Supporting Information – Part 2

Stereoselective Synthesis of Unnatural (2*S*,3*S*)-6-Hydroxy-4-Sphingenine-Containing Sphingolipids

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Content

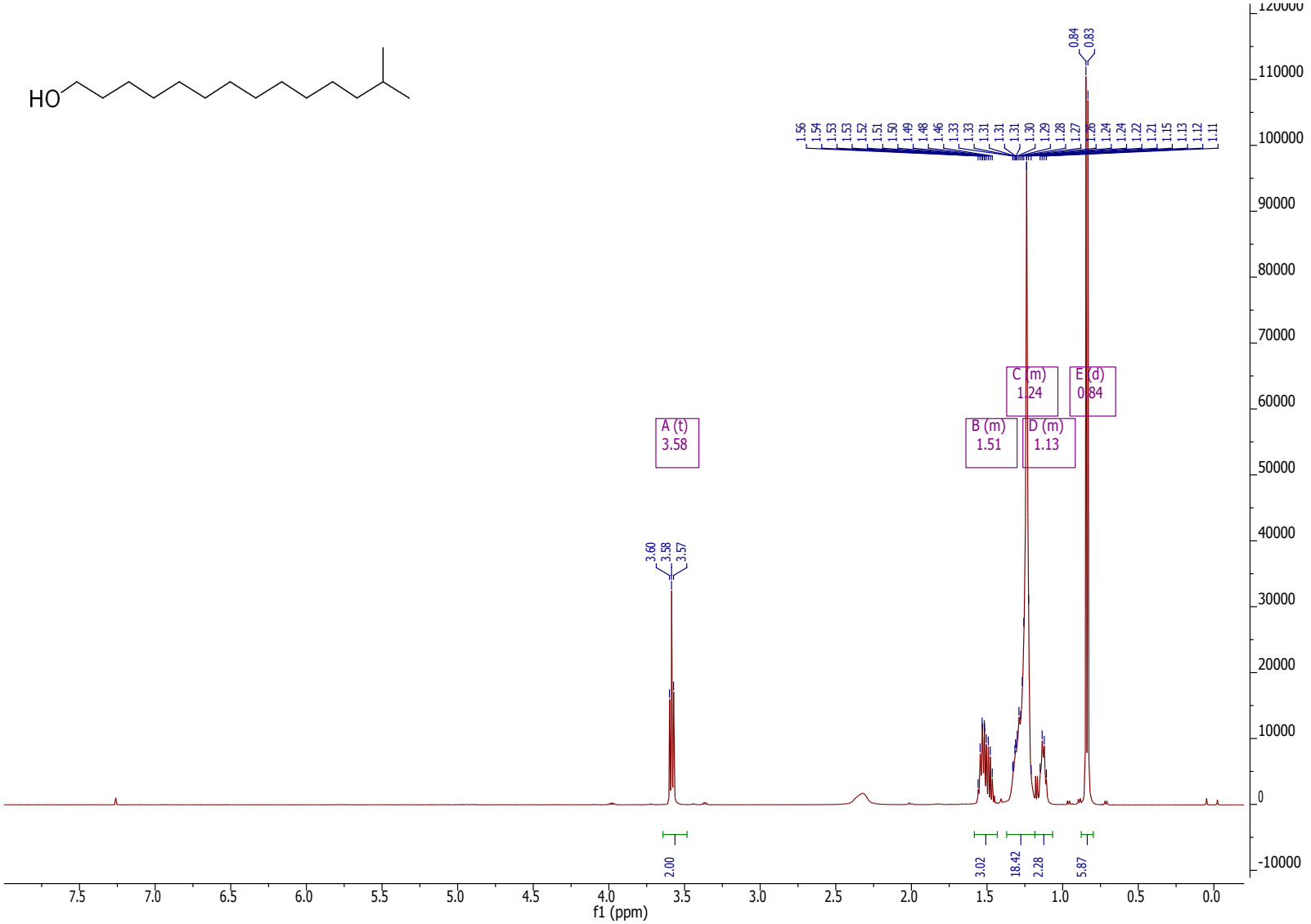

Figure 1. ^{1}H NMR (500 MHz, $CDCl_3$) of 13-methyltetradecanol (A).

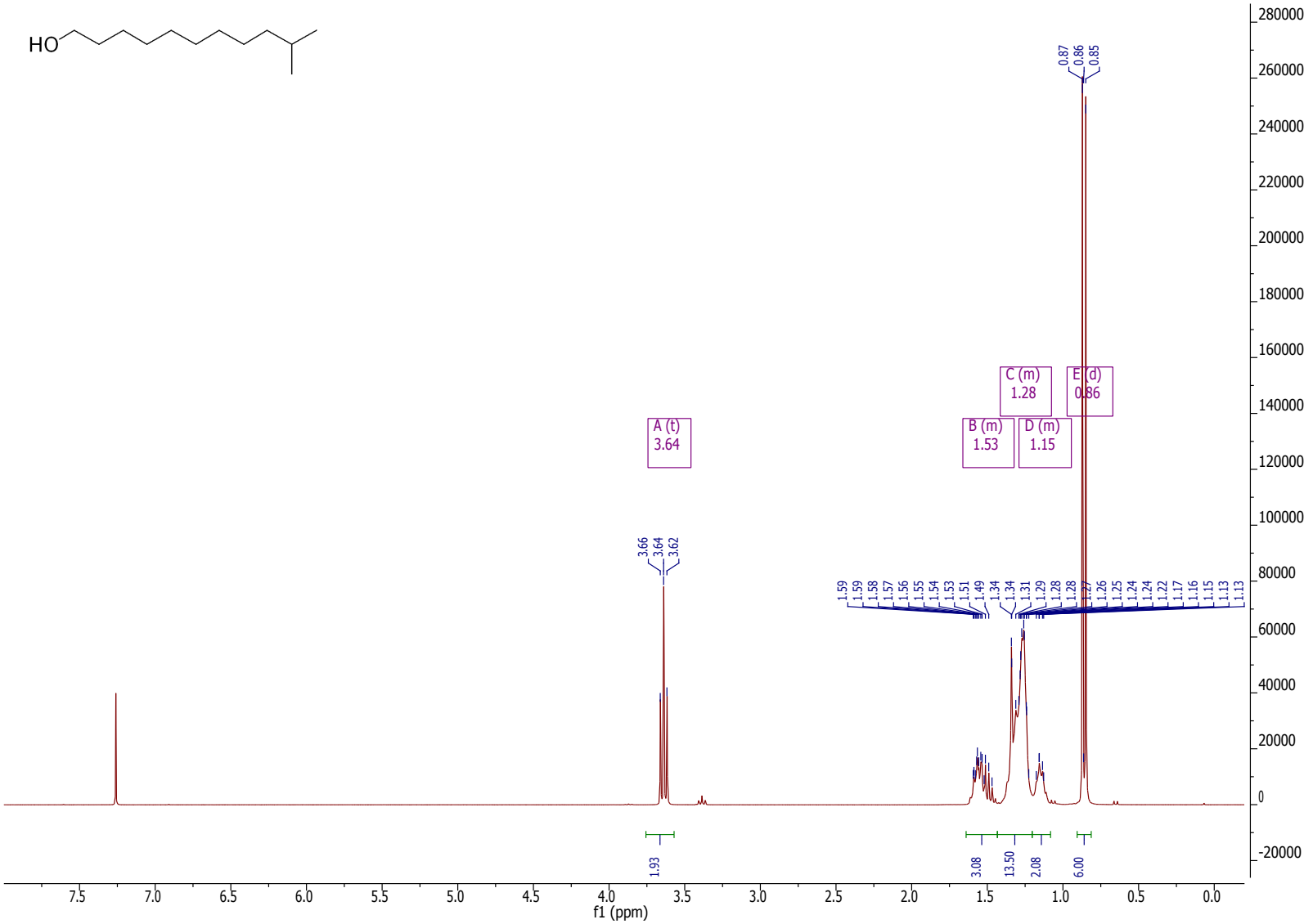

Figure 2. ^{1}H-NMR (300 MHz, $CDCl_3$) of 10-methylundecanol (B).

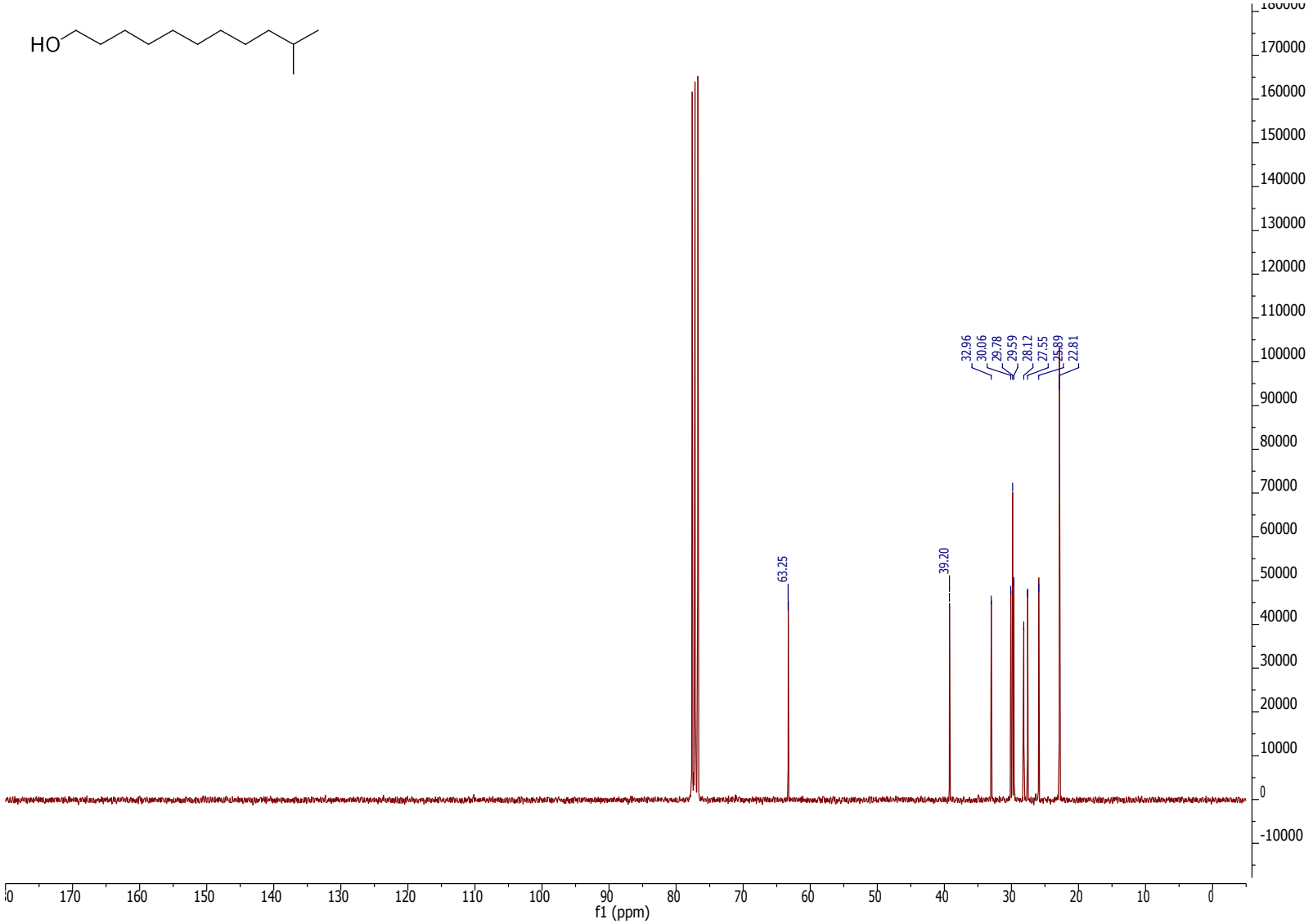

Figure 3. ^{13}C-NMR (75 MHz, $CDCl_3$) of 10-methylundecanol (B).

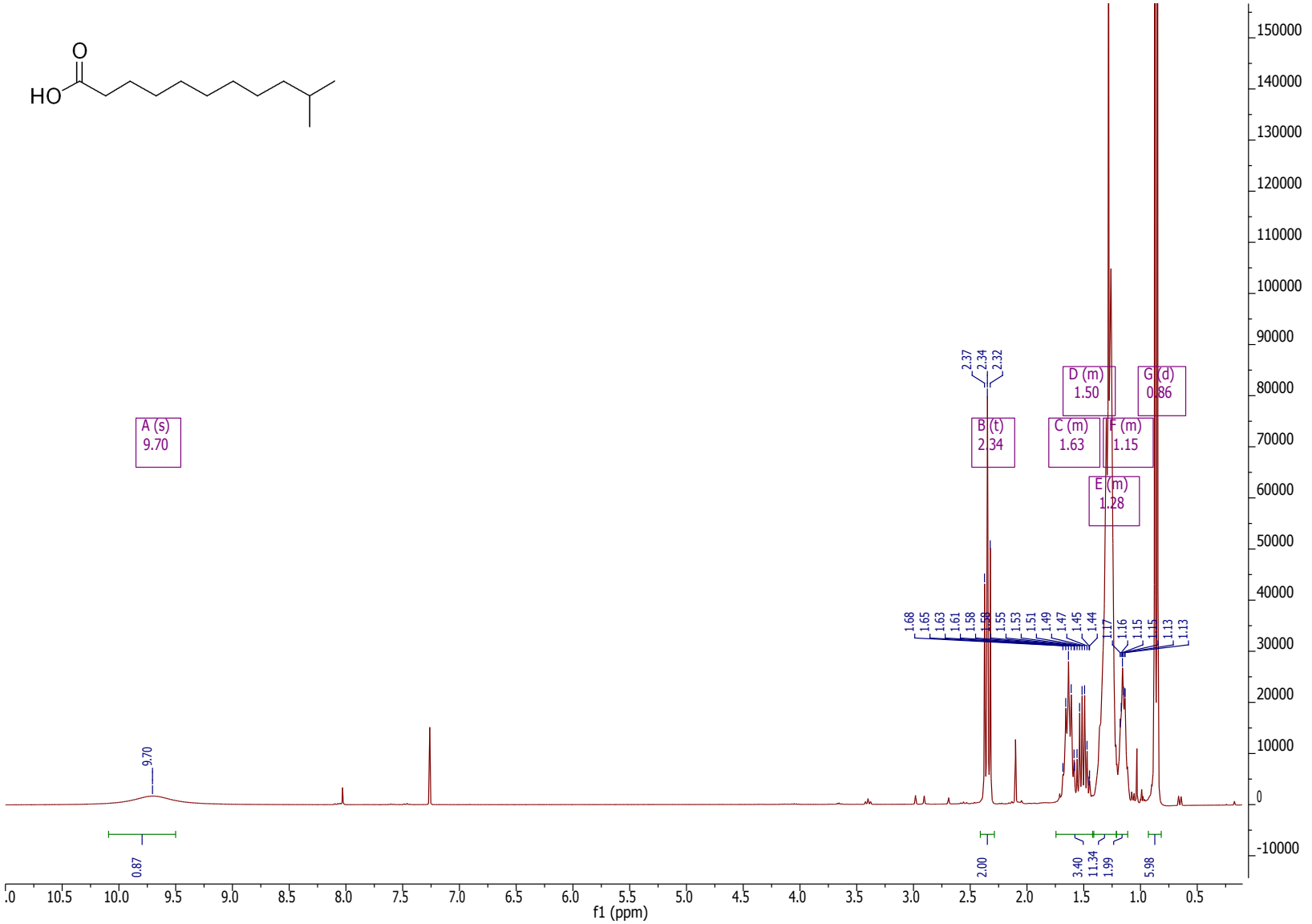

Figure 4. ^{1}H-NMR (300 MHz, $CDCl_3$) of 10-methylundecanoic acid (13a).

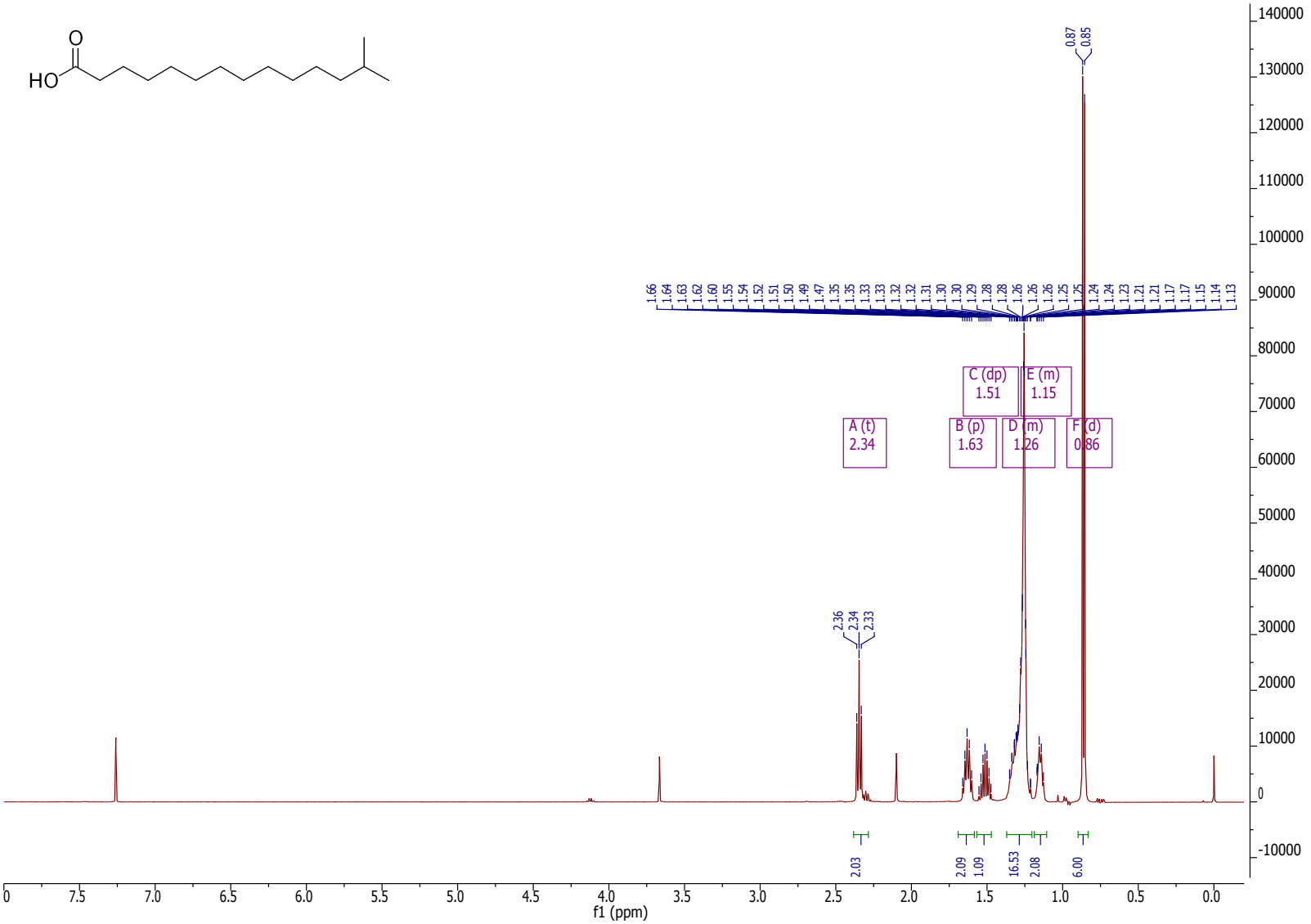

Figure 5. ^{1}H-NMR (500 MHz, $CDCl_3$) of 13-methyltetradecanoic acid (13b).

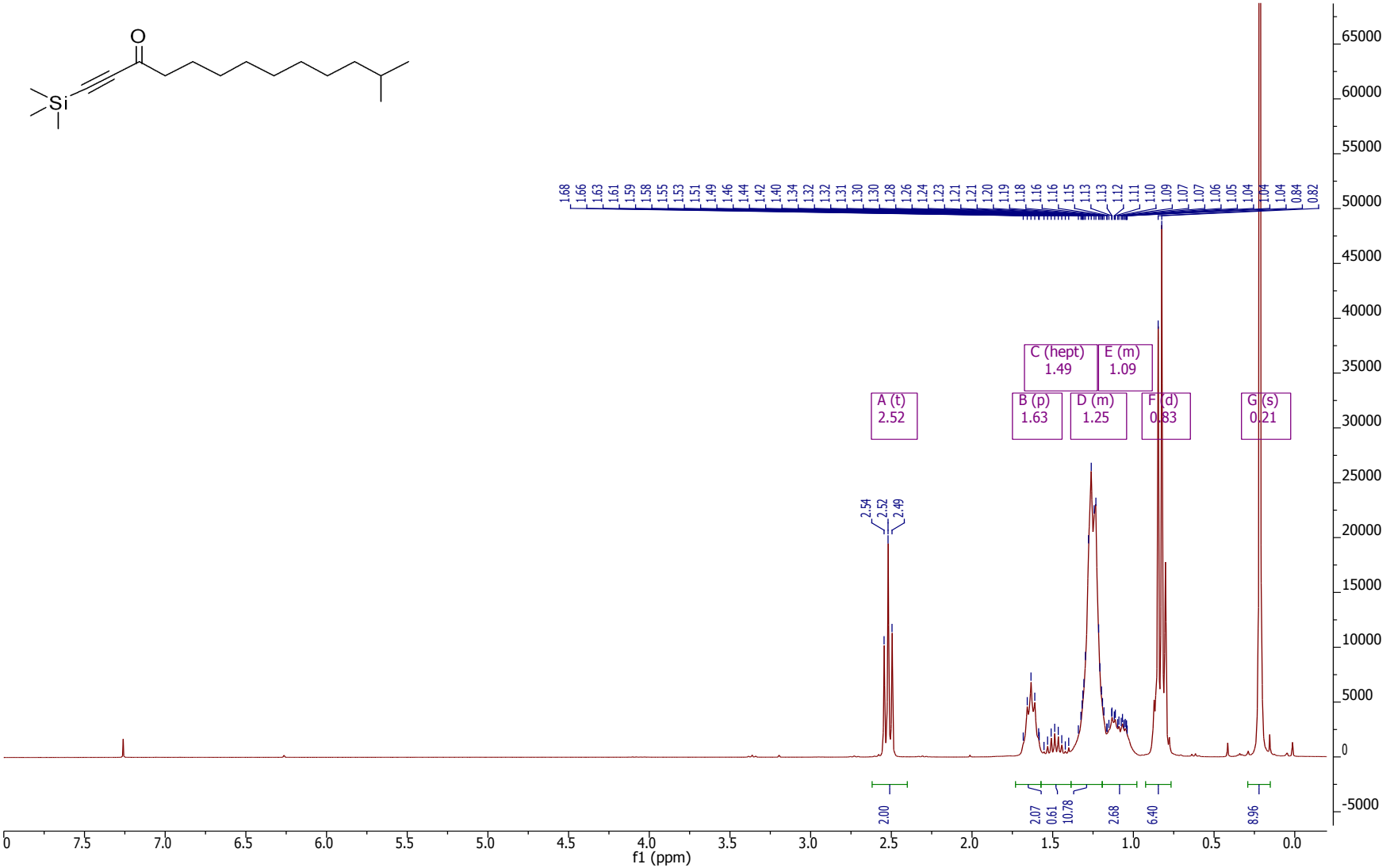

Figure 6. ^{1}H-NMR (300 MHz, $CDCl_3$) of 12-methyl-1-(trimethylsilyl)tridec-1-yn-3-one (14a).

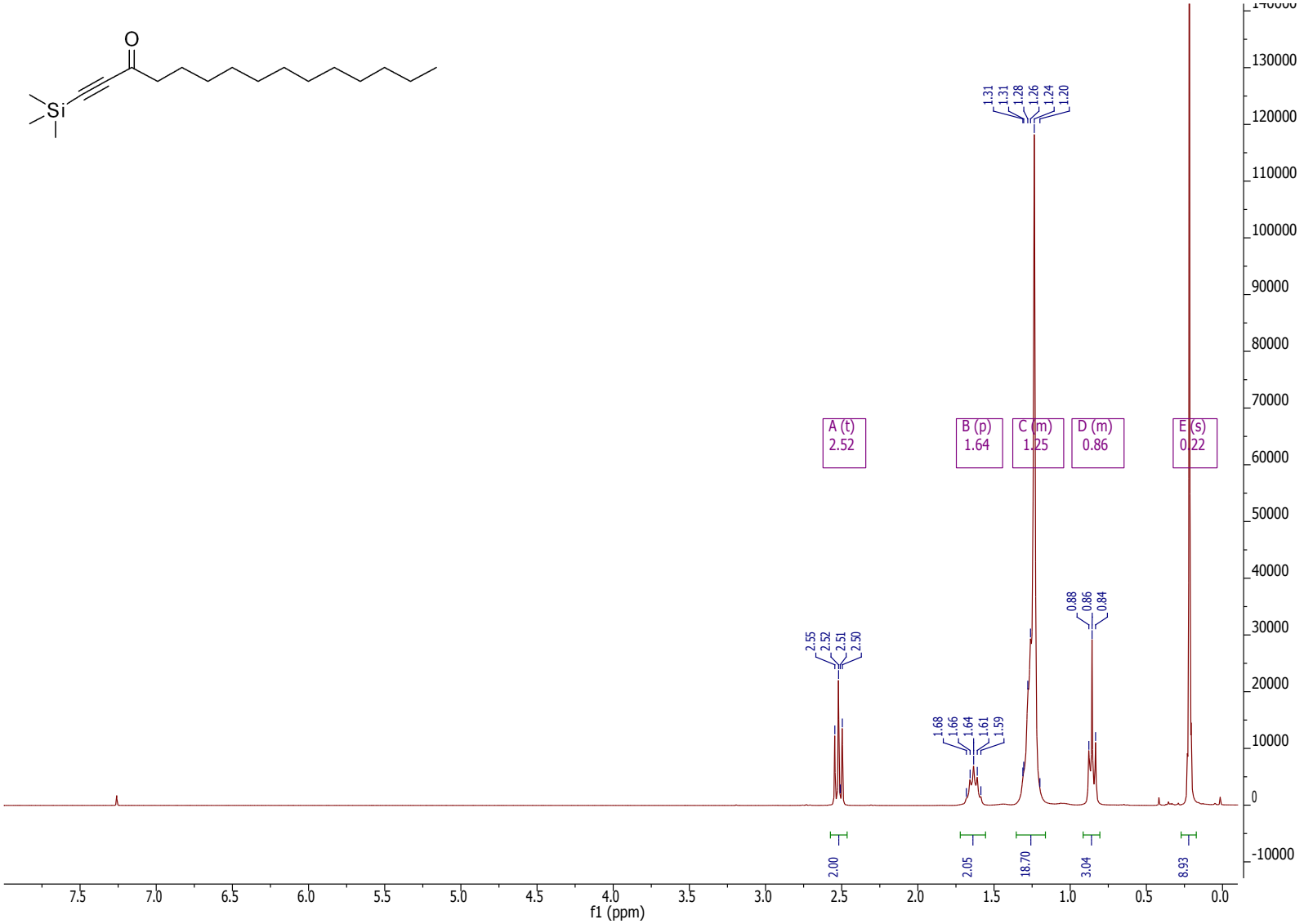

Figure 7. ^{1}H-NMR (300 MHz, $CDCl_3$) of 1-(trimethylsilyl)pentadec-1-yn-3-one (14b).

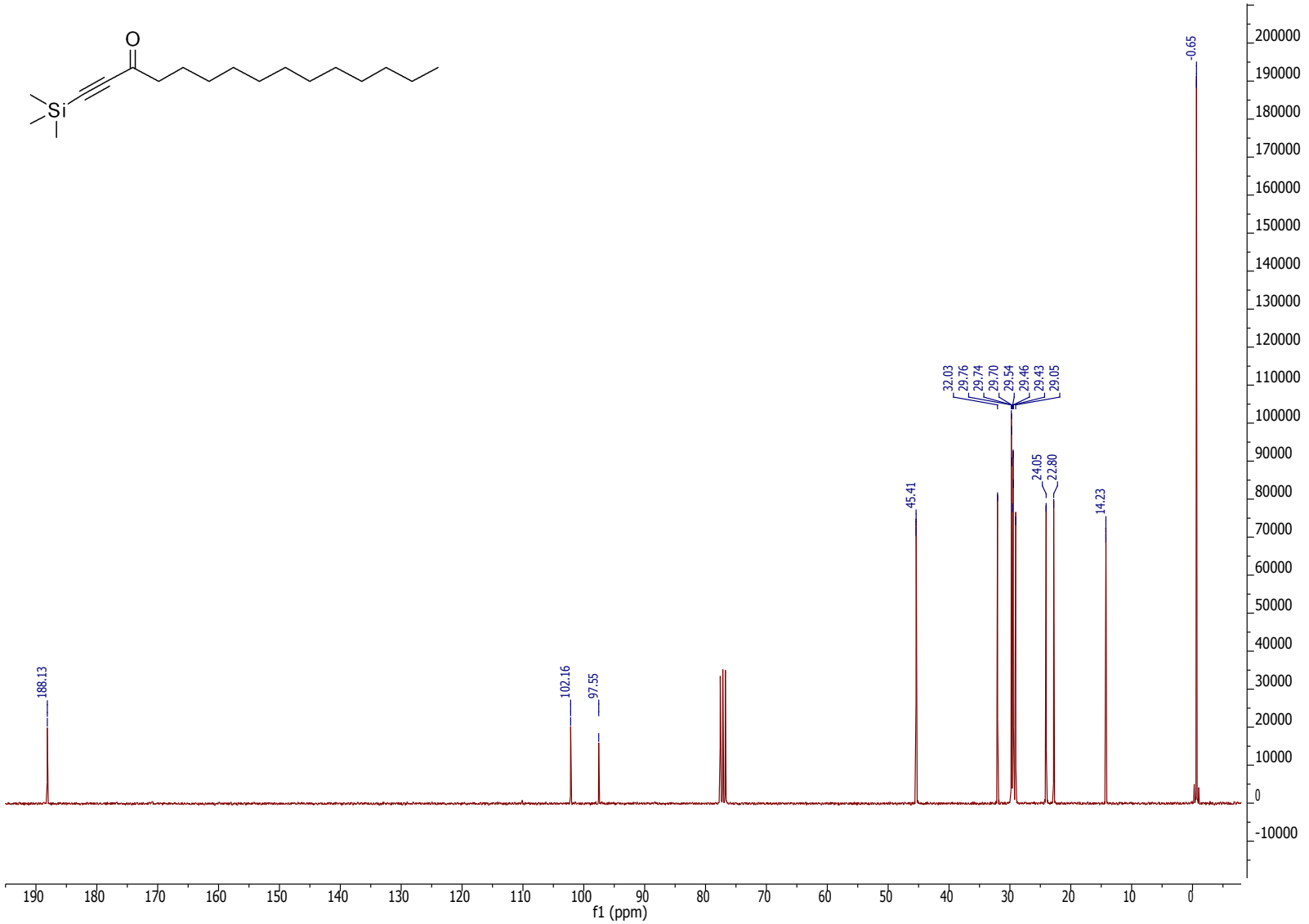

Figure 8. ^{13}C-NMR (75 MHz, $CDCl_3$) of 1-(trimethylsilyl)pentadec-1-yn-3-one (14b).

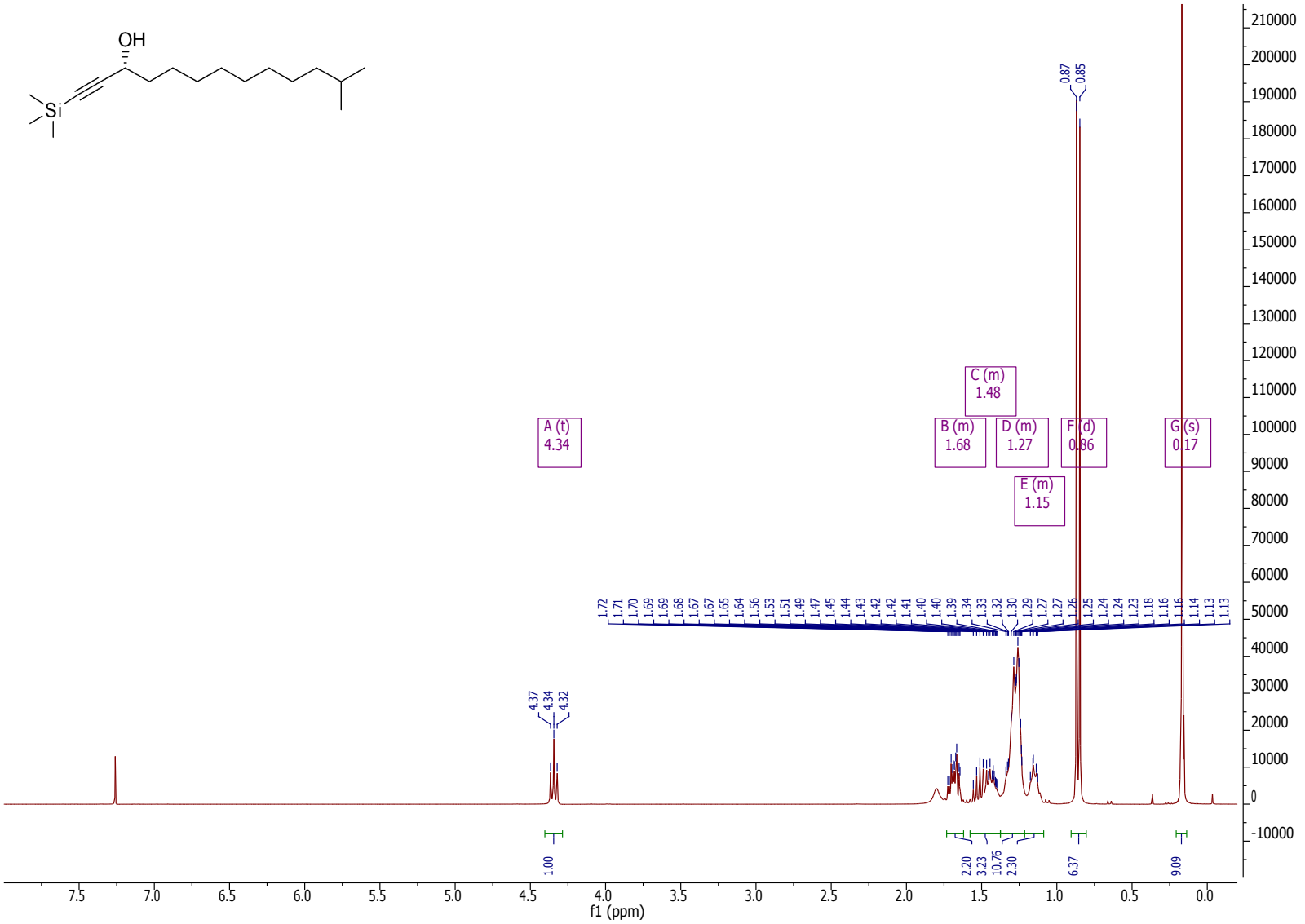

Figure 9. ^{1}H-NMR (300 MHz, $CDCl_3$) of (*R*)-12-methyl-1-tridec-1-yn-3-ol (C).

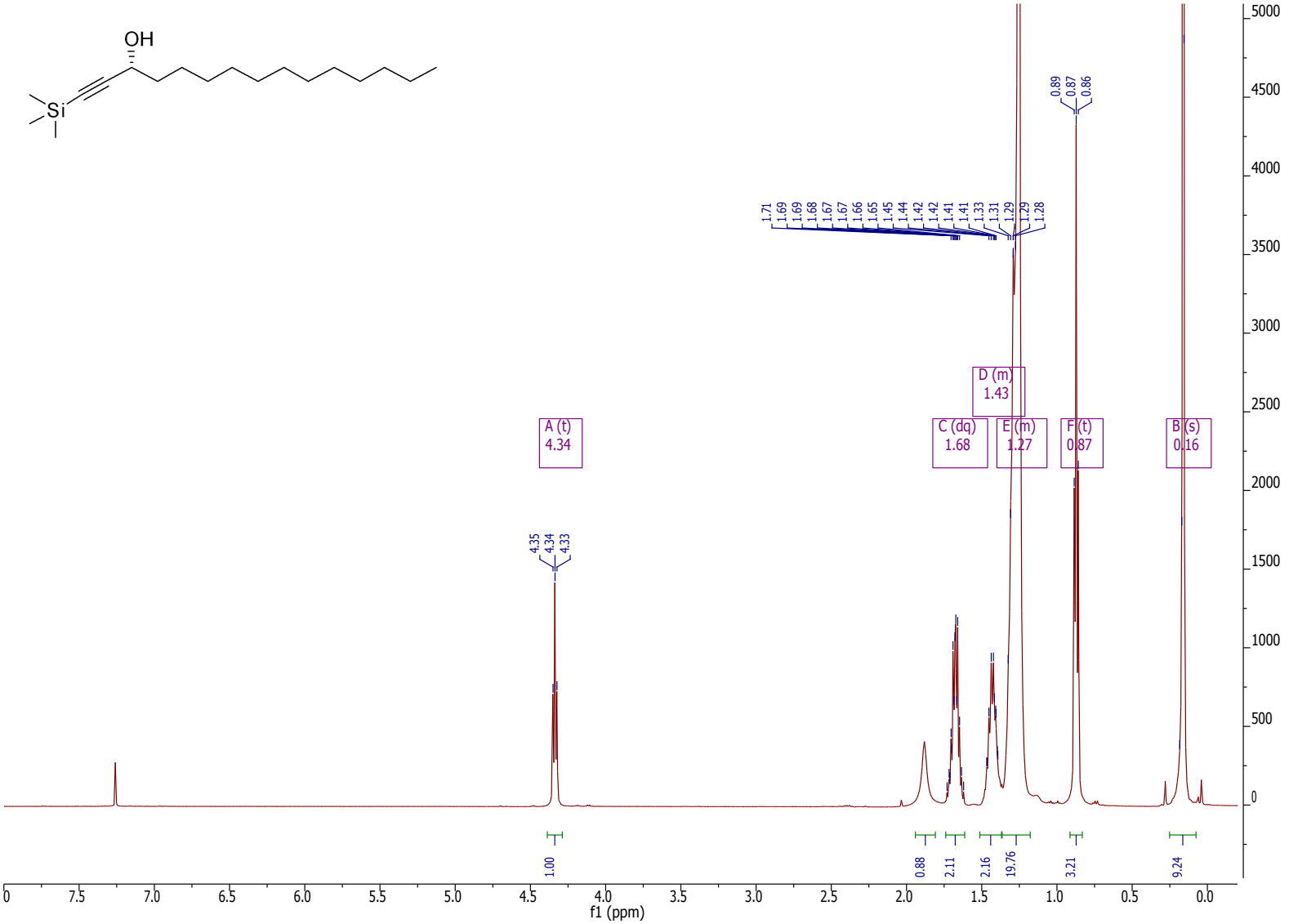

Figure 10. ^{13}C-NMR (500 MHz, $CDCl_3$) of (*R*)-1-(trimethylsilyl)pentadec-1-yn-3-ol (D).

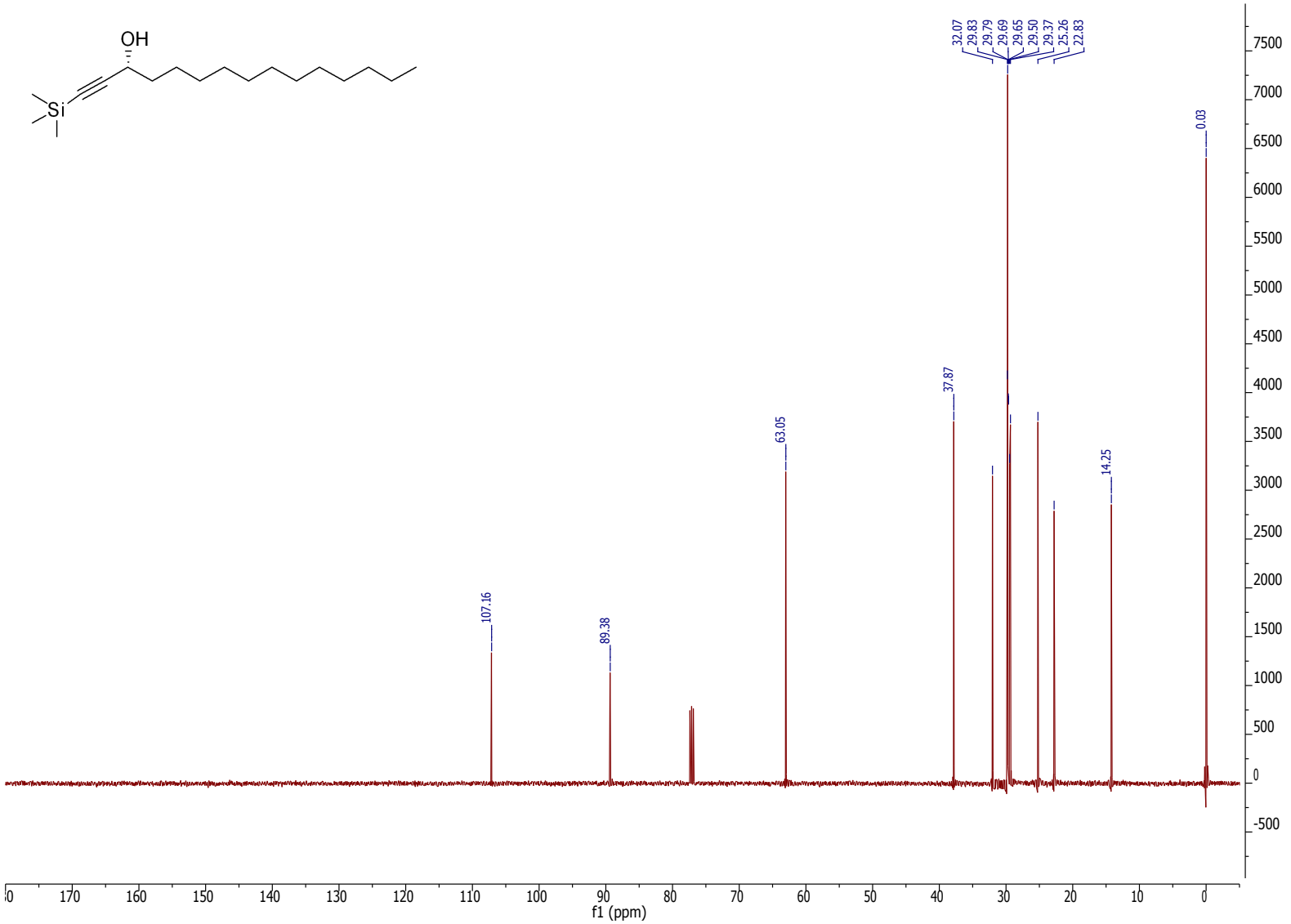

Figure 11. ^{13}C-NMR (126 MHz, $CDCl_3$) of (*R*)-1-(trimethylsilyl)pentadec-1-yn-3-ol (D).

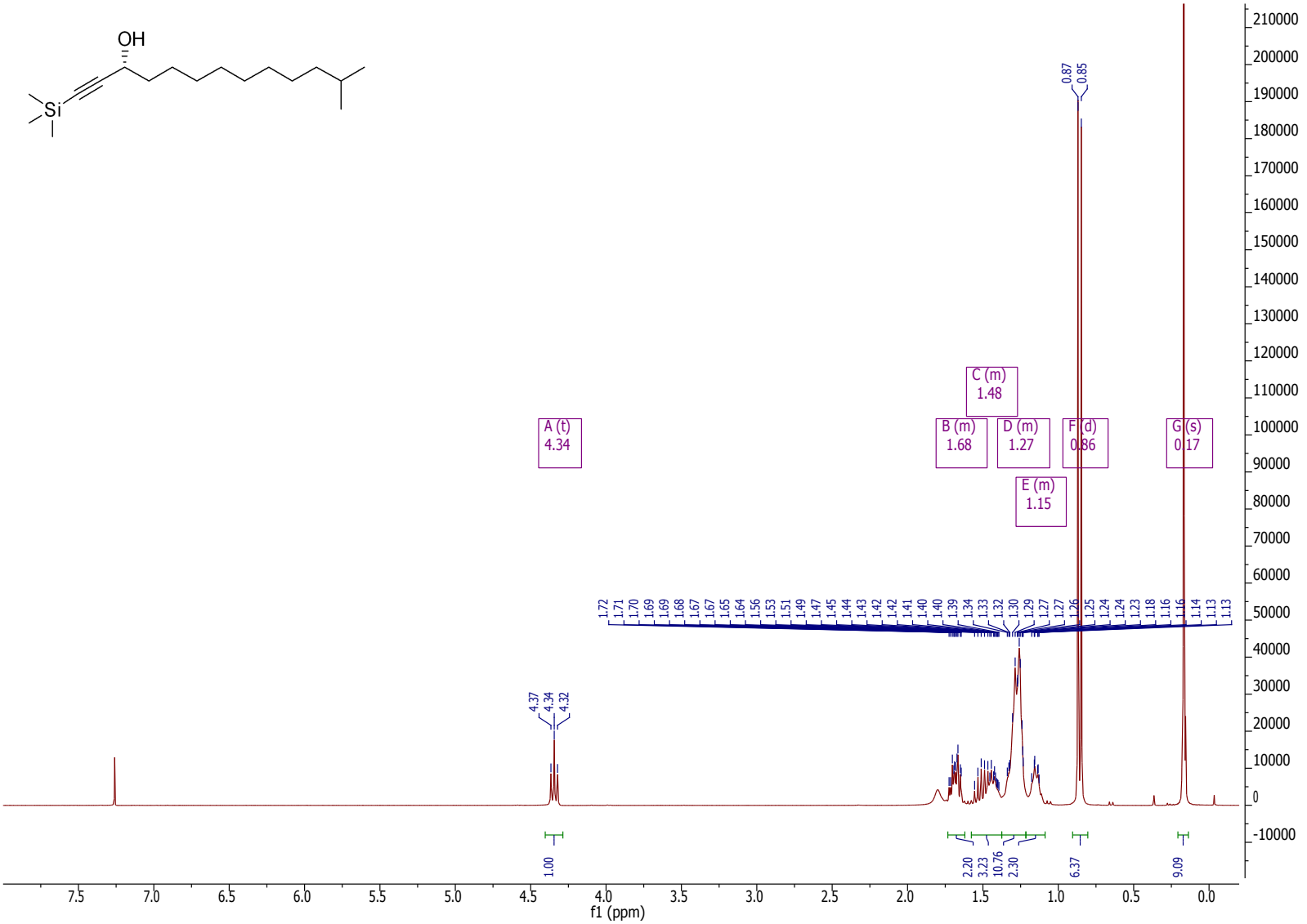

Figure 12. ^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-12-Methyl-1-tridec-1-yn-3-ol (E)

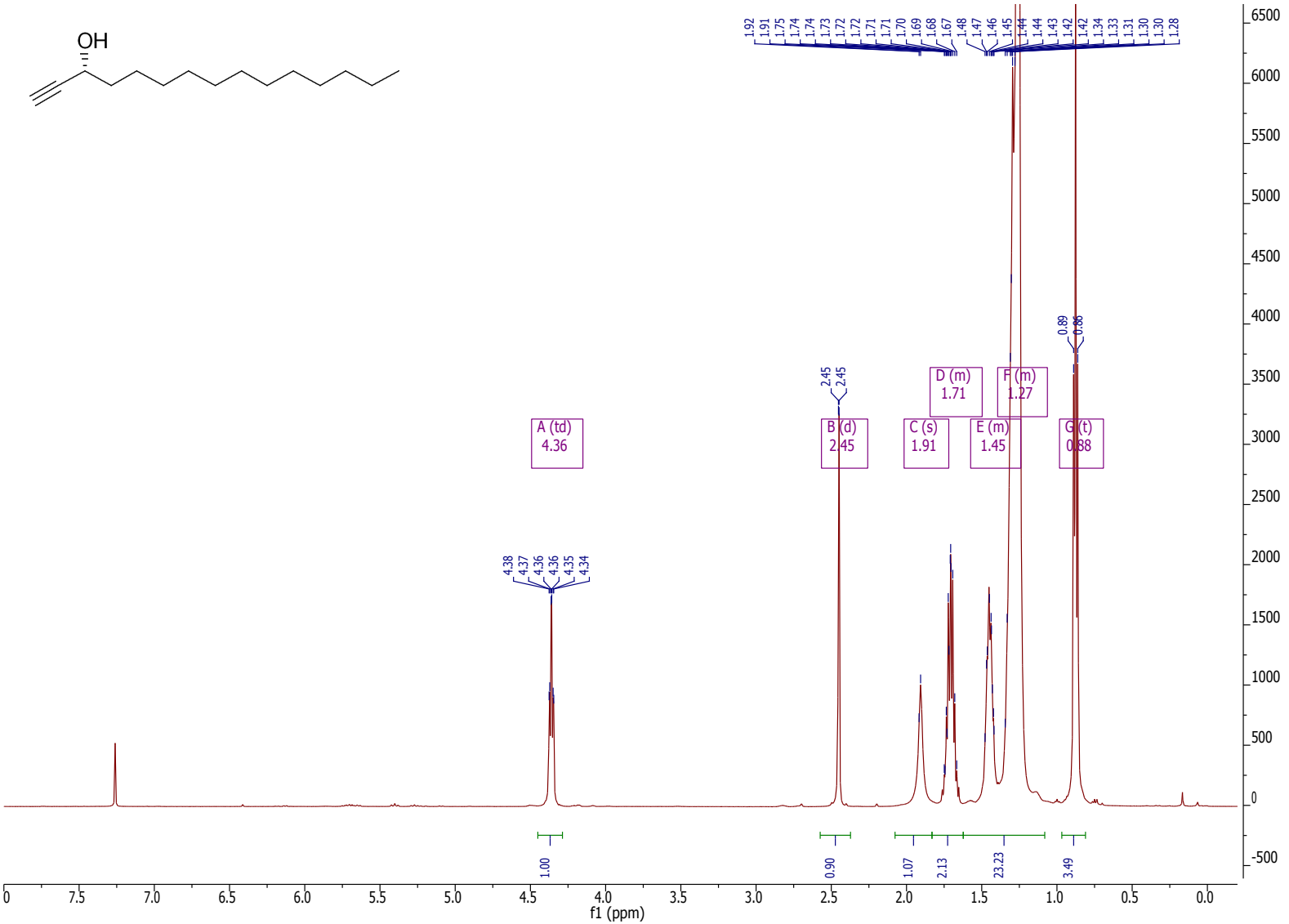

Figure 13. ^{1}H-NMR (500 MHz, $CDCl_3$) of (*R*)-pentadec-1-yn-3-ol (F).

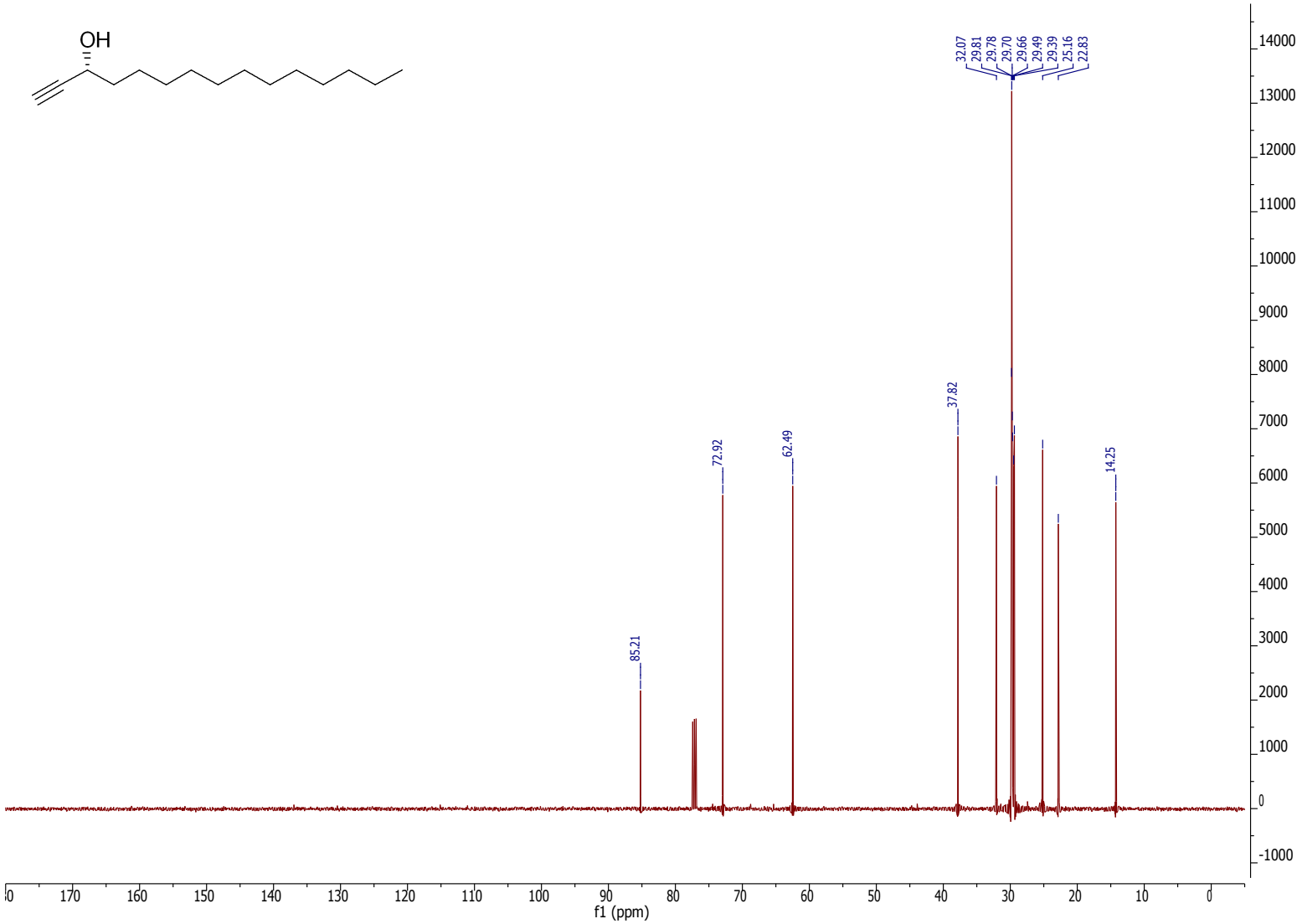

Figure 14. ^{13}C-NMR (126 MHz, $CDCl_3$) of (*R*)-pentadec-1-yn-3-ol (F).

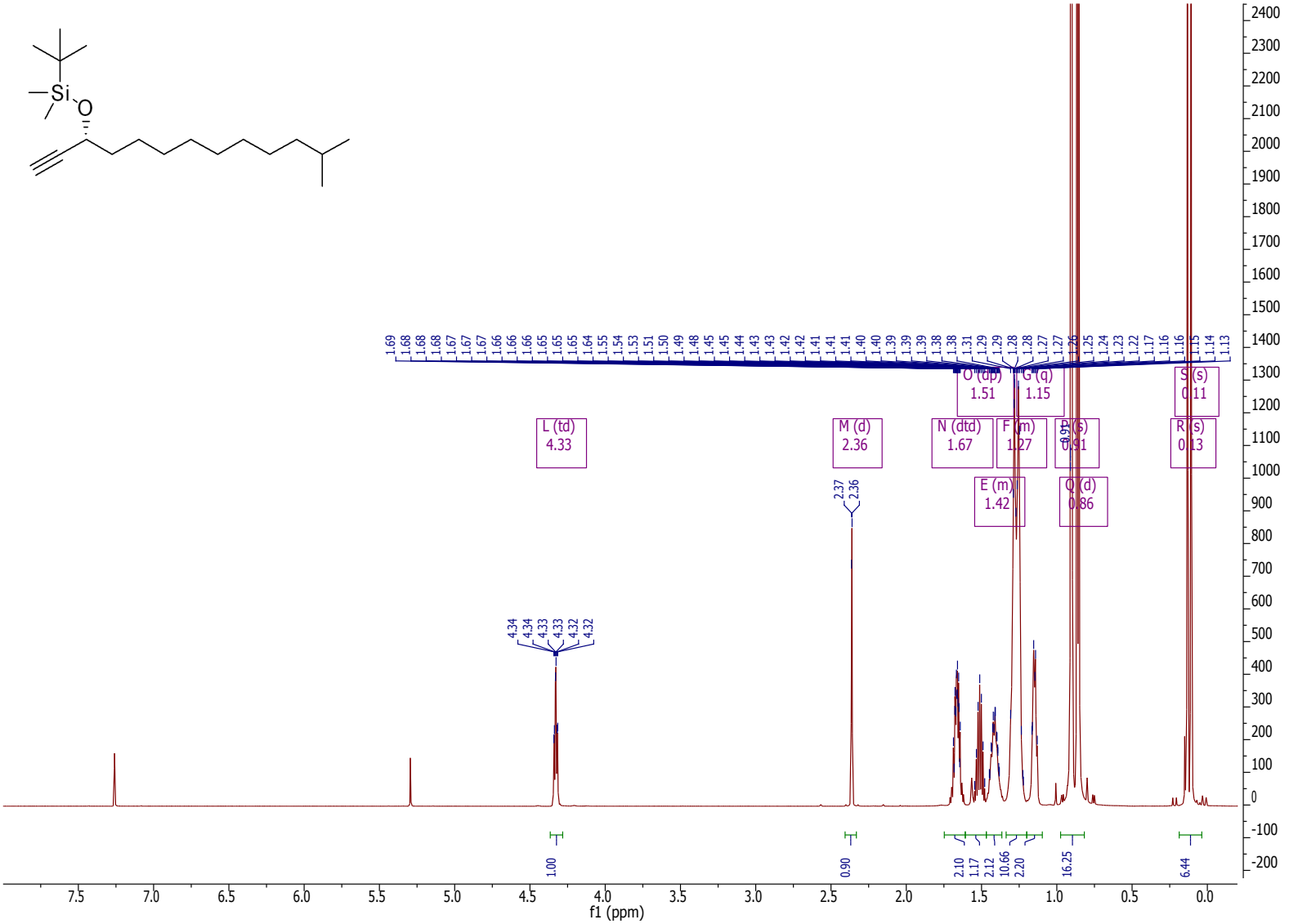

Figure 15. ^{1}H-NMR (600 MHz, $CDCl_3$) of (*R*)-*tert*-butyldimethyl((12-methyl-1-tridec-1-yn-3-yl)oxy)silane (11a).

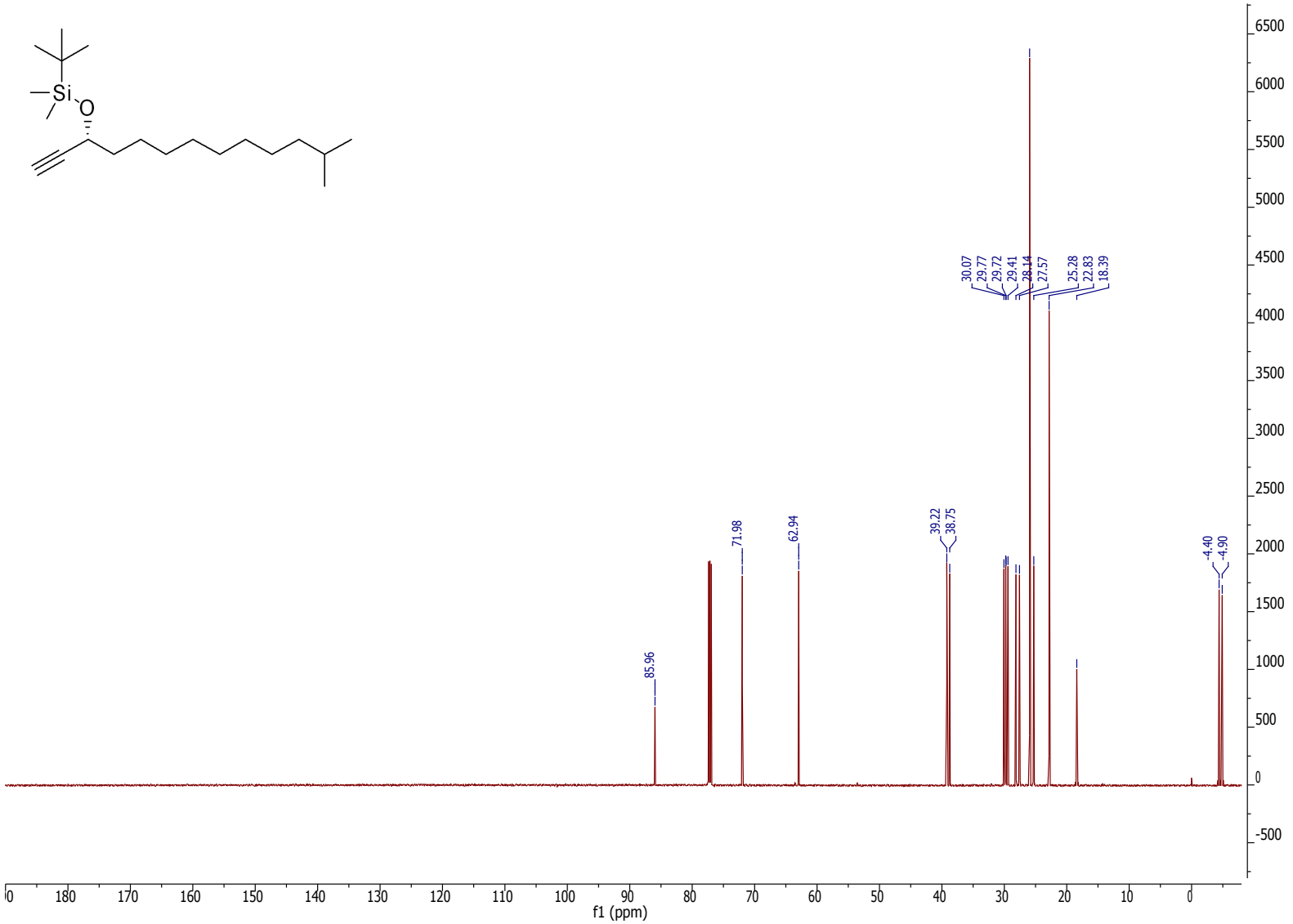

Figure 16. ^{13}C-NMR (151 MHz, $CDCl_3$) of (*R*)-*tert*-butyldimethyl((12-methyl-1-tridec-1-yn-3-yl)oxy)silane (11a).

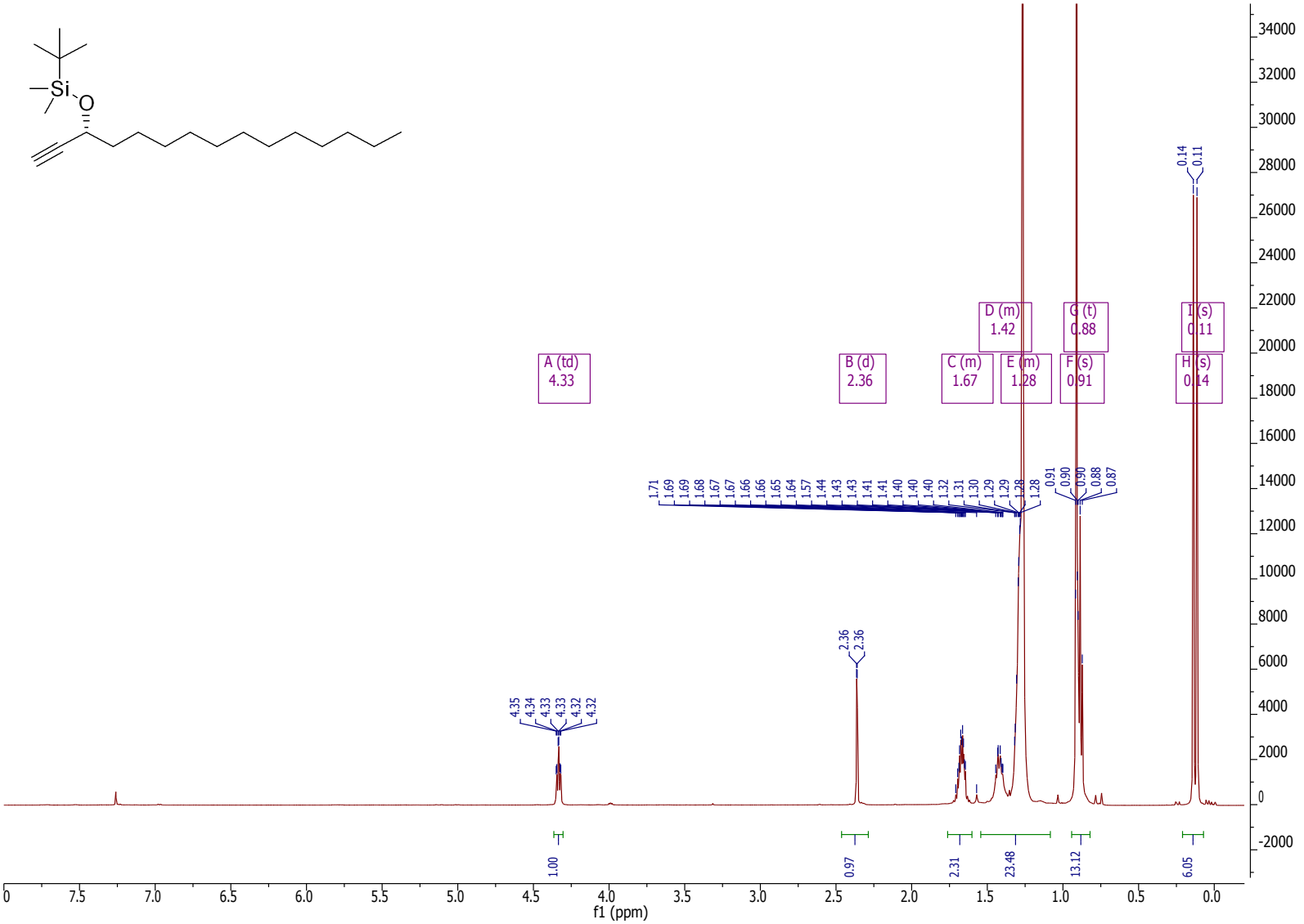

Figure 17. ^{1}H-NMR (500 MHz, $CDCl_3$) of (*R*)-*tert*-butyldimethyl(pentadec-1-yn-3-yloxy)silane (11b).

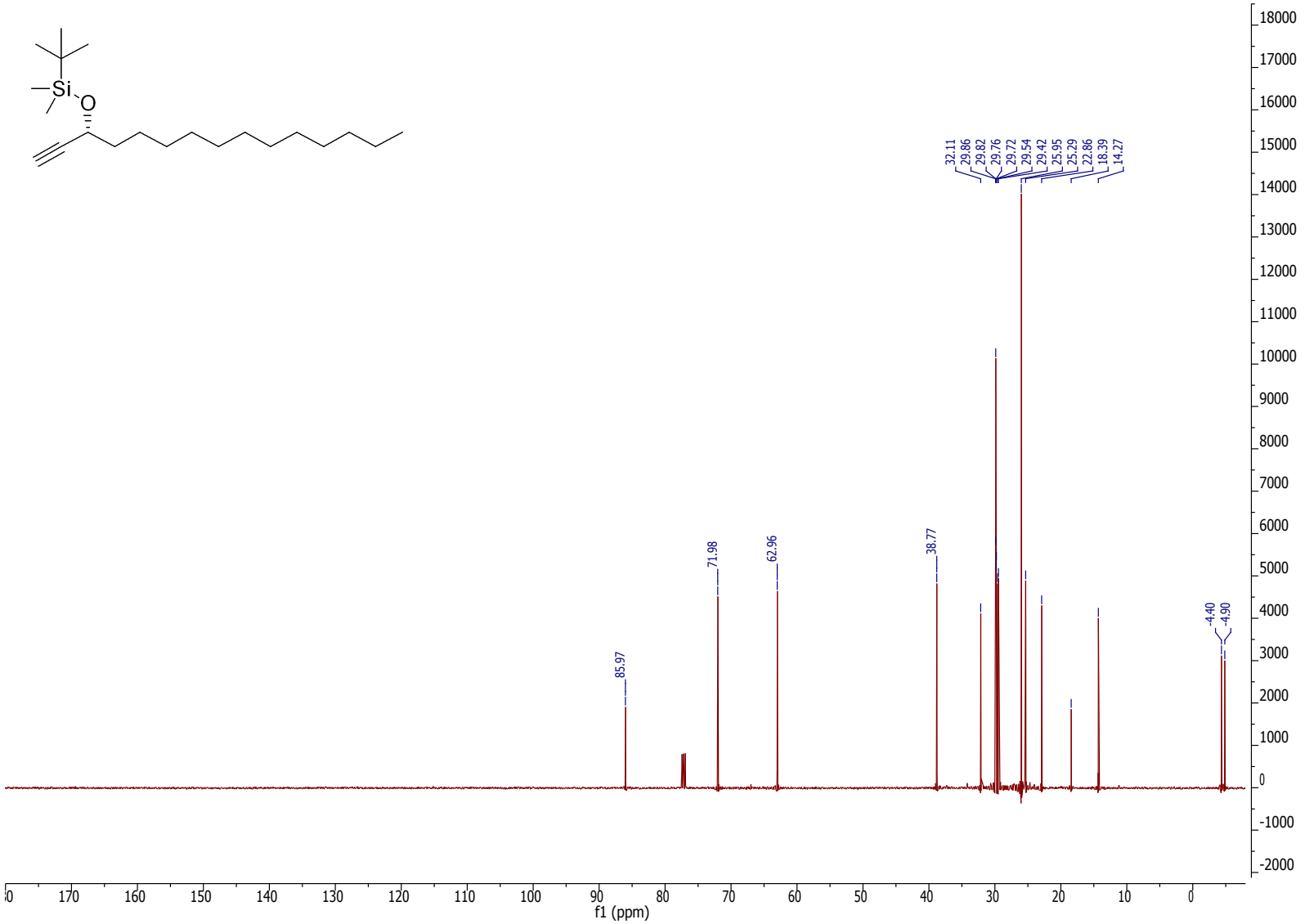

Figure 18. ^{13}C-NMR (126 MHz, $CDCl_3$) of (*R*)-*tert*-butyldimethyl(pentadec-1-yn-3-yloxy)silane (11b).

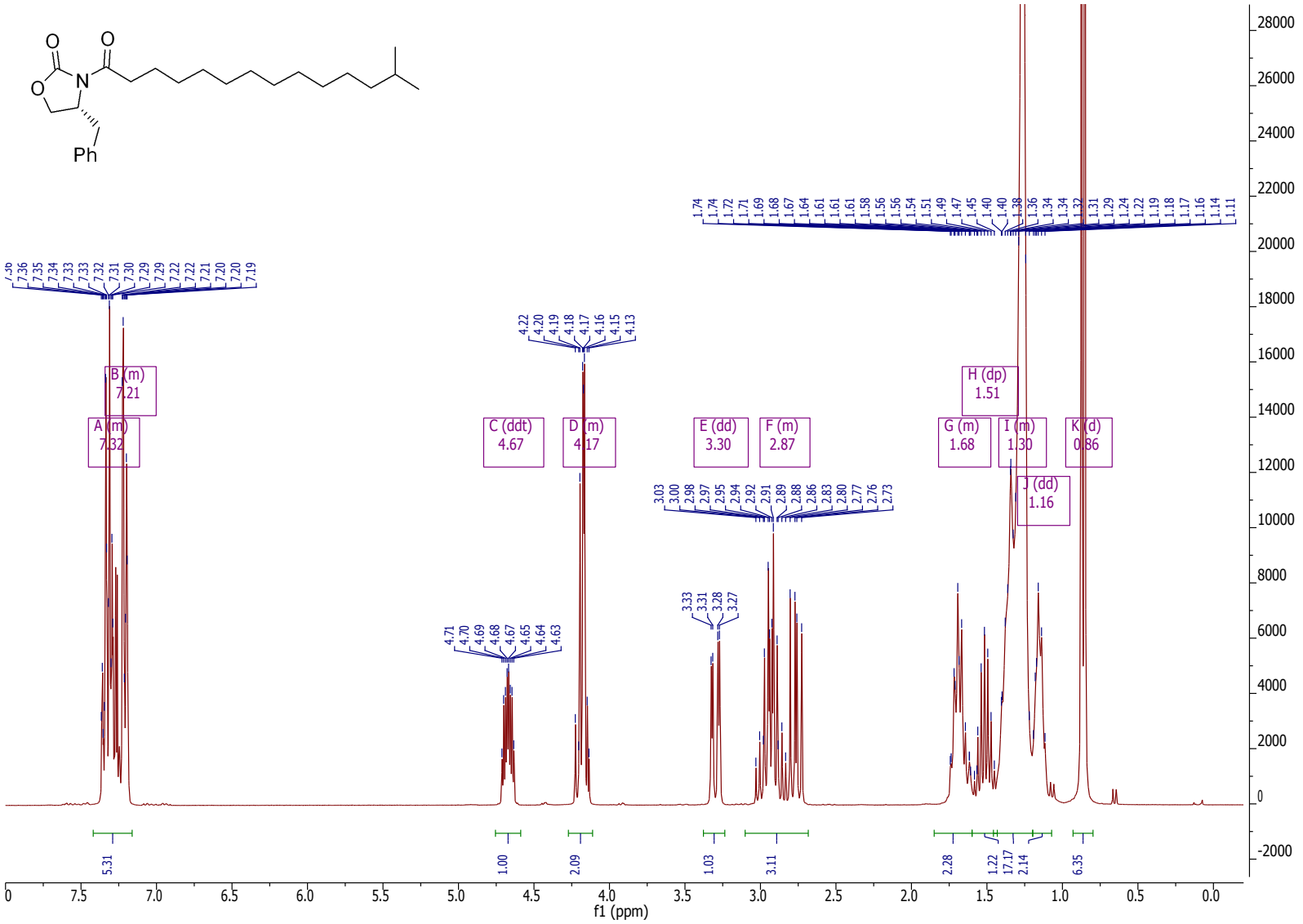

Figure 19. ^{1}H-NMR (300 MHz, $CDCl_3$) of (*R*)-4-benzyl-3-(13-methyltetradecanoyl)oxazolidin-2-one (15a).

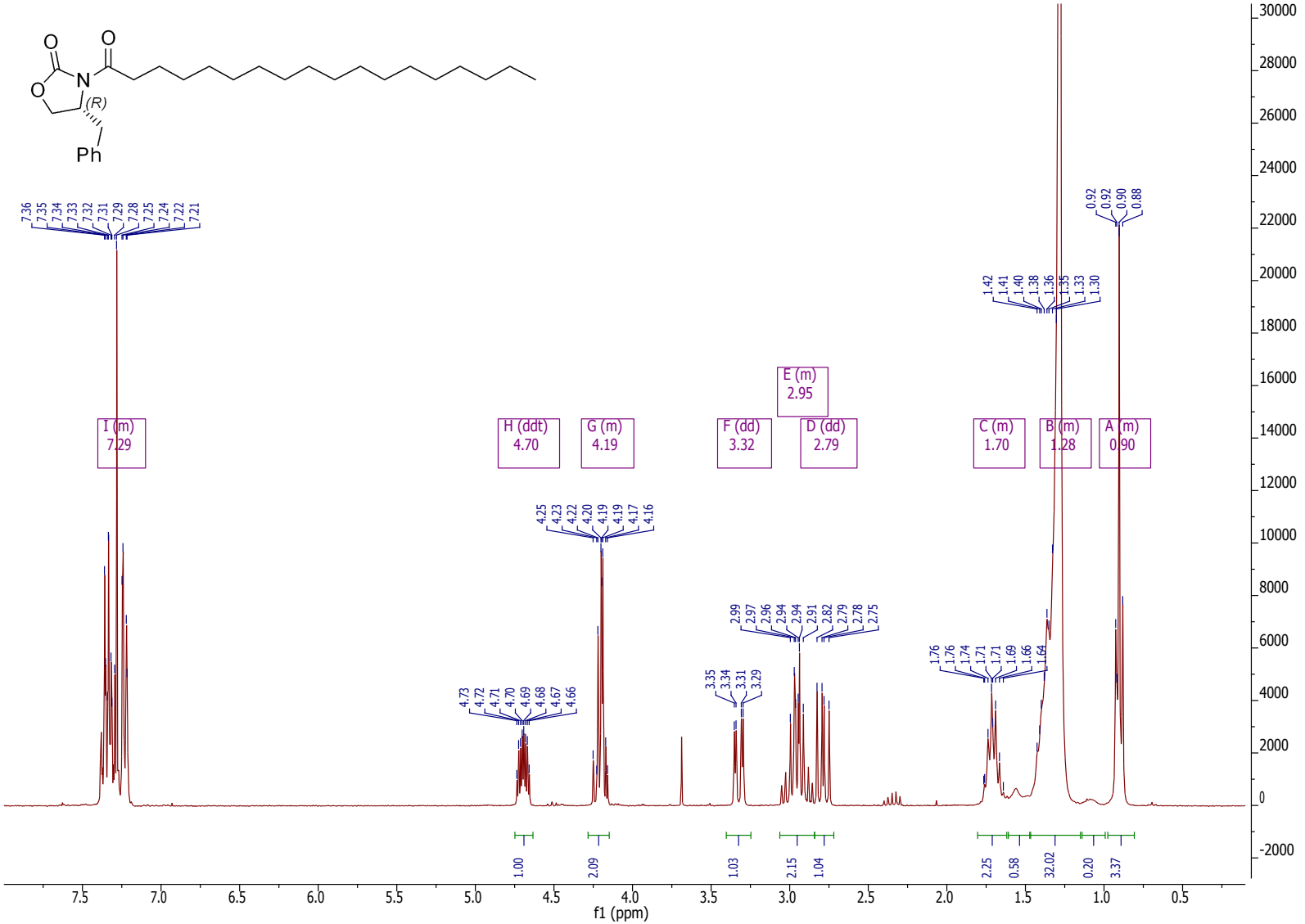

Figure 20. ^{1}H-NMR (75 MHz, $CDCl_3$) of (*R*)-4-benzyl-3-stearoyloxazolidin-2-one (15b).

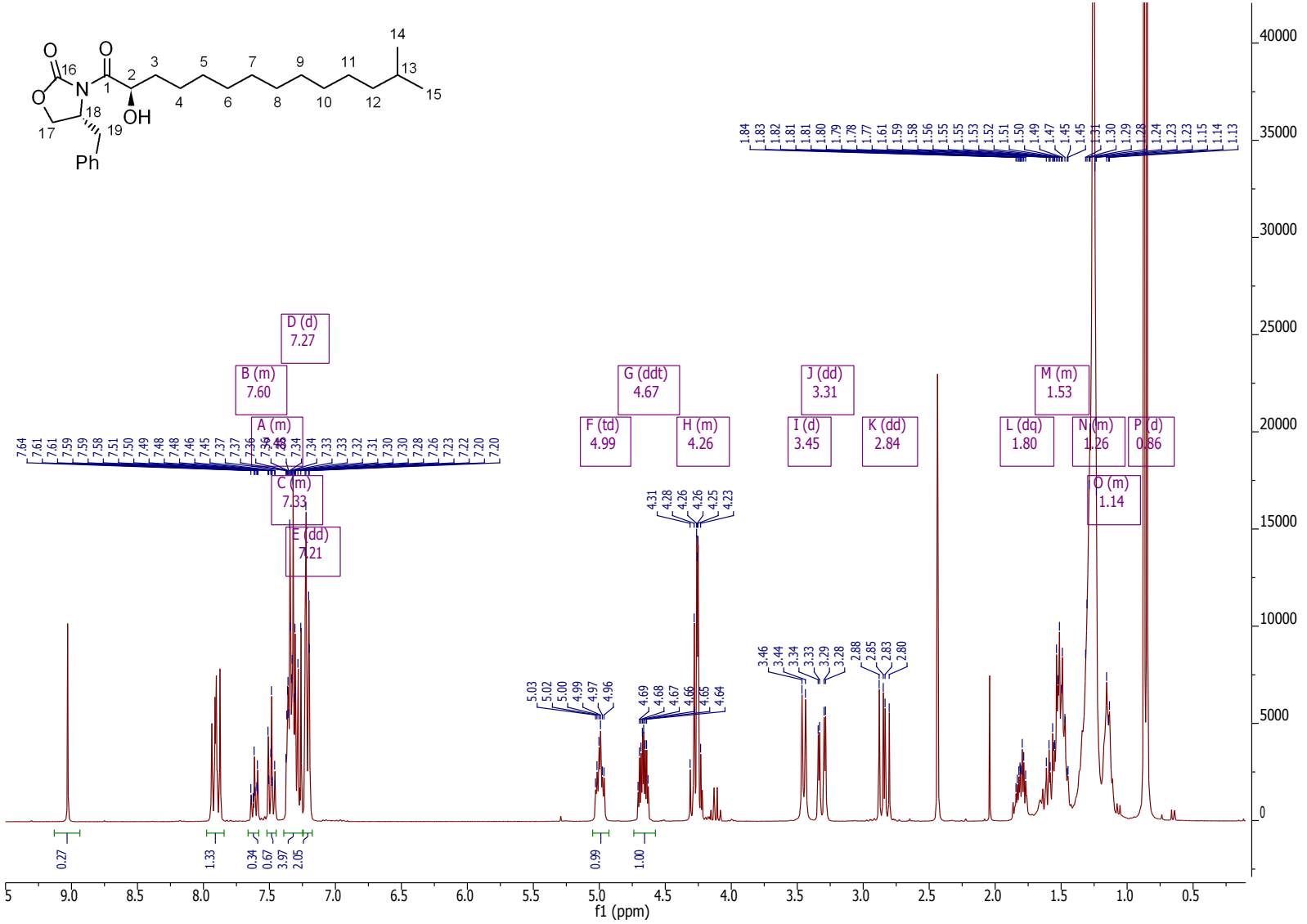

Figure 21. ^{1}H-NMR (300 MHz, $CDCl_3$) of (*R*)-4-benzyl-3-((*R*)-2-hydroxy-13-methyltetradecanoyl)oxazolidin-2-one (G).

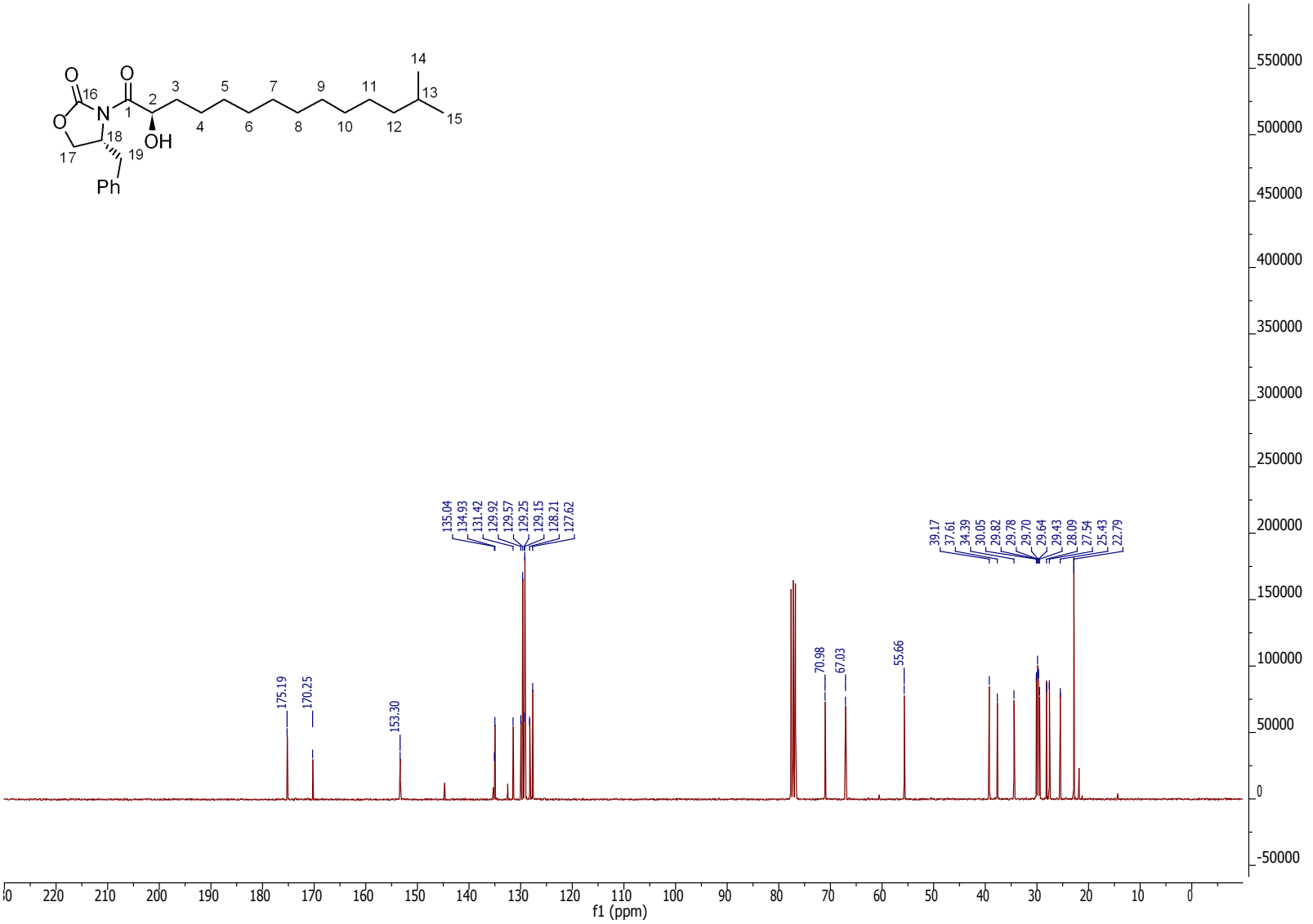

Figure 22. ^{13}C-NMR (75 MHz, $CDCl_3$) of (*R*)-4-benzyl-3-((*R*)-2-hydroxy-13-methyltetradecanoyl)oxazolidin-2-one (G).

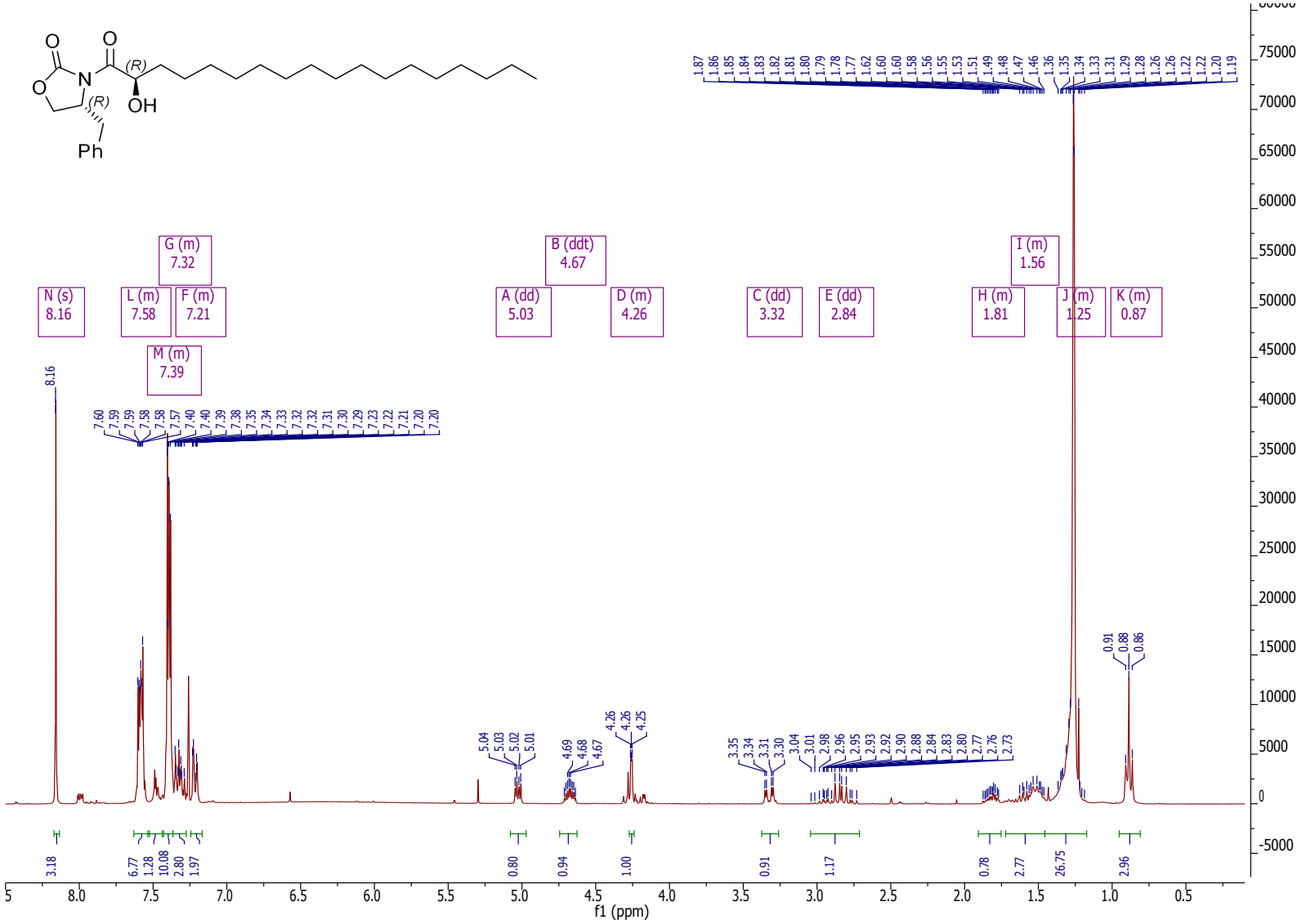

Figure 23. ^{1}H-NMR (300 MHz, $CDCl_3$) of (*R*)-4-benzyl-3-((*R*)-2-hydroxyoctadecanoyl)oxazolidin-2-one (H).

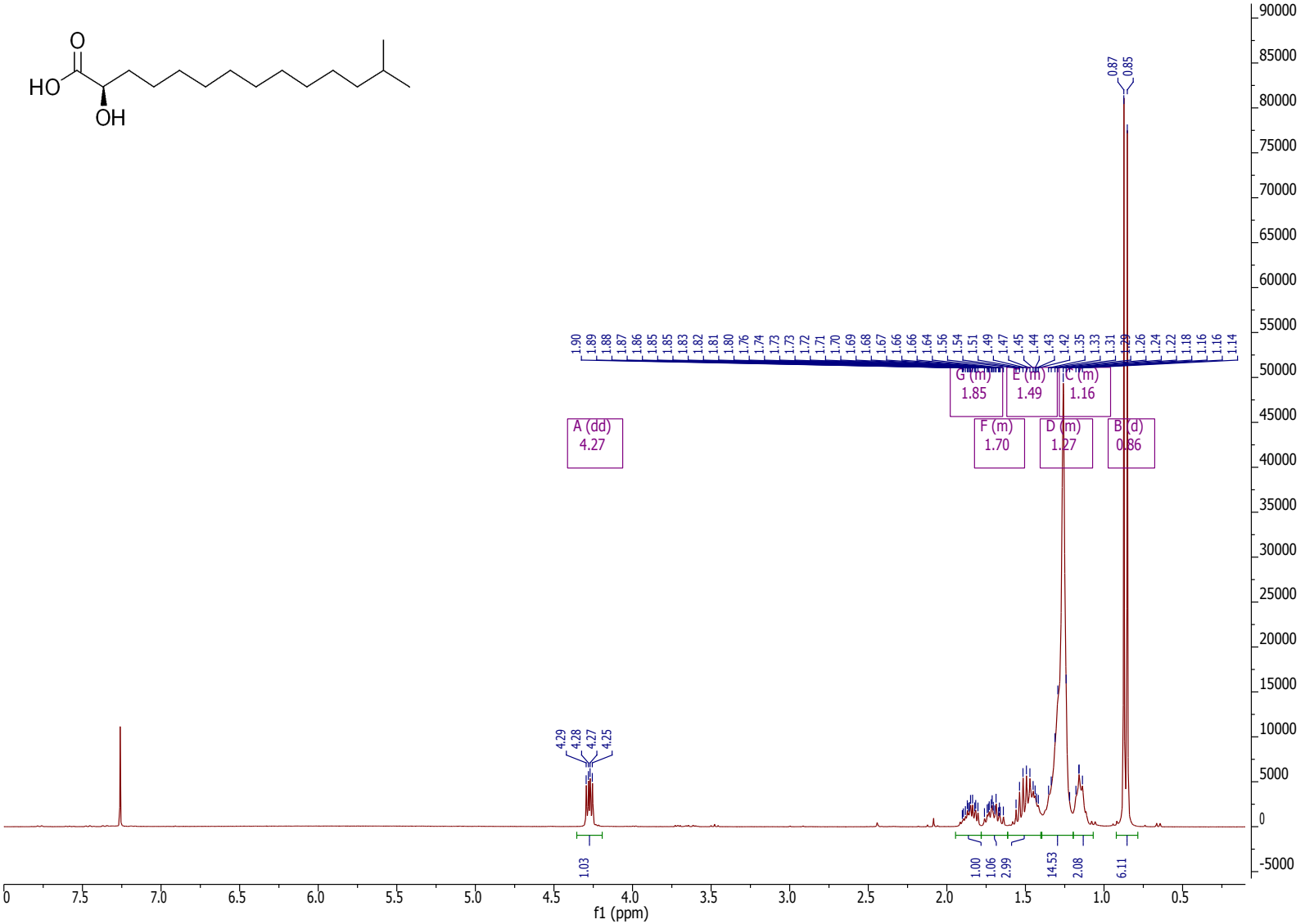

Figure 24. ^{1}H-NMR (300 MHz, $CDCl_3$) of (*R*)-2-hydroxy-13-methyltetradecanoic acid (16a).

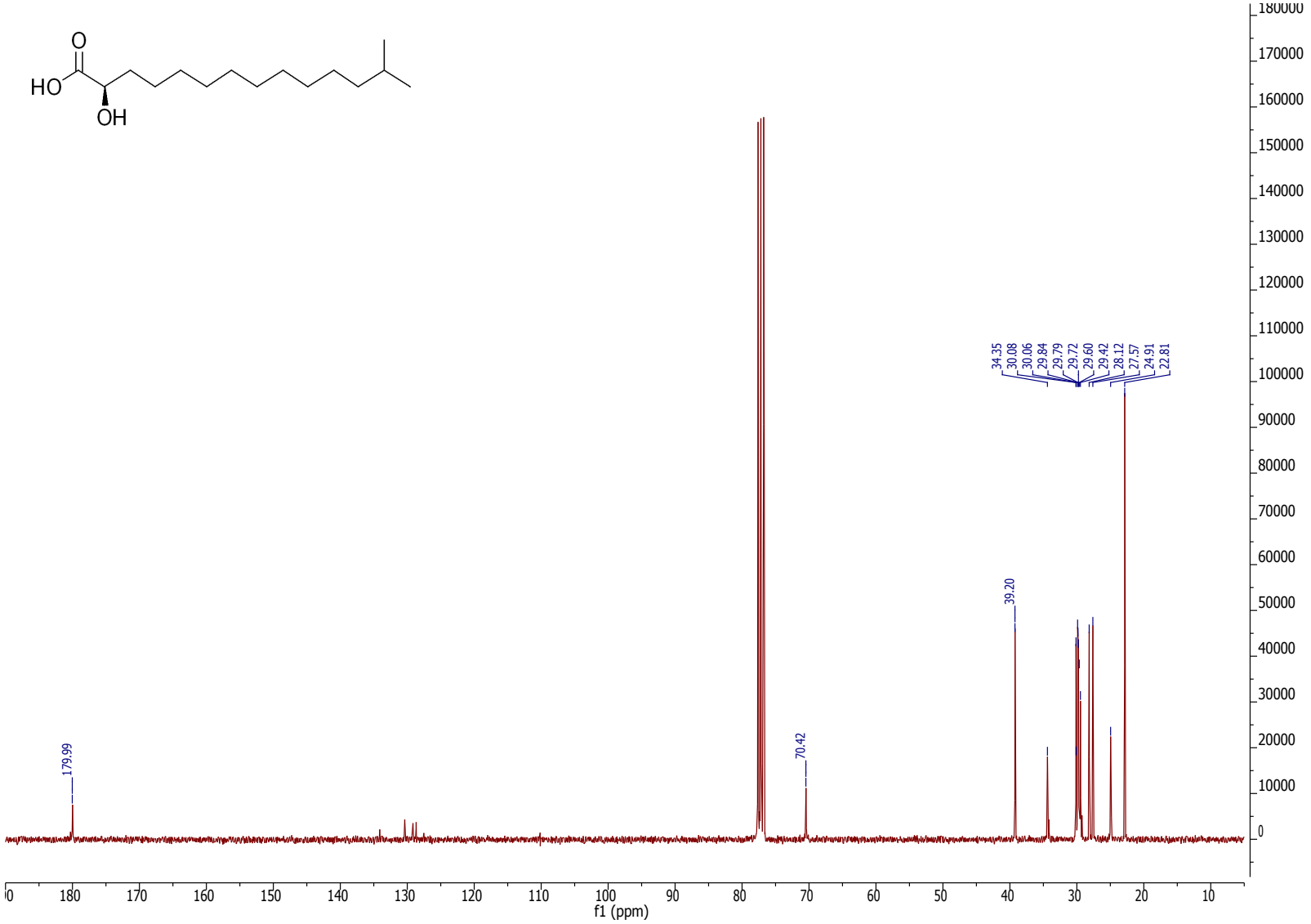

Figure 25. ^{13}C-NMR (75 MHz, $CDCl_3$) of (*R*)-2-Hydroxy-13-methyltetradecanoic acid (16a).

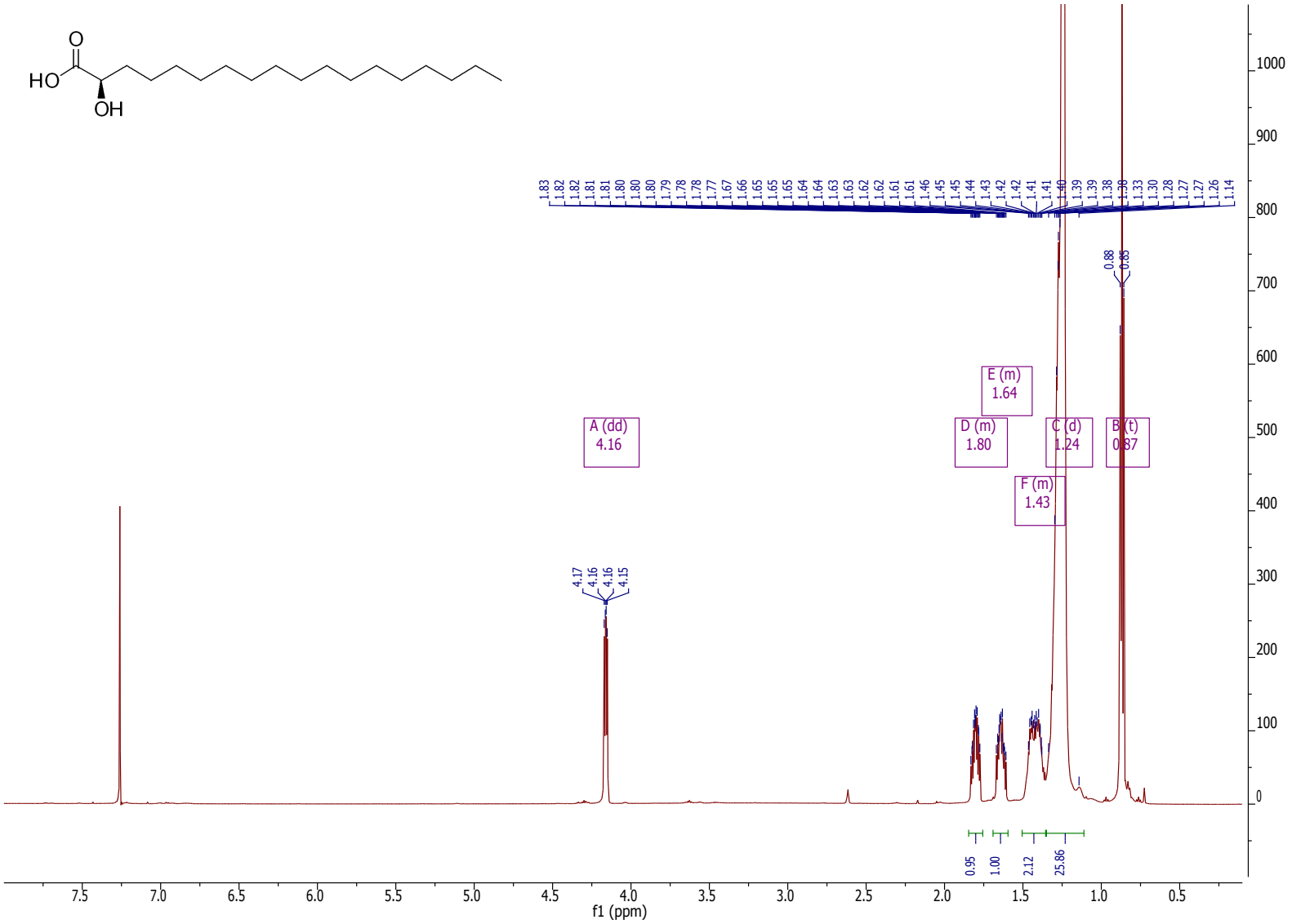

Figure 26. ^{1}H-NMR (600 MHz, $CDCl_3$) of (*R*)-2-hydroxyoctadecanoic acid (16b).

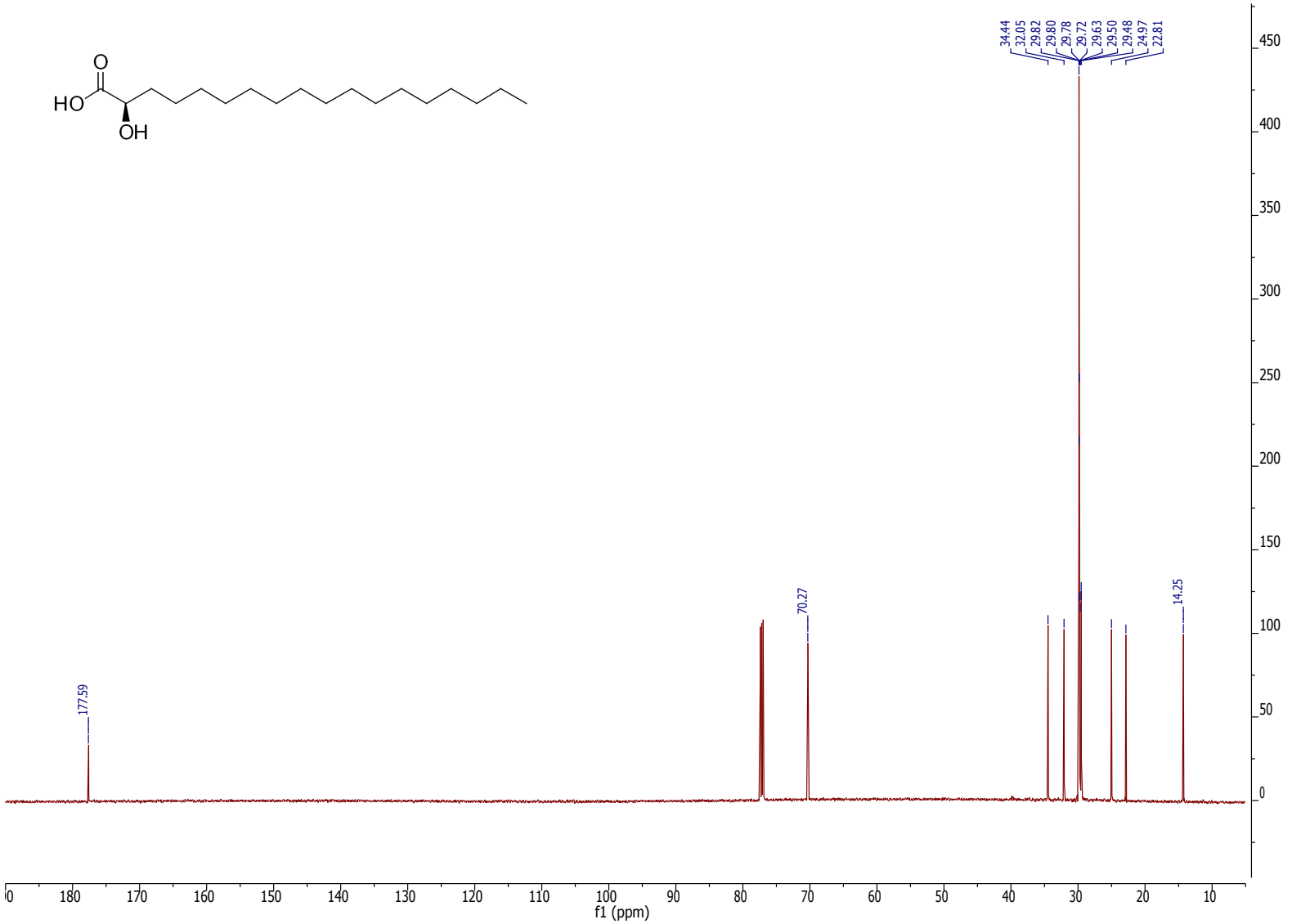

Figure 27. ^{13}C-NMR (151 MHz, $CDCl_3$) of (*R*)-2-hydroxyoctadecanoic acid (16b).

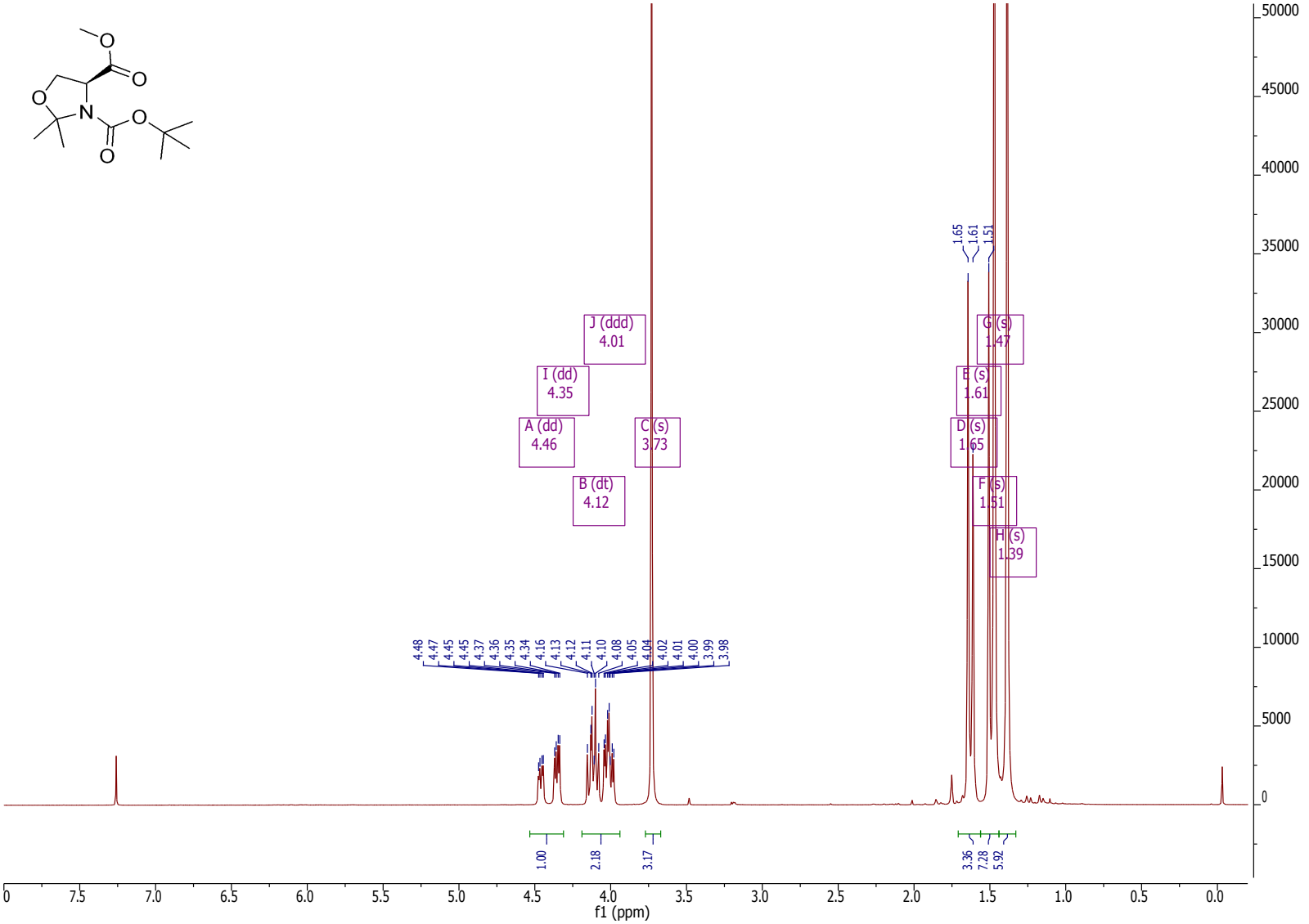

Figure 28. ^{1}H-NMR (300 MHz, $CDCl_3$) of 3-(*tert*-butyl) 4-methyl (*S*)-2,2-dimethyloxazolidine-3,4-dicarboxylate (I).

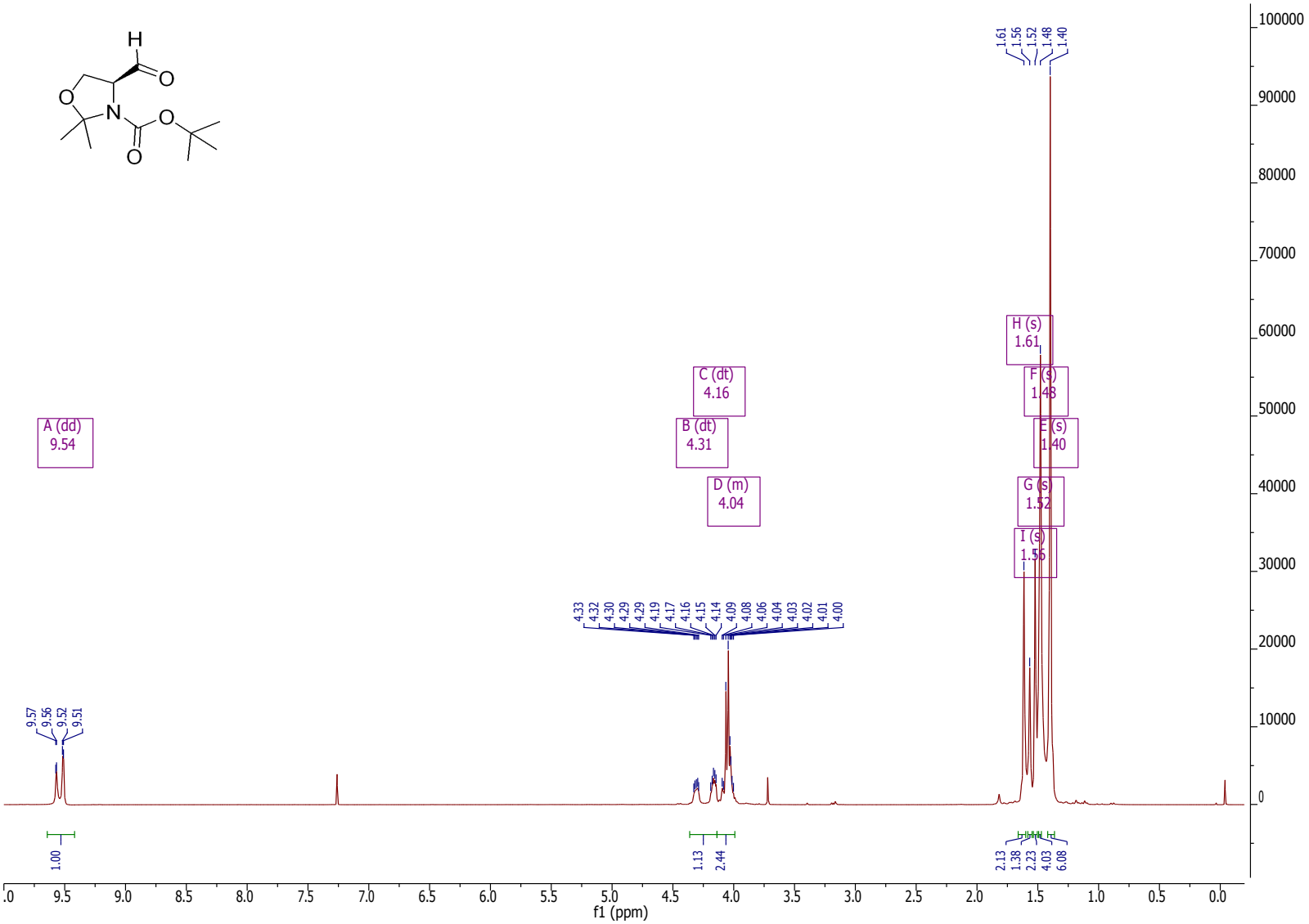

Figure 29. ^{1}H-NMR (300 MHz, $CDCl_3$) of Garner's aldehyde (3).

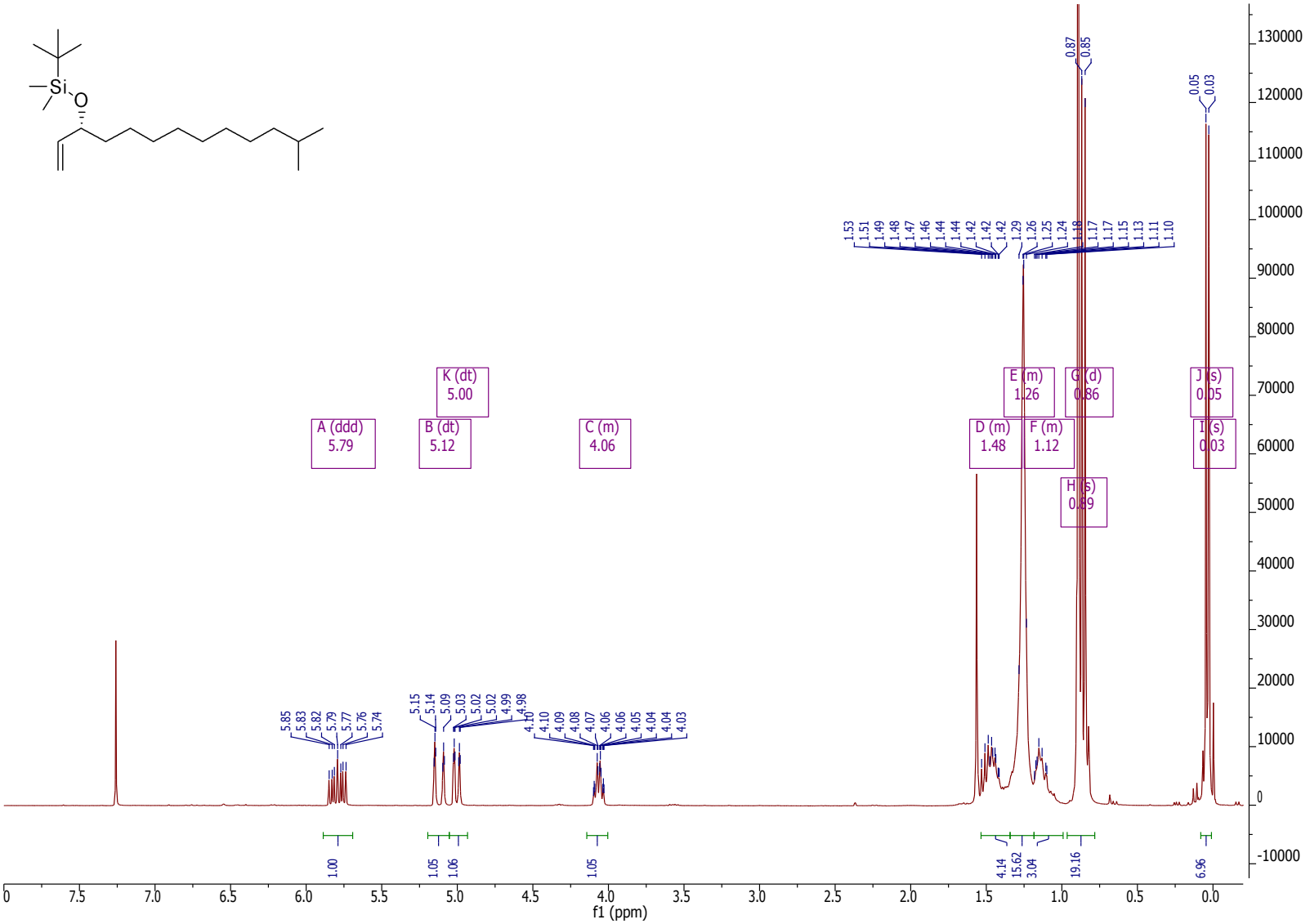

Figure 30. ^{1}H-NMR (300 MHz, $CDCl_3$) of (*R*)-*tert*-butyldimethyl((12-methyltridec-1-en-3-yl)oxy)silane (17).

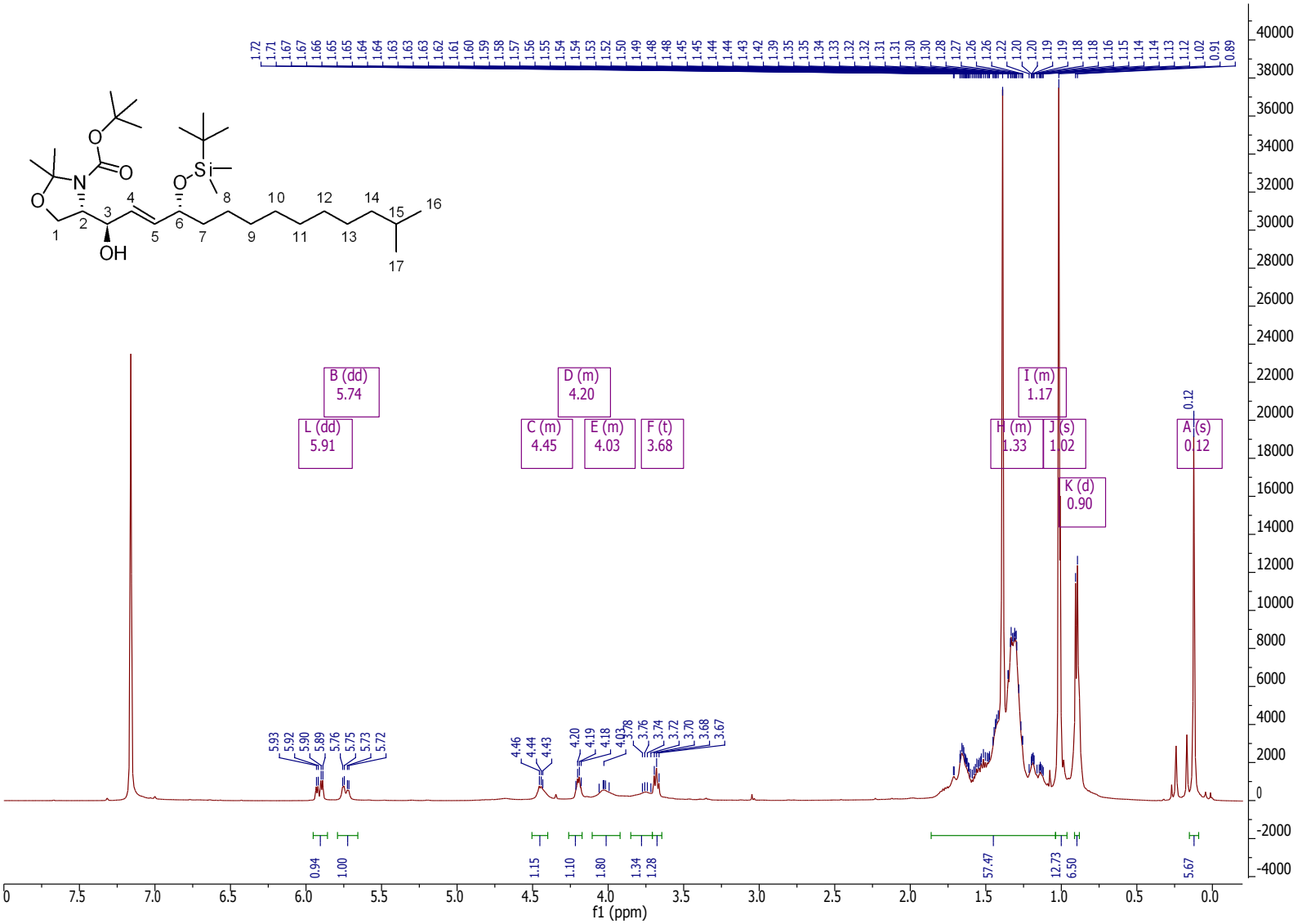

Figure 31. ^{1}H-NMR (500 MHz, C_6D_6, 300 K) of *tert*-butyl (*S*)-4-((1*R*,4*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (12a)

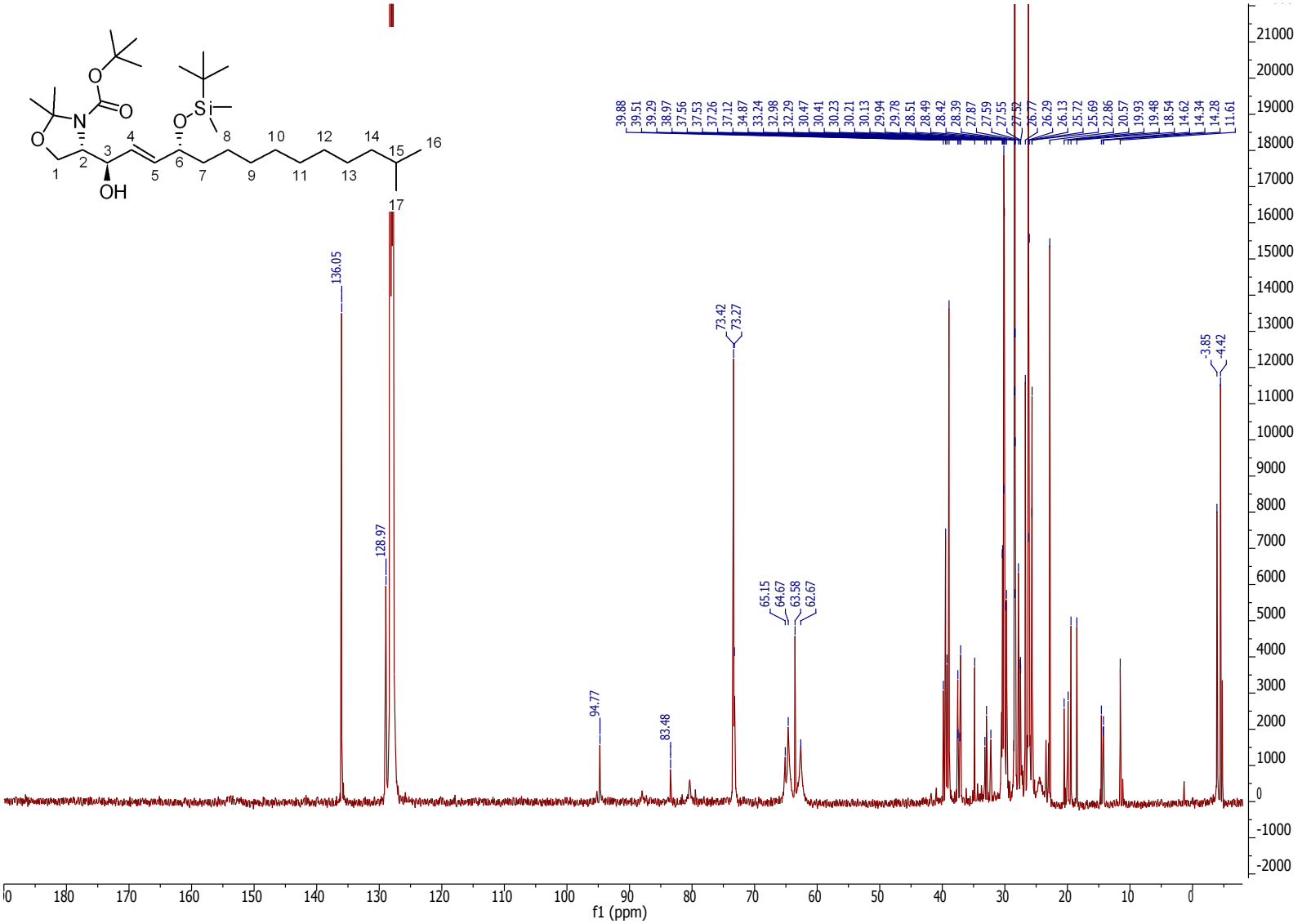

Figure 32. ^{13}C-NMR (126 MHz, C_6D_6, 300 K) of *tert*-butyl (*S*)-4-((1*R*,4*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (12a)

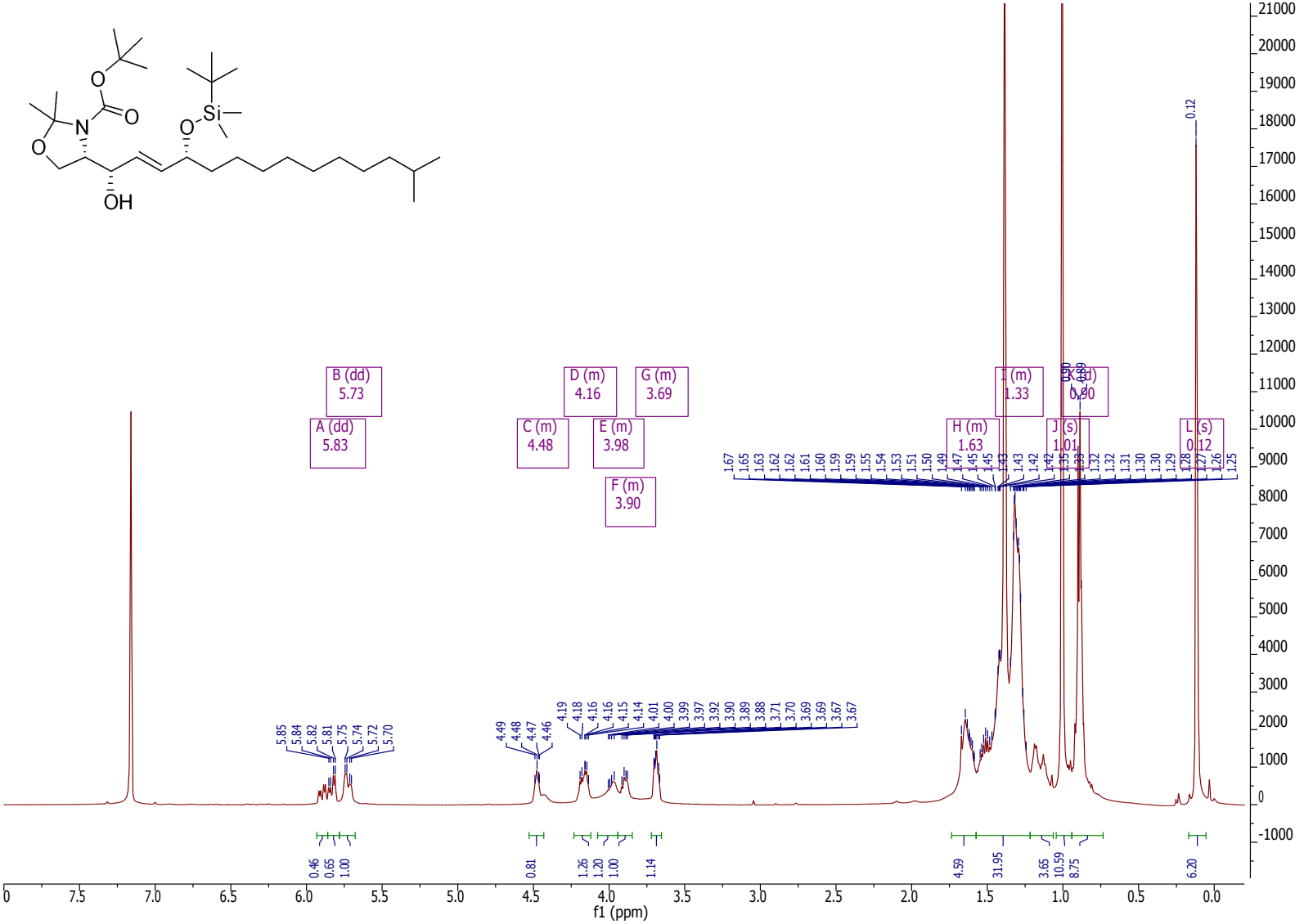

Figure 33. ^{1}H-NMR (500 MHz, C_6D_6, 300 K) of *tert*-butyl (*S*)-4-((1*S*,4*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (12b)

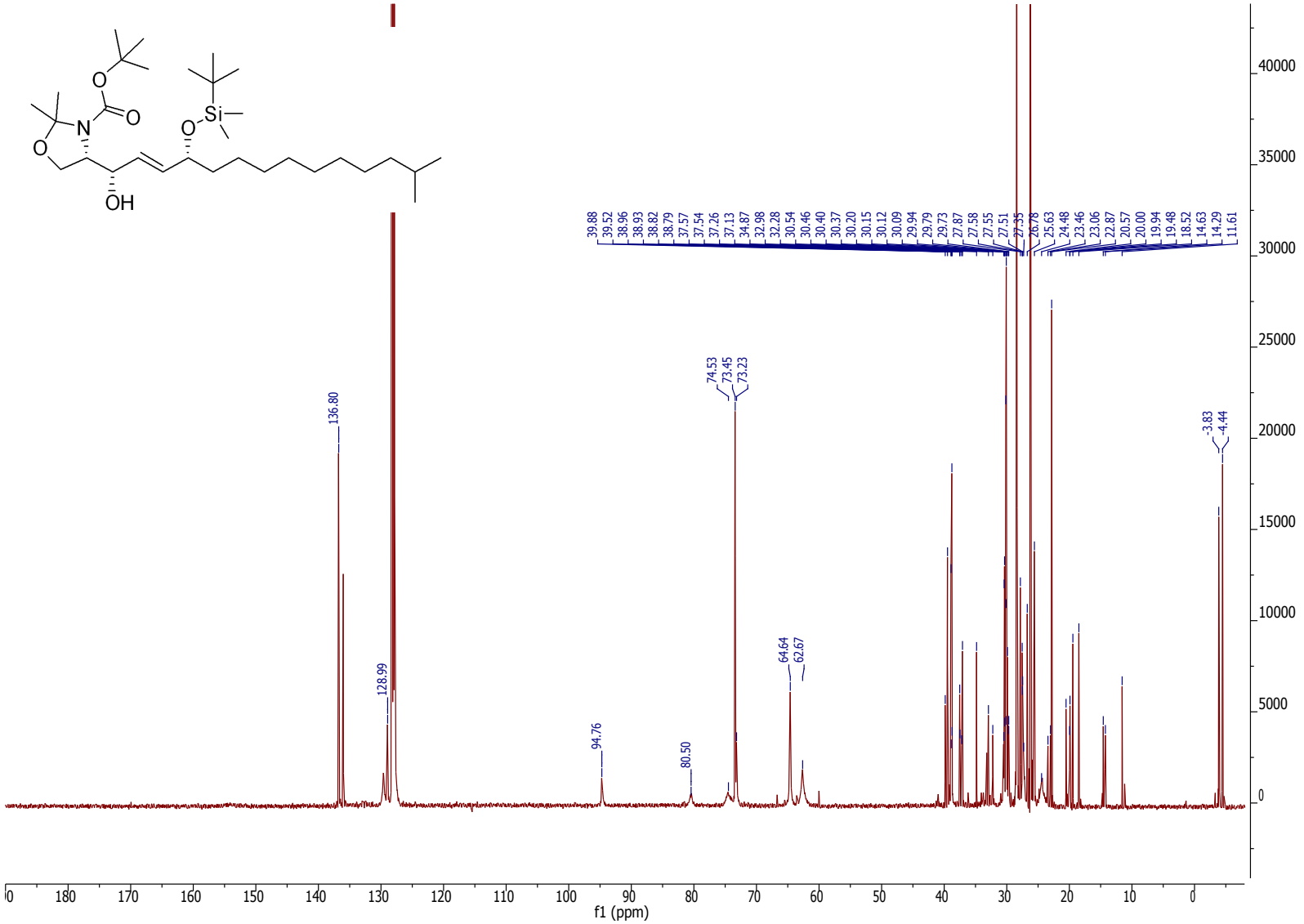

Figure 34. ^{1}H-NMR (126 MHz, C_6D_6, 300 K) of *tert*-butyl (*S*)-4-((1*S*,4*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (12b)

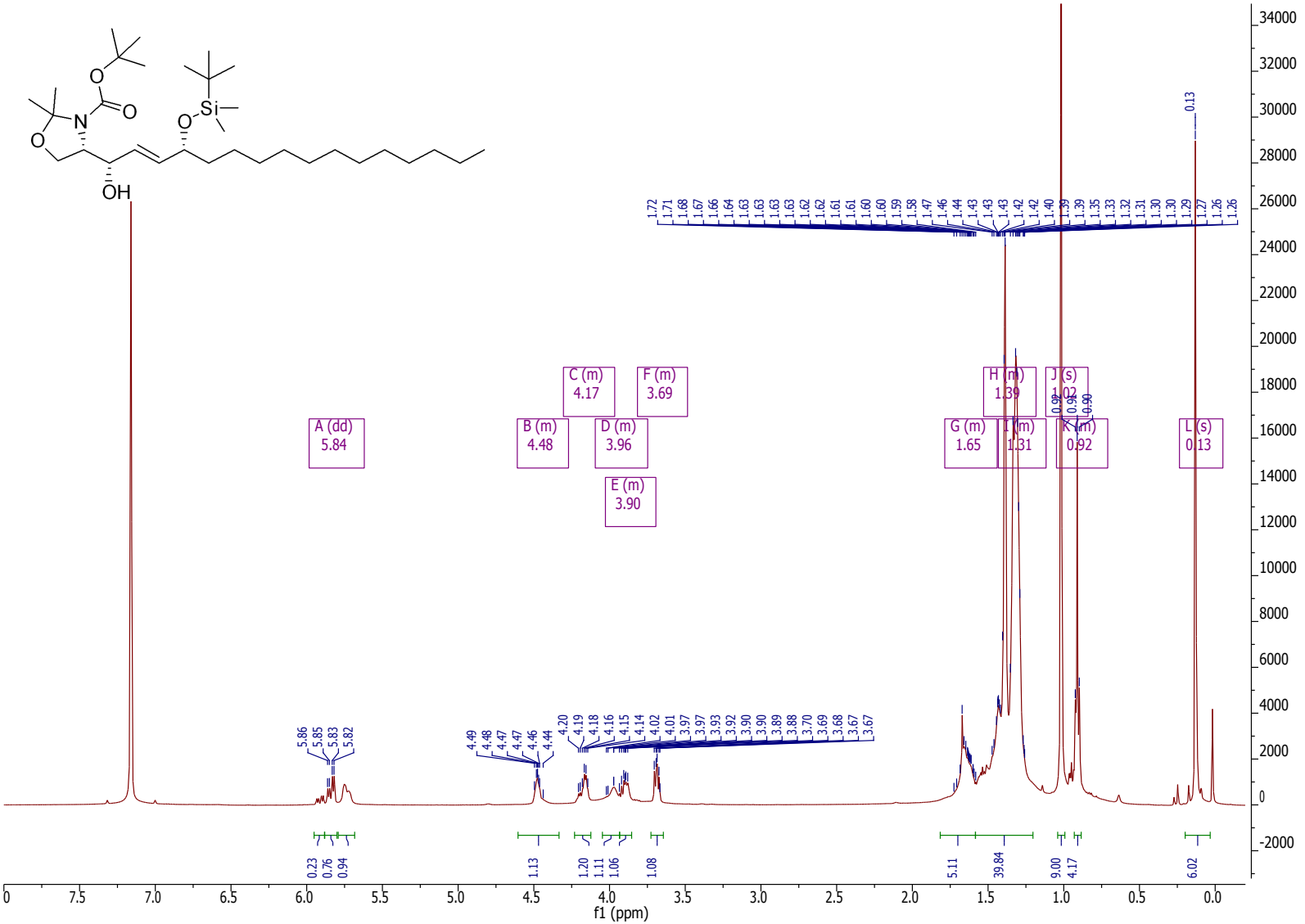

Figure 35. ^{1}H-NMR (500 MHz, C_6D_6, 300 K) of *tert*-butyl (*S*)-4-((1*S*,4*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxyhexadec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (19b).

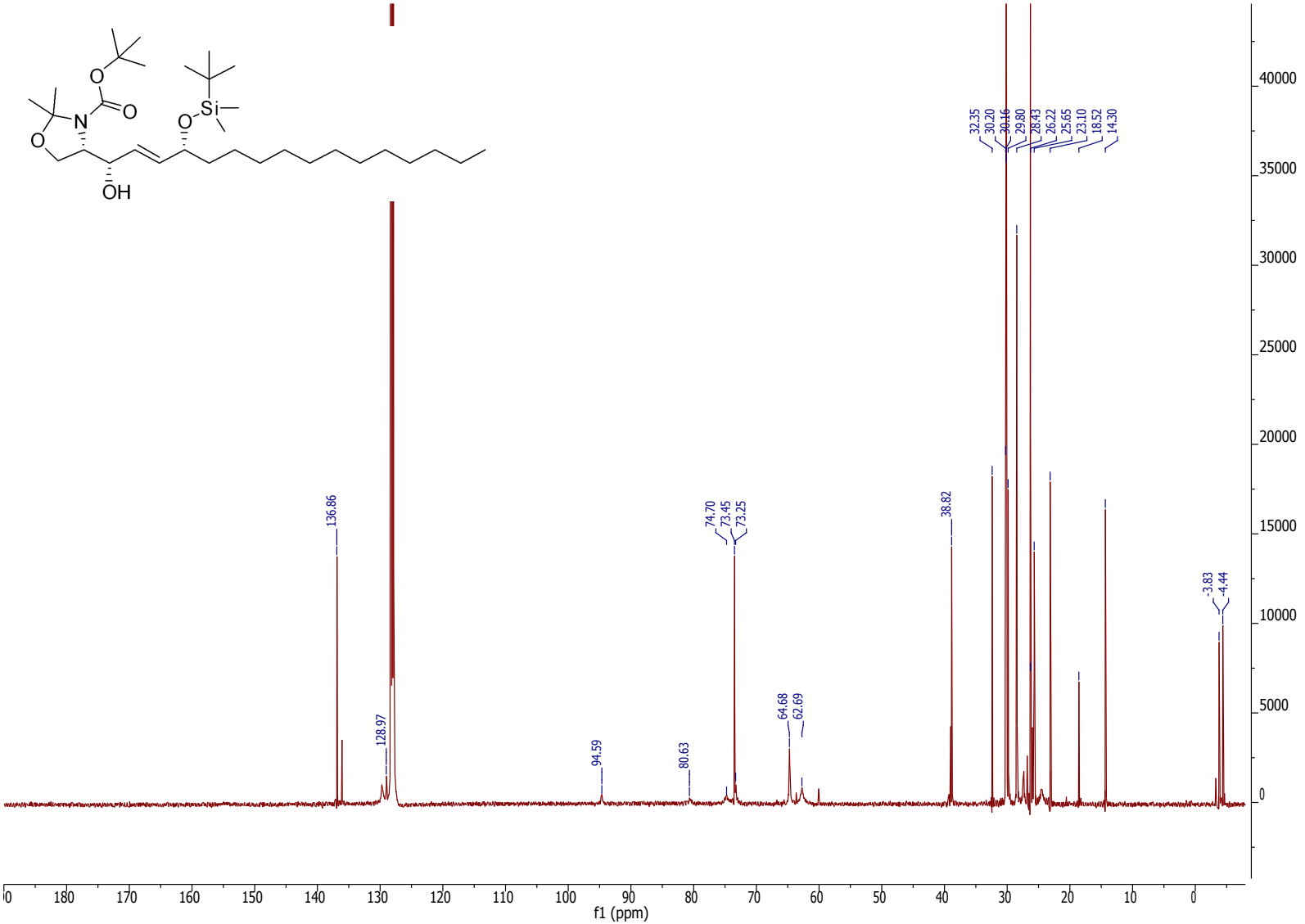

Figure 36. ^{13}C-NMR (126 MHz, C_6D_6, 300 K) of *tert*-butyl (*S*)-4-((1*S*,4*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxyhexadec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (19b).

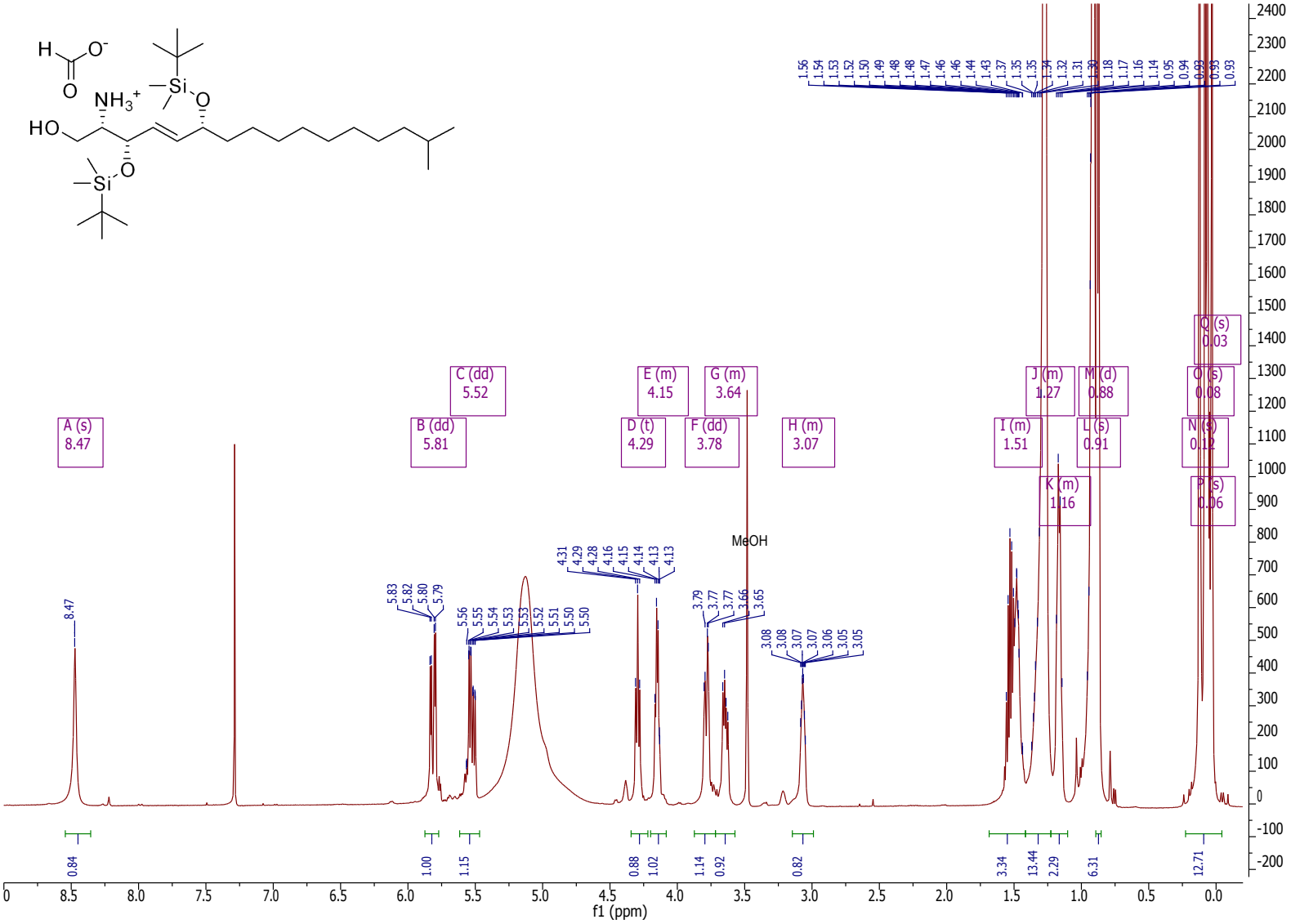

Figure 37. ^{1}H-NMR (500 MHz, $CDCl_3$) of (2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-aminium formate (22).

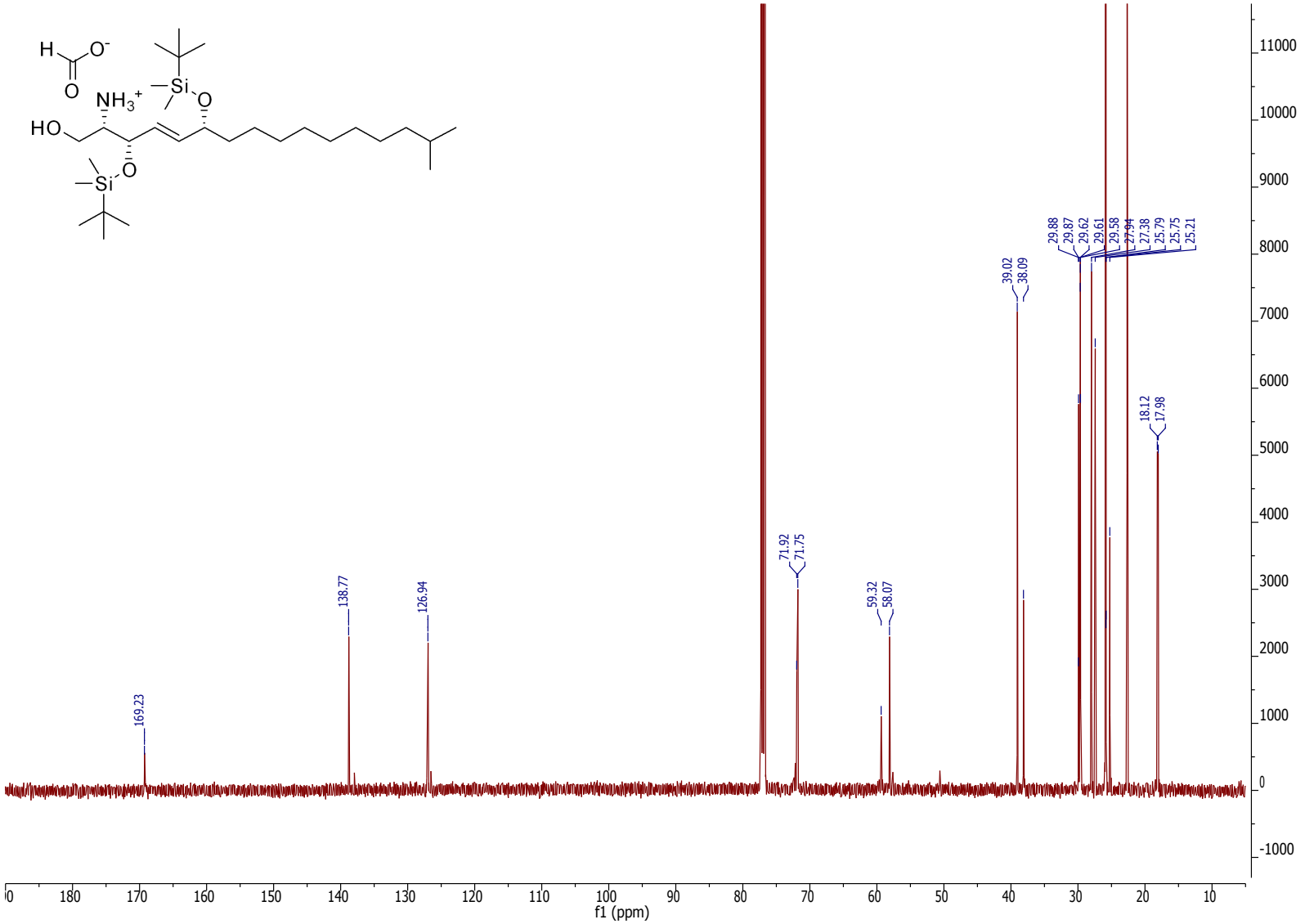

Figure 38. ^{13}C-NMR (126 MHz, $CDCl_3$) of (2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-aminium formate (22).

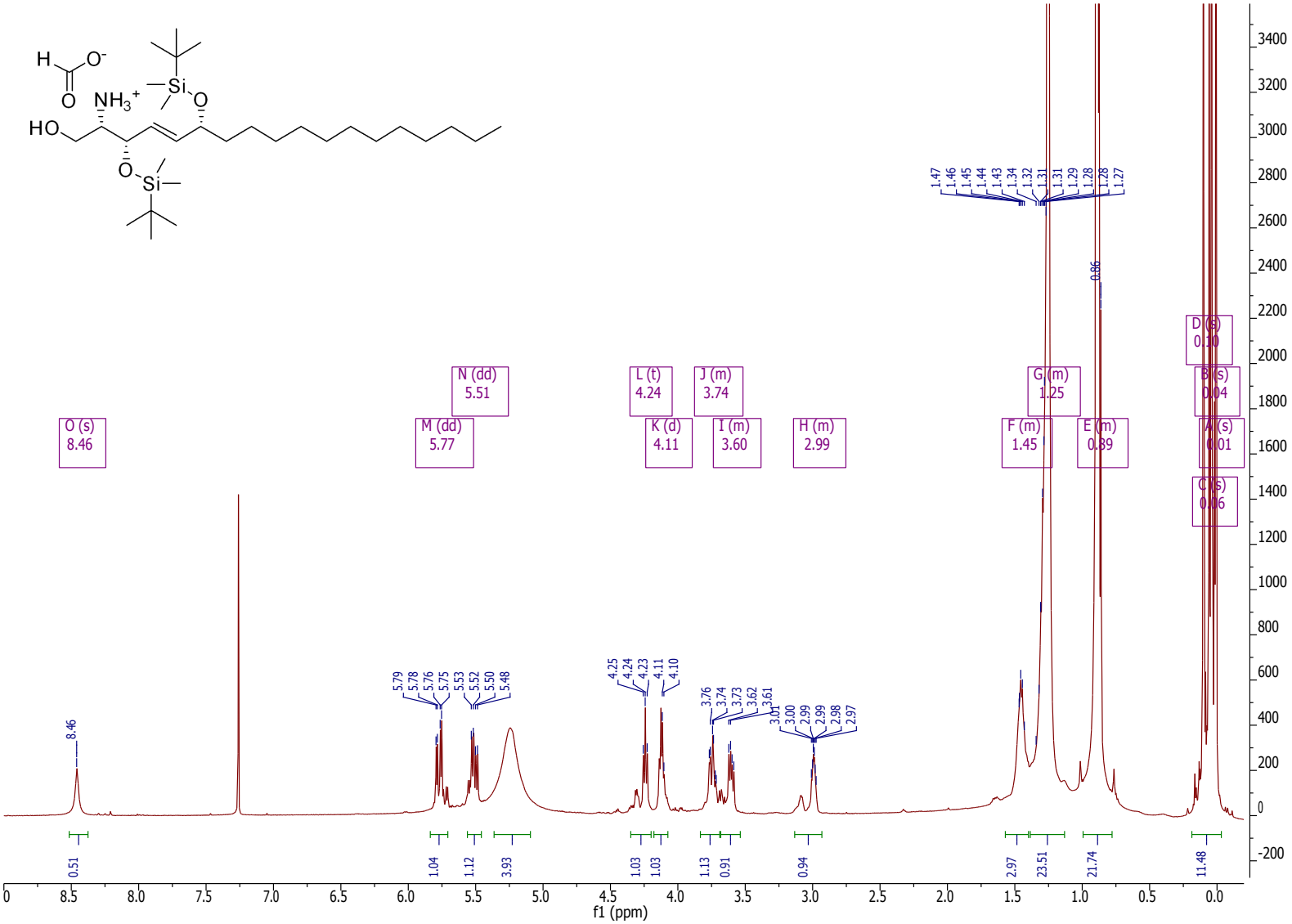

Figure 39. ^{1}H-NMR (500 MHz, $CDCl_3$) of (2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxyoctadec-4-en-2-aminium formate (23).

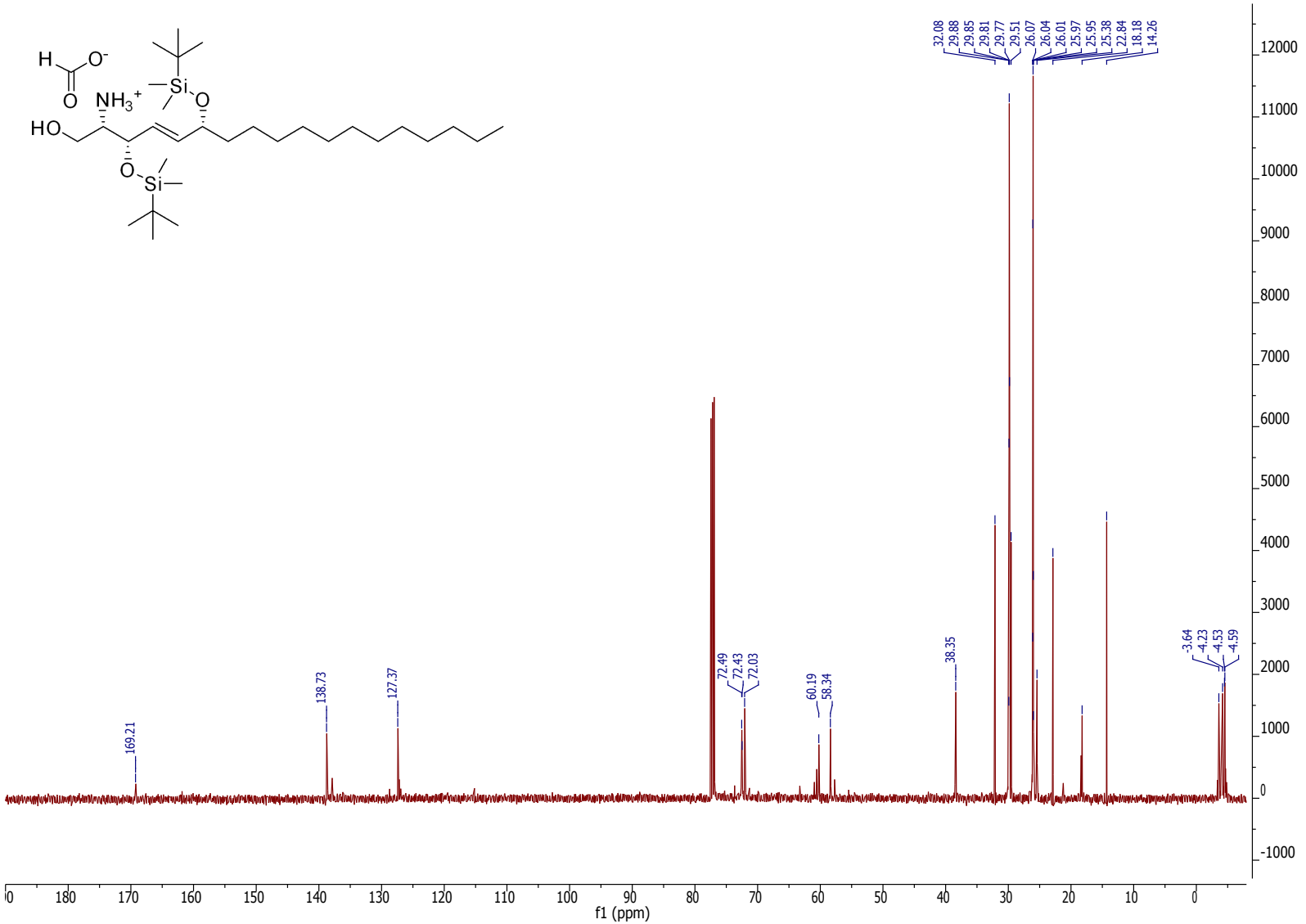

Figure 40. ^{13}C-NMR (126 MHz, $CDCl_3$) of (2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxyoctadec-4-en-2-aminium formate (23)

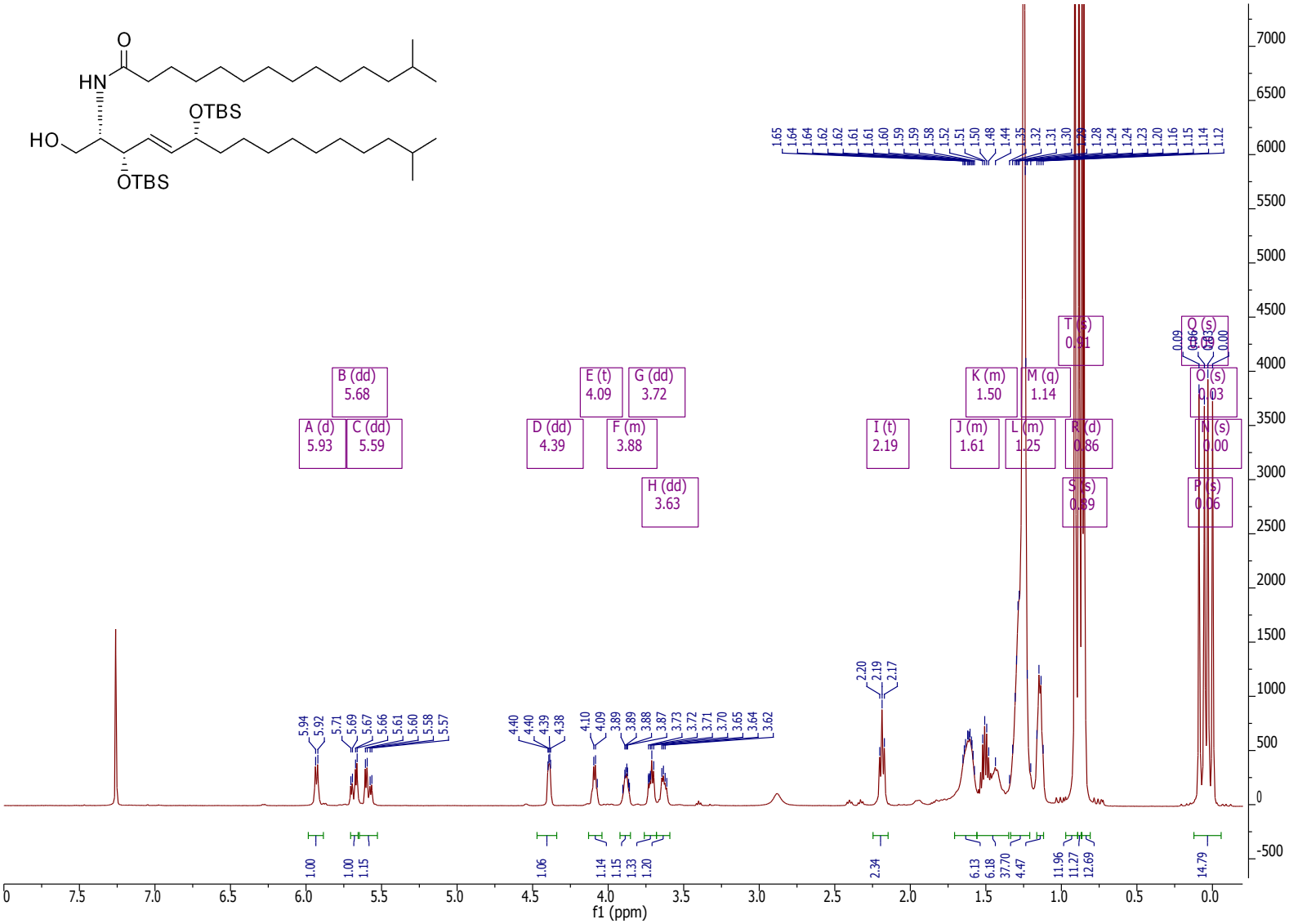

Figure 41. ^{1}H-NMR (500 MHz, $CDCl_3$) of N-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-13-methyltetradecanamide (24).

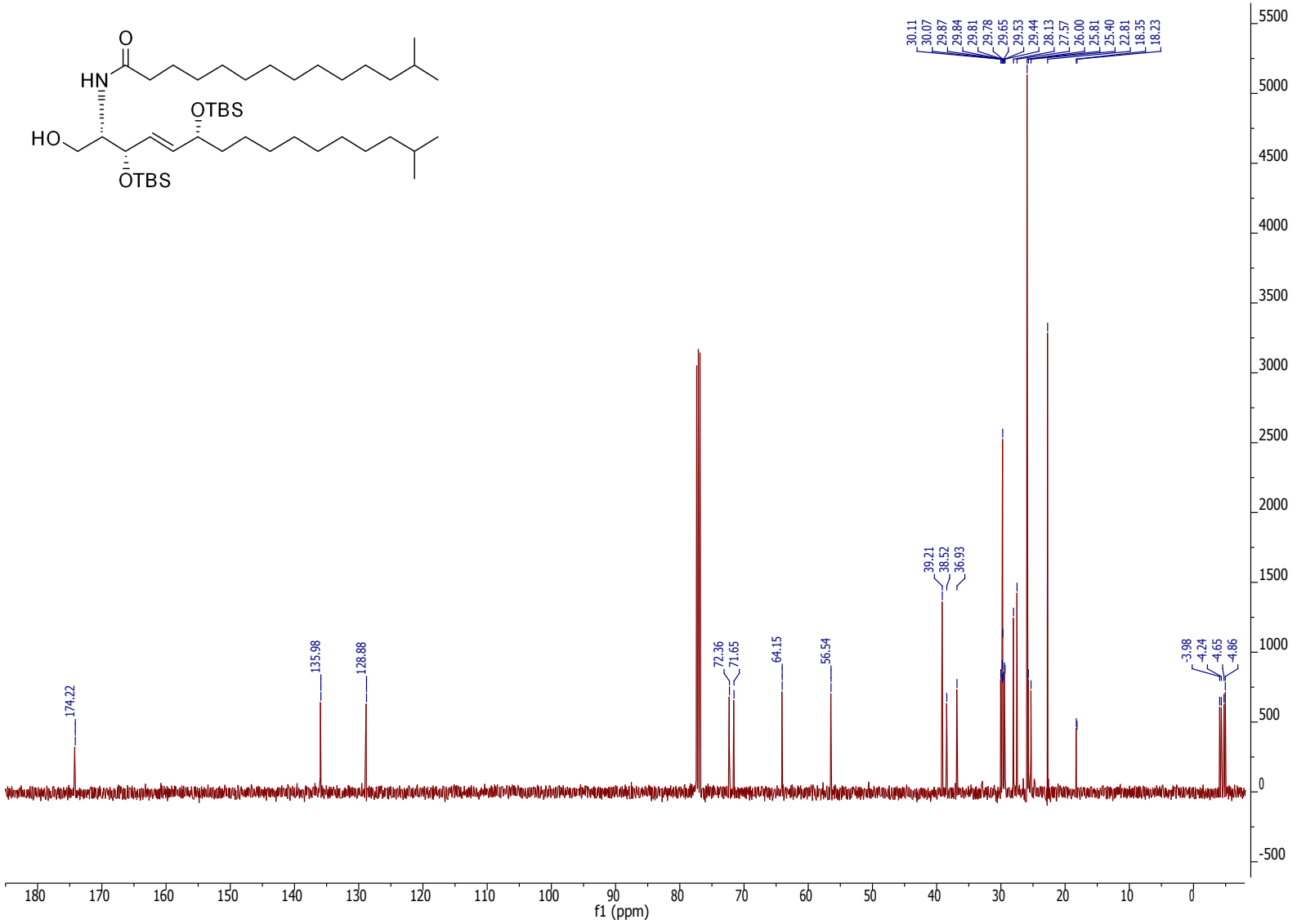

Figure 42. ^{13}**C-NMR (126 MHz, $CDCl_3$) of N-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-13-methyltetradecanamide (24).**

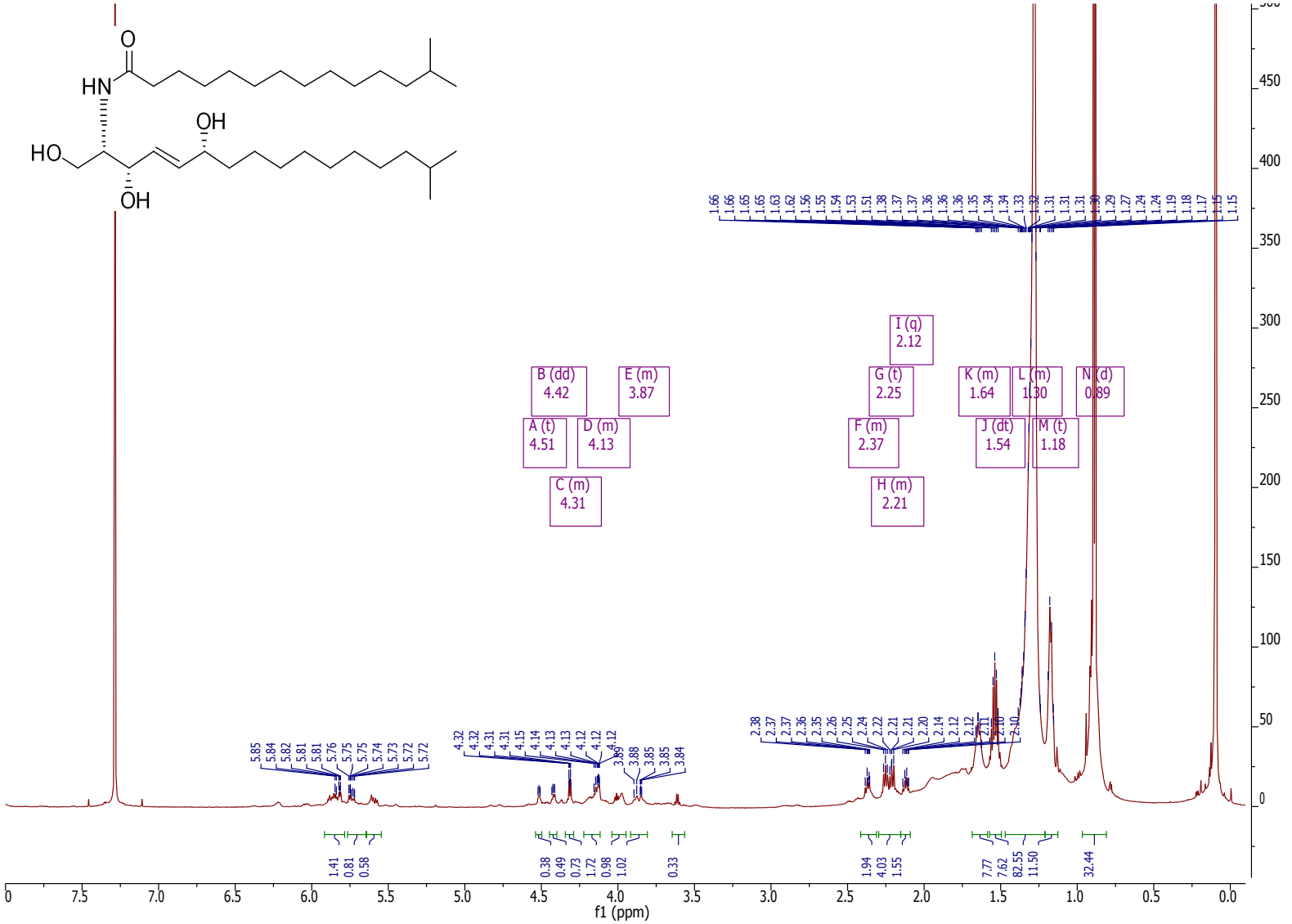

Figure 43. ^{1}H-NMR (600 MHz, $CDCl_3$) of 13-methyl-*N*-((2*S*,3*S*,6*R*,*E*)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (25).

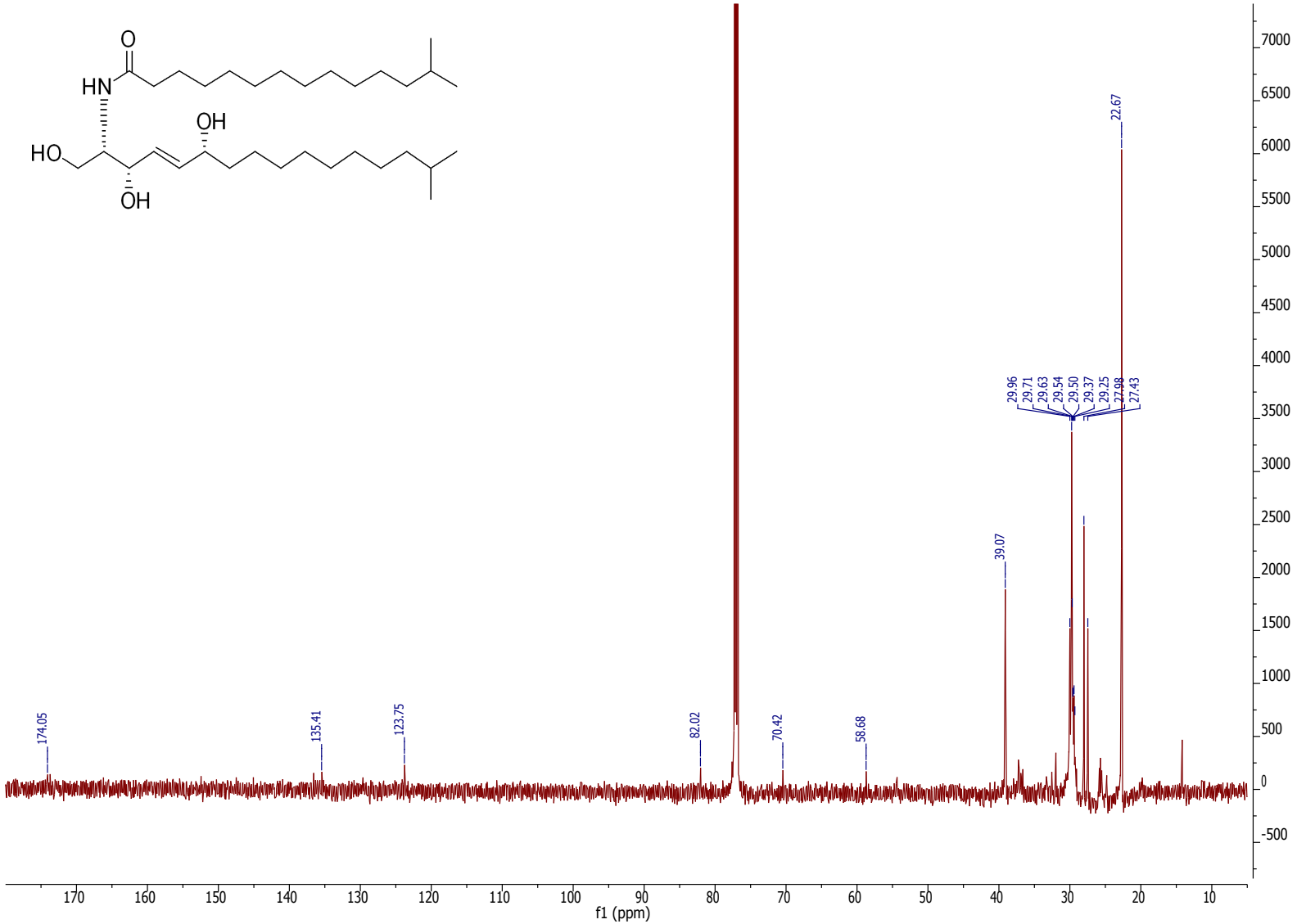

Figure 44. ^{13}C-NMR (151 MHz, $CDCl_3$) of 13-methyl-*N*-((2*S*,3*S*,6*R*,*E*)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (25).

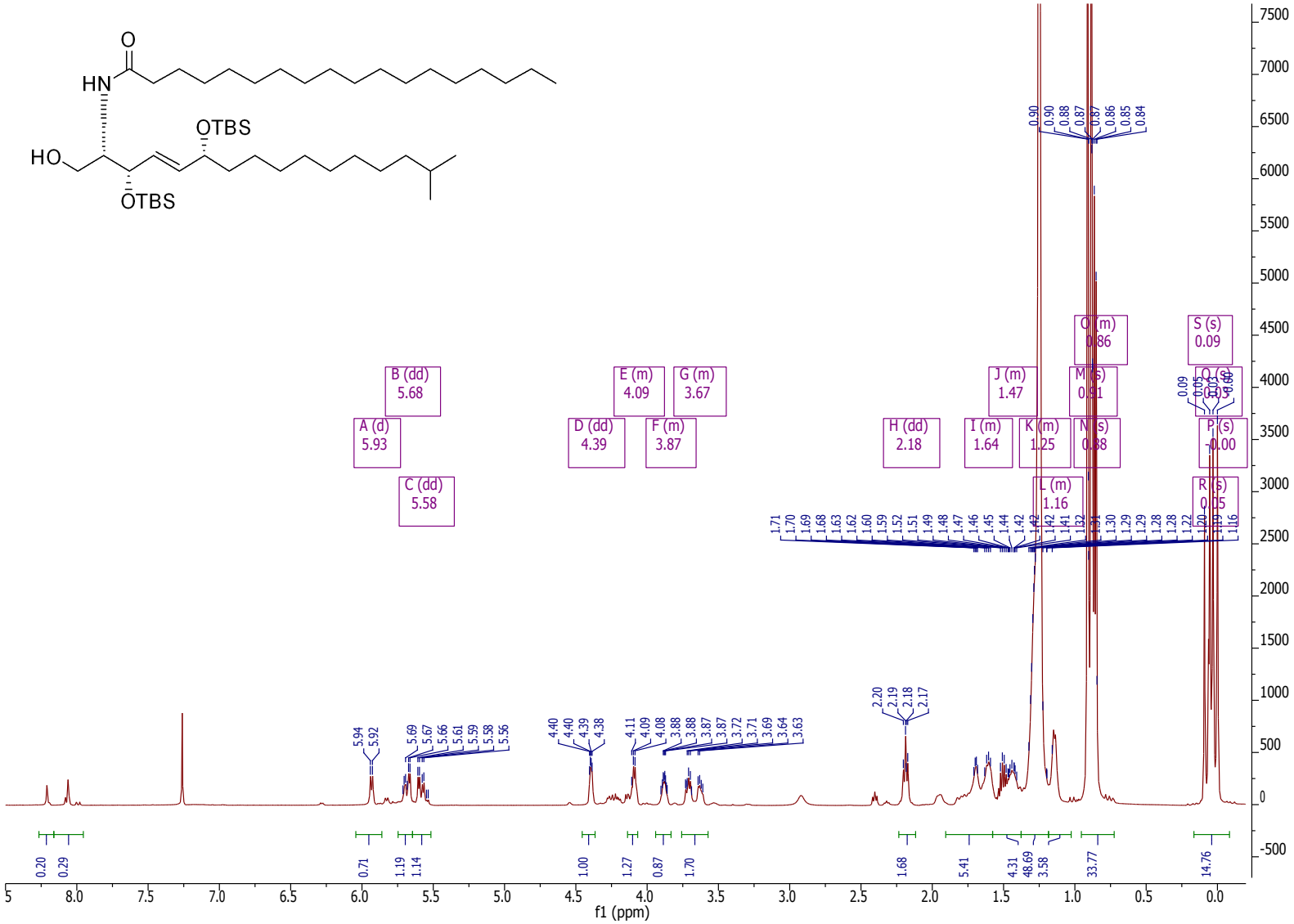

Figure 45. ^{1}H-NMR (500 MHz, $CDCl_3$) of *N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)stearamide (26).

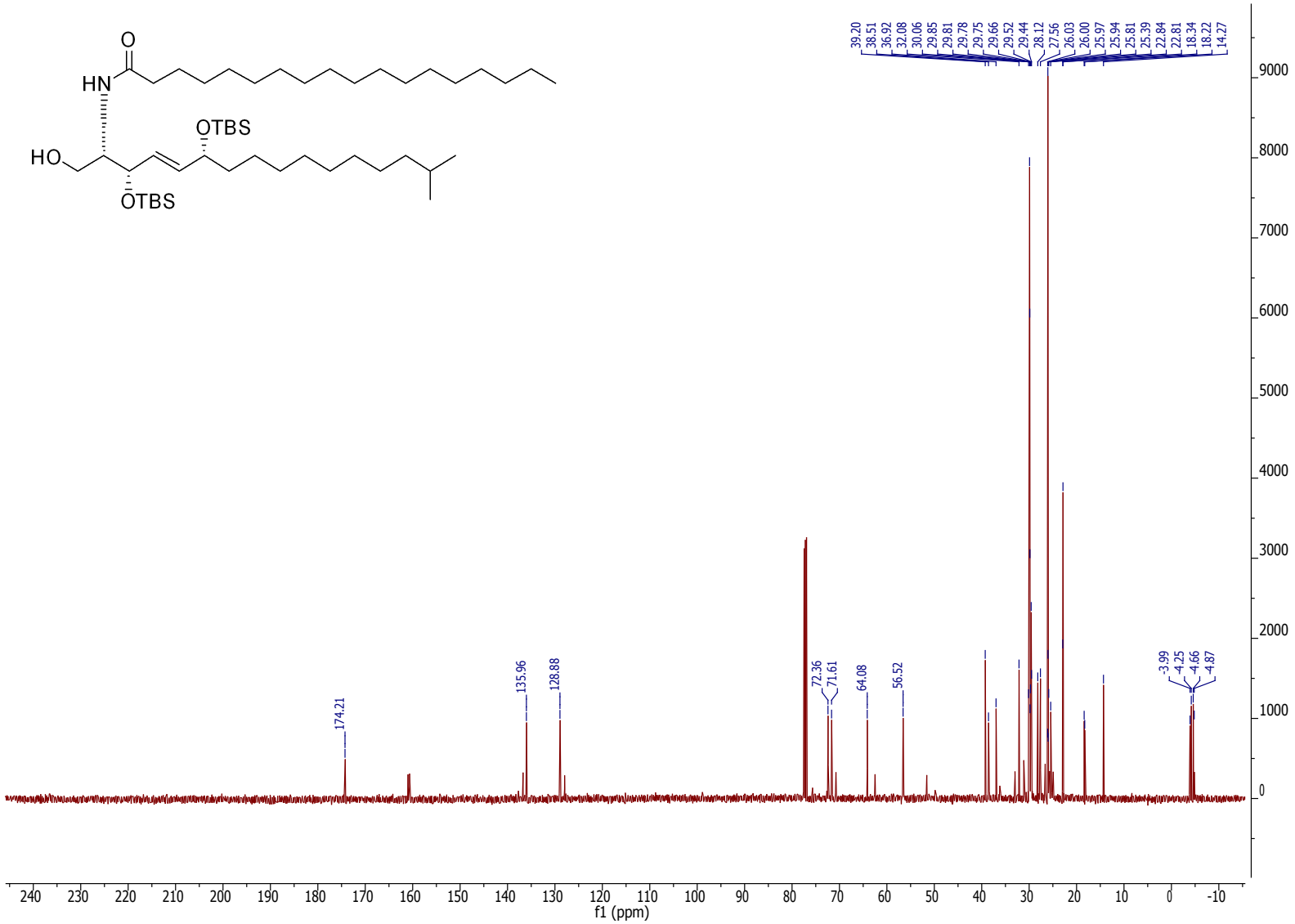

Figure 46. ^{13}C-NMR (126 MHz, $CDCl_3$) of *N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)stearamide (26).

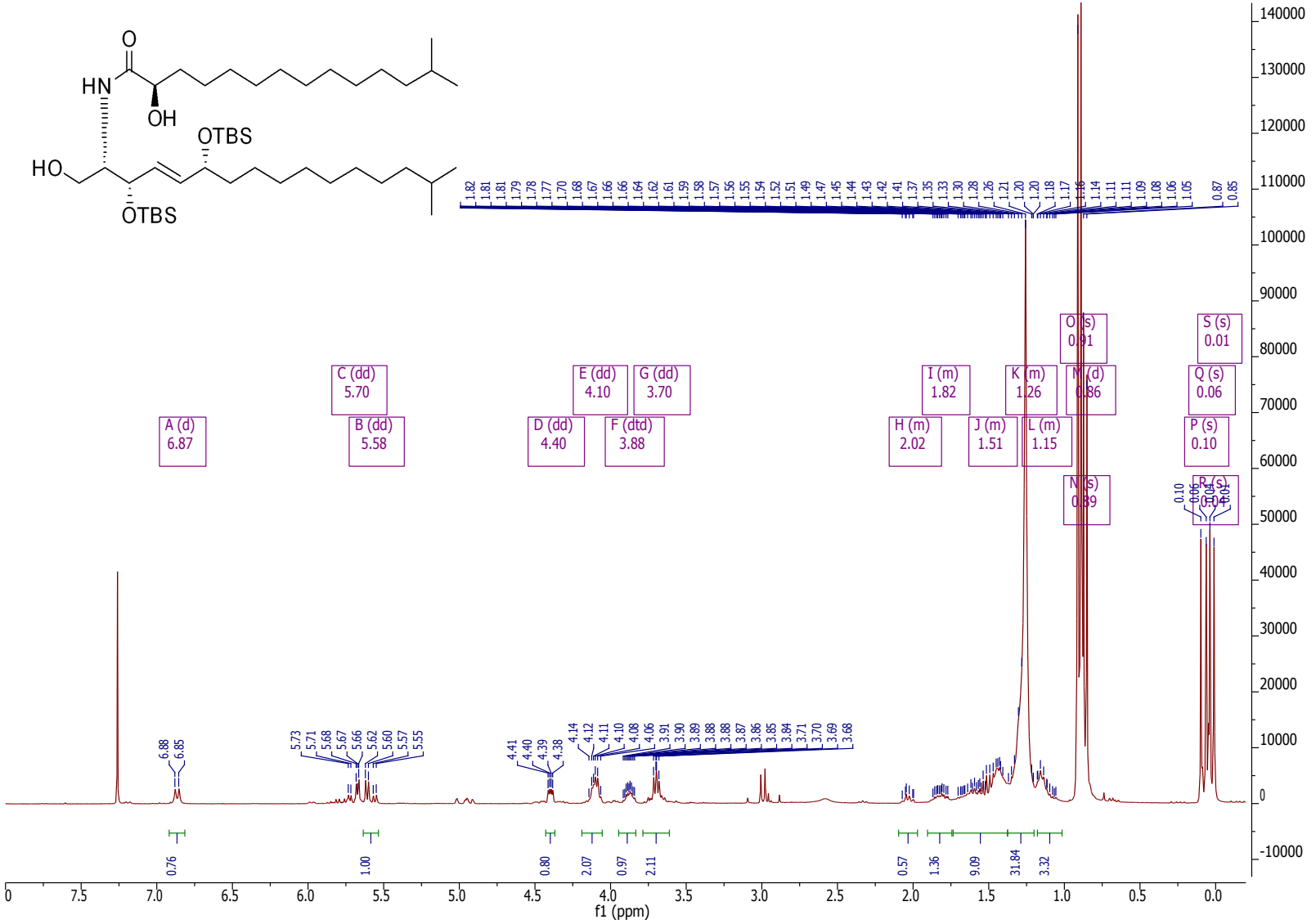

Figure 47. ^{1}H-NMR (300 MHz, $CDCl_3$) of (*R*)-*N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-2-hydroxy-13-methyltetradecanamide (27).

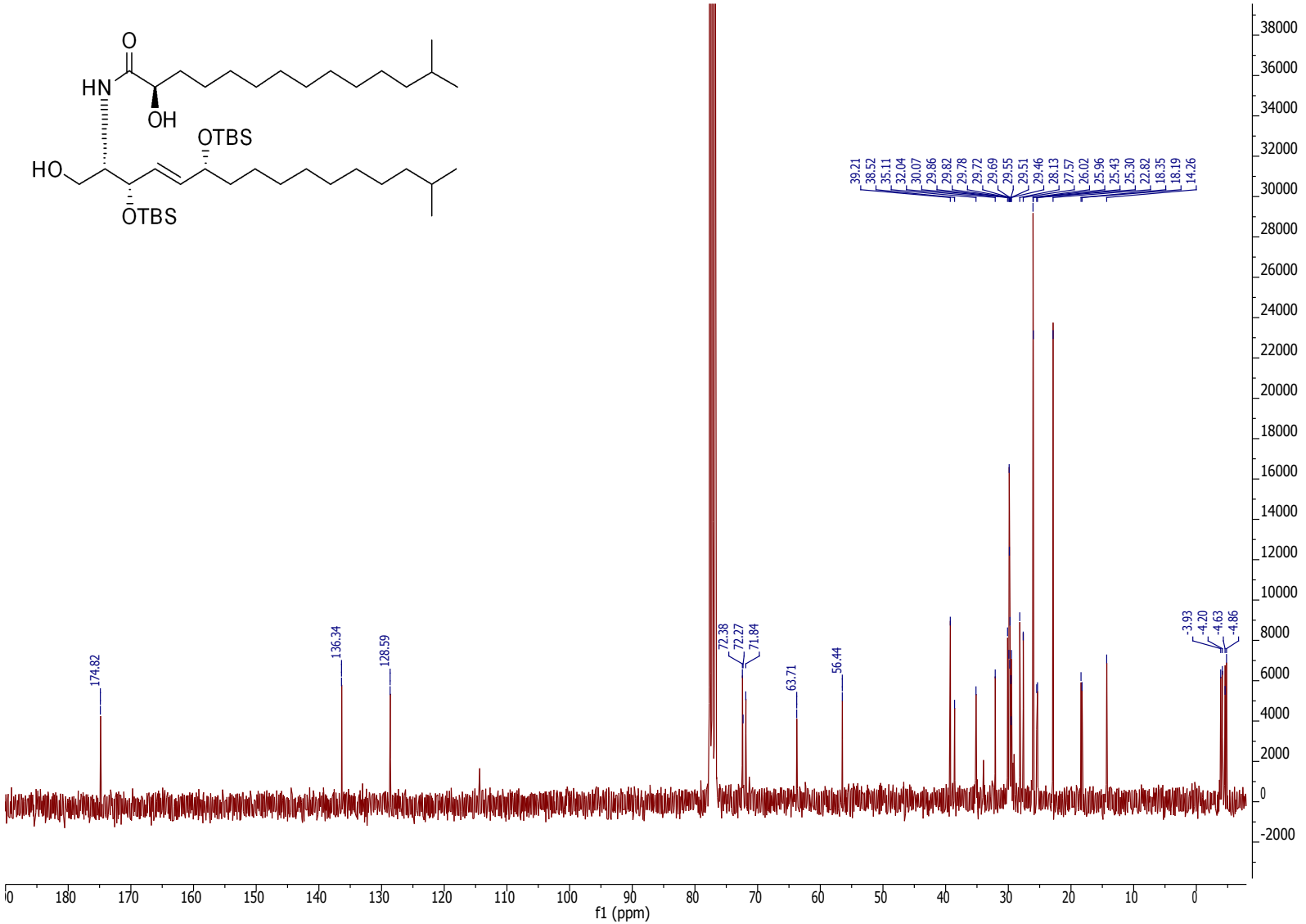

Figure 48. ^{13}C-NMR (75 MHz, $CDCl_3$) of (*R*)-*N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-2-hydroxy-13-methyltetradecanamide (27).

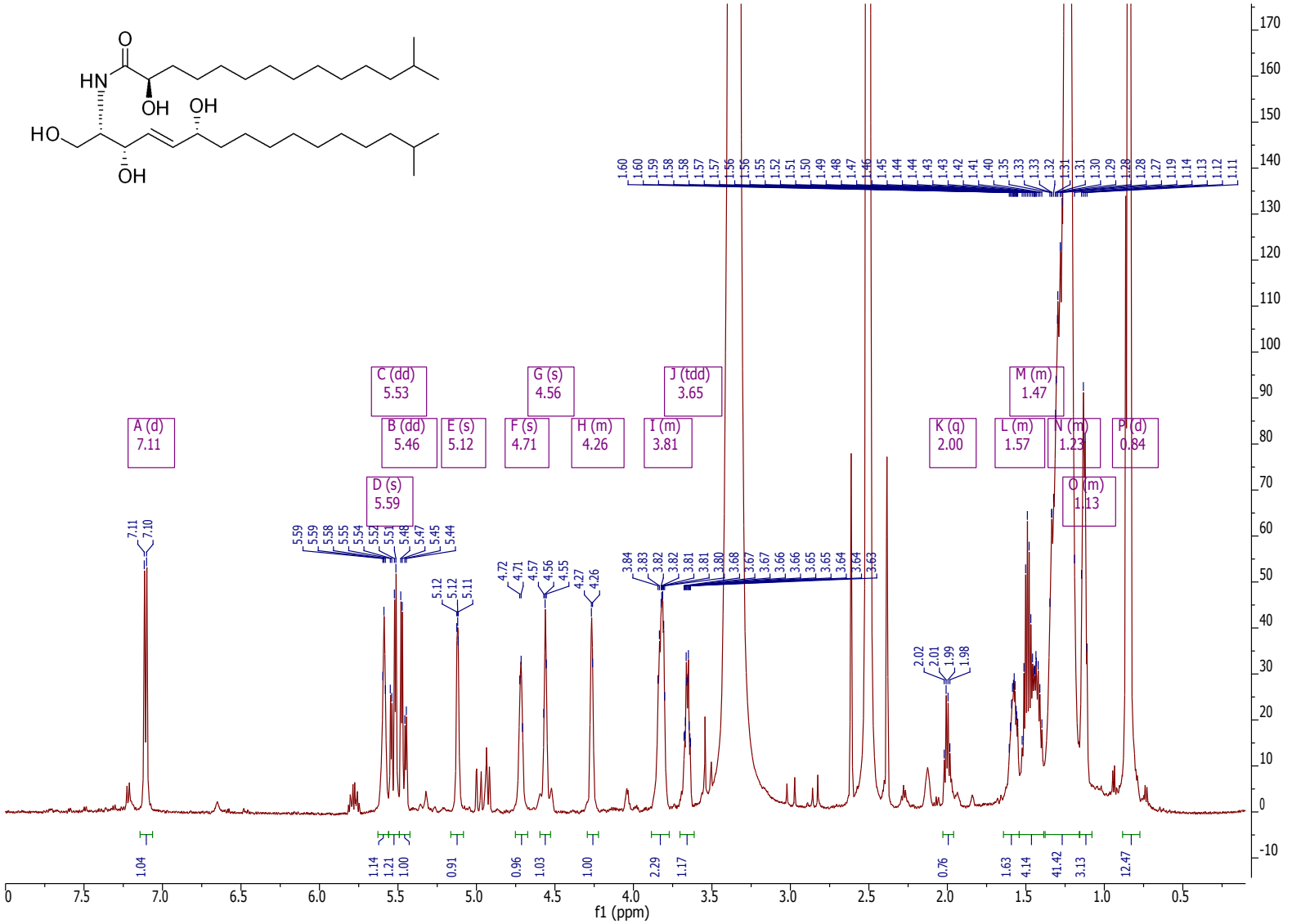

Figure 49. ^{1}H-NMR (600 MHz, DMSO-d_6) of (*R*)-2-hydroxy-13-methyl-*N*-((2*S*,3*S*,6*R*,*E*)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (28).

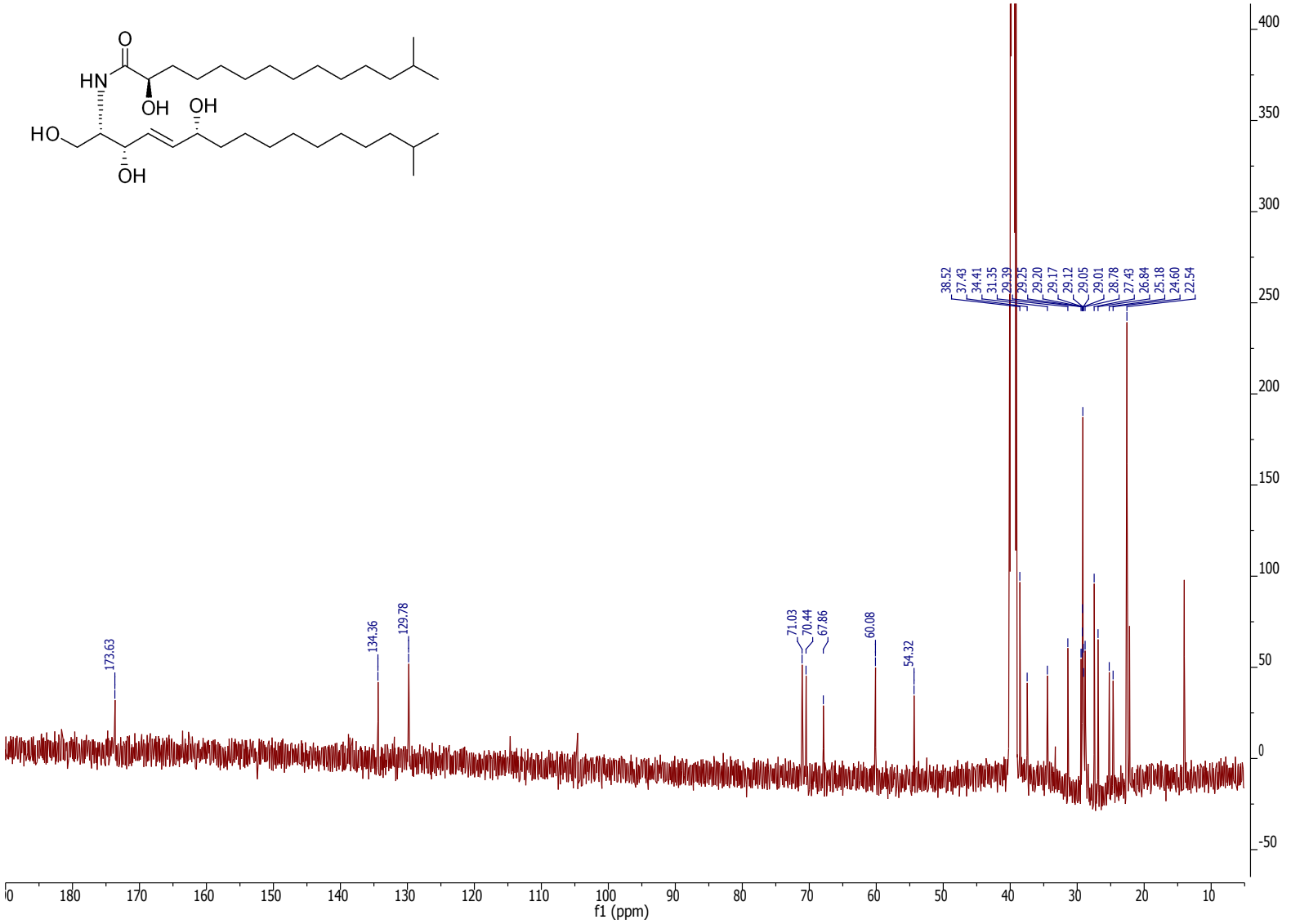

Figure 50. ^{13}C-NMR (151 MHz, DMSO-d_6) of (*R*)-2-hydroxy-13-methyl-*N*-((2*S*,3*S*,6*R*,*E*)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (28).

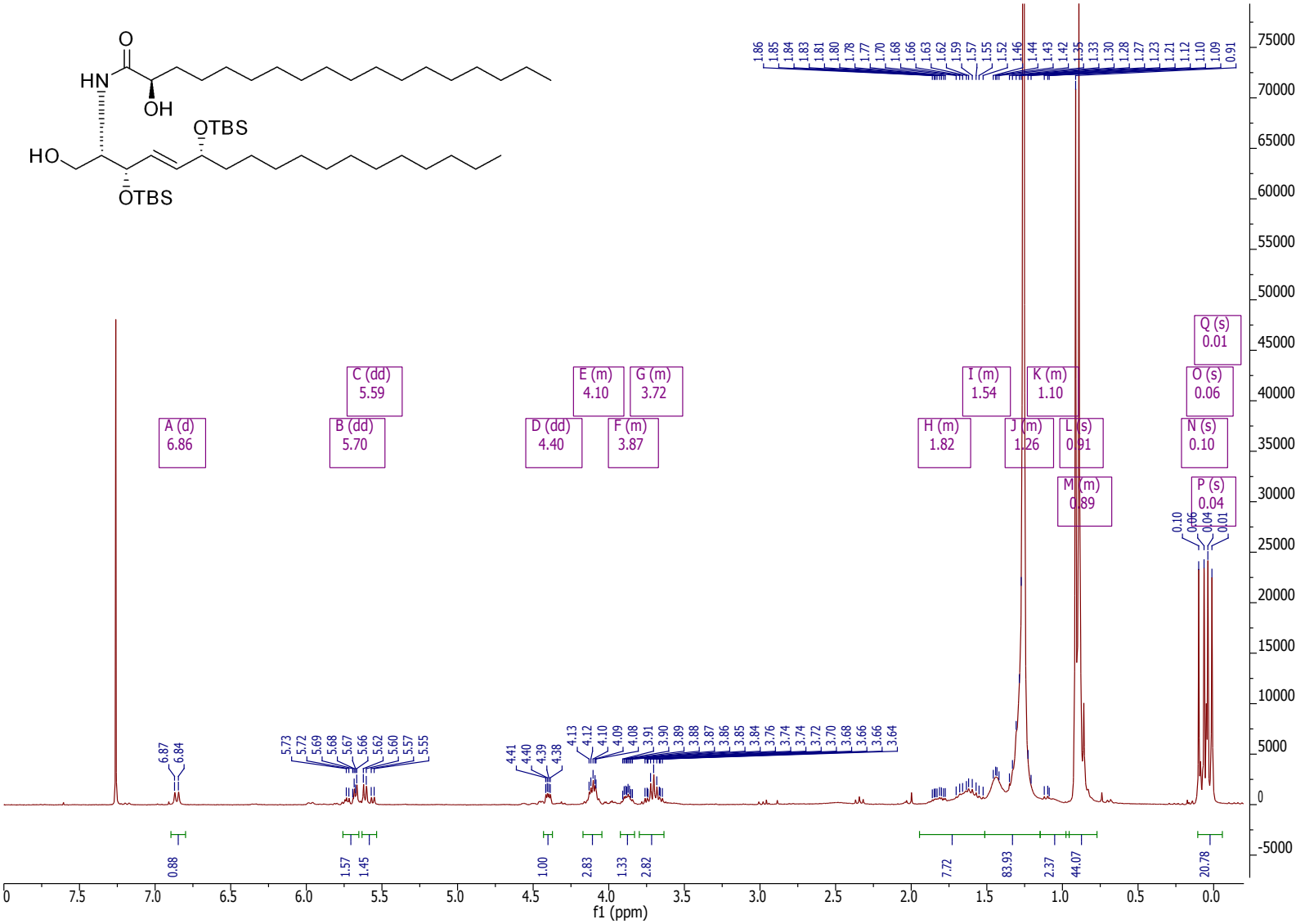

Figure 51. ^{1}H-NMR (300 MHz, $CDCl_3$) of (*R*)-*N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((tert-butyldimethylsilyl)oxy)-1-hydroxyoctadec-4-en-2-yl)-2-hydroxyoctadecanamide (29).

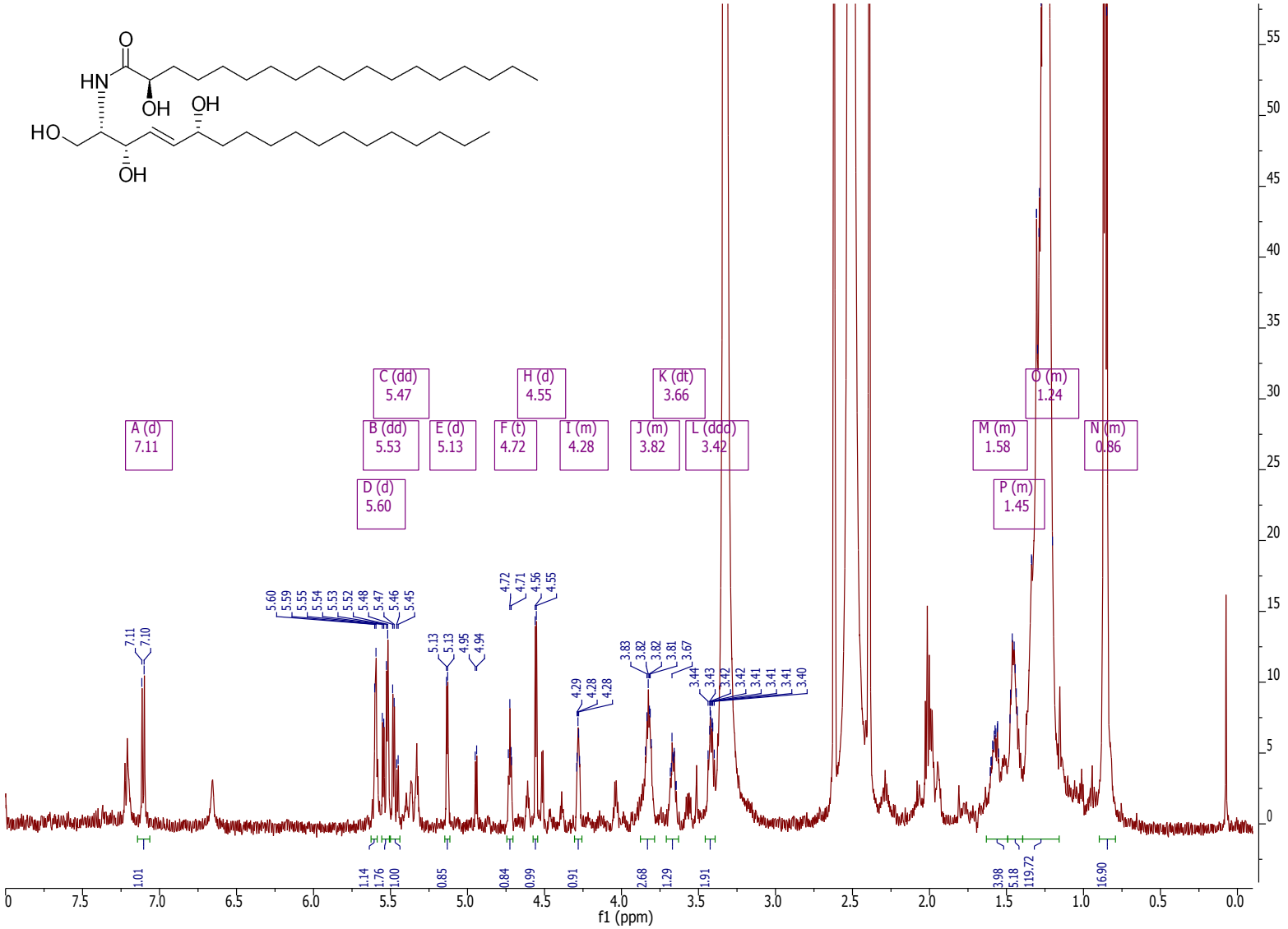

Figure 52. ^{1}H-NMR (600 MHz, DMSO-d_6) of (*R*)-2-hydroxy-*N*-((2*S*,3*S*,6*R*,*E*)-1,3,6-trihydroxyoctadec-4-en-2-yl)octadecanamide (30).

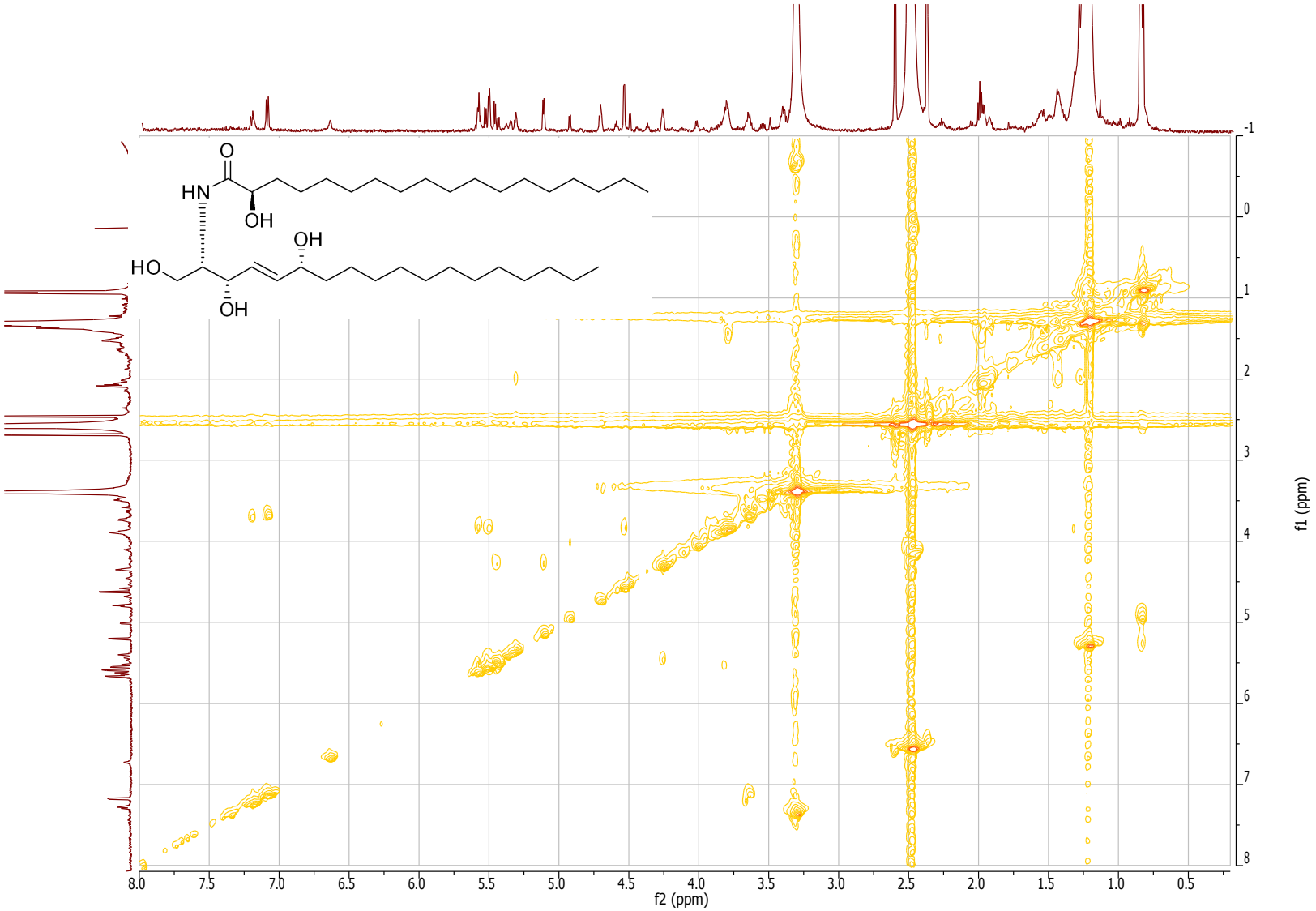

Figure 53. ^{1}H-^{1}H COSY (600 MHz, DMSO-d_6) of (*R*)-2-hydroxy-13-methyl-*N*-((2*S*,3*S*,6*R*,*E*)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (30).

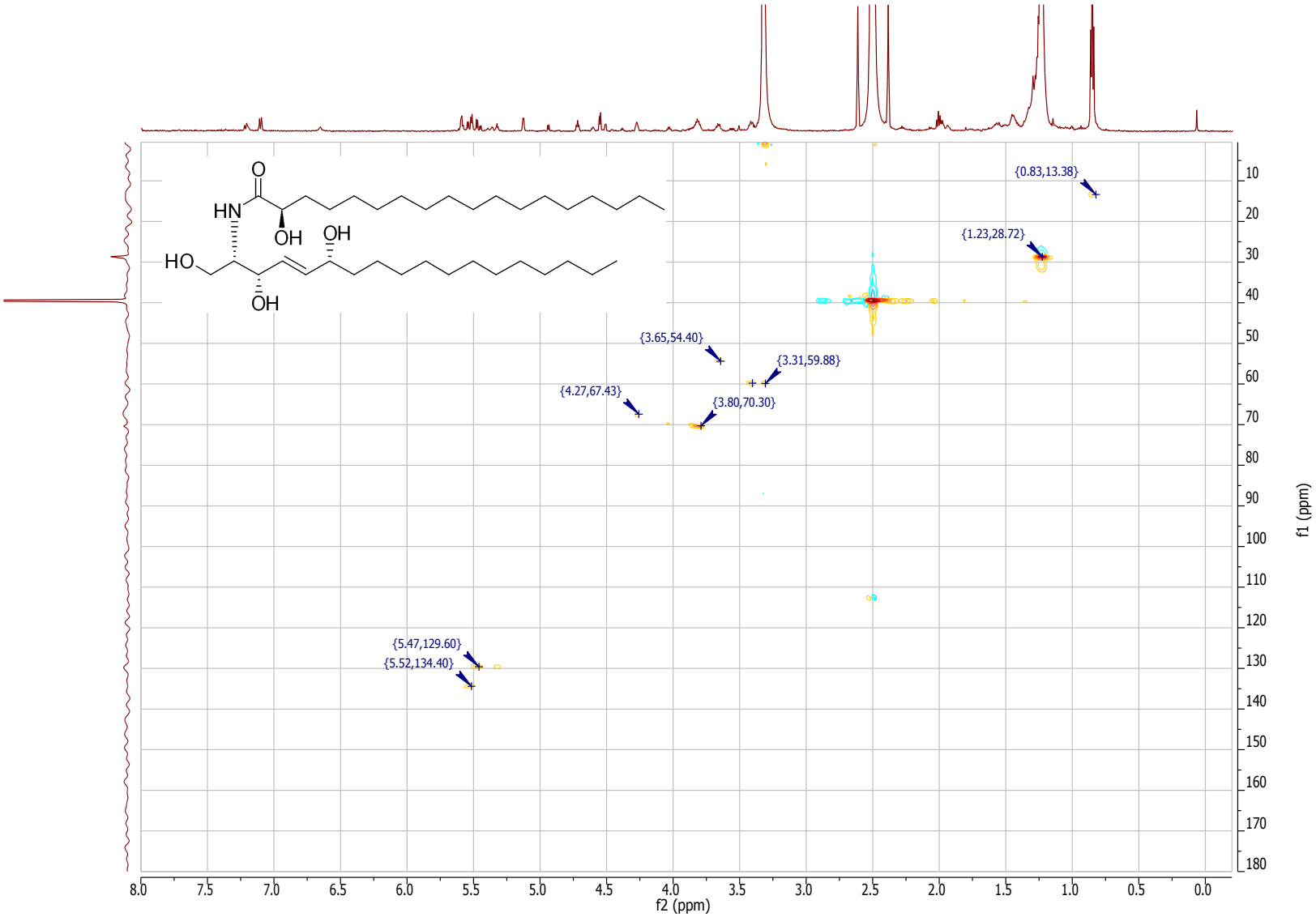

Figure 54. ^{1}H-^{13}C HSQC (*R*)-2-hydroxy-13-methyl-*N*-((2*S*,3*S*,6*R*,*E*)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (30).

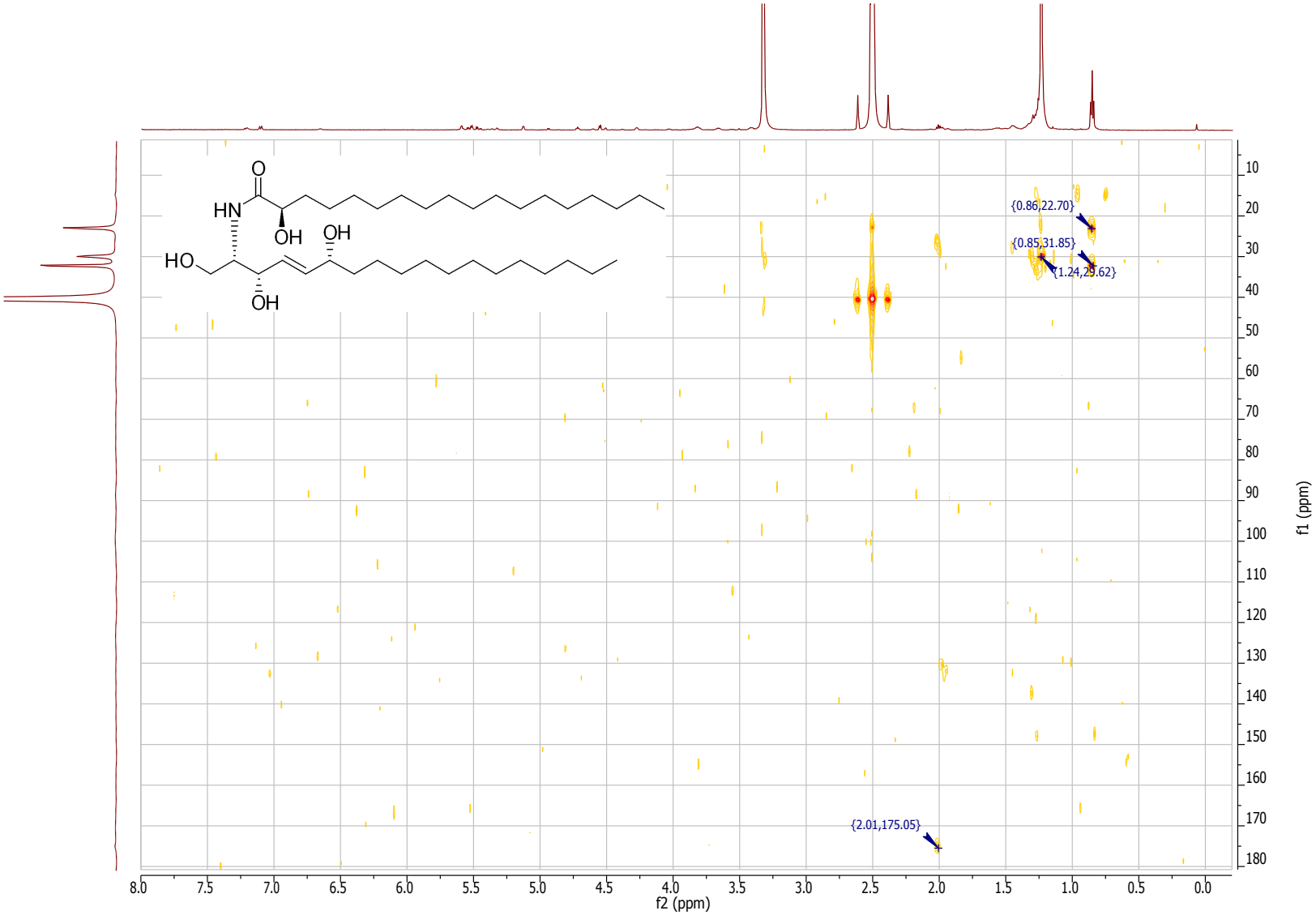

Figure 55. ^{1}H-^{13}C HMBC of (*R*)-2-hydroxy-13-methyl-*N*-((2*S*,3*S*,6*R*,*E*)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (30).

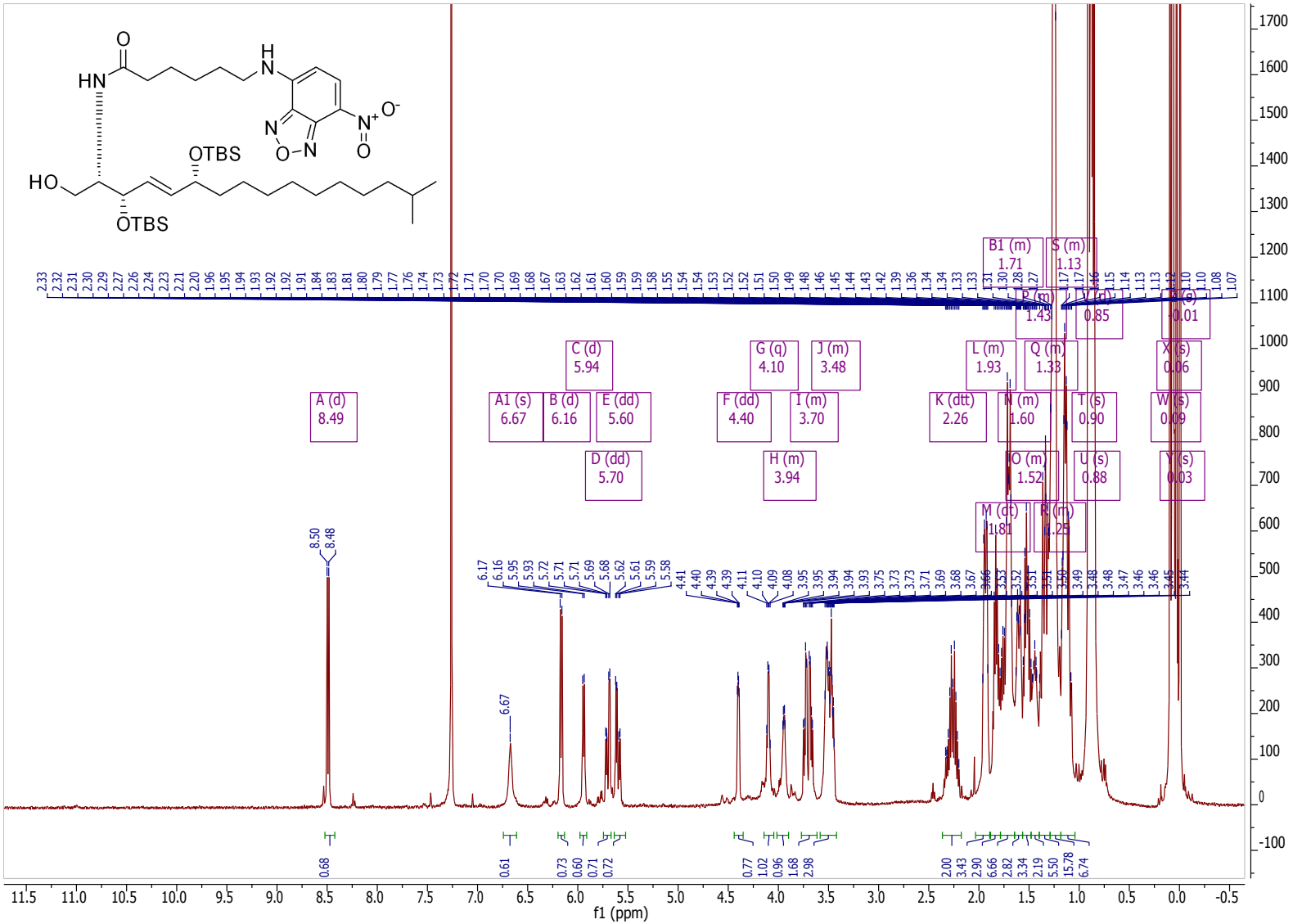

Figure 56. ^{1}H-NMR (500 MHz, $CDCl_3$) of *N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-6-((7-nitrobenzo[c][1,2,5]oxadiazol-4-yl)amino)hexanamide (31).

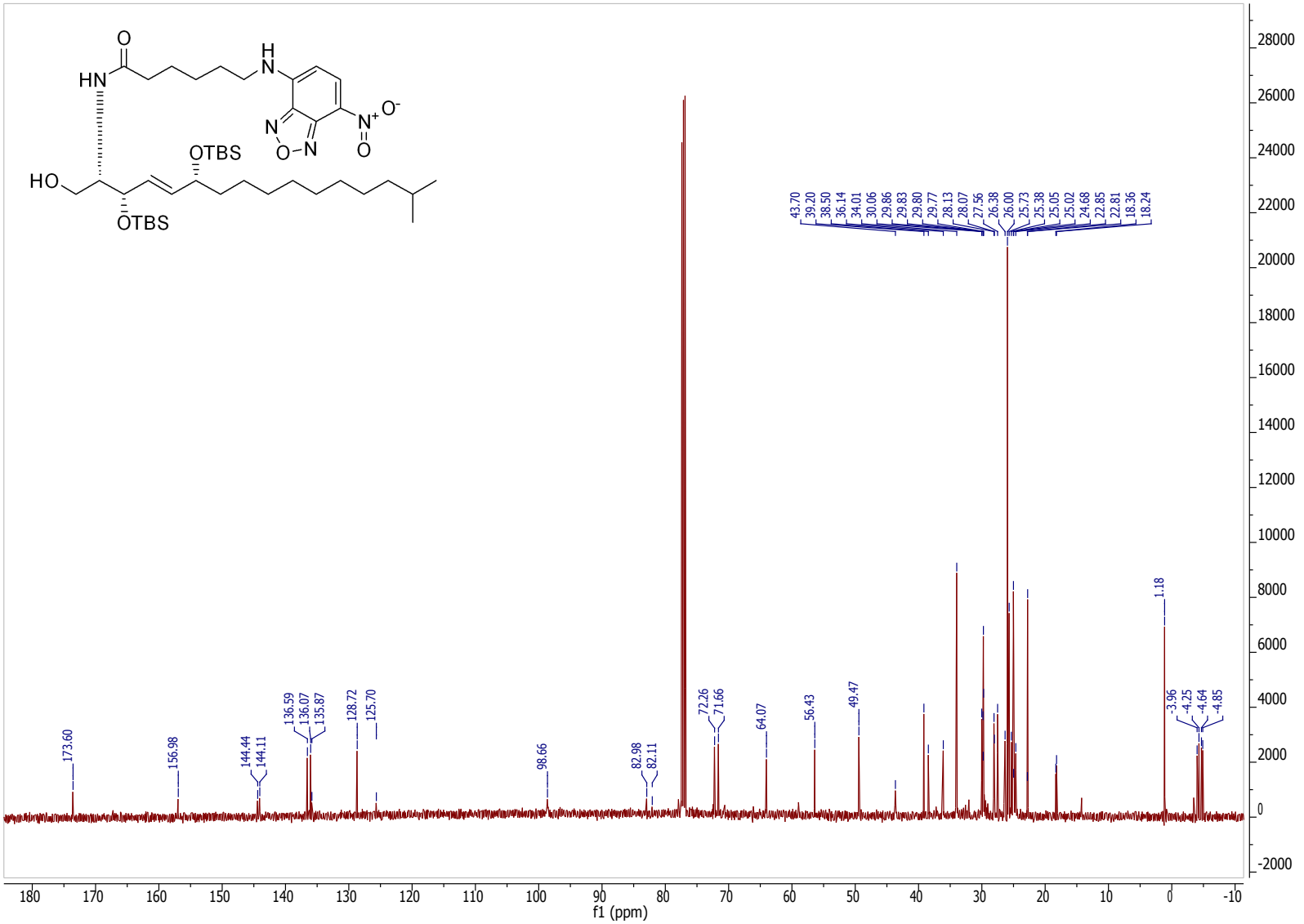

Figure 57. ^{13}C-NMR (126 MHz, $CDCl_3$) of N-((2*S*,3*S*,6*R*,*E*)-3,6-bis((tert-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-6-((7-nitrobenzo[c][1,2,5]oxadiazol-4-yl)amino)hexanamide (31).

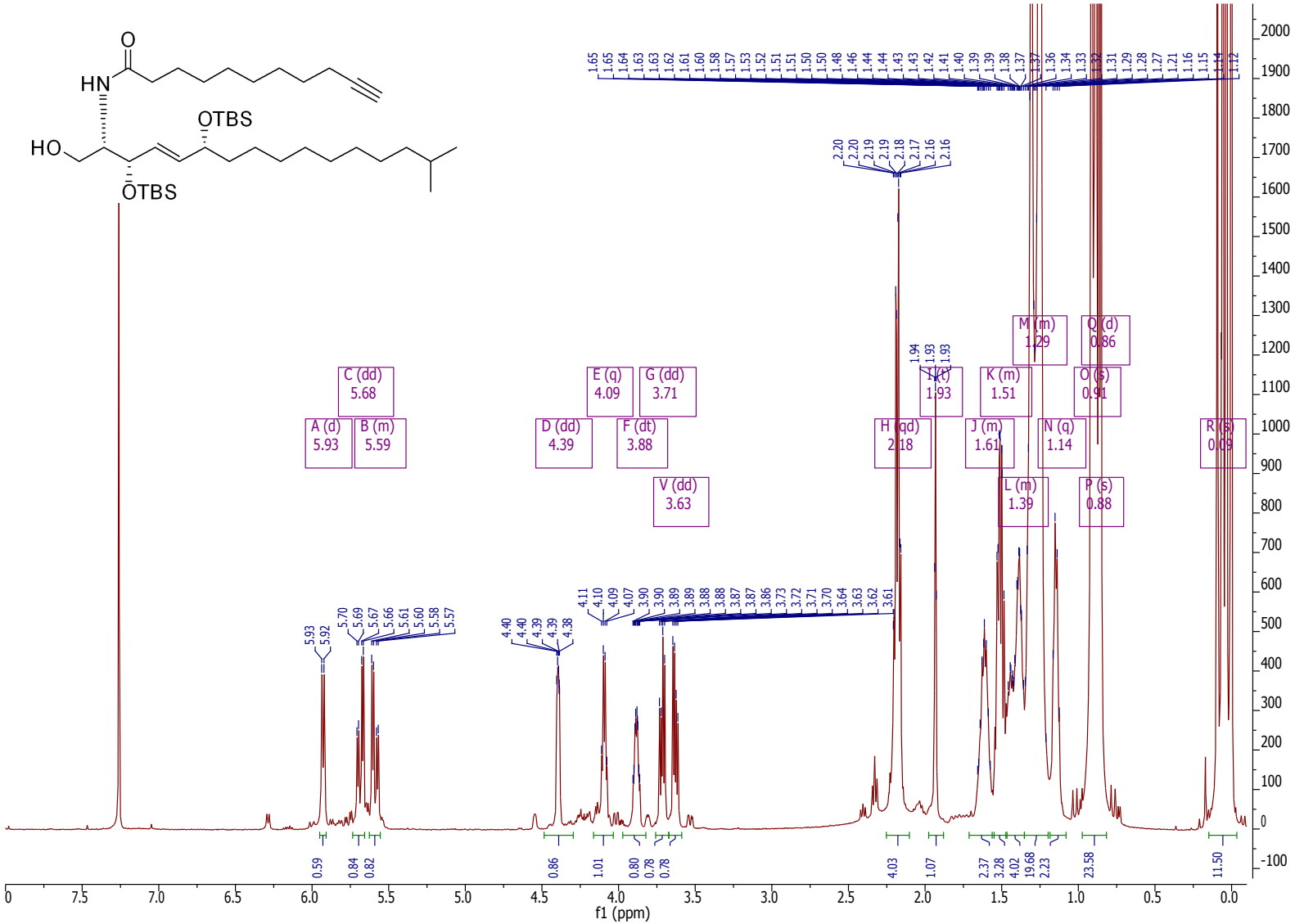

Figure 58 ^{1}H-NMR (500 MHz, $CDCl_3$) of *N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)undec-10-ynamide (32).

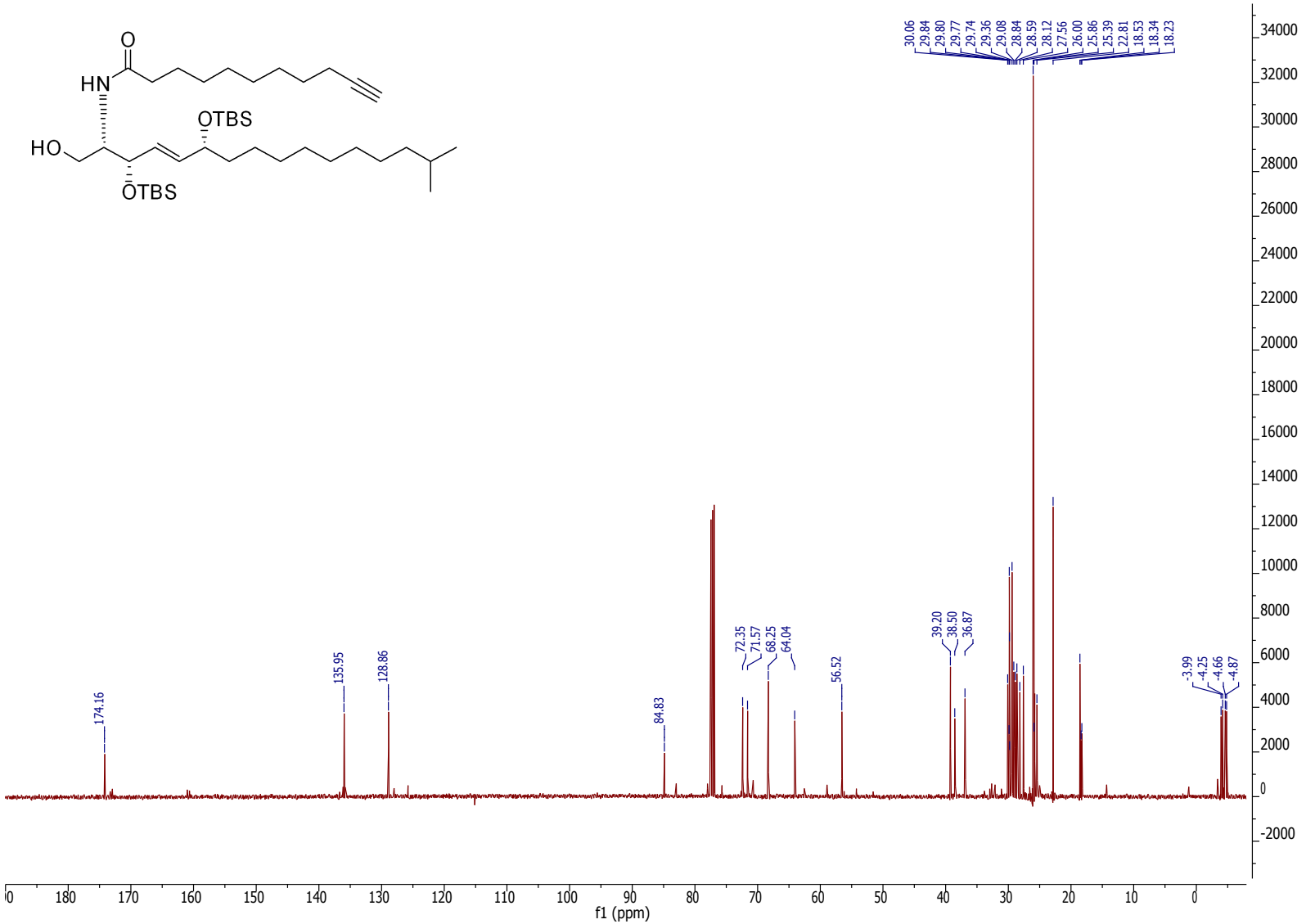

Figure 59. ^{13}C-NMR (126 MHz, $CDCl_3$) of N-((2*S*,3*S*,6*R*,*E*)-3,6-bis((tert-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)undec-10-ynamide (32).