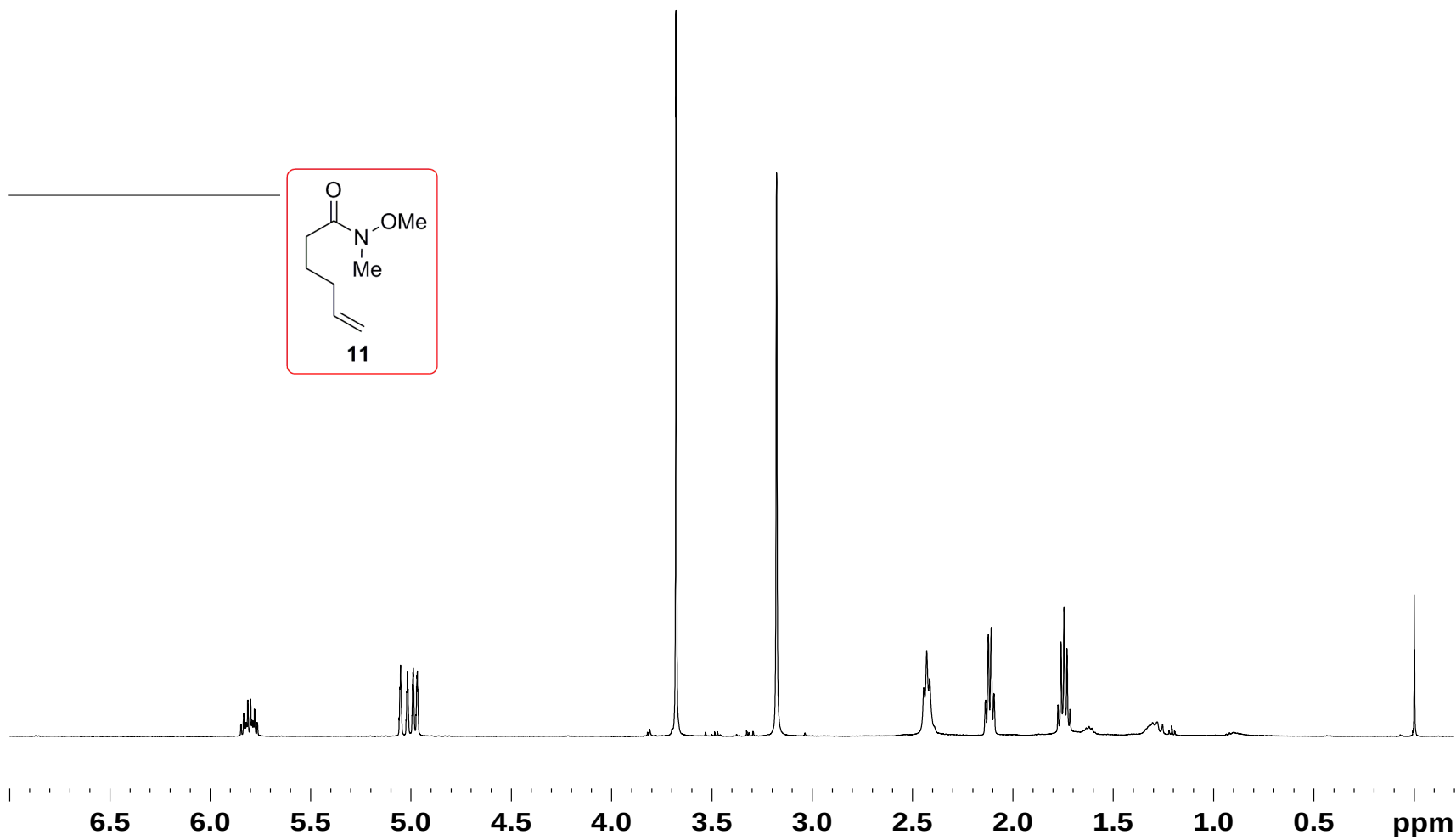


Vinylogous anionic processes in the formation and interconversion of tetracyclic ring systems

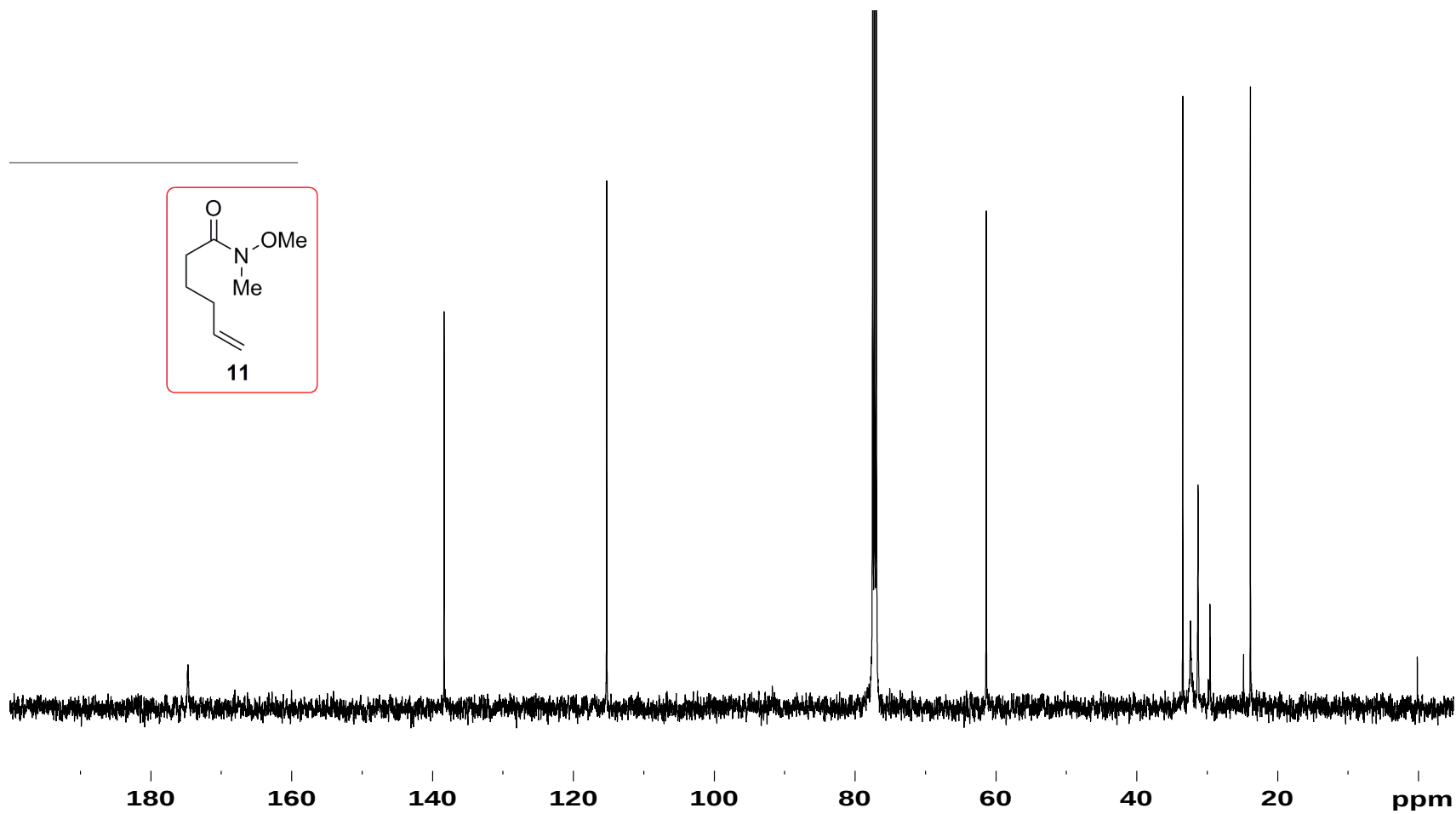
Paul D. Thornton, T. Stanley Cameron and D. Jean Burnell*

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

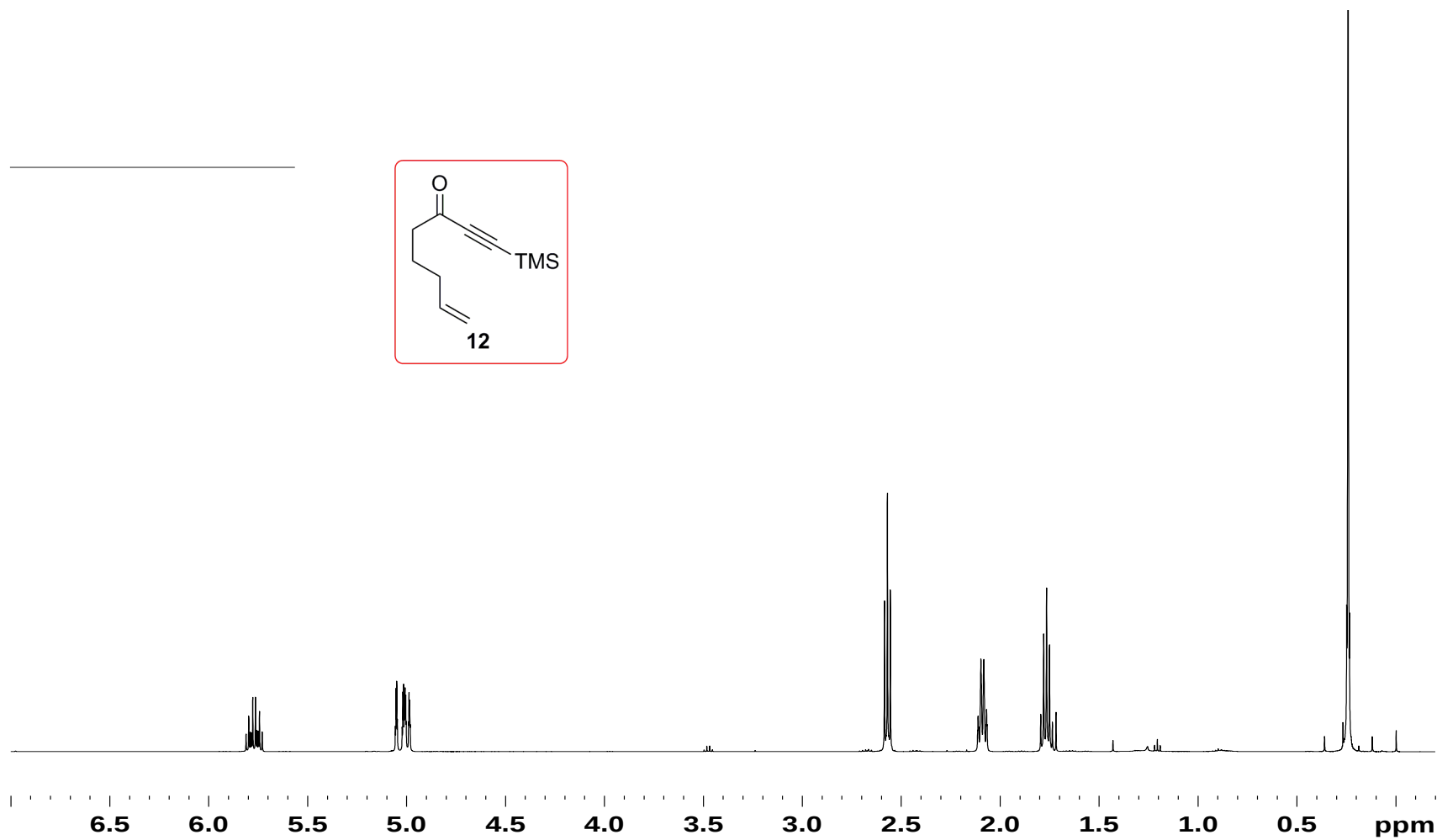
¹H NMR (500 MHz, CDCl₃) of *N*-methoxy-*N*-methyl-5-hexenamide (11)



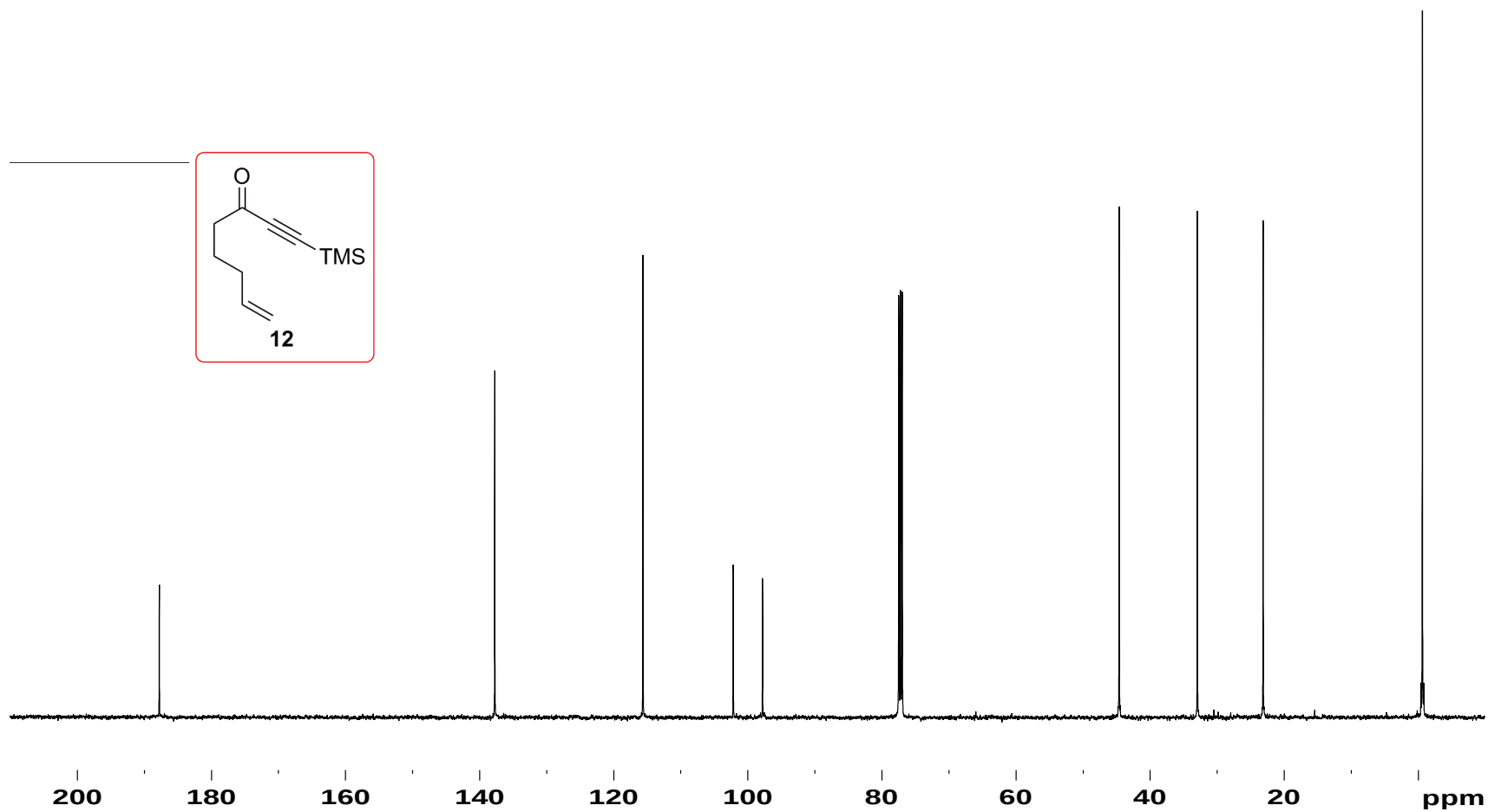
^{13}C NMR (125 MHz, CDCl_3) of *N*-methoxy-*N*-methyl-5-hexenamide (11)



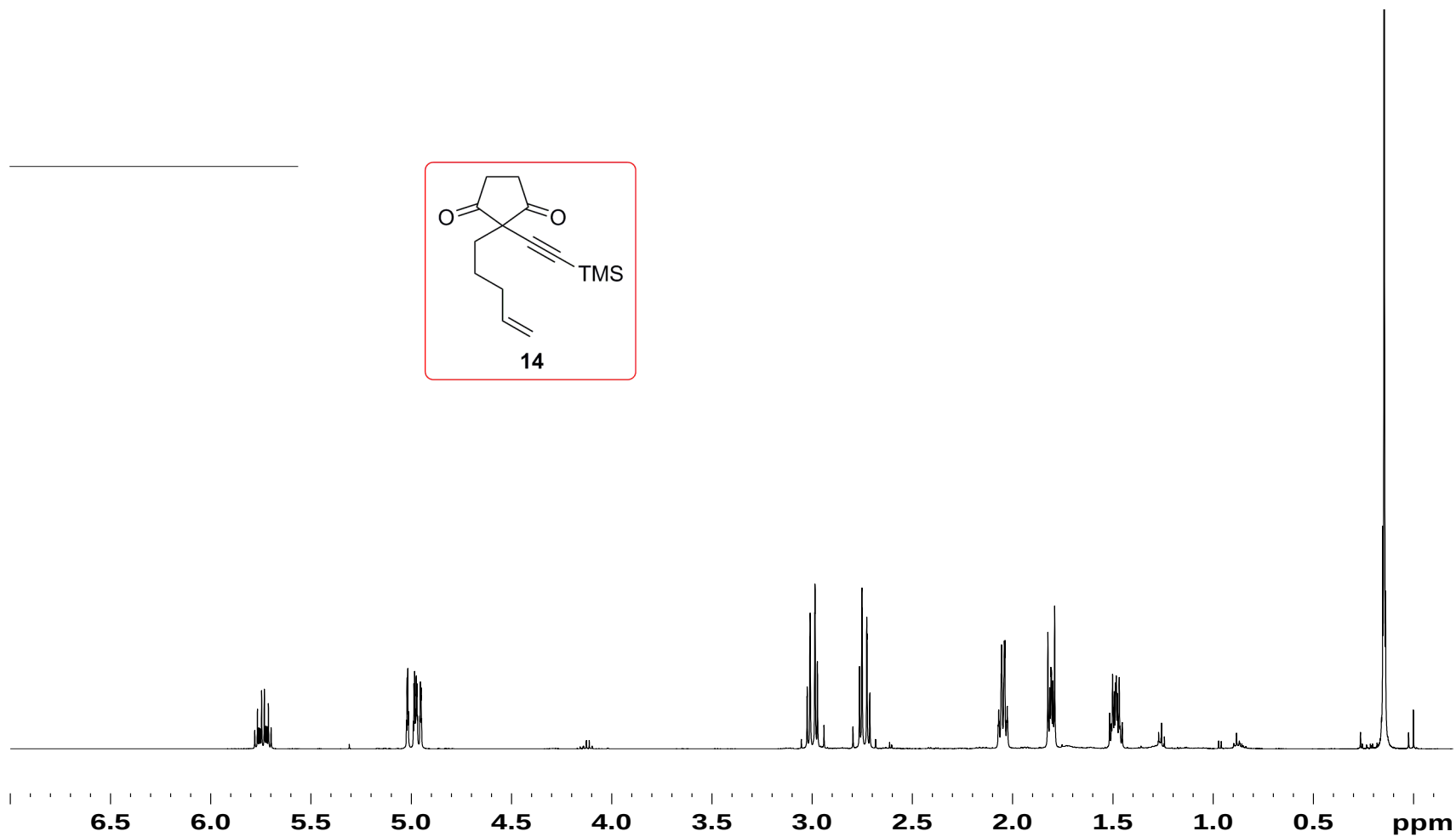
^1H NMR (500 MHz, CDCl_3) of 1-(trimethylsilyl)oct-7-en-1-yn-3-one (12)



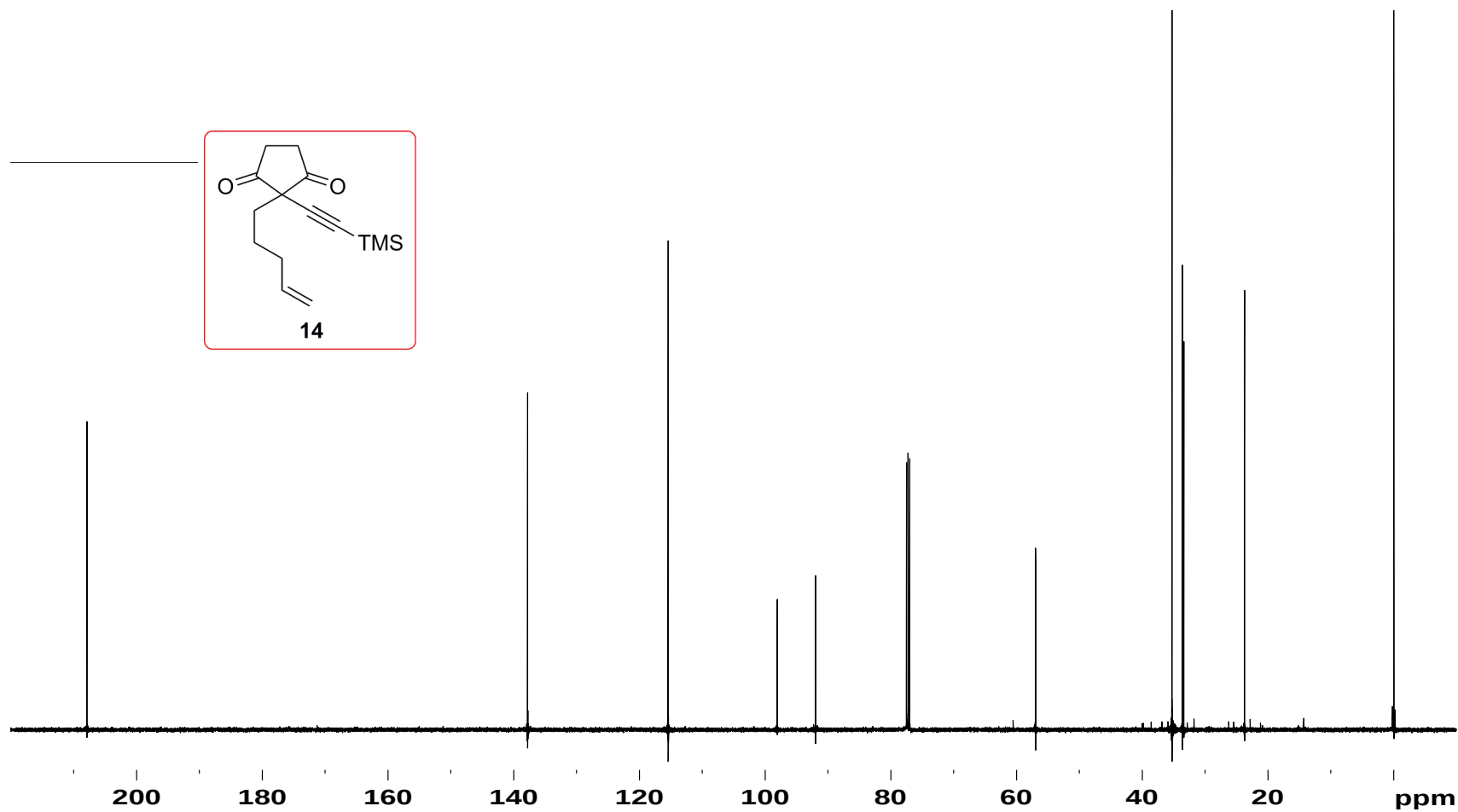
^{13}C NMR (125 MHz, CDCl_3) of 1-(trimethylsilyl)oct-7-en-1-yn-3-one (12)



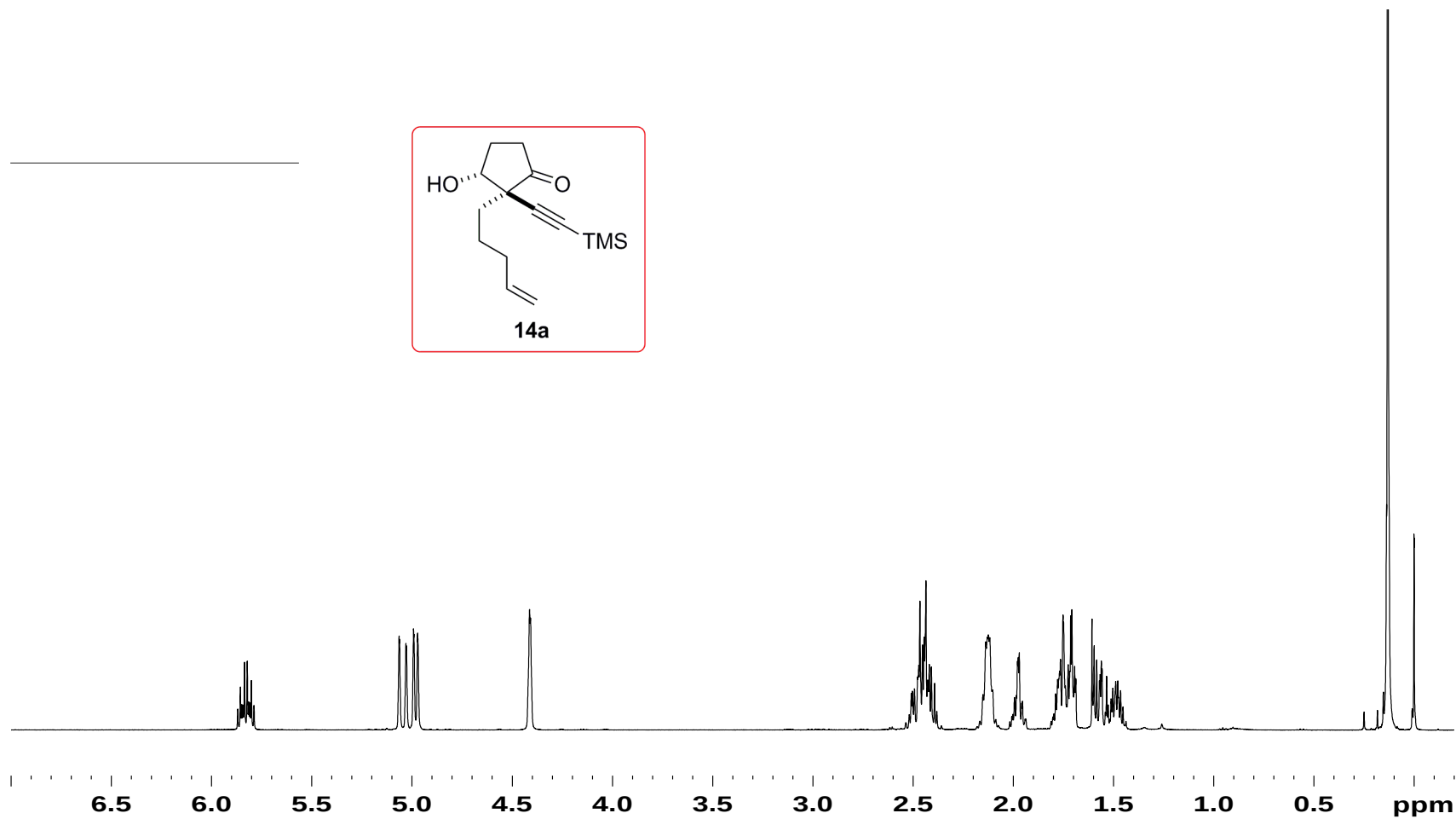
^1H NMR (500 MHz, CDCl_3) of 2-(pent-4-enyl)-2-(2-(trimethylsilyl)ethynyl)cyclopentane-1,3-dione (14)



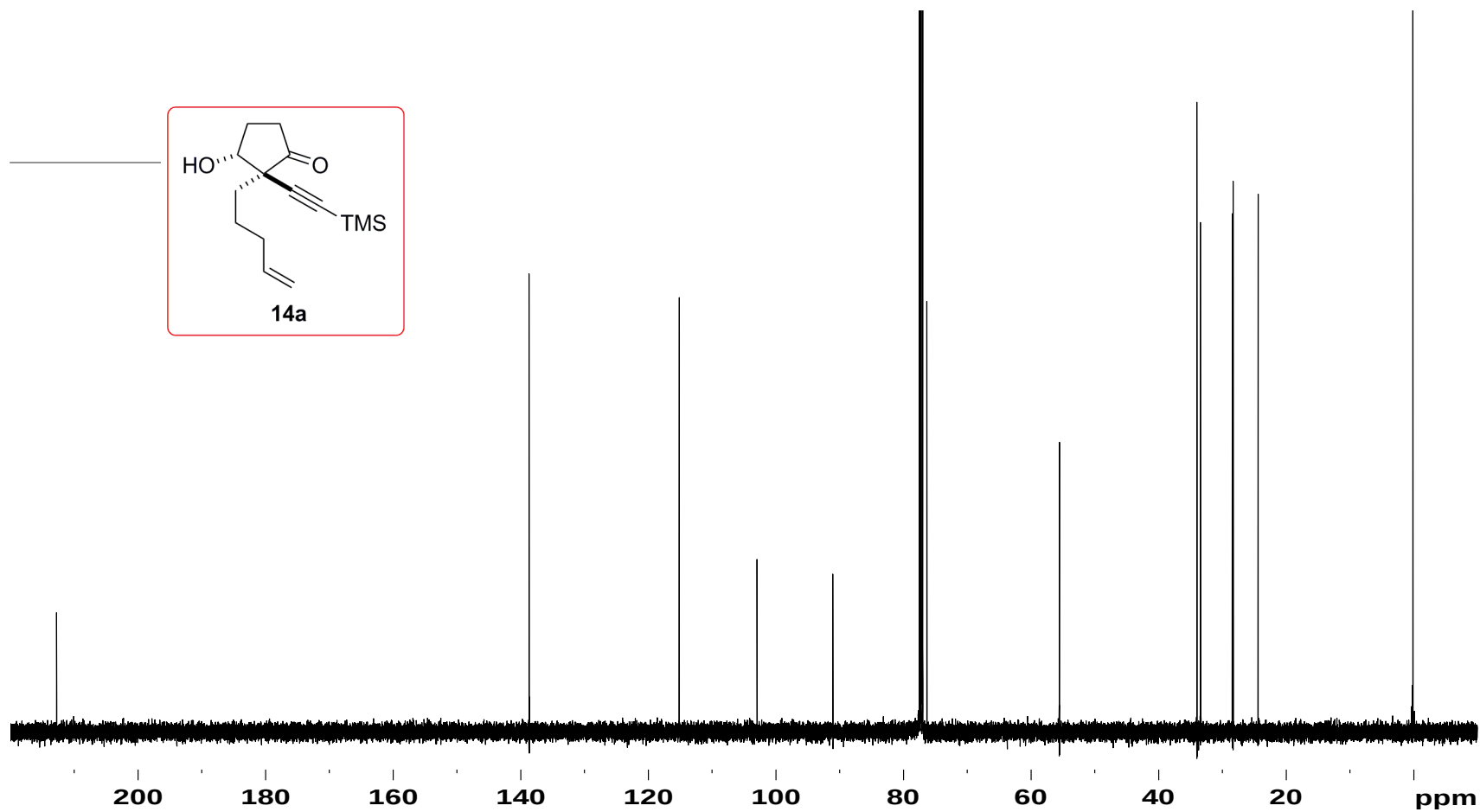
^{13}C NMR (125 MHz, CDCl_3) of 2-(pent-4-enyl)-2-(2-(trimethylsilyl)ethynyl)cyclopentane-1,3-dione (14)



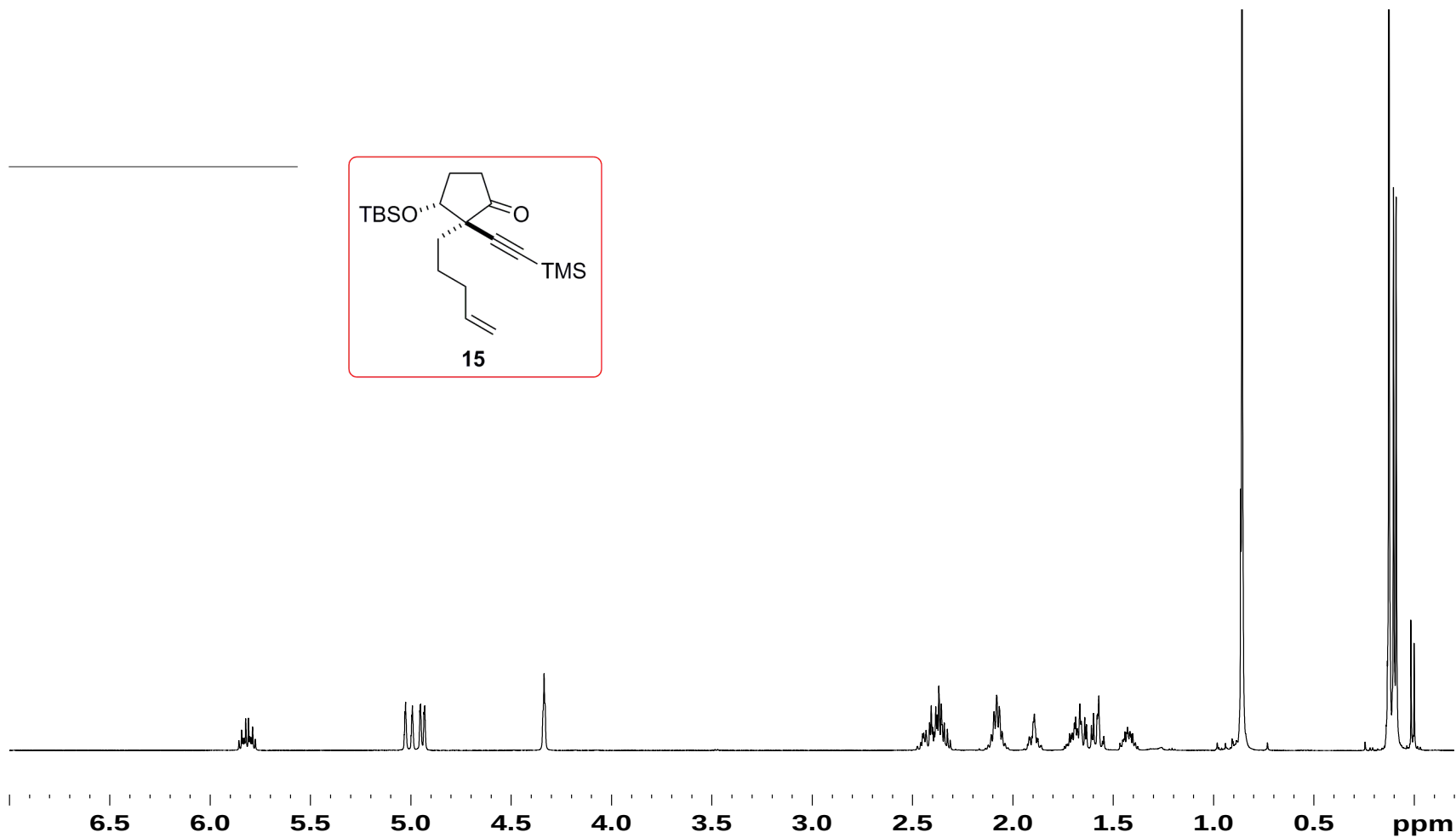
^1H NMR (500 MHz, CDCl_3) of (2*R,3*S**)-3-hydroxy-2-(pent-4-enyl)-2-(2-(trimethylsilyl)ethynyl)cyclopentanone (14a)**



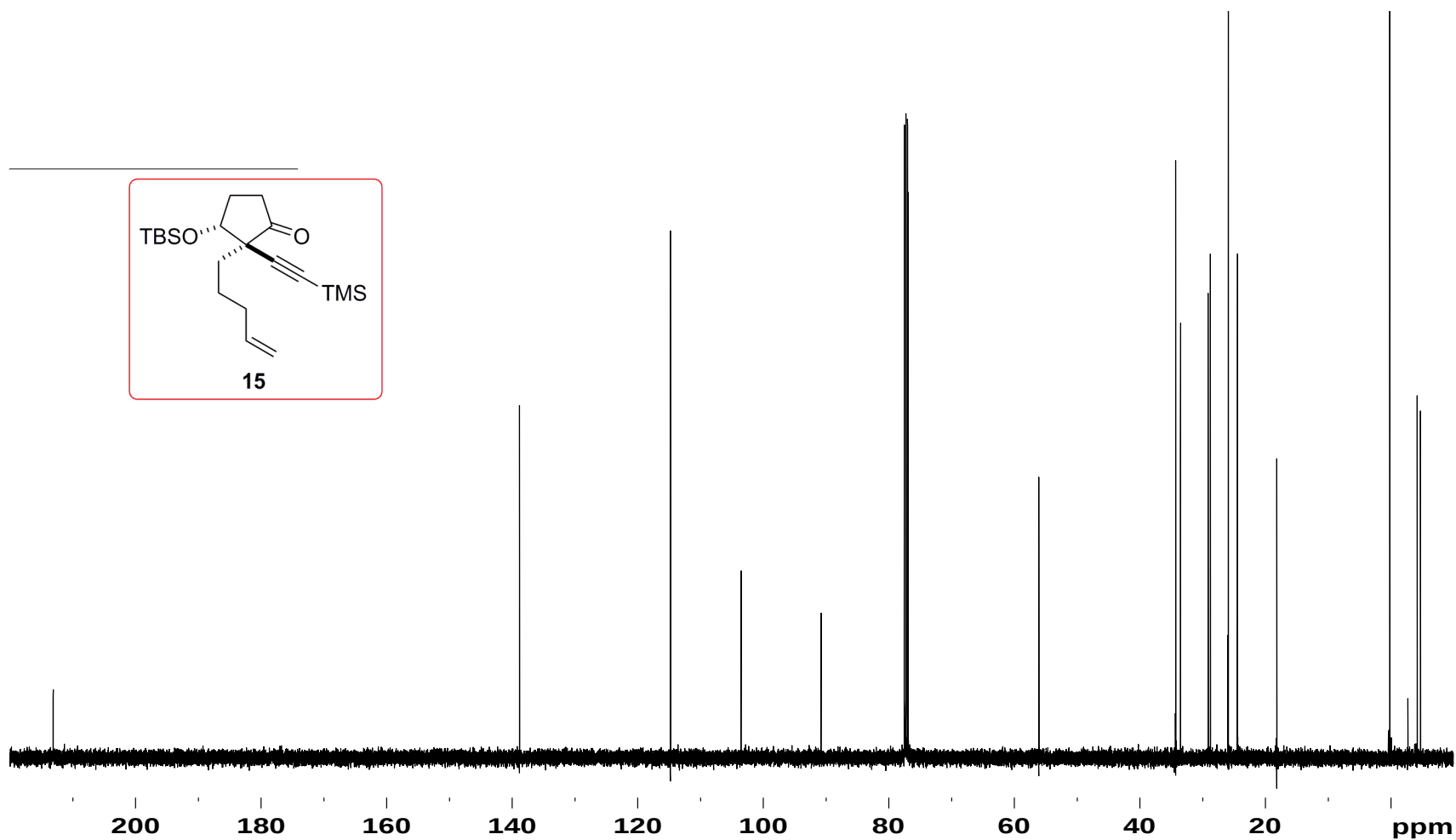
^{13}C NMR (125 MHz, CDCl_3) of (2*R,3*S**)-3-hydroxy-2-(pent-4-enyl)-2-(2-(trimethylsilyl)ethynyl)cyclopentanone (14a)**



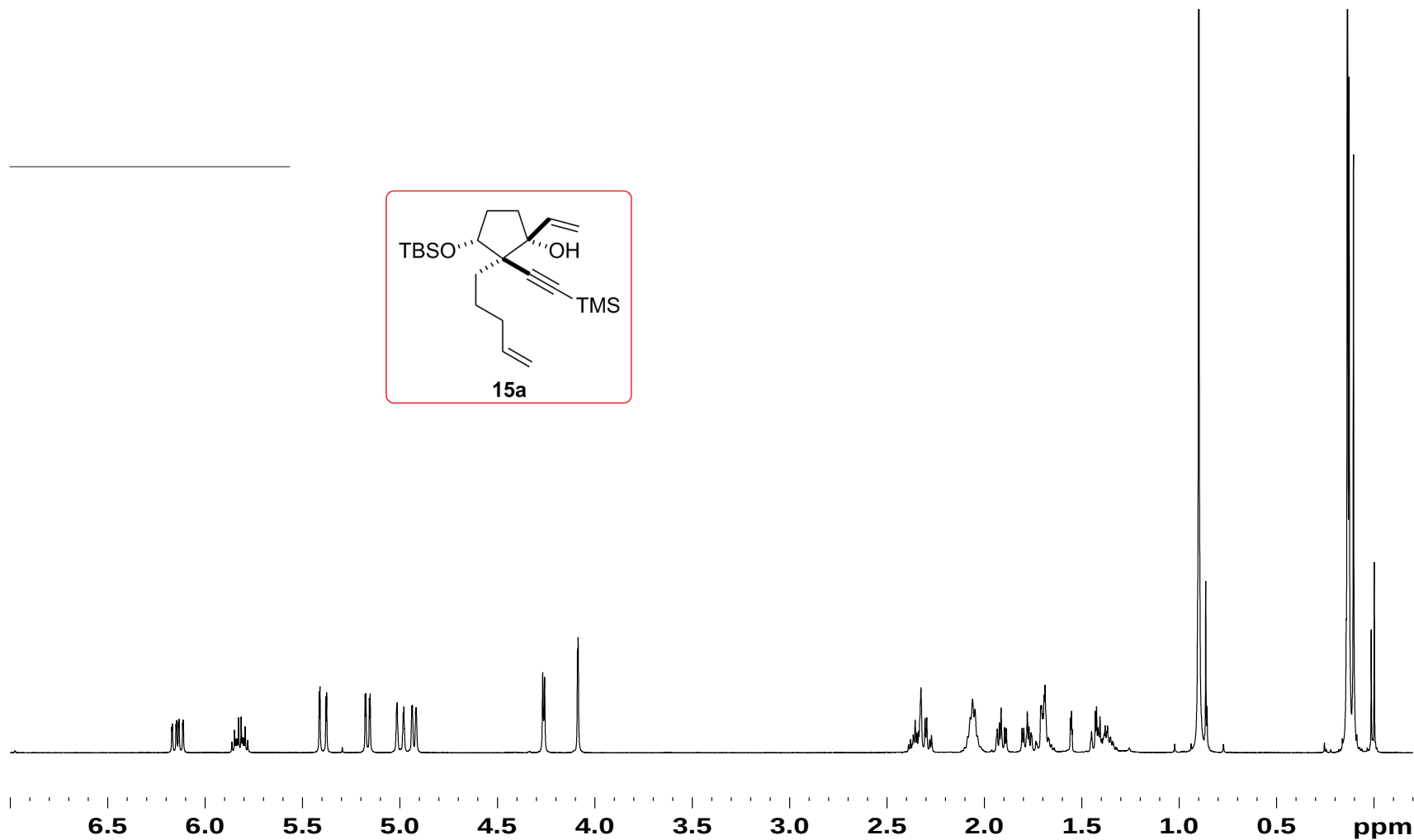
^1H NMR (500 MHz, CDCl_3) of (2*R,3*S**)-3-(*tert*-butyldimethylsilyl)oxy-2-(pent-4-enyl)-2-((trimethylsilyl)ethynyl)cyclopentanone (15)**



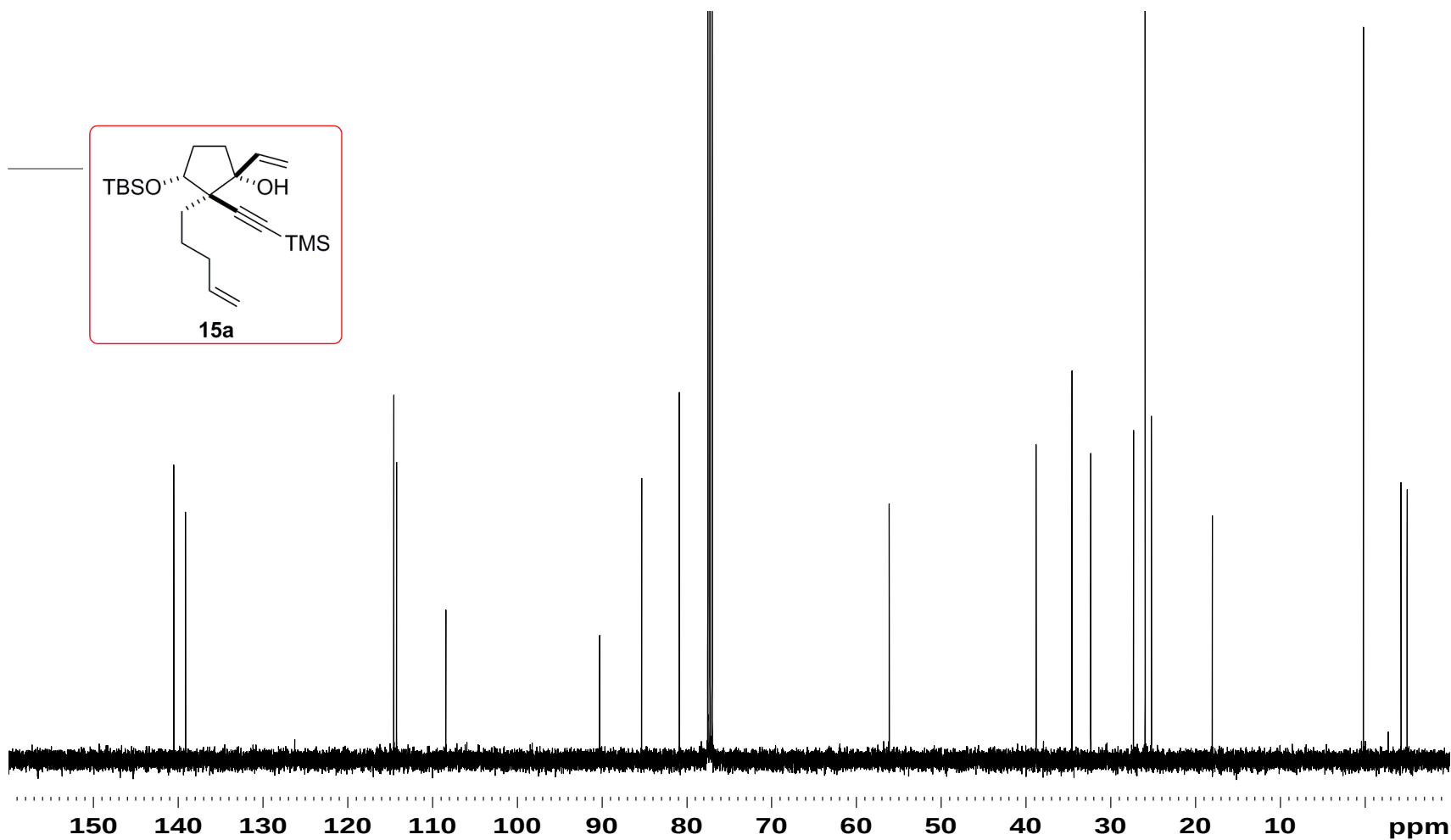
^{13}C NMR (125 MHz, CDCl_3) of (2*R,3*S**)-3-(*tert*-butyldimethylsilyl)oxy-2-(pent-4-enyl)-2-((trimethylsilyl)ethynyl)cyclopentanone (15)**



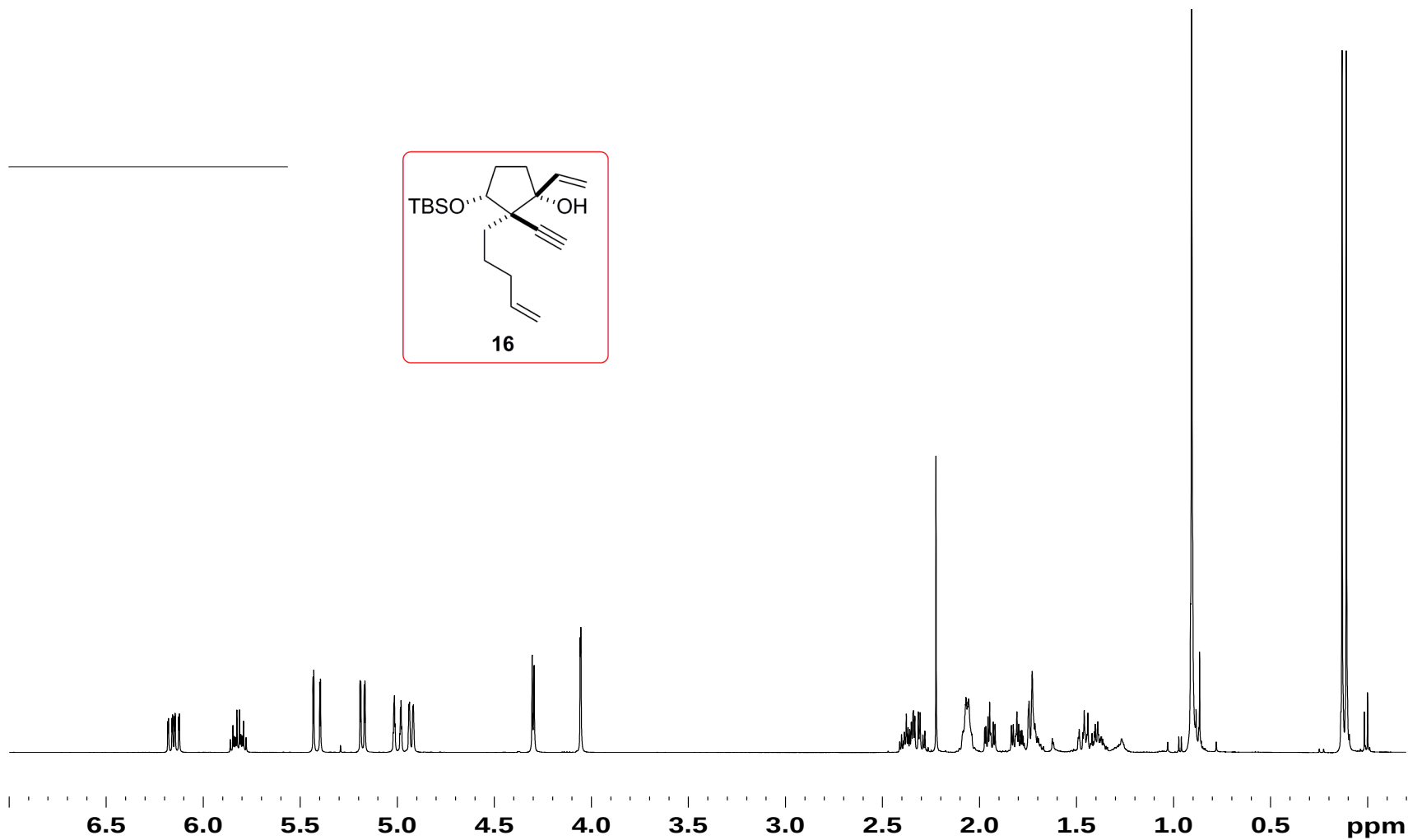
^1H NMR (500 MHz, CDCl_3) of (1*R,2*S**,3*R**)-3-(*tert*-butyldimethylsilyl)oxy-2-((trimethylsilyl)ethynyl)-2-(pent-4-enyl)-1-vinylcyclopentan-1-ol (15a)**



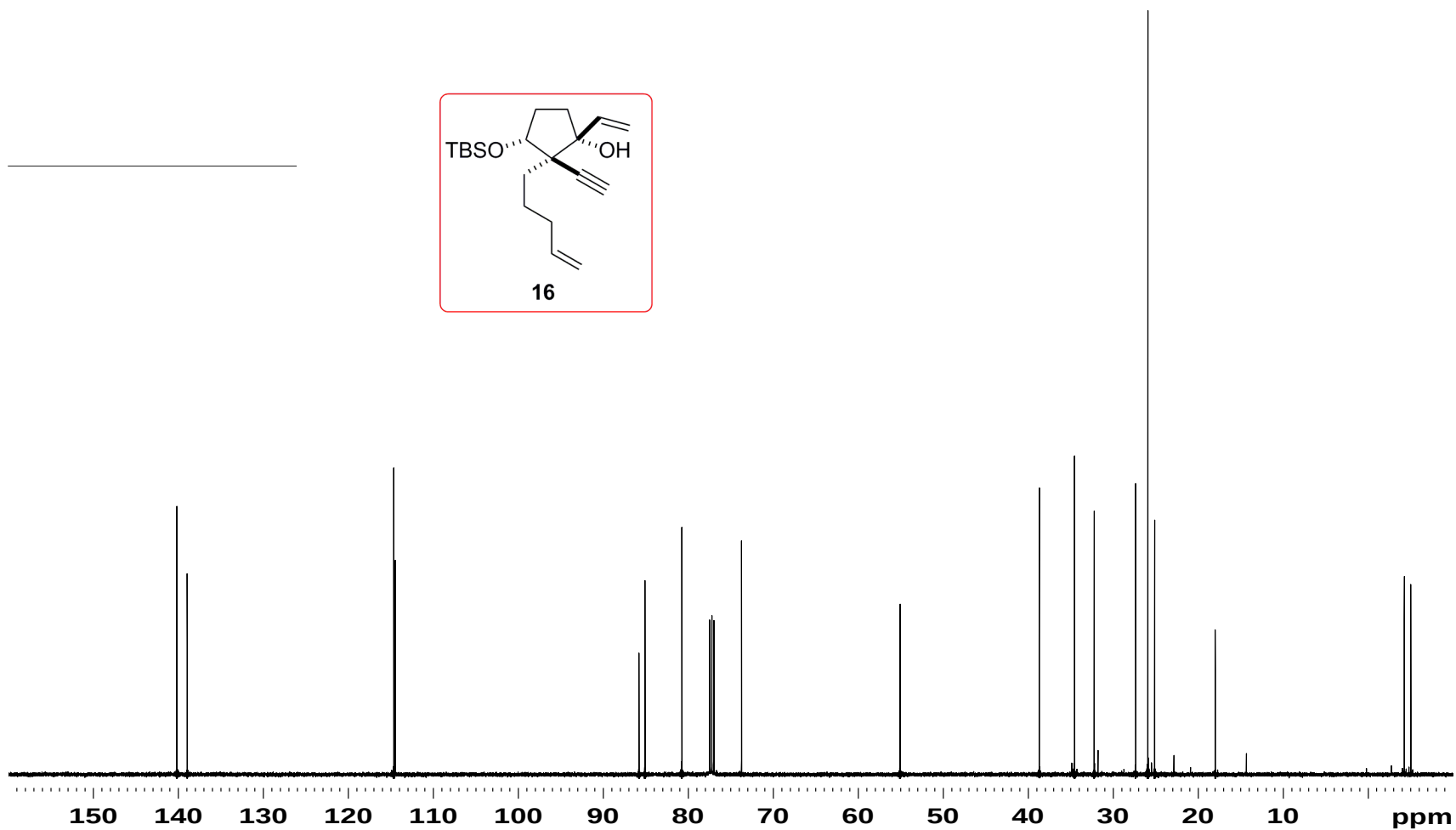
^{13}C NMR (125 MHz, CDCl_3) of (1*R**,2*S**,3*R**)-3-(*tert*-butyldimethylsilyl)oxy-2-((trimethylsilyl)ethynyl)-2-(pent-4-enyl)-1-vinylcyclopentan-1-ol (15a)



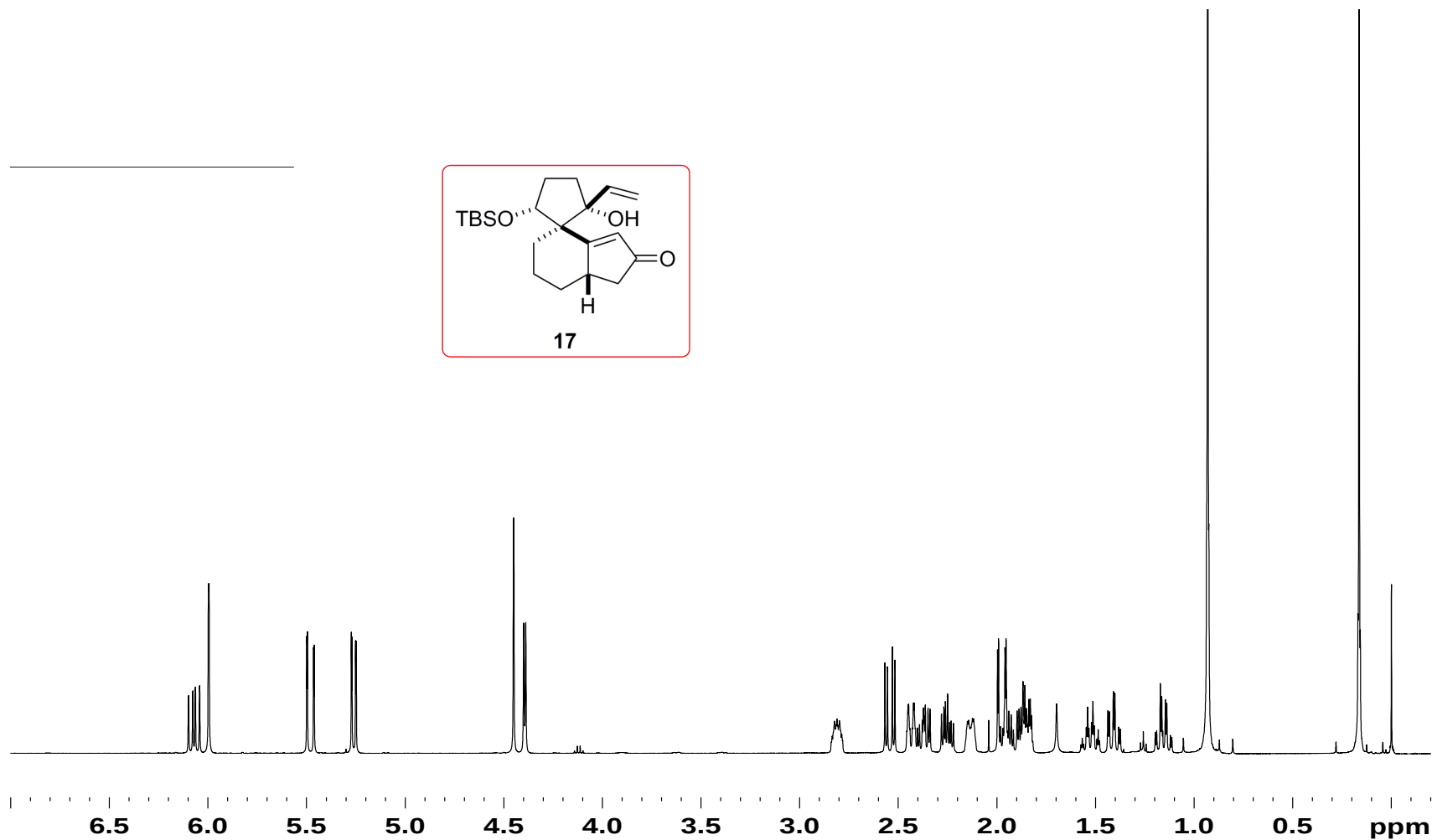
^1H NMR (500 MHz, CDCl_3) of (1*R,2*S**,3*S**)-3-(*tert*-butyldimethylsilyl)oxy-2-ethynyl-2-(pent-4-enyl)-1-vinylcyclopentan-1-ol (16)**



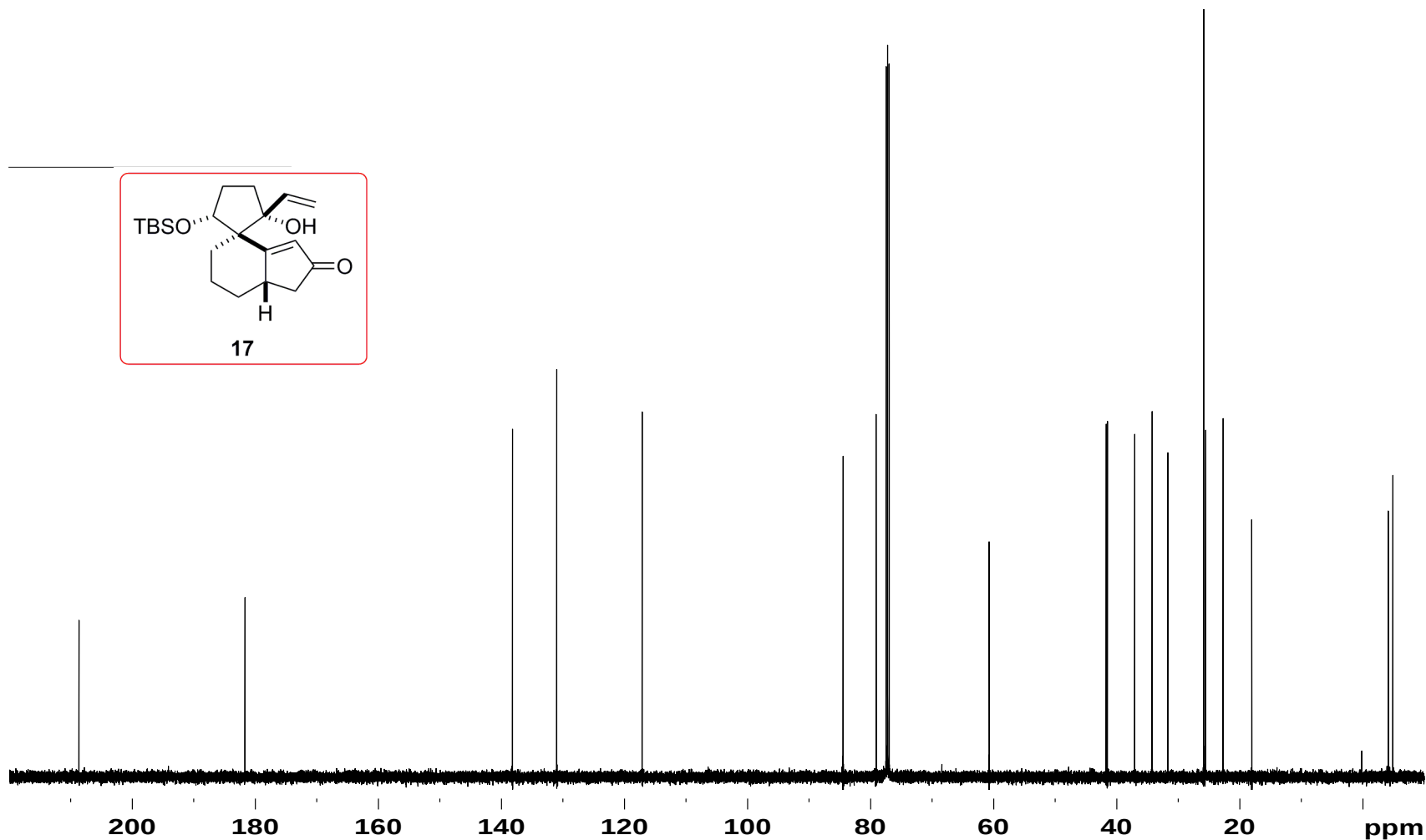
^{13}C NMR (125 MHz, CDCl_3) of (1*R,2*S**,3*S**)-3-(*tert*-butyldimethylsilyl)oxy-2-ethynyl-2-(pent-4-enyl)-1-vinylcyclopentan-1-ol (16)**



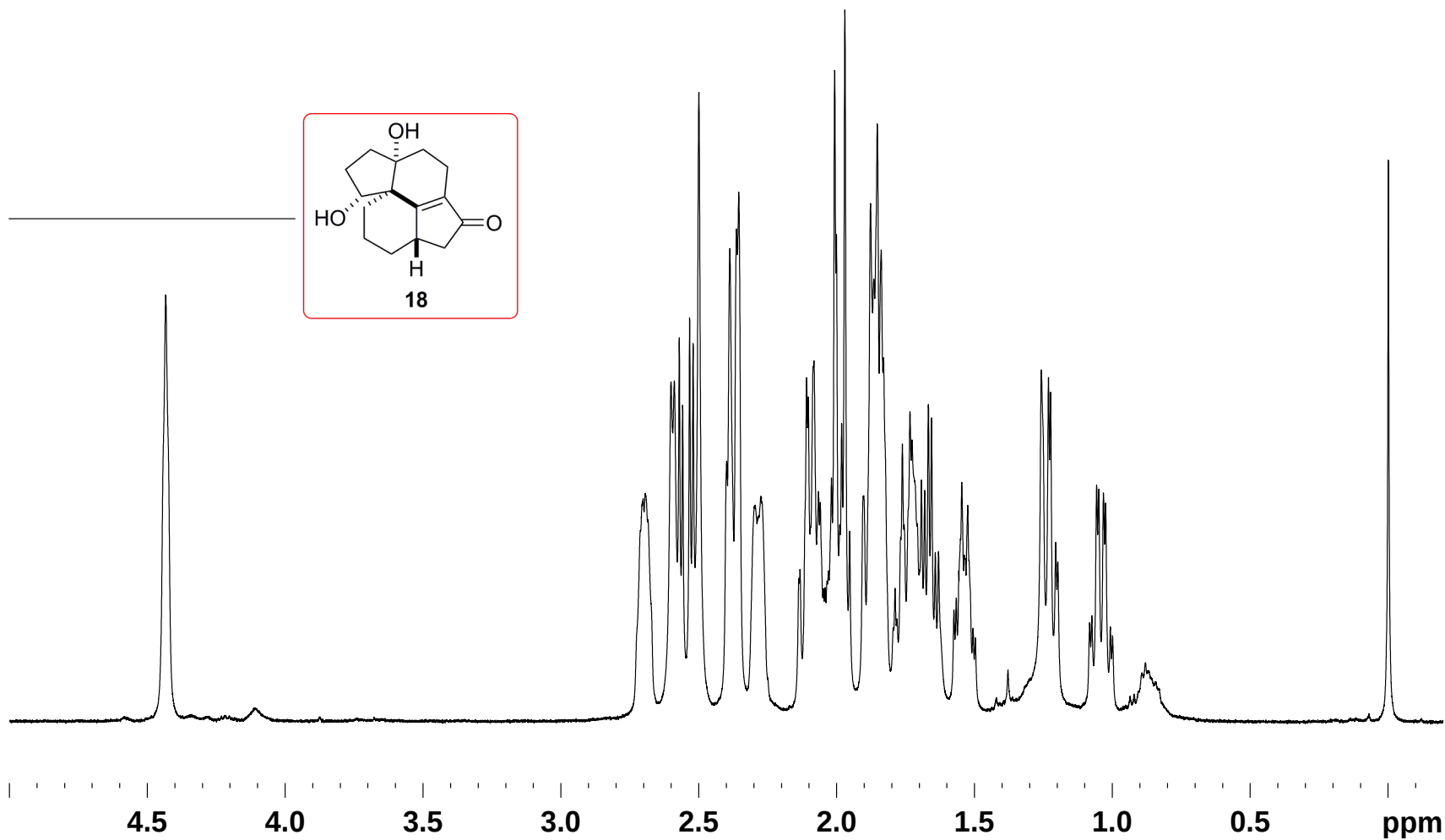
¹H NMR (500 MHz, CDCl₃) of (1*R,2*R**,7*a*'*R**,5*R**)-5-(*tert*-butyldimethylsilyl)oxy-5',6',7',7*a*'-tetrahydro-2-hydroxy-2-vinylspiro[cyclopentane-1,4'-inden]-2'(1'*H*)-one (17)**



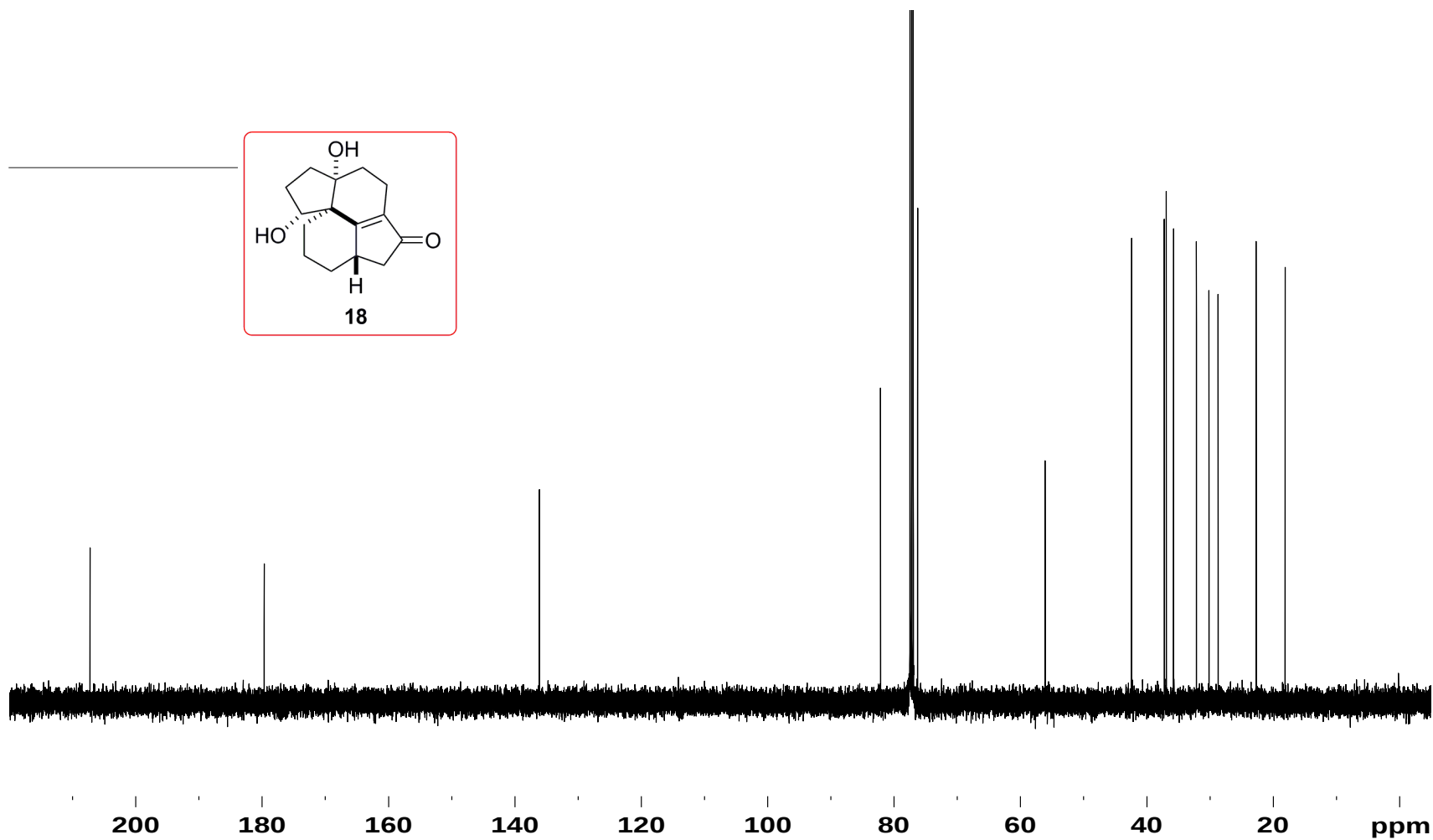
^{13}C NMR (125 MHz, CDCl_3) of (1*R**,2*R**,7*a*'*R**,5*R**)-5-(*tert*-butyldimethylsilyl)oxy-5',6',7',7*a*'-tetrahydro-2-hydroxy-2-vinylspiro[cyclopentane-1,4'-inden]-2'(1'*H*)-one (17)



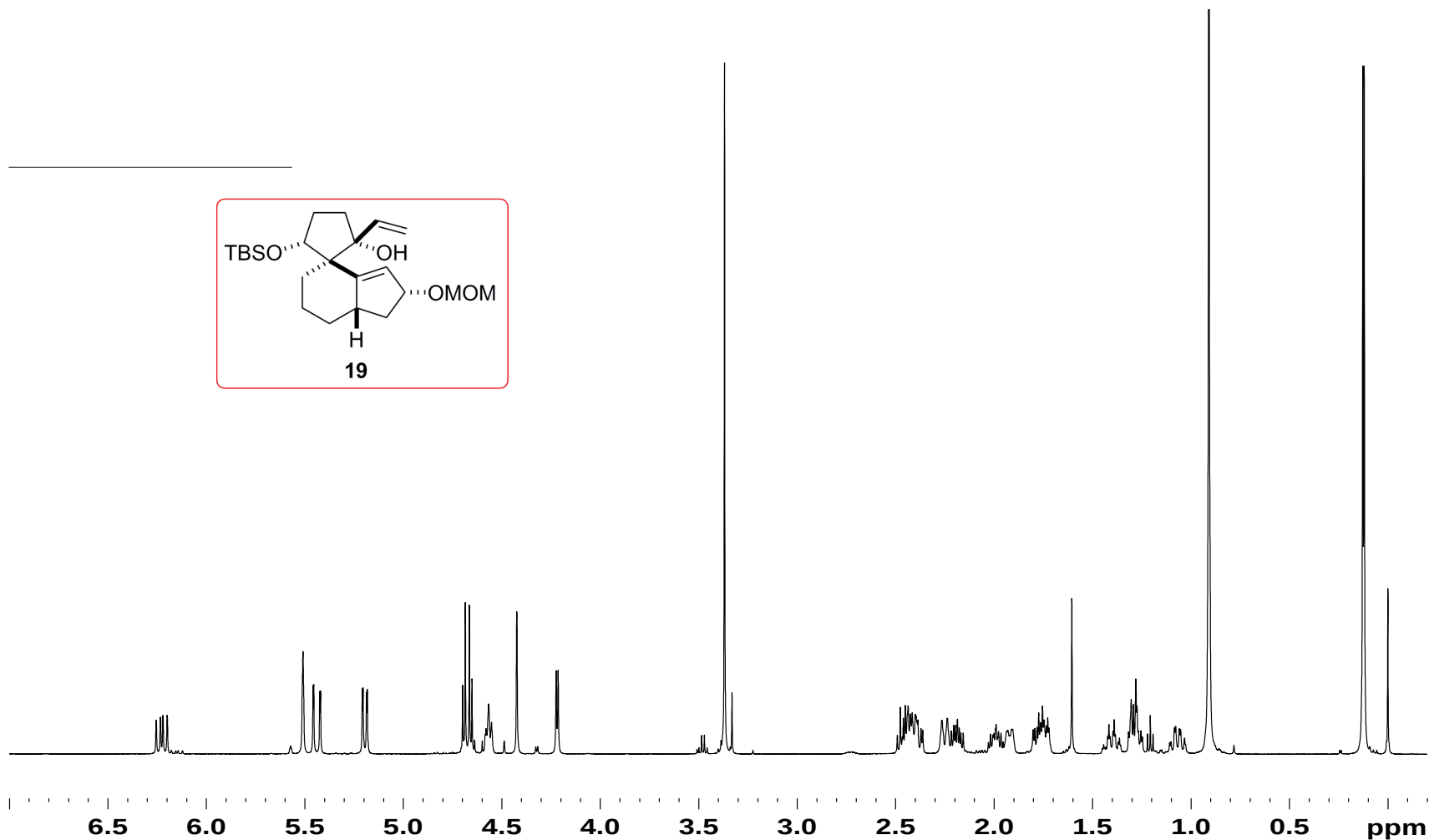
¹H NMR (500 MHz, CDCl₃) of (3*aR,7*aR**,10*S**,10*aR**)-2,3,3*a*,4,6,7,7*a*,8,9,10-decahydro-7*a*,10-dihydroxycyclopenta[*f*]acenaphthalen-5(1*H*)-one (18)**



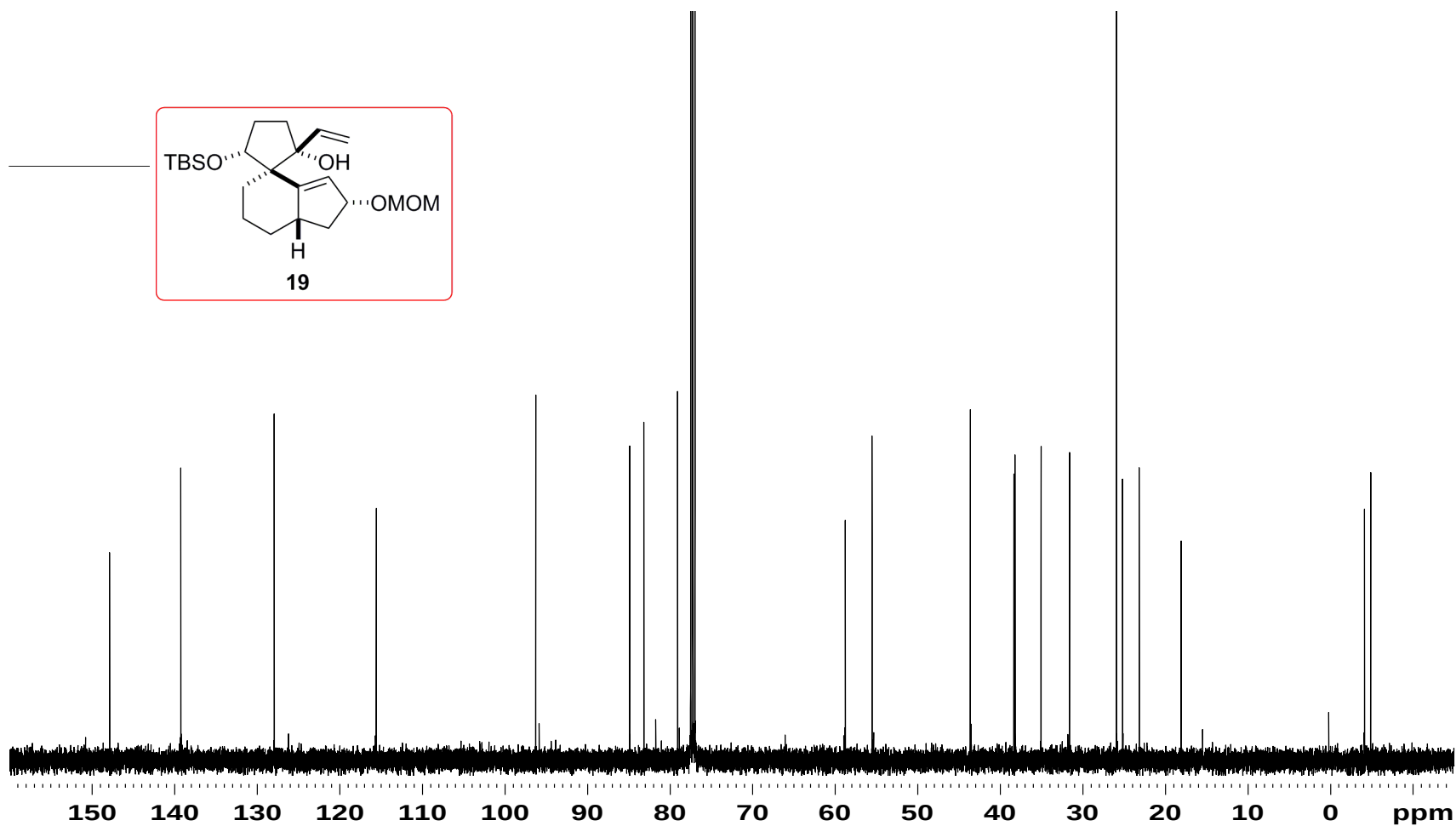
^{13}C NMR (125 MHz, CDCl_3) of (3*aR,7*aR**,10*S**,10*aR**)-2,3,3*a*,4,6,7,7*a*,8,9,10-decahydro-7*a*,10-dihydroxycyclopenta[*f*]acenaphthalen-5(1*H*)-one (18)**



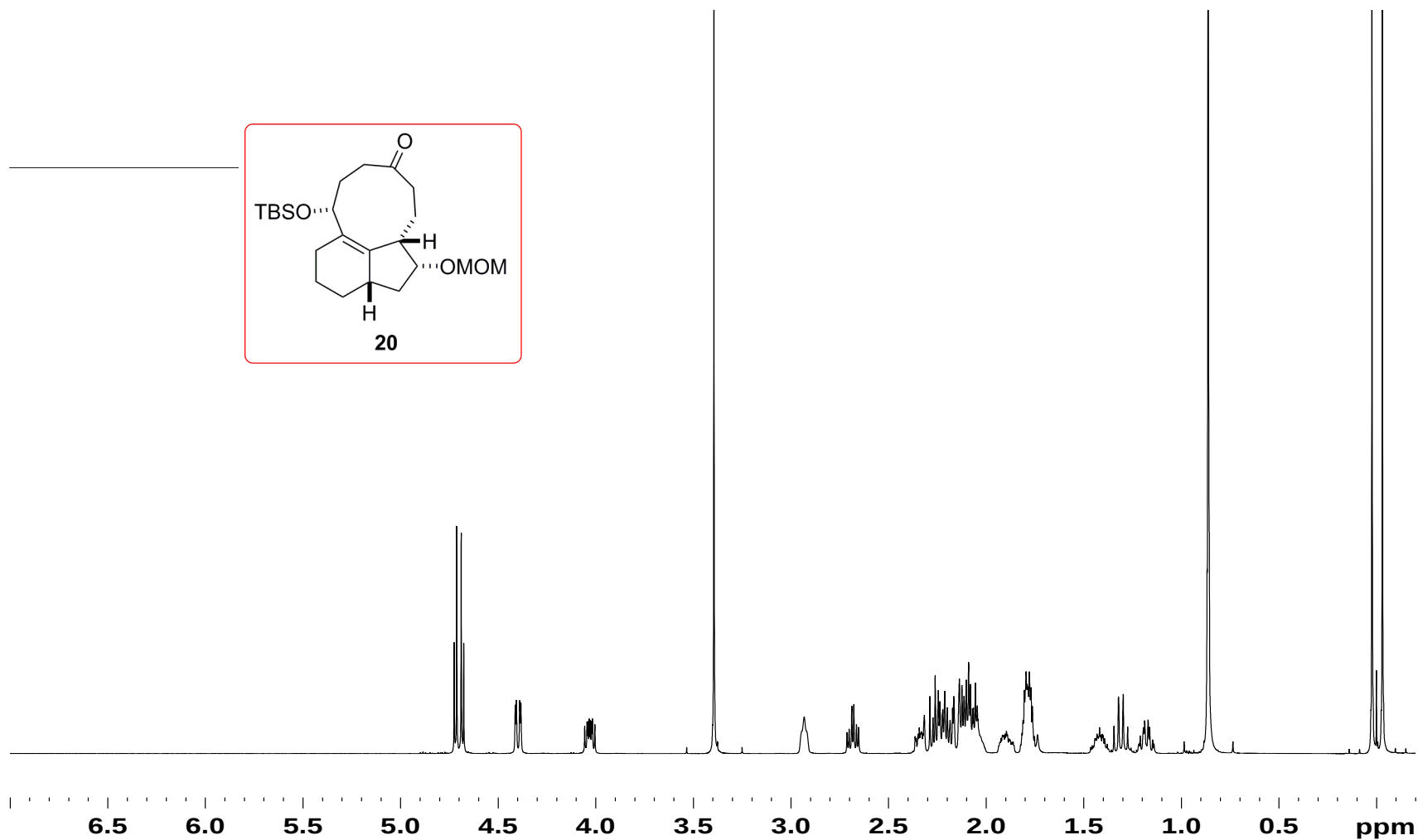
^1H NMR (500 MHz, CDCl_3) of (1*R,2*R**,7*a*'*R**,5*R**)-5-(*tert*-butyldimethylsilyl)oxy-2-hydroxy-2-vinyl-5',6',7',7*a*'-tetrahydro-2'-(methoxymethoxy)spiro[cyclopentane-1,4'-inden]-2'-ol (19)**



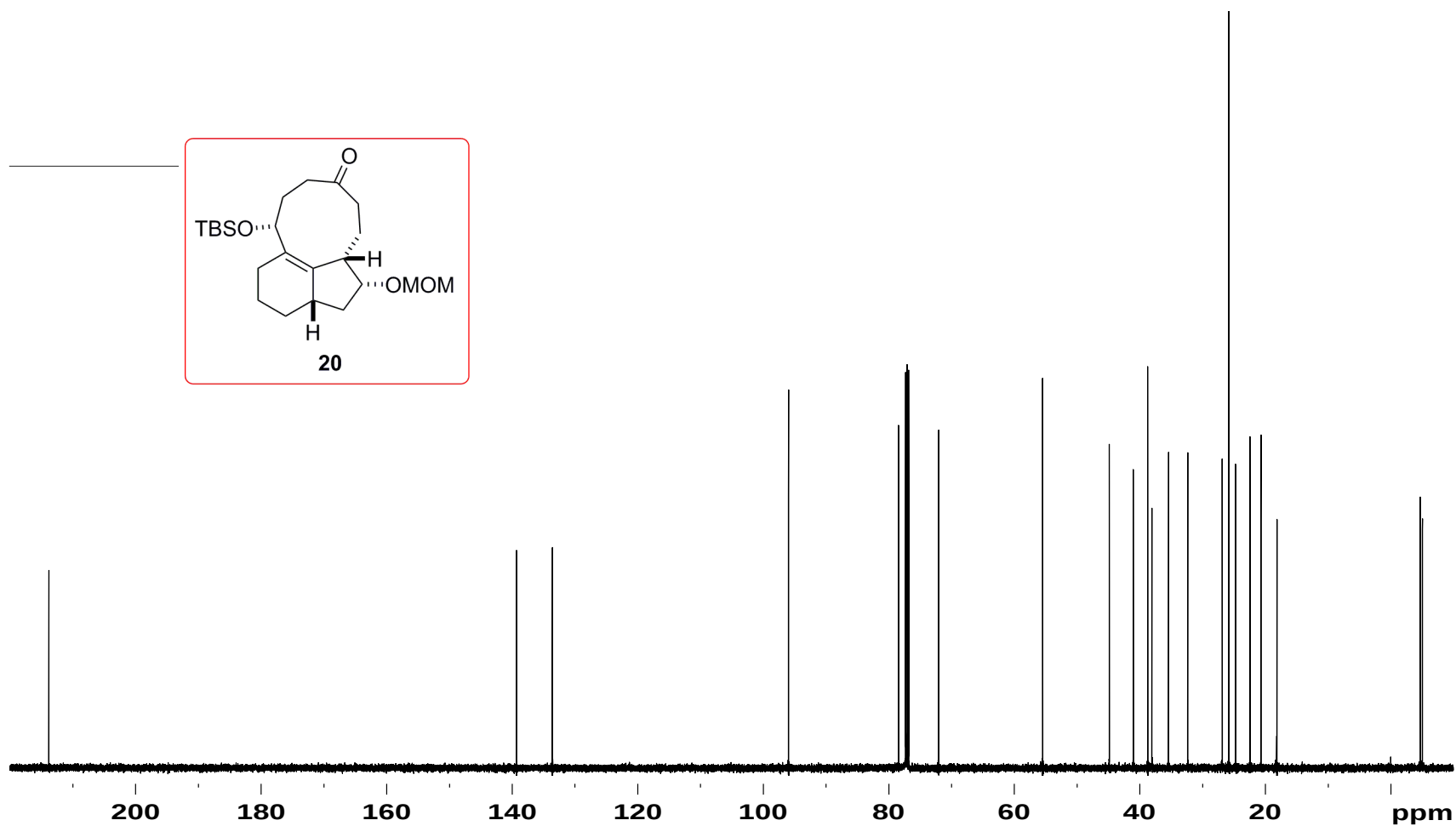
^{13}C NMR (125 MHz, CDCl_3) of (1*R**,2*R**,7*a*'*R**,5*R**)-5-(*tert*-butyldimethylsilyl)oxy-2-hydroxy-2-vinyl-5',6',7',7*a*'-tetrahydro-2'-(methoxymethoxy)spiro[cyclopentane-1,4'-inden]-2'-ol (19)



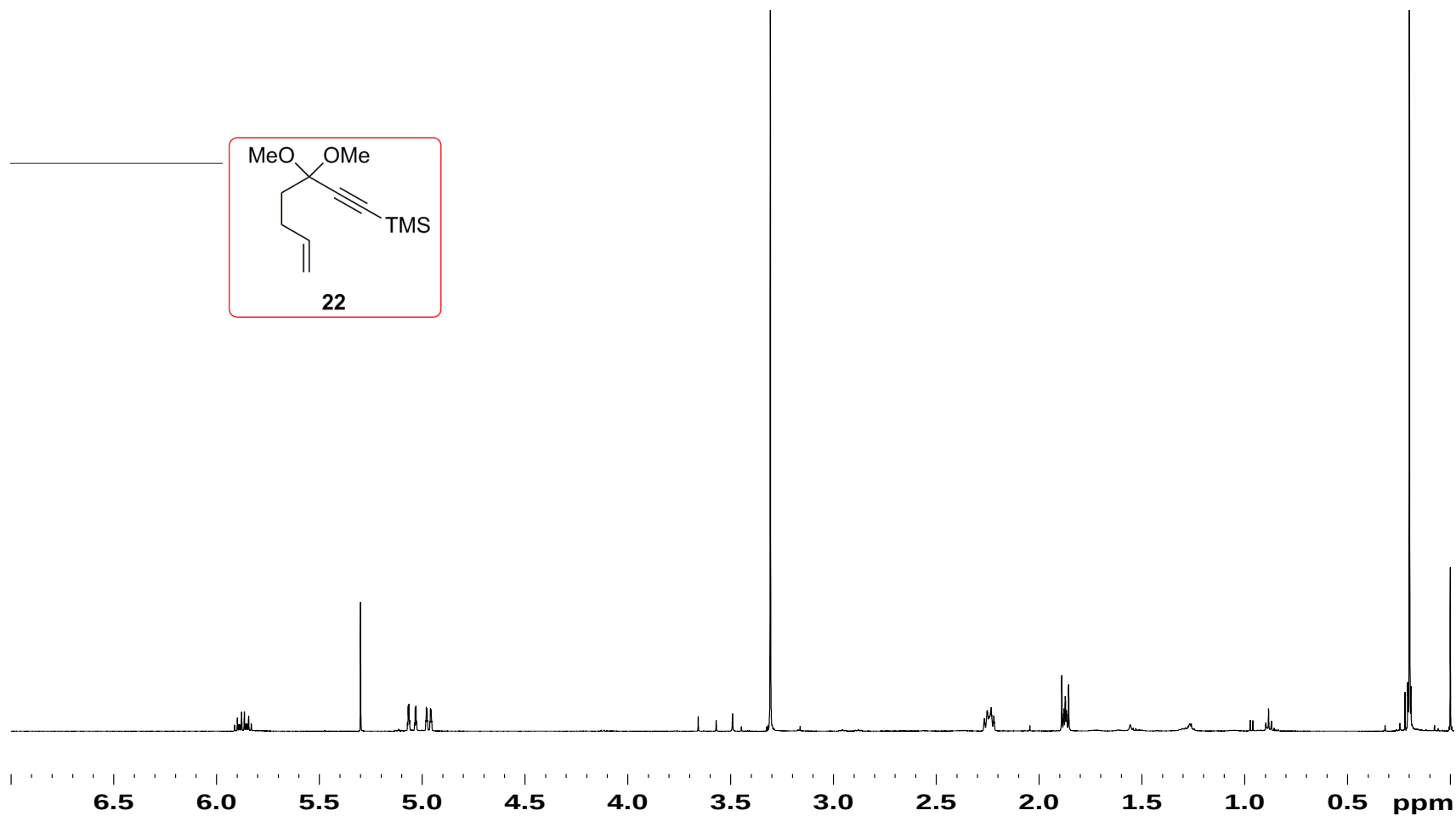
^1H NMR (500 MHz, CDCl_3) of (1*R,2*aS**,6*R**,11*aS**)-6-(*tert*-butyldimethylsilyl)oxy-2*a*,3,4,5,6,7,8,10,11,11*a*-decahydro-1-(methoxymethoxy)-1*H*-cyclonona[*cd*]inden-9(2*H*)-one (20)**



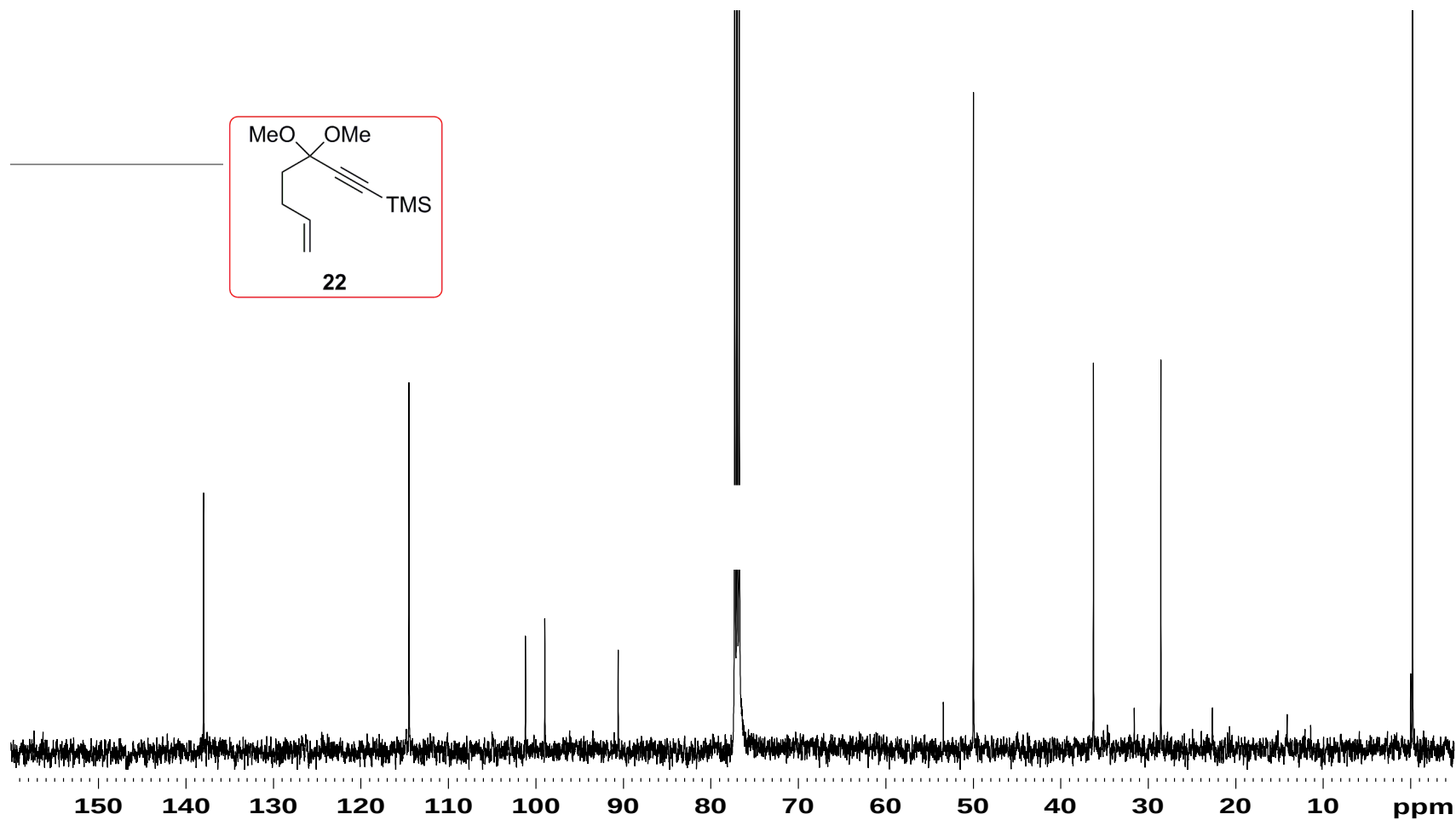
^{13}C NMR (125 MHz, CDCl_3) of (1*R,2*aS**,6*R**,11*aS**)-6-(*tert*-butyldimethylsilyl)oxy-2*a*,3,4,5,6,7,8,10,11,11*a*-decahydro-1-(methoxymethoxy)-1*H*-cyclonona[*cd*]inden-9(2*H*)-one (20)**



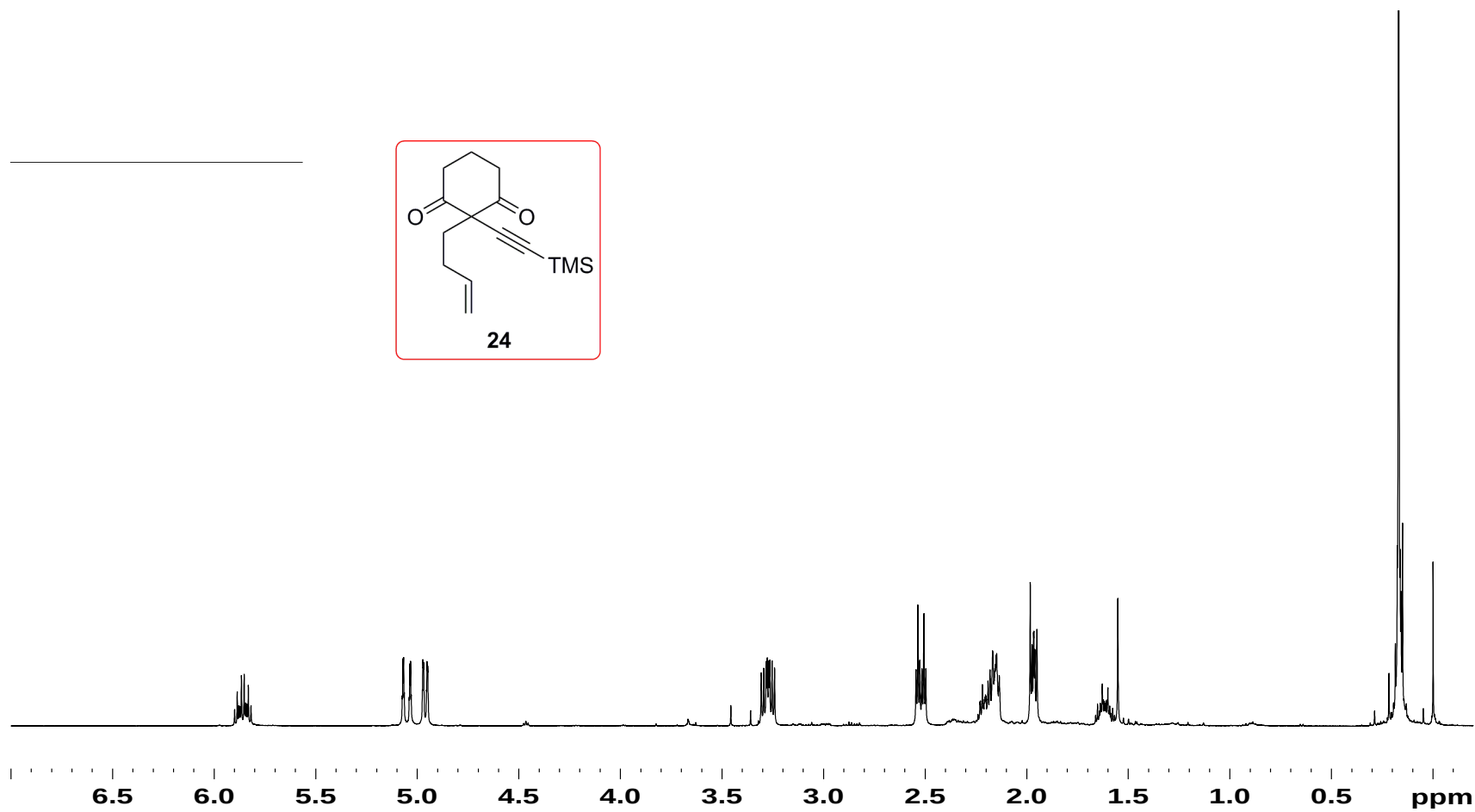
^1H NMR (500 MHz, CDCl_3) of 3,3-dimethoxy-1-(trimethylsilyl)hept-6-en-1-yne (22)



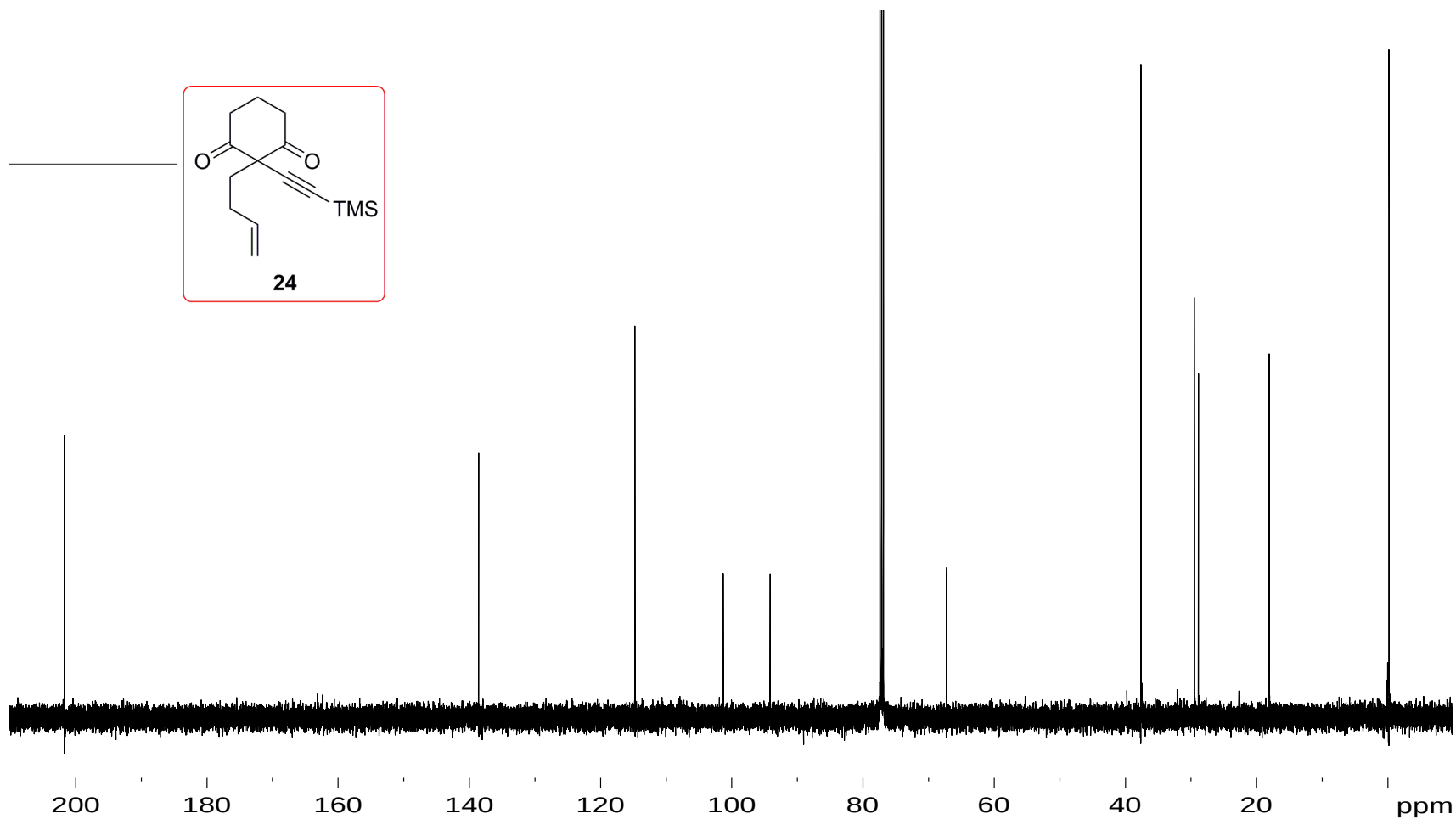
^{13}C NMR (125 MHz, CDCl_3) of 3,3-dimethoxy-1-(trimethylsilyl)hept-6-en-1-yne (22)



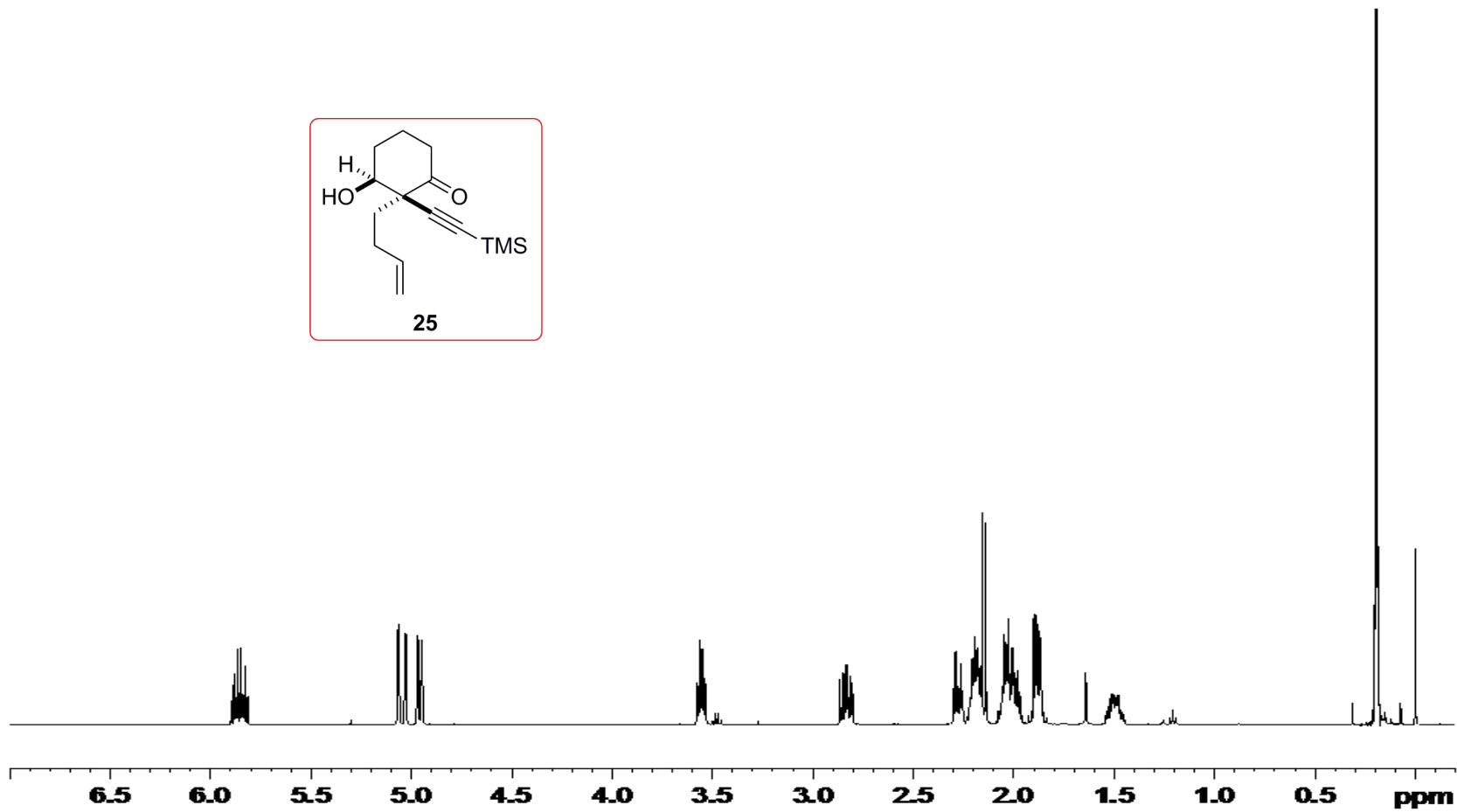
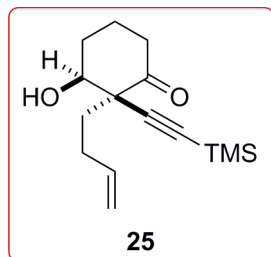
^1H NMR (500 MHz, CDCl_3) of 2-(but-3-enyl)-2-((trimethylsilyl)ethynyl)cyclohexane-1,3-dione (24)



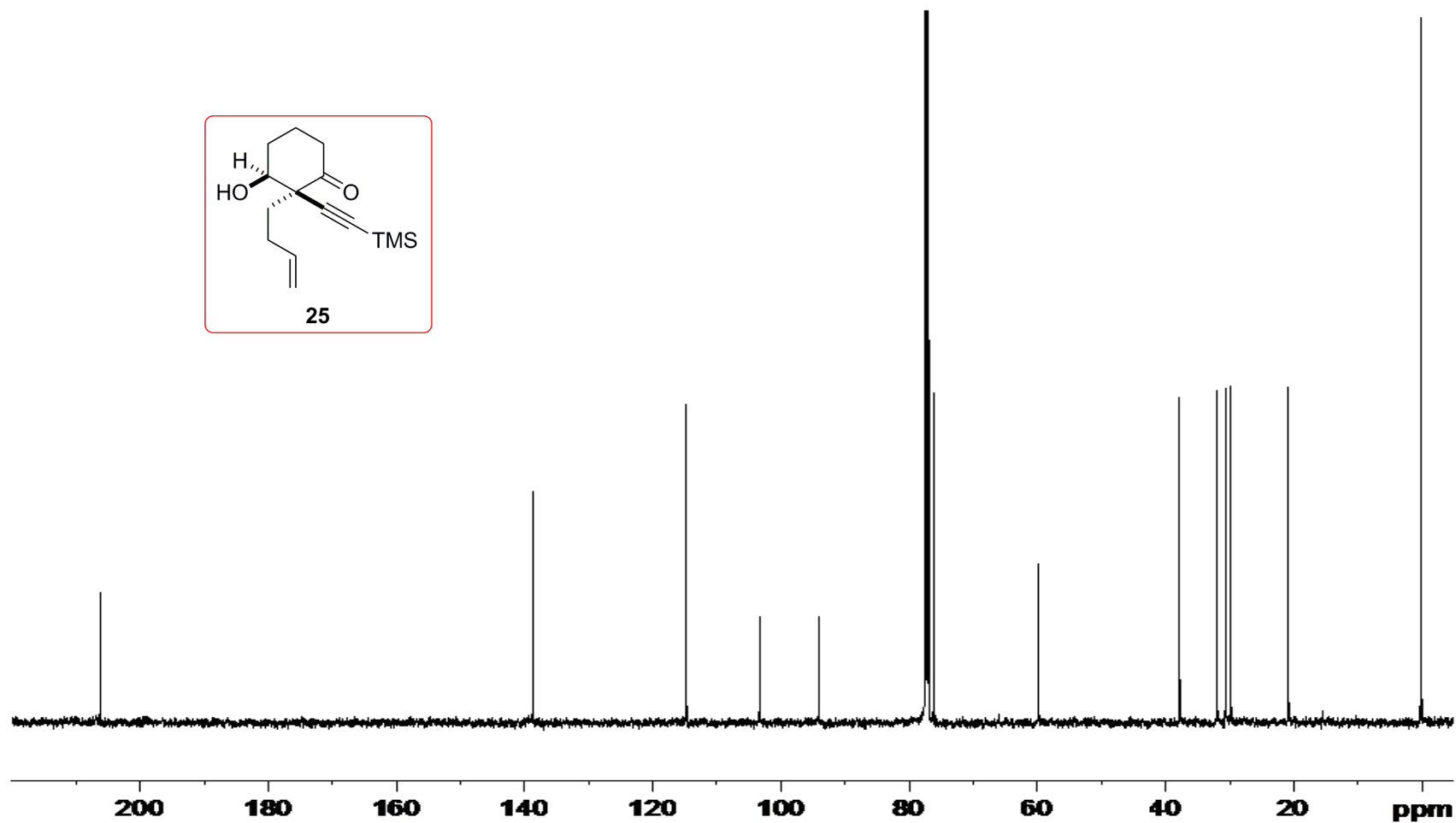
^{13}C NMR (125 MHz, CDCl_3) of 2-(but-3-enyl)-2-((trimethylsilyl)ethynyl)cyclohexane-1,3-dione (24)



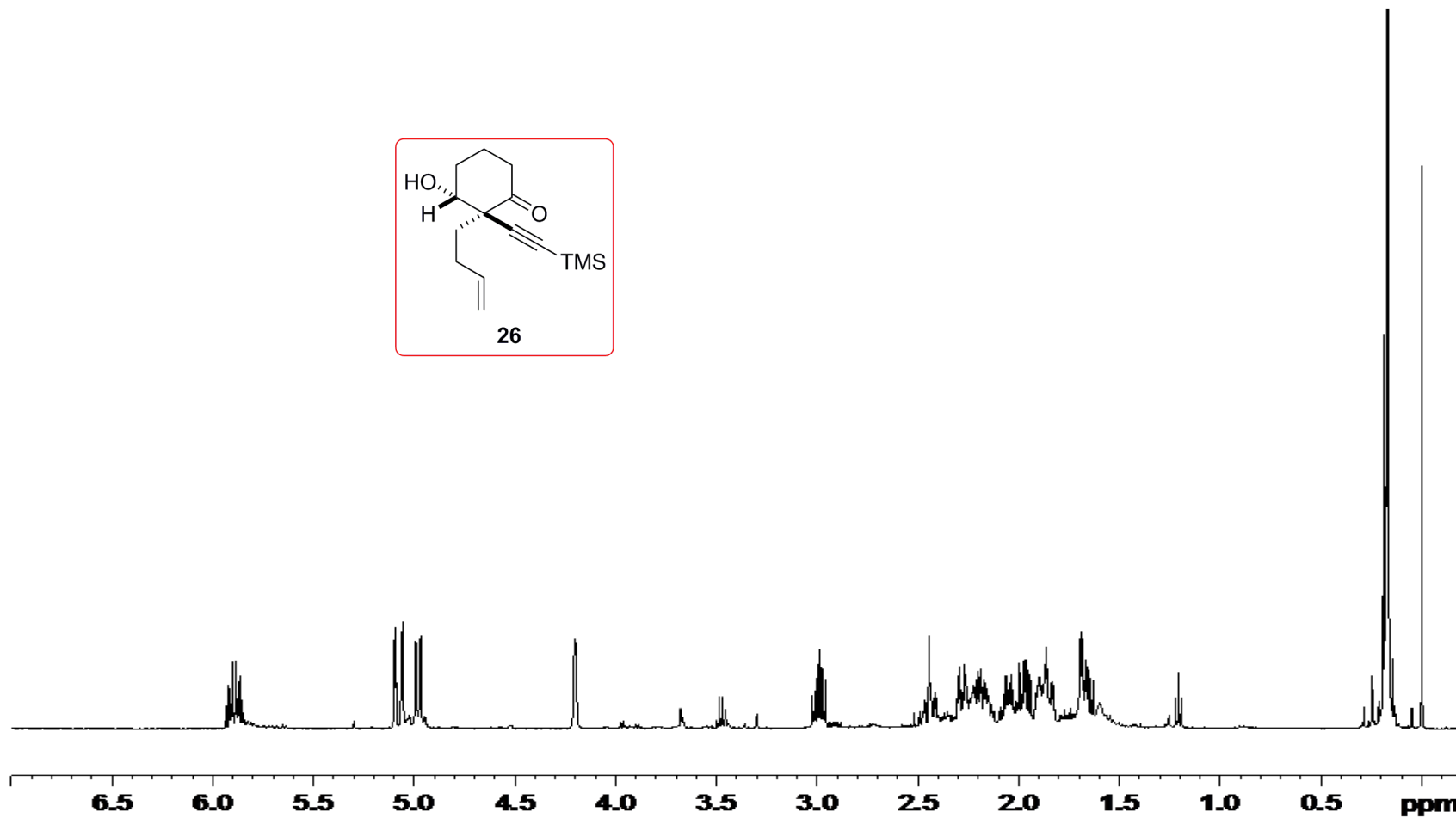
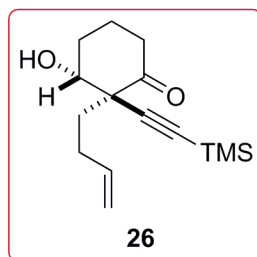
^1H NMR (500 MHz, CDCl_3) of (2*R,3*R**)-2-(but-3-enyl)-3-hydroxy-2-((trimethylsilyl)ethynyl)cyclohexanone (25)**



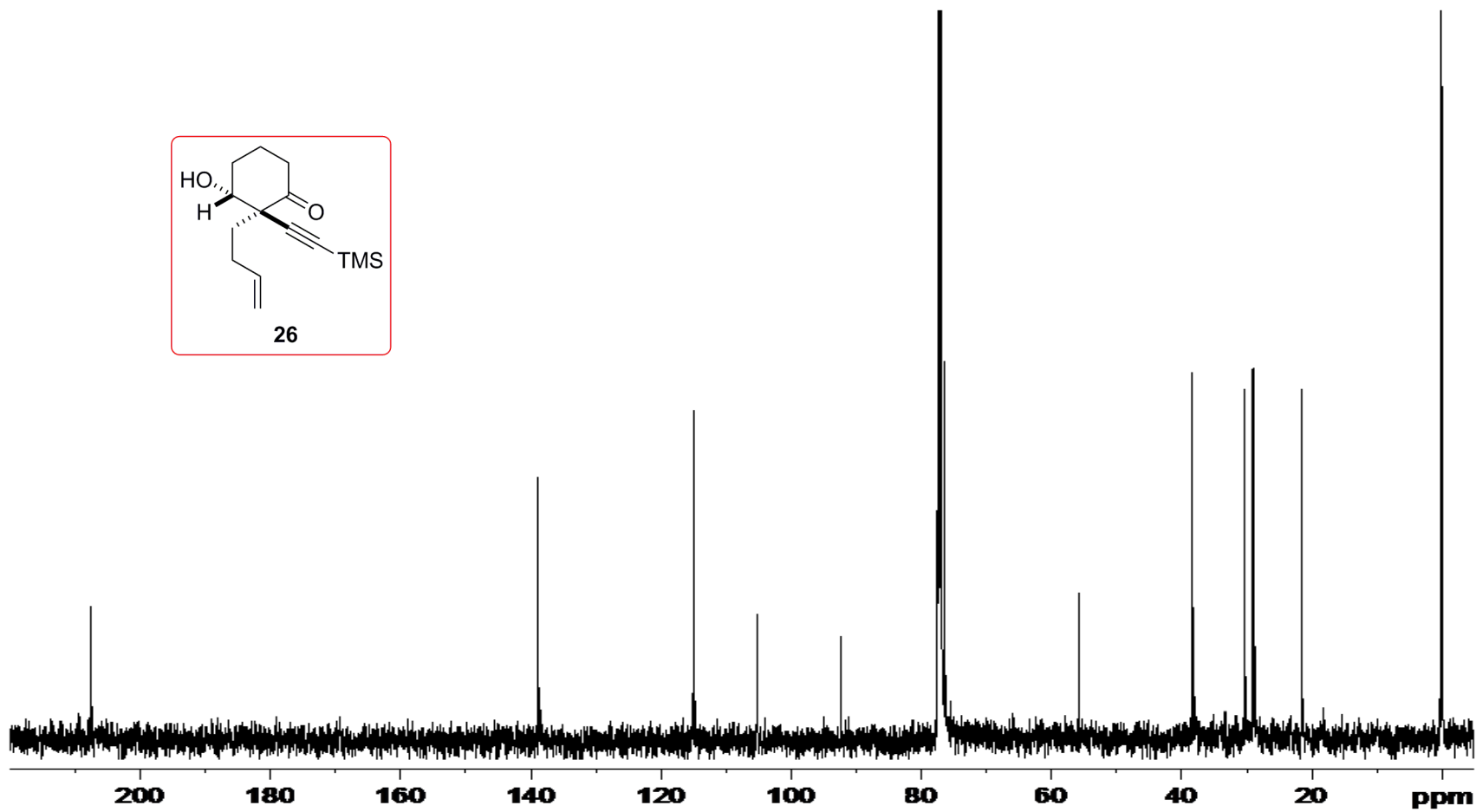
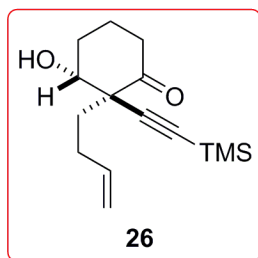
^{13}C NMR (125 MHz, CDCl_3) of (2*R**,3*R**)-2-(but-3-enyl)-3-hydroxy-2-((trimethylsilyl)ethynyl)cyclohexanone (25)



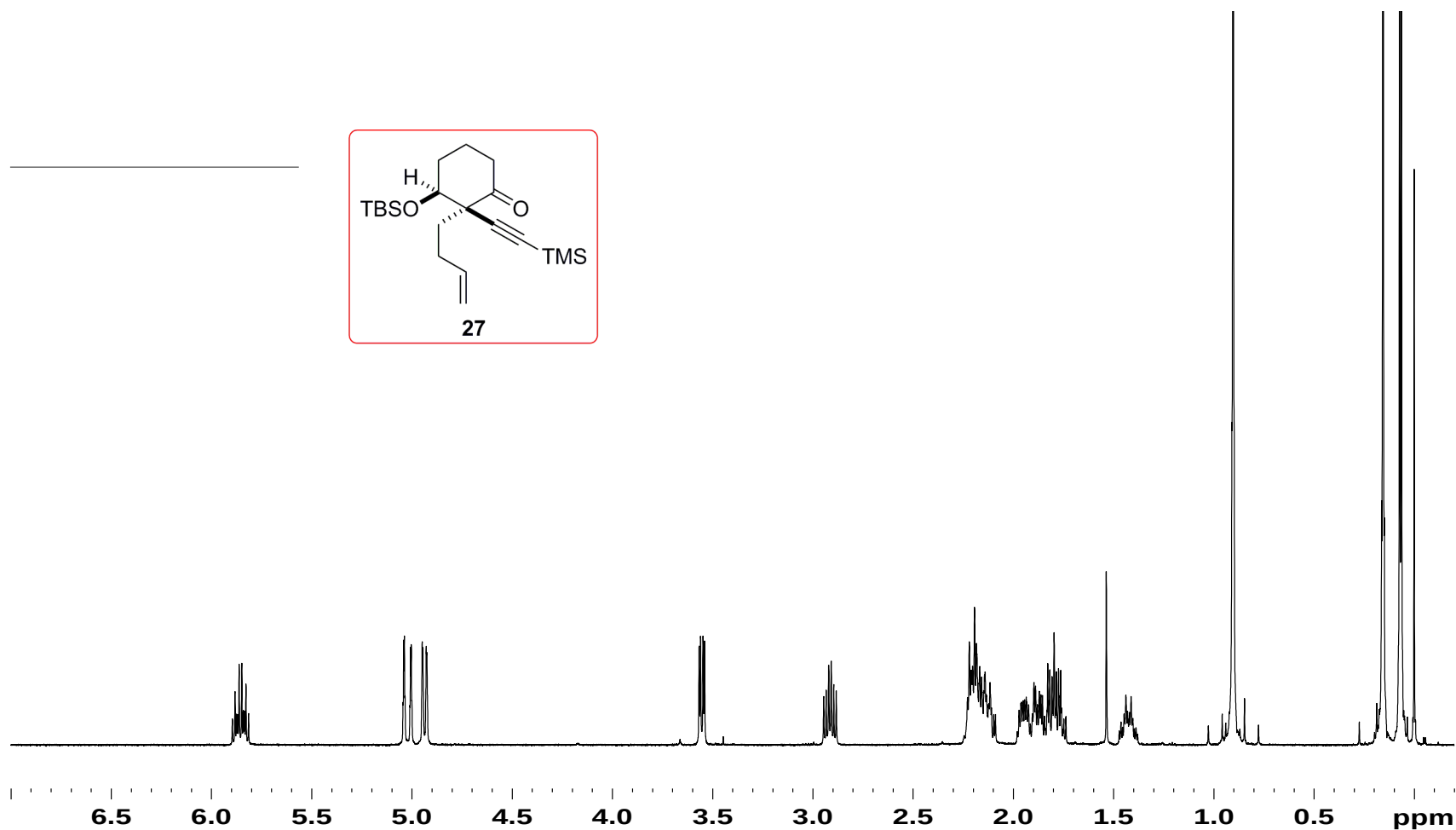
¹H NMR (500 MHz, CDCl₃) of (2*R,3*S**)-2-(but-3-enyl)-3-hydroxy-2-((trimethylsilyl)ethynyl)cyclohexanone (26)**



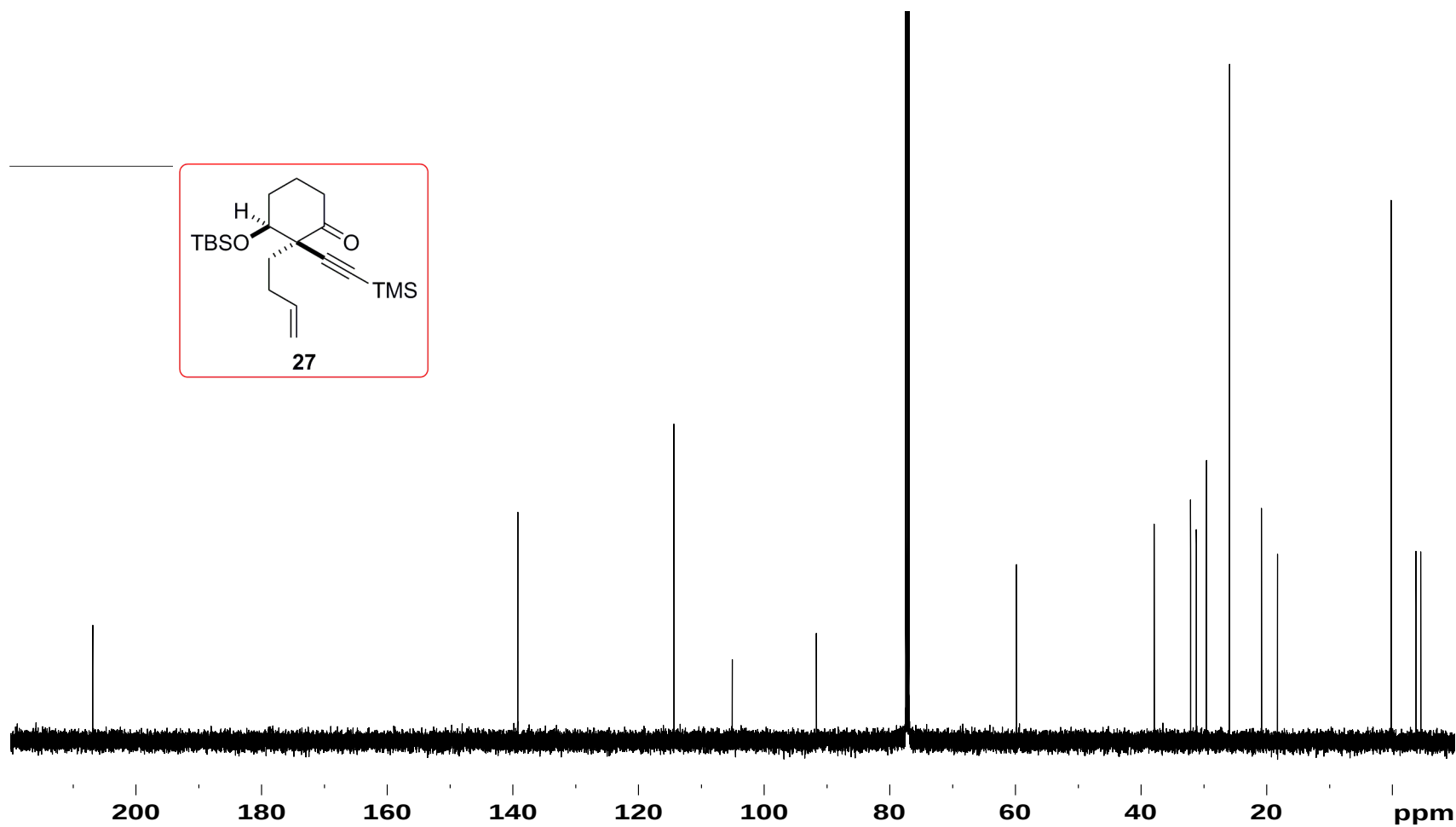
^{13}C NMR (125 MHz, CDCl_3) of (2*R**,3*S**)-2-(but-3-enyl)-3-hydroxy-2-((trimethylsilyl)ethynyl)cyclohexanone (26)



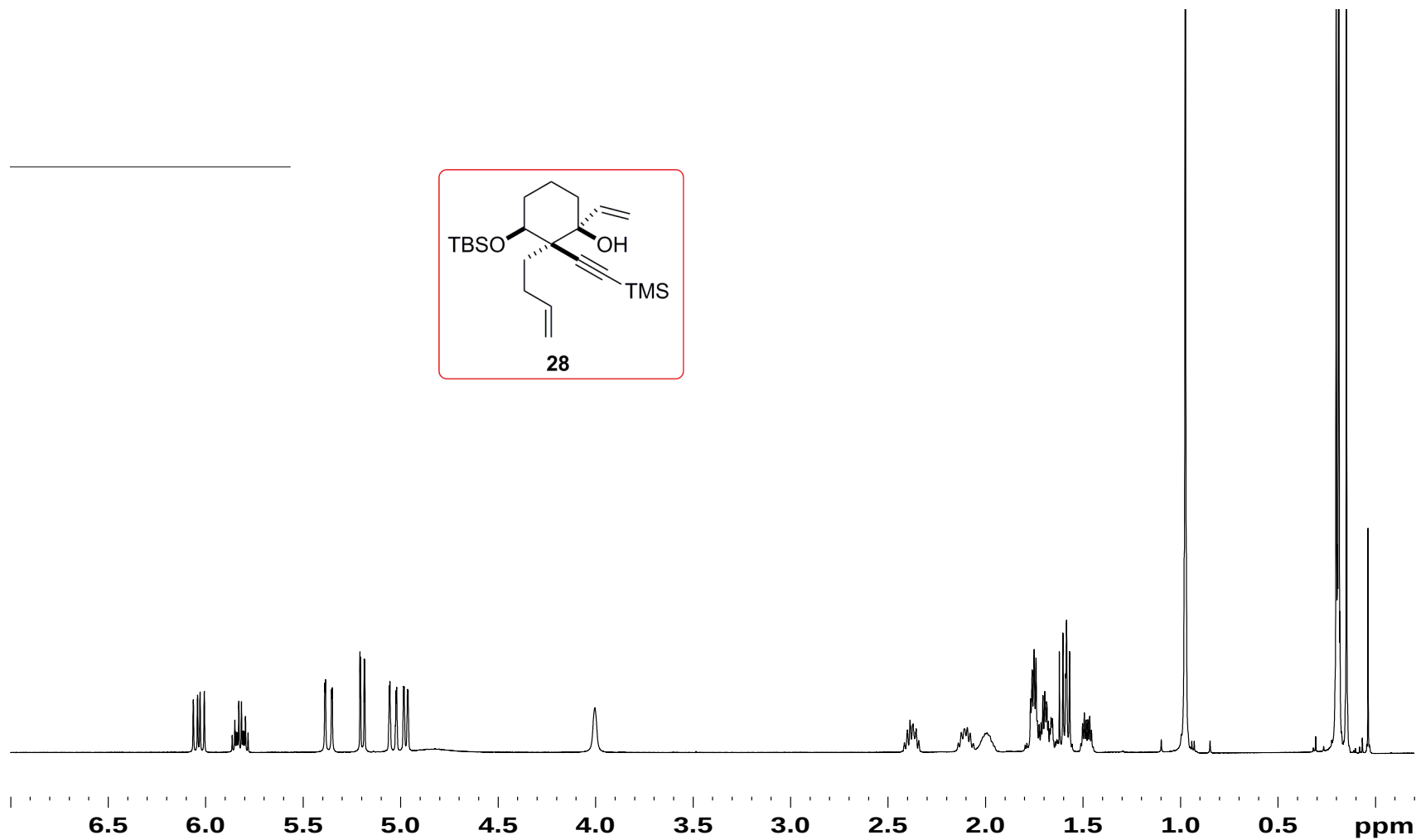
^1H NMR (500 MHz, CDCl_3) of (2*R,3*R**)-2-(but-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2-((trimethylsilyl)ethynyl)cyclohexanone (27)**



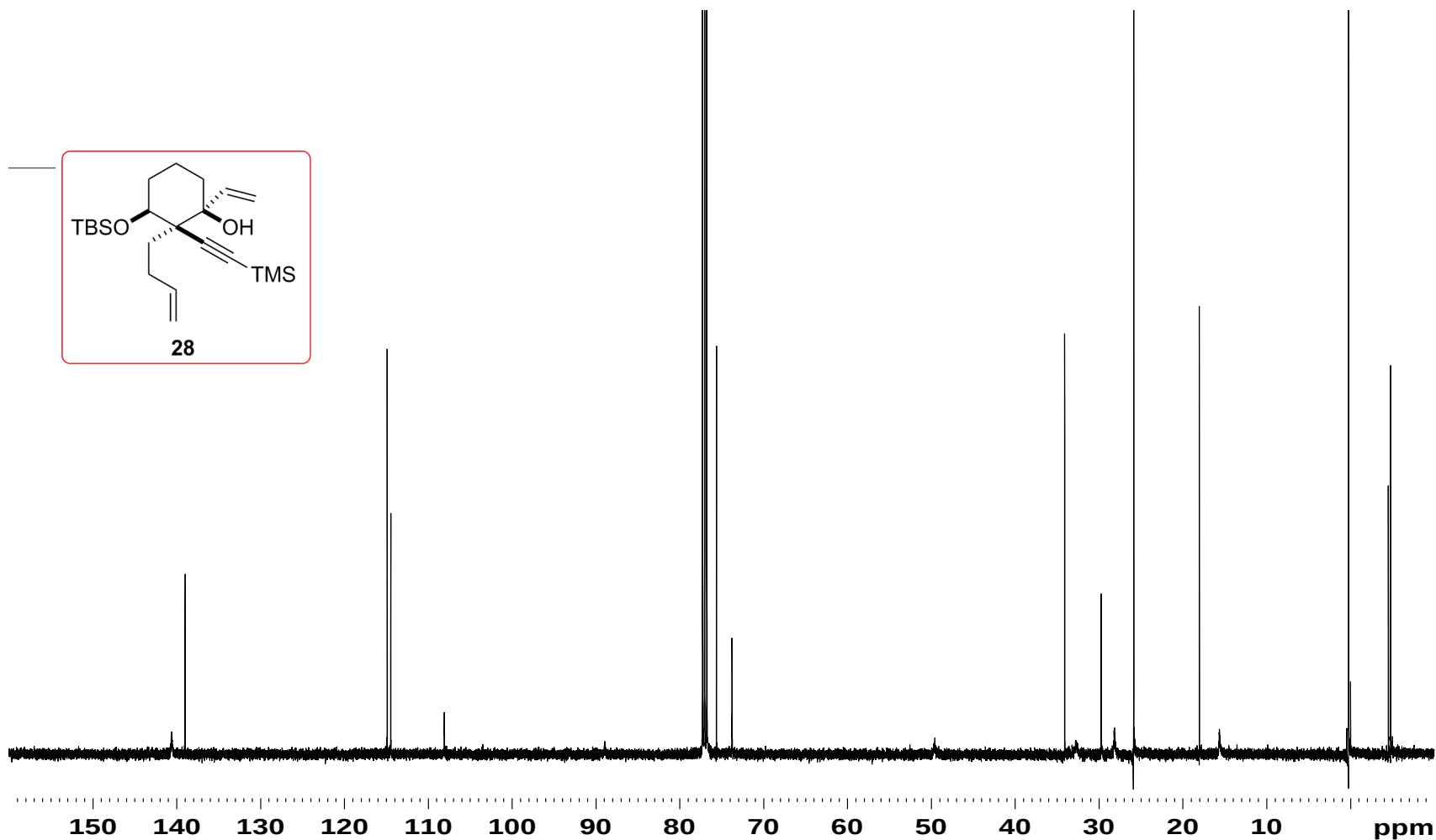
^{13}C NMR (125 MHz, CDCl_3) of (2*R,3*R**)-2-(but-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2-((trimethylsilyl)ethynyl)cyclohexanone (27)**



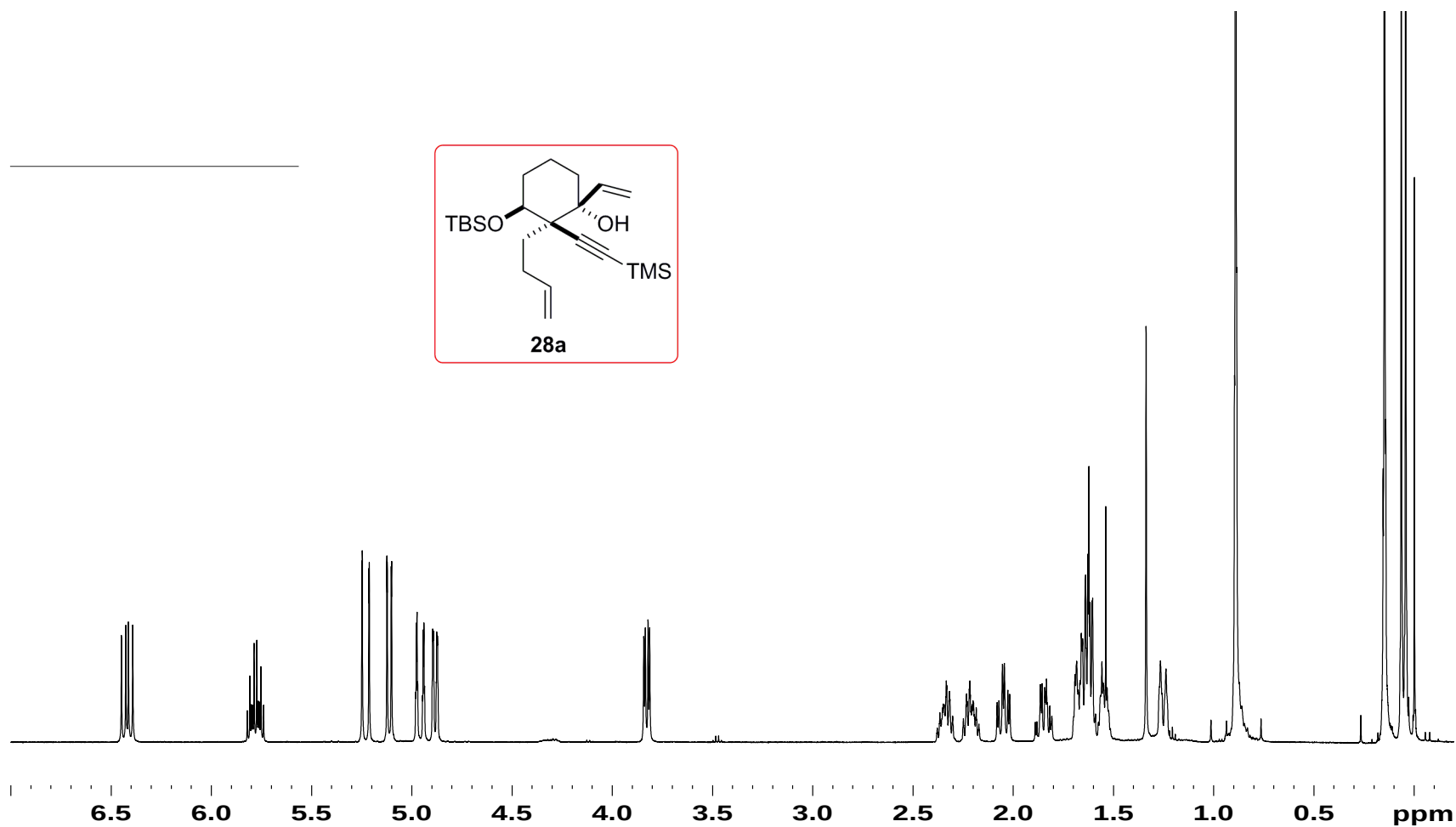
^1H NMR (500 MHz, CDCl_3) of (1*R,2*R**,3*R**)-2-(but-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2-((trimethylsilyl)ethynyl)-1-vinylcyclohexanol (28)**



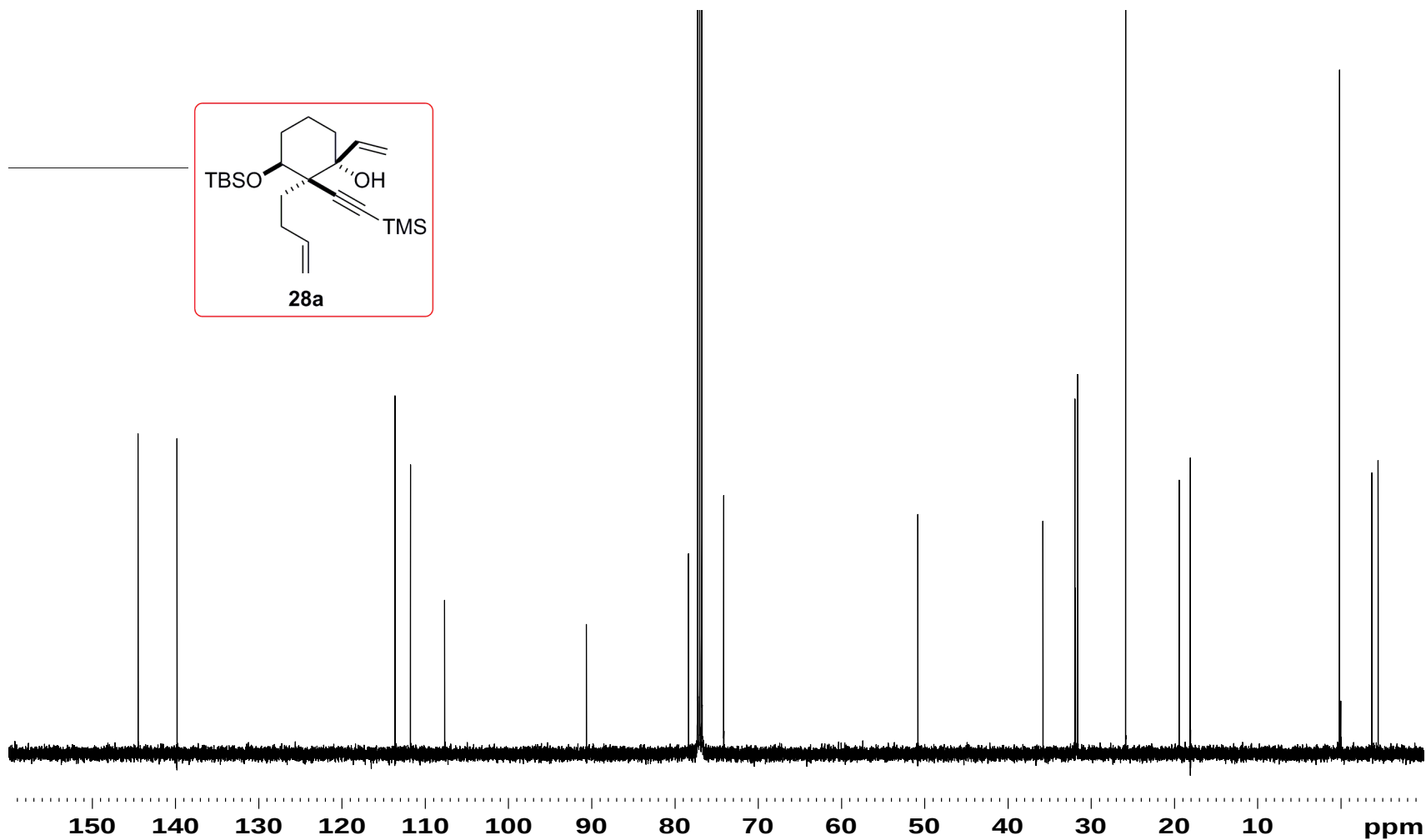
^{13}C NMR (125 MHz, CDCl_3) of (1*R,2*R**,3*R**)-2-(but-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2-((trimethylsilyl)ethynyl)-1-vinylcyclohexanol (28)**

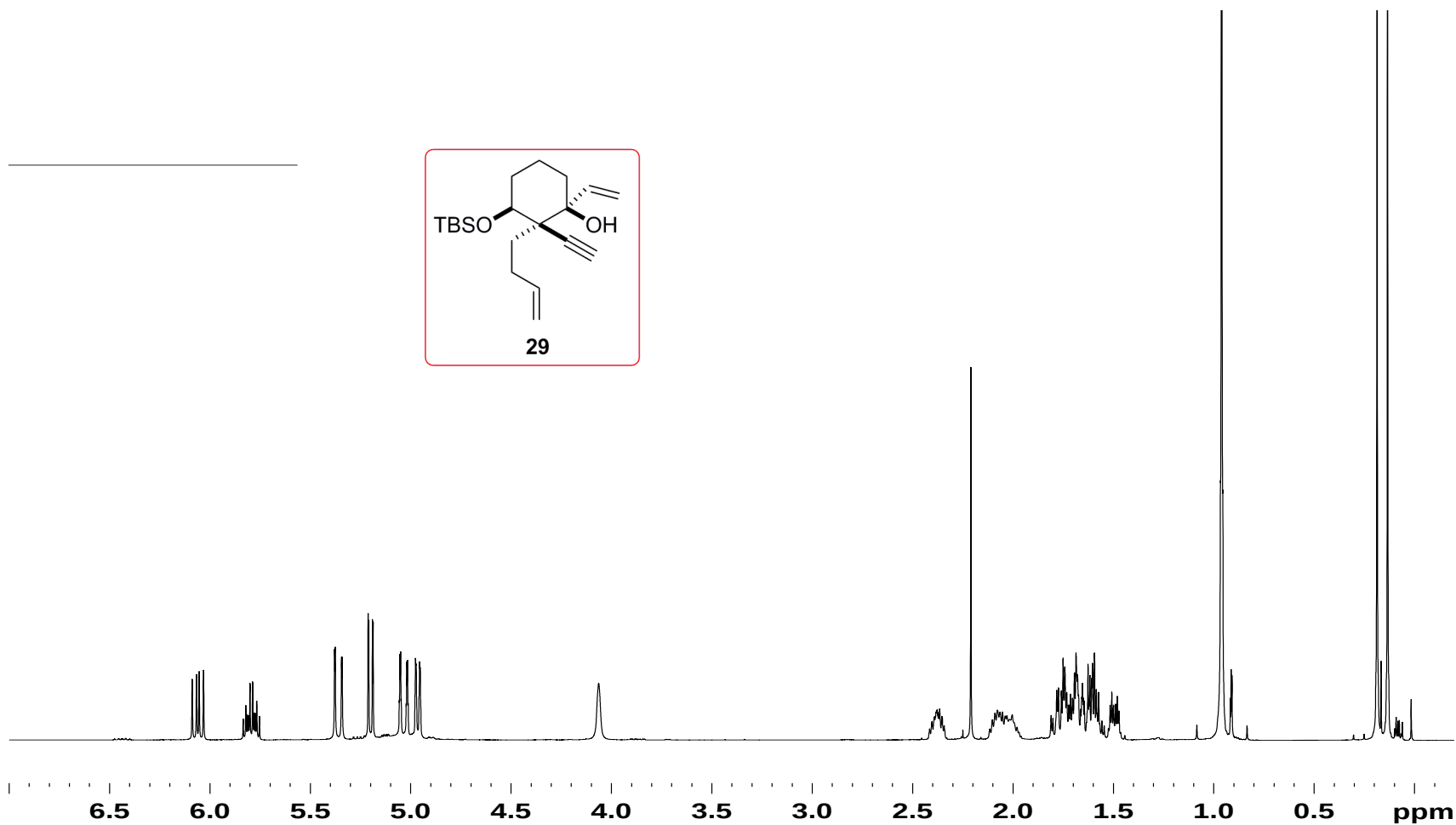


^1H NMR (500 MHz, CDCl_3) of (1*R,2*S**,3*S**)-2-(but-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2-((trimethylsilyl)-ethynyl)-1-vinylcyclohexanol (28a)**

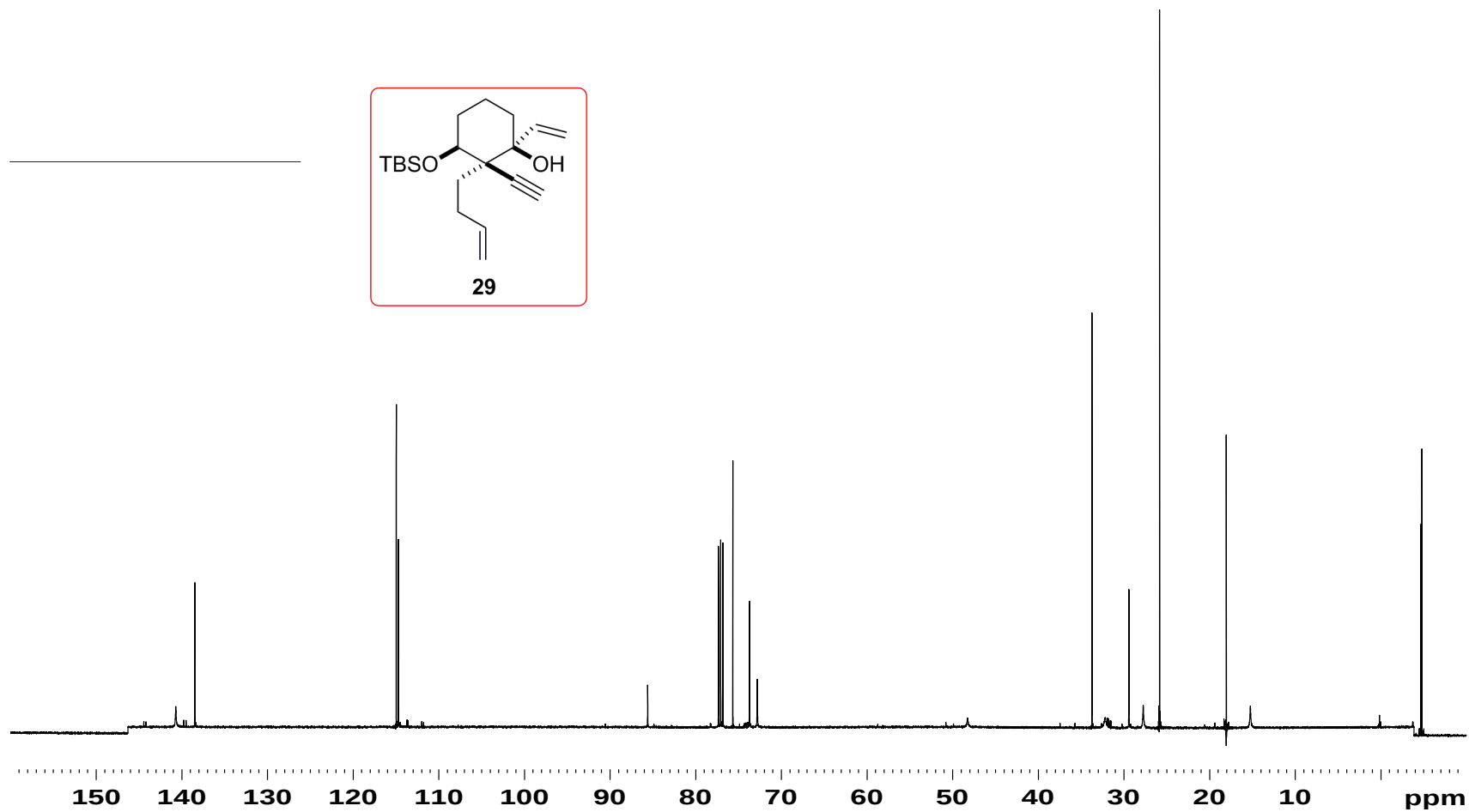


^{13}C NMR (125 MHz, CDCl_3) of (1*R**,2*S**,3*S**)-2-(but-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2-((trimethylsilyl)-ethynyl)-1-vinylcyclohexanol (28a)

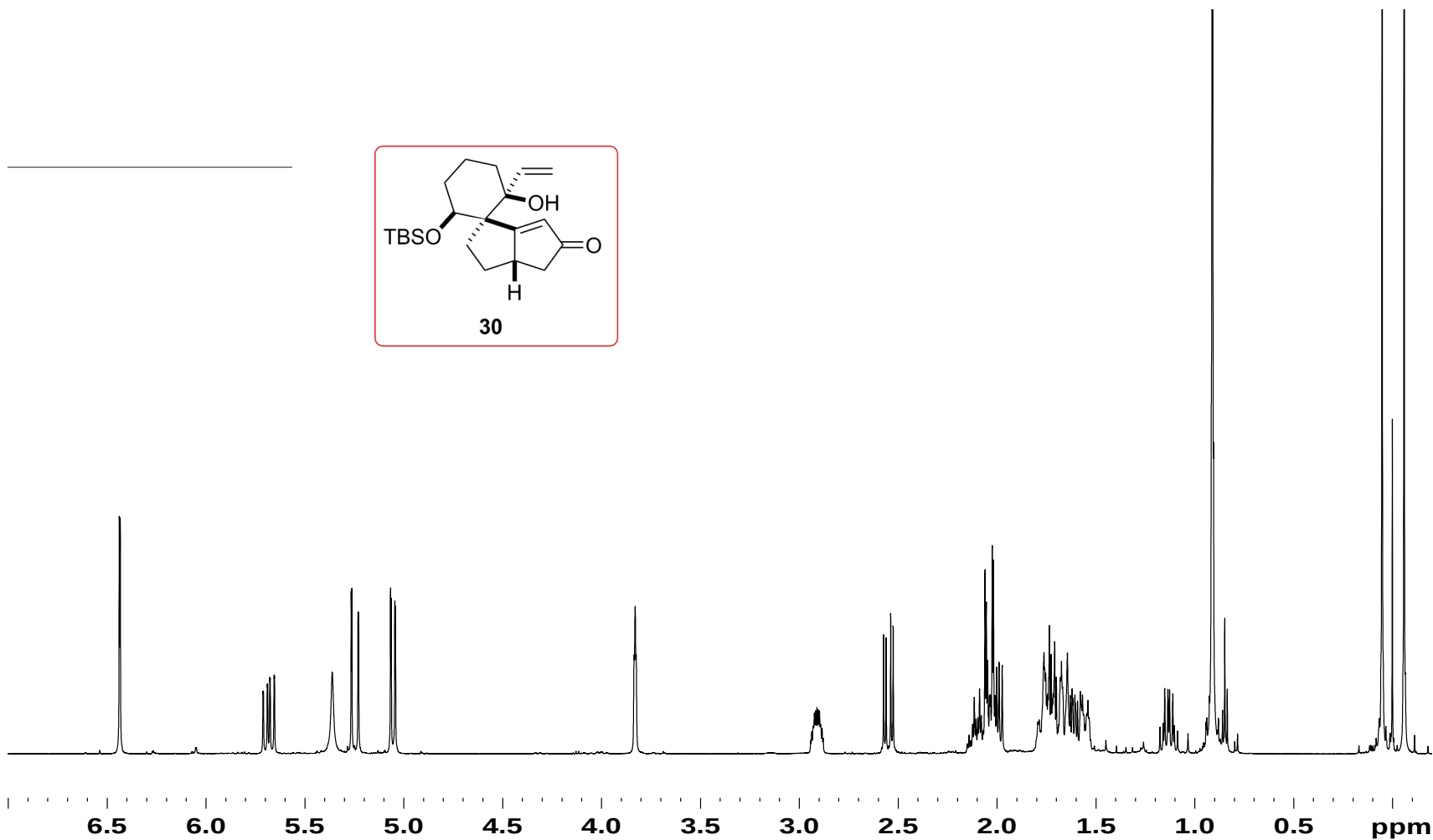


¹H NMR (500 MHz, CDCl₃) of (1*R**,2*R**,3*R**)-2-(but-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2-ethynyl-1-vinylcyclohexanol (29)

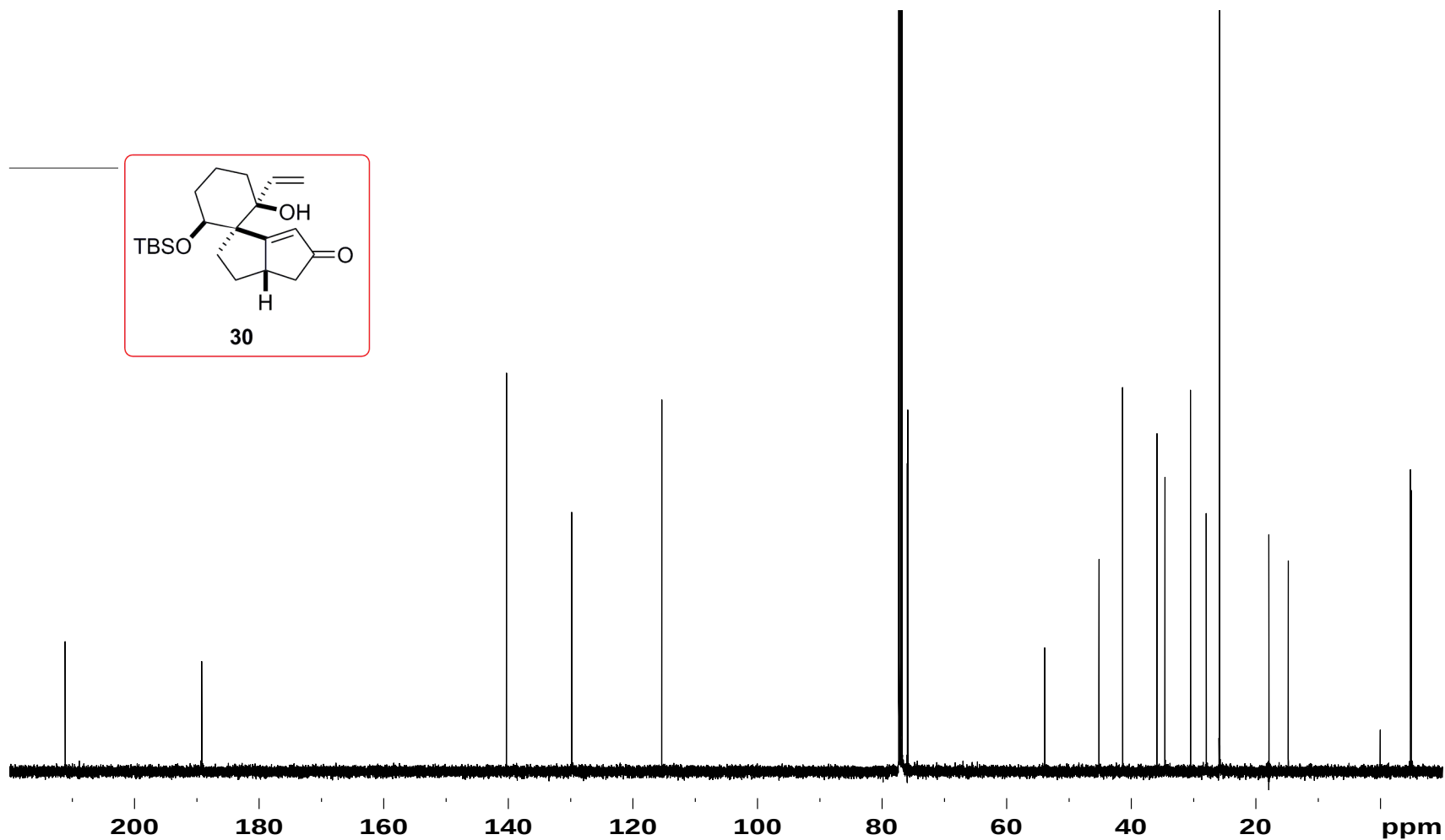
^{13}C NMR (125 MHz, CDCl_3) of (1*R,2*R**,3*R**)-2-(but-3-enyl)-3-(*tert*-butyldimethylsilyl)oxy-2-ethynyl-1-vinylcyclohexanol (29)**



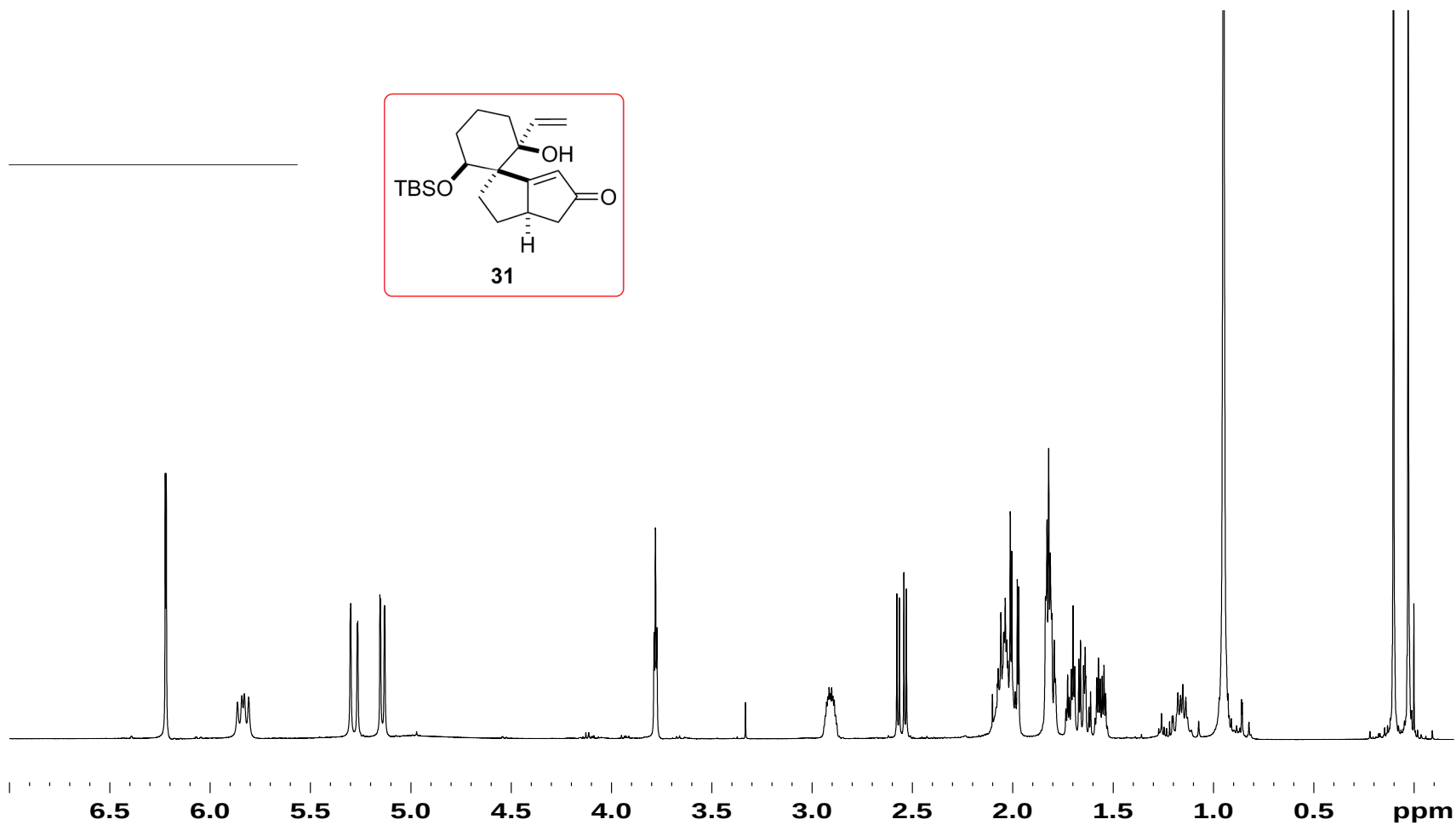
^1H NMR (500 MHz, CDCl_3) of (1*R,2*R**,3*a*'*R**,6*R**)-6-(*tert*-butyldimethylsilyloxy)-2-hydroxy-2-vinyl-3*a*',4'-dihydro-2'*H*-spiro-[cyclohexane-1,1'-pentalen]-5'(3'*H*)-one (30)**



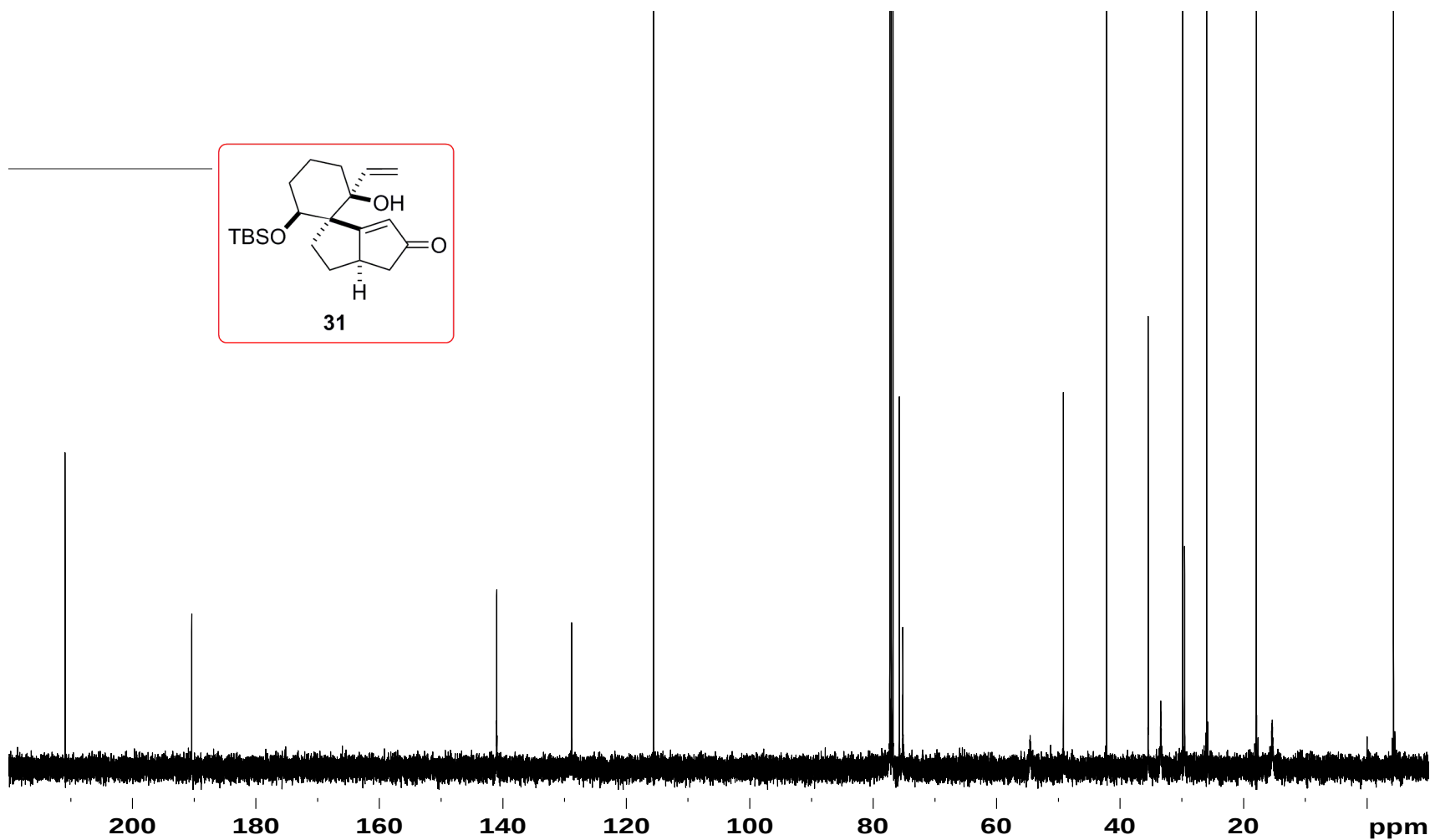
^{13}C NMR (125 MHz, CDCl_3) of (1*R**,2*R**,3*a*'*R**,6*R**)-6-(*tert*-butyldimethylsilyloxy)-2-hydroxy-2-vinyl-3*a*',4'-dihydro-2'*H*-spiro[cyclohexane-1,1'-pentalen]-5'(3'*H*)-one (30)



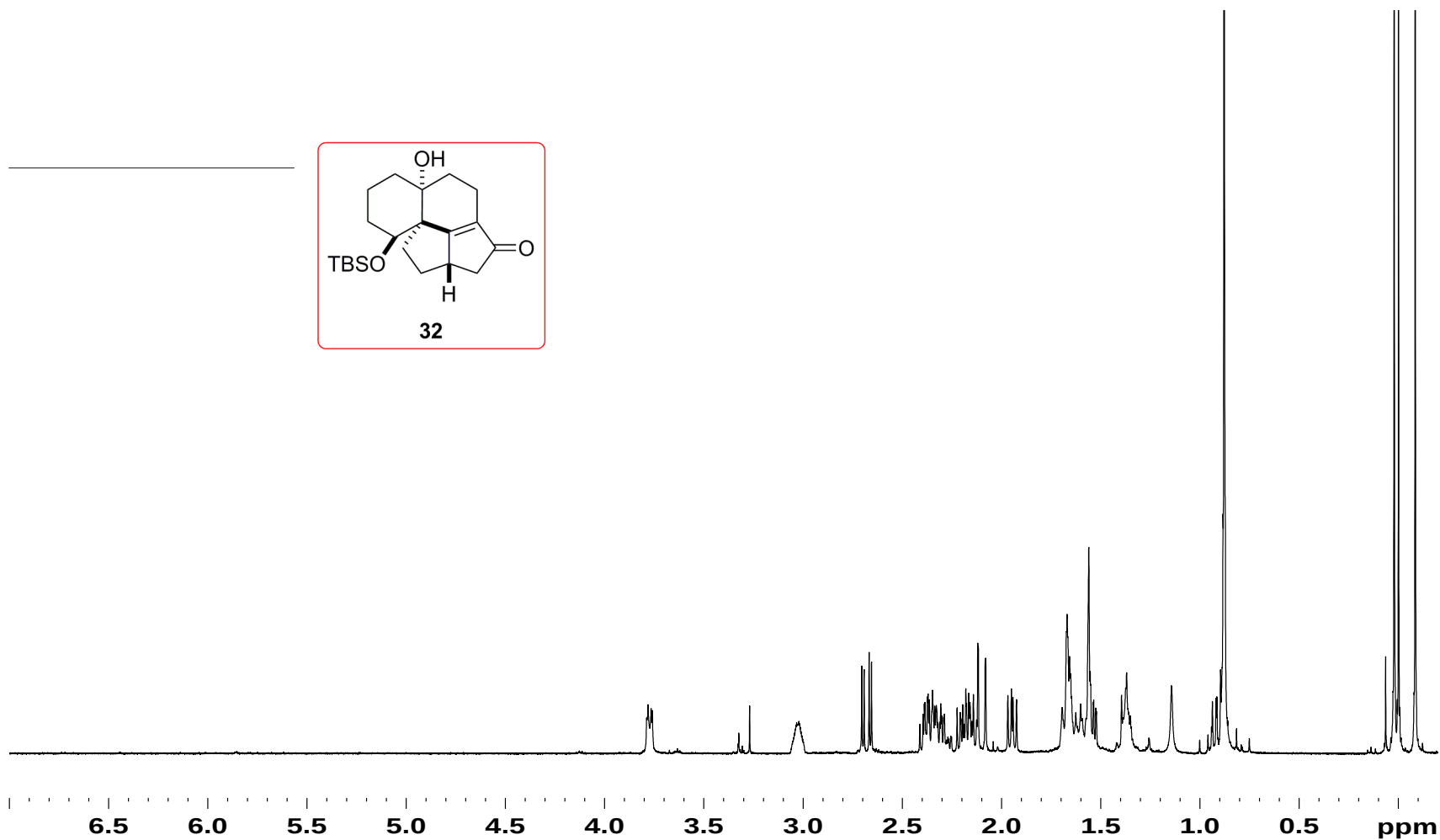
¹H NMR (500 MHz, CDCl₃) of (1*R,2*R**,3*a*'*S**,6*R**)-6-(*tert*-butyldimethylsilyloxy)-2-hydroxy-2-vinyl-3*a*',4'-dihydro-2'*H*-spiro-[cyclohexane-1,1'-pentalen]-5'(3'*H*)-one (31)**



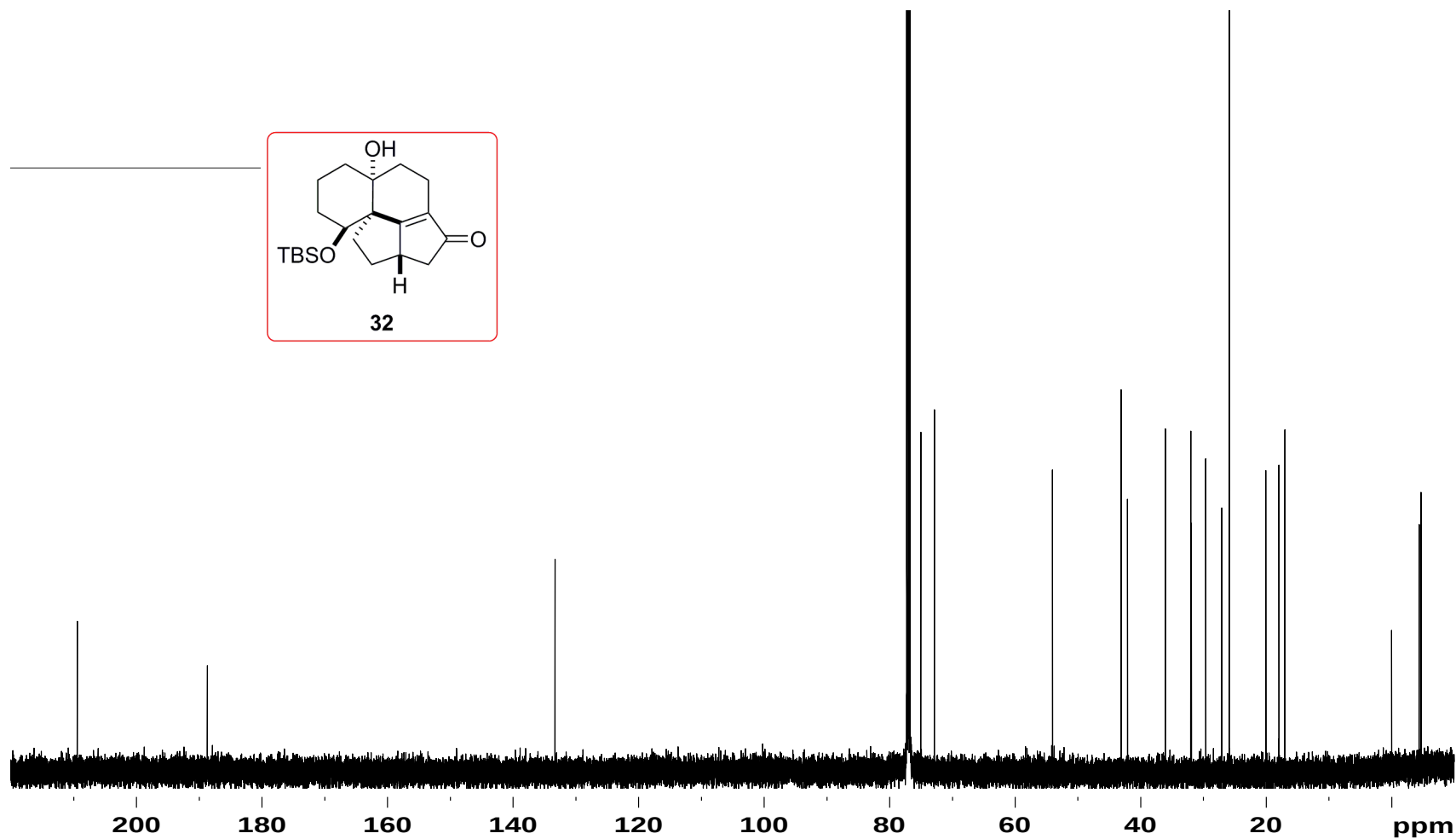
^{13}C NMR (125 MHz, CDCl_3) of (1*R**,2*R**,3*a*'*S**,6*R**)-6-(*tert*-butyldimethylsilyloxy)-2-hydroxy-2-vinyl-3*a*',4'-dihydro-2'*H*-spiro[cyclohexane-1,1'-pentalen]-5'(3'*H*)-one (31)



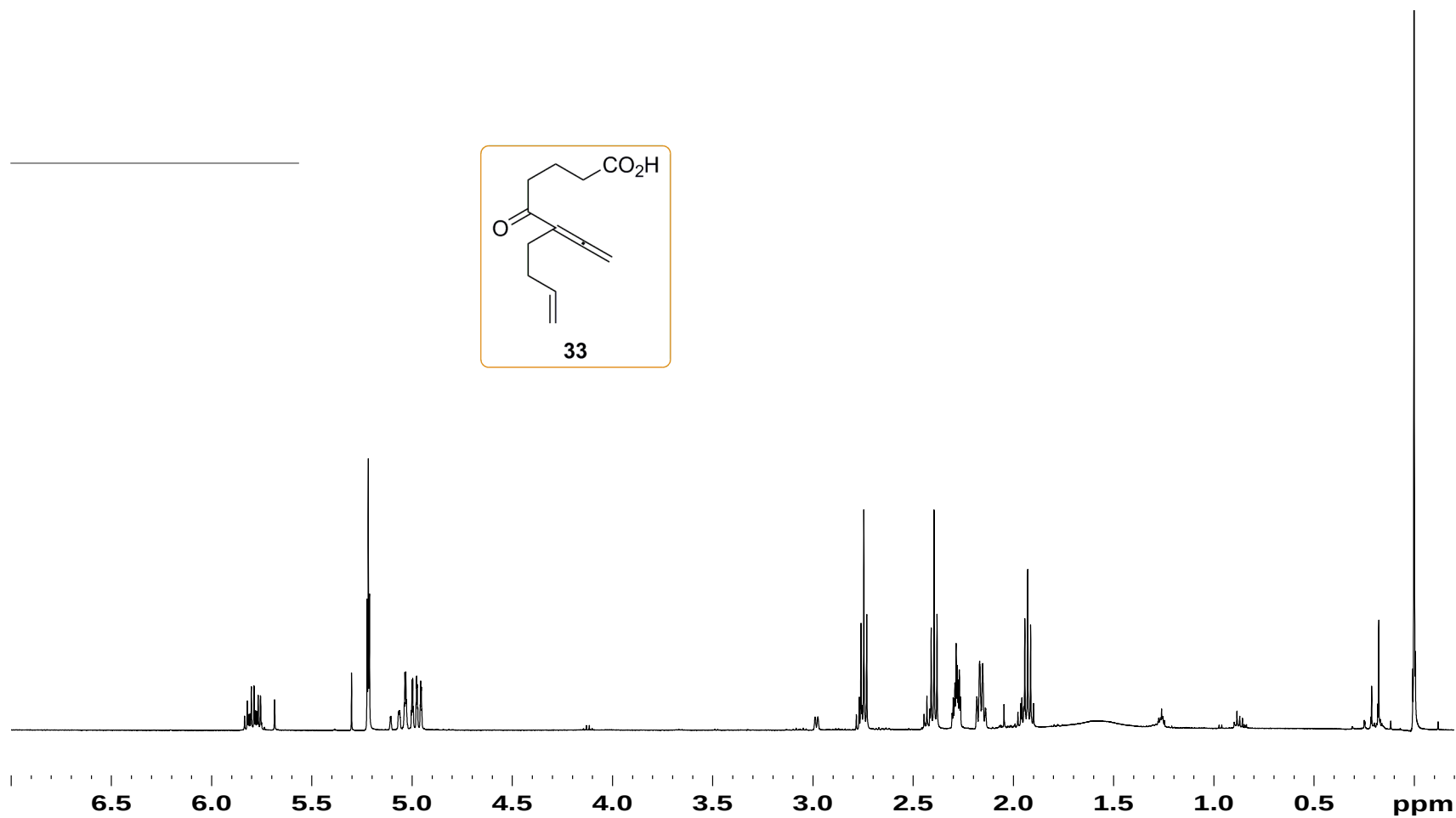
¹H NMR (500 MHz, CDCl₃) of (4*aR,8*R**,8*aR**,10*aR**)-8-(*tert*-butyldimethylsilyl)oxy-3,4,4*a*,5,6,7,8,9,10,10*a*-decahydro-4*a*-hydroxy-1*H*-pentaleno[1,6-*ja*]naphthalene-2(1*H*)-one (32)**



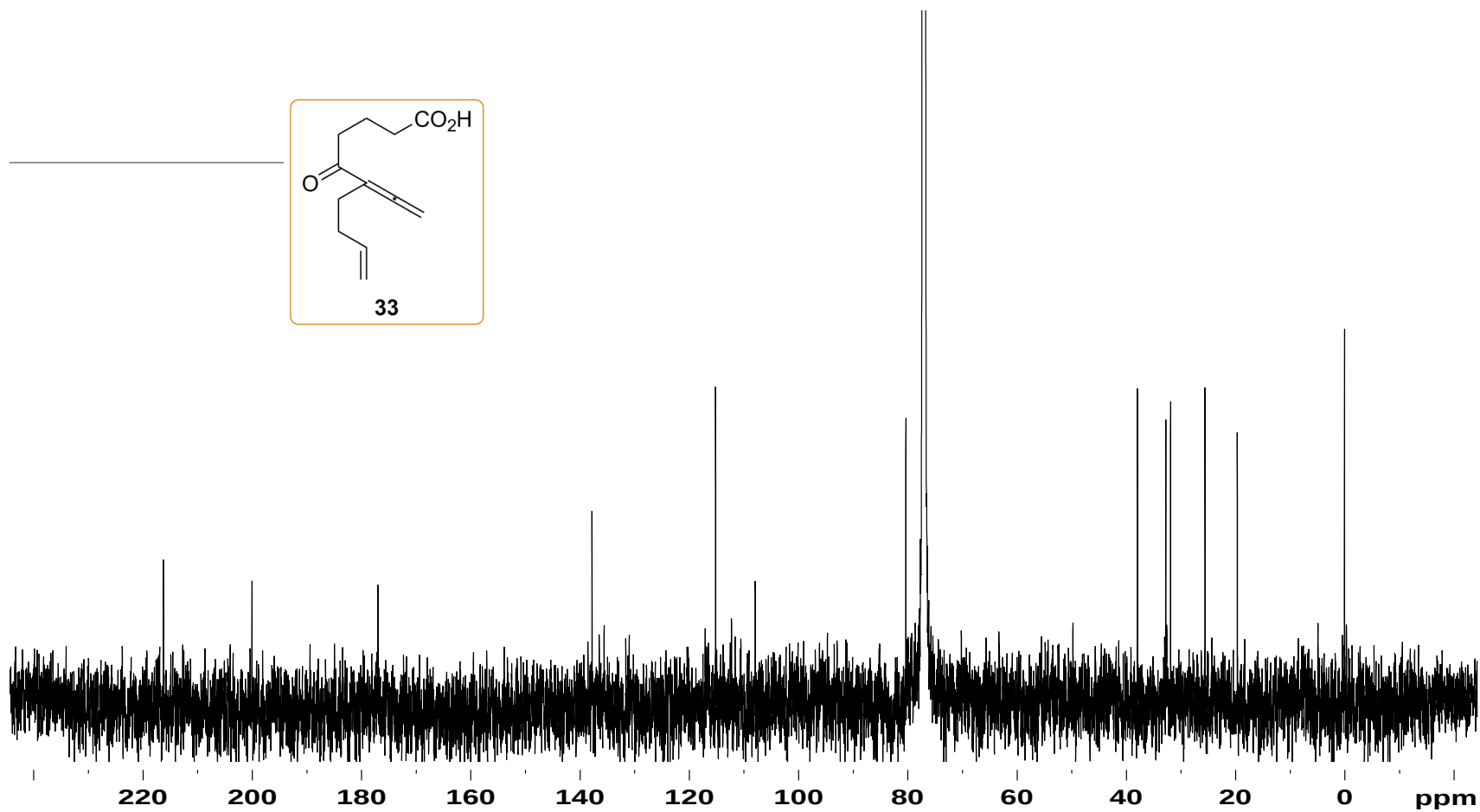
¹³C NMR (125 MHz, CDCl₃) of (4aR*,8R*,8aR*,10aR*)-8-(*tert*-butyldimethylsilyl)oxy-3,4,4a,5,6,7,8,9,10,10a-decahydro-4a-hydroxy-1*H*-pentaleno[1,6-*ja*]naphthalene-2(1*H*)-one (32)



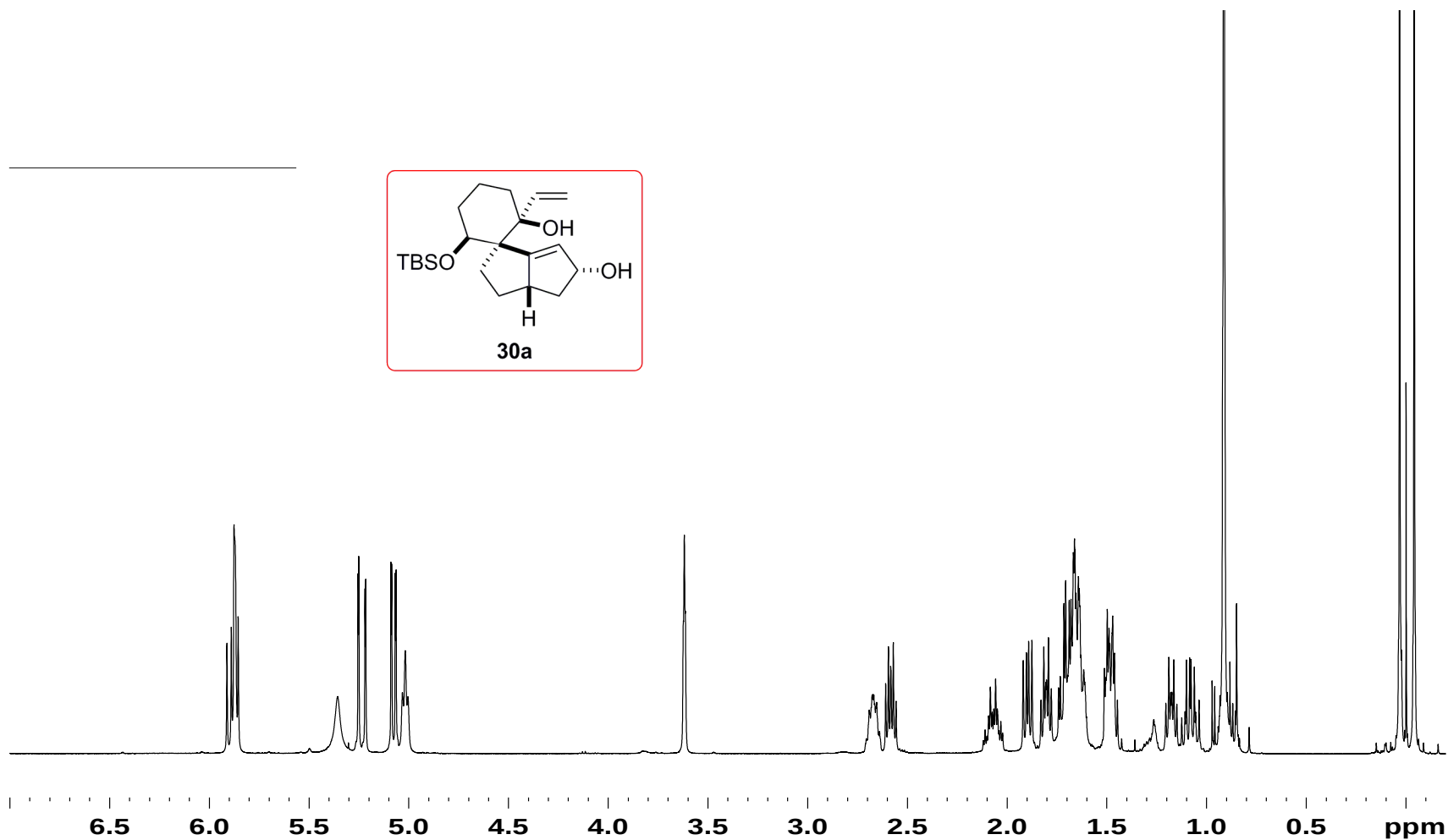
^1H NMR (500 MHz, CDCl_3) of 5-oxo-6-vinylidenedec-9-enoic acid (33)



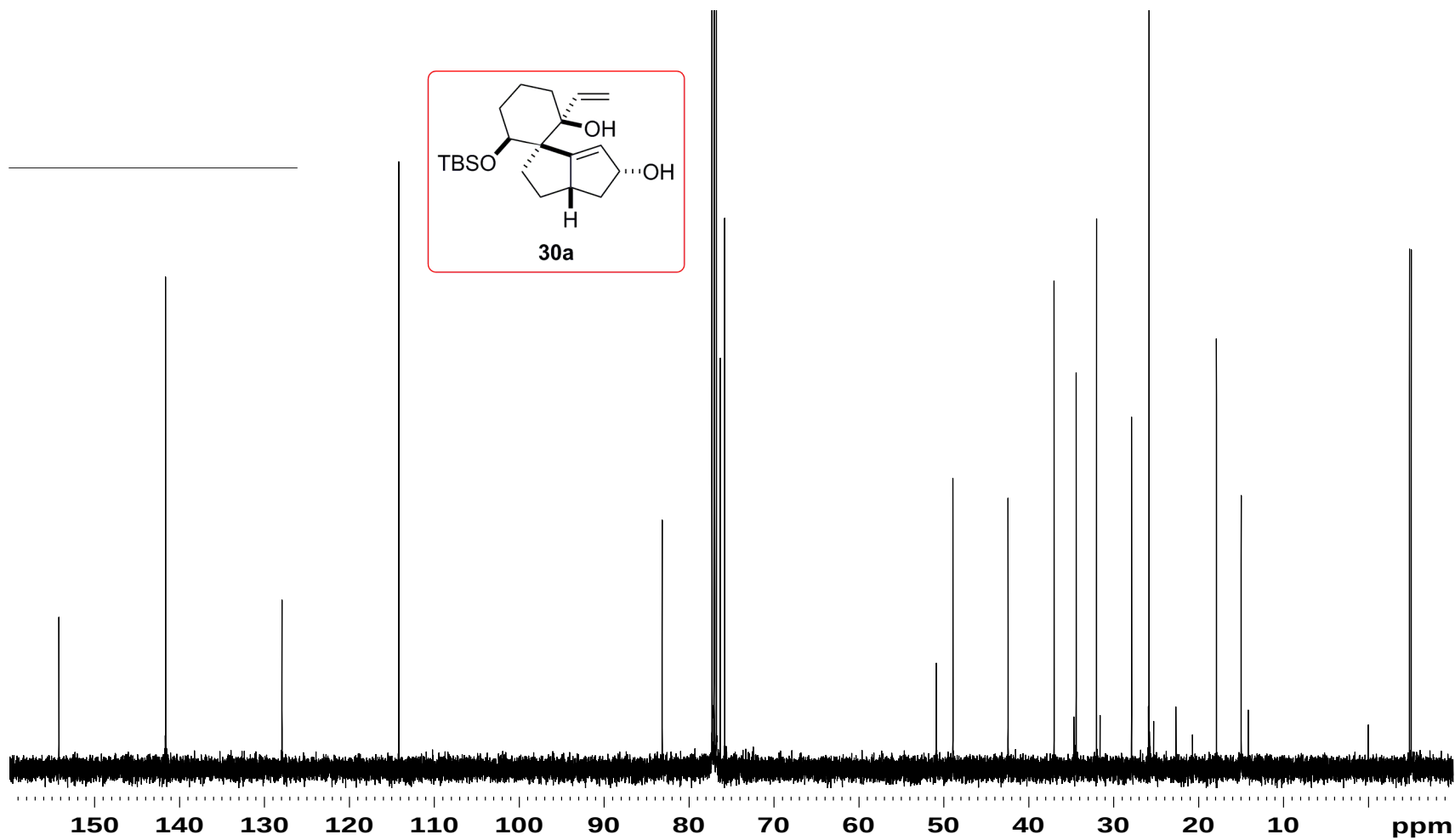
^{13}C NMR (125 MHz, CDCl_3) of 5-oxo-6-vinylidenedec-9-enoic acid (33)



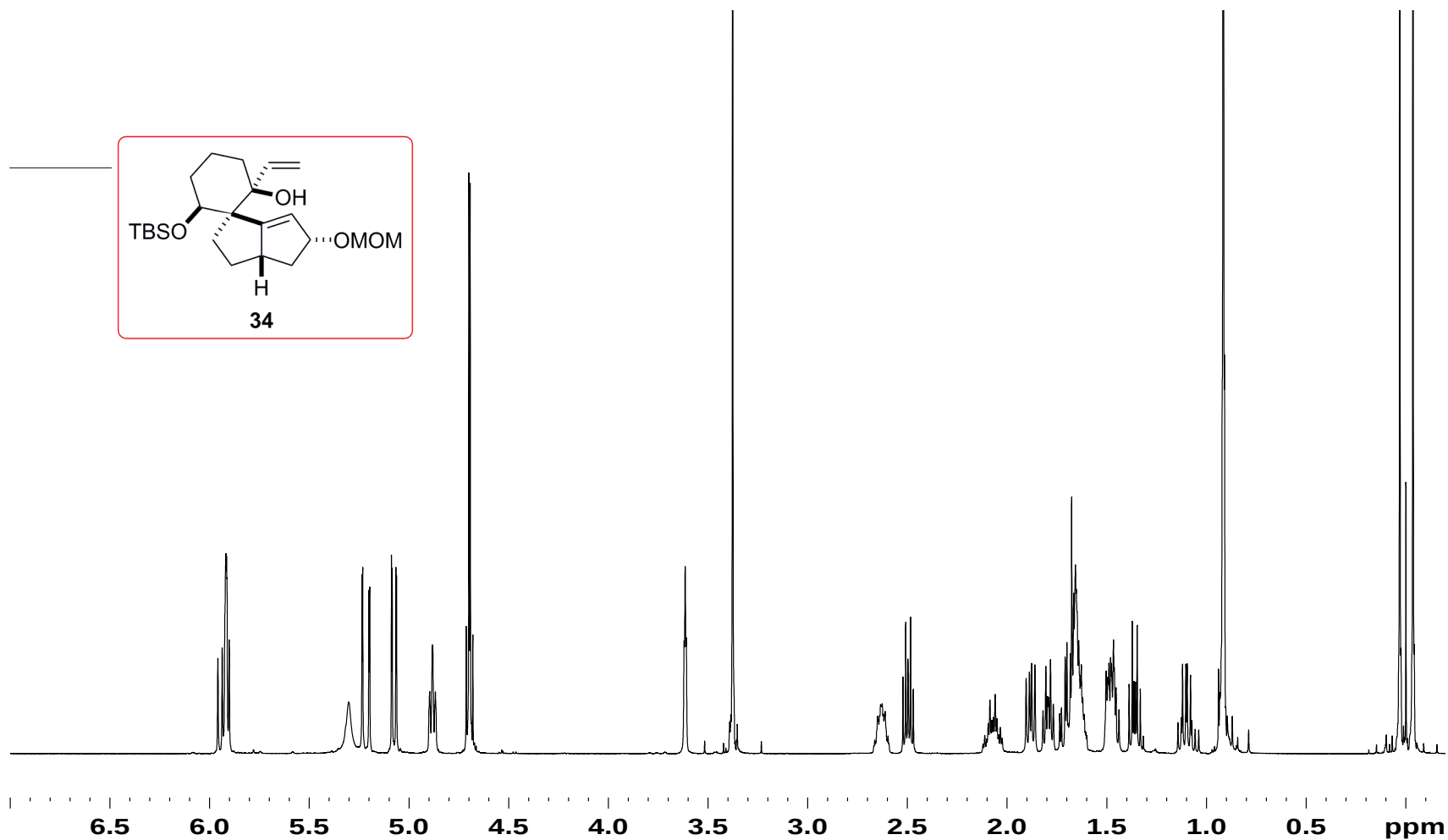
^1H NMR (500 MHz, CDCl_3) of (1*R,2*R**,3*a*'*R**,5'*S**,6*R**)-6-(*tert*-butyldimethylsilyloxy)-2-vinyl-3',3*a*',4',5'-tetrahydro-2'*H*-spiro[cyclohexane-1,1'-pentalene]-2,5'-diol (30a)**



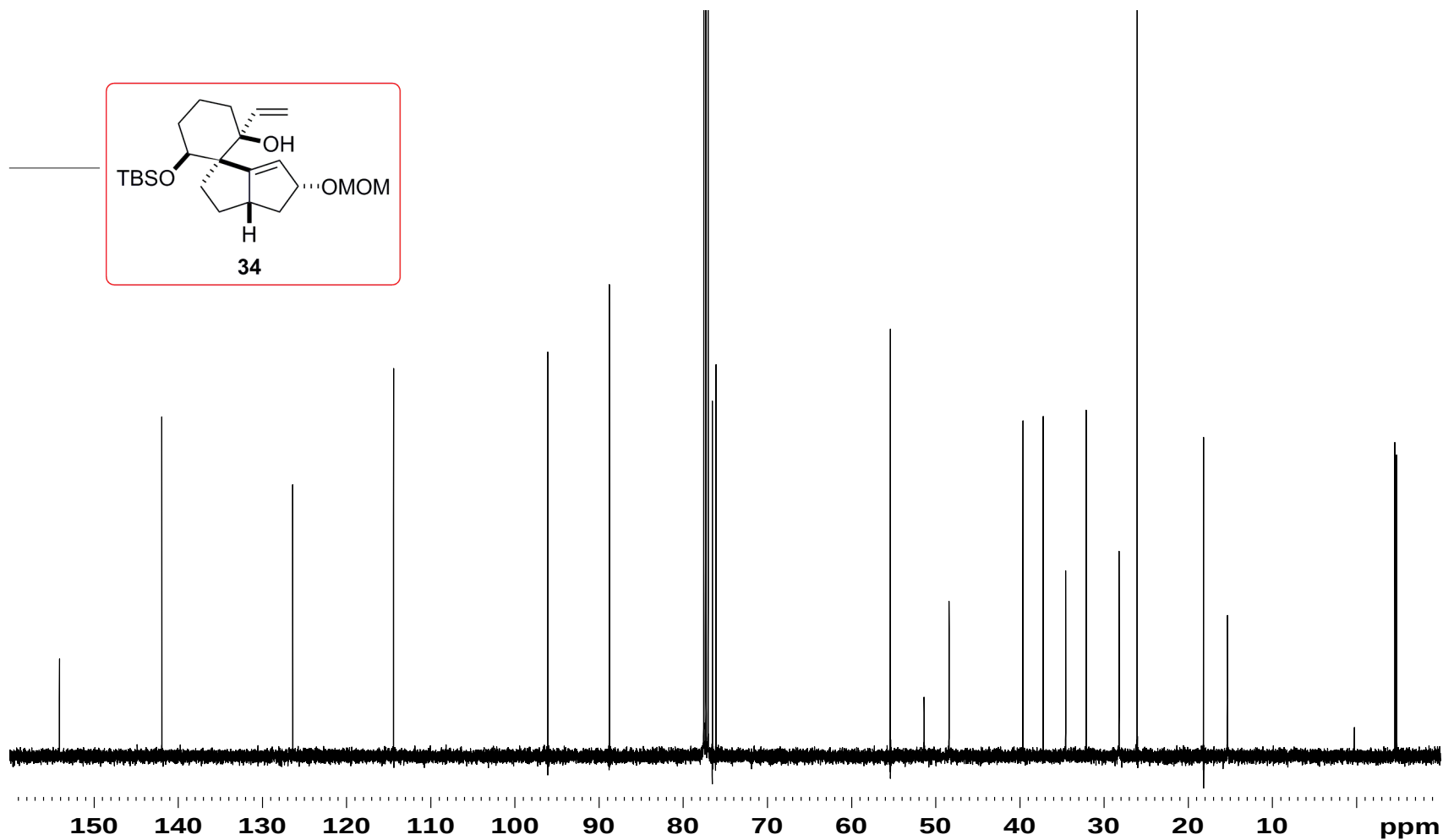
^{13}C NMR (125 MHz, CDCl_3) of (1*R,2*R**,3*a*'*R**,5'*S**,6*R**)-6-(*tert*-butyldimethylsilyloxy)-2-vinyl-3',3*a*',4',5'-tetrahydro-2'*H*-spiro[cyclohexane-1,1'-pentalene]-2,5'-diol (30a)**



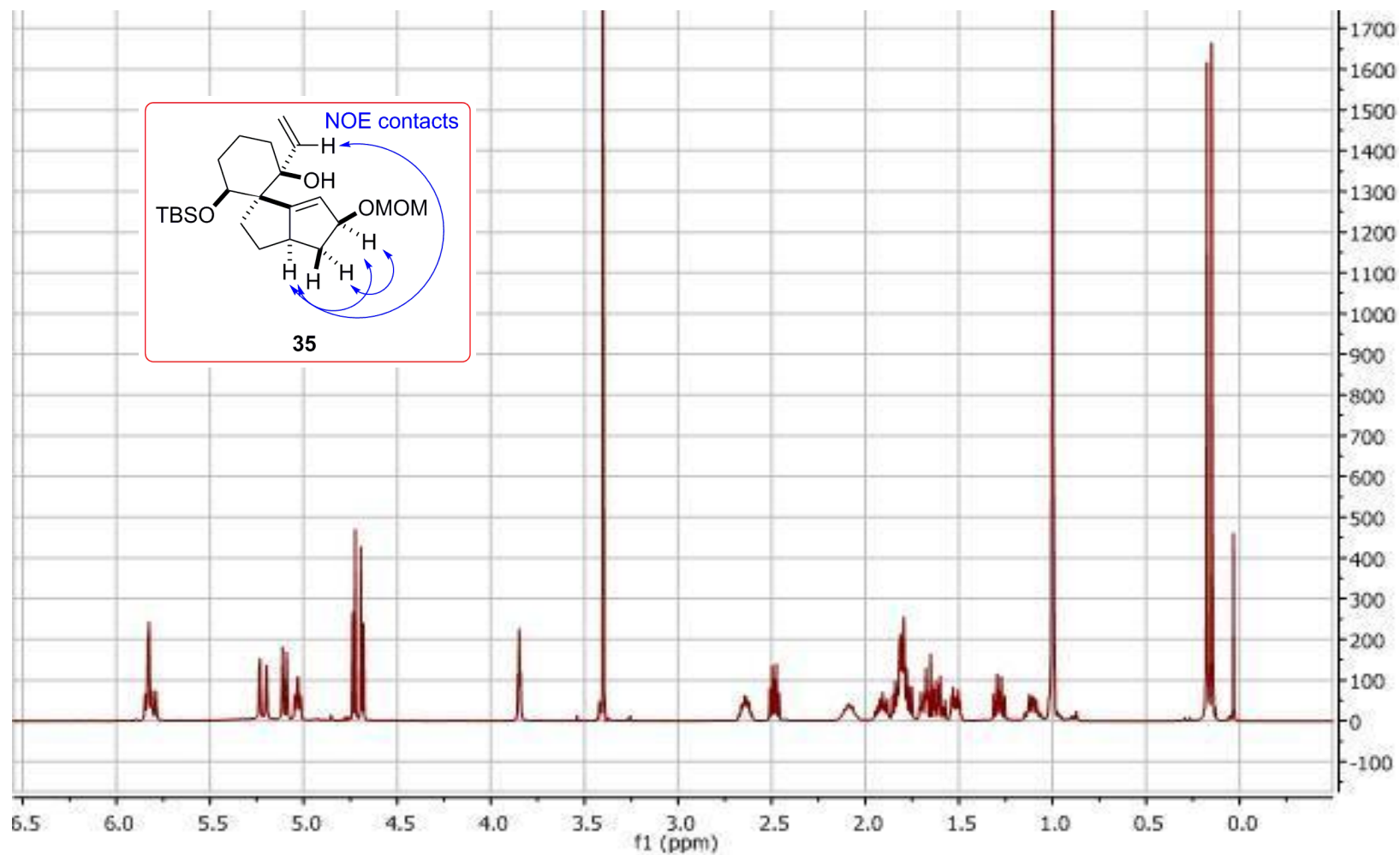
^1H NMR (500 MHz, CDCl_3) of (1*R,2*R**,3*a*'*R**,5'*S**,6*R**)-6-(*tert*-butyldimethylsilyloxy)-5'-(methoxymethoxy)-2-vinyl-3',3*a*',4',5'-tetrahydro-2'*H*-spiro[cyclohexane-1,1'-pentalen]-2-ol (34)**



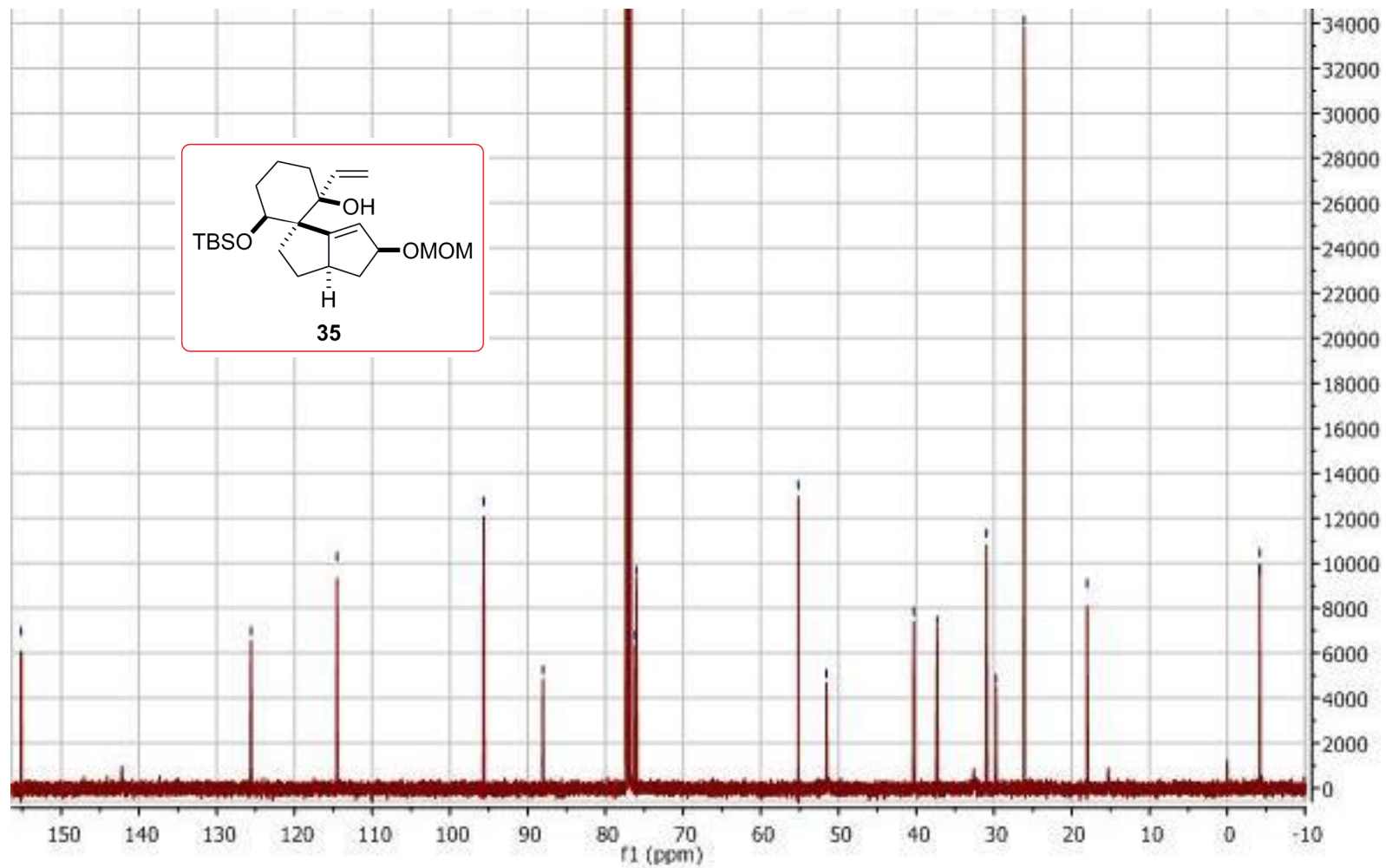
^{13}C NMR (125 MHz, CDCl_3) of (1*R,2*R**,3*a*'*R**,5'*S**,6*R**)-6-(*tert*-butyldimethylsilyloxy)-5'-(methoxymethoxy)-2-vinyl-3',3*a*',4',5'-tetrahydro-2'*H*-spiro[cyclohexane-1,1'-pentalen]-2-ol (34)**



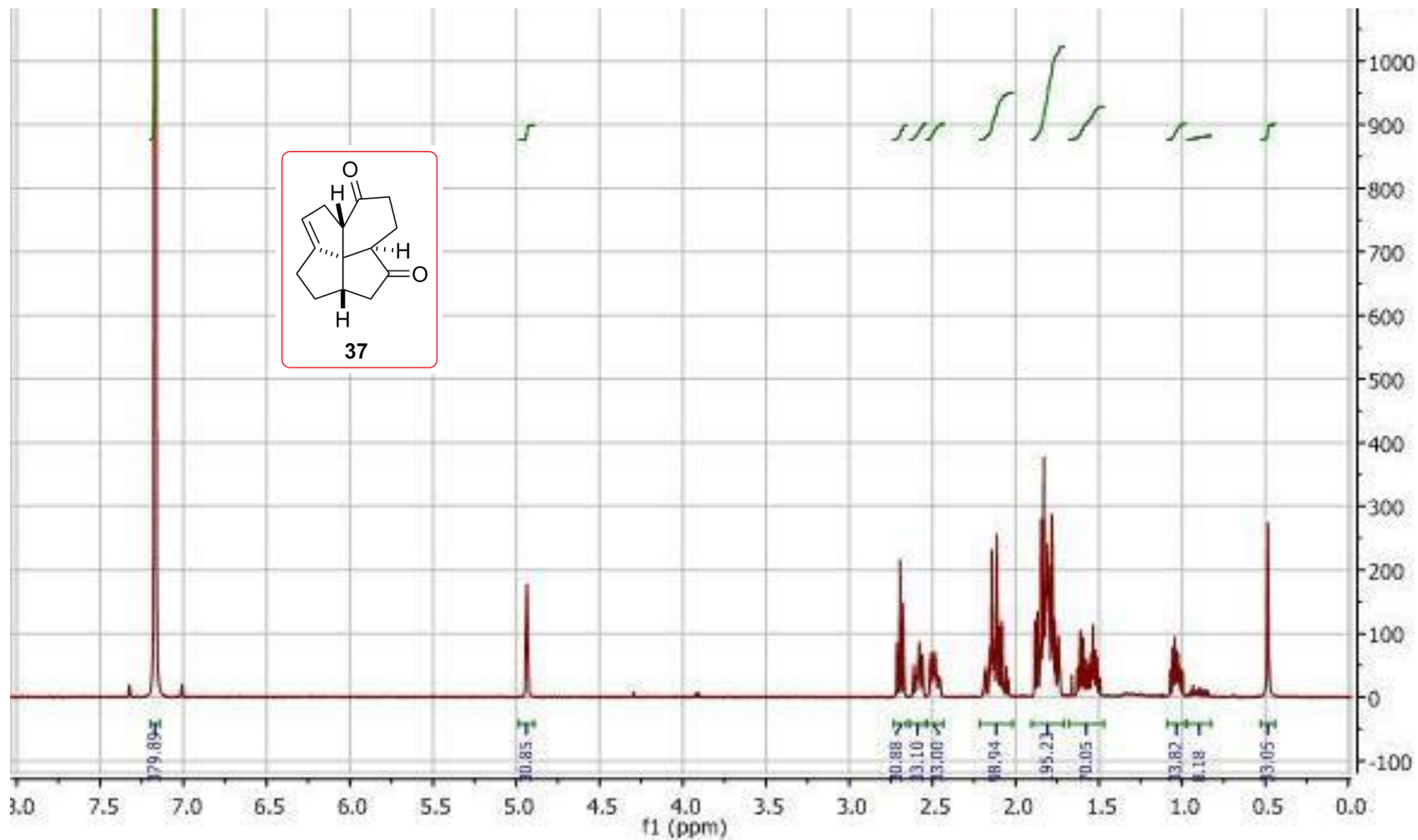
^1H NMR (500 MHz, CDCl_3) of (1*R,2*R**,3*a*'*S**,5'*R**,6*R**)-6-(*tert*-butyldimethylsilyloxy)-5'-(methoxymethoxy)-2-vinyl-3',3*a*',4',5'-tetrahydro-2'*H*-spiro[cyclohexane-1,1'-pentalen]-2-ol (35)**



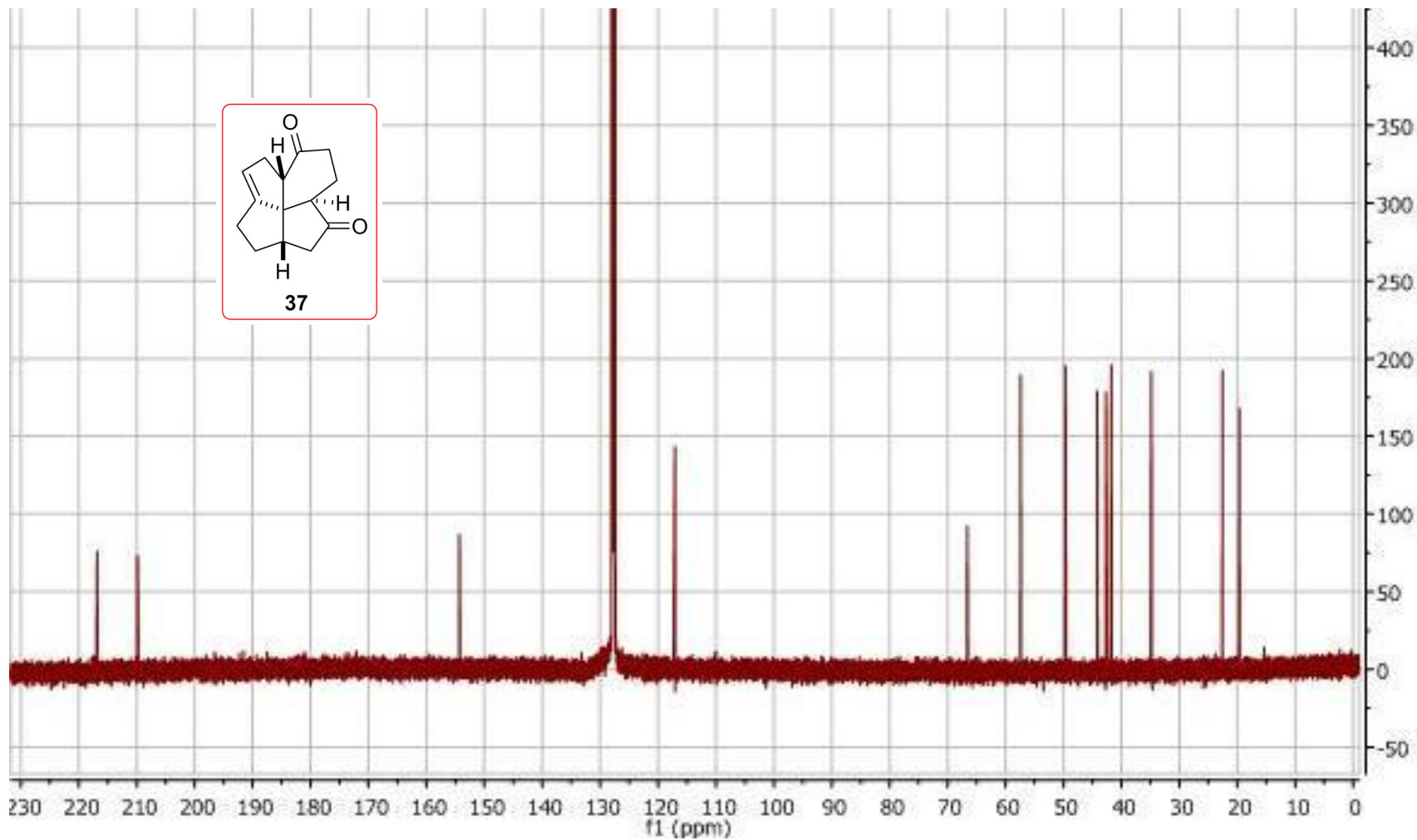
^{13}C NMR (125 MHz, CDCl_3) of (1*R,2*R**,3*a*'*S**,5'*R**,6*R**)-6-(*tert*-butyldimethylsilyloxy)-5'-(methoxymethoxy)-2-vinyl-3',3*a*',4',5'-tetrahydro-2'*H*-spiro[cyclohexane-1,1'-pentalen]-2-ol (35)**



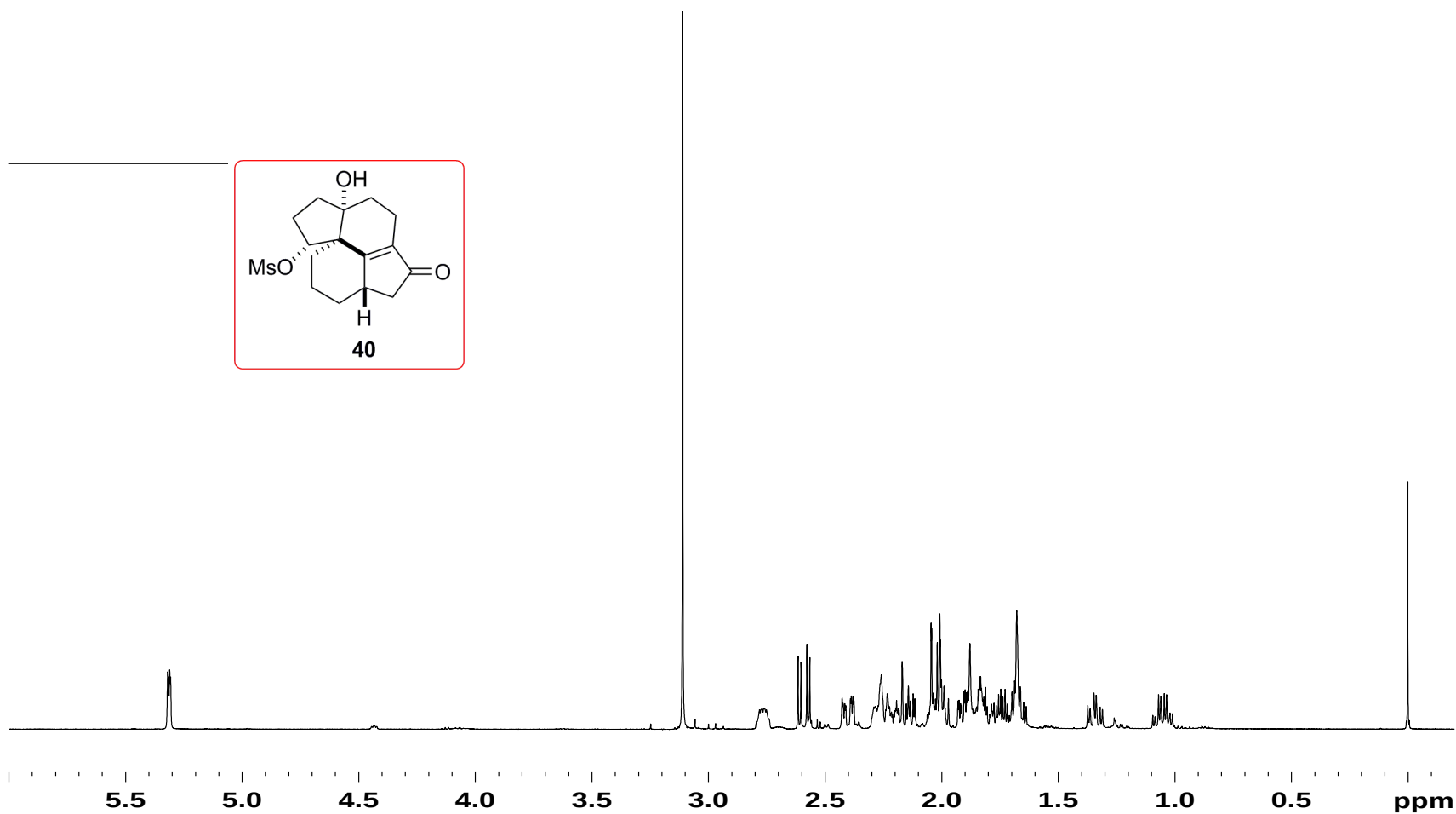
¹H NMR (500 MHz, C₆D₆) of (2*aR,6*aS**,9*aR**,9*bR**)-2,2*a*,3,4,6,6*a*,9,9*a*-octahydro-1*H*-pentaleno[1,6-*dc*]indene-1,7(8*H*)-dione (37)**



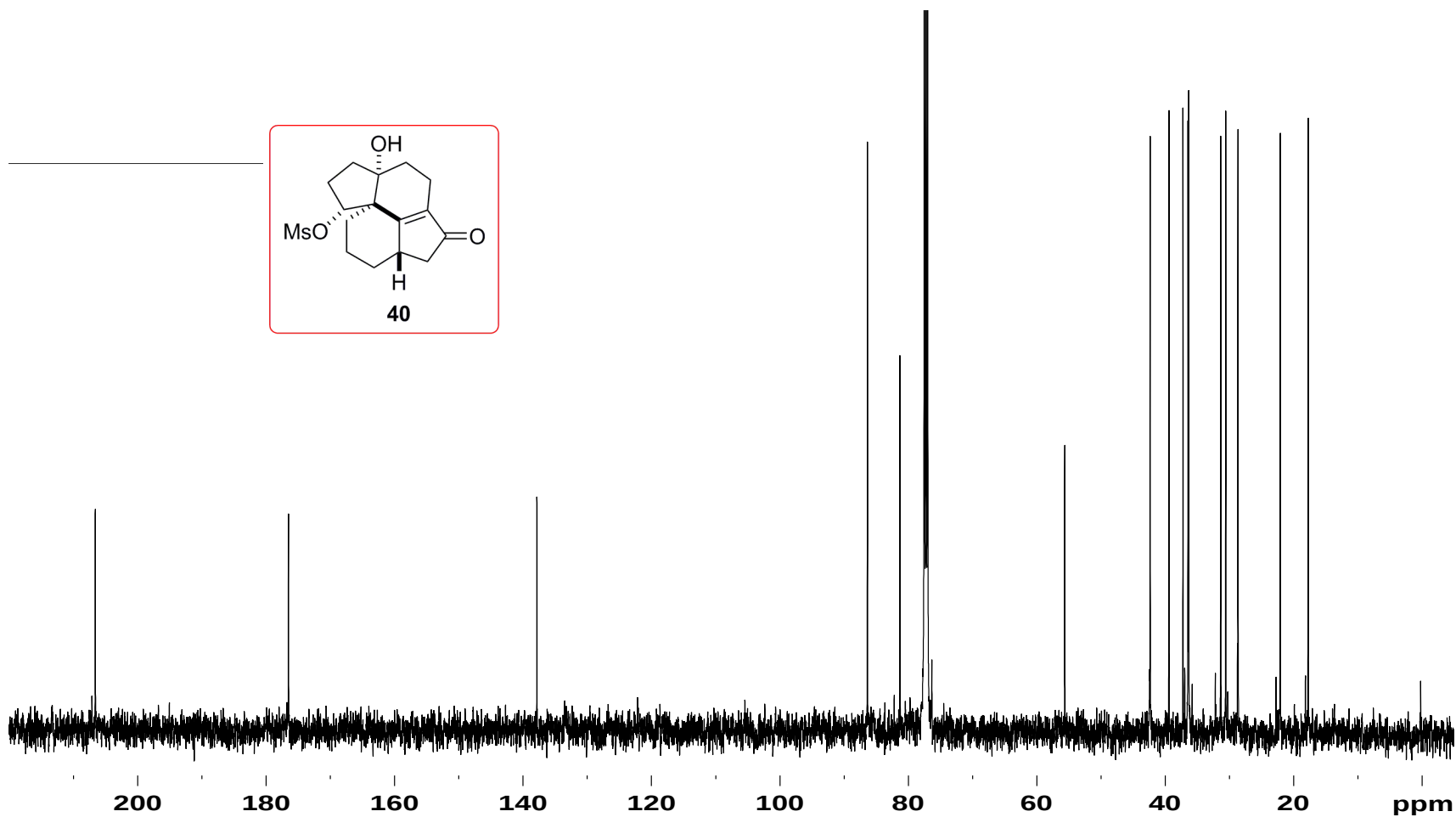
^{13}C NMR (125 MHz, C_6D_6) of $(2aR^*,6aS^*,9aR^*,9bR^*)$ -2,2a,3,4,6,6a,9,9a-octahydro-1H-pentaleno[1,6-dc]indene-1,7(8H)-dione (37)



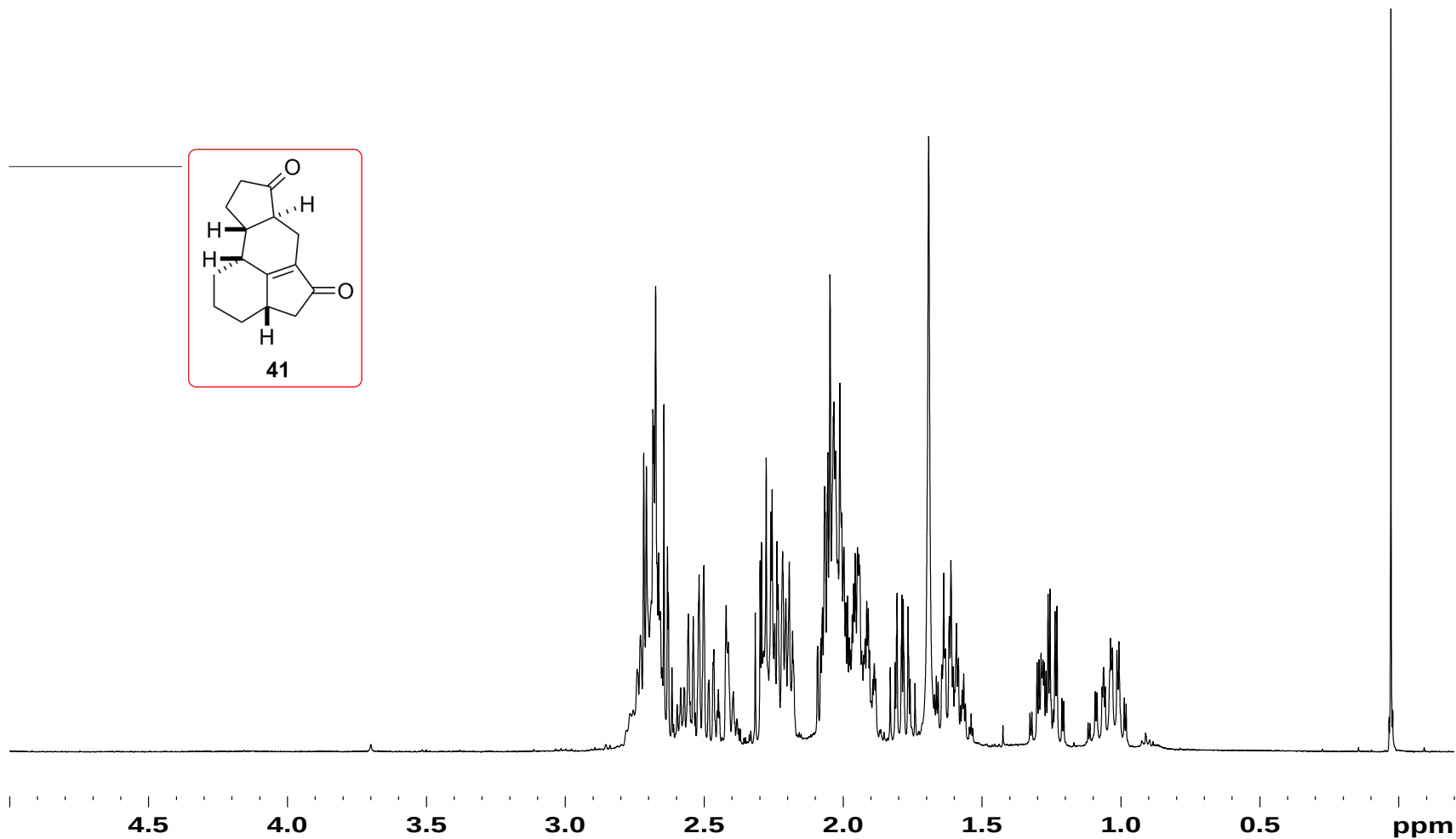
^1H NMR (500 MHz, CDCl_3) of (3*aR,7*aR**,10*S**,10*aR**)-2,3,3*a*,4,6,7,7*a*,8,9,10-decahydro-7*a*-hydroxy-5-oxocyclopenta[*f*]-acenaphthalen-10-yl methanesulfonate (40)**



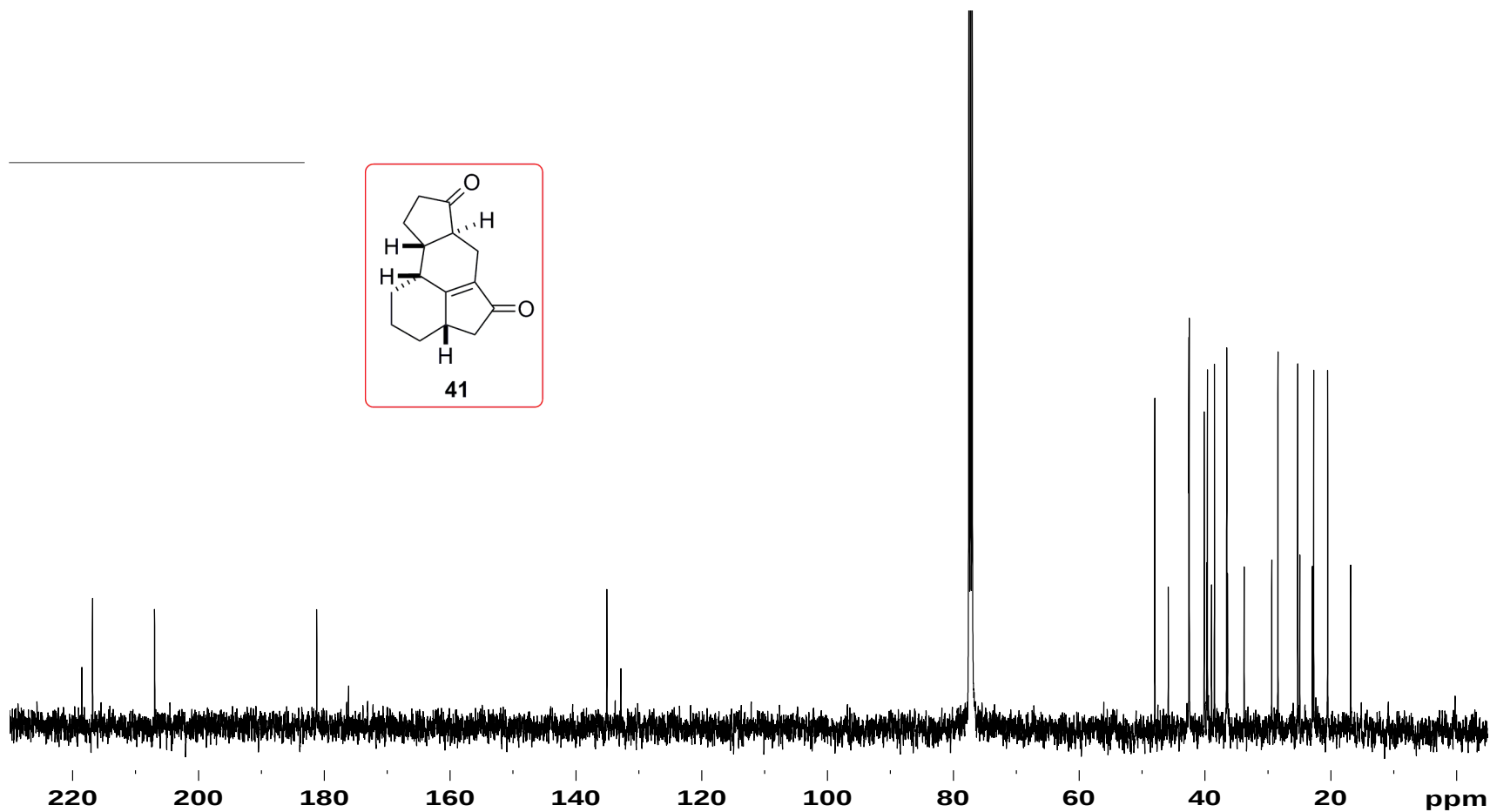
^{13}C NMR (125 MHz, CDCl_3) of (3*aR,7*aR**,10*S**,10*aR**)-2,3,3*a*,4,6,7,7*a*,8,9,10-decahydro-7*a*-hydroxy-5-oxocyclopenta[*f*]-acenaphthalen-10-yl methanesulfonate (40)**



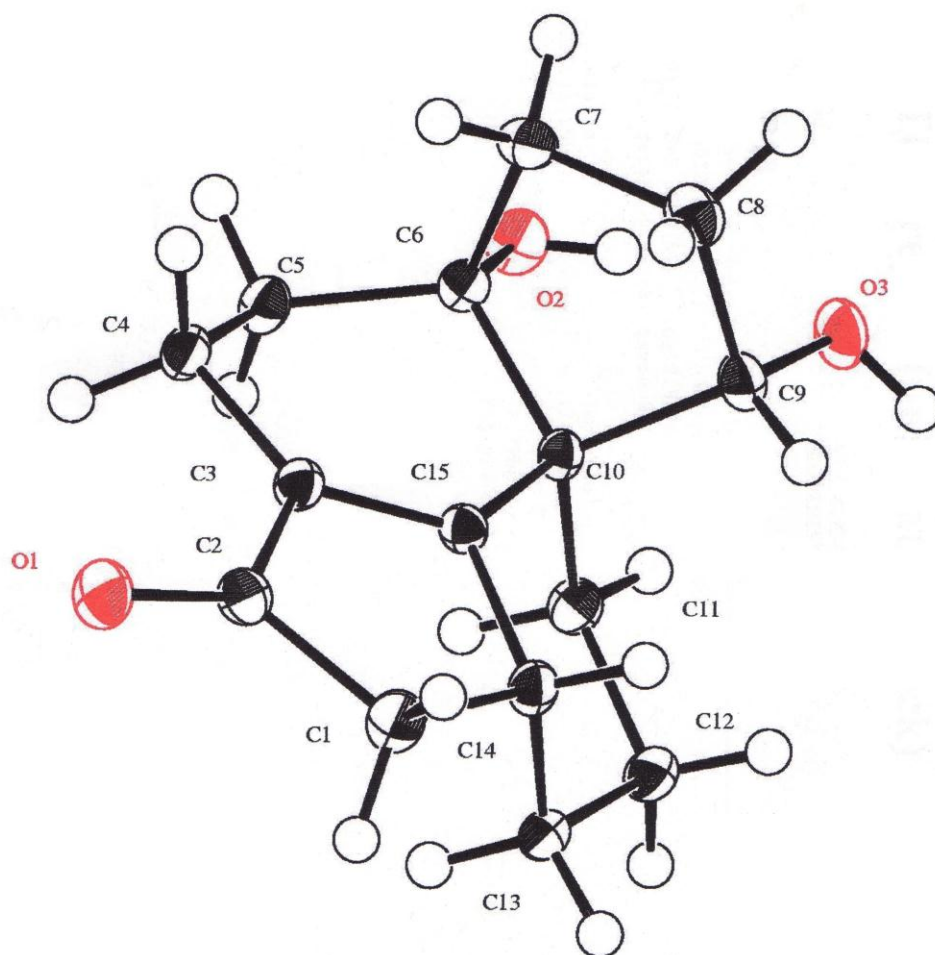
¹H NMR (500 MHz, CDCl₃) of (3*aR,6*aR**,9*aR**,9*bS**)-2,3,3*a*,4,6,6*a*,9,9*a*-octahydro-1*H*-cyclopenta[*e*]acenaphthalene-5,7(8*H*,9*bH*)-dione (41) (containing *ca.* 25% of the isomer epimeric α to the "top" ketone)**



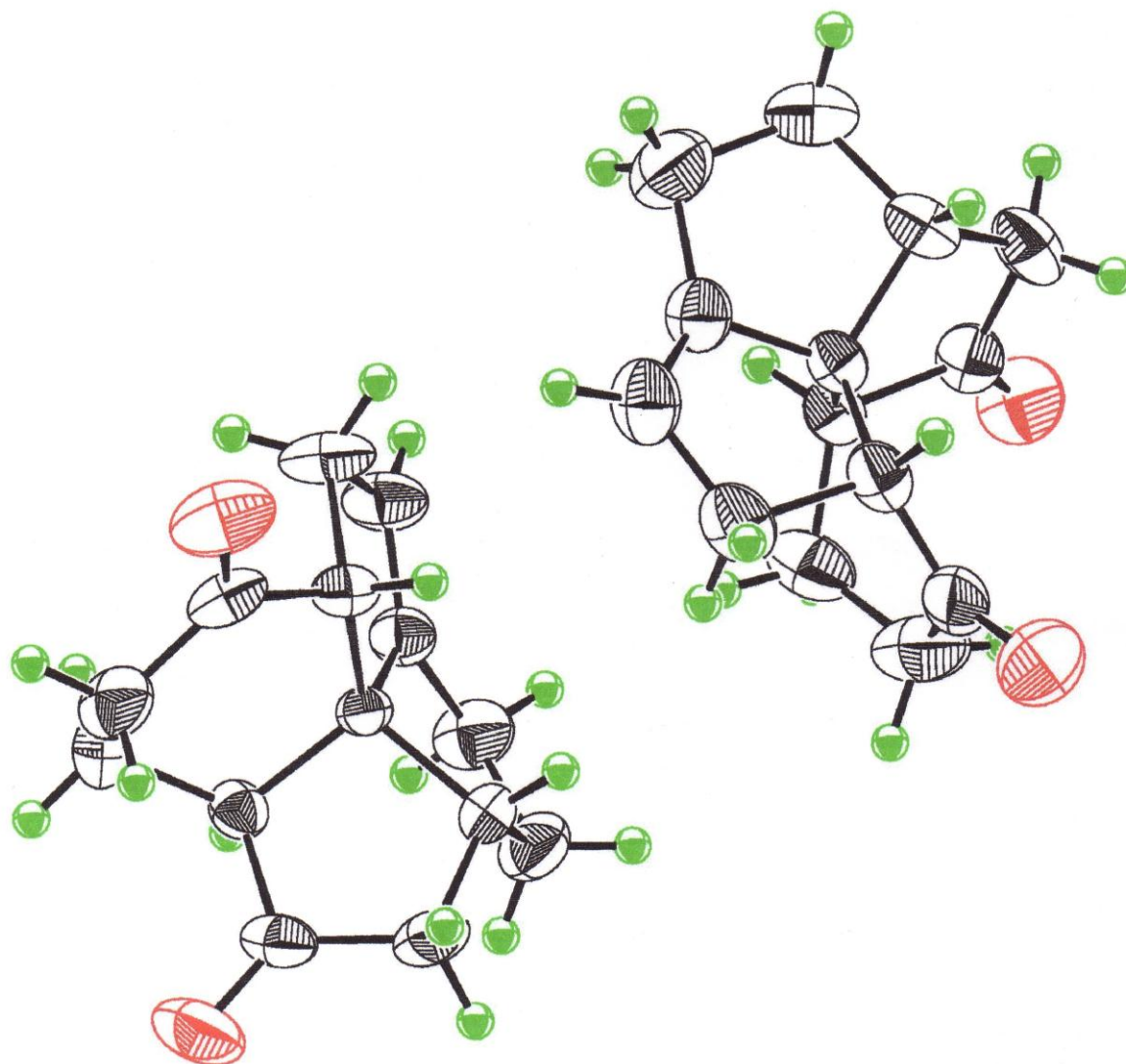
¹³C NMR (125 MHz, CDCl₃) of (3*aR,6*aR**,9*aR**,9*bS**)-2,3,3*a*,4,6,6*a*,9,9*a*-octahydro-1*H*-cyclopenta[*e*]acenaphthalene-5,7(8*H*,9*bH*)-dione (41) (containing *ca.* 25% of the isomer epimeric α to the "top" ketone)**



X-Ray crystal structure of (3*aR,7*aR**,10*S**,10*aR**)-2,3,3*a*,4,6,7,7*a*,8,9,10-decahydro-7*a*,10-dihydroxycyclopenta[*f*]acenaphthalen-5(1*H*)-one (18)**



X-Ray crystal structure of (2*aR,6*aS**,9*aR**,9*bR**)-2,2*a*,3,4,6,6*a*,9,9*a*-octahydro-1*H*-pentaleno-
[1,6-*dc*]indene-1,7(8*H*)-dione (37)**



X-Ray crystal structure of (3*aR,6*aR**,9*aR**,9*bS**)-2,3,3*a*,4,6,6*a*,9,9*a*-octahydro-1*H*-cyclopenta[*e*]-acenaphthalene-5,7(8*H*,9*bH*)-dione (41)**

