Radical allylation of vinyl perfluorocyclic sulfonamides leading to 1,1,2,2,3,3-hexafluorohex-5-ene-1-sulfonamides

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General information

Thin layer chromatography (TLC) was performed on Merck precoated plates (silica gel 60 F254, Art 05554) and visualized by fluorescence quenching under exposure to UV light, or by staining with either $KMn_2O_7/K_2CO_3/NaOH/H_2O$ or $12MoO_3/H_3PO_4/EtOH$. Reaction products were purified by flash chromatography on silica gel. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-ECZ500 (^1H: 500 MHz, $^{13}C\{^1H\}\{^{19}F\}$: 126 MHz) spectrometer, and are referenced to the residual solvent peak of (^1H: 7.26 ppm; $^{13}C\{^1H\}\{^{19}F\}$: 77.00 ppm). Split patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Melting points were measured on a OptiMelt MPA100. High-resolution mass spectra were recorded on a UPLC® ACQUITY UltraPerformance LC TOF-MS : LCT Premier XE or JMS-T100LP mass spectrometer.

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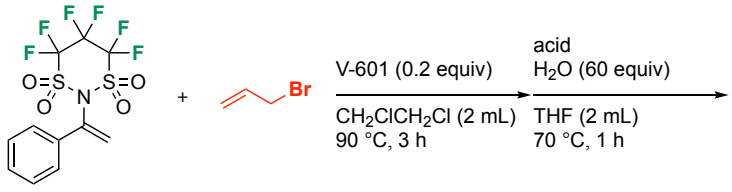
Screening of the acids



1a
0.5 mmol

2a
5 equiv

3a

4a

entry	acid	**3a** (%)[a]	**4a** (%)[a]
1	Nafion	82	88
2	CF_3SO_3H	74	81
3	H_2SO_4	80	84

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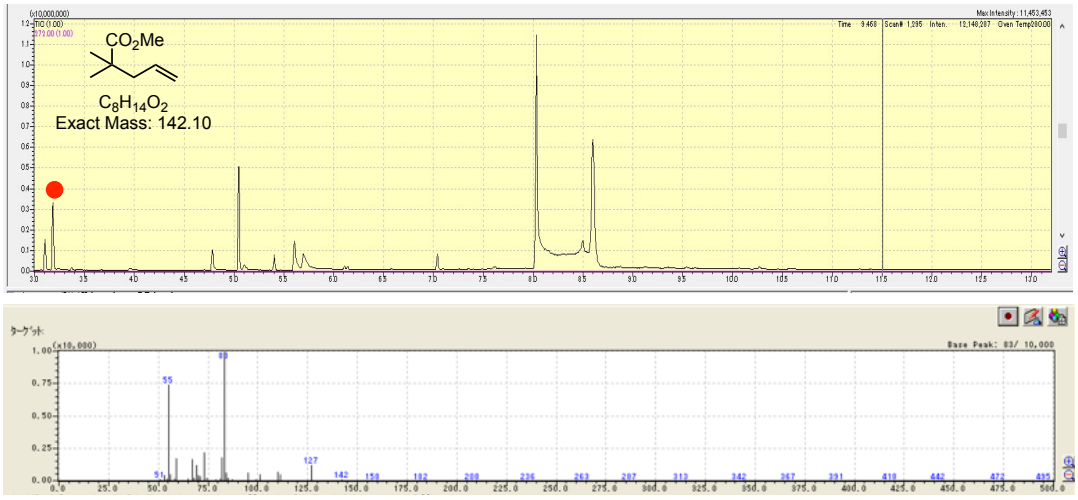
Confirmation of methyl 2,2-dimethylpent-4-enoate (**8**) by GC-MS analysis



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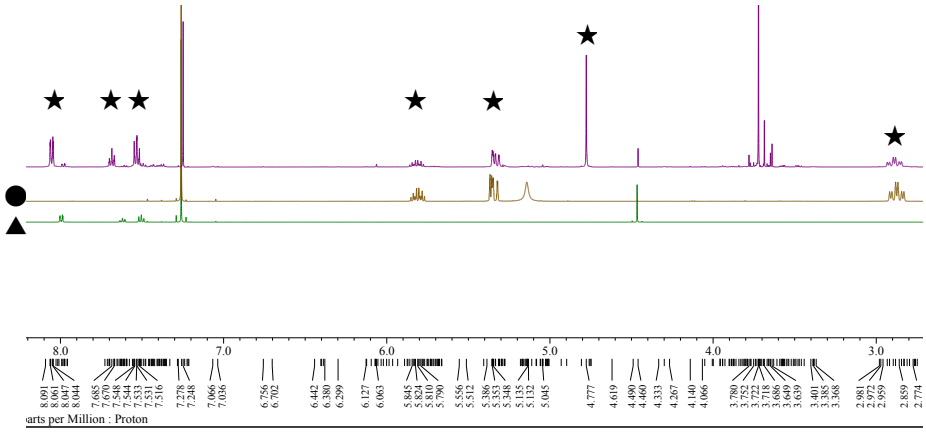
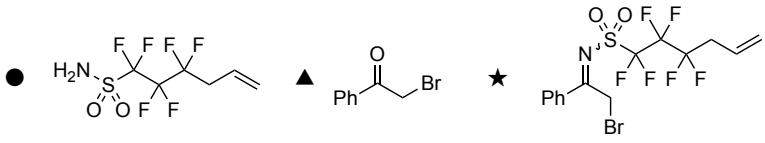
Confirmation of imine **6a** by ^{1}H NMR analysis





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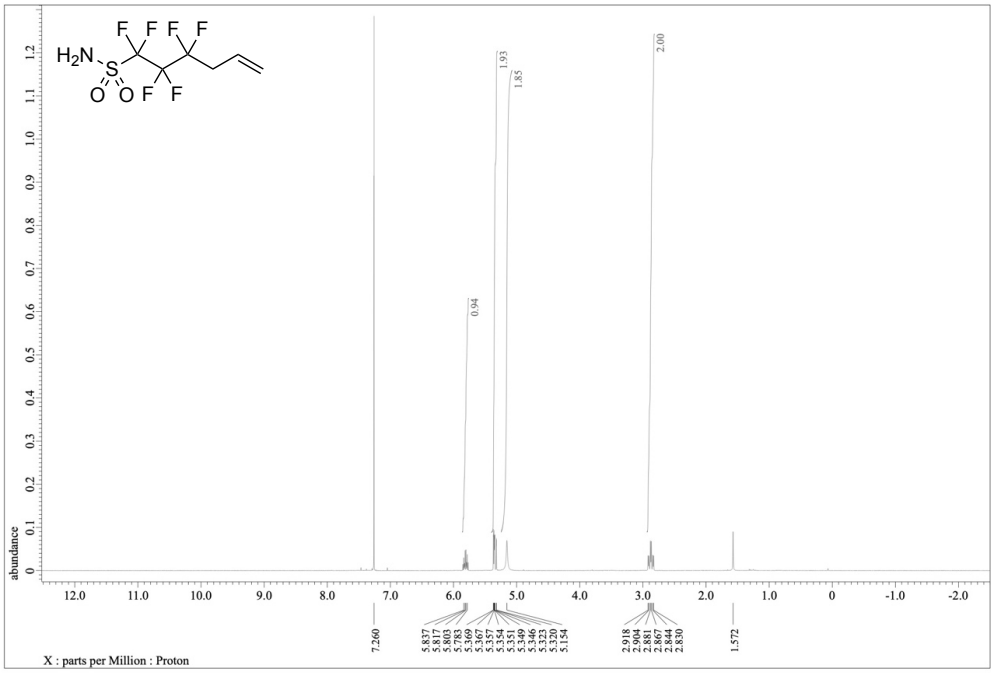
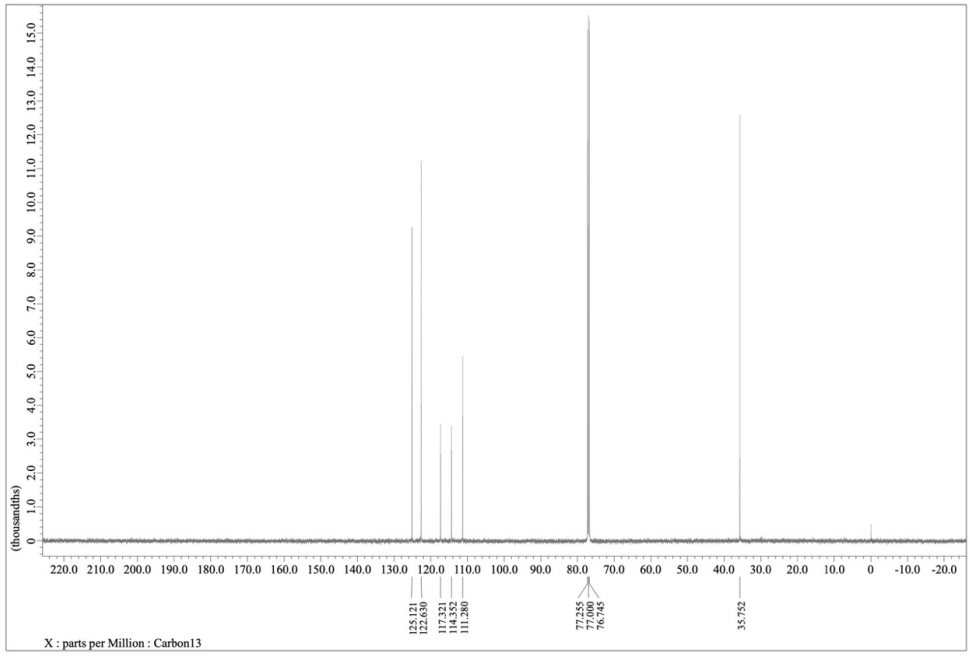
1,1,2,2,3,3-hexafluorohex-5-ene-1-sulfonamide (**3a**)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H}{^{19}F} NMR (126 MHz, $CDCl_3$)



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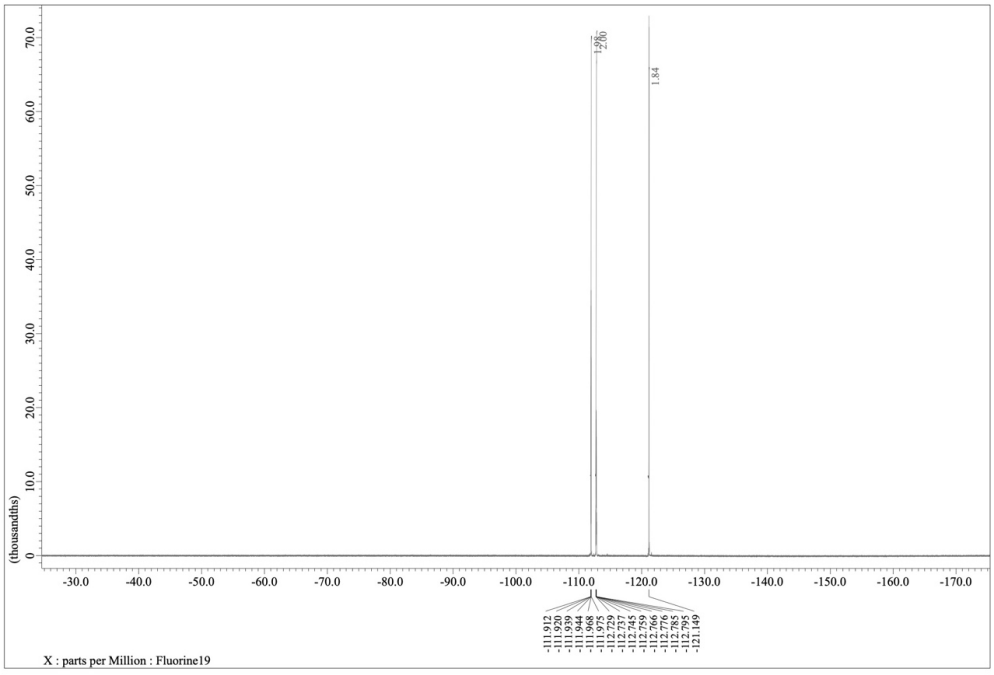
^{19}F NMR (470 MHz, $CDCl_3$)



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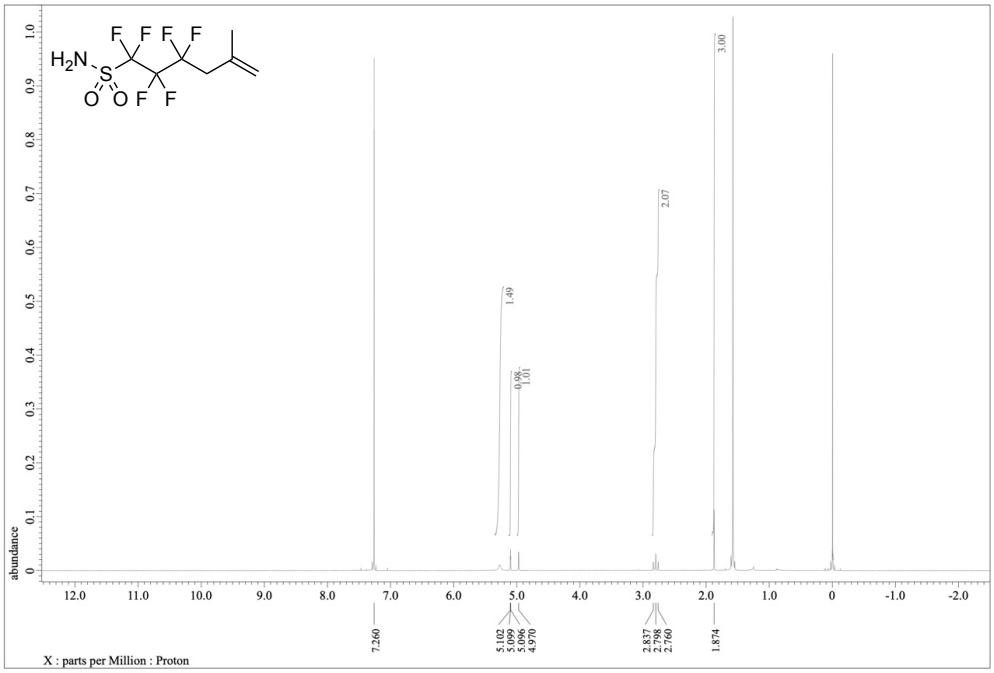
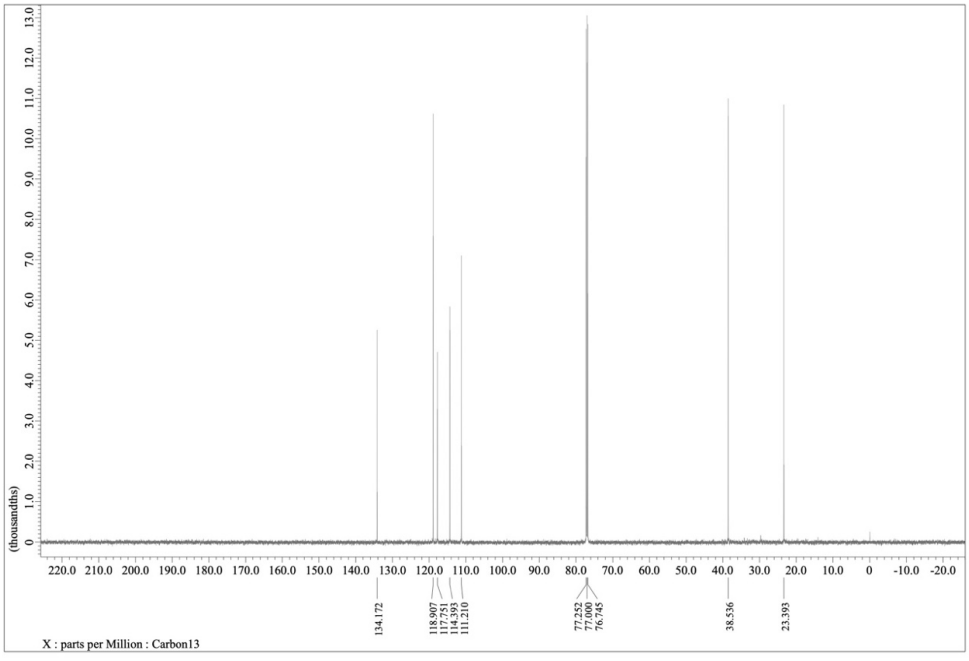
1,1,2,2,3,3-hexafluoro-5-methylhex-5-ene-1-sulfonamide (**3b**)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H}{^{19}F} NMR (126 MHz, $CDCl_3$)



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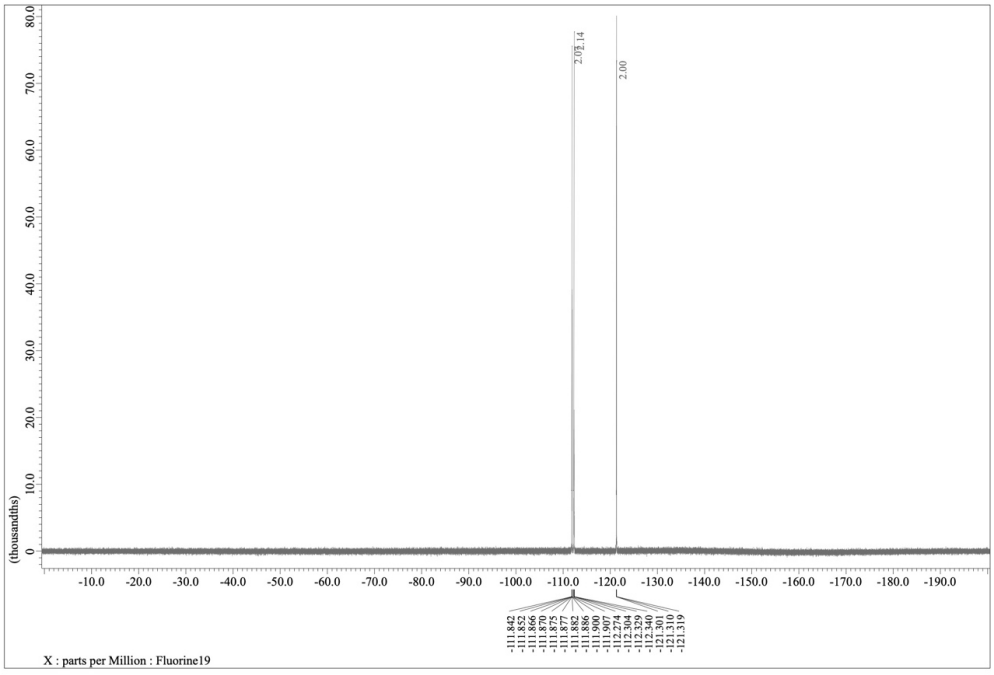

5-bromo-1,1,2,2,3,3-hexafluorohex-5-ene-1-sulfonamide (**3c**)

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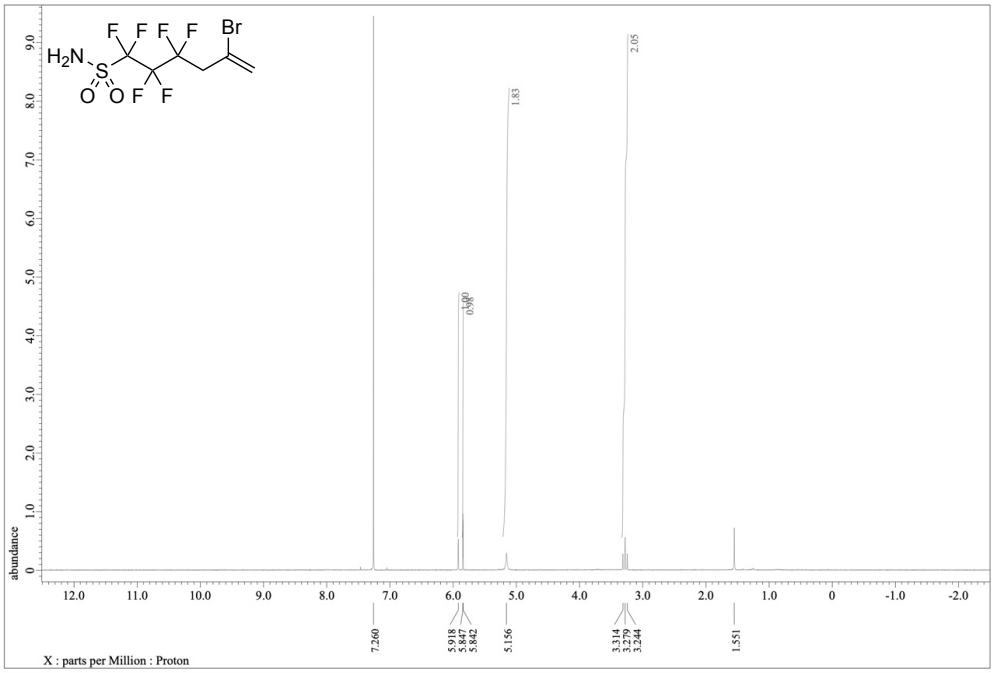
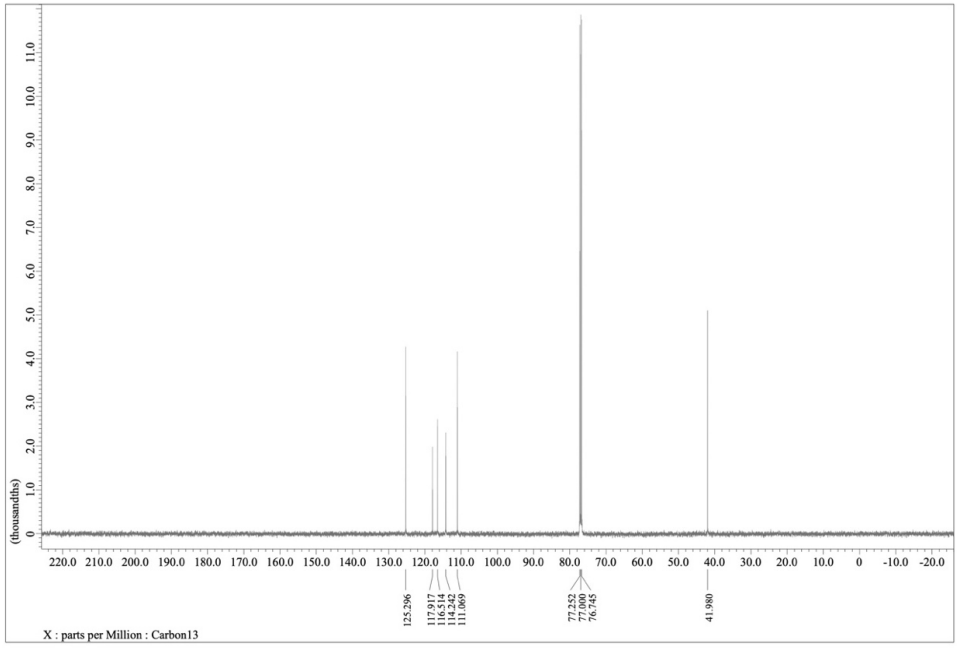
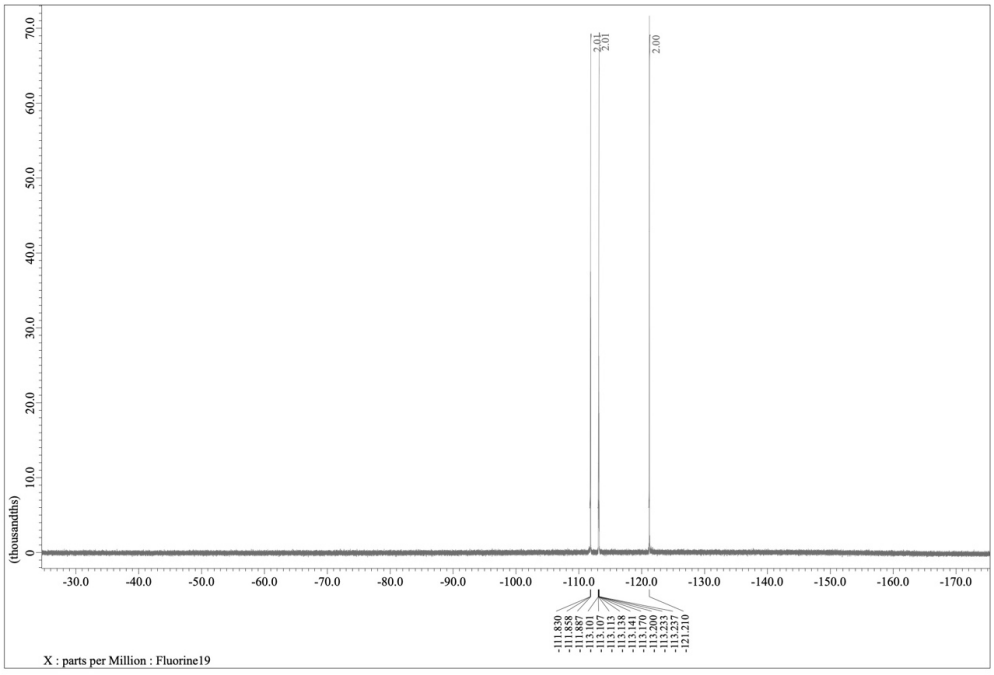


^{13}C{^{1}H}{^{19}F} NMR (126 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$)



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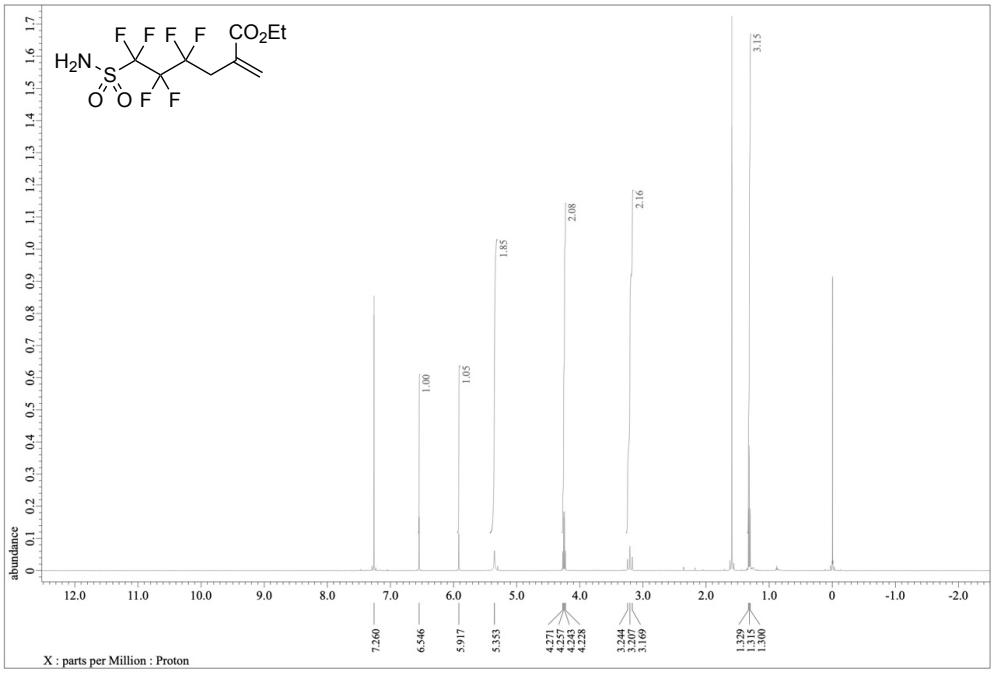
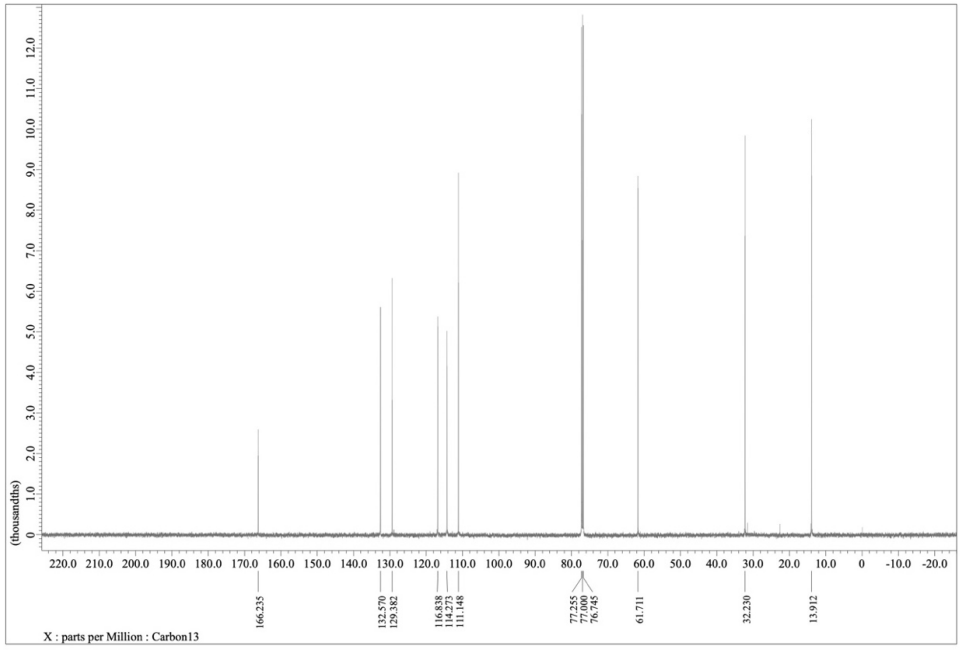
ethyl 4,4,5,5,6,6-hexafluoro-2-methylene-6-sulfamoylhexanoate (**3d**)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H}{^{19}F} NMR (126 MHz, $CDCl_3$)



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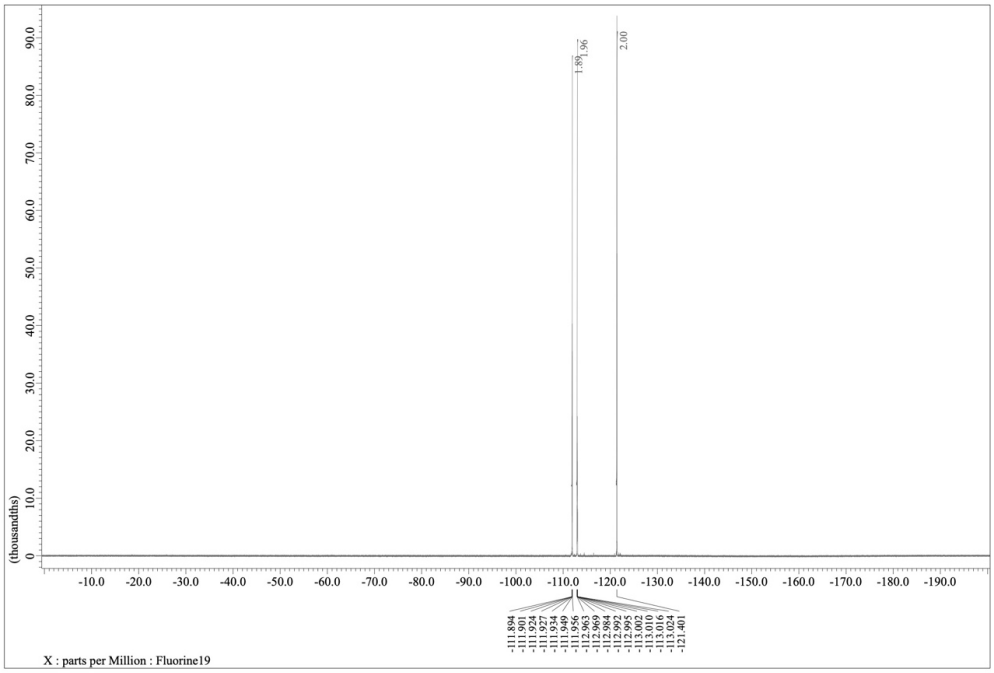
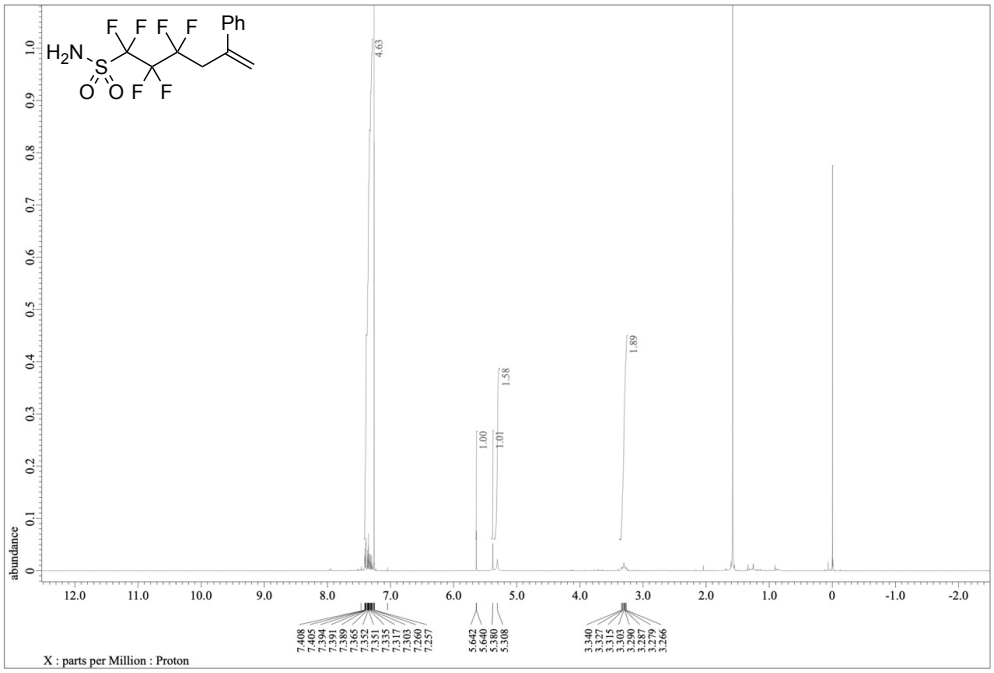
^{19}F NMR (470 MHz, $CDCl_3$)

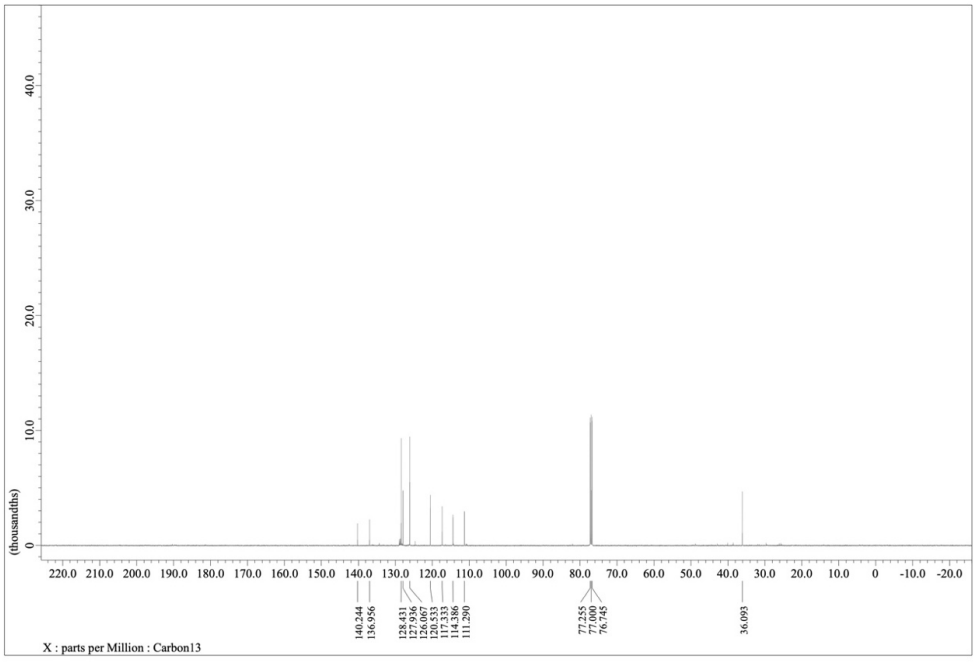


1,1,2,2,3,3-hexafluoro-5-phenylhex-5-ene-1-sulfonamide (**3e**)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H}{^{19}F} NMR (126 MHz, $CDCl_3$)



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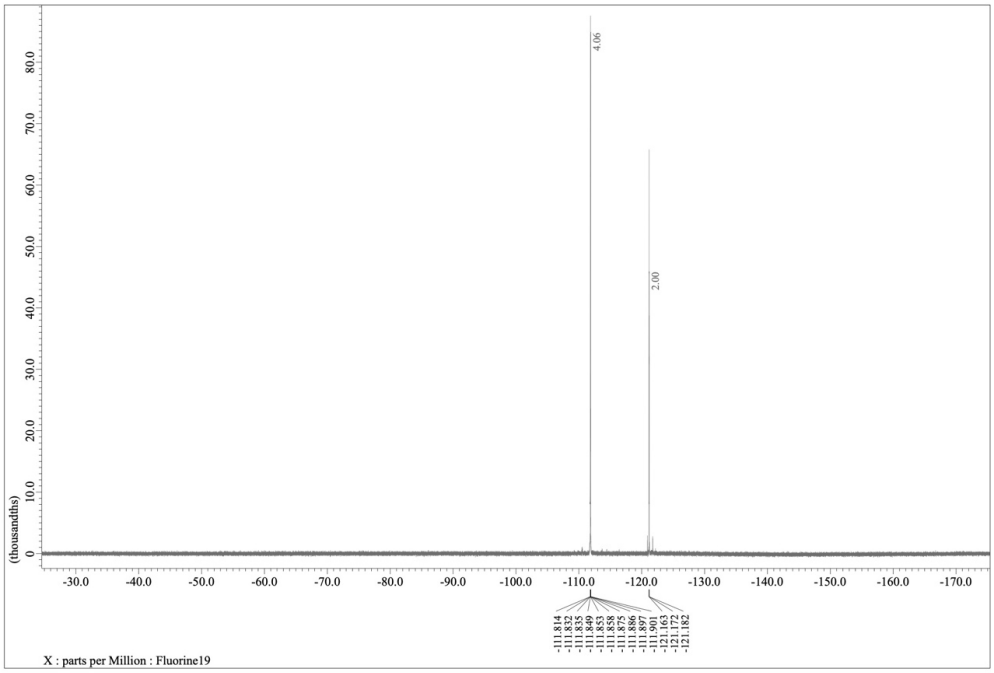

1,1,2,2,3,3,6,6-octafluorohex-5-ene-1-sulfonamide (**3f**)

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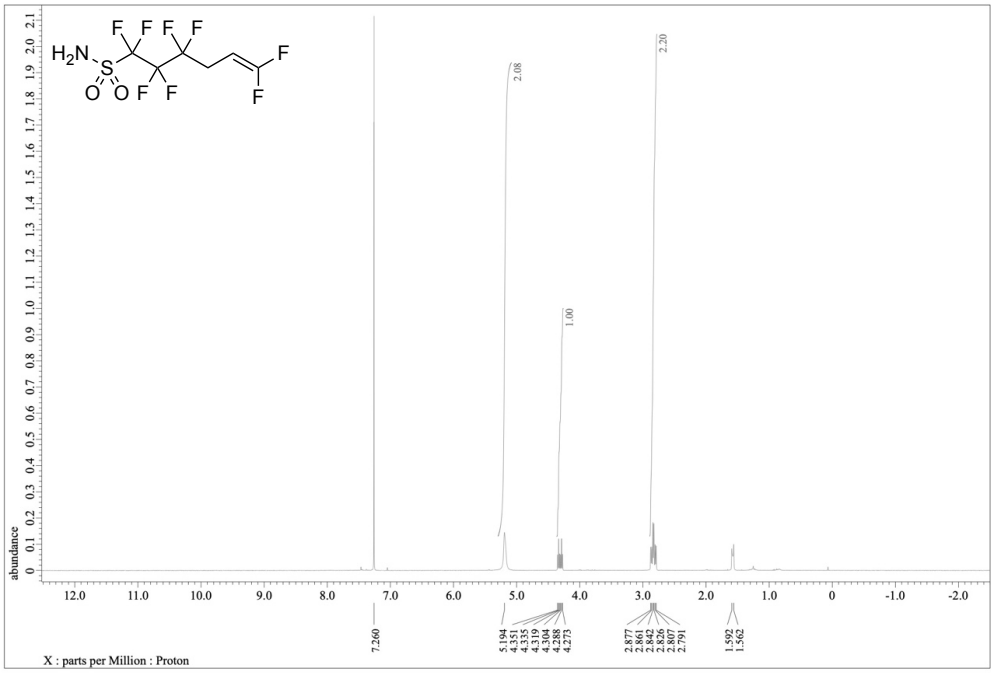
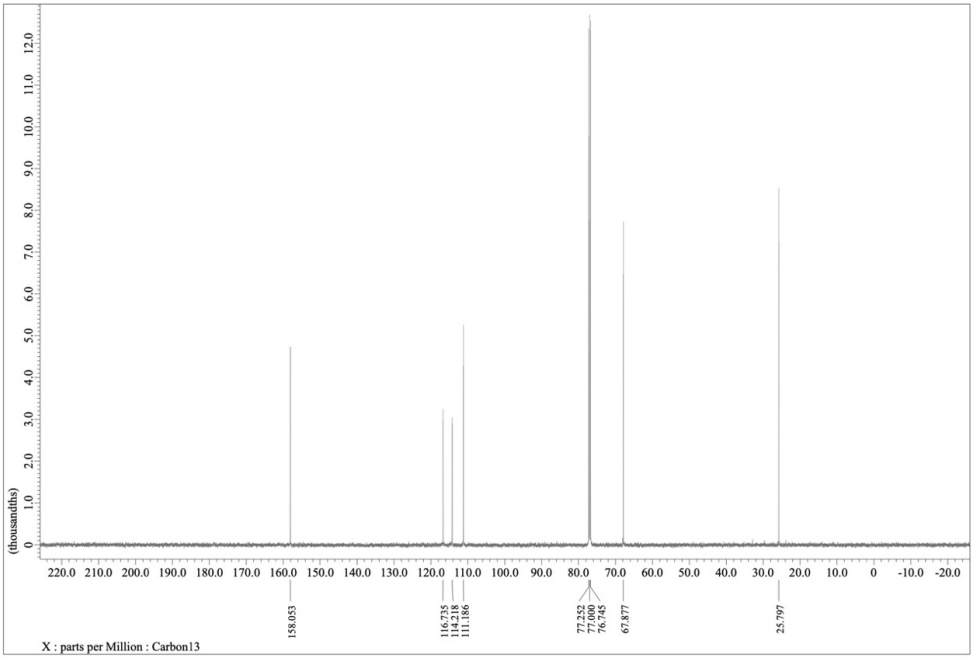


^{13}C{^{1}H}{^{19}F} NMR (126 MHz, $CDCl_3$)



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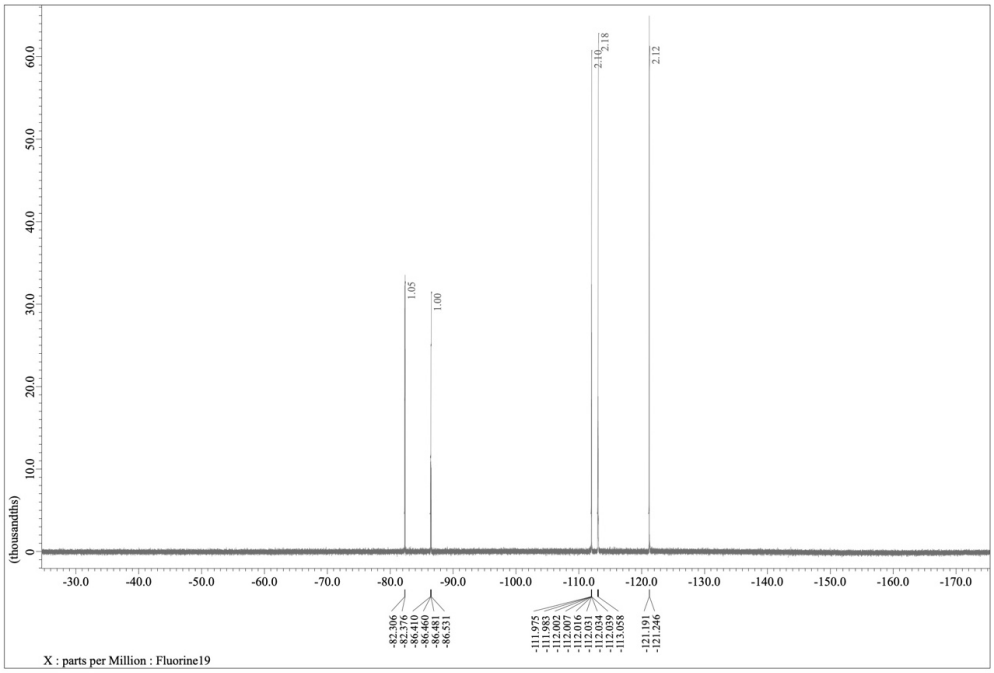
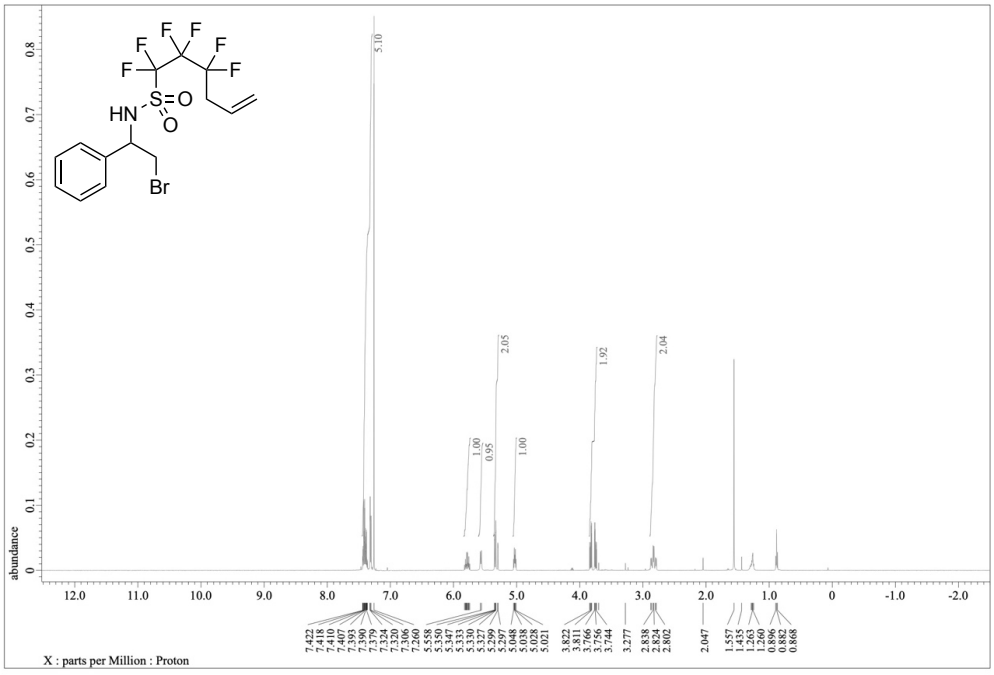


N-(2-bromo-1-phenylethyl)-1,1,2,2,3,3-hexafluorohex-5-ene-1-sulfonamide (**7a**)

^{1}H NMR (500 MHz, $CDCl_3$)



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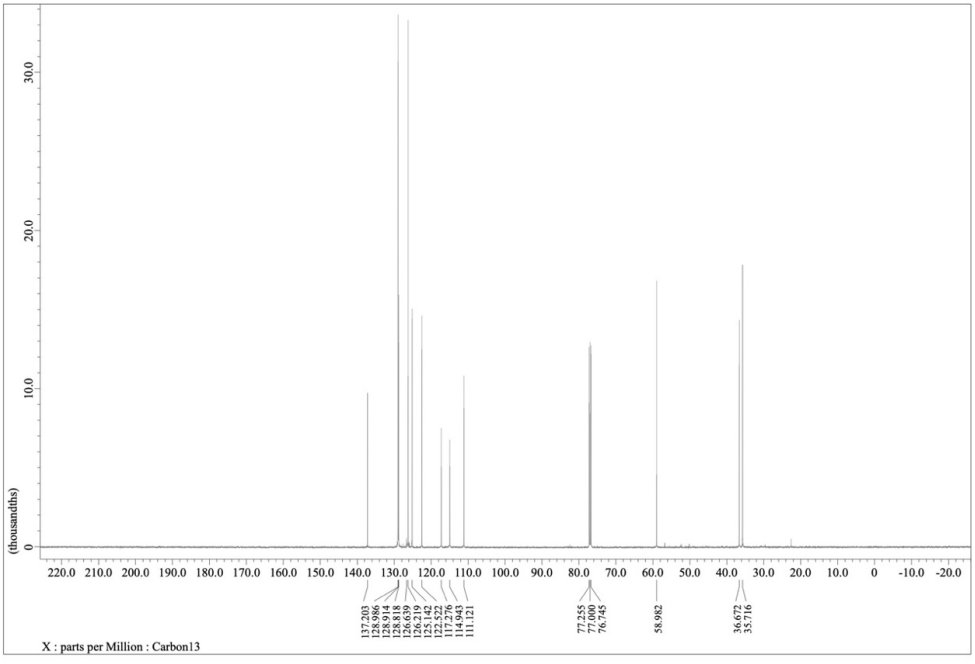

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^{19}F NMR (470 MHz, $CDCl_3$)