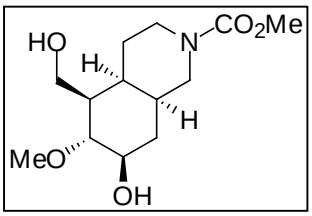
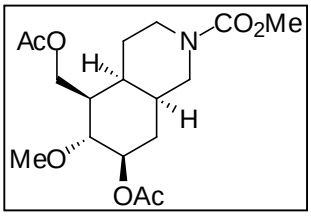
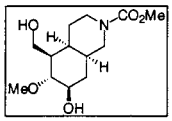


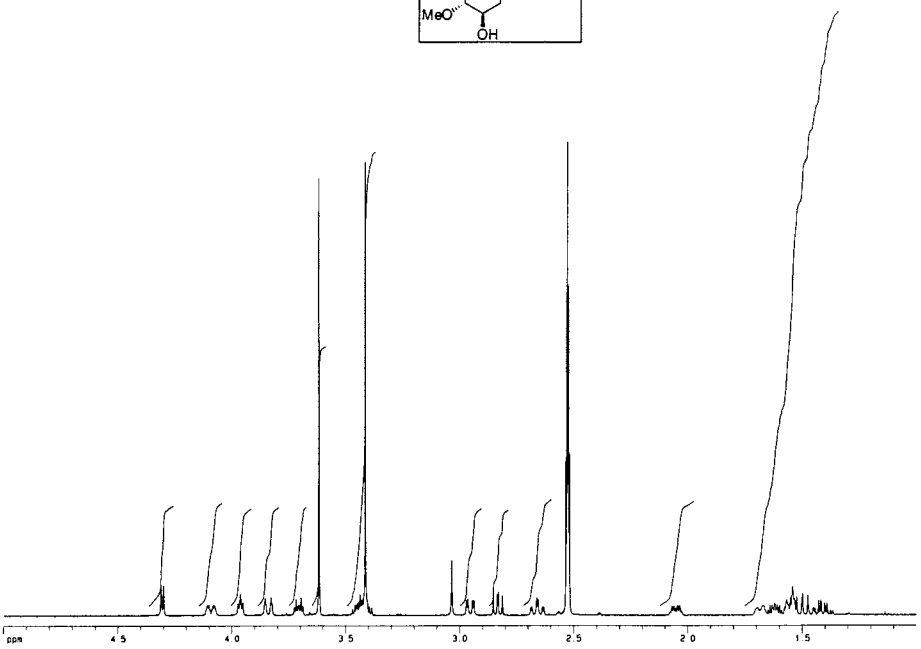
Diol 13: To a solution of **12** (0.1 g, 0.23 mmol) in MeOH (4 mL) was added 10% Pd-C (5 mg). The solution was purged with N_2 and then placed under a H_2 atmosphere. The reaction mixture was stirred for 6 h then filtered through celite and concentrated. The residue was chromatographed (10% MeOH / CH_2Cl_2) to afford 63 mg (100%) of diol **13** as a colorless oil. ^{1}H NMR (DMSO @ 363 K) 4.31 (d, *J* = 5.4 Hz, 1 H), 4.09 (ddt, *J* = 13.1, 4.6, 2.3 Hz, 1 H), 3.96 (t, *J* = 5.1 Hz, 1 H), 3.84 (d, *J* = 13.2 Hz, 1 H), 3.71 (dt, *J* = 10.6, 4.3 Hz, 1 H), 3.62 (s, 3 H), 3.47-3.38 (m, 2 H), 3.41 (s, 3 H), 2.95 (dd, *J* = 13.1, 3.3 Hz, 1 H), 2.83 (dd, *J* = 11.1, 8.8 Hz, 1 H), 2.66 (td, *J* = 13.0, 3.2 Hz, 1 H), 2.04-2.02 (m, 1 H), 1.71-1.65 (m, 1 H), 1.65-1.59 (m, 1 H), 1.58-1.51 (m, 2 H), 1.50 (dd, *J* = 13.0, 11.3 Hz, 1 H), 1.41 (qd, *J* = 12.9, 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 156.2, 85.2, 75.0, 63.7, 60.4, 52.5, 48.6, 46.4, 44.2, 37.1, 34.6, 31.9, 21.4; IR (NaCl, neat) cm-1 3429, 2933, 2894, 1681, 1101; HRMS(CI) calculated for $C_{13}H_{24}NO_5$ (MH^+) 274.1654, observed 274.1656.



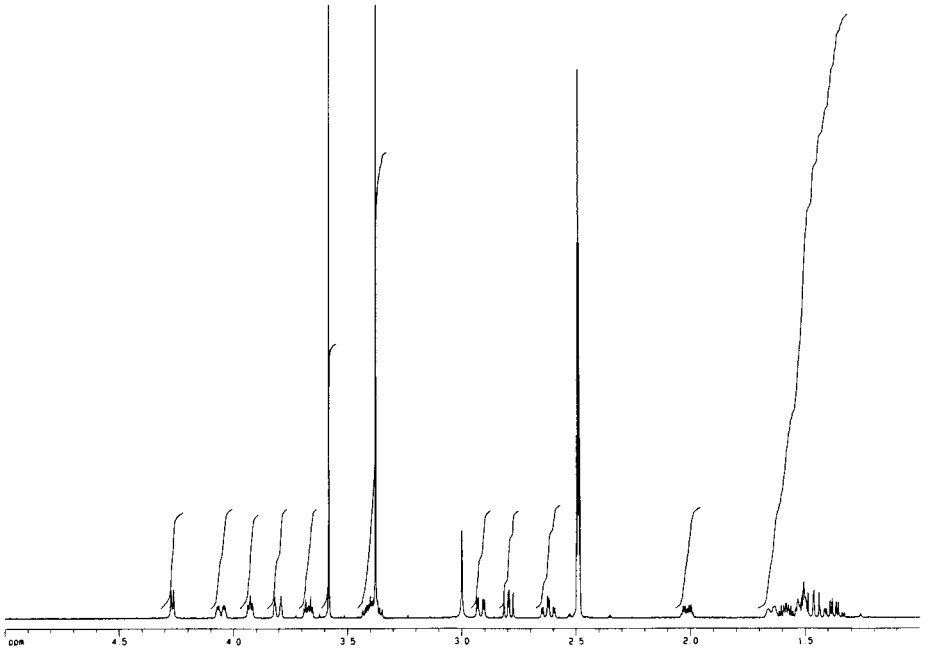
Diacetate 2: To a solution of diol (31 mg, 0.11 mmol) in pyridine (4 mL) at 0 °C was added catalytic DMAP followed by Ac_2O (0.4 g, 3.96 mmol). The cooling bath was removed and the solution was stirred for 90 min. The reaction was quenched with ice (1 g) and partitioned with H_2O (5 mL) and Et_2O (5 mL). The organics were separated and washed with 1% HCl (5 mL), brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed (1:1 EtOAc / Hexane) to afford 22 mg (55%) of **2** as a colorless oil. ^{1}H NMR (DMSO @ 363 K) 4.74 (ddd, *J* = 11.6, 9.3, 5.3 Hz, 1 H), 4.21 (dd, *J* = 11.2, 3.; Hz, 1 H), 4.09-4.03 (m, 1 H), 4.05 (dd, *J* = 11.1, 8.8 Hz, 1 H), 3.80 (br d, *J* = 13.3 Hz, 1 H), 3.58 (s, 3 H), 3.32 (s, 3 H), 3.24 (dd, *J* = 10.7, 9.3 Hz, 1 H), 2.94 (dd, *J* = 13.3, 3.2 Hz, 1 H), 2.65 (td, *J* = 12.9, 3.3 Hz, 1 H), 2.01 (s, 3 H) 2.00 (s, 3 H), 2.01-1.94 (m, 2 H), 1.87-1.80 (m, 1 H), 1.65 (dt, *J* = 12.8, 4.1 Hz, 1 H), 1.56-1.40 (m, 3 H); ^{13}C NMR (C_6D_6) δ 170.2, 169.8, 156.2, 78.9, 77.6, 63.2, 60.1, 52.6, 48.8, 44.7, 44.4, 36.6, 34.6, 29.7, 21.6, 21.2, 20.8; IR (NaCl, neat) cm^{-1} 2951, 1731, 1704, 1453, 1026; HRMS (CI) calculated for $C_{17}H_{27}NO_4$ (M^+) 357.1787, observed 357.1784.

Synthetic diol (sms-4-95 in dmso @ 363 K)

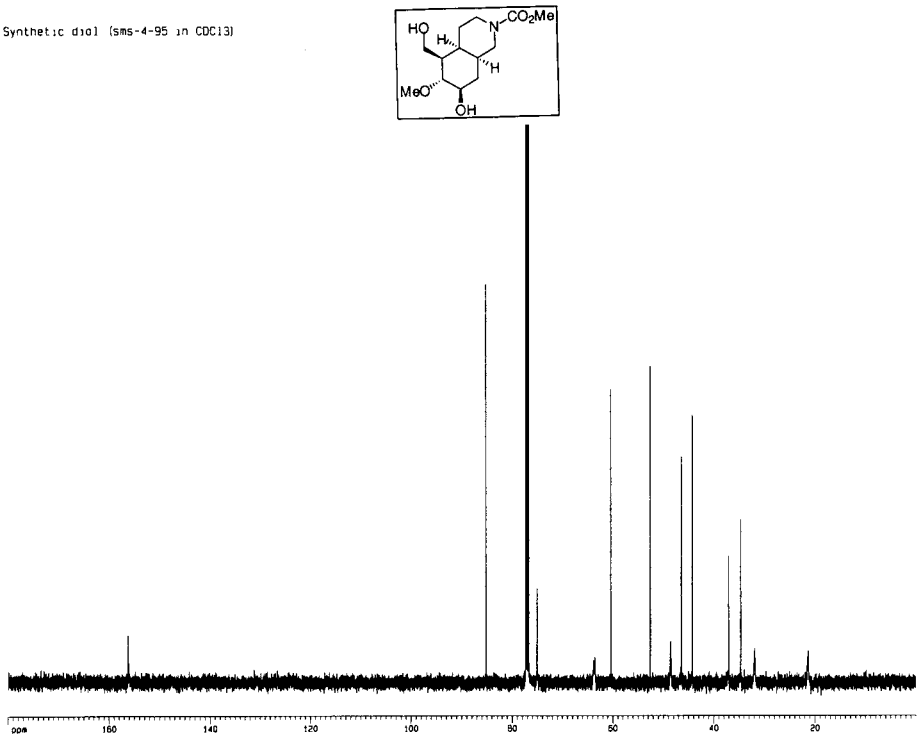




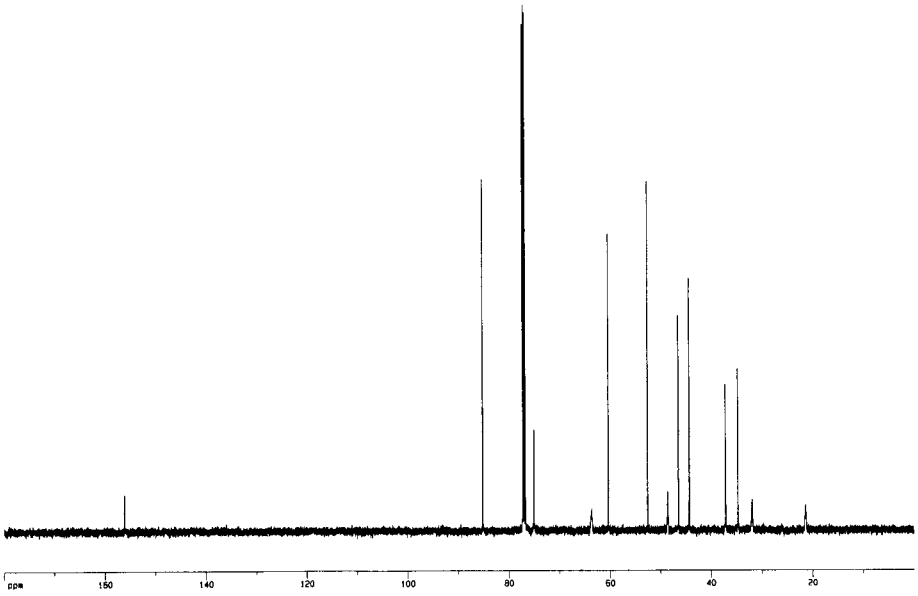
Natural diol derived from reserpine (sms-4-106 in dmso @ 363 K)

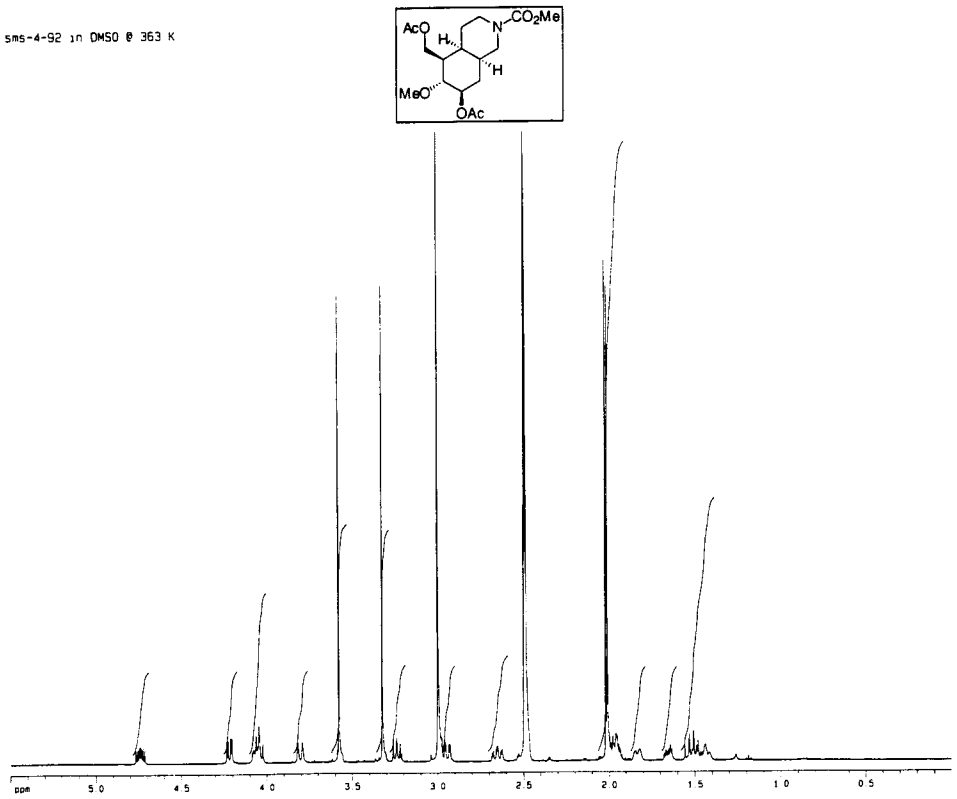


Synthetic diol (sms-4-95 in CDCl3)



Natural diol derived from reserpine (sms-4-106 in CDCL3)




sms-4-92 in DMSO @ 363 K
AcO
H
N
CO2Me
H
MeO
OAc
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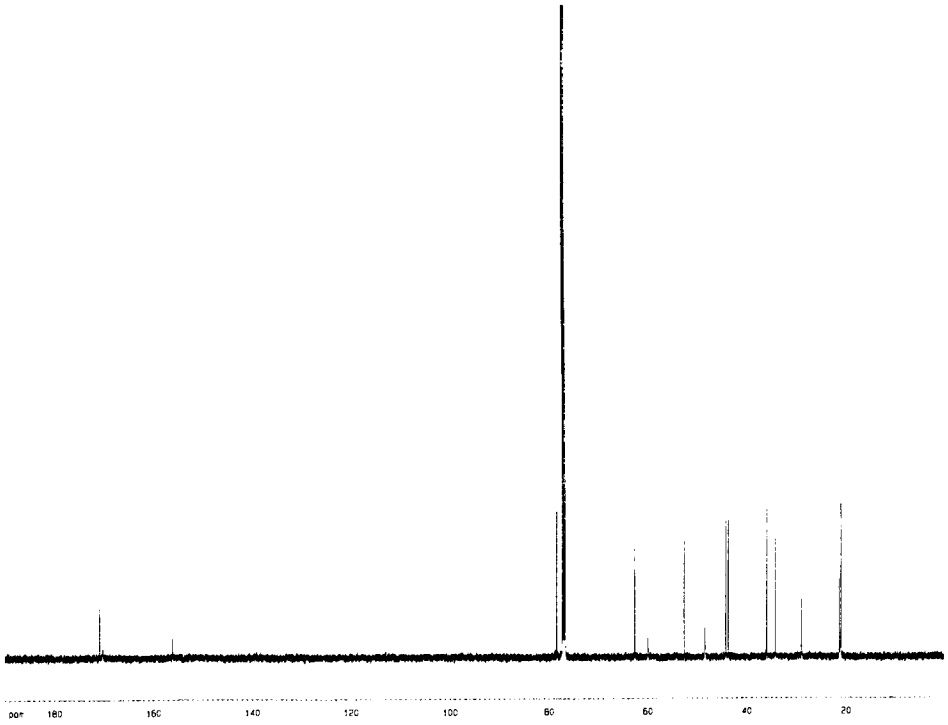
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


ppm
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160
140
120
100
80
60
40
20