

Ene reactions of 2-borylated α -methylstyrenes: a practical route to 4-methylenechromanes and derivatives.

Chaima Boureghda,^{a,b} Aurélie Macé,^a Fabienne Berrée,^a Thierry Roisnel,^a Abdelmadjid Debaché,^{b*} and Bertrand Carboni^{a*}

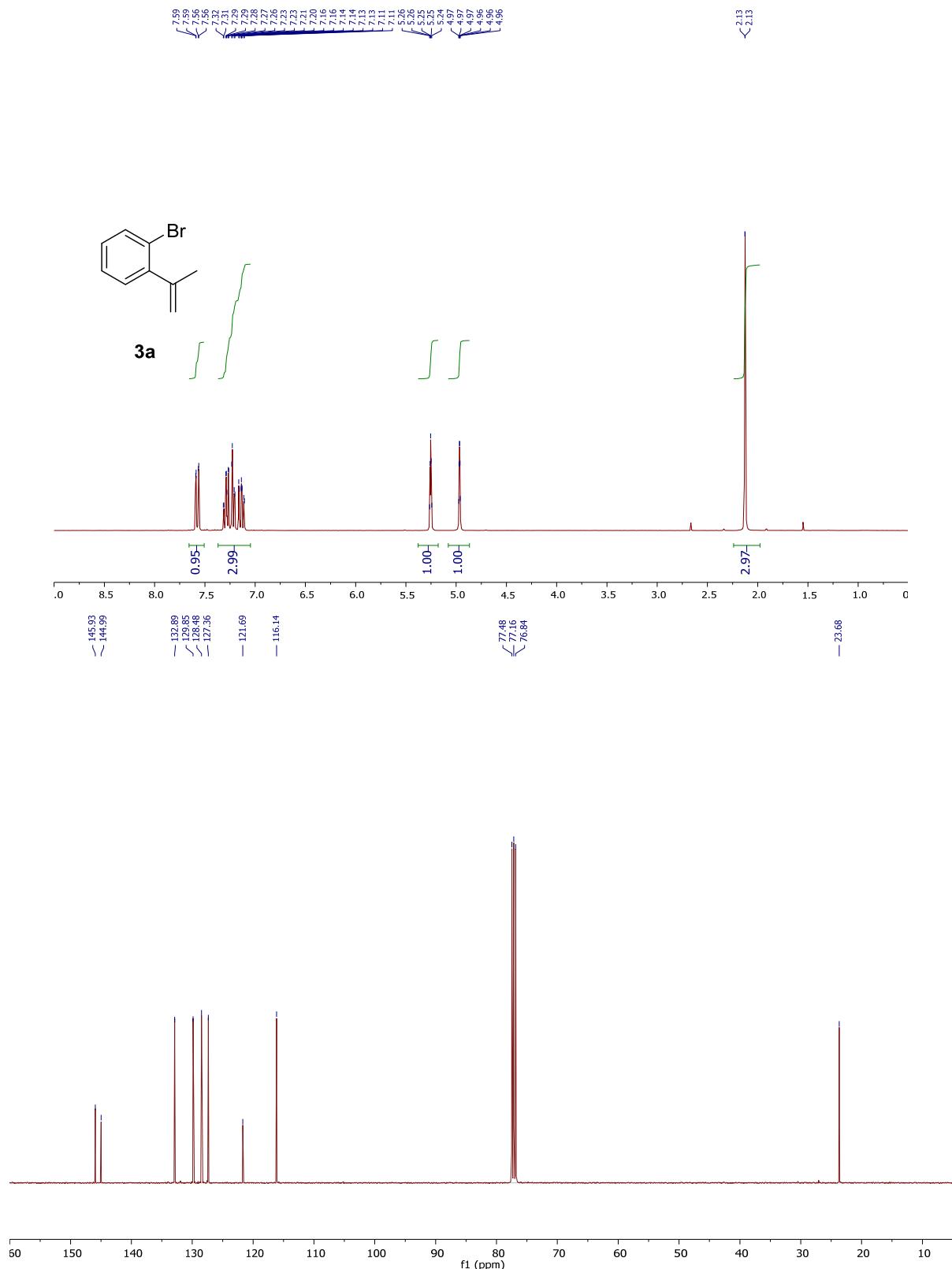
^a Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France.

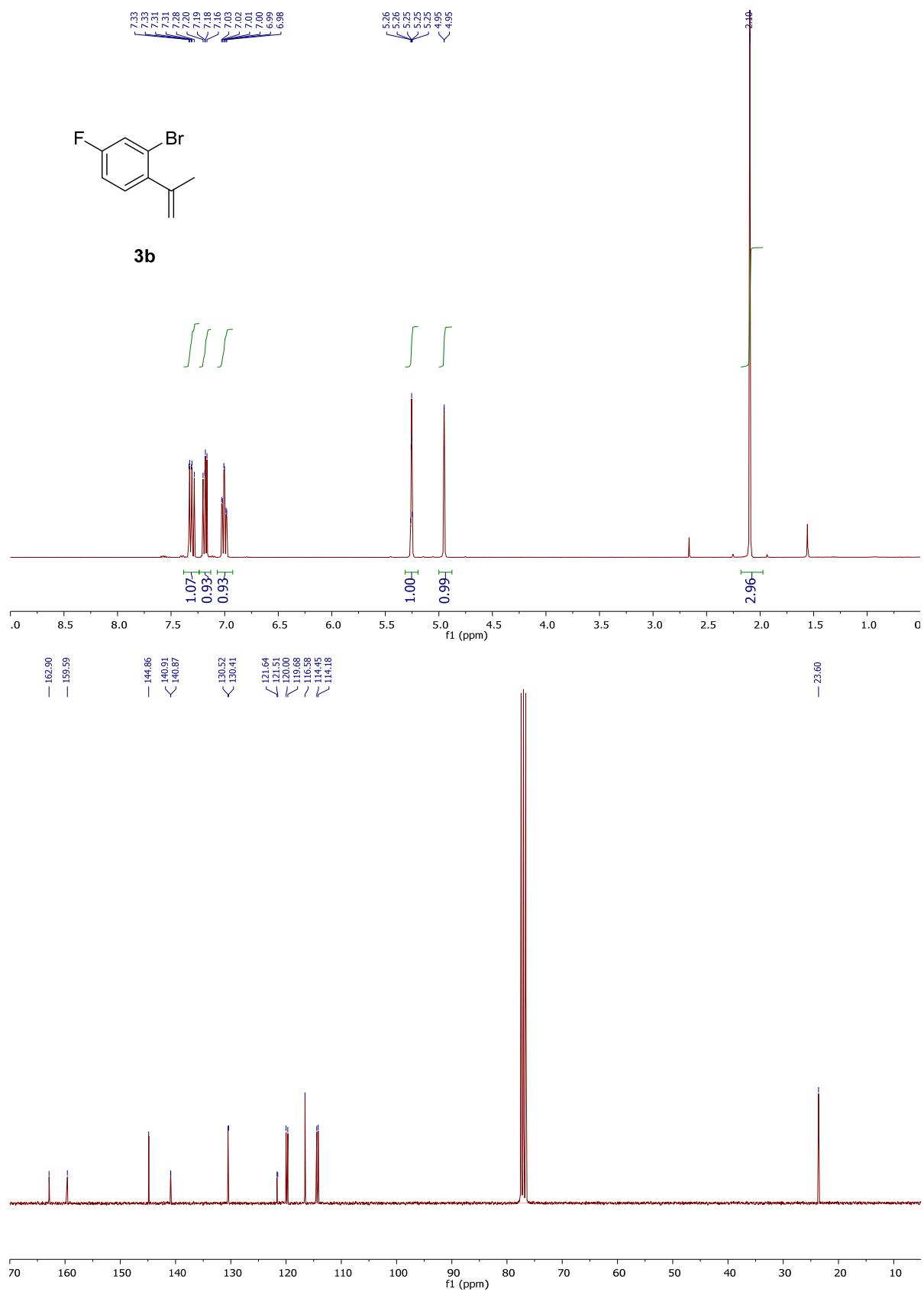
^b Laboratoire de Synthèse des Molécules d'Intérêts Biologiques, Université des Frères Mentouri-Constantine, 25000 Constantine, Algérie.

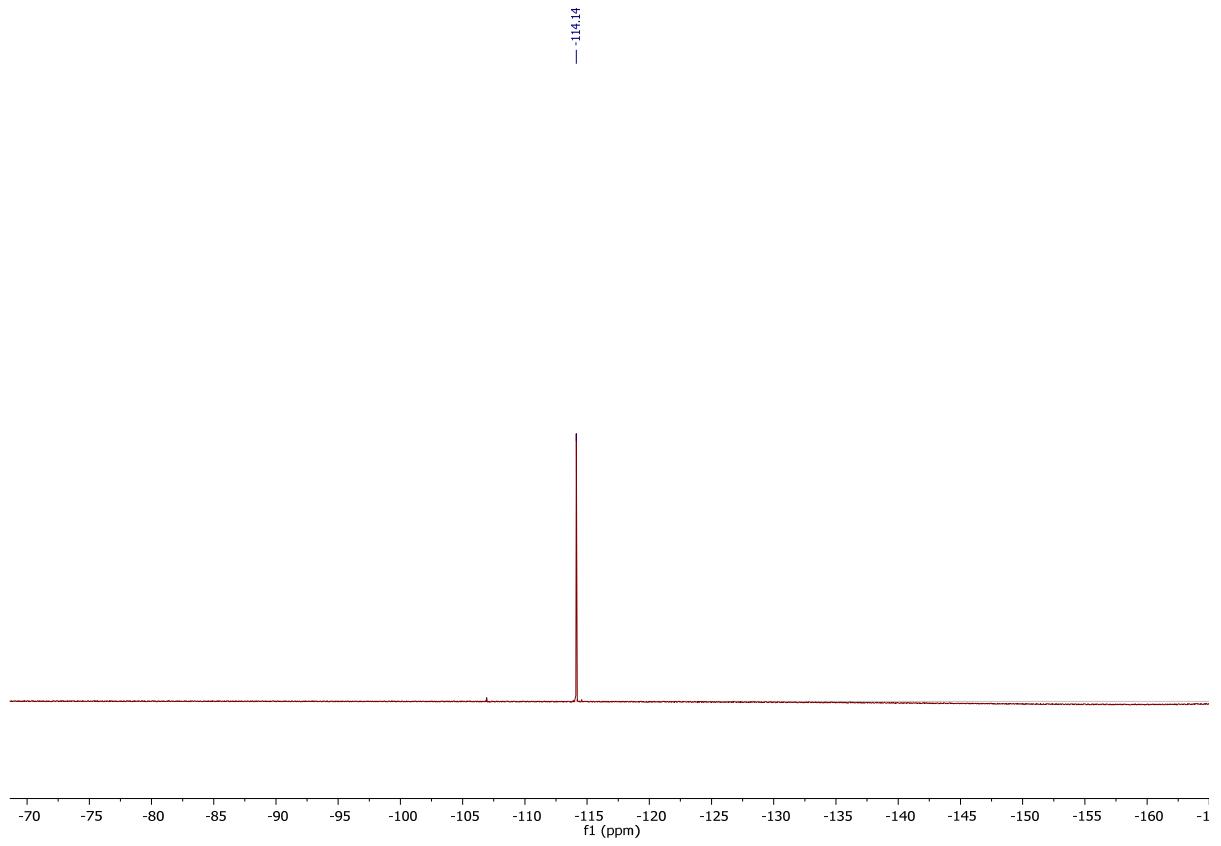
Table of contents

I.	2-Bromo α -methylstyrenes 3a-f	2
II.	Pinacol (2-(prop-1-en-2-yl)phenyl)boronic esters 4a-f from 3a-f	9
III.	B-MIDA derivatives 6a,g-i	21
IV.	Pinacol (2-(prop-1-en-2-yl)phenyl)boronic esters 4g-i from 6g-i	29
V.	Ene reactions: example of compounds 7a and 8a	35
VI.	Oxidation of boronates 7 to phenols 9	39
VII.	Access to 4-methylenechromanes 1 from 9	48
VIII.	Isomerisation of 1 to 10	57
IX.	Hydrogenation of 1a to 11a	62
X.	Other functional transformations of 7a	63

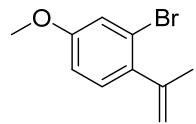
I. 2-Bromo α -methyl styrenes 3a-f



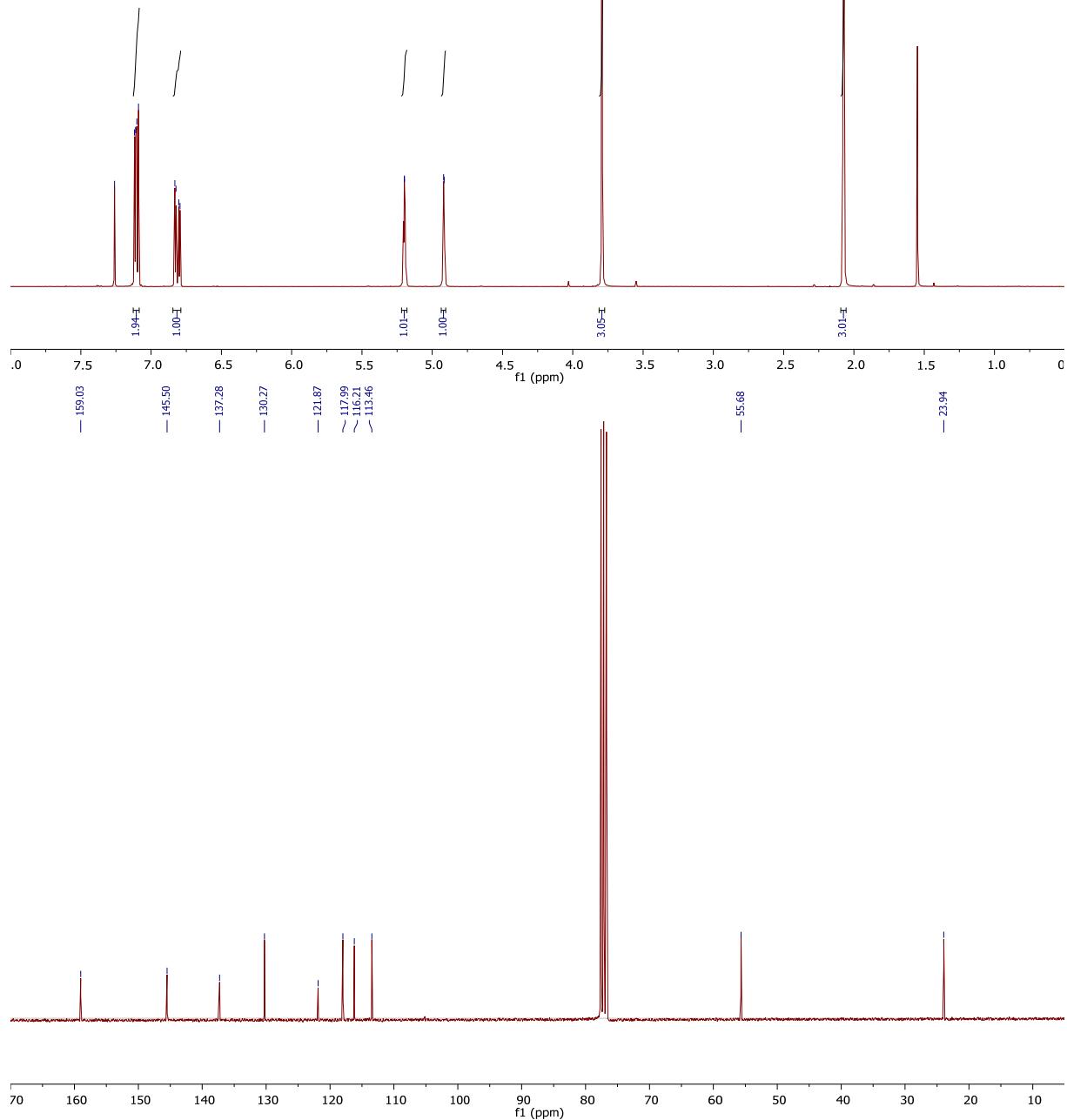


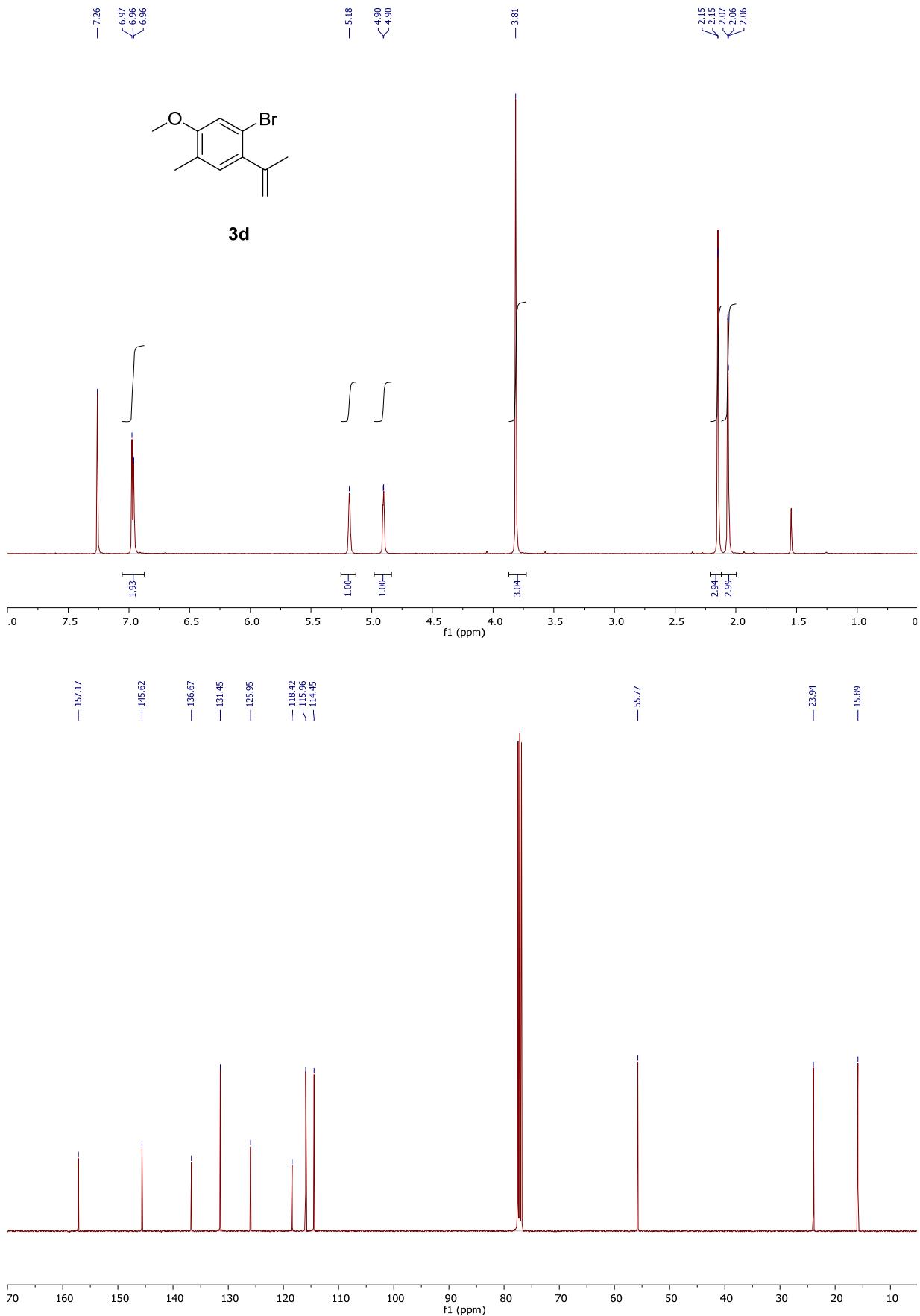


7.26
7.12
7.11
7.09
6.99
6.83
6.82
6.80
6.79



3c





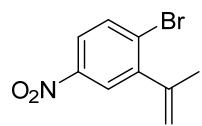
8.06
8.05
7.99
7.98
7.96
7.95
7.75
7.72

— 7.26

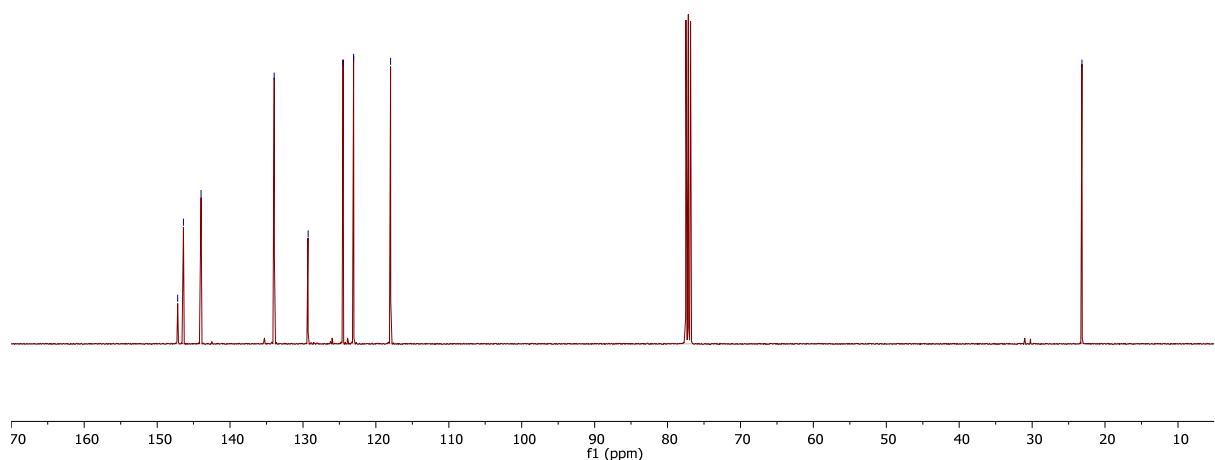
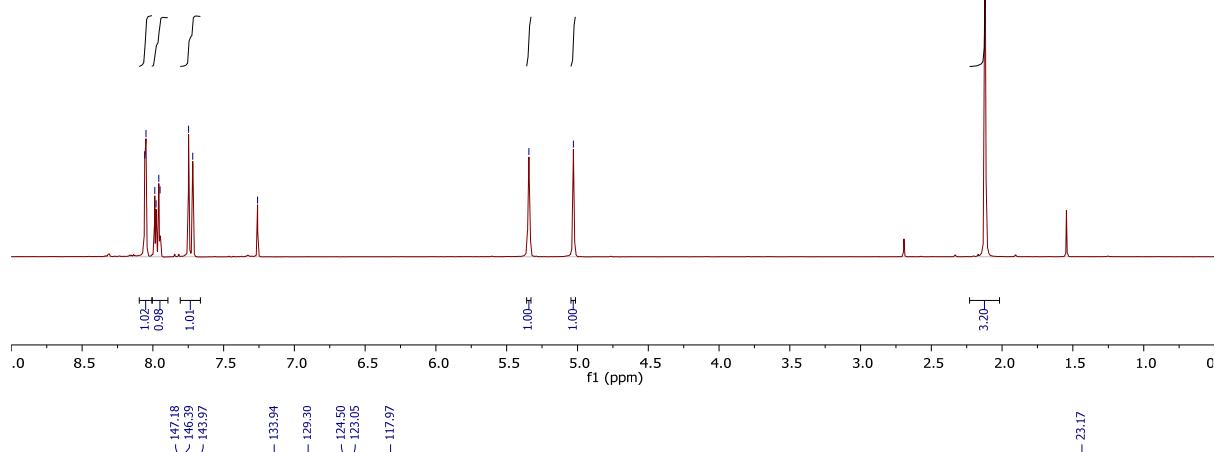
— 5.34

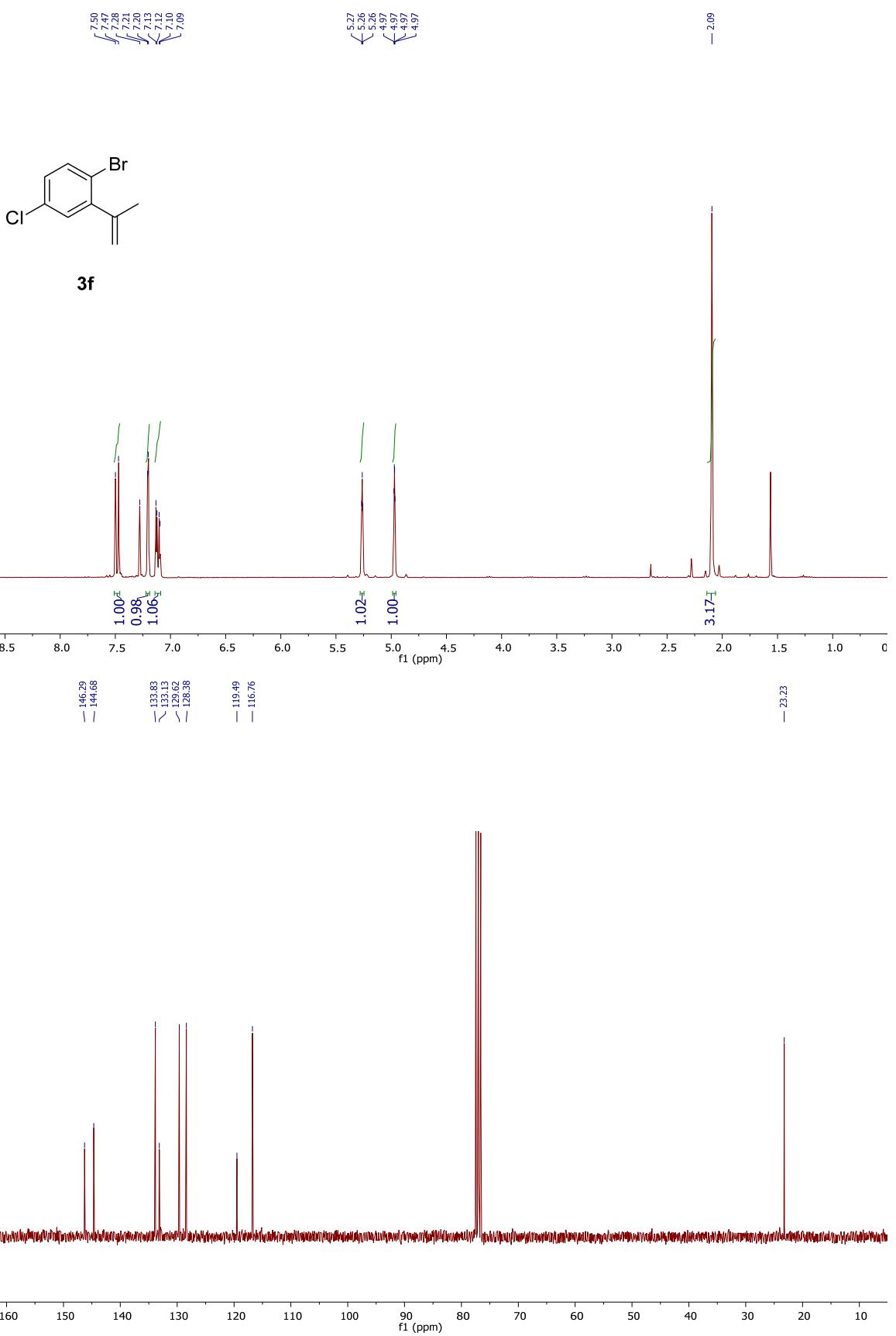
— 5.03

— 2.12

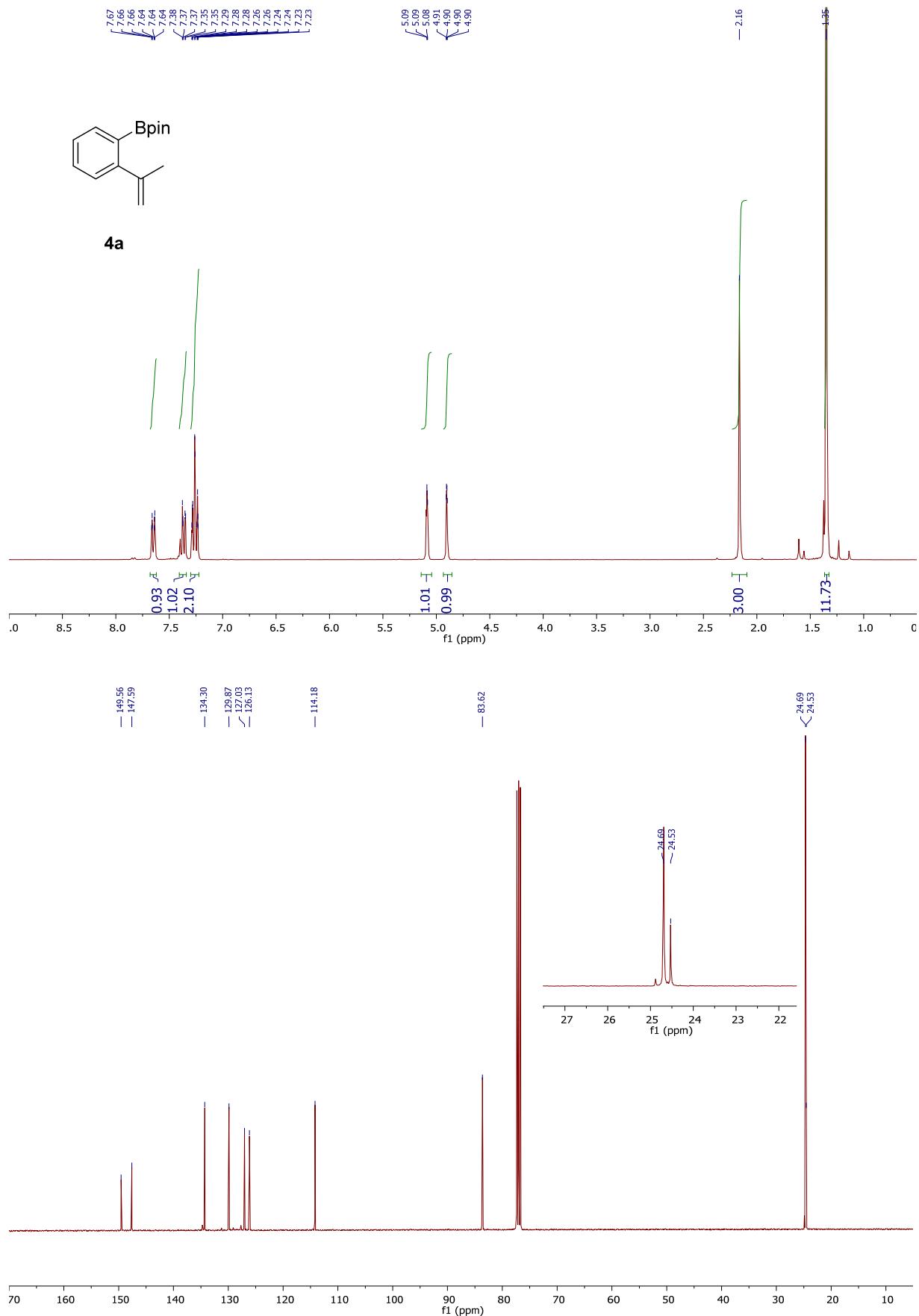


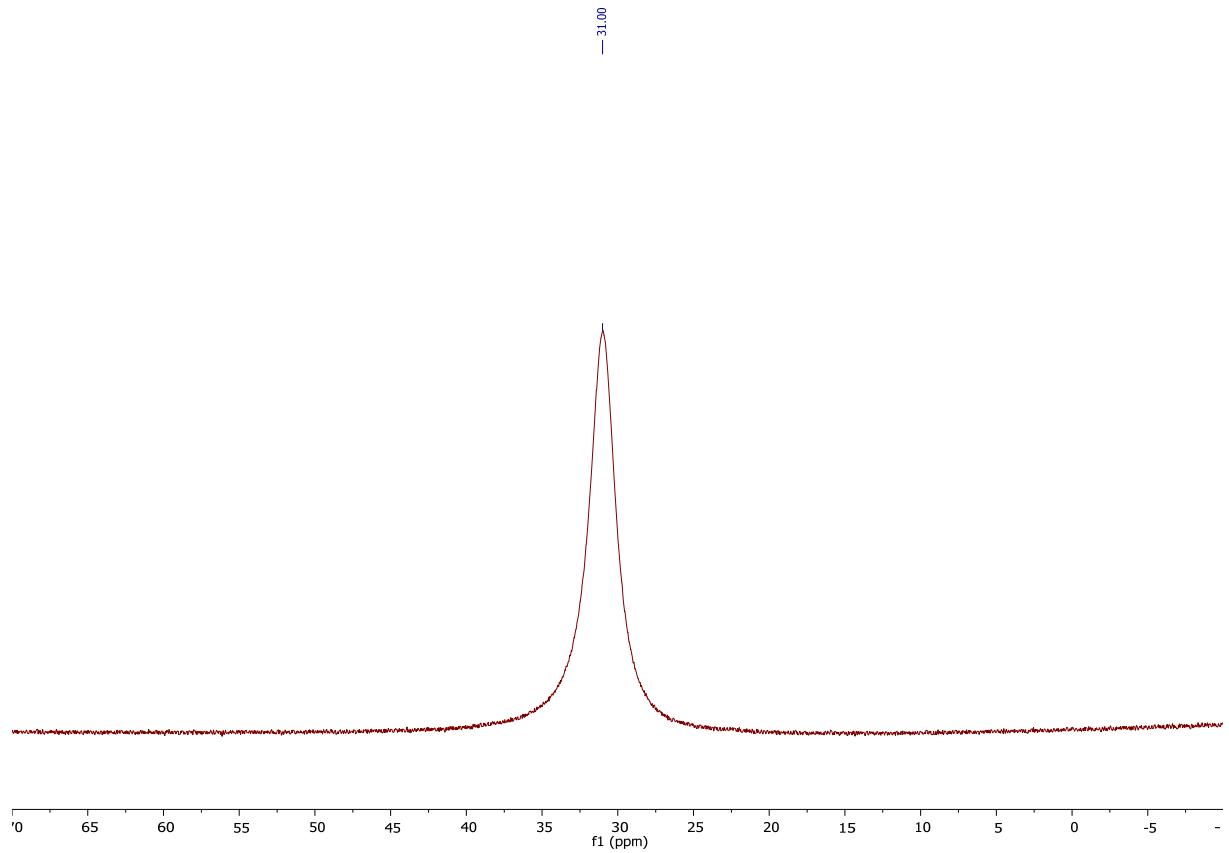
3e





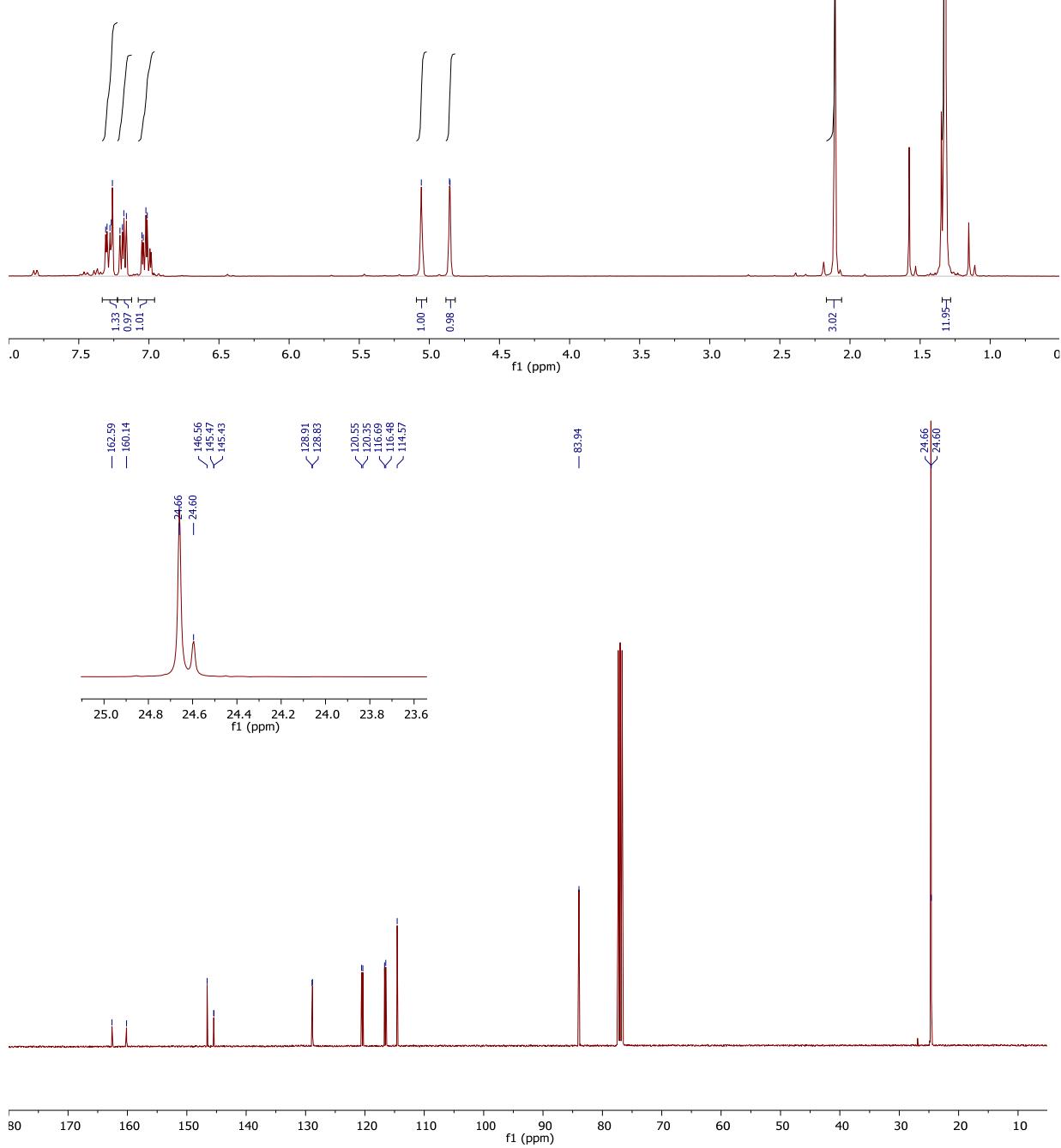
II. Pinacol (2-(prop-1-en-2-yl)phenyl)boronic esters 4a-f from α -methyl styrenes 3a-f

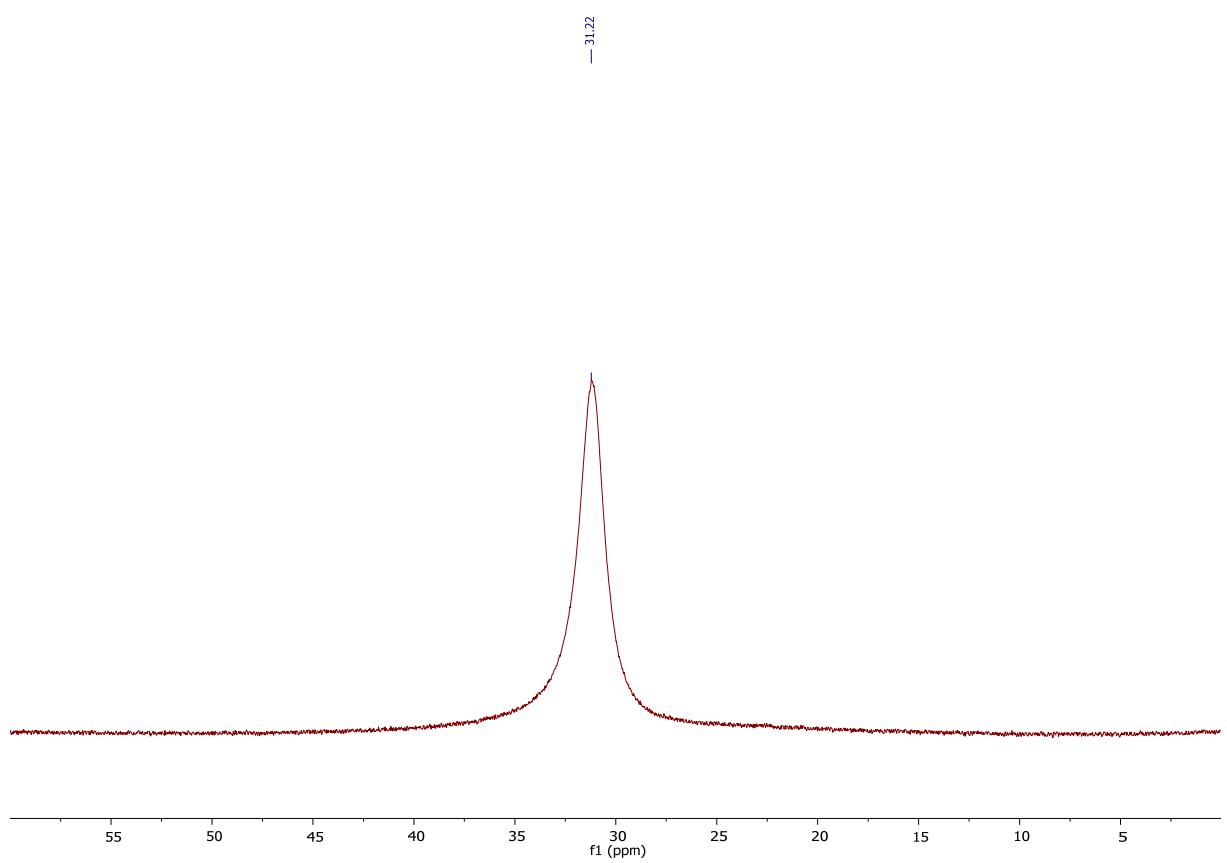
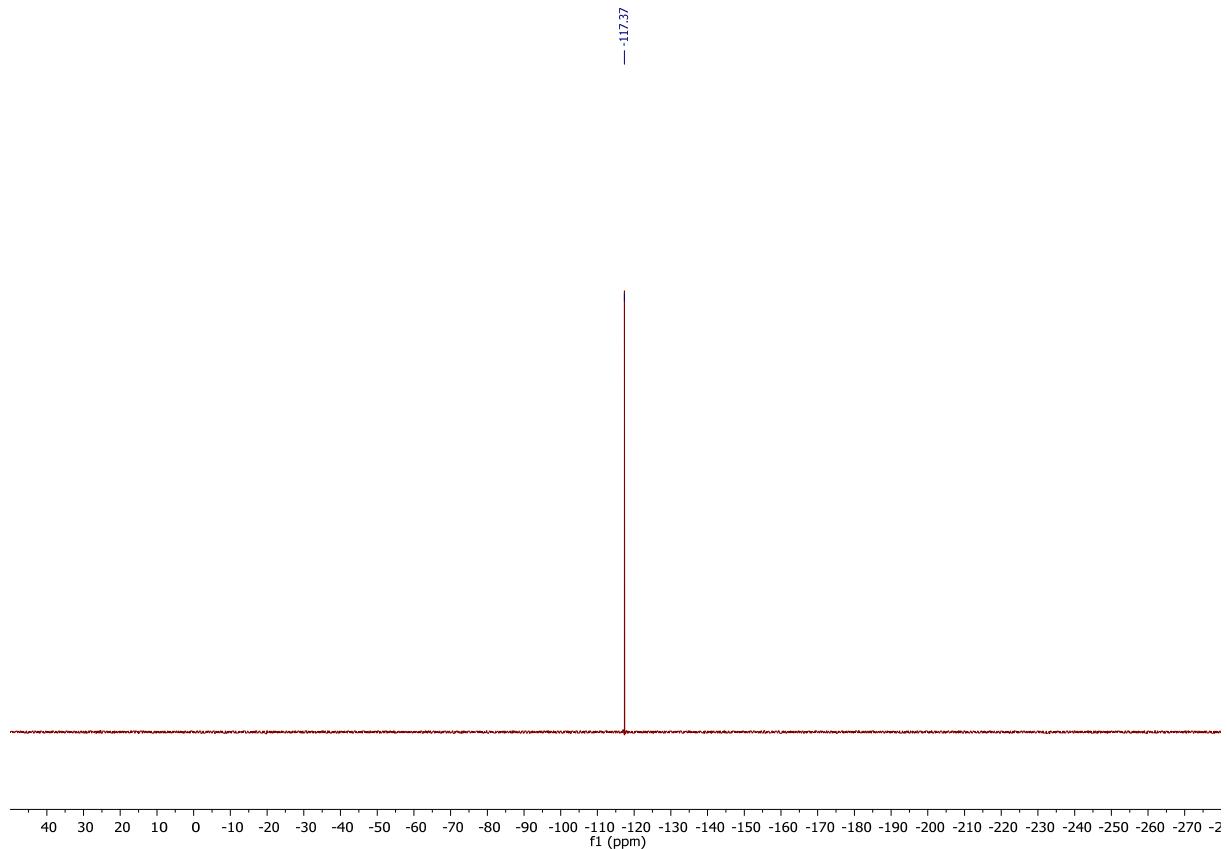


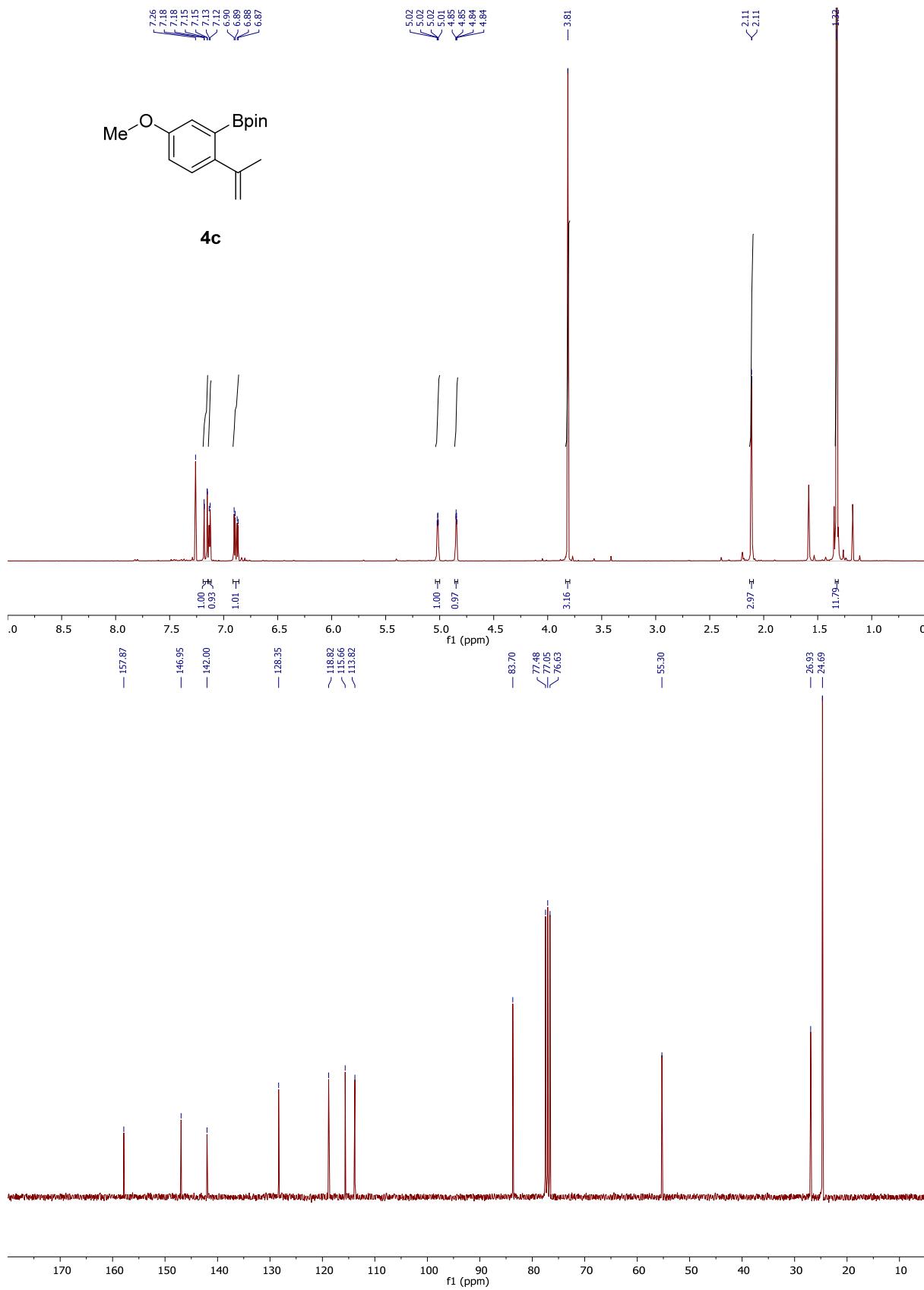


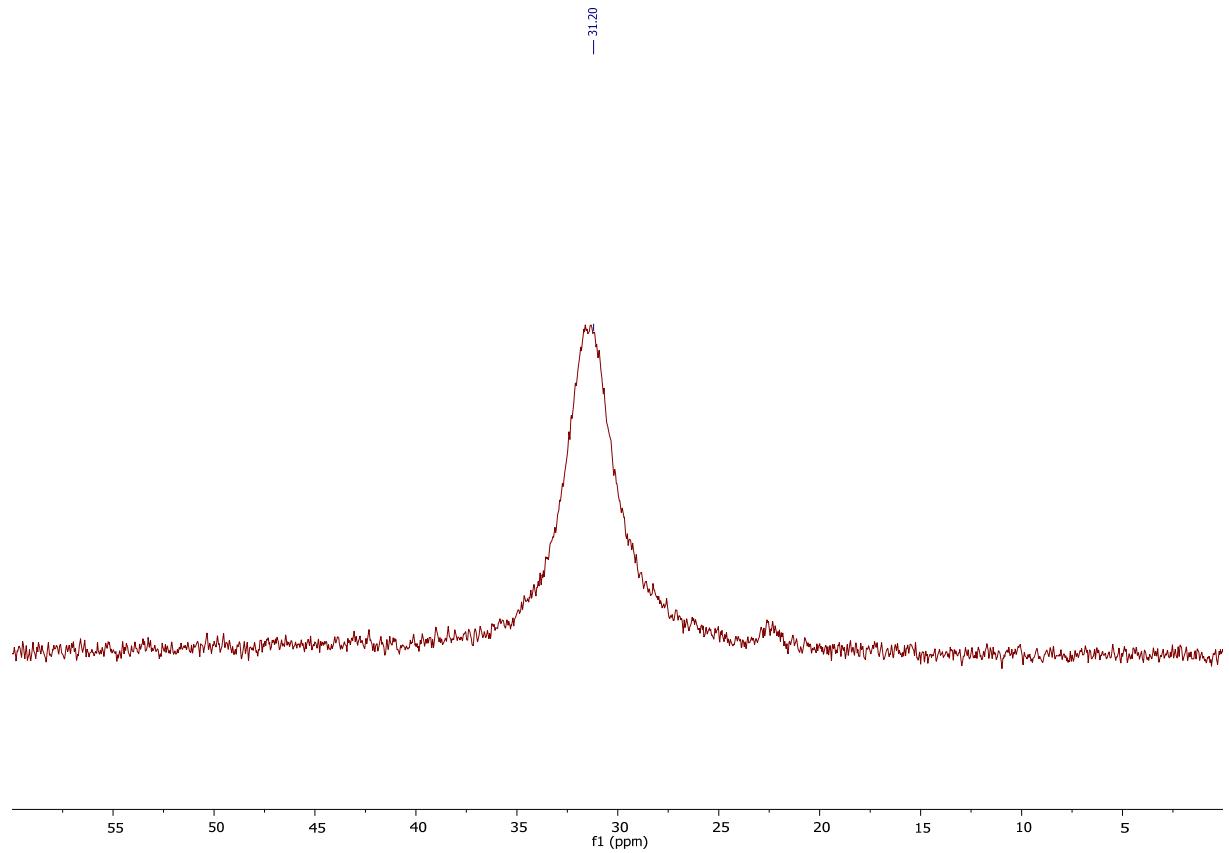


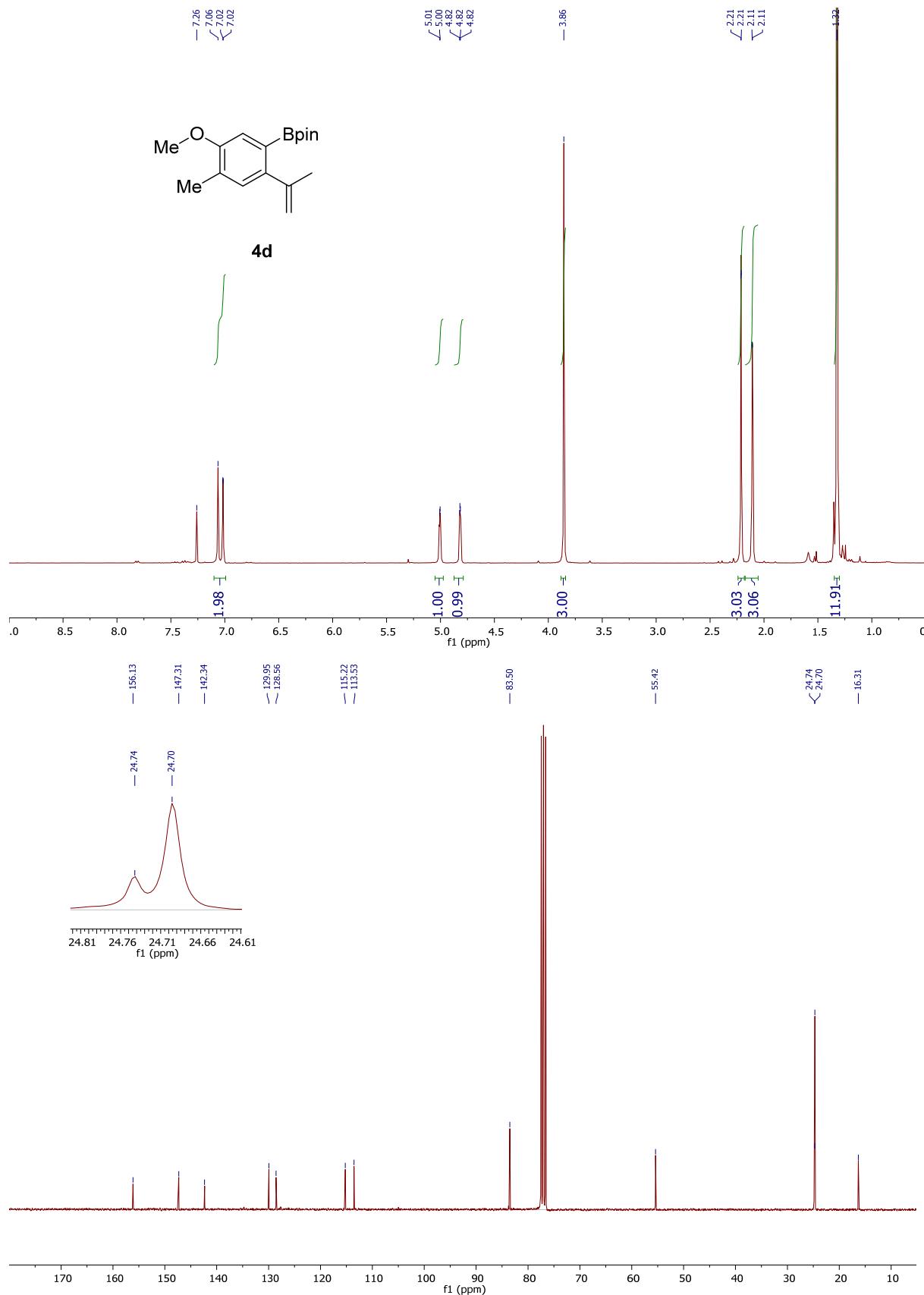
4b

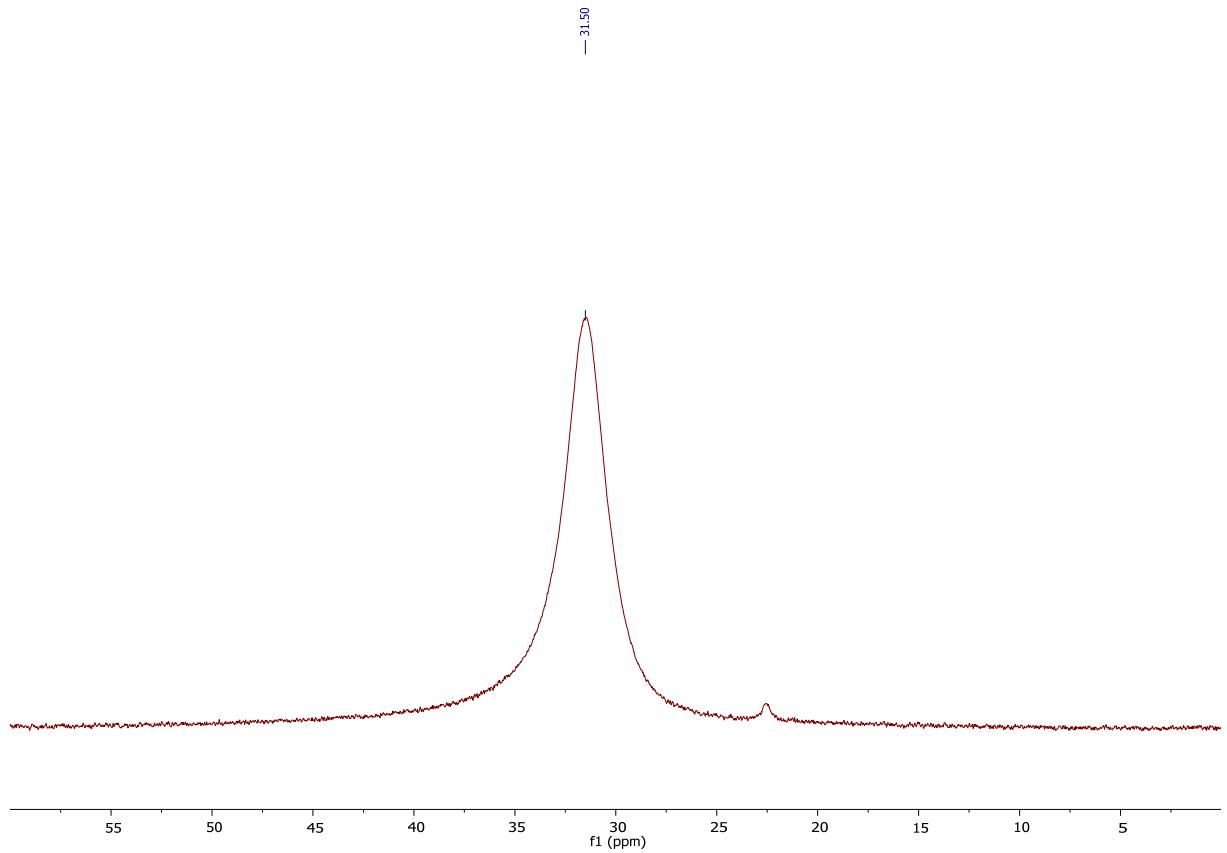


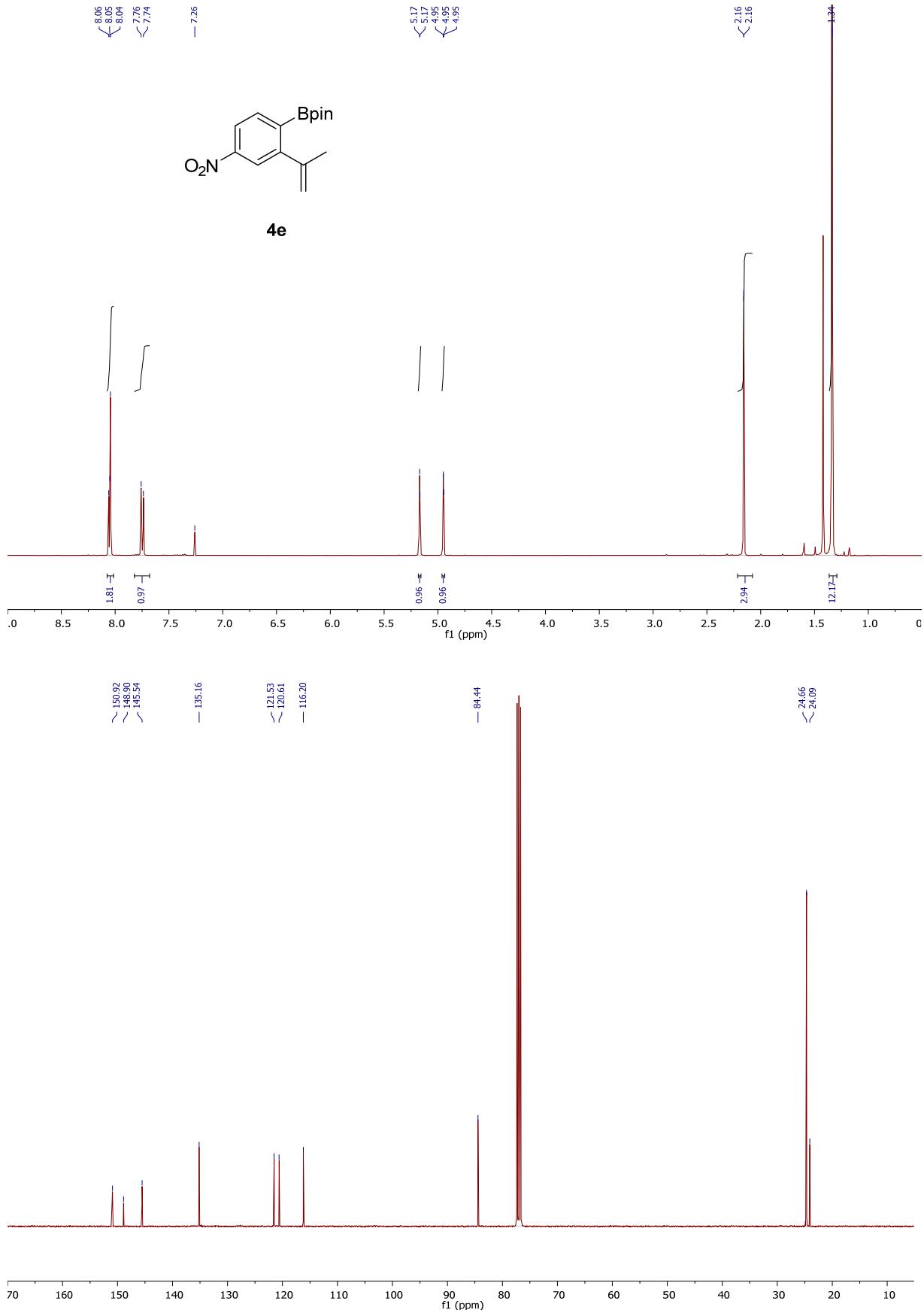


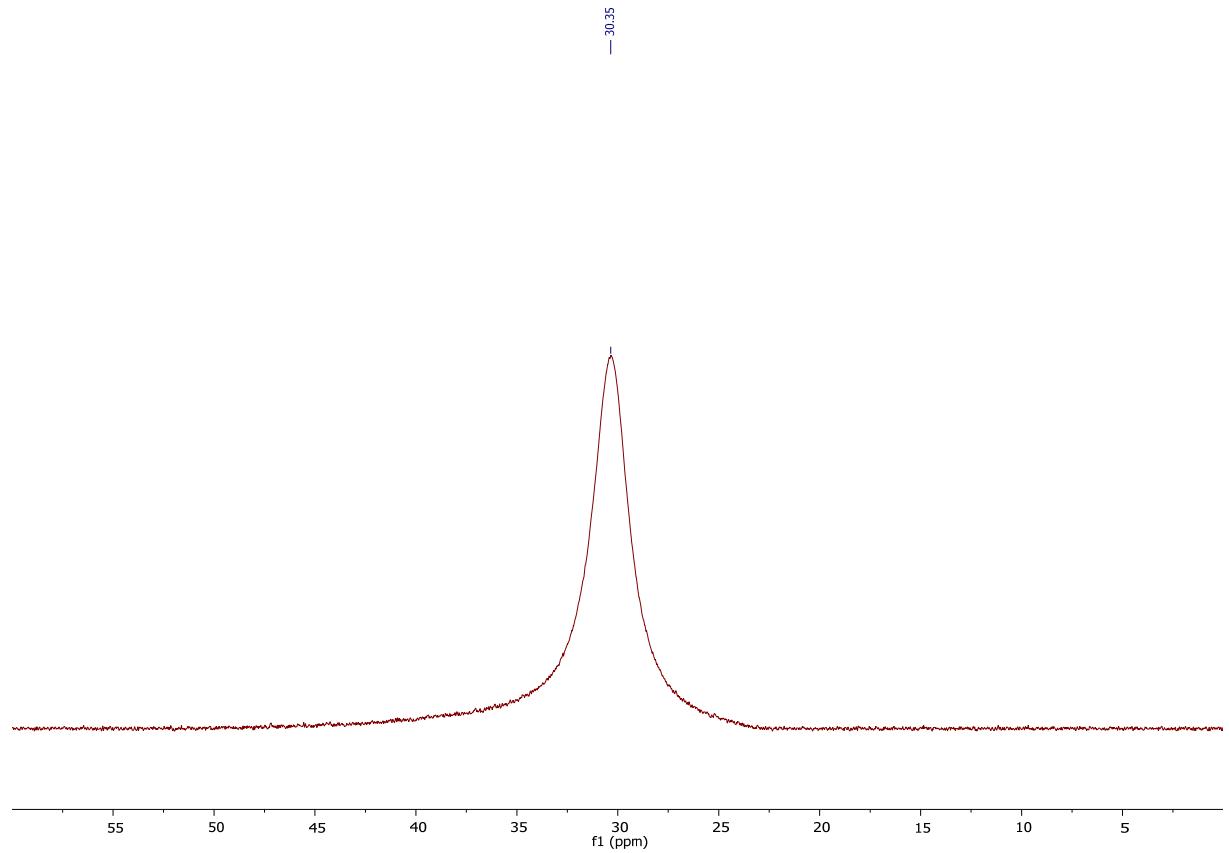


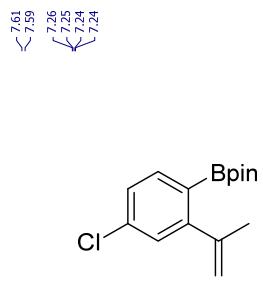




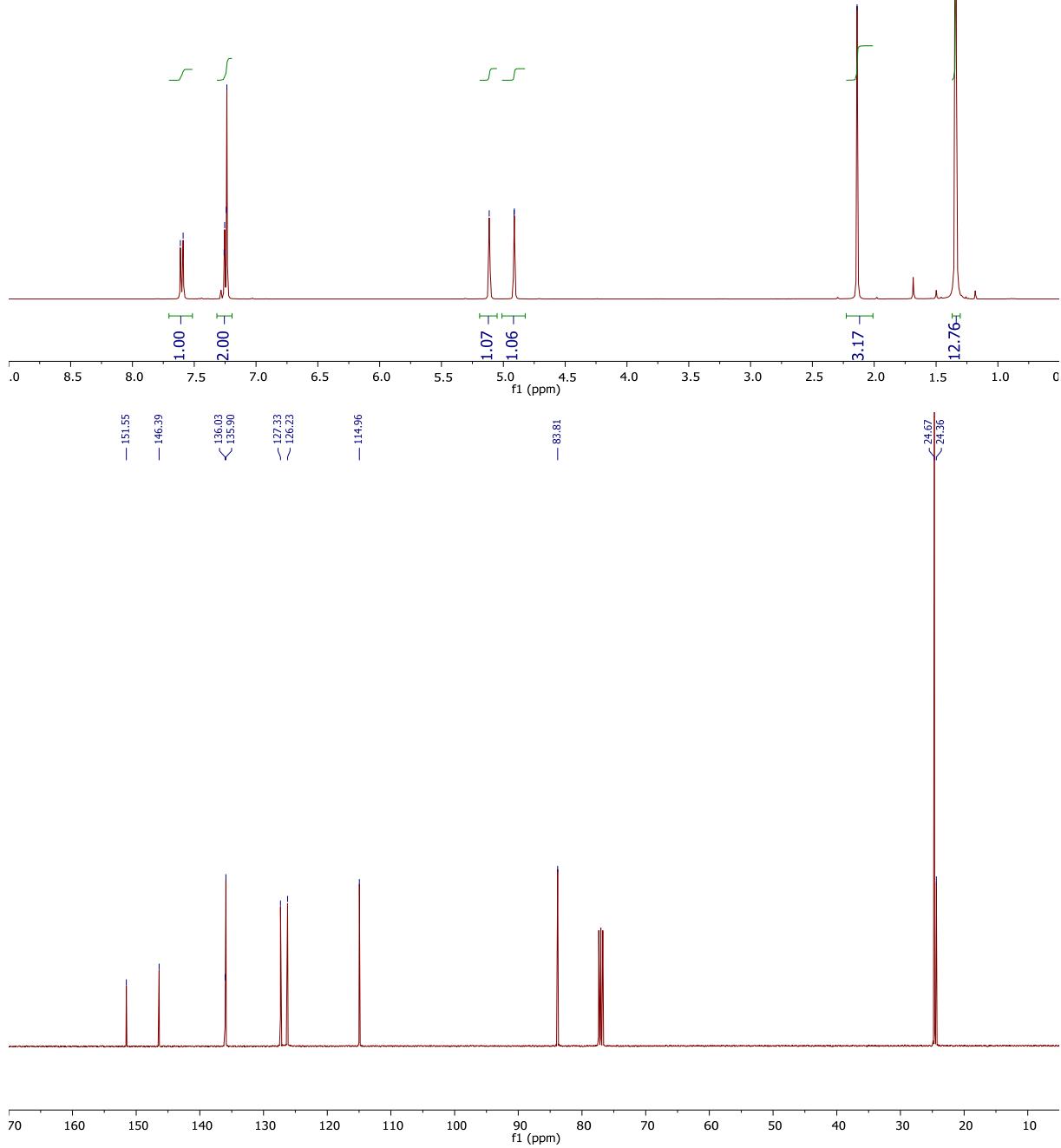


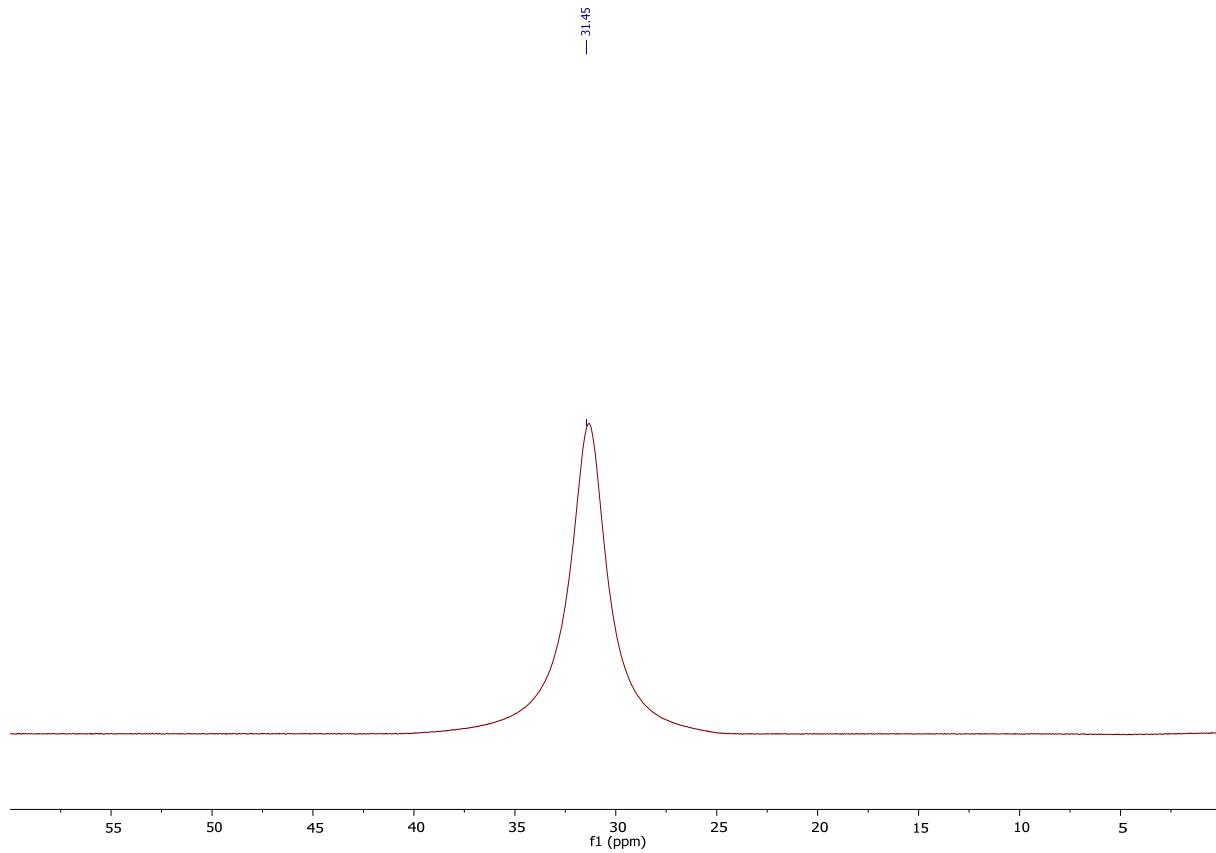




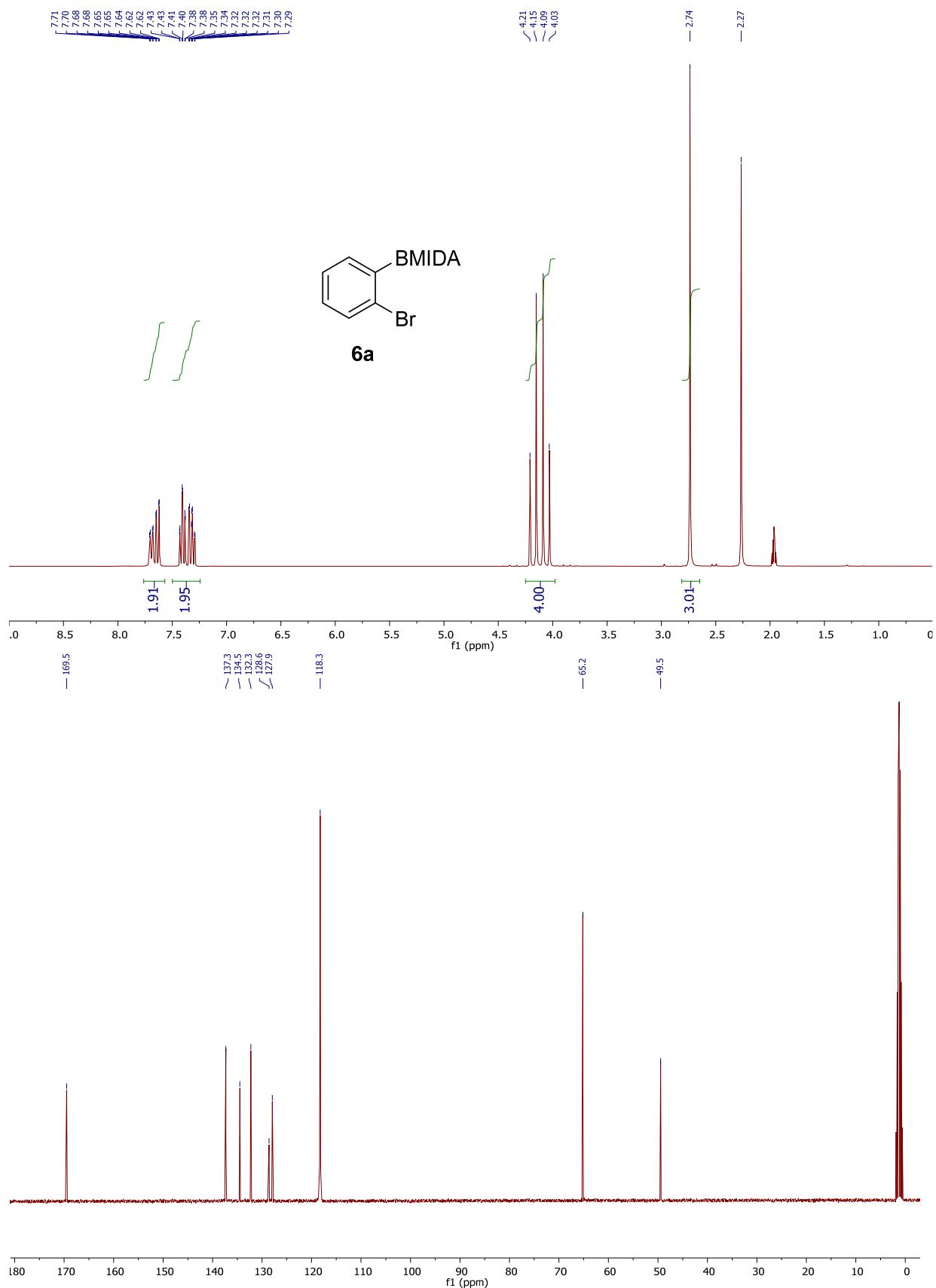


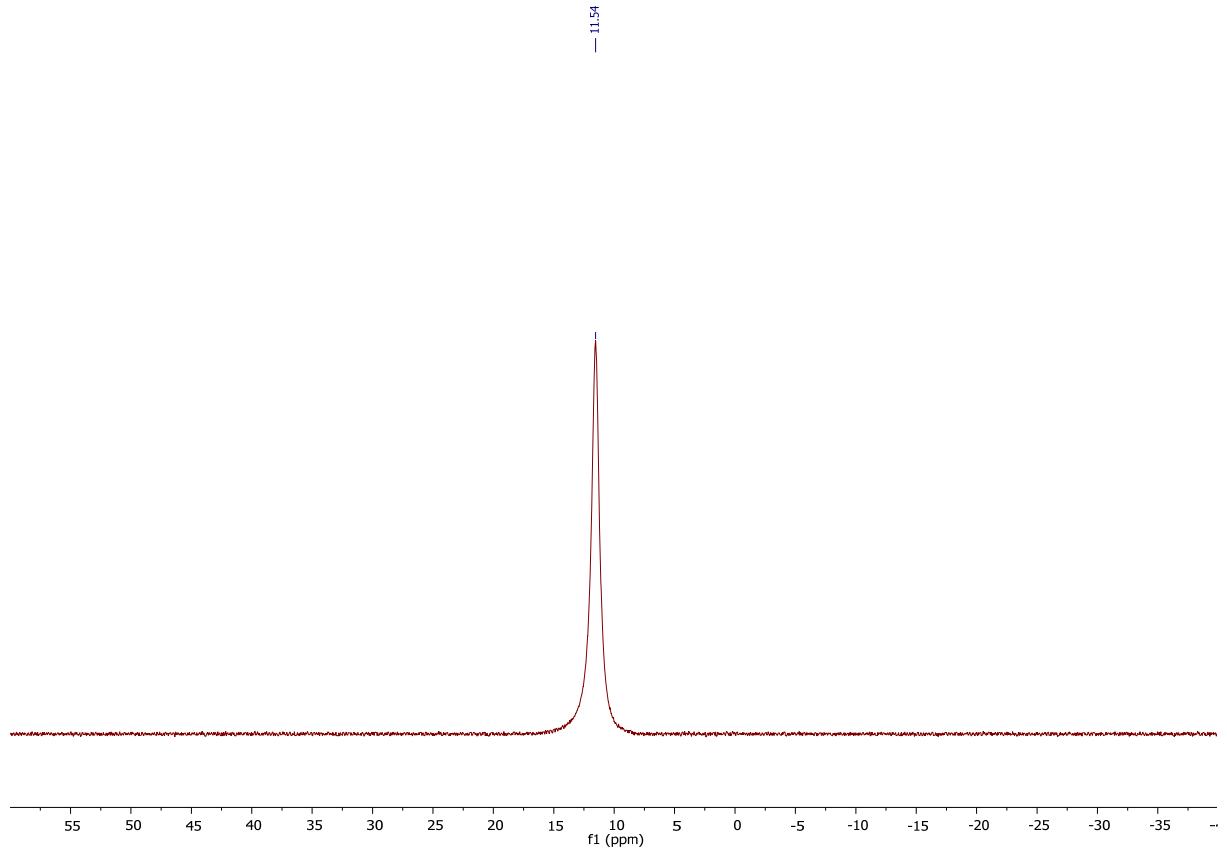
4f

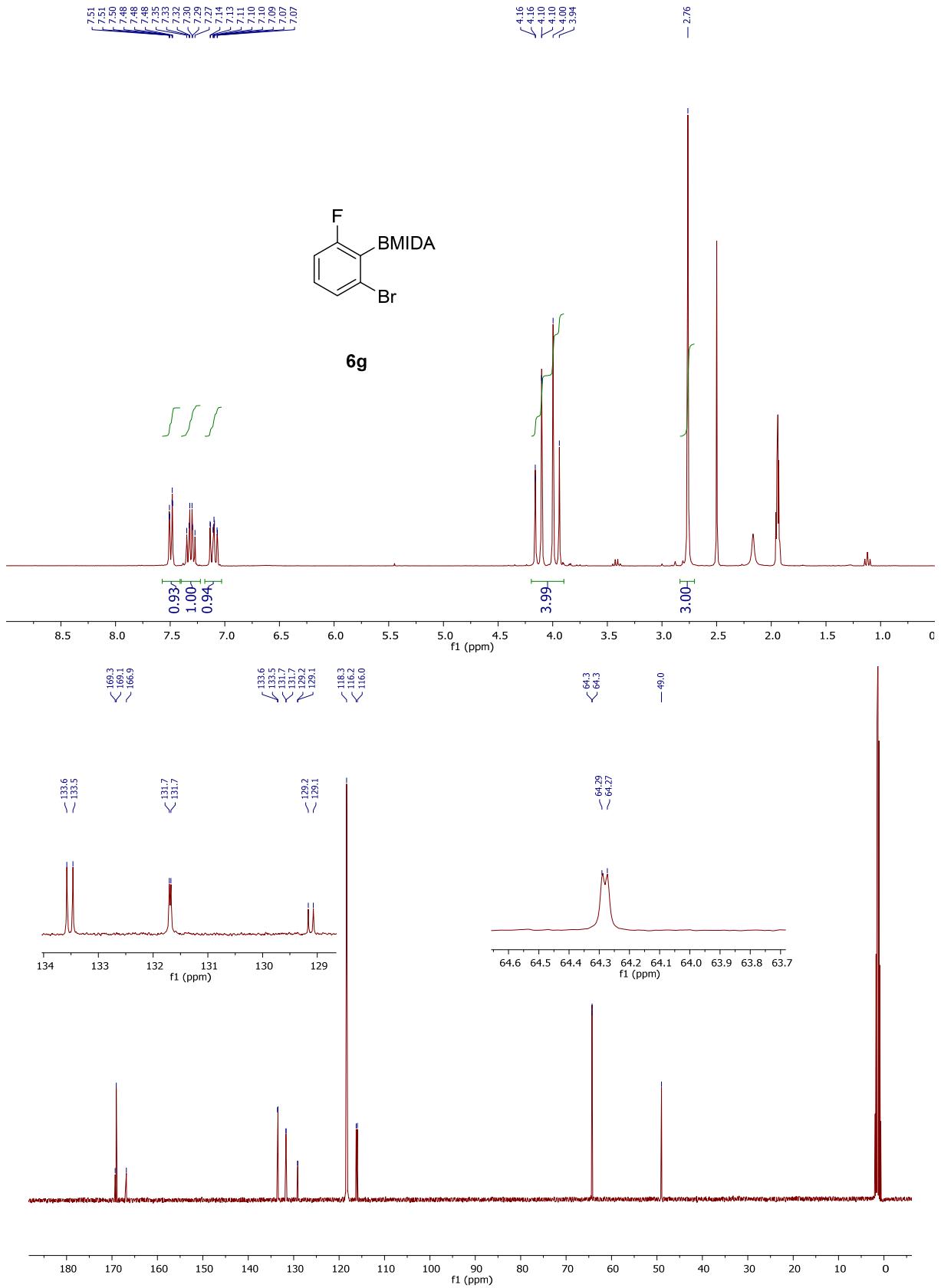


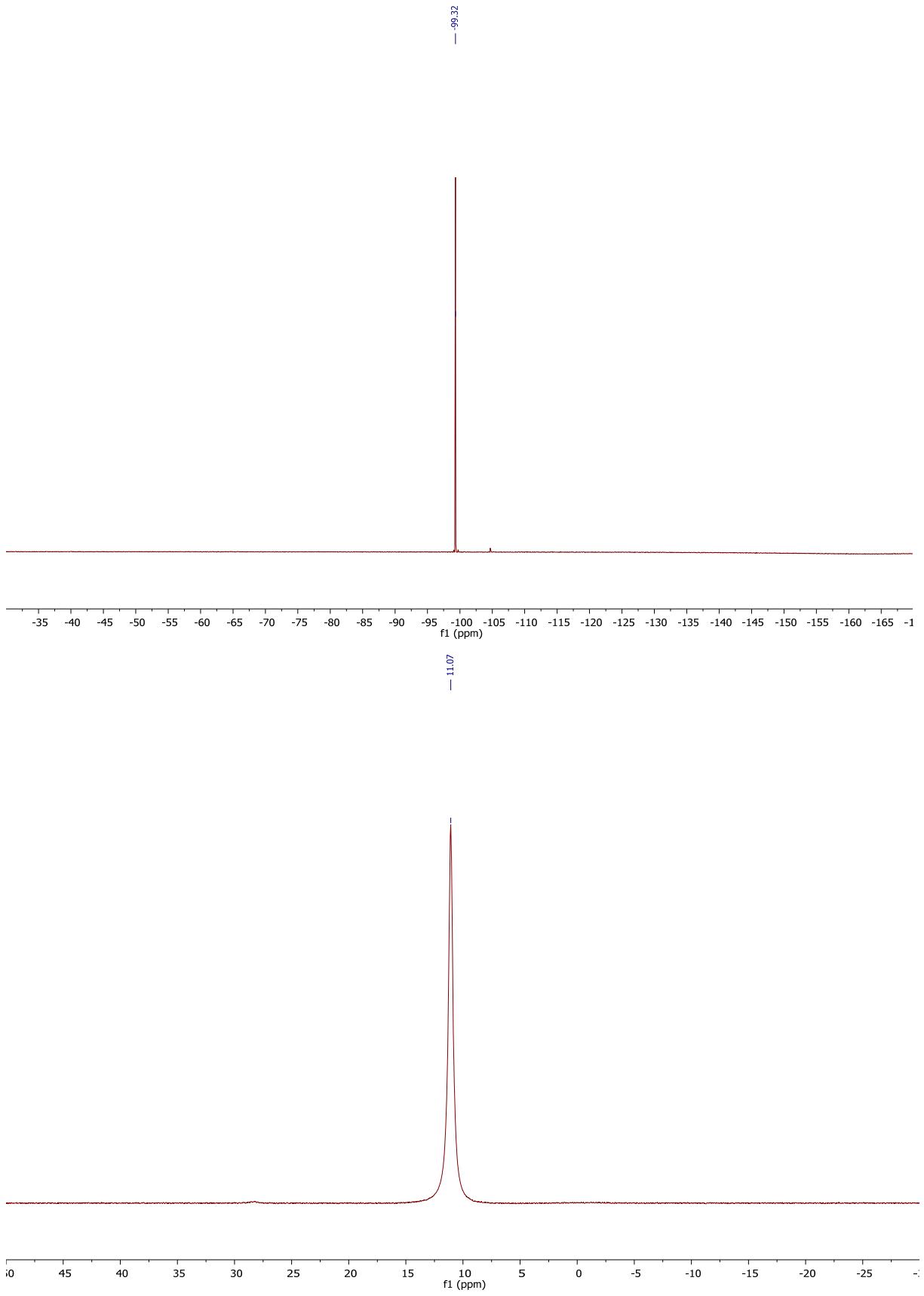


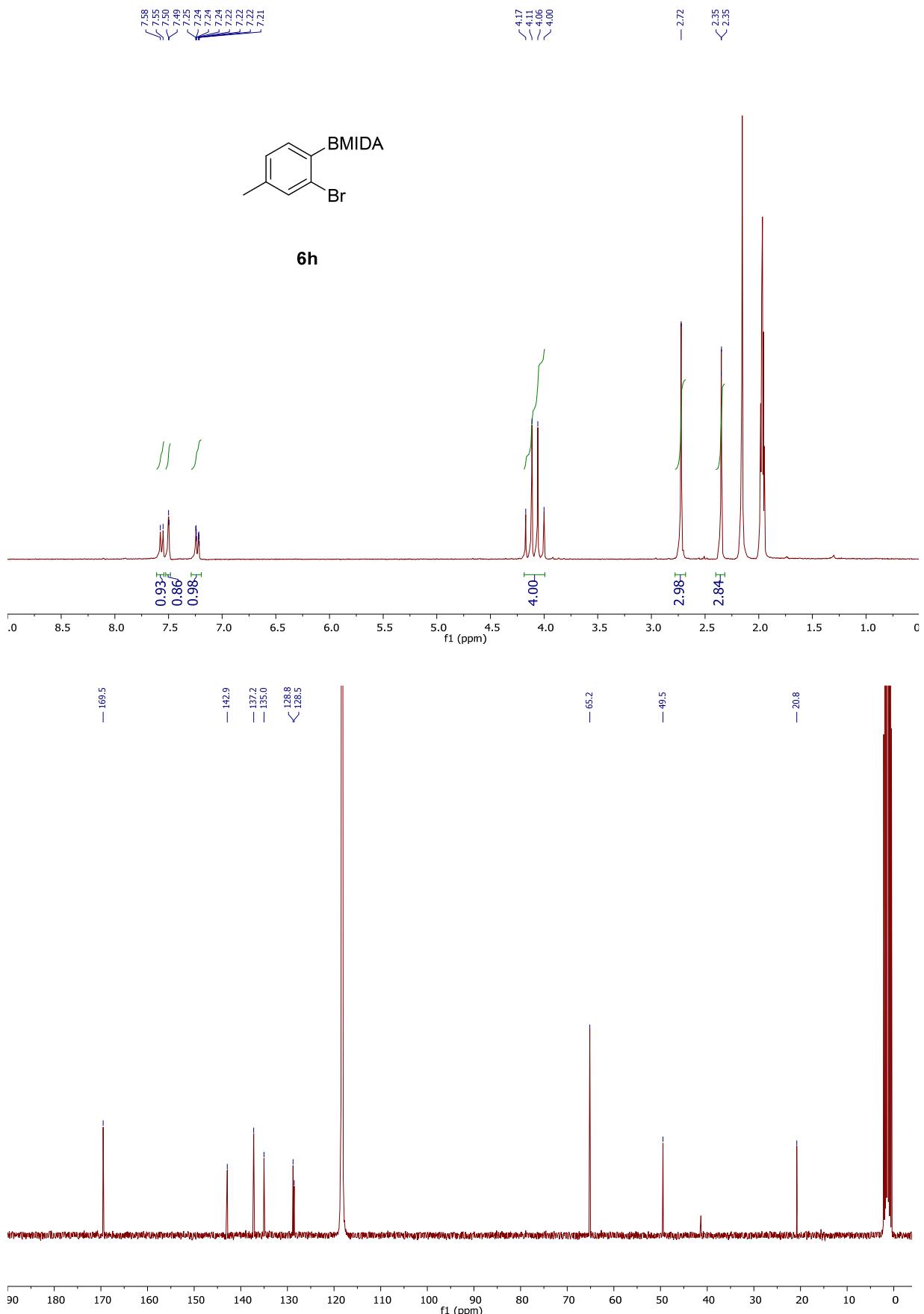
III. B-MIDA derivatives 6a,g-i

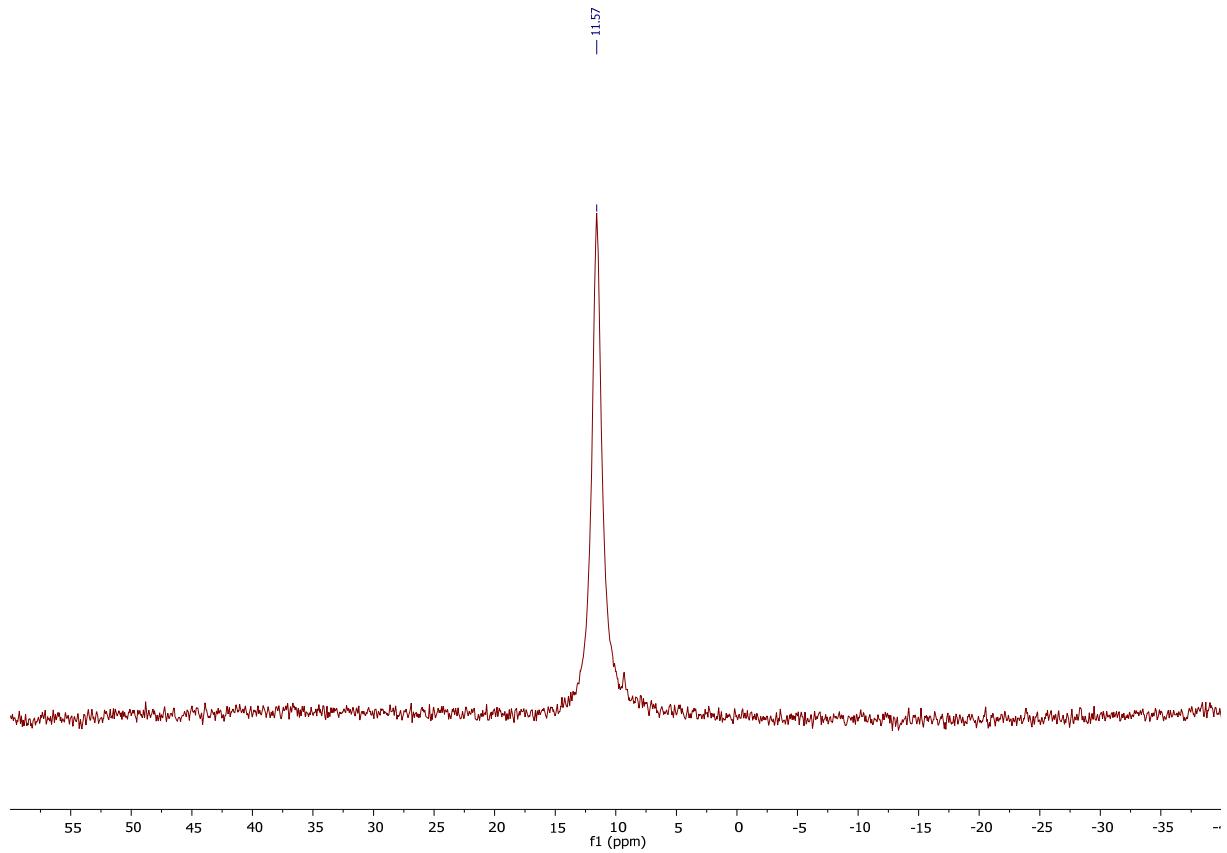


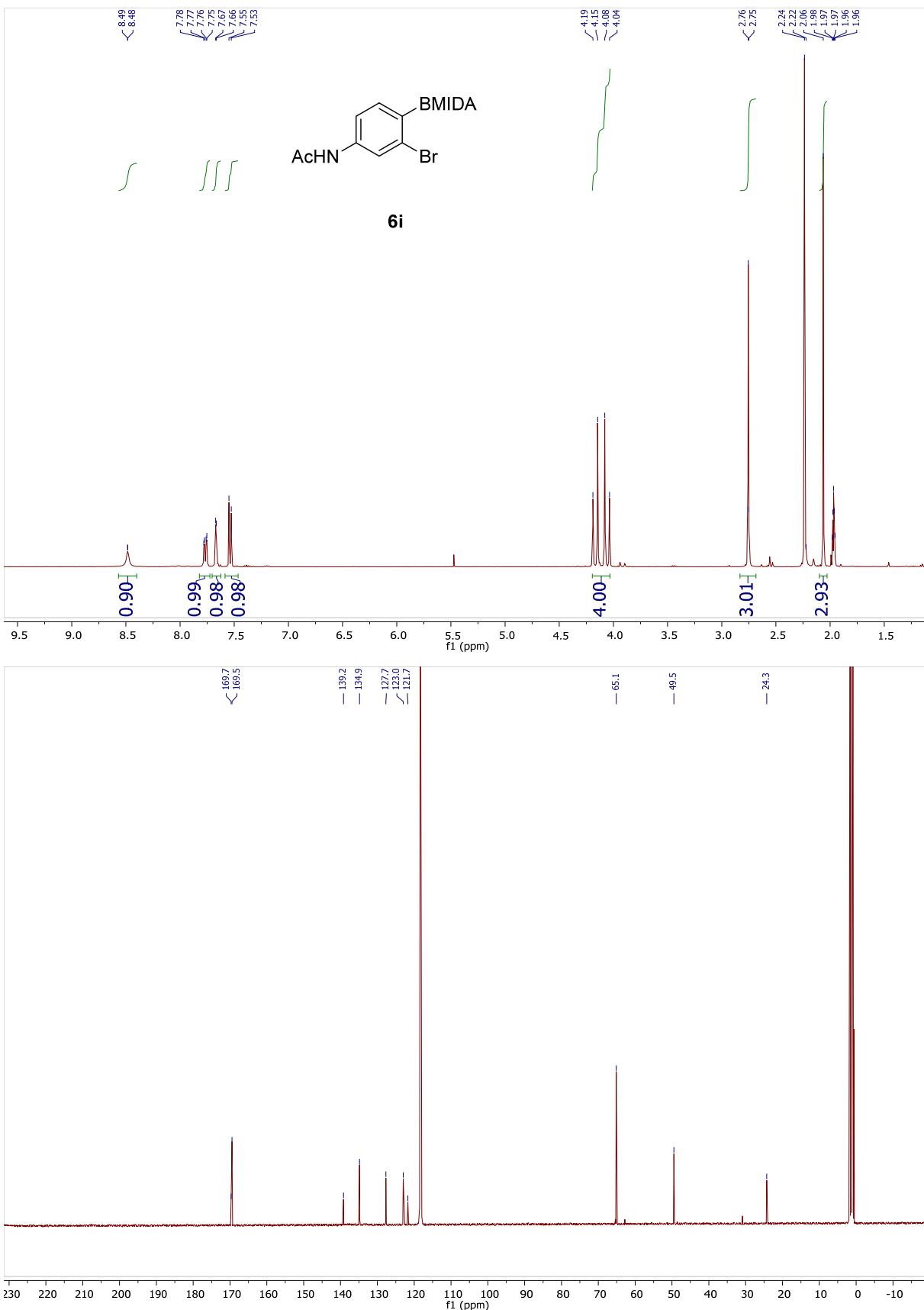


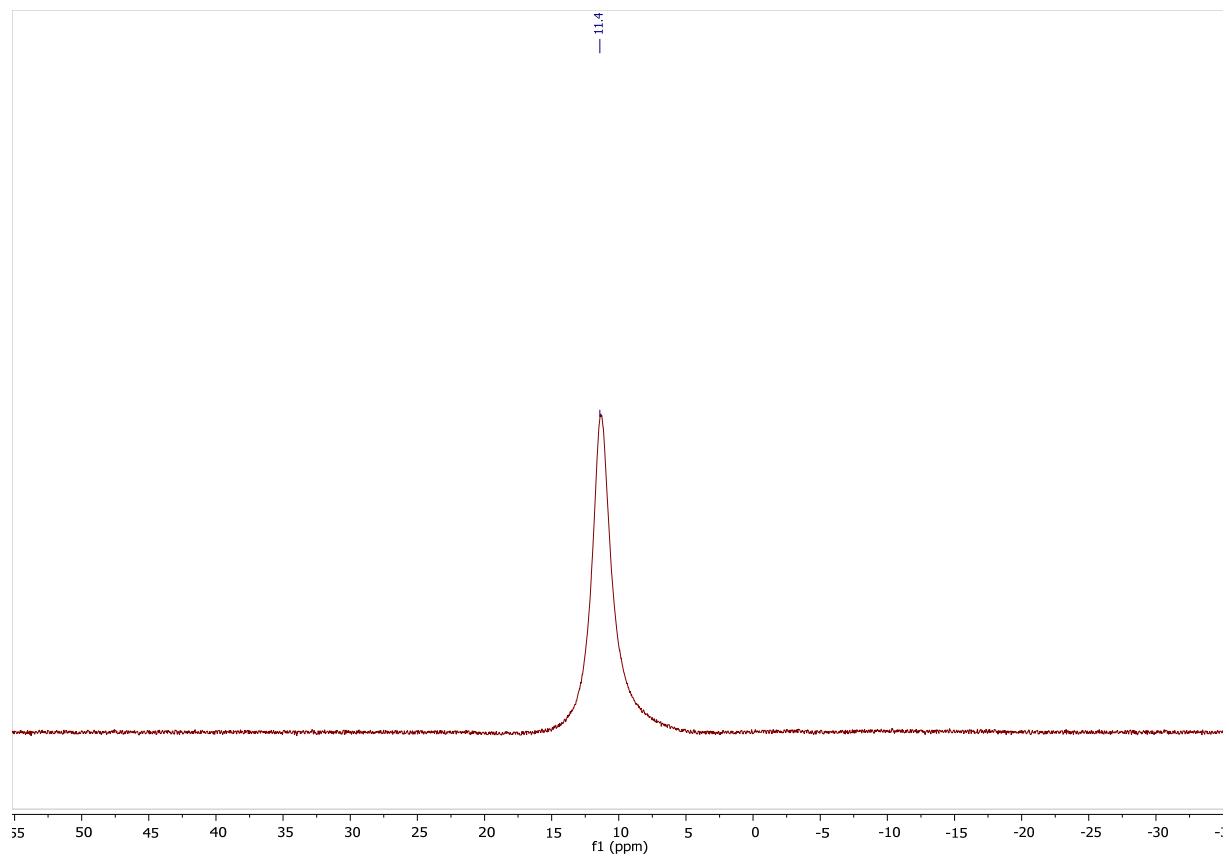




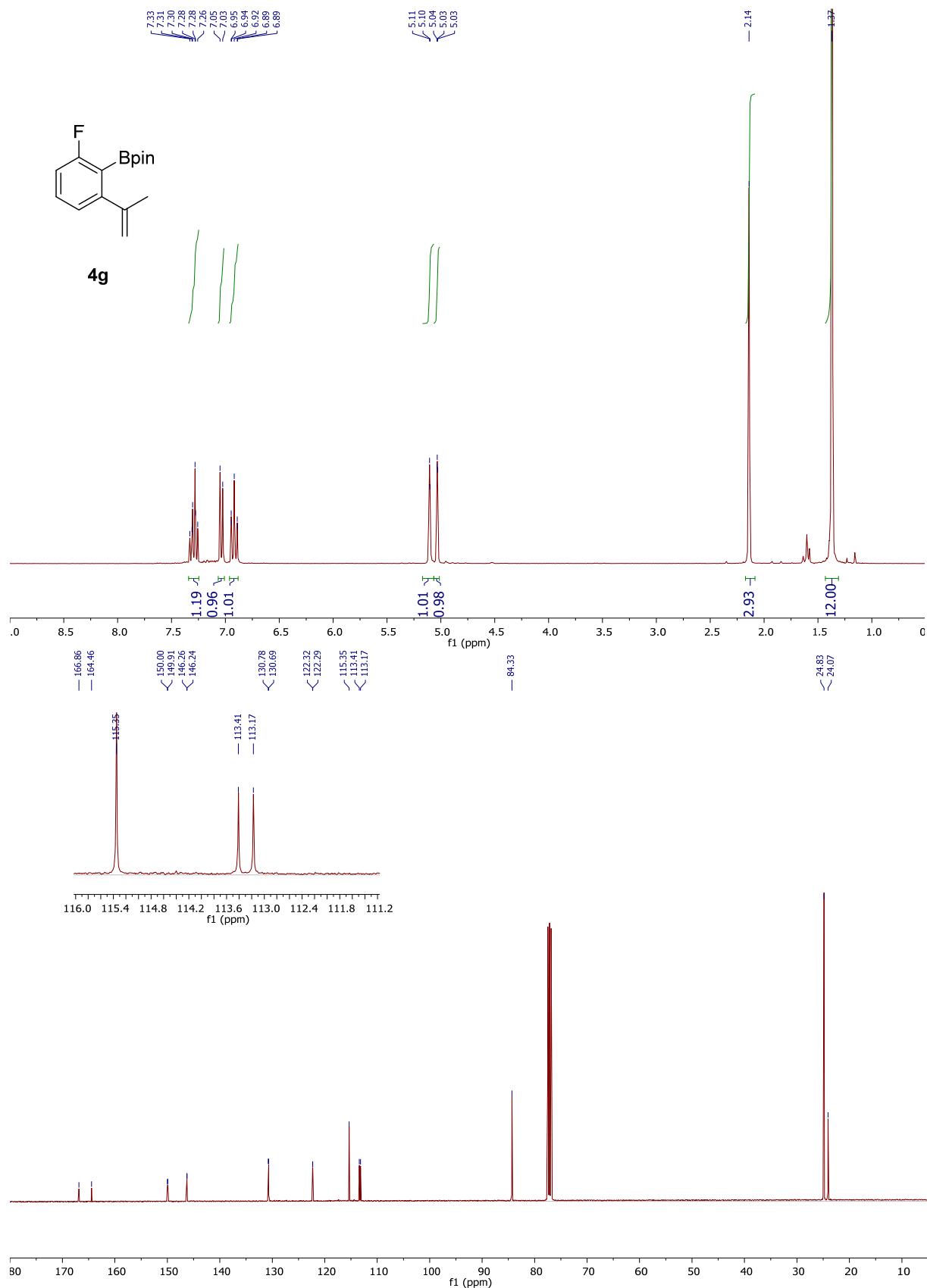


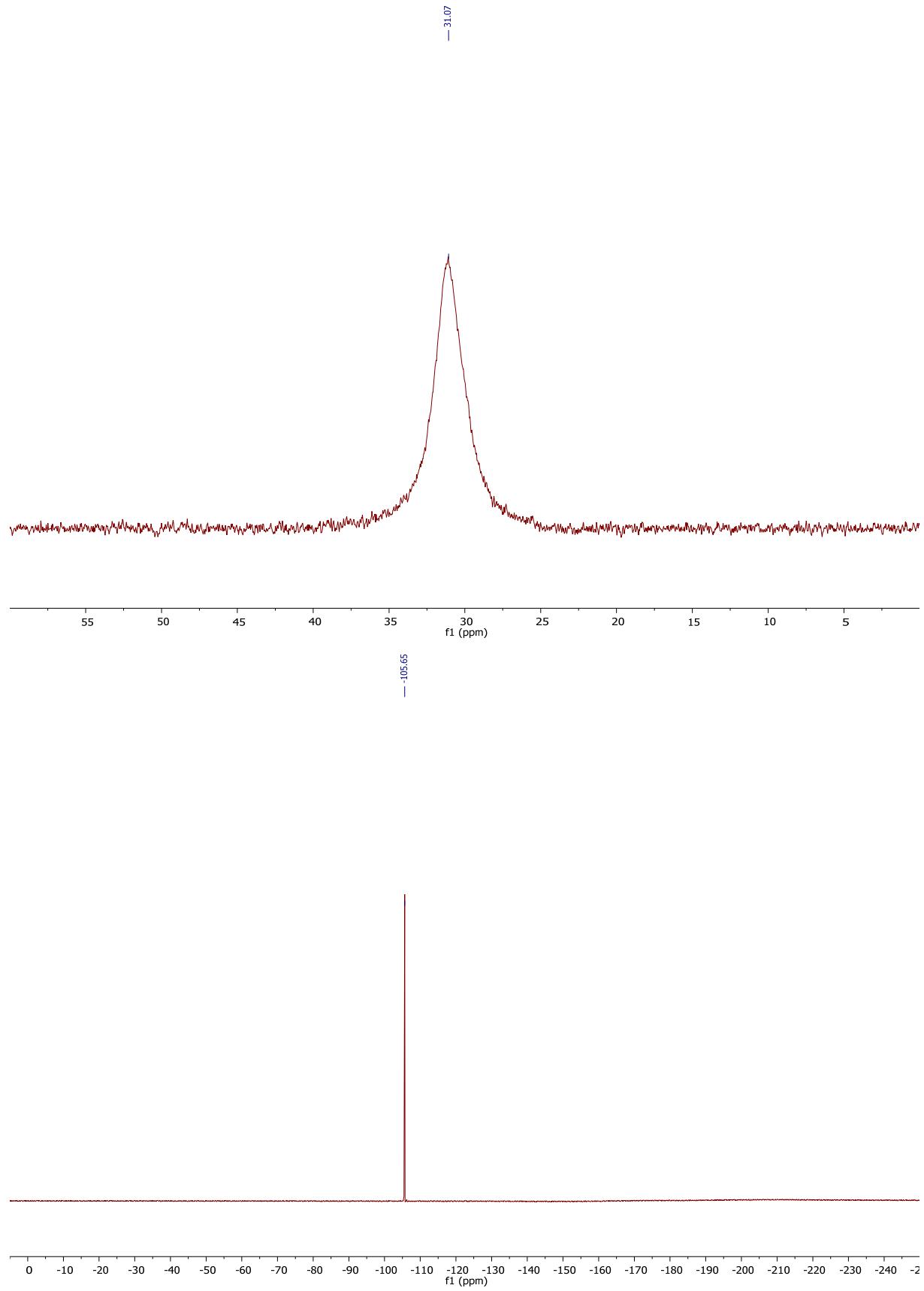


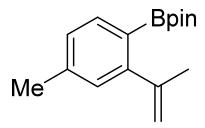




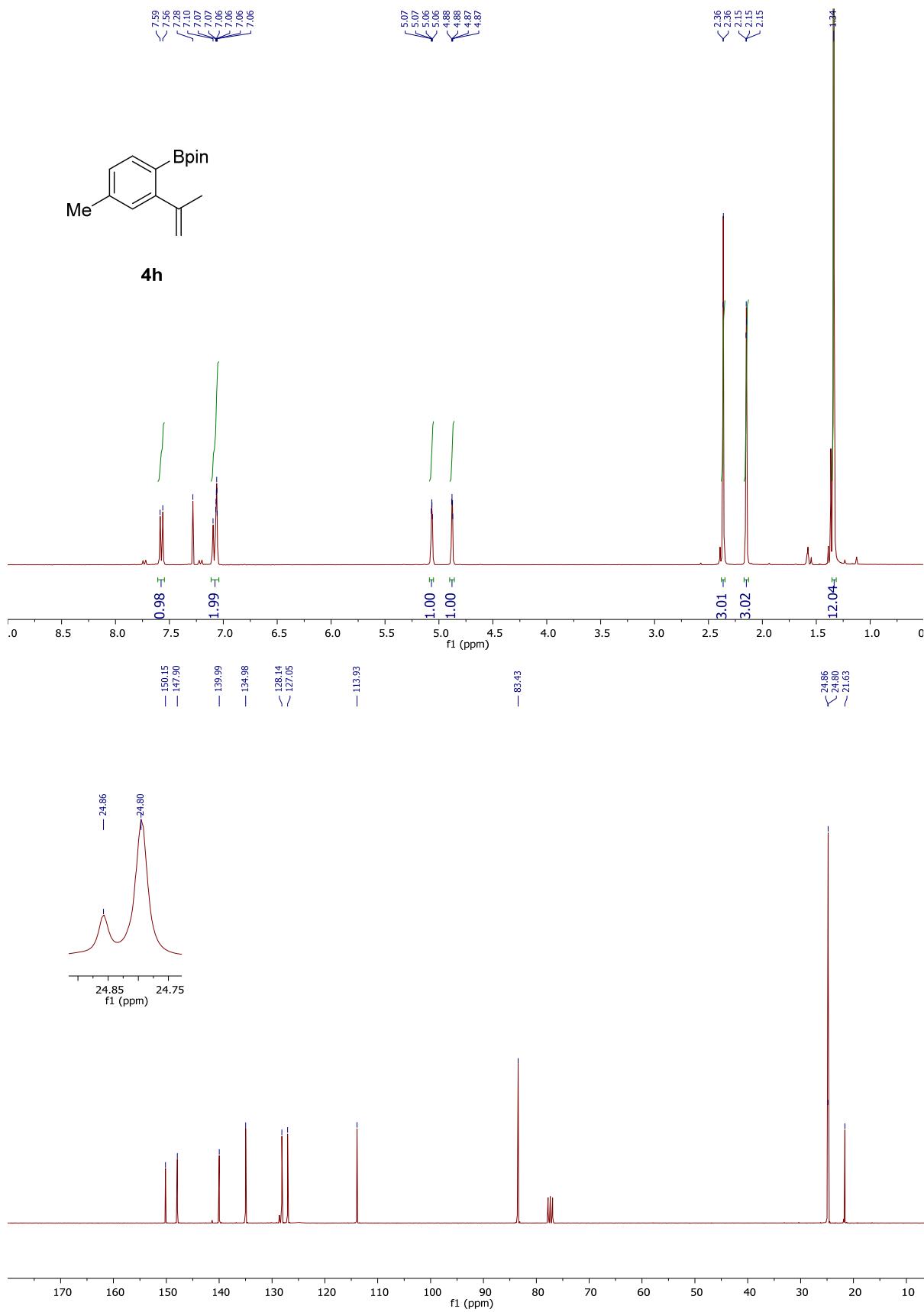
IV. Pinacol (2-(prop-1-en-2-yl)phenyl)boronic esters **4g-i from **6g-i****

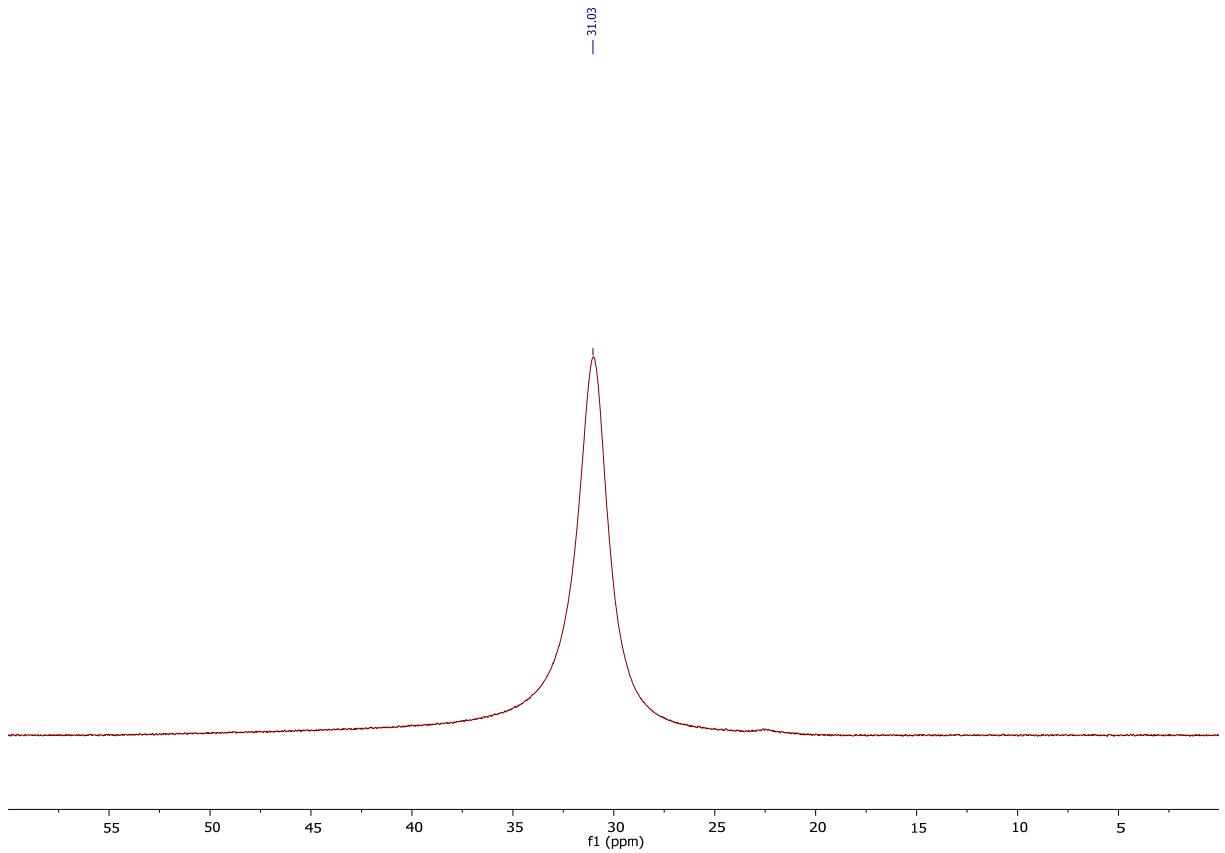


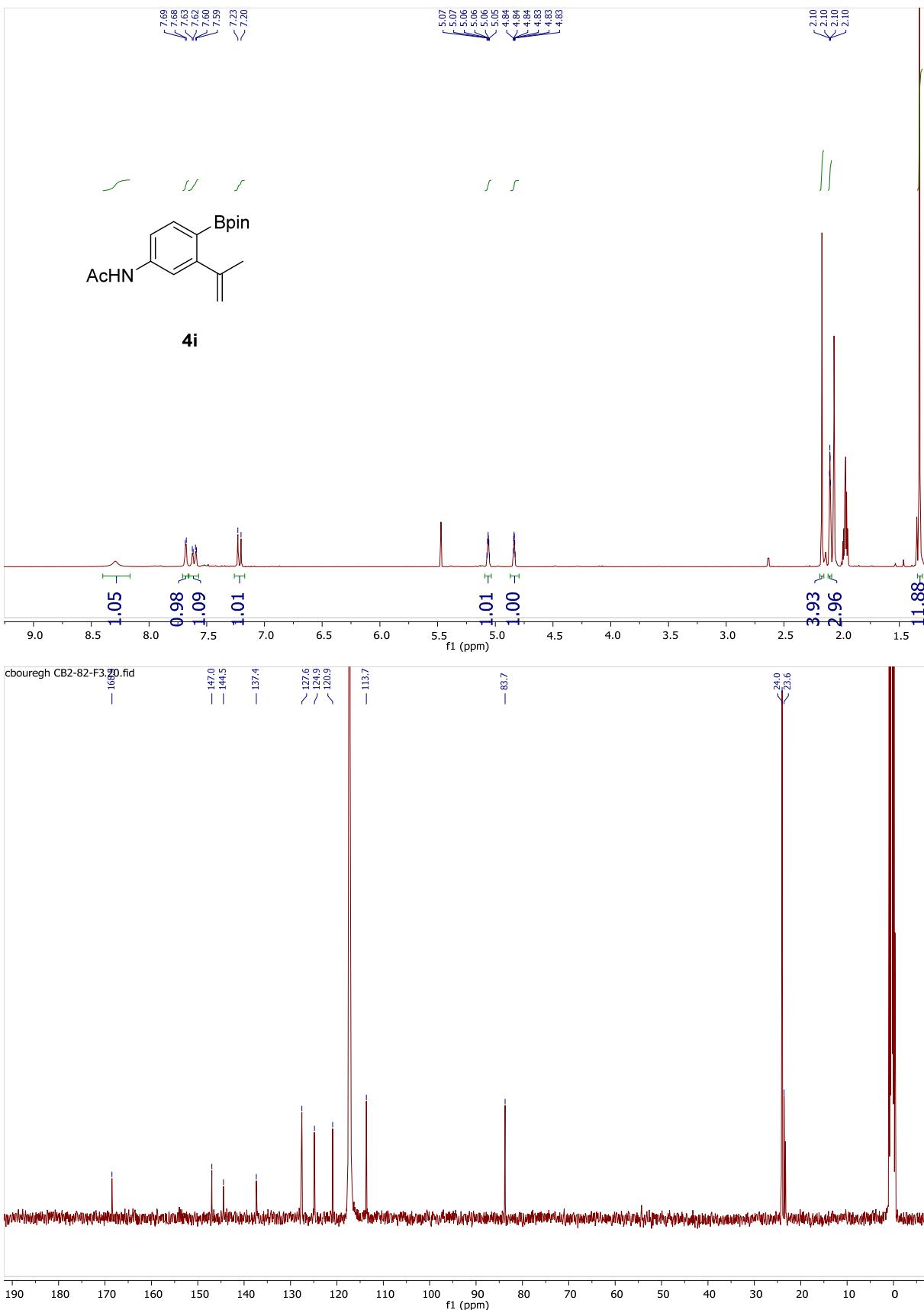


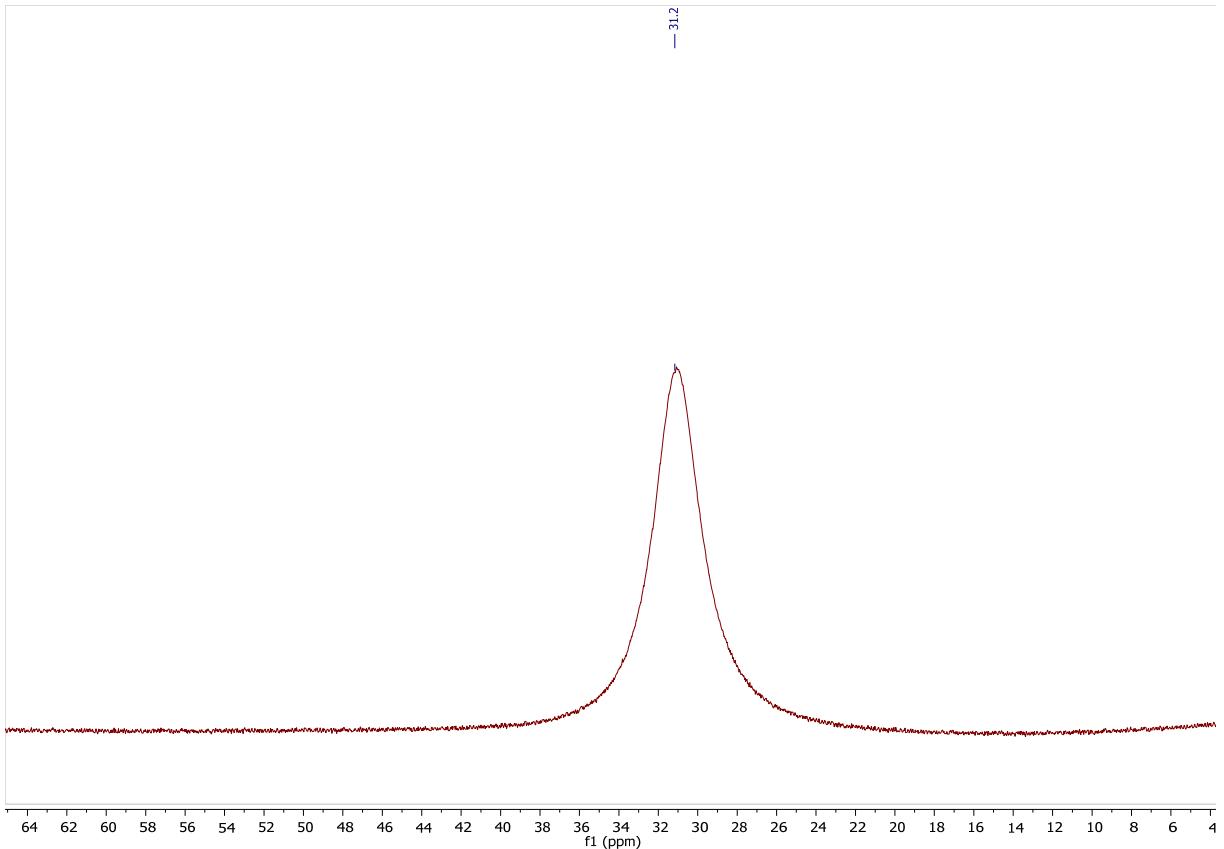


4h



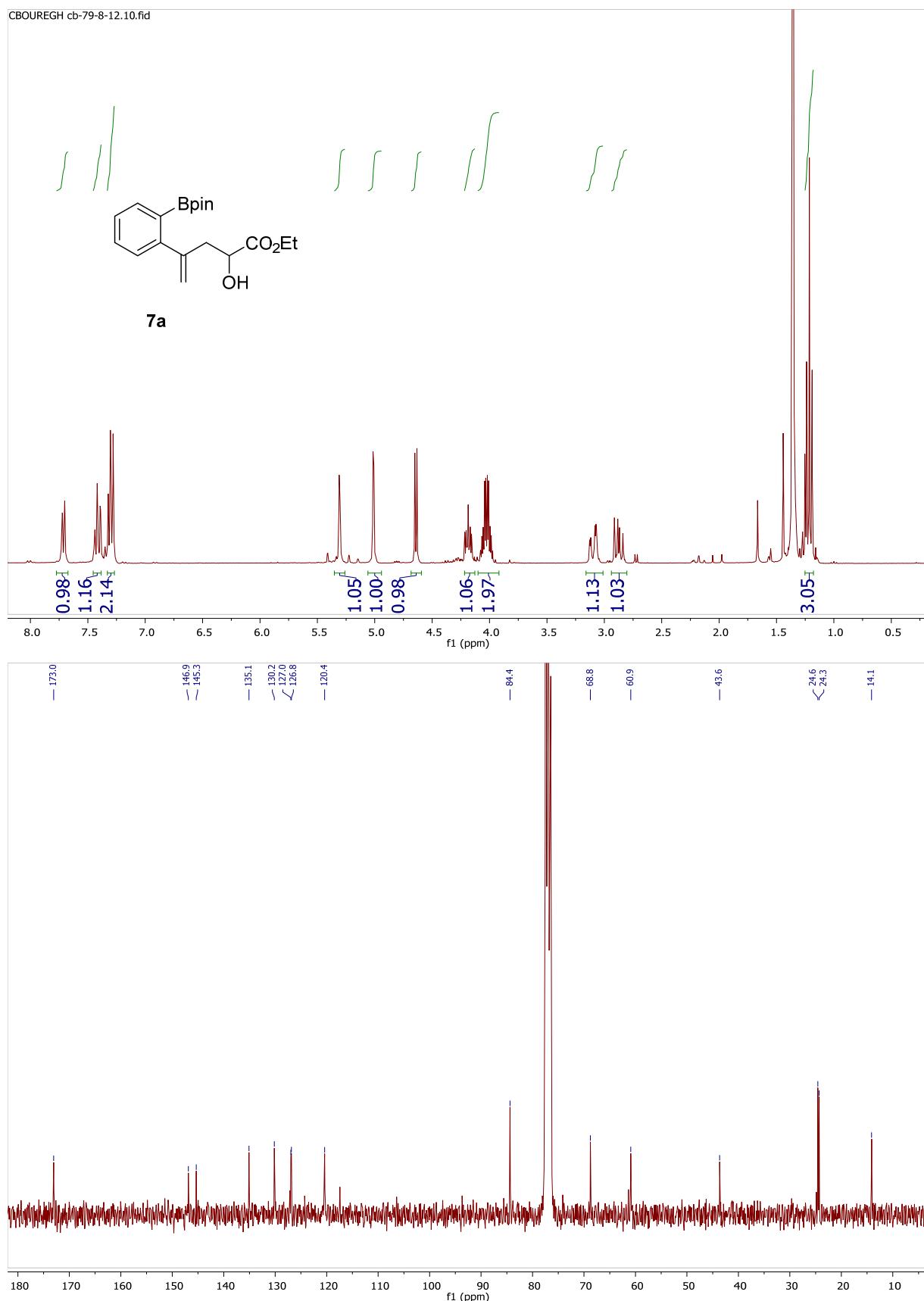


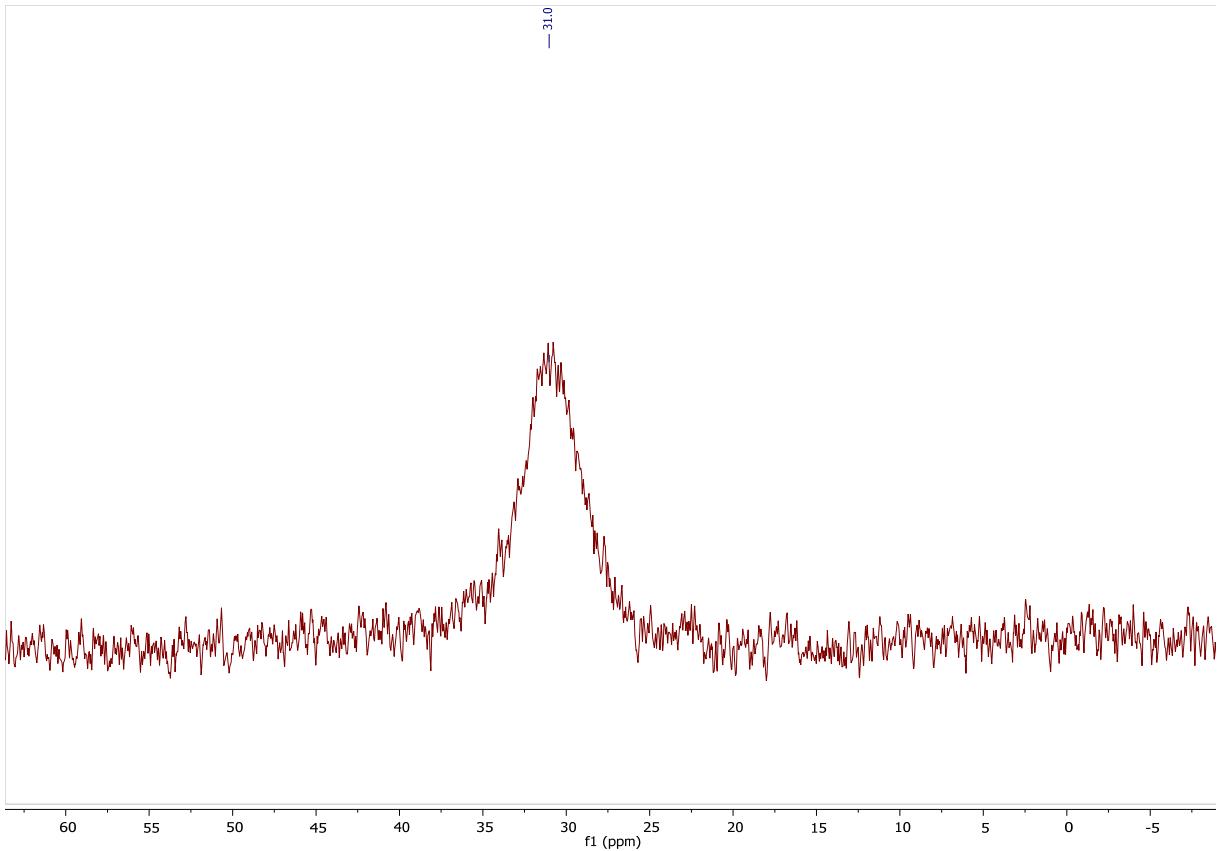


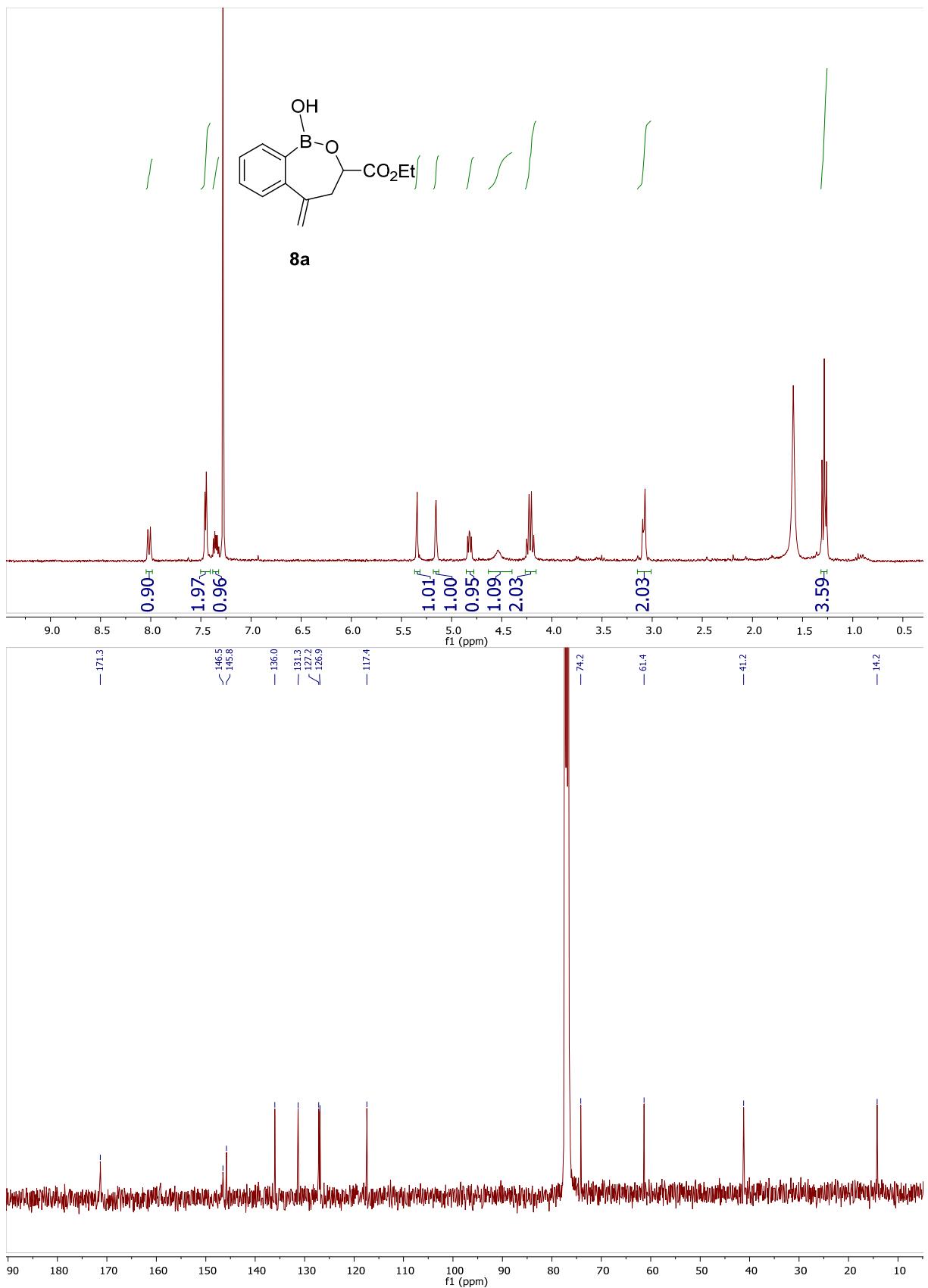


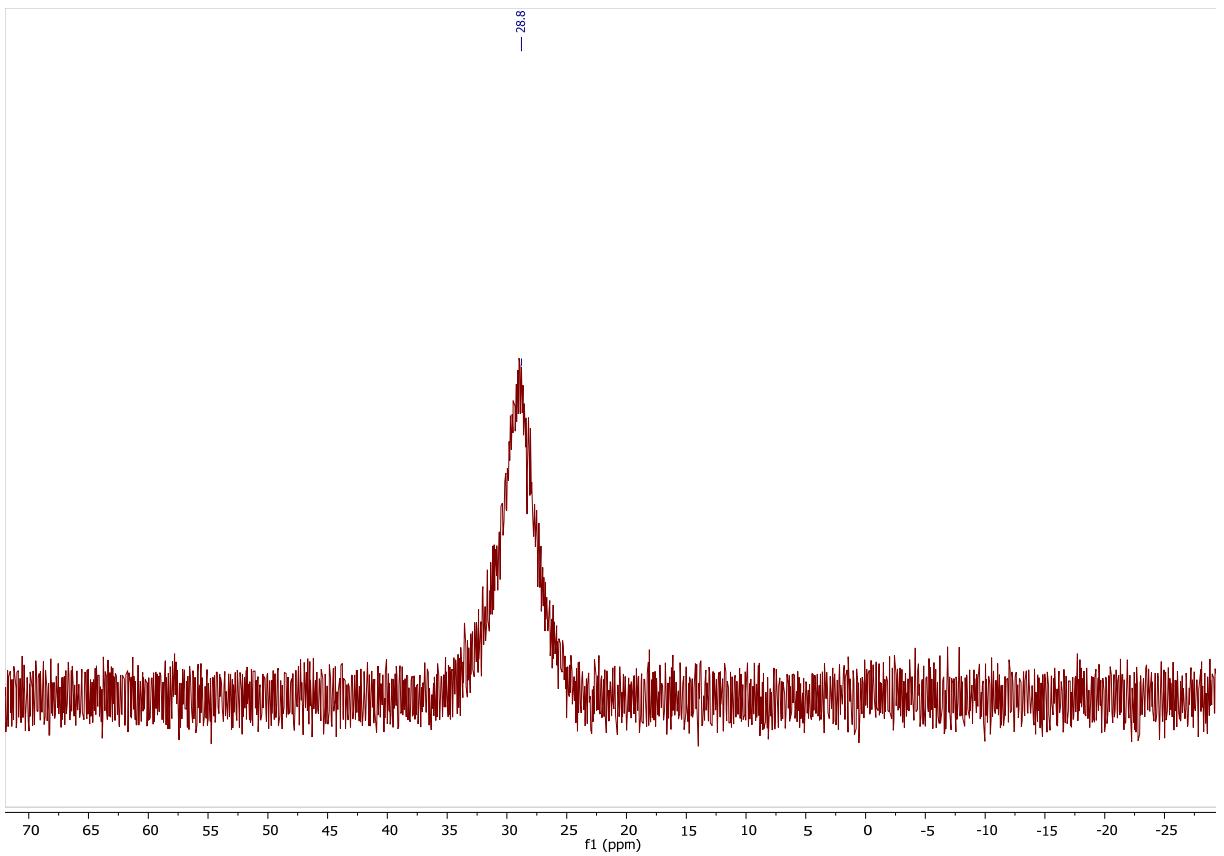
V. Ene reactions: Examples of compounds 7a and 8a

CBOUREGH cb-79-8-12.10.fid

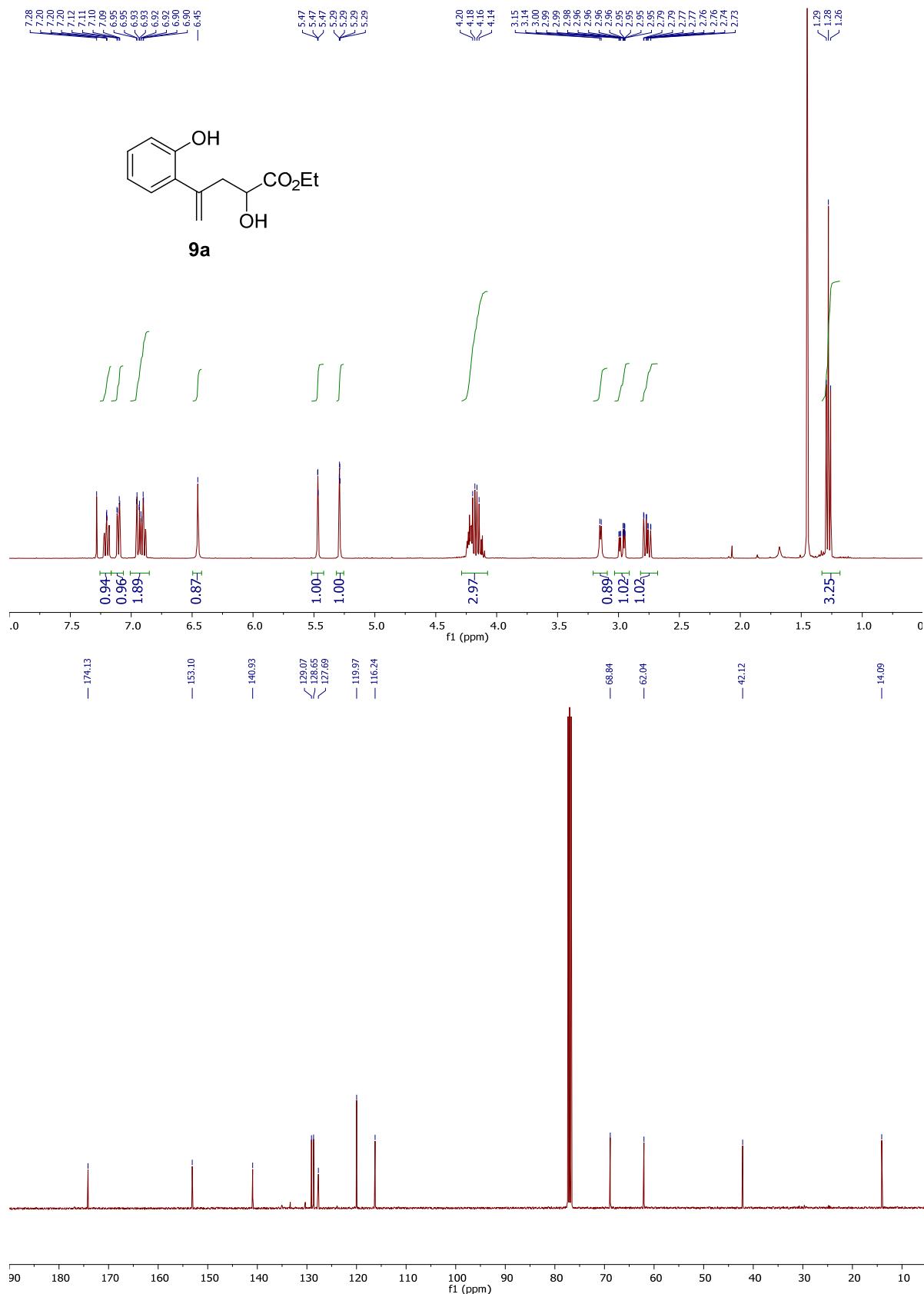


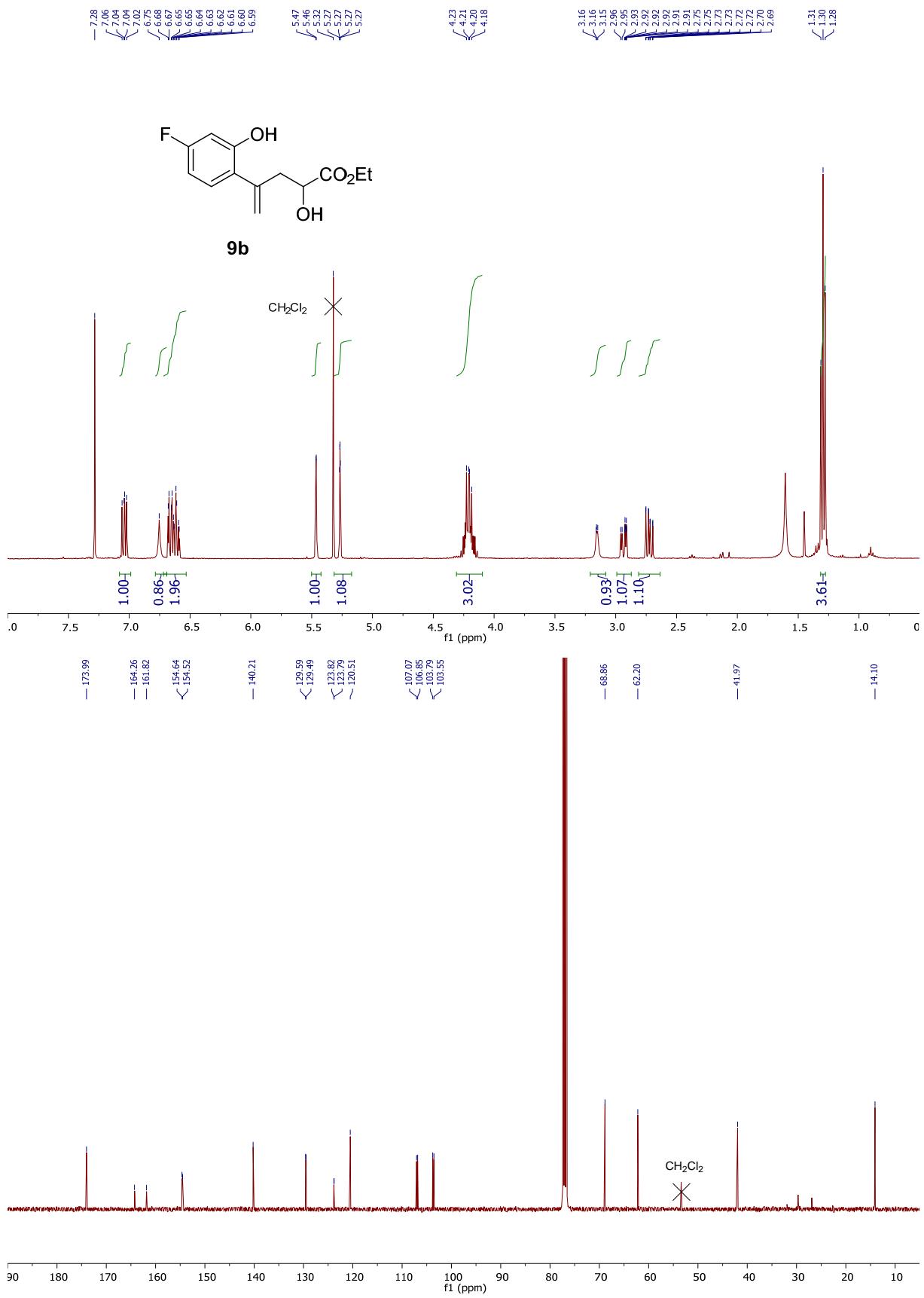


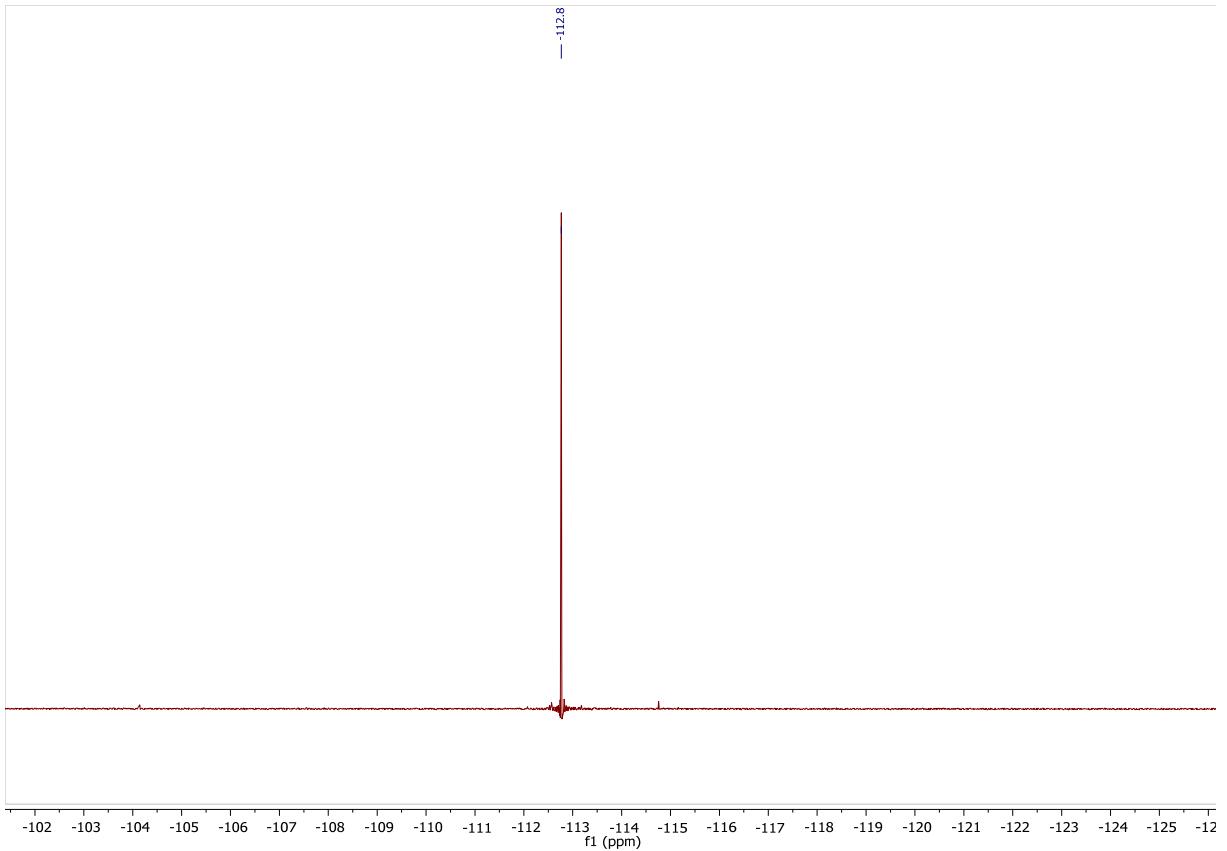


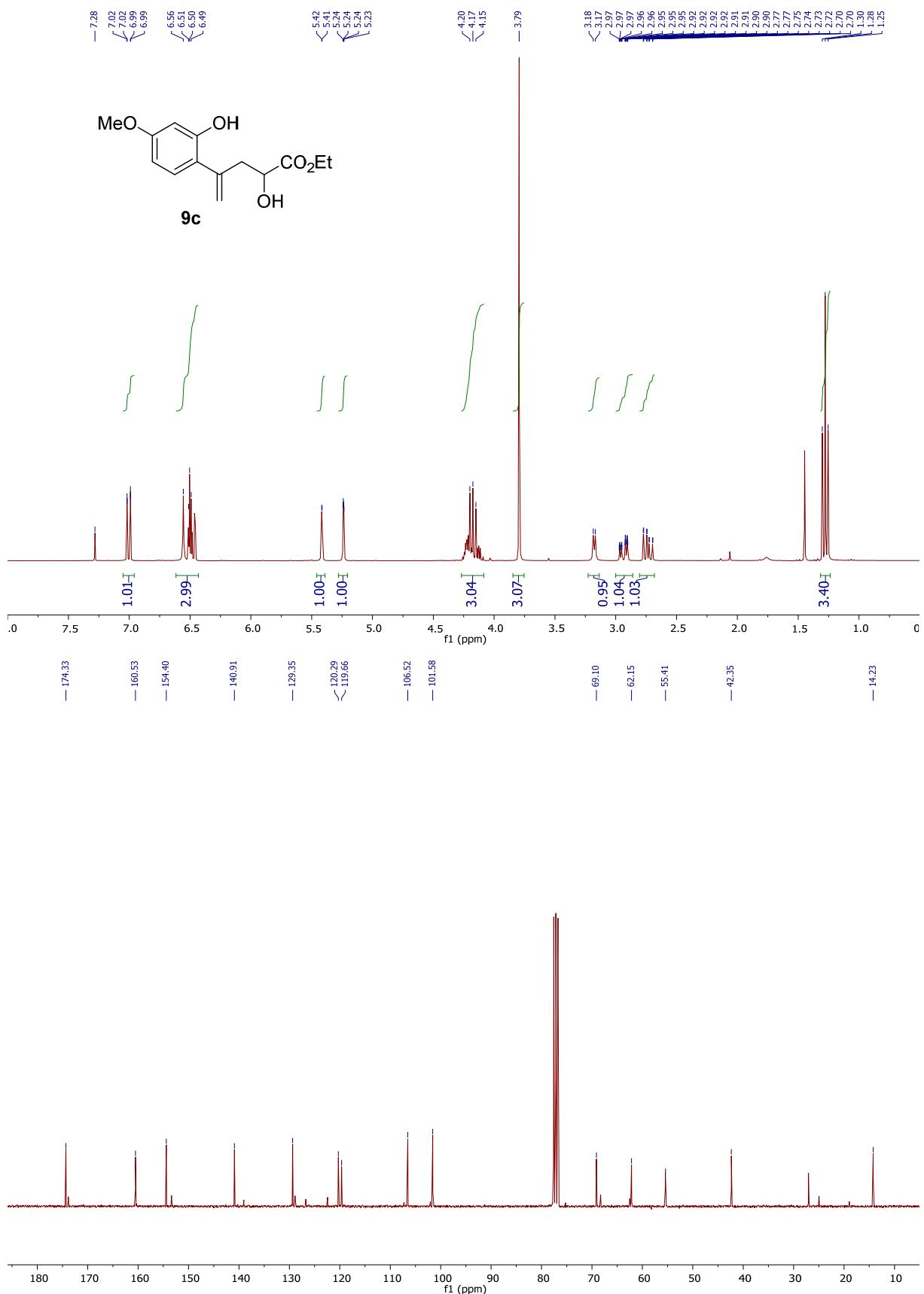


VI. Oxidation of boronates 7 to phenols 9

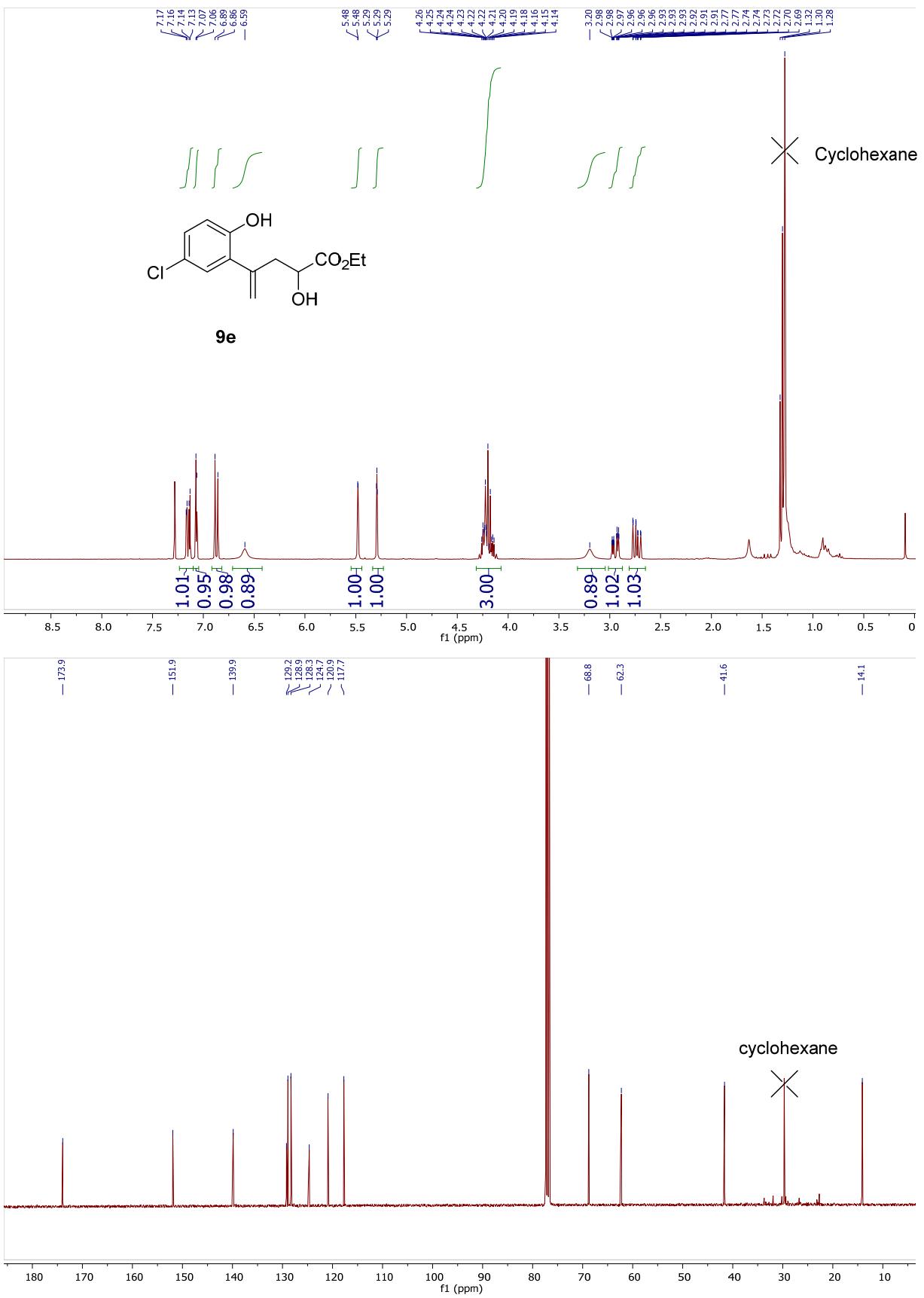


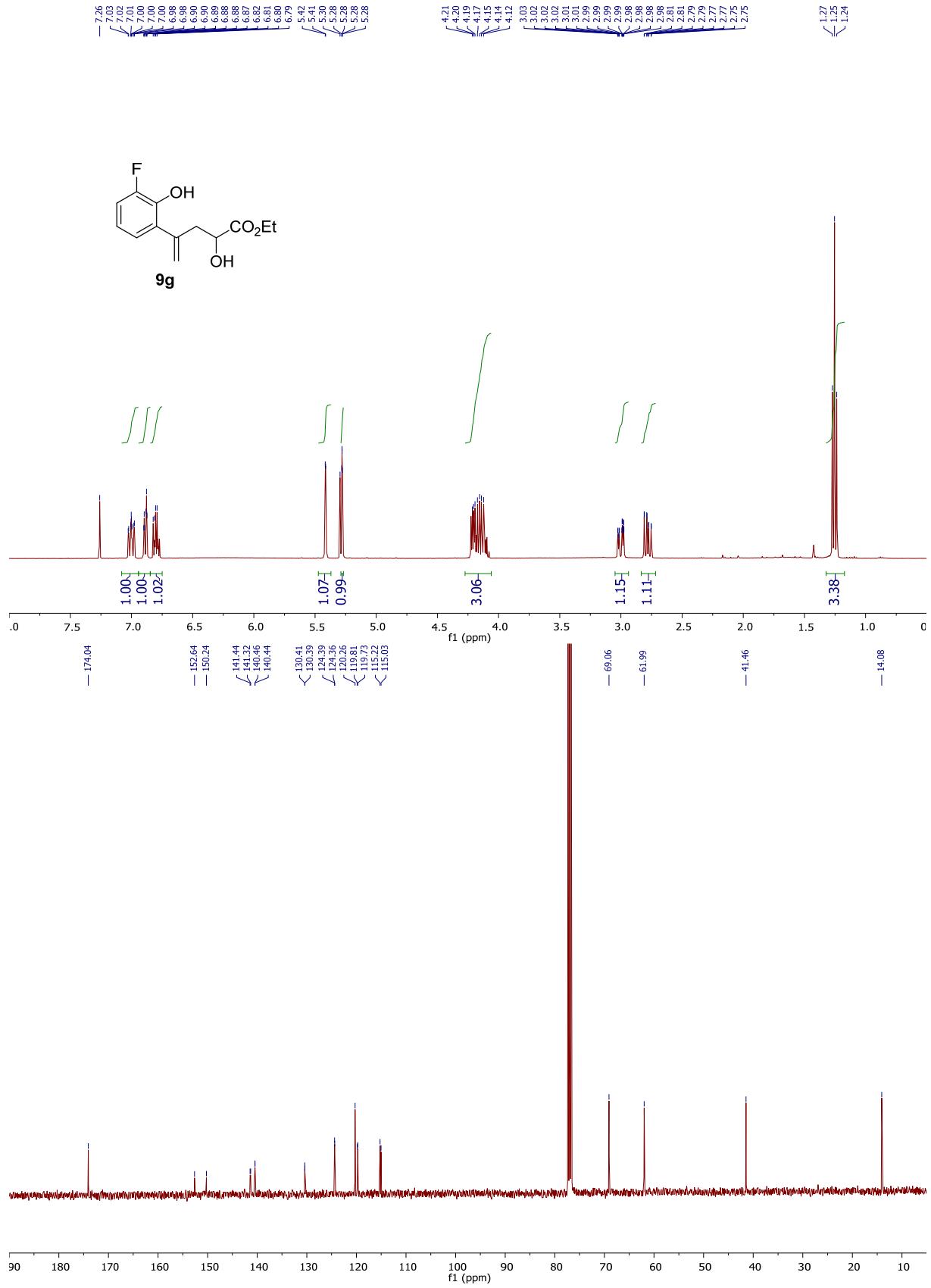


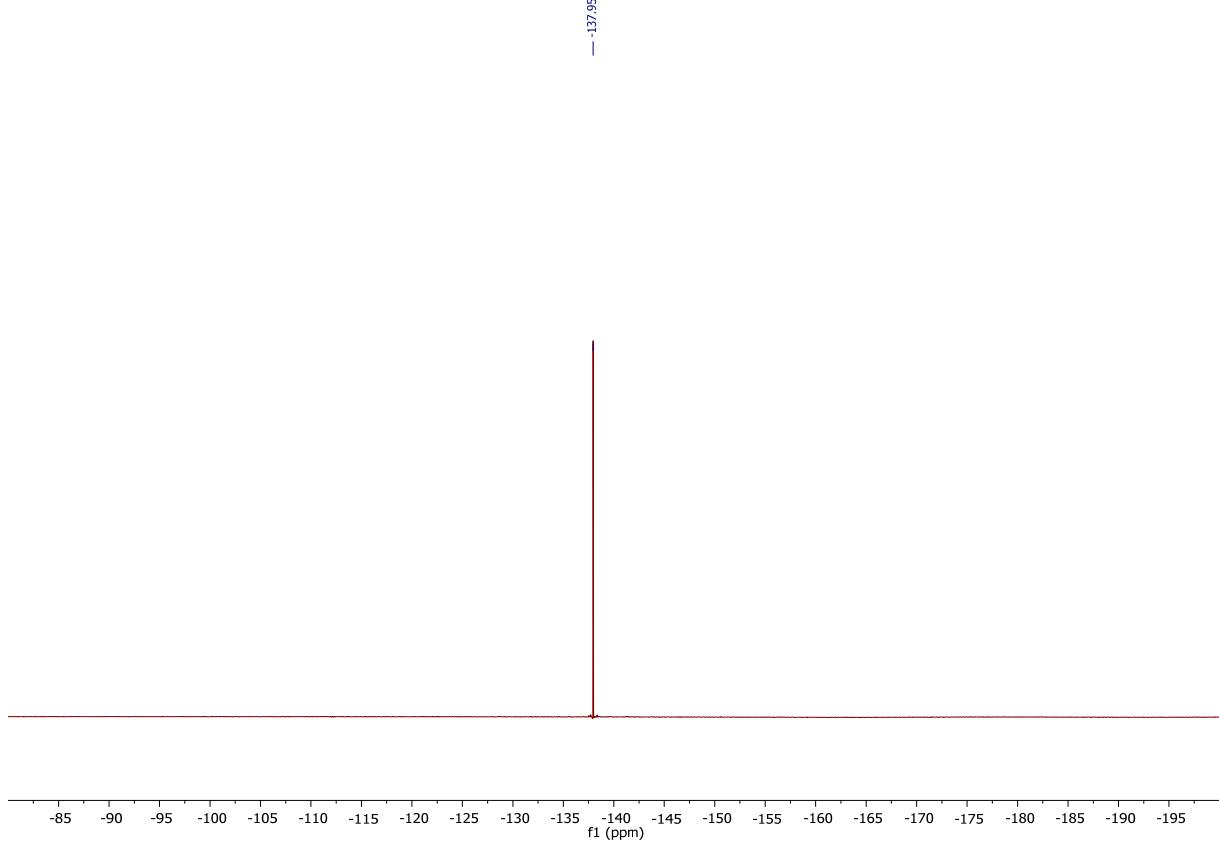


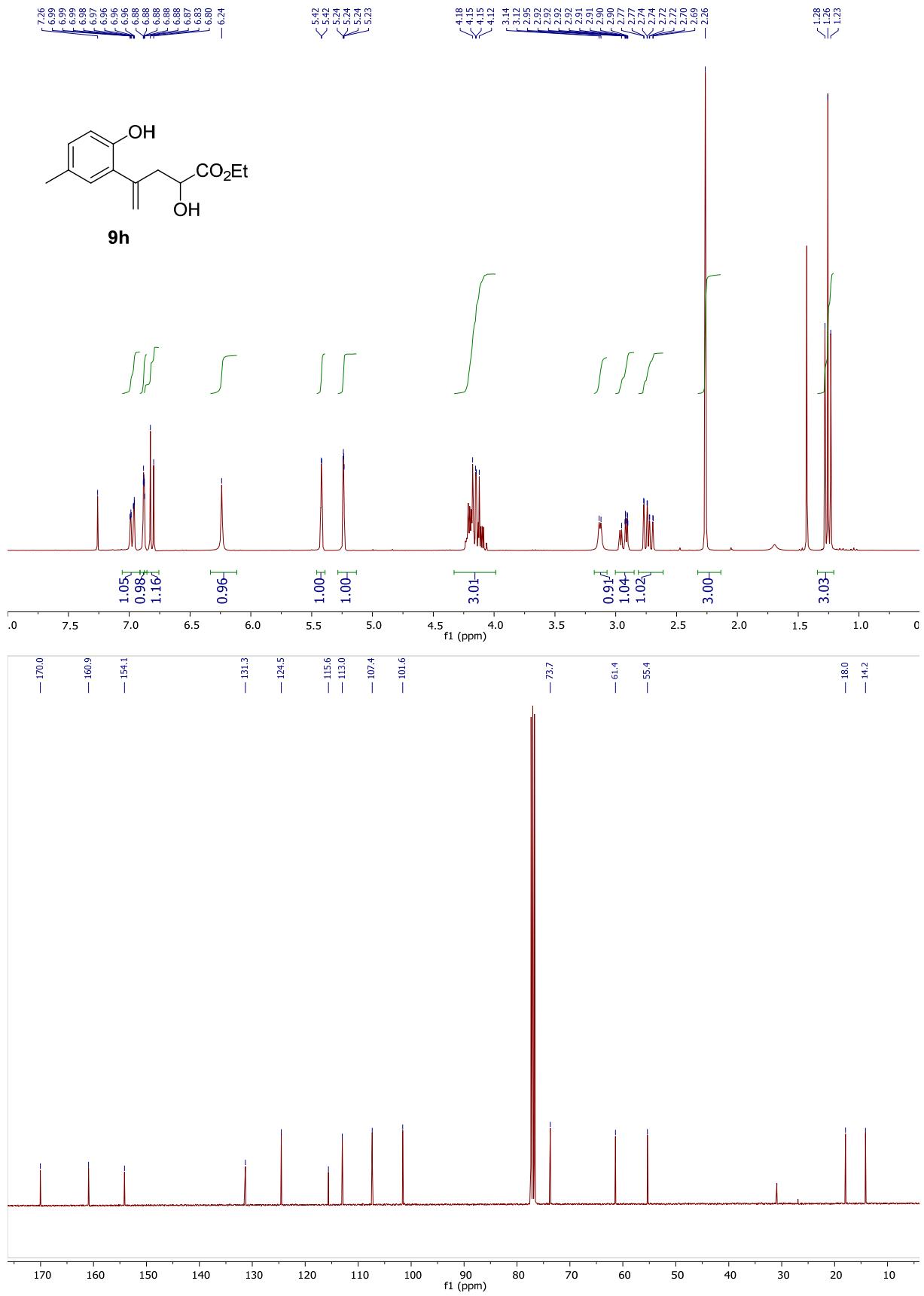


The ¹³C NMR was recorded 12 hours after the ¹H spectrum, which explains the presence of small amounts of the isomerized product.

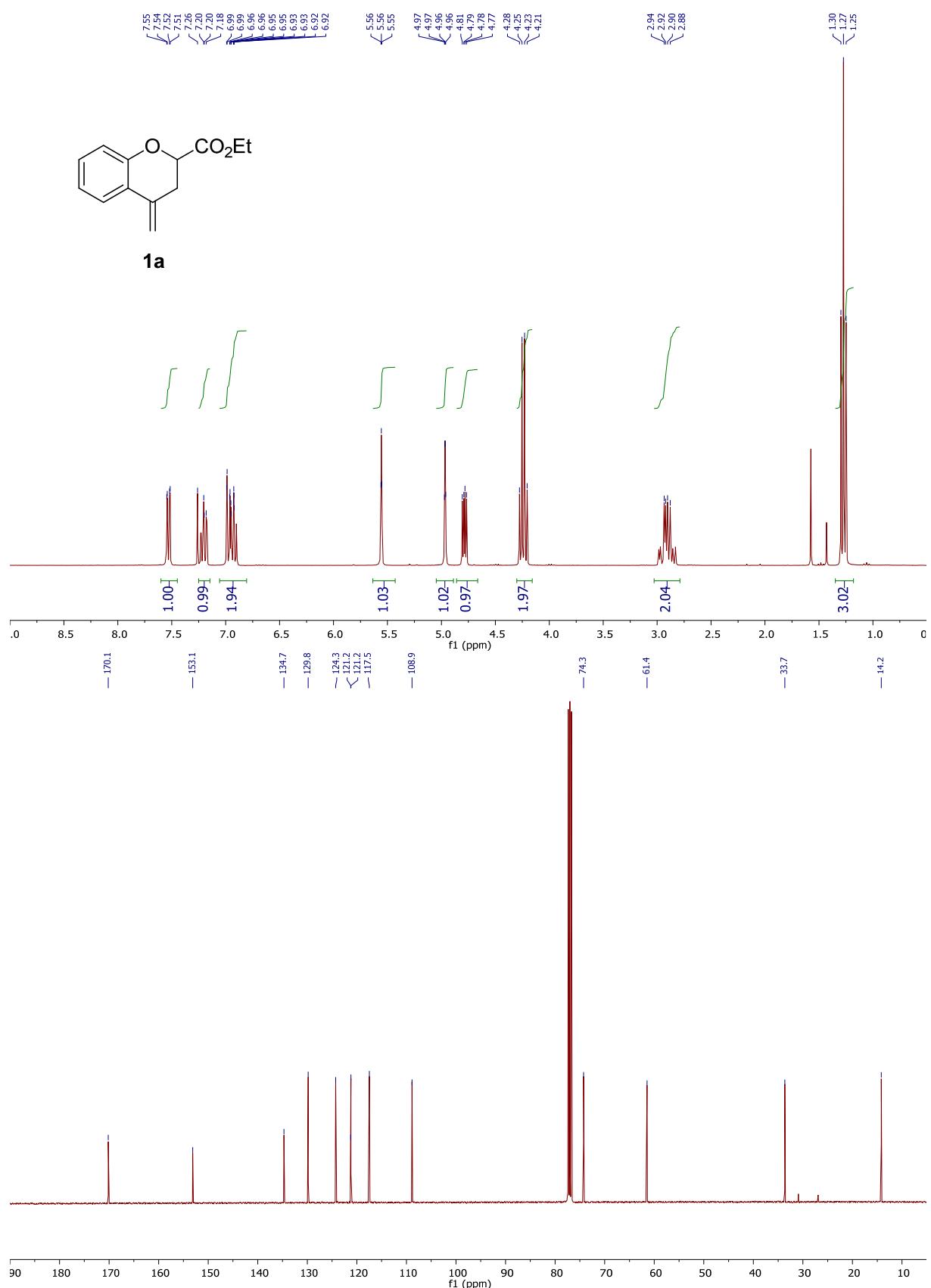


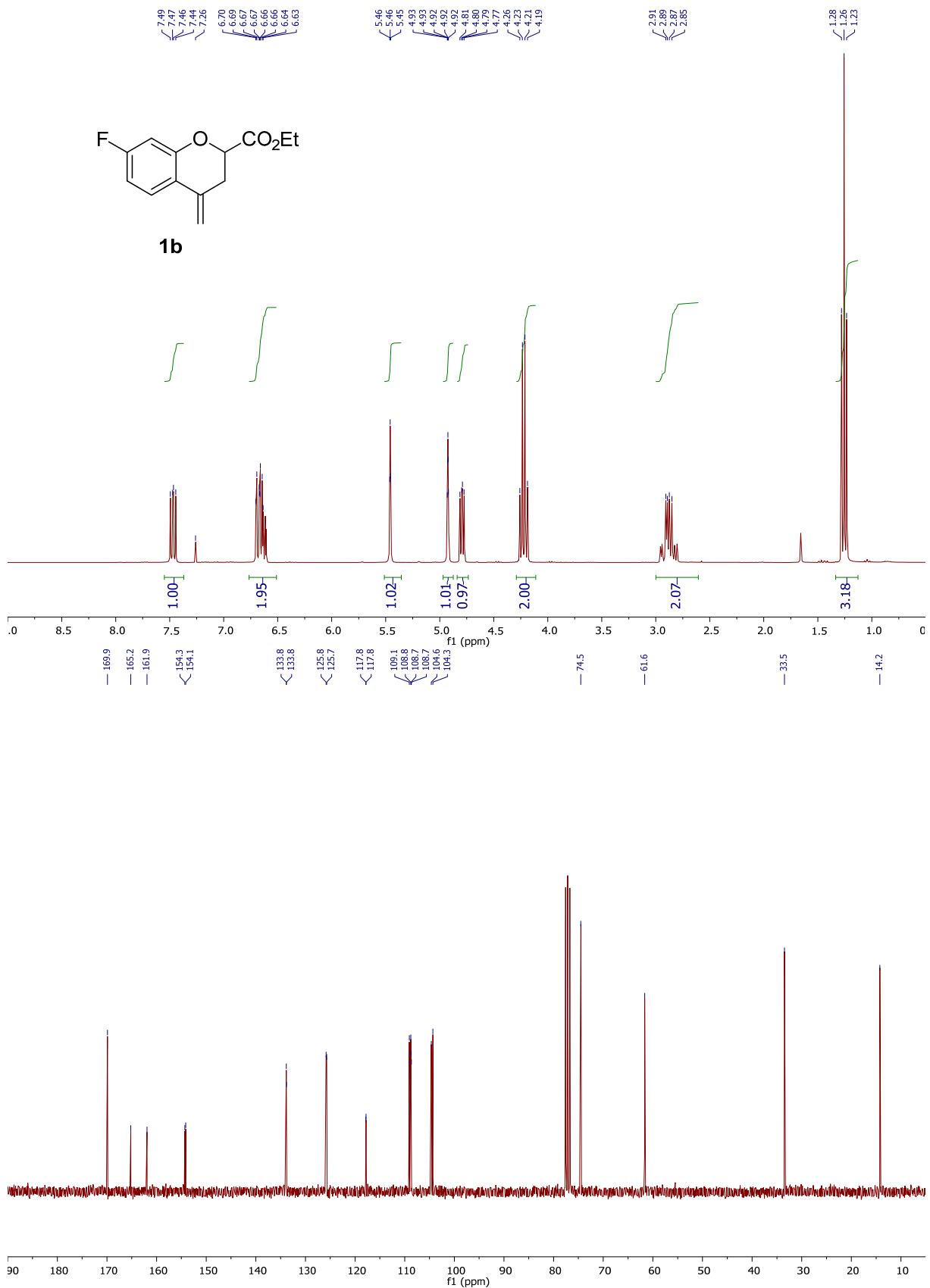


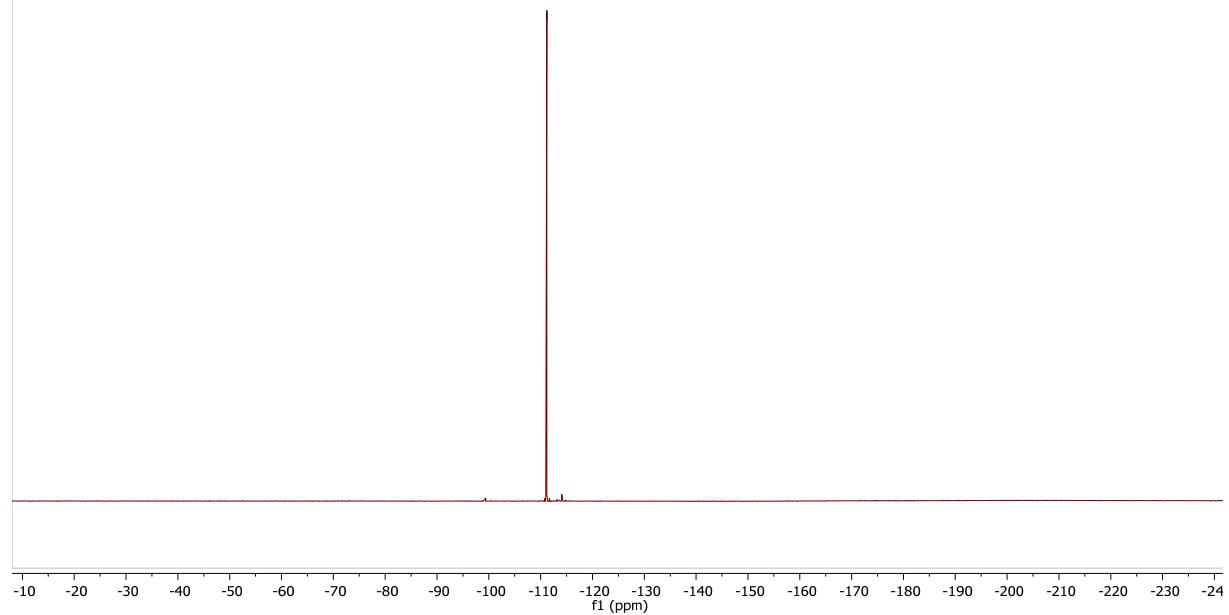


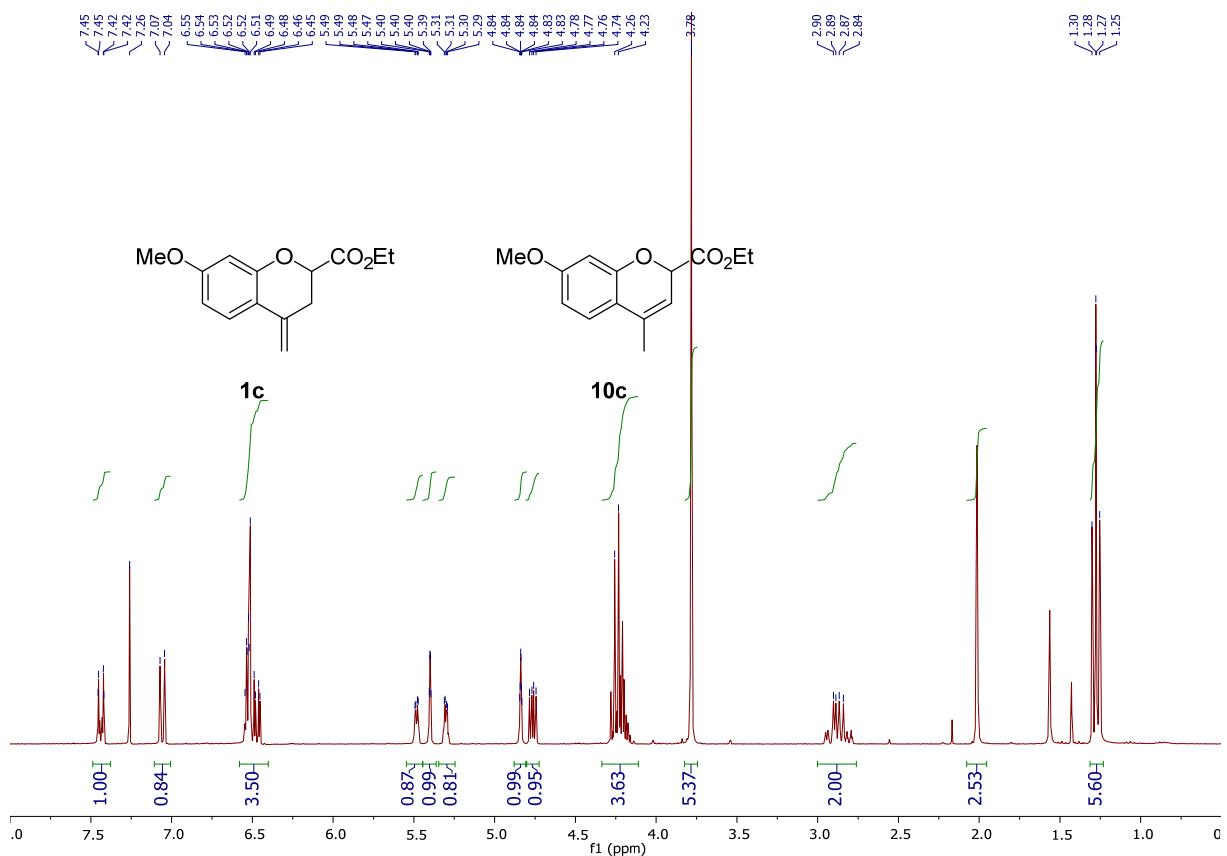


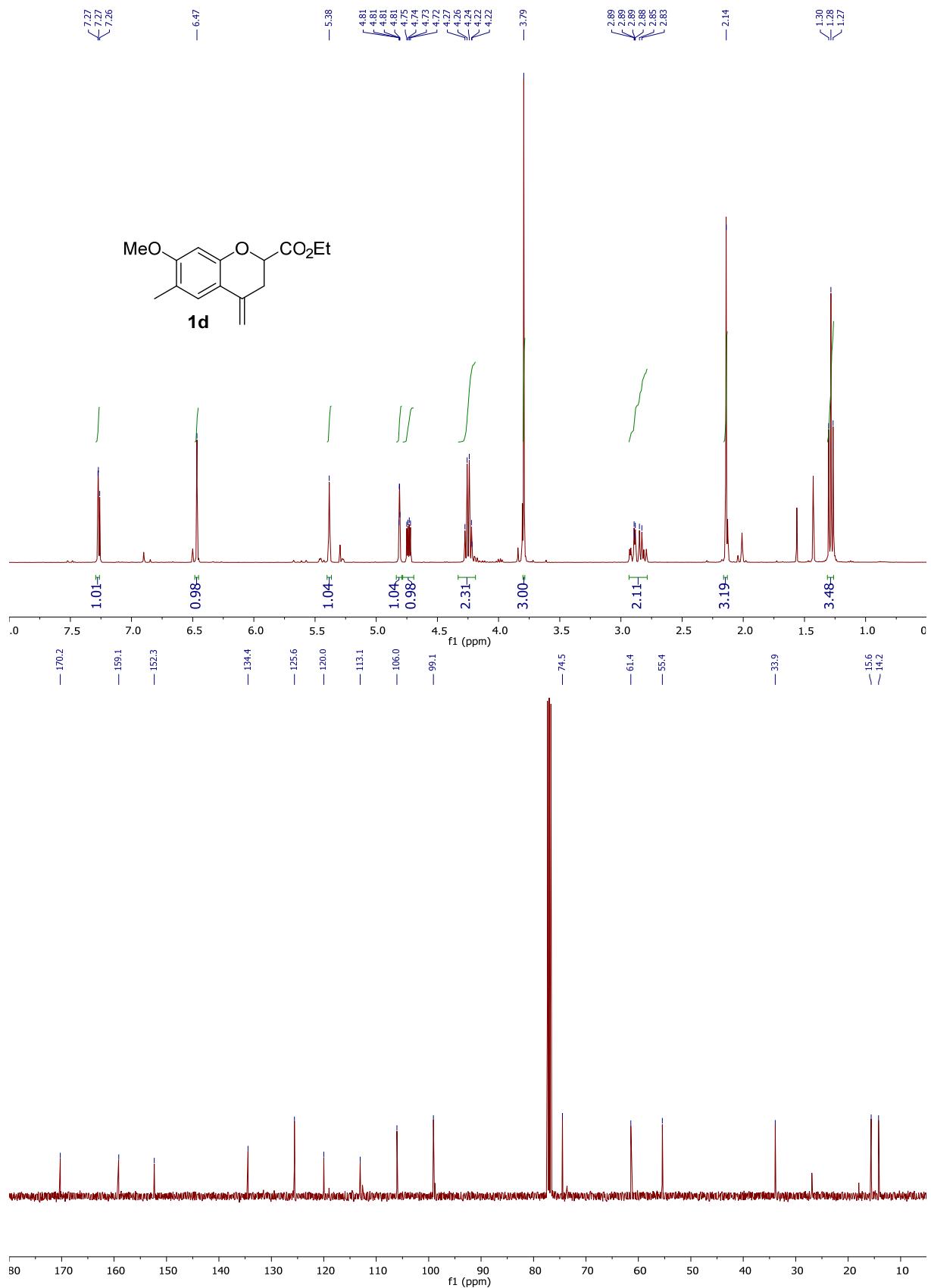
VII. Access to 4-methylenechromanes **1** from **9**

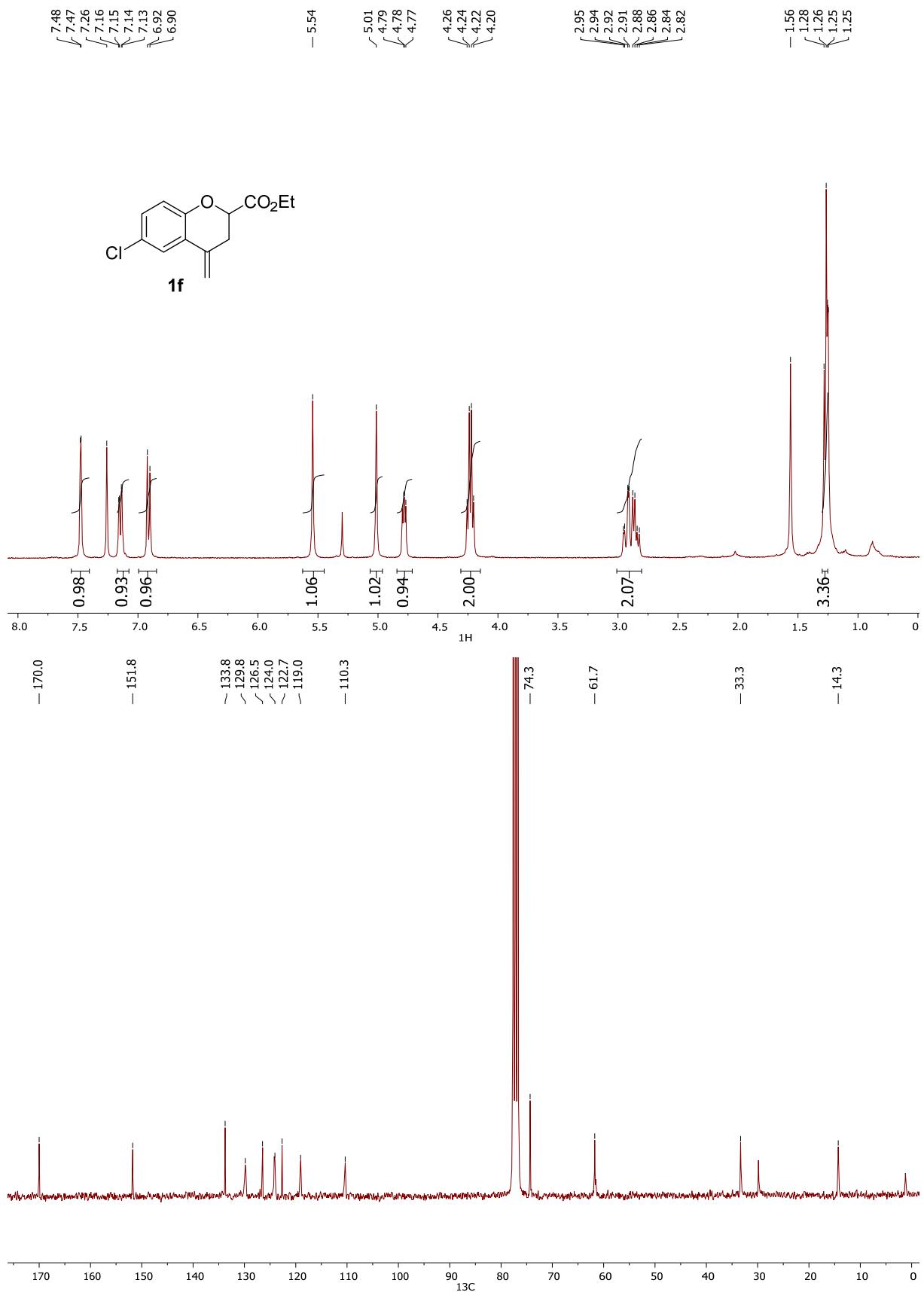


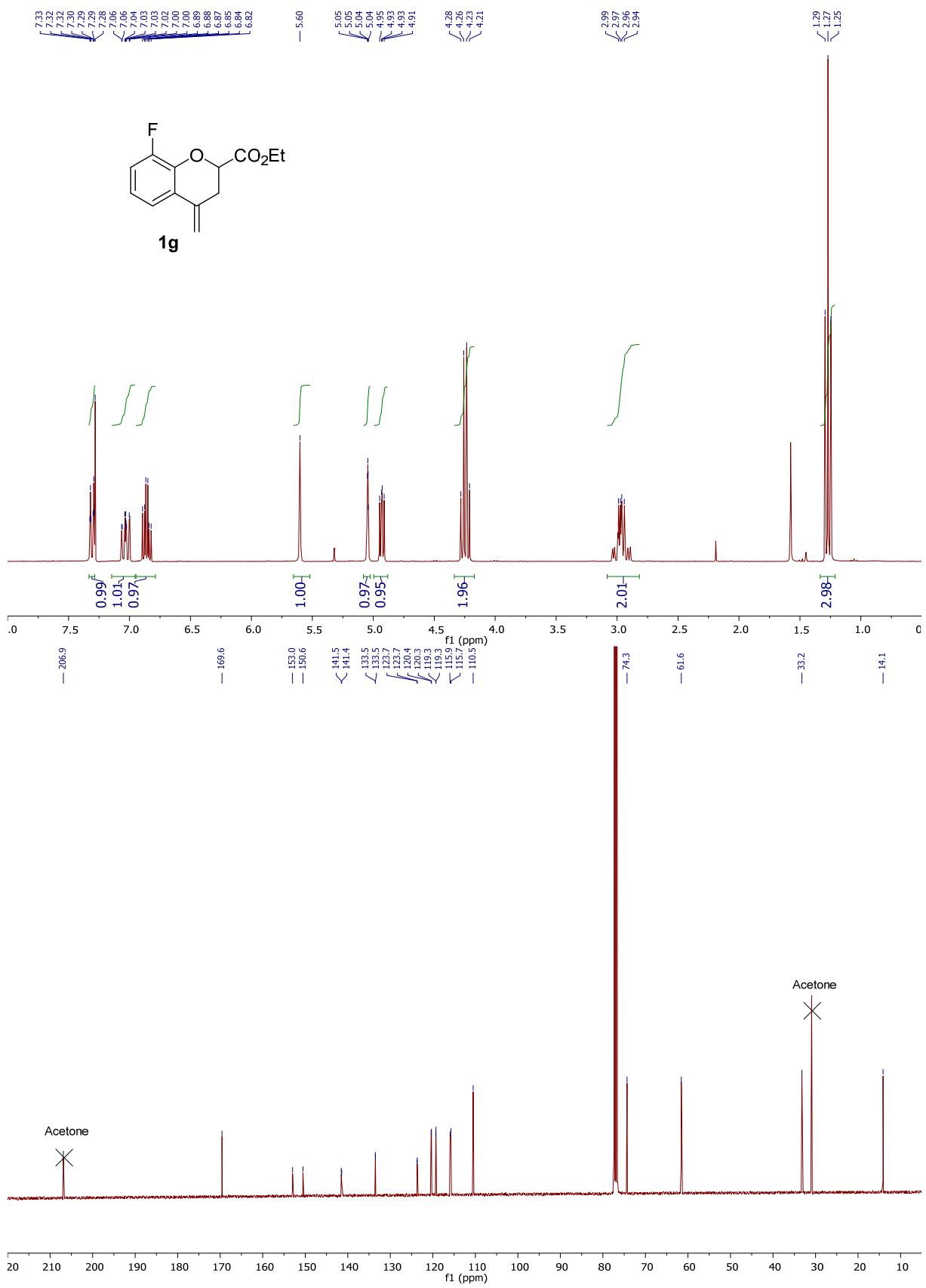


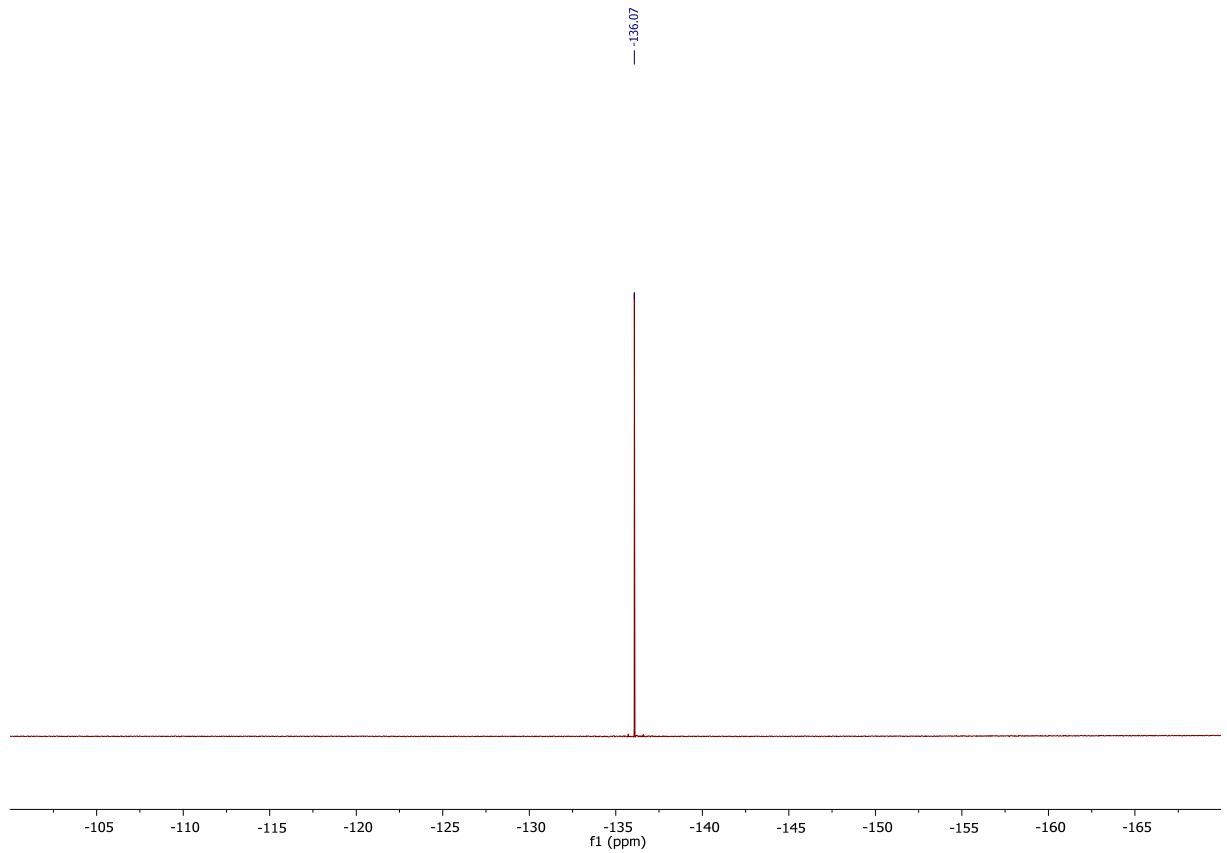


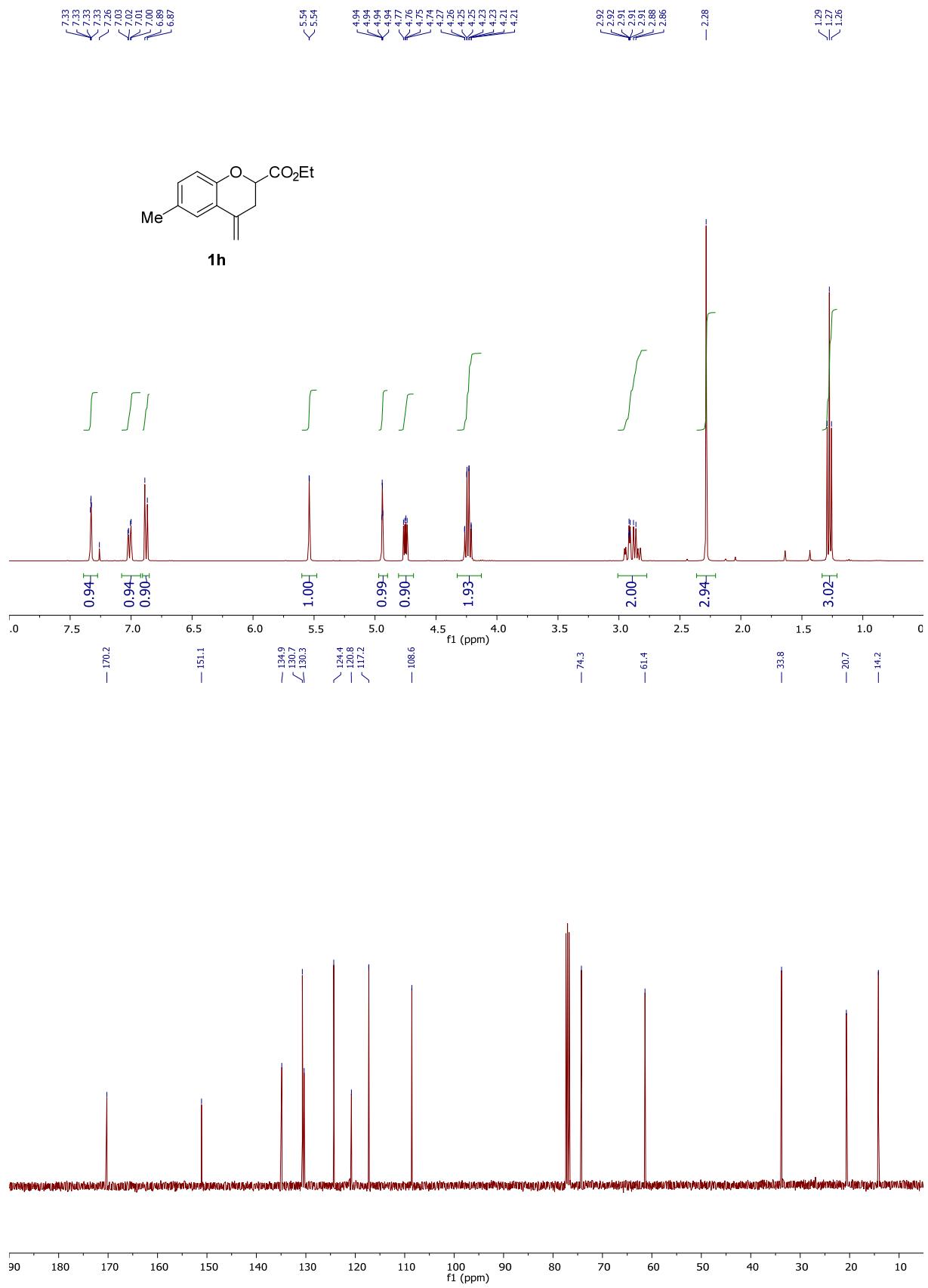




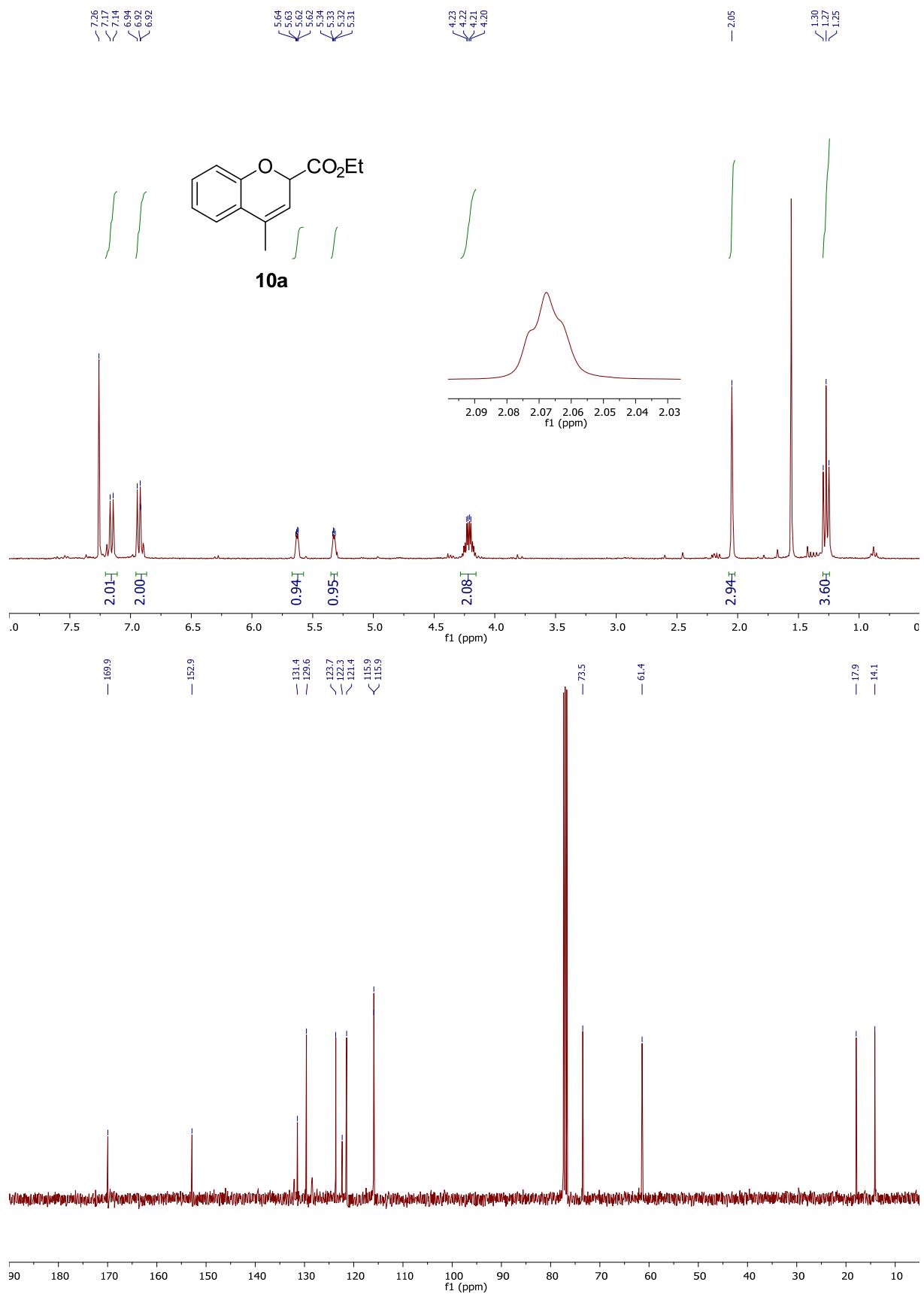


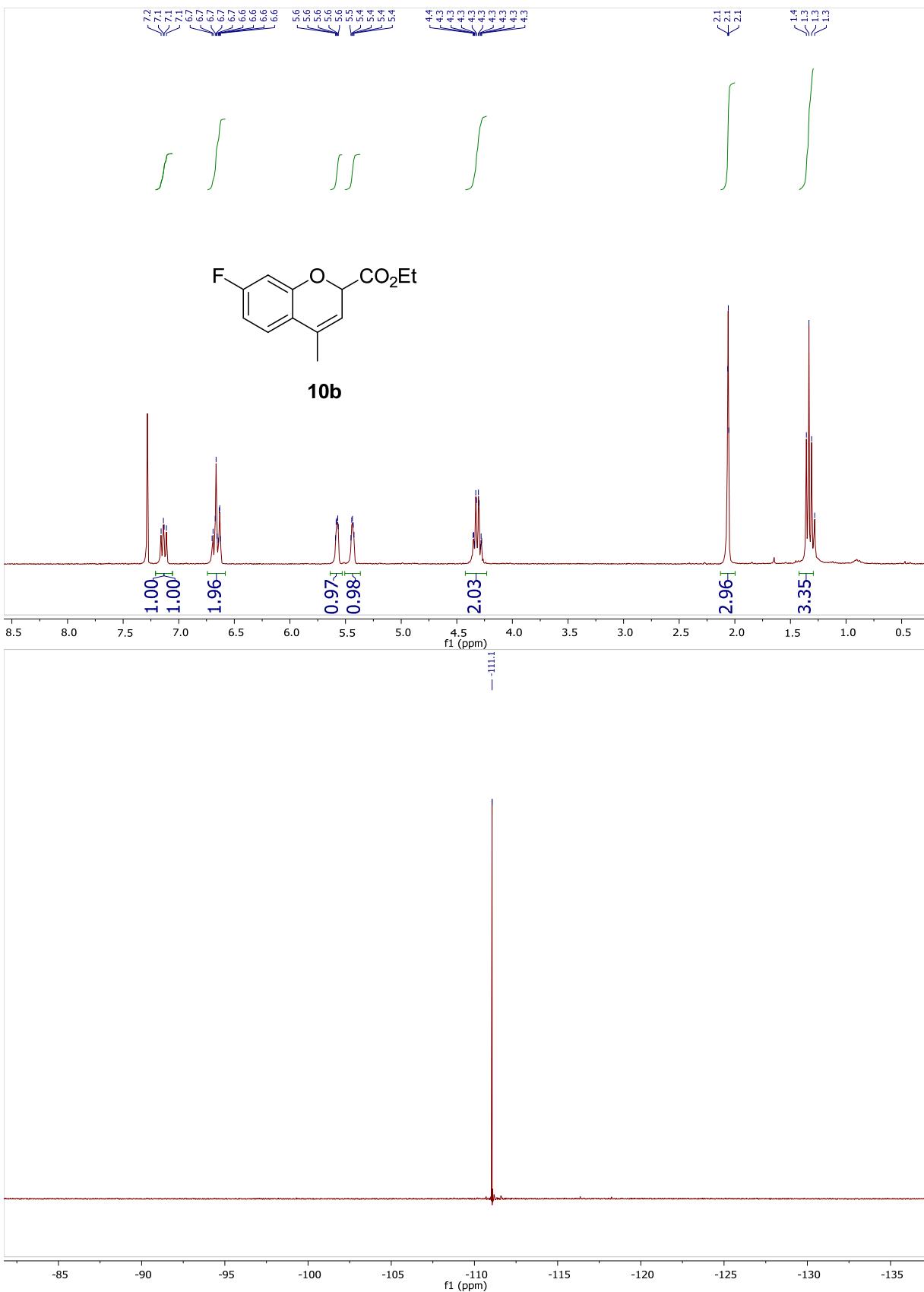


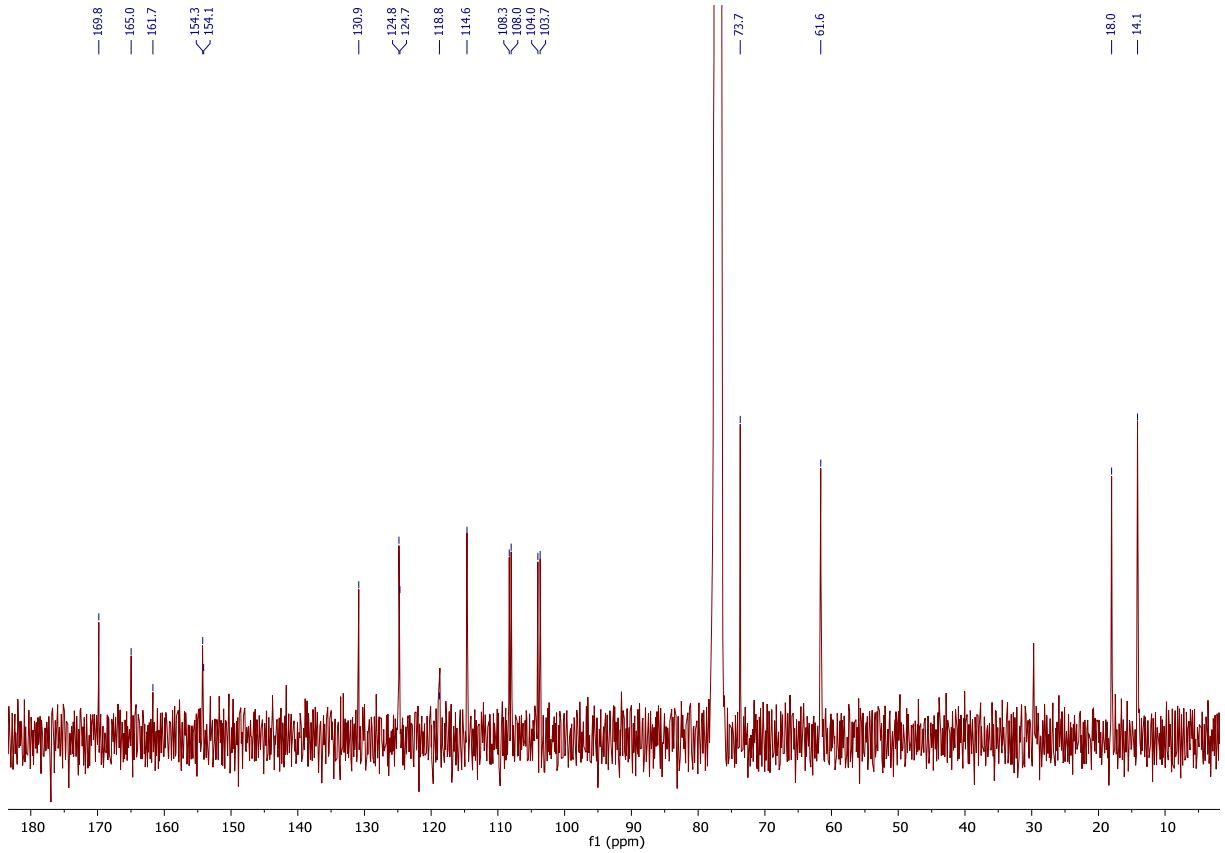


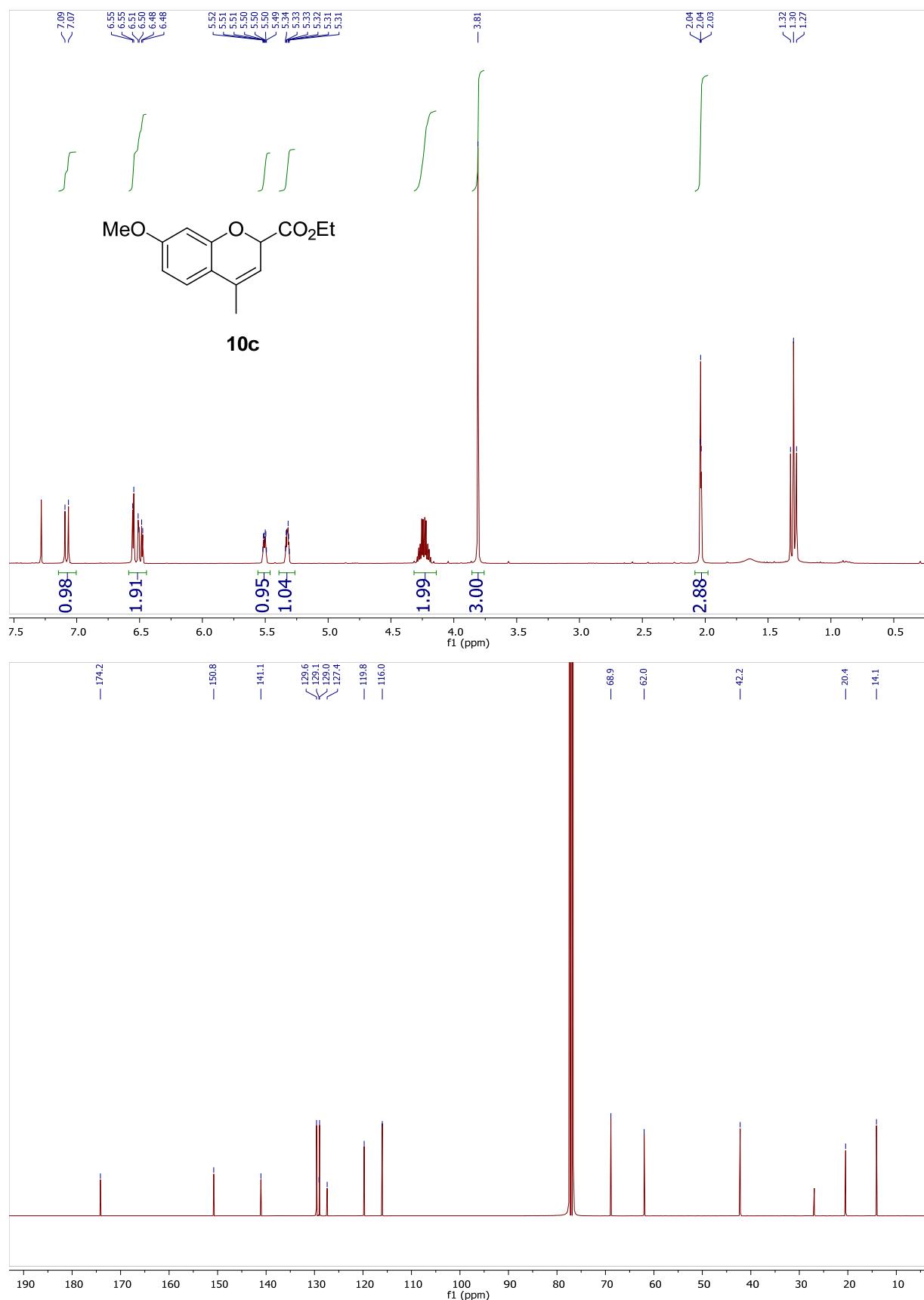


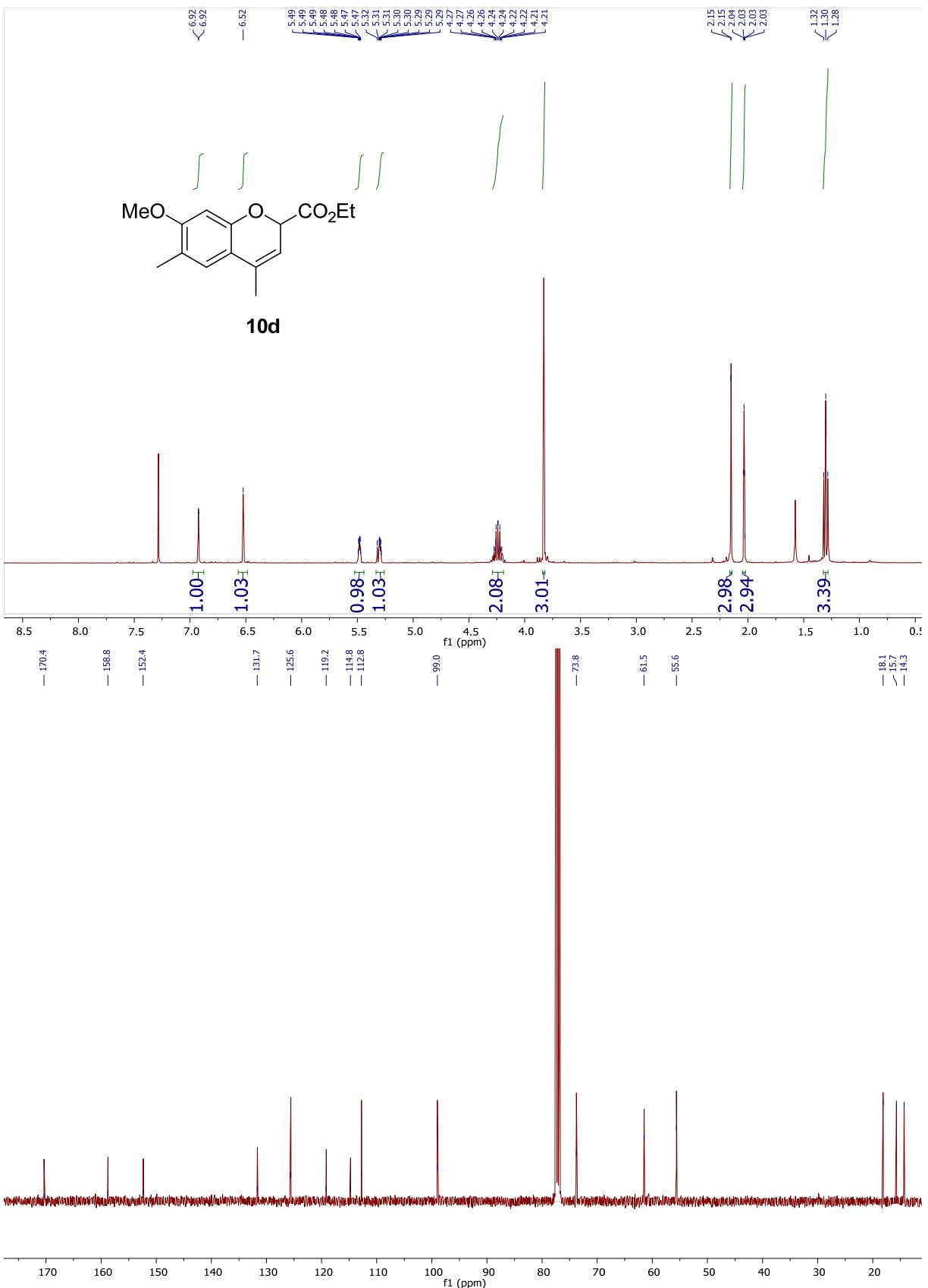
VIII. Isomerisation of 1 to 10



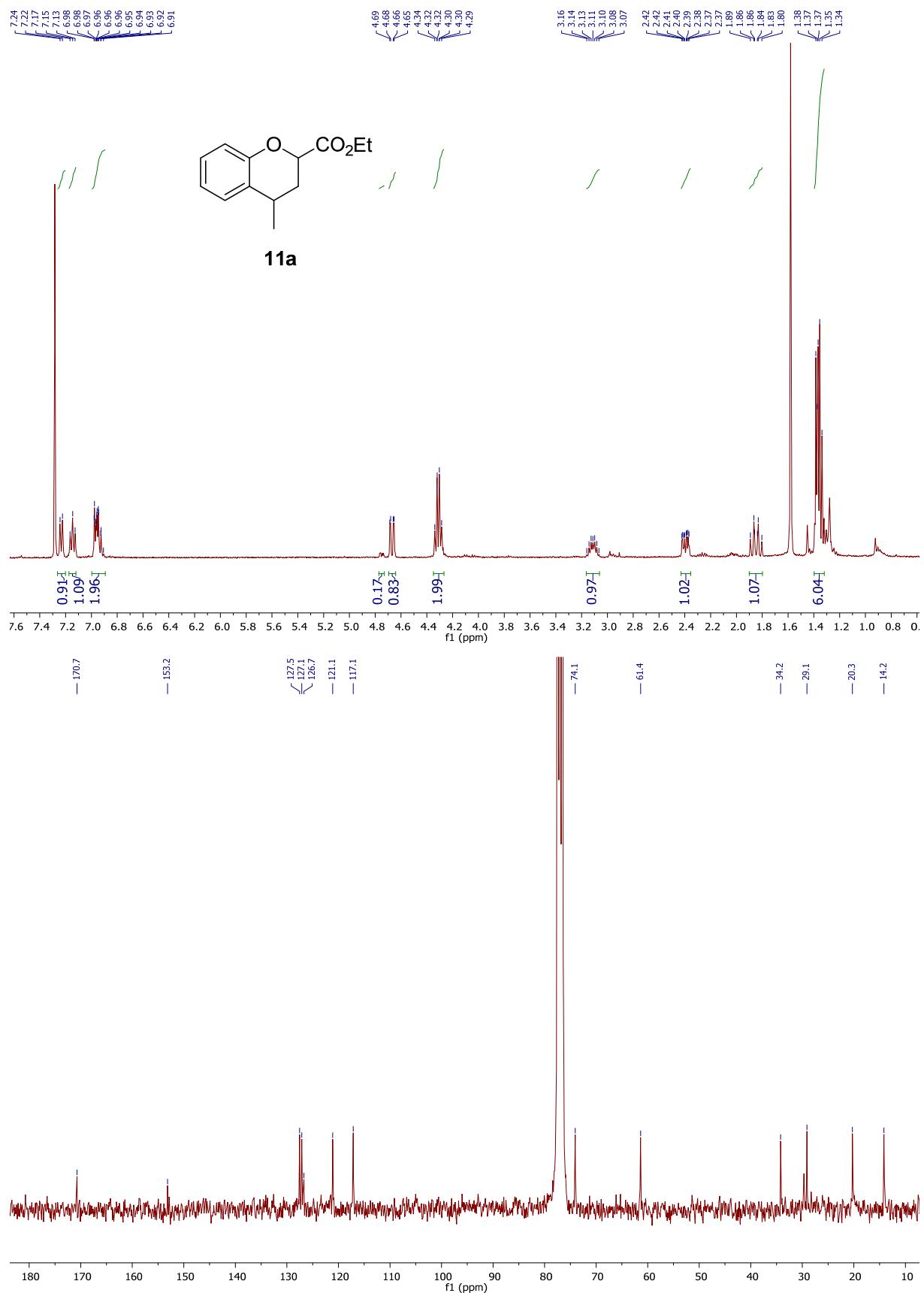








IX. Hydrogenation of 1a to 11a



X. Other functional transformations of **1a**

