Supplementary Material for Chemical Communications

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Enantioselective formal synthesis of uleine alkaloids from phenylglycinol-derived bicyclic lactams

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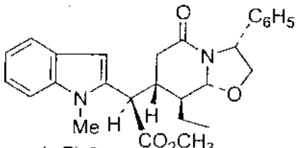
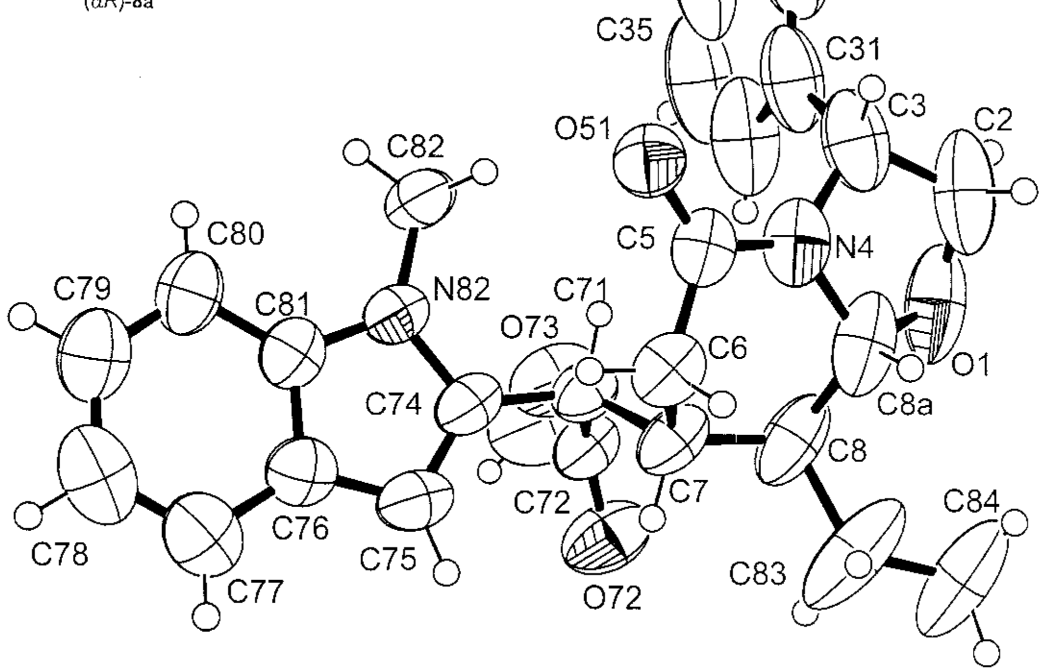
Contents:

- Complete X-ray crystallographic data for (α*R*)-**8a**
- ^{1}H and ^{13}C NMR spectra of new compounds



O
N
C6H5
O
N
Me
H
H
CO2CH3

(αR)-**8a**



C33
C34
C32
C35
C31
O51
C3
C2
C82
C5
N4
C80
C79
C81
N82
C71
O73
C6
O1
C74
C8a
C8
C84
C72
C7
C78
C76
C75
C83
O72
C77

Table 1. Crystal data and structure refinement for (α*R*)-**8a**.

Identification code	(α*R*)-**8a**	
Empirical formula	C27 H30 N2 O4	
Formula weight	446.53	
Temperature	294(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.931(2) Å	α= 90°.
	b = 9.5990(10) Å	β= 90°.
	c = 28.080(9) Å	γ = 90°.
Volume	2407.3(10) $Å^3$	
Z	4	
Density (calculated)	1.232 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	952	
Crystal size	0.69 x 0.36 x 0.12 mm^3	
Theta range for data collection	2.24 to 28.44°.	
Index ranges	0<=h<=11, -12<=k<=0, 0<=l<=37	
Reflections collected	3440	
Independent reflections	3440	
Completeness to theta = 28.44°	100.0 %	
Max. and min. transmission	0.9901 and 0.9451	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3440 / 1 / 312	
Goodness-of-fit on F^2	0.968	
Final R indices [I>2sigma(I)]	R1 = 0.0458, wR2 = 0.1321	
R indices (all data)	R1 = 0.0981, wR2 = 0.1451	
Absolute structure parameter	4(2)	
Extinction coefficient	0.0074(17)	
Largest diff. peak and hole	0.165 and -0.197 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (αR)-**8a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(4)	4283(3)	2311(3)	8595(1)	78(1)
N(82)	5079(3)	7284(2)	8433(1)	59(1)
O(1)	2846(3)	1131(3)	9118(1)	116(1)
O(51)	5519(2)	3473(2)	8021(1)	71(1)
O(72)	3211(3)	6122(3)	9810(1)	98(1)
O(73)	1845(3)	6527(3)	9165(1)	100(1)
C(2)	2749(5)	397(4)	8673(2)	124(2)
C(3)	3289(4)	1445(3)	8303(2)	96(1)
C(31)	2038(4)	2245(4)	8064(2)	102(1)
C(32)	1658(5)	1913(5)	7593(2)	131(2)
C(33)	430(7)	2534(6)	7386(3)	160(2)
C(34)	-379(7)	3478(6)	7640(4)	175(3)
C(35)	-30(6)	3877(5)	8096(3)	153(2)
C(36)	1230(4)	3225(4)	8319(2)	123(2)
C(5)	5340(3)	3191(3)	8441(1)	62(1)
C(6)	6221(3)	3830(3)	8837(1)	68(1)
C(7)	5159(3)	4329(3)	9239(1)	69(1)
C(71)	4185(3)	5512(3)	9036(1)	62(1)
C(73)	729(5)	7224(6)	9452(2)	143(2)
C(74)	5128(3)	6732(3)	8888(1)	62(1)
C(82)	4117(4)	6822(3)	8044(1)	75(1)
C(75)	6127(3)	7463(3)	9157(1)	74(1)
C(77)	7790(3)	9585(3)	8936(1)	85(1)
C(78)	8132(4)	10461(4)	8556(2)	94(1)
C(79)	7438(4)	10281(4)	8118(1)	88(1)
C(80)	6414(4)	9266(3)	8036(1)	76(1)
C(81)	6071(3)	8382(3)	8414(1)	63(1)
C(76)	6739(3)	8522(3)	8866(1)	68(1)
C(72)	3049(4)	6051(3)	9395(1)	68(1)
C(8)	4268(4)	3088(4)	9440(1)	90(1)
C(8A)	4222(4)	1870(3)	9095(1)	92(1)

C(83)	4975(6)	2591(6)	9919(2)	144(2)
C(84)	4373(8)	1484(9)	10193(2)	149(3)
C(83A)	4975(6)	2591(6)	9919(2)	144(2)
C(84A)	4449(17)	3133(19)	10313(4)	125(5)

Table 3. Bond lengths [Å] and angles [°] for (α*R*)-**8a**.

N(4)-C(5)	1.338(4)
N(4)-C(3)	1.468(4)
N(4)-C(8A)	1.467(4)
N(82)-C(81)	1.378(4)
N(82)-C(74)	1.383(3)
N(82)-C(82)	1.459(3)
O(1)-C(8A)	1.421(4)
O(1)-C(2)	1.439(5)
O(51)-C(5)	1.221(3)
O(72)-C(72)	1.176(3)
O(73)-C(72)	1.335(4)
O(73)-C(73)	1.446(4)
C(2)-C(3)	1.524(5)
C(3)-C(31)	1.513(5)
C(31)-C(36)	1.386(6)
C(31)-C(32)	1.400(7)
C(32)-C(33)	1.377(7)
C(33)-C(34)	1.362(8)
C(34)-C(35)	1.371(11)
C(35)-C(36)	1.433(7)
C(5)-C(6)	1.494(4)
C(6)-C(7)	1.551(4)
C(7)-C(8)	1.539(4)
C(7)-C(71)	1.540(4)
C(71)-C(74)	1.500(4)
C(71)-C(72)	1.522(4)
C(74)-C(75)	1.362(4)
C(75)-C(76)	1.414(4)
C(77)-C(78)	1.392(5)
C(77)-C(76)	1.400(4)
C(78)-C(79)	1.390(5)
C(79)-C(80)	1.356(5)
C(80)-C(81)	1.393(4)
C(81)-C(76)	1.410(4)

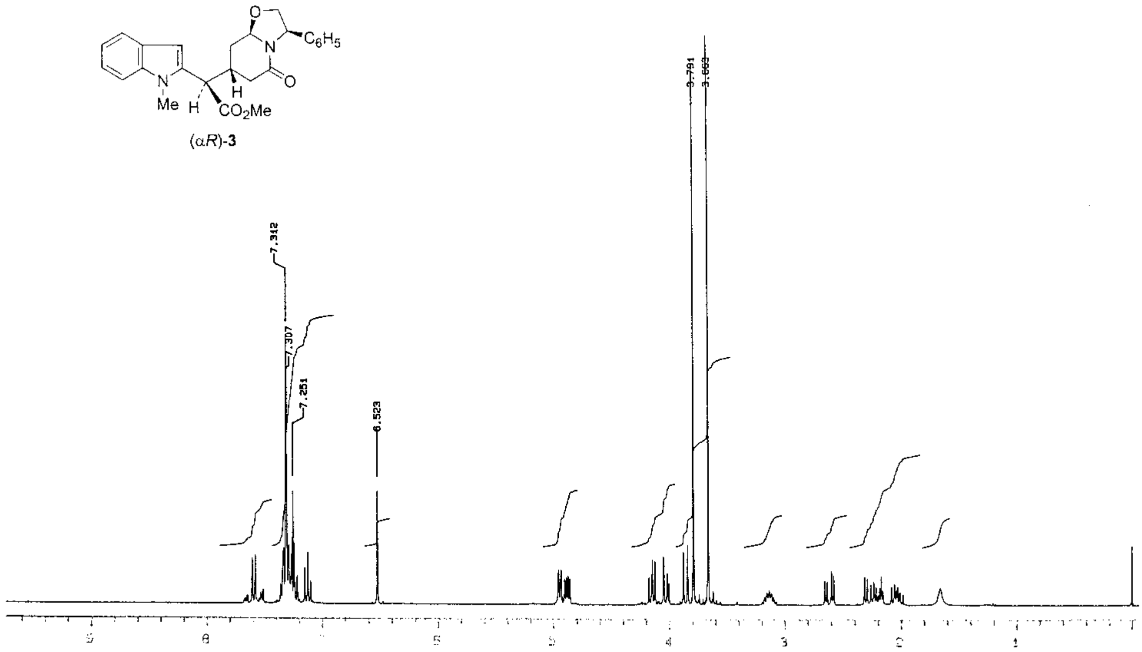
C(8)-C(8A)	1.519(5)
C(8)-C(83)	1.560(5)
C(83)-C(84)	1.418(8)
C(5)-N(4)-C(3)	127.1(3)
C(5)-N(4)-C(8A)	121.2(3)
C(3)-N(4)-C(8A)	110.5(3)
C(81)-N(82)-C(74)	108.0(2)
C(81)-N(82)-C(82)	125.5(2)
C(74)-N(82)-C(82)	126.4(2)
C(8A)-O(1)-C(2)	104.8(3)
C(72)-O(73)-C(73)	116.3(3)
O(1)-C(2)-C(3)	104.5(3)
N(4)-C(3)-C(31)	114.1(3)
N(4)-C(3)-C(2)	100.6(3)
C(31)-C(3)-C(2)	113.8(3)
C(36)-C(31)-C(32)	121.1(4)
C(36)-C(31)-C(3)	120.0(5)
C(32)-C(31)-C(3)	118.8(4)
C(33)-C(32)-C(31)	119.6(6)
C(34)-C(33)-C(32)	119.2(7)
C(33)-C(34)-C(35)	123.7(6)
C(34)-C(35)-C(36)	117.7(6)
C(31)-C(36)-C(35)	118.6(5)
O(51)-C(5)-N(4)	123.0(3)
O(51)-C(5)-C(6)	124.0(3)
N(4)-C(5)-C(6)	113.0(3)
C(5)-C(6)-C(7)	110.3(2)
C(8)-C(7)-C(71)	114.5(2)
C(8)-C(7)-C(6)	110.1(2)
C(71)-C(7)-C(6)	107.59(19)
C(74)-C(71)-C(72)	107.0(2)
C(74)-C(71)-C(7)	111.2(2)
C(72)-C(71)-C(7)	112.4(2)
C(75)-C(74)-N(82)	109.5(2)
C(75)-C(74)-C(71)	128.1(2)

N(82)-C(74)-C(71)	122.4(3)
C(74)-C(75)-C(76)	107.7(2)
C(78)-C(77)-C(76)	118.7(3)
C(79)-C(78)-C(77)	120.4(4)
C(80)-C(79)-C(78)	122.7(3)
C(79)-C(80)-C(81)	117.2(3)
N(82)-C(81)-C(80)	129.6(3)
N(82)-C(81)-C(76)	108.0(2)
C(80)-C(81)-C(76)	122.3(3)
C(77)-C(76)-C(81)	118.7(3)
C(77)-C(76)-C(75)	134.6(3)
C(81)-C(76)-C(75)	106.7(3)
O(72)-C(72)-O(73)	124.0(3)
O(72)-C(72)-C(71)	126.5(3)
O(73)-C(72)-C(71)	109.4(2)
C(8A)-C(8)-C(7)	112.1(2)
C(8A)-C(8)-C(83)	109.0(3)
C(7)-C(8)-C(83)	110.0(4)
O(1)-C(8A)-N(4)	102.7(3)
O(1)-C(8A)-C(8)	112.2(3)
N(4)-C(8A)-C(8)	112.7(3)
C(84)-C(83)-C(8)	122.9(6)

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for (αR)-**8a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(4)	68(1)	67(1)	98(2)	9(1)	28(1)	9(1)
N(82)	64(1)	63(1)	49(1)	2(1)	0(1)	11(1)
O(1)	101(2)	74(2)	174(3)	43(2)	66(2)	18(2)
O(51)	74(1)	74(1)	66(1)	-3(1)	16(1)	2(1)
O(72)	105(2)	128(2)	60(1)	2(1)	19(1)	38(2)
O(73)	87(1)	131(2)	83(1)	-5(1)	9(1)	51(2)
C(2)	96(3)	58(2)	218(5)	26(3)	48(3)	12(2)
C(3)	71(2)	63(2)	153(3)	-2(2)	26(2)	2(2)
C(31)	61(2)	65(2)	181(4)	11(3)	20(2)	-13(2)
C(32)	94(3)	86(3)	212(5)	11(4)	-13(3)	-33(3)
C(33)	119(4)	104(4)	258(7)	39(4)	-52(5)	-43(4)
C(34)	95(4)	81(3)	350(11)	47(6)	-29(6)	-21(3)
C(35)	90(3)	81(3)	287(8)	25(5)	29(4)	-10(3)
C(36)	68(2)	78(2)	225(5)	26(3)	27(3)	9(2)
C(5)	54(1)	58(1)	75(2)	6(1)	18(1)	13(1)
C(6)	59(1)	77(2)	69(2)	7(2)	10(1)	17(2)
C(7)	72(2)	82(2)	54(1)	16(1)	13(1)	24(2)
C(71)	67(2)	67(2)	51(1)	3(1)	6(1)	14(2)
C(73)	123(3)	188(5)	118(3)	-15(3)	19(3)	89(4)
C(74)	70(2)	67(2)	49(1)	5(1)	5(1)	19(2)
C(82)	96(2)	78(2)	52(1)	9(1)	-10(1)	5(2)
C(75)	81(2)	86(2)	54(1)	1(2)	-11(2)	8(2)
C(77)	72(2)	71(2)	112(2)	-6(2)	-12(2)	14(2)
C(78)	62(2)	69(2)	152(3)	-7(2)	2(2)	9(2)
C(79)	75(2)	76(2)	113(3)	18(2)	10(2)	12(2)
C(80)	72(2)	67(2)	87(2)	16(2)	11(2)	10(2)
C(81)	60(1)	59(2)	69(2)	5(1)	4(1)	14(1)
C(76)	61(1)	68(2)	74(2)	1(2)	-6(1)	13(2)
C(72)	78(2)	70(2)	57(2)	6(1)	9(1)	21(2)
C(8)	87(2)	99(2)	83(2)	41(2)	36(2)	40(2)
C(8A)	81(2)	71(2)	123(3)	33(2)	49(2)	28(2)

C(83)	138(4)	196(5)	99(3)	87(3)	43(3)	67(4)
C(84)	126(5)	180(7)	140(5)	108(6)	27(4)	33(5)
C(83A)	138(4)	196(5)	99(3)	87(3)	43(3)	67(4)
C(84A)	116(11)	161(15)	97(9)	7(10)	-39(9)	-22(12)



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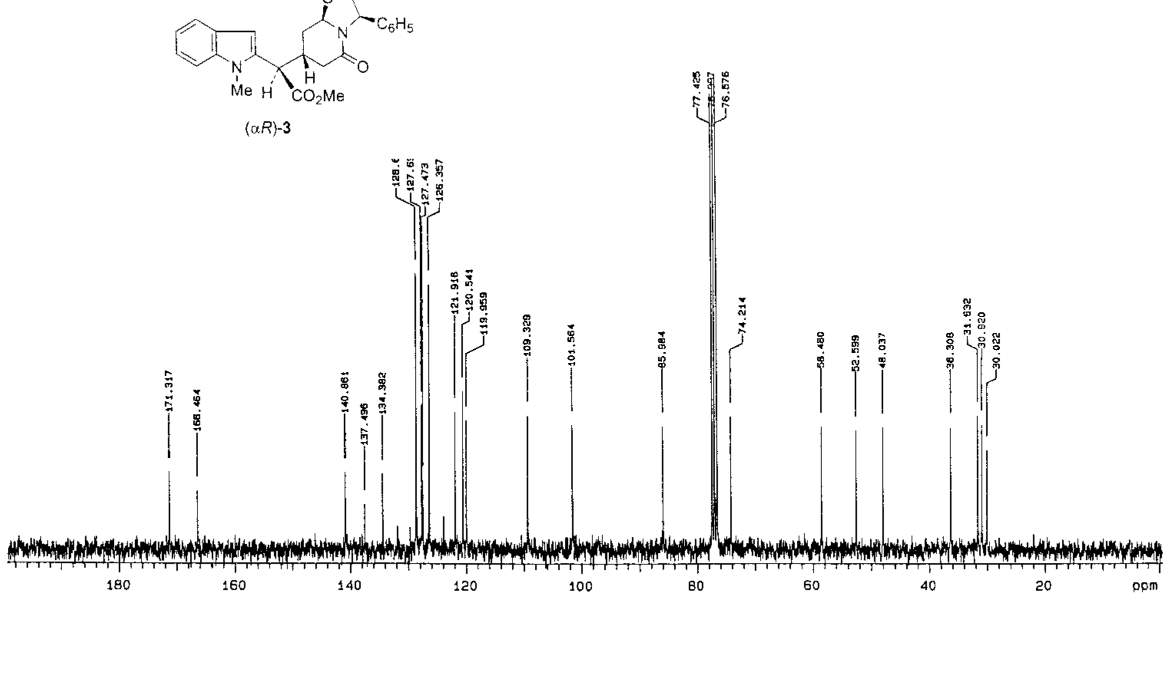
7.251
6.523
3.791
3.663



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109.329
101.564
85.984
77.425
76.576
74.214
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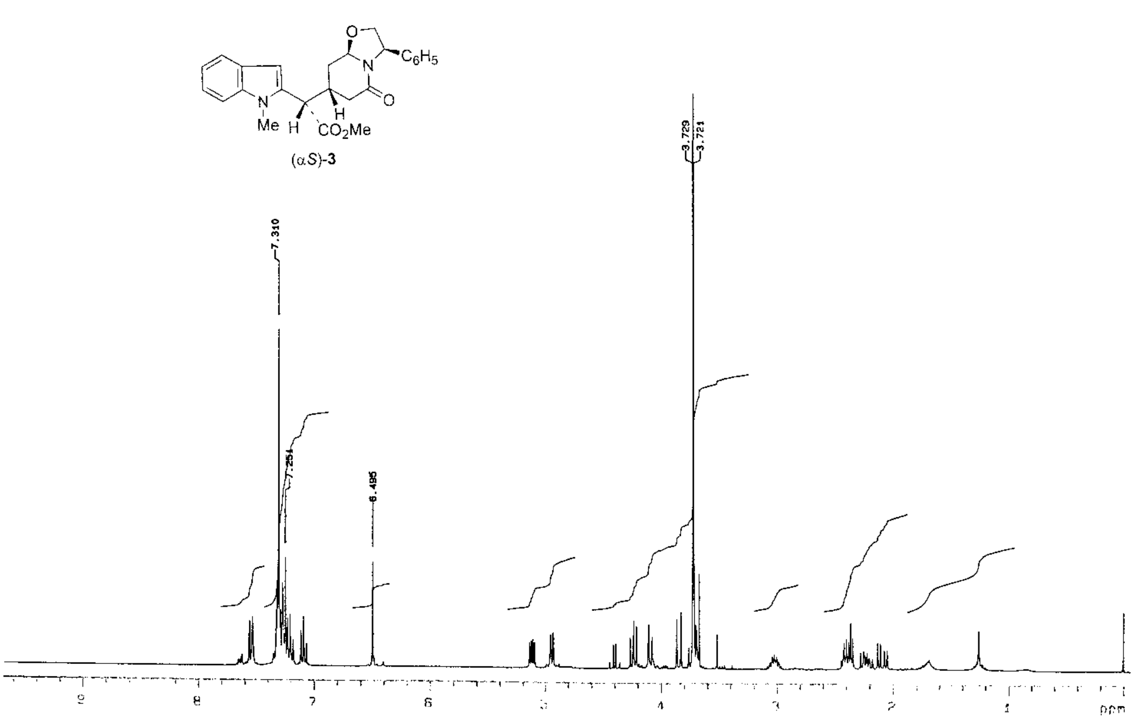
140
120
100
80
60
40
20
ppm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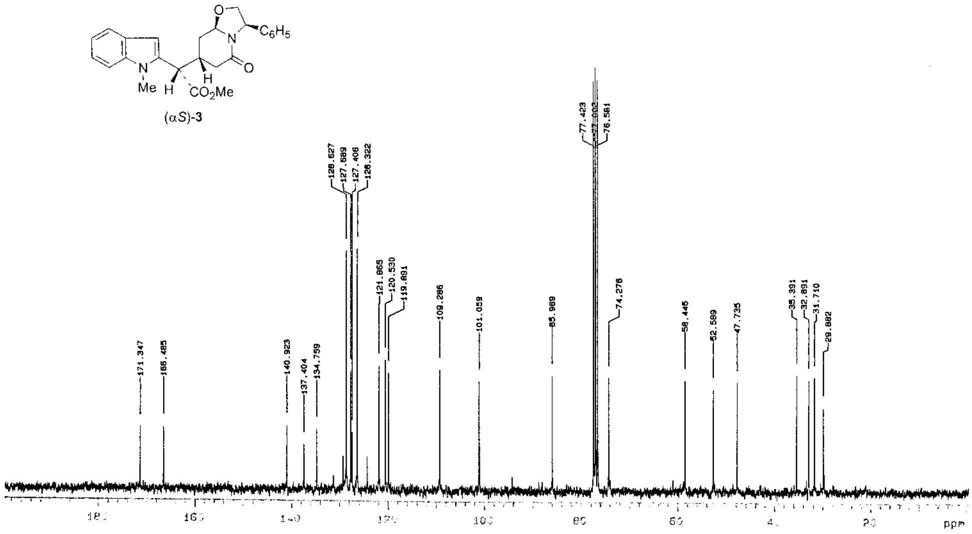
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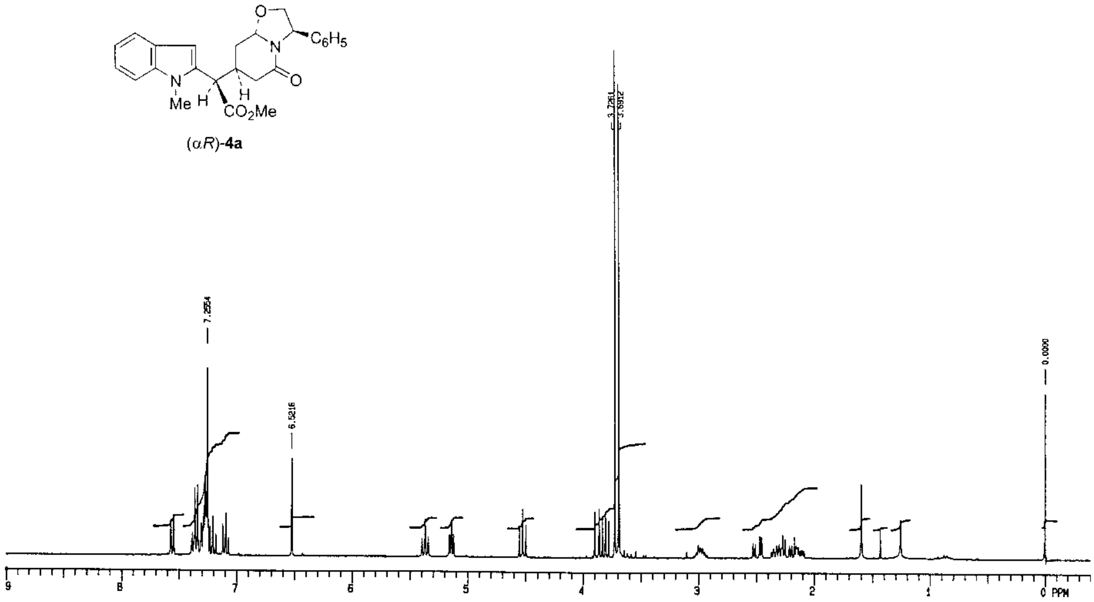

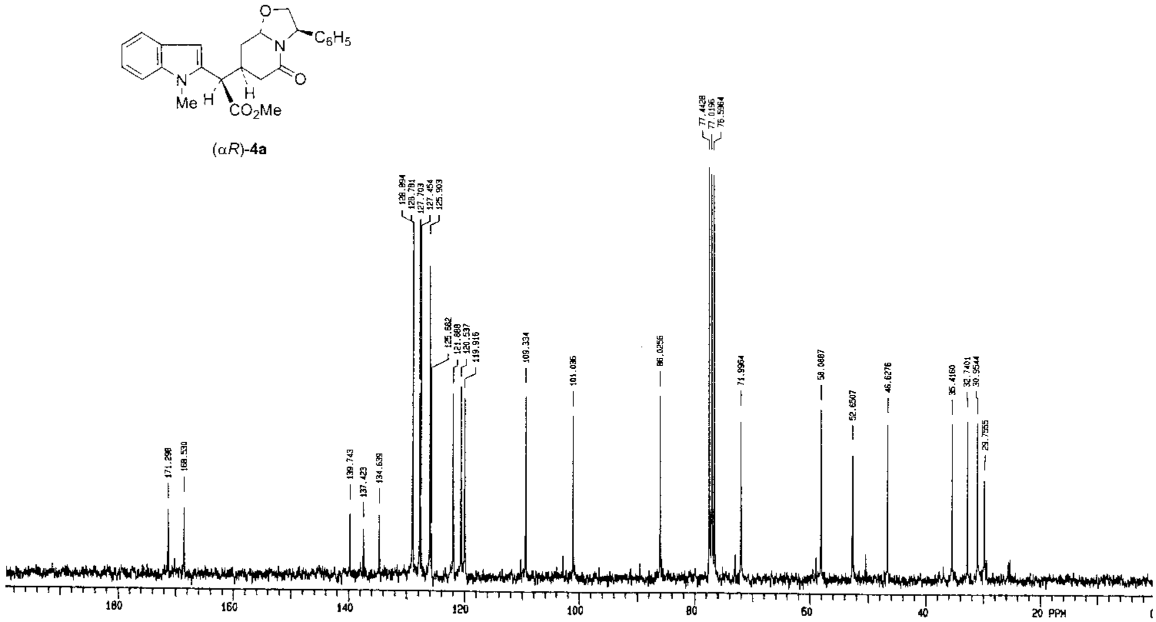

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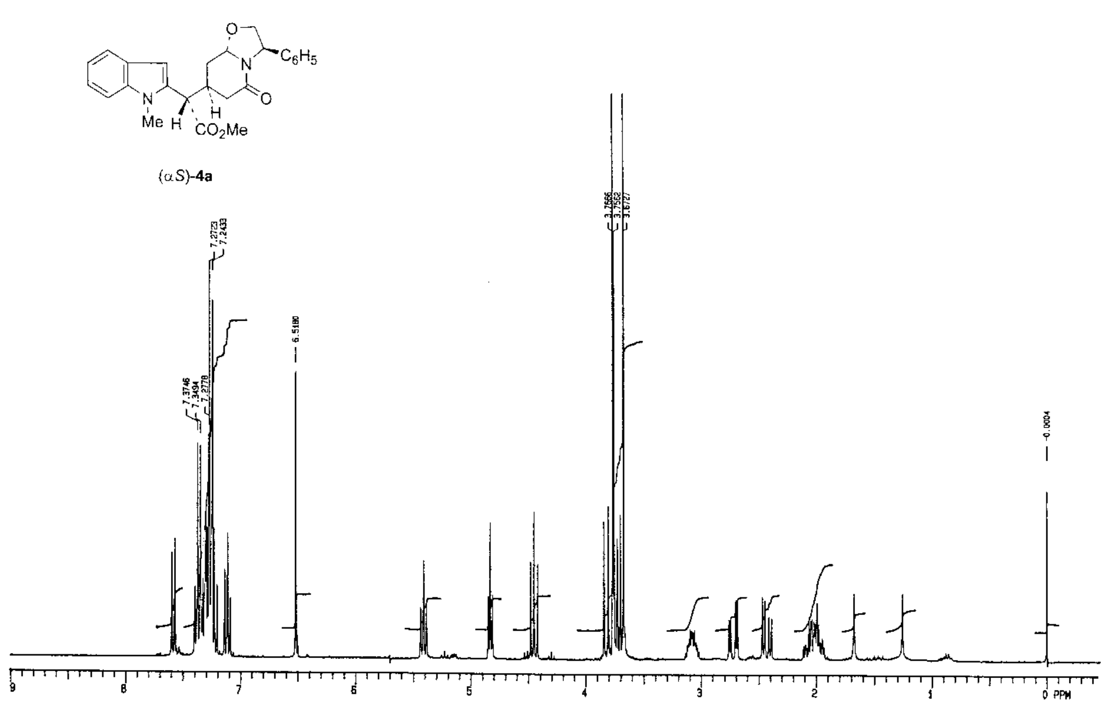

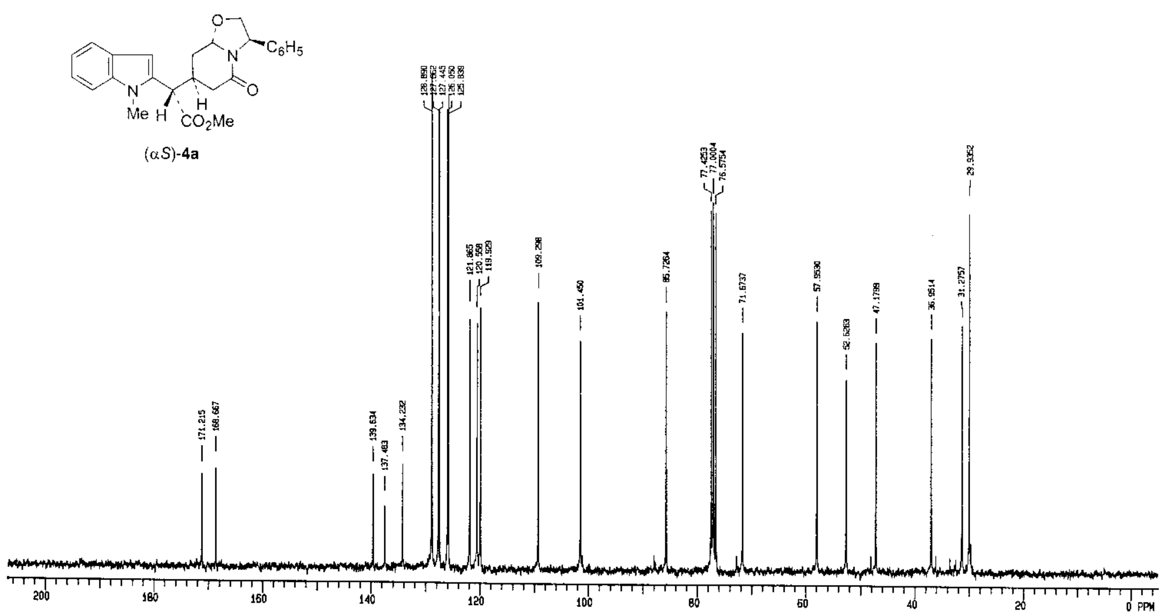

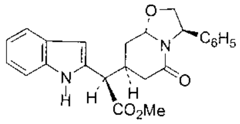
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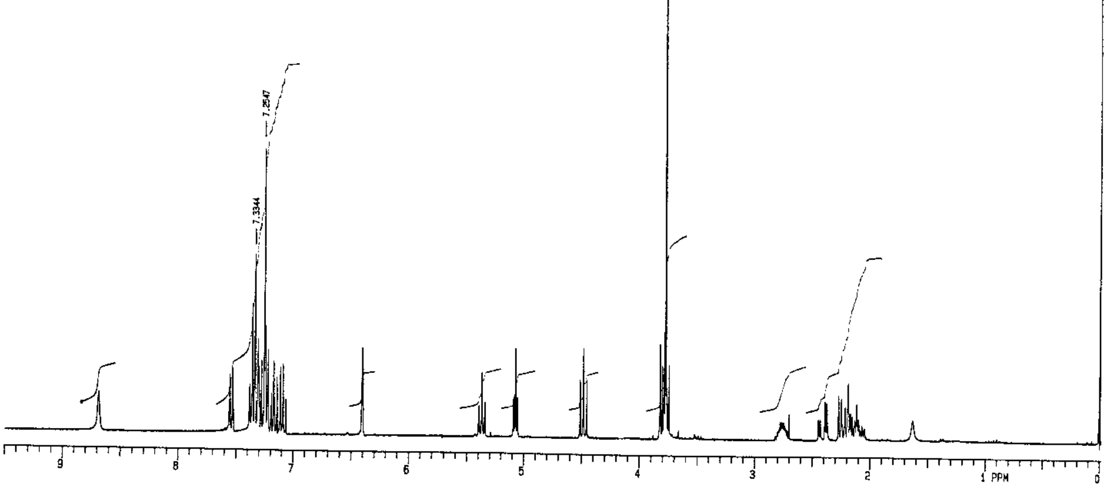
H
H
H
O
CO2Me

(αR)-**4b**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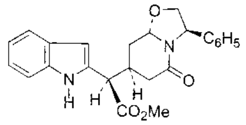
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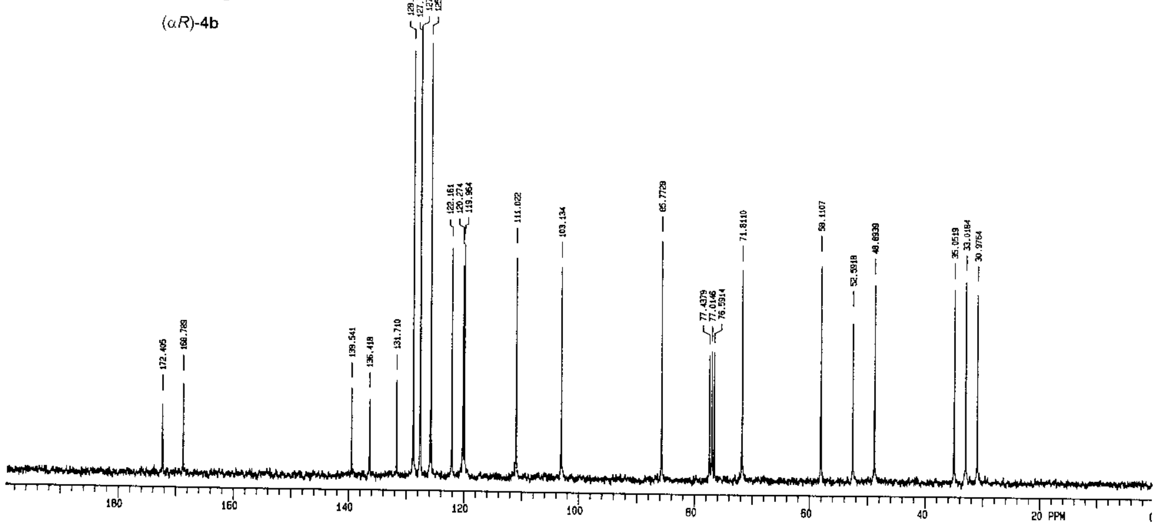
H
O
CO2Me

(αR)-**4b**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77.4379
77.0146
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71.8110
58.1107
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140
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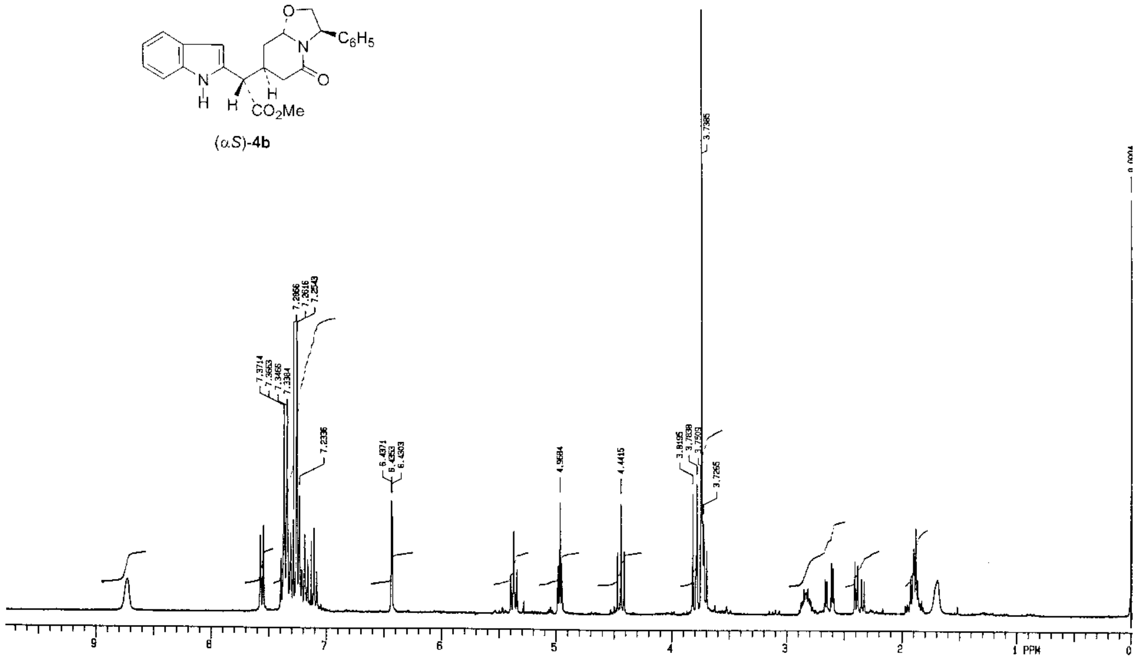
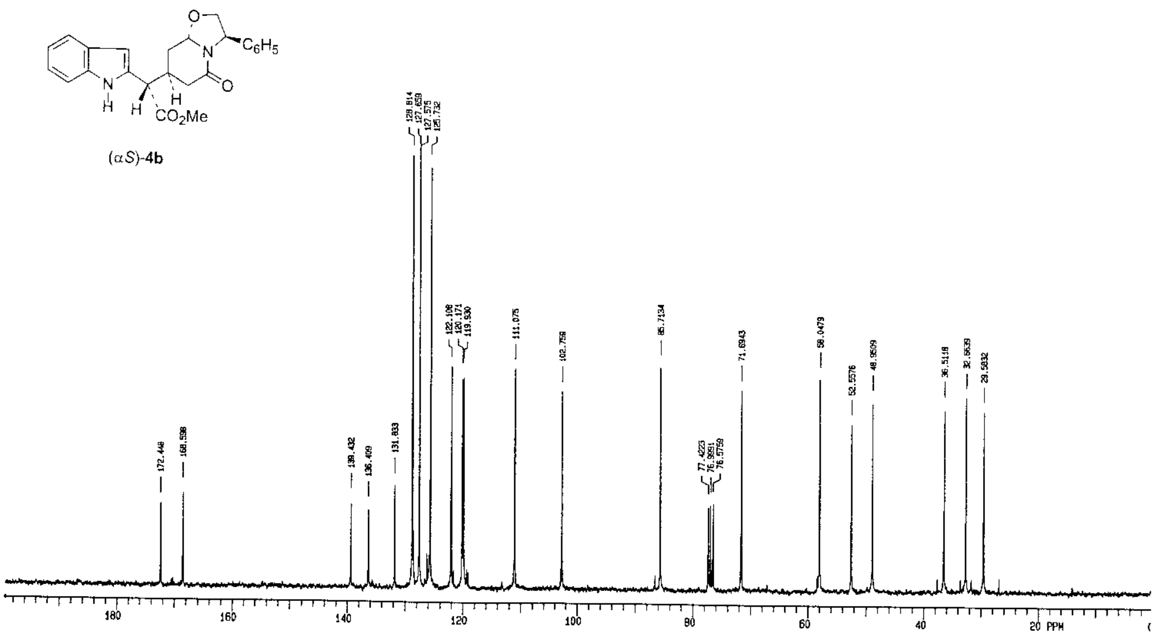
80
60
40
20 PPM



(αS)-**4b**



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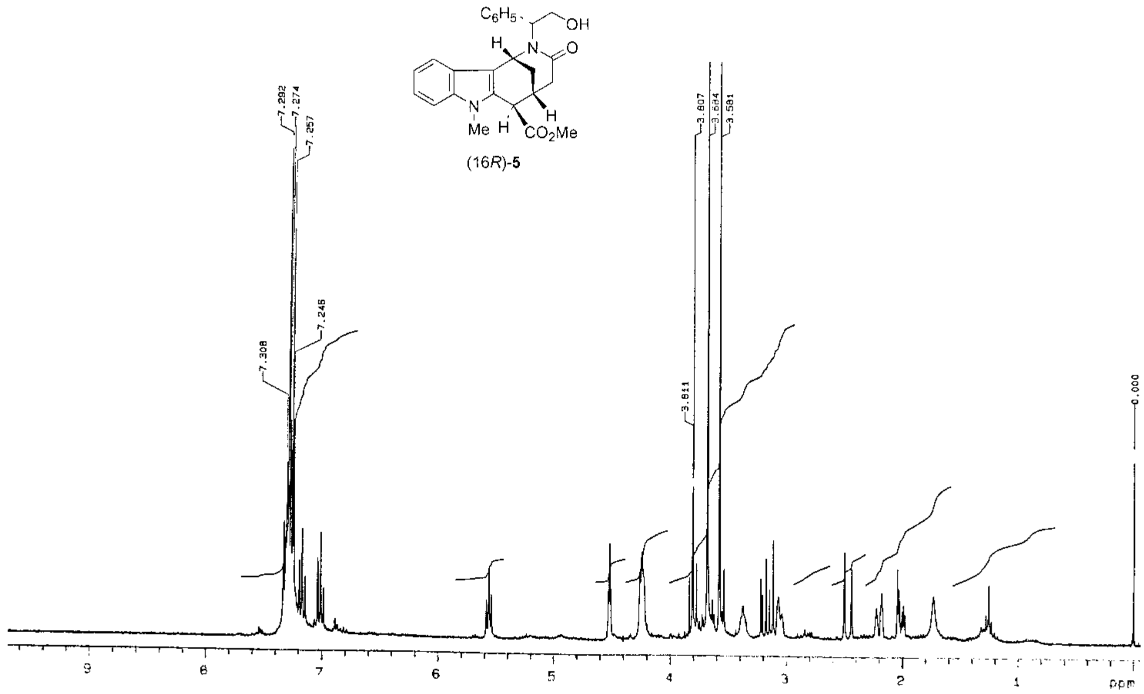
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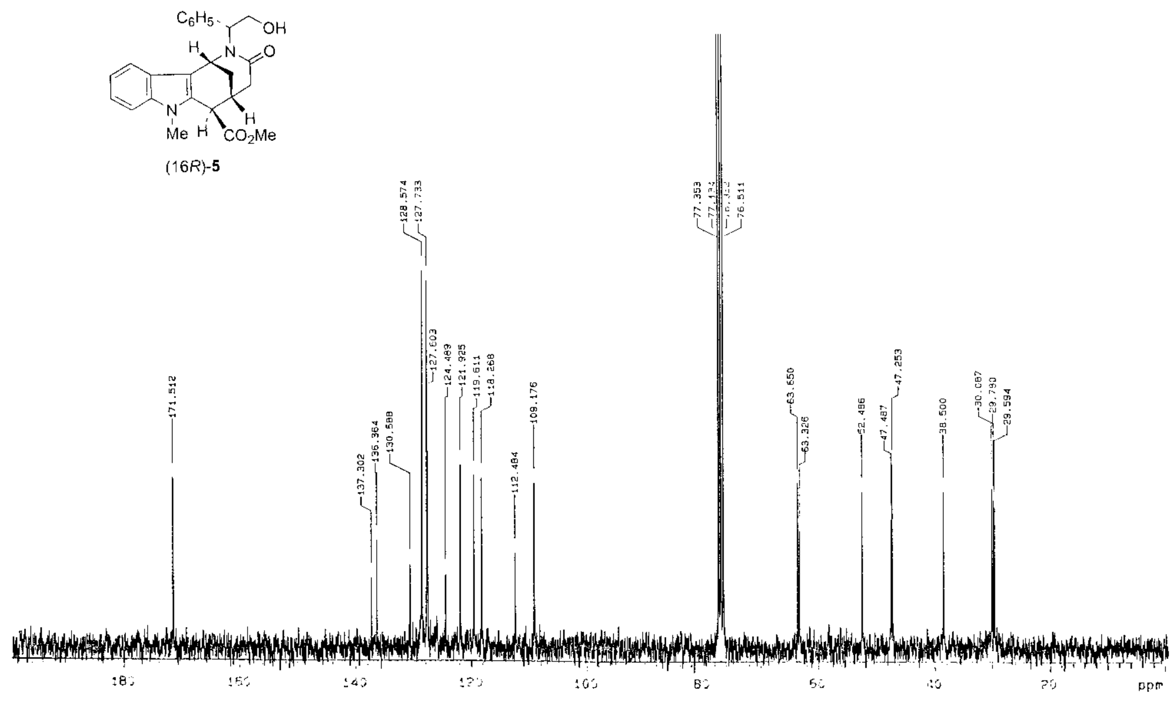
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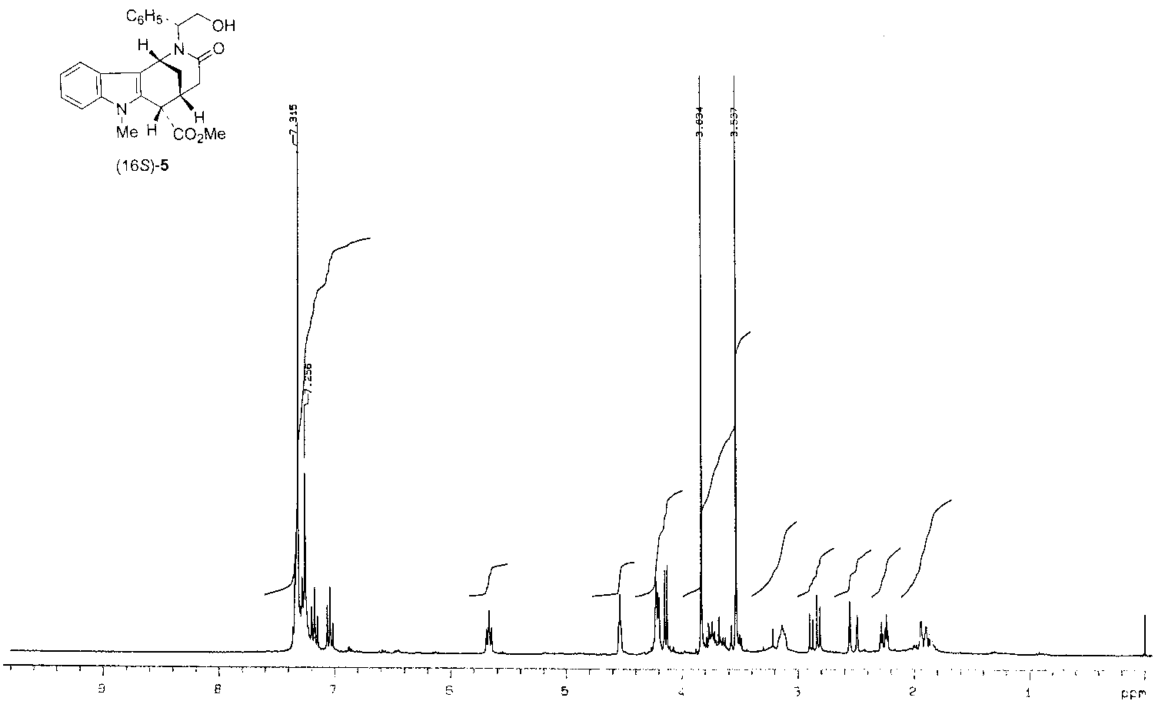
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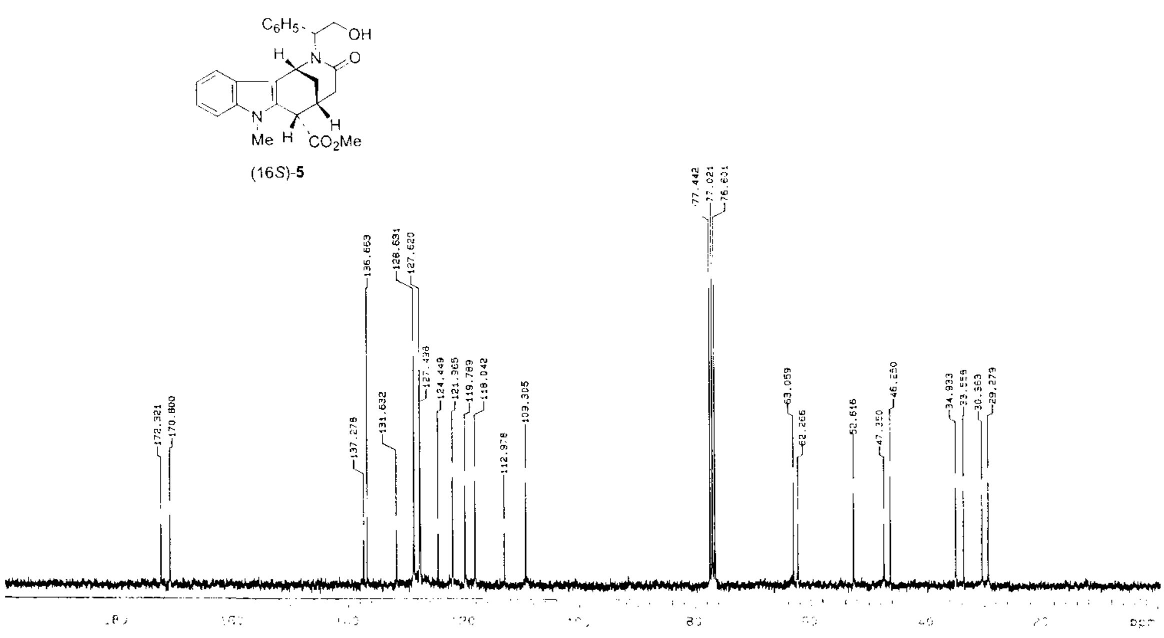
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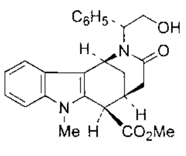
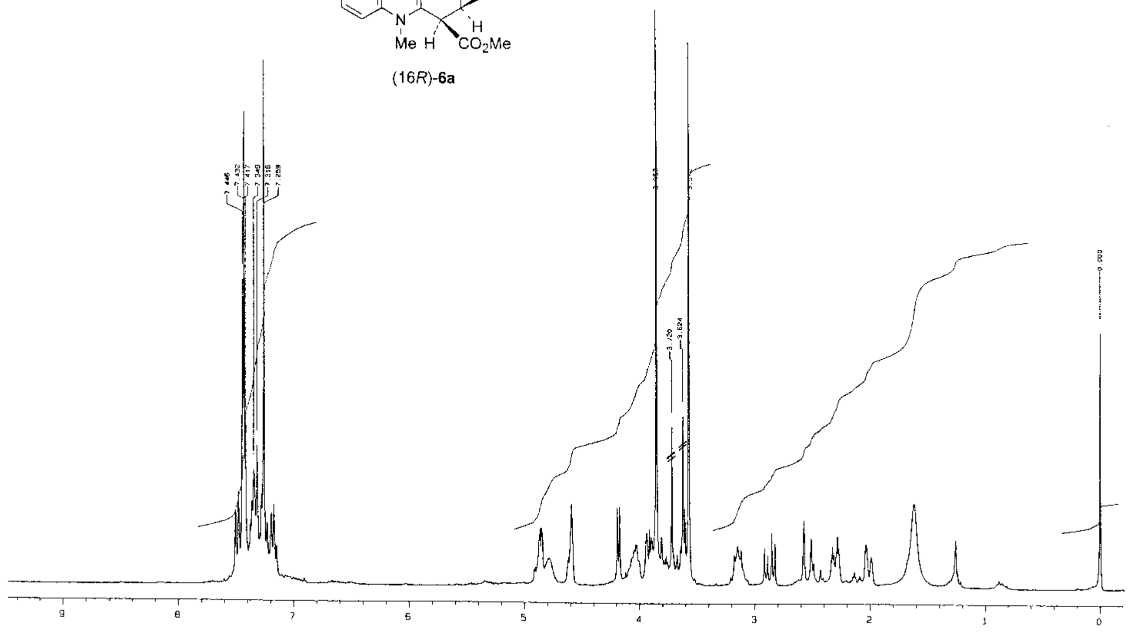
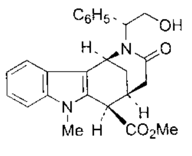
29.279
ppm

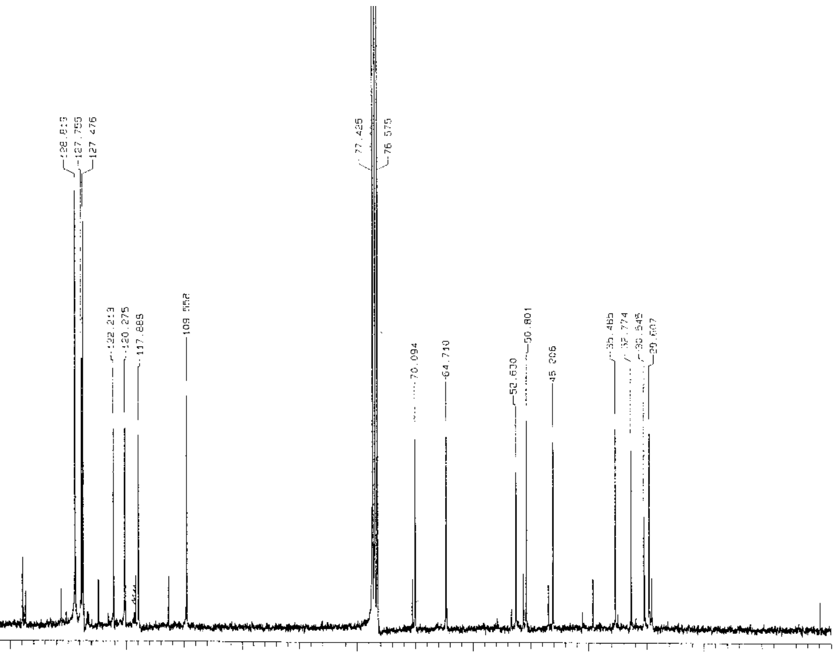


(16*R*)-**6a**





(16*R*)-**6a**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127.755
127.476
122.213
120.275
117.889
109.552
77.425
76.575
70.094
64.710
52.630
50.801
45.206
35.465
32.774
30.545
29.607
ppm

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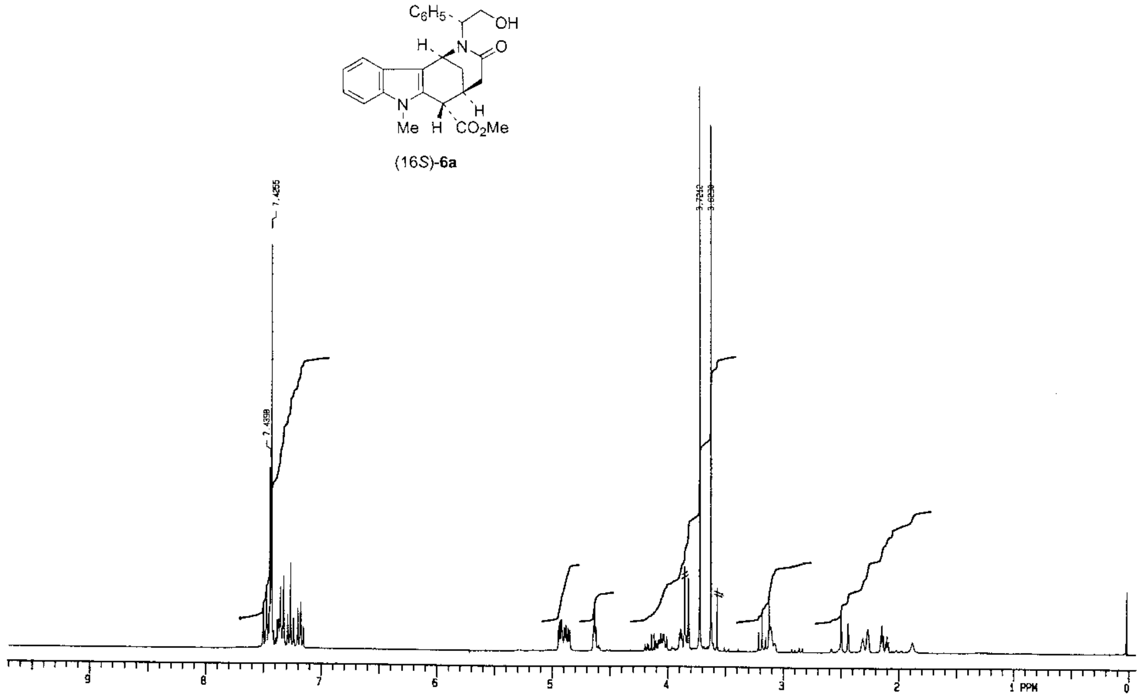
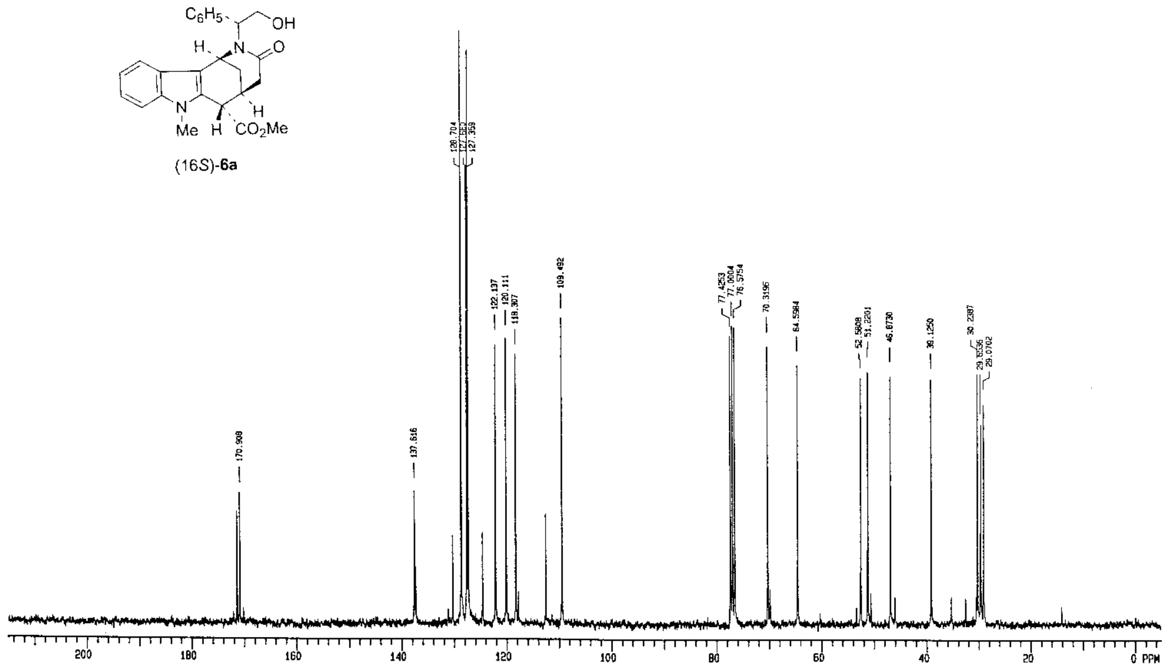
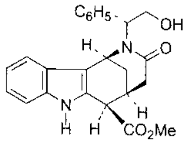


(16*S*)-**6a**

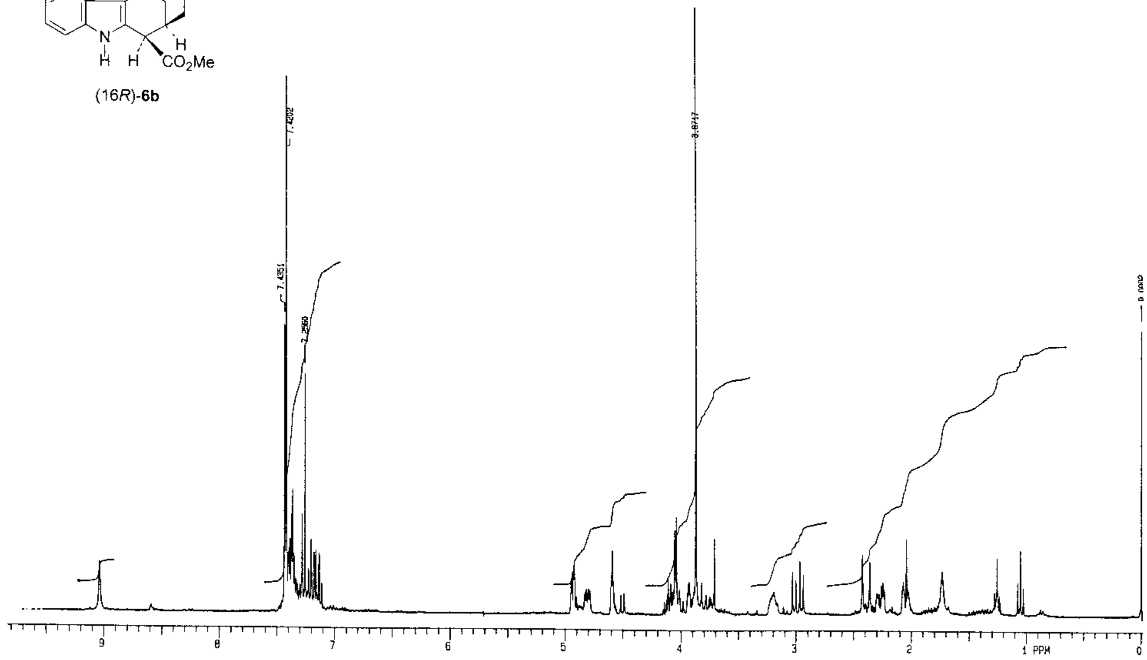


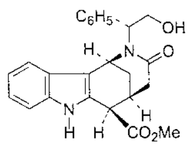
(16*S*)-**6a**

Supplementary Material for Chemical Communications

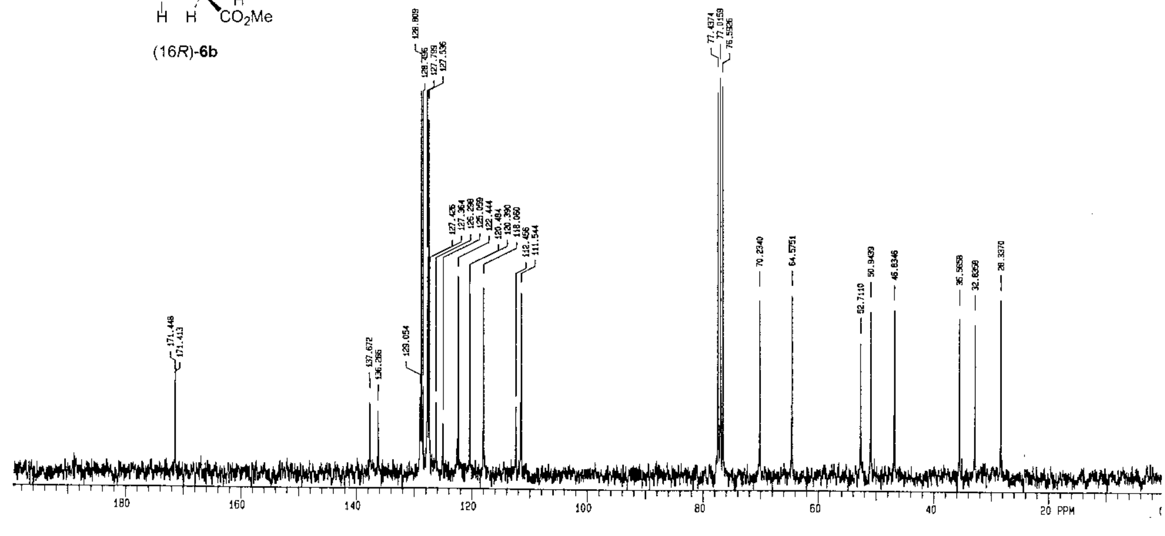


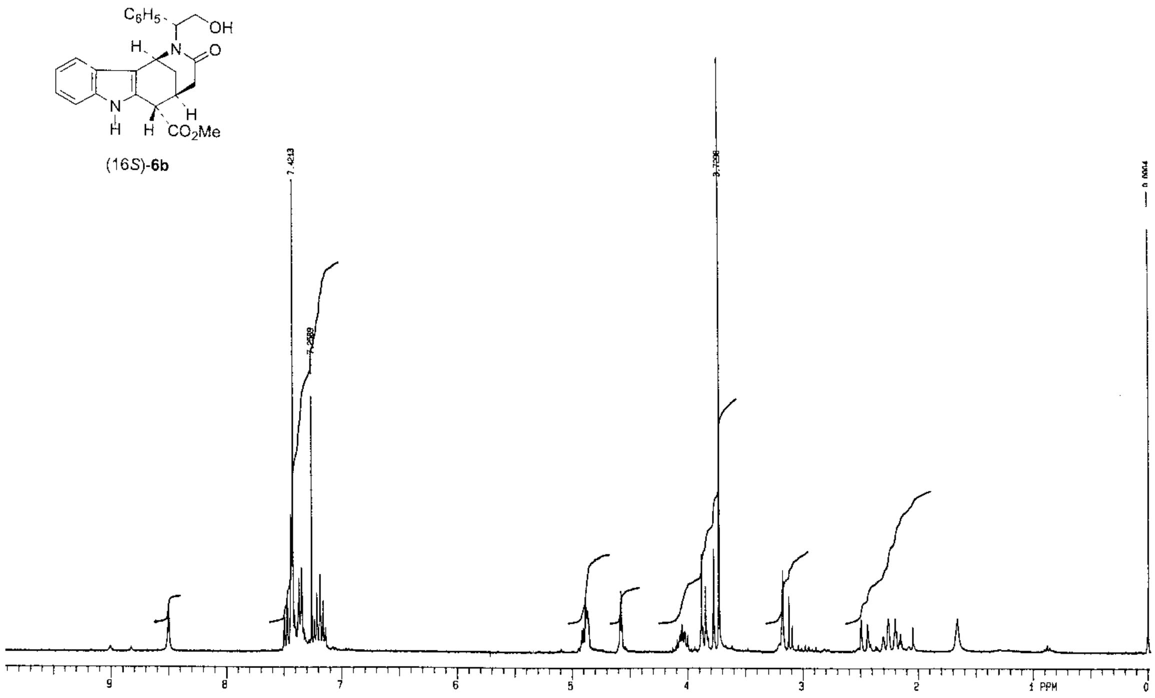
(16*R*)-**6b**



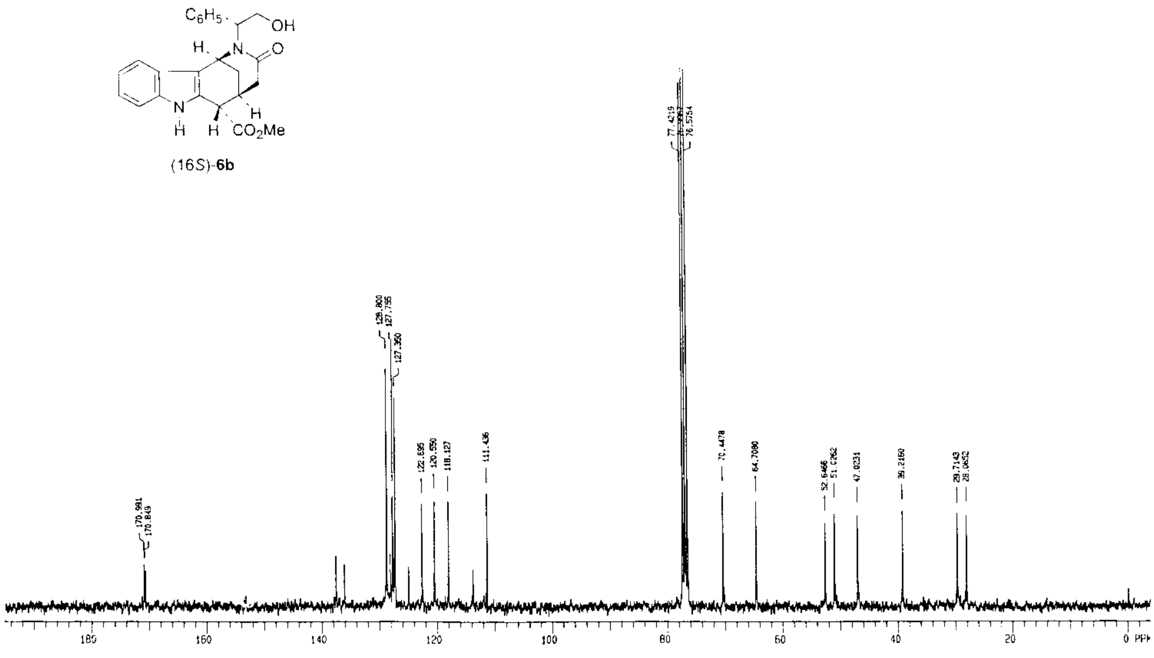


(16*R*)-**6b**



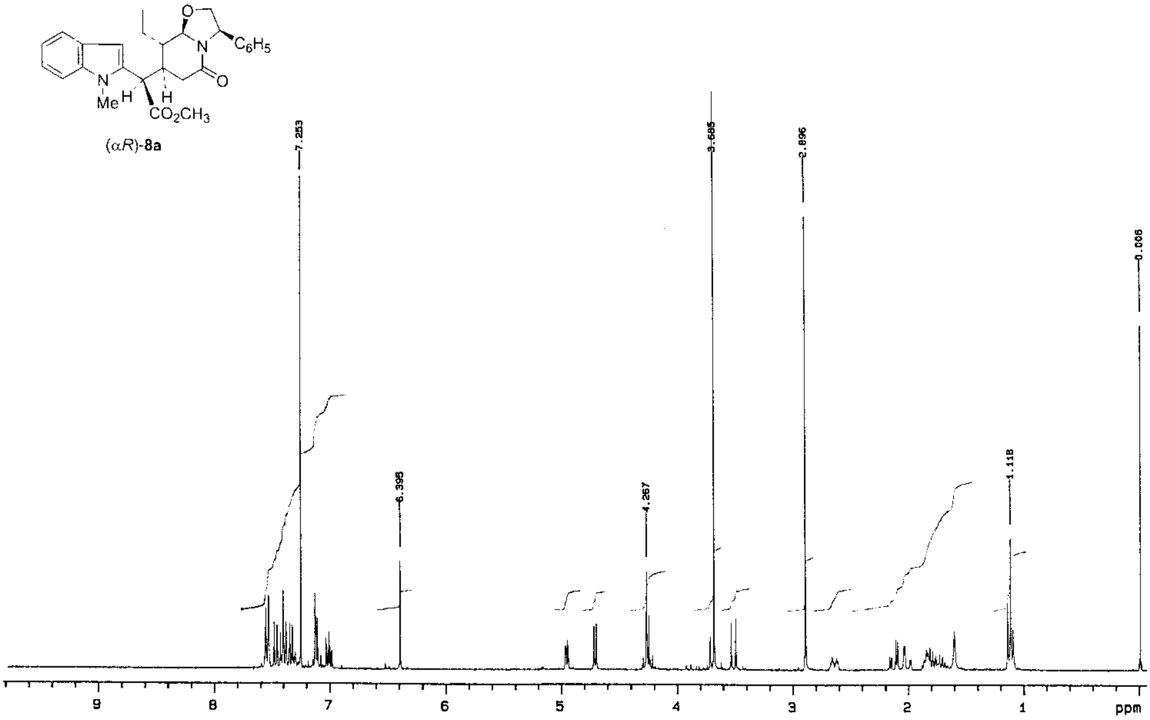


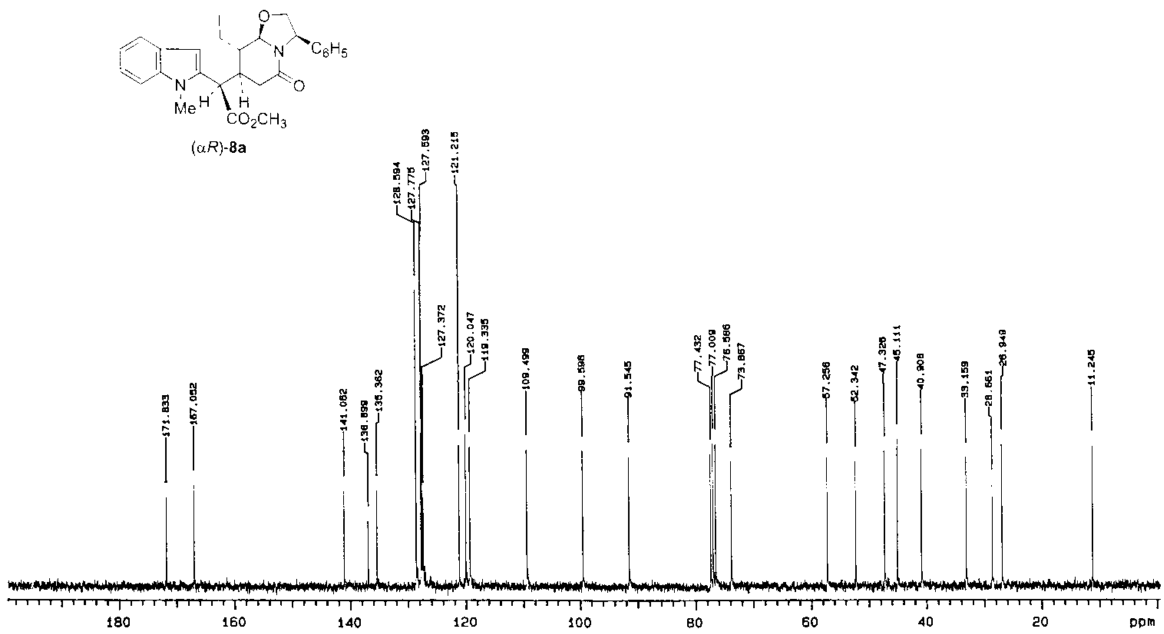
(16*S*)-**6b**



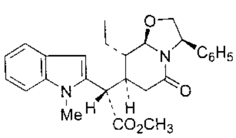
(16*S*)-**6b**

Supplementary Material for Chemical Communications

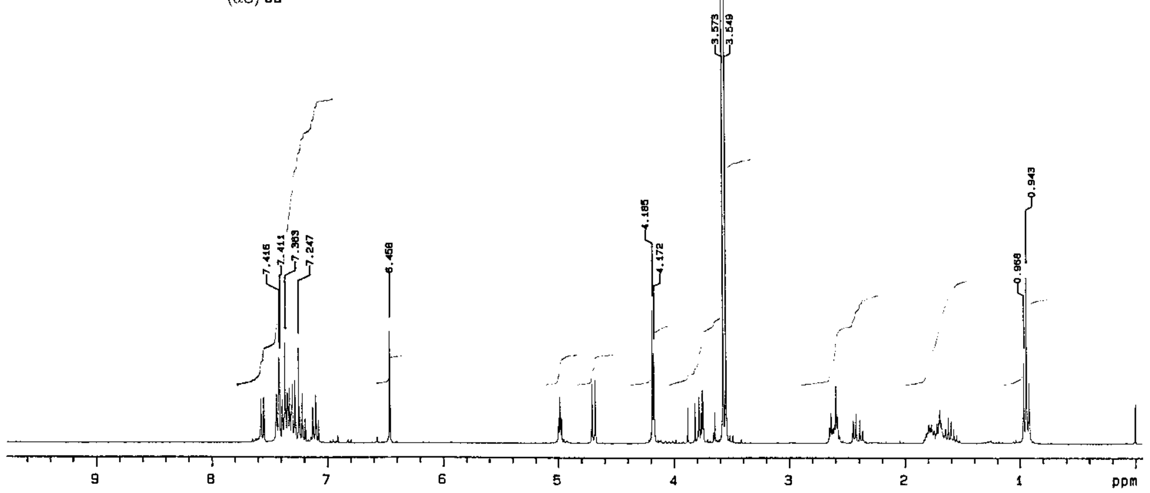


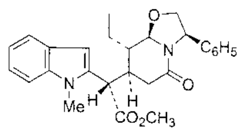


Supplementary Material for Chemical Communications

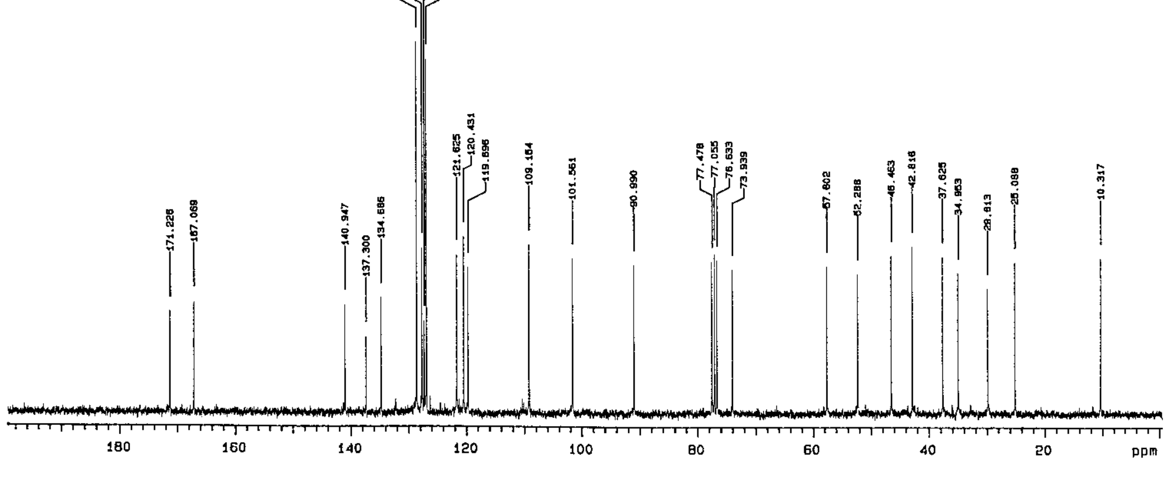


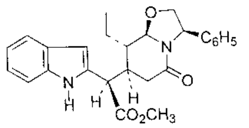
(αS)-8a



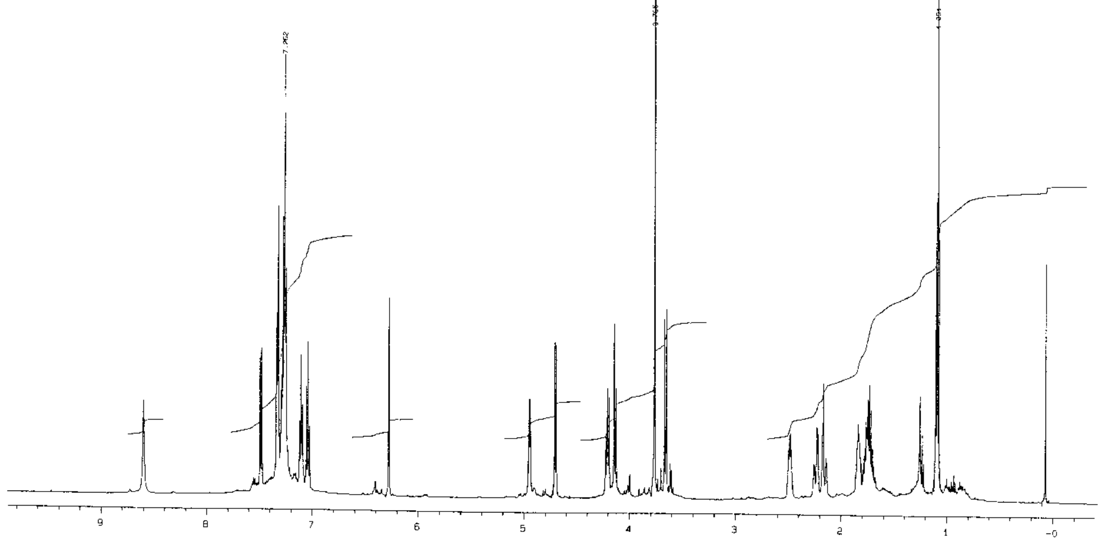


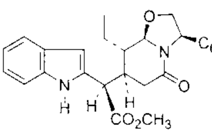
(αS)-8a



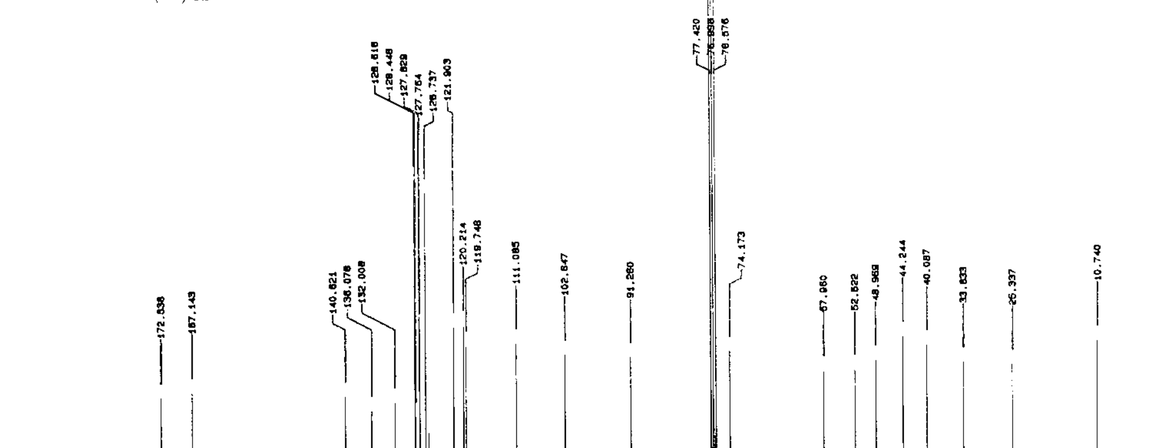


(αR)-8b





(αR)-8b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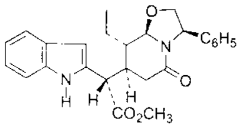
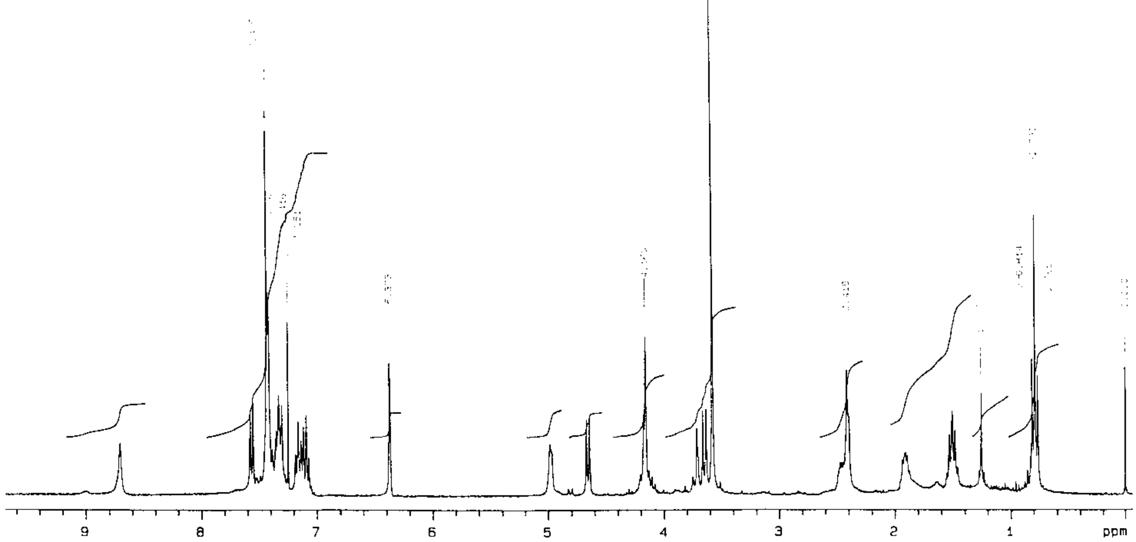
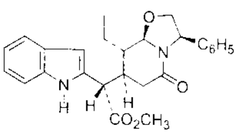
167.143
140.621
136.078
132.008
128.616
128.448
127.829
127.754
126.737
121.903
120.214
119.748
111.085
102.647
91.280
77.420
76.998
76.576
74.173
57.960
52.522
48.969
44.244
40.087
33.633
25.337
10.740
160
140
120
100
80
60
40
20
ppm

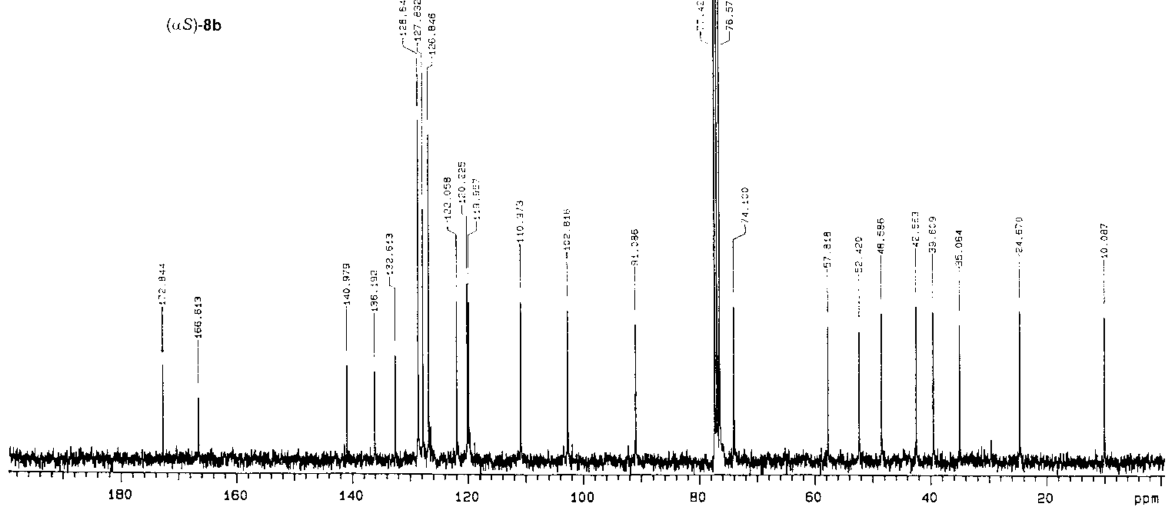

C6H5
O
N
H
H
H
CO2CH3

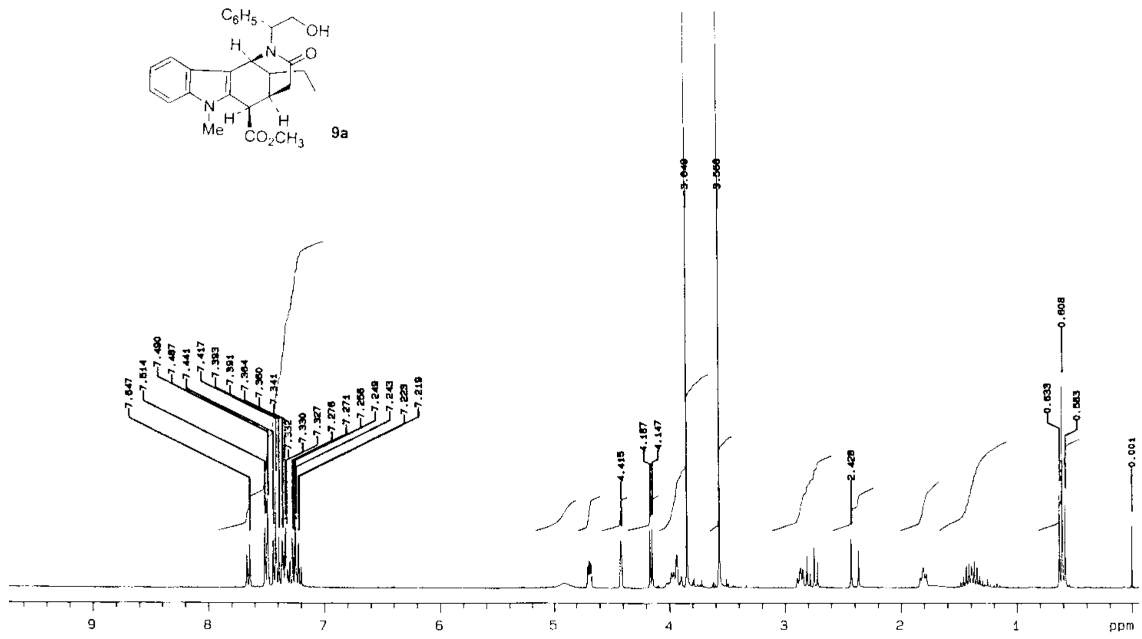
(αS)-8b

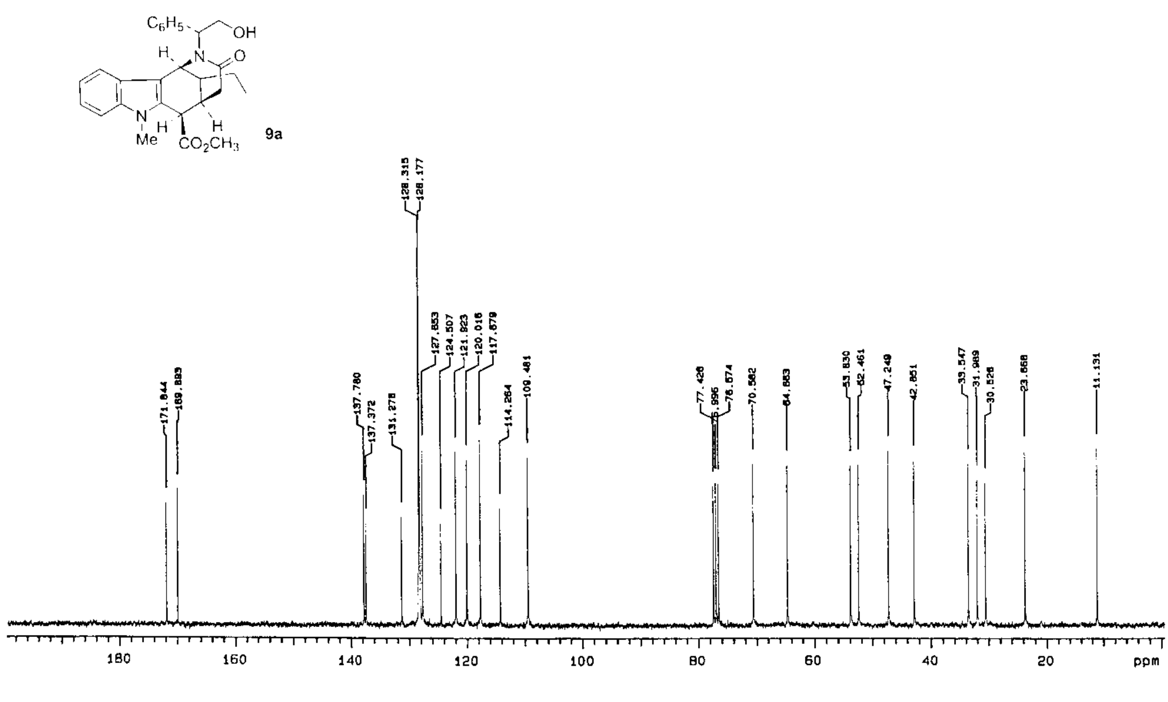

9
8
7
6
5
4
3
2
1
ppm

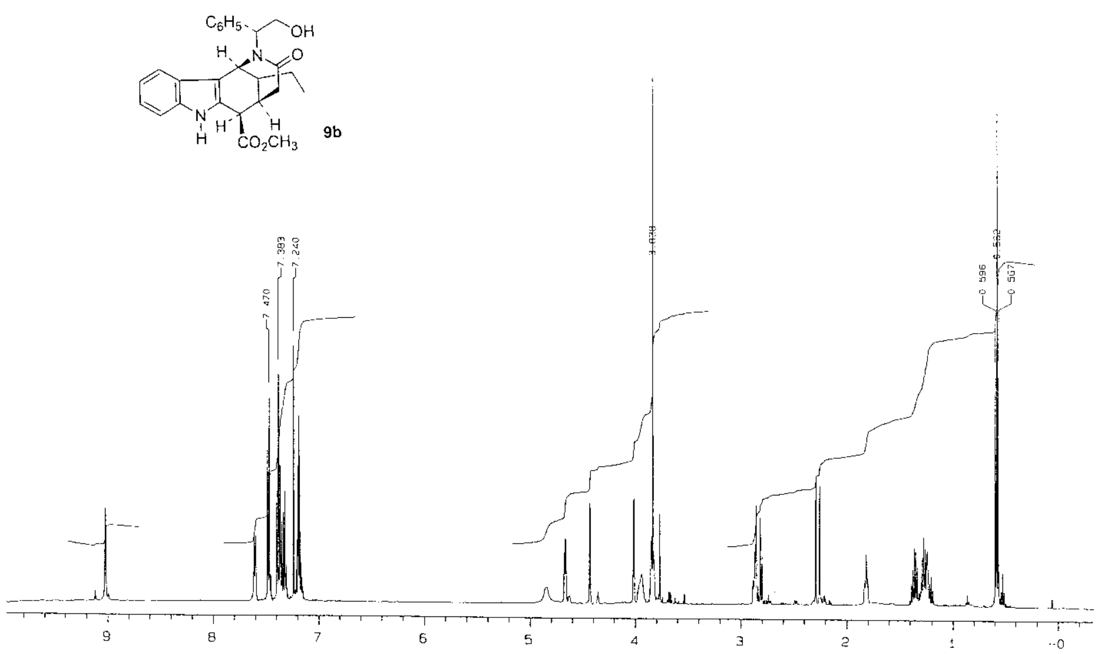

C6H5
O
N
H
H
H
CO2CH3

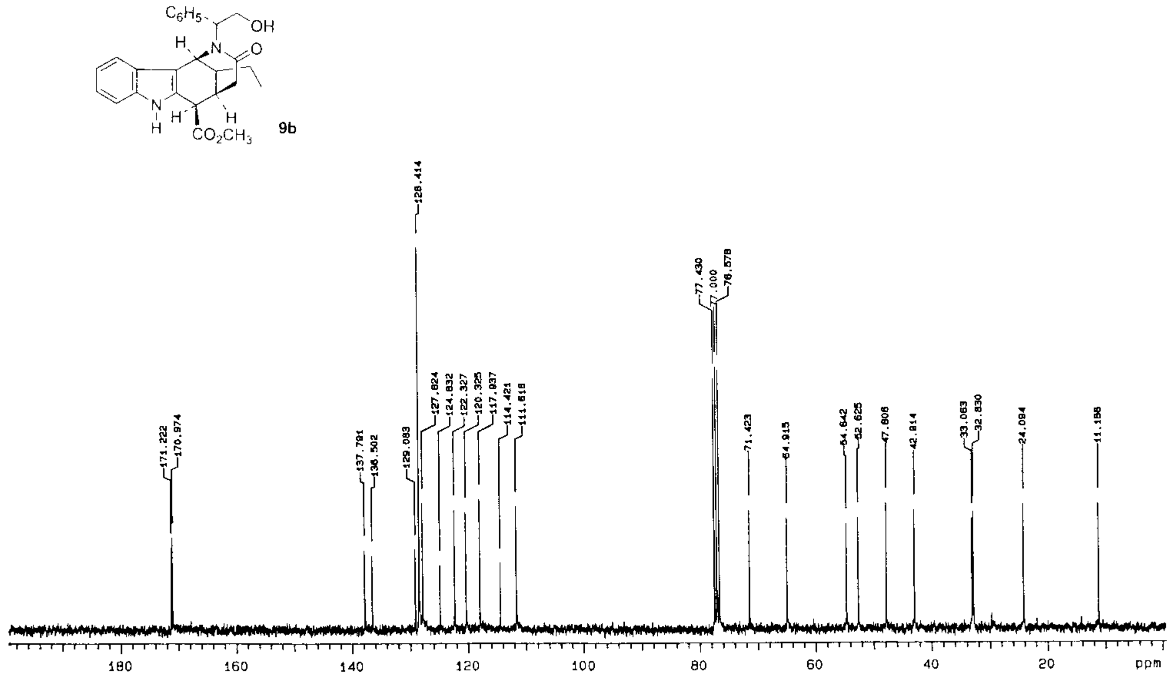
(αS)-8b


172.844
166.613
140.979
136.192
132.613
128.645
127.632
126.846
122.058
120.225
119.927
110.973
102.818
91.086
77.423
76.577
74.100
57.818
52.420
48.586
42.553
39.609
35.064
24.670
10.087
180
160
140
120
100
80
60
40
20
ppm






9b


9b
ppm

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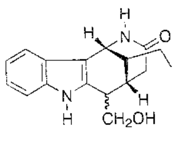
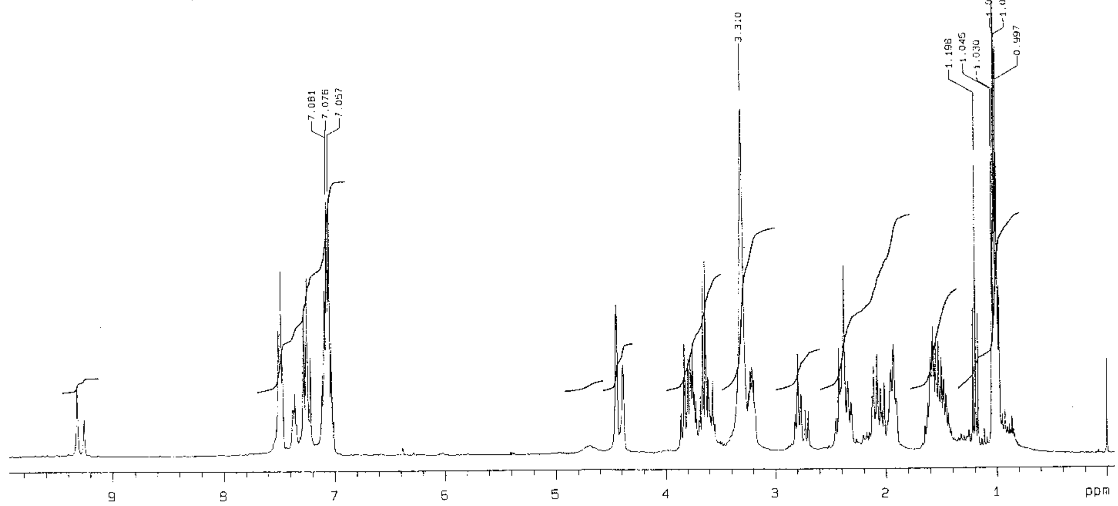
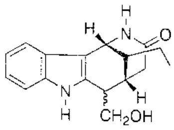
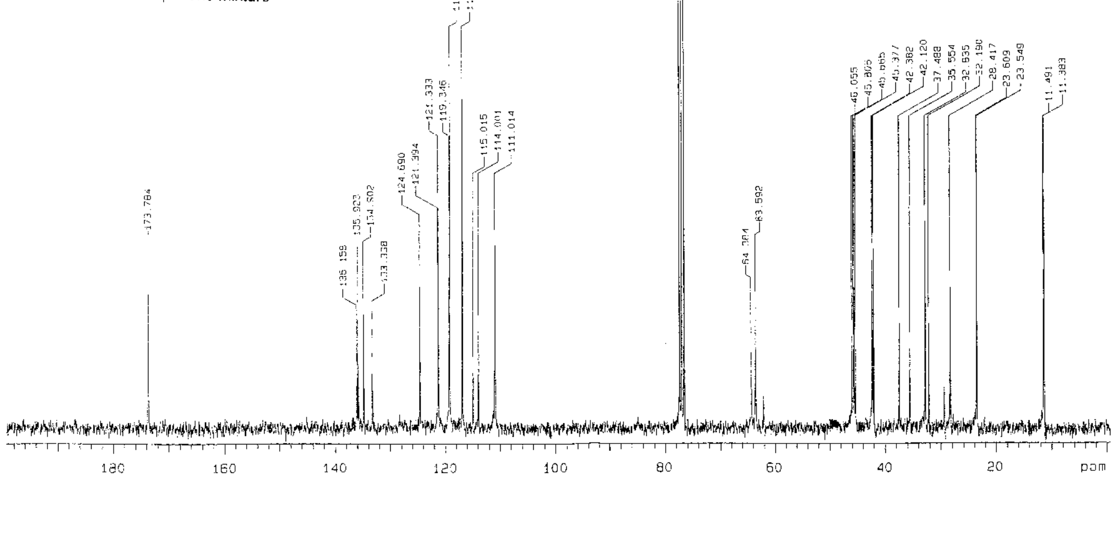


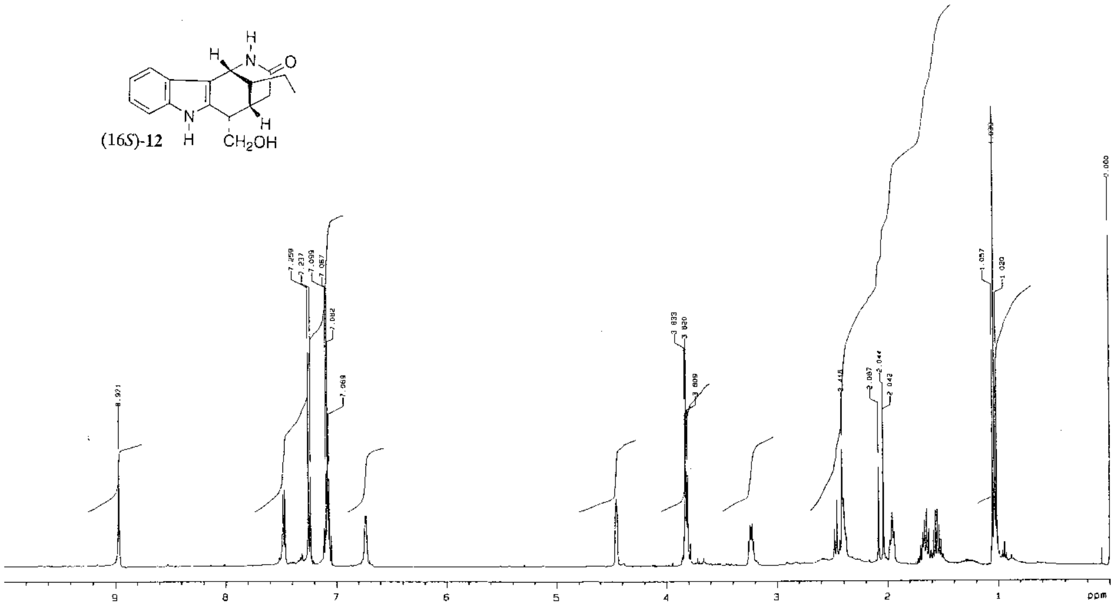
12 epimeric mixture

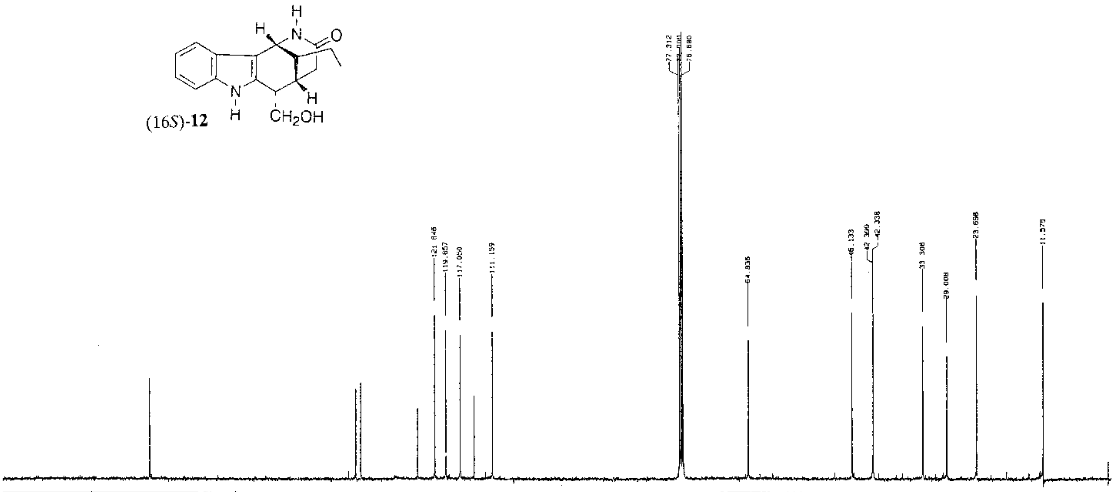


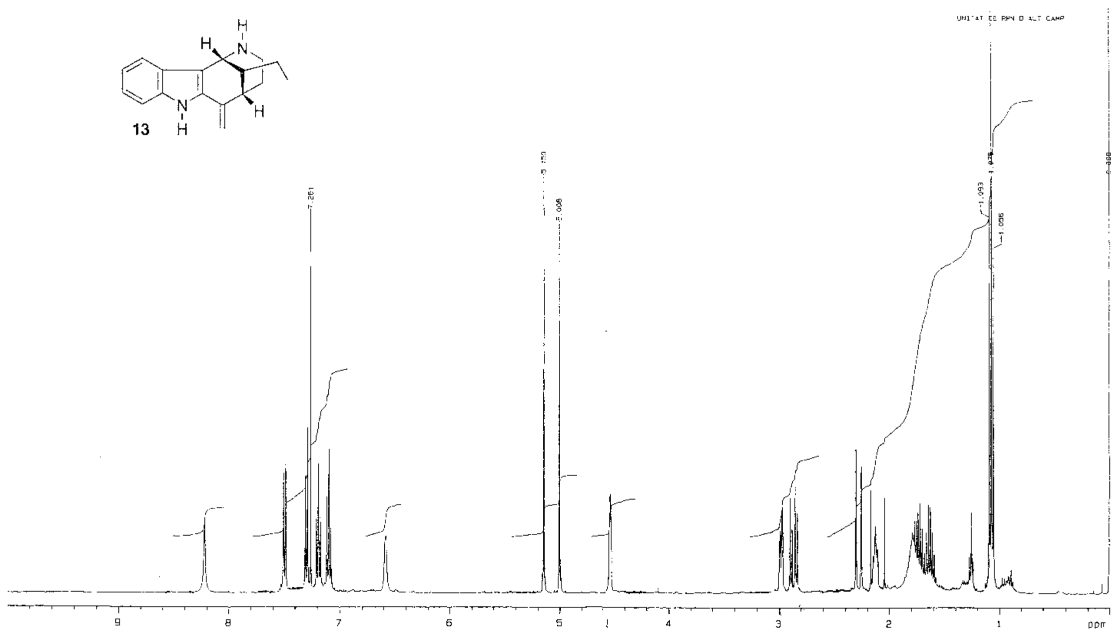


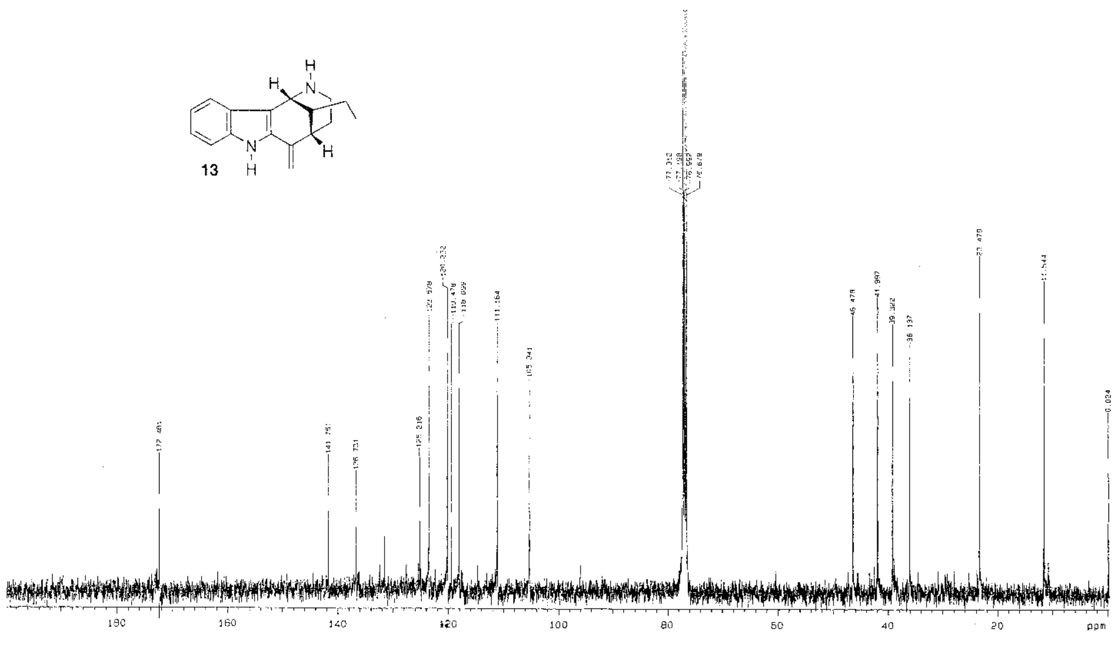
12 epimeric mixture




(16S)-12
H
N
O
H
N
H
H
CH2OH
8.971
3.833
3.820
1.057
1.029
0.000
9
8
7
6
5
4
3
2
1
ppm


(16S)-12
H
N
O
H
N
H
H
CH2OH
121.648
119.657
117.050
111.199
76.890
64.835
46.133
42.308
33.306
29.008
23.656
11.575
180
160
140
120
100
80
60
40
20
ppm





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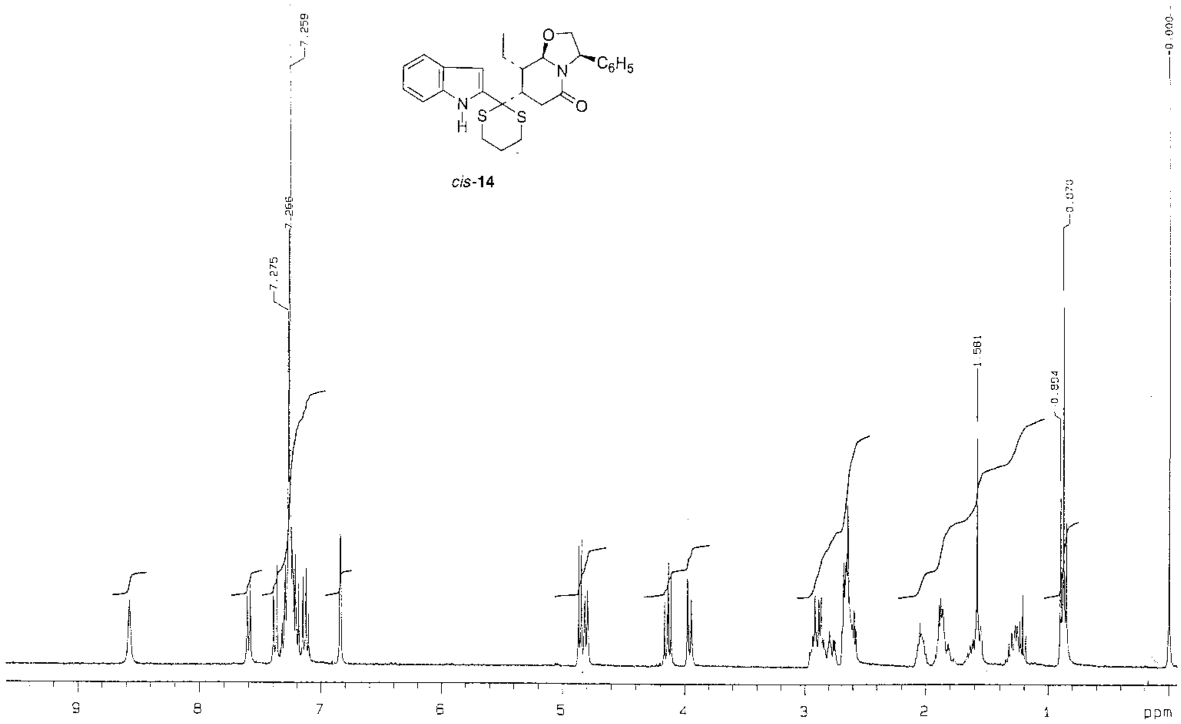
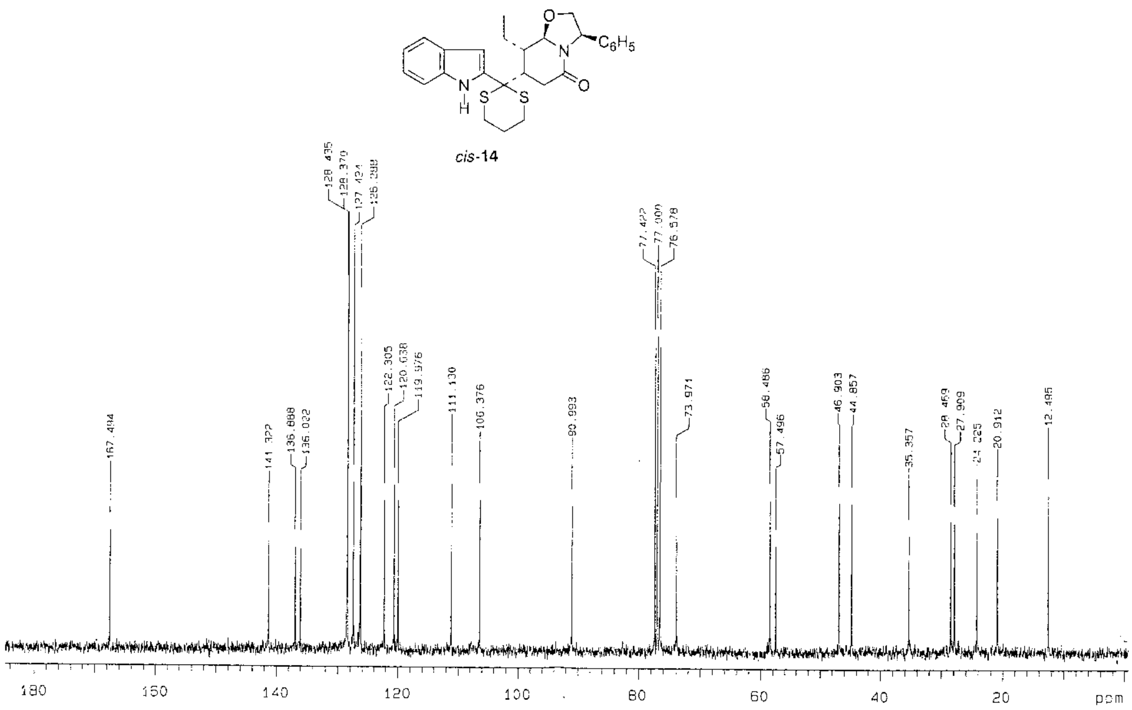
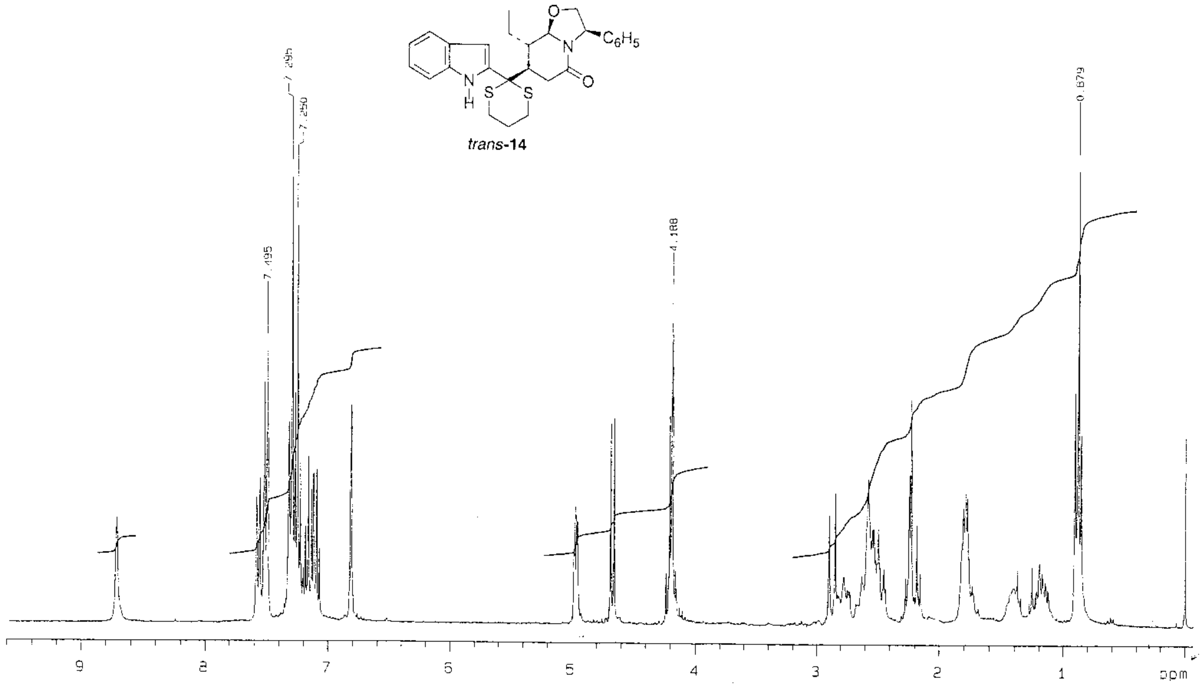
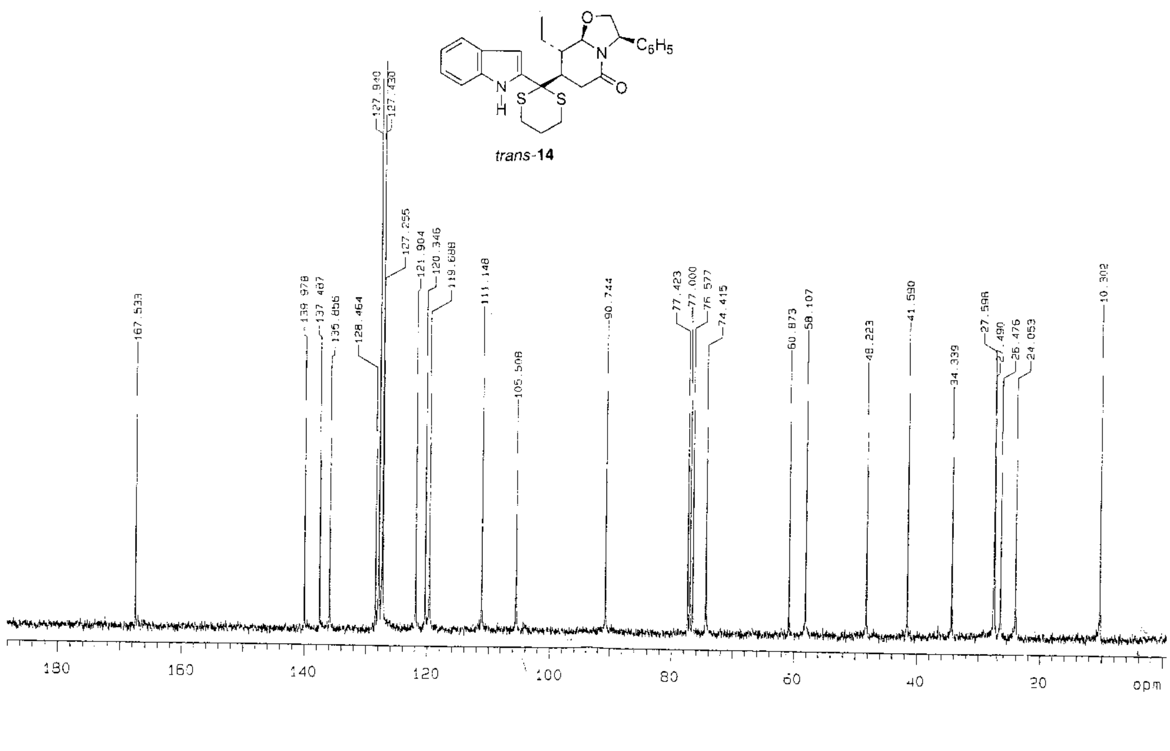
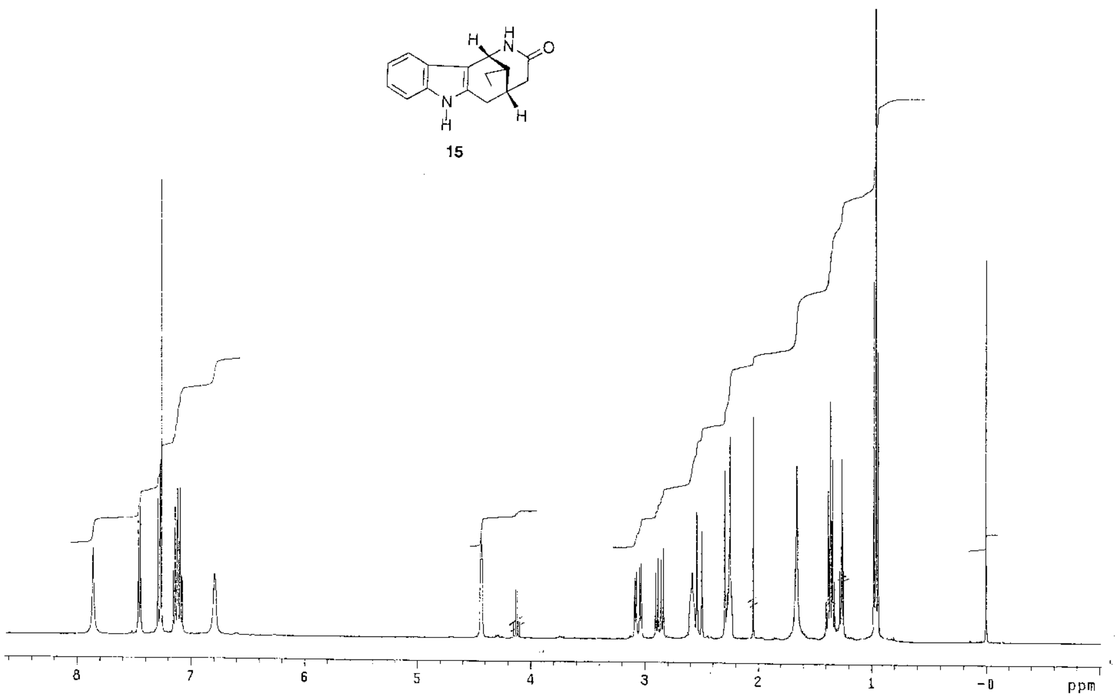


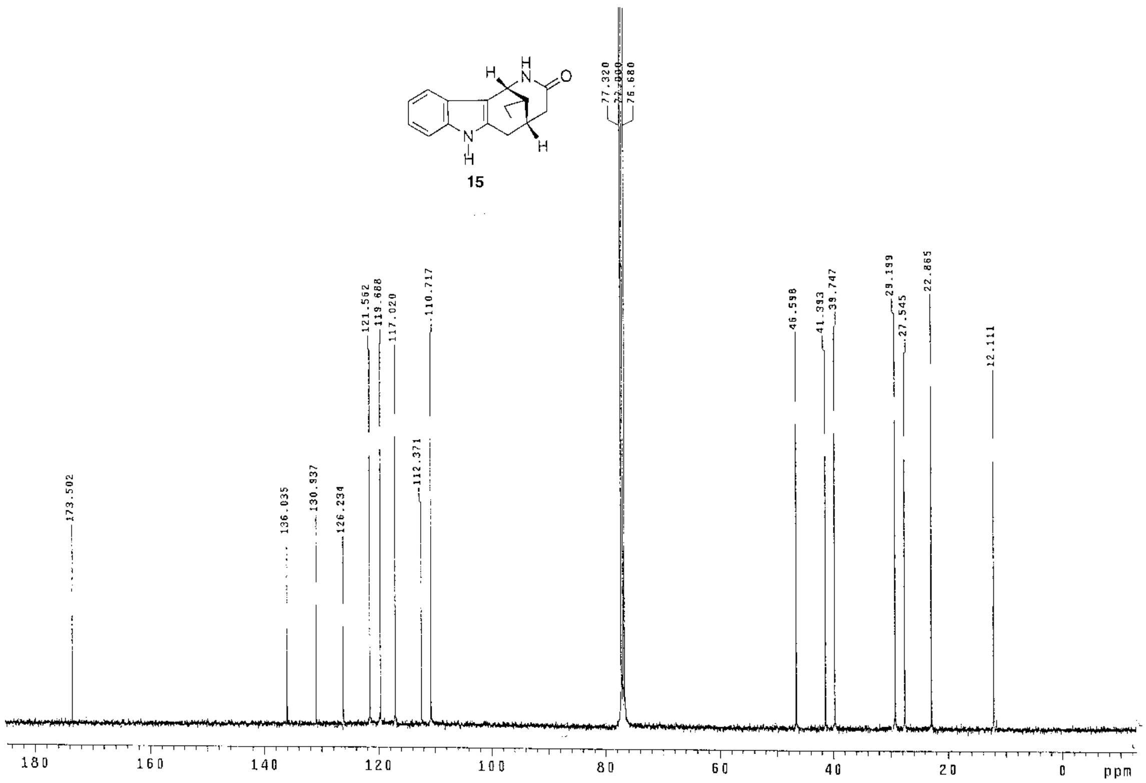


Supplementary Material for Chemical Communications






H
N
O
N
H
H
15
8
7
6
5
4
3
2
1
-0
ppm


H
N
O
N
H
H
15
173.502
136.035
130.937
126.234
121.562
119.668
117.020
112.371
110.717
77.320
77.000
76.680
46.598
41.393
39.747
29.199
27.545
22.865
12.111
180
160
140
120
100
80
60
40
20
0
ppm