

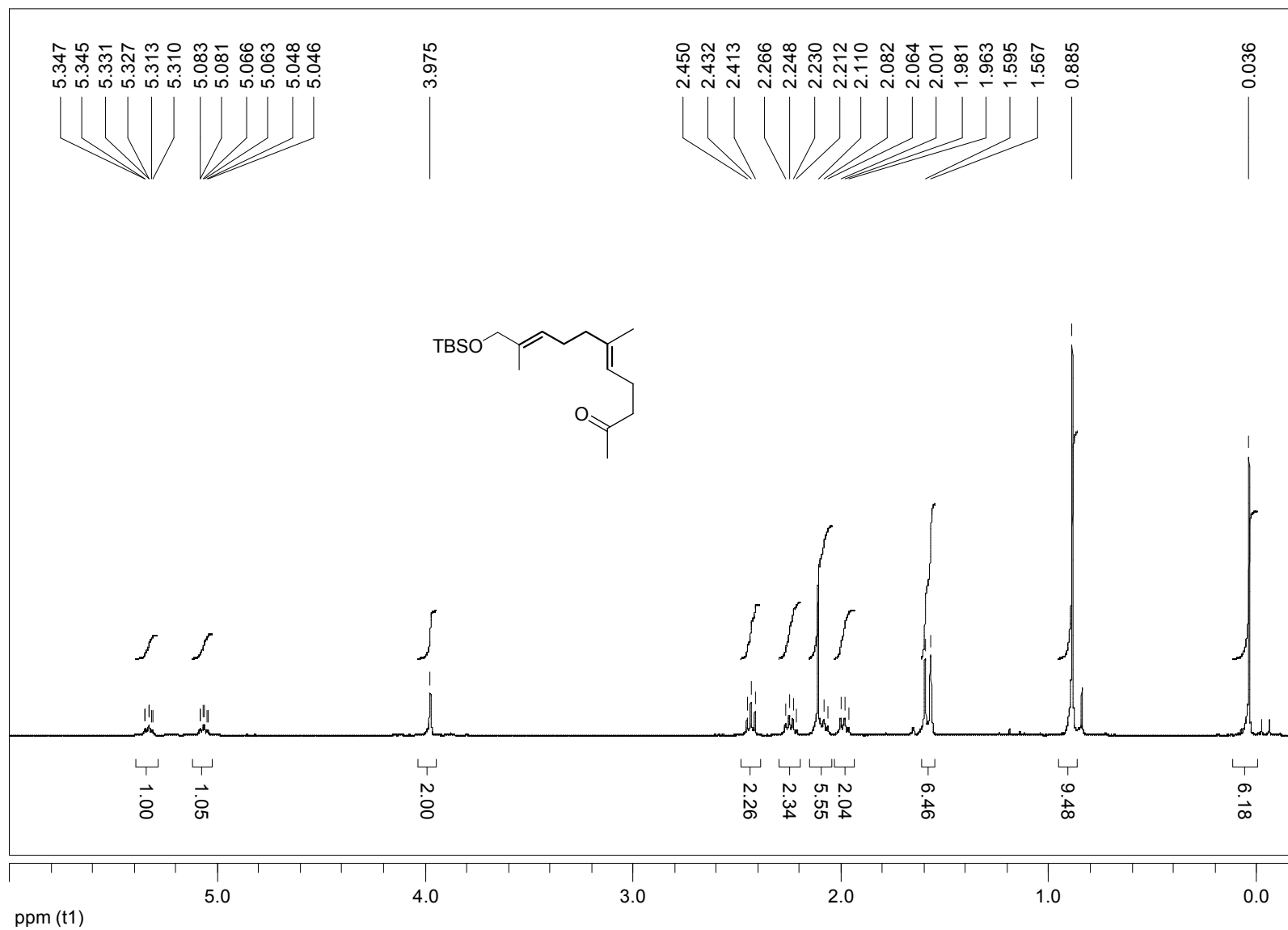
Synthesis of (±)-Likonide B (Smenochromene D) using a Regioselective Claisen Rearrangement, Separation of the Enantiomers and Stereochemical Assignment

Marjorie Bruder, Stephen J. Smith, Alexander J. Blake and Christopher J. Moody

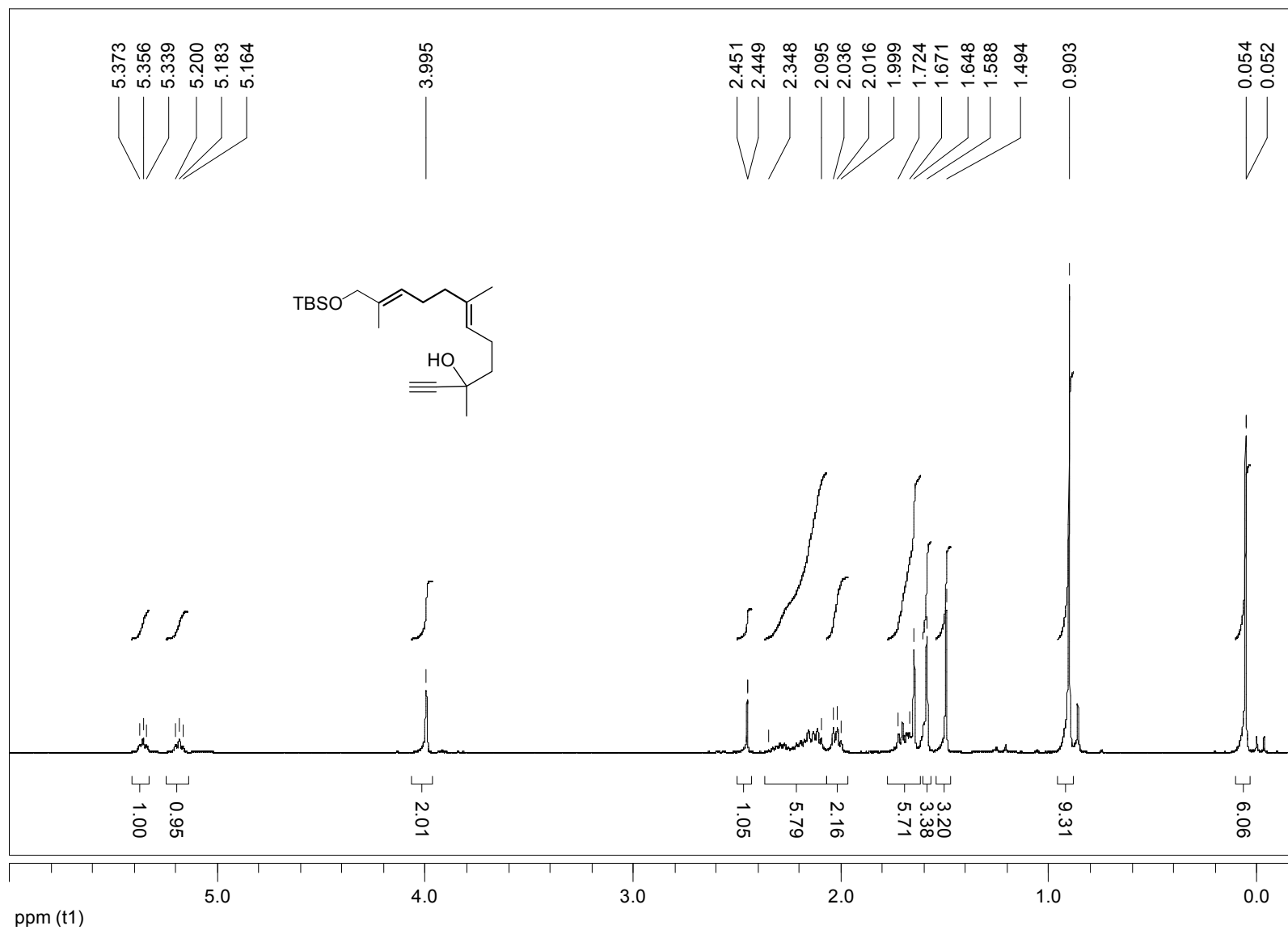
NMR data

^1H and ^{13}C NMR spectra were recorded using a Bruker AV400 instrument (400 MHz ^1H frequency, 100 MHz ^{13}C frequency) in CDCl_3 , unless otherwise specified.

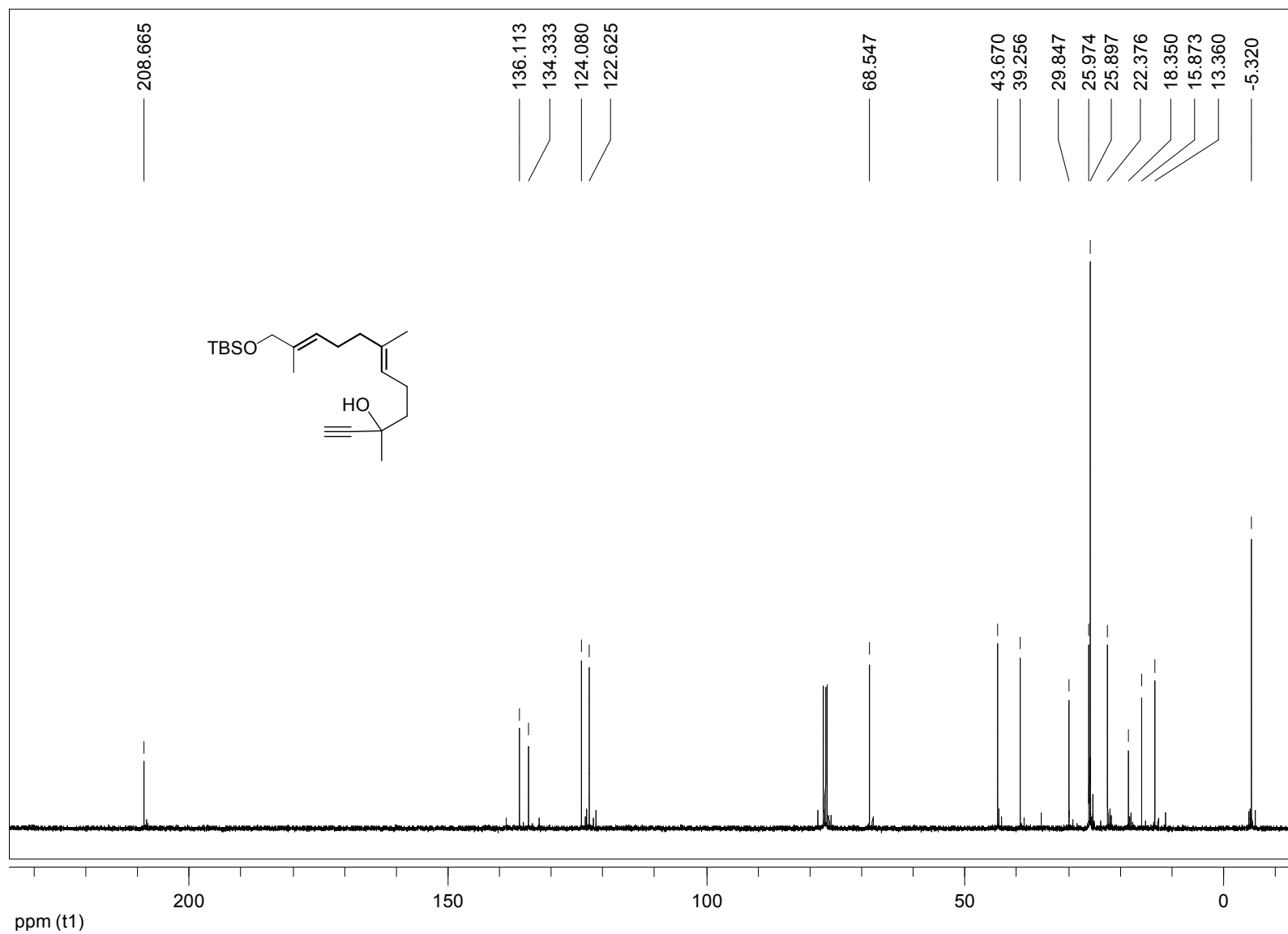
(5*E*,9*E*)-6,10-Dimethyl-11-*tert*-butyldimethylsiloxyundeca-5,9-dien-2-one **8**

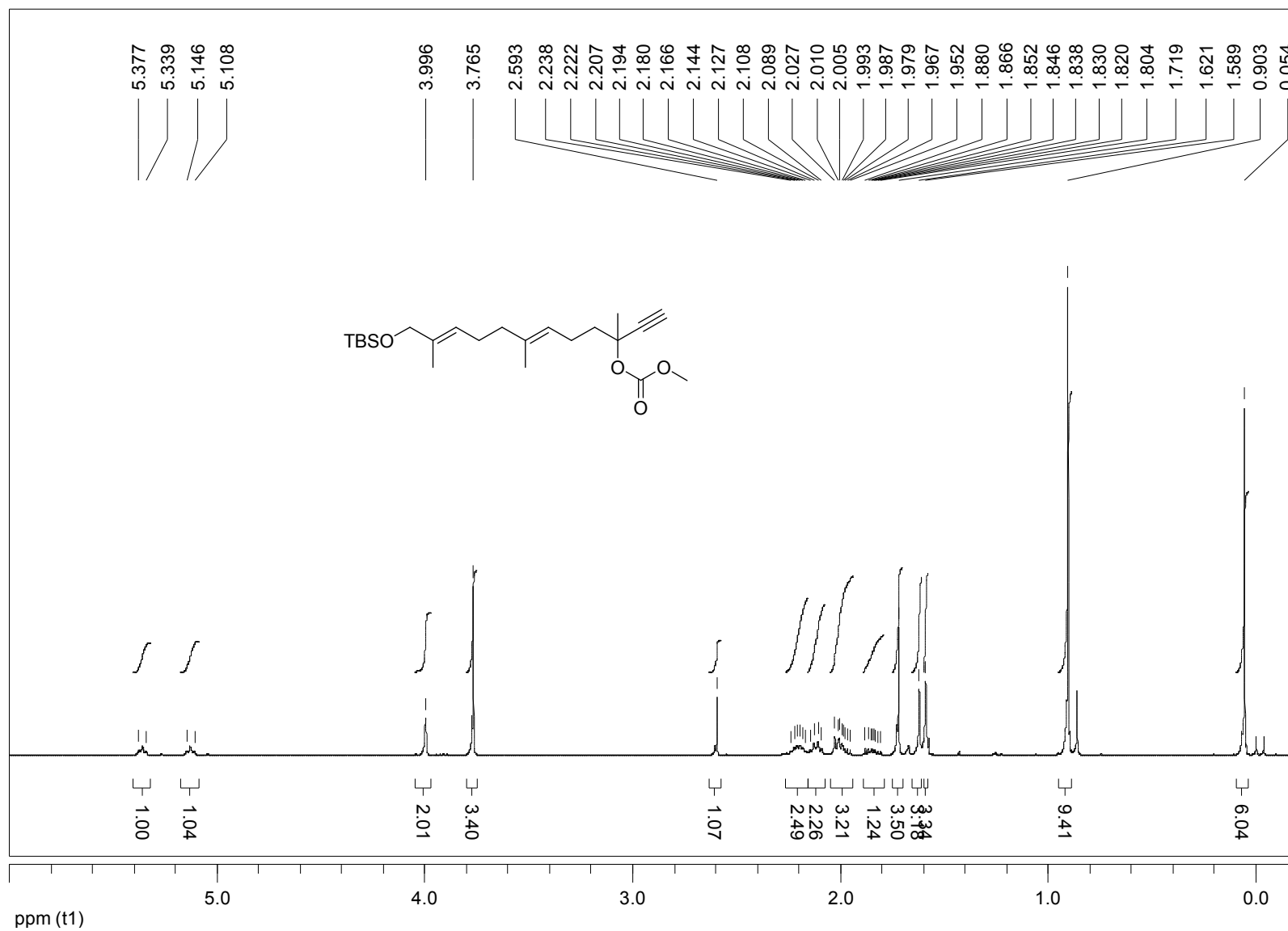


(6*E*,10*E*)-12-*tert*-Butyldimethylsiloxy-3,7,11-trimethyldodeca-6,10-dien-1-yn-3-ol **9**

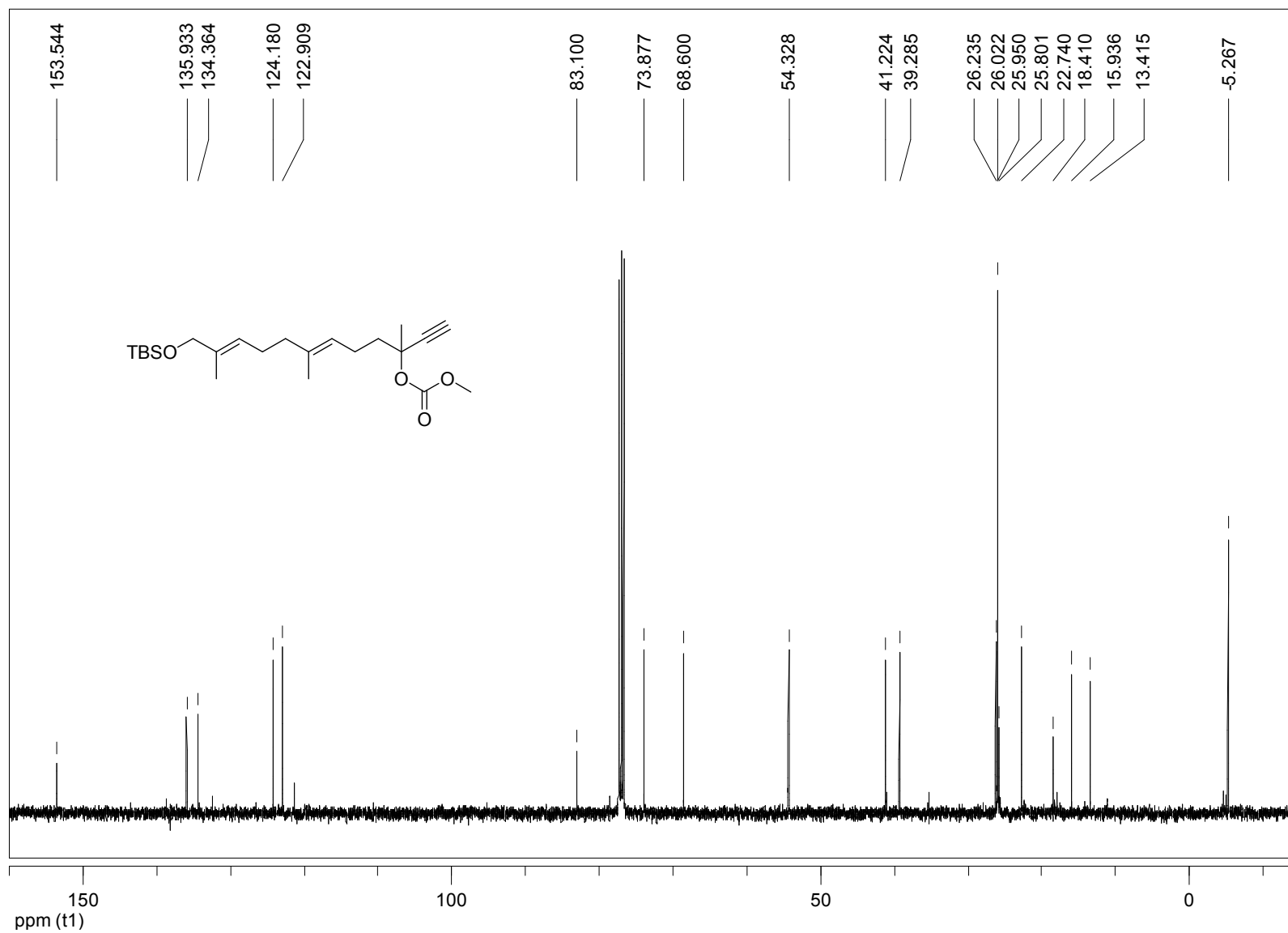


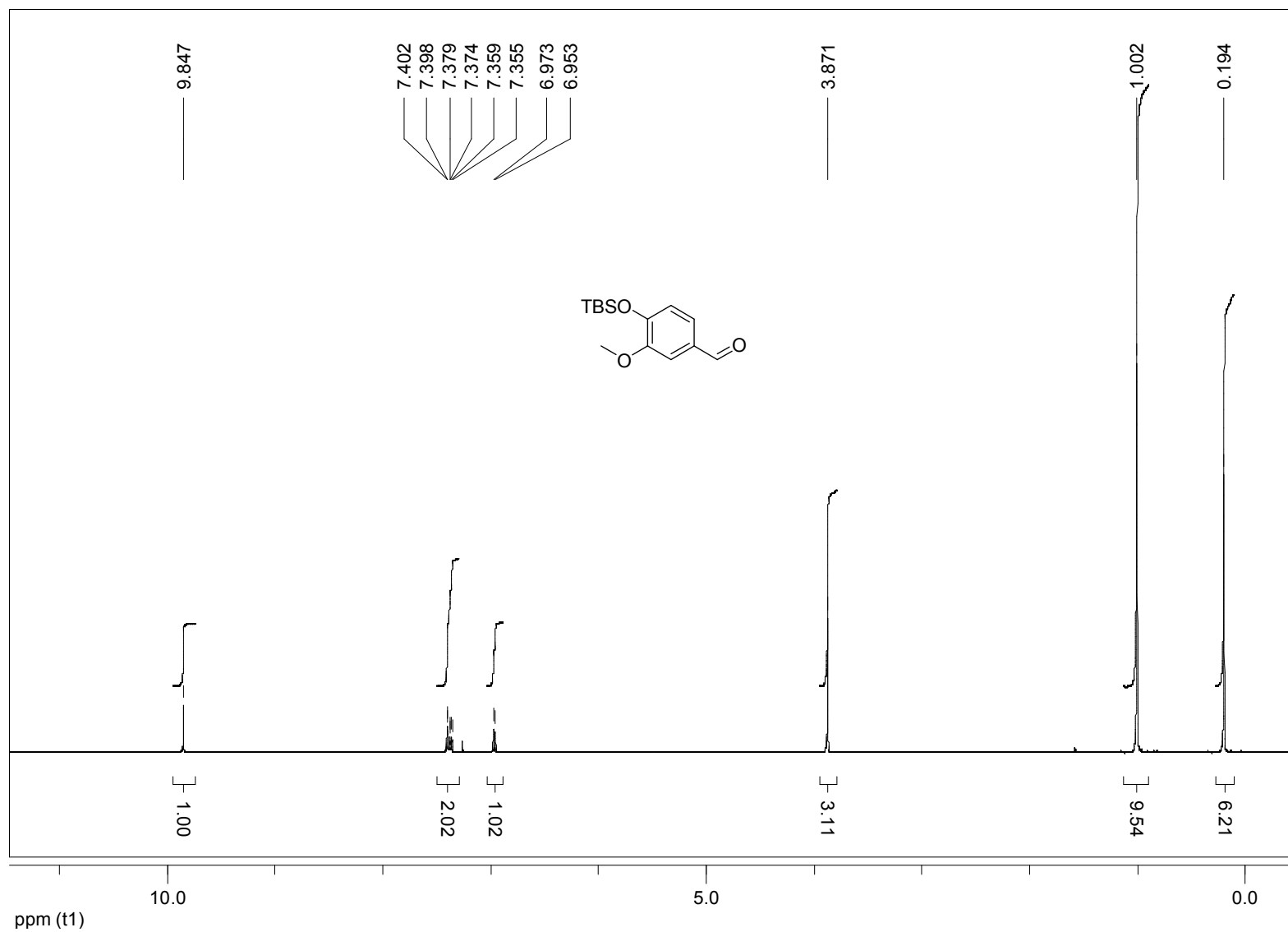
(6*E*,10*E*)-12-*tert*-Butyldimethylsiloxy-3,7,11-trimethyldodeca-6,10-dien-1-yn-3-ol **9**

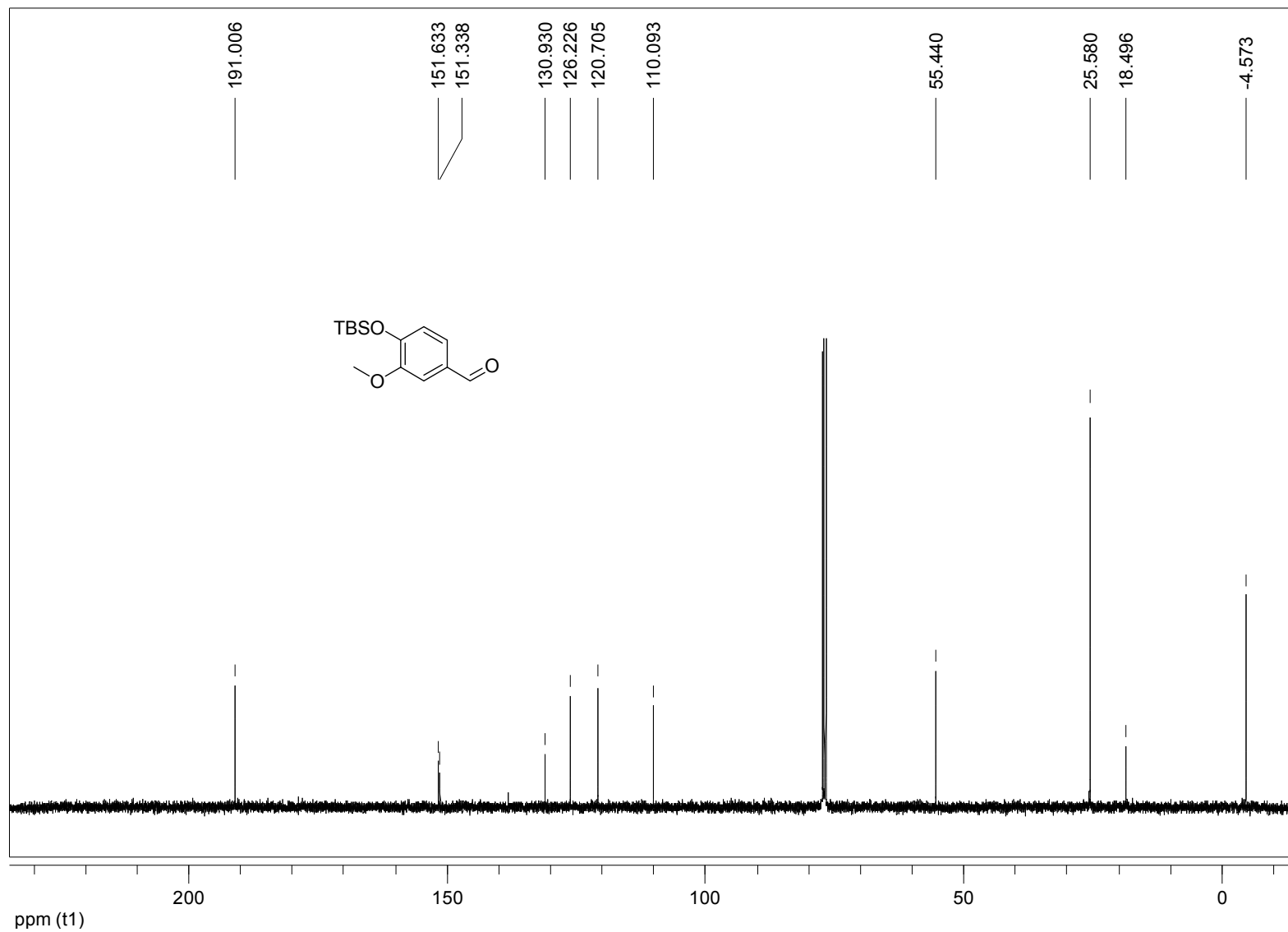


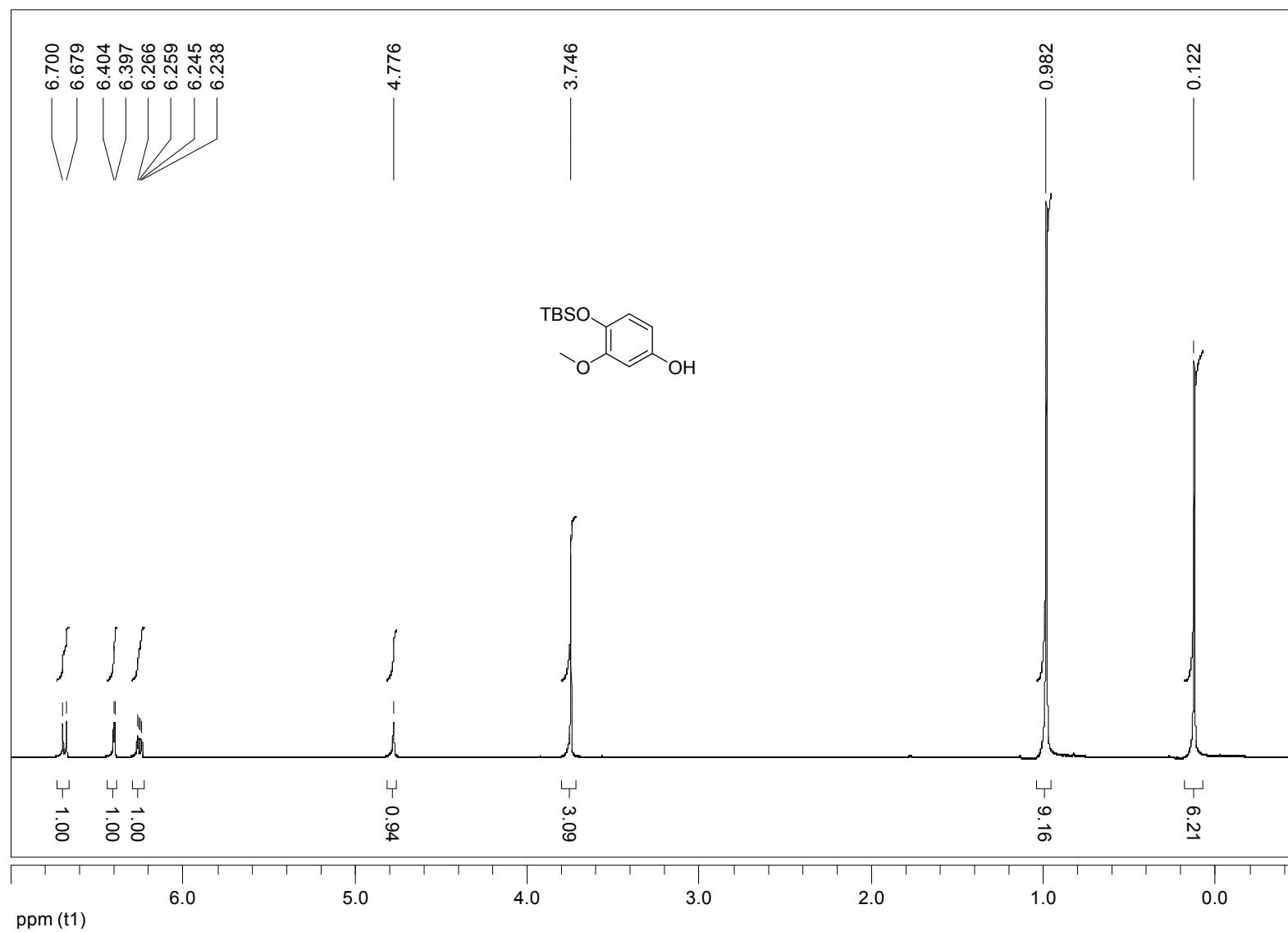
(6E,10E)-12-*tert*-Butyldimethylsiloxy-3,7,11-trimethyldodeca-6,10-dien-1-yn-3-ol methyl carbonate **10**

(6*E*,10*E*)-12-*tert*-Butyldimethylsiloxy-3,7,11-trimethyldodeca-6,10-dien-1-yn-3-ol methyl carbonate **10**



4-*tert*-Butyldimethylsilyloxy-3-methoxybenzaldehyde

4-*tert*-Butyldimethylsilyloxy-3-methoxybenzaldehyde

4-*tert*-Butyldimethylsiloxy-3-methoxyphenol **11**

6.700
6.679
6.404
6.397
6.266
6.259
6.245
6.238

4.776

3.746

0.982

0.122

1.00

1.00

1.00

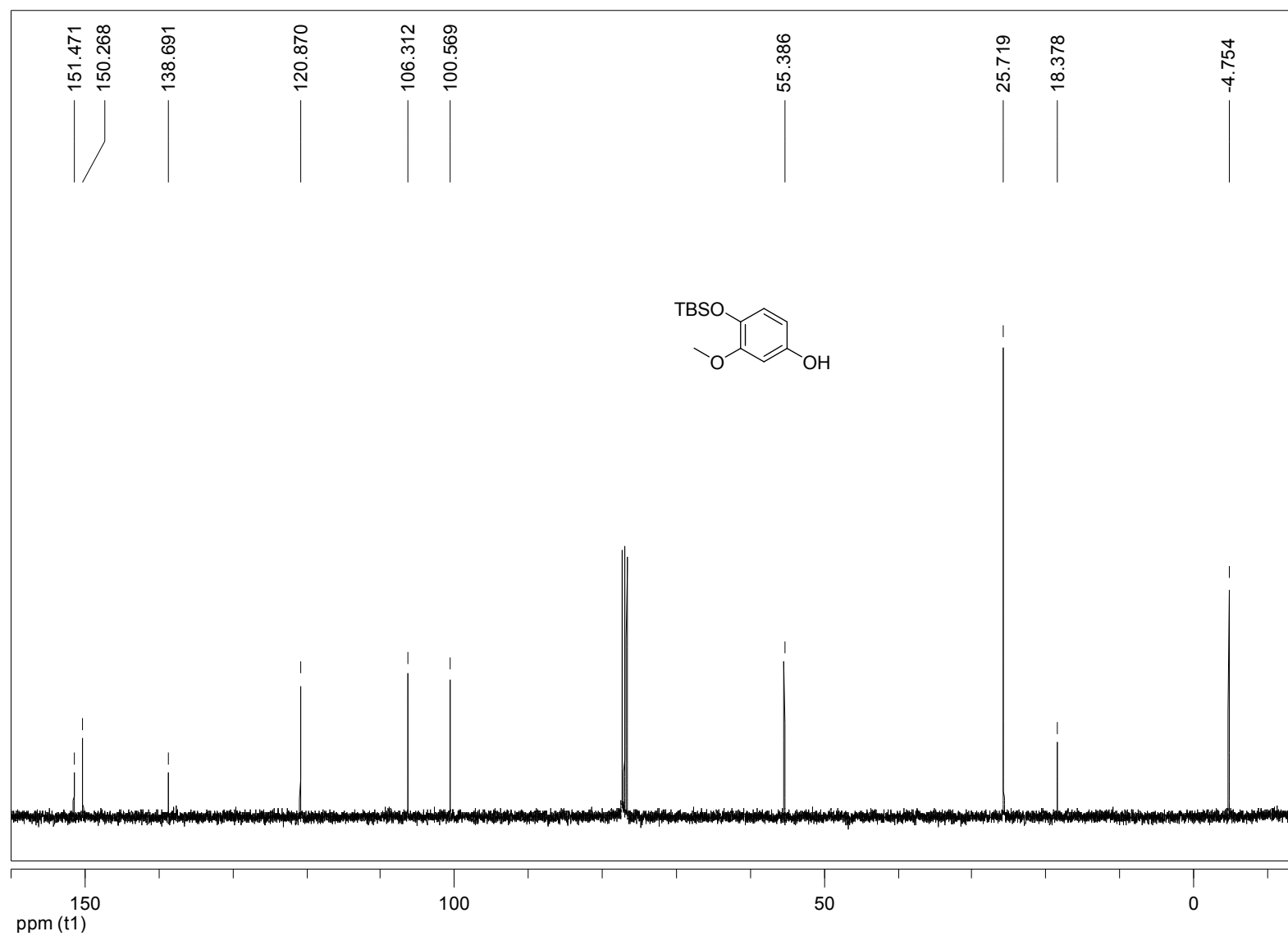
0.94

3.09

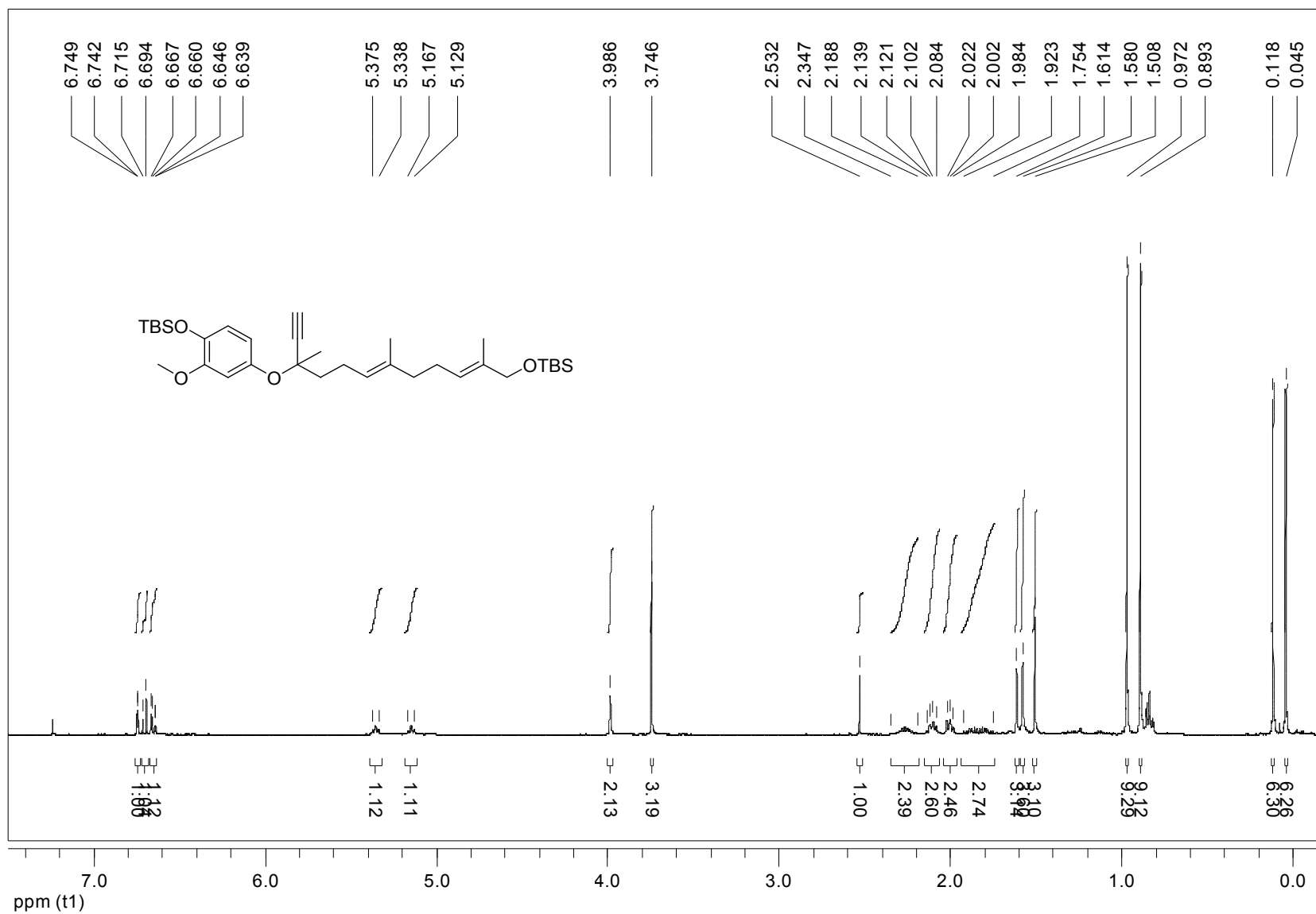
9.16

6.21

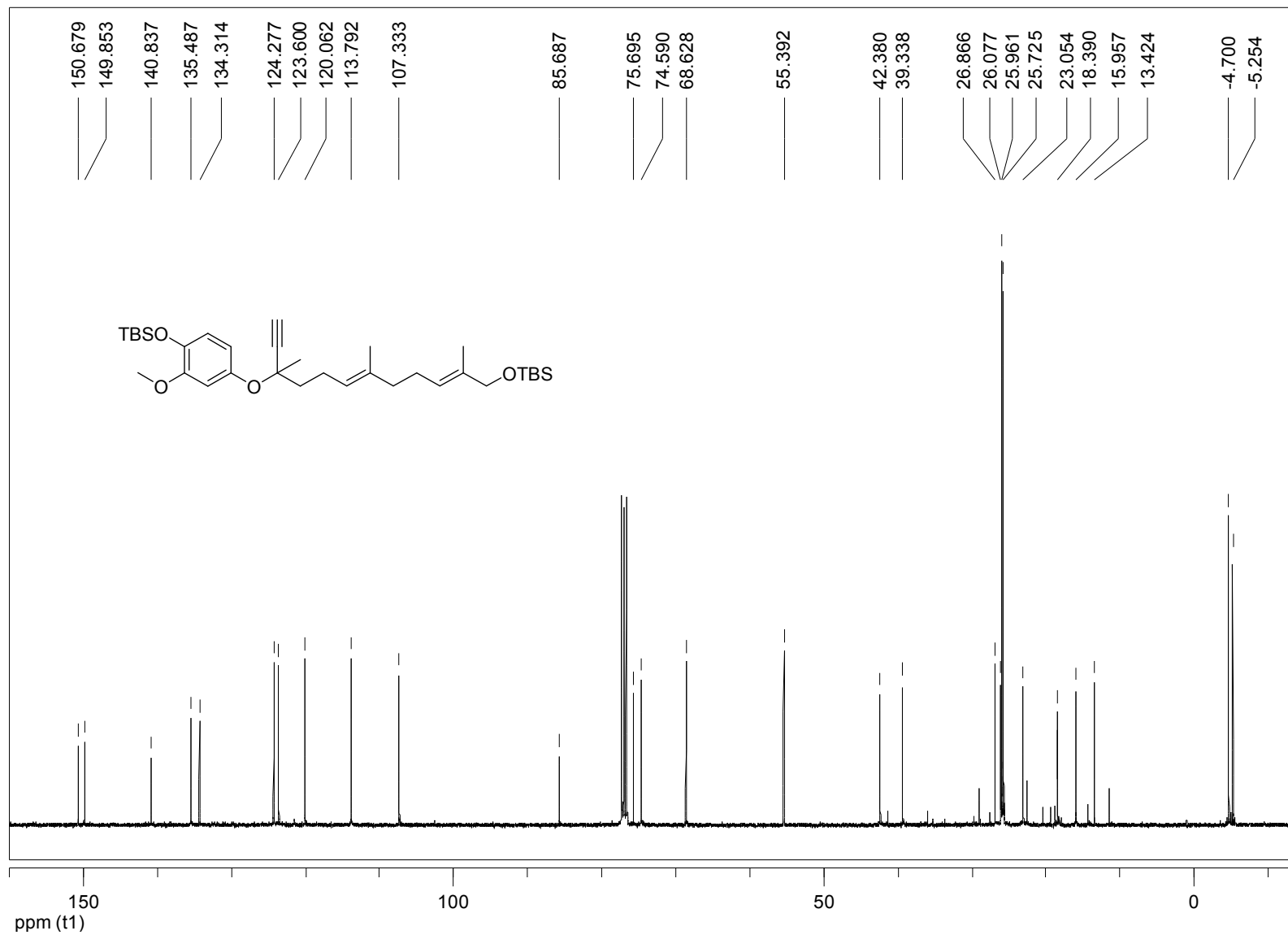
ppm (t1)

4-*tert*-Butyldimethylsiloxy-3-methoxyphenol **11**

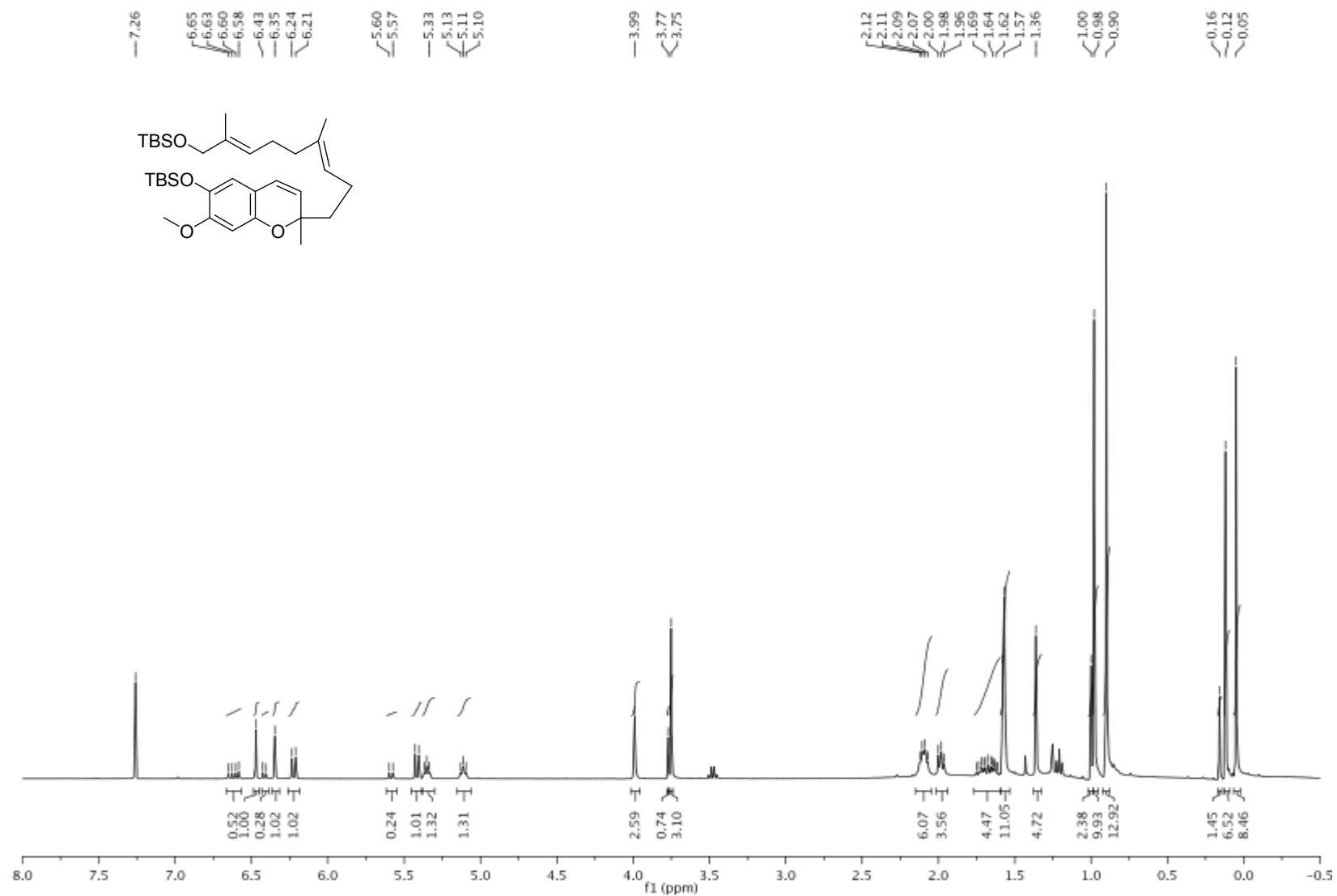
1-*tert*-Butyldimethylsiloxy-4-[(6'*E*,10'*E*)-12'-*tert*-butyldimethylsiloxy-3',7',11'-tri-methyldodeca-6',10'-dien-1'-yn-3'-yloxy]-2-methoxybenzene **12**



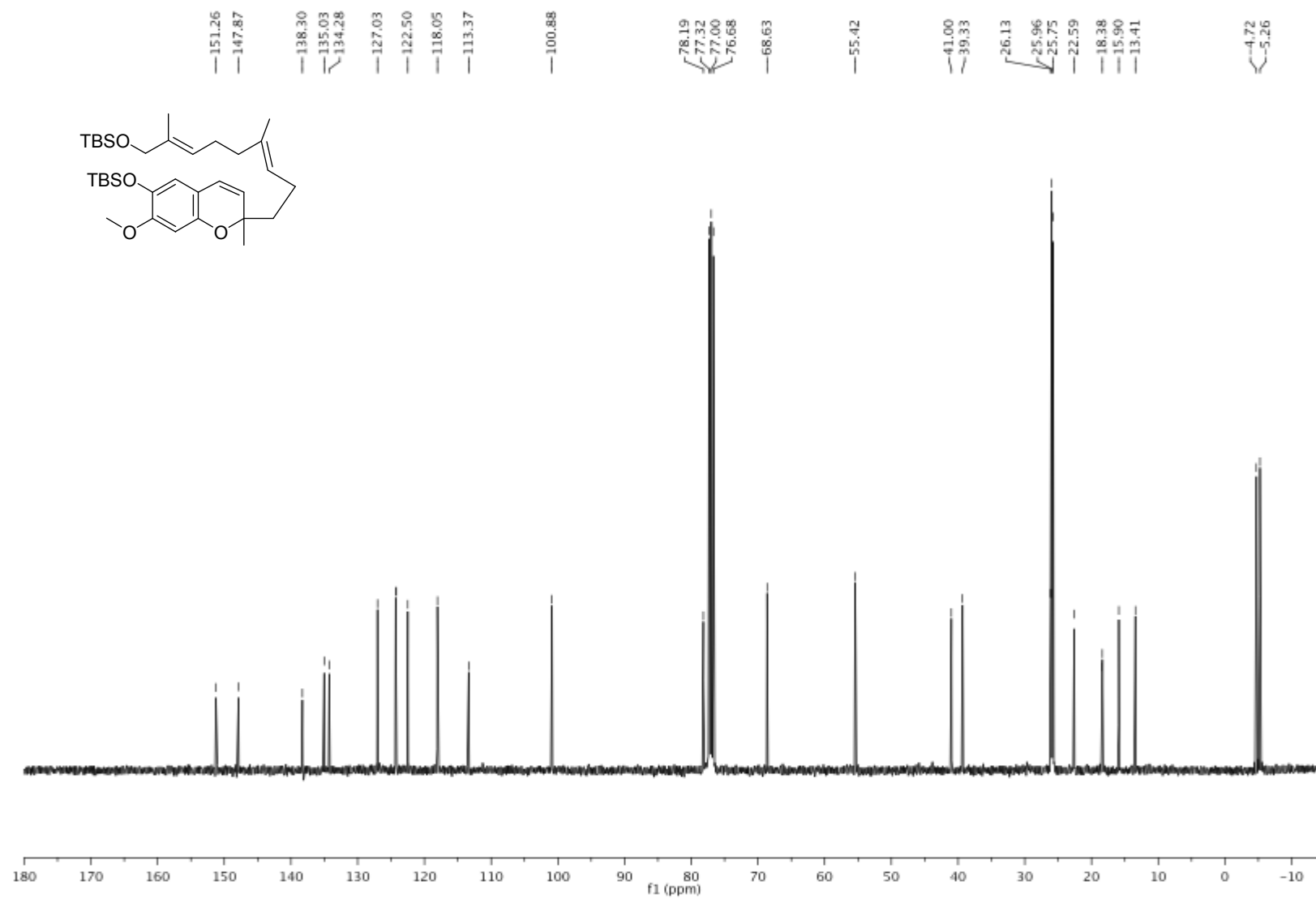
1-*tert*-Butyldimethylsiloxy-4-[(6'*E*,10'*E*)-12'-*tert*-butyldimethylsiloxy-3',7',11'-tri-methyldodeca-6',10'-dien-1'-yn-3'-yloxy]-2-methoxybenzene **12**



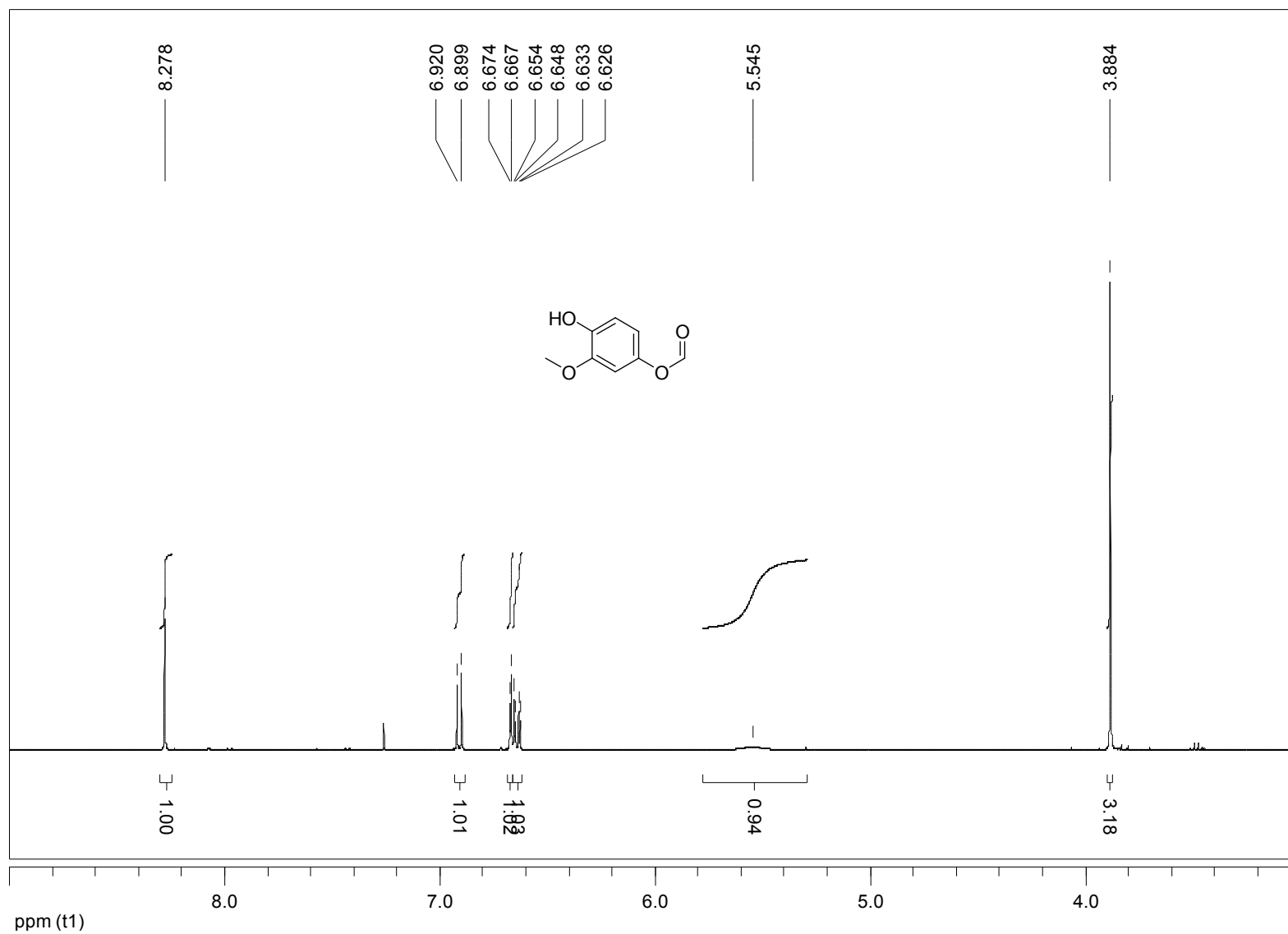
6-*tert*-Butyldimethylsilyl-2-[(3'*E*,7'*E*)-9'-*tert*-butyldimethylsilyloxy-4',8'-dimethyl-nona-3',7'-dienyl]-7-methoxy-2-methyl-2*H*-chromen-6-ol **13**



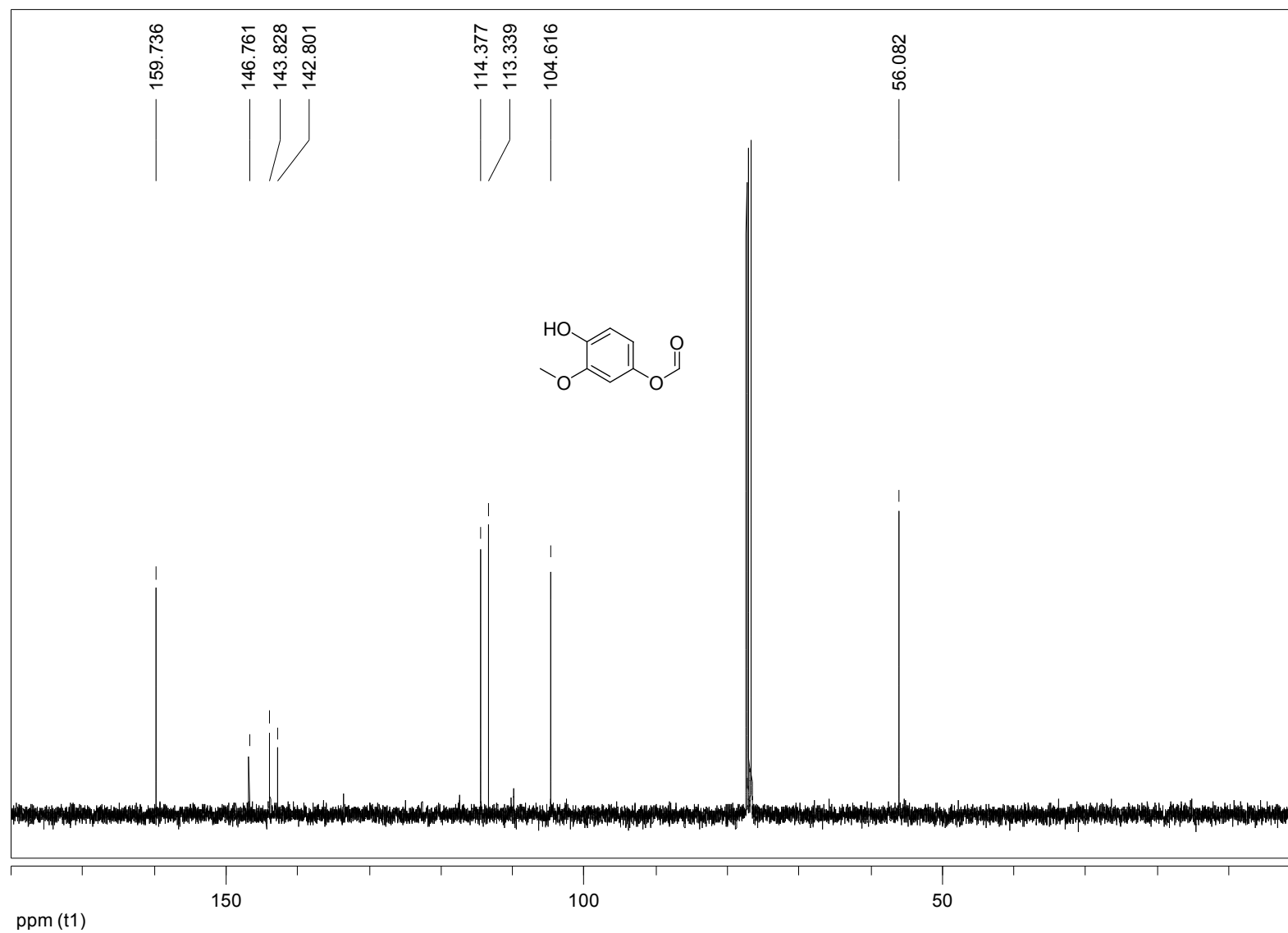
6-*tert*-Butyldimethylsilyl-2-[(3'*E*,7'*E*)-9'-*tert*-butyldimethylsilyloxy-4',8'-dimethyl-nona-3',7'-dienyl]-7-methoxy-2-methyl-2*H*-chromen-6-ol **13**

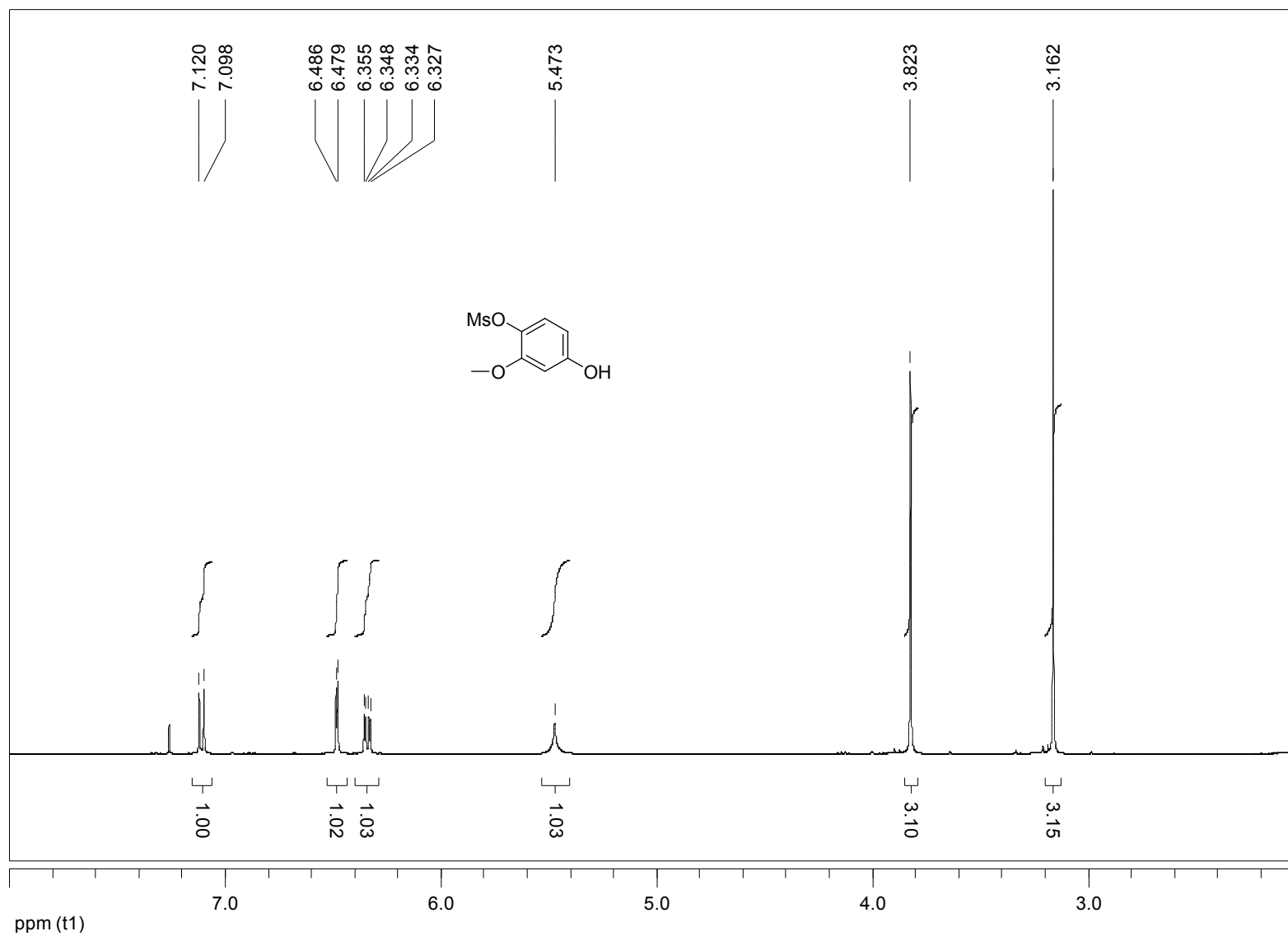


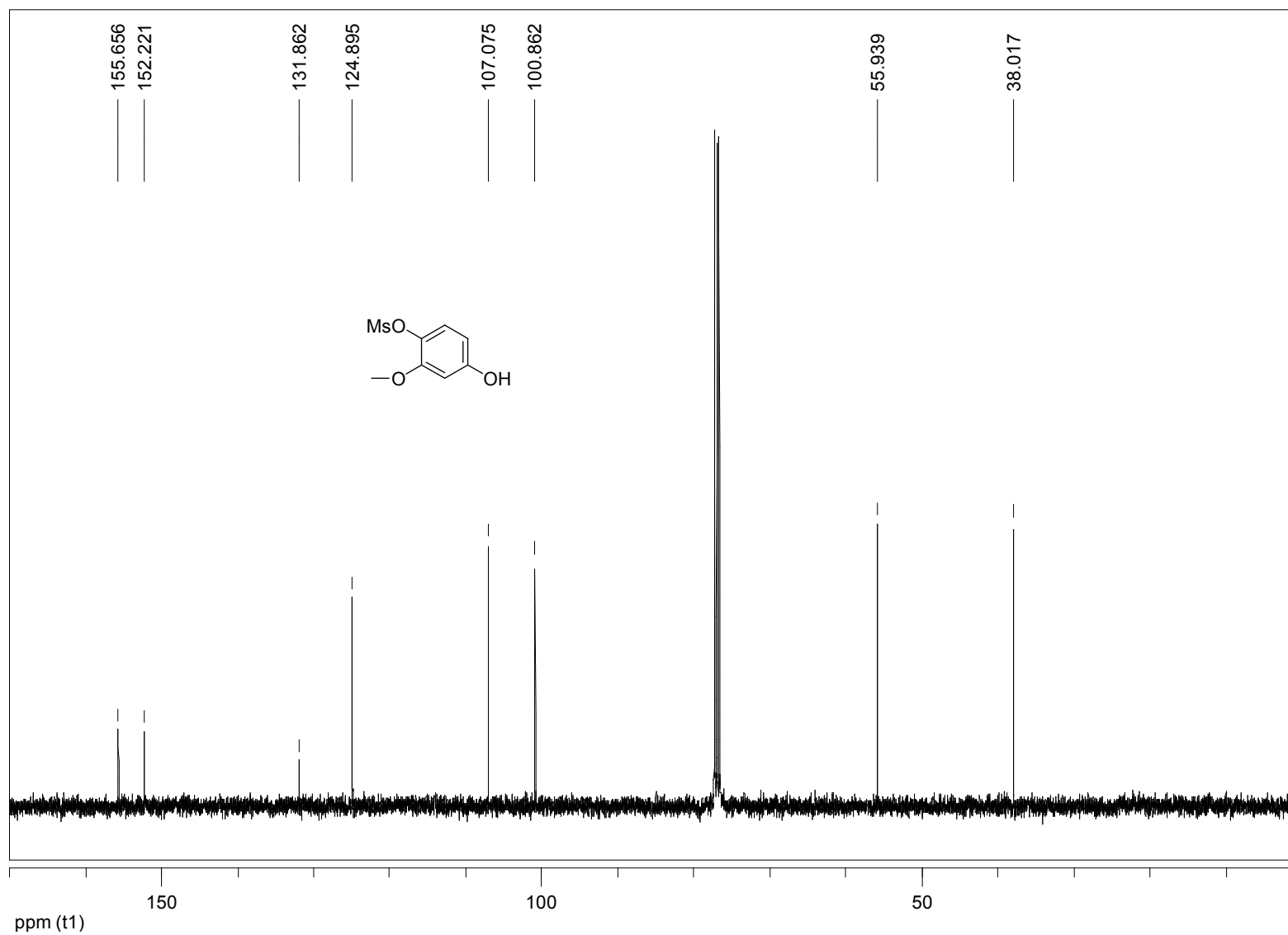
4-Hydroxy-3-methoxyphenyl formate



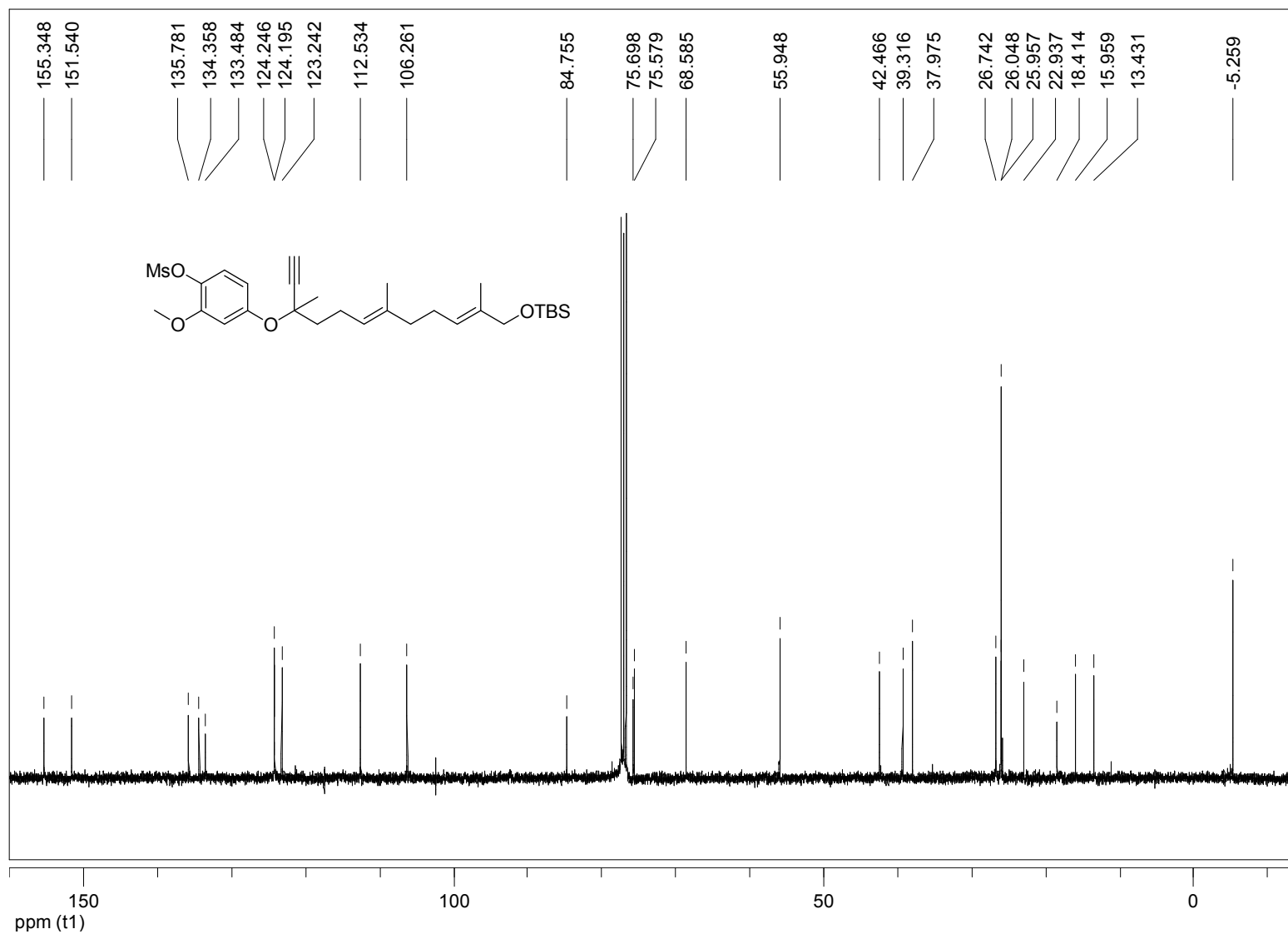
4-Hydroxy-3-methoxyphenyl formate

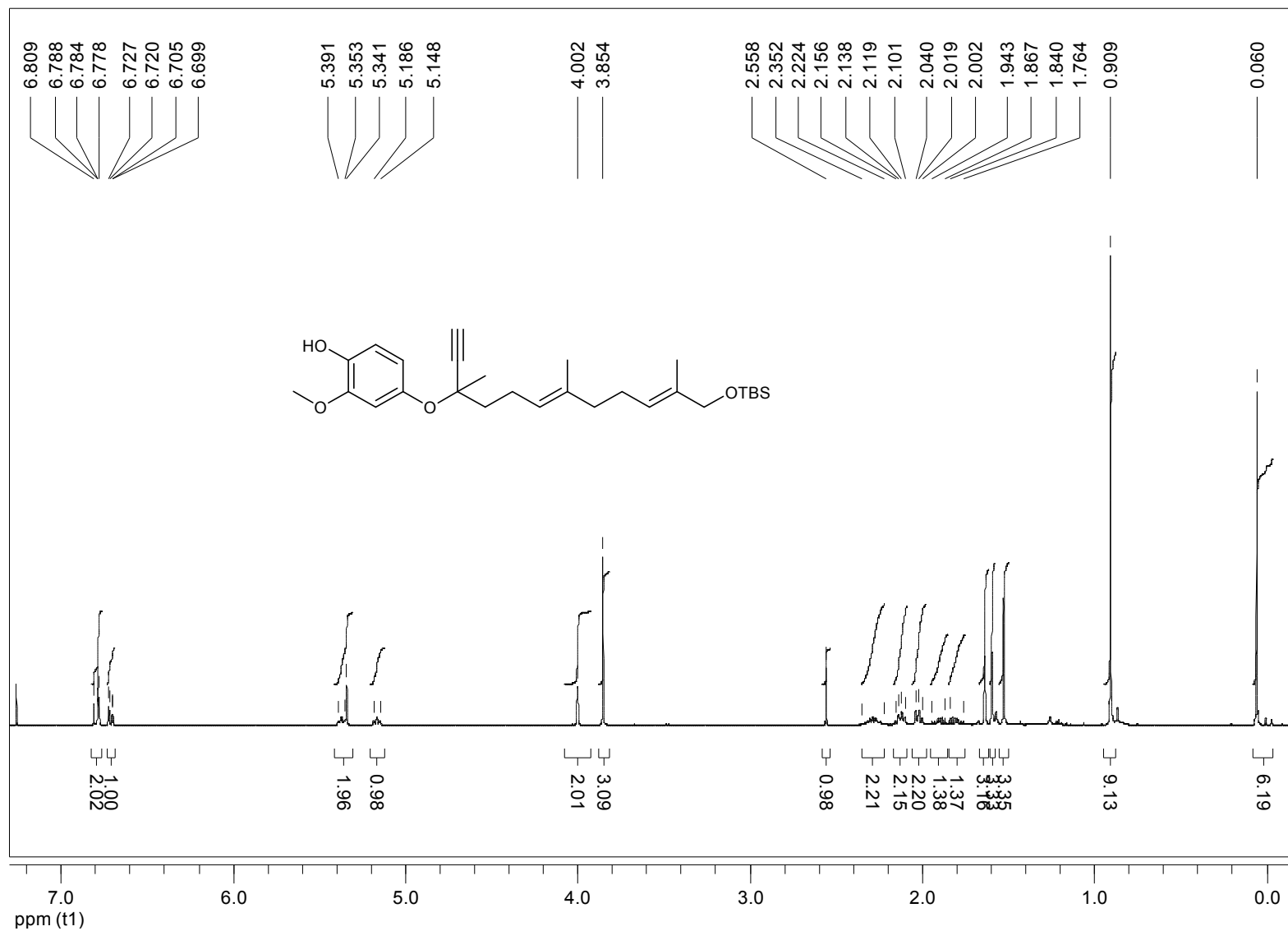


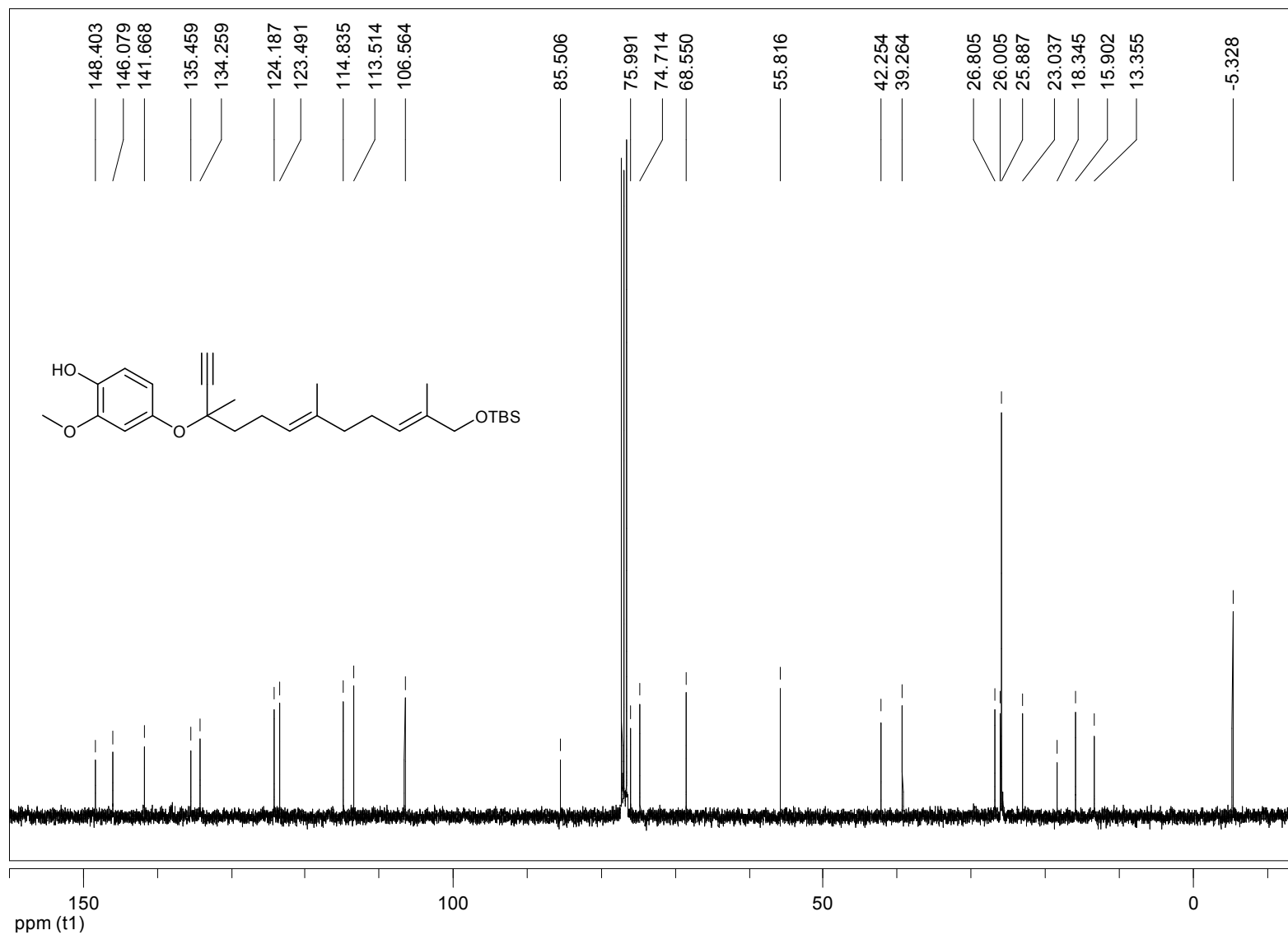
4-Methanesulfonyloxy-3-methoxyphenol **14**

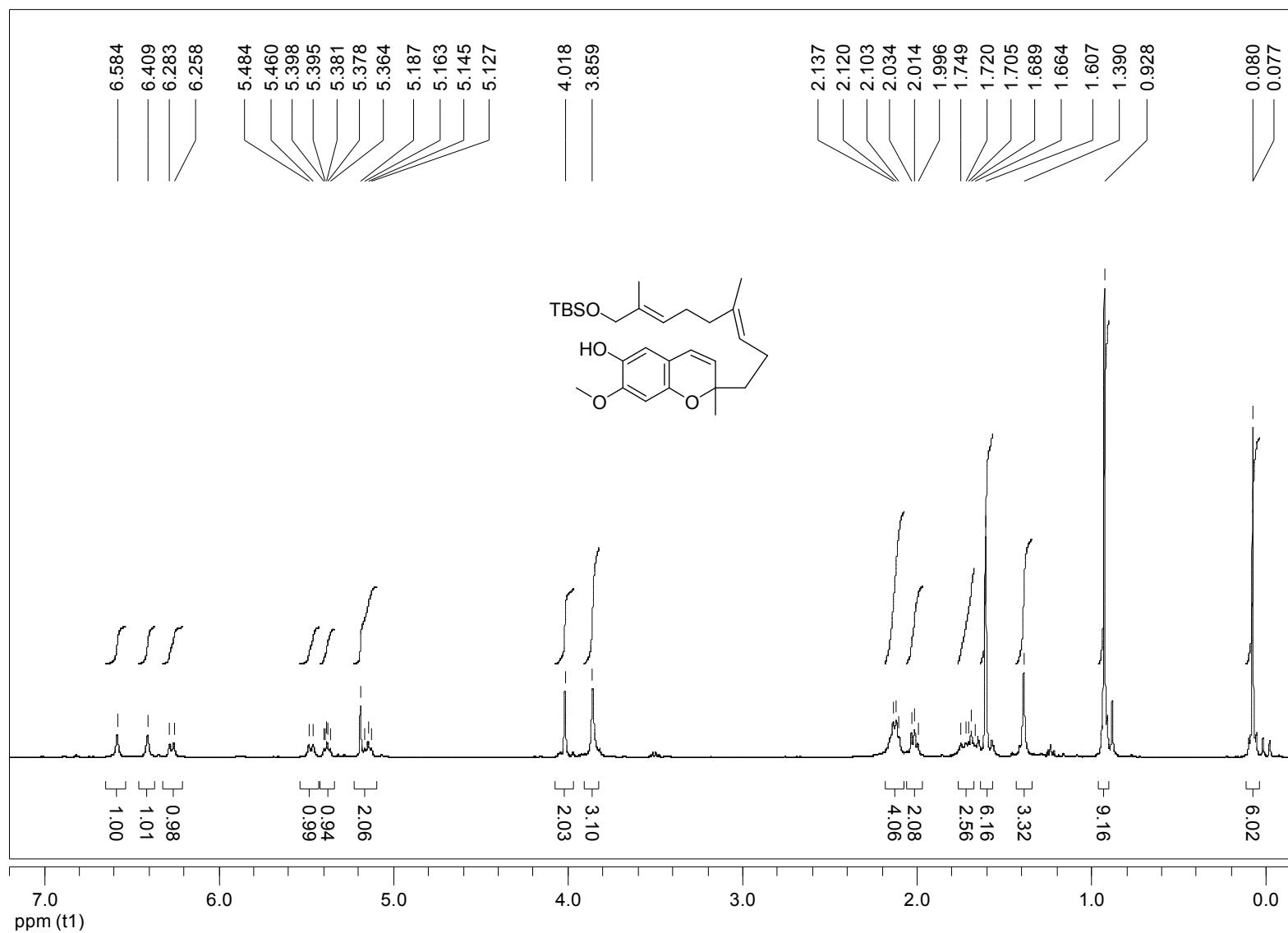
4-Methanesulfonyloxy-3-methoxyphenol **14**

4-Methanesulfonyloxy-3-methoxy-((6'*E*,10'*E*)-12'-*tert*-butyldimethylsiloxy-3',7',11'-trimethyldodeca-6',10'-dien-1'-yn-3'-yloxy) benzene **15**

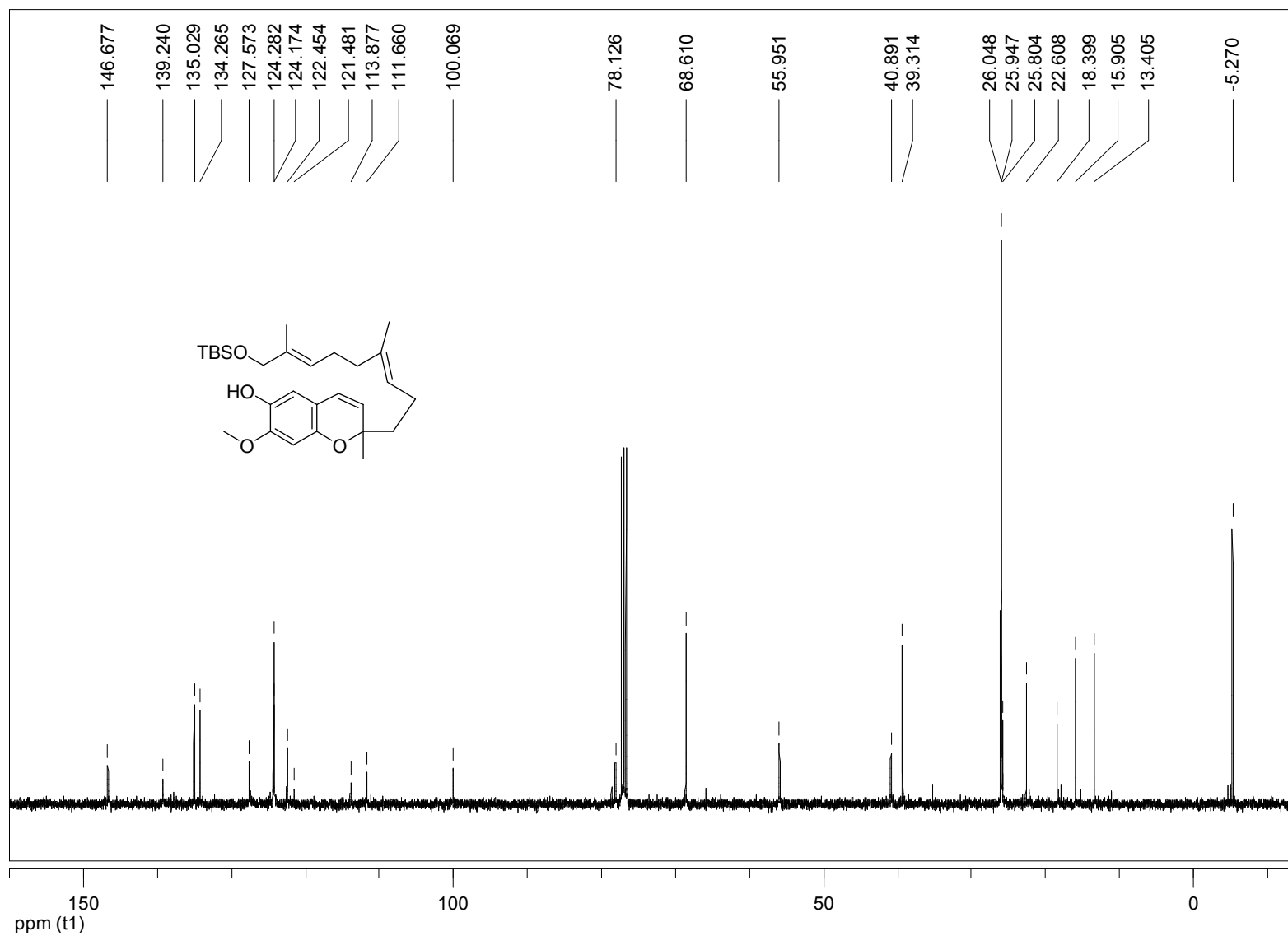


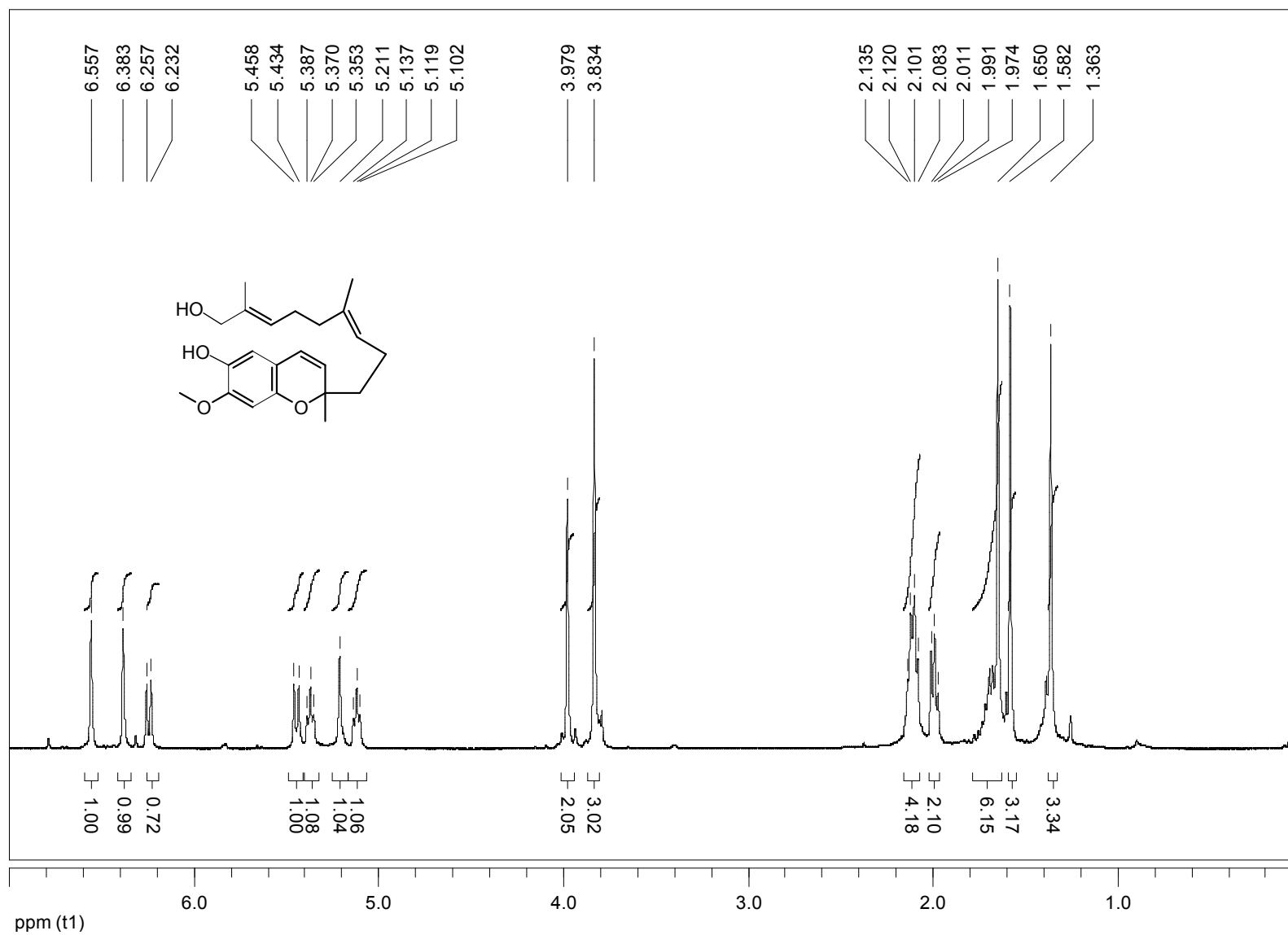
4-[(6'*E*,10'*E*)-12'-*tert*-butyldimethylsiloxy-3',7',11'-trimethyldodeca-6',10'-dien-1'-yn-3'-yloxy]-2-methoxyphenol **16**

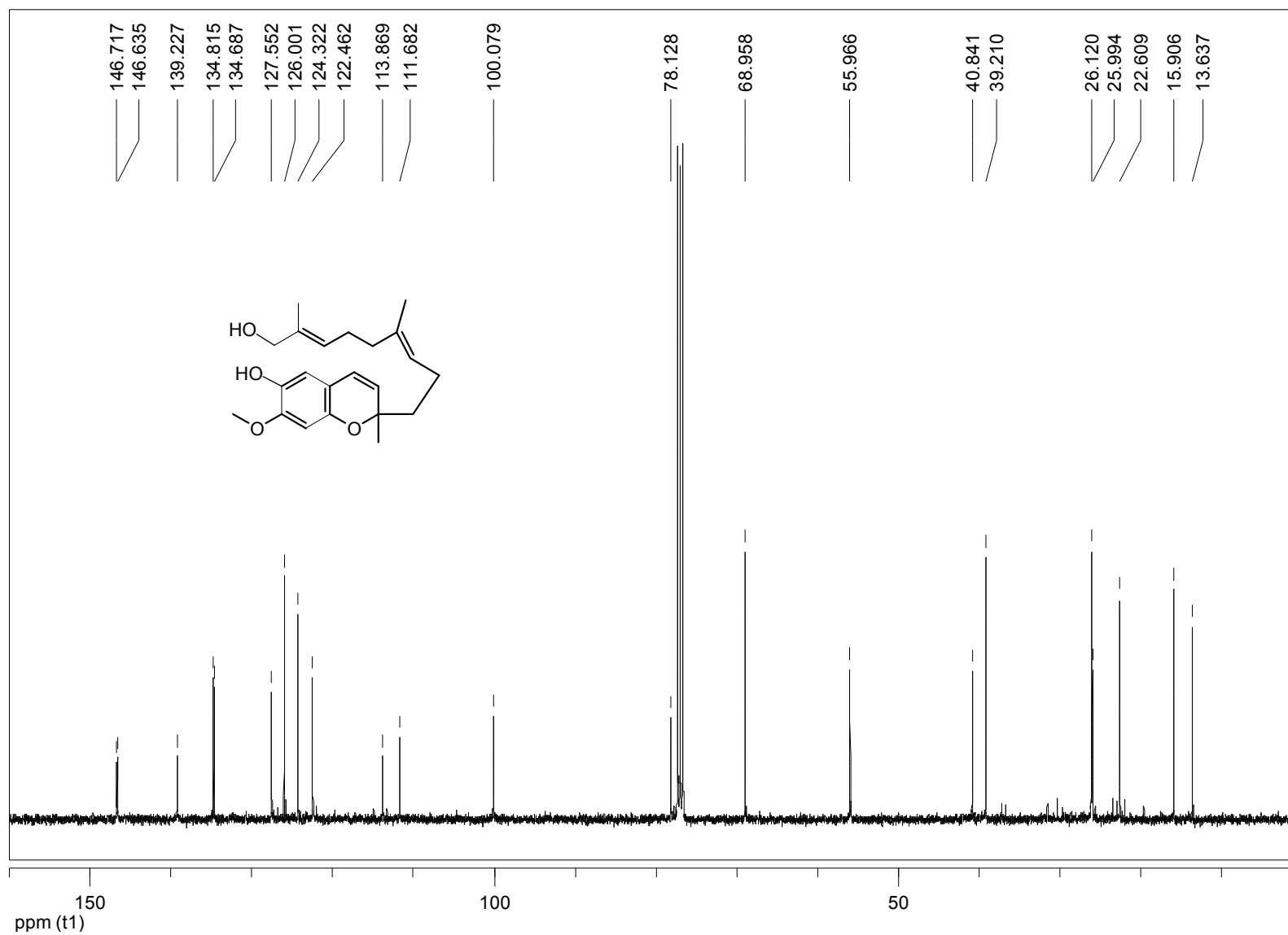
4-[(6'*E*,10'*E*)-12'-*tert*-butyldimethylsiloxy-3',7',11'-trimethyldodeca-6',10'-dien-1'-yn-3'-yloxy]-2-methoxyphenol **16**

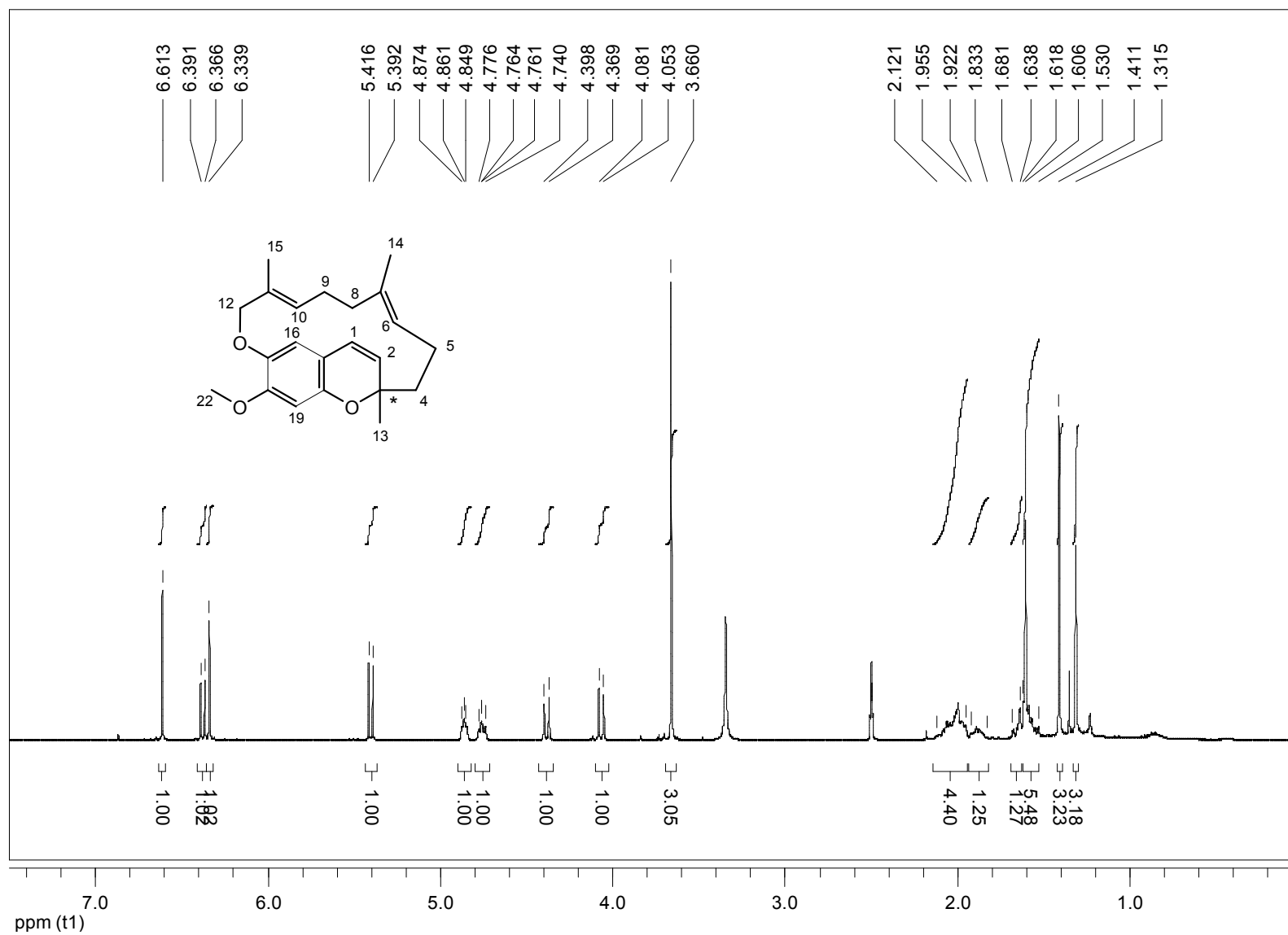
2-[(3'E,7'E)-9'-tert-Butyldimethylsiloxy-4',8'-dimethylnona-3',7'-dienyl]-7-methoxy-2-methyl-2H-chromen-6-ol **17**

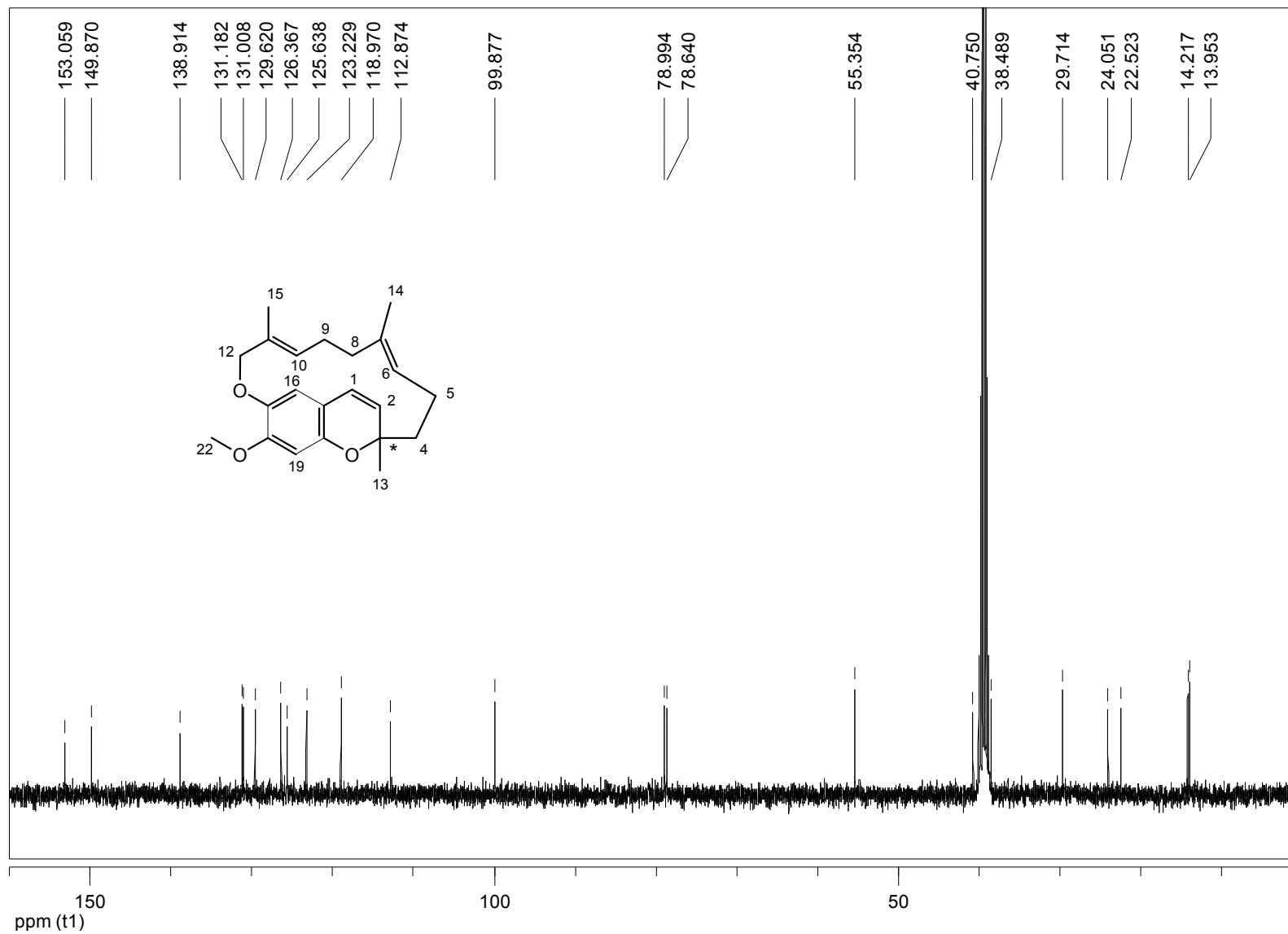
2-[(3'E,7'E)-9'-tert-Butyldimethylsiloxy-4',8'-dimethylnona-3',7'-dienyl]-7-methoxy-2-methyl-2H-chromen-6-ol 17



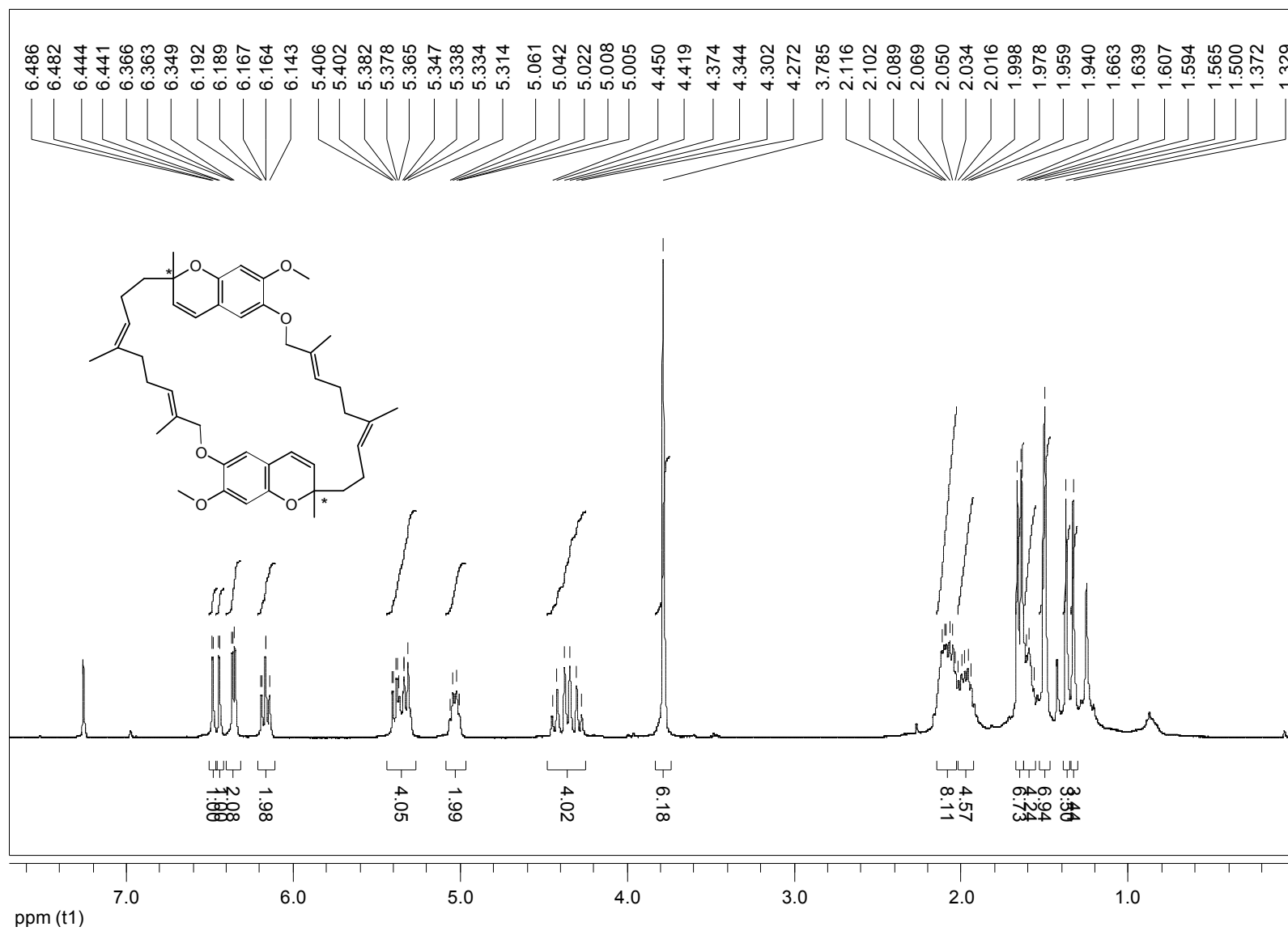
2-[(3'*E*,7'*E*)-9'-hydroxy-4',8'-dimethylnona-3',7'-dienyl]-7-methoxy-2-methyl-2*H*-chromen-6-ol **18**

2-[(3'*E*,7'*E*)-9'-hydroxy-4',8'-dimethylnona-3',7'-dienyl]-7-methoxy-2-methyl-2*H*-chromen-6-ol **18**

(\pm) -Likonide B [(\pm) -smenochromene D] (DMSO)

(\pm) -Likonide B [(\pm) -smenochromene D] (DMSO)

Dimer 19



Dimer 19

