

A stereoselective, Sm(II)–mediated approach to decorated *cis*– hydrindanes: synthetic studies on faurinone and pleuromutilin

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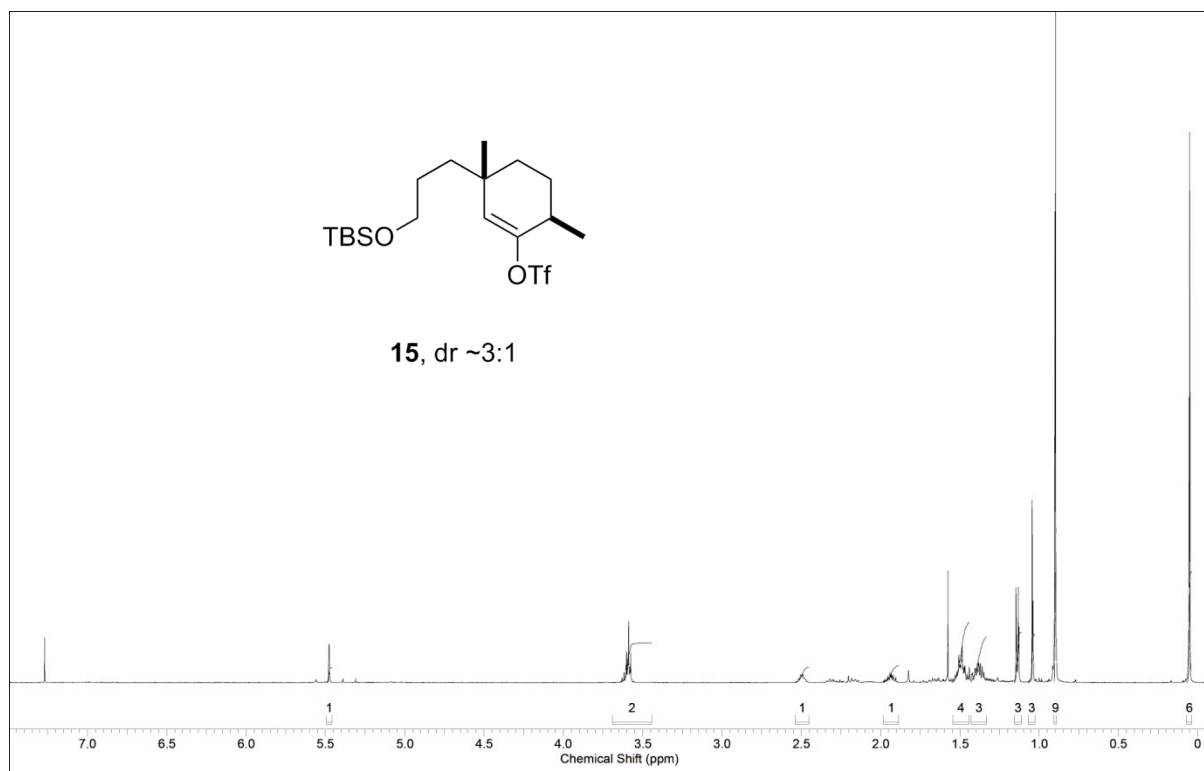
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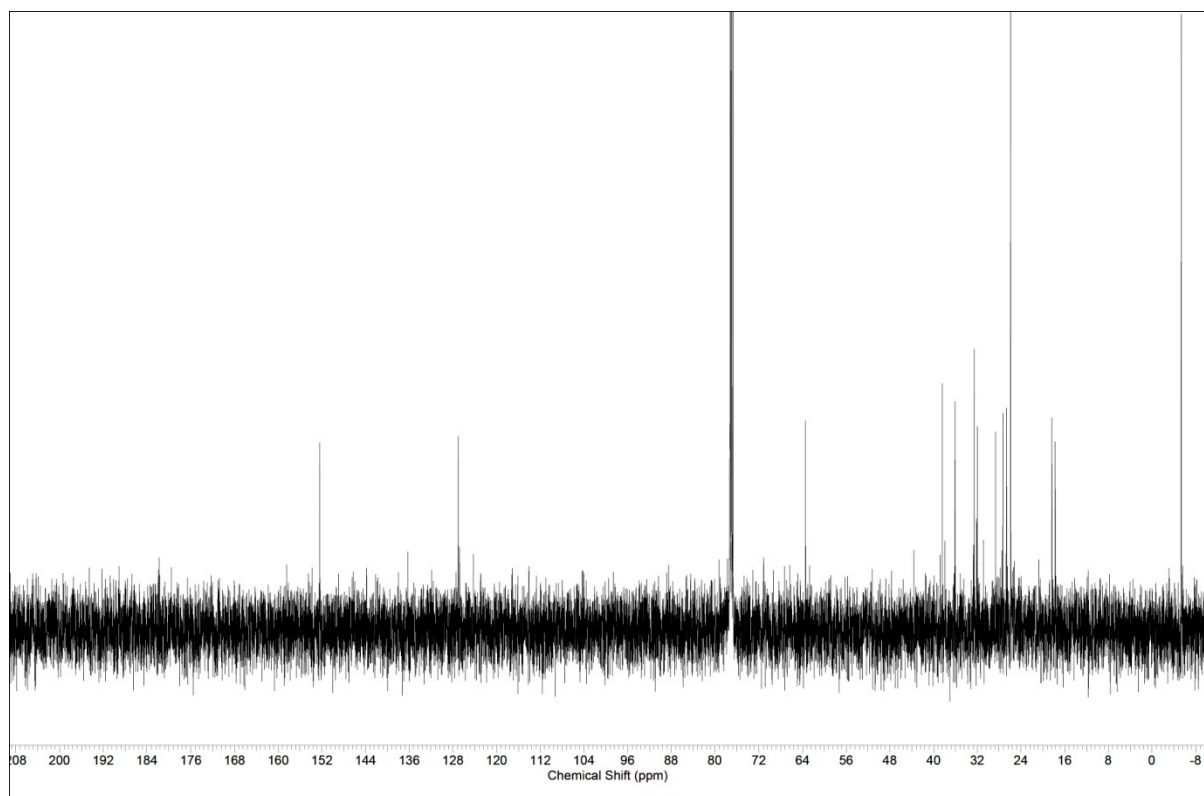
S2 – S43 NMR spectra

S44 X-ray structure of **59**

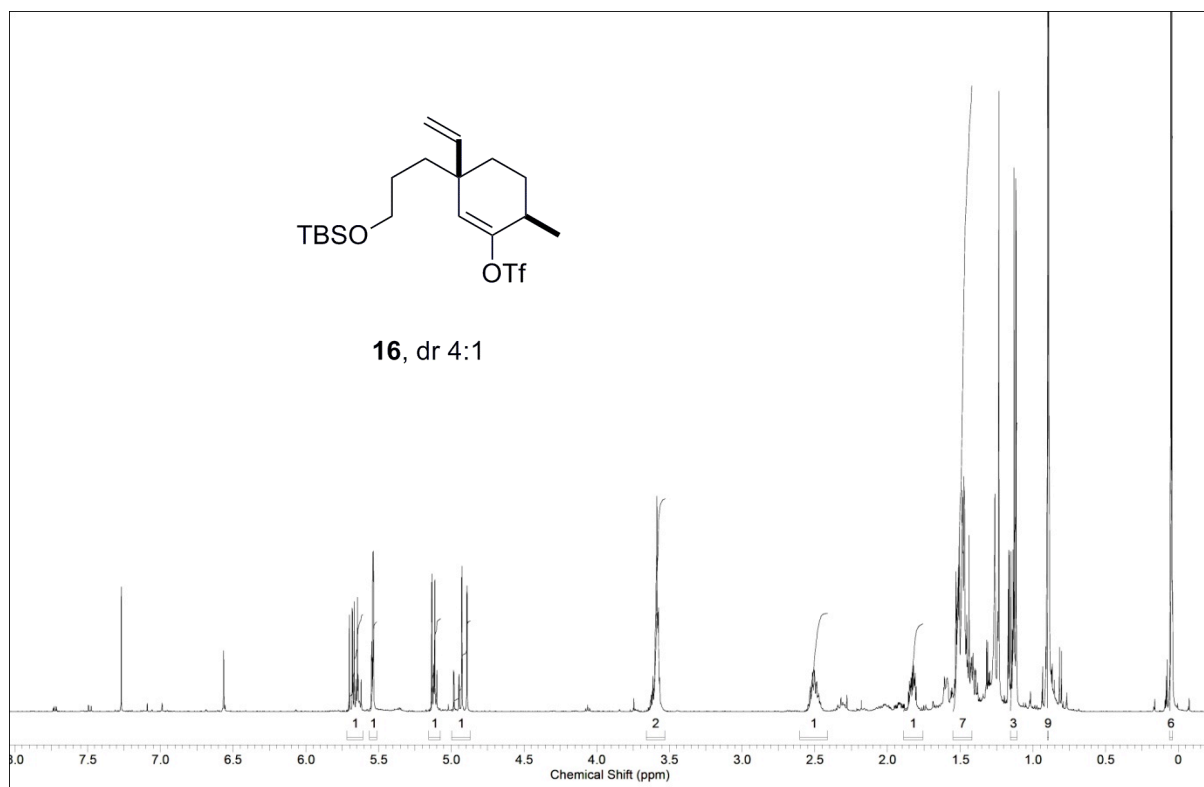
rac-(3*S*,6*R*)-3-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-3,6-dimethylcyclohex-1-en-1-yl
trifluoromethanesulfonate **15**, ¹H-NMR (500 MHz, CDCl₃):



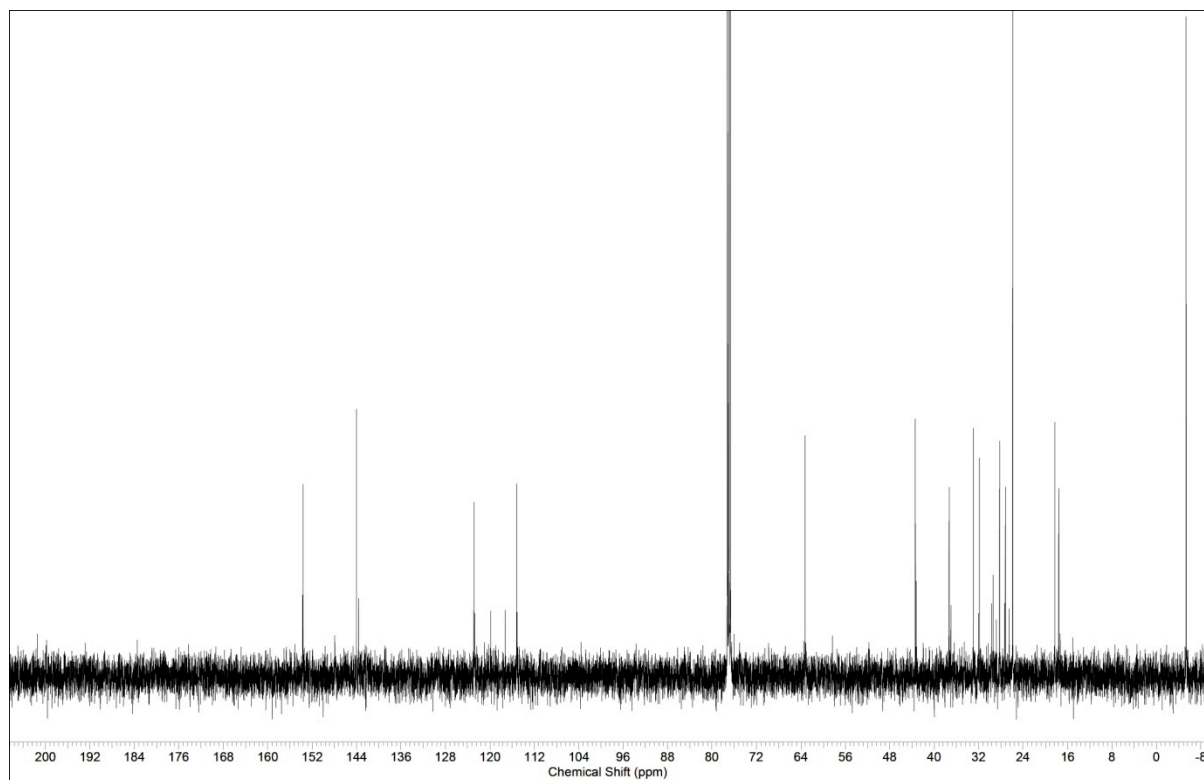
rac-(3*S*,6*R*)-3-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-3,6-dimethylcyclohex-1-en-1-yl
trifluoromethanesulfonate **15**, ¹³C-NMR (125 MHz, CDCl₃):



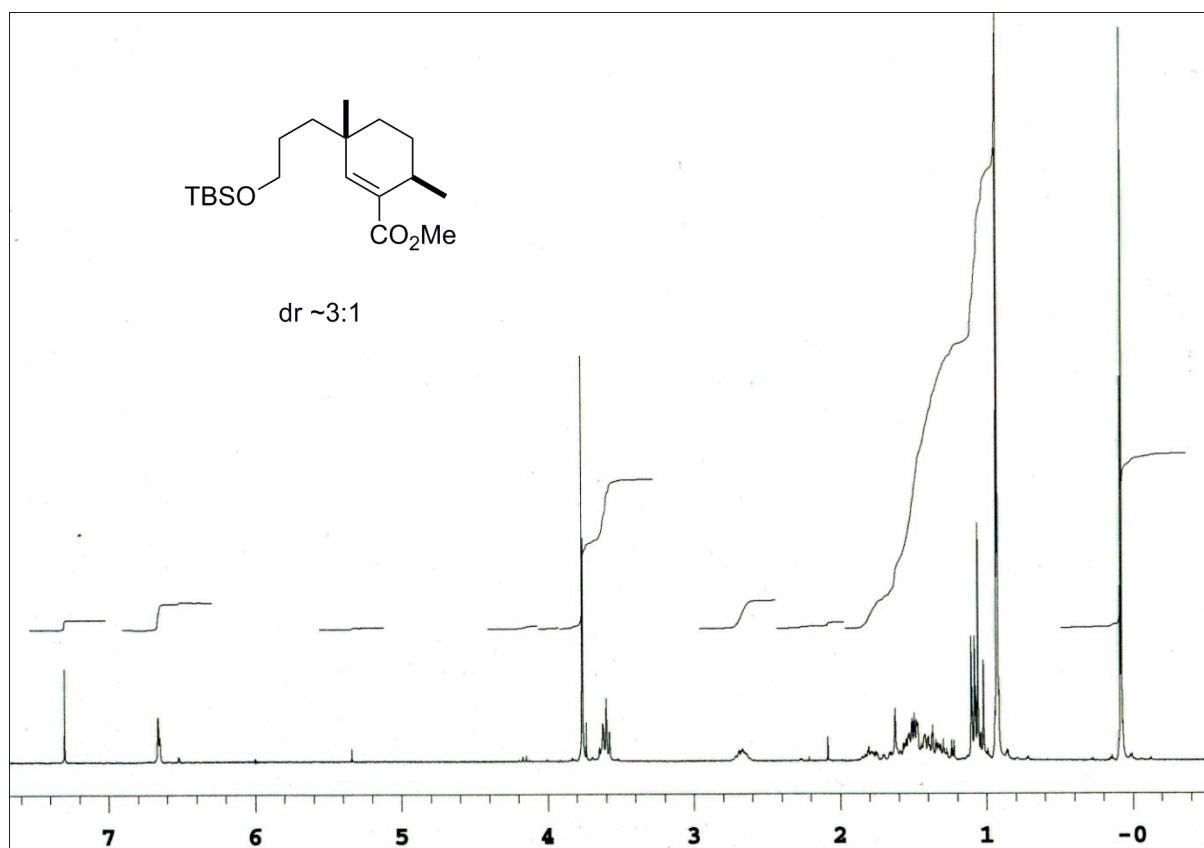
rac-(3*S*,6*R*)-3-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-6-methyl-3-vinylcyclohex-1-en-1-yl trifluoromethanesulfonate **16**, $^1\text{H-NMR}$ (500 MHz, CDCl_3):



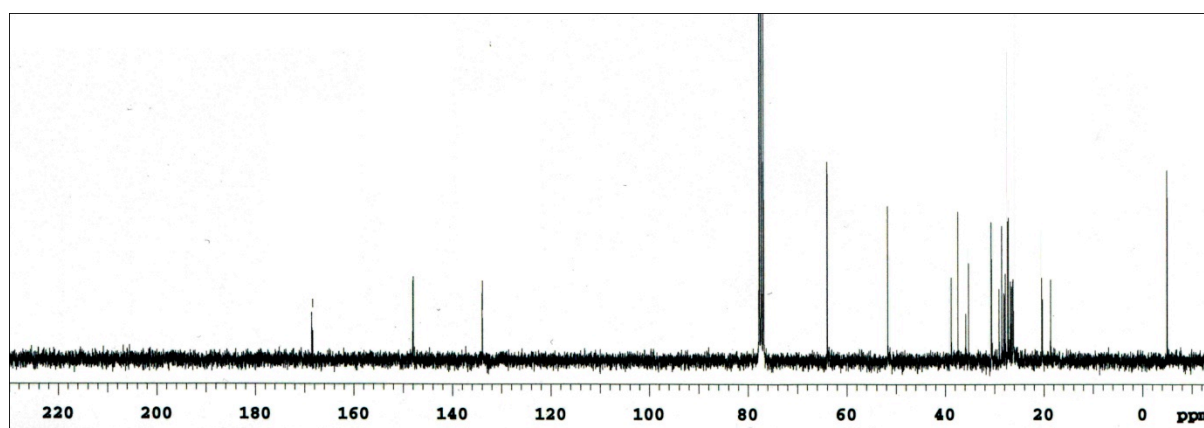
rac-(3*S*,6*R*)-3-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-6-methyl-3-vinylcyclohex-1-en-1-yl trifluoromethanesulfonate **16**, $^{13}\text{C-NMR}$ (125 MHz, CDCl_3):



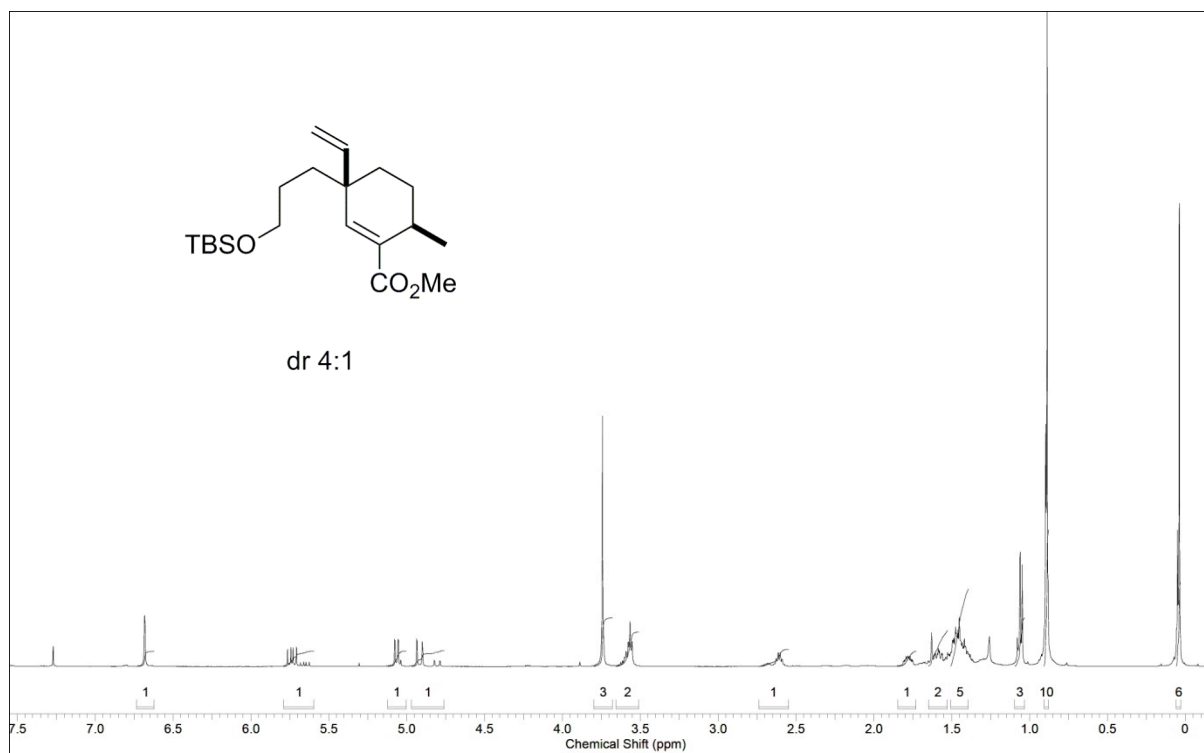
rac-(3*S*,6*R*)-methyl 3-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-3,6-dimethylcyclohex-1-enecarboxylate, $^1\text{H-NMR}$ (300 MHz, CDCl_3):



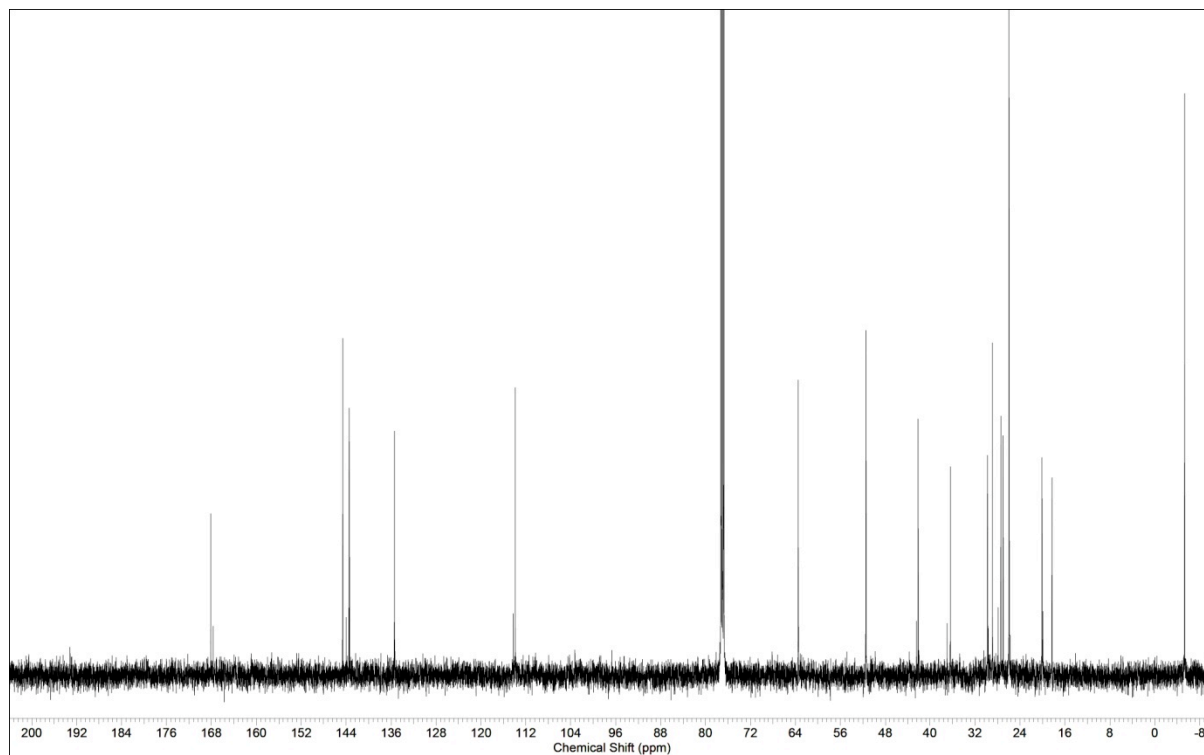
rac-(3*S*,6*R*)-methyl 3-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-3,6-dimethylcyclohex-1-enecarboxylate, $^{13}\text{C-NMR}$ (75 MHz, CDCl_3):



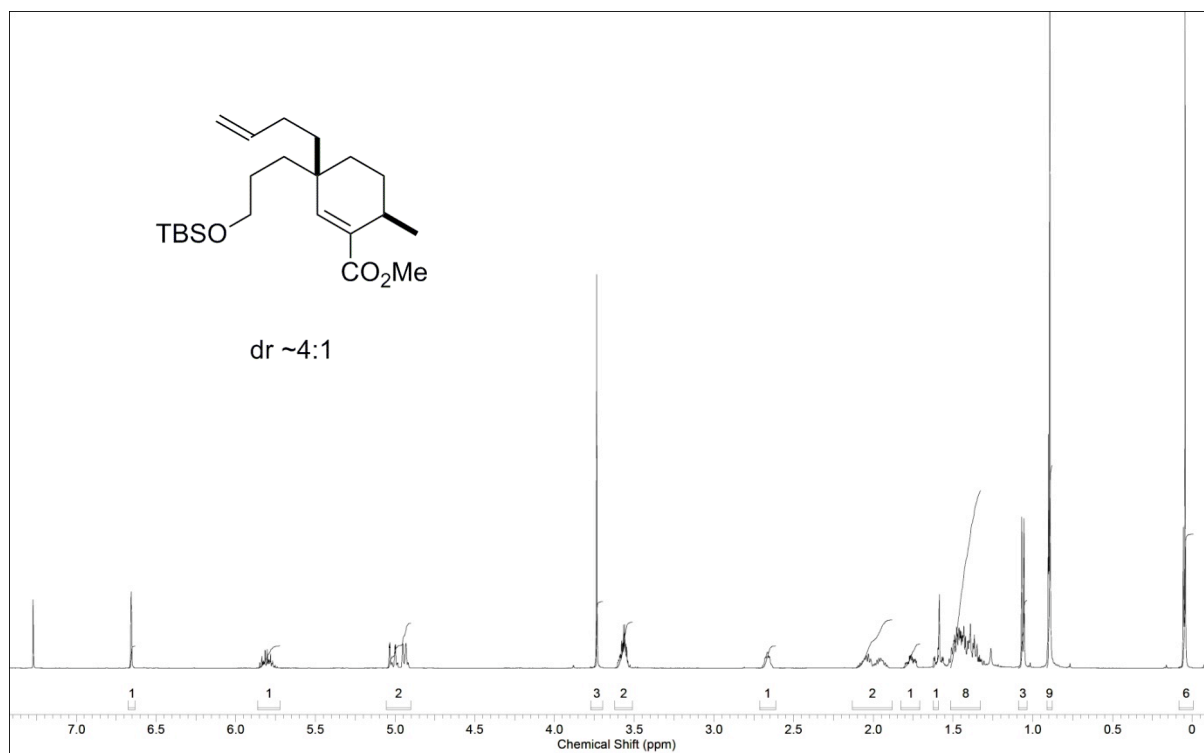
rac-(3*S*,6*R*)-methyl 3-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-6-methyl-3-vinylcyclohex-1-enecarboxylate, $^1\text{H-NMR}$ (500 MHz, CDCl_3):



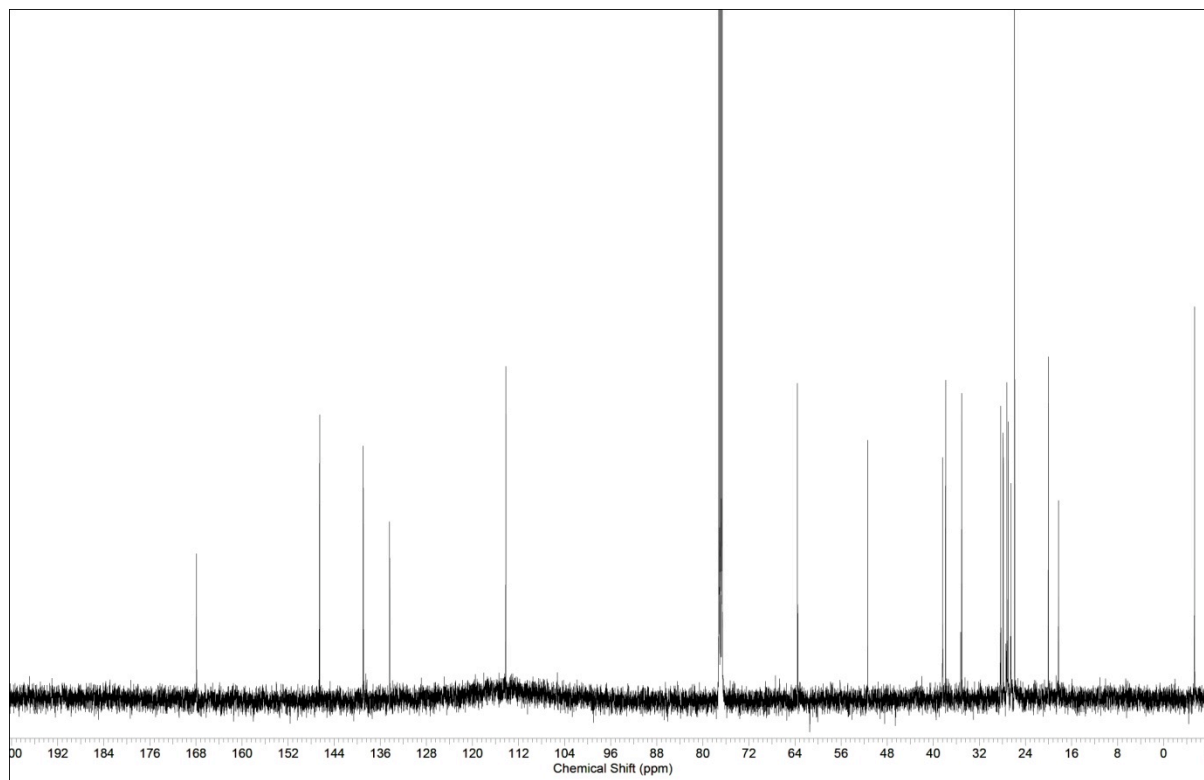
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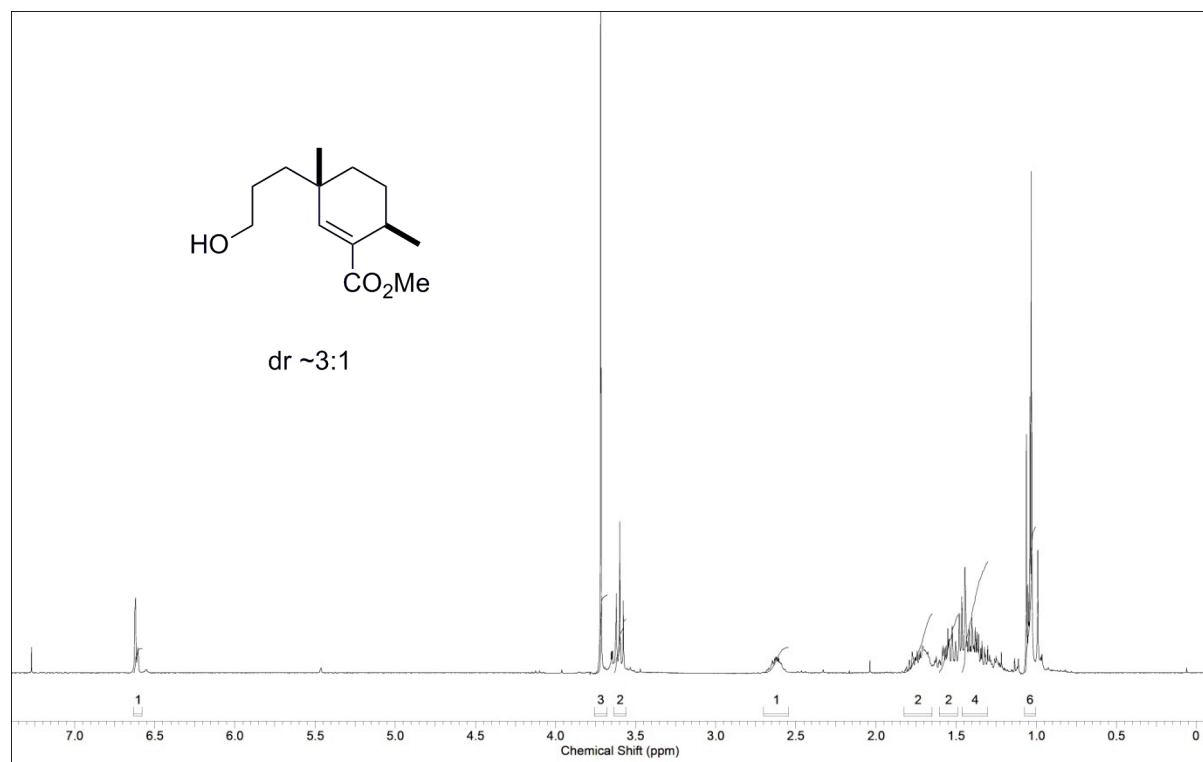
rac-(3*S*,6*R*)-methyl 3-(but-3-en-1-yl)-3-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-6-methylcyclohex-1-enecarboxylate, ¹H-NMR (500 MHz, CDCl₃):



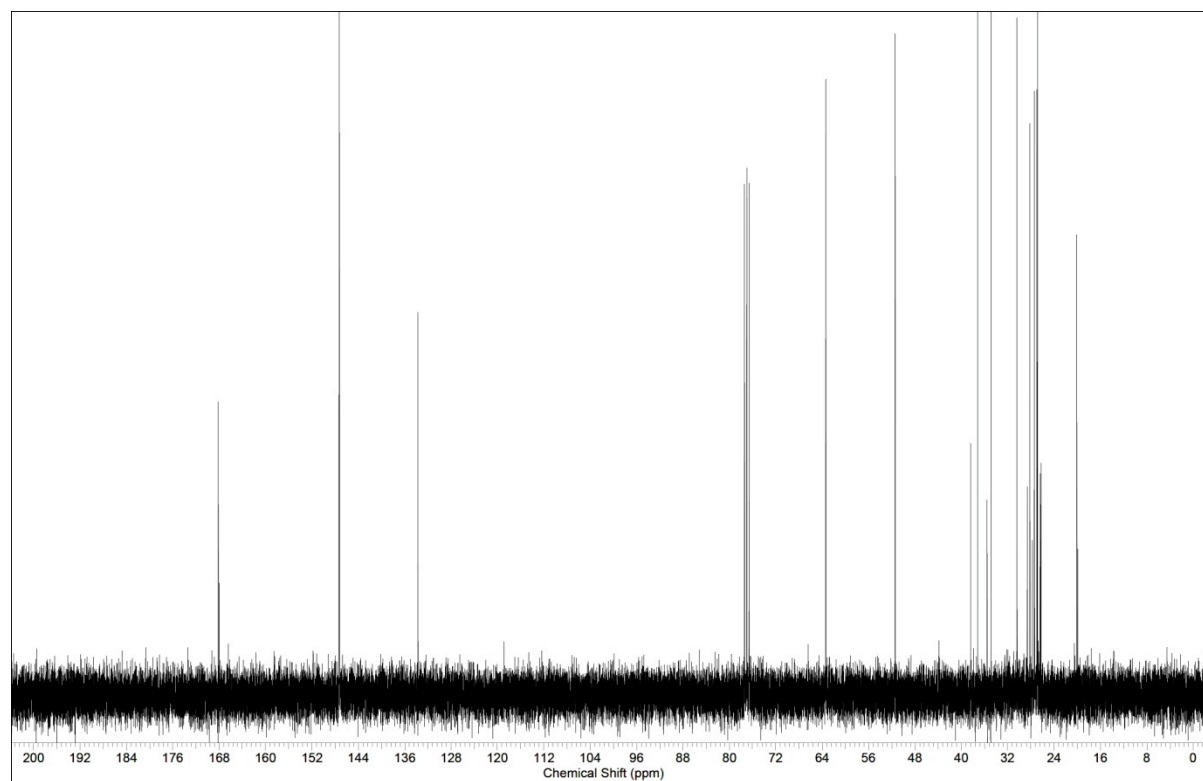
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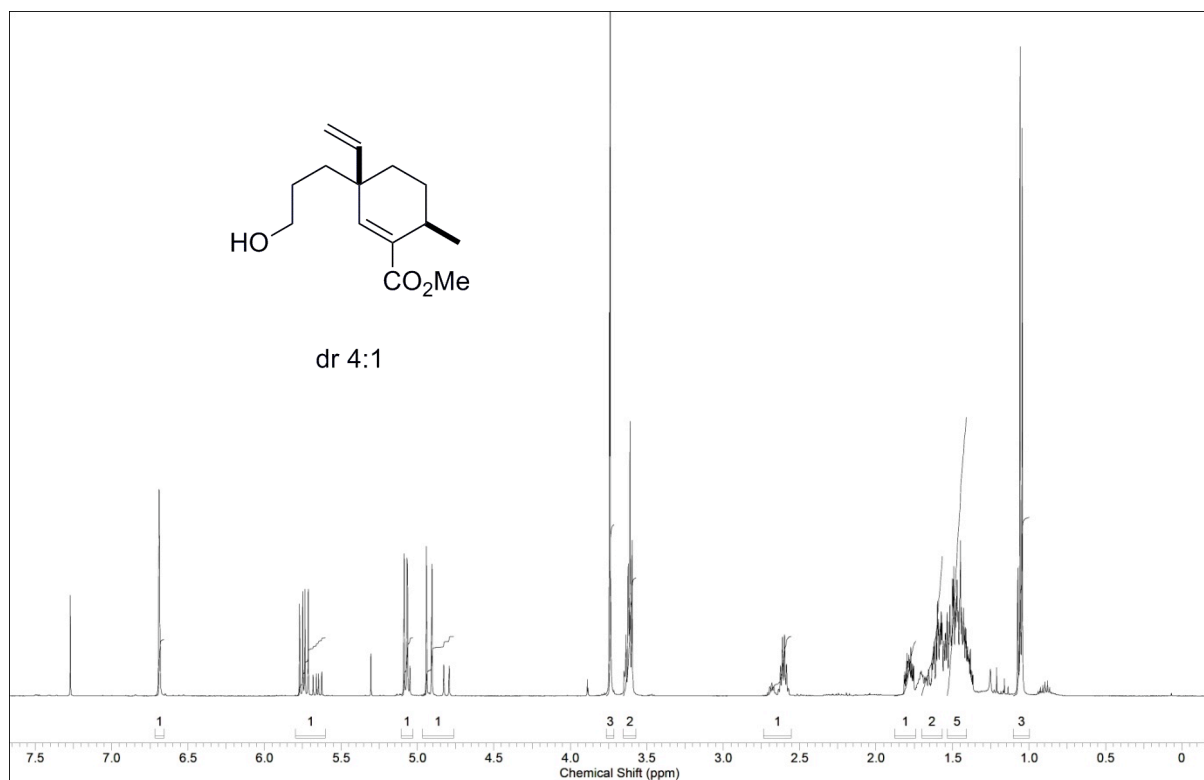
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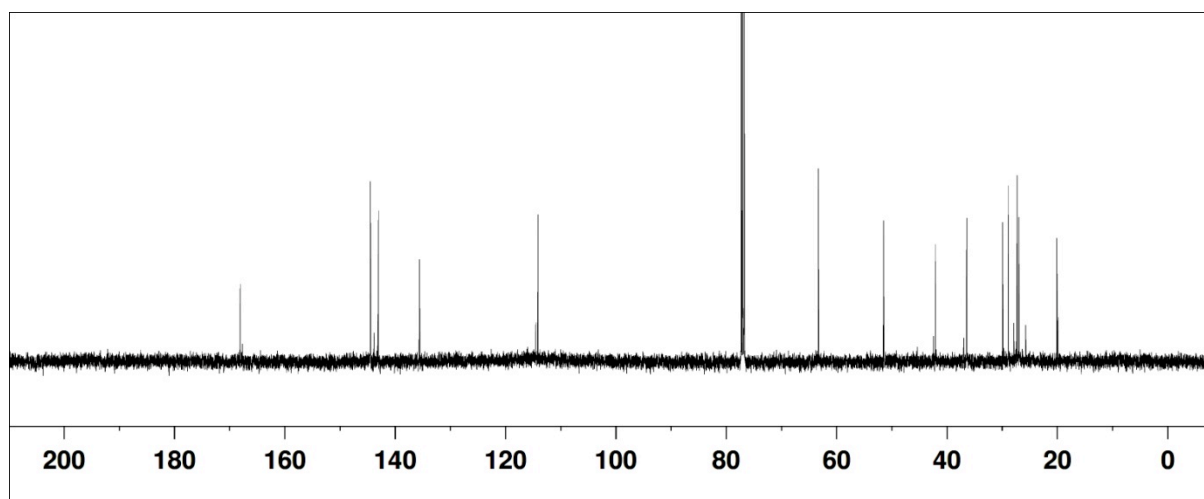
rac-(3*S*,6*R*)-methyl 3-(3-hydroxypropyl)-3,6-dimethylcyclohex-1-enecarboxylate, $^{13}\text{C-NMR}$ (75 MHz, CDCl_3):



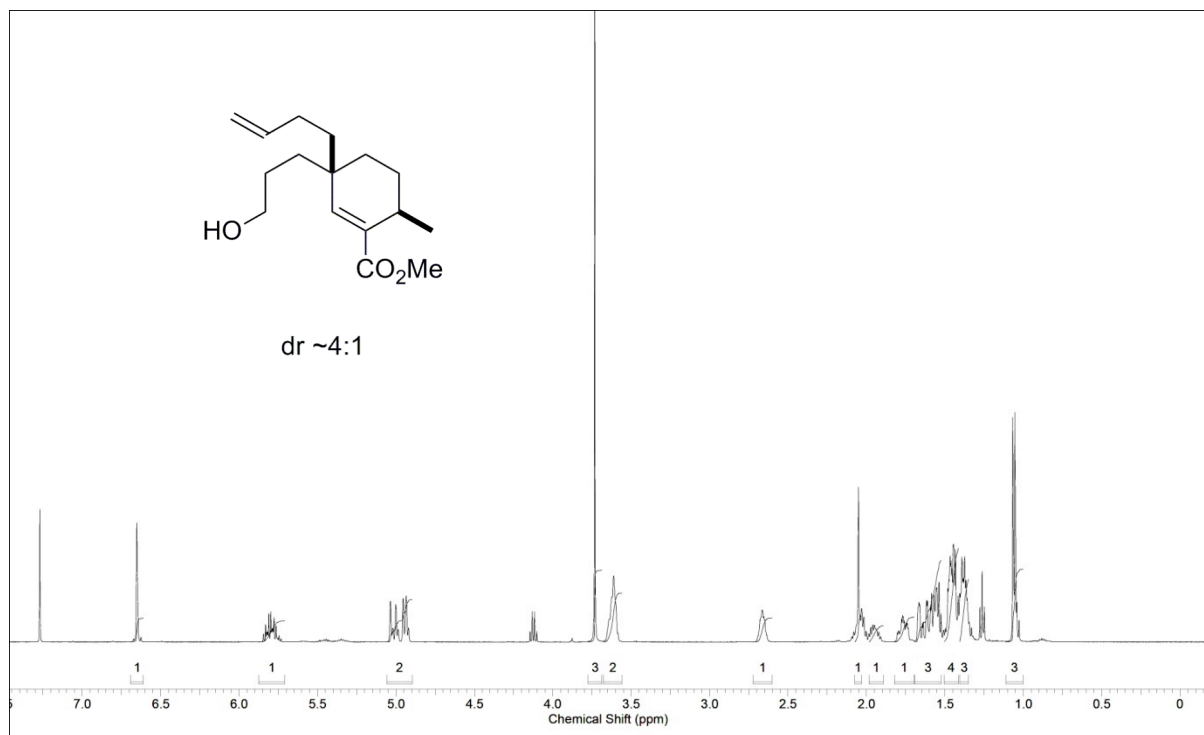
rac-(3*S*,6*R*)-methyl 3-(3-hydroxypropyl)-6-methyl-3-vinylcyclohex-1-enecarboxylate, ¹H-NMR (500 MHz, CDCl₃):



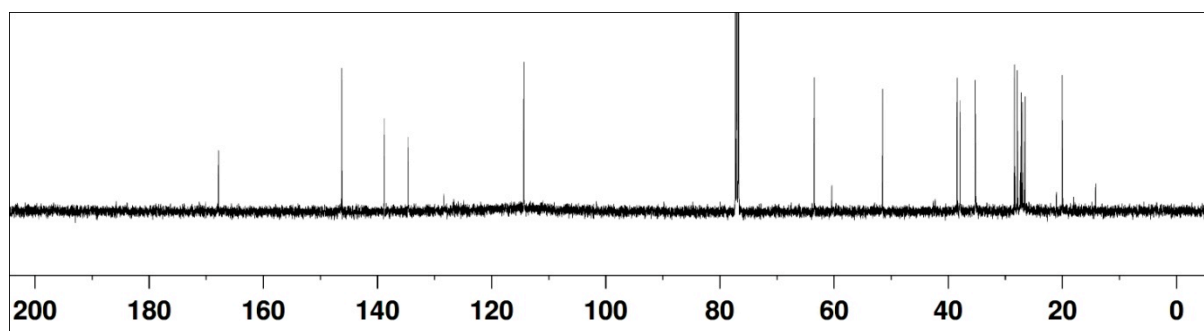
rac-(3*S*,6*R*)-methyl 3-(3-hydroxypropyl)-6-methyl-3-vinylcyclohex-1-enecarboxylate, ¹³C-NMR (125 MHz, CDCl₃):



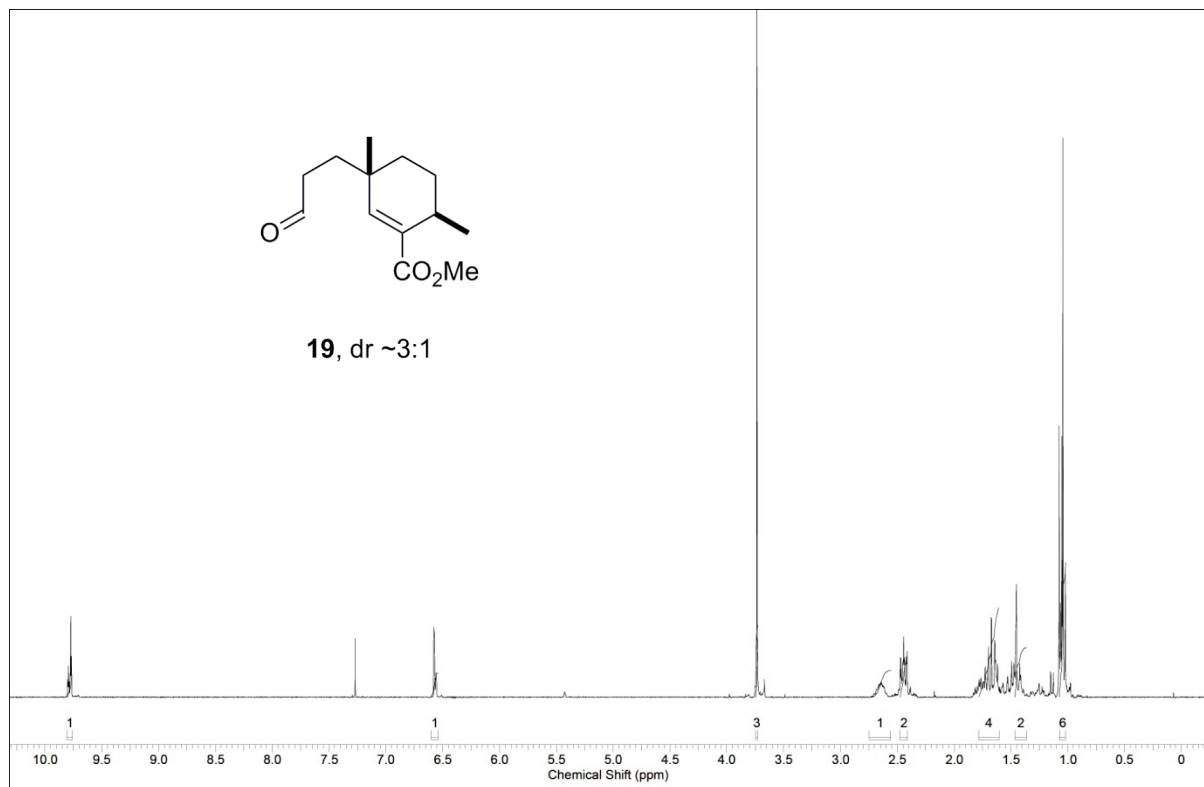
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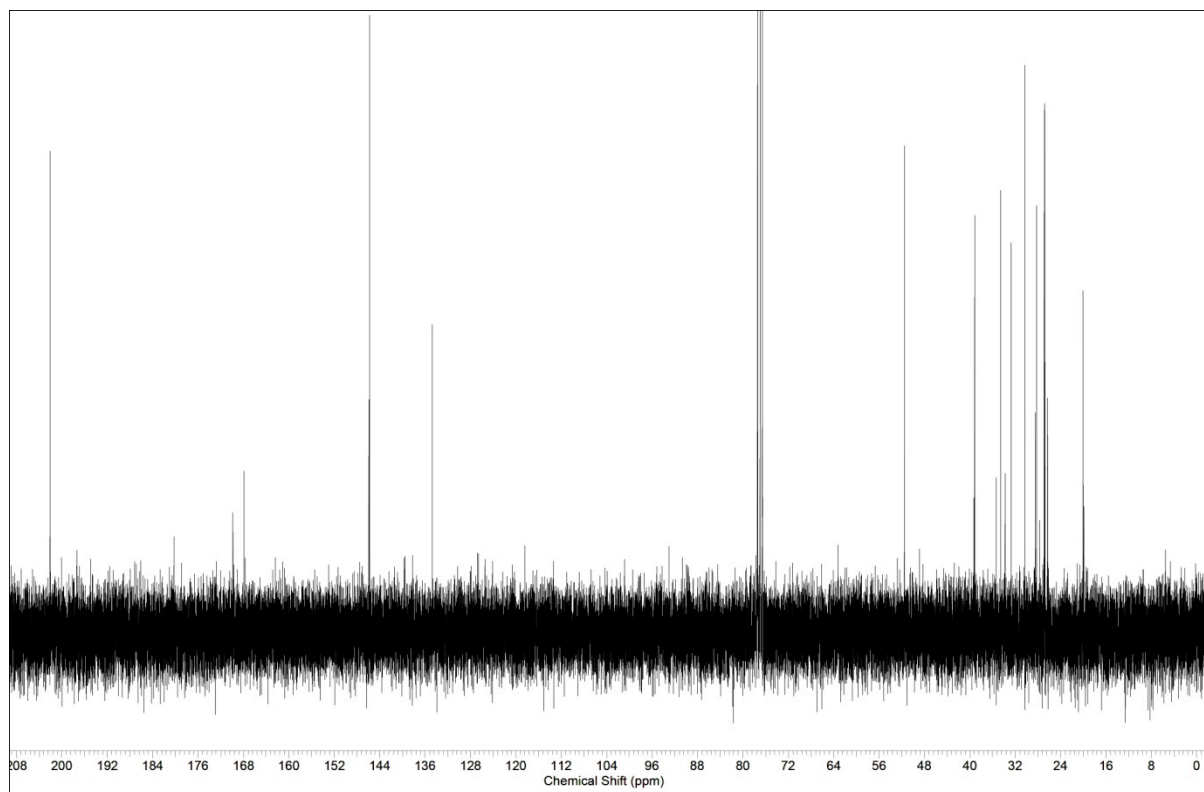
rac-(3*S*,6*R*)-methyl 3-(but-3-en-1-yl)-3-(3-hydroxypropyl)-6-methylcyclohex-1-enecarboxylate, ^{13}C -NMR (125 MHz, CDCl_3):



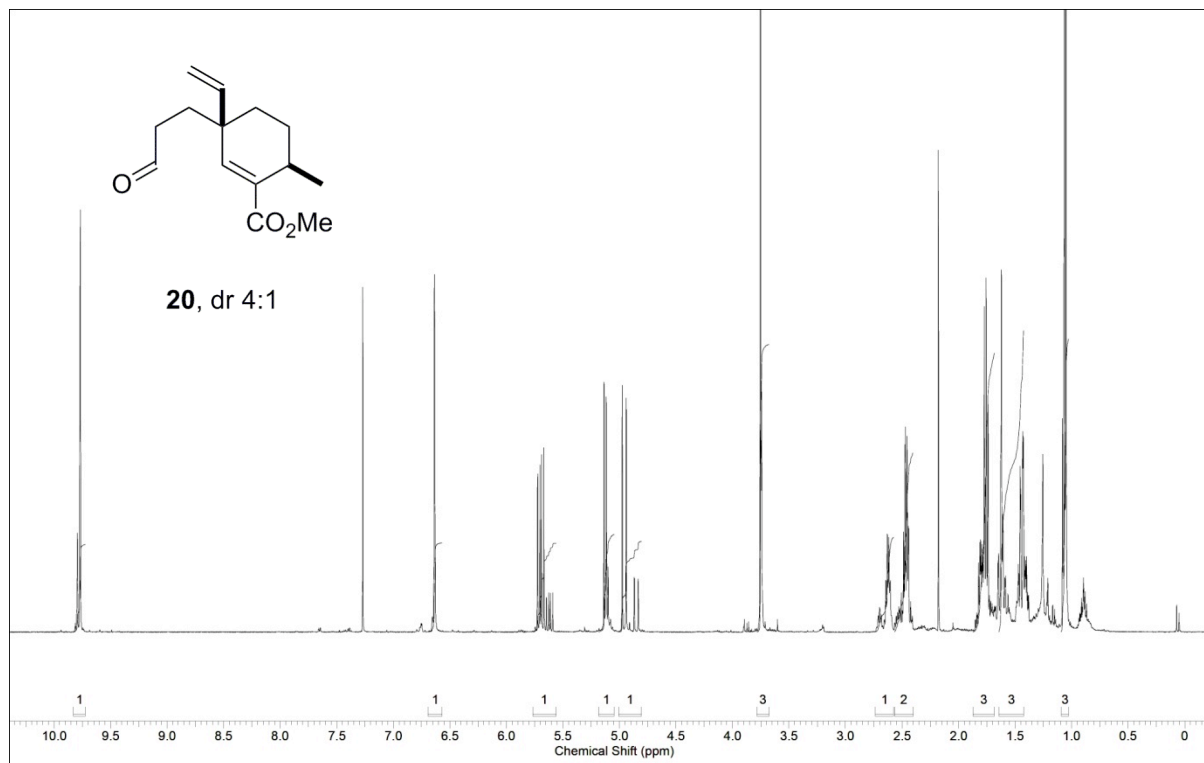
rac-(3*S*,6*R*)-methyl 3,6-dimethyl-3-(3-oxopropyl)cyclohex-1-enecarboxylate **19**, $^1\text{H-NMR}$ (300 MHz, CDCl_3):



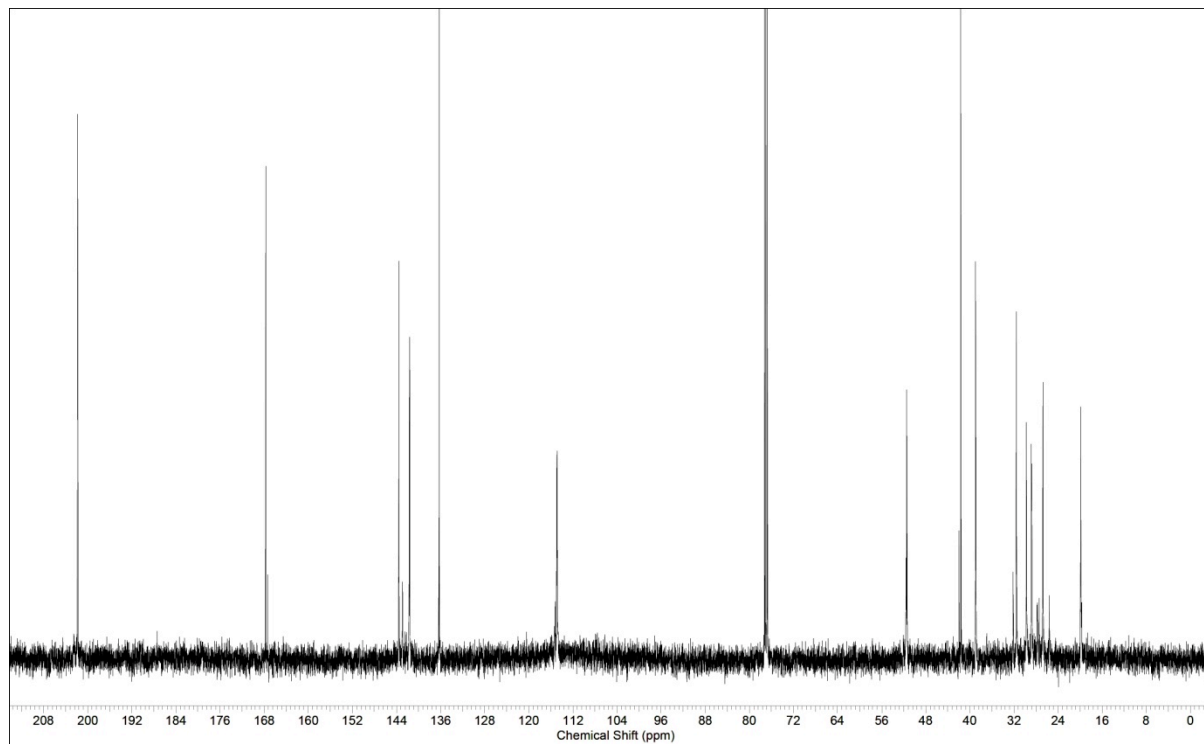
rac-(3*S*,6*R*)-methyl 3,6-dimethyl-3-(3-oxopropyl)cyclohex-1-enecarboxylate **19**, $^{13}\text{C-NMR}$ (75 MHz, CDCl_3):



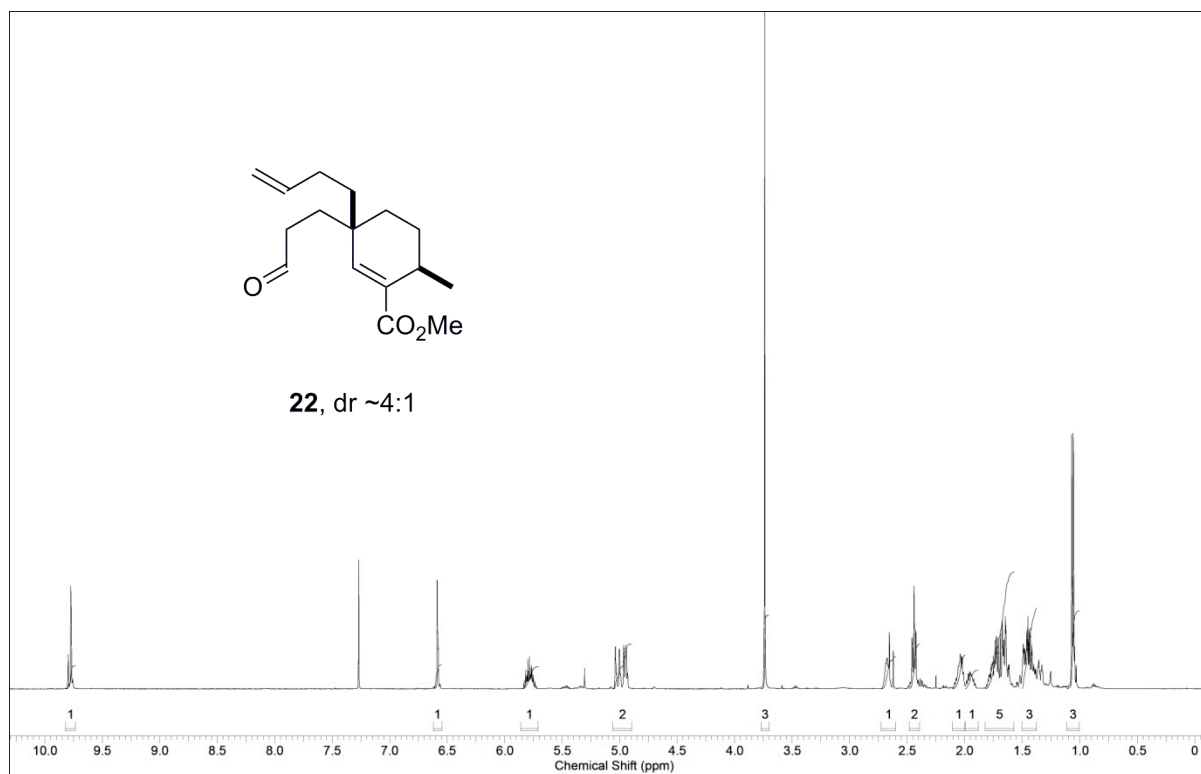
rac-(3*S*,6*R*)-methyl 6-methyl-3-(3-oxopropyl)-3-vinylcyclohex-1-enecarboxylate **20**, ¹H-NMR (500 MHz, CDCl₃):



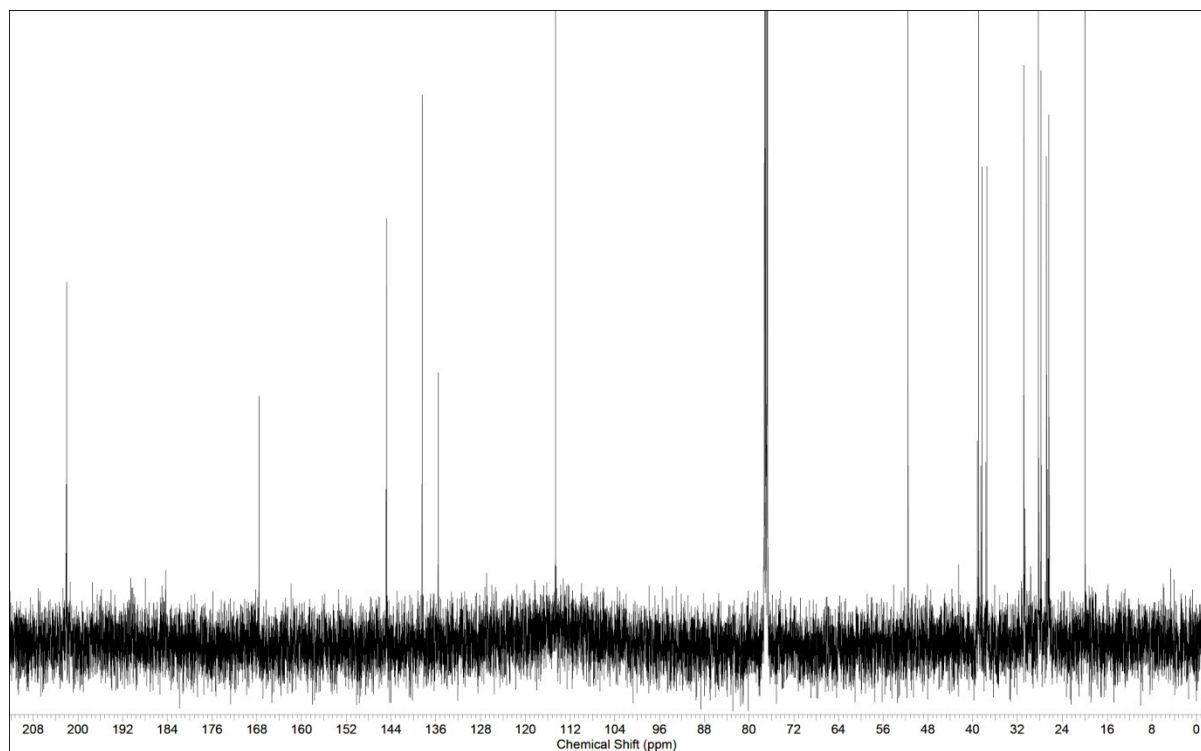
rac-(3*S*,6*R*)-methyl 6-methyl-3-(3-oxopropyl)-3-vinylcyclohex-1-enecarboxylate **20**, ¹³C-NMR (125 MHz, CDCl₃):



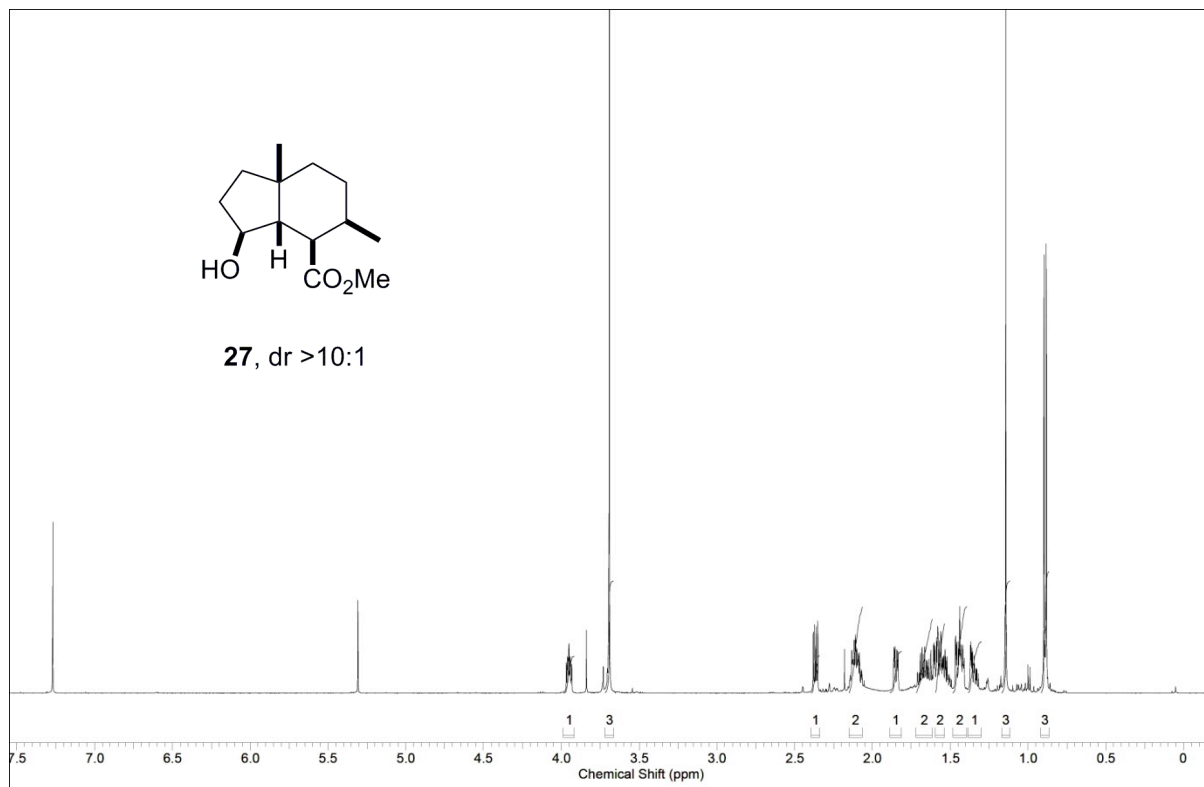
rac-(3*S*,6*R*)-methyl 3-(but-3-en-1-yl)-6-methyl-3-(3-oxopropyl)cyclohex-1-enecarboxylate **22**, ¹H-NMR (500 MHz, CDCl₃):



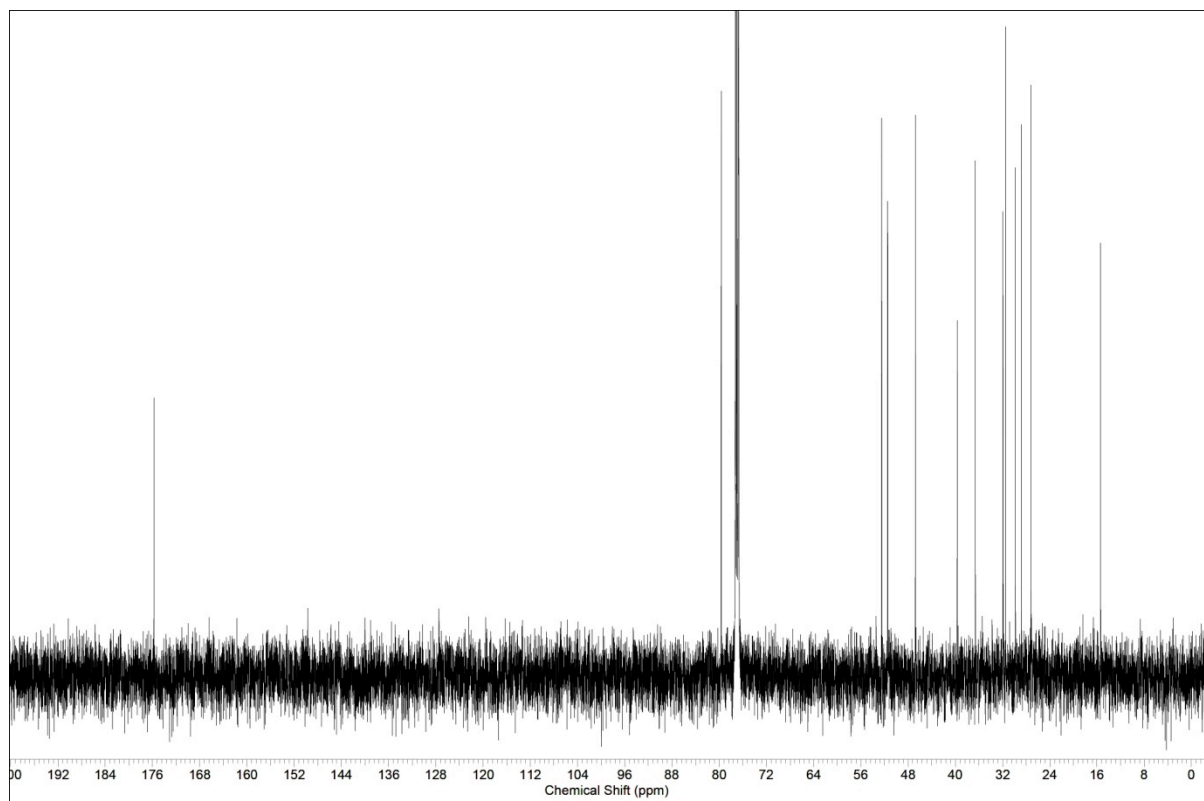
rac-(3*S*,6*R*)-methyl 3-(but-3-en-1-yl)-6-methyl-3-(3-oxopropyl)cyclohex-1-enecarboxylate **22**, ¹³C-NMR (125 MHz, CDCl₃):



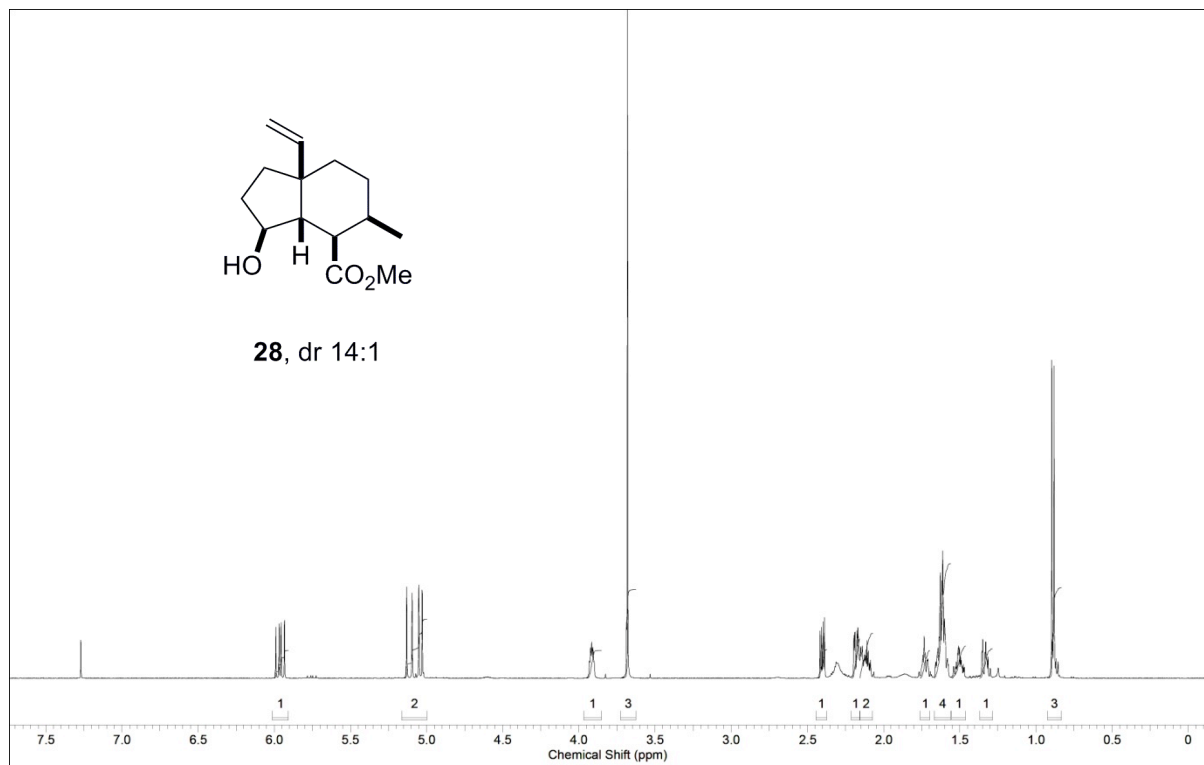
rac-(3*S*,3*aS*,4*R*,5*R*,7*aS*)-methyl 3-hydroxy-5,7*a*-dimethyloctahydro-1*H*-indene-4-carboxylate **27**, ¹H-NMR (500 MHz, CDCl₃):



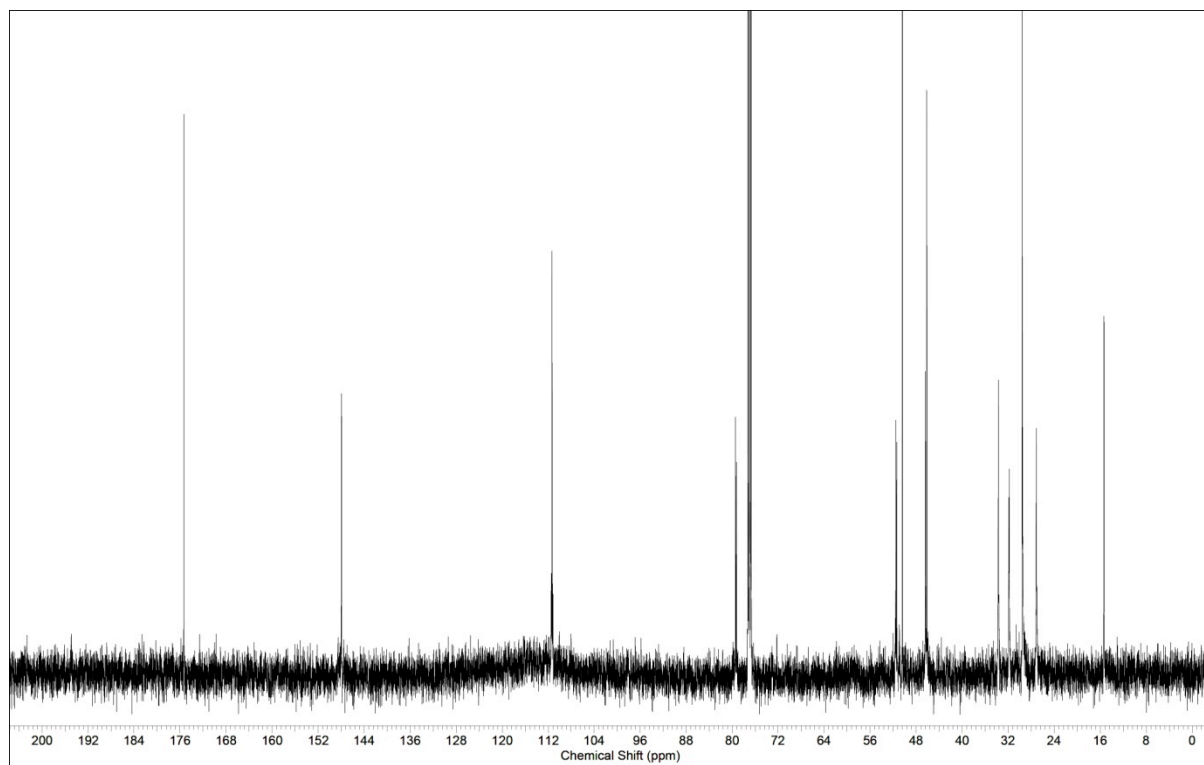
rac-(3*S*,3*aS*,4*R*,5*R*,7*aS*)-methyl 3-hydroxy-5,7*a*-dimethyloctahydro-1*H*-indene-4-carboxylate **27**, ¹³C-NMR (125 MHz, CDCl₃):



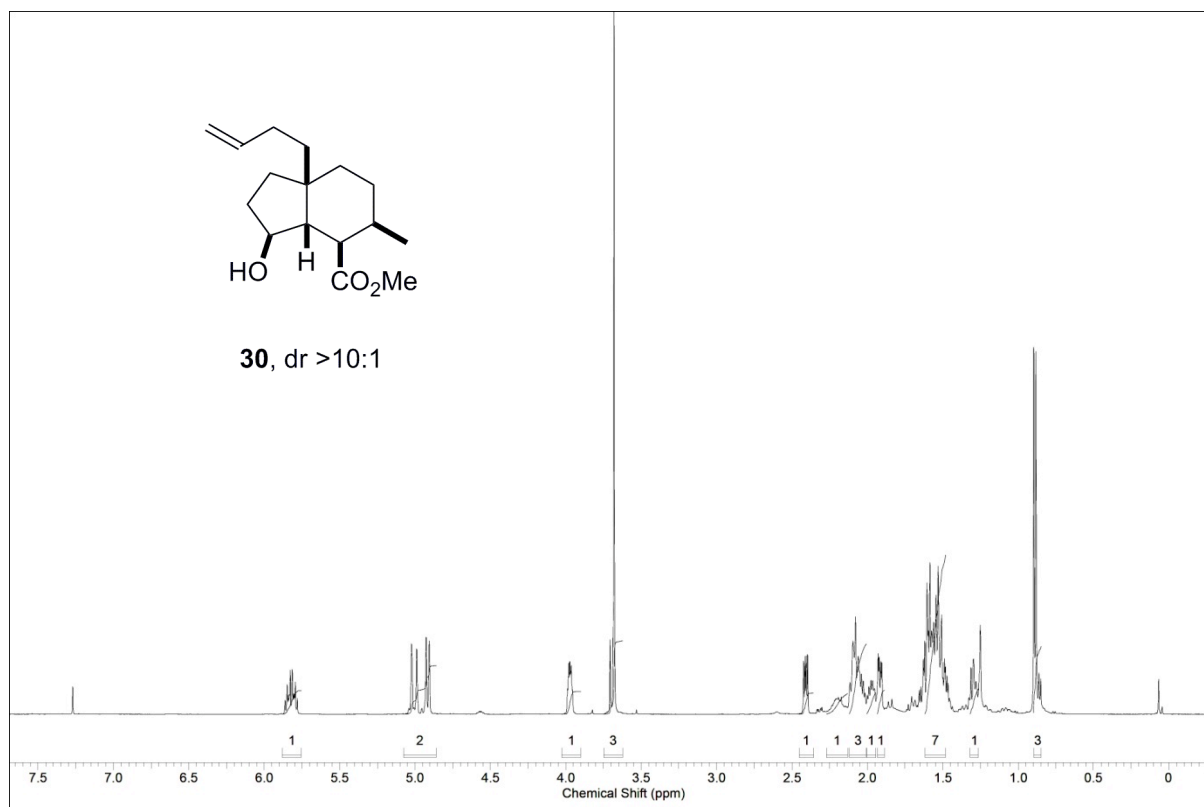
rac-(3*S*,3*aS*,4*R*,5*R*,7*aS*)-methyl 3-hydroxy-5-methyl-7*a*-vinyl-octahydro-1*H*-indene-4-carboxylate **28**,
¹H-NMR (300 MHz, CDCl₃):



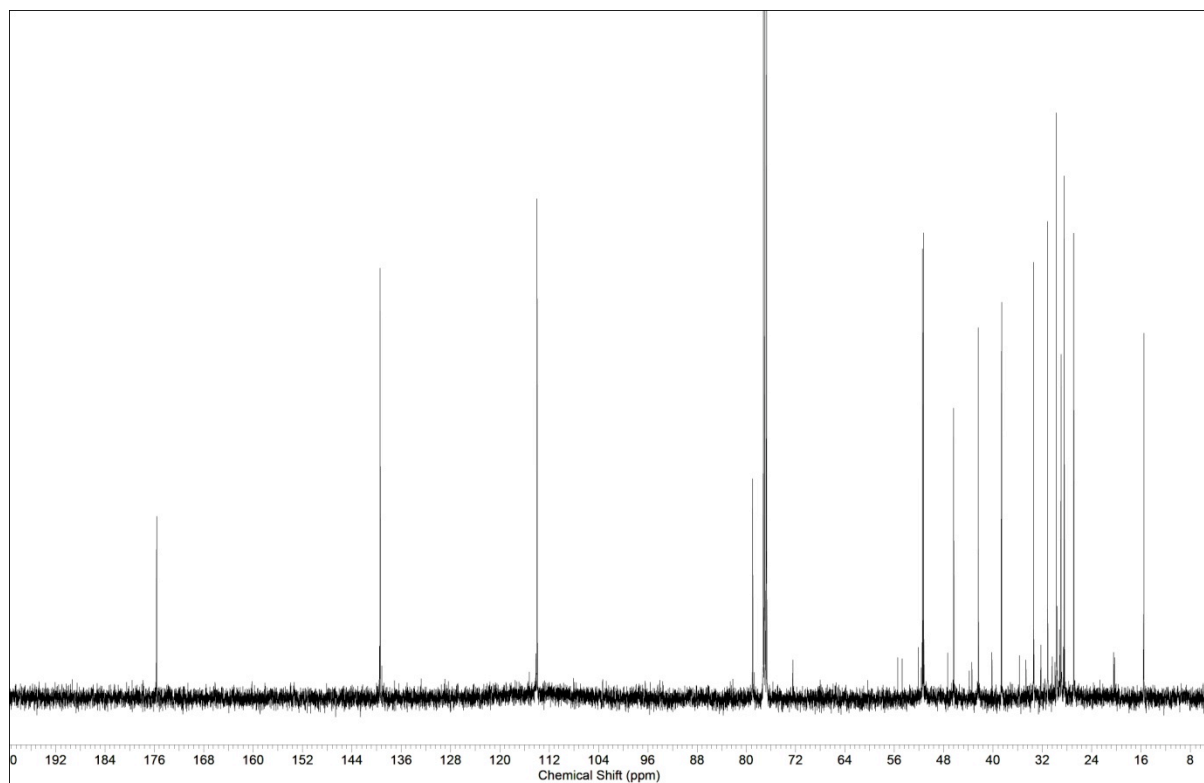
rac-(3*S*,3*aS*,4*R*,5*R*,7*aS*)-methyl 3-hydroxy-5-methyl-7*a*-vinyl-octahydro-1*H*-indene-4-carboxylate **28**,
¹³C-NMR (75 MHz, CDCl₃):



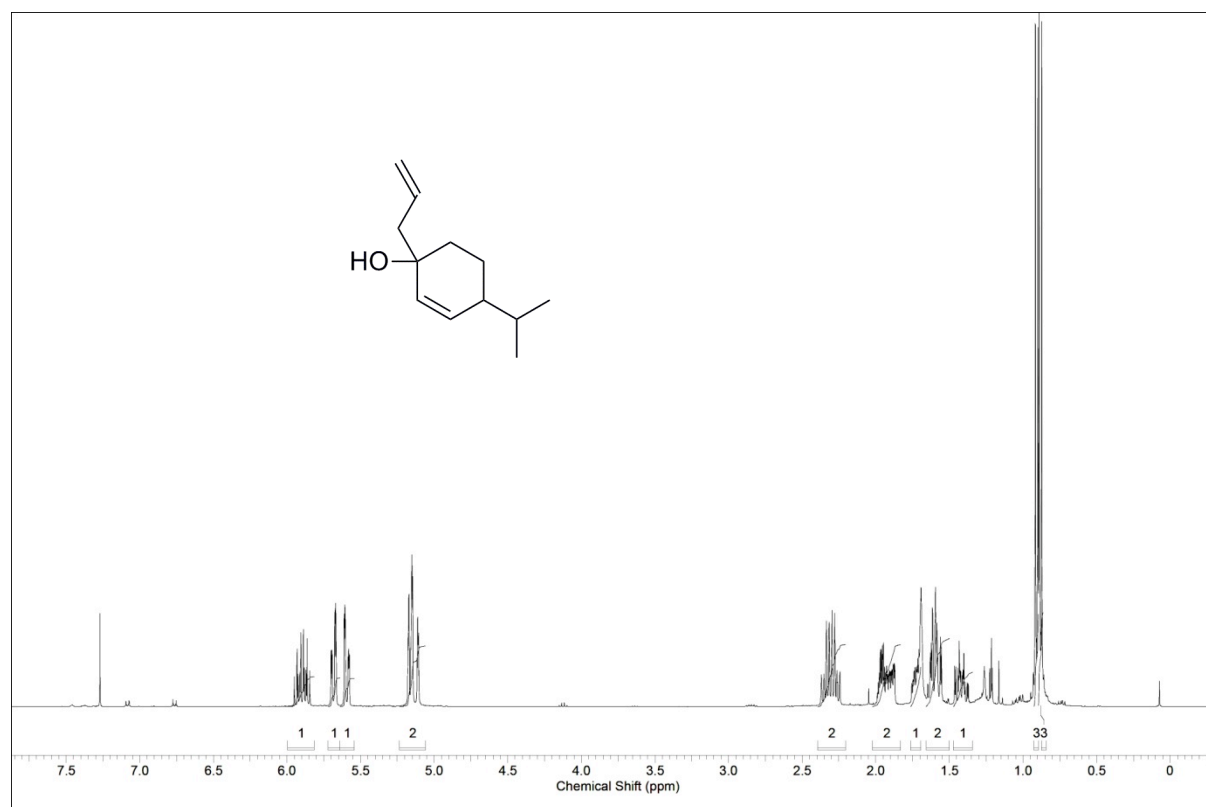
rac-(3*S*,3*aS*,4*R*,5*R*,7*aS*)-methyl 7*a*-(but-3-en-1-yl)-3-hydroxy-5-methyloctahydro-1*H*-indene-4-carboxylate **30**, ¹H-NMR (500 MHz, CDCl₃):



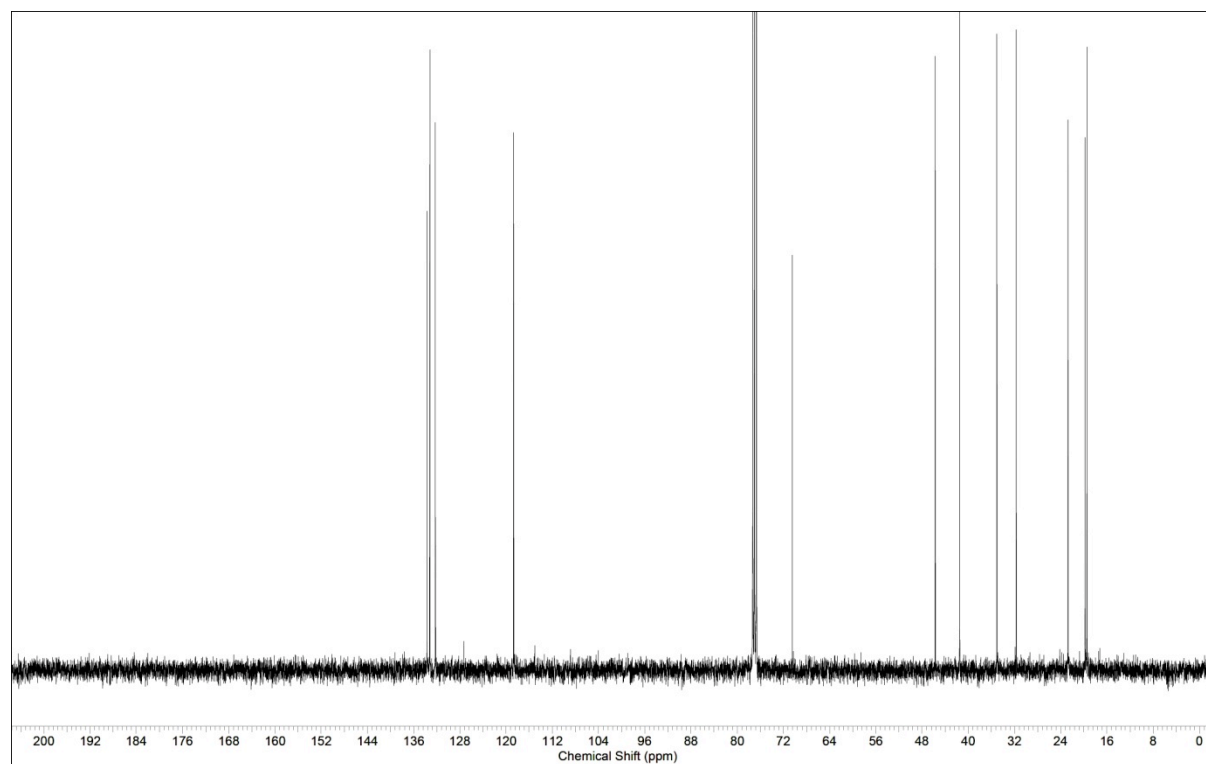
rac-(3*S*,3*aS*,4*R*,5*R*,7*aS*)-methyl 7*a*-(but-3-en-1-yl)-3-hydroxy-5-methyloctahydro-1*H*-indene-4-carboxylate **30**, ¹³C-NMR (125 MHz, CDCl₃):



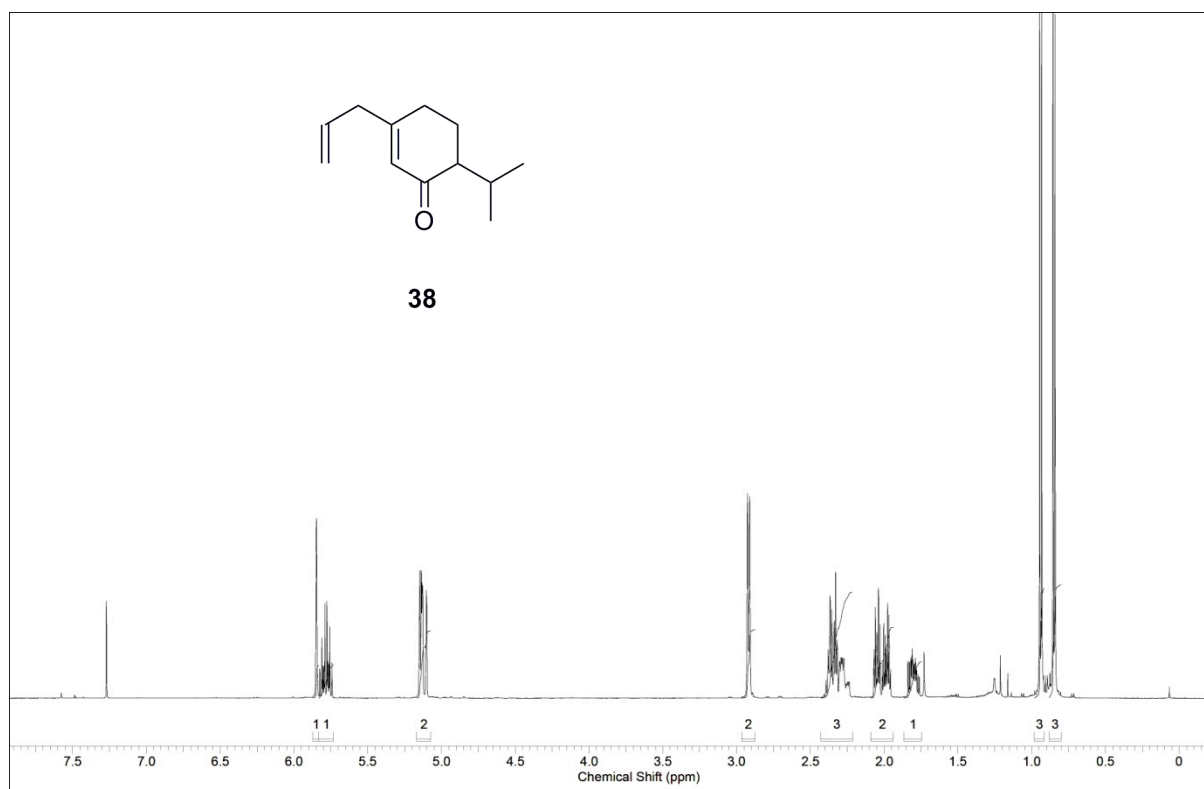
1-allyl-4-isopropylcyclohex-2-enol, $^1\text{H-NMR}$ (400 MHz, CDCl_3):



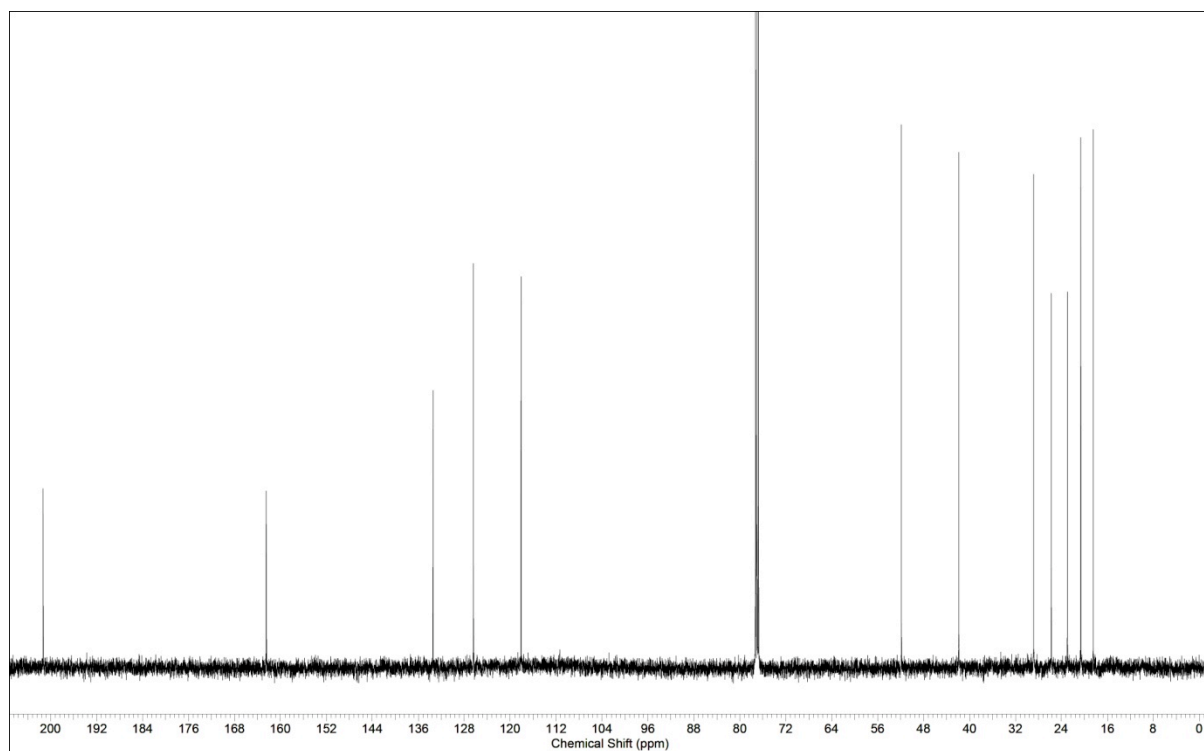
1-allyl-4-isopropylcyclohex-2-enol, $^{13}\text{C-NMR}$ (100 MHz, CDCl_3):



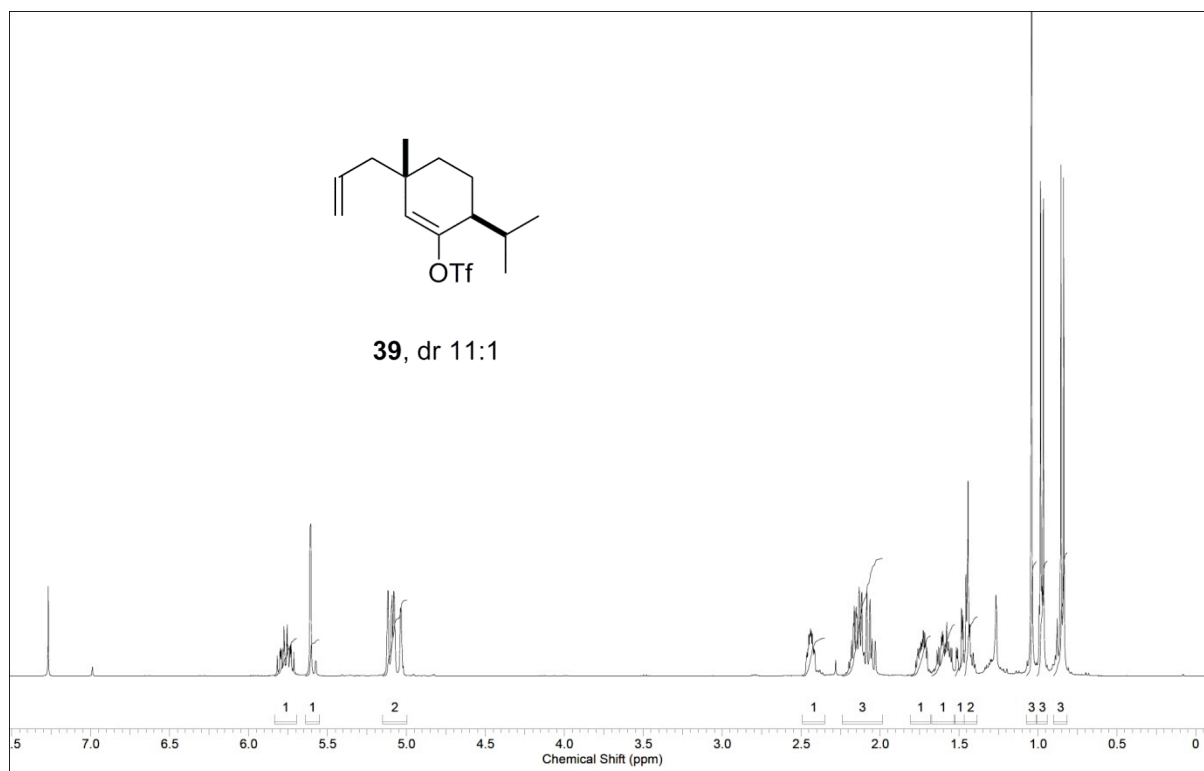
3-allyl-6-isopropylcyclohex-2-enone **38**, $^1\text{H-NMR}$ (400 MHz, CDCl_3):



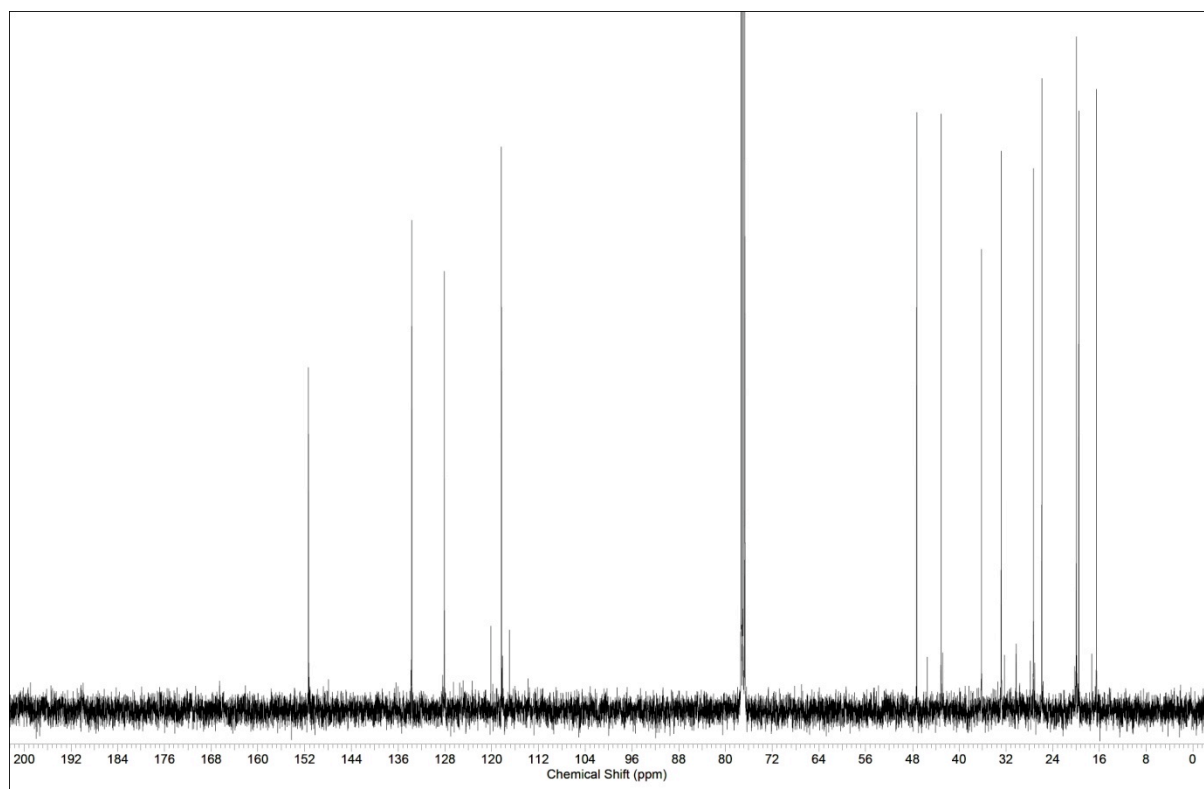
3-allyl-6-isopropylcyclohex-2-enone **38**, $^{13}\text{C-NMR}$ (100 MHz, CDCl_3):



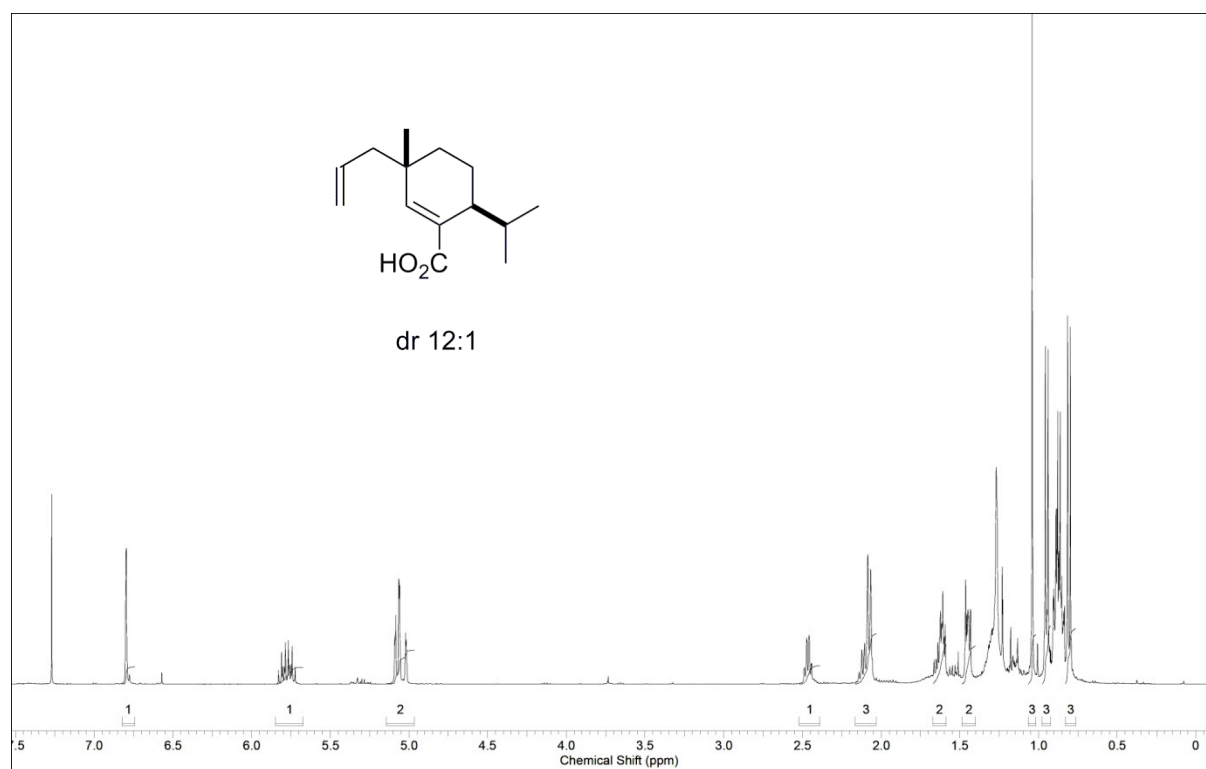
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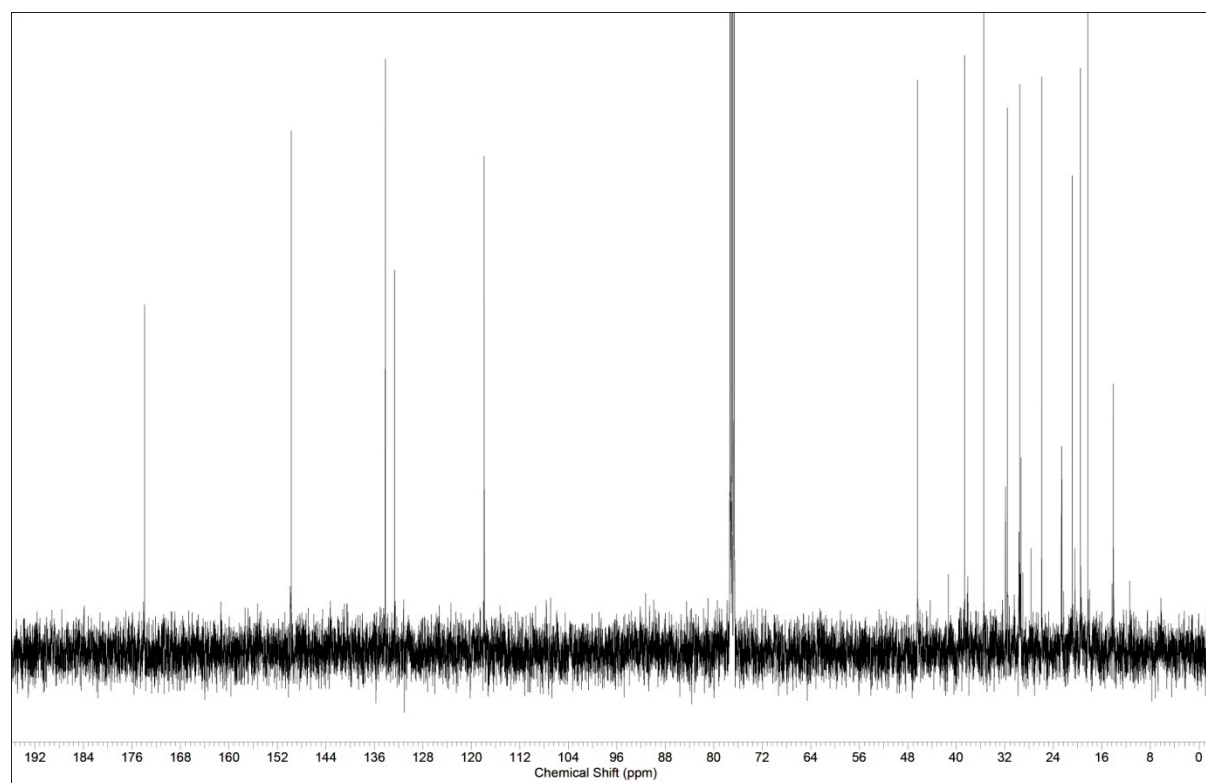
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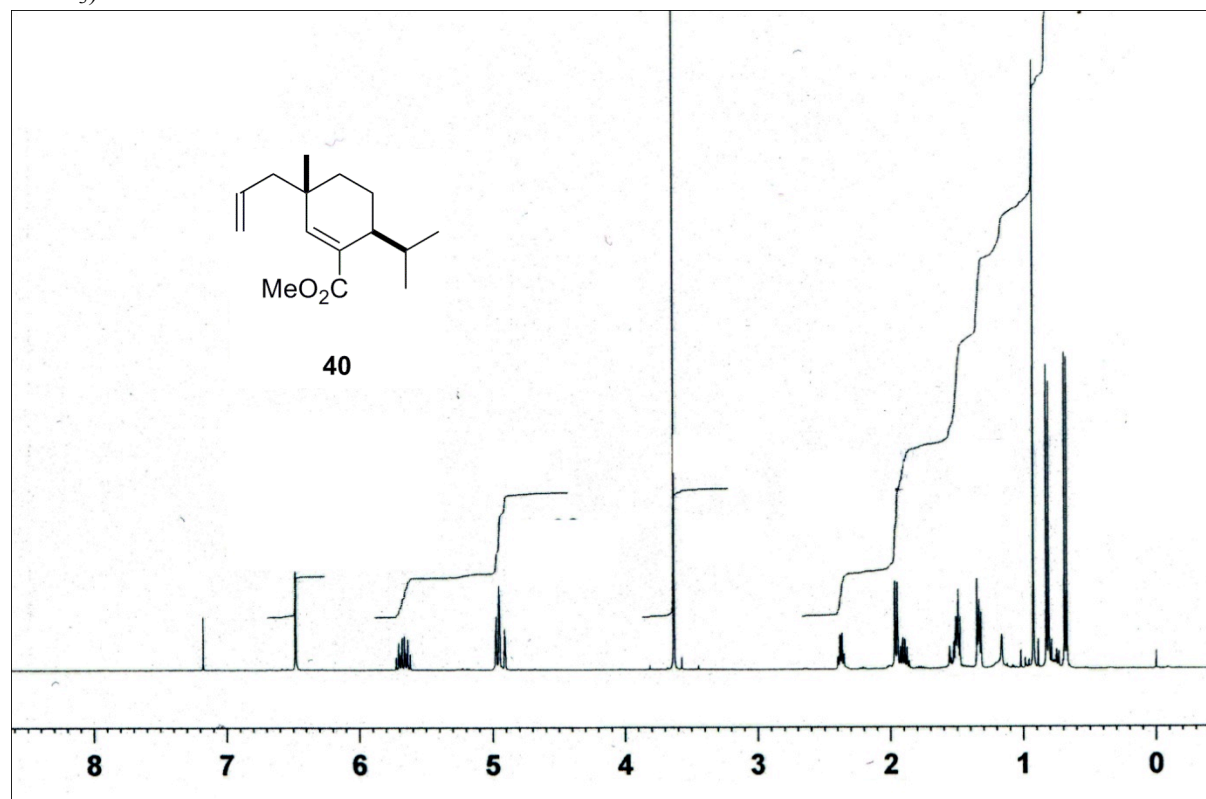
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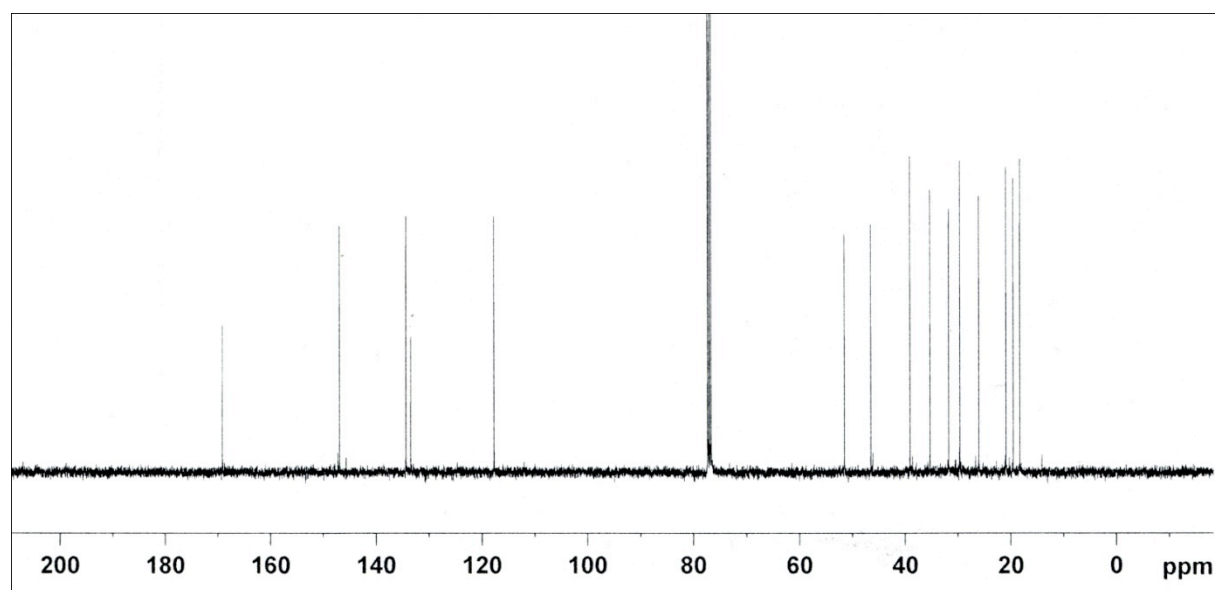
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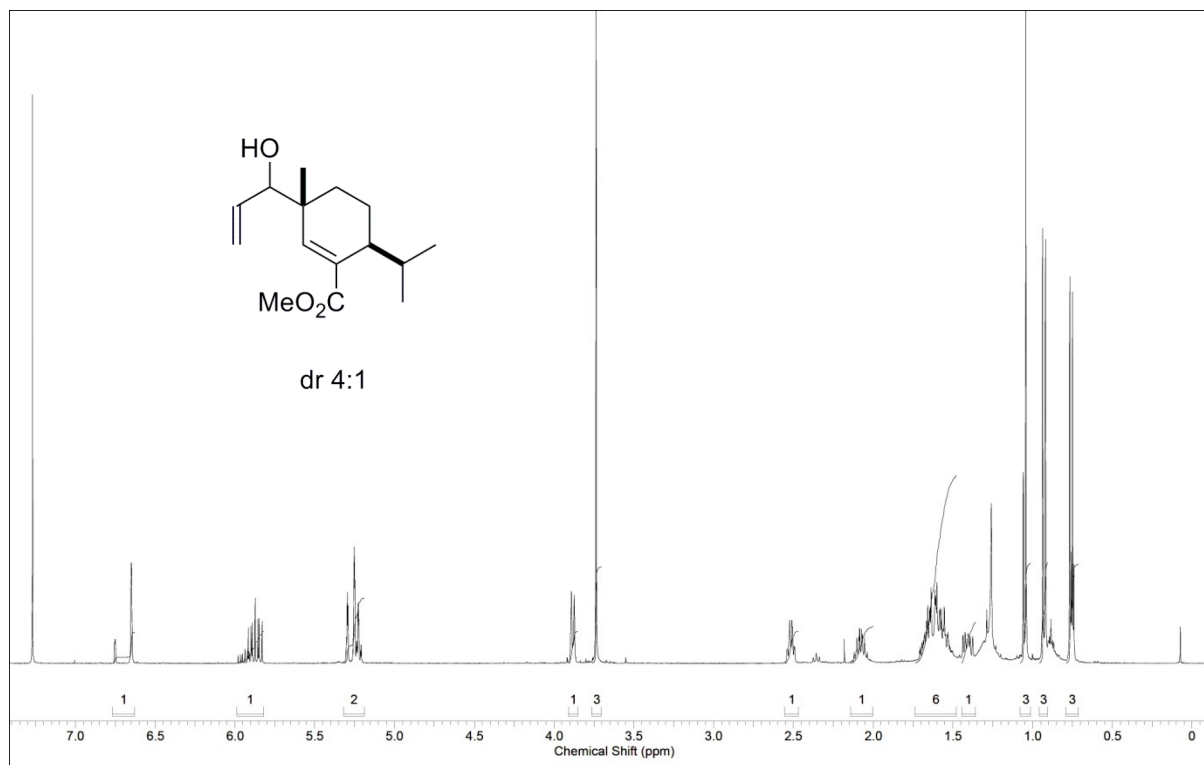
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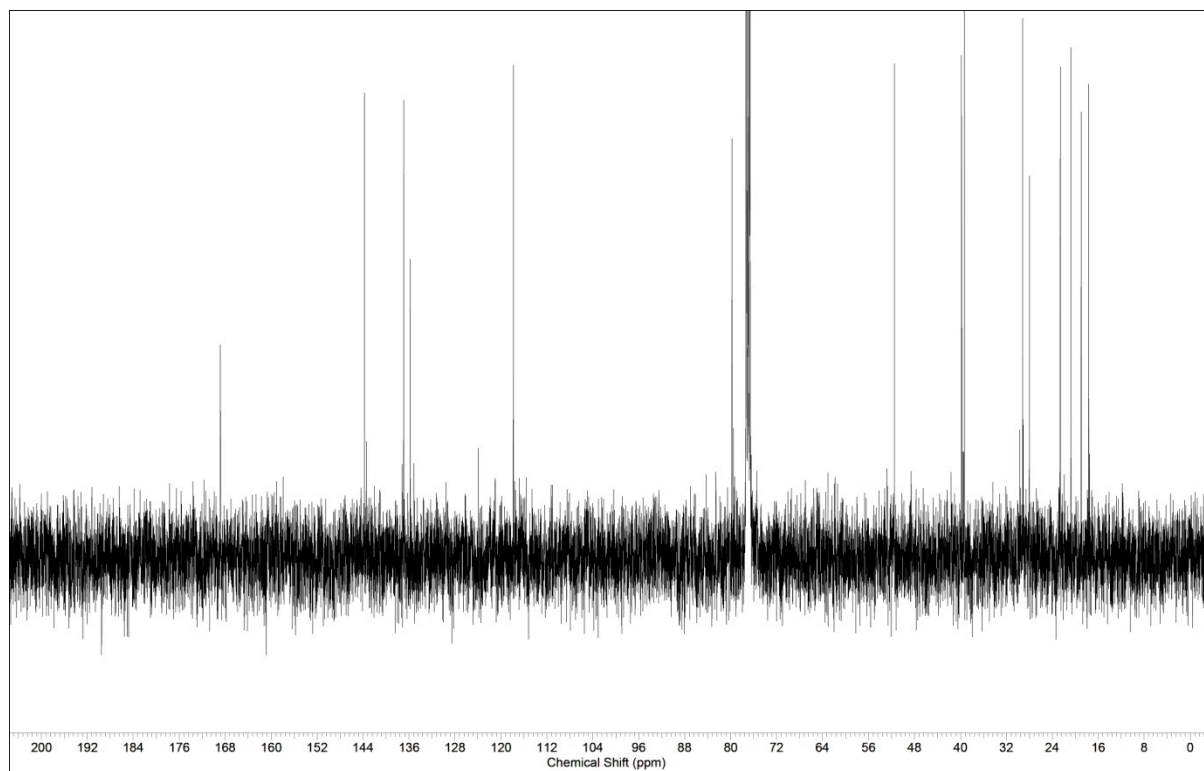
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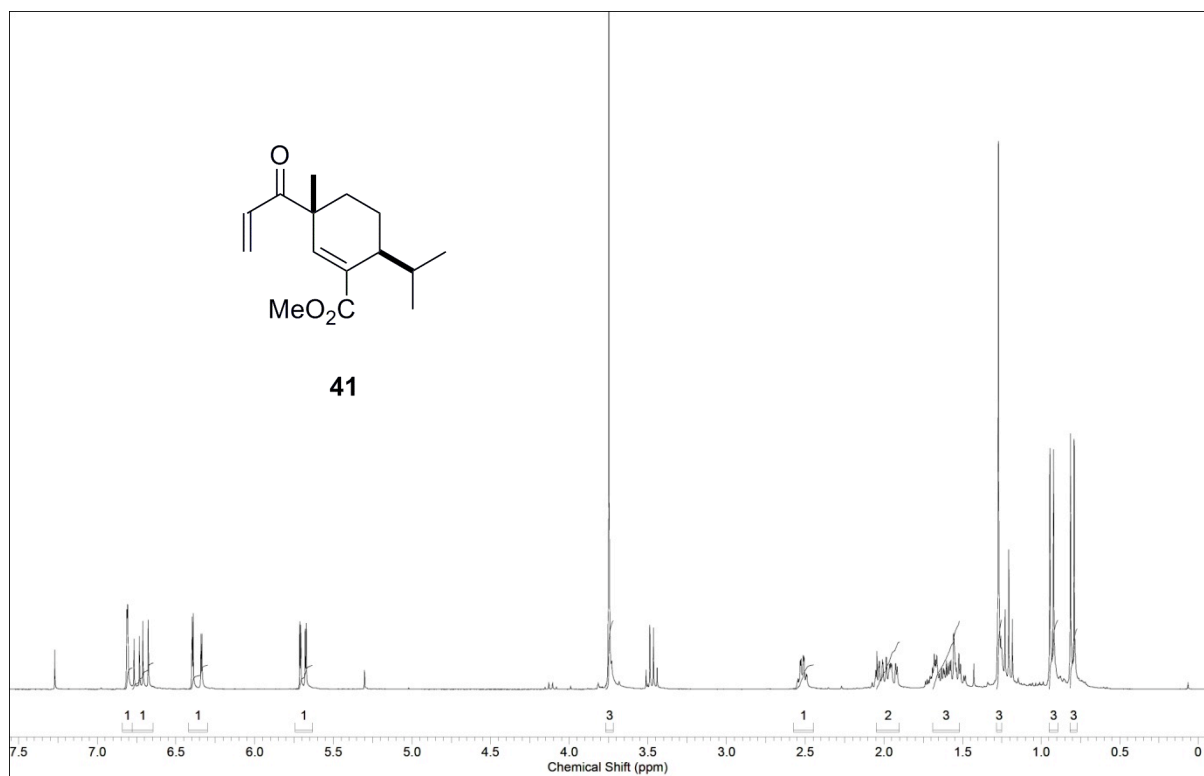
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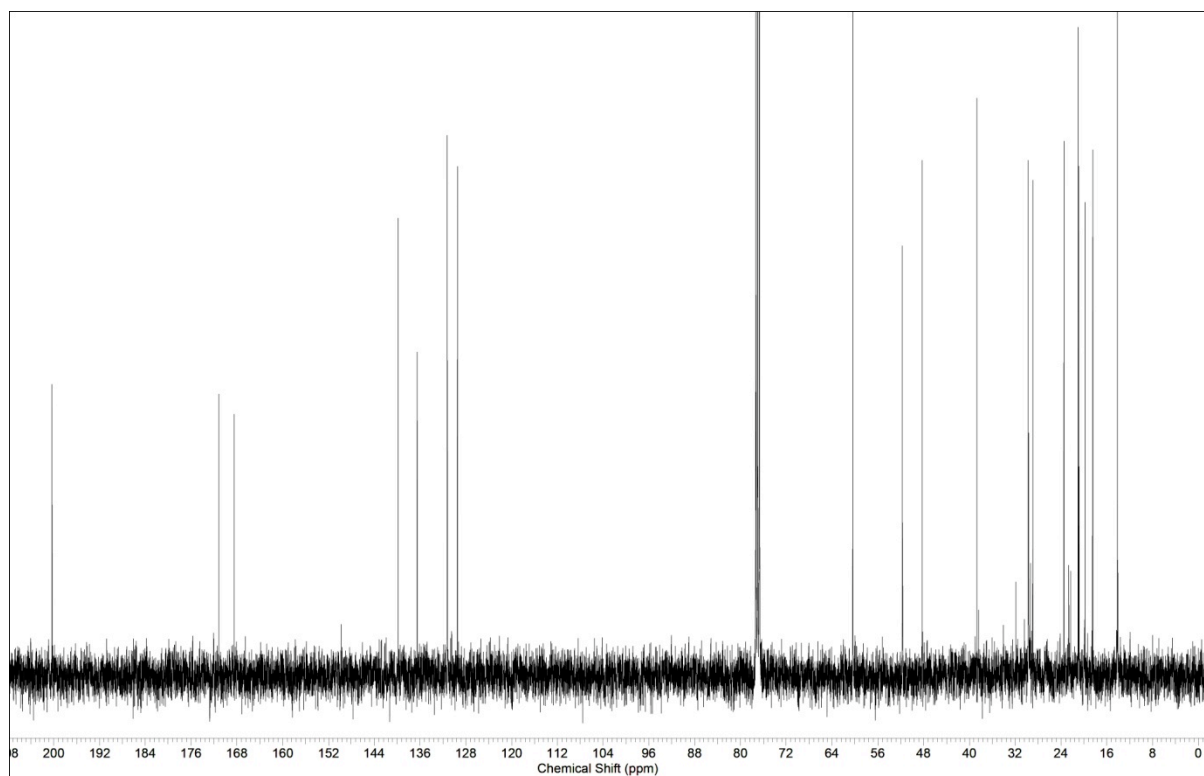
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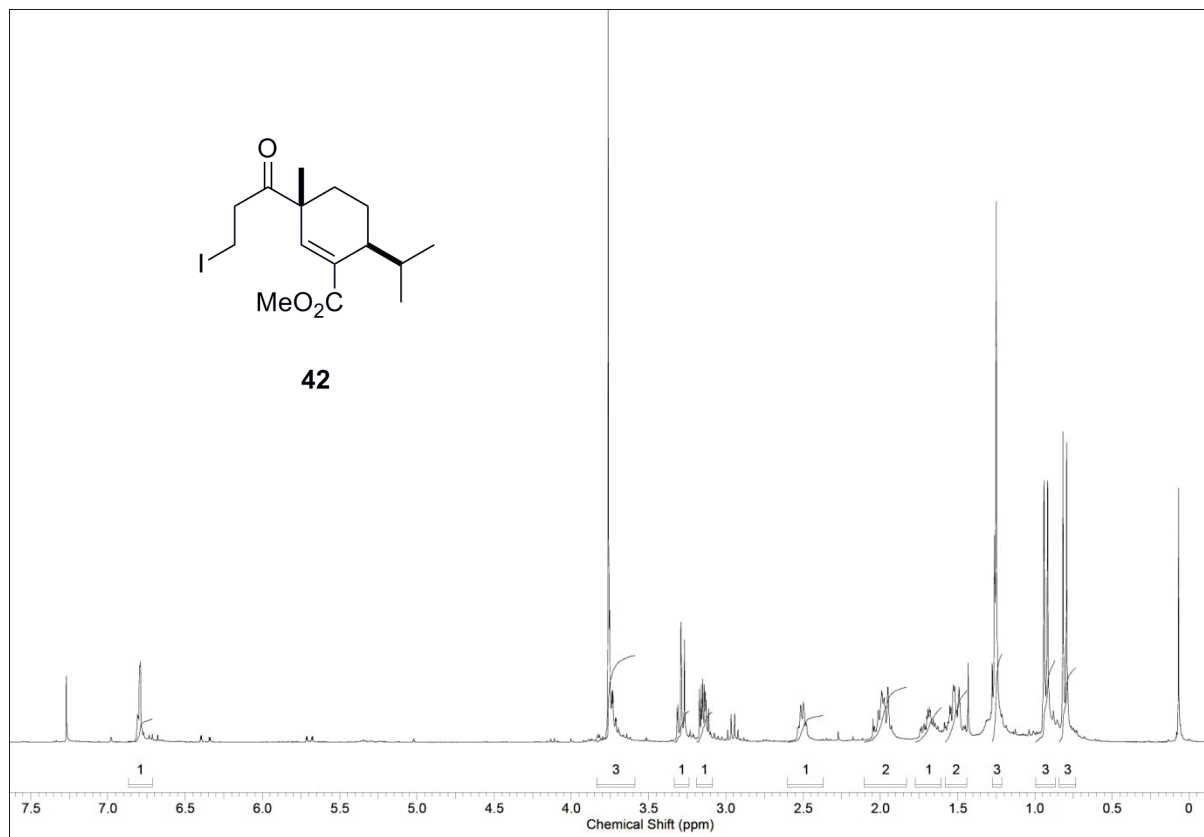
rac-(3*R*,6*S*)-methyl 3-acryloyl-6-isopropyl-3-methylcyclohex-1-enecarboxylate **41**, $^1\text{H-NMR}$ (300 MHz, CDCl_3):



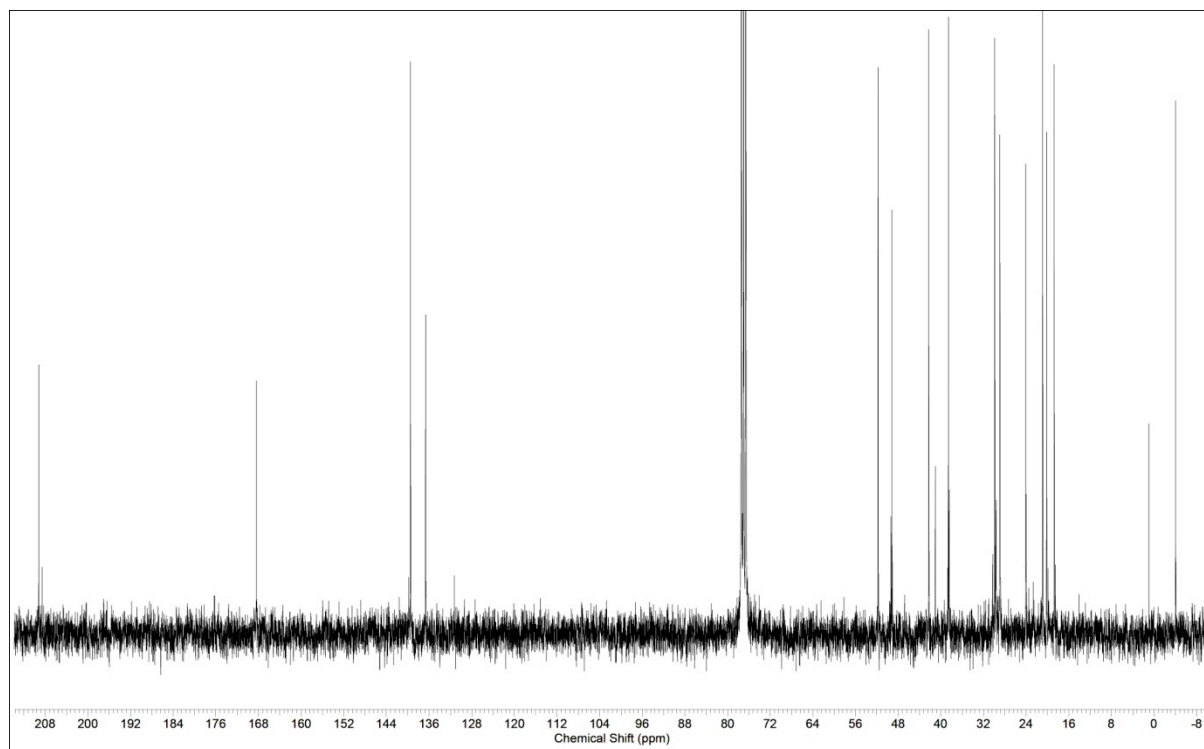
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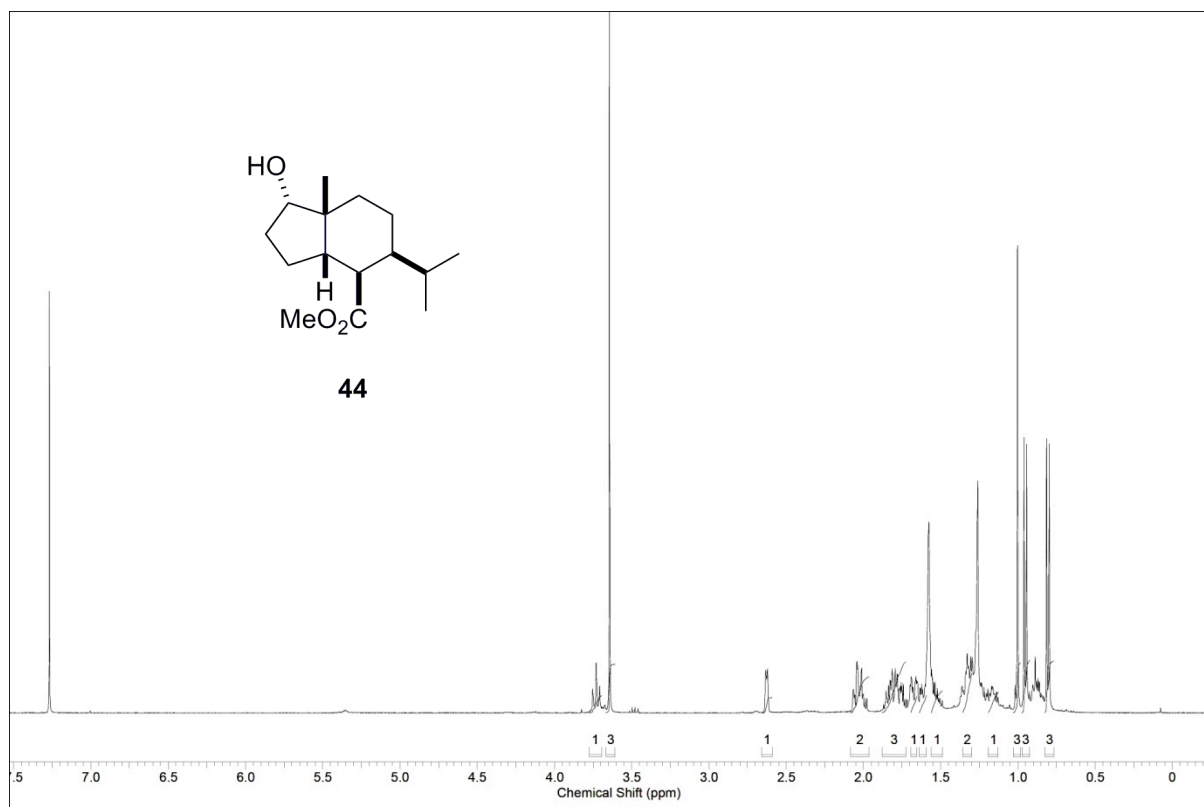
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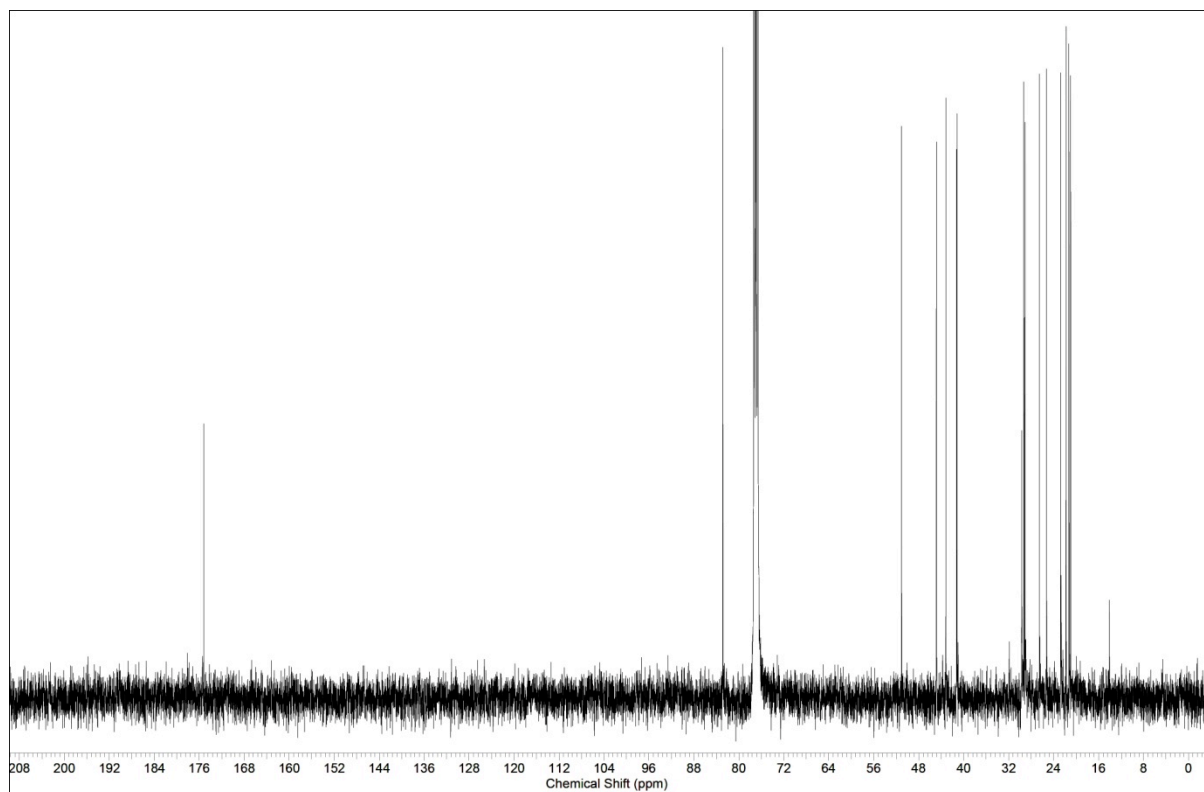
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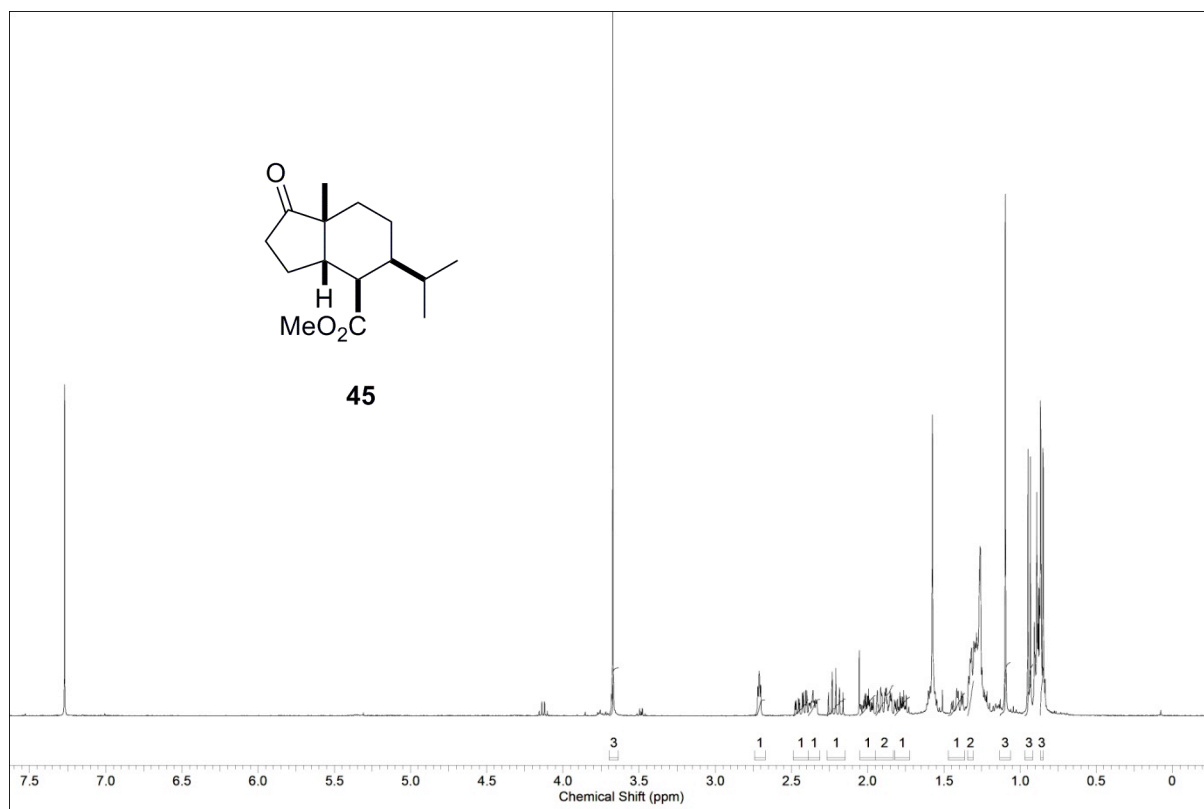
rac-(1*S*,3*aS*,4*R*,5*S*,7*aR*)-methyl 1-hydroxy-5-isopropyl-7*a*-methyloctahydro-1*H*-indene-4-carboxylate **44**, ¹H-NMR (400 MHz, CDCl₃):



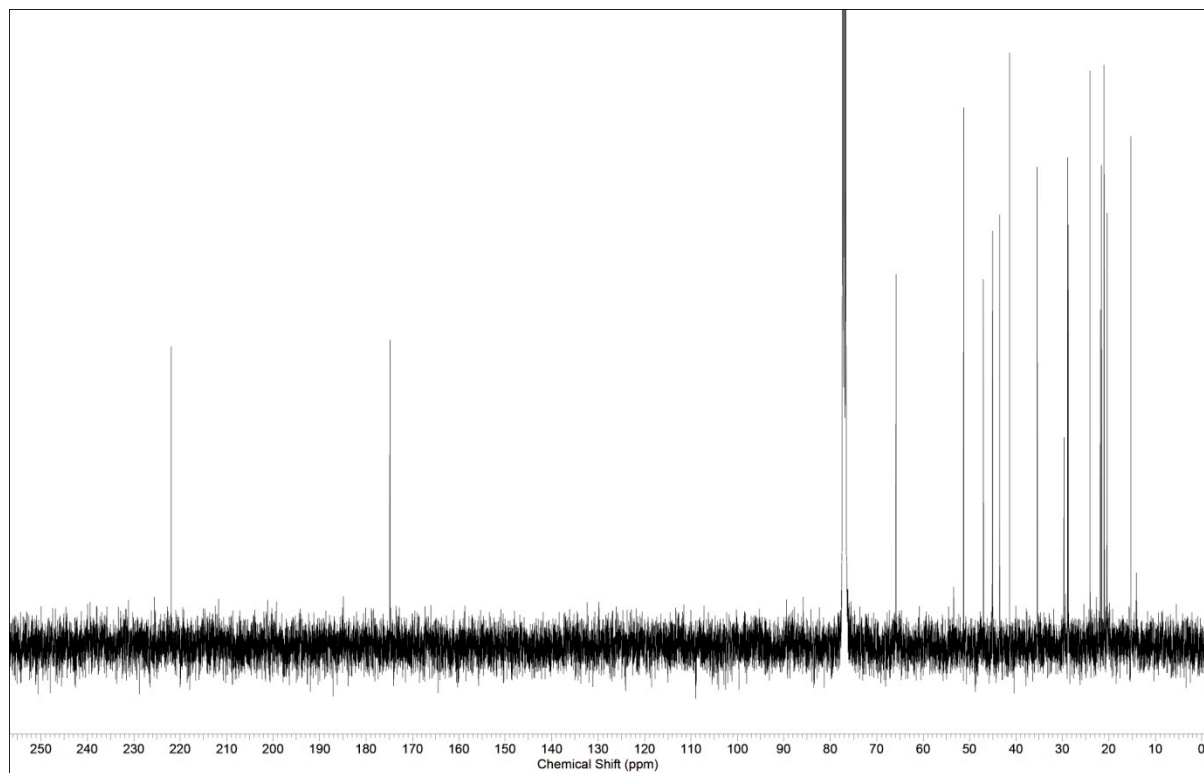
rac-(1*S*,3*aS*,4*R*,5*S*,7*aR*)-methyl 1-hydroxy-5-isopropyl-7*a*-methyloctahydro-1*H*-indene-4-carboxylate **44**, ¹³C-NMR (100 MHz, CDCl₃):



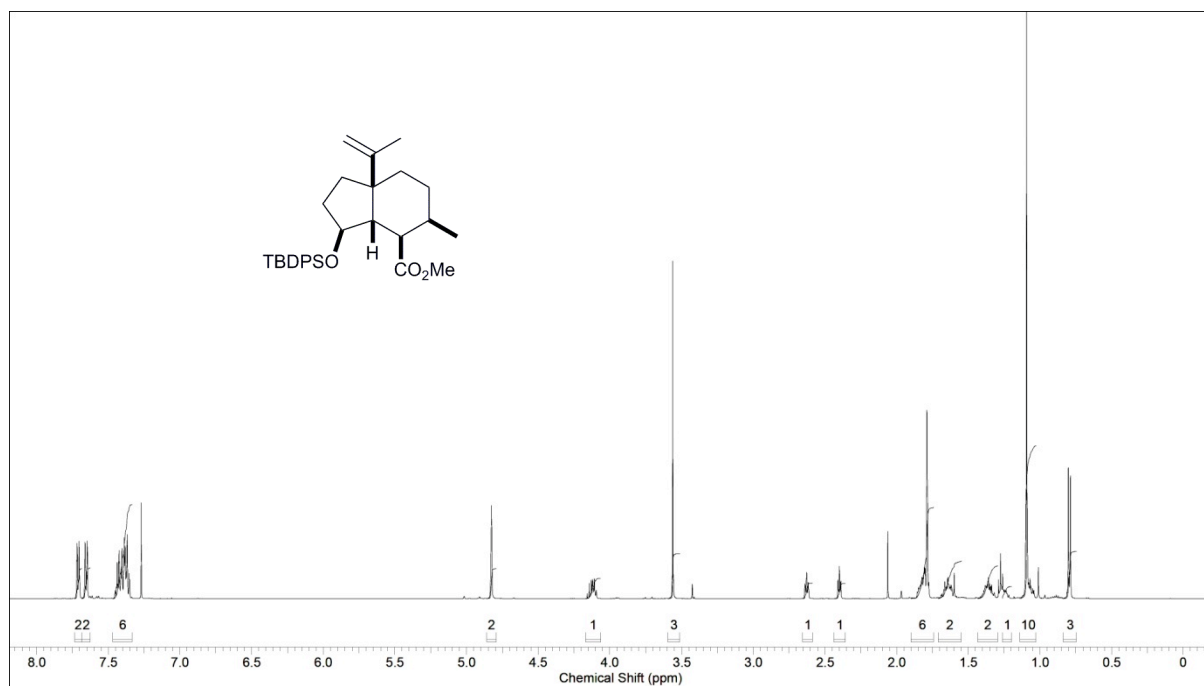
rac-(3*aS*,4*R*,5*S*,7*aR*)-methyl 5-isopropyl-7*a*-methyl-1-oxooctahydro-1*H*-indene-4-carboxylate **45**, ^1H -NMR (400 MHz, CDCl_3):



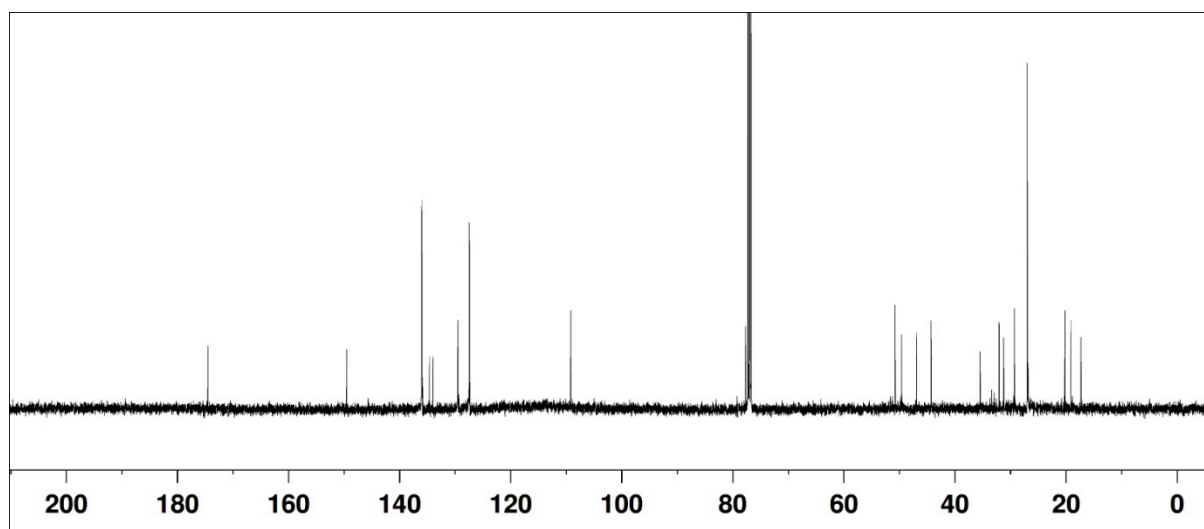
rac-(3*aS*,4*R*,5*S*,7*aR*)-methyl 5-isopropyl-7*a*-methyl-1-oxooctahydro-1*H*-indene-4-carboxylate **45**, ^{13}C -NMR (100 MHz, CDCl_3):



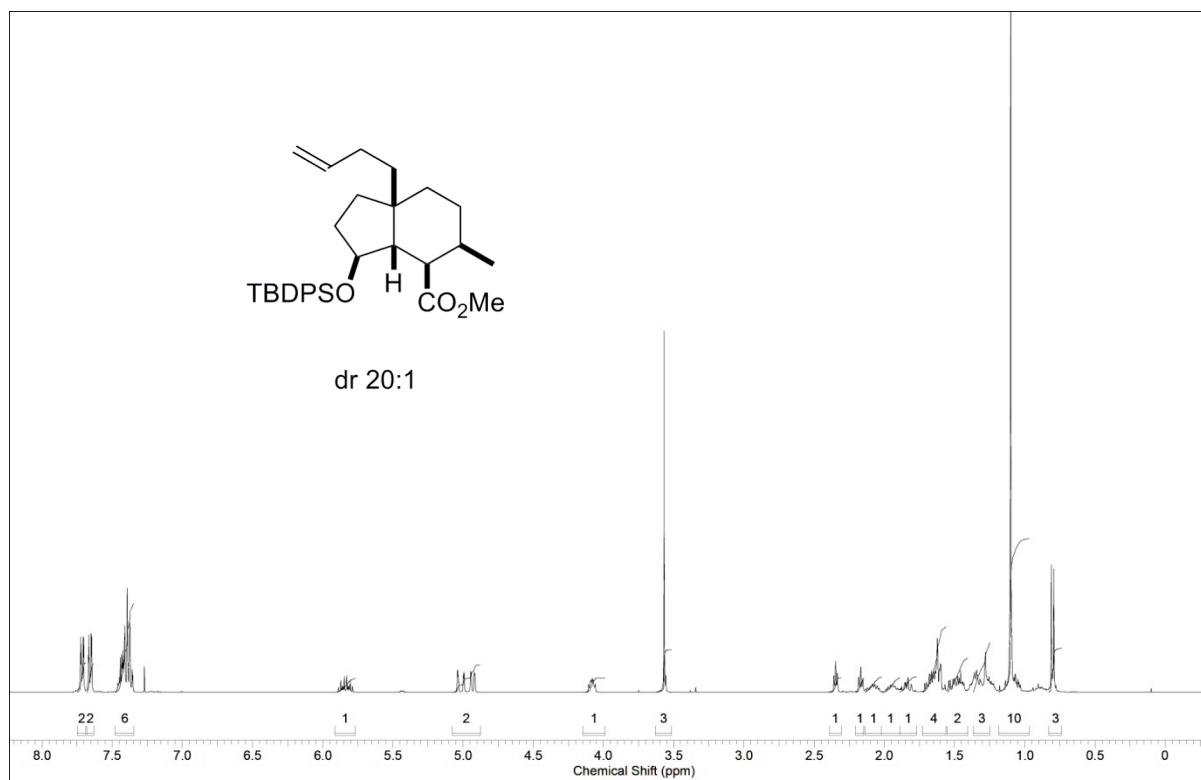
rac-(3*S*,3*aS*,4*R*,5*R*,7*aR*)-methyl 3-((*tert*-butyldiphenylsilyl)oxy)-5-methyl-7*a*-(prop-1-en-2-yl)octahydro-1*H*-indene-4-carboxylate, ¹H-NMR (500 MHz, CDCl₃):



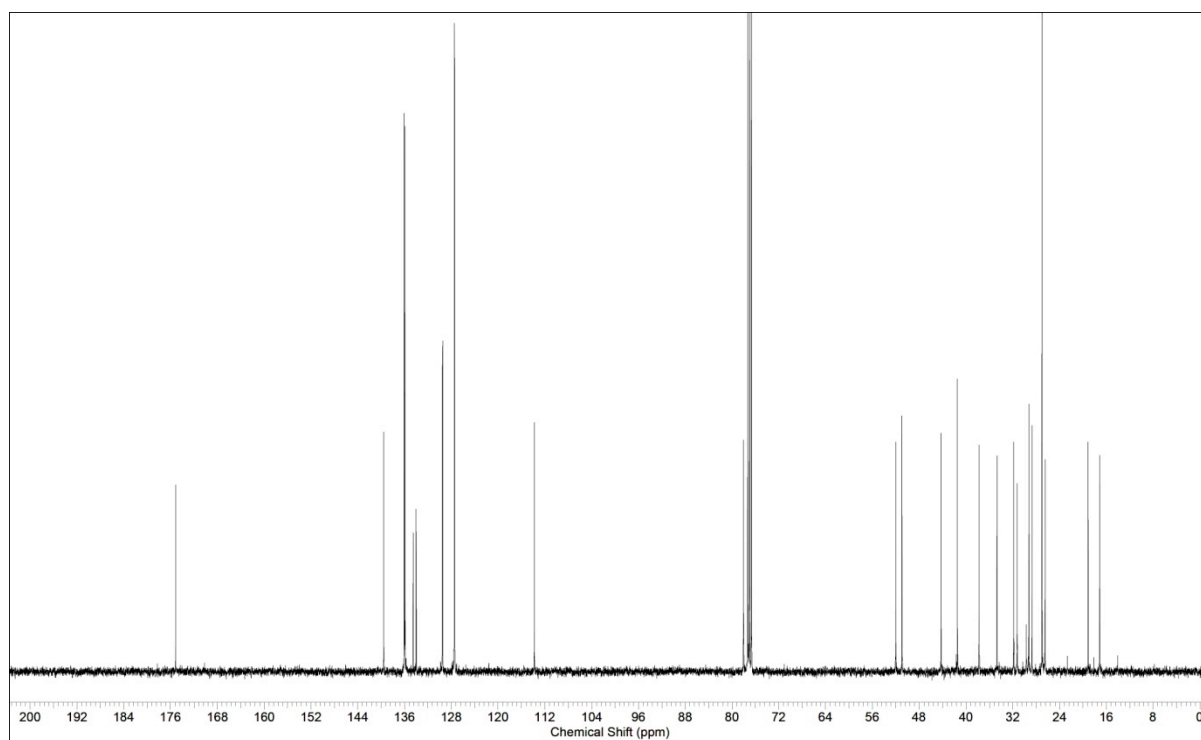
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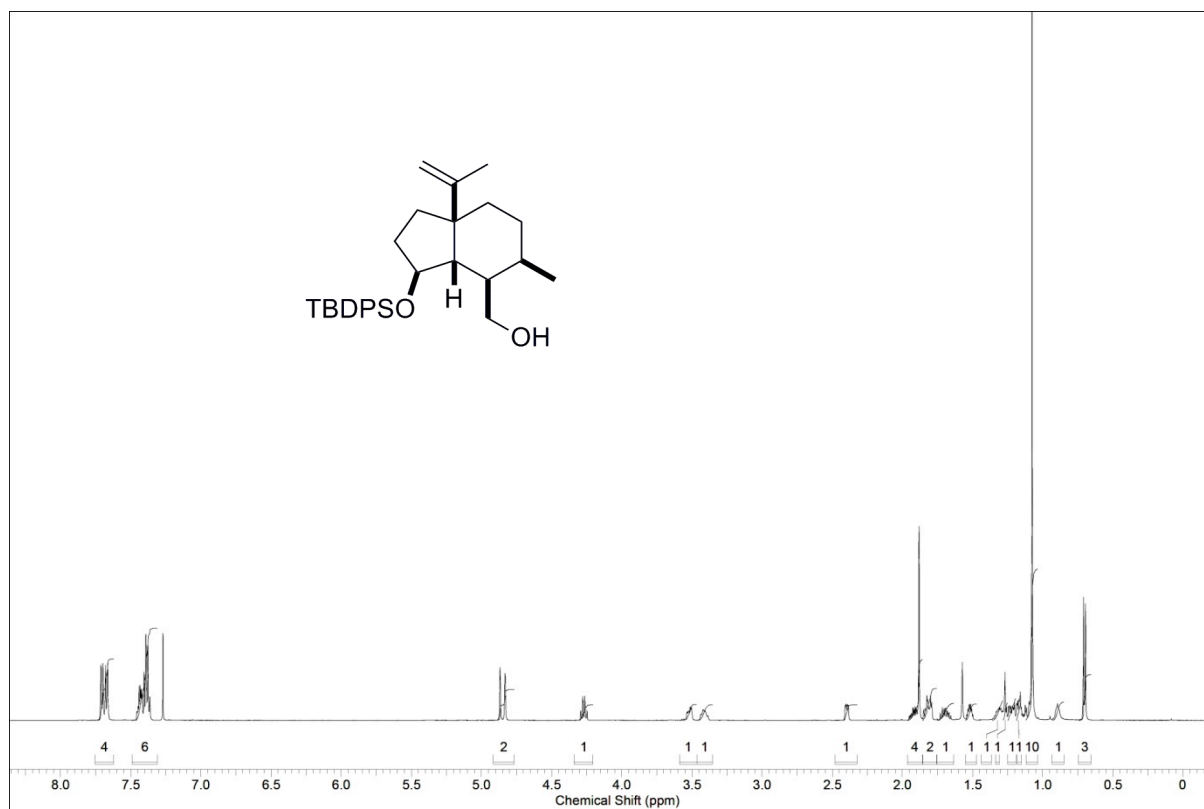
rac- (3*S*,3*aS*,4*R*,5*R*,7*aS*)-methyl 7*a*-(but-3-en-1-yl)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyloctahydro-1*H*-indene-4-carboxylate, ¹H-NMR (400 MHz, CDCl₃):



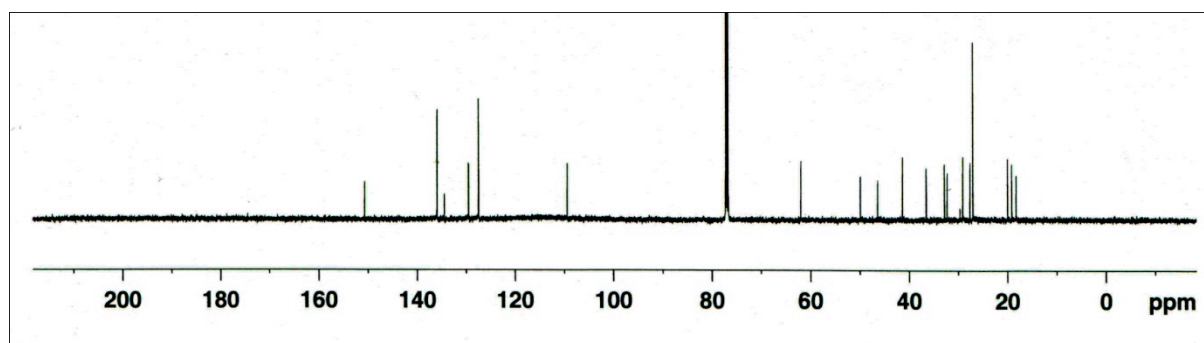
rac- (3*S*,3*aS*,4*R*,5*R*,7*aS*)-methyl 7*a*-(but-3-en-1-yl)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyloctahydro-1*H*-indene-4-carboxylate, ¹³C-NMR (100 MHz, CDCl₃):



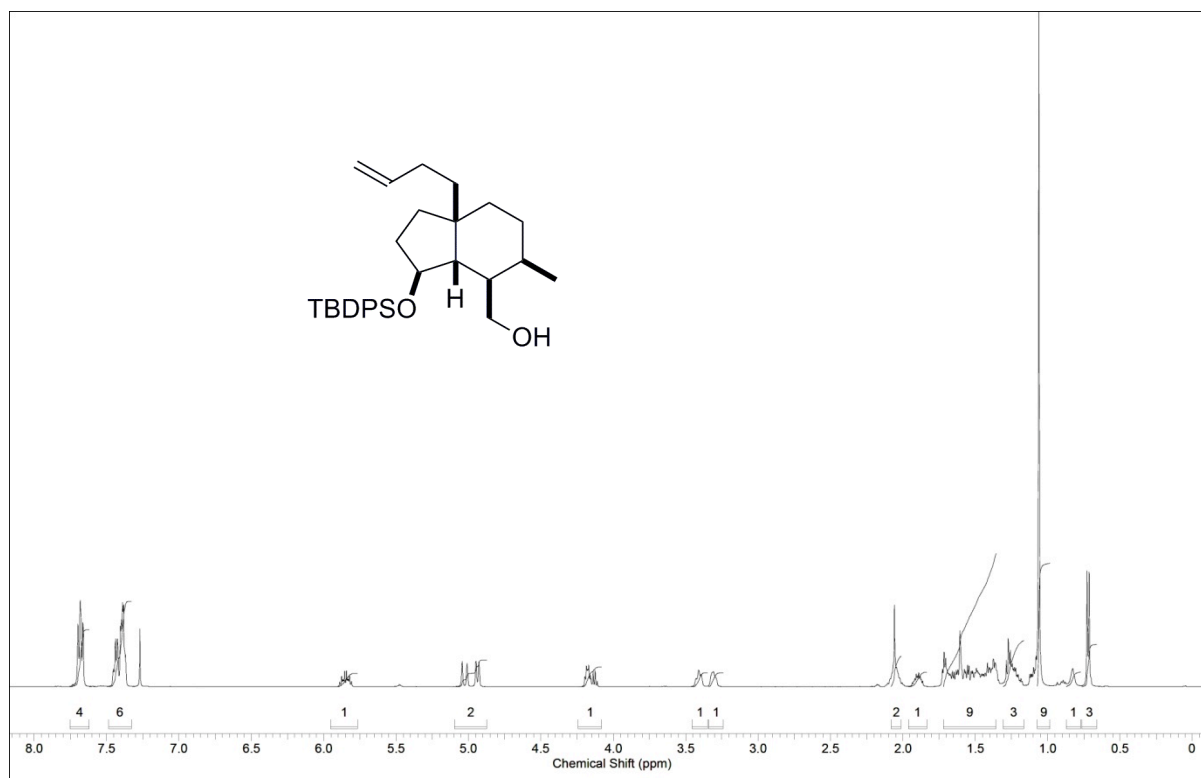
rac-((3*S*,3*aS*,4*R*,5*R*,7*aR*)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyl-7*a*-(prop-1-en-2-yl)octahydro-1*H*-inden-4-yl)methanol, ¹H-NMR (500 MHz, CDCl₃):



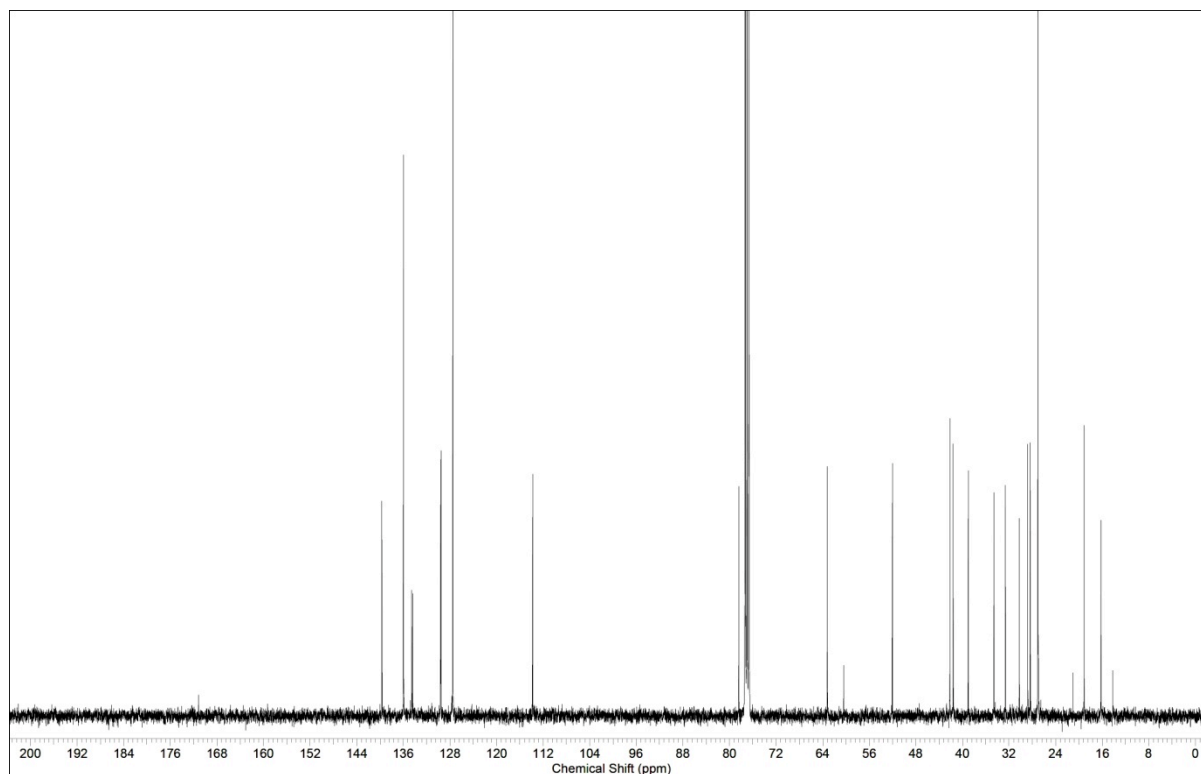
rac-((3*S*,3*aS*,4*R*,5*R*,7*aR*)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyl-7*a*-(prop-1-en-2-yl)octahydro-1*H*-inden-4-yl)methanol, ¹³C-NMR (125 MHz, CDCl₃):



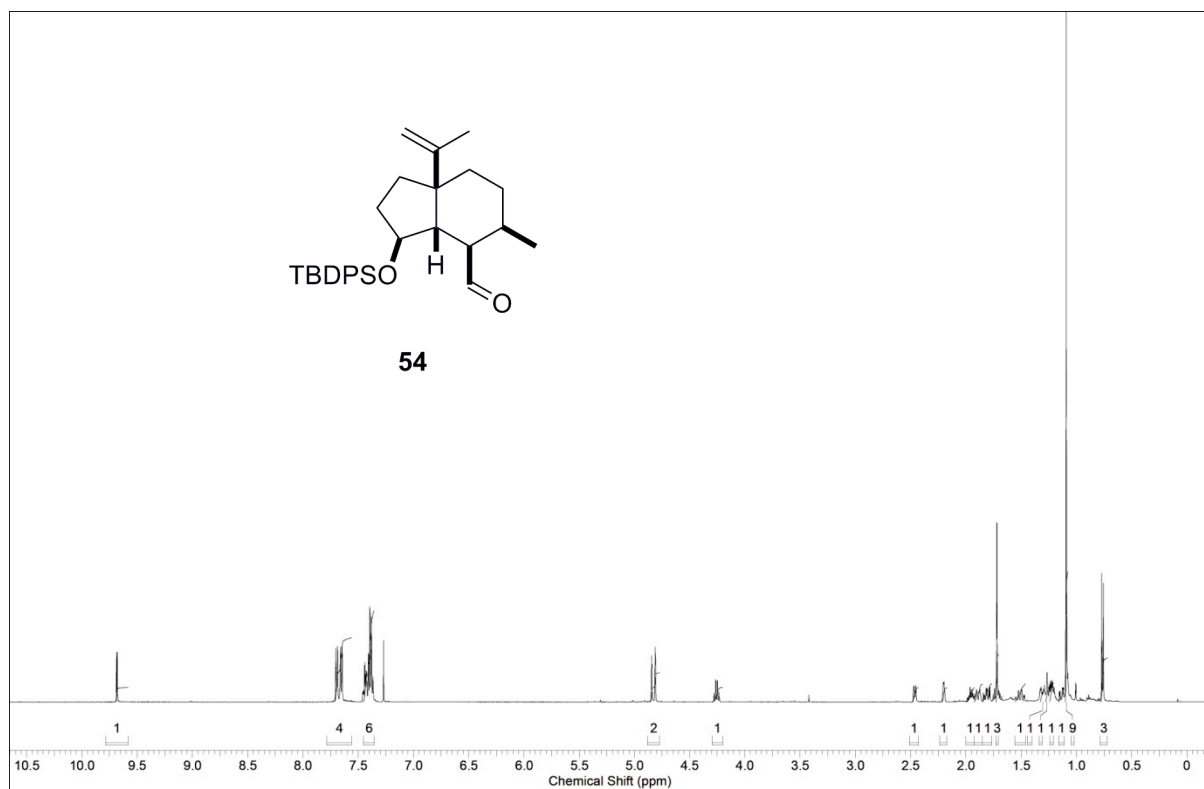
rac-((3*S*,3*aS*,4*R*,5*R*,7*aS*)-7*a*-(but-3-en-1-yl)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyloctahydro-1*H*-inden-4-yl)methanol, ¹H-NMR (500 MHz, CDCl₃):



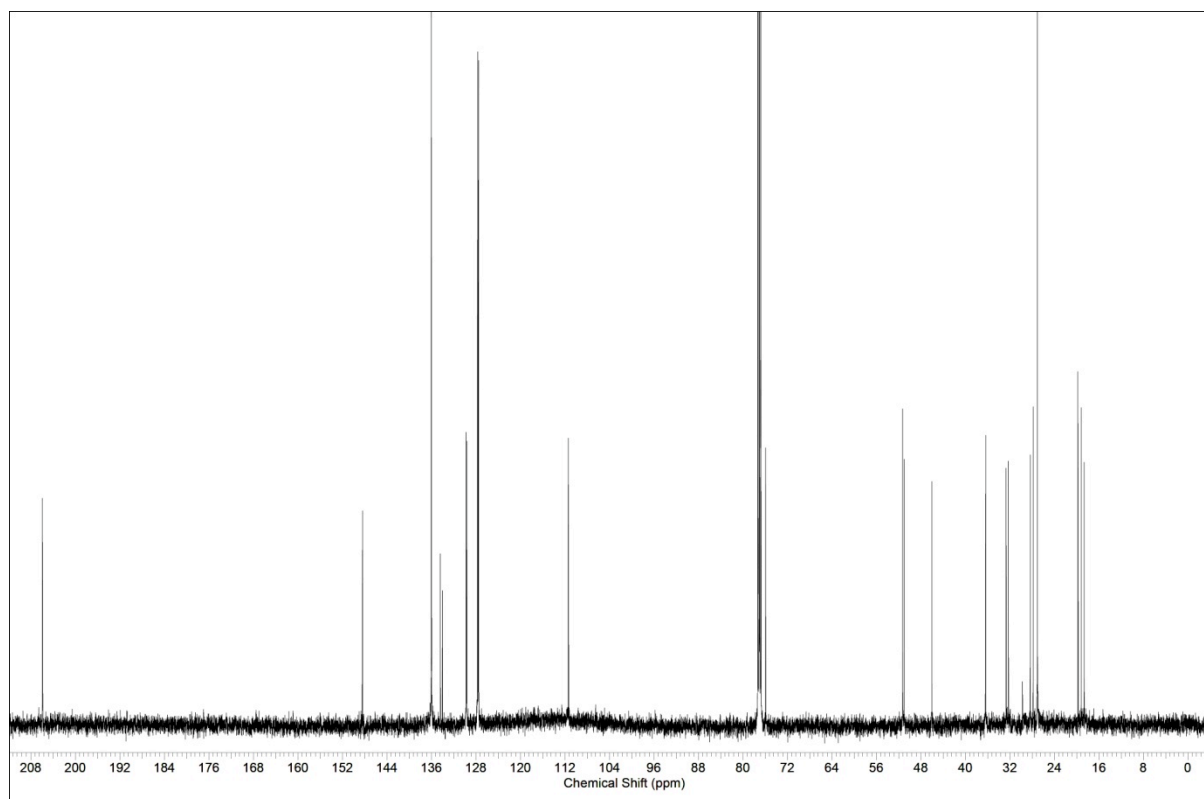
rac-((3*S*,3*aS*,4*R*,5*R*,7*aS*)-7*a*-(but-3-en-1-yl)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyloctahydro-1*H*-inden-4-yl)methanol, ¹³C-NMR (125 MHz, CDCl₃):



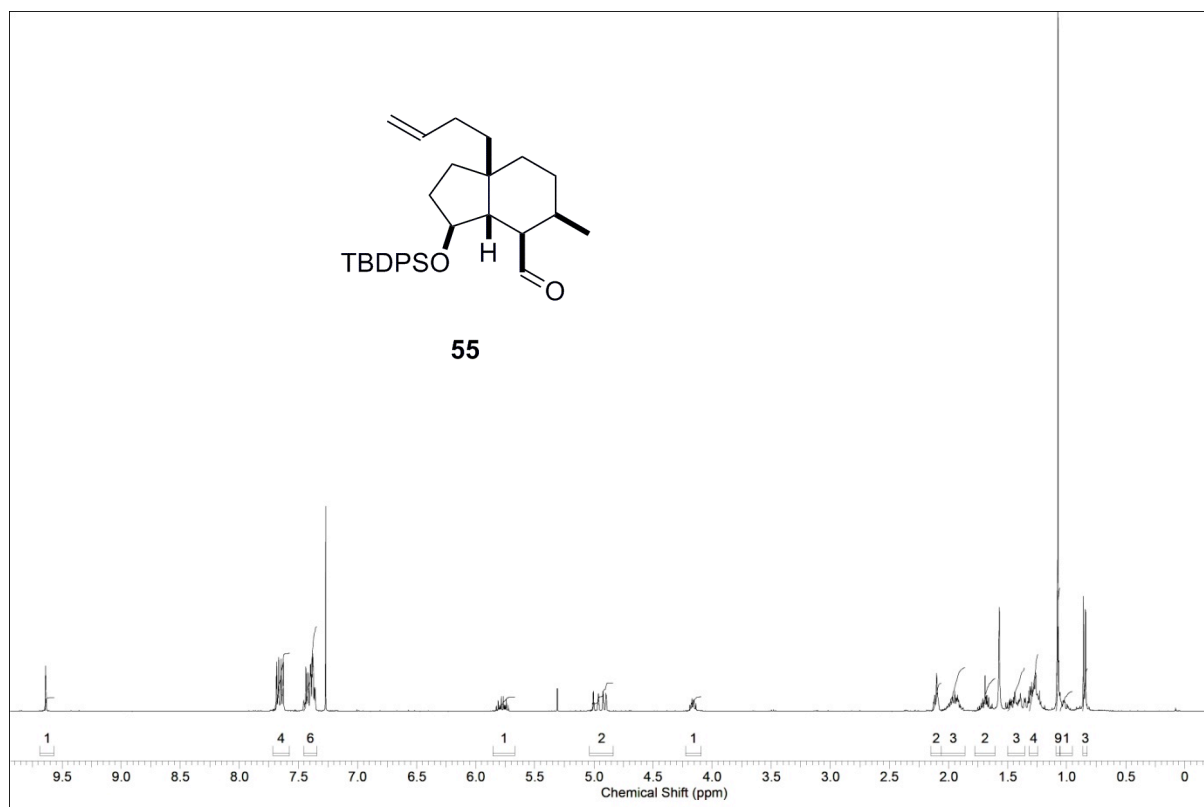
rac-(3*S*,3*aS*,4*R*,5*R*,7*aR*)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyl-7*a*-(prop-1-en-2-yl)octahydro-1*H*-indene-4-carbaldehyde **54**, ¹H-NMR (500 MHz, CDCl₃):



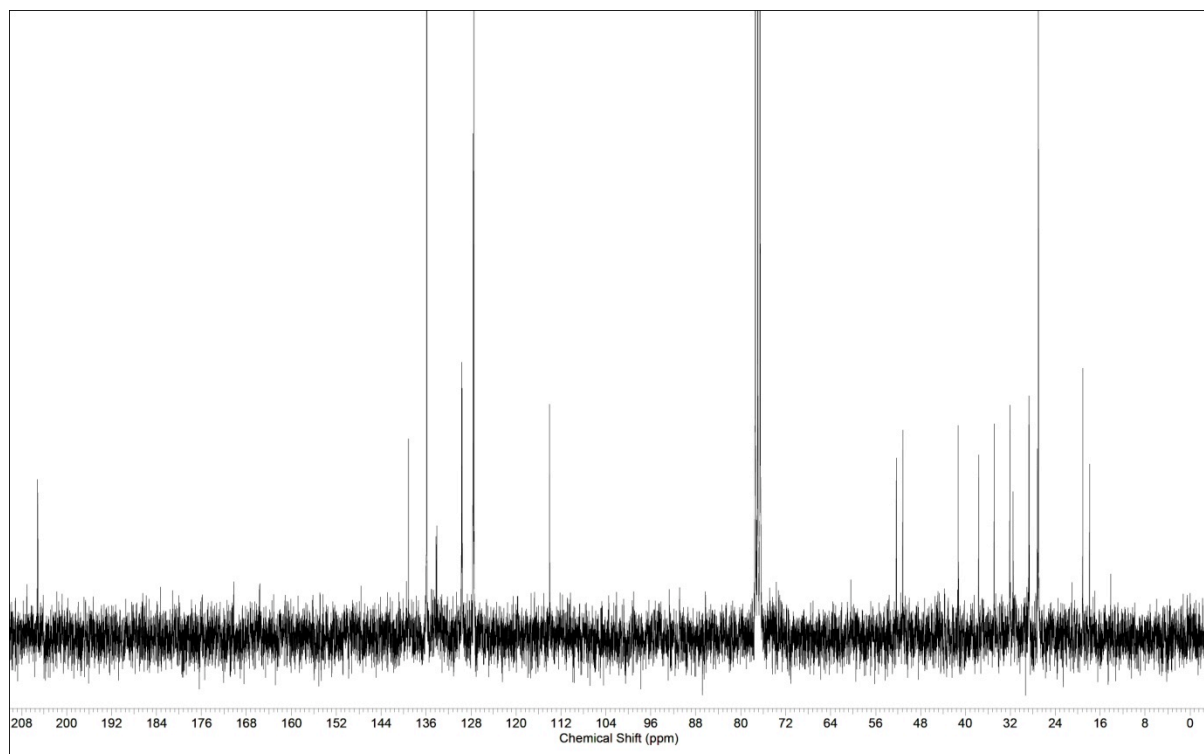
rac-(3*S*,3*aS*,4*R*,5*R*,7*aR*)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyl-7*a*-(prop-1-en-2-yl)octahydro-1*H*-indene-4-carbaldehyde **54**, ¹³C-NMR (125 MHz, CDCl₃):



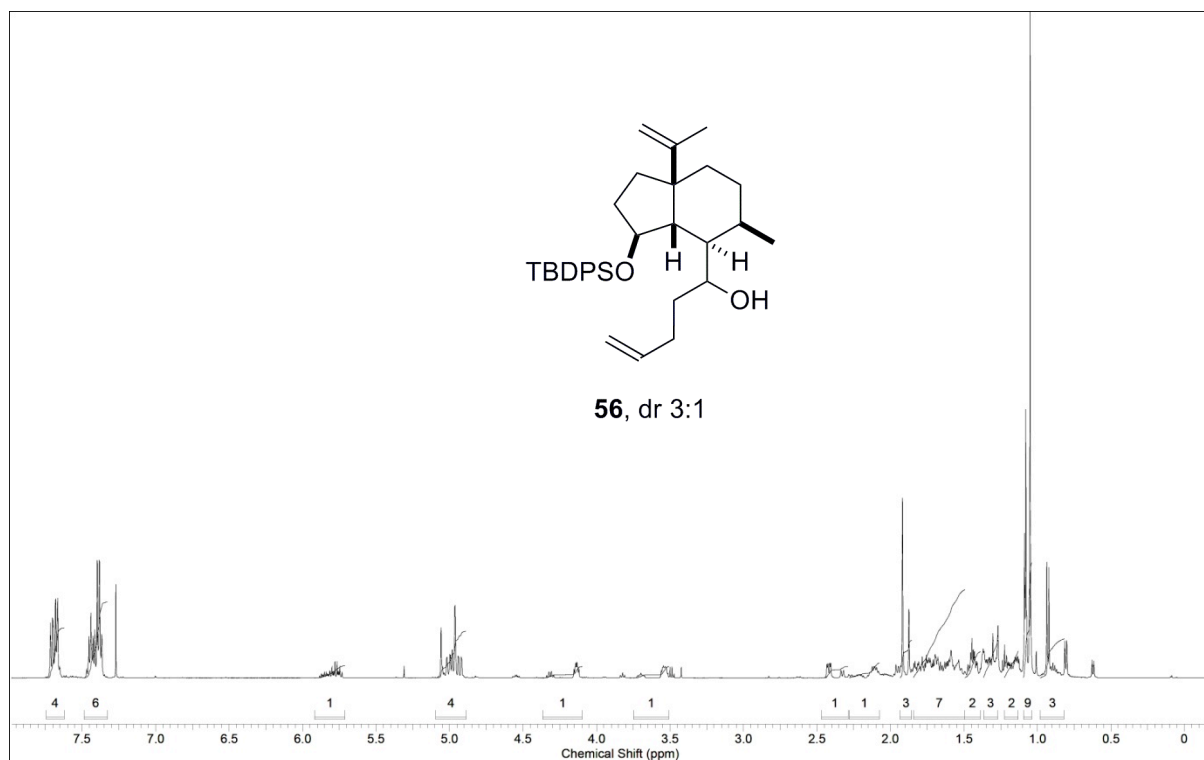
rac-(3*S*,3*aS*,4*R*,5*R*,7*aS*)-7*a*-(but-3-en-1-yl)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyloctahydro-1*H*-indene-4-carbaldehyde **55**, $^1\text{H-NMR}$ (400 MHz, CDCl_3):



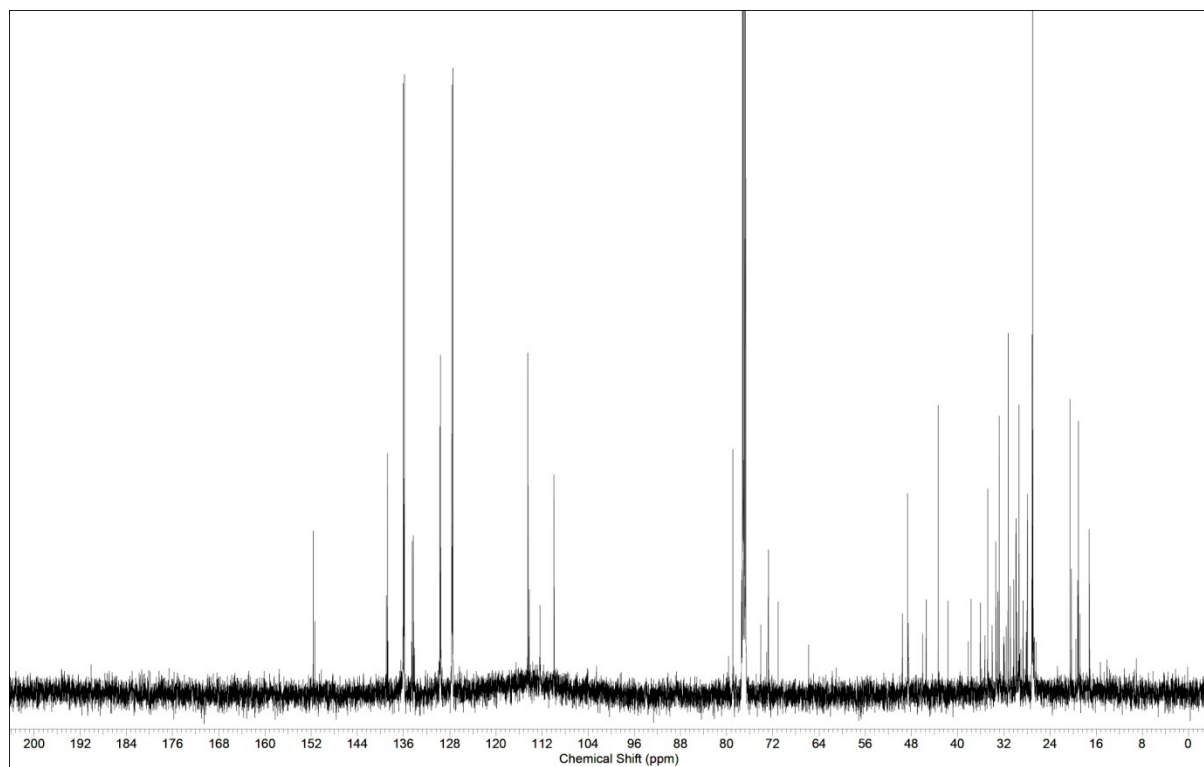
rac-(3*S*,3*aS*,4*R*,5*R*,7*aS*)-7*a*-(but-3-en-1-yl)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyloctahydro-1*H*-indene-4-carbaldehyde **55**, $^{13}\text{C-NMR}$ (100 MHz, CDCl_3):



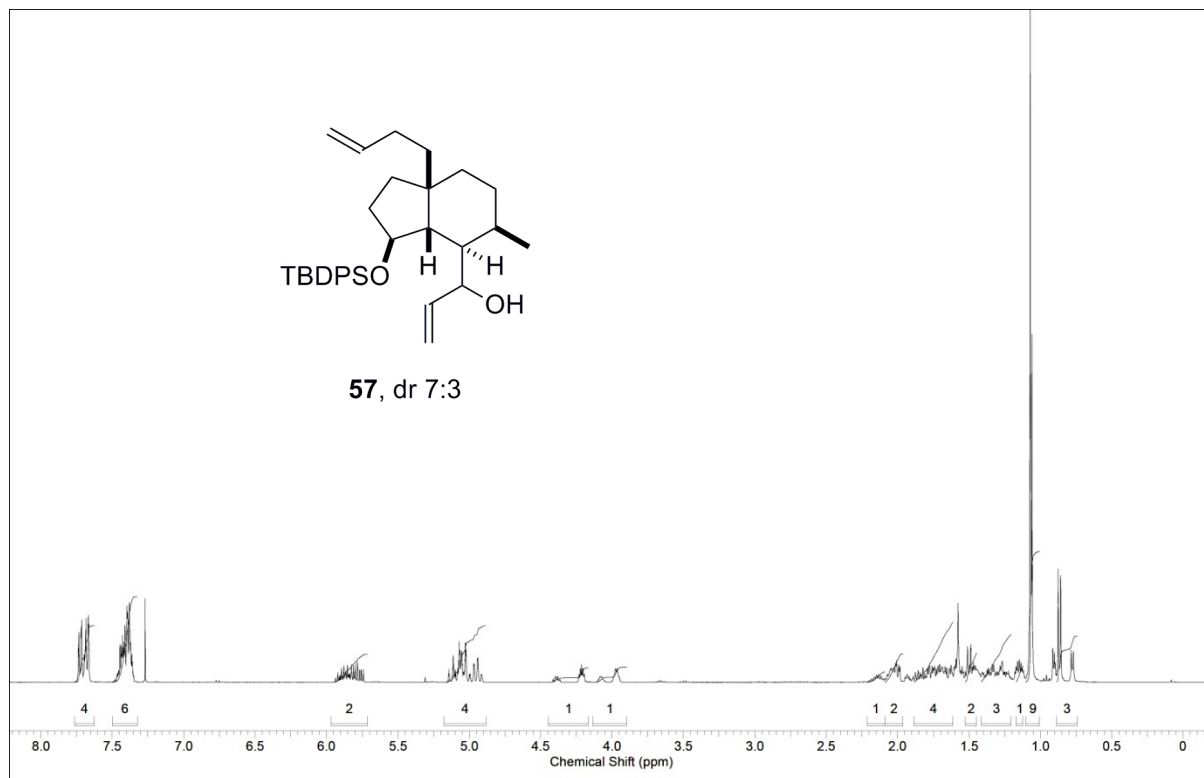
rac-(*S*)-1-((3*S*,3*aS*,4*R*,5*R*,7*aR*)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyl-7*a*-(prop-1-en-2-yl)octahydro-1*H*-inden-4-yl)pent-4-en-1-ol **56**, ¹H-NMR (300 MHz, CDCl₃):



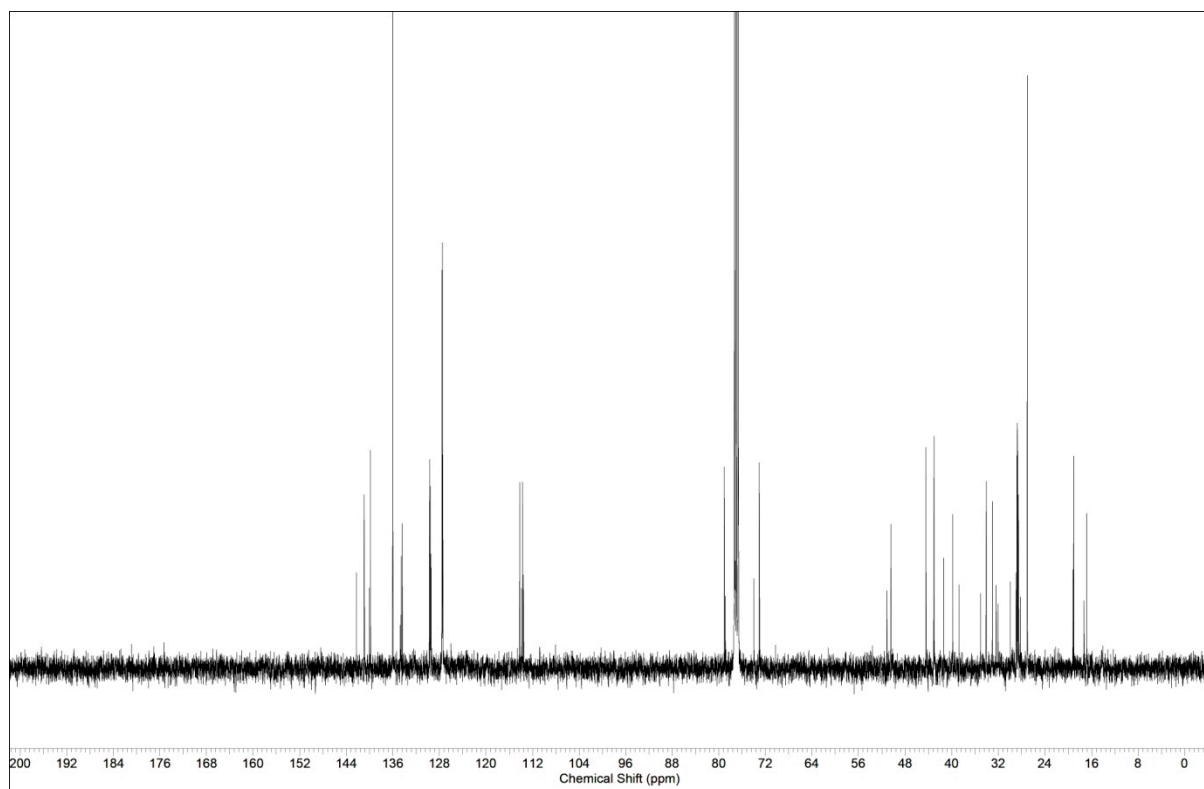
rac-(*S*)-1-((3*S*,3*aS*,4*R*,5*R*,7*aR*)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyl-7*a*-(prop-1-en-2-yl)octahydro-1*H*-inden-4-yl)pent-4-en-1-ol **56**, ¹³C-NMR (75 MHz, CDCl₃):



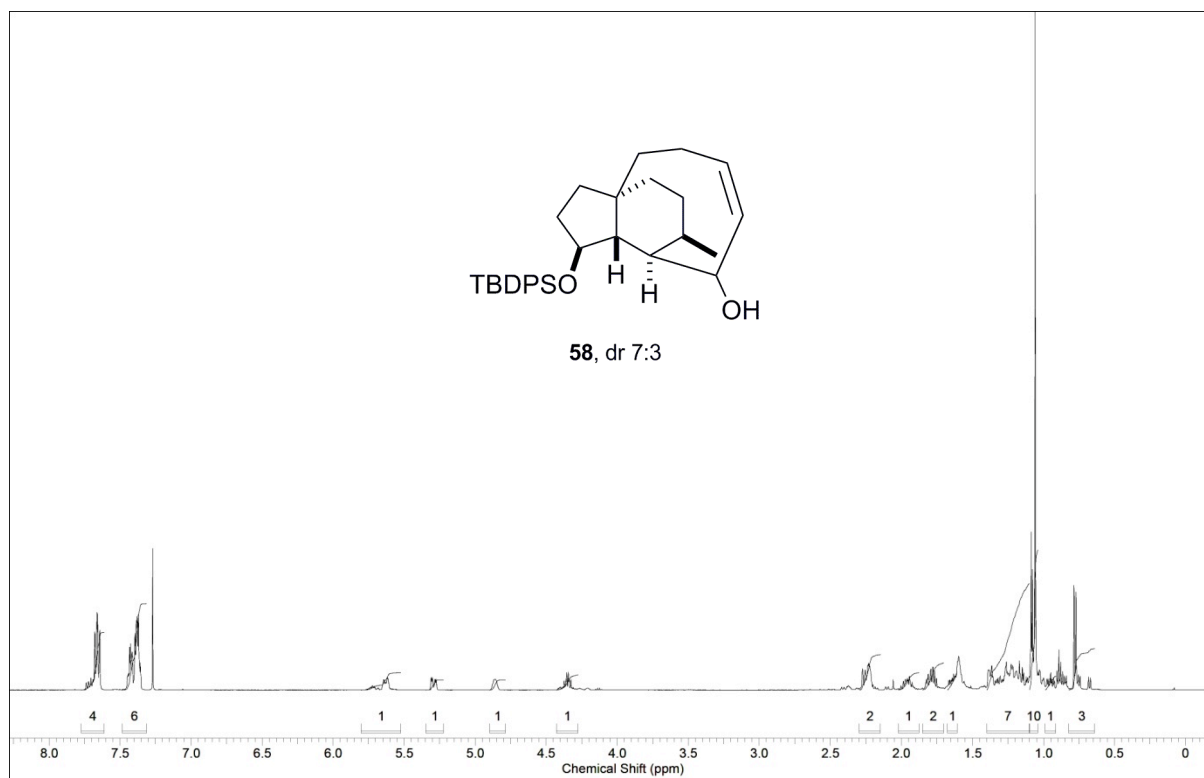
rac-(*S*)-1-((3*S*,3*aS*,4*R*,5*R*,7*aS*)-7*a*-(but-3-en-1-yl)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyloctahydro-1*H*-inden-4-yl)prop-2-en-1-ol **57**, ¹H-NMR (400 MHz, CDCl₃):



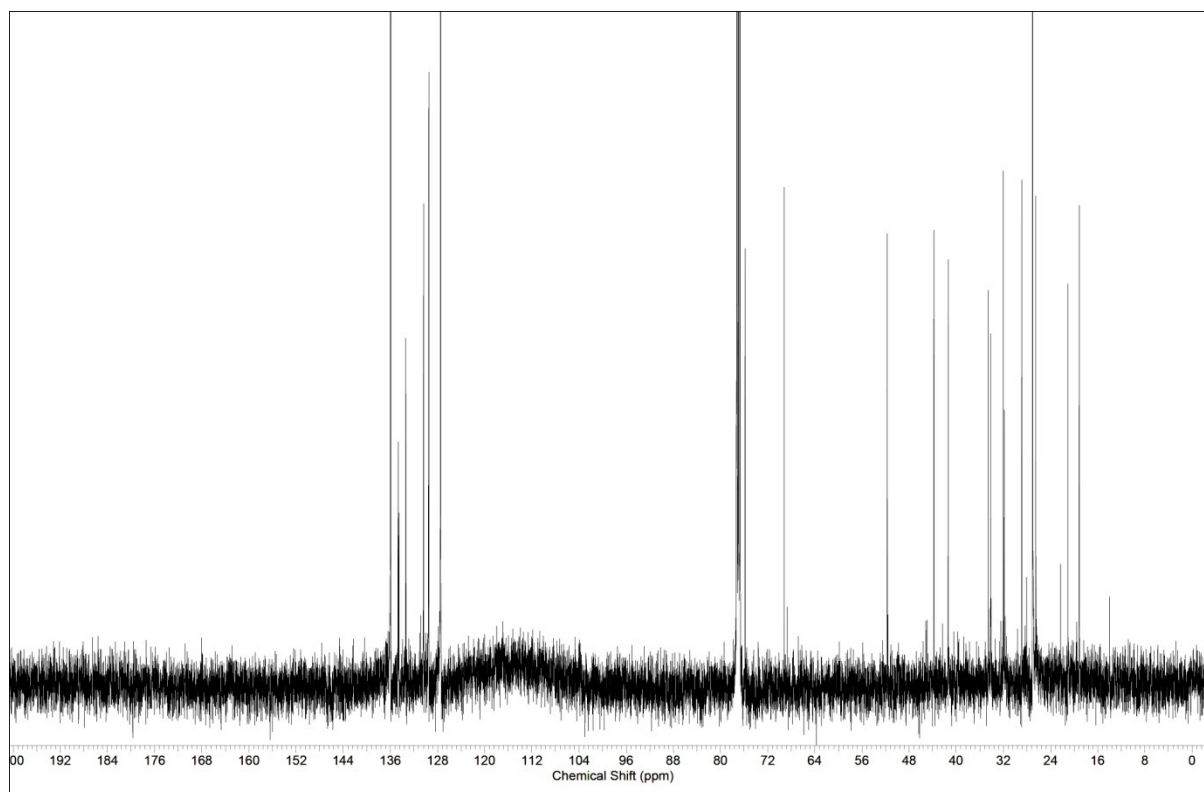
rac-(*S*)-1-((3*S*,3*aS*,4*R*,5*R*,7*aS*)-7*a*-(but-3-en-1-yl)-3-((*tert*-butyldiphenylsilyl)oxy)-5-methyloctahydro-1*H*-inden-4-yl)prop-2-en-1-ol **57**, ¹³C-NMR (100 MHz, CDCl₃):



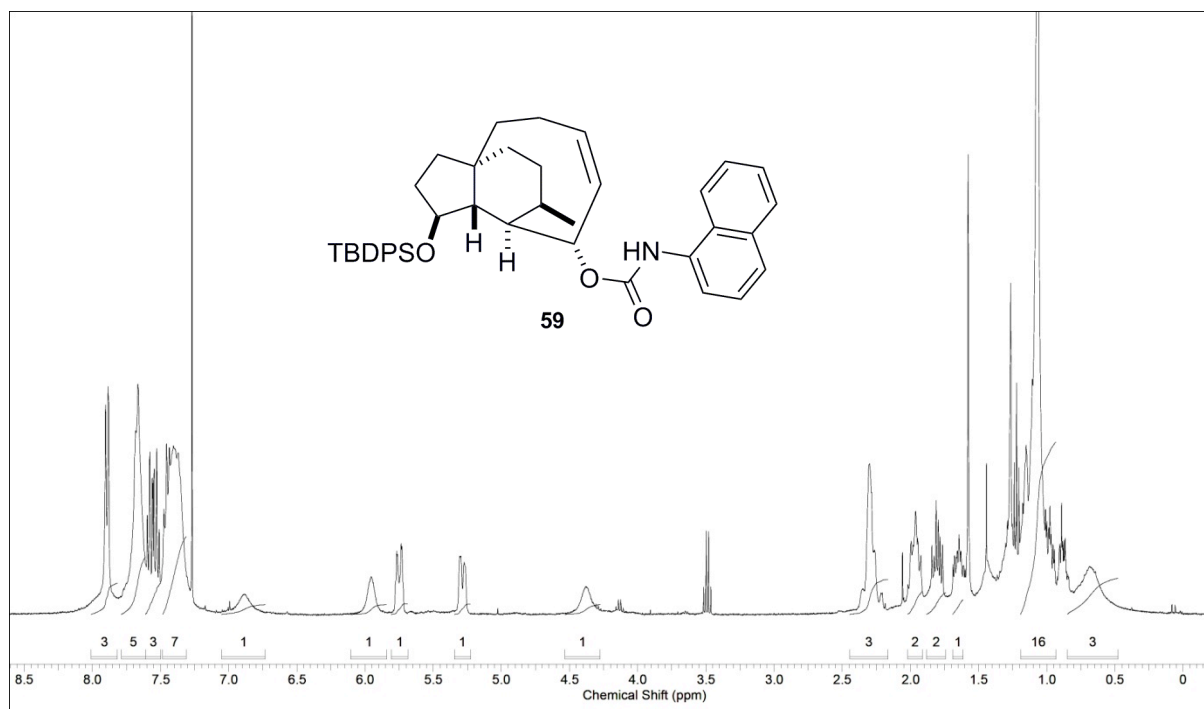
rac-(3*S*,3*aS*,4*R*,9*aS*,12*R*,*Z*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-1,2,3,3*a*,4,5,8,9-octahydro-4,9*a*-propanocyclopenta[8]annulen-5-ol **58**, $^1\text{H-NMR}$ (500 MHz, CDCl_3):



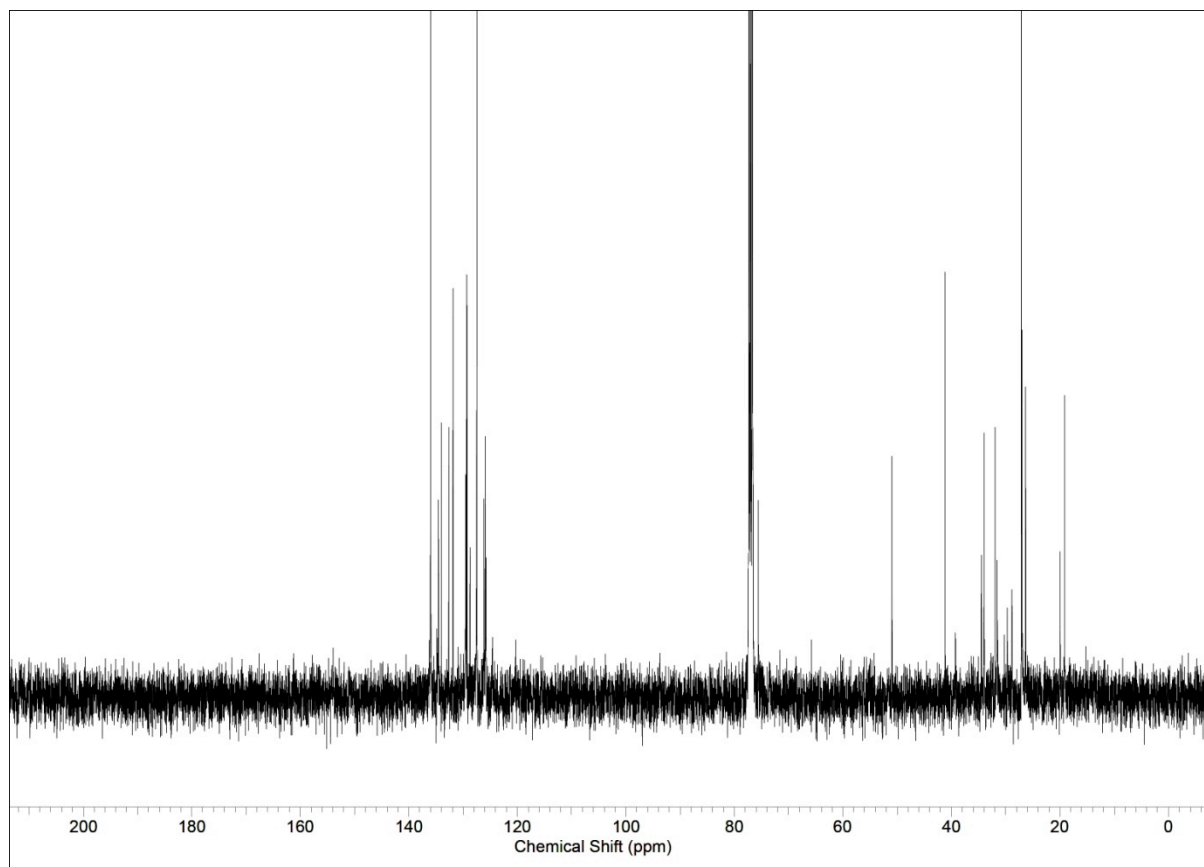
rac-(3*S*,3*aS*,4*R*,9*aS*,12*R*,*Z*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-1,2,3,3*a*,4,5,8,9-octahydro-4,9*a*-propanocyclopenta[8]annulen-5-ol **58**, $^{13}\text{C-NMR}$ (125 MHz, CDCl_3):



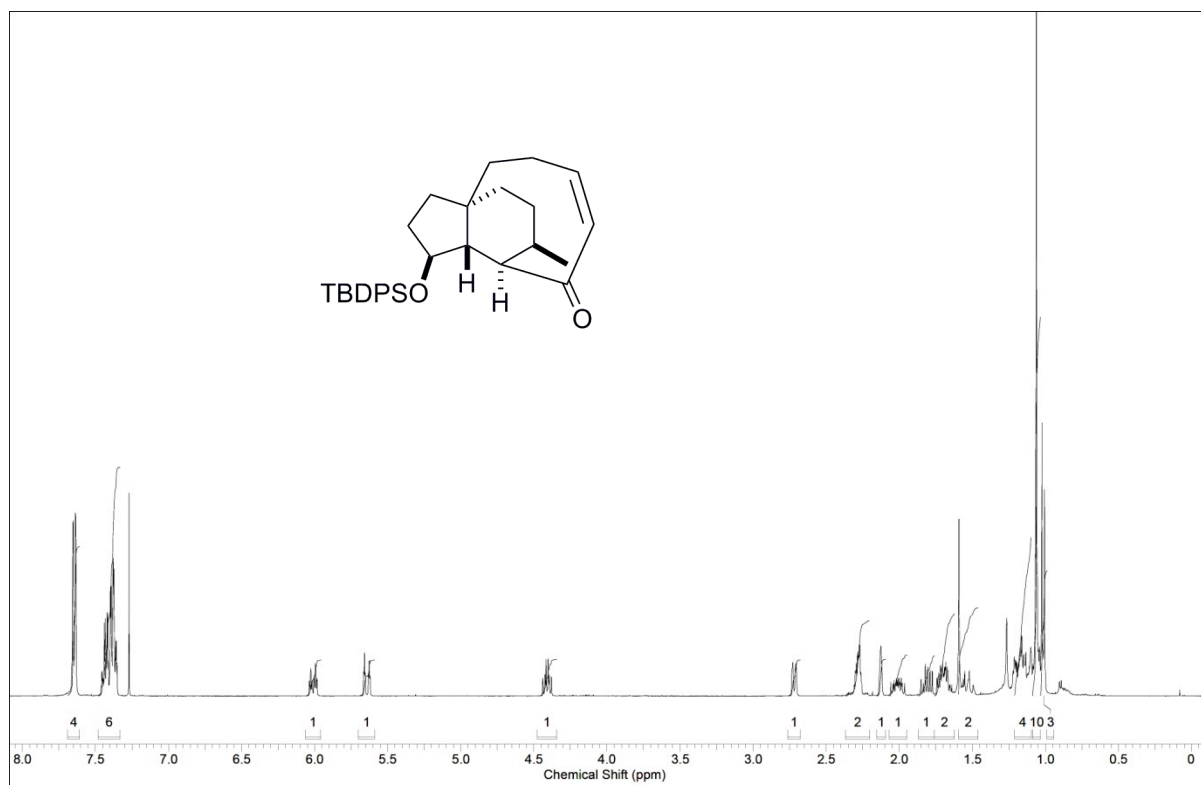
rac-(3*S*,3*aS*,4*R*,5*S*,9*aS*,12*R*,*Z*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-1,2,3,3*a*,4,5,8,9-octahydro-4,9*a*-propanocyclopenta[8]annulen-5-yl naphthalen-1-ylcarbamate **59**, $^1\text{H-NMR}$ (400 MHz, CDCl_3):



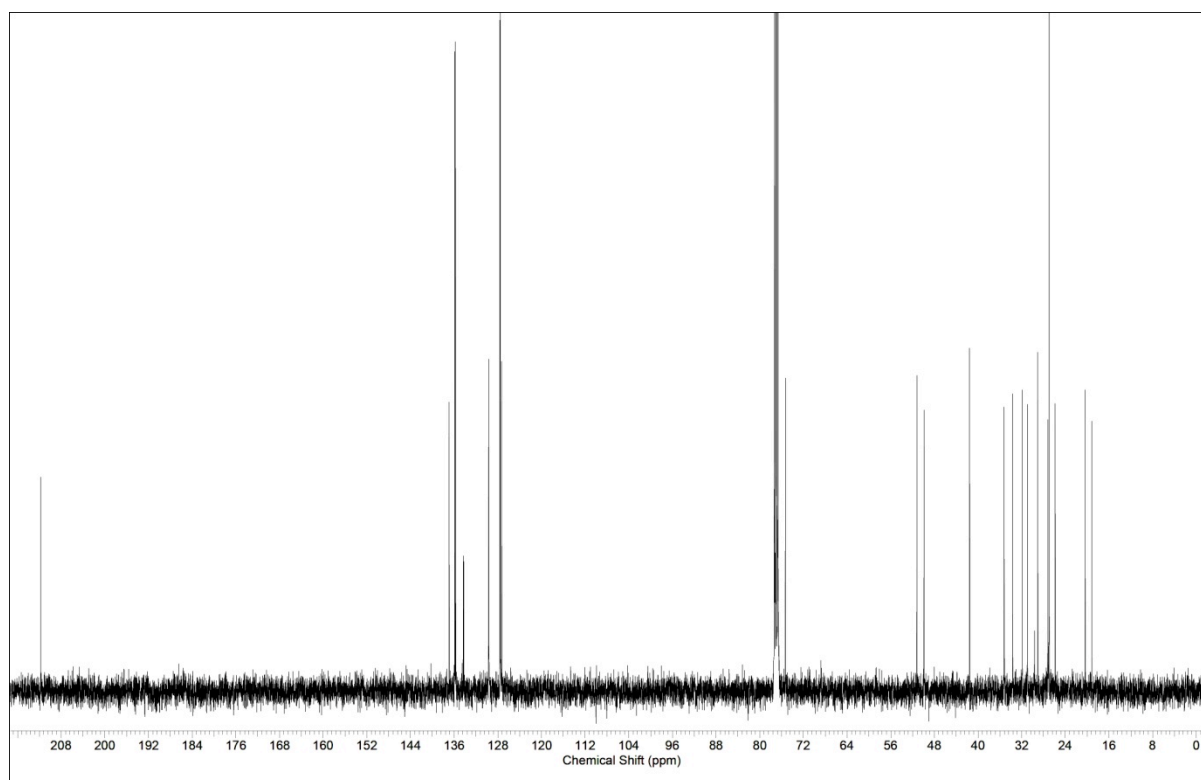
rac-(3*S*,3*aS*,4*R*,5*S*,9*aS*,12*R*,*Z*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-1,2,3,3*a*,4,5,8,9-octahydro-4,9*a*-propanocyclopenta[8]annulen-5-yl naphthalen-1-ylcarbamate **59**, $^{13}\text{C-NMR}$ (75 MHz, CDCl_3):



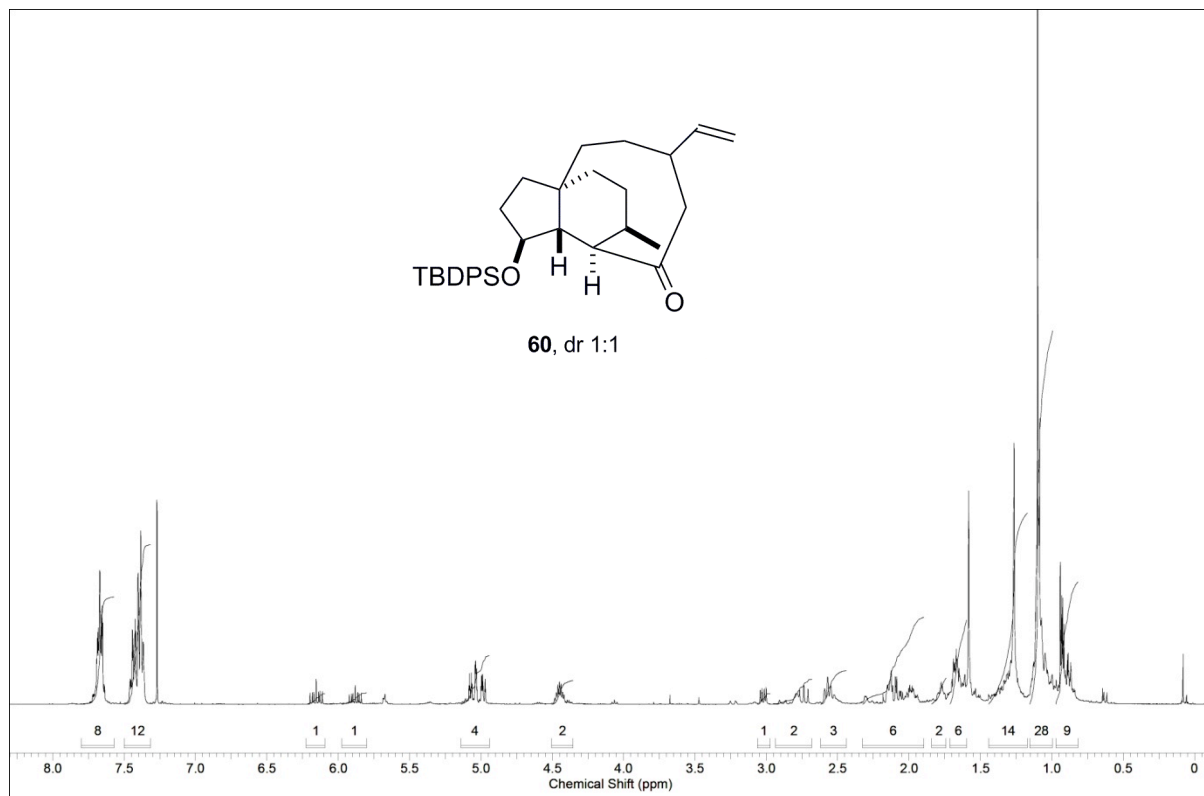
rac-(3*S*,3*aS*,4*R*,9*aS*,12*R*,*Z*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-2,3,3*a*,4,8,9-hexahydro-4,9a-propanocyclopenta[8]annulen-5(1*H*)-one, ¹H-NMR (400 MHz, CDCl₃):



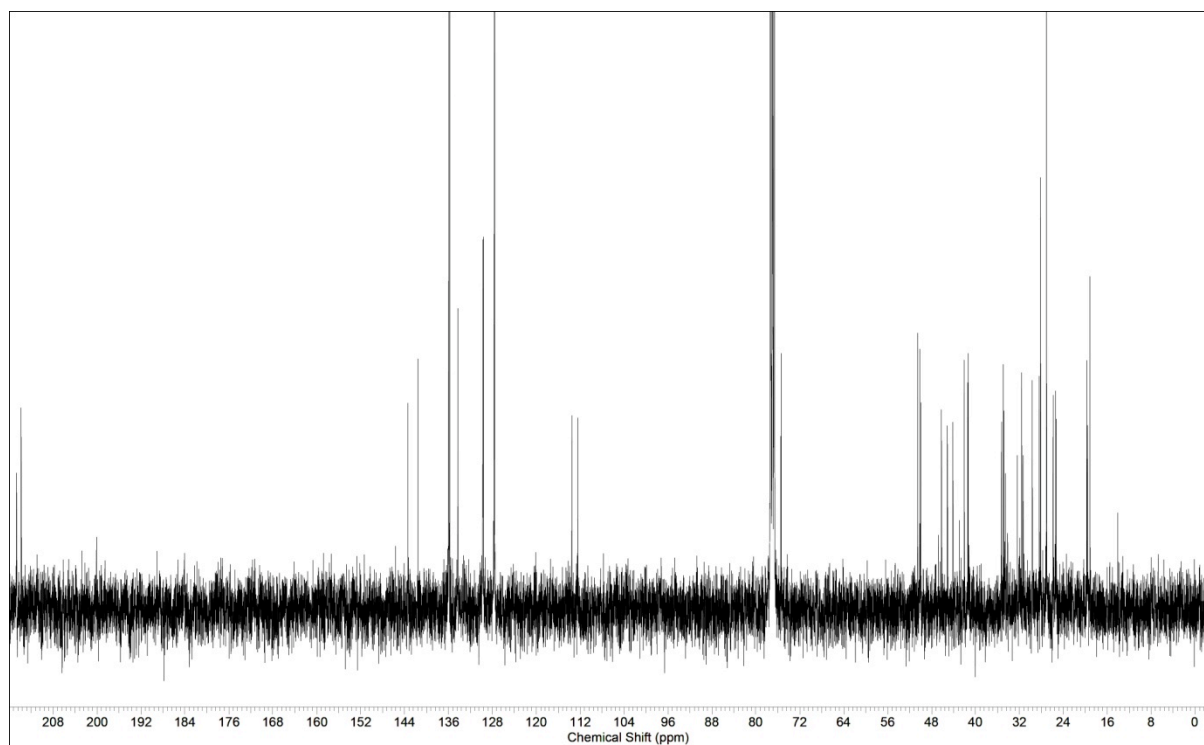
rac-(3*S*,3*aS*,4*R*,9*aS*,12*R*,*Z*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-2,3,3*a*,4,8,9-hexahydro-4,9a-propanocyclopenta[8]annulen-5(1*H*)-one, ¹³C-NMR (100 MHz, CDCl₃):



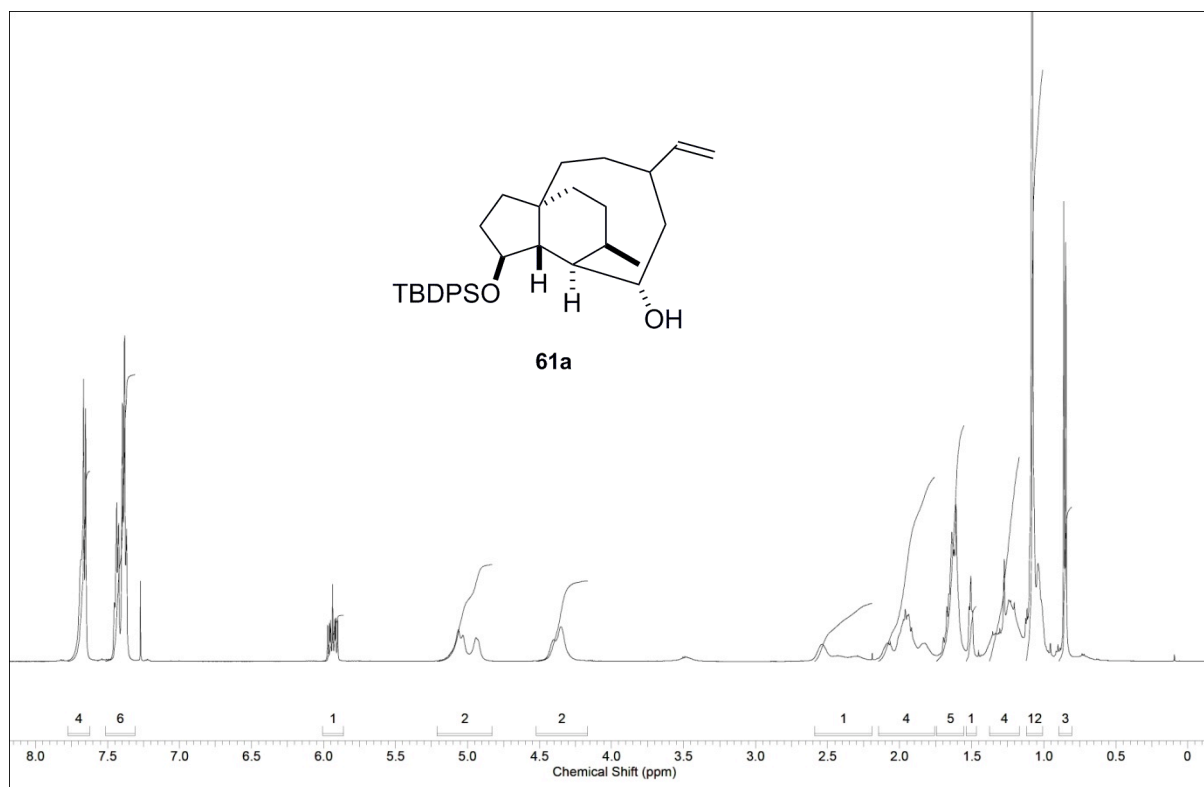
rac-(3*S*,3*aS*,4*R*,9*aR*,12*R*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-7-vinyloctahydro-4,9a-propanocyclopenta[8]annulen-5(1*H*)-one **60**, ¹H-NMR (400 MHz, CDCl₃):



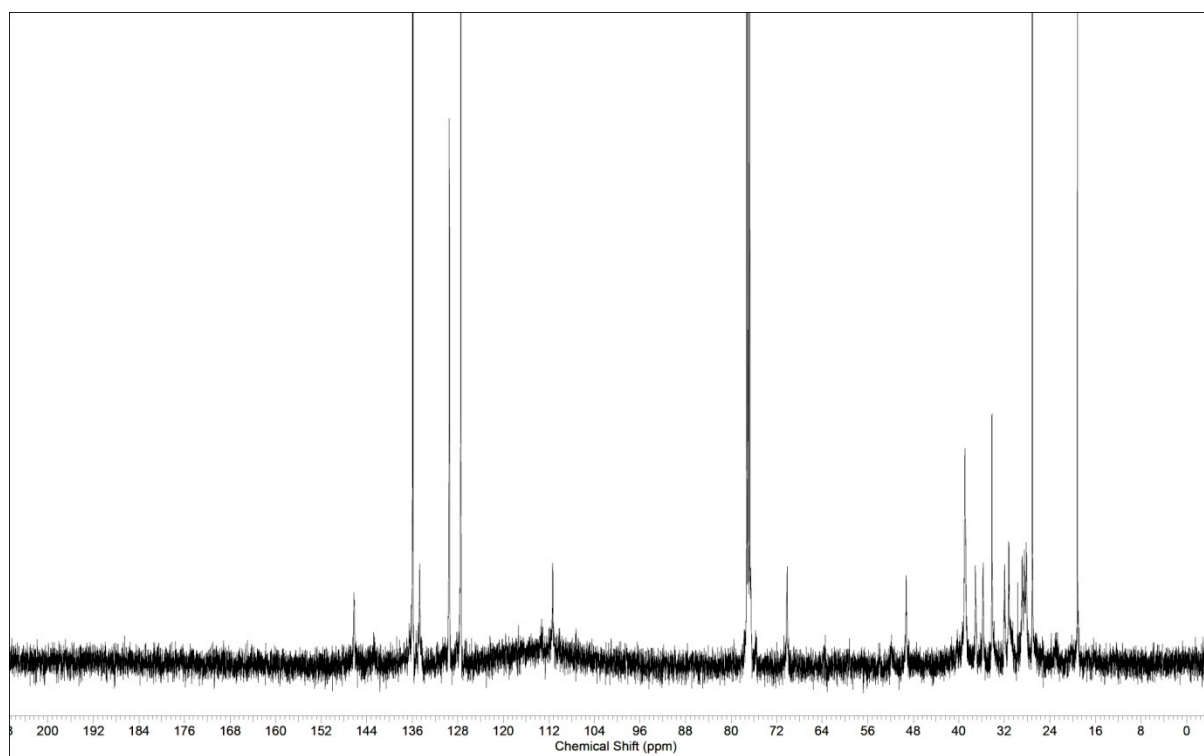
rac-(3*S*,3*aS*,4*R*,9*aR*,12*R*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-7-vinyloctahydro-4,9a-propanocyclopenta[8]annulen-5(1*H*)-one **60**, ¹³C-NMR (75 MHz, CDCl₃):



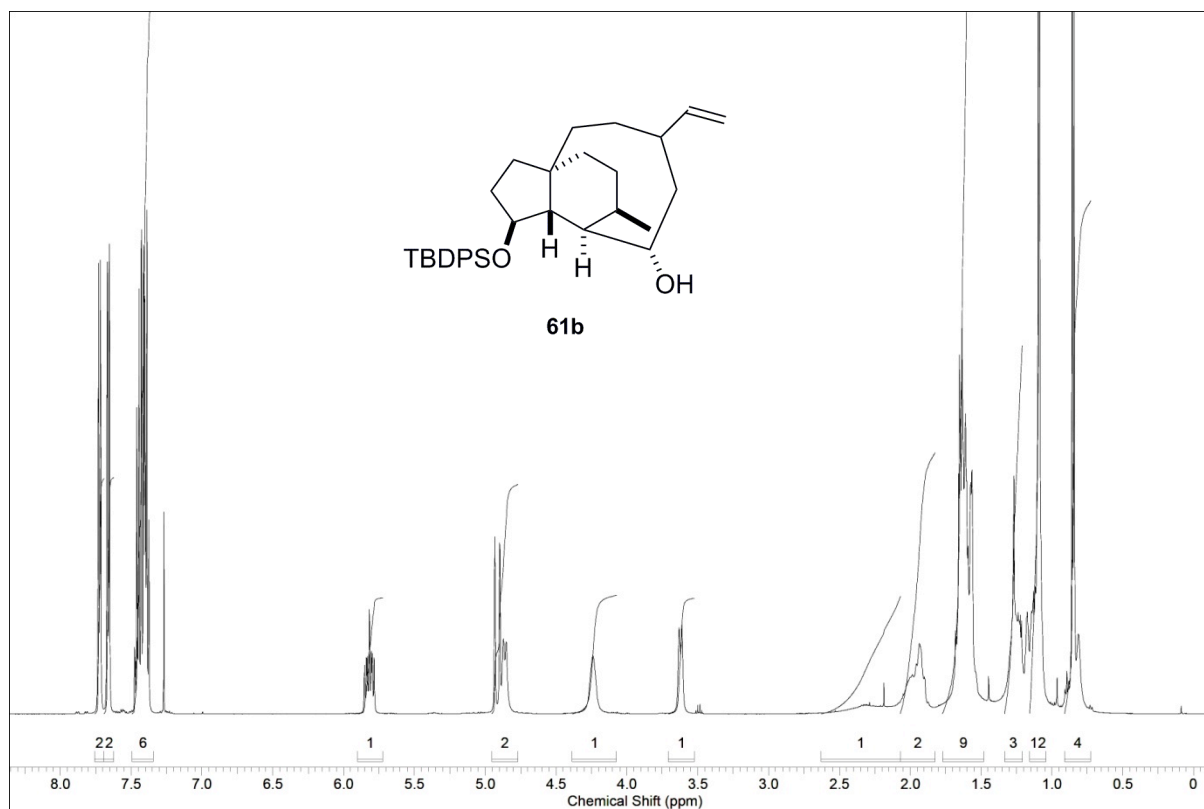
rac-(3*S*,3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-7-vinyldecahydro-4,9*a*-propanocyclopenta[8]annulen-5-ol **61a**, ¹H-NMR (300 MHz, CDCl₃):



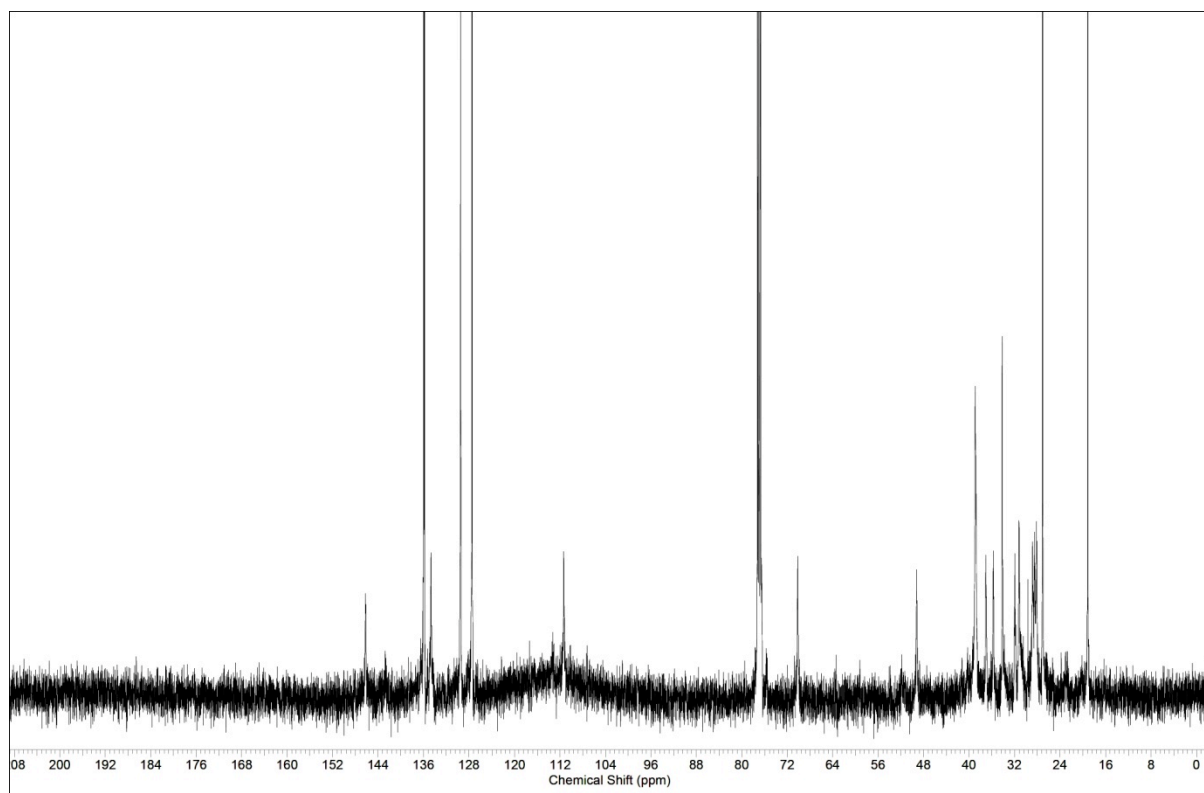
rac-(3*S*,3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-7-vinyldecahydro-4,9*a*-propanocyclopenta[8]annulen-5-ol **61a**, ¹³C-NMR (75 MHz, CDCl₃):



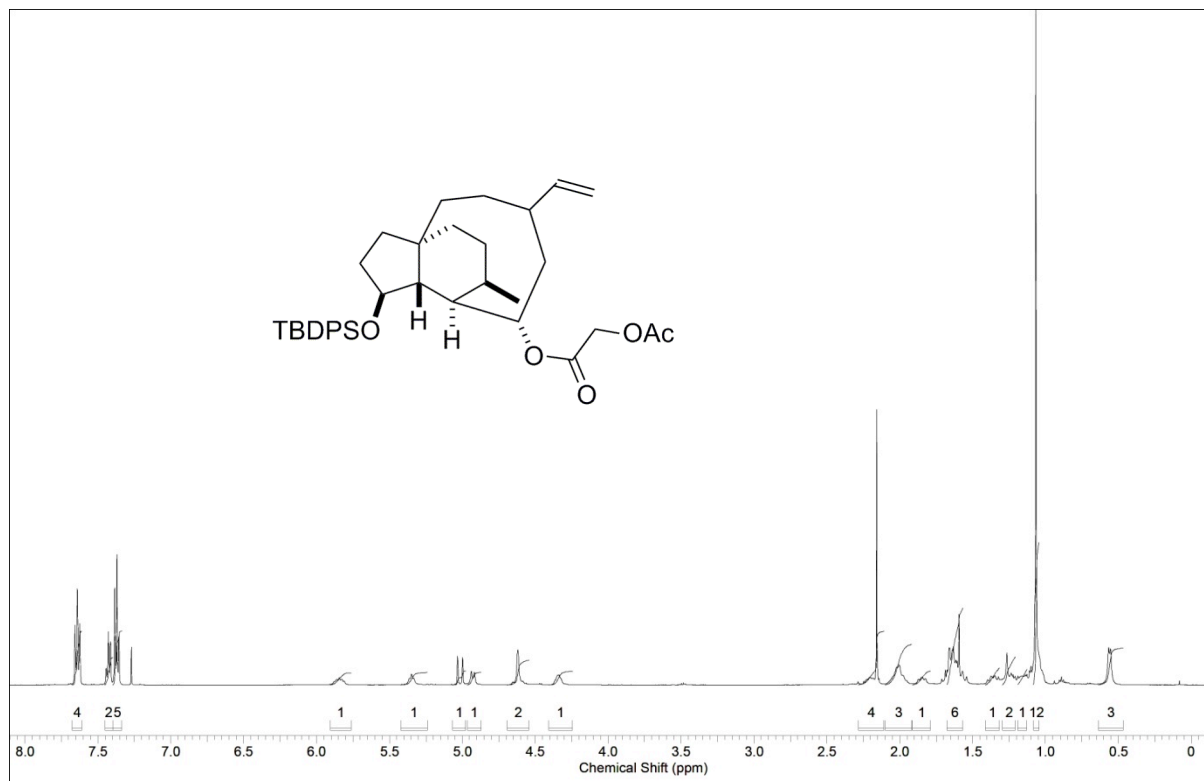
rac-(3*S*,3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-7-vinyldecahydro-4,9*a*-propanocyclopenta[8]annulen-5-ol **61b**, $^1\text{H-NMR}$ (300 MHz, CDCl_3):



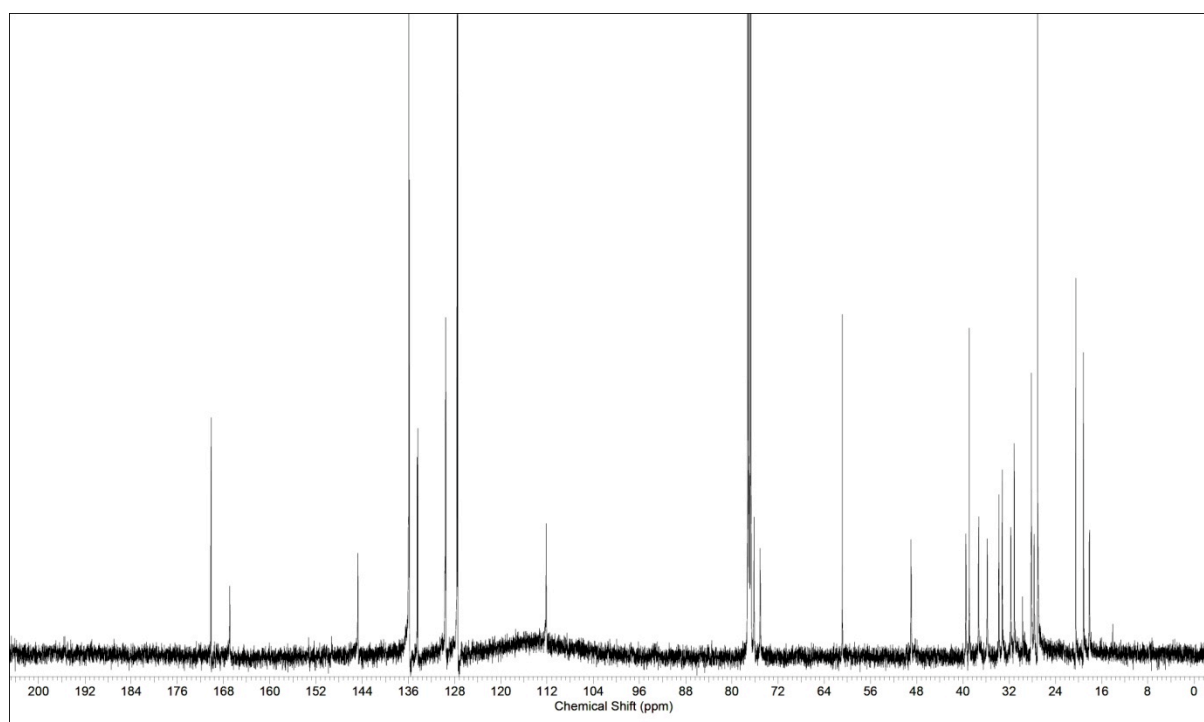
rac-(3*S*,3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-7-vinyldecahydro-4,9*a*-propanocyclopenta[8]annulen-5-ol **61b**, $^{13}\text{C-NMR}$ (75 MHz, CDCl_3):



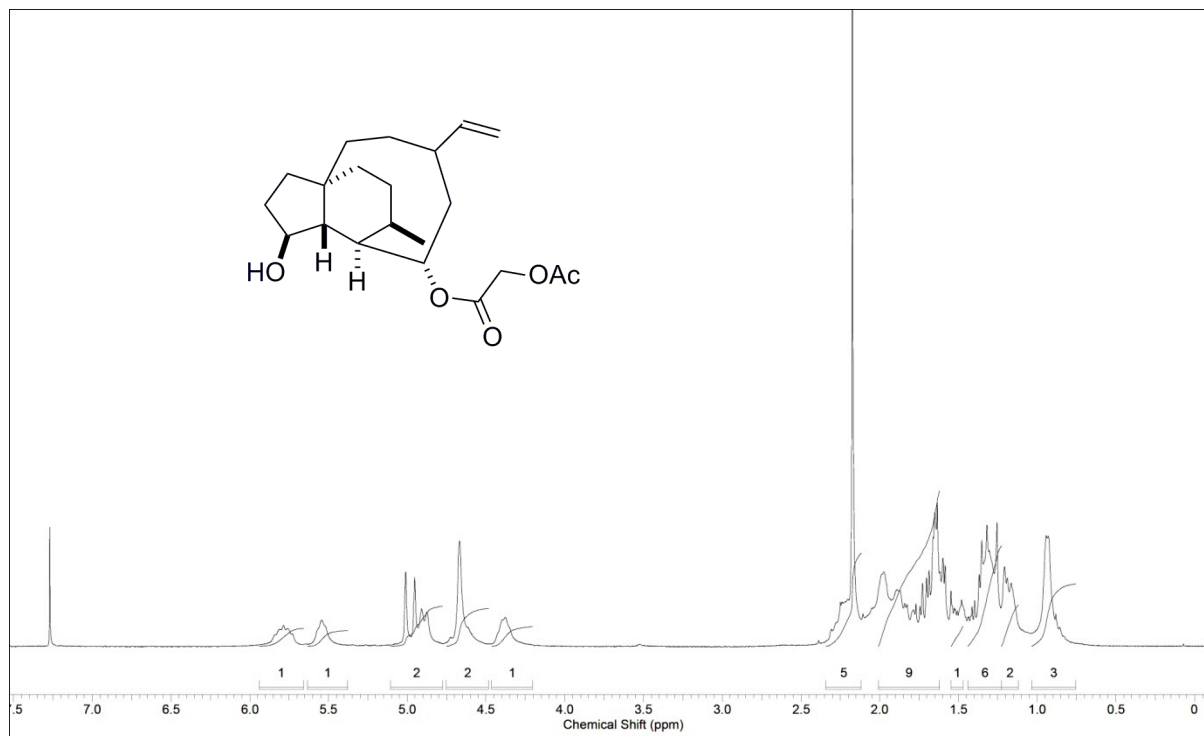
rac-(3*S*,3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-7-vinyldecahydro-4,9*a*-propanocyclopenta[8]annulen-5-yl 2-acetoxyacetate, ¹H-NMR (500 MHz, CDCl₃):



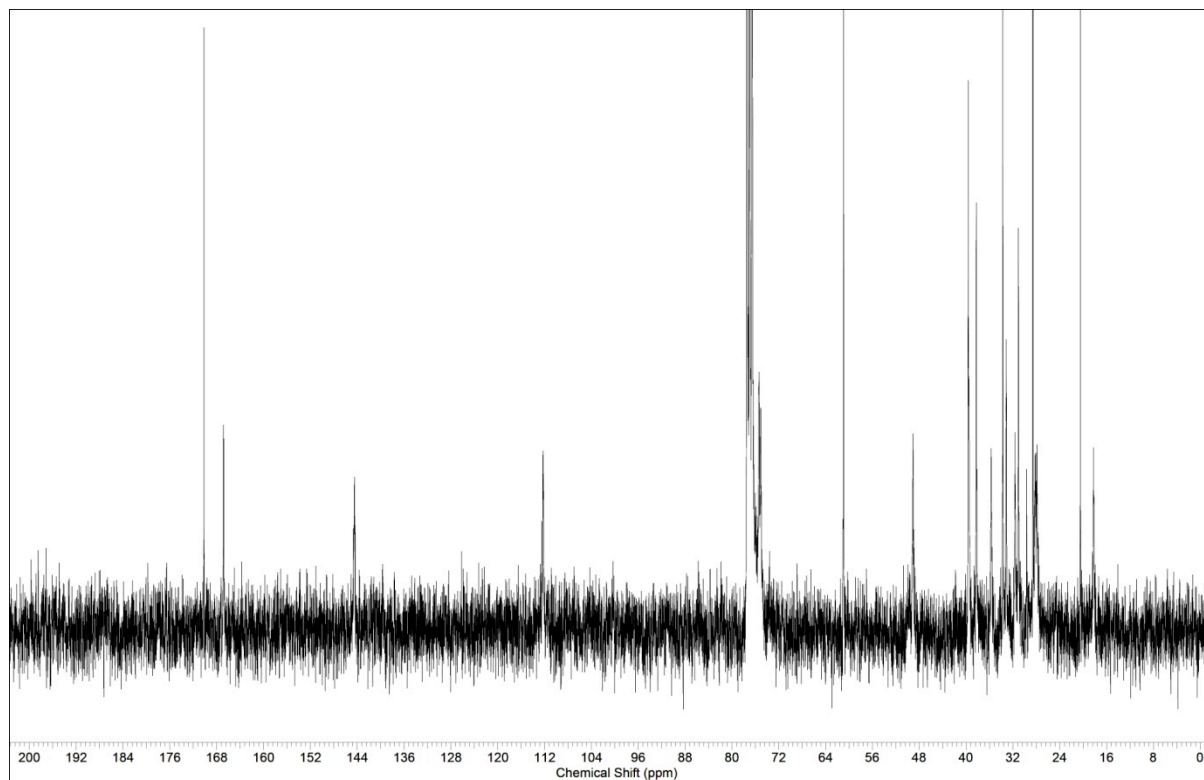
rac-(3*S*,3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-3-((*tert*-butyldiphenylsilyl)oxy)-12-methyl-7-vinyldecahydro-4,9*a*-propanocyclopenta[8]annulen-5-yl 2-acetoxyacetate, ¹³C-NMR (125 MHz, CDCl₃):



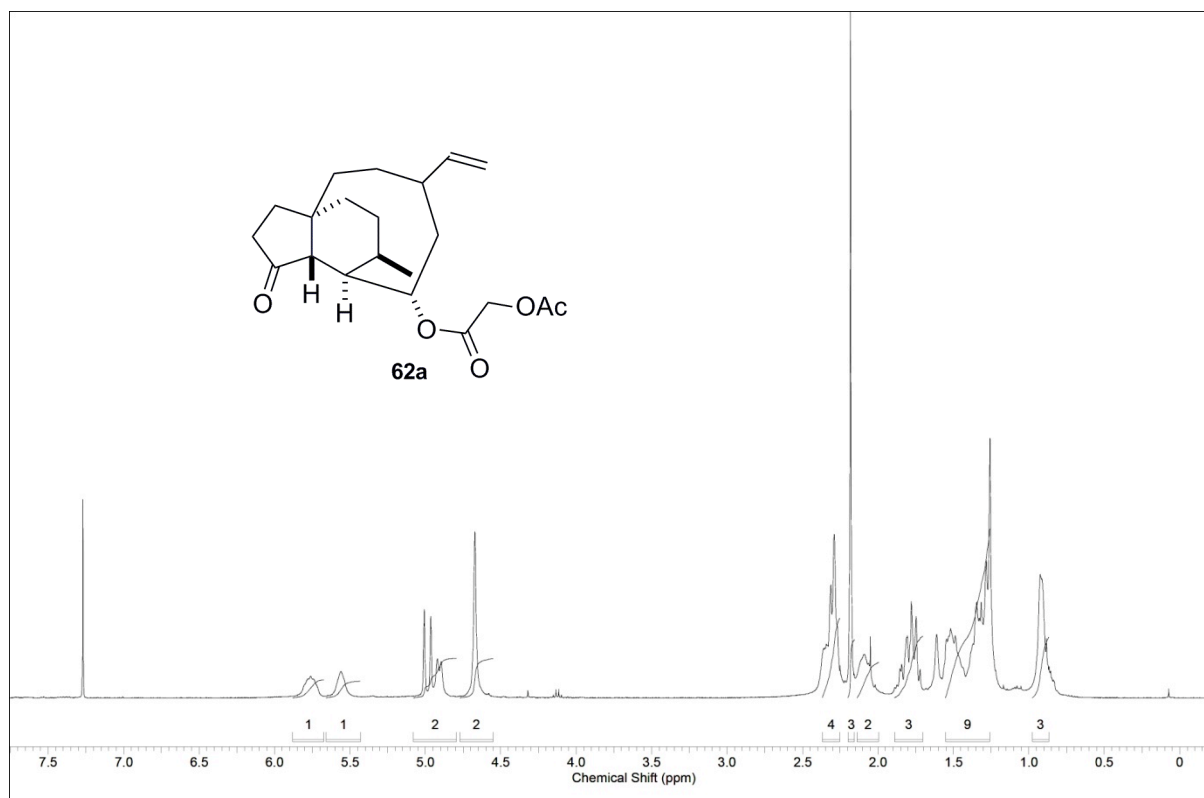
rac-(3*S*,3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-3-hydroxy-12-methyl-7-vinyldecahydro-4,9a-propanocyclopenta[8]annulen-5-yl 2-acetoxyacetate, ¹H-NMR (300 MHz, CDCl₃):



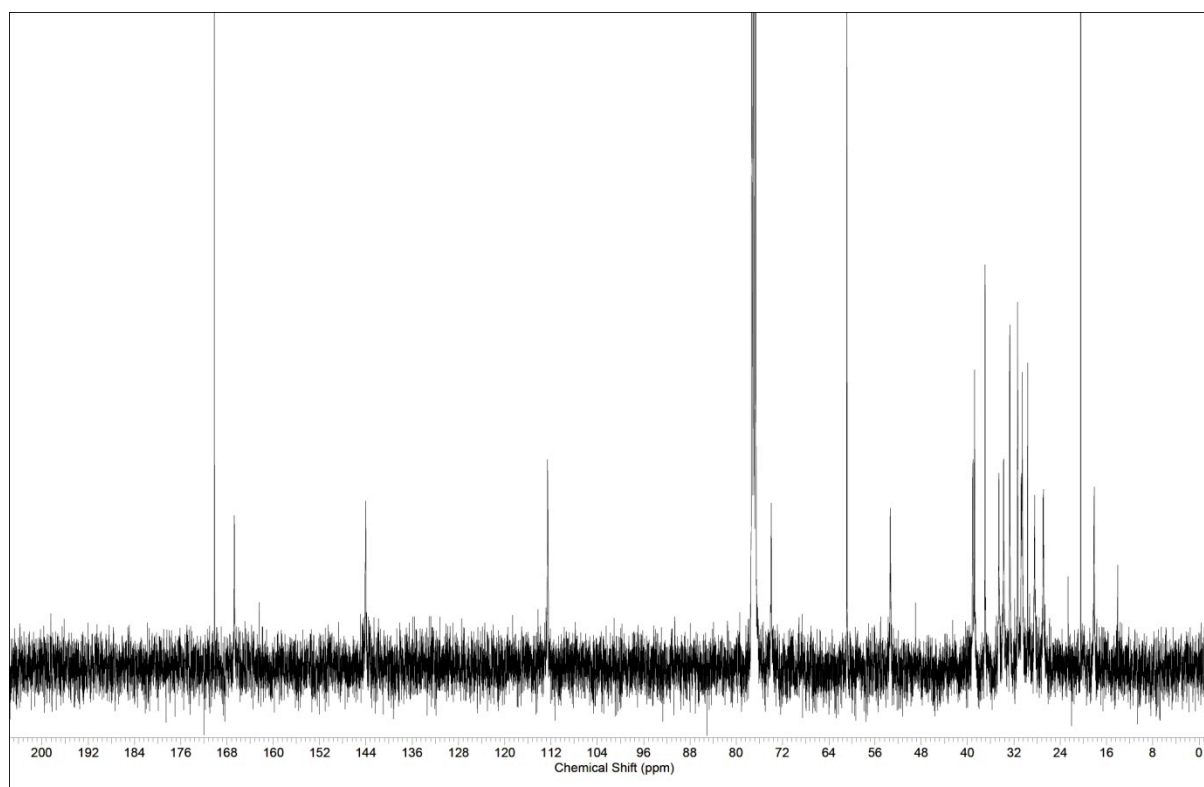
rac-(3*S*,3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-3-hydroxy-12-methyl-7-vinyldecahydro-4,9a-propanocyclopenta[8]annulen-5-yl 2-acetoxyacetate, ¹³C-NMR (75 MHz, CDCl₃):



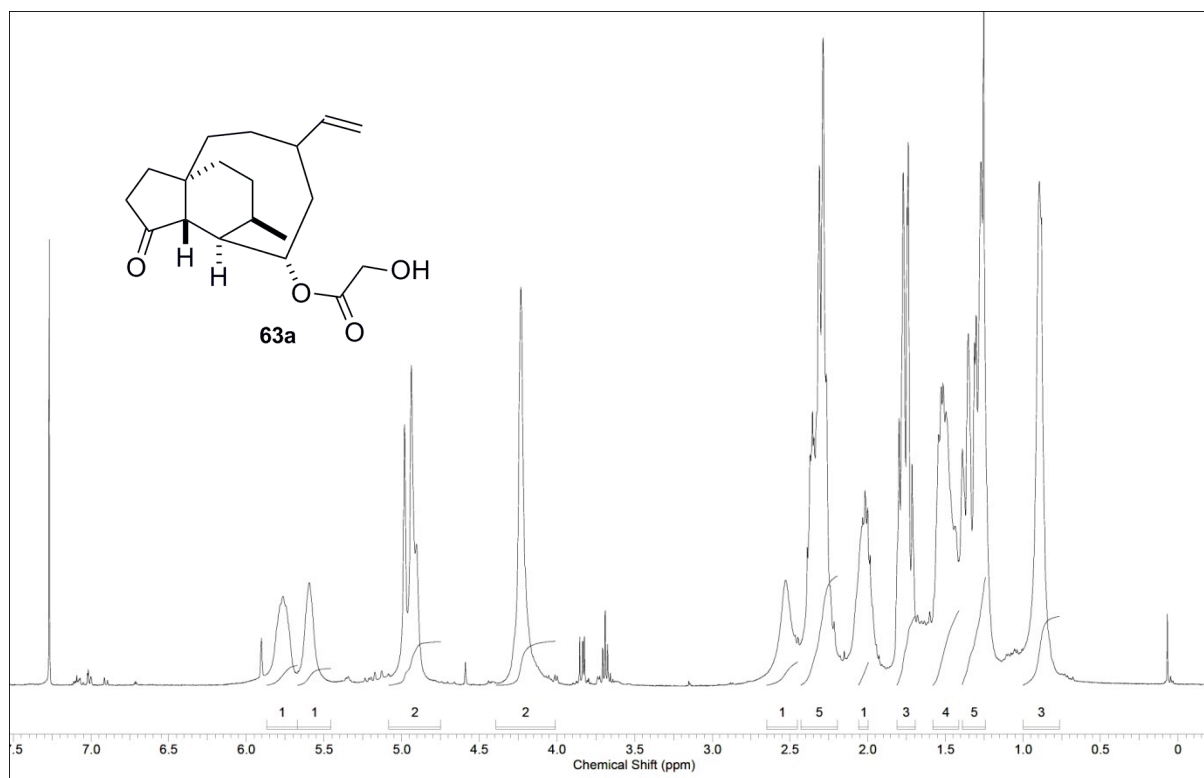
rac-(3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-12-methyl-3-oxo-7-vinyldecahydro-4,9a-propanocyclopenta[8]annulen-5-yl 2-acetoxyacetate **62a**, $^1\text{H-NMR}$ (300 MHz, CDCl_3):



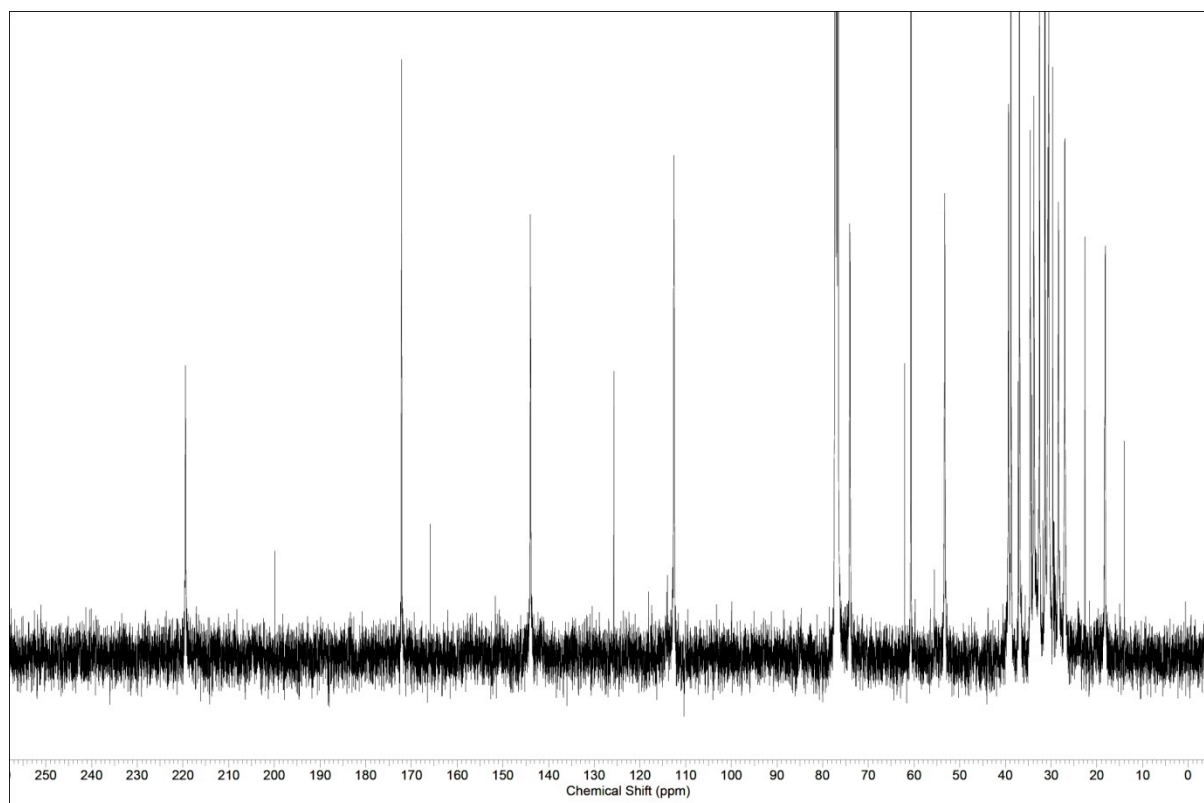
rac-(3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-12-methyl-3-oxo-7-vinyldecahydro-4,9a-propanocyclopenta[8]annulen-5-yl 2-acetoxyacetate **62a**, $^{13}\text{C-NMR}$ (75 MHz, CDCl_3):



rac-(3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-12-methyl-3-oxo-7-vinyldecahydro-4,9a-propanocyclopenta[8]annulen-5-yl 2-hydroxyacetate **63a**, $^1\text{H-NMR}$ (400 MHz, CDCl_3):



rac-(3*aS*,4*R*,5*S*,7*S* or 7*R*,9*aR*,12*R*)-12-methyl-3-oxo-7-vinyldecahydro-4,9a-propanocyclopenta[8]annulen-5-yl 2-hydroxyacetate **63a**, $^{13}\text{C-NMR}$ (100 MHz, CDCl_3):



X-ray structure of **59**

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