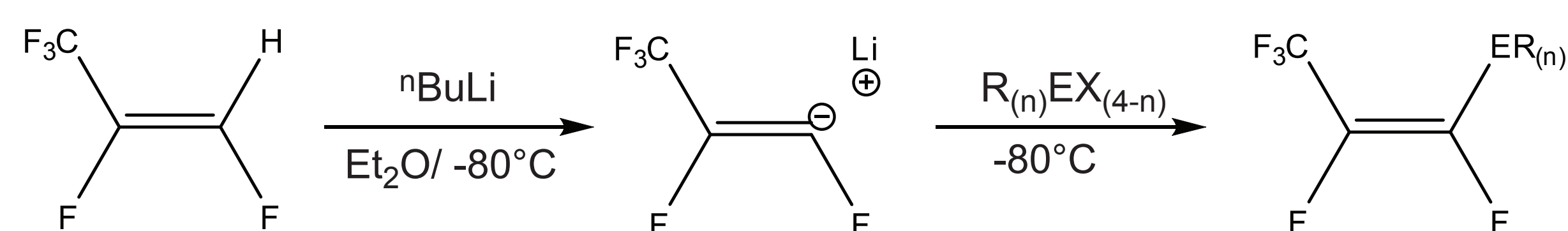


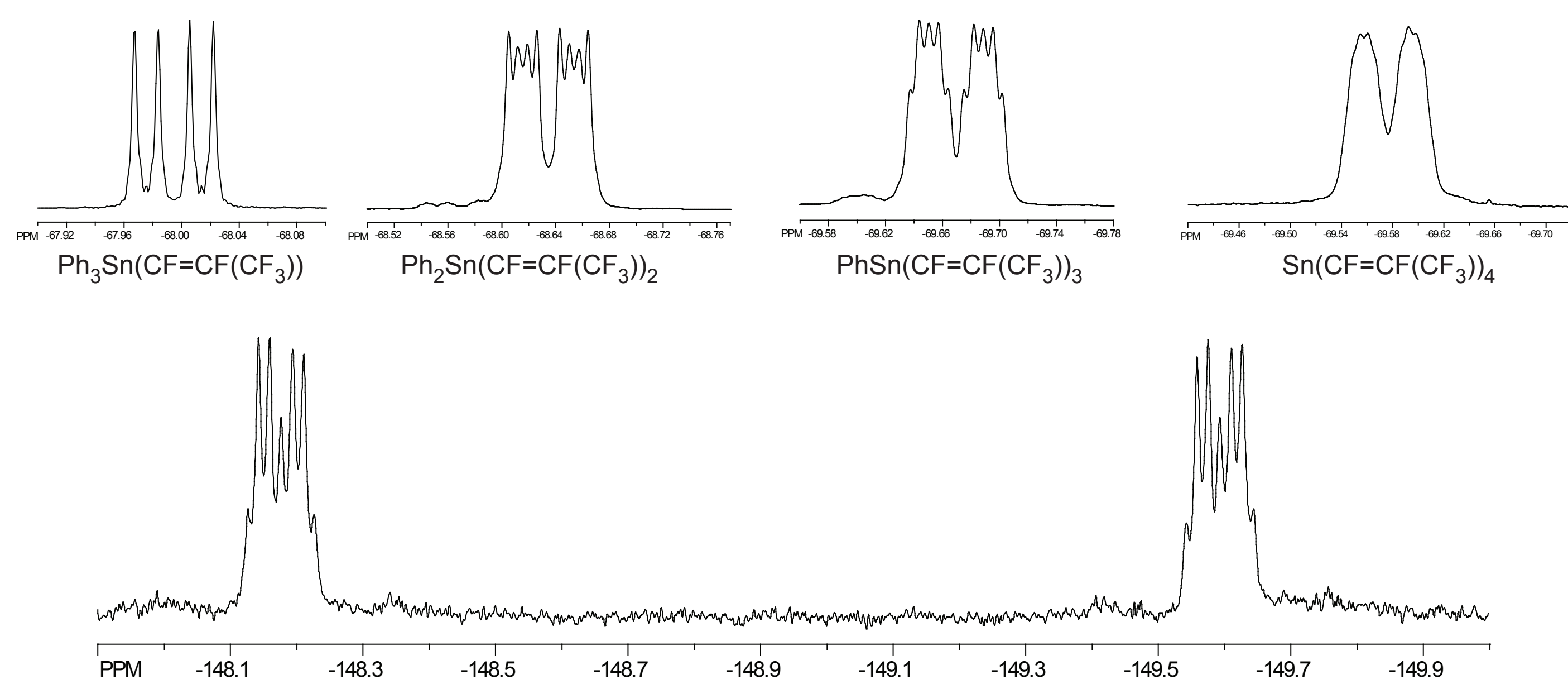
Synthesis of New Compounds Based on (Z)-HFC-1225ye and the use of $\text{Bu}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$ as a Perfluoropropenyl Transfer Reagent.

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Z-perfluoropropenyl lithium ($\text{CF}_3\text{CF}=\text{CFLi}$) can be synthesised by reacting (Z)-HFC-1225ye ($\text{CF}_3\text{CF}=\text{CFH}$) with one equivalent of $^n\text{BuLi}$. The resulting perfluoropropenyl lithium can then be reacted *in situ* with a number of electrophiles as per the scheme below:

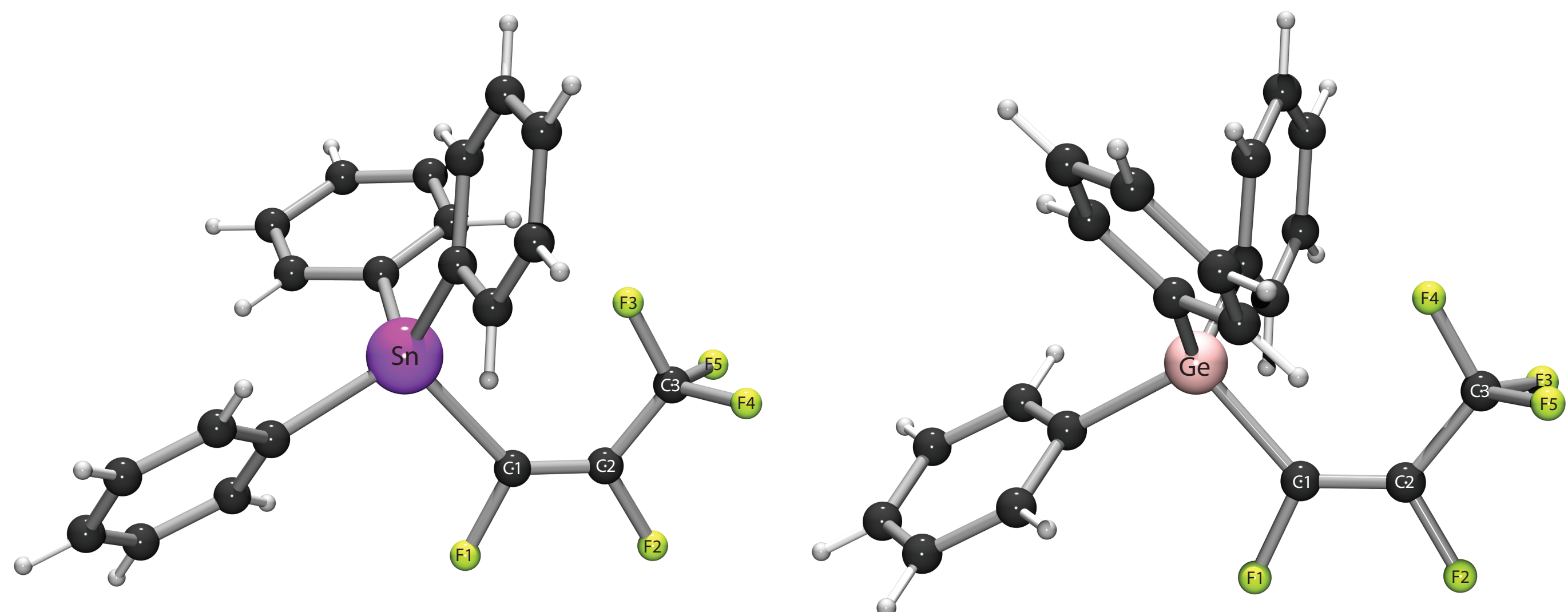


Reactions with Ph_3SnCl , Ph_2SnCl_2 , PhSnCl_3 and SnCl_4 resulted in the expected products in good yield. ^{19}F $\{^1\text{H}\}$ NMR spectra of the CF_3 signal shows coupling to the two other fluorines (see below left) and, on increasing substitution, through-space coupling to a fluorine on the neighbouring $\text{CF}=\text{CF}(\text{CF}_3)$ group(s), resulting in additional doublet, triplet and quartet patterns.



$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $\text{Ph}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$ showed a ddq splitting pattern as expected $\delta_{\text{Sn}} -148.9$ (ddq $J_{\text{SnF}} 211.4, 7.62, 2.50$ Hz)

Similarly Z-perfluoropropenyl lithium was reacted with Bu_3SnCl , Bu_2SnCl_2 , Ph_3GeBr and Ph_3PbCl affording $\text{Bu}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$, $\text{Bu}_2\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))_2$, $\text{Ph}_3\text{Ge}(\text{CF}=\text{CF}(\text{CF}_3))$ and $\text{Ph}_3\text{Pb}(\text{CF}=\text{CF}(\text{CF}_3))$ respectively in good yields. Of these $\text{Bu}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$ has been reported previously by Burton *et al.* using a different method¹.



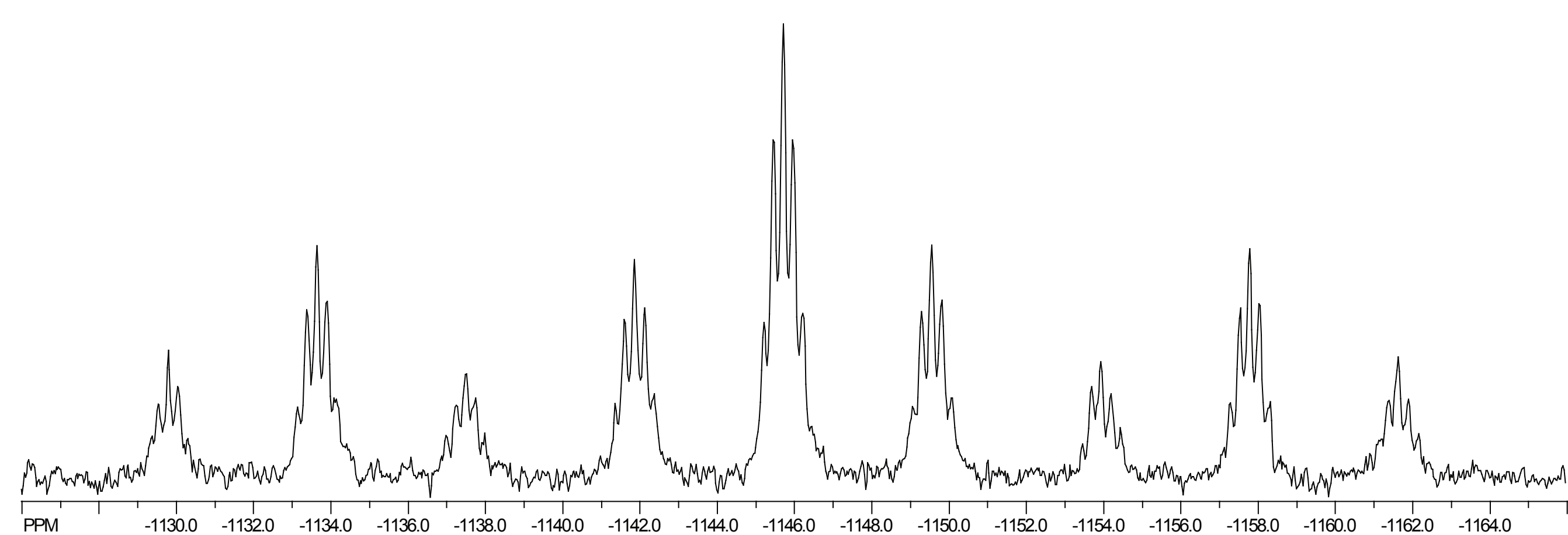
X-Ray crystal structure of $\text{Ph}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$

Selected bond lengths (Å) and bond angles (°): Sn-C1 2.170(13), C1-F1 1.371(14), C1=C2 1.329(17), C2-F2 1.375(19), C2-C3 1.480(19), C3-F3 1.317(17), C3-F4 1.328(17), C3-F5 1.324(17), Sn-C1-C2 132.9, Sn-C1-F1 112.7, F1-C1-C2 115.0, C1-C2-C3 129.3, C1-C2-F1 121.1, F2-C2-C3 109.4.

X-Ray crystal structure of $\text{Ph}_3\text{Ge}(\text{CF}=\text{CF}(\text{CF}_3))$

Selected bond lengths (Å) and bond angles (°): Ge-C1 1.893(5), C1-F1 1.357(6), C1=C2 1.321(8), C2-F2 1.355(7), C2-C3 1.488(8), C3-F3 1.332(7), C3-F4 1.337(8), C3-F5 1.334(6), Ge-C1-C2 132.2, Ge-C1-F1 112.7, F1-C1-C2 115.1, C1-C2-C3 129.0, C1-C2-F2 120.6, F2-C2-C3 110.4.

Z-perfluoropropenyl lithium was also reacted with PhHgCl and HgCl_2 producing $\text{PhHg}(\text{CF}=\text{CF}(\text{CF}_3))$ and $\text{Hg}(\text{CF}=\text{CF}(\text{CF}_3))_2$ respectively in good yields.

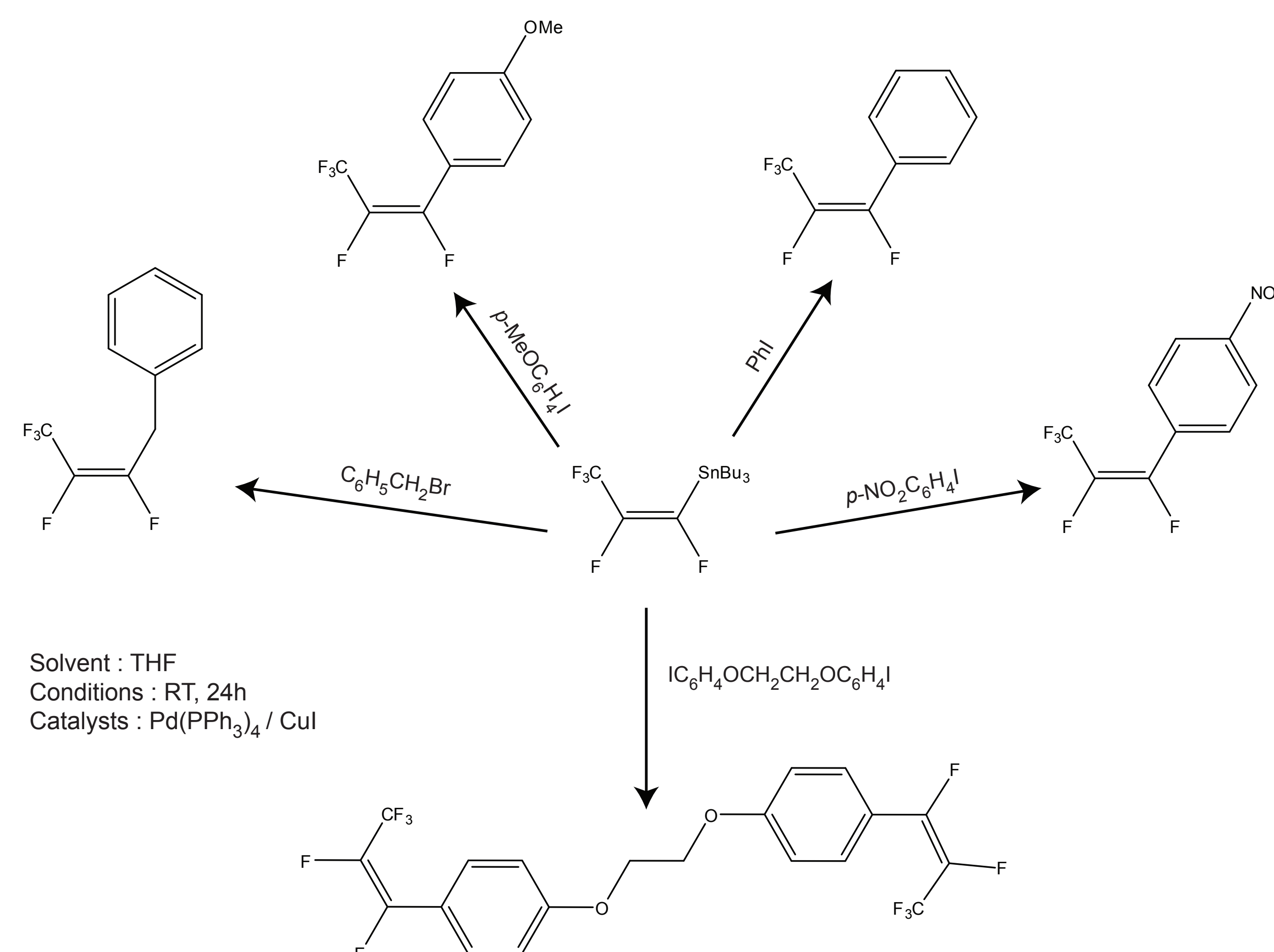


^{199}Hg $\{^1\text{H}\}$ NMR spectrum of $\text{Hg}(\text{CF}=\text{CF}(\text{CF}_3))_2$ showed a ttsept splitting pattern as expected. $\delta_{\text{Hg}} -1145.7$ (ttsept $J_{\text{HgF}} 864.1, 275.9, 17.8$ Hz)

Using a Stille-Liebeskind cross-coupling reaction $\text{Bu}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$ has been successfully used as a reliable source of the perfluoropropenyl group with $\text{Pd}(\text{PPh}_3)_4$ as the catalyst. Copper iodide was added as a co-catalyst due to its ability to increase the rate of reaction². Thus $\text{Bu}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$ reacts with an aryl iodide or benzyl bromide in the presence of the catalyst and co-catalyst at room temperature yielding the expected phenylperfluoropropenes and phenylpentafluorobutene.

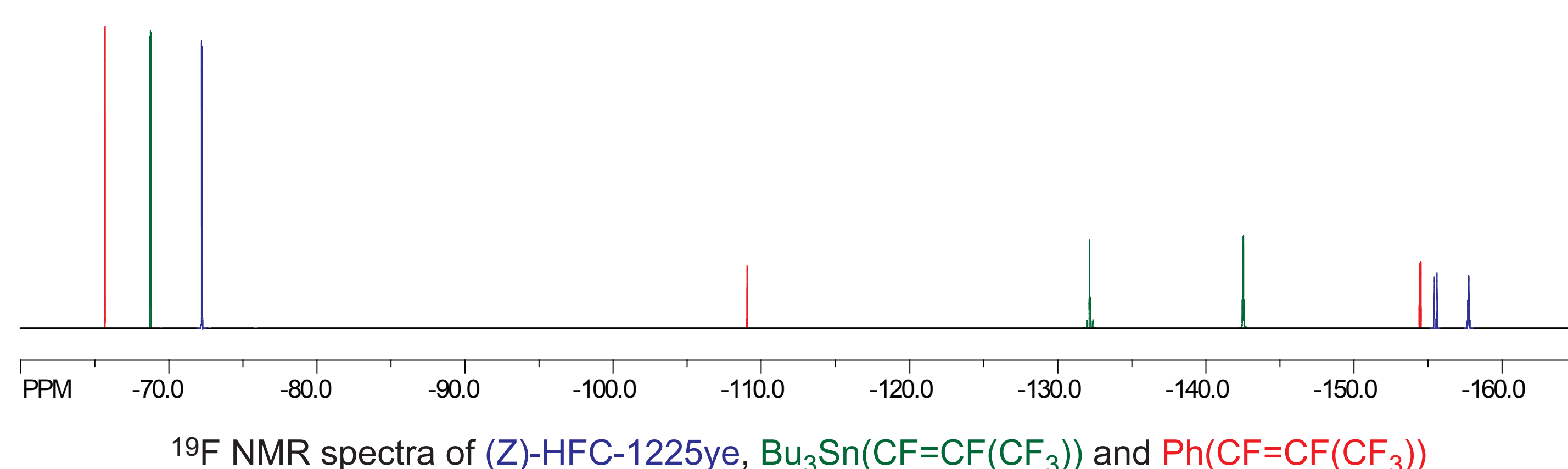
As outlined below reactions using PhI , $p\text{-NO}_2\text{C}_6\text{H}_4\text{I}$, $p\text{-MeOC}_6\text{H}_4\text{I}$, $(\text{IC}_6\text{H}_4\text{OCH}_2)_2$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ yielded the subsequent arylperfluoropropenes $\text{PhCF}=\text{CF}(\text{CF}_3)$, $p\text{-NO}_2\text{C}_6\text{H}_4\text{CF}=\text{CF}(\text{CF}_3)$, $p\text{-MeOC}_6\text{H}_4\text{CF}=\text{CF}(\text{CF}_3)$, $((\text{CF}_3)\text{CF}=\text{CF}(\text{C}_6\text{H}_4\text{OCH}_2))_2$ and phenylpentafluorobutene $\text{PhCH}_2\text{CF}=\text{CF}(\text{CF}_3)$ in good yields.

All were confirmed by ^{19}F NMR spectroscopy and by comparison to previously reported values where possible³, with the $p\text{-NO}_2$ substituted and bis-substituted phenyl ether systems also being characterised using MS.



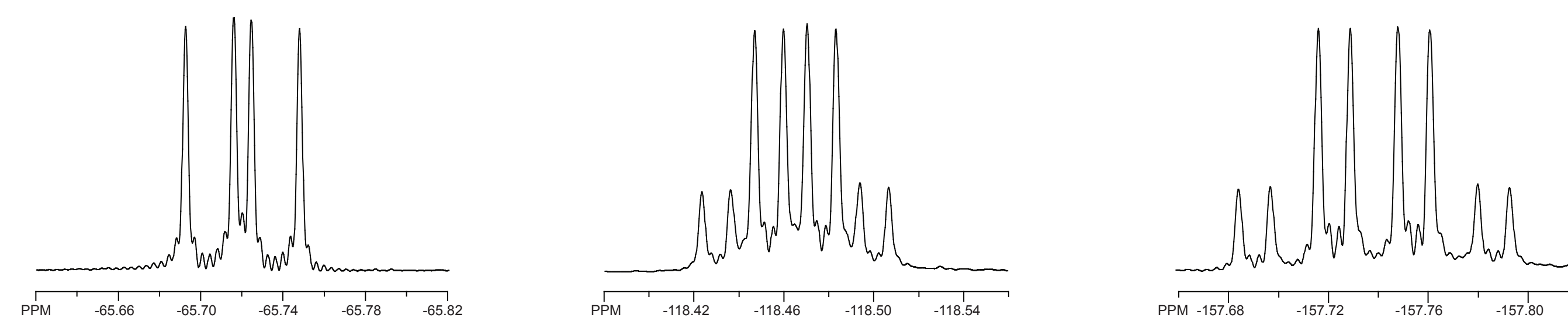
Solvent: THF
Conditions: RT, 24h
Catalysts: $\text{Pd}(\text{PPh}_3)_4$ / CuI

$\text{Ph}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$ was tested as an alternative to $\text{Bu}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$ as a source of the perfluoropropenyl group. The reaction did proceed but with a much lower conversion rate; 10% for $\text{Ph}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$ opposed to >95% for $\text{Bu}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$.



^{19}F NMR spectra of (Z)-HFC-1225ye, $\text{Bu}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$ and $\text{Ph}(\text{CF}=\text{CF}(\text{CF}_3))$

The cross-coupling reaction progression can be tracked by the use of ^{19}F NMR spectroscopy due to the large changes in chemical shift between starting materials and desired products



$^{19}\text{F}\{^1\text{H}\}$ NMR Spectra of $\text{PhCH}_2\text{CF}=\text{CF}(\text{CF}_3)$. $\delta_{\text{F}} -65.7$ (dd $J_{\text{FF}} 12.1, 8.8$ Hz $-\text{CF}=\text{CF}(\text{CF}_3)$), -118.5 (qd $J_{\text{FF}} 8.8, 4.8$ Hz $-\text{CF}=\text{CF}(\text{CF}_3)$), -157.7 (qd $J_{\text{FF}} 12.1, 4.8$ Hz $-\text{CF}=\text{CF}(\text{CF}_3)$).

(Z)-HFC-1225-ye has been shown to be a convenient starting material for the generation of main group perfluoropropenyl systems. $\text{Bu}_3\text{Sn}(\text{CF}=\text{CF}(\text{CF}_3))$ can be used as a source of the perfluoropropenyl group and will transfer Z-($\text{CF}=\text{CF}(\text{CF}_3)$) via a cross-coupling reaction into a variety of activated and deactivated aromatic systems including $p\text{-MeOC}_6\text{H}_4\text{I}$ and $p\text{-NO}_2\text{C}_6\text{H}_4\text{I}$