

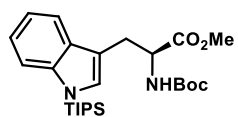
Total Synthesis of Verruculogen and Fumitremorgin A Enabled by Ligand-controlled C–H Borylation

Yu Feng,[‡] Dane Holte,[‡] Jochen Zoller, Shigenobu Umekiya, Leah R. Simke,
and Phil S. Baran*

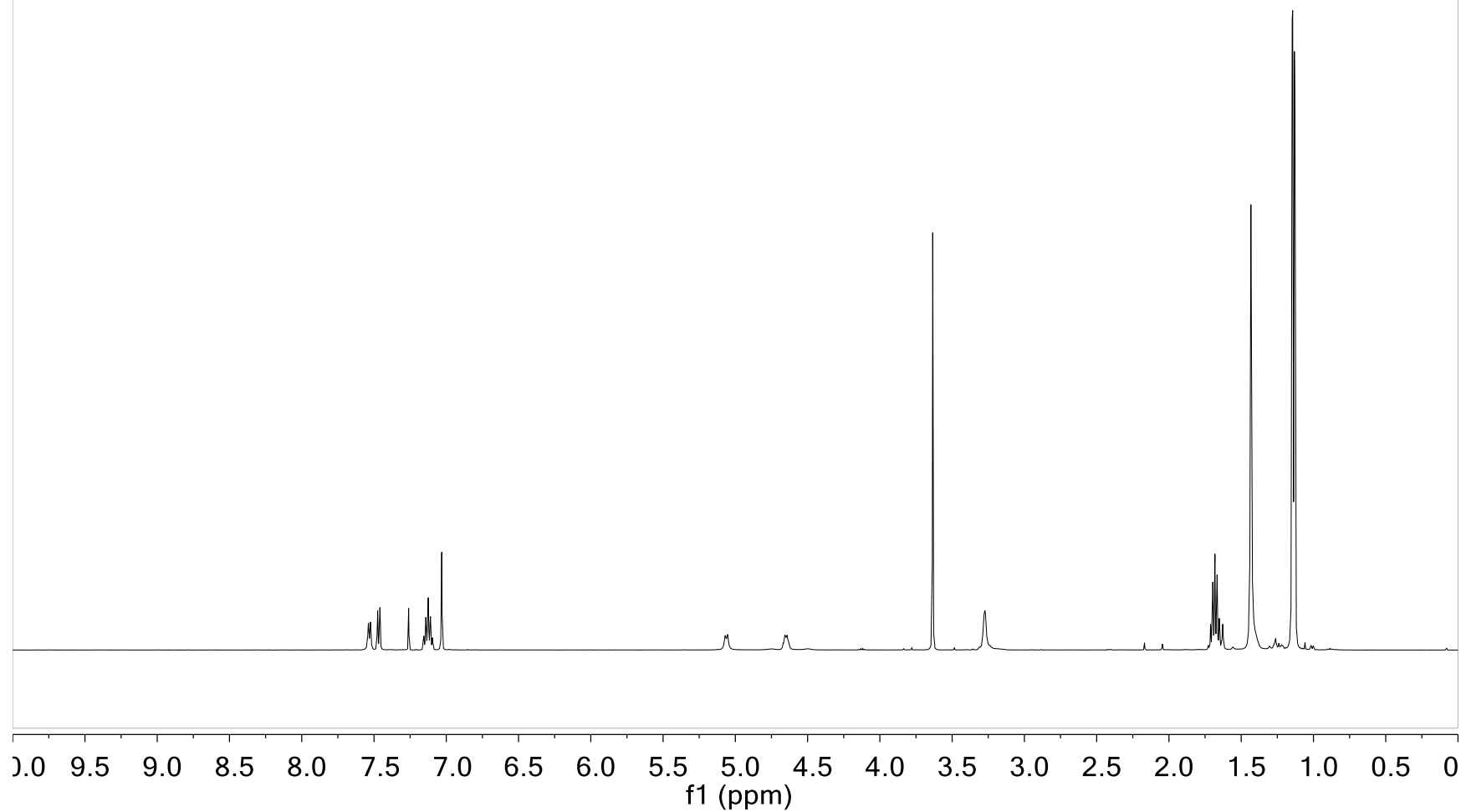
*Department of Chemistry, The Scripps Research Institute,
10550 North Torrey Pines Road, La Jolla, California 92037*

SUPPORTING INFORMATION

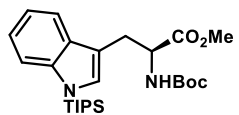
SPECTRA FOR NEW COMPOUNDS



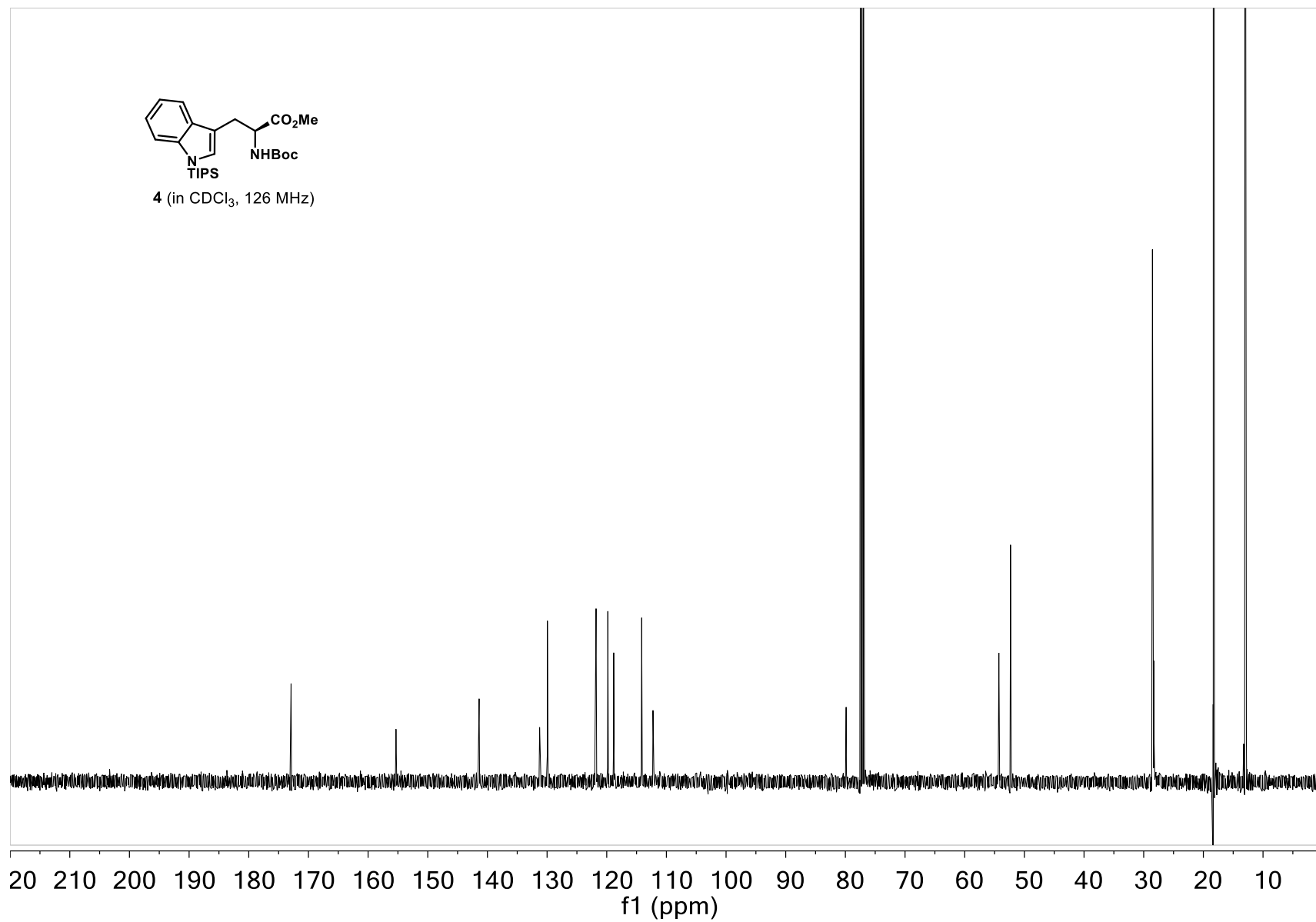
4 (in CDCl₃, 500 MHz)



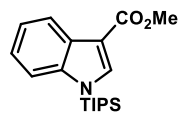
SS2



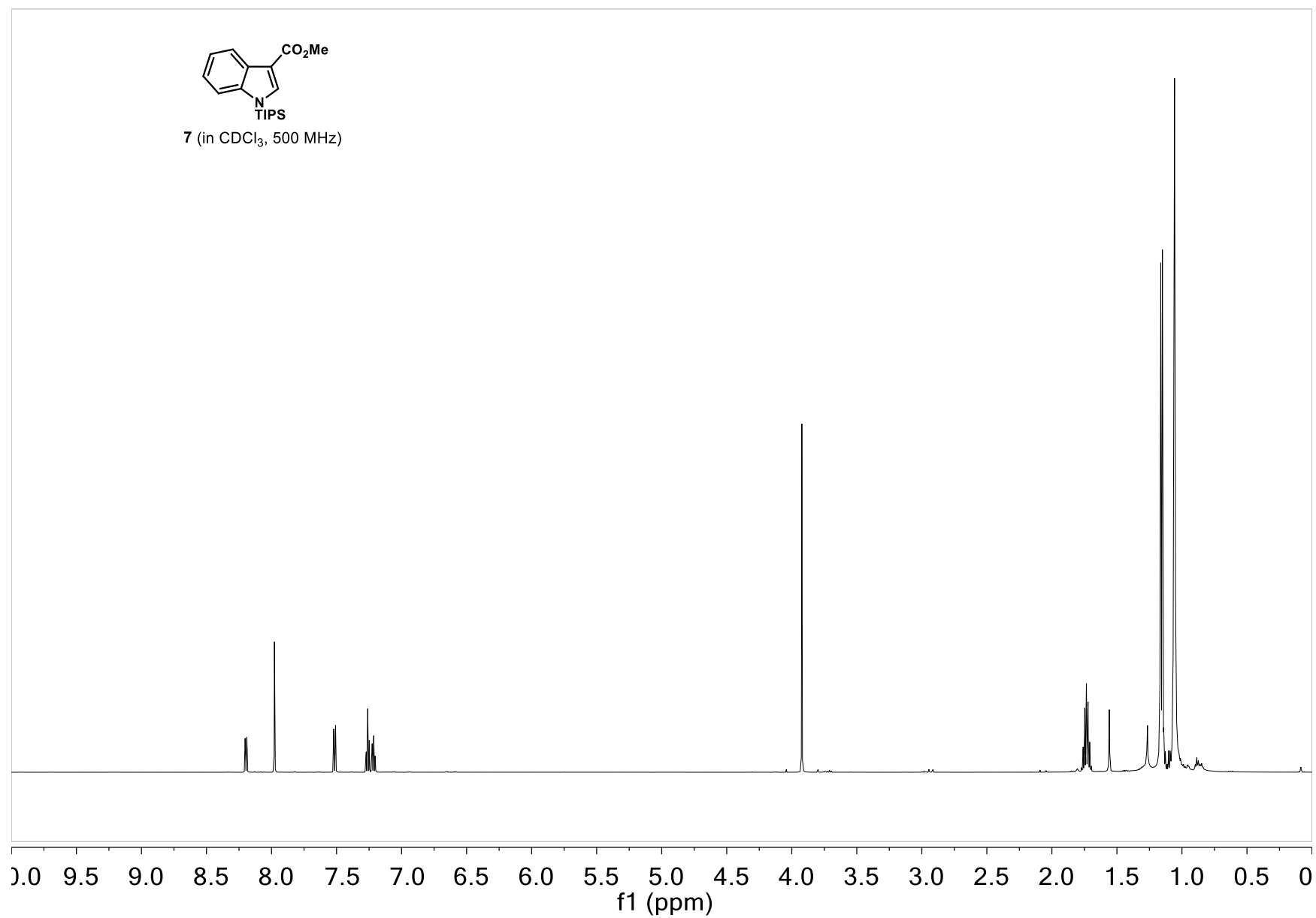
4 (in CDCl₃, 126 MHz)



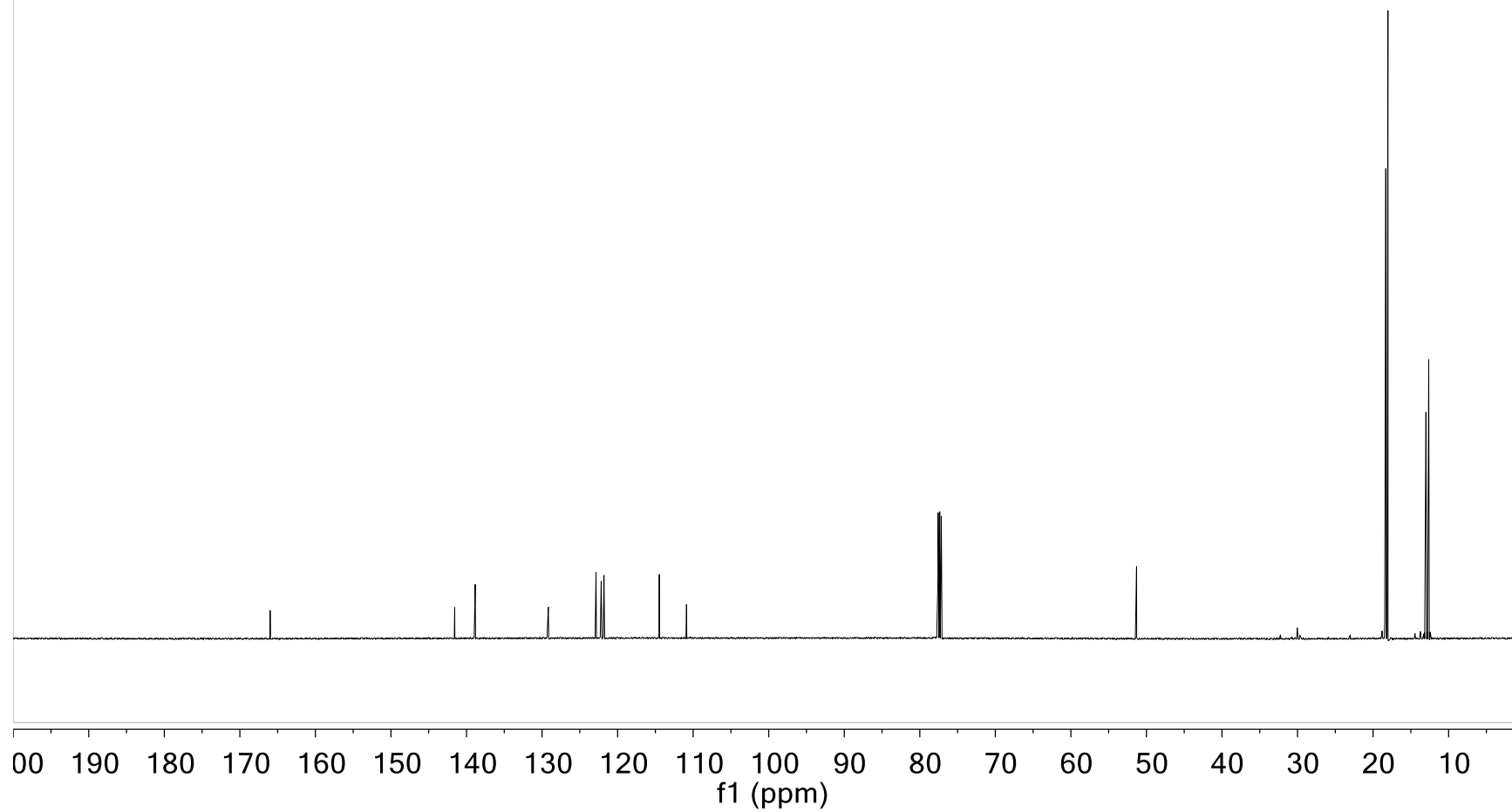
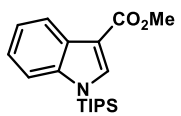
SS3

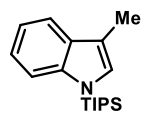


7 (in CDCl₃, 500 MHz)

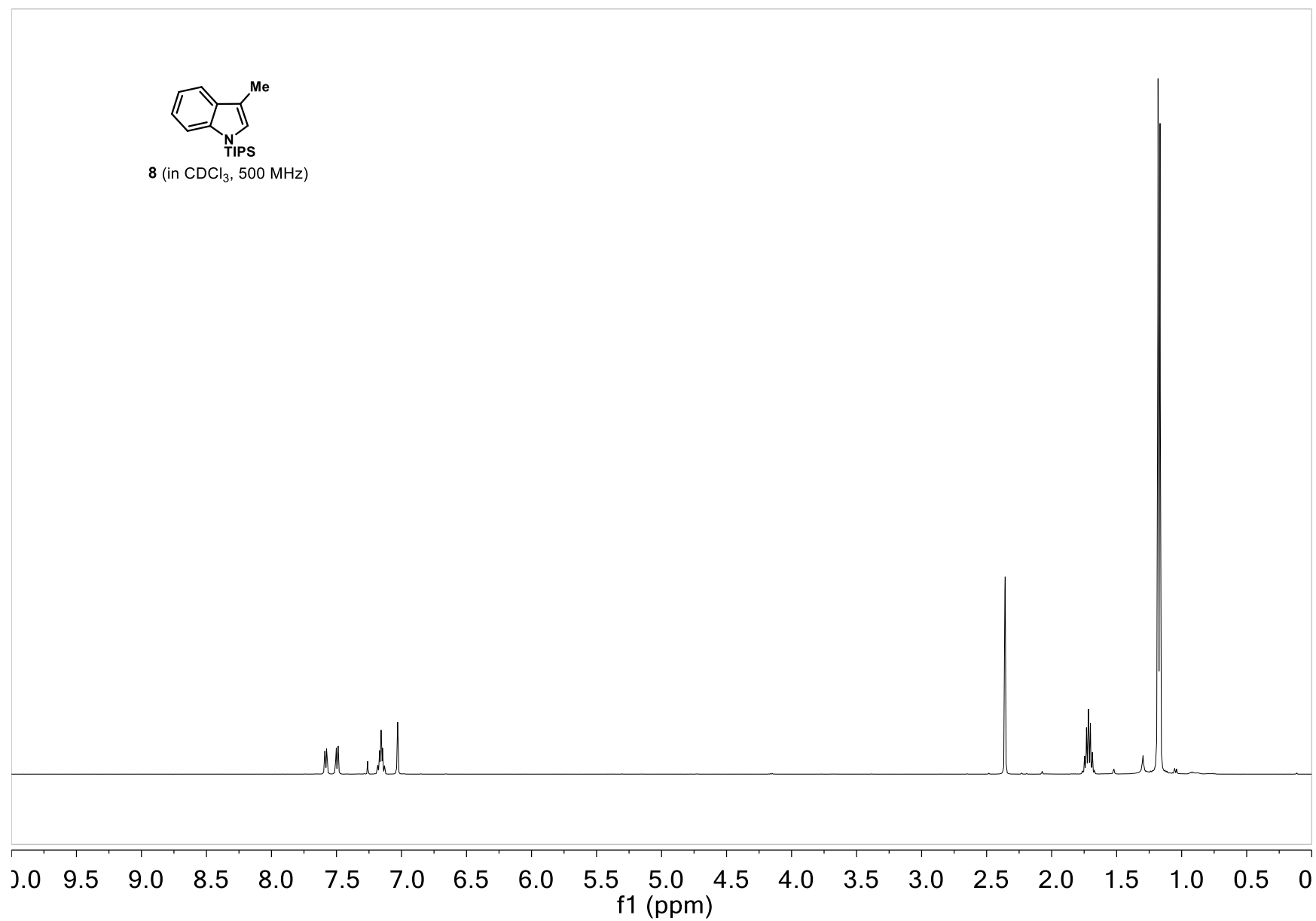


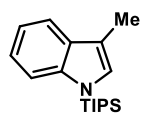
SS4



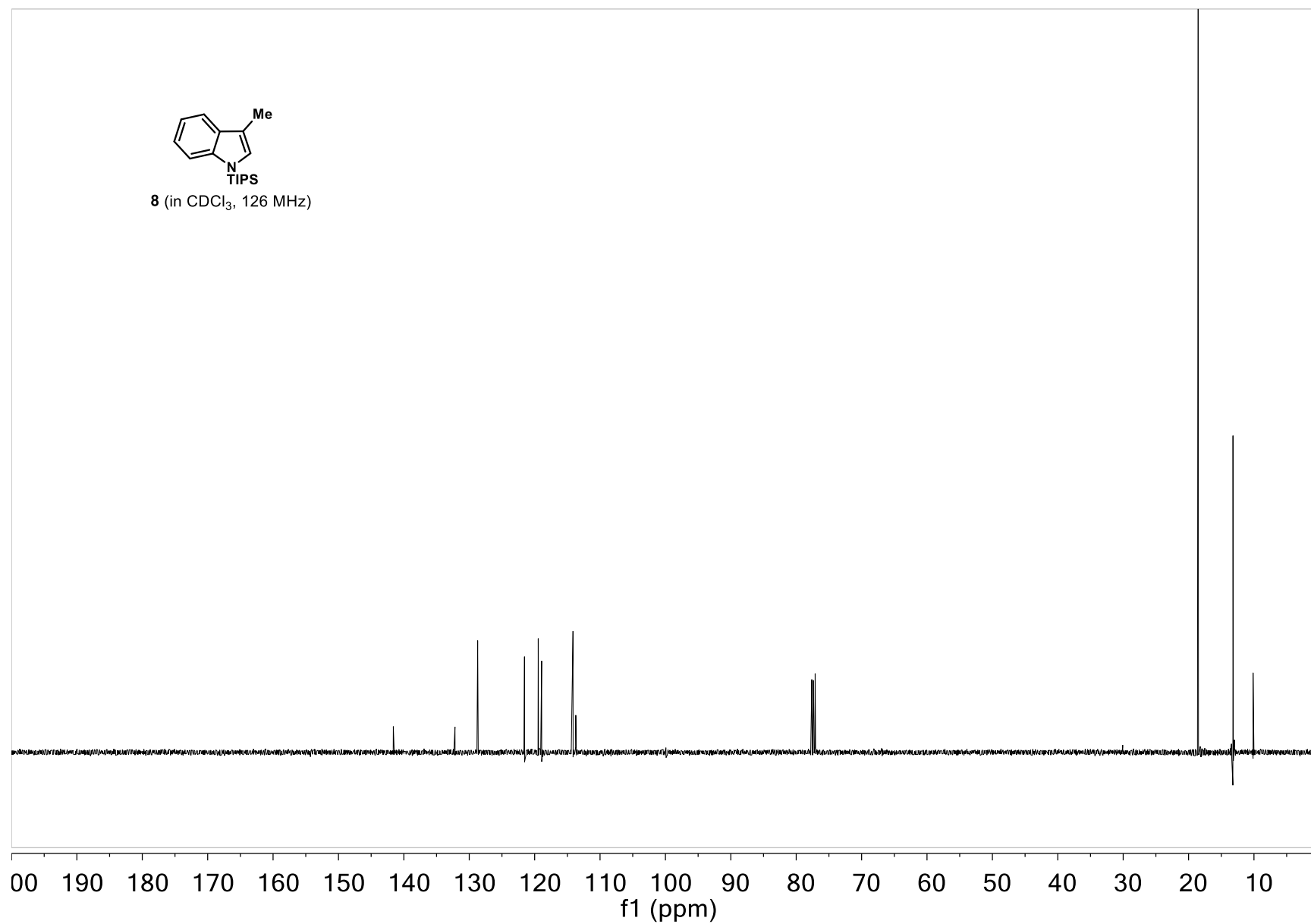


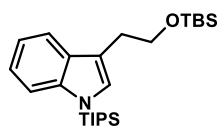
8 (in CDCl₃, 500 MHz)



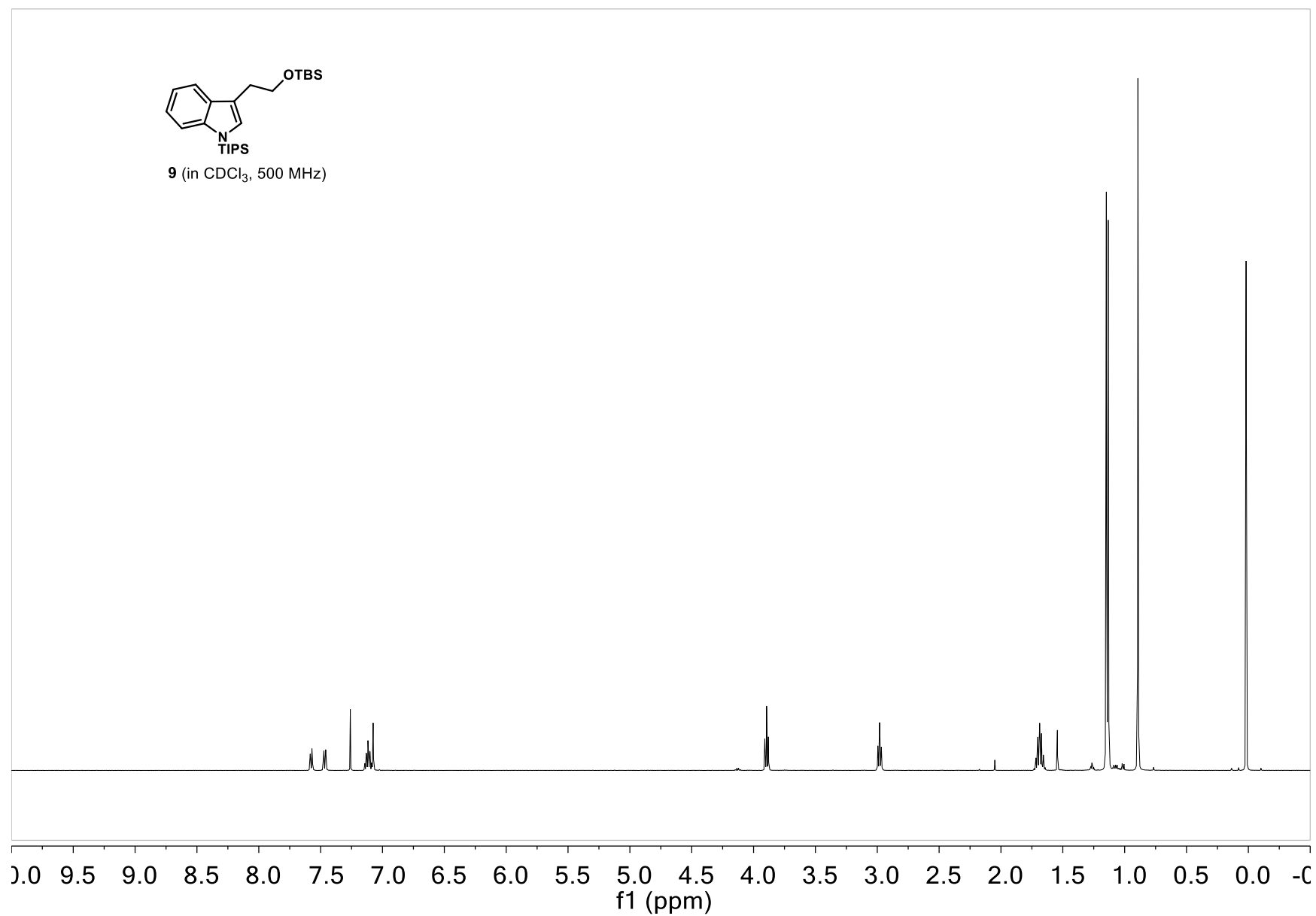


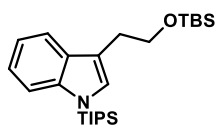
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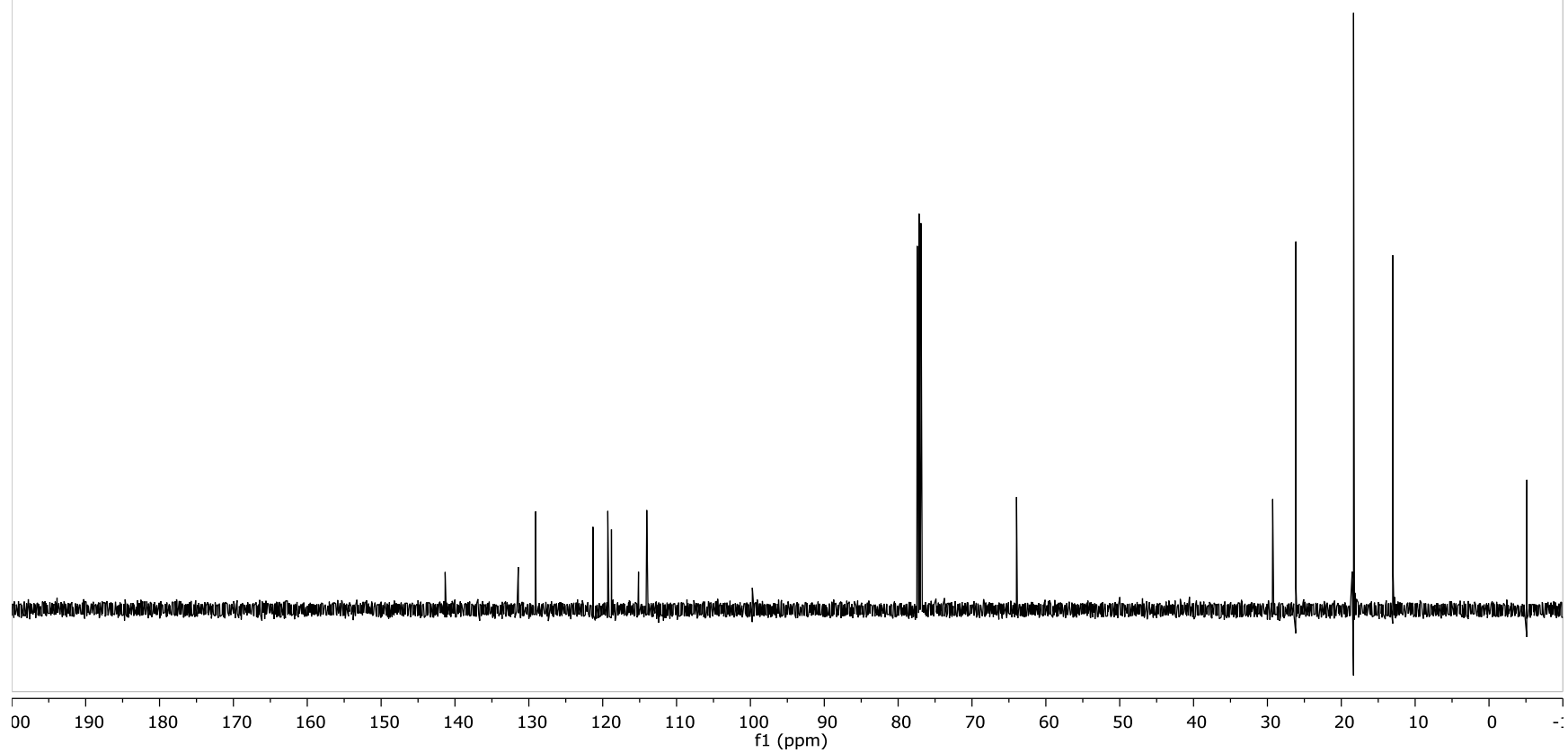


9 (in CDCl₃, 500 MHz)

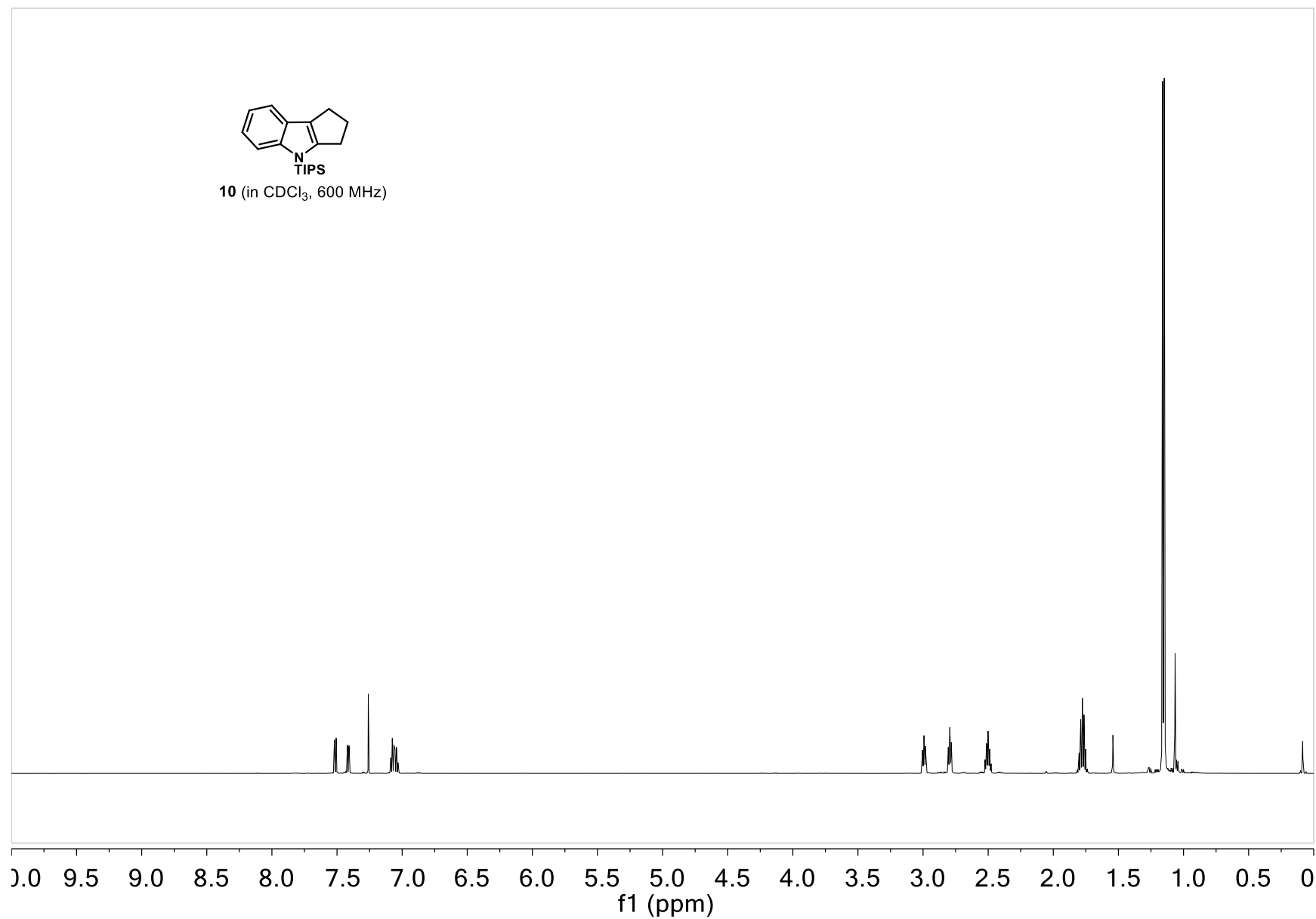
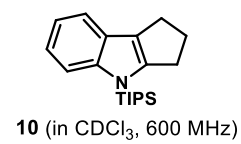


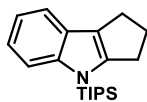


9 (in CDCl₃, 126 MHz)

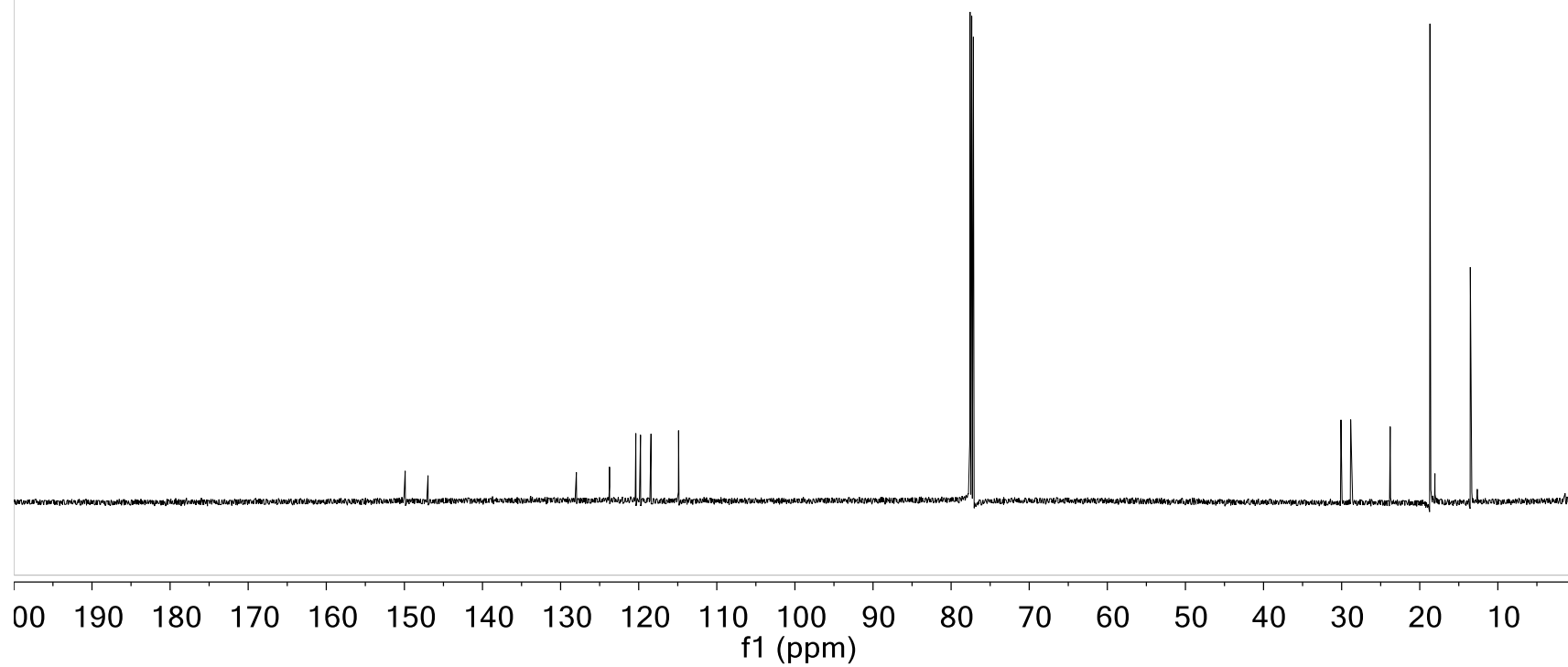


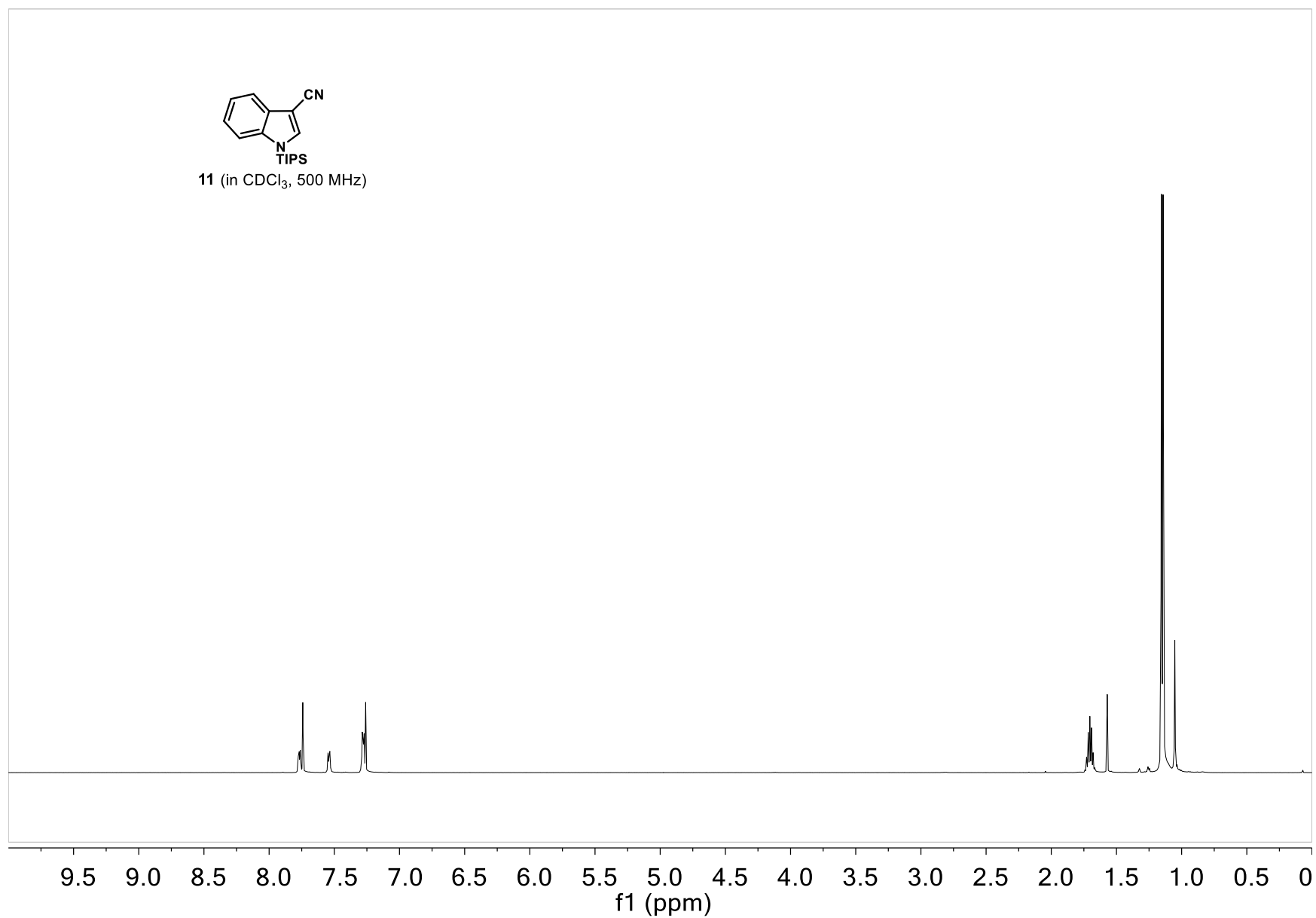
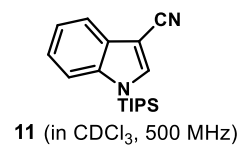
SS9



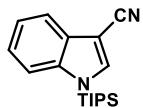


10 (in CDCl₃, 126 MHz)

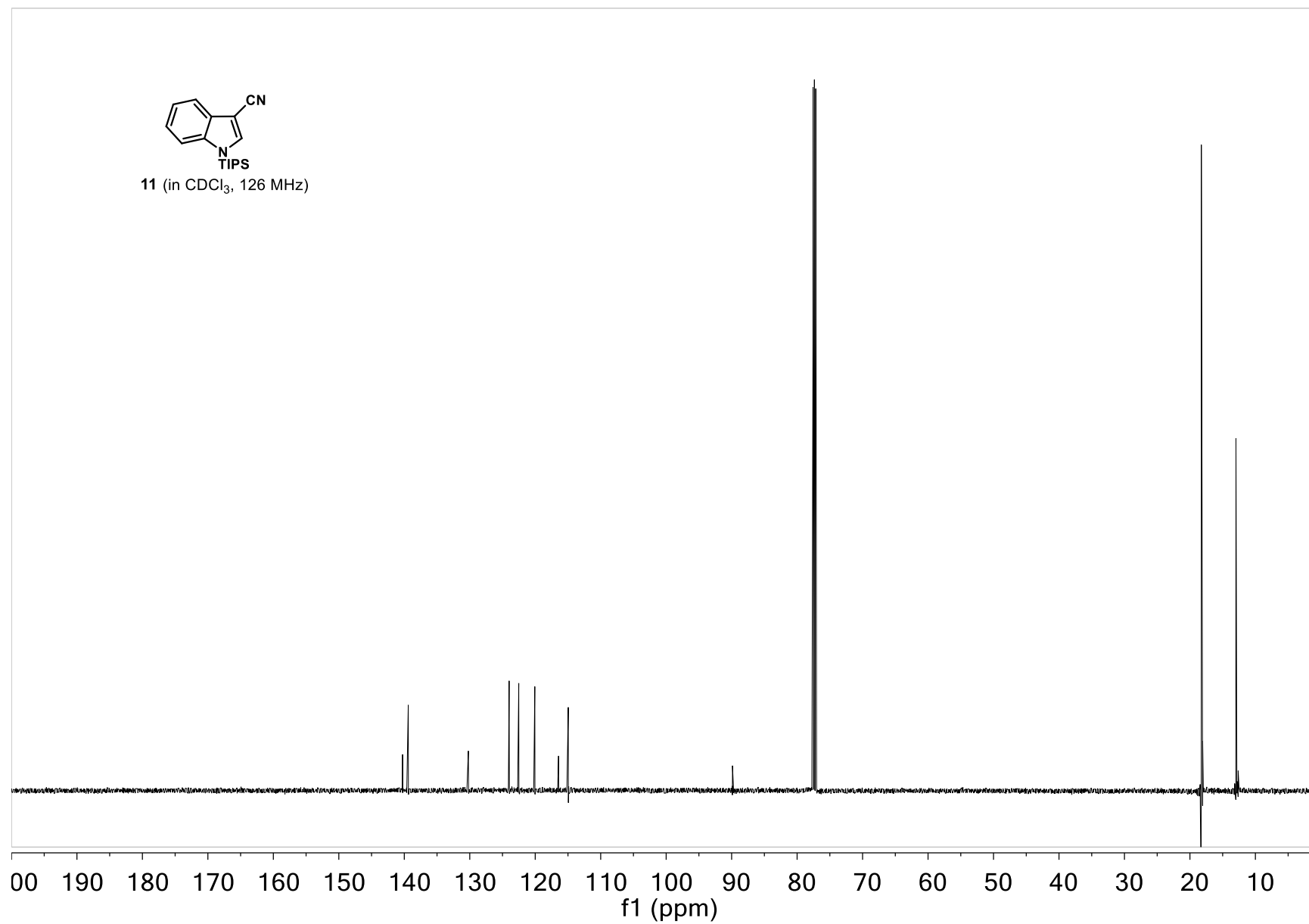


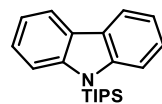


SS12

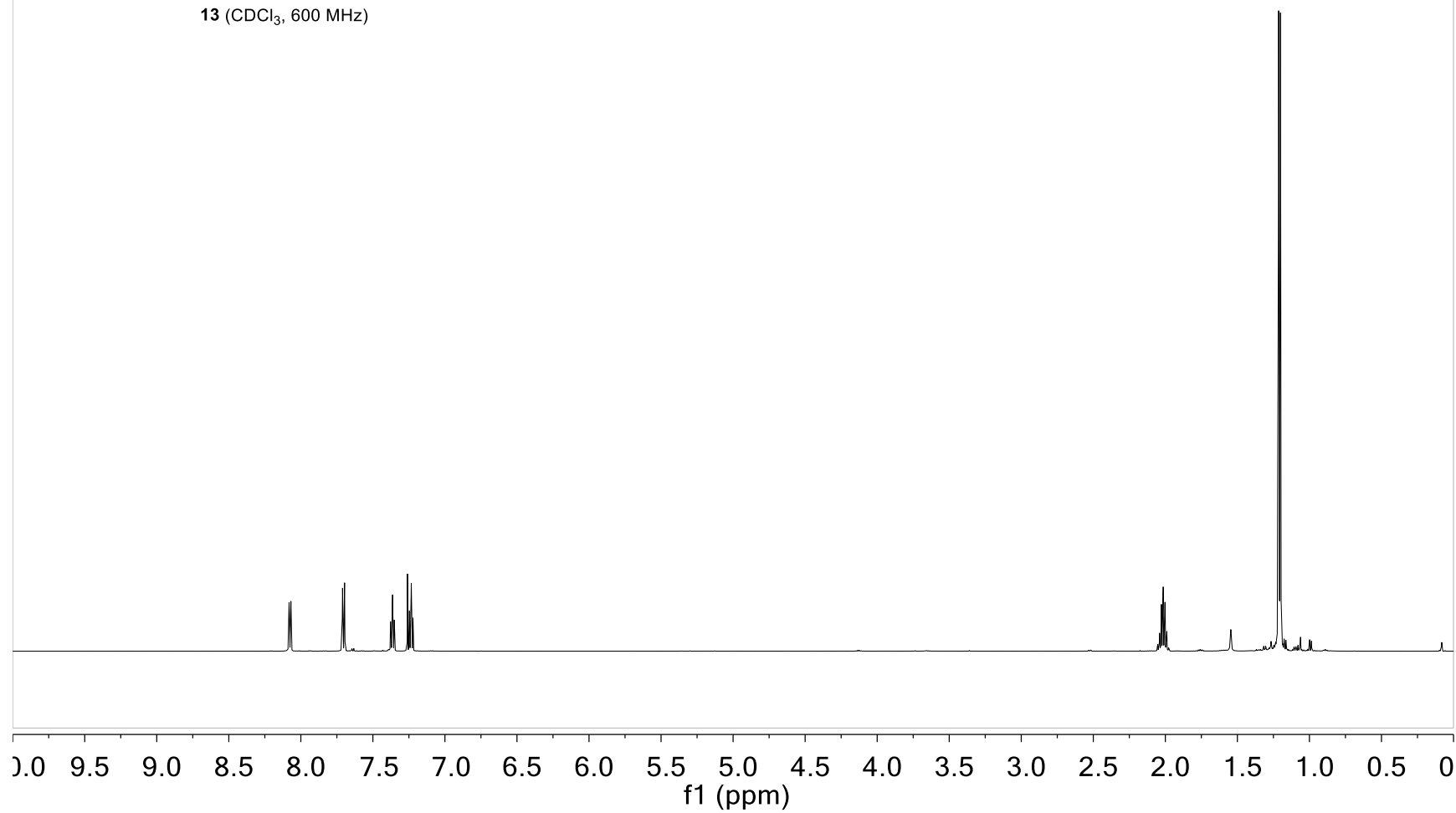


11 (in CDCl₃, 126 MHz)

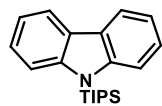




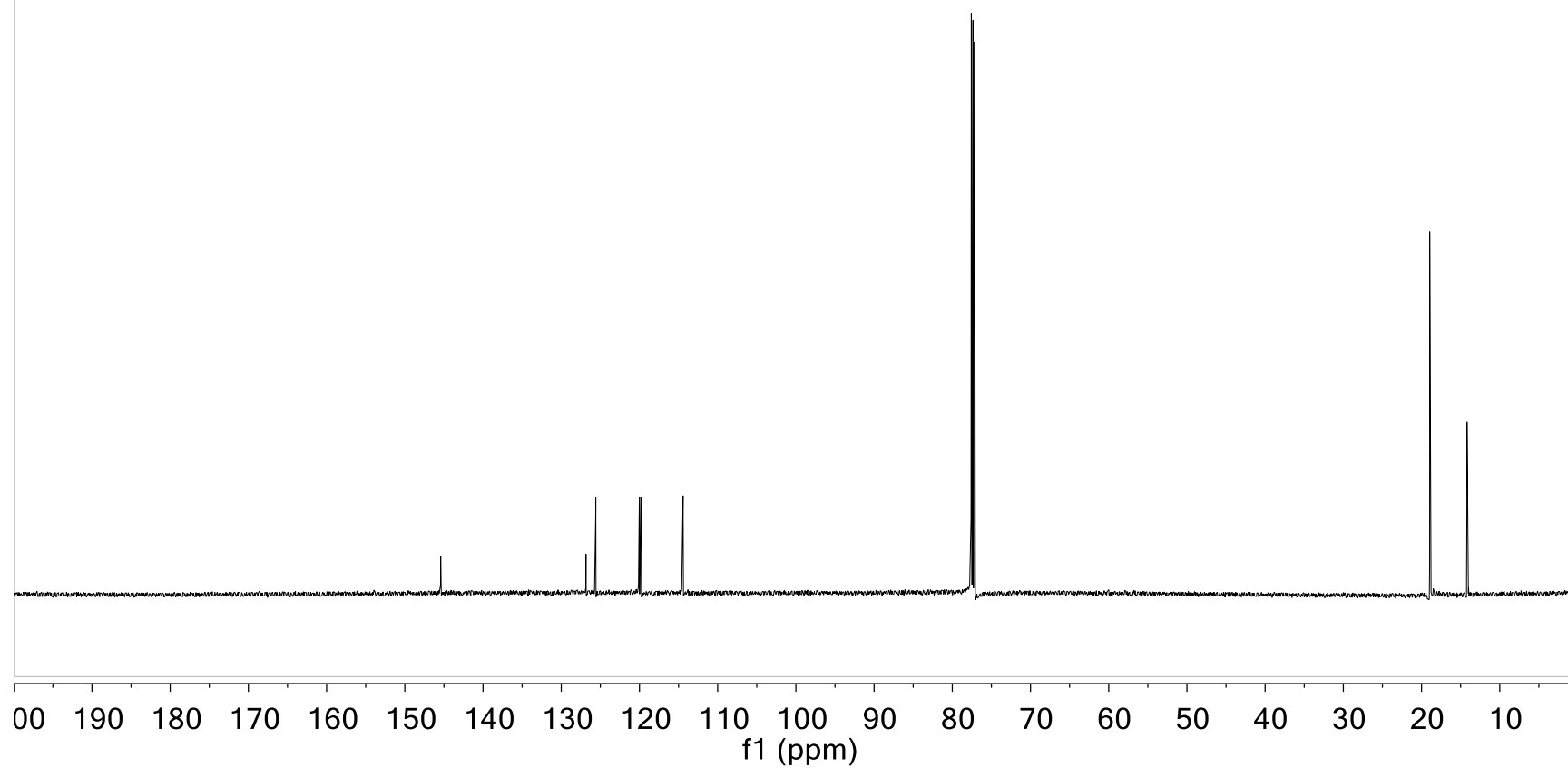
13 (CDCl₃, 600 MHz)

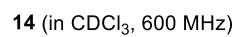


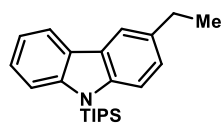
SS14



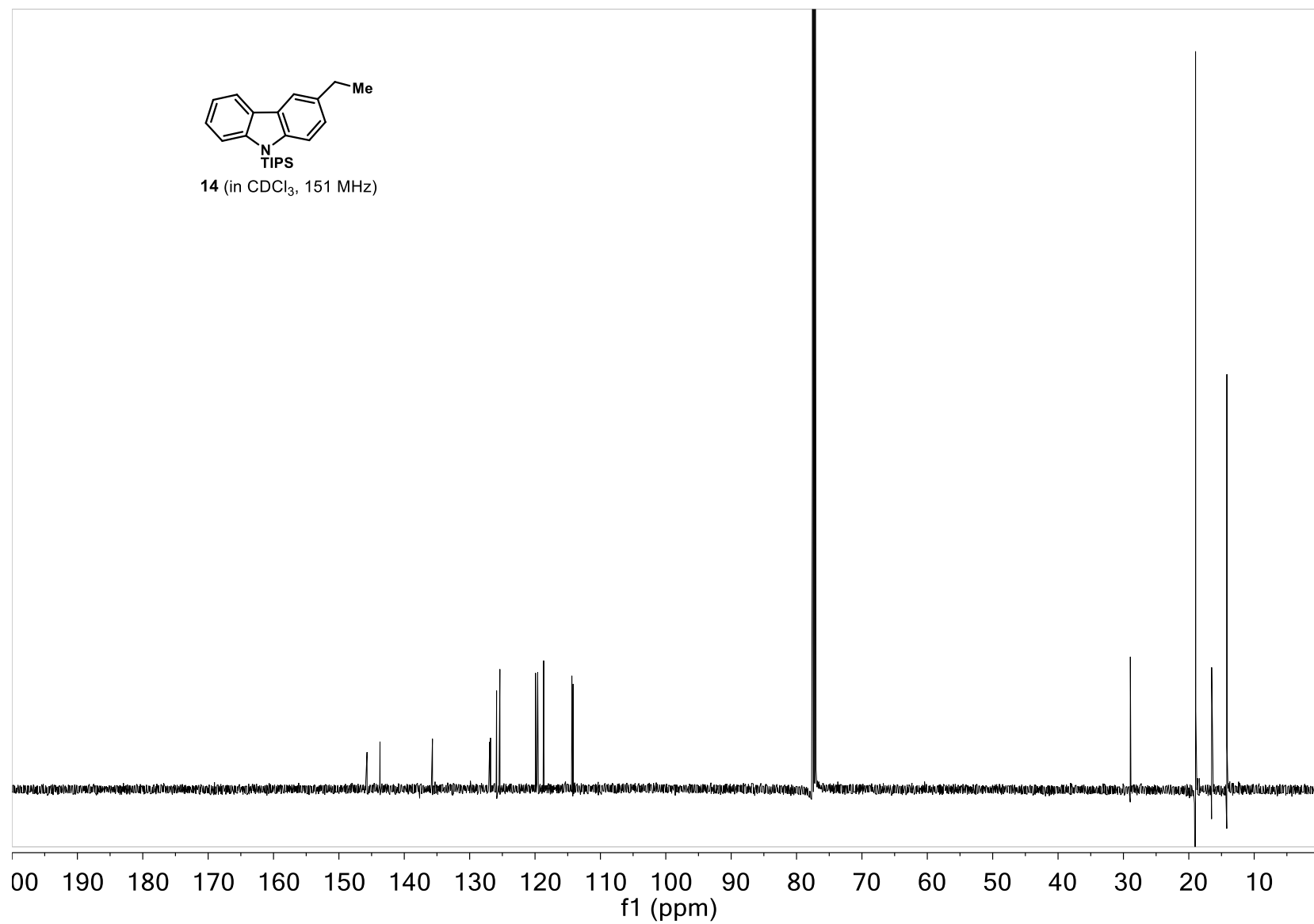
13 (CDCl₃, 151 MHz)

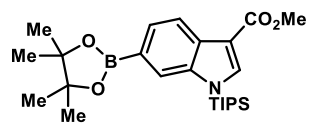




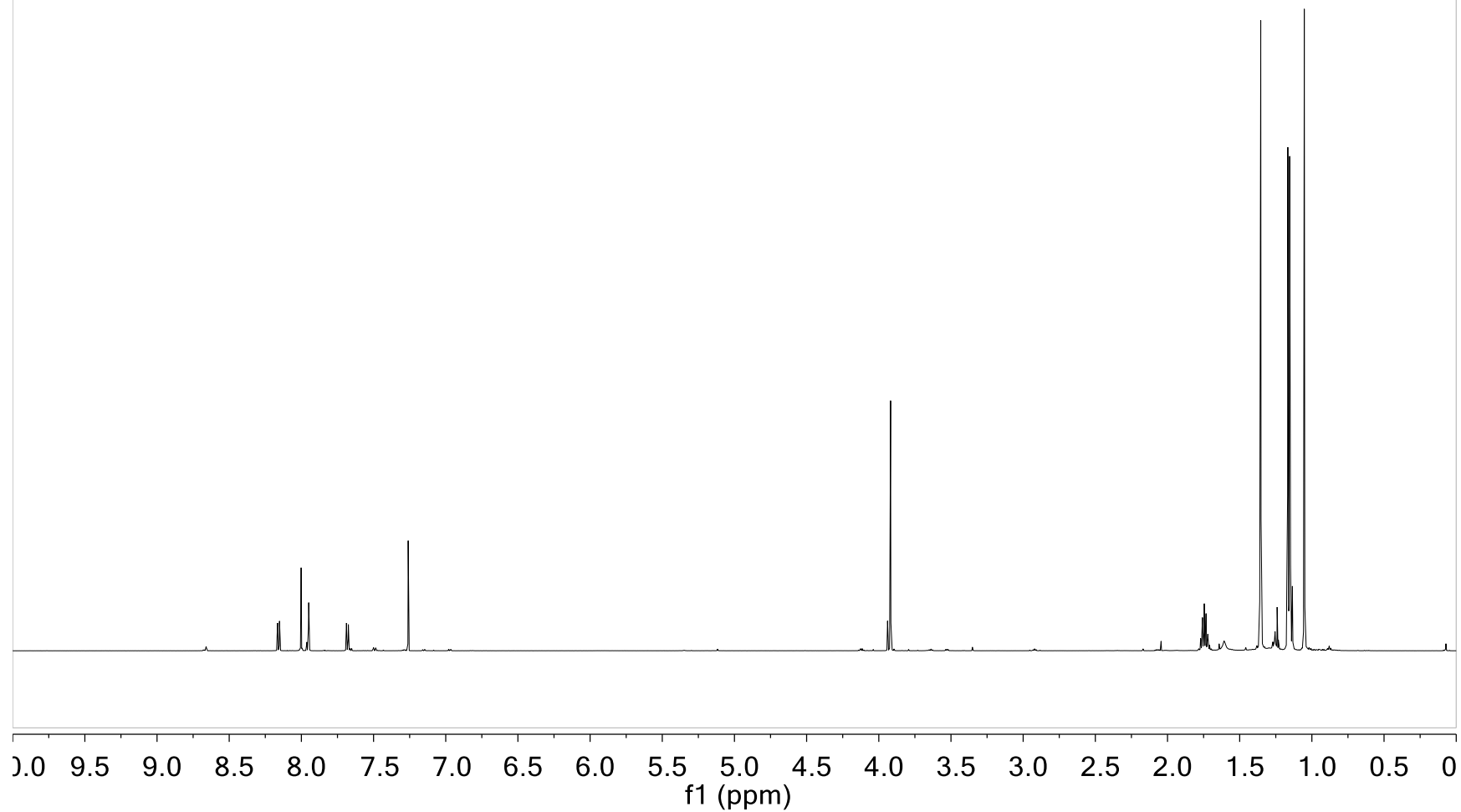


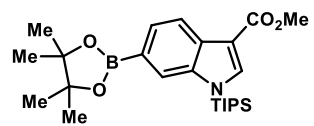
14 (in CDCl₃, 151 MHz)



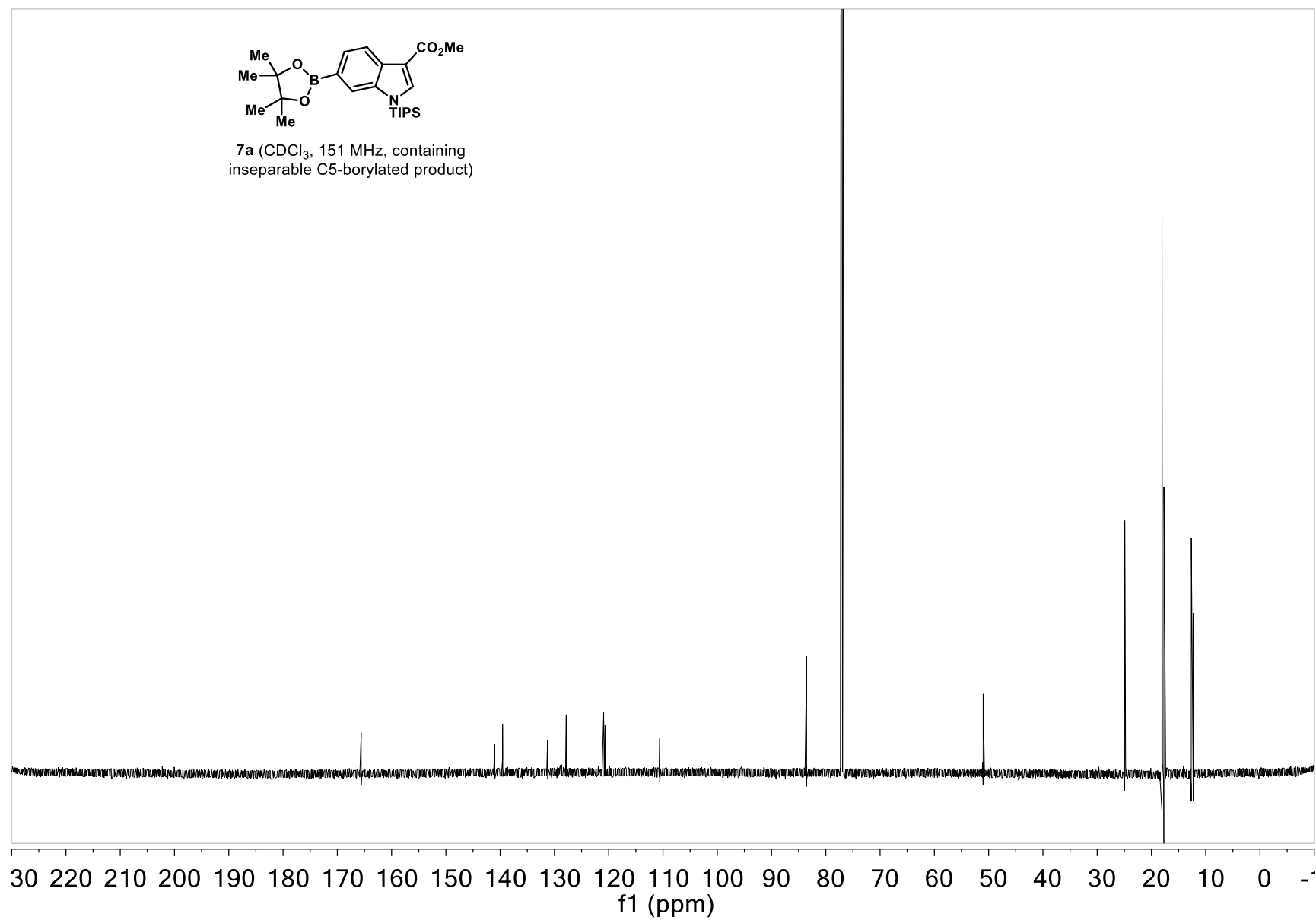


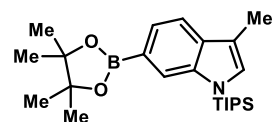
7a (CDCl₃, 600 MHz, containing inseparable C5-borylated product)



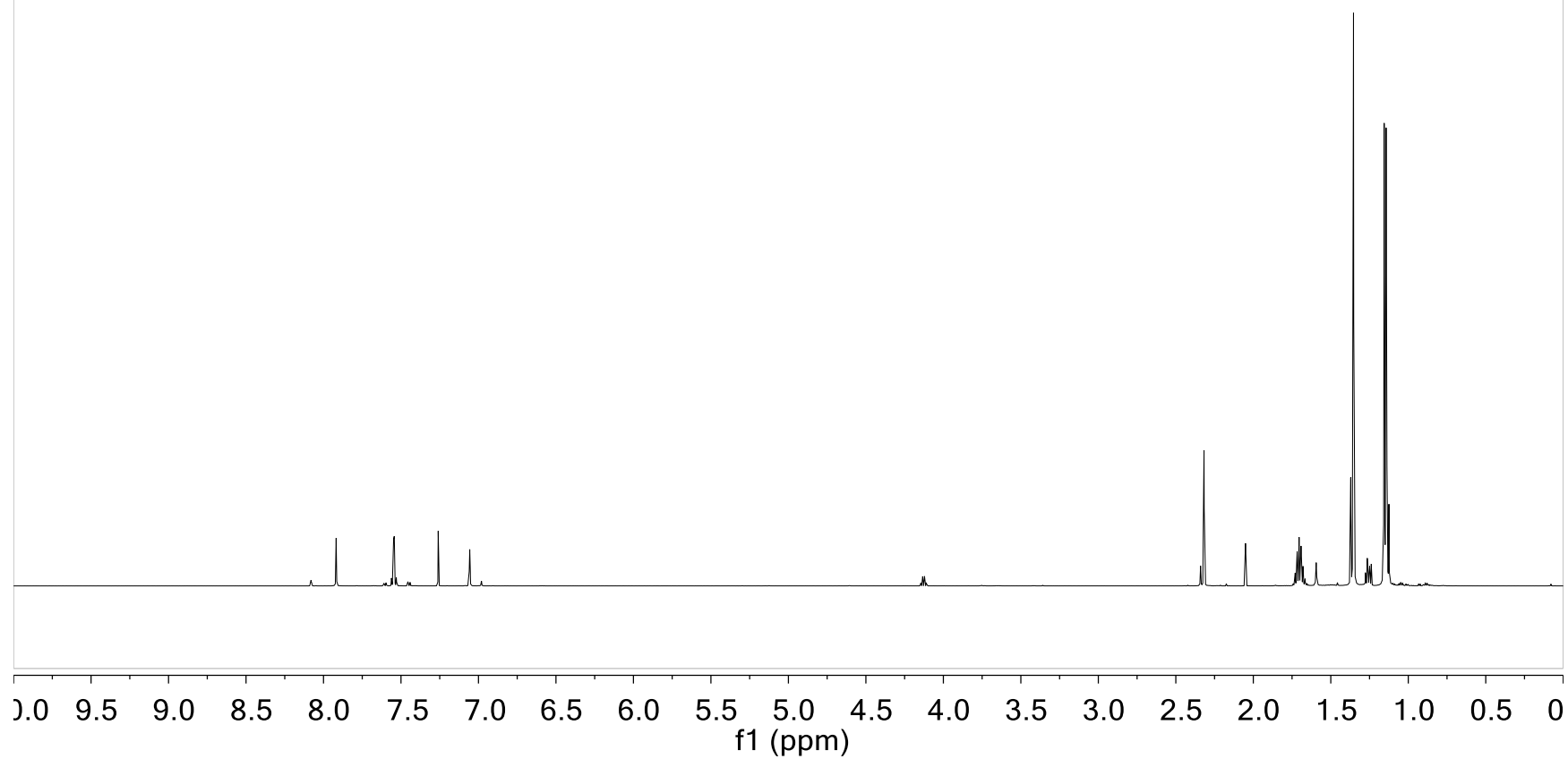


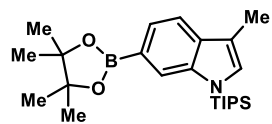
7a (CDCl₃, 151 MHz, containing inseparable C5-borylated product)



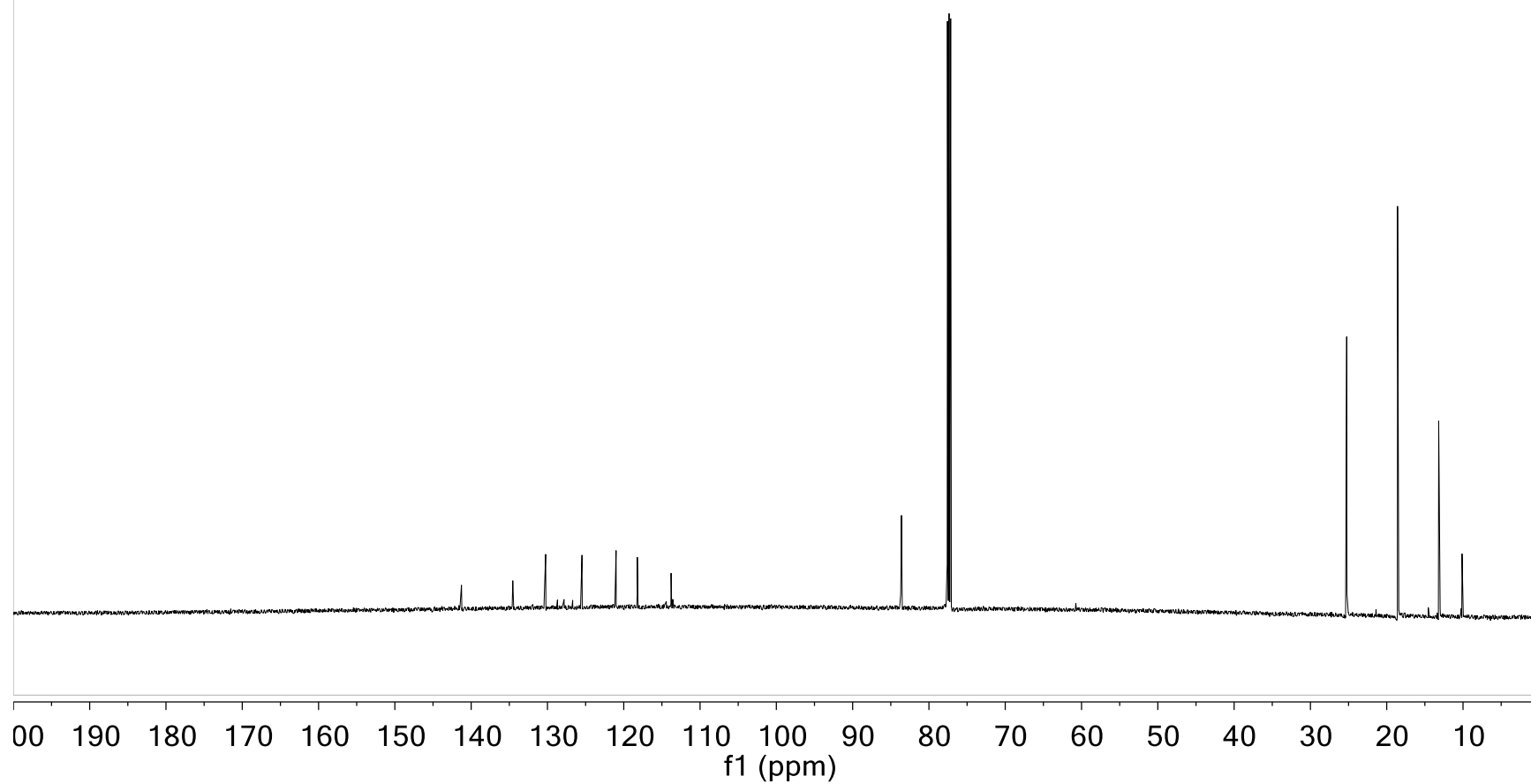


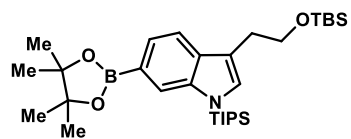
8a (in CDCl₃, 600 MHz, containing inseparable C5-borylated product)



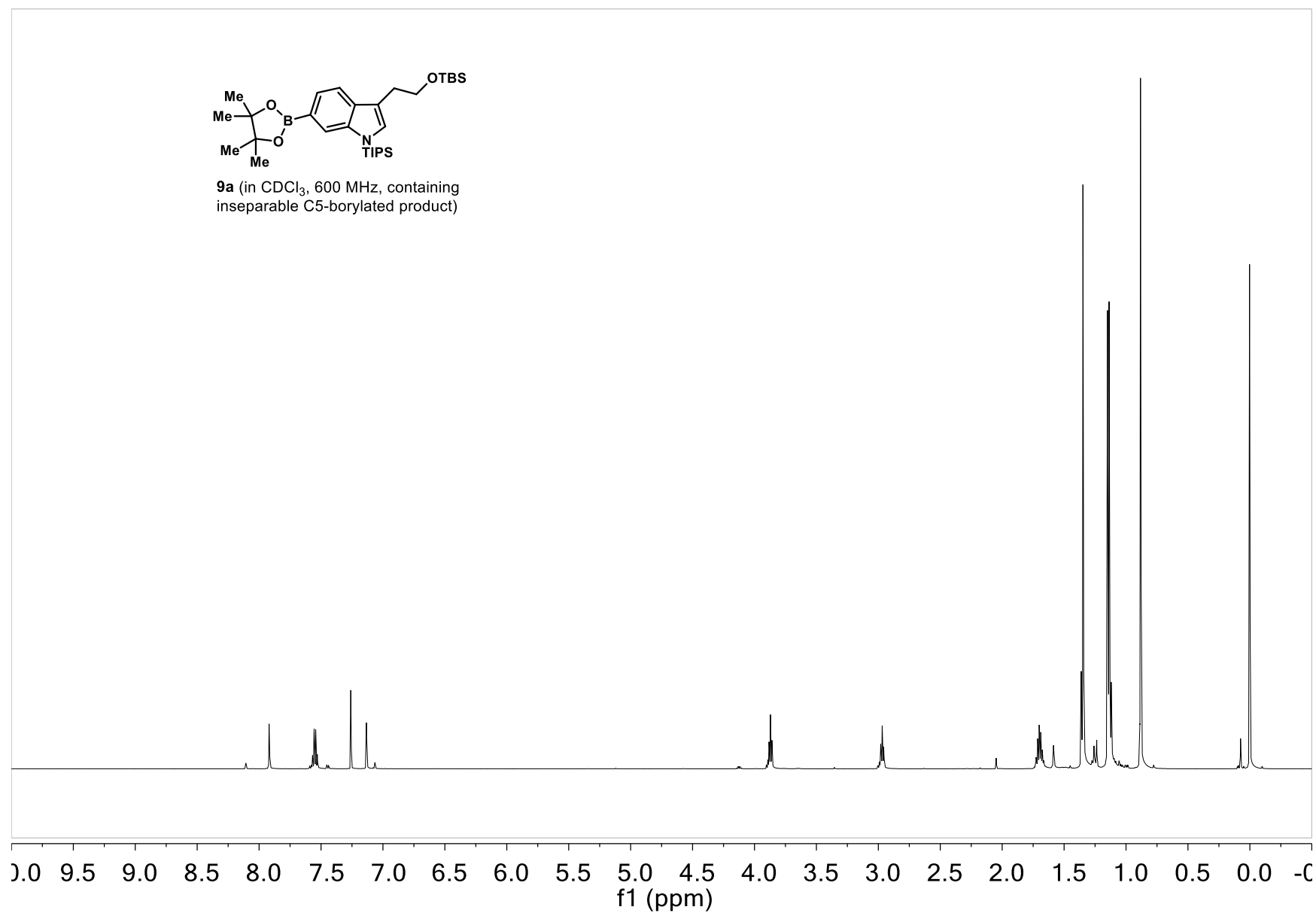


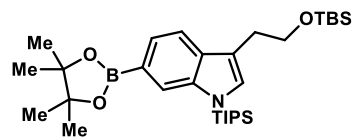
8a (in CDCl₃, 151 MHz, containing inseparable C5-borylated product)



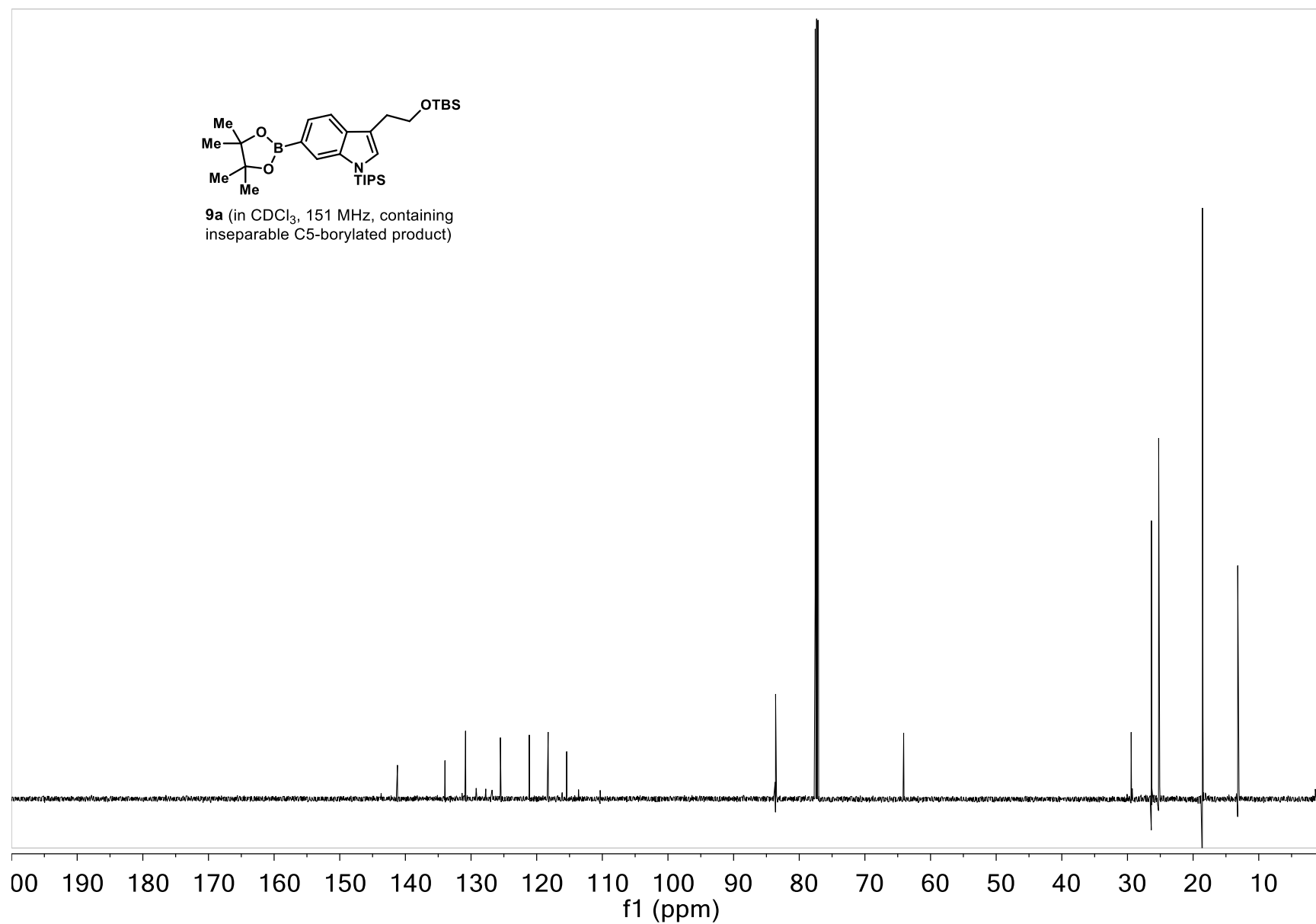


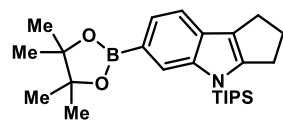
9a (in CDCl₃, 600 MHz, containing inseparable C5-borylated product)



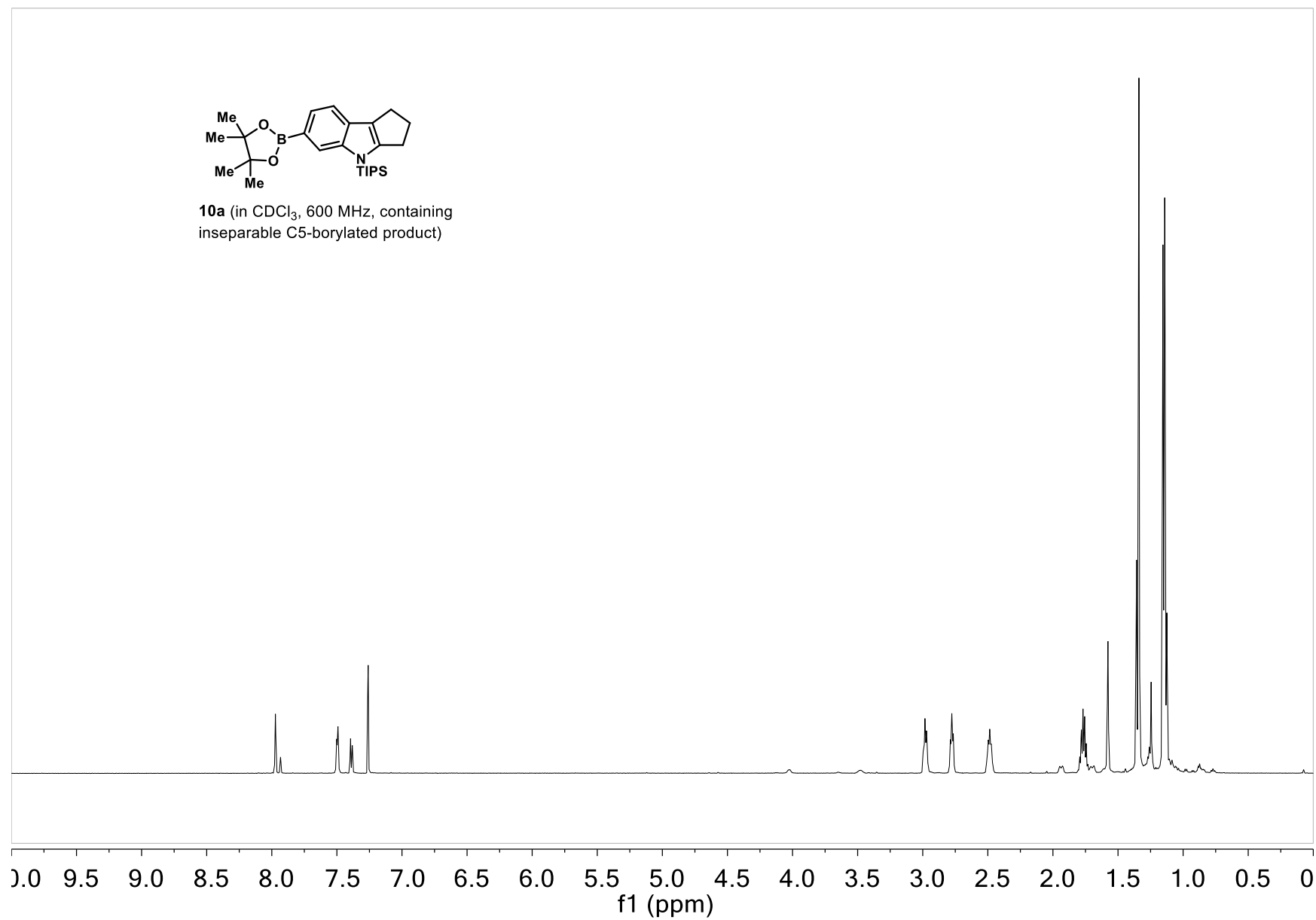


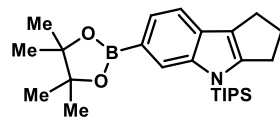
9a (in CDCl₃, 151 MHz, containing inseparable C5-borylated product)



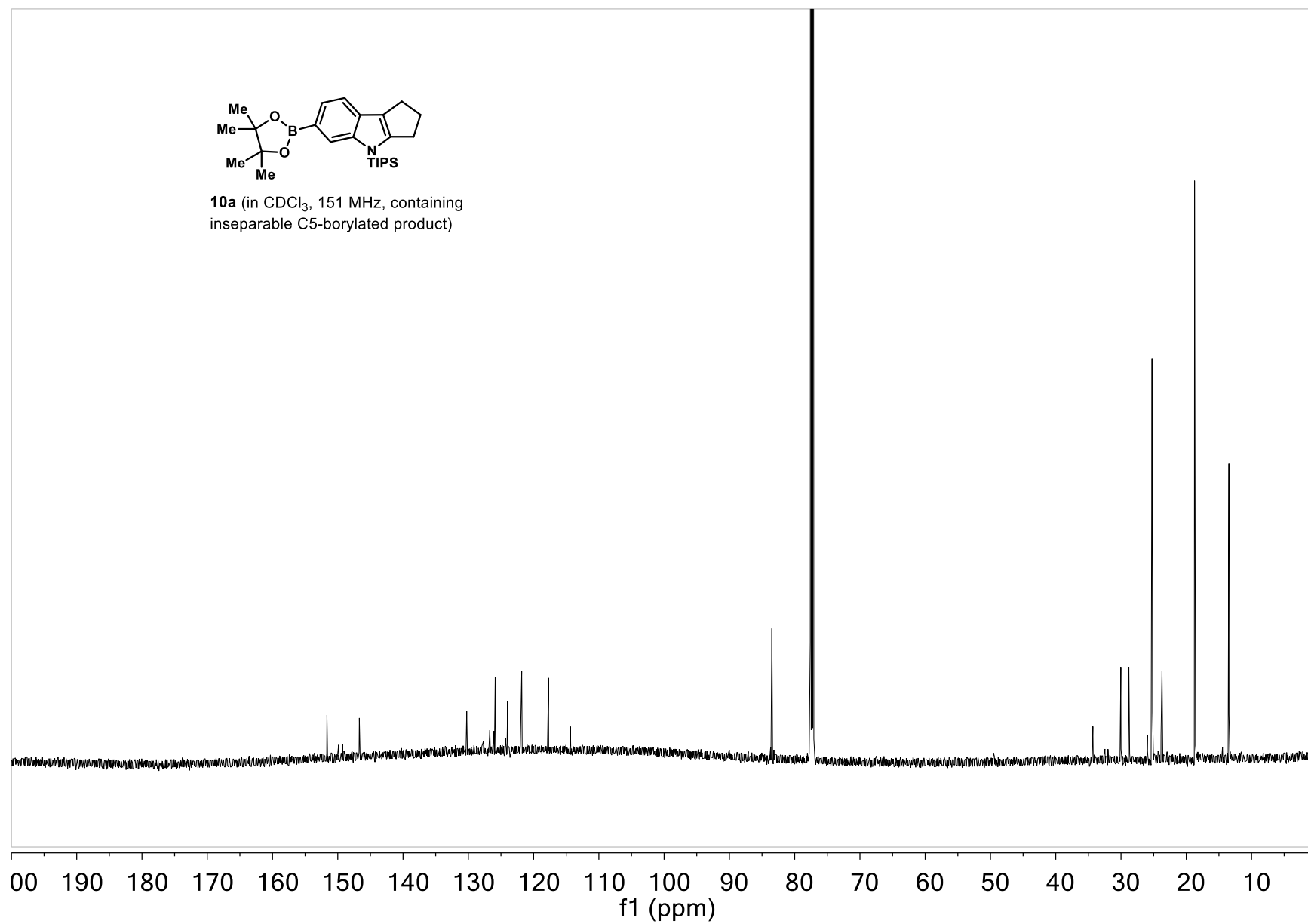


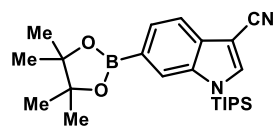
10a (in CDCl₃, 600 MHz, containing inseparable C5-borylated product)



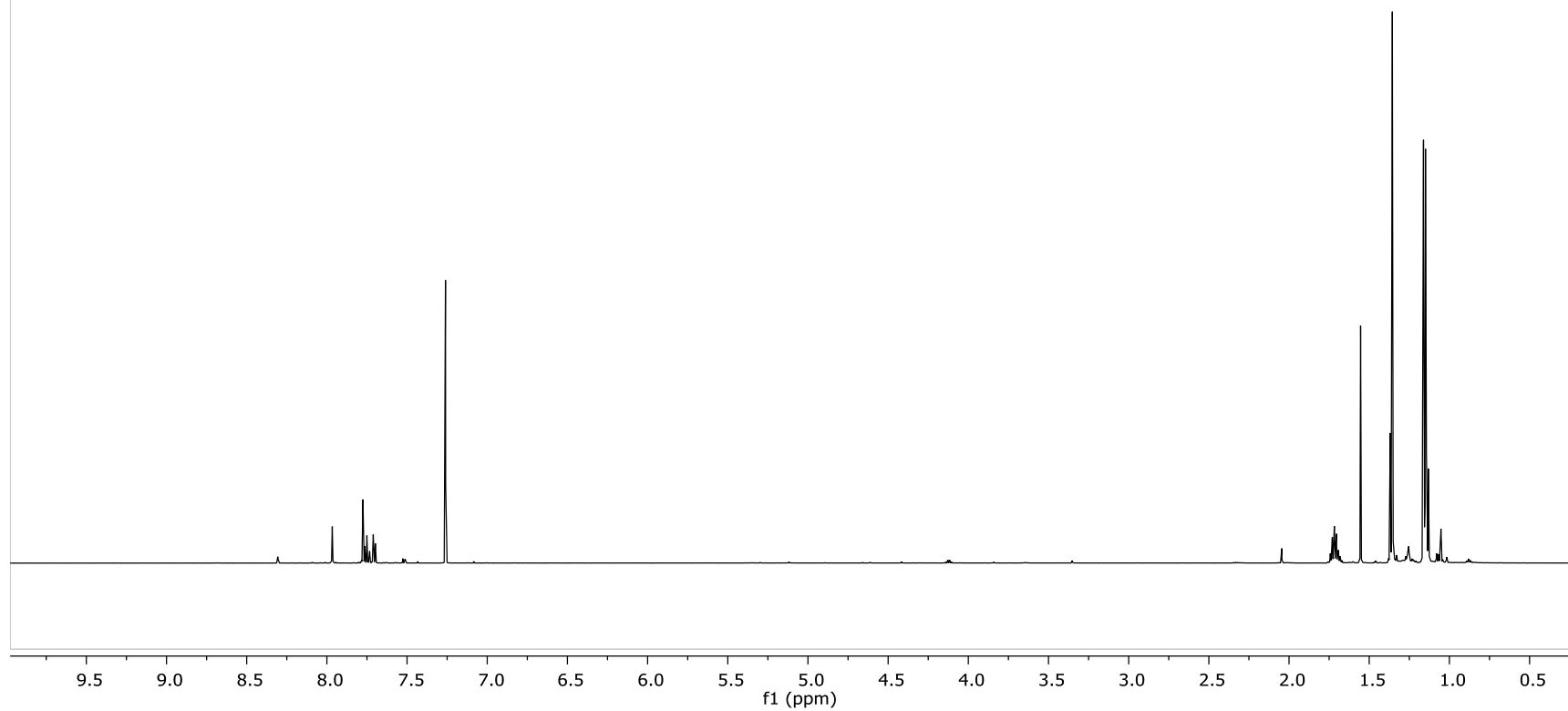


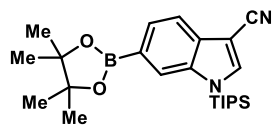
10a (in CDCl₃, 151 MHz, containing inseparable C5-borylated product)



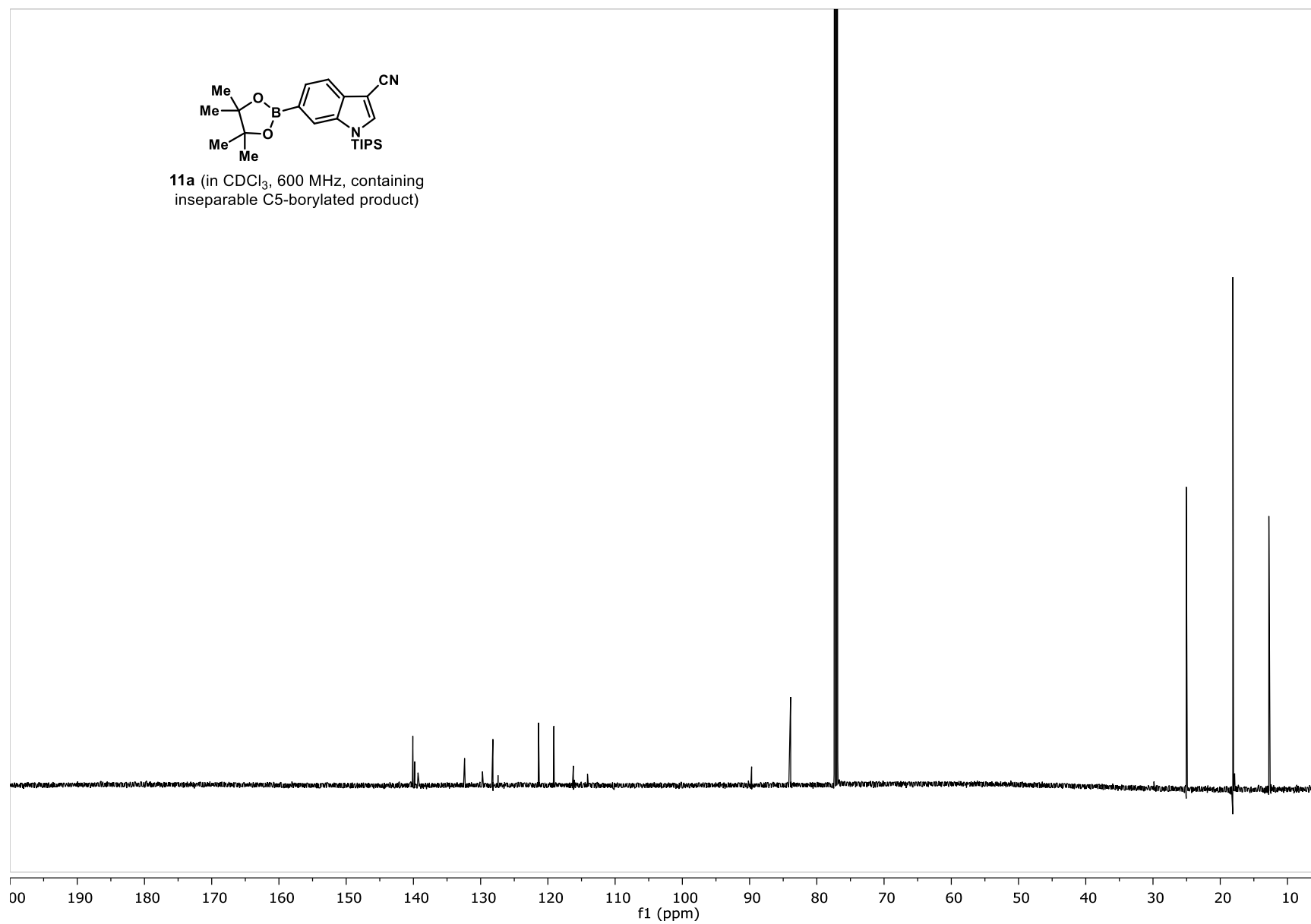


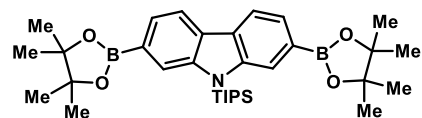
11a (in CDCl₃, 151 MHz, containing inseparable C5-borylated product)



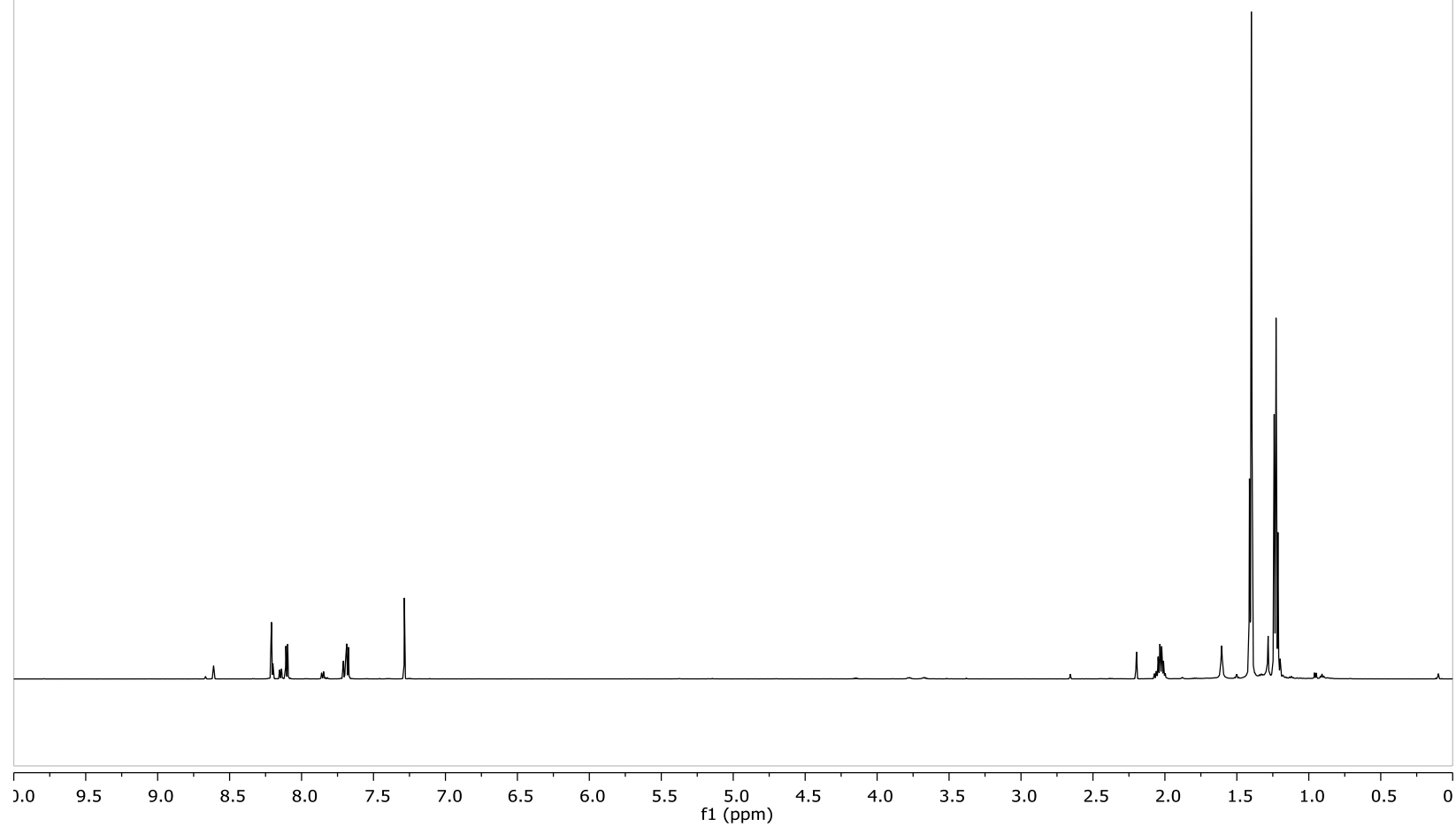


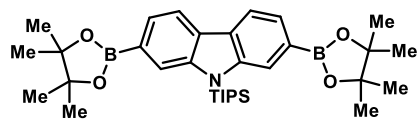
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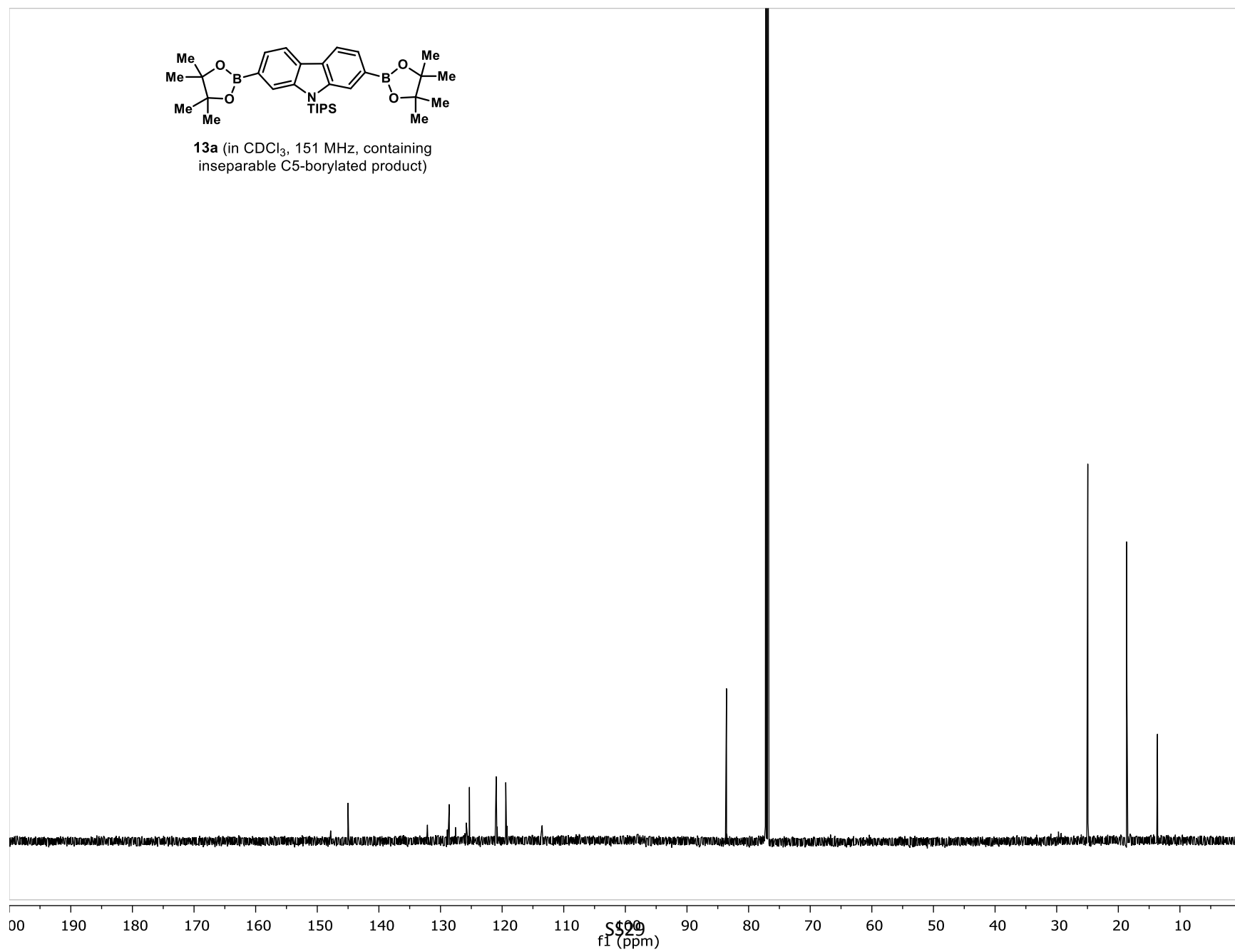


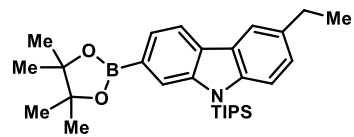
13a (in CDCl₃, 600 MHz, containing inseparable C5-borylated product)



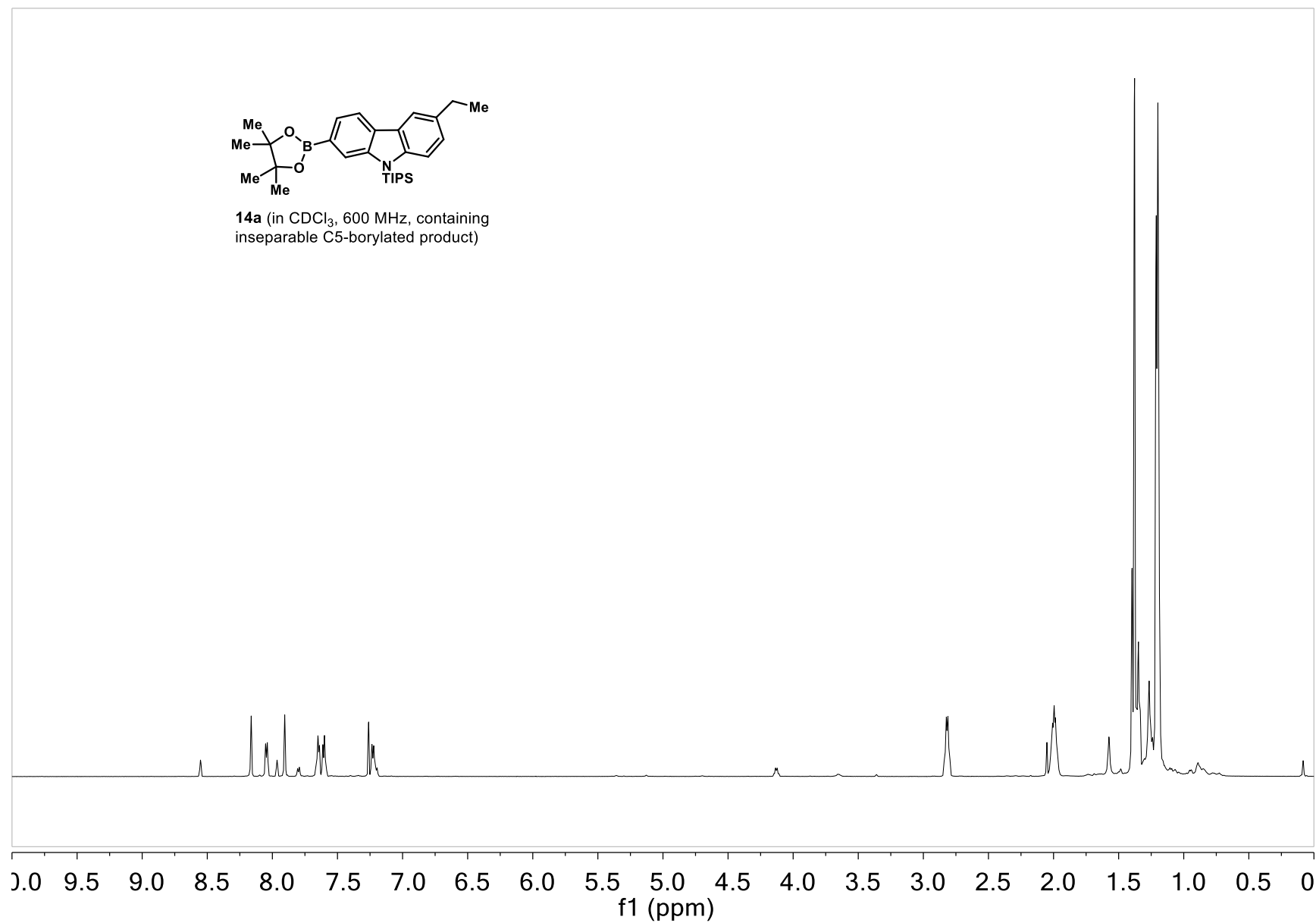


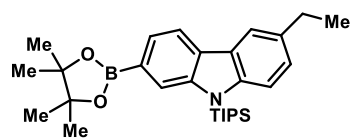
13a (in CDCl₃, 151 MHz, containing inseparable C5-borylated product)



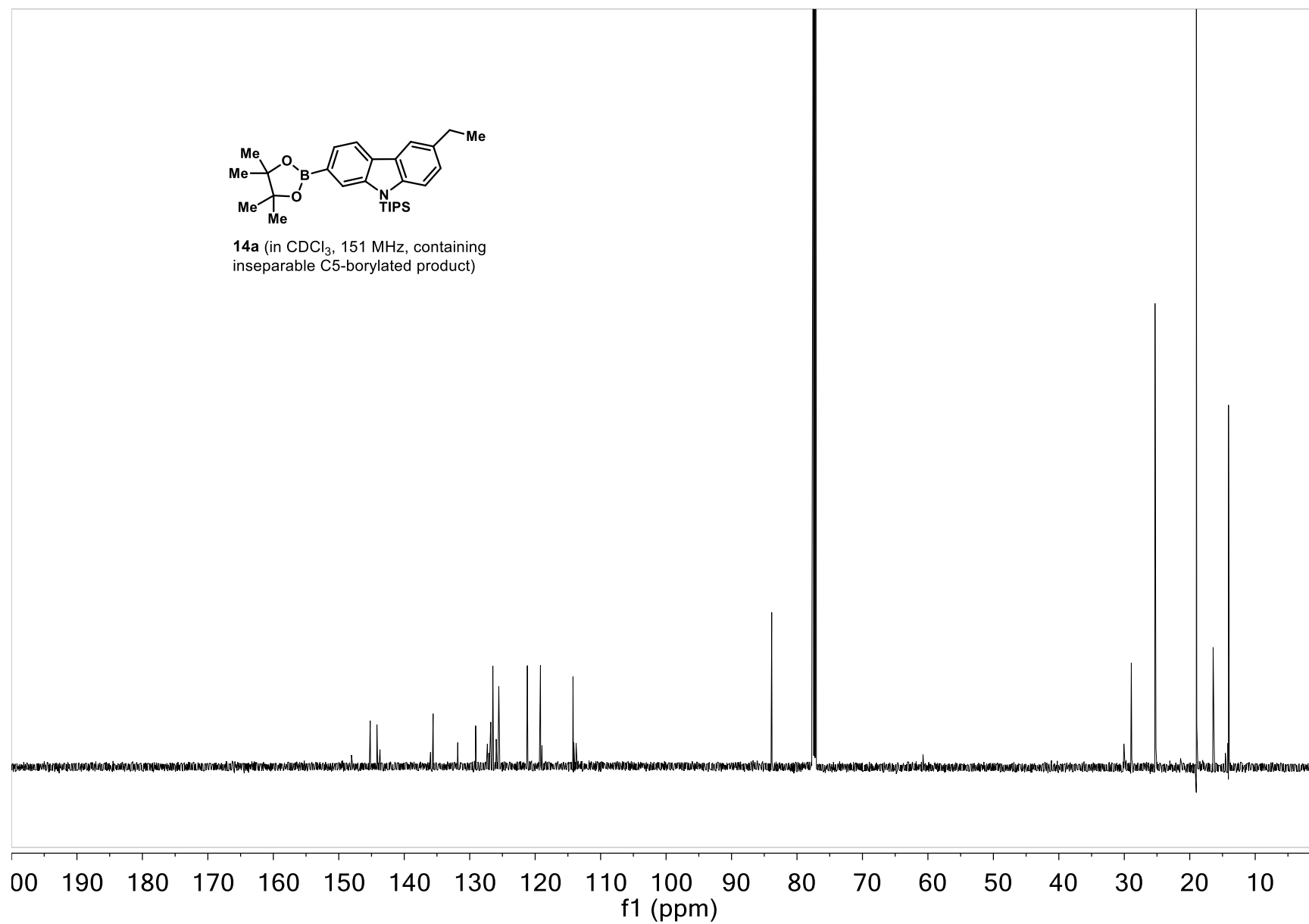


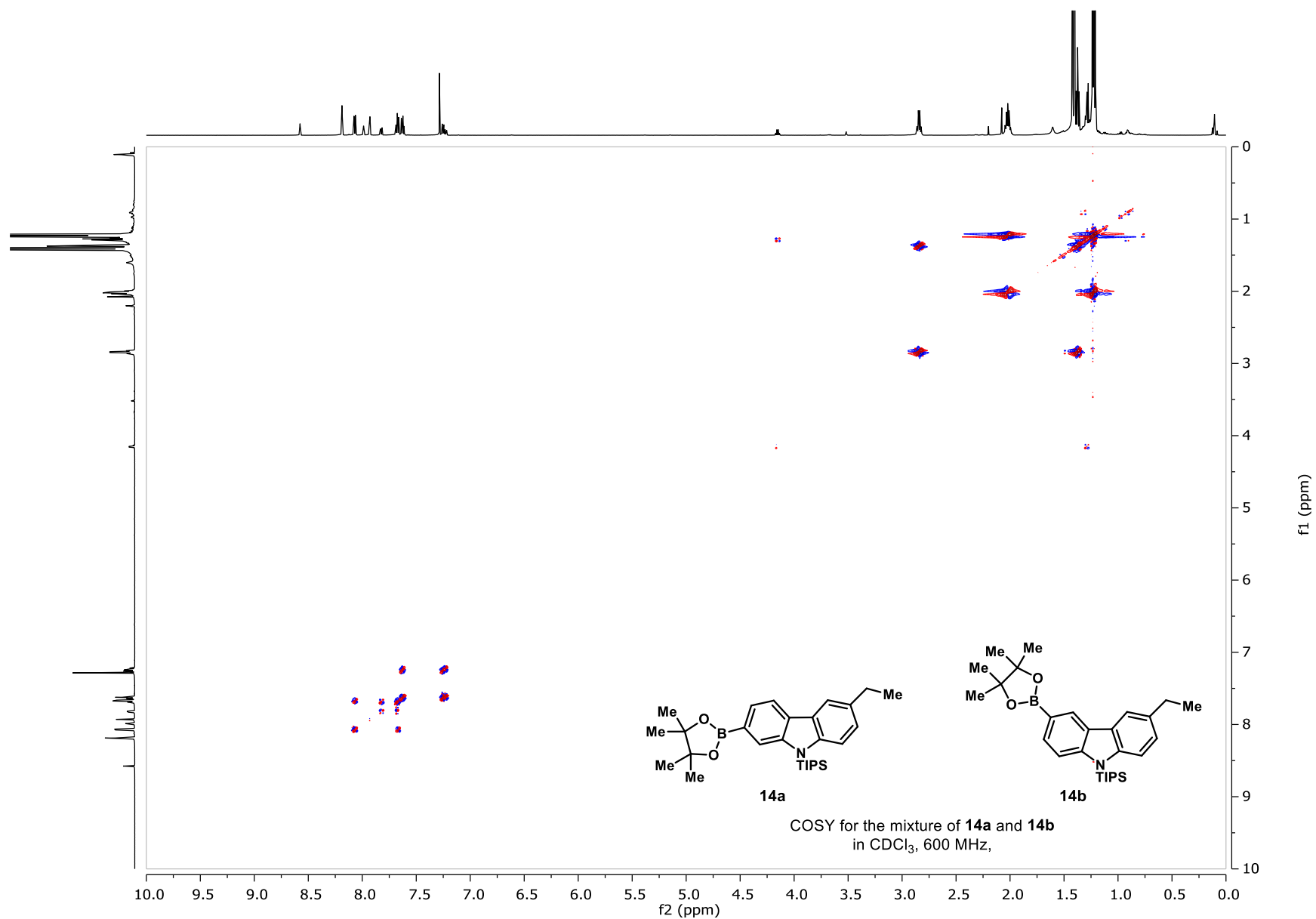
14a (in CDCl₃, 600 MHz, containing inseparable C5-borylated product)

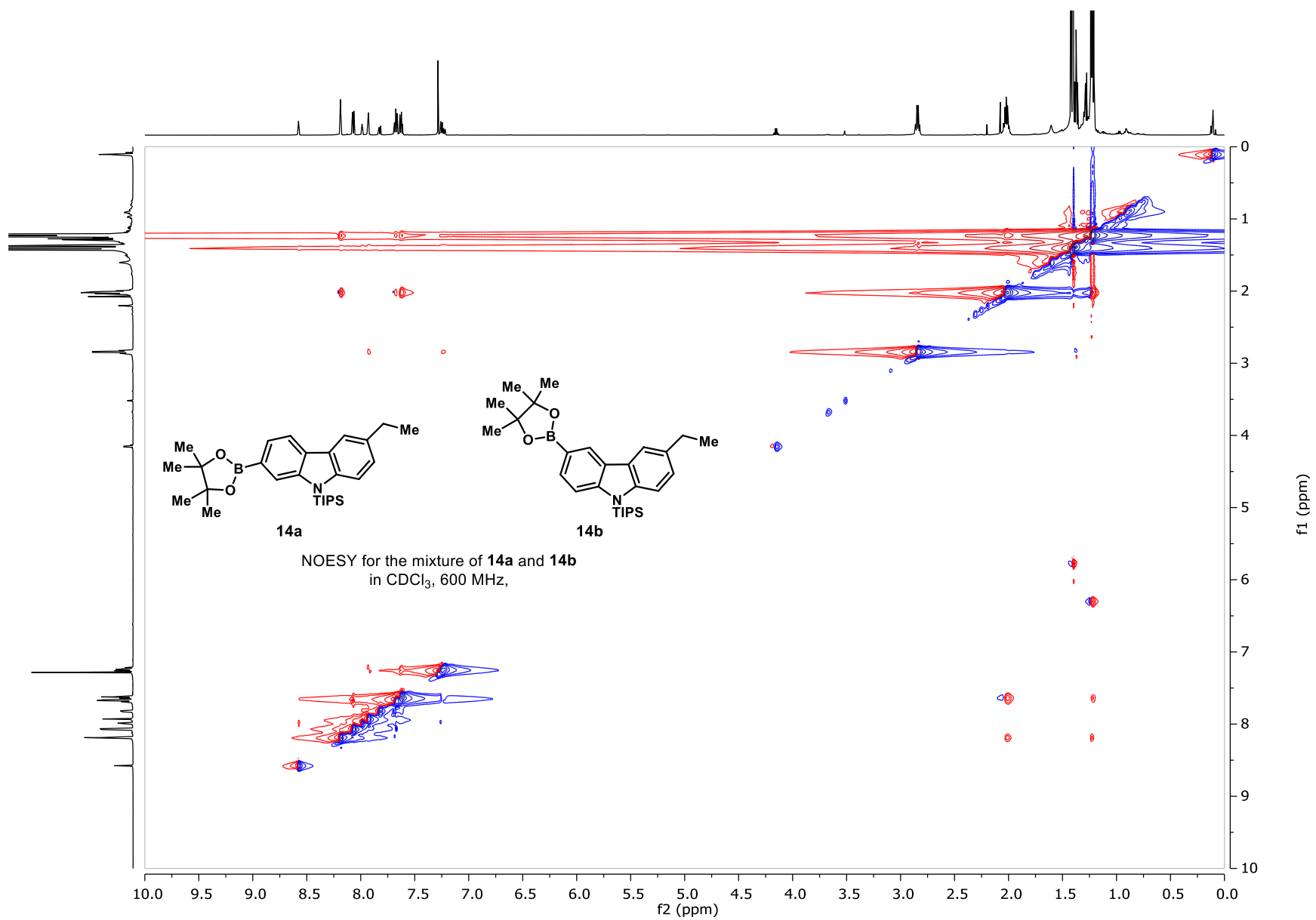


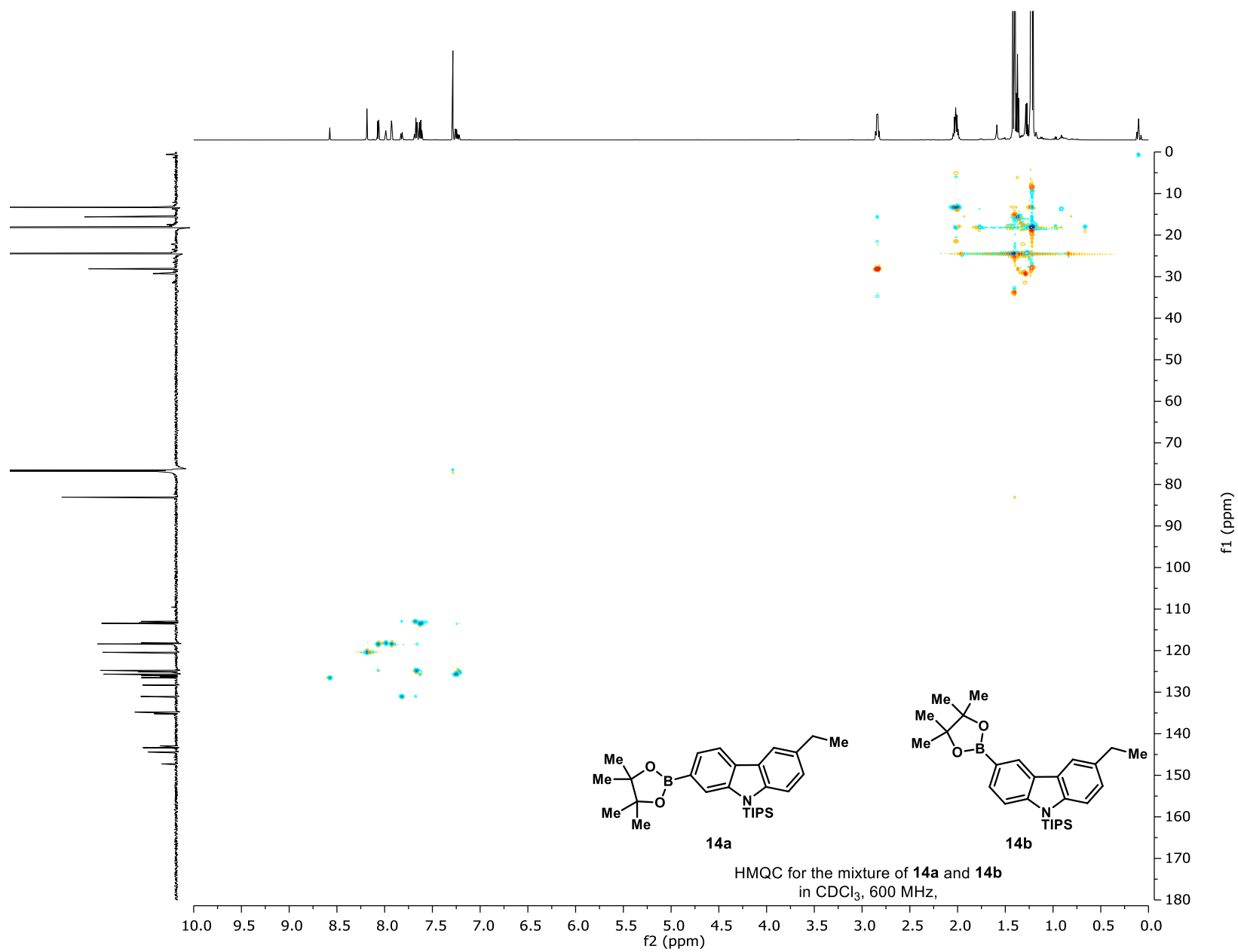


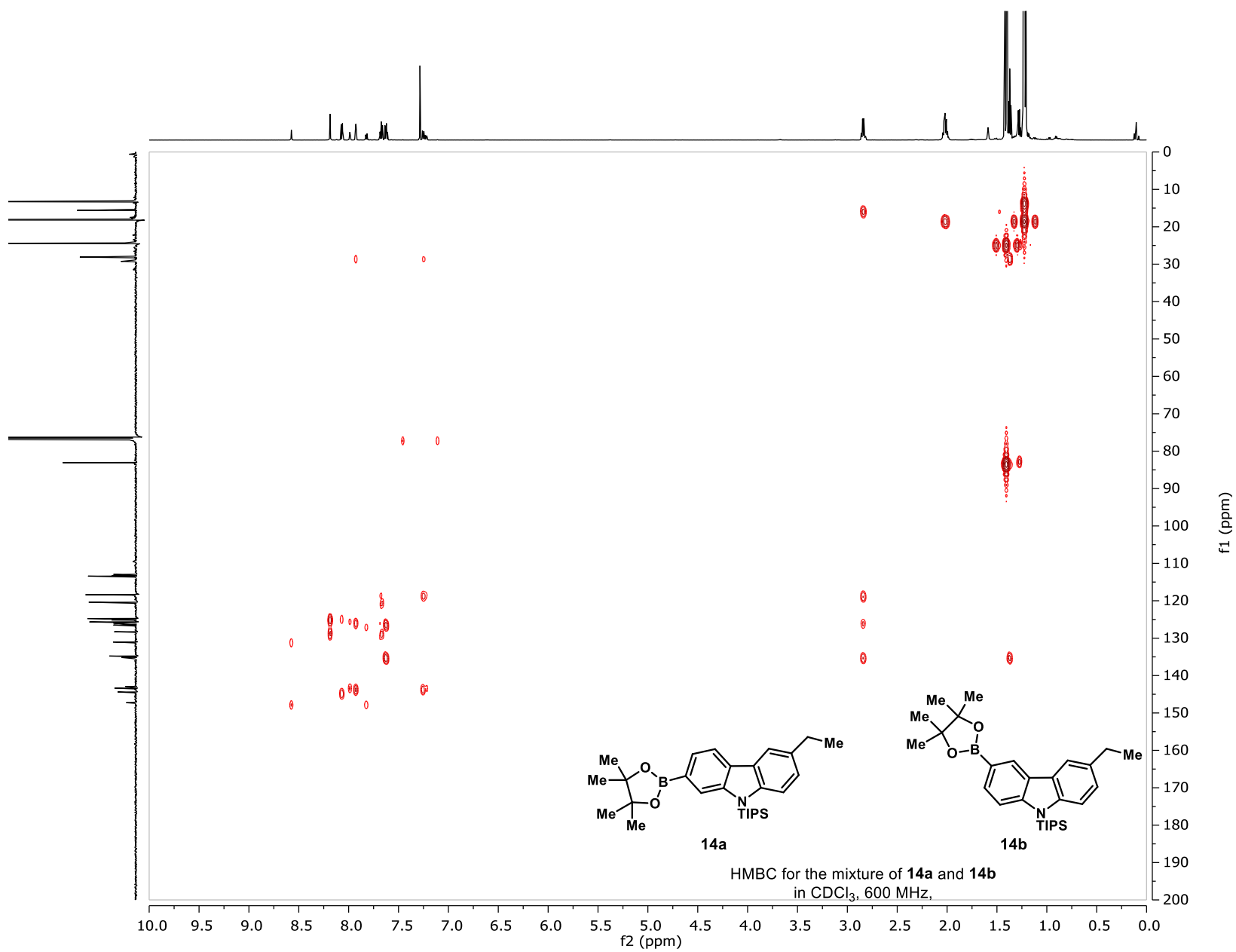
14a (in CDCl₃, 151 MHz, containing inseparable C5-borylated product)

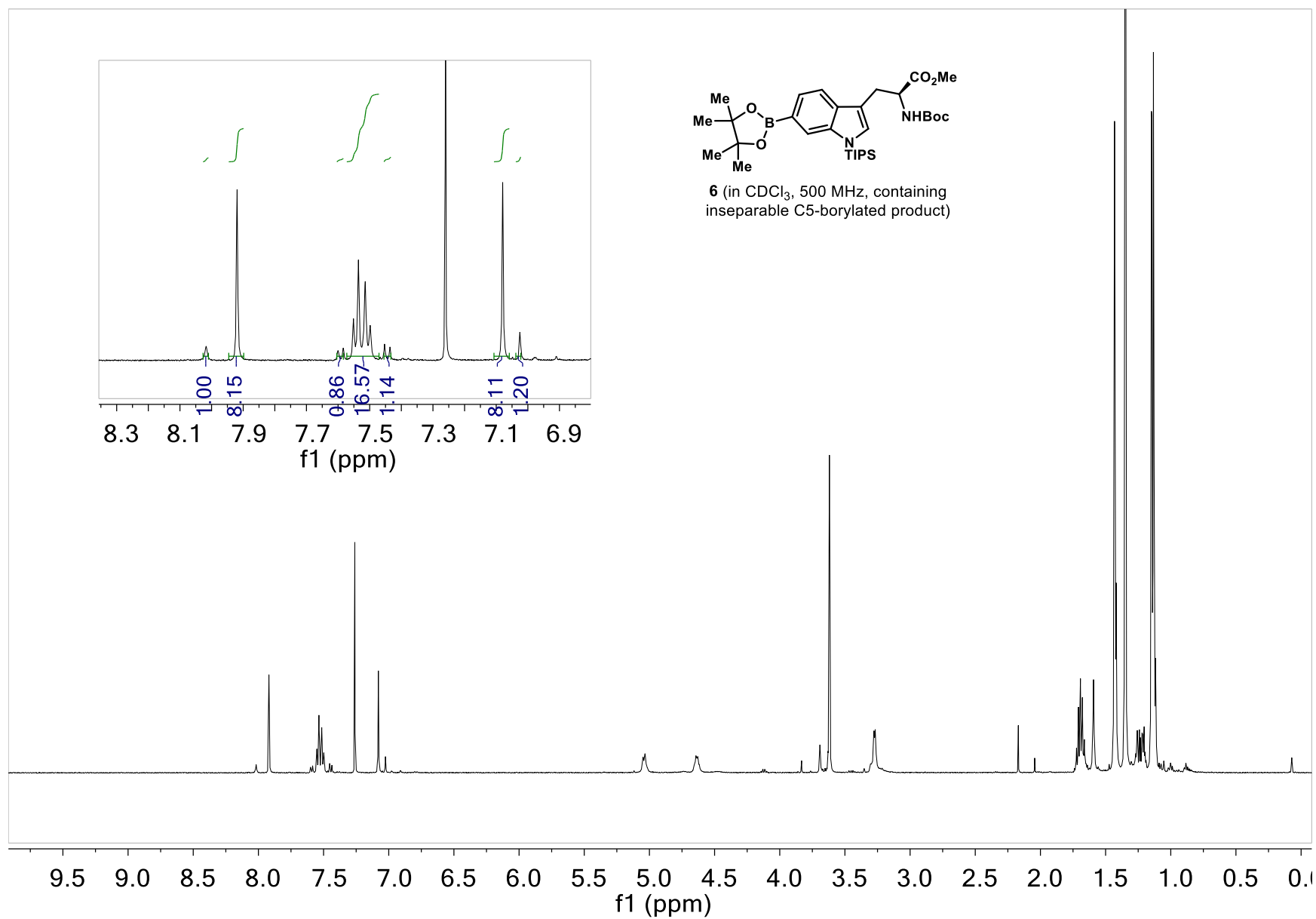


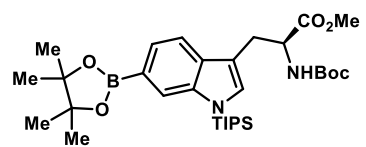




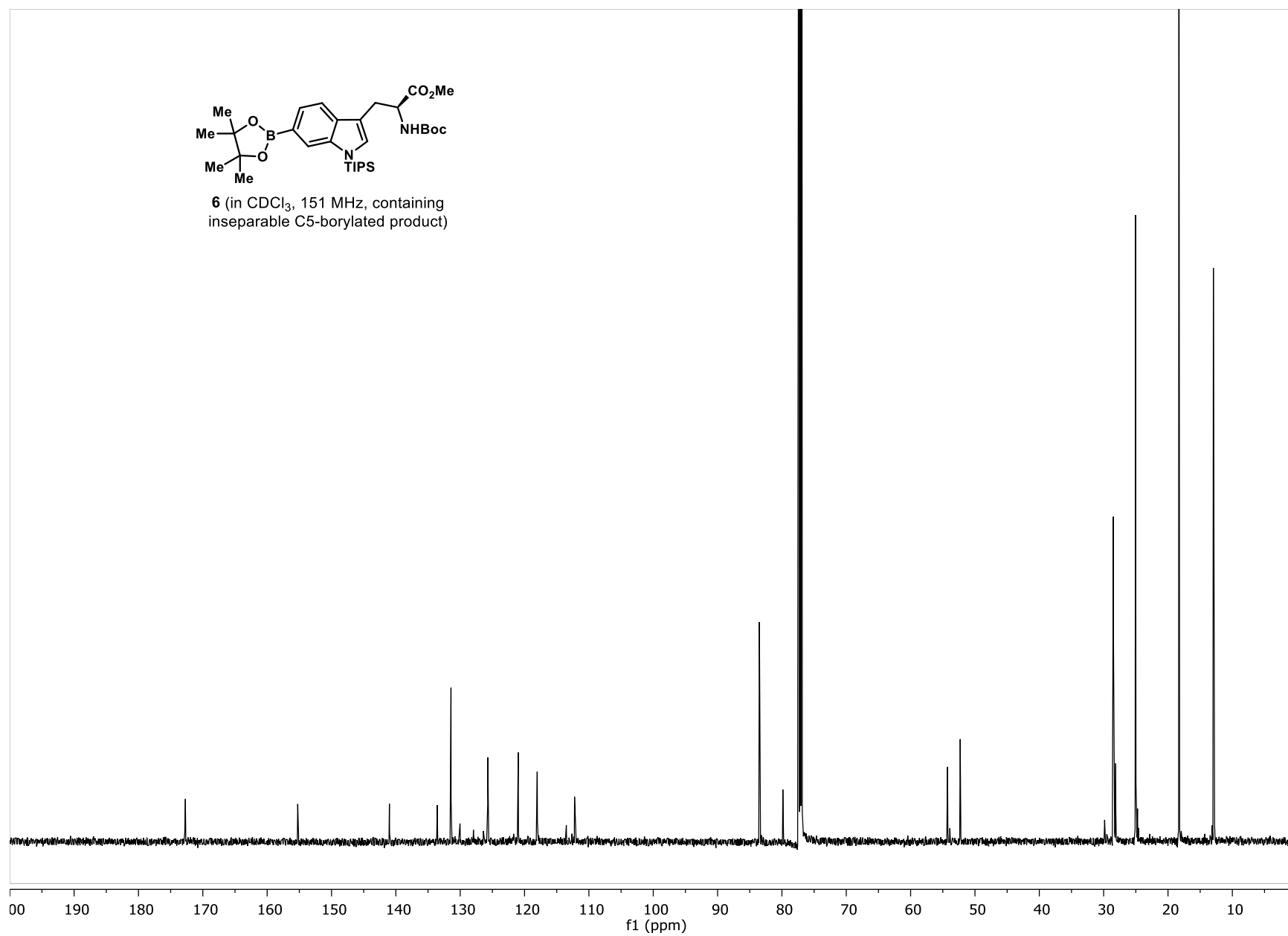




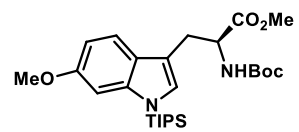




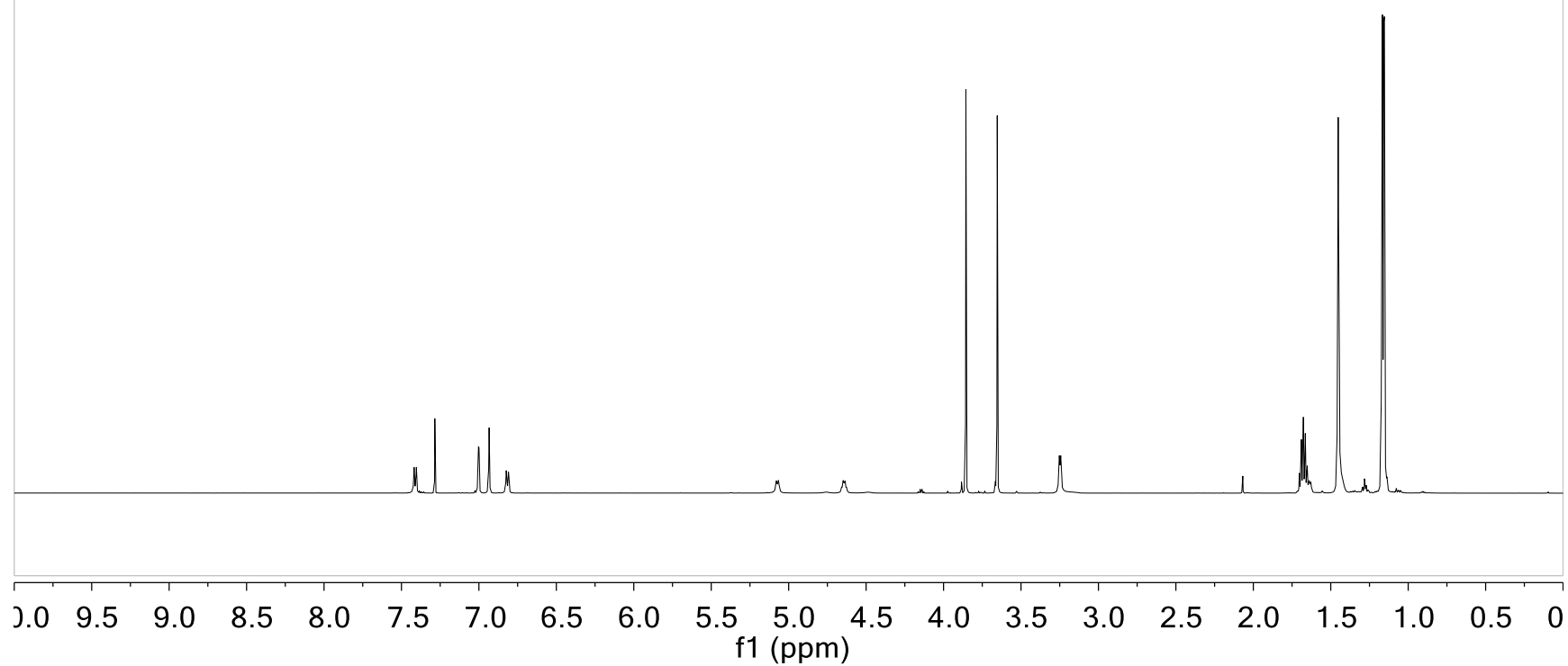
6 (in CDCl₃, 151 MHz, containing inseparable C5-borylated product)



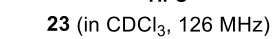
SS37

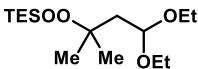


23 (in CDCl₃, 500 MHz)

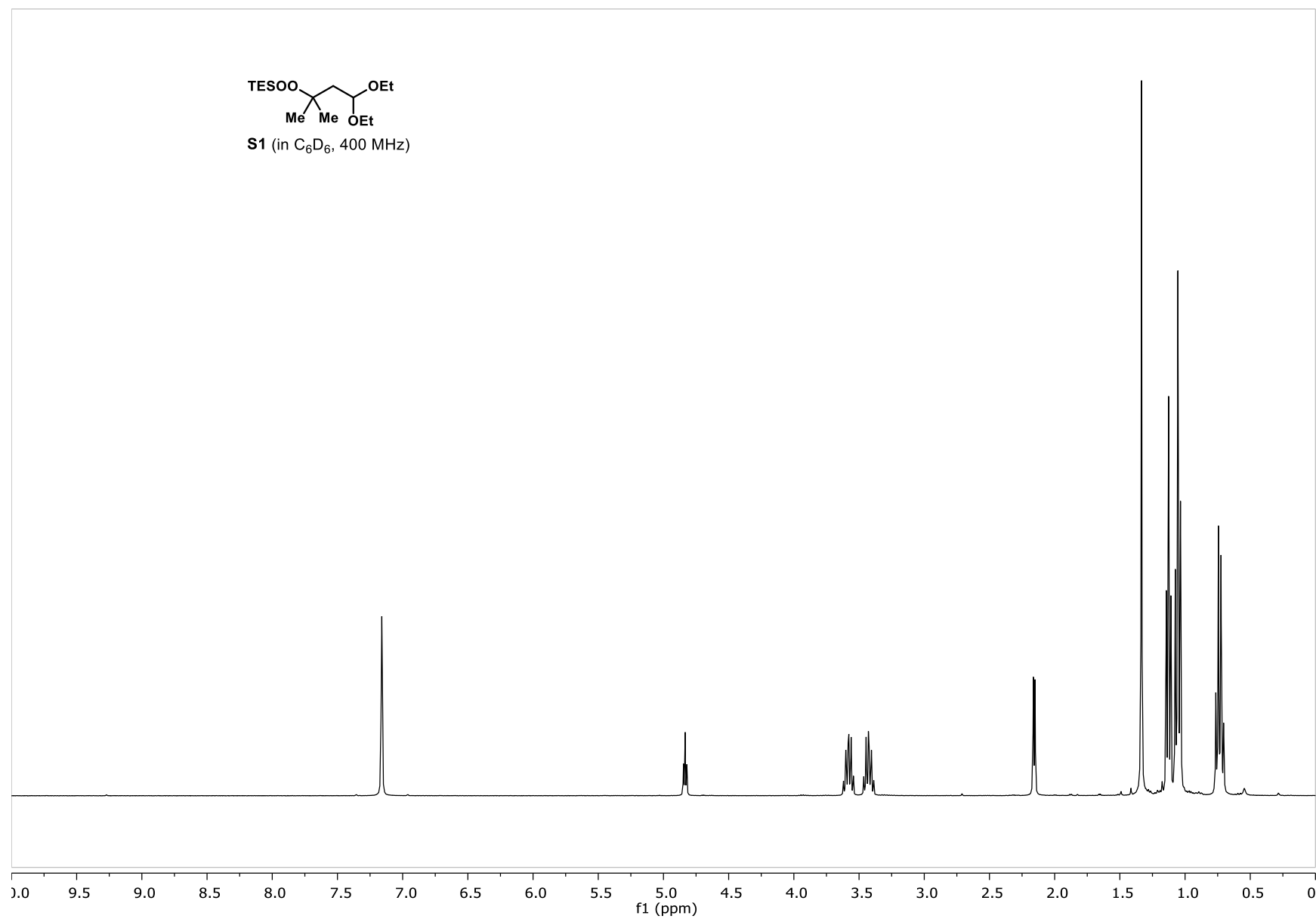


SS38

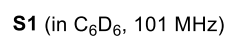


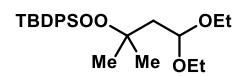


S1 (in C₆D₆, 400 MHz)

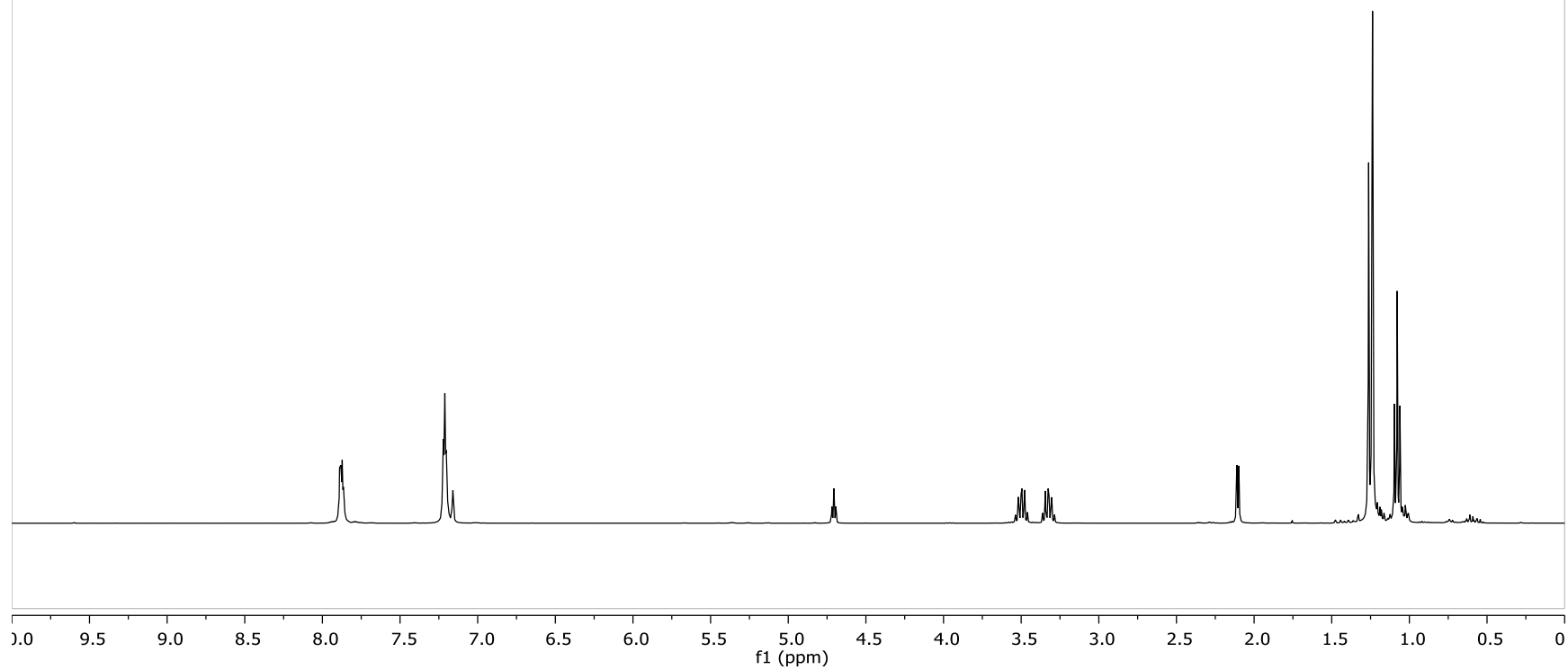


SS40

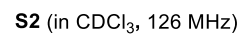


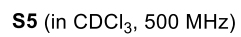


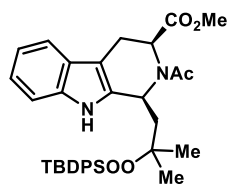
S2 (in CDCl₃, 500 MHz)



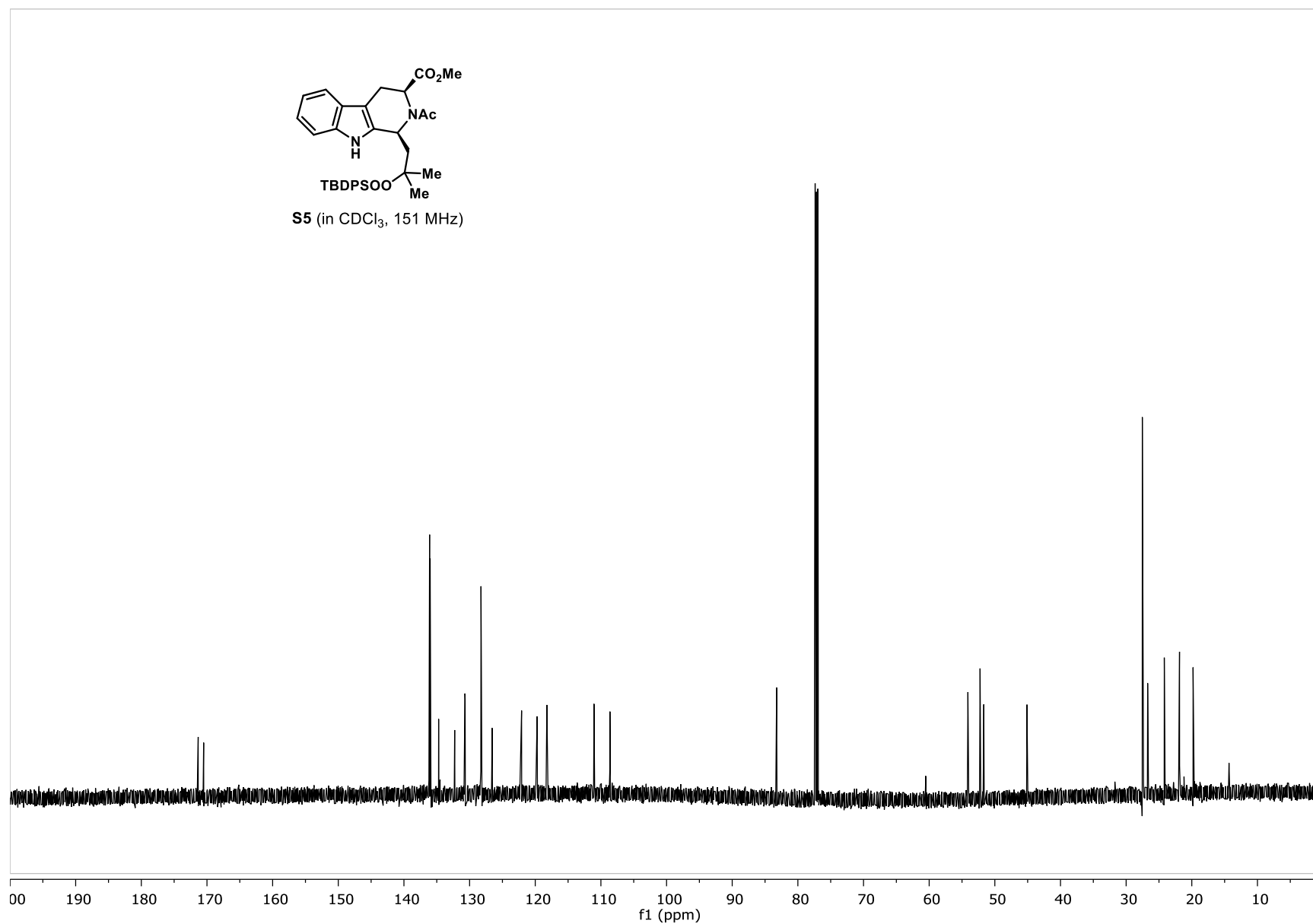
SS42

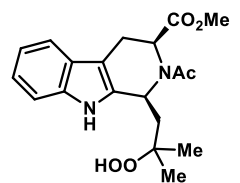




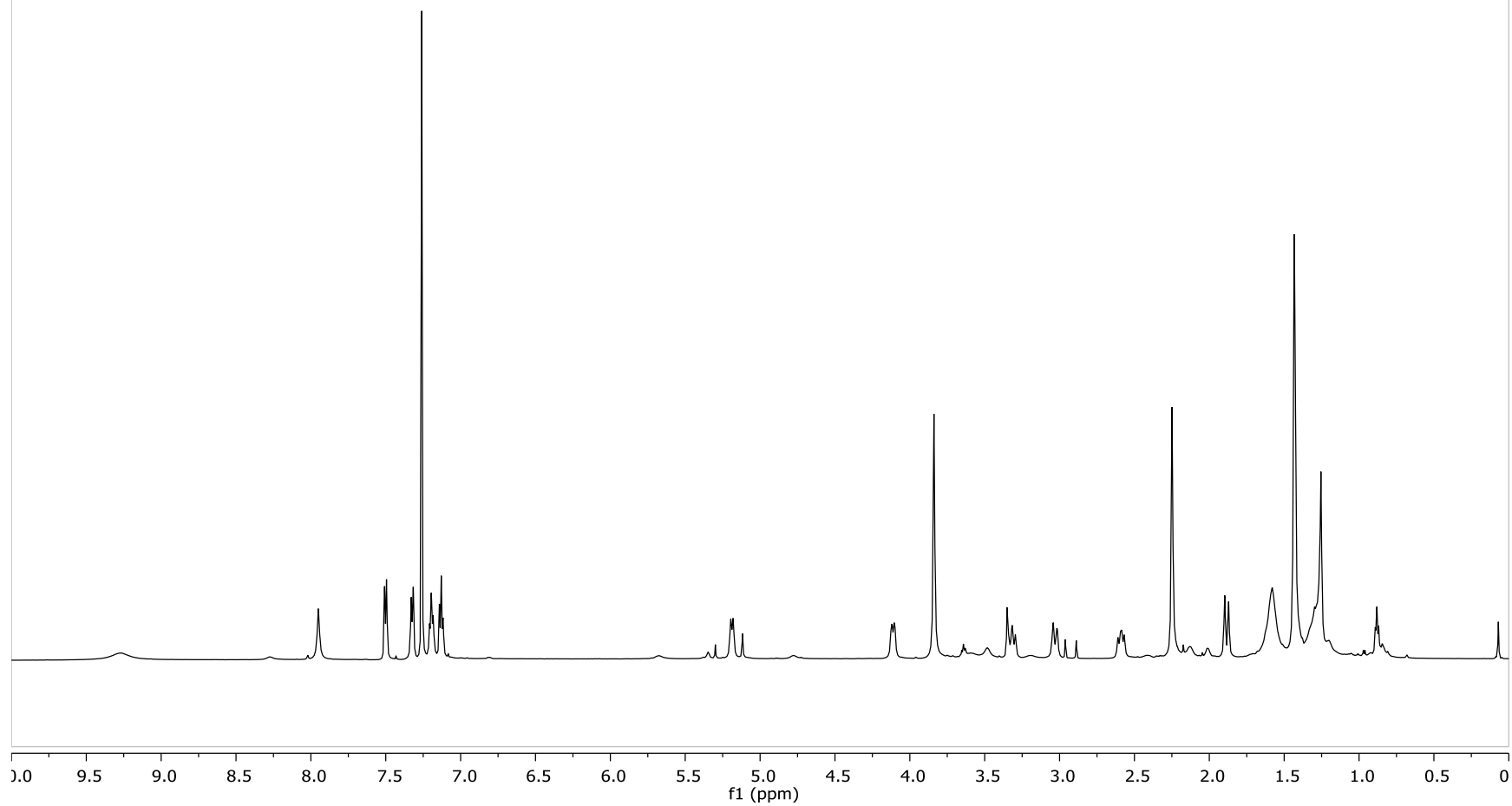


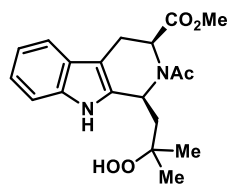
S5 (in CDCl₃, 151 MHz)



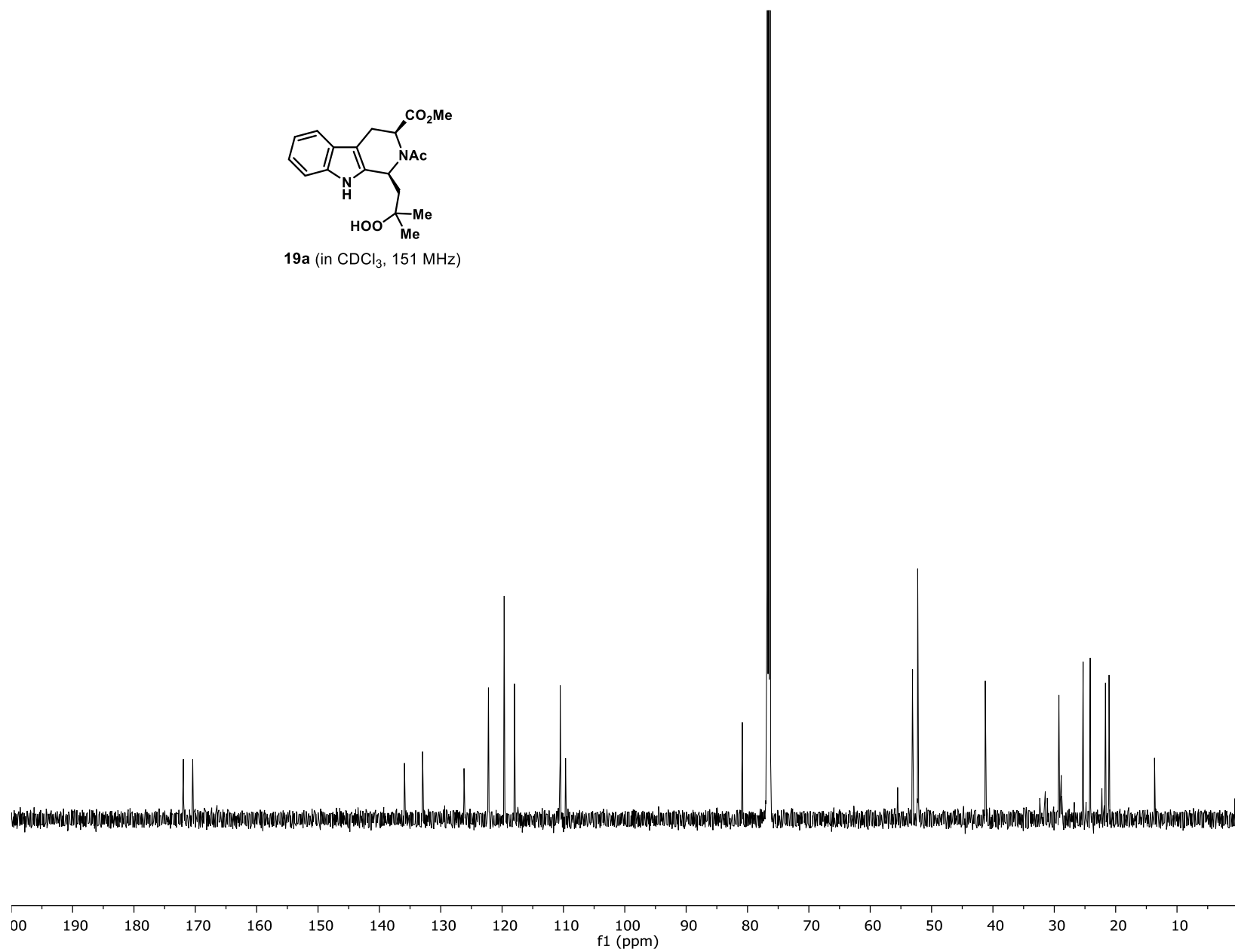


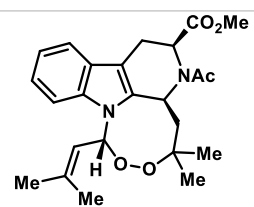
19a (in CDCl₃, 600 MHz)



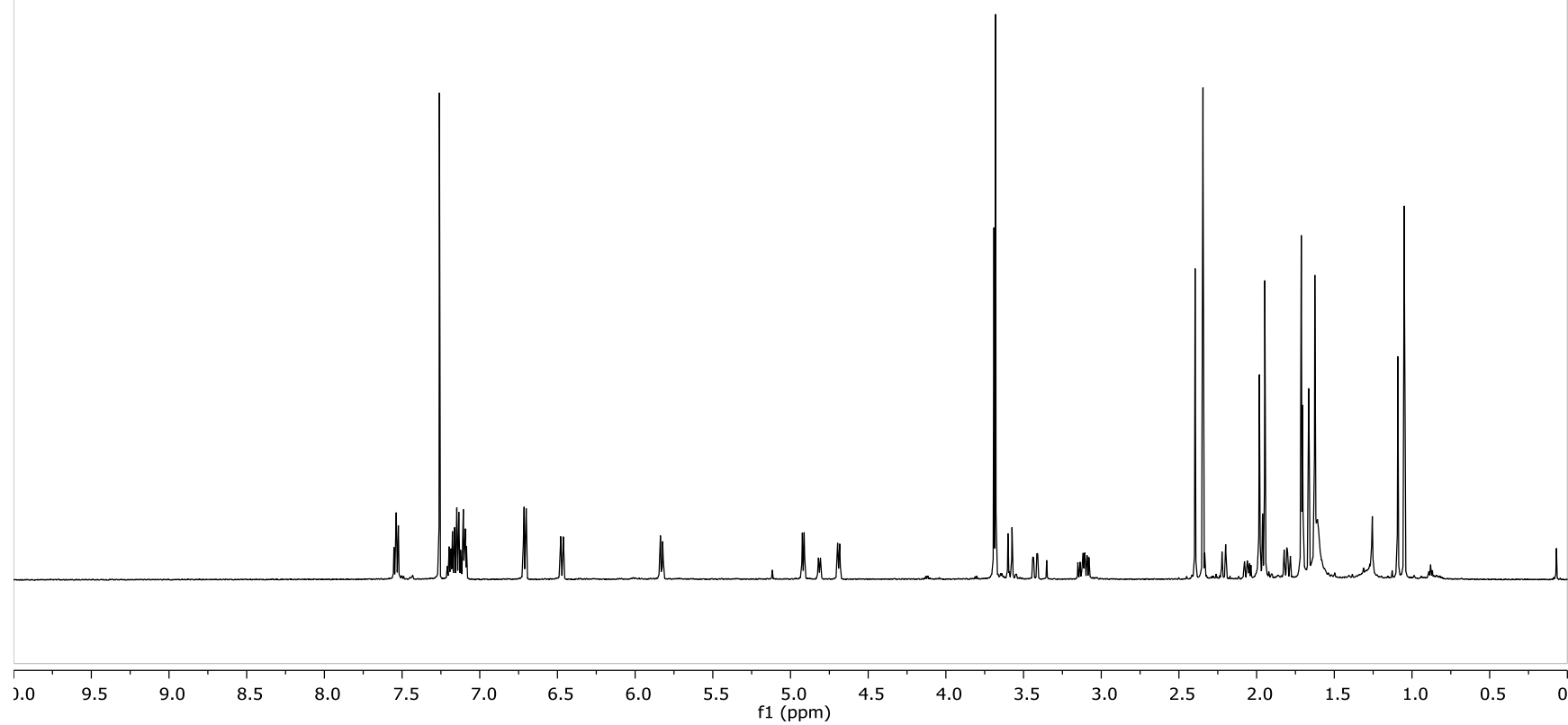


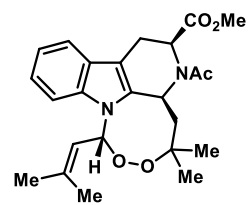
19a (in CDCl₃, 151 MHz)



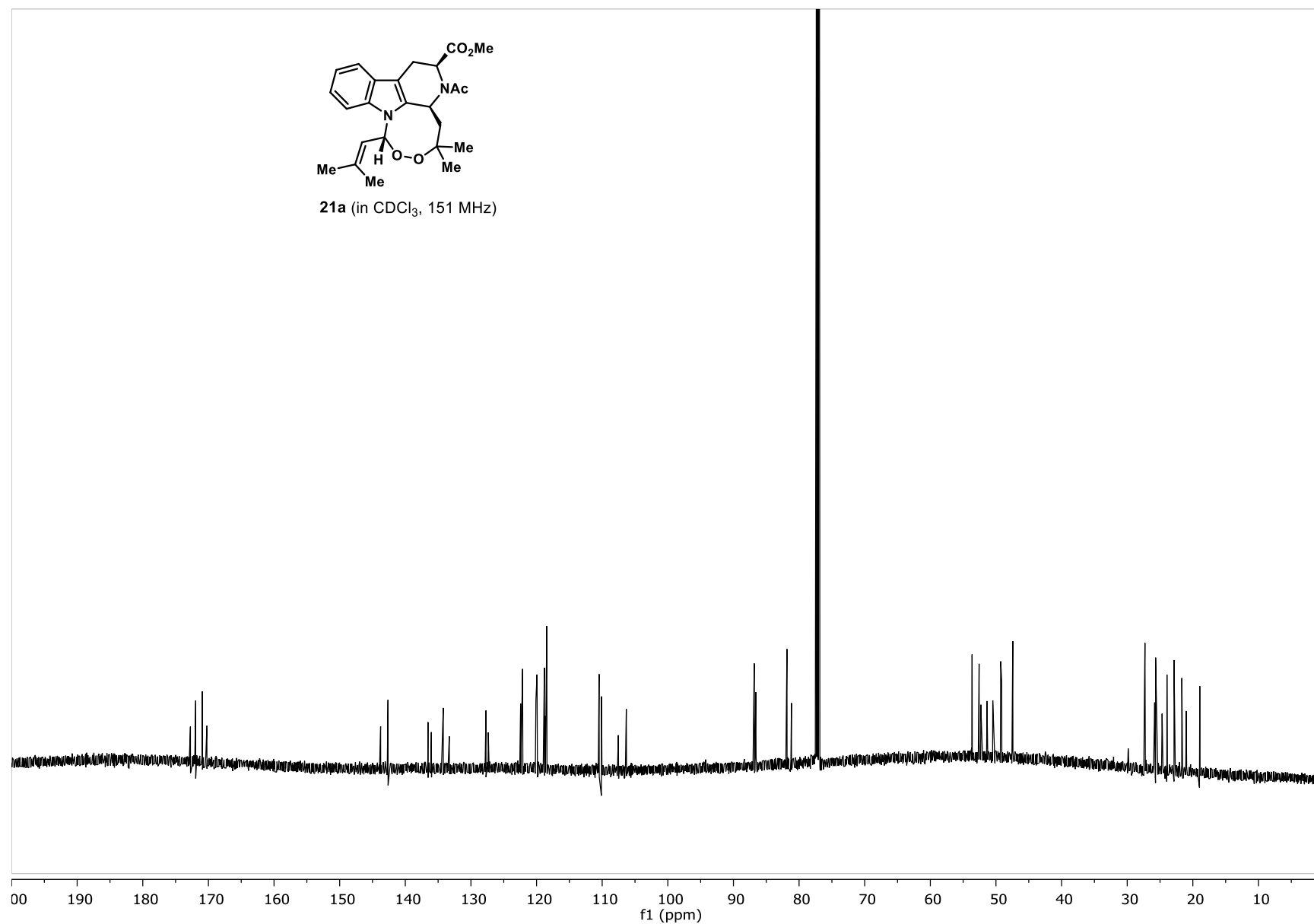


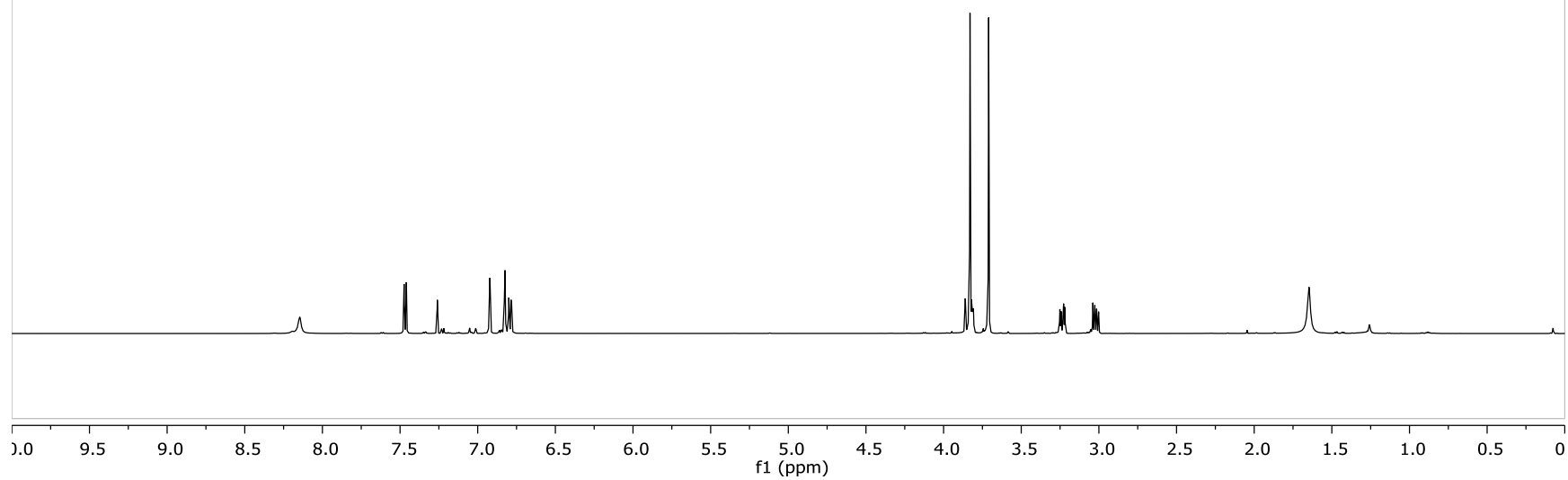
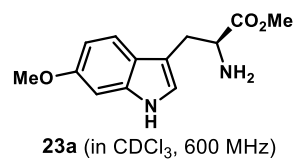
21a (in CDCl₃, 600 MHz)



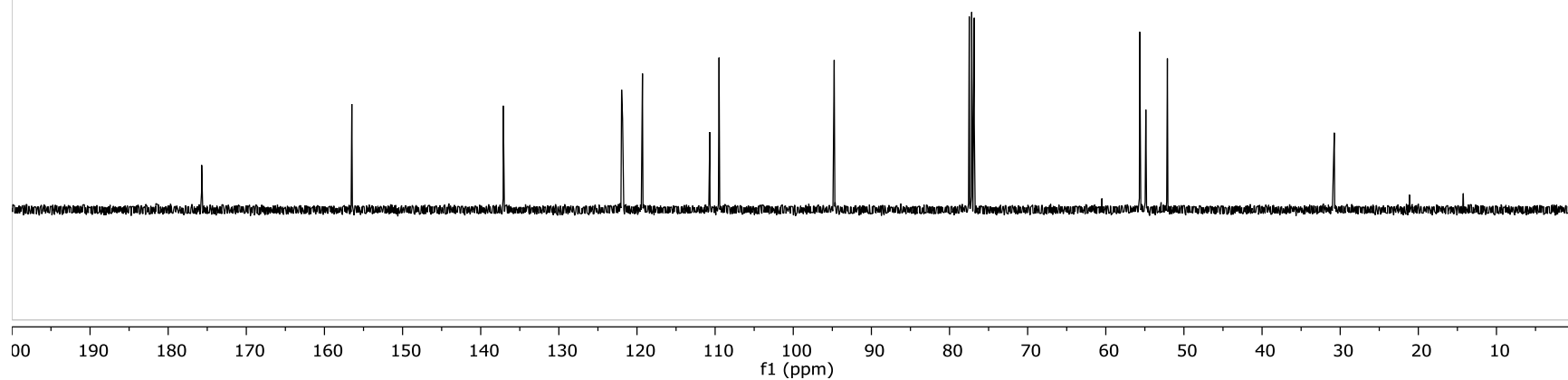
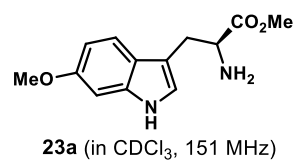


21a (in CDCl₃, 151 MHz)

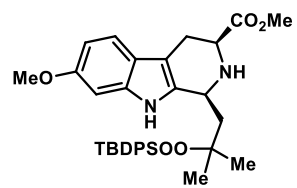




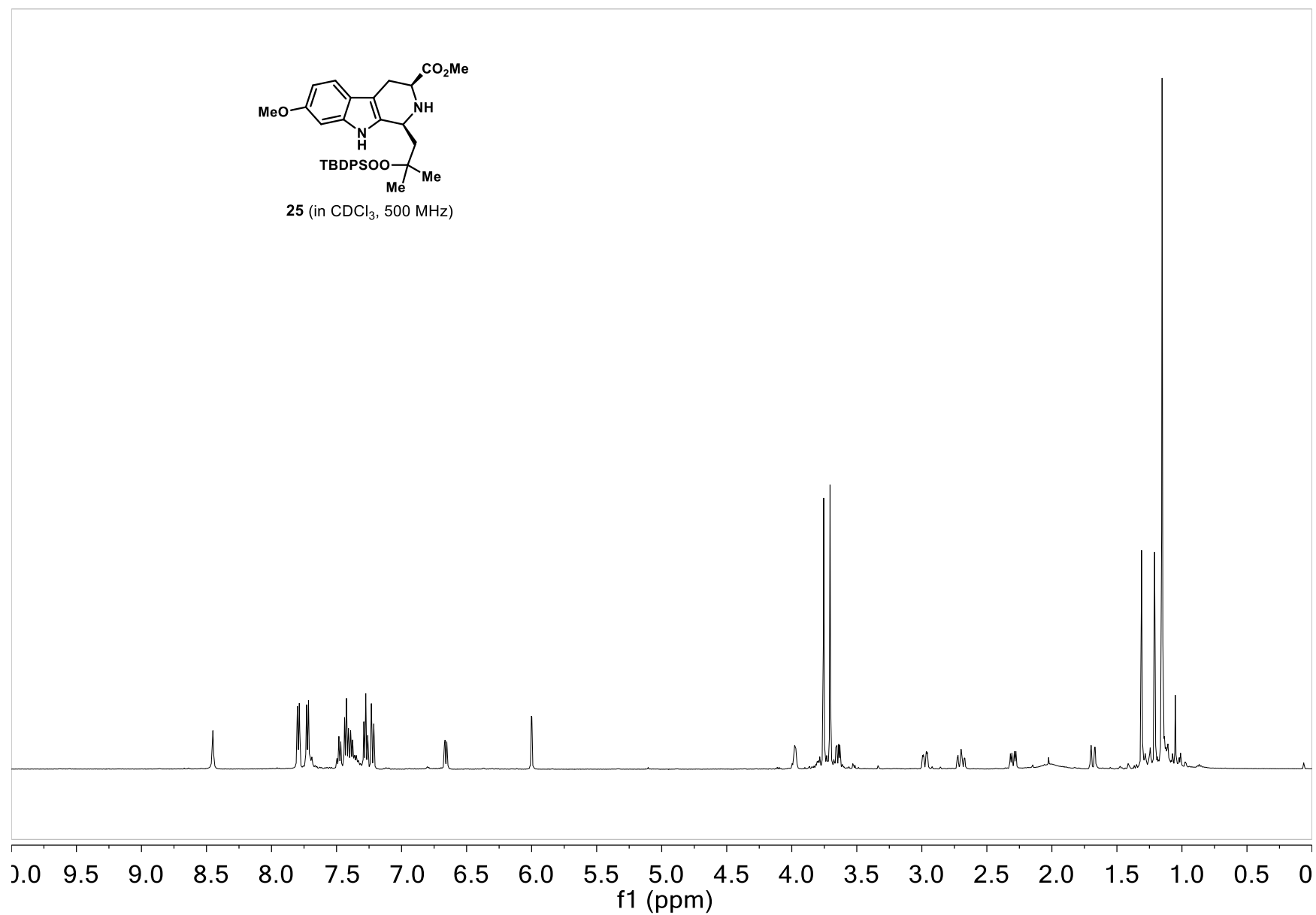
SS50

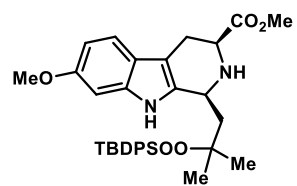


SS51

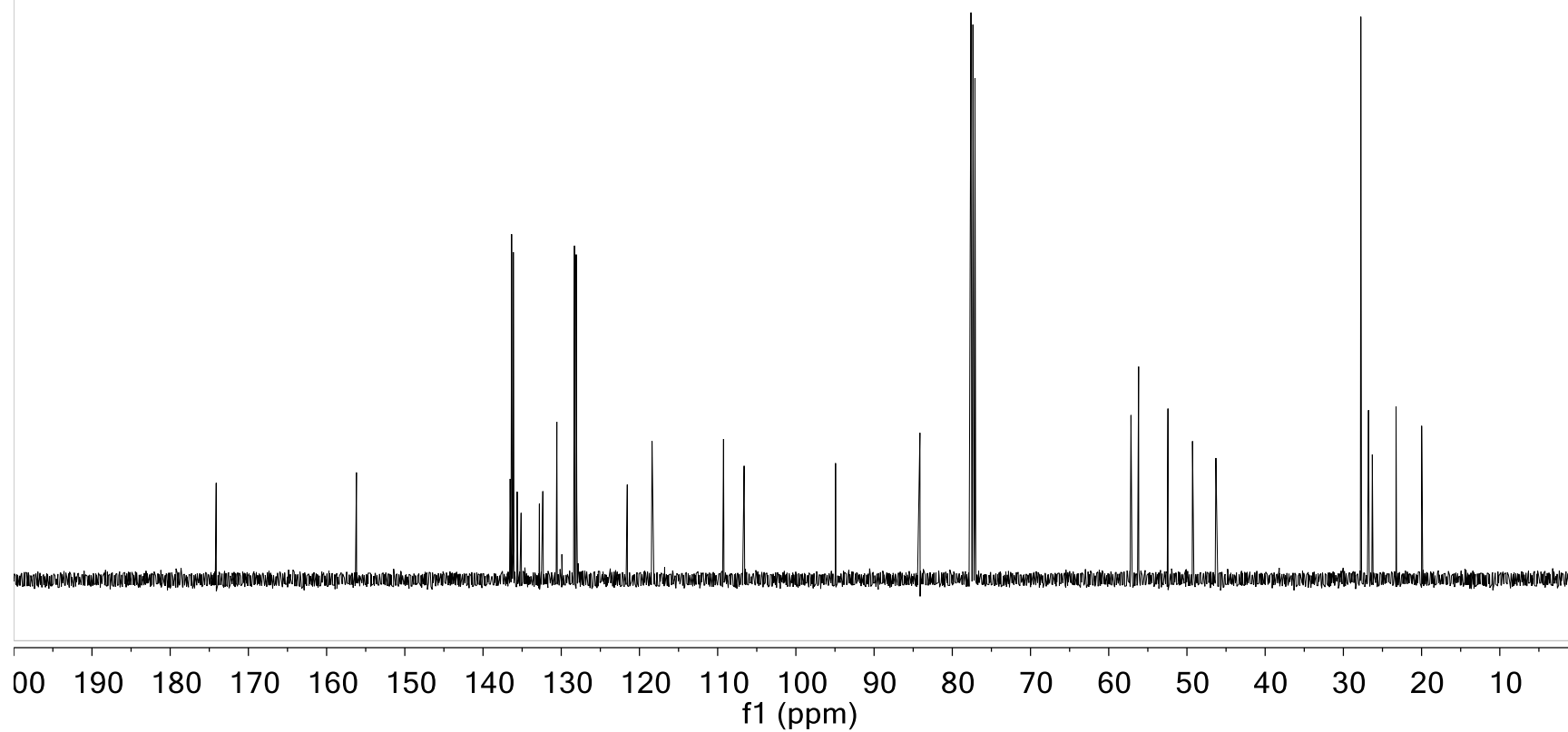


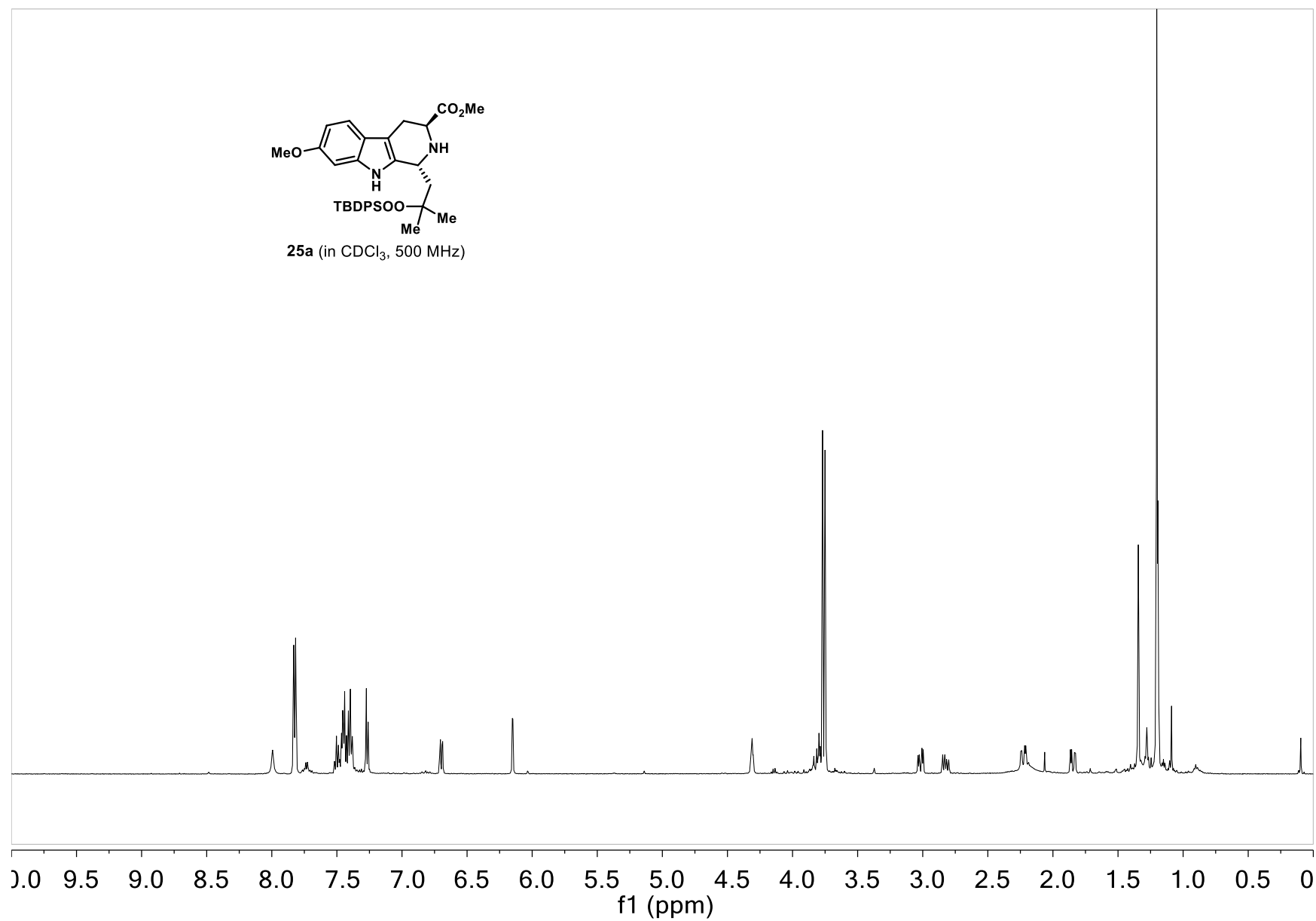
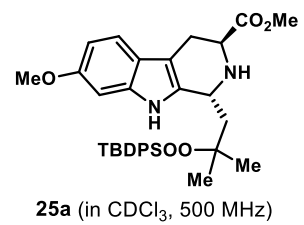
25 (in CDCl_3 , 500 MHz)

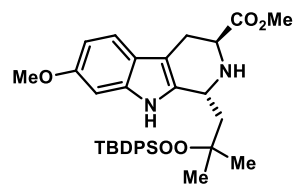




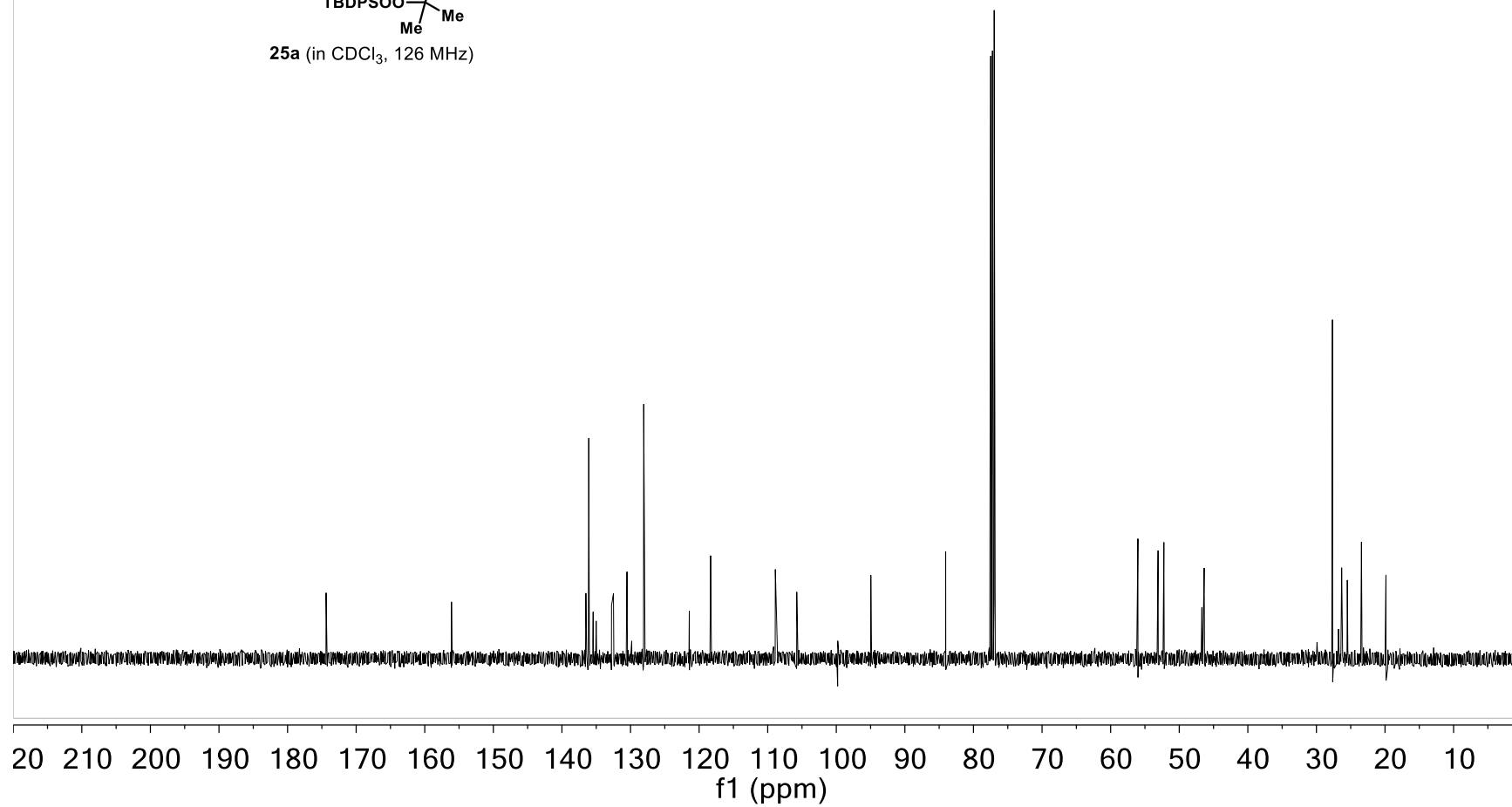
25 (in CDCl₃, 126 MHz)

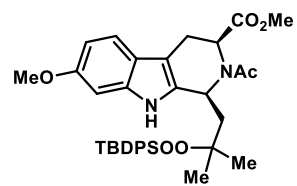




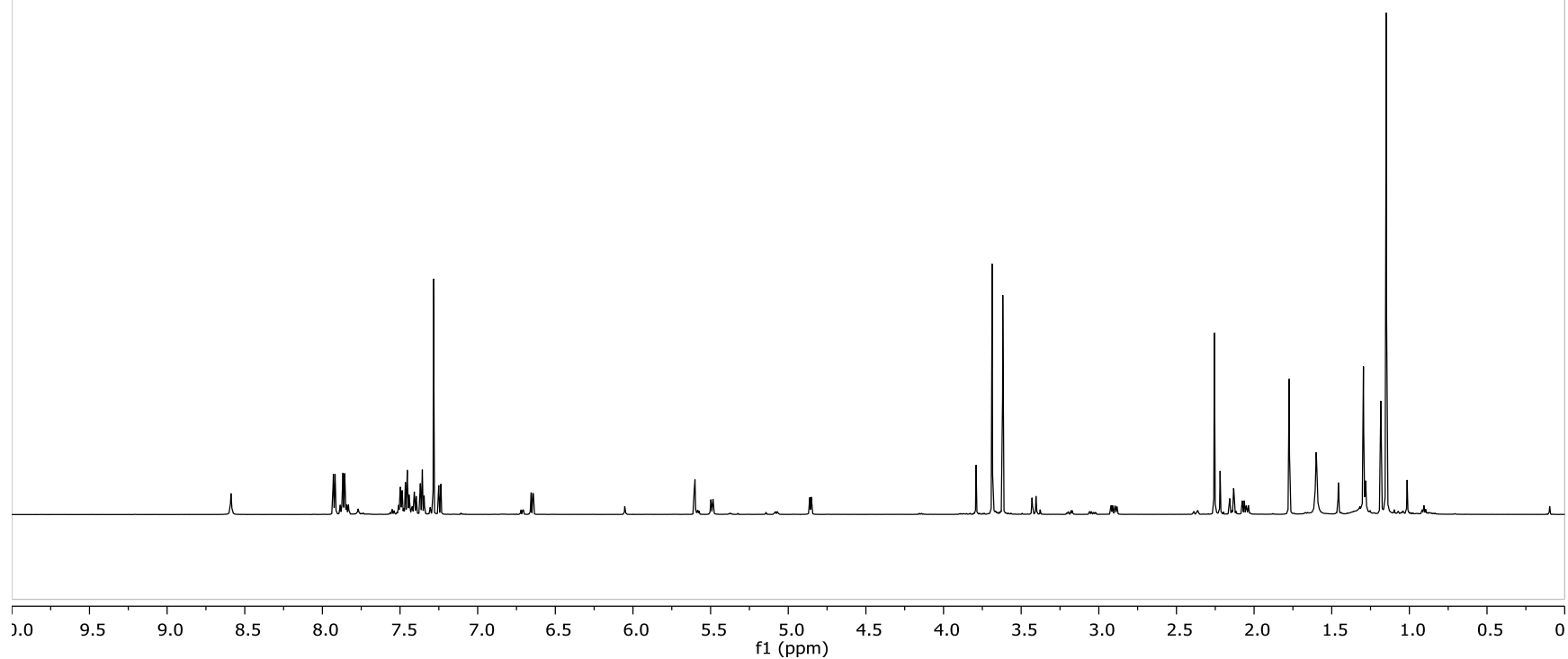


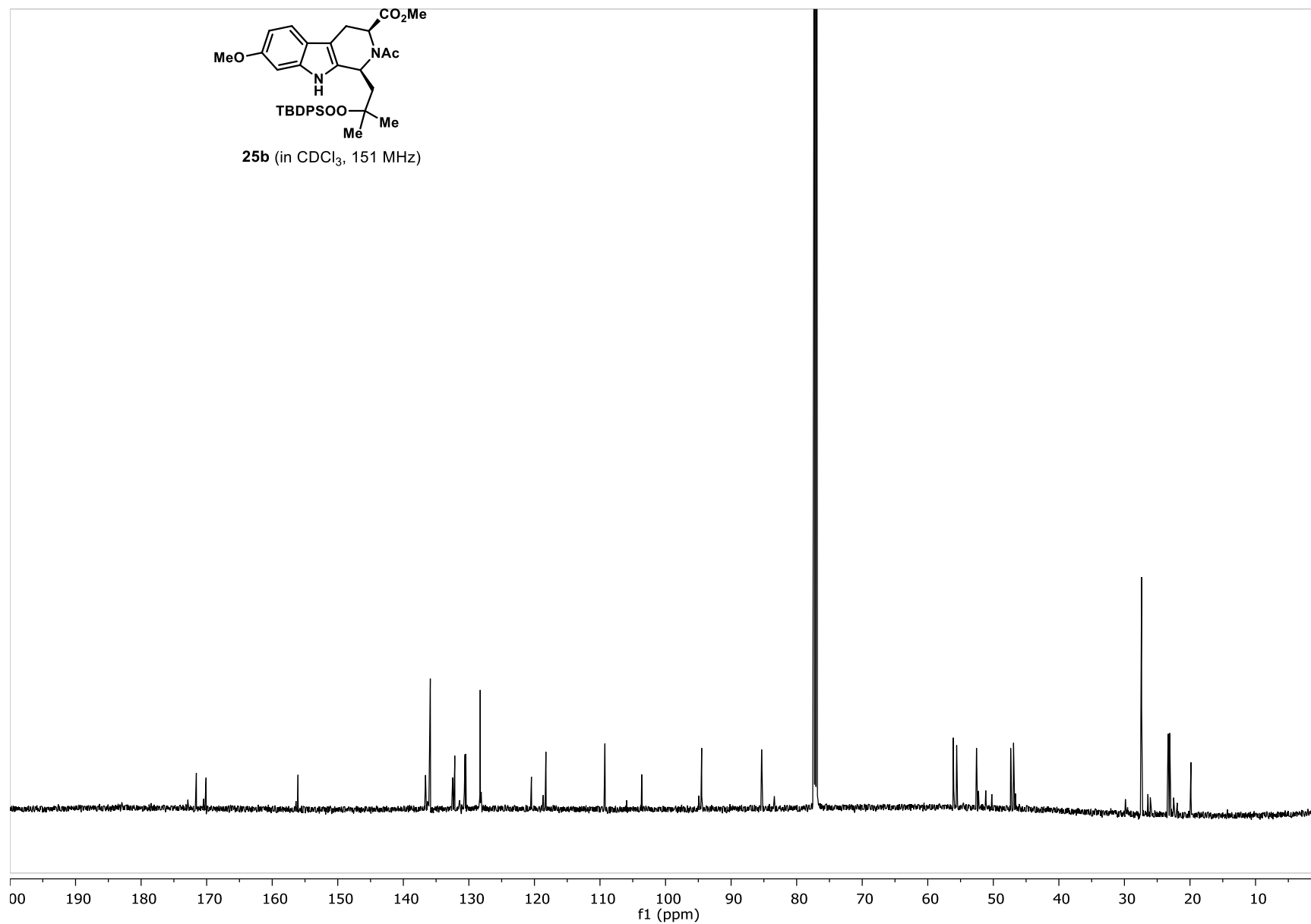
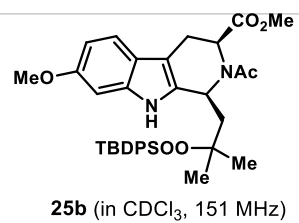
25a (in CDCl₃, 126 MHz)

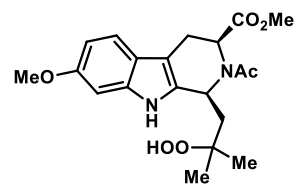




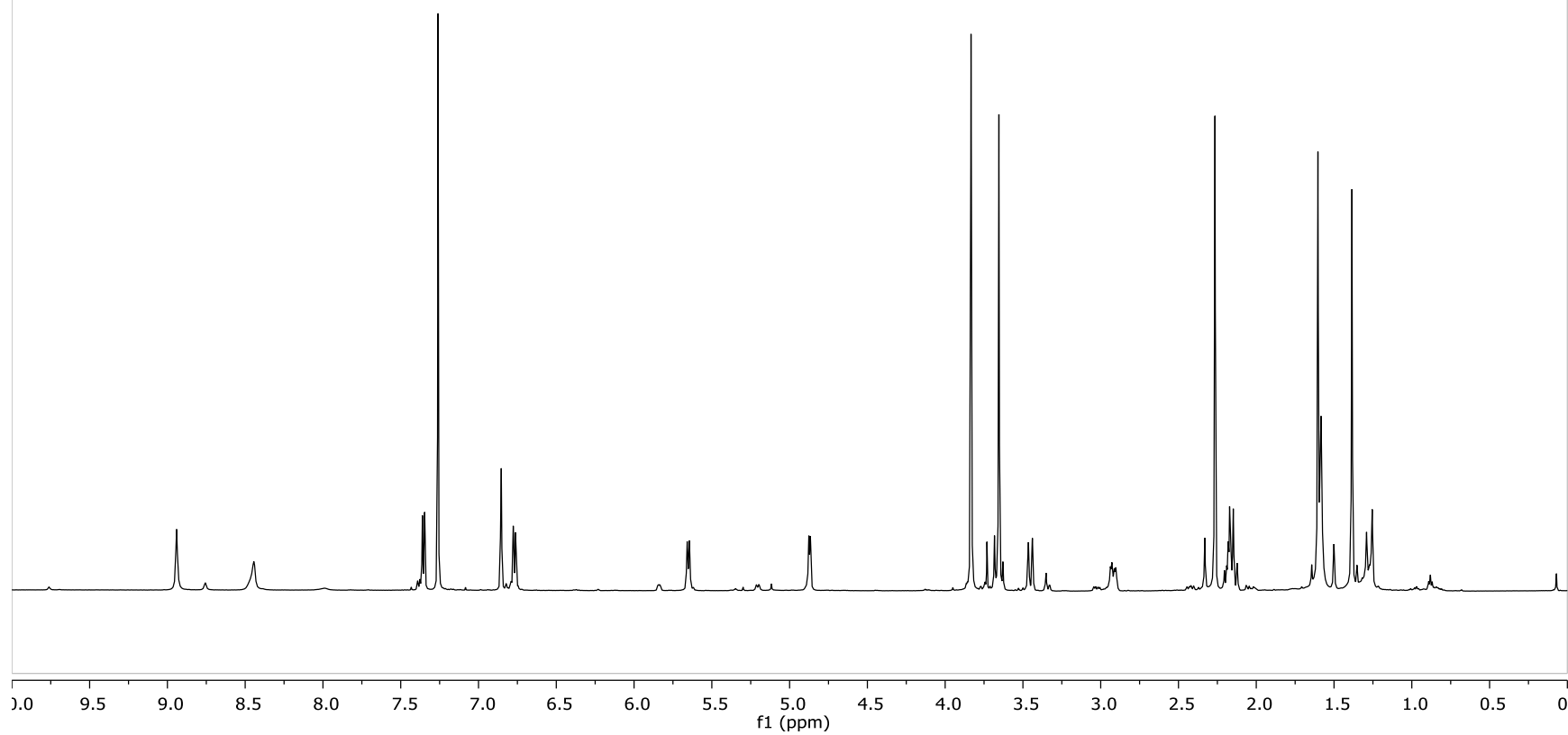
25b (in CDCl₃, 500 MHz)

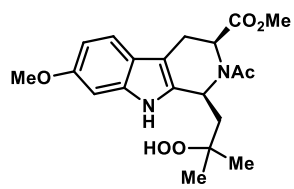




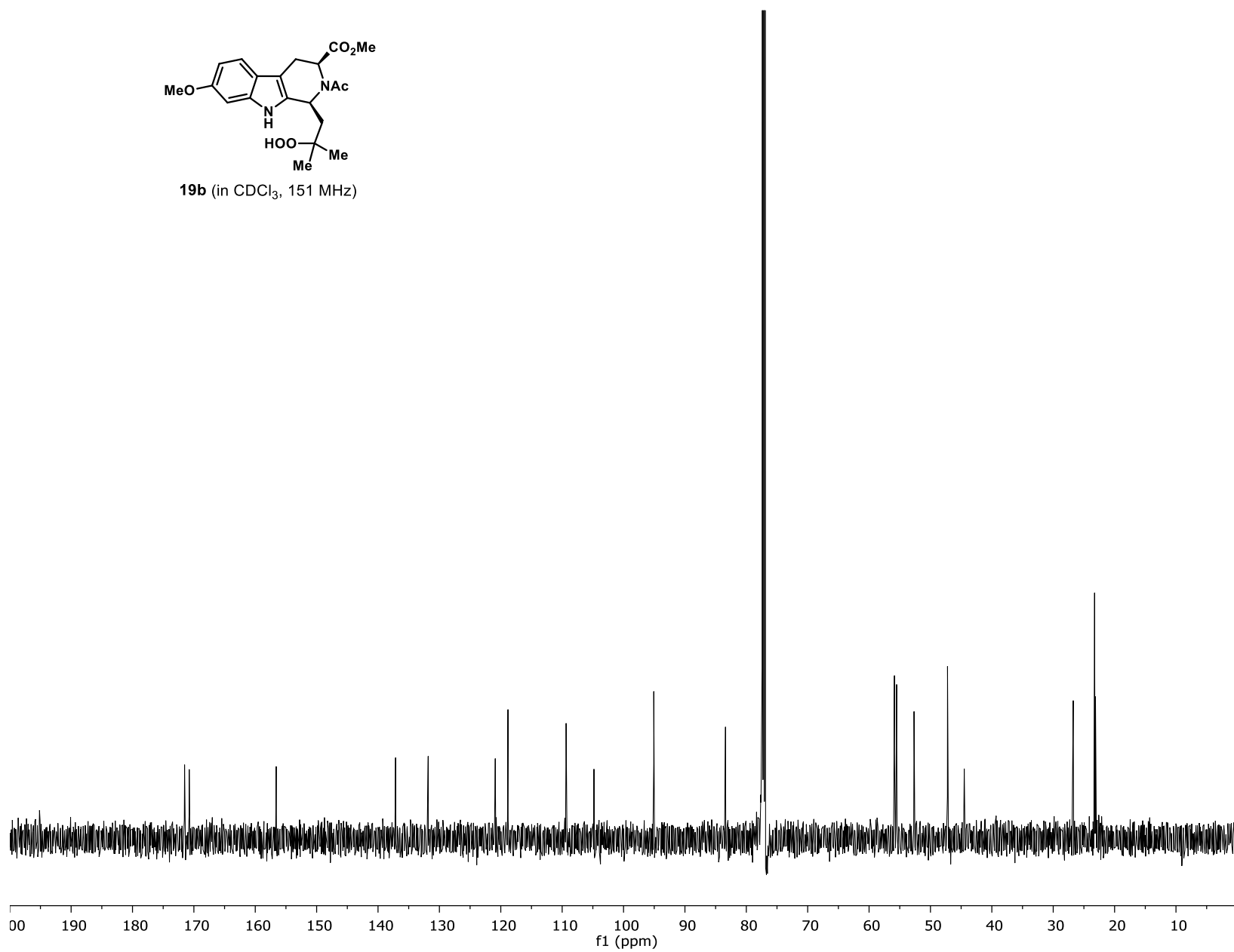


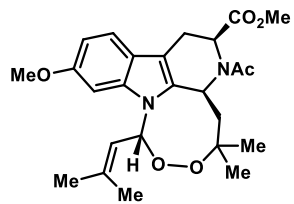
19b (in CDCl₃, 600 MHz)



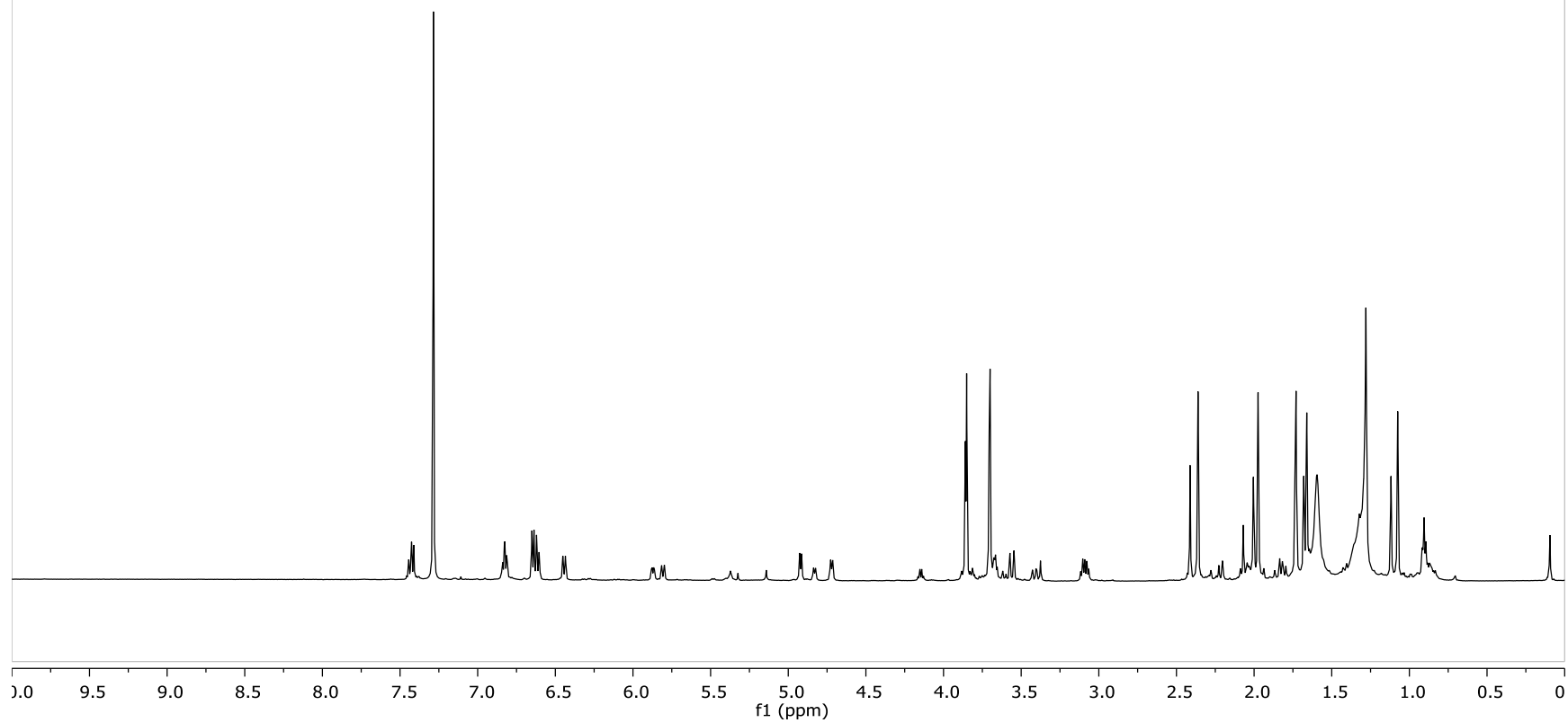


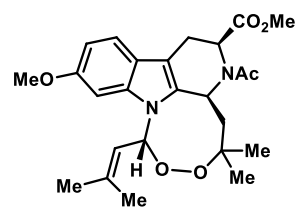
19b (in CDCl₃, 151 MHz)



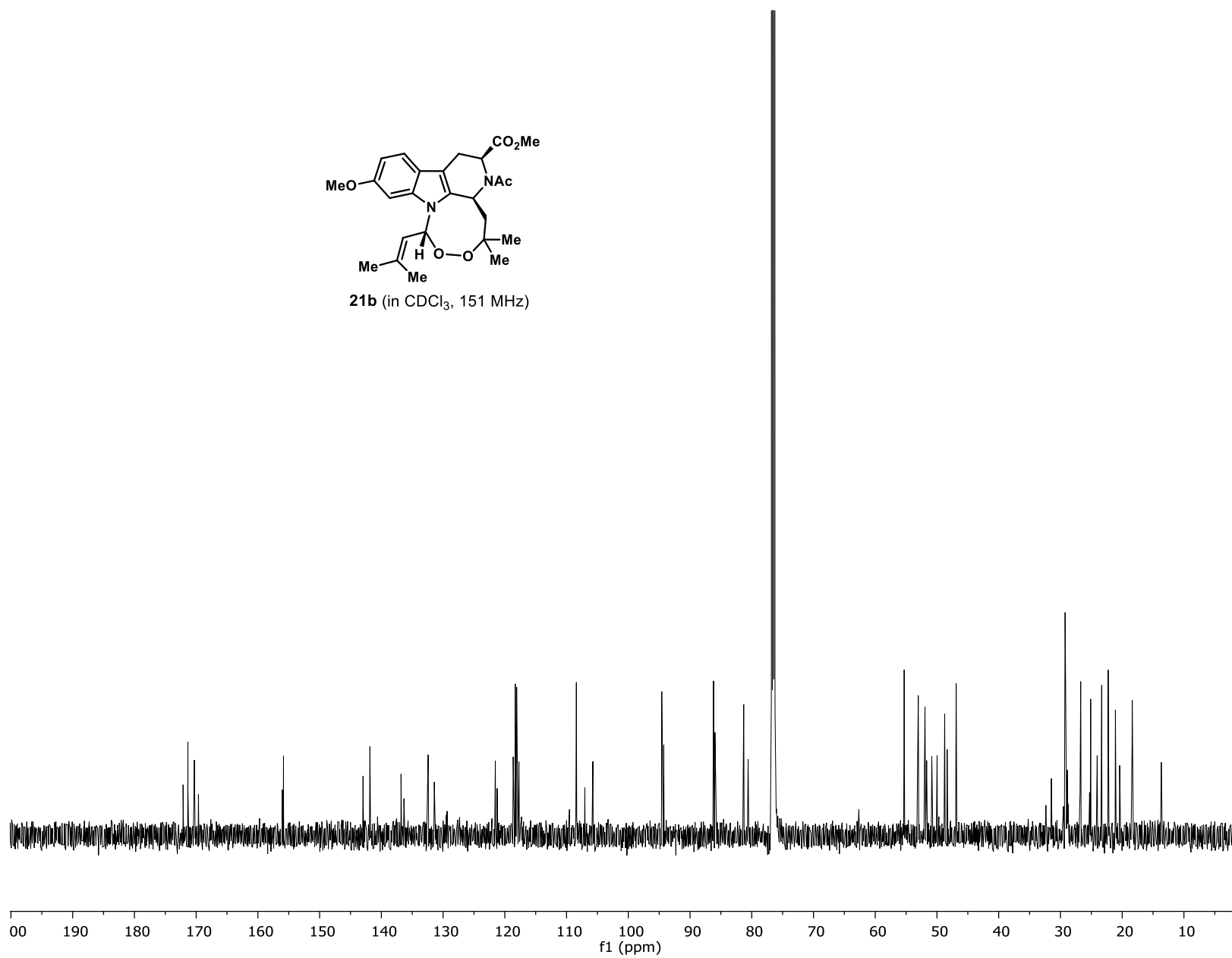


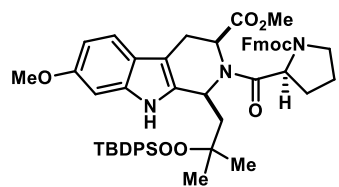
21b (in CDCl₃, 600 MHz)



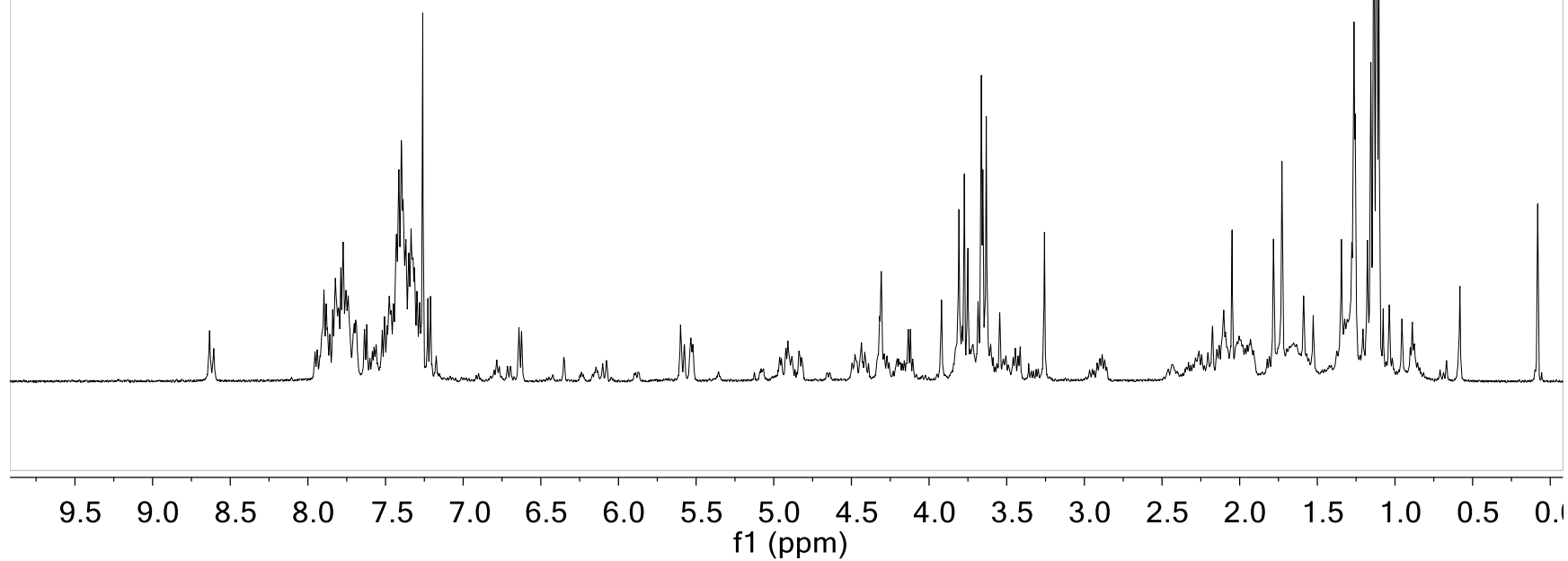


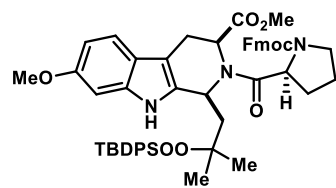
21b (in CDCl₃, 151 MHz)



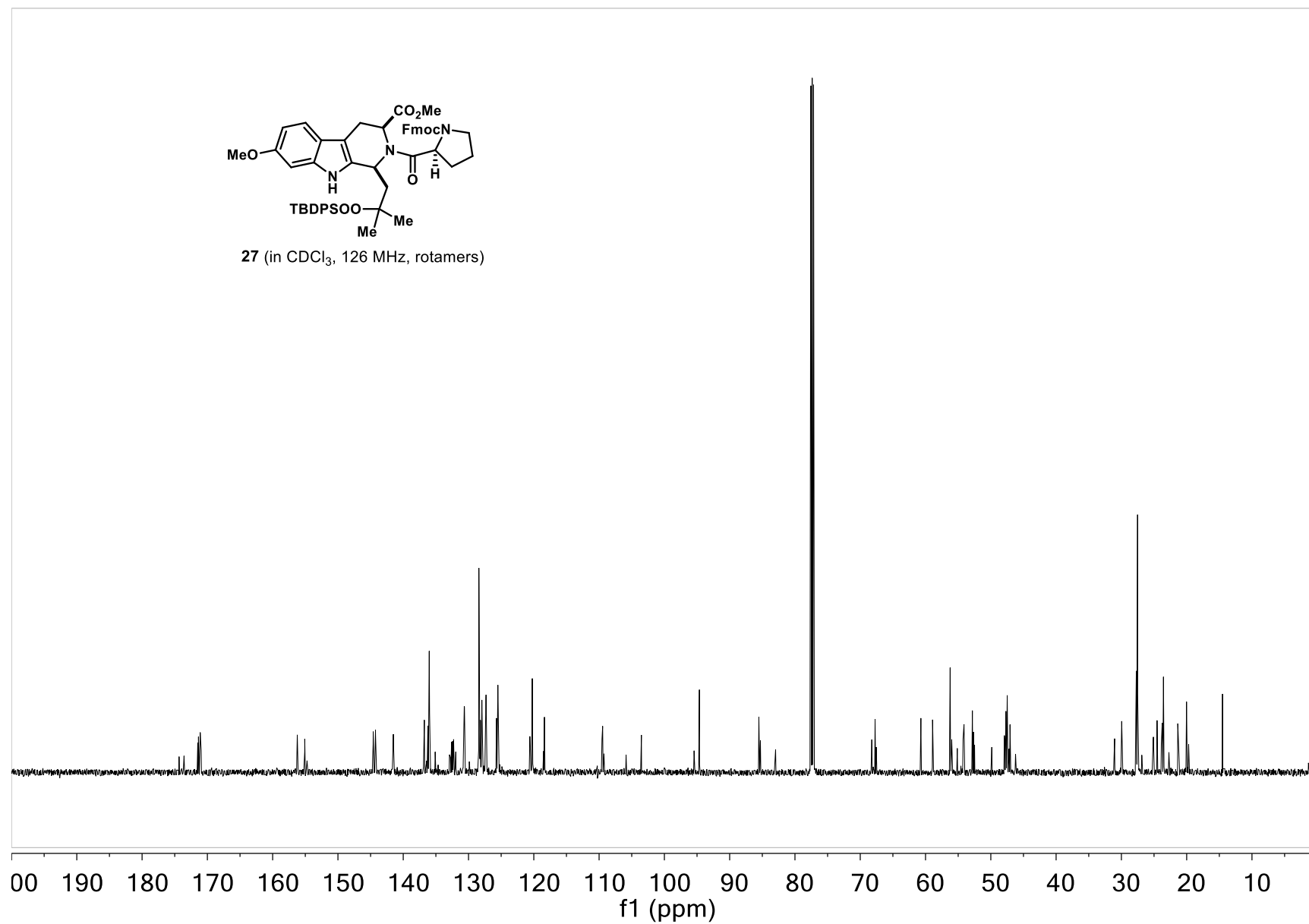


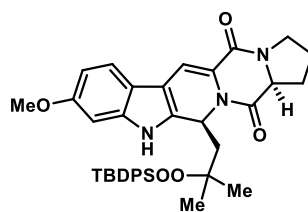
27 (in CDCl₃, 500 MHz, rotamers)



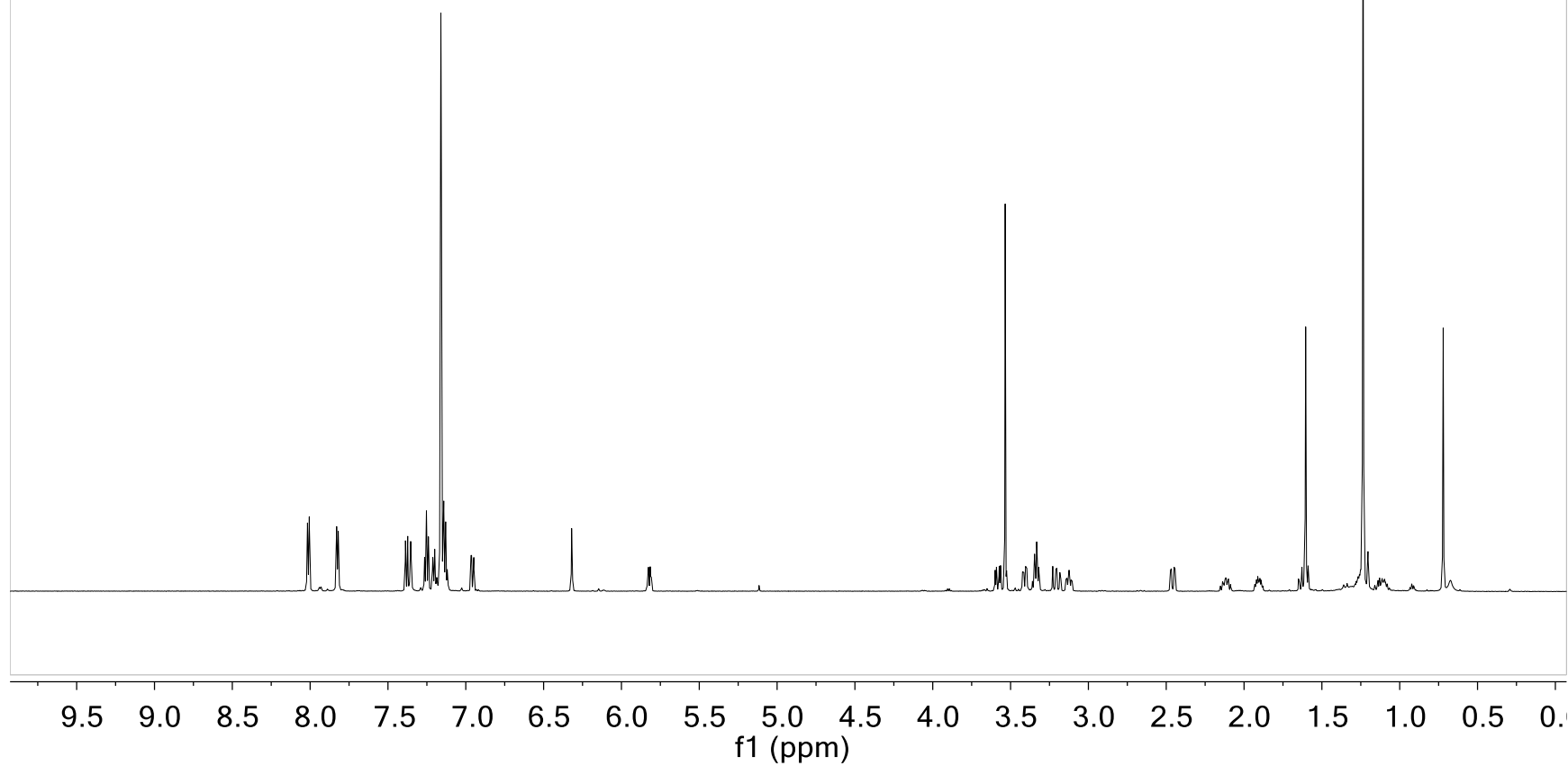


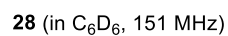
27 (in CDCl₃, 126 MHz, rotamers)

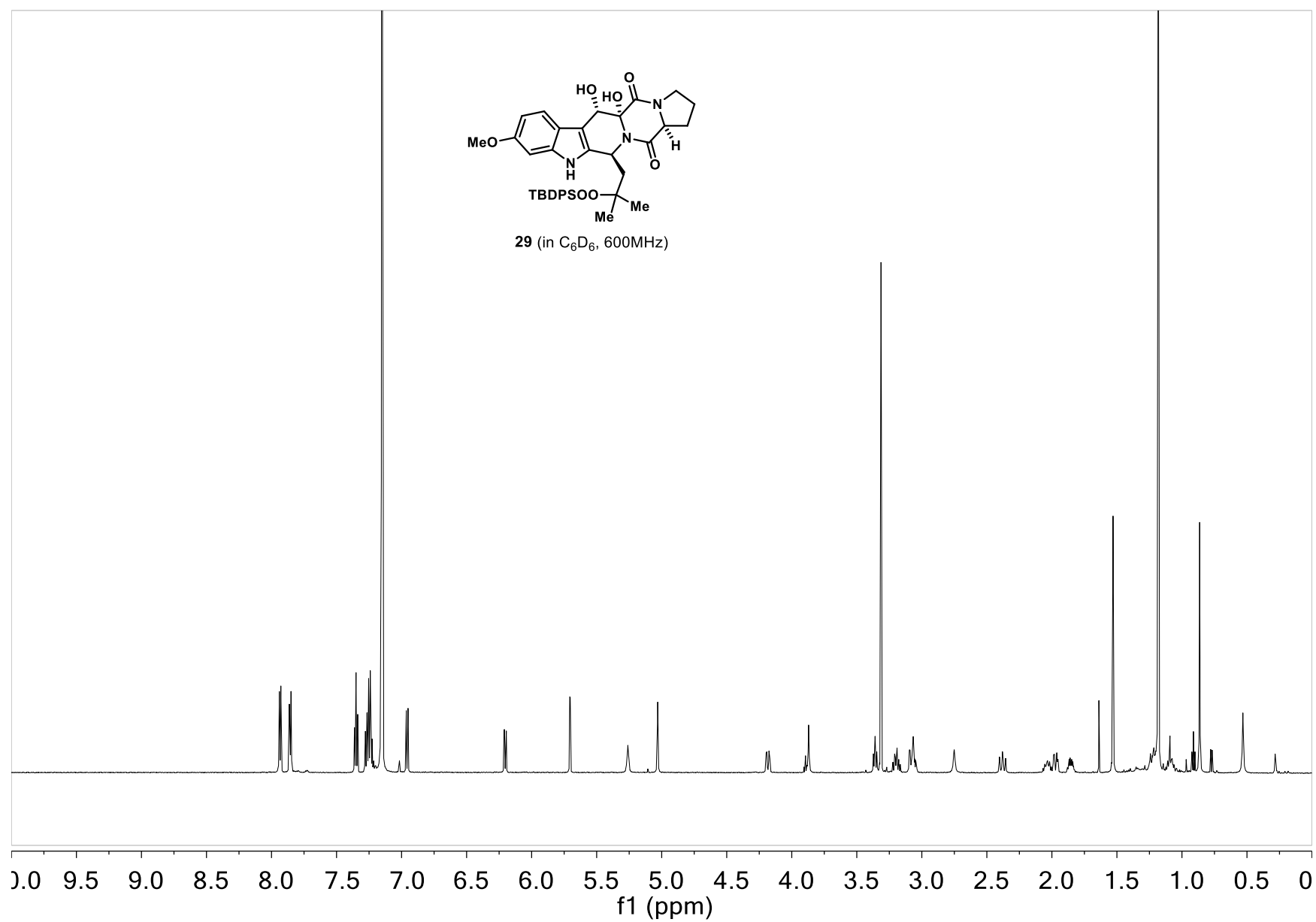




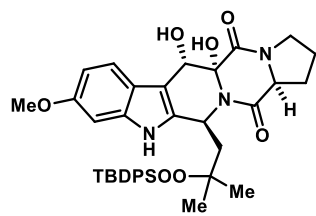
28 (in C₆D₆, 600 MHz)



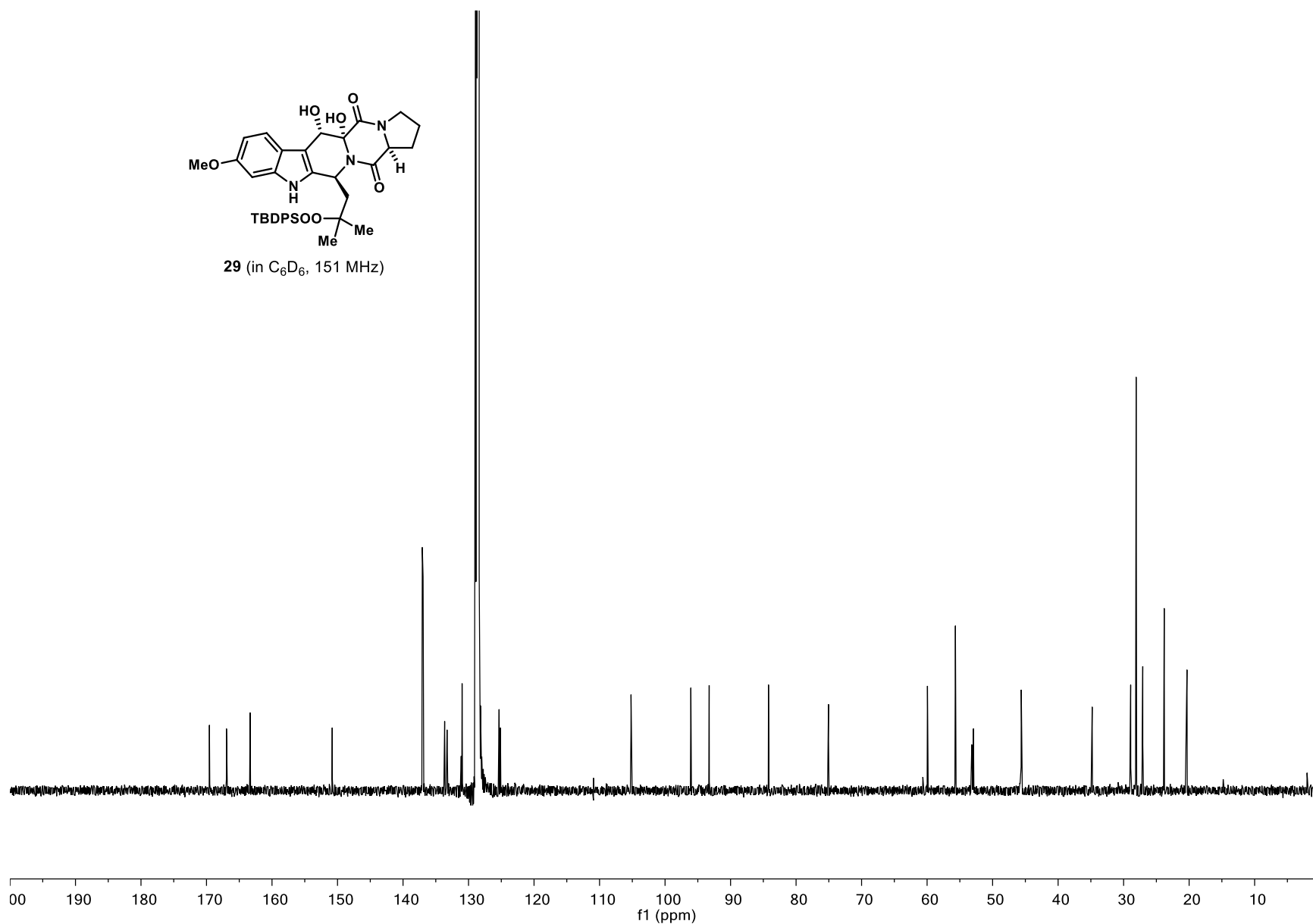


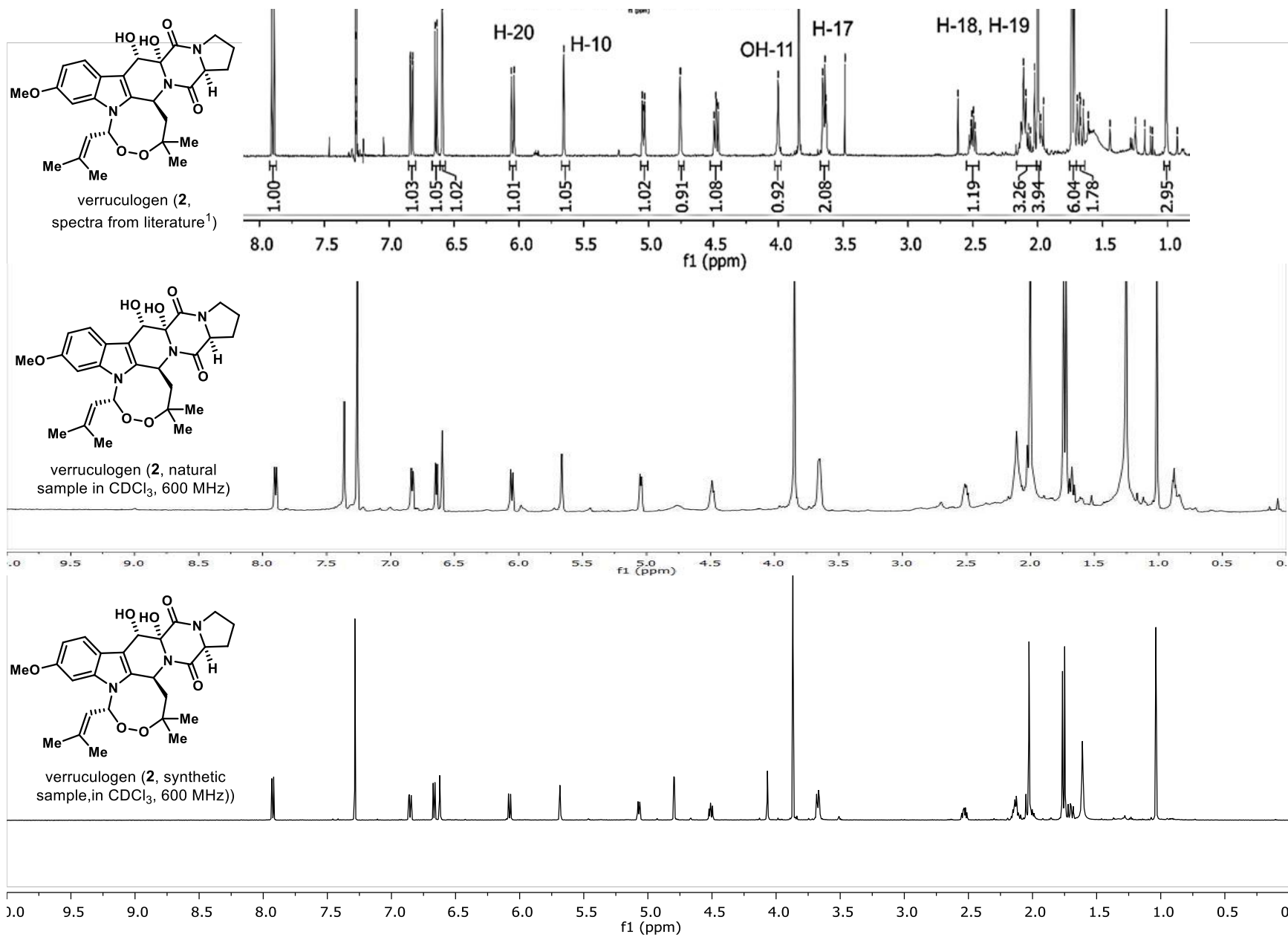


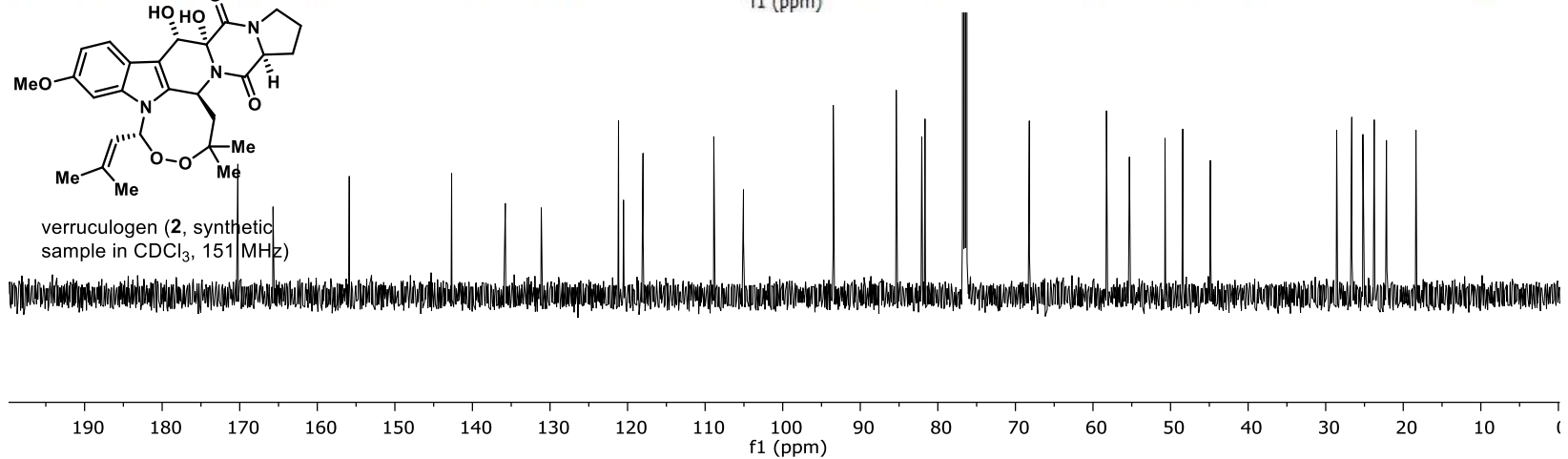
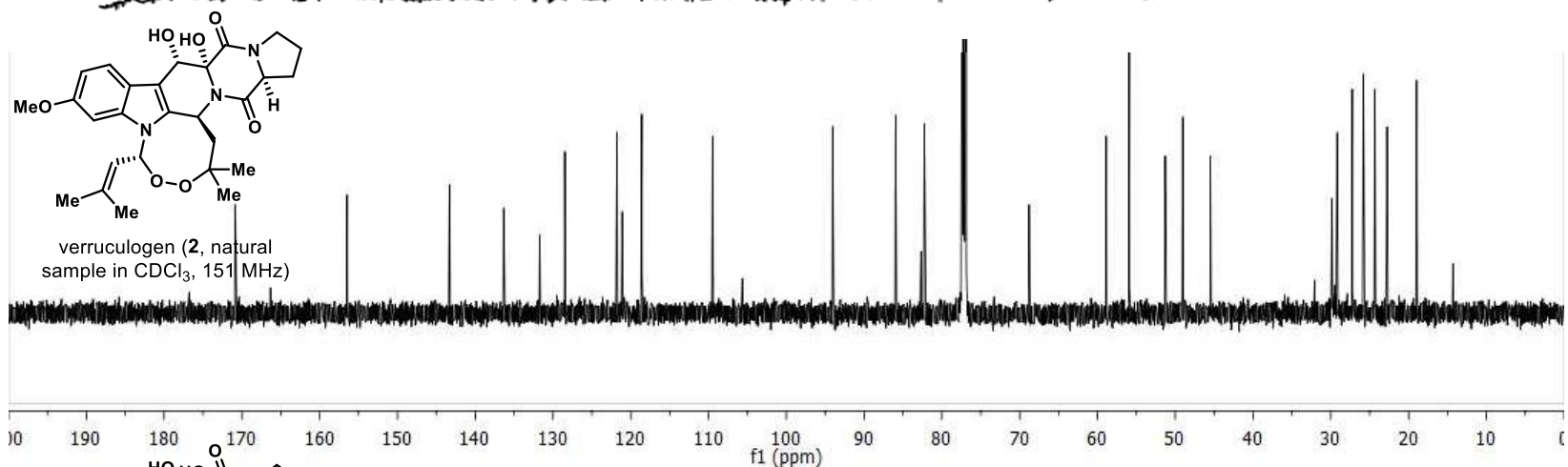
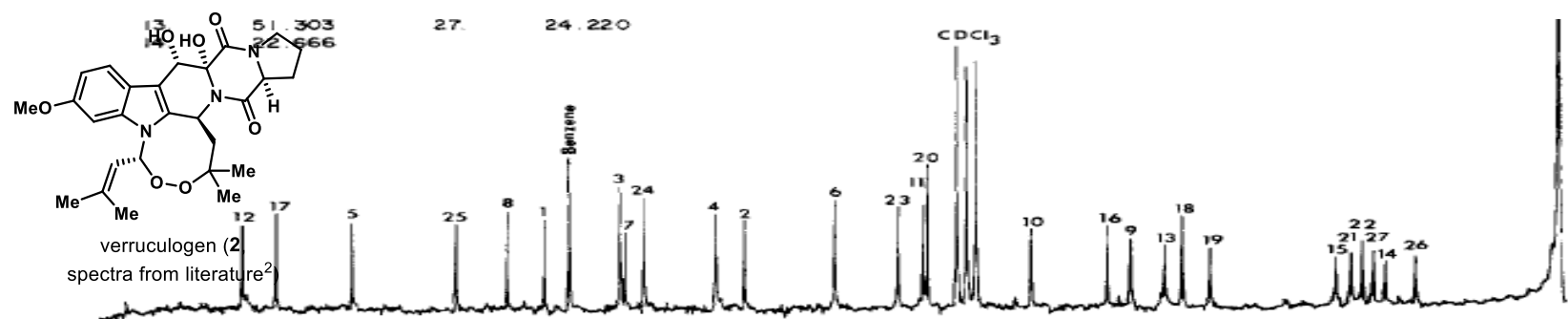
29 (in C₆D₆, 600MHz)

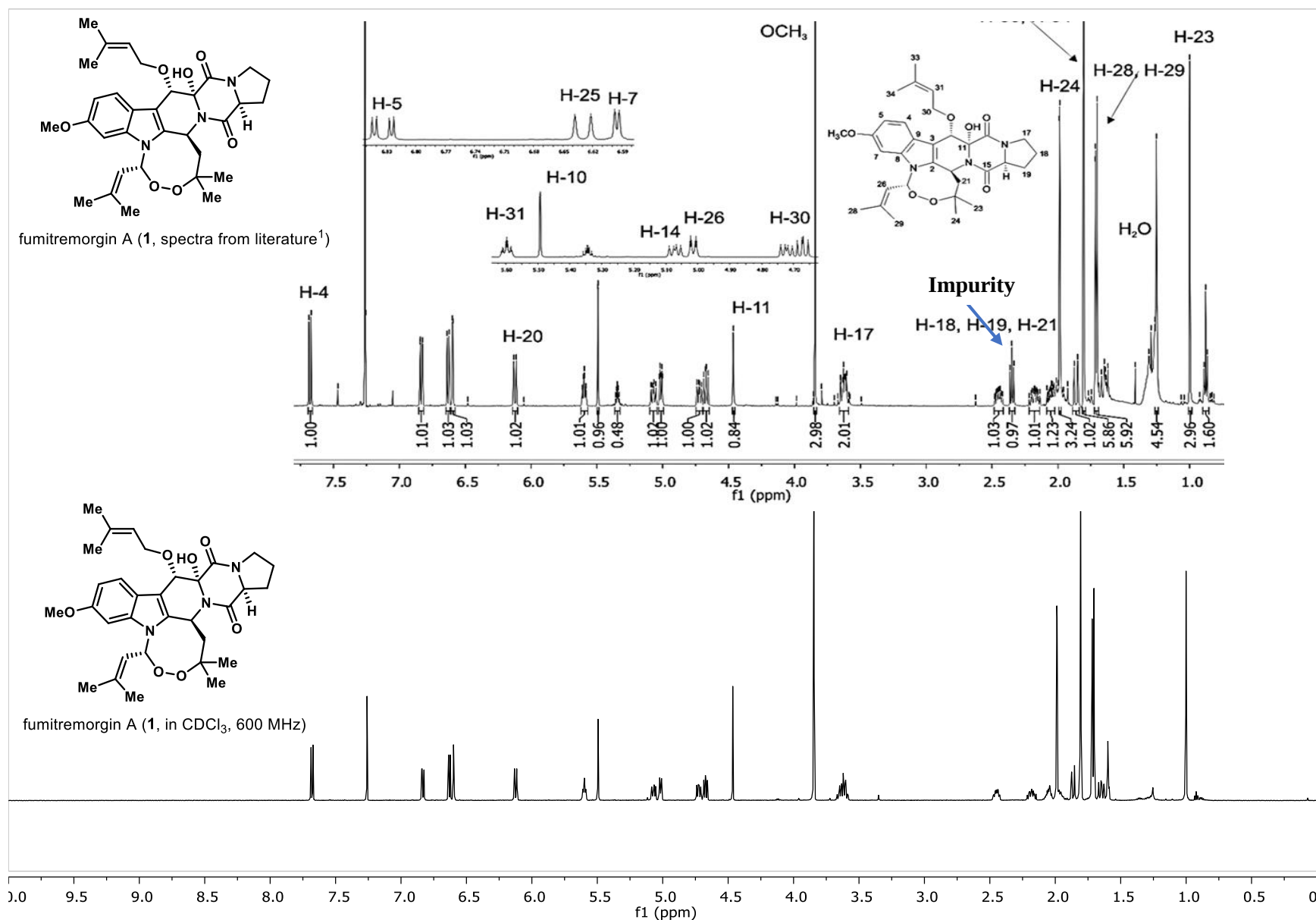


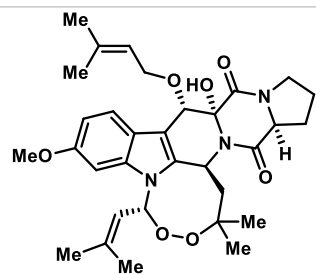
29 (in C₆D₆, 151 MHz)



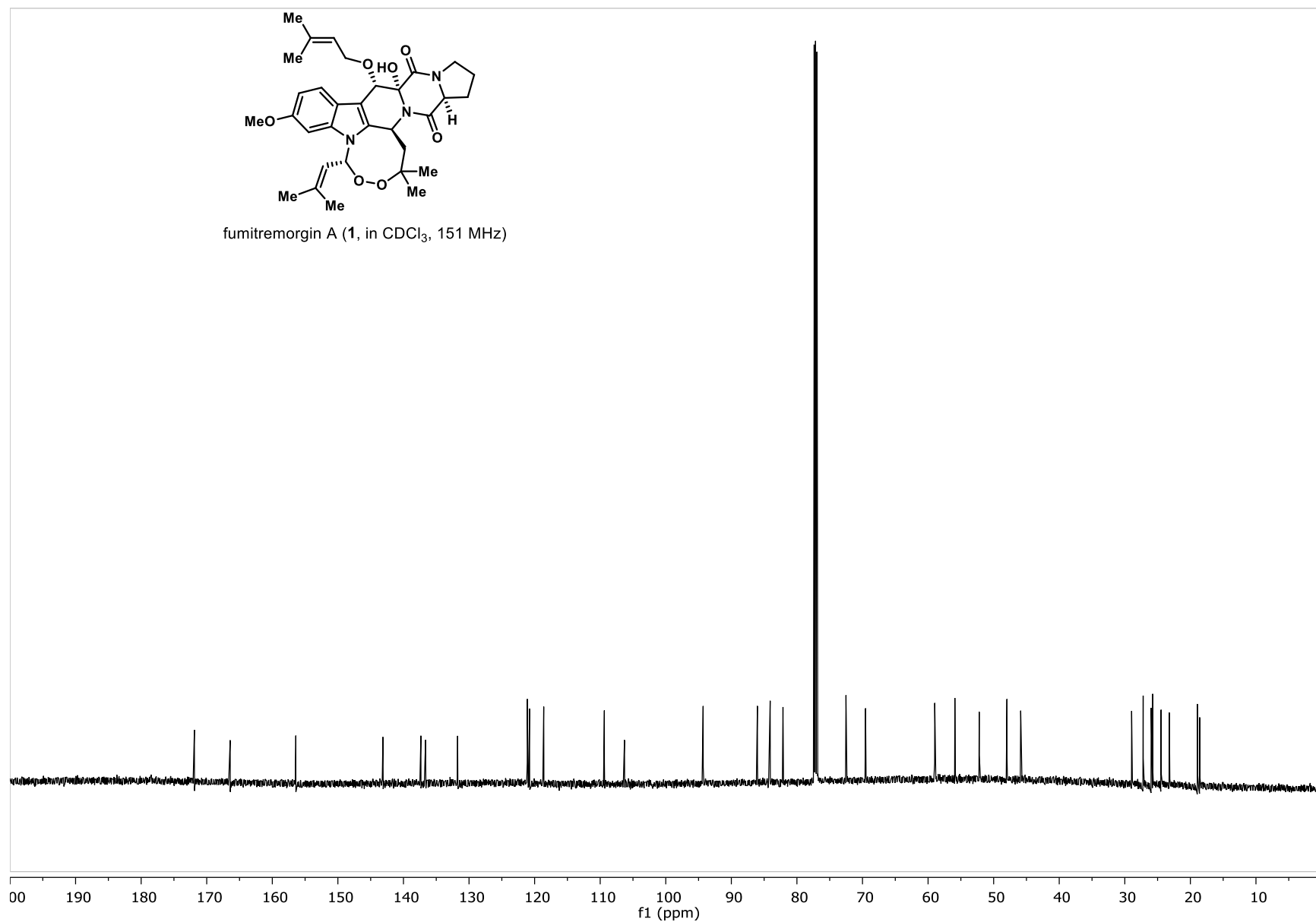


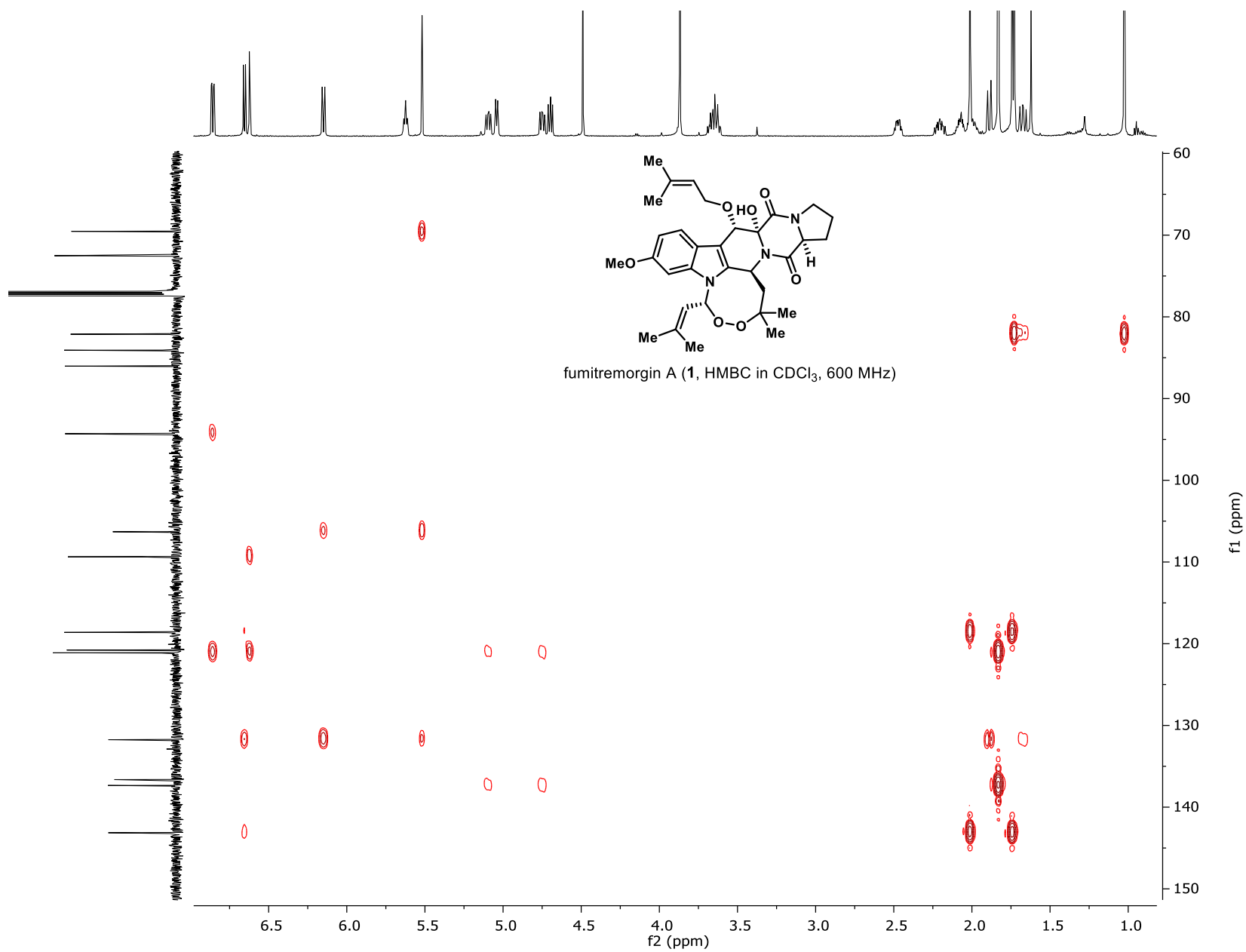






fumitremorgin A (1, in CDCl₃, 151 MHz)





SS73

Reference:

1. Erlangung des Doktorgrades, Ph.D. thesis, Chemische, molekularbiologische und biochemische Untersuchungen zur Biosynthese von Mykotoxinen aus Ascomyceten, der Philipps-Universität Marburg, **2014**.
2. Cole, R. J.; Kirksey, J. W.; Cox, R. H.; Clardy, J. *J. Agric. Food Chem.*, **1975**, 23, 1015.