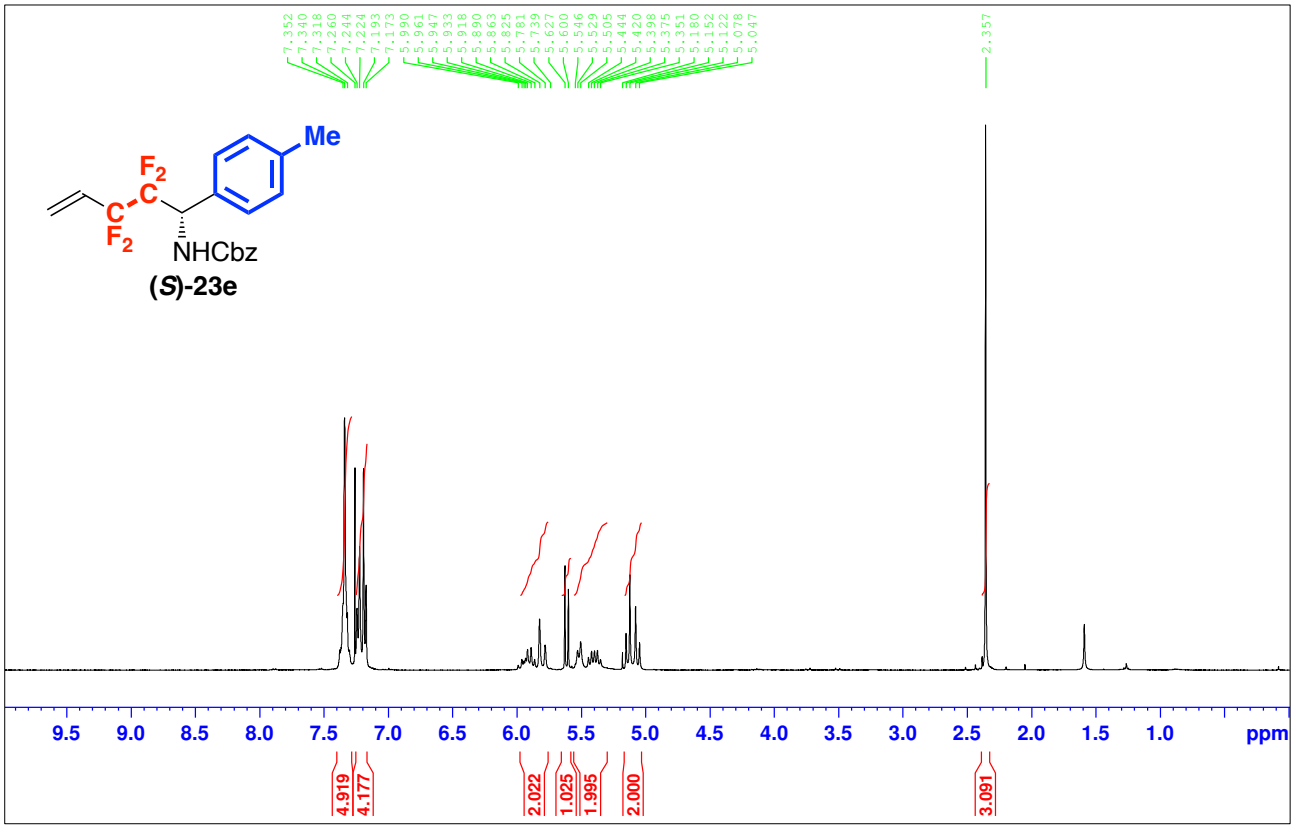


No.	Rt	Area(%)
1	19.85	50.086
2	51.5	49.914
		100

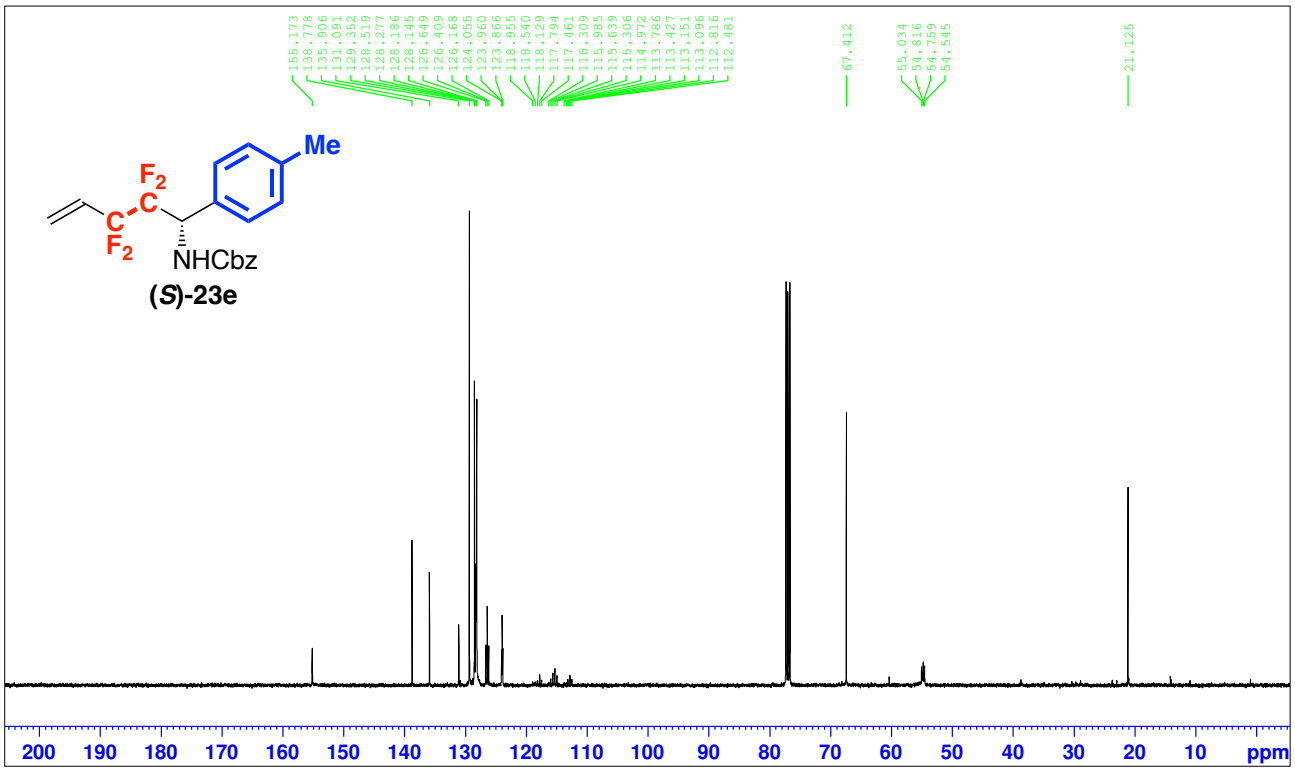


No.	Rt	Area(%)
1	19.72	95.216
2	49.41	4.784
		100

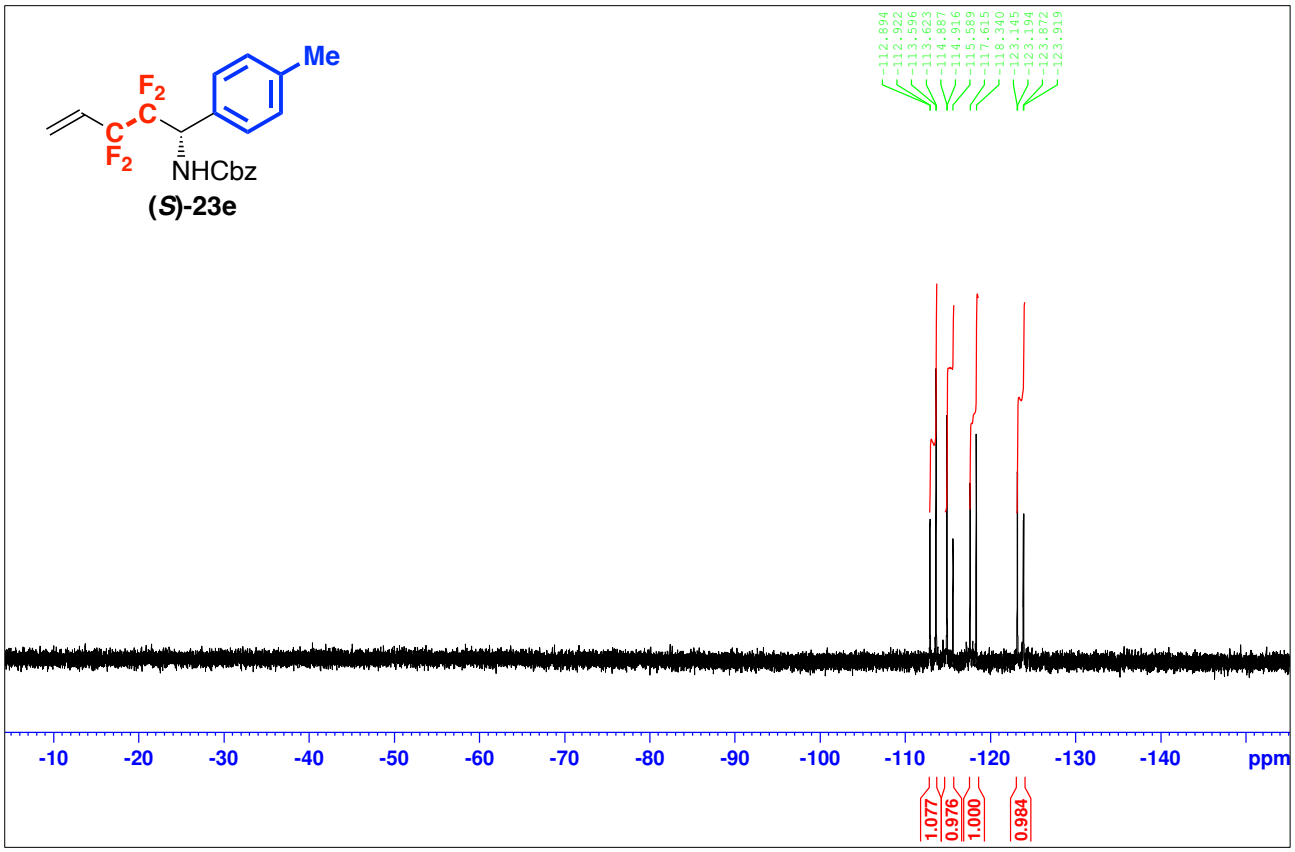
^{1}H NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-methylphenylpent-4-en-1-yl)carbamate (**(*S*)-23e**)



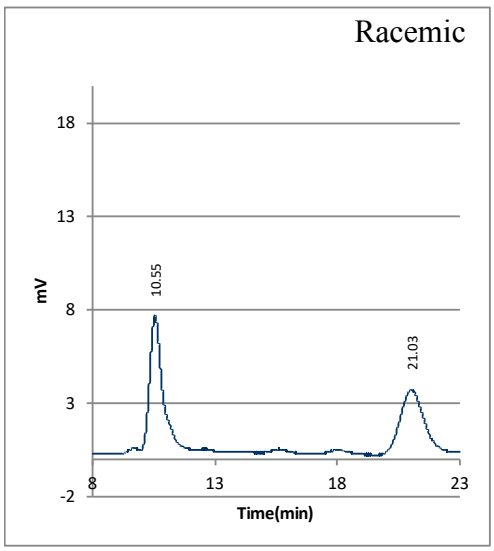
^{13}C NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-methylphenylpent-4-en-1-yl)carbamate (**(*S*)-23e**)



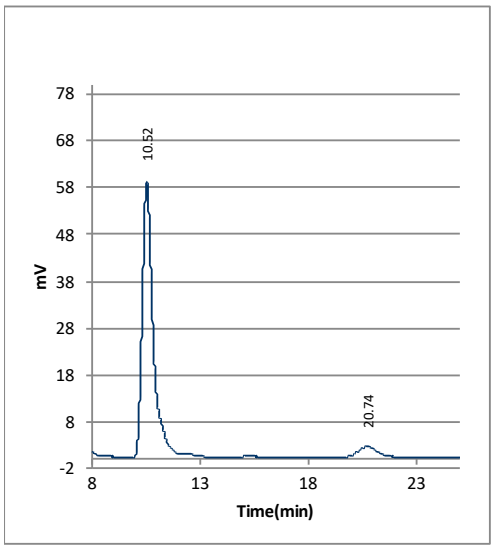
^{19}F NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(4-methylphenylpent-4-en-1-yl)carbamate (**(*S*)-23e**)



Chromatograph in HPLC for **(*S*)-23e**

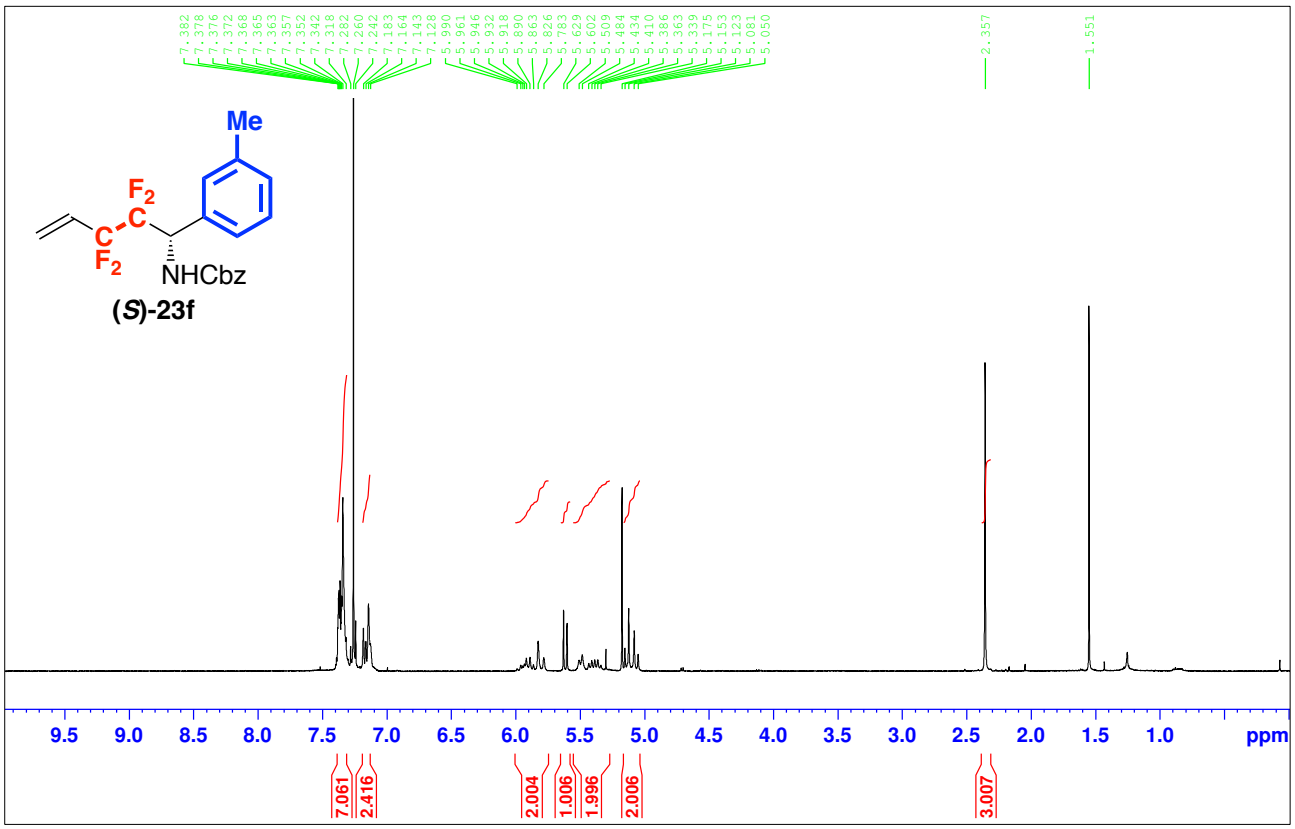


No.	Rt	Area(%)
1	10.55	49.92
2	21.03	50.08
		100

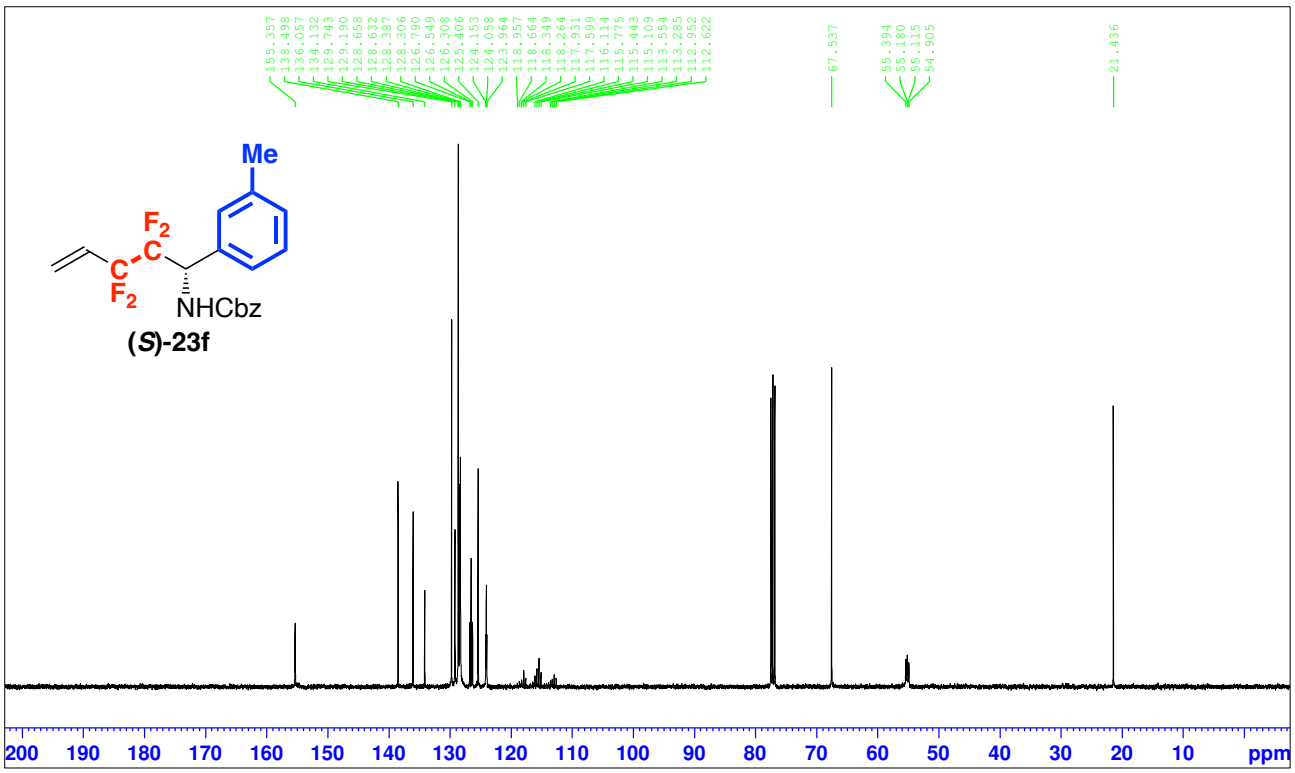


No.	Rt	Area(%)
1	10.52	95.043
2	20.74	4.957
		100

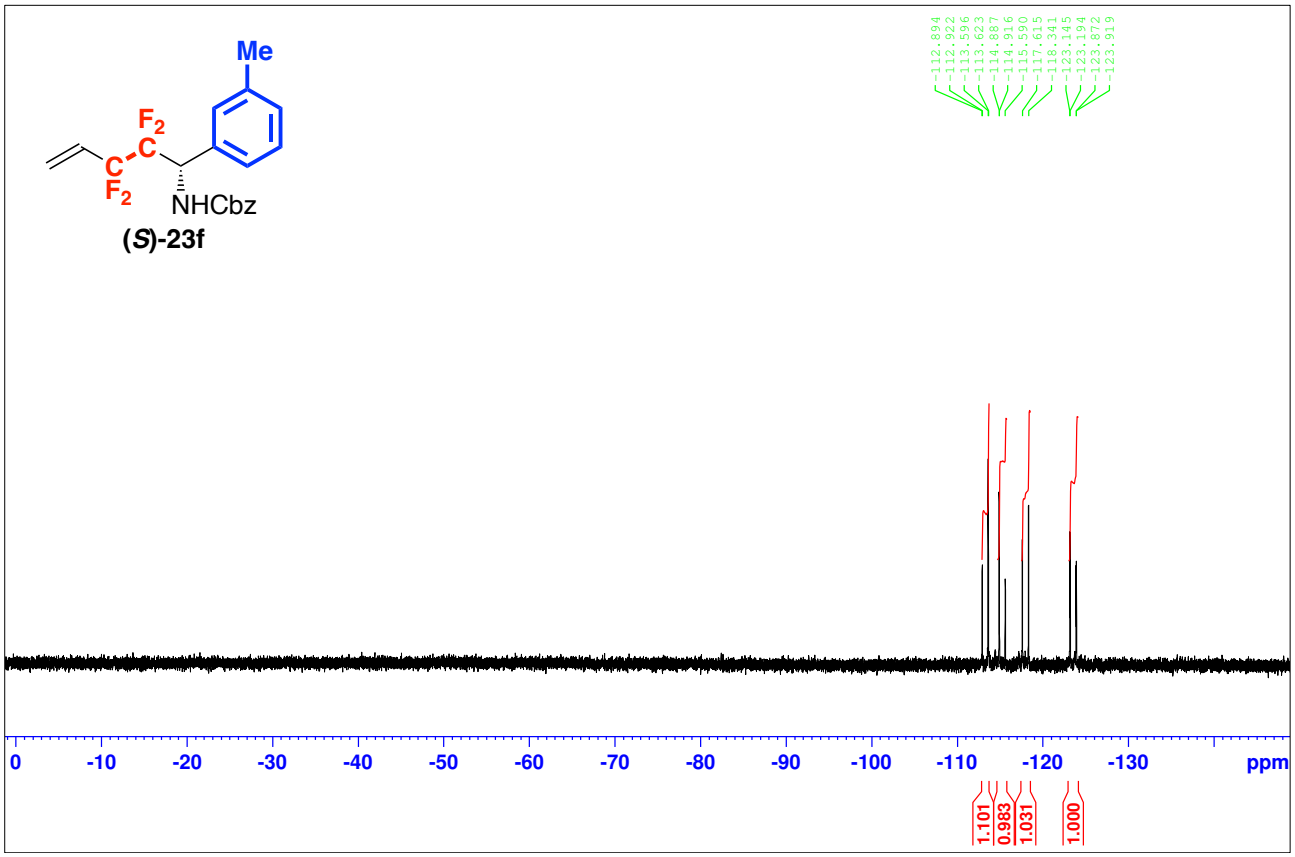
^{1}H NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(3-methylphenylpent-4-en-1-yl)carbamate (**(*S*)-23f**)



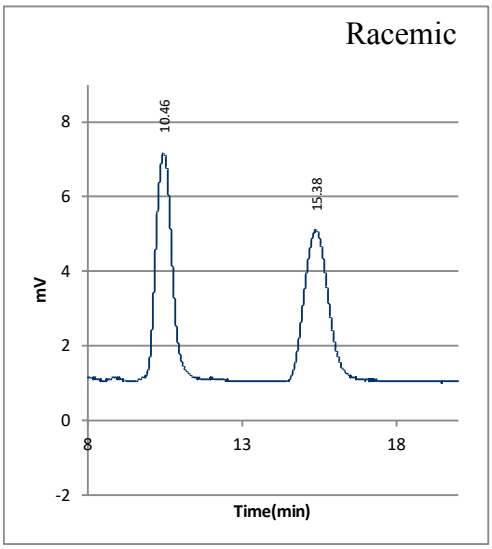
^{13}C NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(3-methylphenylpent-4-en-1-yl)carbamate (**(*S*)-23f**)



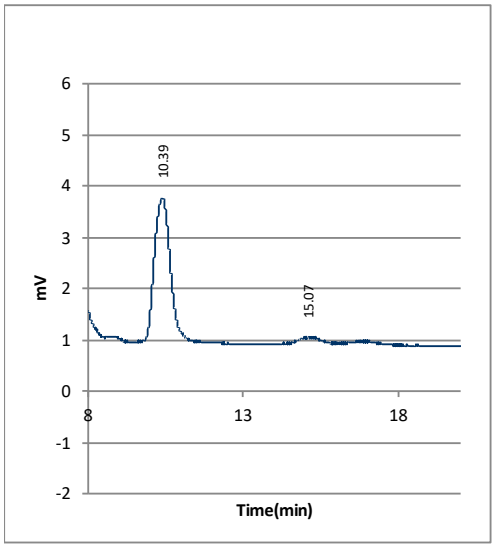
^{19}F NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(3-methylphenylpent-4-en-1-yl)carbamate ((***S*)-23f**)



Chromatograph in HPLC for **(*S*)-23f**

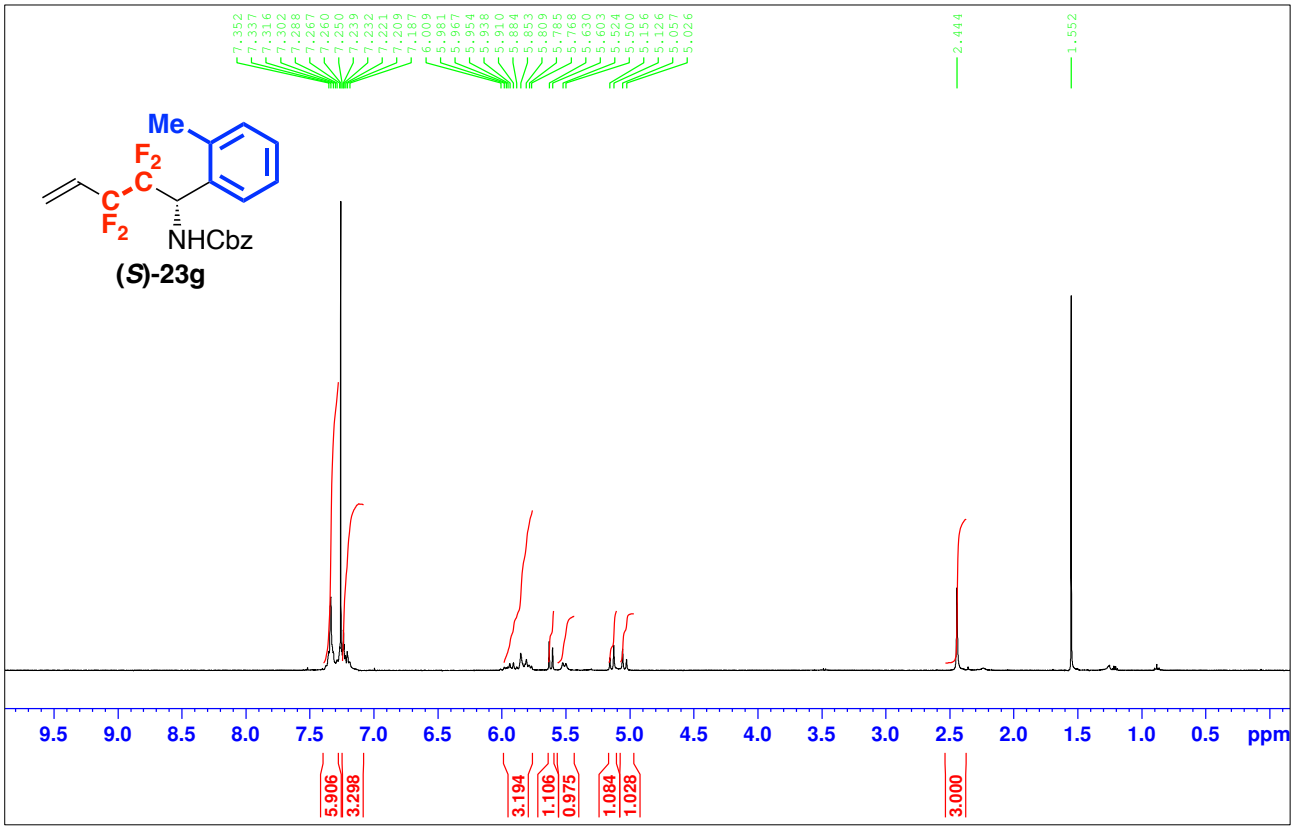


No.	Rt	Area(%)
1	10.46	50.086
2	15.38	49.914
		100

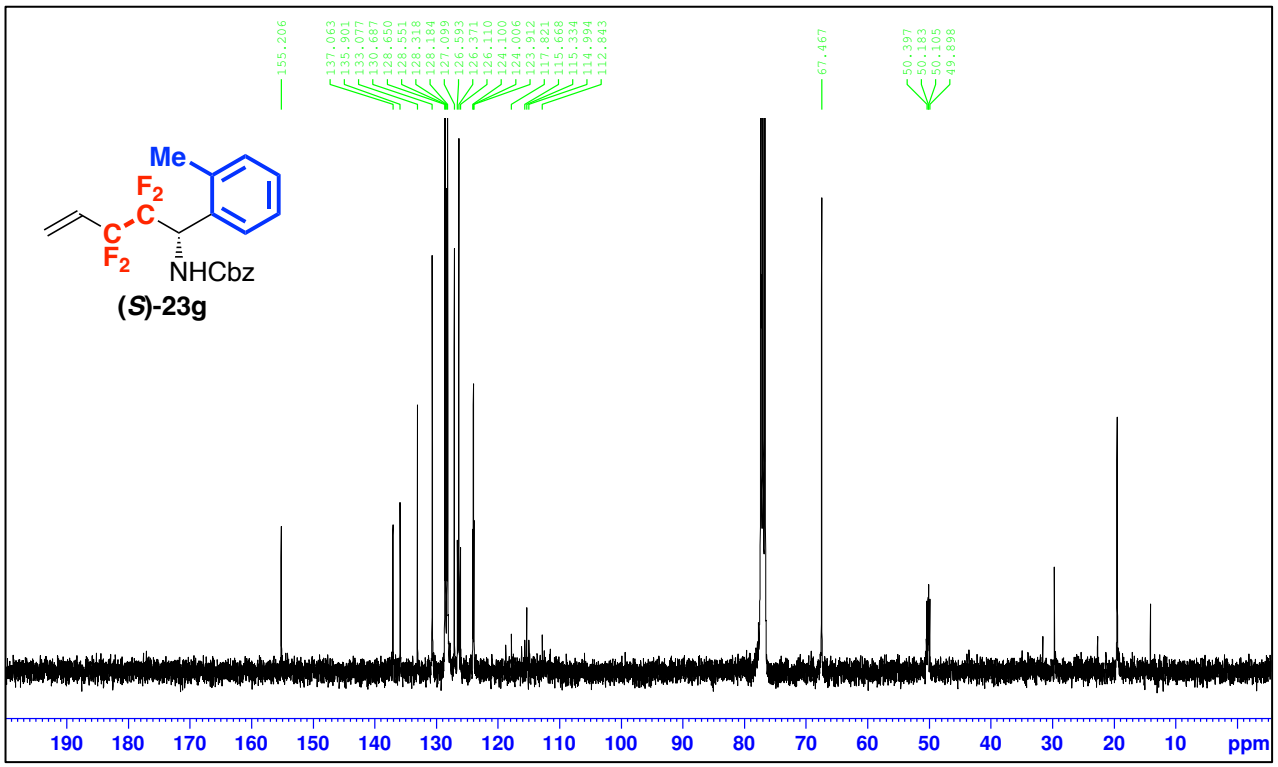


No.	Rt	Area(%)
1	10.39	95.504
2	15.07	4.496
		100

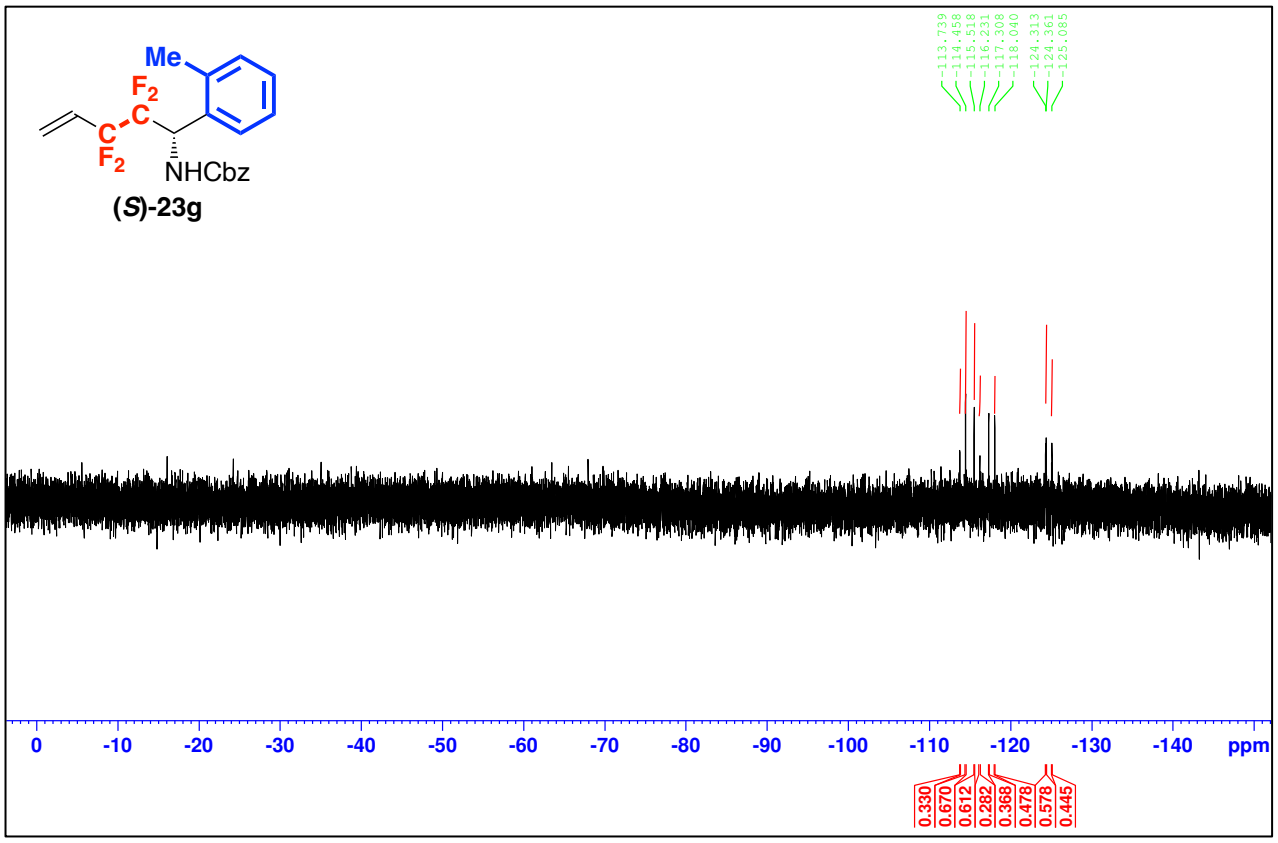
^{1}H NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(2-methylphenylpent-4-en-1-yl)carbamate ((***S***)-23g)



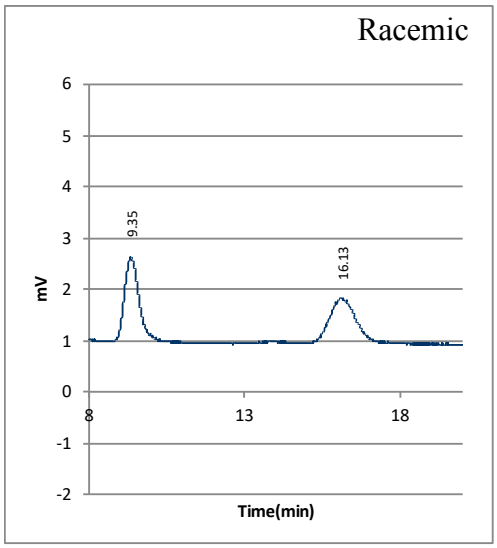
^{13}C NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(2-methylphenylpent-4-en-1-yl)carbamate ((***S***)-23g)



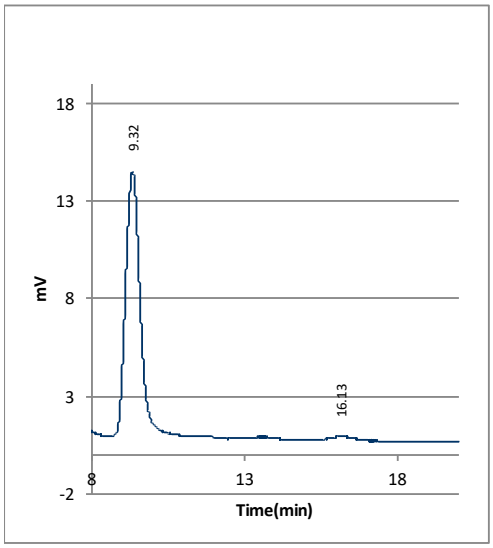
^{19}F NMR Spectrum of (*S*)-benzyl *N*-(2,2,3,3-tetrafluoro-1-(2-methylphenylpent-4-en-1-yl)carbamate (**(*S*)-23g**)



Chromatograph in HPLC for **(*S*)-23g**



No.	Rt	Area(%)
1	9.35	49.913
2	16.13	50.087
		100



No.	Rt	Area(%)
1	9.32	97.056
2	16.13	2.944
		100