



## Supporting Information

for

### **Asymmetric synthesis of fluorinated derivatives of aromatic and $\gamma$ -branched amino acids via a chiral Ni(II) complex**

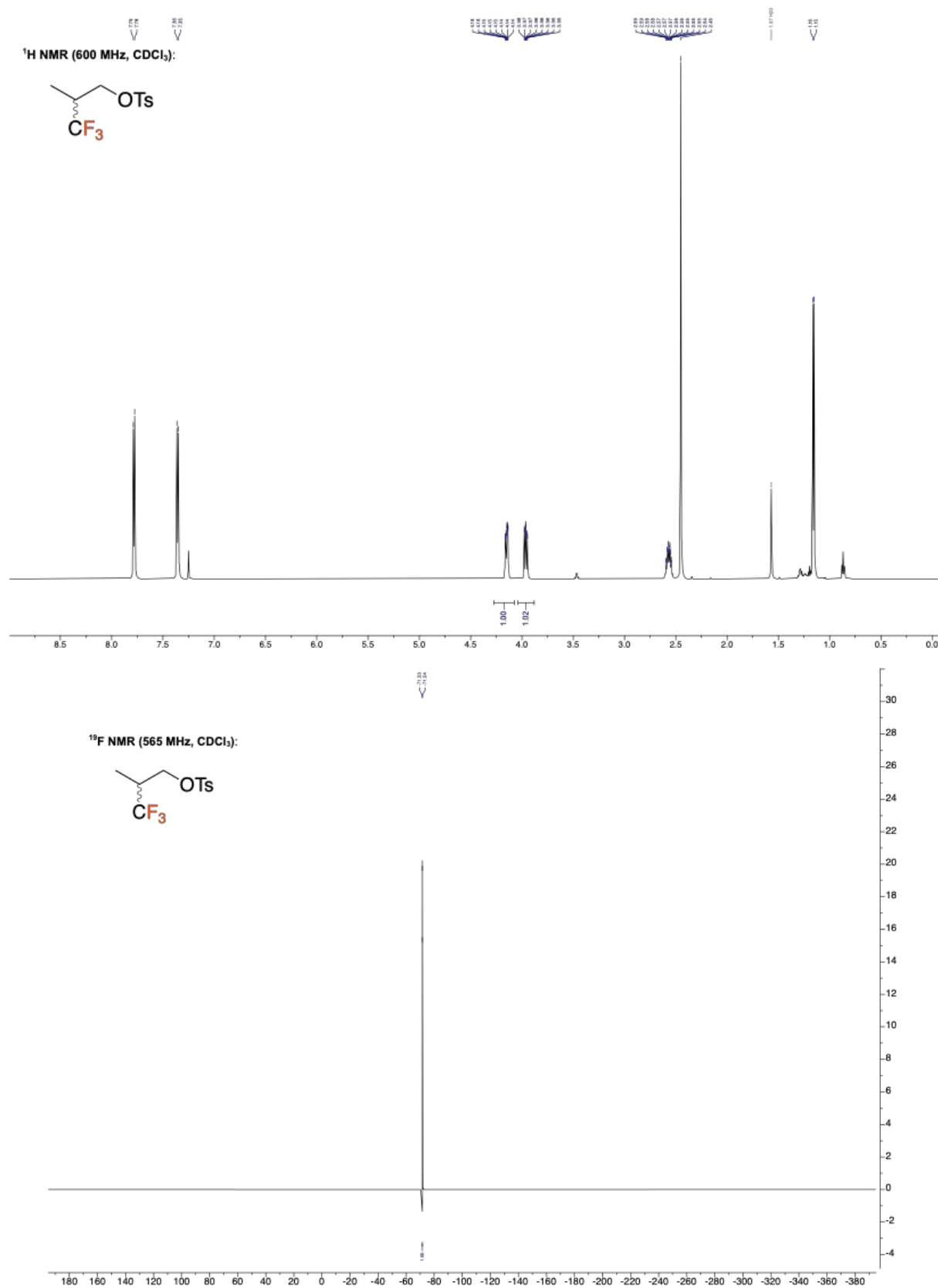
Maurizio Iannuzzi, Thomas Hohmann, Michael Dyrks, Kilian Haoues,  
Katarzyna Salamon-Krokosz and Beate Kokschi

*Beilstein J. Org. Chem.* **2025**, 21, 659–669. doi:10.3762/bjoc.21.52

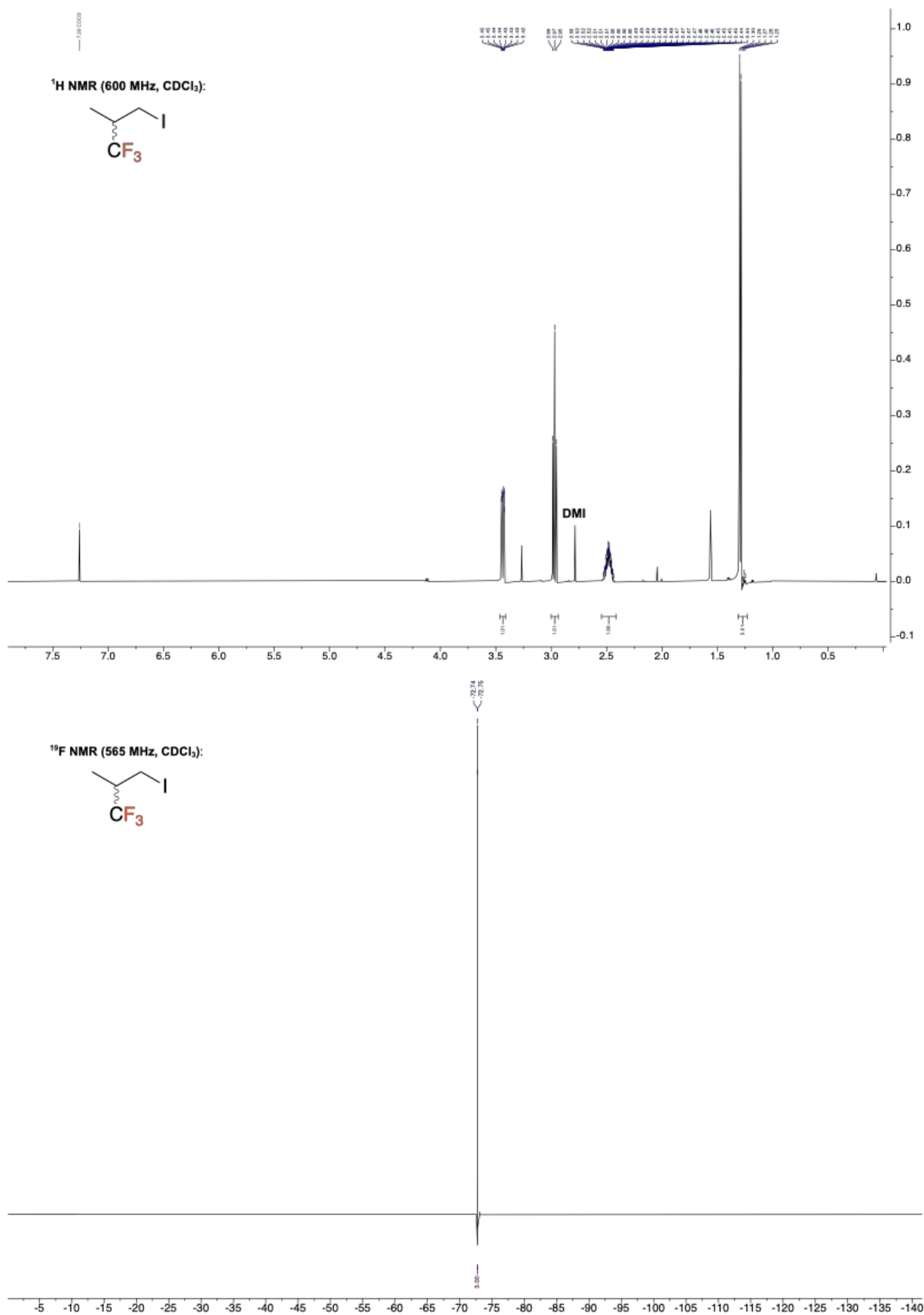
### **NMR spectra and HPLC chromatograms**

## NMR spectra and HPLC chromatograms

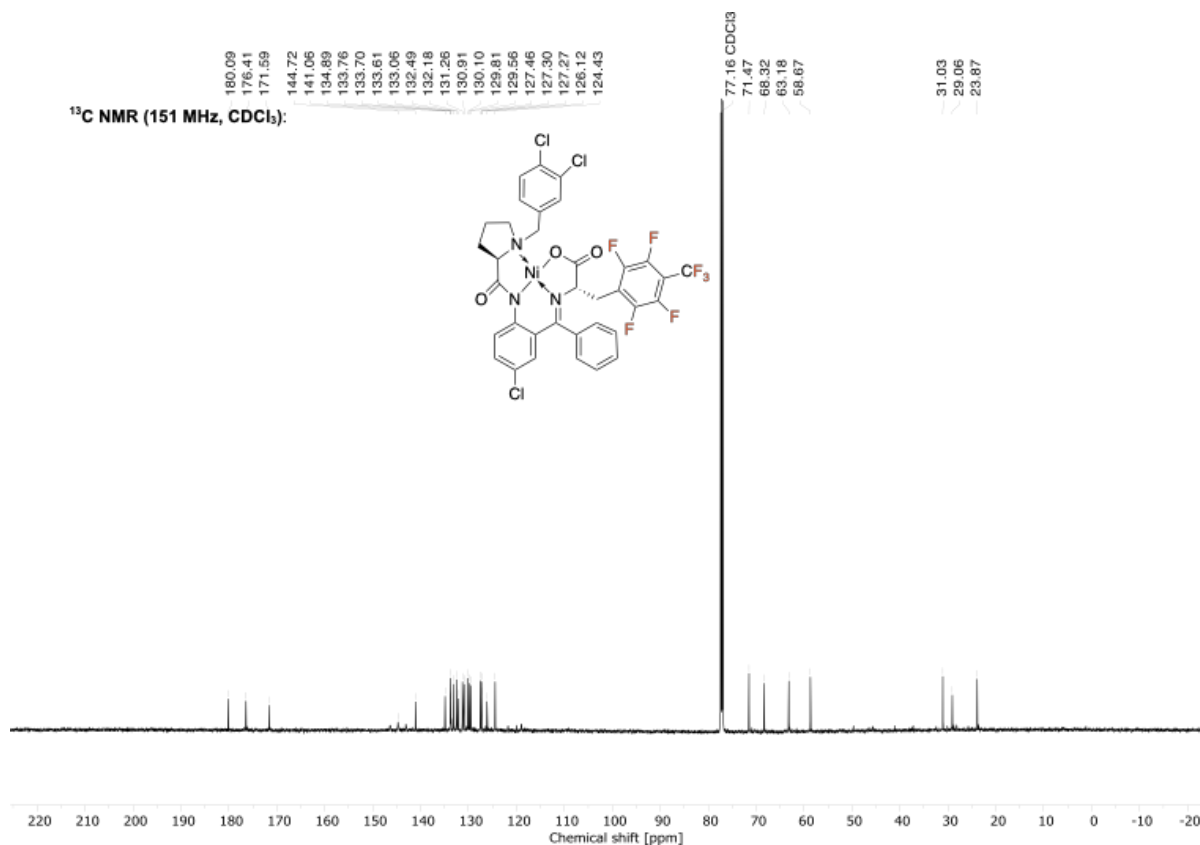
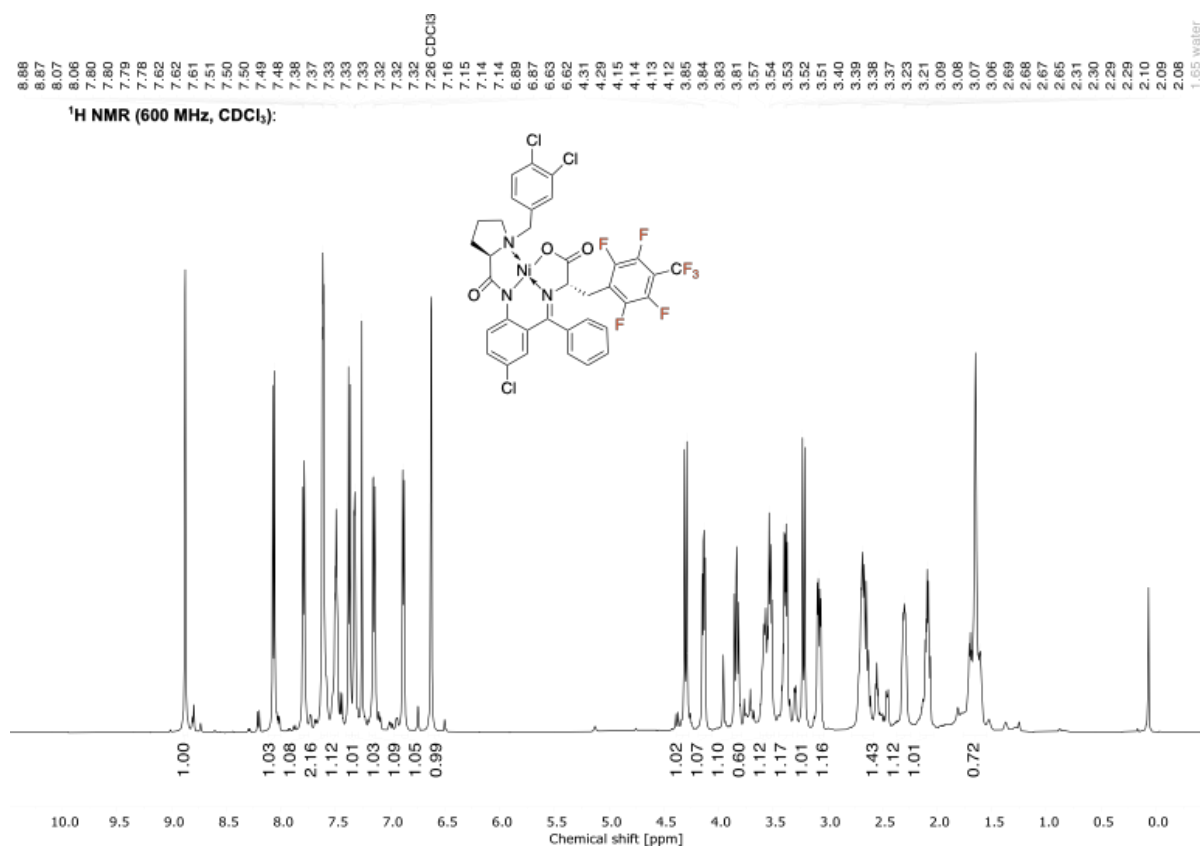
### 3,3,3-Trifluoro-2-methylpropyl 4-methylbenzene-1-sulfonate (**9**)



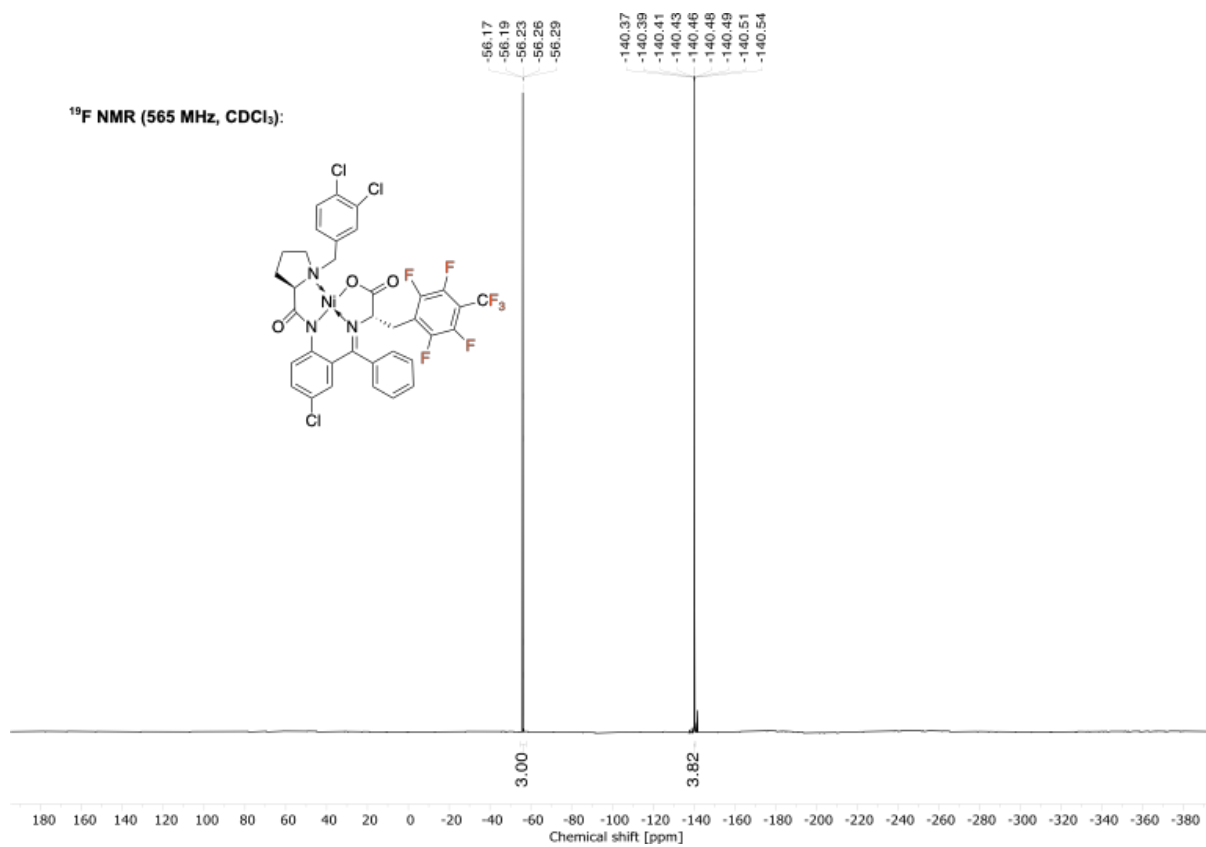
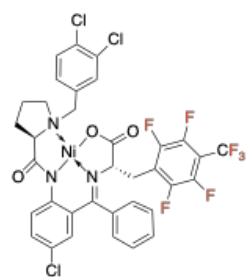
1,1,1-Trifluoro-3-iodo-2-methylpropane (**10**)



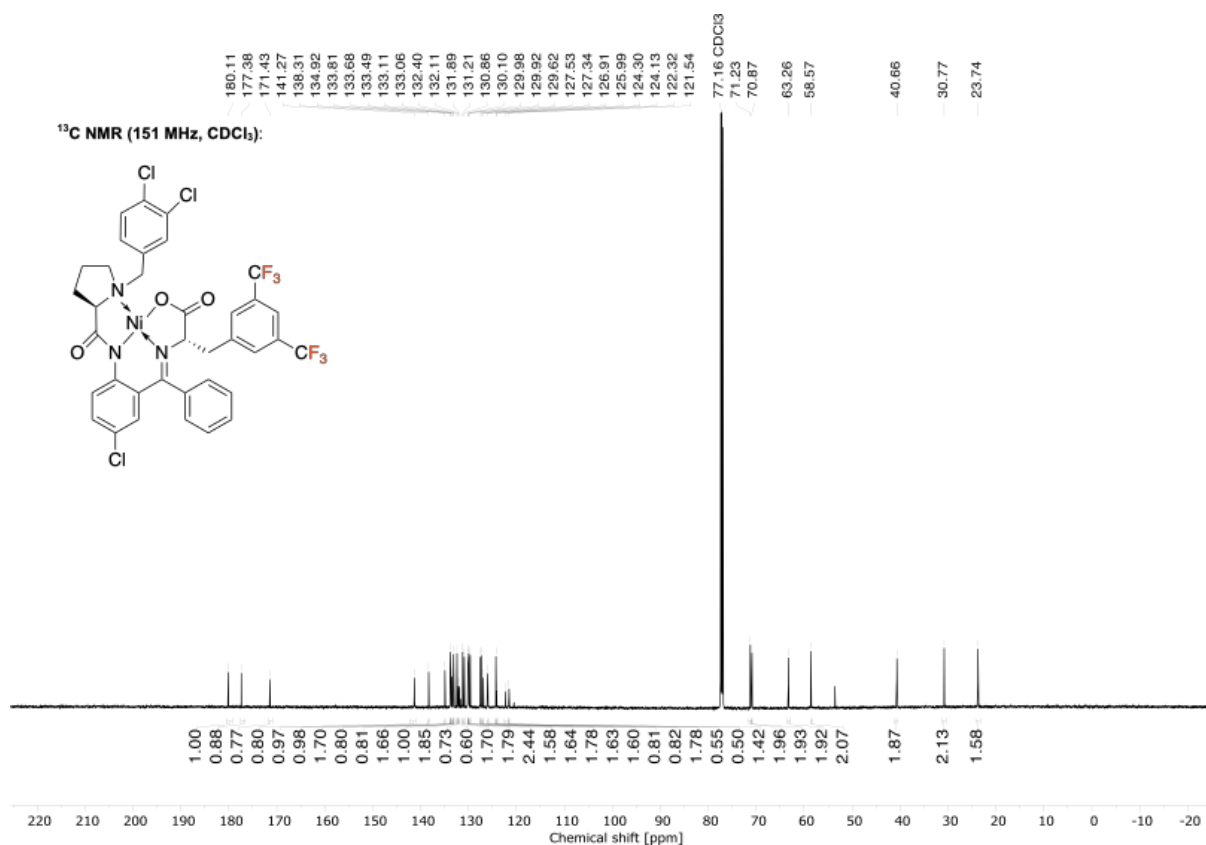
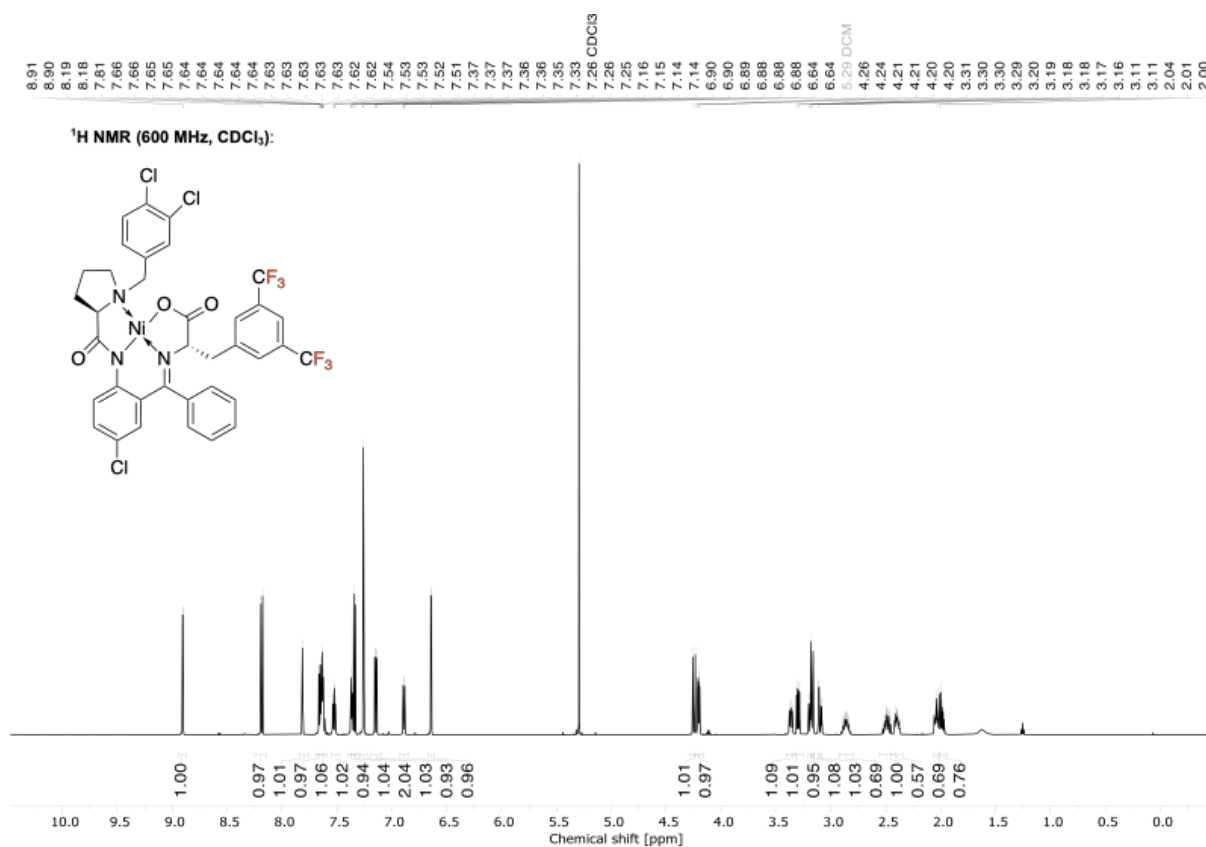
*Ni(II)*-Schiff base complex of [2.3.5.6*F*]TfMePhe **6**

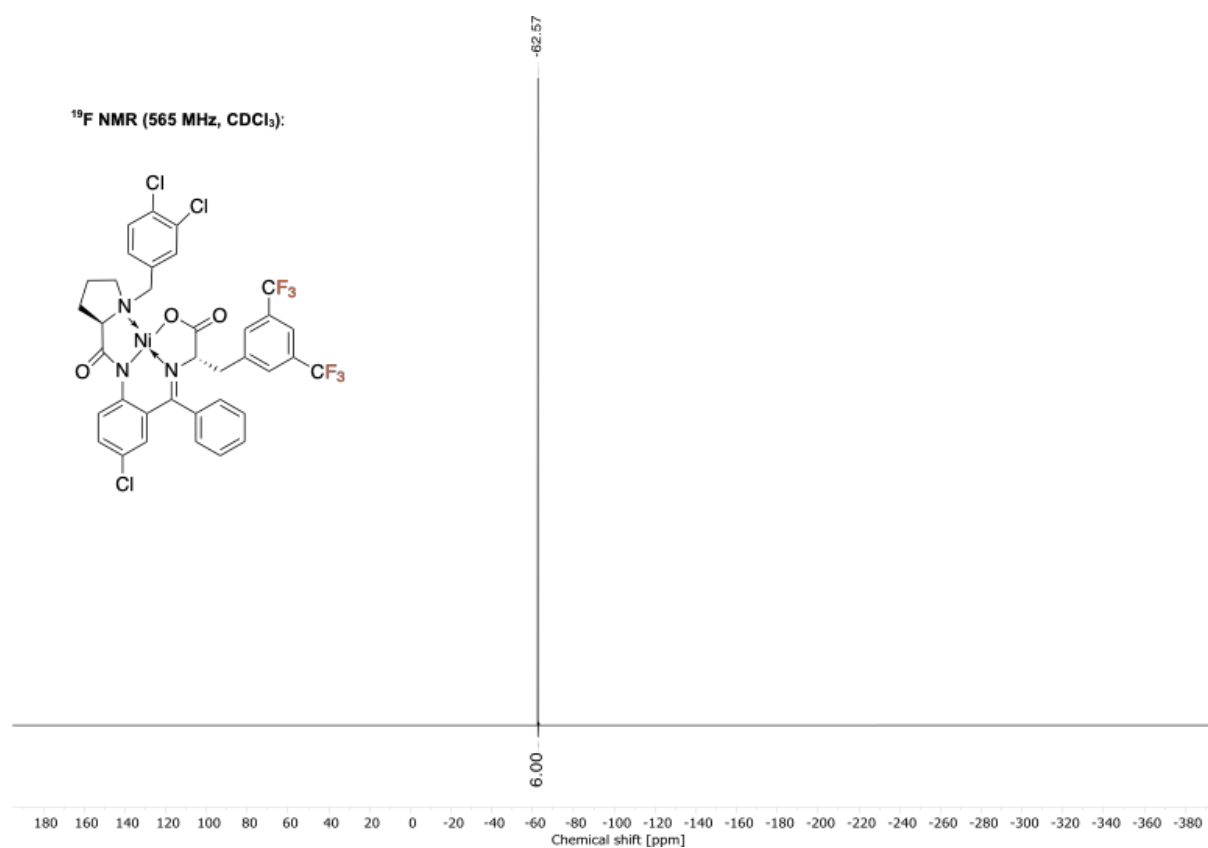


**<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):**

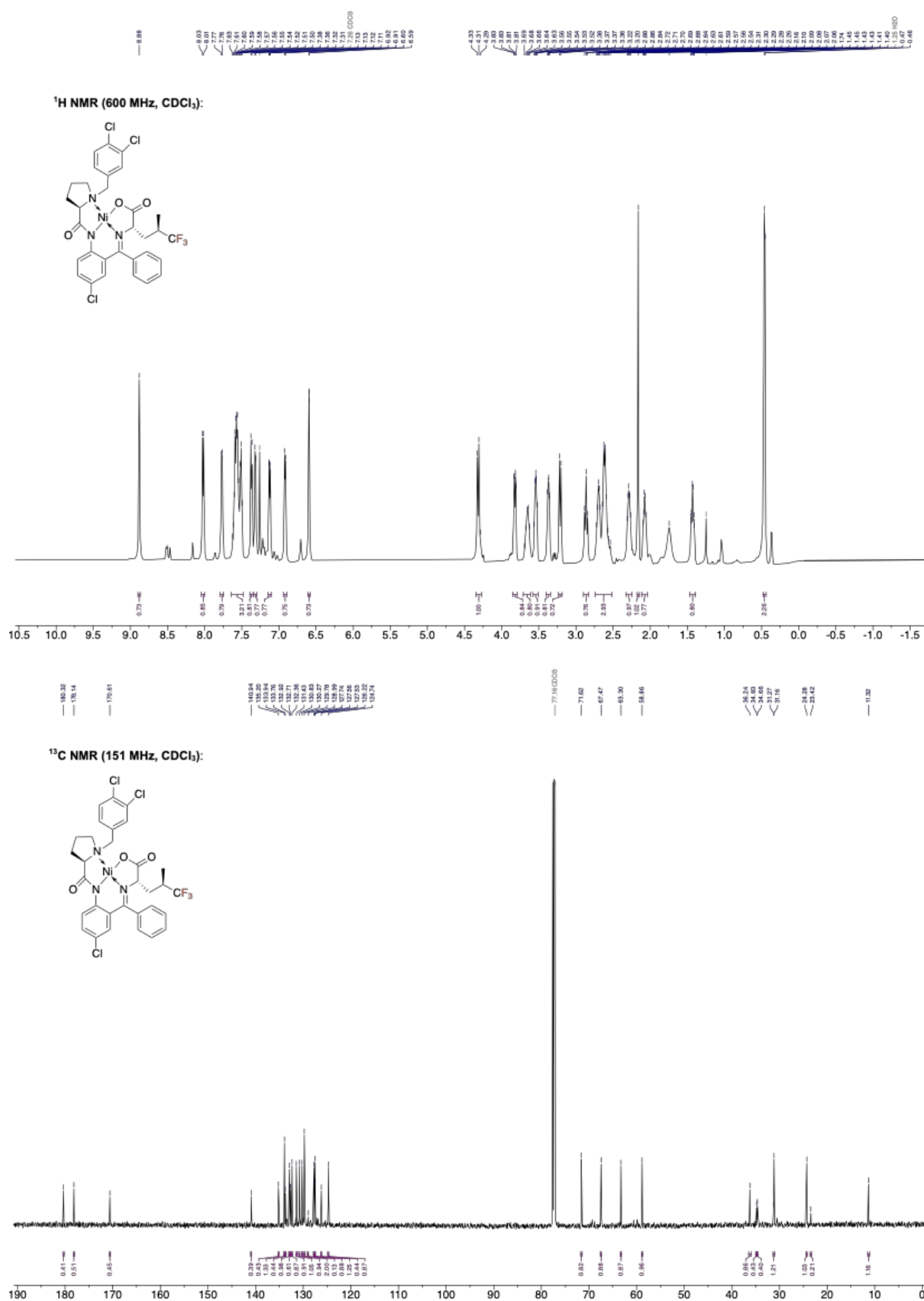


*Ni(II)*-Schiff base complex of bisTfMePhe **7**

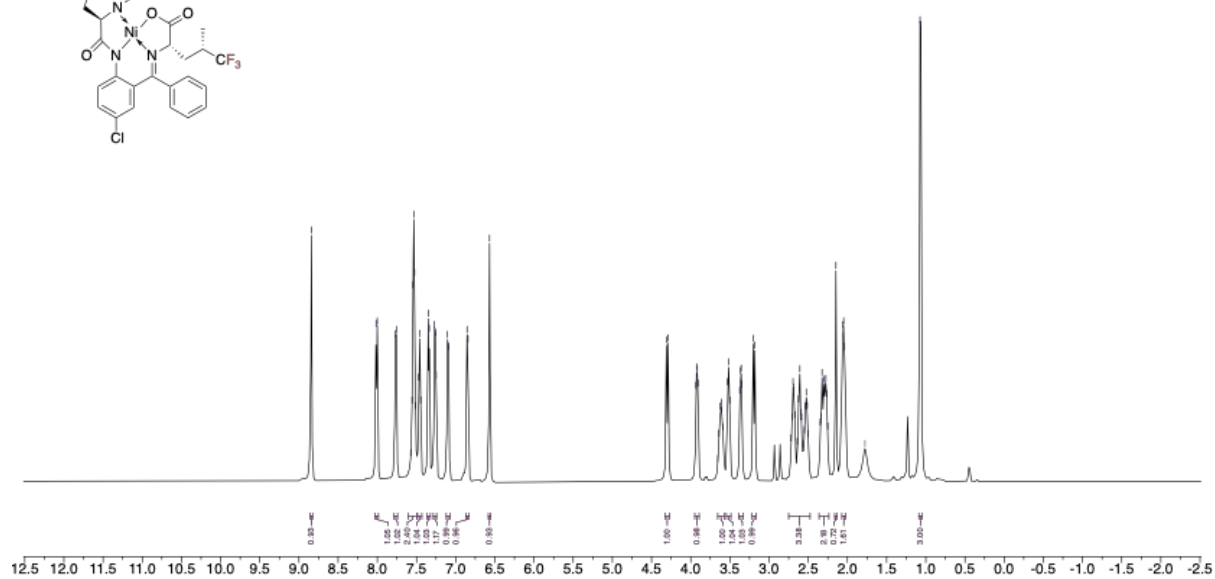
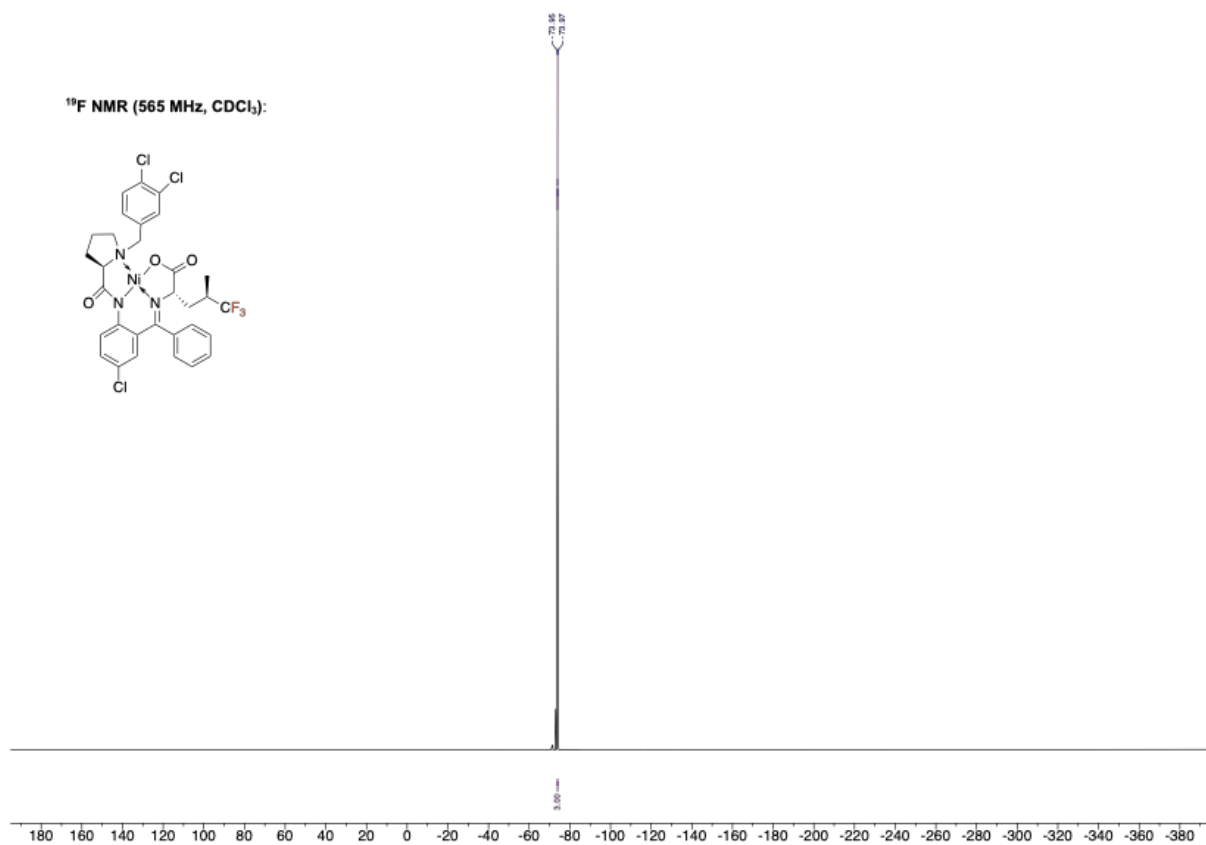


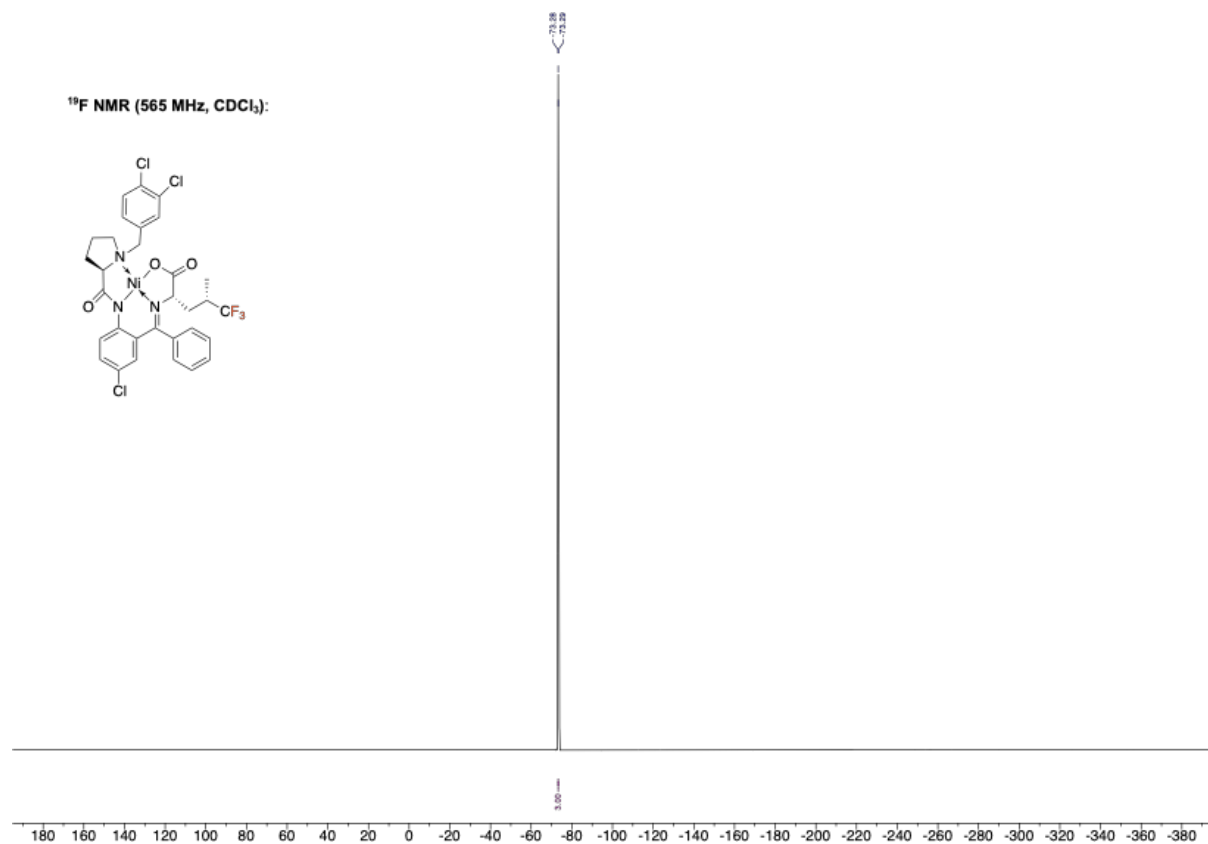


*Ni(II)*-Schiff base complexes of (2*S*,4*R*)-TfLeu **11a**, (2*S*,4*S*)-TfLeu **11b**

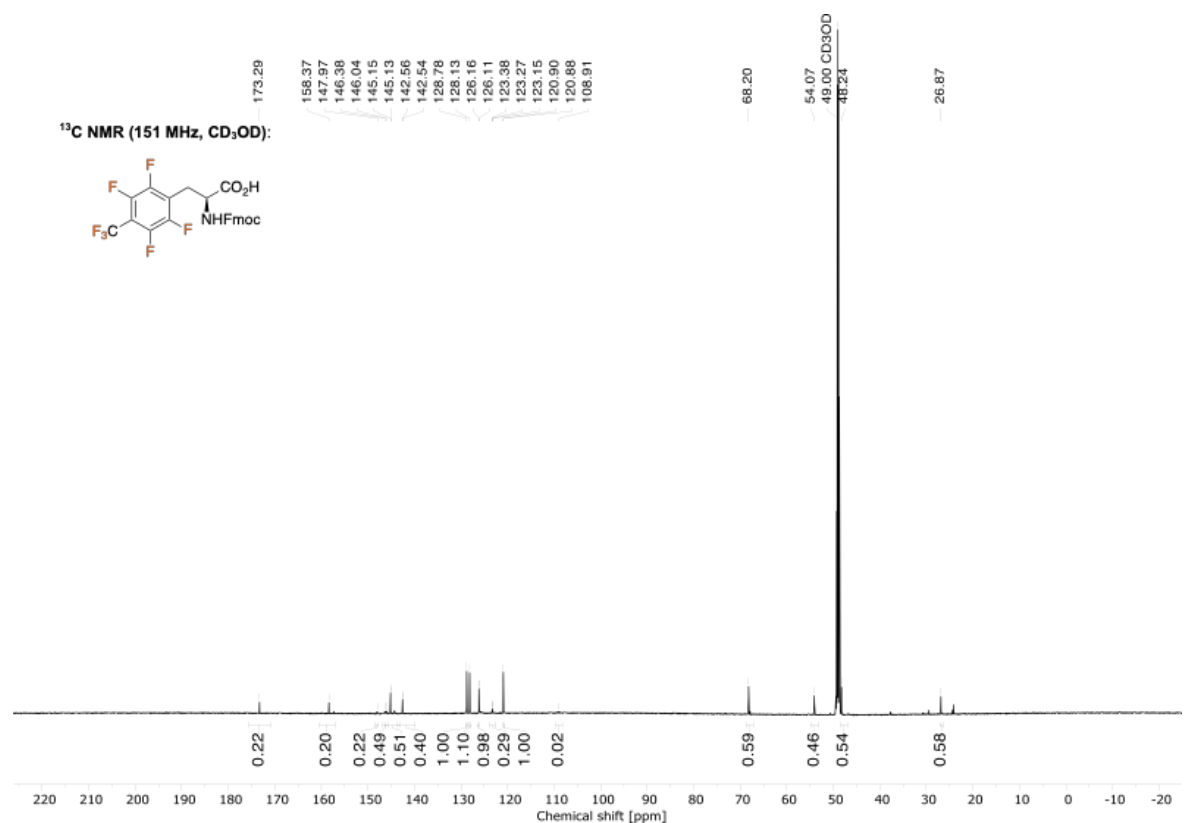
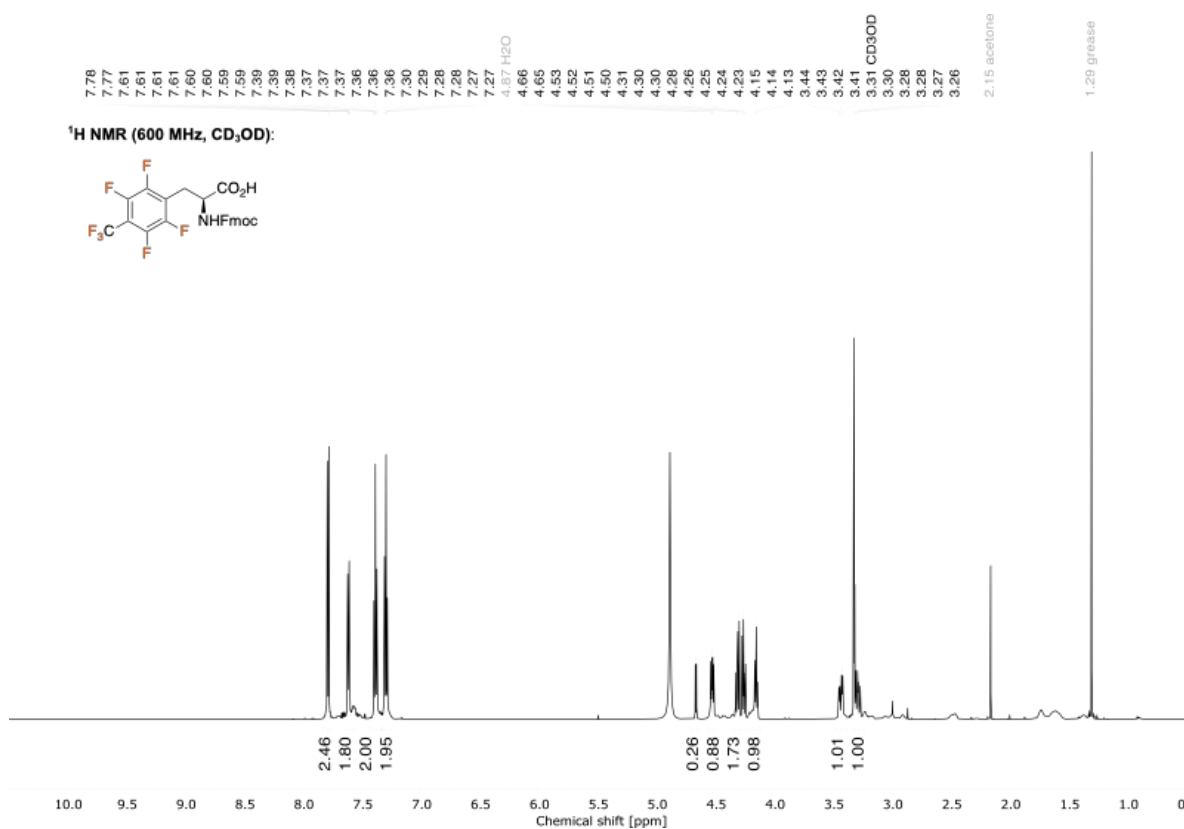


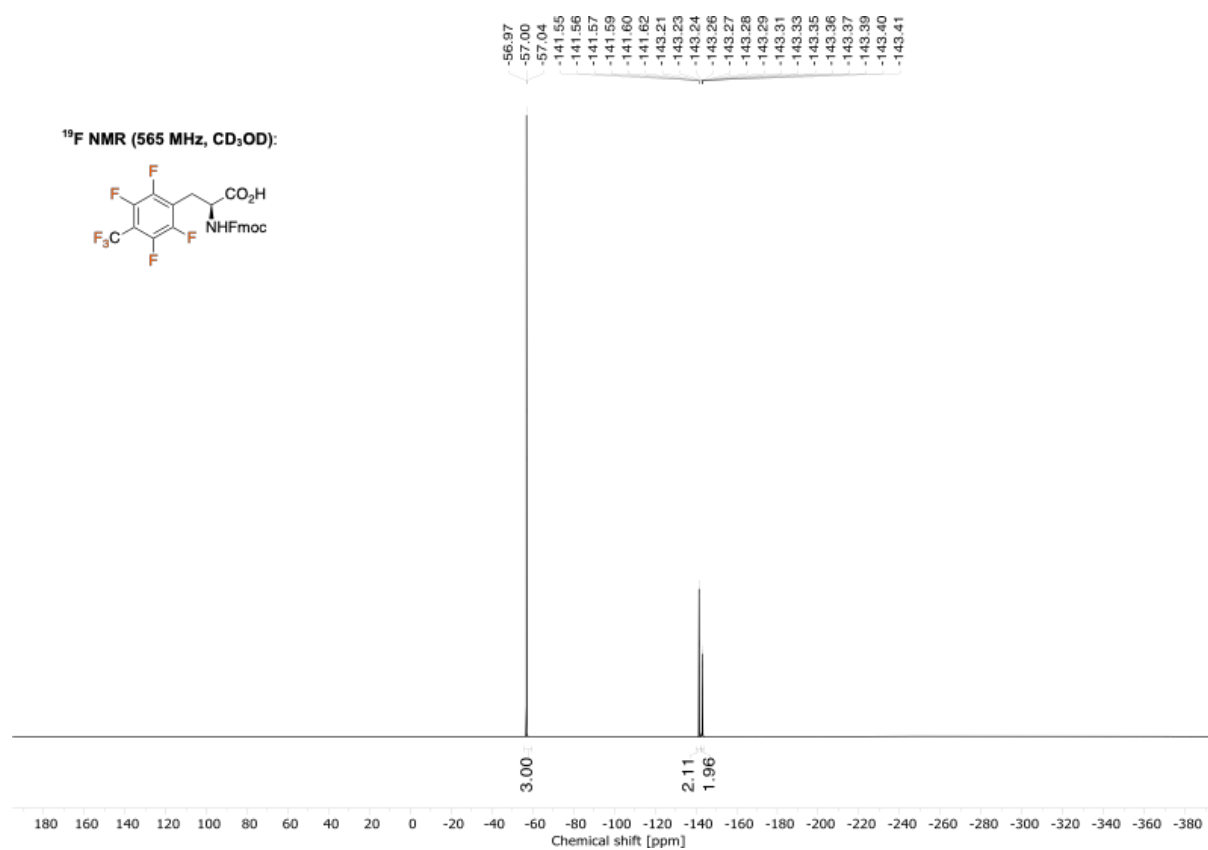




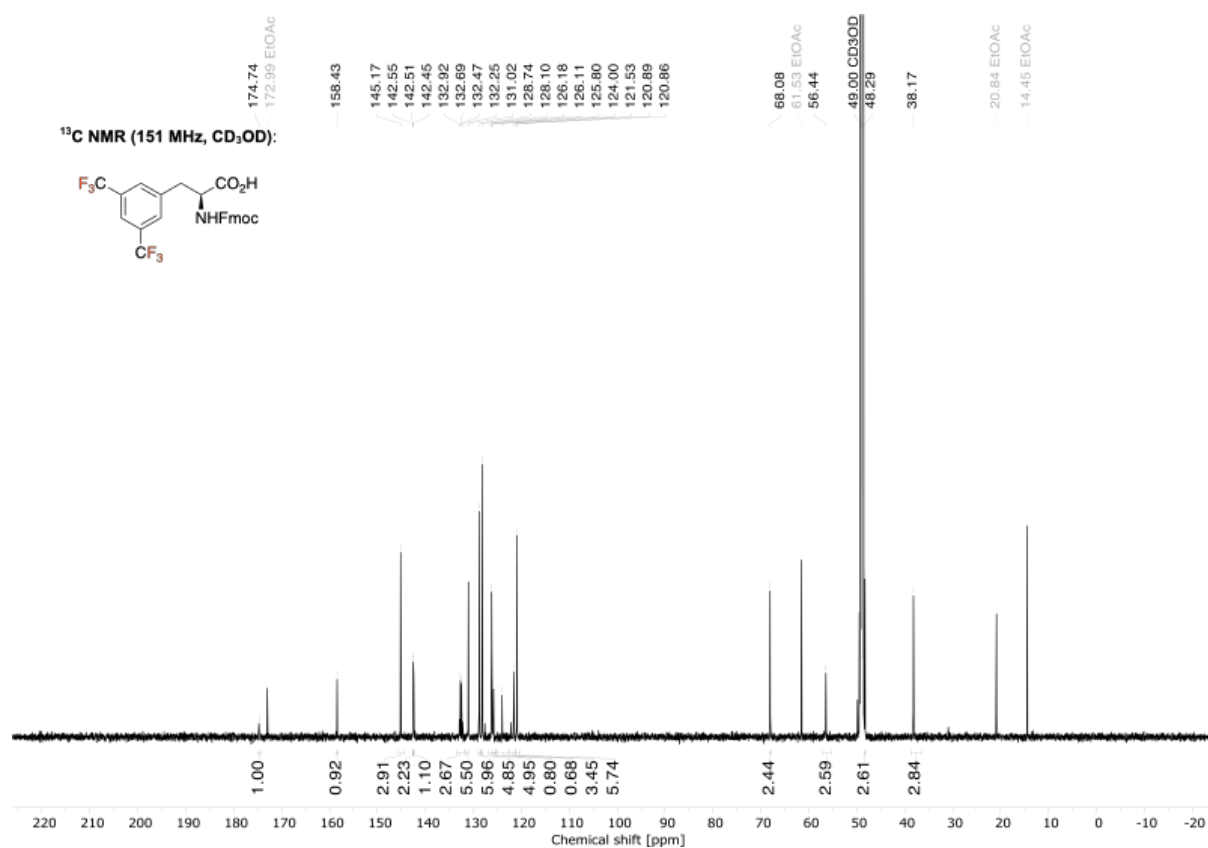
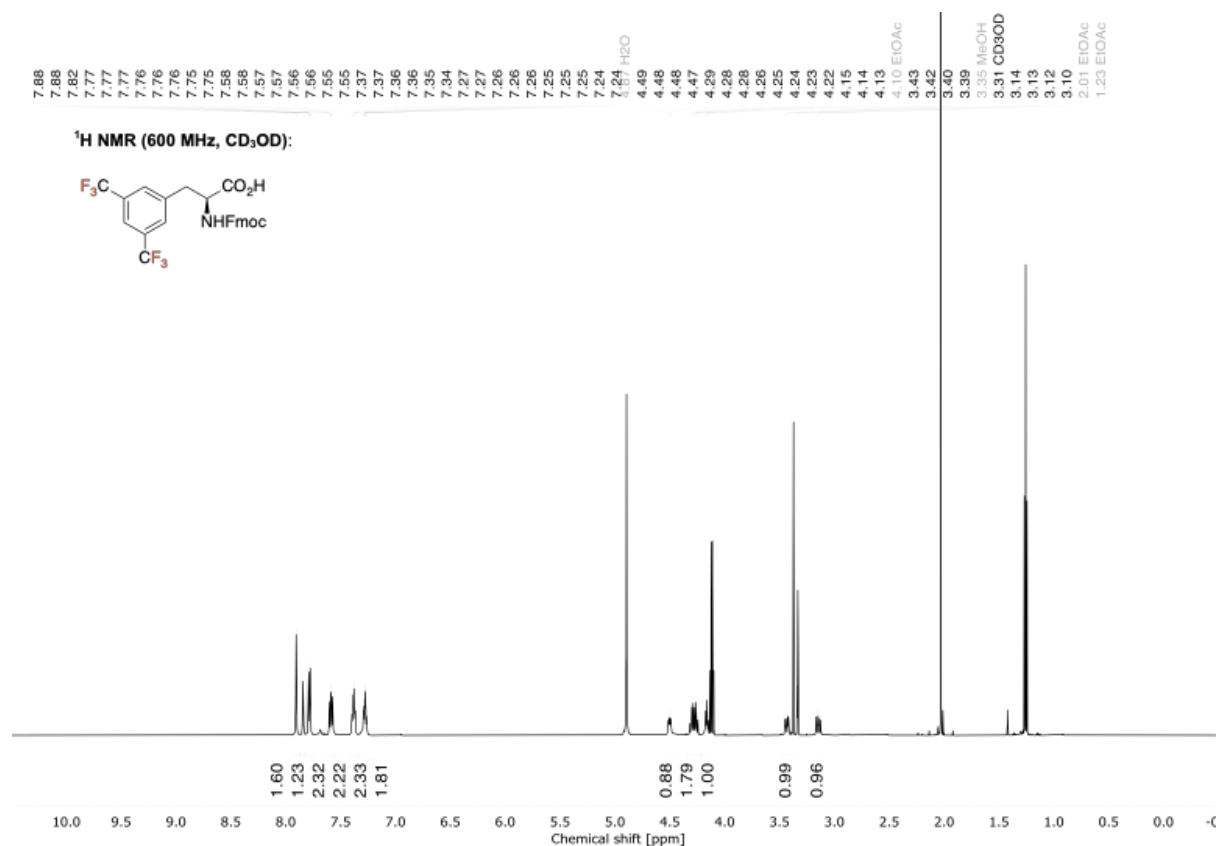


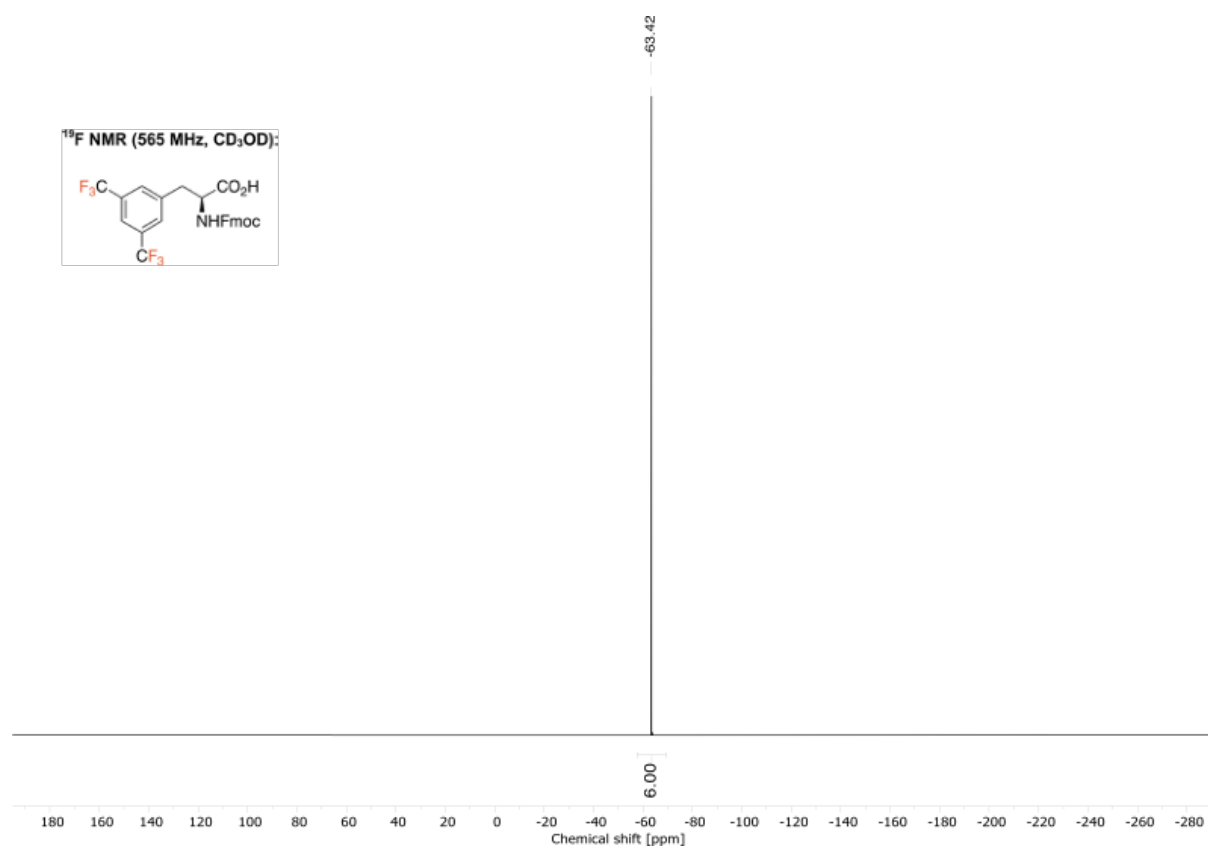
(S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)propanoic acid [tetrafluoro(trifluoromethyl)phenylalanine, [2.3.5.6F]TfMePhe] **2**



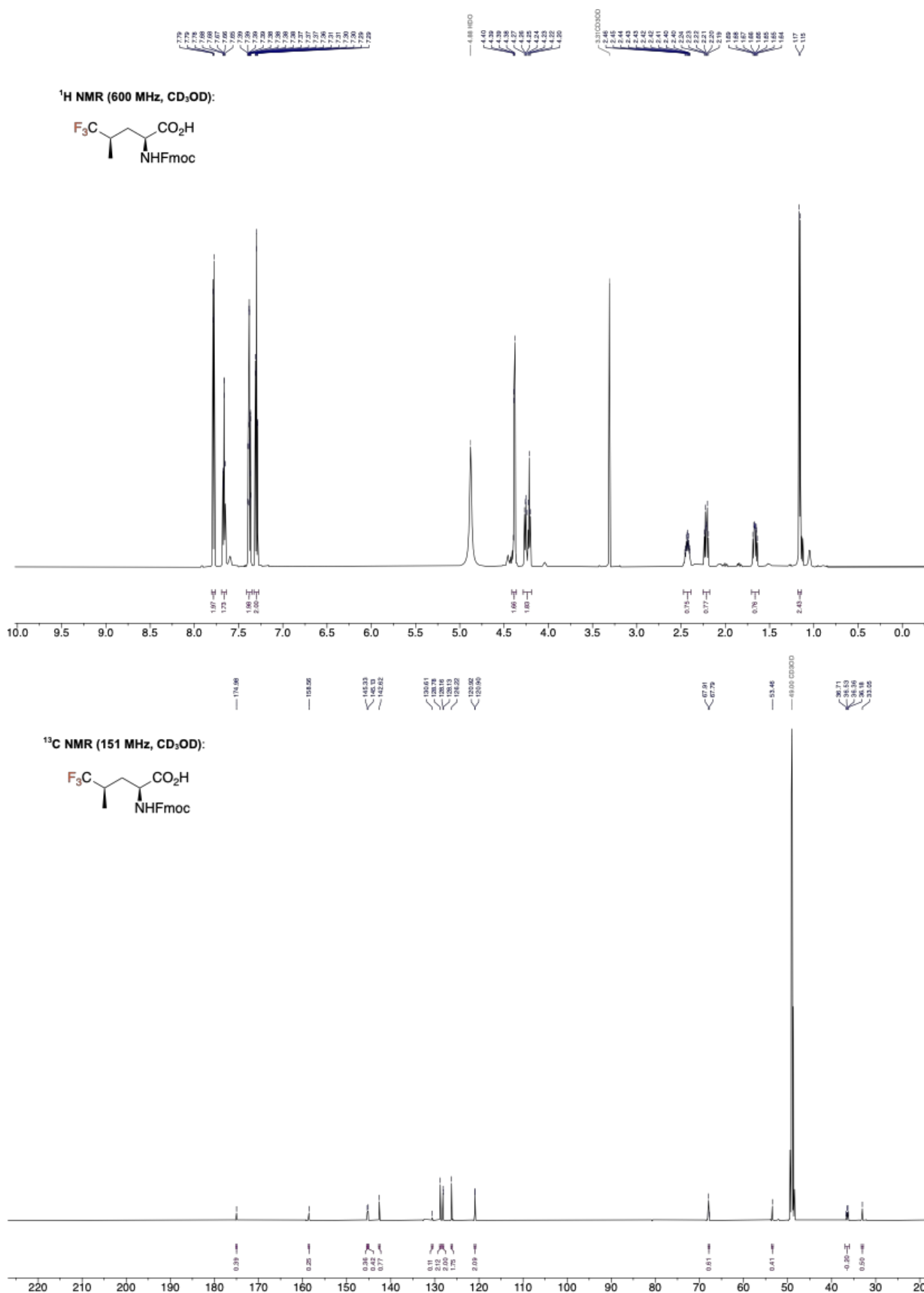


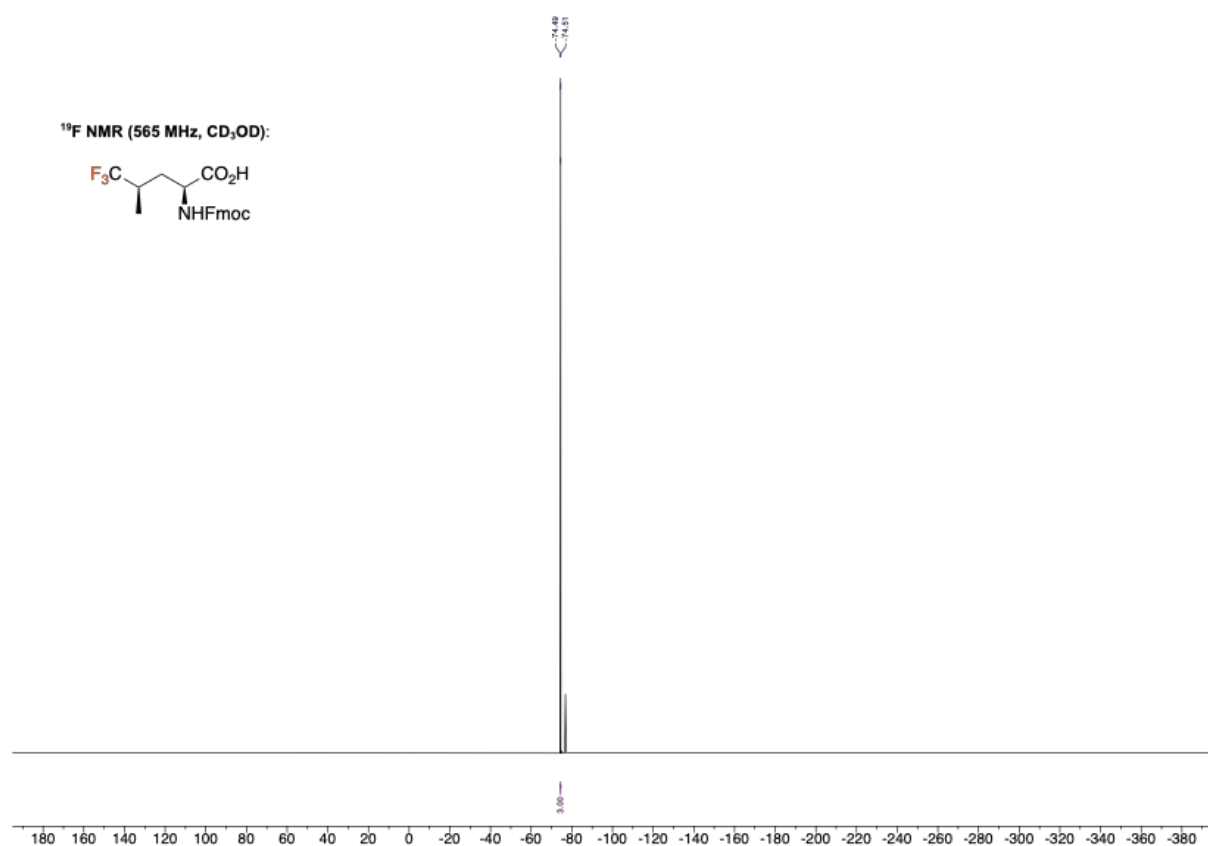
(S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(3,5-bis(trifluoromethyl)phenyl)propanoic acid [bis(trifluoromethyl)phenylalanine, bisTfMePhe] **3**



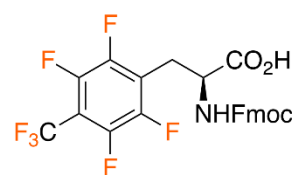
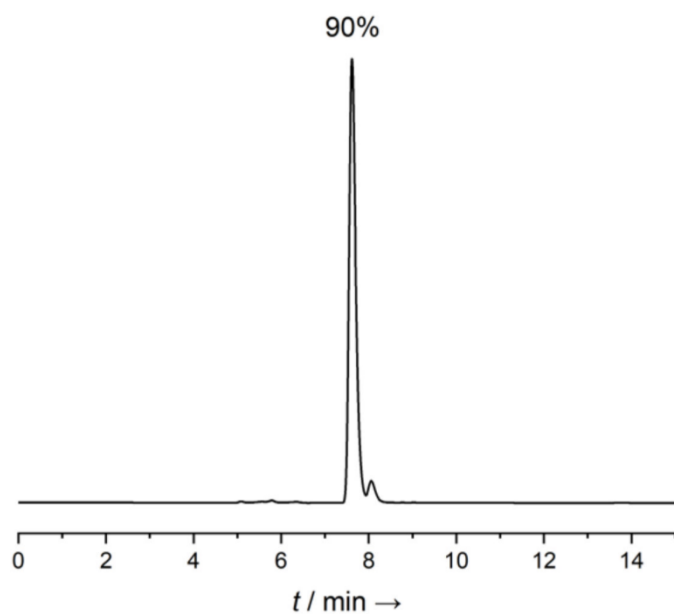


(2*S*,4*R*)-2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)-5,5,5-trifluoro-4-methylpentanoic acid  
[Trifluoroleucine, TfLeu] **12a**



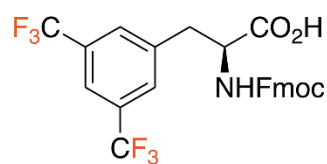
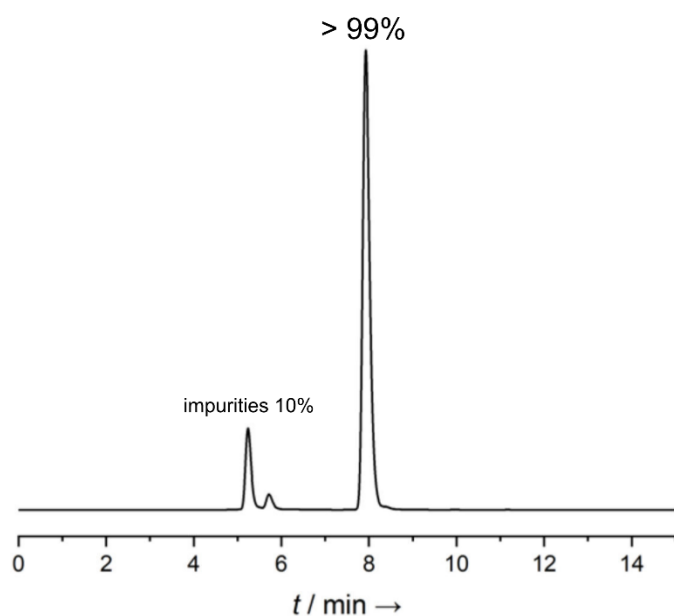






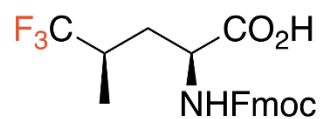
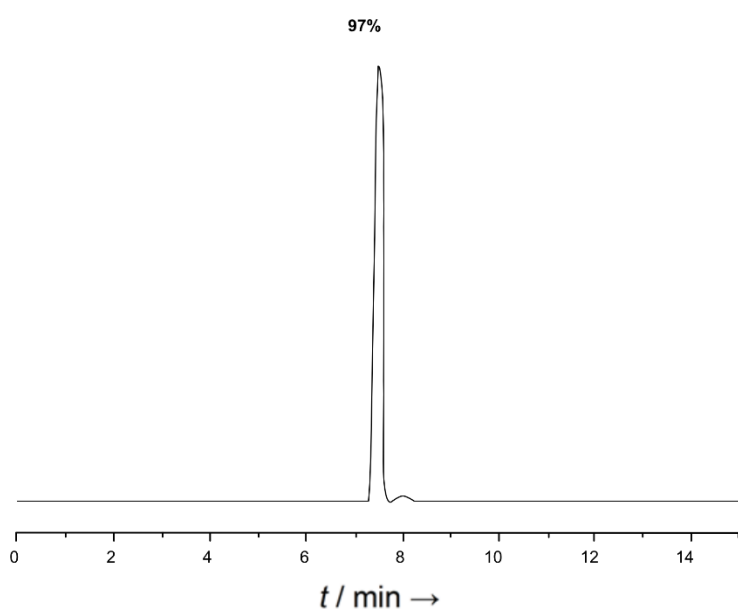
Chiral HPLC, Method:

MeCN:MeOH:H<sub>2</sub>O = 148:850:2, 15 min



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In order to validate the separation efficiency of the HPLC method to determine the enantiomeric purity of the fluorinated amino acids in our previous publication racemic mixtures of the corresponding fluorinated amino acids were prepared by a procedure described by Yamada et al. and subsequently analyzed [1].

## References

1. Yamada, S.H., C.; Yoshioka, R.; Chibata, I. , *Method for the racemization of optically active amino acids*. Journal of Organic Chemistry, 1983. **48**(6): p. 843-846.