

## Supplementary Information

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### Studies directed toward the synthesis of hedycoropyrans: total synthesis of des-hydroxy (–)-hedycoropyran B (*ent*- rhoiptelol B)

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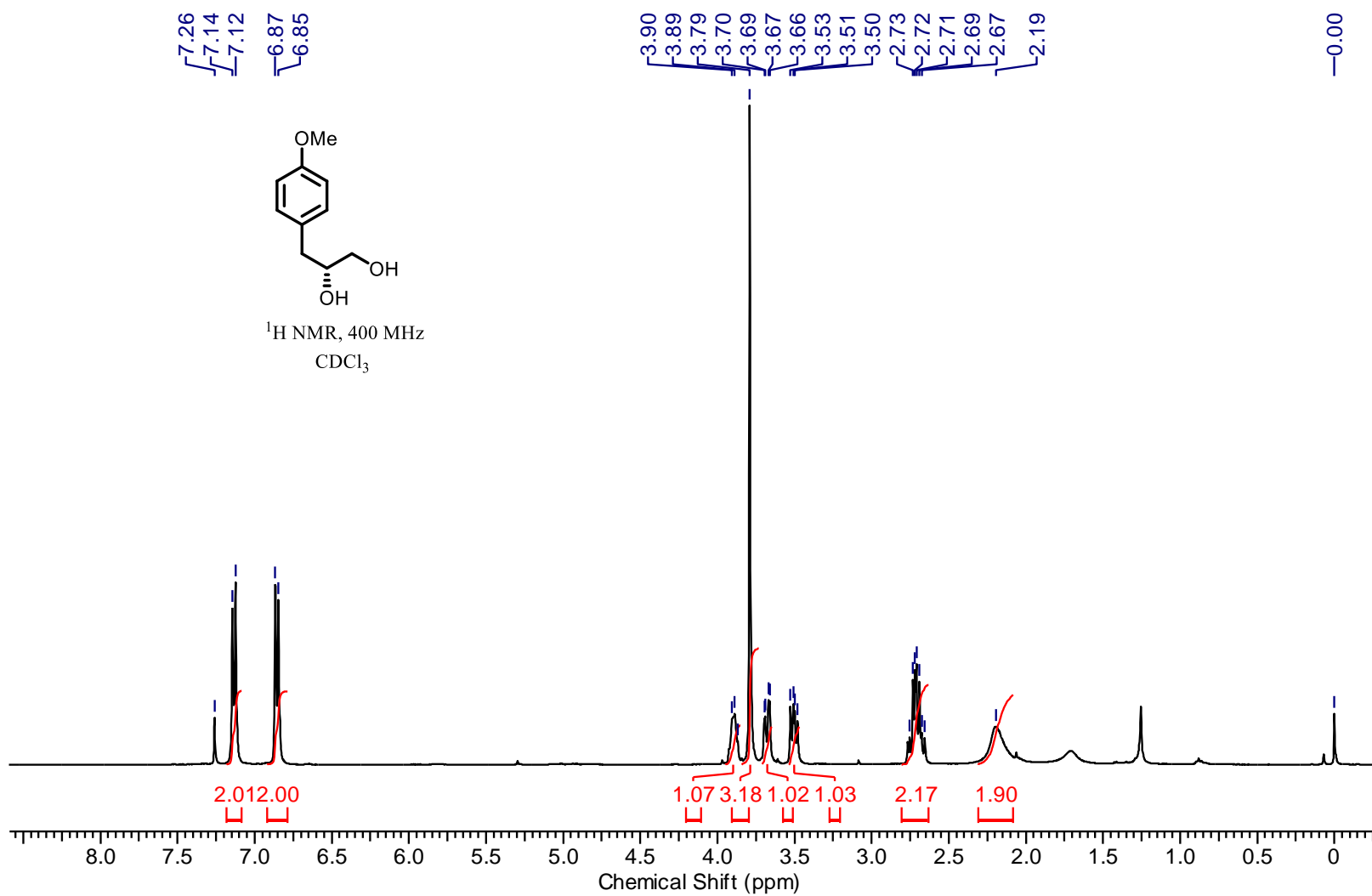
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#### Table of Contents

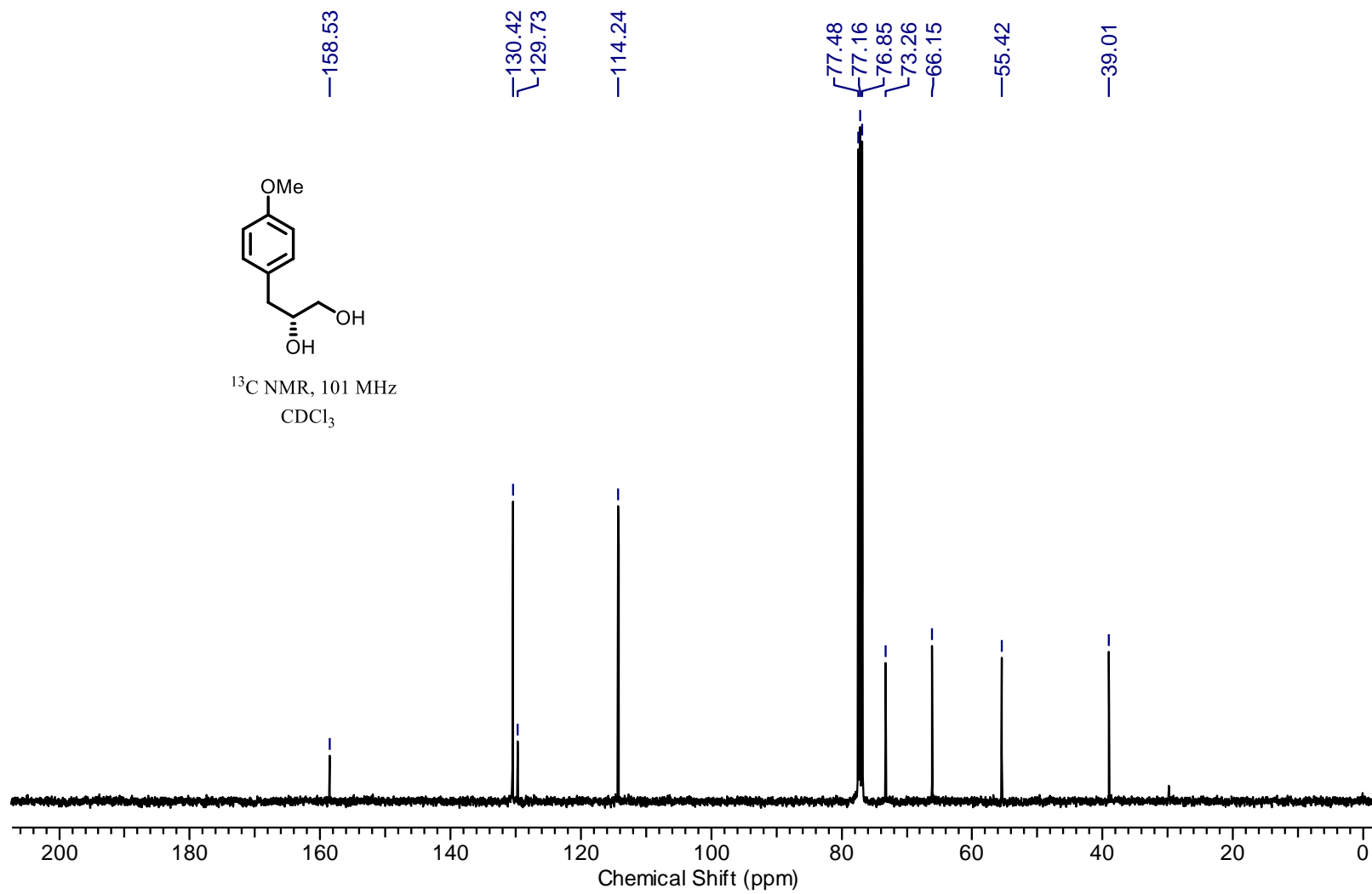
S. No	Contents	Page
1.	<sup>1</sup> H and <sup>13</sup> C NMR Spectra	S3-S113
2.	2D-NMR Spectra of 4-((2 <i>S</i> , 4 <i>R</i> , 6 <i>R</i> )-6-(( <i>R</i> )-2-(4-(( <i>tert</i> -butyldimethylsilyl)oxy)phenyl)-1-hydroxyethyl)-4-hydroxytetrahydro-2 <i>H</i> -pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate ( <b>34</b> )	S114-S118
3.	Table S1. NMR data comparison of synthesized, natural and first synthesis of rhoiptelol B	S119-S120

# 1. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

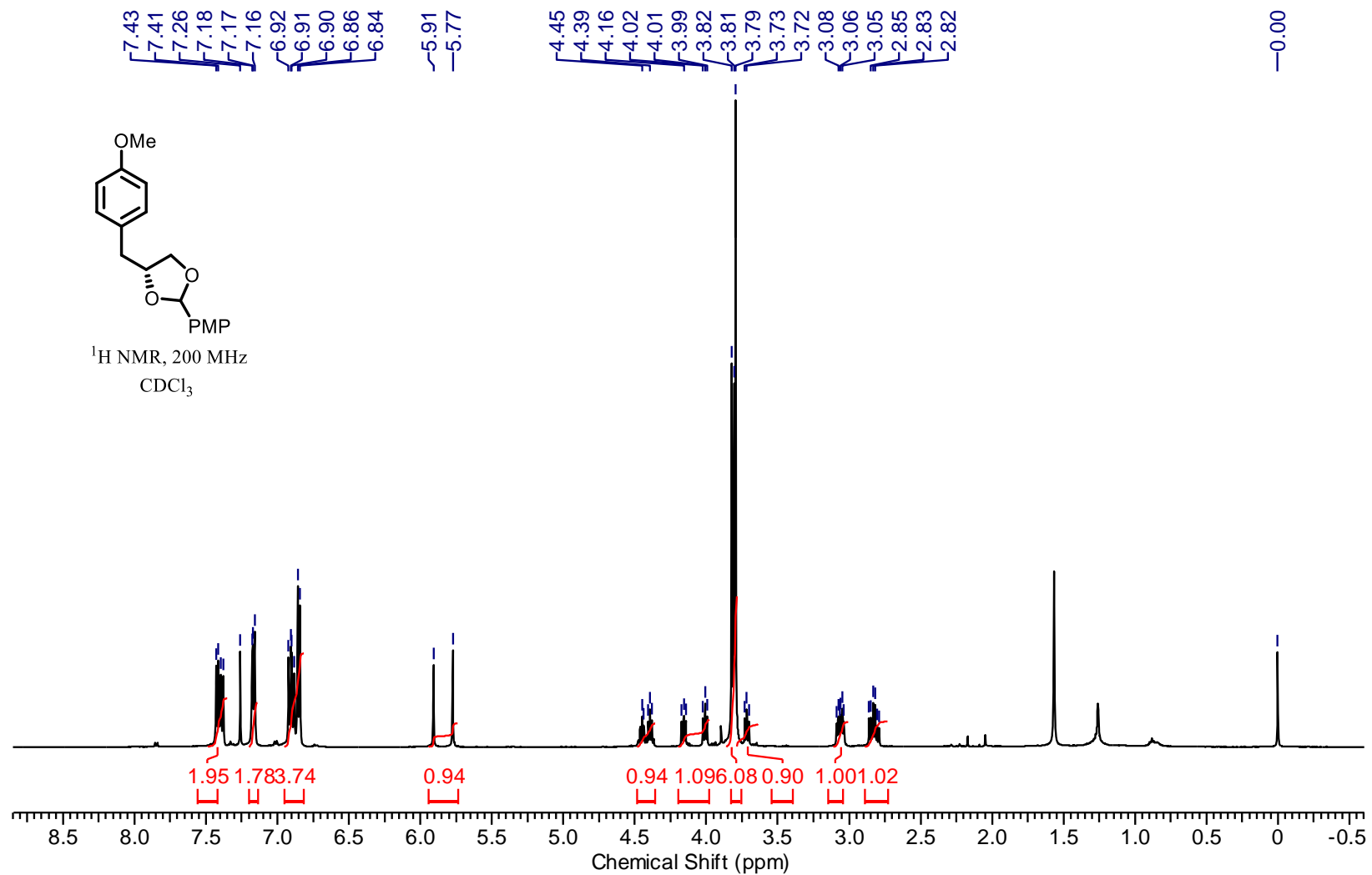
*(R)*-3-(4-Methoxyphenyl)propane-1,2-diol (**S1**):



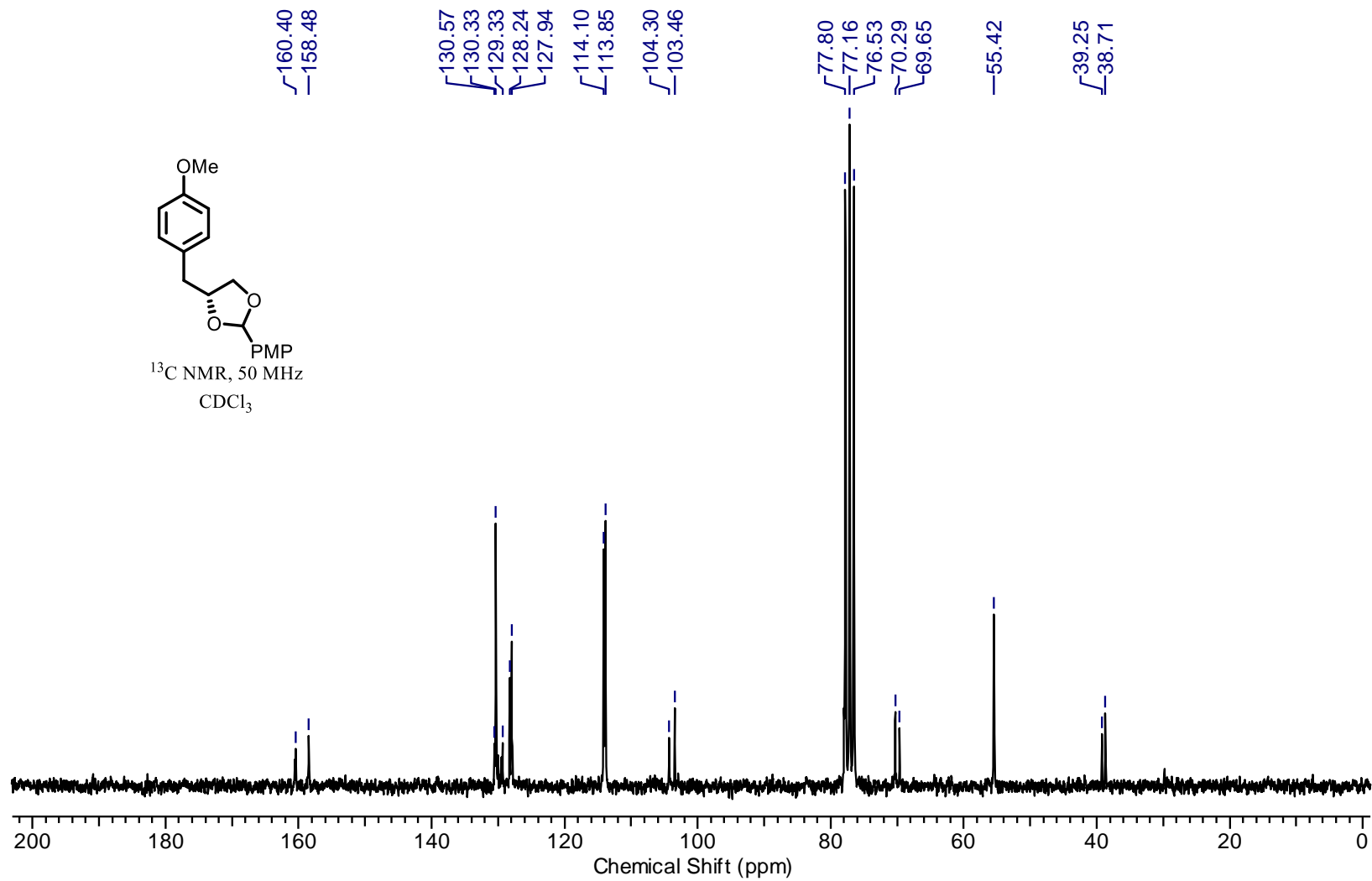
*(R)*-3-(4-Methoxyphenyl)propane-1,2-diol (**S1**):



(4R)-4-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1,3-dioxolane (**11**):

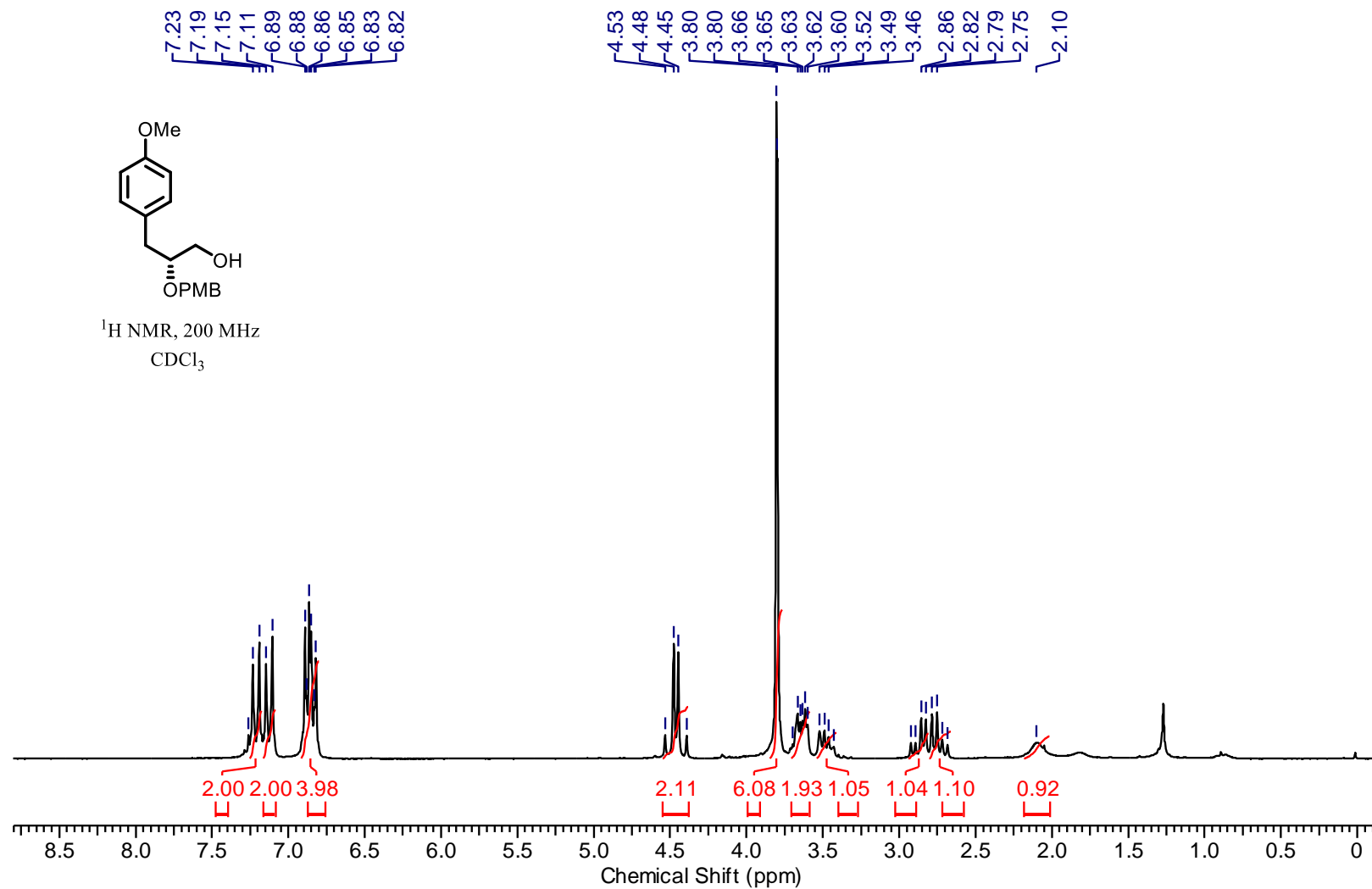


(4R)-4-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1,3-dioxolane (**11**):

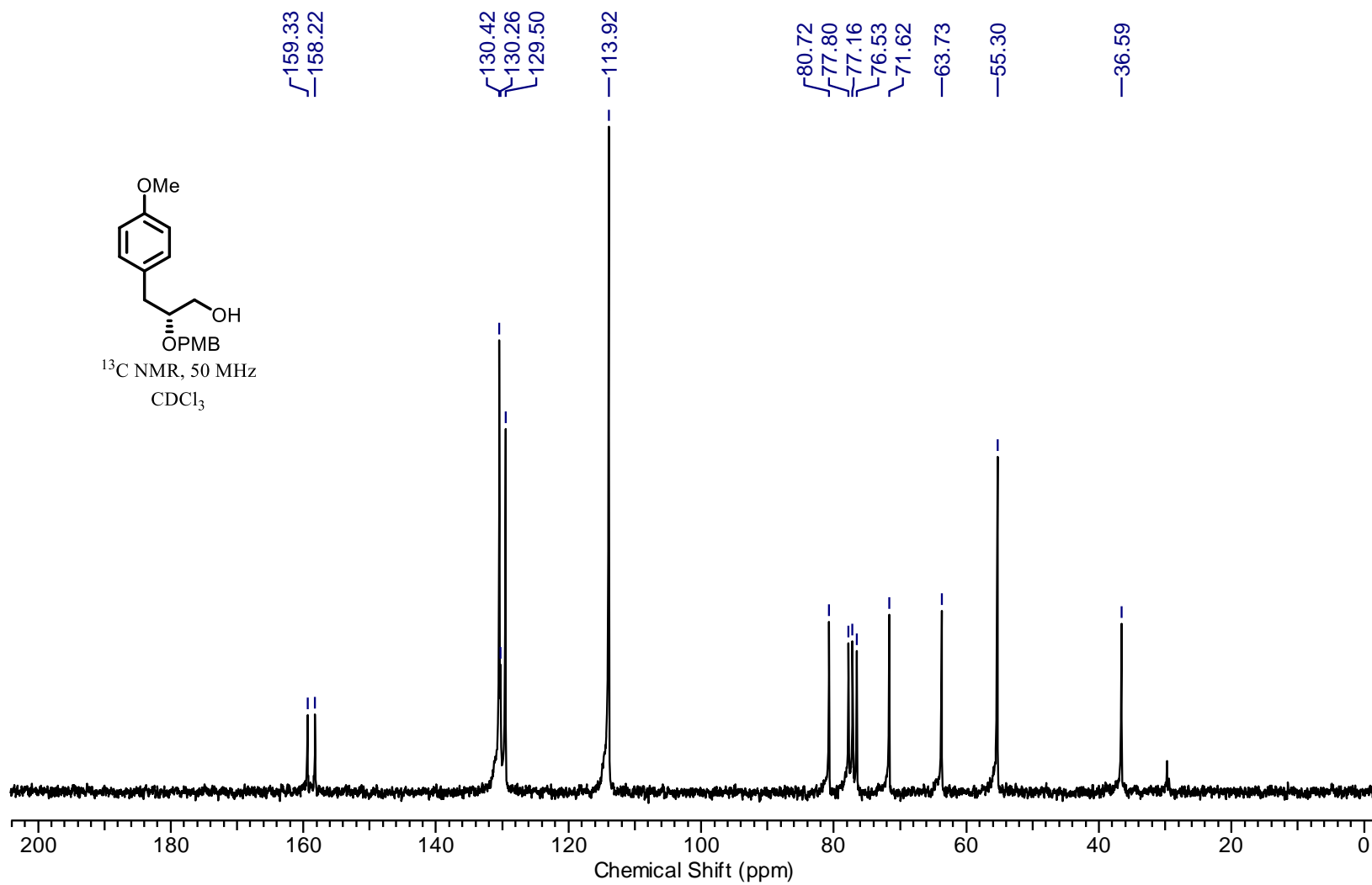


(R)-2-(4-

*Methoxybenzyl)oxy)-3-(4-methoxyphenyl)propan-1-ol (S2):*

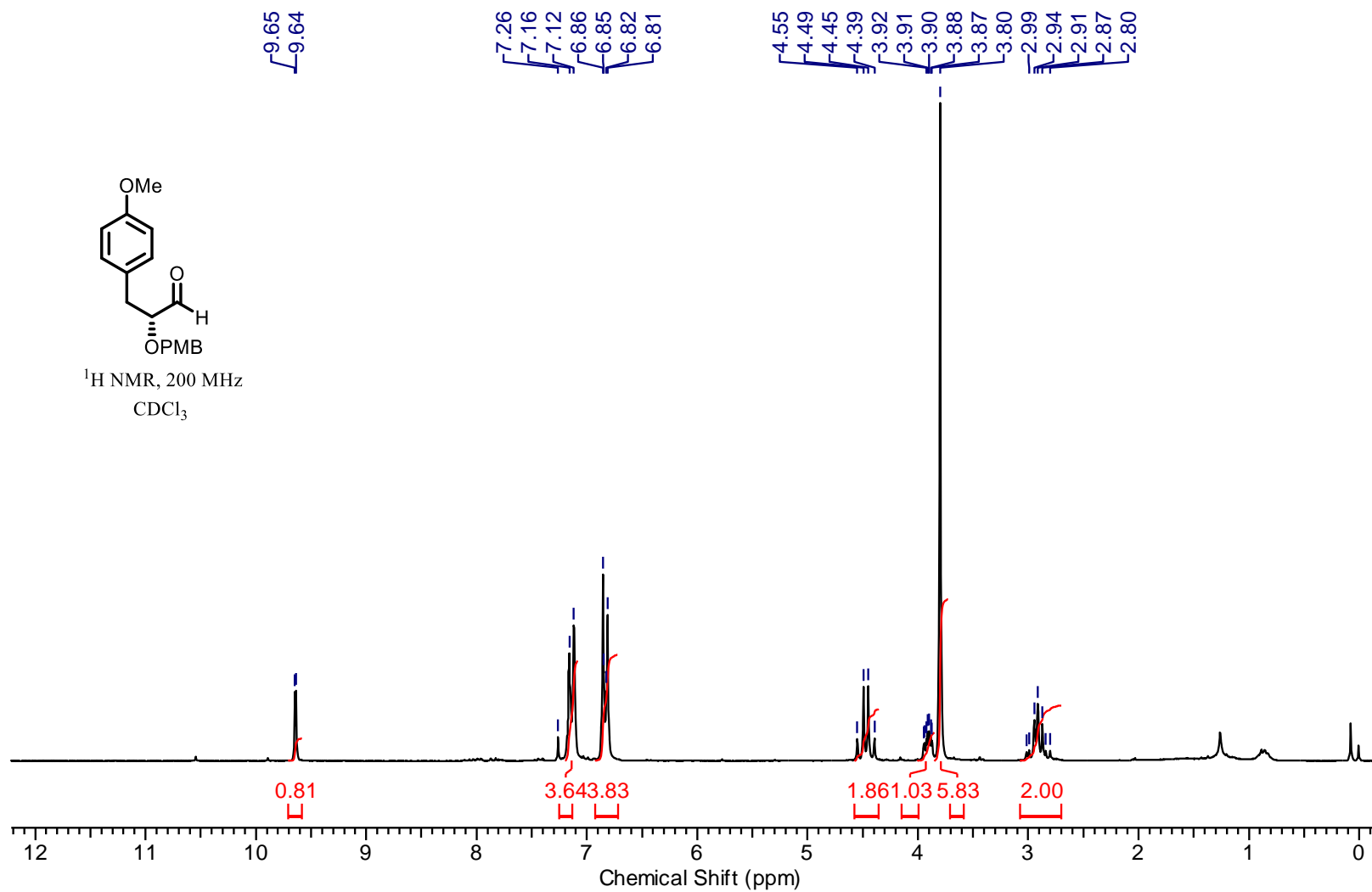


*(R)*-2-((4-Methoxybenzyl)oxy)-3-(4-methoxyphenyl)propan-1-ol (**S2**):

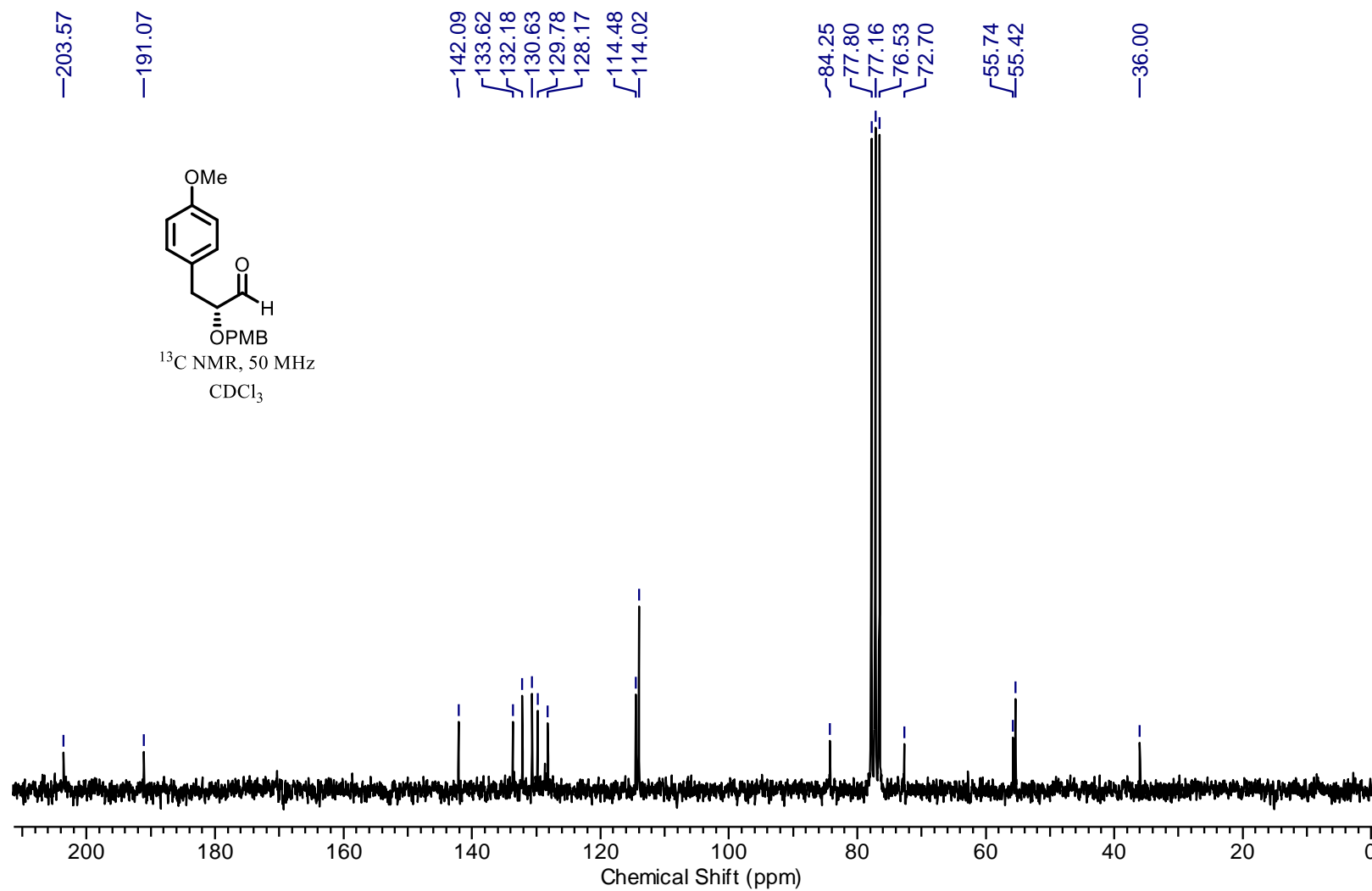




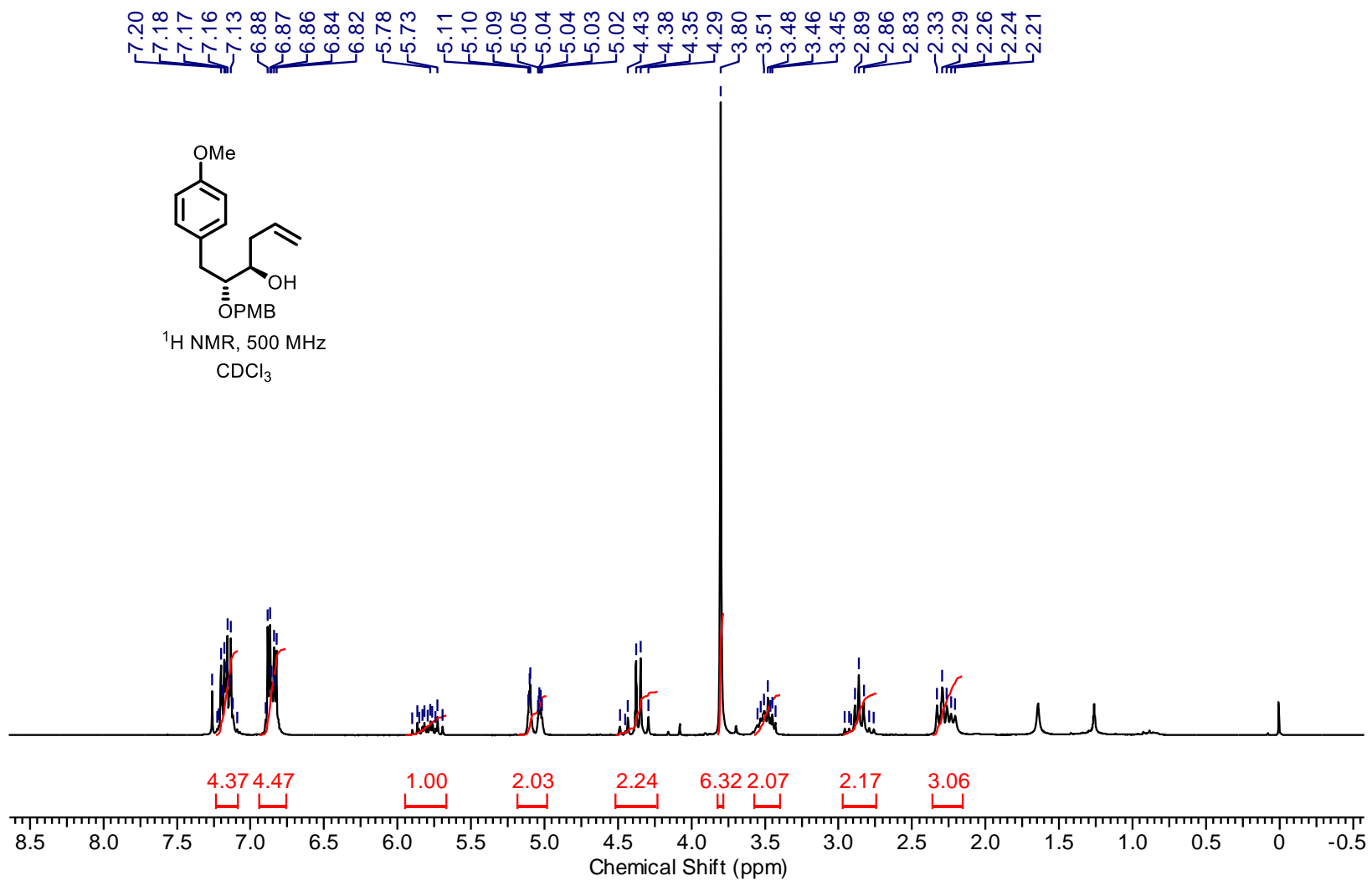
*(R)*-2-((4-Methoxybenzyl)oxy)-3-(4-methoxyphenyl)propanal (**12**):



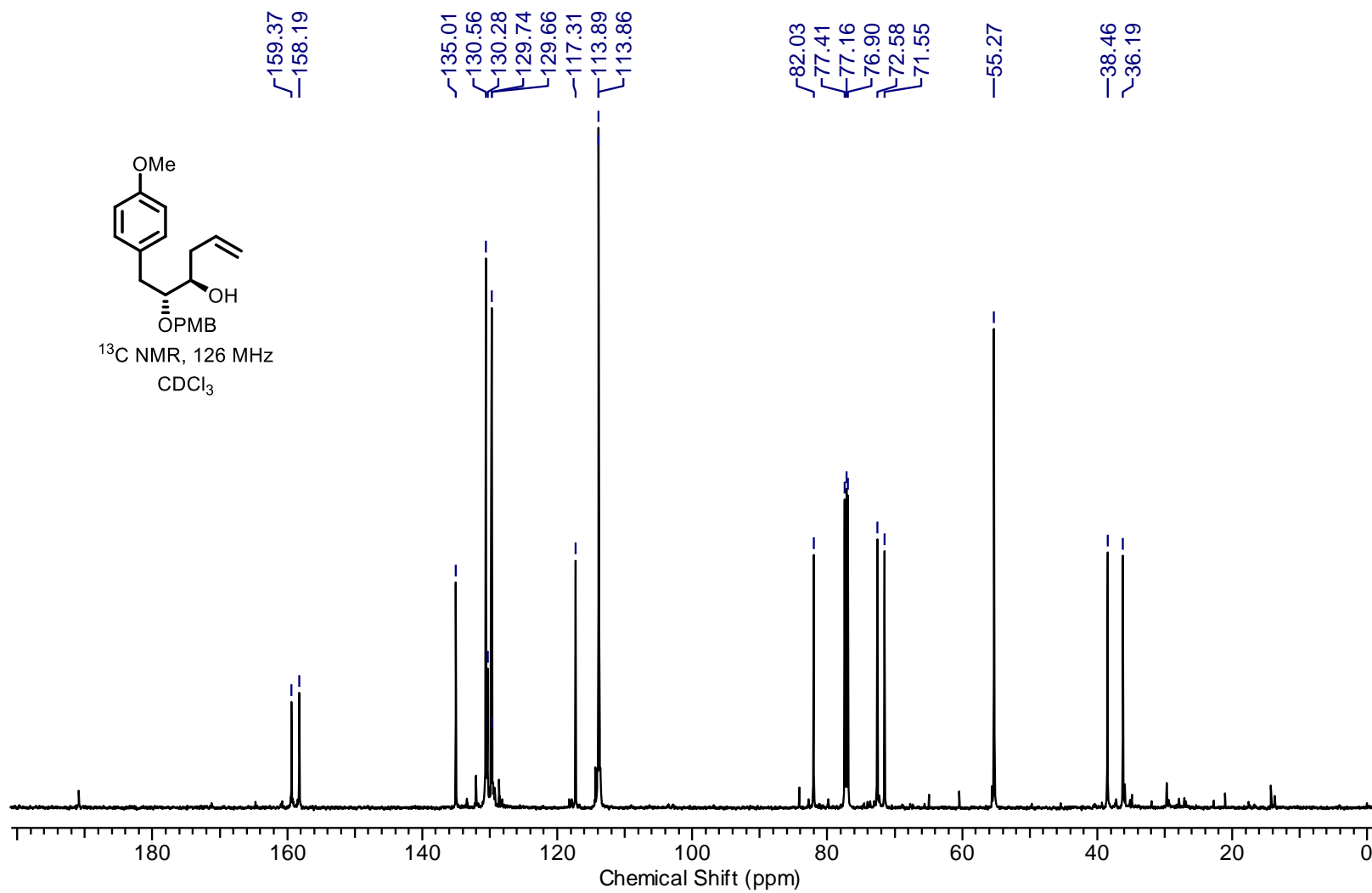
*(R)*-2-((4-Methoxybenzyl)oxy)-3-(4-methoxyphenyl)propanal (**12**):



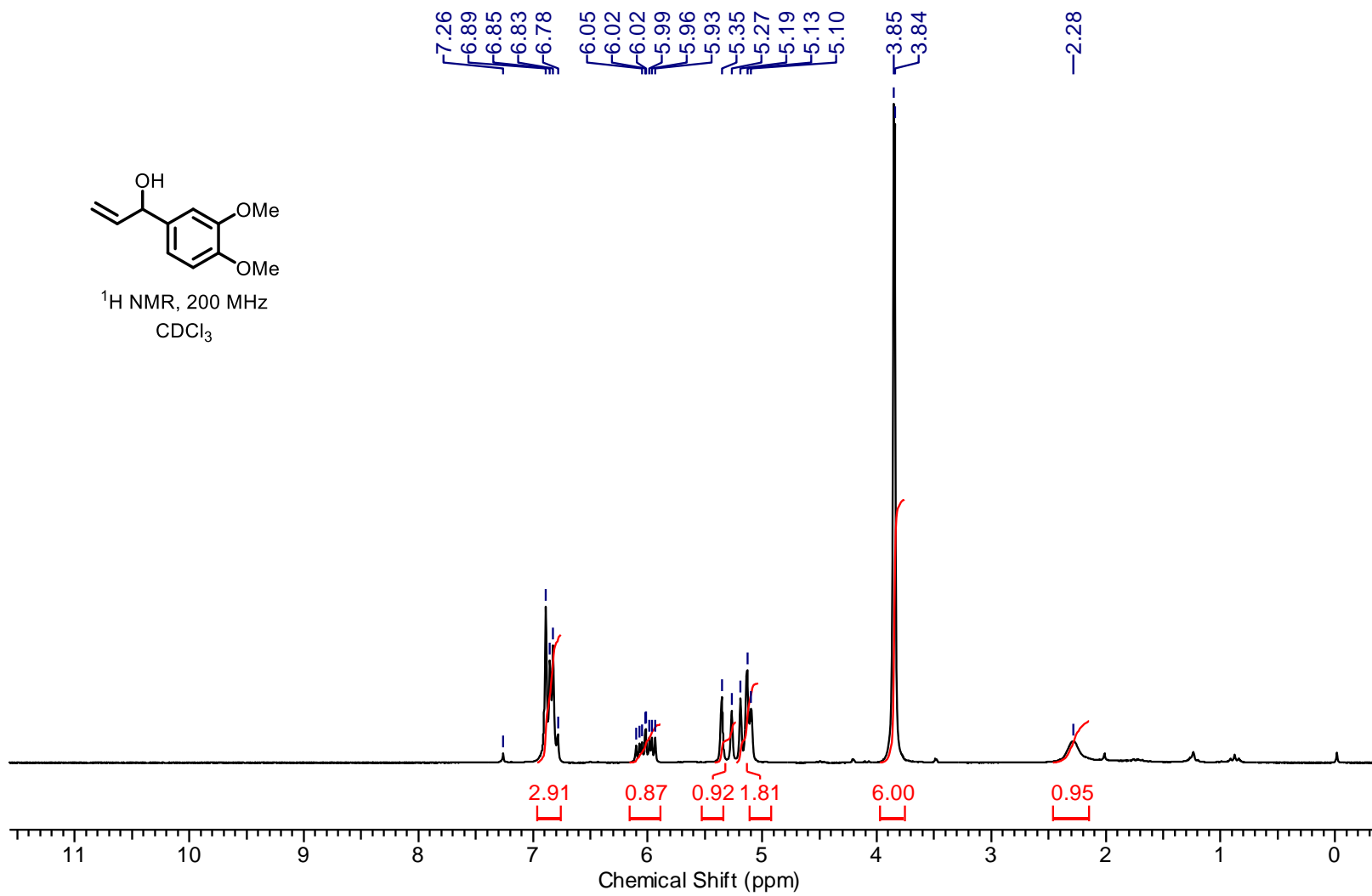
(2*R*, 3*R*)-2-((4-Methoxybenzyl)oxy)-1-(4-methoxyphenyl)hex-5-ene-3-ol (**7**):



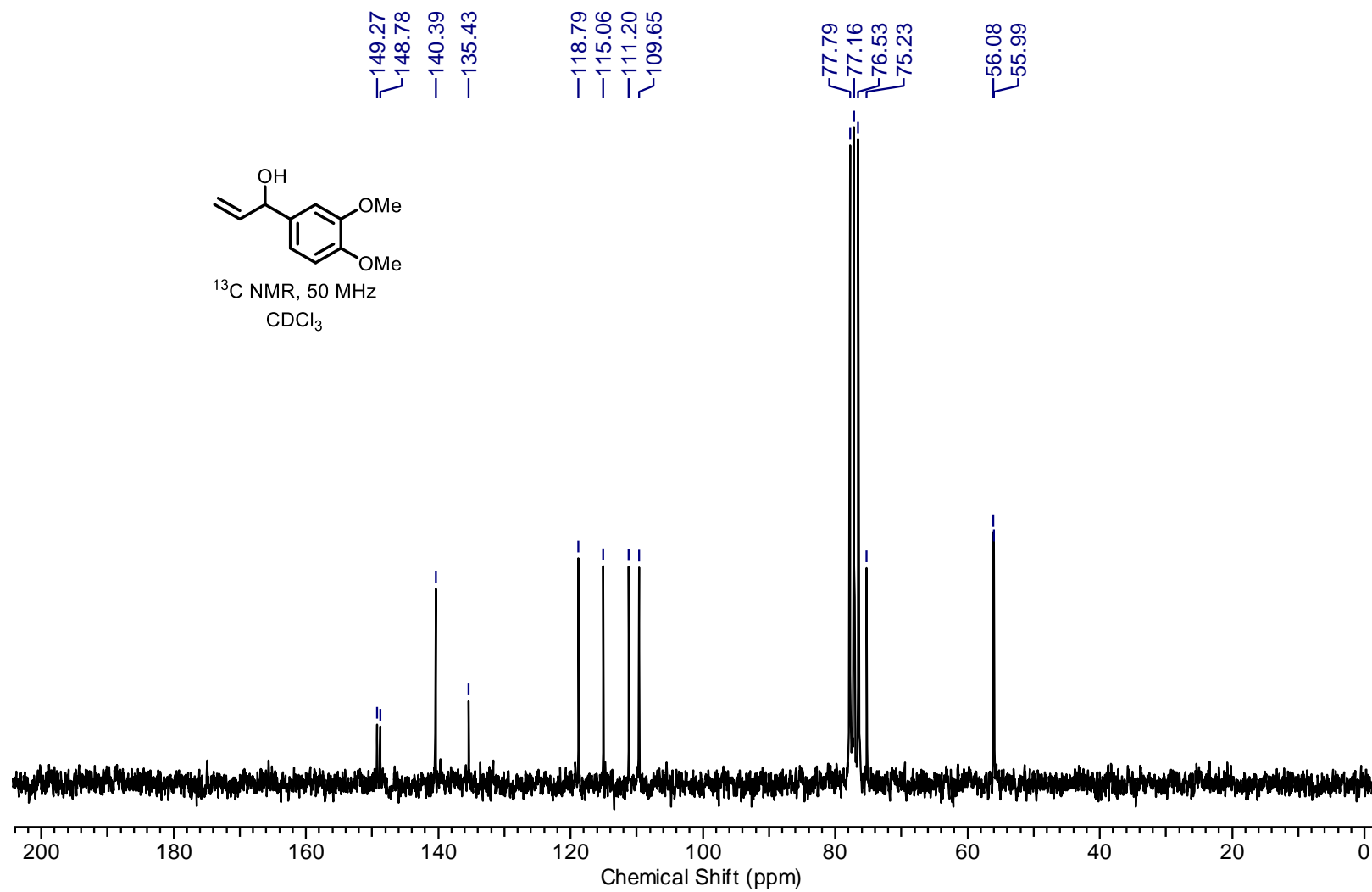
(2*R*, 3*R*)-2-((4-Methoxybenzyl)oxy)-1-(4-methoxyphenyl)hex-5-ene-3-ol (**7**):



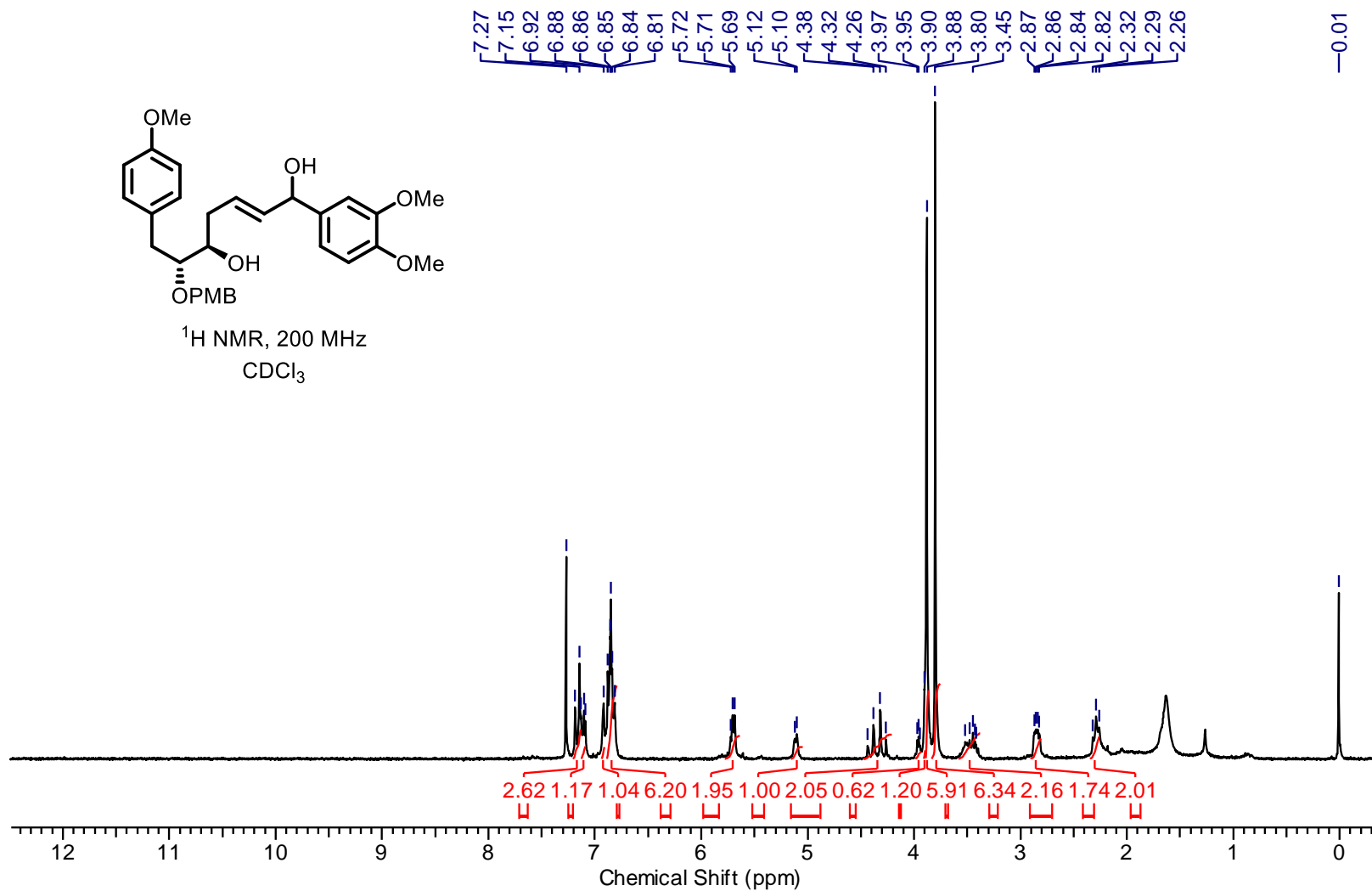
1-(3,4-Dimethoxyphenyl)prop-2-en-1-ol (**8**):



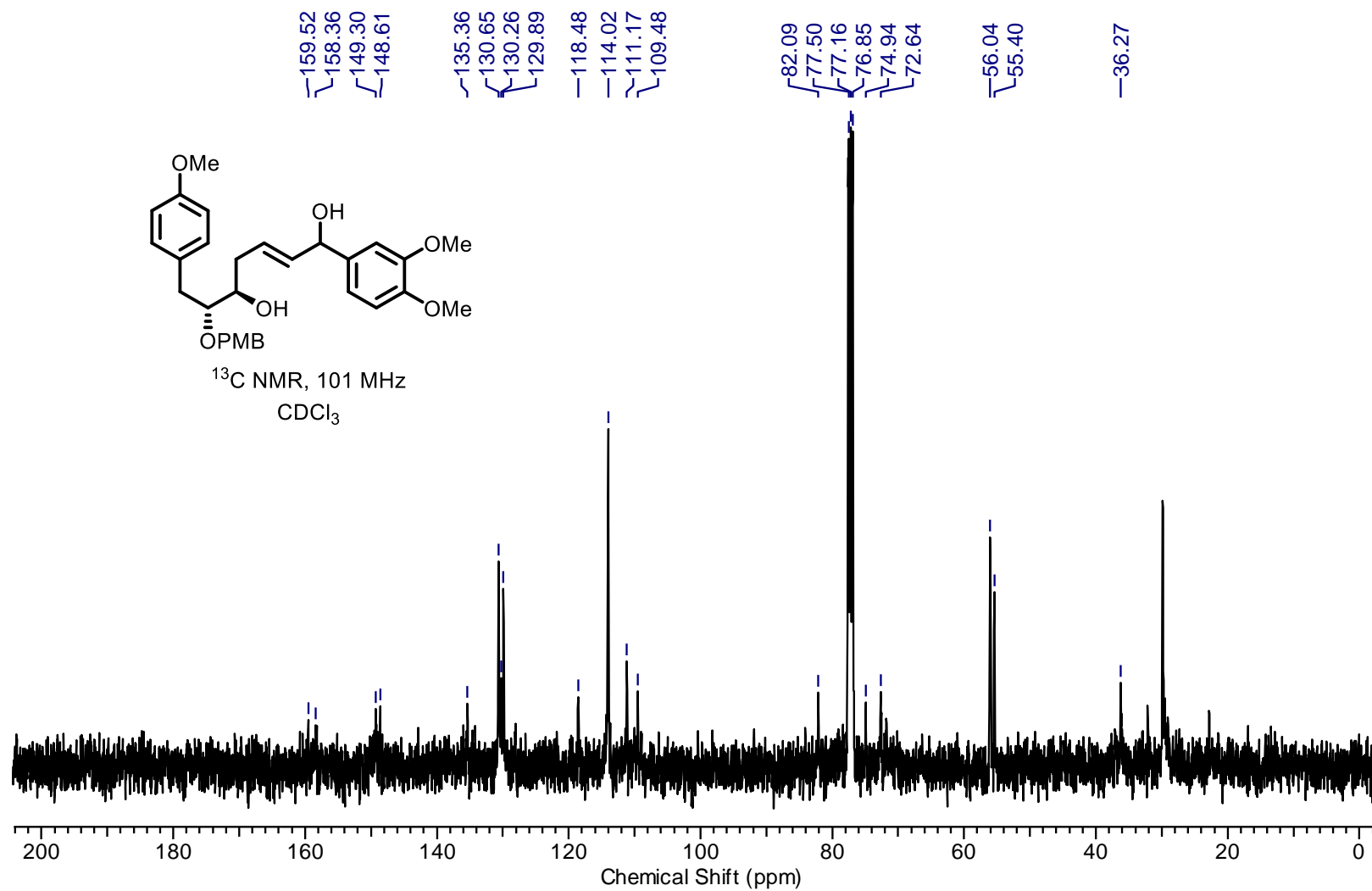
*1-(3,4-Dimethoxyphenyl)prop-2-en-1-ol (8)*:



(5*R*, 6*R*, *E*)-1-(3,4-Dimethoxyphenyl)-6-((4-methoxybenzyl)oxy)-7-(4-methoxyphenyl)hept-2-ene-1,5-diol (**6**):

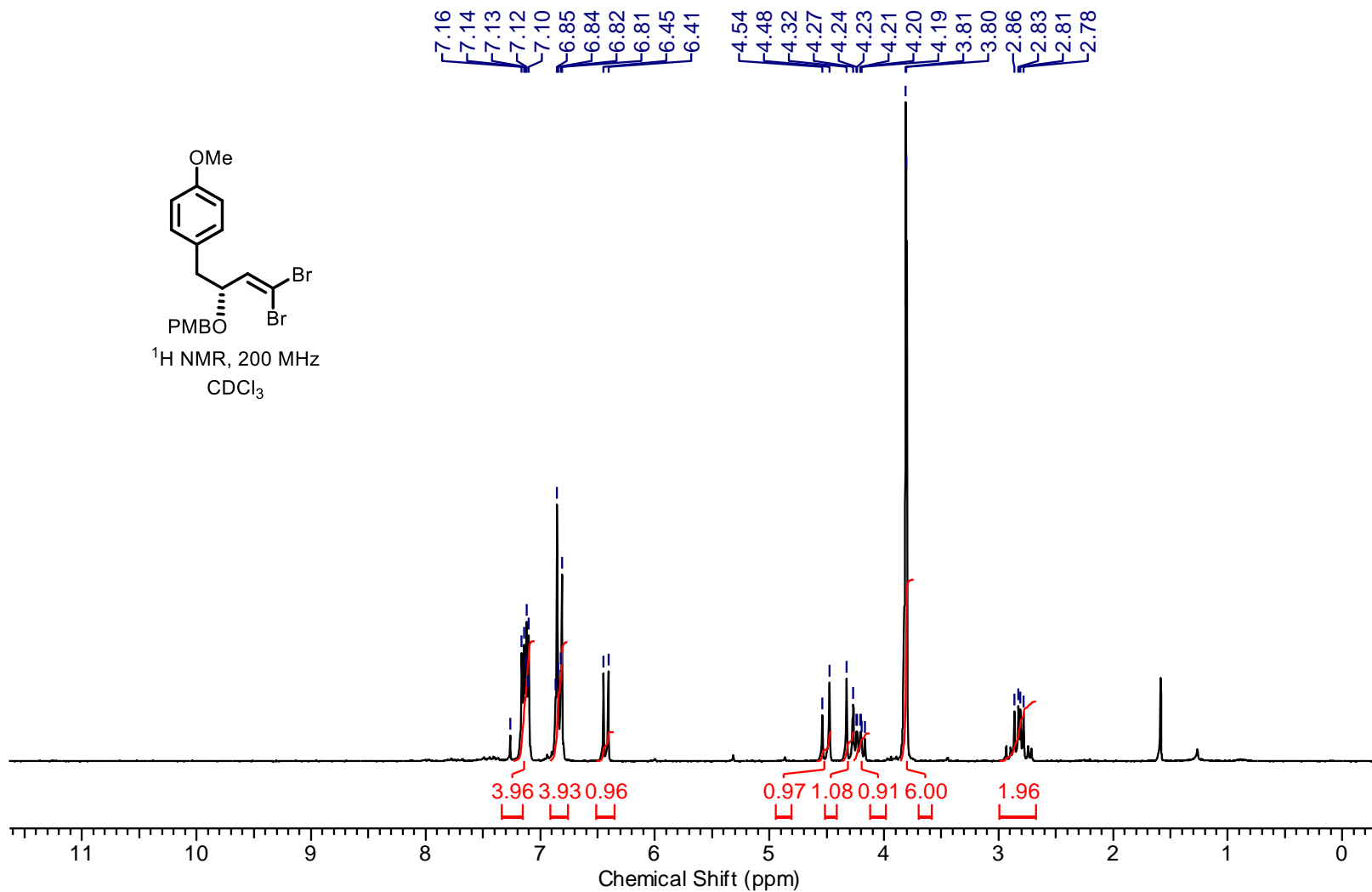


(5*R*, 6*R*, *E*)-1-(3,4-Dimethoxyphenyl)-6-((4-methoxybenzyl)oxy)-7-(4-methoxyphenyl)hept-2-ene-1,5-diol (**6**):

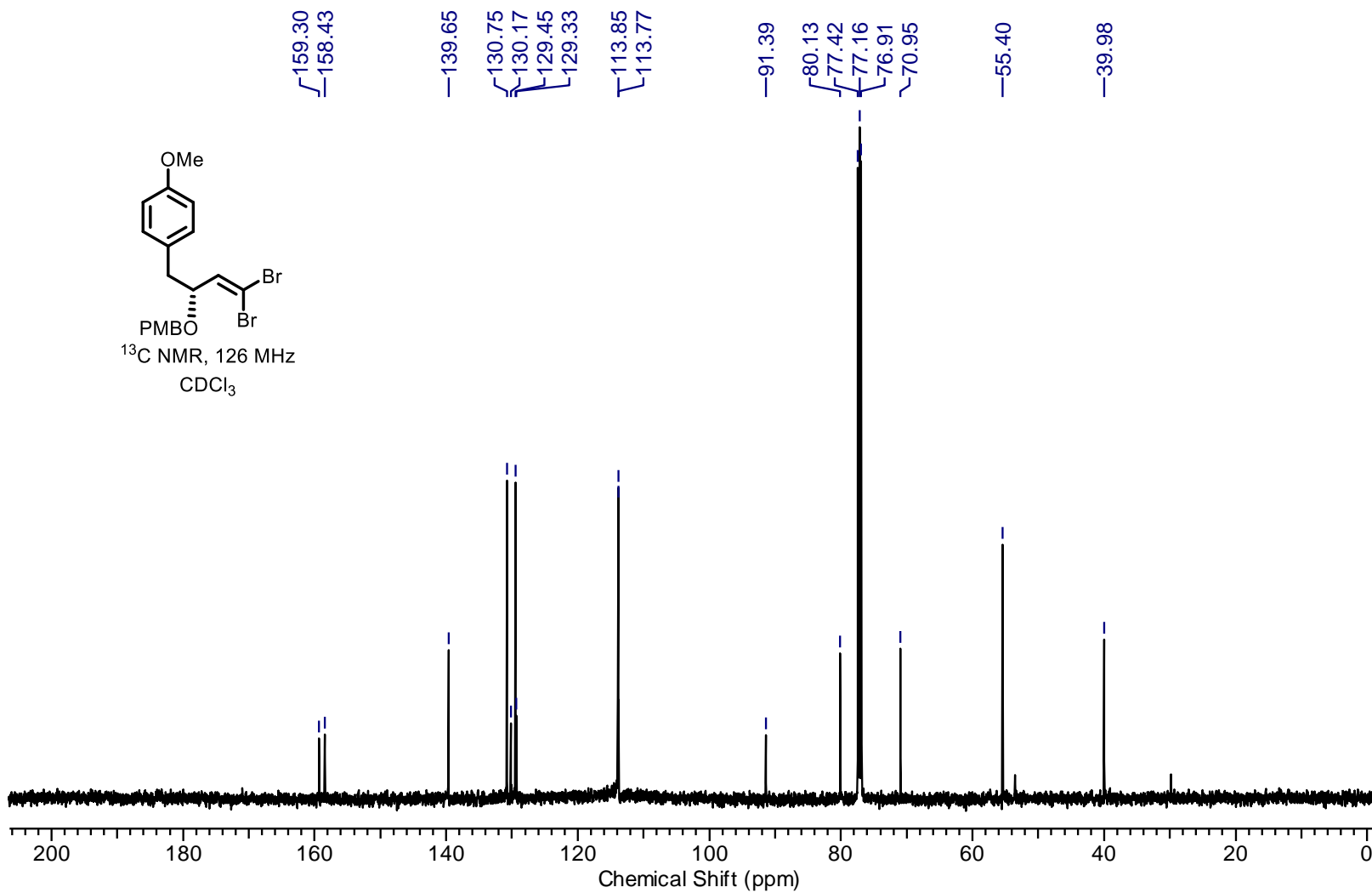




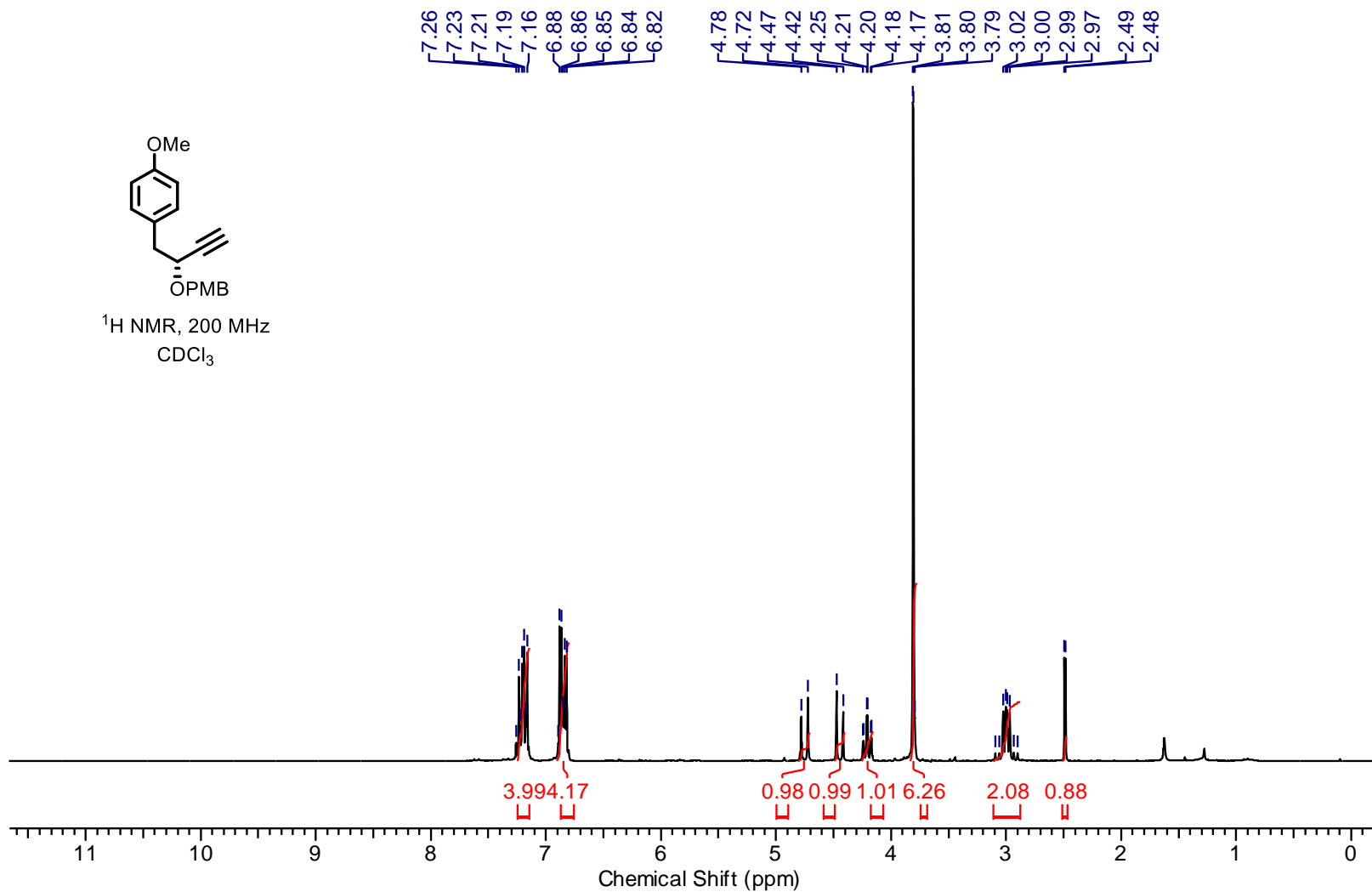
*(R)*-1-(((4,4-Dibromo-1-(4-methoxyphenyl)but-3-en-2-yl)oxy)methyl)-4-methoxybenzene (**S3**):



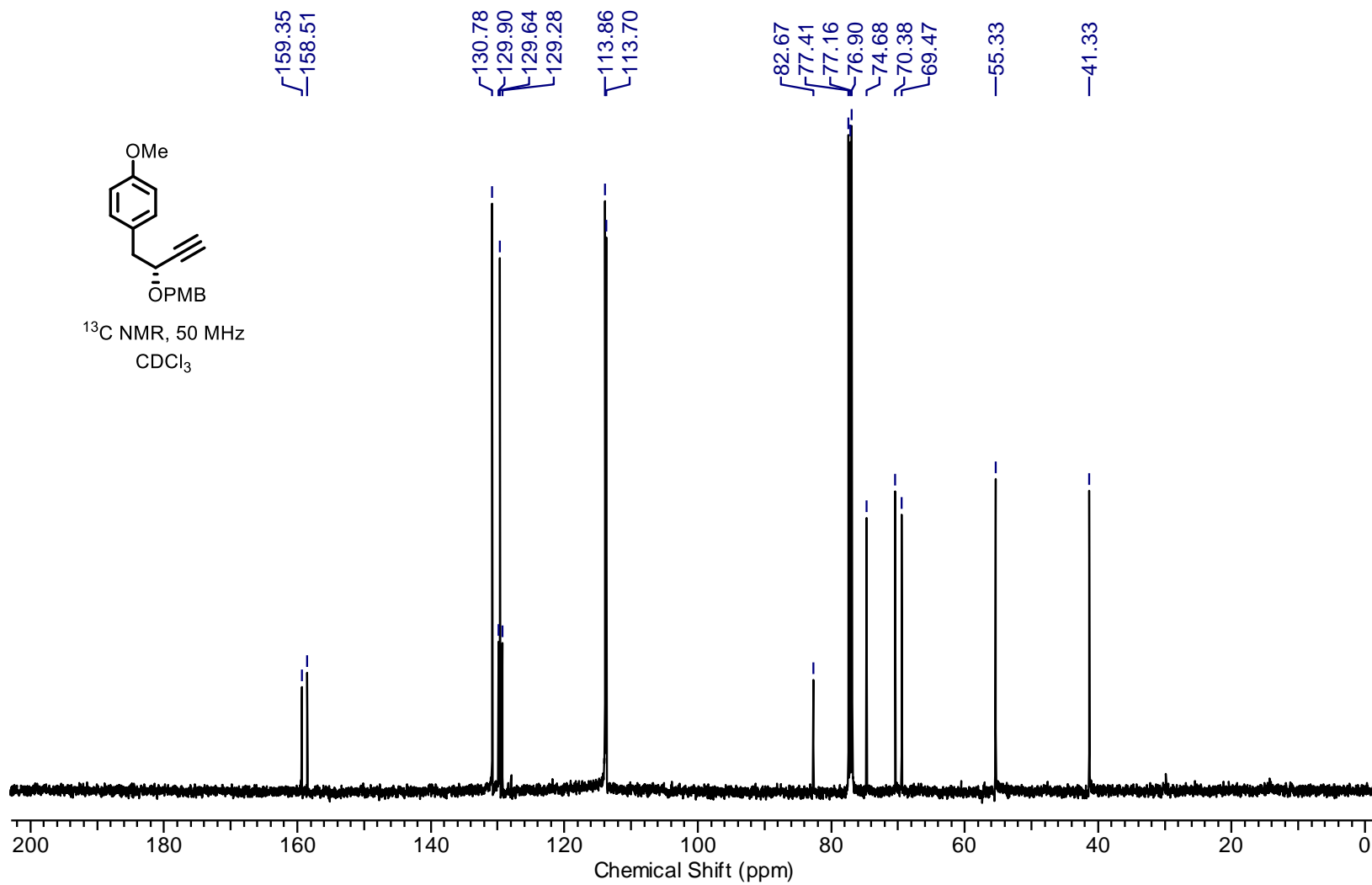
*(R)*-1-(((4,4-Dibromo-1-(4-methoxyphenyl)but-3-en-2-yl)oxy)methyl)-4-methoxybenzene (**S3**):



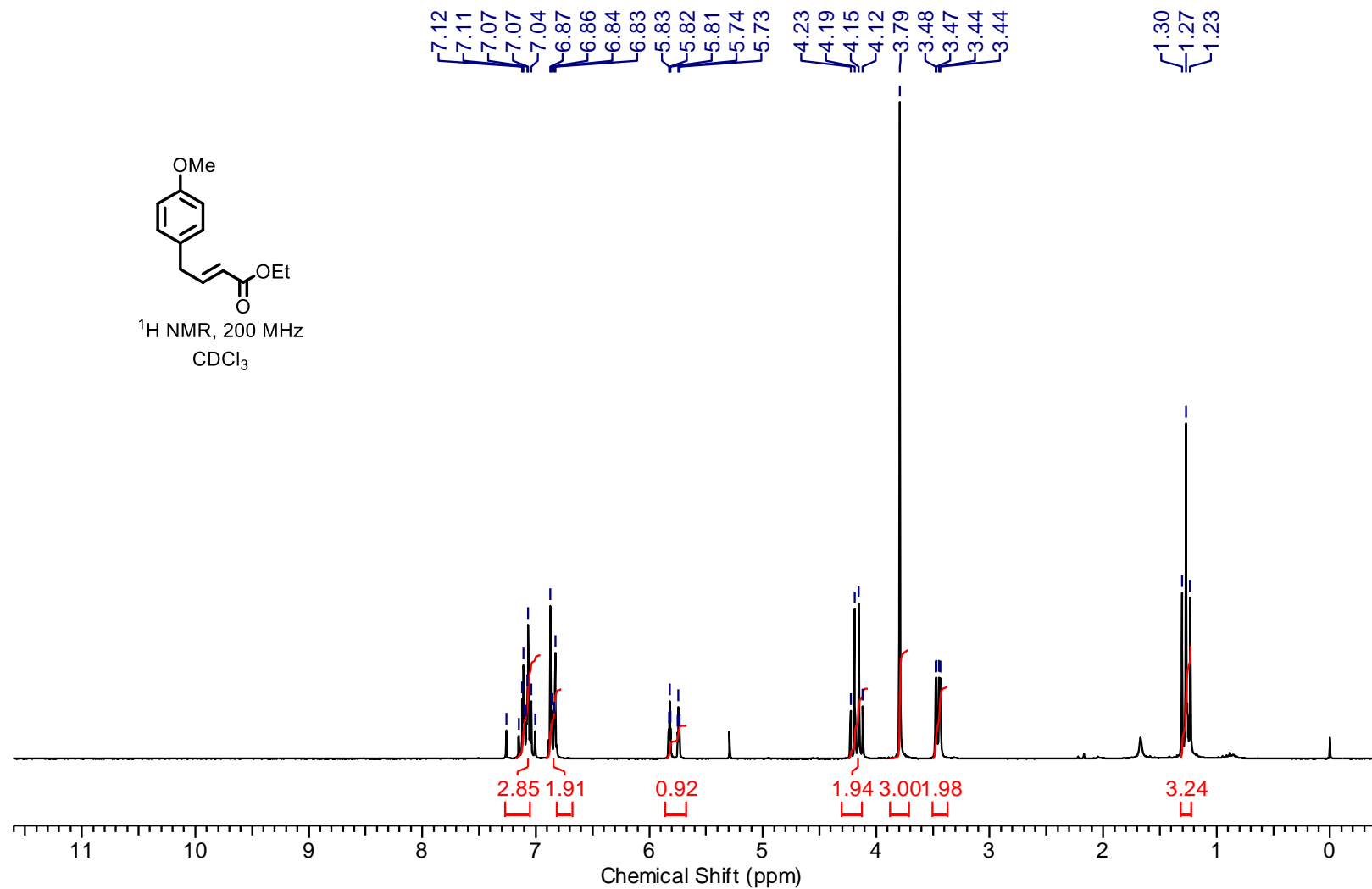
*(R)*-1-Methoxy-4-(2-((4-methoxybenzyl)oxy)but-3-yn-1-yl)benzene (**15**):



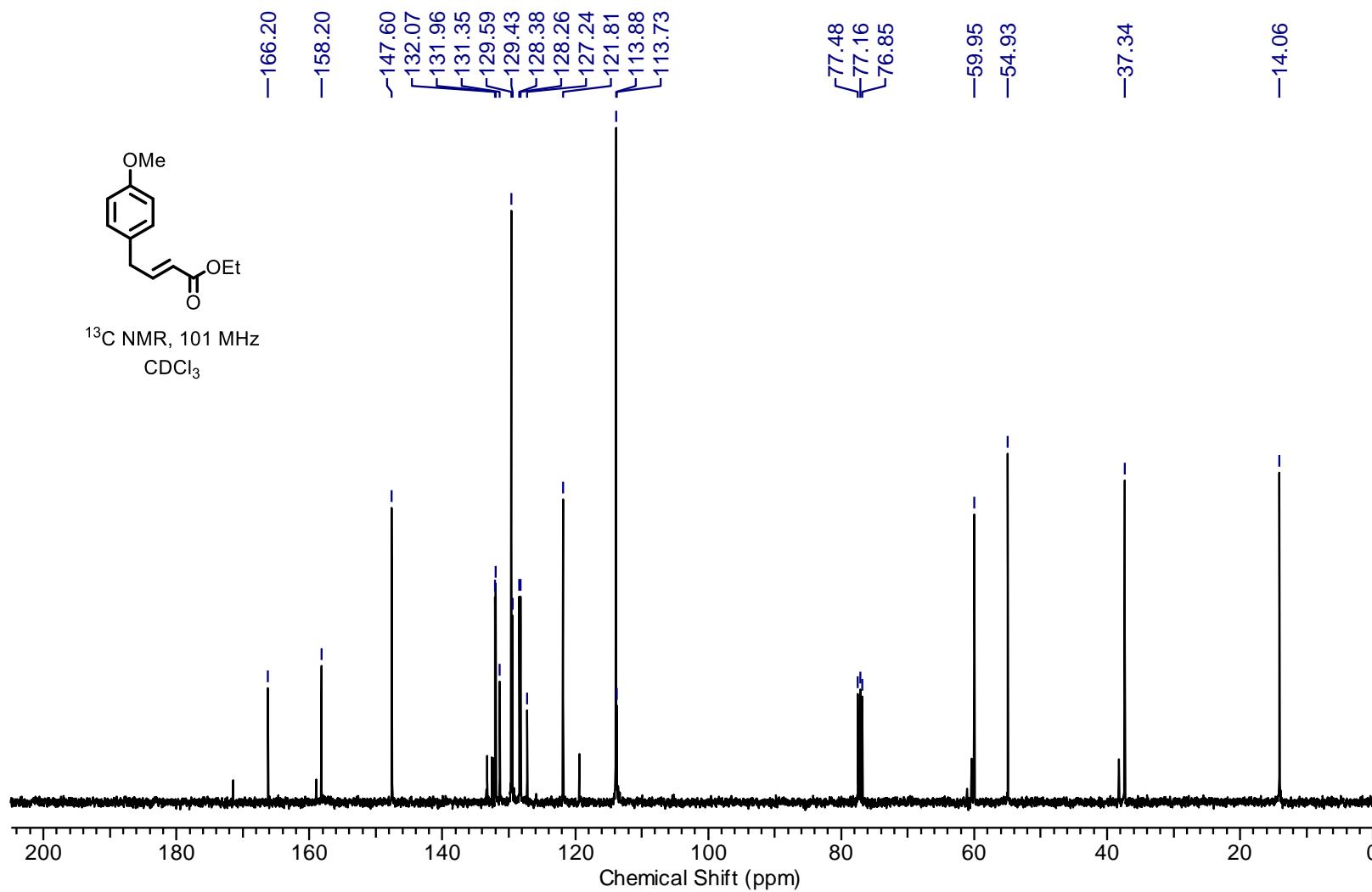
*(R)*-1-Methoxy-4-((4-methoxybenzyl)oxy)but-3-yn-1-yl)benzene (**15**):



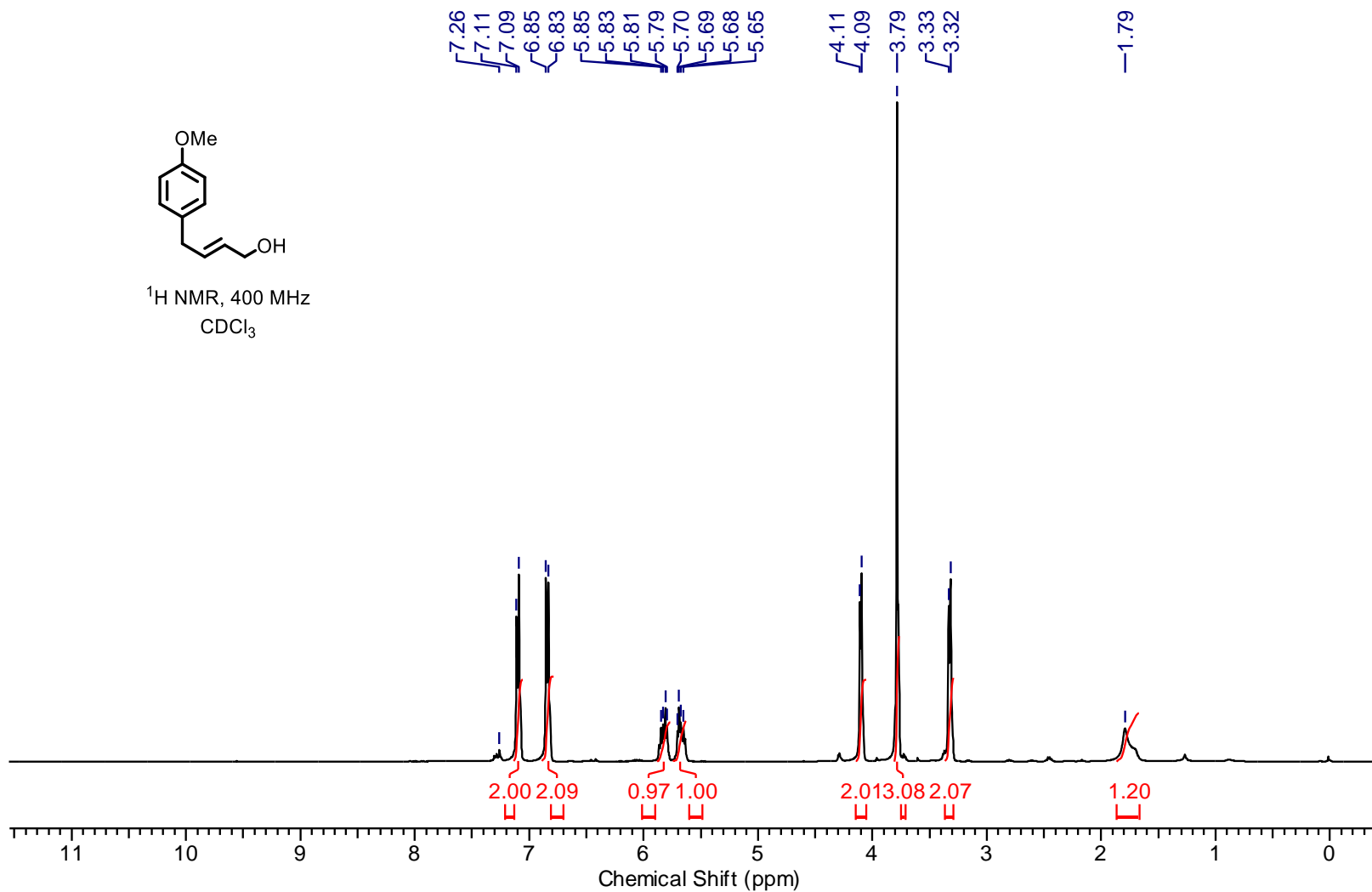
Ethyl (E)-4-(4-methoxyphenyl)but-2-enoate (**17**):



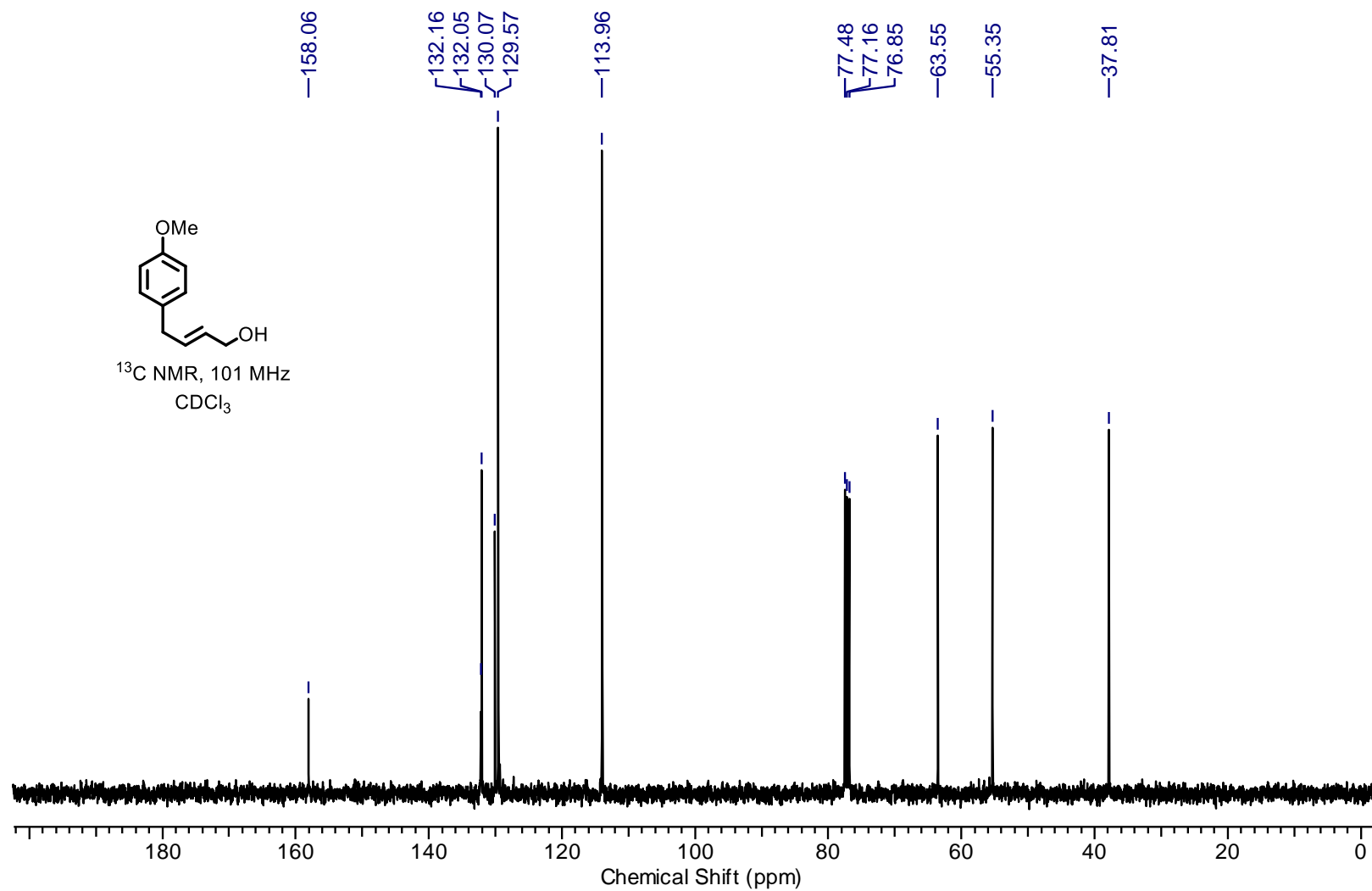
Ethyl (E)-4-(4-methoxyphenyl)but-2-enoate (**17**):



(E)-4-(4-Methoxyphenyl)but-2-en-1-ol (**S4**):

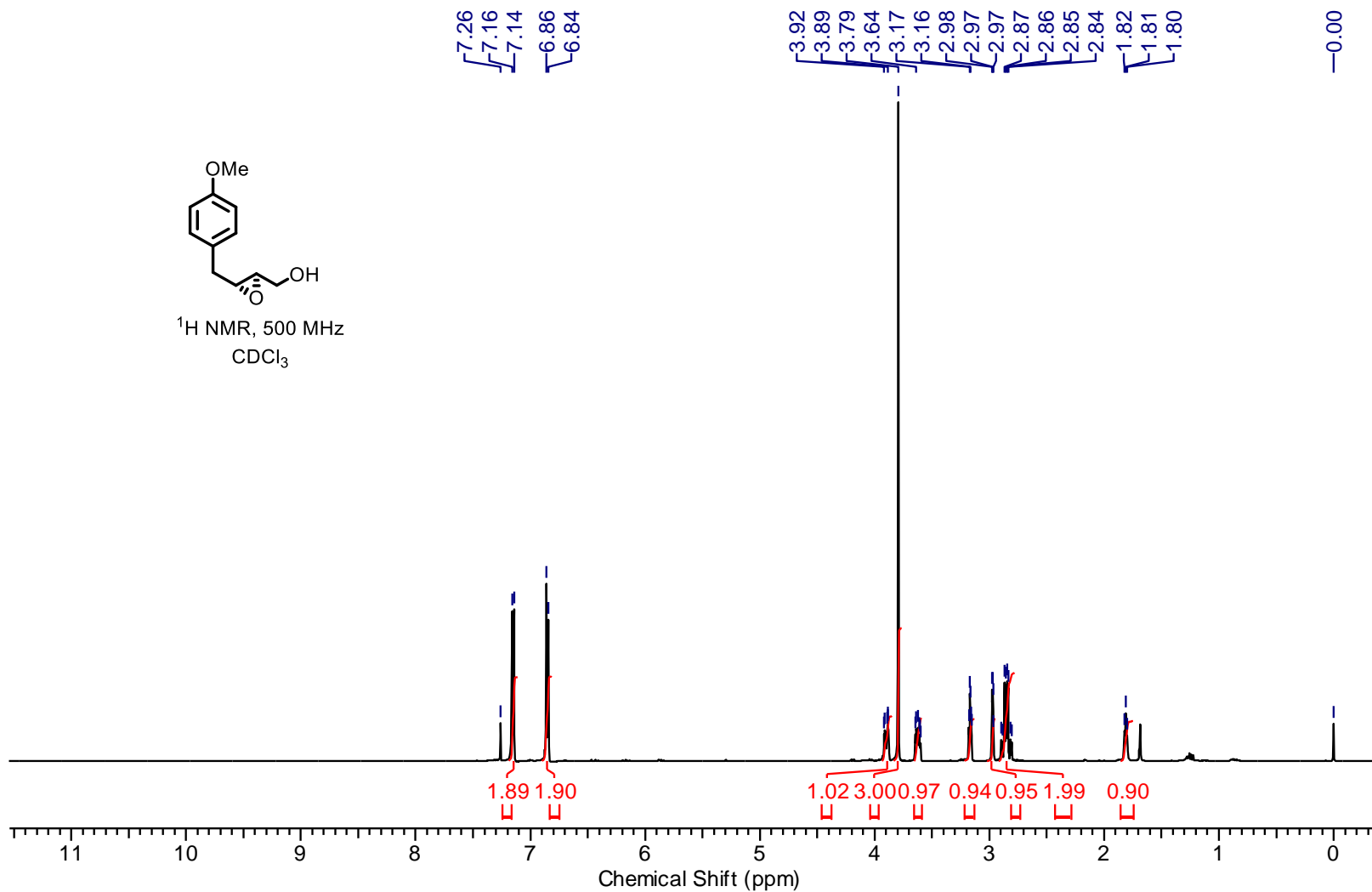


*(E)*-4-(4-Methoxyphenyl)but-2-en-1-ol (**S4**):

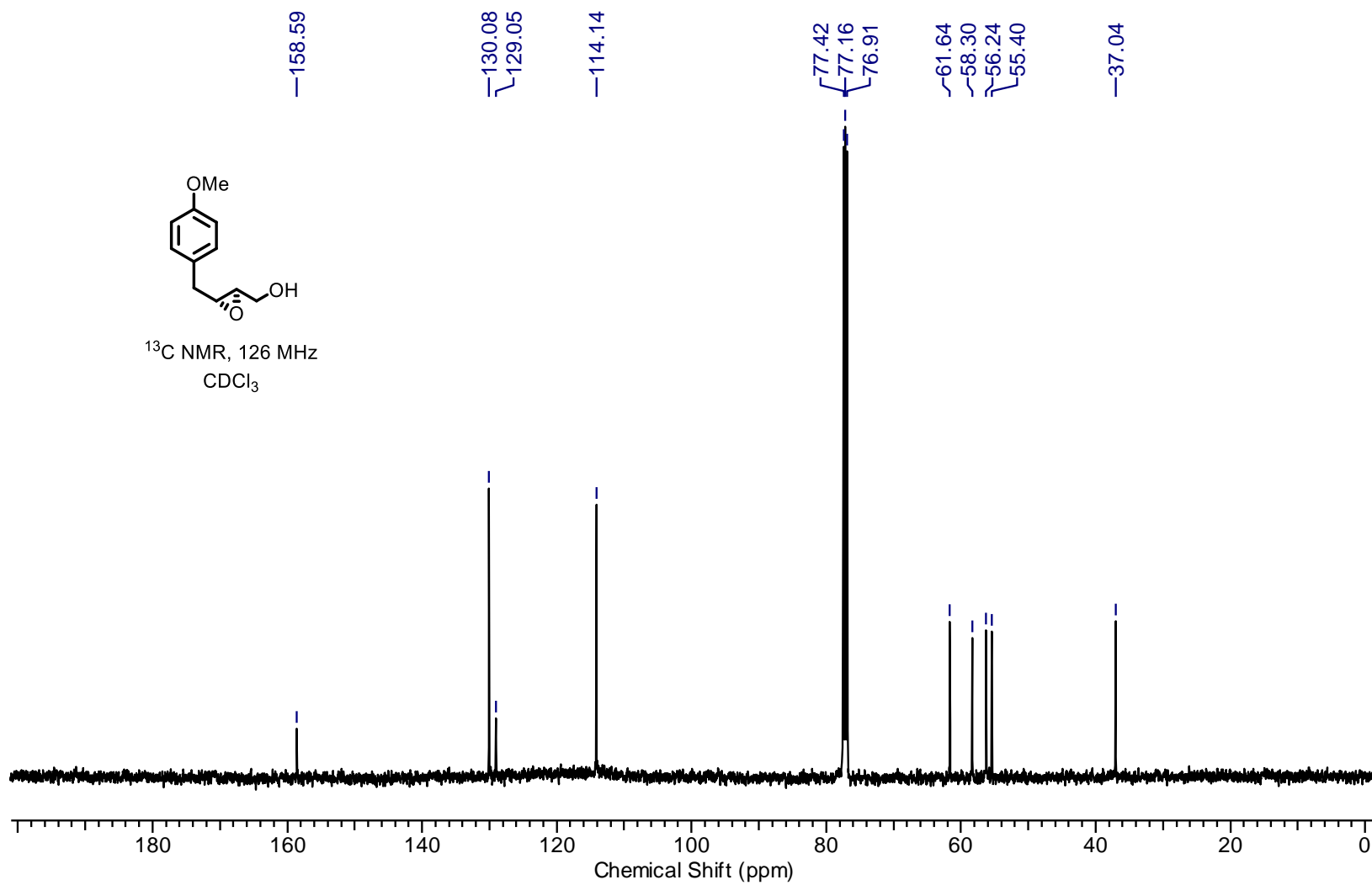




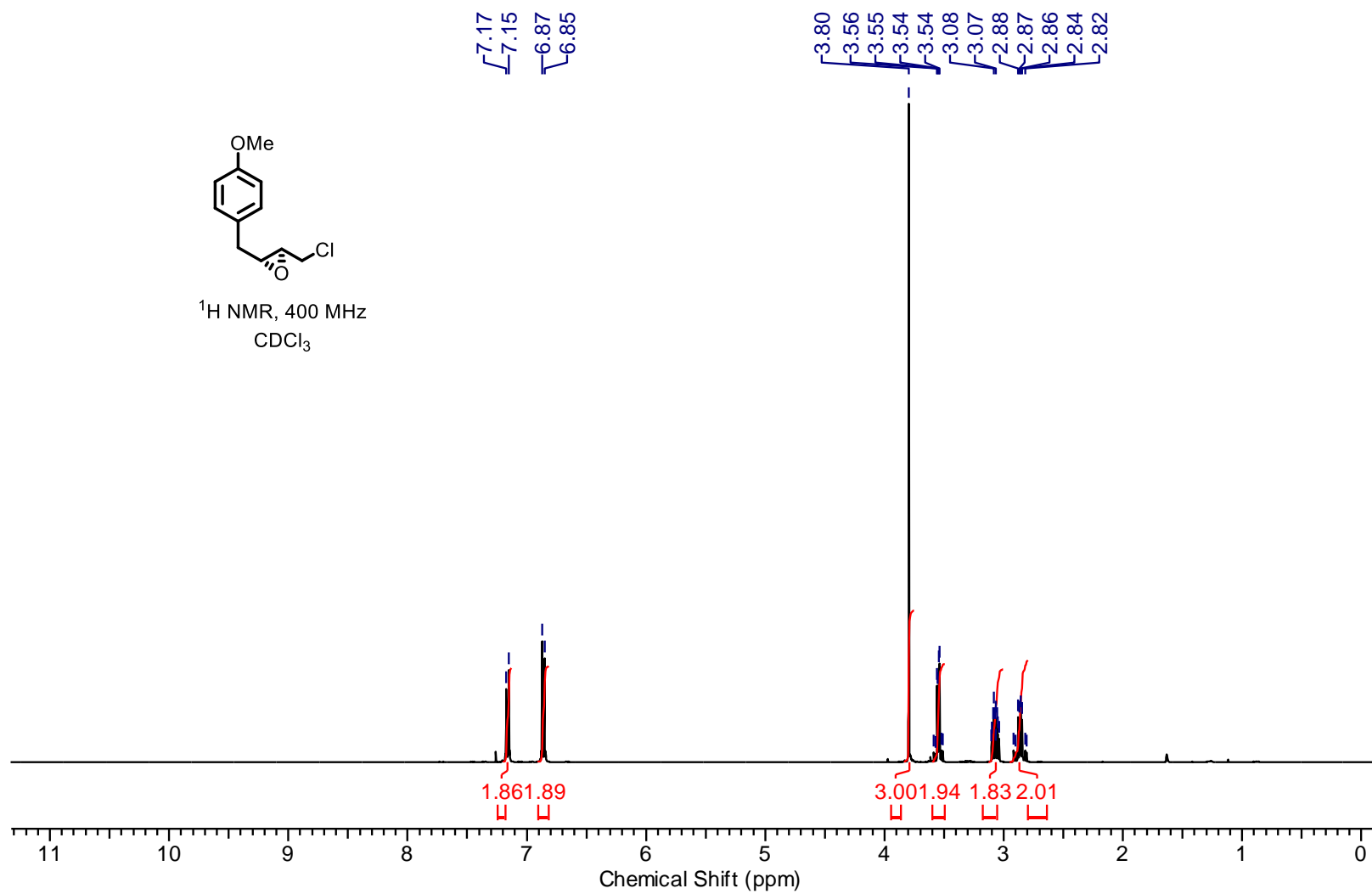
*((2R, 3R)*-3-(4-Methoxybenzyl)oxiran-2-yl)methanol (**18**):



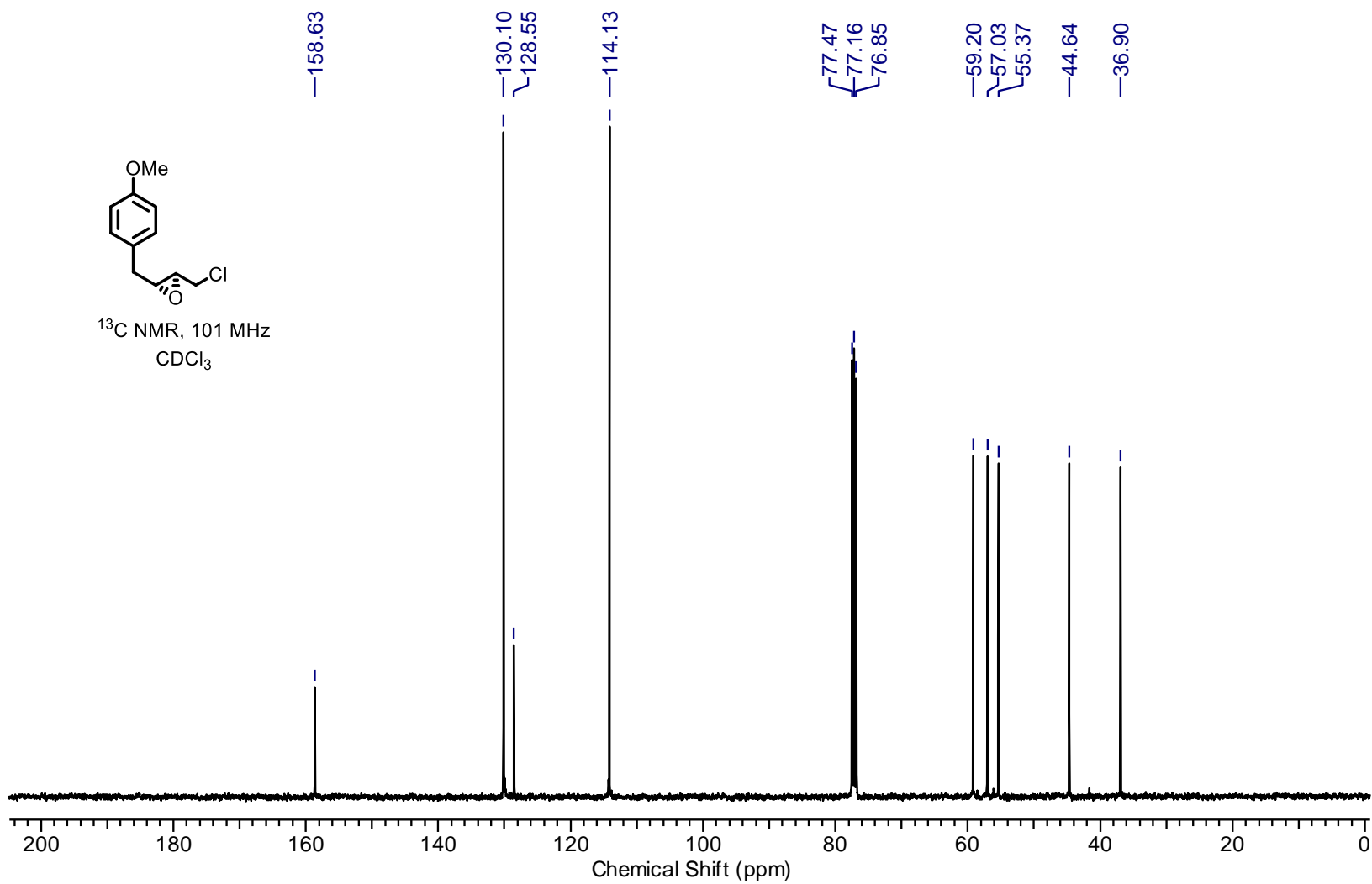
*((2R, 3R)*-3-(4-Methoxybenzyl)oxiran-2-yl)methanol (**18**):



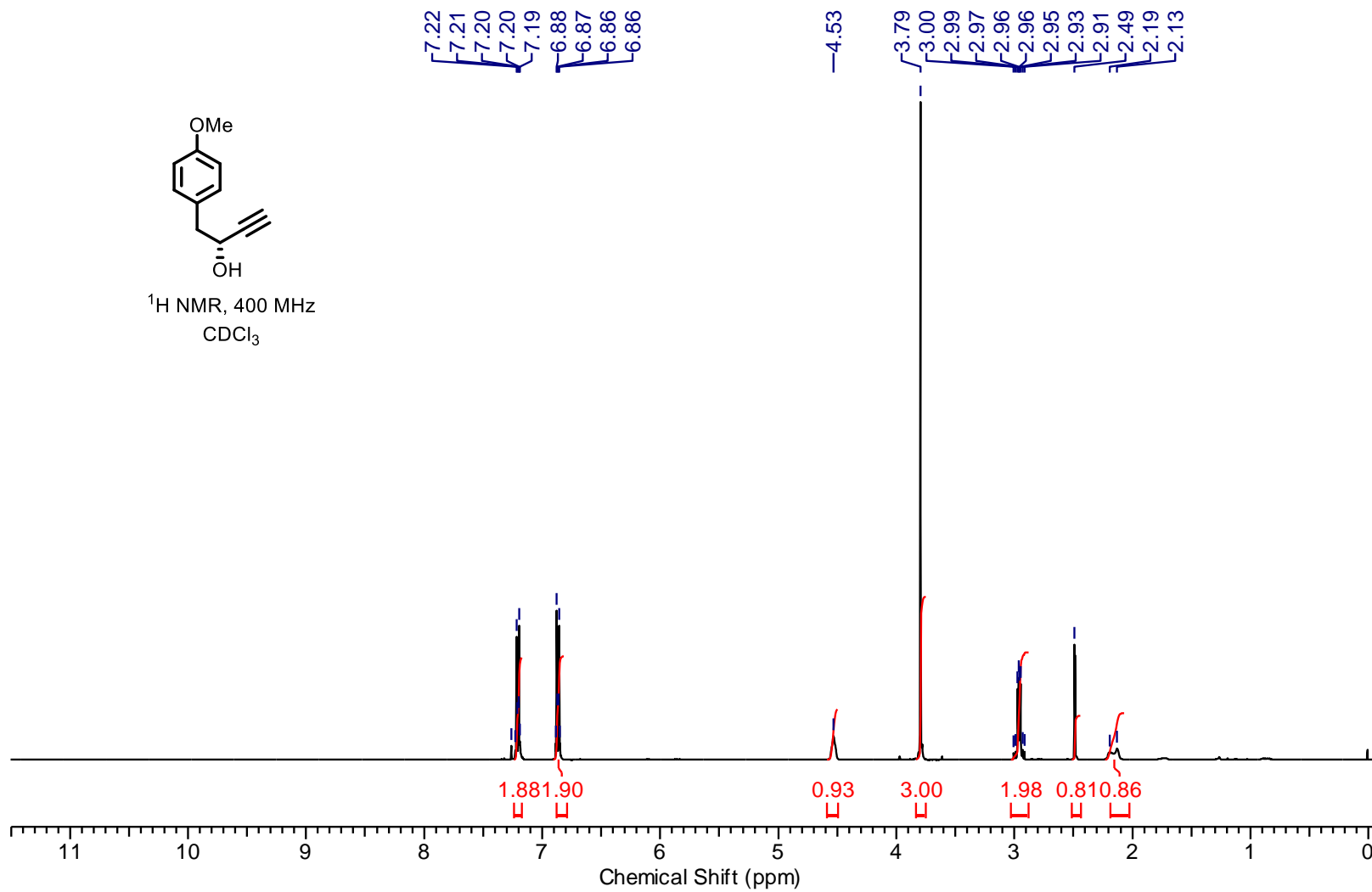
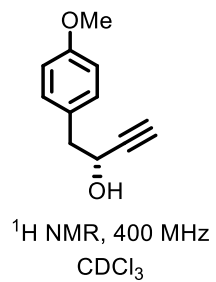
(2*S*, 3*R*)-2-(Chloromethyl)-3-(4-methoxybenzyl)oxirane (**19**):



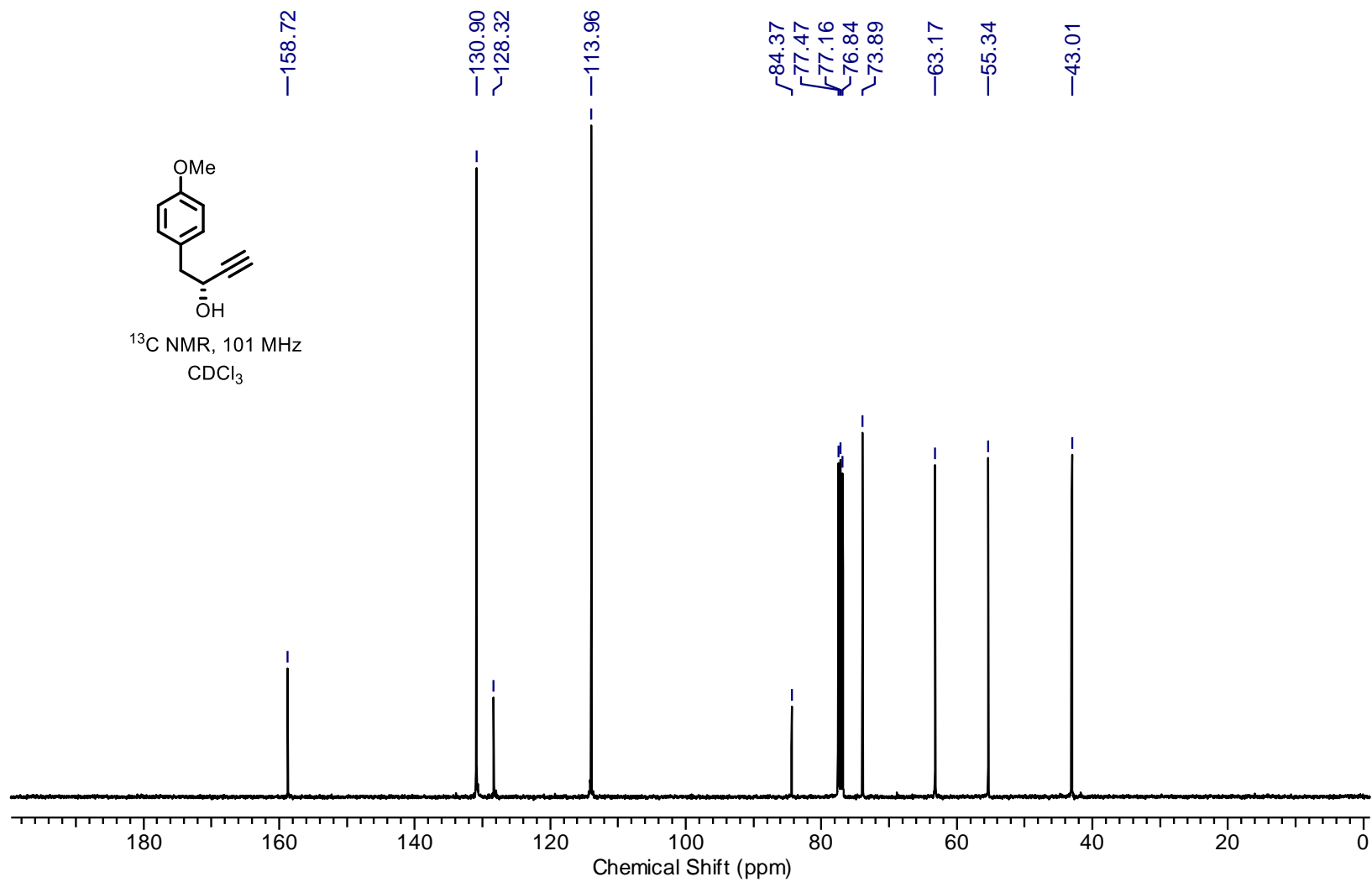
(2*S*, 3*R*)-2-(Chloromethyl)-3-(4-methoxybenzyl)oxirane (**19**):



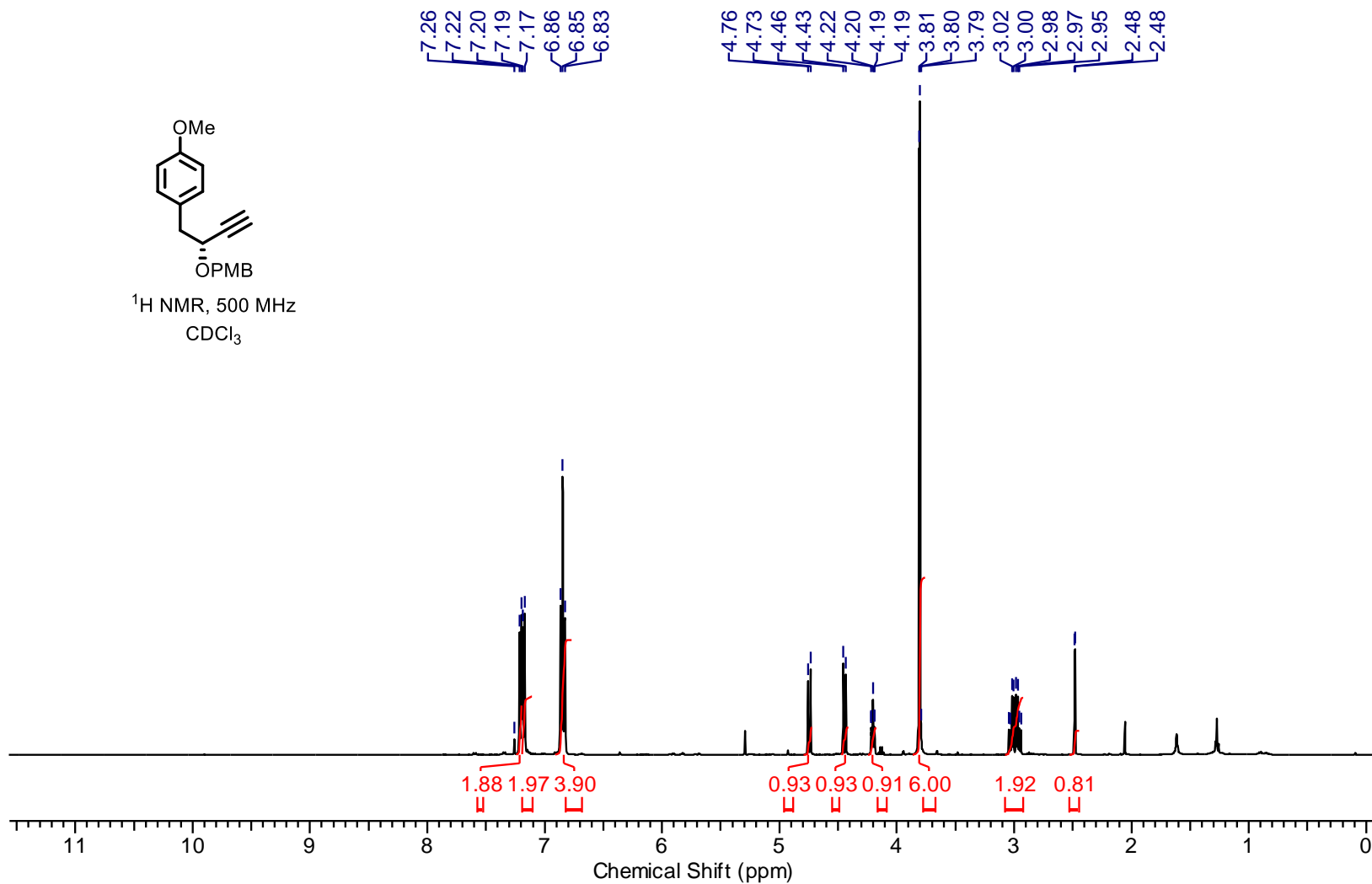
*(R)*-1-(4-Methoxyphenyl)but-3-yn-2-ol (**S5**):



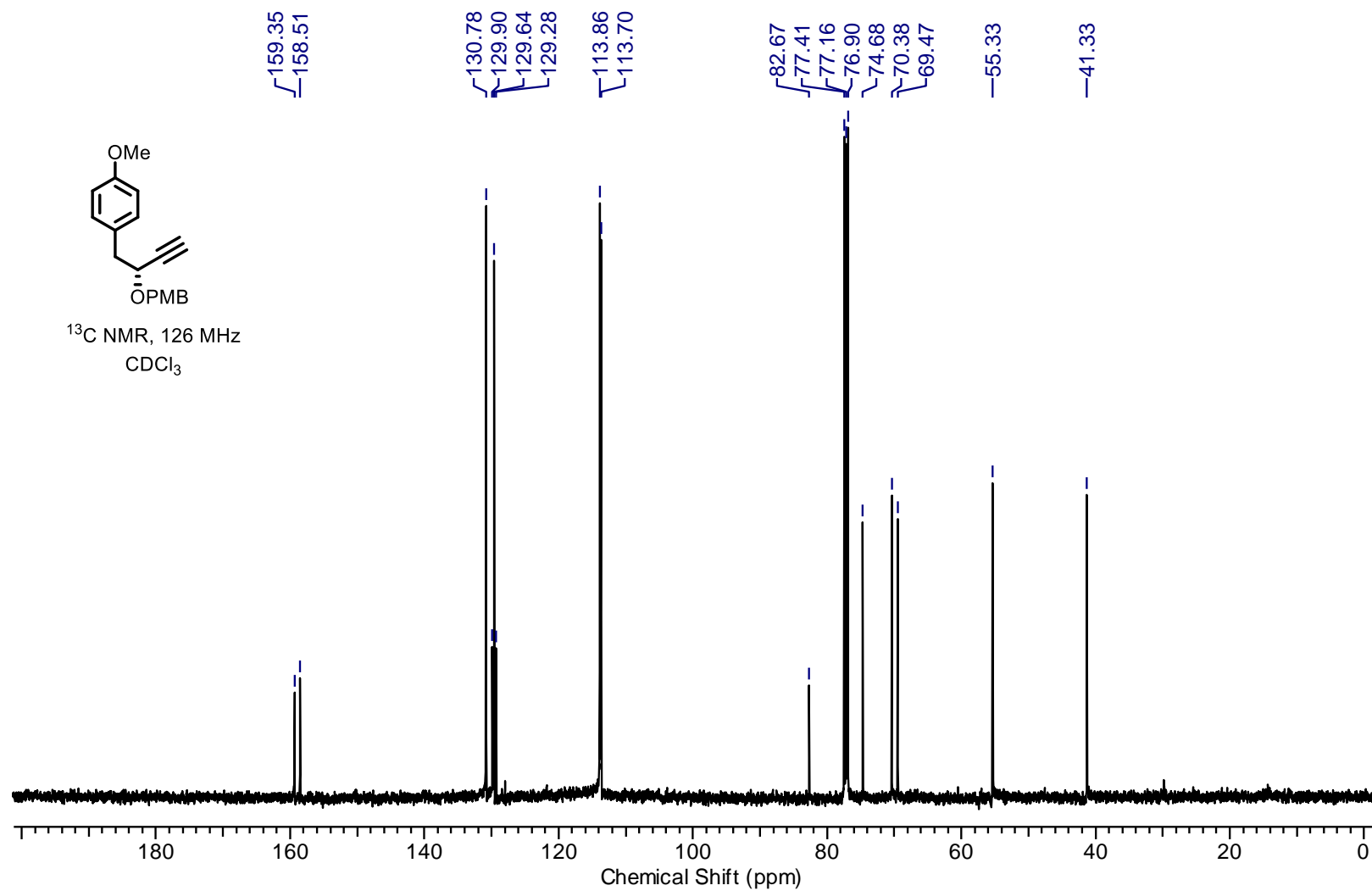
*(R)*-1-(4-Methoxyphenyl)but-3-yn-2-ol (**S5**):



*(R)*-1-Methoxy-4-(2-((4-methoxybenzyl)oxy)but-3-yn-1-yl)benzene (**15**):

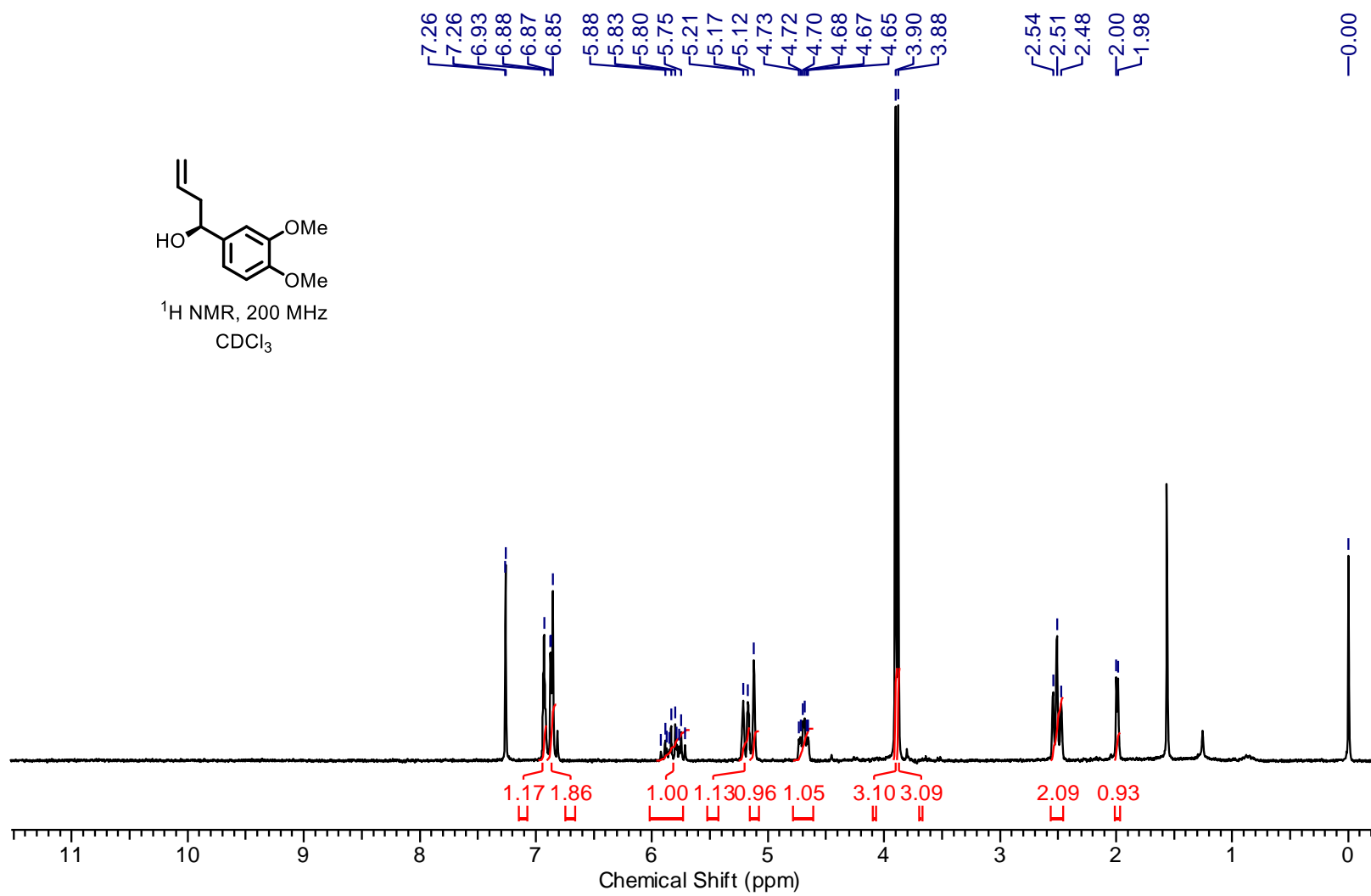


*(R)*-1-Methoxy-4-(2-((4-methoxybenzyl)oxy)but-3-yn-1-yl)benzene (**15**):

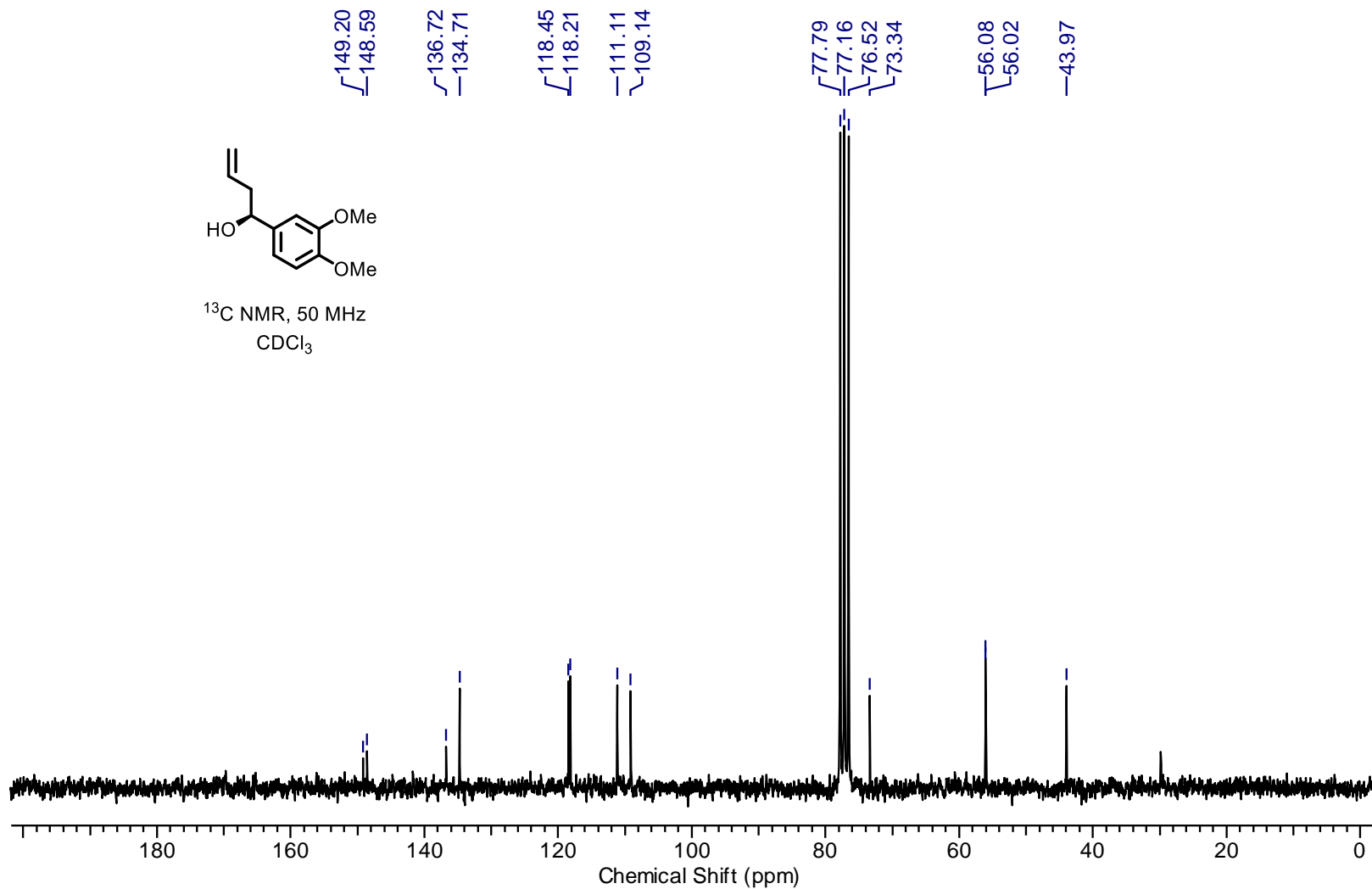




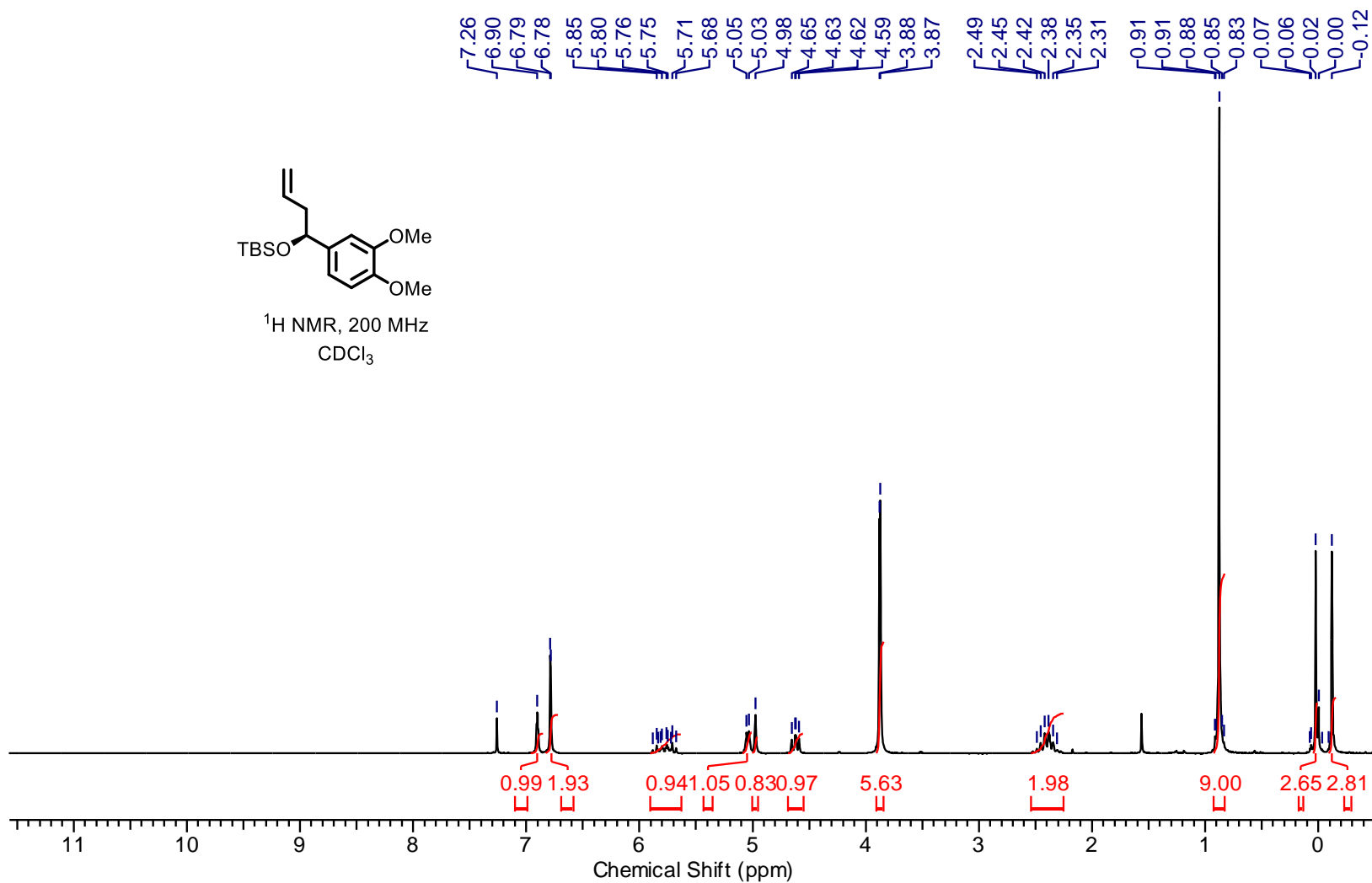
*(S)*-1-(3,4-Dimethoxyphenyl)but-3-en-1-ol (**20**):



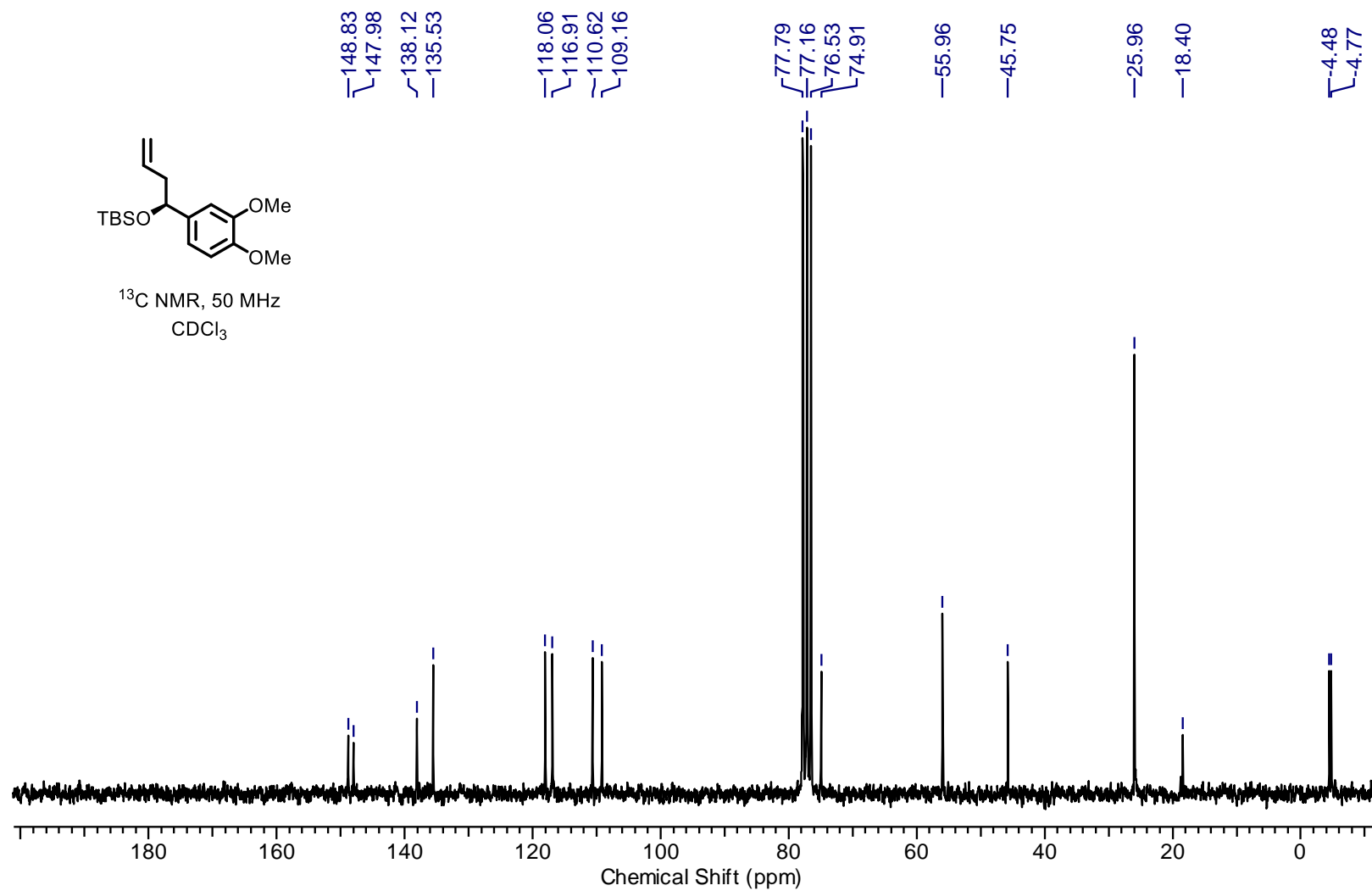
(S)-1-(3,4-Dimethoxyphenyl)but-3-en-1-ol (**20**):



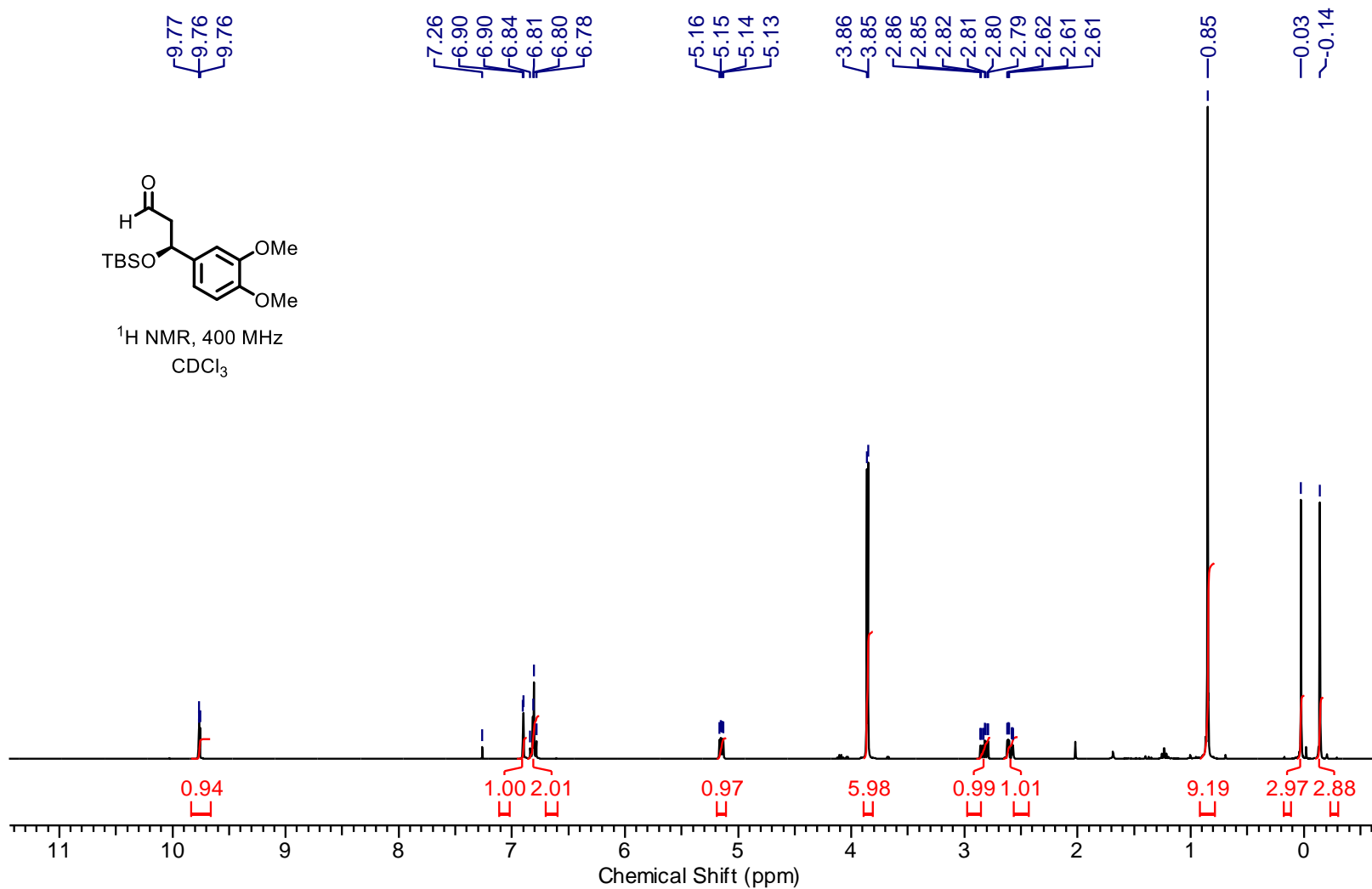
(*S*)-Tert-butyl((1-(3,4-dimethoxyphenyl)but-3-en-1-yl)oxy)dimethylsilane (**S6**):



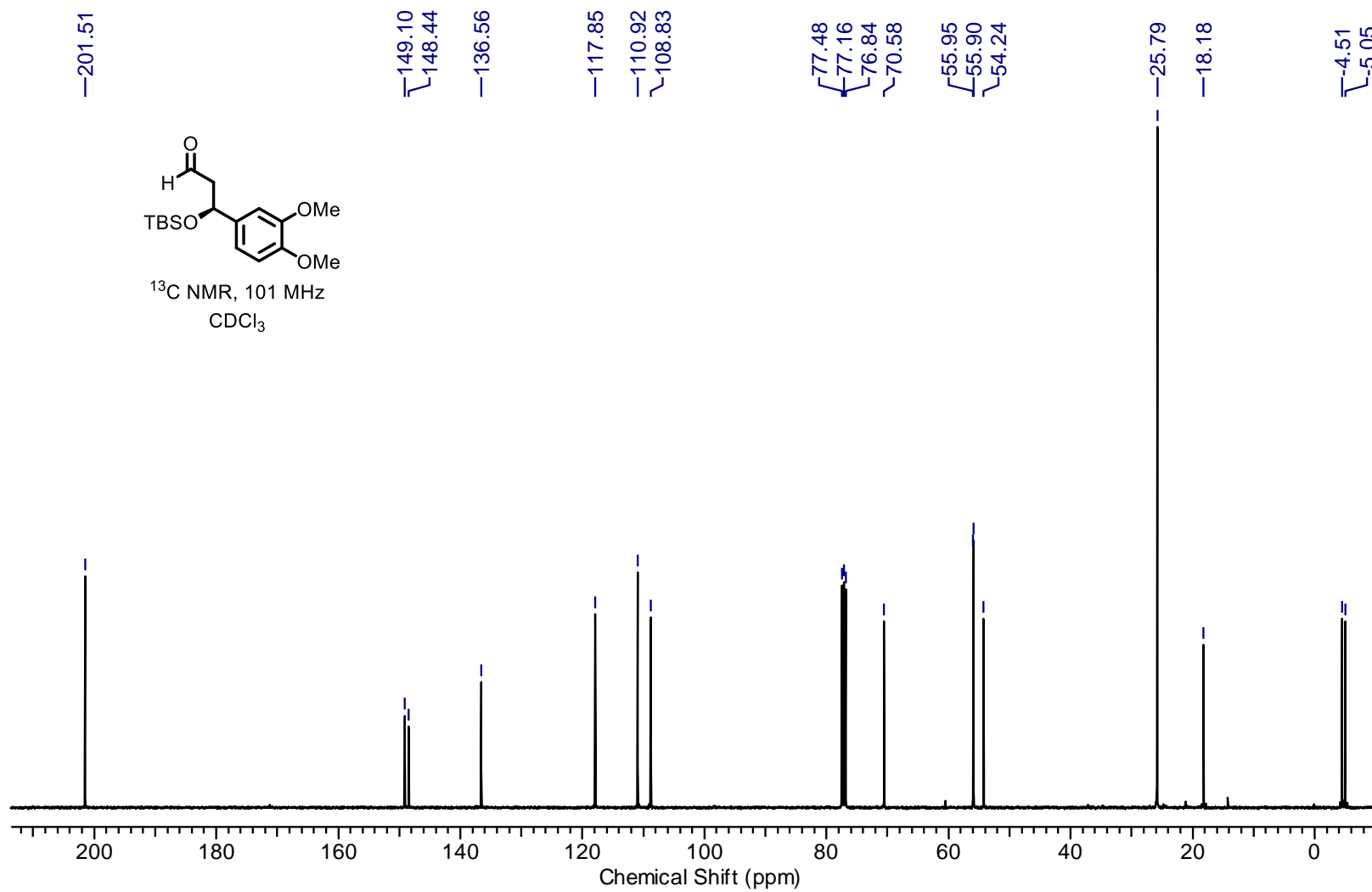
*(S)*-Tert-butyl((1-(3,4-dimethoxyphenyl)but-3-en-1-yl)oxy)dimethylsilane (**S6**):



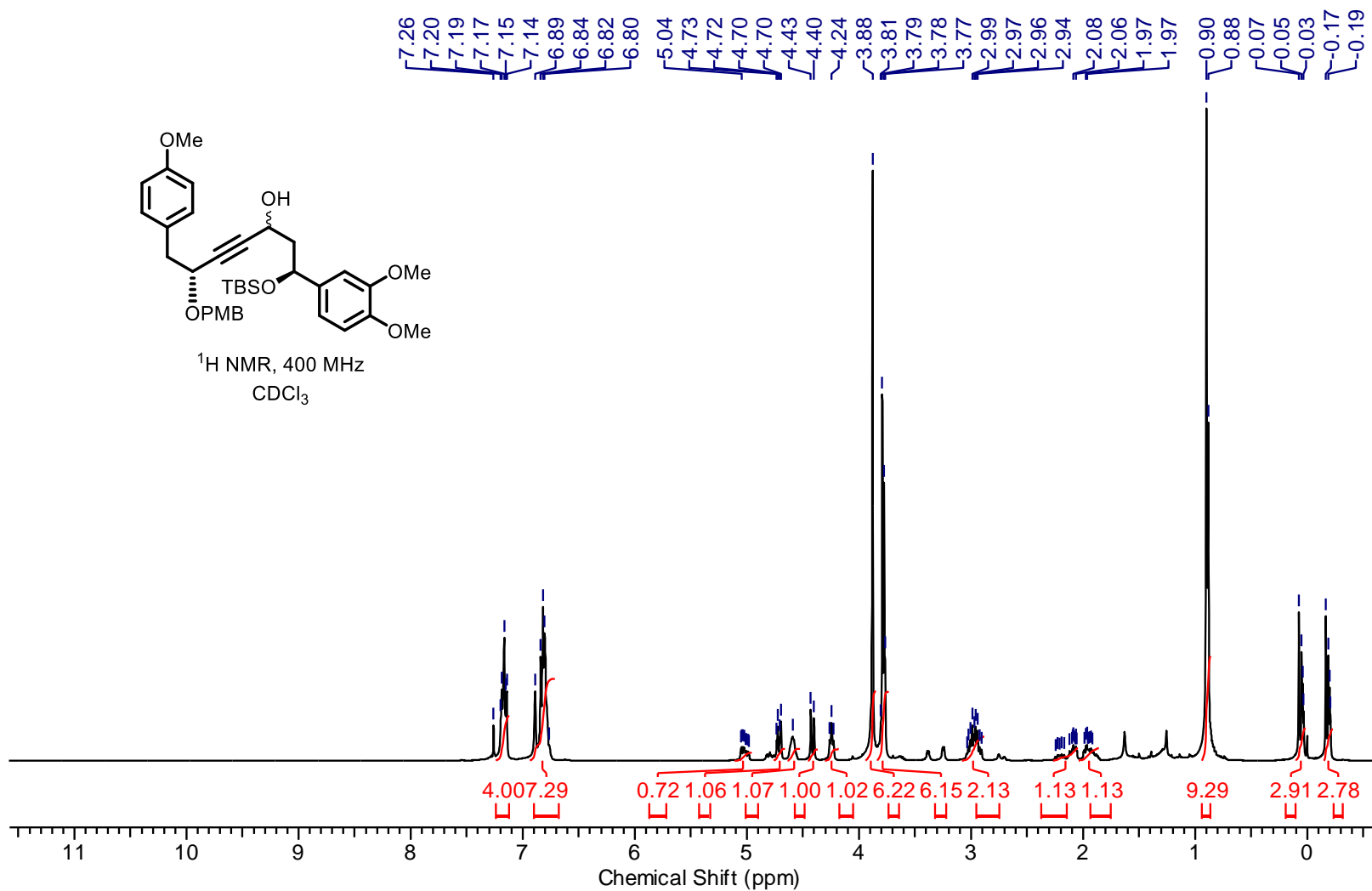
(S)-3-((Tert-butyl dimethylsilyl)oxy)-3-(3,4-dimethoxyphenyl)propanal (**16**):



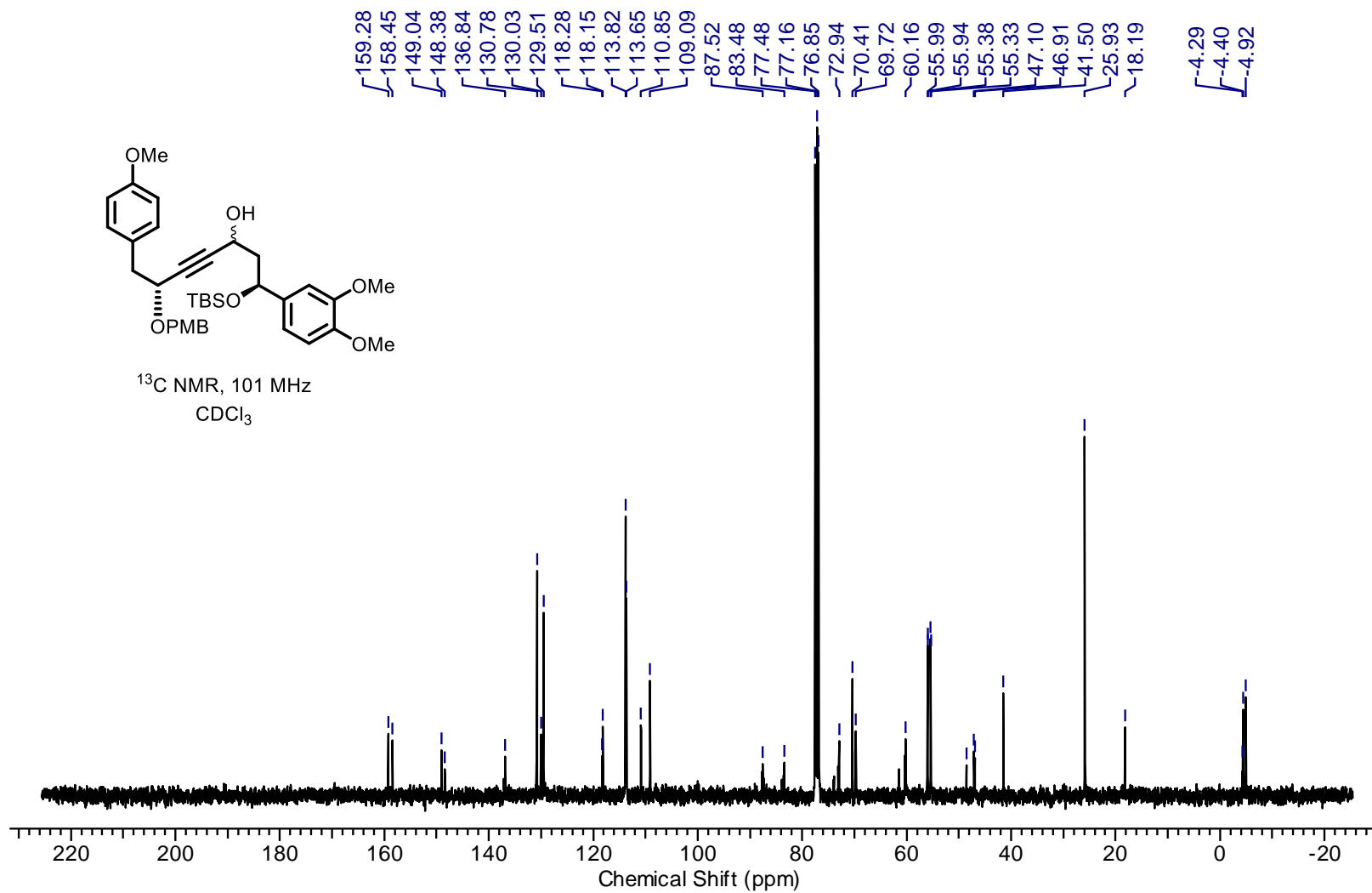
(*S*)-3-((*Tert*-butyldimethylsilyl)oxy)-3-(3,4-dimethoxyphenyl)propanal (**16**):



(1*S*, 6*R*)-1-((*Tert*-butyldimethylsilyl)oxy)-1-(3,4-dimethoxyphenyl)-6-((4-methoxybenzyl)-oxy)-7-(4-methoxyphenyl)hept-4-yn-3-ol (**21**):

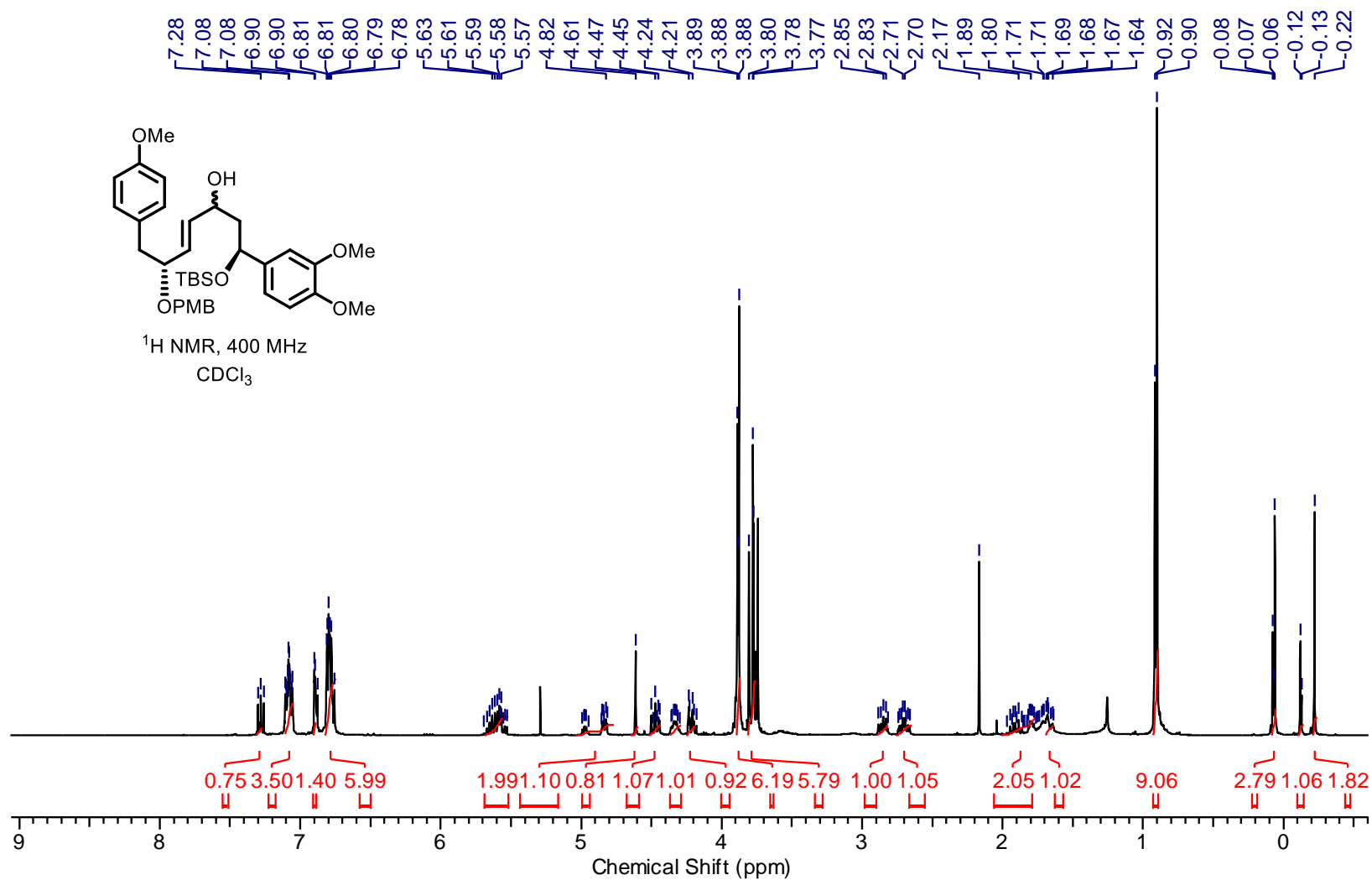


(1*S*, 6*R*)-1-((*Tert*-butyldimethylsilyl)oxy)-1-(3,4-dimethoxyphenyl)-6-((4-methoxybenzyl)-oxy)-7-(4-methoxyphenyl)hept-4-yn-3-ol (**21**):

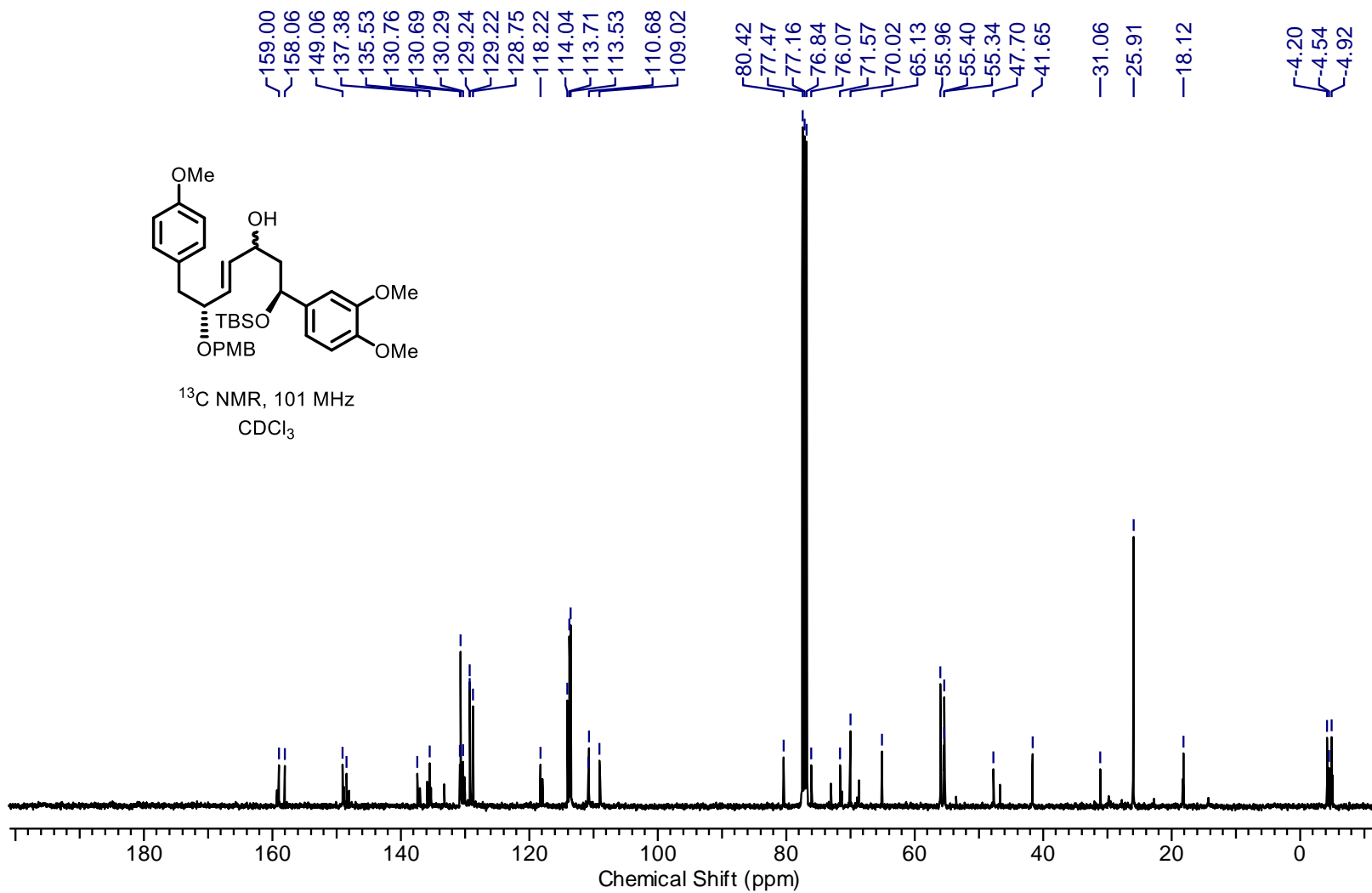




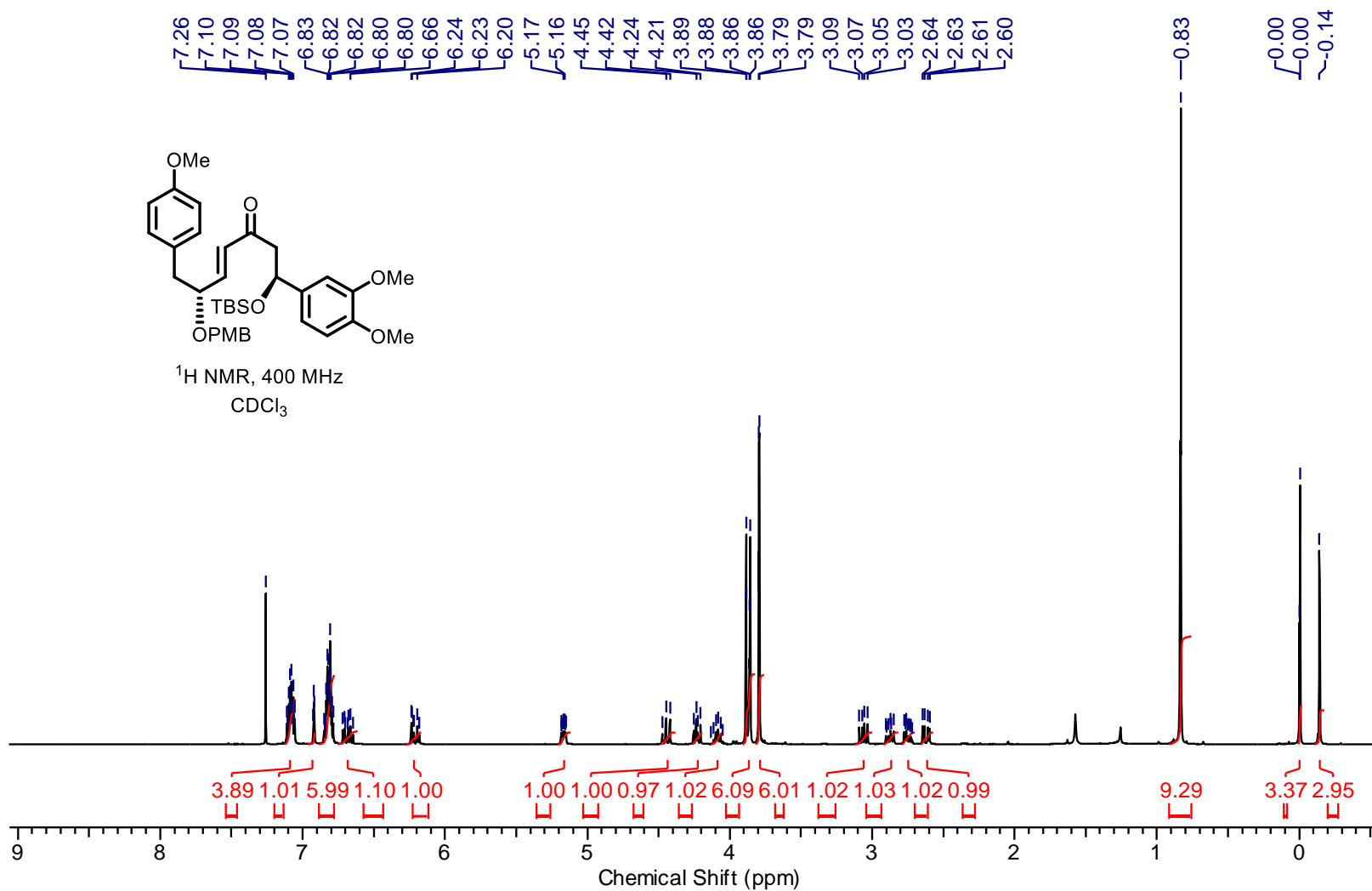
(1*S*, 6*R*, *E*)-1-((*Tert*-butyldimethylsilyl)oxy)-1-(3,4-dimethoxyphenyl)-6-((4-methoxybenzyl)-oxy)-7-(4-methoxyphenyl)hept-4-en-3-ol (**S7**):



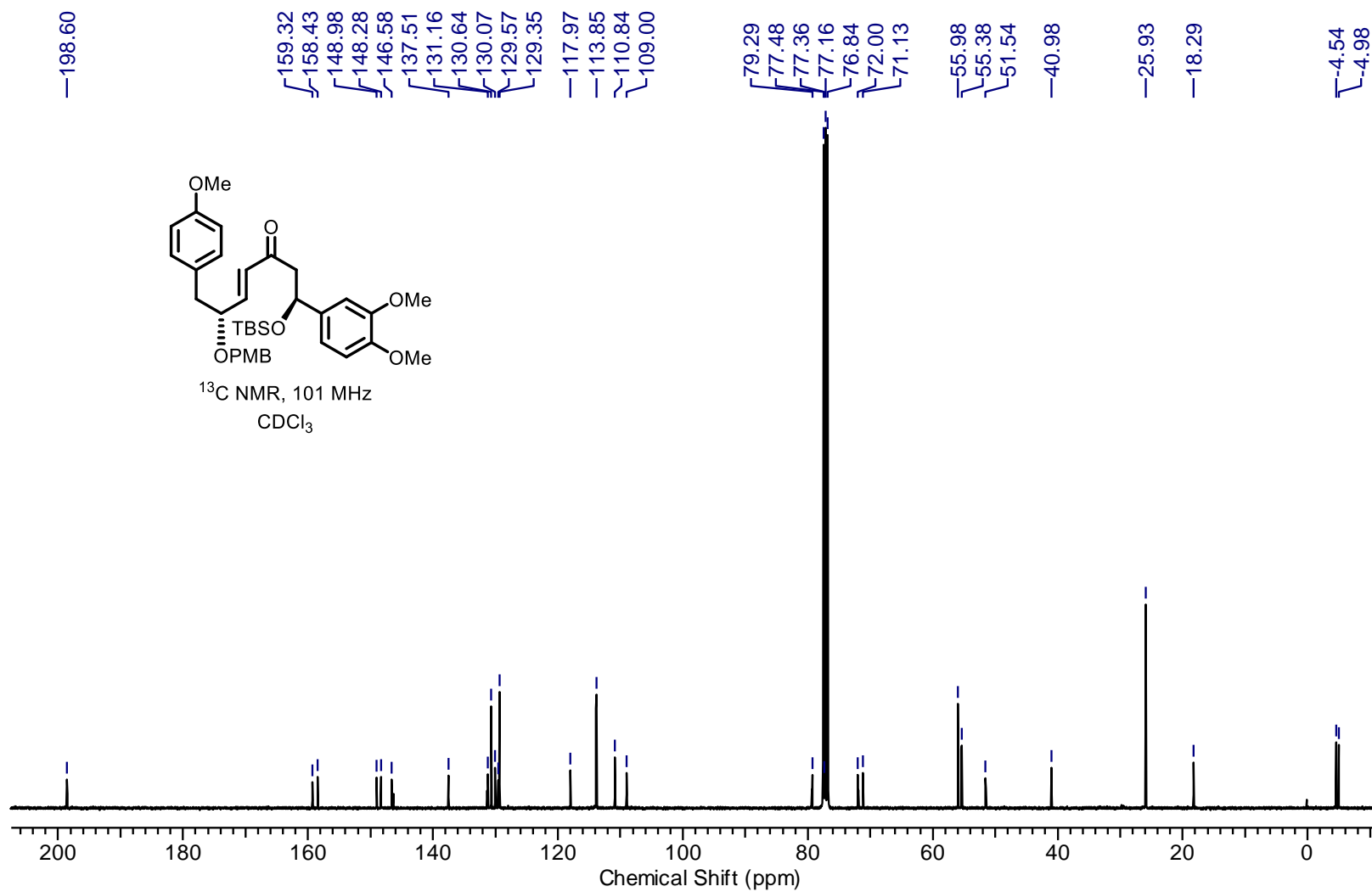
(1*S*, 6*R*, *E*)-1-((*Tert*-butyldimethylsilyl)oxy)-1-(3,4-dimethoxyphenyl)-6-((4-methoxybenzyl)-oxy)-7-(4-methoxyphenyl)hept-4-en-3-ol (**S7**):



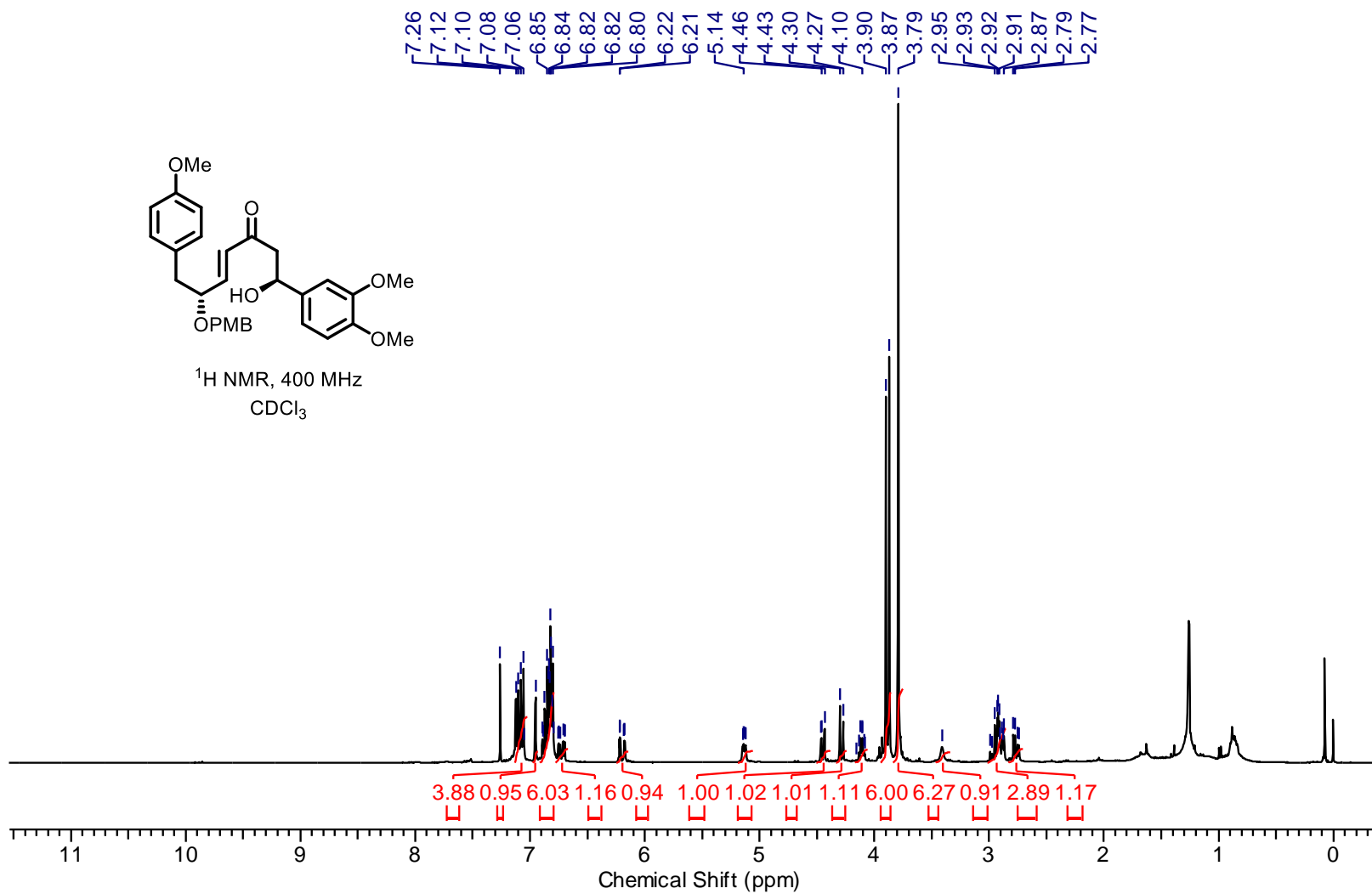
(1*S*, 6*R*, *E*)-1-((*Tert*-butyldimethylsilyl)oxy)-1-(3,4-dimethoxyphenyl)-6-((4-methoxybenzyl)-oxy)-7-(4-methoxyphenyl)hept-4-en-3-one (**14**):



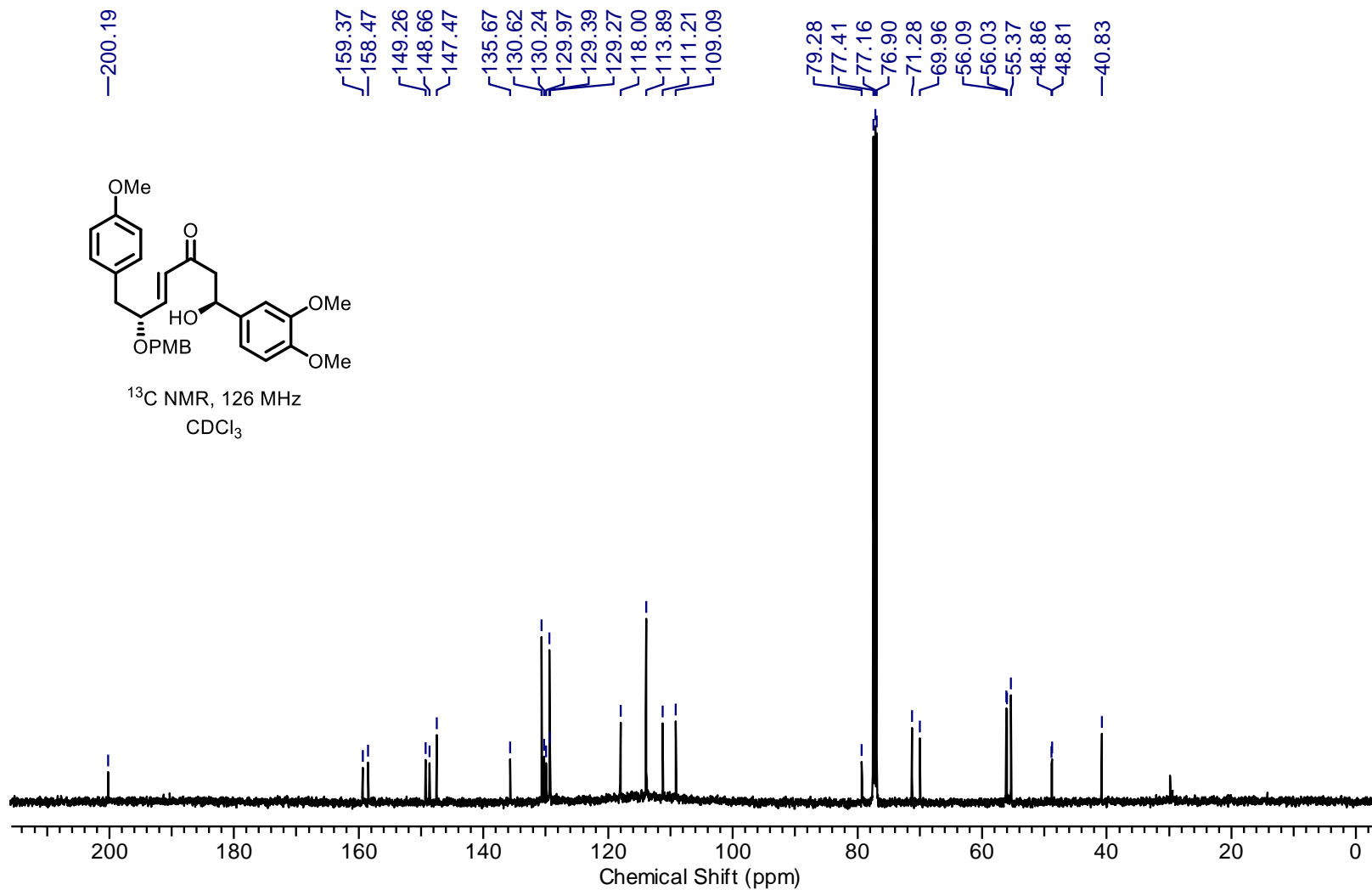
(1*S*, 6*R*, *E*)-1-((*Tert*-butyldimethylsilyl)oxy)-1-(3,4-dimethoxyphenyl)-6-((4-methoxybenzyl)-oxy)-7-(4-methoxyphenyl)hept-4-en-3-one (**14**):



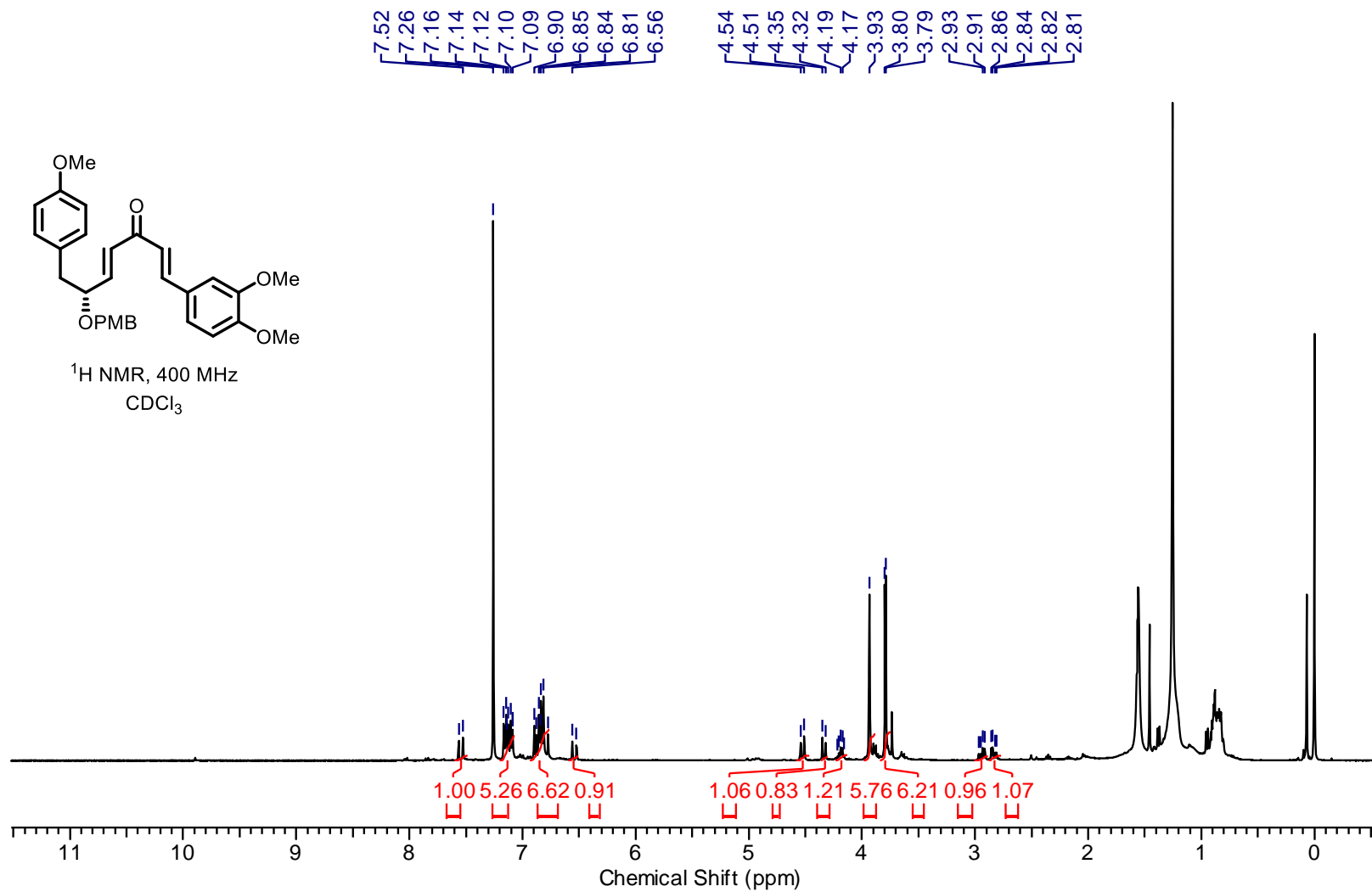
(1*S*, 6*R*, *E*)-1-(3,4-Dimethoxyphenyl)-1-hydroxy-6-((4-methoxybenzyl)oxy)-7-(4-methoxyphenyl)-hept-4-en-3-one (**22**):



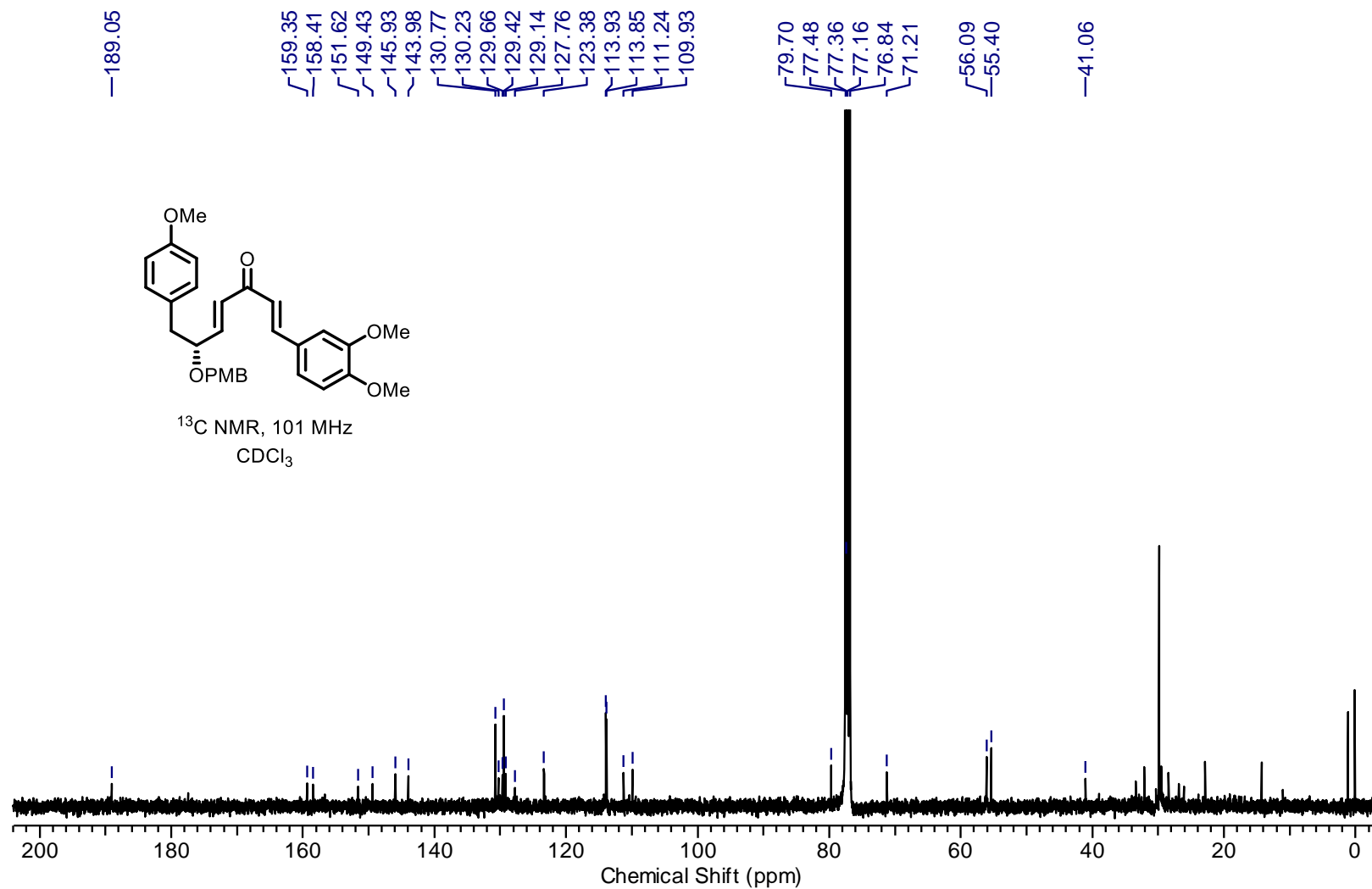
(1*S*, 6*R*, *E*)-1-(3,4-Dimethoxyphenyl)-1-hydroxy-6-((4-methoxybenzyl)oxy)-7-(4-methoxyphenyl)-hept-4-en-3-one (**22**):



(*R*, *1E*, *4E*)-1-(3,4-Dimethoxyphenyl)-6-((4-methoxybenzyl)oxy)-7-(4-methoxyphenyl)hepta-1,4-dien-3-one (**24**):

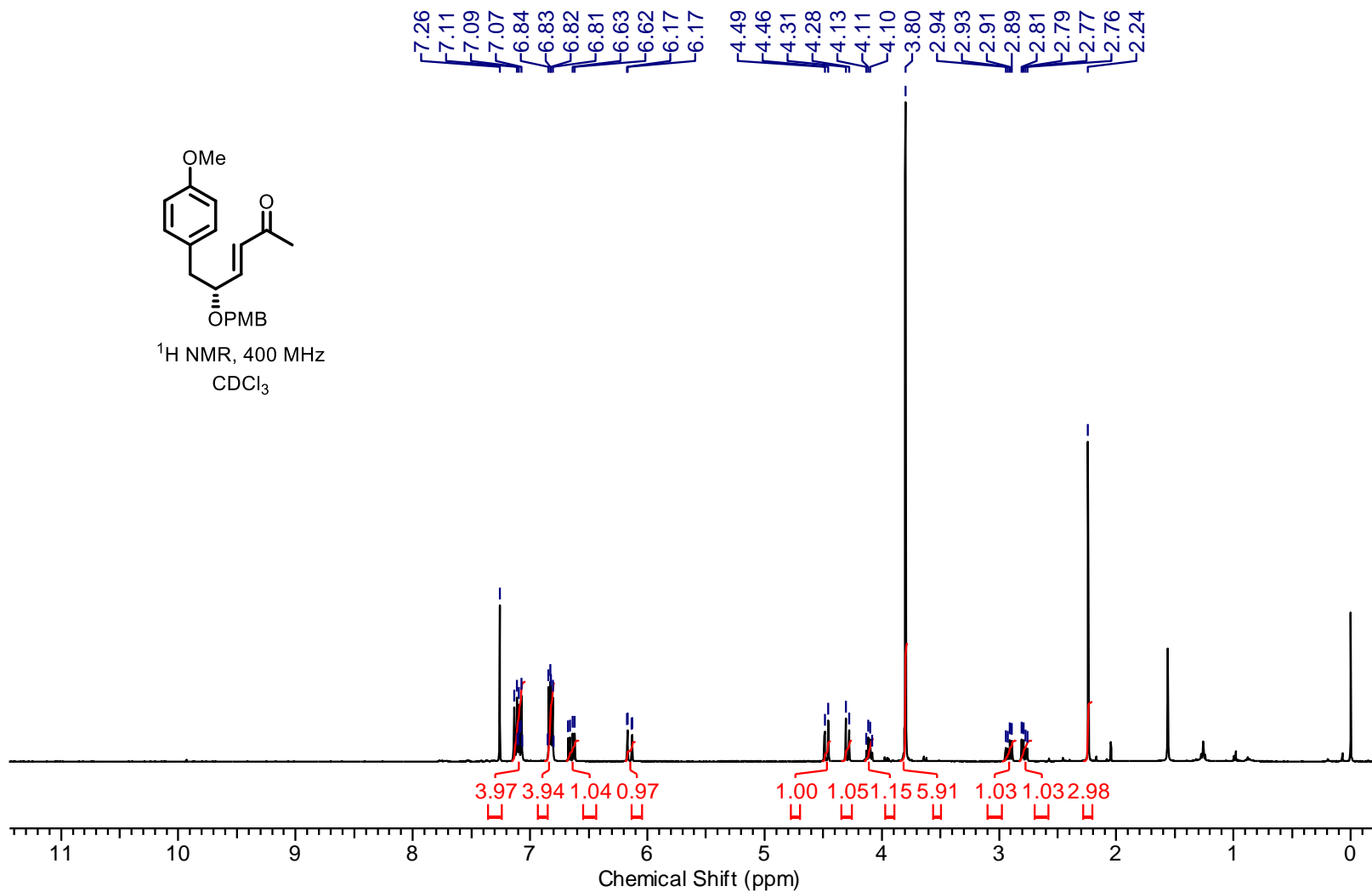


(*R*, *1E*, *4E*)-1-(3,4-Dimethoxyphenyl)-6-((4-methoxybenzyl)oxy)-7-(4-methoxyphenyl)hepta-1,4-dien-3-one (**24**):

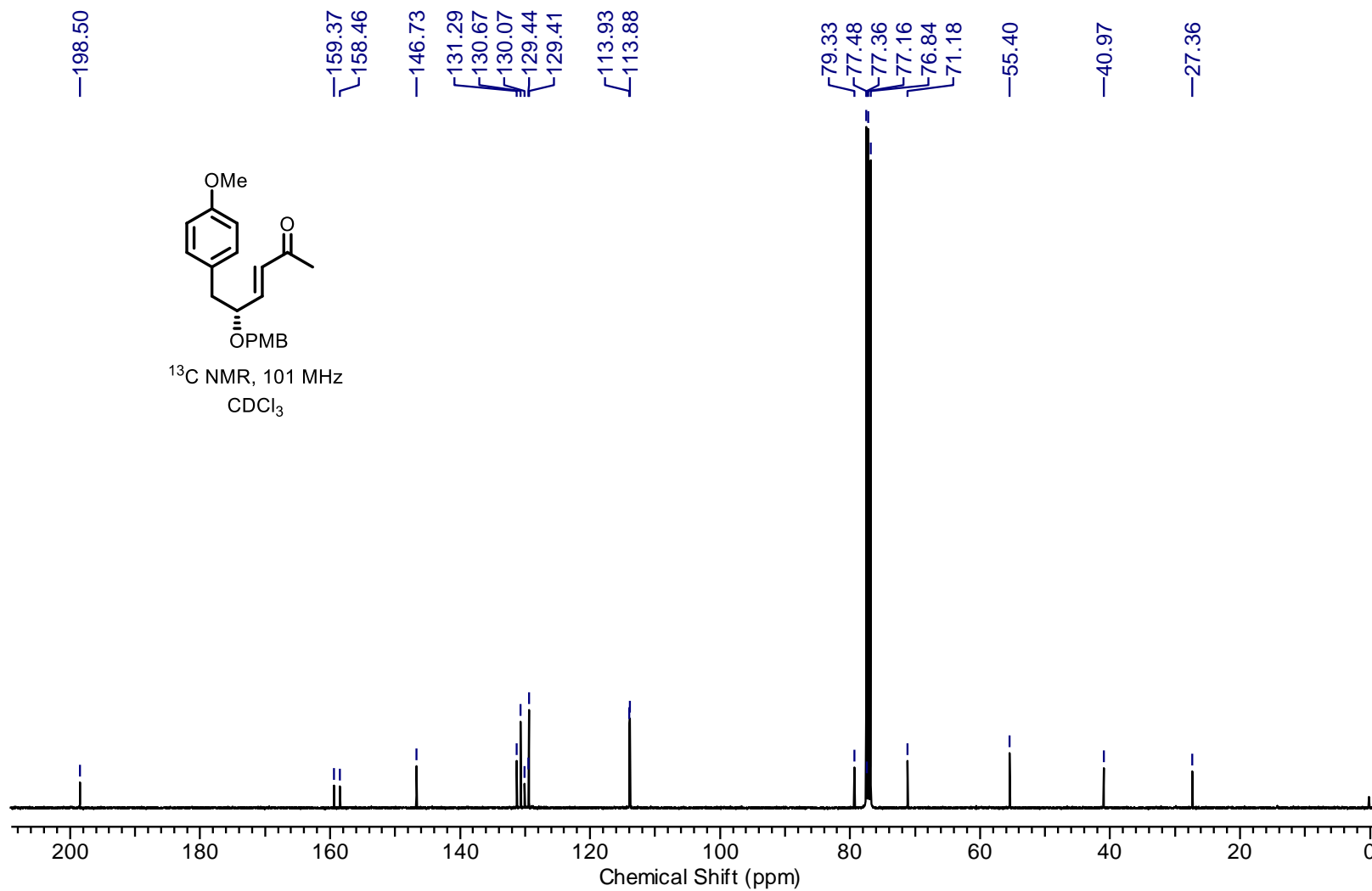




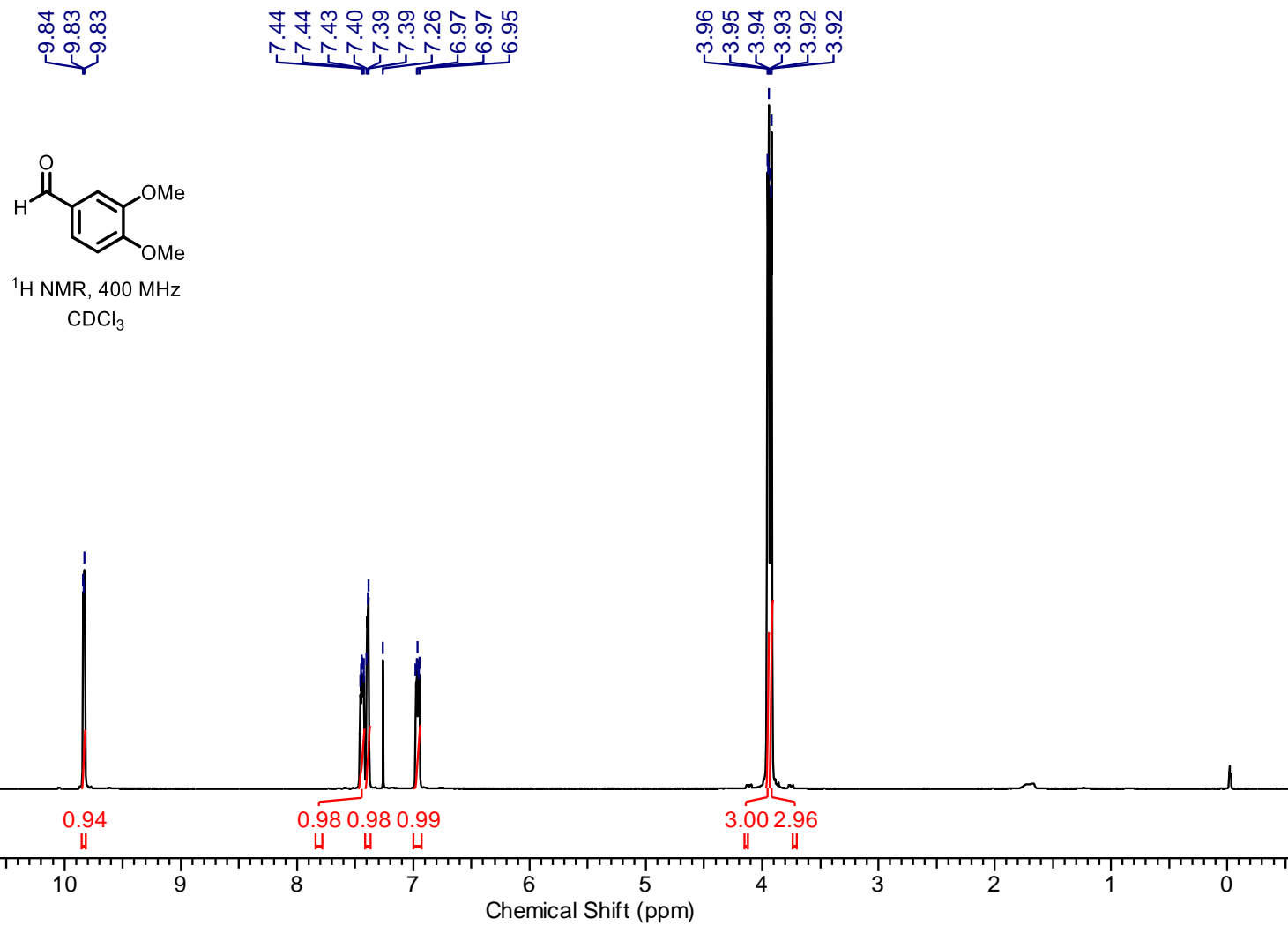
(R, E)-5-((4-Methoxybenzyl)oxy)-6-(4-methoxyphenyl)hex-3-en-2-one (**25**):



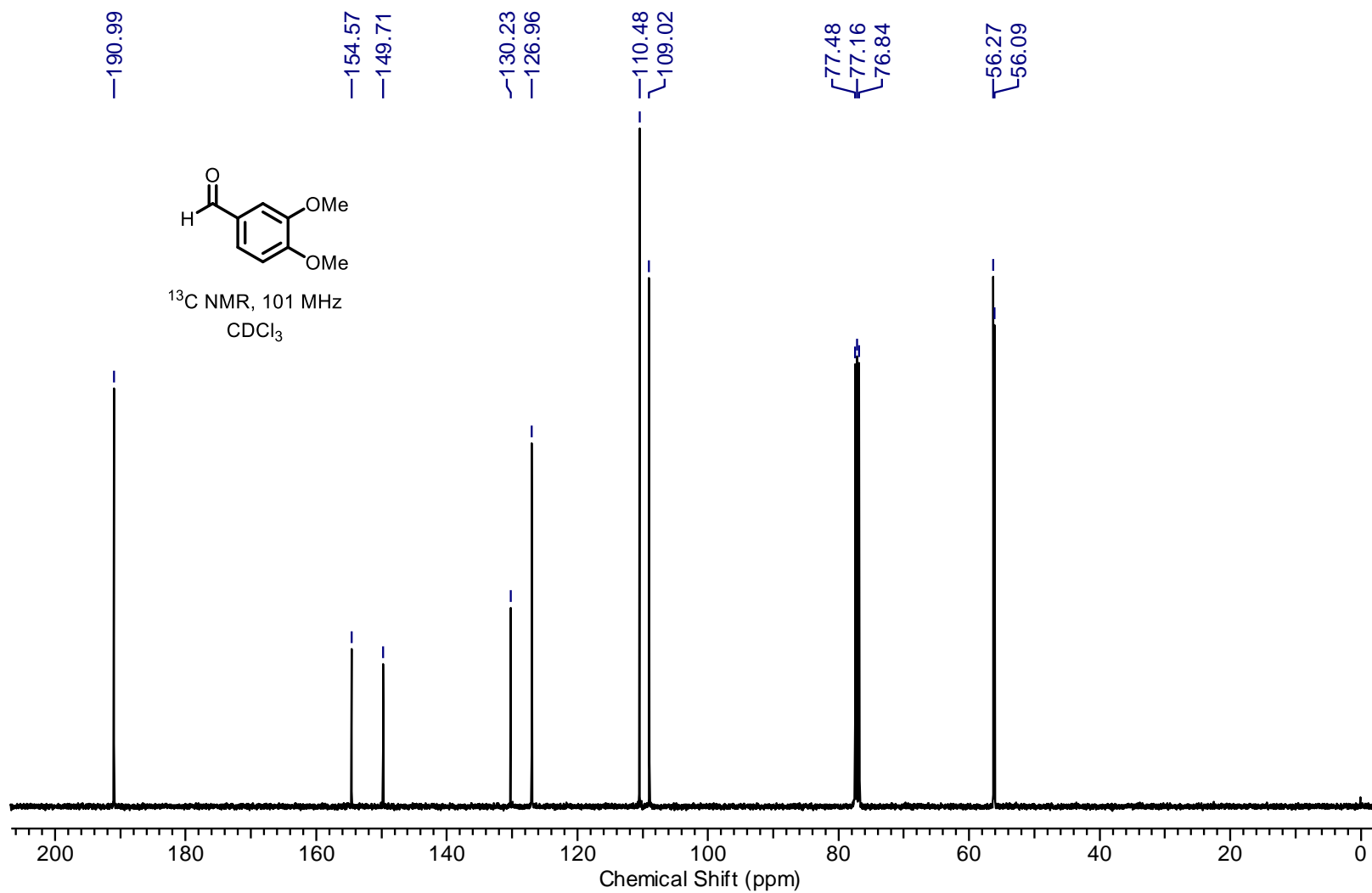
(*R, E*)-5-((4-Methoxybenzyl)oxy)-6-(4-methoxyphenyl)hex-3-en-2-one (**25**):



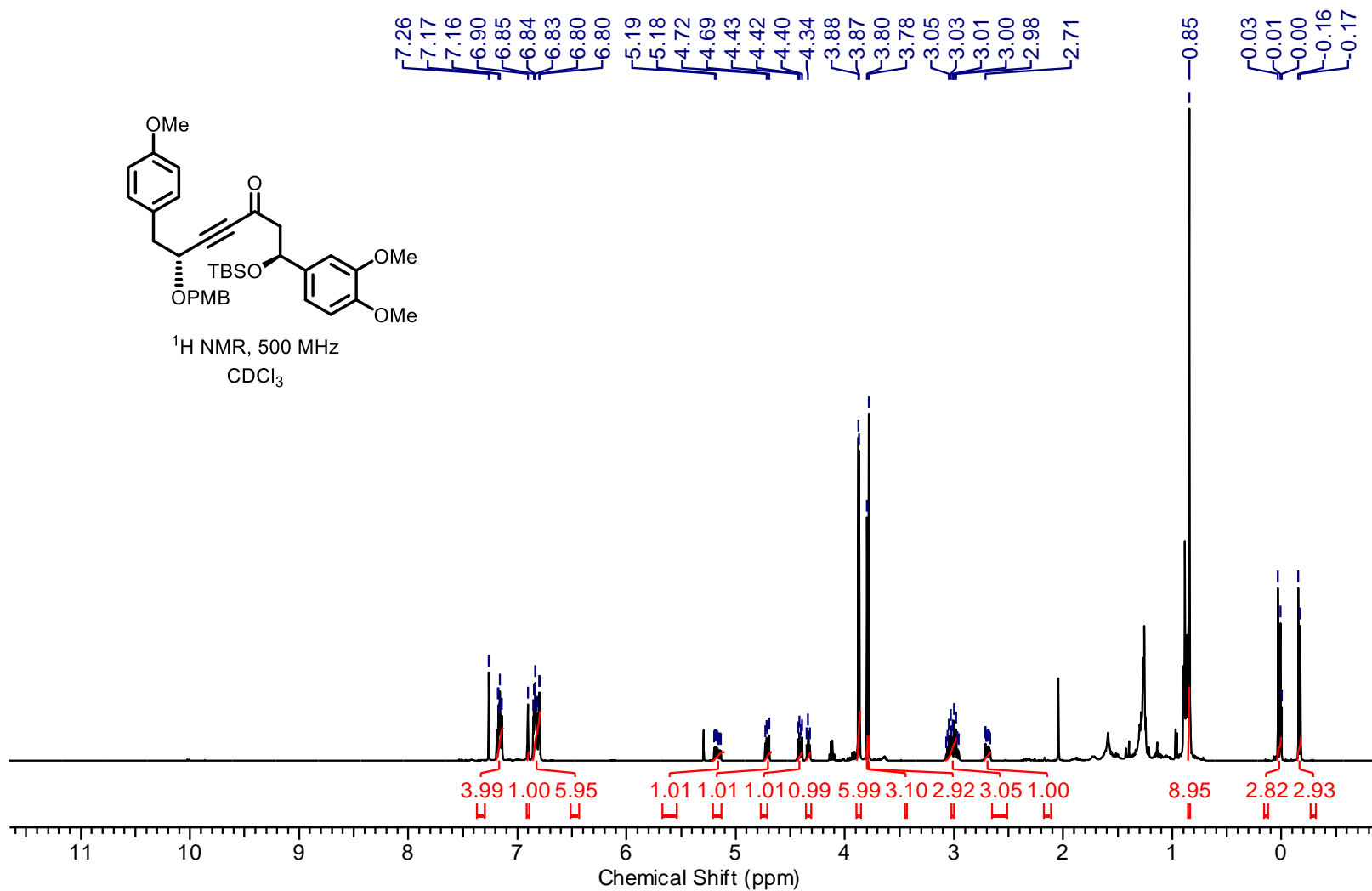
3,4-Dimethoxybenzaldehyde (**10**):



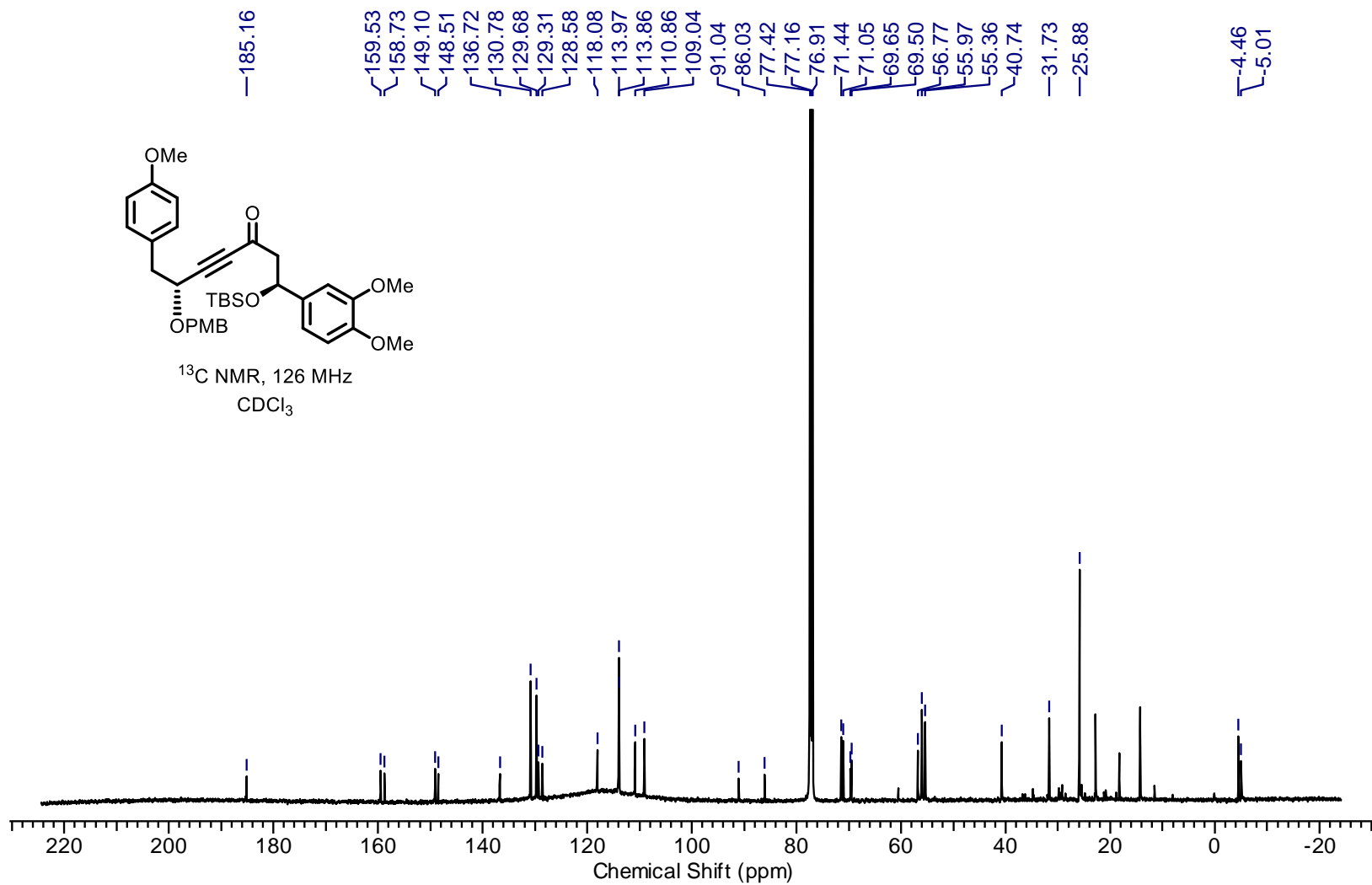
3,4-Dimethoxybenzaldehyde (**10**):



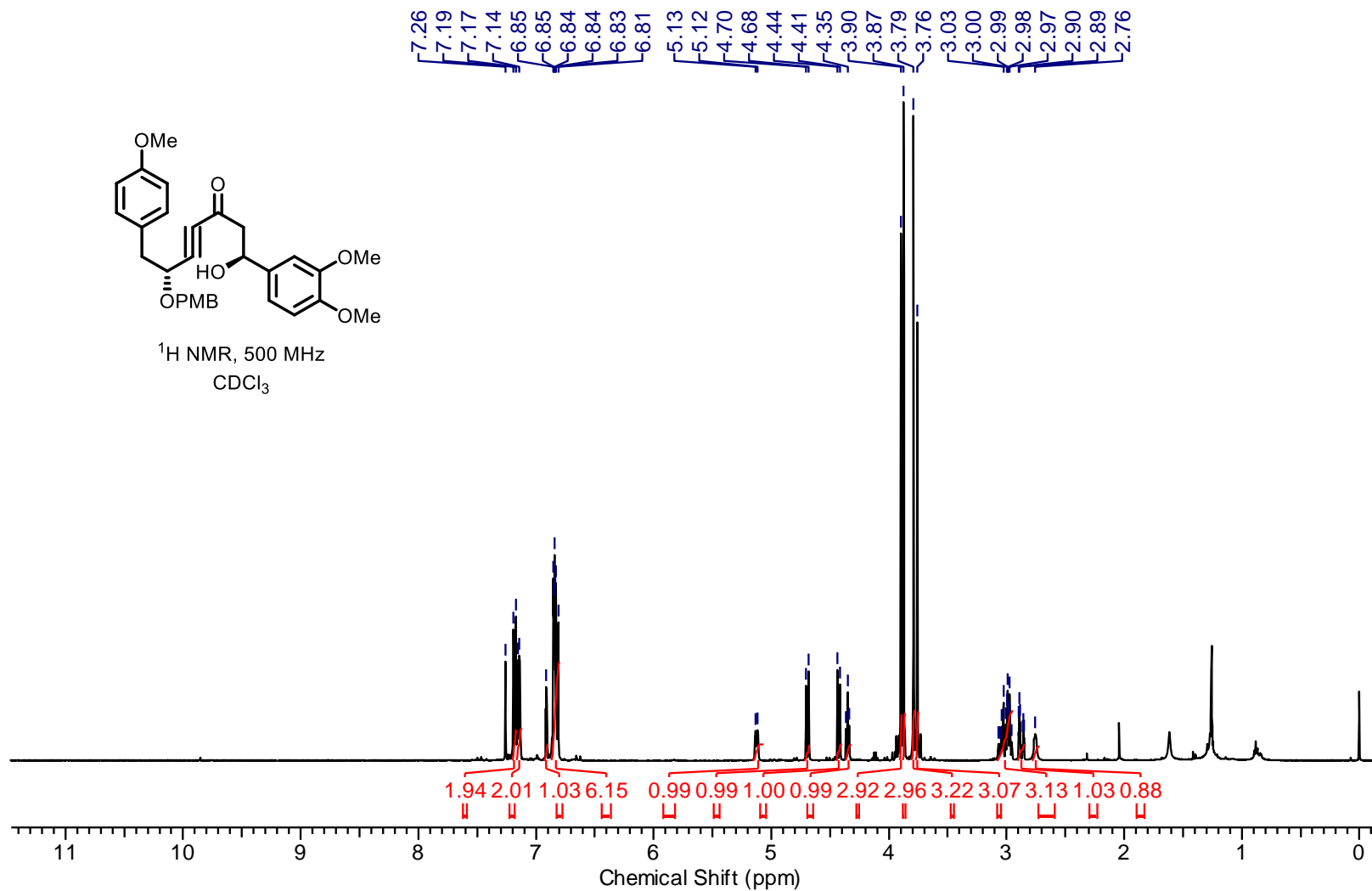
(1*S*, 6*R*)-1-((*Tert*-butyldimethylsilyl)oxy)-1-(3,4-dimethoxyphenyl)-6-((4-methoxybenzyl)-oxy)-7-(4-methoxyphenyl)hept-4-yn-3-one (**14a**):



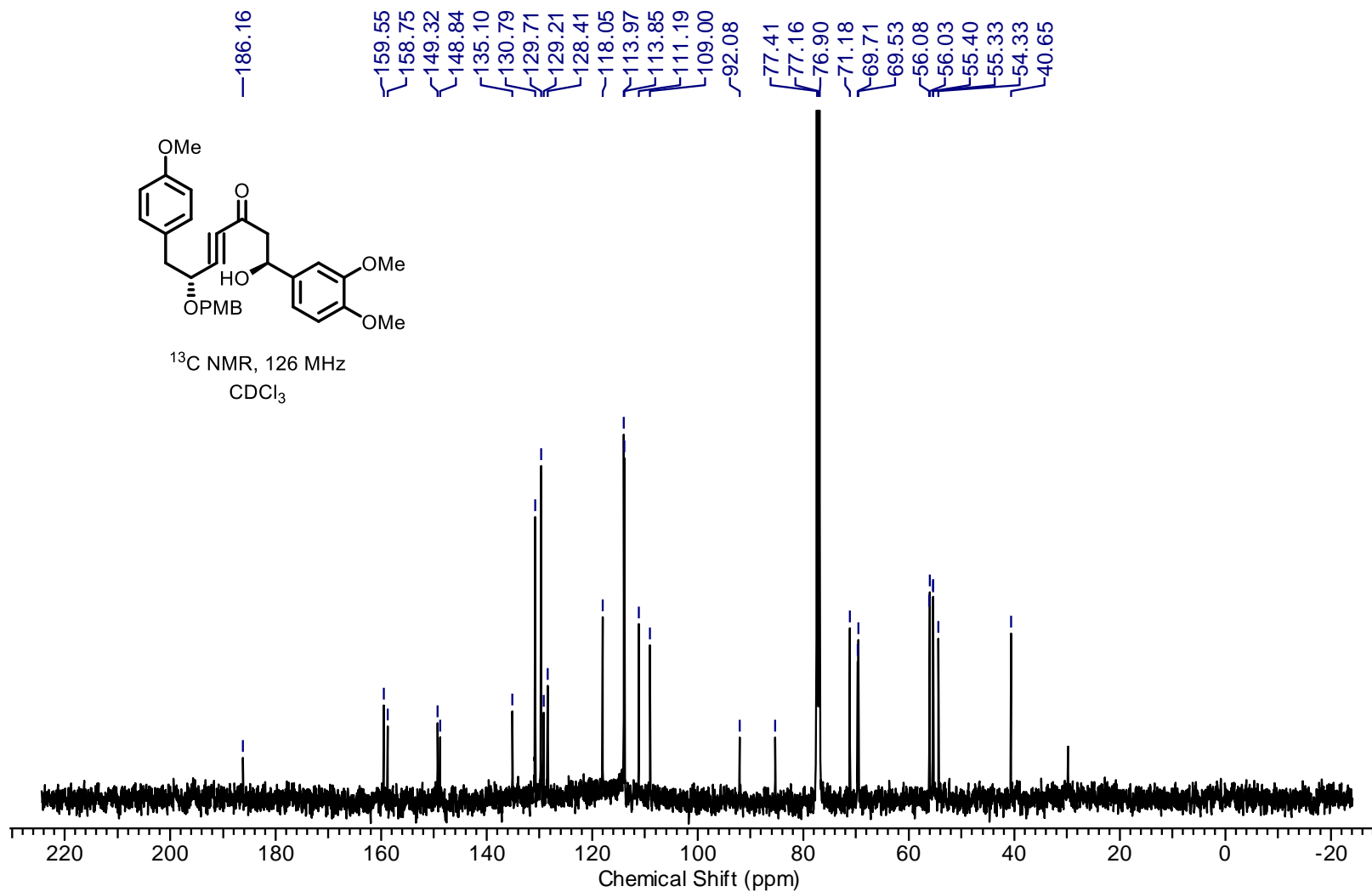
(1*S*, 6*R*)-1-((*Tert*-butyldimethylsilyl)oxy)-1-(3,4-dimethoxyphenyl)-6-((4-methoxybenzyl)-oxy)-7-(4-methoxyphenyl)hept-4-yn-3-one (**14a**):



(1*S*, 6*R*)-1-(3,4-Dimethoxyphenyl)-1-hydroxy-6-((4-methoxybenzyl)oxy)-7-(4-methoxyphenyl)hept-4-yn-3-one (**22a**):

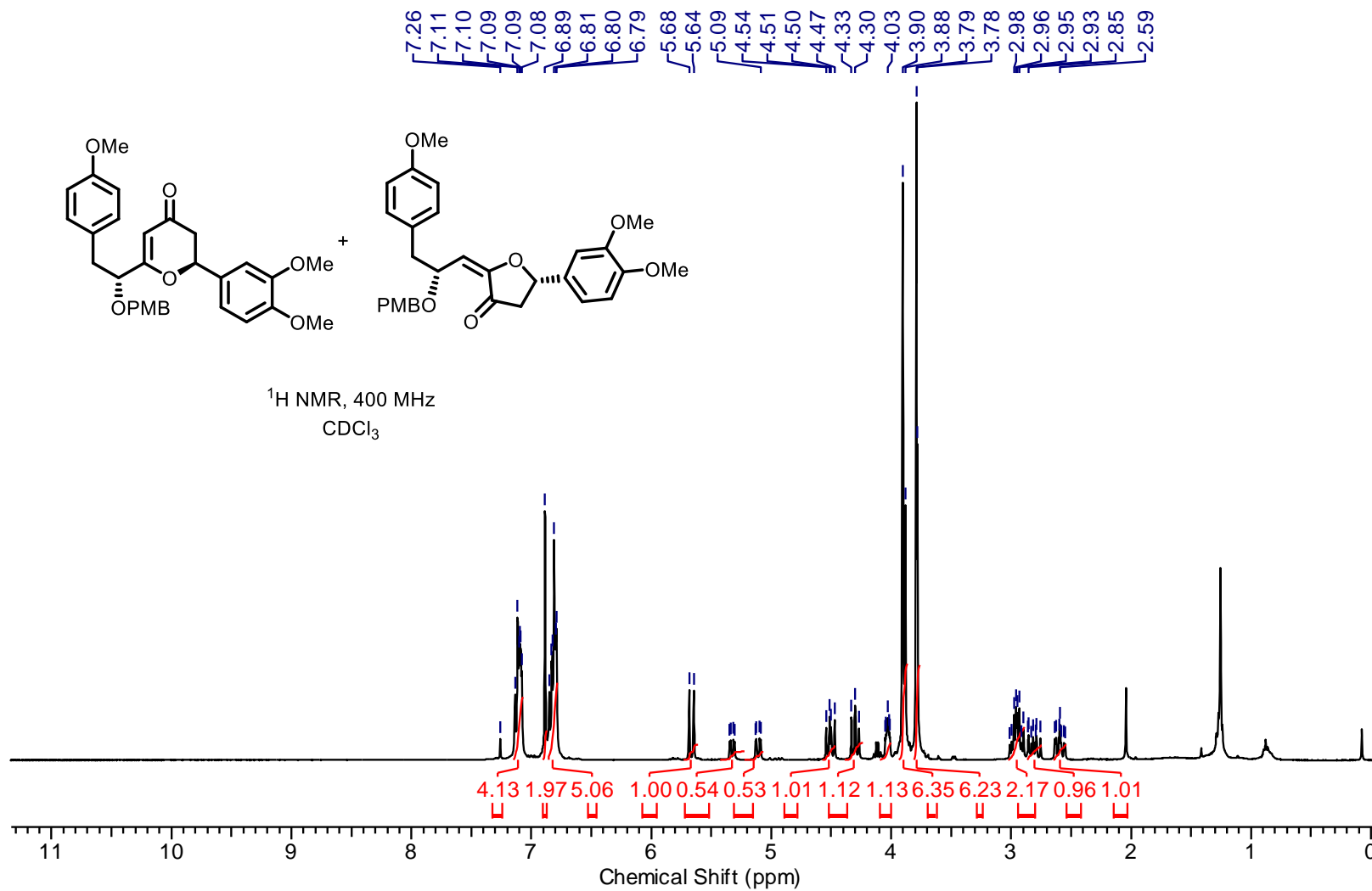


(1*S*, 6*R*)-1-(3,4-Dimethoxyphenyl)-1-hydroxy-6-((4-methoxybenzyl)oxy)-7-(4-methoxyphenyl)hept-4-yn-3-one (**22a**):

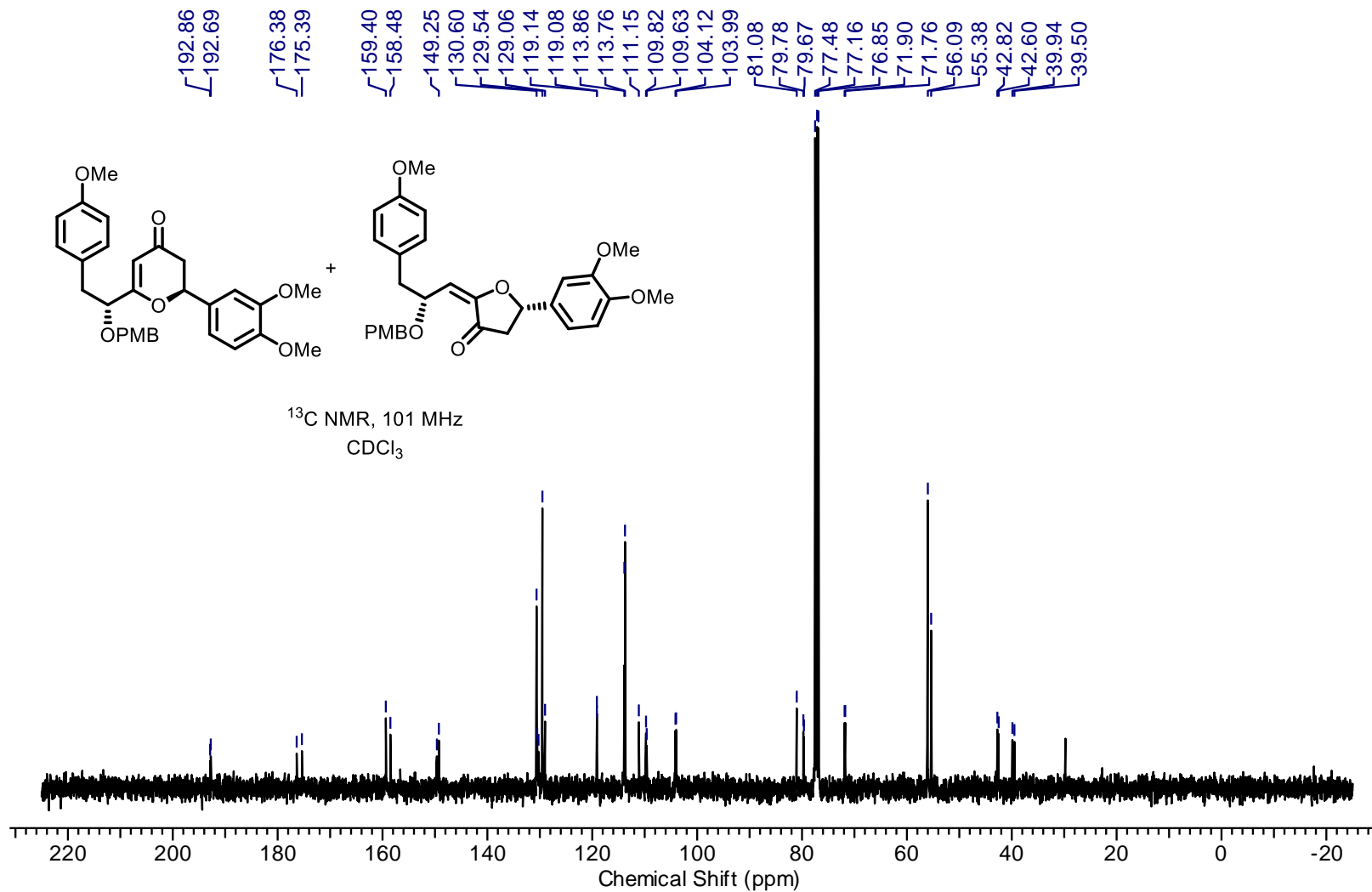




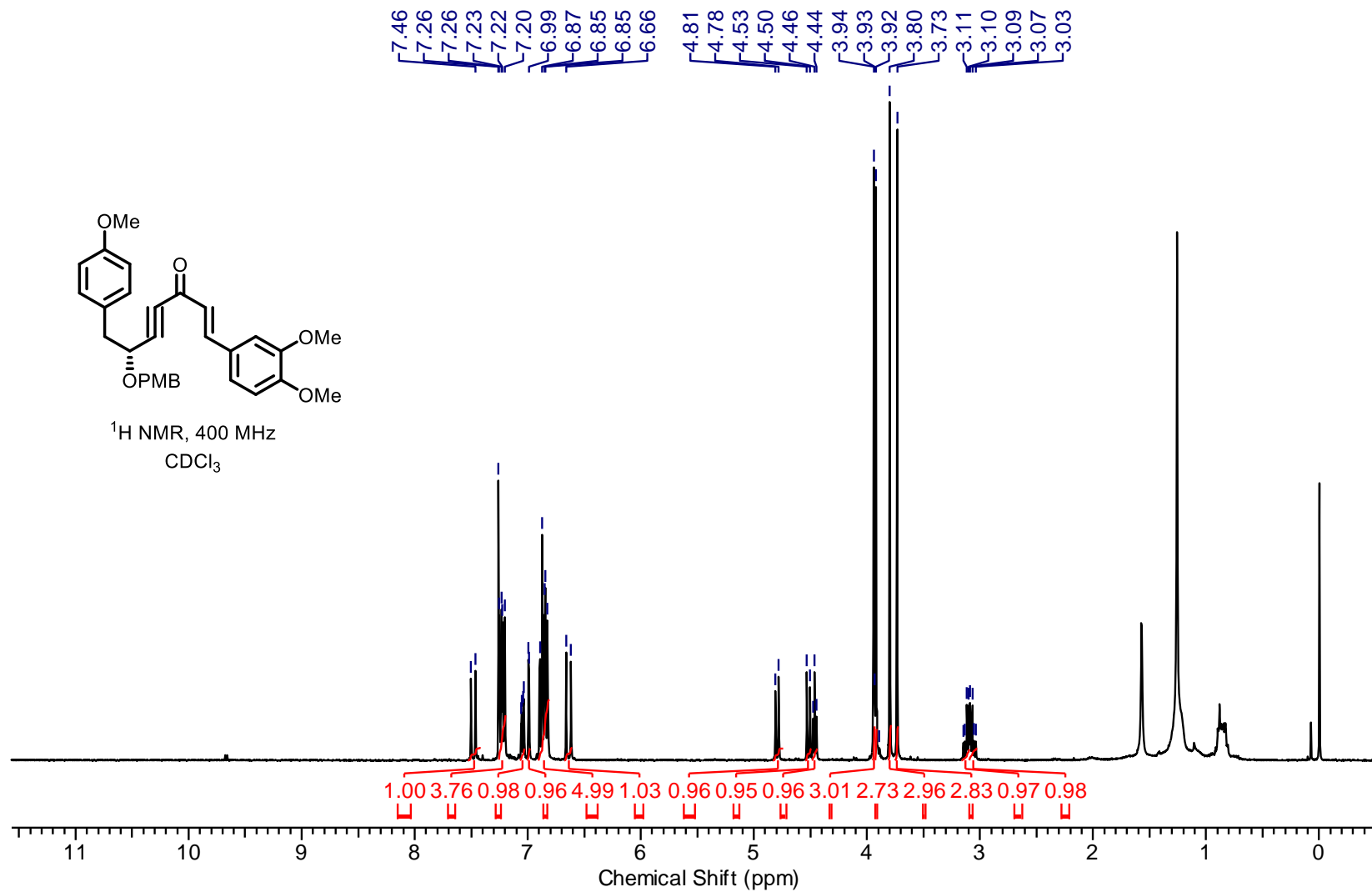
(*S*)-2-(3,4-Dimethoxyphenyl)-6-((*R*)-1-(4-methoxybenzyl)oxy)-2-(4-methoxyphenyl)ethyl)-2,3-dihydro-4*H*-pyran-4-one (**23a**) and (*S*, *E*)-5-(3,4-dimethoxyphenyl)-2-((*R*)-2-(4-methoxybenzyl)oxy)-3-(4-methoxyphenyl)propylidene)dihydrofuran-3(2*H*)-one (**26**):



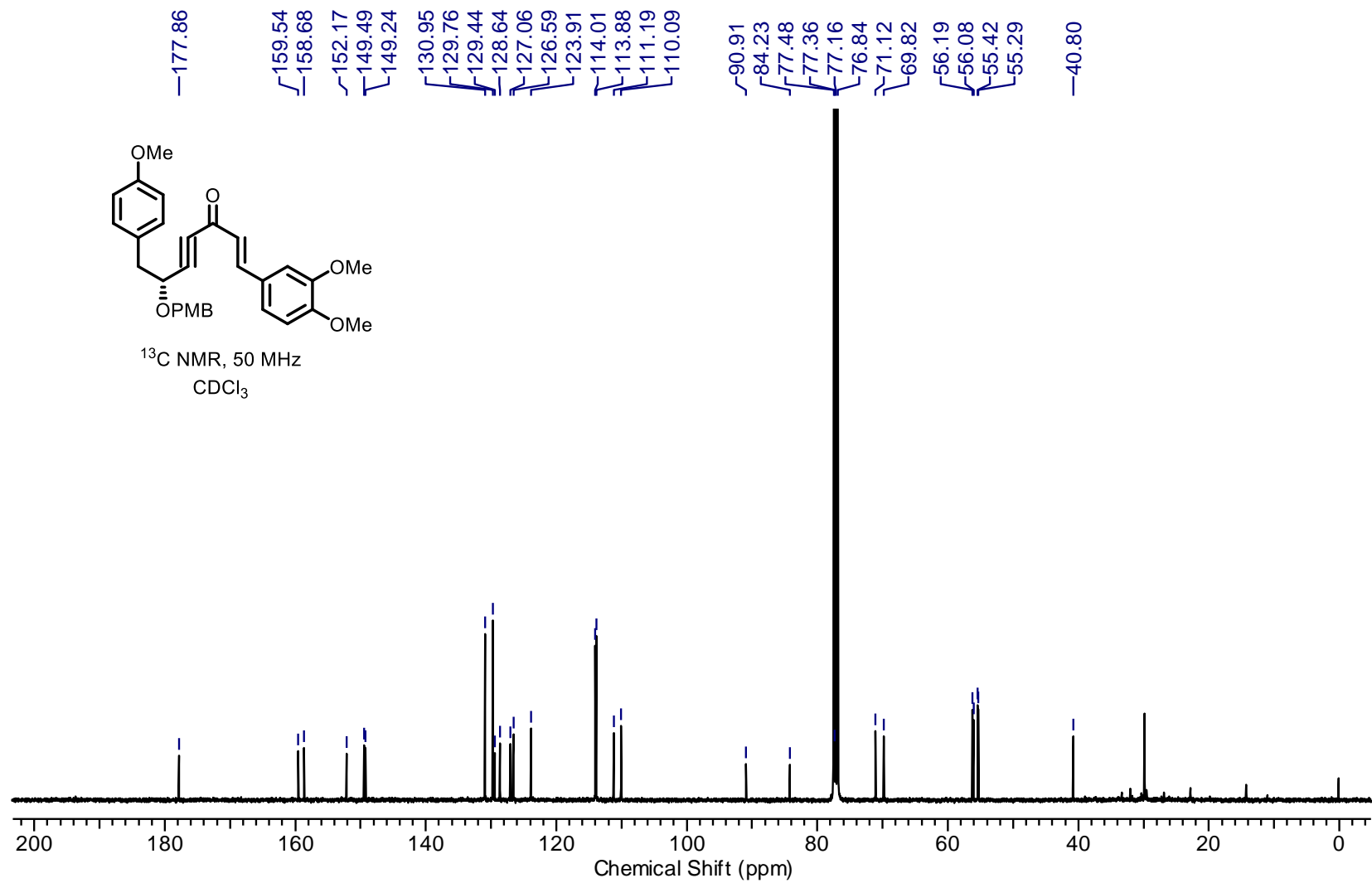
(*S*)-2-(3,4-Dimethoxyphenyl)-6-((*R*)-1-(4-methoxybenzyl)oxy)-2-(4-methoxyphenyl)ethyl)-2,3-dihydro-4*H*-pyran-4-one (**23a**) and (*S*, *E*)-5-(3,4-dimethoxyphenyl)-2-((*R*)-2-(4-methoxybenzyl)oxy)-3-(4-methoxyphenyl)propylidene)dihydrofuran-3(2*H*)-one (**26**):



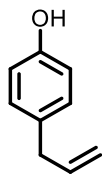
(R, E)-1-(3,4-Dimethoxyphenyl)-6-((4-methoxybenzyl)oxy)-7-(4-methoxyphenyl)hept-1-en-4-yn-3-one (24a):



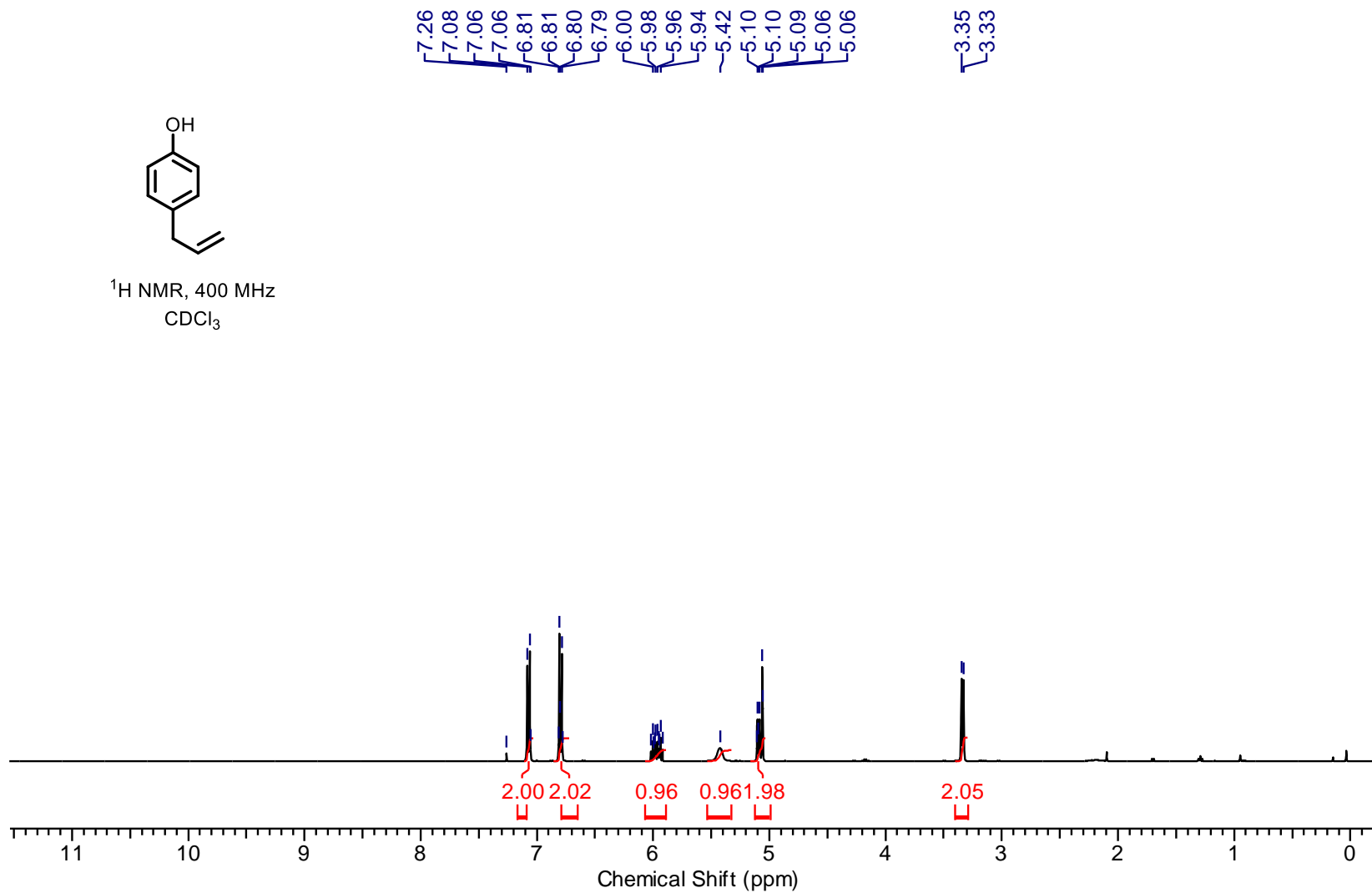
(*R, E*)-1-(3,4-Dimethoxyphenyl)-6-((4-methoxybenzyl)oxy)-7-(4-methoxyphenyl)hept-1-en-4-yn-3-one (**24a**):



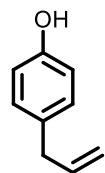
4-Allylphenol (**S8**)



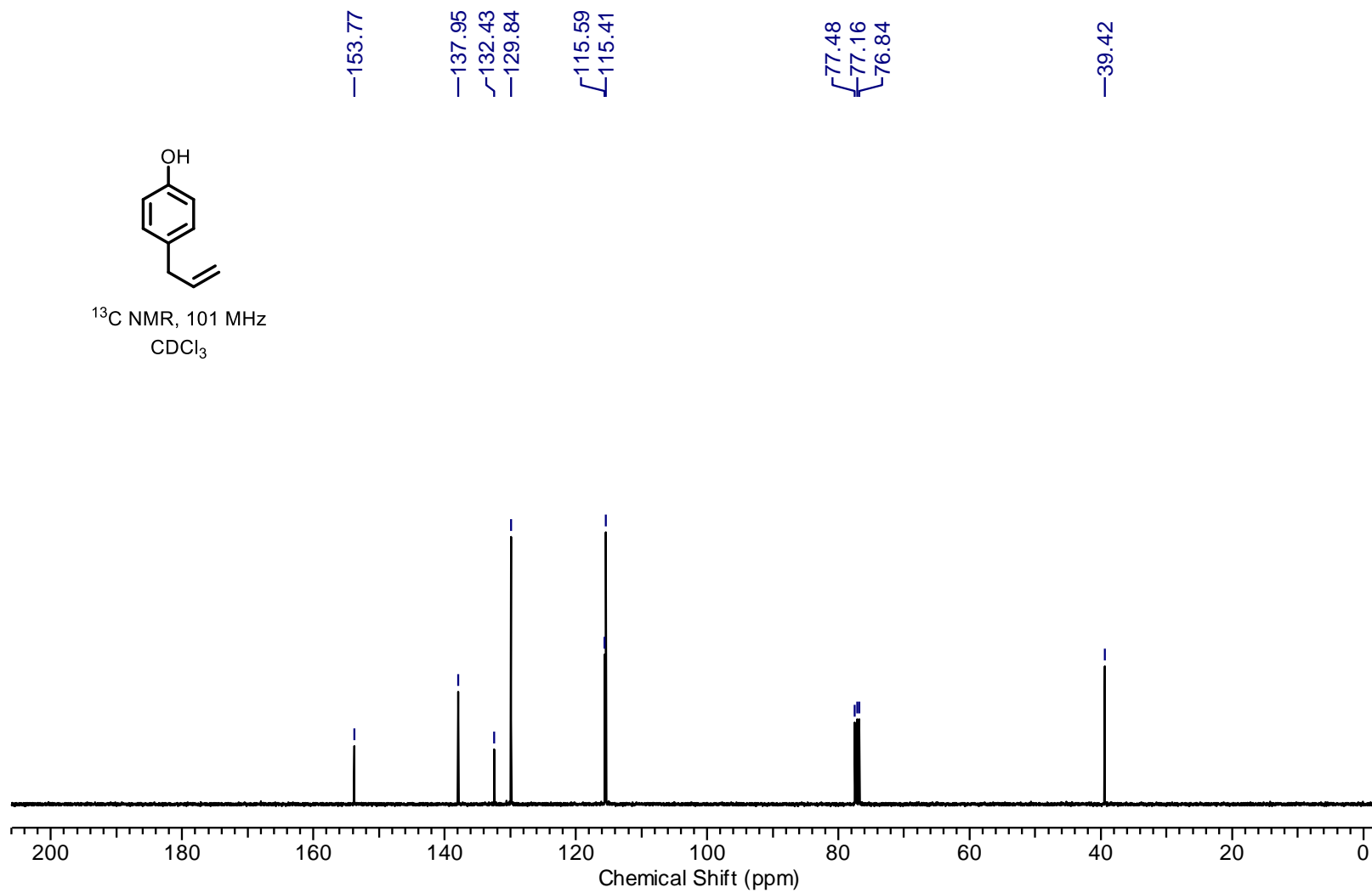
<sup>1</sup>H NMR, 400 MHz  
CDCl<sub>3</sub>



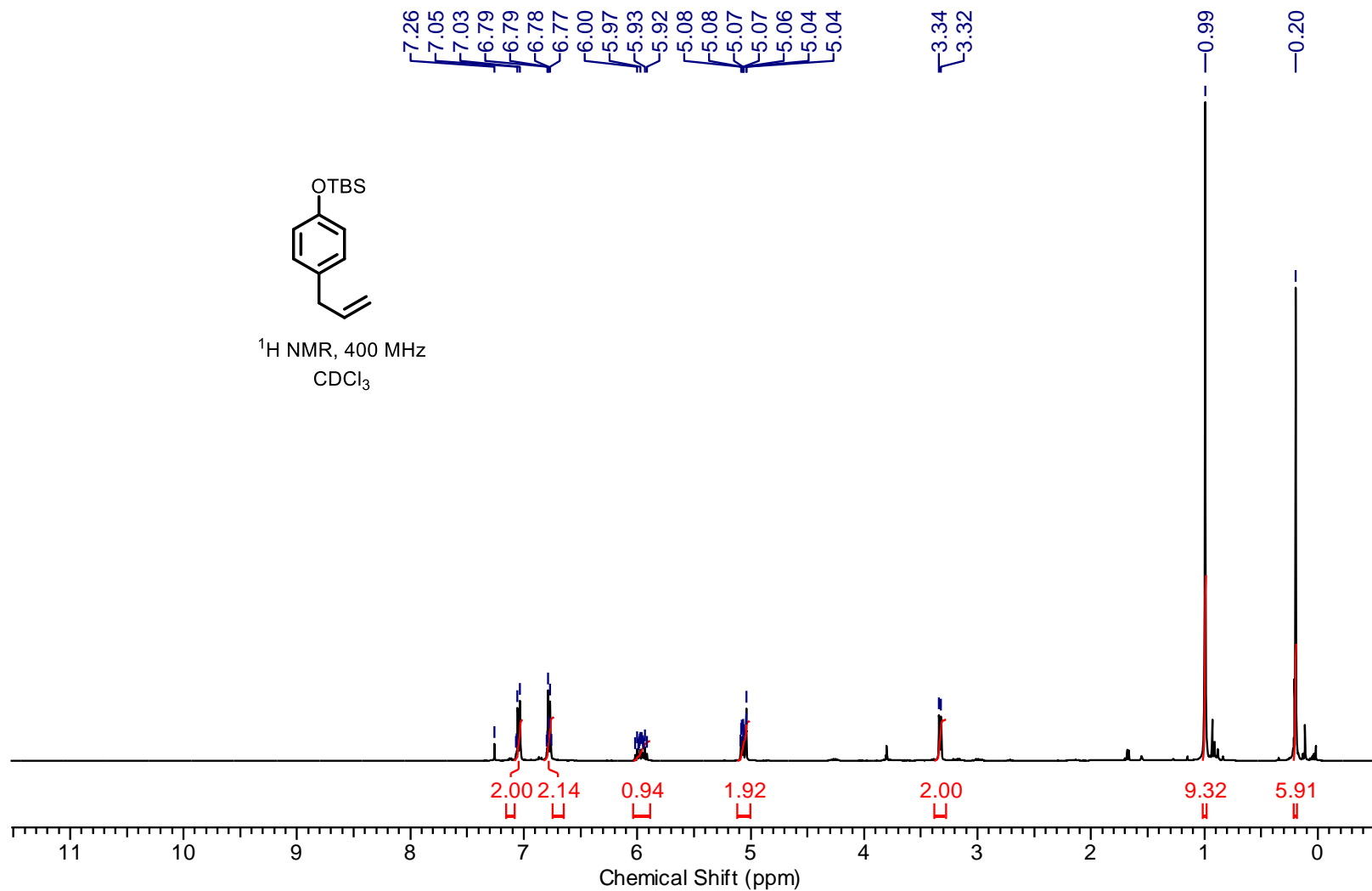
4-Allylphenol (**S8**)



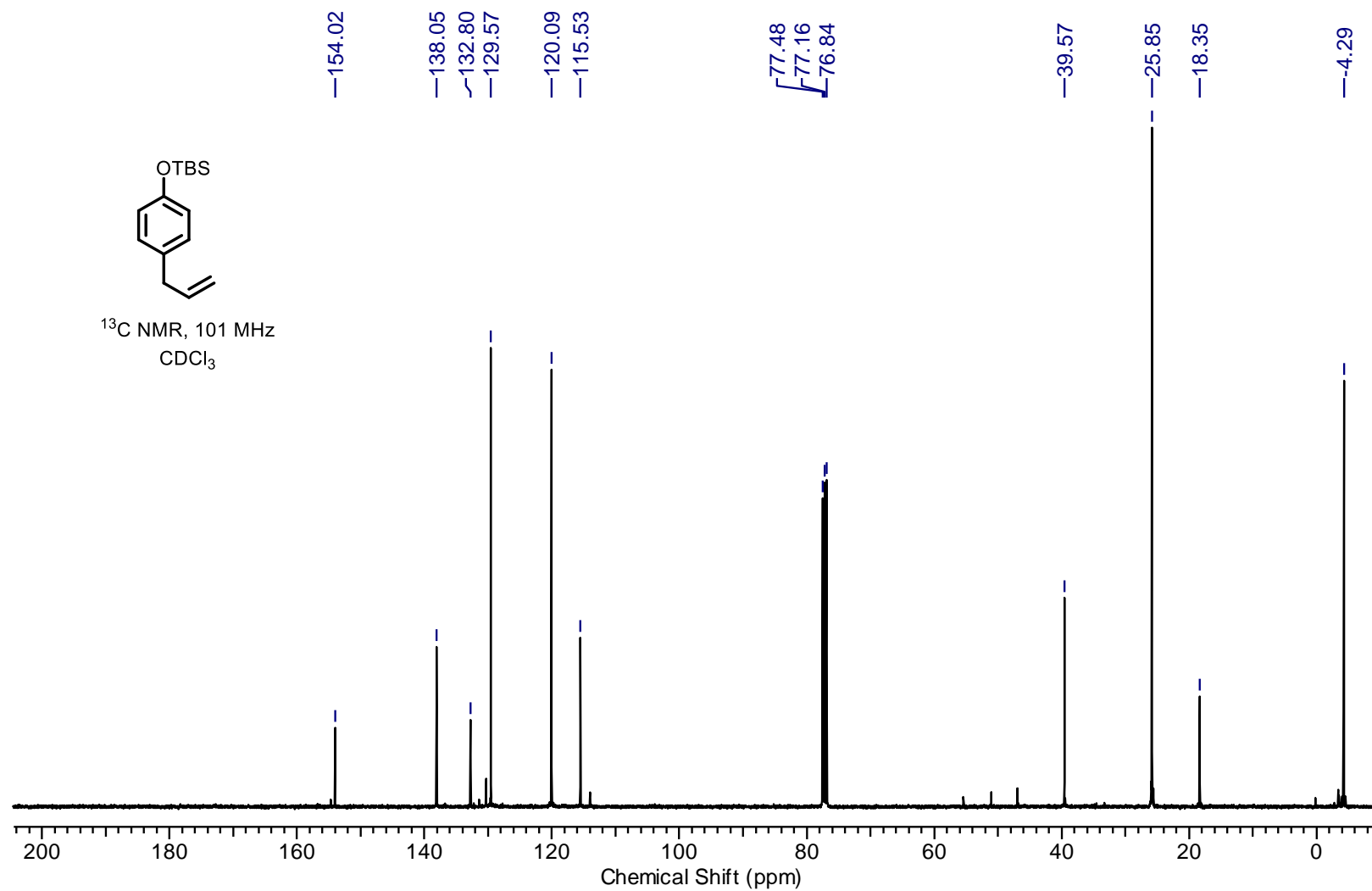
<sup>13</sup>C NMR, 101 MHz  
CDCl<sub>3</sub>



(4-Allylphenoxy)(tert-butyl)dimethylsilane (**9a**):

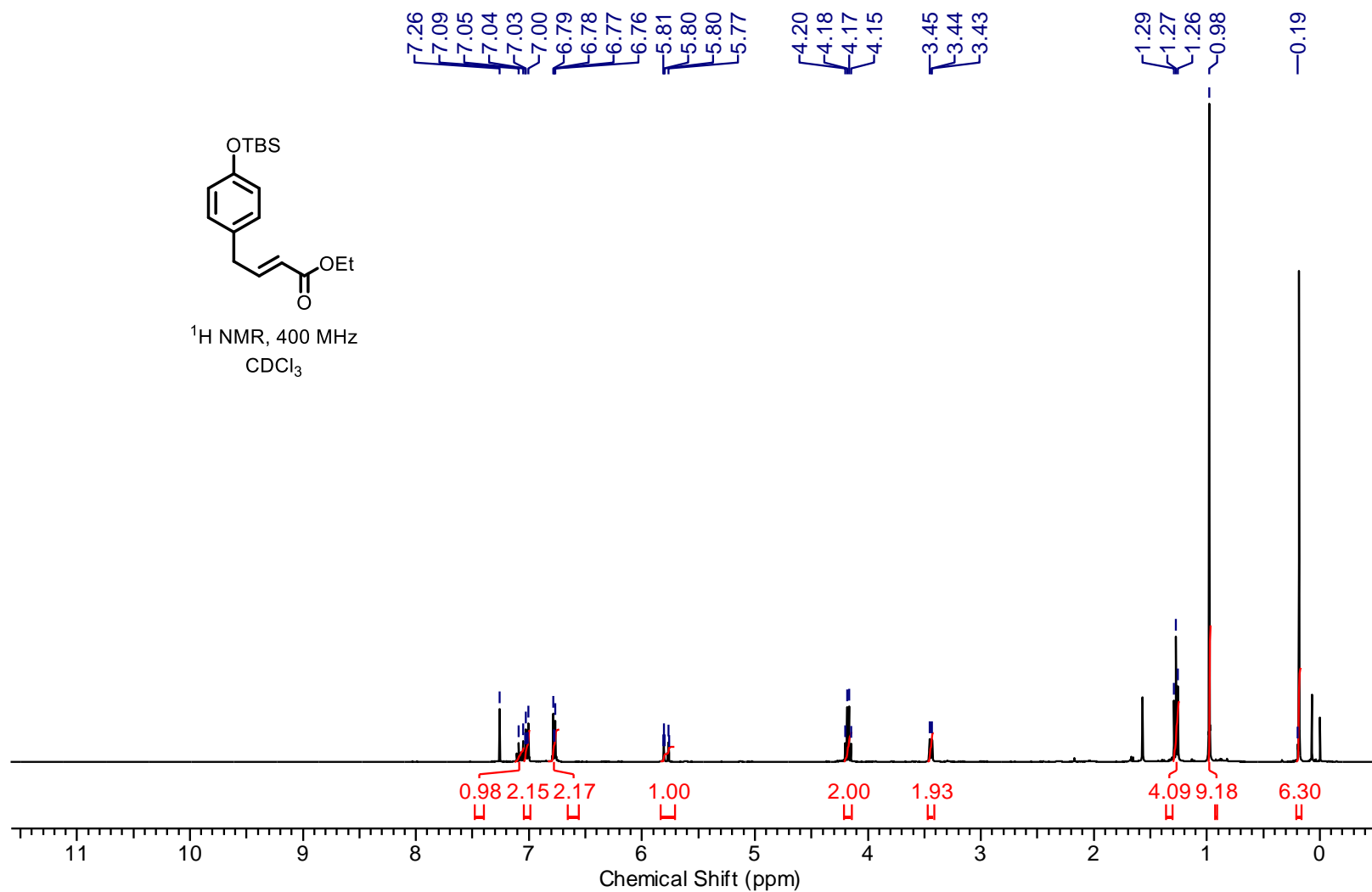


(4-Allylphenoxy)(tert-butyl)dimethylsilane (**9a**):

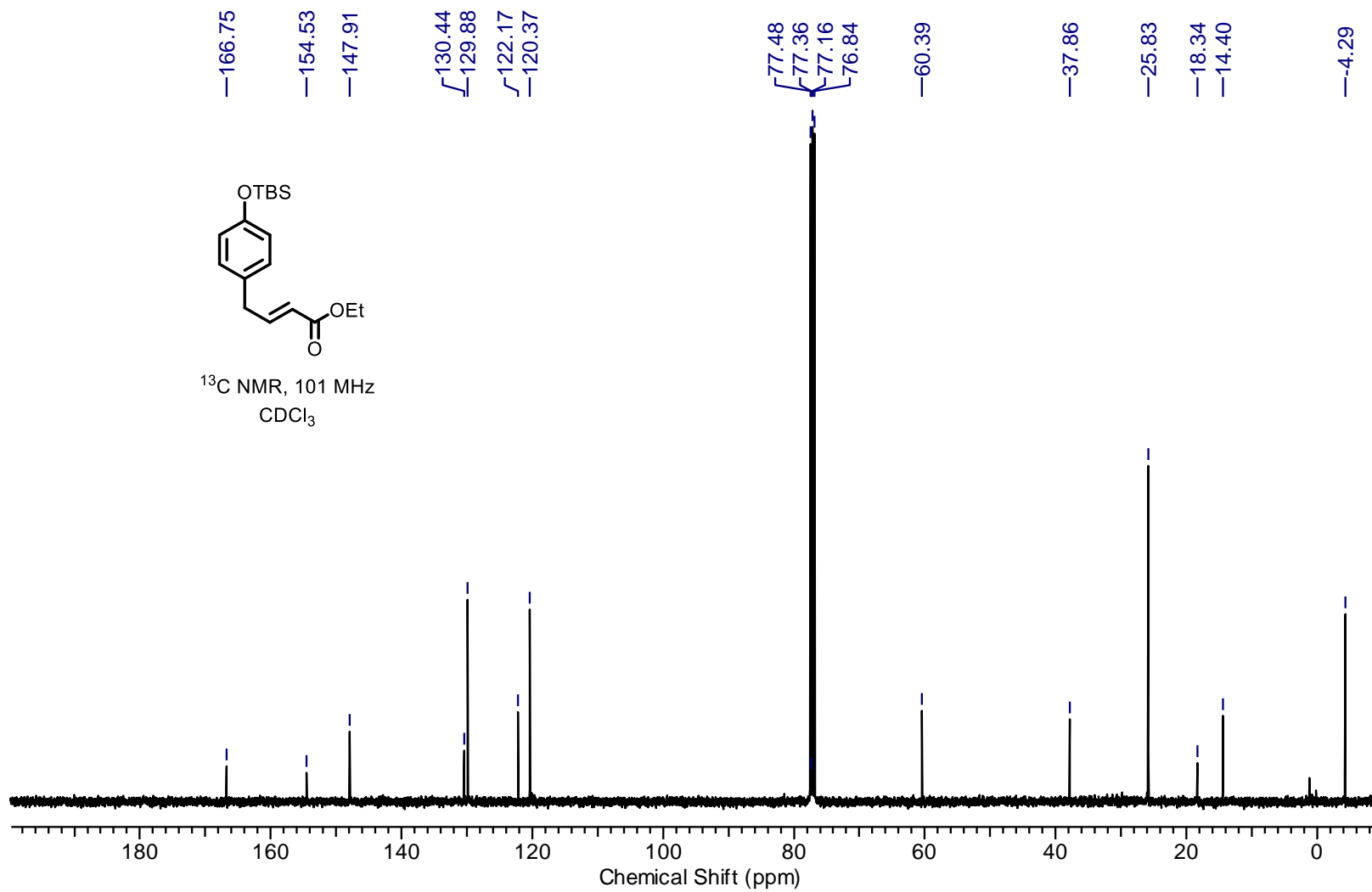




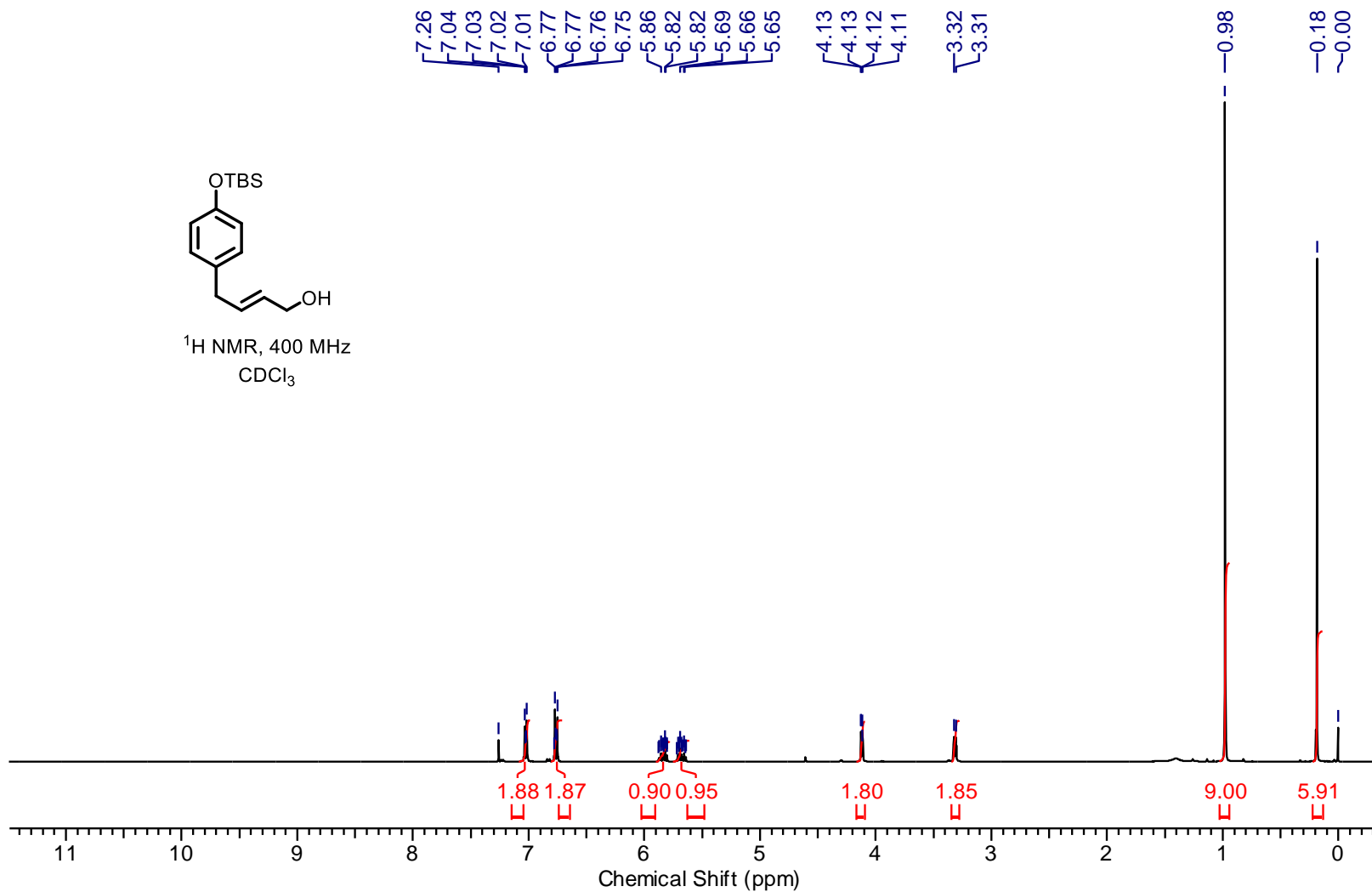
Ethyl-(E)-4-(4-((tert-butyl)dimethylsilyloxy)phenyl)but-2-enoate (**17a**):



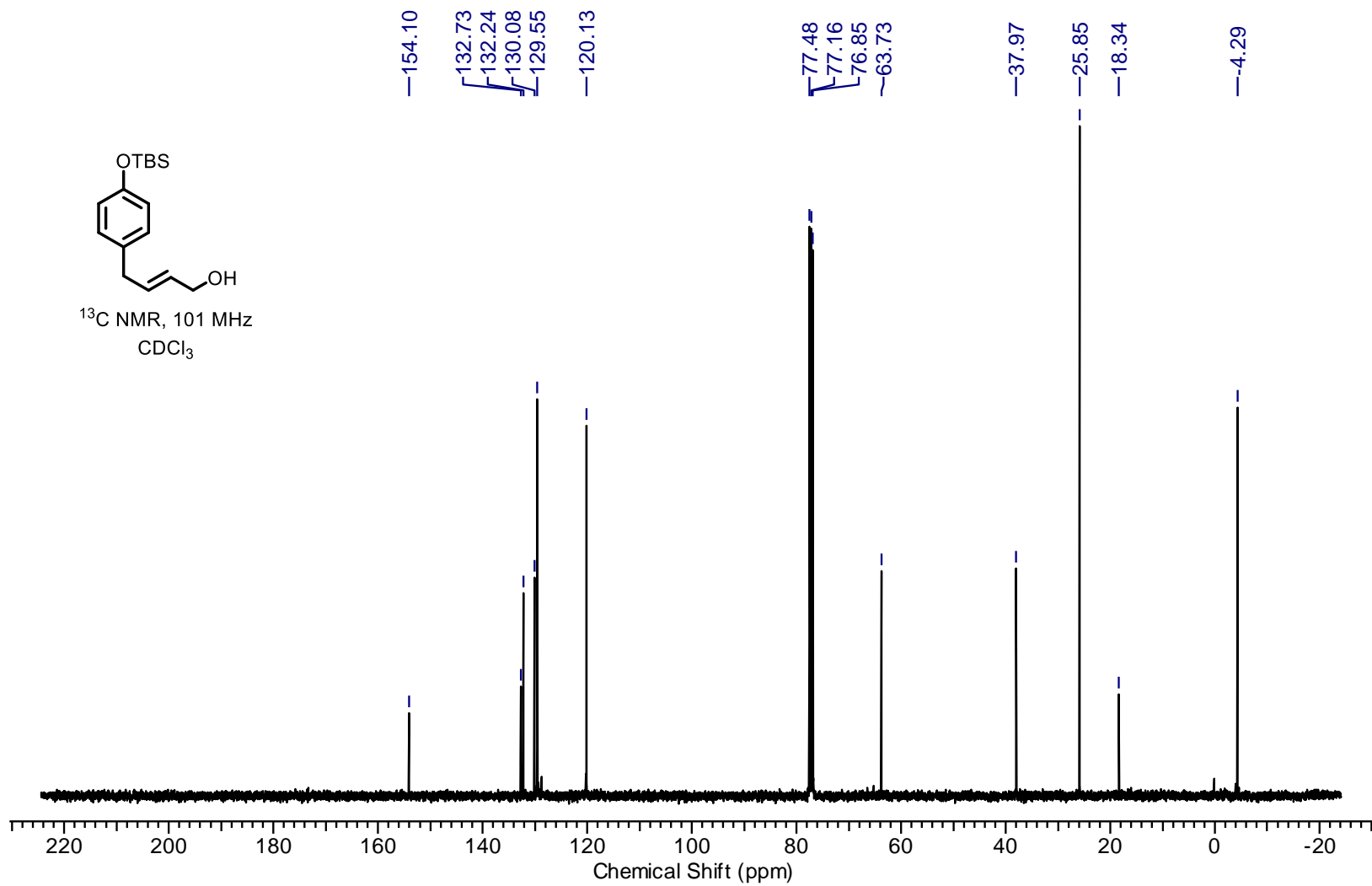
Ethyl-(E)-4-(4-((tert-butyl)dimethylsilyloxy)phenyl)but-2-enoate (**17a**):



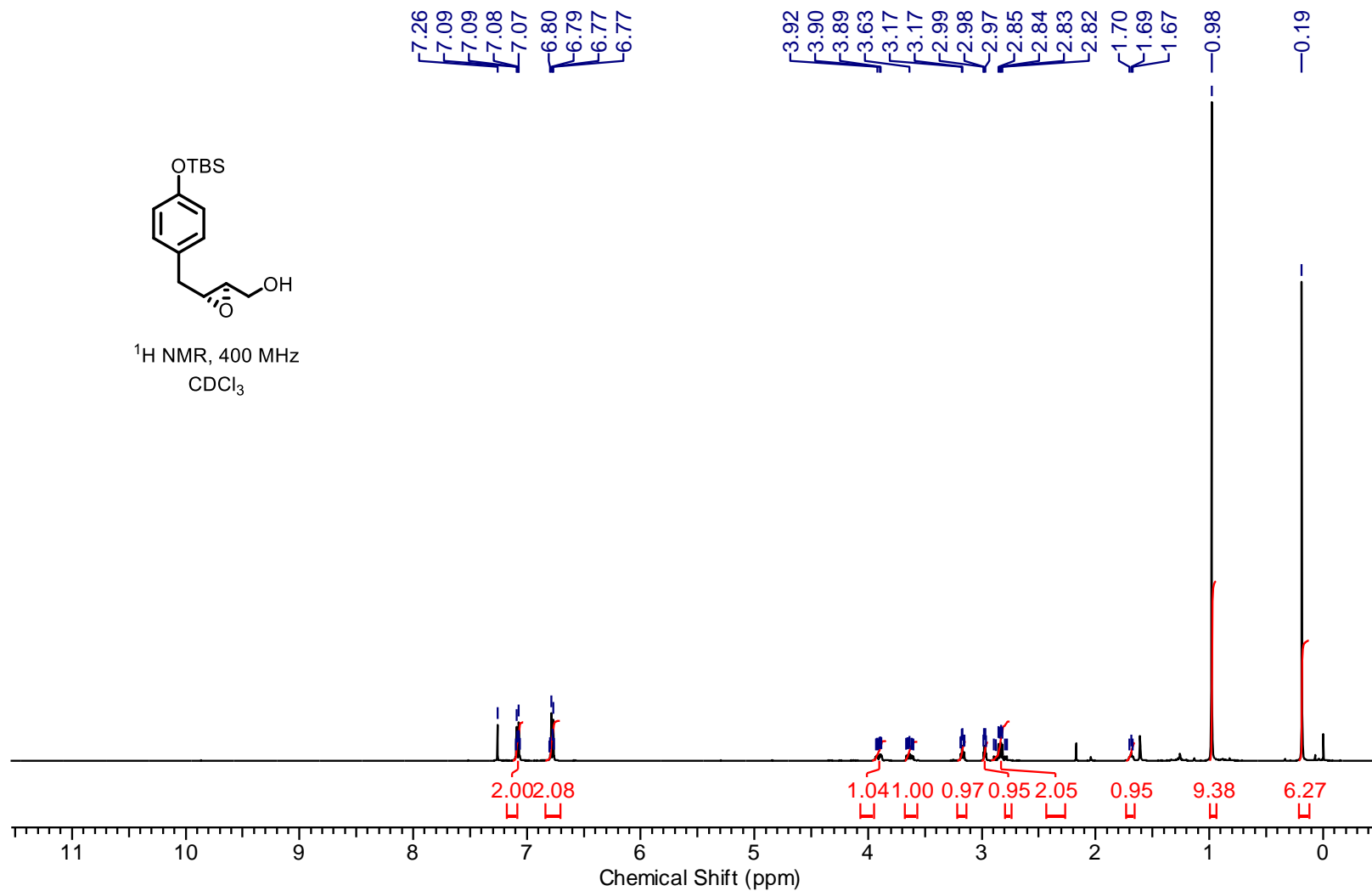
(E)-4-(4-((Tert-butyl dimethylsilyl)oxy)phenyl)but-2-en-1-ol (**S4a**):



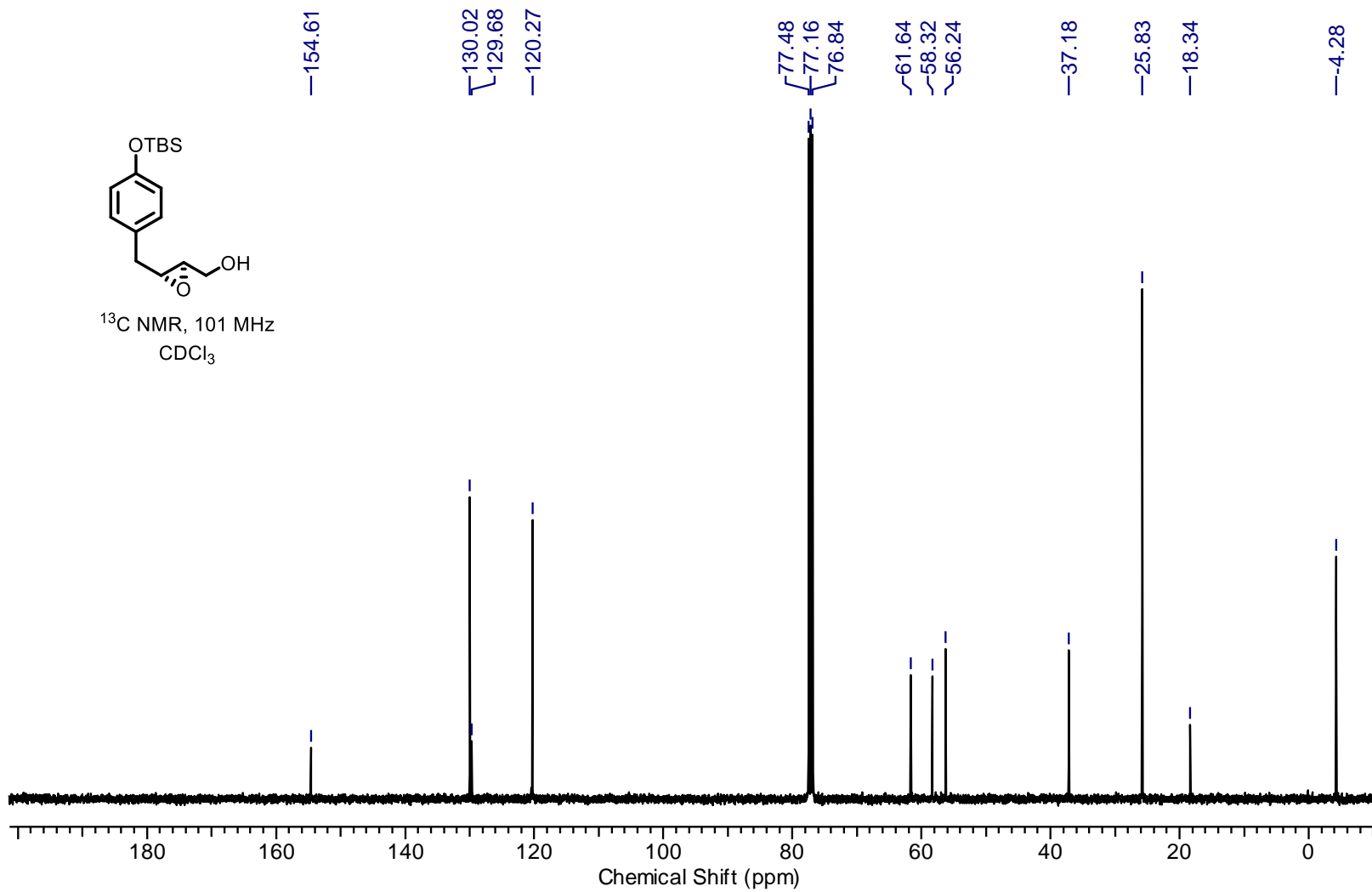
(E)-4-(4-((Tert-butyl dimethylsilyl)oxy)phenyl)but-2-en-1-ol (**S4a**):



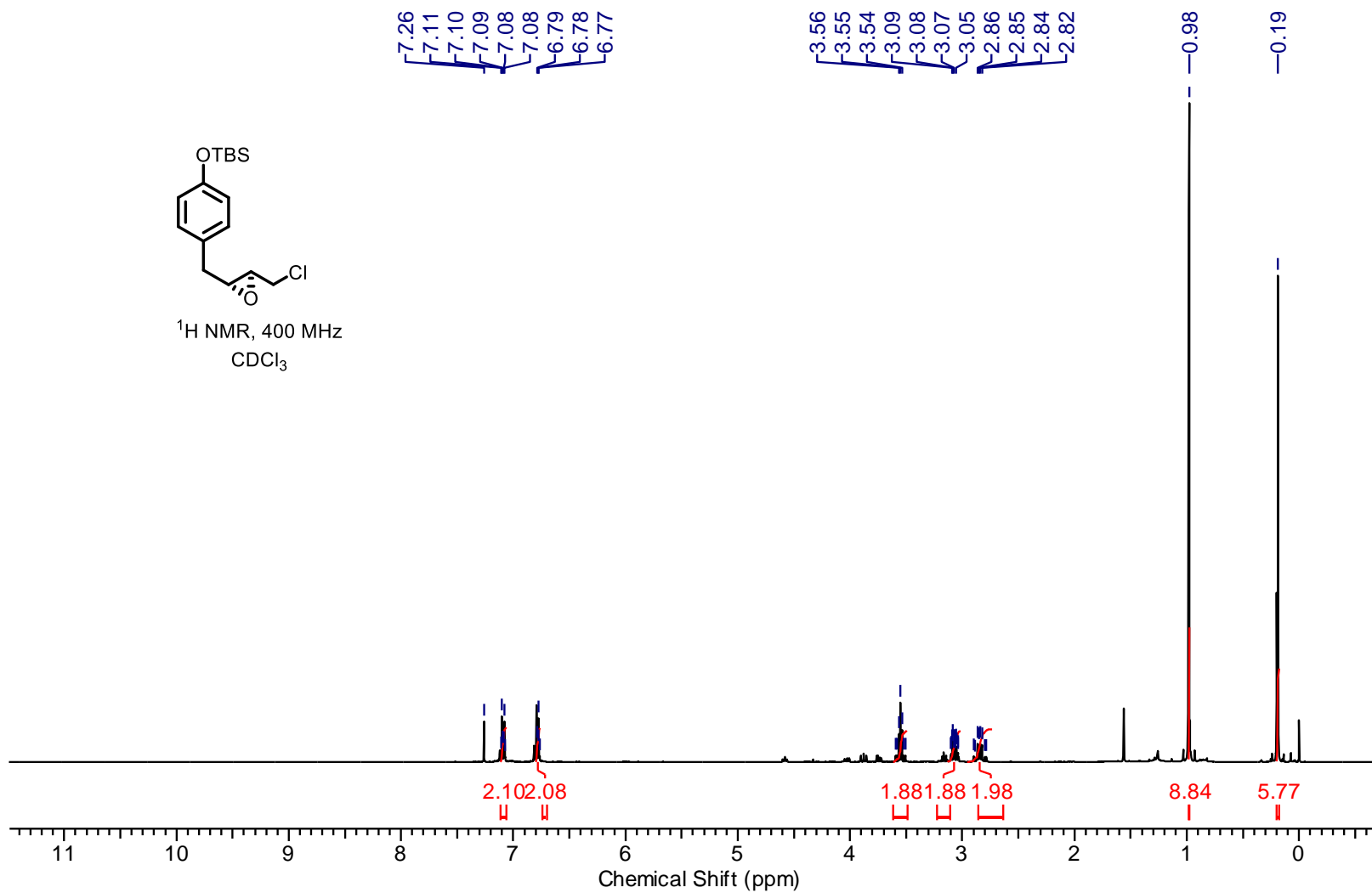
*((2R, 3R)*-3-(4-((*Tert*-butyldimethylsilyl)oxy)benzyl)oxiran-2-yl)methanol (**18a**):



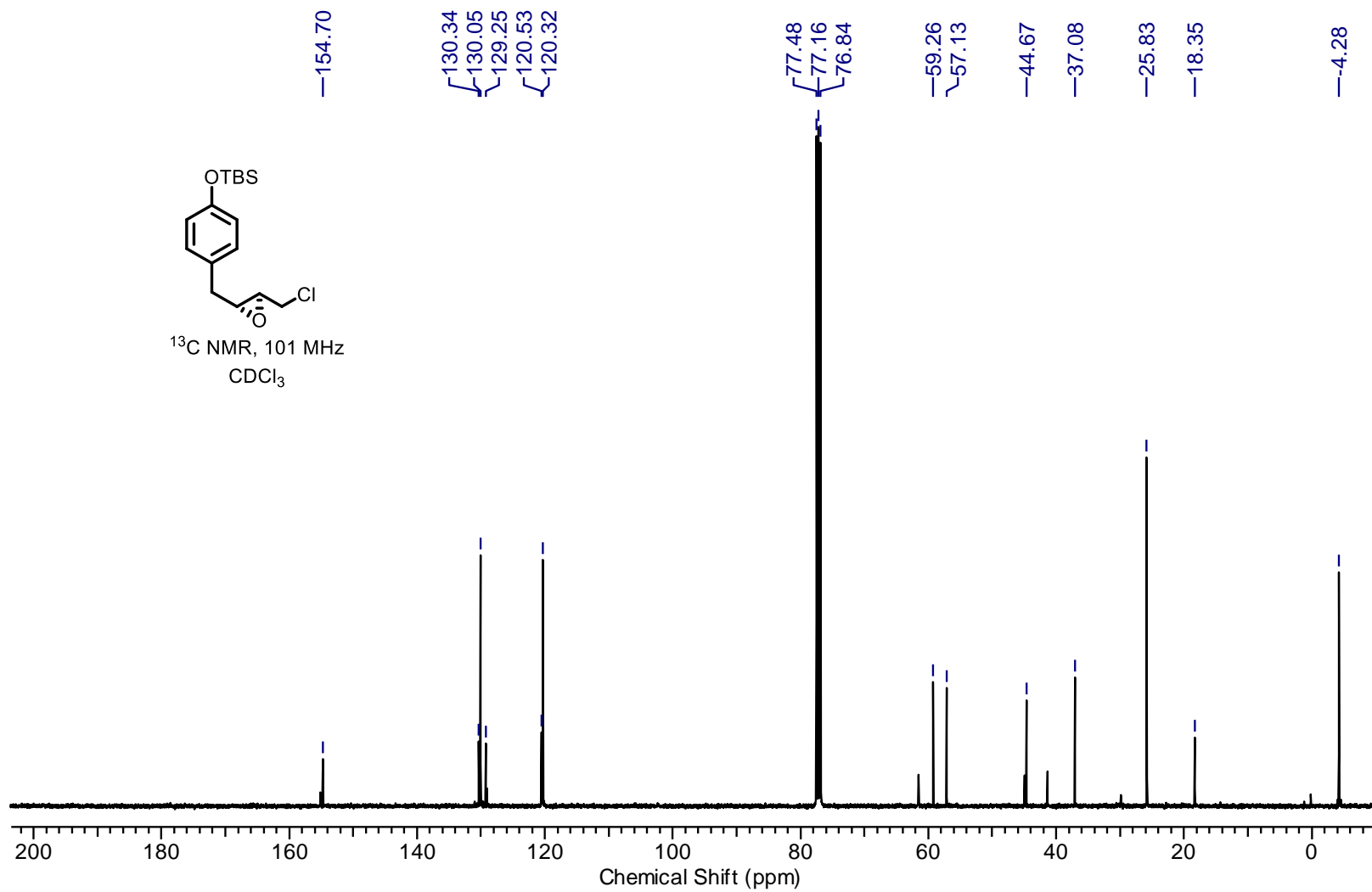
*((2R, 3R)*-3-(4-((*Tert*-butyldimethylsilyl)oxy)benzyl)oxiran-2-yl)methanol (**18a**):



*Tert-butyl(4-(((2R,3S)-3-(chloromethyl)oxiran-2-yl)methyl)phenoxy)dimethylsilane (19a):*

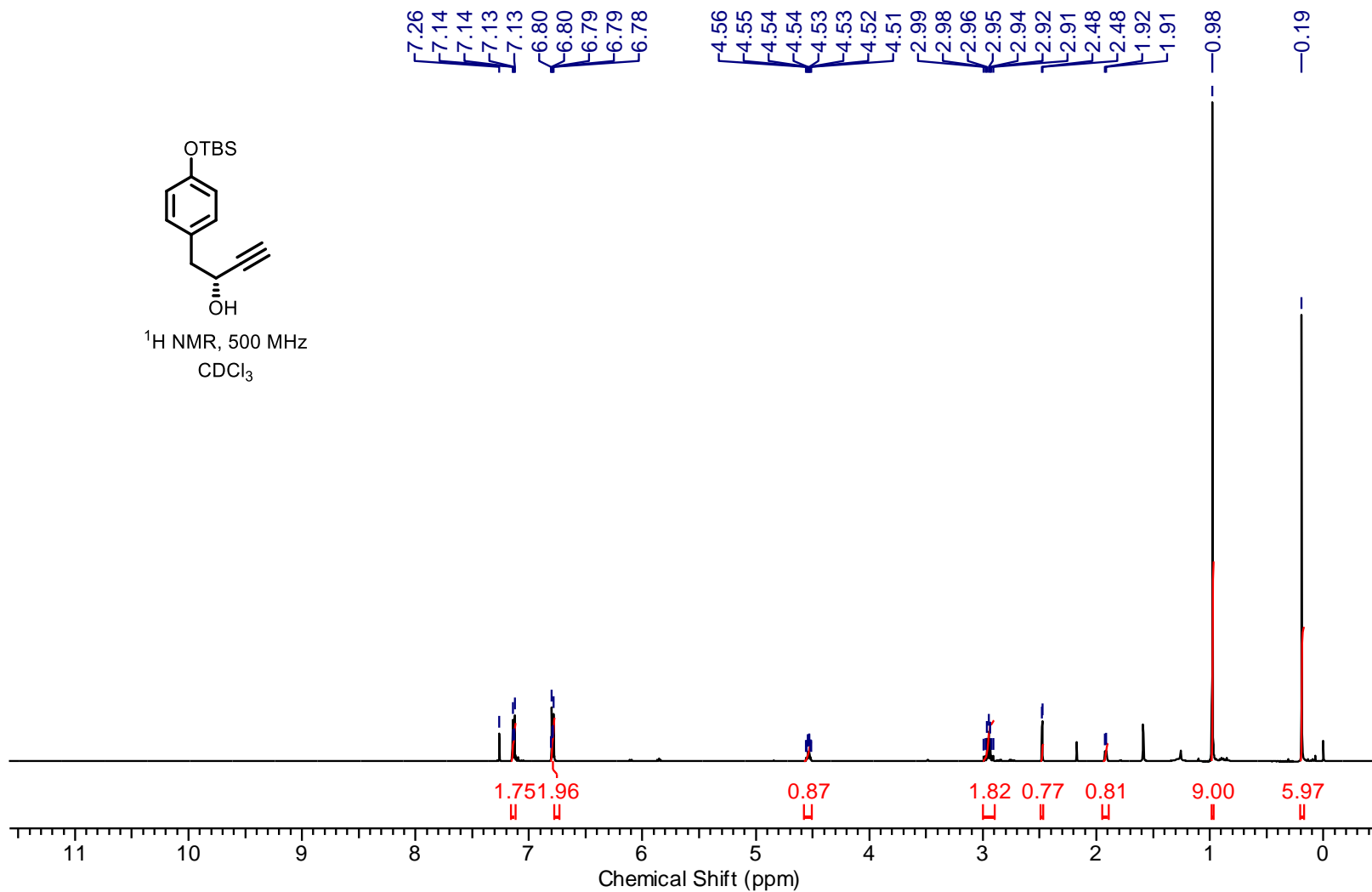


*Tert-butyl(4-(((2R,3S)-3-(chloromethyl)oxiran-2-yl)methyl)phenoxy)dimethylsilane (19a):*

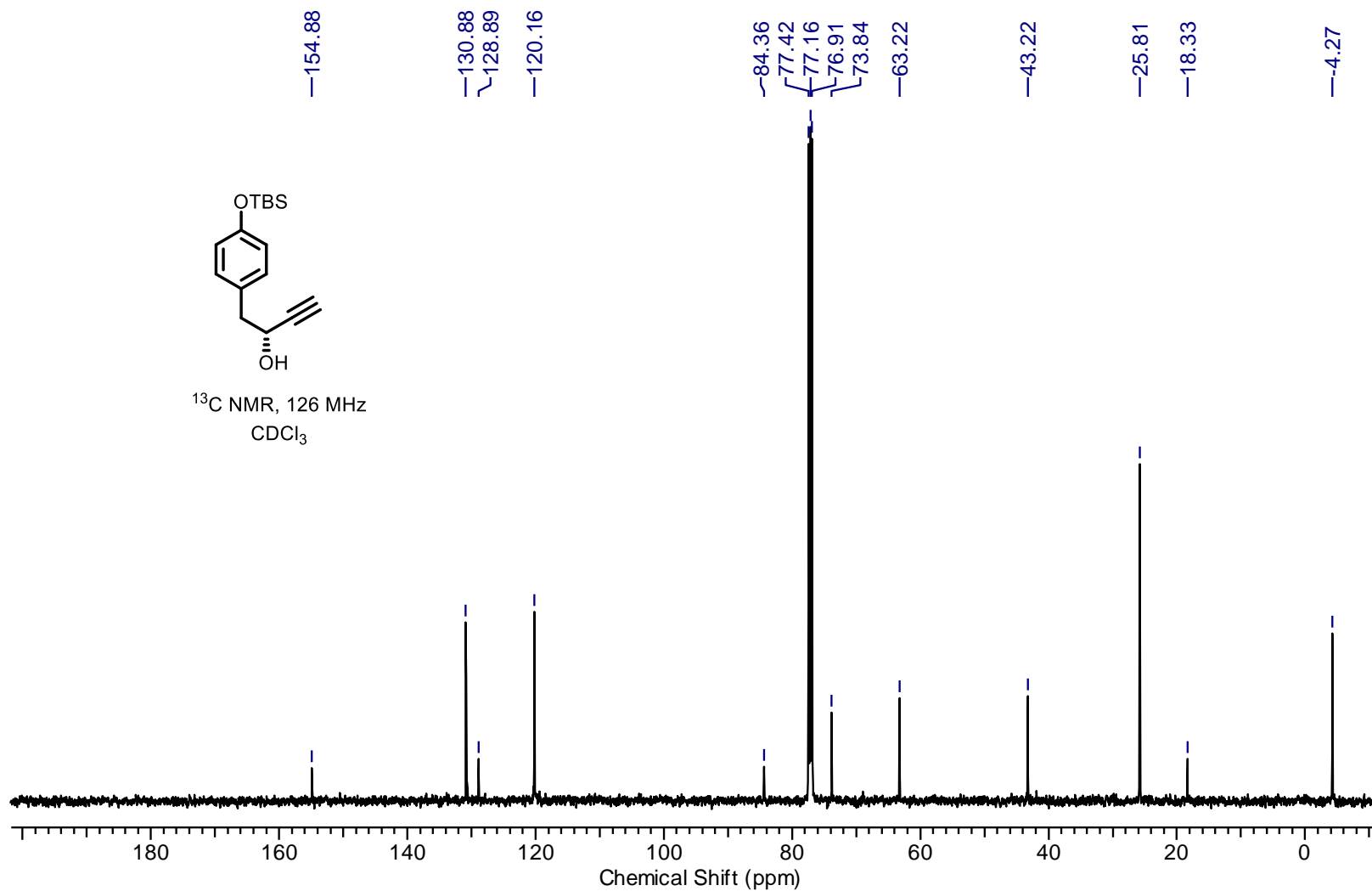




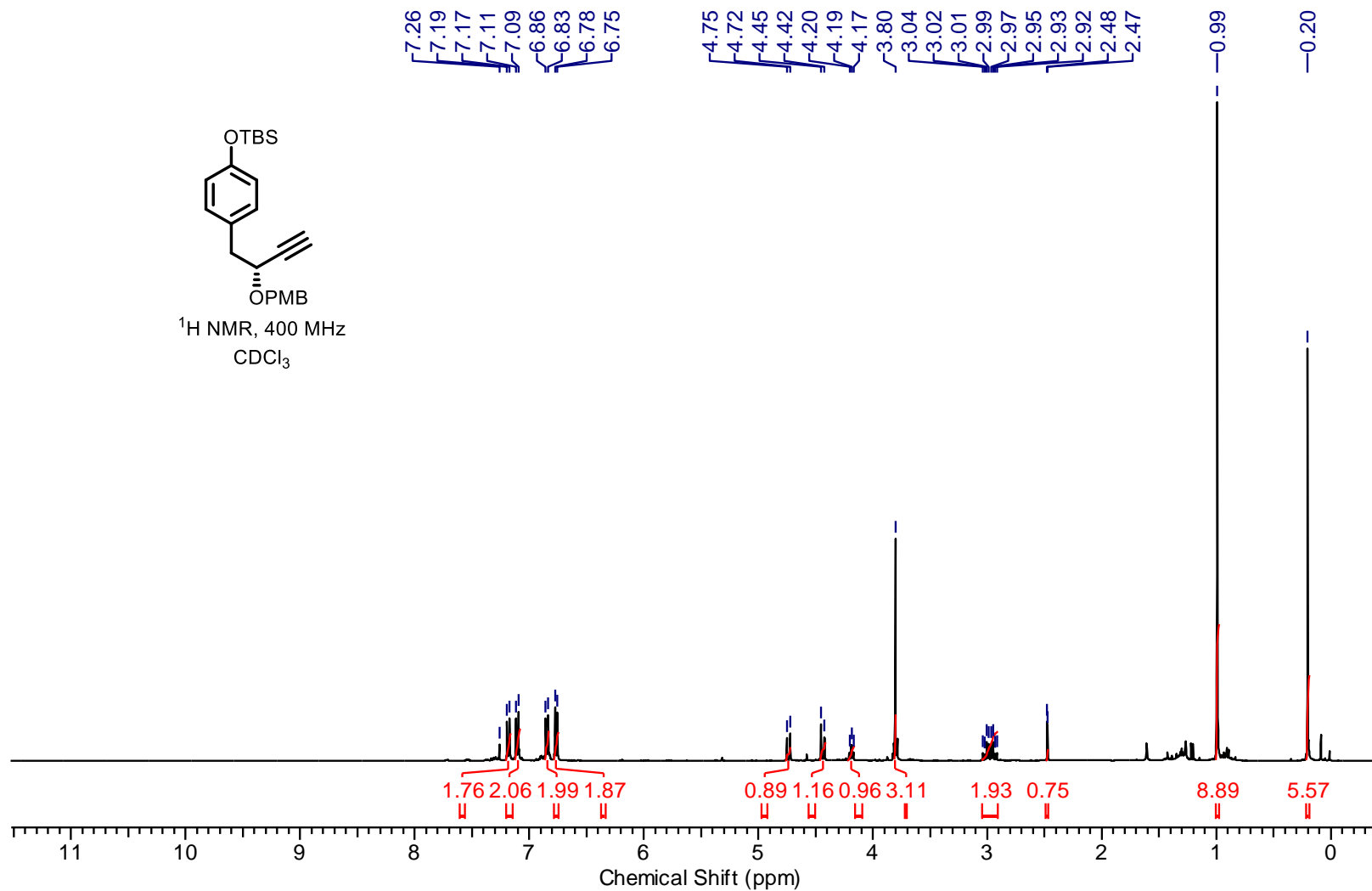
*(R)*-1-(4-((*Tert*-butyldimethylsilyl)oxy)phenyl)but-3-yn-2-ol (**S5a**):



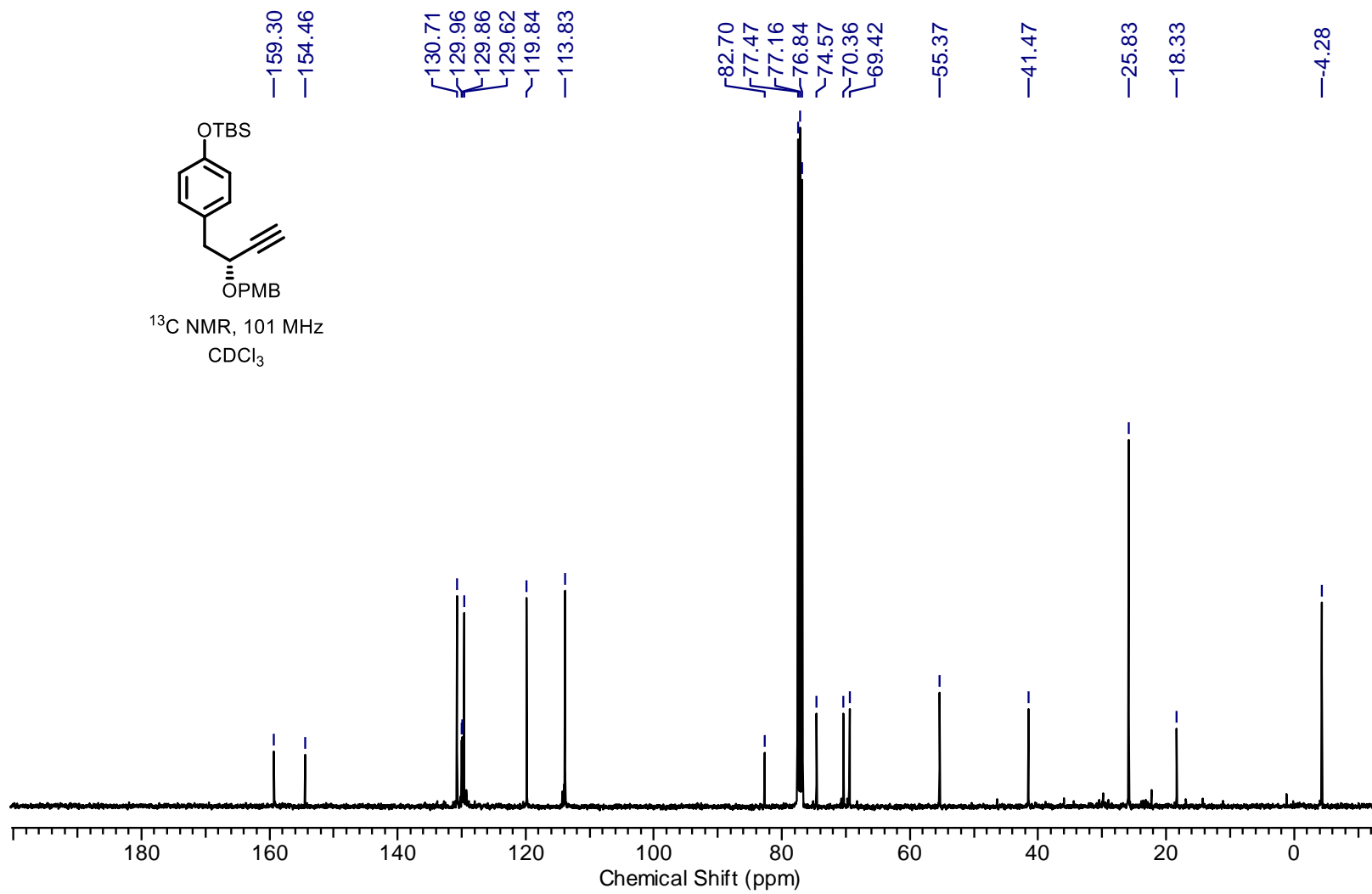
*(R)*-1-(4-((*Tert*-butyldimethylsilyloxy)phenyl)but-3-yn-2-ol (**S5a**):



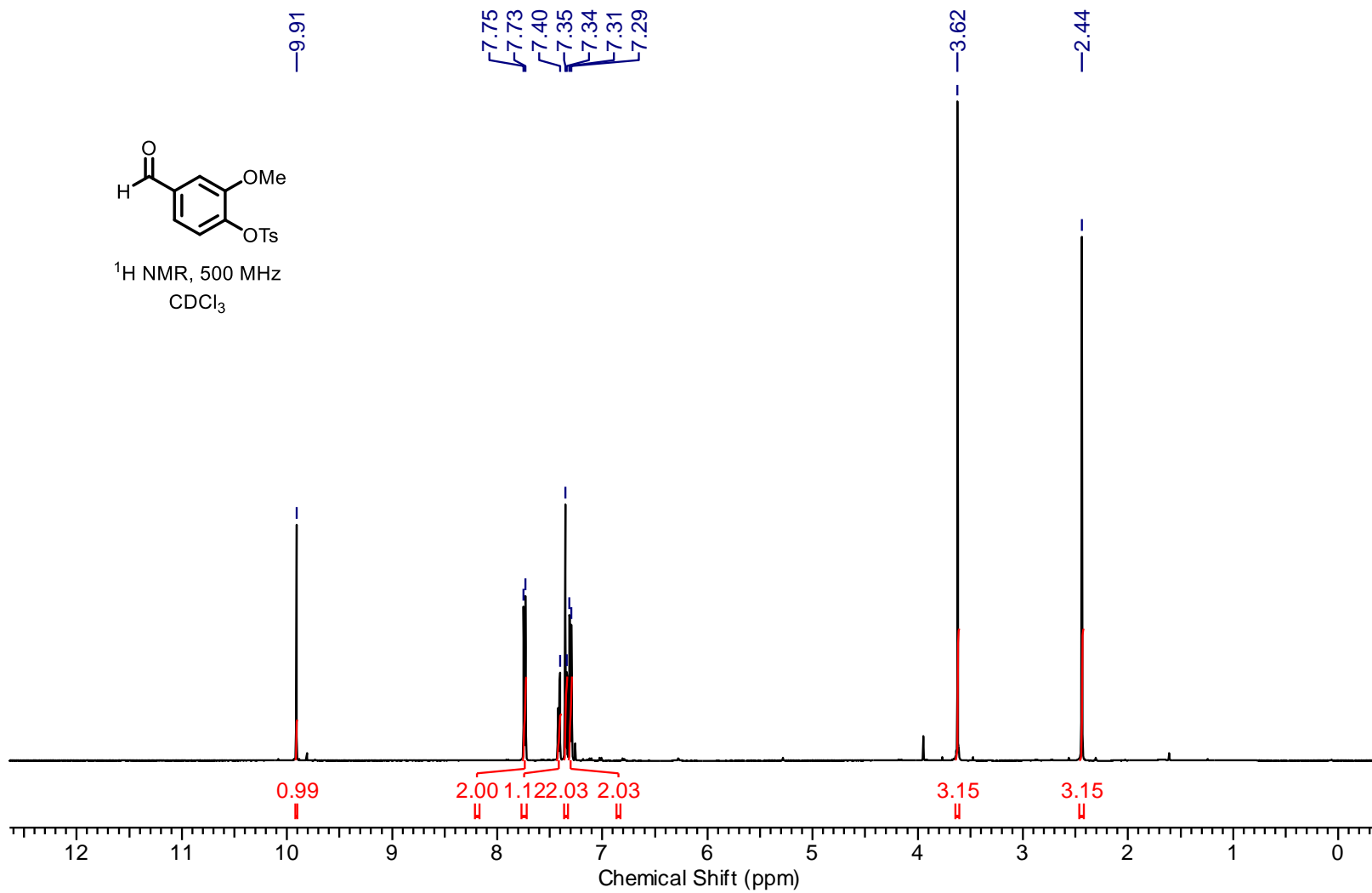
(R)-Tert-butyl(4-(2-((4-methoxybenzyl)oxy)but-3-yn-1-yl)phenoxy)dimethylsilane (**15a**):



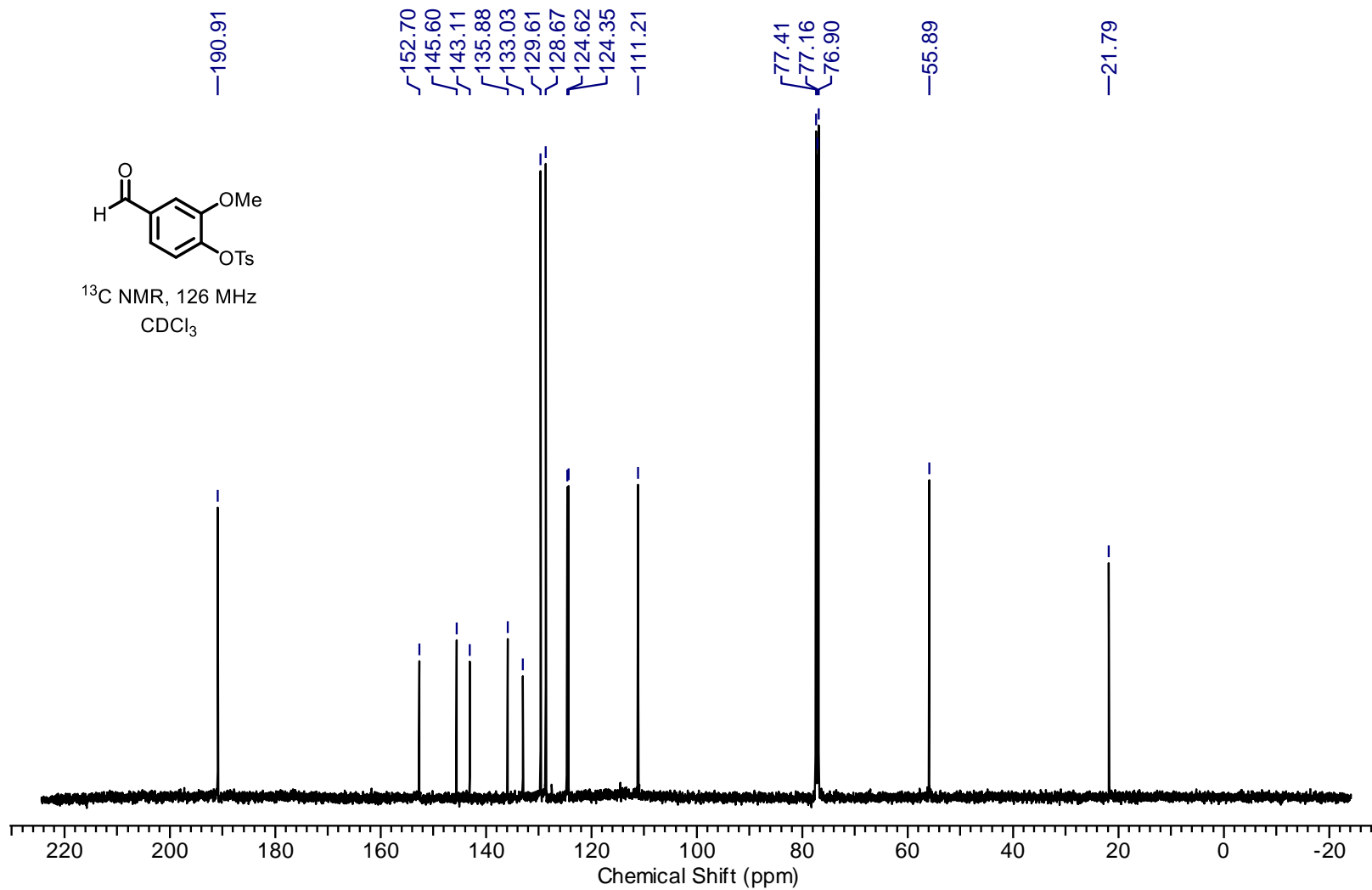
*(R)*-Tert-butyl(4-(2-((4-methoxybenzyl)oxy)but-3-yn-1-yl)phenoxy)dimethylsilane (**15a**):



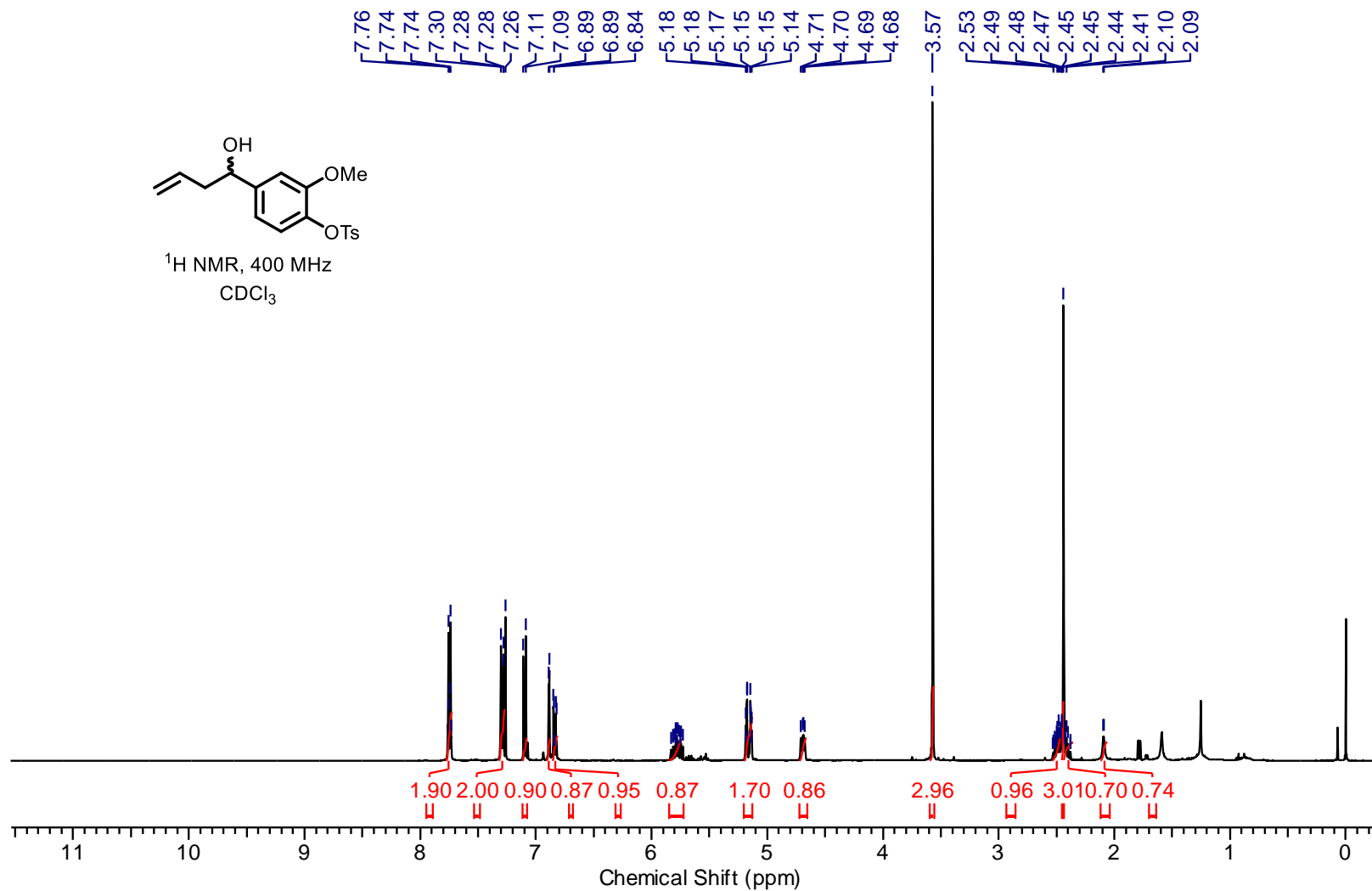
4-Formyl-2-methoxyphenyl-4-methylbenzenesulfonate (**10a**):



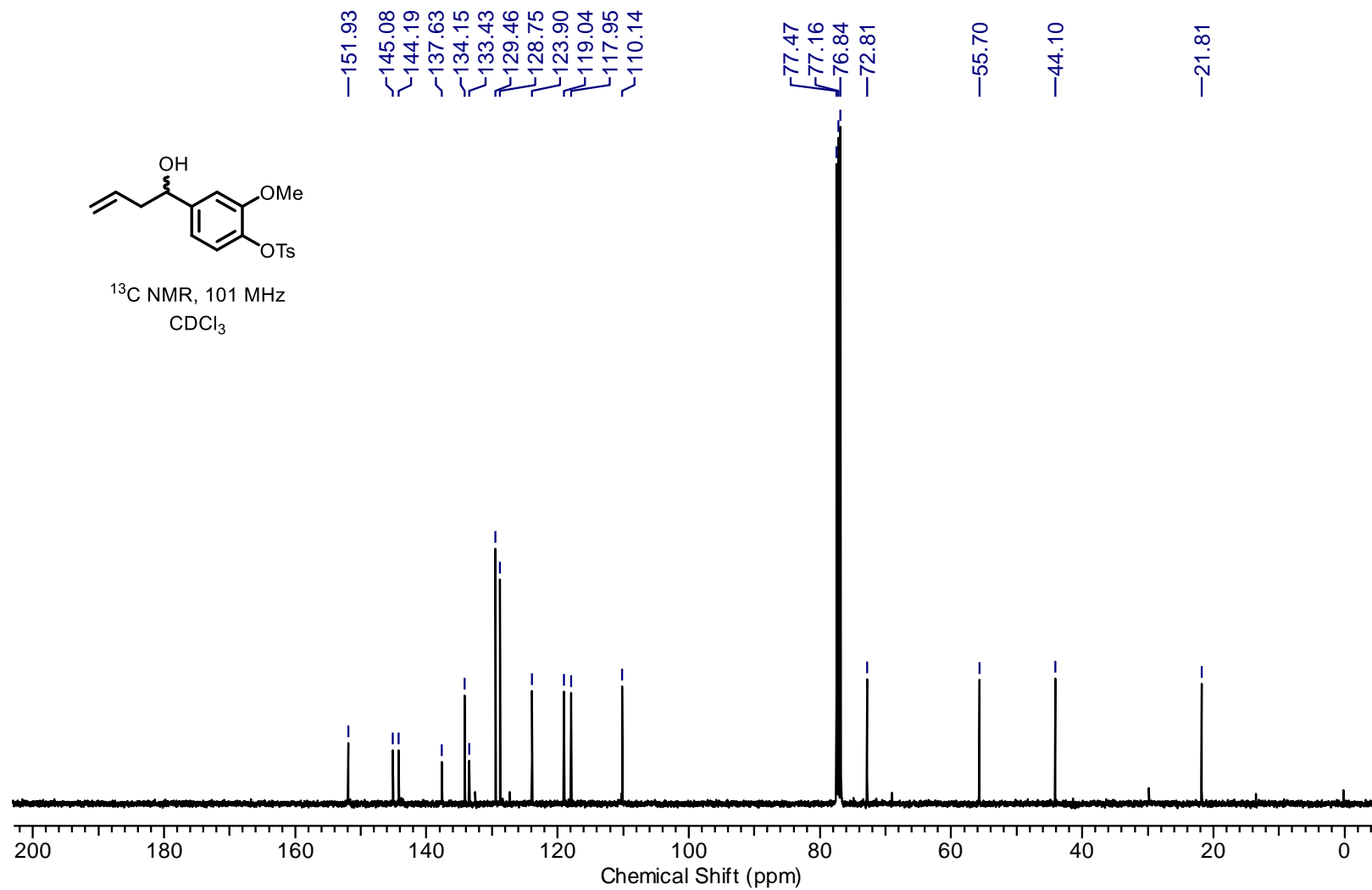
4-Formyl-2-methoxyphenyl-4-methylbenzenesulfonate (**10a**):



4-(1-Hydroxybut-3-en-1-yl)-2-methoxyphenyl 4-methylbenzenesulphonate (**S9**):

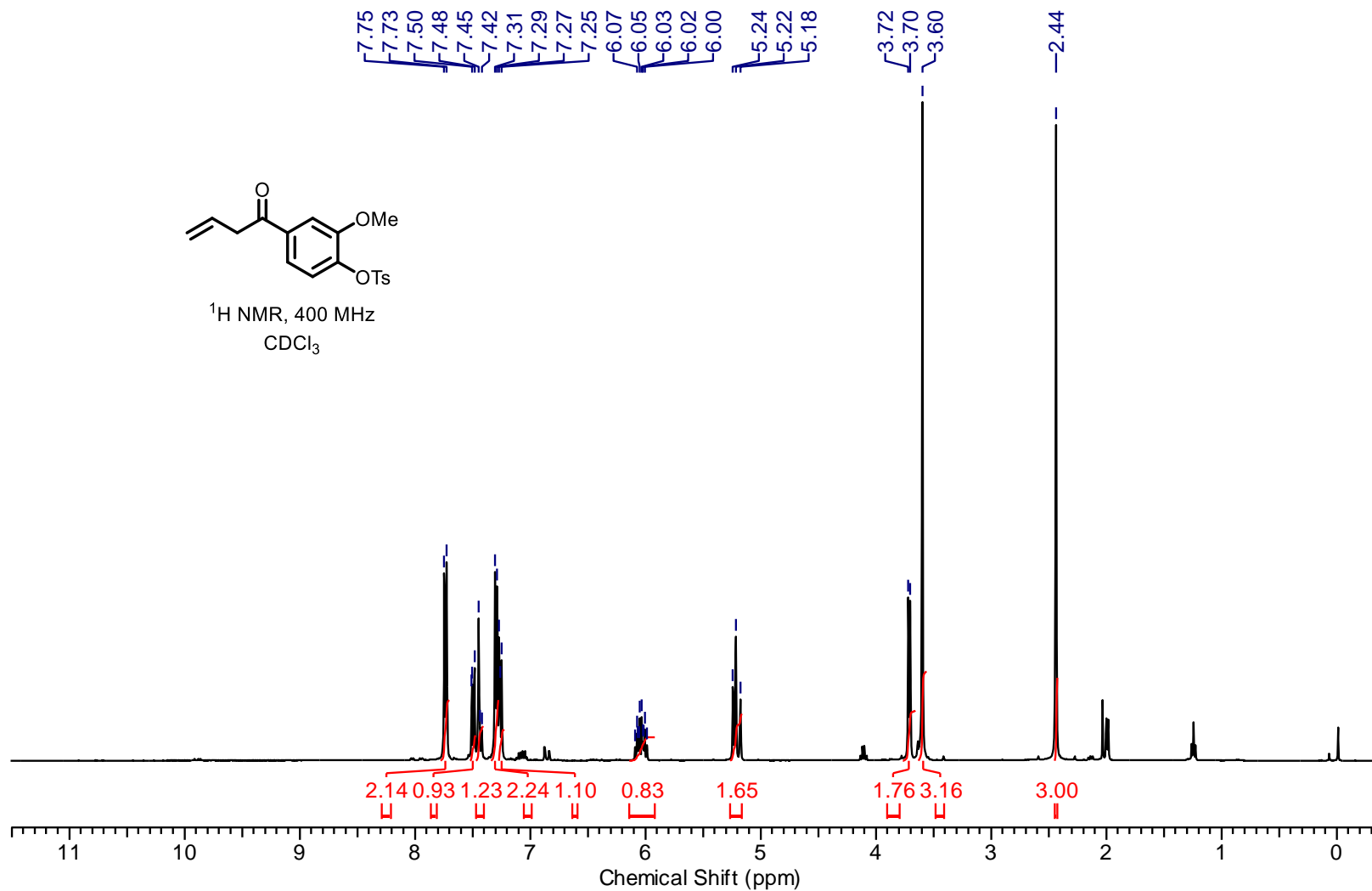


4-(1-Hydroxybut-3-en-1-yl)-2-methoxyphenyl 4-methylbenzenesulphonate (**S9**):

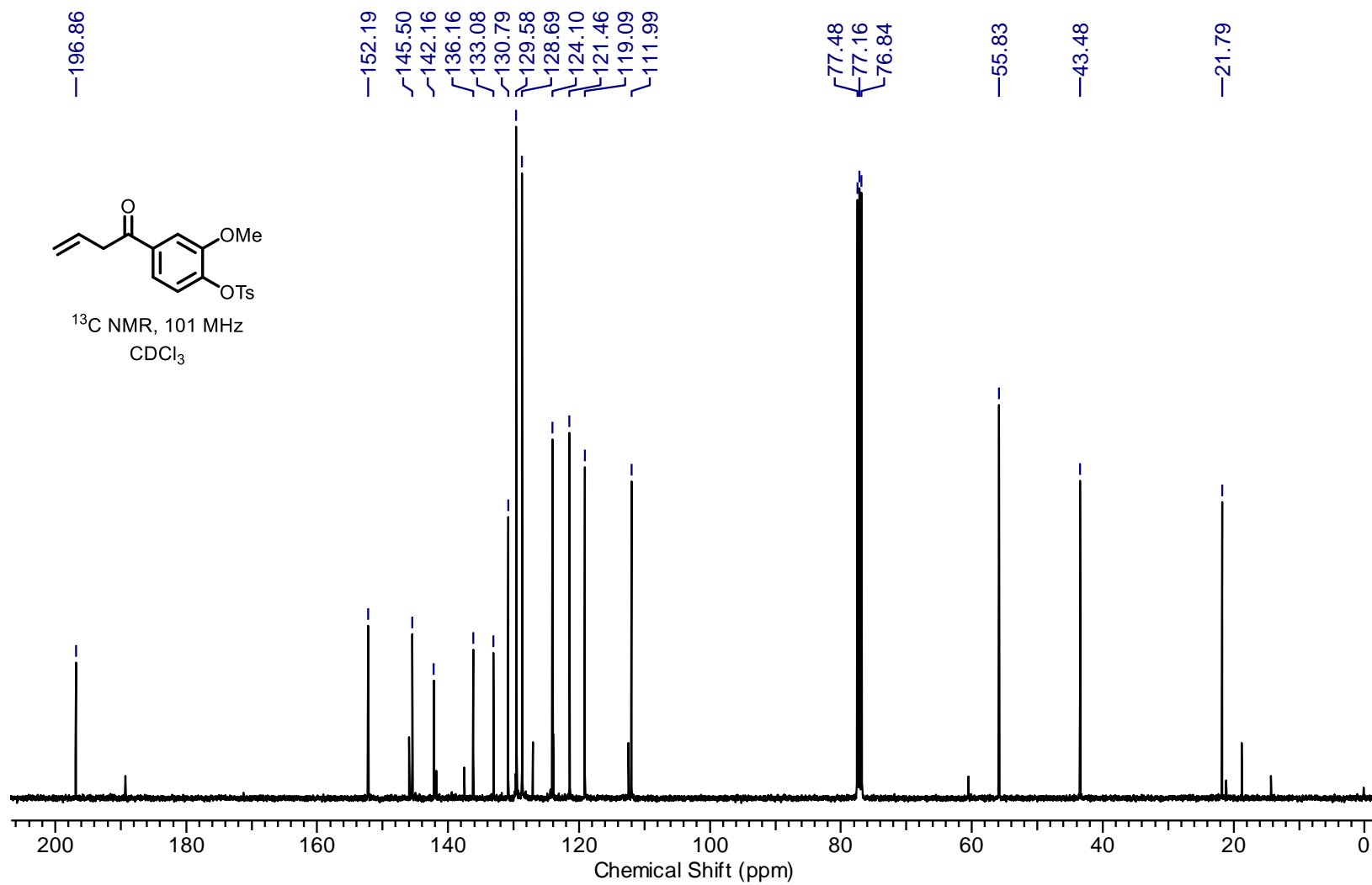




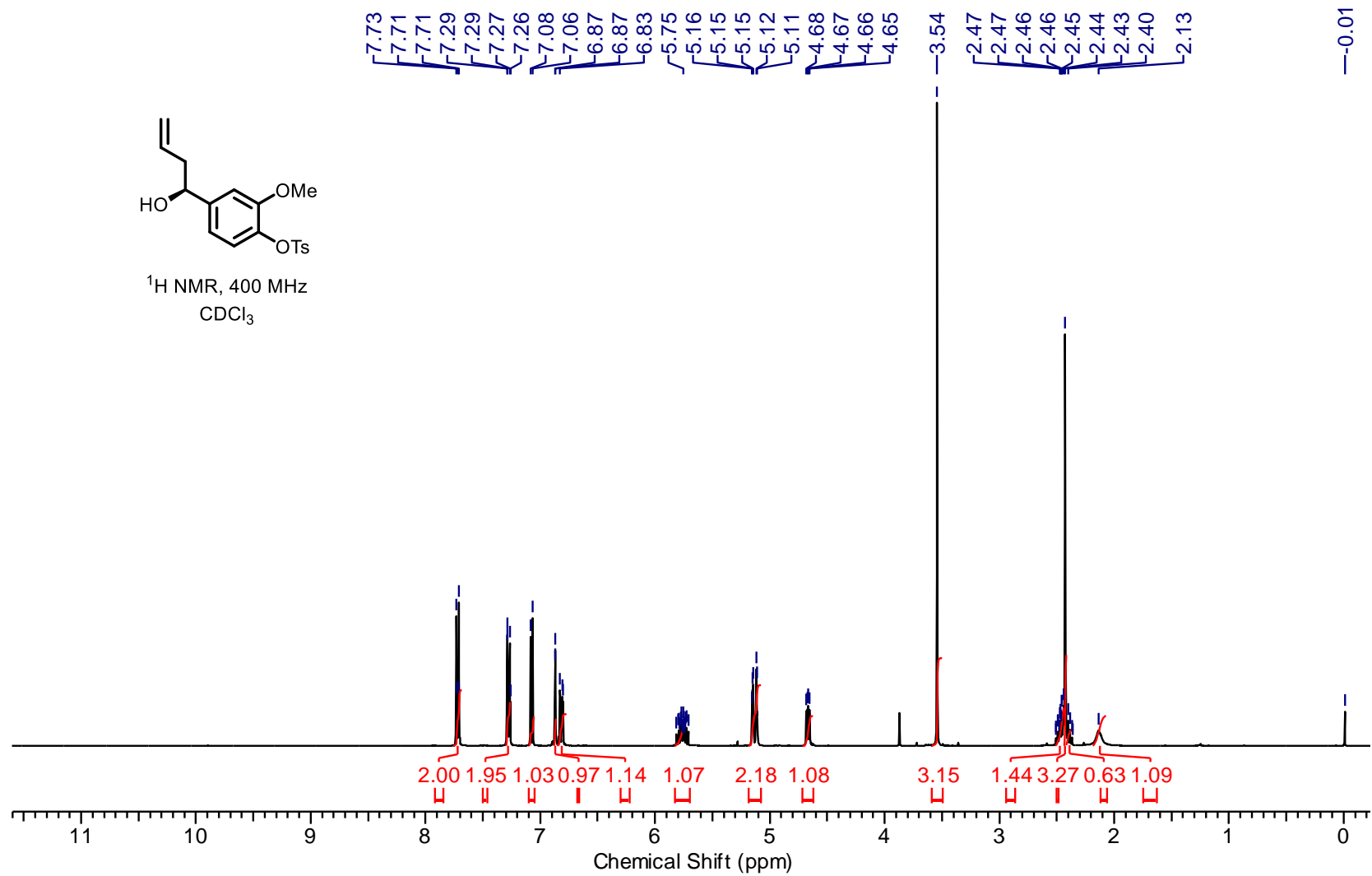
4-(But-3-enoyl)-2-methoxyphenyl-4-methylbenzenesulfonate (**28**):



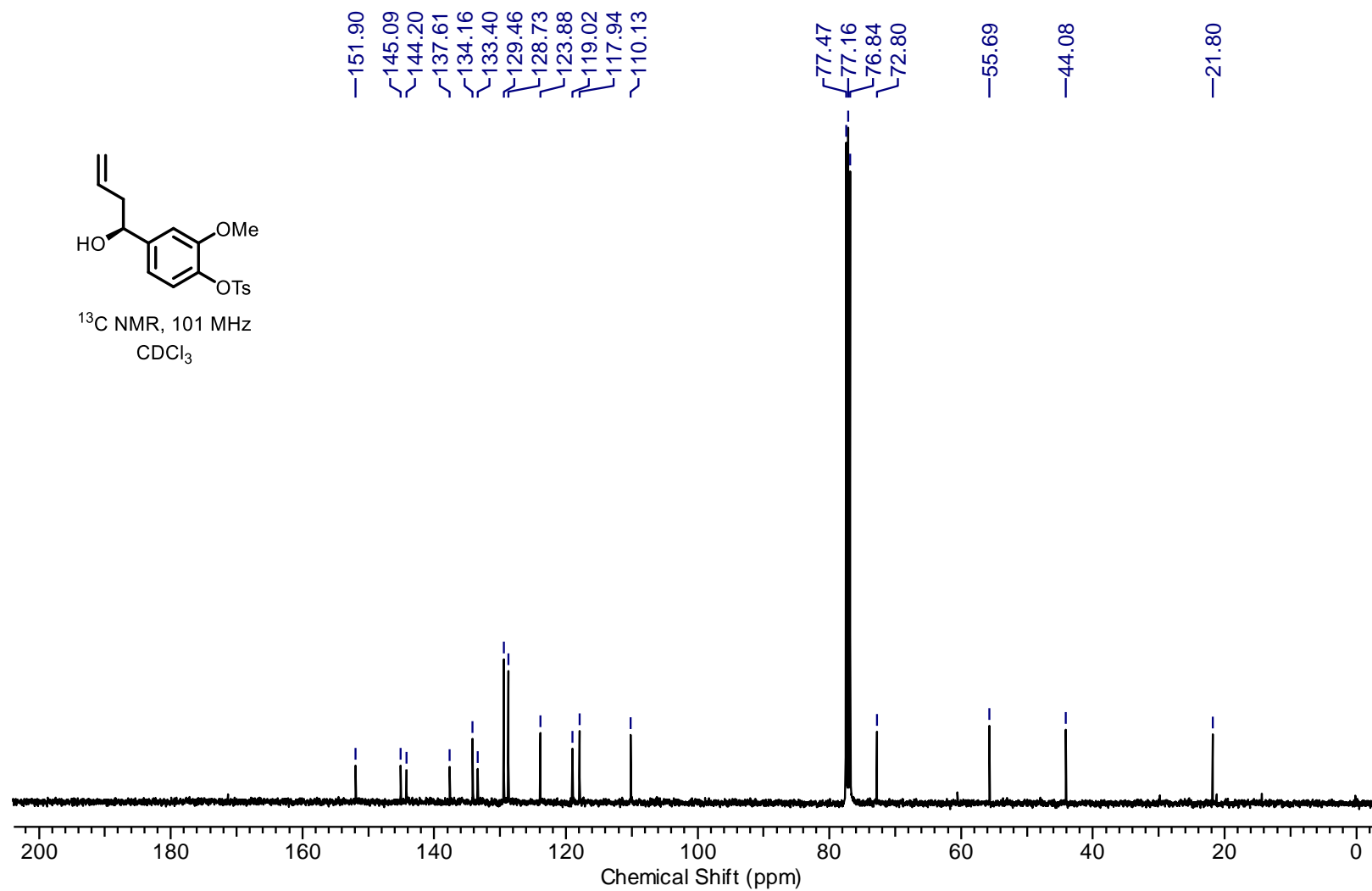
4-(But-3-enoyl)-2-methoxyphenyl-4-methylbenzenesulfonate (**28**):



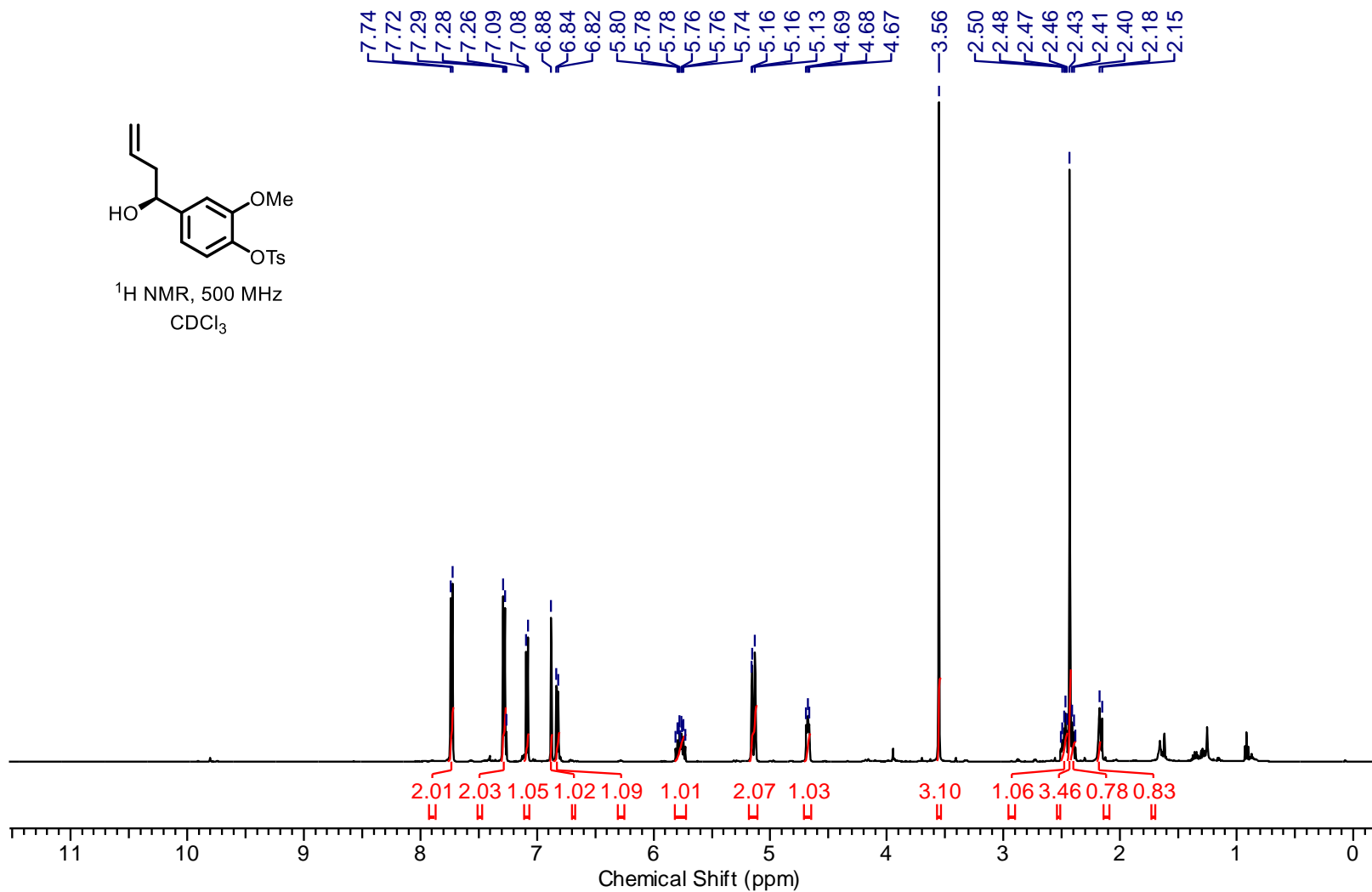
(S)-4-(1-Hydroxybut-3-en-1-yl)-2-methoxyphenyl-4-methylbenzenesulphonate (**20a**) (prepared from **28**)



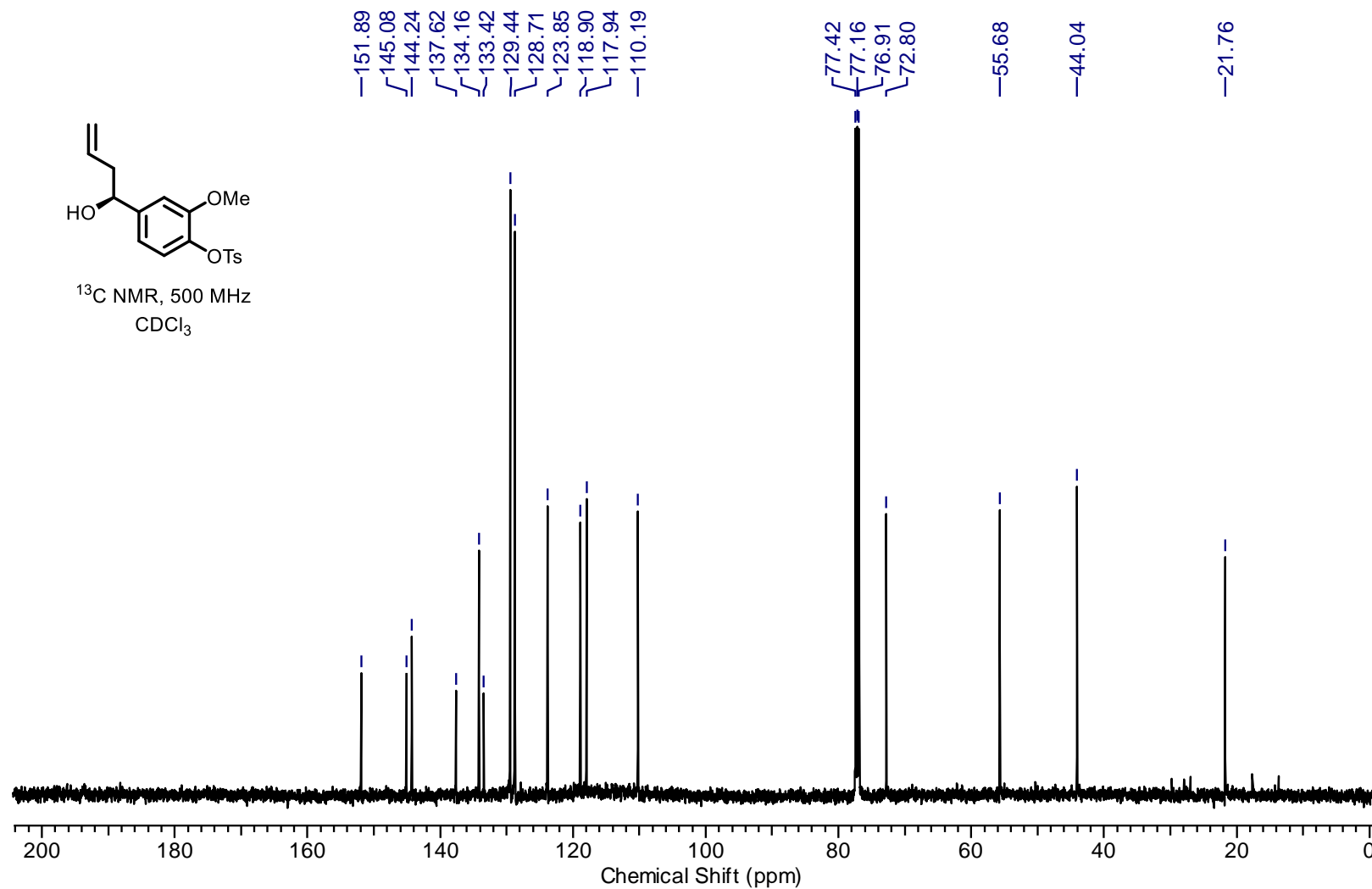
(S)-4-(1-Hydroxybut-3-en-1-yl)-2-methoxyphenyl-4-methylbenzenesulphonate (**20a**) (prepared from **28**)



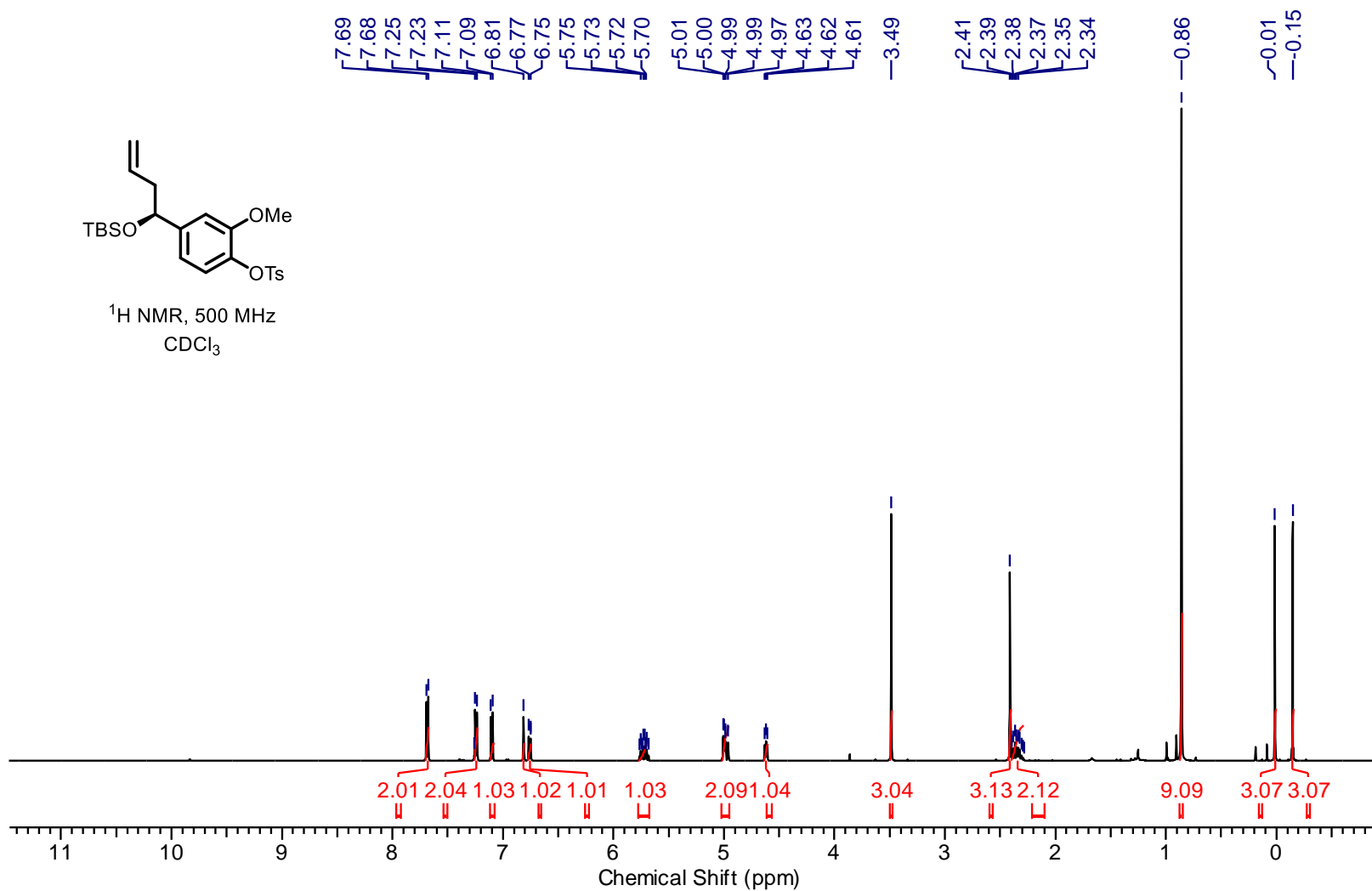
(S)-4-(1-Hydroxybut-3-en-1-yl)-2-methoxyphenyl-4-methylbenzenesulphonate (**20a**) (prepared from **10a**):



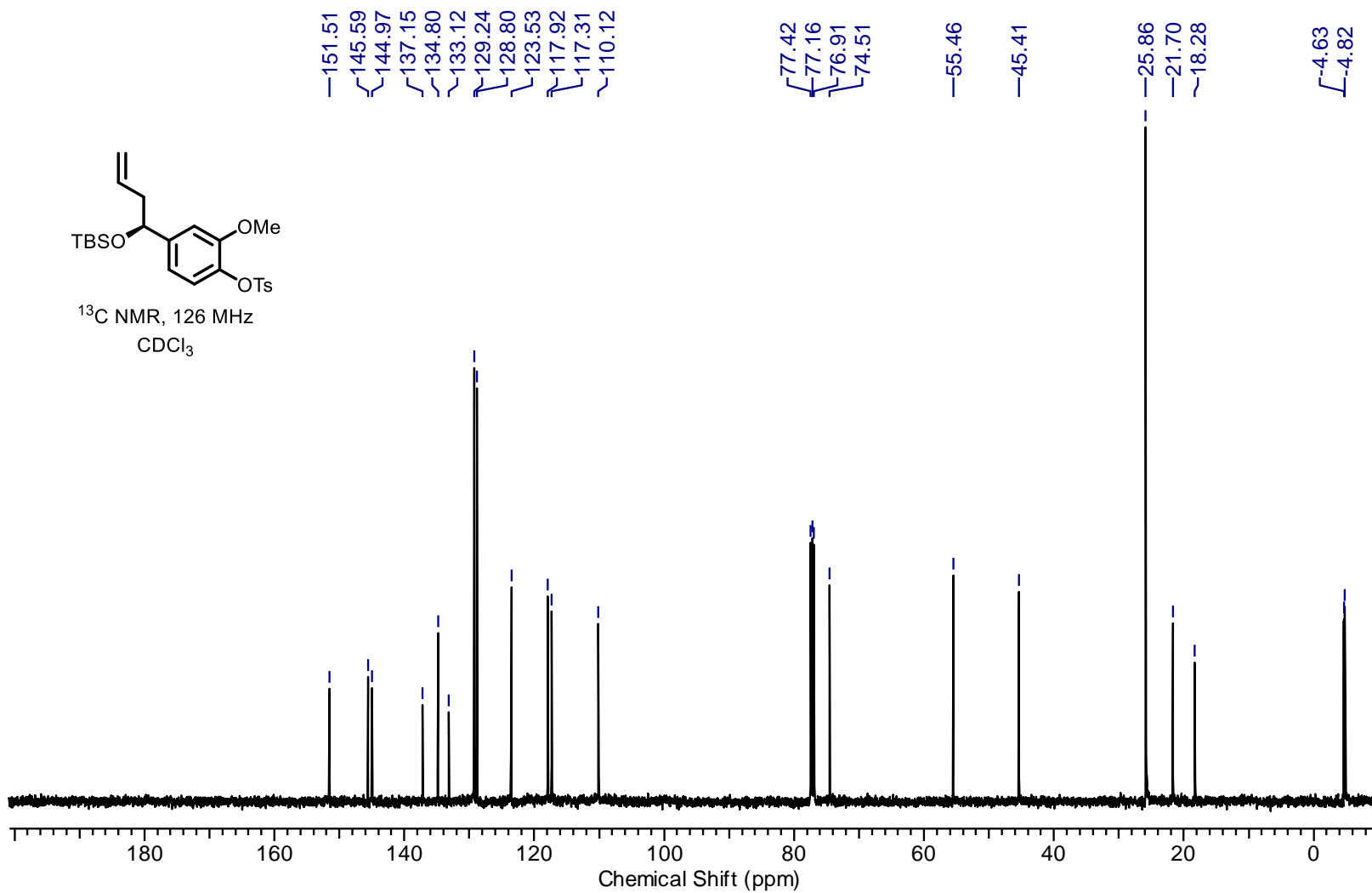
(*S*)-4-(1-Hydroxybut-3-en-1-yl)-2-methoxyphenyl-4-methylbenzenesulphonate (**20a**) (prepared from **10a**):



(S)-4-(1-((Tert-butyl dimethylsilyl)oxy)but-3-en-1-yl)-2-methoxyphenyl-4-methylbenzene-sulphonate (**S6a**):

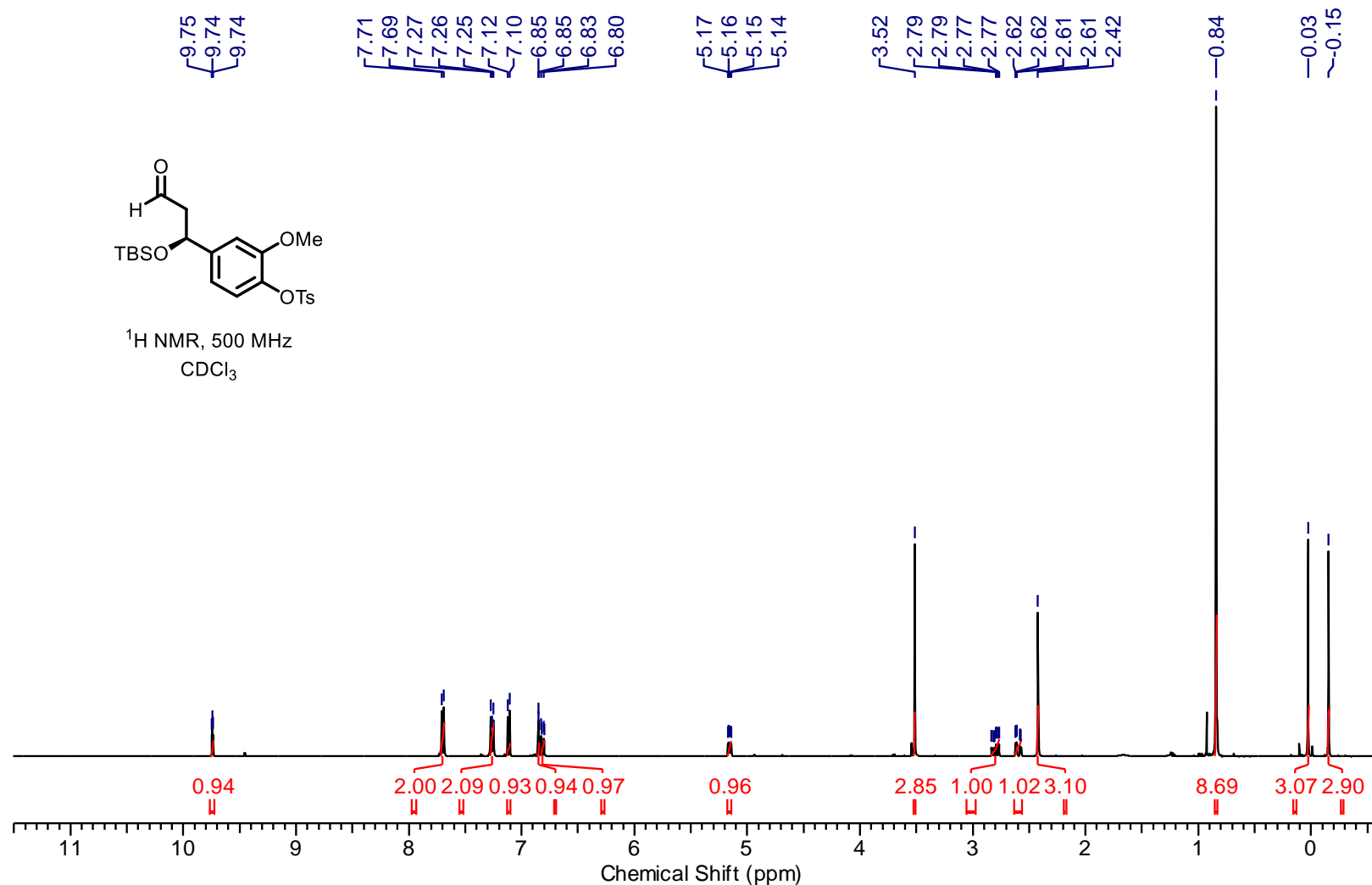


(S)-4-(1-((Tert-butyl dimethylsilyl)oxy)but-3-en-1-yl)-2-methoxyphenyl-4-methylbenzene-sulphonate (**S6a**):

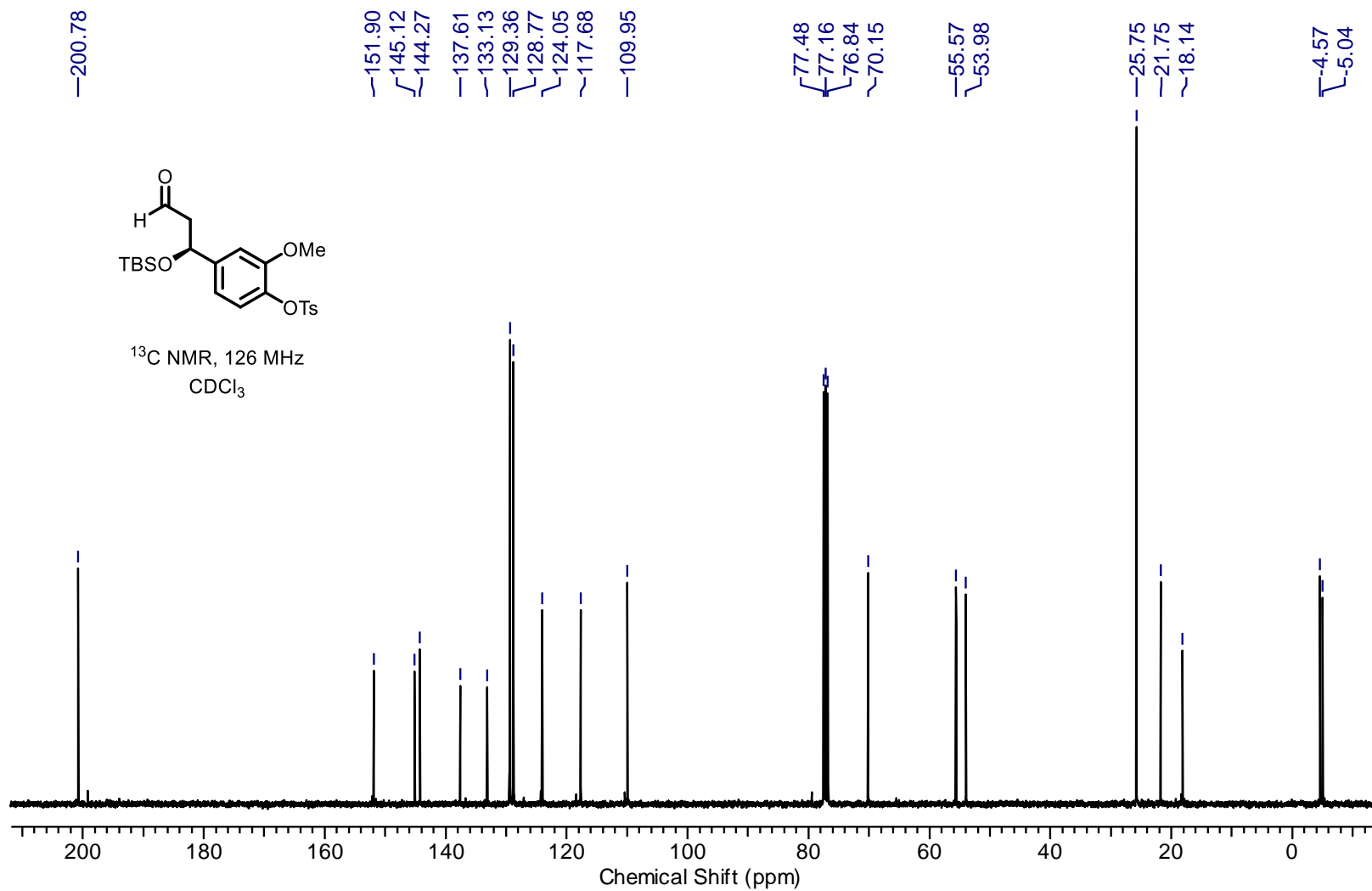




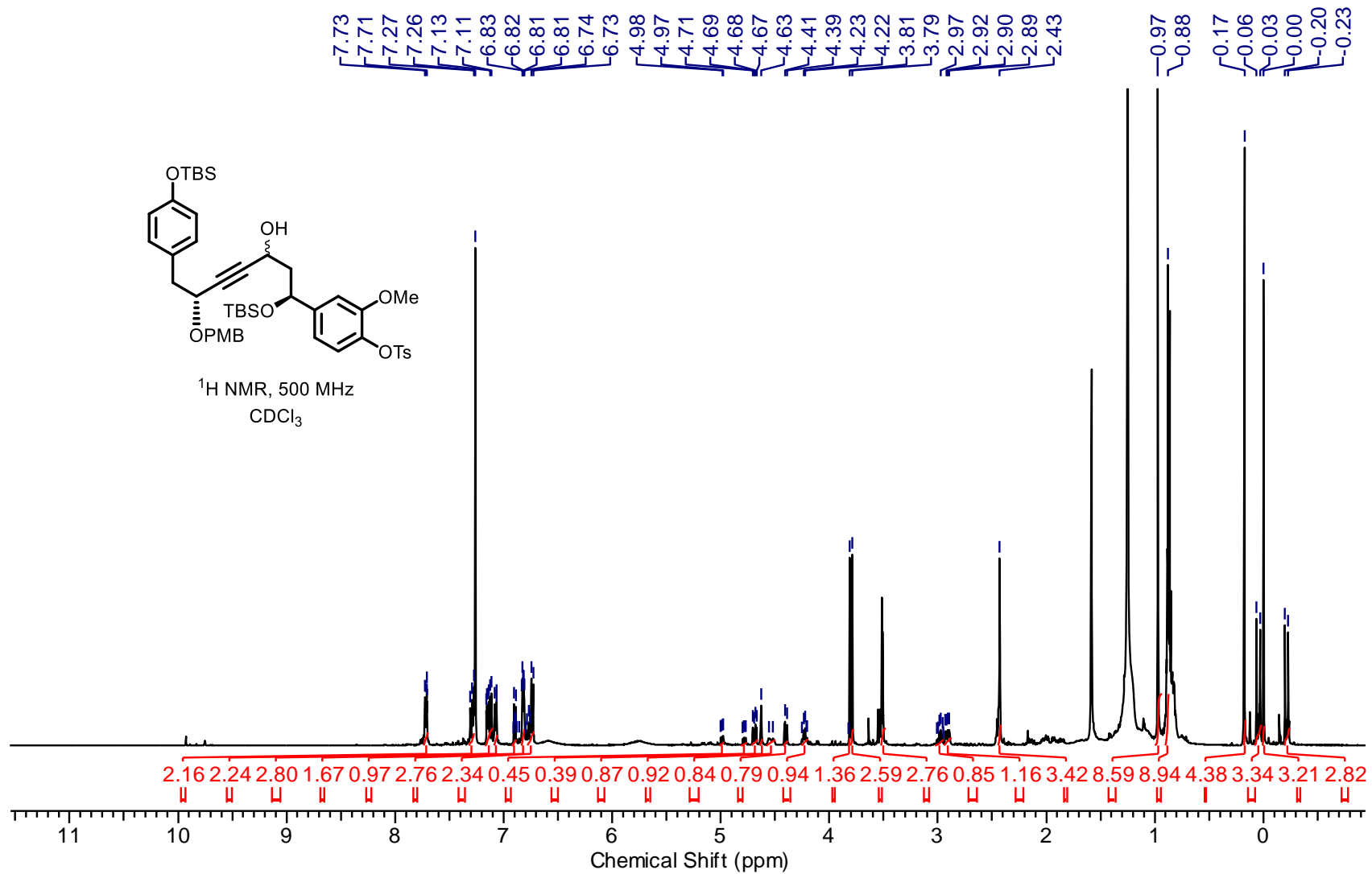
(S)-4-(1-((Tert-butyl dimethylsilyl)oxy)-3-oxopropyl)-2-methoxyphenyl-4-methylbenzene-sulfonate (**16a**):



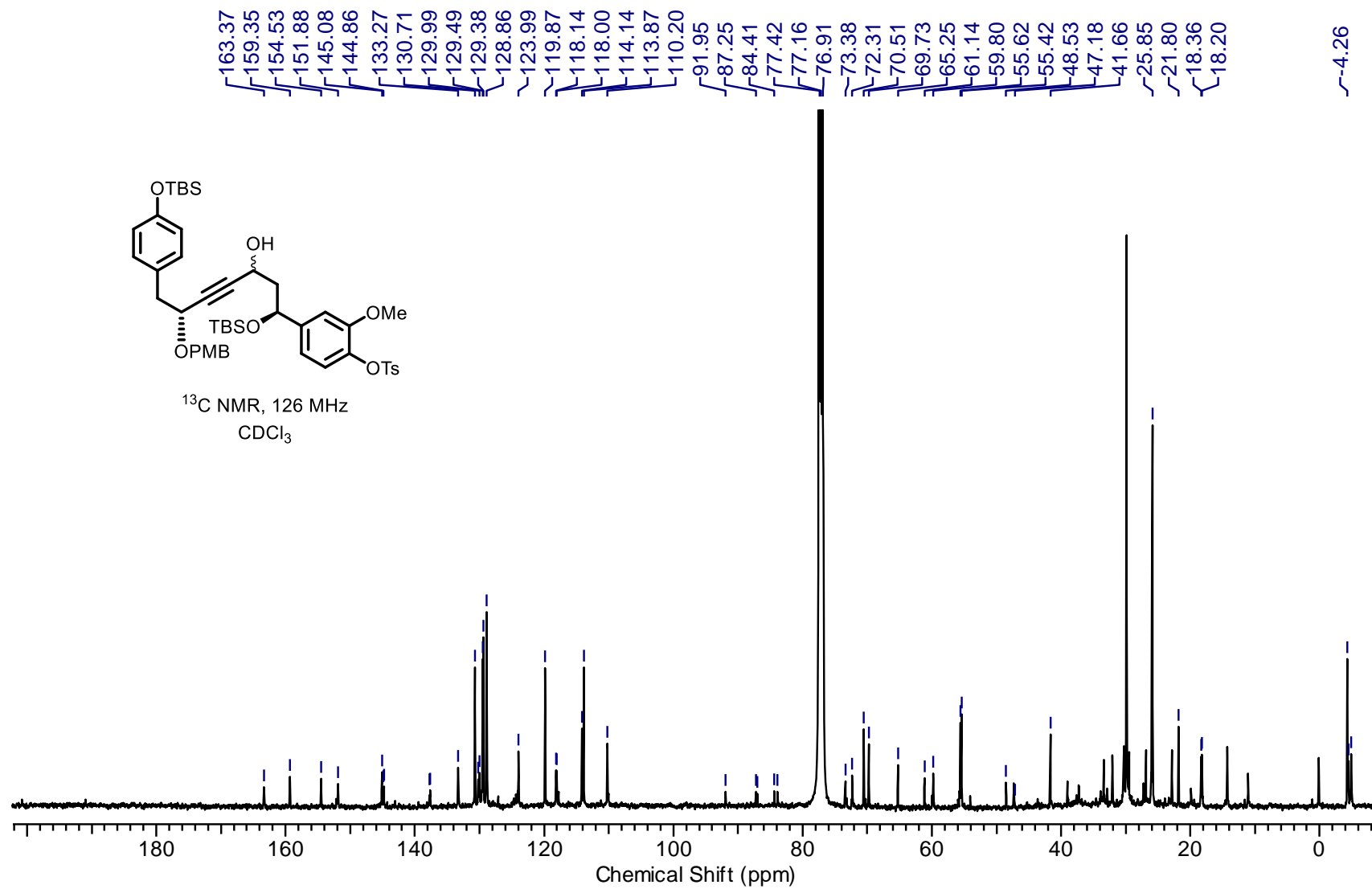
(S)-4-(1-((Tert-butyl dimethylsilyl)oxy)-3-oxopropyl)-2-methoxyphenyl-4-methylbenzene-sulfonate (**16a**):



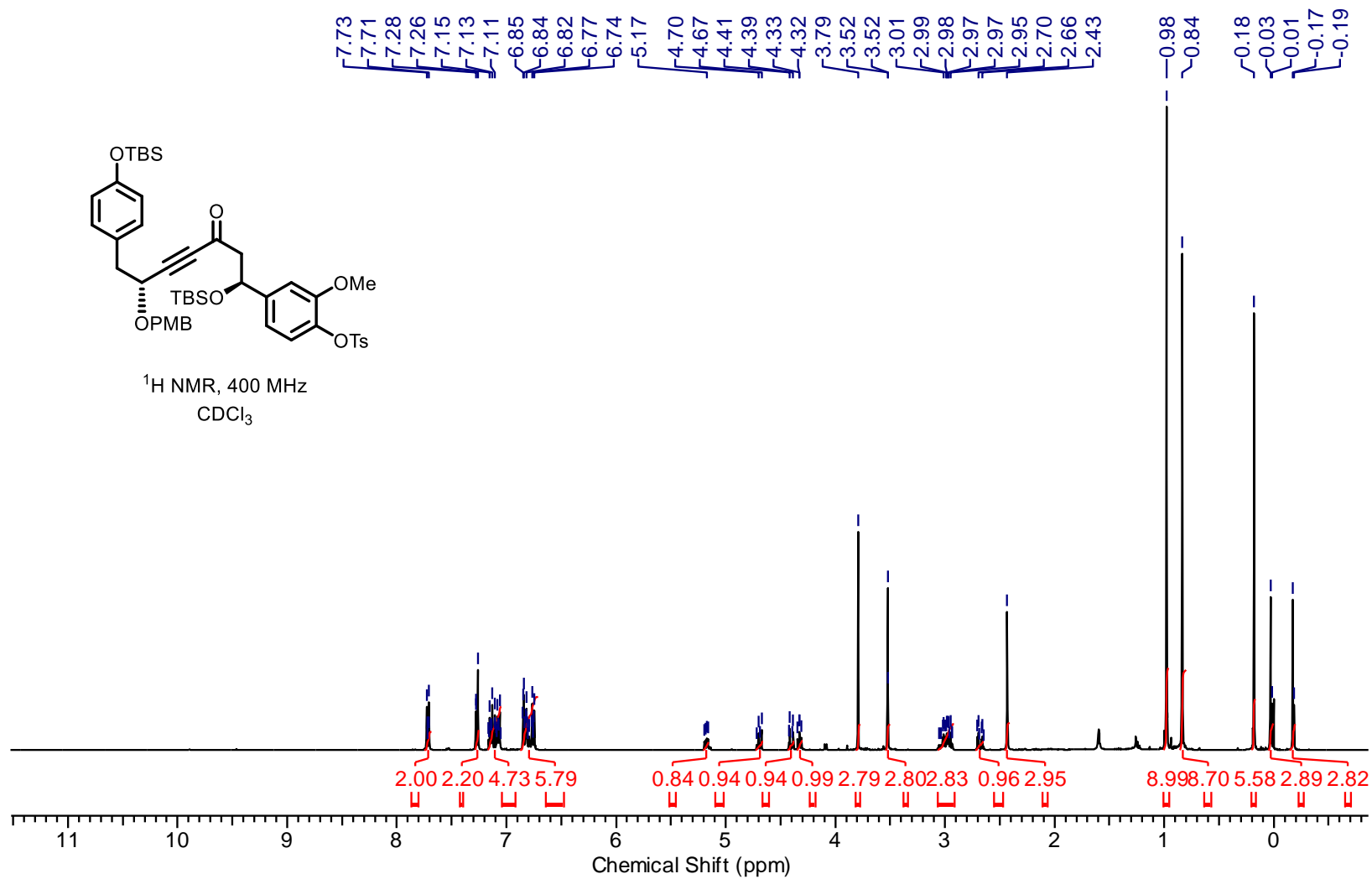
4-((1*S*, 6*R*)-1-((*Tert*-butyldimethylsilyl)oxy)-7-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-3-hydroxy-6-((4-methoxybenzyl)oxy)hept-4-yn-1-yl)-2-methoxyphenyl-4-methylbenzene-sulfonate (**21a**):



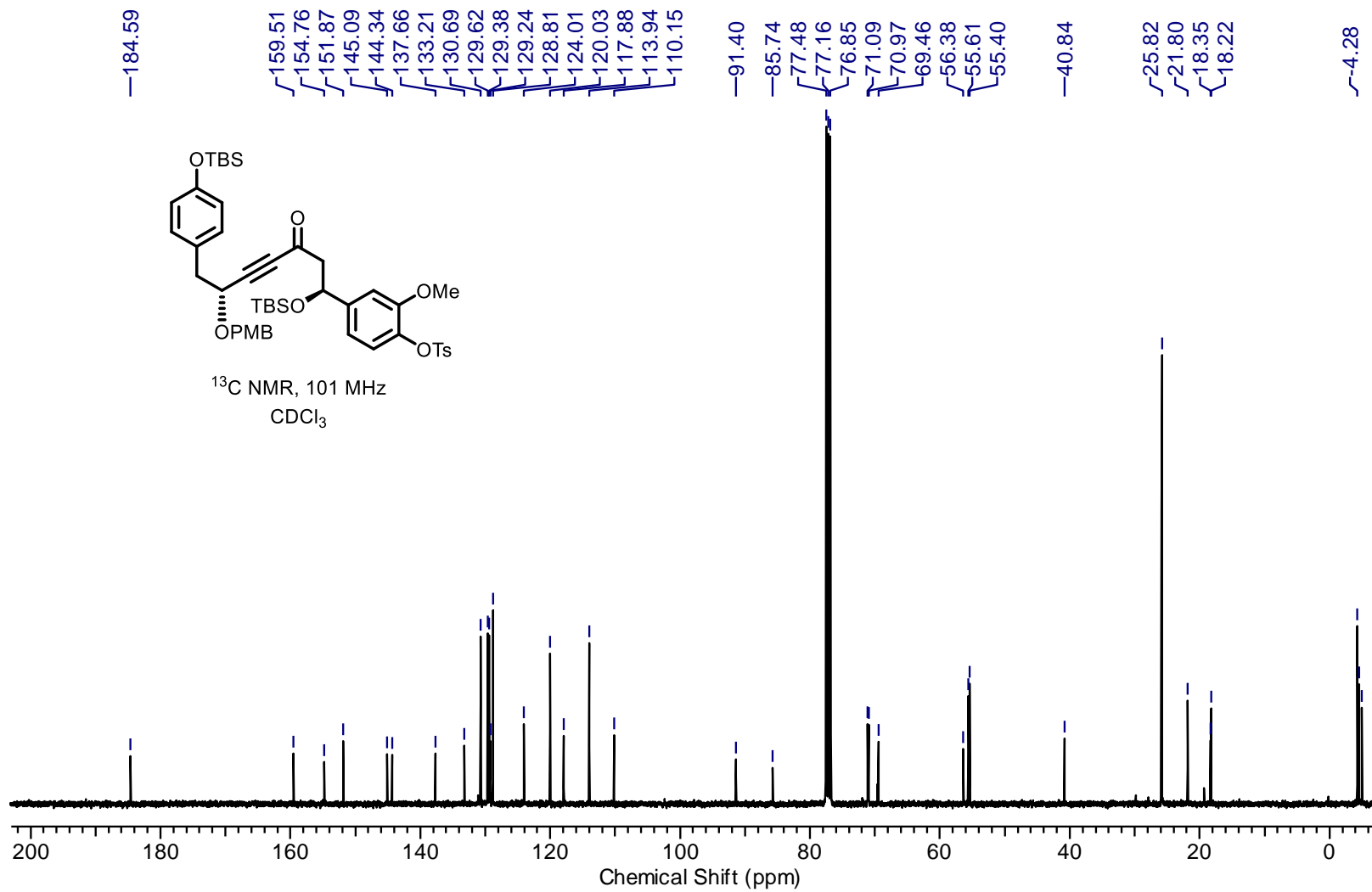
4-((1*S*, 6*R*)-1-((*Tert*-butyldimethylsilyl)oxy)-7-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-3-hydroxy-6-((4-methoxybenzyl)oxy)hept-4-yn-1-yl)-2-methoxyphenyl-4-methylbenzene-sulfonate (**21a**):



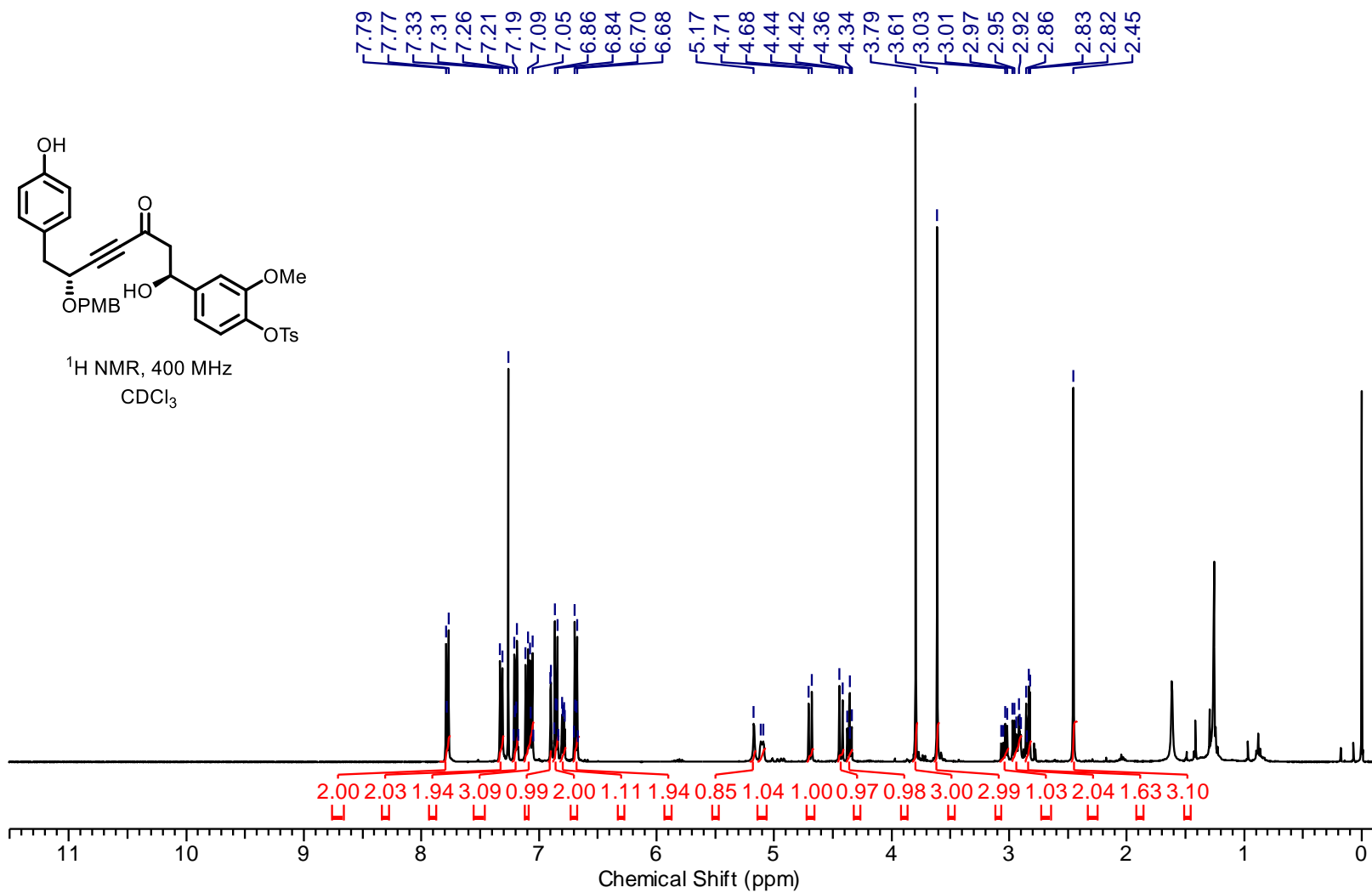
4-((1*S*, 6*R*)-1-((*Tert*-butyldimethylsilyl)oxy)-7-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-6-((4-methoxybenzyl)oxy)-3-oxohept-4-yn-1-yl)-2-methoxyphenyl-4-methylbenzenesulfonate (**14b**):



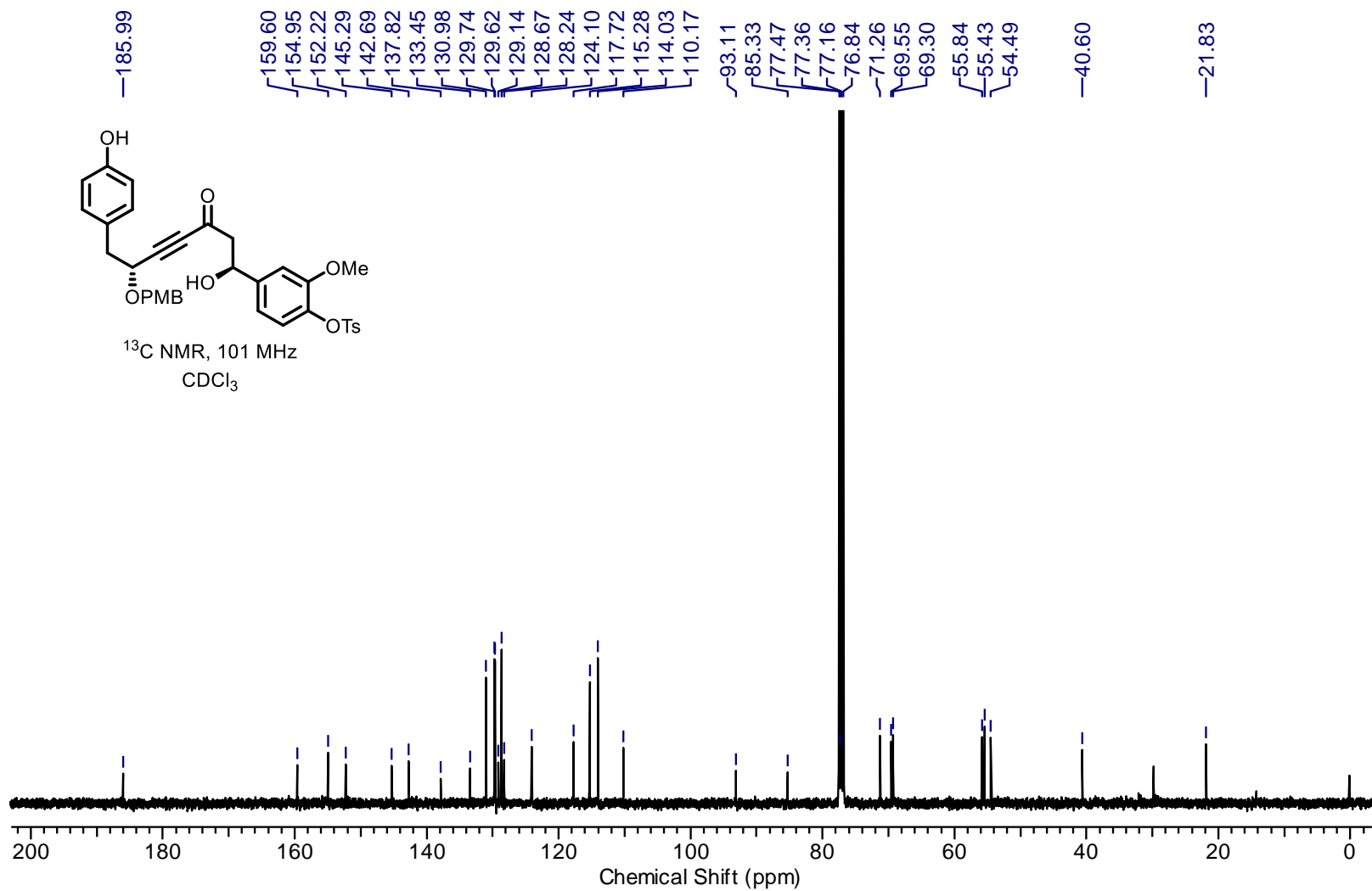
4-((1*S*, 6*R*)-1-((*Tert*-butyldimethylsilyl)oxy)-7-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-6-((4-methoxybenzyl)oxy)-3-oxohept-4-yn-1-yl)-2-methoxyphenyl-4-methylbenzenesulfonate (**14b**):



4-((1*S*, 6*R*)-7-(4-((*Tert*-butyldimethylsilyl)oxy)phenyl)-1-hydroxy-6-((4-methoxybenzyl)-oxy)-3-oxohept-4-yn-1-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**29**):

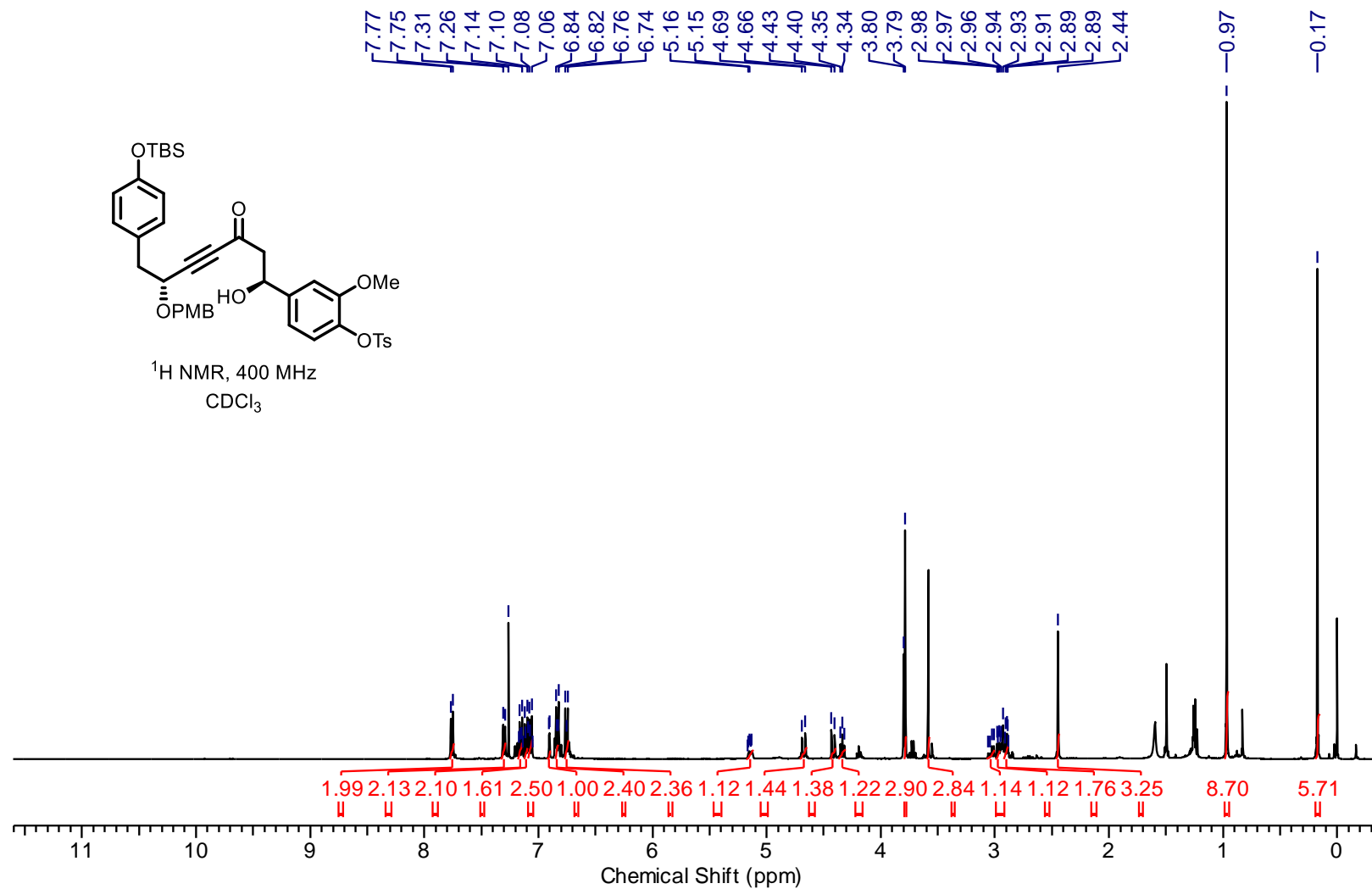


4-((1*S*, 6*R*)-7-(4-((*Tert*-butyldimethylsilyl)oxy)phenyl)-1-hydroxy-6-((4-methoxybenzyl)-oxy)-3-oxohept-4-yn-1-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**29**):

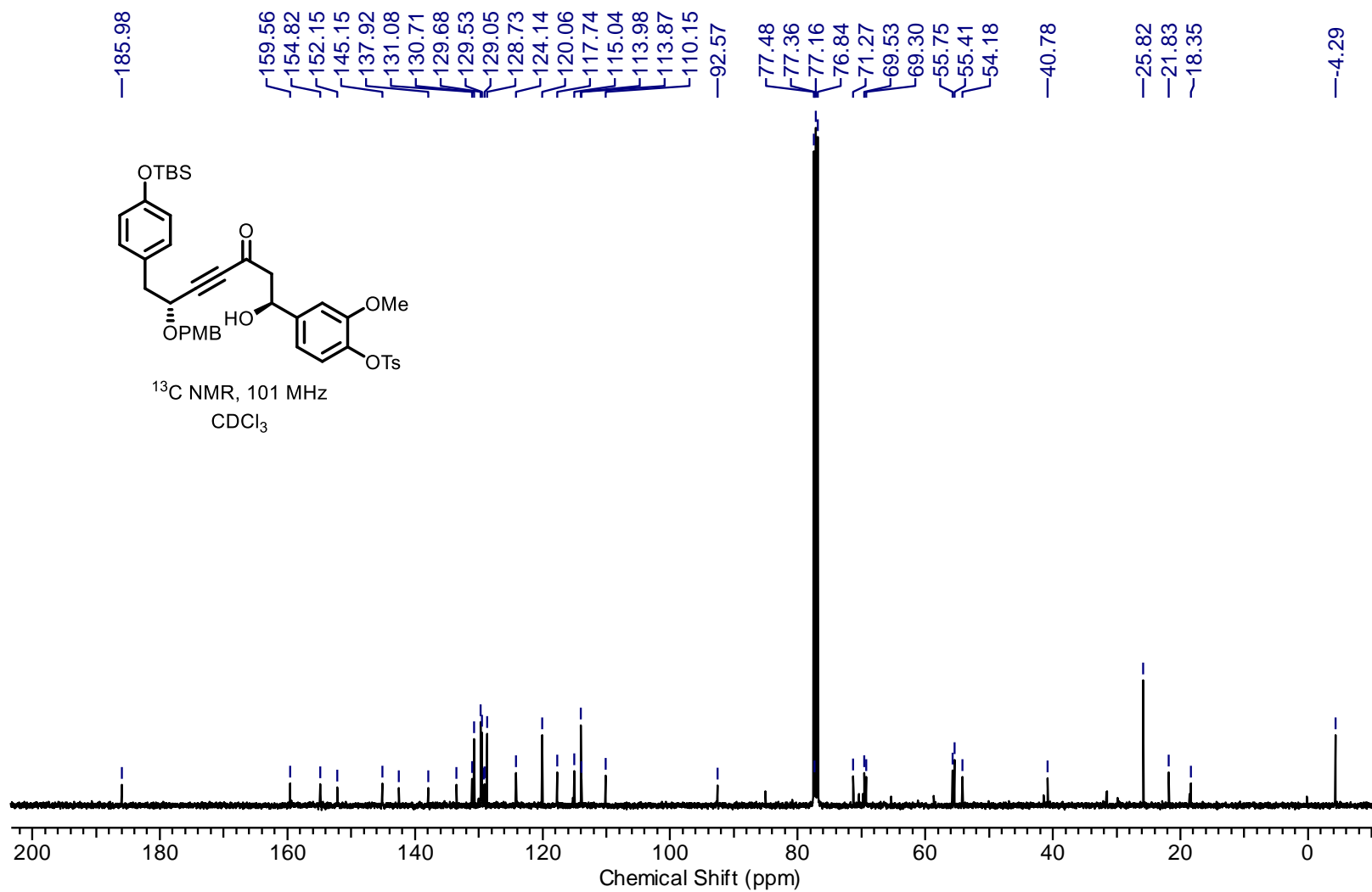




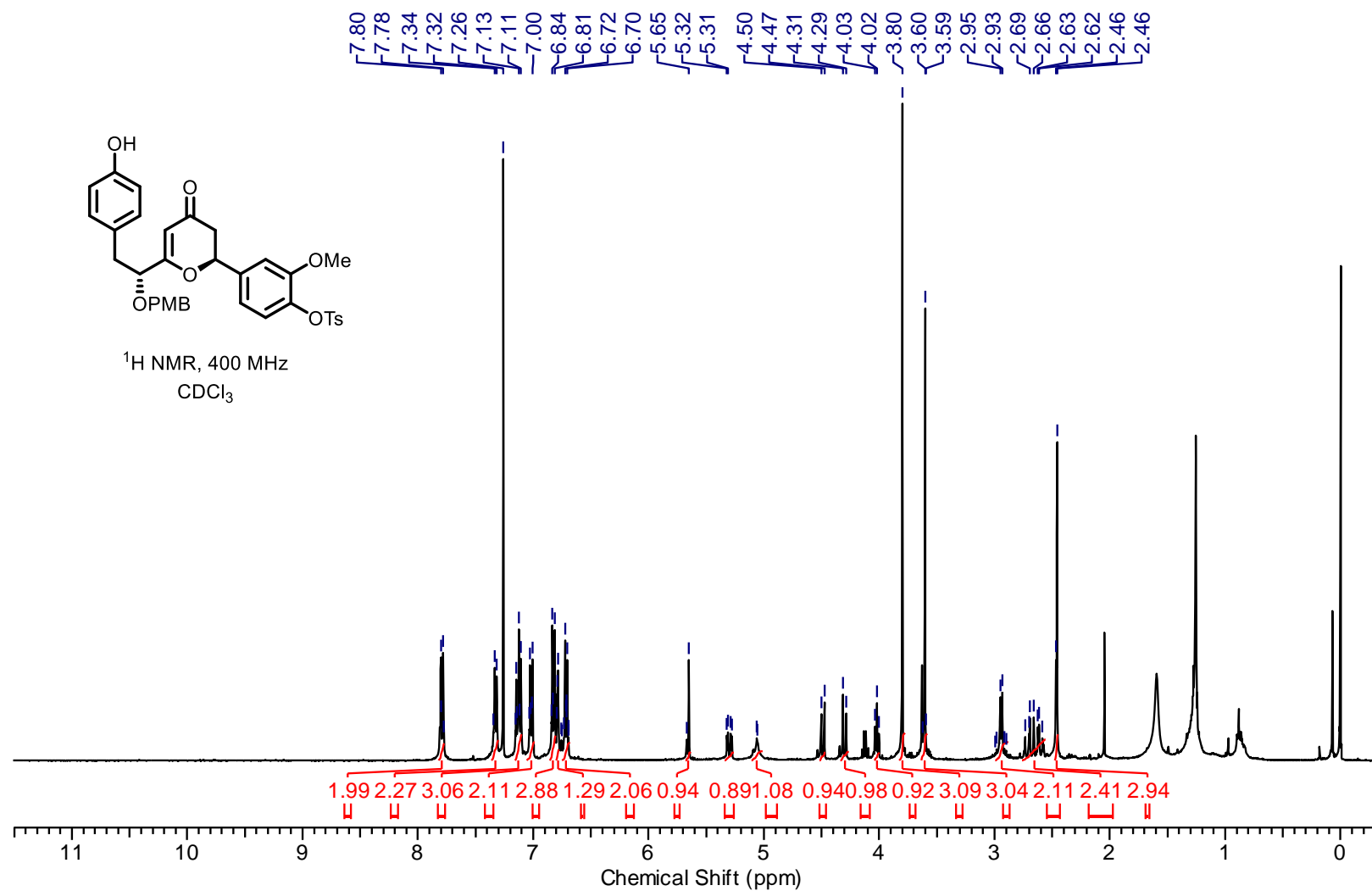
4-((1*S*, 6*R*)-1-Hydroxy-7-(4-hydroxyphenyl)-6-((4-methoxybenzyl)oxy)-3-oxohept-4-yn-1-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**30**):



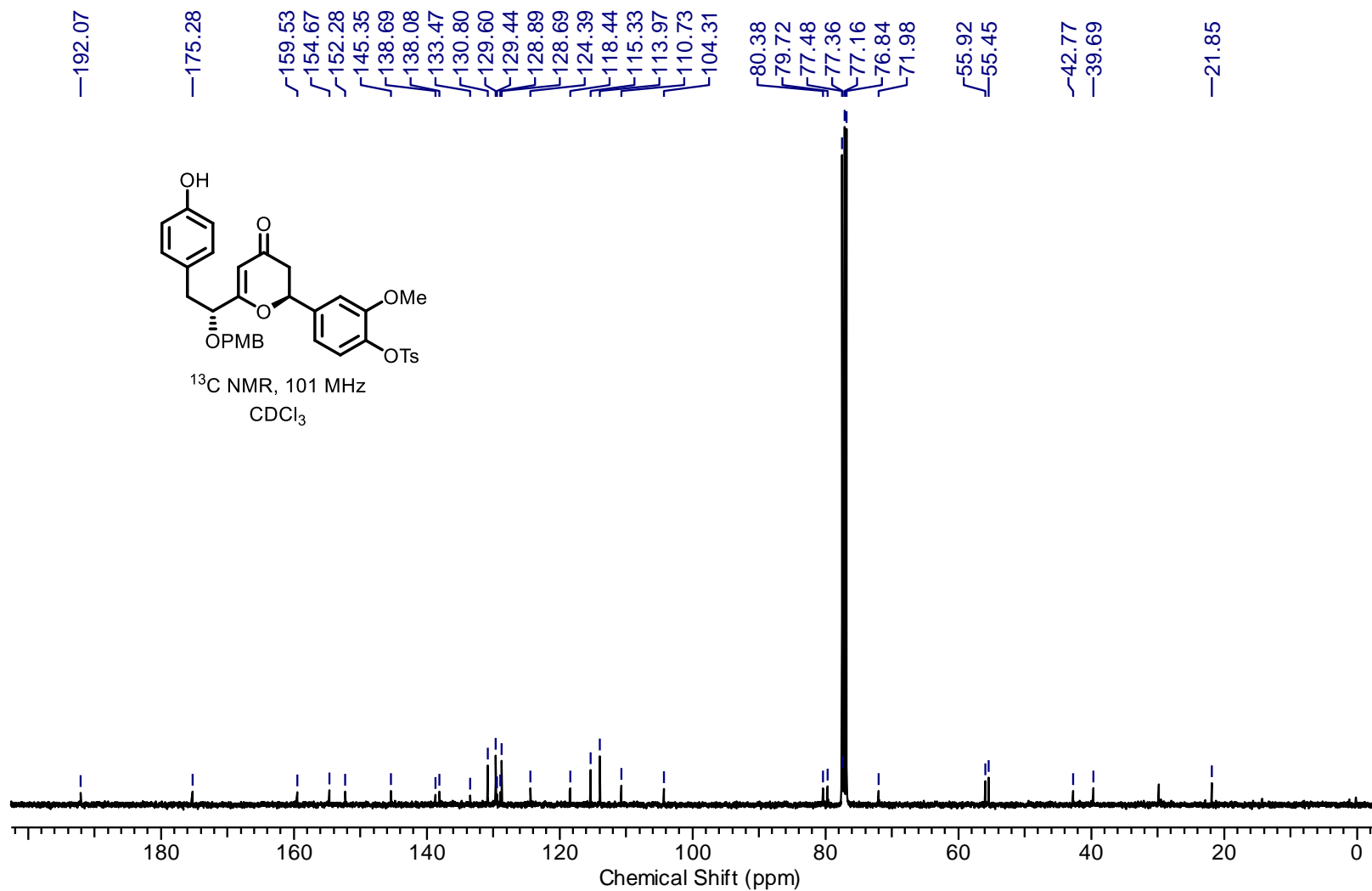
4-((1*S*, 6*R*)-1-Hydroxy-7-(4-hydroxyphenyl)-6-((4-methoxybenzyl)oxy)-3-oxohept-4-yn-1-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**30**):



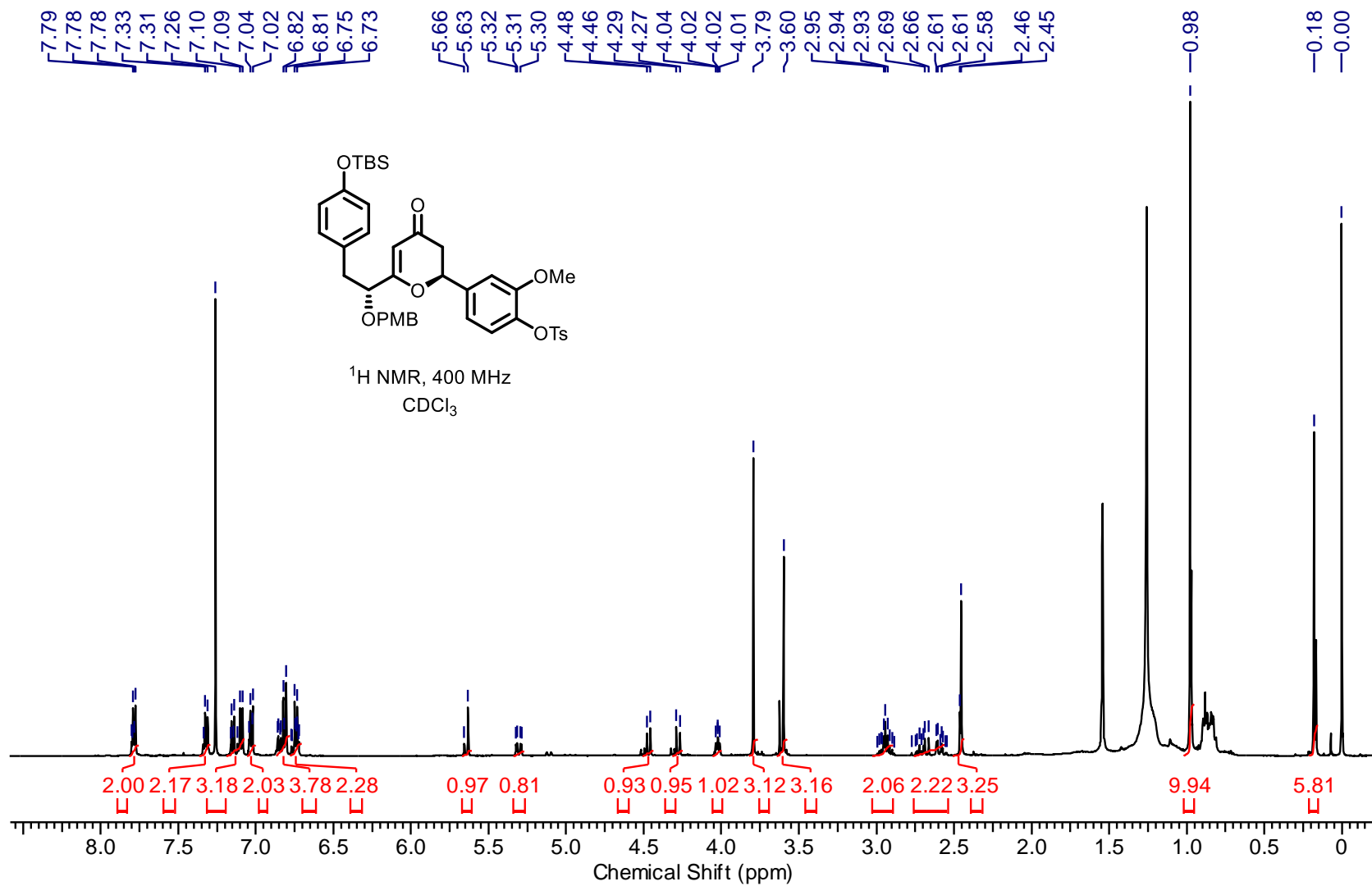
4-((*S*)-6-((*R*)-2-(4-Hydroxyphenyl)-1-((4-methoxybenzyl)oxy)ethyl)-4-oxo-3,4-dihydro-2H-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**31**):



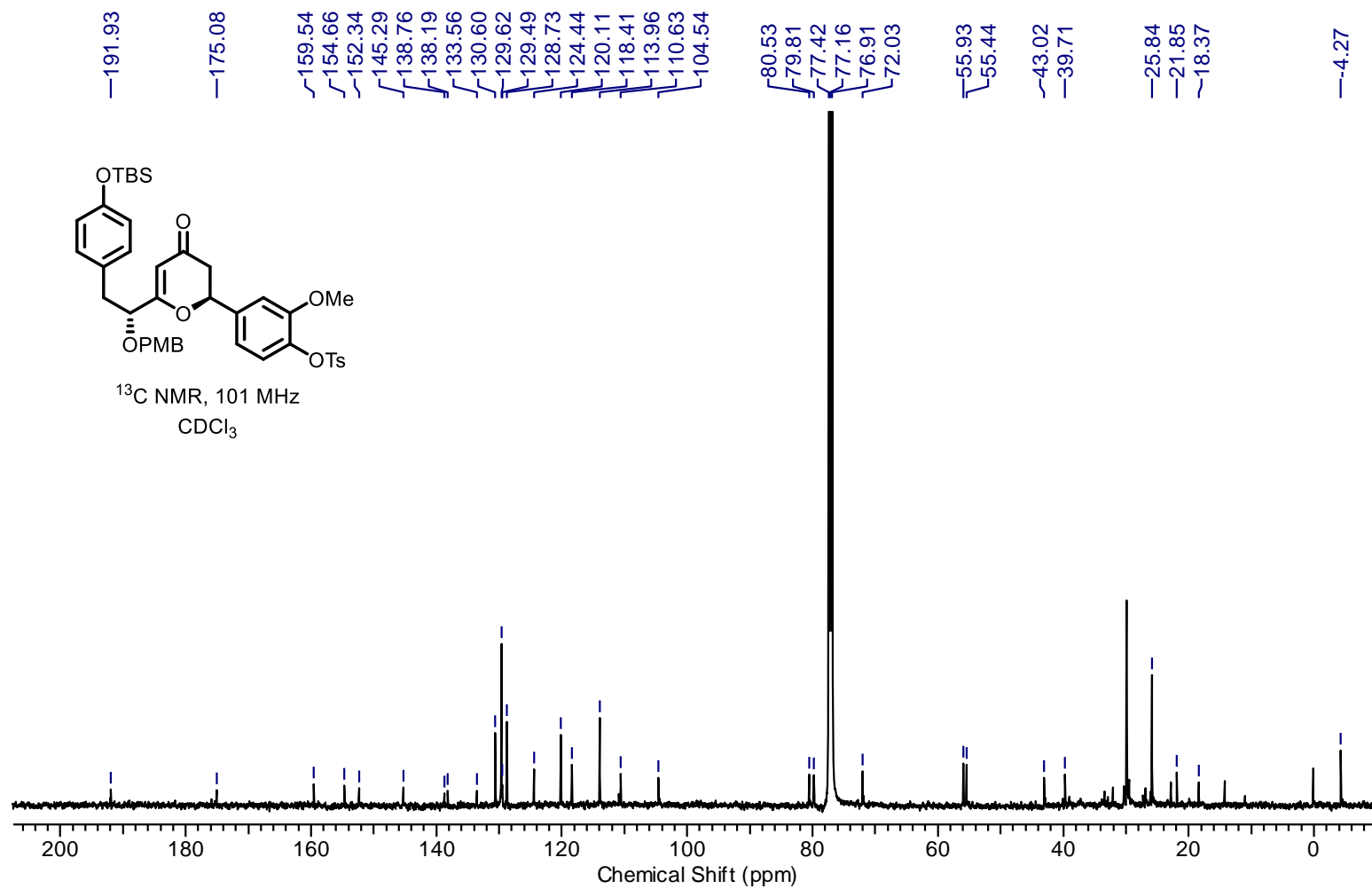
4-((*S*)-6-((*R*)-2-(4-Hydroxyphenyl)-1-((4-methoxybenzyl)oxy)ethyl)-4-oxo-3,4-dihydro-2H-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**31**):



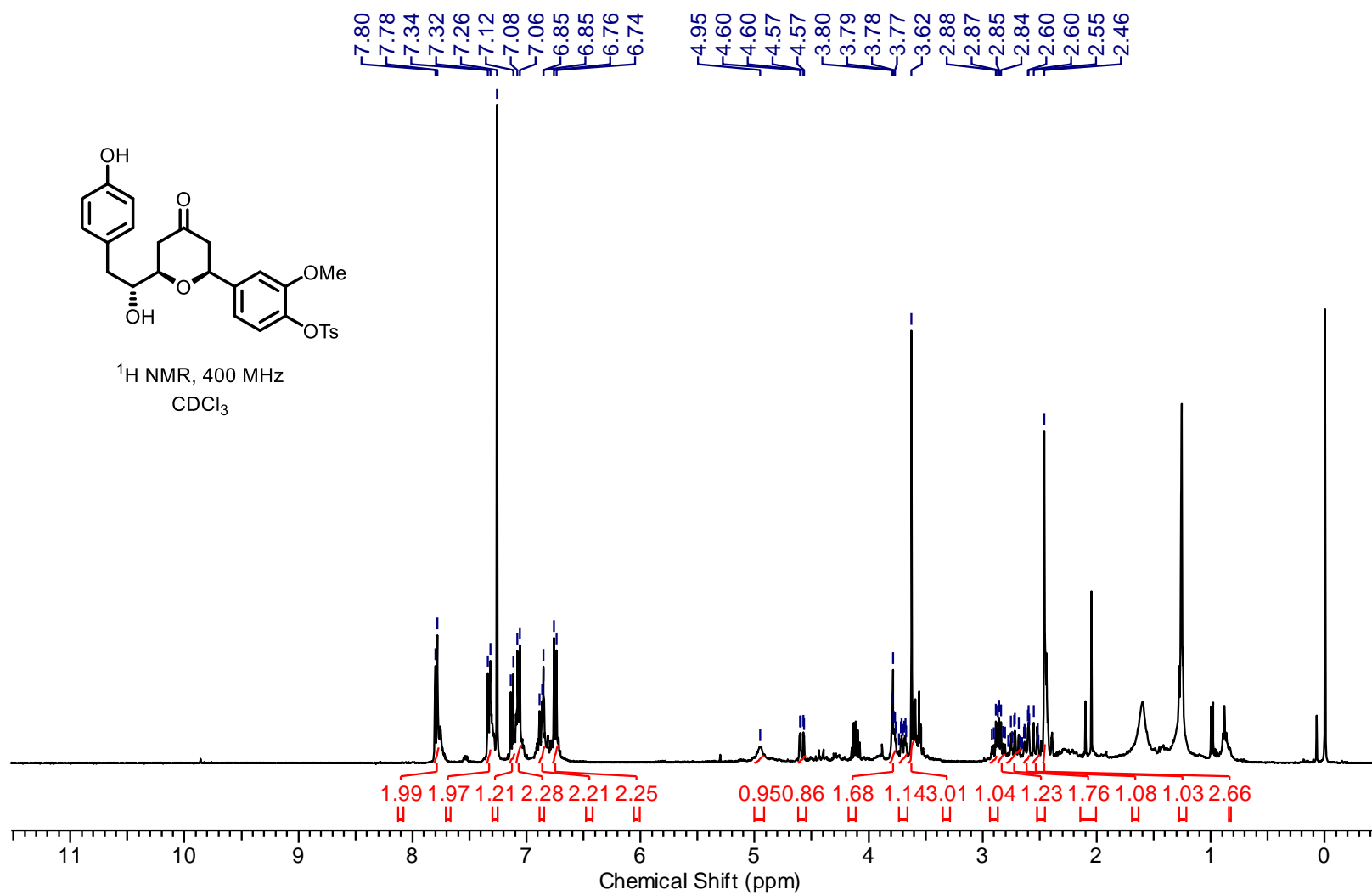
4-((*S*)-6-((*R*)-2-(4-((*Tert*-butyldimethylsilyl)oxy)phenyl)-1-((4-methoxybenzyl)oxy)ethyl)-4-oxo-3,4-dihydro-2*H*-pyran-2-yl)-2-methoxyphenyl-4-methylbenzenesulfonate (**32**):



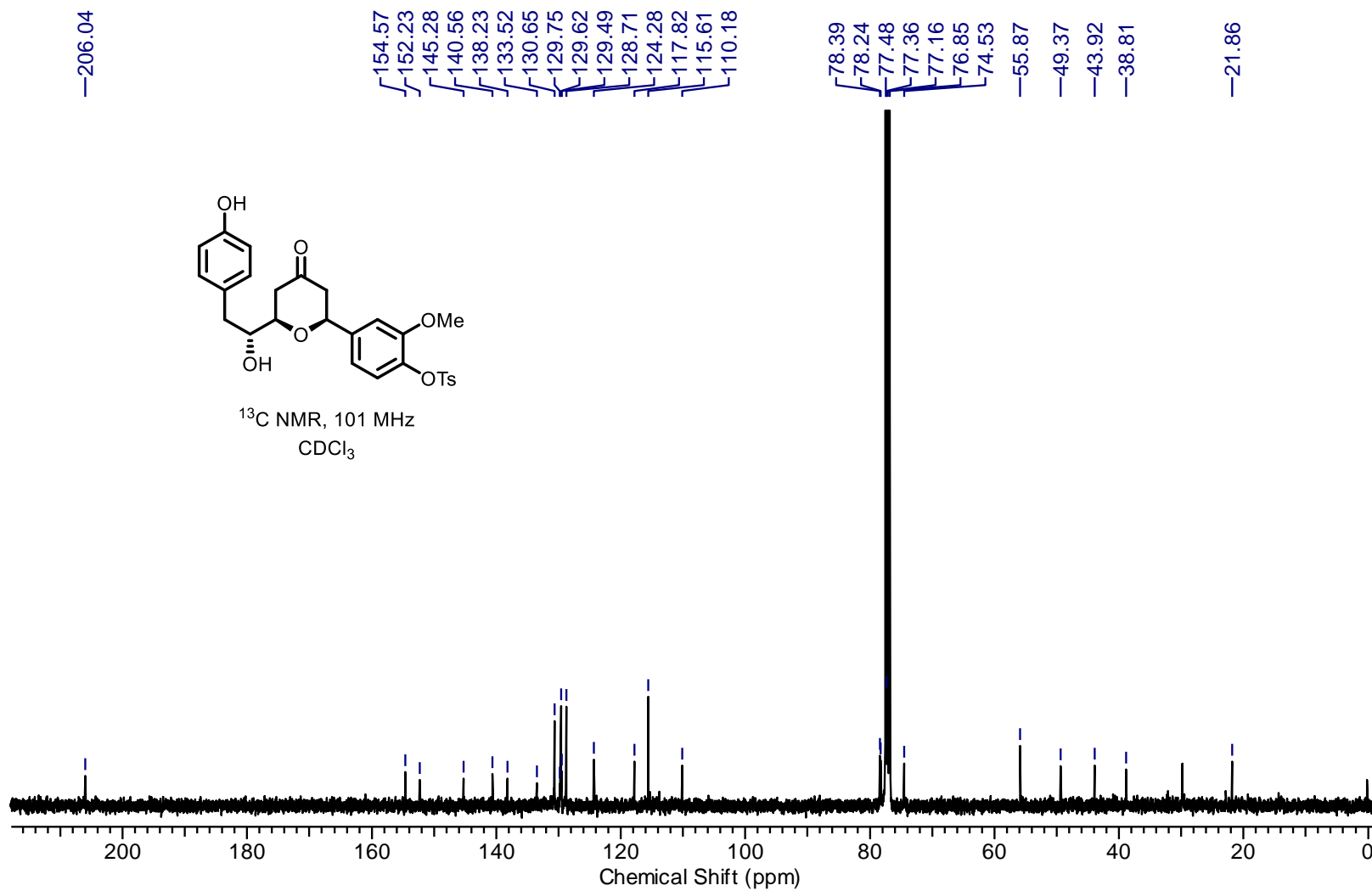
4-((*S*)-6-((*R*)-2-(4-((*Tert*-butyldimethylsilyl)oxy)phenyl)-1-((4-methoxybenzyl)oxy)ethyl)-4-oxo-3,4-dihydro-2*H*-pyran-2-yl)-2-methoxyphenyl-4-methylbenzenesulfonate (**32**):



4-((2*S*, 6*R*)-6-((*R*)-1-Hydroxy-2-(4-hydroxyphenyl)ethyl)-4-oxotetrahydro-2*H*-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**S10**):

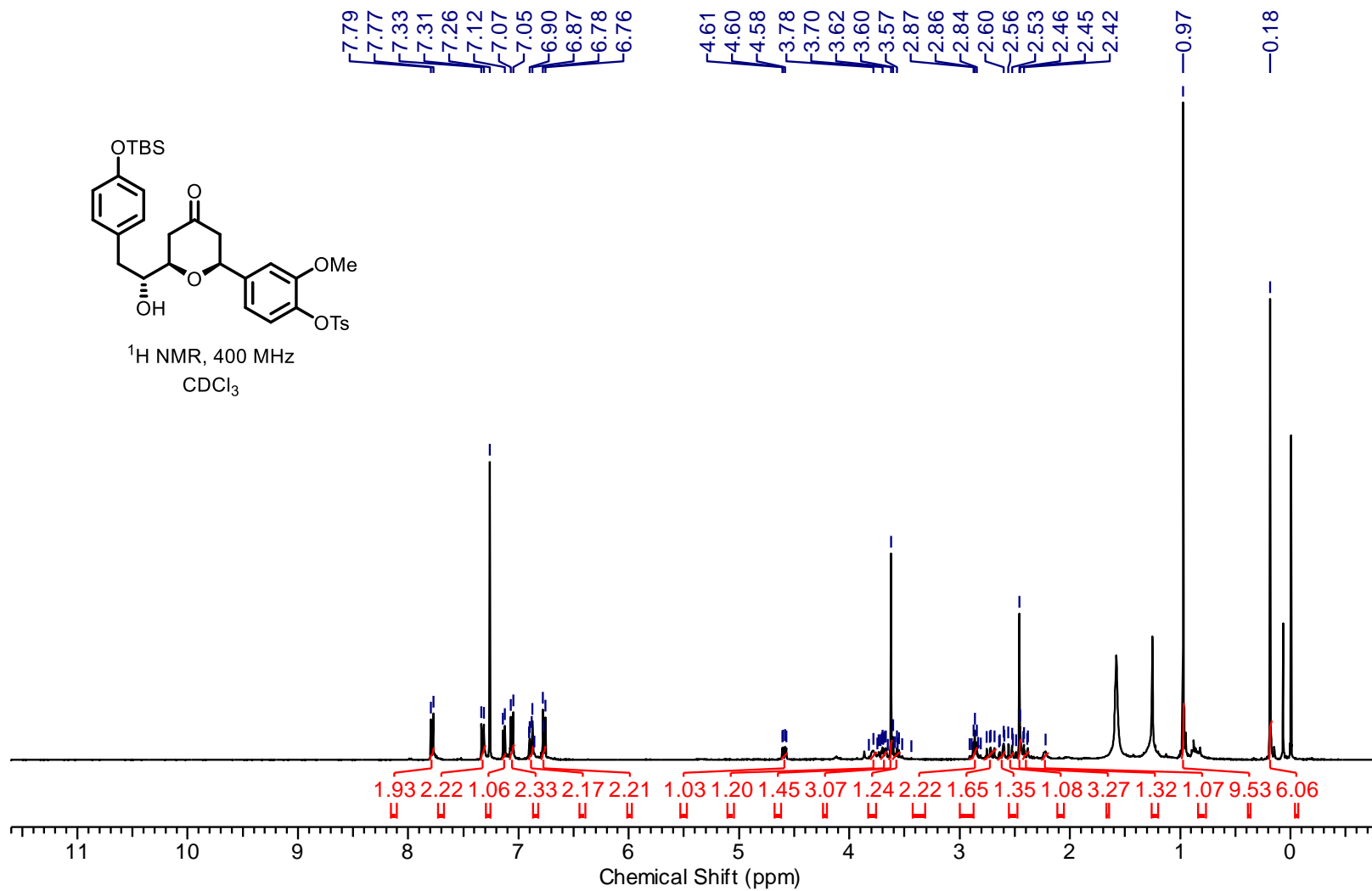


4-((2*S*, 6*R*)-6-((*R*)-1-Hydroxy-2-(4-hydroxyphenyl)ethyl)-4-oxotetrahydro-2*H*-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**S10**):

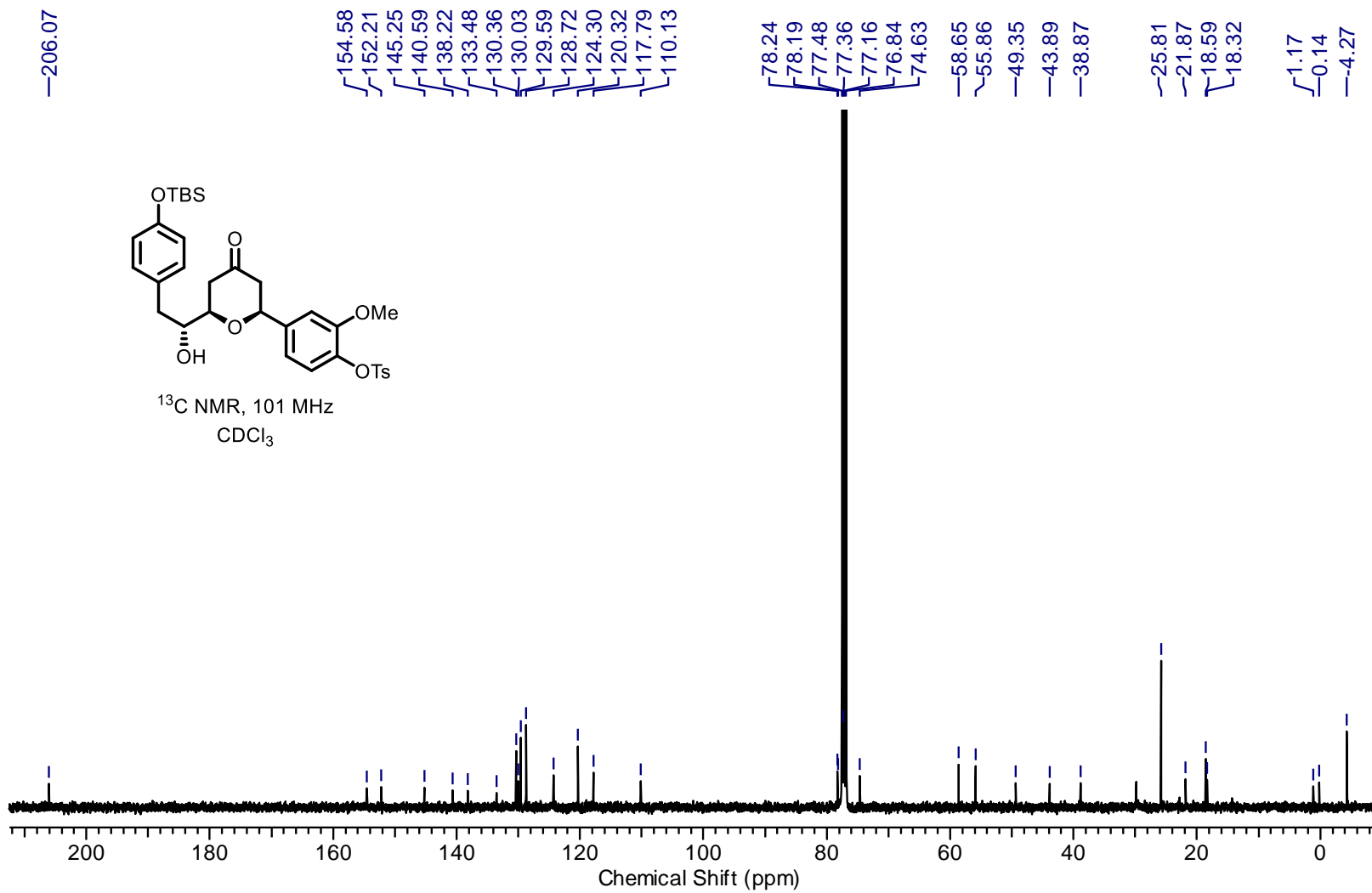




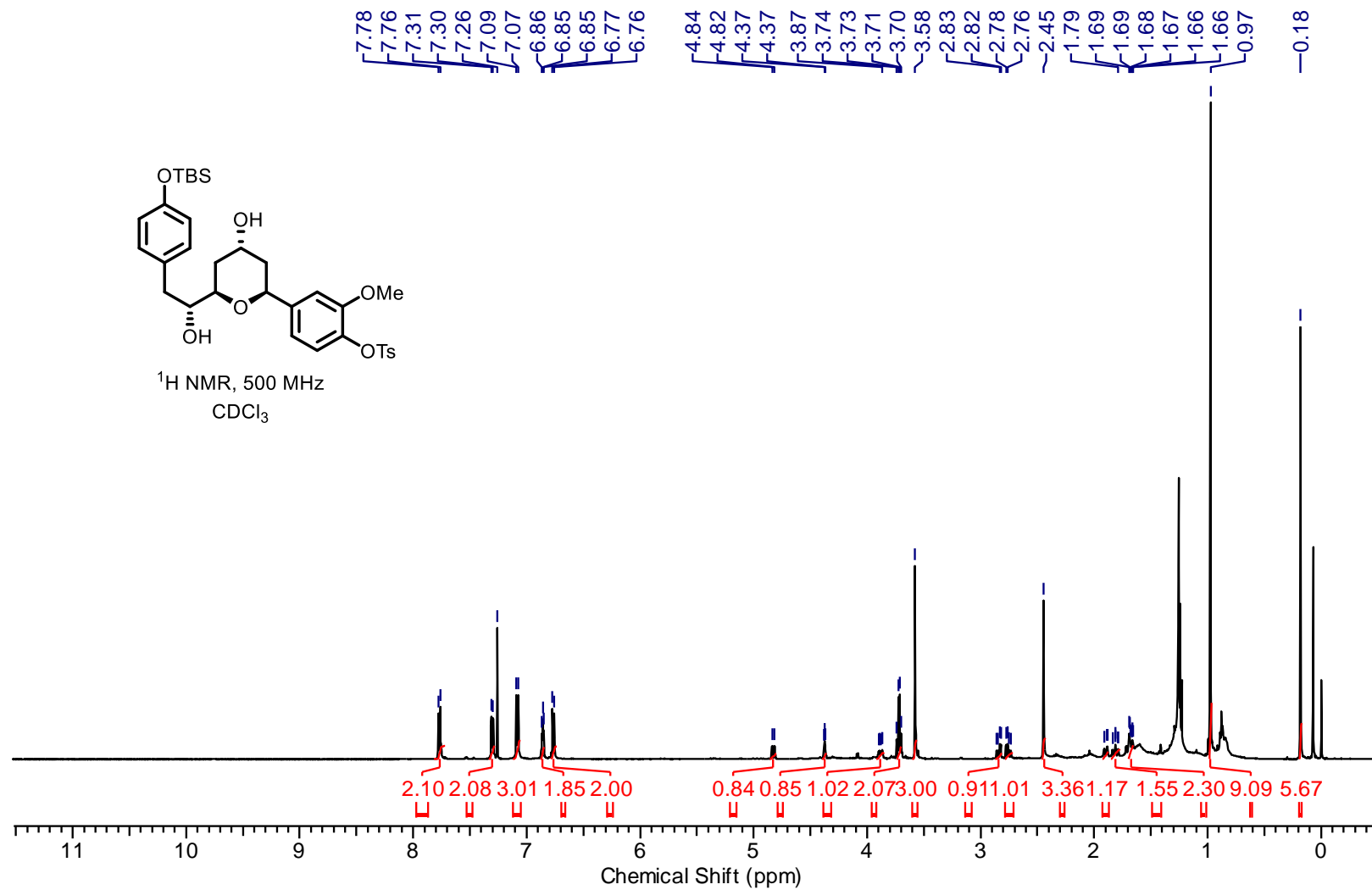
4-((2*S*, 6*R*)-6-((*R*)-2-(4-((*Tert*-butyldimethylsilyl)oxy)phenyl)-1-hydroxyethyl)-4-oxotetrahydro-2*H*-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (S11):



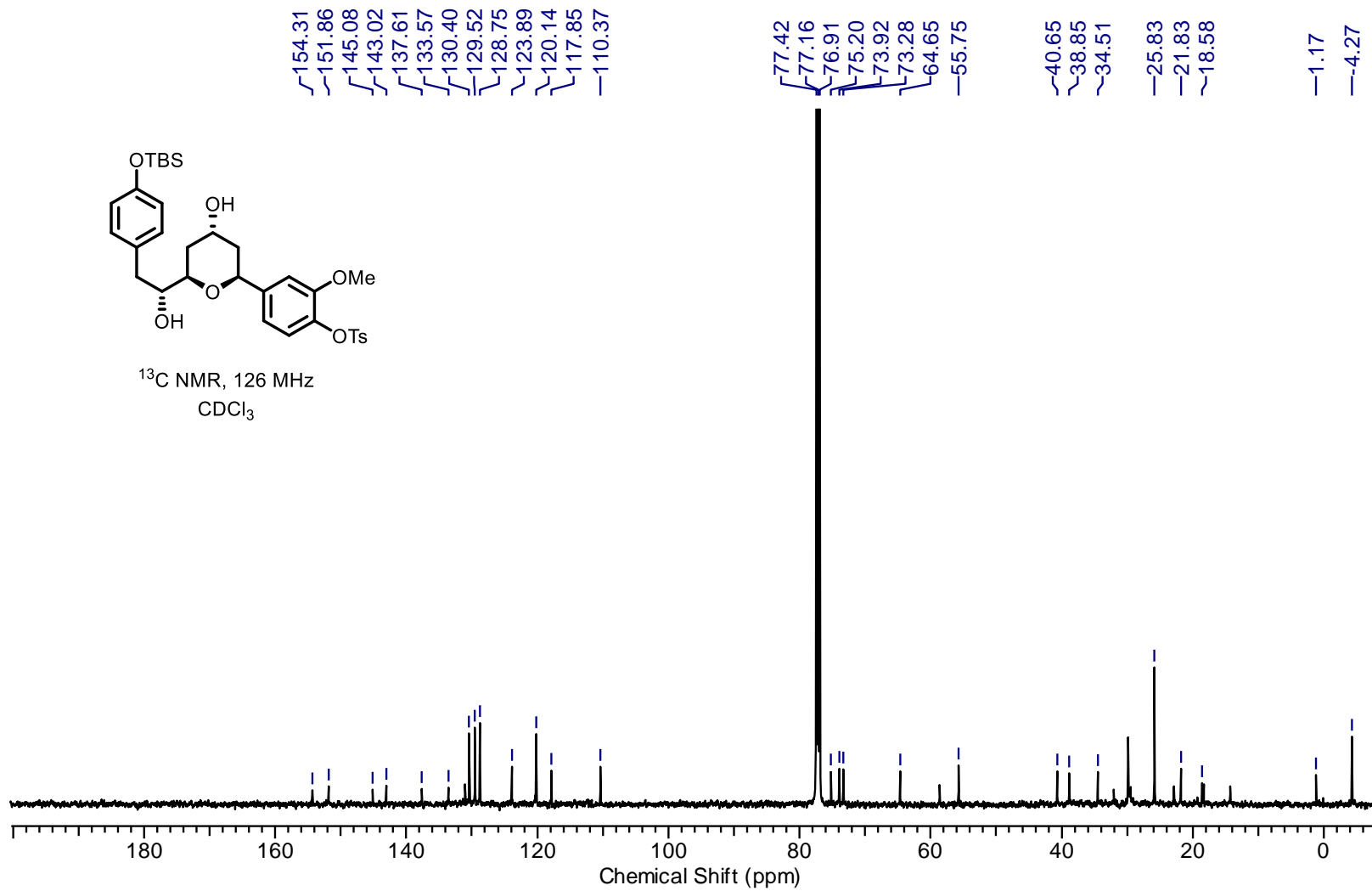
4-((2*S*, 6*R*)-6-((*R*)-2-(4-((*Tert*-butyldimethylsilyl)oxy)phenyl)-1-hydroxyethyl)-4-oxotetrahydro-2*H*-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (S11):



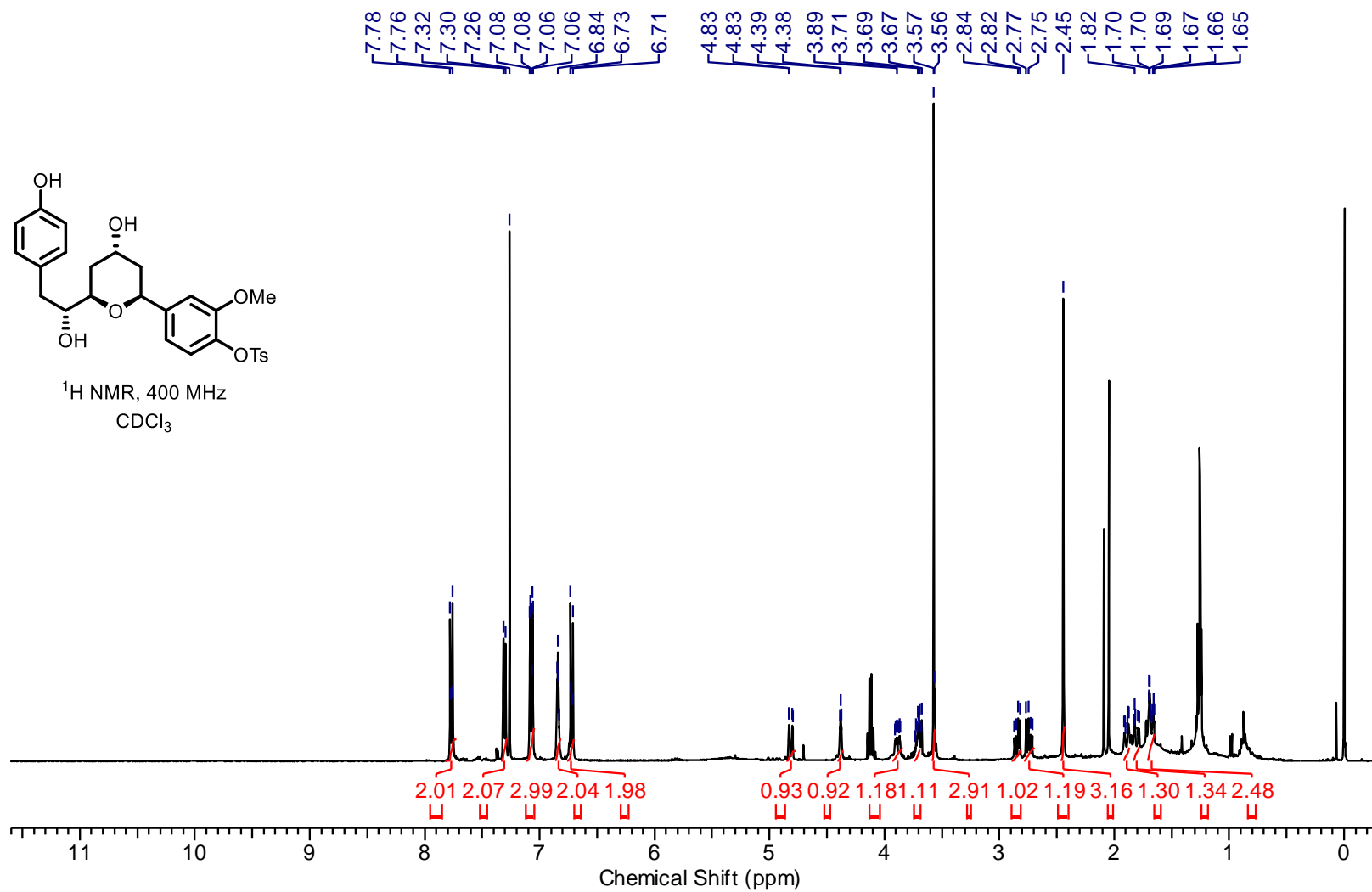
4-((2*S*, 4*R*, 6*R*)-6-((*R*)-2-(4-((*Tert*-butyldimethylsilyl)oxy)phenyl)-1-hydroxyethyl)-4-hydroxytetra-hydro-2*H*-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**34**):



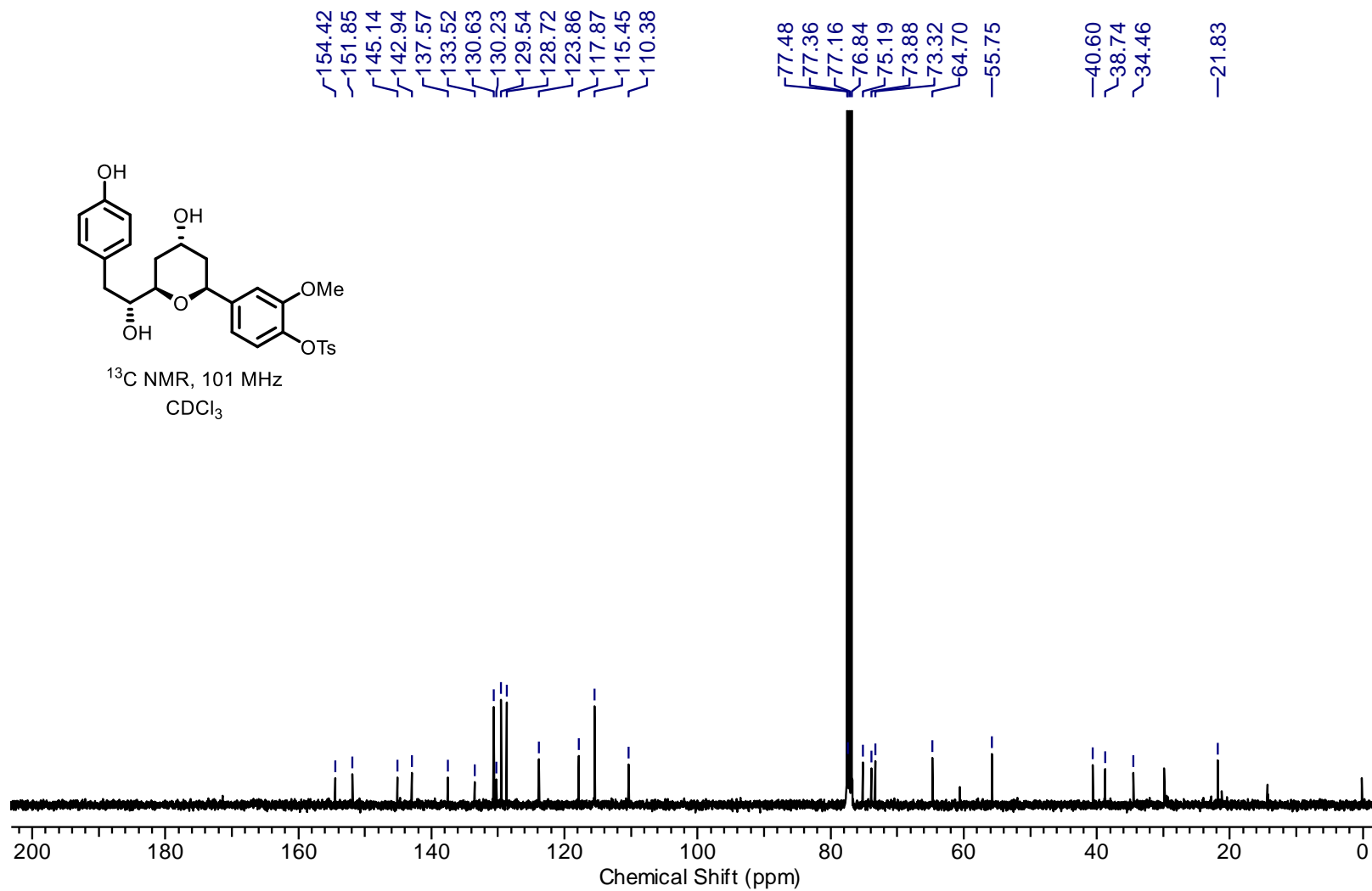
4-((2*S*, 4*R*, 6*R*)-6-((*R*)-2-(4-((*Tert*-butyldimethylsilyl)oxy)phenyl)-1-hydroxyethyl)-4-hydroxytetra-hydro-2*H*-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**34**):



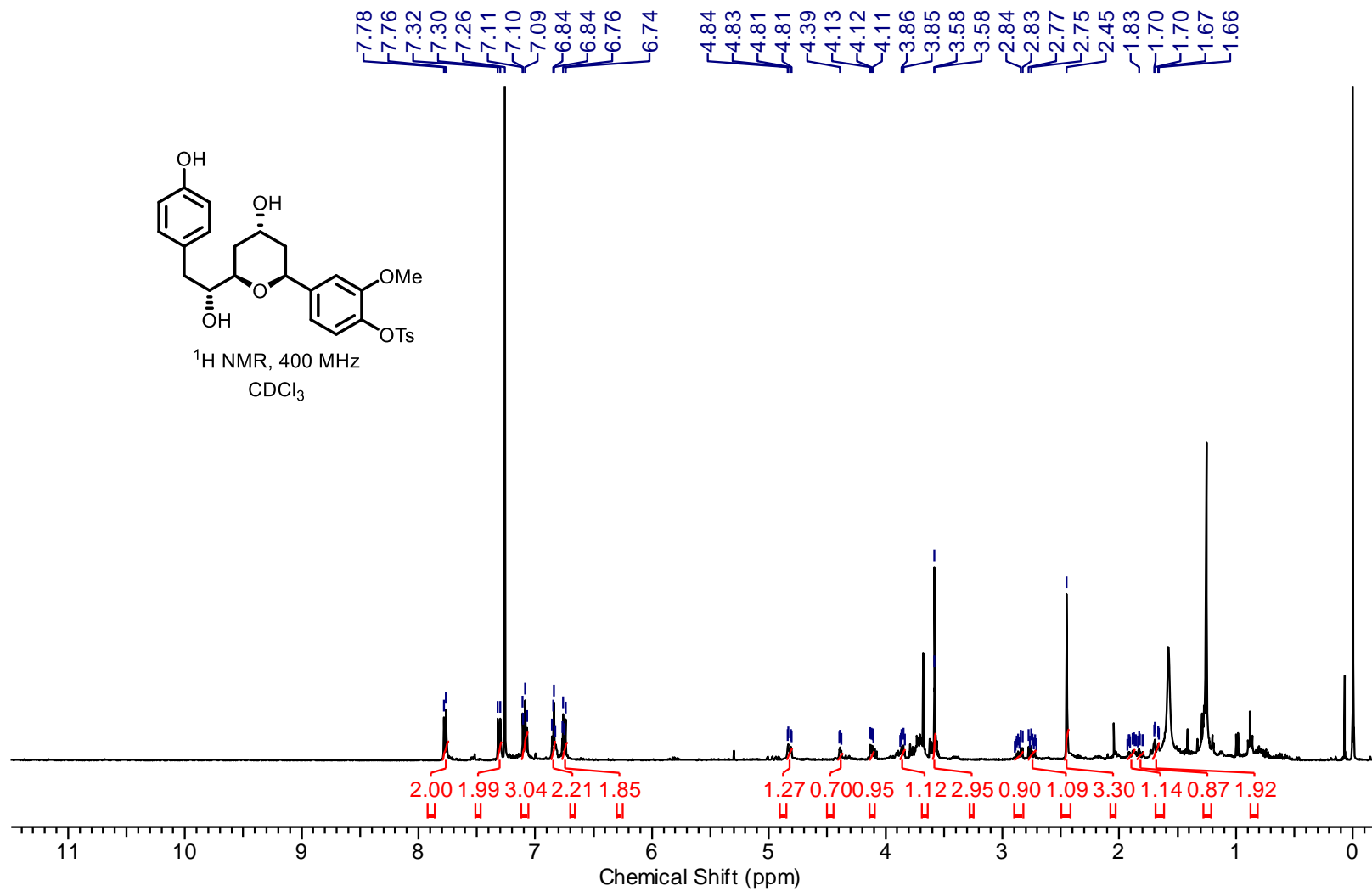
4-((2*S*, 4*R*, 6*R*)-4-Hydroxy-6-((*R*)-1-hydroxy-2-(4-hydroxyphenyl)ethyl)tetrahydro-2*H*-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**35**) (using *LS-Selectride*):



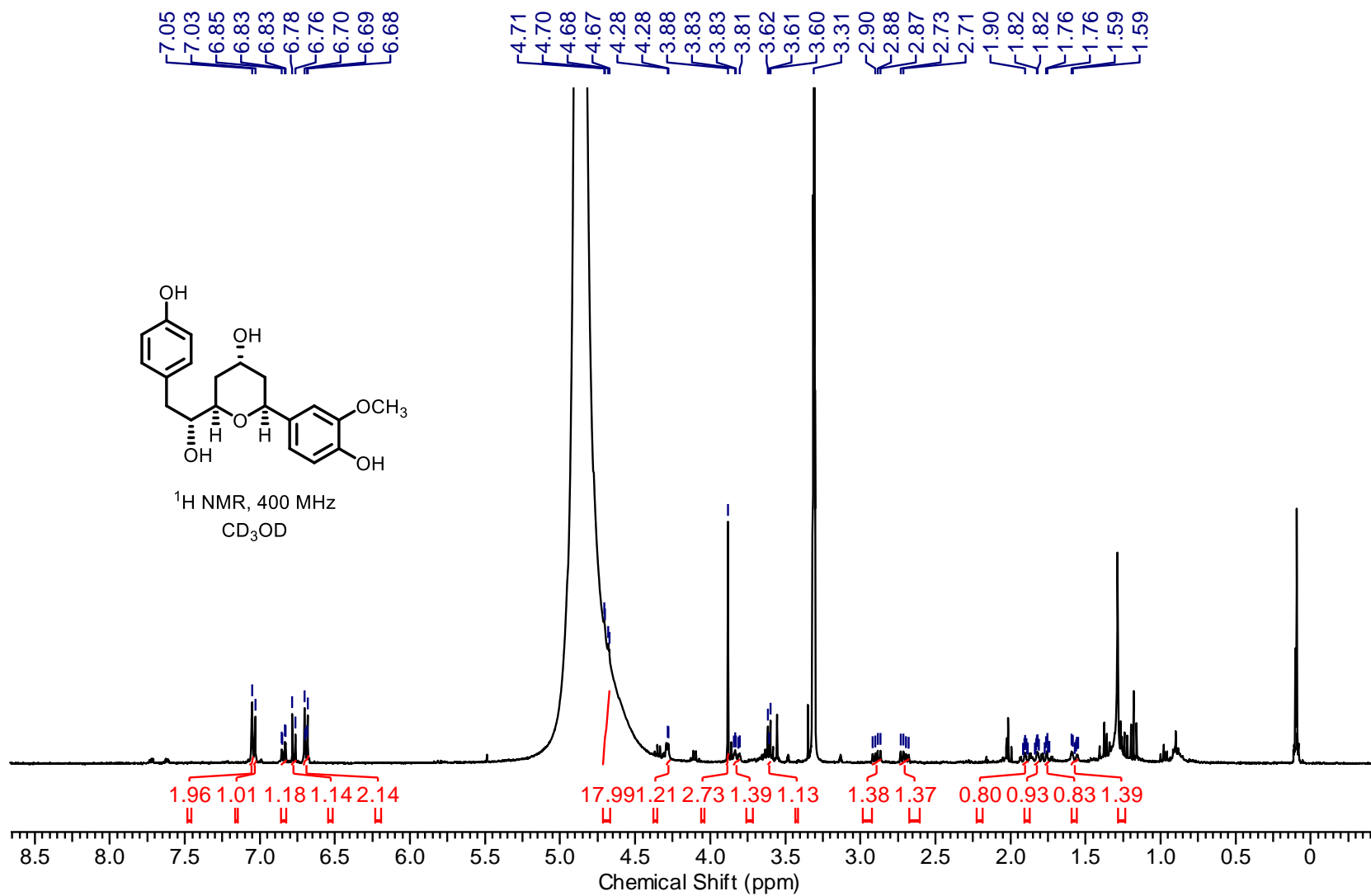
4-((2*S*, 4*R*, 6*R*)-4-Hydroxy-6-((*R*)-1-hydroxy-2-(4-hydroxyphenyl)ethyl)tetrahydro-2*H*-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**35**) (using LS-Selectride):



4-((2*S*, 4*R*, 6*R*)-4-Hydroxy-6-((*R*)-1-hydroxy-2-(4-hydroxyphenyl)ethyl)tetrahydro-2*H*-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**35**) (using TBAF):

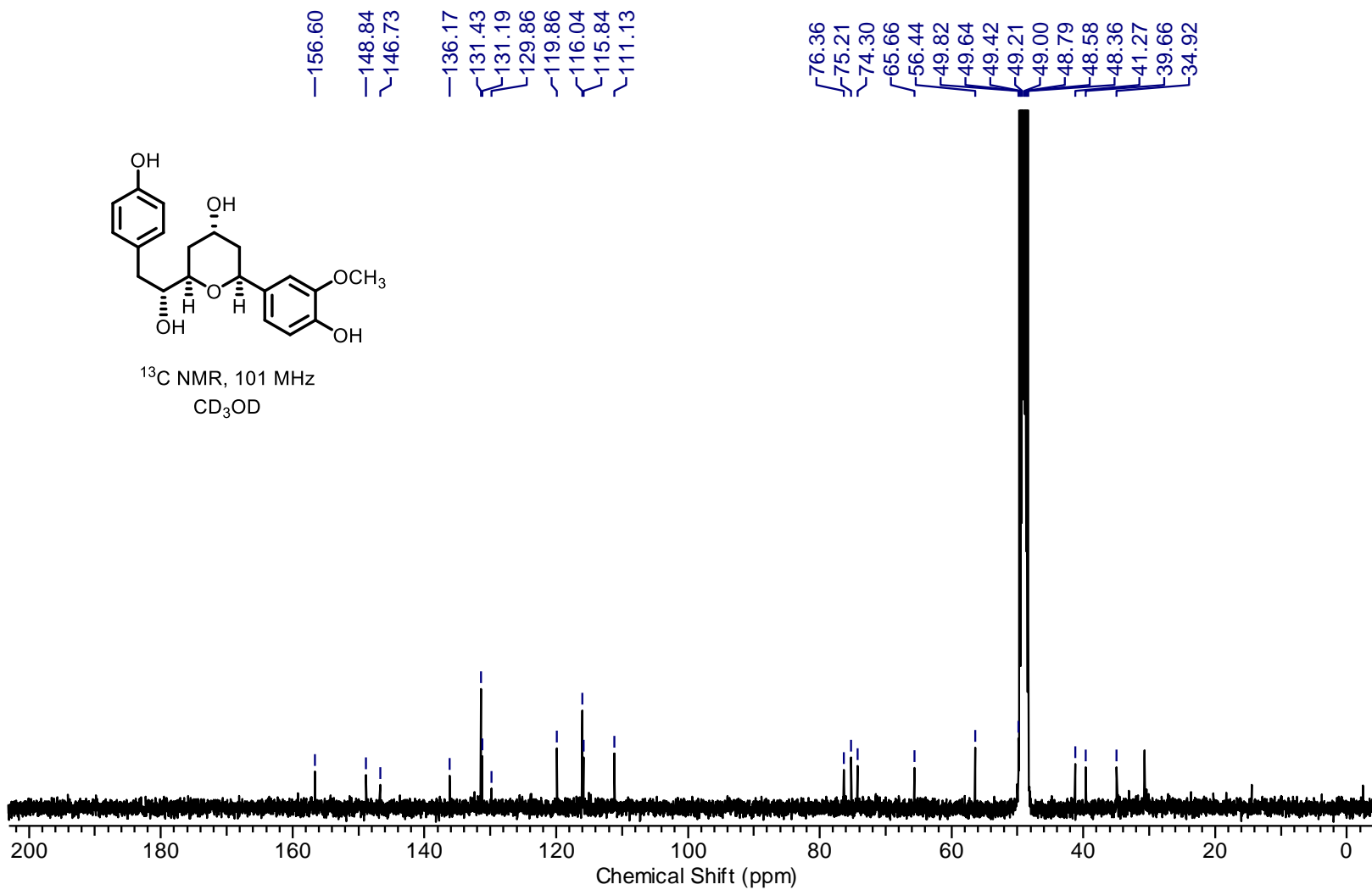


*ent*-Rhoiptelol B (**3a**):

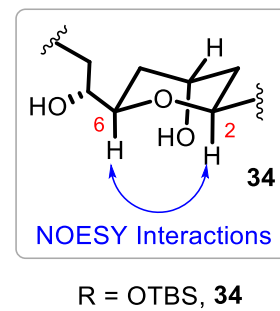
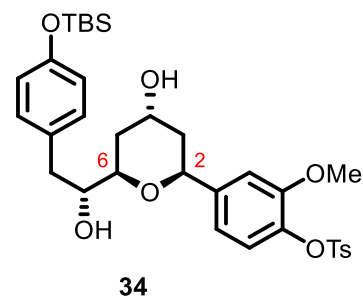




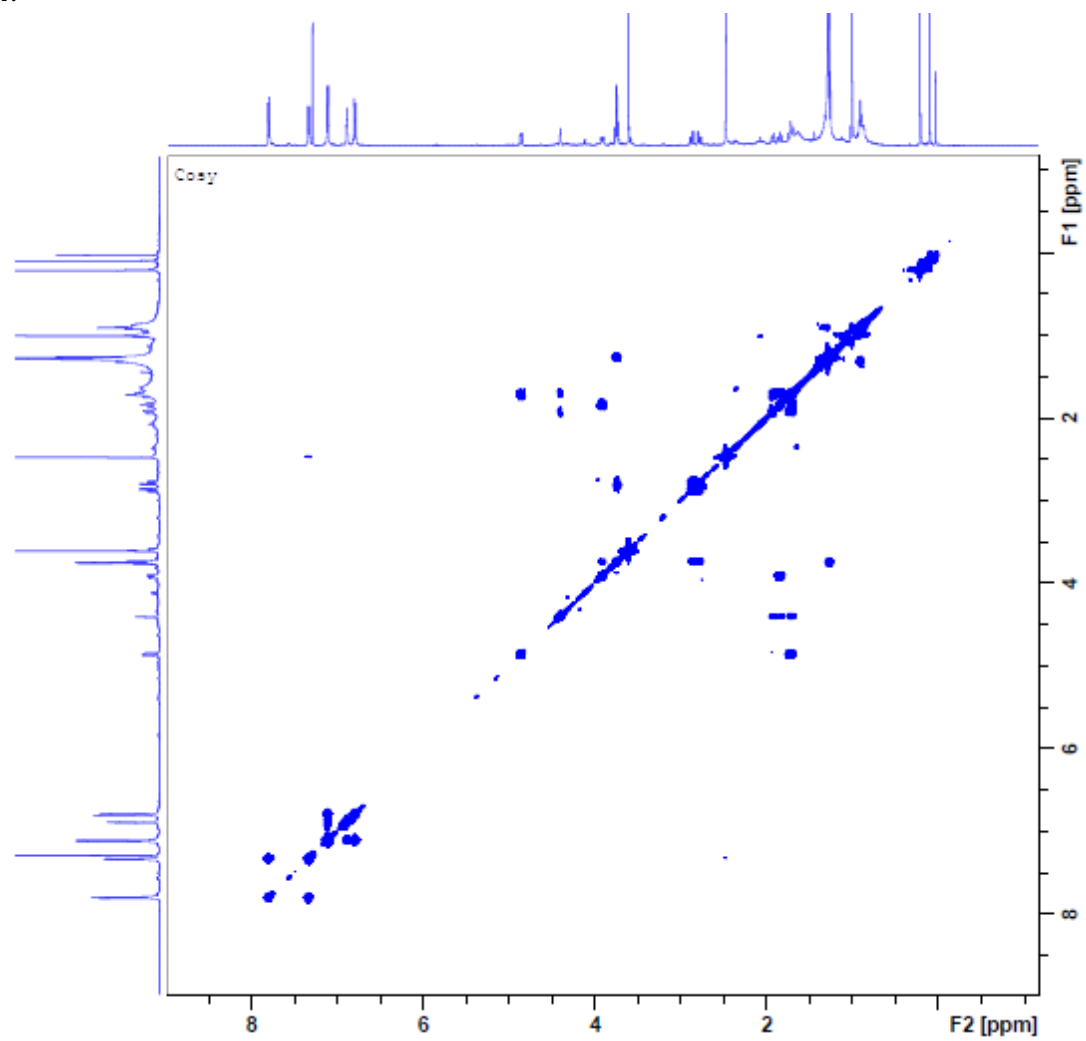
*ent*-Rhoiptelol B (**3a**):



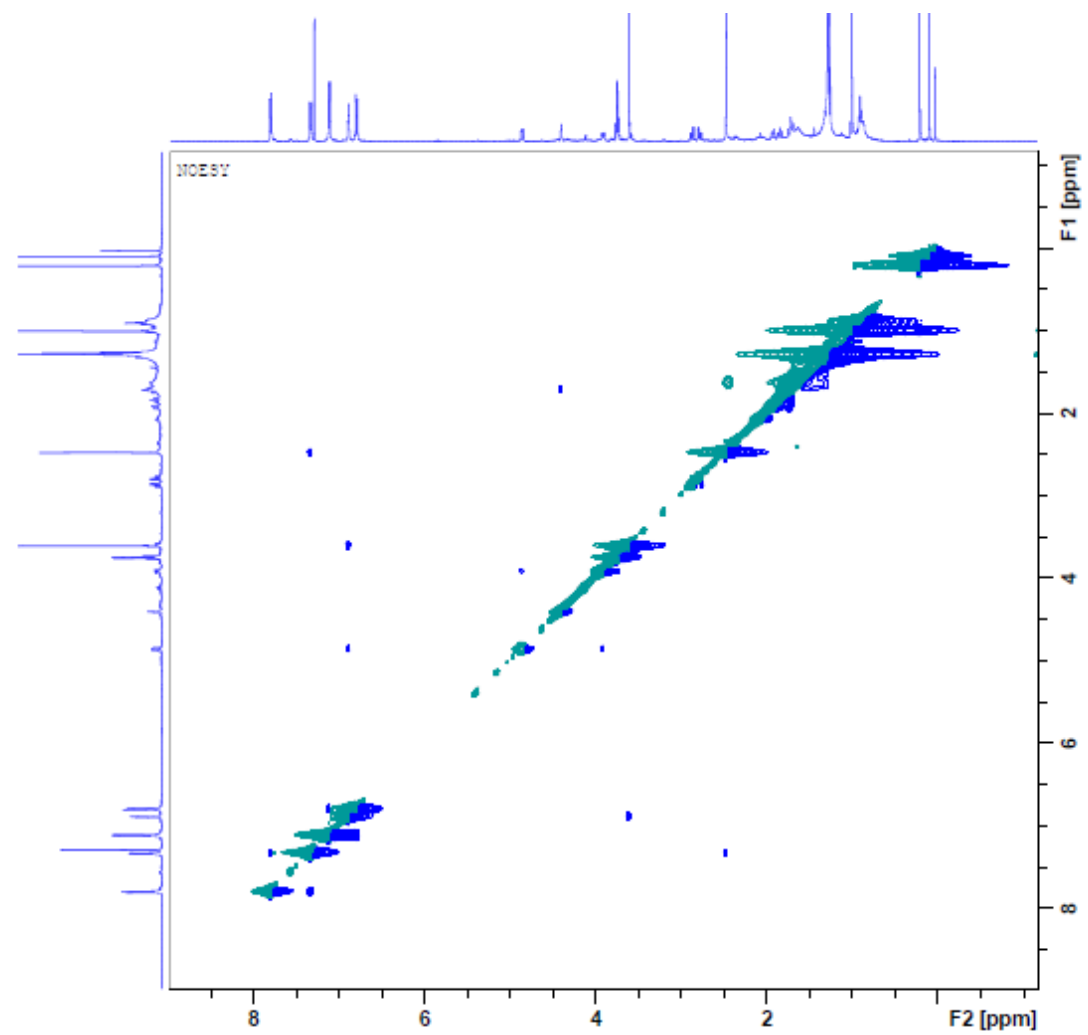
2. 2D-NMR Spectra of 4-((2*S*, 4*R*, 6*R*)-6-((*R*)-2-(4-((*tert*-butyldimethyl-silyl)oxy)phenyl)-1-hydroxyethyl)-4-hydroxytetrahydro-2*H*-pyran-2-yl)-2-methoxyphenyl 4-methylbenzenesulfonate (**34**):



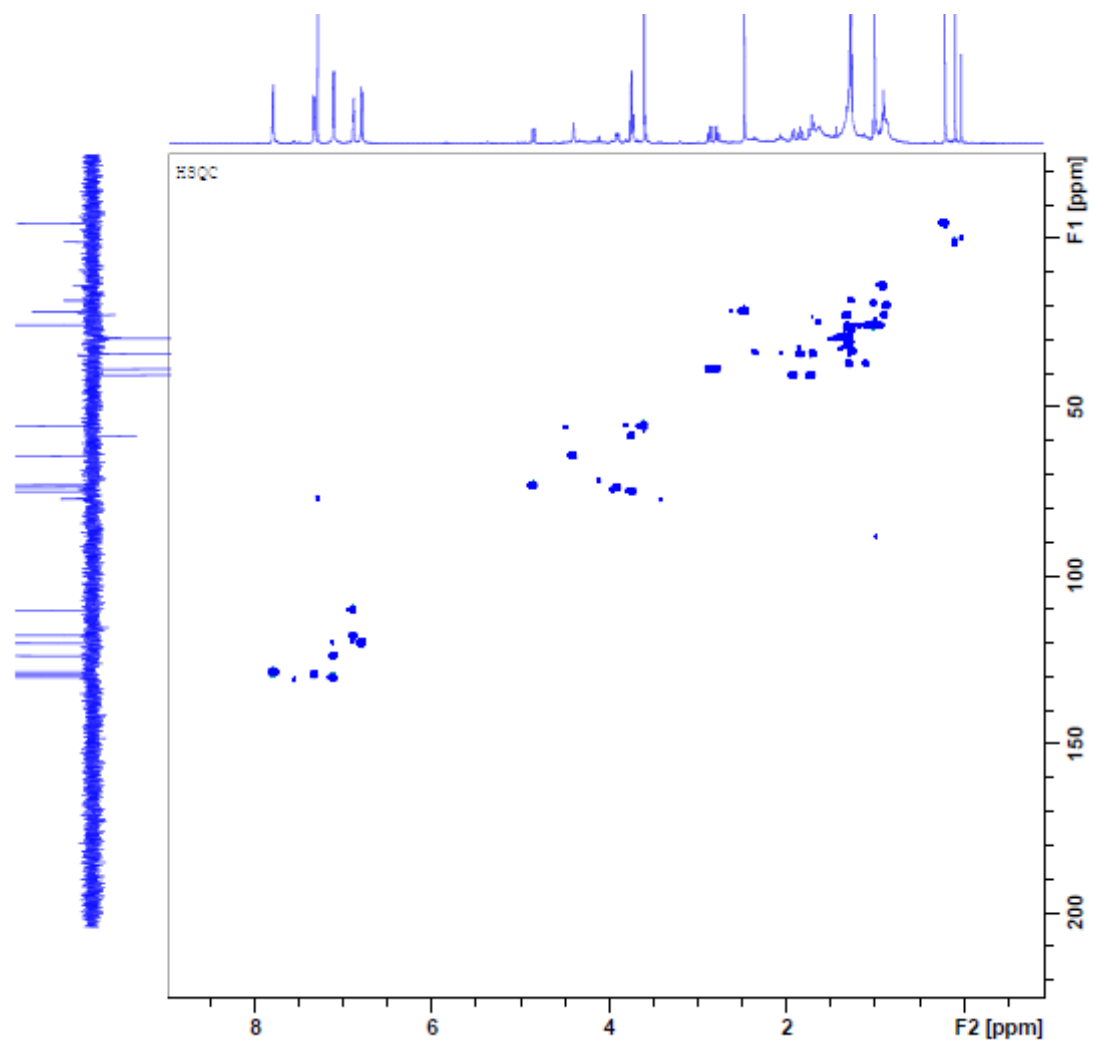
a) COSY spectra of **34**:



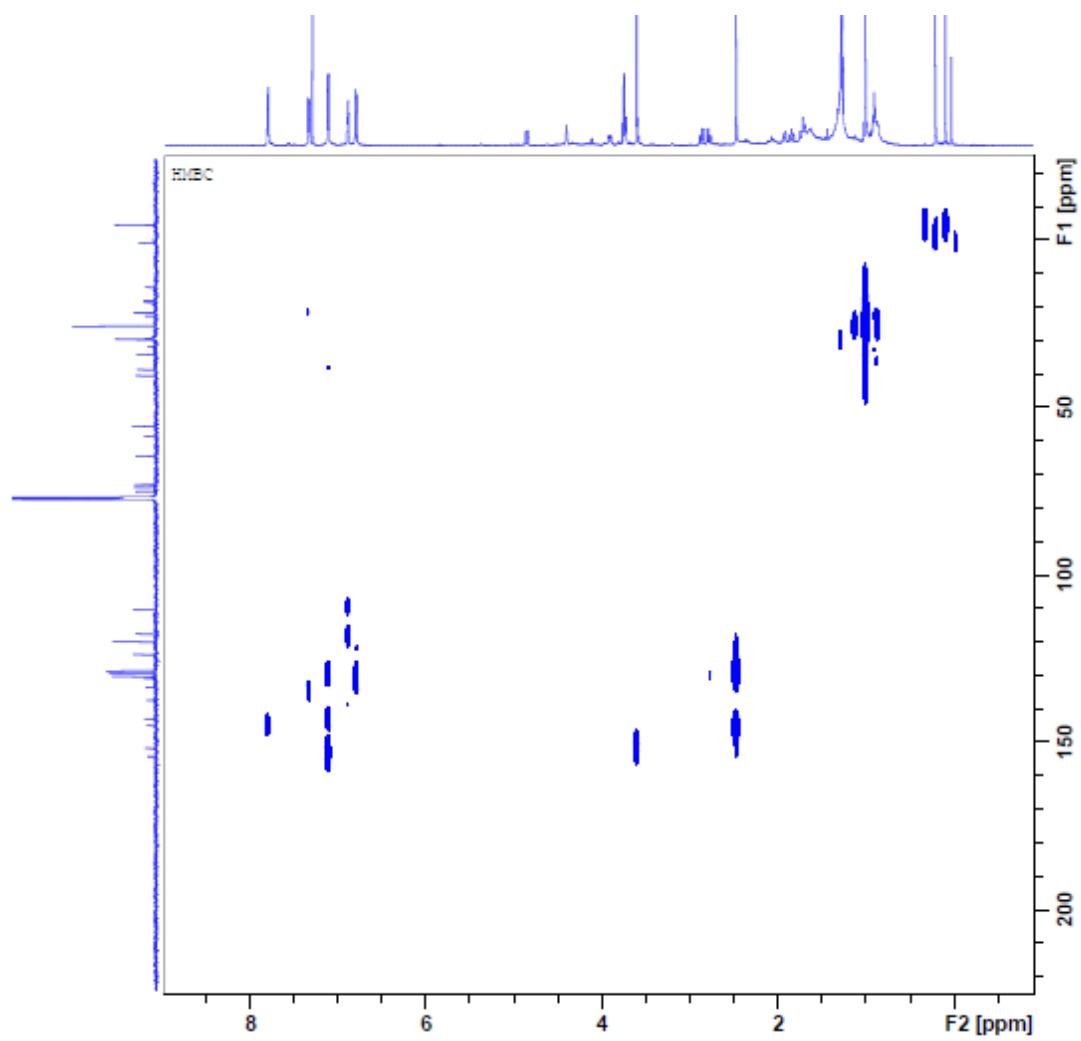
a) NOESY spectra of **34**:



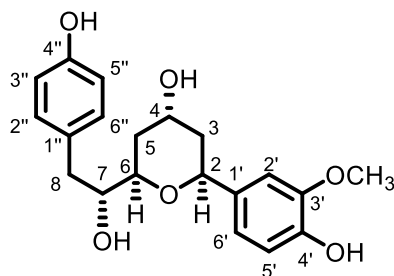
b) HSQC spectra of **34**:



c) HMBC spectra of **34**:



**3. Table S1.** Comparison of NMR data of rhoiptelol B (**3a**) (Our work, Natural (Isolated) and First synthesised)



**ent-Rhoiptelol B (3a)**

Position	Our Work ( <i>ent</i> - Rhoiptelol B)		Natural Rhoiptelol B (Isolated)		First Synthesis of Rhoiptelol B	
	$\delta_H$ ( $J$ in Hz)	$\delta_C$	$\delta_H$ ( $J$ in Hz)	$\delta_C$	$\delta_H$ ( $J$ in Hz)	$\delta_C$
2	4.69 (1H, <i>dd</i> , $J = 2.25, 11.51$ Hz)	75.2	4.69 (1H, <i>dd</i> , $J = 3, 11$ Hz)	75.2 d	4.69 (1H, <i>dd</i> , $J = 11.1, 3.0$ Hz)	75.2
3	1.76 (1H, <i>d</i> , $J = 2.88$ Hz) 1.84-1.80 (1H, <i>m</i> )	41.3	1.75 (1H, <i>ddd</i> , $J = 3, 11, 12$ Hz, <i>ax</i> ) 1.84 (1H, <i>dd</i> , $J = 3, 12$ Hz, <i>eq</i> )	41.3 t	1.74 (1H, <i>ddd</i> , $J = 13.9, 11.3, 3.0$ Hz) 1.83 (1H, <i>dd</i> , $J = 14.5, 2.6$ Hz)	41.3
4	4.28 (1H, <i>m</i> )	65.7	4.27 (1H, <i>t</i> , $J = 3$ Hz)	65.6 d	4.27 (1H, <i>t</i> , $J = 3.0$ Hz)	65.7
5	1.57-1.54 (1H, <i>m</i> ) 1.92-1.89 (1H, <i>m</i> )	34.9	1.57 (1H, <i>dd</i> , $J = 2, 13$ Hz, <i>eq</i> ) 1.89 (1H, <i>dt</i> , $J = 3, 13$ Hz, <i>ax</i> )	34.9 t	1.55 (1H, <i>dd</i> , $J = 13.4, 2.0$ Hz) 1.92 (1H, <i>dd</i> , $J = 13.5, 3.0$ Hz)	35.0
6	3.85-3.82 (1H, <i>m</i> )	74.3	3.82 (1H, <i>dt</i> , $J = 13, 3$ Hz)	74.3 d	3.81 (1H, <i>dt</i> , $J = 12.5, 2.89$ Hz)	74.3
7	3.60-3.57 (1H, <i>m</i> )	76.4	3.60, (1H, <i>dt</i> , $J = 3, 7$ Hz)	76.3d	3.59 (1H, <i>dt</i> , $J = 7.0, 3.2$ Hz)	76.4
8	2.71 (1H, <i>dd</i> , $J = 7.25, 13.26$ Hz) 2.89 (1H, <i>dd</i> , $J = 7.00, 13.66$ Hz)	39.7	2.70 (1H, <i>dd</i> , $J = 7, 13$ Hz) 2.89 (1H, <i>dd</i> , $J = 7, 13$ Hz)	39.7 t	2.69 (1H, <i>dd</i> , $J = 13.4, 7.3$ Hz) 2.89 (1H, <i>dd</i> , $J = 13.4, 6.8$ Hz)	39.7
1'		136.2		136.1 s		136.2
2'	7.05 (2H, <i>br. s</i> )	111.1	7.04 (1H, <i>br s</i> )	111.1 d	7.04 (1H, <i>br. s</i> )	111.1
3'		148.8		148.8 s		148.8

4'		146.7		146.7 s		146.8
5'	6.77 (1H, d, $J = 8.13$ Hz)	115.8	6.77 (1H, d, $J = 8$ Hz)	115.8 d	6.76 (1H, d, $J = 8.1$ Hz)	115.9
6'	6.84 (1H, dd, $J = 1.88, 8.38$ Hz)	119.9	6.84 (1H, dd, $J = 2, 8$ Hz)	119.8 d	6.83 (1H, dd, $J = 8.1, 1.9$ Hz)	119.8
1''		129.9		131.1 s		131.2
2''	7.03 (1H, s)	131.4	7.03 (1H, d, $J = 8$ Hz)	131.4 d	7.03 (2H, d, $J = 8.1$ Hz)	131.4
3''	6.71-6.68 (2H, m)	116.0	6.69 (1H, d, $J = 8$ Hz)	116.0 d	6.68 (2H, d, $J = 8.1$ Hz)	116.0
4''		156.6		156.6 s		156.7
5''		115.8	6.69 (1H, d, $J = 8$ Hz)	116.0 d		116.0
6''		131.4	7.03 (1H, d, $J = 8$ Hz)	131.4 d		131.5
OMe	3.88 (3H, s)	56.4	3.87 (3H, s)	56.4 q	3.87 (1H, s)	56.4

**THE END**