

ESTUDO QUÍMICO E ATIVIDADE ANTIBACTERIANA DO CAULE DE *Aristolochia esperanzae* Kuntze (ARISTOLOCHIACEAE)

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Asarinina (**1**): p.f. 120,2–121,8 °C; CG/EM $t_R = 53,916$ min, m/z 354,2 [M]⁺, 178,0, 149,0 (pico base), 135,1, 131,0 e 77,0; IV ($\nu_{\max}/\text{cm}^{-1}$) 3090, 3025, 3010, 2950, 2910, 2890, 2835, 1650, 1630, 1610, 1515, 1505, 1480, 1405, 1265, 1280, 1050, 1030, 970, 775 e 755; RMN de ¹H (400 MHz; CDCl₃) δ_H 6,84 (s; H-2' e H-2''), 6,80 (m; H-6' e H-6''), 6,77 (m; H-5' e H-5''), 5,95 (s; O-CH₂-O), 4,82 (d, $J = 5,2$ Hz; H-6), 4,39 (d, $J = 7,1$ Hz; H-2), 4,09 (d, $J = 10,2$ Hz; H-4 β),

3,84 (m; H-8 α) 3,82 (m; H-4 α), 3,31 (m; H-7), 3,29 (m, H-8 β) e 2,86 (m; H-3); RMN de ¹³C (100 MHz; CDCl₃) δ_C 148,0 (C-3''), 147,7 (C-3'), 147,2 (C-4''), 146,6 (C-4'), 135,1 (C-1''), 132,3 (C-1'), 119,6 (C-2''), 118,7 (C-2'), 108,2 (C-5' e C-5''), 106,6 (C-6''), 106,4 (C-6'), 101,1 (O-CH₂-O''), 100,9 (O-CH₂-O'), 87,7 (C-2), 82,0 (C-6), 70,9 (C-4), 69,7 (C-8), 54,7 (C-3) e 50,2 (C-7).

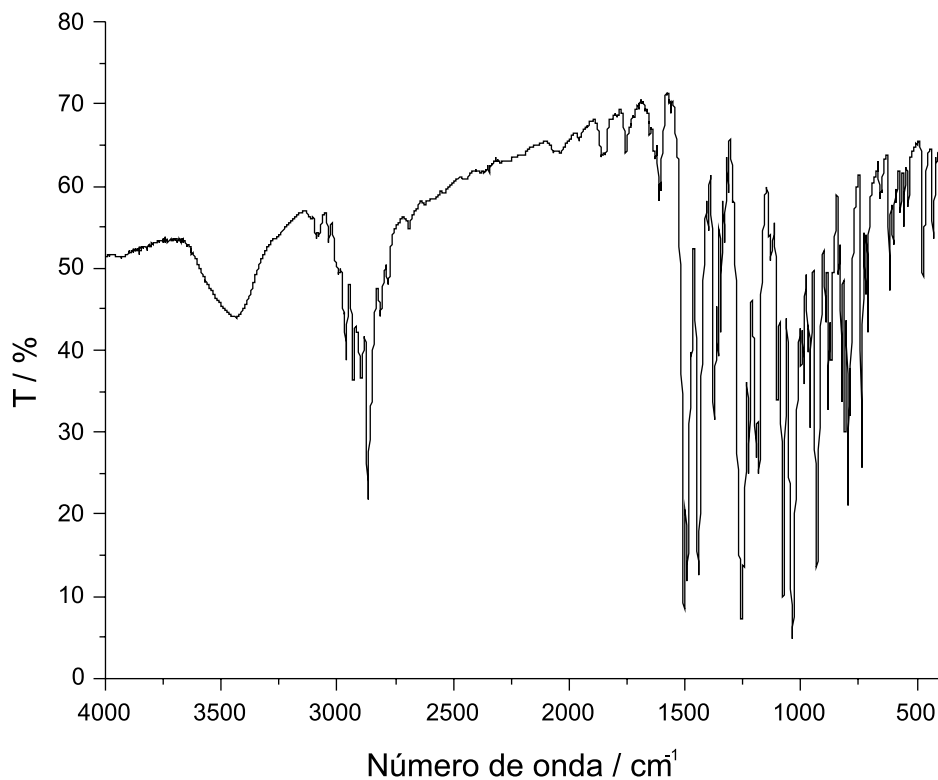


Figura 1S. Espectro de absorção na região do IV de **1** (asarinina; KBr; cm^{-1})

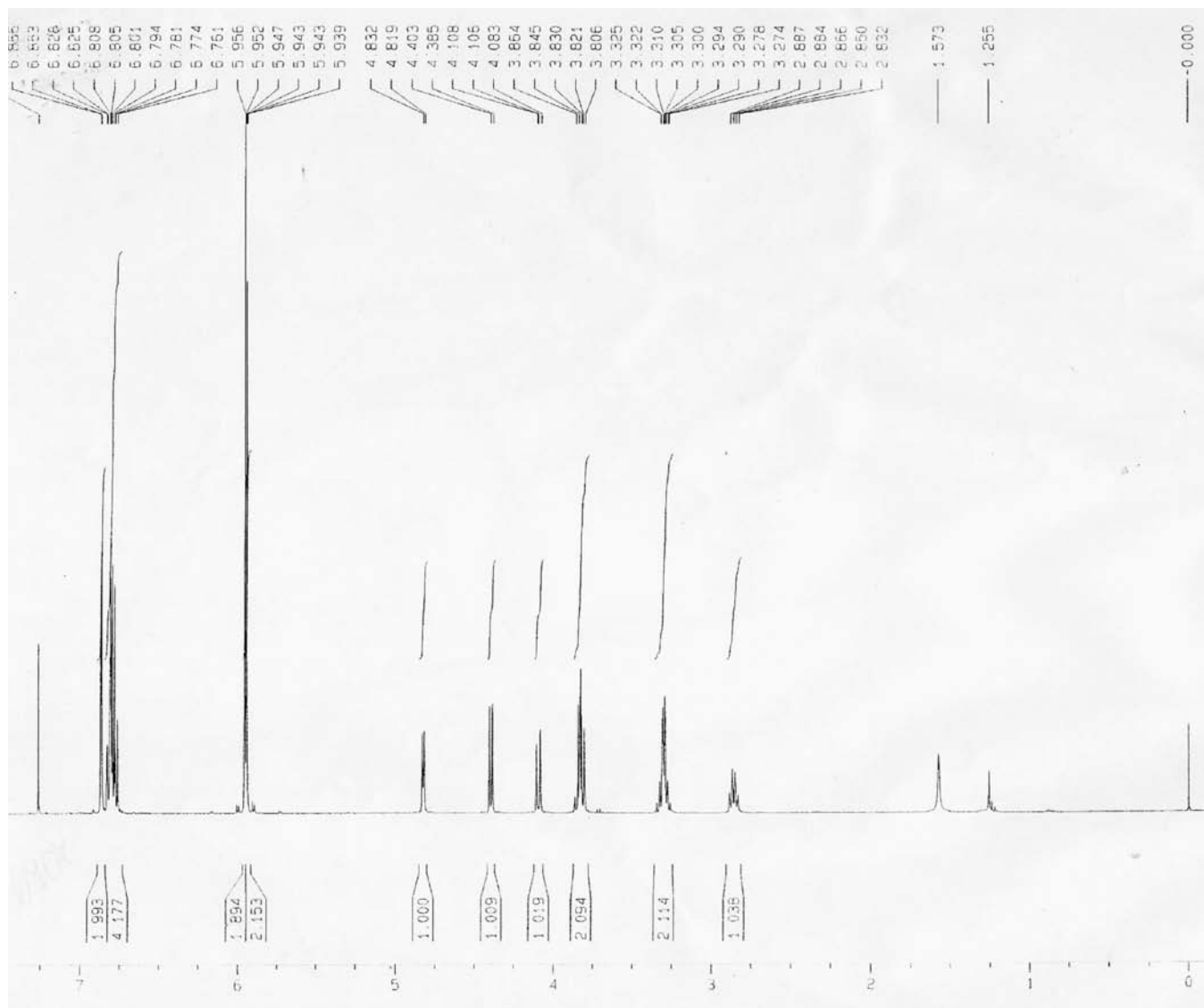


Figura 2S. Espectro de RMN de ^1H de **1** (asarinina; 400 MHz; CDCl_3).

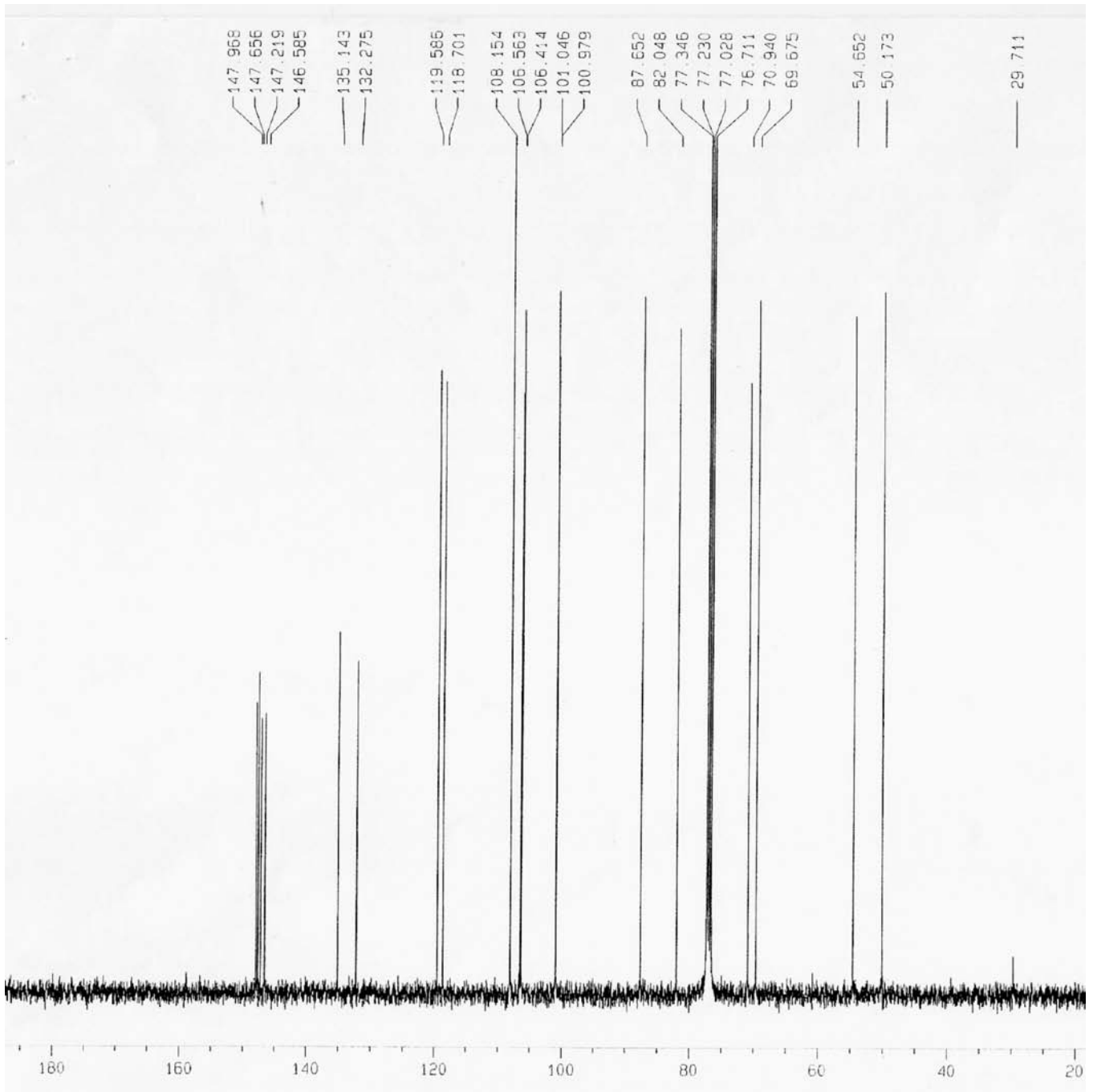


Figura 3S. Espectro de RMN de ^{13}C de **1** (asarina; 100 MHz; CDCl_3)

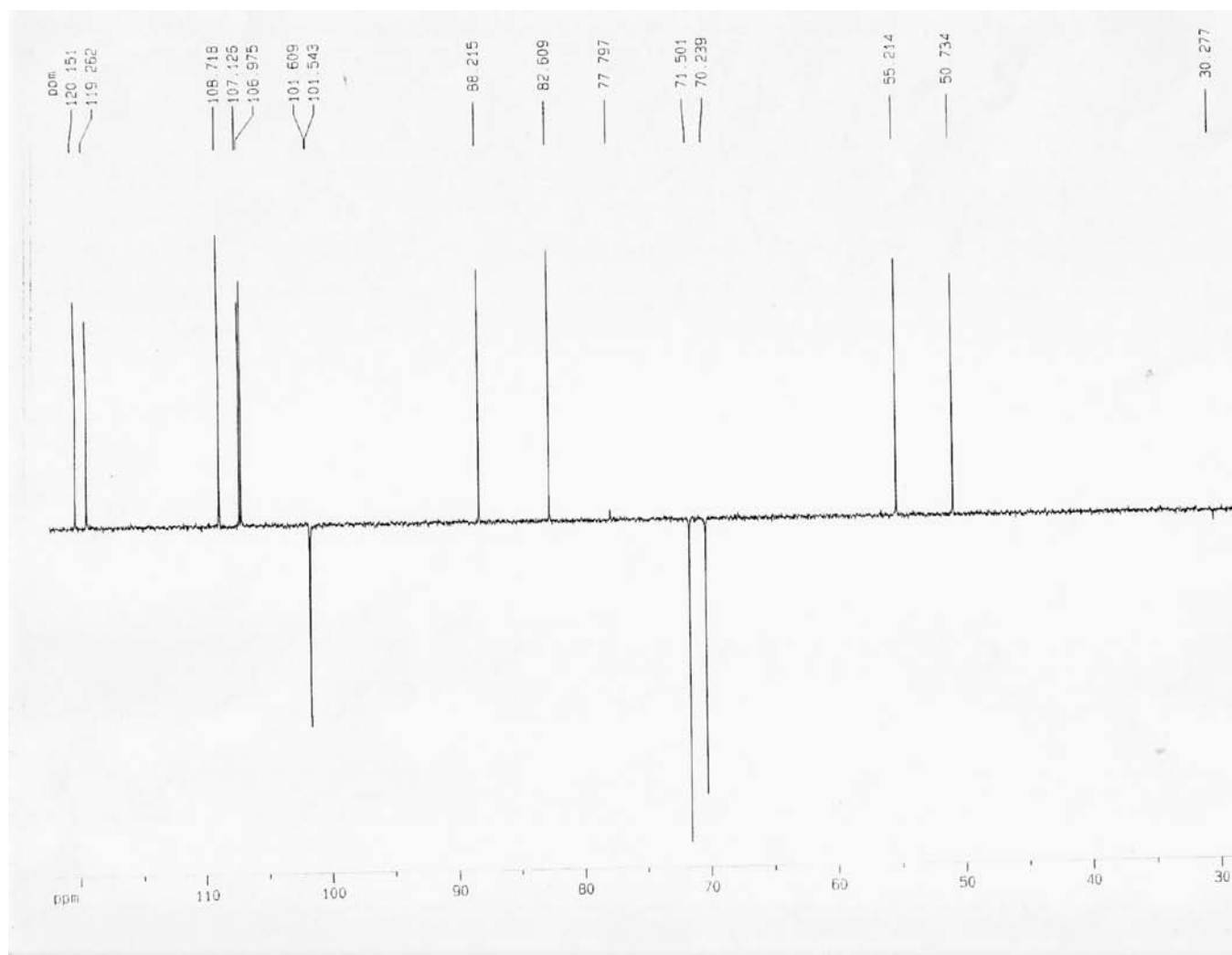


Figura 4S. Subespectro DEPT 135° de **1** (asarinina; 100 MHz; CDCl₃)

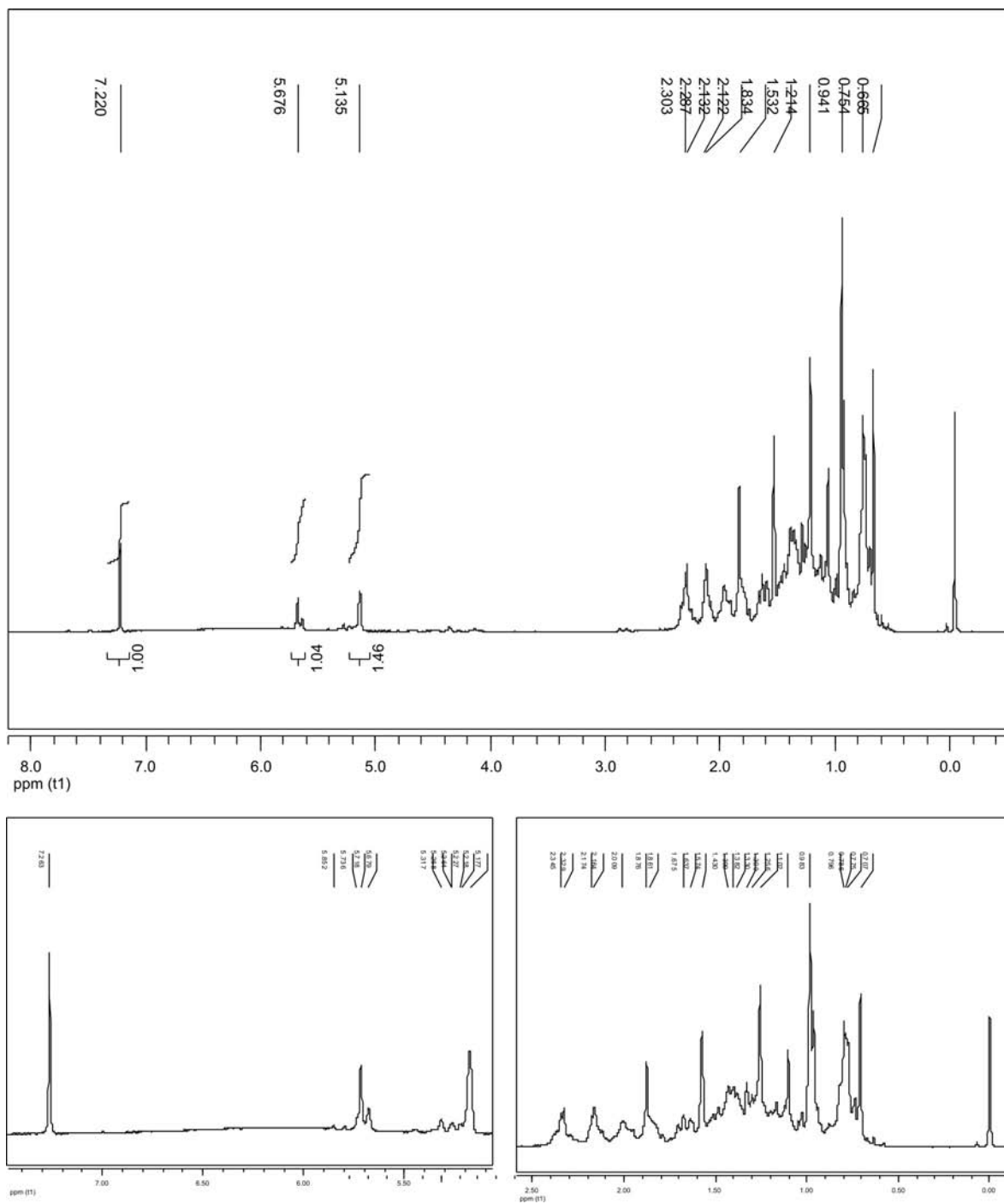


Figura 5S. Espectro de RMN de ¹H (400 MHz; CDCl₃) de mistura dos fitoconstituintes 2 (ácido populifólico) e 3 (ácido 2-oxopopulifólico) (superior) e expansões (inferior)

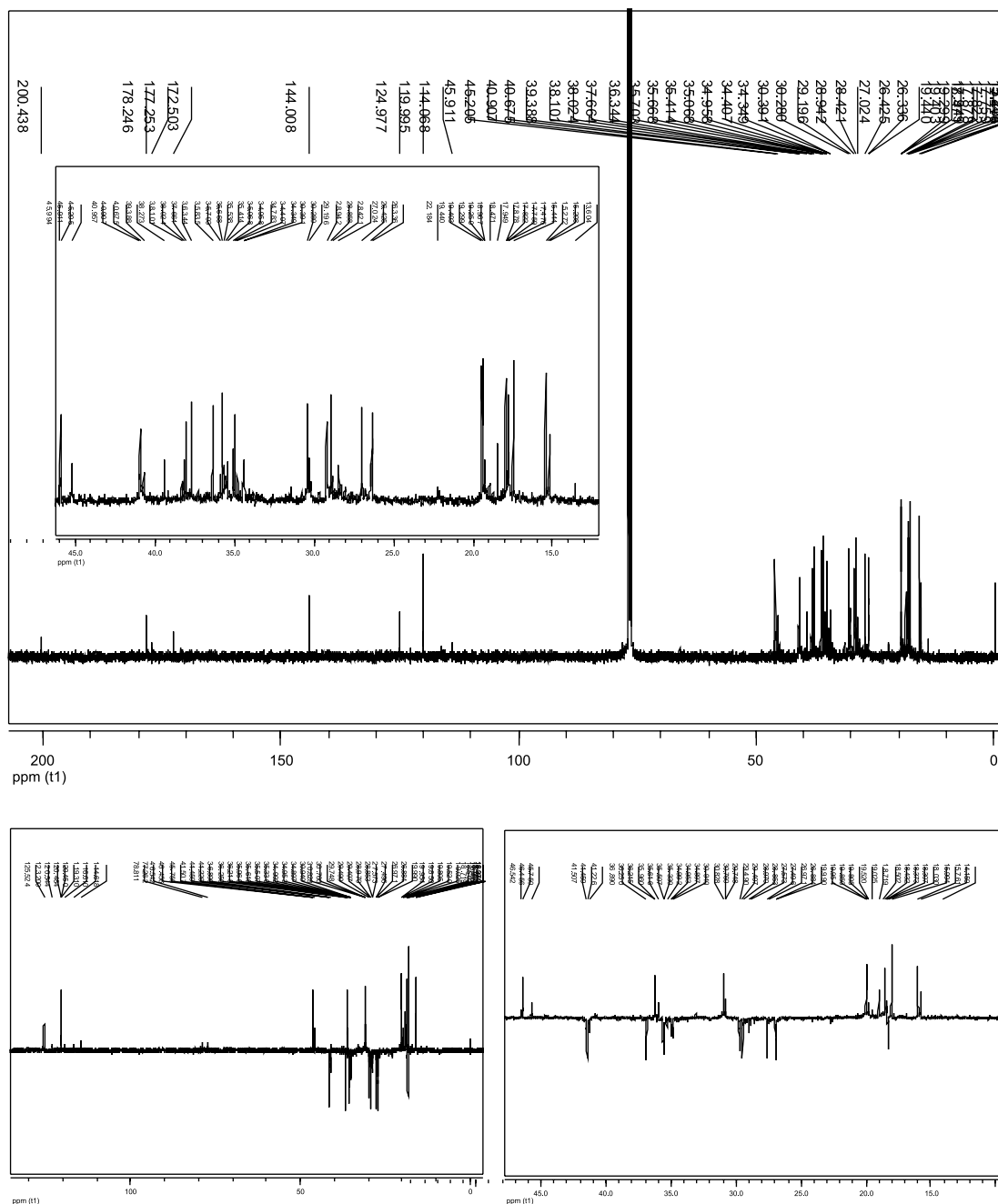


Figura 6S. Espectro de RMN de ^{13}C (superior) e subspectro DEPT 135 $^\circ$ (inferior) de mistura dos fitoconstituintes 2 (ácido populifólico) e 3 (ácido 2-oxopulifólico) (100 MHz; CDCl_3)

Ácido aristolóquico II (**4**): IV ($\nu_{\text{máx}}/\text{cm}^{-1}$) 3200-2600 (banda larga), 3153, 3056, 3026, 2919, 2794, 1682, 1662, 1621, 1509, 1478, 1428, 1375, 1363, 1320, 1263, 1186, 1166, 1039, 1004, 944, 843 e 724; RMN de ^1H (400 MHz; CDCl_3) δ_{H} 10,79 (s; CO_2H), 8,51 (d; $J = 8,0$ Hz; H-5), 7,95 (d; $J = 7,6$ Hz; H-8), 7,62 (s; H-2), 7,59-7,55 (m; H-6 e H-7); 7,12 (s; H-9) e 6,48 (s; $\text{O}-\text{CH}_2-\text{O}$); RMN de ^{13}C (100 MHz;

CDCl_3) δ_{C} 168,0 (CO_2H), 148,7 (C-3), 146,7 (C-4), 135,0 (C-10), 133,9 (C-10a), 128,6 (C-8), 127,4 (C-6), 126,2 (C-5), 125,1 (C-7), 125,0 (C-4b), 123,8 (C-8a), 119,1 (C-1), 110,8 (C-4a), 105,1 (C-2), 104,2 (C-9) e 103,1 ($\text{O}-\text{CH}_2-\text{O}$); CG/EM $t_{\text{R}} = 53,304$ min, m/z 264,1 $[\text{M} - \text{NO}_2]^+$, 263,2 (pico base), 237,2, 236,1, 208,9, 207,8, 178,2, 152,6, 151,2 e 131,1.

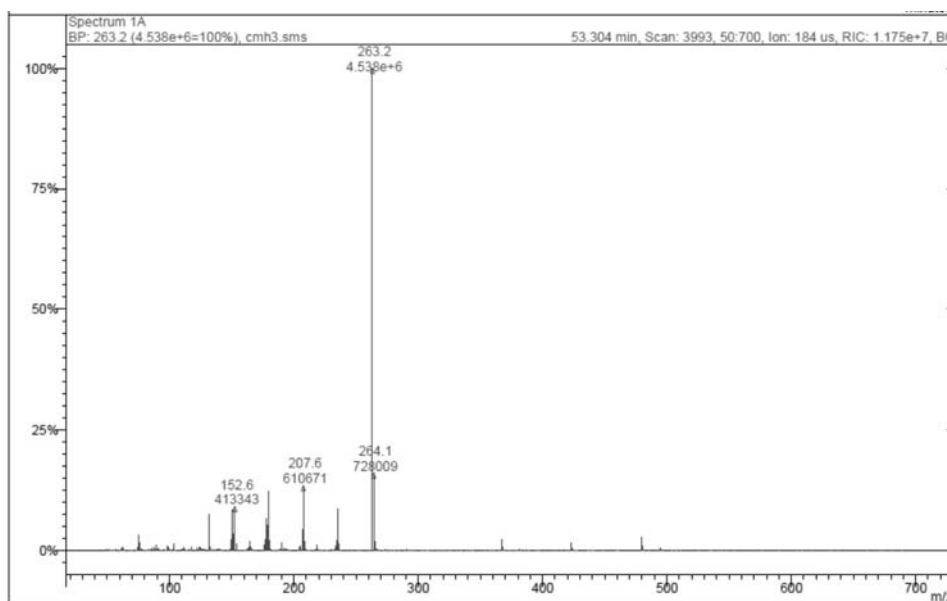


Figura 7S. Espectro de massas de **4** (ácido aristolóquico II)

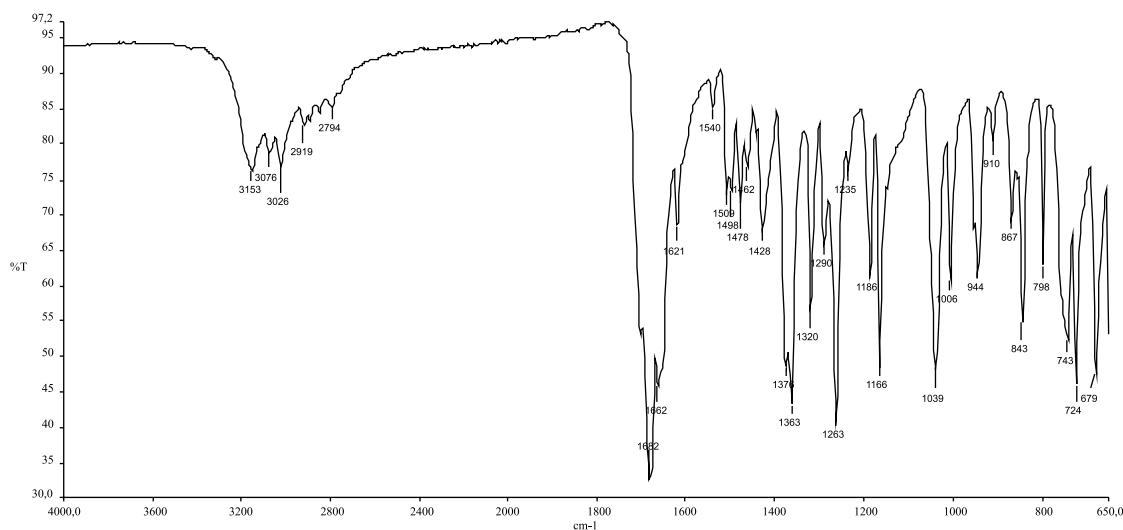


Figura 8S. Espectro de absorção na região do IV de **4** (ácido aristolóquico II; KBr; cm^{-1})

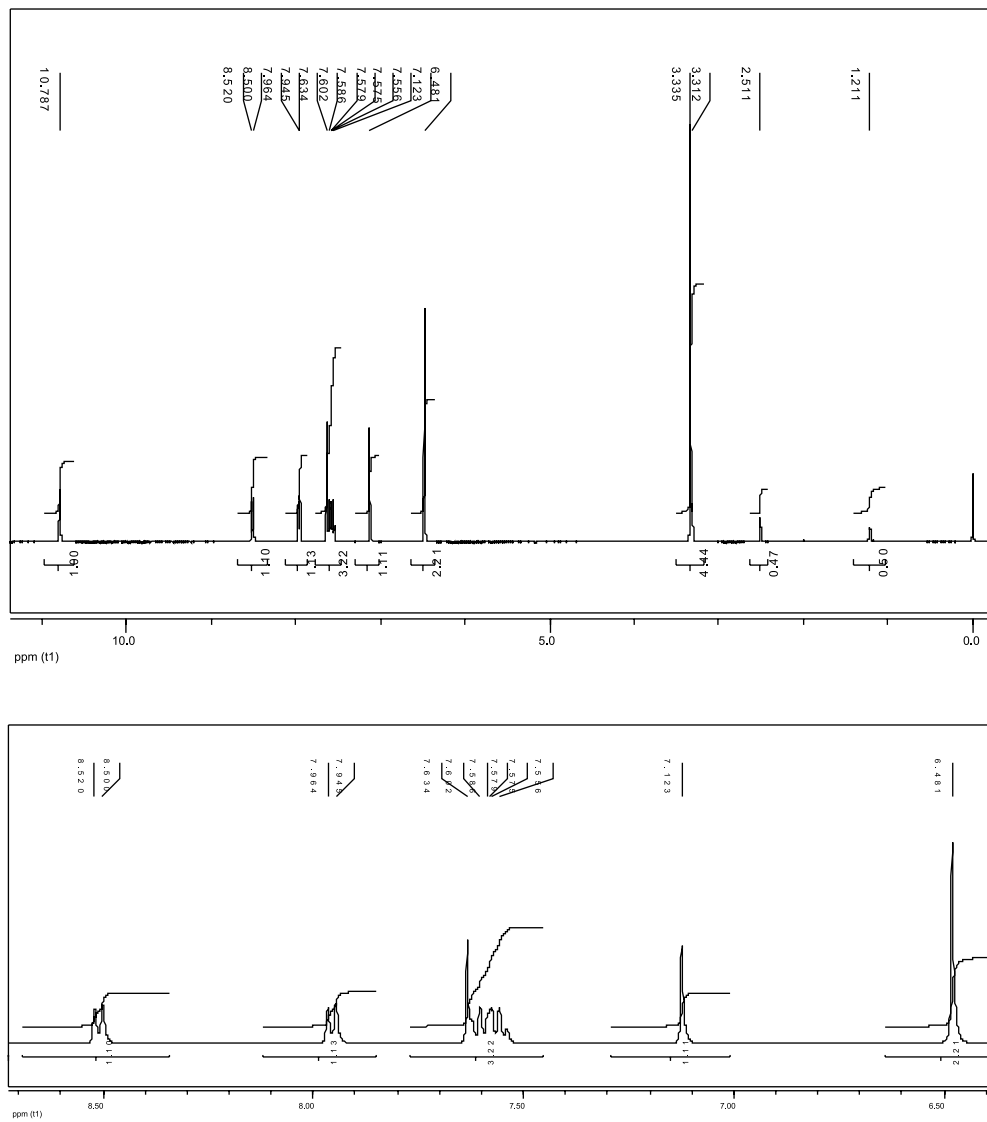


Figura 9S. Espectro de RMN de ^1H de 4 (ácido aristolóquico II) e expansão correspondente (400 MHz; DMSO-d_6)

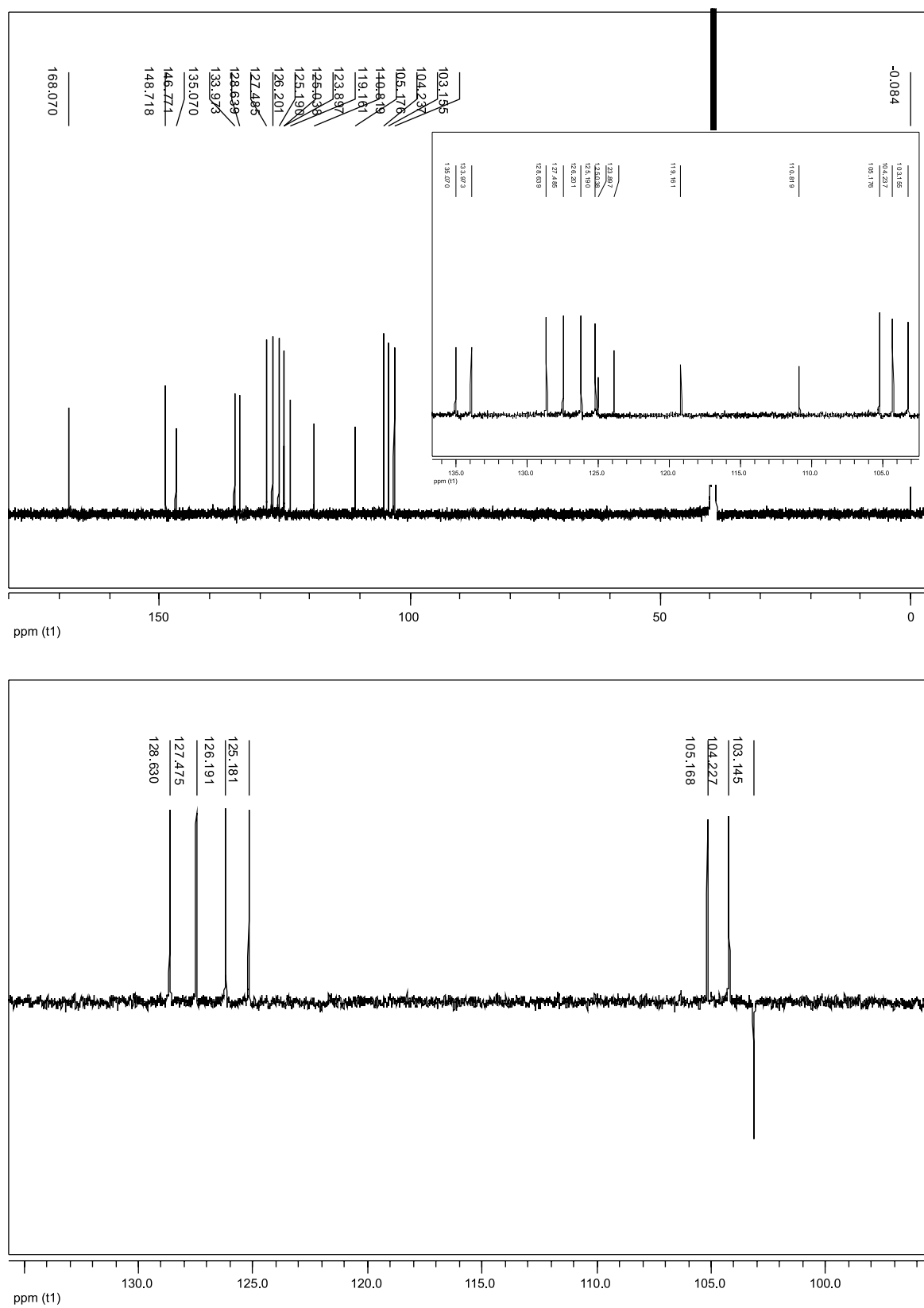


Figura 10S. Espectro de RMN de ^{13}C (superior) e subspectro DEPT 135° (inferior) de 4 (ácido aristolóquico II; 100 MHz; DMSO-d_6)

Aristolactama AII (**5**): IV ($\nu_{\text{máx}}/\text{cm}^{-1}$) 3300-2750 (banda larga), 3255, 3194, 2979, 1699, 1624, 1500, 1422, 1355, 1328, 1292, 1241, 1181, 1153, 1124, 1096, 1056, 1033, 984, 905, 875, 848, 803 e 753; RMN de ^1H (400 MHz; CDCl_3) δ_{H} 10,66 (s; NH), 10,14 (s; OH), 9,15 (d; $J = 8,8$ Hz; H-5), 7,86 (d; $J = 7,6$ Hz; H-8), 7,66 (s; H-2), 7,57-7,50 (m; H-6 e H-7), 7,06 (s; H-9) e 4,07 (s; CH_3O); RMN de

^{13}C (100 MHz; CDCl_3) δ_{C} 168,5 (HNC=O), 151,9 (C-3), 148,6 (C-4), 135,2 (C-10), 134,6 (C-8a), 128,5 (C-8), 126,8 (C-7), 126,6 (C-5), 126,0 (C-4b), 124,8 (C-6), 122,4 (C-10a), 121,7 (C-1), 120,3 (C-4a), 113,3 (C-2), 103,6 (C-9) e 59,2 (CH_3O); CG/EM $t_{\text{R}} = 53,770$ min, m/z 266,3 $[\text{M}+1]^+$, 265,4 $[\text{M}]^+$ (pico base), 250,6, 222,6, 166,6 e 139,6.

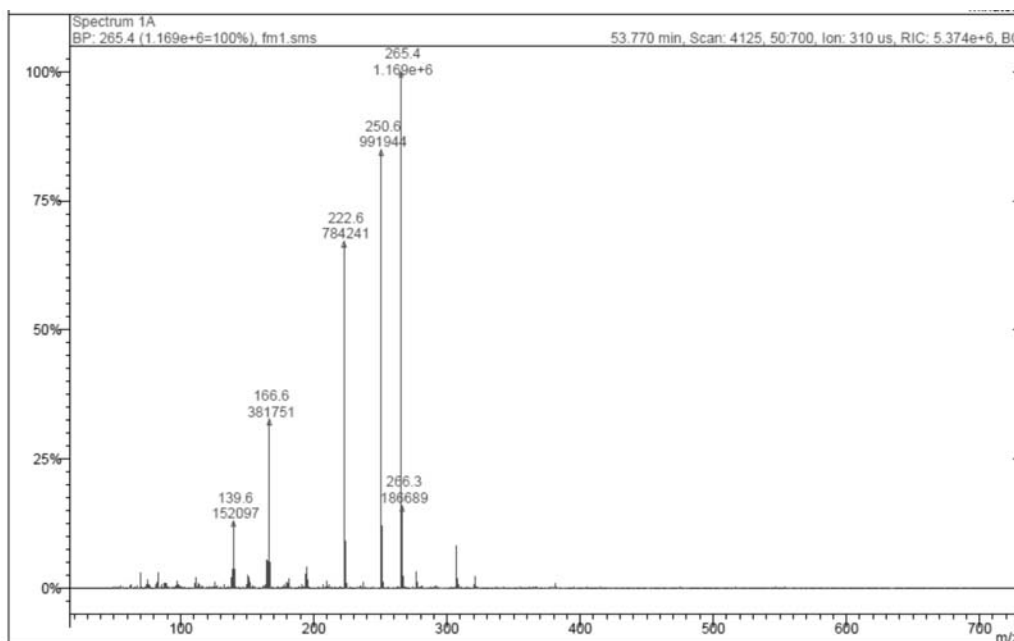


Figura 11S. Espectro de massas de **5** (aristolactama AII)

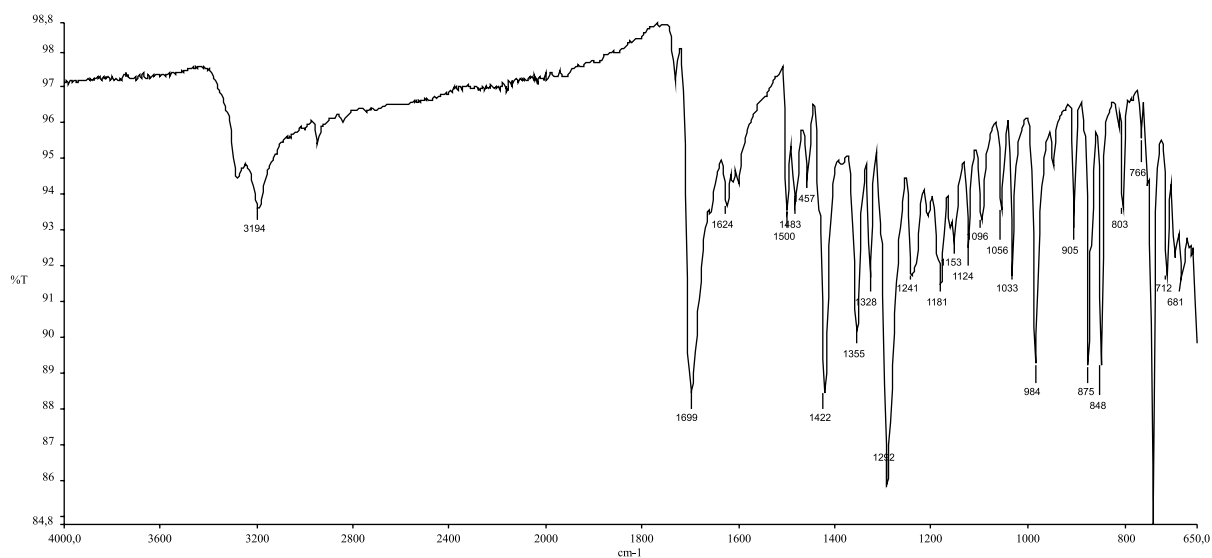


Figura 12S. Espectro de absorção na região do IV de **5** (aristolactama AII; KBr; cm^{-1})

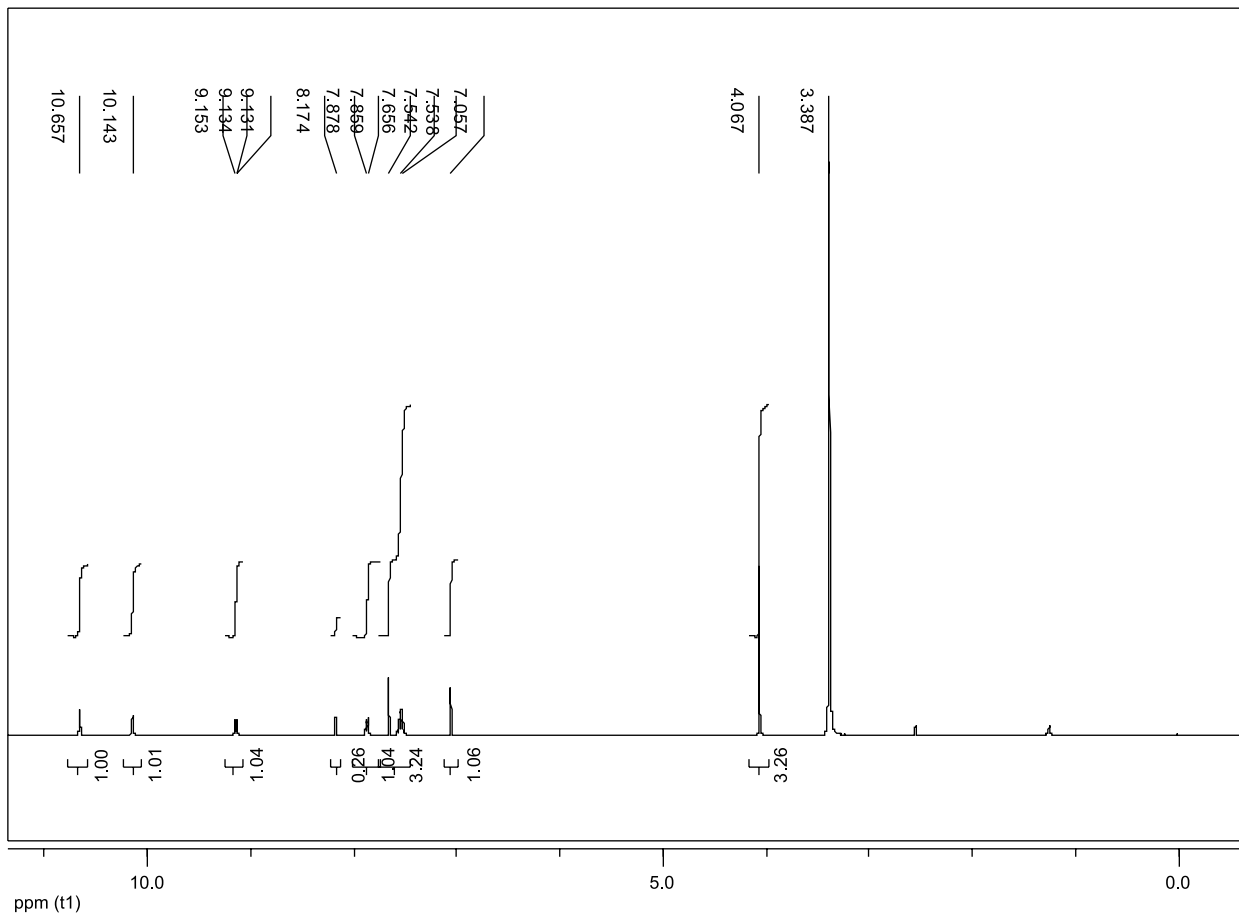


Figura 13S. Espectro de RMN de ^1H de 5 (aristolactama AII; 400 MHz; DMSO-d_6)

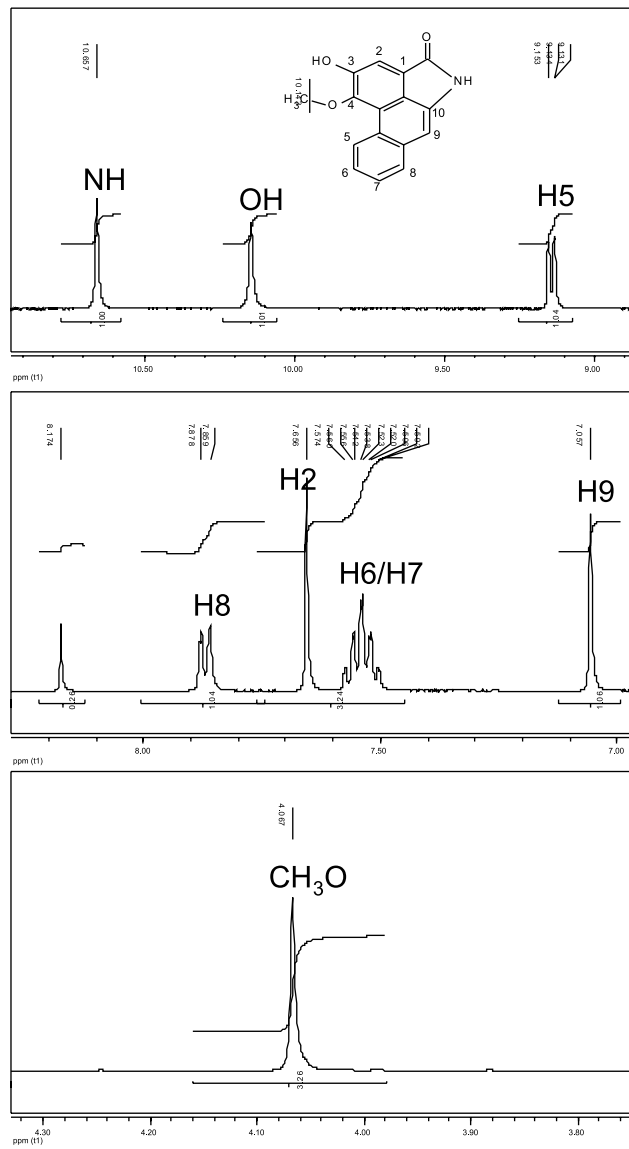


Figura 14S. Expansões do espectro de RMN de ^1H de 5 (aristolactama AII; 400 MHz; $\text{DMSO-}d_6$)

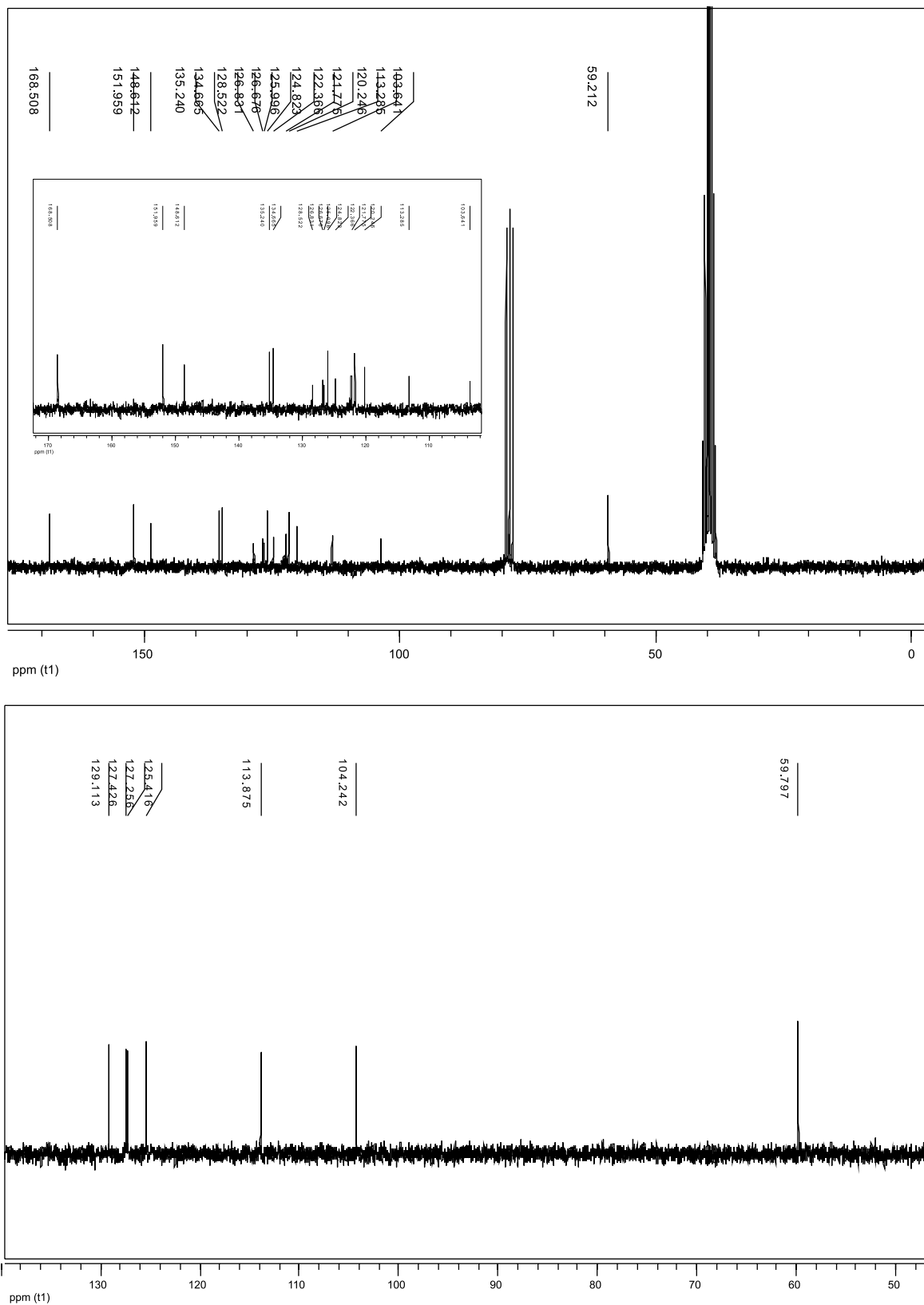


Figura 15S. Espectro de RMN de ¹³C (superior) e subspectro DEPT 135° (inferior) de 5 (aristolactama AII; 100 MHz; DMSO-d₆)

Aristolactama A1a (**6**): IV ($\nu_{\text{máx}}/\text{cm}^{-1}$) 3300-2750 (banda larga), 3255, 3197, 2977, 1690, 1619, 1503, 1422, 1355, 1328, 1292, 1240, 1181, 1153, 1124, 1104, 1055, 1037, 984, 901, 868, 846, 803 e 755; RMN de ^1H (400 MHz; CDCl_3) δ_{H} 10,49 (s; NH), 9,89 (s; C-3-OH), 9,10 (d, $J=9,2$ Hz; H-5), 7,90 (s; C-8-OH), 7,80 (d, $J=7,2$ Hz; H-7),

7,67 (s; H-2), 7,51 (dd, $J=9,2$ e $7,2$ Hz; H-6), 7,01 (s; H-9) e 4,07 (s; CH_3O); RMN de ^{13}C (100 MHz; CDCl_3) δ_{C} 167,6 (C=O), 150,7 (C-3), 147,4 (C-4), 134,1 (C-8a e C-10), 133,4 (C-8), 127,2 (C-7), 125,6 (C-5), 124,9 (C-4b), 123,6 (C-6), 121,4 (C-10a), 120,7 (C-1), 119,1 (C-4a), 112,2 (C-2), 102,5 (C-9) e 58,1 (CH_3O).

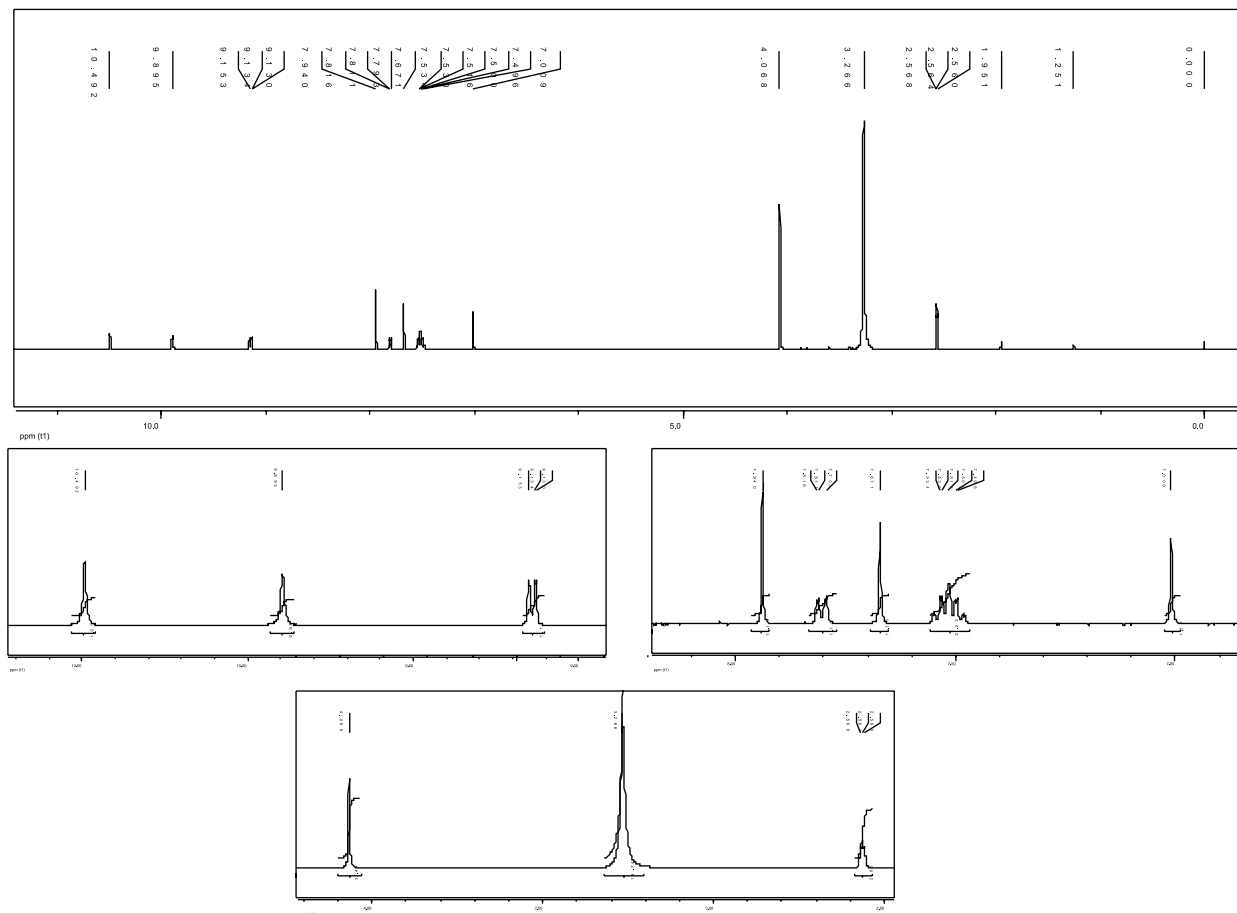


Figura 16S. Espectro de RMN de ^1H de **6** e expansões correspondentes (aristolactama A1a; 400 MHz; CDCl_3)

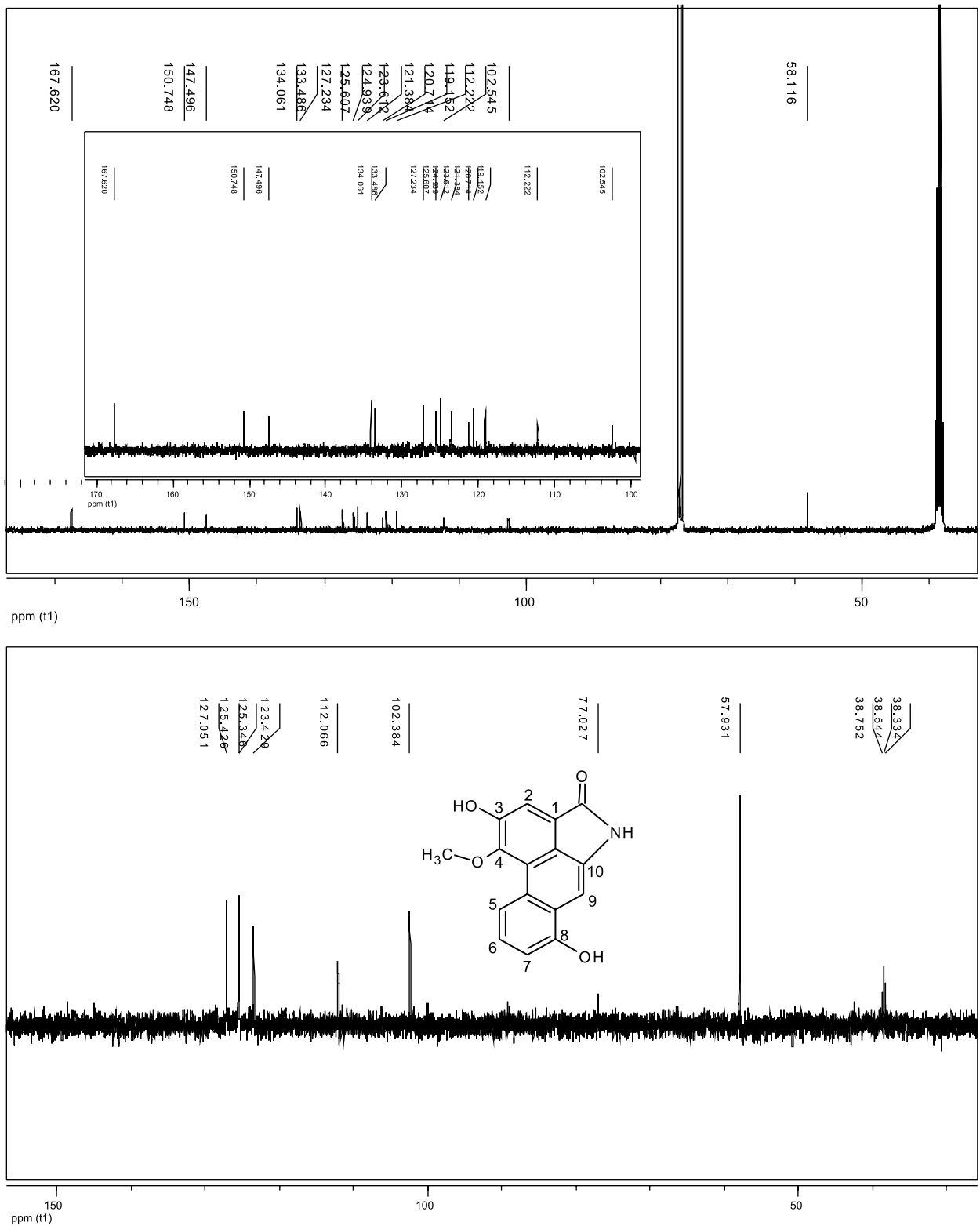


Figura 17S. Espectro de RMN de ^{13}C (superior) e subspectro DEPT 135° (inferior) de 6 e expansões correspondentes (aristolactama A1a; 100 MHz; CDCl_3)

β -Cubebina (**7**): p.f. 122,7–128,0 °C; IV ($\nu_{\text{máx}}/\text{cm}^{-1}$) 3332 (banda larga), 2948, 2926, 2897, 2781, 1608, 1495, 1484, 1439, 1365, 1356, 1238, 1185, 1118, 1096, 1037, 1006, 922 e 807; RMN de ^1H (400 MHz; CDCl_3) δ_{H} 6,67 (s; H-2'), 6,66 (m; H-5 e H-5'), 6,62 (m; H-6'), 6,56 (m; H-2), 6,52 (m; H-6), 5,87 (s; O-CH₂-O), 5,85 (s; O-CH₂-O'), 5,15 (d, $J = 13,2$ Hz; H-9), 4,03 (dd, $J = 8,4$ e $4,3$ Hz; H-9' β), 3,50 (dd, $J = 8,4$ e $6,1$; H-9' α), 2,90 (m; H-7a), 2,86 (sl; OH), 2,70 (m;

H-7'a), 2,62 (m; H-7b), 2,50 (m; H-7'b), 2,37 (m; H-8') e 1,93 (m; H-8); RMN de ^{13}C (100 MHz; CDCl_3) δ_{C} 147,7 (C-3), 147,5 (C-3'), 145,9 (C-4'), 145,7 (C-4), 134,5 (C-1'), 133,8 (C-1), 121,6 (C-6'), 121,3 (C-6), 109,3 (C-2'), 108,9 (C-2), 108,2 (C-5), 108,1 (C-5'), 108,8 (O-CH₂-O e O-CH₂-O'), 98,8 (C-9), 72,5 (C-9'), 51,9 (C-8), 42,9 (C-8'), 38,8 (C-7') e 33,6 (C-7).

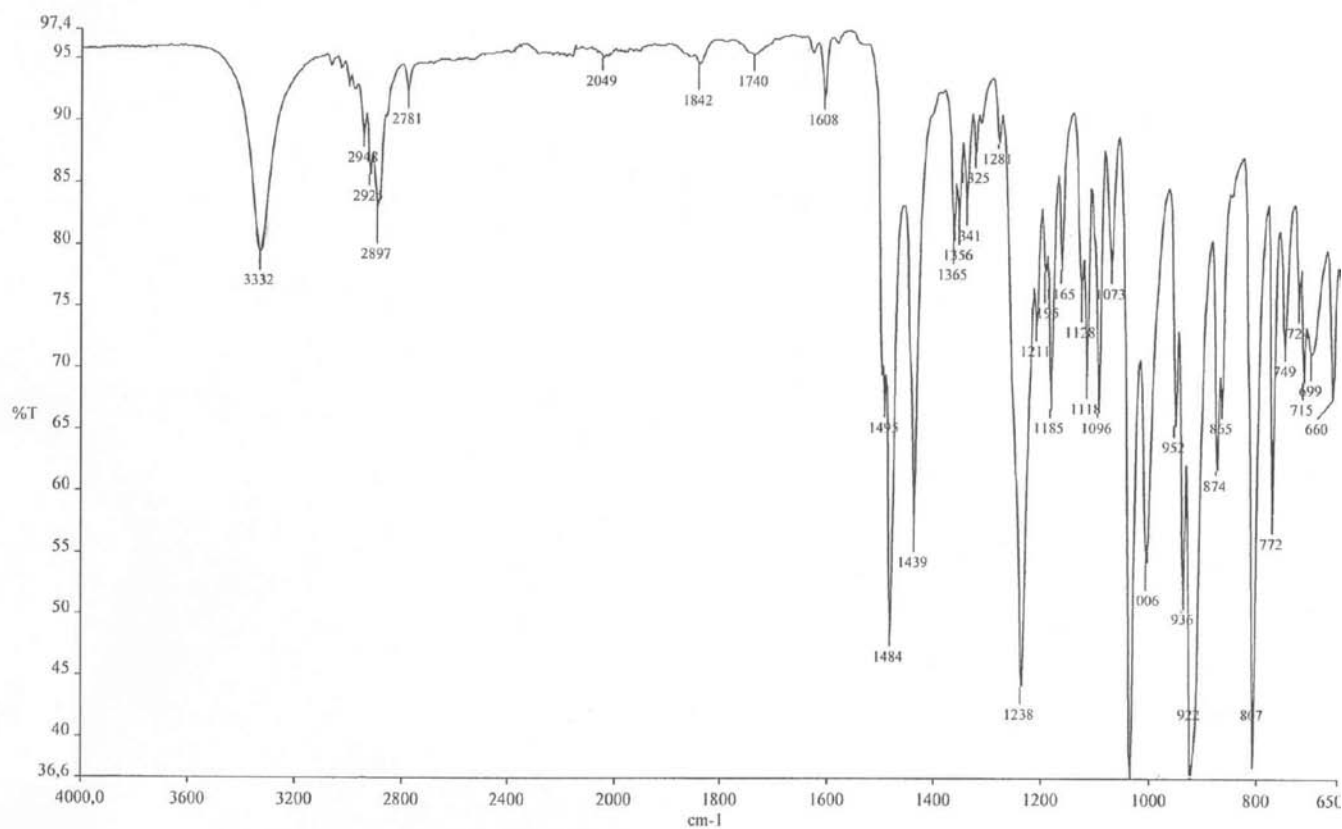
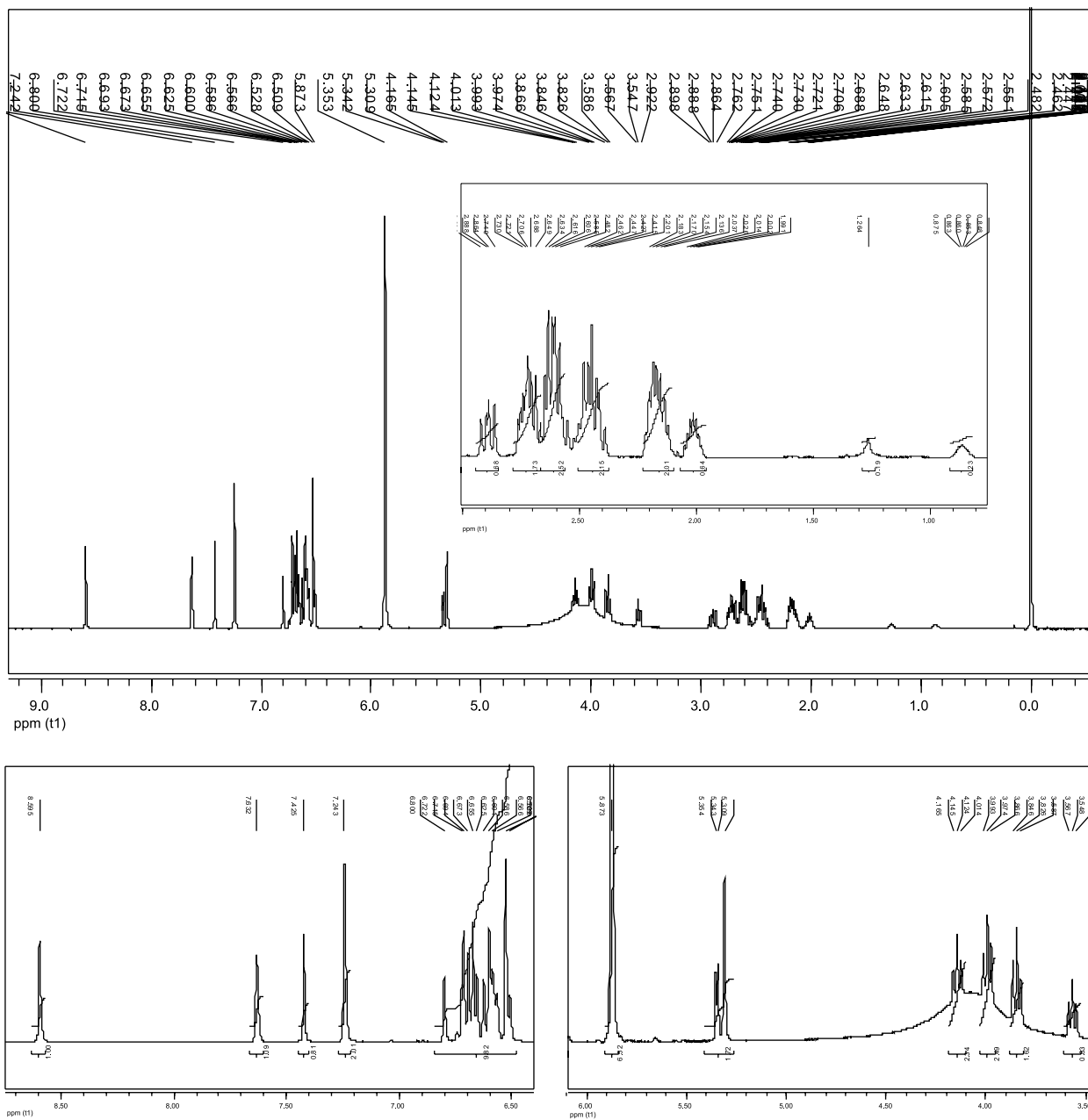


Figura 18S. Espectro de absorção na região do IV de **7** (β -cubebina; KBr; cm^{-1})



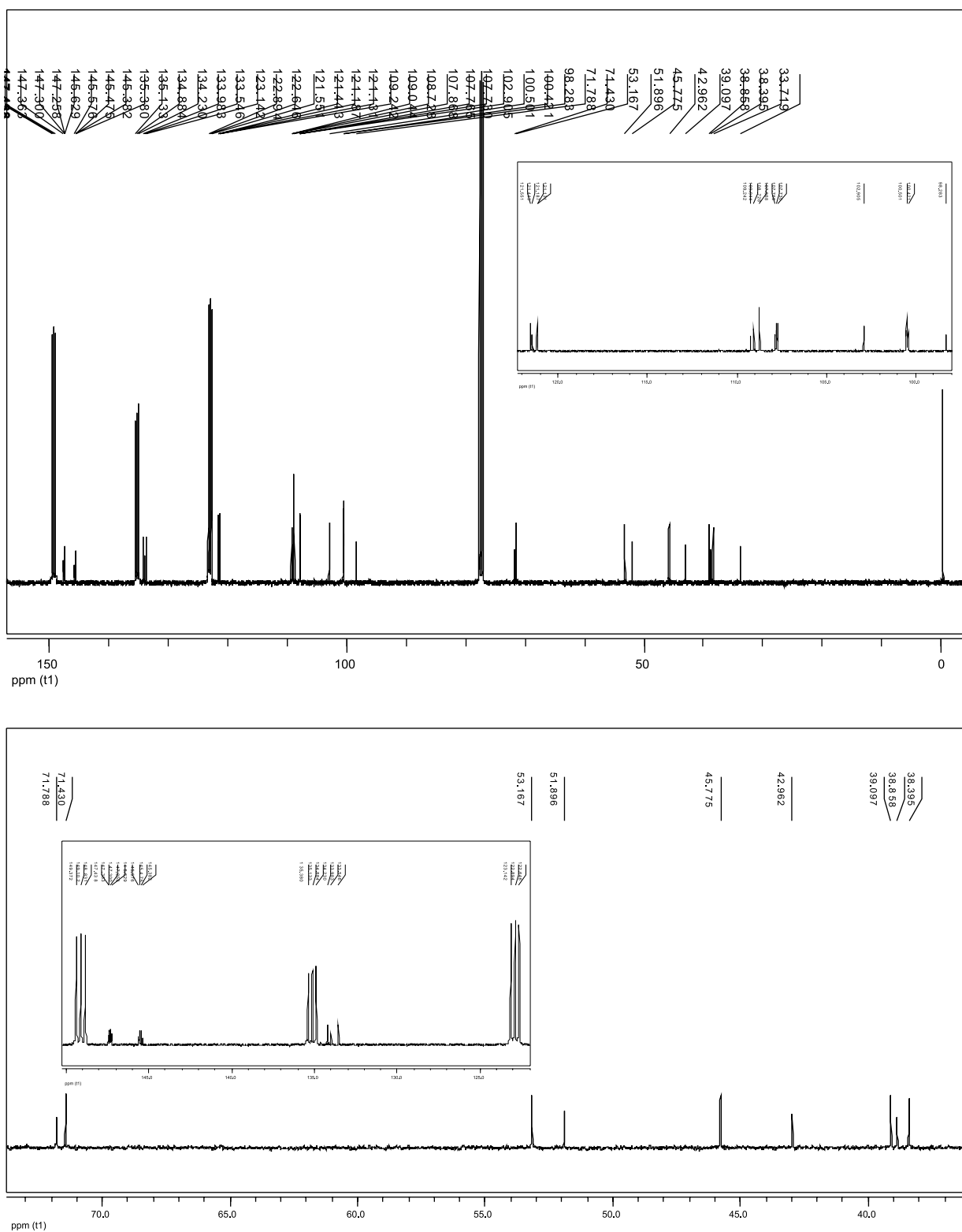


Figura 20S. Espectro de RMN de ^{13}C de 7 e expansões (β -cubebina; 100 MHz; CDCl_3 com gotas de piridina)

Ácido aristolóquico I (**8**): IV ($\nu_{\text{máx}}/\text{cm}^{-1}$) 3200-2600 (banda larga), 1684, 1622, 1593, 1524, 1504, 1468, 1448, 1416, 1370, 1345, 1265, 1247, 1147, 1115, 1039, 997, 945, 921, 900, 803 e 722; RMN de ^1H (400 MHz; CDCl_3) δ_{H} 13,32 (sl; CO_2H), 8,61 (d, $J = 8,4$ Hz; H-5), 8,56 (s; H-9), 7,83 (t, $J = 8,4$ Hz; H-6), 7,80 (s; H-2), 7,34 (d, $J = 8,4$ Hz; H-7), 6,48 (s; $\text{O}-\text{CH}_2-\text{O}$) e 4,05 (s; OCH_3); RMN de ^{13}C (100

MHz; CDCl_3) δ_{C} 167,5 (CO_2H), 156,1 (C-8), 146,4 (C-10), 145,9 (C-3), 145,6 (C-4), 131,4 (C-6), 129,7 (C-10a), 124,0 (C-4a), 119,4 (C-9), 118,7 (C-8a), 118,3 (C-5), 117,1 (C-4b), 116,7 (C-1), 112,0 (C-2), 108,7 (C-7), 102,8 ($\text{O}-\text{CH}_2-\text{O}$) e 56,1 (OCH_3); CG/EM $t_{\text{R}} = 59,980$ min, m/z 294,3 [M] $^+$, 280,8 (pico base), 252,4, 251,2, 224,3, 195,8, 163,3, 139,6 e 137,8.

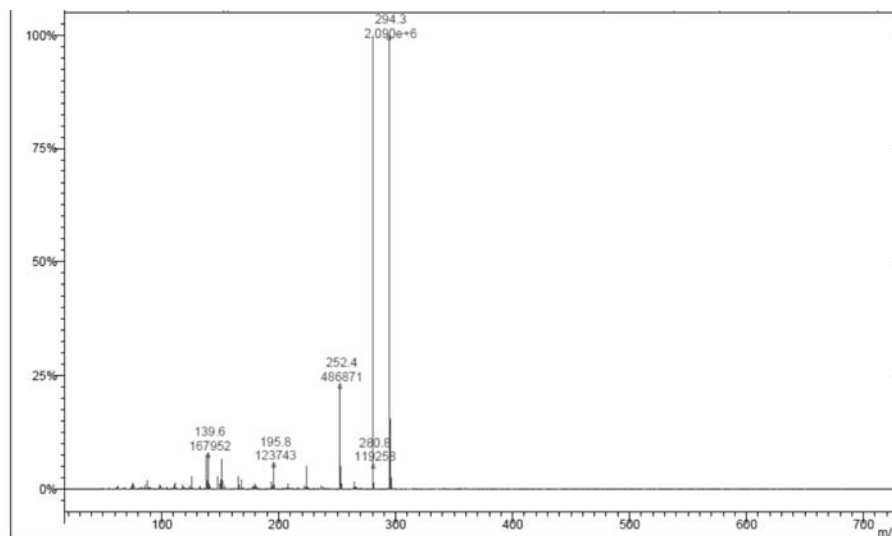


Figura 21S. Espectro de massas de **8** (ácido aristolóquico I)

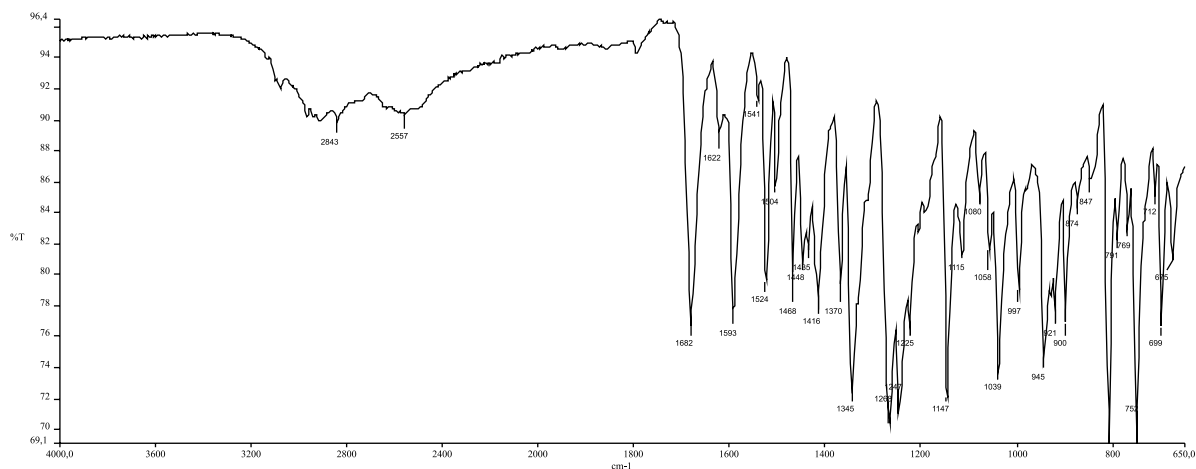


Figura 22S. Espectro de absorção na região do IV de **8** (ácido aristolóquico I; KBr; cm^{-1})

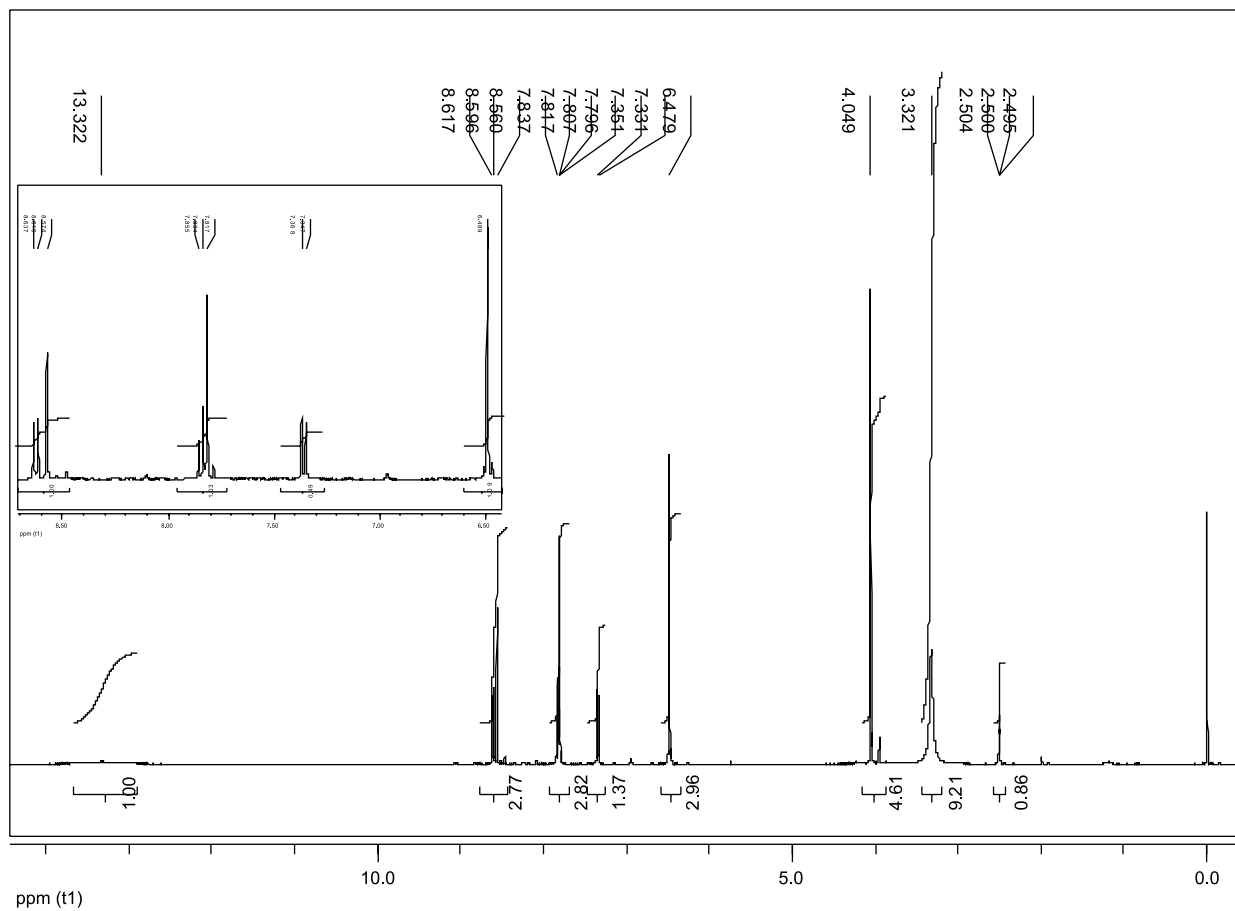


Figura 23S. Espectro de RMN de ^1H de 8 (ácido aristolóquico I; 400 MHz; DMSO-d_6)

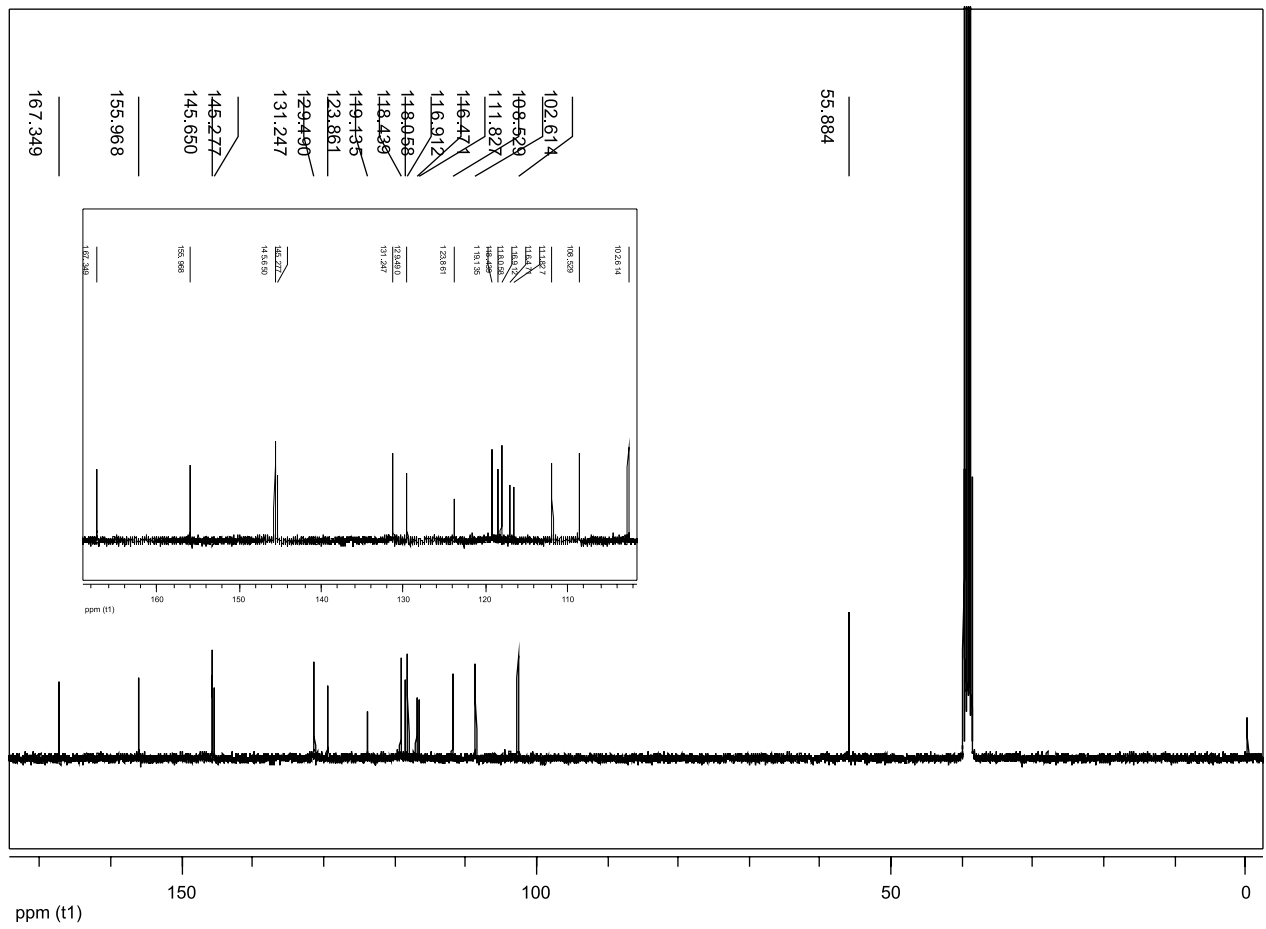


Figura 24S. Espectro de RMN de ^{13}C de **8** (ácido aristolóquico I; 100 MHz; $DMSO-d_6$)

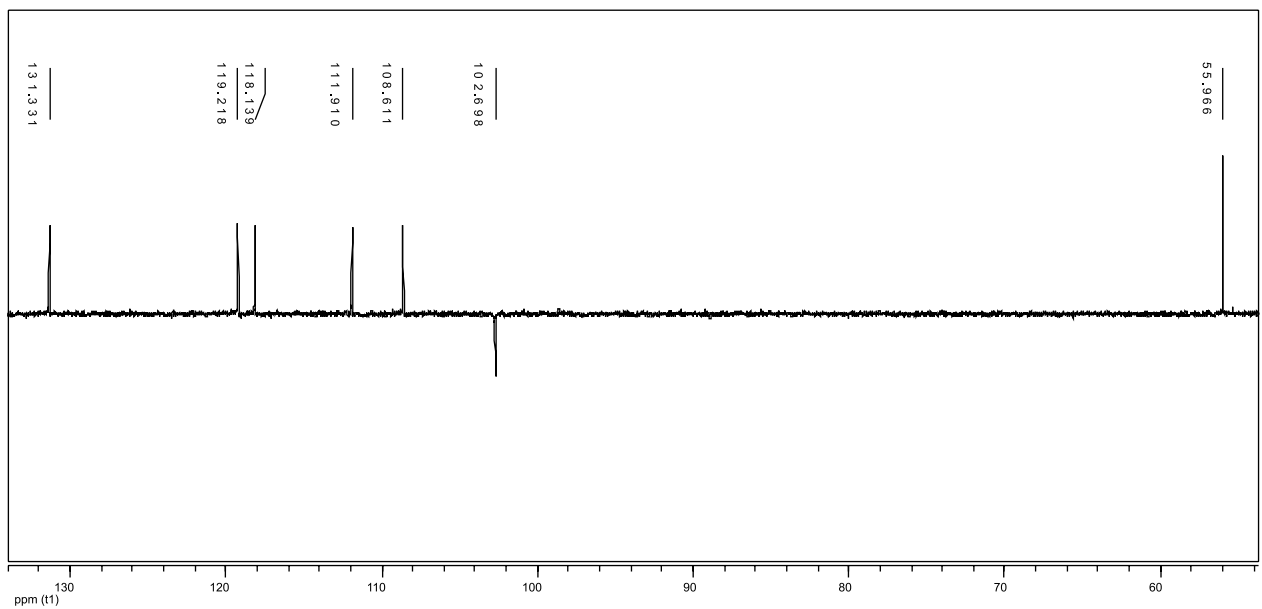


Figura 25S. Subespectro DEPT 135° de **8** (ácido aristolóquico I; 100 MHz; $DMSO-d_6$)

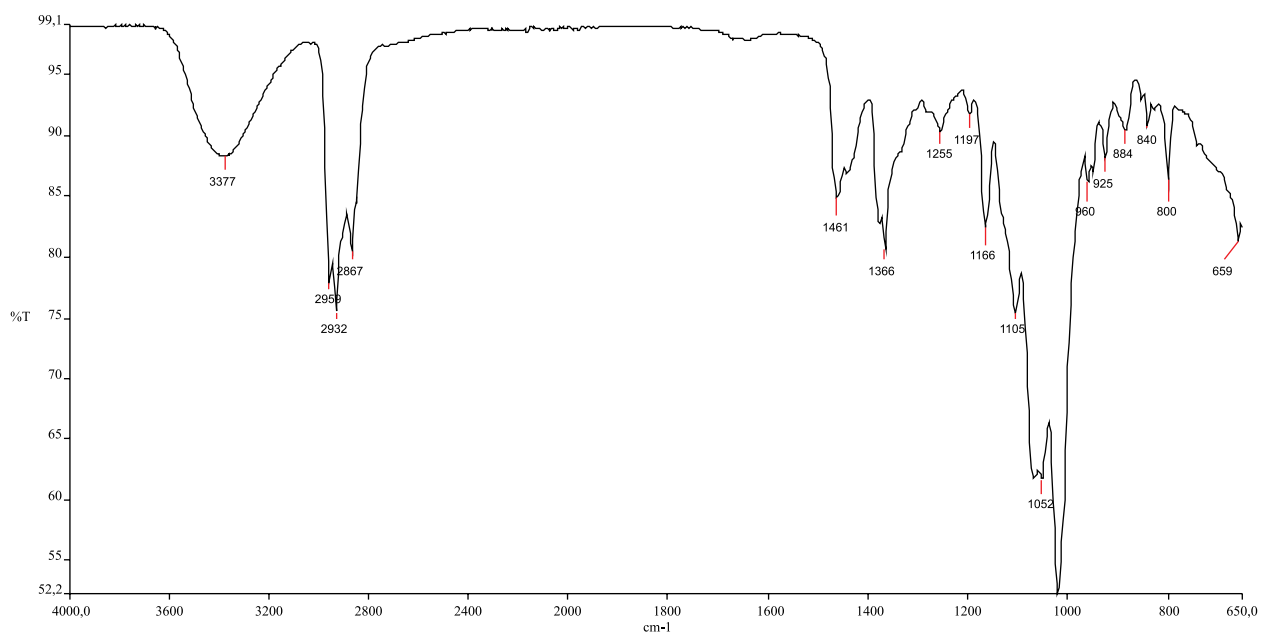


Figura 26S. Espectro de absorção na região do IV de **9** (sitosterol-3-O- β -D-glicopiranosídeo; KBr; cm^{-1})

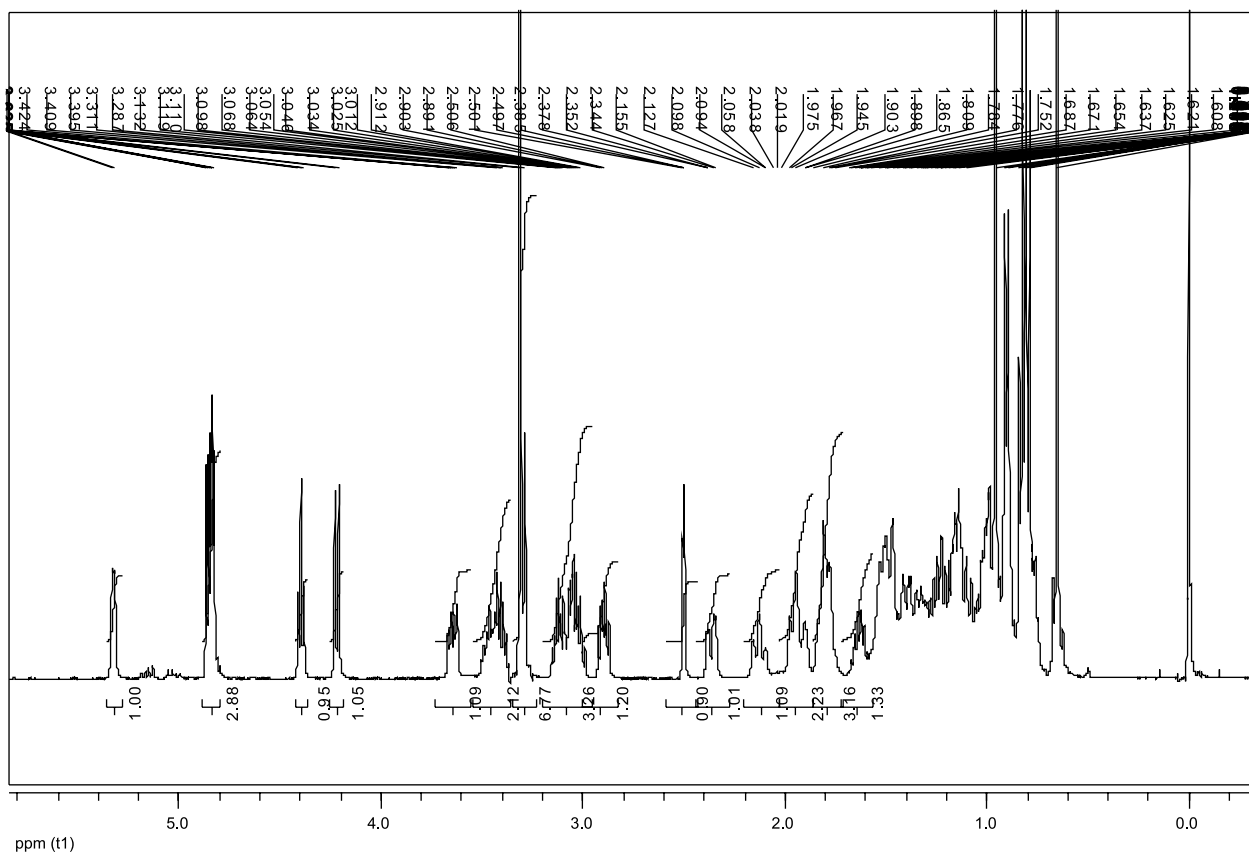


Figura 27S. Espectro de RMN de ^1H de **9** (sitosterol-3-O- β -D-glicopiranosídeo; 400 MHz; $\text{DMSO}-d_6$)

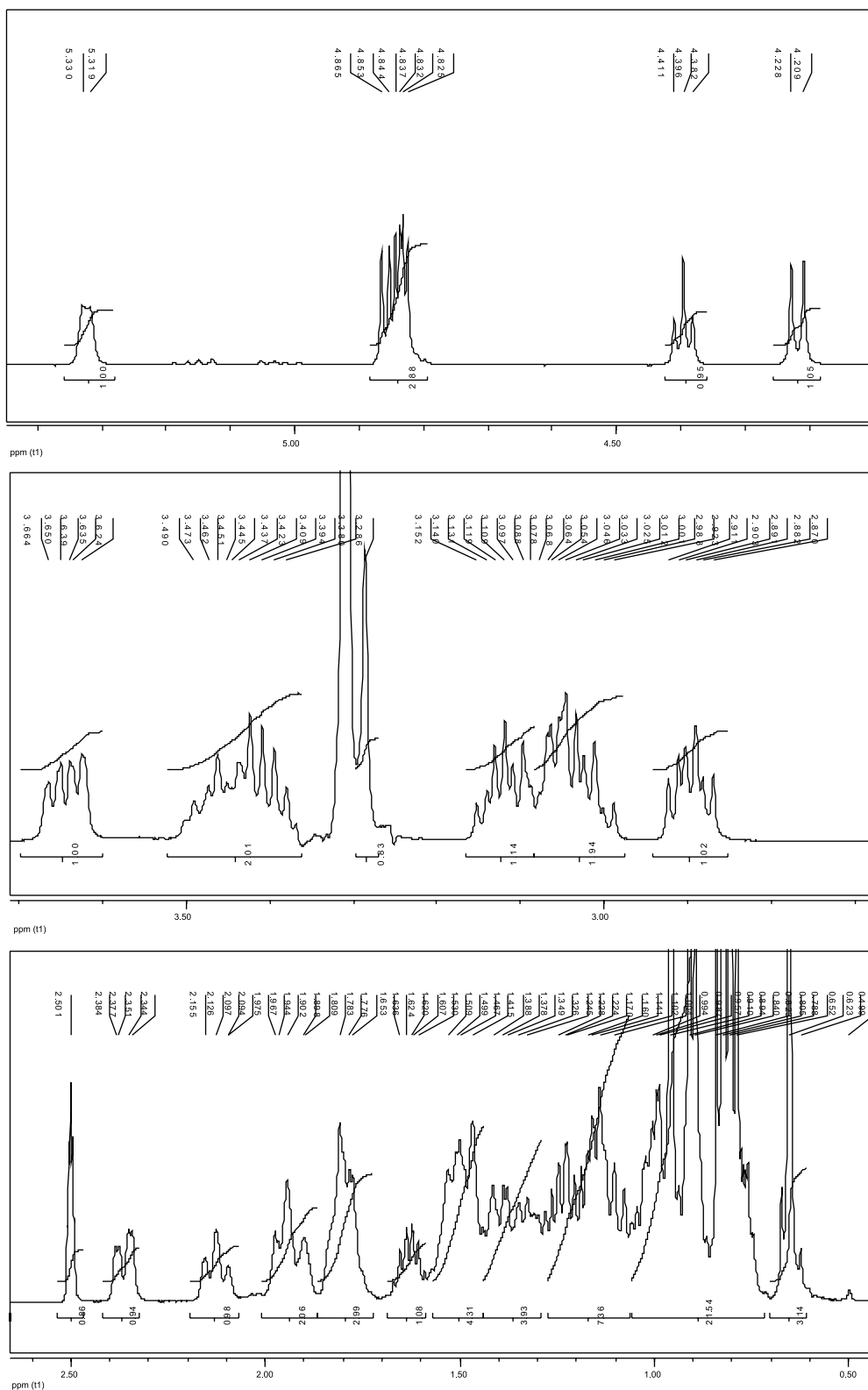


Figura 28S. Expansões do espectro de RMN de ¹H de 9 (sitosterol-3-O-β-D-glicopiranosídeo; 400 MHz; DMSO-d₆)

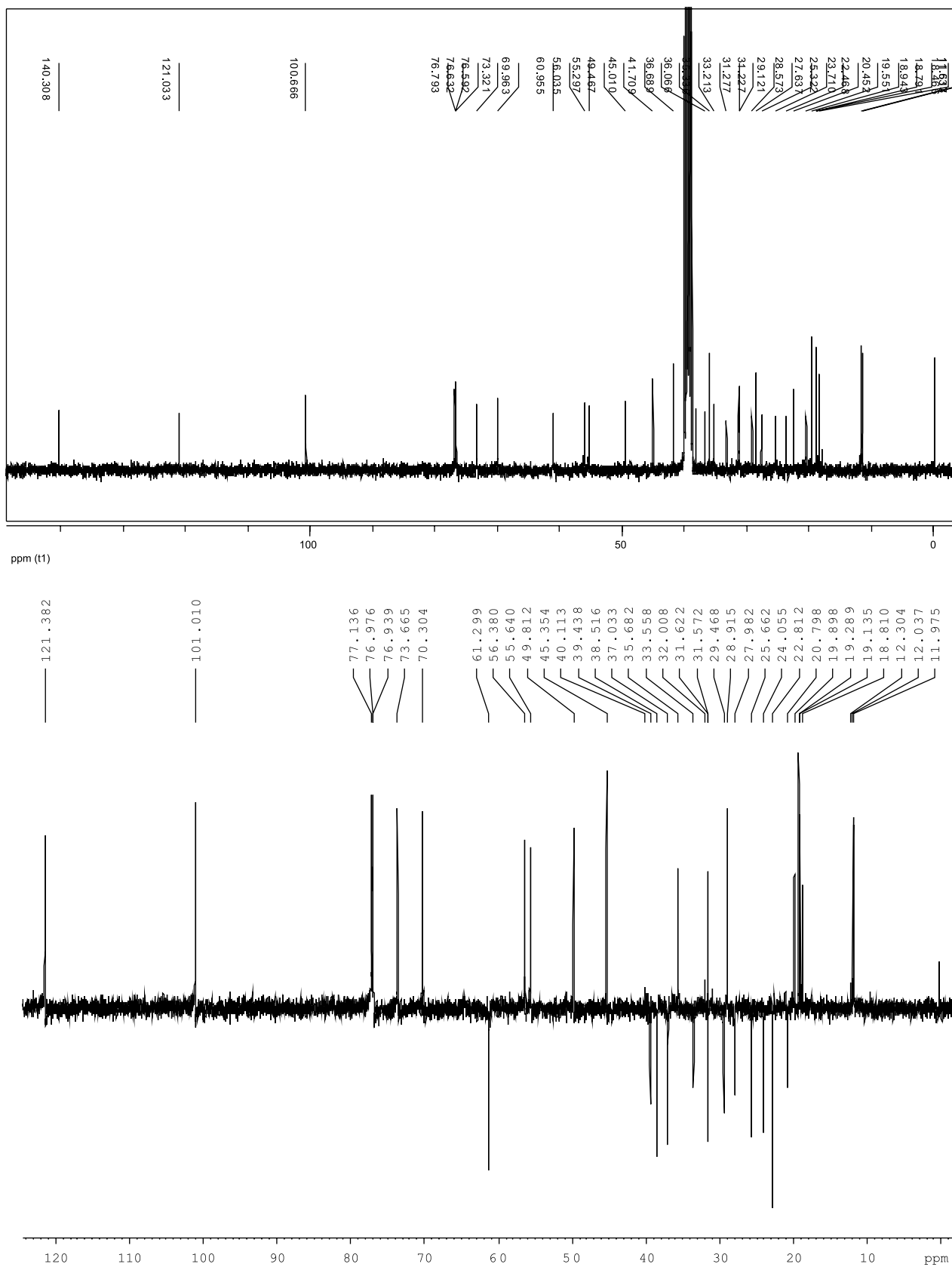


Figura 29S. Espectro de RMN de ^{13}C (superior) e subspectro DEPT 135° (inferior) de **9** (sitosterol-3-O- β -D-glicopiranosídeo; 100 MHz; DMSO-d_6)

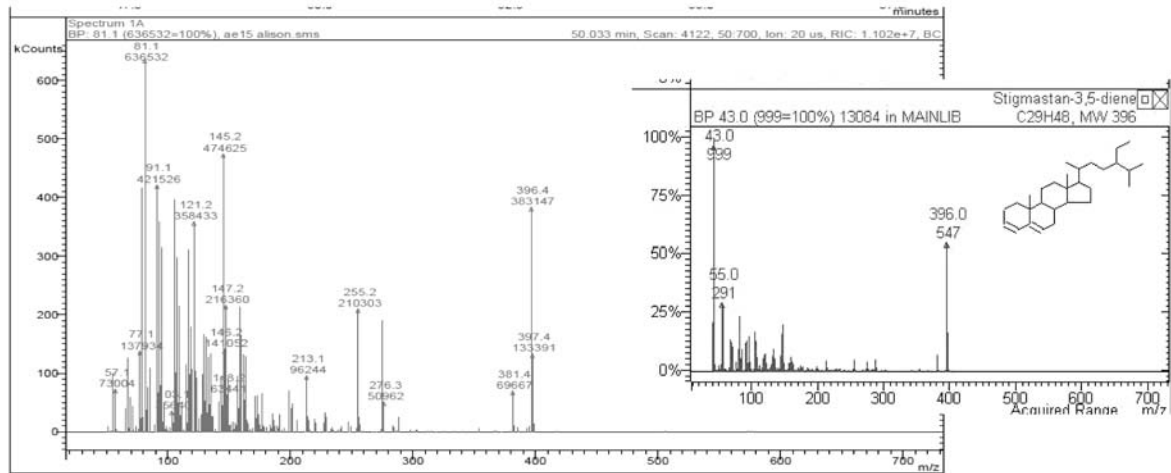


Figura 30S. Espectro de massas de 10 (estigmastan-3,5-dieno) e espectro de massas correspondente do banco de dados NIST (2005).