

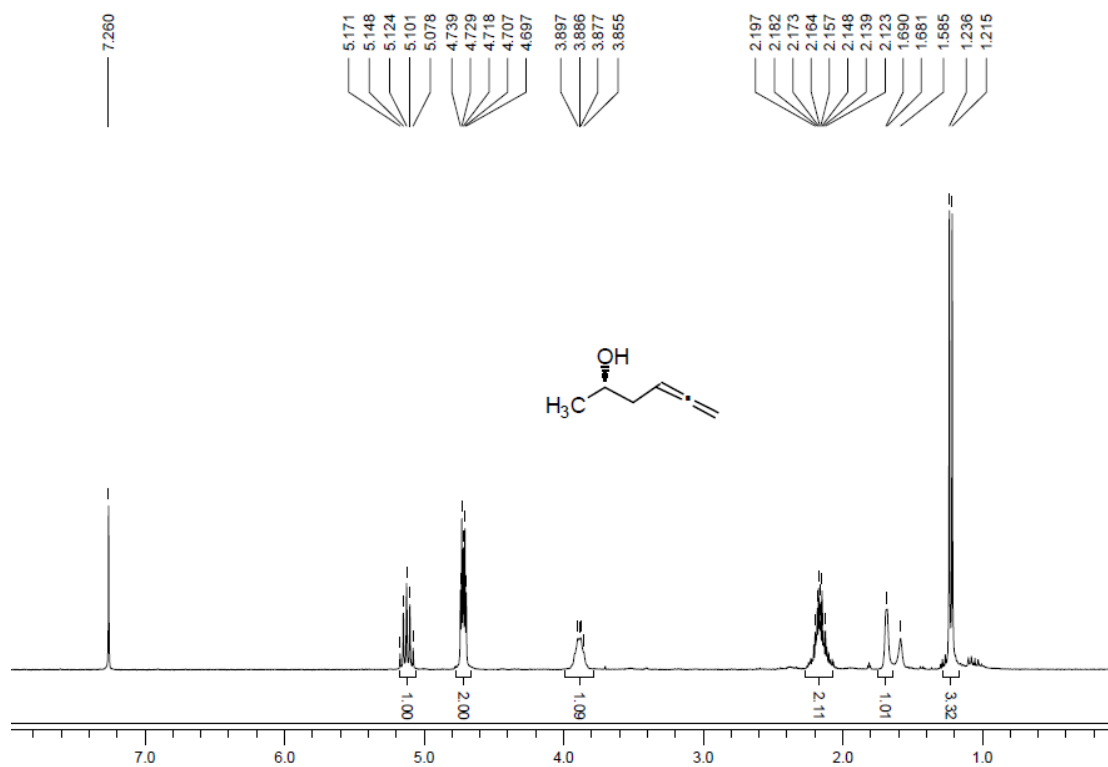
A Synthesis of (-)-Sedinine by Allene Cyclisation and Iminium Ion Chemistry

Spectroscopic data

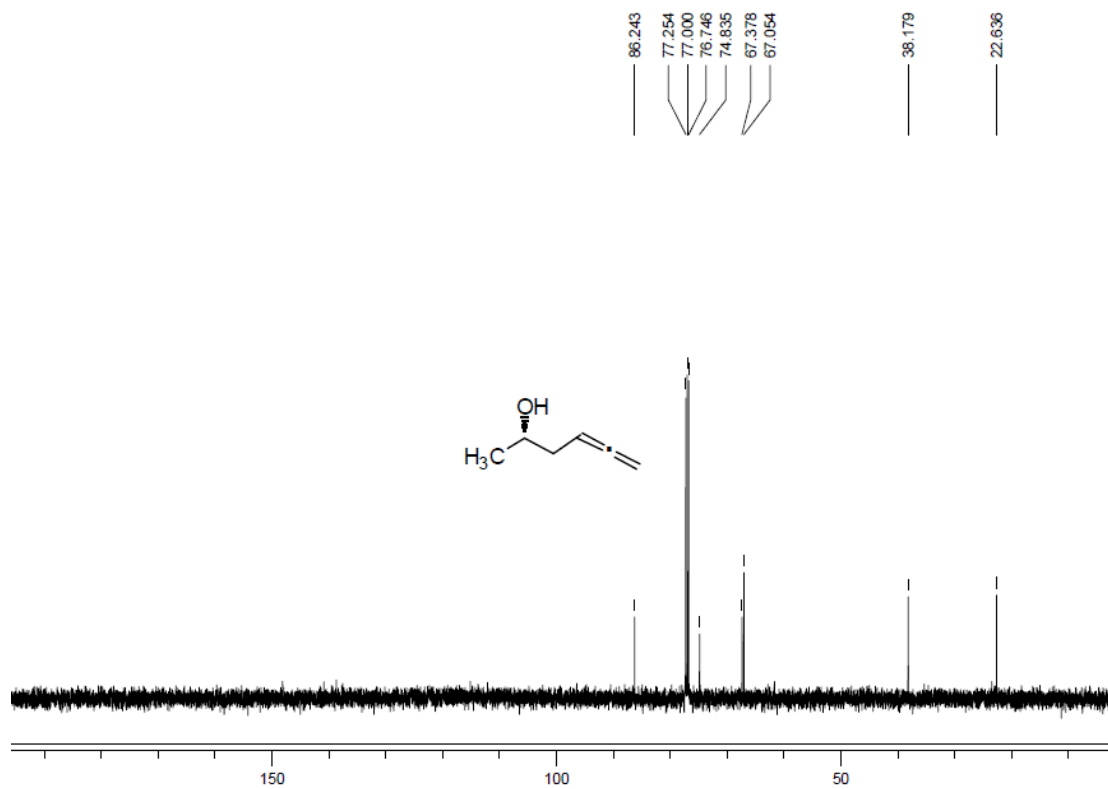
Roderick W. Bates,* and Yongna Lu

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link Singapore 637371

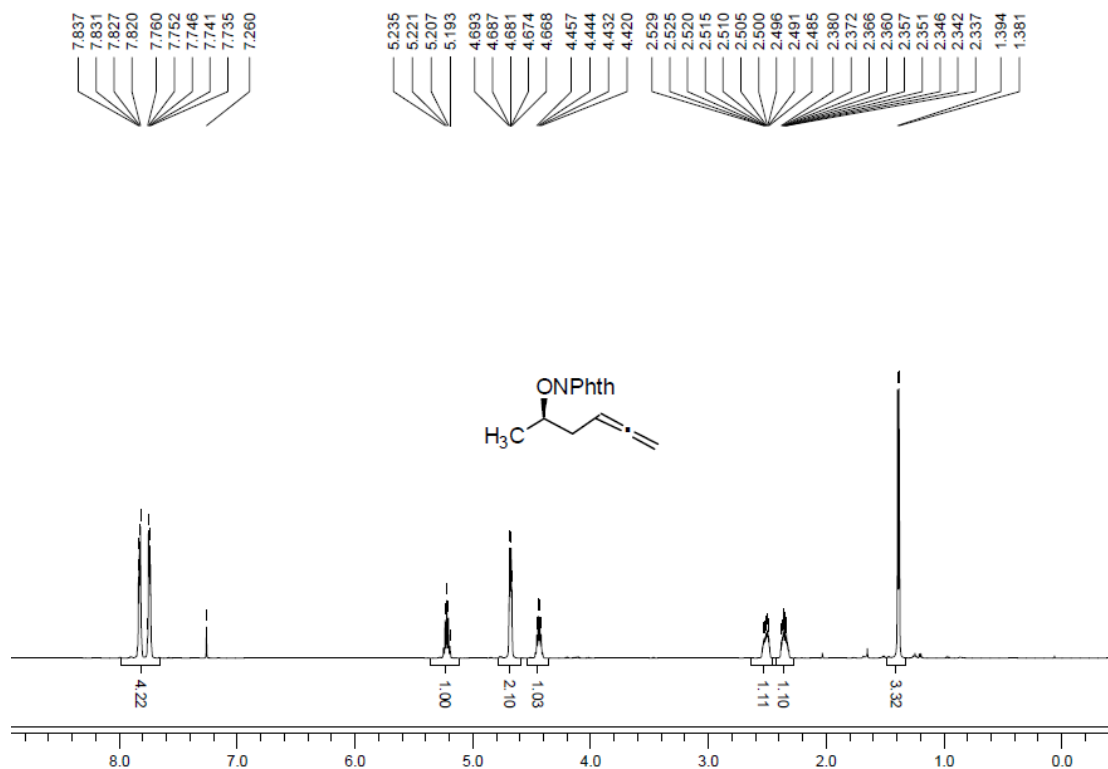
(S)-hexa-4,5-dien-2-ol (6)	2
(R)-2-(hexa-4,5-dien-2-yloxy)isoindoline-1,3-dione (7)	3
(R)-O-(Hexa-4,5-dien-2-yl)hydroxylamine (8)	6
<i>N</i> -tert-Butoxycarbonyl (R)-hexa-4,5-dien-2-hydroxylamine (9)	7
(5R)-tert-Butyl 5-methyl-3-vinylisoxazolidine-2-carboxylate (10)	8
tert-Butyl ((3R, 5R)-5-hydroxyhex-1-en-3-yl)carbamate (11a)	9
tert-butyl ((3S,5R)-5-hydroxyhex-1-en-3-yl)carbamate (11b)	10
(2S,4R,6R)-tert-Butyl 2-(3-bromopropyl)-6-methyl-4-vinyl-1,3-oxazinane-3-carboxylate (12a)	11
(2R,4R,6R)-tert-butyl-2-(3-bromopropyl)-6-methyl-4-vinyl-1,3-oxazinane-3-carboxylate (12b)	12
(2S,4R,6R)-tert-Butyl 2-allyl-6-methyl-4-vinyl-1,3-oxazinane -3-carboxylate (13)	13
(1S,3R,5R)-tert-Butyl 3-methyl-2-oxa-9-azabicyclo[3.3.1]non-6-ene-9-carboxylate (14)	14
(2R)-tert-Butyl 5,6-dihydro-2-((R)-2-hydroxypropyl)-6-methoxypyridine-1(2H)- carboxylate (15)	15
(3R,4aR)-4,4a,7,8-Tetrahydro-8-methoxy-3-methylpyrido [1,2-c][1,3] oxazin-1(3H) -one (16)	16
(3R,4aR,8S)-3-methyl-8-(2-oxo-2-phenyleth-yl)-4,4a,7,8-tetrahydropyrido [1,2-c][1,3] oxazin-1(3H)-one (17a)	17
(3R,4aR,8R)-3-methyl-8-(2-oxo-2-phenyleth-yl)-4,4a,7,8-tetrahydropyrido[1,2-c][1,3] oxazin-1(3H)-one (17b)	18
(2R,6S)-tert-Butyl 2-((R)-2-hydroxypropyl)-6- (2-oxo-2-phenylethyl)-5,6-dihydro pyri- dine-1(2H)-carboxylate (19)	19
(2R,6S)-tert-Butyl 6-((S)-2-hydroxy-2-phenylethyl)-2-((R)-2- hydroxypropyl)-5,6-di -hydropyridine-1(2H)-carboxylate (21a)	20
(2R,6S)-tert-Butyl 6-((R)-2-hydroxy-2-phenylethyl)-2-((R)-2-hydroxypropyl)-5,6-di -hydropyridine-1(2H)-carboxylate (21b)	21
(R)-1-((2R,6S)-1,2,5,6-Tetrahydro-6-((S)-2-hydroxy-2-phenylethyl)-1-methylpyridin -2-yl)propan-2-ol (sedinine) (1)	22



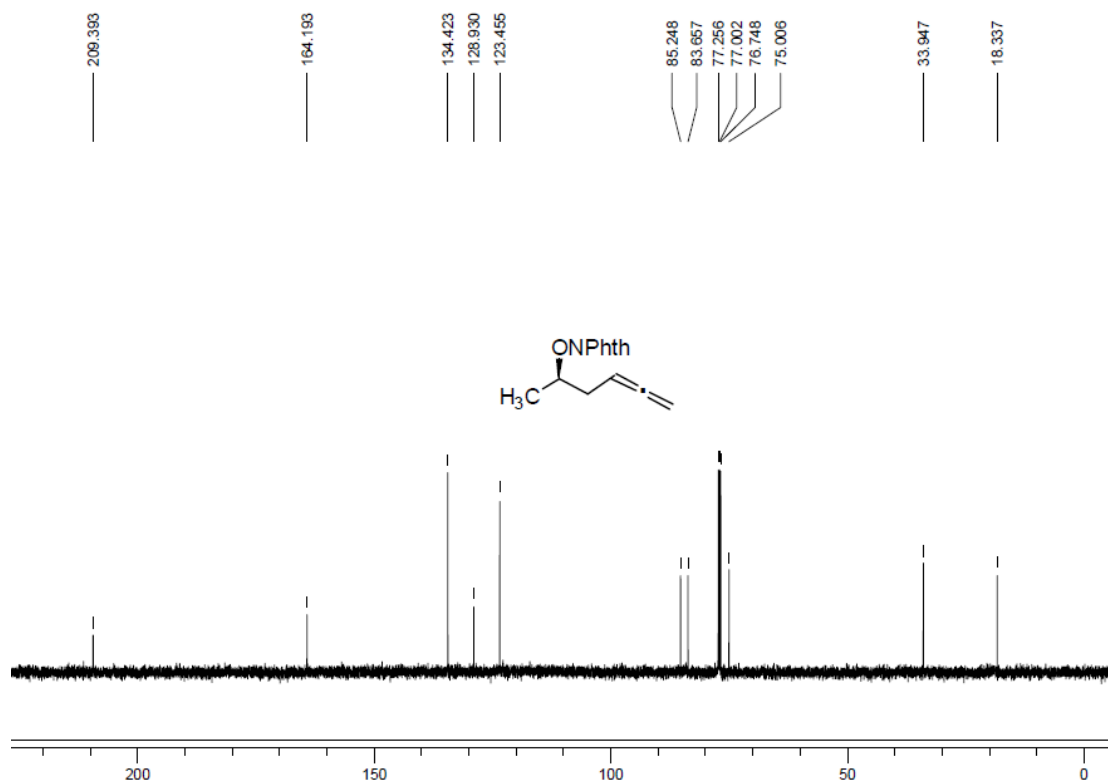
¹H NMR spectrum of (S)-Hexa-4,5-dien-2-ol (6) (CDCl₃, 300MHz)



¹³C NMR spectrum of (S)-Hexa-4,5-dien-2-ol (6) (CDCl₃, 125MHz)

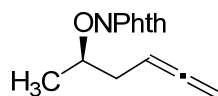


¹H NMR spectrum of **(R)-2-(Hexa-4,5-dien-2-yloxy)isoindoline-1,3-dione (7)** (CDCl₃, 500MHz)

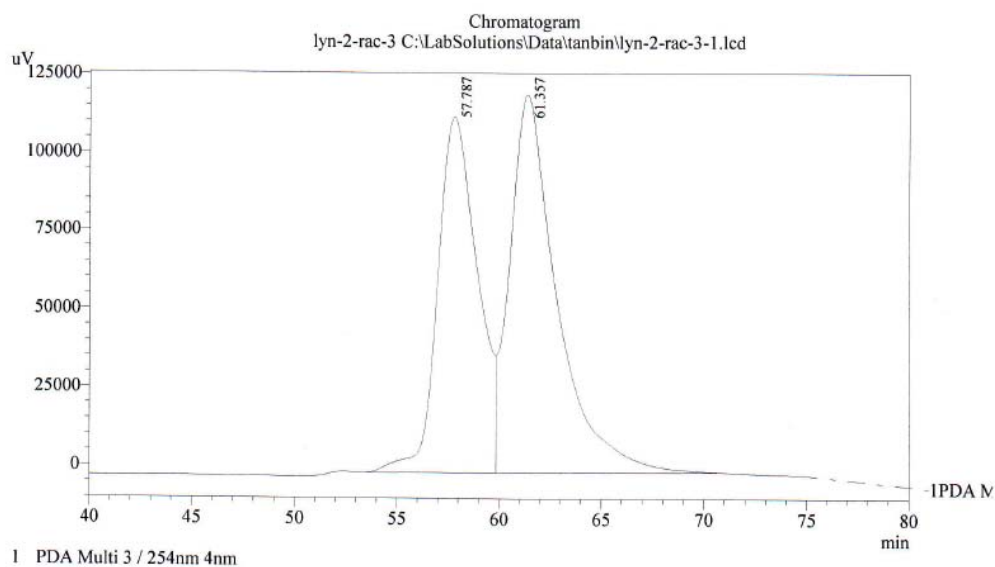


¹³C NMR spectrum of **(R)-2-(Hexa-4,5-dien-2-yloxy)isoindoline-1,3-dione (7)** (CDCl₃, 125MHz)

Chiral HPLC analysis for compound 7: **(R)-2-(Hexa-4,5-dien-2-yloxy)isoindoline-1,3-dione**



Time: 2009Apr281358
 Reaction name:
 Substrate:
 Sample name: lny-2-rac
 Catalyst:
 Solvent:
 Temperature:
 Chiral column: OJ-H
 Eluent: 99% hexane 1%IPA
 Flow rate: 0.3mL/min

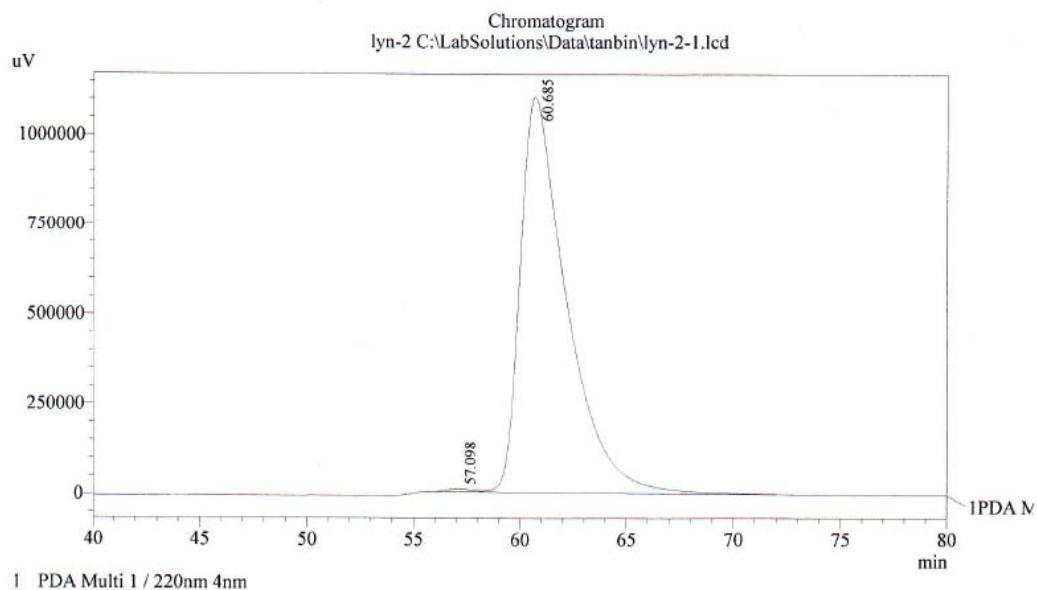


PDA Ch3 254nm 4nm

PeakTable

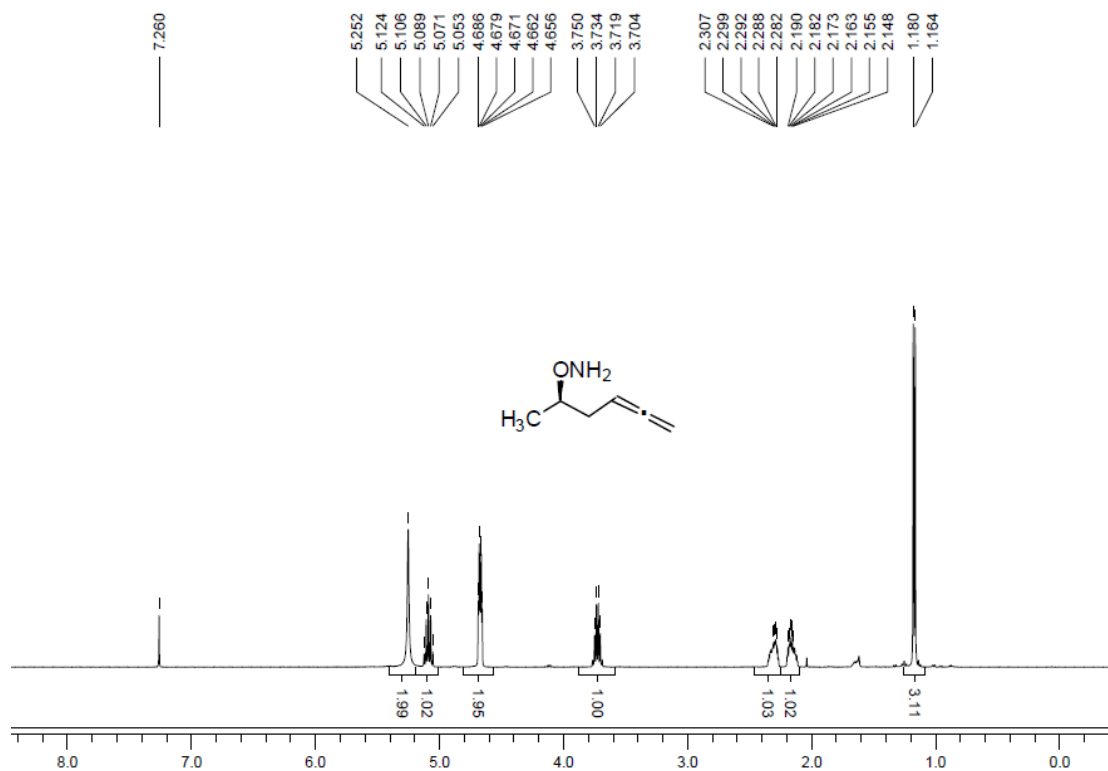
Peak#	Ret. Time	Area	Height	Area %	Height %
1	57.787	15448643	113740	44.255	48.496
2	61.357	19459744	120796	55.745	51.504
Total		34908388	234536	100.000	100.000

Time: 2009Apr281359
 Reaction name:
 Substrate:
 Sample name: lny-2
 Catalyst:
 Solvent:
 Temperature:
 Chiral column: OJ-H
 Eluent: 99% hexane 1%IPA
 Flow rate: 0.3mL/min

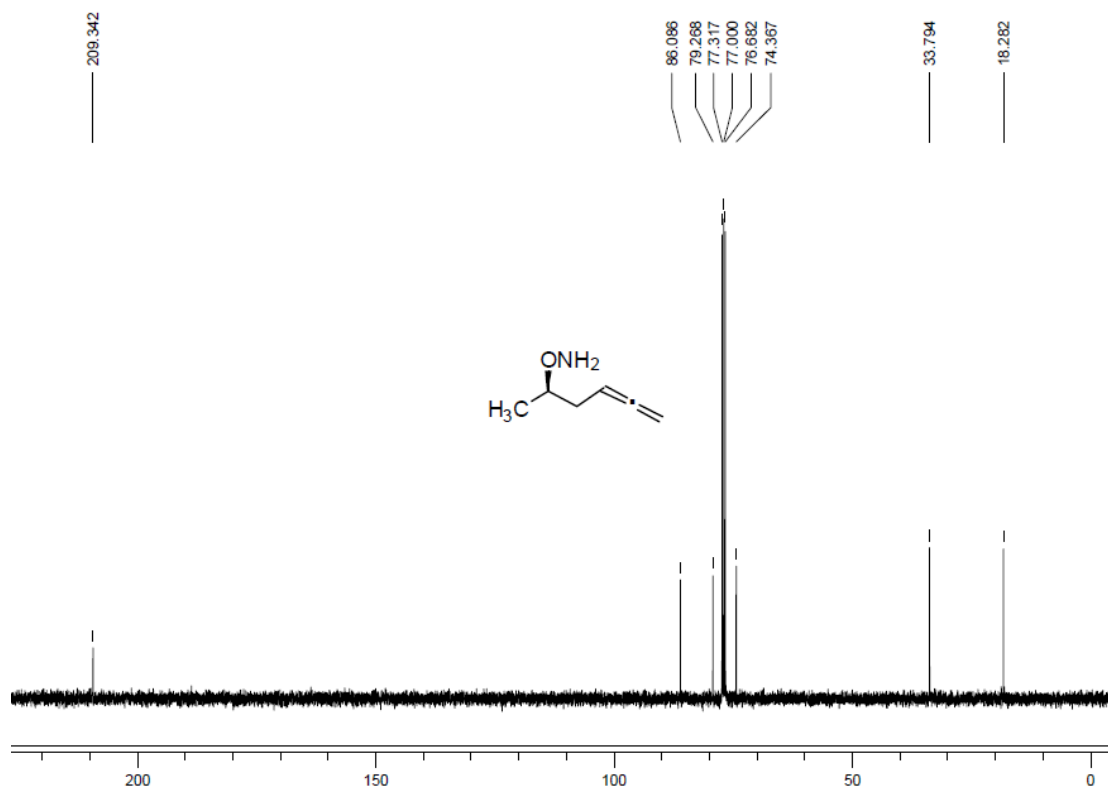


PeakTable

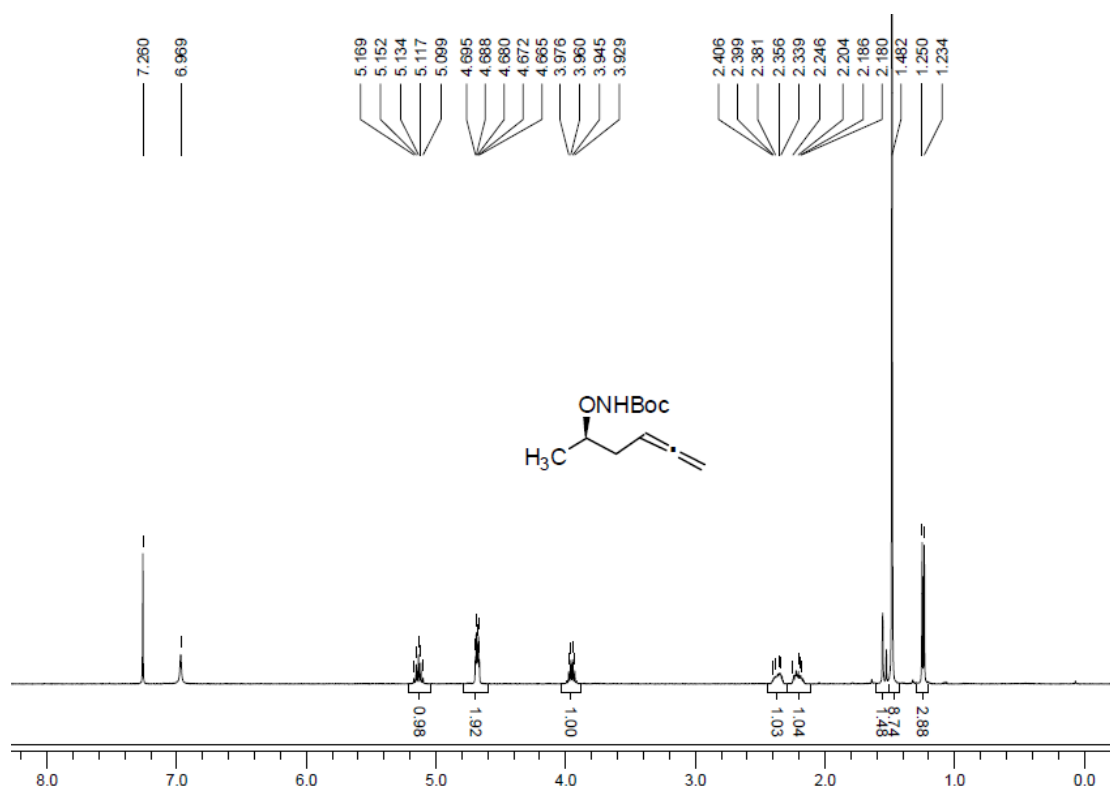
PDA Ch1 220nm 4nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	57.098	600916	7941	0.357	0.715
2	60.685	167806486	1102827	99.643	99.285
Total		168407402	1110768	100.000	100.000



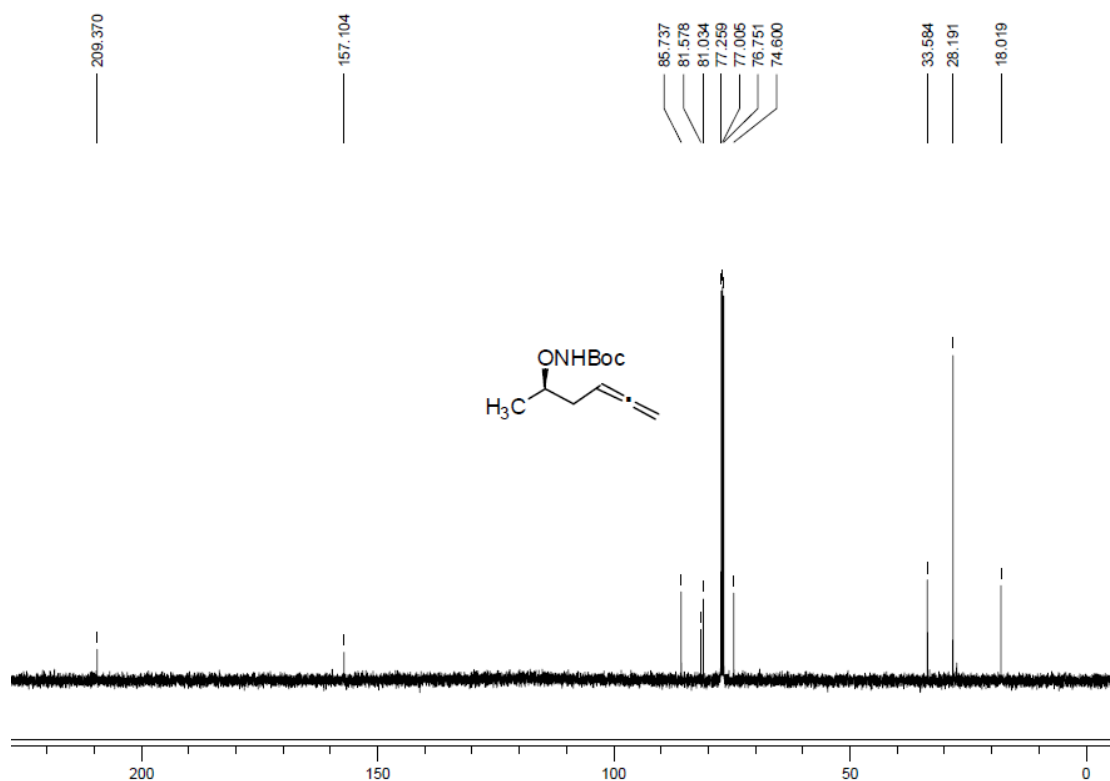
¹H NMR spectrum of (*R*)-O-(Hexa-4,5-dien-2-yl)hydroxylamine (**8**) (CDCl₃, 400MHz)



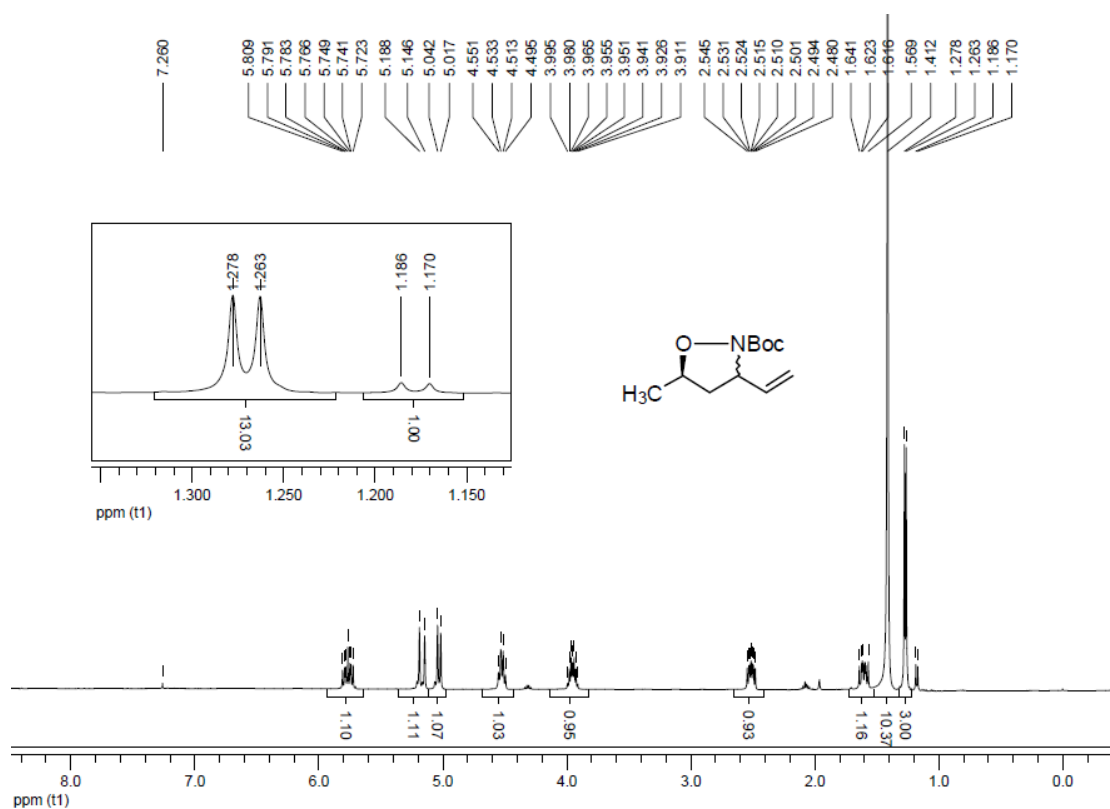
¹³C NMR spectrum of (*R*)-O-(Hexa-4,5-dien-2-yl)hydroxylamine (**8**) (CDCl₃, 100MHz)



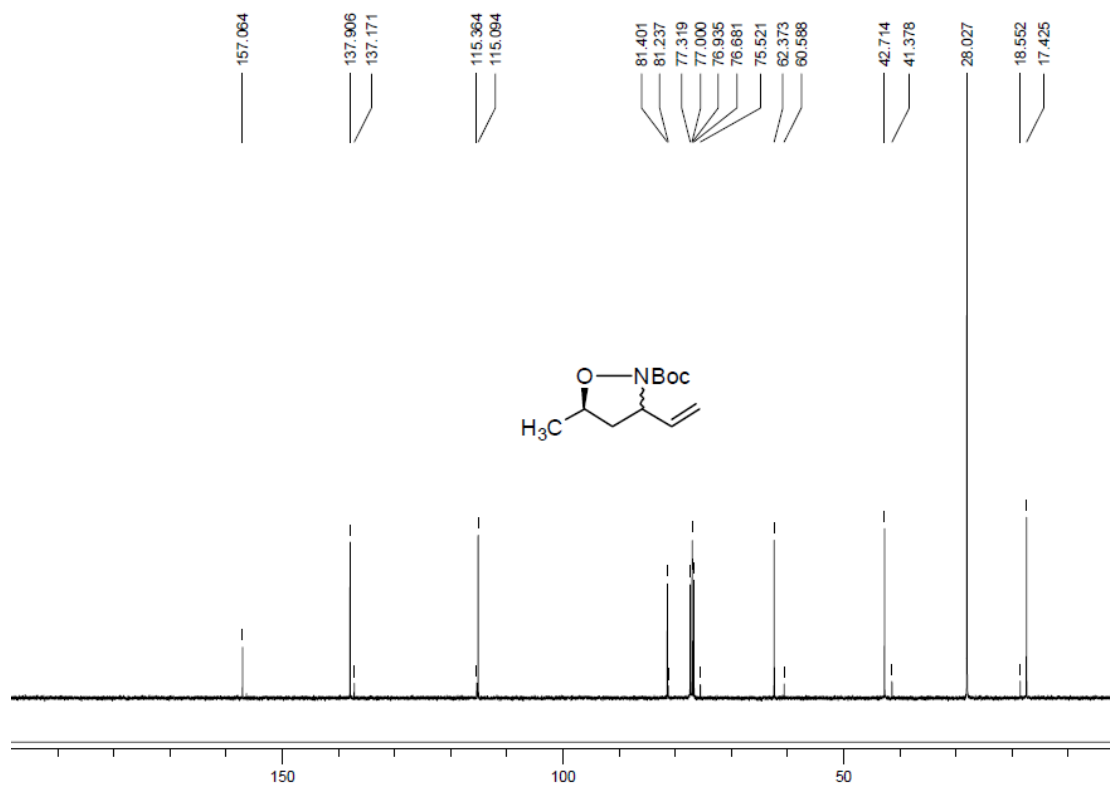
¹H NMR spectrum of *N*-*tert*-Butoxycarbonyl (*R*)-hexa-4,5-dien-2-hydroxylamine (9) (CDCl₃, 400MHz)



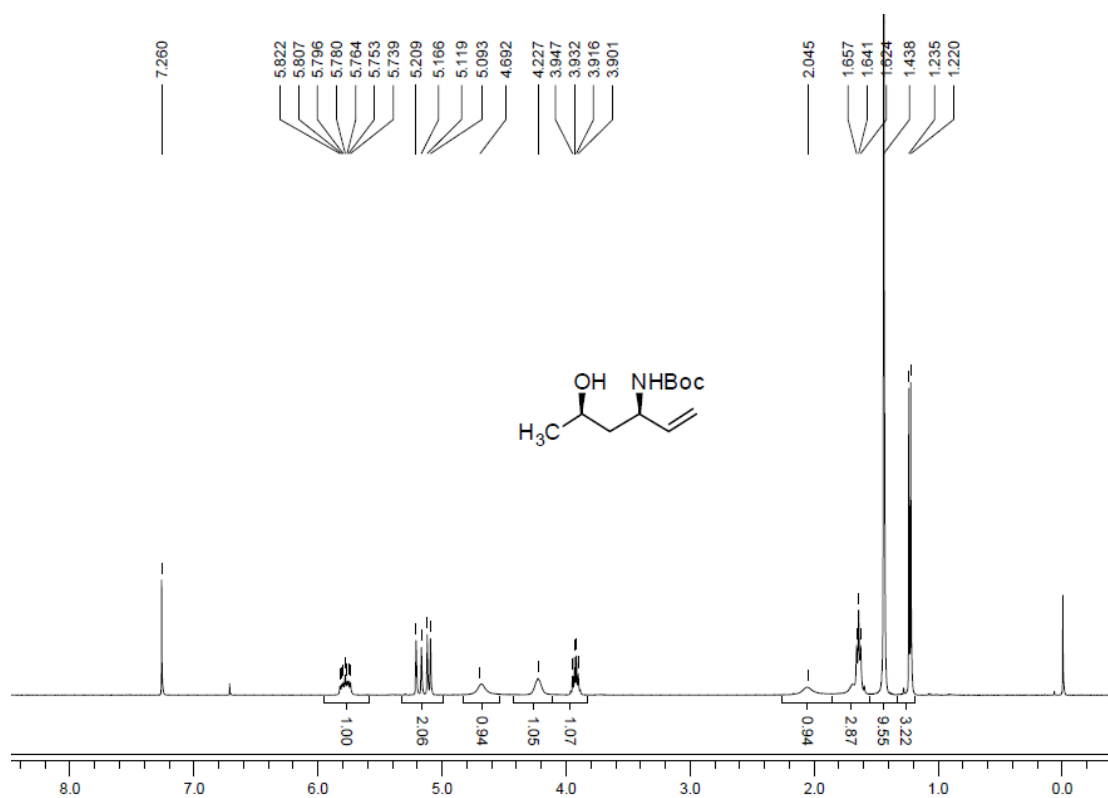
¹³C NMR spectrum of *N*-*tert*-Butoxycarbonyl (*R*)-hexa-4,5-dien-2-hydroxylamine (9) (CDCl₃, 75MHz)



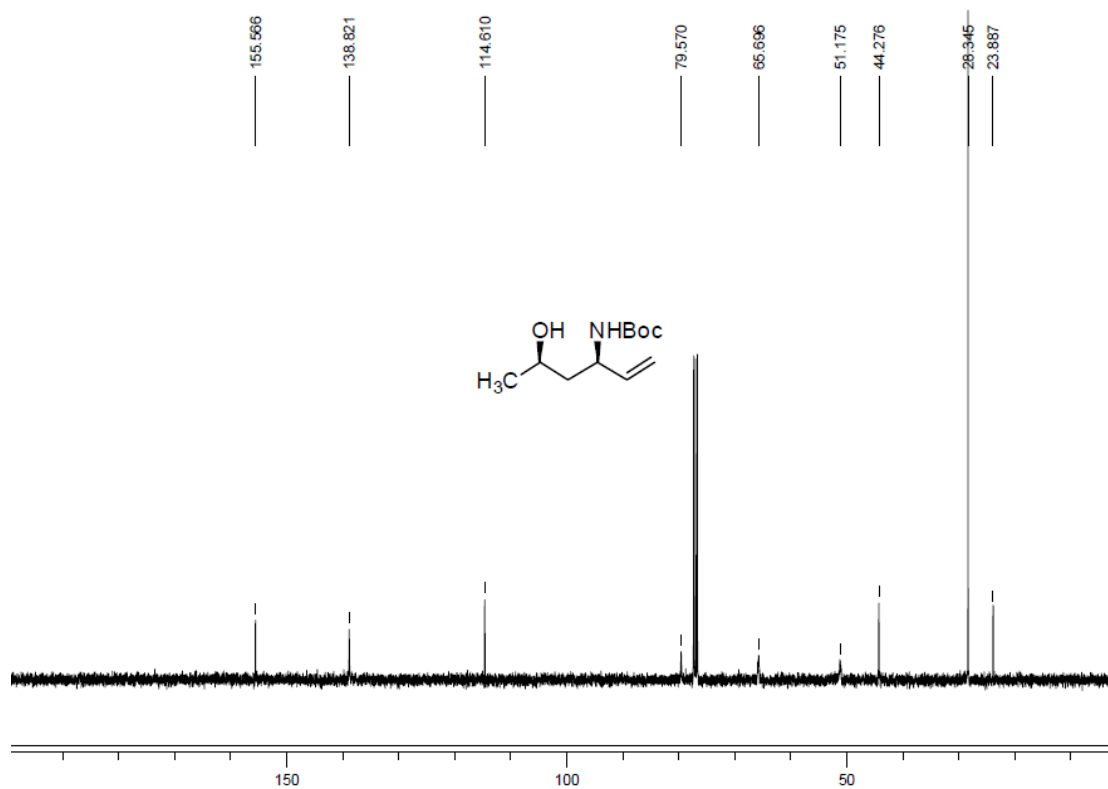
¹H NMR spectrum of (5R)-tert-Butyl 5-methyl-3-vinylisoxazolidine-2-carboxylate (10) (CDCl₃, 300MHz)



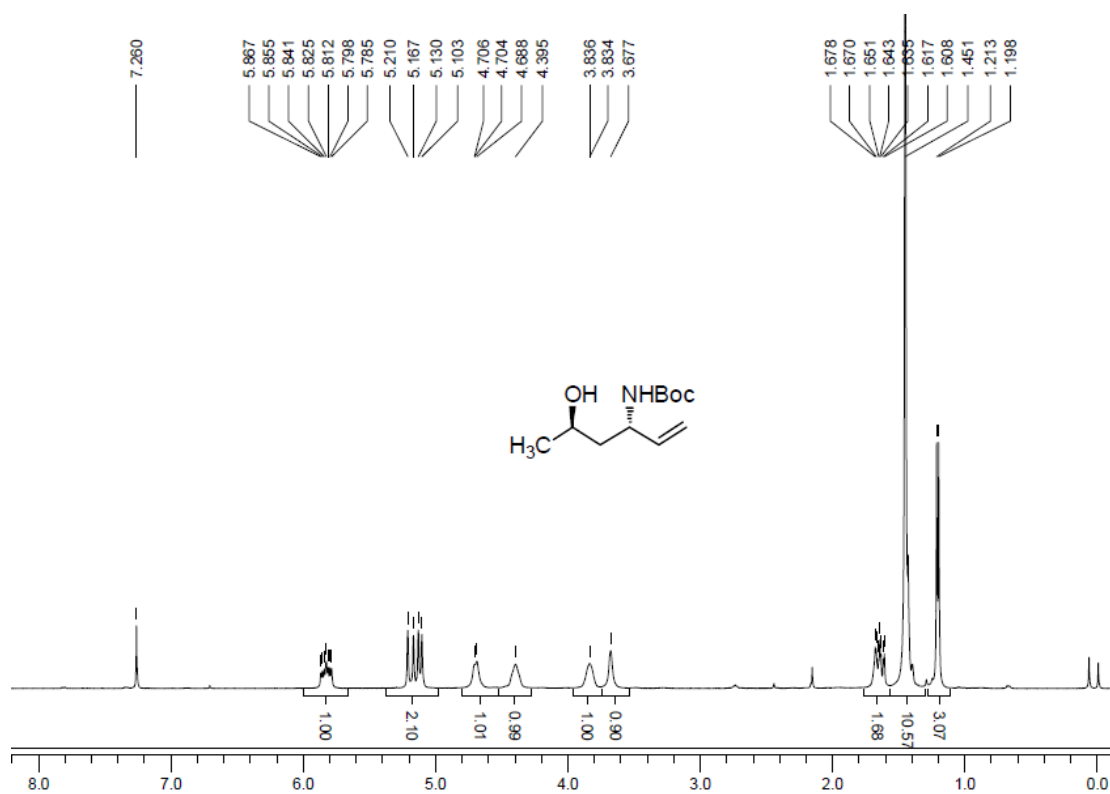
¹³C NMR spectrum of (5R)-tert-Butyl 5-methyl-3-vinylisoxazolidine-2-carboxylate (10) (CDCl₃, 75MHz)



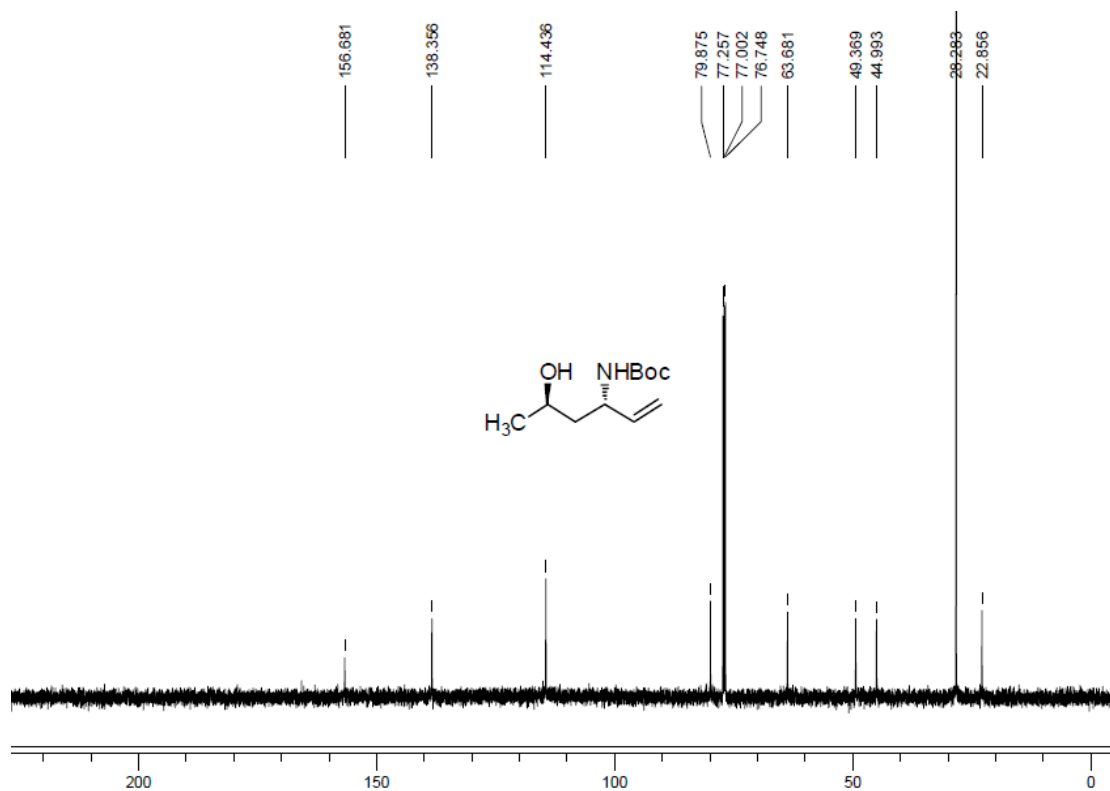
¹H NMR spectrum of *tert*-Butyl ((3*R*, 5*R*)-5-hydroxyhex-1-en-3-yl)carbamate (11a) (CDCl₃, 400MHz)



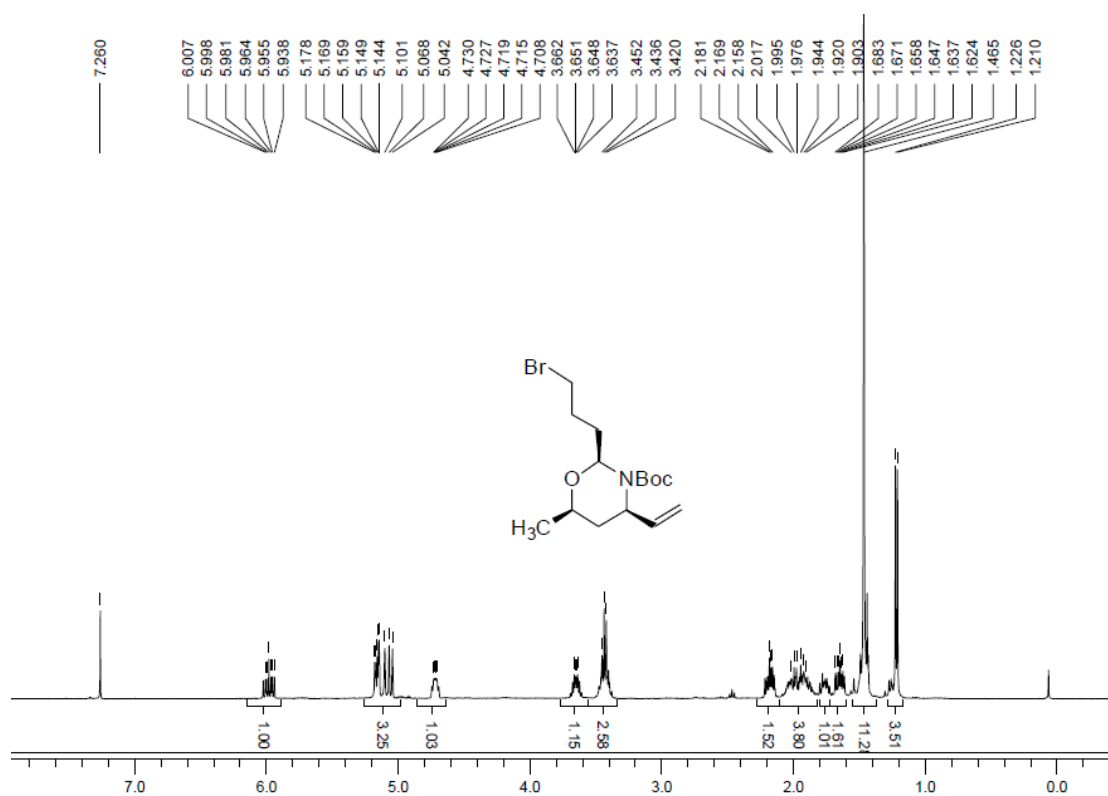
¹³C NMR spectrum of *tert*-Butyl ((3*R*, 5*R*)-5-hydroxyhex-1-en-3-yl)carbamate (11a) (CDCl₃, 100MHz)



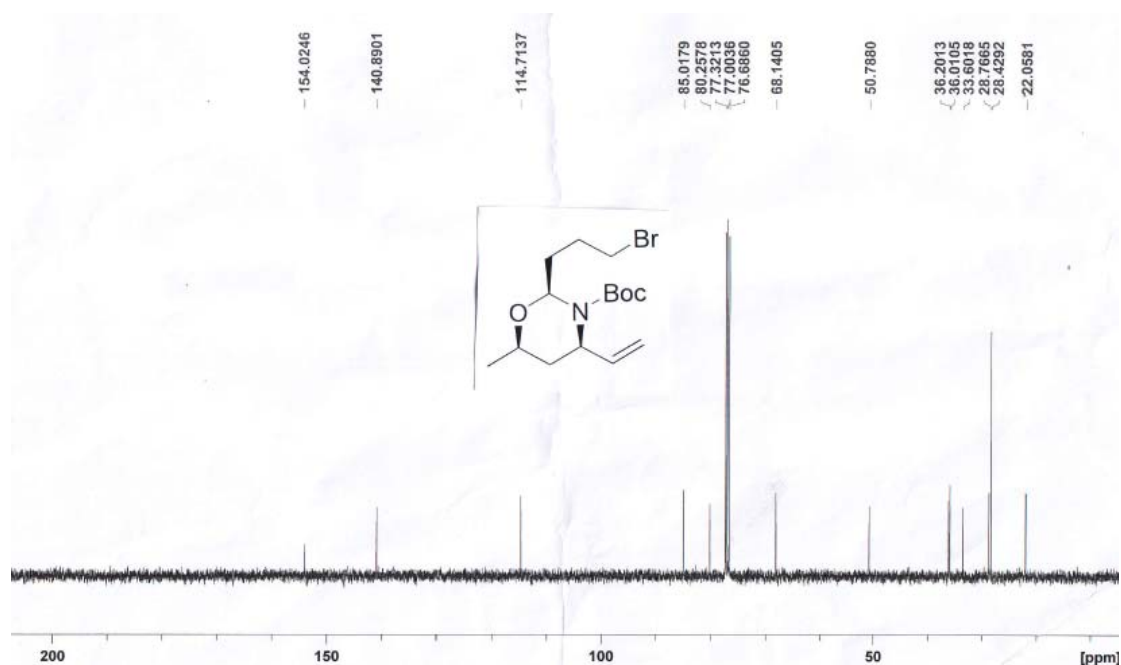
¹H NMR spectrum of *tert*-butyl ((3*S*,5*R*)-5-hydroxyhex-1-en-3-yl)carbamate (11b) (CDCl₃, 400MHz)



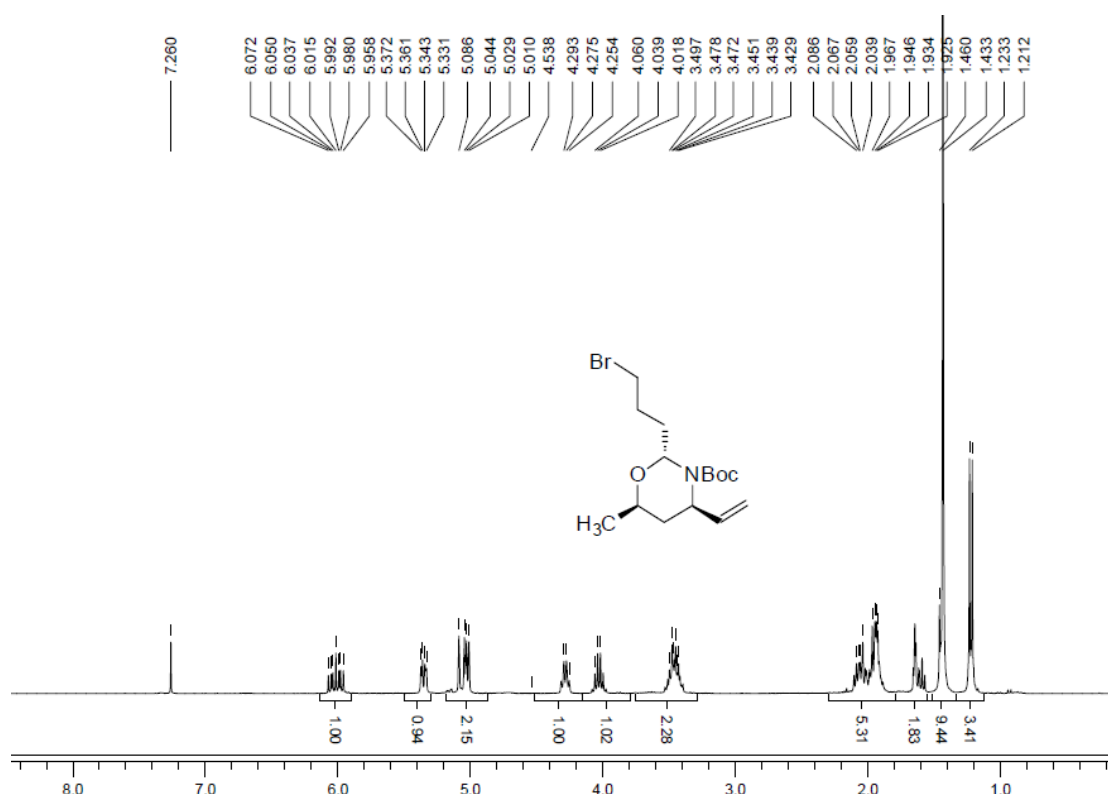
¹³C NMR spectrum of *tert*-butyl ((3*S*,5*R*)-5-hydroxyhex-1-en-3-yl)carbamate (11b) (CDCl₃, 125MHz)



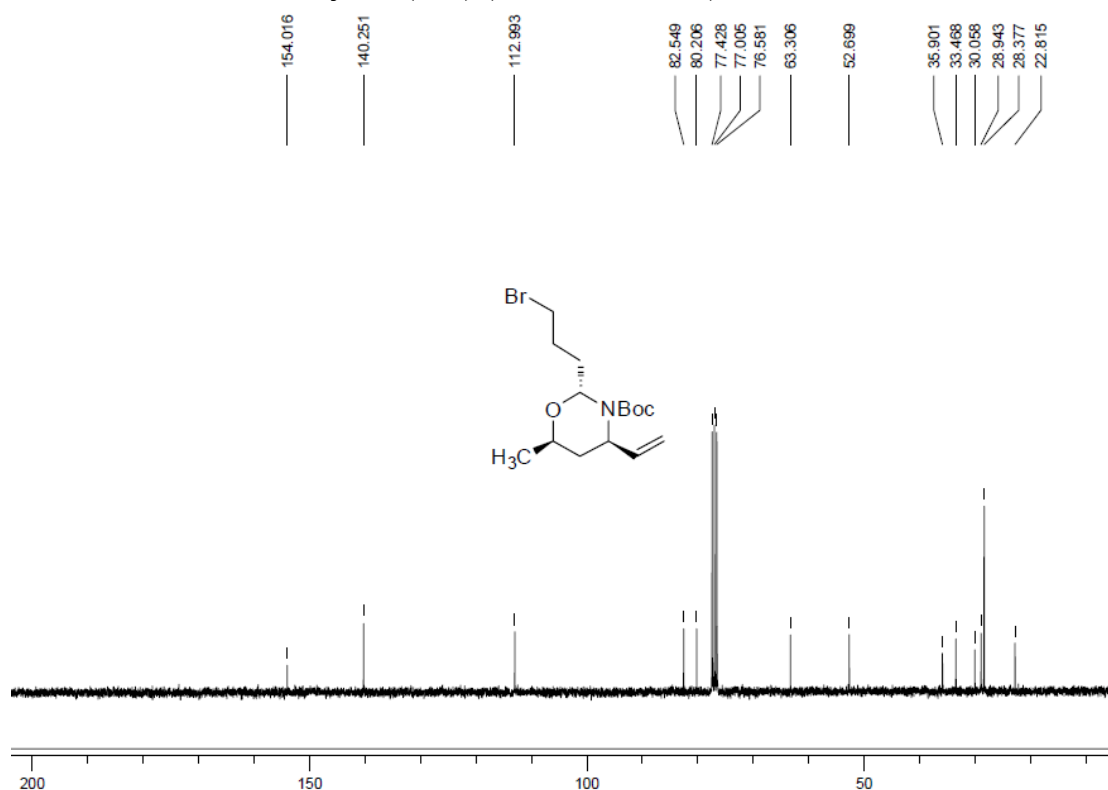
¹H NMR spectrum of (2S,4R,6R)-tert-Butyl 2-(3-bromopropyl)-6-methyl-4-vinyl-1,3-oxazinane-3-carboxylate (12a) (CDCl₃, 400MHz)



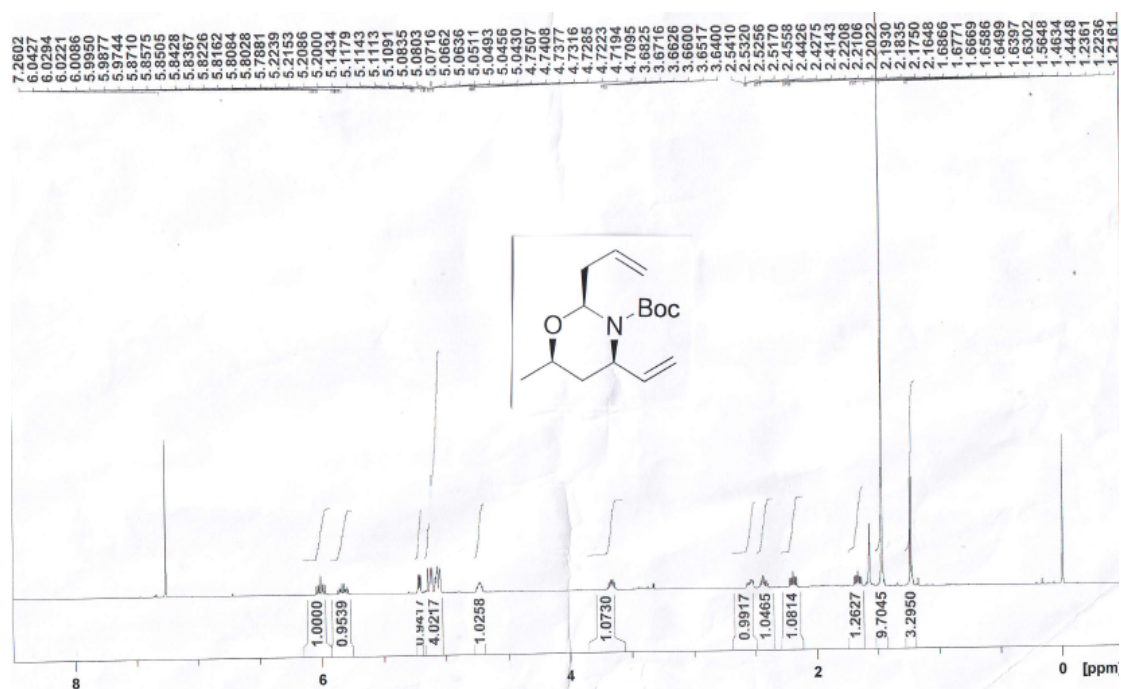
¹³C NMR spectrum of (2S,4R,6R)-tert-Butyl 2-(3-bromopropyl)-6-methyl-4-vinyl-1,3-oxazinane-3-carboxylate (12a) (CDCl₃, 100MHz)



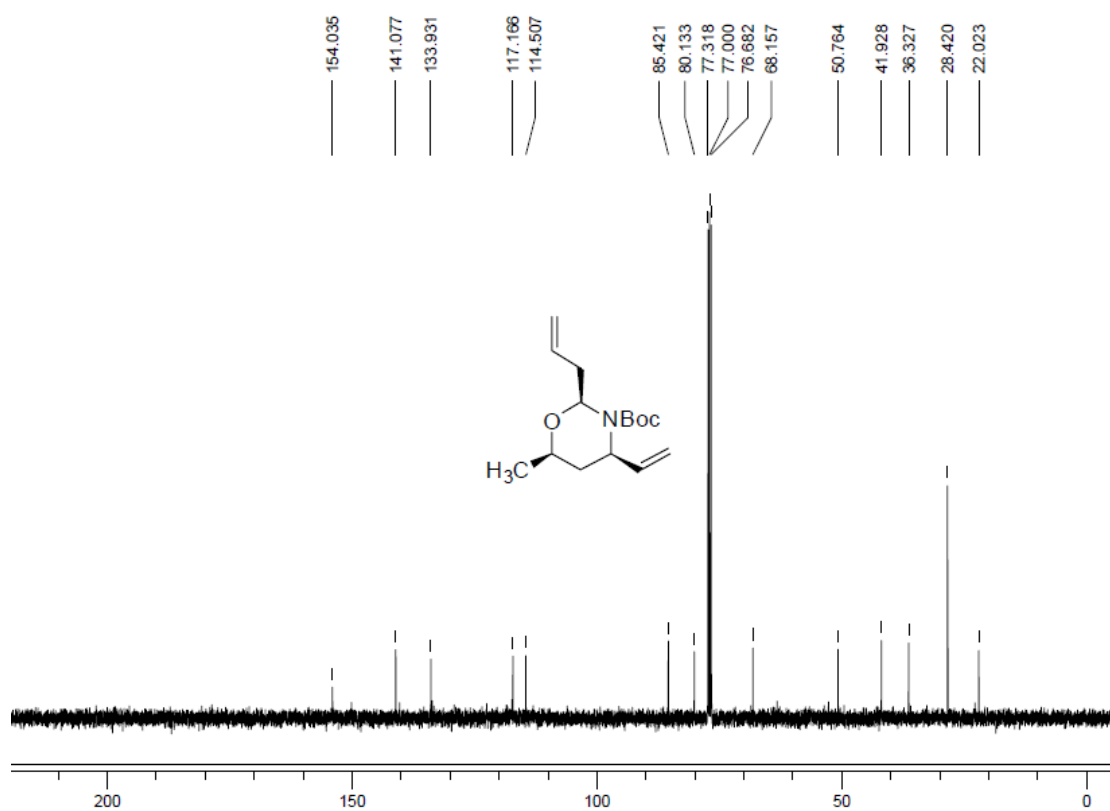
¹H NMR spectrum of (2R,4R,6R)-tert-butyl-2-(3-bromopropyl)-6-methyl-4-vinyl 1,3-oxazinane-3-carboxylate (12b) (CDCl₃, 300MHz)



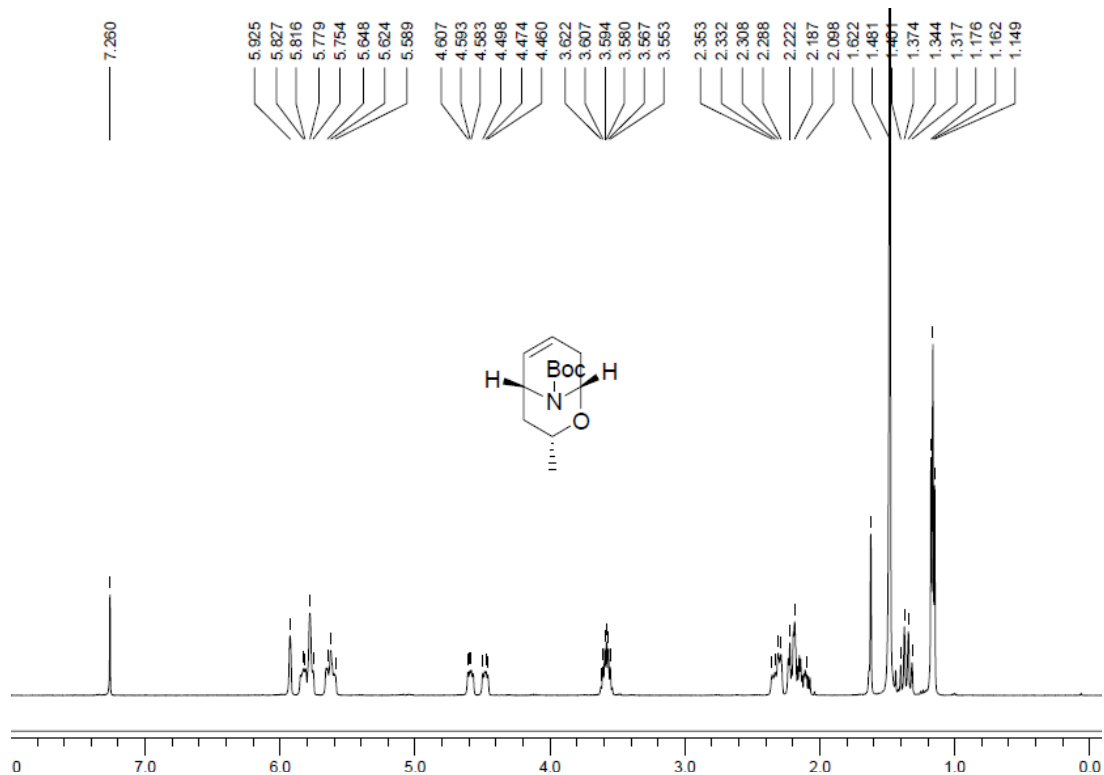
¹³C NMR spectrum of (2R,4R,6R)-tert-butyl-2-(3-bromopropyl)-6-methyl-4-vinyl 1,3-oxazinane-3-carboxylate (12b) (CDCl₃, 75MHz)



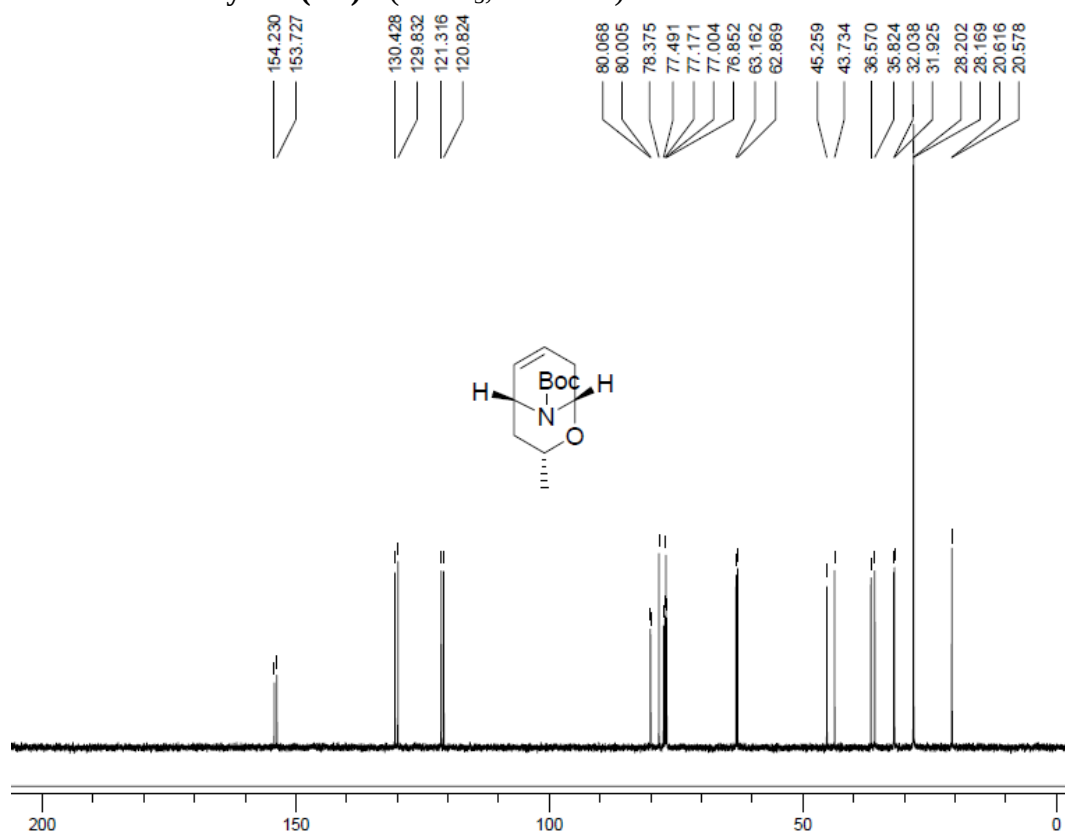
¹H NMR spectrum of (2S,4R,6R)-tert-Butyl 2-allyl-6-methyl-4-vinyl-1,3-oxazinane-3-carboxylate (13) (CDCl₃, 500MHz)



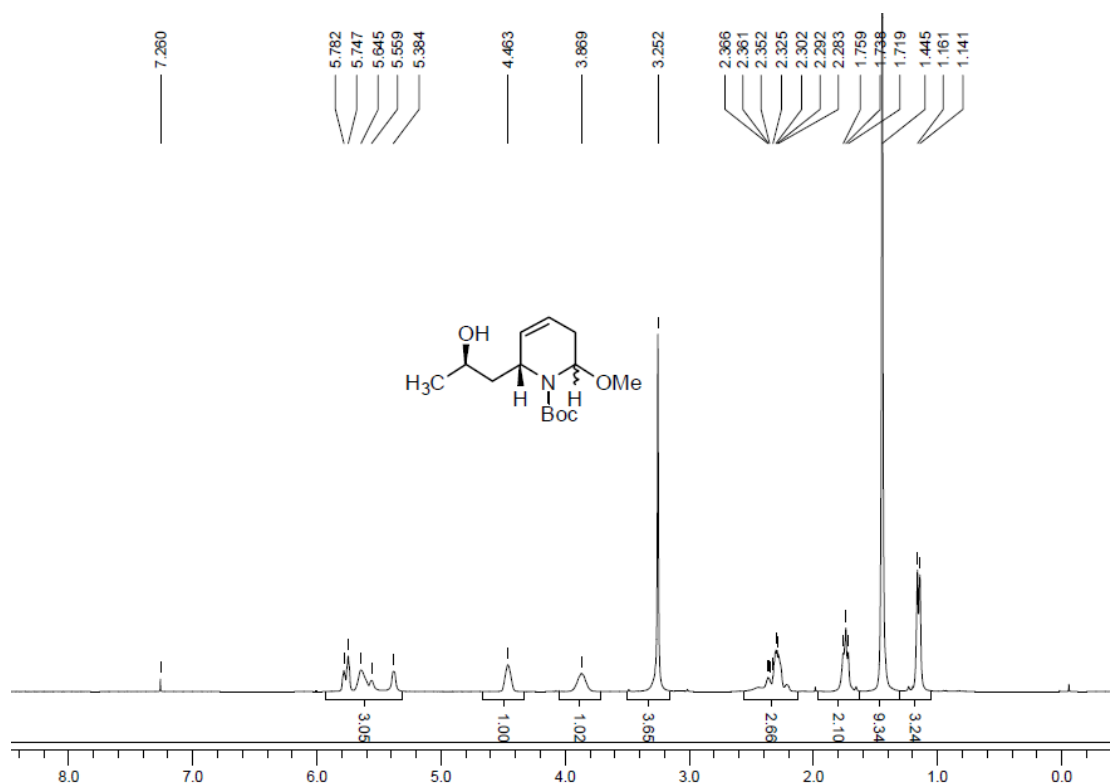
¹³C NMR spectrum of (2S,4R,6R)-tert-Butyl 2-allyl-6-methyl-4-vinyl-1,3-oxazinane-3-carboxylate (13) (CDCl₃, 100MHz)



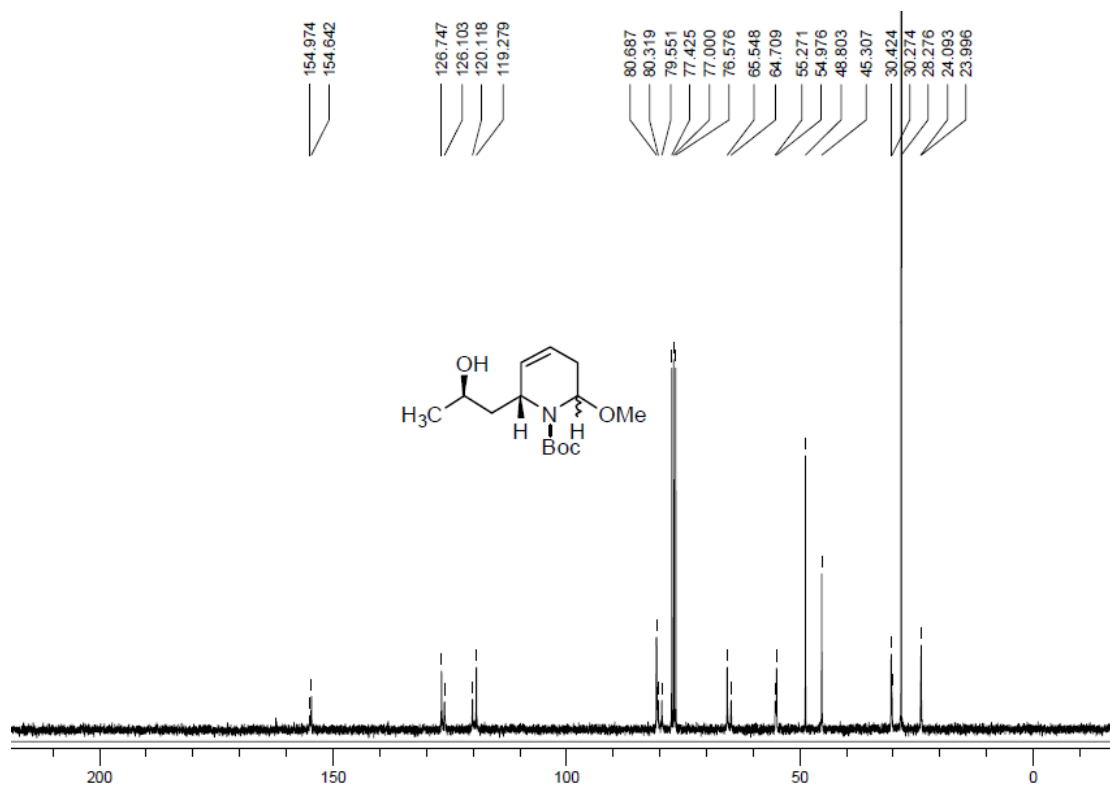
¹H NMR spectrum of (1S,3R,5R)-tert-Butyl 3-methyl-2-oxa-9-azabicyclo[3.3.1]non-6-ene-9-carboxylate (14) (CDCl₃, 400MHz)



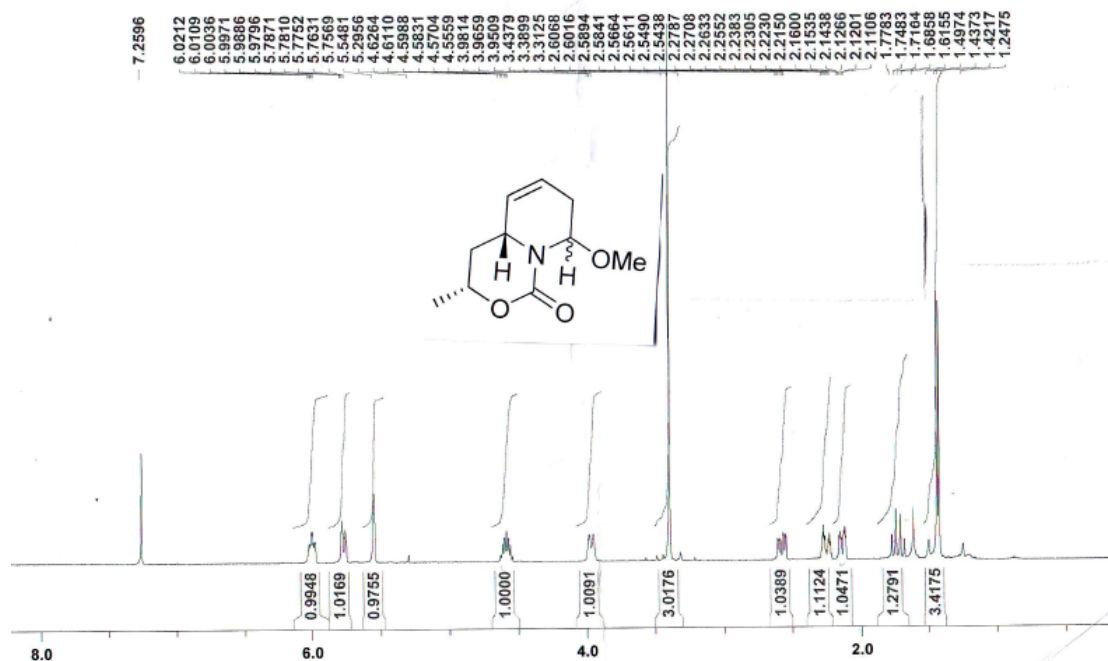
¹³C NMR spectrum of (1S,3R,5R)-tert-Butyl 3-methyl-2-oxa-9-azabicyclo[3.3.1]non-6-ene-9-carboxylate (14) (CDCl₃, 100MHz)



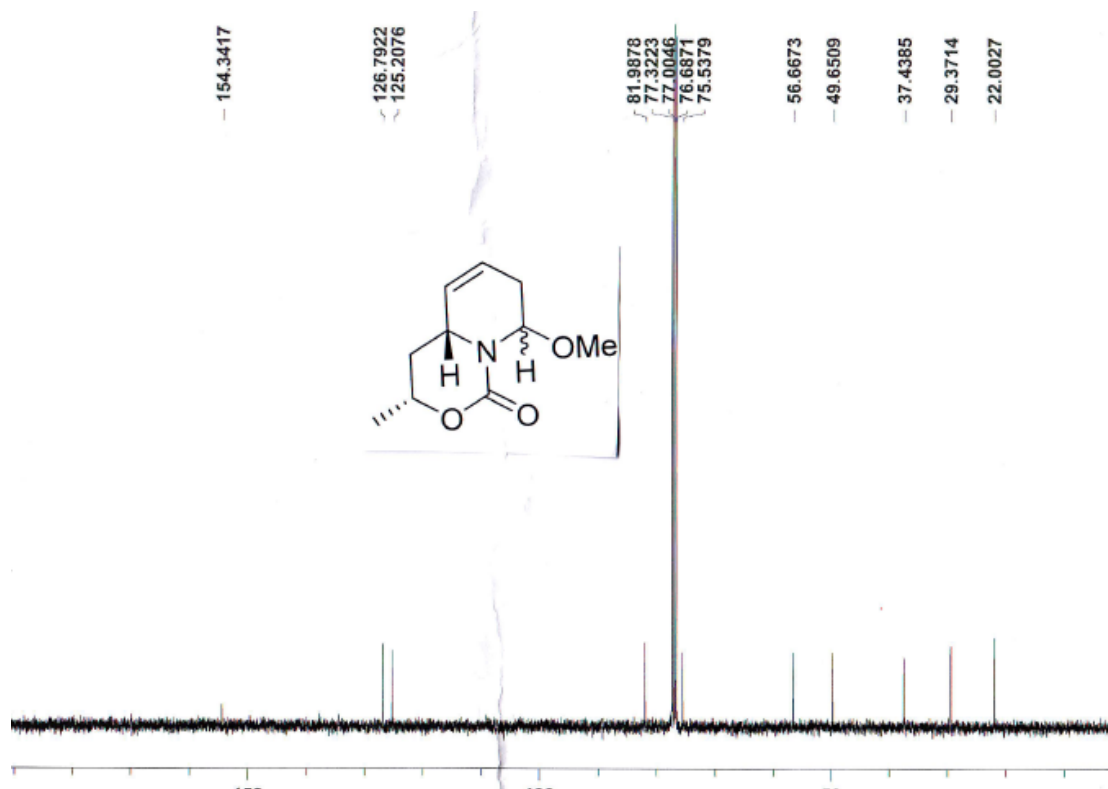
¹H NMR spectrum of (2*R*)-*tert*-Butyl 5,6-dihydro-2-((*R*)-2-hydroxypropyl)-6-methoxypyridine-1(2*H*)-carboxylate (15) (CDCl₃, 300MHz)



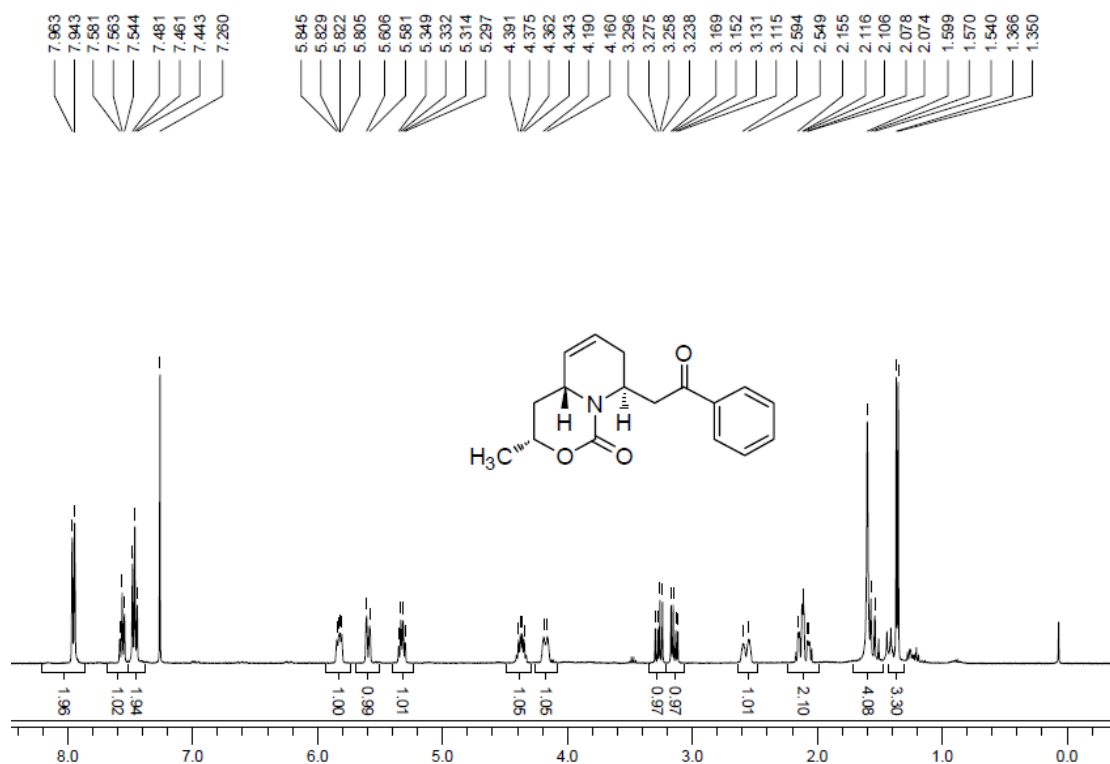
¹³C NMR spectrum of (2*R*)-*tert*-Butyl 5,6-dihydro-2-((*R*)-2-hydroxypropyl)-6-methoxypyridine-1(2*H*)-carboxylate (15) (CDCl₃, 100MHz)



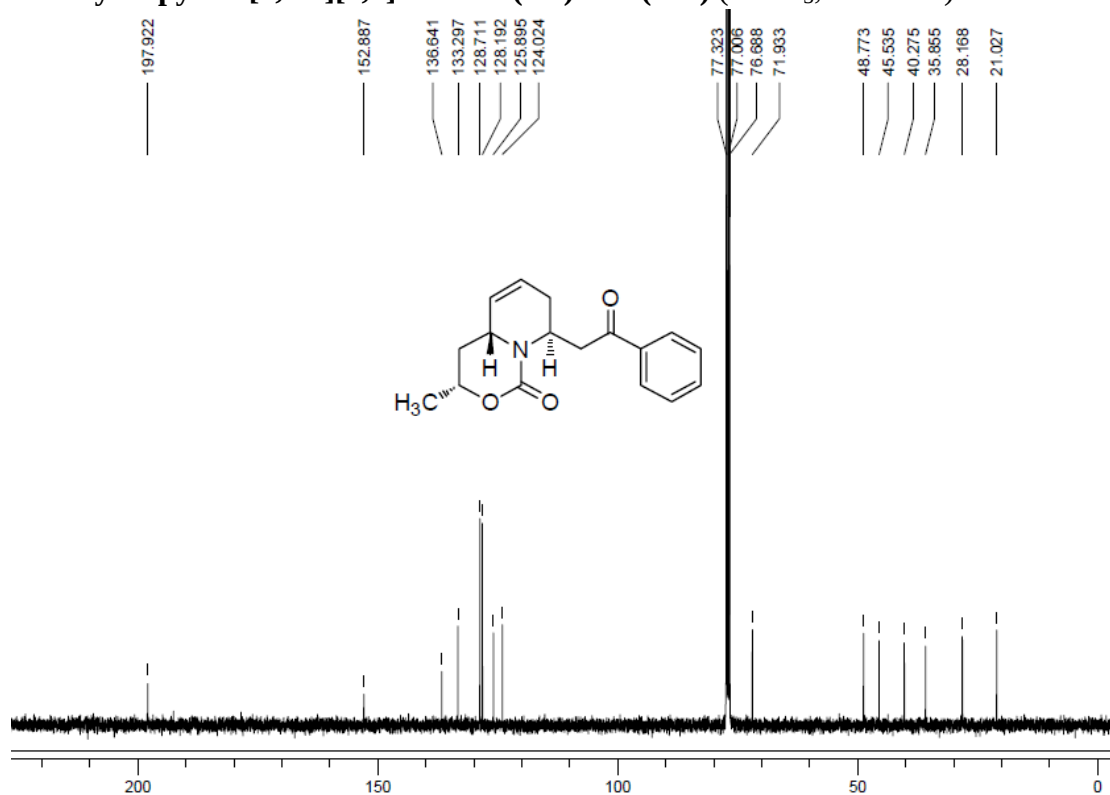
¹H NMR spectrum of (3*R*,4*aR*)-4,4*a*,7,8-Tetrahydro-8-methoxy-3-methylpyrido [1,2-*c*][1,3]oxazin-1(3*H*)-one (16) (CDCl₃, 400MHz)



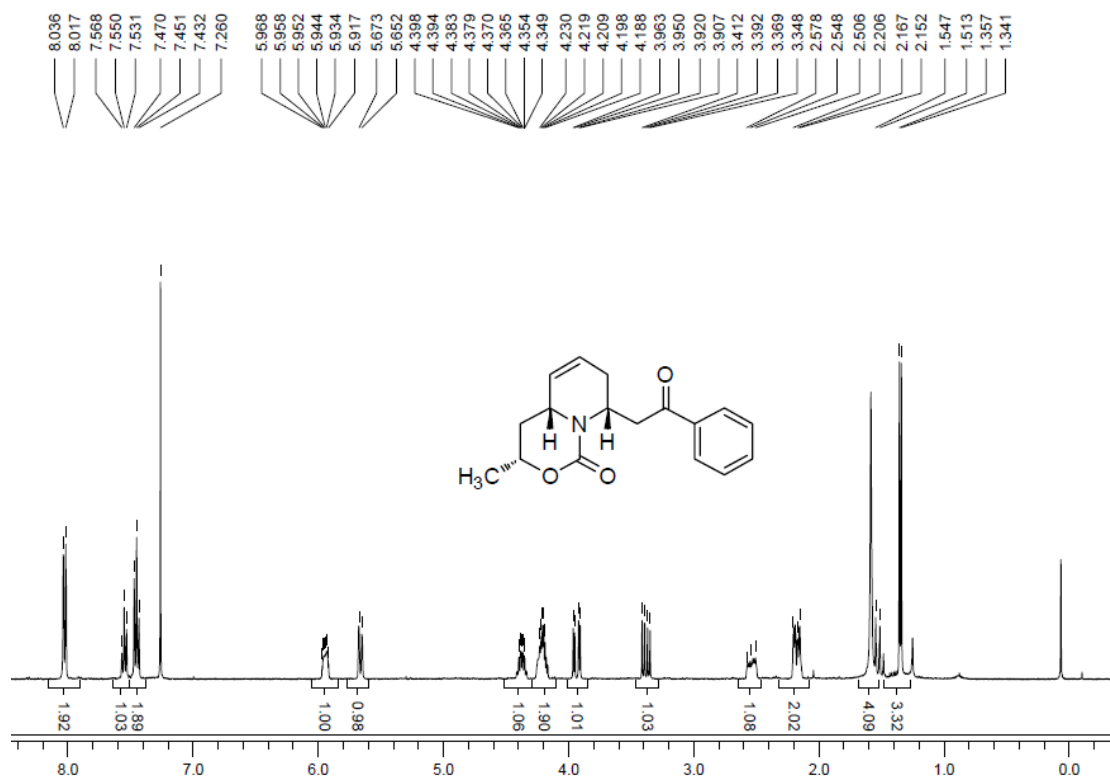
¹³C NMR spectrum of (3*R*,4*aR*)-4,4*a*,7,8-Tetrahydro-8-methoxy-3-methylpyrido [1,2-*c*][1,3]oxazin-1(3*H*)-one (16) (CDCl₃, 100MHz)



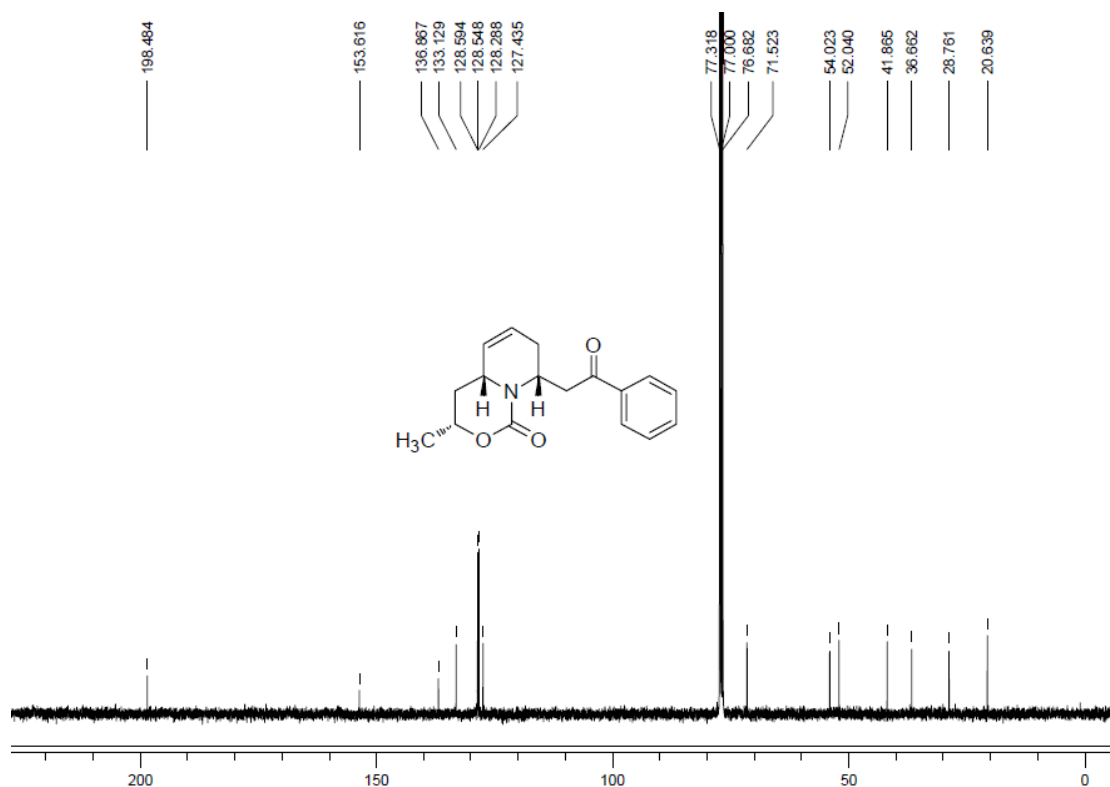
¹H NMR spectrum of (3R,4aR,8S)-3-methyl-8-(2-oxo-2-phenyleth-yl)-4,4a,7,8-tetrahydropyrido[1,2-c][1,3]oxazin-1(3H)-one (17a) (CDCl₃, 400MHz)



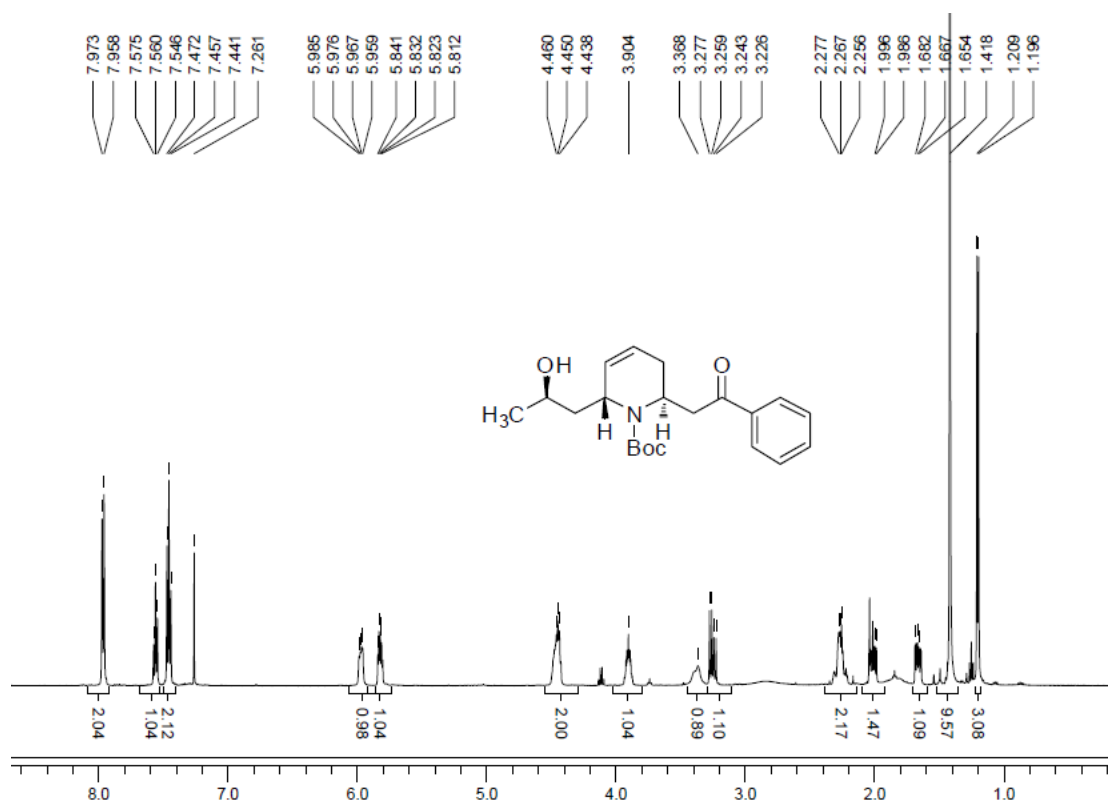
¹³C NMR spectrum of (3R,4aR,8S)-3-methyl-8-(2-oxo-2-phenyleth-yl)-4,4a,7,8-tetrahydropyrido[1,2-c][1,3]oxazin-1(3H)-one (17a) (CDCl₃, 100MHz)



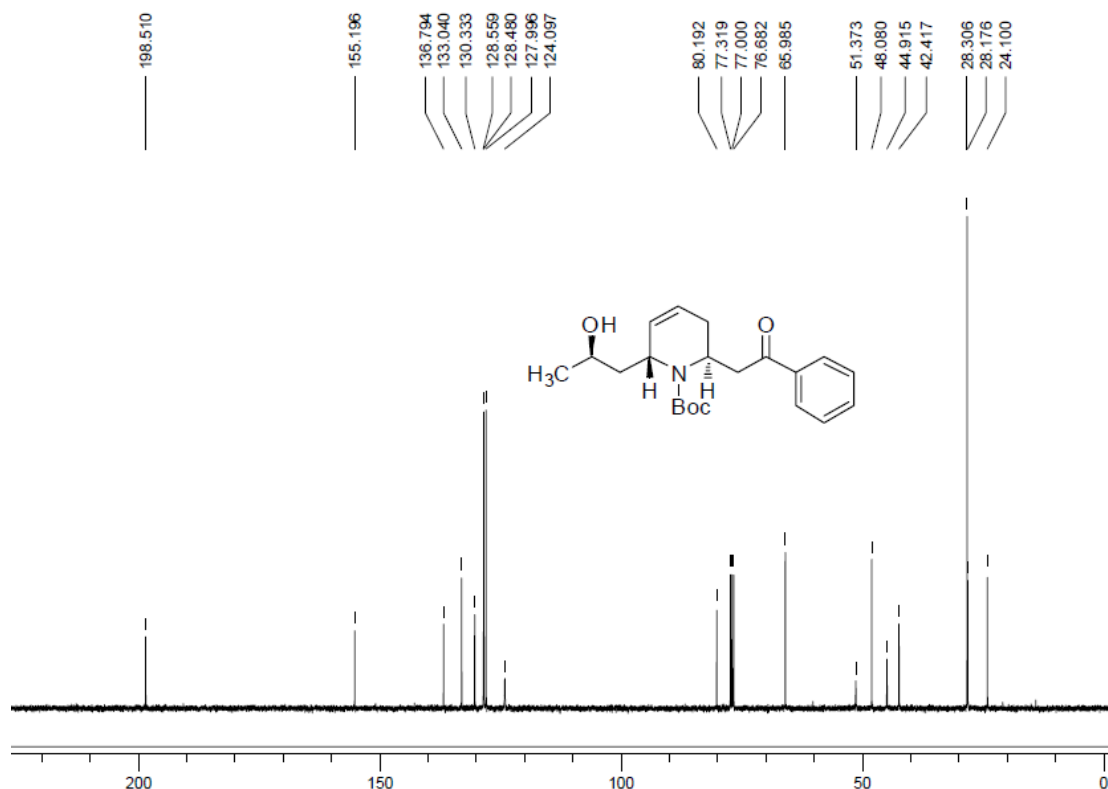
¹H NMR spectrum of (3*R*,4*aR*,8*R*)-3-methyl-8-(2-oxo-2-phenyleth-yl)-4,4*a*,7,8-tetrahydropyrido[1,2-*c*][1,3]oxazin-1(3*H*)-one (17b) (CDCl₃, 500MHz)



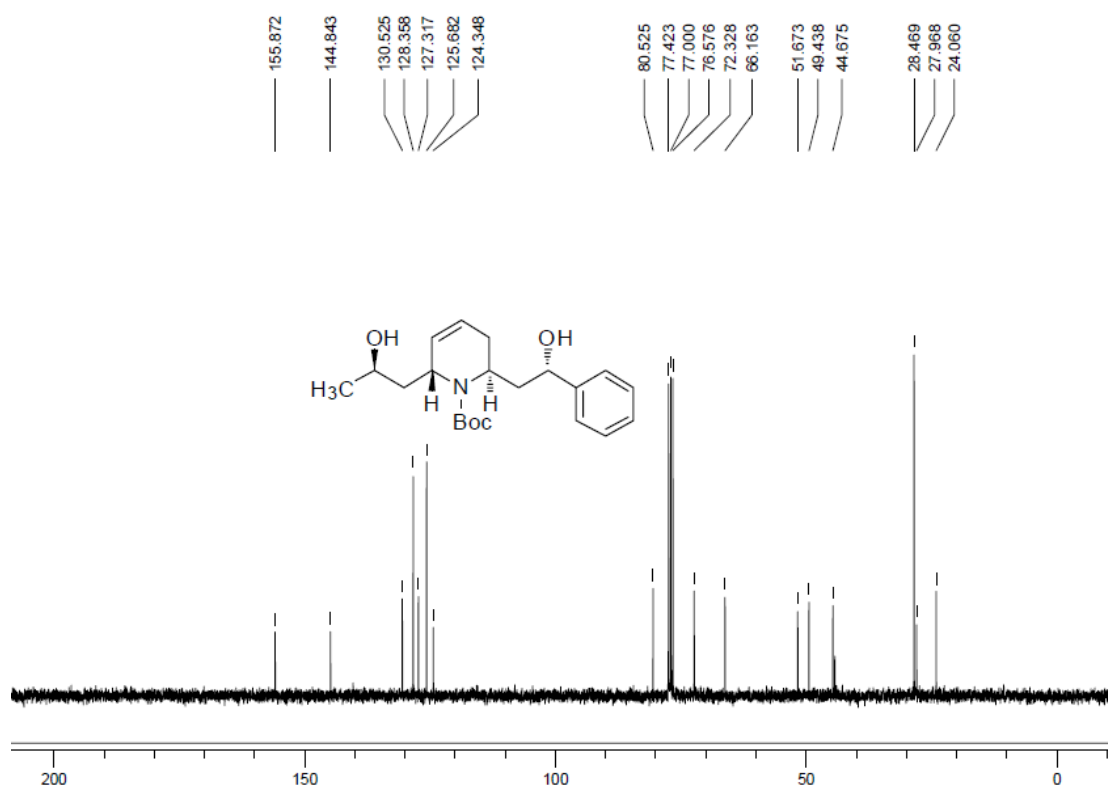
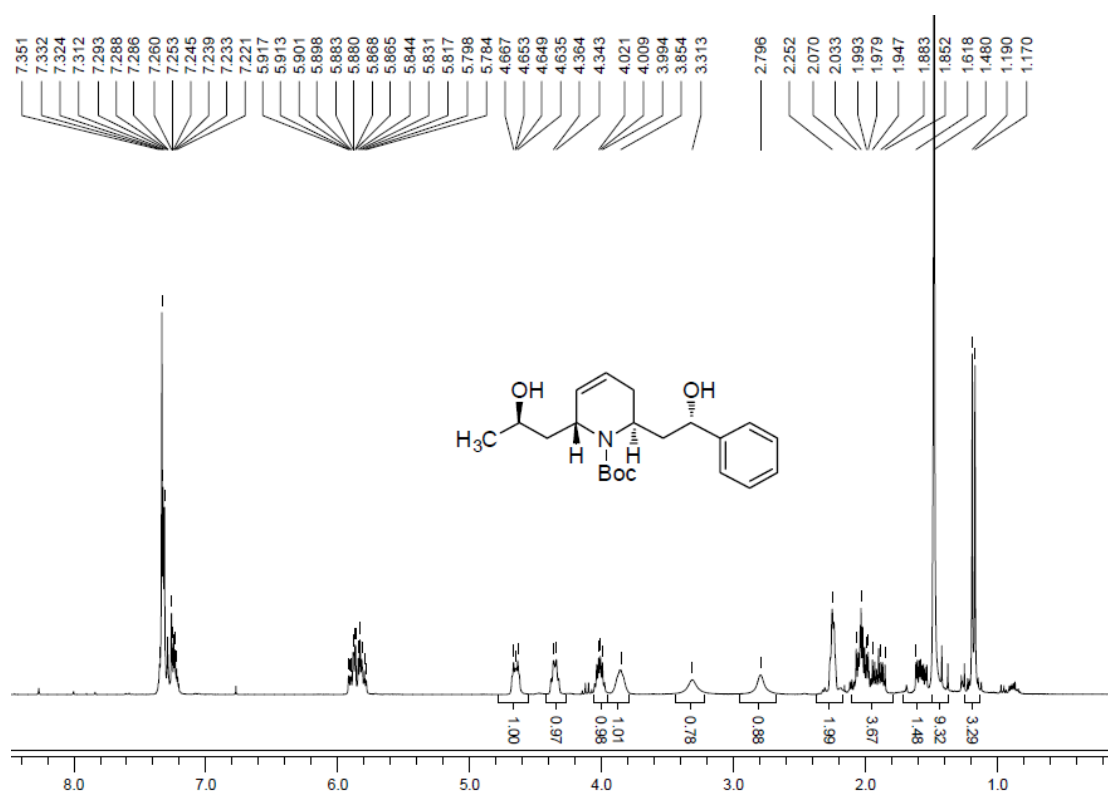
¹³C NMR spectrum of (3*R*,4*aR*,8*R*)-3-methyl-8-(2-oxo-2-phenyleth-yl)-4,4*a*,7,8-tetrahydropyrido[1,2-*c*][1,3]oxazin-1(3*H*)-one (17b) (CDCl₃, 100MHz)

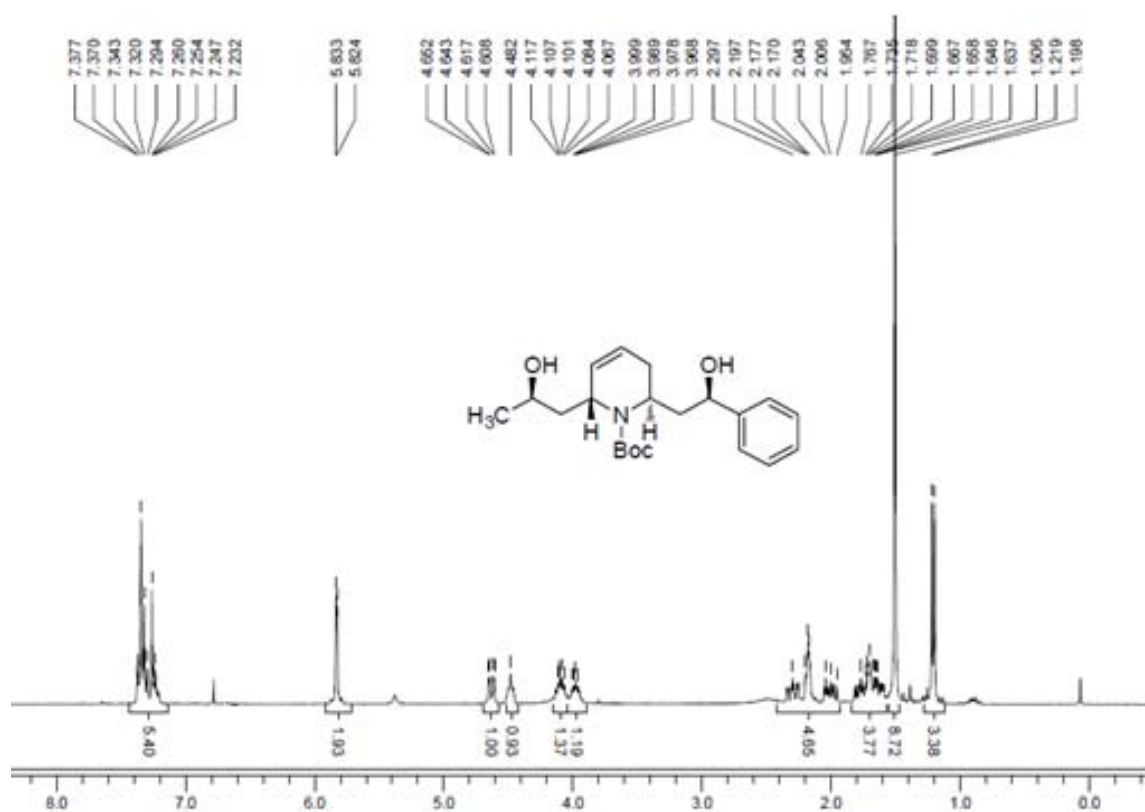


¹H NMR spectrum of (2R,6S)-tert-Butyl 2-((R)-2-hydroxypropyl)-6-(2-oxo-2-phenylethyl)-5,6-dihydro pyridine-1(2H)-carboxylate (19) (CDCl₃, 500MHz)

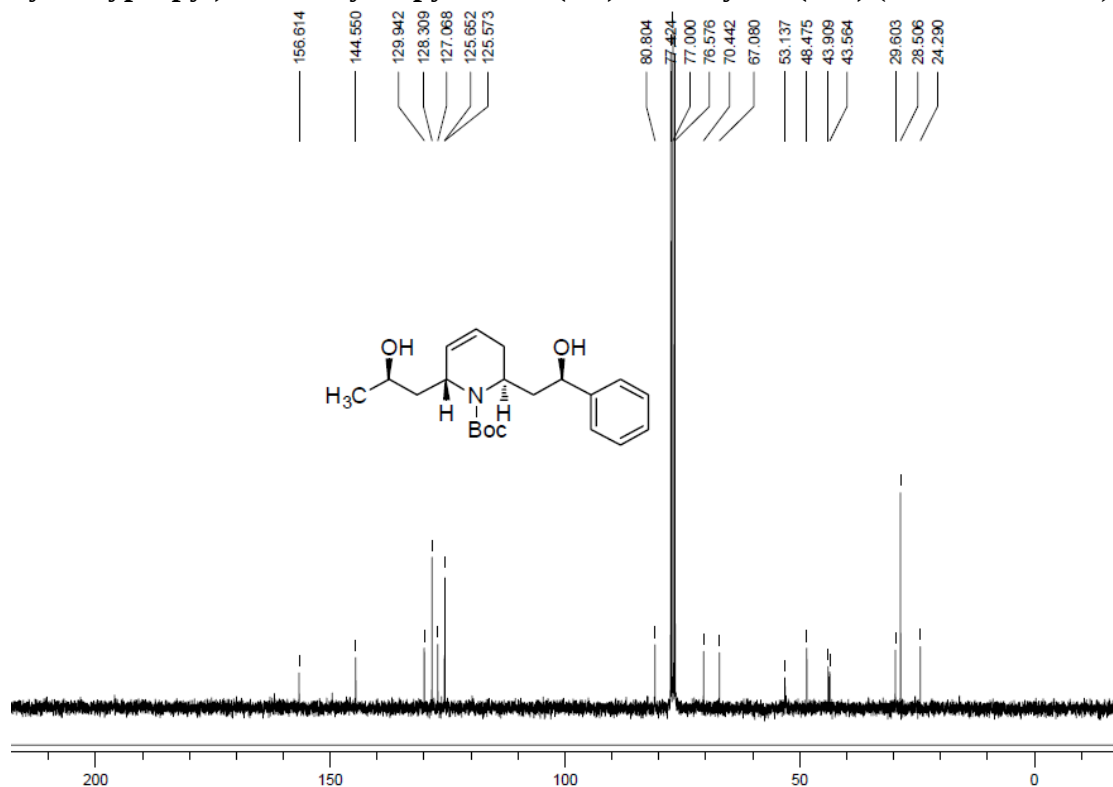


¹³C NMR spectrum of (2R,6S)-tert-Butyl 2-((R)-2-hydroxypropyl)-6-(2-oxo-2-phenylethyl)-5,6-dihydro pyridine-1(2H)-carboxylate (19) (CDCl₃, 100MHz)

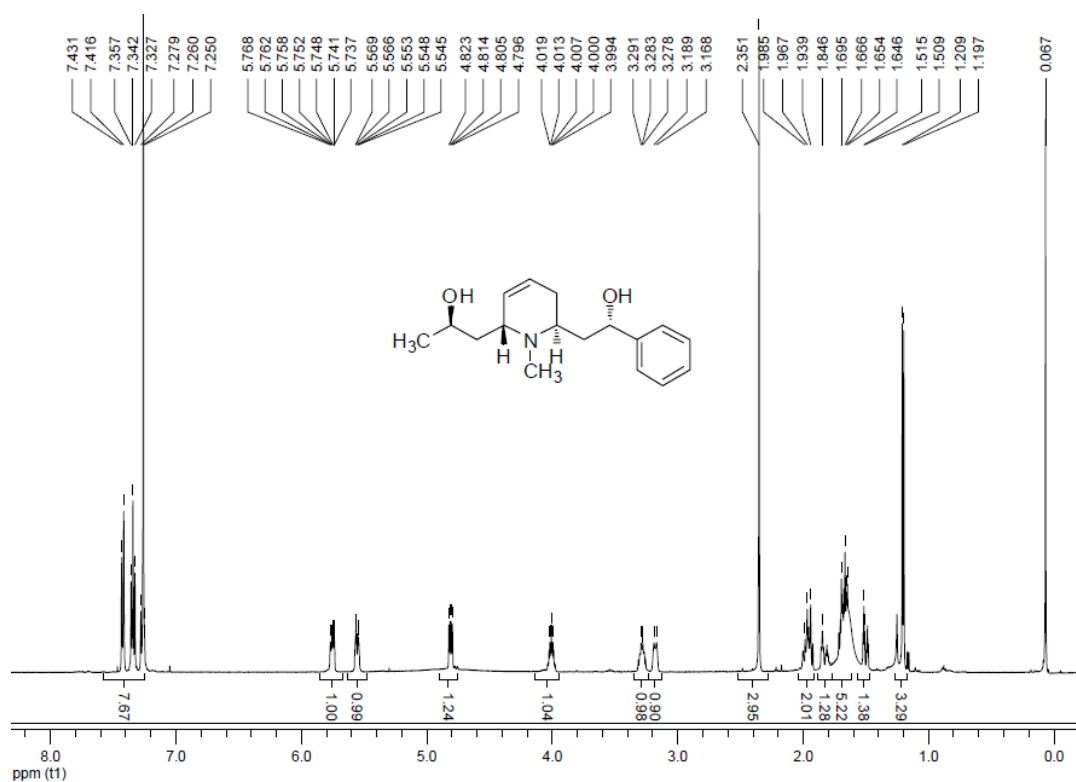




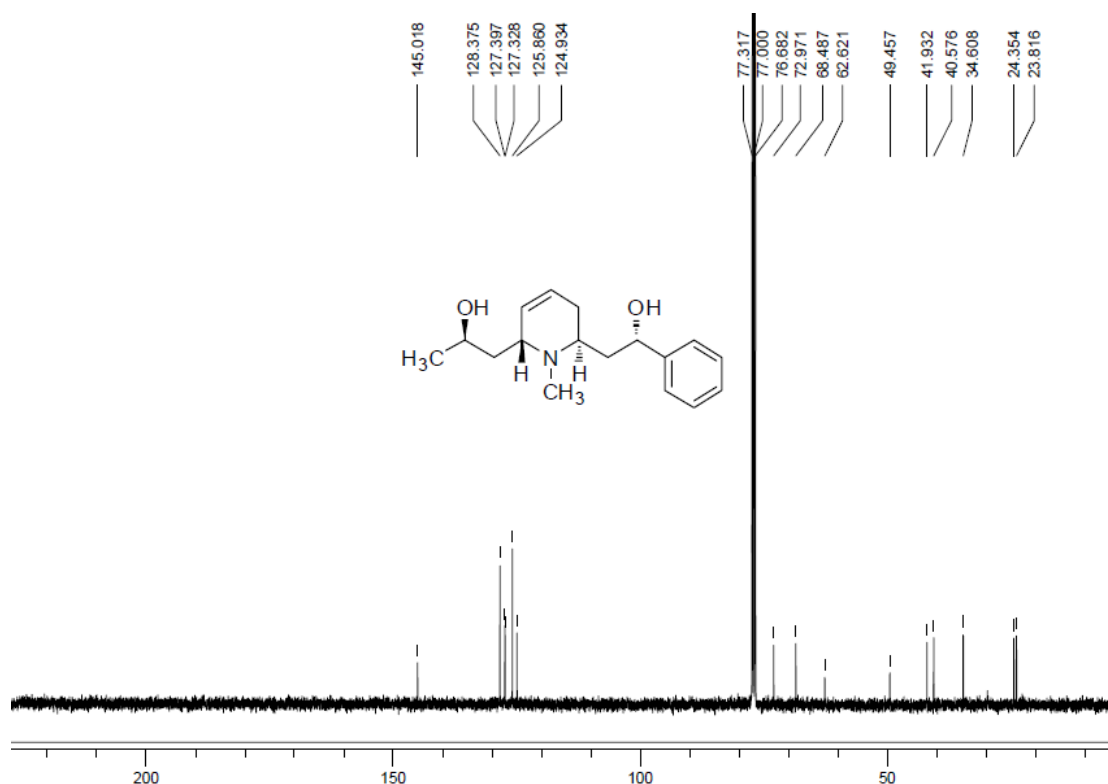
¹H NMR spectrum of (2*R*,6*S*)-*tert*-Butyl 6-((*R*)-2-hydroxy-2-phenylethyl)-2-((*R*)-2-hydroxypropyl)-5,6-di-hydropyridine-1(2*H*)-carboxylate (21b) (CDCl₃, 300MHz)



¹³C NMR spectrum of (2*R*,6*S*)-*tert*-Butyl 6-((*R*)-2-hydroxy-2-phenylethyl)-2-((*R*)-2-hydroxypropyl)-5,6-di-hydropyridine-1(2*H*)-carboxylate (21b) (CDCl₃, 75MHz)



¹H NMR spectrum of **(R)-1-((2R,6S)-1,2,5,6-Tetrahydro-6-((S)-2-hydroxy-2-phenylethyl)-1-methylpyridin-2-yl)propan-2-ol (1)** (CDCl₃, 500MHz)



¹³C NMR spectrum of **(R)-1-((2R,6S)-1,2,5,6-Tetrahydro-6-((S)-2-hydroxy-2-phenylethyl)-1-methylpyridin-2-yl)propan-2-ol (1)** (CDCl₃, 100MHz)