

Supplementary Material

Spirocyclization reactions and antiproliferative activity of indole phytoalexins 1-methoxybrassinin and its 1-substituted derivatives

Mariana Budovská,^{*a} Martina Bago Pilátová,^b Viera Tischlerová,^b and Ján Mojžiš^b

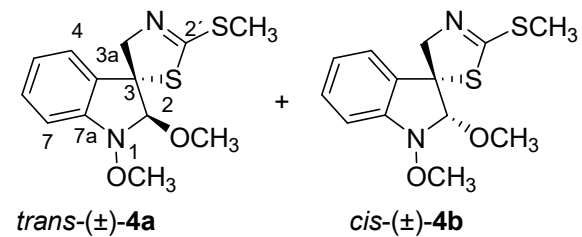
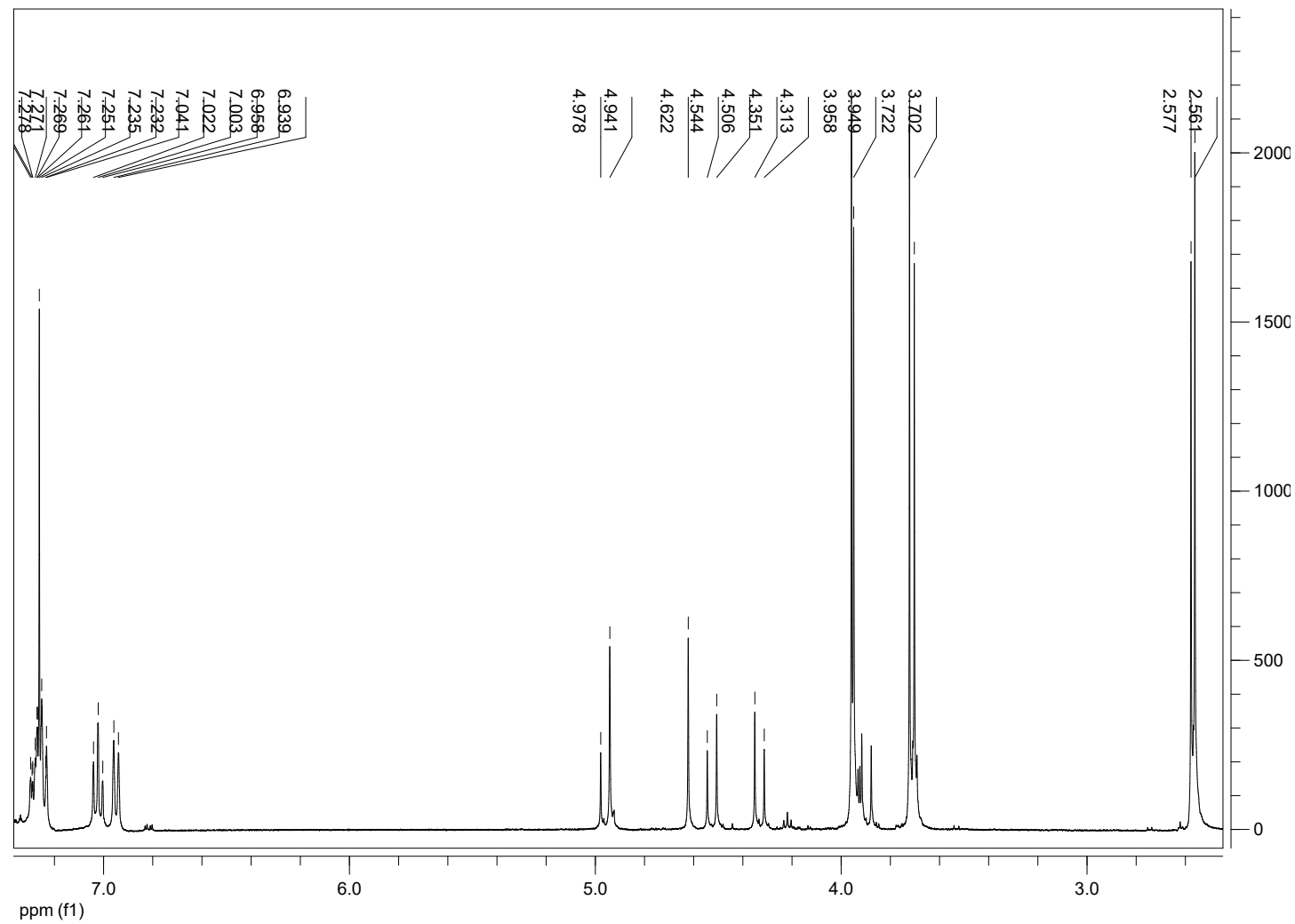
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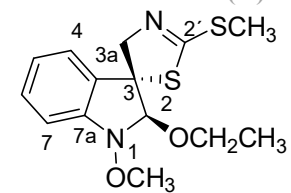
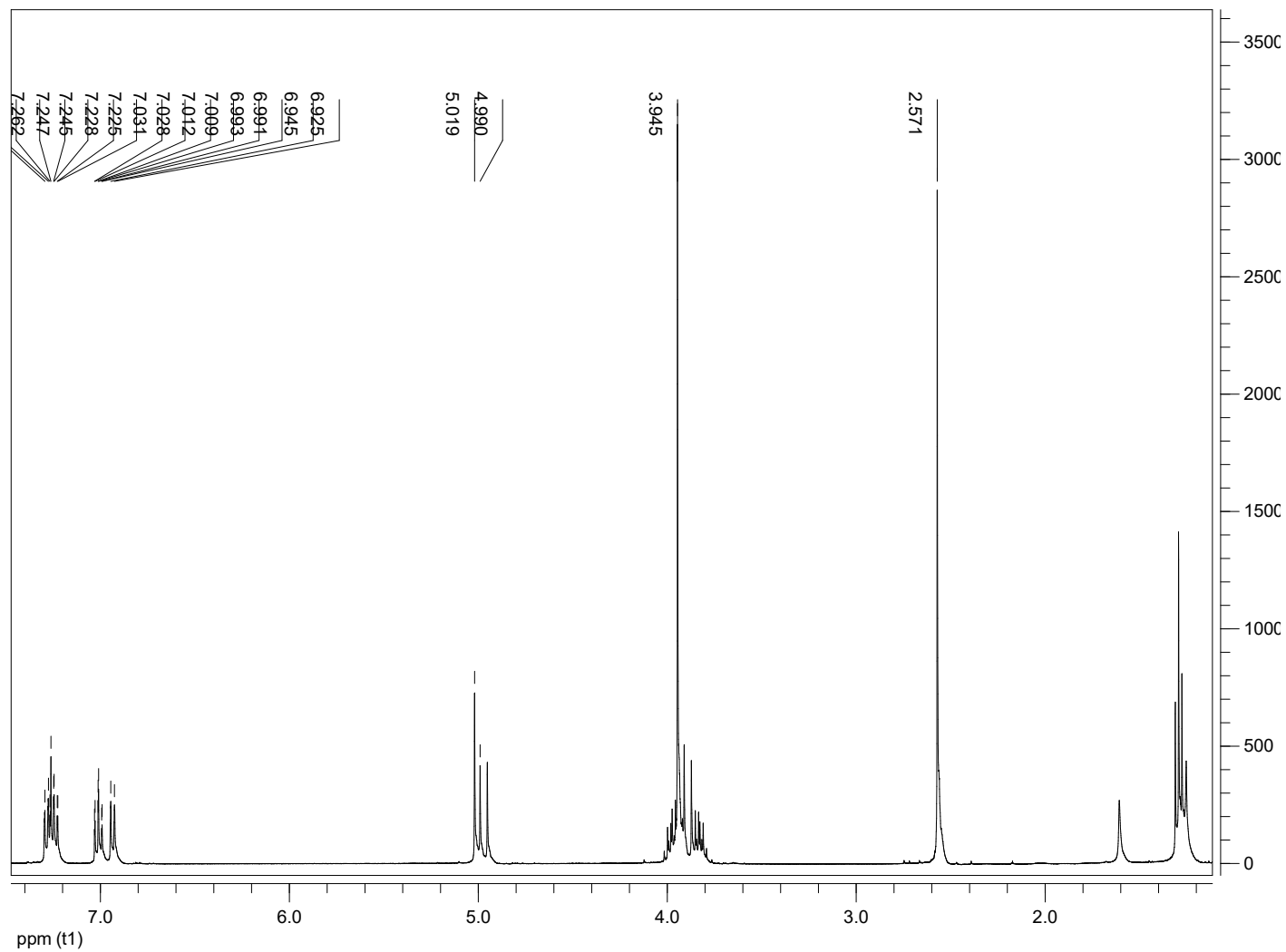
^b*Department of Pharmacology, Faculty of Medicine, P. J. Šafárik University, SNP 1,
040 66 Košice, Slovak Republic*

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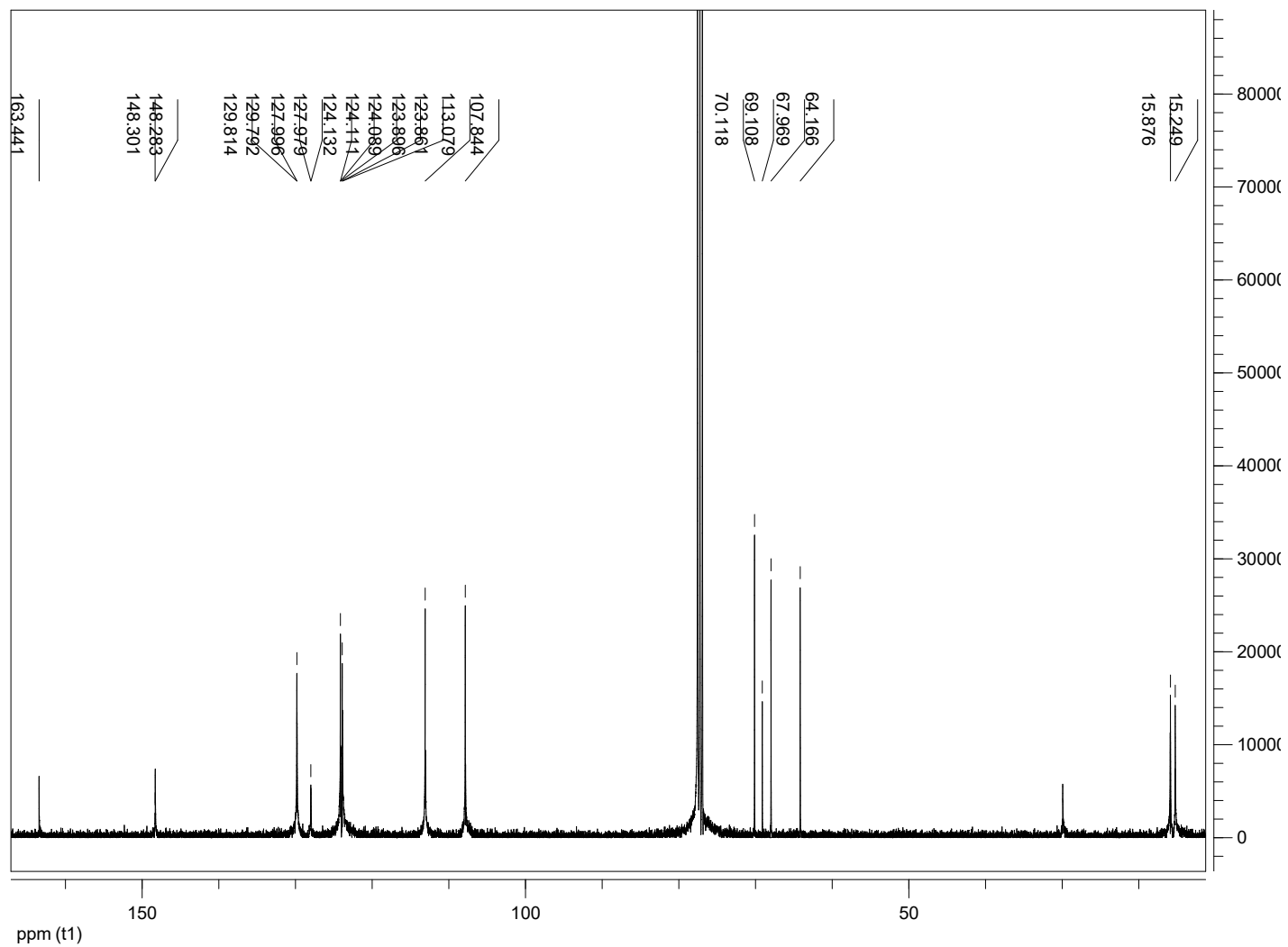
1. Experimental section

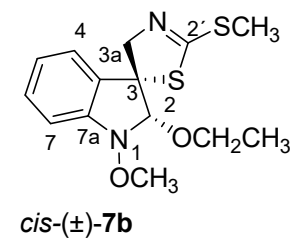
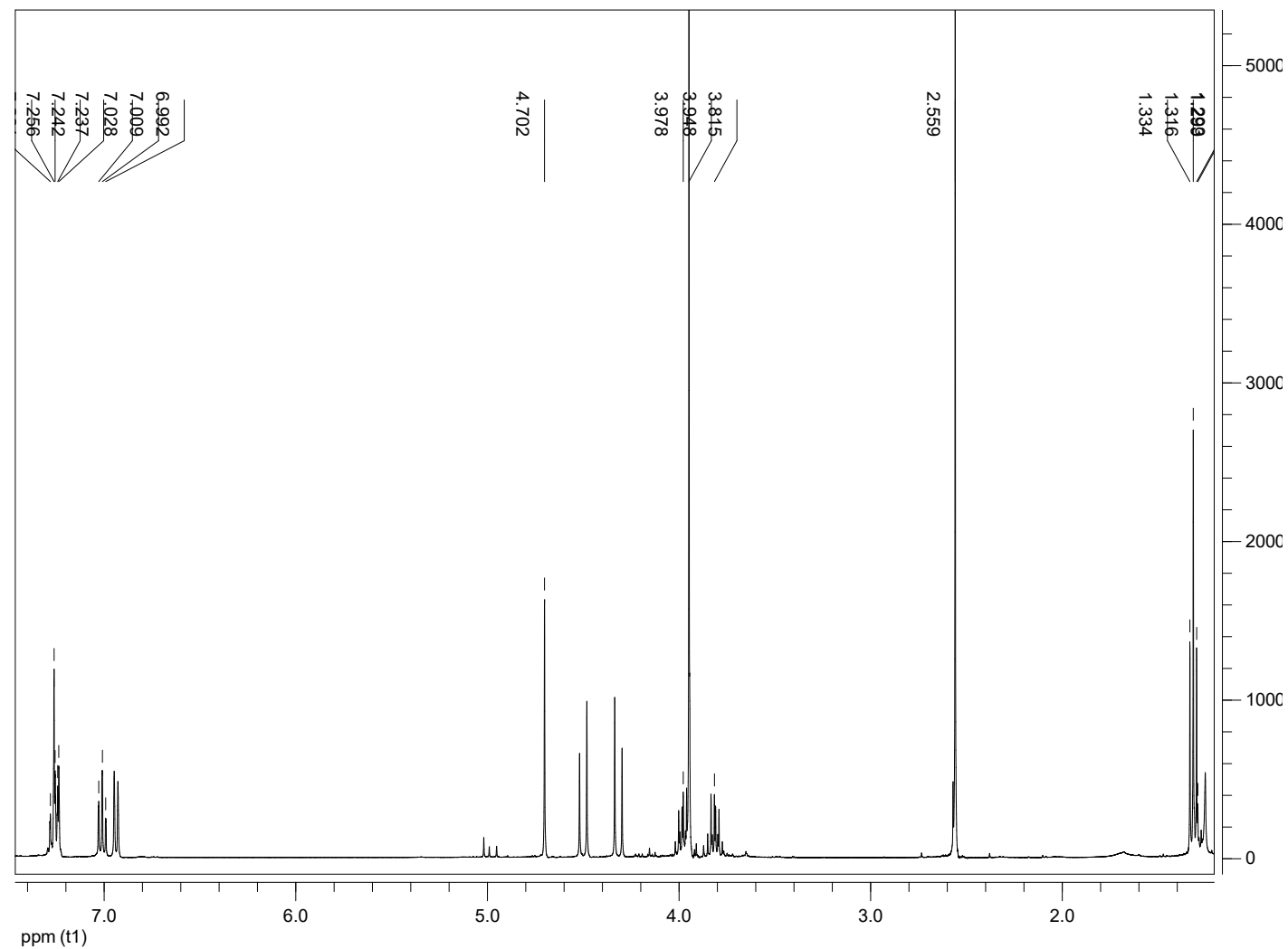
¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were measured on a Varian Mercury Plus spectrometer.

***trans*-(±)- and *cis*-(±)-1-Methoxyspirobrassinol methyl ether [*trans*-(±)-4a and *cis*-(±)-4b]**¹H NMR spectrum of mixture *trans*-(±)-4a and *cis*-(±)-4b in CDCl₃

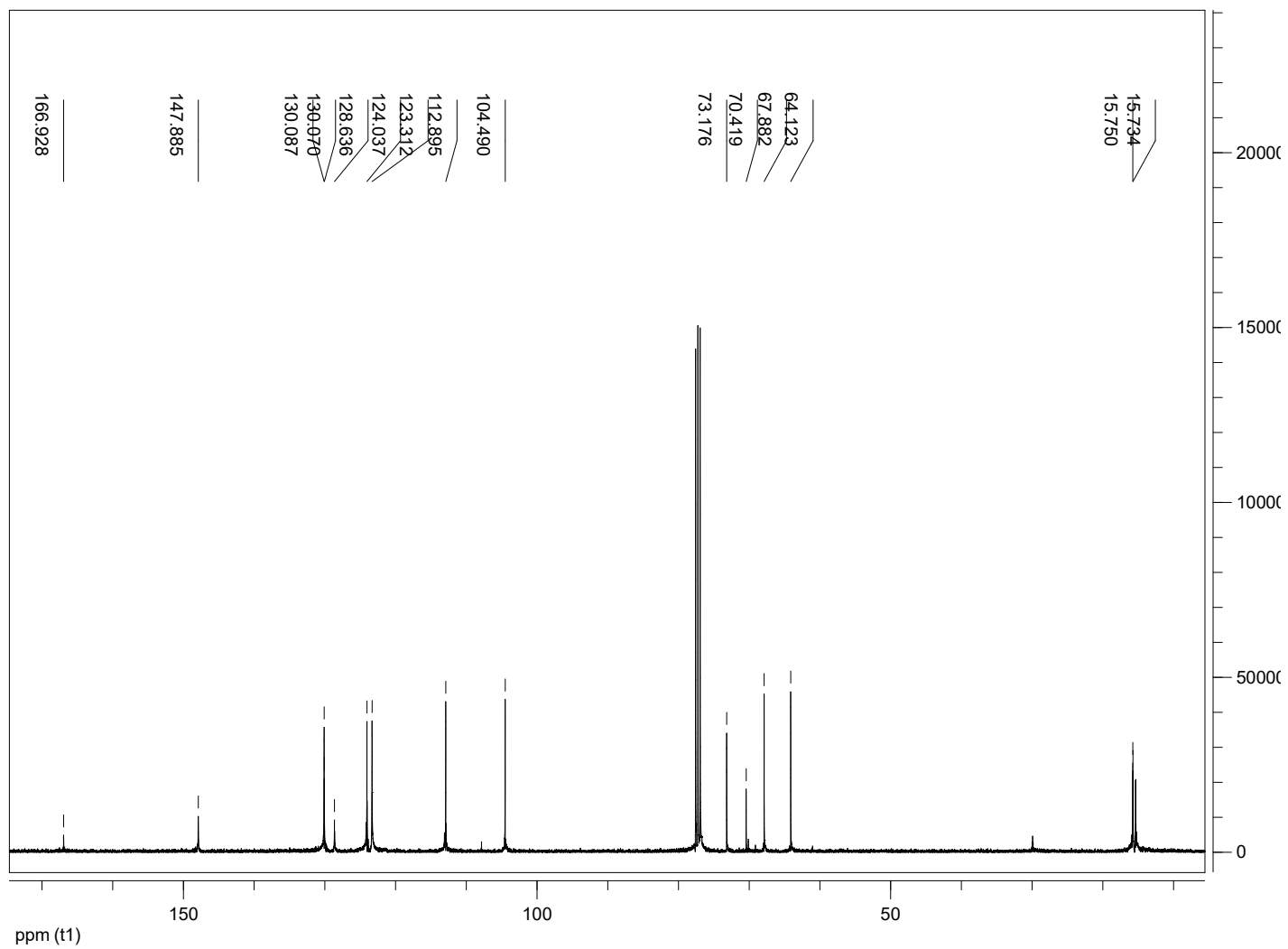
trans*-(±)-1-Methoxyspirobrassinol ethyl ether [*trans*-(±)-7a]**¹H NMR spectrum of *trans*-(±)-7a in CDCl₃trans*-(±)-7a**

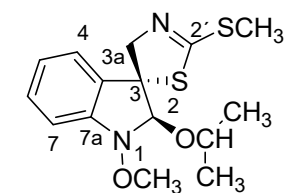
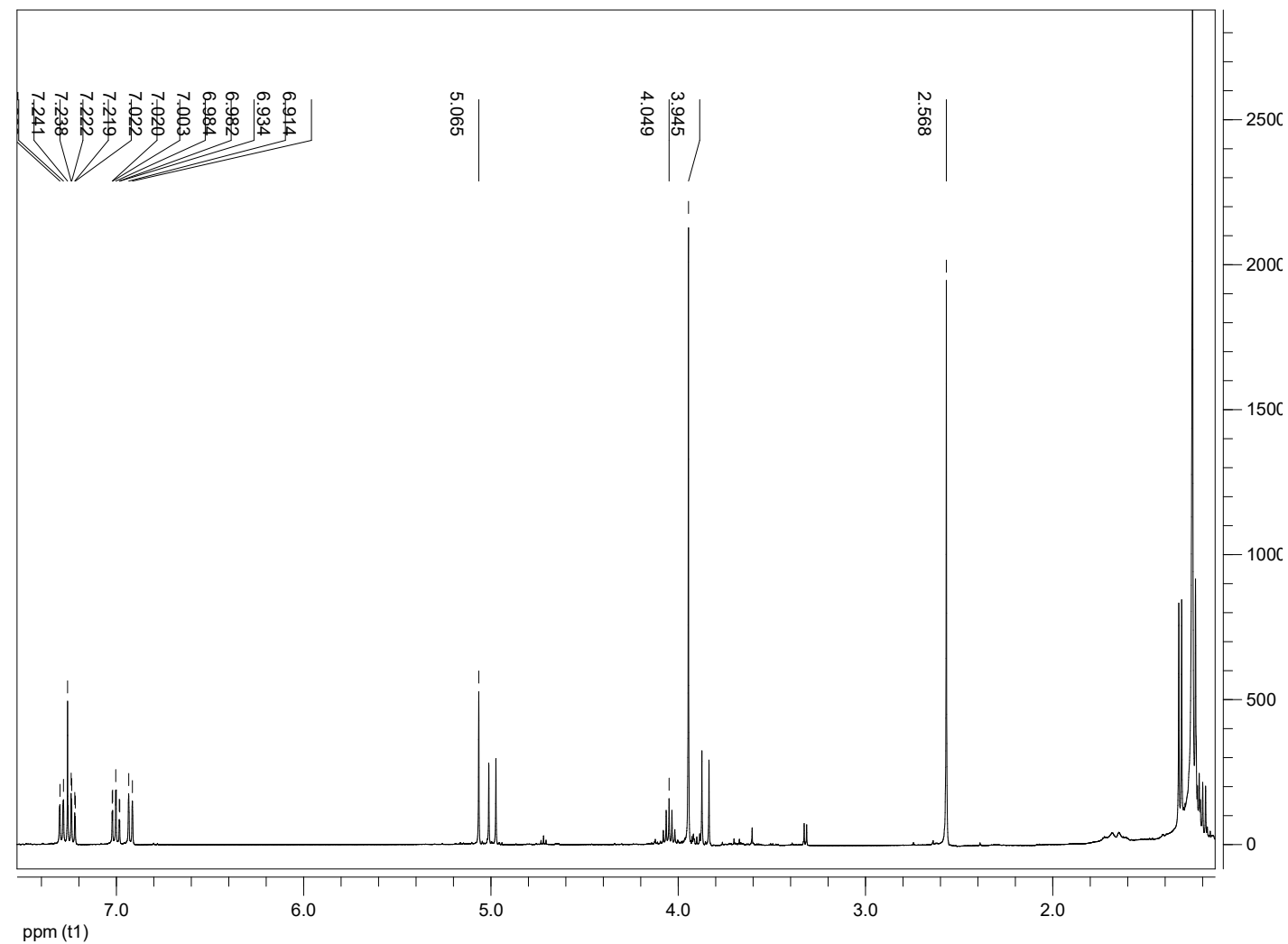
^{13}C NMR spectrum of *trans*-(±)-**7a** in CDCl_3



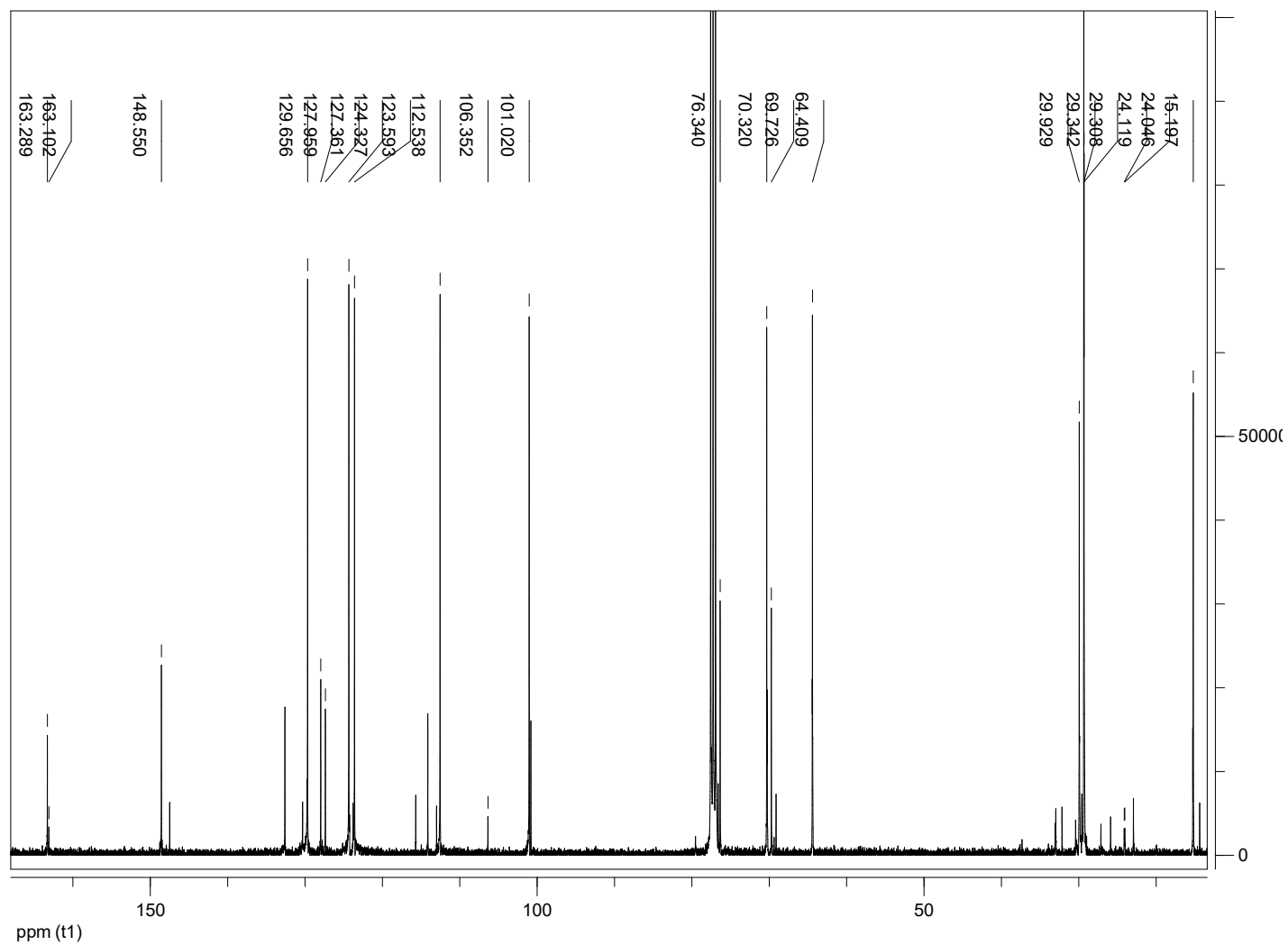
***cis*-(±)-1-Methoxyspirobrassinol ethyl ether [*cis*-(±)-7b]**¹H NMR spectrum of *cis*-(±)-7b in CDCl₃

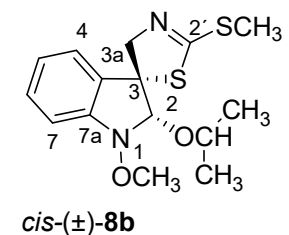
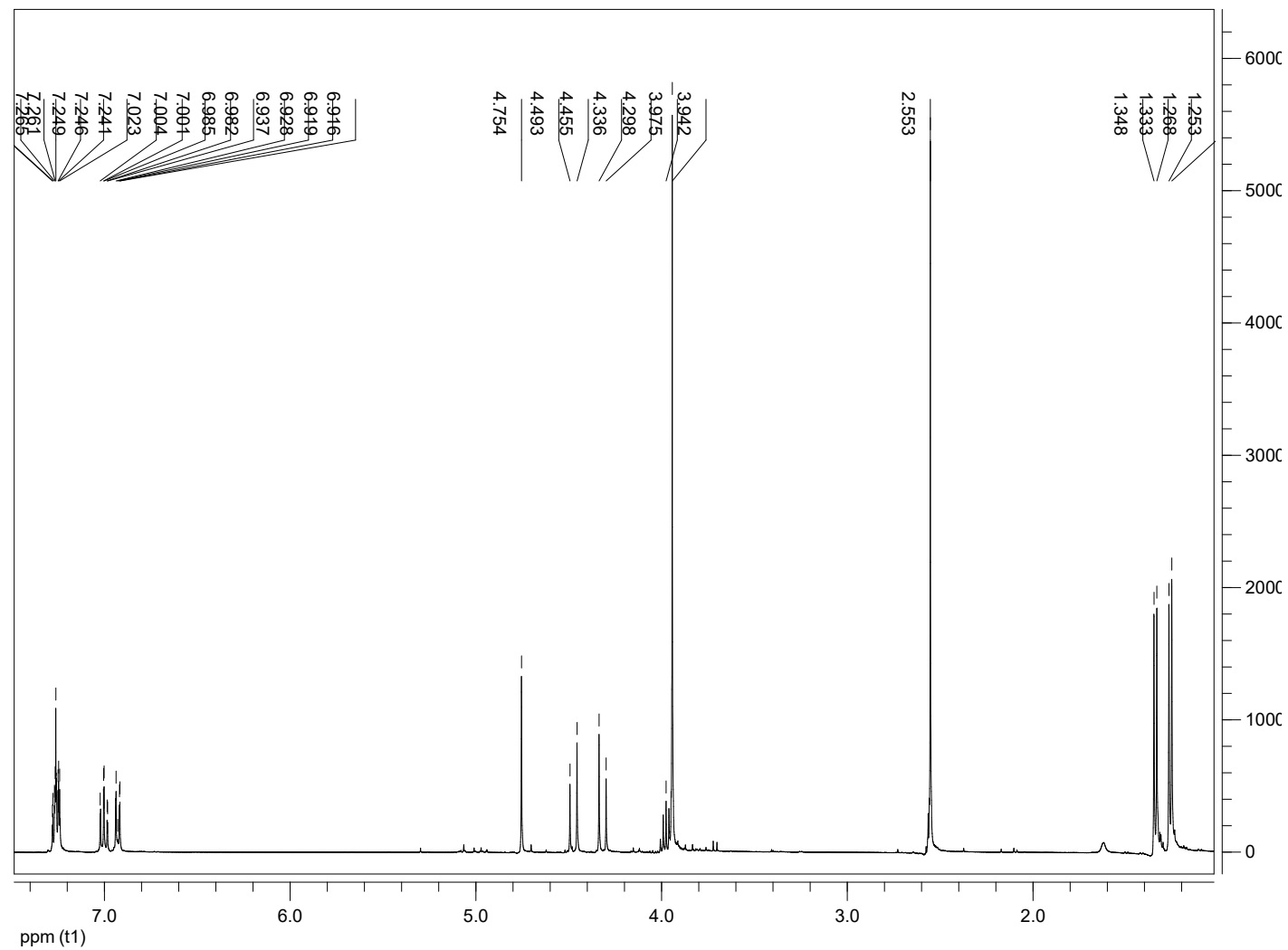
^{13}C NMR spectrum of *cis*-(±)-**7b** in CDCl_3



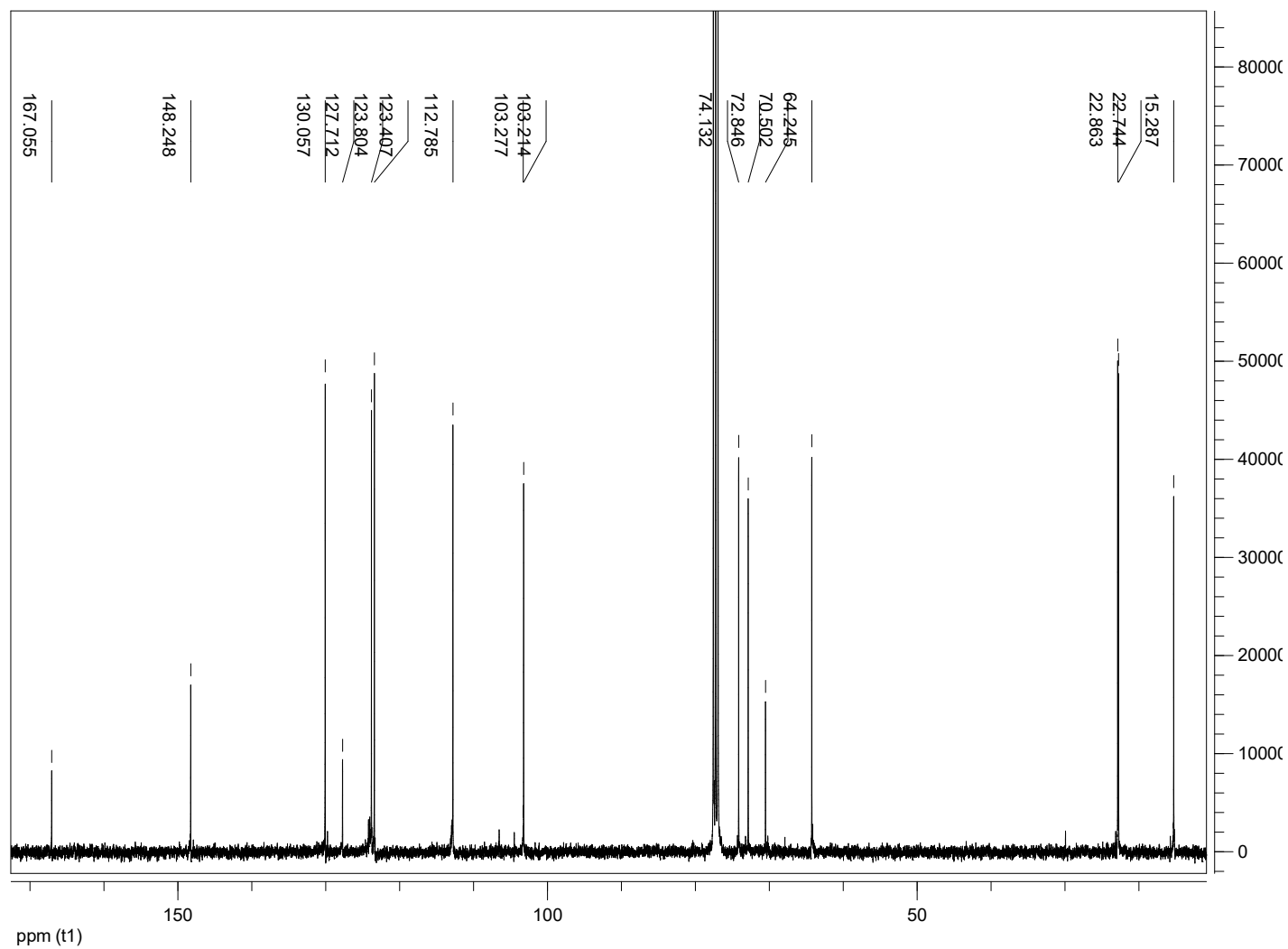
***trans*-(±)-1-Methoxyspirobrassinol isopropyl ether [*trans*-(±)-8a]**¹H NMR spectrum of *trans*-(±)-8a in CDCl₃*trans*-(±)-8a

^{13}C NMR spectrum of *trans*-(±)-**8a** in CDCl_3

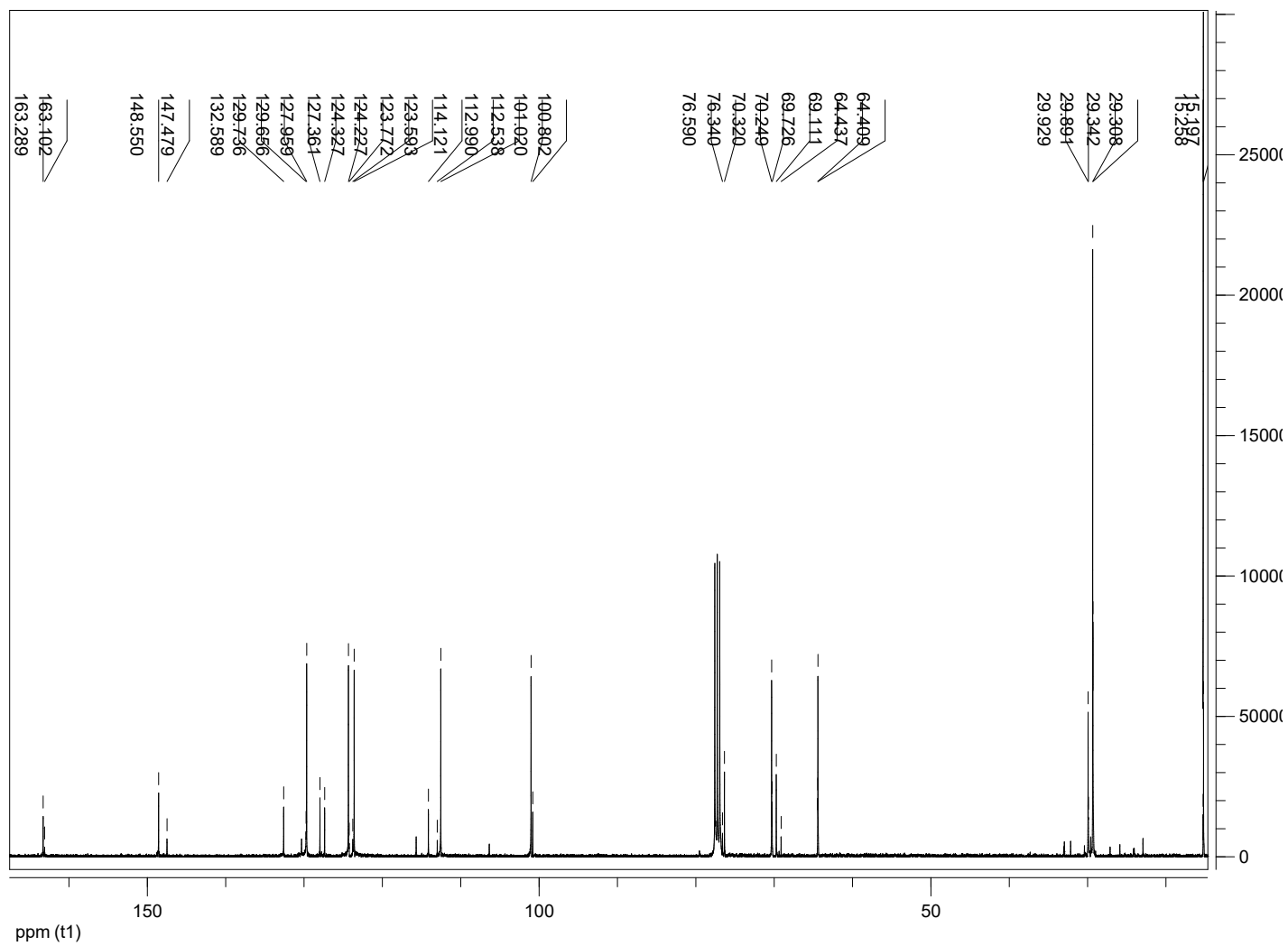


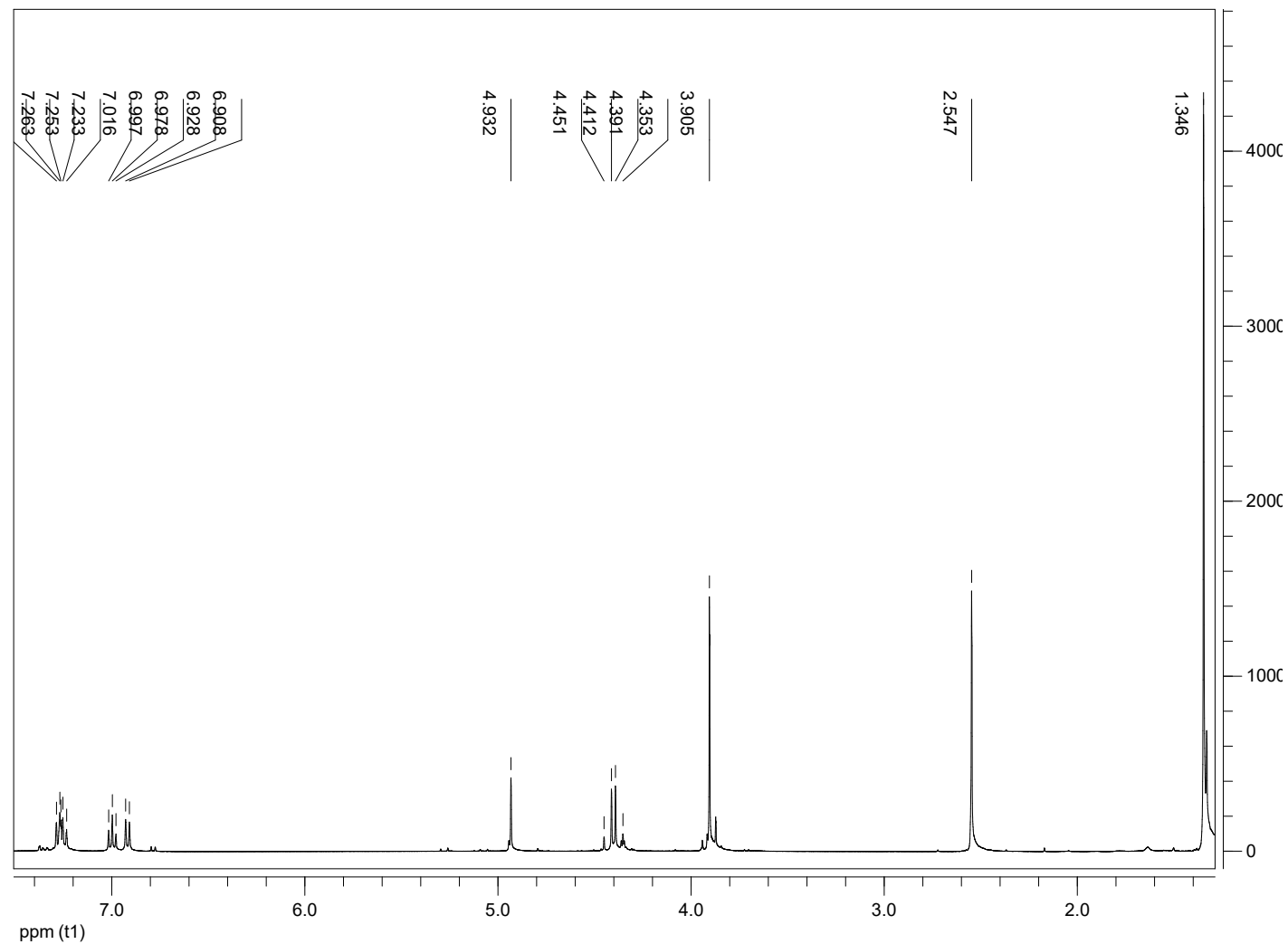
***cis*-(±)-1-Methoxyspirobrassinol isopropyl ether [*cis*-(±)-8b]**¹H NMR spectrum of *cis*-(±)-8b in CDCl₃

^{13}C NMR spectrum of *cis*-(±)-**8b** in CDCl_3

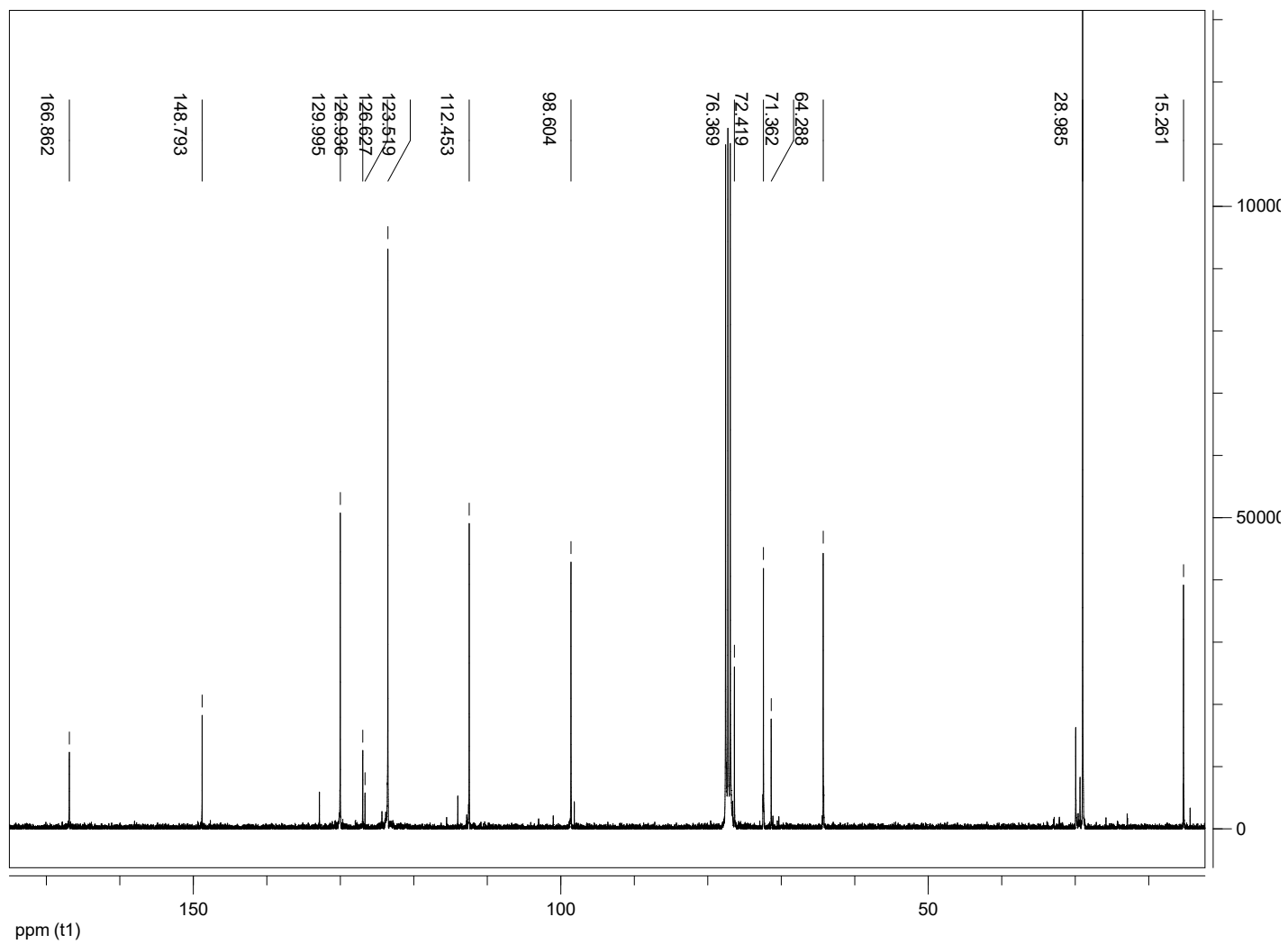


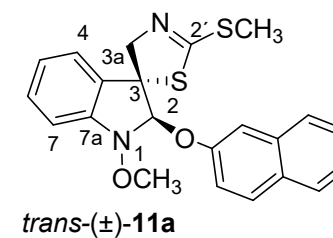
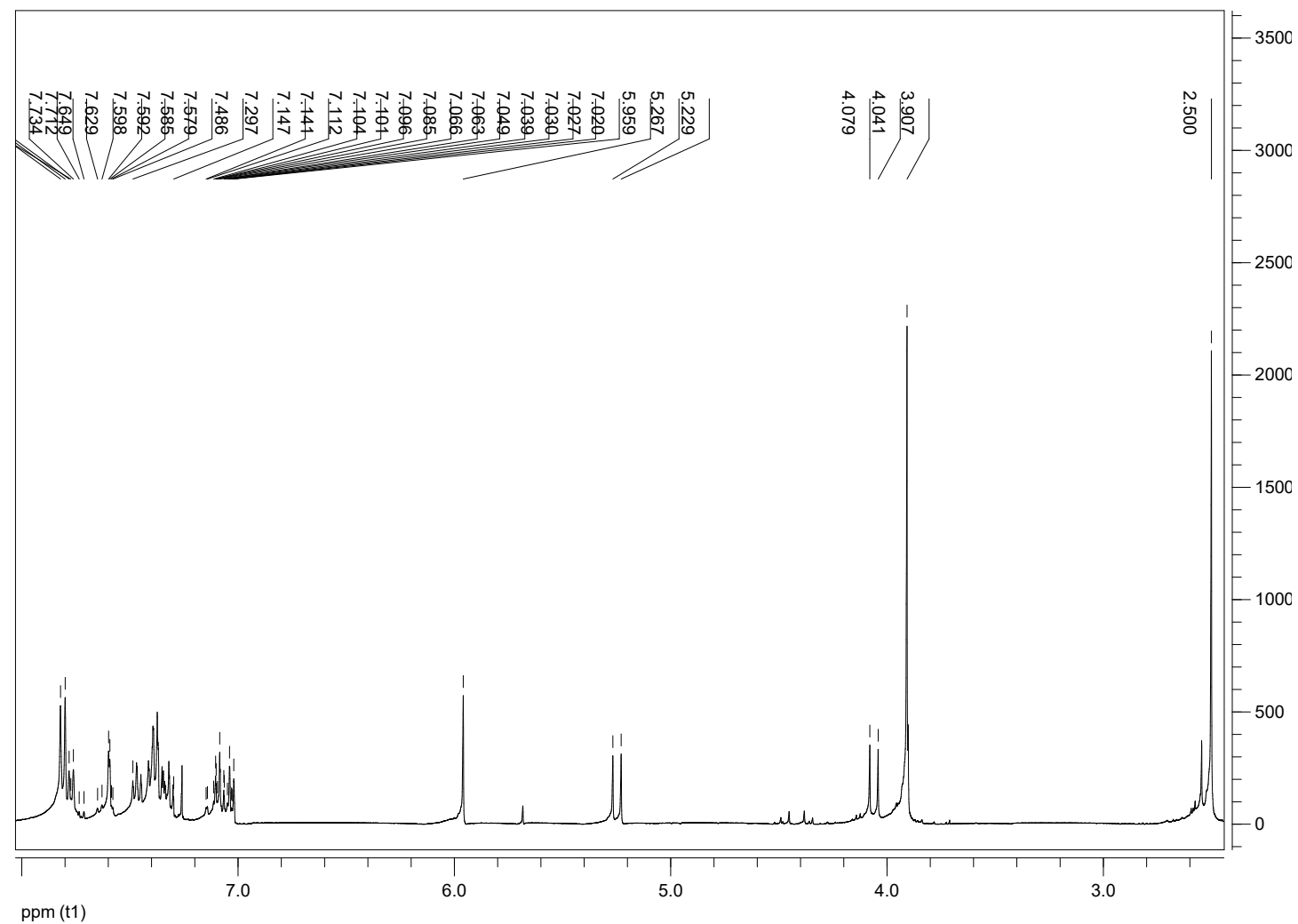
^{13}C NMR spectrum of *trans*-(±)-**9a** in CDCl_3



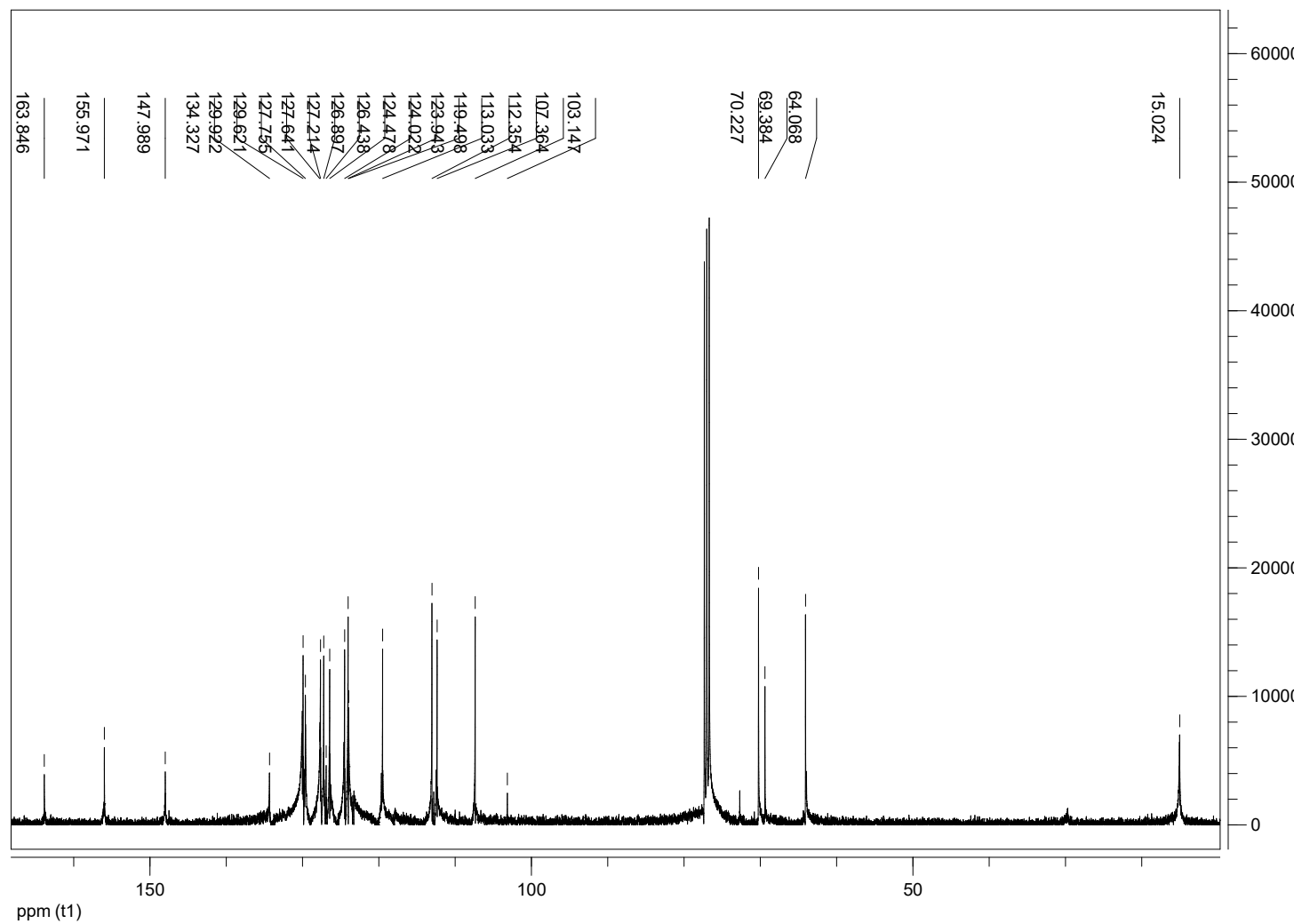
***cis*-(±)-1-Methoxyspirobrassinol *tert*-butyl ether [*cis*-(±)-9b]**¹H NMR spectrum of *cis*-(±)-9b in CDCl₃

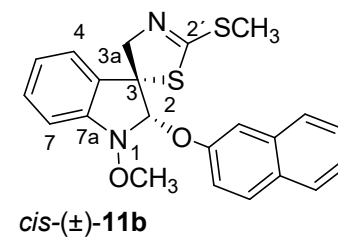
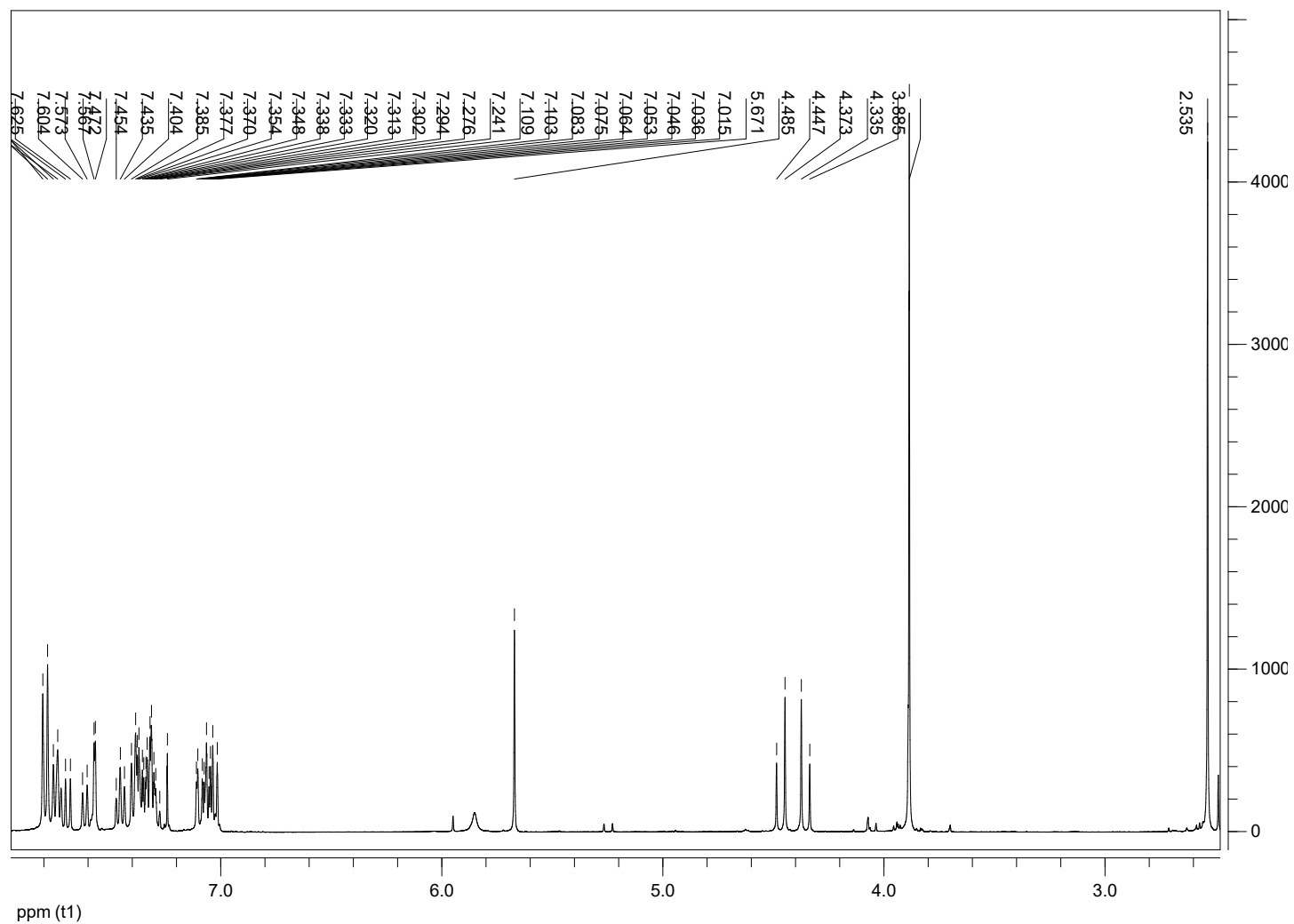
^{13}C NMR spectrum of *cis*-(±)-**9b** in CDCl_3

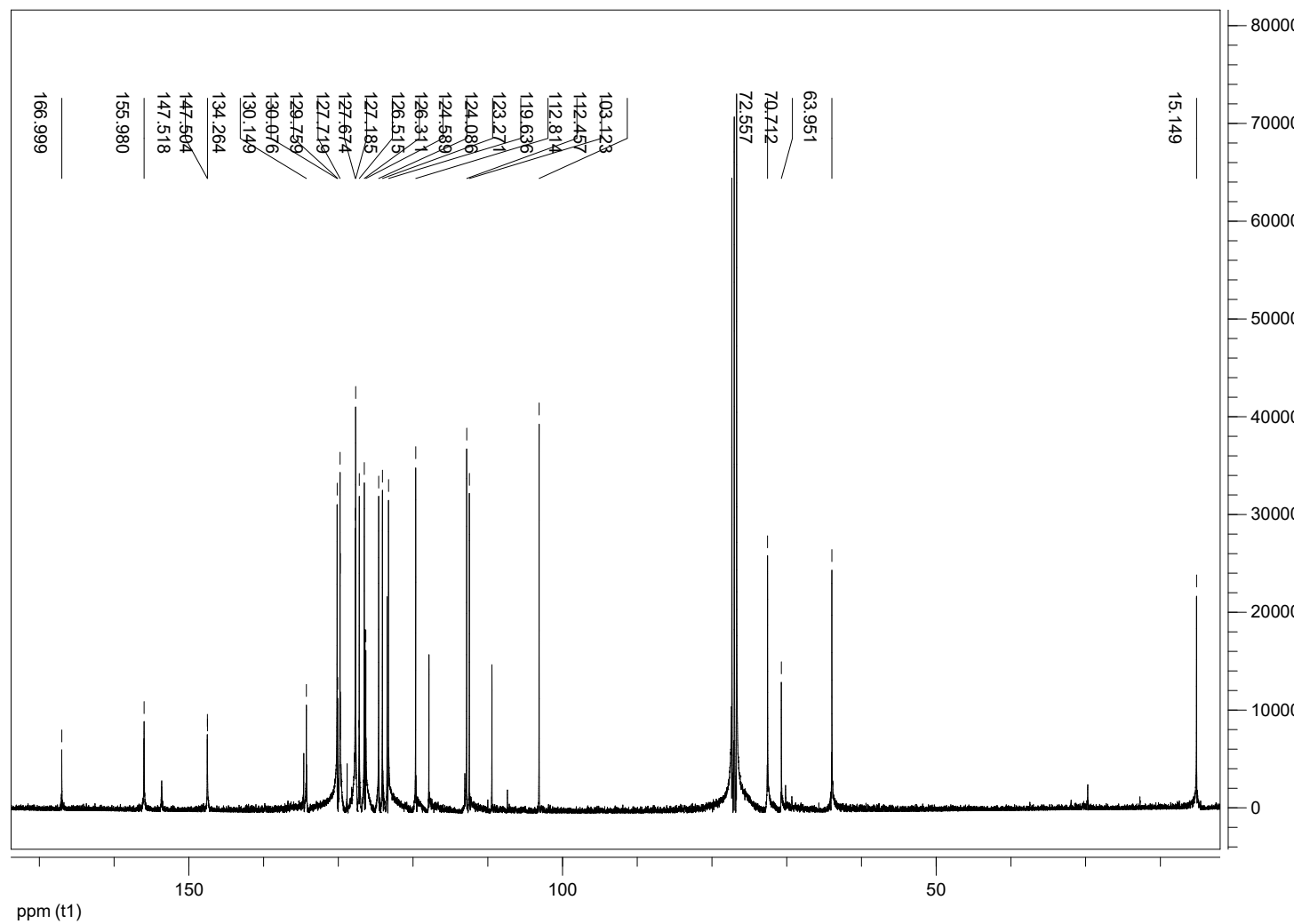


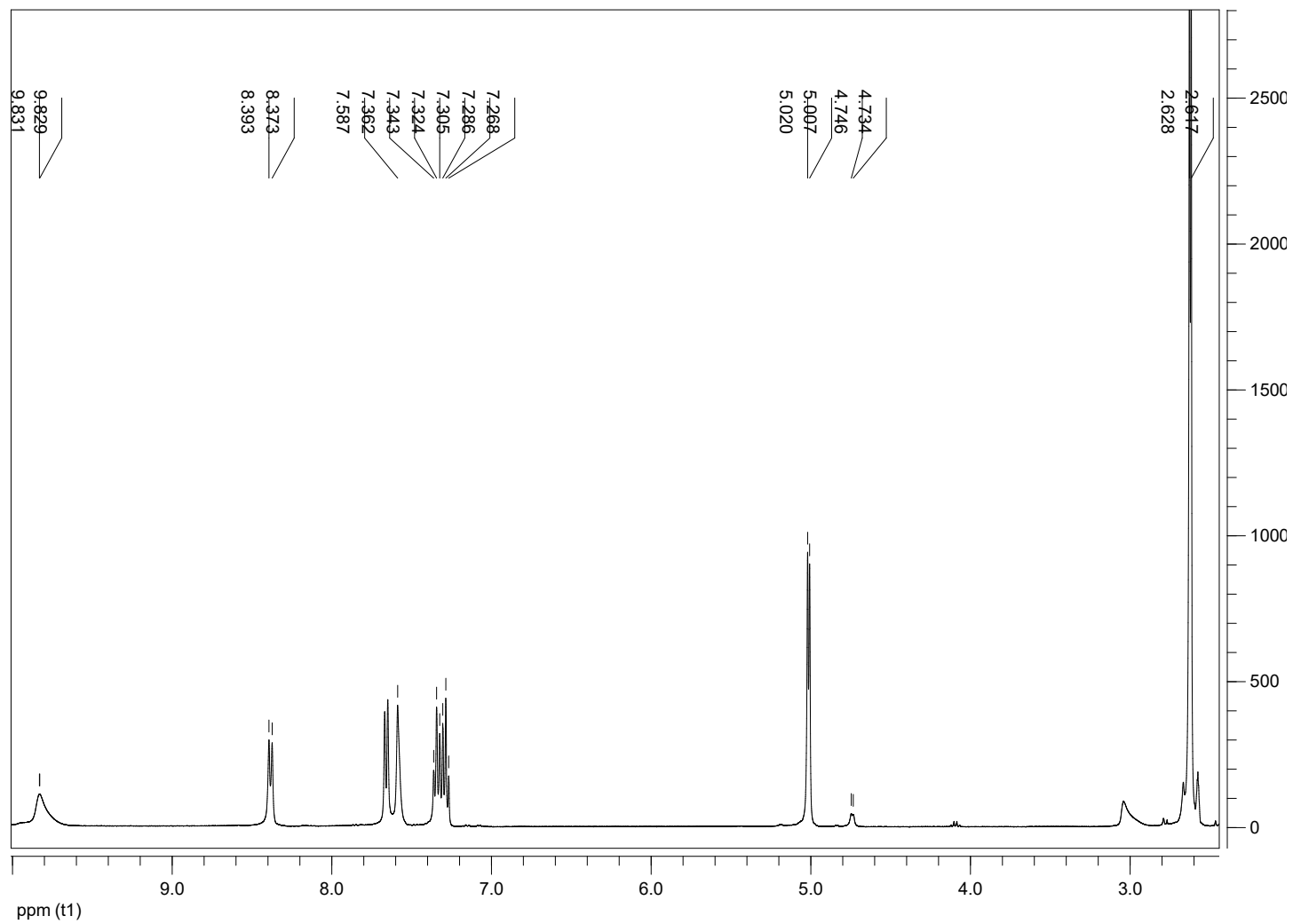
***trans*-(±)-1-Methoxyspirobrassinol naphth-2-yl ether [*trans*-(±)-11a]**¹H NMR spectrum of *trans*-(±)-11a in CDCl₃

^{13}C NMR spectrum of *trans*-(±)-11a in CDCl_3

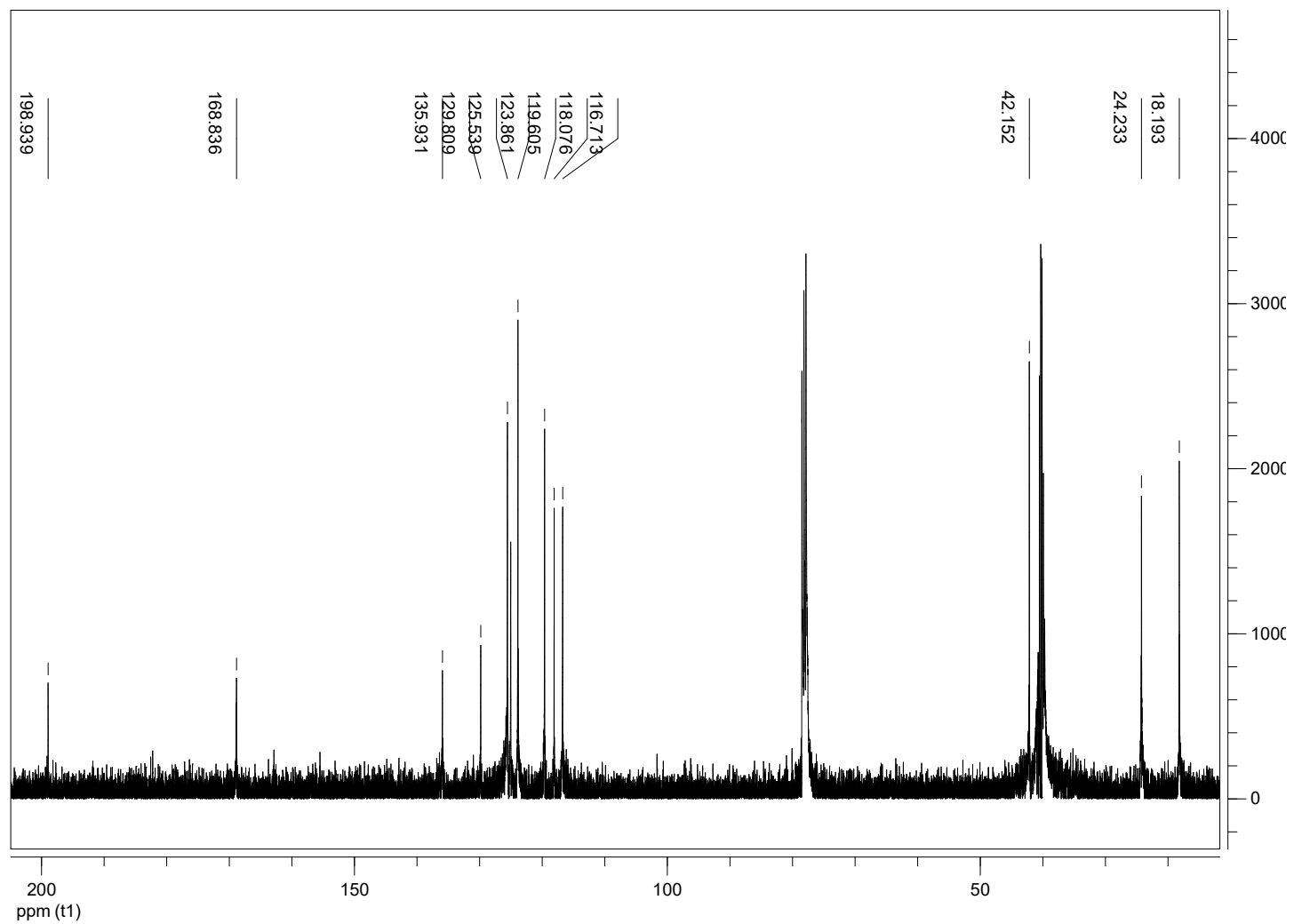


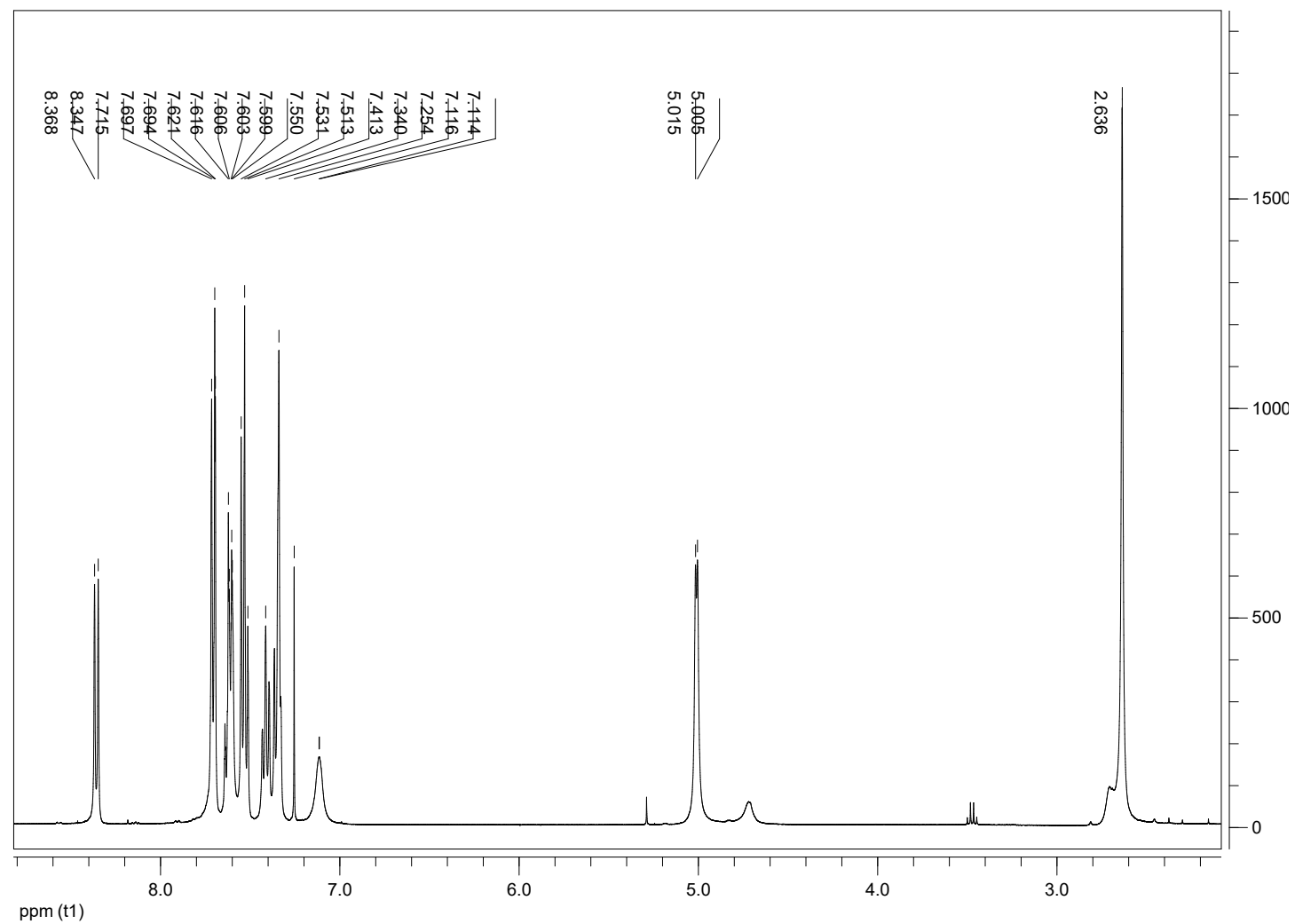
***cis*-(±)-1-Methoxyspirobrassinol naphth-2-yl ether [*cis*-(±)-11b]**¹H NMR spectrum of *cis*-(±)-11b in CDCl₃

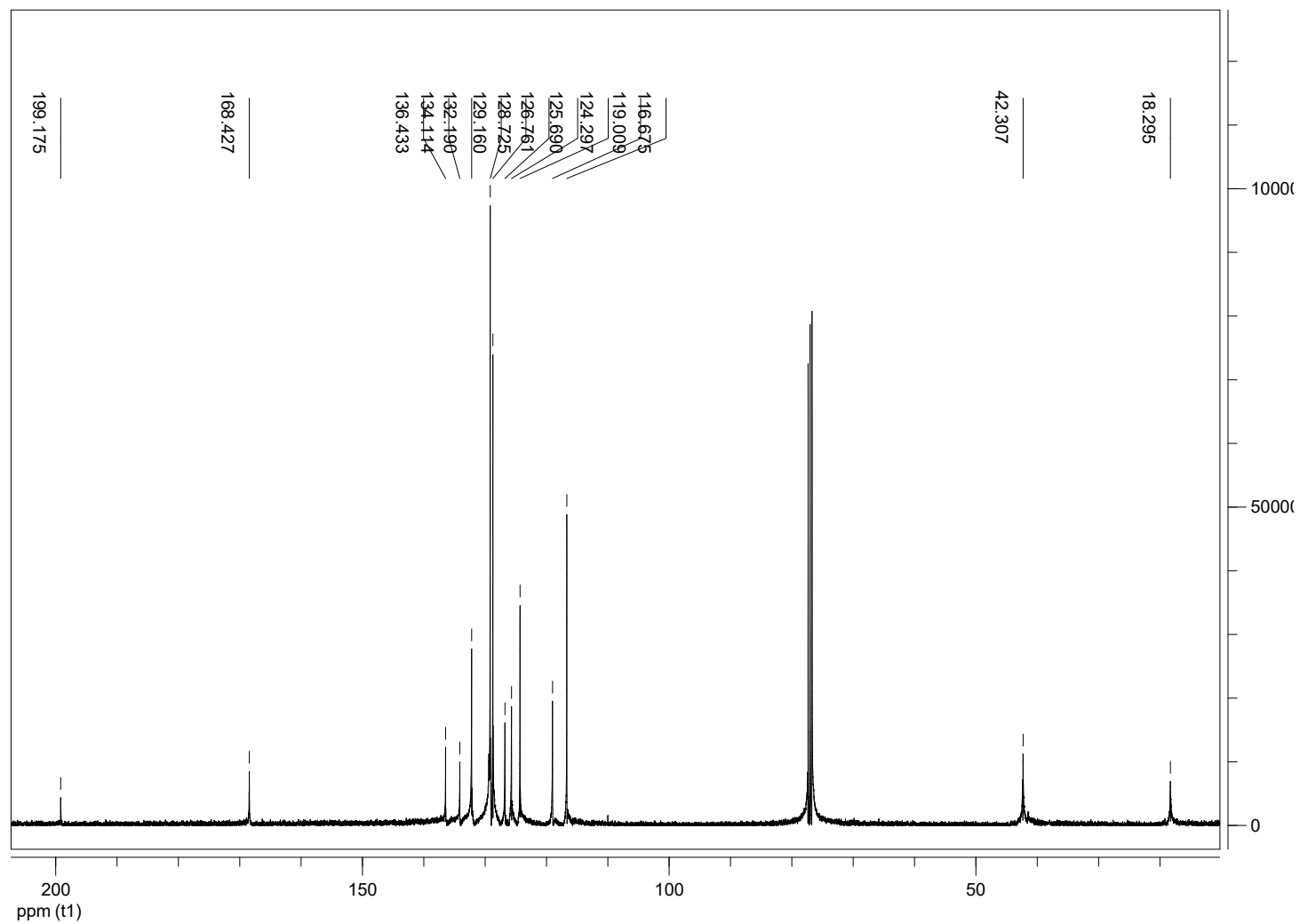
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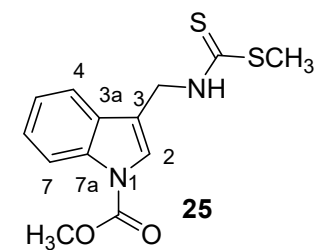
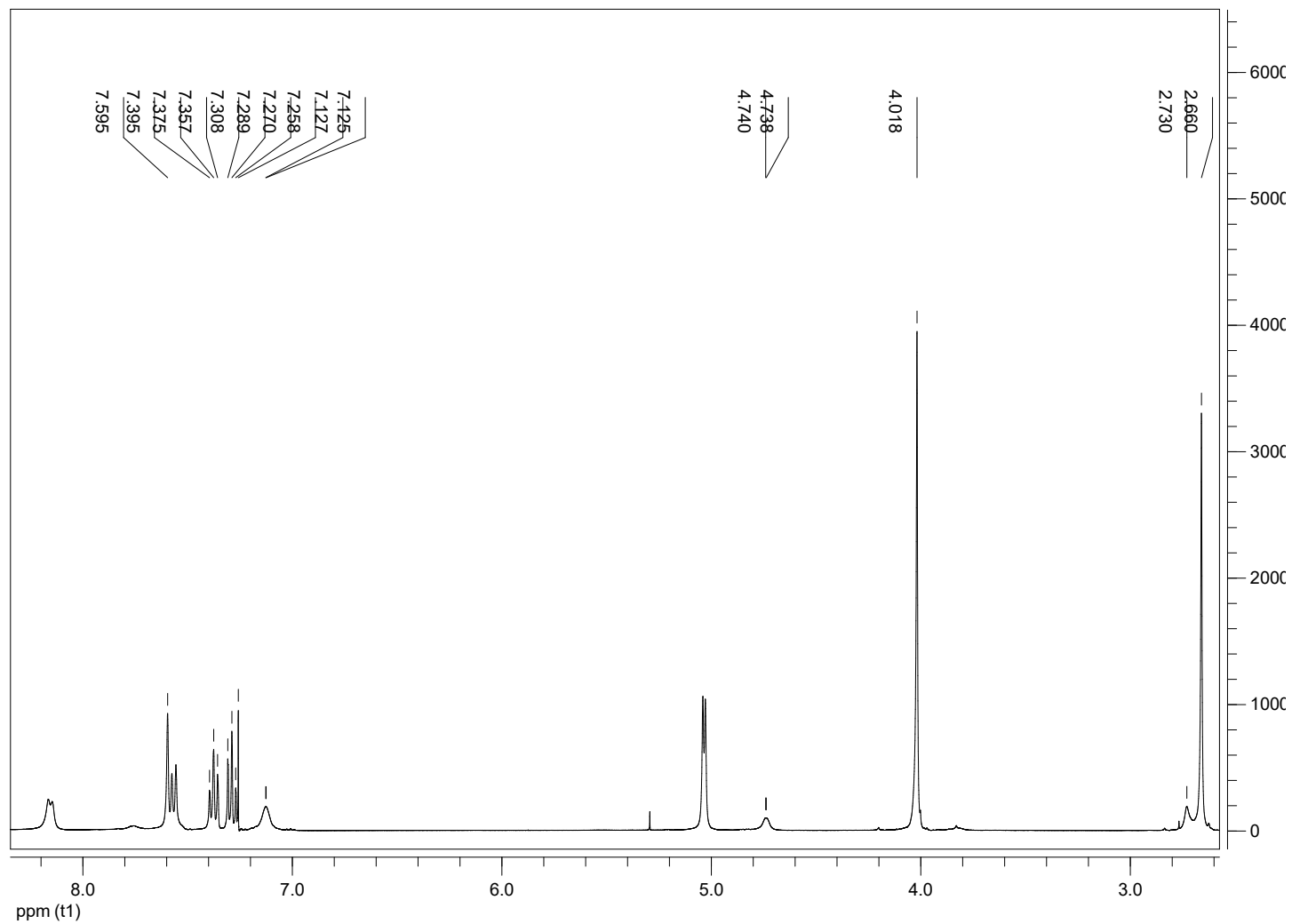
1-Acetylbrassinin (23)¹H NMR spectrum of **23** in DMSO-*d*₆

^{13}C NMR spectrum of **23** in $\text{DMSO-}d_6$

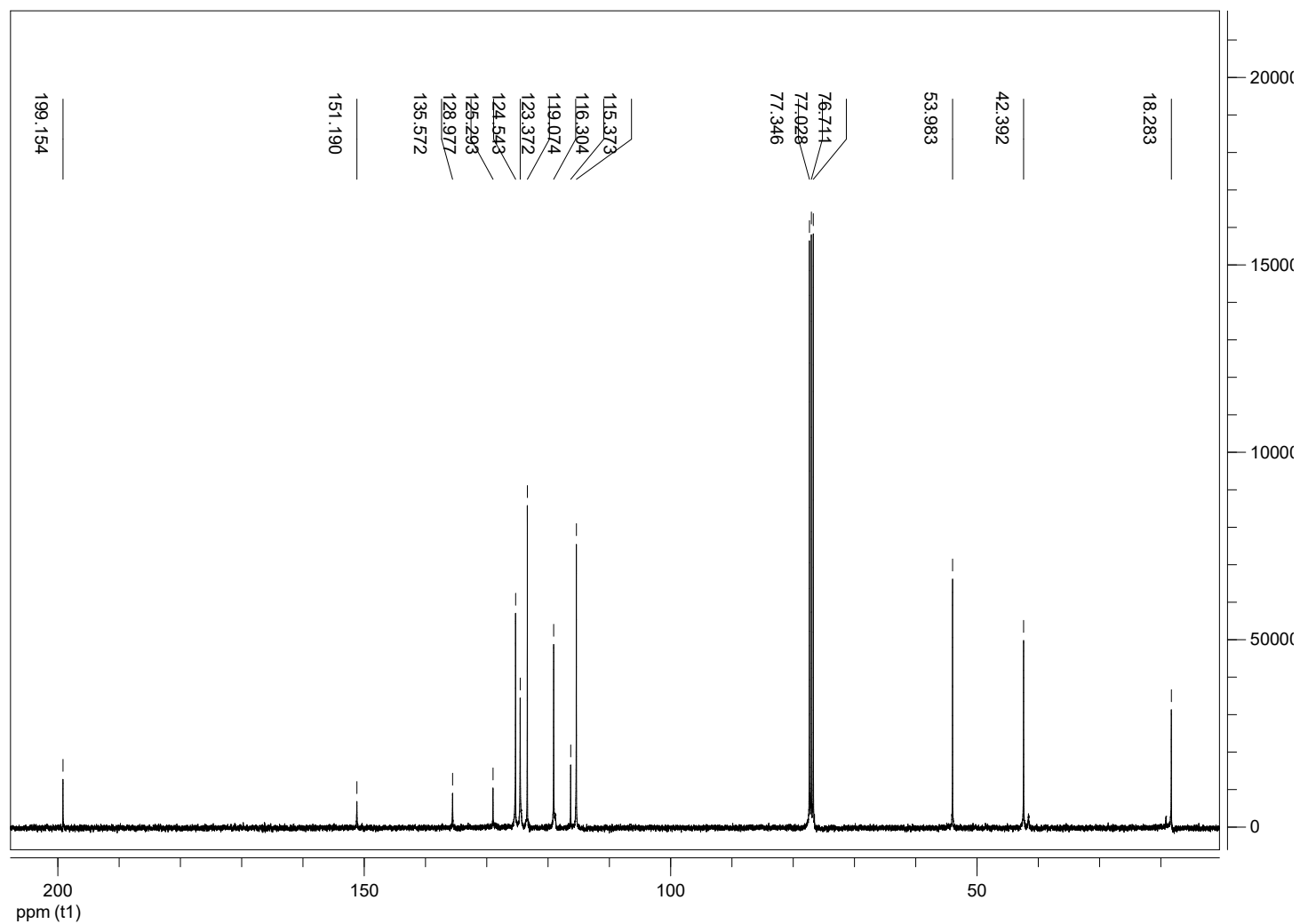


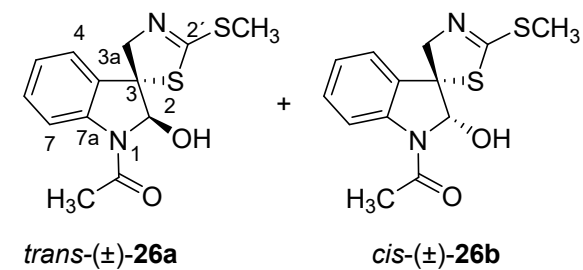
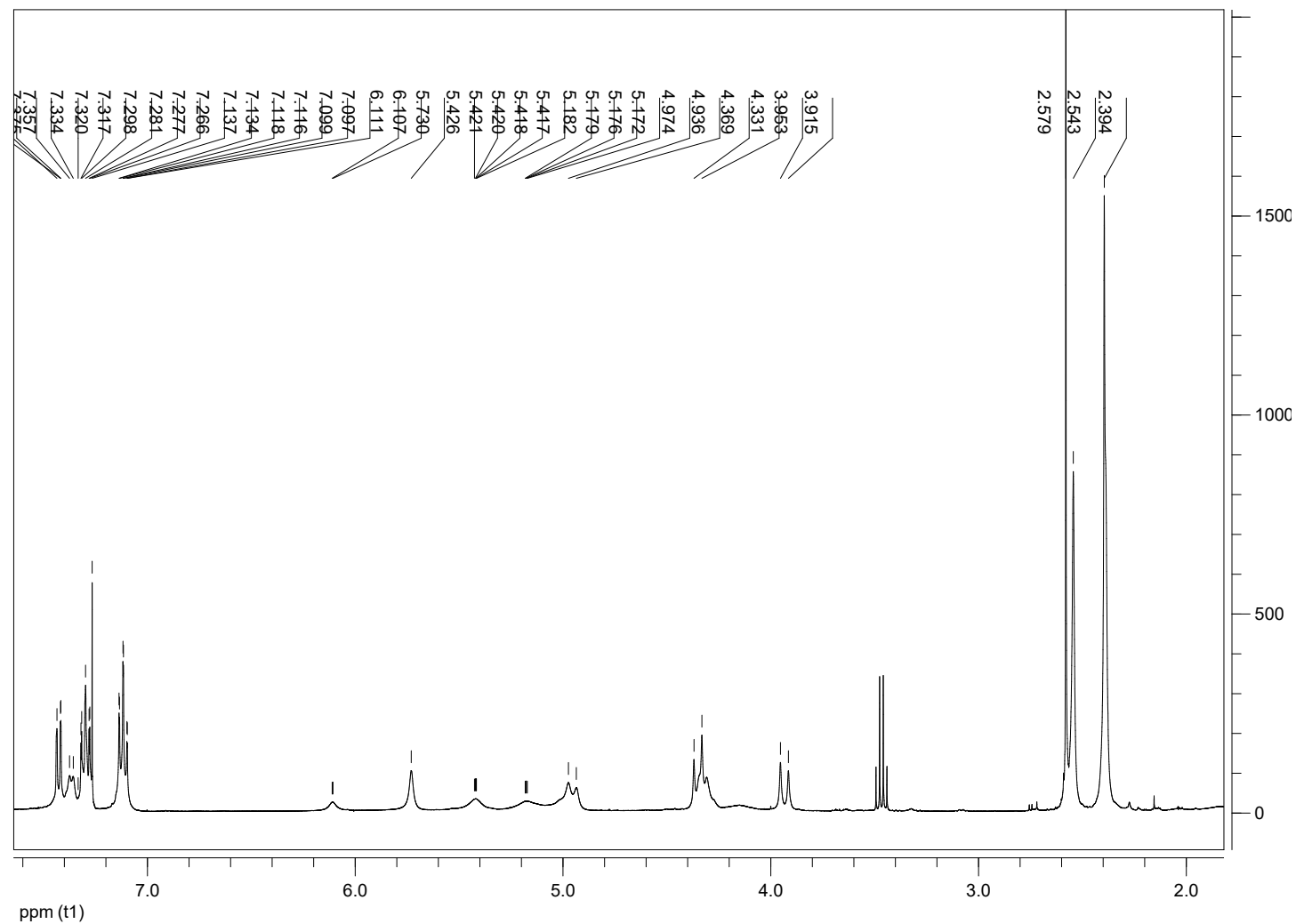
1-Benzoylbrassinin (24)¹H NMR spectrum of **24** in CDCl₃

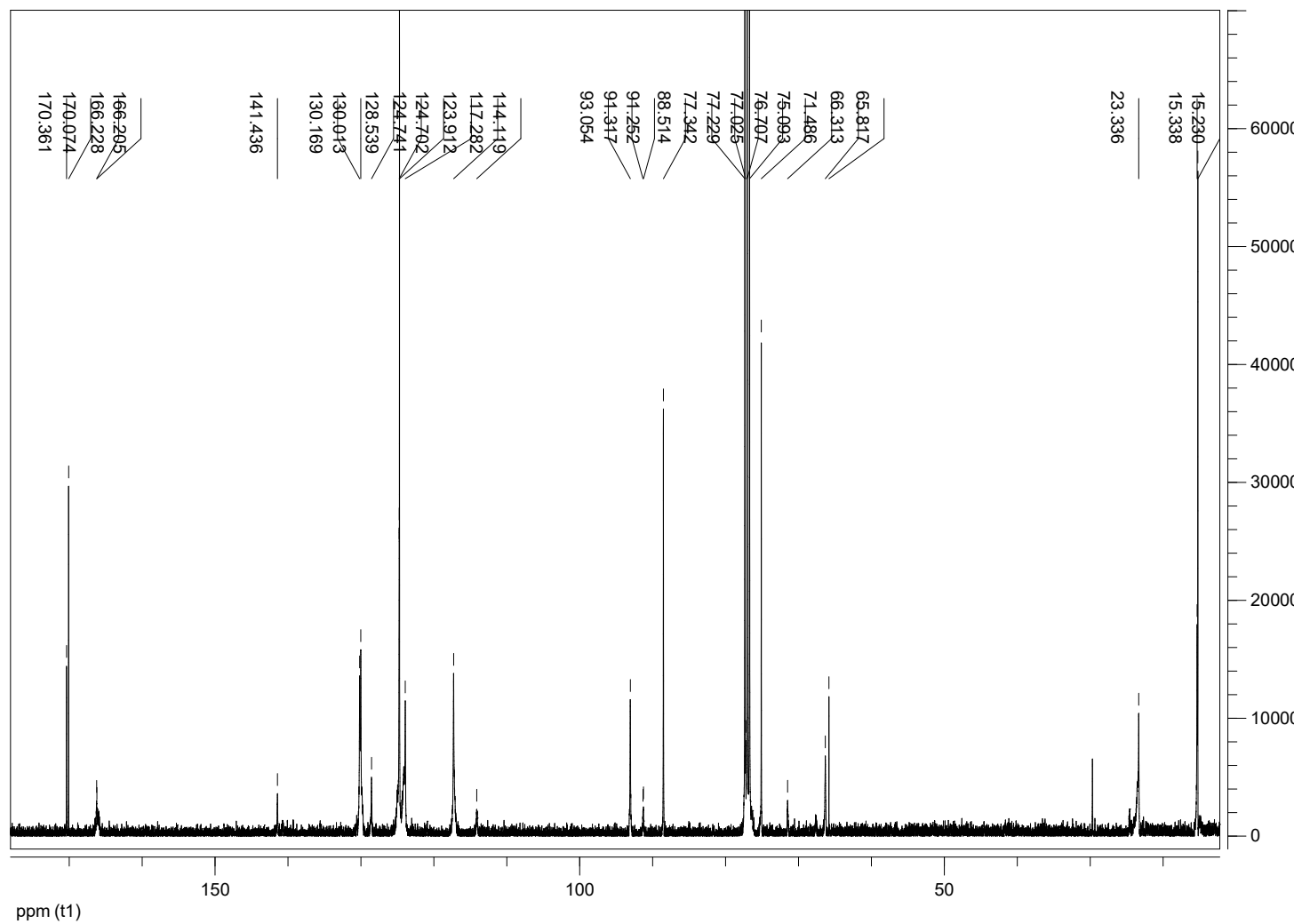
^{13}C NMR spectrum of **24** in CDCl_3 

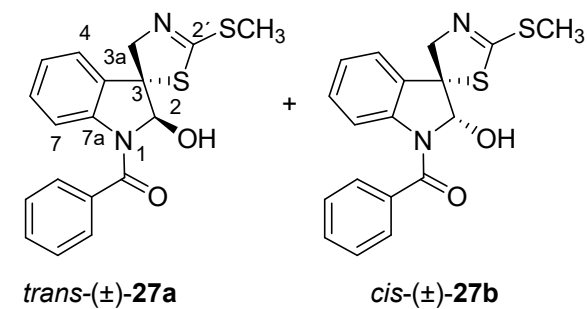
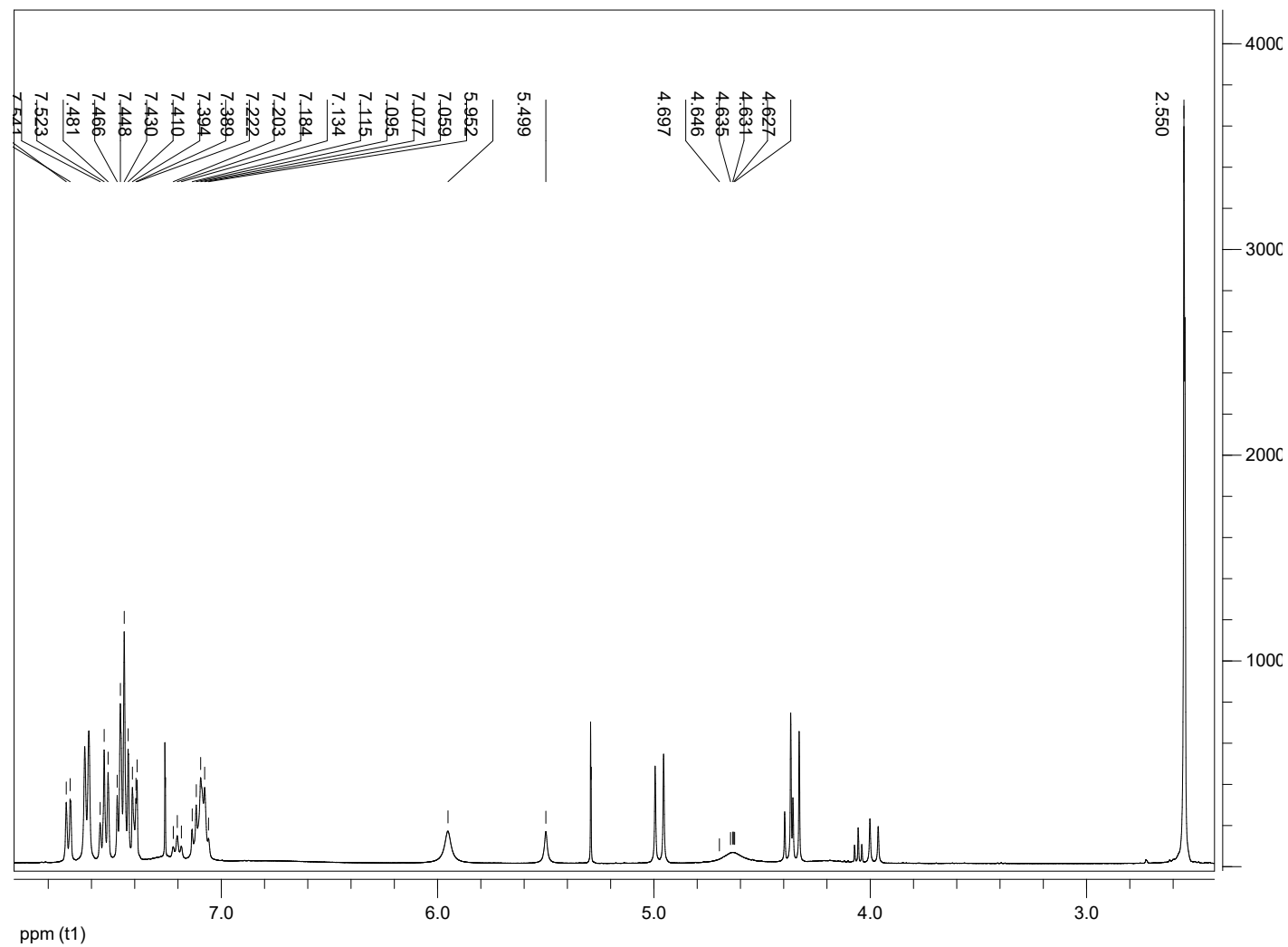
1-(Methoxycarbonyl)brassinin (25)¹H NMR spectrum of **25** in CDCl₃

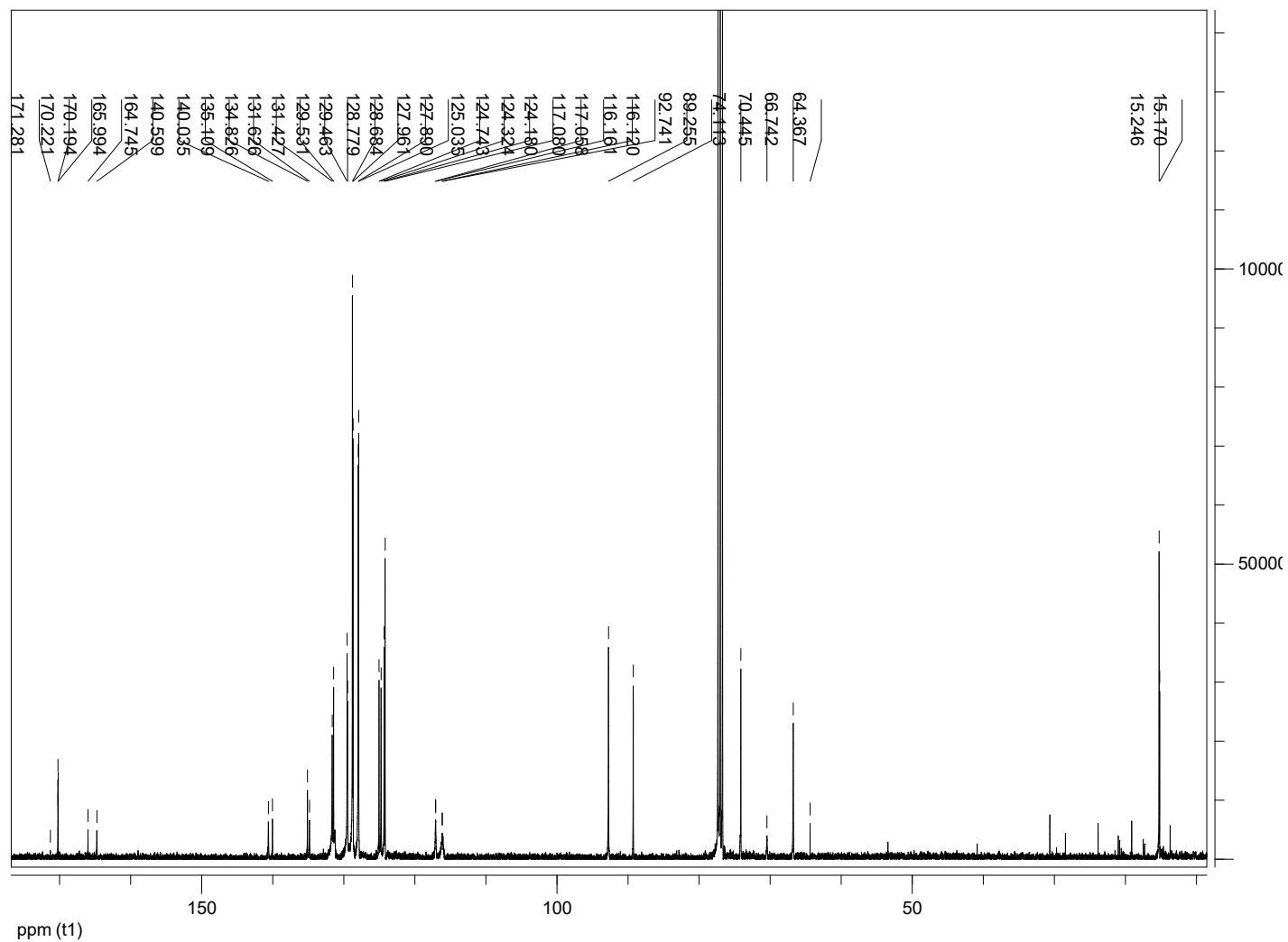
^{13}C NMR spectrum of **25** in CDCl_3

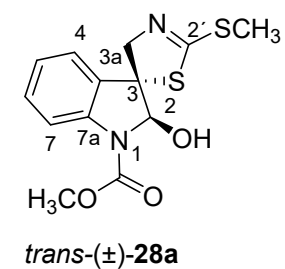
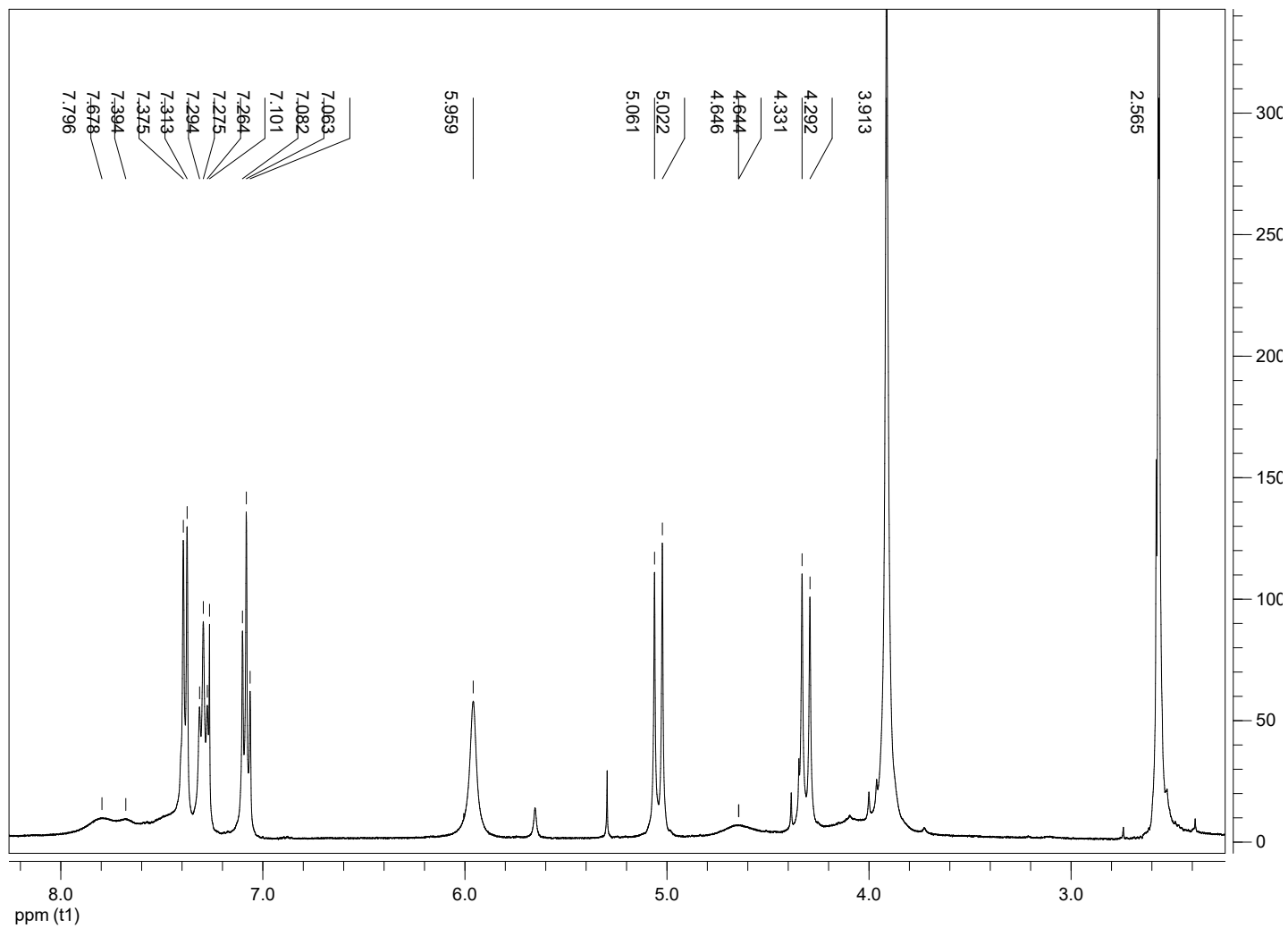


***trans*-(±)- and *cis*-(±)-1-Acetylspirobrassinol [*trans*-(±)-26a and *cis*-(±)-26b]**¹H NMR spectrum of mixture *trans*-(±)-26a and *cis*-(±)-26b in CDCl₃

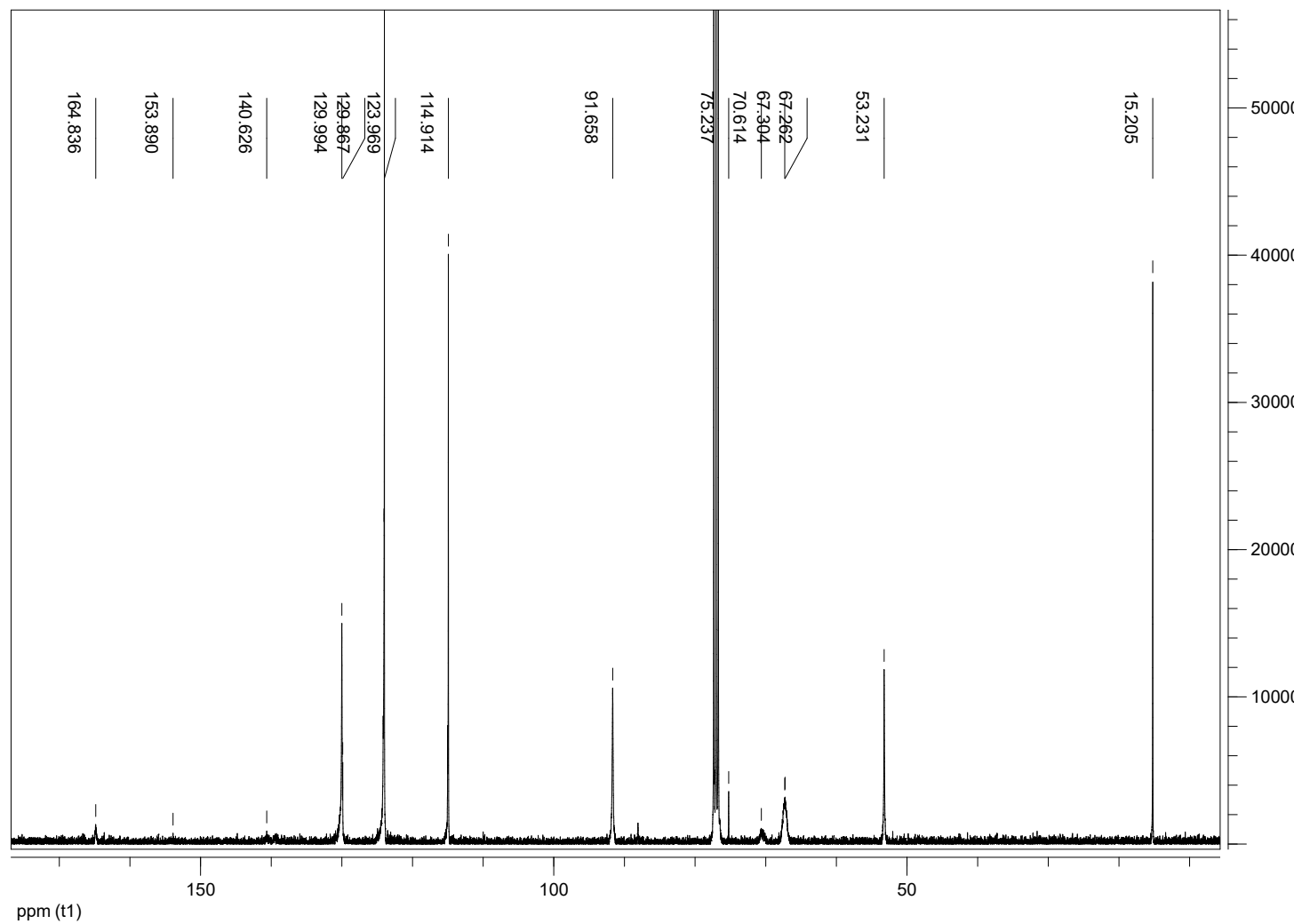
^{13}C NMR spectrum of mixture *trans*-(±)-26a and *cis*-(±)-26b in CDCl_3 

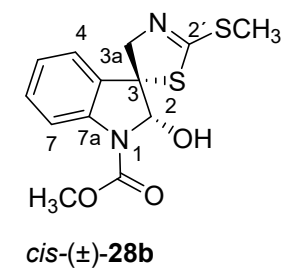
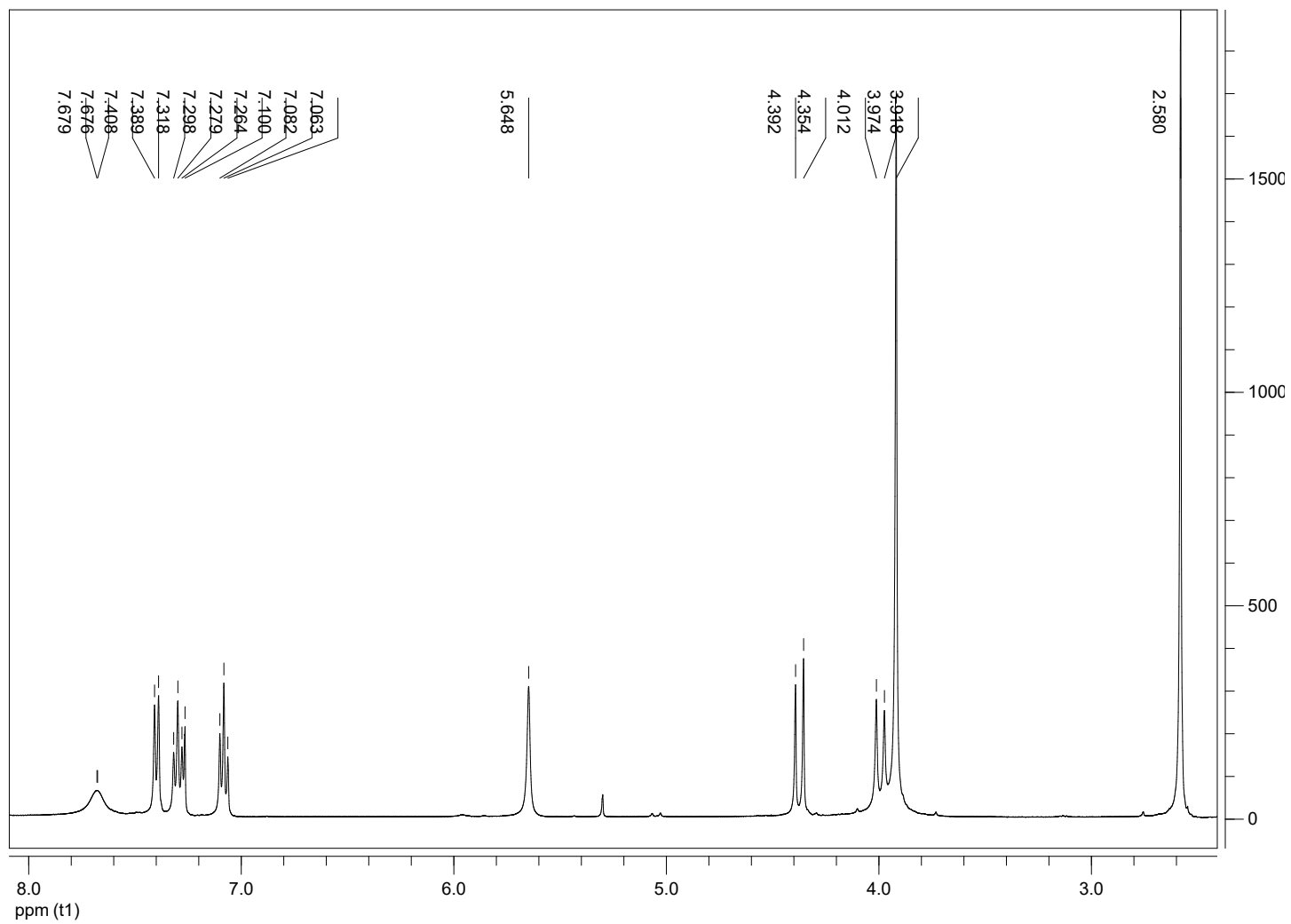
***trans*-(±)- and *cis*-(±)-1-Benzoylspirobrassinol [*trans*-(±)-27a and *cis*-(±)-27b]**¹H NMR spectrum of mixture *trans*-(±)-27a and *cis*-(±)-27b in CDCl₃

^{13}C NMR spectrum of mixture *trans*-(±)-27a and *cis*-(±)-27b in CDCl_3 

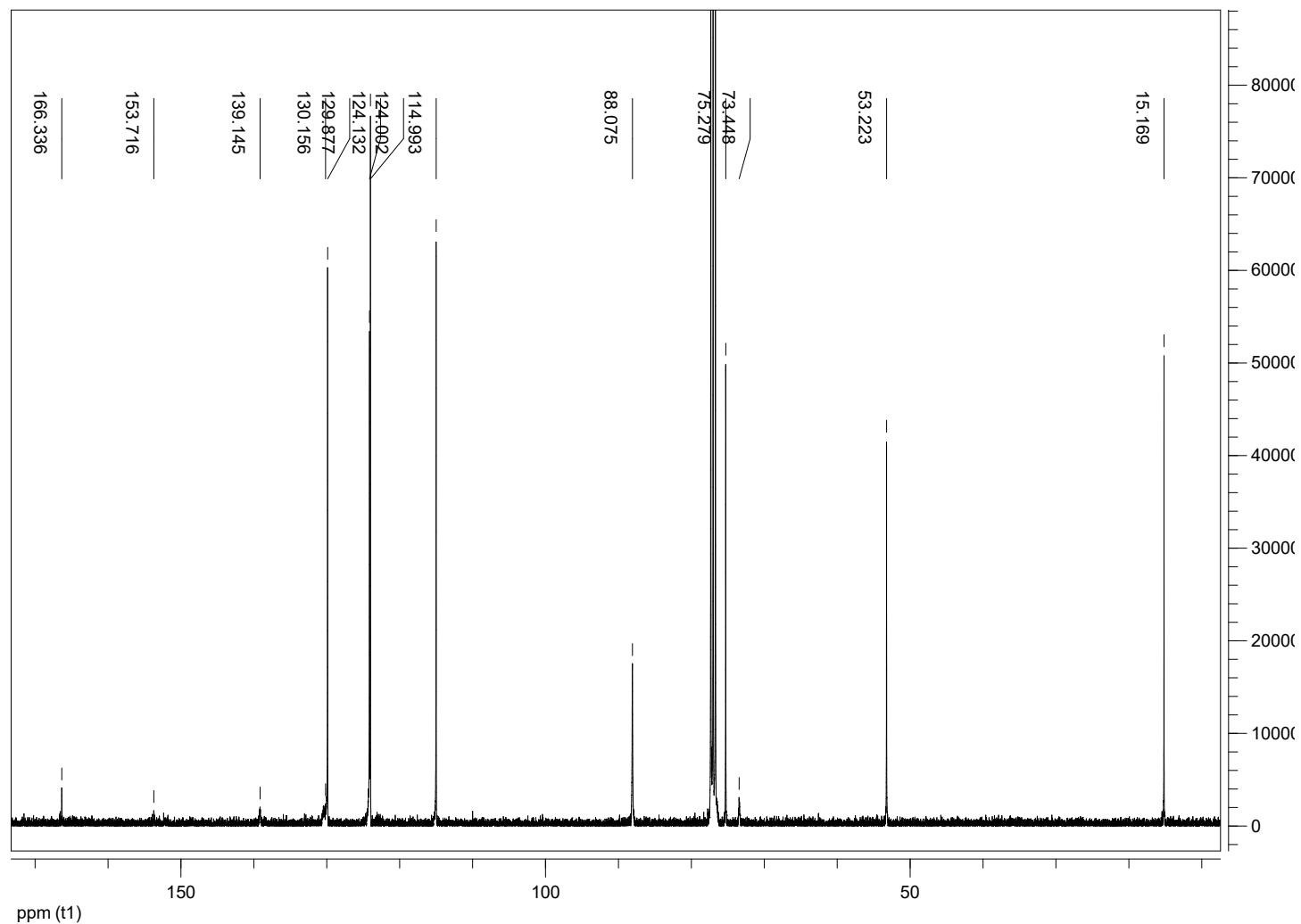
***trans*-(±)-1-Methoxycarbonylspirobrassinol [*trans*-(±)-28a]**¹H NMR spectrum of *trans*-(±)-28a in CDCl₃

^{13}C NMR spectrum of *trans*-(±)-**28a** in CDCl_3

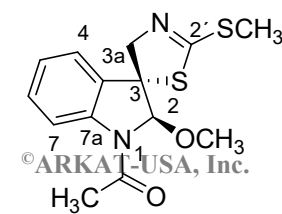


***cis*-(±)-1-Methoxycarbonylspirobrassinol [*cis*-(±)-28b]**¹H NMR spectrum of *cis*-(±)-28b in CDCl₃

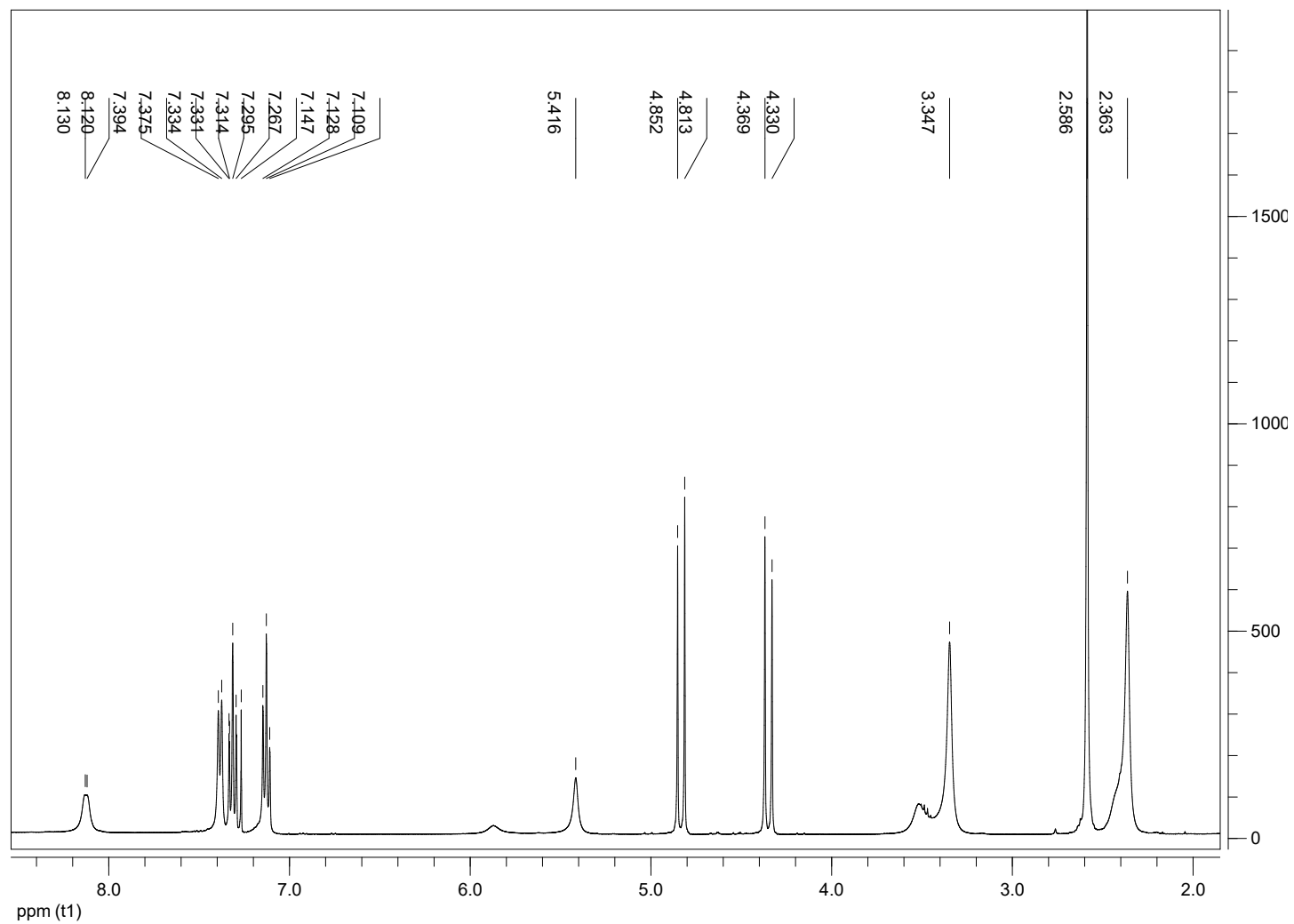
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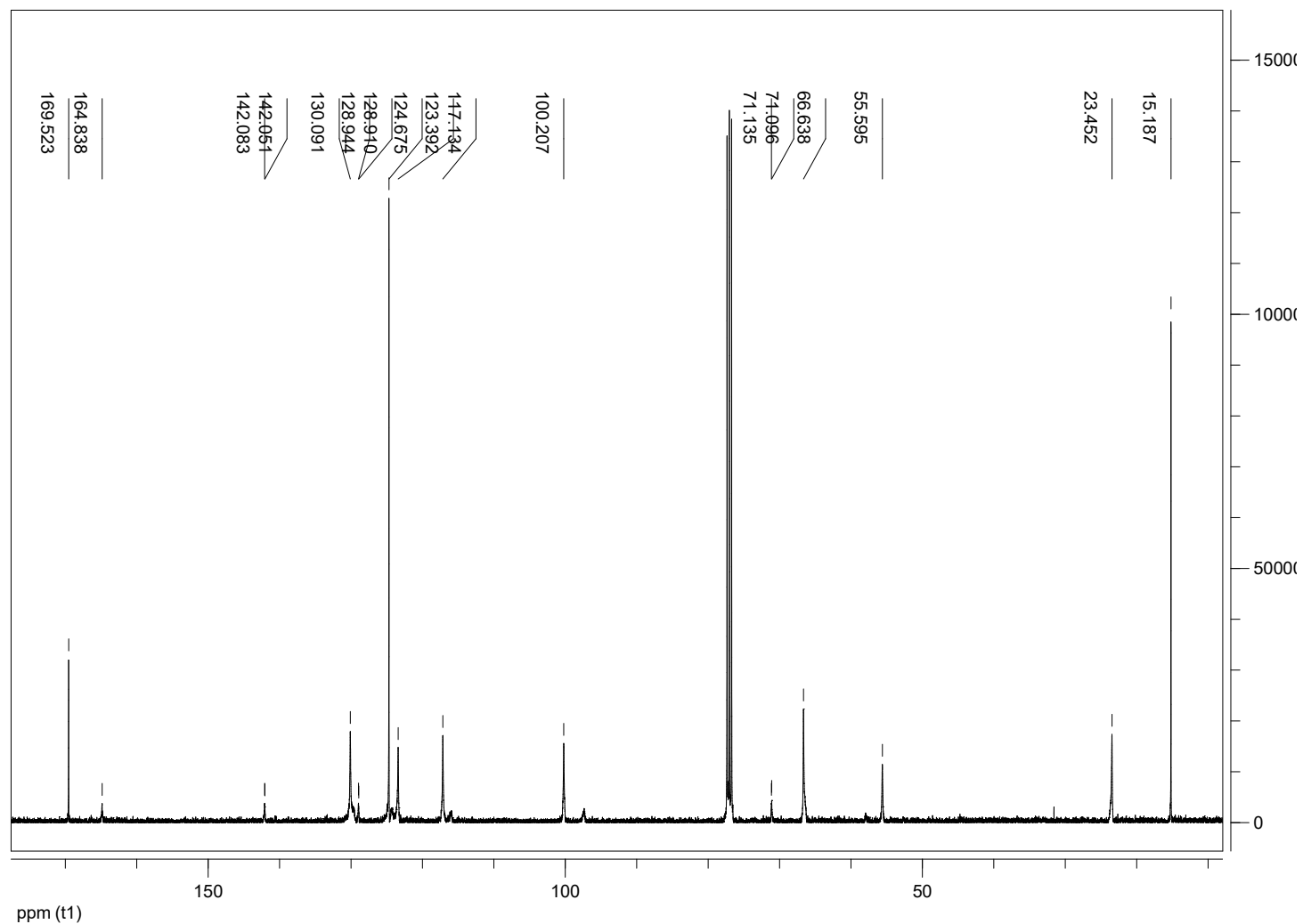


trans-(±)-1-Acetylspirobrassinol methyl ether [*trans*-(±)-**30a**]

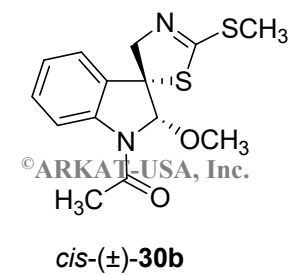


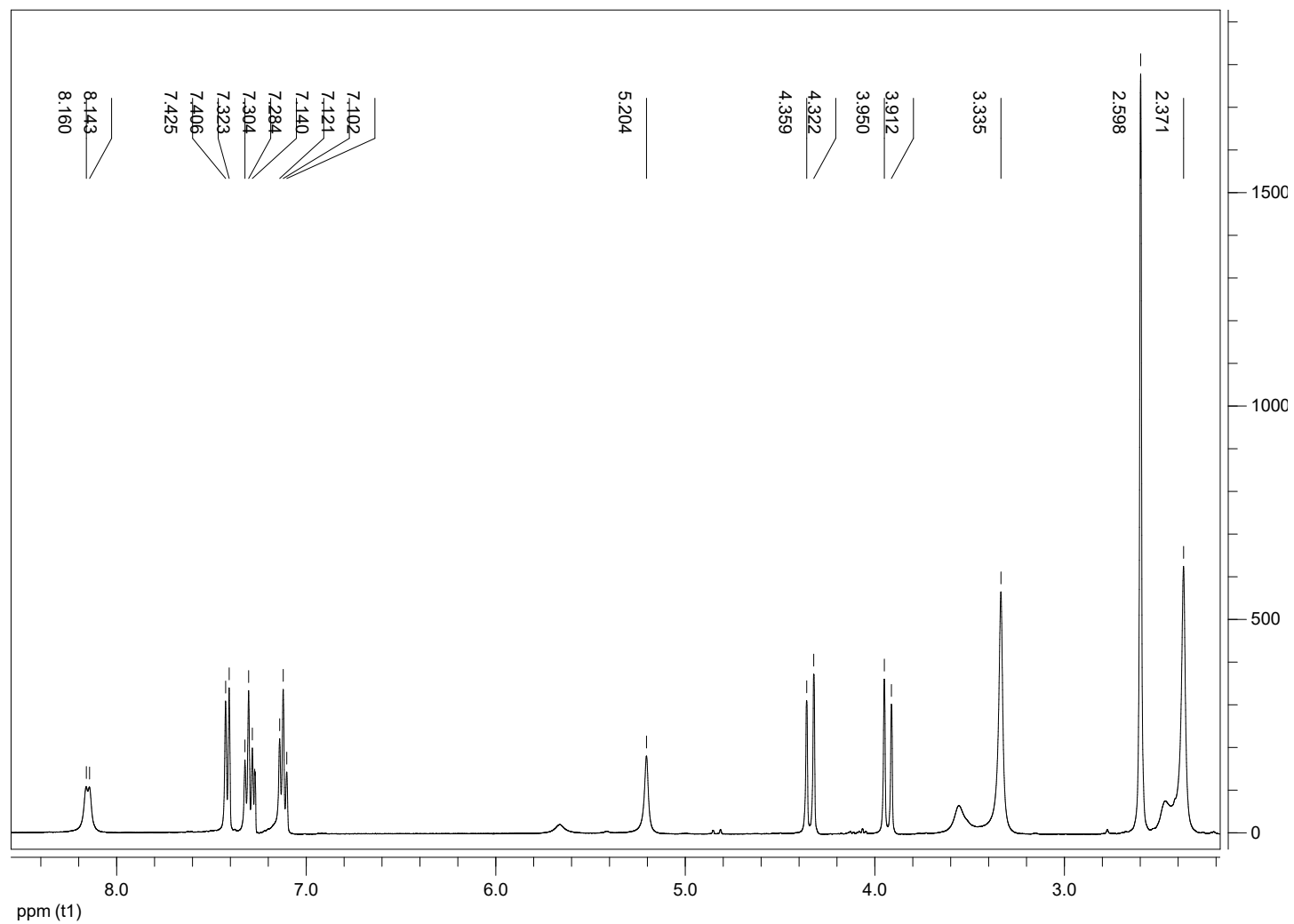
trans-(±)-**30a**

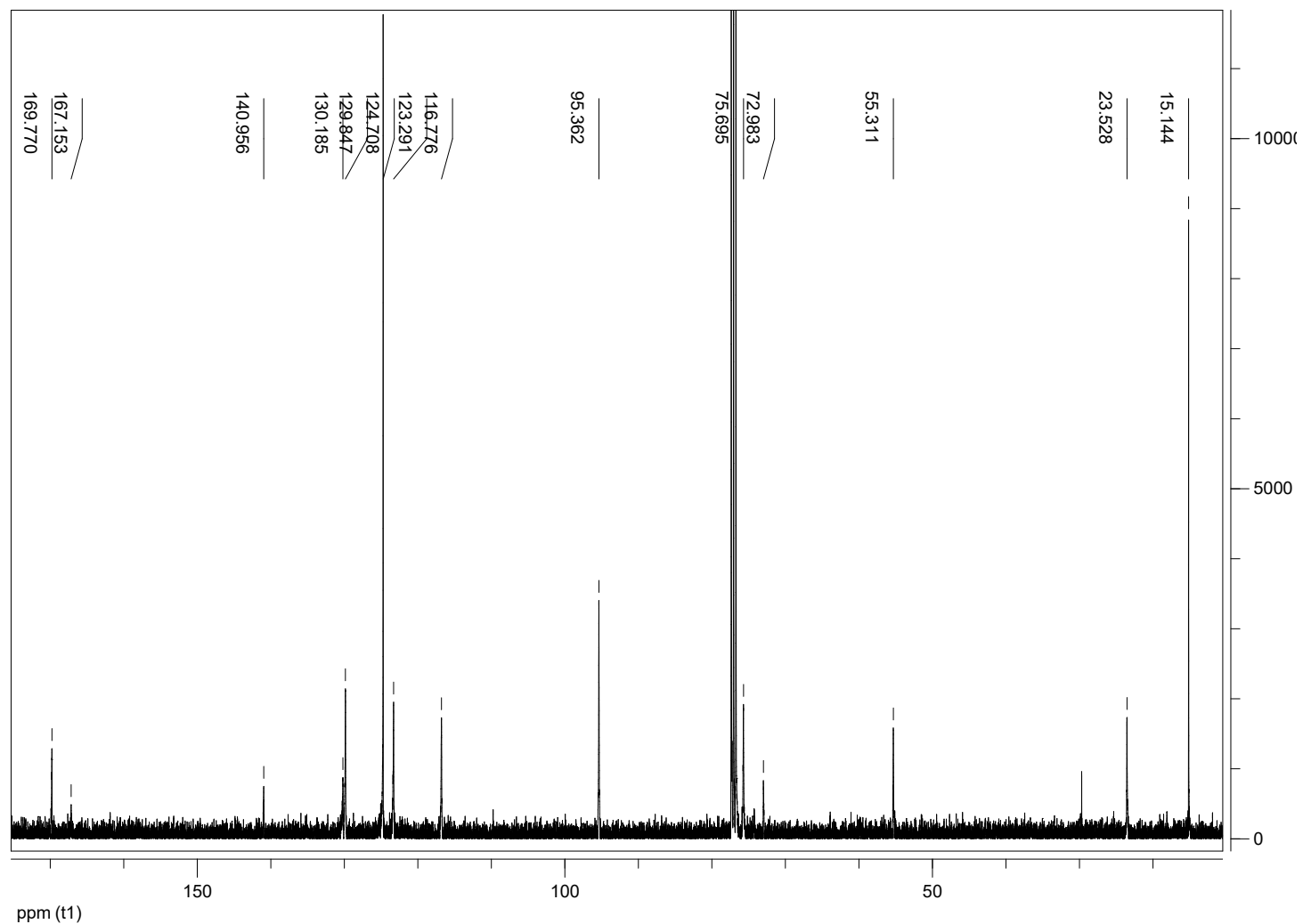
^1H NMR spectrum of *trans*-(±)-**30a** in CDCl_3  ^{13}C NMR spectrum of *trans*-(±)-**30a** in CDCl_3



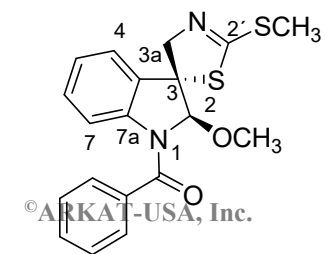
cis-(±)-1-Acetylspirobrasinol methyl ether [(±)-30b]



^1H NMR spectrum of *cis*-(±)-**30b** in CDCl_3  ^{13}C NMR spectrum of *cis*-(±)-**30b** in CDCl_3

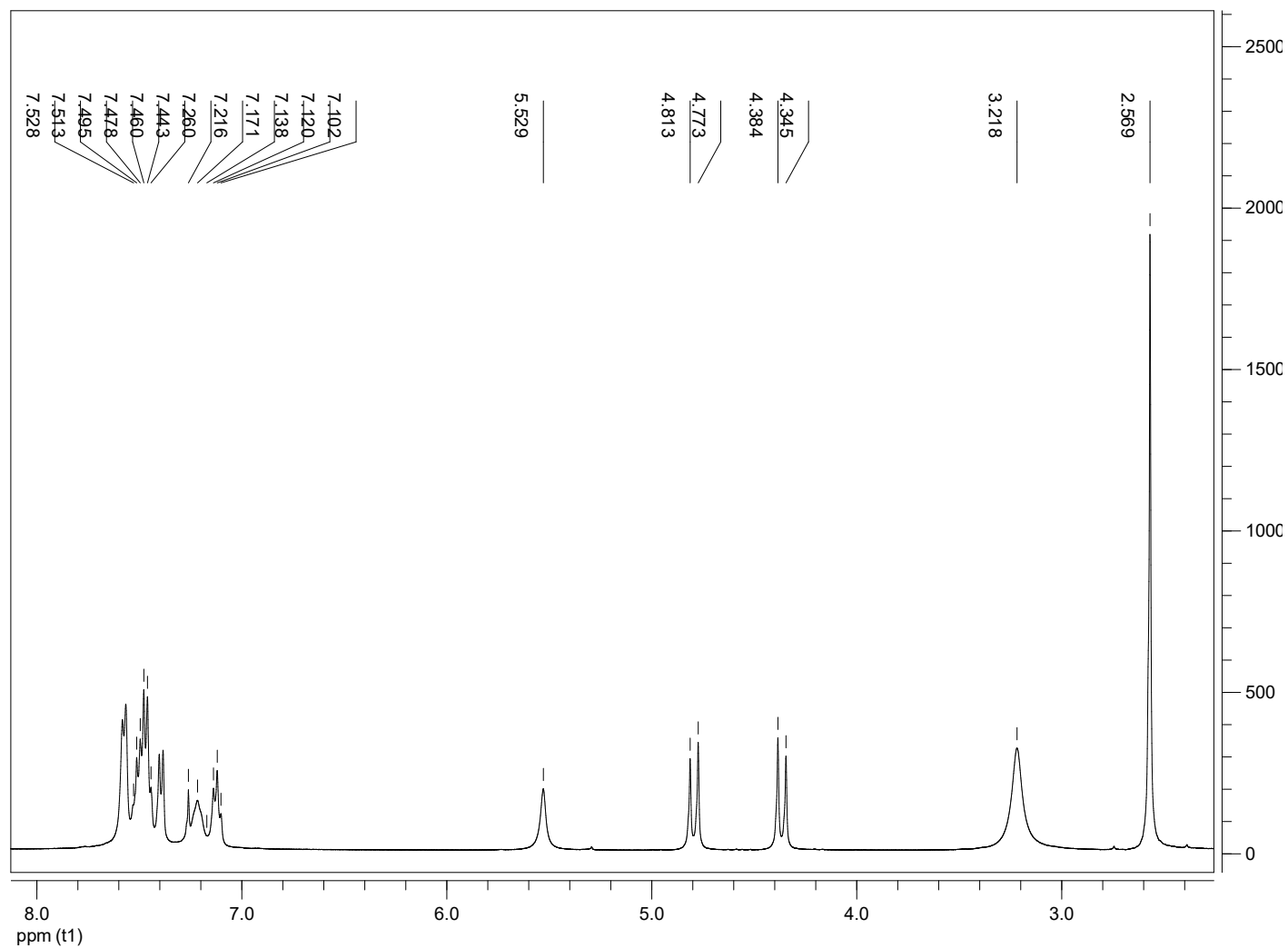


trans-(±)-1-Benzoylspirobrasinol methyl ether [(±)-31a]

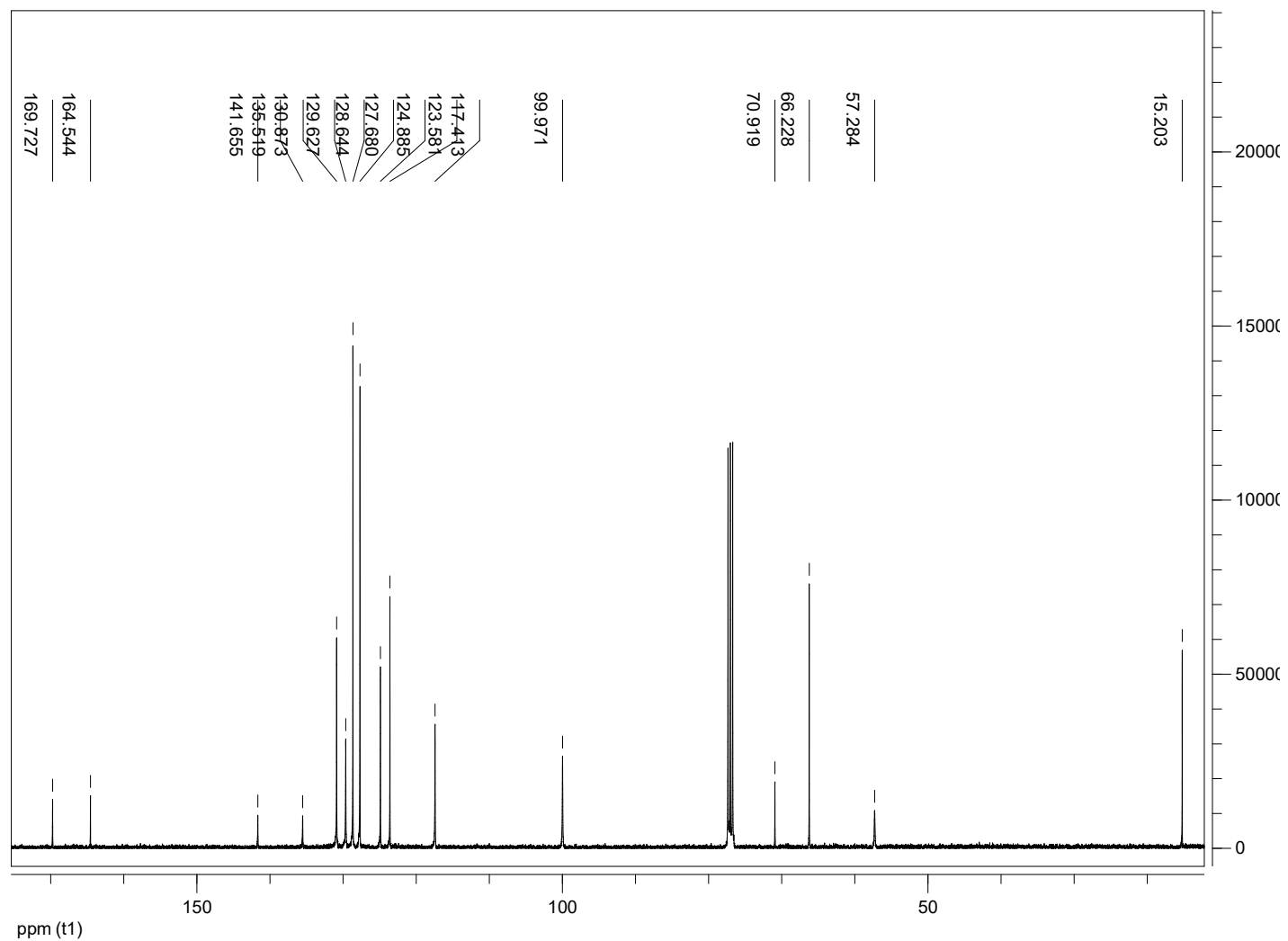


trans-(±)-31a

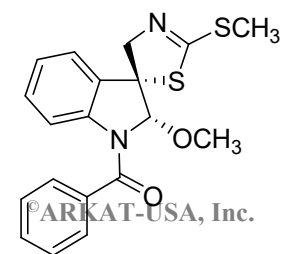
^1H NMR spectrum of *trans*-(±)-**31a** in CDCl_3



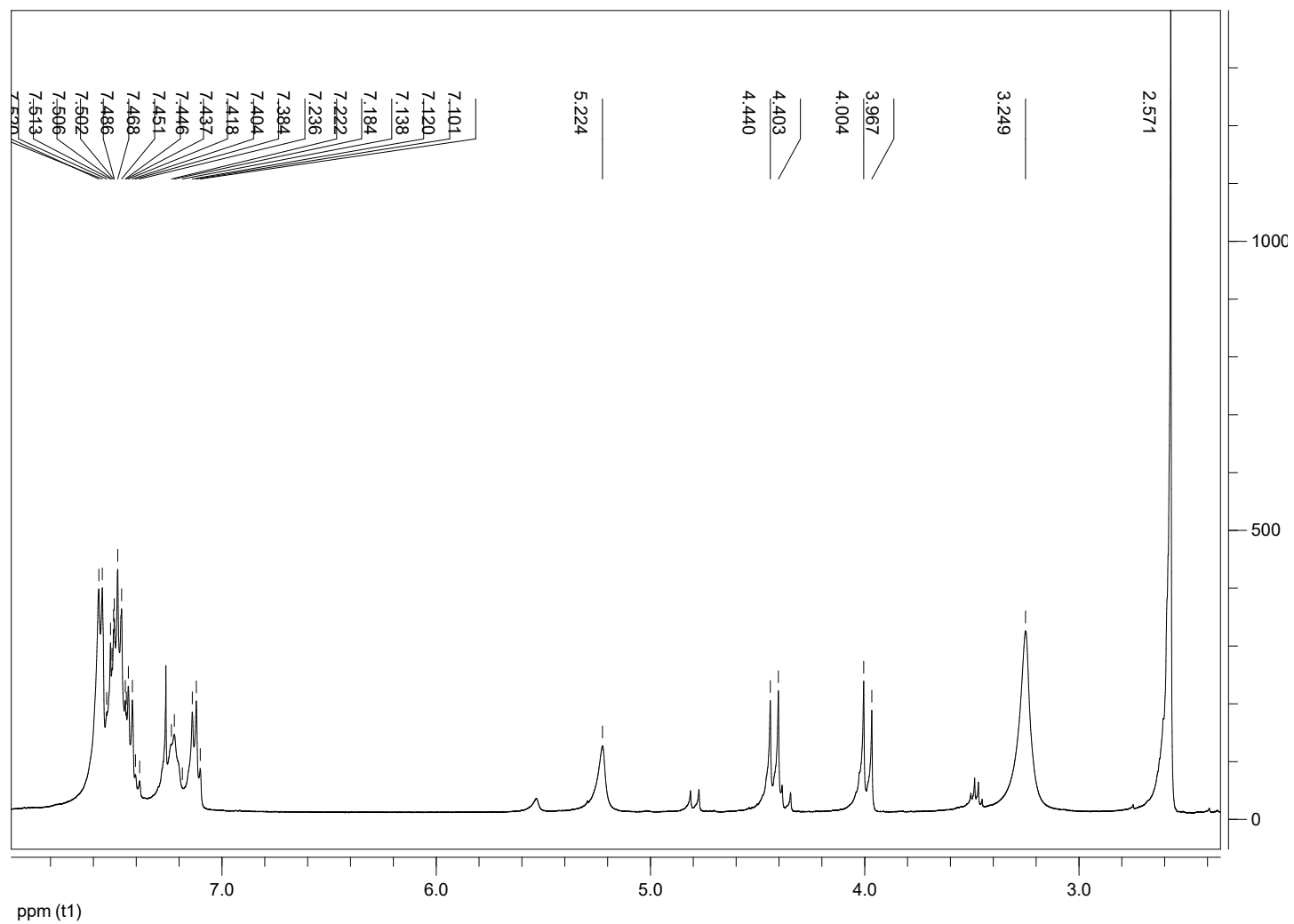
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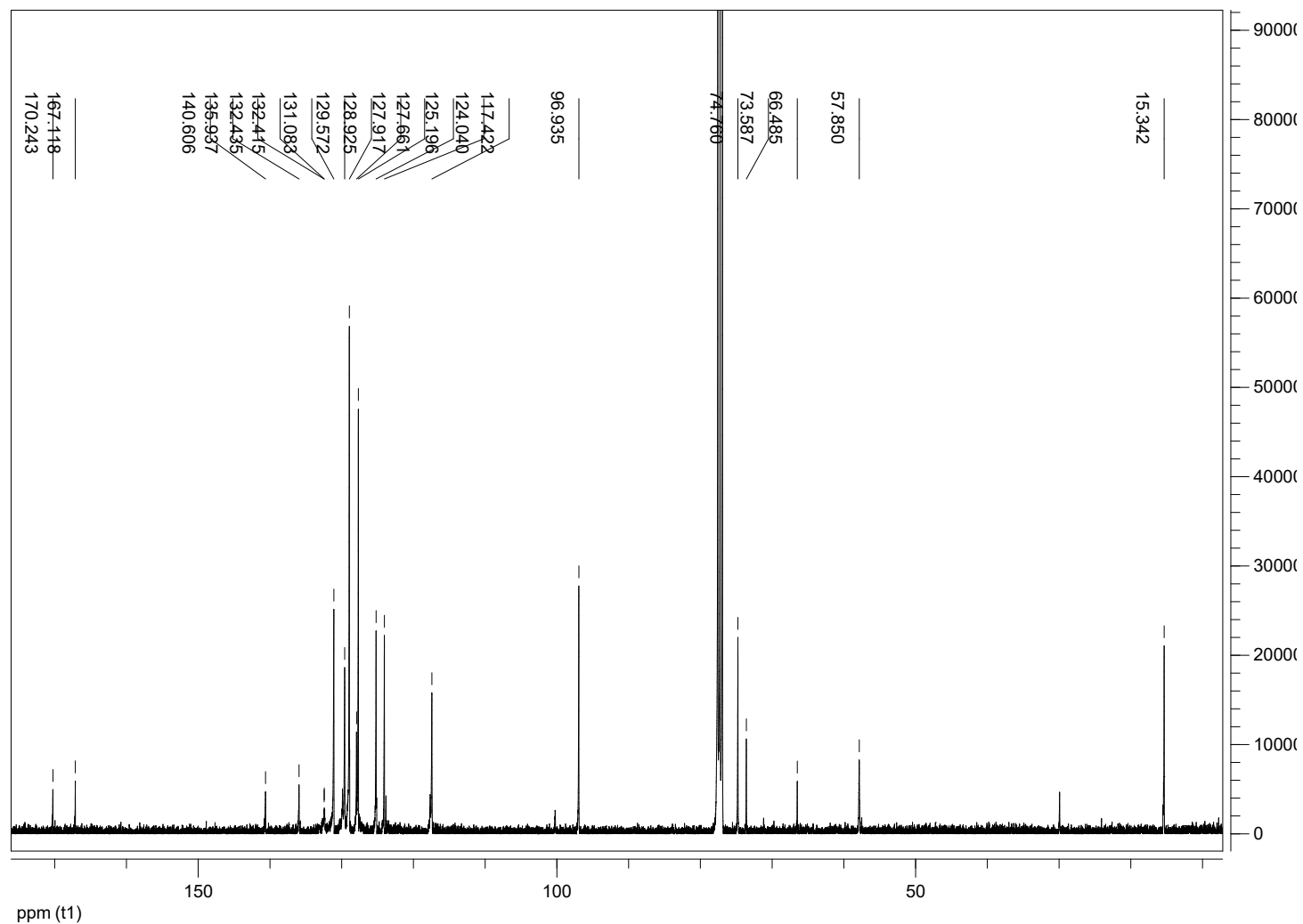


***cis*-(±)-1-Benzoylspirobrasinol methyl ether [(±)-31b]**

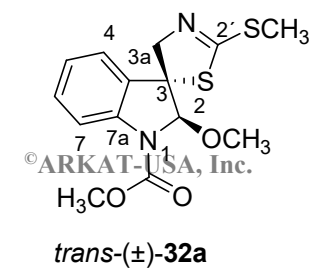


***cis*-(±)-31b**

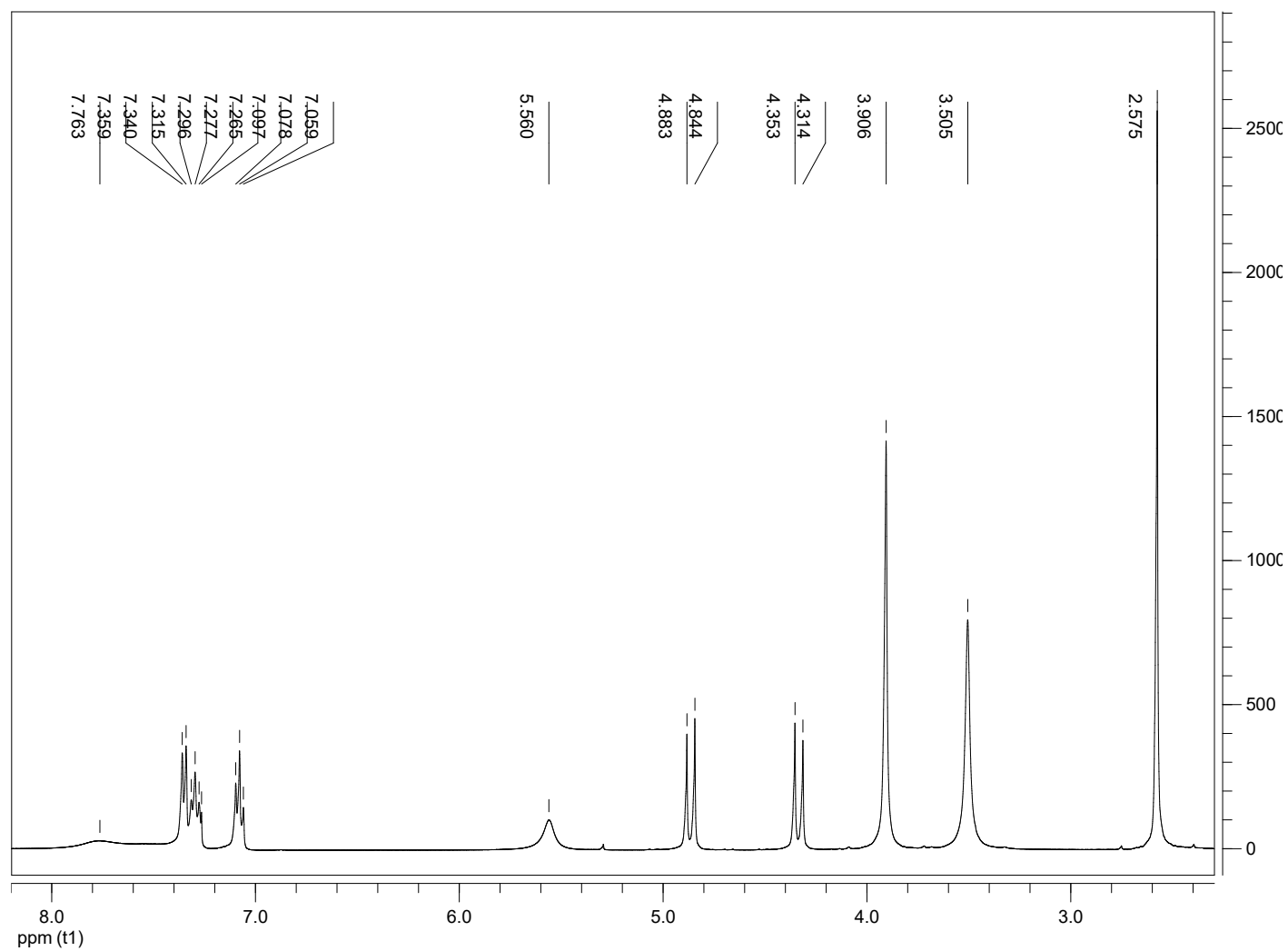
^1H NMR spectrum of *cis*-(±)-**31b** in CDCl_3  ^{13}C NMR spectrum of *cis*-(±)-**31b** in CDCl_3



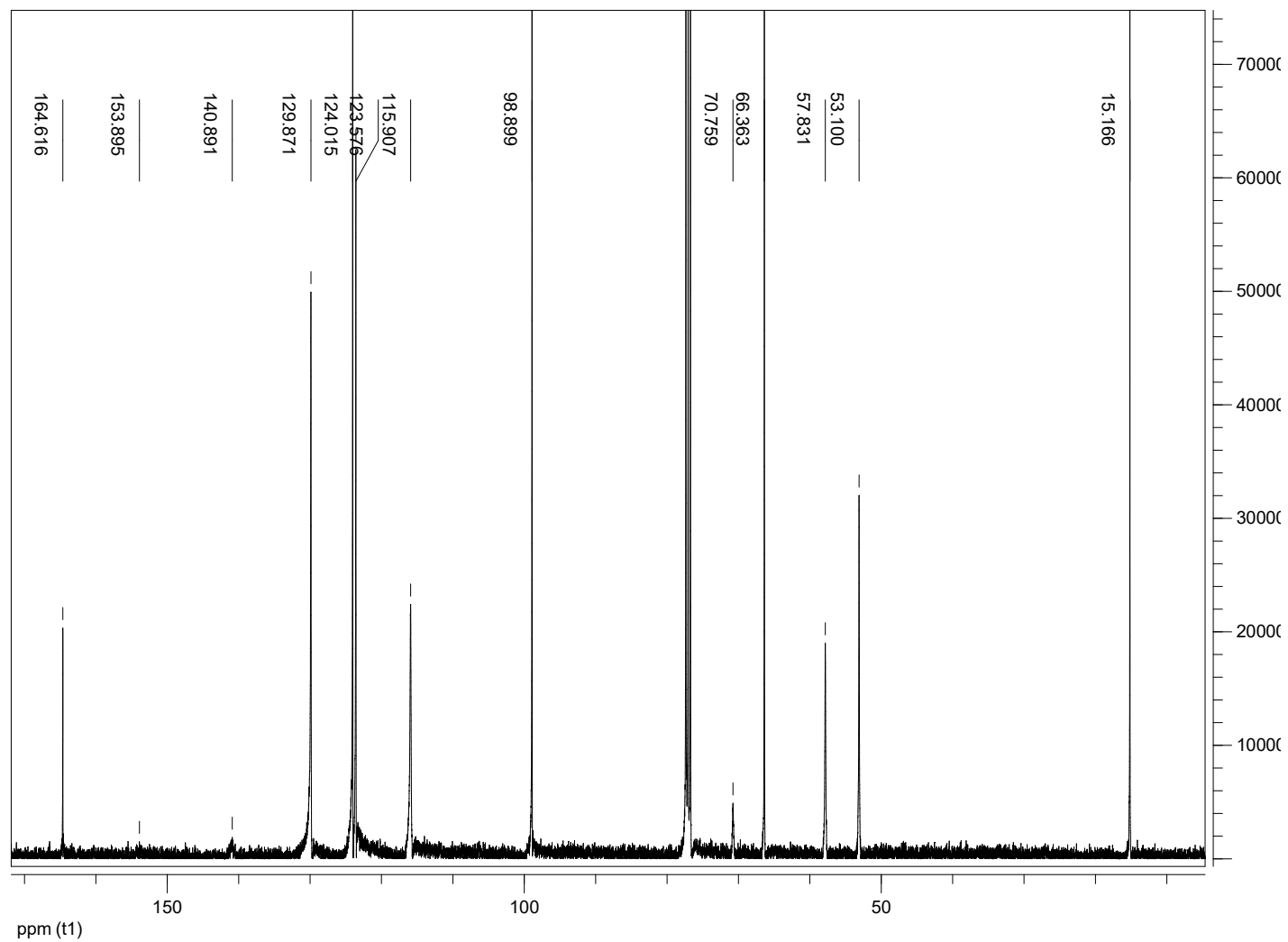
trans-(±)-1-Methoxycarbonylspirobrasinol methyl ether [(±)-32a]



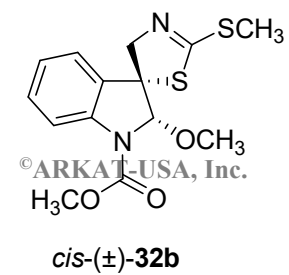
^1H NMR spectrum of *trans*-(±)-**32a** in CDCl_3



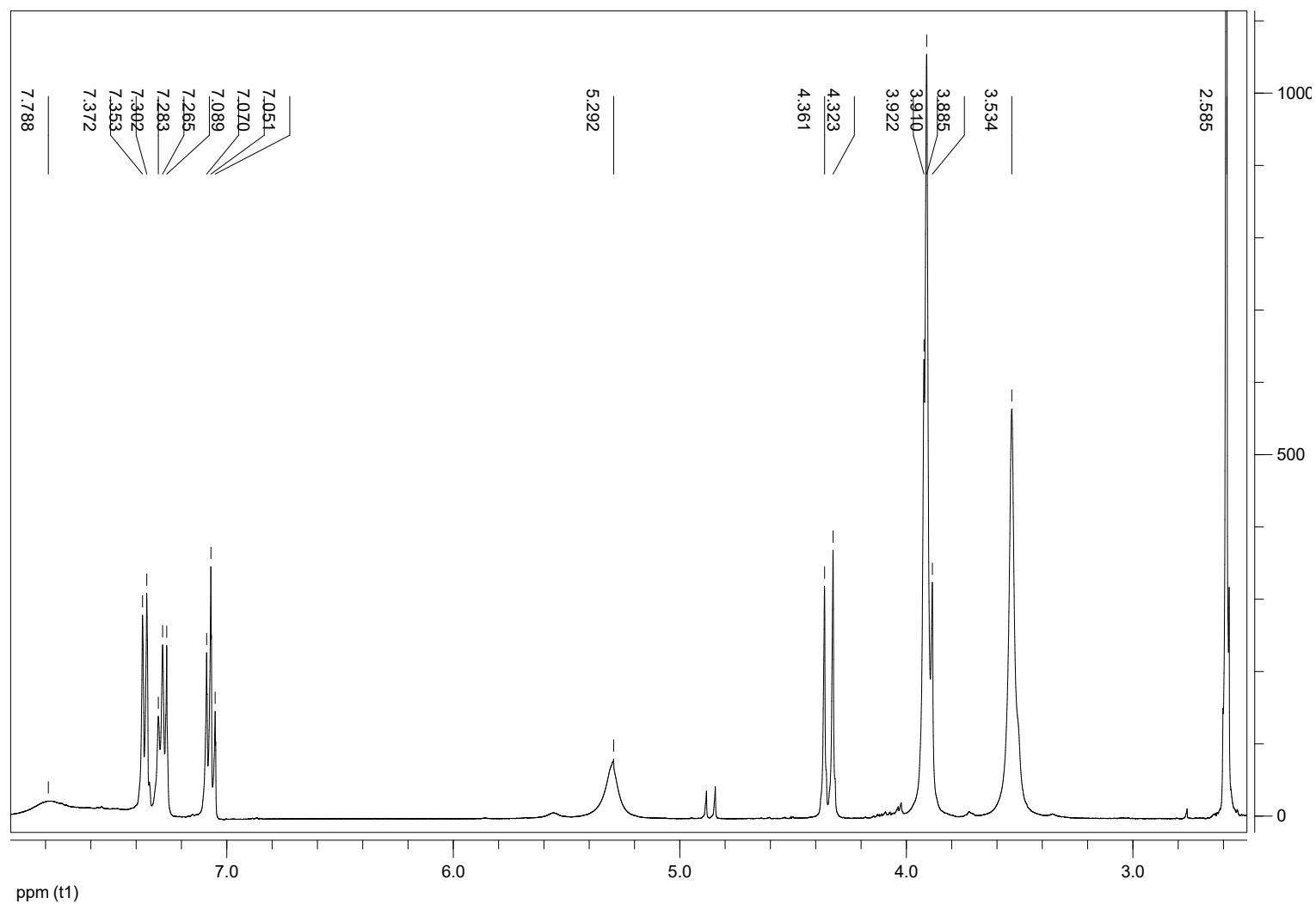
^{13}C NMR spectrum of *trans*-(±)-**32a** in CDCl_3



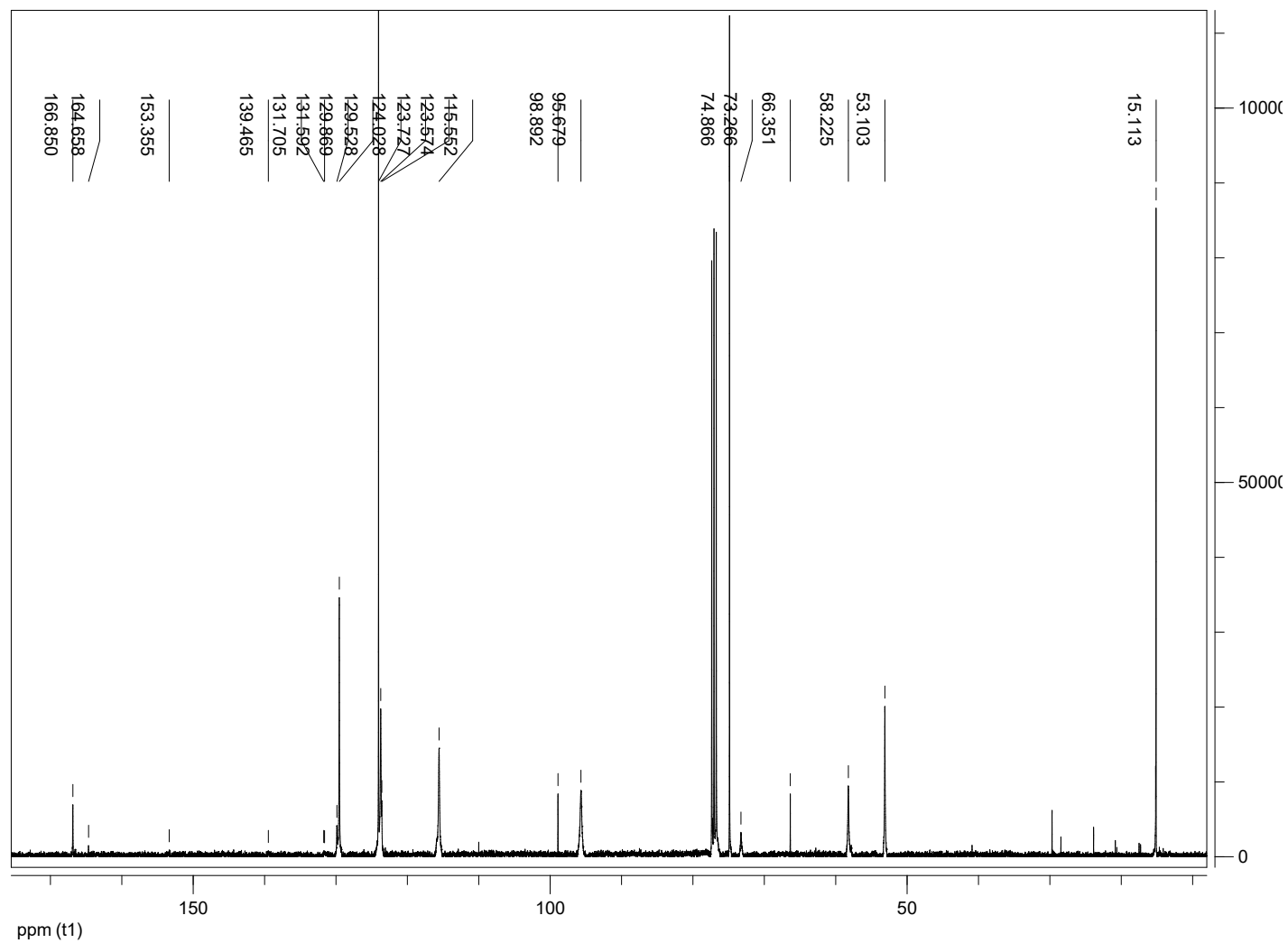
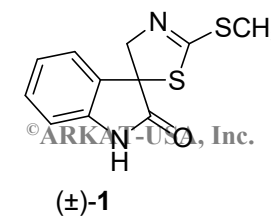
cis-(±)-1-Methoxycarbonylspirobrasinol methyl ether [(±)-32b]

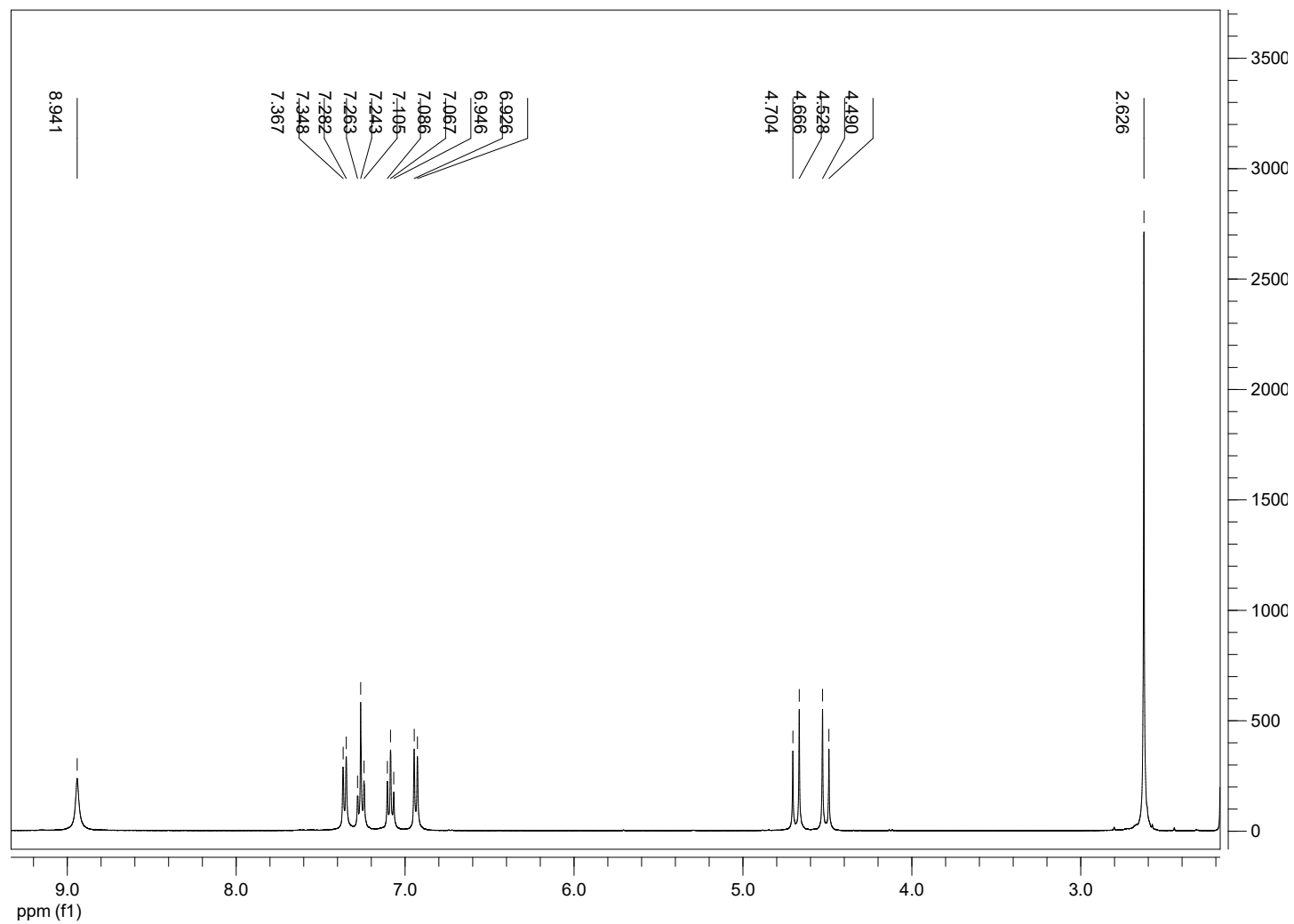
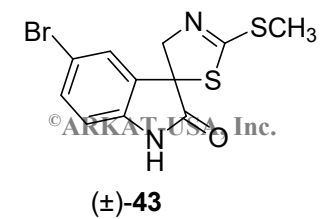


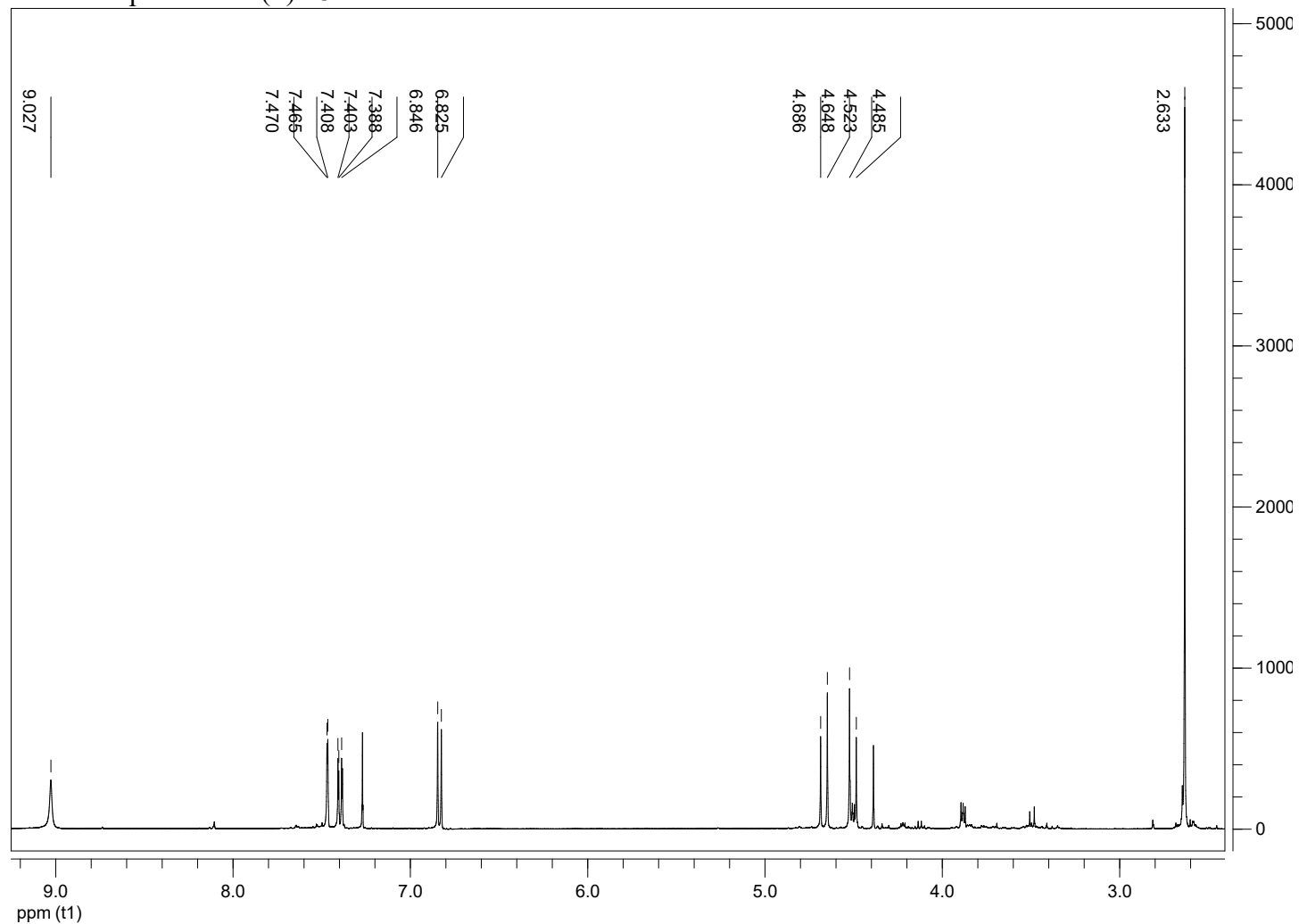
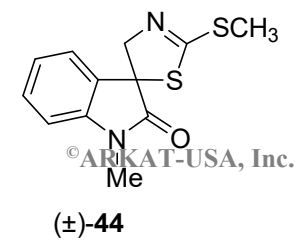
^1H NMR spectrum of *cis*-(±)-**32b** in CDCl_3



^{13}C NMR spectrum of *cis*-(±)-**32b** in CDCl_3

**Spirobrassinin [(±)-1]**

^1H NMR spectrum of (\pm)-15-Bromospirobrassinin [(\pm)-43]

^1H NMR spectrum of (\pm)-**43**1-Methylspirobrassinin [(\pm)-**44**]

^1H NMR spectrum of (\pm)-44