

Supporting Information II

Stereoselective Synthesis of a Monocyclic Peloruside A Analog

Christoph W. Wullschleger,⁺ Jürg Gertsch,[‡] Karl-Heinz Altmann^{*,†}

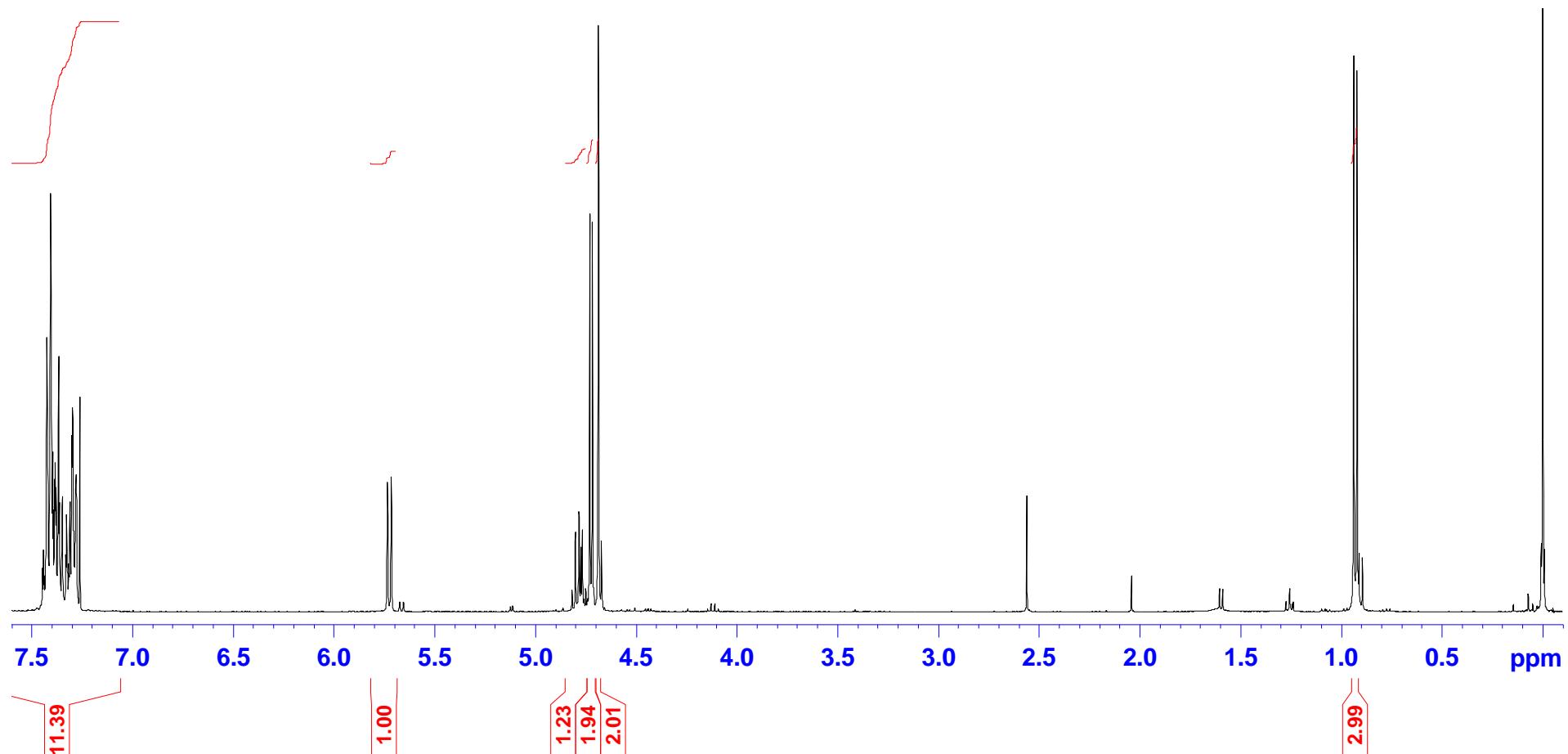
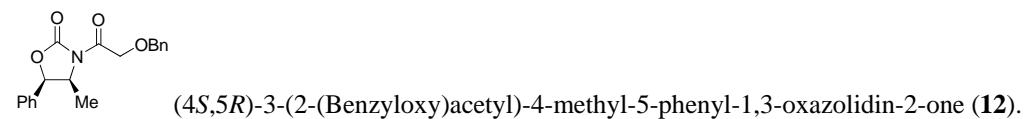
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Bern, Bühlstrasse 28, CH-3012 Bern, Switzerland

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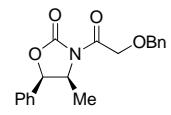
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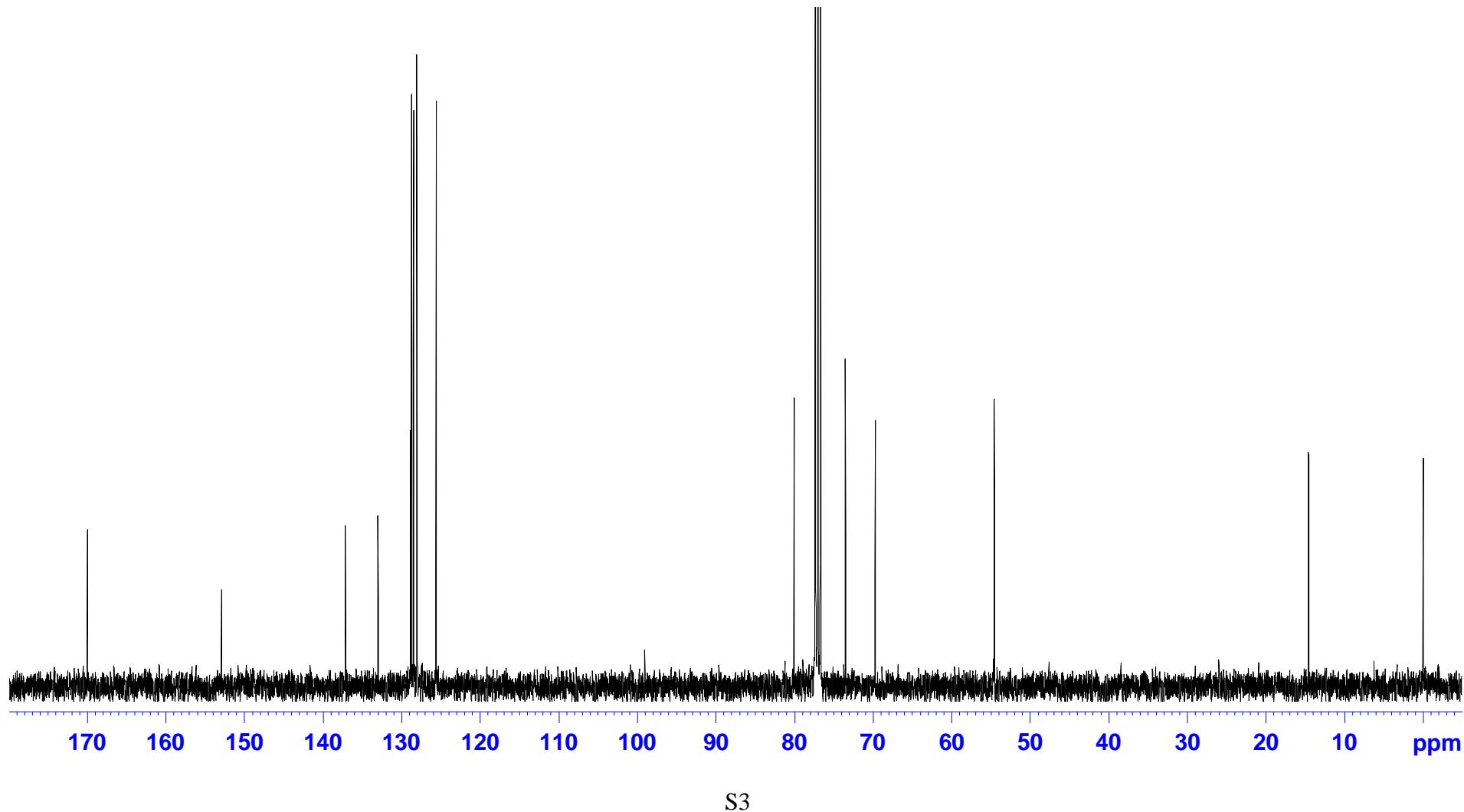
Synthesis of building block **6**



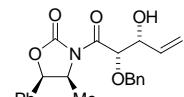
S2



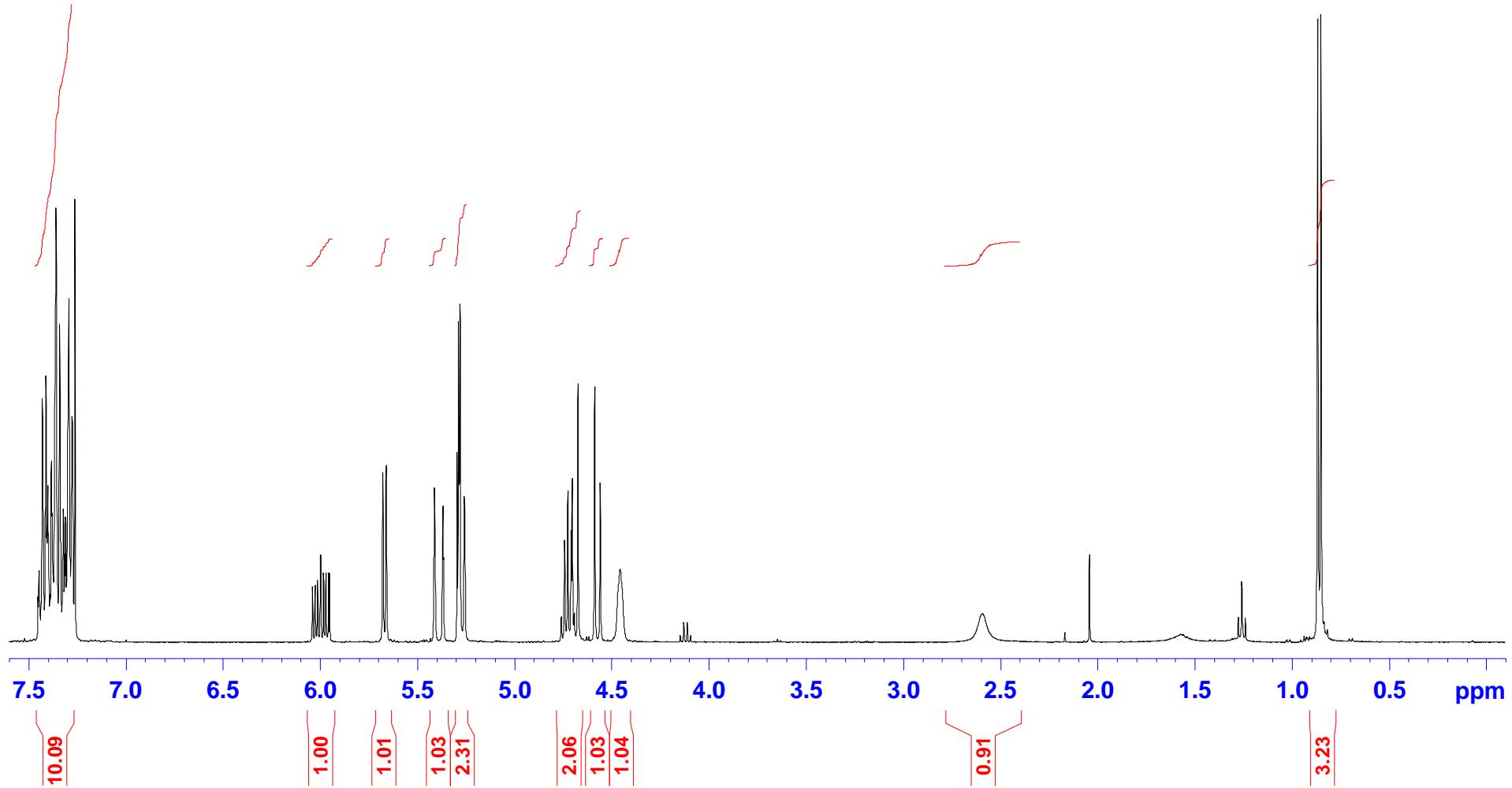
(4*S*,5*R*)-3-(2-(Benzylxy)acetyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one (**12**).

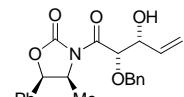


S3

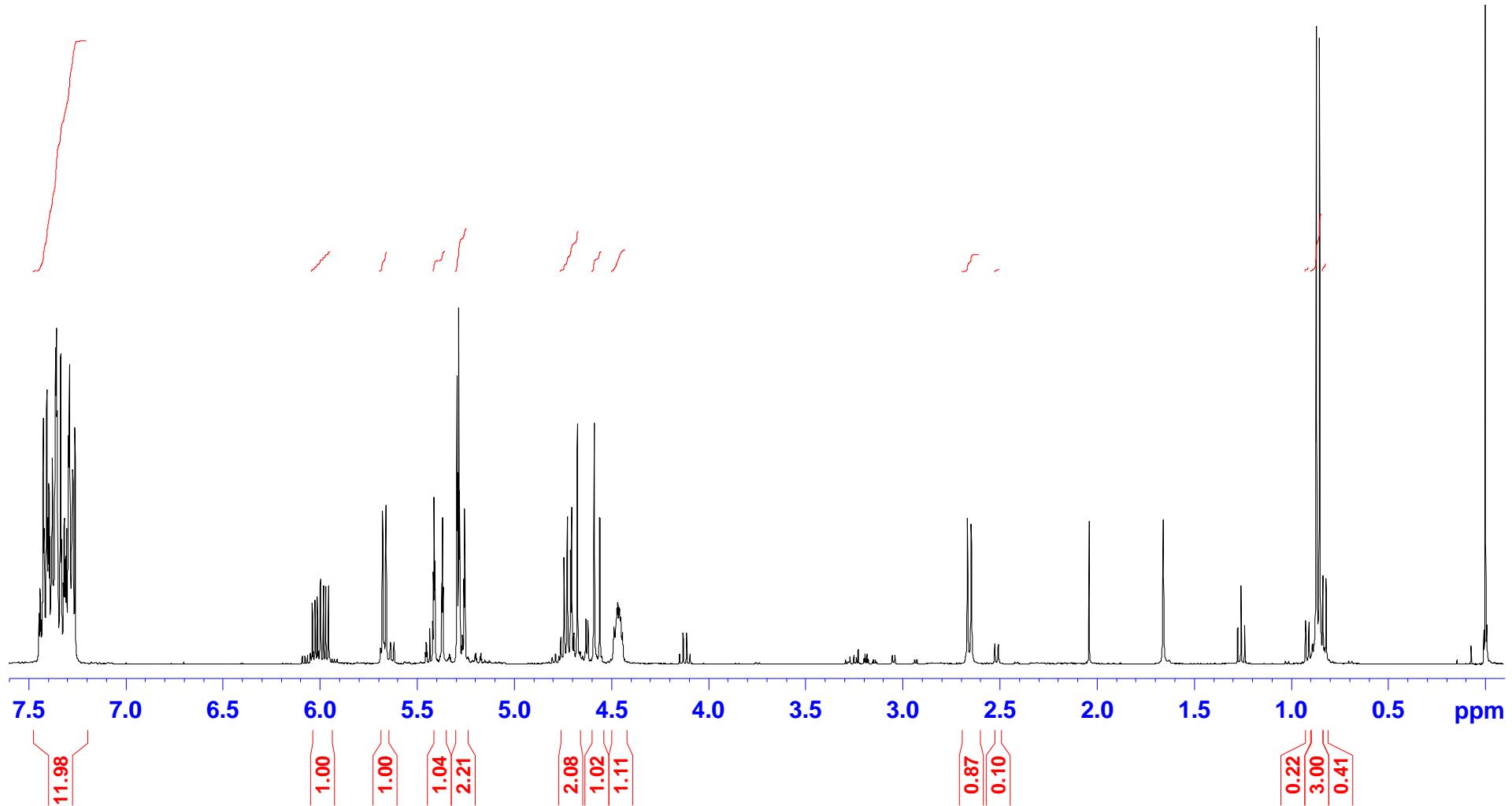


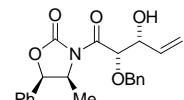
(4*S*,5*R*)-3-((2*S*,3*R*)-2-(Benzylxy)-3-hydroxypent-4-enoyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one (**13**, diastereomerically pure, with Bu₂BOTf).



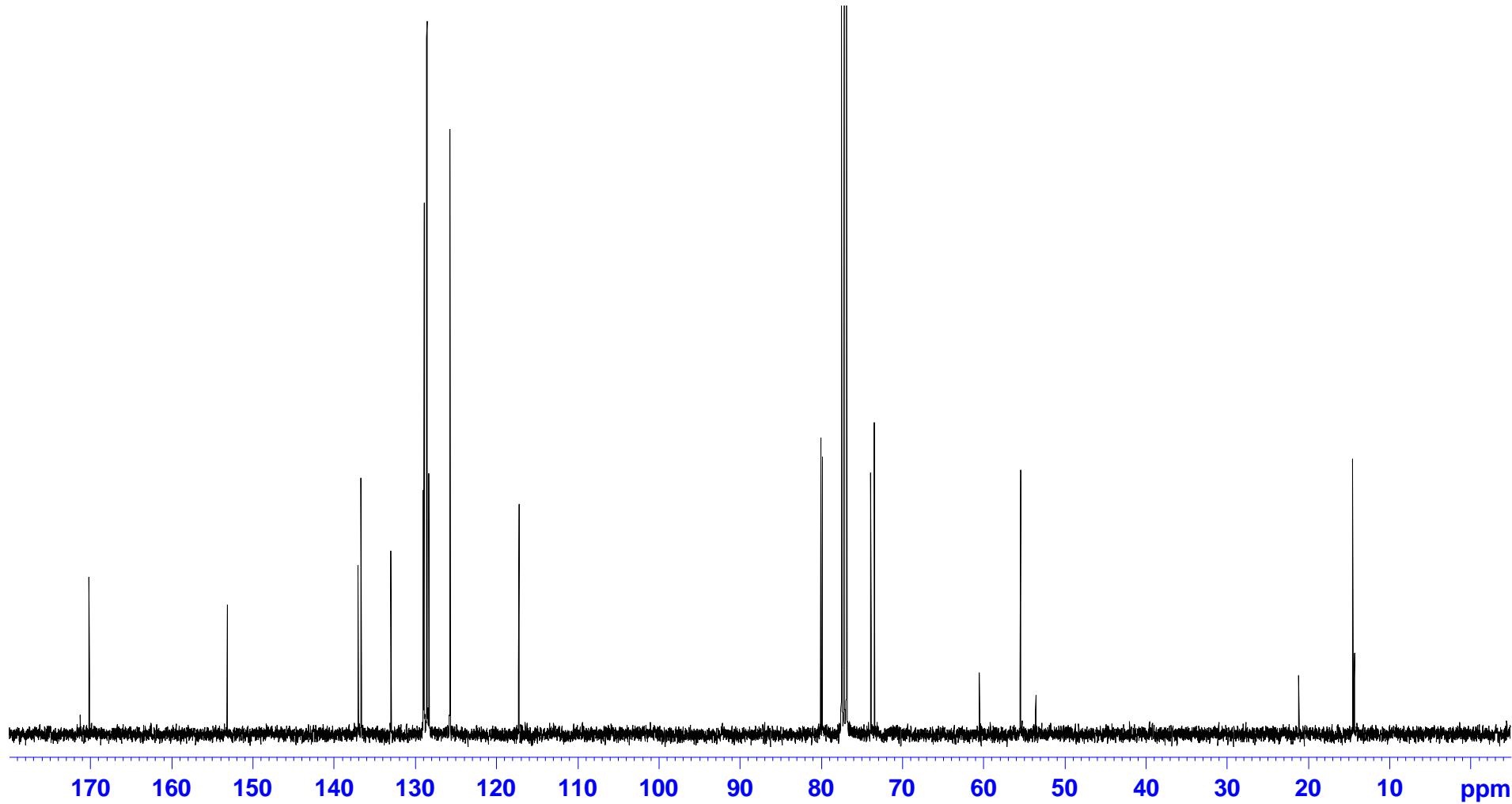


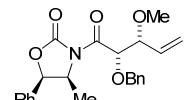
(4*S*,5*R*)-3-((2*S*,3*R*)-2-(Benzylxy)-3-hydroxypent-4-enoyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one (**13**, 14:2:1 mixture, with TiCl₄)



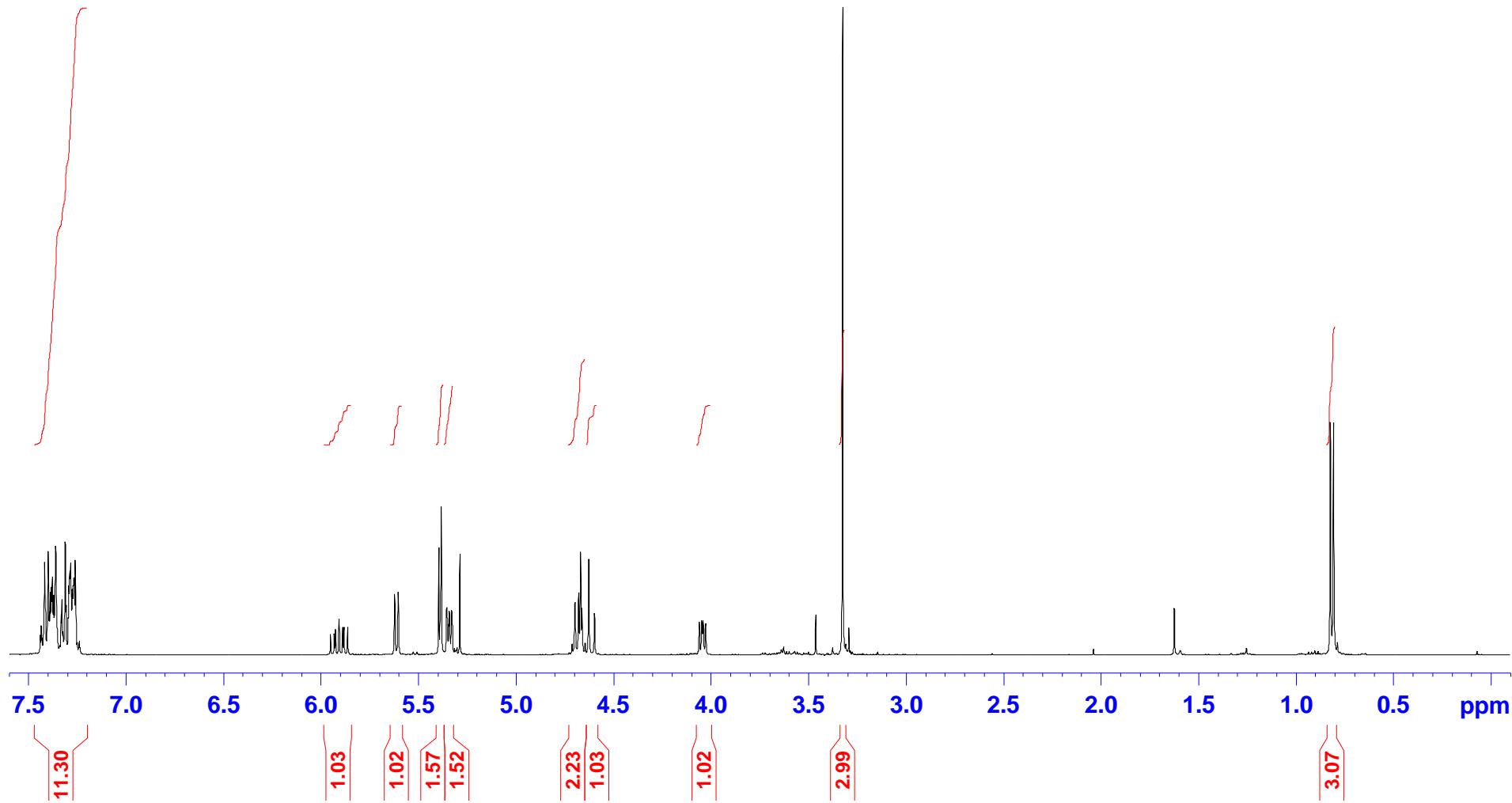


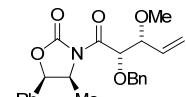
(4*S*,5*R*)-3-((2*S*,3*R*)-2-(Benzylxy)-3-hydroxypent-4-enoyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one (**13**, diastereomerically pure, with Bu₂BOTf).



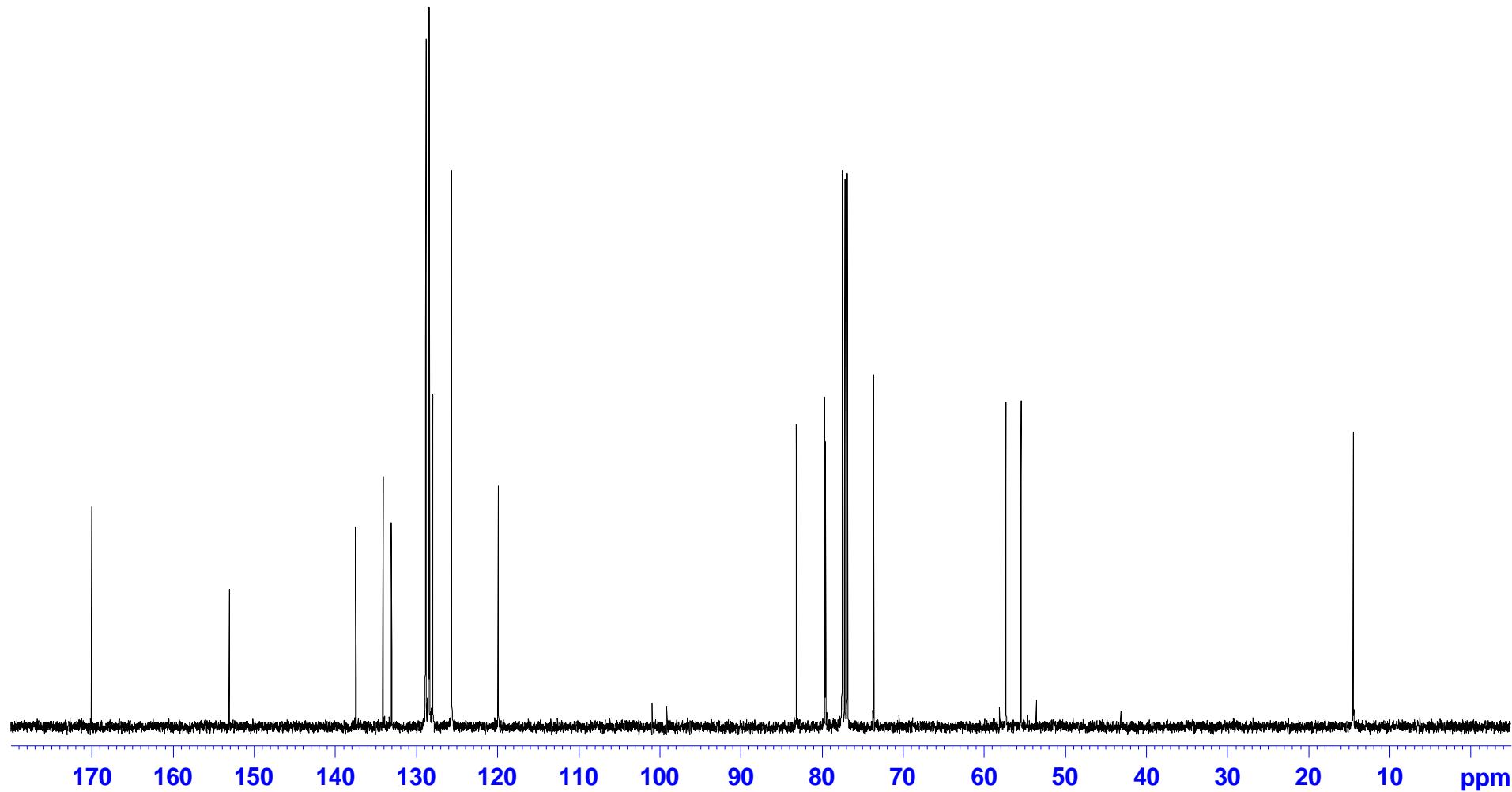


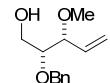
(4*S*,5*R*)-3-((2*S*,3*R*)-2-(Benzylxy)-3-methoxypent-4-enoyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one (**C**).



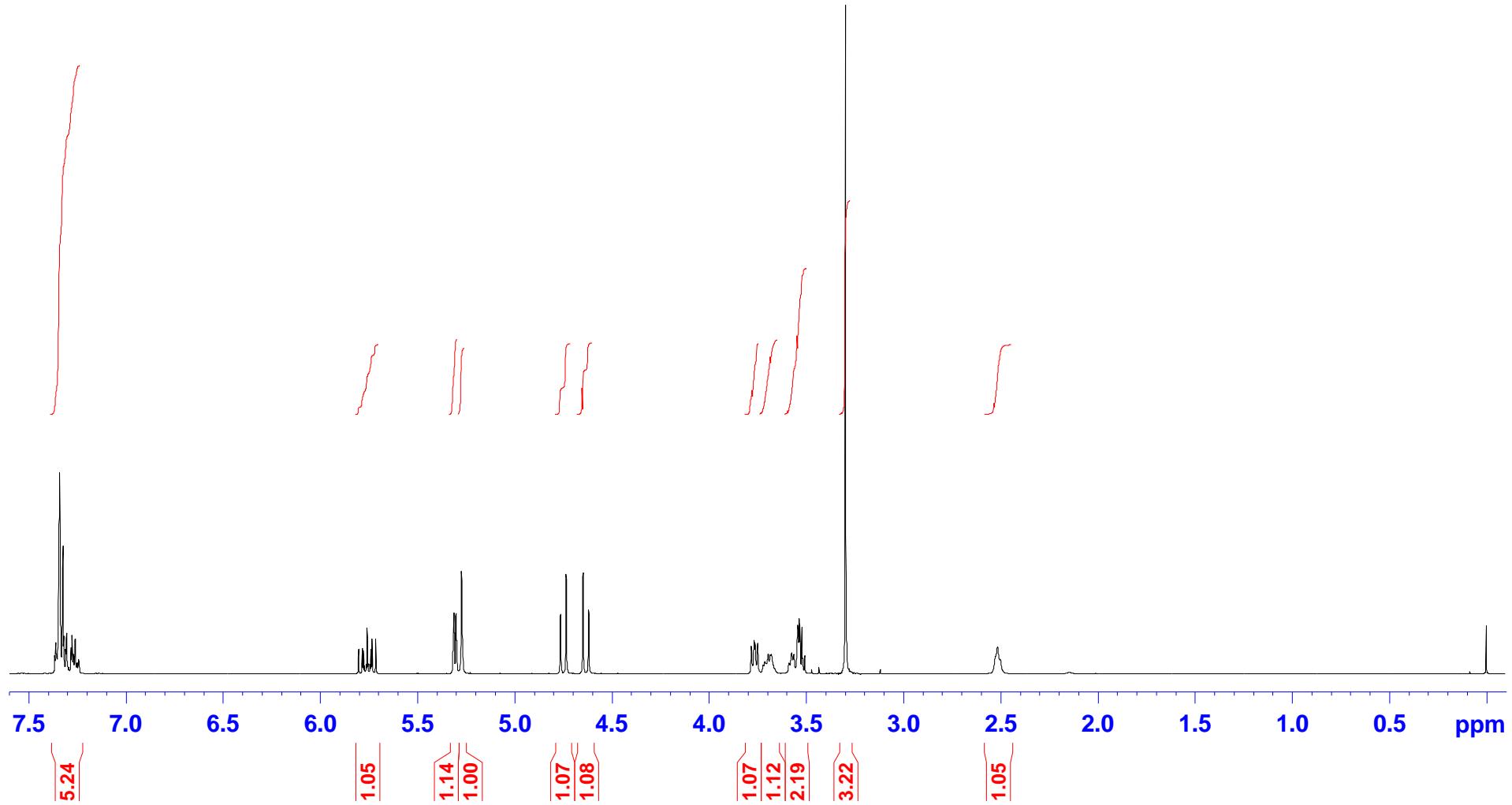


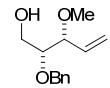
(4*S*,5*R*)-3-((2*S*,3*R*)-2-(Benzylxy)-3-methoxypent-4-enoyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one (**C**).



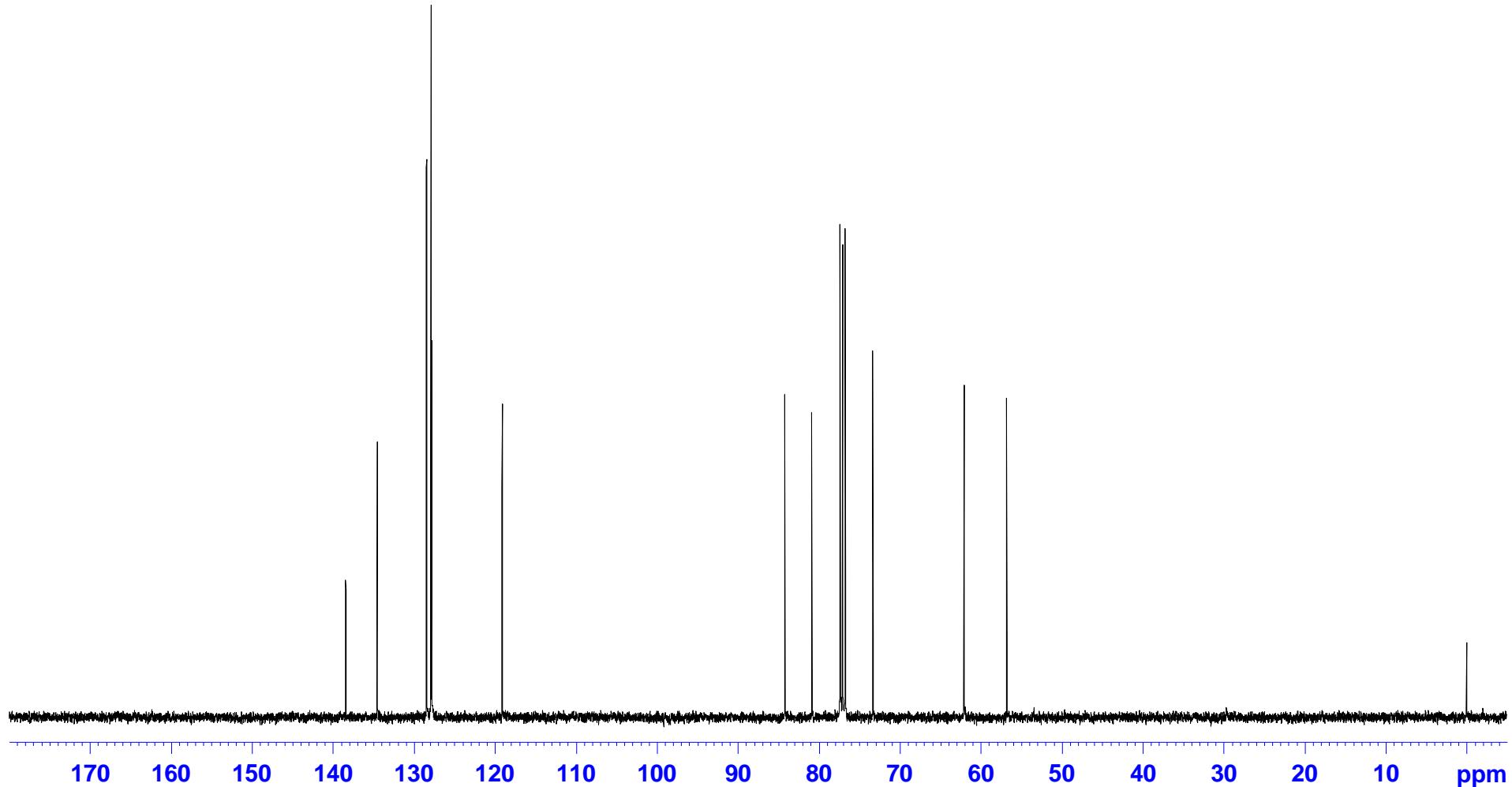


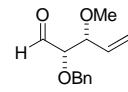
(*2R,3R*)-2-(Benzylxy)-3-methoxypent-4-en-1-ol (**14**).



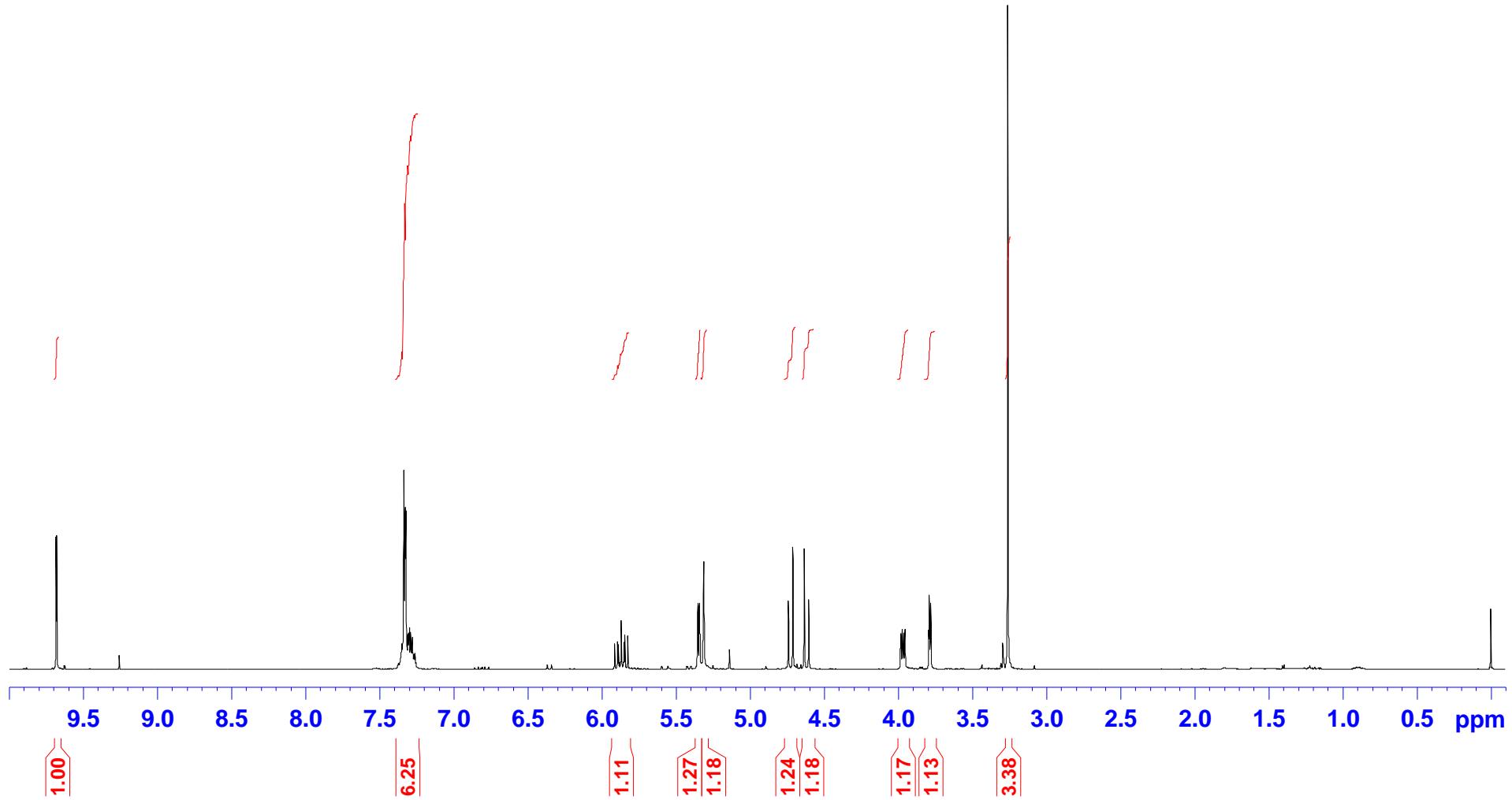


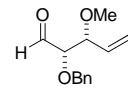
(*2R,3R*)-2-(Benzylxy)-3-methoxypent-4-en-1-ol (**14**).



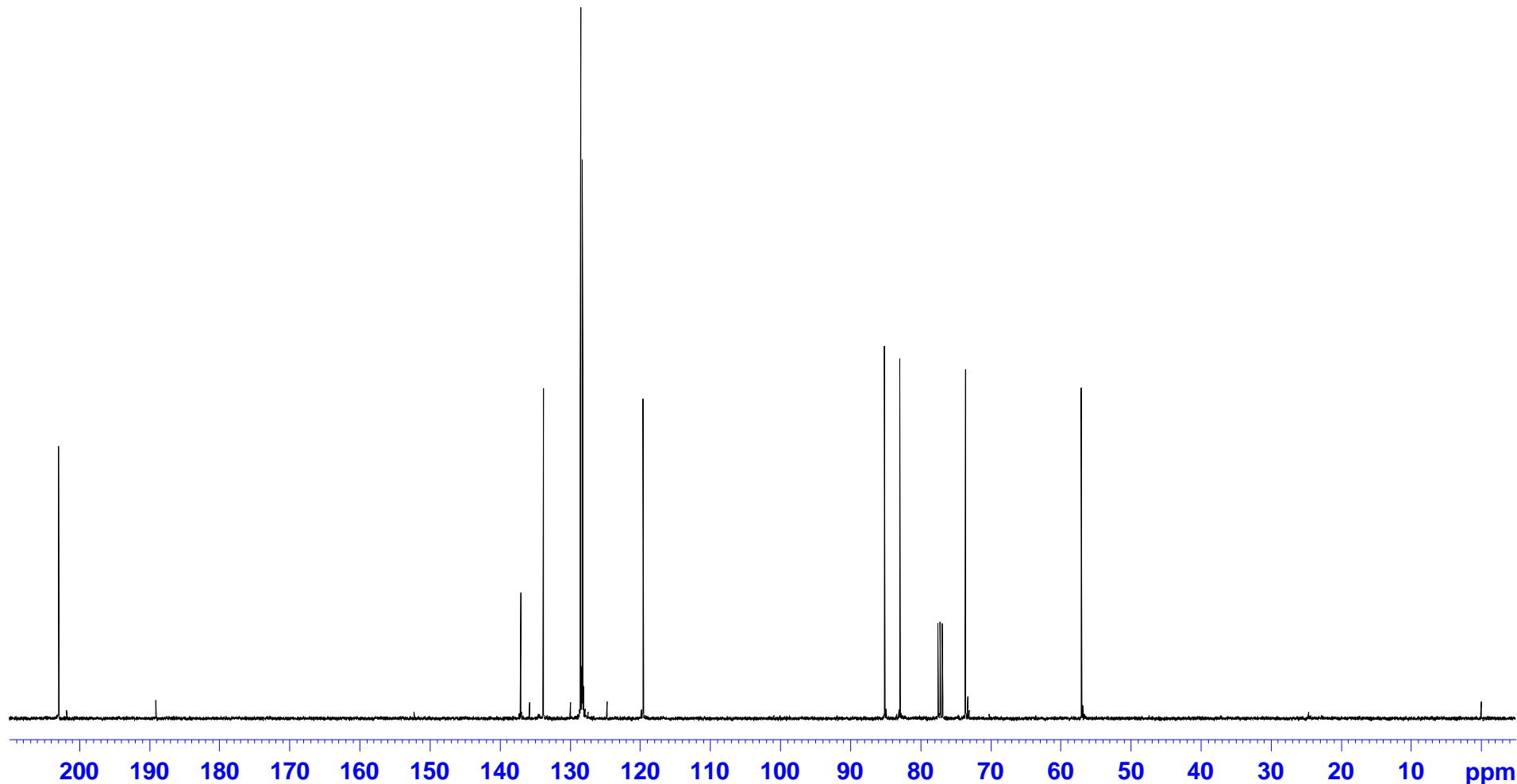


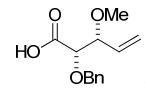
(2*S*,3*R*)-2-(Benzylxy)-3-methoxypent-4-enal (**D**).



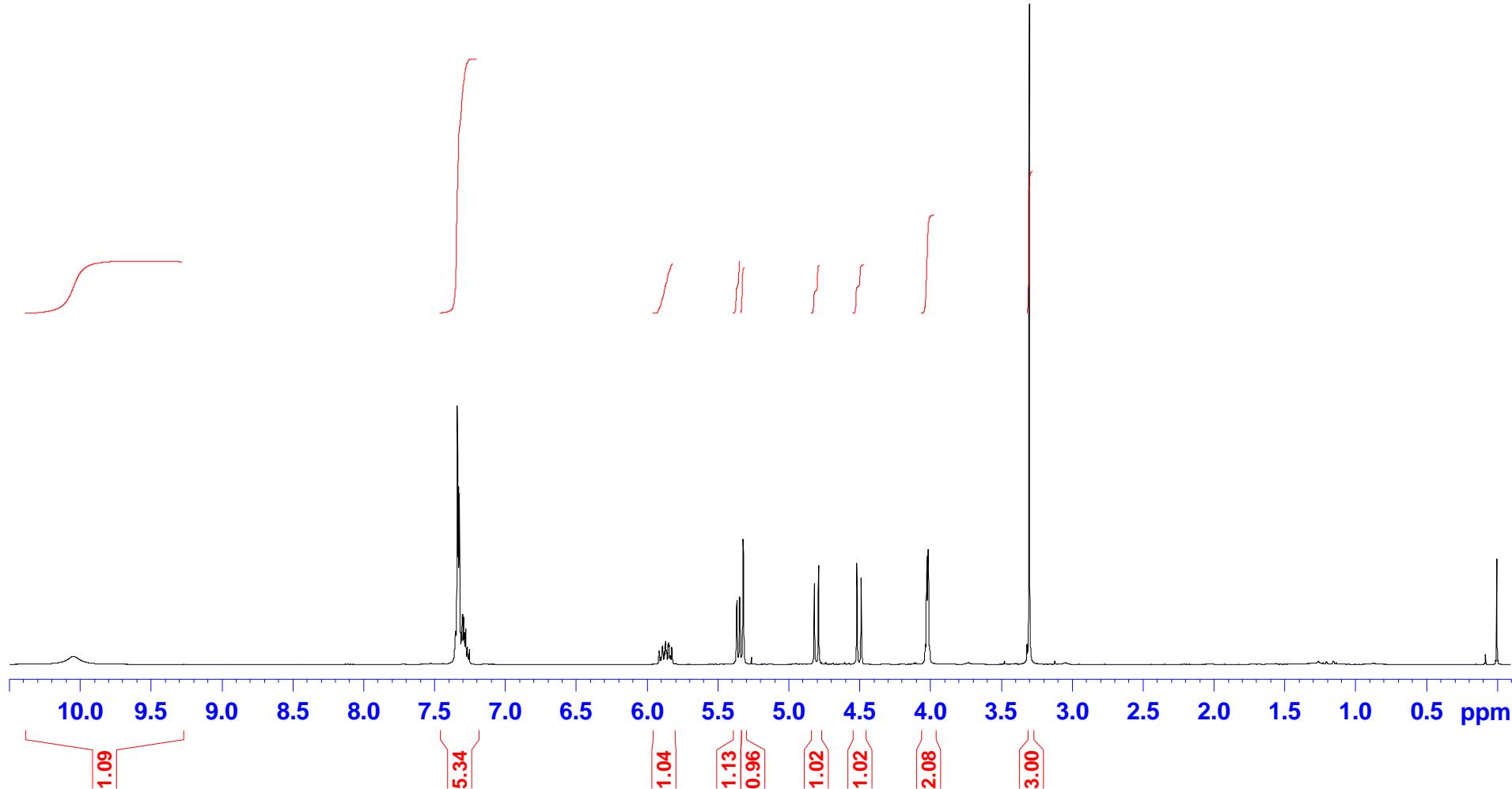


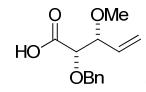
(2*S*,3*R*)-2-(Benzylxy)-3-methoxypent-4-enal (**D**).



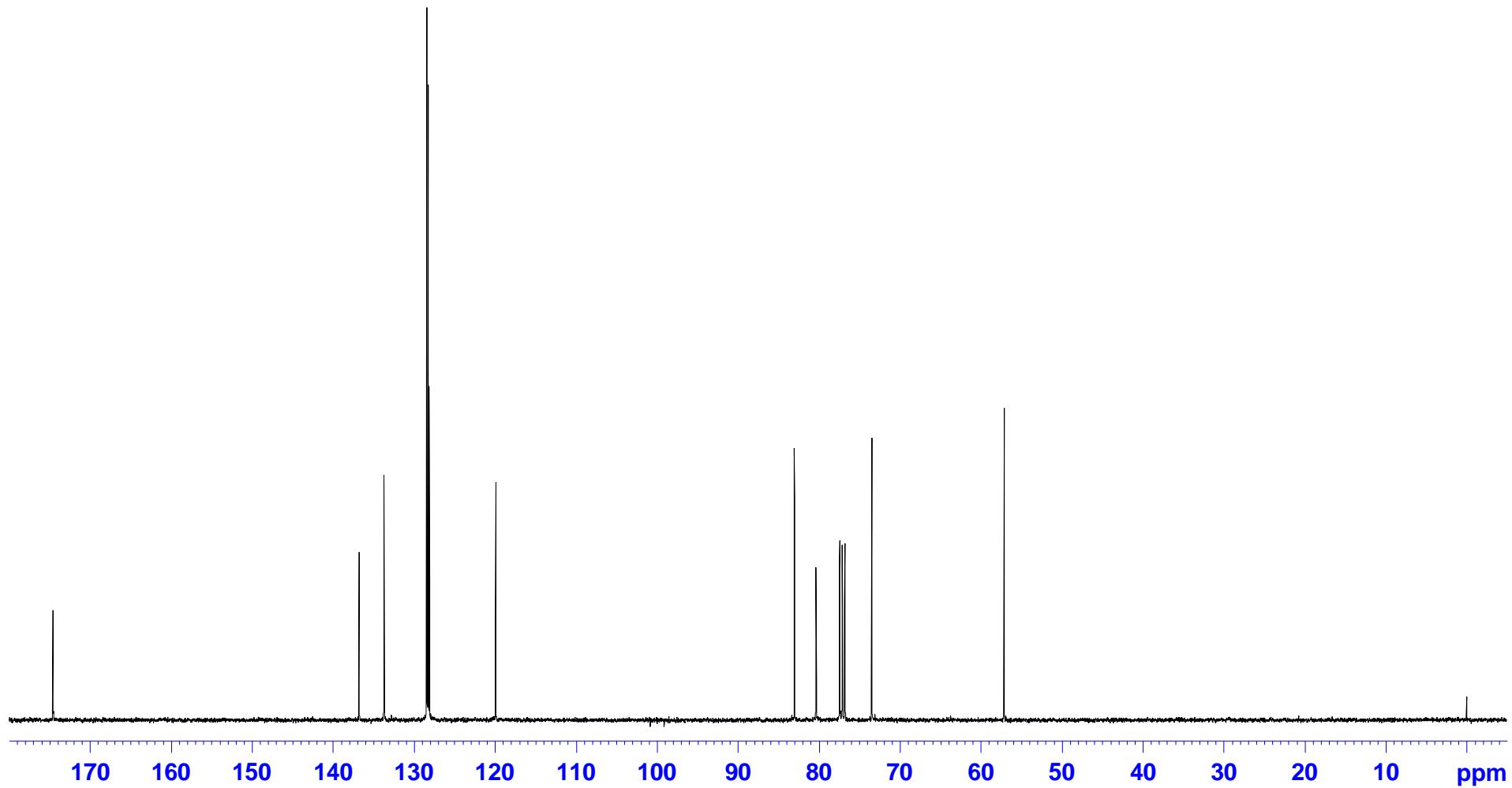


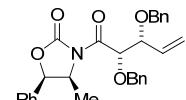
(2*S*,3*R*)-2-(Benzylxy)-3-methoxypent-4-enoic acid (**6**).



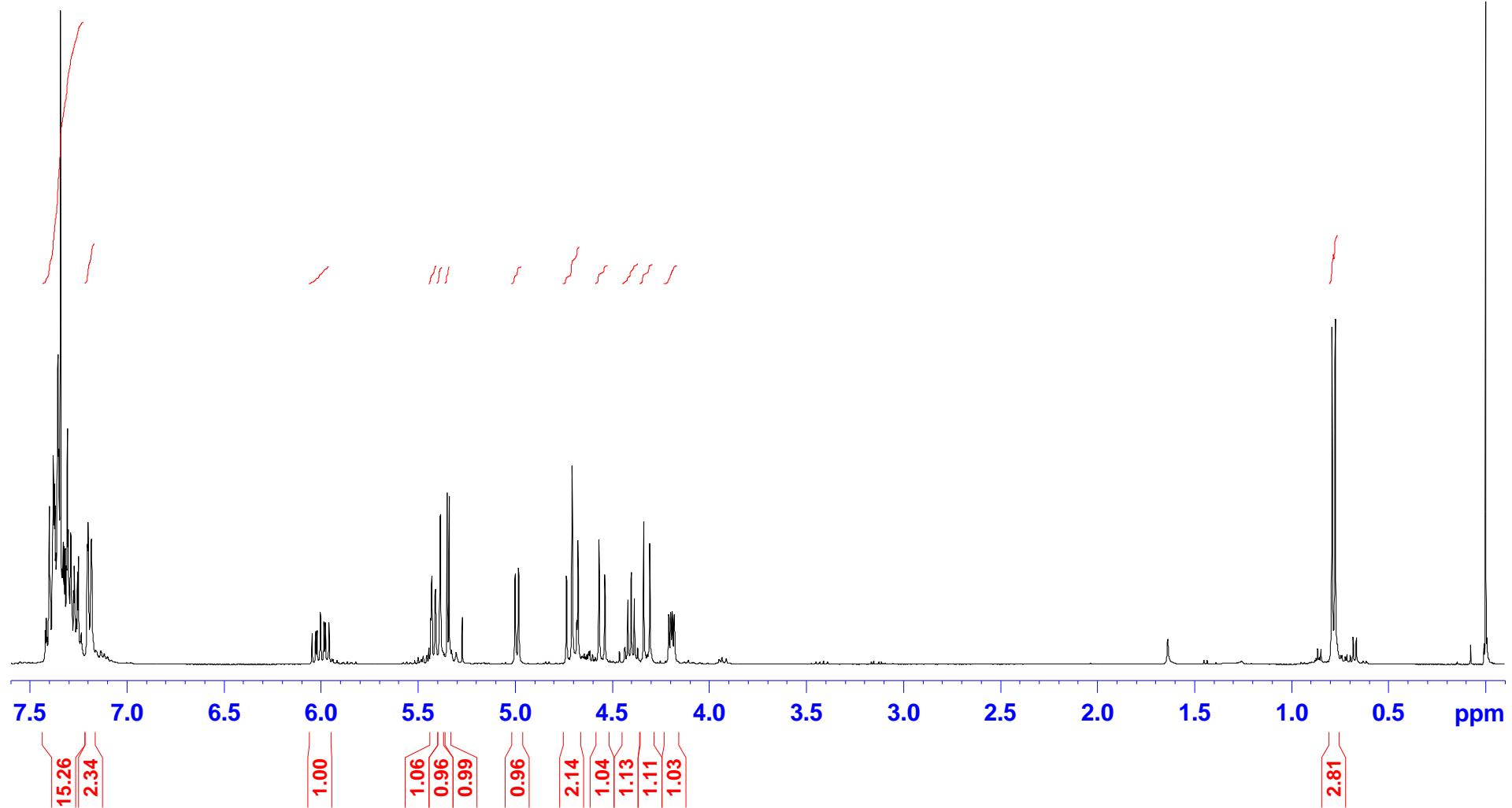


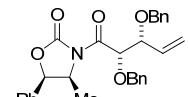
(2*S*,3*R*)-2-(Benzylxy)-3-methoxypent-4-enoic acid (**6**).



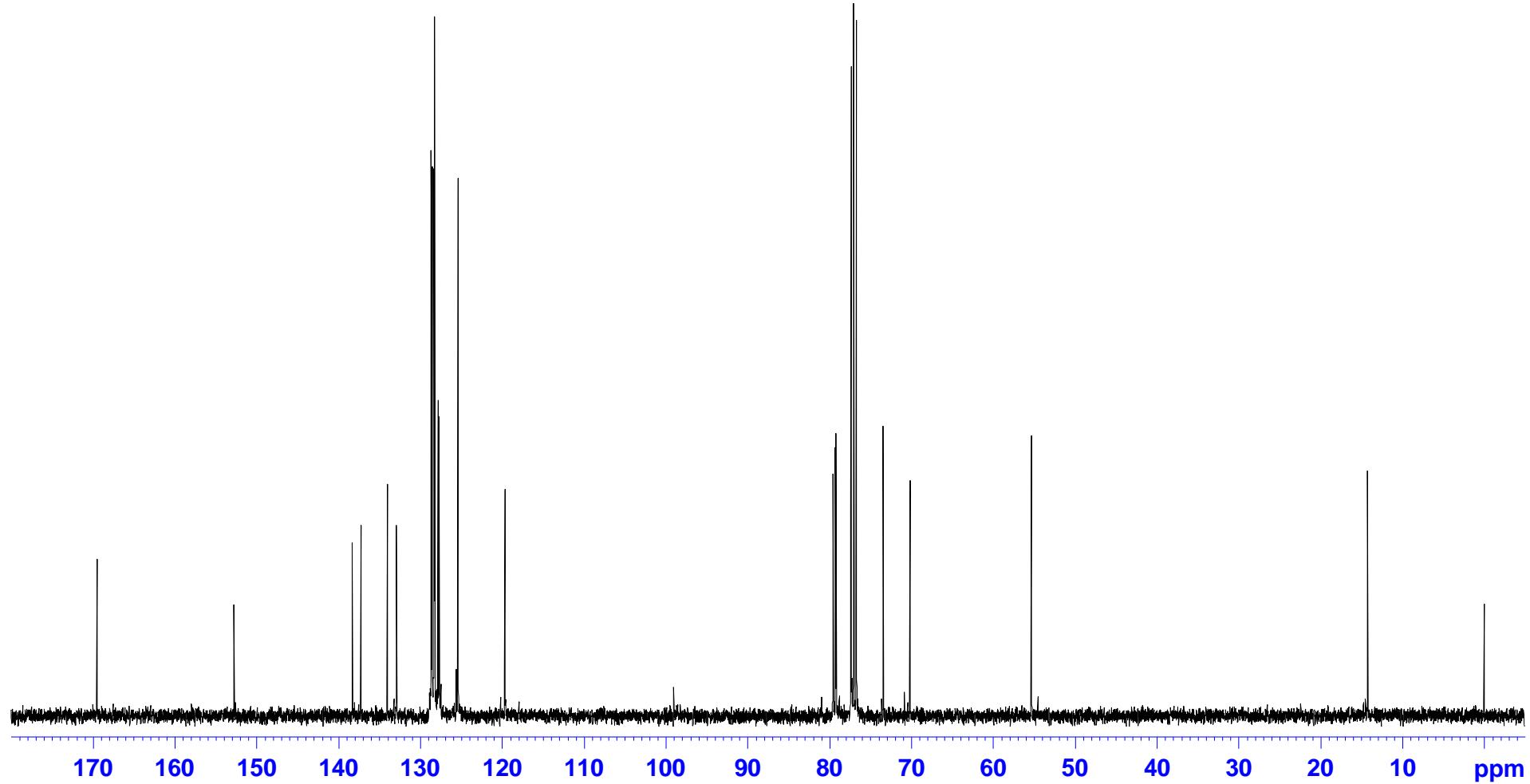


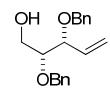
(4*S*,5*R*)-3-((2*S*,3*R*)-2,3-Bis(benzyloxy)pent-4-enoyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one (**E**).



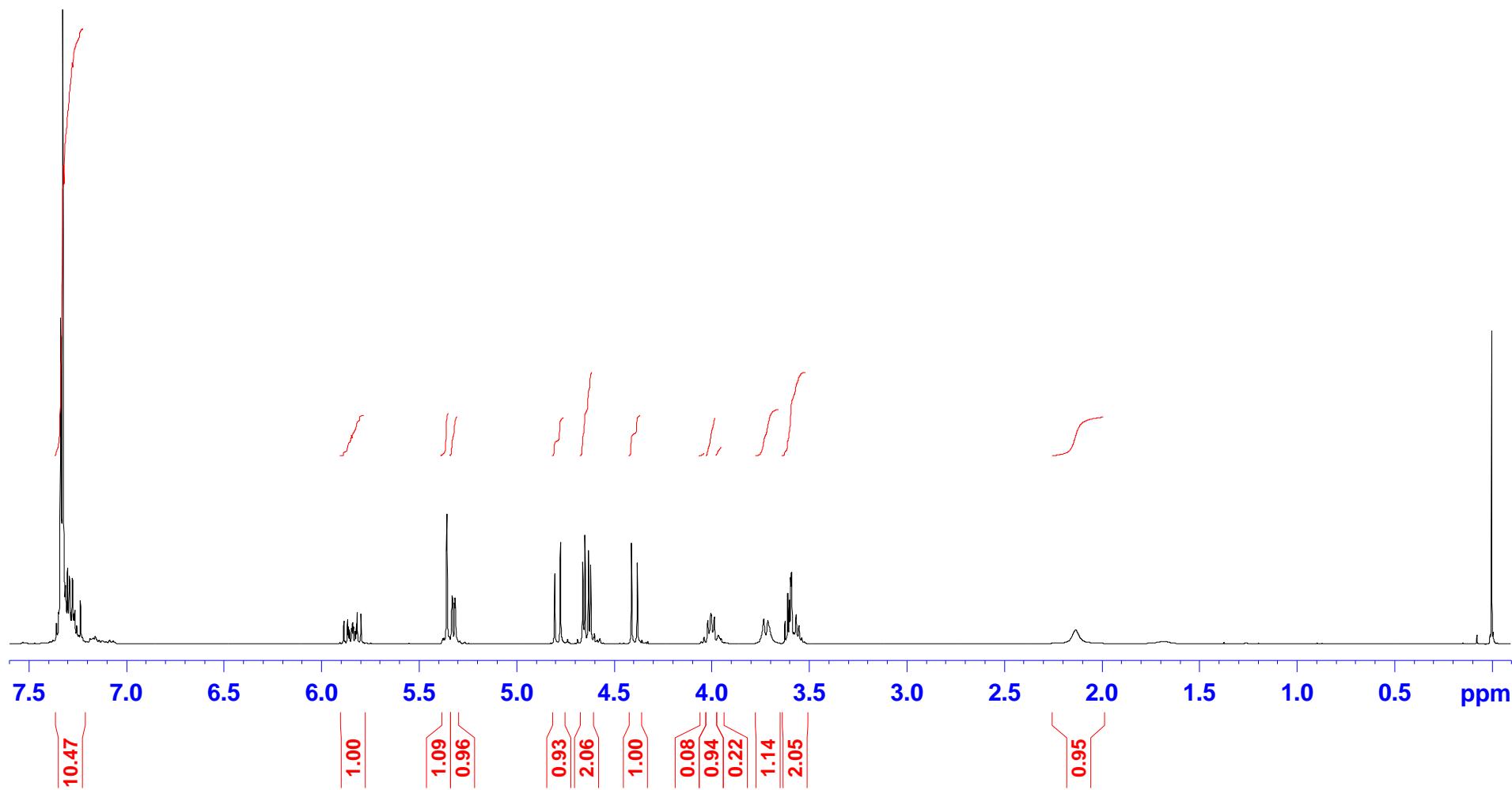


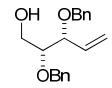
(4*S*,5*R*)-3-((2*S*,3*R*)-2,3-Bis(benzyloxy)pent-4-enoyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one (**E**).



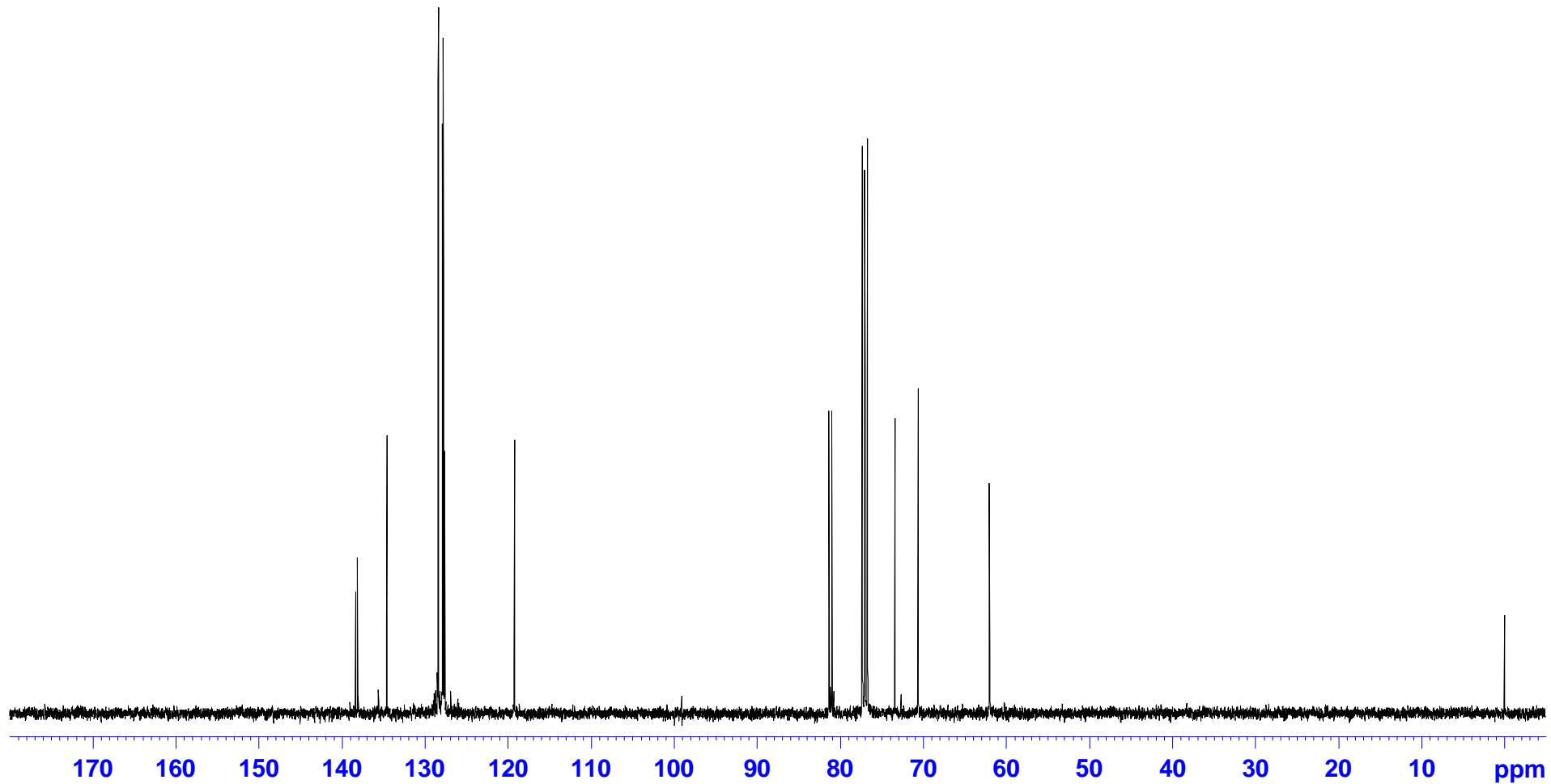


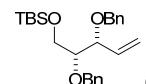
(2*R*,3*R*)-2,3-Bis(benzyloxy)pent-4-en-1-ol (**15**).



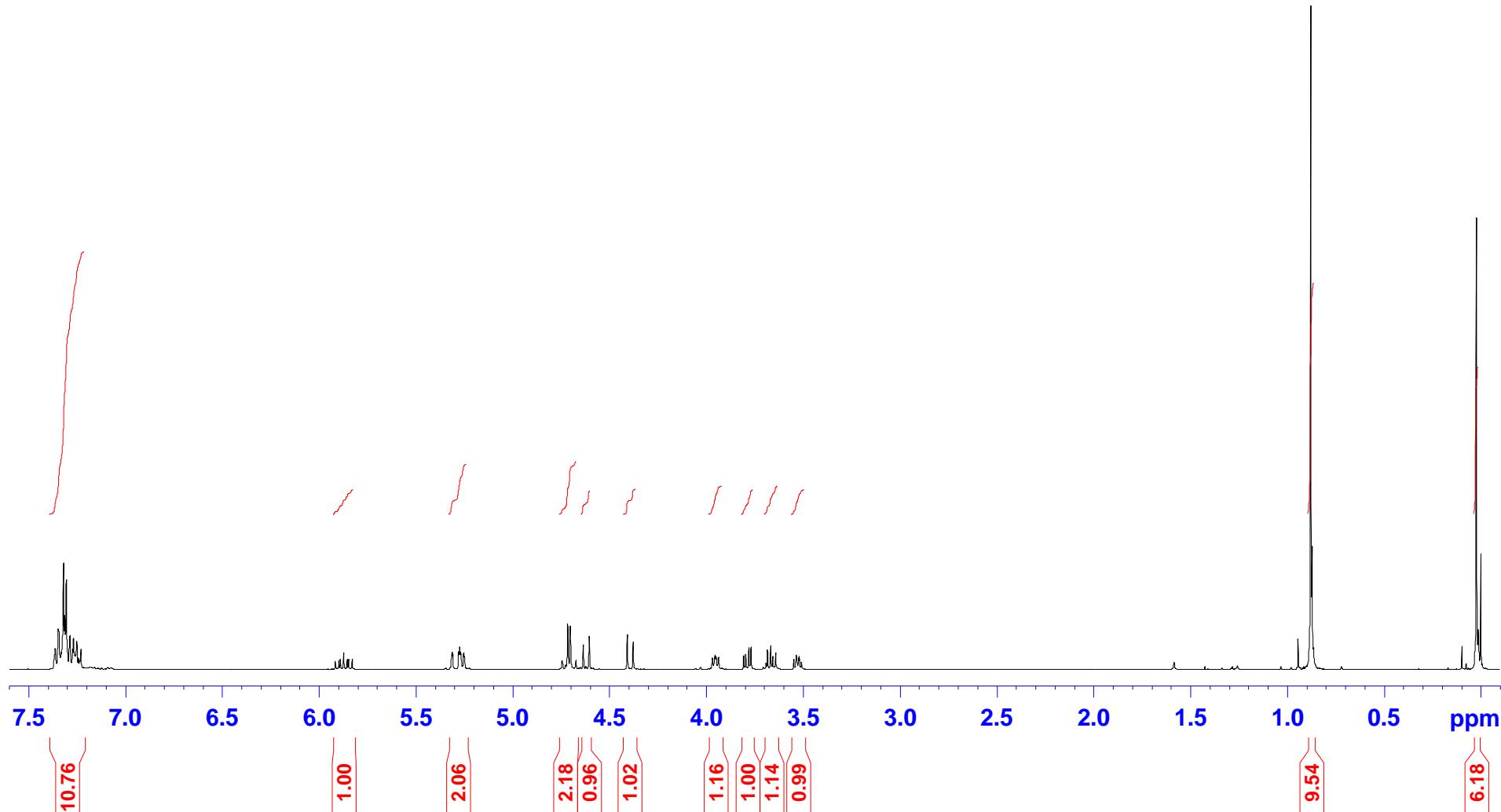


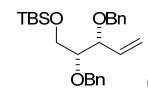
(*2R,3R*)-2,3-Bis(benzyloxy)pent-4-en-1-ol (**15**).



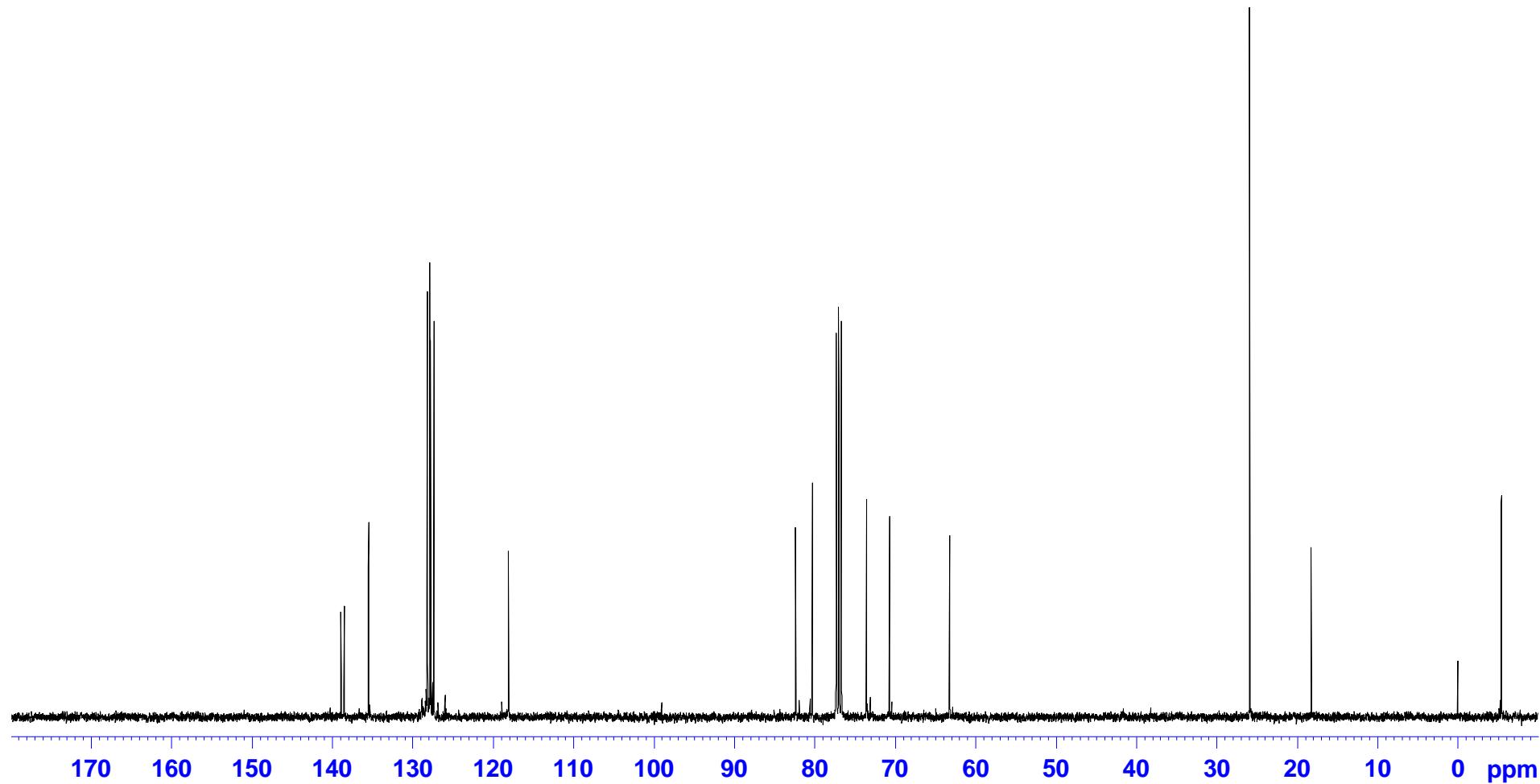


((2*R*,3*R*)-2,3-Bis(benzyloxy)pent-4-enyloxy)(*tert*-butyl)dimethylsilane (**16**).

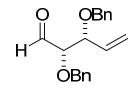




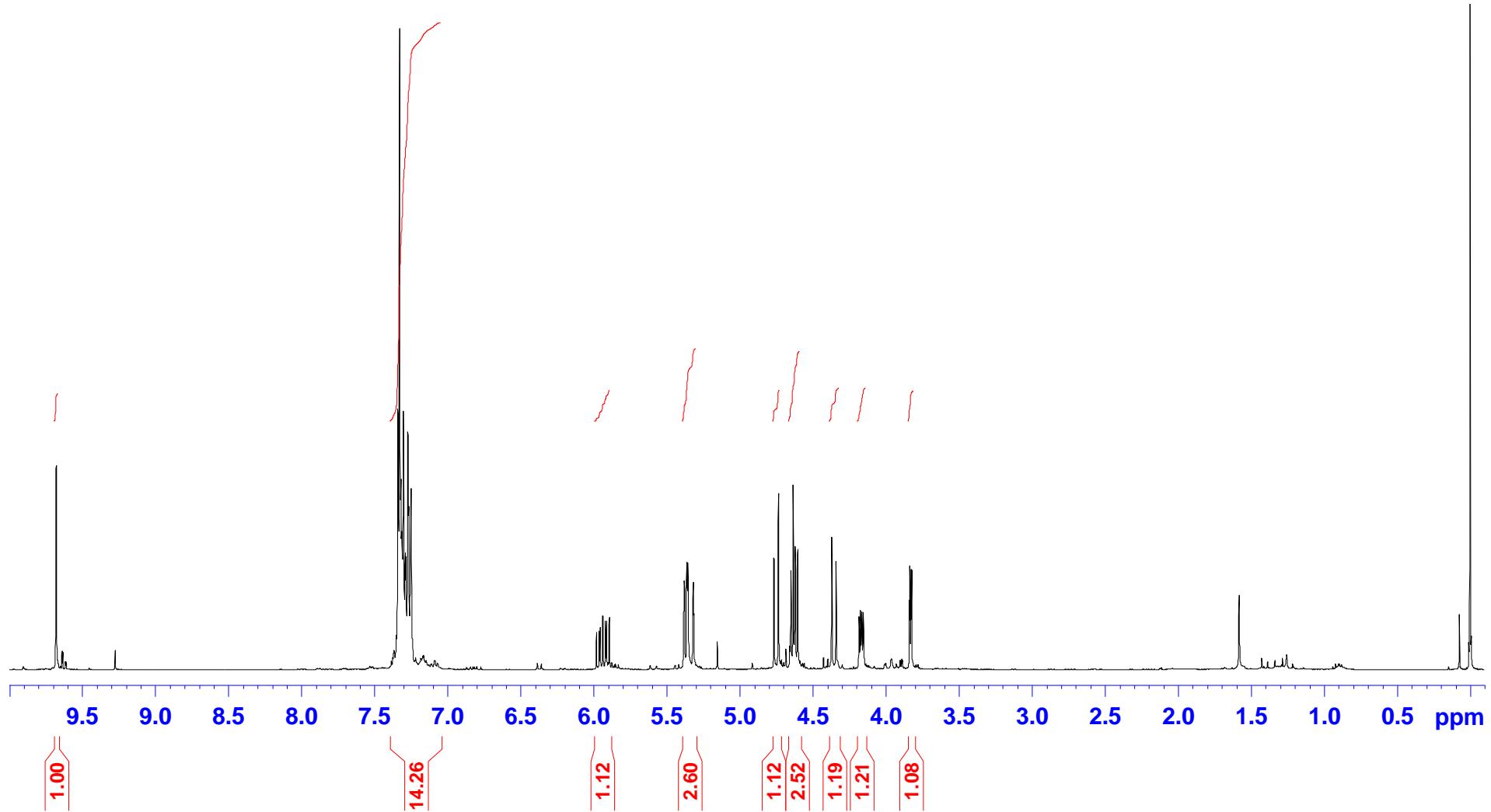
((2*R*,3*R*)-2,3-Bis(benzyloxy)pent-4-enyloxy)(*tert*-butyl)dimethylsilane (**16**).

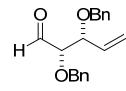


S20

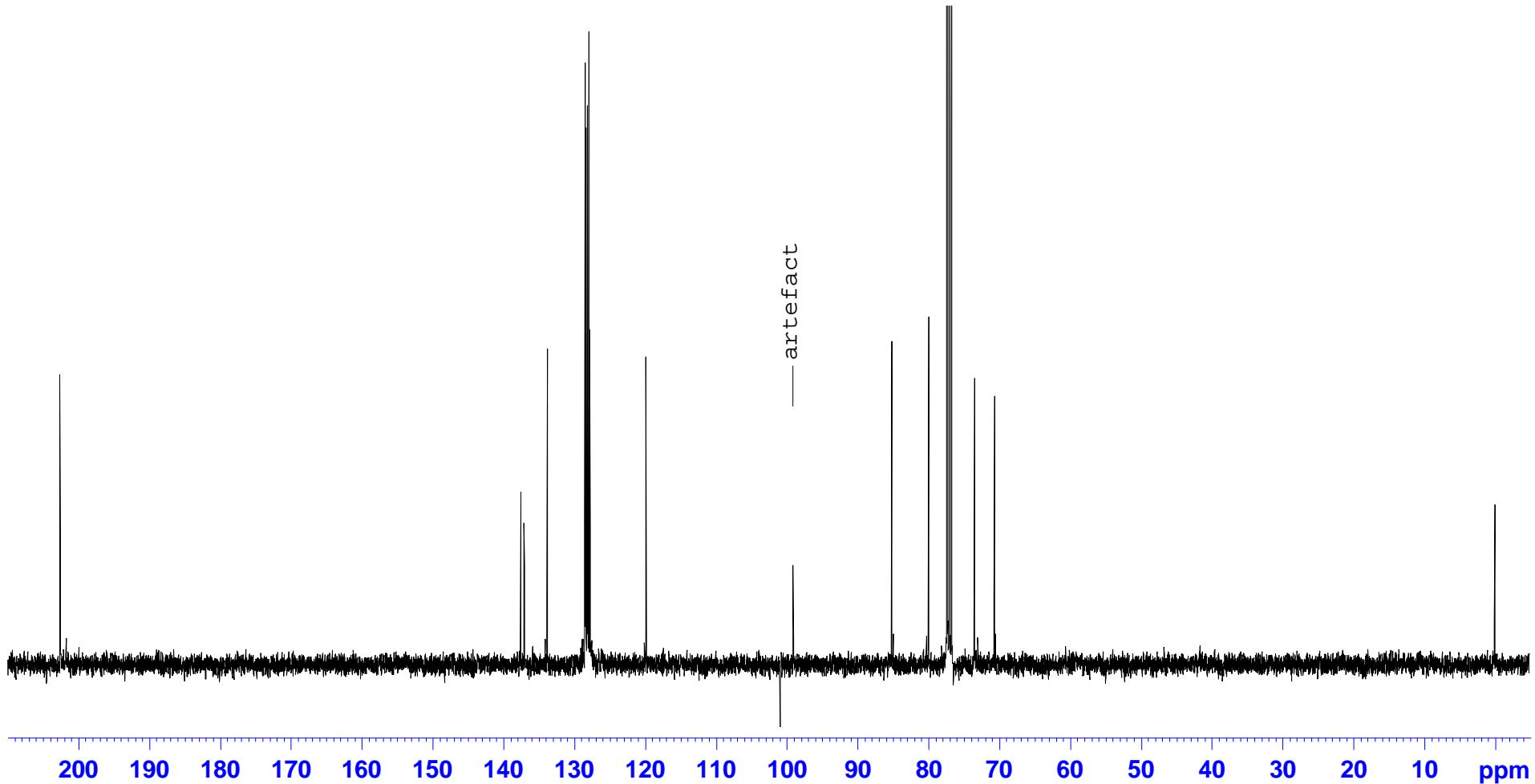


(2*S*,3*R*)-2,3-bis(benzyloxy)pent-4-enal (**17**).

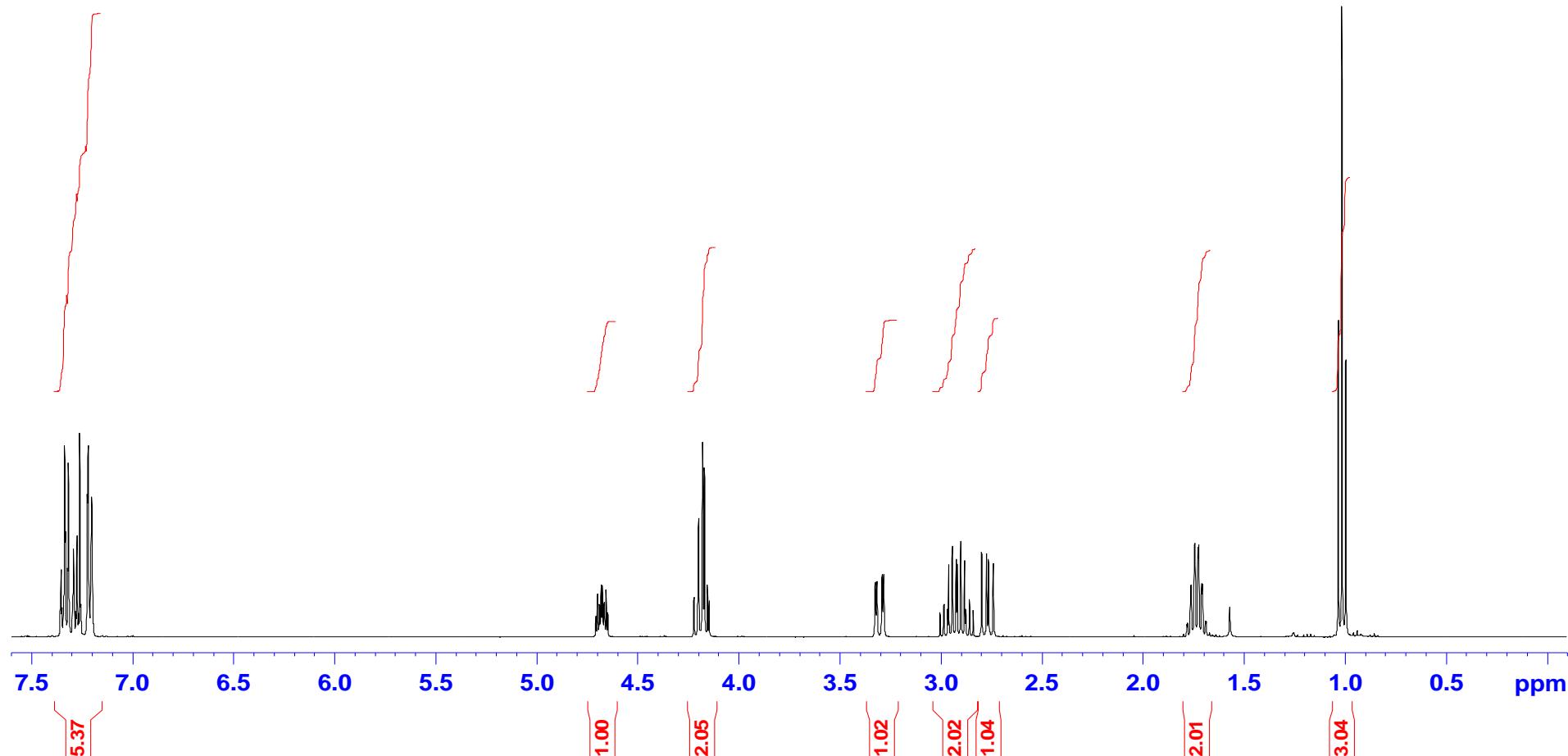
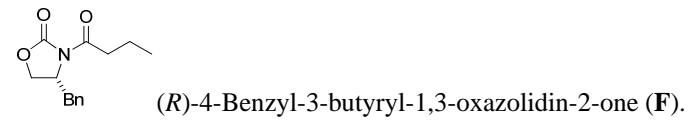


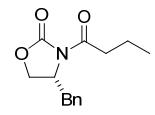


(2*S*,3*R*)-2,3-bis(benzyloxy)pent-4-enal (**17**).

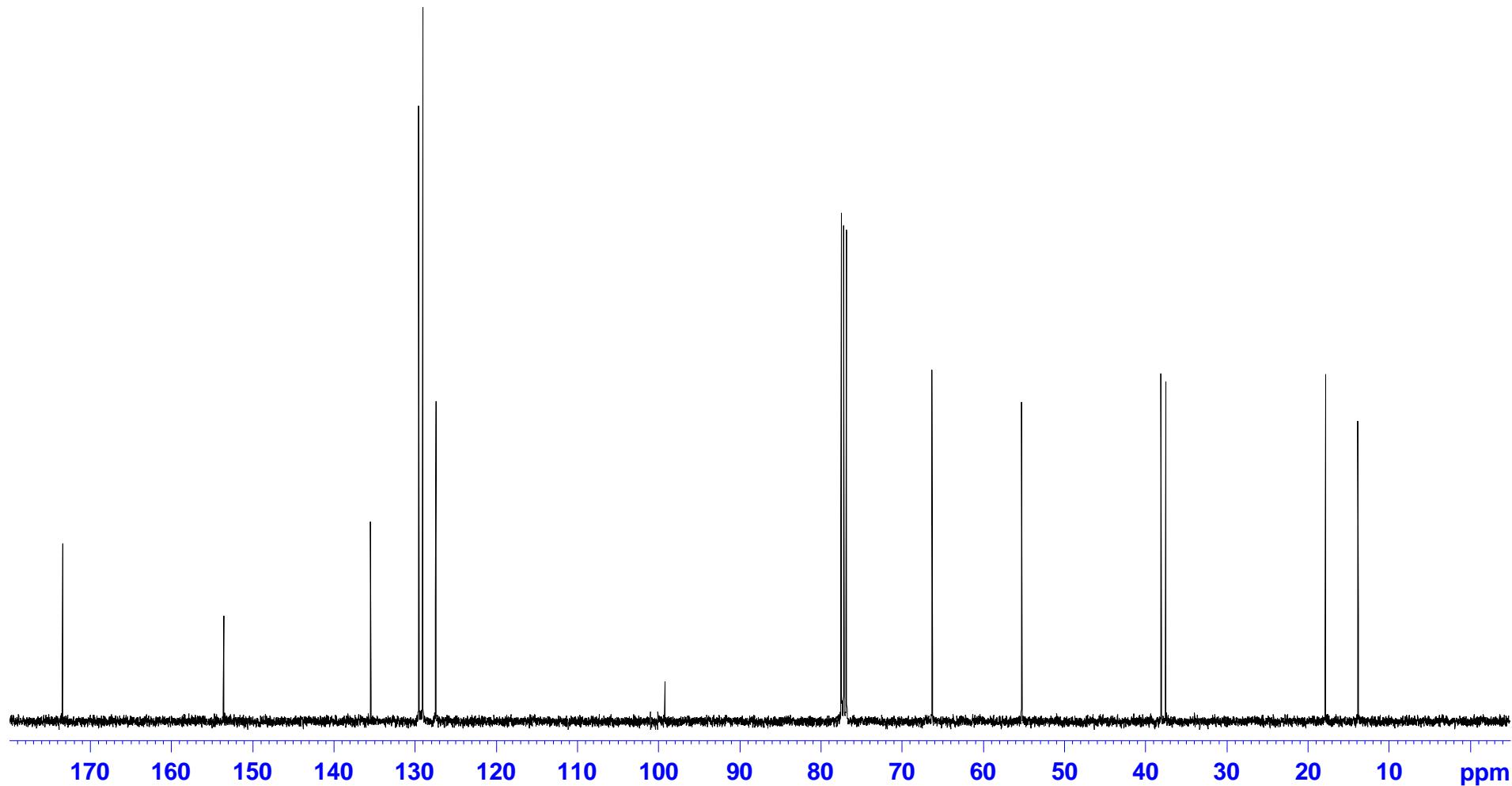


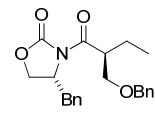
Synthesis of vinyl iodide 7



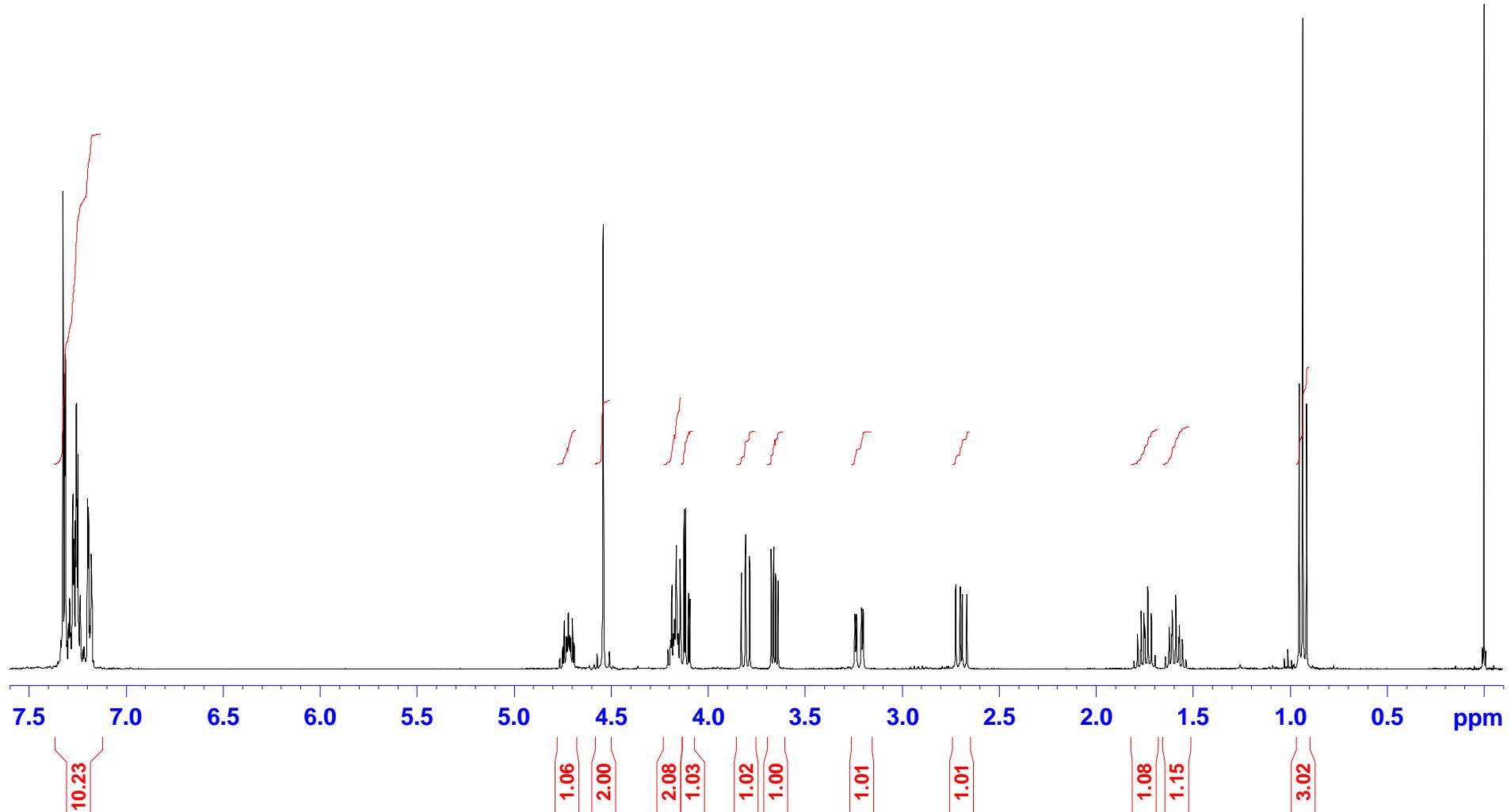


(*R*)-4-Benzyl-3-butryl-1,3-oxazolidin-2-one (**F**).

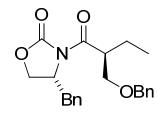




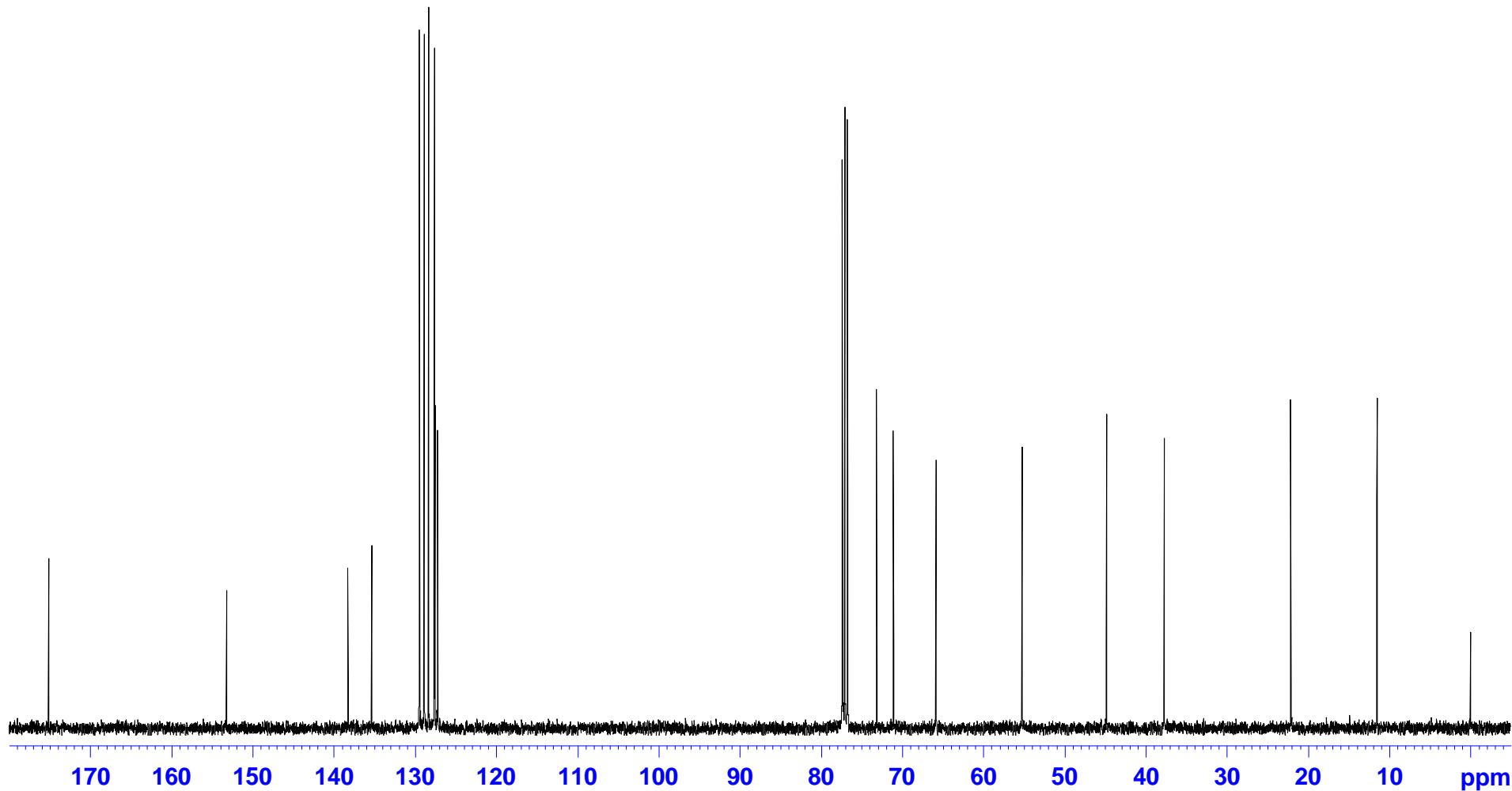
(*R*)-4-benzyl-3-((*S*)-2-(benzyloxymethyl)butanoyl)-1,3-oxazolidin-2-one (**18**).

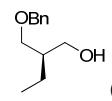


S25

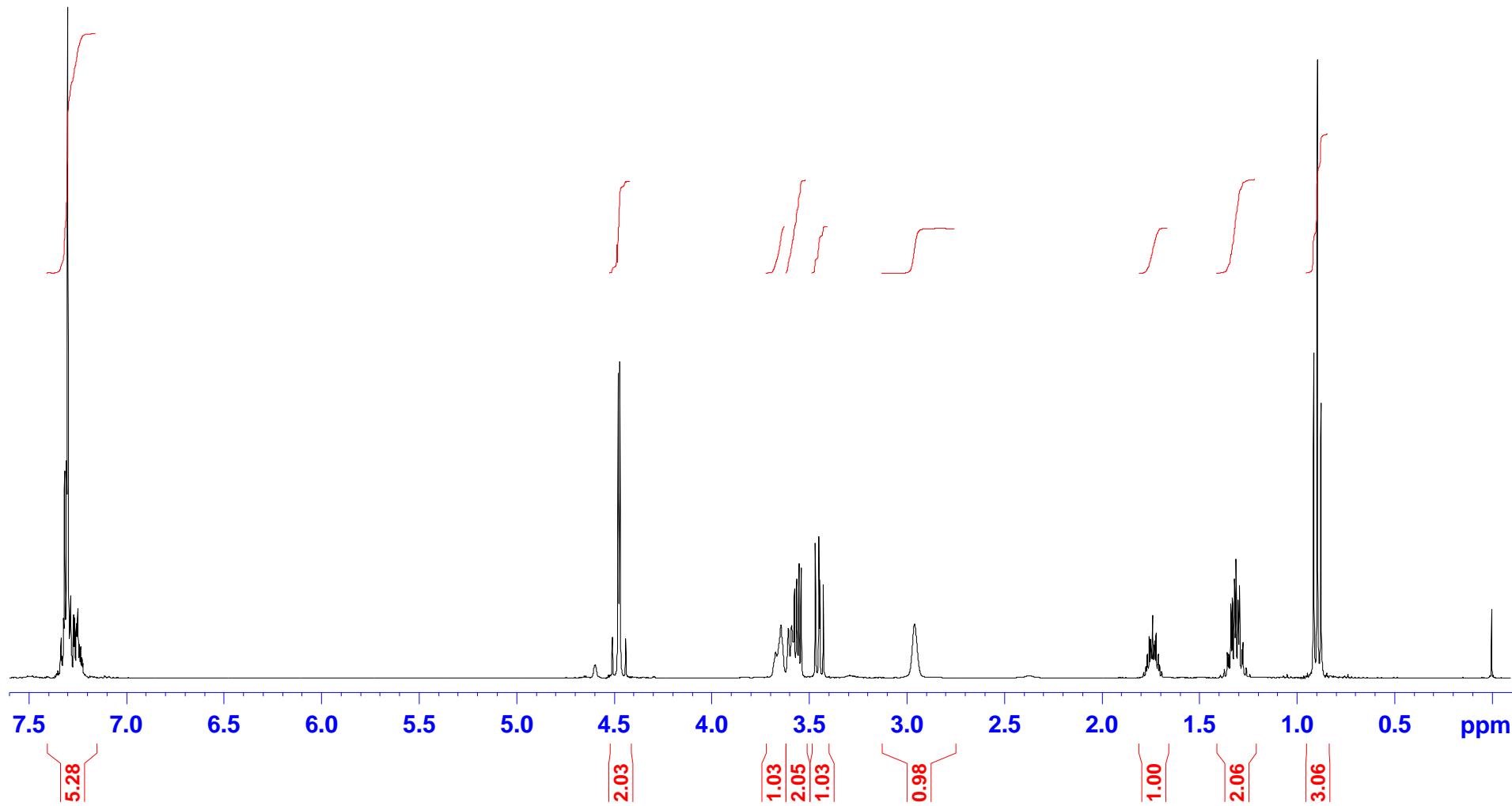


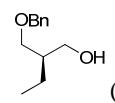
(*R*)-4-benzyl-3-((*S*)-2-(benzyloxymethyl)butanoyl)-1,3-oxazolidin-2-one (**18**).



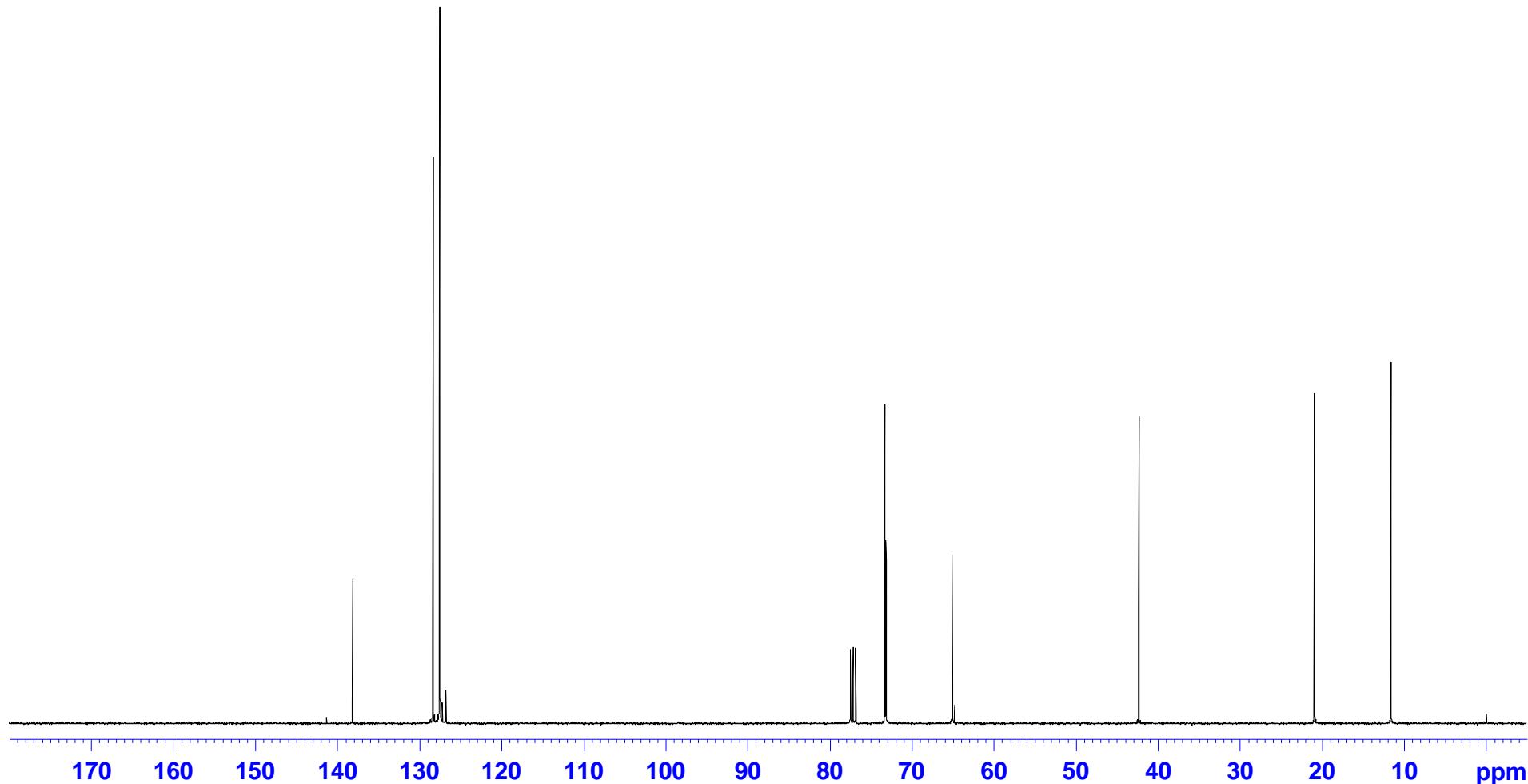


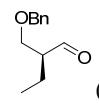
(*R*)-2-(Benzylloxymethyl)butan-1-ol (**19**).



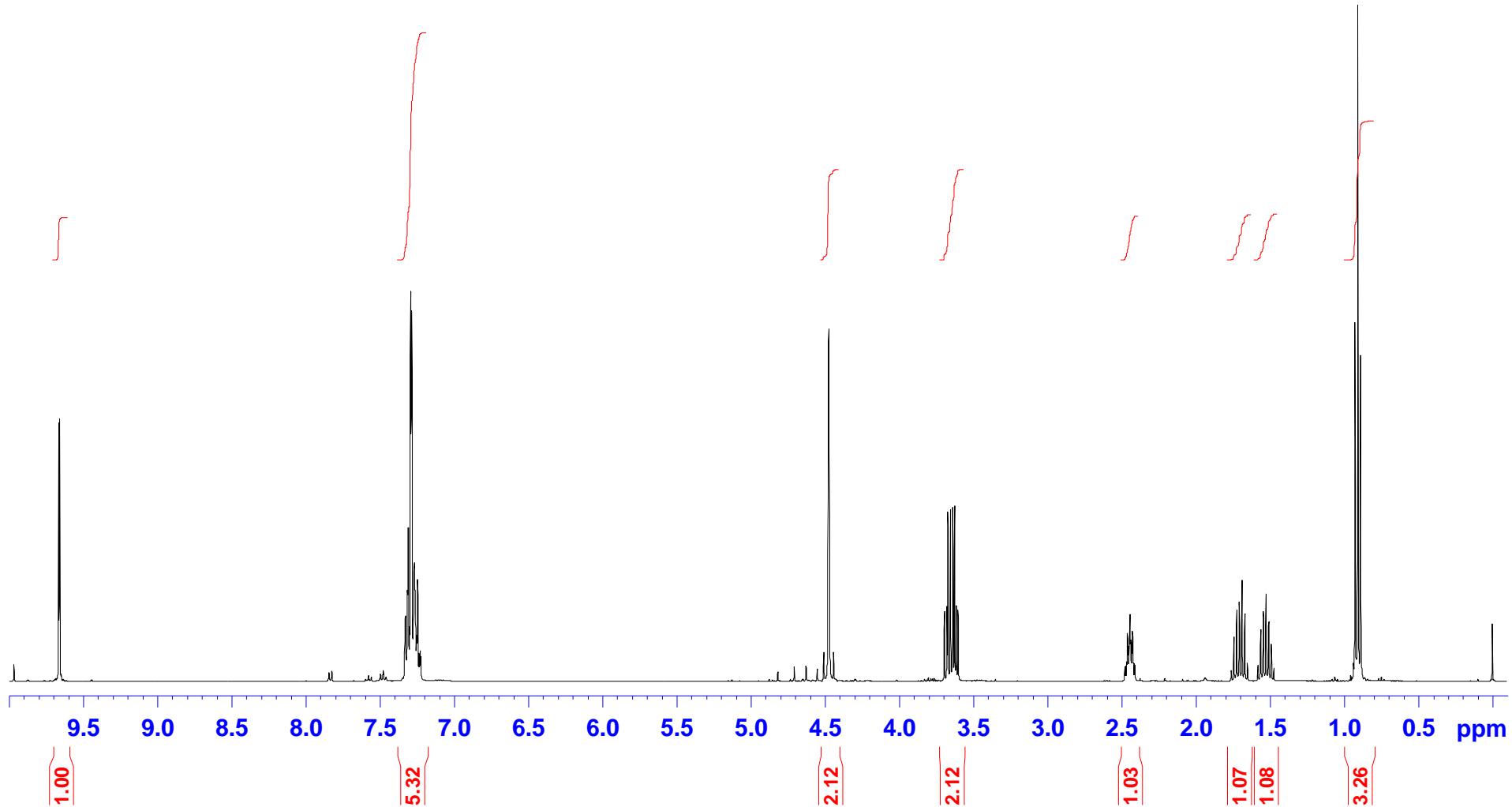


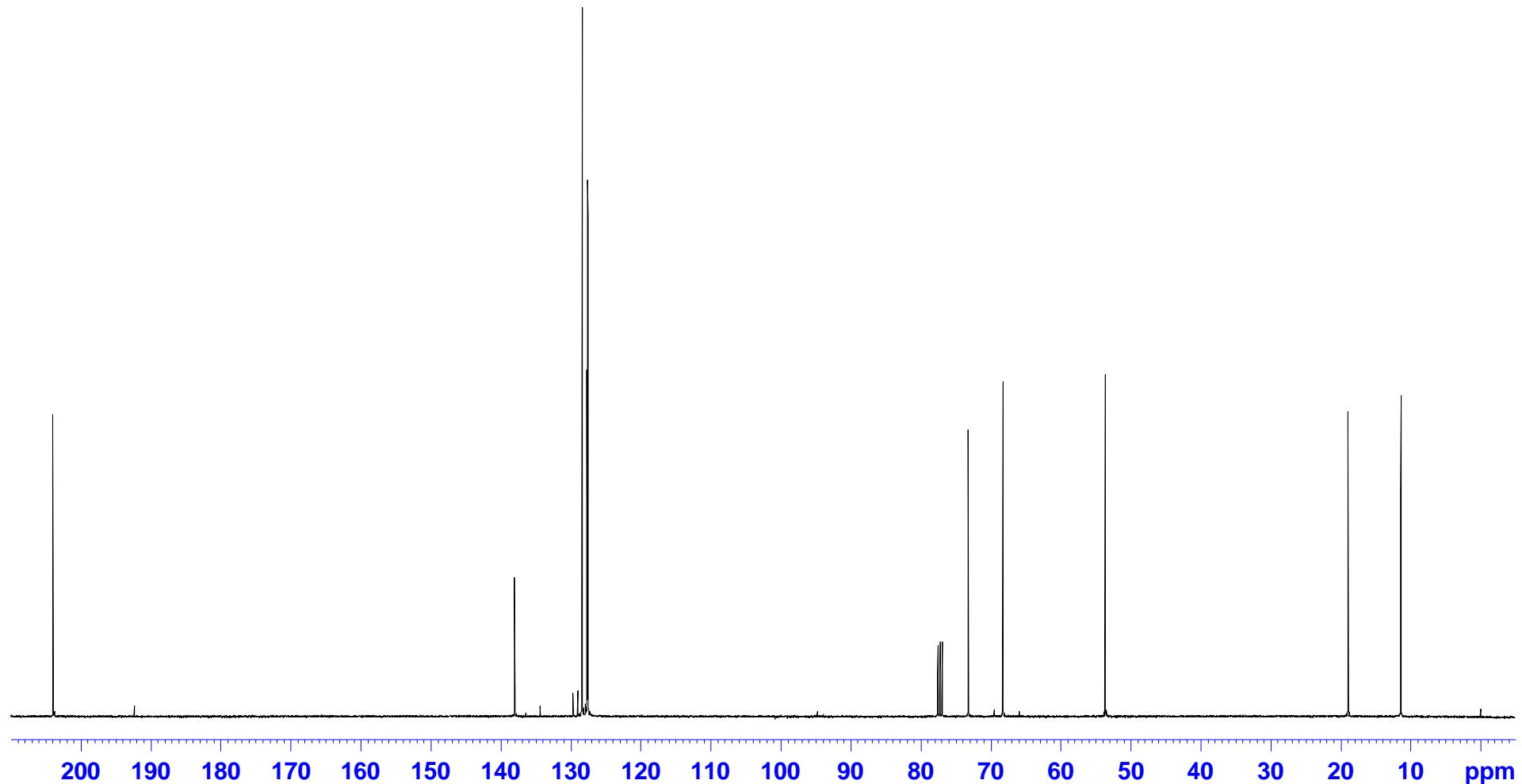
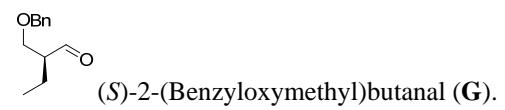
(*R*)-2-(Benzylloxymethyl)butan-1-ol (**19**).



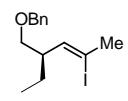


(S)-2-(Benzylloxymethyl)butanal (**G**).

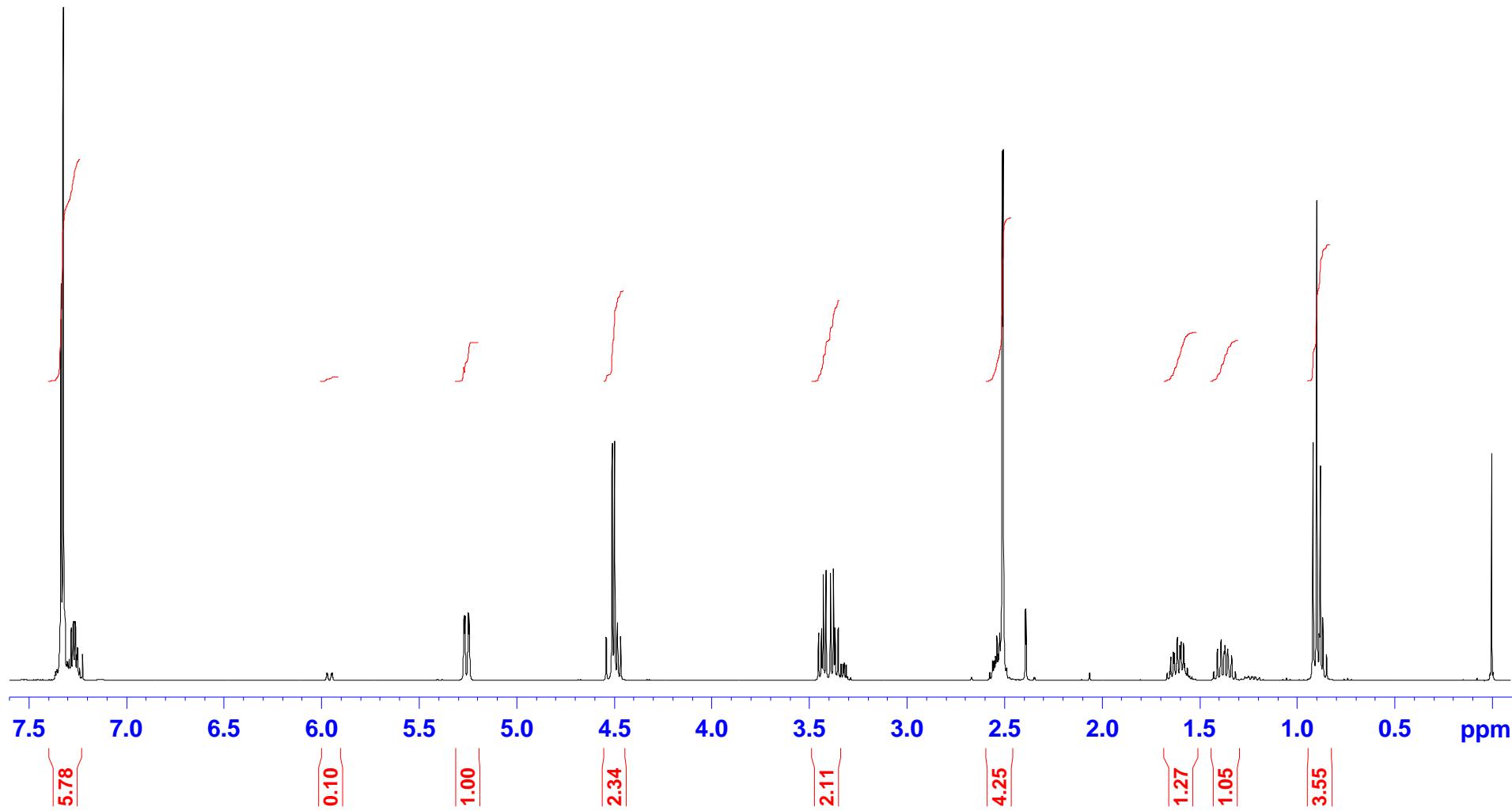


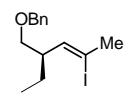


S30

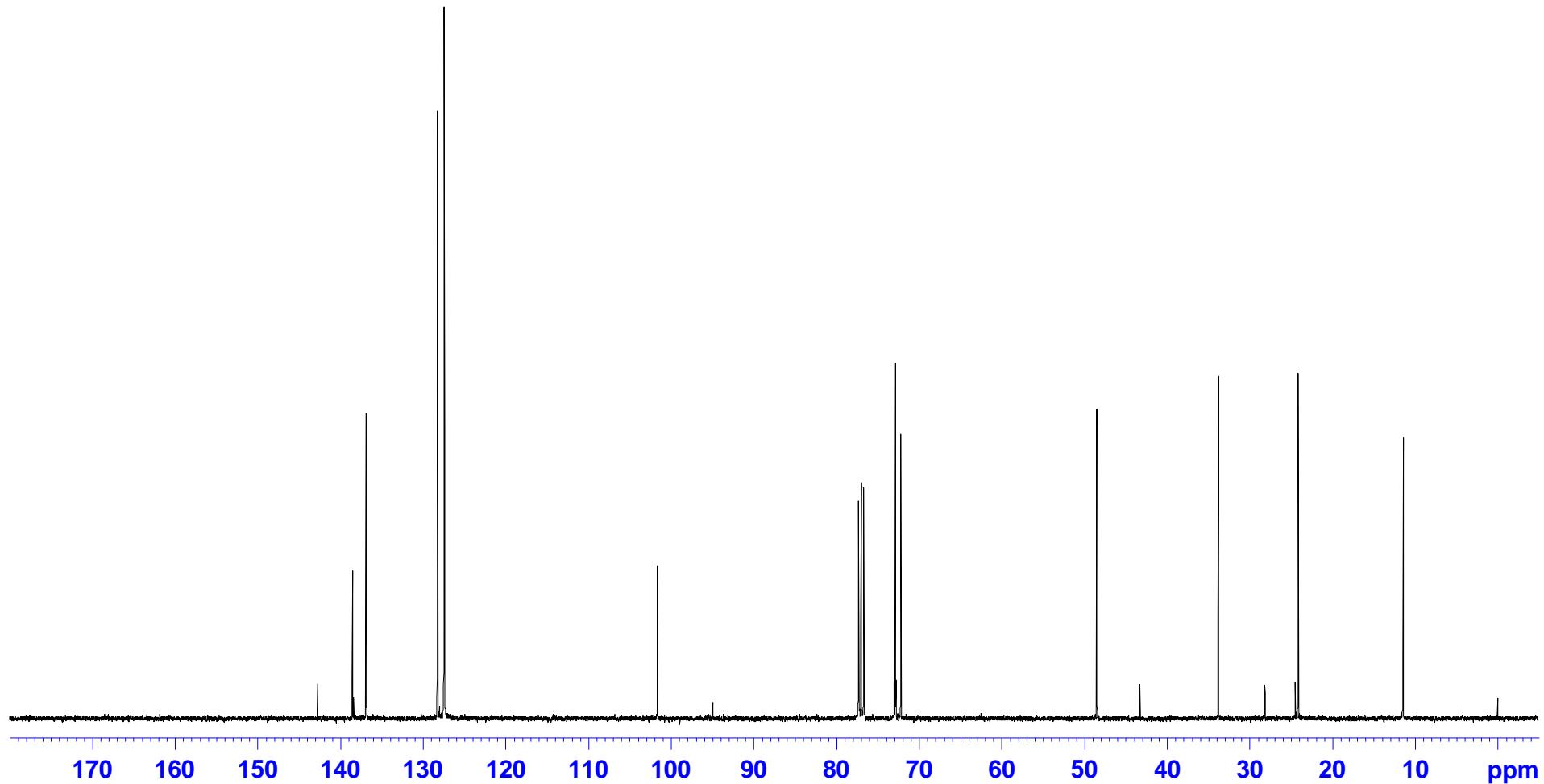


(*R,Z*)-((2-Ethyl-4-iodopent-3-enyloxy)methyl)benzene (**7**).



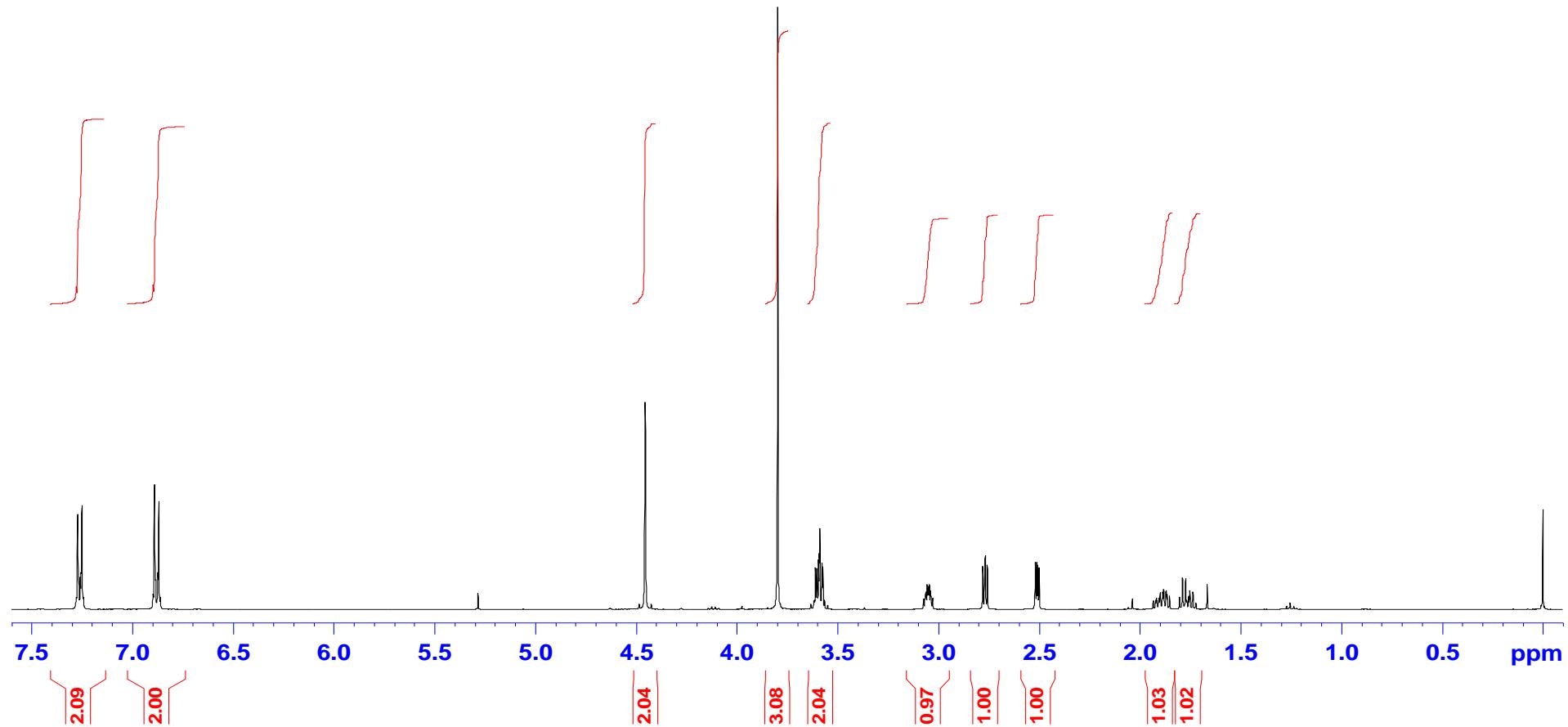


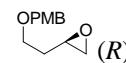
(*R,Z*)-((2-Ethyl-4-iodopent-3-enyloxy)methyl)benzene (**7**).



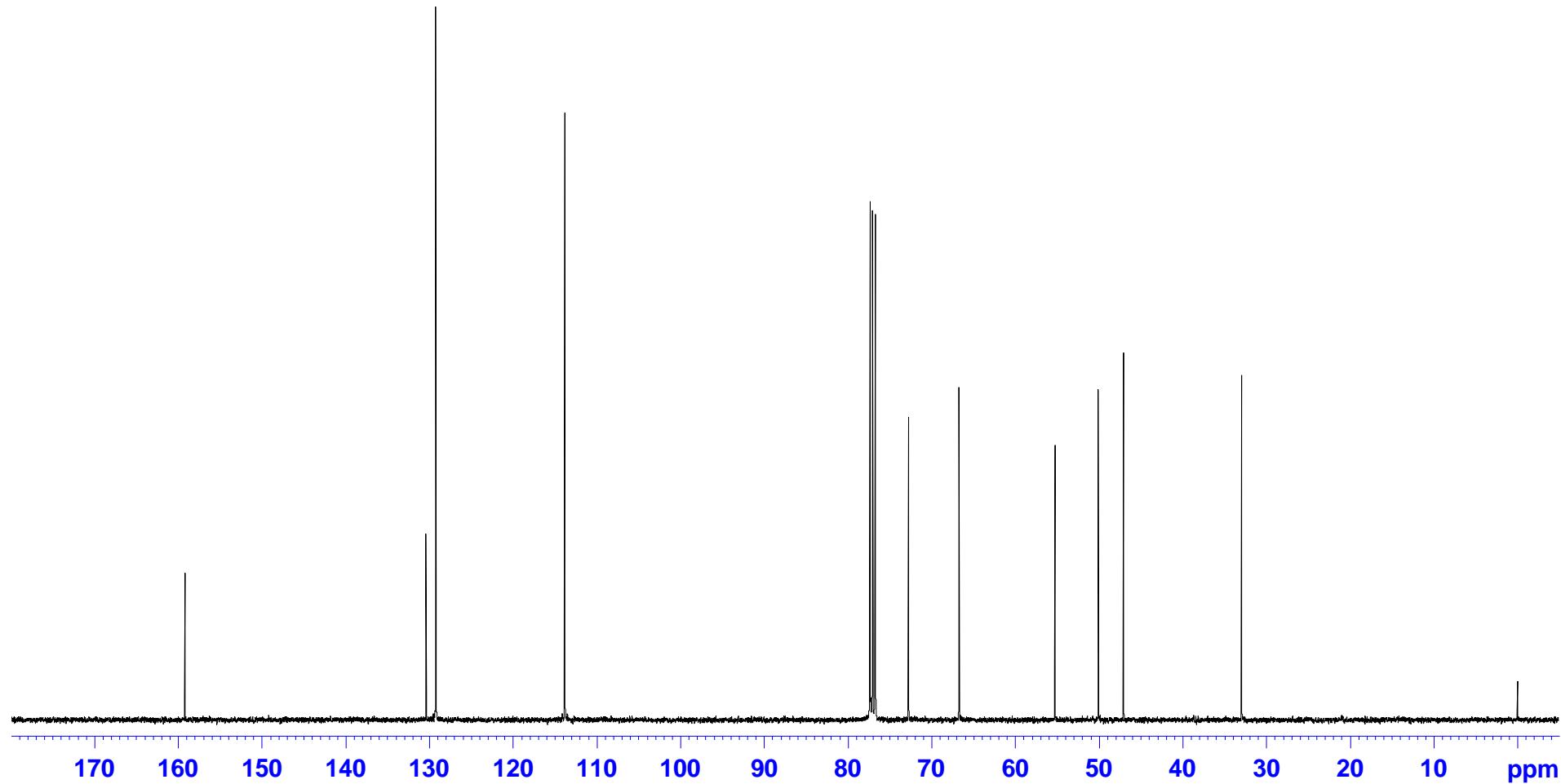
Synthesis of building block **8**

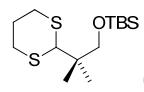
O=C[C@H]1CCOP(=O)([O-])C=C1 (*R*)-2-(4-Methoxybenzyloxy)ethyl oxirane (**10**).



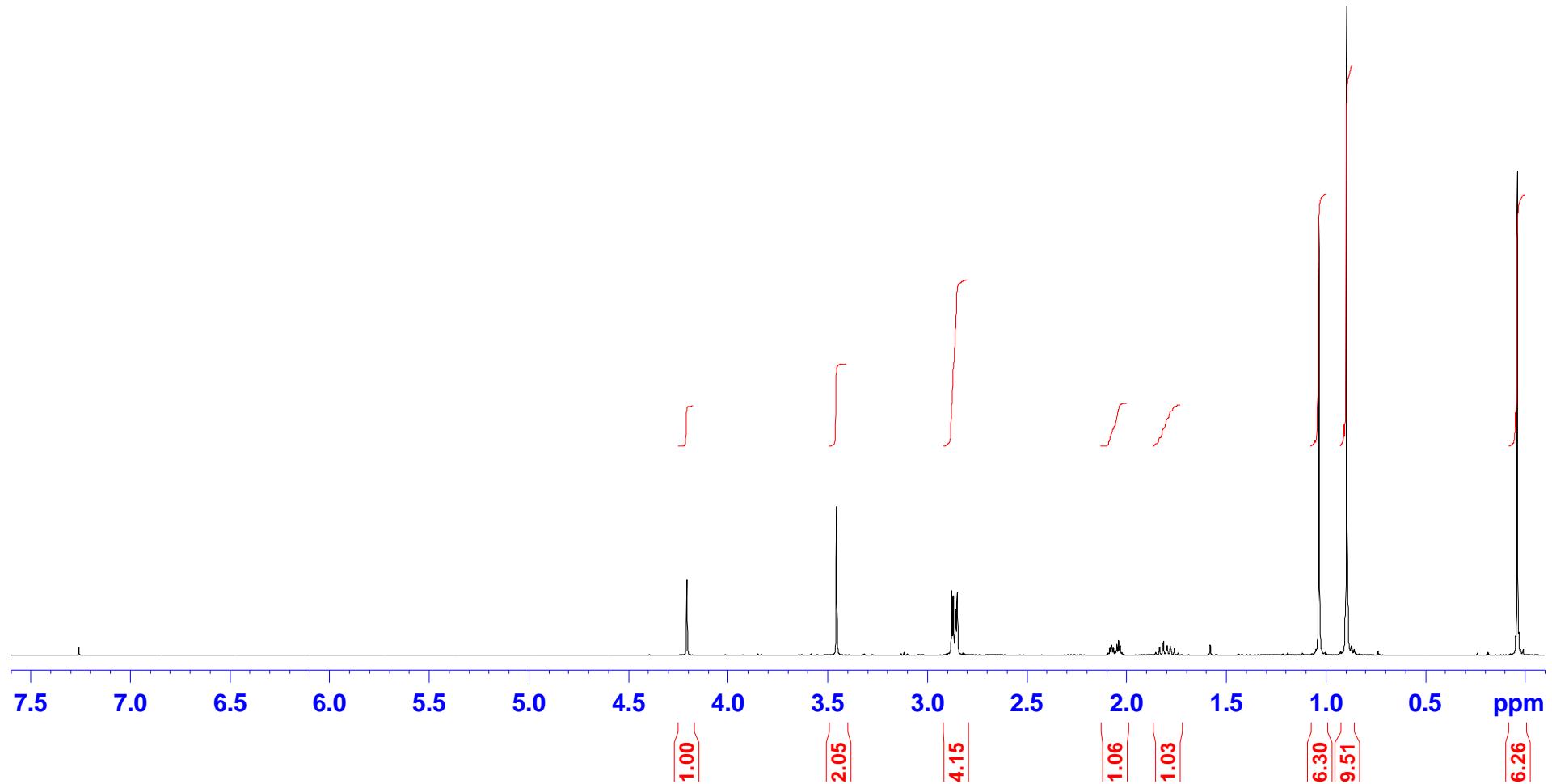


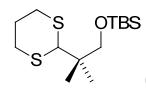
(*R*)-2-(2-(4-Methoxybenzyloxy)ethyl)oxirane (**10**).



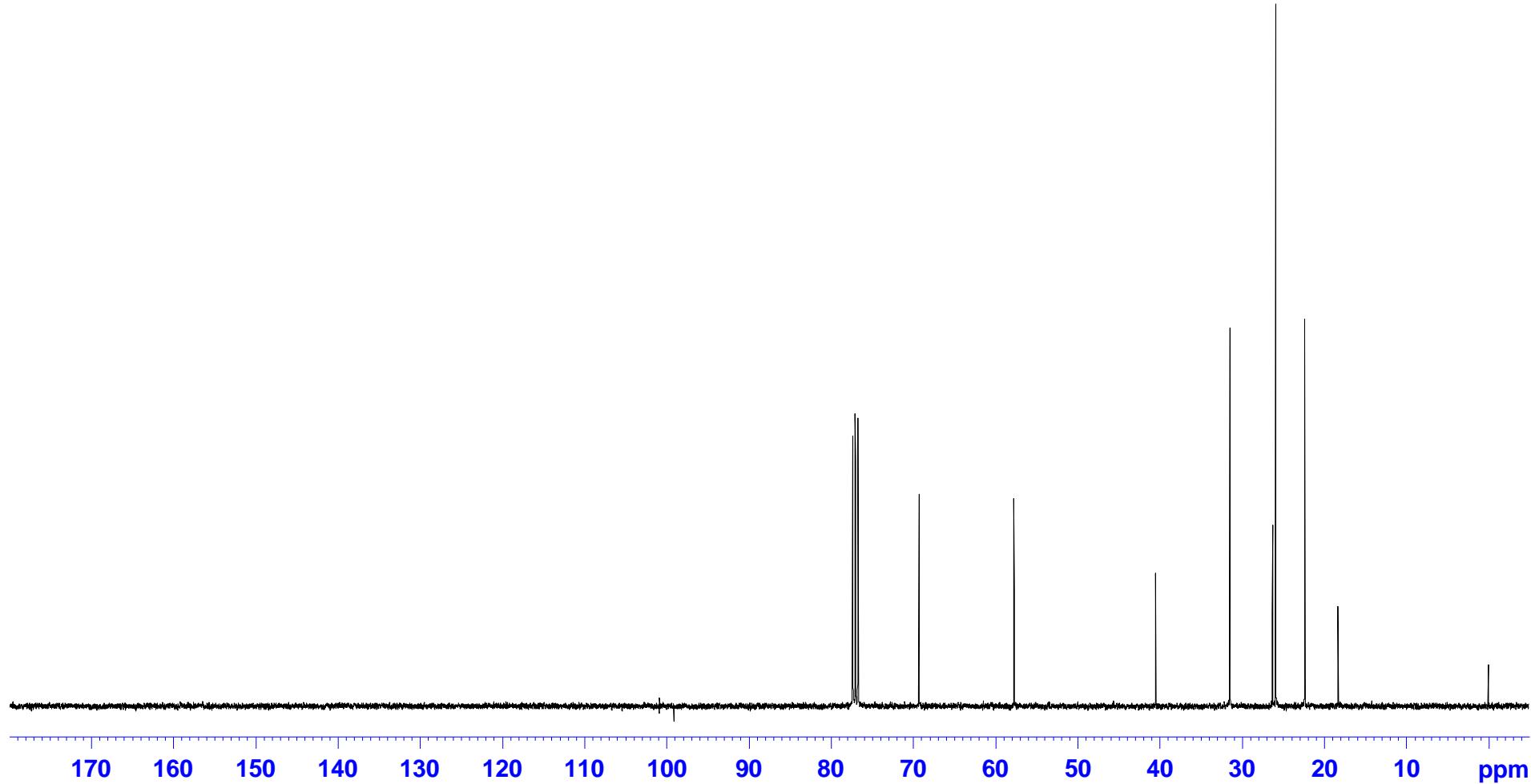


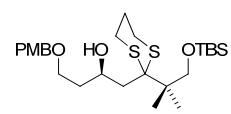
(2-(1,3-Dithian-2-yl)-2-methylpropoxy)(*tert*-butyl)dimethylsilane (**11**).



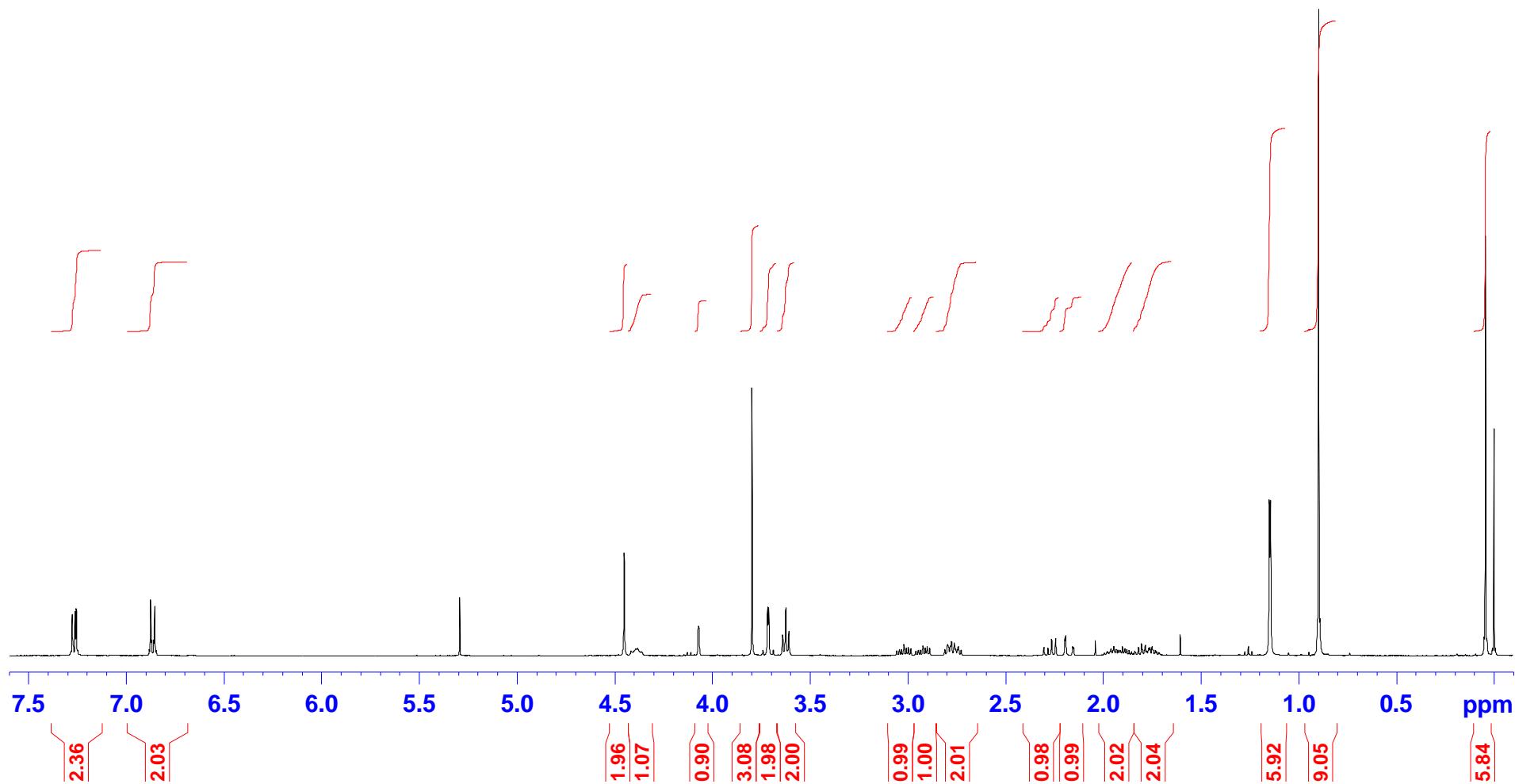


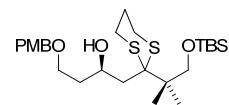
(2-(1,3-Dithian-2-yl)-2-methylpropoxy)(*tert*-butyl)dimethylsilane (**11**).



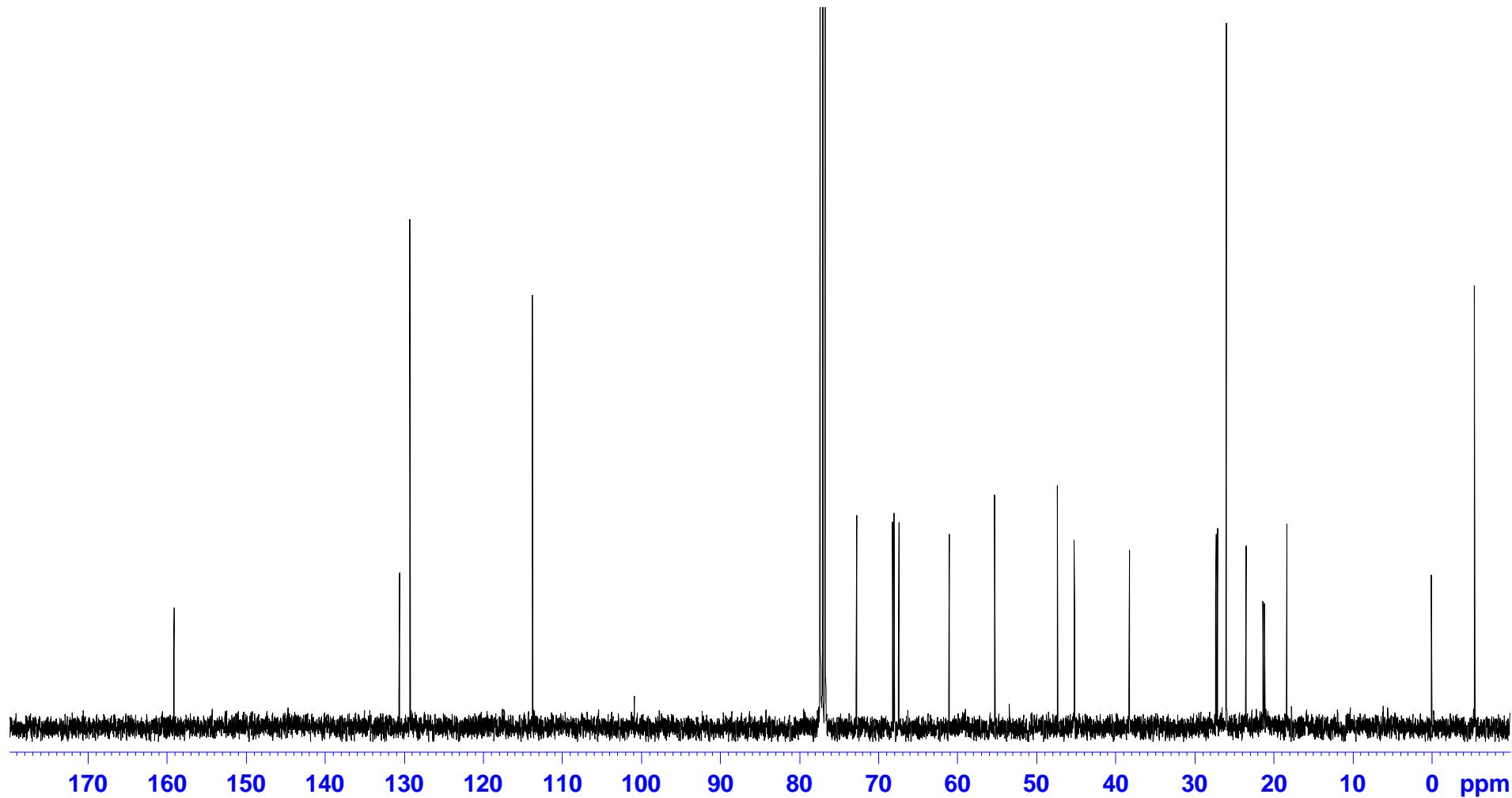


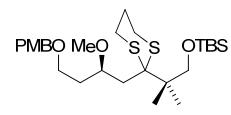
(*R*)-1-(2-(1-(*tert*-Butyldimethylsilyloxy)-2-methylpropan-2-yl)-1,3-dithian-2-yl)-4-(4-methoxybenzyloxy)butan-2-ol (**M**).



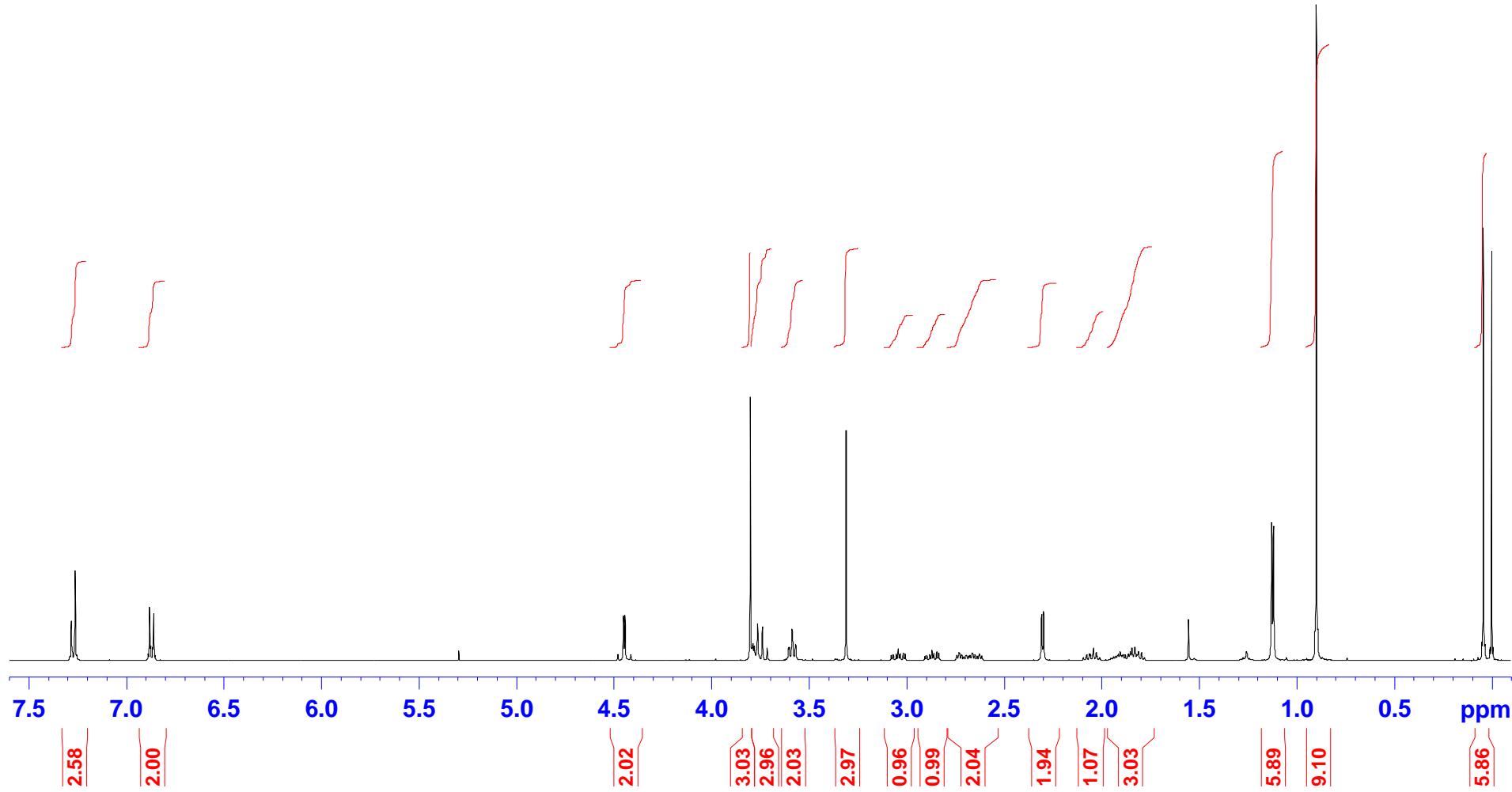


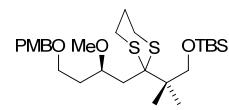
(*R*)-1-(2-(1-(*tert*-Butyldimethylsilyloxy)-2-methylpropan-2-yl)-1,3-dithian-2-yl)-4-(4-methoxybenzyloxy)butan-2-ol (**M**).



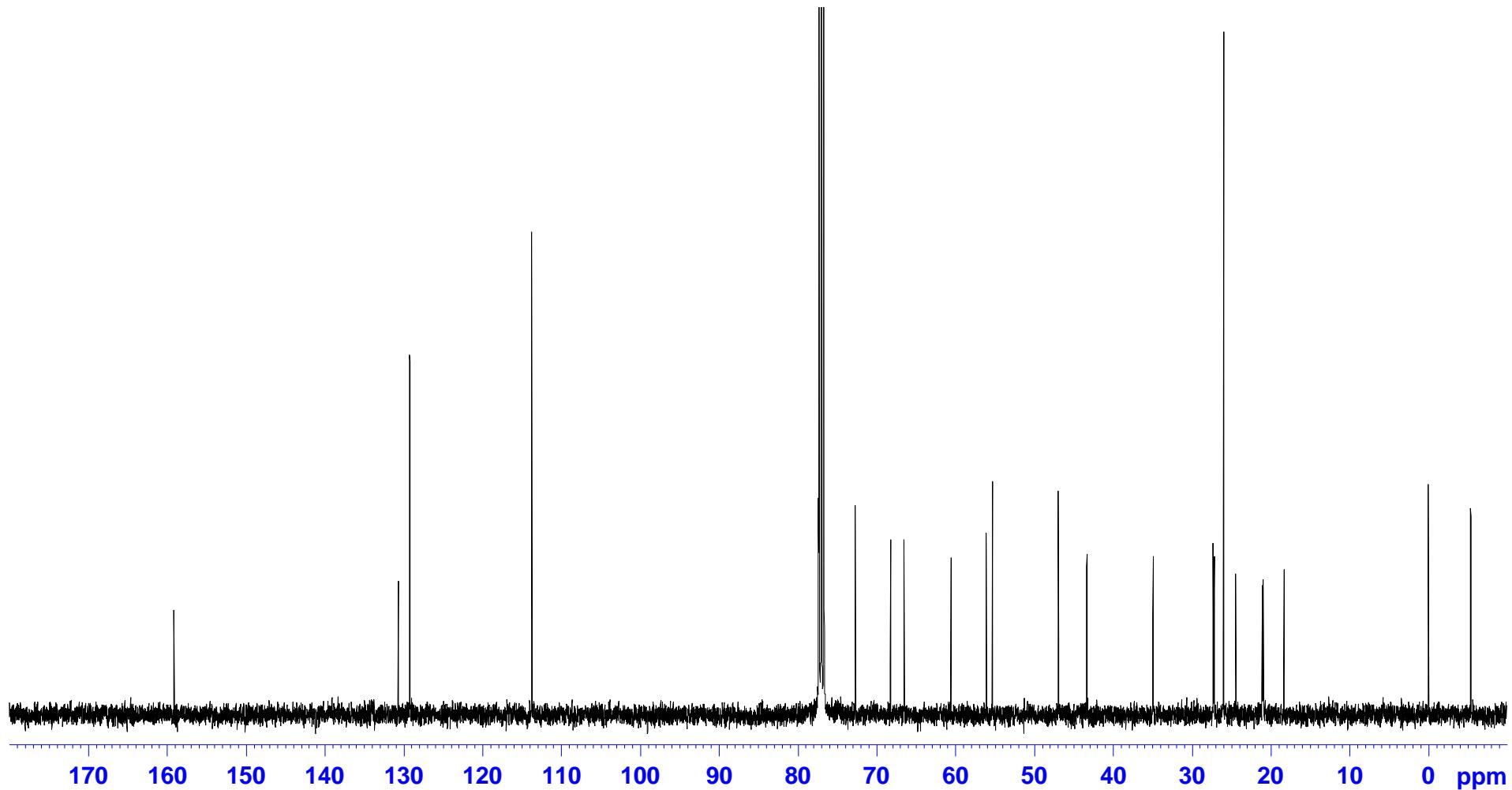


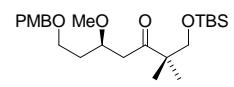
(*R*)-*tert*-Butyl(2-(2-methoxy-4-(4-methoxybenzyloxy)butyl)-1,3-dithian-2-yl)-2-methylpropoxydimethylsilane (**20**).



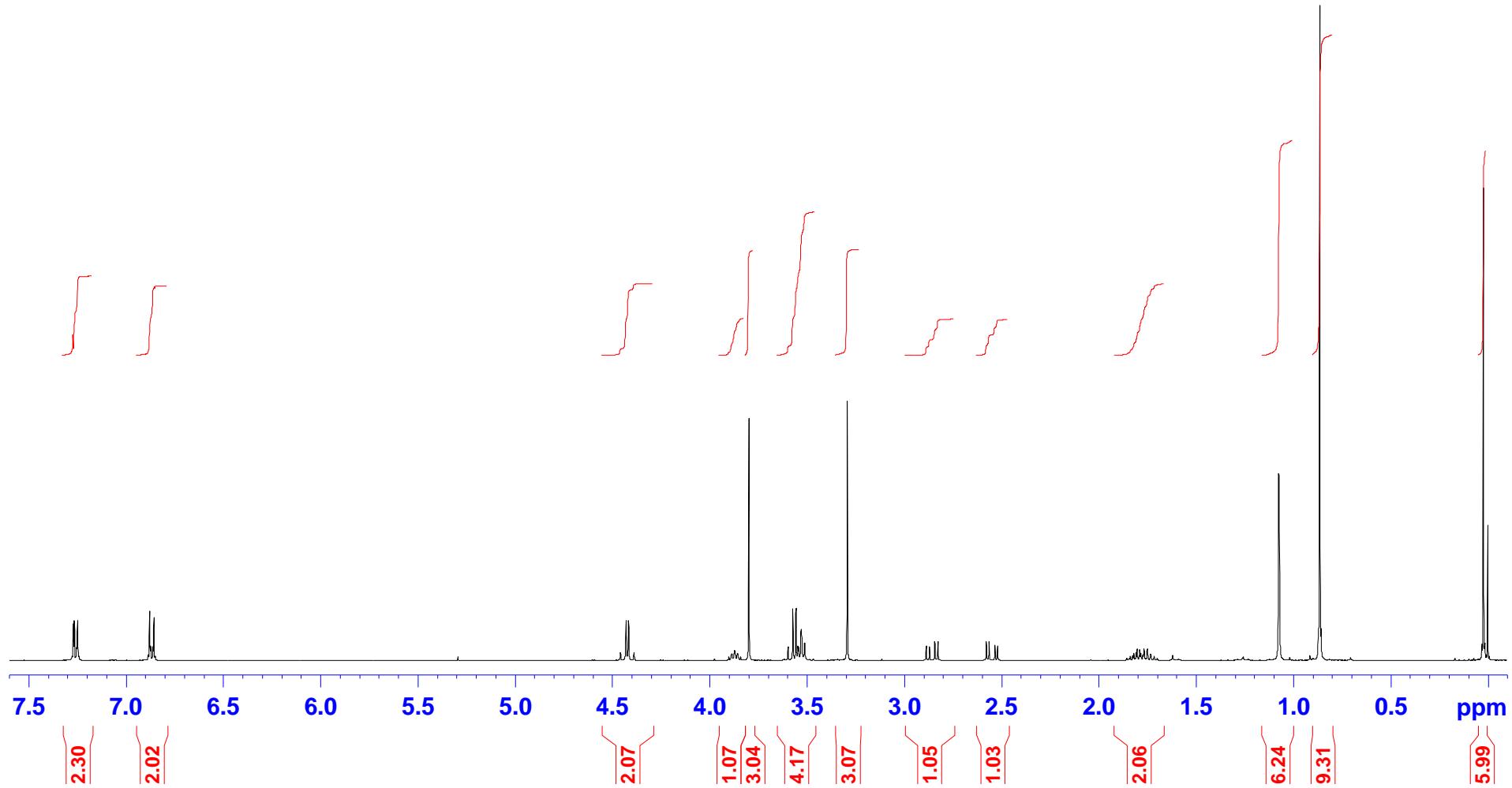


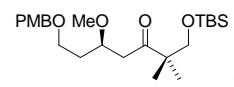
(*R*)-*tert*-Butyl(2-(2-methoxy-4-(4-methoxybenzyloxy)butyl)-1,3-dithian-2-yl)-2-methylpropoxy)dimethylsilane (**20**).



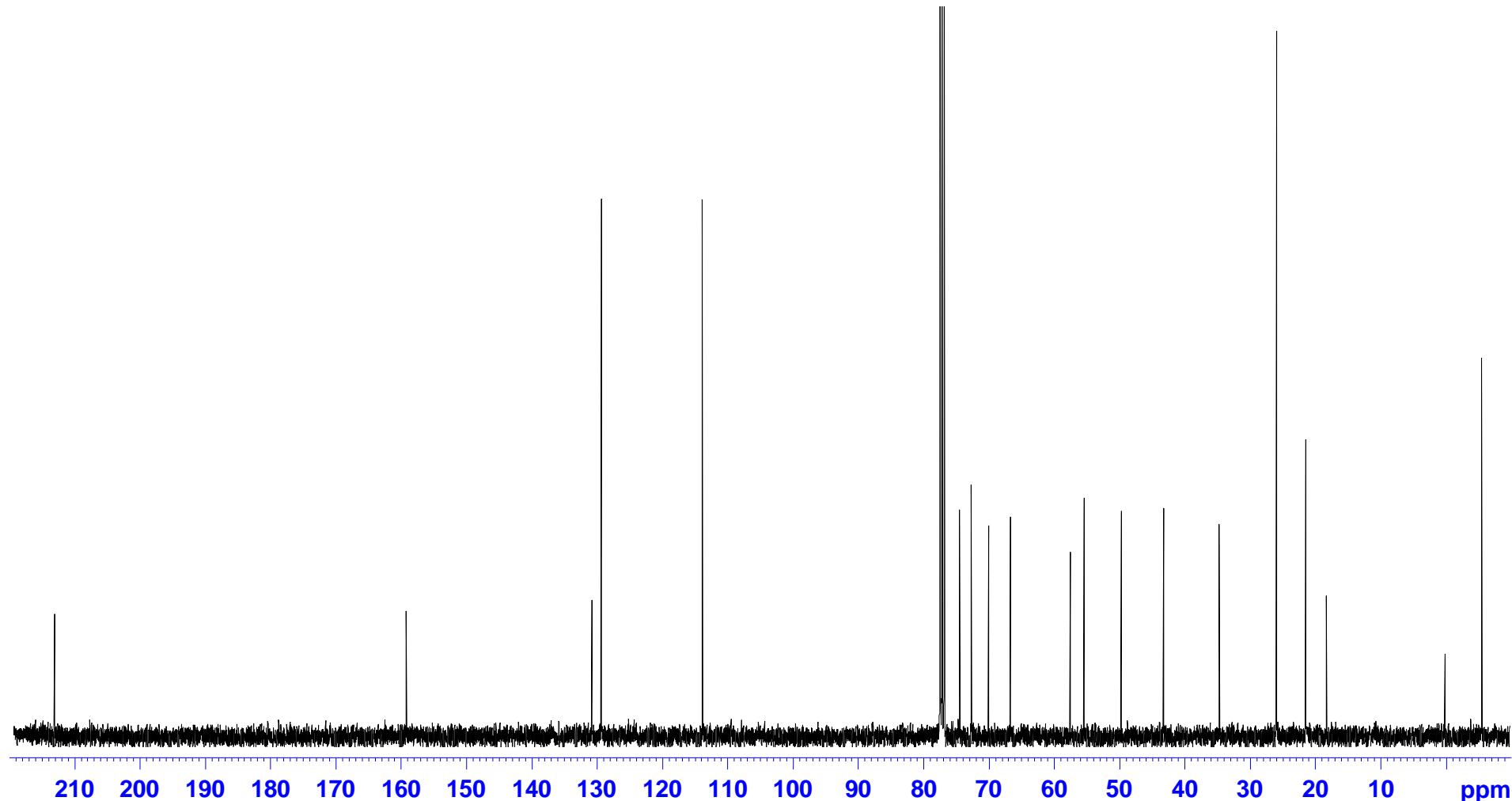


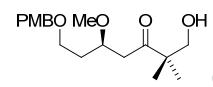
(*R*)-1-(*tert*-Butyldimethylsilyloxy)-5-methoxy-7-(4-methoxybenzyloxy)-2,2-dimethylheptan-3-one (**N**).



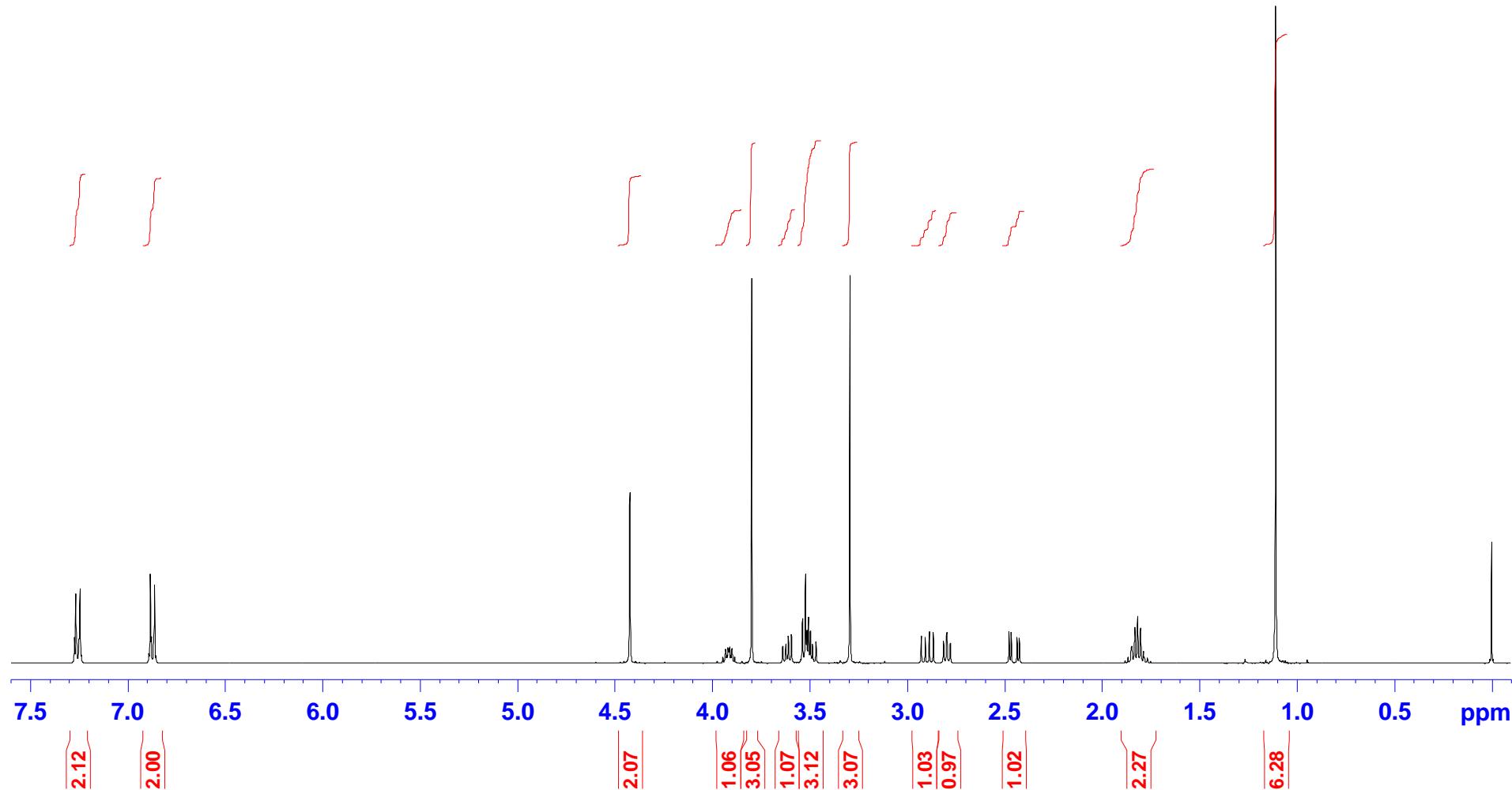


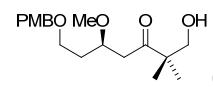
(*R*)-1-(*tert*-Butyldimethylsilyloxy)-5-methoxy-7-(4-methoxybenzyloxy)-2,2-dimethylheptan-3-one (**N**).



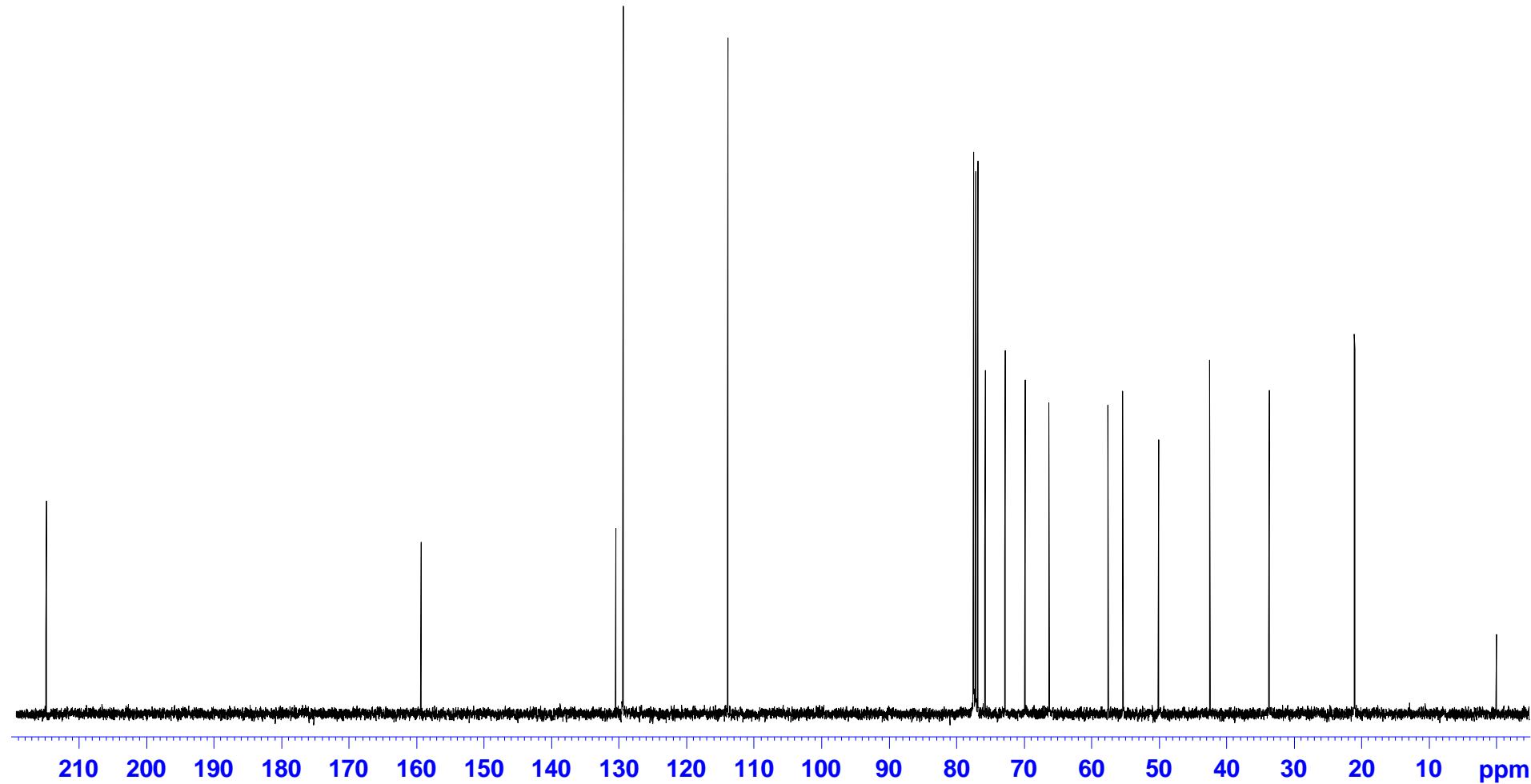


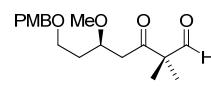
(*R*)-1-Hydroxy-5-methoxy-7-(4-methoxybenzyloxy)-2,2-dimethylheptan-3-one (**O**).



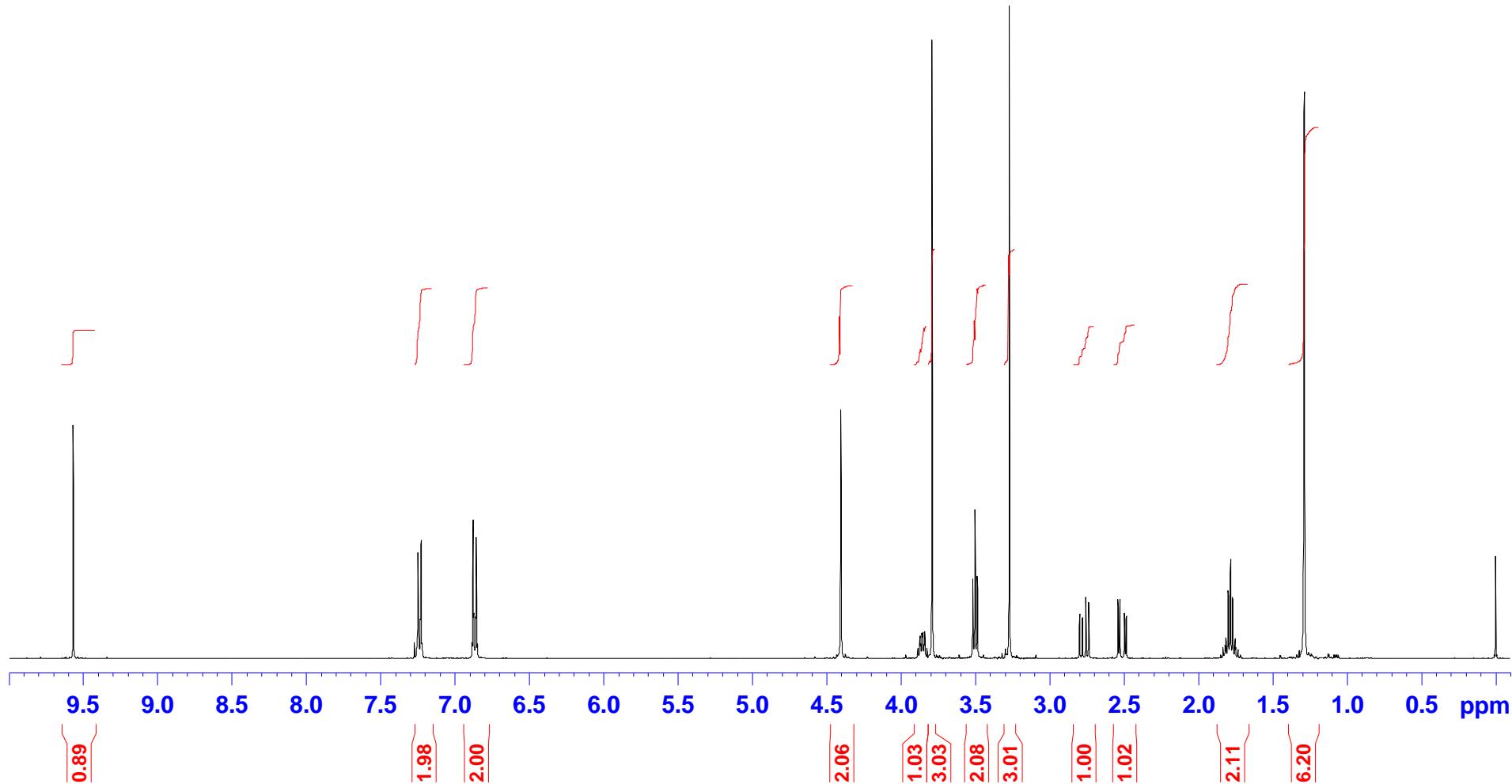


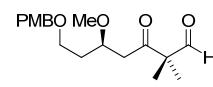
(*R*)-1-Hydroxy-5-methoxy-7-(4-methoxybenzyloxy)-2,2-dimethylheptan-3-one (**O**).



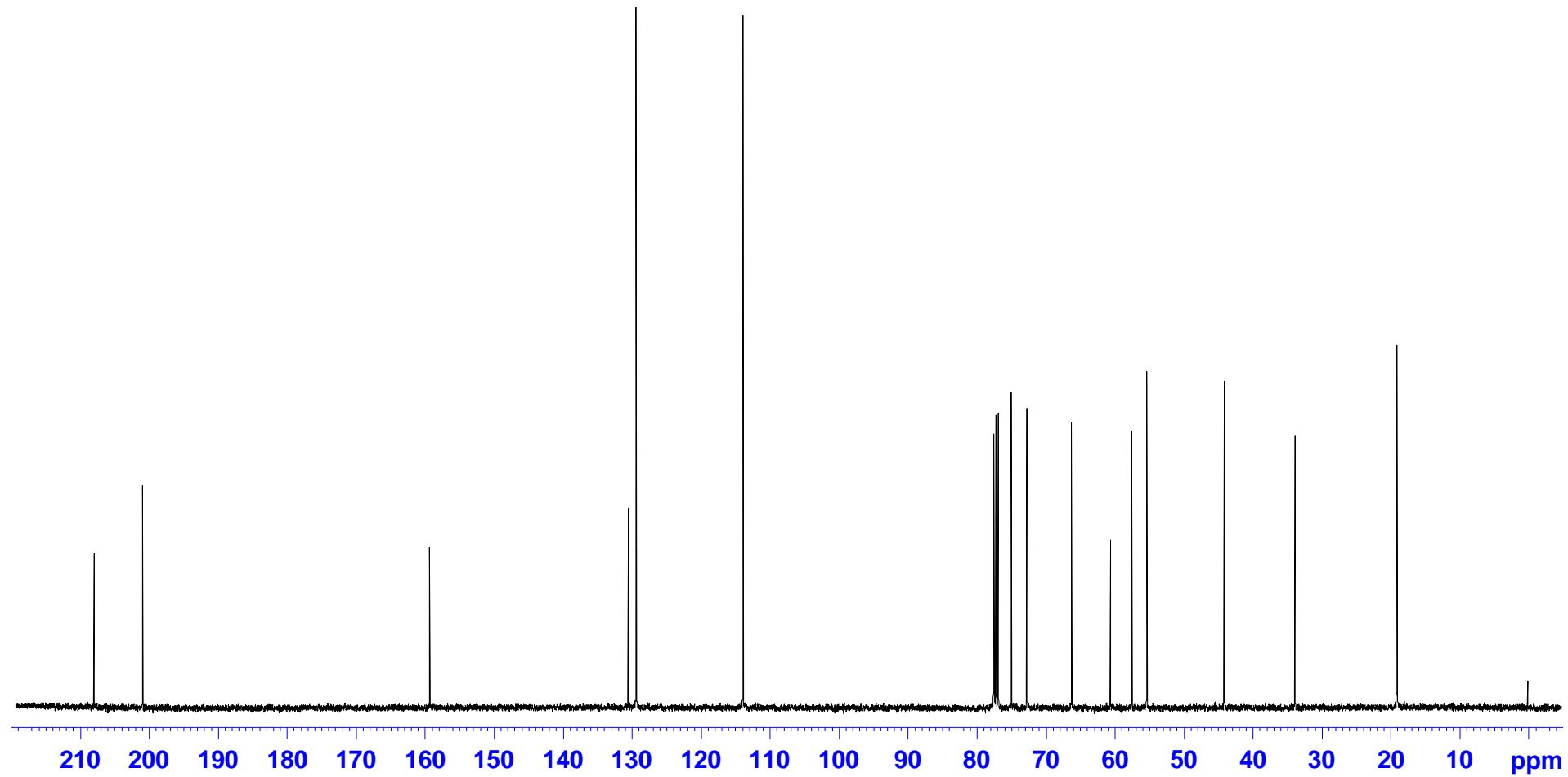


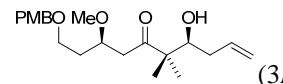
(*R*)-5-Methoxy-7-(4-methoxybenzyloxy)-2,2-dimethyl-3-oxoheptanal (**9**).



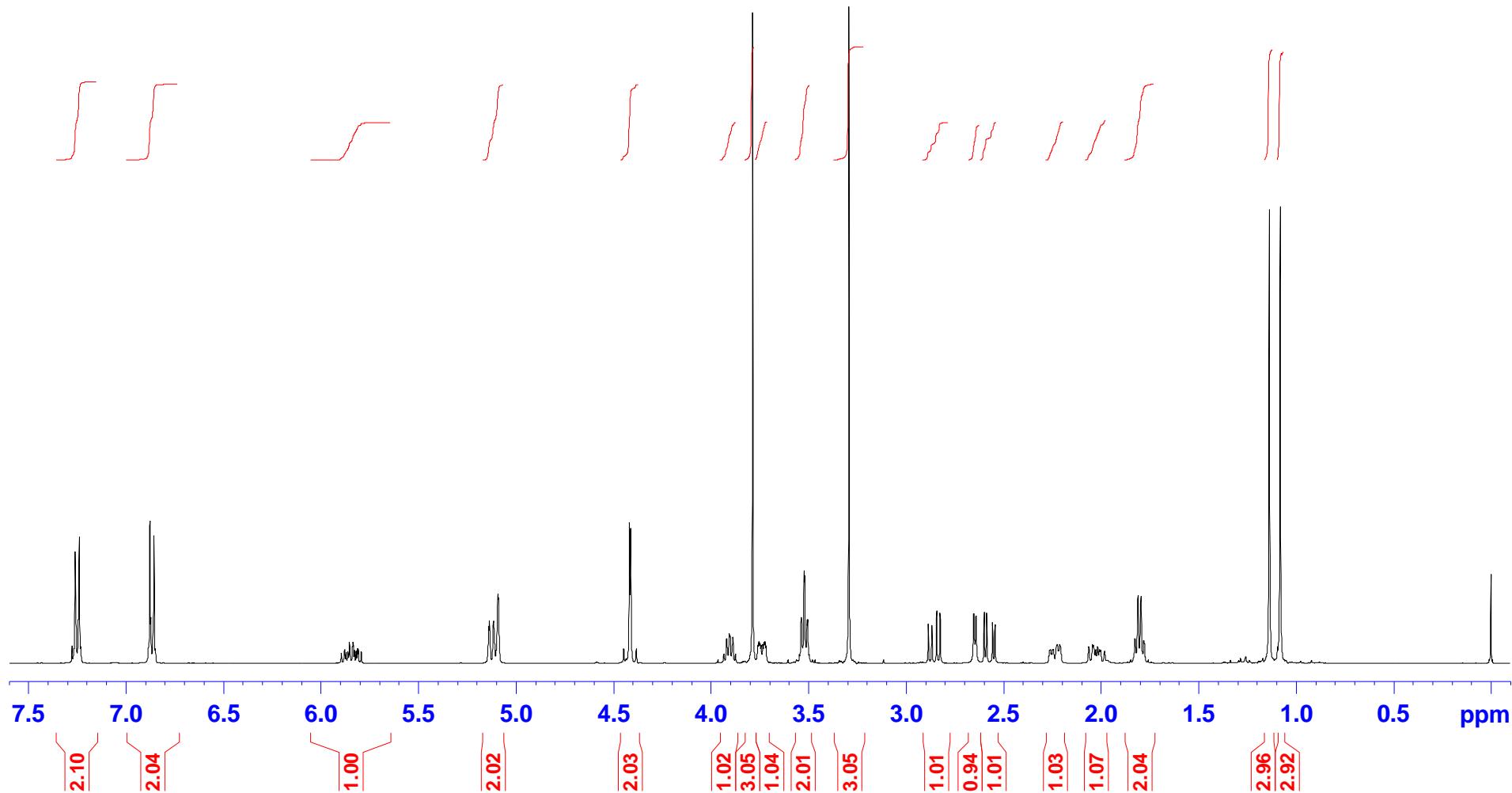


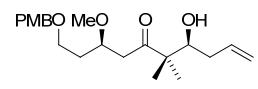
(*R*)-5-Methoxy-7-(4-methoxybenzyloxy)-2,2-dimethyl-3-oxoheptanal (**9**).



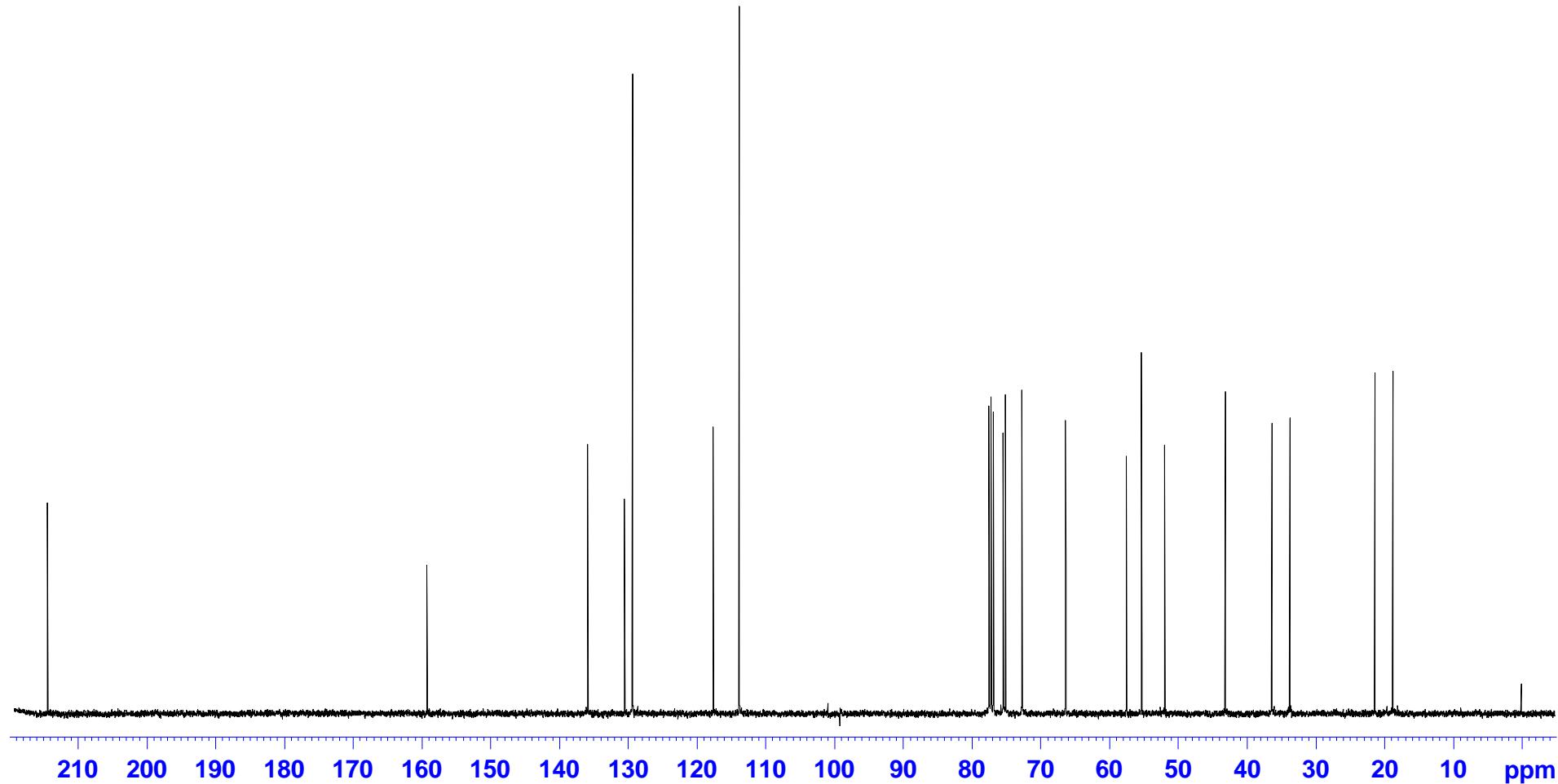


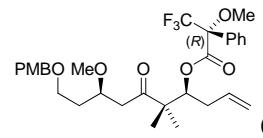
(*3R,7S*)-7-Hydroxy-3-methoxy-1-(4-methoxybenzyloxy)-6,6-dimethyldec-9-en-5-one (**21**).



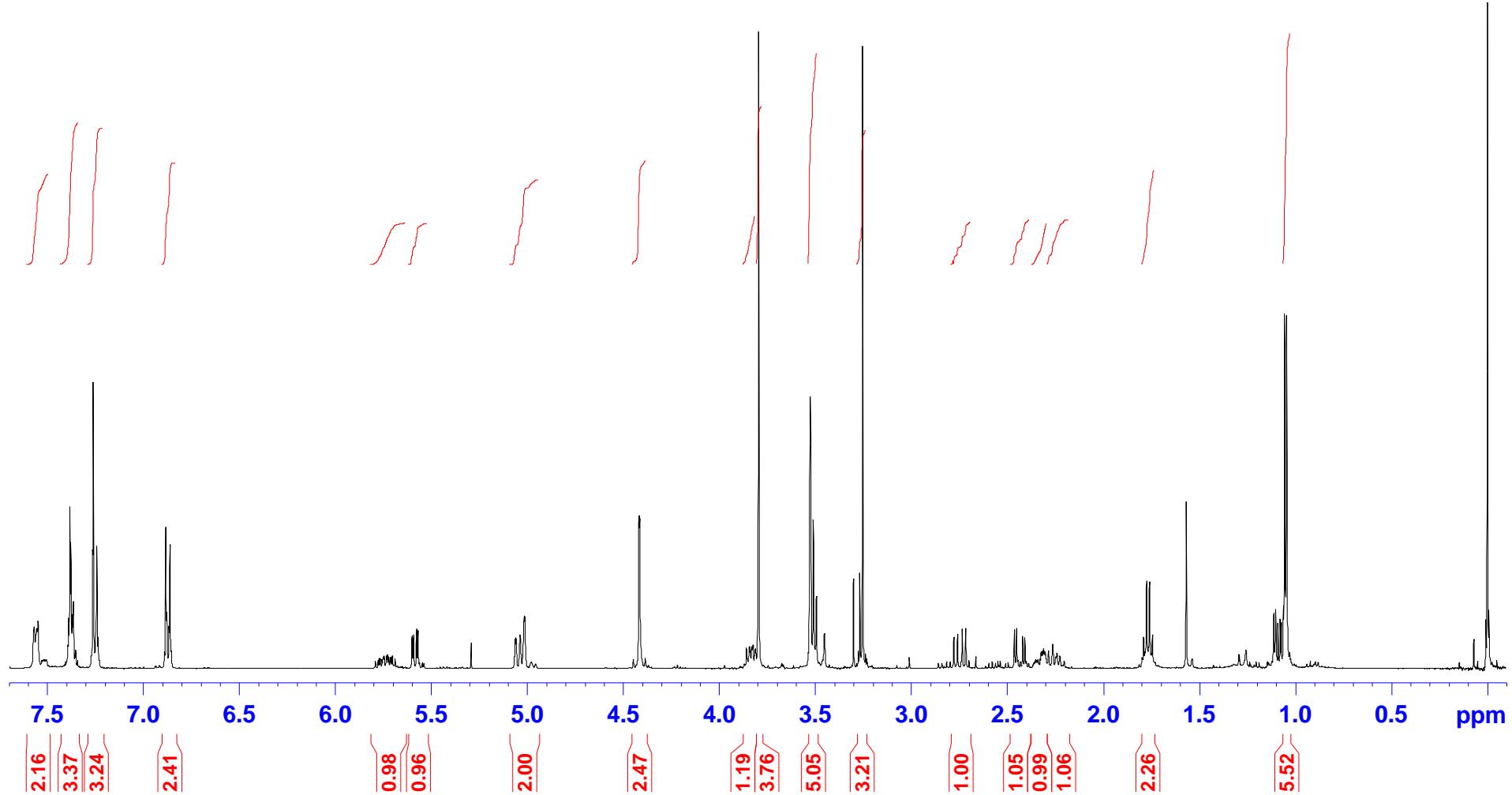


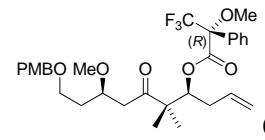
(*3R,7S*)-7-Hydroxy-3-methoxy-1-(4-methoxybenzyloxy)-6,6-dimethyldec-9-en-5-one (**21**).



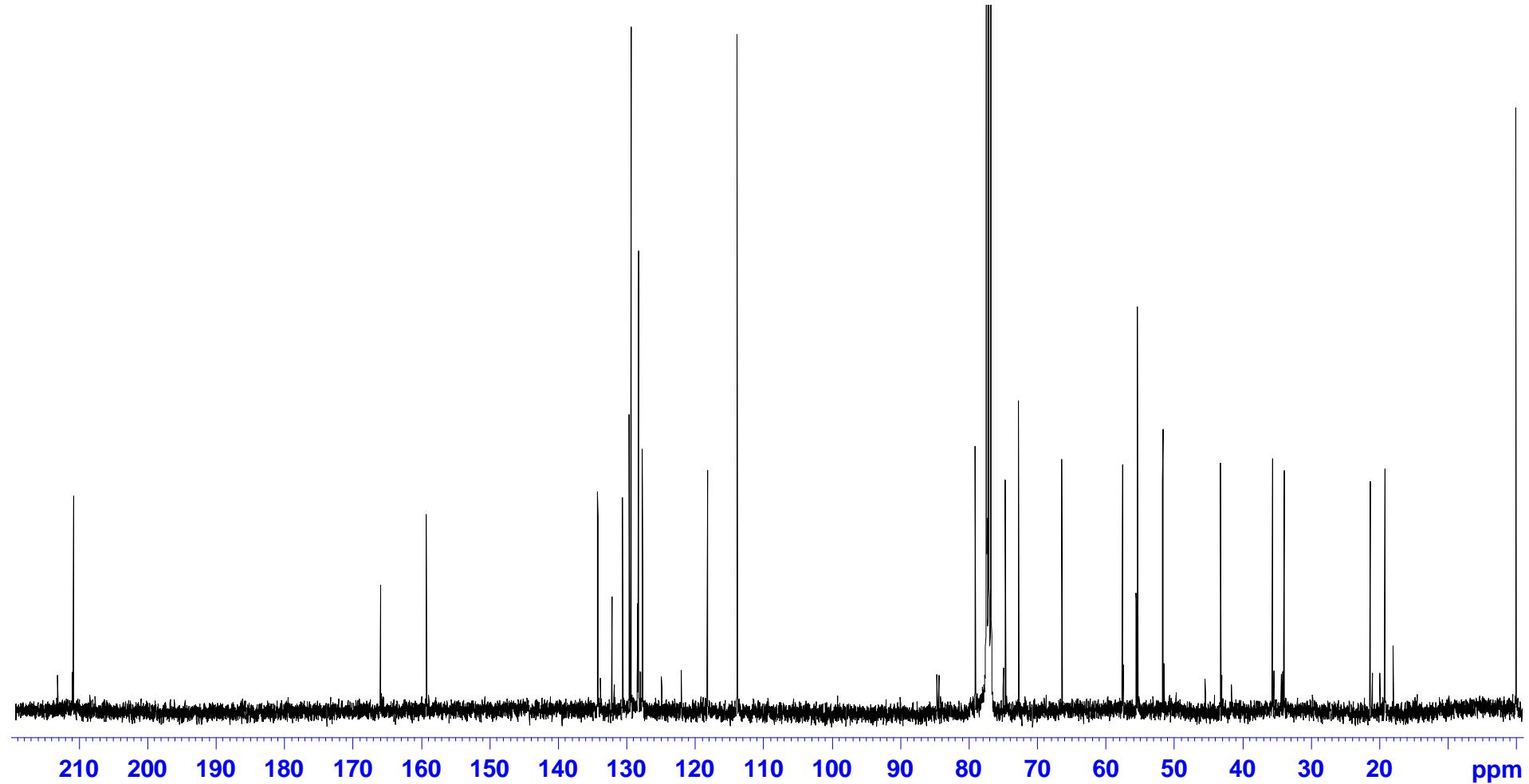


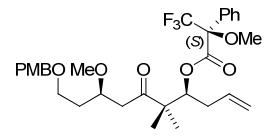
(*R*)-((4*S*,8*R*)-8-Methoxy-10-(4-methoxybenzyloxy)-5,5-dimethyl-6-oxodec-1-en-4-yl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**Q**).



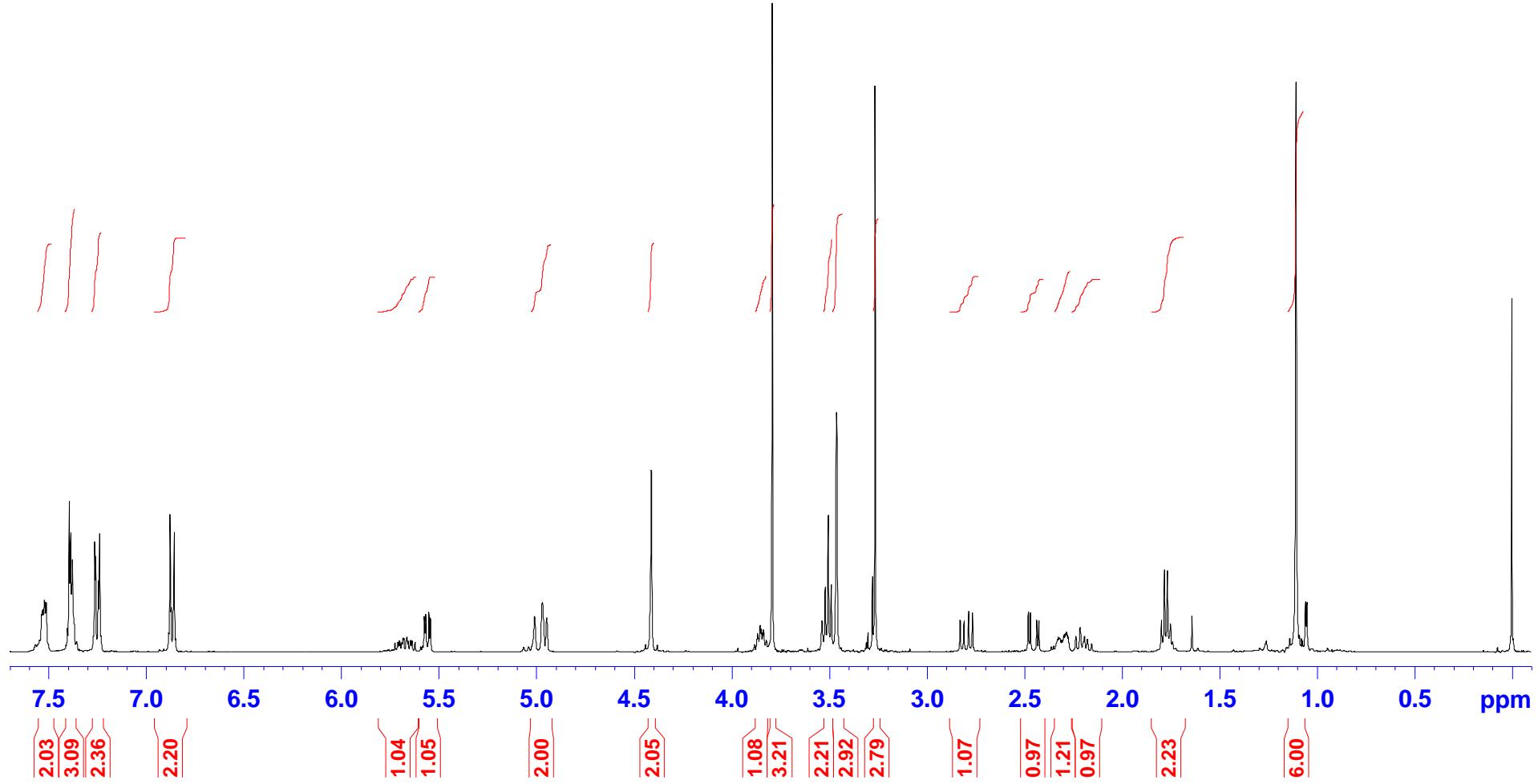


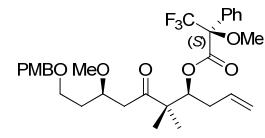
(*R*)-((4*S*,8*R*)-8-Methoxy-10-(4-methoxybenzyloxy)-5,5-dimethyl-6-oxodec-1-en-4-yl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**Q**).



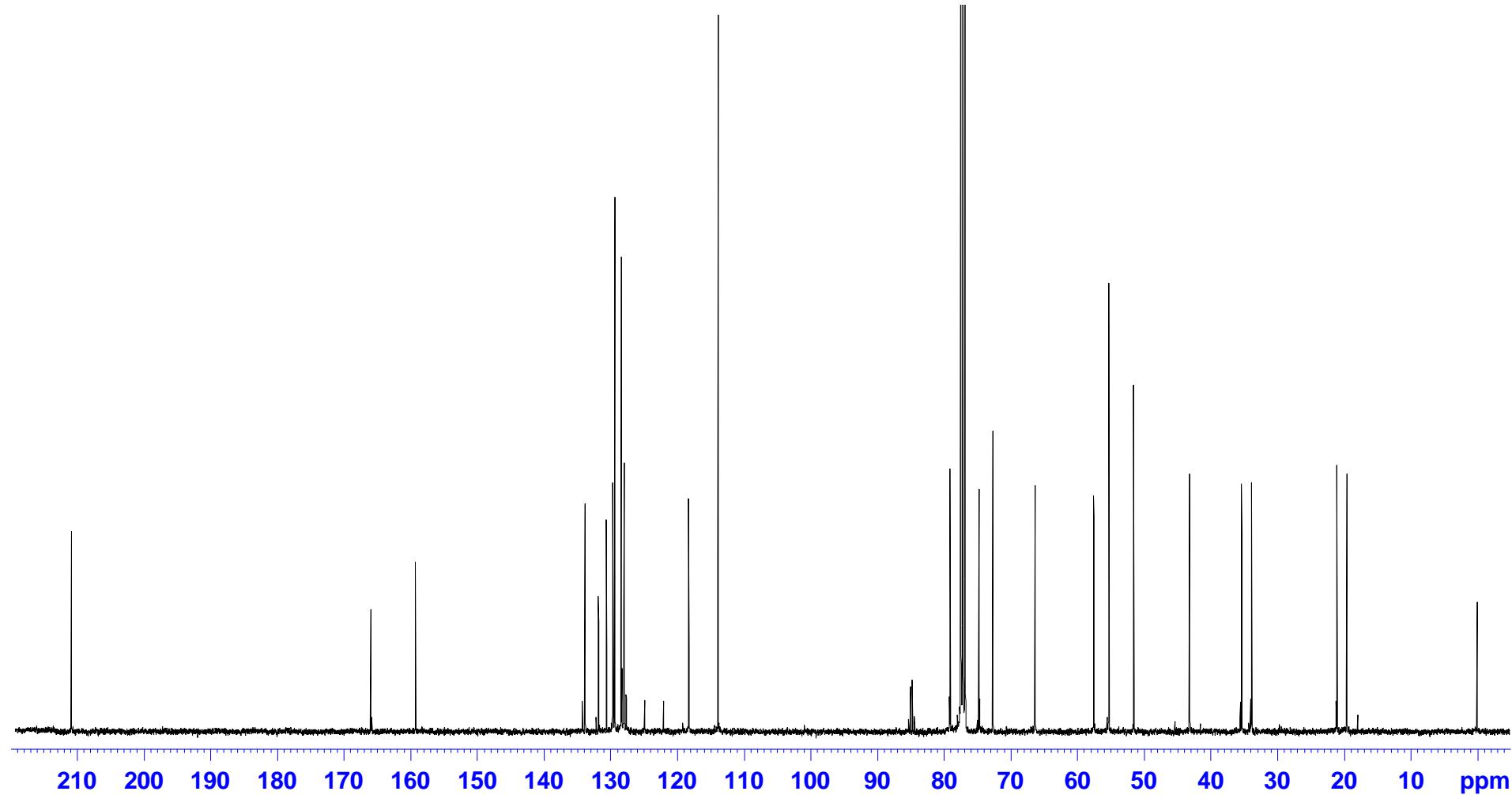


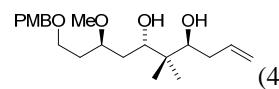
(*S*)-((4*S*,8*R*)-8-Methoxy-10-(4-methoxybenzyl)oxo-5,5-dimethyl-6-oxodec-1-en-4-yl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**R**).



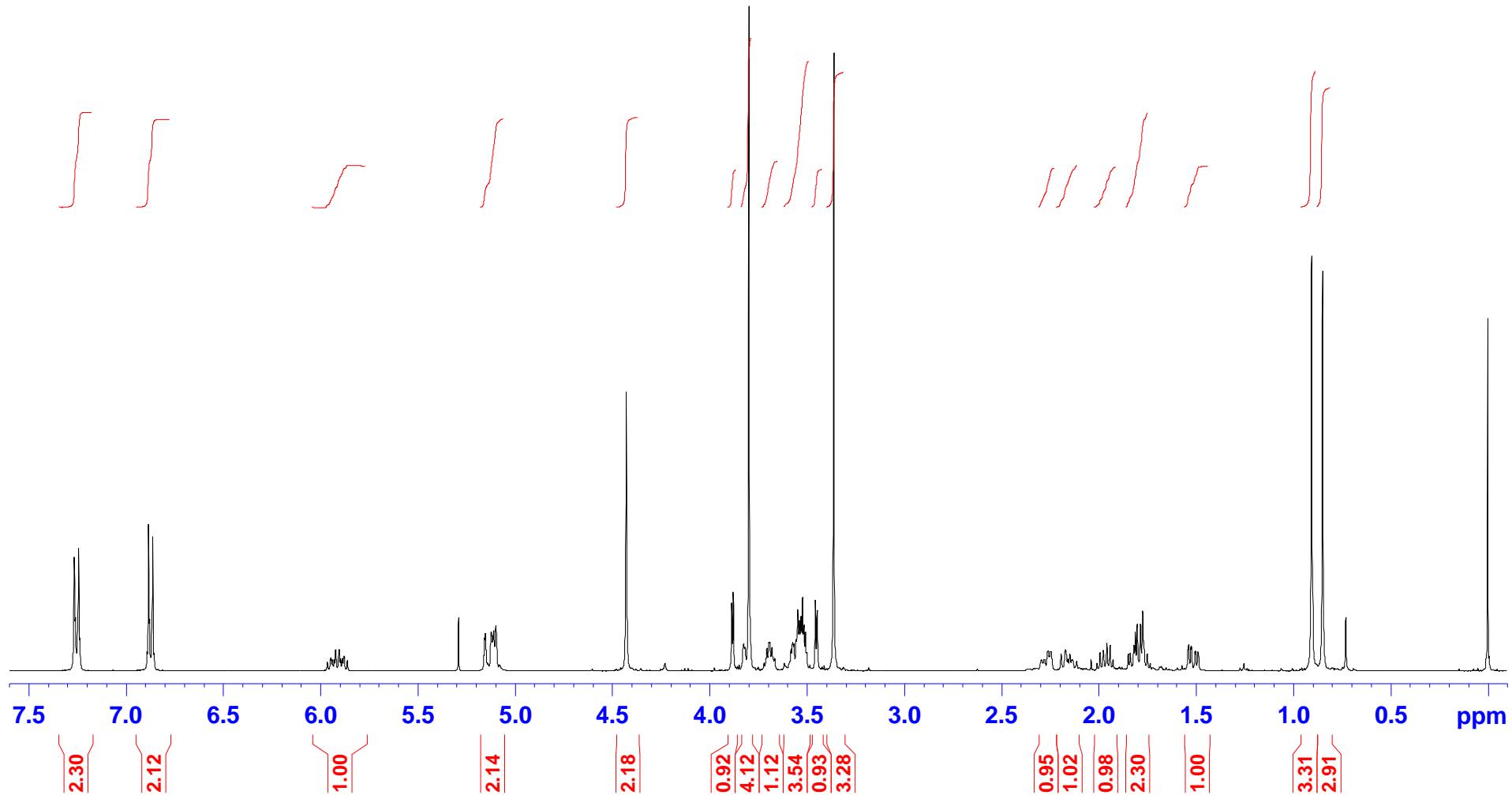


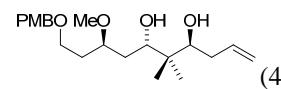
(*S*)-((4*S*,8*R*)-8-Methoxy-10-(4-methoxybenzyl)oxo-5,5-dimethyl-6-oxodec-1-en-4-yl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**R**).



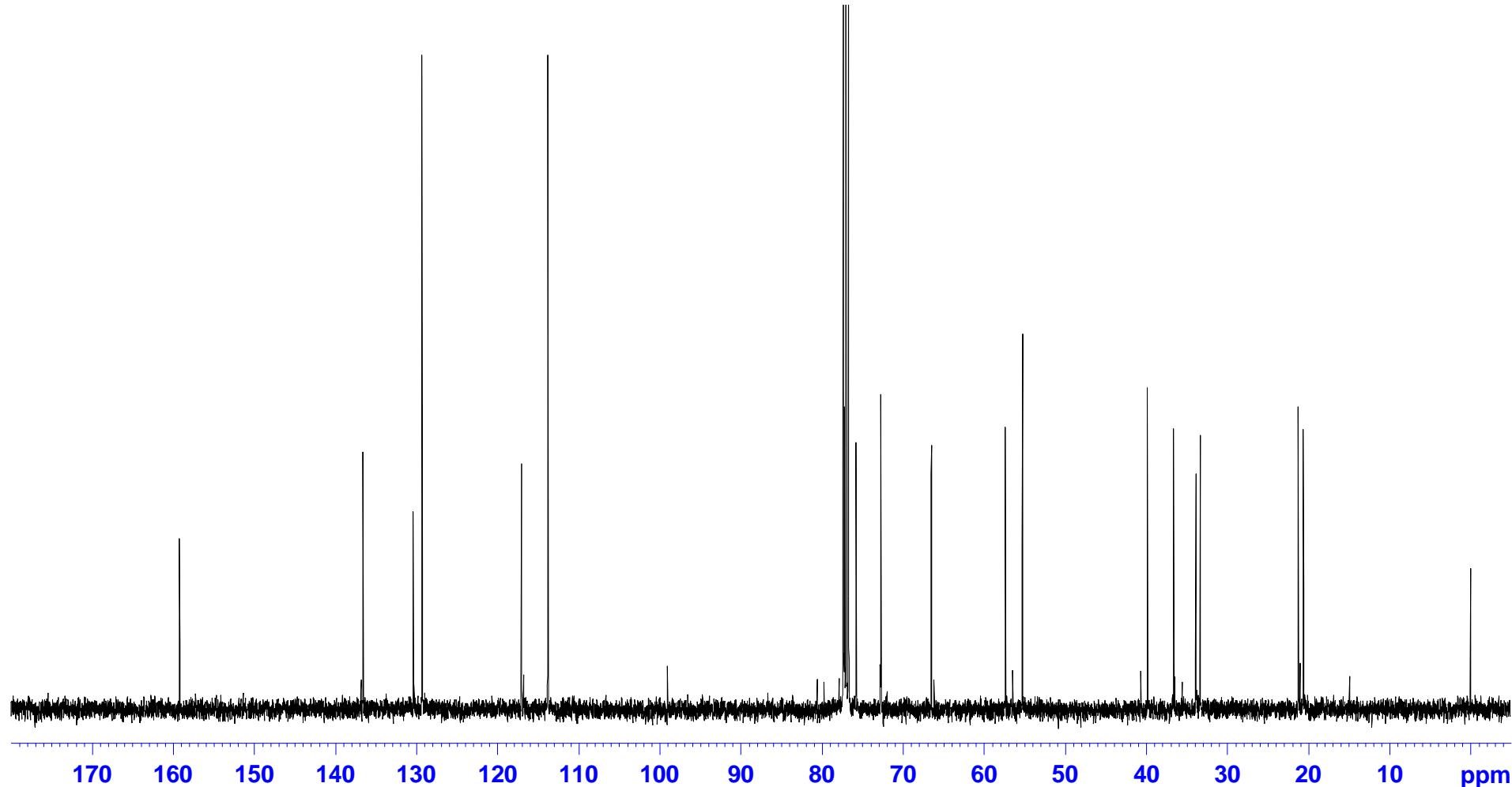


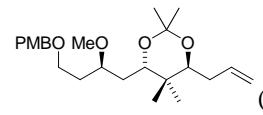
(4*S*,6*S*,8*R*)-8-Methoxy-10-(4-methoxybenzyloxy)-5,5-dimethyldec-1-ene-4,6-diol (**S**).



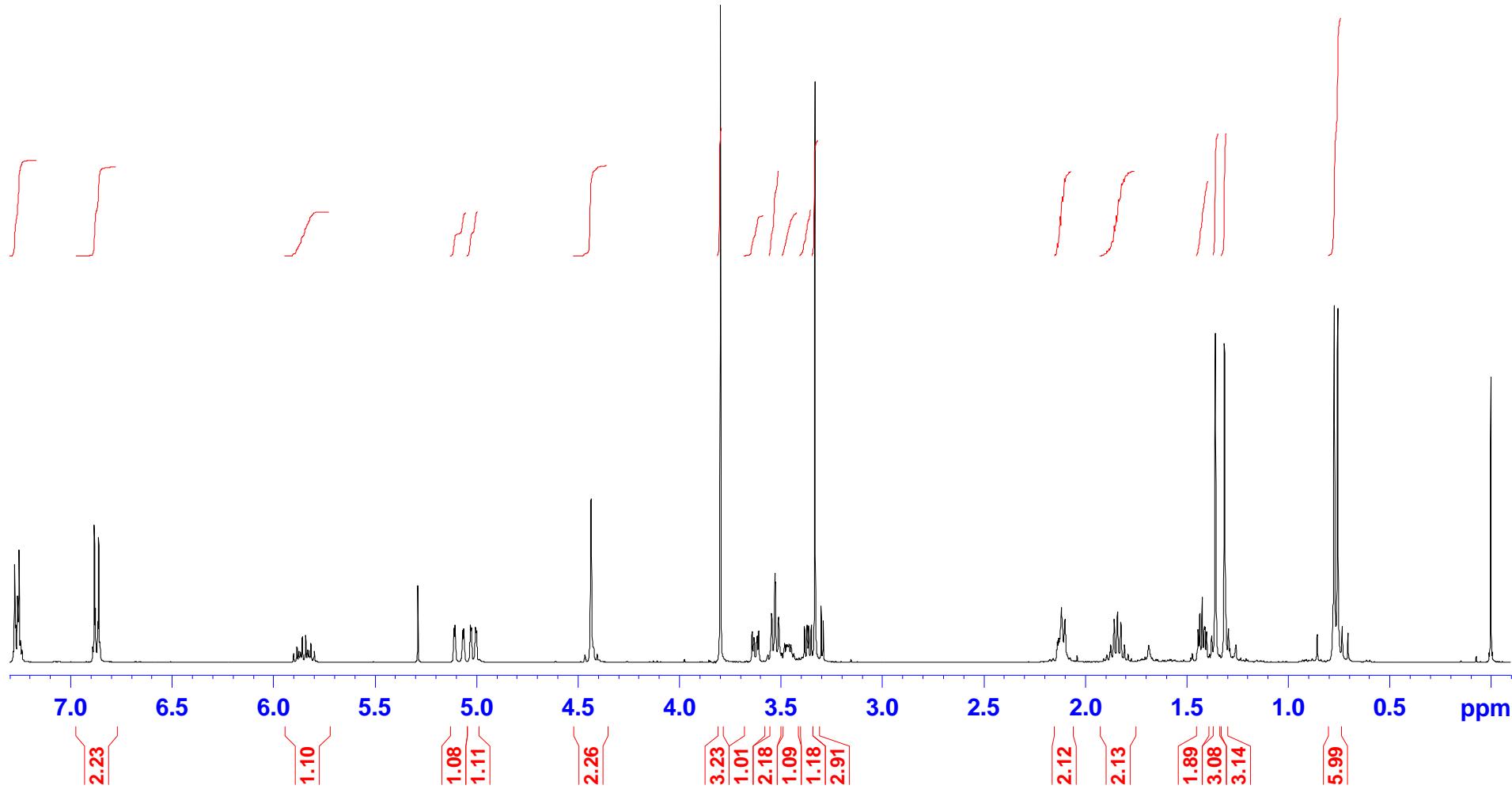


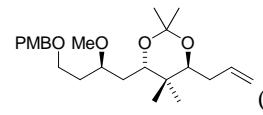
(4*S*,6*S*,8*R*)-8-Methoxy-10-(4-methoxybenzyloxy)-5,5-dimethyldec-1-ene-4,6-diol (**S**).



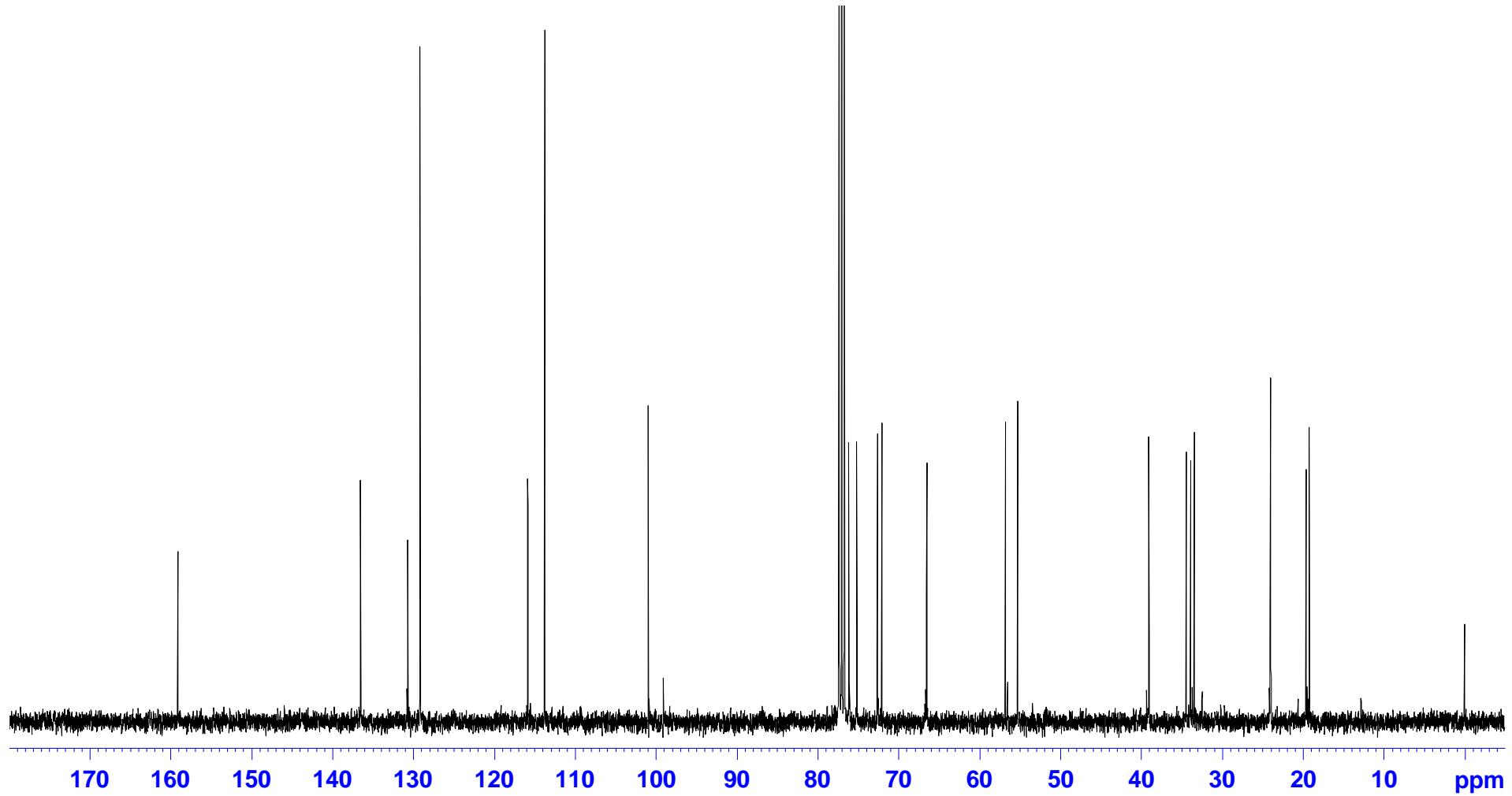


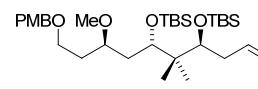
(4*S*,6*S*)-4-Allyl-6-((*R*)-2-methoxy-4-(4-methoxybenzyloxy)butyl)-2,2,5,5-tetramethyl-1,3-dioxane (**T**).



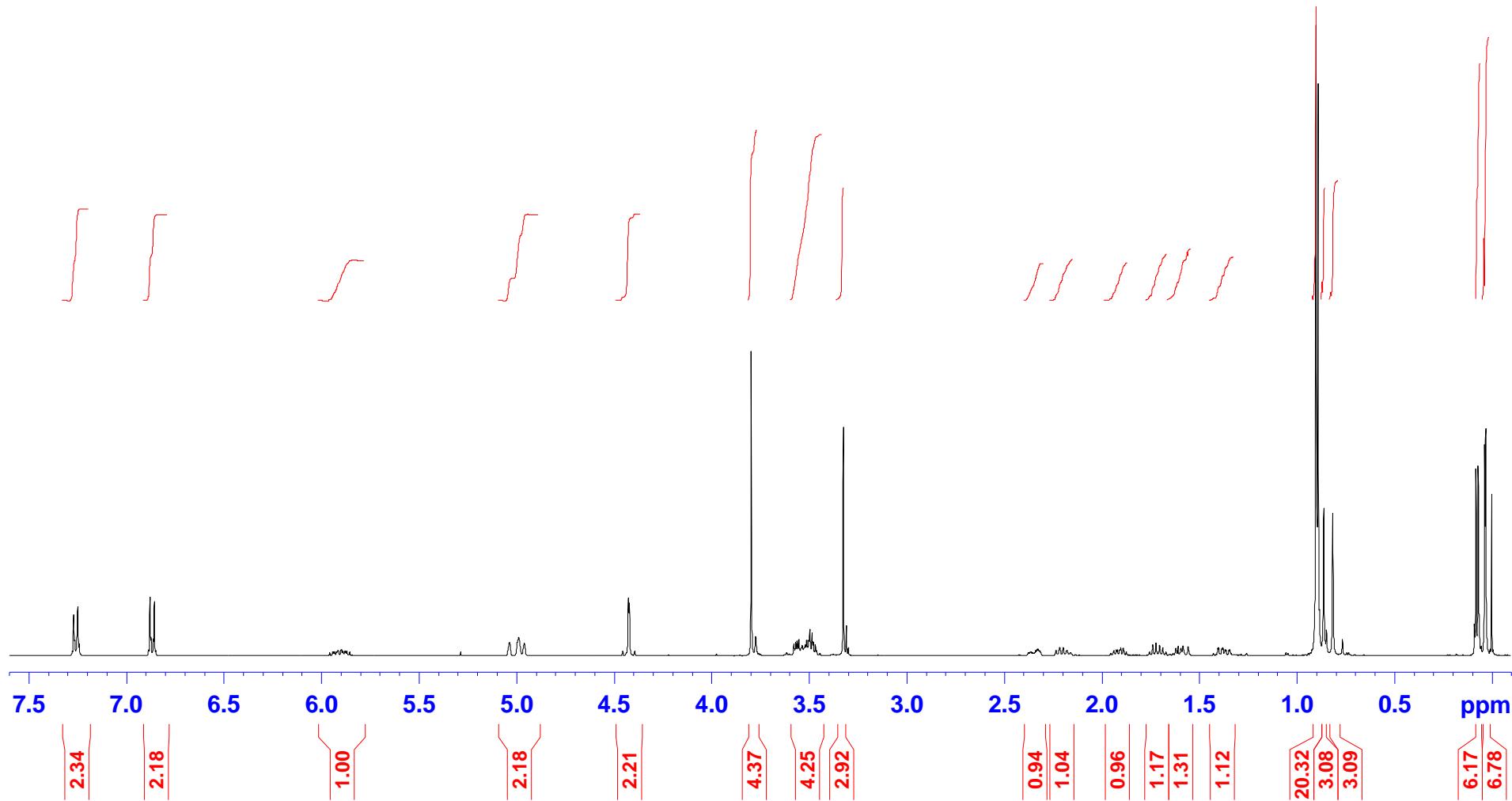


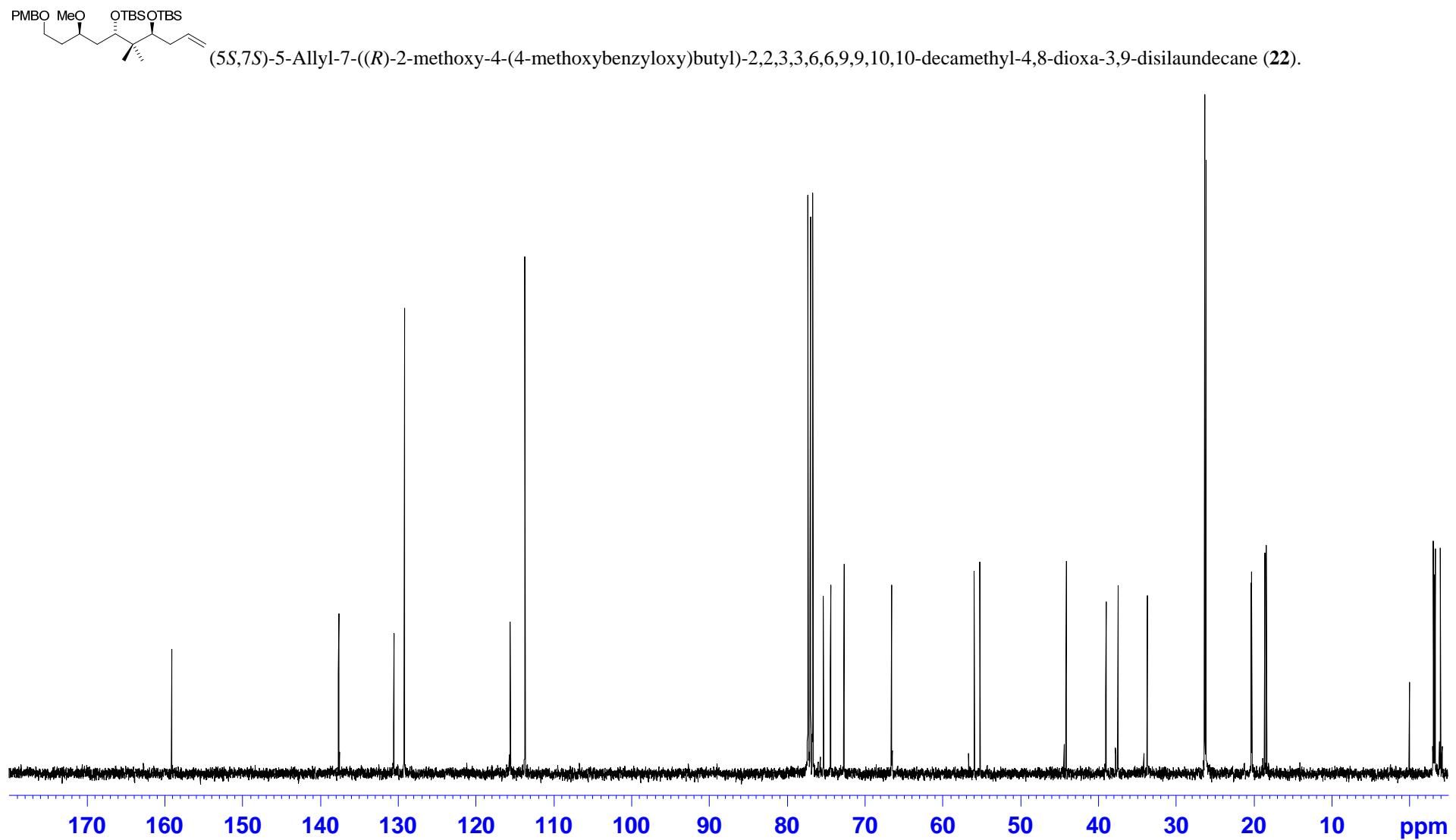
(4*S*,6*S*)-4-Allyl-6-((*R*)-2-methoxy-4-(4-methoxybenzyloxy)butyl)-2,2,5,5-tetramethyl-1,3-dioxane (**T**).

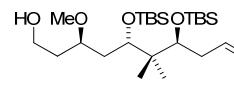




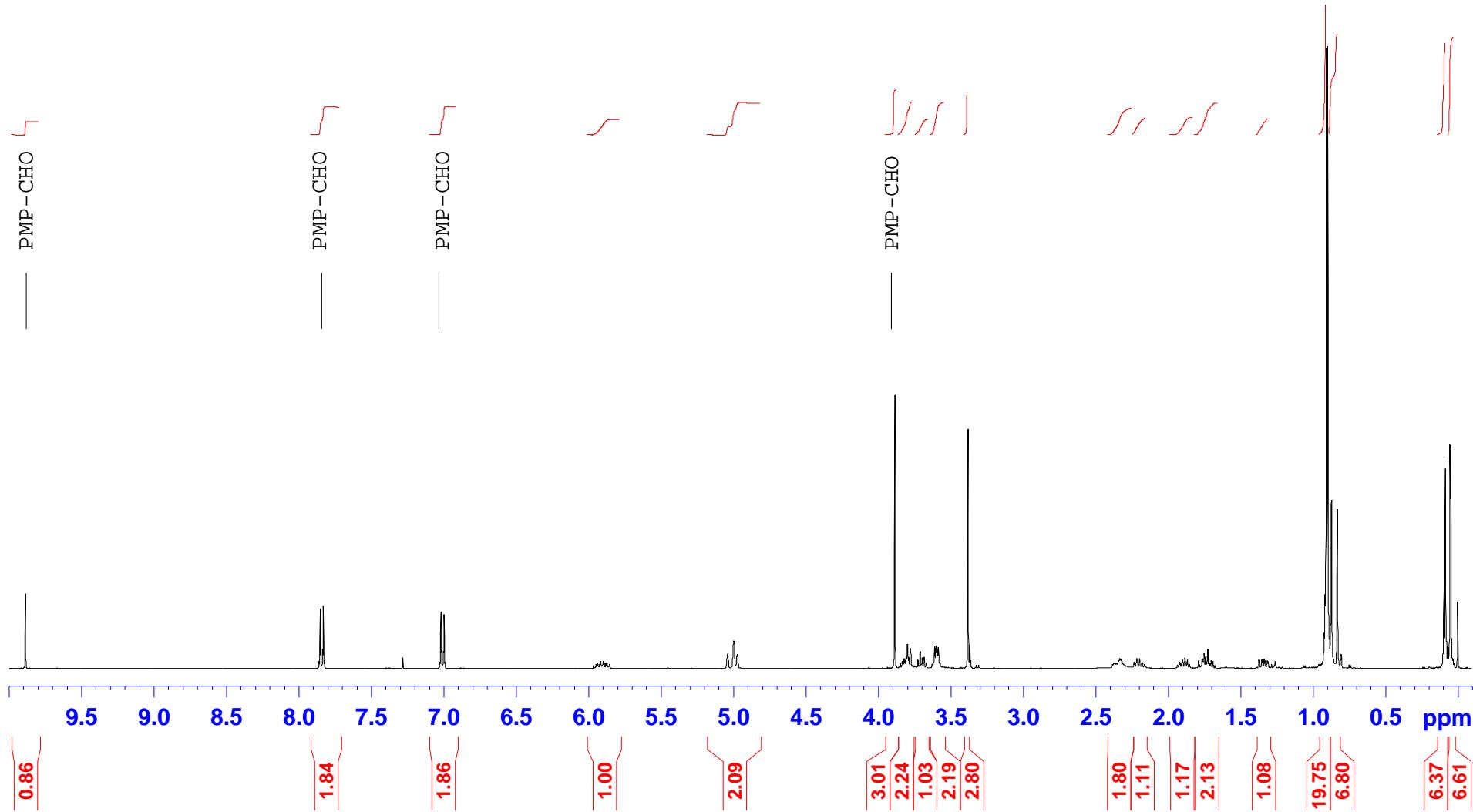
(5*S*,7*S*)-5-Allyl-7-((*R*)-2-methoxy-4-(4-methoxybenzyloxy)butyl)-2,2,3,3,6,6,9,9,10,10-decamethyl-4,8-dioxa-3,9-disilaundecane (**22**).

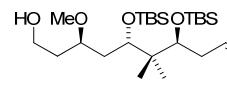




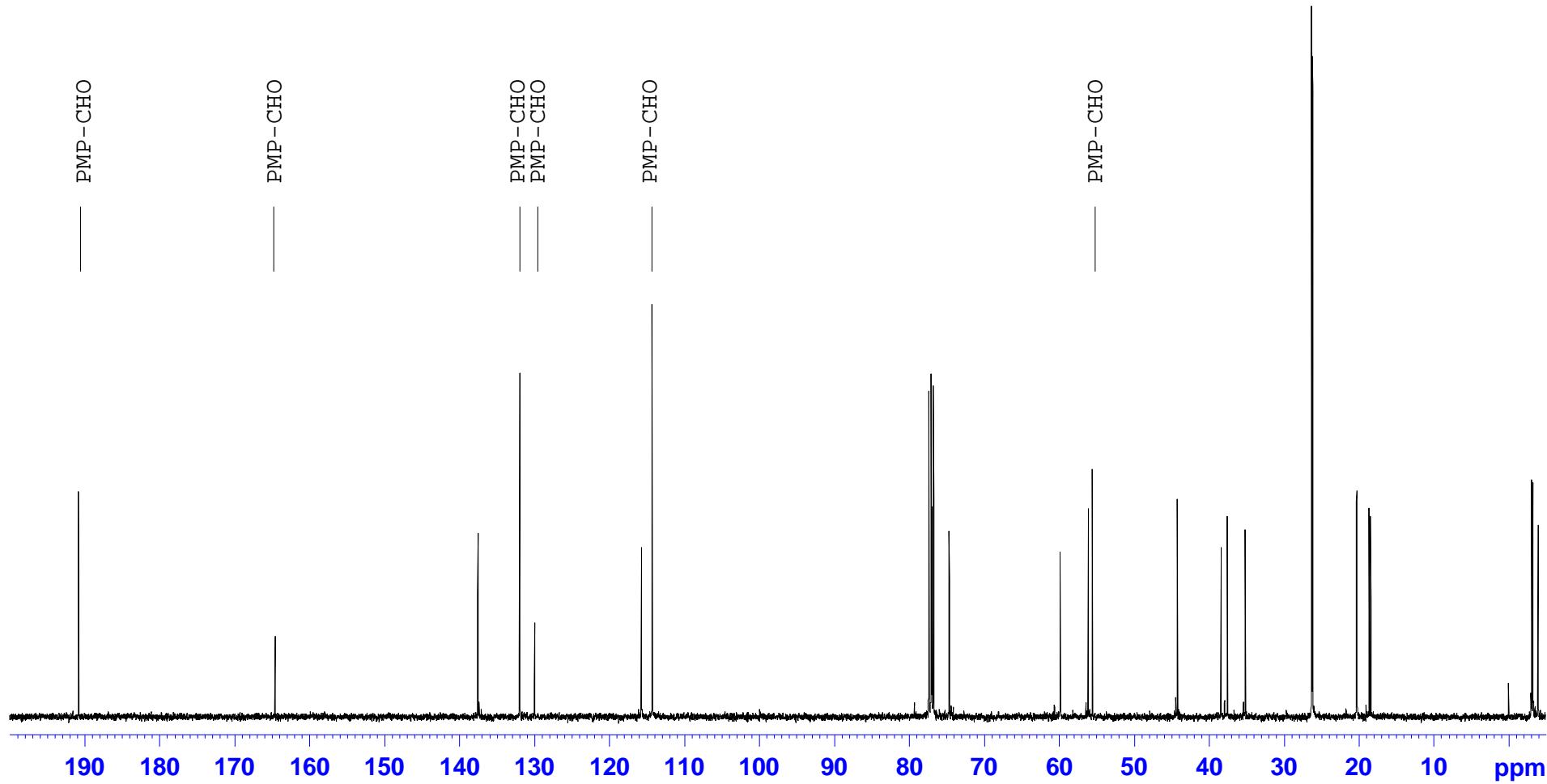


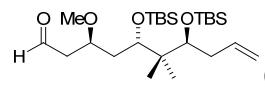
(3*R*,5*S*,7*S*)-5,7-Bis(*tert*-butyldimethylsilyloxy)-3-methoxy-6,6-dimethyldec-9-en-1-ol (**U**).



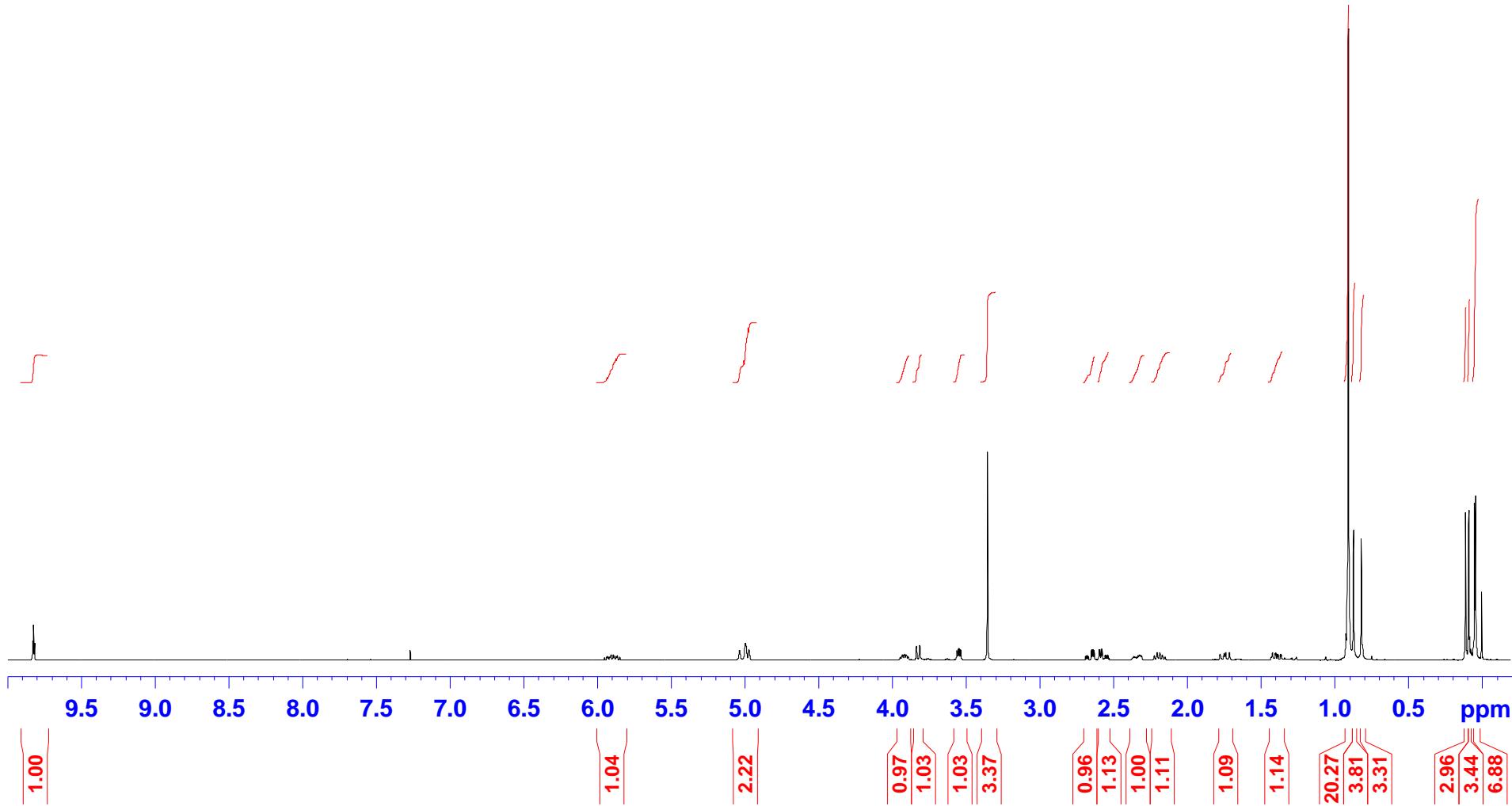


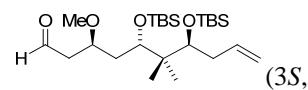
(3*R*,5*S*,7*S*)-5,7-Bis(*tert*-butyldimethylsilyloxy)-3-methoxy-6,6-dimethyldec-9-en-1-ol (**U**).



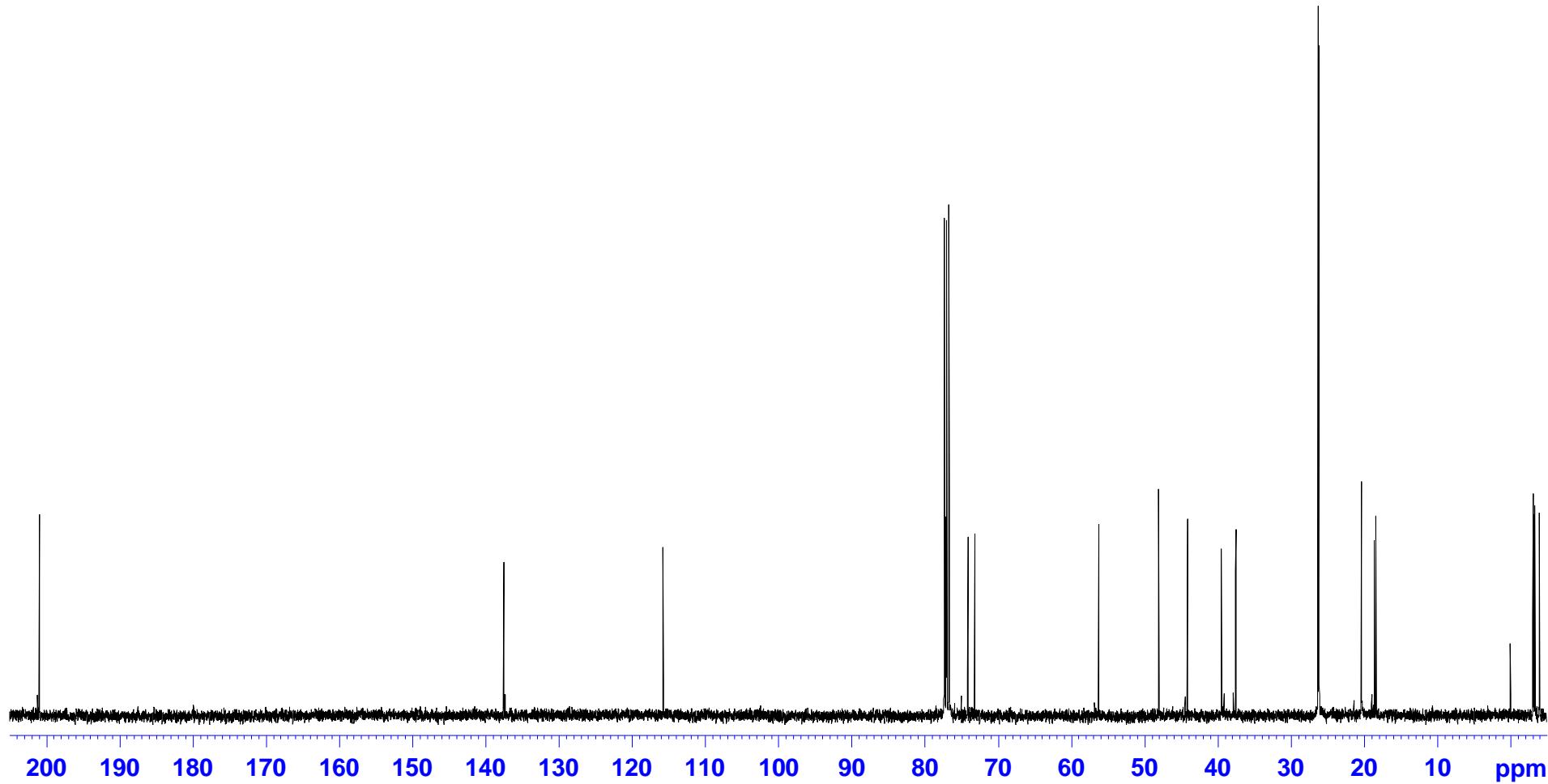


(*3S,5S,7S*)-5,7-Bis(*tert*-butyldimethylsilyloxy)-3-methoxy-6,6-dimethyldec-9-enal (**8**).

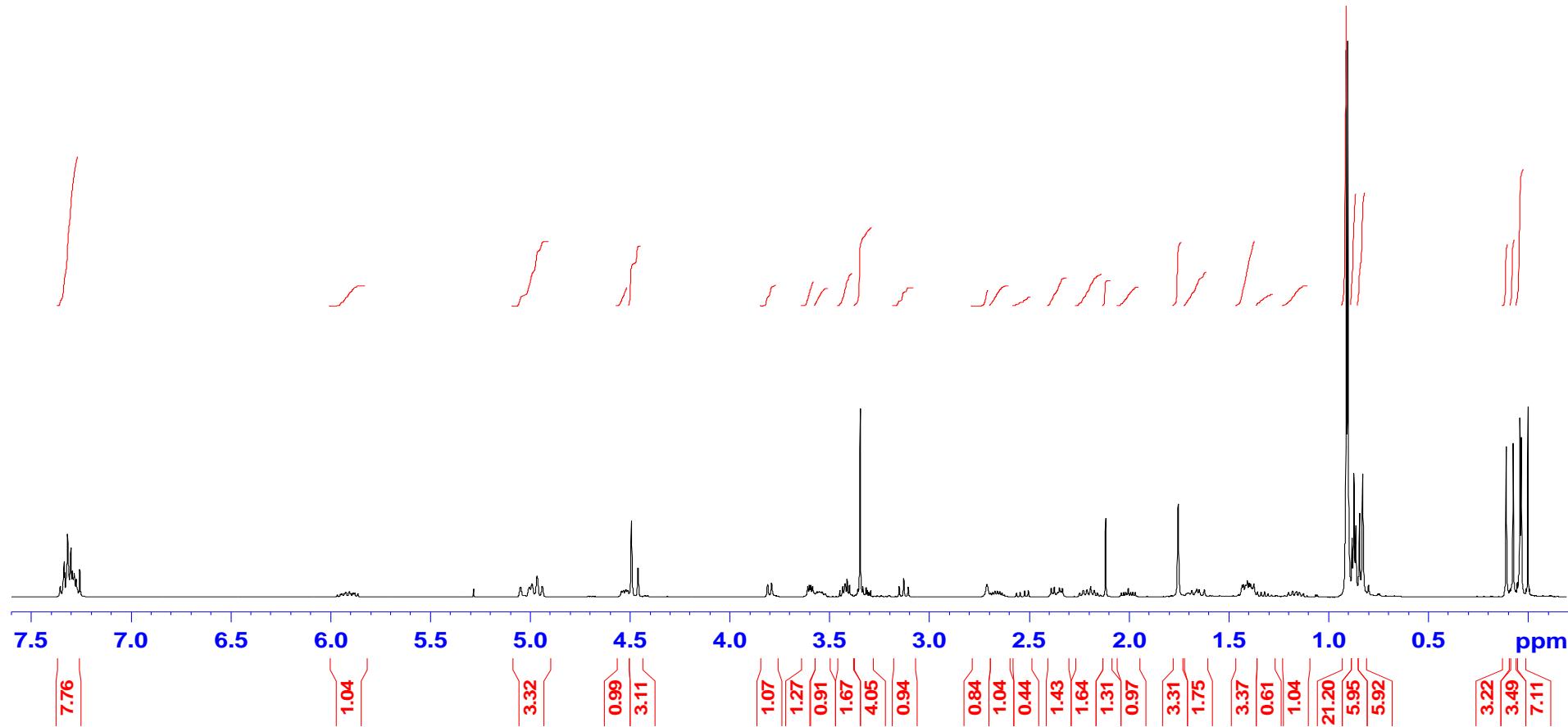
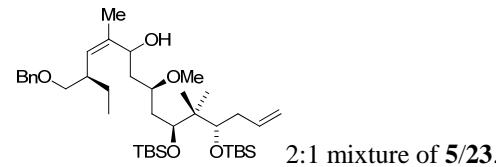


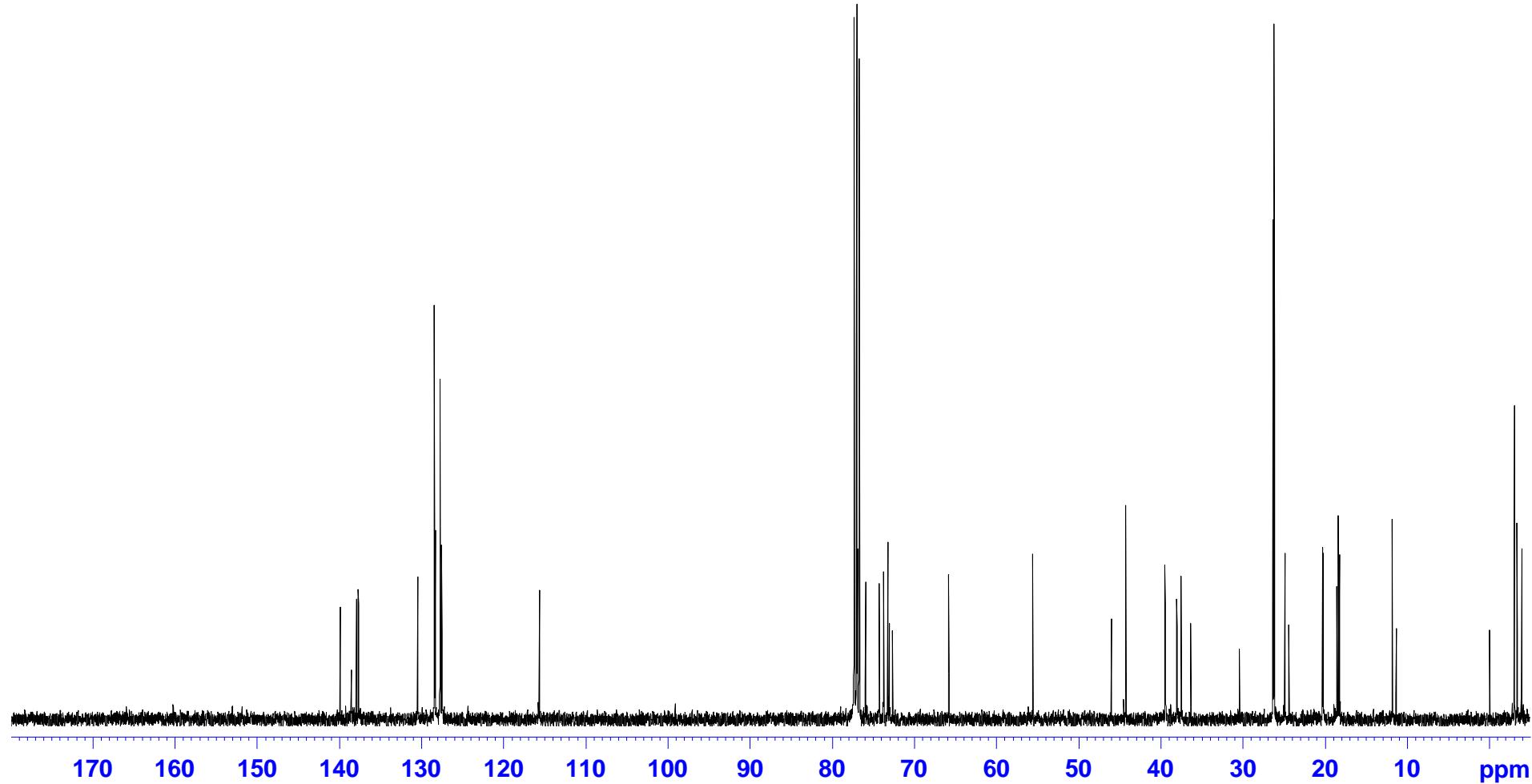
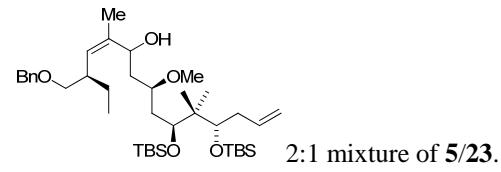


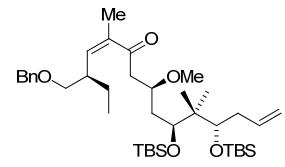
(*3S,5S,7S*)-5,7-Bis(*tert*-butyldimethylsilyloxy)-3-methoxy-6,6-dimethyldec-9-enal (**8**).



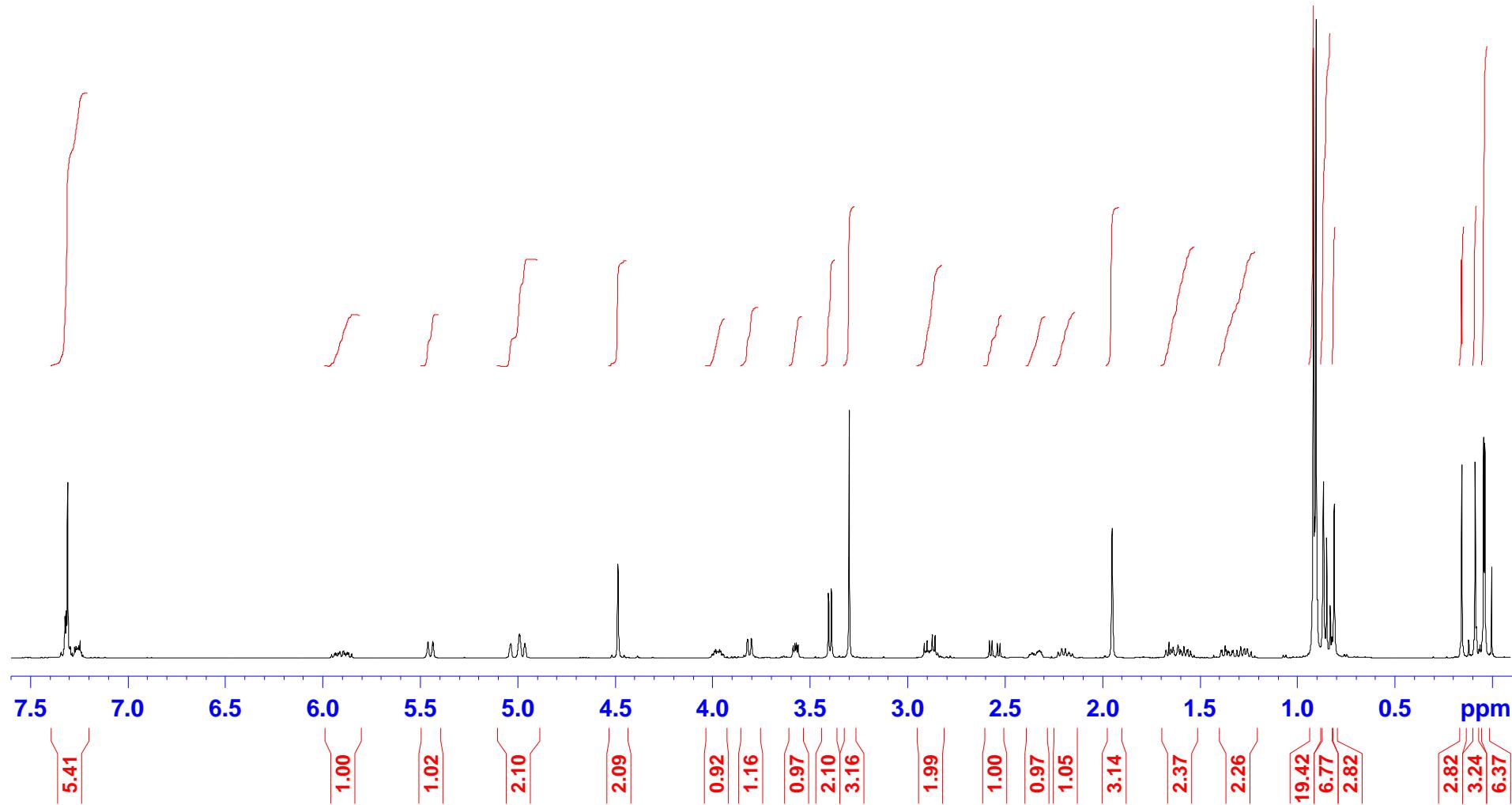
Assembly of target structure **4**

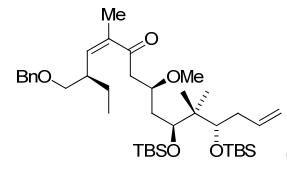




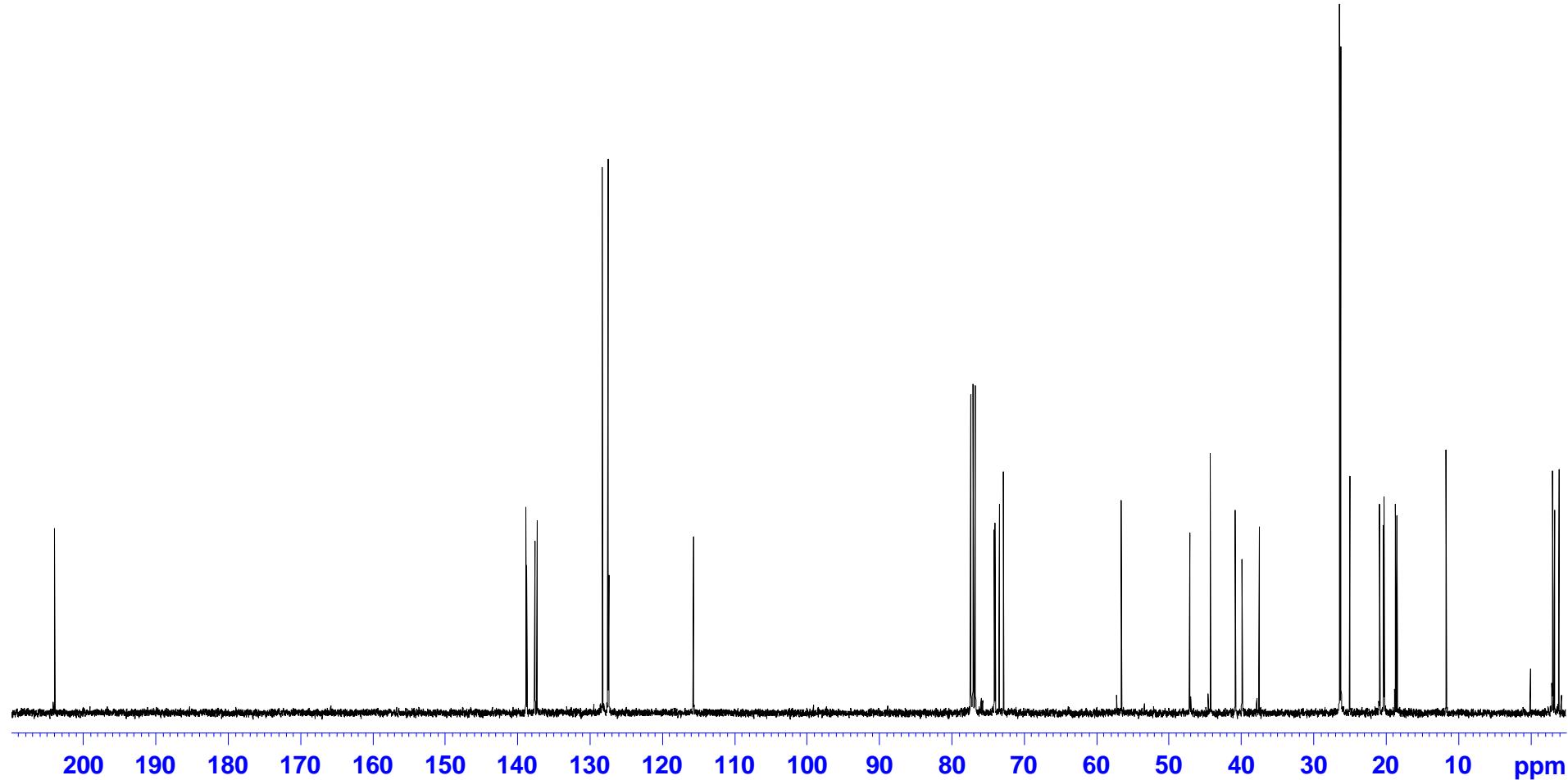


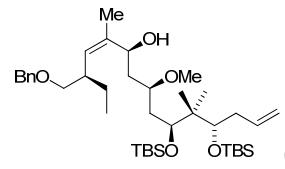
(3*R*,8*S*,10*S*,12*S*,*Z*)-3-(Benzylxymethyl)-10,12-bis(tert-butyldimethylsilyloxy)-8-methoxy-5,11,11-trimethylpentadeca-4,14-dien-6-one (**V**).



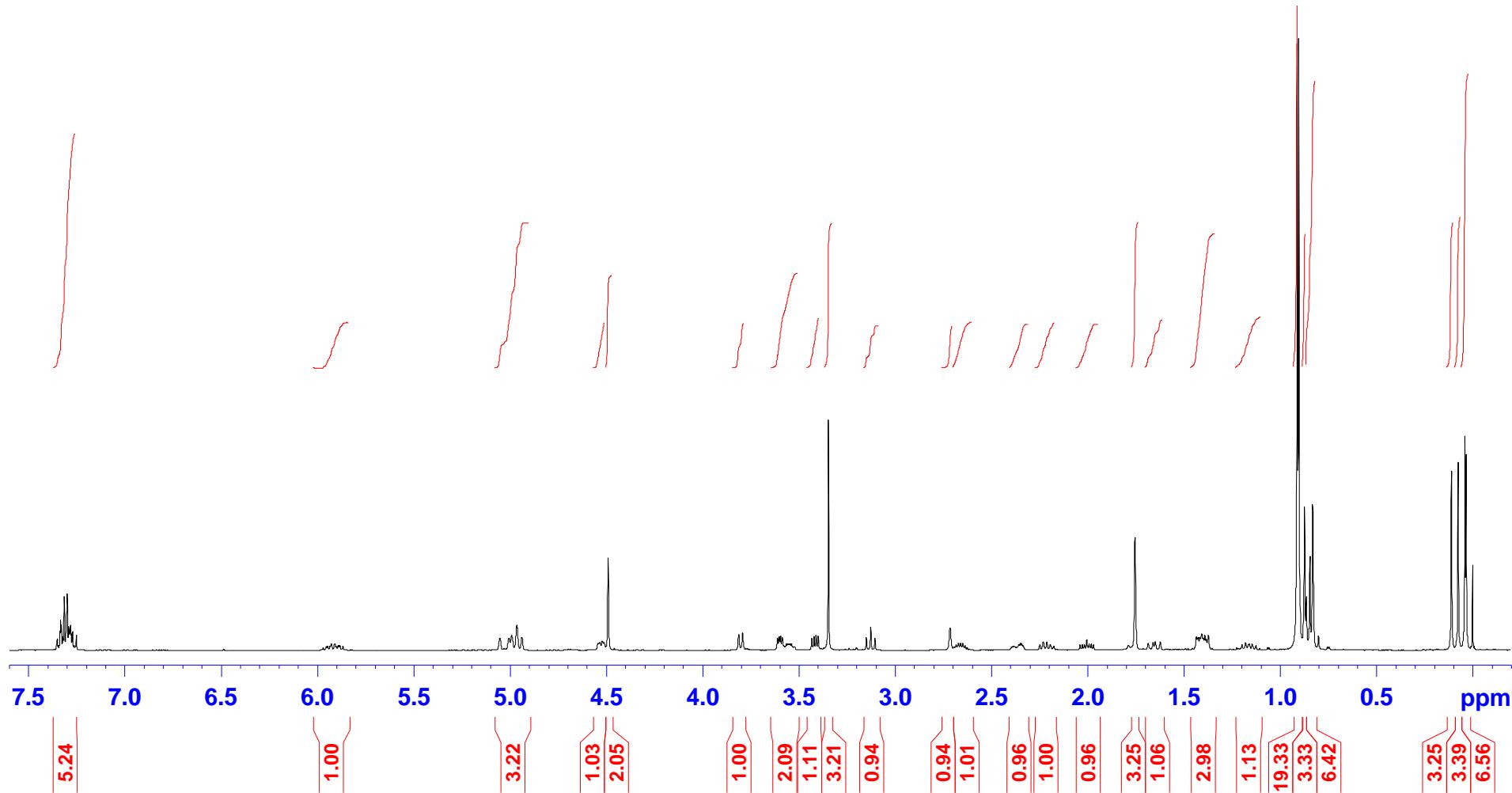


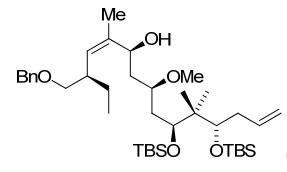
(*3R,8S,10S,12S,Z*)-3-(Benzylxymethyl)-10,12-bis(tert-butyldimethylsilyloxy)-8-methoxy-5,11,11-trimethylpentadeca-4,14-dien-6-one (**V**).



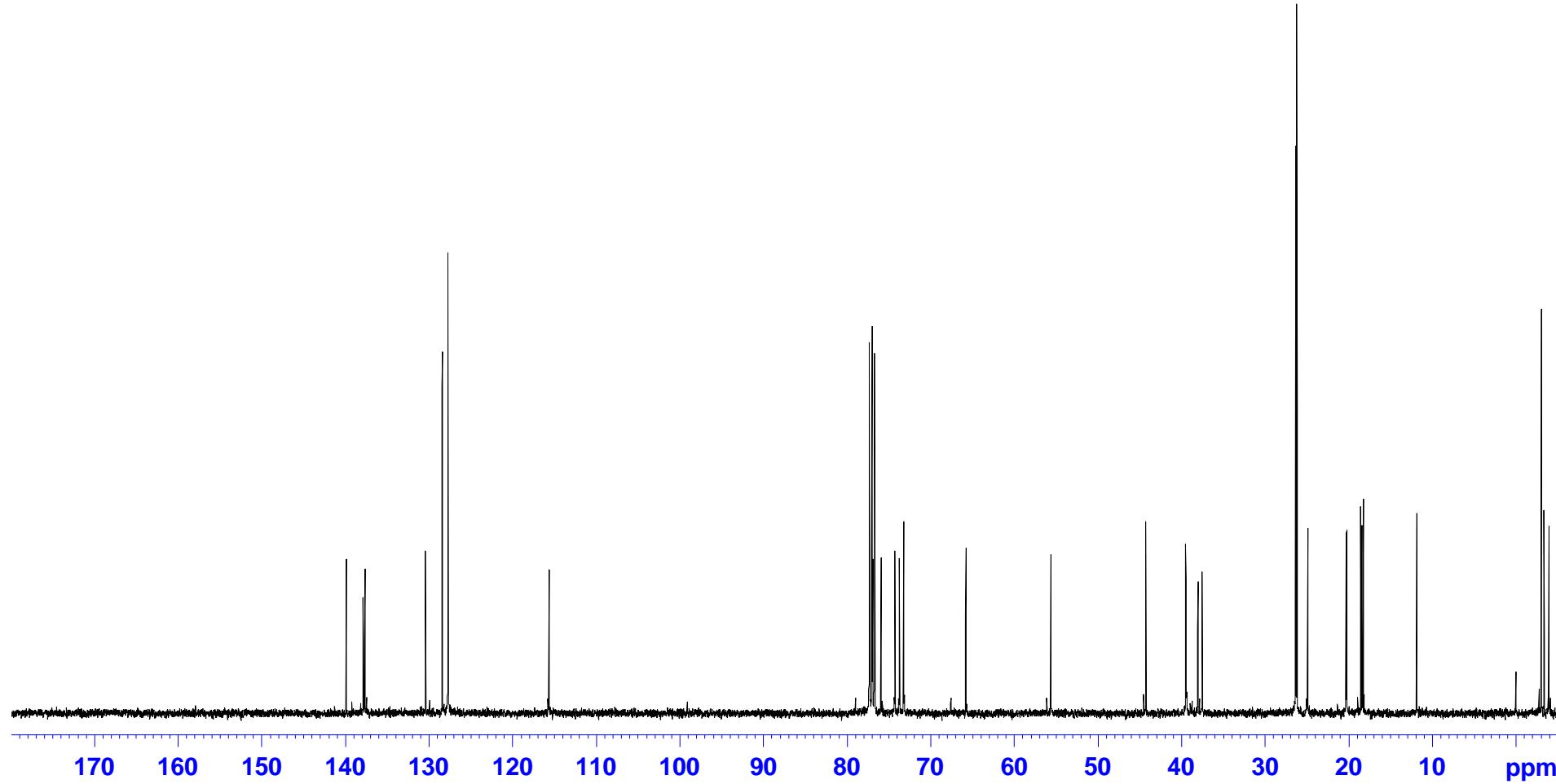


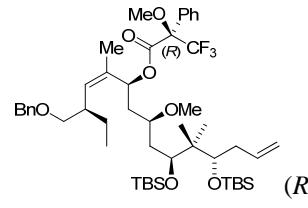
(3*R*,6*S*,8*R*,10*S*,12*S*,*Z*)-3-(Benzylxymethyl)-10,12-bis(*tert*-butyldimethylsilyloxy)-8-methoxy-5,11,11-trimethylpentadeca-4,14-dien-6-ol (**5**).



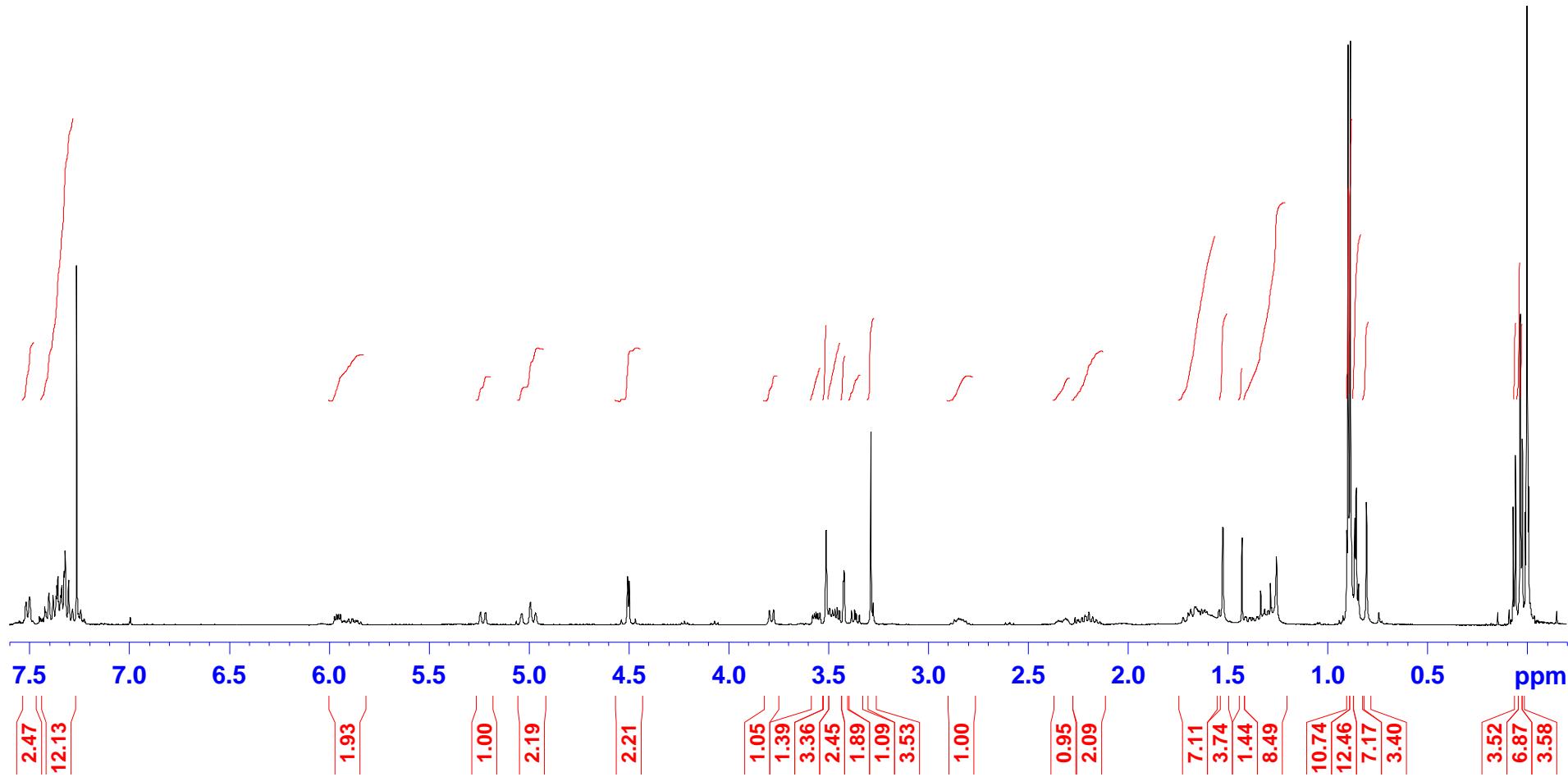


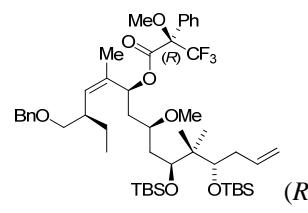
(3*R*,6*S*,8*R*,10*S*,12*S*,*Z*)-3-(Benzylloxymethyl)-10,12-bis(*tert*-butyldimethylsilyloxy)-8-methoxy-5,11,11-trimethylpentadeca-4,14-dien-6-ol (**5**).



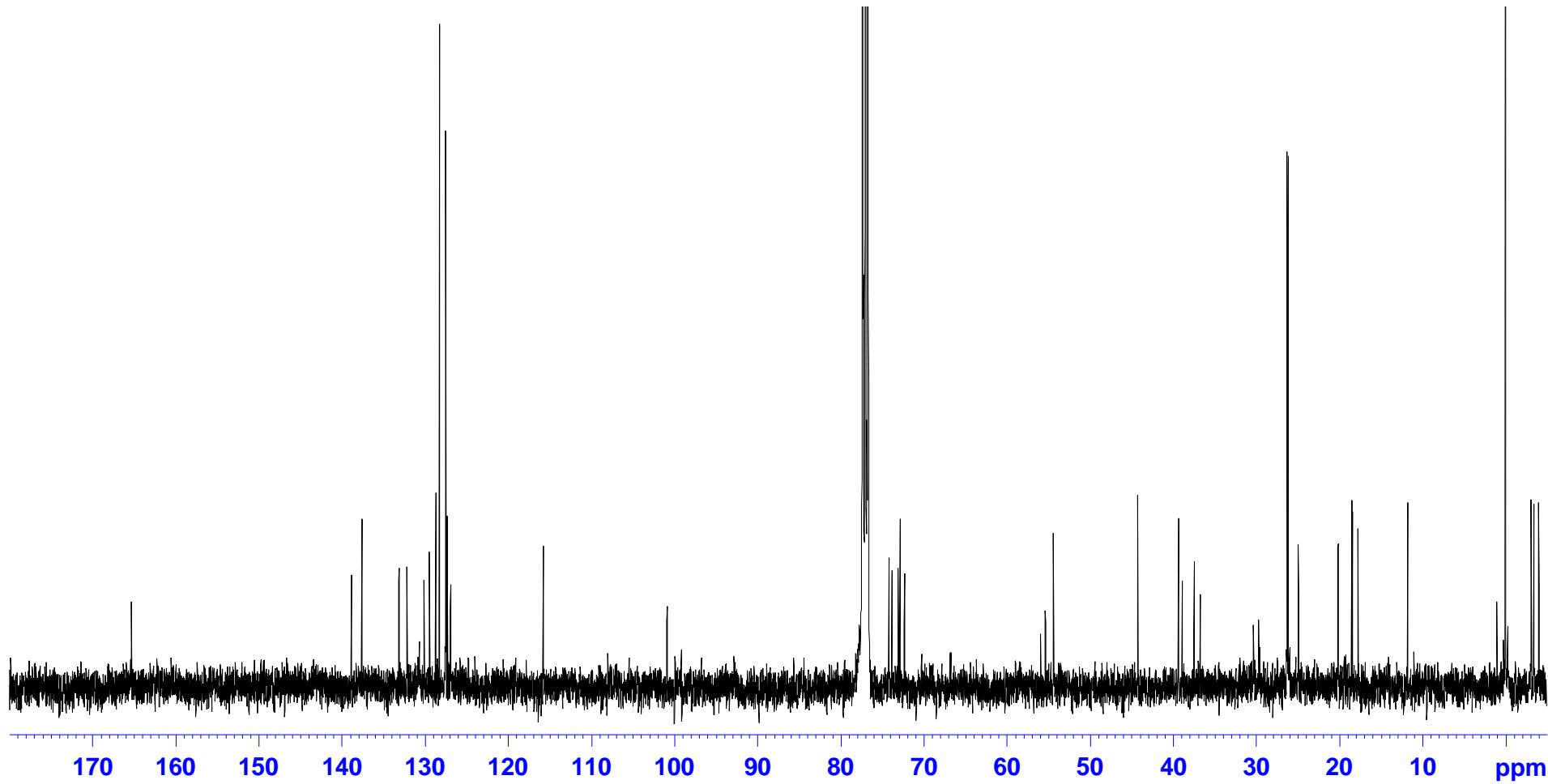


(R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**W**).

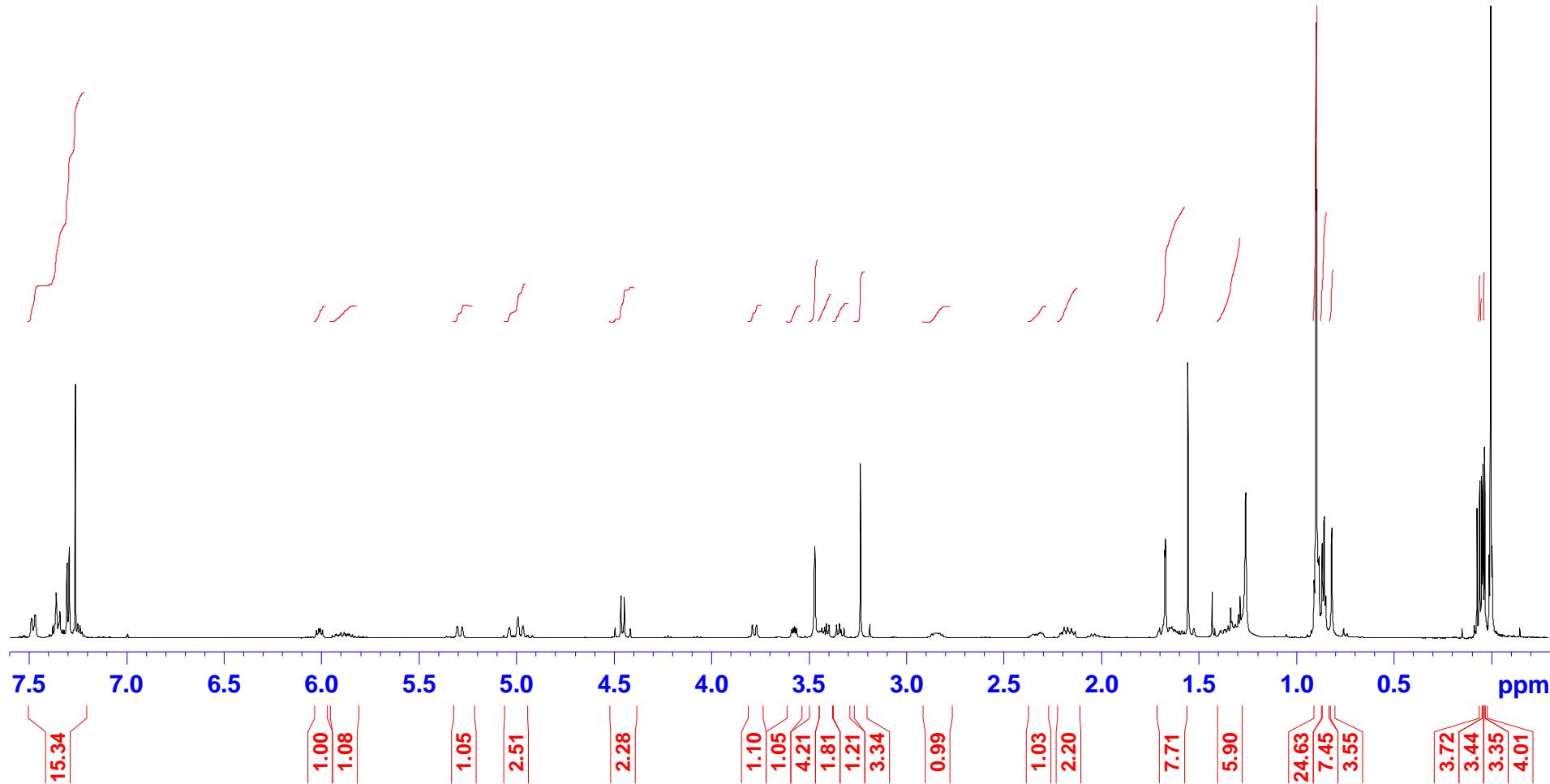
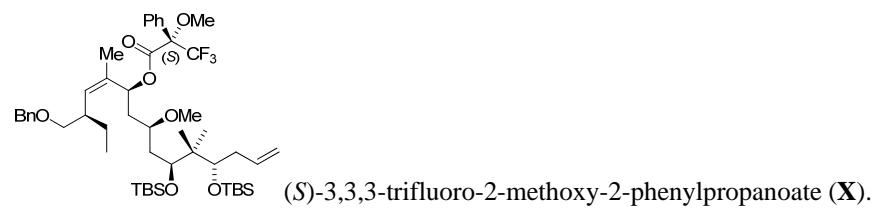


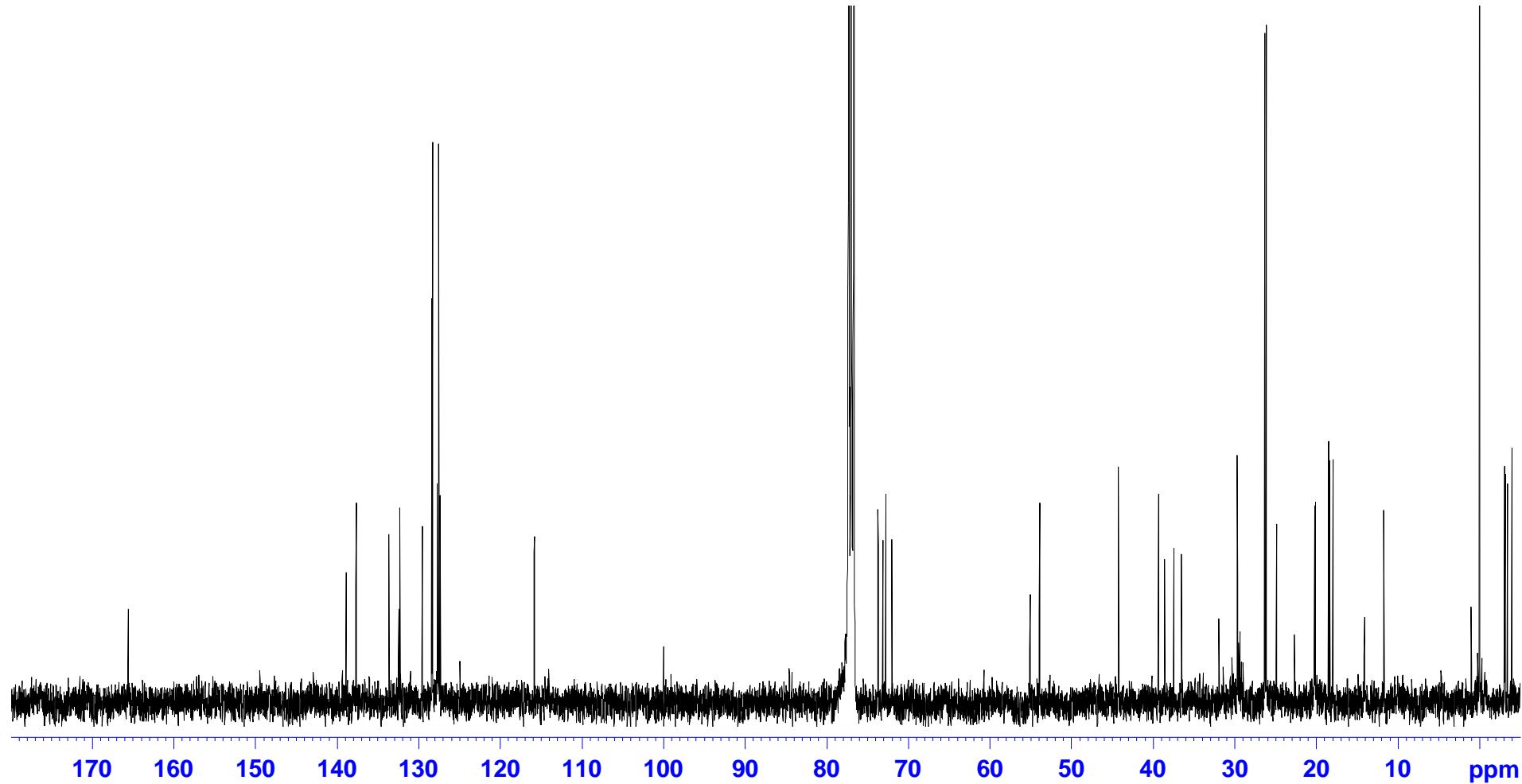
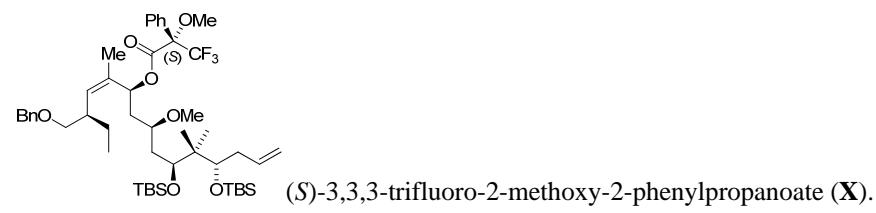


(*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**W**).

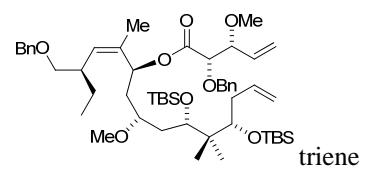


S70

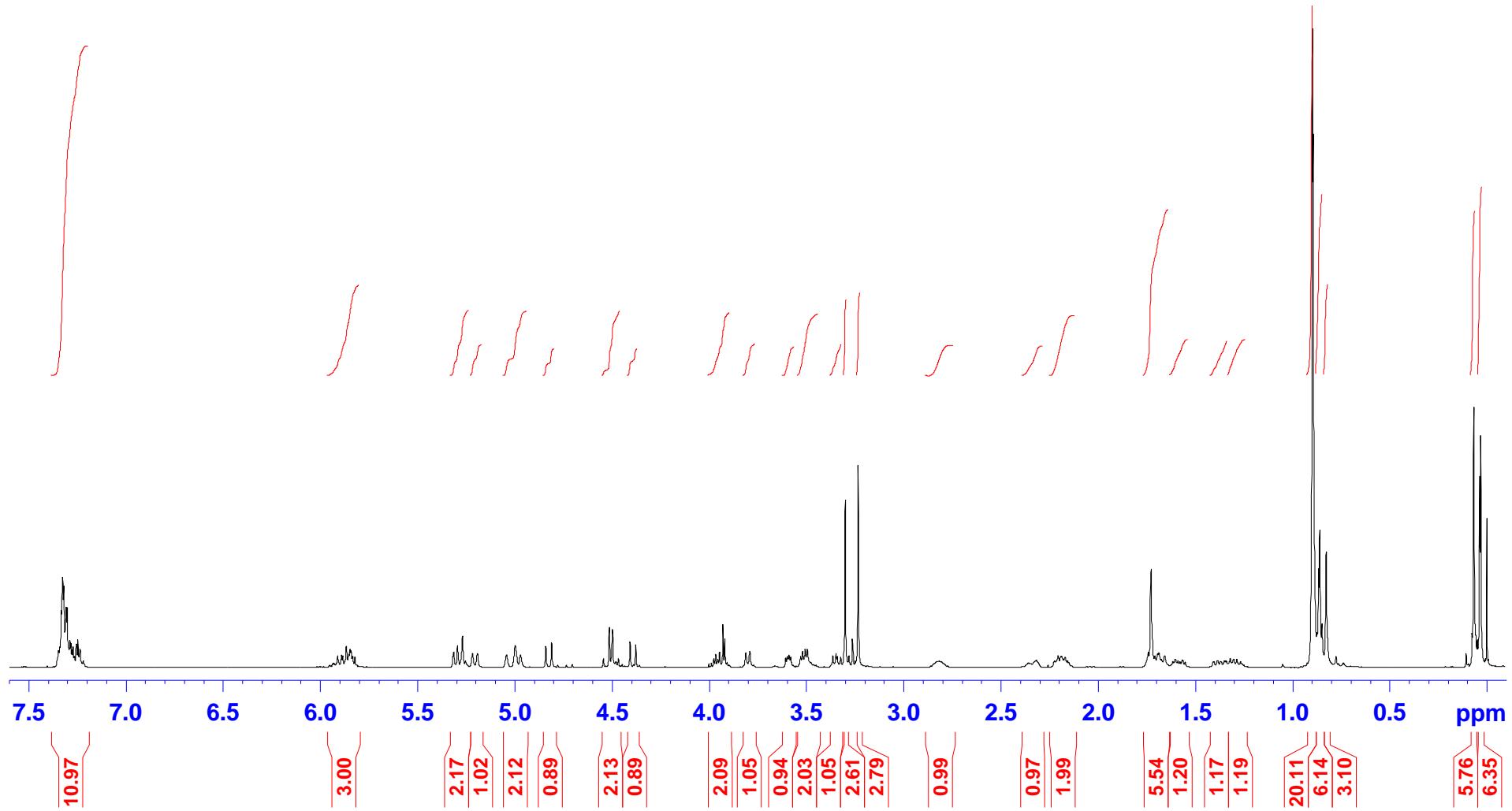


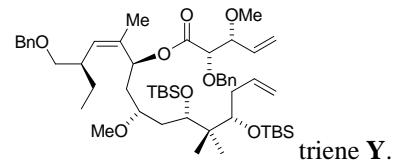


S72

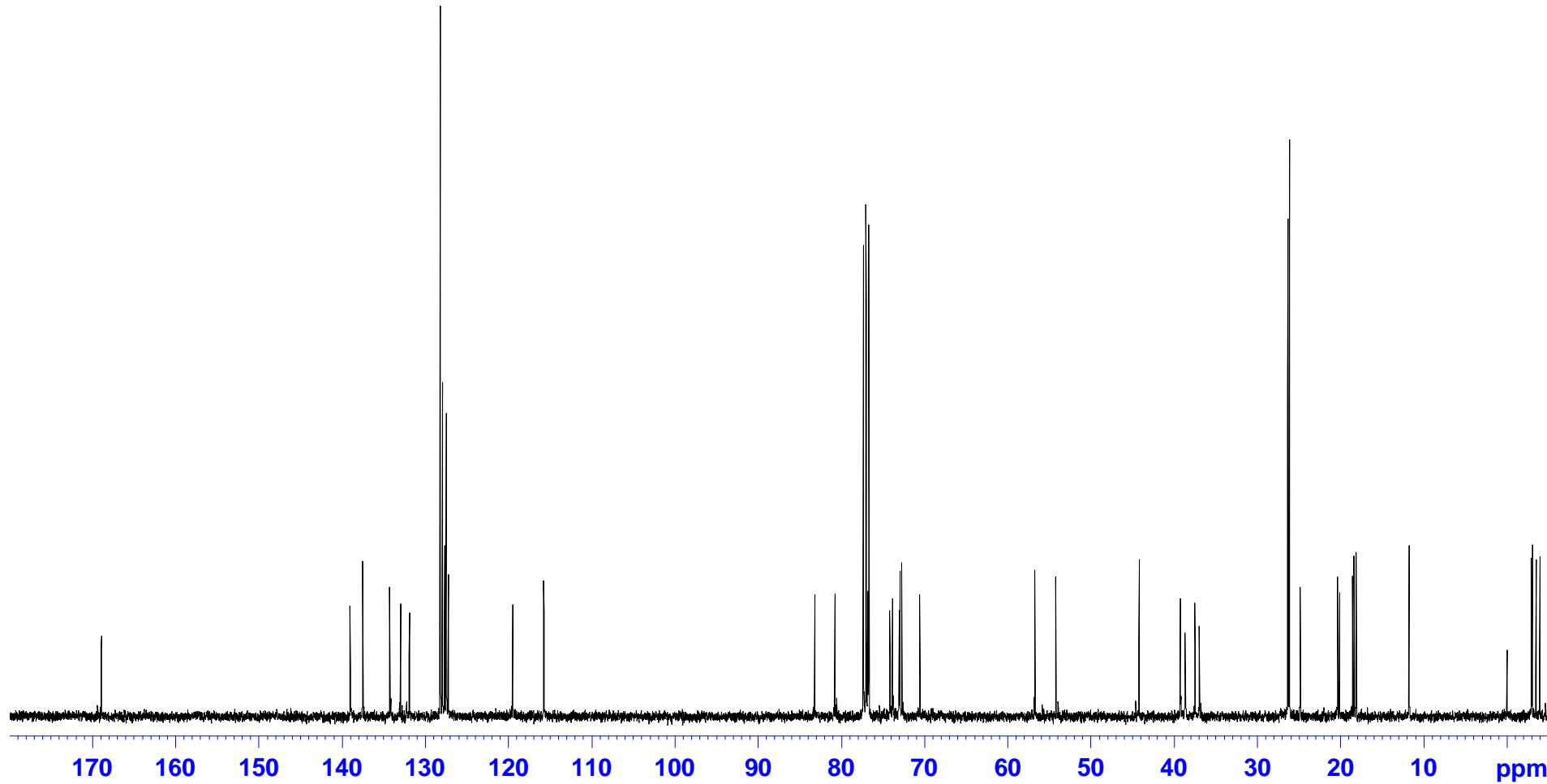


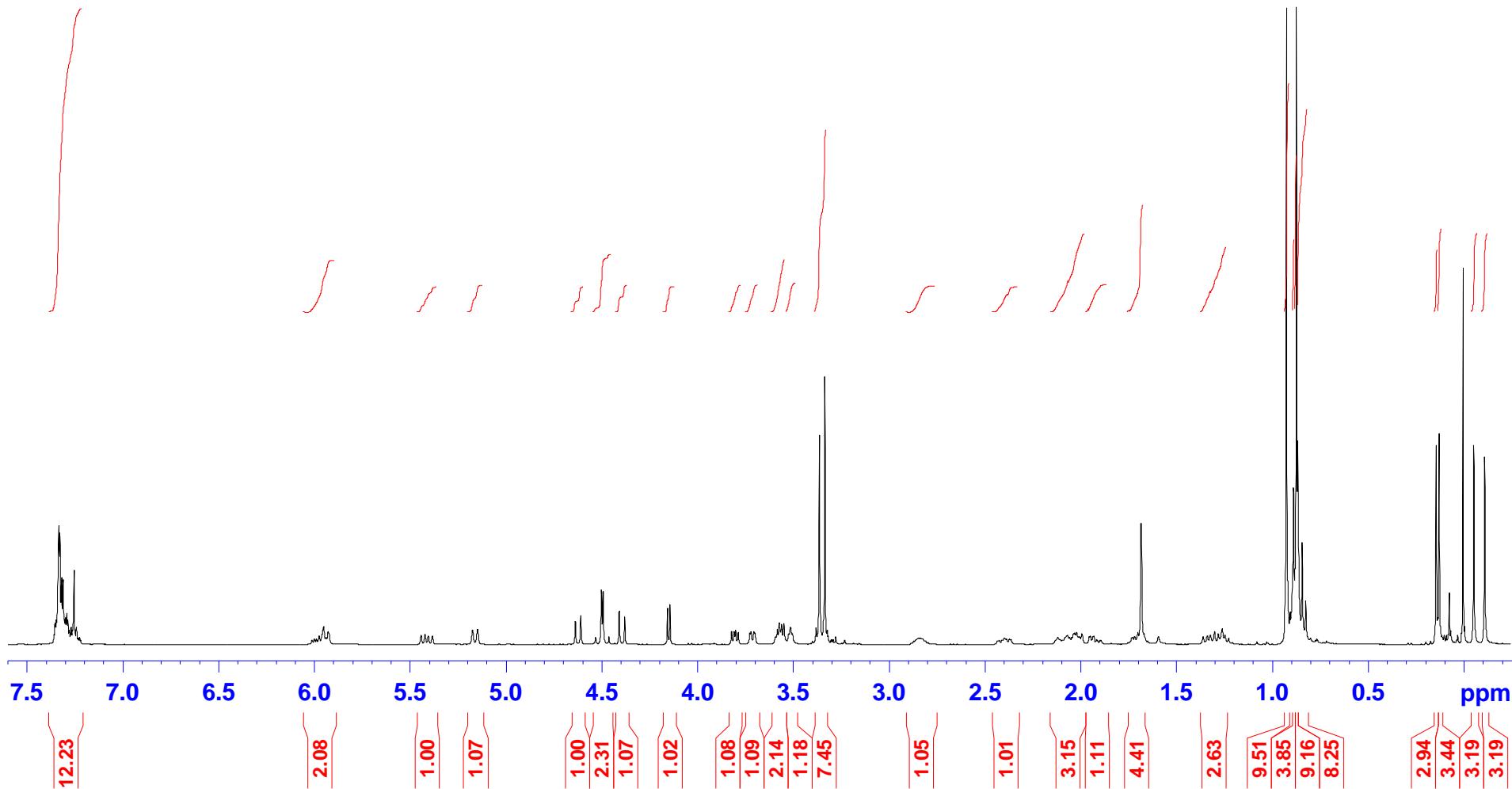
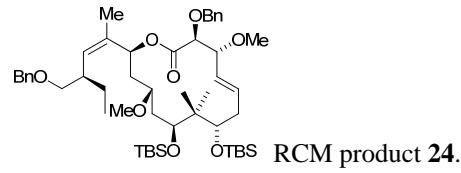
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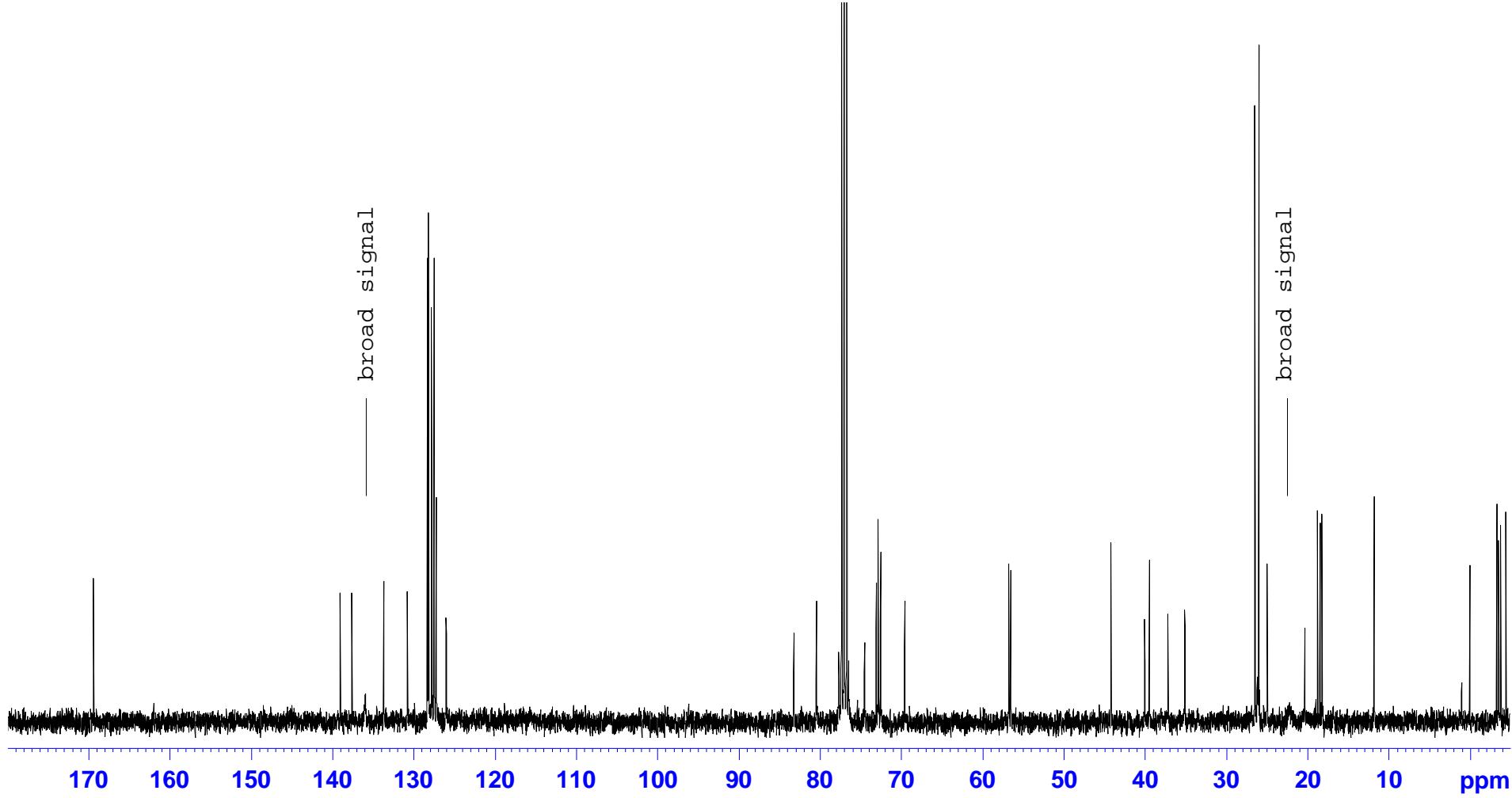
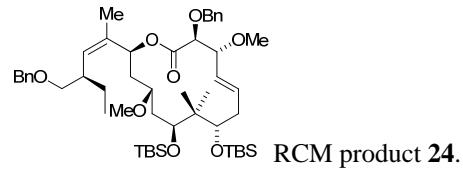


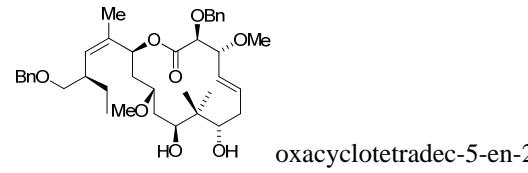


triene Y.

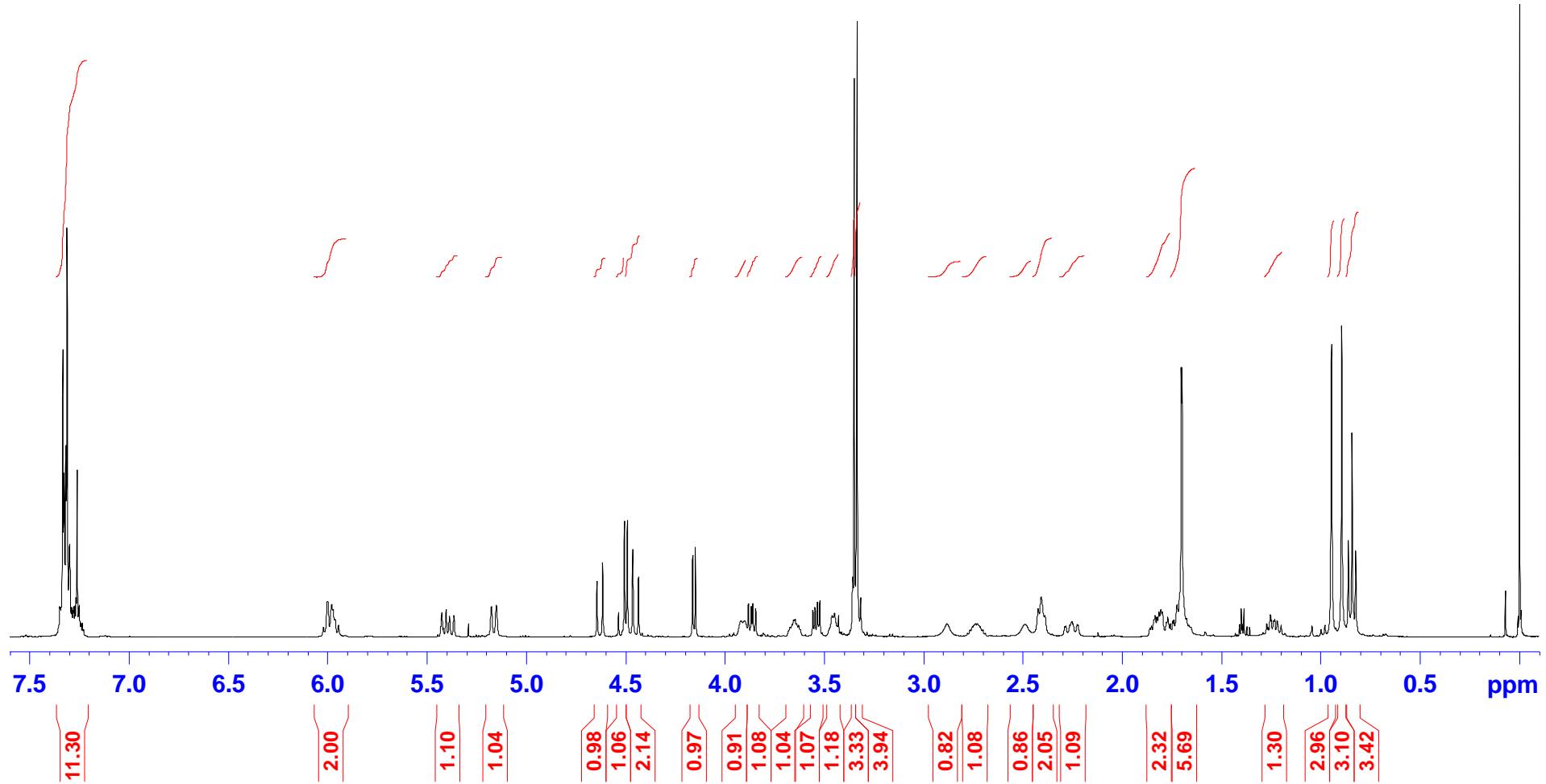


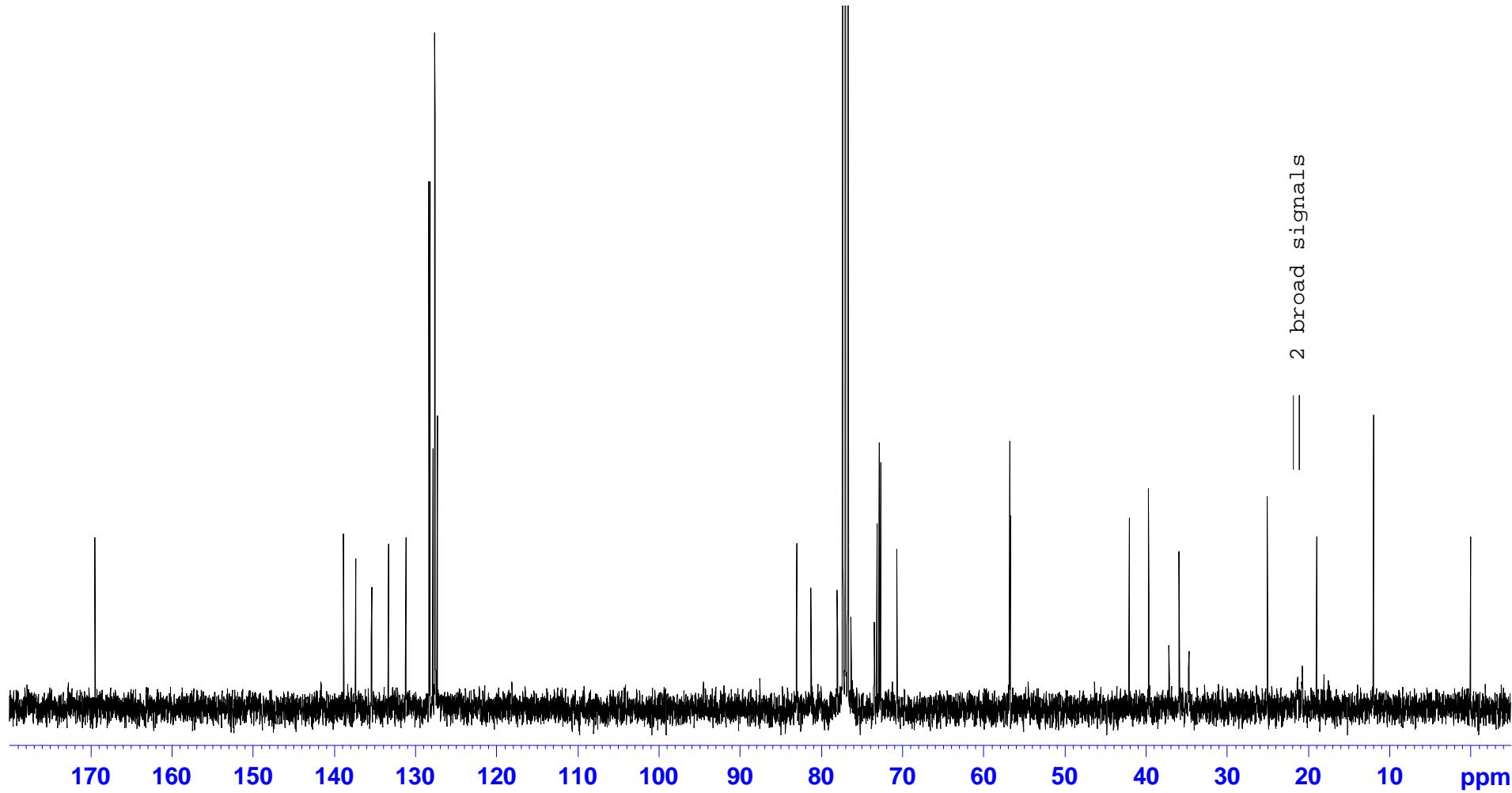
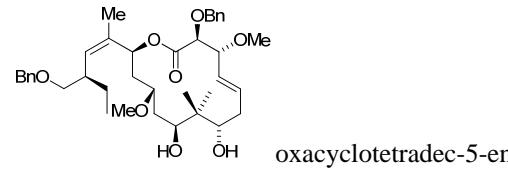


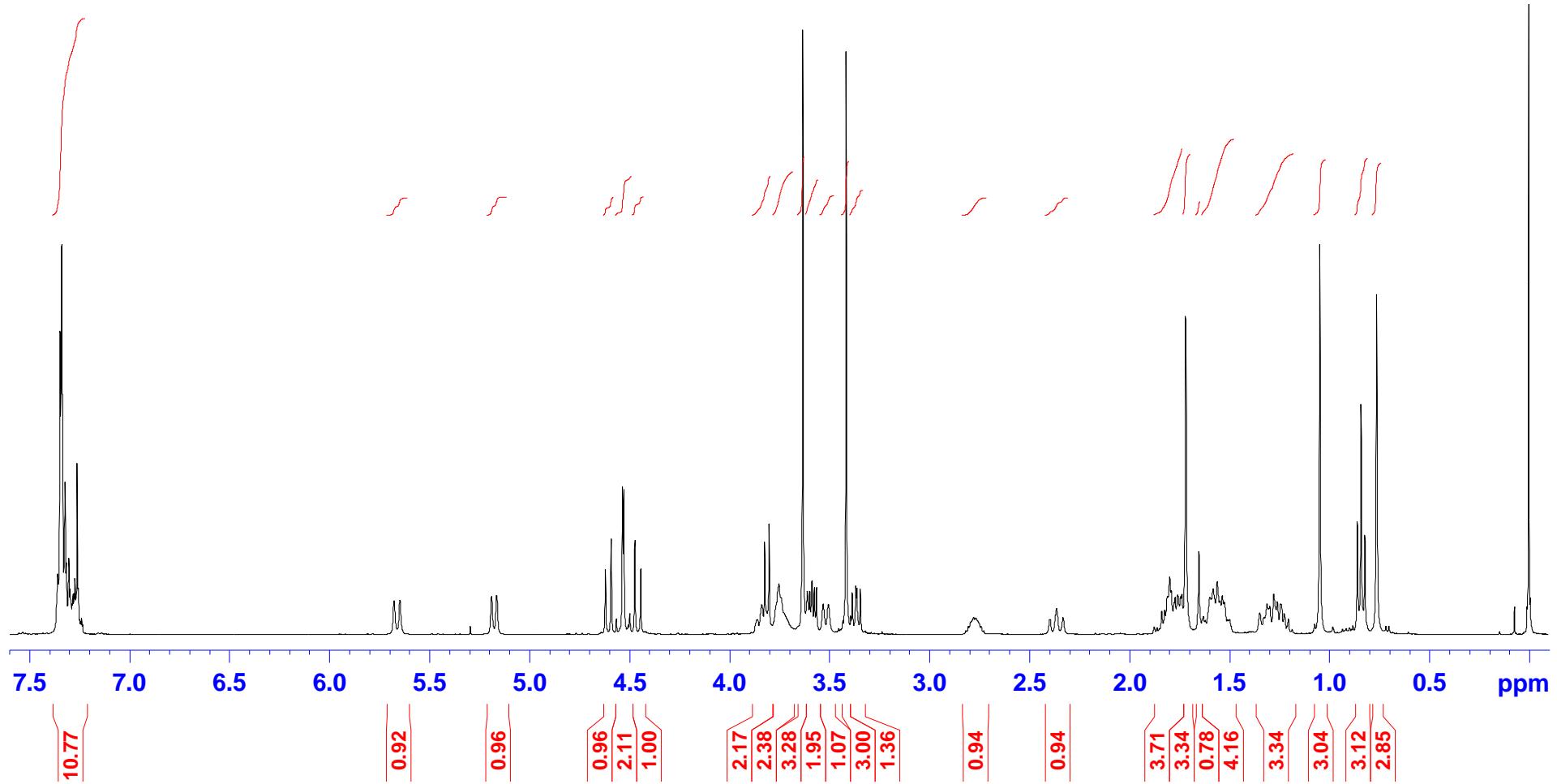
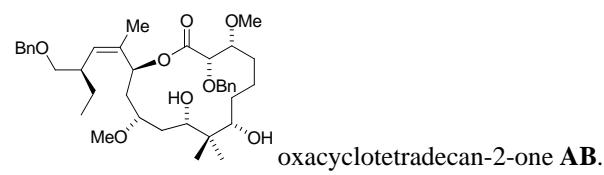


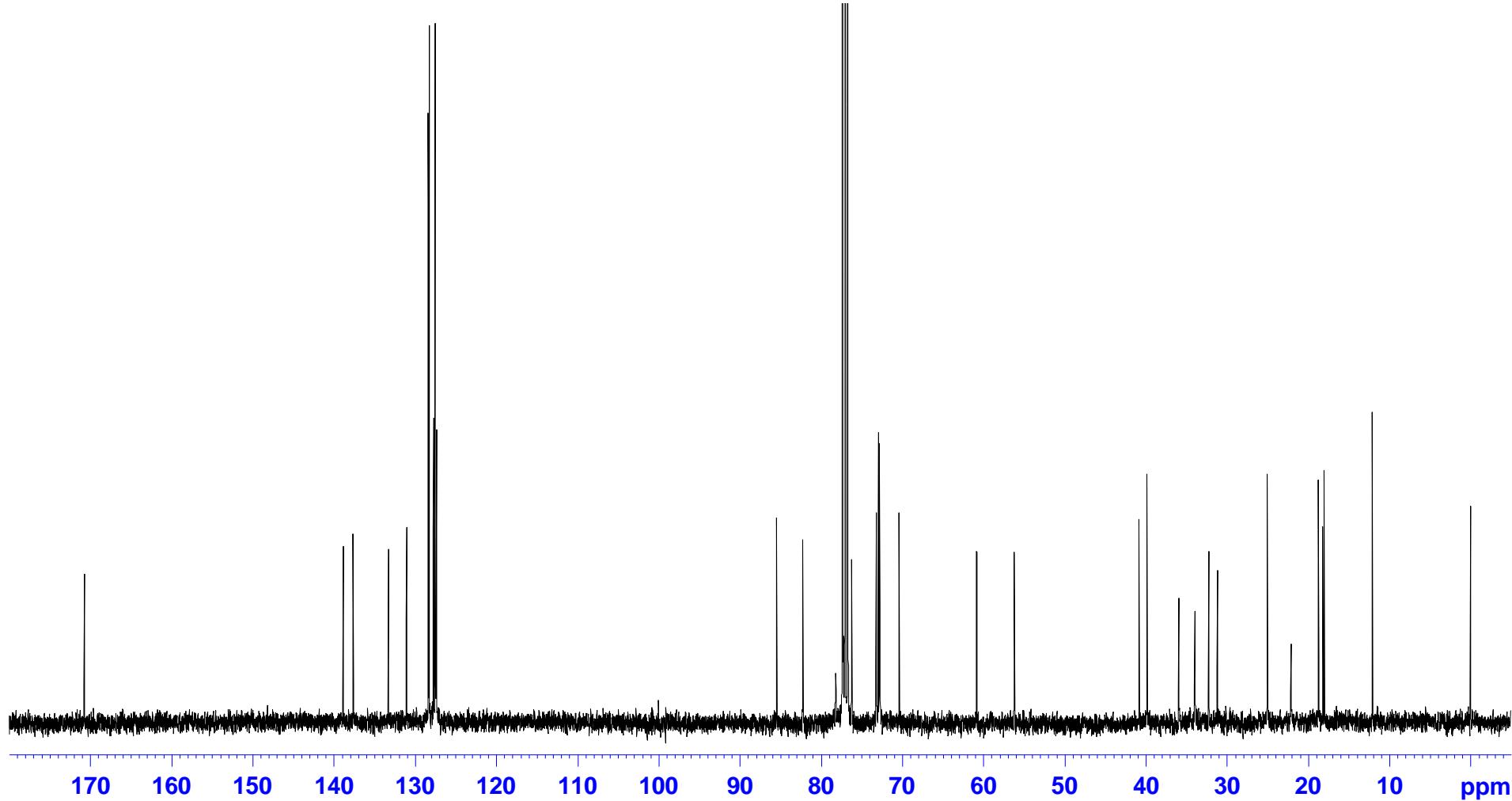
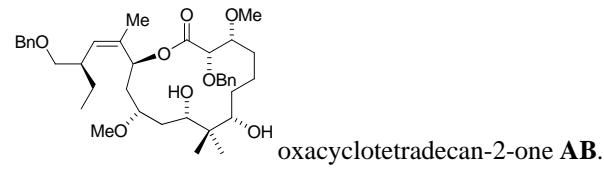


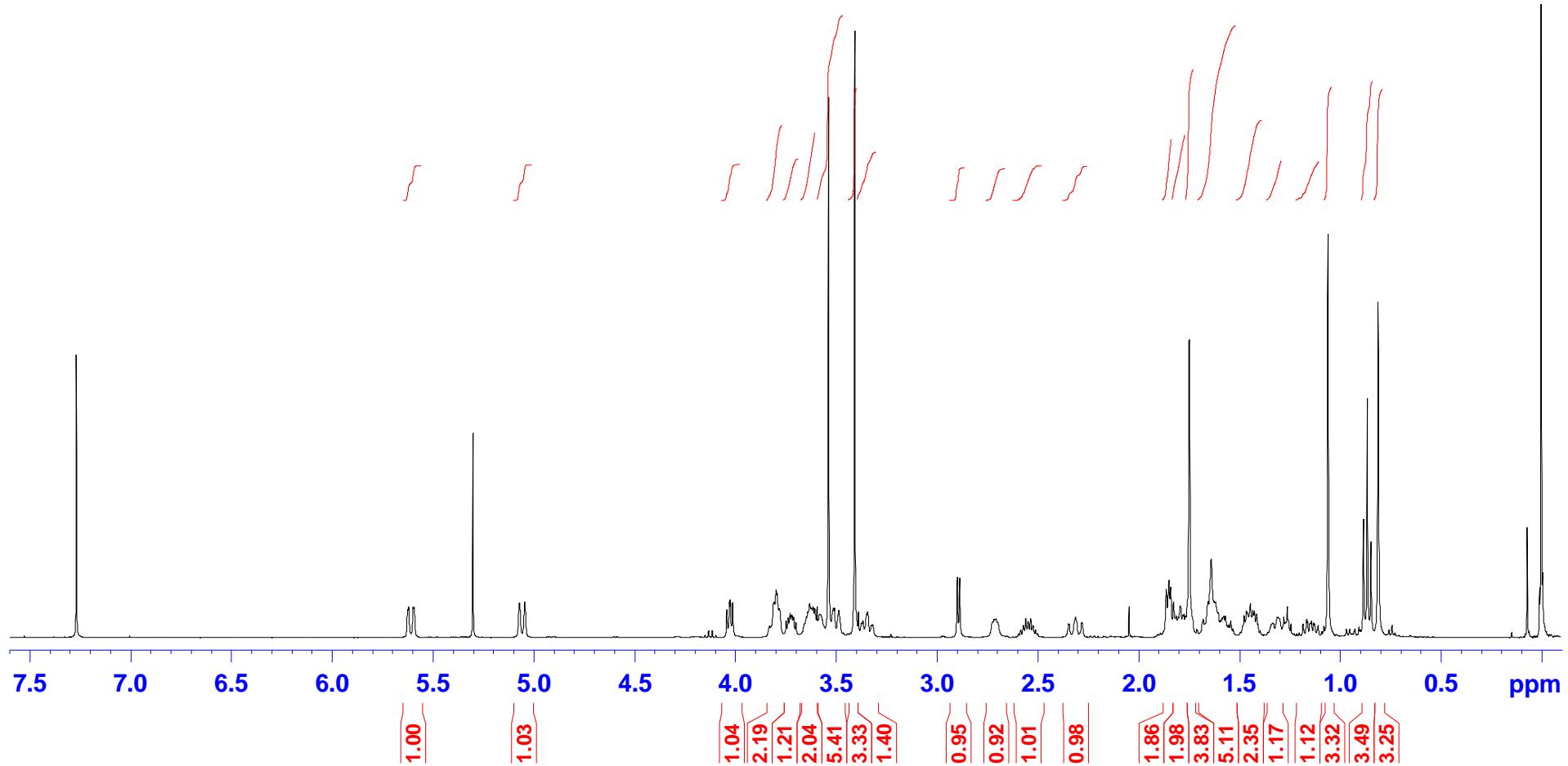
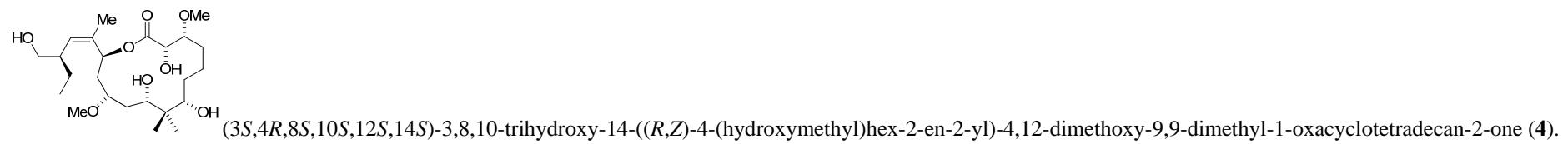
oxacyclotetradec-5-en-2-one **Z**.

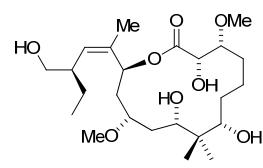












(*3S,4R,8S,10S,12S,14S*)-3,8,10-trihydroxy-14-((*R,Z*)-4-(hydroxymethyl)hex-2-en-2-yl)-4,12-dimethoxy-9,9-dimethyl-1-oxacyclotetradecan-2-one (**4**).

