

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).....	4
Figure 2. ¹ H-NMR (300 MHz, CDCl ₃) of 10-methylundecanol (B).	5
Figure 3. ¹³ C-NMR (75 MHz, CDCl ₃) of 10-methylundecanol (B).	6
Figure 4. ¹ H-NMR (300 MHz, CDCl ₃) of 10-methylundecanoic acid (13a).	7
Figure 5. ¹ H-NMR (500 MHz, CDCl ₃) of 13-methyltetradecanoic acid (13b).	8
Figure 6. ¹ H-NMR (300 MHz, CDCl ₃) of 12-methyl-1-(trimethylsilyl)tridec-1-yn-3-one (14a).	9
Figure 7. ¹ H-NMR (300 MHz, CDCl ₃) of 1-(trimethylsilyl)pentadec-1-yn-3-one (14b).	10
Figure 8. ¹³ C-NMR (75 MHz, CDCl ₃) of 1-(trimethylsilyl)pentadec-1-yn-3-one (14b).	11
Figure 9. ¹ H-NMR (300 MHz, CDCl ₃) of (<i>R</i>)-12-methyl-1-tridec-1-yn-3-ol (C).	12
Figure 10. ¹³ C-NMR (500 MHz, CDCl ₃) of (<i>R</i>)-1-(trimethylsilyl)pentadec-1-yn-3-ol (D).	13
Figure 11. ¹³ C-NMR (126 MHz, CDCl ₃) of (<i>R</i>)-1-(trimethylsilyl)pentadec-1-yn-3-ol (D).	14
Figure 13. ¹ H NMR (500 MHz, CDCl ₃) of (<i>R</i>)-12-Methyl-1-tridec-1-yn-3-ol (E)	15
Figure 14. ¹ H-NMR (500 MHz, CDCl ₃) of (<i>R</i>)-pentadec-1-yn-3-ol (F).	16
Figure 15. ¹³ C-NMR (126 MHz, CDCl ₃) of (<i>R</i>)-pentadec-1-yn-3-ol (F).	17
Figure 16. ¹ H-NMR (600 MHz, CDCl ₃) of (<i>R</i>)- <i>tert</i> -butyldimethyl((12-methyl-1-tridec-1-yn-3-yl)oxy)silane (11a).....	18
Figure 17. ¹³ C-NMR (151 MHz, CDCl ₃) of (<i>R</i>)- <i>tert</i> -butyldimethyl((12-methyl-1-tridec-1-yn-3-yl)oxy)silane (11a).....	19
Figure 18. ¹ H-NMR (500 MHz, CDCl ₃) of (<i>R</i>)- <i>tert</i> -butyldimethyl(pentadec-1-yn-3-yloxy)silane (11b).	20
Figure 19. ¹³ C-NMR (126 MHz, CDCl ₃) of (<i>R</i>)- <i>tert</i> -butyldimethyl(pentadec-1-yn-3-yloxy)silane (11b).	21
Figure 20. ¹ H-NMR (300 MHz, CDCl ₃) of (<i>R</i>)-4-benzyl-3-(13-methyltetradecanoyl)oxazolidin-2-one (15a).	22
Figure 21. ¹ H-NMR (75 MHz, CDCl ₃) of (<i>R</i>)-4-benzyl-3-stearoyloxazolidin-2-one (15b).	23
Figure 22. ¹ H-NMR (300 MHz, CDCl ₃) of (<i>R</i>)-4-benzyl-3-((<i>R</i>)-2-hydroxy-13-methyltetradecanoyl)oxazolidin-2-one (G).	24
Figure 23. ¹³ C-NMR (75 MHz, CDCl ₃) of (<i>R</i>)-4-benzyl-3-((<i>R</i>)-2-hydroxy-13-methyltetradecanoyl)oxazolidin-2-one (G).....	25

Figure 24. ¹ H-NMR (300 MHz, CDCl ₃) of (<i>R</i>)-4-benzyl-3-((<i>R</i>)-2-hydroxyoctadecanoyl)oxazolidin-2-one (H).	26
Figure 25. ¹ H-NMR (300 MHz, CDCl ₃) of (<i>R</i>)-2-hydroxy-13-methyltetradecanoic acid (16a).	27
Figure 26. ¹³ C-NMR (75 MHz, CDCl ₃) of (<i>R</i>)-2-Hydroxy-13-methyltetradecanoic acid (16a).	28
Figure 27. ¹ H-NMR (600 MHz, CDCl ₃) of (<i>R</i>)-2-hydroxyoctadecanoic acid (16b).	29
Figure 28. ¹³ C-NMR (151 MHz, CDCl ₃) of (<i>R</i>)-2-hydroxyoctadecanoic acid (16b).	30
Figure 29. ¹ H-NMR (300 MHz, CDCl ₃) of 3-(<i>tert</i> -butyl) 4-methyl (<i>S</i>)-2,2-dimethyloxazolidine-3,4-dicarboxylate (I).	31
Figure 30. ¹ H-NMR (300 MHz, CDCl ₃) of Garner's aldehyde (3).	32
Figure 31. ¹ H-NMR (300 MHz, CDCl ₃) of (<i>R</i>)- <i>tert</i> -butyldimethyl((12-methyltridec-1-en-3-yl)oxy)silane (17).	33
Figure 32. ¹ H-NMR (500 MHz, C ₆ D ₆ , 300 K) of <i>tert</i> -butyl (<i>S</i>)-4-((1 <i>R</i> ,4 <i>R</i> , <i>E</i>)-4-((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (12a)	34
Figure 33. ¹³ C-NMR (126 MHz, C ₆ D ₆ , 300 K) of <i>tert</i> -butyl (<i>S</i>)-4-((1 <i>R</i> ,4 <i>R</i> , <i>E</i>)-4-((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (12a)	35
Figure 34. ¹ H-NMR (500 MHz, C ₆ D ₆ , 300 K) of <i>tert</i> -butyl (<i>S</i>)-4-((1 <i>S</i> ,4 <i>R</i> , <i>E</i>)-4-((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (12b)	36
Figure 35. ¹ H-NMR (126 MHz, C ₆ D ₆ , 300 K) of <i>tert</i> -butyl (<i>S</i>)-4-((1 <i>S</i> ,4 <i>R</i> , <i>E</i>)-4-((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (12b)	37
Figure 36. ¹ H-NMR (500 MHz, C ₆ D ₆ , 300 K) of <i>tert</i> -butyl (<i>S</i>)-4-((1 <i>S</i> ,4 <i>R</i> , <i>E</i>)-4-((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxyhexadec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (19b)	38
Figure 37. ¹³ C-NMR (126 MHz, C ₆ D ₆ , 300 K) of <i>tert</i> -butyl (<i>S</i>)-4-((1 <i>S</i> ,4 <i>R</i> , <i>E</i>)-4-((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxyhexadec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (19b)	39
Figure 38. ¹ H-NMR (500 MHz, CDCl ₃) of (2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-aminium formate (22).	40
Figure 39. ¹³ C-NMR (126 MHz, CDCl ₃) of (2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-aminium formate (22).	41
Figure 40. ¹ H-NMR (500 MHz, CDCl ₃) of (2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxyoctadec-4-en-2-aminium formate (23).	42
Figure 41. ¹³ C-NMR (126 MHz, CDCl ₃) of (2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxyoctadec-4-en-2-aminium formate (23)	43
Figure 42. ¹ H-NMR (500 MHz, CDCl ₃) of N-((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-13-methyltetradecanamide (24).	44
Figure 43. ¹³ C-NMR (126 MHz, CDCl ₃) of N-((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-13-methyltetradecanamide (24).	45

Figure 44. ¹ H-NMR (600 MHz, CDCl ₃) of 13-methyl- <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (25).	46
Figure 45. ¹³ C-NMR (151 MHz, CDCl ₃) of 13-methyl- <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (25).....	47
Figure 46. ¹ H-NMR (500 MHz, CDCl ₃) of <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)stearamide (26).	48
Figure 47. ¹³ C-NMR (126 MHz, CDCl ₃) of <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)stearamide (26).	49
Figure 48. ¹ H-NMR (300 MHz, CDCl ₃) of (<i>R</i>)- <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-2-hydroxy-13-methyltetradecanamide (27).	50
Figure 49. ¹³ C-NMR (75 MHz, CDCl ₃) of (<i>R</i>)- <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-2-hydroxy-13-methyltetradecanamide (27).....	51
Figure 50. ¹ H-NMR (600 MHz, DMSO- <i>d</i> ₆) of (<i>R</i>)-2-hydroxy-13-methyl- <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (28).	52
Figure 51. ¹³ C-NMR (151 MHz, DMSO- <i>d</i> ₆) of (<i>R</i>)-2-hydroxy-13-methyl- <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (28).	53
Figure 52. ¹ H-NMR (300 MHz, CDCl ₃) of (<i>R</i>)- <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxyoctadec-4-en-2-yl)-2-hydroxyoctadecanamide (29).	54
Figure 53. ¹ H-NMR (600 MHz, DMSO- <i>d</i> ₆) of (<i>R</i>)-2-hydroxy- <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-1,3,6-trihydroxyoctadec-4-en-2-yl)octadecanamide (30).	55
Figure 54. ¹ H- ¹ H COSY (600 MHz, DMSO- <i>d</i> ₆) of (<i>R</i>)-2-hydroxy-13-methyl- <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (30).	56
Figure 55. ¹ H- ¹³ C HSQC (<i>R</i>)-2-hydroxy-13-methyl- <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (30).	57
Figure 56. ¹ H- ¹³ C HMBC of (<i>R</i>)-2-hydroxy-13-methyl- <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (30).	58
Figure 57. ¹ H-NMR (500 MHz, CDCl ₃) of <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-6-((7-nitrobenzo[<i>c</i>][1,2,5]oxadiazol-4-yl)amino)hexanamide (31).....	59
Figure 58. ¹³ C-NMR (126 MHz, CDCl ₃) of <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-6-((7-nitrobenzo[<i>c</i>][1,2,5]oxadiazol-4-yl)amino)hexanamide (31).....	60
Figure 59. ¹ H-NMR (500 MHz, CDCl ₃) of <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)undec-10-ynamide (32).	61
Figure 60. ¹³ C-NMR (126 MHz, CDCl ₃) of <i>N</i> -((2 <i>S</i> ,3 <i>S</i> ,6 <i>R</i> , <i>E</i>)-3,6-bis((<i>tert</i> -butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)undec-10-ynamide (32).	62

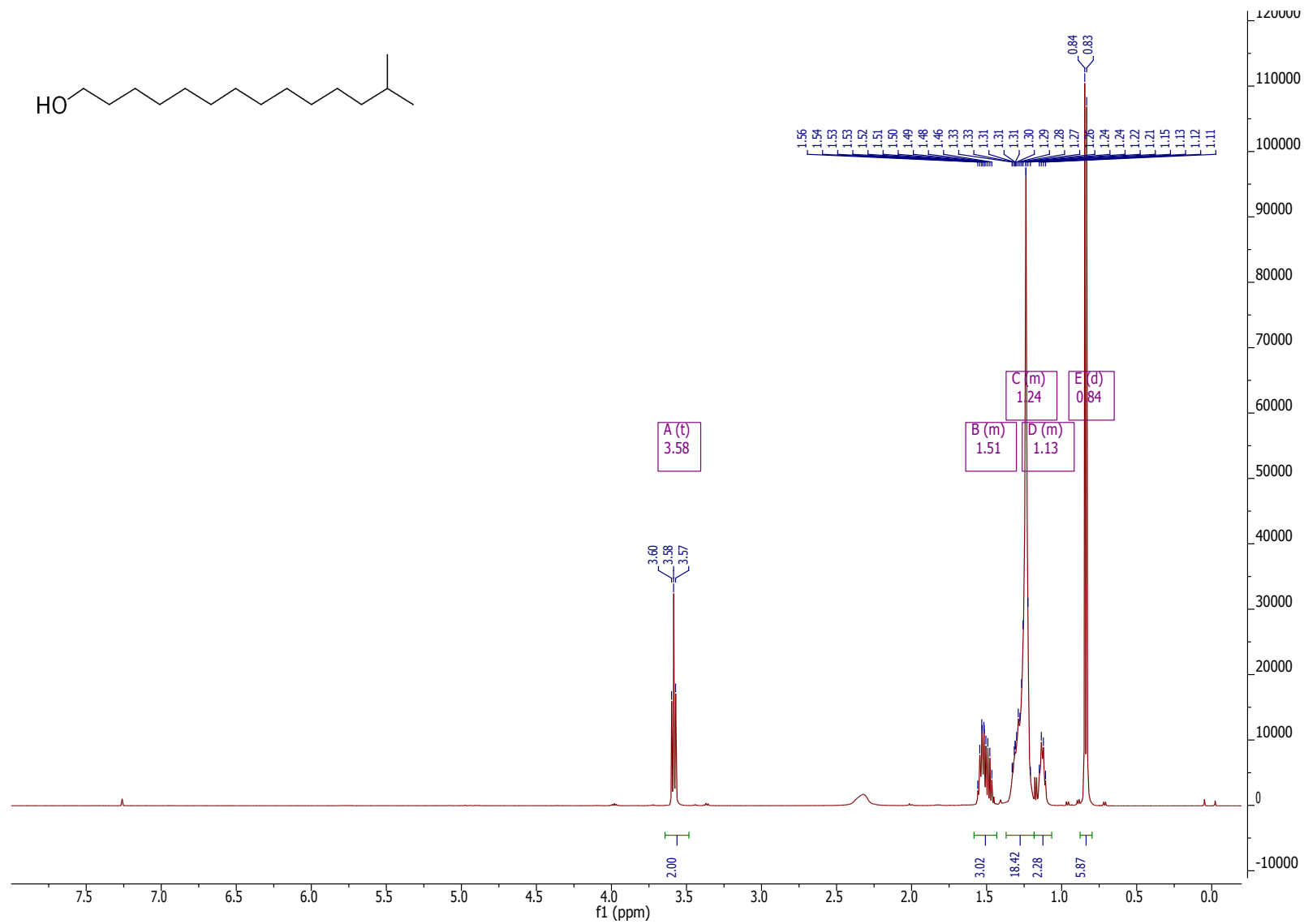
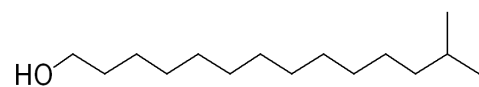


Figure 1. ^1H NMR (500 MHz, CDCl_3) of 13-methyltetradecanol (A).

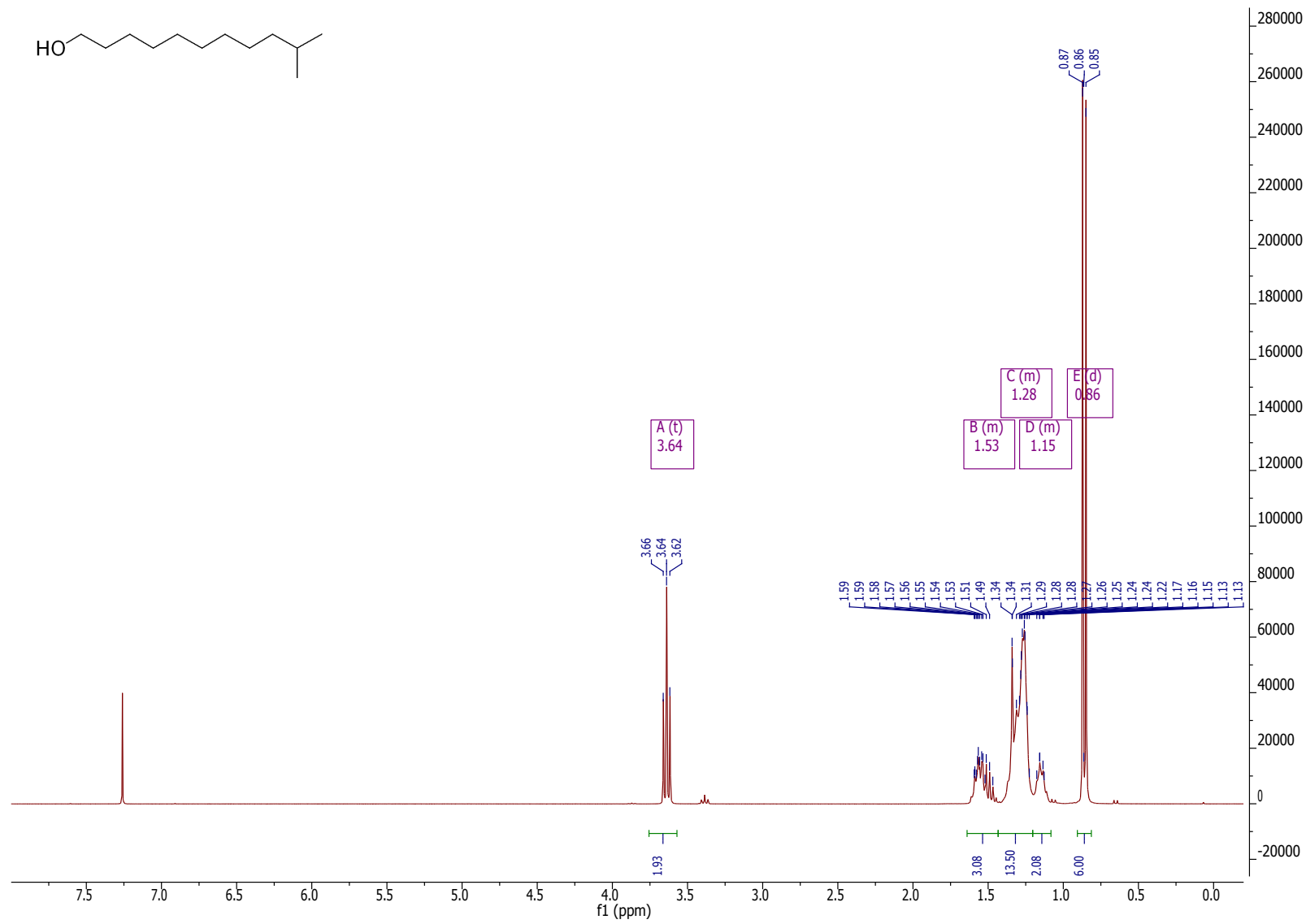
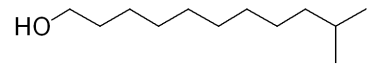


Figure 2. ¹H-NMR (300 MHz, CDCl₃) of 10-methylundecanol (B).

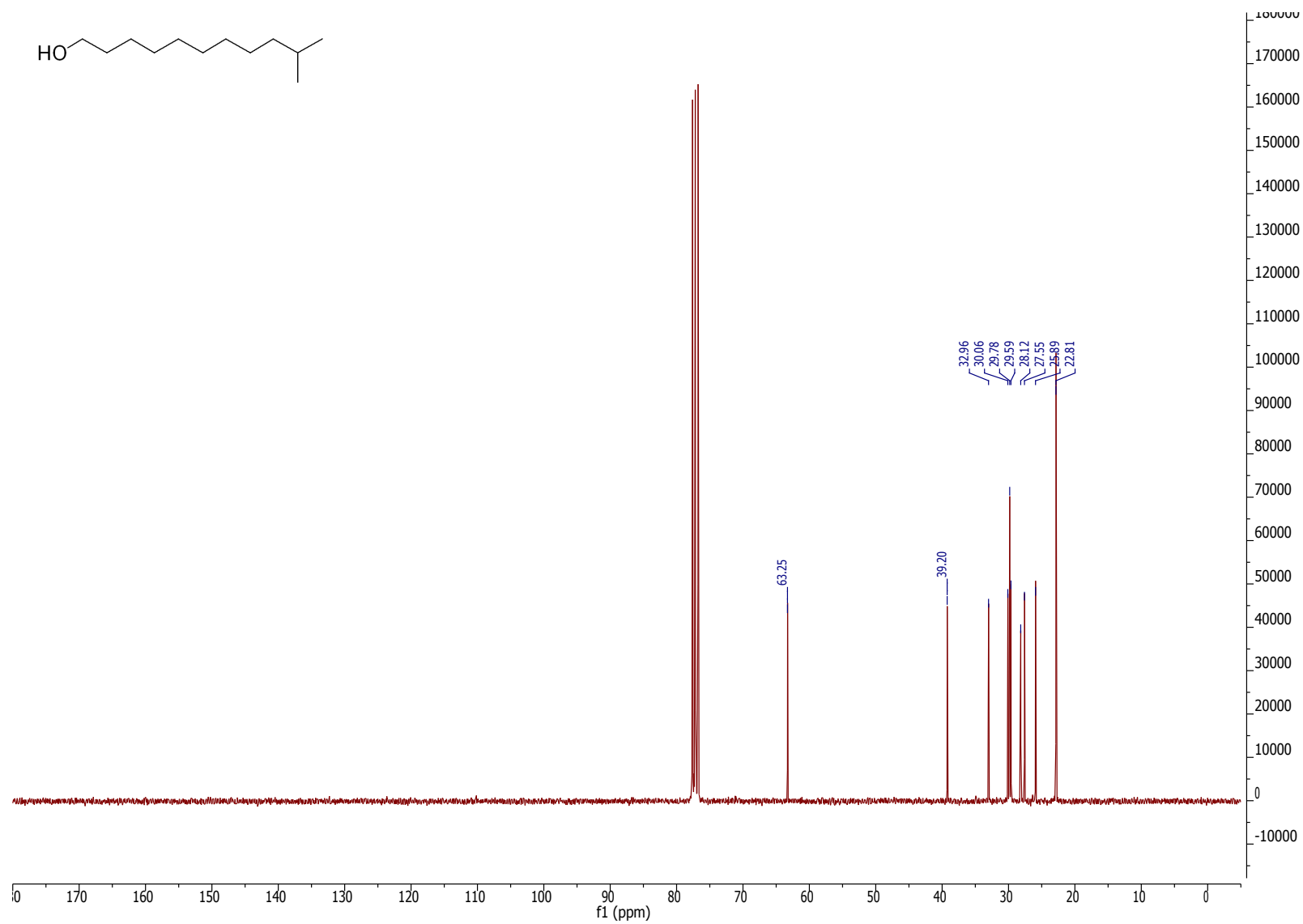
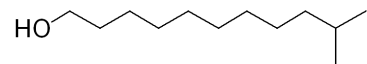


Figure 3. ^{13}C -NMR (75 MHz, CDCl_3) of 10-methylundecanol (B).

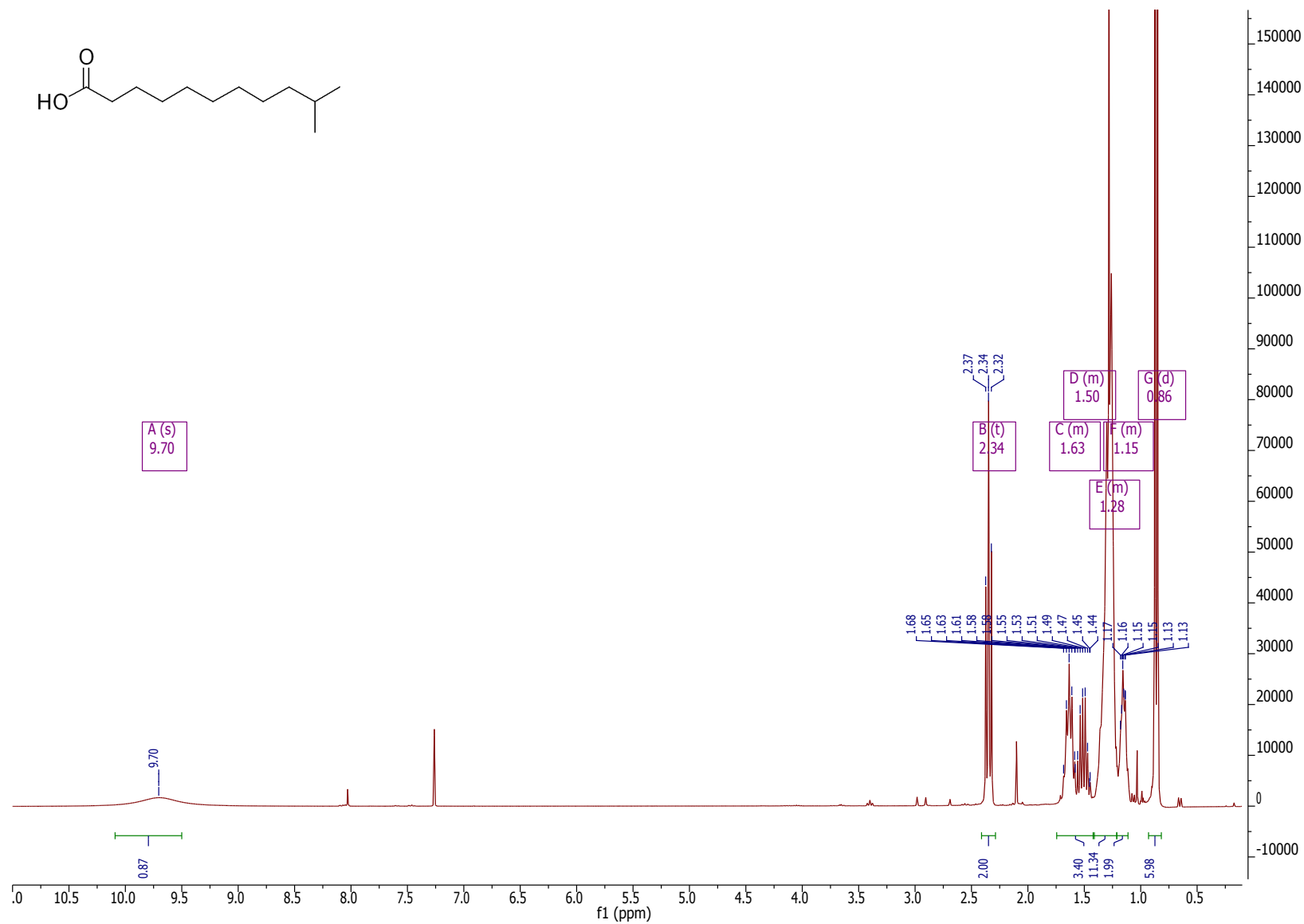
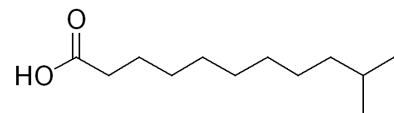


Figure 4. ¹H-NMR (300 MHz, CDCl₃) of 10-methylundecanoic acid (13a).

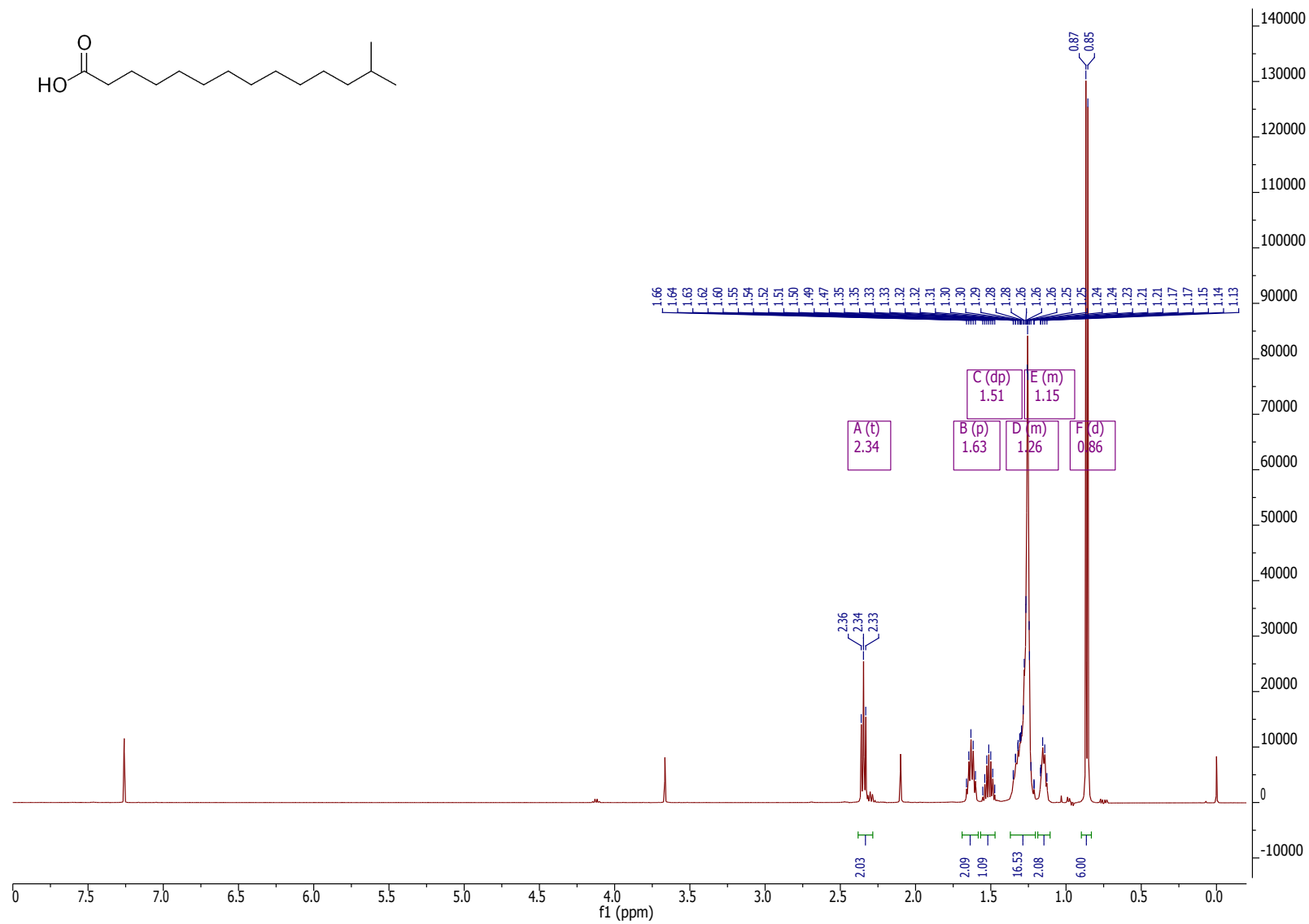
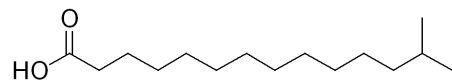


Figure 5. ¹H-NMR (500 MHz, CDCl₃) of 13-methyltetradecanoic acid (13b).

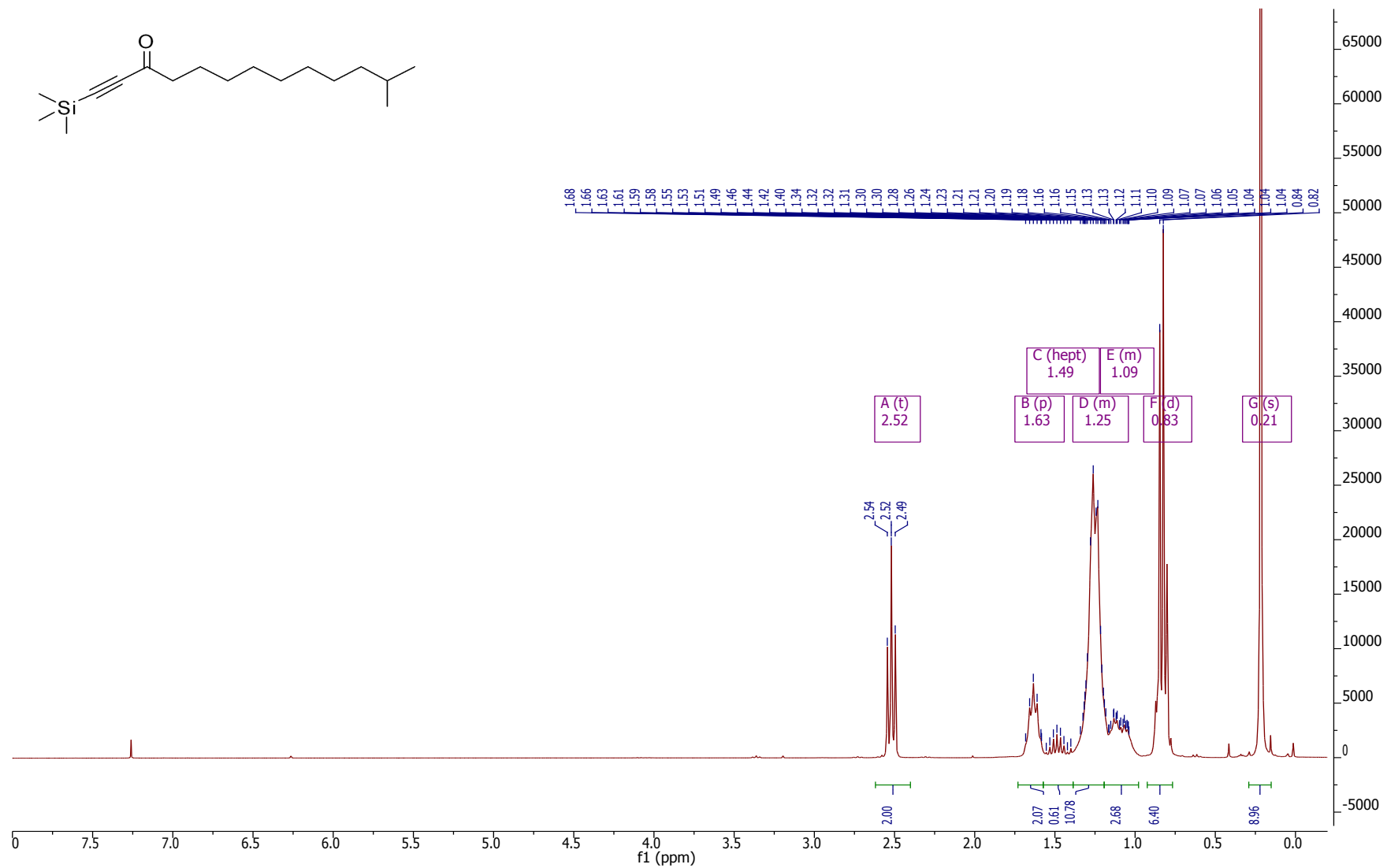


Figure 6. ¹H-NMR (300 MHz, CDCl₃) of 12-methyl-1-(trimethylsilyl)tridec-1-yn-3-one (14a).

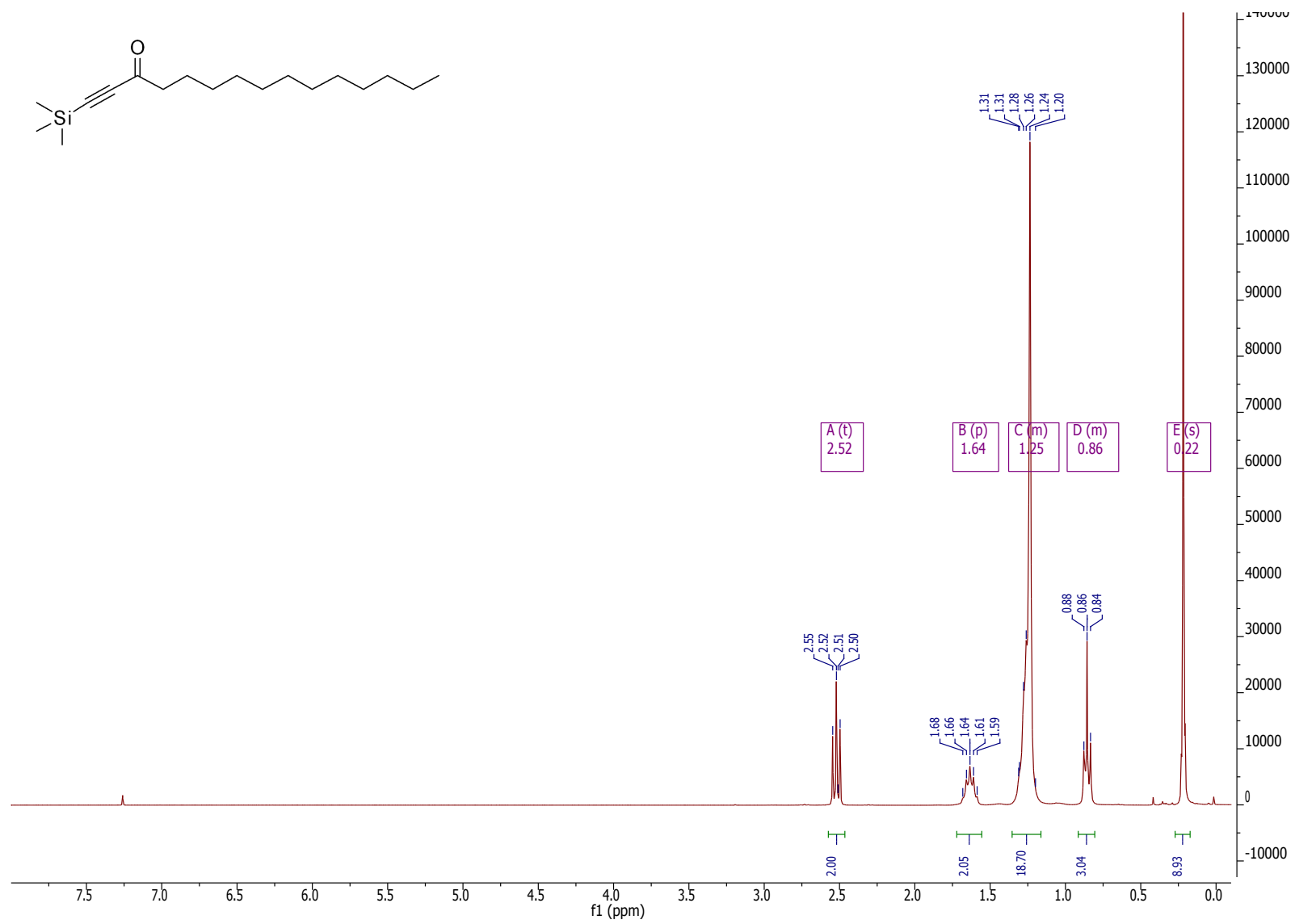


Figure 7. ¹H-NMR (300 MHz, CDCl₃) of 1-(trimethylsilyl)pentadec-1-yn-3-one (14b).

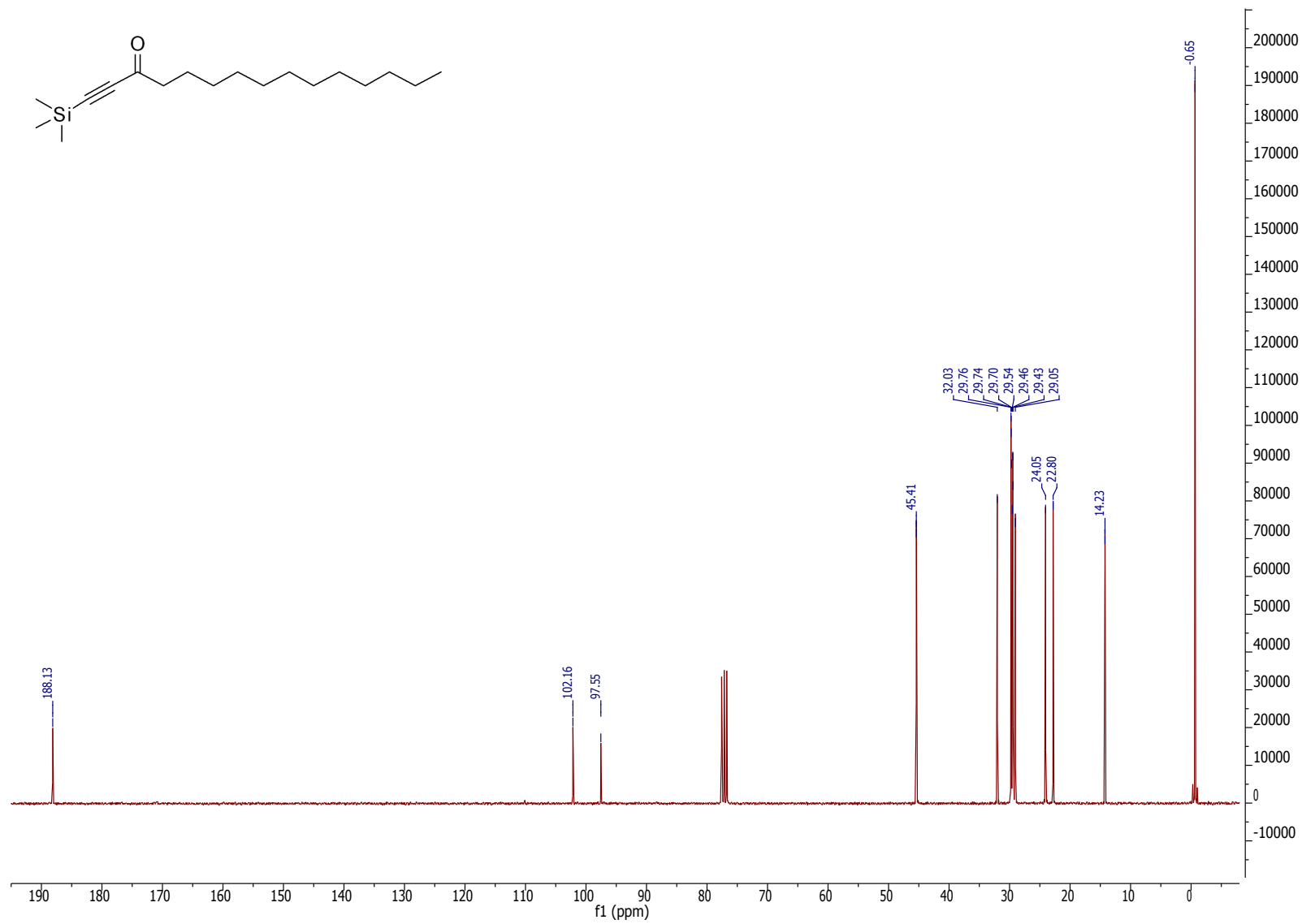


Figure 8. ¹³C-NMR (75 MHz, CDCl₃) of 1-(trimethylsilyl)pentadec-1-yn-3-one (14b).

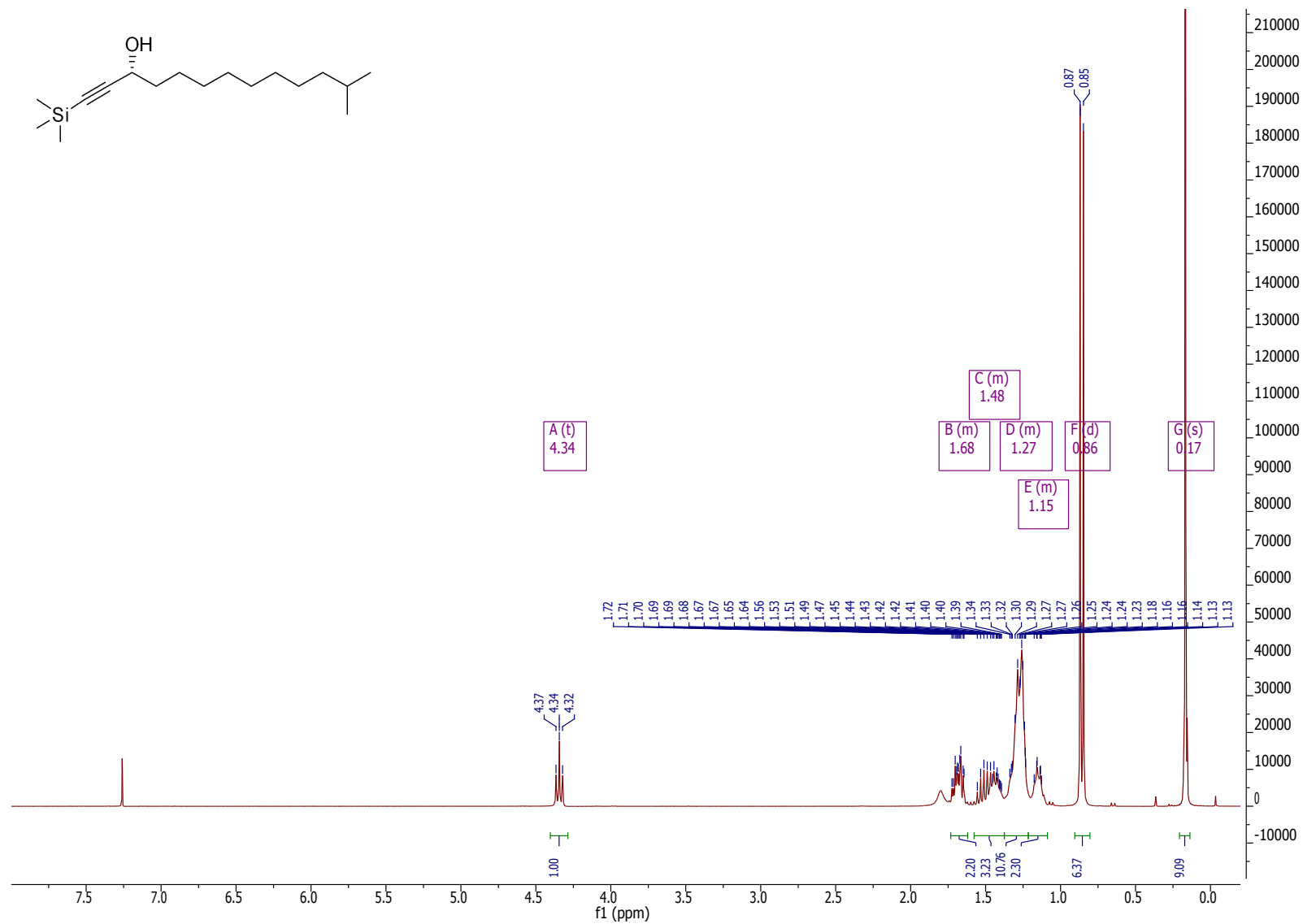


Figure 9. ¹H-NMR (300 MHz, CDCl₃) of (R)-12-methyl-1-tridec-1-yn-3-ol (C).

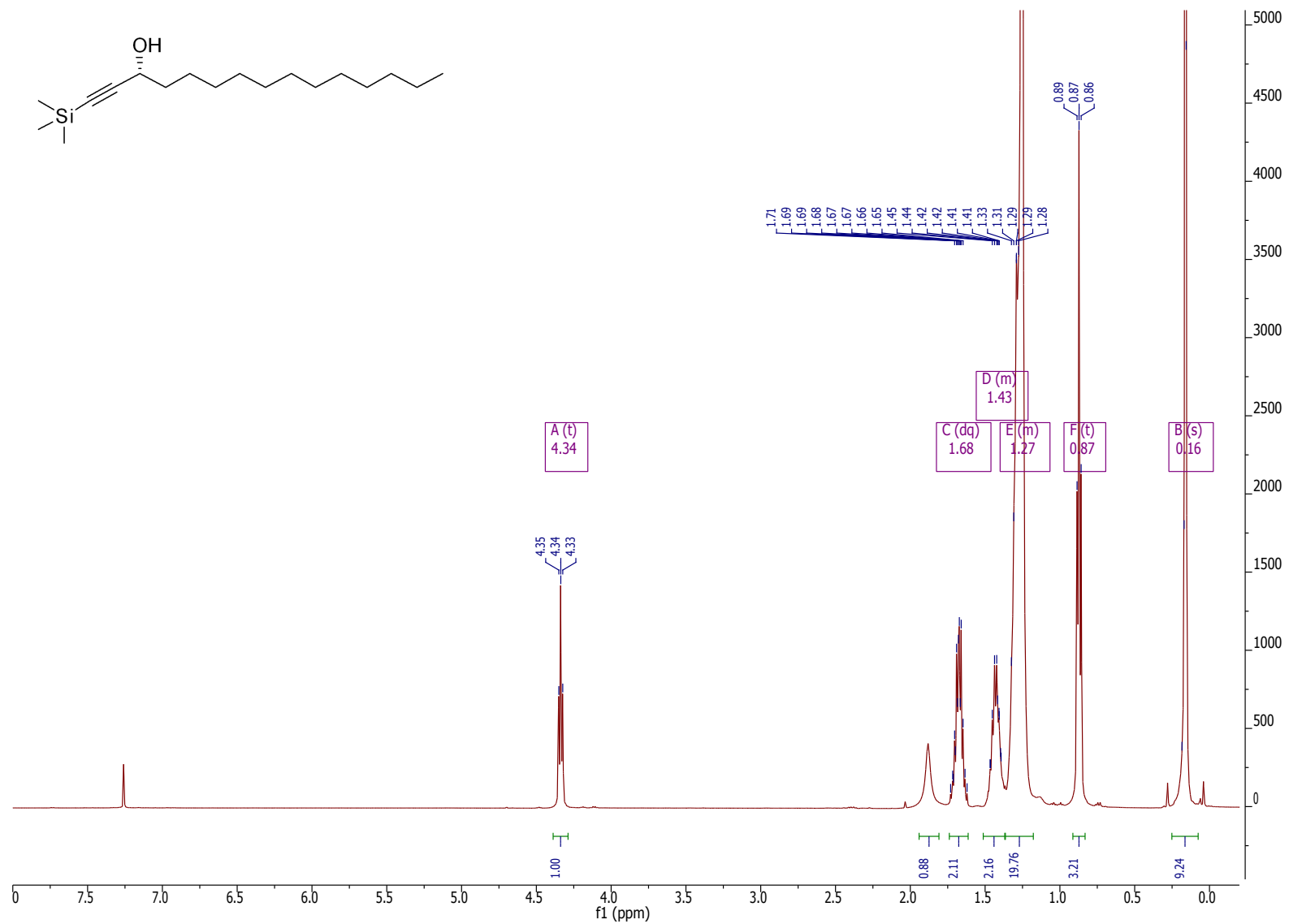


Figure 10. ¹³C-NMR (500 MHz, CDCl₃) of (R)-1-(trimethylsilyl)pentadec-1-yn-3-ol (D).

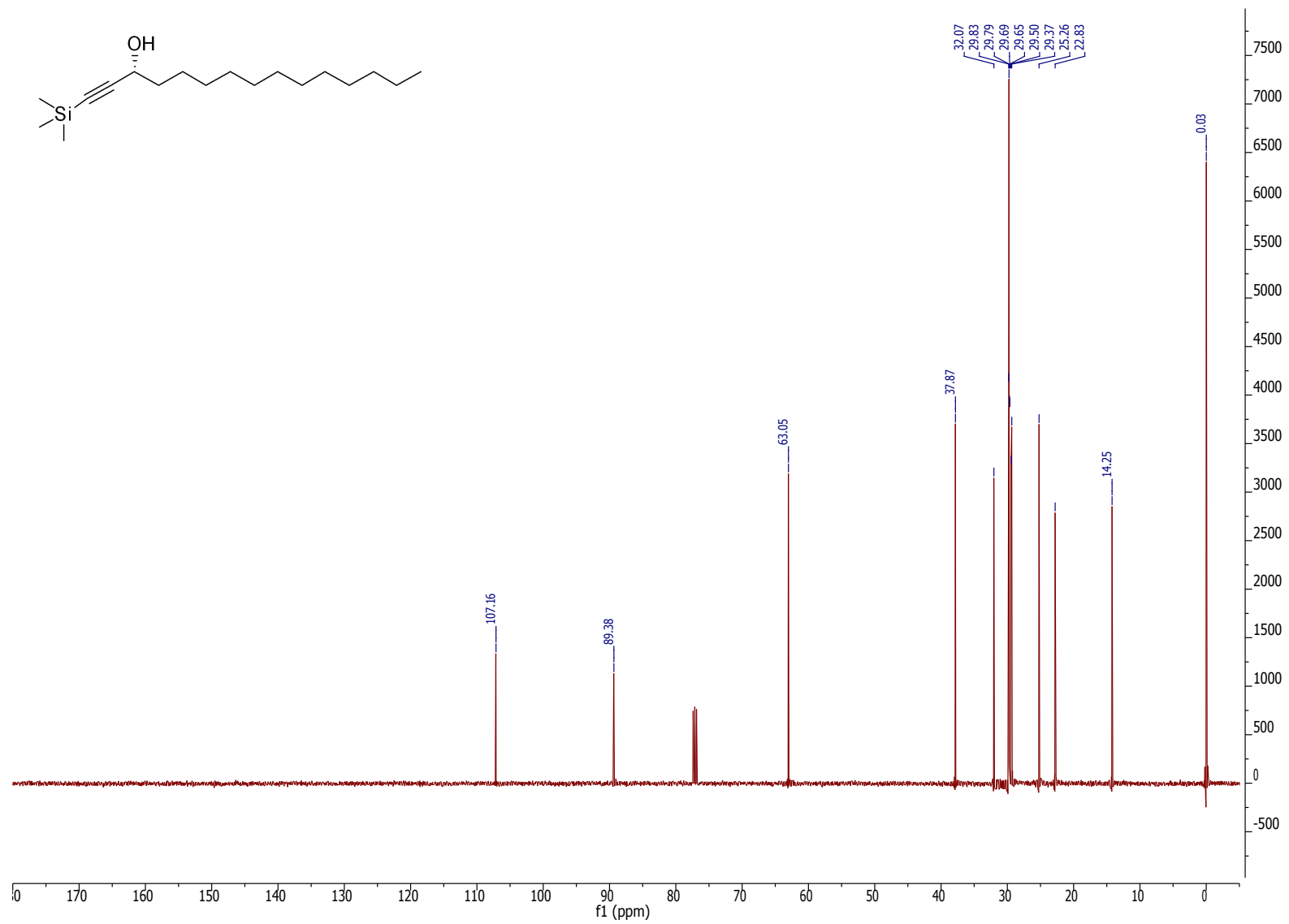


Figure 11. ¹³C-NMR (126 MHz, CDCl₃) of (*R*)-1-(trimethylsilyl)pentadec-1-yn-3-ol (D).

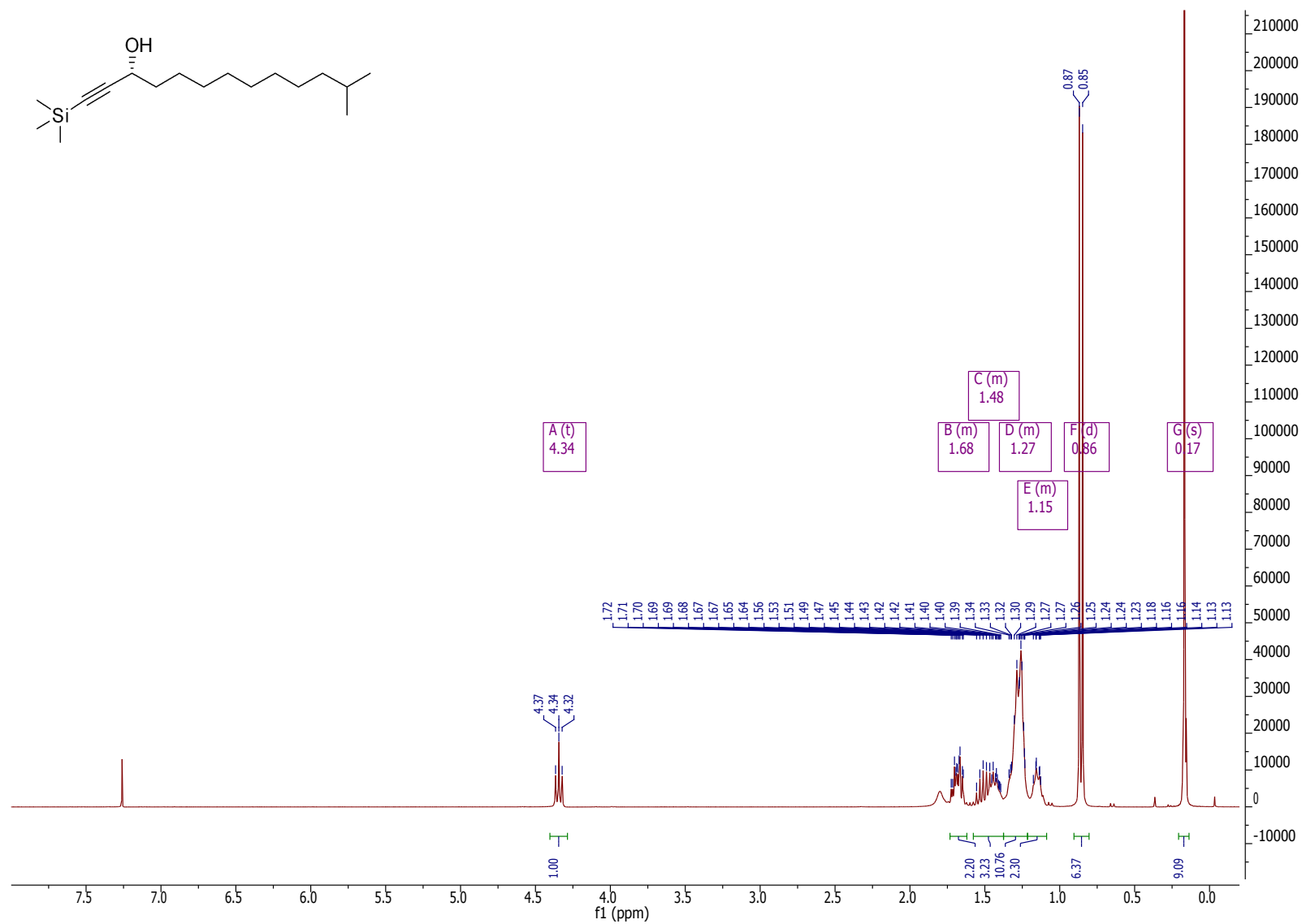


Figure 12. ¹H NMR (500 MHz, CDCl₃) of (R)-12-Methyl-1-tridec-1-yn-3-ol (E)

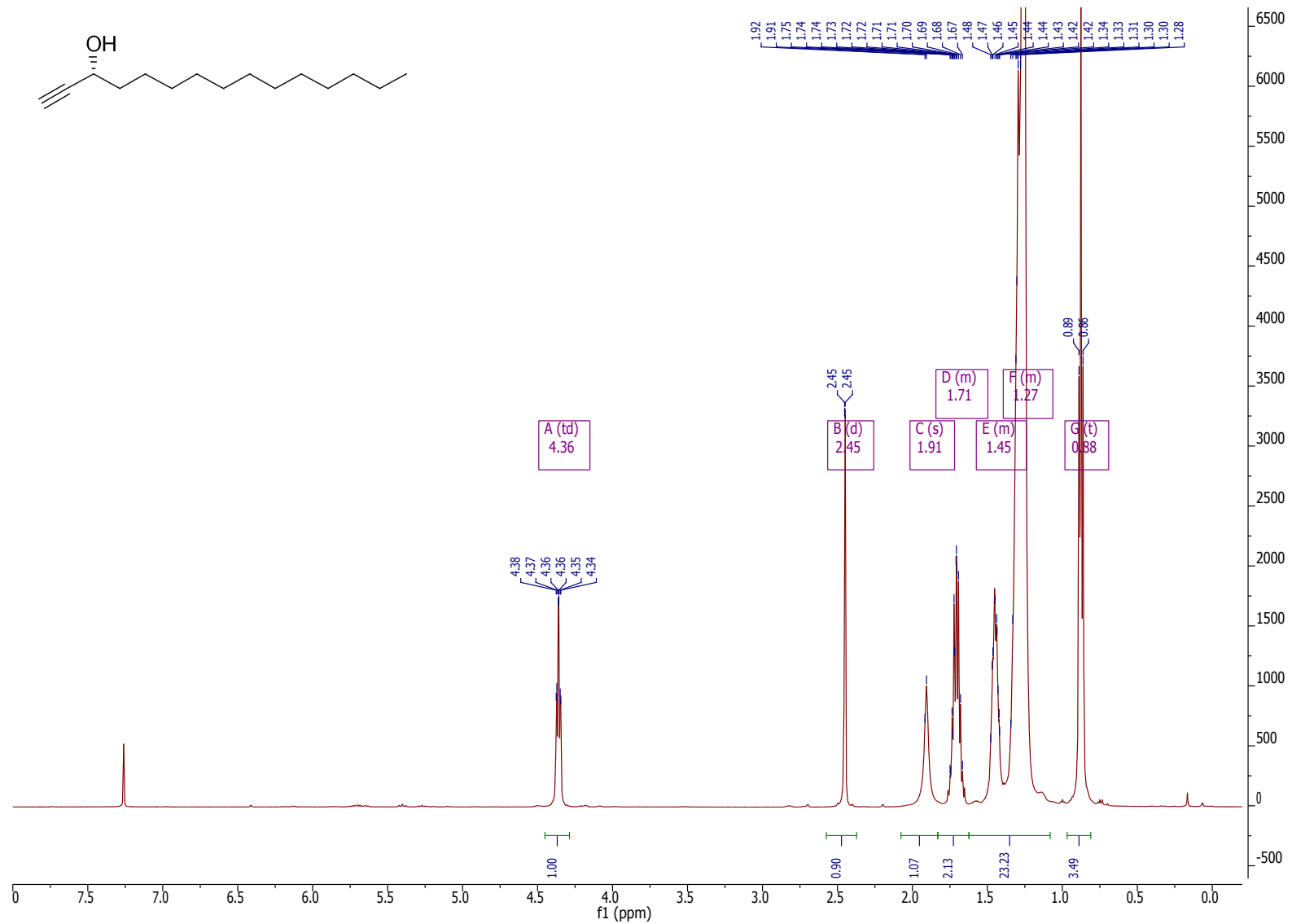


Figure 13. ¹H-NMR (500 MHz, CDCl₃) of (R)-pentadec-1-yn-3-ol (F).

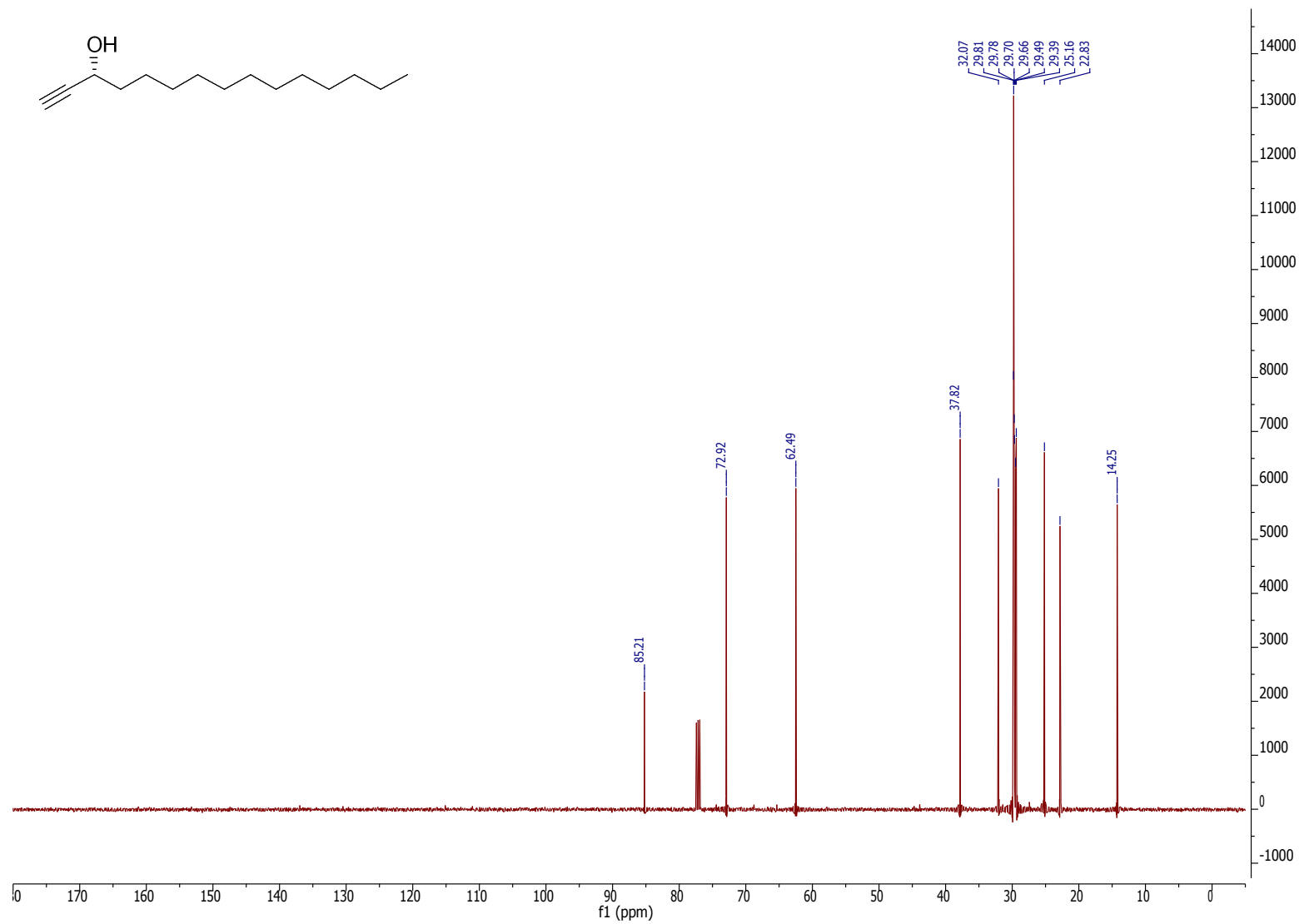


Figure 14. ¹³C-NMR (126 MHz, CDCl₃) of (R)-pentadec-1-yn-3-ol (F).

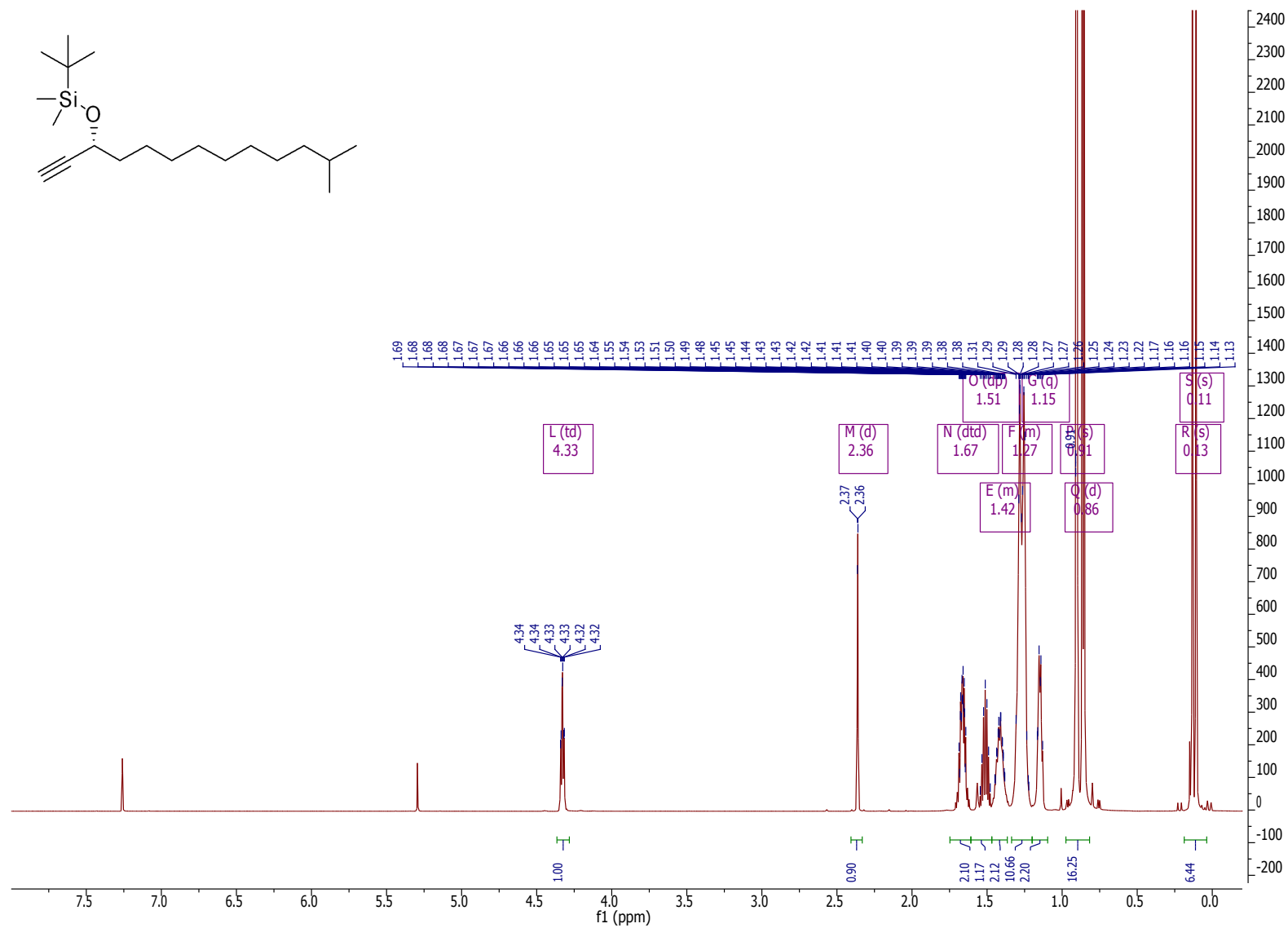


Figure 15. ¹H-NMR (600 MHz, CDCl₃) of *(R)*-*tert*-butyldimethyl((12-methyl-1-tridec-1-yn-3-yl)oxy)silane (11a).

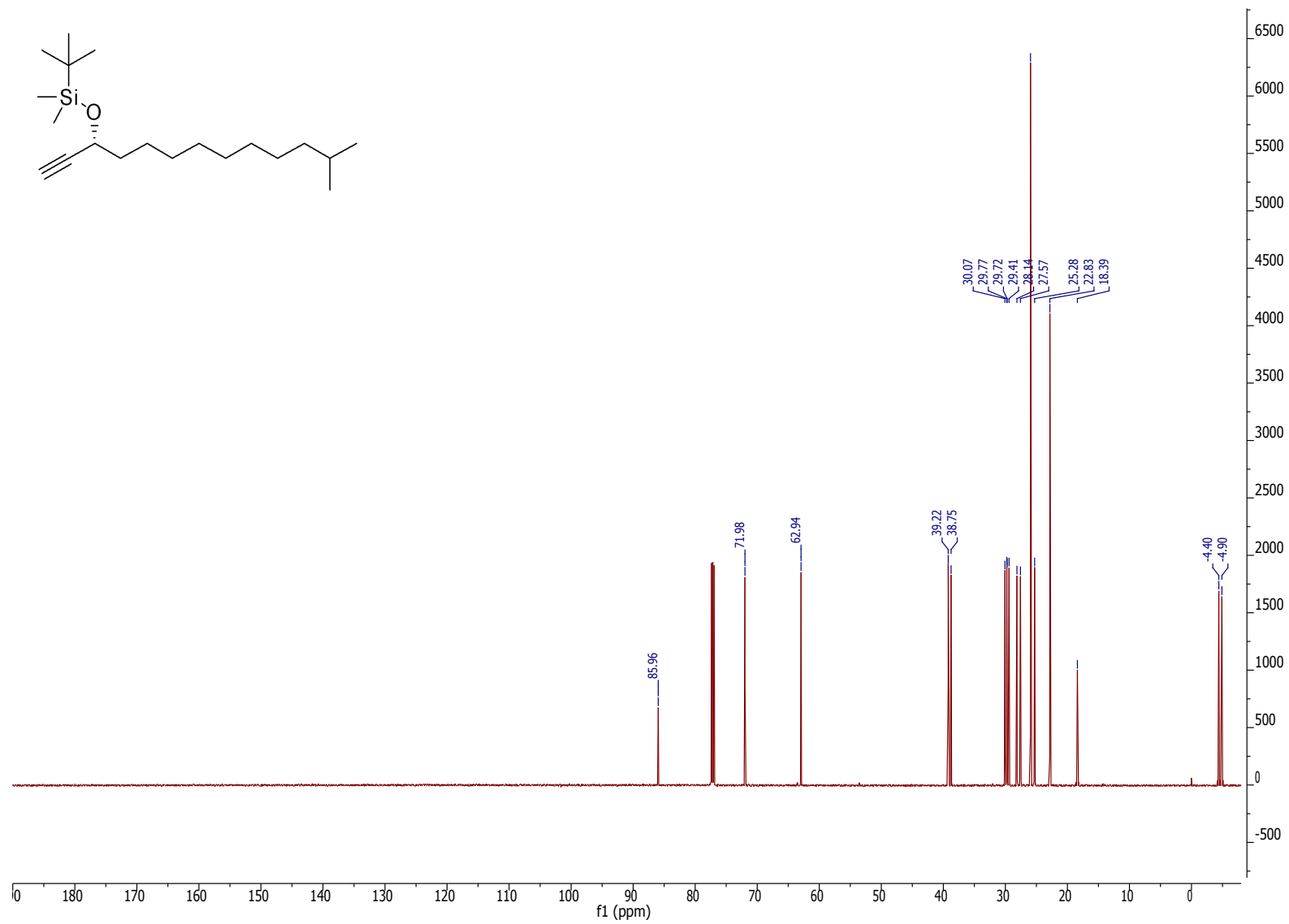


Figure 16. ¹³C-NMR (151 MHz, CDCl₃) of (R)-tert-butyl dimethyl((12-methyl-1-tridec-1-yn-3-yl)oxy)silane (11a).

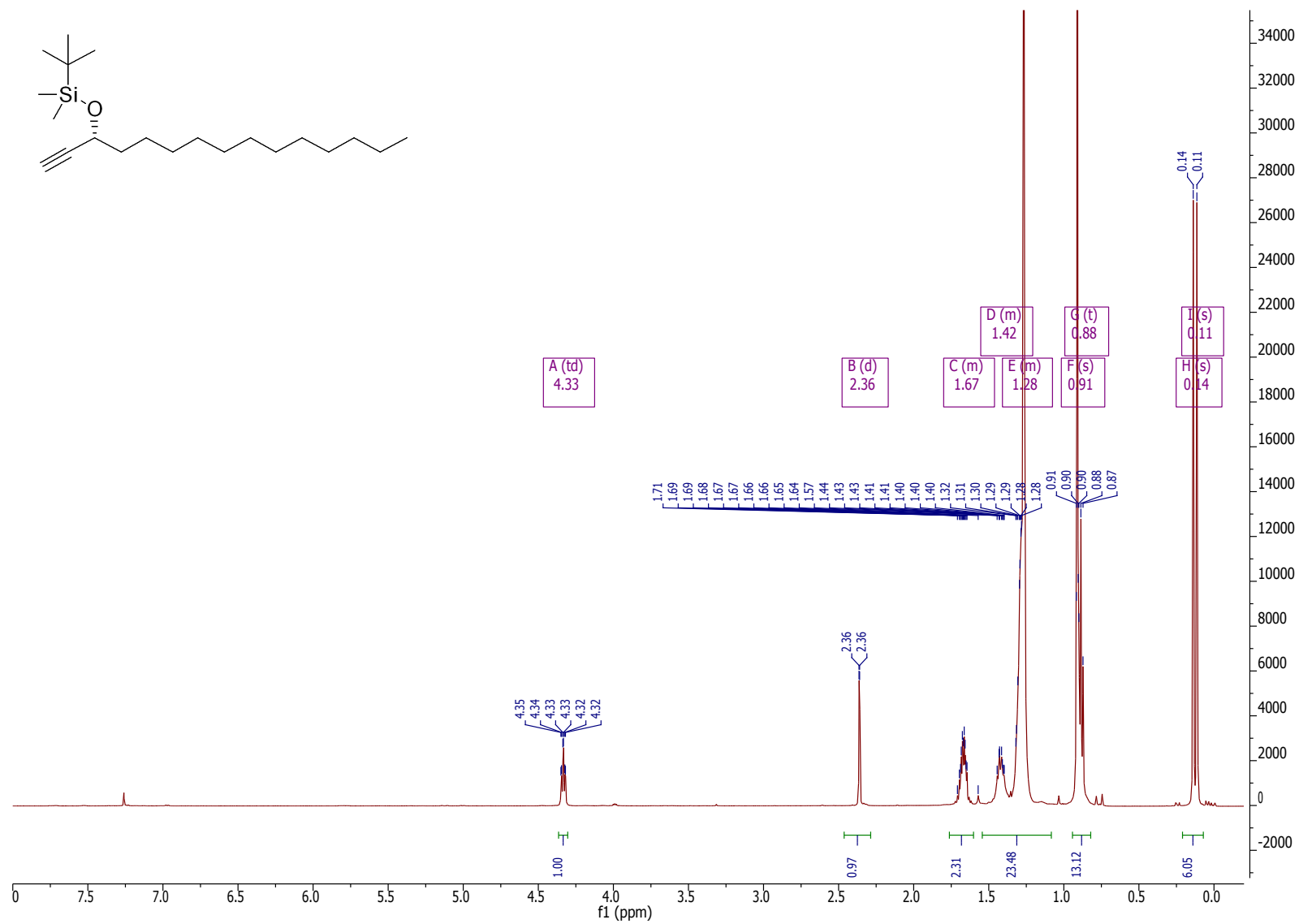


Figure 17. ¹H-NMR (500 MHz, CDCl₃) of *(R)*-*tert*-butyl dimethyl (pentadec-1-yn-3-yloxy)silane (11b).

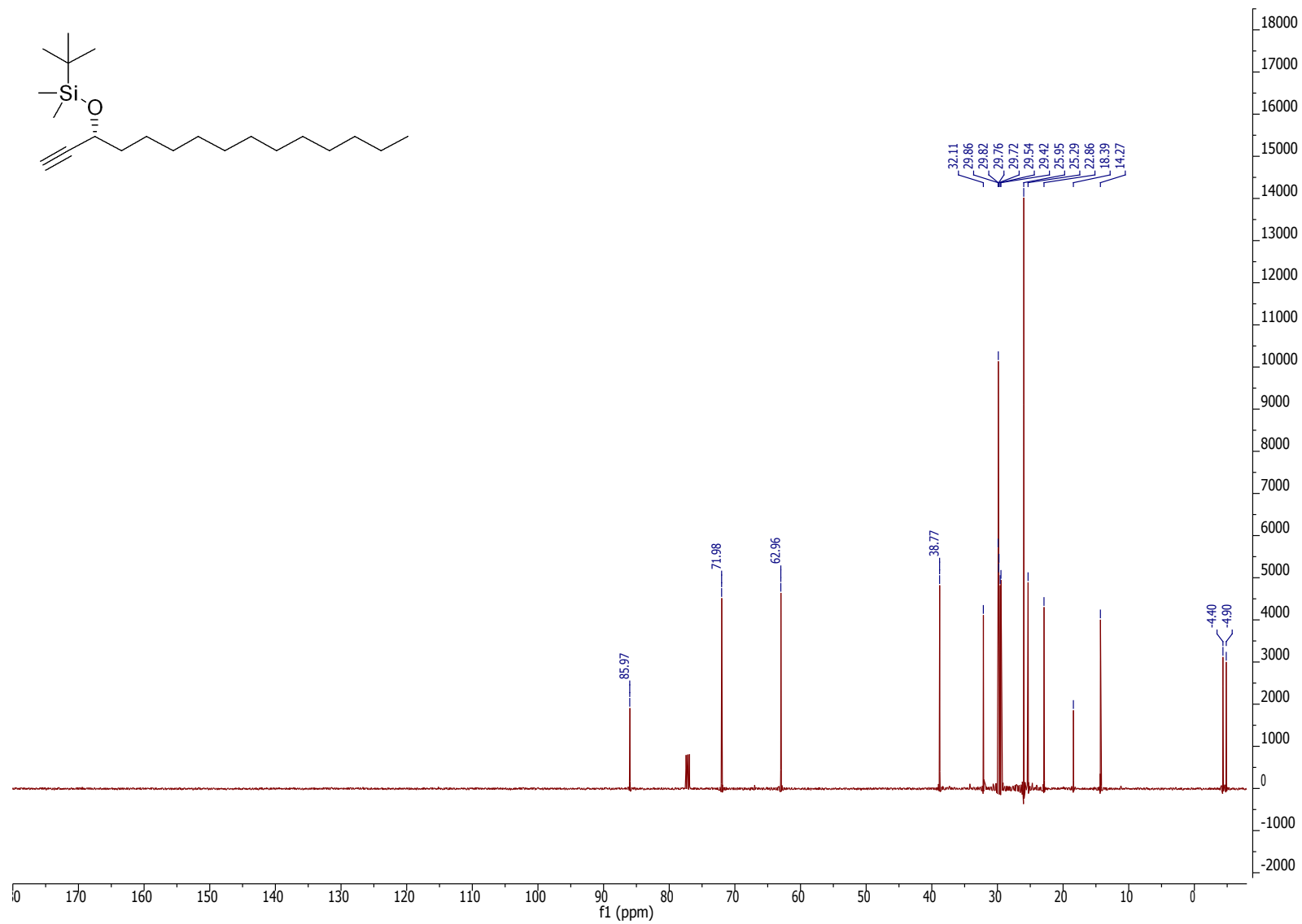


Figure 18. ¹³C-NMR (126 MHz, CDCl₃) of *(R)*-tert-butyl dimethyl(pentadec-1-yn-3-yloxy)silane (11b).

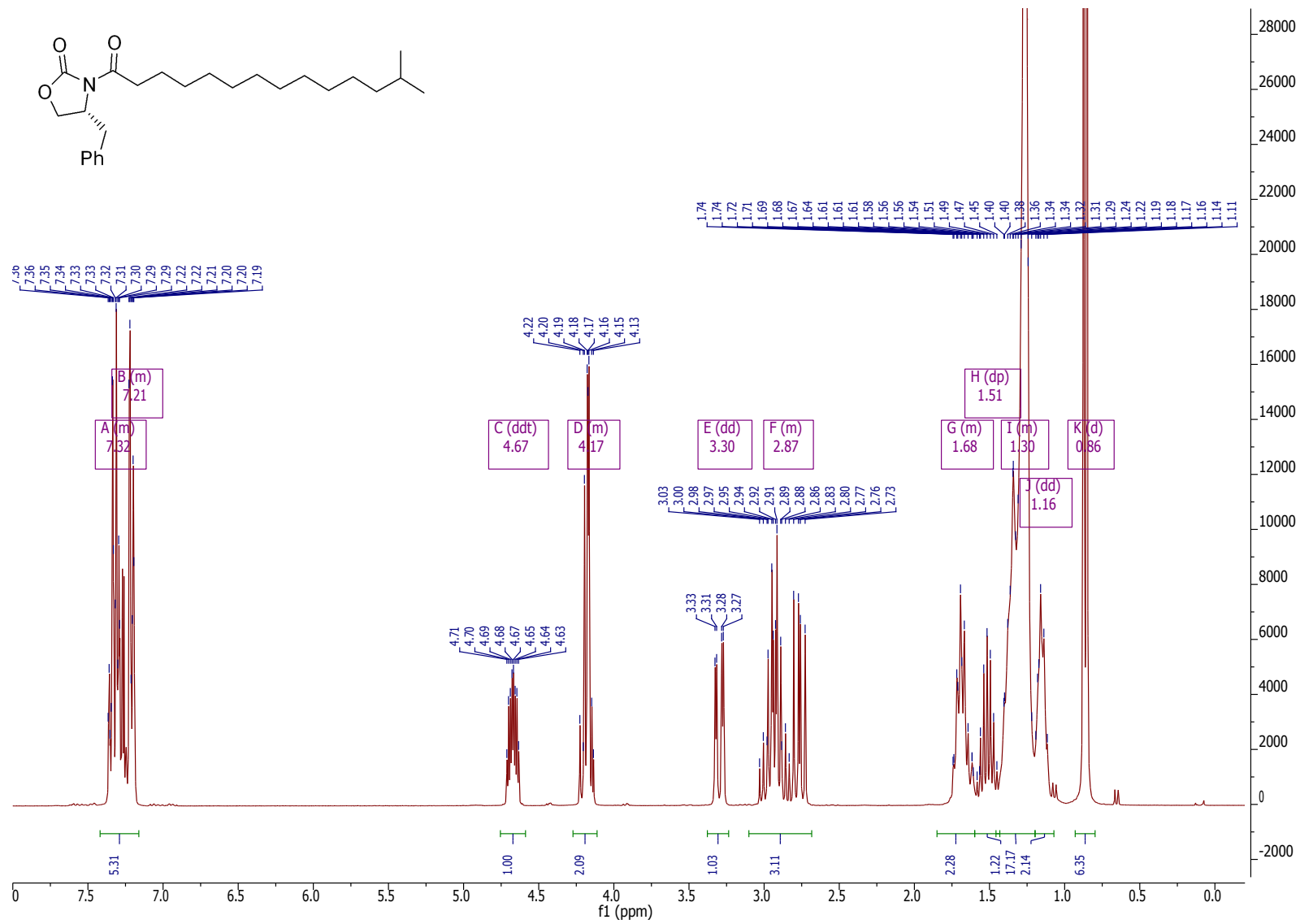


Figure 19. ¹H-NMR (300 MHz, CDCl₃) of (R)-4-benzyl-3-(13-methyltetradecanoyl)oxazolidin-2-one (15a).

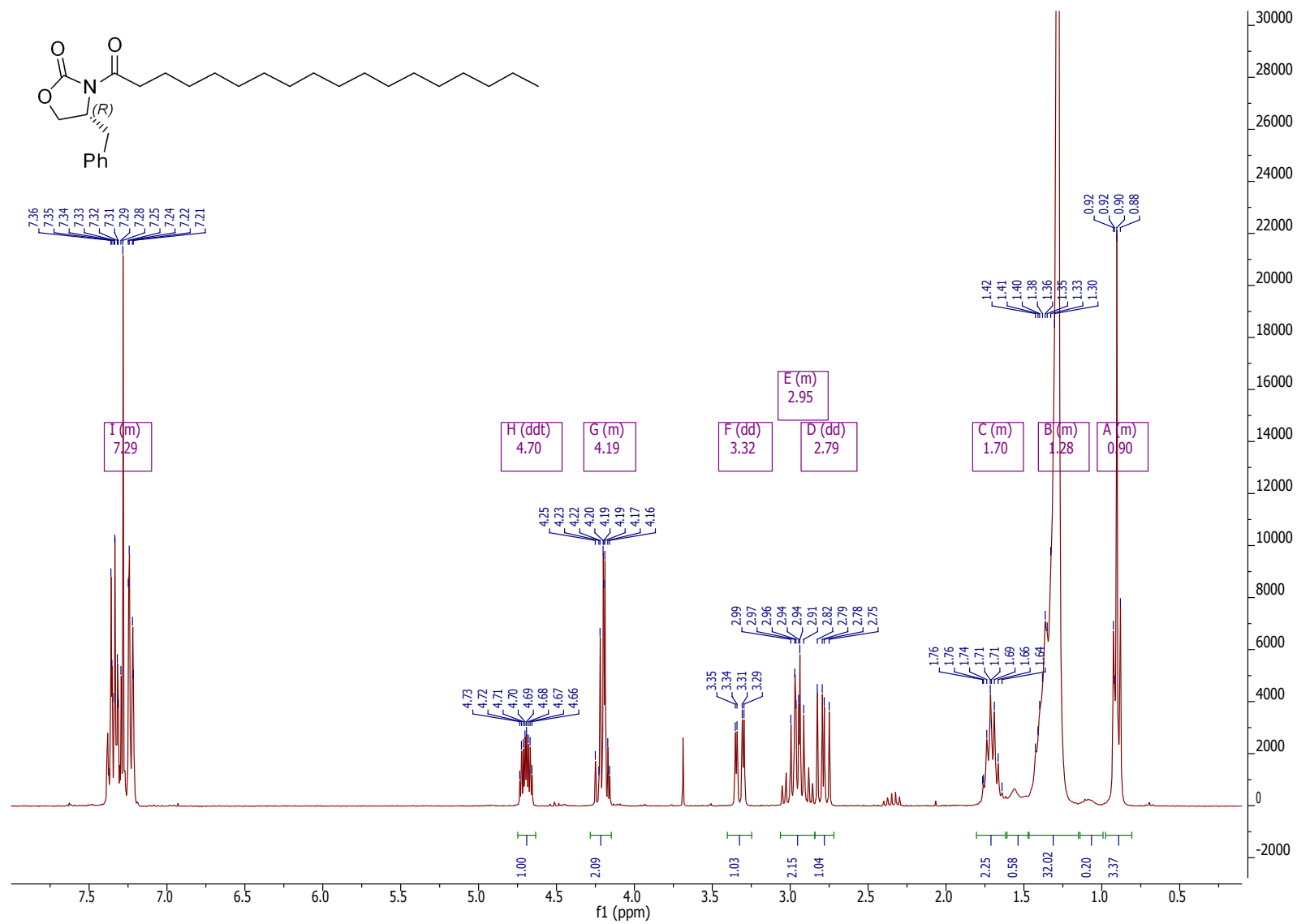


Figure 20. ¹H-NMR (75 MHz, CDCl₃) of (R)-4-benzyl-3-stearoyloxazolidin-2-one (15b).

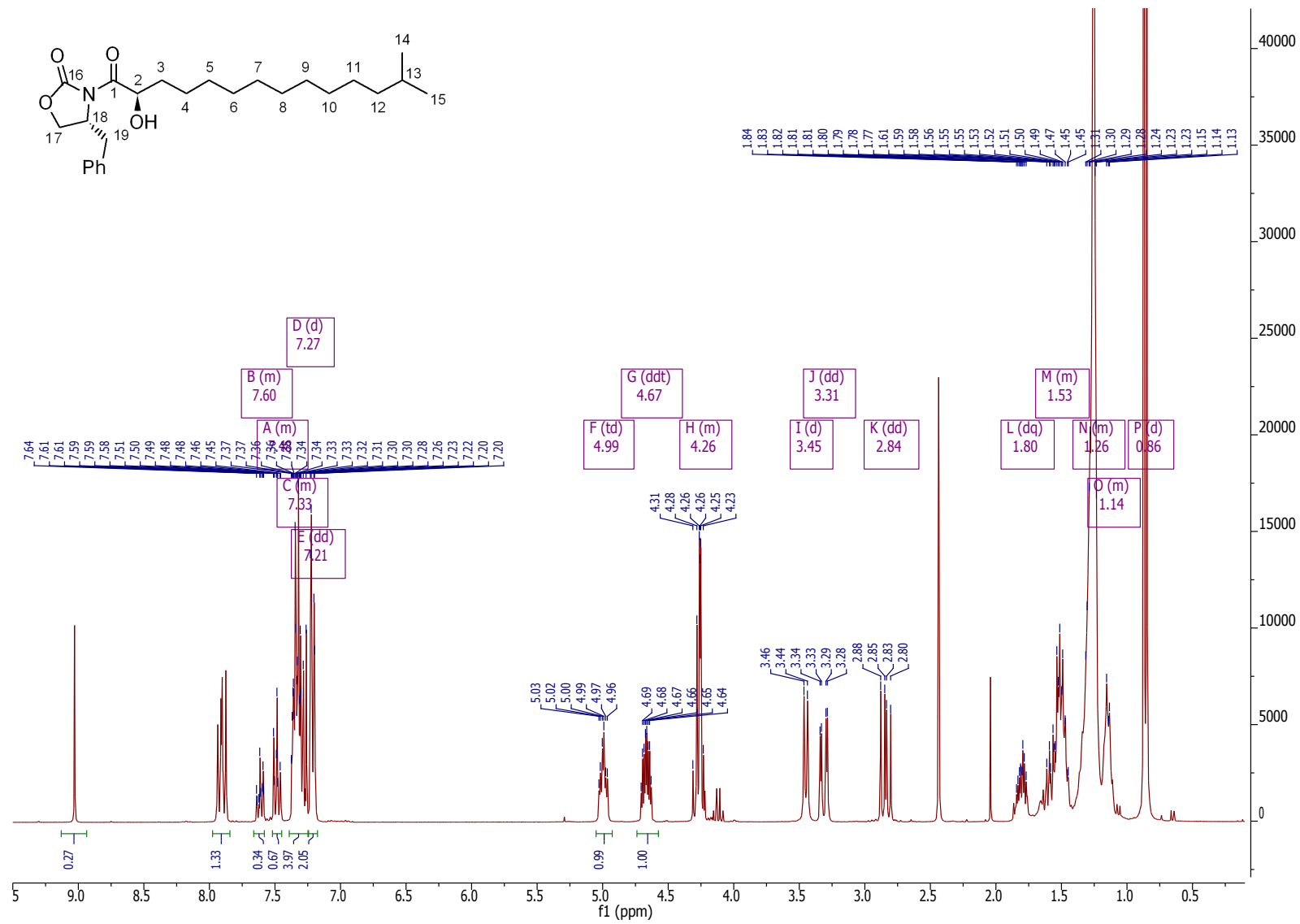


Figure 21. $^1\text{H-NMR}$ (300 MHz, CDCl_3) of *(R)*-4-benzyl-3-((*R*)-2-hydroxy-13-methyltetradecanoyl)oxazolidin-2-one (**G**).

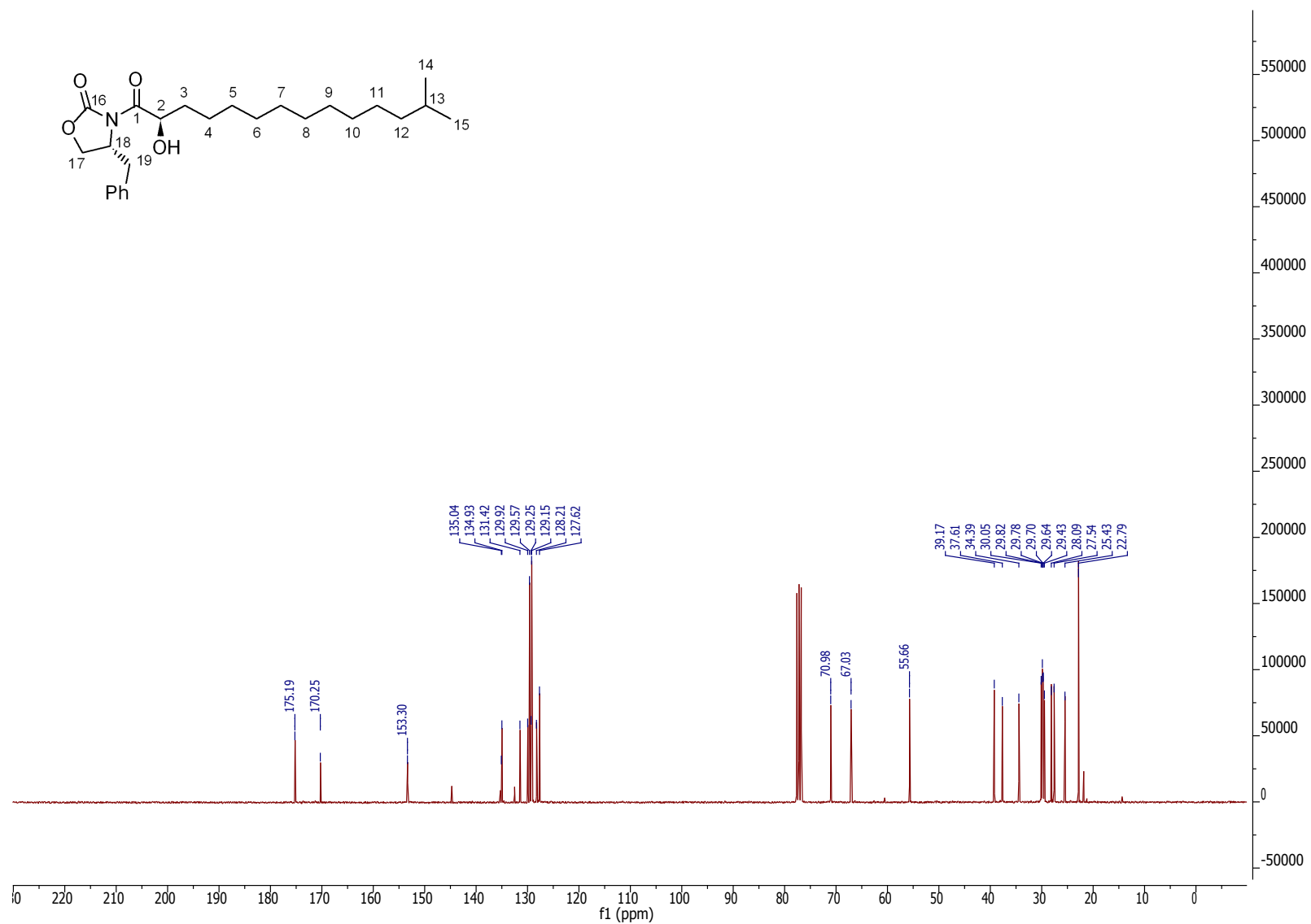


Figure 22. ¹³C-NMR (75 MHz, CDCl₃) of (R)-4-benzyl-3-((R)-2-hydroxy-13-methyltetradecanoyl)oxazolidin-2-one (G).

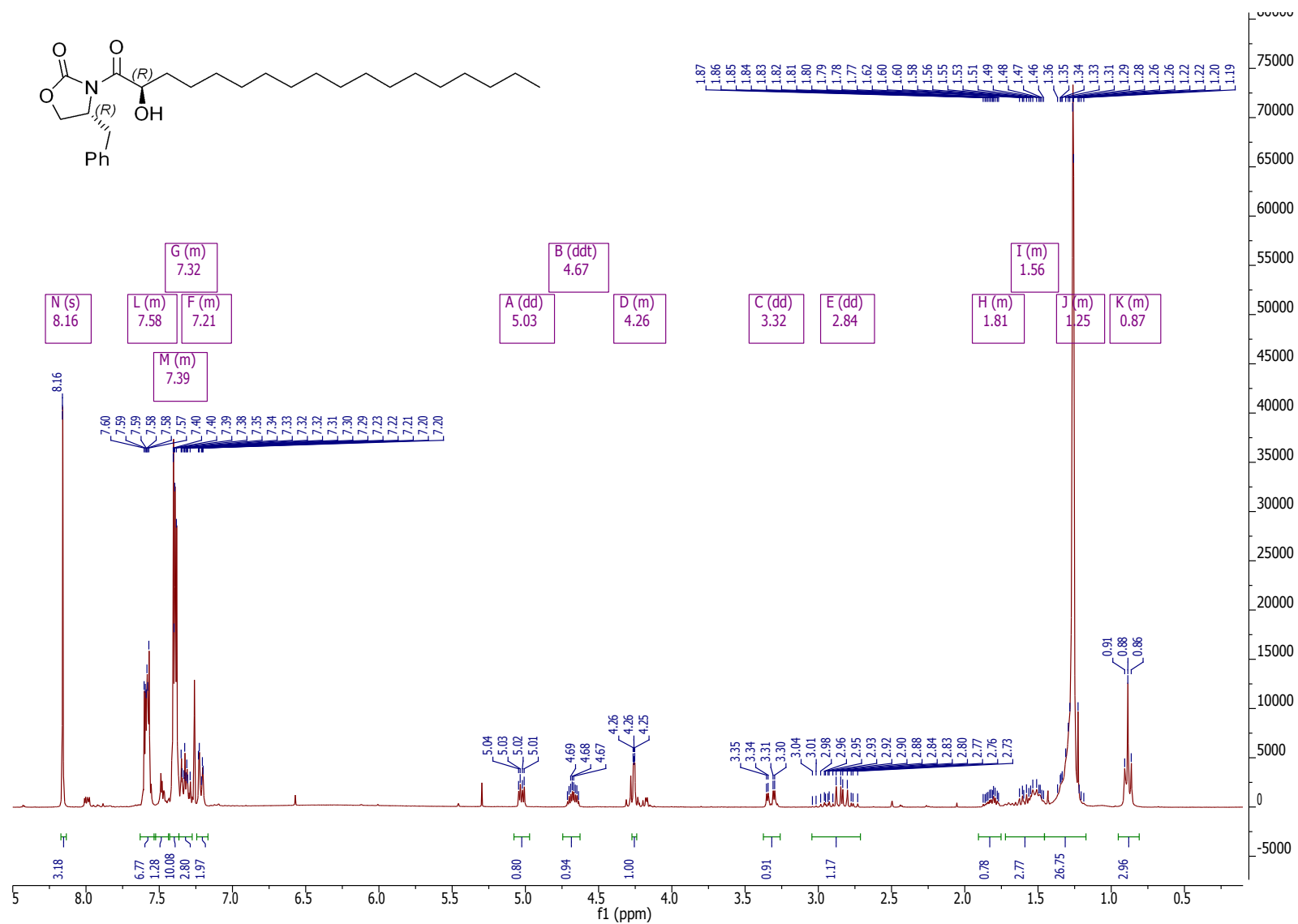


Figure 23. ¹H-NMR (300 MHz, CDCl₃) of (R)-4-benzyl-3-((R)-2-hydroxyoctadecanoyl)oxazolidin-2-one (H).

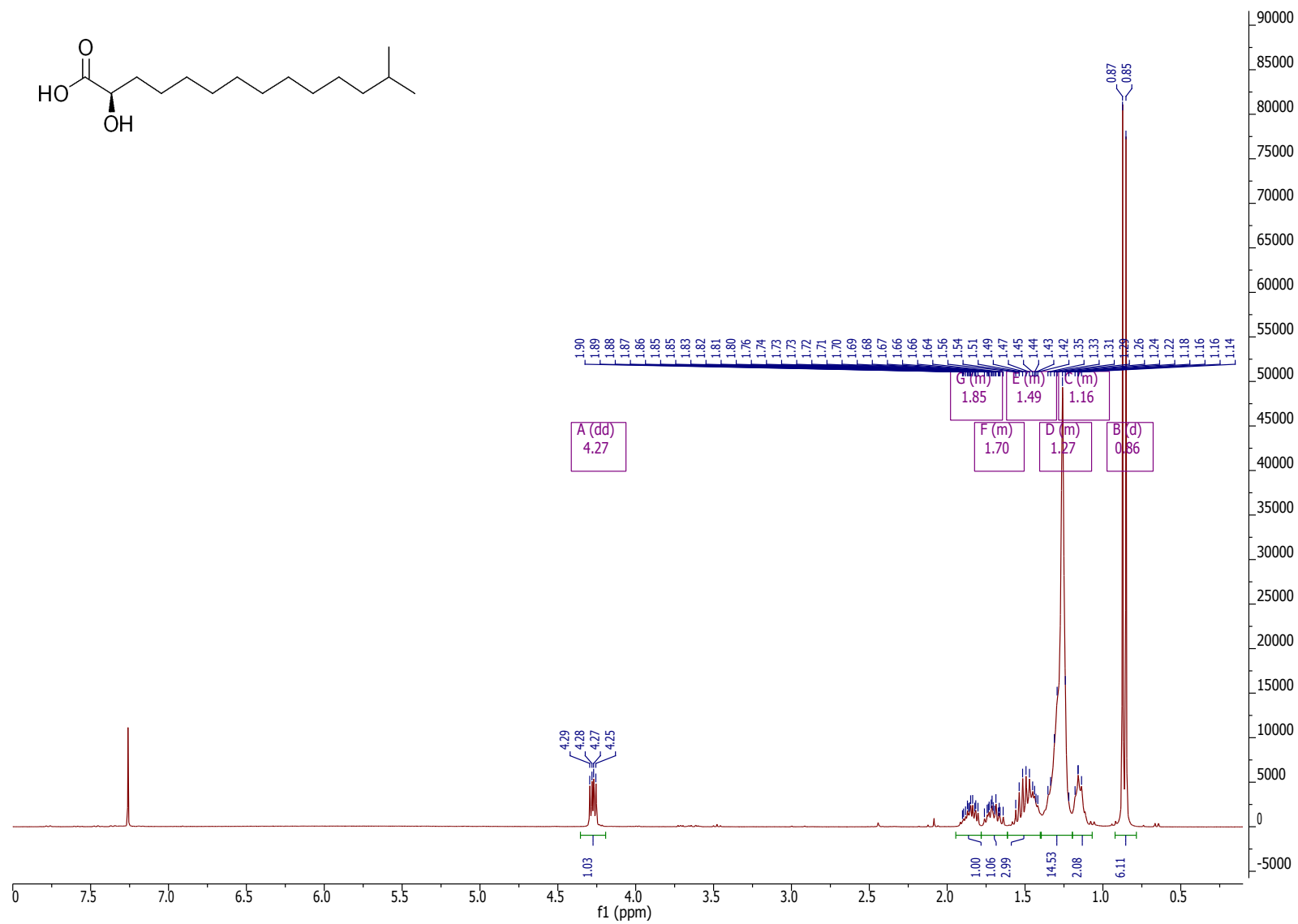


Figure 24. ¹H-NMR (300 MHz, CDCl₃) of (R)-2-hydroxy-13-methyltetradecanoic acid (16a).

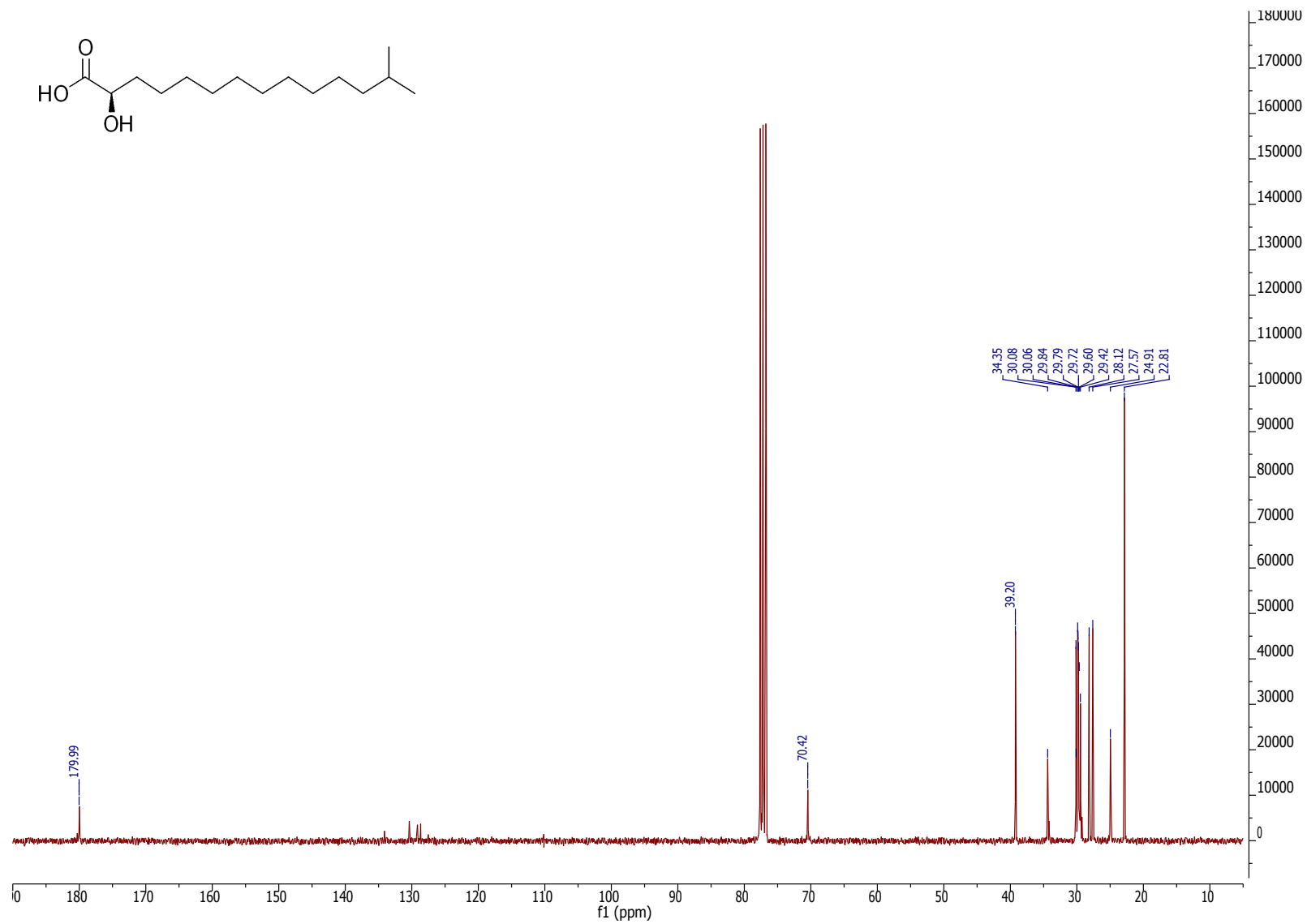


Figure 25. ¹³C-NMR (75 MHz, CDCl₃) of (R)-2-Hydroxy-13-methyltetradecanoic acid (16a).

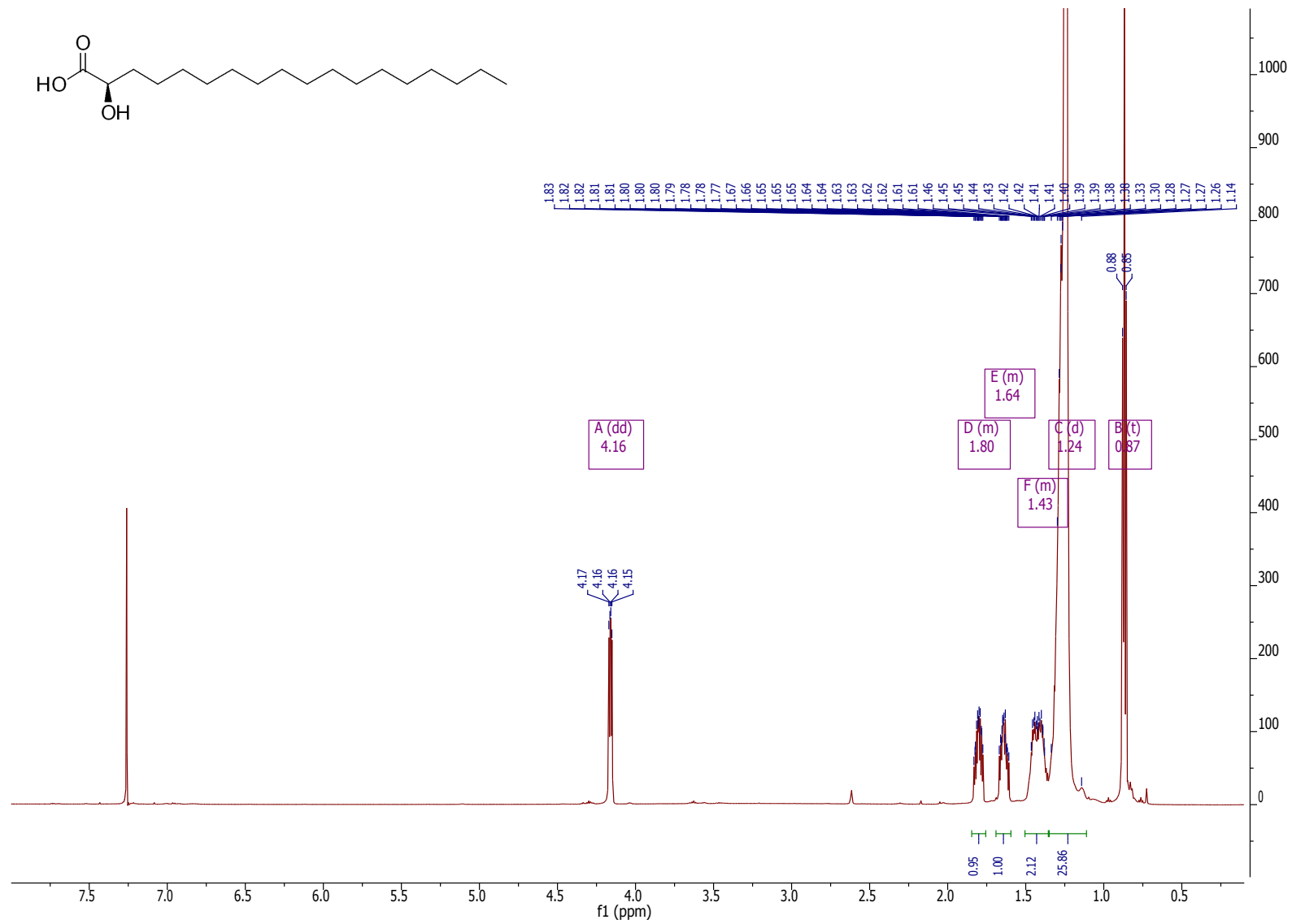


Figure 26. ¹H-NMR (600 MHz, CDCl₃) of *(R)*-2-hydroxyoctadecanoic acid (16b).

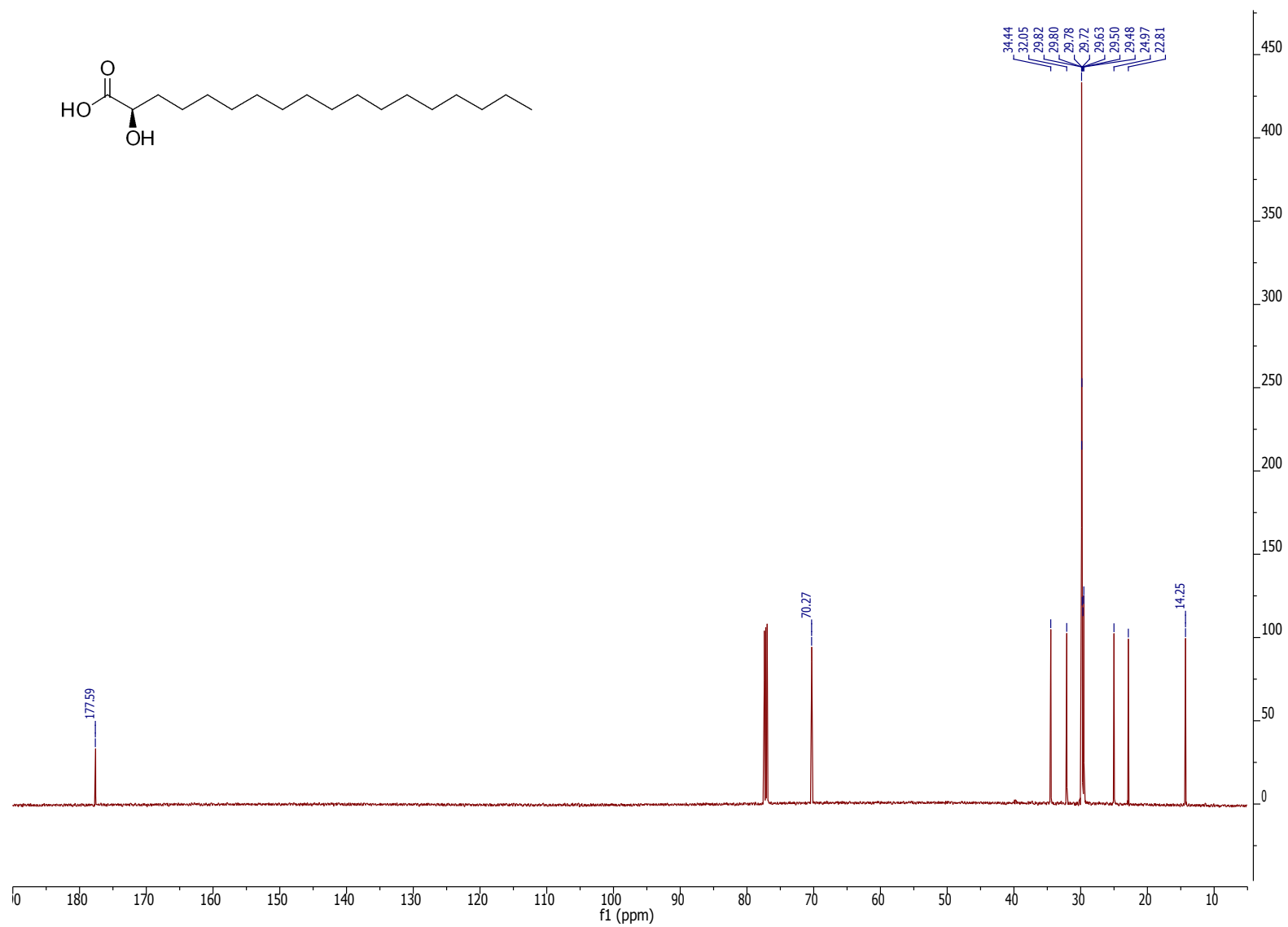


Figure 27. ¹³C-NMR (151 MHz, CDCl₃) of (R)-2-hydroxyoctadecanoic acid (16b).

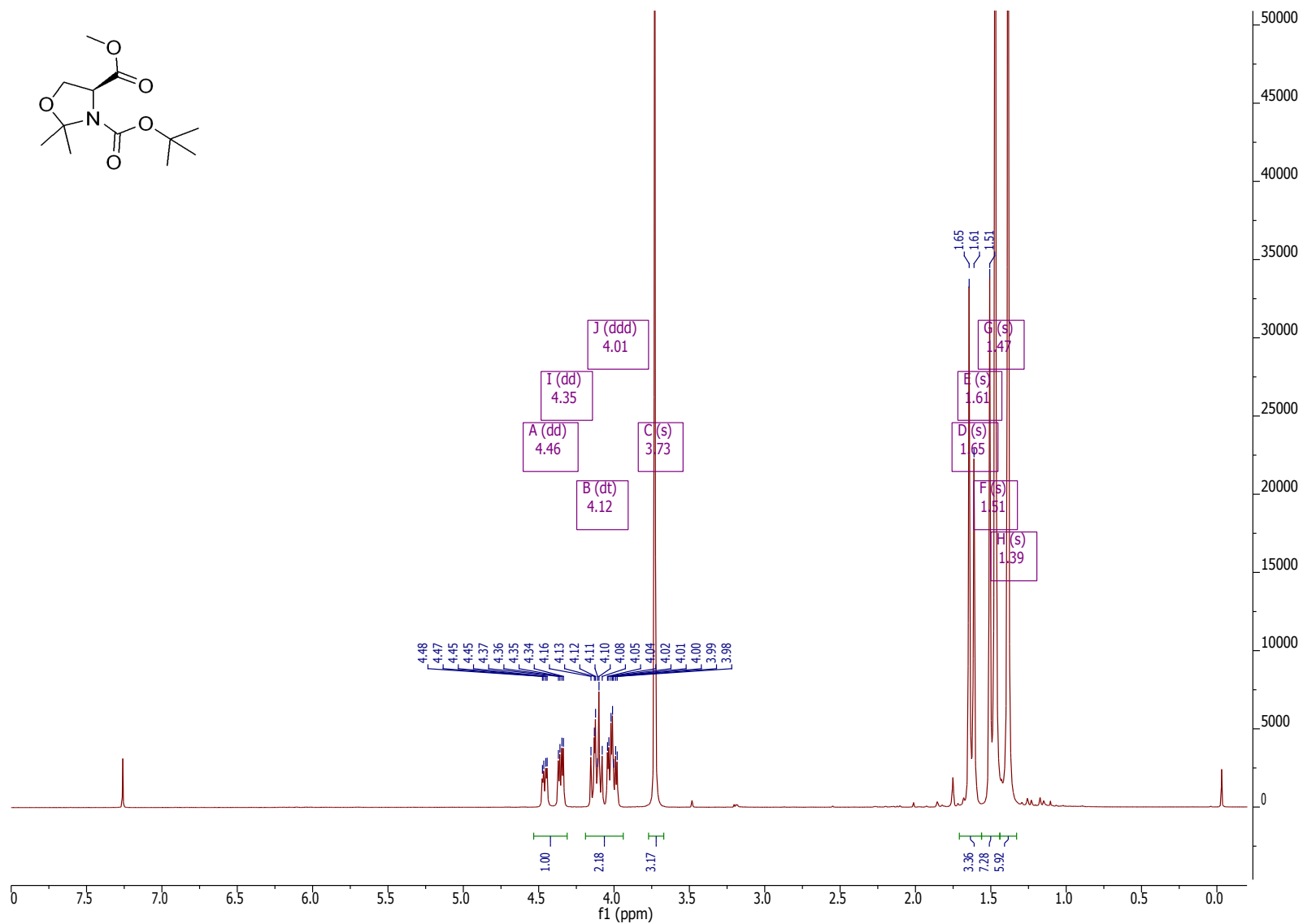


Figure 28. ¹H-NMR (300 MHz, CDCl₃) of 3-(*tert*-butyl) 4-methyl (*S*)-2,2-dimethyloxazolidine-3,4-dicarboxylate (I).

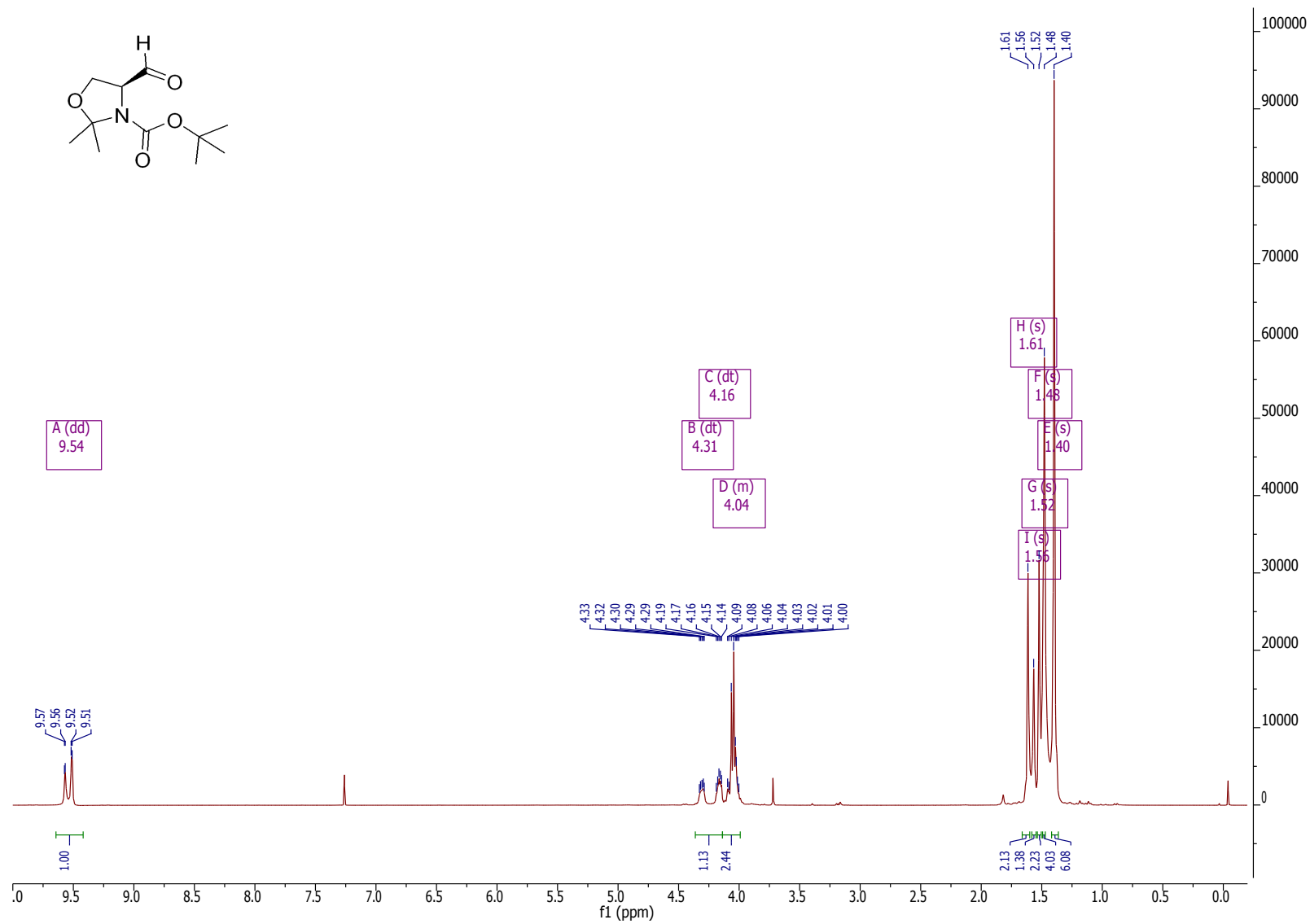


Figure 29. ¹H-NMR (300 MHz, CDCl₃) of Garner's aldehyde (3).

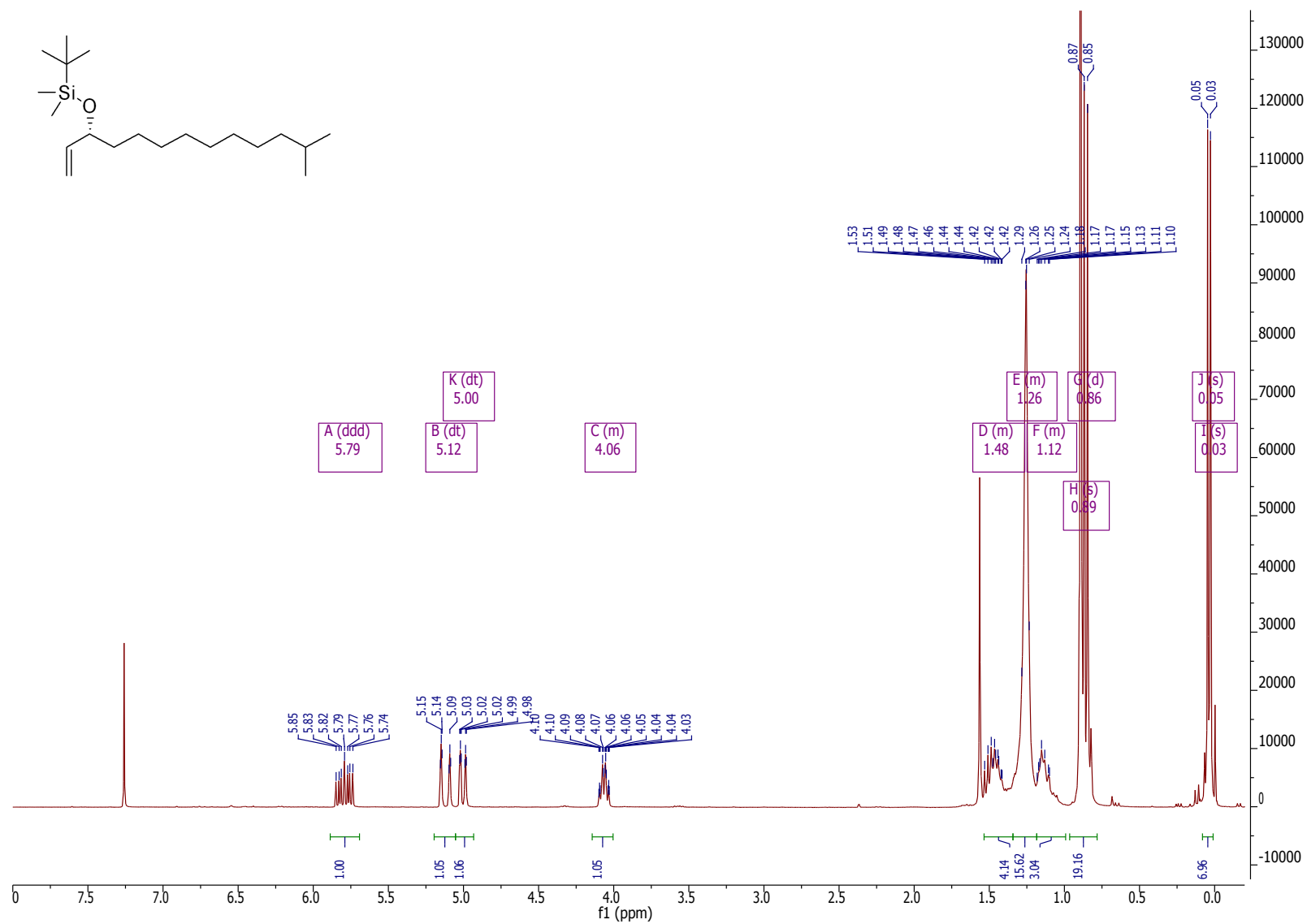


Figure 30. ¹H-NMR (300 MHz, CDCl₃) of *(R)*-tert-butyl dimethyl((12-methyltridec-1-en-3-yl)oxy)silane (17).

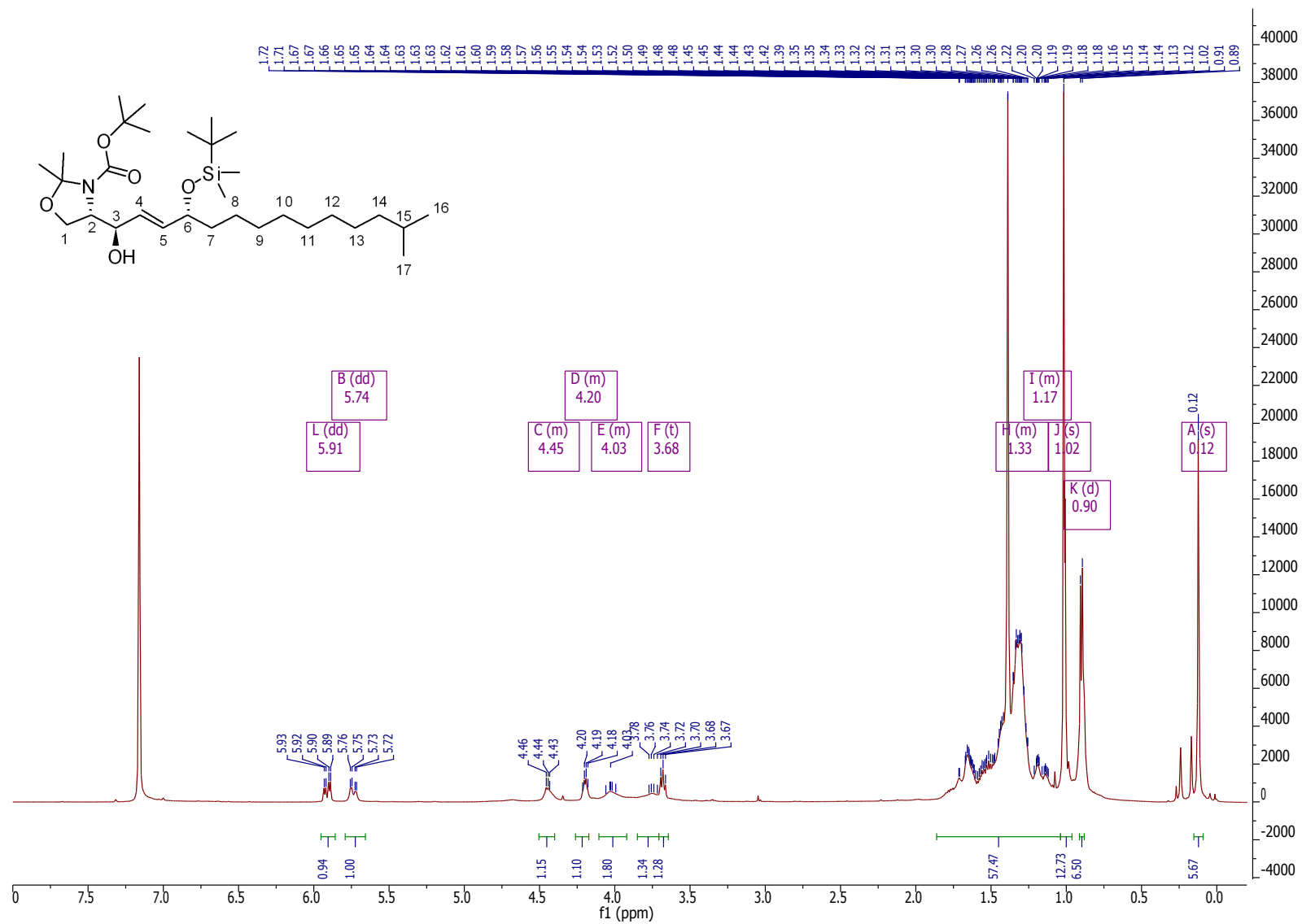


Figure 31. ¹H-NMR (500 MHz, C₆D₆, 300 K) of *tert*-butyl (*S*)-4-((1*R*,4*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (**12a**)

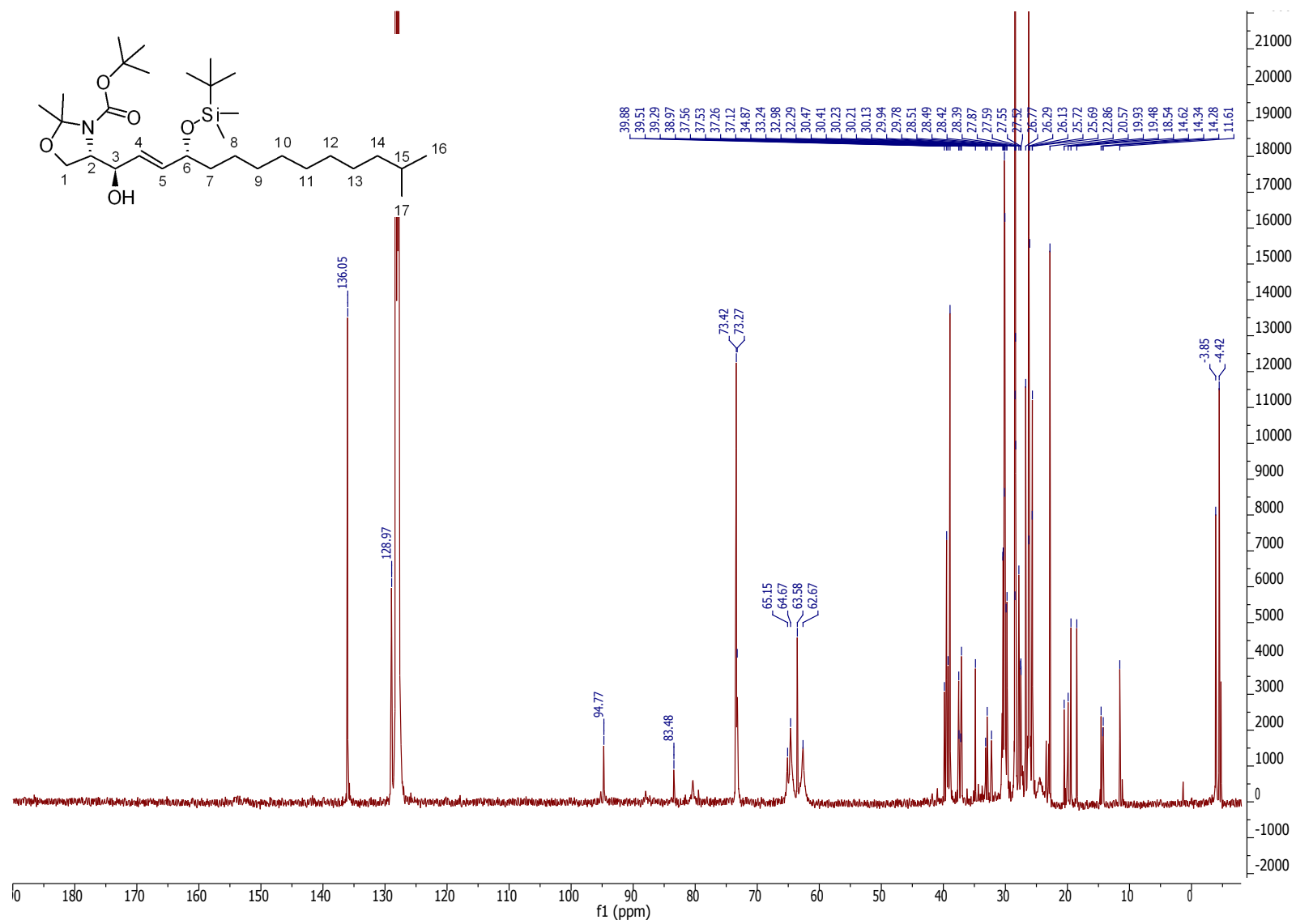


Figure 32. ^{13}C -NMR (126 MHz, C_6D_6 , 300 K) of *tert*-butyl (*S*)-4-((1*R*,4*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (12a)

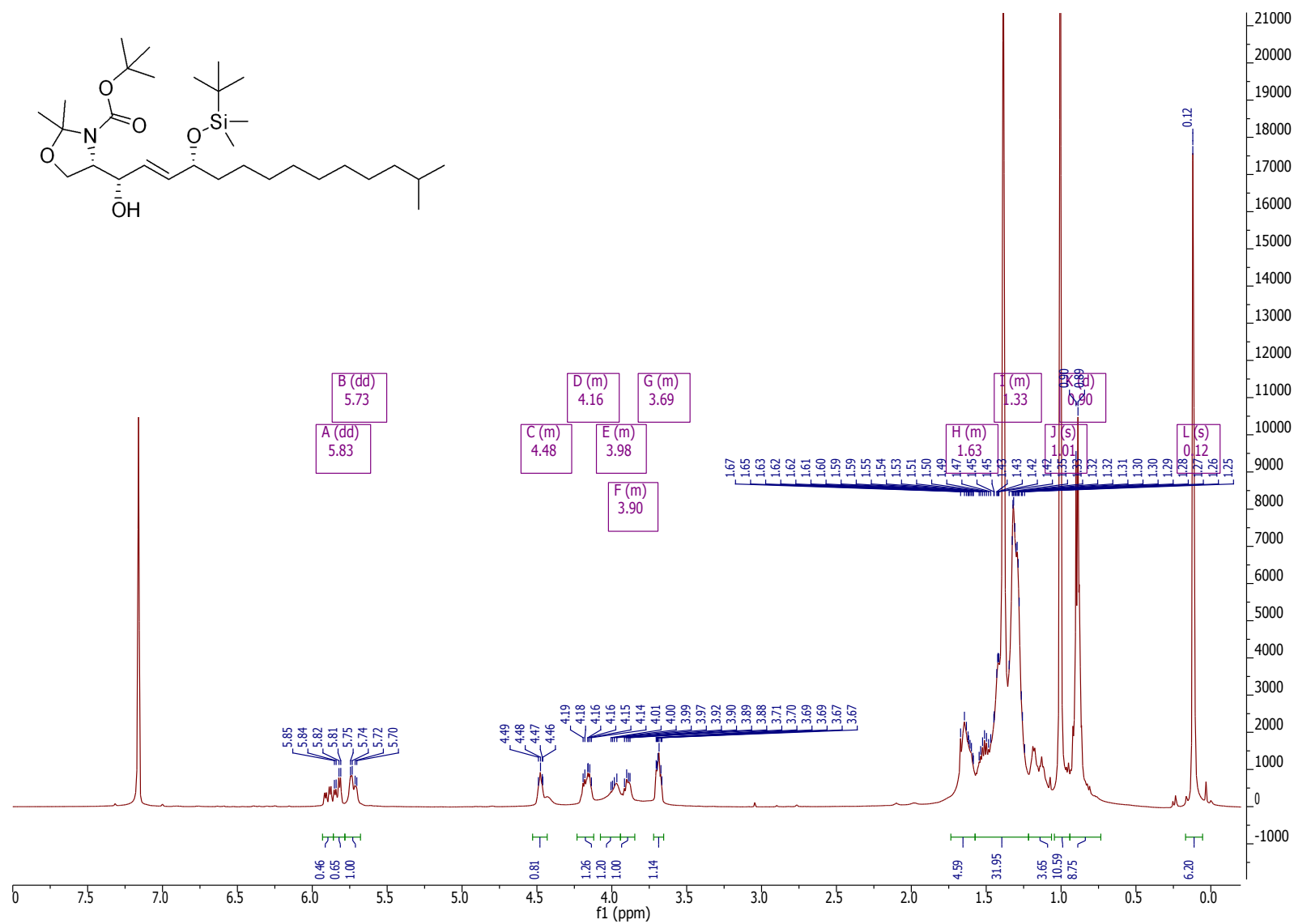


Figure 33. $^1\text{H-NMR}$ (500 MHz, C_6D_6 , 300 K) of *tert*-butyl (*S*)-4-((1*S*,4*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (**12b**)

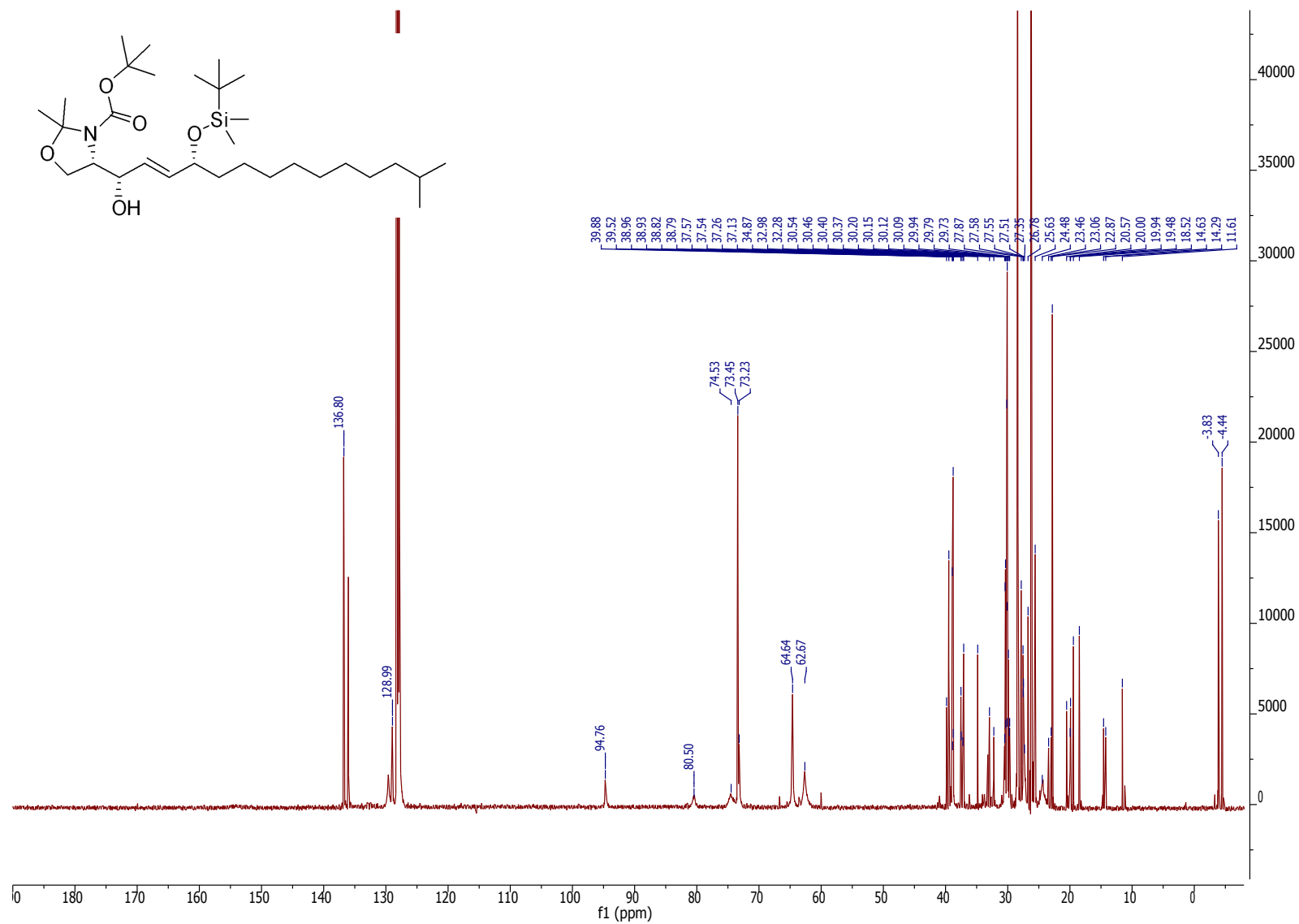


Figure 34. ¹H-NMR (126 MHz, C₆D₆, 300 K) of *tert*-butyl (S)-4-((1S,4R,E)-4-((*tert*-butyl dimethylsilyl)oxy)-1-hydroxy-13-methyltetradec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (12b)

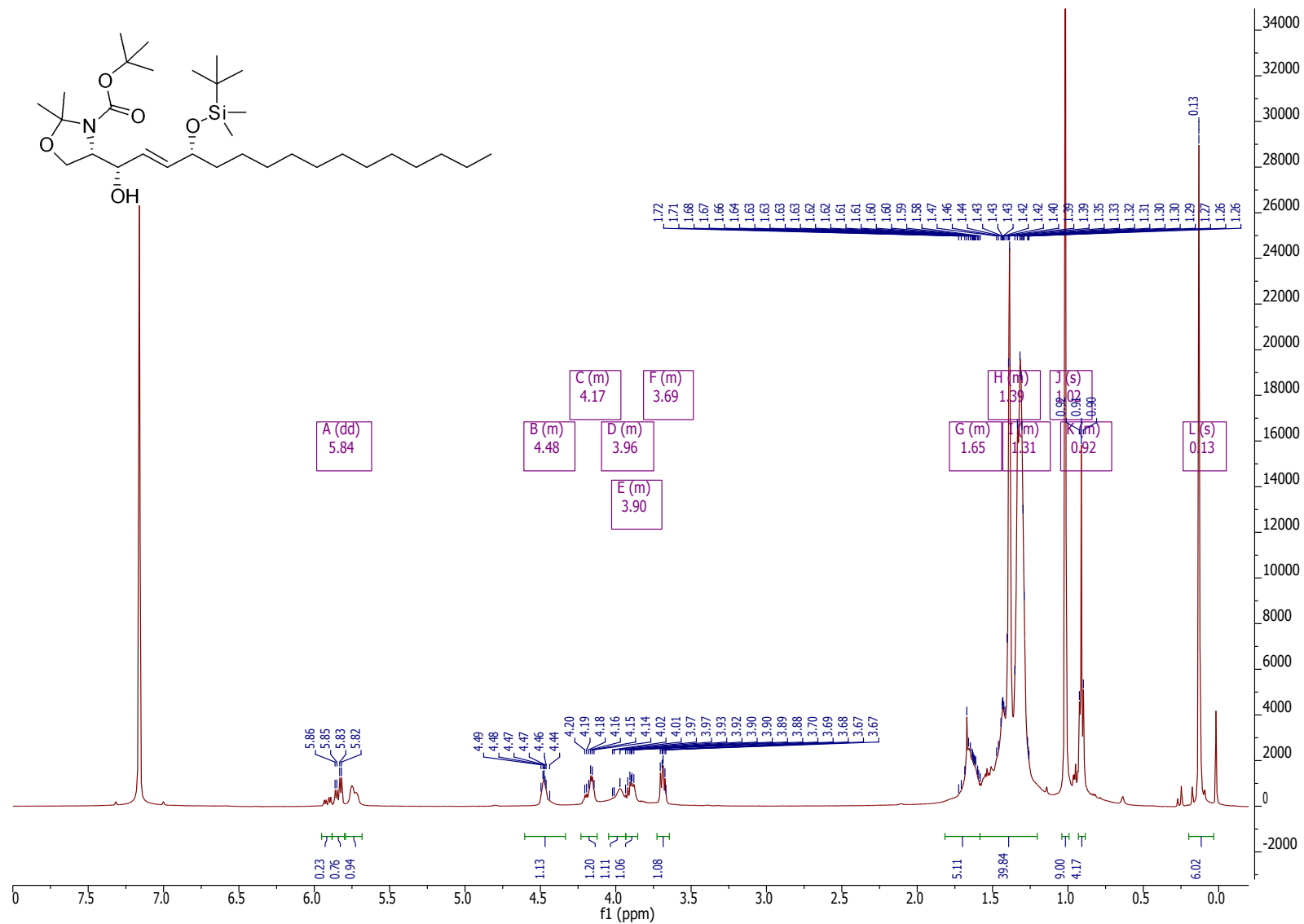


Figure 35. ¹H-NMR (500 MHz, C₆D₆, 300 K) of *tert*-butyl (S)-4-((1S,4R,E)-4-((*tert*-butyl dimethylsilyl)oxy)-1-hydroxyhexadec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (19b).

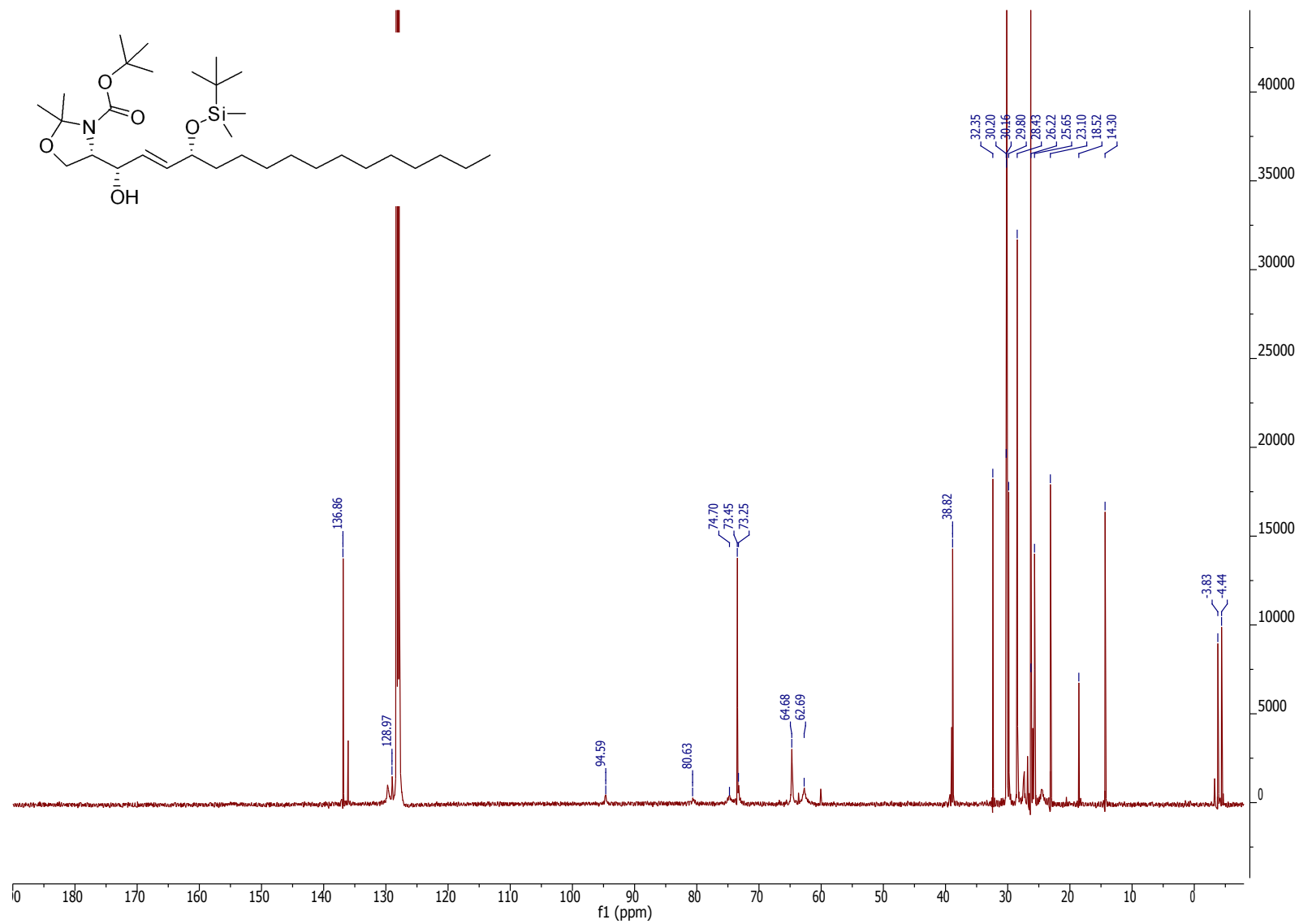


Figure 36. ^{13}C -NMR (126 MHz, C_6D_6 , 300 K) of *tert*-butyl (S)-4-((1S,4R,E)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxyhexadec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (19b).

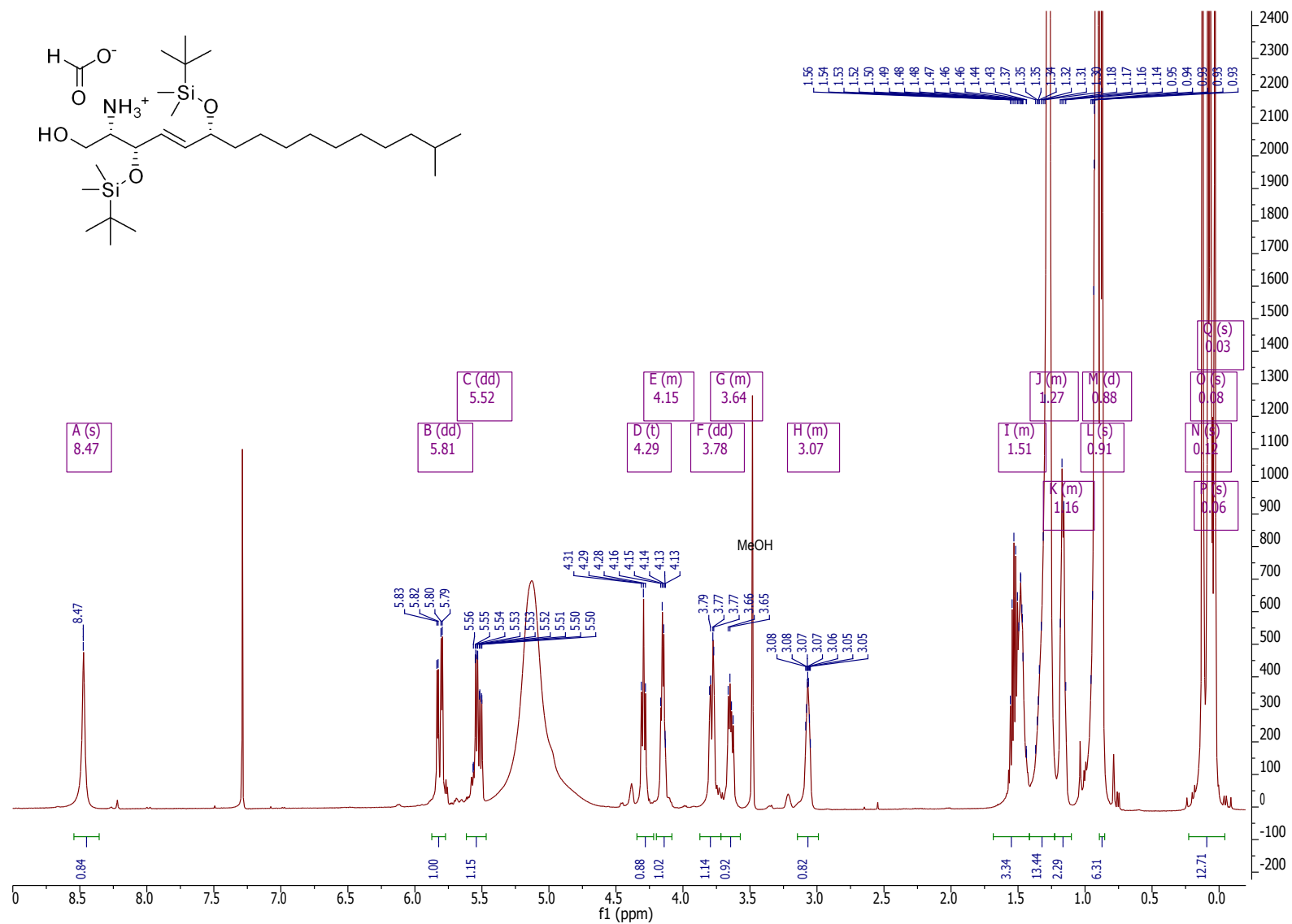


Figure 37. ¹H-NMR (500 MHz, CDCl₃) of (2S,3S,6R,E)-3,6-bis(tert-butyl dimethylsilyloxy)-1-hydroxy-15-methylhexadec-4-en-2-aminium formate (22).

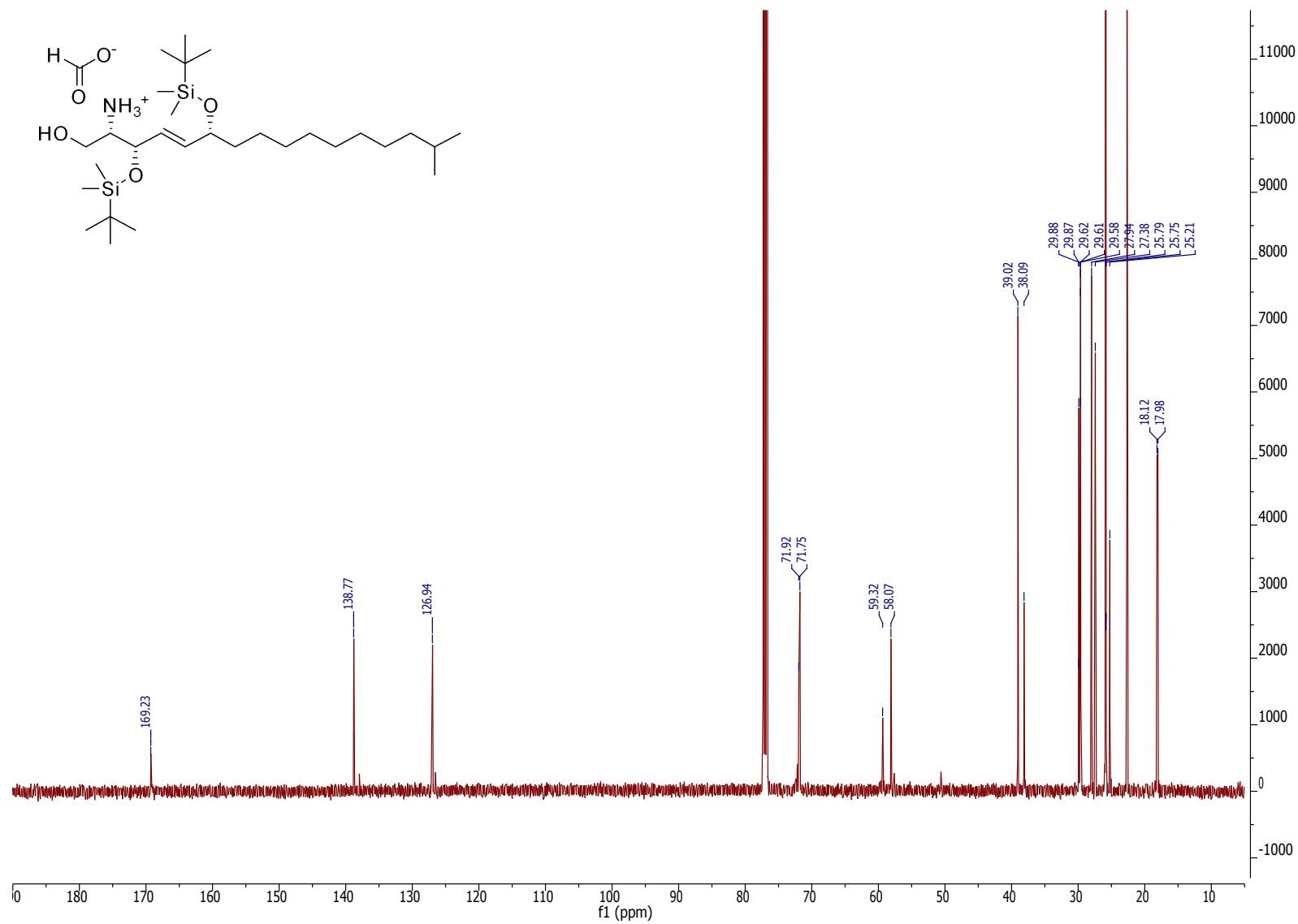


Figure 38. $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) of (2S,3S,6R,E)-3,6-bis((tert-butyl)dimethylsilyloxy)-1-hydroxy-15-methylhexadec-4-en-2-aminium formate (22).

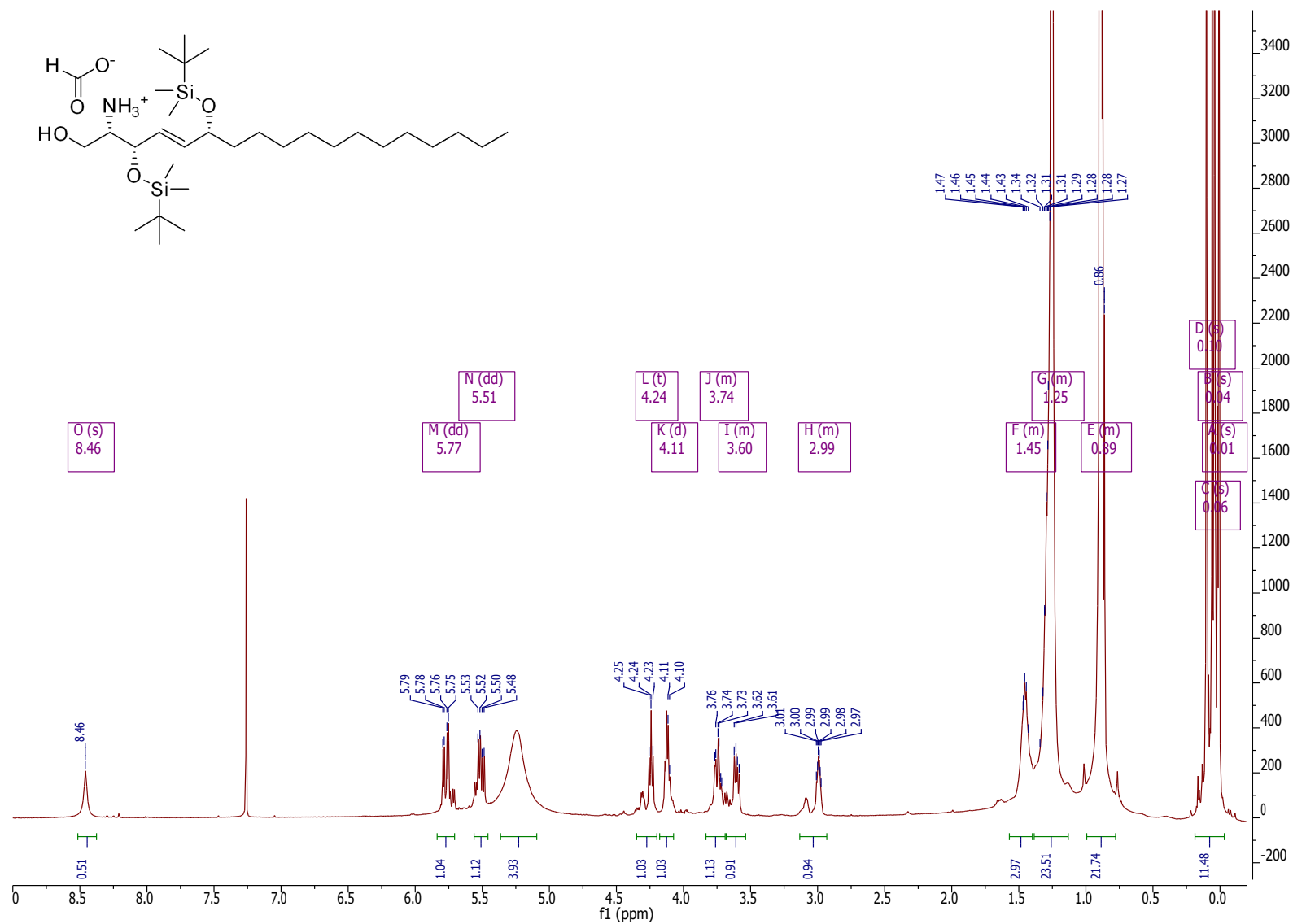


Figure 39. ¹H-NMR (500 MHz, CDCl₃) of (2S,3S,6R,E)-3,6-bis(tert-butylidimethylsilyloxy)-1-hydroxyoctadec-4-en-2-aminium formate (23).

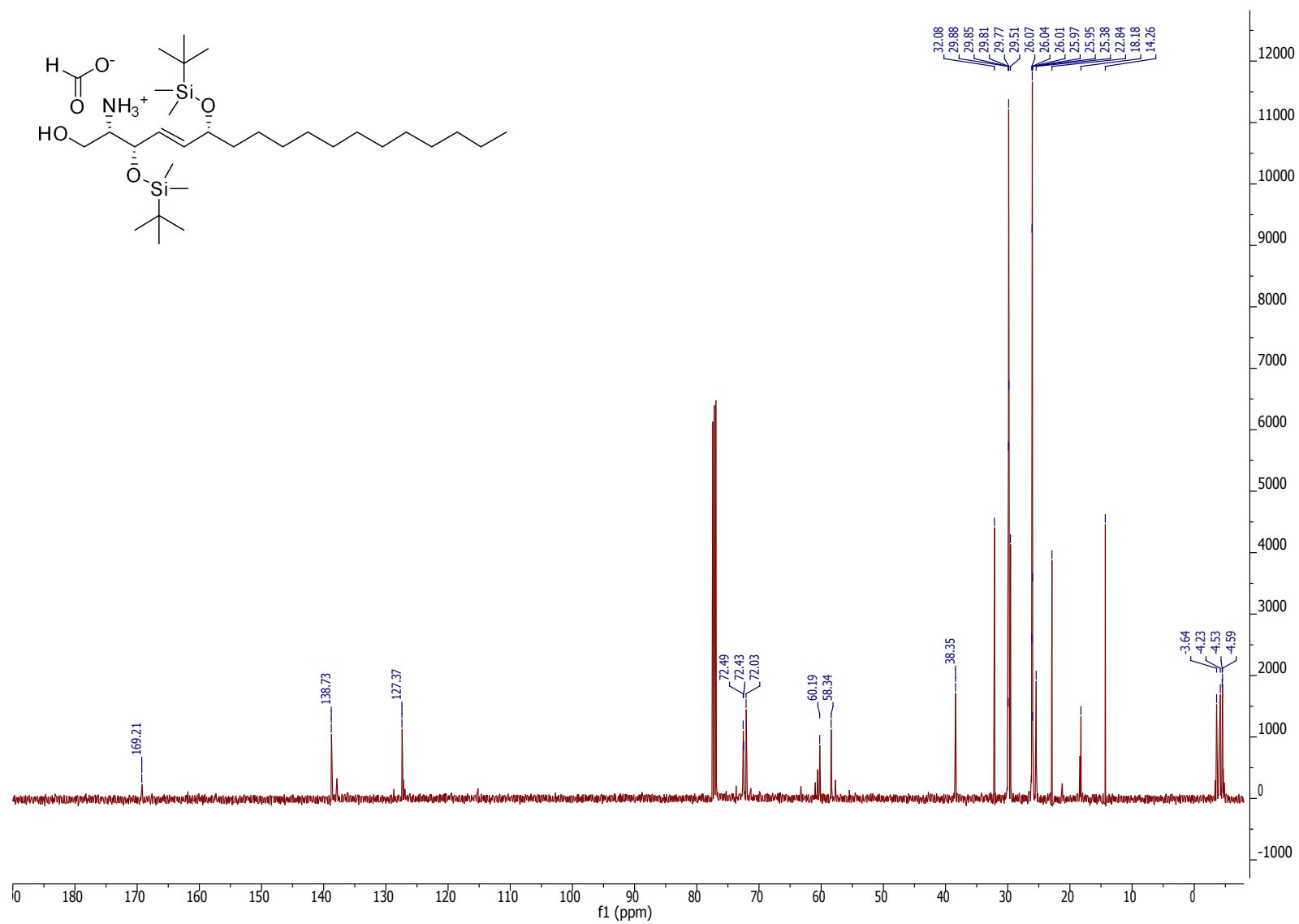


Figure 40. $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) of (2S,3S,6R,E)-3,6-bis((tert-butylidimethylsilyl)oxy)-1-hydroxyoctadec-4-en-2-aminium formate (23)

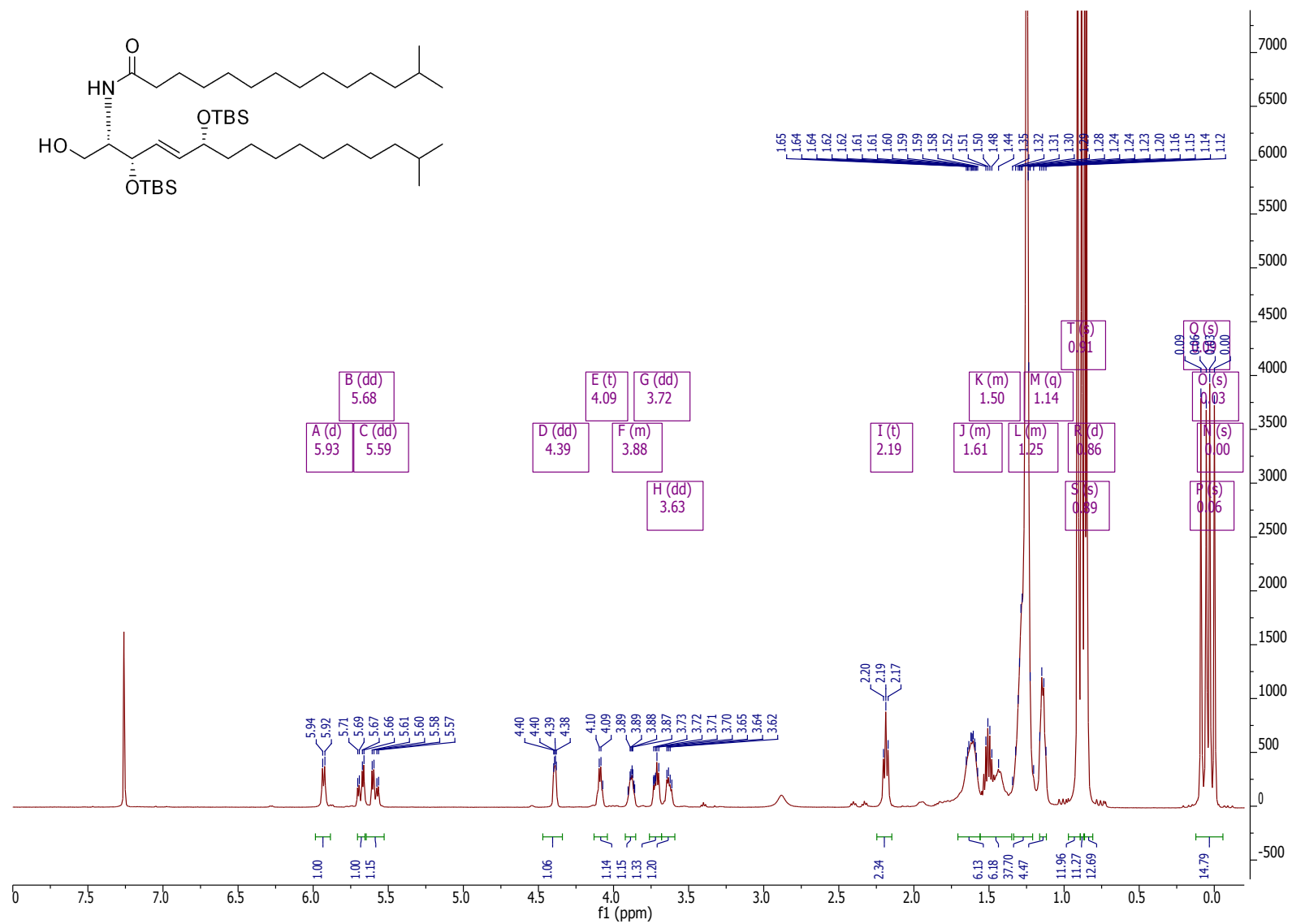


Figure 41. ¹H-NMR (500 MHz, CDCl₃) of *N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-13-methyltetradecanamide (**24**).

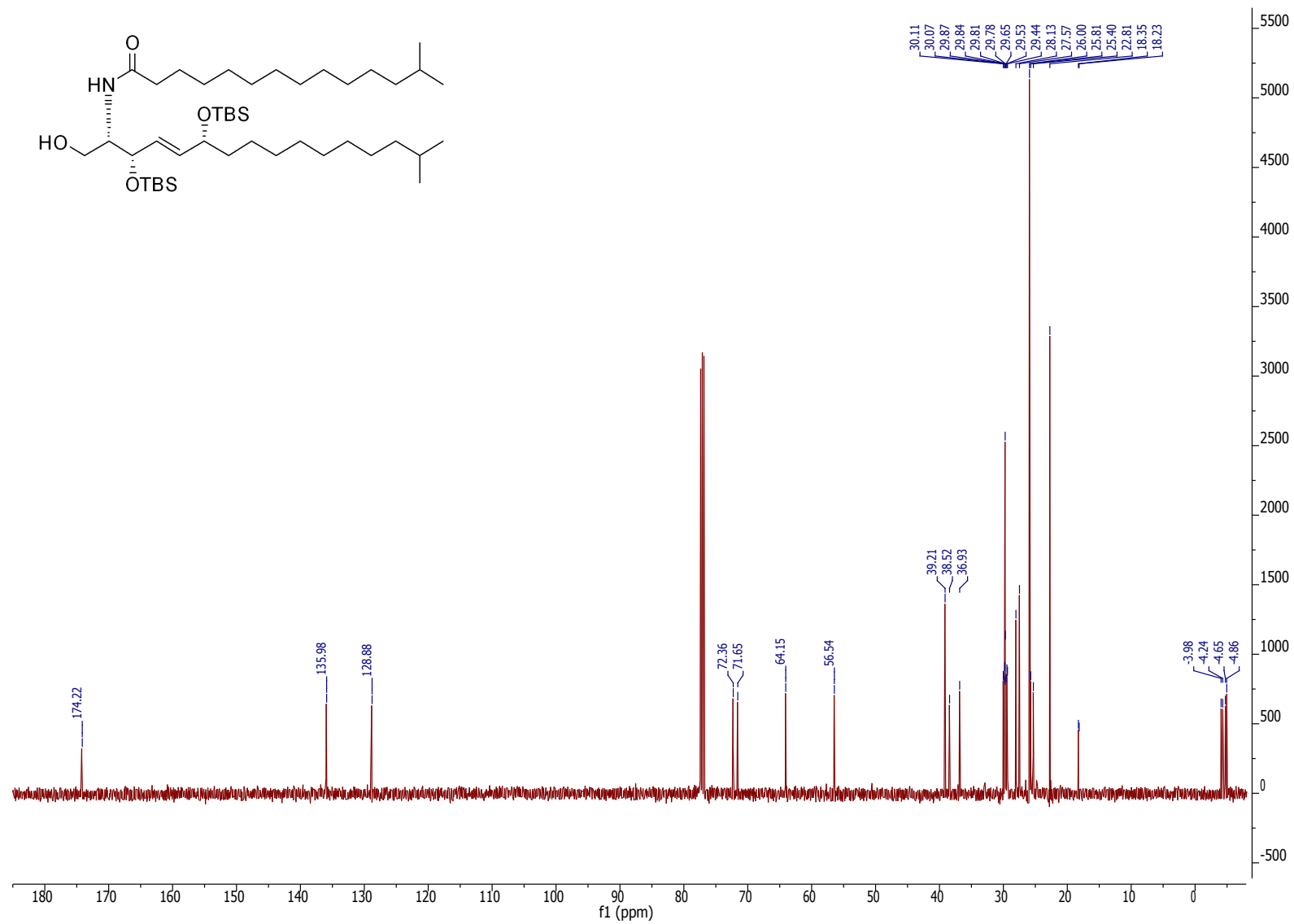


Figure 42. ¹³C-NMR (126 MHz, CDCl₃) of N-((2S,3S,6R,E)-3,6-bis((tert-butylidimethylsilyloxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-13-methyltetradecanamide (24).

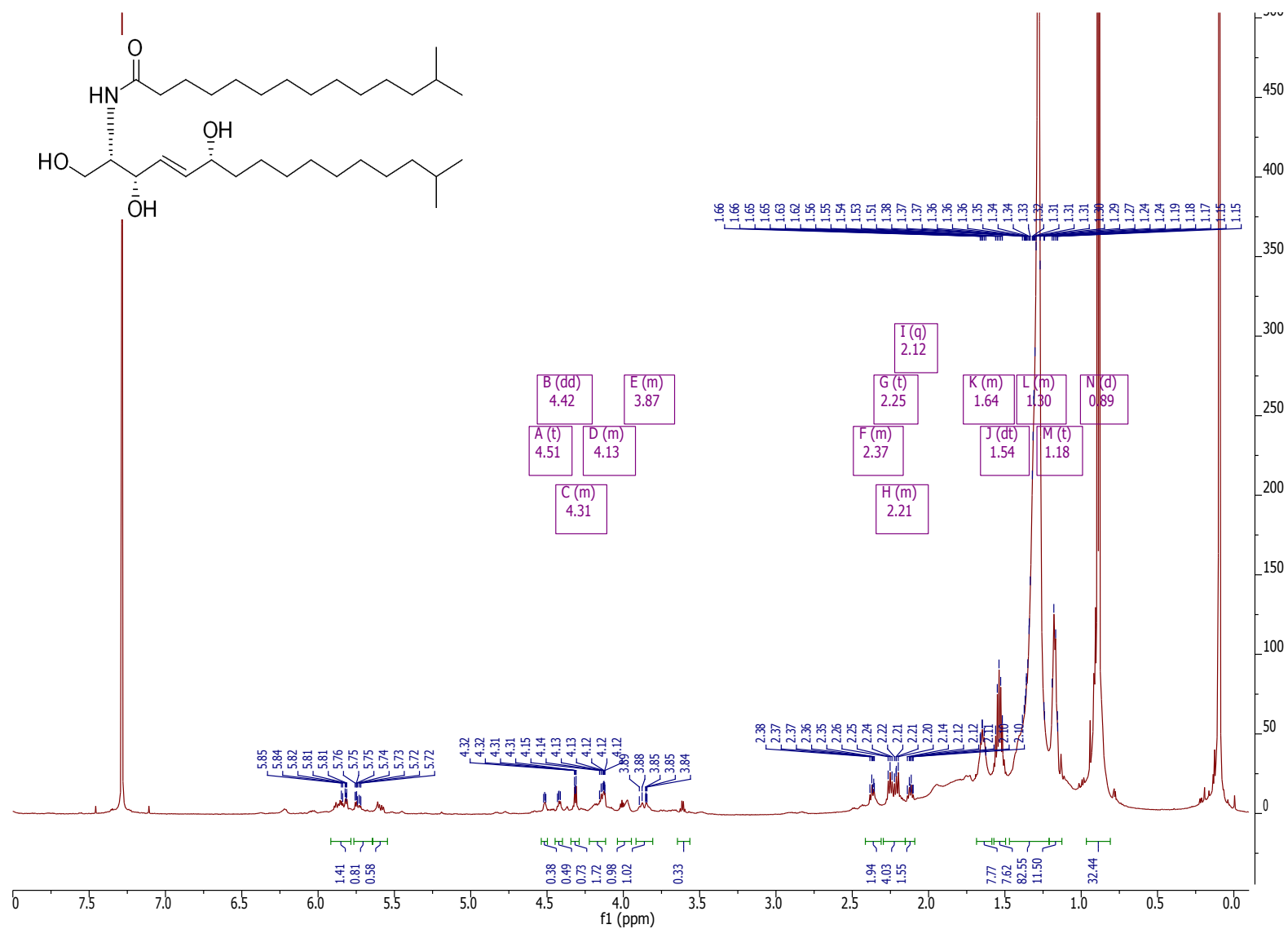


Figure 43. ¹H-NMR (600 MHz, CDCl₃) of 13-methyl-N-((2S,3S,6R,E)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (25).

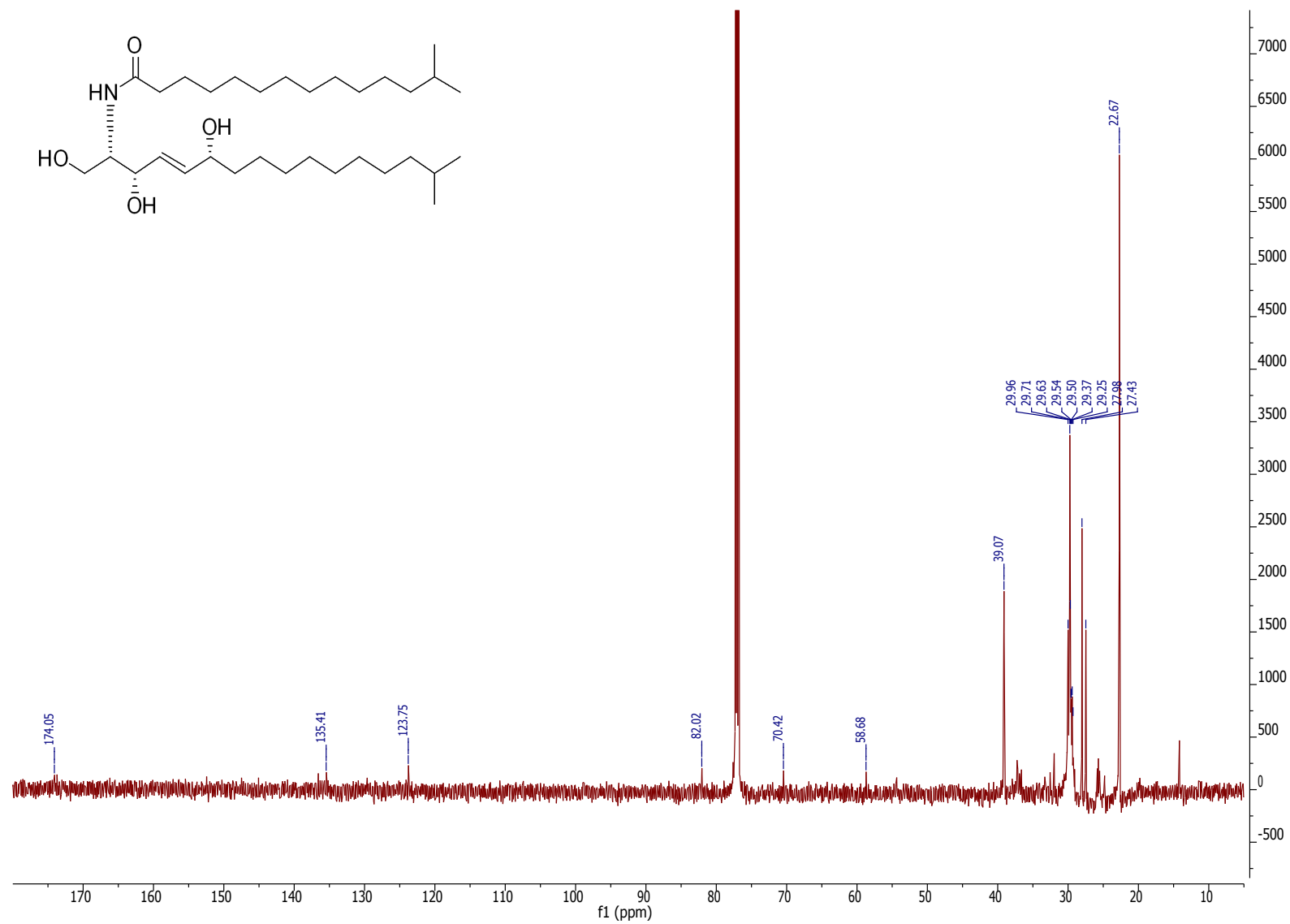


Figure 44. ¹³C-NMR (151 MHz, CDCl₃) of 13-methyl-N-((2S,3S,6R,E)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (25).

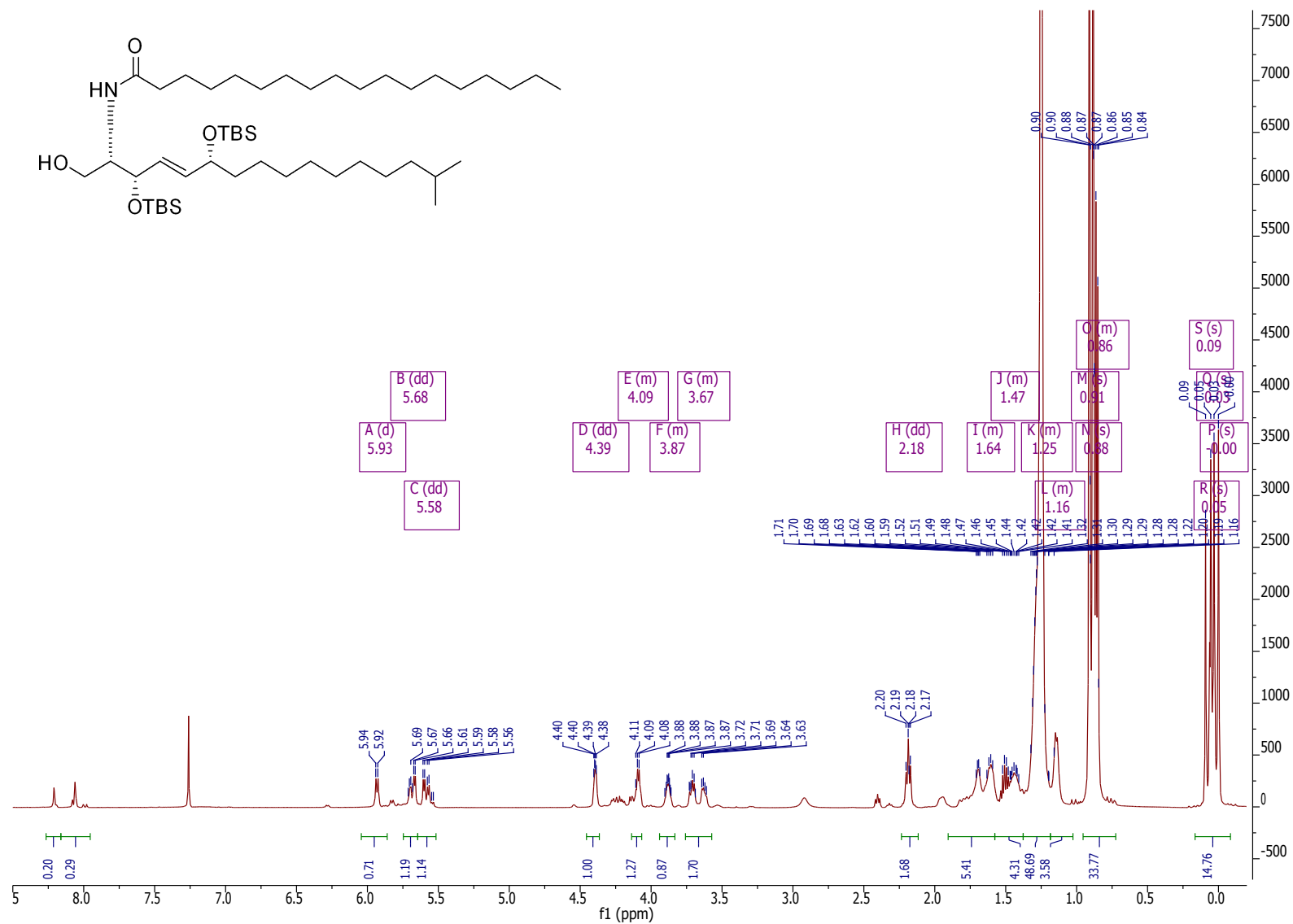


Figure 45. ¹H-NMR (500 MHz, CDCl₃) of *N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyl)dimethylsilyloxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)stearamide (**26**).

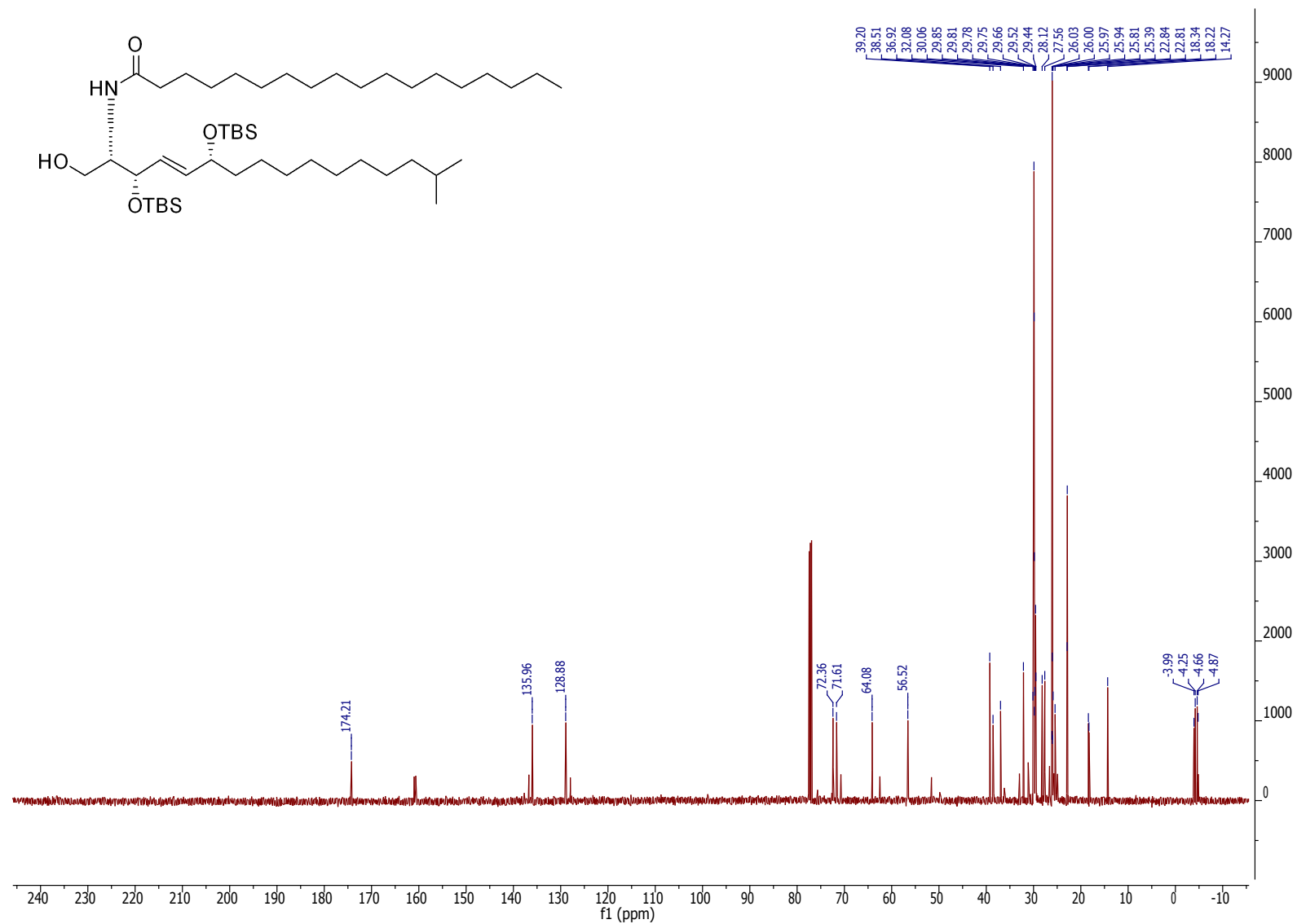


Figure 46. ¹³C-NMR (126 MHz, CDCl₃) of *N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis(*tert*-butyldimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)stearamide (26).

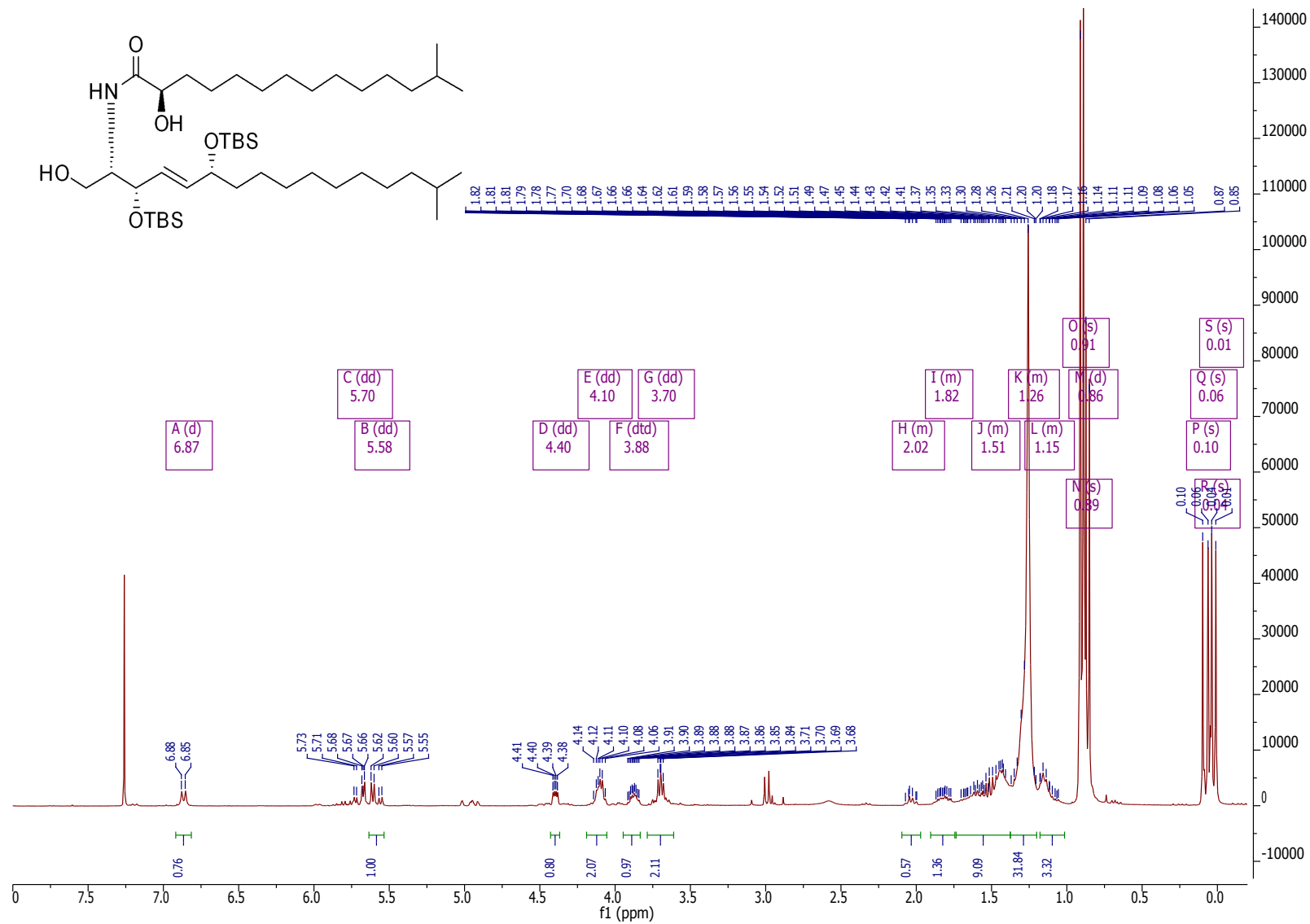


Figure 47. ¹H-NMR (300 MHz, CDCl₃) of (*R*)-*N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyloxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-2-hydroxy-13-methyltetradecanamide (27).

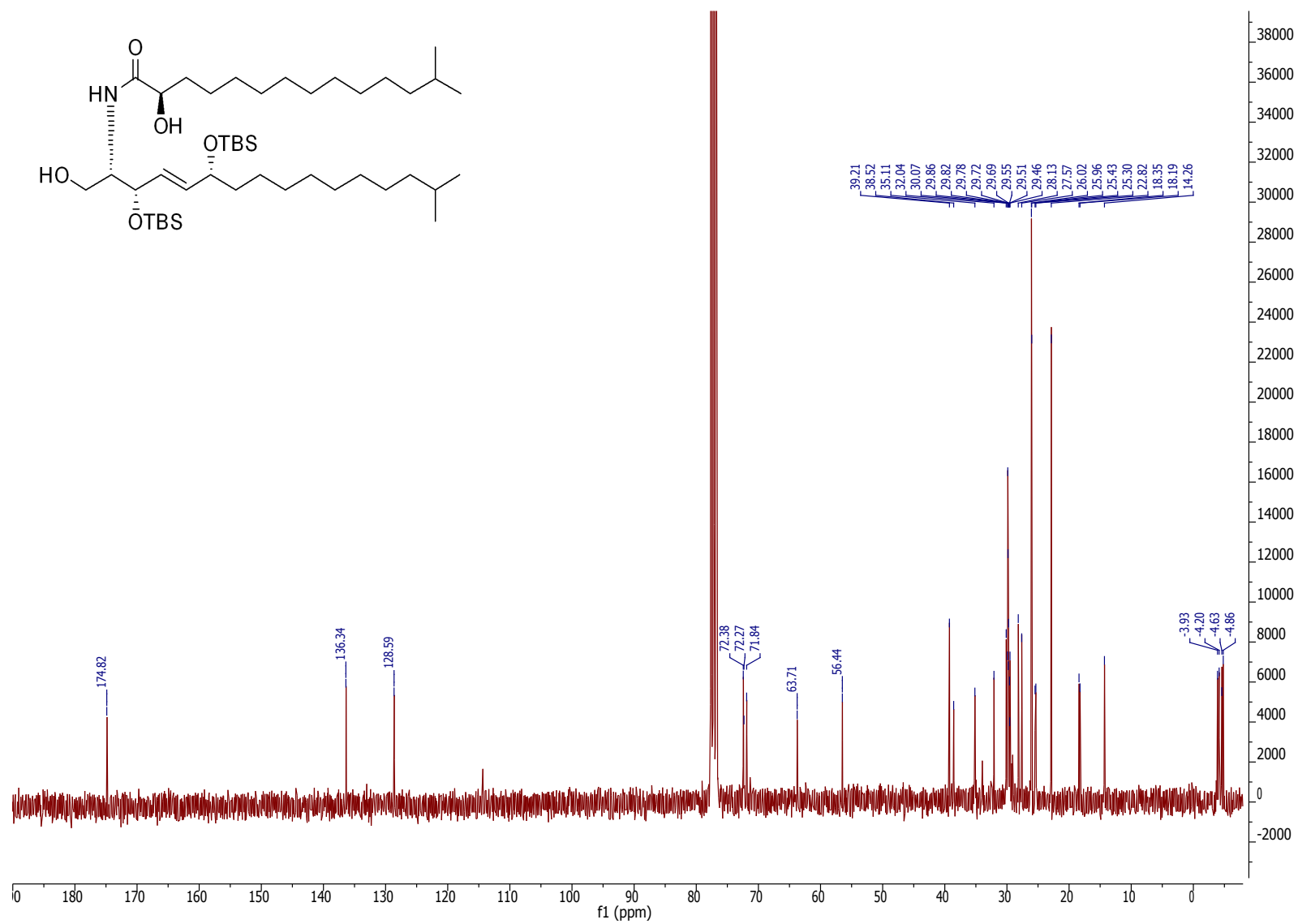


Figure 48. ¹³C-NMR (75 MHz, CDCl₃) of *(R)*-*N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis(*tert*-butyldimethylsilyloxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-2-hydroxy-13-methyltetradecanamide (27).

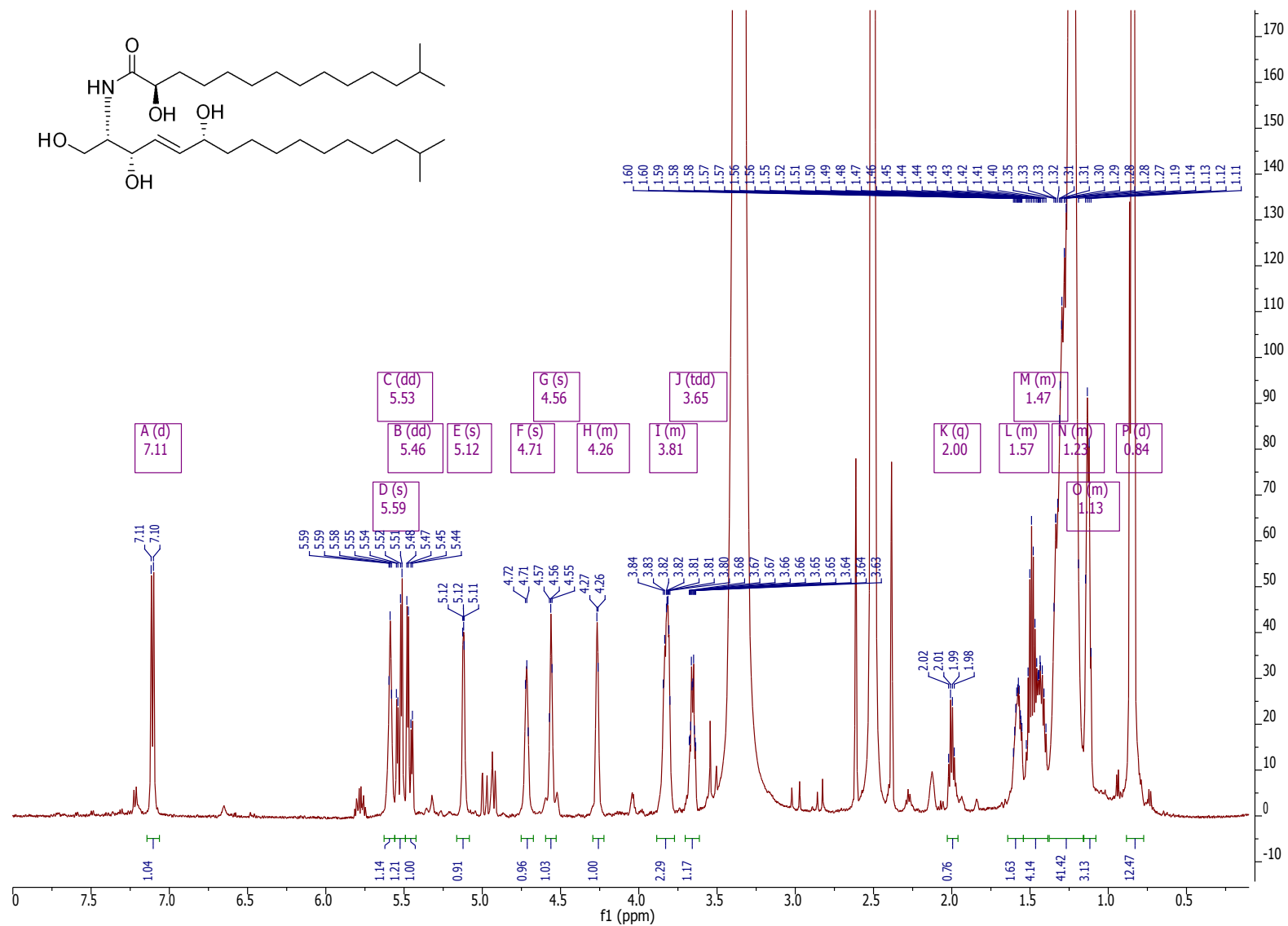


Figure 49. ¹H-NMR (600 MHz, DMSO-d₆) of (R)-2-hydroxy-13-methyl-N-((2S,3S,6R,E)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (28).

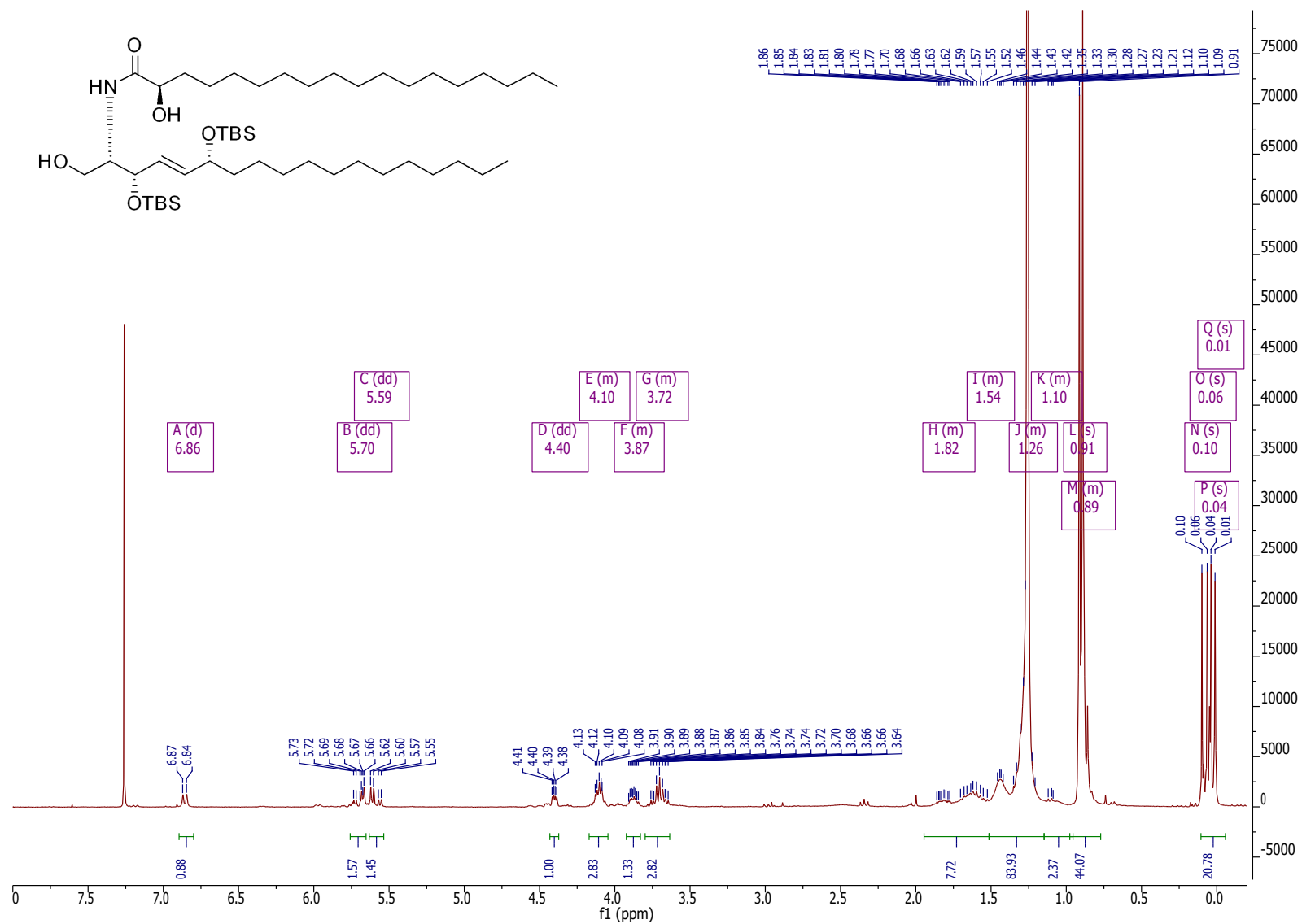


Figure 51. ¹H-NMR (300 MHz, CDCl₃) of *(R)*-*N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxyoctadec-4-en-2-yl)-2-hydroxyoctadecanamide (29).

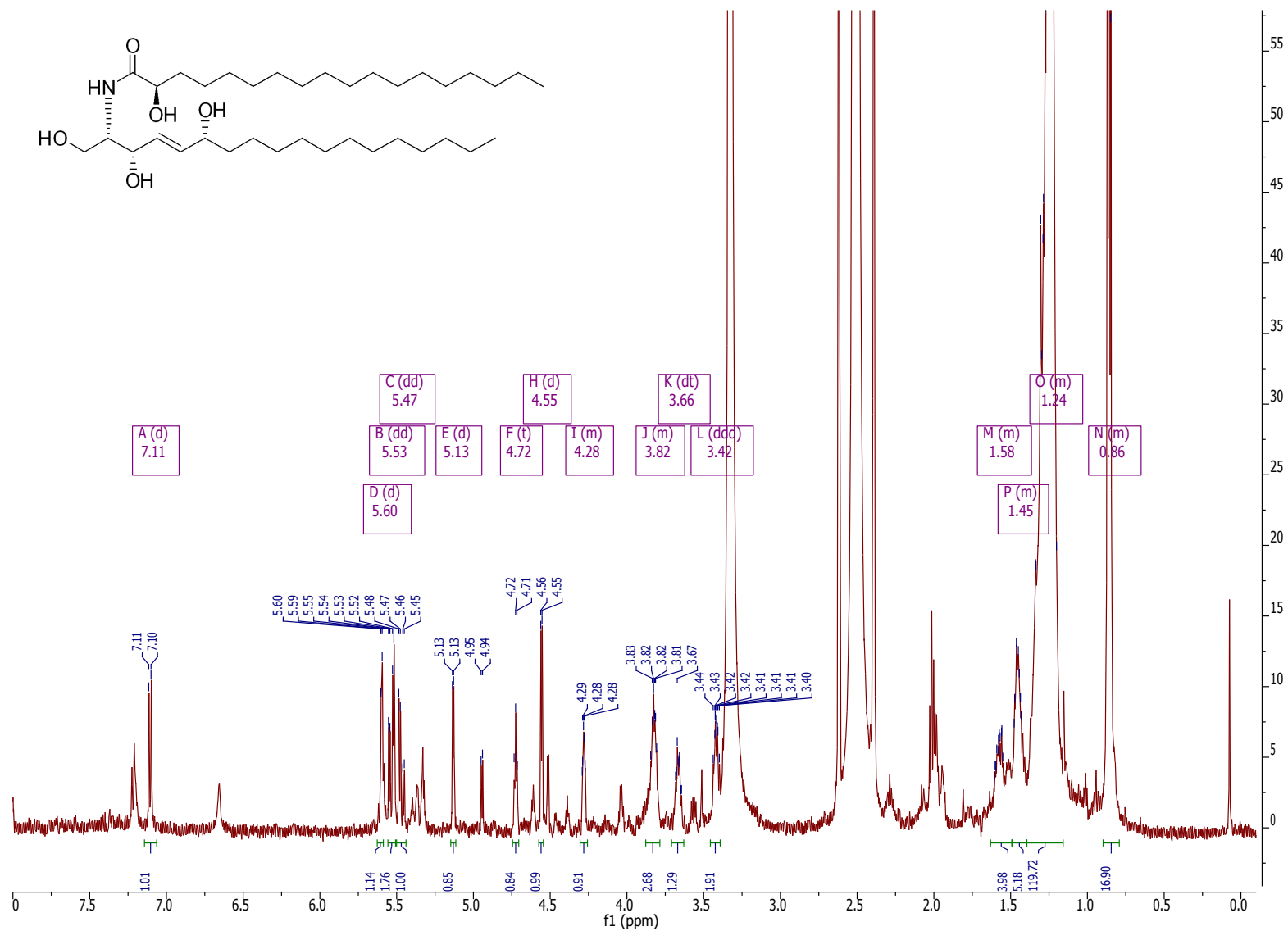


Figure 52. ¹H-NMR (600 MHz, DMSO-d₆) of (R)-2-hydroxy-N-((2S,3S,6R,E)-1,3,6-trihydroxyoctadec-4-en-2-yl)octadecanamide (30).

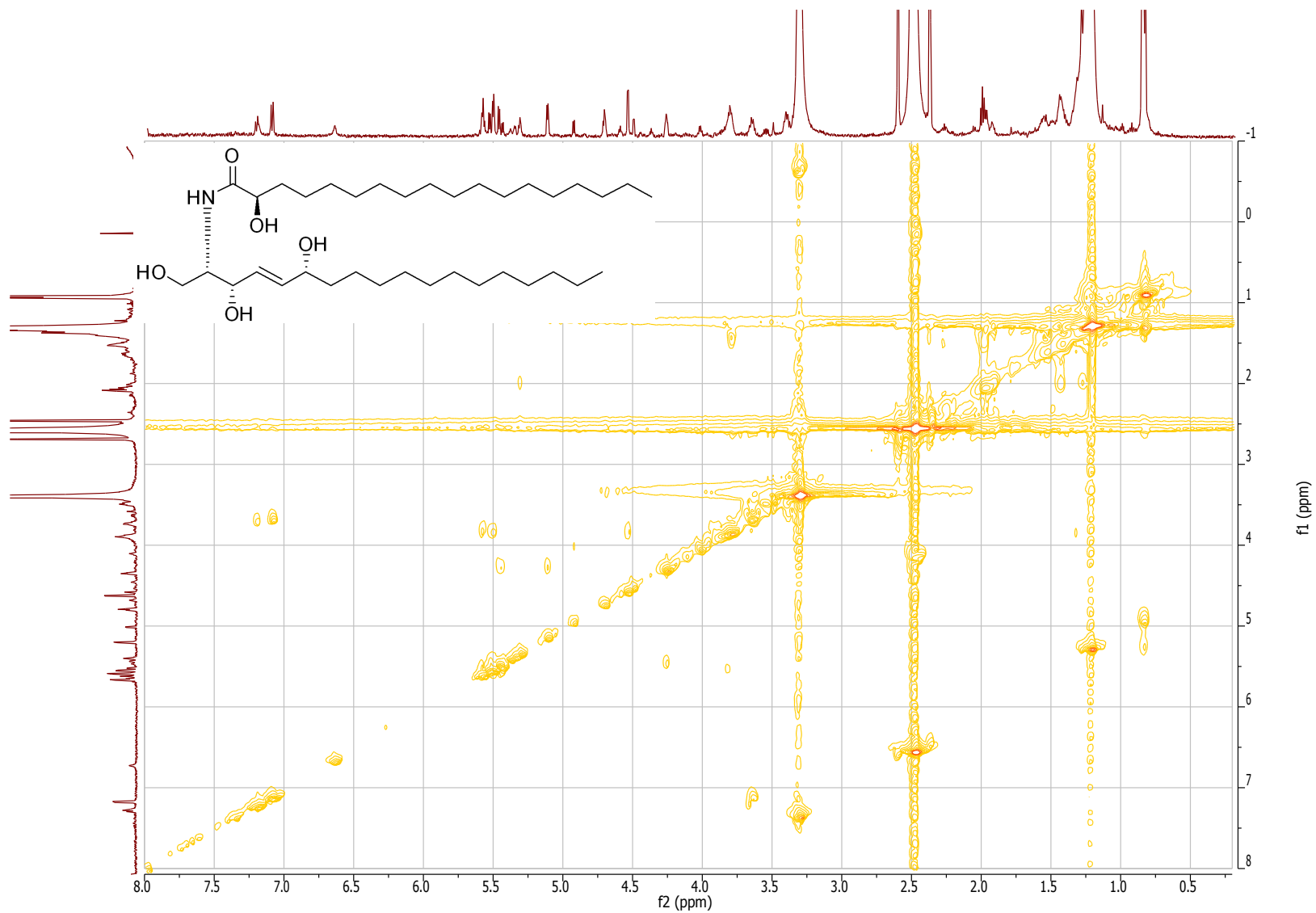


Figure 53. ^1H - ^1H COSY (600 MHz, $\text{DMSO-}d_6$) of *(R)*-2-hydroxy-13-methyl-*N*-((*2S,3S,6R,E*)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (30).

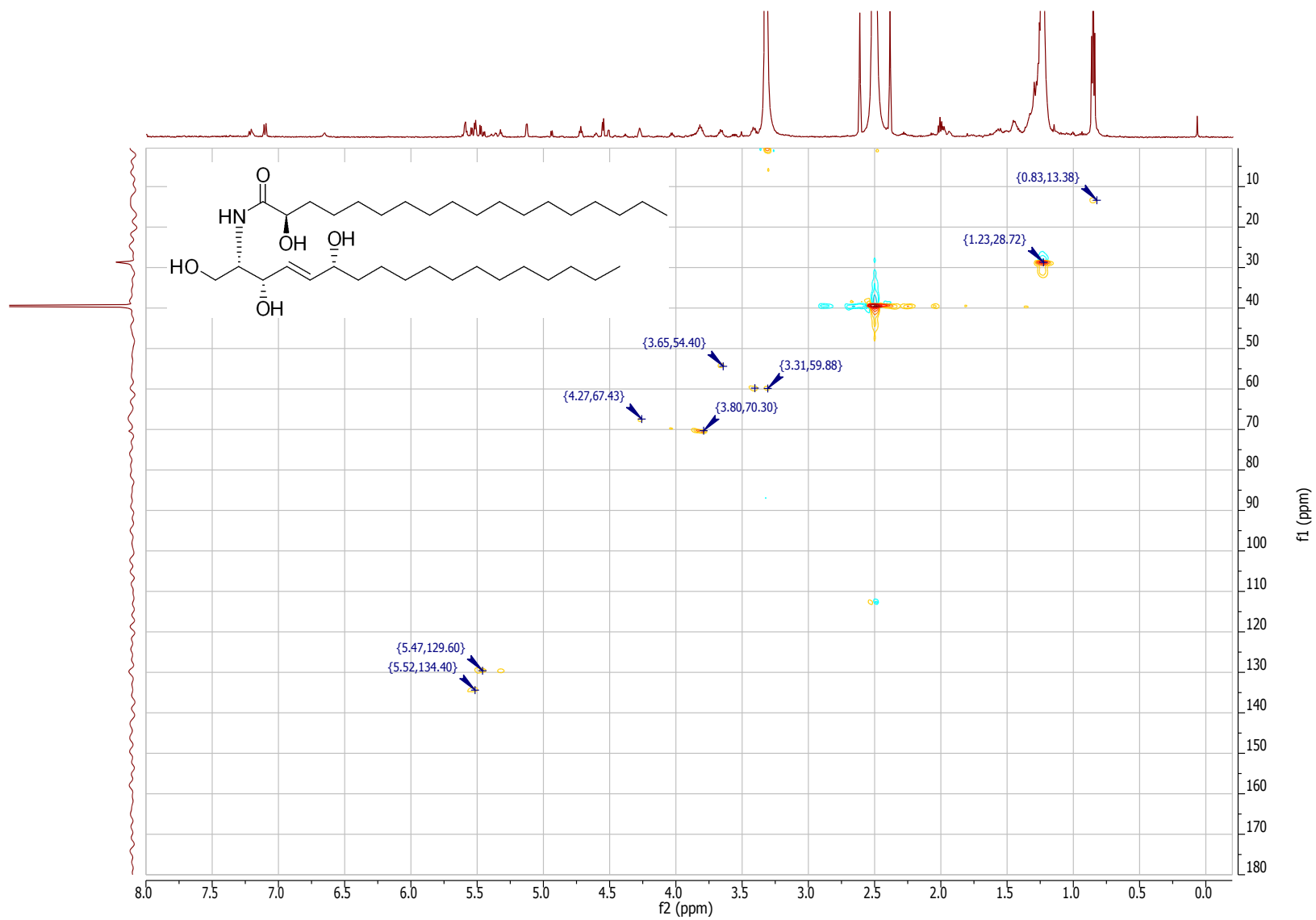


Figure 54. ^1H - ^{13}C HSQC (R)-2-hydroxy-13-methyl-N-((2S,3S,6R,E)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (30).

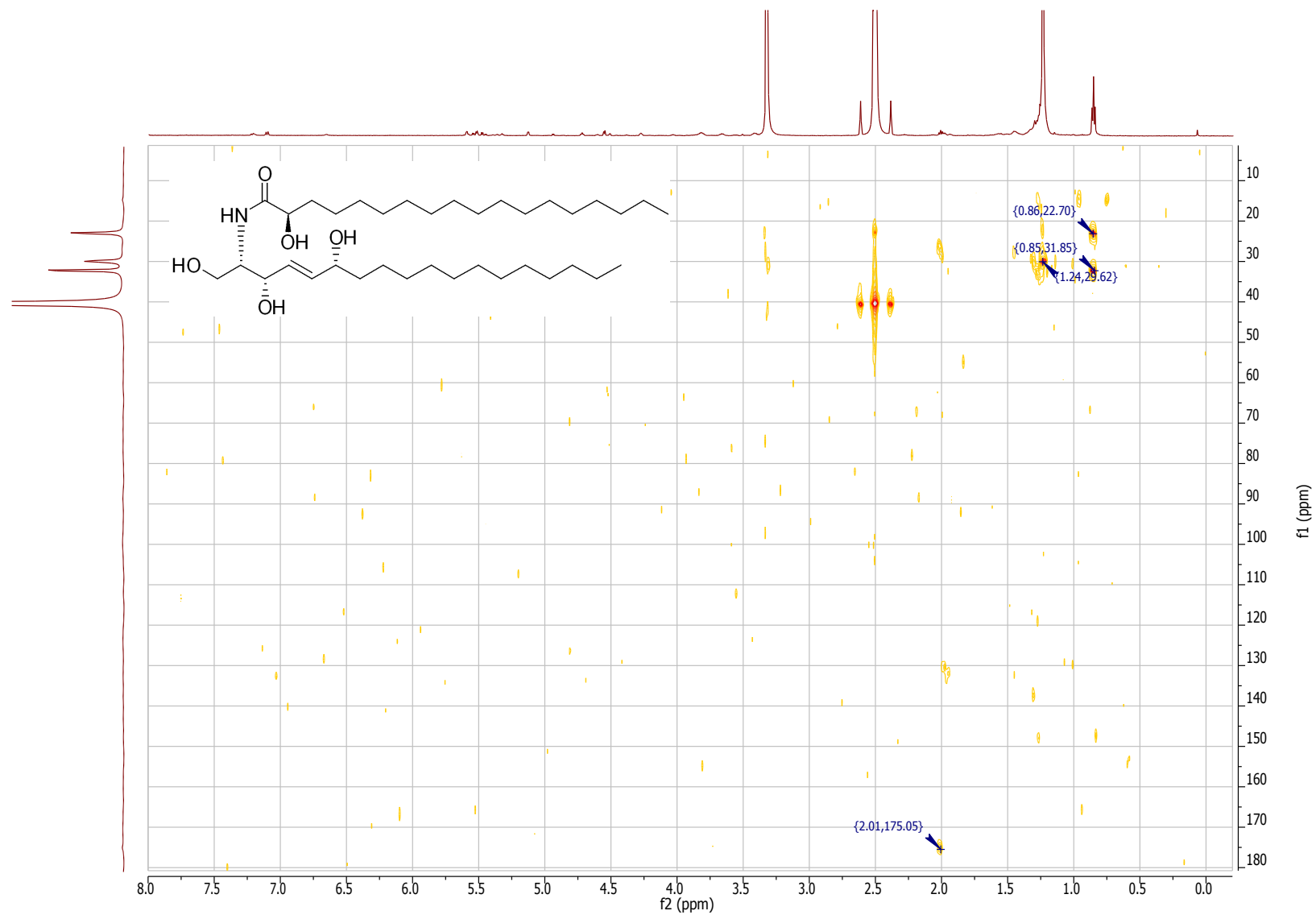


Figure 55. ^1H - ^{13}C HMBC of (R)-2-hydroxy-13-methyl-N-((2S,3S,6R,E)-1,3,6-trihydroxy-15-methylhexadec-4-en-2-yl)tetradecanamide (30).

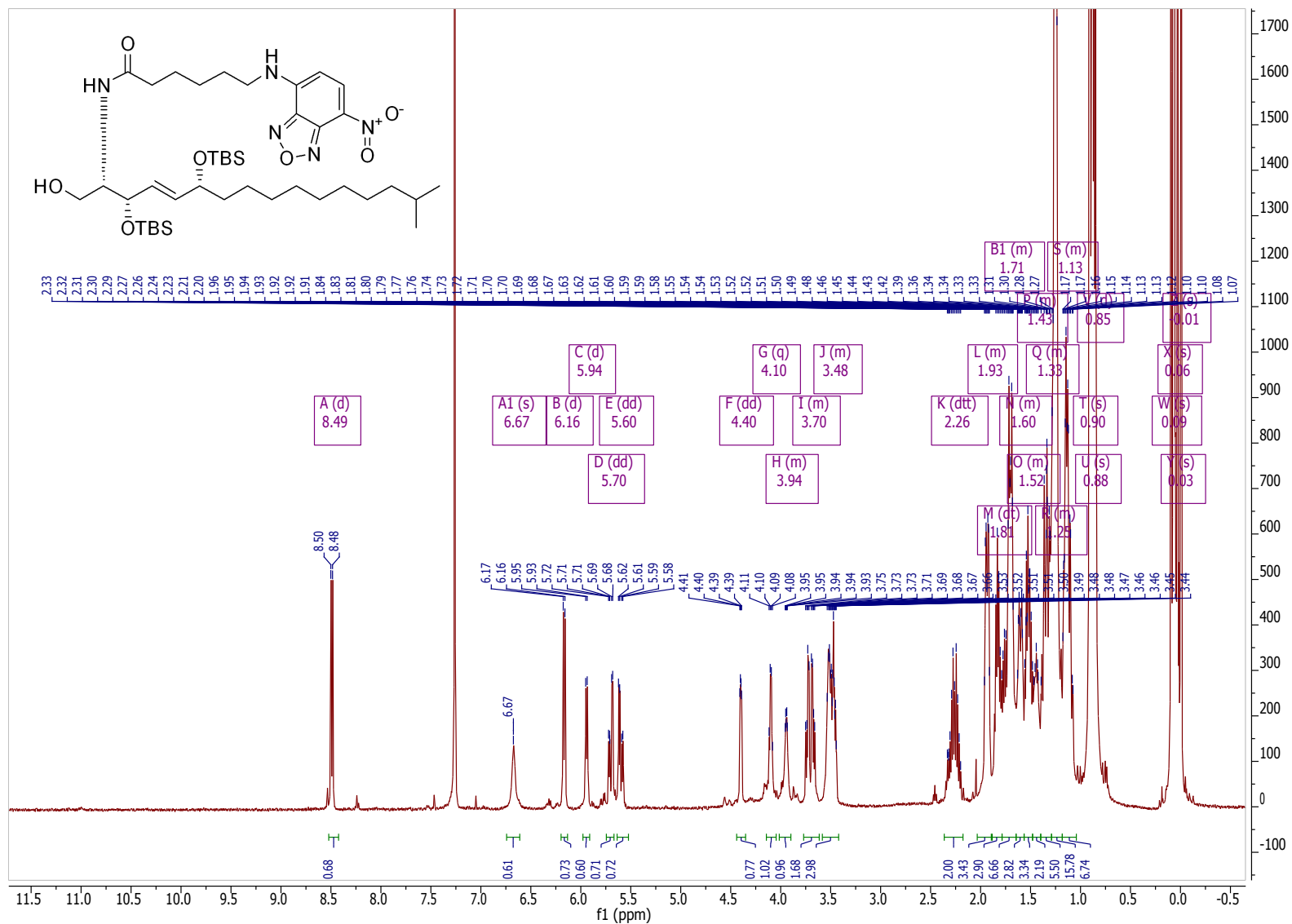


Figure 56. ¹H-NMR (500 MHz, CDCl₃) of *N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis(*tert*-butyldimethylsilyloxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-6-((7-nitrobenzo[*c*][1,2,5]oxadiazol-4-yl)amino)hexanamide (**31**).

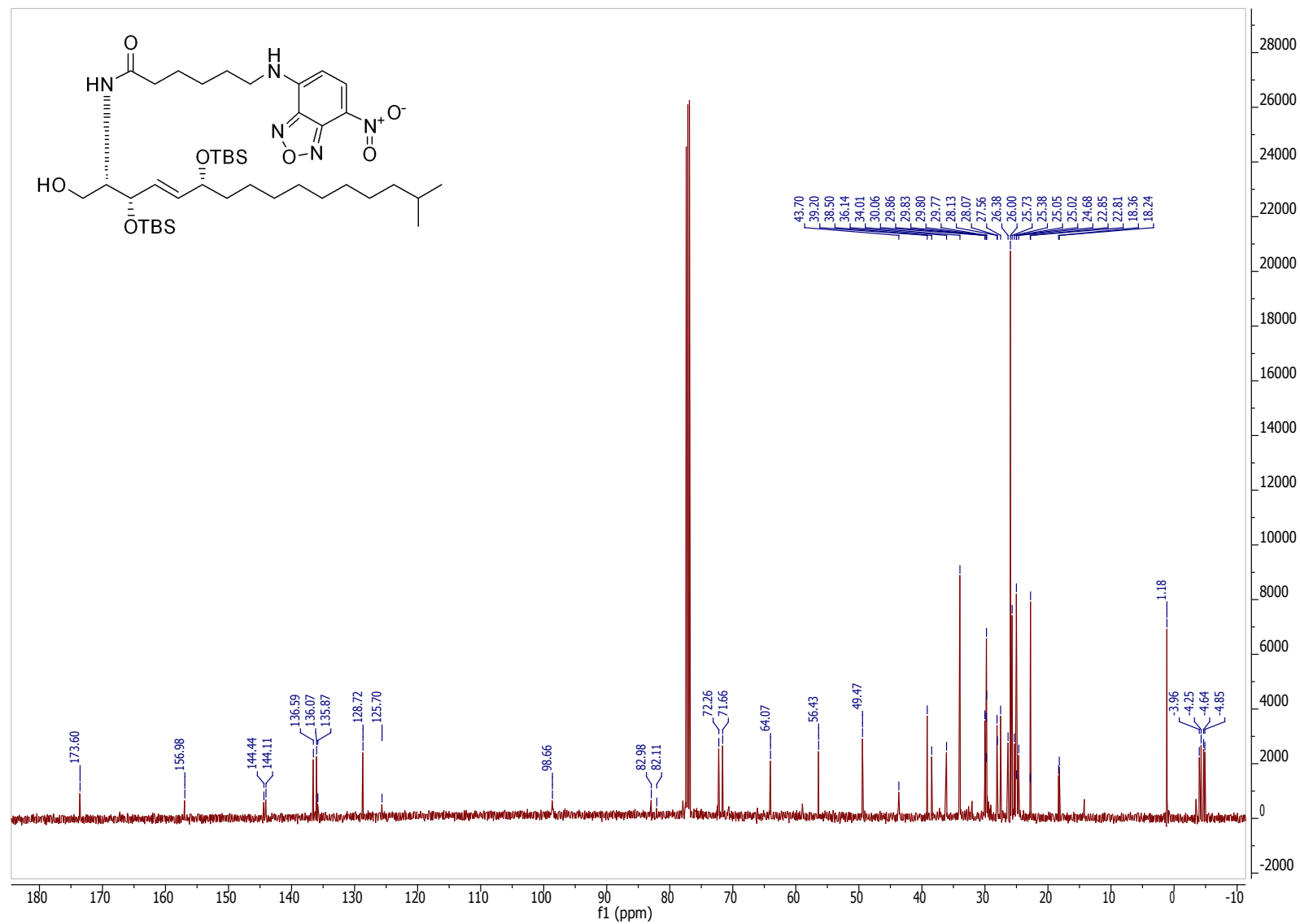


Figure 57. ^{13}C -NMR (126 MHz, CDCl_3) of *N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyloxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)-6-((7-nitrobenzo[*c*][1,2,5]oxadiazol-4-yl)amino)hexanamide (**31**).

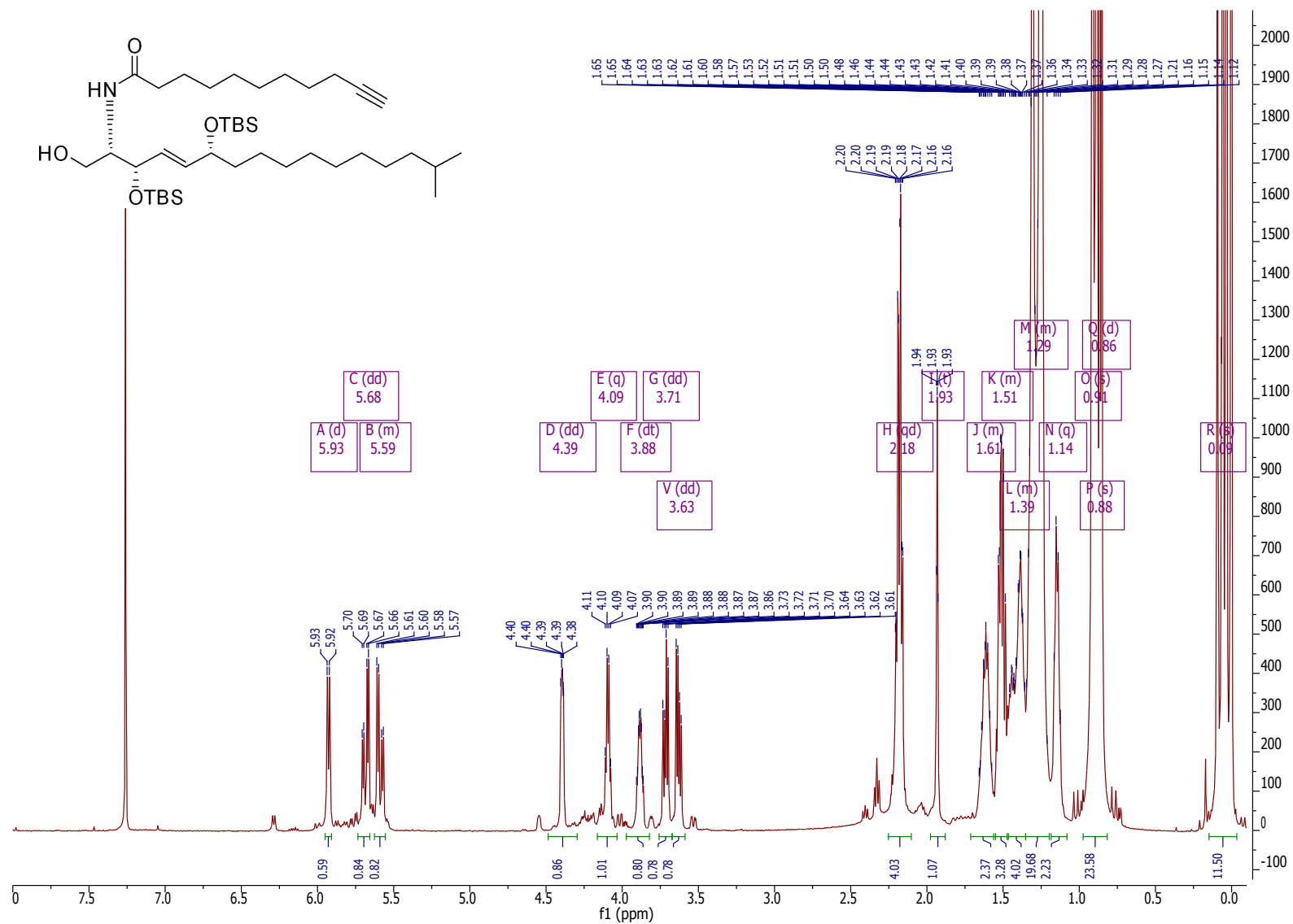


Figure S8 ¹H-NMR (500 MHz, CDCl₃) of *N*-((2*S*,3*S*,6*R*,*E*)-3,6-bis((*tert*-butyldimethylsilyloxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)undec-10-ynamide (32).

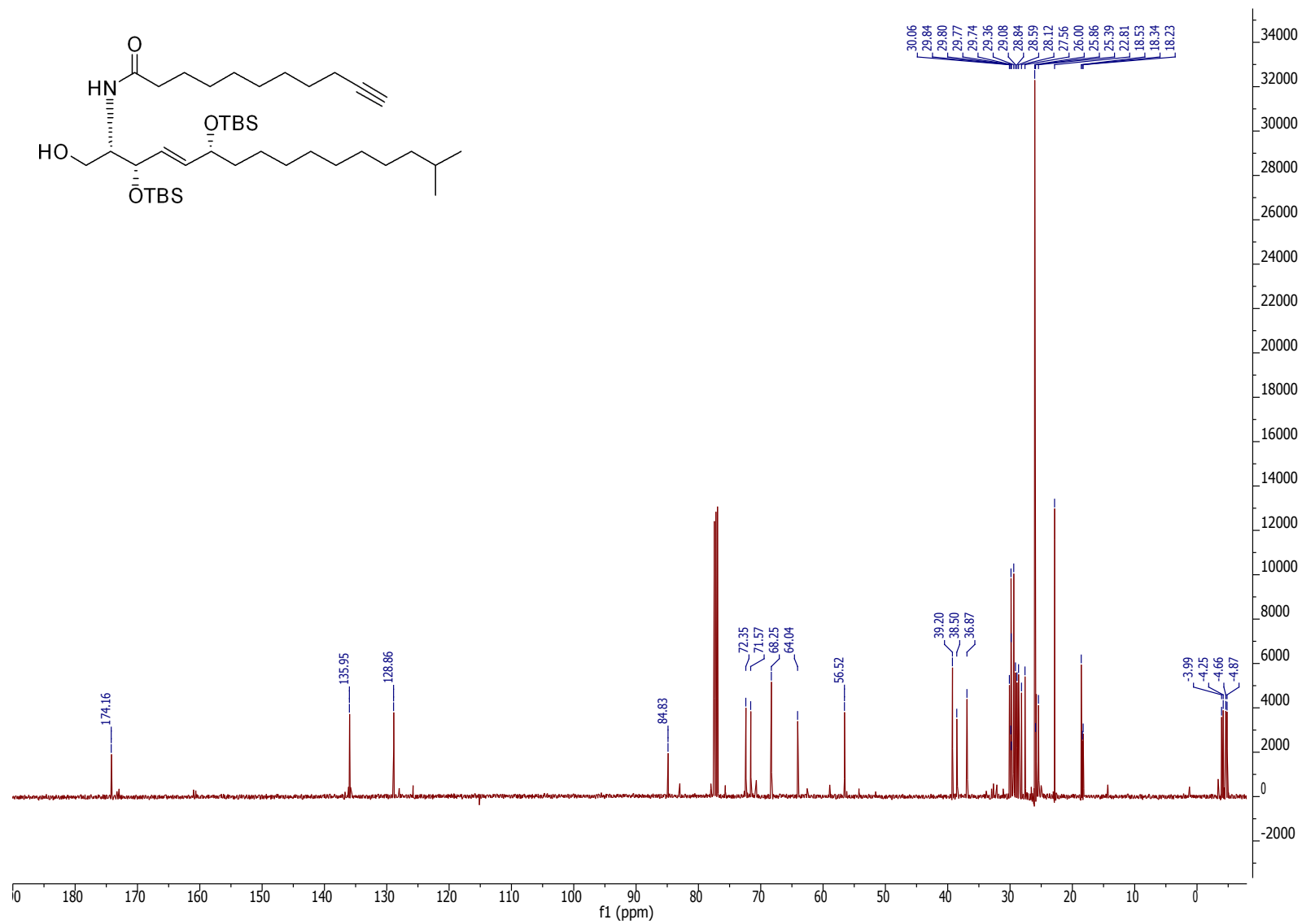


Figure 59. ¹³C-NMR (126 MHz, CDCl₃) of N-((2S,3S,6R,E)-3,6-bis((tert-butylidimethylsilyl)oxy)-1-hydroxy-15-methylhexadec-4-en-2-yl)undec-10-ynamide (32).