Electronic Supplementary Information

Regioselective synthesis of di-*C*-glycosylflavones possessing anti-inflammation activities

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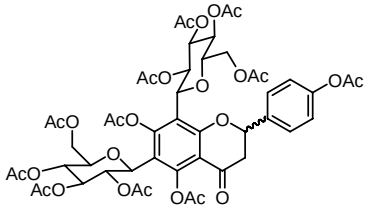
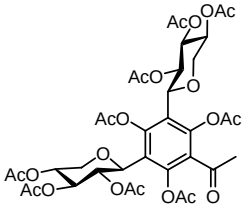
5,7,4'-Triacetoxy-6,8-di-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)flavanone (2aaAc)



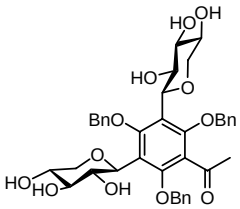
According to the previously reported method,[15] a mixture of (±)-naringenin (**1**, 136 mg, 0.5 mmol), D-glucose (270 mg, 1.5 mmol), and $Sc(OTf)_3$ (74 mg, 0.15 mmol) in EtOH (2 mL)/H_2O (1 mL) was heated at reflux for 16 h. The mixture was cooled and concentrated under reduced pressure. The crude product of **2aa** was treated with Ac_2O (3 mL) in pyridine (3 mL) for 24 h at room temperature. The reaction mixture was partitioned between 1 M HCl and EtOAc. The organic phase was washed with 1 M HCl and brine, dried over anhydrous $MgSO_4$, filtered, and then concentrated by rotary evaporation. By column chromatography on silica gel (EtOAc/hexane, 1:1 to 2:1) the desired product **2aaAc** was obtained (< 20% yield) by contamination with mono-*C*-glycosylation and other products as shown by the ^{1}H NMR spectrum.

3,5-Di-(*C*-β-D-xylopyranosyl)acetophenone peracetate (5bbAc).



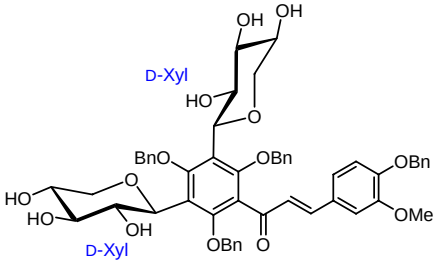
For analytical purpose, the crude sample of **5bb** was treated with Ac_2O in pyridine for 12 h at room temperature to give **5bbAc**. $C_{36}H_{42}O_{21}$; colorless solid, mp 140–142 °C; TLC (EtOAc/hexane, 1:1) R_f = 0.20; $[\alpha]^{25}_D$ –2.45 (*c* 4.7, EtOAc); IR ν_{max} (neat) 2940, 2858, 1783, 1754, 1597, 1369, 1219, 1169, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.55 (1 H, br s), 5.42 (1 H, br s), 5.26–5.14 (2 H, m), 4.96 (2 H, br s), 4.65 (1 H, d, *J* = 9.2 Hz), 4.26 (1 H, br s), 4.10–4.03 (2 H, m), 3.33 (1 H, t, *J* = 9.8 Hz), 3.22 (1 H, t, *J* = 10.4 Hz), 2.37 (3 H, s), 2.35 (3 H, s), 2.26 (3 H, s), 2.24 (3 H, s), 2.00 (12 H, s), 1.87 (3 H, s), 1.69 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.0, 169.9 (2 ×), 169.6 (3 ×), 169.1, 167.9, 167.7, 167.4, 150.4, 147.9, 146.0, 128.6, 122.1, 119.9, 73.7 (3 ×), 73.1, 70.2, 69.7, 69.0, 68.9, 67.4, 67.3, 30.0, 21.1 (2 ×), 20.9 (2 ×), 20.8, 20.8, 20.7, 20.4, 20.2; HRMS (ESI) calcd for $C_{36}H_{42}O_{21}Na$: 833.2116, found: *m*/*z* 833.2108 [M + Na]$^+$.

2,4,6-Tribenzyloxy-3,5-di-(*C*-β-D-xylopyranosyl)acetophenone (5bbBn).



Compound **5bb** was treated with $PhCH_2Br$ and K_2CO_3 in dry DMF at room temperature for 12 h to give **5bbBn**. $C_{39}H_{42}O_{12}$; TLC ($CHCl_3$/MeOH, 5:1) R_f = 0.25; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (3 H, d, *J* = 7.2 Hz), 7.41–7.19 (14 H, m), 7.10 (1 H, d, *J* = 6.8 Hz), 5.05 (2 H, t, *J* = 9.2 Hz), 4.97 (1 H, d, *J* = 10.8 Hz), 4.80–4.71 (6 H, m), 4.48 (2 H, t, *J* = 11 Hz), 4.27 (1 H, br s), 4.05 (1 H, br s), 3.88 (2 H, br s), 3.38 (2 H, br s), 3.26 (2 H, br s), 3.14 (1 H, br s), 3.02 (1 H, br s), 2.90 (4 H, s), 2.31 (3 H, br s); HRMS (ESI) calcd for $C_{39}H_{43}O_{12}$: 703.2755, found: *m*/*z* 703.2751 $[M + H]^+$.

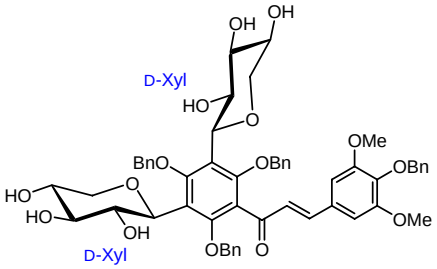
2,4,6,4'-Tetrabenzyloxy-3'-methoxy-3,5-di-*C*-(β-D-xylopyranosyl)chalcone (7bb2)



Alkylation of **5bbBn** (270 mg, 0.385 mmol) with 4-(benzyloxy)-3-methoxybenzaldehyde (280 mg, 1.15 mmol), by a procedure similar to that for **7bb1,** gave compound **7bb2** (245 mg, 69%). $C_{54}H_{54}O_{14}$; yellow prisms, mp 136.4–138.7 °C; TLC ($CHCl_3$/MeOH, 10:1) R_f = 0.15; $[\alpha]^{25}_D$ –40.84 (*c* 3.2, EtOAc); IR ν_{max} (neat) 3400, 2929, 1576, 1509, 1455, 1268, 1136, 1085 cm^{-1}; ^{1}H NMR (a mixture of rotamers, $CDCl_3$, 400 MHz) δ 7.46 (1 H, d, *J* = 15.6 Hz), 7.41–7.04 (20 H, m), 6.96–6.94 (2 H, m), 6.85 (1 H, d, *J* = 15.6 Hz), 6.76 (1 H, d, *J* = 8 Hz), 5.16–5.05 (3 H, m), 5.01–4.92 (2 H, m), 4.78 (2 H, d, *J* = 9.6 Hz), 4.70 (1 H, t, *J* = 10 Hz), 4.52 (2 H, t, *J* = 11.6 Hz), 4.22 (1 H, t, *J* = 9.2 Hz), 4.08 (1 H, t, *J* = 9 Hz), 3.87 (2 H, d, *J* = 5.6 Hz), 3.79 (3 H, s), 3.36–3.32 (1 H, m), 3.24–3.16 (3 H, m), 3.13–3.04 (2 H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.1, 161.1, 157.8, 157.2, 150.8, 149.5, 146.6, 136.7, 136.6, 136.3, 128.6–125.7 (4 ×), 123.8,

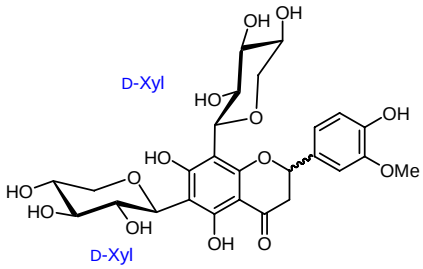
123.6, 122.4, 113.1, 110.7, 80.0 (2 ×), 79.1 (2 ×), 78.7 (2 ×), 76.1 (2 ×), 75.9 (2 ×), 71.5, 70.8 (2 ×), 70.1, 56.1; HRMS (ESI) calcd for $C_{54}H_{54}O_{14}Na$: 949.3406, found: *m*/*z* 949.3400 $[M + Na]^+$.

2,4,6,4'-Tetrabenzyloxy-3',5'-dimethoxy-3,5-di-*C*-(β-D-xylopyranosyl)chalcone (7bb3)



Alkylation of **5bbBn** (215 mg, 0.3 mmol) with 4-(benzyloxy)-3,5-di-methoxybenzaldehyde (245 mg, 0.9 mmol), by a procedure similar to that for **7bb1,** gave compound **7bb3** (183 mg, 64%). $C_{55}H_{56}O_{15}$; yellow prisms, mp 142.0–144.1 °C; TLC ($CHCl_3$/MeOH, 10:1) R_f = 0.13; $[\alpha]^{25}_D$ –36.33 (*c* 3.3, EtOAc); IR ν_{max} (neat) 3400, 2878, 1577, 1498, 1454, 1418, 1128, 1089 cm^{-1}; ^1H NMR (a mixture of rotamers, $CDCl_3$, 400 MHz) δ 7.47–7.05 (21 H, m), 6.88 (1 H, d, *J* = 15.6 Hz), 6.64 (2 H, s), 5.10 (1 H, d, *J* = 10.4 Hz), 5.04–4.93 (3 H, m), 4.78 (2 H, d, *J* = 9.6 Hz), 4.69 (2 H, t, *J* = 11.4 Hz), 4.54 (2 H, t, *J* = 10.8 Hz), 4.23 (1 H, t, *J* = 9.2 Hz), 4.10 (1 H, t, *J* = 8.8 Hz), 3.89 (2 H, br s), 3.74 (6 H, s), 3.36–3.32 (1 H, m), 3.26–3.20 (3 H, m), 3.18–3.05 (2 H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.0, 161.3, 157.9, 157.2, 153.5 (2 ×), 146.5, 139.5, 137.4, 136.7, 136.2, 129.8–126.8 (4 ×), 123.7, 122.5, 106.2 (2 ×), 80.0 (2 ×), 79.2 (2 ×), 78.7 (2 ×), 76.1 (2 ×), 75.9 (2 ×), 71.4, 70.9, 70.1 (2 ×), 56.4 (2 ×); HRMS (ESI) calcd for $C_{55}H_{56}O_{15}Na$: 979.3511, found: *m*/*z* 979.3501 $[M + Na]^+$.

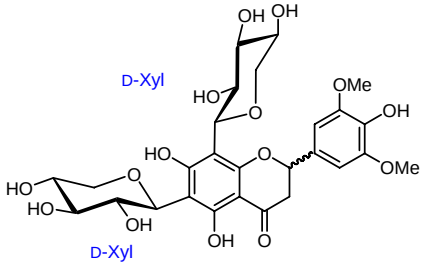
5,7,4'-Trihydroxy-3'-methoxy-6,8-di-*C*-(β-D-xylopyranosyl)flavanone (8bb2)



By a procedure similar to that for **8bb1**, the acid-catalyzed cyclization of **7bb2** (200 mg, 0.216 mmol) and subsequent hydrogenolysis of the benzyl group gave **8bb2** (85 mg, 70%). $C_{26}H_{30}O_{14}$; TLC (Me_2CO/EtOAc/H_2O/HOAc, 30:30:5:1) R_f = 0.23; ^1H NMR (CD_3OD, 400 MHz) δ 7.17, 7.13 (total 1 H, each s), 6.95–6.90 (1 H, m), 6.82 (1 H, d, *J* = 8.4 Hz), 5.44–5.38 (1 H, m),

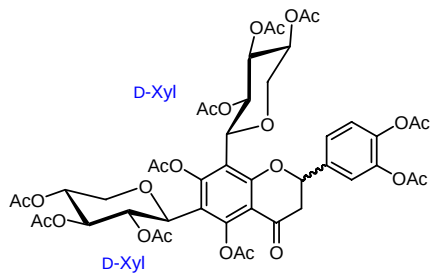
4.80–4.71 (2 H, m), 4.04–3.88 (7 H, m), 3.70–3.52 (2 H, m), 3.48–3.37 (3 H, m), 3.29–3.23 (1 H, m), 3.16–3.07 (1 H, m), 2.90–2.76 (1 H, m); ^{13}C NMR (CD_3OD, 150 MHz) δ 197.3, 164.2, 161.9/161.2, 147.7, 146.5/146.4, 130.3, 130.0, 118.8/118.7, 114.7/114.6, 110.2, 109.7, 104.3/103.8, 102.1/101.9, 79.1/78.9, 78.4 (2 ×), 75.0 (2 ×), 71.6, 71.5, 70.2, 70.1, 69.9 (2 ×), 55.2, 42.8; HRMS (ESI) calcd for $C_{26}H_{30}O_{14}Na$: 589.1528, found: *m*/*z* 589.1555 $[M + Na]^+$.

4',5,7-Trihydroxy-3',5'-dimethoxy-6,8-di-*C*-(β-D-xylopyranosyl)flavanone (8bb3)



By a procedure similar to that for **8bb1**, the acid-catalyzed cyclization of **7bb3** (110 mg, 0.115 mmol) and subsequent hydrogenolysis of the benzyl group gave **8bb3** (52 mg, 76%). $C_{27}H_{32}O_{15}$; TLC (Me_2CO/EtOAc/H_2O/HOAc, 30:30:5:1) R_f = 0.22; ^{1}H NMR (CD_3OD, 400 MHz) δ 6.84 (1 H, s), 6.79 (1 H, s), 5.44–5.38 (1 H, m), 4.78–4.72 (2 H, m), 4.05–3.88 (10 H, m), 3.69–3.60 (1 H, m), 3.52 (1 H, br s), 3.43–3.35 (3 H, m), 3.26–3.23 (1 H, m), 3.20–3.05 (1 H, m), 2.91–2.78 (1 H, m); ^{13}C NMR (CD_3OD, 100 MHz) δ 197.4/197.2, 164.2, 161.9/161.2, 147.9/147.8 (2 ×), 135.2/135.0, 129.9, 129.5, 104.3/104.1, 103.7, 103.3 (2 ×), 102.3/102.1, 79.3, 78.7, 78.6, 75.3 (2 ×), 71.9 (2 ×), 70.4 (2 ×), 70.2 (2 ×), 56.0 (2 ×), 43.2; HRMS (ESI) calcd for $C_{27}H_{32}O_{15}Na$: 619.1633, found: *m*/*z* 619.1649 $[M + Na]^+$.

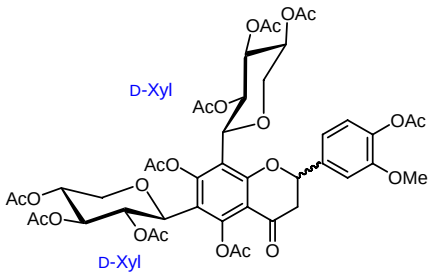
5,7,3',4'-Tetraacetoxy-6,8-di-*C*-(hexa-*O*-acetyl-β-D-xylopyranose)flavanone (8bb1Ac).



Compound **8bb1** was treated with Ac_2O in pyridine (6 mL) for 12 h at room temperature to give **8bb1Ac**. $C_{45}H_{48}O_{24}$; pale-yellow amorphous solids; mp 154–156 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.24; IR ν_{max} (neat) 2924, 2854, 1754, 1695, 1603, 1369, 1219, 1035 cm^{-1}; ^{1}H NMR

($CDCl_3$, 400 MHz) δ 7.42–7.39 (2 H, m), 7.3 (1 H, d, *J* = 8.4 Hz), 5.78–5.72 (2 H, m), 5.51 (1 H, t, *J* = 9.4 Hz), 5.27–5.21 (2 H, m), 5.01–4.95 (1 H, m), 4.86–4.80 (1 H, m), 4.61 (1 H, d, *J* = 9.6 Hz), 4.32–4.25 (2 H, m), 4.13 (1 H, dd, *J* = 11.6, 5.6 Hz), 3.35 (1 H, t, *J* = 11.2 Hz), 3.25 (1 H, t, *J* = 10.8 Hz), 2.93 (1 H, t, *J* = 15.4 Hz), 2.78 (1 H, dd, *J* = 16.8, 2.8 Hz), 2.44 (3 H, s), 2.42 (3 H, s), 2.31 (3 H, s), 2.29 (3 H, s), 2.05 (3 H, s), 2.02 (6 H, s), 1.99 (3 H, s), 1.89 (3 H, s), 1.77 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 188.1, 170.1, 169.9, 169.7, 169.3, 167.9 (2 ×), 167.8 (3 ×), 167.6, 162.1, 154.7, 149.7, 142.3, 141.8, 137.1, 123.9, 123.1, 120.2, 116.9, 115.6, 111.9, 78.2, 73.9, 73.5, 73.4, 72.6, 69.5 (2 ×), 69.0, 68.4, 67.6, 67.1, 45.4, 21.2, 21.0 (3 ×), 20.8 (2 ×), 20.8, 20.7, 20.4, 20.3; HRMS (ESI) calcd for $C_{45}H_{48}O_{24}Na$: 995.2428, found: *m*/*z* 995.2427 $[M + Na]^+$.

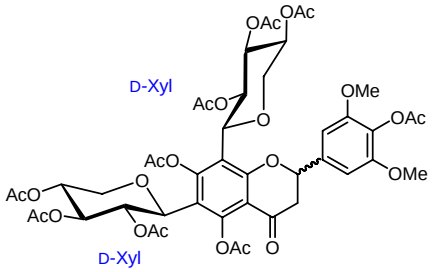
5,7,4'-Triacetoxy-6,8-di-*C*-(hexa-*O*-acetyl-β-D-xylopyranose)-3'-methoxyflavanone (8bb2Ac)



By a procedure similar to that for **8bb1Ac**, acetylation of **8bb2** (120 mg, 0.21 mmol) gave **8bb2Ac** (137 mg). $C_{44}H_{48}O_{23}$; Pale-yellow amorphous solids; mp 149–151 °C; TLC (EtOAc/hexane, 1.5:1) R_f = 0.25; IR ν_{max} (neat) 2924, 2853, 1754, 1695, 1603, 1369, 1220, 1164, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22 (1 H, s), 7.11 (1 H, d, *J* = 8.4 Hz), 7.04 (1 H, d, *J* = 8.0 Hz), 5.80 (1 H, t, *J* = 9.6 Hz), 5.69 (1 H, d, *J* = 12.0 Hz), 5.52 (1 H, t, *J* = 9.2 Hz), 5.27–5.21 (2 H, m), 5.01–4.95 (1 H, m), 4.79–4.73 (1 H, m), 4.61 (1 H, d, *J* = 9.2 Hz), 4.28–4.22 (2 H, m), 4.13 (1 H, dd, *J* = 11.6, 5.2 Hz), 3.88 (3 H, s), 3.34 (1 H, t, *J* = 10.8 Hz), 3.24 (1 H, t, *J* = 10.6 Hz), 2.96 (1 H, t, *J* = 15.4 Hz), 2.76 (1 H, dd, *J* = 17, 2.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 188.8, 170.2 (2 ×), 170.2 (2 ×), 170.0, 169.8, 169.0, 168.2, 167.9, 162.6, 155.1, 151.6, 150.0, 139.8, 137.3, 123.3, 117.7, 117.1, 115.8, 112.2, 109.7, 79.3, 74.2, 73.8, 73.7, 72.9, 69.8, 69.4 (2 ×), 68.7, 67.9, 67.4, 56.3, 45.8, 21.6, 21.3, 21.1 (2 ×), 21.0 (3 ×), 20.7, 20.6; HRMS (ESI) calcd for $C_{44}H_{49}O_{23}$; 945.2659, found: *m*/*z* 945.2649 $[M + H]^+$.

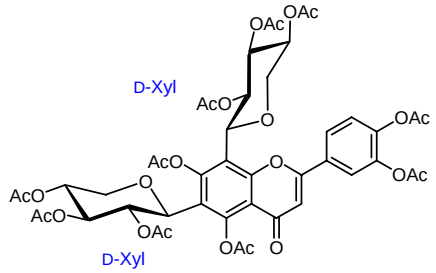
3',5'-Dimethoxy-5,7,4'-tri-acetoxy-6,8-di-*C*-(hexa-*O*-acetyl-β-D-xylopyranose)flavanone

(8bb3Ac)



By a procedure similar to that for **8bb1Ac**, acetylation of **8bb3** (70 mg, 0.117 mmol) gave **8bb3Ac** (74 mg). $C_{45}H_{50}O_{24}$; colorless solid, mp 168–170 °C; TLC (EtOAc/hexane, 1.5:1) R_f = 0.32; IR ν_{max} (neat) 2922, 2851, 1754, 1695, 1604, 1369, 1220, 1163, 1132, 1035 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.78 (2 H, s), 5.8 (1 H, t, J = 9.8 Hz), 5.66 (1 H, d, J = 11.6 Hz), 5.51 (1 H, t, J = 9.6 Hz), 5.24 (2 H, dd, J = 17, 9.4 Hz), 5.01–4.95 (1 H, m), 4.76–4.70 (1 H, m), 4.61 (1 H, d, J = 9.2 Hz), 4.27–4.22 (2 H, m), 4.13 (1 H, dd, J = 11.2, 5.6 Hz), 3.85 (6 H, s), 3.34 (1 H, t, J = 11 Hz), 3.23 (1 H, t, J = 10.8 Hz), 2.96 (1 H, dd, J = 16.8, 14 Hz), 2.75 (1 H, dd, J = 16.8, 2.4 Hz), 2.44 (3 H, s), 2.41 (3 H, s), 2.33 (3 H, s), 2.05 (3 H, s), 2.02 (3 H, s), 1.99 (6 H, s), 1.90 (3 H, s), 1.77 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 188.7, 170.1, 170.1, 169.9, 169.7, 169.4, 168.7, 168.6, 168.1, 167.8, 162.5, 155.0, 152.5 (2 ×), 149.9, 136.9, 128.5, 116.9, 115.8, 112.2, 102.0 (2 ×), 79.6, 74.2, 73.7, 73.6, 72.8, 69.9, 69.7, 69.3, 68.6, 67.9, 67.3, 56.4 (2 ×), 46.0, 21.5, 21.2 (2 ×), 21.0, 21.0, 20.9, 20.8, 20.6, 20.5; HRMS (ESI) calcd for $C_{45}H_{50}O_{24}Na$: 997.2584, found: m/z 997.2560 $[M + Na]^+$.

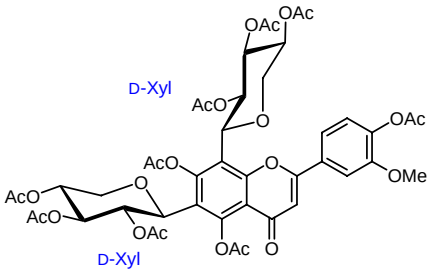
5,7,3',4'-Tetraacetoxy-6,8-di-*C*-(hexa-*O*-acetyl-β-D-xylopyranosyl)flavone (9bb1Ac).



Flavanone **8bb1Ac** was treated with I_2 in DMSO at 130 °C for 3 h to give **9bb1Ac**. $C_{45}H_{46}O_{24}$; colorless solid, mp 163–165 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.16; $[\alpha]^{25}_D$ –5.33 (*c* 2.3, EtOAc); IR ν_{max} (neat) 2926, 1754, 1651, 1604, 1369, 1217, 1036 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.87 (1 H, d, J = 7.2 Hz), 7.71 (1 H, s), 7.46 (1 H, d, J = 8.4 Hz), 6.55 (1 H, s), 5.67 (1 H, t, J =

9.4 Hz), 5.57 (1 H, br s), 5.37 (1 H, t, *J* = 9.4 Hz), 5.27 (1 H, t, *J* = 9.4 Hz), 5.15–5.09 (1 H, m), 5.05–4.98 (1 H, m), 4.73 (1 H, d, *J* = 9.6 Hz), 4.48 (1 H, d, *J* = 10 Hz), 4.40 (1 H, dd, *J* = 11.2, 5.6 Hz), 4.15 (1 H, dd, *J* = 11.6, 5.6 Hz), 3.40–3.35 (2 H, m), 2.49 (3 H, s), 2.46 (3 H, s), 2.34 (3 H, s), 2.32 (3 H, s), 2.06 (6 H, s), 2.03 (3 H, s), 2.01 (3 H, s), 1.86 (3 H, s), 1.75 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.8, 170.3, 170.1 (2 ×), 169.9 (2 ×), 169.7 (2 ×), 168.1 (2 ×), 167.7 , 161.1, 156.7, 153.0, 149.3, 145.1, 143.0, 130.0, 124.9, 124.7, 121.8, 119.4, 117.7, 115.4, 109.6, 74.5, 73.9 (2 ×), 73.1 , 69.7 (2 ×), 69.3 (2 ×), 68.2, 67.5, 21.6, 21.3, 21.0 (6 ×), 20.6 (2 ×); HRMS (ESI) calcd for $C_{45}H_{47}O_{24}$: 971.2452, found: *m*/*z* 971.2450 $[M + H]^+$.

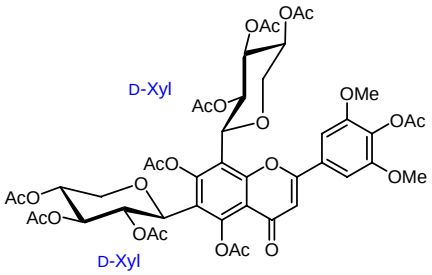
5,7,4'-Triacetoxy-6,8-di-*C*-(hexa-*O*-acetyl-β-D-xylopyranosyl)-3'-methoxyflavone (9bb2Ac)



By a procedure similar to that for **9bb1Ac**, oxidation of **8bb2Ac** (173 mg, 0.18 mmol) with I_2 (14 mg, 0.055 mmol) in DMSO and subsequent reacetylation gave **9bb2Ac** (120 mg, 70%). $C_{44}H_{46}O_{23}$; colorless solid, mp 155–157 °C; TLC (EtOAc/hexane, 1.5:1) R_f = 0.13; $[\alpha]^{25}_D$ –3.63 (*c* 2.3, EtOAc); IR ν_{max} (neat) 2924, 1754, 1650, 1603, 1368, 1224, 1042 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60 (1 H, d, *J* = 8.4 Hz), 7.37 (1 H, s) , 7.29 (1 H, d, *J* = 8.4 Hz) , 6.53 (1 H, s), 5.74 (1 H, t, *J* = 9.6 Hz), 5.57 (1 H, t, *J* = 8.8 Hz), 5.35 (1 H, t, *J* = 9.4 Hz), 5.27 (1 H, t, *J* = 9.2 Hz), 5.15–5.08 (1 H, m), 5.05–4.98 (1 H, m), 4.73 (1 H, d, *J* = 10 Hz), 4.48 (1 H, d, *J* = 10 Hz), 4.34 (1 H, dd, *J* = 11.4, 5.4 Hz), 4.15 (1 H, dd, *J* = 11.4, 5.4 Hz), 3.91 (3 H, s), 3.40–3.33 (2 H, m), 2.48 (3 H, s), 2.45 (3 H, s), 2.34 (3 H, s), 2.05 (6 H, s), 2.02 (3 H, s), 1.99 (3 H, s), 1.86 (3 H, s), 1.77 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.8, 170.1, 170.0, 169.9 169.8, 169.6 (2 ×), 168.5, 168.0, 167.9, ,162.3, 156.7, 152.9, 151,8, 149.2, 142.8, 130.3, 123.9, 119.7, 119.2, 117.5, 115.3, 110.4, 109.6, 74.3, 73.6 (2 ×), 72.9, 69.5, 69.4, 69.2 (2 ×), 68.0, 67.3, 56.4, 21.5, 21.2, 20.9 (4 ×), 20.5, 20.5 (2 ×); HRMS (ESI) calcd for $C_{44}H_{46}O_{23}Na$: 965.2322, found: *m*/*z* 965.2333 $[M + Na]^+$.

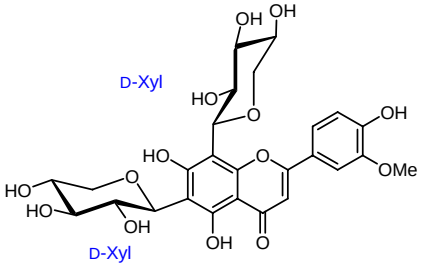
5,7,4'-Triacetoxy-6,8-di-*C*-(hexa-*O*-acetyl-β-D-xylopyranosyl)-3',5'-dimethoxyflavone

(9bb3Ac)



By a procedure similar to that for **9bb1Ac**, oxidation of **8bb3Ac** (40 mg, 0.041 mmol) with I_2 (3.2 mg, 0.012 mmol) in DMSO and subsequent reacetylation gave **9bb3Ac** (32 mg, 80%). $C_{45}H_{48}O_{24}$; colorless solid, mp 172–173 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.18; $[\alpha]^{25}_D$ −12.1 (*c* 3.0, EtOAc); IR ν_{max} (neat) 2934, 1756, 1652, 1601, 1367, 1218, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.09 (2 H, s), 6.48 (1 H, s), 5.84 (1 H, t, *J* = 9 Hz), 5.59 (1 H, br s), 5.35–5.21 (2 H, m), 5.05–4.94 (2 H, m), 4.73 (1 H, d, *J* = 9.2 Hz), 4.47 (1 H, d, *J* = 9.6 Hz), 4.31 (1 H, dd, *J* = 11.4, 5.8 Hz), 4.16 (1 H, dd, *J* = 11.2, 5.6 Hz), 3.92 (6 H, s), 3.41–3.30 (2 H, m), 2.50 (3 H, s), 2.46 (3 H, s), 2.35 (3 H, s), 2.06 (3 H, s), 2.03 (6 H, s), 1.99 (3 H, s), 1.86 (3 H, s), 1.75 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.4, 169.8 (2 ×), 169.8, 169.7, 169.4, 168.1 (2 ×), 167.9, 167.7, 163.1, 156.6, 152.7 (2 ×), 149.1, 131.5, 130.0, 119.1, 116.9, 115.1, 110.5, 103.7 (2 ×), 102.6, 74.2, 73.8, 73.4, 72.7, 69.6 (2 ×), 69.0 (2 ×), 68.3, 67.2, 56.6 (2 ×), 21.3, 21.2, 21.0, 20.8, 20.7, 20.7, 20.5, 20.3, 20.2; HRMS (ESI) calcd for $C_{45}H_{49}O_{24}$: 973.2608, found: *m*/*z* 973.2592 $[M + H]^+$.

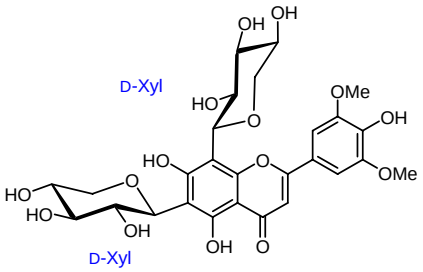
6,8-Di-*C*-(β-D-xylopyranosyl)-5,7,4'-trihydroxy-3'-methoxyflavone (9bb2)



By a procedure similar to that for **9bb1**, saponification of **9bb2Ac** (19 mg, 0.02 mmol) with sodium methoxide (23 mg, 0.43 mmol) in methanol gave **9bb2** (10 mg, 88%). $C_{26}H_{28}O_{14}$; colorless solid, mp 195–197 °C; TLC (Me_2CO/EtOAc/H_2O/HOAc, 30:30:5:1) R_f = 0.23; IR ν_{max} (KBr) 3398, 2921, 2866, 1646, 1626, 1579, 1514, 1434, 1354, 1292, 1212, 1087, 1056 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz) δ 7.52 (2 H, br s), 6.93 (1 H, d, *J* = 8.4 Hz), 6.62 (1 H, s), 4.85 (2 H, covered by the signal of methanol), 4.61 (1 H, br s), 4.14–3.90 (7 H, m), 3.77–3.65 (3 H, m), 3.49–3.38 (3 H, m); ^{13}C NMR (CD_3OD, 100 MHz) δ 184.1, 166.1, 163.1, 161.3, 156.5, 152.0,

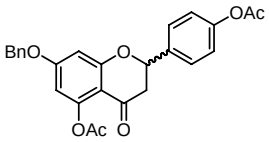
149.3, 123.7, 122.0, 116.8, 110.8, 108.9, 105.3, 104.1 (2 ×), 80.2 (2 ×), 79.9, 76.6, 73.4, 73.1, 72.0, 71.7, 71.4 (2 ×), 56.9; HRMS (ESI) calcd for $C_{26}H_{27}O_{14}$: 563.1401, found: *m*/*z* 563.1400 $[M - H]^-$.

6,8-Di-*C*-(β-D-xylopyranosyl)-5,7,4'-trihydroxy-3',5'-dimethoxyflavone (9bb3)



By a procedure similar to that for **9bb1**, saponification of **9bb3Ac** (10 mg, 0.01 mmol) with sodium methoxide (11 mg, 0.21 mmol) in methanol gave **9bb3** (5 mg, 84%). $C_{27}H_{30}O_{15}$; colorless solid, mp 207–208 °C; TLC (Me_2CO/EtOAc/H_2O/HOAc, 30:30:5:1) R_f = 0.22; IR ν_{max} (KBr) 3434, 2900, 2854, 1649, 1625, 1581, 1516, 1465, 1353, 1217, 1121, 1088, 1057 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz) δ 7.27 (2 H, s), 6.63 (1 H, s), 4.99 (1 H, br s), 4.85 (2 H, covered by the signal of methanol), 4.14–4.02 (3 H, m), 3.96 (6 H, s), 3.74–3.64 (3 H, m), 3.46–3.35 (4 H, m); HRMS (ESI) calcd for $C_{27}H_{29}O_{15}$: 593.1506, found: *m*/*z* 593.1509 $[M - H]^-$.

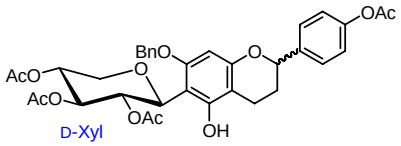
4',5-Diacetoxy-7-benzyloxyflavanone (10).



Treatment of (±)-naringenin with K_2CO_3 (1 equiv) and benzyl bromide (1.3 equiv) in anhydrous DMF at room temperature for 12 h gave a selective monobenzylation product, which reacted with Ac_2O in pyridine by catalysis of 4-dimethylaminopyridine for 4 h at room temperature to give compound **10**. $C_{26}H_{22}O_7$; colorless foam; TLC (EtOAc/hexane, 1:5) R_f = 0.25; IR (film) 2955, 1783, 1672, 1441, 1128 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.44 (2 H, d, *J* = 8.5 Hz), 7.38–7.33 (5 H, m), 7.13 (2 H, d, *J* = 8.5 Hz), 6.47 (1 H, d, *J* = 2.4 Hz), 6.35 (1 H, d, *J* = 2.4 Hz), 5.43 (1 H, dd, *J* = 13.5, 2.7 Hz), 5.05 (2 H, s), 2.97 (1 H, dd, *J* = 16.6, 13.5 Hz), 2.70 (1 H, dd, *J* = 16.6, 2.7 Hz), 2.37 (3 H, s), 2.29 (3 H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.5, 169.5,

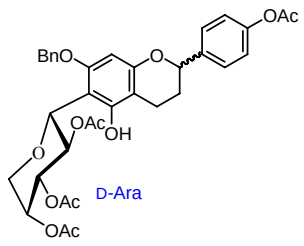
169.3, 164.6, 164.0, 151.8, 150.8, 135.9, 135.4, 128.7 (2 ×), 128.4, 127.5 (2 ×), 127.3 (2 ×), 122.0 (2 ×), 108.0, 105.4, 100.3, 78.9, 70.5, 45.0, 21.1 (2 ×); HRMS calcd for $C_{26}H_{23}O_7$ (M^+ + H): 447.1444, found: *m*/*z* 447.1447.

4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-7-benzyloxy-5-hydroxyflavan (12bBn)



By a procedure similar to that for **12aBn**, glycosylation of flavan **11** (1.95 g, 5 mmol) with 2,3,4-tri-*O*-acetyl-D-xylopyranosyl trichloroacetimidate (2.31 g, 5.5 mmol) gave compound **12bBn** (2.46 g, 76%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{35}H_{36}O_{12}$; White prisms, mp 207–209 °C; TLC (EtOAc/hexane, 1:2) R_f = 0.4; IR (film) 3421, 2933, 1712, 1628, 1342, 1179 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (1 H, d, *J* = 8.2 Hz), 7.41–7.32 (6 H, m), 7.09–7.07 (2 H, m), 6.06 (0.5 H, s), 6.04 (0.5 H, s), 5.35–5.33 (2 H, m), 5.10–5.08 (2 H, m), 4.98–4.88 (3 H, m), 4.28 (1 H, dd, *J* = 11.3, 5.6 Hz), 3.45 (1 H, dd, *J* = 10.9, 5.5 Hz), 2.78–2.74 (1 H, m), 2.67–2.61 (1 H, m), 2.29 (3 H, s), 2.20–2.13 (1 H, m), 2.08–2.02 (8 H, m), 1.80–1.78 (3 H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 170.0, 169.6, 169.2, 156.8, 155.3/155.2, 155.12/155.10, 150.24/150.21, 139.0, 136.8, 128.7/128.6 (2 ×), 128.0, 127.38, 127.33 (2 ×), 127.09/127.06 (2 ×), 121.6 (2 ×), 104.1/104.0, 101.5/101.4, 92.8/92.7, 75.03/75.00, 73.4/73.3, 70.7/70.6, 70.27/70.24, 69.38/69.36, 67.37/67.34, 29.5/29.3, 21.2, 20.8, 20.7, 20.4, 19.2/19.1; HRMS (ESI) calcd for $C_{35}H_{37}O_{12}$: 649.2280, found: *m*/*z* 649.2233 $[M + H]^+$. HRMS calcd for $C_{35}H_{36}NaO_{12}$: 671.2104, found: *m*/*z* 671.2121 $[M + Na]^+$.

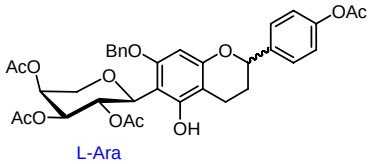
4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-7-benzyloxy-5-hydroxyflavan (12cBn)



By a procedure similar to that for **12aBn**, glycosylation of flavan **11** (1.95 g, 5 mmol) with

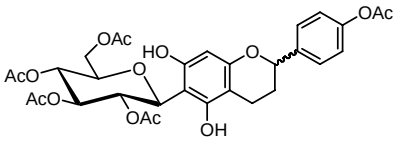
2,3,4-tri-*O*-acetyl-D-arabinopyranosyl trichloroacetimidate (2.31 g, 5.5 mmol) gave compound **12cBn** (2.27 g, 70%) as an inseparable mixture of diastereomers with rotamers. $C_{35}H_{36}O_{12}$; White foam; TLC (EtOAc/hexane, 1:2) R_f = 0.4; IR (film) 3533, 2912, 1756, 1641, 1299, 1176 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.40–7.31 (7 H, m), 7.08 (2 H, d, *J* = 7.1 Hz), 6.11–6.06 (1 H, m), 5.64–5.62 (1 H, m), 5.42 (1 H, s), 5.13–5.06 (2 H, m), 4.97–4.86 (3 H, m), 4.08 (1 H, d, *J* = 12.7 Hz), 3.77 (1 H, d, *J* = 13.1 Hz), 2.81–2.59 (2 H, m), 2.27 (3 H, s), 2.20 (3 H, s), 2.15–1.99 (5 H, m), 1.87–1.80 (3 H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6/170.4, 170.2/170.1, 169.5/169.3, 169.16/169.12, 156.8, 155.49/155.46, 155.09, 150.25, 139.1, 136.9, 128.6/128.5 (2 ×), 127.9, 127.6/127.5, 127.3/127.2 (2 ×), 127.09/127.07 (2 ×), 121.6 (2 ×), 104.05, 102.4, 92.7/92.6, 77.5, 74.5, 71.8, 70.2, 68.6, 68.4, 29.5, 21.1, 21.0, 20.7, 20.5, 19.2; HRMS calcd for $C_{35}H_{36}NaO_{12}$: 671.2104, found: *m*/*z* 671.2123 $[M + Na]^+$.

4'-Acetoxy-6-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)-7-benzyloxy-5-hydroxyflavan (12dBn)



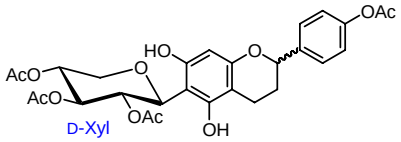
By a procedure similar to that for **12aBn**, glycosylation of flavan **11** (1.95 g, 5 mmol) with 2,3,4-tri-*O*-acetyl-L-arabinopyranosyl trichloroacetimidate (2.31 g, 5.5 mmol) gave compound **12dBn** (2.11 g, 65%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{35}H_{36}O_{12}$; White prisms, mp 115–118 °C; TLC (EtOAc/hexane, 1:1) R_f = 0.35; IR ν_{max} (neat) 3392, 2934, 1749, 1626, 1370, 1218 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.76 (0.6 H, s, OH), 7.72 (0.4 H, s, OH), 7.42–7.31 (7 H, m), 7.10–7.07 (2 H, m), 6.08 (0.4 H, s), 6.06 (0.6 H, s), 5.67–5.59 (1 H, m), 5.43 (1 H, br), 5.14 (1 H, dd, *J* = 10.0, 3.2 Hz), 5.07 (1 H, d, *J* = 10.0 Hz), 5.01–4.88 (3 H, m), 4.11 (1 H, dd, *J* = 13.2, 2.4 Hz), 3.80 (1 H, d, *J* = 13.2 Hz), 2.87–2.79 (1 H, m), 2.71–2.65 (1 H, m), 2.30 (3 H, s), 2.23–2.17 (4 H, m), 2.08–1.93 (4 H, m), 1.82 (1.8 H, s), 1.81 (1.2 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 169.7, 169.0, 168.7/168.7, 156.4, 155.1/155.1, 154.8/154.7, 149.9, 138.8, 136.6, 128.4 (2 ×), 127.7, 127.0 (2 ×), 126.8/126.7 (2 ×), 121.3 (2 ×), 103.8/103.7, 102.2/102.0, 92.5/92.4, 77.4/77.2, 74.4/74.3, 71.7, 70.1/70.0, 68.4, 68.2/68.2 (2 ×), 29.5/29.3, 21.1, 20.9, 20.7, 20.5, 19.2; HRMS (ESI) calcd for $C_{35}H_{36}O_{12}Na$: 671.2104, found: *m*/*z* 671.2108 $[M + Na]^+$.

4'-Acetoxy-6-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-5,7-dihydroxyflavan (12a).



Hydrogenolysis of **12aBn** on Pd/C in CH_3OH/EtOAc for 1 h at room temperature afforded **12a** as an inseparable mixture of diastereomers (existing as rotamers). $C_{31}H_{34}O_{14}$; colorless foam; TLC (EtOAc/hexane, 1:1) R_f = 0.45; IR (film) 3521, 2913, 1741, 1652, 1327, 1156 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.38–7.36 (2 H, m), 7.07–7.05 (2 H, m), 5.88 (1 H, s), 5.36–5.33 (2 H, m), 5.28–5.25 (1 H, m), 5.19–5.05 (1 H, m), 4.92 (0.5 H, d, J = 10.0 Hz), 4.87 (0.5 H, d, J = 10.3 Hz), 4.30–4.28 (1 H, m), 4.25–4.09 (2 H, m), 3.86 (1 H, d, J = 9.9 Hz), 2.79–2.71 (1 H, m), 2.66–3.59 (1 H, m), 2.28 (3 H, s), 2.15–1.98 (12 H, m), 1.85 (1.5 H, s), 1.83 (1.5 H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 170.7, 170.4, 169.6, 169.4, 156.6, 154.6 (br), 152.7 (br), 150.1, 139.0, 127.29/127.24, 121.6, 103.5 (br), 100.5, 100.4, 96.0/95.9 (br), 90.1, 76.18/76.12, 74.2/73.8, 73.7/71.0, 70.8/70.7, 69.8/68.4, 67.8/67.2, 61.9/61.4, 29.4/29.3, 21.1, 20.79/20.70, 20.6, 20.4, 20.3, 19.1/19.0; HRMS calcd for $C_{31}H_{34}NaO_{14}$: 653.1846, found: m/z 653.1851 $[M + Na]^+$.

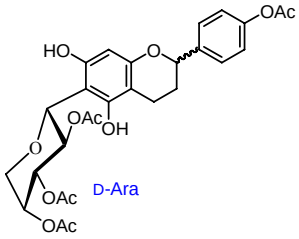
4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-5,7-dihydroxyflavan (12b)



By a procedure similar to that **12a**, hydrogenolysis of **12bBn** (519 mg, 0.8 mmol) on Pd/C gave compound **12b** (371 mg, 83%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{28}H_{30}O_{12}$; White prisms, mp 227–230 °C; TLC (EtOAc/hexane, 1:1) R_f = 0.5; IR (film) 3554, 2923, 1752, 1612, 1333, 1112 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 (2 H, d, J = 8.4 Hz), 7.06 (2 H, d, J = 8.4 Hz), 5.87 (1 H, s), 5.37–5.34 (1 H, m), 5.31–5.26 (1 H, m), 5.11–5.08 (1 H, m), 4.97 (1 H, dd, J = 10.1, 1.4 Hz), 4.93–4.87 (1 H, m), 4.30 (1 H, dd, J = 11.3, 5.6 Hz), 3.46 (1 H, t, J = 11.1 Hz), 2.72–2.69 (1 H, m), 2.61–2.58 (1 H, m), 2.28 (3 H, s), 2.19–1.85 (10 H, m), 1.85 (1.5 H, s), 1.83 (1.5 H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 170.0, 169.6, 169.2, 156.6, 154.6 (br), 152.8 (br), 150.2, 139.0, 127.27/127.23, 127.1, 121.5, 103.5 (br), 100.6/100.5, 98.36/98.30 (br), 96.1/96.0, 75.19/75.17, 73.4/73.3, 71.1, 71.0, 69.2, 67.4, 29.4/29.3,

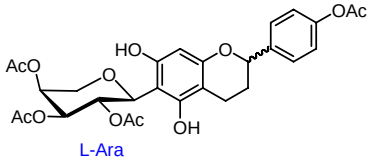
21.1, 20.77/20.71, 20.4/20.3, 19.05/19.02, 14.1; HRMS calcd for $C_{28}H_{30}NaO_{12}$: 581.1635, found: *m*/*z* 581.1633 $[M + Na]^+$.

4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-5,7-dihydroxyflavan (12c)



By a procedure similar to that **12a**, hydrogenolysis of **12cBn** (649 mg, 1 mmol) on Pd/C, gave compound **12c** (474 mg, 85%) as an inseparable mixture of diastereomers with rotamers. $C_{28}H_{30}O_{12}$; White foam; TLC (EtOAc/hexane, 1:1) R_f = 0.5; IR (film) 3510, 2981, 1721, 1651, 1331, 1216 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 (2 H, d, *J* = 7.4 Hz), 7.06 (2 H, d, *J* = 7.4 Hz), 5.86 (1 H, br s), 5.61–5.55 (1 H, m), 5.42 (1 H, br s), 5.18–5.11 (1 H, m), 4.95–4.88 (2 H, m), 4.11 (1 H, d, *J* = 13.1 Hz), 3.80 (1 H, d, *J* = 13.1 Hz), 2.75–2.68 (1 H, m), 2.65–2.57 (1 H, m), 2.28 (3 H, s), 2.205 (1.5 H, s), 2.200 (1.5 H, s), 2.13–1.99 (7 H, m), 1.87 (1.5 H, s), 1.85 (1.5 H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 170.2, 169.6, 169.3/169.2, 156.5, 155.2 (br), 152.5 (br), 150.1, 139.1, 127.28/127.22, 127.1, 121.6, 103.4 (br), 101.3/101.1, 96.1, 95.5 (br), 78.4/78.3, 74.7/74.6, 71.6, 68.6 (2 ×), 68.5, 29.4/29.3, 21.1, 21.0, 20.8/20.7, 20.5, 19.0; HRMS calcd for $C_{28}H_{30}NaO_{12}$: 581.1635, found: *m*/*z* 581.1639 $[M + Na]^+$.

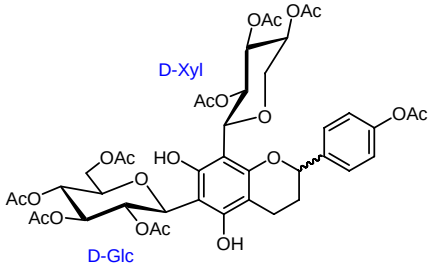
4'-Acetoxy-6-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)-5,7-dihydroxyflavan (12d)



By a procedure similar to that **12a**, hydrogenolysis of **12dBn** (1.12 g, 1.72 mmol) on Pd/C, gave compound **12d** (815 mg, 85%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{28}H_{30}O_{12}$; White prisms, mp 118.5–120 °C; TLC (EtOAc/hexane, 1:1) R_f = 0.15; IR ν_{max} (neat) 3400, 2925, 1747, 1632, 1370, 1221 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.38 (2 H, d, *J* = 8.4 Hz), 7.08–7.06 (2 H, m), 5.89 (1 H, br), 5.62–5.55 (1 H, m), 5.43 (1 H, br), 5.17 (2 H, dd, *J* = 9.6, 3.2 Hz), 4.95–4.90 (2 H, m), 4.13 (1 H, dd, *J* = 12.8, 2 Hz), 3.82 (1 H, d, *J* = 12.8 Hz), 2.72 (1 H, br), 2.66–2.61 (1 H, m), 2.29 (3 H, s), 2.22 (1.5 H, s), 2.21 (1.5 H, s), 2.19–2.13 (1 H, m), 2.09–2.03 (1 H, m), 2.00 (3 H, s), 1.89 (1.5 H, s), 1.87 (1.5 H, s); ^{13}C NMR ($CDCl_3$, 100

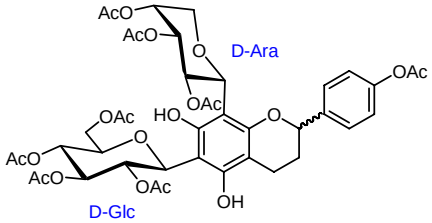
MHz) δ 170.2, 170.0/170.0, 169.5, 169.2/169.1, 156.2, 154.8, 152.6, 149.8, 138.9, 127.0 (2 ×), 121.3/121.3 (2 ×), 102.9, 101.1/101.0, 95.4, 74.5/74.4, 71.6/71.5, 68.6 (2 ×), 68.5, 68.3, 29.5/29.3, 21.1, 21.0/20.9, 20.7, 20.5, 19.1; HRMS (ESI) calcd for $C_{28}H_{30}O_{12}Na$: 581.1635, found: *m*/*z* 581.1624 $[M + Na]^+$.

4'-Acetoxy-6-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-5,7-dihydroxyflavan (13ab)



By a procedure similar to that for **13aa**, glycosylation of glycosylflavan **12a** (400 mg, 0.63 mmol) with 2,3,4-tri-*O*-acetyl-D-xylopyranosyl trichloroacetimidate (320 mg, 0.76 mmol) gave compound **13ab** (420 mg, 75%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{42}H_{48}O_{21}$; Colorless foam; TLC (EtOAc/hexane, 1:1) R_f = 0.45; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (0.3 H, d, *J* = 5.5 Hz), 7.45 (0.5 H, d, *J* = 8.4 Hz), 7.41–7.35 (1.8 H, m), 7.14–7.10 (0.7 H, m), 7.07–7.06 (0.7 H, m), 5.37–4.87 (10 H, m), 4.65 (0.5 H, br s), 4.35–4.21 (1.5 H, m), 4.17–4.08 (2 H, m), 4.01–3.93 (0.5 H, m), 3.90–3.82 (1 H, m), 3.48–3.39 (0.5 H, m), 2.81–2.75 (1 H, m), 2.65–2.57 (1 H, m), 2.30–1.65 (26 H, 8 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{42}H_{48}NaO_{21}$: 911.2586, found: *m*/*z* 911.2591 $[M + Na]^+$.

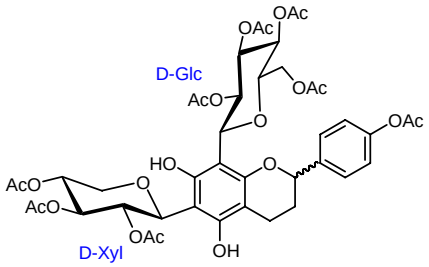
4'-Acetoxy-6-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-5,7-dihydroxyflavan (13ac)



By a procedure similar to that for **13aa**, glycosylation of glycosylflavan **12a** (450 mg, 0.71 mmol) with 2,3,4-tri-*O*-acetyl-D-arabinopyranosyl trichloroacetimidate (340 mg, 0.85 mmol) gave compound **13ac** (510 mg, 81%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{42}H_{48}O_{21}$; Colorless foam; TLC (EtOAc/hexane, 1:1) R_f = 0.42; ^{1}H NMR (600 MHz,

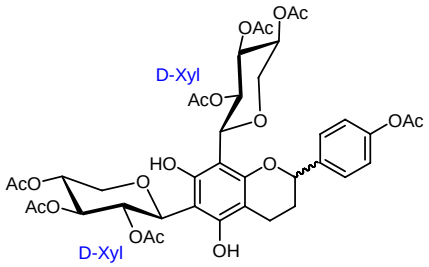
$CDCl_3$) δ 7.71 (0.5 H, d, *J* = 14.2 Hz), 7.57 (0.5 H, d, *J* = 8.4 Hz), 7.41 (0.75 H, d, *J* = 8.4 Hz), 7.36 (0.75 H, d, *J* = 8.4 Hz), 7.13–7.09 (1.5 H, m), 5.61–5.18 (8 H, m), 5.11–4.71 (2 H, m), 4.31–4.29 (1 H, m), 4.16–3.94 (3 H, m), 3.87–3.85 (1 H, m), 3.79–3.76 (1 H, m), 2.85–2.69 (1 H, m), 2.67–2.54 (1 H, m), 2.30–1.65 (26 H, 8 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{42}H_{48}NaO_{21}$ (M^+ + Na): 911.2586, found: *m*/*z* 911.2593.

4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-8-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-gluco pyranosyl)-5,7-dihydroxyflavan (13ba)



By a procedure similar to that for **13aa**, glycosylation of glycosylflavan **12b** (460 mg, 0.82 mmol) with 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl trichloroacetimidate (486 mg, 0.98 mmol), gave compound **13ba** (545 mg, 75%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{45}H_{48}O_{21}$; Colorless foam; TLC (EtOAc/hexane, 1:1) R_f = 0.45; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43–7.36 (3 H, m), 7.13–7.06 (2 H, m), 5.52–5.10 (4 H, m), 4.99–4.71 (6 H, m), 4.33–4.17 (2 H, m), 4.16–3.98 (2 H, m), 3.90–3.44 (1 H, m), 2.79–2.72 (1 H, m), 2.65–2.51 (1 H, m), 2.31–1.80 (26 H, 8 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{45}H_{48}NaO_{21}$: 911.2586, found: *m*/*z* 911.2590 $[M + Na]^+$.

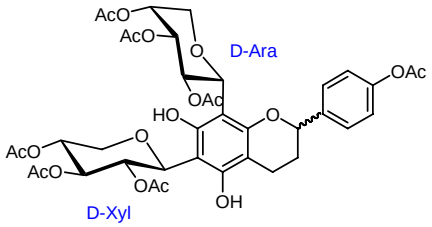
4'-Acetoxy-6,8-di-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-5,7-dihydroxyflavan (13bb)



By a procedure similar to that for **13aa**, glycosylation of glycosylflavan **12b** (400 mg, 0.72 mmol) with 2,3,4-tri-*O*-acetyl-D-xylopyranosyl trichloroacetimidate (364 mg, 0.87 mmol) gave compound **13bb** (420 mg, 71%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{39}H_{44}O_{19}$; Colorless foam; TLC (EtOAc/hexane, 1:1) R_f = 0.45; ^{1}H NMR (600 MHz,

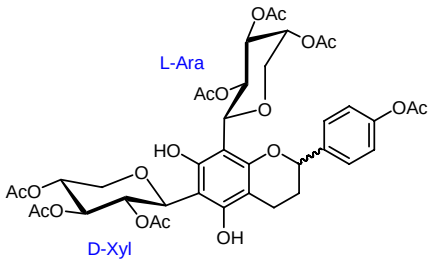
$CDCl_3$) δ 7.43–7.31 (2 H, m), 7.14–7.06 (2 H, m), 5.36–5.17 (4 H, m), 5.15–4.81 (6 H, m), 4.73 (0.5 H, br s), 4.65 (0.5 H, br s), 4.30–3.92 (3 H, m), 3.50–3.35 (1 H, m), 2.79–2.71 (1 H, m), 2.66–2.57 (1 H, m), 2.30–1.80 (23 H, 7 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{39}H_{44}NaO_{19}$: 839.2374, found: *m*/*z* 839.2381 $[M + Na]^+$.

4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-5,7-dihydroxyflavan (13bc)



By a procedure similar to that for **13aa**, glycosylation of glycosylflavan **12b** (600 mg, 1.08 mmol) with 2,3,4-tri-*O*-acetyl-D-arabinopyranosyl trichloroacetimidate (546 mg, 1.3 mmol) gave compound **13bc** (457 mg, 52%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{39}H_{44}O_{19}$; Colorless foam; TLC (EtOAc/hexane, 1:1) R_f = 0.43; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42–7.35 (2 H, m), 7.13–7.06 (2 H, m), 5.59–5.20 (5 H, m), 5.13–4.73 (5.5 H, m), 4.30–3.94 (3 H, m), 3.78–3.44 (1.5 H, m), 2.80–2.63 (1 H, m), 2.62–2.50 (1 H, m), 2.30–1.67 (23 H, 7 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{39}H_{44}NaO_{19}$: 839.2374, found: *m*/*z* 839.2379 $[M + Na]^+$.

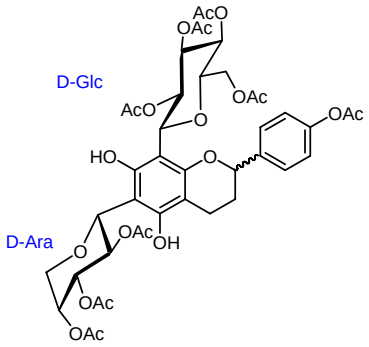
4'-Acetoxy-6-*C*-(tri-*O*-acetyl-β-D-xylopyranosyl)-8-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)-5,7-dihydroxyflavan (13bd)



By a procedure similar to that for **13aa**, glycosylation of glycosylflavan **12b** (1.46 g, 2.61 mmol) with 2,3,4-tri-*O*-acetyl-L-arabinopyranosyl trichloroacetimidate (2.2 g, 5.22 mmol) gave compound **13bd** (1.7 g, 80%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{39}H_{44}O_{19}$; White prisms, mp 238–240 °C; TLC (EtOAc/hexane, 3:2) R_f = 0.42; IR ν_{max} (neat) 3387, 2939, 1752, 1619, 1369, 1219 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (0.5 H, s, OH),

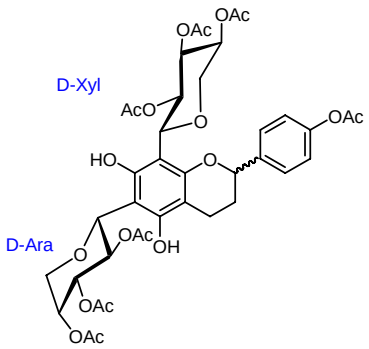
7.65 (0.5 H, s, OH), 7.41 (1 H, d, J = 8.8 Hz), 7.35 (1 H, d, J = 8.8 Hz), 7.33 (0.5 H, s, OH), 7.31 (0.5 H, s, OH), 7.13–7.08 (2 H, m), 5.53–5.37 (3 H, m), 5.33–5.27 (1 H, m), 5.14–4.97 (4 H, m), 4.87–4.82 (1 H, m), 4.30–4.25 (1 H, m), 4.10–4.05 (1 H, m), 3.80–3.75 (1 H, m), 3.45 (1 H, t, J = 11.2 Hz), 2.83–2.71 (1 H, m), 2.68–2.57 (1 H, m), 2.31 (3 H, s, 1 × OAc), 2.22 (3 H, s, 1 × OAc), 2.19–2.10 (1 H, m), 2.06 (3 H, s, 1 × OAc), 2.03 (3 H, s, 1 × OAc), 2.02–1.96 (6 H, m, 2 × OAc), 1.93–1.89 (1 H, m), 1.86 (1.5 H, s, 0.5 × OAc), 1.81 (1.5 H, s, 0.5 × OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 169.8, 169.7, 169.5, 169.4, 169.1/169.0, 168.1/168.0, 154.7/154.7, 152.9/152.8, 152.8/152.7, 149.8/149.6, 139.0/138.3, 126.6/126.0 (2 ×), 121.3 (2 ×), 102.4, 102.0/102.0, 101.2, 77.1/77.1, 74.2, 74.1/74.0, 73.7, 71.8/71.7, 70.3, 69.0, 68.4, 68.1, 67.9, 67.1, 30.6/28.6, 21.0, 20.8, 20.6 (3 ×), 20.6, 20.4, 19.6/18.8; HRMS (ESI) calcd for $C_{39}H_{44}O_{19}Na$: 839.2374, found: m/z 839.2369 $[M + Na]^+$.

4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-8-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-5,7-dihydroxyflavan (13ca)



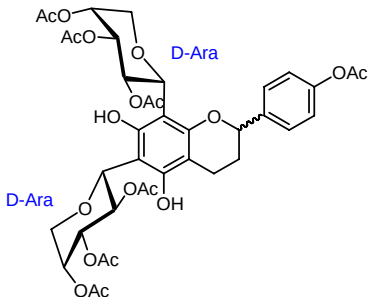
By a procedure similar to that for **13aa**, glycosylation of glycosylflavan **12c** (340 mg, 0.61 mmol) with 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl trichloroacetimidate (361 mg, 0.74 mmol), gave compound **13ca** (462 mg, 85%) as an inseparable mixture of diastereomers (existing rotamers). $C_{45}H_{48}O_{21}$; Colorless foam; TLC (EtOAc/hexane, 1:1) R_f = 0.45; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42–7.33 (3 H, m), 7.13–7.10 (2 H, m), 5.61–5.20 (6 H, m), 5.17–5.00 (3 H, m), 4.95–4.79 (1 H, m), 4.30–4.19 (1 H, m), 4.14–4.00 (2.5 H, m), 3.84–3.78 (1.5 H, m), 2.80–2.70 (1 H, m), 2.66–2.54 (1 H, m), 2.31–1.80 (26 H, 8 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{45}H_{48}NaO_{21}$: 911.2586, found: m/z 911.2589 $[M + Na]^+$.

4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-5,7-dihydroxyflavan (13cb)



By a procedure similar to that for **13aa**, glycosylation of glycosylflavan **12c** (400 mg, 0.72 mmol) with 2,3,4-tri-*O*-acetyl-D-xylopyranosyl trichloroacetimidate (364 mg, 0.87 mmol) gave compound **13cb** (350 mg, 60%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{39}H_{44}O_{19}$; Colorless foam; TLC (EtOAc/hexane, 1:1) R_f = 0.44; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.32 (2 H, m), 7.14–7.10 (2 H, m), 5.54–5.42 (2 H, m), 5.32–5.13 (3.5 H, m), 5.07–4.18 (4.5 H, m), 4.26–4.21 (1 H, m), 4.16–4.04 (2 H, m), 3.84–3.79 (1 H, m), 3.45–3.39 (1 H, m), 2.78–2.71 (1 H, m), 2.63–2.54 (1 H, m), 2.30–1.75 (23 H, 7 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{39}H_{44}NaO_{19}$: 839.2374, found: *m*/*z* 839.2369 $[M + Na]^+$.

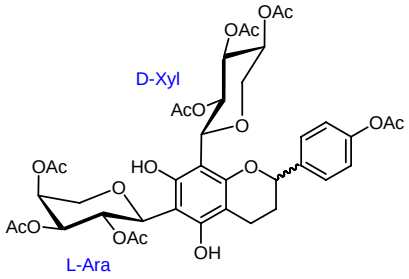
4'-Acetoxy-6,8-di-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-5,7-dihydroxyflavan (13cc)



By a procedure similar to that for **13aa**, glycosylation of glycosylflavan **12c** (300 mg, 0.54 mmol) with 2,3,4-tri-*O*-acetyl-D-arabinopyranosyl trichloroacetimidate (274 mg, 0.65 mmol) gave compound **13cc** (310 mg, 70%) as an inseparable mixture of diastereomers (existing rotamers). $C_{39}H_{44}O_{19}$; Colorless foam; TLC (EtOAc/hexane, 1:1) R_f = 0.43; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43–7.34 (2 H, m), 7.13–7.07 (2 H, m), 5.60–5.38 (3 H, m), 5.32–5.20 (3 H, m), 5.16–4.75 (4 H, m), 4.48–4.41 (0.5 H, m), 4.12–3.94 (2.5 H, m), 3.87–3.71 (2 H, m), 2.85–2.67 (1 H, m), 2.66–2.51 (1 H, m), 2.30–1.80 (23 H, 7 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{39}H_{44}NaO_{19}$: 839.2374, found: *m*/*z* 839.2380 $[M + Na]^+$.

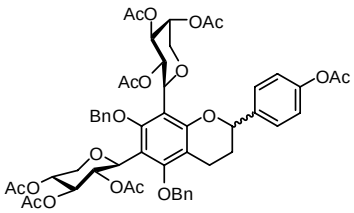
4'-Acetoxy-6-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)-8-*C*-(tri-*O*-acetyl-β-D-xylopyranosyl)-5,

7-dihydroxyflavan (13db)



By a procedure similar to that for **13aa**, glycosylation of glycosylflavan **12d** (810 mg, 1.45 mmol) with 2,3,4-tri-*O*-acetyl-D-xylopyranosyl trichloroacetimidate (1.22 g, 2.90 mmol) gave compound **13db** (766 mg, 65%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{39}H_{44}O_{19}$; White prisms, mp 162–163 °C; TLC (EtOAc/hexane, 3:2) R_f = 0.39; IR ν_{max} (neat) 3395, 2940, 1754, 1620, 1370, 1219 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.67 (0.4 H, br, OH), 7.61 (0.6 H, br, OH), 7.44 (1 H, d, *J* = 8.4 Hz), 7.37 (1 H, d, *J* = 8.4 Hz), 7.34 (0.4 H, s, OH), 7.32 (0.4 H, s, OH), 7.15–7.09 (2 H, m), 5.61–5.54 (1 H, m), 5.42 (1 H, br), 5.32–4.99 (6 H, m), 4.90–4.86 (1 H, m), 4.24 (1 H, dd, *J* = 11.2, 5.6 Hz), 4.09 (1 H, dt, *J* = 13.6, 2 Hz), 3.80 (1 H, d, *J* = 13.6 Hz), 3.47–3.41 (1 H, m), 2.88–2.72 (1 H, m), 2.68–2.59 (1 H, m), 2.31 (3 H, s, 1 × OAc), 2.24–2.16 (4 H, m, 1 × OAc and 1 × C_3-H), 2.08–1.98 (12 H, m, 4 × OAc), 1.95–1.67 (4 H, m, 1 × OAc and 1 × C_3-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 169.9/169.8, 169.7, 169.6, 169.4, 169.2/169.2, 168.3/168.3, 155.2, 153.2/153.0, 152.2, 149.9/149.7, 139.2/138.4, 126.8/126.1 (2 ×), 121.5/121.5 (2 ×), 102.8, 102.8/102.7, 100.4/100.3, 77.1, 74.7, 73.8, 73.6, 72.0, 70.6/70.5, 69.0, 68.7, 68.2, 67.7/67.7, 67.3, 31.0/28.5, 21.2/21.1, 21.0, 20.8, 20.7, 20.6, 20.5, 20.4, 19.7/18.8; HRMS (ESI) calcd for $C_{39}H_{44}O_{19}Na$: 839.2374, found: *m*/*z* 839.2366 $[M + Na]^+$.

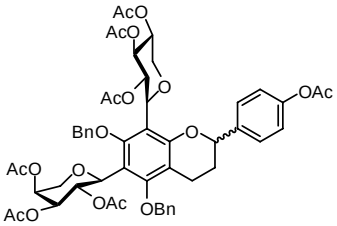
4'-Acetoxy-5,7-di-benzoxy-6-*C*-(tri-*O*-acetyl-β-D-xylopyranosyl)-8-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)flavan (13bdBn)



To a solution of **13bd** (1.38 g, 1.69 mmol) and K_2CO_3 (934 mg, 6.76 mmol) in anhydrous DMF (5 mL) was added benzyl bromide (808 μL, 6.76 mmol) dropwise and stirred at room temperature for 12 h. The mixture was evaporated in vacuo and partitioned between H_2O and EtOAc. The organic phase was washed with water and brine, dried over anhydrous $MgSO_4$,

filtered and concentrated. The residue was purified by flash column chromatography (EtOAc/hexane, 2:3) to yield **13bdBn** (1.43 g, 84%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{53}H_{56}O_{19}$; white prisms, mp 222–222.8 °C; TLC (EtOAc/hexane, 3:2) R_f = 0.61; IR ν_{max} (neat) 2933, 1746, 1587, 1367, 1220 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.74–7.55 (2 H, m), 7.52–7.28 (10 H, m), 7.15–7.06 (2 H, m), 6.41–5.50 (2 H, m), 5.28–5.00 (4 H, m), 4.97–4.89 (2 H, m), 4.80–4.55 (5 H, m), 4.09–3.88 (2 H, m), 3.76–3.18 (2 H, m), 3.07–2.72 (2 H, m), 2.28 (3 H, s, 1 × OAc), 2.16–2.11 (1 H, m), 2.01–1.71 (16 H, m, 5 × OAc and 1 × C_3-H), 1.50 (3 H, s, 1 × OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 170.1, 170.1/169.9, 169.8/169.7, 169.4/169.1, 168.9/168.8, 168.4/168.1, 158.8/158.5, 157.2, 156.7/156.7, 150.2/149.9, 139.2/138.4, 137.2/137.1, 136.3, 128.7/128.5 (2 ×), 128.4/128.1 (2 ×), 127.7/127.4 (2 ×), 127.3 (2 ×), 127.2/127.0 (2 ×), 126.2, 125.5, 121.6/121.3 (2 ×), 114.8/114.7, 114.4/114.2, 112.6/111.9, 79.2/79.1, 78.5/77.8, 75.8/75.6, 74.7/74.4, 74.0/73.9, 73.4, 72.8/72.5, 70.6/70.1, 69.2, 68.7/68.5, 68.4/68.3, 66.9/66.8, 66.7/66.6, 30.5/29.3, 21.5/21.1, 20.8 (2 ×), 20.7 (2 ×), 20.5/20.5, 20.4/20.3, 20.0/19.6; HRMS (ESI) calcd for $C_{53}H_{56}O_{19}Na$: 1019.3314, found: *m*/*z* 1019.3311 $[M + Na]^+$.

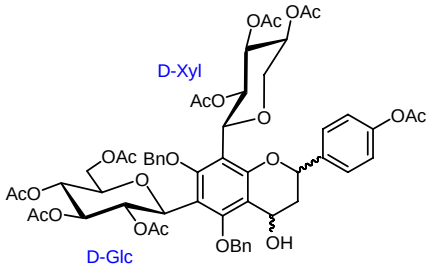
4'-Acetoxy-5,7-di-benzoxy-6-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)-8-*C*-(tri-*O*-acetyl-β-D-xylopyranosyl)flavan (13dbBn)



By a procedure similar to that for **13bdBn**, compound **13db** (780 mg, 0.95 mmol) was treated with benzyl bromide (460 μL, 3.82 mmol) in the presence of K_2CO_3 (530 mg, 3.82 mmol) in anhydrous DMF (5 mL) to give **13dbBn** (836 mg, 88%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{53}H_{56}O_{19}$; White prisms, mp 125–127 °C; TLC (EtOAc/hexane, 3:2) R_f = 0.65; IR ν_{max} (neat) 2925, 1749, 1588, 1367, 1220 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.62–7.24 (12 H, m), 7.16–7.08 (2 H, m), 6.43–6.20 (1 H, m), 6.03–5.94 (1 H, m), 5.60–5.45 (1 H, m), 5.26–4.56 (10 H, m), 4.24–3.26 (4 H, m), 2.94–2.56 (2 H, m), 2.29 (3 H, s, 1 × OAc), 2.09–1.73 (17 H, m, 5 × OAc and 2 × C_3-H), 1.46–1.37 (3 H, m, 1 × OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 169.7, 169.5/169.3, 169.1/169.0, 168.8, 168.6, 168.2/167.8, 158.7/158.1, 157.2/156.5, 156.0/155.9, 149.8/149.4, 138.5, 138.1/137.9, 136.1/135.9,

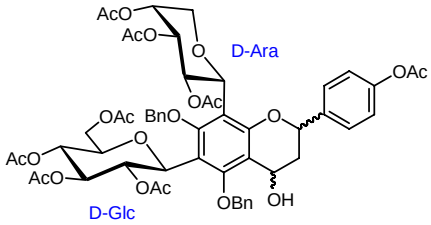
128.5/128.2 (2 ×), 127.9 (2 ×), 127.5/127.0 (2 ×), 126.8, 126.6/125.9, 125.5 (2 ×), 125.1 (2 ×), 121.4/121.1 (2 ×), 115.0/114.8, 114.0/113.8, 112.2/111.8, 78.3/78.1, 76.5/76.3, 75.8/74.7, 74.2/74.1, 73.9/73.7, 73.1/72.9, 72.7, 69.3/69.1, 68.9/68.8, 68.6, 68.4, 68.1/67.3, 66.7/66.3, 28.9/28.2, 20.8, 20.5 (3 ×), 20.3, 20.2, 20.1, 19.6/19.5; HRMS (ESI) calcd for $C_{53}H_{56}O_{19}Na$: 1019.3314, found: *m*/*z* 1019.3326 $[M + Na]^+$.

4'-Acetoxy-6-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-5,7-dibenzyloxy-4-hydroxyflavan (14abBn)



By a procedure similar to that for **14aaBn**, the subsequent benzylation and oxidation of **13ab** (420 mg, 0.47 mmol) gave compound **14abBn** (375 mg, 73%) as an inseparable diastereomeric mixture (existing as rotamers). $C_{56}H_{60}O_{22}$; Light-yellow foam; TLC (EtOAc/hexane, 1:1) R_f = 0.35; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75–7.34 (12 H, m), 7.16–7.06 (2 H, m), 6.44–6.06 (2 H, m), 5.46–4.56 (12.5 H, m), 4.21–3.28 (5.5 H, m), 2.31–1.71 (26 H, 8 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{56}H_{60}NaO_{22}$: 1107.3474, found: *m*/*z* 1107.3468 $[M + Na]^+$.

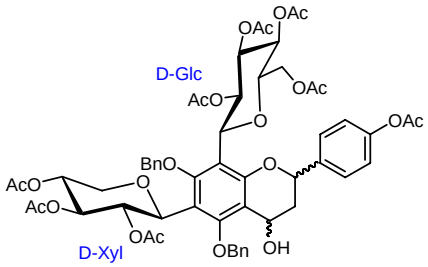
4'-Acetoxy-6-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-5,7-dibenzyloxy-4-hydroxyflavan (14acBn)



By a procedure similar to that for **14aaBn**, the subsequent benzylation and oxidation of **13ac** (510 mg, 0.57 mmol) gave compound **14acBn** (390 mg, 63%) as an inseparable diastereomeric mixture (existing as rotamers). $C_{56}H_{60}O_{22}$; Light-yellow foam; TLC (EtOAc/hexane, 1:1) R_f = 0.32; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65–7.26 (12 H, m), 7.20–7.14 (1 H, m), 7.12–7.07 (1 H, m), 6.22 (0.4 H, t, J = 9.6 Hz), 6.04 (0.3 H, t, J = 9.6 Hz), 5.96 (0.3 H, t, J = 9.6 Hz), 5.47–4.60 (14.5 H, m), 4.24–3.84 (3.5 H, m), 3.67–3.55 (0.8 H, m), 3.05 (0.2 H, t, J = 9.6 Hz), 2.29–1.66

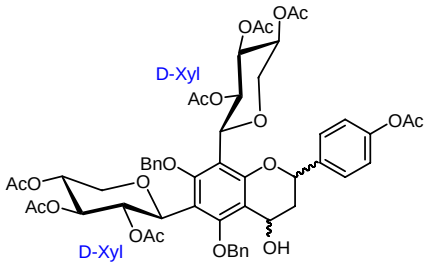
(26 H, 8 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{56}H_{60}NaO_{22}$: 1107.3474, found: *m*/*z* 1107.3468 $[M + Na]^+$.

4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-8-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-gluco pyranosyl)-5,7-dibenzyloxy-4-hydroxyflavan (14baBn)



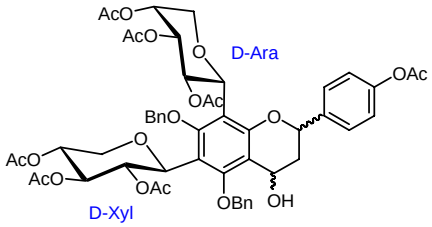
By a procedure similar to that for **14aaBn**, the subsequent benzylation and oxidation of **13ba** (545 mg, 0.62 mmol) gave compound **14baBn** (444 mg, 66%) as an inseparable diastereomeric mixture (existing as rotamers). $C_{56}H_{60}O_{22}$; Light-yellow foam; TLC (EtOAc/hexane, 1:1) R_f = 0.35; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48–7.36 (12 H, m), 7.23–7.17 (2 H, m), 6.15–6.11 (0.5 H, m), 5.38–5.31 (2.5 H, m), 5.24–4.79 (11 H, m), 4.66–4.63 (0.5 H, m), 4.22–4.08 (3.5 H, m), 3.98–3.46 (2 H, m), 2.32–1.72 (26 H, 8 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{56}H_{60}NaO_{22}$: 1107.3474, found: *m*/*z* 1107.3481 $[M + Na]^+$.

4'-Acetoxy-6,8-di-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-5,7-dibenzyloxy-4-hydroxyflavan (14bbBn)



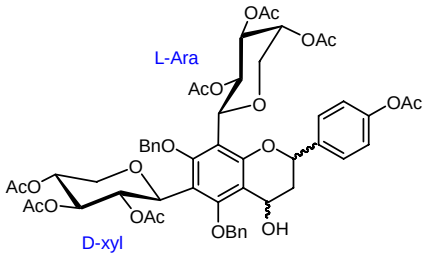
By a procedure similar to that for **14aaBn**, the subsequent benzylation and oxidation of **13bb** (420 mg, 0.51 mmol) gave compound **14bbBn** (210 mg, 41%) as an inseparable diastereomeric mixture (existing as rotamers). $C_{53}H_{56}O_{20}$; Light-yellow foam; TLC (EtOAc/hexane, 1:1) R_f = 0.38; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60–7.33 (12 H, m), 7.18–7.09 (2 H, m), 6.19–5.98 (0.5 H, m), 5.39–5.07 (7 H, m), 5.03–4.55 (7.5 H, m), 4.24–3.93 (2 H, m), 3.85–3.74 (1 H, m), 3.61–3.24 (1 H, m), 2.40–1.78 (23 H, 7 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{53}H_{56}NaO_{20}$: 1035.3263, found: *m*/*z* 1035.3272 $[M + Na]^+$.

4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-5,7-dibenzoxy-4-hydroxyflavan (14bcBn)



By a procedure similar to that for **14aaBn**, the subsequent benzylation and oxidation of **13bc** (457 mg, 0.56 mmol) gave compound **14bcBn** (357 mg, 63%) as an inseparable diastereomeric mixture (existing as rotamers). $C_{53}H_{56}O_{20}$; Light-yellow foam; TLC (EtOAc/hexane, 1:1) R_f = 0.38; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58–7.25 (12 H, m), 7.15–7.11 (2 H, m), 5.38–5.29 (5 H, m), 5.27–5.13 (5 H, m), 5.11–4.93 (4 H, m), 4.76–4.57 (1.5 H, m), 4.20–4.08 (0.5 H, m), 4.08–3.80 (2 H, m), 3.77–3.61 (1 H, m), 2.29–1.99 (23 H, 7 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{53}H_{56}NaO_{20}$: 1035.3263, found: *m*/*z* 1035.3271 $[M + Na]^+$.

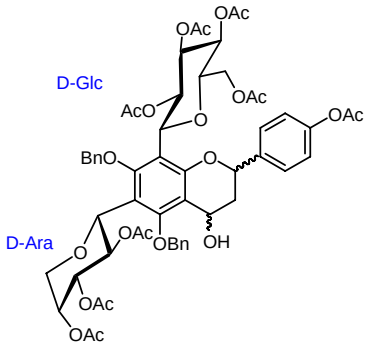
4'-Acetoxy-6-*C*-(tri-*O*-acetyl-β-D-xylopyranosyl)-8-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)-5,7-benzyloxy-4-hydroxyflavan (14bdBn)



By a procedure similar to that for **14aaBn**, the subsequent benzylation and oxidation of **13bd** (1.56 g, 1.57 mmol) gave compound **14bdBn** (1.44 g, 90%) as an inseparable diastereomeric mixture (existing as rotamers). $C_{53}H_{56}O_{20}$; white prisms, mp 255–256 °C; TLC (EtOAc/hexane, 3:2) R_f = 0.42; IR ν_{max} (neat) 3482, 2937, 1749, 1588, 1368, 1221 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62 (2 H, d, *J* = 8.4 Hz), 7.57–7.31 (10 H, m), 7.09 (2 H, d, *J* = 8.4 Hz), 6.22–6.08 (1 H, m), 5.99–5.81 (1 H, m), 5.39 (1 H, d, *J* = 11.6 Hz), 5.32–5.07 (4 H, m), 5.04–4.92 (3 H, m), 4.82–4.78 (2 H, m), 4.75–4.73 (1 H, d, *J* = 10 Hz), 4.71–4.59 (1 H, m), 4.11 (1 H, dd, *J* = 10.8, 5.2 Hz), 3.98 (1 H, d, *J* = 13.2 Hz), 3.48 (1 H, d, *J* = 13.2 Hz), 3.22 (1 H, t, *J* = 10.8 Hz), 2.28 (3 H, s), 2.21–2.14 (1 H, m), 2.09–2.05 (1 H, m), 2.00 (3 H, s), 1.98 (3 H, s), 1.93 (3 H, s), 1.84 (3 H, s), 1.79–1.72 (4 H, m), 1.50 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 170.0, 169.8, 169.7, 169.3, 168.9, 168.2, 160.6, 158.5, 156.6, 150.0, 138.3, 136.8, 136.0, 128.7 (2 ×), 128.6/128.5 (2

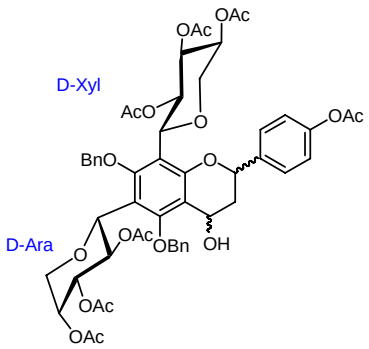
×), 128.4/127.9 (2 ×), 127.7/127.6 (2 ×), 127.1/126.9 (2 ×), 126.3, 125.4, 121.6/121.3 (2 ×), 115.4, 115.3, 114.7, 79.4, 78.3, 74.5/74.1, 74.0 (2 ×), 73.8, 72.8/72.4, 70.5, 69.1, 68.6, 68.3, 66.9, 66.5, 59.4, 37.7, 21.1, 20.7, 20.7 (2 ×), 20.5/20.4, 20.3, 20.3; HRMS (ESI) calcd for $C_{53}H_{56}O_{20}Na$: 1035.3263, found: *m*/*z* 1035.3268 $[M + Na]^+$.

4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-8-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-5,7-dibenzyloxy-4-hydroxyflavan (14caBn)



By a procedure similar to that for **14aaBn**, the subsequent benzylation and oxidation of **13ca** (462 mg, 052 mmol) gave compound **14caBn** (367 mg, 65%) as an inseparable diastereomeric mixture (existing as rotamers). $C_{56}H_{60}O_{22}$; Light-yellow foam; TLC (EtOAc/hexane, 1:1) R_f = 0.35; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65–7.25 (12 H, m), 7.21–7.15 (2 H, m), 6.48–6.25 (1 H, m), 6.00–5.67 (1 H, m), 5.32–4.71 (12 H, m), 4.17–4.09 (2 H, m), 4.06–3.87 (2.5 H, m), 3.65–3.55 (1 H, m), 3.40–3.31 (0.5 H, m), 2.31–1.70 (26 H, 8 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{56}H_{60}NaO_{22}$: 1107.3474, found: *m*/*z* 1107.3482 $[M + Na]^+$.

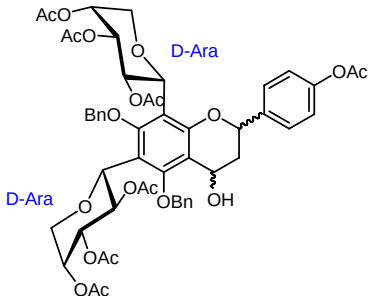
4'-Acetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)- 5,7-dibenzyloxy-4-hydroxyflavan (14cbBn)



By a procedure similar to that for **14aaBn**, the subsequent benzylation and oxidation of **13cb** (350 mg, 0.43 mmol) gave compound **14cbBn** (170 mg, 39%) as an inseparable diastereomeric mixture (existing as rotamers). $C_{53}H_{56}O_{20}$; Light-yellow foam; TLC (EtOAc/hexane, 1:1) R_f =

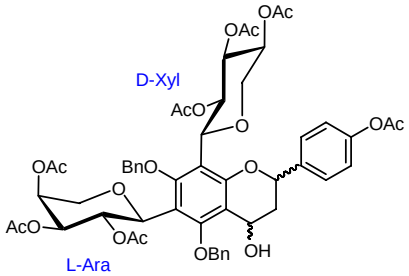
0.38; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62–7.37 (12 H, m), 7.16–7.08 (2 H, m), 6.48–5.63 (1 H, m), 5.35–4.65 (13.5 H, m), 4.14–4.10 (2 H, m), 3.63–3.55 (2 H, m), 3.35–3.03 (0.5 H, m), 2.30–1.73 (23 H, 7 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{53}H_{56}NaO_{20}$: 1035.3263, found: *m*/*z* 1035.3274 $[M + Na]^+$.

4'-Acetoxy-6,8-di-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-5,7-dibenzyloxy-4-hydroxyflavan (14ccBn)



By a procedure similar to that for **14aaBn**, the subsequent benzylation and oxidation of **13cc** (310 mg, 0.38 mmol) gave compound **14ccBn** (262 mg, 68%) as an inseparable diastereomeric mixture (existing as rotamers). $C_{53}H_{56}O_{20}$; Light-yellow foam; TLC (EtOAc/hexane, 1:1) R_f = 0.35; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50–7.26 (12 H, m), 7.21–7.09 (2 H, m), 6.21–6.13 (0.5 H, m), 5.35–4.72 (15.5 H, m), 4.20–3.91 (1 H, m), 3.80–3.38 (2 H, m), 2.28–1.82 (23 H, 7 × OAc; C_3-H_a and H_b); HRMS calcd for $C_{53}H_{56}NaO_{20}$: 1035.3263, found: *m*/*z* 1035.3275 $[M + Na]^+$.

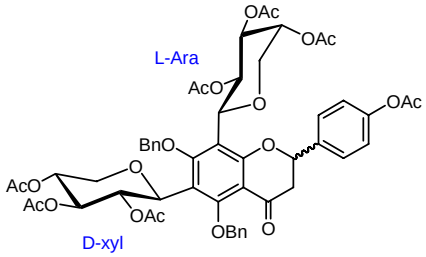
4'-Acetoxy-6-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)-8-*C*-(tri-*O*-acetyl-β-D-xylopyranosyl)-5,7-dibenzyloxy-4-hydroxyflavan (14dbBn)



By a procedure similar to that for **14aaBn**, the subsequent benzylation and oxidation of **13db** (810 mg, 0.81 mmol) gave compound **14dbBn** (800 mg, 96%) as an inseparable diastereomeric mixture (existing as rotamers). $C_{53}H_{56}O_{20}$; White prisms, mp 133–135 °C; TLC (EtOAc/hexane, 3:2) R_f = 0.44; IR ν_{max} (neat) 3486, 2933, 1750, 1589, 1369, 1222 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62–7.25 (12 H, m), 7.16–7.08 (2 H, m), 6.43–6.39 (0.5 H, m), 6.22 (0.5 H, t, *J* = 9.6 Hz), 6.04–5.66 (1.5 H, m), 5.59 (0.5 H, d, *J* = 12.8 Hz), 5.48–5.08 (4 H, m), 5.02–4.63

(7 H, m), 4.21–3.97 (2 H, m), 3.59–3.54 (1 H, m), 3.33–3.30 (0.3 H, m), 2.80 (0.7 H, t, J = 11.2 Hz), 2.28 (3 H, s, 1 × OAc), 2.21–1.95 (10 H, m, 3 × OAc and 1 × C_4-H), 1.92–1.89 (3 H, m, 1 × OAc), 1.85–1.66 (5 H, m, 1 × OAc and 2 × C_3-H), 1.57–1.41 (3 H, m, 1 × OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.2, 170.0, 169.8, 169.7, 169.4, 169.1, 168.3, 160.6, 158.8, 156.0, 149.7, 138.2, 138.0, 136.1, 128.7/128.5 (2 ×), 128.4/128.2 (2 ×), 127.5 (2 ×), 127.3/127.3, 127.2/127.1, 126.3 (2 ×), 125.5 (2 ×), 121.4 (2 ×), 115.8, 115.0, 114.7, 78.5, 78.2, 74.1, 73.8, 73.2, 72.7, 72.2, 69.2, 68.8, 68.5, 68.3, 67.7, 66.5, 59.4, 37.9, 21.1, 20.7 (2 ×), 20.7 (2 ×), 20.5/20.3, 19.9/19.8; HRMS (ESI) calcd for $C_{53}H_{56}O_{20}Na$: 1035.3263, found: m/z 1035.3265 $[M + Na]^+$.

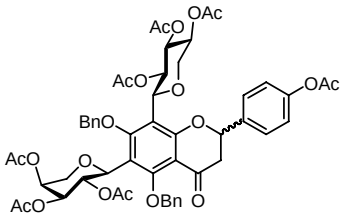
4'-Acetoxy-5,7-di-benzoxy-6-*C*-(tri-*O*-acetyl-β-D-xylopyranosyl)-8-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)flavanone (15bdBn).



Compound **14bdBn** was oxidized with PDC in CH_2Cl_2 for 4 h at refluxing to give **15bdBn** as an inseparable mixture of diastereomers (existing as rotamers). $C_{53}H_{54}O_{20}$; colorless foam; TLC (EtOAc/hexane, 3:2) R_f = 0.50; IR ν_{max} (neat) 2938, 1747, 1692, 1576, 1370, 1222 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (1 H, d, J = 8.8 Hz), 7.70–7.30 (11 H, m), 7.17–7.15 (2 H, m), 6.43–6.13 (1 H, m), 5.74–5.65 (1 H, m), 5.55 (0.5 H, d, J = 12.4 Hz), 5.35 (0.5 H, d, J = 10.8 Hz), 5.22–5.09 (2 H, m), 5.05 (1 H, t, J = 9.6 Hz), 4.98–4.87 (2 H, m), 4.83–4.57 (5 H, m), 4.03–3.88 (2 H, m), 3.45–3.34 (1 H, m), 3.19–2.62 (3 H, m), 2.30 (3 H, s, 1 × OAc), 2.02–1.70 (15 H, m, 5 × OAc), 1.31–1.21 (3 H, m, 1 × OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 188.1, 170.0, 169.7/169.6, 169.6, 169.5, 169.1, 168.4, 168.3, 165.3, 163.6, 159.9, 150.6, 136.2, 136.1 (2 ×), 128.6/128.4 (2 ×), 128.3/128.3 (2 ×), 128.2/128.1 (2 ×), 128.1/128.0 (2 ×), 127.8/127.6, 127.3/127.2, 127.0/126.9 (2 ×), 121.6/121.5 (2 ×), 117.3, 114.5, 111.1, 79.2/79.0, 78.2, 73.6, 72.8, 72.7, 72.2, 70.0, 68.9/68.8, 68.0, 67.9, 67.7, 66.8, 66.3, 46.0, 20.8, 20.5, 20.5, 20.4, 20.3, 20.1, 19.5; HRMS

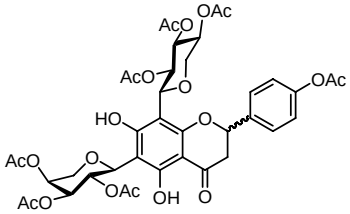
(ESI) calcd for $C_{53}H_{54}O_{20}Na$: 1033.3106, found: *m*/*z* 1033.3097 $[M + Na]^+$.

4'-Acetoxy-5,7-di-benzoxy-6-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)-8-*C*-(tri-*O*-acetyl-β-D-xylopyranosyl)flavanone (15dbBn)



By a procedure similar to that for **15bdBn**, compound **14dbBn** (700 mg, 0.691 mmol) was treated with PDC (1.04 g, 2.764 mmol) to afford **15dbBn** (600 mg, 86%) as an inseparable mixture of diastereomers (existing as rotamers). $C_{53}H_{54}O_{20}$; White foam; TLC (EtOAc/hexane, 3:2) R_f = 0.50; IR ν_{max} (neat) 2939, 1750, 1692, 1577, 1369, 1222 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.67–7.28 (12 H, m), 7.19–7.12 (2 H, m), 6.08–5.96 (1 H, m), 5.87–5.70 (1 H, m), 5.59–5.47 (1 H, m), 5.35–5.04 (3 H, m), 4.95–4.91 (2 H, m), 4.85–4.61 (5 H, m), 3.97–3.77 (2 H, m), 3.48–3.41 (1 H, m), 3.21–2.69 (3 H, m), 2.27 (3 H, s, 1 × OAc), 2.09–1.68 (15 H, m, 5 × OAc), 1.53–1.24 (3 H, m, 1 × OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 188.5/188.2, 169.9/169.7, 169.5/169.5, 169.4/169.3, 169.0, 168.6/168.5, 168.4/168.3, 168.1/168.0, 165.4/165.2, 163.7/163.2, 159.9/159.7, 150.5/150.1, 137.3/137.2, 136.2/135.8, 135.5/135.1, 128.5/128.3 (2 ×), 128.2/128.2 (2 ×), 128.1/127.9 (2 ×), 127.8/127.1, 126.9/126.9, 126.2/126.0 (2 ×), 125.1/125.0 (2 ×), 121.5/121.4 (2 ×), 118.3/117.7, 114.9/114.3, 112.2/111.2, 78.7/78.5, 78.1/78.0, 73.8/73.7, 73.4/73.2, 72.8/72.7, 72.6/72.5, 72.4/72.3, 68.8/68.7, 68.4, 68.2, 67.9/67.7, 67.5/67.4, 66.4/66.2, 45.2/44.1, 20.8, 20.4 (2 ×), 20.3 (2 ×), 20.2/20.0, 19.6; HRMS (ESI) calcd for $C_{53}H_{54}O_{20}Na$: 1033.3106, found: *m*/*z* 1033.3102 $[M + Na]^+$.

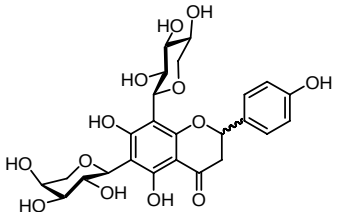
4'-Acetoxy-6-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)-8-*C*-(tri-*O*-acetyl-β-D-xylopyranosyl)-5,7-di-hydroxyflavanone (15db)



By a procedure similar to that for **15bd**, hydrogenolysis of compound **15dbBn** (260 mg, 0.256 mmol) gave **15db** (167 mg, 83%) as an inseparable mixture (existing as rotamers).

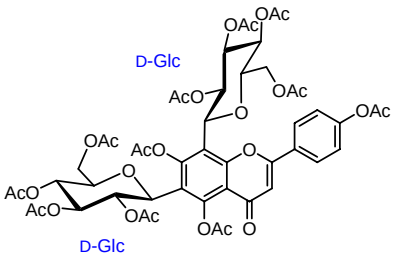
$C_{39}H_{42}O_{20}$; White prisms, mp 156–158 °C; TLC (EtOAc/hexane, 3:2) R_f = 0.37; IR ν_{max} (neat) 3299, 2922, 1748, 1632, 1369, 1219 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 12.60 (1 H, br, OH), 8.70 (1 H, br, OH), 7.56 (1 H, d, *J* = 8.8 Hz), 7.44 (1 H, d, *J* = 8.8 Hz), 7.19 (2 H, d, *J* = 8.8 Hz), 5.79 (1 H, br), 5.67 (1 H, d, *J* = 12 Hz), 5.47–5.26 (4 H, m), 5.16 (1 H, d, *J* = 9.6 Hz), 4.98 (1 H, t, *J* = 9.6 Hz), 4.90 (1 H, d, *J* = 9.6 Hz), 4.14–4.10 (2 H, m), 3.82 (1 H, d, *J* = 13.6 Hz), 3.38 (1 H, t, *J* = 11.2 Hz), 3.03 (1 H, br), 2.84–2.80 (1 H, m), 2.31–2.31 (3 H, m, 1 × OAc), 2.25 (3 H, s, 1 × OAc), 2.08–1.95 (12 H, m, 4 × OAc), 1.84–1.79 (3 H, m, 1 × OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.4, 169.3, 169.1, 168.9 (2 ×), 168.4, 168.4, 168.0, 162.9, 161.7, 160.3, 149.8, 135.3, 126.6/126.2 (2 ×), 121.5/121.5 (2 ×), 102.7, 101.6 (2 ×), 78.5/78.1, 73.9, 73.6, 73.1, 71.3, 71.1, 69.4, 68.4, 68.2, 67.4, 66.9, 42.8, 21.3 (2 ×), 20.9, 20.9, 20.8, 20.7, 20.5; HRMS (ESI) calcd for $C_{39}H_{41}O_{20}$: 829.2191, found: *m*/*z* 829.2169 $[M - H]^-$.

6-*C*-α-L-arabinopyranosyl-8-*C*-β-D-xylopyranosyl-4,5,7-trihydroxyflavanone (2db)



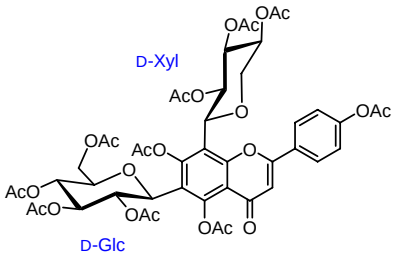
By a procedure similar to that for **2bd**, saponification of **15db** (114.7 mg, 0.138 mmol) gave **2db** (70 mg, 95%).$C_{25}H_{28}O_{13}$; yellow prisms, mp > 220 °C (decomposed); IR ν_{max} (neat) 3367, 2923, 1631, 1542, 1448, 1375, 1238, 1079 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz) δ 7.32 (2 H, t, *J* = 8.4 Hz), 6.79 (2 H, d, *J* = 8.4 Hz), 5.29–5.23 (1 H, m), 4.78–4.76 (1 H, m), 4.65–4.57 (2 H, m), 4.31 (1 H, br), 3.93–3.84 (3 H, m), 3.62 (1 H, d, *J* = 12.4 Hz), 3.57–3.51 (2 H, m), 3.34–3.31 (1 H, m), 3.22 (1 H, t, *J* = 11.2 Hz), 2.95–2.87 (1 H, m), 2.66–2.57 (1 H, m); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 189.2/189.1, 179.1, 161.9, 160.2/160.0, 156.7/156.6, 130.4, 126.9/126.8 (2 ×), 114.7 (2 ×), 107.1/107.0, 105.6, 96.3/96.2, 79.3, 76.3/76.1, 75.1 (3 ×), 71.1/70.8, 70.2, 70.1, 69.7, 69.1, 67.7, 41.7/41.6; HRMS (ESI) calcd for $C_{25}H_{27}O_{13}$: 535.1452, found: *m*/*z* 535.1455 $[M - H]^-$.

5,7,4'-Triacetoxy-6,8-di-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)flavone (3aaAc).[15]



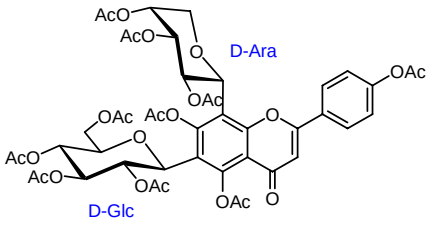
Compound **14aaBn** was treated with DDQ in chlorobenzene for 24 h at 140 °C to give a crude diglycosylapigenin derivative, which was subjected to hydrogenolysis on Pd/C in CH_3OH/EtOAc for 1 h at room temperature, followed by peracetylation with Ac_2O in pyridine to give **3aaAc**. $C_{49}H_{52}O_{26}$; white solid, mp 149–151 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.28; $[\alpha]_D^{20}$ = +19.1 (*c* = 1.0, $CHCl_3$) [lit.[15] $[\alpha]_D^{21}$ = +18.5 (*c* = 0.79, $CHCl_3$)]; IR (film) 3455, 2929, 1785, 1763, 1657, 1632, 1421, 1010 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.04 (2 H, d, *J* = 8.4 Hz), 7.36 (2 H, d, *J* = 8.4 Hz), 6.63 (1 H, s), 5.90 (1 H, t, *J* = 9.5 Hz), 5.66 (1 H, br s), 5.44 (1 H, t, *J* = 9.7 Hz), 5.39 (1 H, t, *J* = 9.7 Hz), 5.27 (1 H, t, *J* = 9.4 Hz), 5.12 (1 H, t, *J* = 9.9 Hz), 4.78 (1 H, d, *J* = 10.1 Hz), 4.55 (1 H, d, *J* = 10.1 Hz), 4.42 (1 H, dd, *J* = 12.5, 4.6 Hz), 4.25 (1 H, dd, *J* = 12.7, 4.0 Hz), 4.16 (1 H, dd, *J* = 12.7, 2.2 Hz), 3.91 (1 H, dd, *J* = 12.5, 1.3 Hz), 3.78 (1 H, br d, *J* = 6.3 Hz), 3.72 (1 H, ddd, *J* = 9.7, 4.6, 1.3 Hz), 2.52 (3 H, s), 2.46 (3 H, s), 2.32 (3 H, s), 2.07 (3 H, s), 2.03 (3 H, s), 2.02 (3 H, s), 1.99 (3 H, s), 1.96 (3 H, s), 1.89 (3 H, s), 1.85 (3 H, s), 1.72 (3 H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.9, 170.8, 170.4, 170.3, 170.2, 169.8, 169.64, 169.60, 168.9, 168.1, 167.5, 161.6, 156.8, 153.6, 153.1, 149.5, 128.6, 127.8 (2 ×), 127.6, 122.7 (2 ×), 118.8, 116.9, 115.3, 108.8, 74.2, 74.1, 73.8, 72.6, 69.3, 69.1, 68.2, 68.1, 68.0, 67.92, 61.90, 61.7, 21.3, 21.2, 21.1, 21.0, 20.9, 20.78, 20.76, 20.66, 20.62, 20.4, 20.2; HRMS calcd for $C_{49}H_{52}NaO_{26}$: 1079.2645, found: *m*/*z* 1079.2652 $[M + Na]^+$.

5,7,4'-Triacetoxy-6-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)flavone (3abAc)



By a procedure similar to that for **3aaAc**, compound **14abBn** (120 mg, 0.11 mmol) was subjected to oxidation (with DDQ), debenzylation and acetylation to give **3abAc** (55 mg, 51% overall yield). $C_{46}H_{48}O_{24}$; White solid, mp 133–135 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.33; $[\alpha]_D^{20}$ = –5.2 (*c* = 1.0, $CHCl_3$); IR (film) 3421, 2899, 1756, 1721, 1632, 1611, 1473, 1129, 1021 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.96 (2 H, d, *J* = 8.6 Hz), 7.35 (2 H, d, *J* = 8.6 Hz), 6.57 (1 H, s), 5.70–5.65 (2 H, m), 5.38 (1 H, t, *J* = 9.6 Hz), 5.27 (1 H, t, *J* = 9.4 Hz), 5.21–5.16 (1 H, m), 5.13 (1 H, t, *J* = 9.8 Hz), 4.81 (1 H, br d, *J* = 10.0 Hz), 4.47 (1 H, d, *J* = 9.8 Hz), 4.43 (1 H, dd, *J* = 12.5, 4.3 Hz), 4.36 (1 H, dd, *J* = 11.5, 5.6 Hz), 3.92 (1 H, d, *J* = 12.1 Hz), 3.78 (1 H, br t, *J* = 3.4 Hz), 3.38 (1 H, t, *J* = 11.1 Hz), 2.53 (3 H, s), 2.46 (3 H, s), 2.32 (3 H, s), 2.07 (3 H, s), 2.04 (3 H, s), 2.02 (3 H, s), 2.00 (3 H, s), 1.98 (3 H, s), 1.86 (3 H, s), 1.74 (3 H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.9, 170.4, 170.3, 170.2, 170.0, 169.85, 169.80, 169.6, 169.0, 168.1, 167.6, 161.9, 156.8, 153.5, 152.8, 149.3, 128.8, 127.9 (2 ×), 122.7 (2 ×), 118.7, 117.4, 115.3, 108.9, 74.3, 74.2, 73.4, 72.6, 69.5, 69.1, 68.9, 68.1, 68.0, 67.7, 61.8, 21.3, 21.2, 20.77, 20.74, 20.65, 20.61, 20.49, 20.45, 20.27, 20.22; HRMS calcd for $C_{46}H_{49}O_{24}$: 985.2614, found: *m*/*z* 985.2621 $[M + H]^+$.

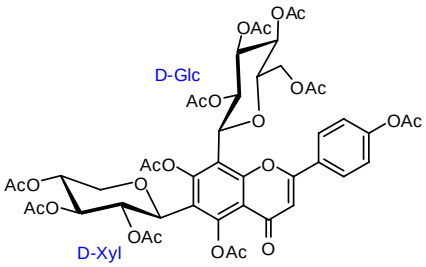
5,7,4'-Triacetoxy-6-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)flavone (3acAc)



By a procedure similar to that for **3aaAc**, compound **14acBn** (141 mg, 0.13 mmol) was subjected to oxidation (with DDQ), debenzylation and acetylation to give **3acAc** (78 mg, 61% overall yield). $C_{46}H_{48}O_{24}$; White solid, mp 141–143 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.33; $[\alpha]_D^{20}$ = +24.7 (*c* = 1.0, $CHCl_3$); IR (film) 3451, 2955, 1783, 1771, 1661, 1650, 1453, 1128, 1010 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.79 (2 H, d, *J* = 7.9 Hz), 7.29 (2 H, d, *J* = 7.9 Hz), 6.54 (1 H, s), 5.63 (1 H, t, *J* = 9.8 Hz), 5.47 (1 H, br s), 5.26–5.13 (5 H, m), 4.94 (1 H, br d, *J* = 9.1 Hz),

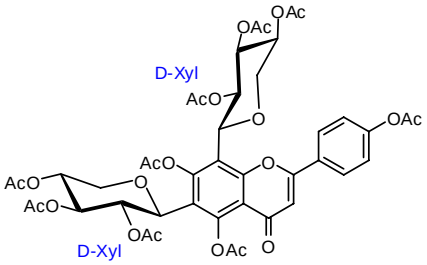
4.42 (1 H, br d, *J* = 8.6 Hz), 4.09 (1 H, d, *J* = 12.9 Hz), 3.95 (1 H, d, *J* = 12.9 Hz), 3.82 (1 H, d, *J* = 13.4 Hz), 3.77 (1 H, dd, *J* = 9.7, 2.8 Hz), 2.45 (3 H, s), 2.44 (3 H, s), 2.31 (3 H, s), 2.24 (3 H, s), 2.04 (3 H, s), 2.10 (3 H, s), 1.99 (3 H, s), 1.98 (3 H, s), 1.96 (3 H, s), 1.72 (3 H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.9, 170.5, 170.4, 170.3, 170.1, 169.5, 169.4, 168.9, 168.5, 168.17, 168.10, 161.4, 155.0, 154.5, 153.5, 148.8, 128.5, 127.5 (2 ×), 122.9 (2 ×), 120.8, 117.3, 114.4, 108.8, 74.8, 73.6, 72.5, 72.0, 70.2, 69.7, 69.3, 68.7, 68.3, 68.0, 62.0, 21.4, 21.3, 21.1, 21.0, 20.8, 20.7, 20.6, 20.4, 20.2, 19.9; HRMS calcd for $C_{46}H_{49}O_{24}$: 985.2614, found: *m*/*z* 985.2620 $[M + H]^+$.

5,7,4'-Triacetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-8-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)flavone (3baAc)



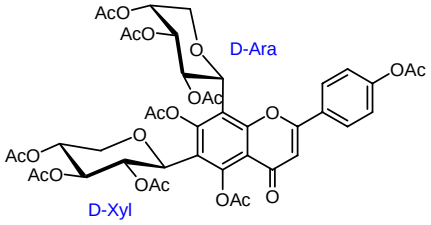
By a procedure similar to that for **3aaAc**, compound **14baBn** (110 mg, 0.10 mmol) was subjected to oxidation (with DDQ), debenzylation and acetylation to give **3baAc** (49 mg, 49% overall yield). $C_{46}H_{48}O_{24}$; White solid, mp 130–132 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.33; $[\alpha]_D^{20}$ = –63.3 (*c* = 1.0, $CHCl_3$); IR (film) 3443, 2971, 1772, 1759, 1621, 1512, 1422, 1028 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (1.5 H, d, *J* = 8.6 Hz), 7.85–7.81 (0.5 H, m), 7.37–7.31 (2 H, m), 6.62 (0.5 H, s), 6.55 (0.5 H, s), 5.97–5.82 (0.7 H, m), 5.45–5.18 (3.8 H, m), 5.11 (0.7 H. br s), 5.06 (0.7 H, br s), 4.78 (0.5 H. br s), 4.71 (1.5 H, br s), 4.71 (0.2 H, dd, *J* = 12.5, 4.8 Hz), 4.26–4.21 (1.1 H, m), 4.16–4.05 (1.9 H, m), 4.03–3.95 (0.3 H, m), 3.91–3.82 (1.6 H, m), 2.41–2.32 (9 H, 3 × OAc), 2.15–2.12 (6 H, 2 × OAc), 2.10–1.95 (9 H, 3 × OAc), 1.87–1.68 (6 H, 2 × OAc); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.0/175.9, 170.76/170.73, 170.5/170.2, 170.3, 169.9/169.8, 169.6/169.5, 169.4/169.3, 169.0/168.97, 168.91, 168.4/168.3, 167.98/167.91, 161.5/161.4, 161.2/159.9, 157.3/156.6 (br), 153.5/153.3, 152.4/148.4 (br), 129.0/128.8, 127.8/127.6 (2 ×), 122.9/122.7 (2 ×), 120.1, 117.3/115.5 (br), 108.8, 108.5/108.2, 76.5, 74.7/74.1, 73.9, 73.2/73.1, 71.8/71.6, 68.6, 68.4/67.8, 68.1/67.5, 66.1/65.8, 65.3/65.0, 62.2/61.9, 21.2, 21.1, 20.9, 20.85, 20.81, 20.7, 20.68, 20.64, 20.45, 20.3; HRMS calcd for $C_{46}H_{49}O_{24}$: 985.2614, found: *m*/*z* 985.2619 $[M + H]^+$.

5,7,4'-Triacetoxy-6,8-di-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)flavone (3bbAc)



By a procedure similar to that for **3aaAc**, compound **14bbBn** (134 mg, 0.13 mmol) was subjected to oxidation (with DDQ), debenzylation and acetylation to give **3bbAc** (63 mg, 52% overall yield). $C_{43}H_{44}O_{22}$; White solid, mp 136–138 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.35; $[\alpha]_D^{20}$ = –20.6 (c = 1.0, $CHCl_3$); IR (film) 3457, 2921, 1785, 1762, 1653, 1650, 1423, 1172, 1012 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, at 40 °C) δ 7.95–7.84 (2 H, m), 7.33 (1 H, d, J = 7.4 Hz), 7.22 (1 H, d, J = 7.4 Hz), 6.56 (1 H, s), 5.80–5.45 (1 H, m), 5.32 (1 H, t, J = 9.5 Hz), 5.23 (1 H, t, J = 9.5 Hz), 5.13–5.03 (2 H, m), 4.89–4.58 (3 H, m), 4.31–4.17 (1 H, m), 4.13 (0.5 H, dd, J = 11.2, 5.0 Hz), 4.06 (0.5 H, d, J = 13.6 Hz), 4.01 (0.5 H, d, J = 11.7 Hz), 3.89 (0.5 H, d, J = 13.6 Hz), 3.44 (0.5 H, t, J = 10.9 Hz), 3.36 (0.5 H, t, J = 10.9 Hz), 2.43–2.29 (9 H, 3 × OAc), 2.13–1.96 (15 H, 5 × OAc), 1.77–1.67 (3 H, 1 × OAc); ^{13}C NMR (150 MHz, $CDCl_3$, at 40 °C) δ 176.0/175.9, 170.0/169.9, 169.8, 169.5, 169.3, 168.8, 168.6, 168.1, 168.0, 167.9, 161.7/161.6, 156.5/154.5, 153.5/153.3, 148.4, 130.0/129.7, 129.0/128.7, 127.8/127.5 (2 ×), 122.7/122.4 (2 ×), 120.4/120.2, 118.3/117.4, 115.6/115.0, 108.9, 74.1, 73.4, 73.0, 71.6, 69.2, 69.1, 68.9, 68.6, 67.5, 67.2, 21.2, 21.1, 21.0, 20.9, 20.8, 20.7, 20.6, 20.4, 20.2; HRMS calcd for $C_{43}H_{45}O_{22}$: 913.2402, found: m/z 913.2408 $[M + H]^+$.

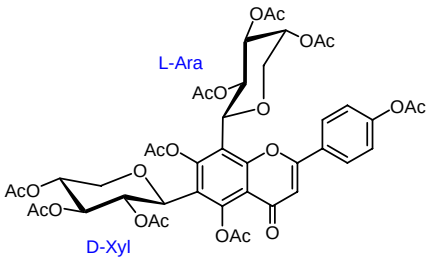
5,7,4'-Triacetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)flavone (3bcAc)



By a procedure similar to that for **3aaAc**, compound **14bcBn** (143 mg, 0.14 mmol) was subjected to oxidation (with DDQ), debenzylation and acetylation to give **3bcAc** (82 mg, 64% overall yield). $C_{43}H_{44}O_{22}$; white solid, mp 137–139 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.31; $[\alpha]_D^{20}$ = +24.1 (c = 1.0, $CHCl_3$); IR (film) 3472, 2918, 1799, 1756, 1661, 1632, 1492, 1176 cm^{-1};

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (0.3 H, br s), 7.80 (1.7 H, d, *J* = 7.7 Hz), 7.30 (2 H, d, *J* = 7.7 Hz), 6.56 (1 H, s), 5.65 (1 H, br t, *J* = 9.5 Hz), 5.58–5.41 (2 H, m), 5.26–5.17 (3 H, m), 5.01 (1.3 H, br s), 4.83 (0.7 H, br s), 4.16 (1 H, dd, *J* = 11.3, 5.5 Hz), 4.10 (1 H, d, *J* = 13.1 Hz), 3.81 (1 H, d, *J* = 13.1 Hz), 3.36 (1 H, t, *J* = 10.7 Hz), 2.46–2.41 (6 H, 2 × OAc), 2.32–2.24 (6 H, 2 × OAc), 2.04–1.96 (9 H, 3 × OAc), 1.72 (3 H, s, 1 × OAc), 1.52 (3 H, s, 1 × OAc); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.9, 170.5, 170.3, 170.1, 170.0, 169.7, 169.4, 168.9, 168.2, 168.1, 161.5, 155.0, 154.4, 153.5, 148.9, 128.9/128.5, 127.5 (2 ×), 122.9 (2 ×), 121.1, 117.4, 114.4/114.1, 108.9, 74.1, 73.6, 72.9, 72.0, 70.4, 69.7, 68.9, 68.7, 68.4, 67.3, 21.3, 21.1, 20.9, 20.8, 20.76, 20.72, 20.4, 20.0, 19.9; HRMS calcd for $C_{43}H_{45}O_{22}$: 913.2402, found: *m*/*z* 913.2409 $[M + H]^+$.

5,7,4'-Triacetoxy-6-*C*-(tri-*O*-acetyl-β-D-xylopyranosyl)-8-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)flavone (3bdAc)



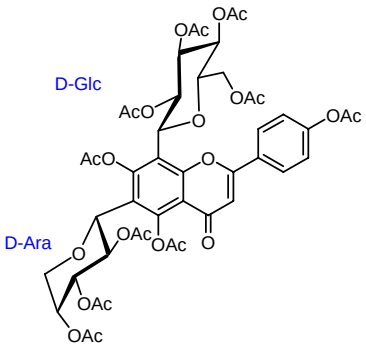
By a procedure similar to that for **3aaAc**, compound **14bdBn** (100 mg, 0.098 mmol) was subjected to oxidation (with DDQ), debenzylation and acetylation to give **3bdAc** (20.5 mg, 23% overall yield).

Alternatively, a solution of **15bd** (88 mg, 0.111 mmol) in DMSO (5 mL) was stirred with iodine (5.6 mg, 0.022 mmol) at 140 °C for 4 h. The mixture was quenched by addition of aqueous $Na_2S_2O_3$, and extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The crude product was treated with Ac_2O (3 mL) in pyridine (1 mL) and DMAP (10 mg, 0.08 mmol) at room temperature for 4 h. The mixture was quenched by addition of CH_3-OH, concentrated under reduced pressure, and partitioned between 1 M $HCl_{(aq)}$ and EtOAc. After neutralization with saturated $NaHCO_3$, the organic layer was separated, washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was washed with Et_2O to afford **3bdAc** (86 mg, 85% overall yield).

$C_{43}H_{44}O_{22}$; White prisms, mp 183–184 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.19; $[\alpha]^{23}_D$ –5.8 (*c* 3.04, EtOAc); IR ν_{max} (neat) 2922, 1752, 1650, 1368, 1218 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (1.2 H, d, *J* = 8.4 Hz), 7.80 (0.8 H, d, *J* = 8.4 Hz), 7.28 (0.8 H, d, *J* = 8.4 Hz), 7.22 (1.2 H,

d, J = 8.4 Hz), 6.54 (0.4 H, s), 6.47 (0.6 H, s), 6.02 (0.6 H, br), 5.68 (0.4 H, t, J = 9.6 Hz), 5.60–5.57 (1 H, m), 5.50 (0.4 H, br), 5.41 (0.6 H, br), 5.27 (1 H, t, J = 9.6 Hz), 5.19–5.16 (1.4 H, m), 5.08–4.98 (1 H, m), 4.75 (0.6 H, d, J = 9.2 Hz), 4.42 (0.6 H, d, J = 9.6 Hz), 4.36 (0.4 H, d, J = 8 Hz), 4.19–4.07 (2 H, m), 3.85 (0.4 H, d, J = 13.6 Hz), 3.73 (0.6 H, d, J = 13.6 Hz), 3.37 (0.6 H, t, J = 11.2 Hz), 3.25 (0.4 H, t, J = 11.2 Hz), 2.47 (3 H, s, 1 × OAc), 2.44 (3 H, s, 1 × OAc), 2.32–2.30 (3 H, s, 1 × OAc), 2.21–1.92 (15 H, m, 5 × OAc), 1.84–1.79 (3 H, m, 1 × OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.4/175.2, 170.3, 170.0, 169.7/169.6 (2 ×), 169.4, 168.5/168.4, 168.1, 167.8, 167.6, 162.6/160.7, 156.7/154.5, 153.0, 152.7/152.4, 150.2/148.8, 129.2/128.7, 128.6/127.2 (2 ×), 122.5/121.5 (2 ×), 118.9, 117.2, 115.7/115.0, 110.2/108.7, 74.6/73.9, 73.6/73.4, 72.5, 72.1/71.9, 70.4/69.9, 69.4, 68.8, 68.5, 67.8/67.3, 67.0, 21.2, 21.1, 21.0, 20.7, 20.6 (2 ×), 20.5, 20.5/20.2, 20.2/20.0; HRMS (ESI) calcd for $C_{43}H_{44}O_{22}Na$: 935.2222, found: m/z 935.2220 $[M + Na]^+$.

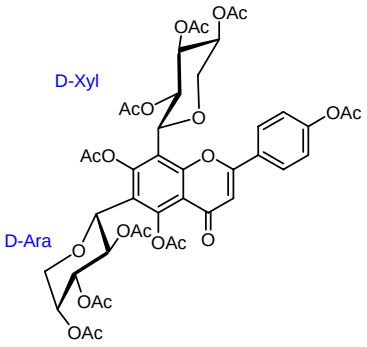
5,7,4'-Triacetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-8-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)flavone (3caAc)



By a procedure similar to that for **3aaAc**, compound **14caBn** (132 mg, 0.12 mmol) was subjected to oxidation (with DDQ), debenzylation and acetylation to give **3caAc** (67 mg, 56% for three steps). $C_{46}H_{48}O_{24}$; white solid, mp 145–147 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.33; $[\alpha]_D^{20}$ = –72.9 (c = 1.0, $CHCl_3$); IR (film) 3453, 2923, 1784, 1765, 1665, 1643, 1421, 1129, 1009 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (1.3 H, d, J = 8.5 Hz), 7.84 (0.7 H, d, J = 8.5 Hz), 7.36 (1.3 H, d, J = 8.5 Hz), 7.32 (0.7 H, d, J = 8.5 Hz), 6.64 (0.6 H, s), 6.55 (0.4 H, s), 6.01 (0.6 H, t, J = 9.8 Hz), 5.70–5.55 (0.8 H, m), 5.49–5.39 (2.4 H, m), 5.36–5.30 (1.4 H, m), 5.23 (0.4 H, t, J = 9.8 Hz), 5.10–5.08 (1 H, m), 4.74 (0.4 H, d, J = 9.7 Hz), 4.70–4.66 (1 H, m), 4.42 (0.4 H, dd, J = 12.6, 4.9 Hz), 4.35 (0.6 H, dd, J = 12.6, 4.9 Hz), 4.09 (0.6 H, d, J = 12.3 Hz), 4.02 (1 H, d, J = 13.4 Hz), 3.75 (0.4 H, d, J = 12.3 Hz), 3.87–3.83 (1 H, m), 3.79–3.74 (1 H, m), 2.48–2.41 (6 H, 2 × OAc), 2.32–2.31 (3 H, 1 × OAc), 2.20–2.16 (3 H, 1 × OAc), 2.05–1.94 (9 H, 3 × OAc),

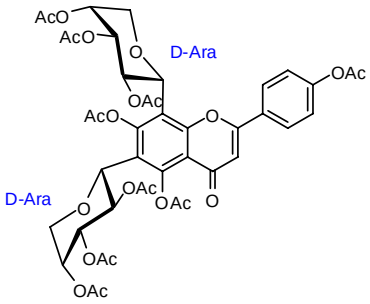
1.89–1.59 (9 H, 3 × OAc); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.1/175.9, 170.8, 170.6/170.5, 170.3, 170.2, 170.1/170.0, 169.8/169.7, 169.5/169.4, 168.9/168.8, 168.5/168.3, 168.1, 161.5/161.4, 157.1, 155.2/154.5, 153.5/153.1, 149.2/148.7, 128.7/128.6, 127.8/127.6 (2 ×), 122.9/122.7 (2 ×), 118.9, 117.6, 115.2, 108.9/108.8, 76.3, 74.0, 73.3/73.1, 72.9, 72.0, 71.8/71.4, 69.4/69.3, 68.69/68.63, 67.9/67.8, 67.2/66.7, 62.1/61.6, 21.3, 21.2, 21.1, 21.0, 20.8, 20.7, 20.67/20.63, 21.5, 20.4, 20.3/20.2; HRMS calcd for $C_{46}H_{49}O_{24}$ (M^+ + H): 985.2614, found: *m*/*z* 985.2621.

5,7,4'-Triacetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-8-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)flavone (3cbAc)



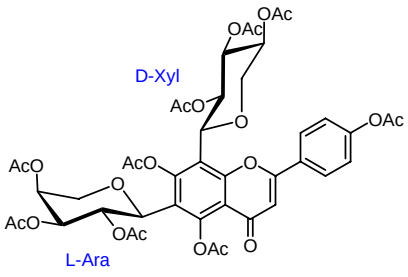
By a procedure similar to that for **3aaAc**, compound **14cbBn** (152 mg, 0.15 mmol) was subjected to oxidation (with DDQ), debenzylation and acetylation to give **3cbAc** (60 mg, 44% for three steps). $C_{43}H_{44}O_{22}$; white solid, mp 138–140 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.33; $[\alpha]_D^{20}$ = –72.8 (*c* = 1.0, $CHCl_3$); IR (film) 3457, 2917, 1736, 1711, 1653, 1624, 1473, 1132, 1024 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95–7.82 (2 H, m), 7.33 (2 H, d, *J* = 8.0 Hz), 6.58 (1 H, br s), 5.89 (0.4 H, br s), 5.64 (0.6 H, br s), 5.45–5.37 (2 H, m), 5.32 (1.8 H, t, *J* = 9.6 Hz), 5.21–5.13 (1.2 H, m), 5.10 (1 H, dd, *J* = 9.7, 3.0 Hz), 4.72 (0.6 H, d, *J* = 9.4 Hz), 4.61 (0.4 H, br d, *J* = 7.7 Hz), 4.31–4.23 (1 H, m), 4.04 (1 H, d, *J* = 13.0 Hz), 3.85–3.76 (1 H, m), 3.52–3.44 (1 H, m), 2.48–2.42 (6 H, 2 × OAc), 2.32–2.27 (3 H, 1 × OAc), 2.19–2.17 (3 H, 1 × OAc), 2.07–1.94 (9 H, 3 × OAc), 1.84–1.66 (6 H, 2 × OAc); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.2 (br), 170.3, 170.1, 170.0, 169.8, 169.0, 168.9, 168.3, 168.2, 168.0, 161.7/161.5 (br), 157.1, 155.3/154.6 (br), 153.4/153.3, 149.0/148.7, 129.0/128.8, 127.8/127.6 (2 ×), 122.8/122.6 (2 ×), 118.9, 117.7, 115.1/114.3, 108.9, 74.2, 73.5, 71.9/71.5, 70.0, 69.3/69.1, 68.8/68.7, 68.19/68.15, 67.8, 67.4, 66.9, 21.29, 21.20, 21.0 (2 ×), 20.7 (2 ×), 20.6, 20.5, 20.4; HRMS calcd for $C_{43}H_{45}O_{22}$: 913.2402, found: *m*/*z* 913.2409 $[M + H]^+$.

5,7,4'-Triacetoxy-6,8-di-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)flavone (3ccAc)



By a procedure similar to that for **3aaAc**, compound **14ccBn** (147 mg, 0.145 mmol) was subjected to oxidation (with DDQ), debenzylation and acetylation to give **3ccAc** (78 mg, 59% for three steps). $C_{43}H_{44}O_{22}$; white solid, mp 136–138 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.33; $[\alpha]_D^{20}$ = +9.8 (*c* = 1.0, $CHCl_3$); IR (film) 3435, 2961, 1788, 1762, 1651, 1649, 1432, 1177, 1014 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.99 (0.5 H, br d, *J* = 7.8 Hz), 7.81 (1.5 H, d, *J* = 8.2 Hz), 7.30–7.27 (2 H, m), 6.61 (0.1 H, br s), 6.54 (0.7 H, s), 6.47 (0.2 H, br s), 5.49–5.44 (1 H, m), 5.40–5.29 (2 H, m), 5.25–5.14 (3 H, m), 5.12–5.08 (1 H, m), 4.09 (1.5 H, d, *J* = 13.1 Hz), 4.03 (0.5 H, d, *J* = 13.1 Hz), 3.91 (1 H, dd, *J* = 10.9, 5.5 Hz), 3.85–3.81 (1 H, m), 3.71 (1 H, t, *J* = 11.1 Hz), 2.43–2.31 (9 H, 3 × OAc), 2.19–2.13 (9 H, 3 × OAc), 1.99–1.96 (9 H, 3 × OAc); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.8, 170.7, 170.2, 170.1, 169.8, 169.1, 169.0, 168.8, 168.6, 168.1, 161.5/161.4, 154.5, 153.5/153.1, 149.2/148.5, 130.0/129.7, 128.7/128.6, 127.8/127.5 (2 ×), 122.9 (2 ×), 122.5/122.3, 117.2 (br), 115.6/115.2 (br), 108.8, 73.7, 72.2, 72.1, 70.6, 69.4, 68.7, 68.6, 66.8, 64.9, 64.8, 21.2, 21.1, 21.0, 20.99, 20.94, 20.8, 20.77, 20.70, 20.0; HRMS calcd for $C_{43}H_{45}O_{22}$: 913.2402, found: *m*/*z* 913.2410 $[M + H]^+$.

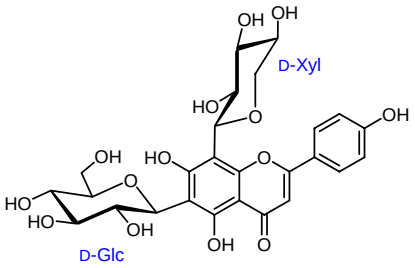
5,7,4'-Triacetoxy-6-*C*-(tri-*O*-acetyl-α-L-arabinopyranosyl)-8-*C*-(tri-*O*-acetyl-β-D-xylopyranosyl)flavone (3dbAc)



By a procedure similar to that for **3aaAc**, compound **14dbBn** (150 mg, 0.148 mmol) was subjected to oxidation (with DDQ), debenzylation and acetylation to give **3dbAc** (30 mg, 22% for three steps). Alternatively, **15db** (50 mg, 0.063 mmol) was heated in DMSO (5 mL) with

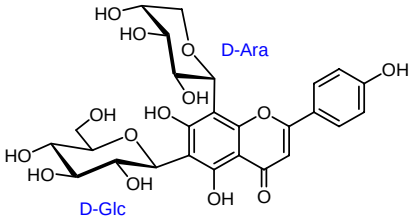
iodine (3.29 mg, 0.013 mmol) at 140 °C for 4 h to give **3dbAc** (41 mg, 71% overall yield) by a procedure similar to that for **3bdAc**. $C_{43}H_{44}O_{22}$; White prisms, mp 170–172 °C; TLC (EtOAc/hexane, 2:1) R_f = 0.19; $[\alpha]^{24}_D$ +4.2 (*c* 2.4, EtOAc); IR ν_{max} (neat) 2923, 1752, 1650, 1369, 1219 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96 (2 H, d, *J* = 8.8 Hz), 7.33 (2 H, d, *J* = 8.8 Hz), 6.57 (1 H, s), 5.77–5.70 (2 H, m), 5.47–5.46 (1 H, m), 5.37 (1 H, t, *J* = 9.6 Hz), 5.23–5.17 (1 H, m), 5.11 (1 H, dd, *J* = 9.6, 3.6 Hz), 4.69 (1 H, d, *J* = 9.6 Hz), 4.51 (1 H, d, *J* = 9.6 Hz), 4.36 (1 H, dd, *J* = 11.2, 5.6 Hz), 4.04 (1 H, d, *J* = 13.6 Hz), 3.77 (1 H, d, *J* = 13.6 Hz), 3.39 (1 H, t, *J* = 11.2 Hz), 2.54 (3 H, s), 2.44 (3 H, s), 2.32 (3 H, s), 2.18 (3 H, s), 2.07 (3 H, s), 1.98 (3 H, s), 1.98 (3 H, s), 1.89 (3 H, s), 1.72 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.6, 169.9, 169.7, 169.6 (2 ×), 169.4 (2 ×), 168.6, 168.1, 167.6, 161.5, 156.3, 153.1, 152.8, 148.9, 128.6, 127.6 (2 ×), 122.5 (2 ×), 118.8, 117.1, 114.9, 108.7, 74.0, 73.4 (2 ×), 71.8, 69.4, 69.3, 69.0, 68.6, 67.6, 66.6, 21.2, 21.1, 21.0, 20.8, 20.7 (2 ×), 20.6, 20.3, 20.3; HRMS (ESI) calcd for $C_{43}H_{44}O_{22}Na$: 935.2222, found: *m*/*z* 935.2219 $[M + Na]^+$.

6-*C*-β-D-Glucopyranosyl-8-*C*-β-D-xylopyranosyl-5,7,4'-trihydroxyflavone (3ab)



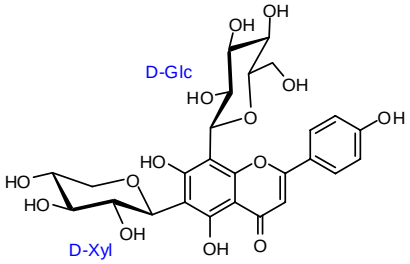
By a procedure similar to that for **3aa**, saponification of **3abAc** (55 mg, 0.056 mmol) gave **3ab** (28 mg) in 89% yield. $C_{26}H_{28}O_{14}$; Yellow powder, mp > 250 °C; $[\alpha]_D^{20}$ = +26.8 (*c* = 0.6, MeOH); IR (film) 3389, 2899, 2856, 1678, 1612, 1507, 1159 cm^{-1}; ^1H NMR (600 MHz, MeOH-d_4, at 40 °C) δ 7.87 (2 H, d, *J* = 8.7 Hz), 6.94 (2 H, d, *J* = 8.7 Hz), 6.61 (1 H, s), 5.00 (1 H, d, *J* = 9.9 Hz, H-1'''$_{ax}$, 8β-Xyl), 4.95 (1 H, d, *J* = 9.8 Hz, H-1''$_{ax}$, 6β-Glc), 4.09 (1 H, dd, *J* = 11.3, 5.6 Hz), 4.07–4.02 (1 H, m), 3.88 (1 H, dd, *J* = 12.3, 2.3 Hz), 3.82–3.75 (2 H, m), 3.68 (0.5 H, s), 3.64 (0.5 H, s), 3.55–3.52 (2 H, m), 3.50–3.47 (2 H, m), 3.41–3.37 (1 H, m); ^{13}C NMR (150 MHz, CD_3OD, at 40 °C) δ 183.4, 165.6, 162.1 (br), 161.9, 160.1 (br), 156.1 (br), 128.9 (br) (2 ×), 122.5, 116.2 (2 ×), 104.6 (br), 103.1, 103.0 (br), 102.7, 81.8, 79.3, 78.5 (br), 75.0 (br), 72.6 (br), 72.2 (br), 71.1, 71.0, 70.9 (br), 70.3 (br), 61.2 (br); HRMS calcd for $C_{26}H_{29}O_{14}$: 565.1557, found: *m*/*z* 565.1564 $[M + H]^+$.

6-*C*-β-D-Glucopyranosyl-8-*C*-α-D-arabinopyranosyl-5,7,4'-trihydroxyflavone (3ac)



By a procedure similar to that for **3aa**, saponification of **3acAc** (78 mg, 0.079 mmol) gave **3ac** (37 mg) in 84% yield. $C_{26}H_{28}O_{14}$; Yellow powder, mp 198–200 °C; $[\alpha]_D^{20}$ = –9.9 (*c* = 1.0, MeOH); IR (film) 3455, 3351, 2918, 1659, 1611, 1532, 1431 cm^{-1}; ^1H NMR (600 MHz, CD_3OD, at 40 °C) δ 7.86–7.81 (2 H, m), 6.91 (2 H, d, *J* = 8.8 Hz), 6.59 (1 H, br s), 4.93 (2 H, br d, *J* > 8.4 Hz, H-1"$_{ax}$ & H-1'"$_{ax}$, 6β-Glc & 8α-Ara), 4.07 (1 H, d, *J* = 12.4 Hz), 4.02 (1 H, s), 3.87 (1 H, dd, *J* = 13.3, 2.1 Hz), 3.79 (1 H, d, *J* = 7.4 Hz), 3.75 (1 H, s), 3.69–3.66 (1.5 H, m), 3.64 (1.5 H, s), 3.52–3.45 (2 H, m), 3.43 (1 H, br s); ^{13}C NMR (150 MHz, MeOH-d_4, at 40 °C) δ 183.4, 165.6, 162.5, 161.8, 160.8/160.3 (br), 155.9 (br), 129.3/129.2 (br) (2 ×), 123.5, 122.3, 116.2 (2 ×), 108.6 (br), 104.3 (br), 102.8, 81.7, 79.1 (br), 76.3 (br), 74.9 (br), 74.4 (br), 71.4 (br), 71.0 (br), 70.4 (br), 70.0 (br), 69.7 (br), 62.0 (br); HRMS calcd for $C_{26}H_{29}O_{14}$: 565.1557, found: *m/z* 565.1562 $[M + H]^+$.

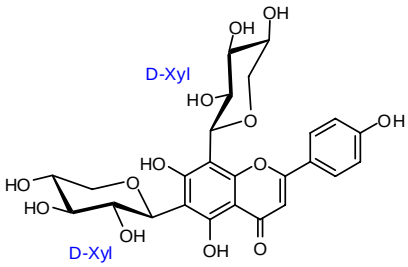
6-*C*-β-D-Xylopyranosyl-8-*C*-β-D-glucopyranosyl-5,7,4'-trihydroxyflavone (3ba)



By a procedure similar to that for **3aa**, saponification of **3baAc** (49 mg, 0.049 mmol) gave **3ba** (23 mg) in 85% yield. $C_{26}H_{28}O_{14}$; Yellow powder, mp 230 °C (dec.); $[\alpha]_D^{20}$ = –68.5 (*c* = 0.5, DMSO); IR (film) 3459, 2978, 1651, 1609, 1574, 1423,1192 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6, Deuterium exchange) δ 8.02 (2 H, d, *J* = 8.8 Hz), 6.89 (2 H, d, *J* = 8.8 Hz), 6.79 (1 H, s), 5.32 (1 H, s, H-1'"$_{eq}$, 8β-Glc), 4.70 (1 H, d, *J* = 9.9 Hz, H-1'"$_{ax}$, 6β-Xyl), 3.97 (1 H, d, *J* = 11.4 Hz), 3.91 (1 H, d, *J* = 12.1 Hz), 3.83–3.80 (1.5 H, m), 3.75 (1 H, d, *J* = 10.4 Hz), 3.60 (0.5 H, d, *J* = 3.4 Hz), 3.51–3.49 (2.5 H, m), 3.39–3.35 (1.5 H, m), 3.25–3.21 (2 H, m); ^{13}C NMR (150 MHz, DMSO-d_6) δ 182.3, 164.1, 162.2, 161.3, 156.8, 154.9, 129.0 (2 ×), 121.5, 115.9 (2 ×), 106.8, 104.8, 103.3, 102.3, 81.9, 78.7, 73.3, 72.5, 71.2, 70.8, 70.6, 69.1, 67.9, 67.2, 61.4; HRMS calcd

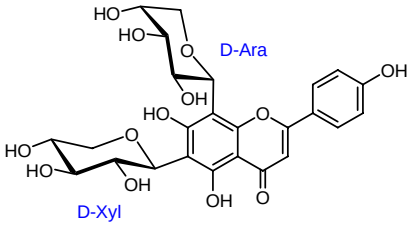
for $C_{26}H_{29}O_{14}$: 565.1557, found: *m*/*z* 565.1561 $[M + H]^+$.

6,8-Di-*C*-β-D-xylopyranosyl-5,7,4'-trihydroxyflavone (3bb)



By a procedure similar to that for **3aa**, saponification of **3bbAc** (63 mg, 0.068 mmol) gave **3bb** (33 mg) in 91% yield. $C_{25}H_{26}O_{13}$; Yellow powder; mp 200 °C (dec.); $[\alpha]_D^{20}$ = –102.7 (*c* = 0.8, DMSO); IR (film) 3429, 2920, 1644, 1578, 1511, 1290 cm^{-1}; ^1H NMR (600 MHz, MeOH-d_4, at 40 °C) δ 7.86 (1 H, d, *J* = 8.8 Hz), 7.79 (1 H, d, *J* = 8.8 Hz), 6.91–6.86 (2 H, m), 6.55 (0.5 H, s), 6.50 (0.5 H, br s), 5.63 (0.5 H, s, H-1'''$_{eq}$, 8β-Xyl), 5.48 (0.5 H, s, H-1'''$_{eq}$, 8β-Xyl), 4.77 (1 H, d, *J* = 9.9 Hz, H-1"$_{ax}$, 6β-Xyl), 4.37 (0.5 H, br t, *J* = 5.3 Hz), 4.20–4.13 (1.5 H, m), 4.07–4.00 (2.5 H, m), 3.95 (0.5 H, dd, *J* = 11.0, 5.4 Hz), 3.83 (0.5 H, s), 3.80 (0.5 H, s), 3.69–3.63 (2.5 H, m), 3.49 (0.5 H, t, *J* = 4.4 Hz), 3.43–3.38 (1 H, m); ^{13}C NMR (150 MHz, DMSO-d_6) δ 182.6, 164.4/163.7, 162.9/162.7, 161.7, 157.3, 155.3, 129.09/129.06 (2 ×), 121.9/121.4, 116.46/116.40 (2 ×), 109.4, 107.2/105.1, 103.7/103.5, 102.94/102.90, 79.6/79.2, 74.7/74.3, 73.3/72.95, 72.7/72.1, 71.5/71.3, 71.1/70.7, 70.4/70.2, 70.1/69.4, 68.5/68.3, 67.5; HRMS calcd for $C_{25}H_{27}O_{13}$: 535.1452, found: *m*/*z* 535.1460 $[M + H]^+$.

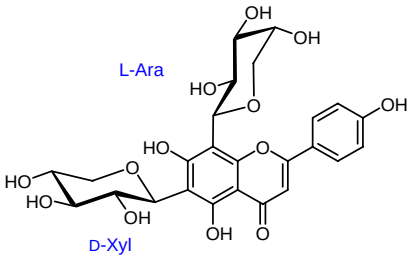
6-*C*-β-D-Xylopyranosyl-8-*C*-α-D-arabinopyranosyl-5,7,4'-trihydroxyflavone (3bc)



By a procedure similar to that for **3aa**, saponification of **3bcAc** (82 mg, 0.090 mmol) gave **3bc** (42 mg) in 87% yield. $C_{25}H_{26}O_{13}$; Yellow powder; mp 240 °C (dec.); $[\alpha]_D^{20}$ = –78.6 (*c* = 0.5, DMSO); IR (film) 3429, 2957, 1696, 1602, 1531, 1151 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_4, Deuterium exchange, at 40 °C) δ 8.00 (2 H, br s), 6.92 (2 H, d, *J* = 8.3 Hz), 6.77 (1 H, s), 4.84 (1 H, br, H-1'''$_{ax}$, 8α-Ara), 4.56 (1 H, br, H-1"$_{ax}$, 6β-Xyl), 3.88 (1.5 H, d, *J* = 11.9 Hz), 3.85 (2.5 H, br s), 3.77–3.65 (1 H, br m), 3.50 (1 H, s), 3.48–3.27 (1 H, m), 3.23–3.02 (3 H, m); ^{13}C NMR

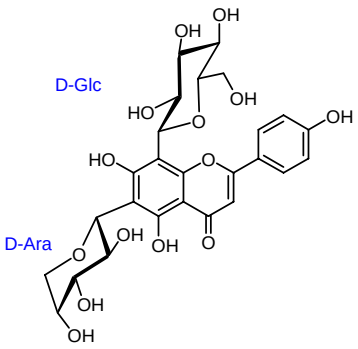
(150 MHz, DMSO-d_6) δ 182.8, 164.2 (br), 161.6, 160.9 (br), 153.9 (br) (2 ×), 129.4 (br) (2 ×), 121.7, 116.4 (2 ×), 109.7 (br), 103.9 (br) (2 ×), 102.9, 79.6 (br), 75.7 (br) 74.3 (br) (2 ×), 72.9, 72.7, 70.8 (br), 70.2 (br) (2 ×), 68.9 (br); HRMS calcd for $C_{25}H_{27}O_{13}$: 535.1452, found: *m*/*z* 535.1456 $[M + H]^+$.

6-*C*-β-D-Xylopyranosyl-8-*C*-α-L-arabinopyranosyl-5,7,4'-trihydroxyflavone (3bd)[14f]



By a procedure similar to that for **3aa**, saponification of **3bdAc** (87 mg, 0.095 mmol) gave **3bd** (49 mg) in 96% yield. $C_{25}H_{26}O_{13}$; yellow prisms, mp > 280 °C (decomposed); $[\alpha]^{26}_D$ –2.8 (*c* 2.2, H_2O); IR ν_{max} (neat) 3328, 2890, 1650, 1580, 1513, 1441, 1359, 1216, 1087 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz) δ 7.95 (2 H, br), 6.90 (2 H, d, *J* = 8.4 Hz), 6.56 (1 H, s), 4.96 (1 H, d, *J* = 9.6 Hz), 4.84 (1 H, covered by the signal of methanol), 4.28–4.23 (2 H, m), 4.05 (1 H, d, *J* = 11.6 Hz), 4.01–3.95 (2 H, m), 3.80 (1 H, d, *J* = 11.6 Hz), 3.69–3.63 (2 H, m), 3.41 (1 H, t, *J* = 8.8 Hz), 3.35–3.31 (1 H, m); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 182.2, 163.7, 161.0 (2 ×), 159.7, 153.6, 128.9 (2 ×), 121.2, 116.0 (2×), 109.1, 103.8, 103.2, 102.5, 79.2, 75.3, 73.9 (2 ×), 70.4 (3 ×), 70.0 (2 ×), 68.6; HRMS (ESI) calcd for $C_{25}H_{25}O_{13}$: 533.1295, found: *m*/*z* 533.1294 $[M - H]^-$.

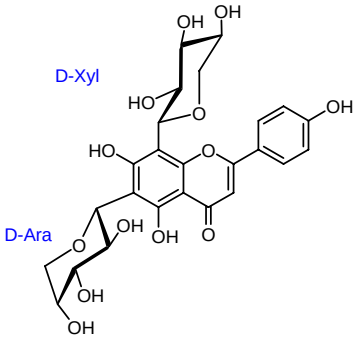
6-*C*-α-D-Arabinopyranosyl-8-*C*-β-D-glucopyranosyl-5,7,4'-trihydroxyflavone (3ca)



By a procedure similar to that for **3aa**, saponification of **3caAc** (67 mg, 0.067 mmol) gave **3ca** (30 mg) in 81% yield. $C_{26}H_{28}O_{14}$; yellow powder; mp 238 °C (dec.); $[\alpha]_D^{20}$ = –50.7 (*c* = 1.2, DMSO); IR (film) 3438, 2979, 2888, 1657, 1598, 1501, 1425, 1201 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6, deuterium exchange) δ 8.02 (2 H, d, *J* = 8.7 Hz), 6.90 (2 H, d, *J* = 8.7 Hz), 6.81 (1 H,

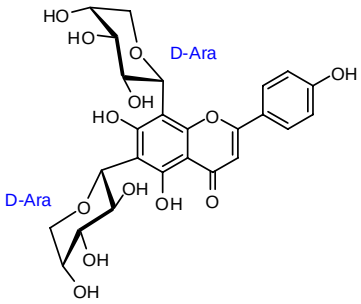
s), 4.71 (1 H, d, J = 9.8 Hz, H-1'''$_{ax}$, 8β-Glc), 4.69 (1 H, d, J = 9.7 Hz, H-1''$_{ax}$, 6α-Ara), 3.85–3.75 (3 H, m), 3.64 (1 H, d, J = 11.6 Hz), 3.55–3.49 (2 H, m), 3.44 (1 H, dd, J = 9.0, 2.3 Hz), 3.38–3.34 (2 H, m), 3.26–3.24 (2 H, m); ^{13}C NMR (150 MHz, DMSO-d_6) δ 182.8, 164.5, 161.7, 161.3, 158.6, 155.6, 129.4 (2 ×), 121.9, 116.3 (2 ×), 108.3, 105.4, 104.2, 102.9, 82.3, 79.1, 74.7, 74.0, 73.7, 71.2, 71.0, 70.5, 70.0, 68.8, 61.7; HRMS calcd for $C_{26}H_{29}O_{14}$: 565.1557, found: m/z 565.1562 $[M + H]^+$.

6-*C*-α-D-Arabinopyranosyl-8-*C*-β-D-xylopyranosyl-5,7,4'-trihydroxyflavone (3cb)



By a procedure similar to that for **3aa**, saponification of **3cbAc** (60 mg, 0.066 mmol) gave **3cb** (29 mg) in 83% yield. $C_{25}H_{26}O_{13}$; yellow powder; mp 210–212 °C; $[\alpha]_D^{20}$ = –112.2 (c = 0.5, DMSO); IR (film) 3447, 2972, 2899, 1675, 1639, 1521, 1421, 1212 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6, deuterium exchange, at 40 °C) δ 7.95 (2 H, d, J = 8.5 Hz), 6.96 (2 H, d, J = 8.5 Hz), 6.82 (1 H, s), 4.70 (2 H, br d, J = 9.4 Hz, H-1'' & H-1''', 6α-Ara & 8β-Xyl), 3.92 (1.5 H, br s), 3.86–3.81 (1.5 H, m), 3.66–3.49 (1 H, m), 3.46 (1 H, dd, J = 9.0, 2.0 Hz), 3.44–3.37 (1 H, m), 3.26–3.17 (4 H, m); ^{13}C NMR (150 MHz, DMSO-d_6) δ 182.8, 164.3, 161.7, 161.4, 158.7, 155.5, 129.0 (2 ×), 121.8, 116.4 (2 ×), 108.4, 105.2, 104.2, 103.1, 79.2, 74.7, 74.1, 71.2, 71.1, 70.7, 70.5, 70.2, 70.0, 68.8; HRMS calcd for $C_{25}H_{27}O_{13}$: 535.1452, found: m/z 535.1458 $[M + H]^+$.

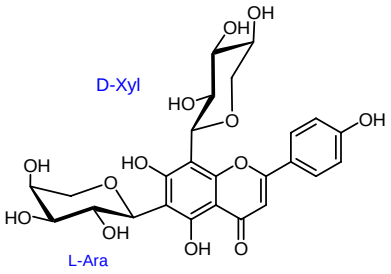
6,8-Di-*C*-α-D-arabinopyranosyl-5,7,4'-trihydroxyflavone (3cc)



By a procedure similar to that for **3aa**, saponification of **3ccAc** (78 mg, 0.086 mmol) gave

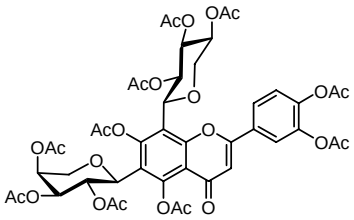
3cc (36 mg) in 79% yield. $C_{25}H_{26}O_{13}$; yellow powder; mp 200–202 °C; $[\alpha]_D^{20}$ = +19.0 (*c* = 0.3, DMSO); IR (film) 3451, 2957, 2901, 1672, 1604, 1519, 1211 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6, deuterium exchange) δ 8.28 (1.6 H, br d, *J* = 7.1 Hz), 8.02 (0.4 H, br d, *J* = 7.1 Hz), 6.92–6.87 (2 H, m), 6.82 (1 H, s), 5.27 (1 H, s, H-1'''$_{eq}$, 8α-Ara), 4.58 (1 H, d, *J* = 9.8 Hz, H-1''$_{ax}$, 6α-Ara), 4.27 (1 H, t, *J* = 9.3 Hz), 3.99–3.91 (1.5 H, m), 3.89–3.78 (3 H, m), 3.76–3.66 (1.5 H, m), 3.55–3.44 (1 H, m), 3.41–3.31 (2 H, m); ^{13}C NMR (150 MHz, DMSO-d_6) δ 182.7, 164.7, 162.7, 161.6, 157.8, 155.6, 130.16/130.12 (2 ×), 121.4, 116.4 (2 ×), 107.3, 105.3, 103.7, 102.2, 75.5, 74.9, 72.3, 71.7, 71.1, 70.3, 69.6, 68.5, 67.0, 63.6; HRMS calcd for $C_{25}H_{27}O_{13}$: 535.1452, found: *m*/*z* 535.1461 $[M + H]^+$.

6-*C*-α-L-Arabinopyranosyl-8-*C*-β-D-xylopyranosyl-5,7,4'-trihydroxyflavone (3db)[14f]



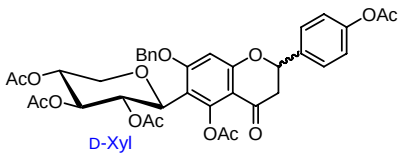
By a procedure similar to that for **3aa**, saponification of **3dbAc** (117 mg, 0.128 mmol) gave **3db** (60 mg) in 88% yield. $C_{25}H_{26}O_{13}$; Yellow prisms, mp > 250 °C (decomposed); $[\alpha]^{19}_D$ –2.0 (*c* 2.8, H_2O); IR ν_{max} (neat) 3326, 2905, 1654, 1582, 1508, 1438, 1356, 1215, 1086 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz) δ 7.79 (2 H, d, *J* = 8.8 Hz), 6.83 (2 H, d, *J* = 8.8 Hz), 6.38 (1 H, s), 5.03 (1 H, d, *J* = 10 Hz, H-1'''$_{ax}$, 8β-Xyl), 4.78 (1 H, d, *J* = 9.6 Hz, H-1'''$_{ax}$, 6α-Ara), 4.57 (1 H, t, *J* = 9.6 Hz), 4.20 (1 H, t, *J* = 10 Hz), 4.05 (1 H, dd, *J* = 11.2, 5.6 Hz), 3.96 (1 H, d, *J* = 11.6 Hz), 3.90 (1 H, br), 3.82–3.77 (1 H, m), 3.68 (1 H, d, *J* = 11.6 Hz), 3.56 (1 H, dd, *J* = 9.6, 2.8 Hz), 3.48 (1 H, t, *J* = 10 Hz), 3.40 (1 H, t, *J* = 11.2 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 180.6, 162.1, 160.6, 159.7, 158.6, 155.3, 128.5/128.0 (2 ×), 121.7, 115.7 (2 ×), 108.6, 104.8, 101.9, 100.7, 79.1, 74.9, 74.6, 74.4, 71.3, 70.5, 70.3, 69.9, 69.7, 68.7; HRMS (ESI) calcd for $C_{25}H_{25}O_{13}$: 533.1295, found: *m*/*z* 533.1296 $[M - H]^-$.

6-*C*-α-L-Arabinopyranosyl-8-*C*-α-D-xylopyranosyl)-3',4',5,7-tetrahydroxyflavone peracetate (18dbAc).



Compound **17db** was heated with iodine in DMSO (2 mL) at 140 °C for 4 h, followed by reacetylation with Ac_2O, to afford **18dbAc**. $C_{45}H_{46}O_{24}$; pale-yellow prisms, mp 186–188 °C; TLC (EtOAc/hexane, 3:2) R_f = 0.12; $[\alpha]^{26}_D$ –4.5 (*c* 0.87, CH_2Cl_2); IR ν_{max} (neat) 2924, 1752, 1649, 1369, 1219 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.87 (1 H, d, *J* = 8.4 Hz), 7.71 (1 H, s), 7.46 (1 H, d, *J* = 8.4 Hz), 6.53 (1 H, s), 5.75–5.67 (2 H, m), 5.47 (1 H, d, *J* = 2.8 Hz), 5.37 (1 H, t, *J* = 9.6 Hz), 5.16–5.10 (2 H, m), 4.69 (1 H, d, *J* = 9.6 Hz), 4.49 (1 H, d, *J* = 9.6 Hz), 4.40 (1 H, dd, *J* = 10.8, 5.2 Hz), 4.04 (1 H, d, *J* = 12.4 Hz), 3.78 (1 H, d, *J* = 13.6 Hz), 3.37 (1 H, t, *J* = 10.8 Hz), 2.55 (3 H, s), 2.45 (3 H, s), 2.34 (3 H, s), 2.32 (3 H, s), 2.18 (3 H, s), 2.06 (3 H, s), 2.01 (3 H, s), 1.98 (3 H, s), 1.89 (3 H, s), 1.73 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.5, 170.1 (2 ×), 169.8 (2 ×), 169.5 (3 ×), 167.8 (2 ×), 167.4 , 160.8, 156.4, 153.0, 149.1, 144.8, 142.7, 129.8, 124.7, 124.5, 121.5, 119.1, 117.2, 114.3, 109.3, 74.2, 73.5 (2 ×), 71.9 , 69.4 (3 ×), 68.7, 67.9, 66.7, 21.3, 21.1, 20.8 (5 ×), 20.7 (2 ×), 20.4; HRMS (ESI) calcd for $C_{45}H_{46}O_{24}Na$: 993.2277, found: *m*/*z* 993.2278 $[M + Na]^+$.

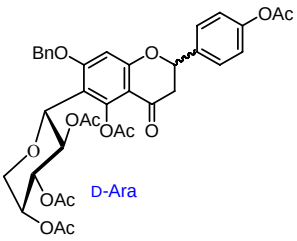
5,4'-Diacetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-7-benzyloxyflavanone (19b)



By a procedure similar to that for **19a**, compound **12bBn** (650 mg, 1 mmol) was subjected to acetylation and a subsequent oxidation with CAN to give flavanone **19b** as a mixture of diastereomers (345 mg, 49%). $C_{37}H_{36}O_{14}$; colorless foam; TLC (EtOAc/hexane, 1:2) R_f = 0.38; ^1H NMR (600 MHz, $CDCl_3$) δ 7.51–7.34 (7 H, m), 7.15–7.11 (2 H, m), 6.47/6.41 (1 H, br s), 5.81 (0.5 H, br s), 5.58–5.28 (1.5 H, m), 5.23–5.13 (3 H, m), 5.10–4.81 (2.5 H, m), 4.56 (0.5 H, br s), 3.33 (1 H, br s), 3.01–2.93 (1 H, m), 2.68–2.66 (1 H, m), 2.42–1.81 (15 H, 5 × OAc);

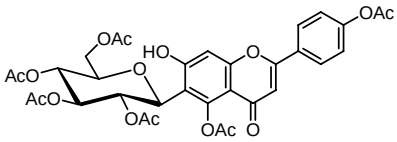
HRMS calcd for $C_{37}H_{36}NaO_{14}$: 727.2003, found: *m*/*z* 727.2009 $[M + Na]^+$.

5,4'-Diacetoxy-6-*C*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-7-benzyloxyflavanone (19c)



By a procedure similar to that for **19a**, compound **12cBn** (649 mg, 1 mmol) was subjected to acetylation and a subsequent oxidation with CAN to give flavanone **19c** (366 mg, 52%) as an inseparable diastereomeric mixture. $C_{37}H_{36}O_{14}$; colorless foam; TLC (EtOAc/hexane, 1:2) R_f = 0.38; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (1 H, br s), 7.43–7.31 (6 H, m), 7.13–7.11 (2 H, m), 6.51–6.42 (1 H, m), 6.13 (0.5 H, br s), 5.85–5.79 (0.5 H, m), 5.44–5.04 (5.5 H, m), 4.90 (0.5 H, d, *J* = 9.0 Hz), 4.08–3.98 (1 H, m), 3.69 (1 H, d, *J* = 13.1 Hz), 3.01–2.95 (1 H, m), 2.70–2.64 (1 H, m), 2.46–1.79 (15 H, 5 × OAc); HRMS calcd for $C_{37}H_{36}NaO_{14}$ (M^+ + Na): 727.2003, found: *m*/*z* 727.2007 $[M + Na]^+$.

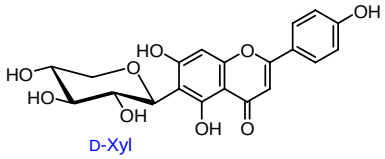
5,7,4'-Trihydroxy-6-*C*-(β-D-glucopyranosyl)flavone peracetate (3aAc).



Flavanone **19a** was treated with iodine in DMSO at 140 °C for 1 h, followed by hydrogenolysis on 10% Pd/C and reacetylation, to afford flavone **3aAc**. $C_{35}H_{34}O_{17}$; colorless foam; TLC (EtOAc/hexane, 1:1) R_f = 0.4; IR (film) 2938, 1721, 1600, 1214, 1135 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, as mixture of rotamers) δ 7.82 (2 H, d, *J* = 8.2 Hz), 7.29 (1 H, s), 7.22 (2 H, d, *J* = 8.2 Hz), 6.57 (1 H, s), 5.68 (0.7 H, t, *J* = 9.5 Hz), 5.61 (0.3 H, t, *J* = 9.5 Hz), 5.29 (1 H, t, *J* = 9.3 Hz), 5.14 (1 H, t, *J* = 9.7 Hz), 4.85–4.81 (1 H, m), 4.39 (1 H, br d, *J* = 13.0 Hz), 3.96 (1 H, br d, *J* = 12.3 Hz), 3.79 (1 H, br d, *J* = 9.4 Hz), 2.46 (3 H, s), 2.45 (3 H, s), 2.30 (3 H, s), 2.15–1.91 (9 H, m), 1.79 (3 H, s); ^{13}C NMR (150 MHz, $CDCl_3$, as mixture of rotamers) δ 176.0, 170.4, 170.2, 169.9, 169.6, 168.9, 168.6, 167.8, 161.7, 157.2, 153.4, 153.3, 148.7, 128.3, 127.6 (2 ×),

122.4 (2 ×), 119.0, 114.5, 111.8, 108.7, 76.5, 74.3, 72.3, 69.5, 68.1, 61.9, 21.3, 21.2, 21.1, 20.7, 20.67, 20.63, 20.4; HRMS calcd for $C_{35}H_{35}O_{17}$: 727.1874, found: *m*/*z* 727.1877 $[M + H]^+$.

5,7,4'-Trihydroxy-6-*C*-(β-D-xylopyranosyl)flavone (3b)

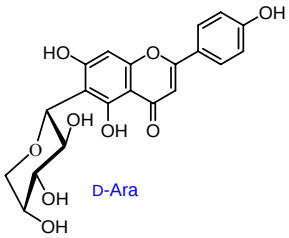


By the procedure similar to that for **3a**, flavone **19b** (224 mg, 0.4 mmol) was oxidized with Me_2SO/I_2, followed by debenzylation and acetylation, to give **3bAc** (204 mg, 78% for three steps). Saponification of **3bAc** (66 mg, 0.1 mmol) gave **3b** (36 mg) in 90% yield.

3bAc: $C_{32}H_{30}O_{15}$; white foam; TLC (EtOAc/hexane, 1:1) R_f = 0.45; IR (film) 2921, 1756, 1621, 1276, 1119 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, as mixture of rotamers) δ 7.83 (2 H, d, *J* = 8.6 Hz), 7.28 (1 H, s), 7.23 (2 H, d, *J* = 8.6 Hz), 6.58 (1 H, s), 5.63 (0.6 H, br s), 5.43 (0.4 H, br s), 5.32–5.27 (1 H, m), 5.04–5.00 (1 H, m), 4.74 (1 H, br s, *J* = 7.2 Hz), 4.15 (1 H, dd, *J* = 11.3, 5.5 Hz), 3.39 (1 H, t, *J* = 10.9 Hz), 2.46 (3 H, s), 2.41 (3 H, s), 2.31 (3 H, s), 2.04 (3 H, s), 2.02 (3 H, s), 1.79 (3 H, s); ^{13}C NMR (150 MHz, $CDCl_3$, as mixture of rotamers) δ 176.1, 170.2, 170.0, 169.0, 168.8, 168.6, 168.1, 161.7, 157.2, 153.4, 148.7, 128.3, 127.6 (2 ×), 124.7, 122.4 (2 ×), 119.4, 114.5, 111.8, 108.7, 73.7, 72.7, 69.8, 69.2, 67.3, 22.6, 21.2, 21.1, 20.7 (2 ×), 20.4; HRMS calcd for $C_{32}H_{30}NaO_{15}$: 677.1482, found: *m*/*z* 677.1485 $[M + Na]^+$.

3b: $C_{20}H_{18}O_9$; yellow powder; mp 198–200 °C; $[\alpha]_D^{20}$ = +19.5 (*c* = 0.6, MeOH); IR (film) 3439, 2919, 1651, 1221, 1173 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.82 (2 H, d, *J* = 8.6 Hz), 6.92 (2 H, d, *J* = 8.6 Hz), 6.58 (1 H, s), 6.48 (1 H, s), 5.33 (0.5 H, t, *J* = 4.9 Hz), 4.79 (1 H, d, *J* = 9.9 Hz, $H_{anomeric}$, 6-β-configuration), 4.23 (1 H, t, *J* = 9.4 Hz), 3.98 (1 H, dd, *J* = 11.1, 5.5 Hz), 3.68–3.64 (1.5 H, m), 3.42 (1 H, t, *J* = 8.9 Hz); ^{13}C NMR (150 MHz, CD_3OD) δ 183.1, 165.3, 164.0, 161.9, 161.4, 157.9, 128.5 (2 ×), 122.2, 116.1 (2 ×), 108.1, 104.3, 103.0, 94.1, 79.4, 75.1, 71.3, 70.7, 70.6; HRMS calcd for $C_{20}H_{19}O_9$: 403.1029, found: *m*/*z* 403.1033 $[M + H]^+$.

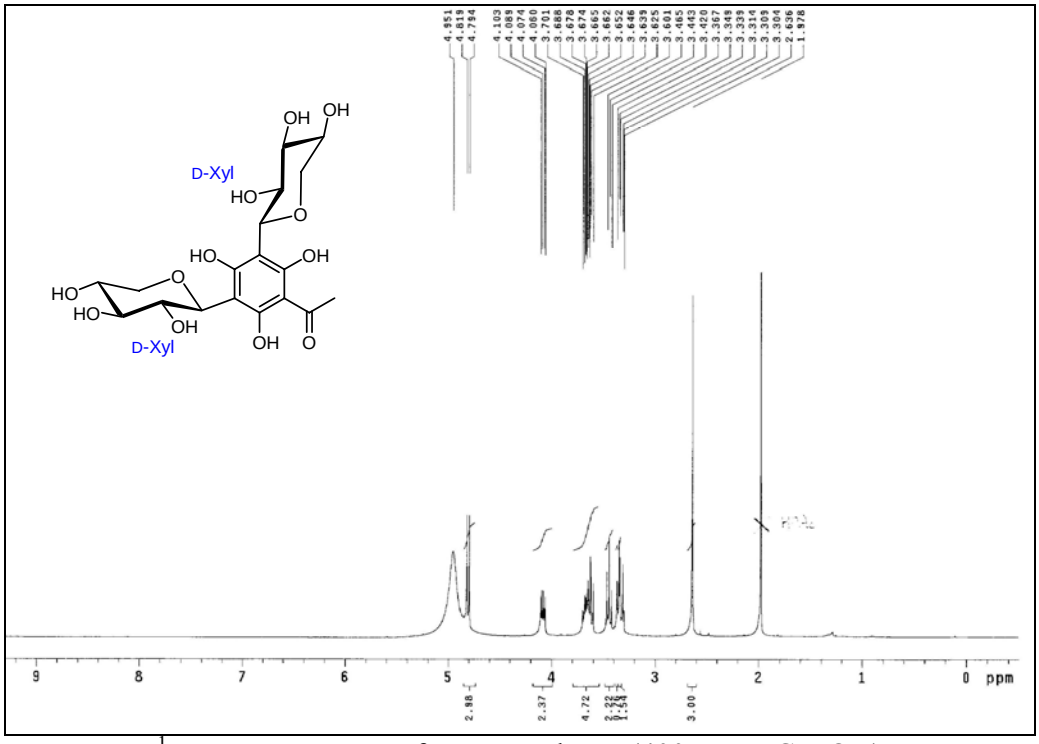
5,7,4'-Trihydroxy-6-*C*-(α-D-arabinopyranosyl)flavone (3c)



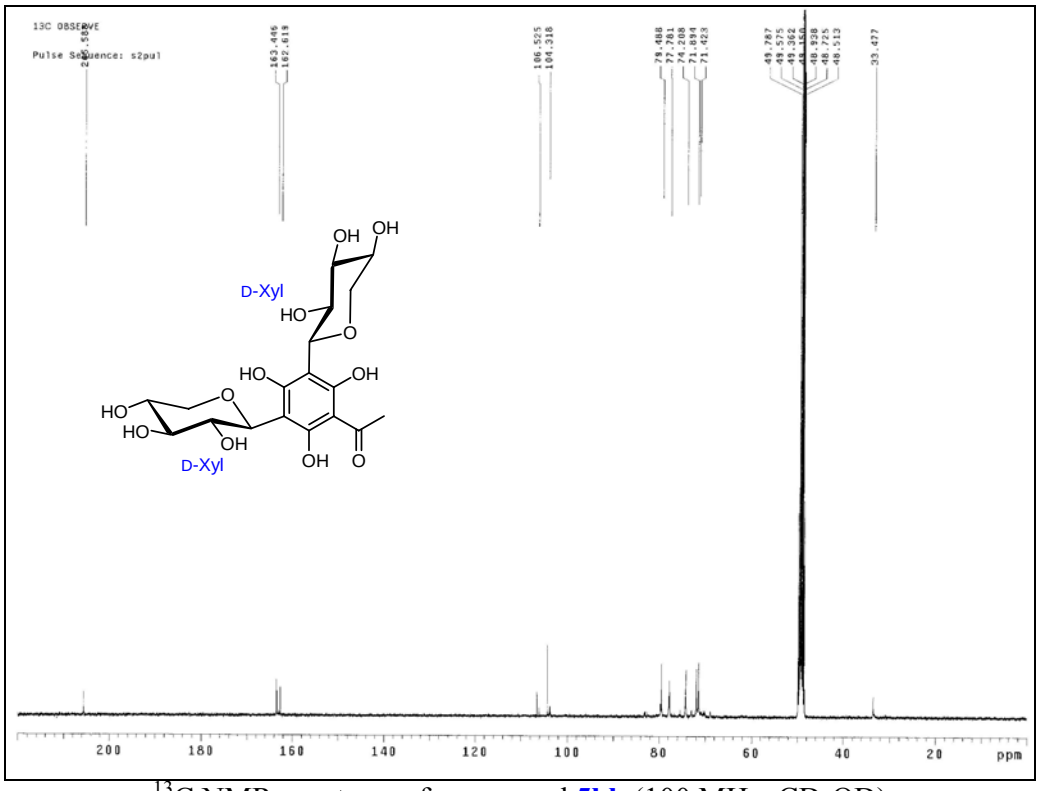
By the procedure similar to that for **3a**, flavone **19c** (280 mg, 0.5 mmol) was oxidized with Me_2SO/I_2, followed by debenzylation and acetylation, to give **3cAc** (256 mg, 78% for three steps). Saponification of **3cAc** (68 mg, 0.1 mmol) gave **3c** (34 mg) in 85% yield.

3cAc: TLC (EtOAc/hexane, 1:1) R_f = 0.45; IR (film) 2922, 1719, 1626, 1216, 1183 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, as mixture of rotamers) δ 7.84 (2 H, d, *J* = 8.7 Hz), 7.30 (1 H, s), 7.24 (2 H, d, *J* = 8.7 Hz), 6.58 (1 H, s), 5.84 (1 H, br d, *J* = 9.4 Hz), 5.47 (1 H, br s), 5.15 (1 H, dd, *J* = 10.1, 3.6 Hz), 4.69 (1 H, d, *J* = 9.4 Hz), 4.04 (1 H, d, *J* = 13.1 Hz), 3.79 (1 H, d, *J* = 13.1 Hz), 2.47 (3 H, s), 2.32 (3 H, s), 2.19 (3 H, s), 2.16 (3 H, s), 1.99 (3 H, s), 1.79 (3 H, s); ^{13}C NMR (150 MHz, $CDCl_3$, as mixture of rotamers) δ 176.1, 170.1, 169.9, 169.2, 168.8, 168.5, 168.3, 161.7, 157.1, 153.4, 148.6, 128.3, 127.59 (2 ×), 127.50, 122.4 (2 ×), 119.3, 114.5, 111.6, 108.6, 73.2, 71.9, 69.2, 68.8, 68.1, 20.8, 20.7, 20.6, 20.5 (2 ×), 20.3; HRMS calcd for $C_{32}H_{30}NaO_{15}$: 677.1482, found: *m*/*z* 677.1488 $[M + Na]^+$.

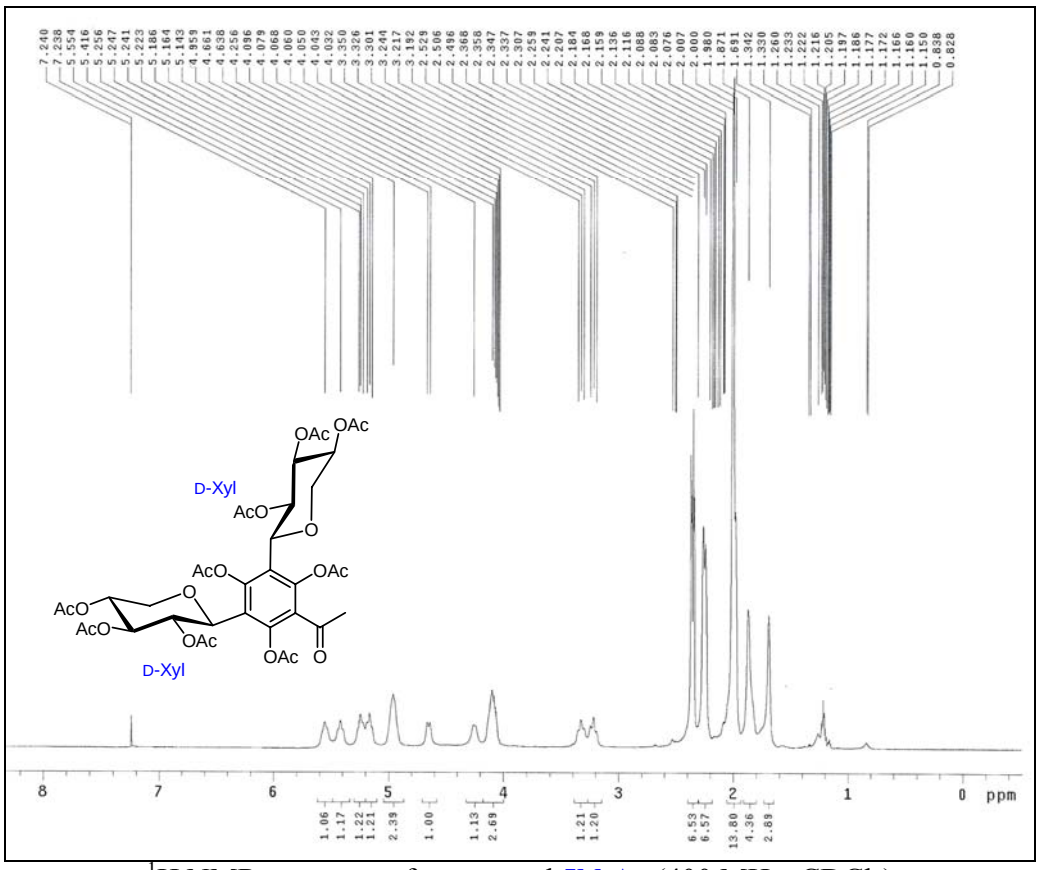
3c: $C_{20}H_{18}O_9$; yellow powder; mp 181–183 °C; $[\alpha]_D^{20}$ = –37.6 (*c* = 0.35, MeOH); IR (film) 3451, 2938, 1661, 1282, 1159 cm^{-1}; ^1H NMR (600 MHz, MeOH-d_4) δ 7.83 (2 H, d, *J* = 8.8 Hz), 6.92 (2 H, d, *J* = 8.8 Hz), 6.59 (1 H, s), 6.51 (1 H, s), 4.79 (1 H, d, *J* = 9.8 Hz, $H_{anomeric}$, 6-α-configuration), 4.24 (1 H, t, *J* = 9.4 Hz), 4.02–3.99 (1 H, m), 3.96 (1 H, br s), 3.72 (1 H, d, *J* = 12.4 Hz), 3.61 (1 H, dd, *J* = 9.2, 3.1 Hz); ^{13}C NMR (150 MHz, MeOH-d_4) δ 183.1, 165.3, 163.8, 161.9, 160.4, 157.8, 128.6 (2 ×), 122.2, 116.1 (2 ×), 108.4, 104.3, 103.0, 94.7, 75.3, 74.9, 71.0, 69.9, 69.8; HRMS calcd for $C_{20}H_{19}O_9$: 403.1029, found: *m*/*z* 403.1028 $[M + H]^+$.



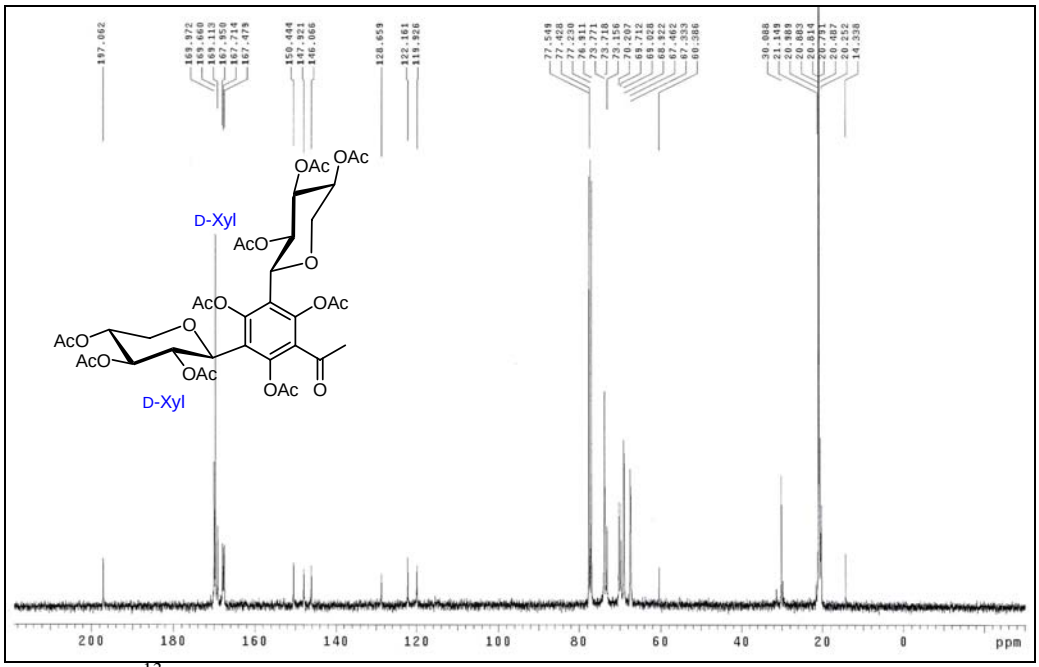
^{1}H NMR spectrum of compound **5bb** (400 MHz, CD_3OD)



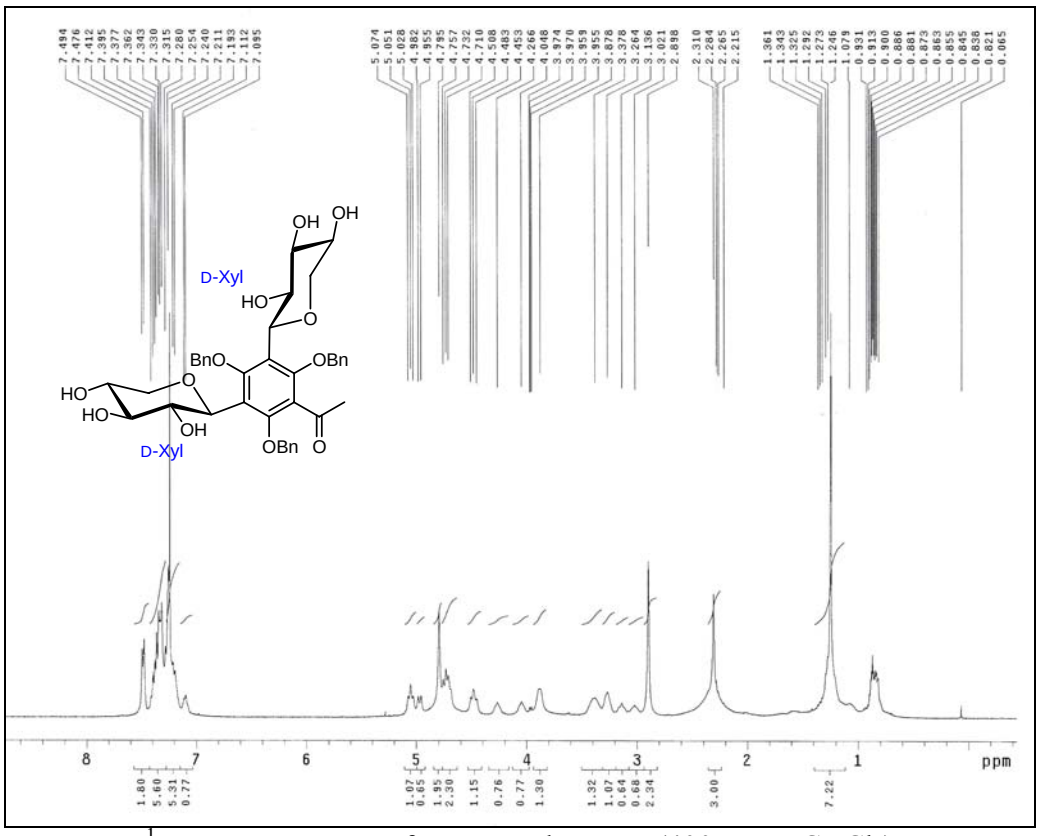
^{13}C NMR spectrum of compound **5bb** (100 MHz, CD_3OD)



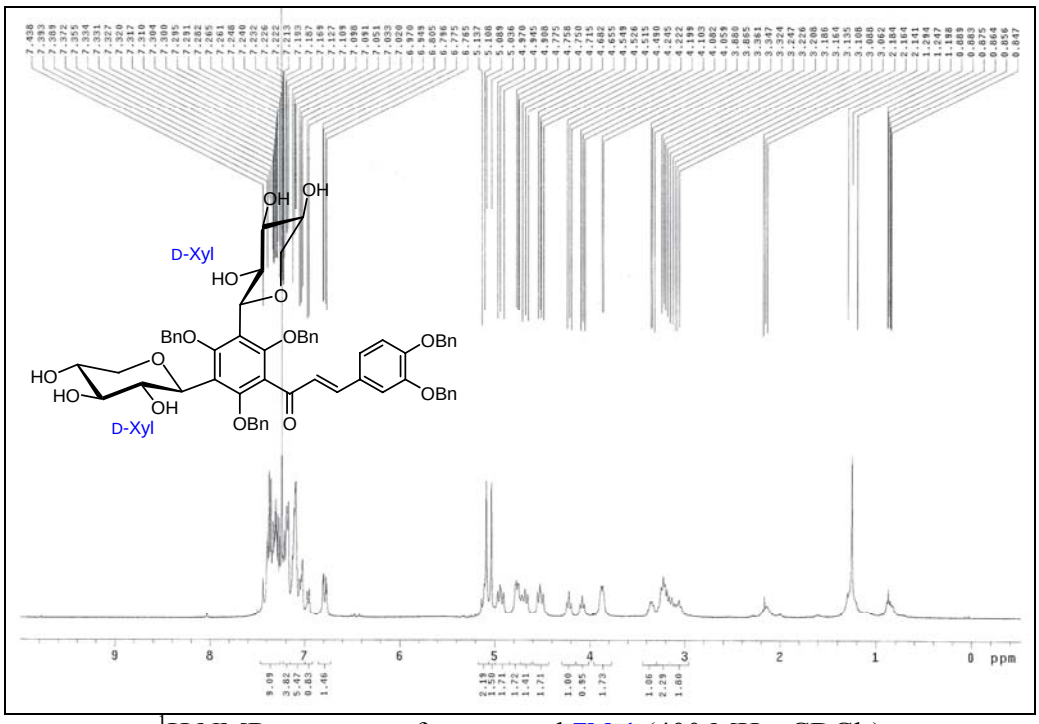
^{1}H NMR spectrum of compound **5bbAc** (400 MHz, $CDCl_3$)



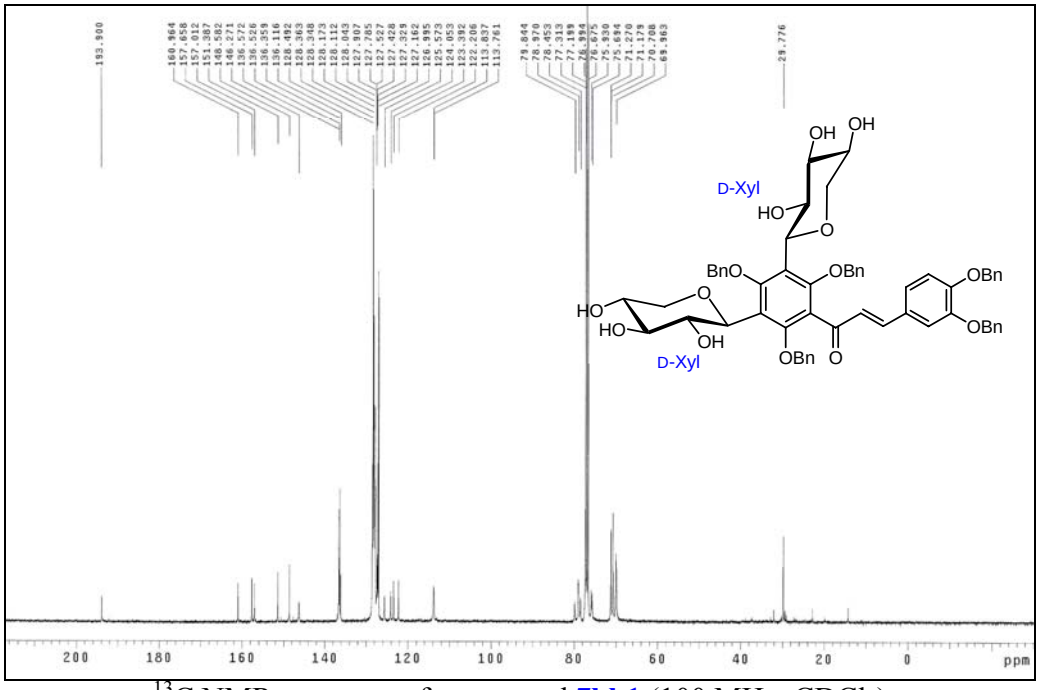
^{13}C NMR spectrum of compound **5bbAc** (100 MHz, $CDCl_3$)



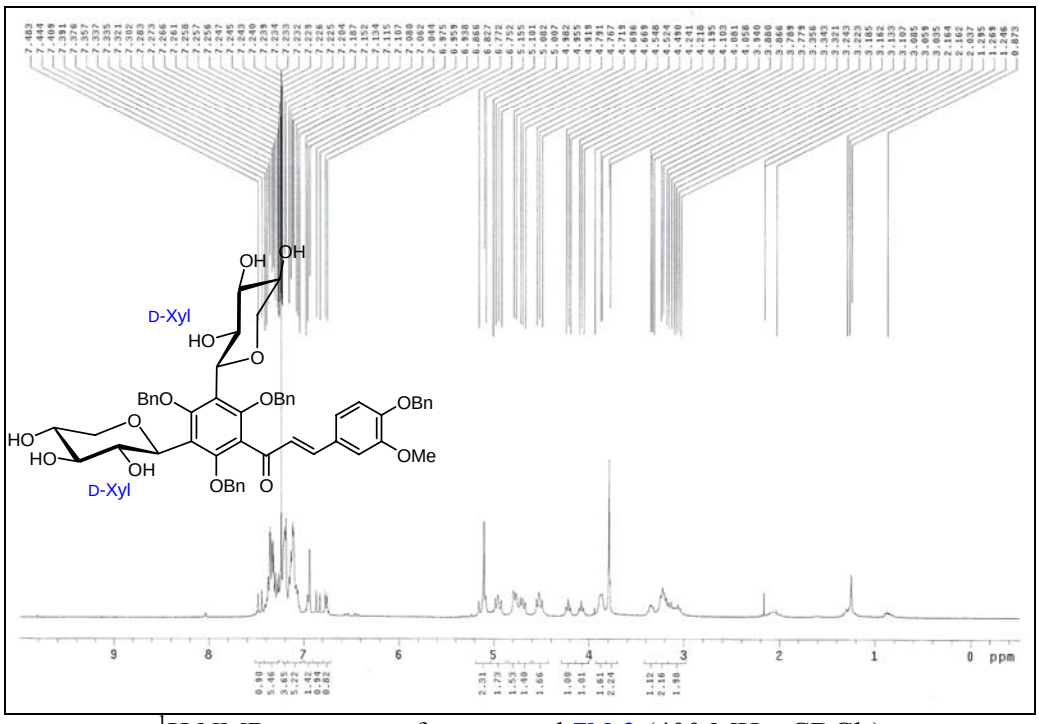
^{1}H NMR spectrum of compound **5bbBn** (400 MHz, $CDCl_3$)



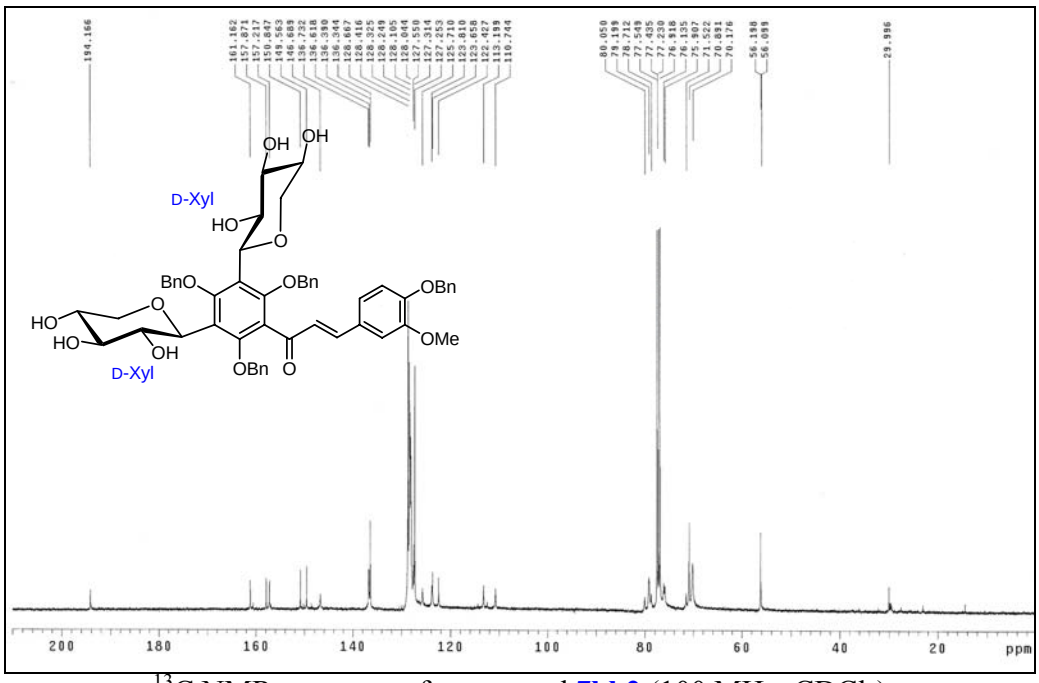
^{1}H NMR spectrum of compound **7bb1** (400 MHz, $CDCl_3$)



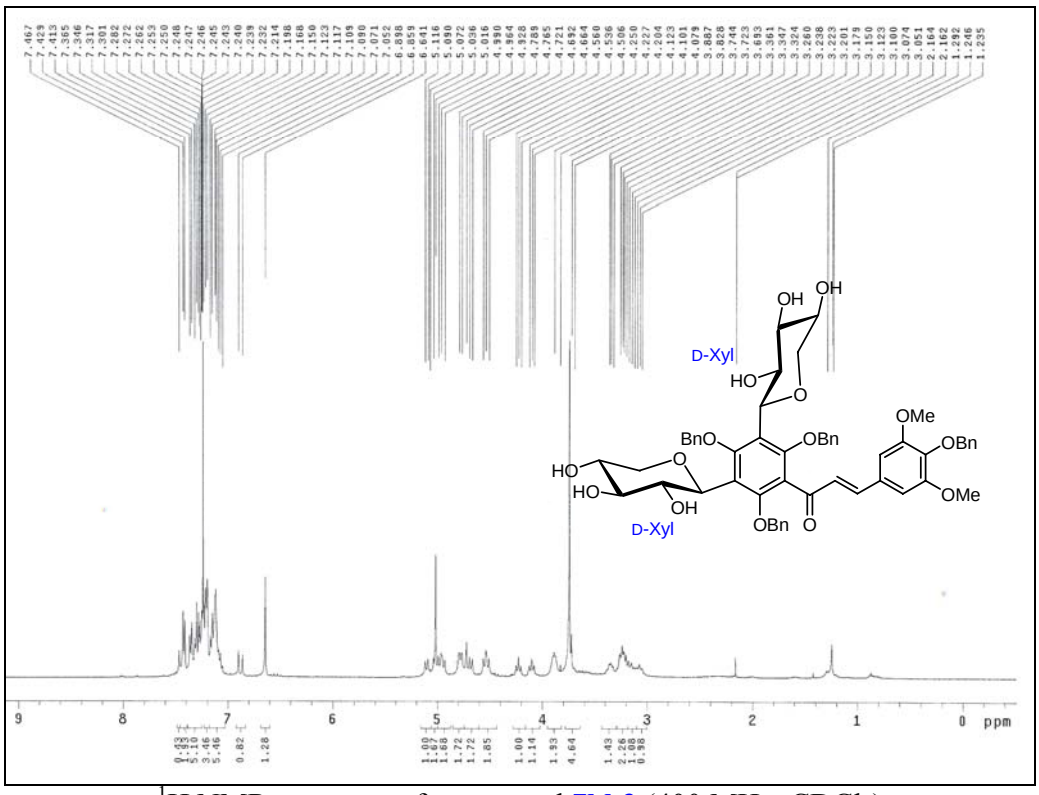
^{13}C NMR spectrum of compound **7bb1** (100 MHz, $CDCl_3$)



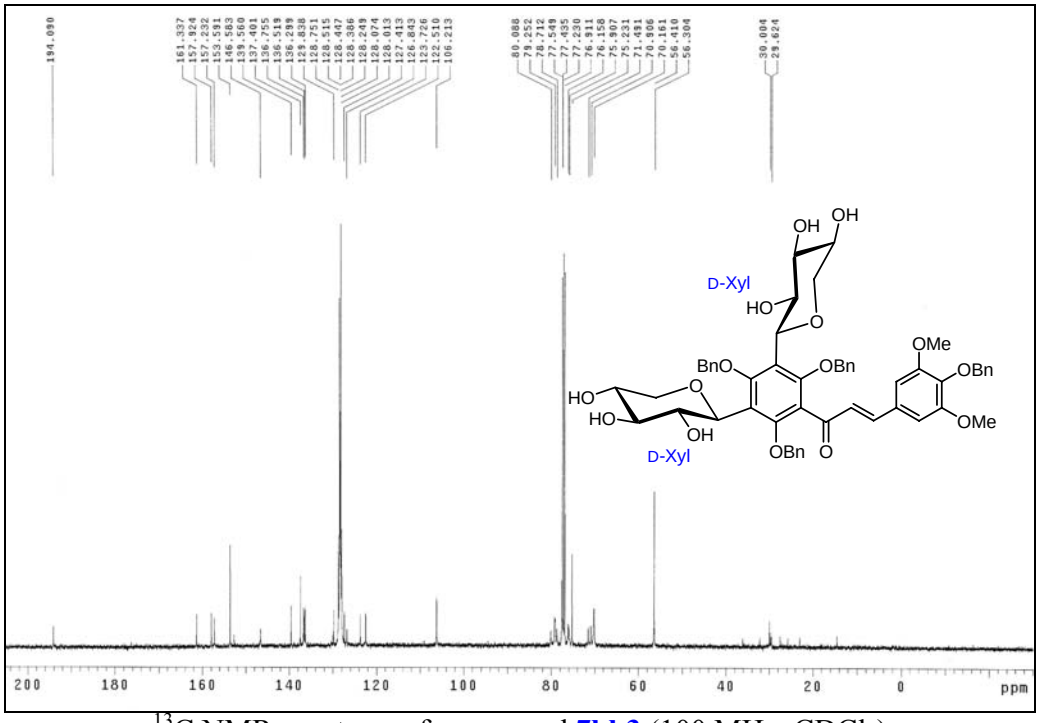
^{1}H NMR spectrum of compound **7bb2** (400 MHz, $CDCl_3$)



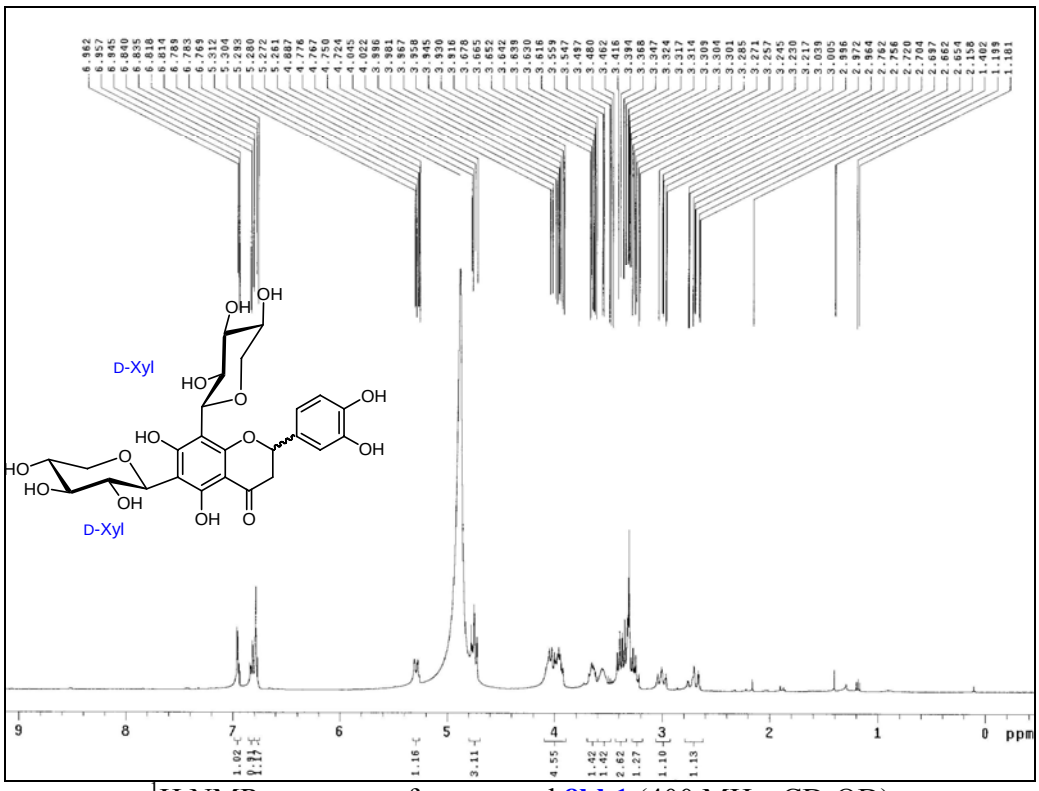
^{13}C NMR spectrum of compound **7bb2** (100 MHz, $CDCl_3$)



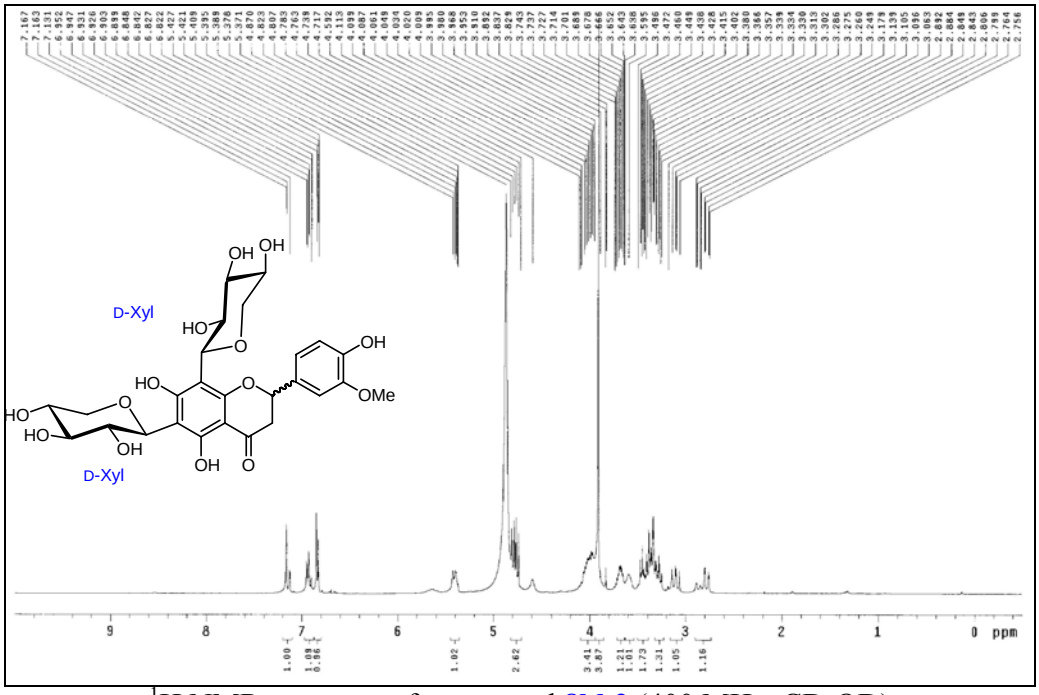
^{1}H NMR spectrum of compound **7bb3** (400 MHz, $CDCl_3$)



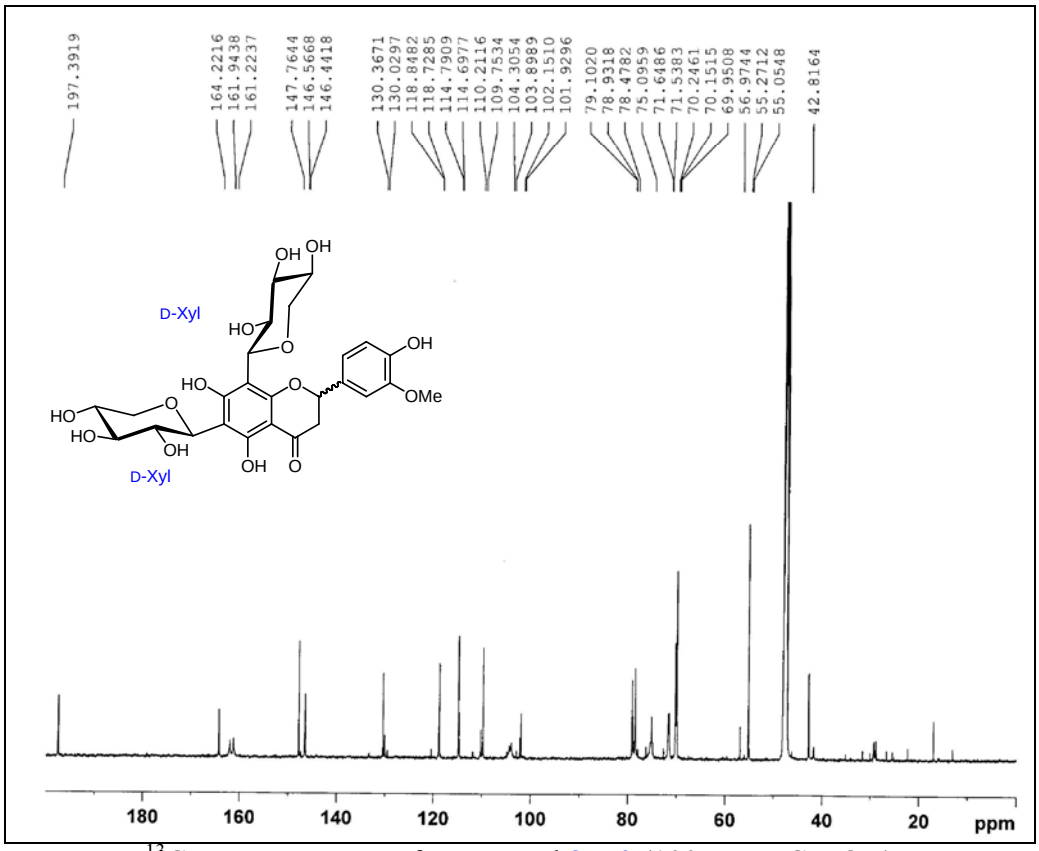
^{13}C NMR spectrum of compound **7bb3** (100 MHz, $CDCl_3$)



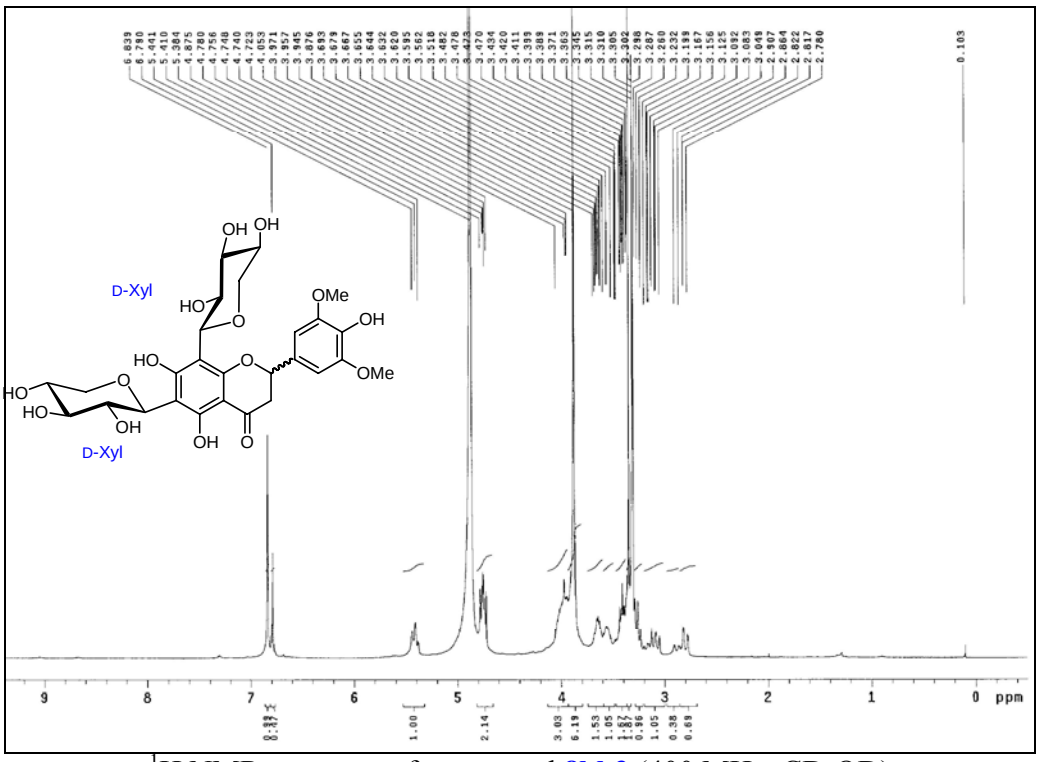
^{1}H NMR spectrum of compound **8bb1** (400 MHz, CD_3OD)



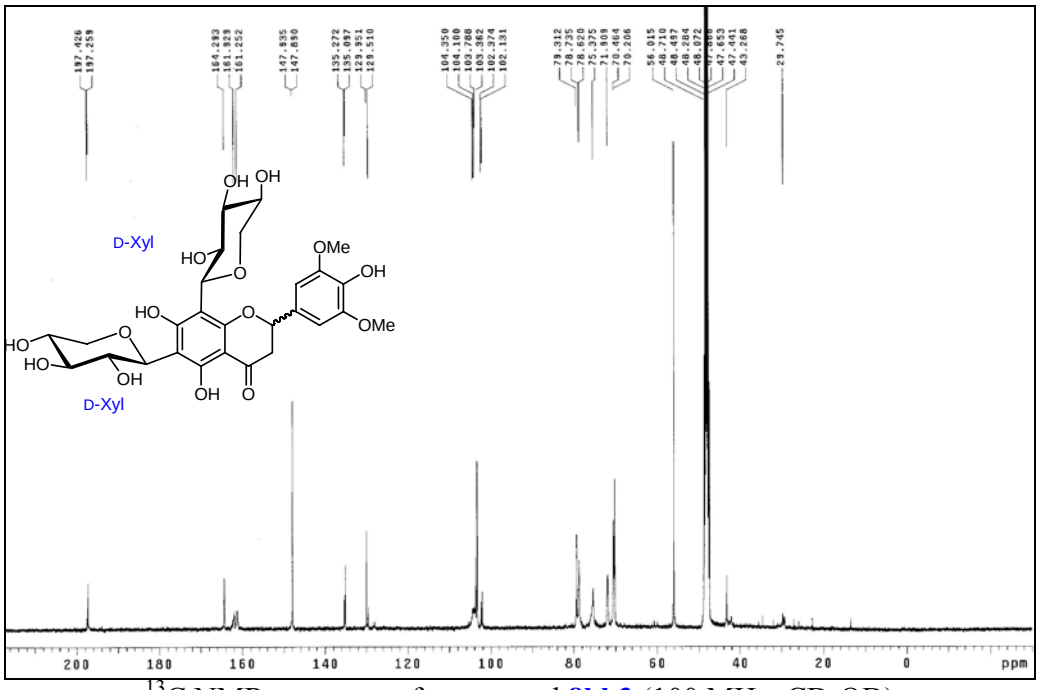
^{1}H NMR spectrum of compound **8bb2** (400 MHz, CD_3OD)



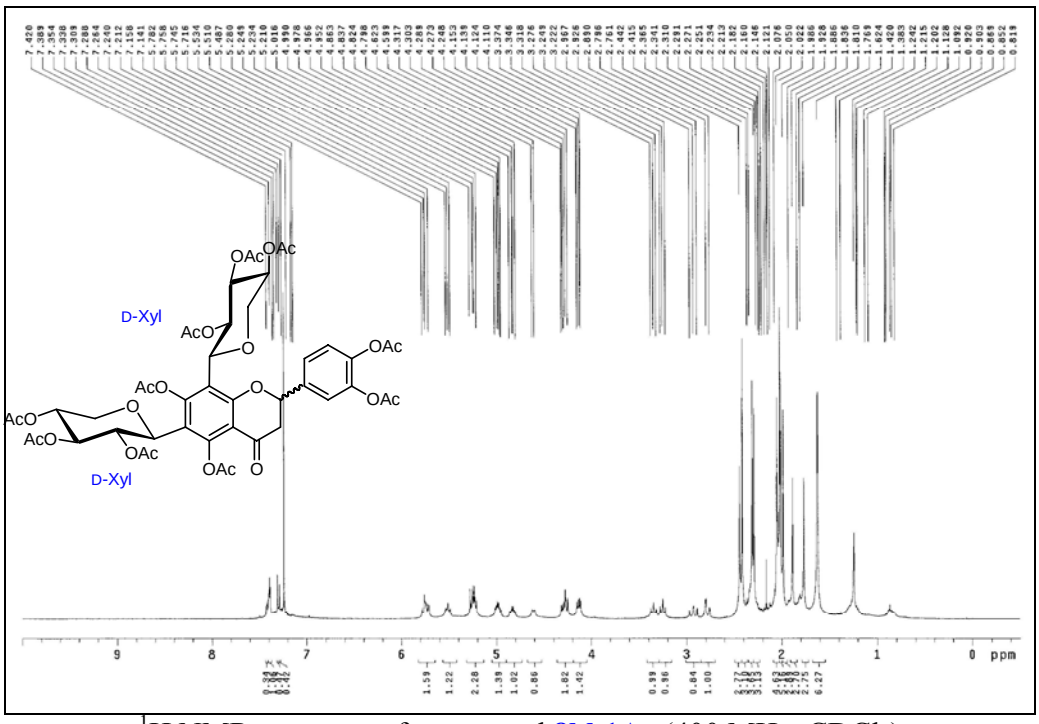
^{13}C NMR spectrum of compound **8bb2** (100 MHz, CD_3OD)



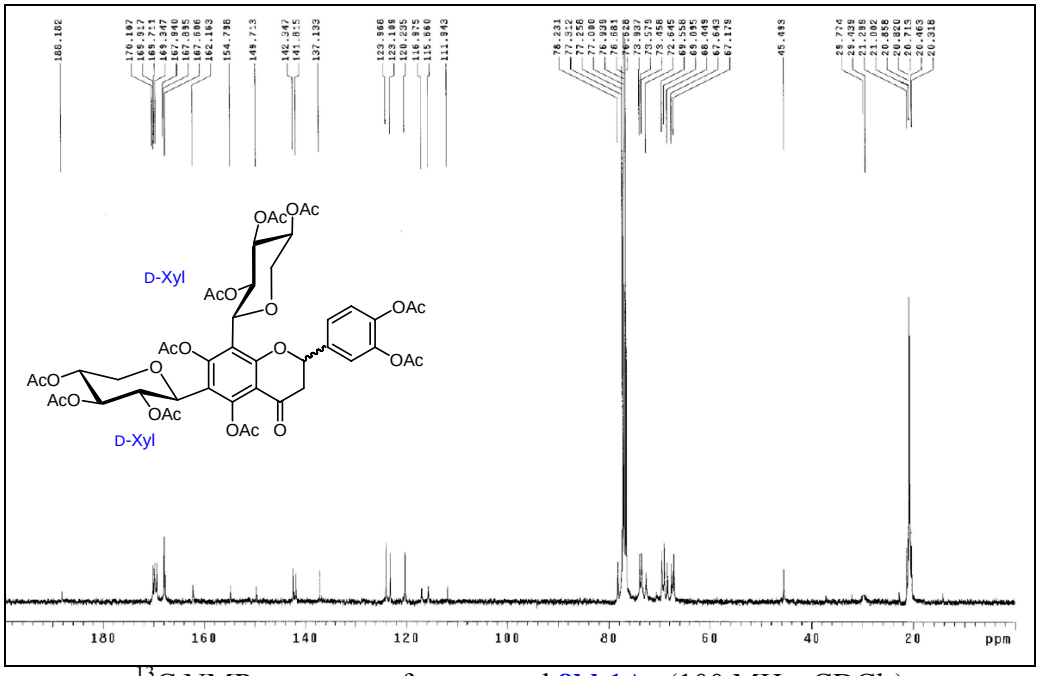
^{1}H NMR spectrum of compound **8bb3** (400 MHz, CD_3OD)



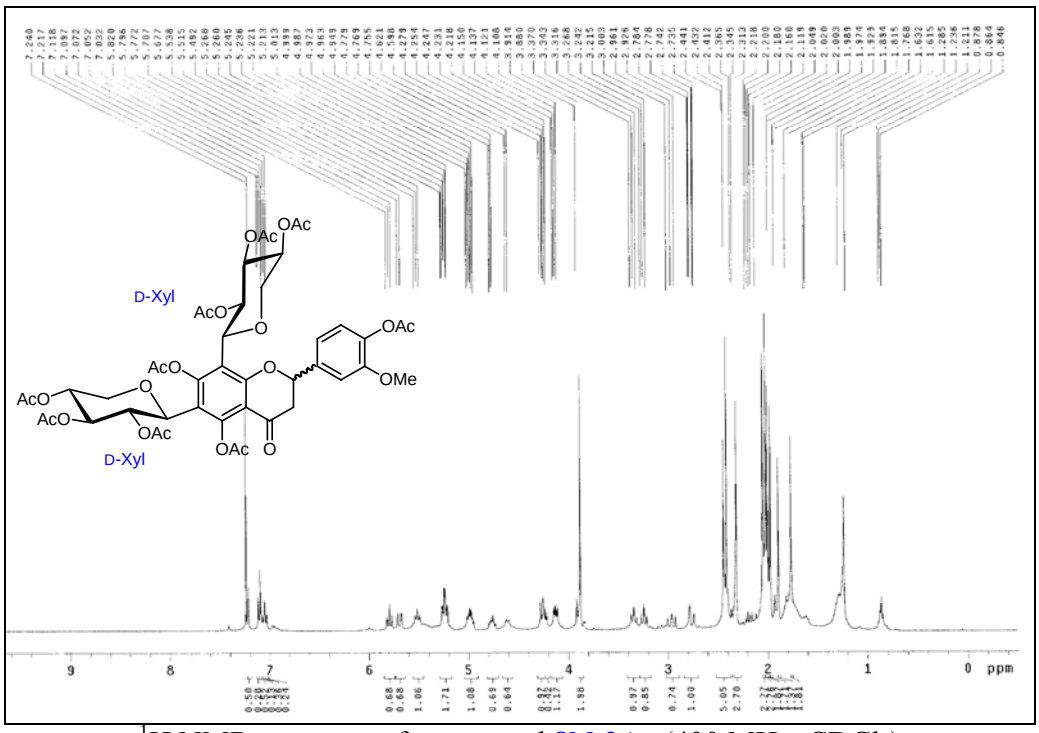
^{13}C NMR spectrum of compound **8bb3** (100 MHz, CD_3OD)



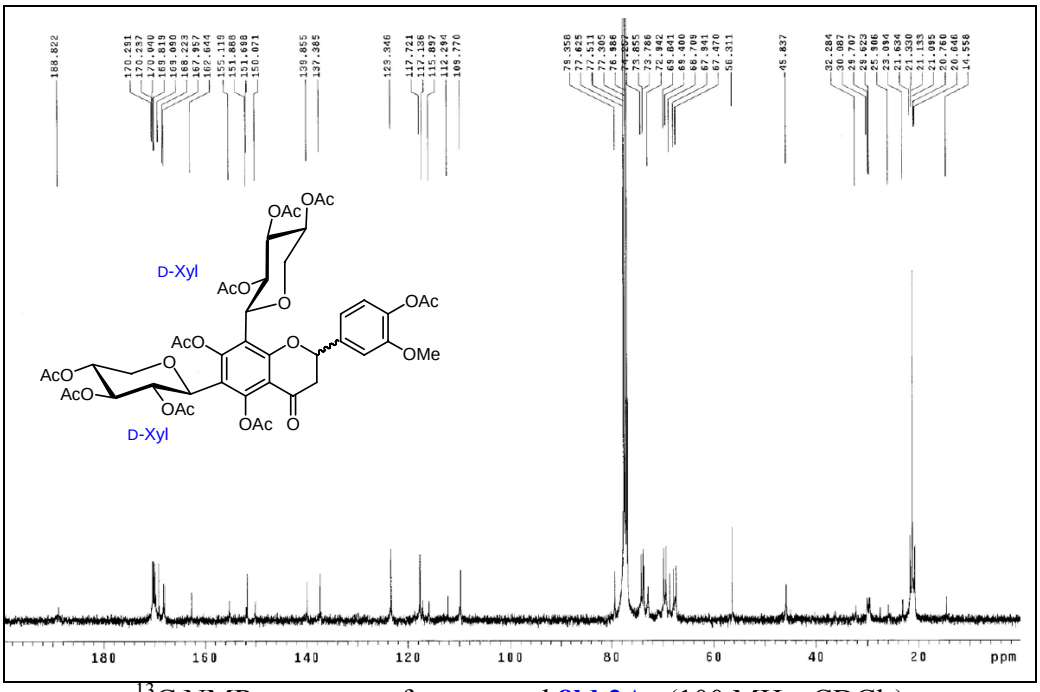
^{1}H NMR spectrum of compound **8bb1Ac** (400 MHz, $CDCl_3$)



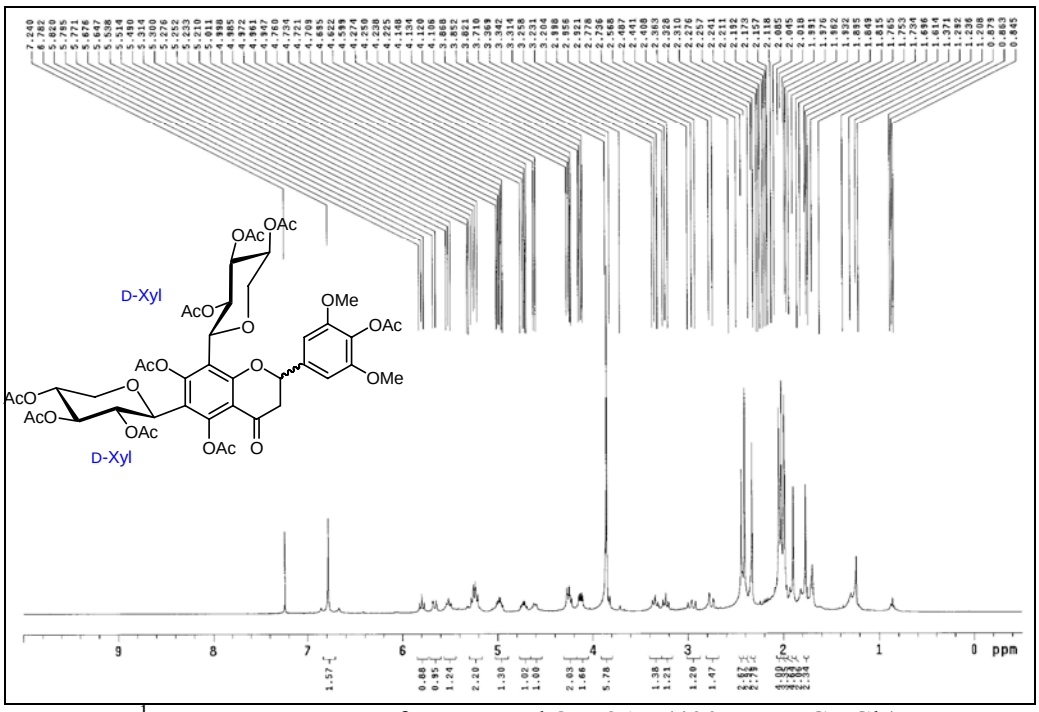
^{13}C NMR spectrum of compound **8bb1Ac** (100 MHz, $CDCl_3$)



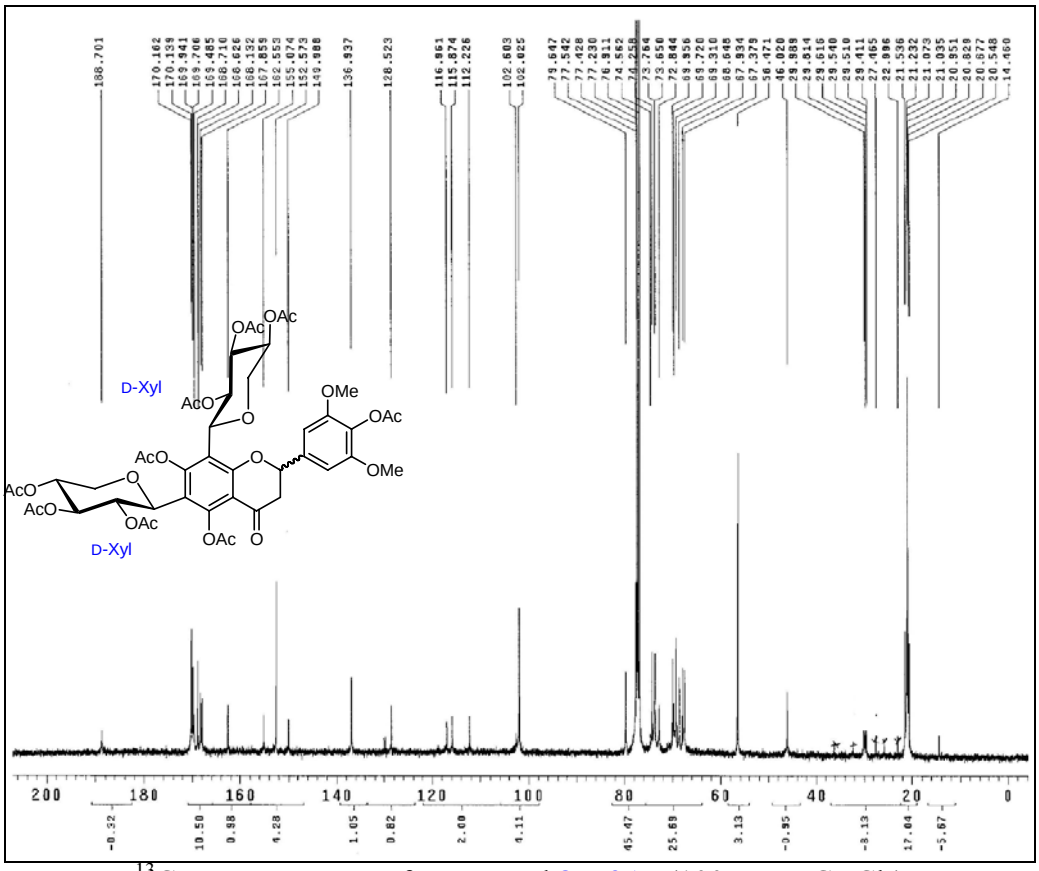
^{1}H NMR spectrum of compound **8bb2Ac** (400 MHz, $CDCl_3$)



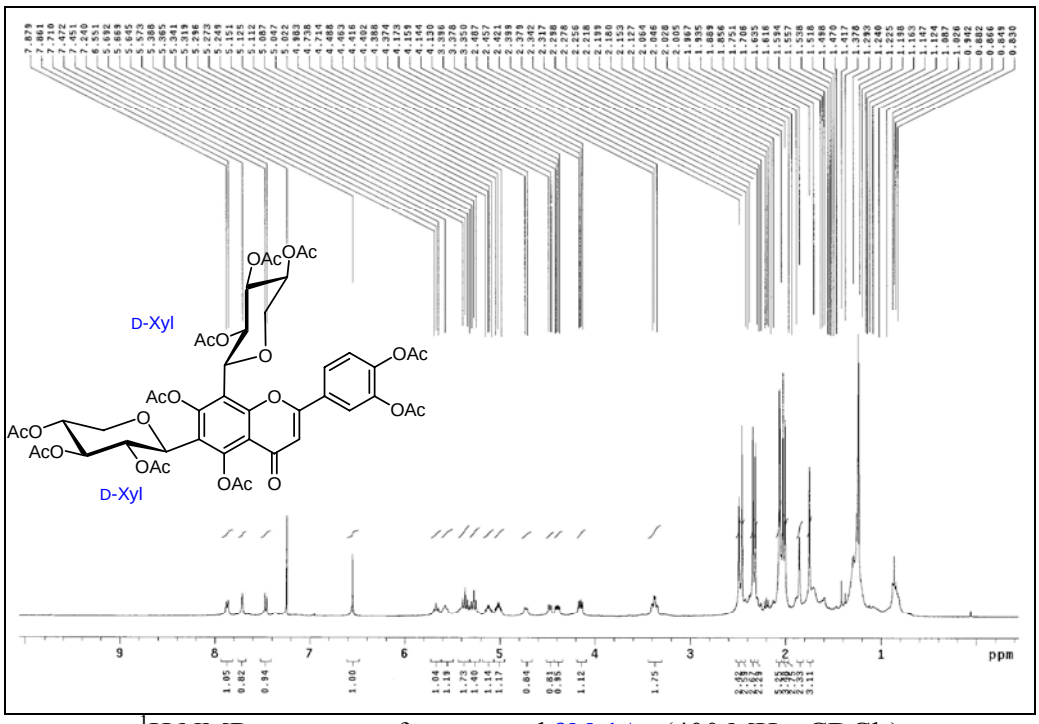
^{13}C NMR spectrum of compound **8bb2Ac** (100 MHz, $CDCl_3$)



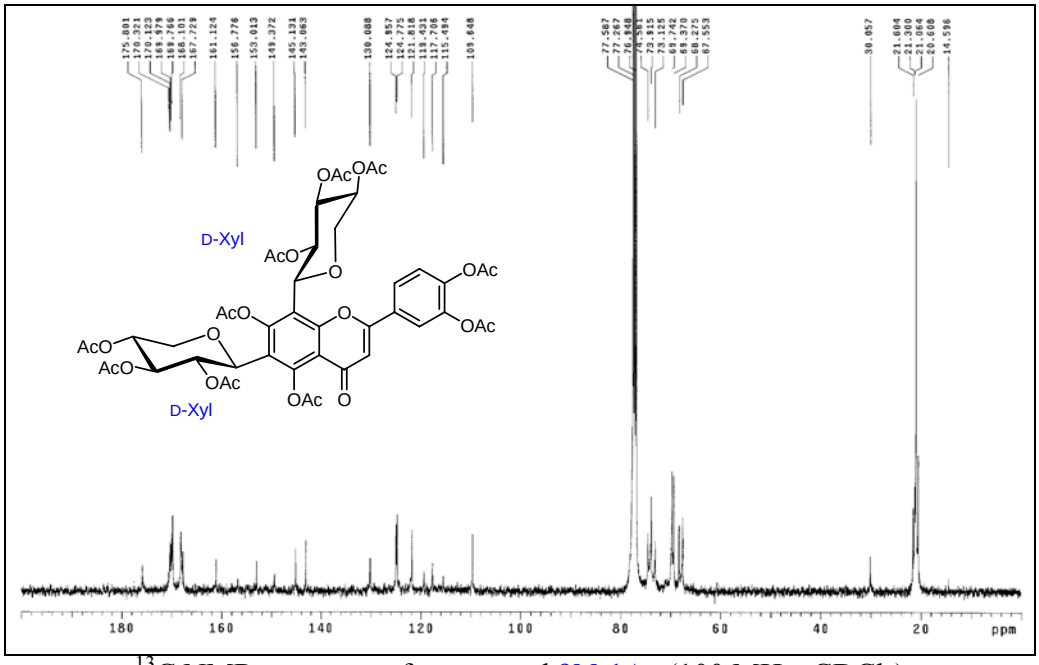
^{1}H NMR spectrum of compound **8bb3Ac** (400 MHz, $CDCl_3$)



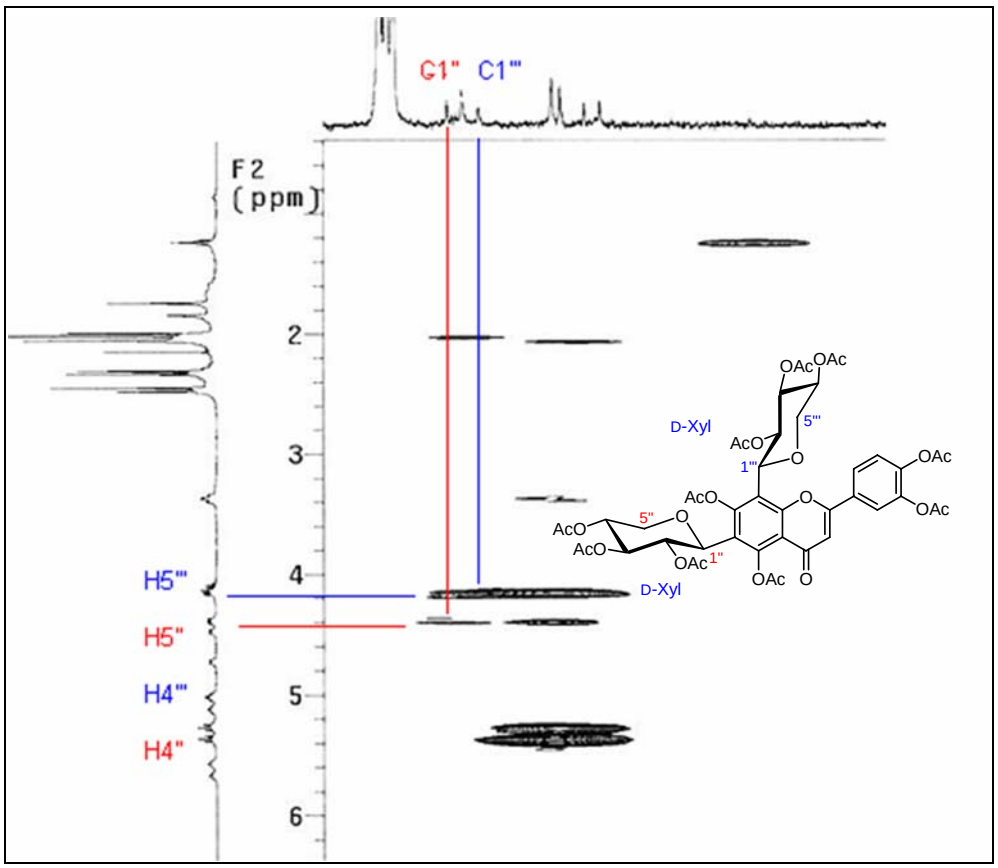
^{13}C NMR spectrum of compound **8bb3Ac** (100 MHz, $CDCl_3$)



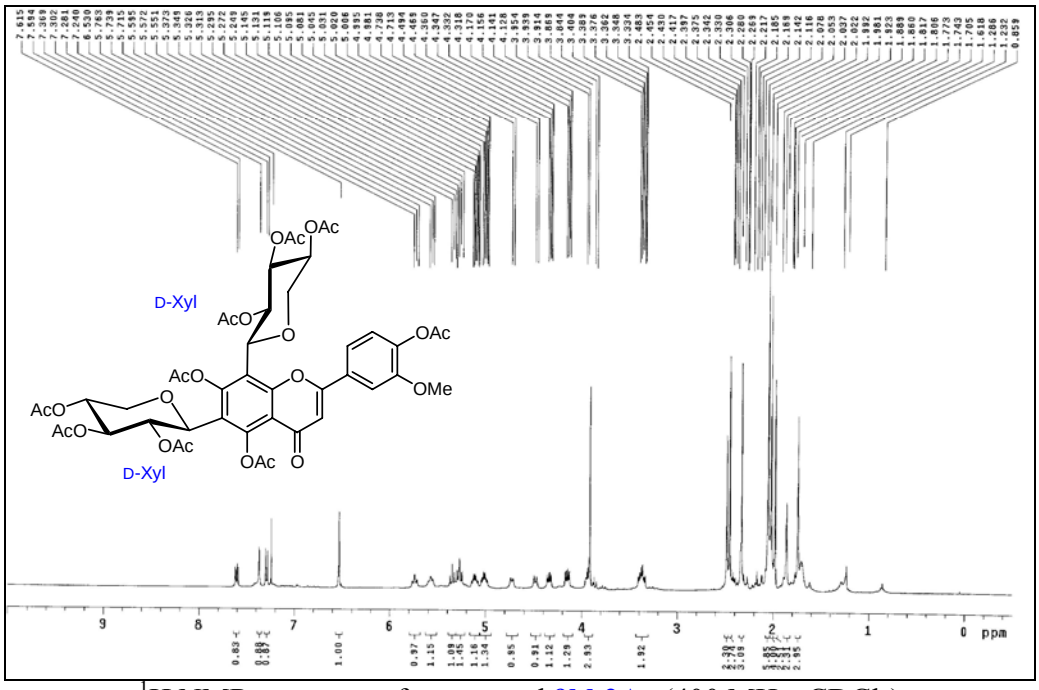
^{1}H NMR spectrum of compound **9bb1Ac** (400 MHz, $CDCl_3$)



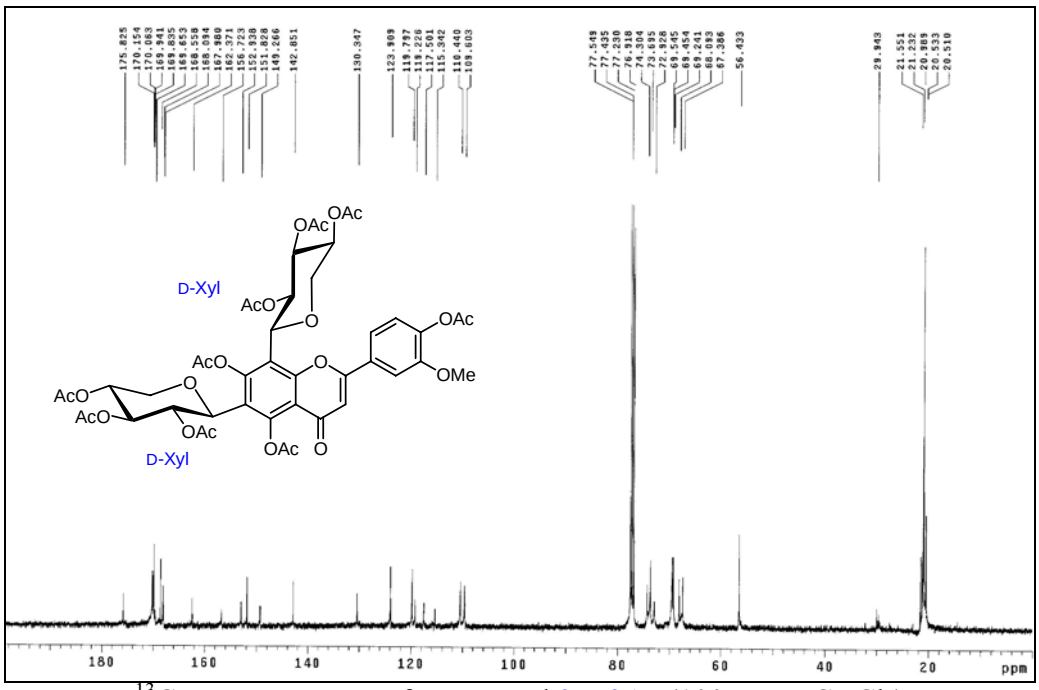
^{13}C NMR spectrum of compound **9bb1Ac** (100 MHz, $CDCl_3$)



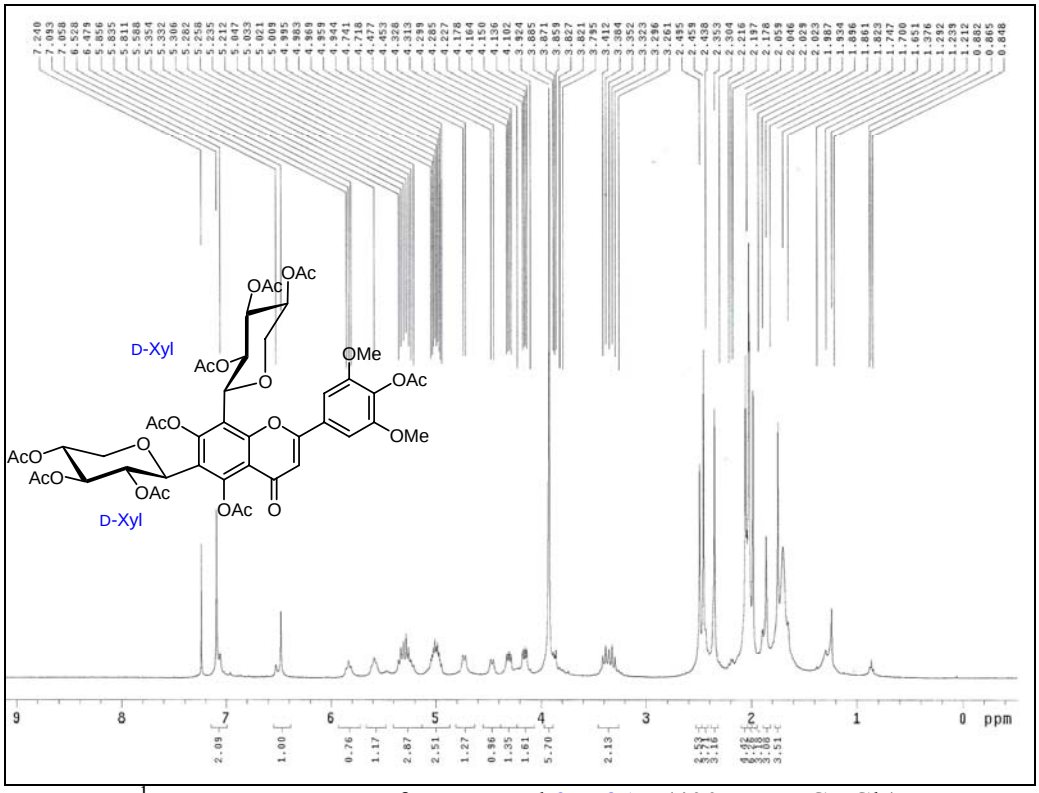
HMBC NMR spectrum of compound **9bb1Ac** (400 MHz, $CDCl_3$)



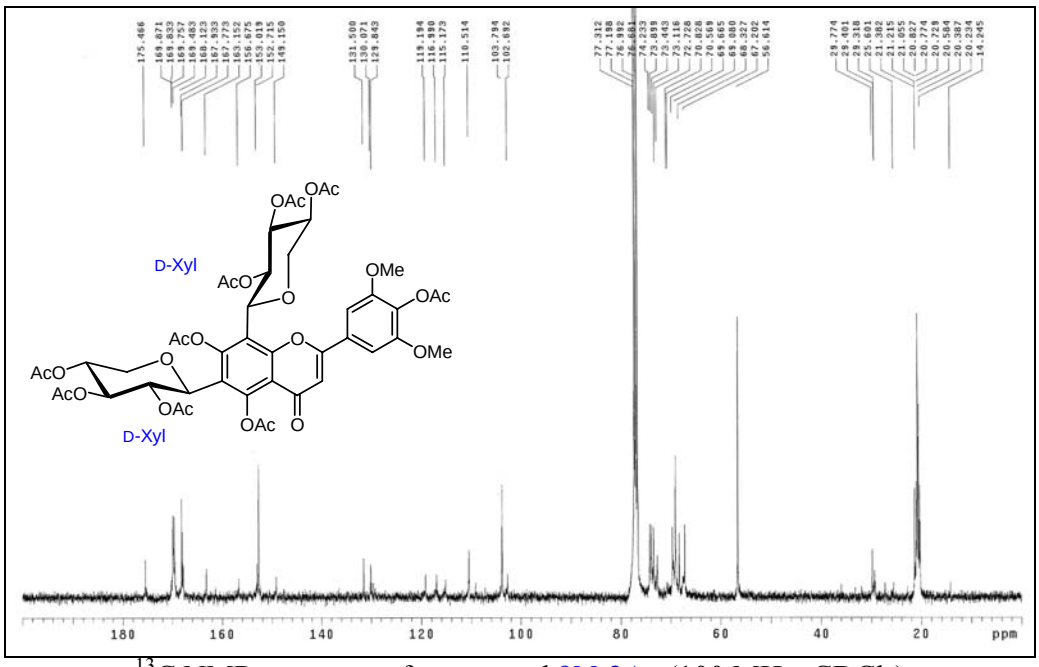
^{1}H NMR spectrum of compound **9bb2Ac** (400 MHz, $CDCl_3$)



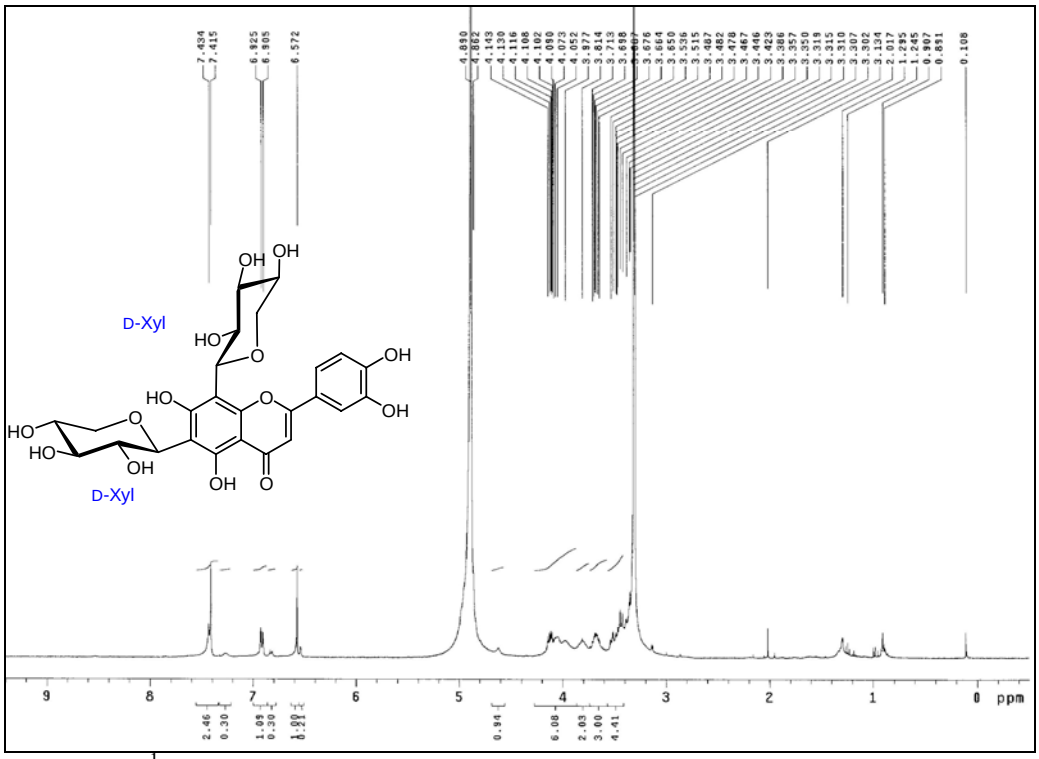
^{13}C NMR spectrum of compound **9bb2Ac** (100 MHz, $CDCl_3$)



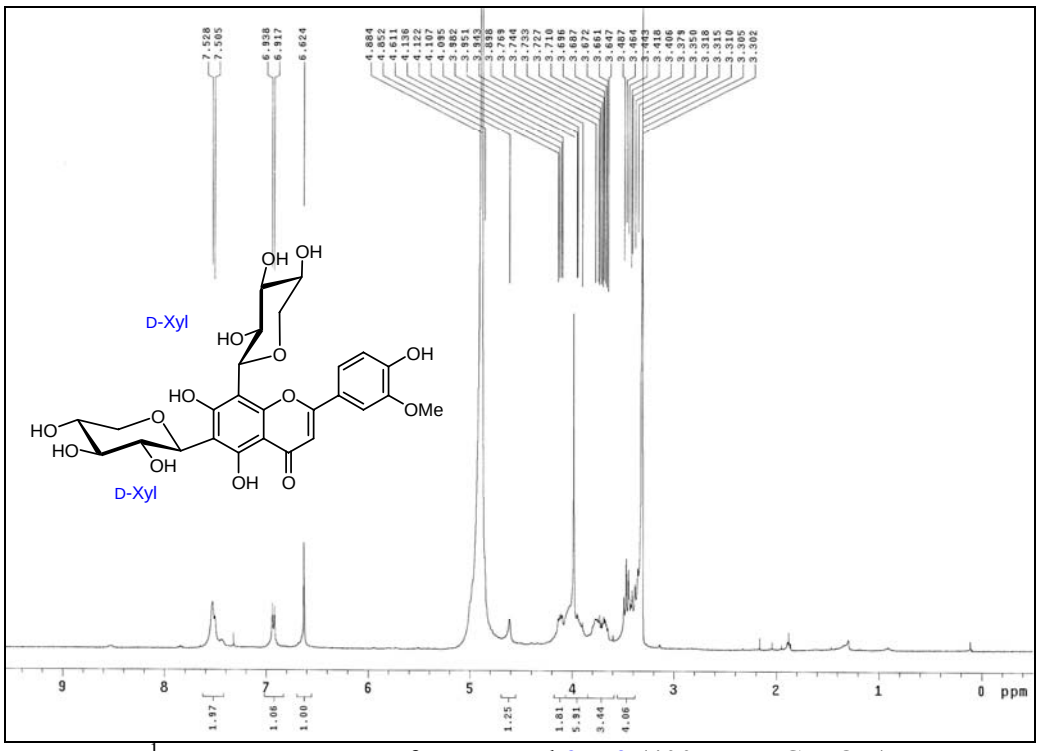
^{1}H NMR spectrum of compound **9bb3Ac** (400 MHz, $CDCl_3$)



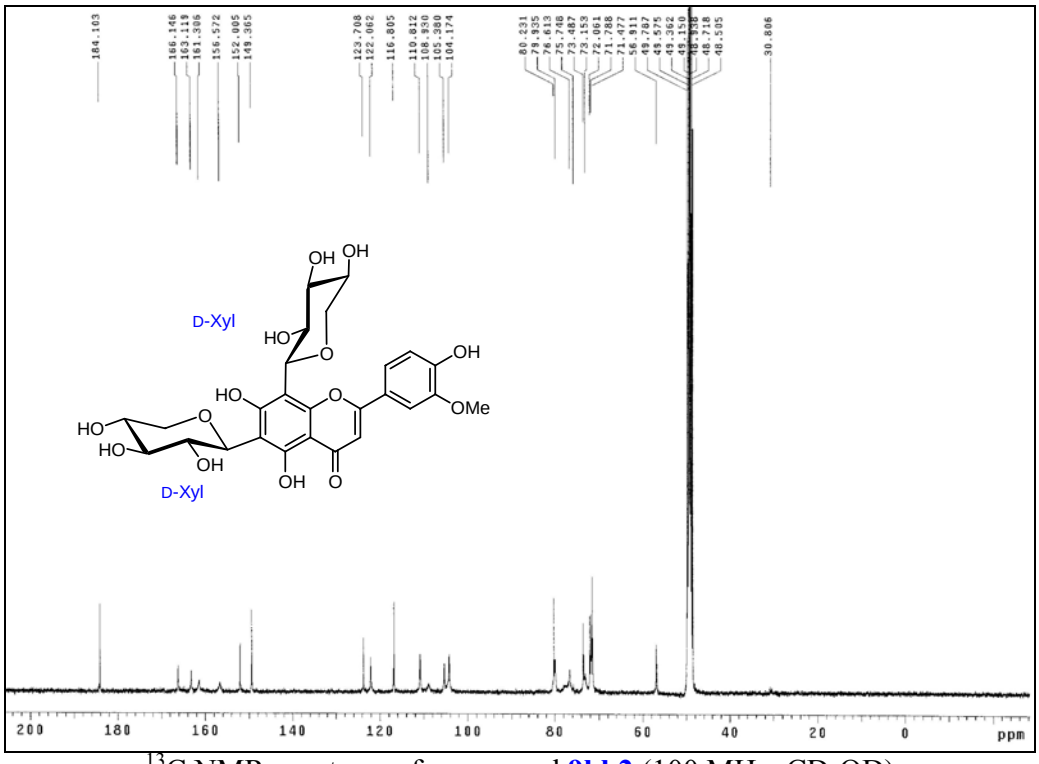
^{13}C NMR spectrum of compound **9bb3Ac** (100 MHz, $CDCl_3$)



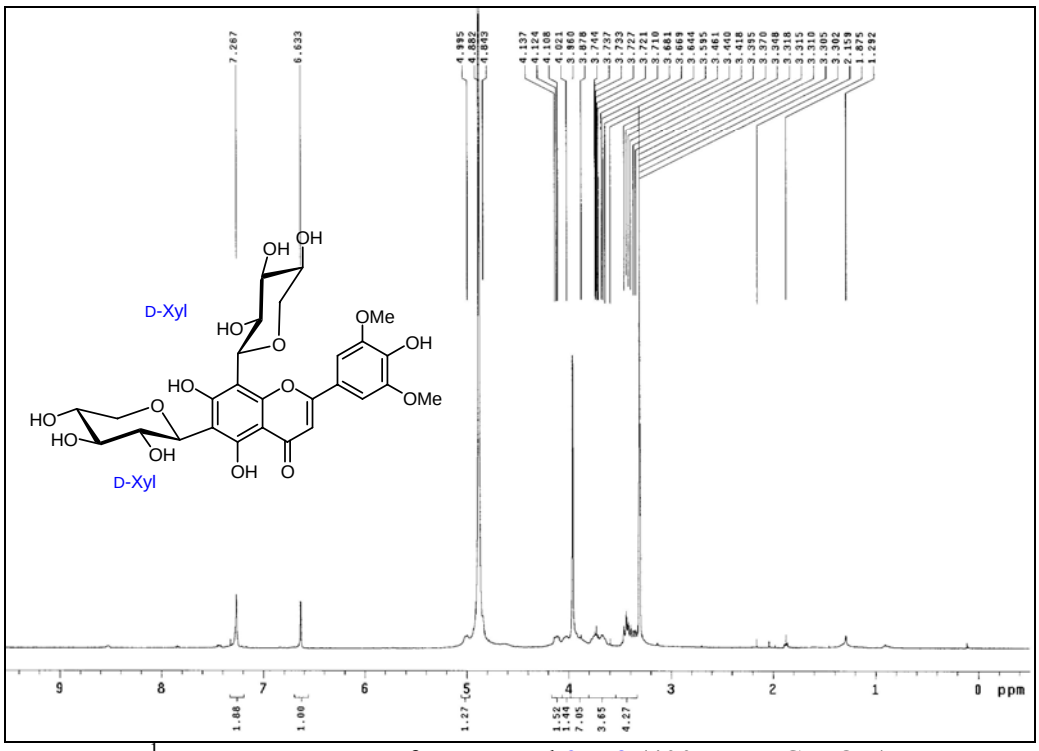
^{1}H NMR spectrum of compound **9bb1** (400 MHz, CD_3OD)



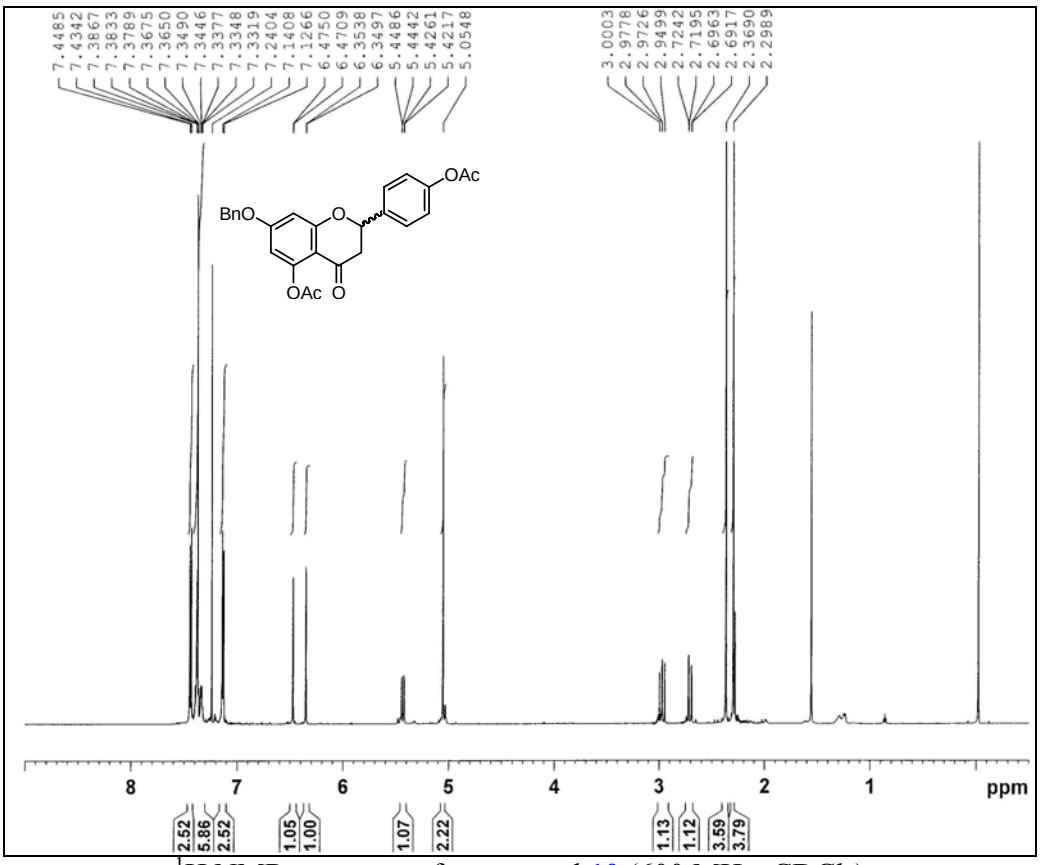
^{1}H NMR spectrum of compound **9bb2** (400 MHz, CD_3OD)



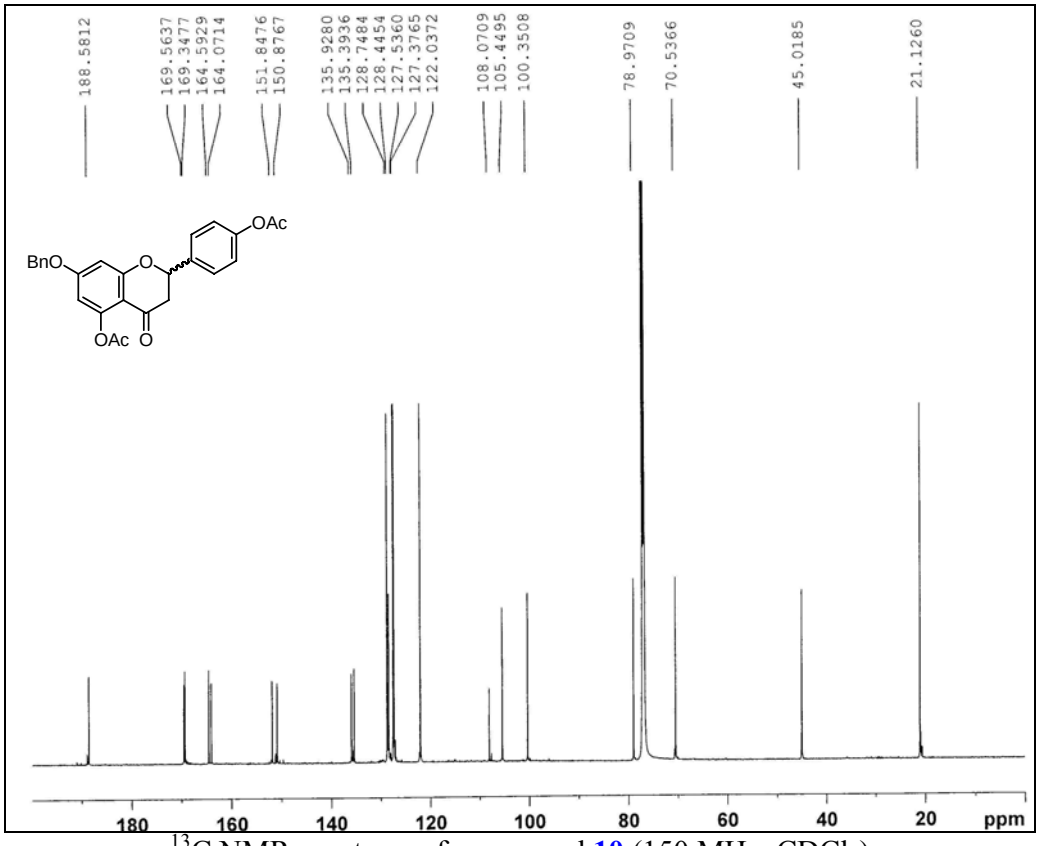
^{13}C NMR spectrum of compound **9bb2** (100 MHz, CD_3OD)



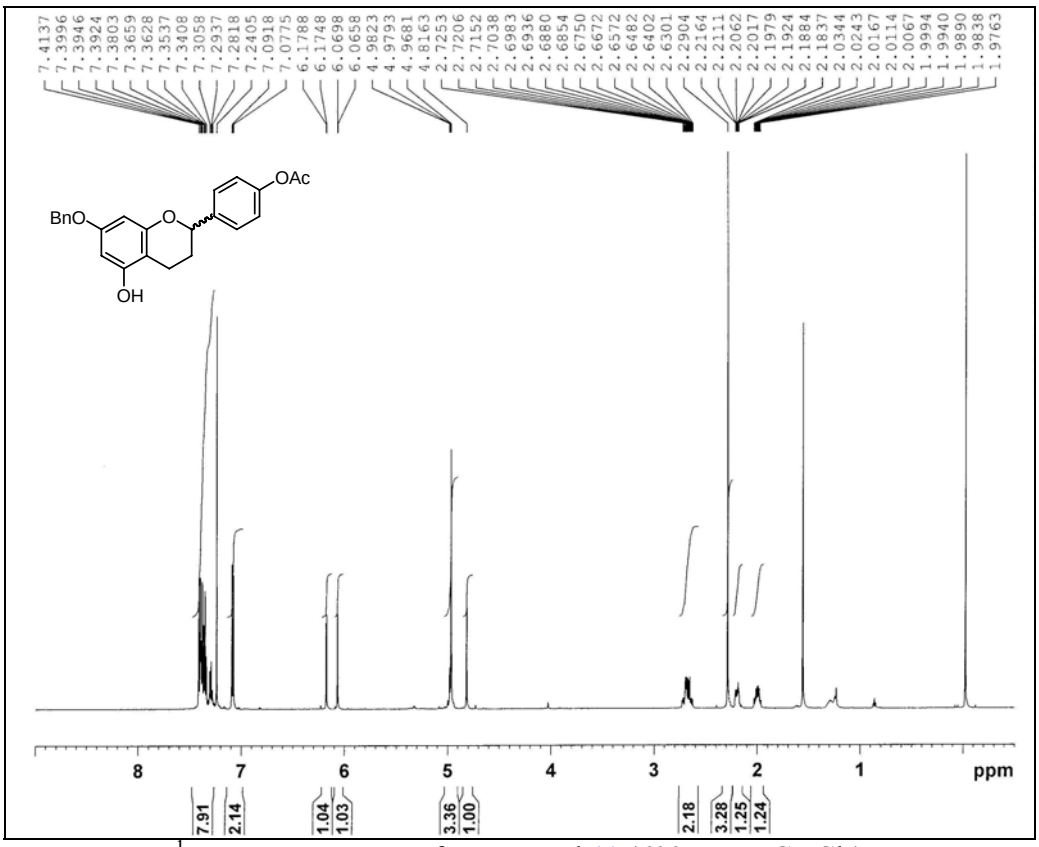
^{1}H NMR spectrum of compound **9bb3** (400 MHz, CD_3OD)



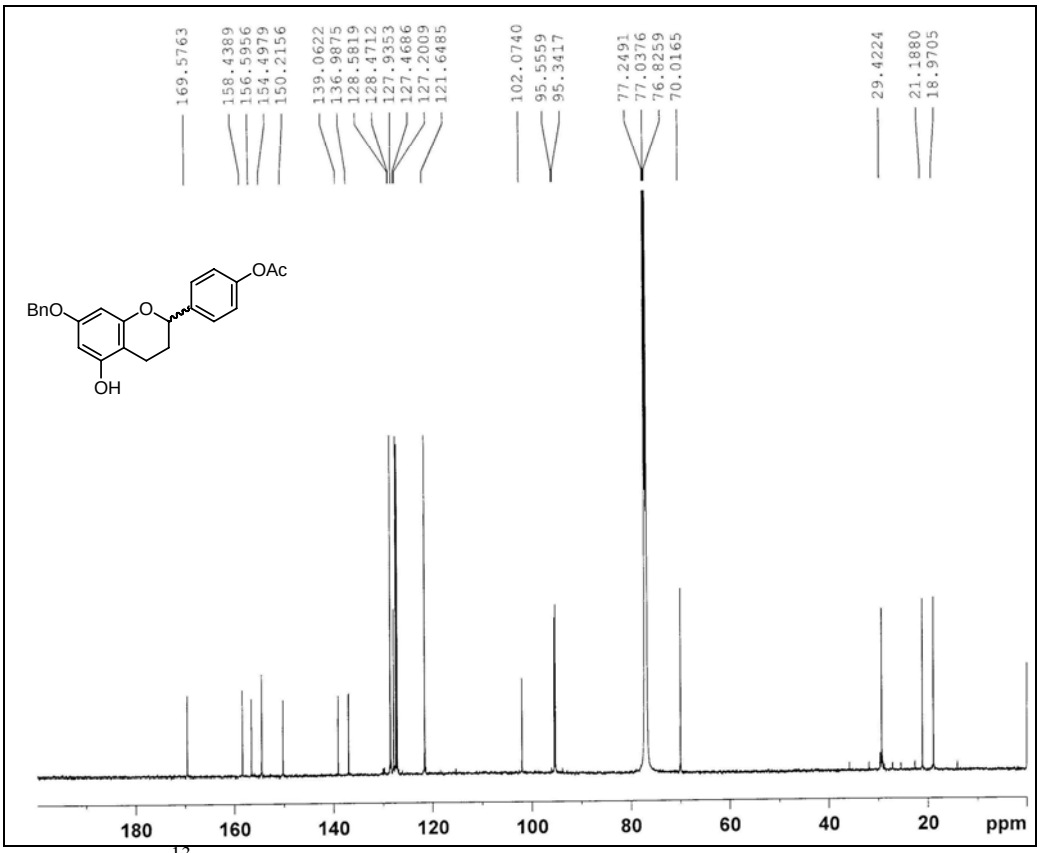
^{1}H NMR spectrum of compound **10** (600 MHz, $CDCl_3$)



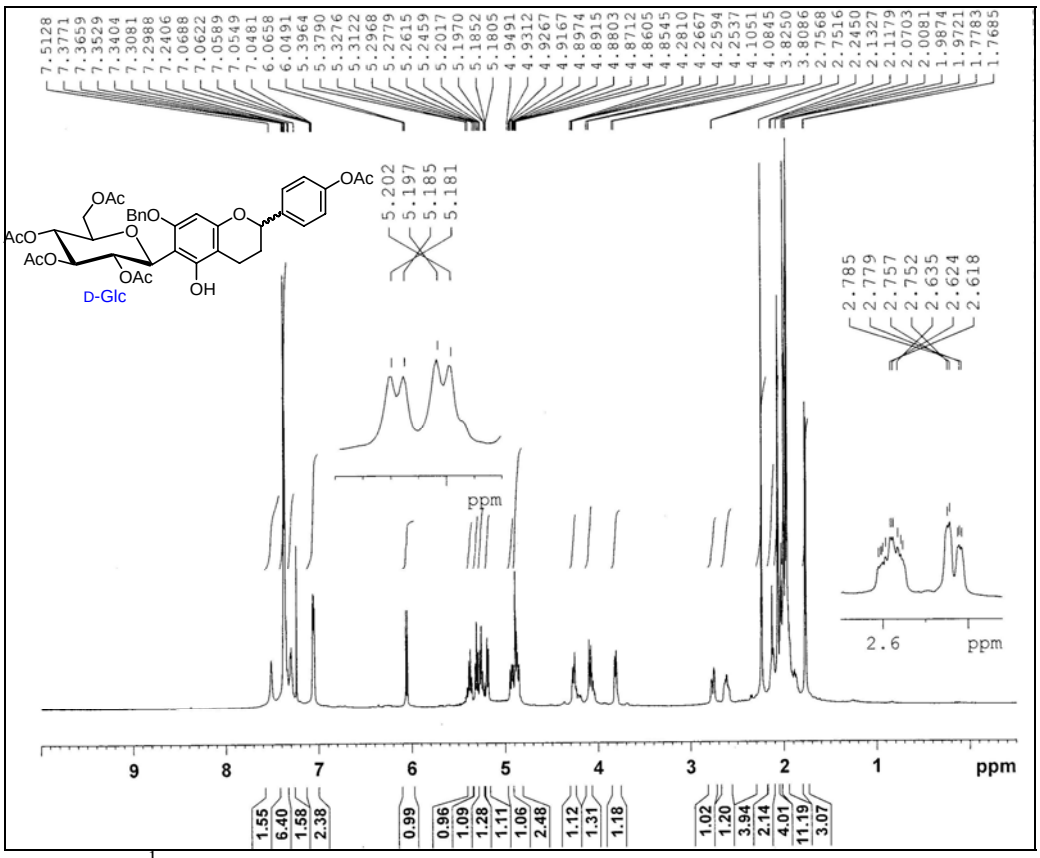
^{13}C NMR spectrum of compound **10** (150 MHz, $CDCl_3$)



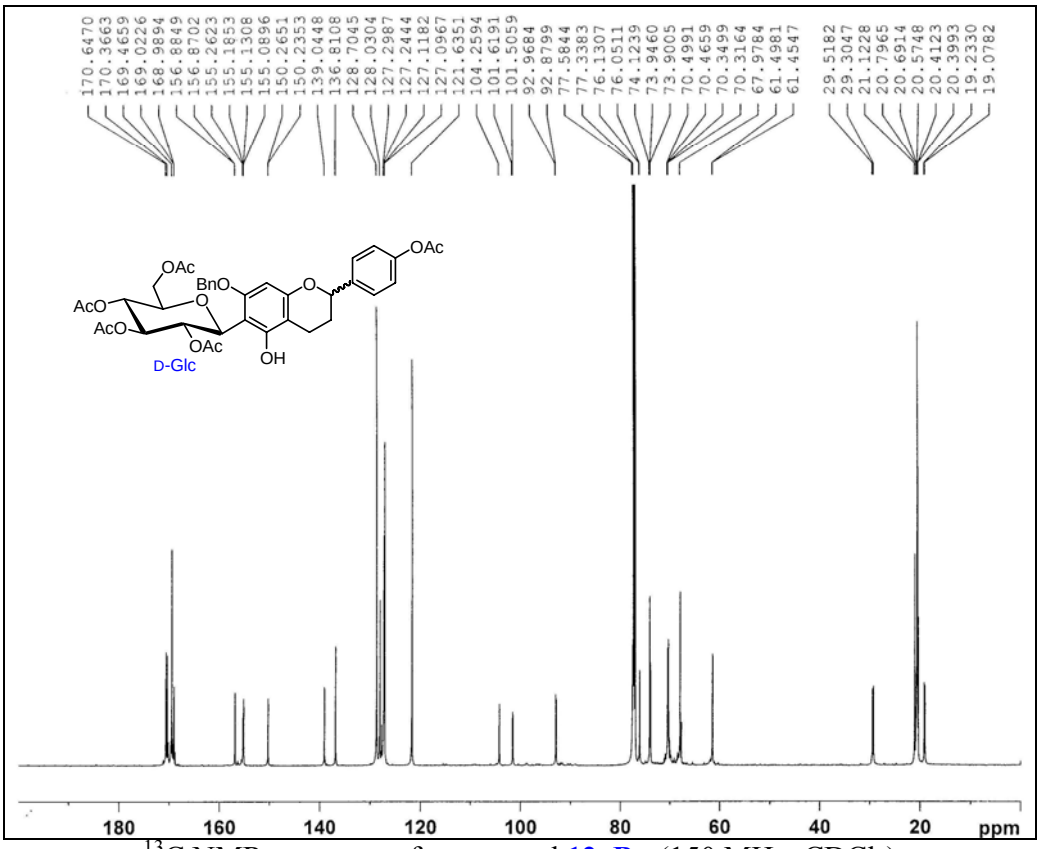
^{1}H NMR spectrum of compound **11** (600 MHz, $CDCl_3$)



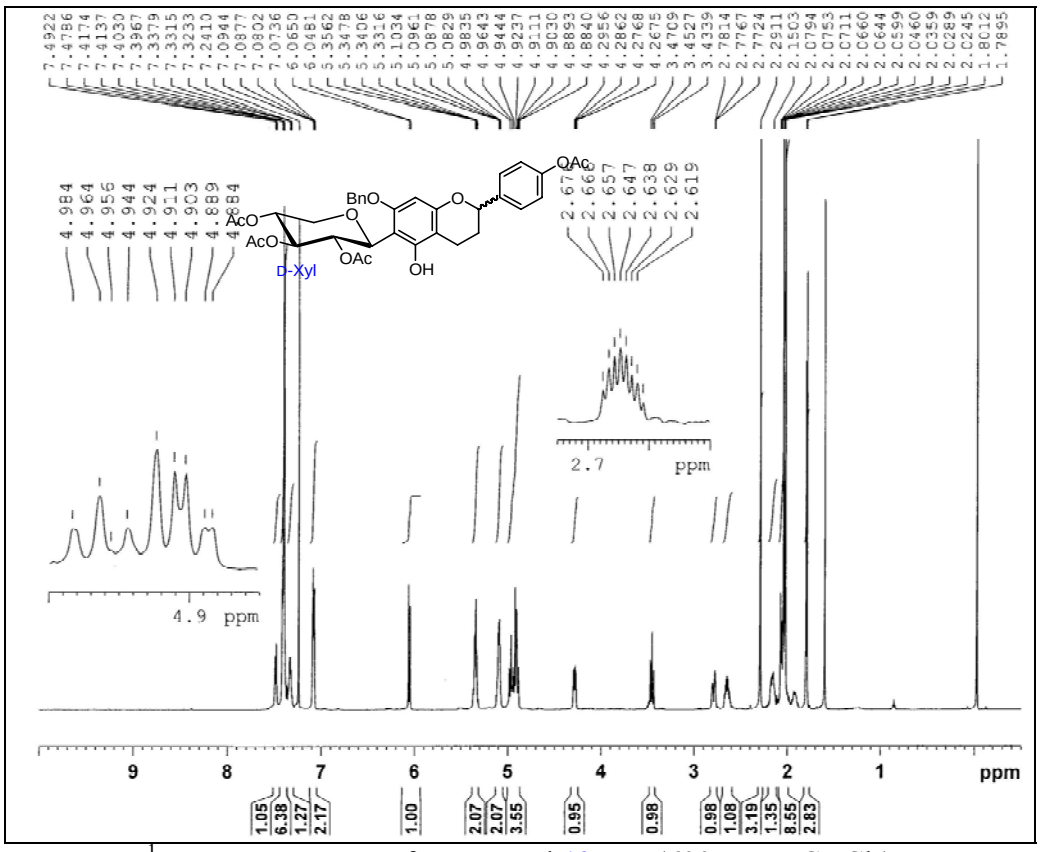
^{13}C NMR spectrum of compound **11** (150 MHz, $CDCl_3$)



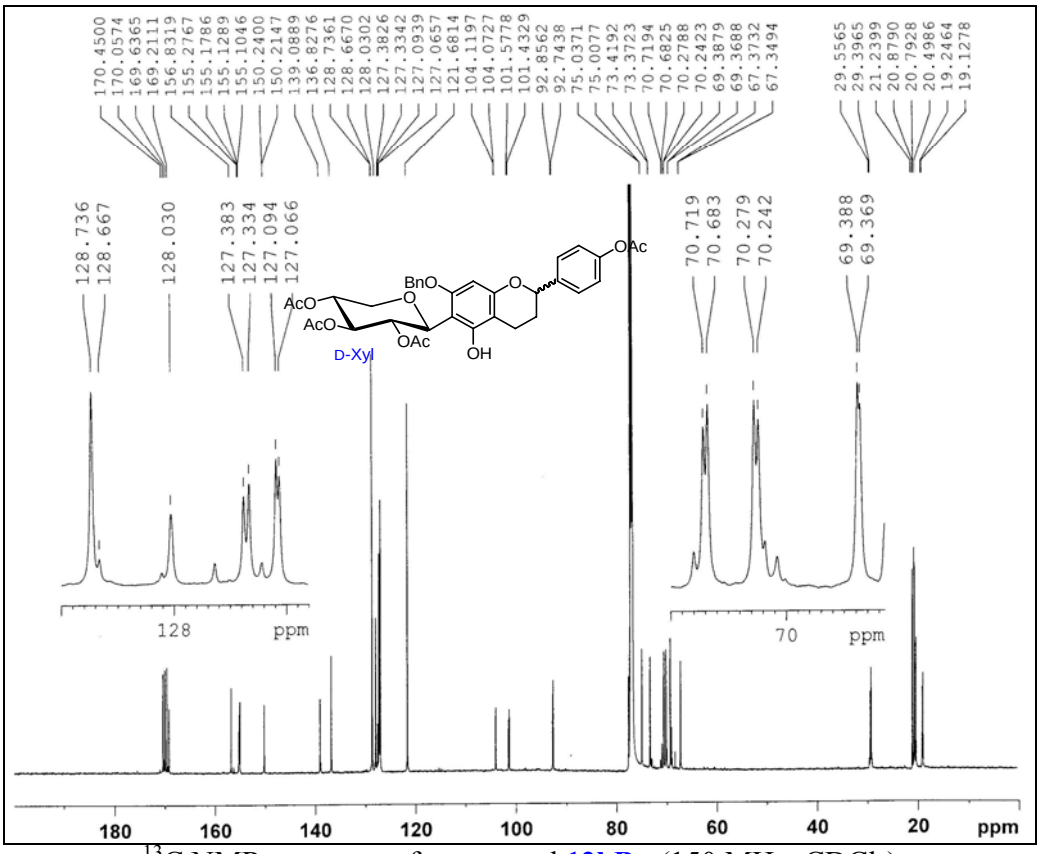
^{1}H NMR spectrum of compound **12aBn** (600 MHz, $CDCl_3$)



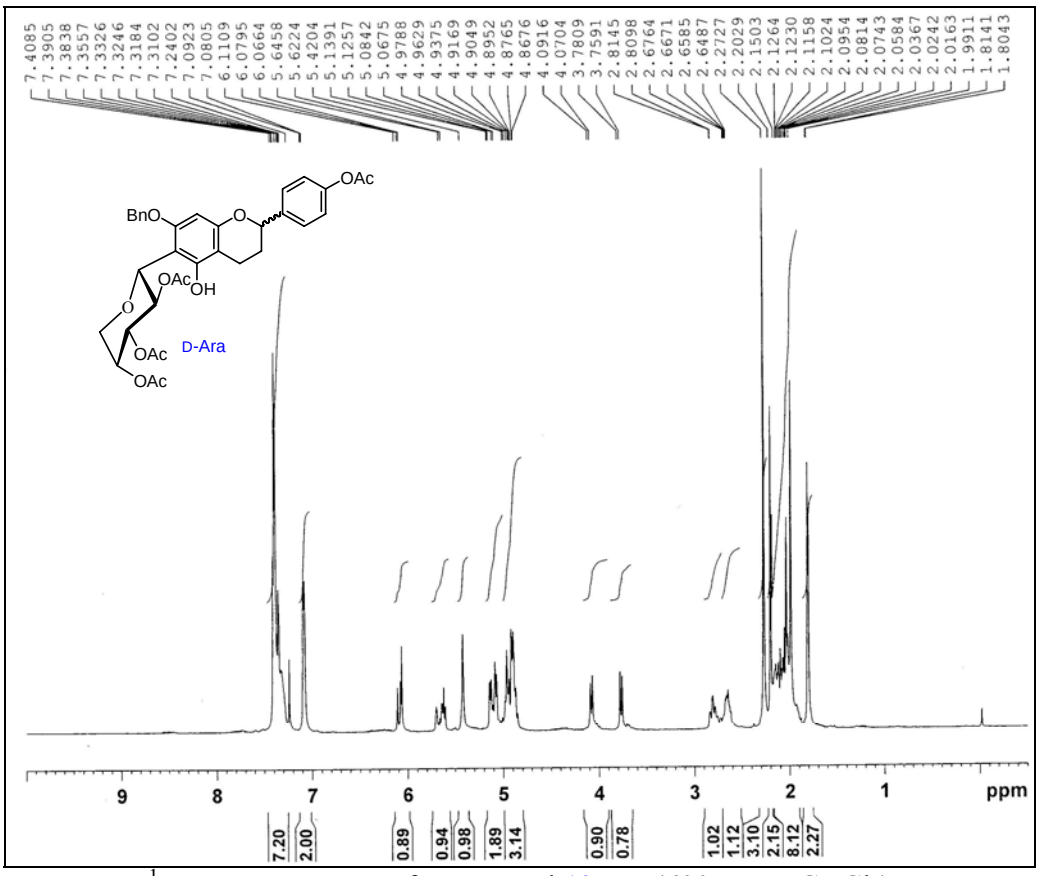
^{13}C NMR spectrum of compound **12aBn** (150 MHz, $CDCl_3$)



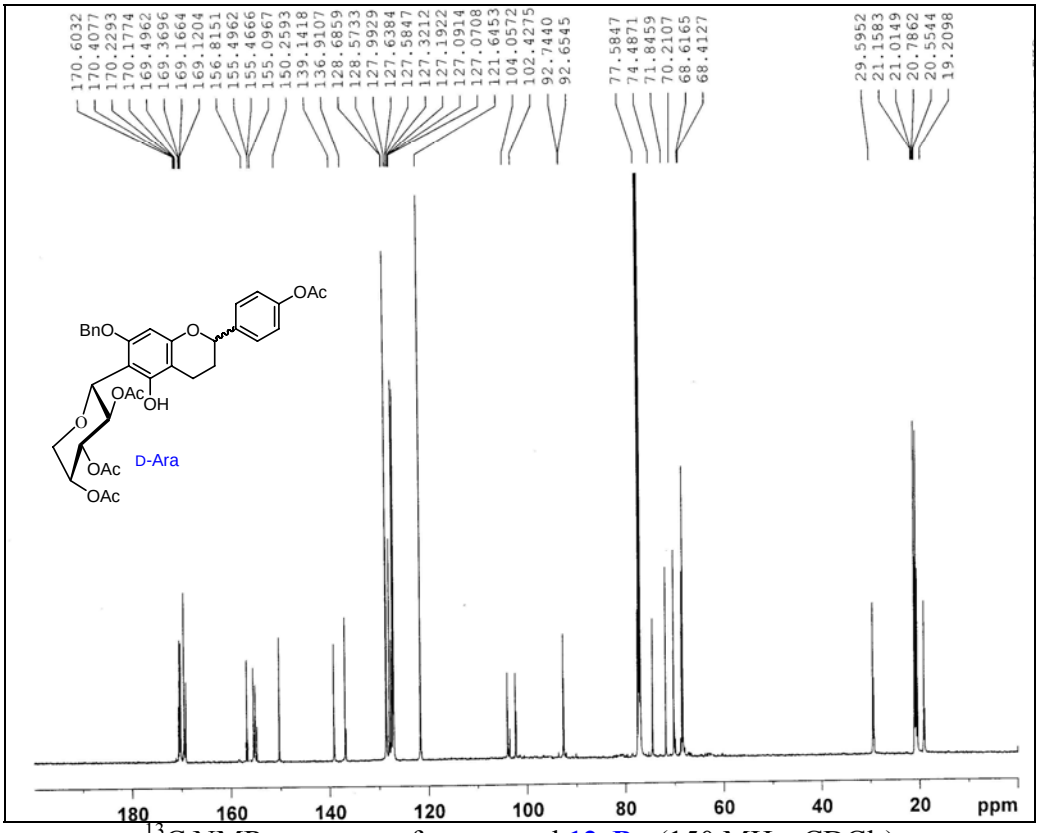
^{1}H NMR spectrum of compound **12bBn** (600 MHz, $CDCl_3$)



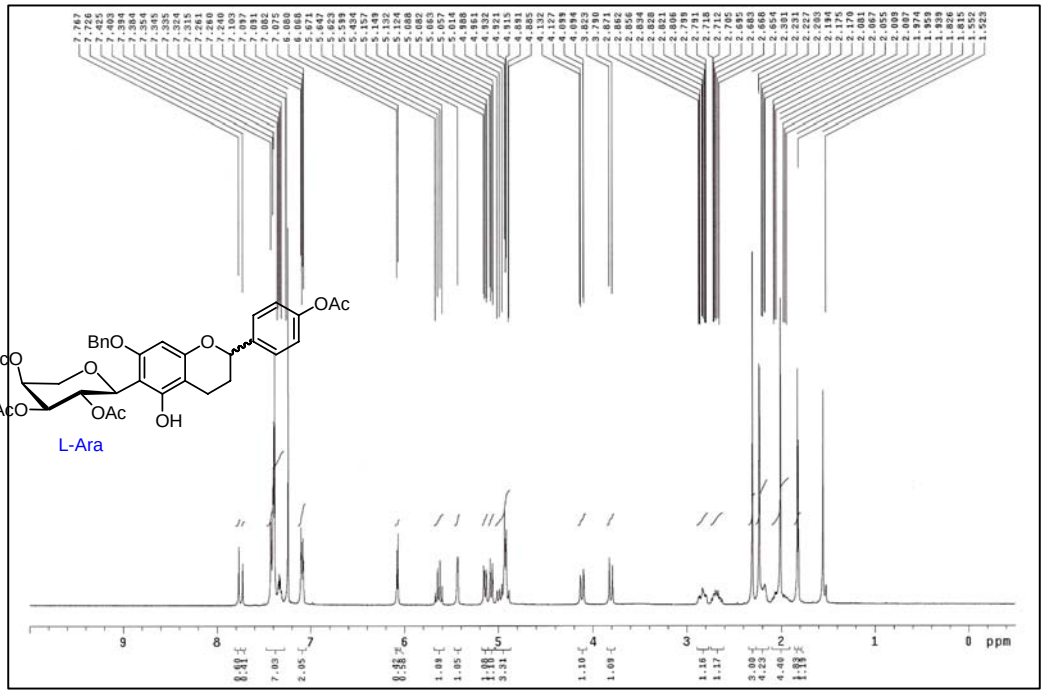
^{13}C NMR spectrum of compound **12bBn** (150 MHz, $CDCl_3$)



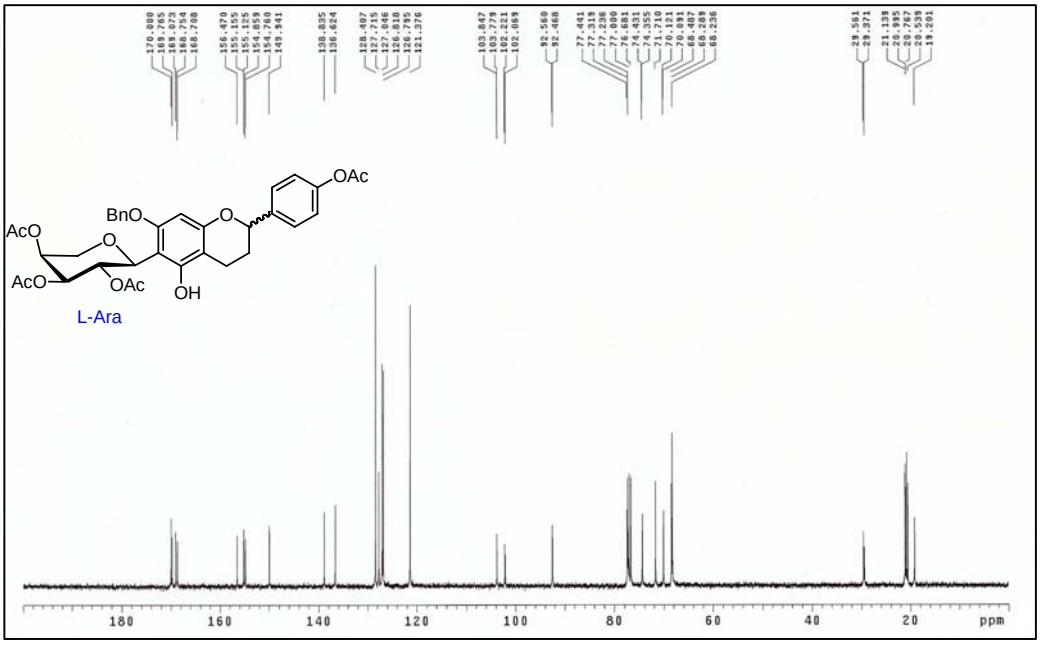
^{1}H NMR spectrum of compound **12cBn** (600 MHz, $CDCl_3$)



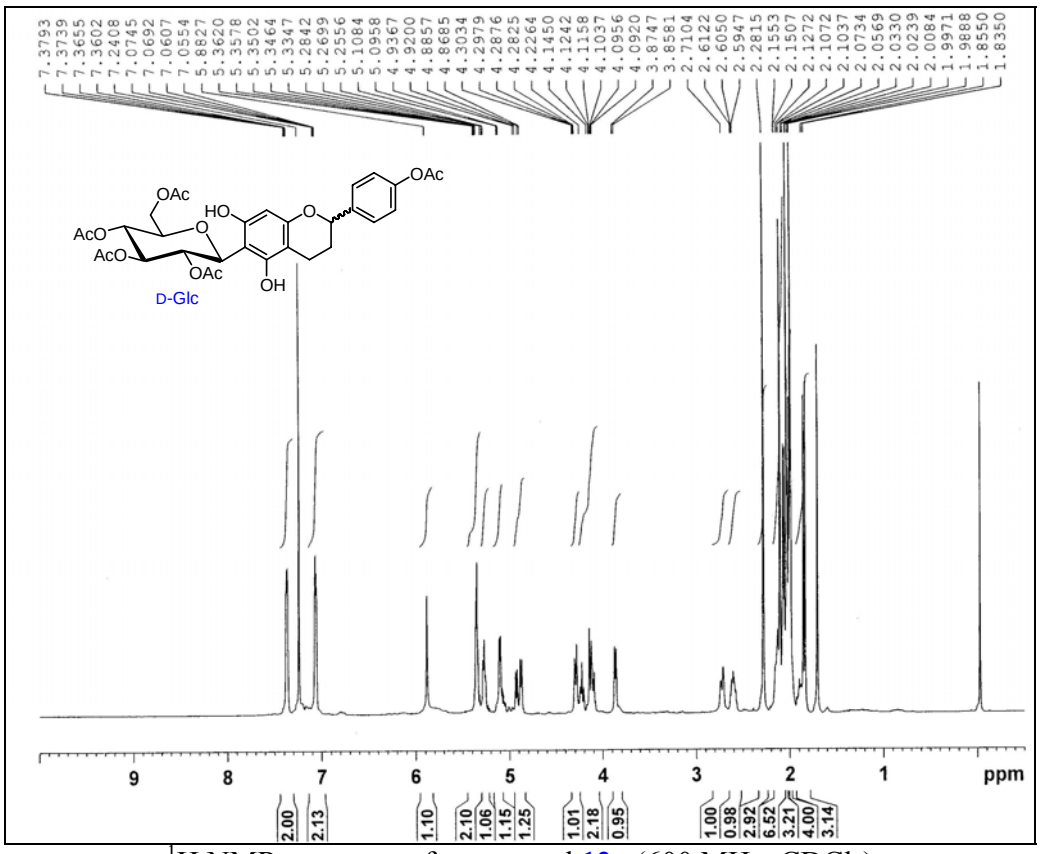
^{13}C NMR spectrum of compound **12cBn** (150 MHz, $CDCl_3$)



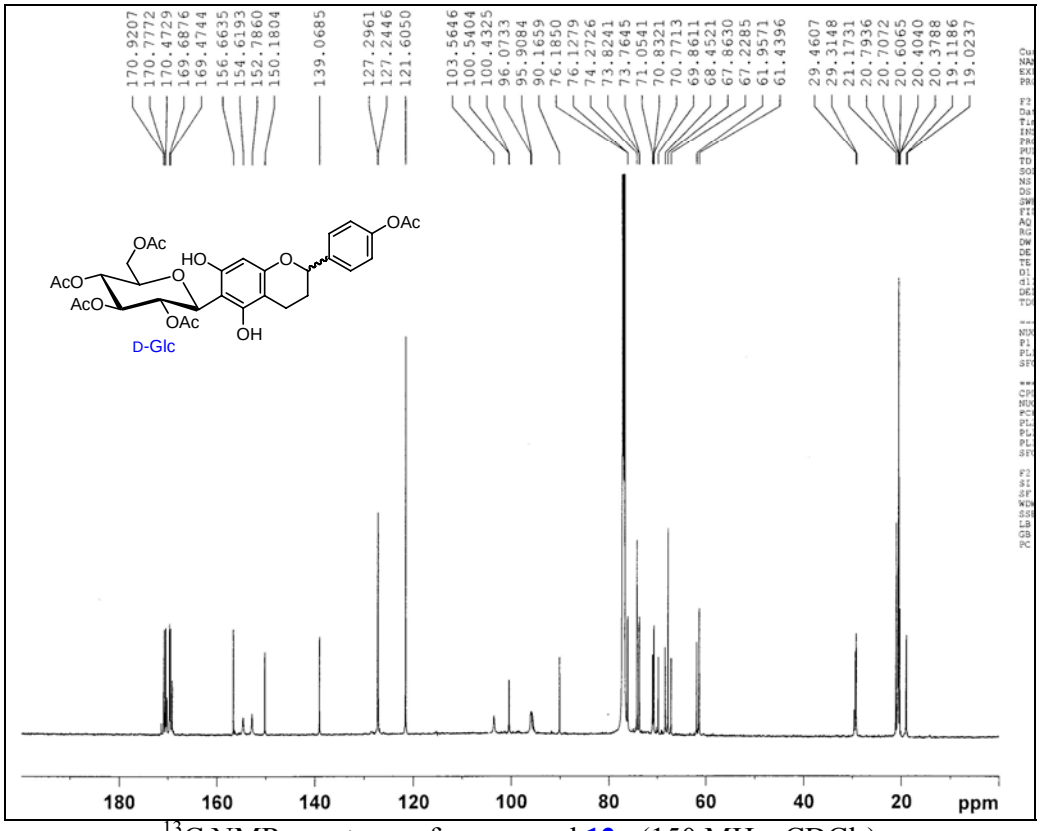
^{1}H NMR spectrum of compound **12dBn** (400 MHz, $CDCl_3$)



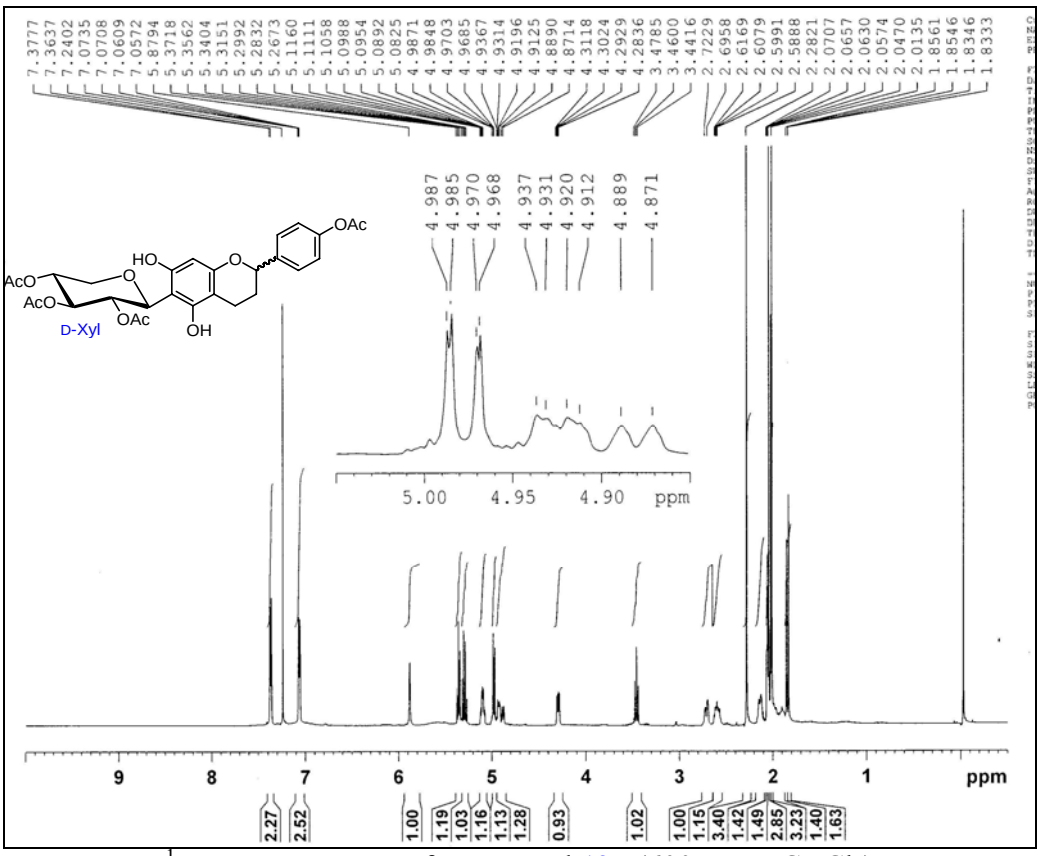
^{13}C NMR spectrum of compound **12dBn** (100 MHz, $CDCl_3$)



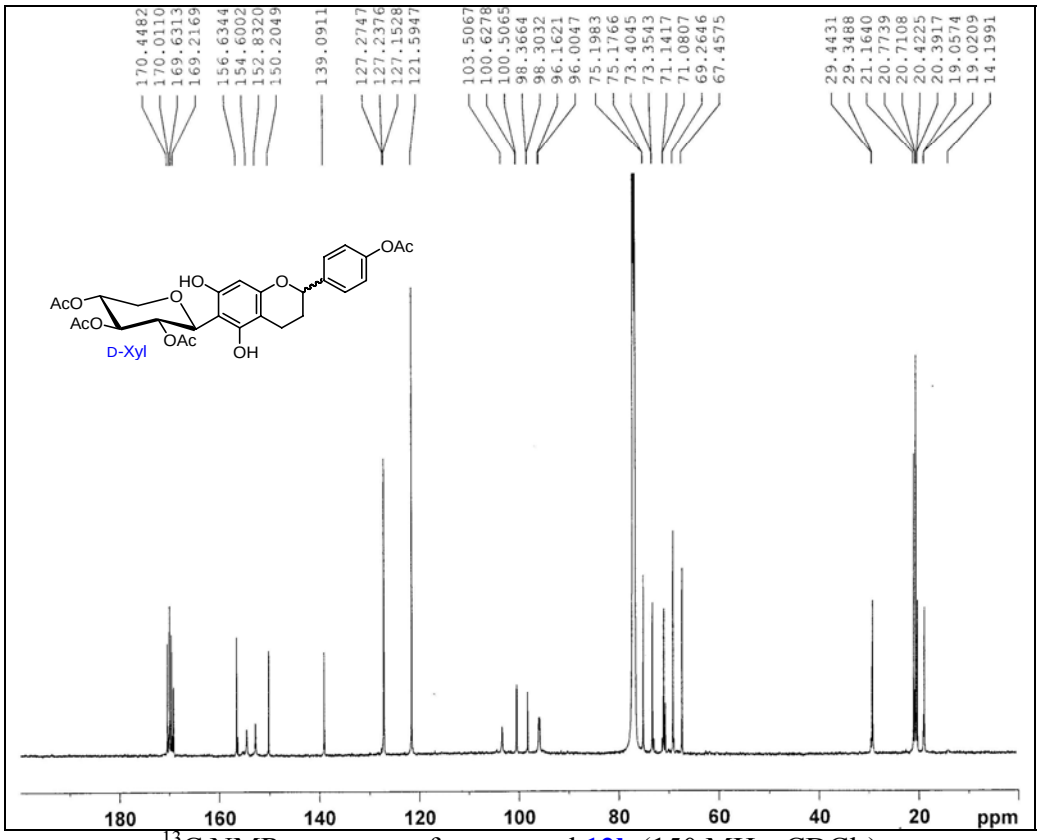
^{1}H NMR spectrum of compound **12a** (600 MHz, $CDCl_3$)



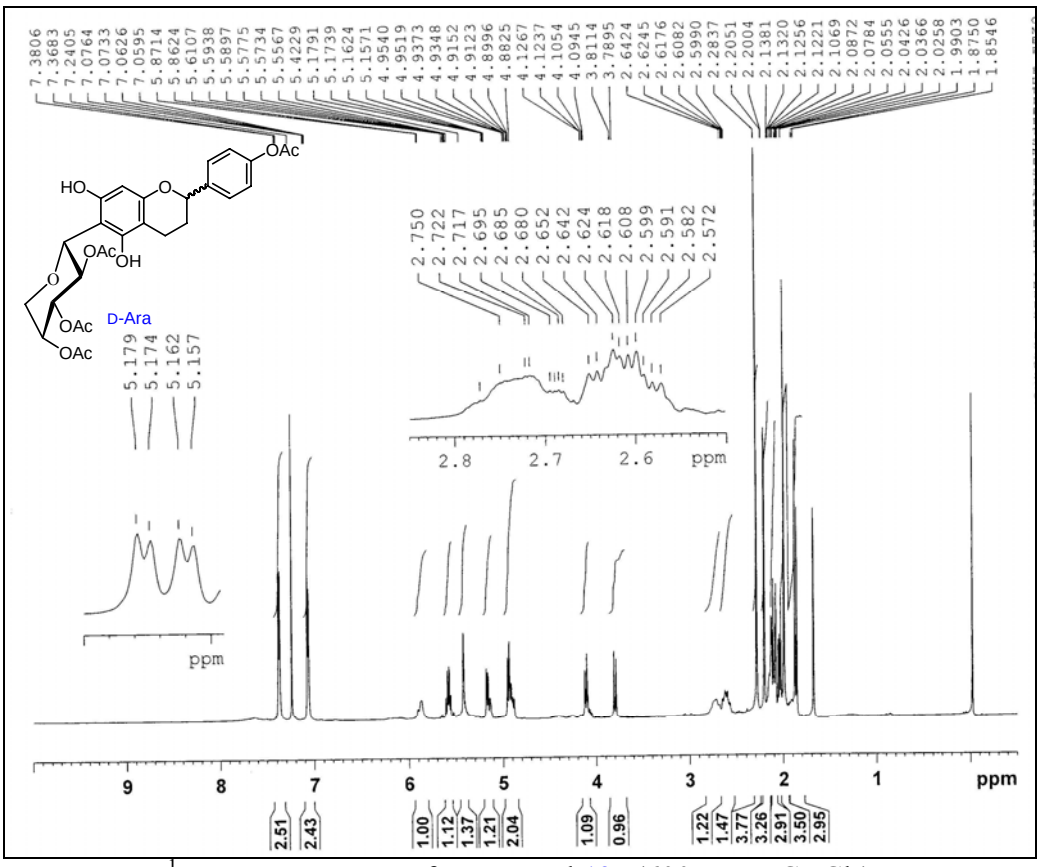
^{13}C NMR spectrum of compound **12a** (150 MHz, $CDCl_3$)



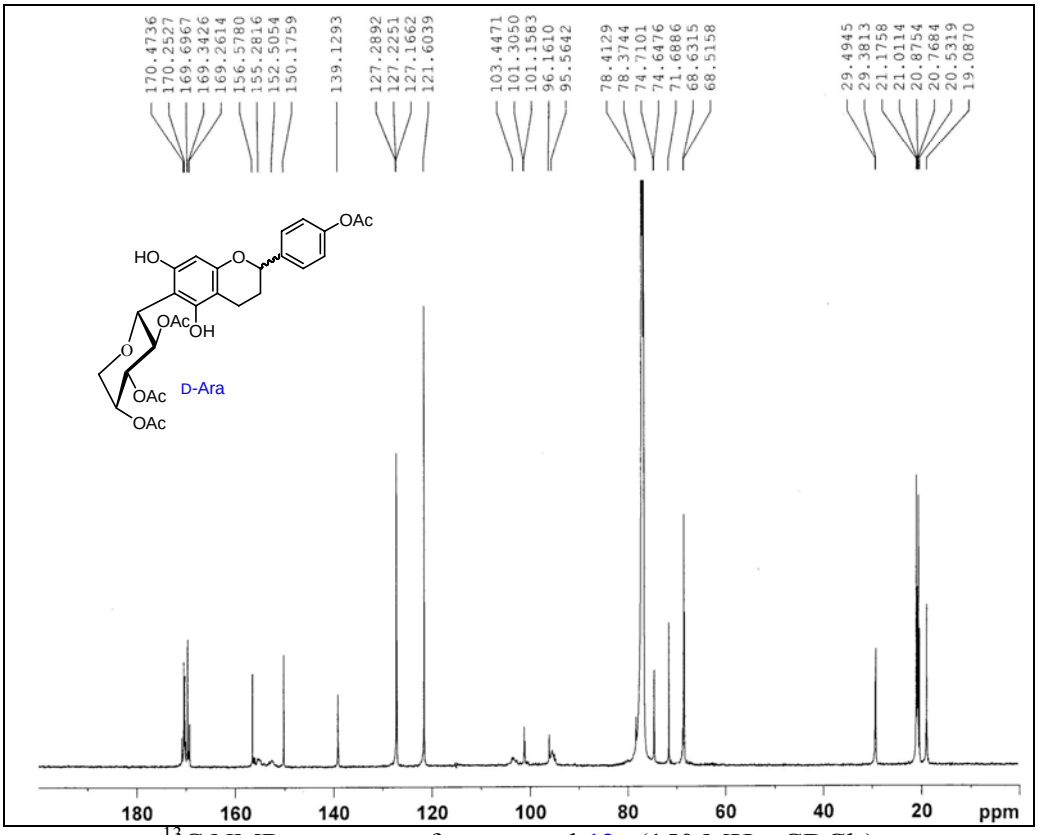
^{1}H NMR spectrum of compound **12b** (600 MHz, $CDCl_3$)



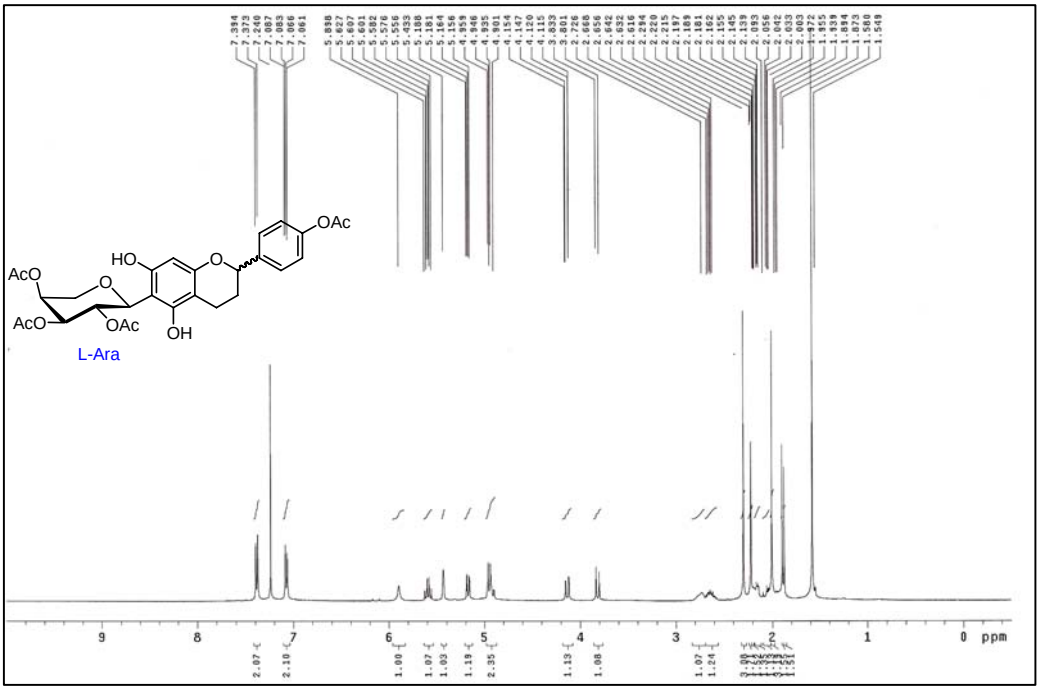
^{13}C NMR spectrum of compound **12b** (150 MHz, $CDCl_3$)



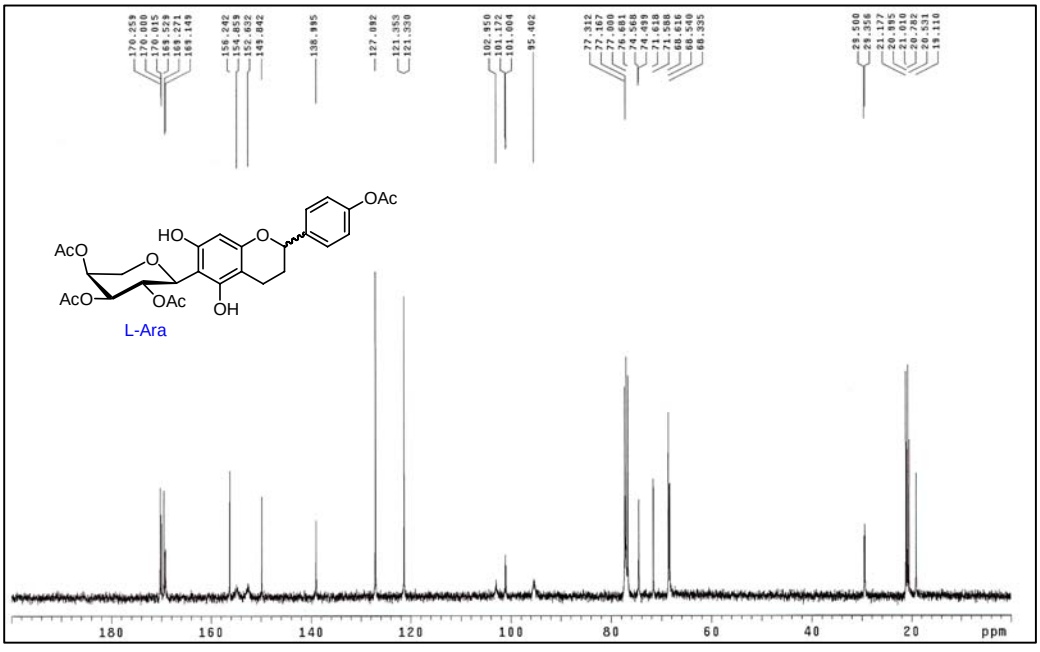
^{1}H NMR spectrum of compound **12c** (600 MHz, $CDCl_3$)



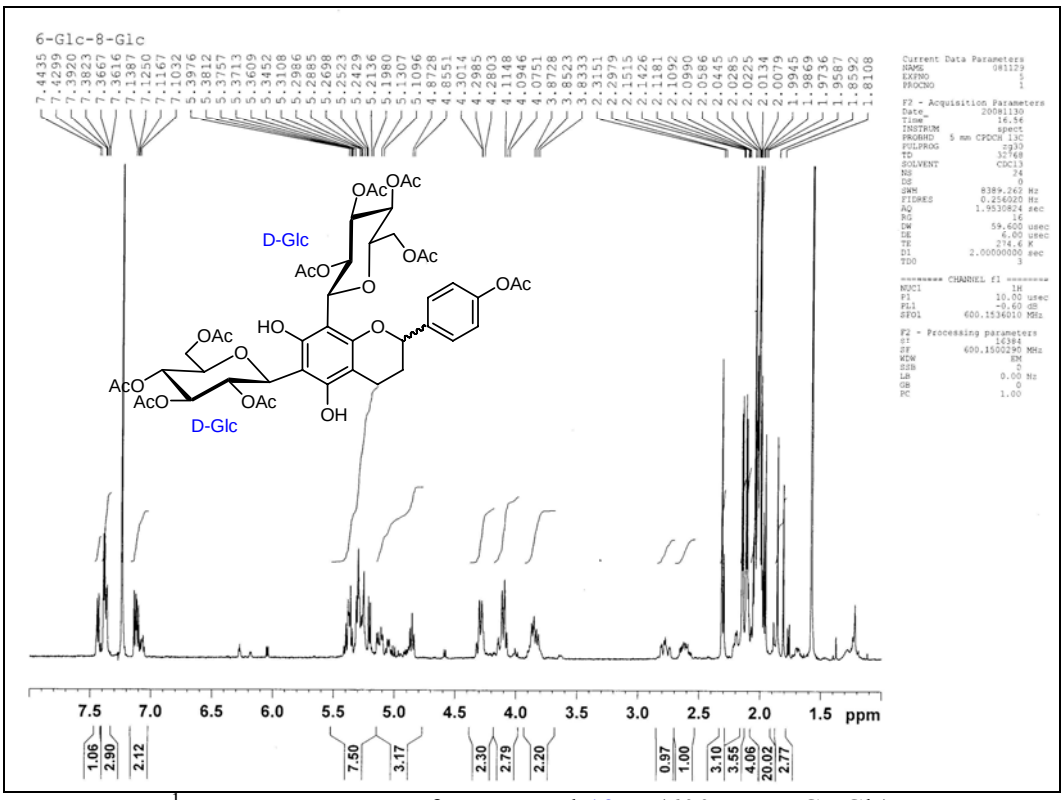
^{13}C NMR spectrum of compound **12c** (150 MHz, $CDCl_3$)



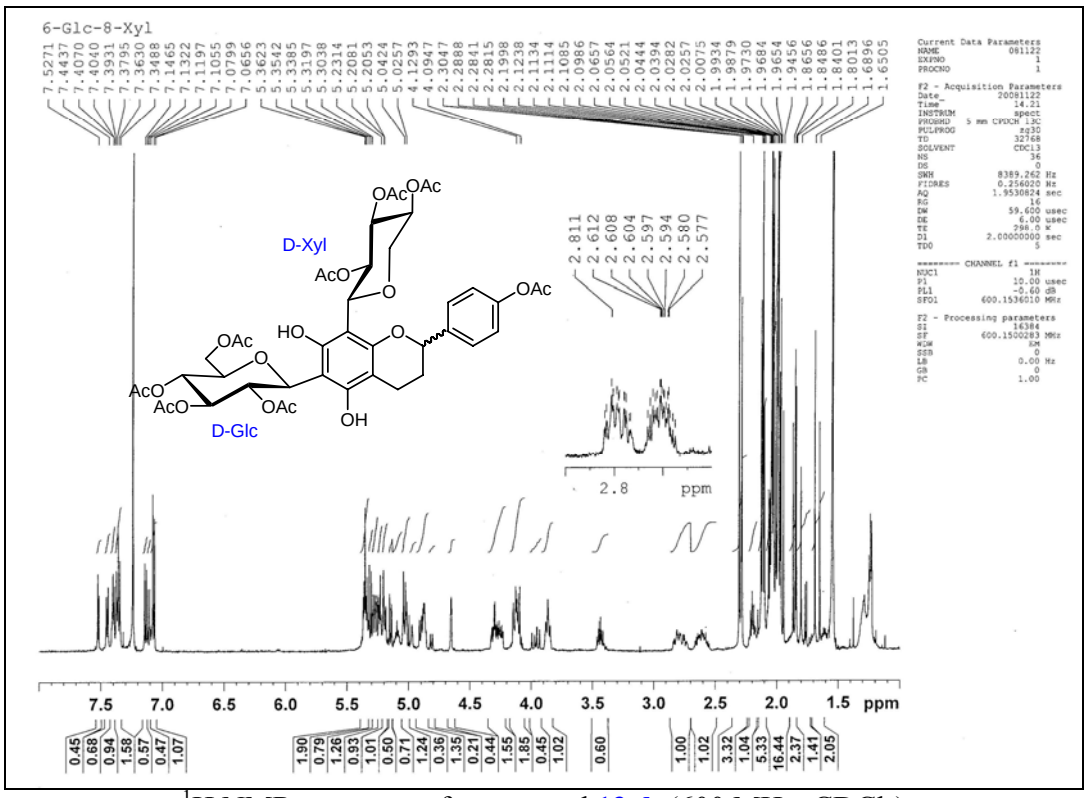
^{1}H NMR spectrum of compound **12d** (400 MHz, $CDCl_3$)



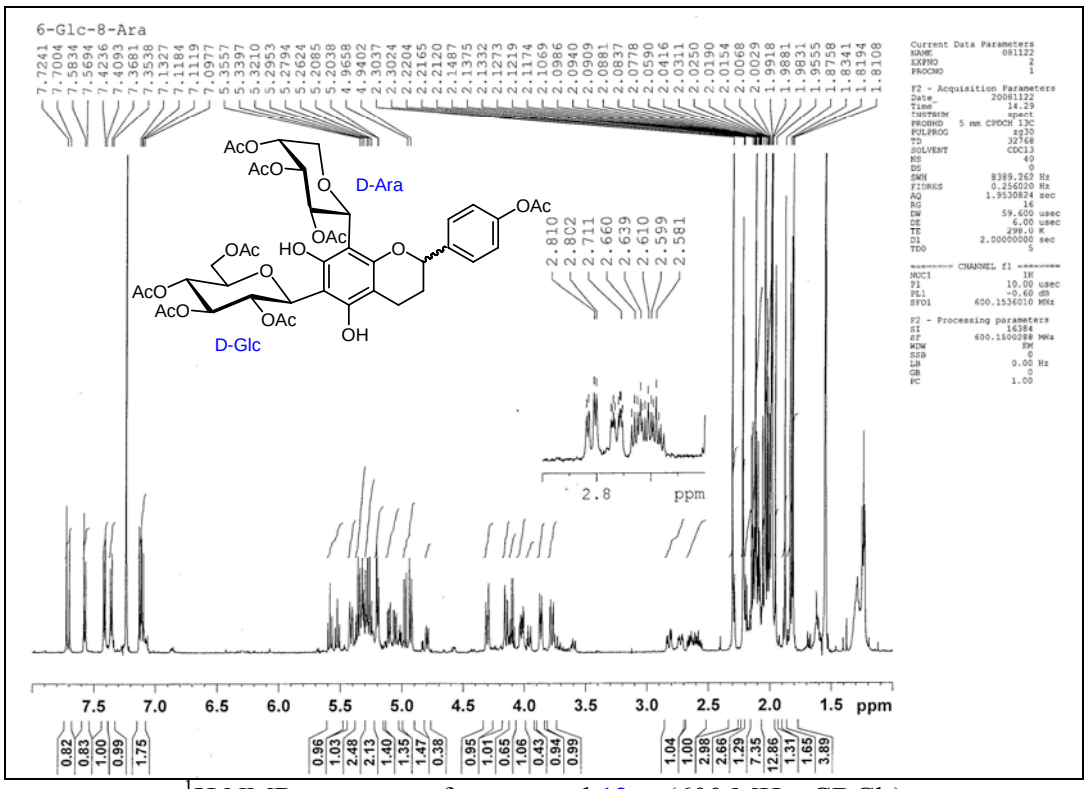
^{13}C NMR spectrum of compound **12d** (100 MHz, $CDCl_3$)



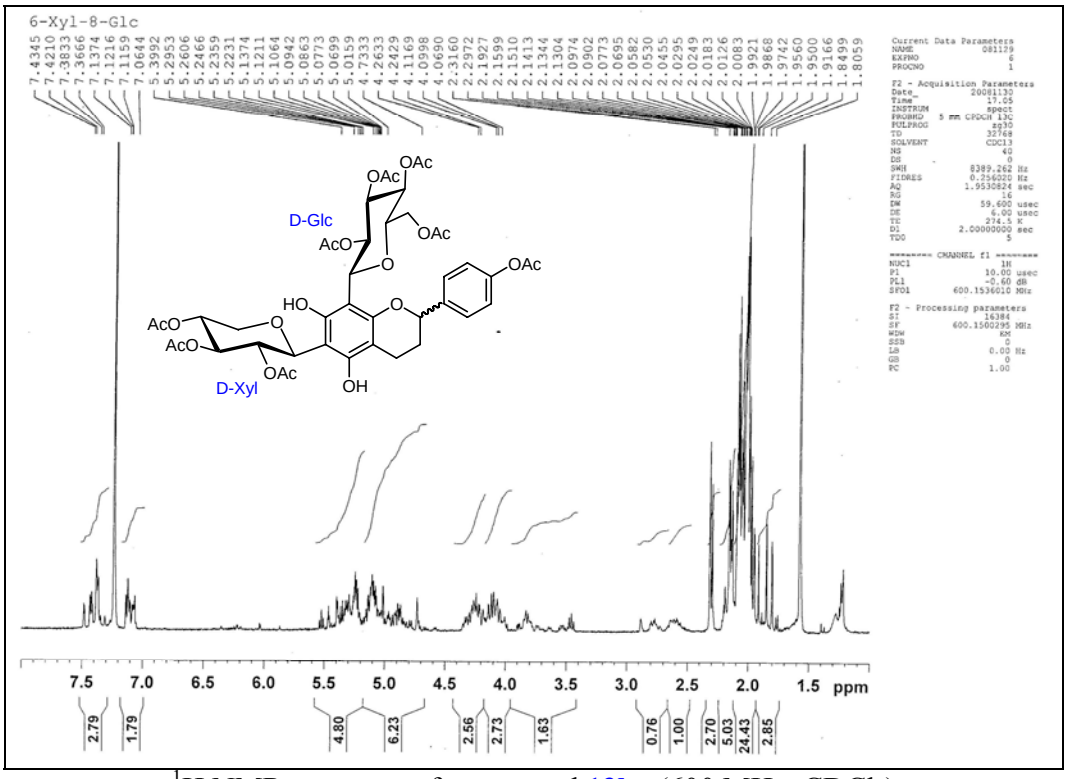
^{1}H NMR spectrum of compound **13aa** (600 MHz, $CDCl_3$)



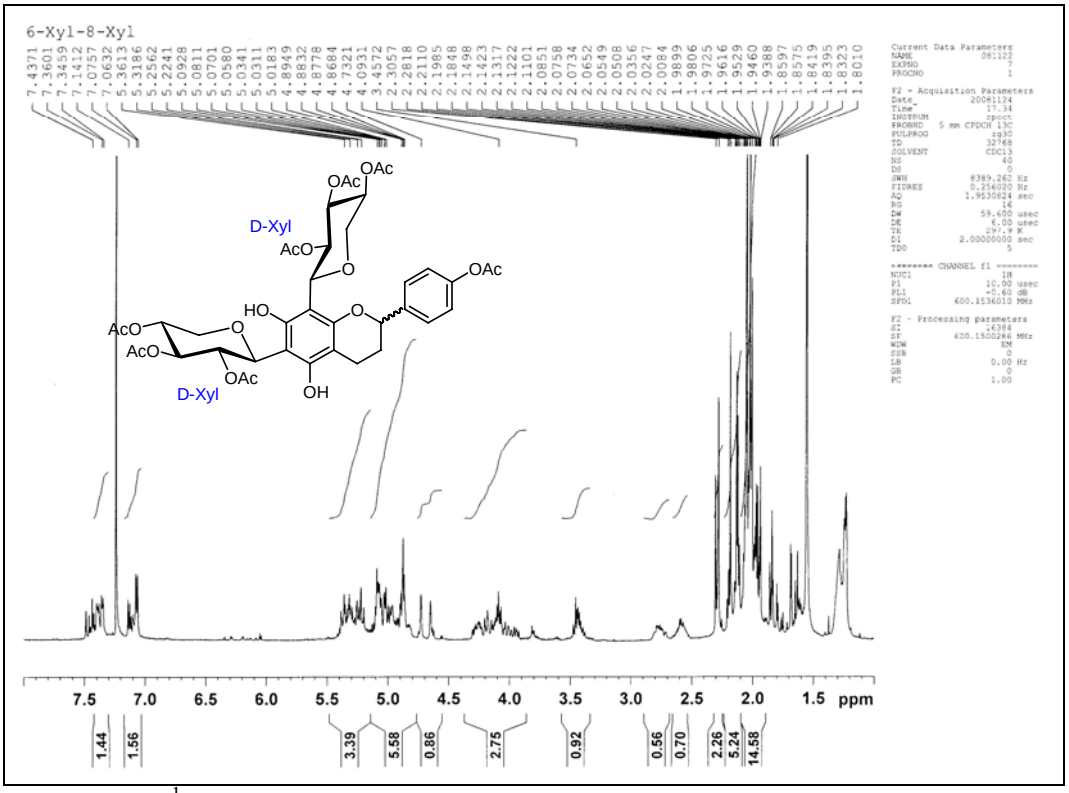
^{1}H NMR spectrum of compound **13ab** (600 MHz, $CDCl_3$)



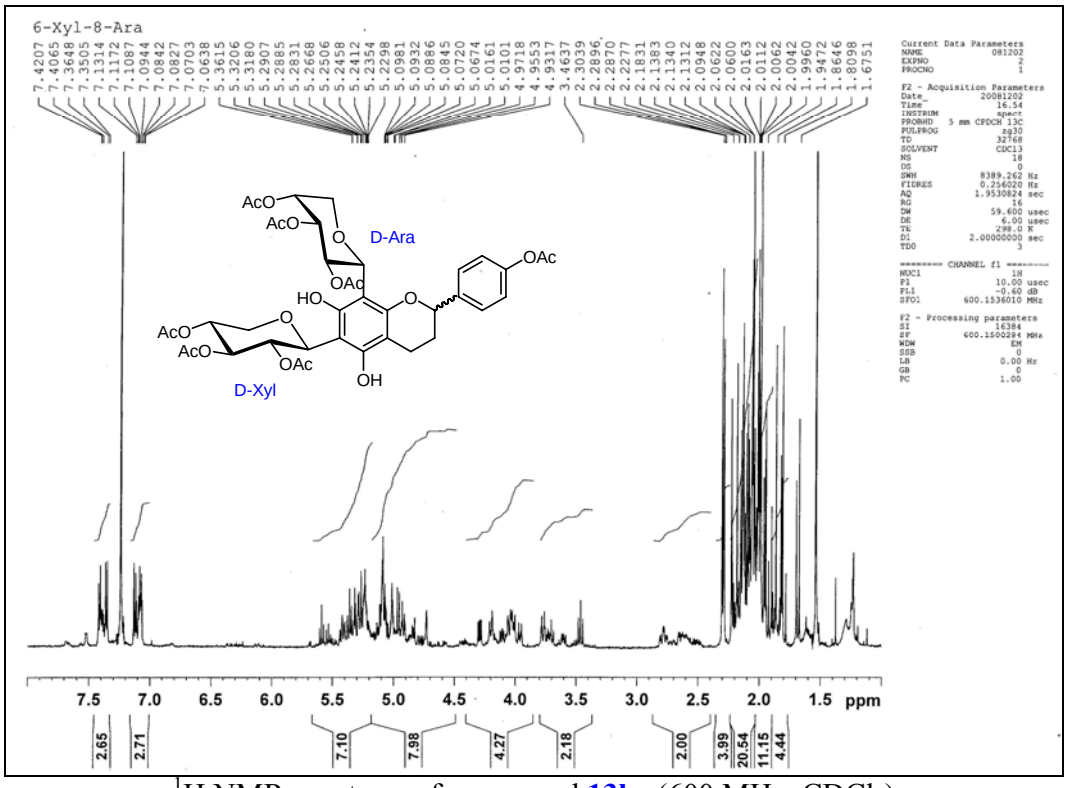
^{1}H NMR spectrum of compound **13ac** (600 MHz, $CDCl_3$)



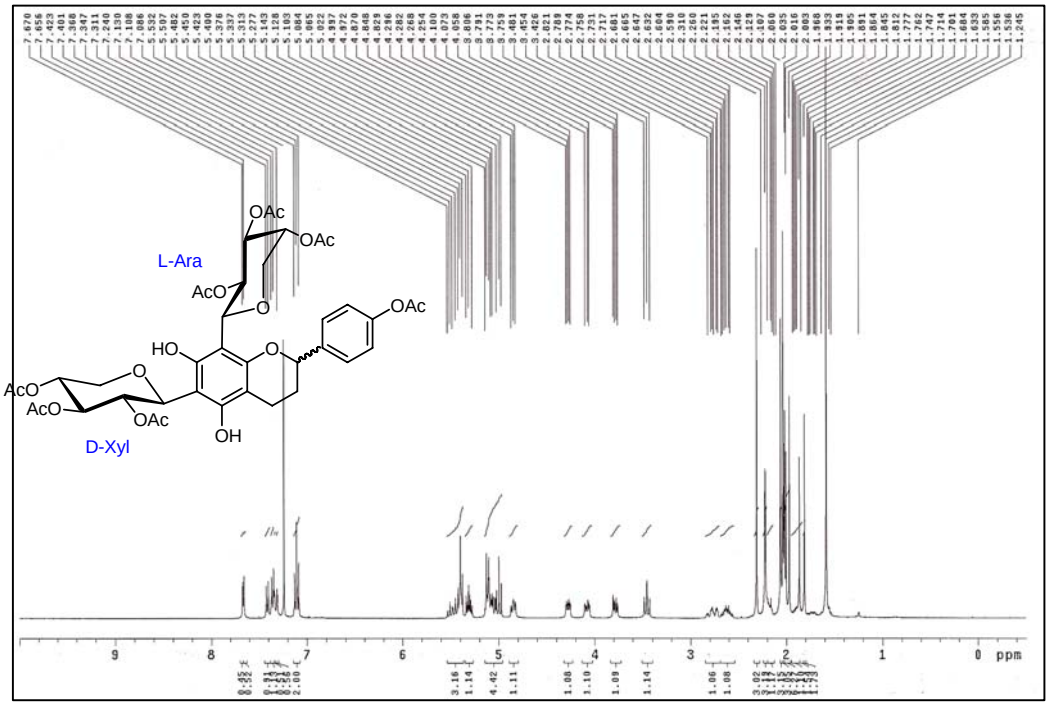
^{1}H NMR spectrum of compound **13ba** (600 MHz, $CDCl_3$)



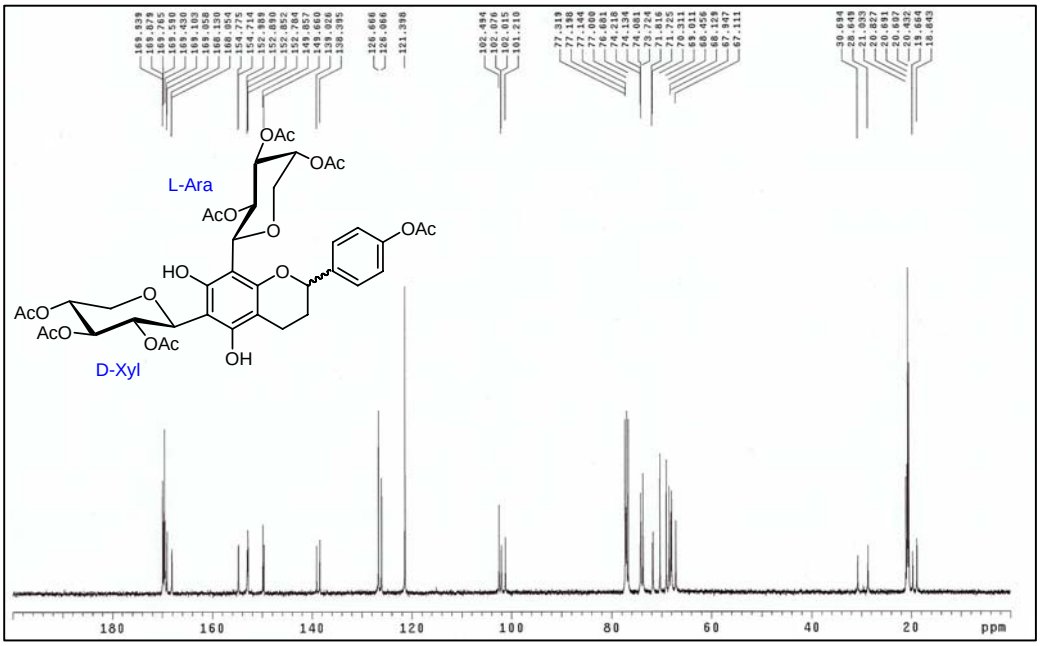
^{1}H NMR spectrum of compound **13bb** (600 MHz, $CDCl_3$)



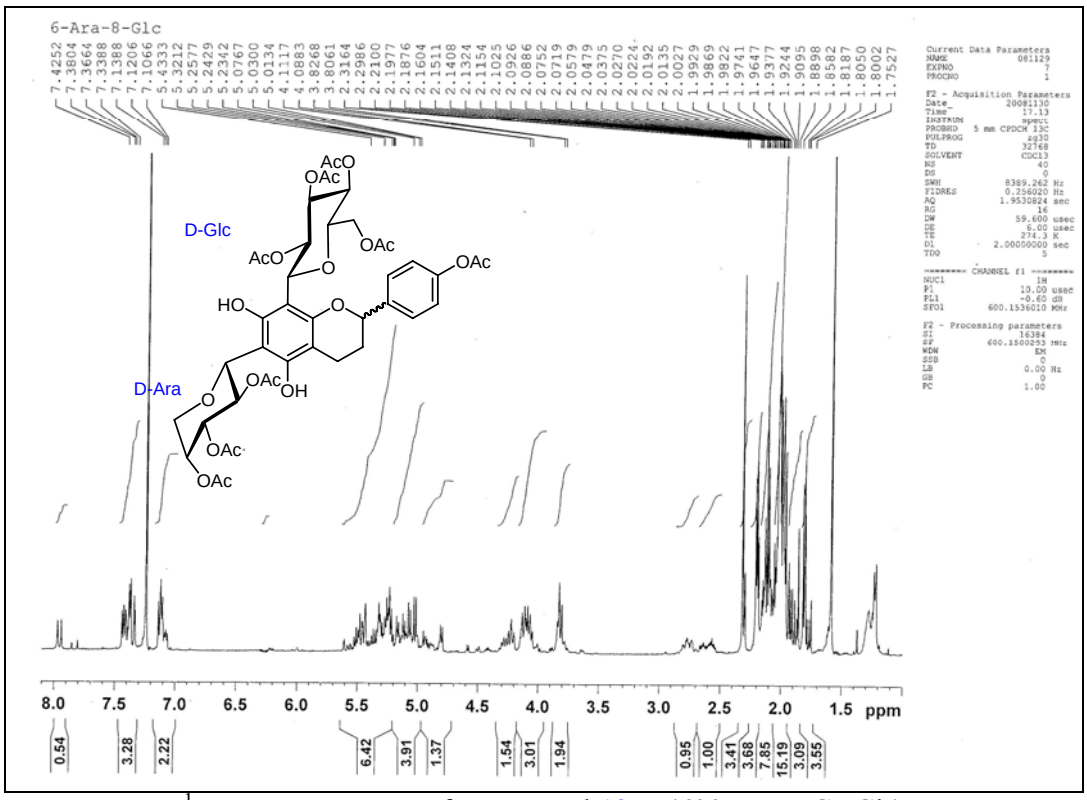
^{1}H NMR spectrum of compound **13bc** (600 MHz, $CDCl_3$)



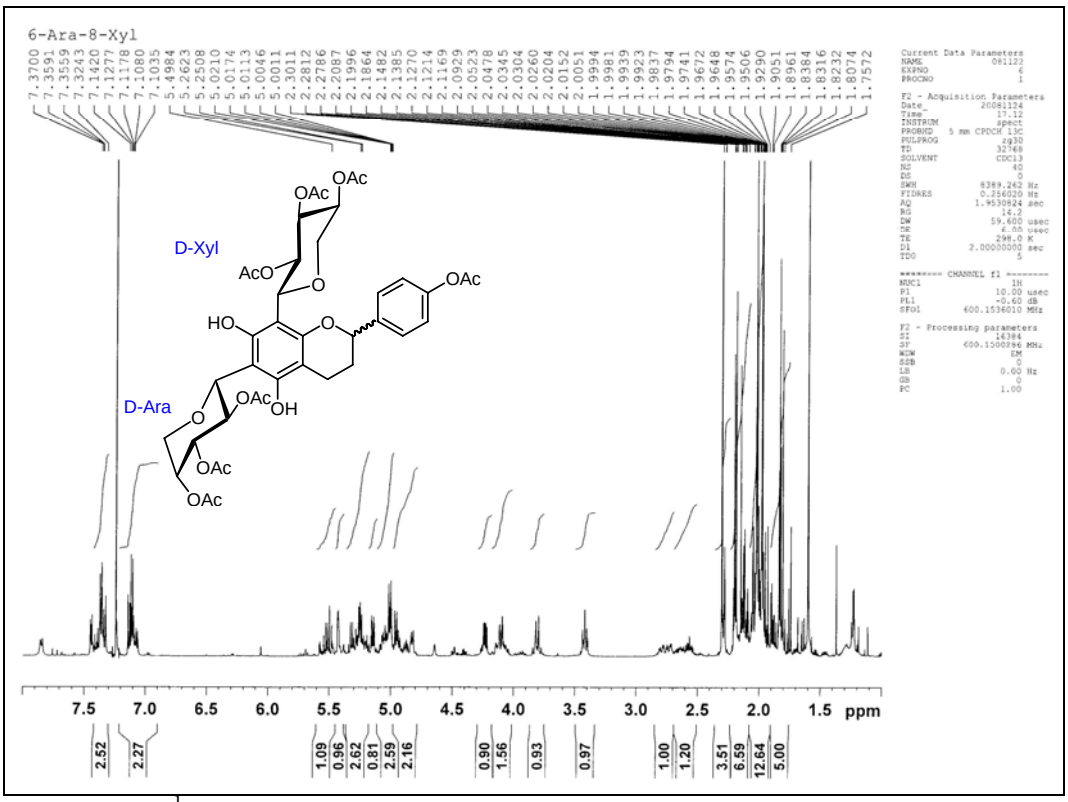
^{1}H NMR spectrum of compound **13bd** (400 MHz, $CDCl_3$)



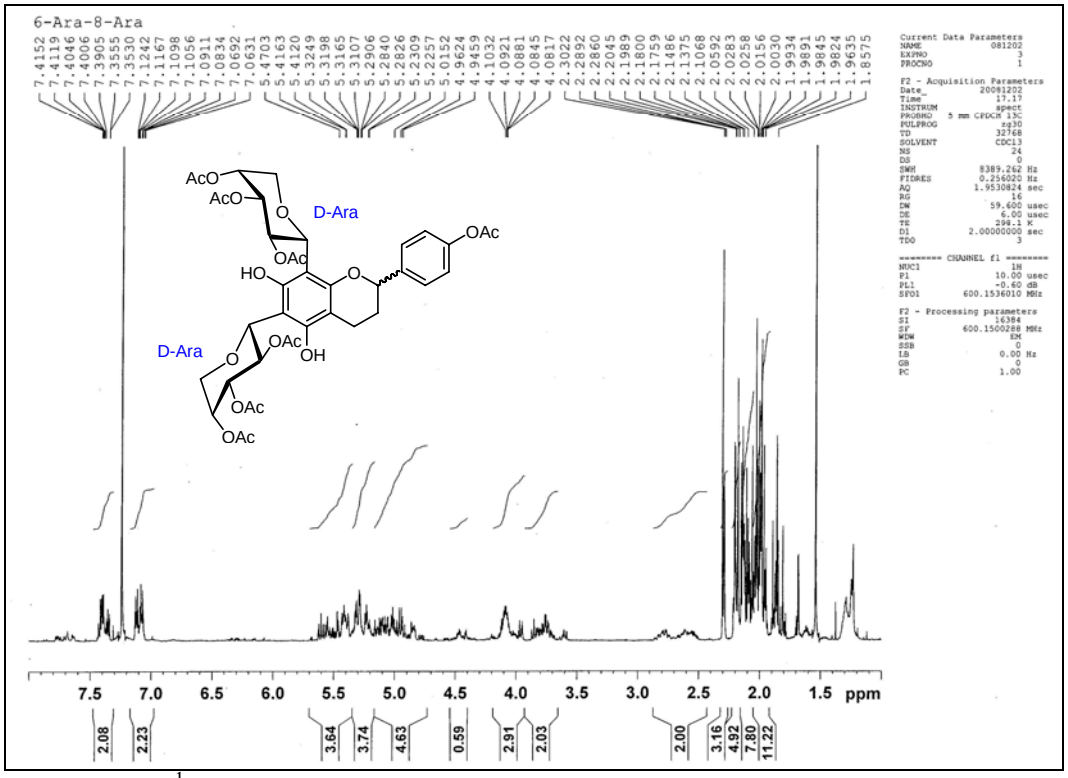
^{13}C NMR spectrum of compound **13bd** (100 MHz, $CDCl_3$)



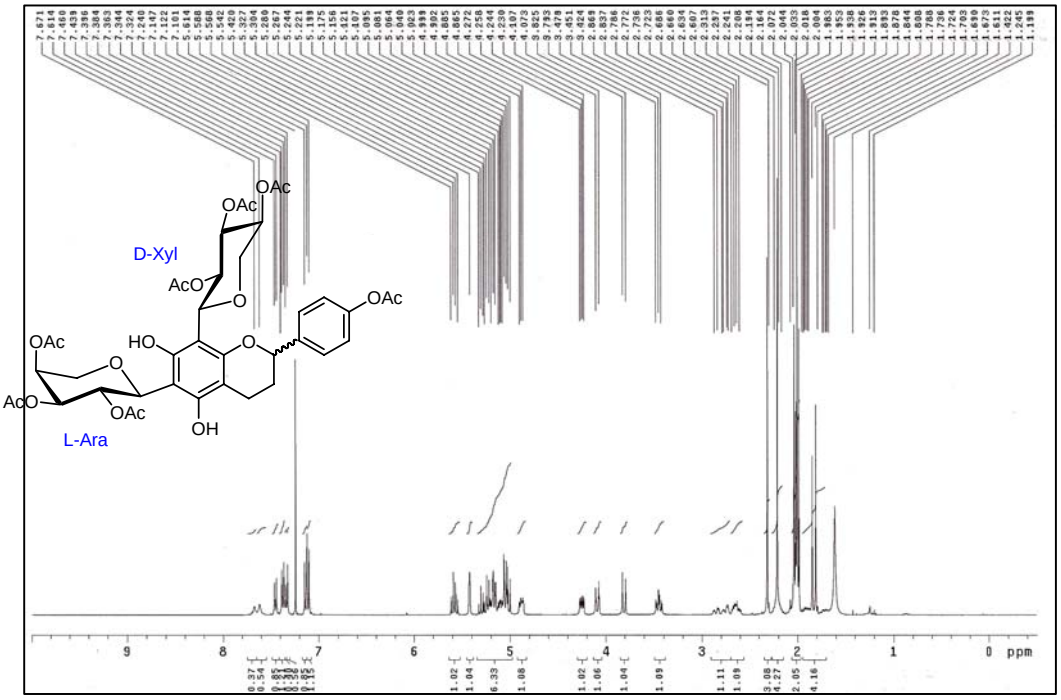
^{1}H NMR spectrum of compound **13ca** (600 MHz, $CDCl_3$)



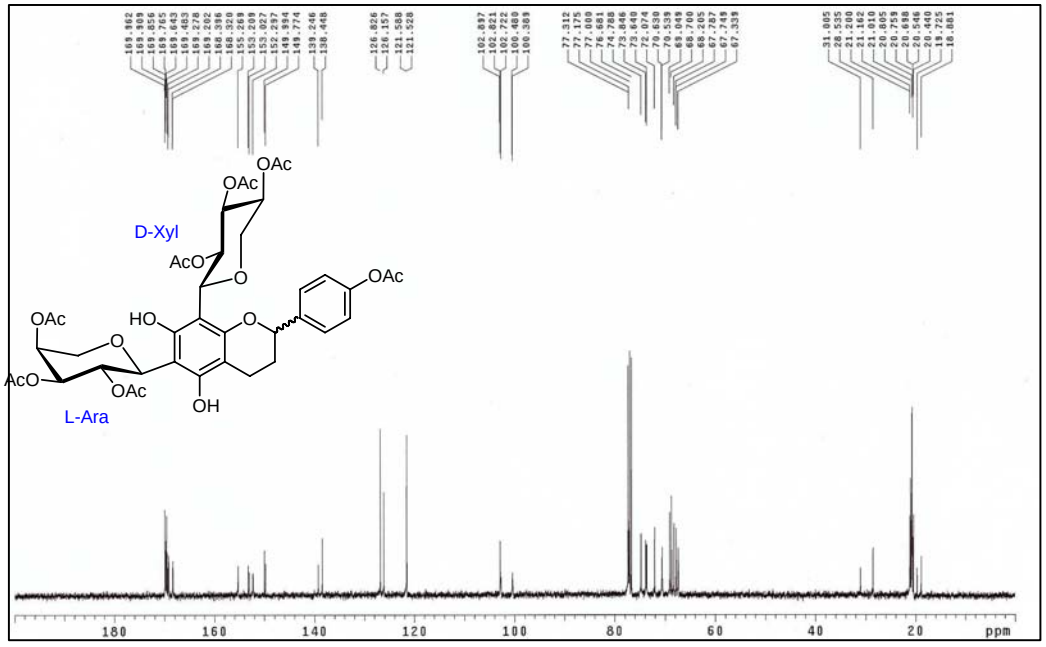
^{1}H NMR spectrum of compound **13cb** (600 MHz, $CDCl_3$)



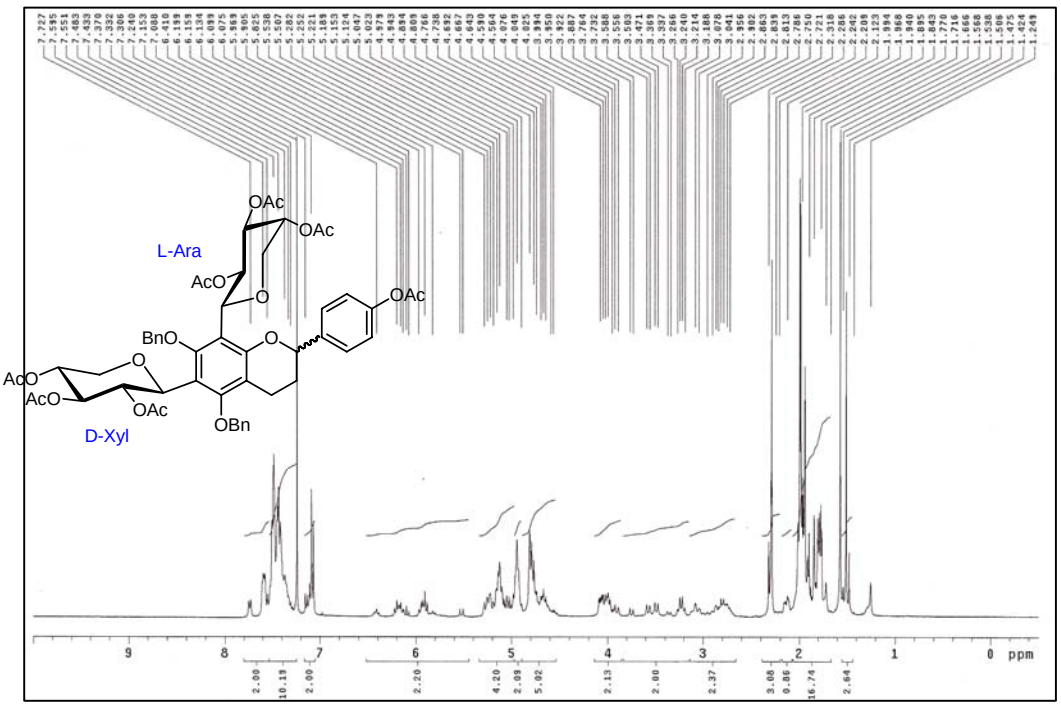
^{1}H NMR spectrum of compound **13cc** (600 MHz, $CDCl_3$)



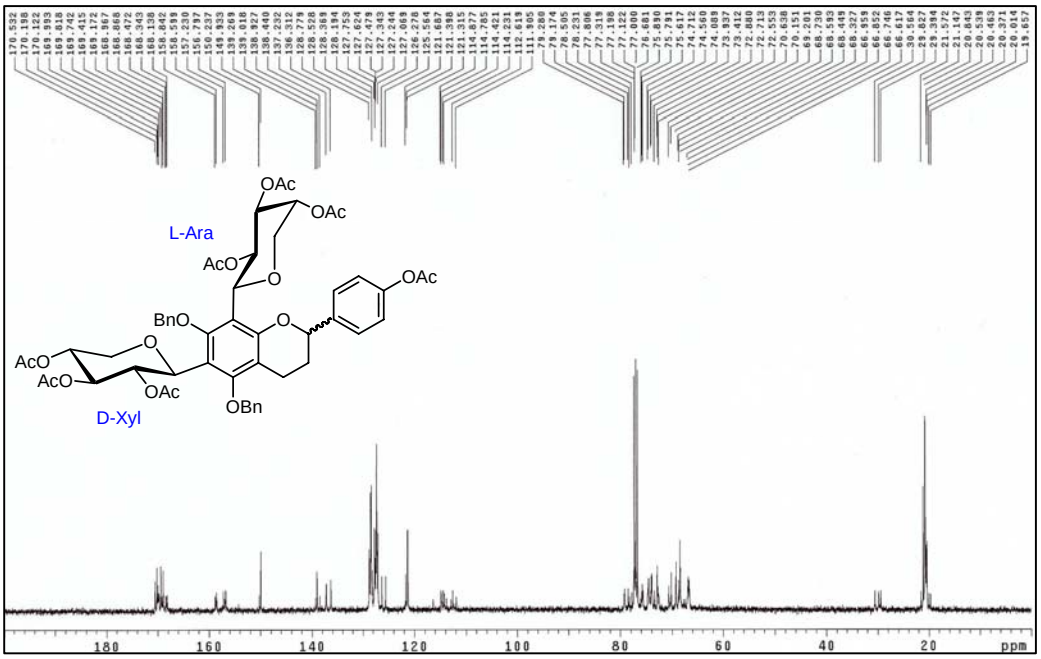
^{1}H NMR spectrum of compound **13db** (400 MHz, $CDCl_3$)



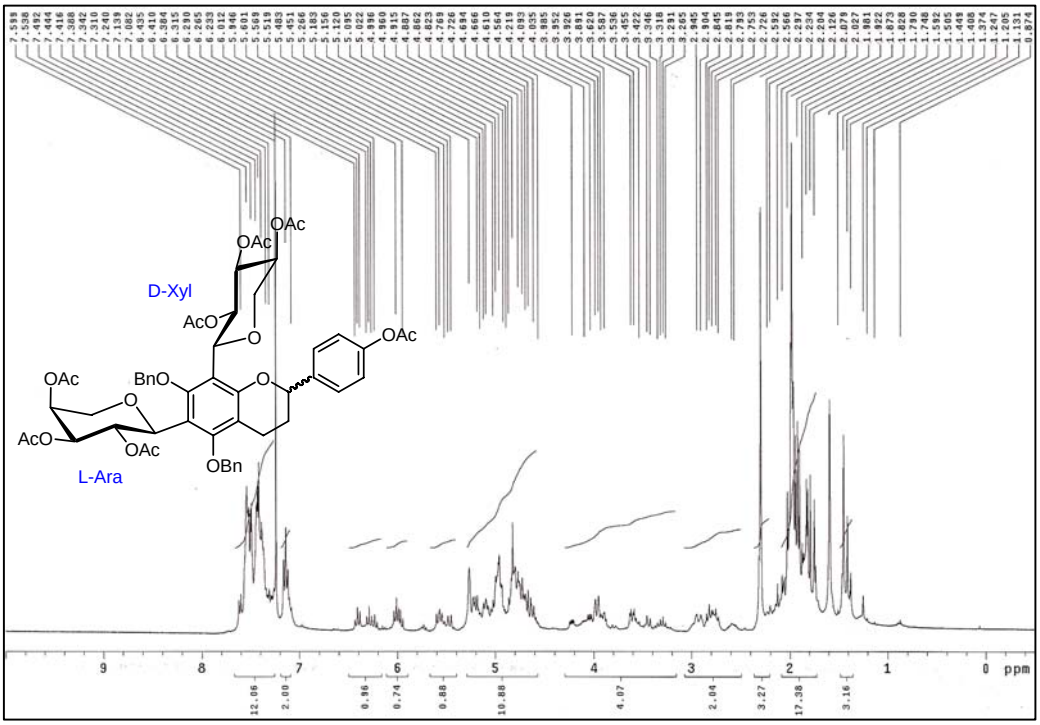
^{13}C NMR spectrum of compound **13db** (100 MHz, $CDCl_3$)



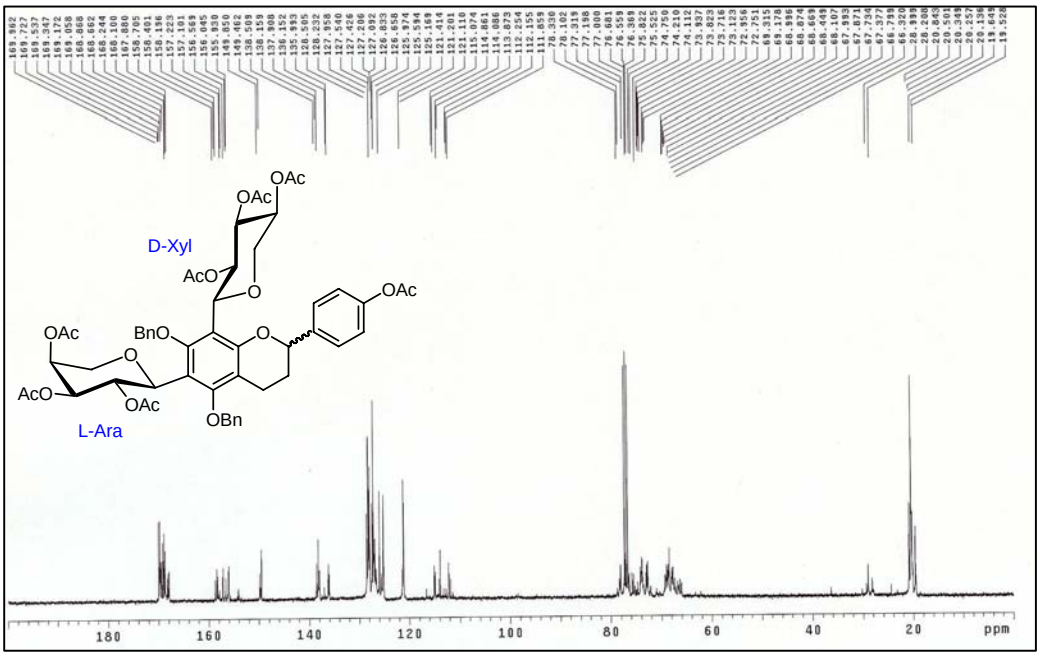
^{1}H NMR spectrum of compound **13bdBn** (400 MHz, $CDCl_3$)



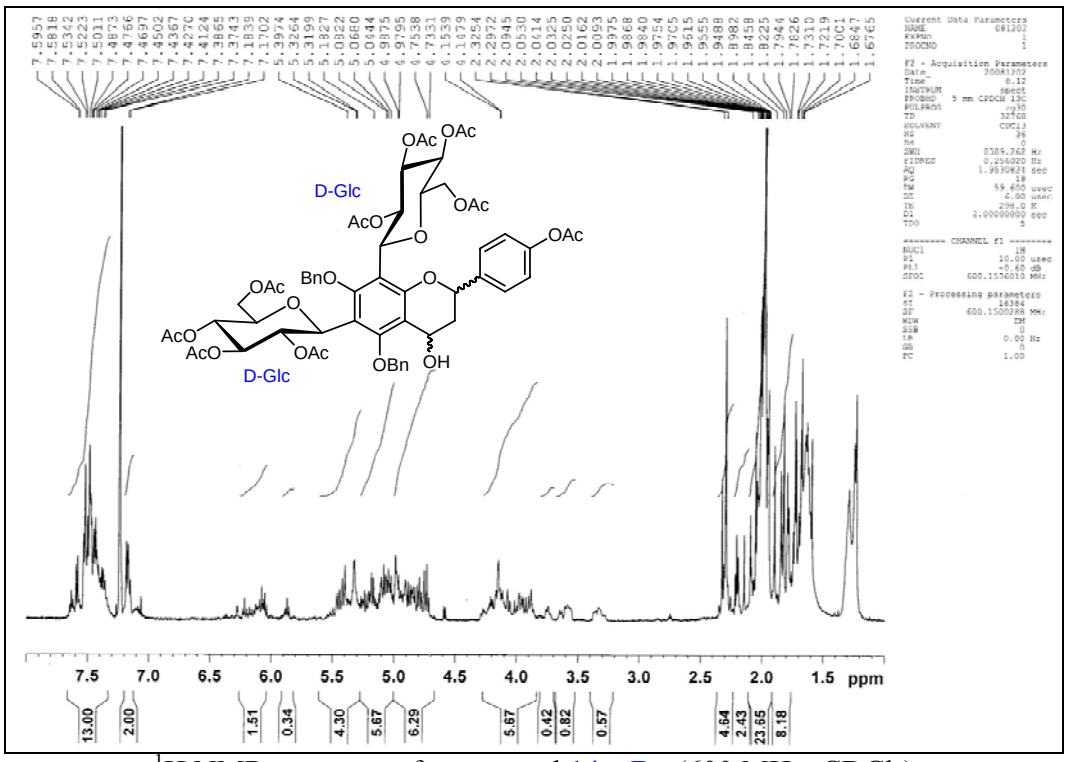
^{13}C NMR spectrum of compound **13bdBn** (100 MHz, $CDCl_3$)



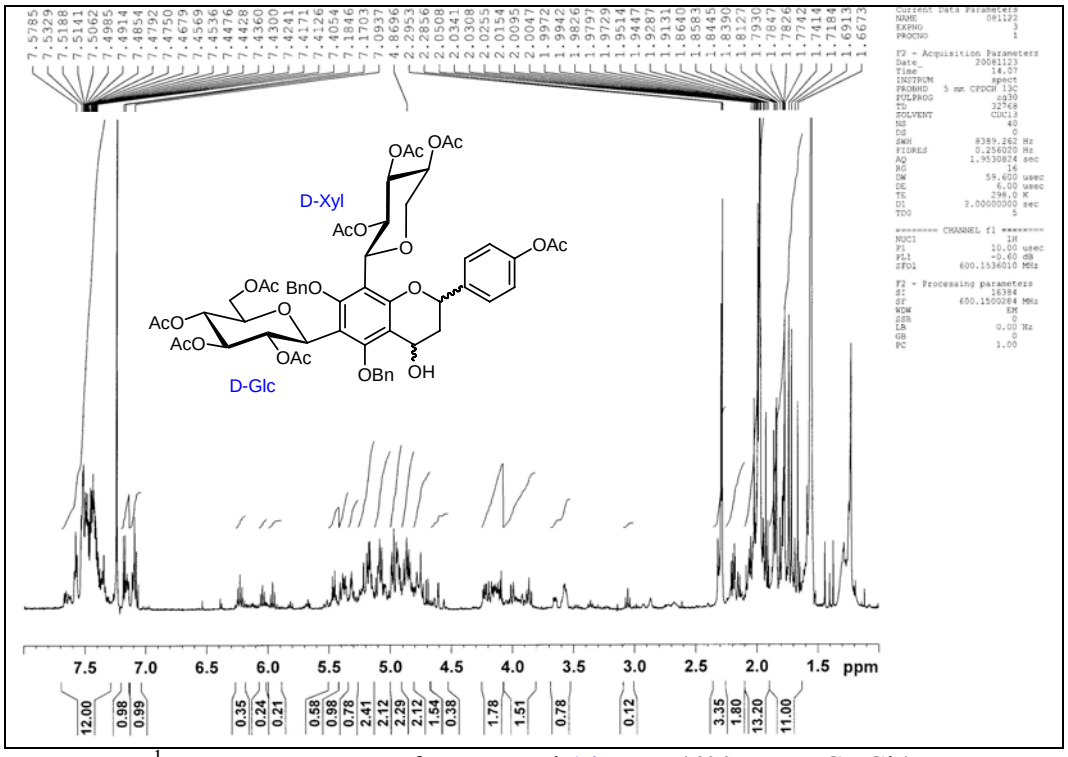
^{1}H NMR spectrum of compound **13dbBn** (400 MHz, $CDCl_3$)



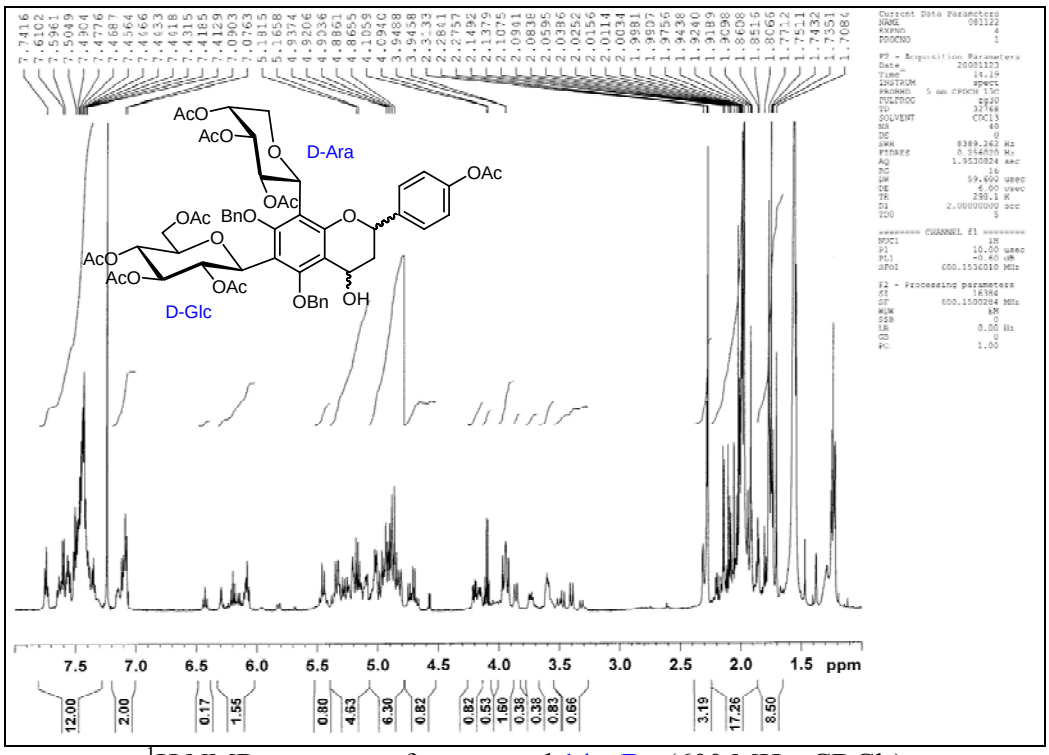
^{13}C NMR spectrum of compound **13dbBn** (100 MHz, $CDCl_3$)



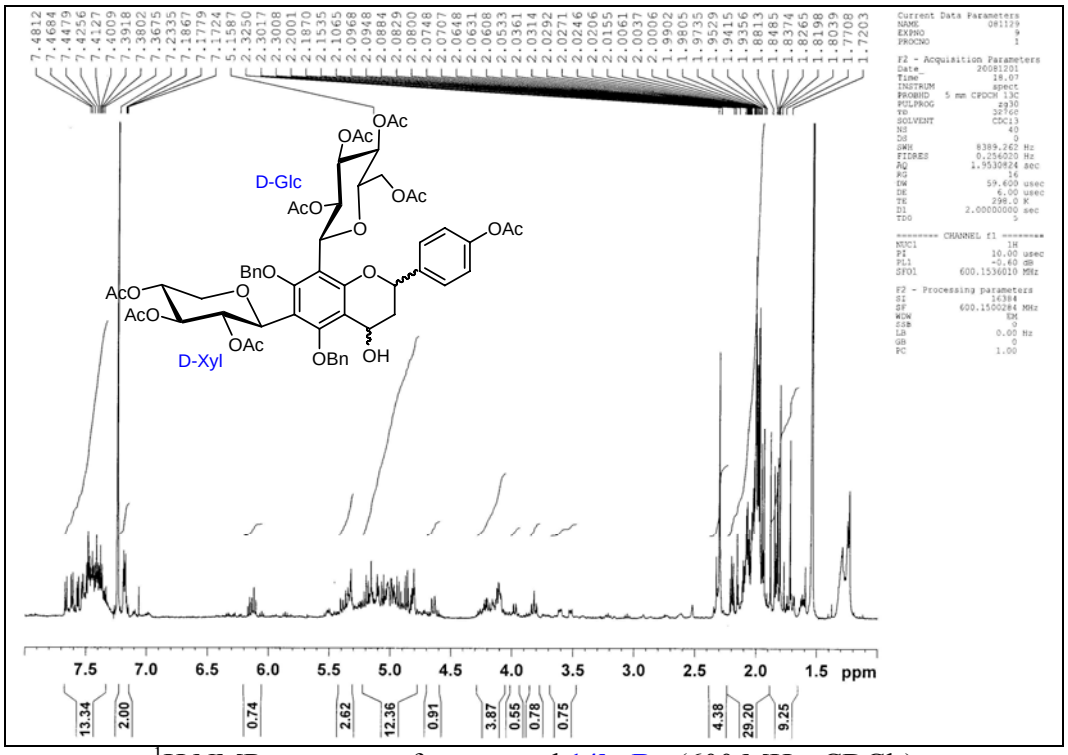
^{1}H NMR spectrum of compound **14aaBn** (600 MHz, $CDCl_3$)



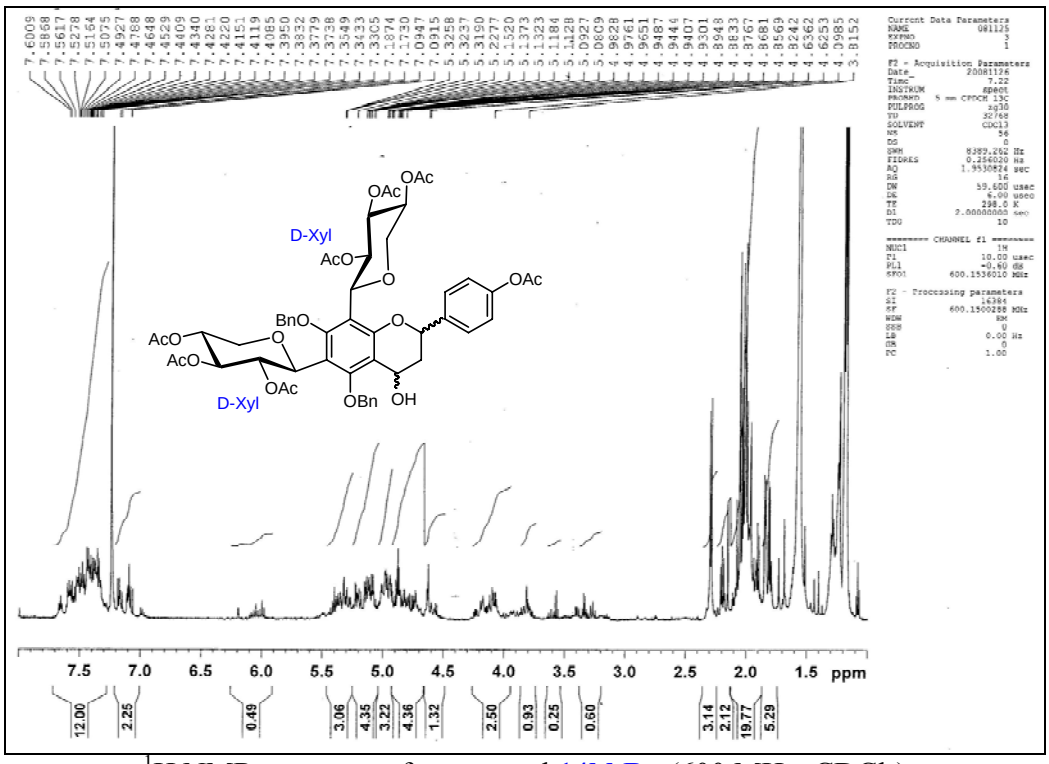
^{1}H NMR spectrum of compound **14abBn** (600 MHz, $CDCl_3$)



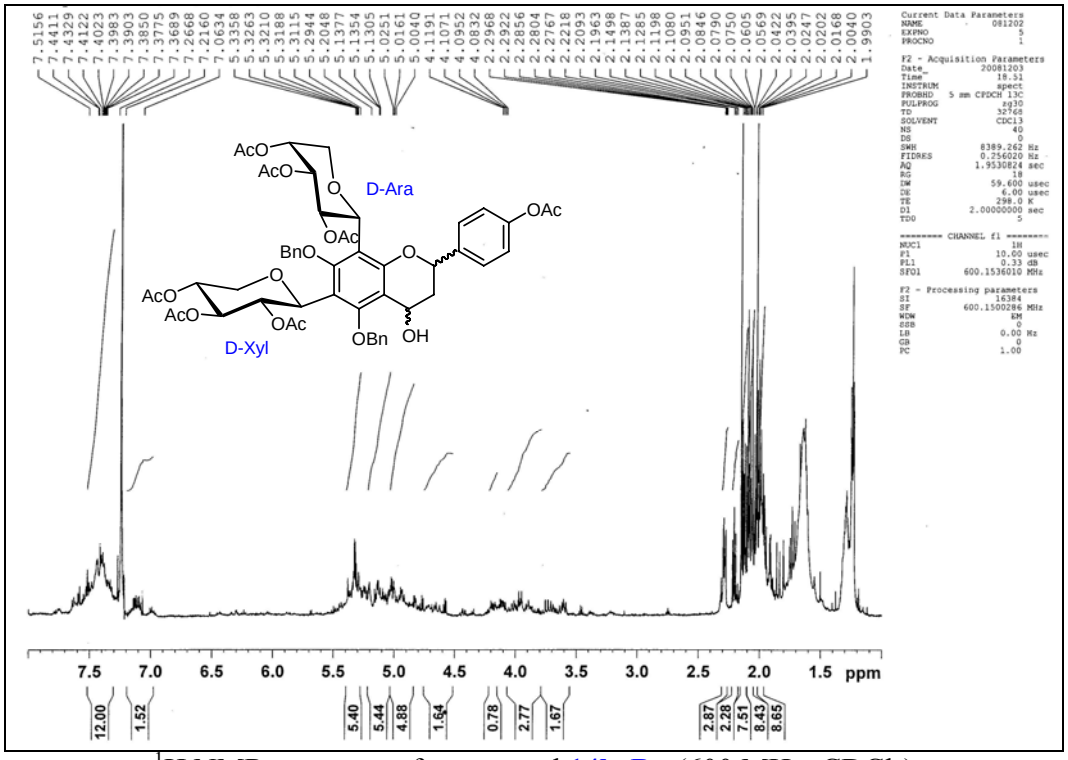
^{1}H NMR spectrum of compound **14acBn** (600 MHz, $CDCl_3$)



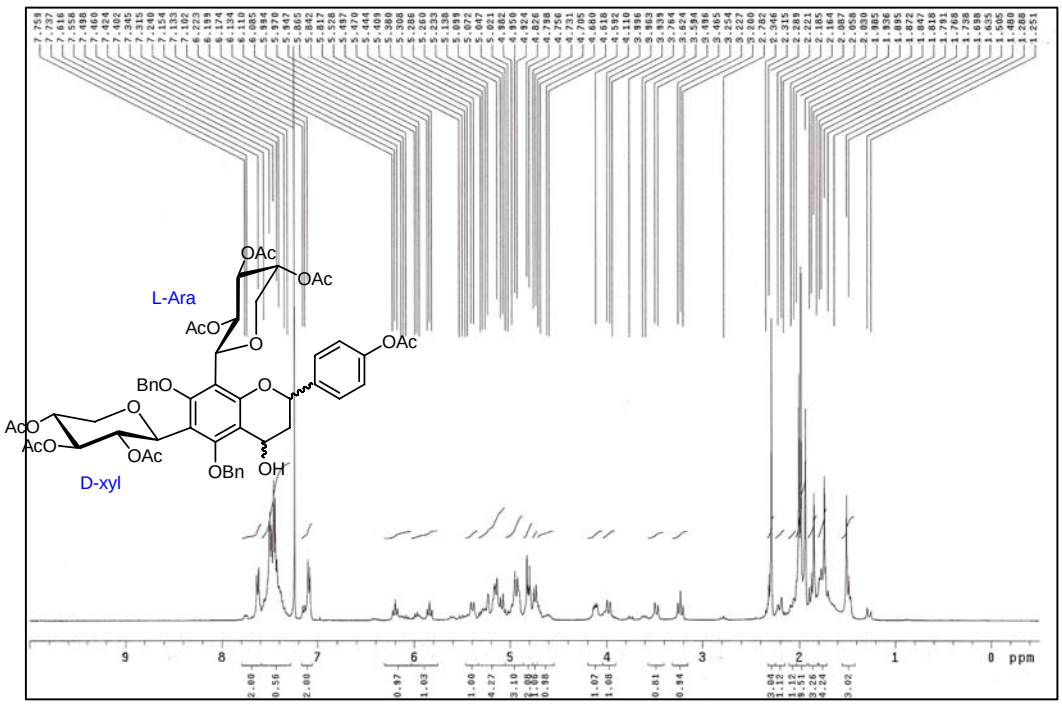
^{1}H NMR spectrum of compound **14baBn** (600 MHz, $CDCl_3$)



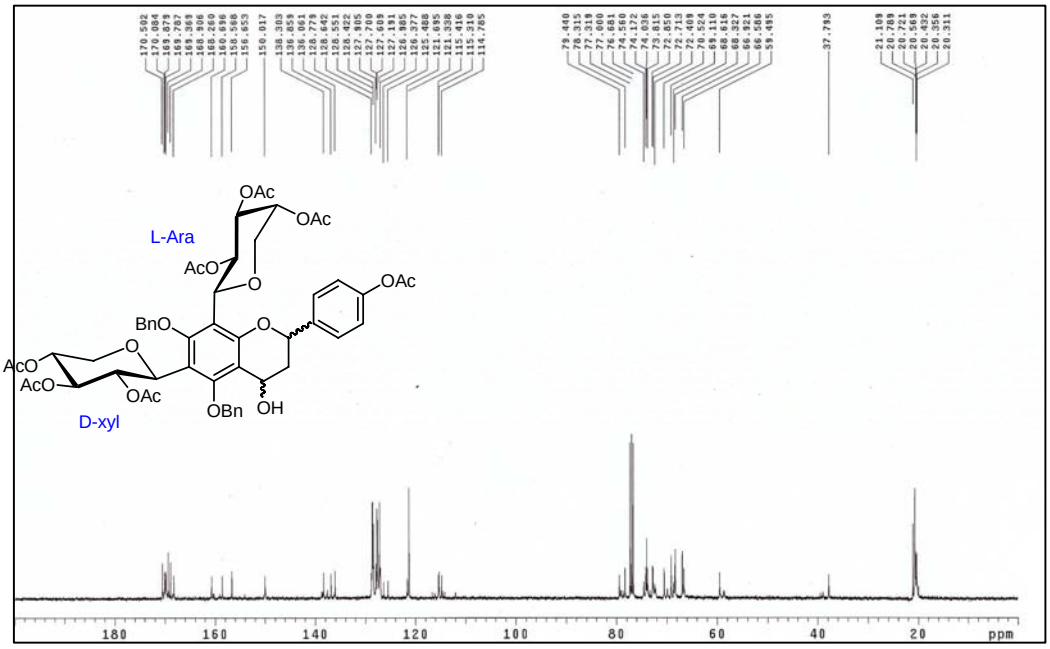
^{1}H NMR spectrum of compound **14bbBn** (600 MHz, $CDCl_3$)



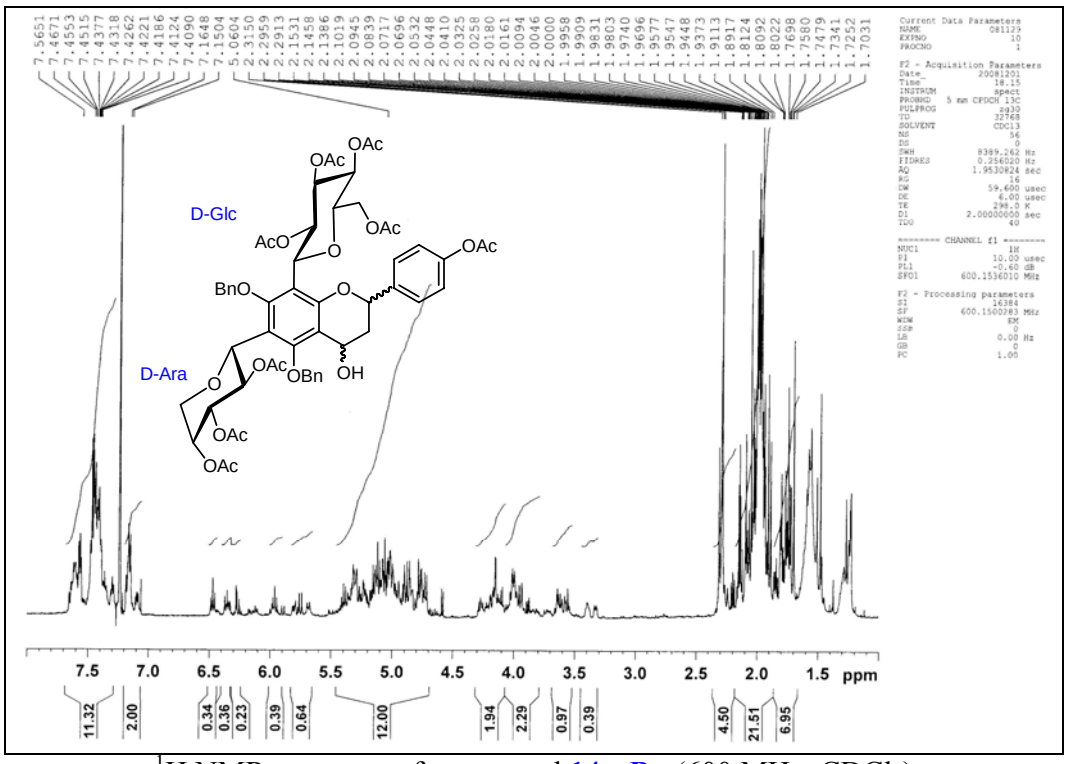
^{1}H NMR spectrum of compound **14bcBn** (600 MHz, $CDCl_3$)



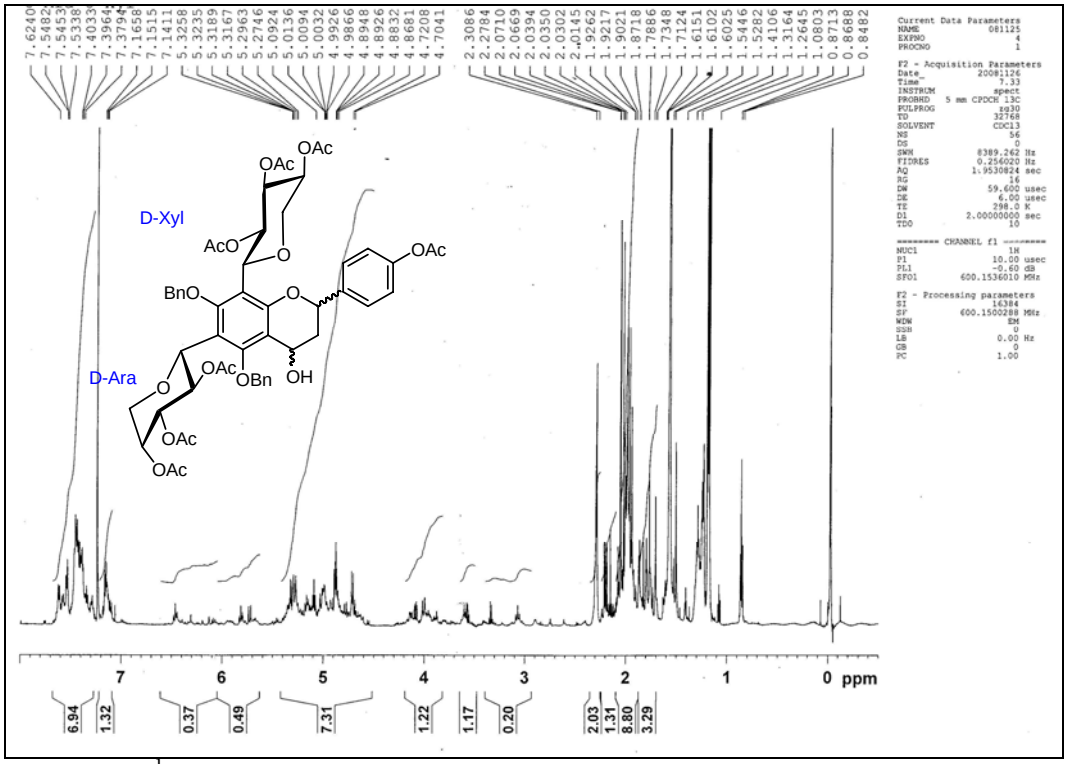
^{1}H NMR spectrum of compound **14bdBn** (400 MHz, $CDCl_3$)



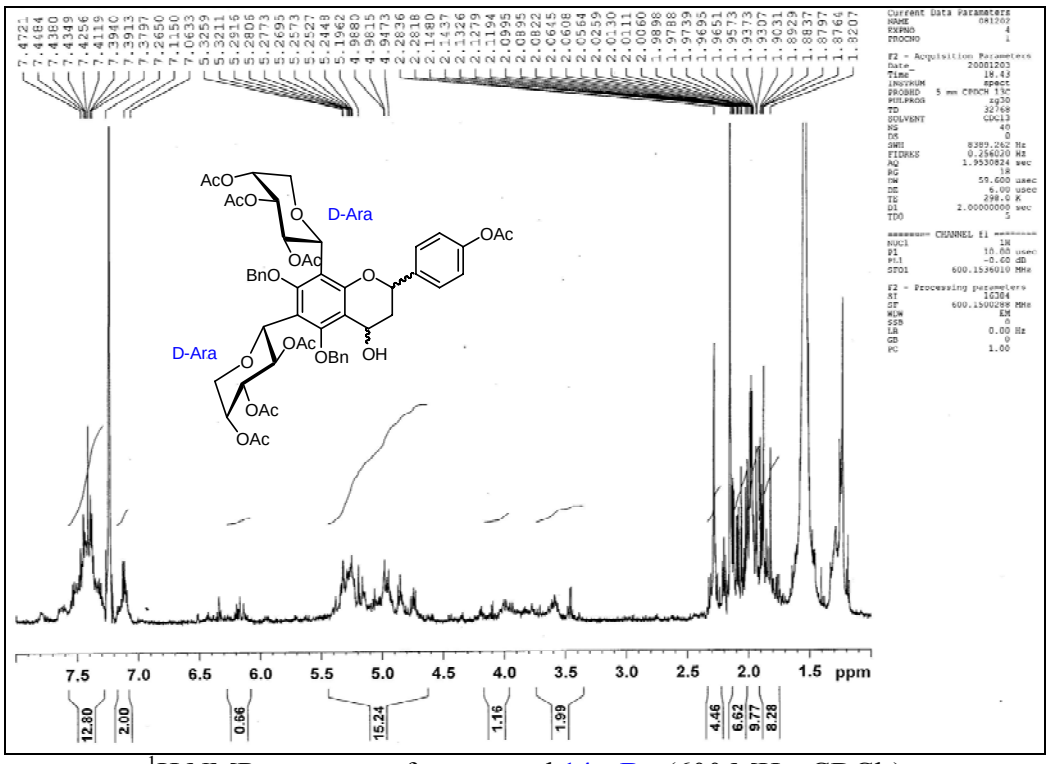
^{13}C NMR spectrum of compound **14bdBn** (100 MHz, $CDCl_3$)



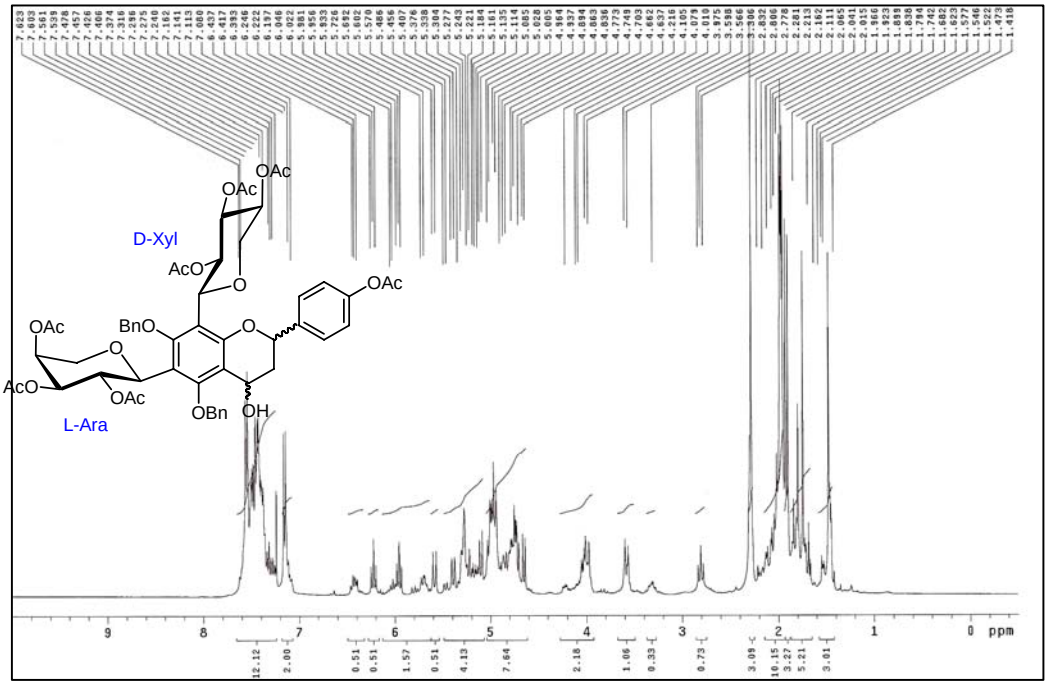
^{1}H NMR spectrum of compound **14caBn** (600 MHz, $CDCl_3$)



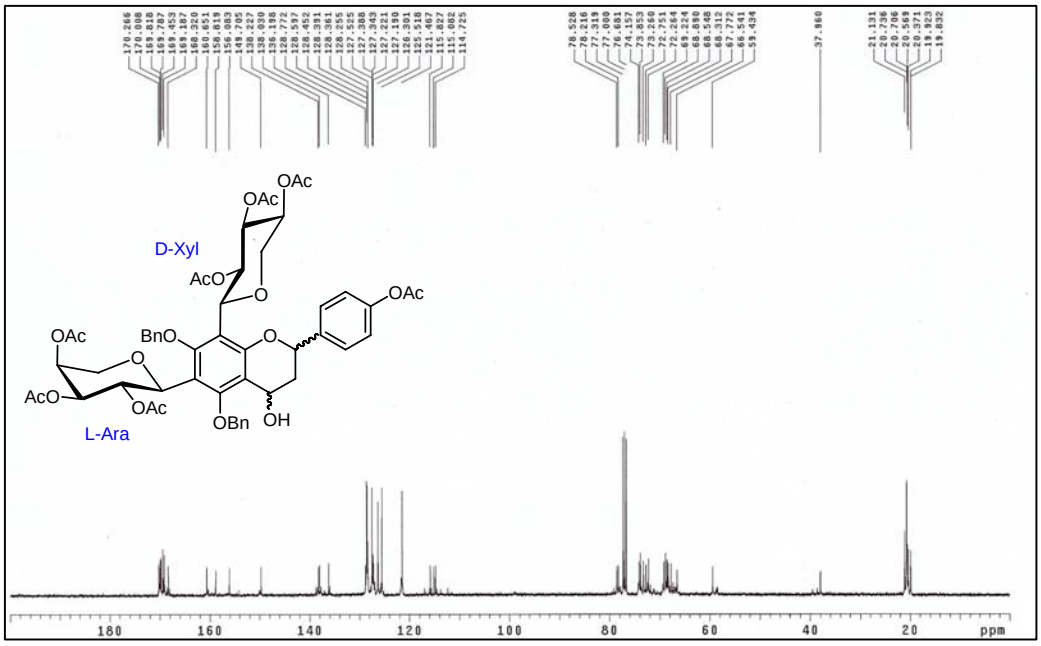
^{1}H NMR spectrum of compound **14cbBn** (600 MHz, $CDCl_3$)



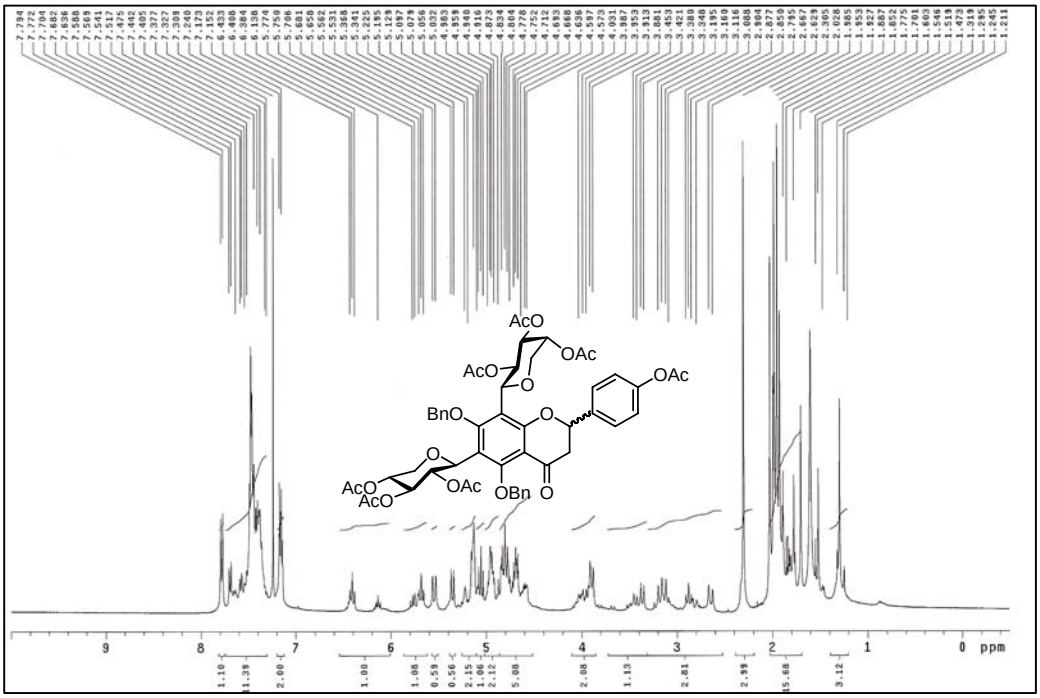
^{1}H NMR spectrum of compound **14ccBn** (600 MHz, $CDCl_3$)



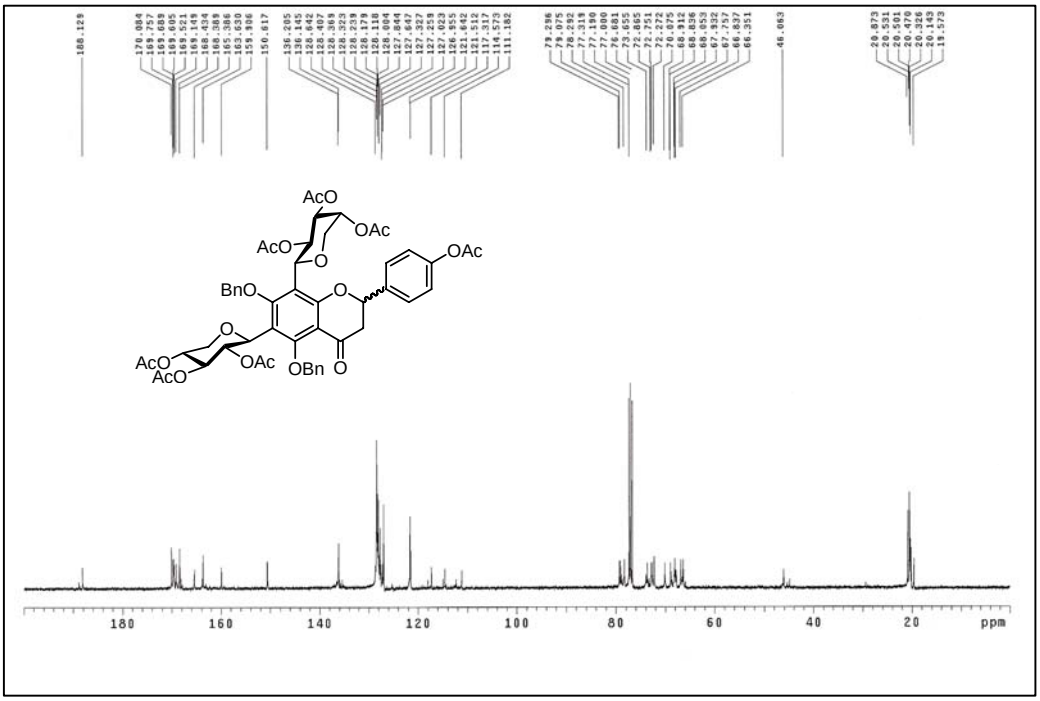
^{1}H NMR spectrum of compound **14dbBn** (400 MHz, $CDCl_3$)



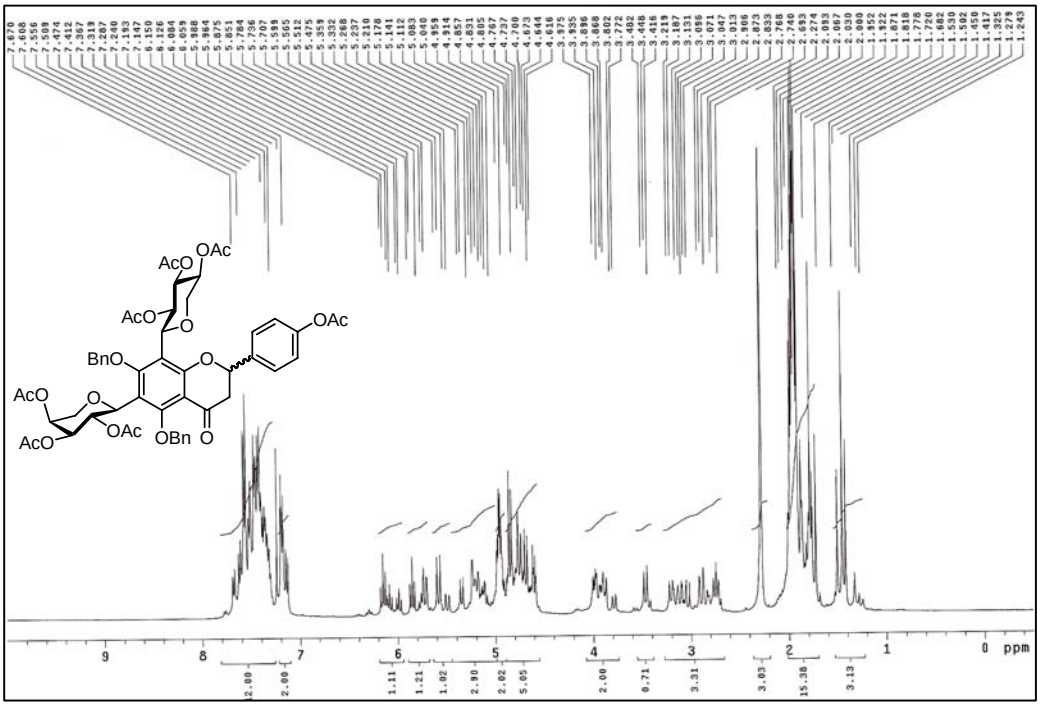
^{13}C NMR spectrum of compound **14dbBn** (100 MHz, $CDCl_3$)



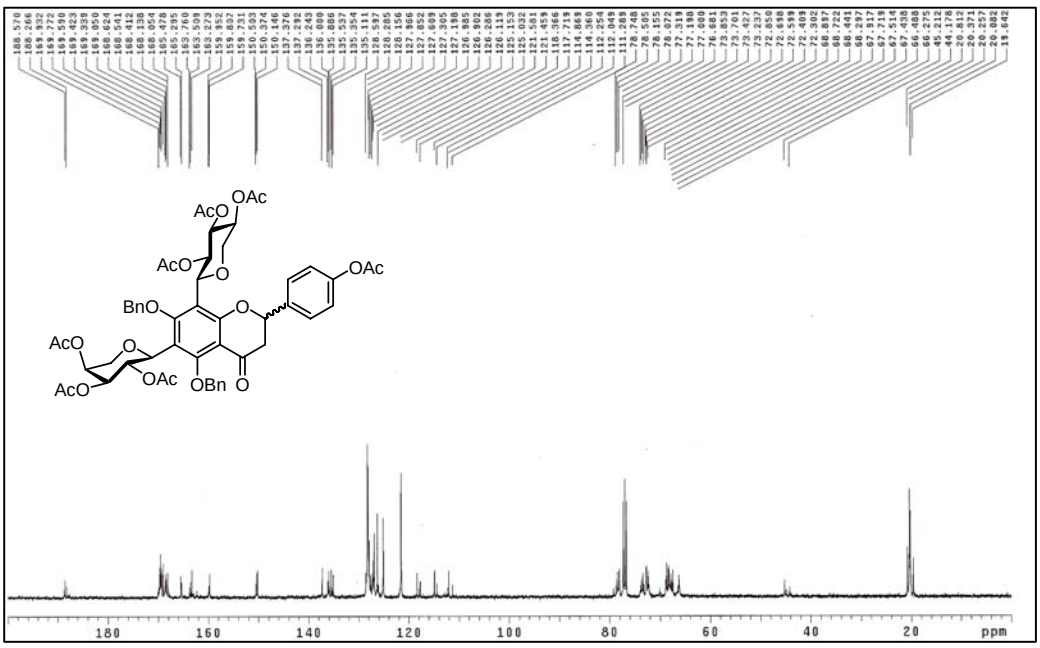
^{1}H NMR spectrum of compound **15bdBn** (400 MHz, $CDCl_3$)



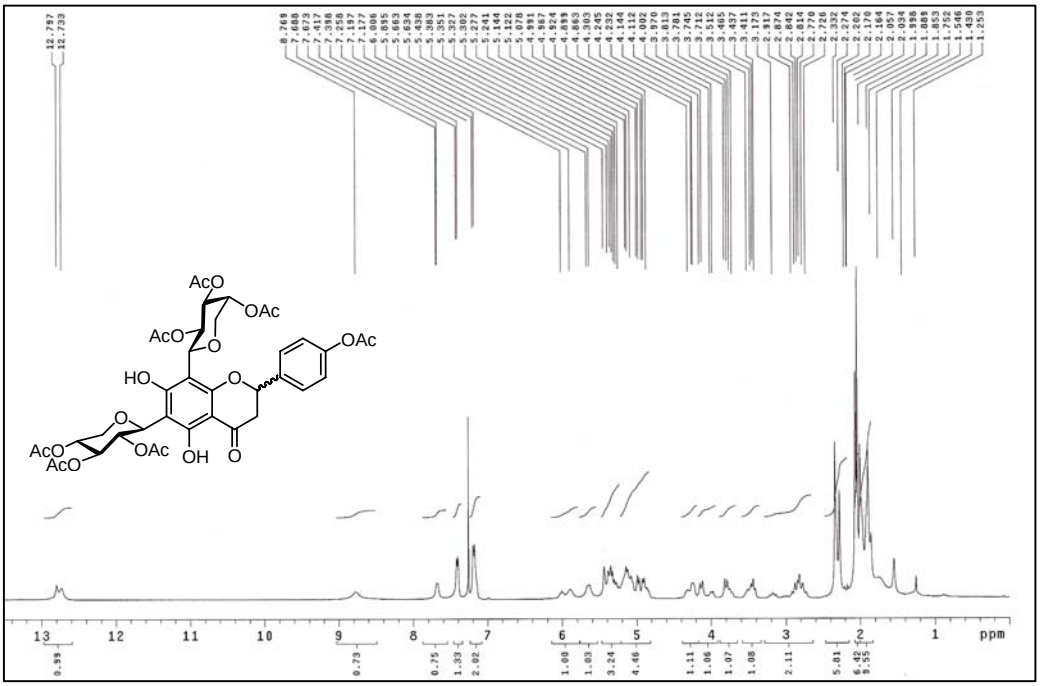
^{13}C NMR spectrum of compound **15bdBn** (100 MHz, $CDCl_3$)



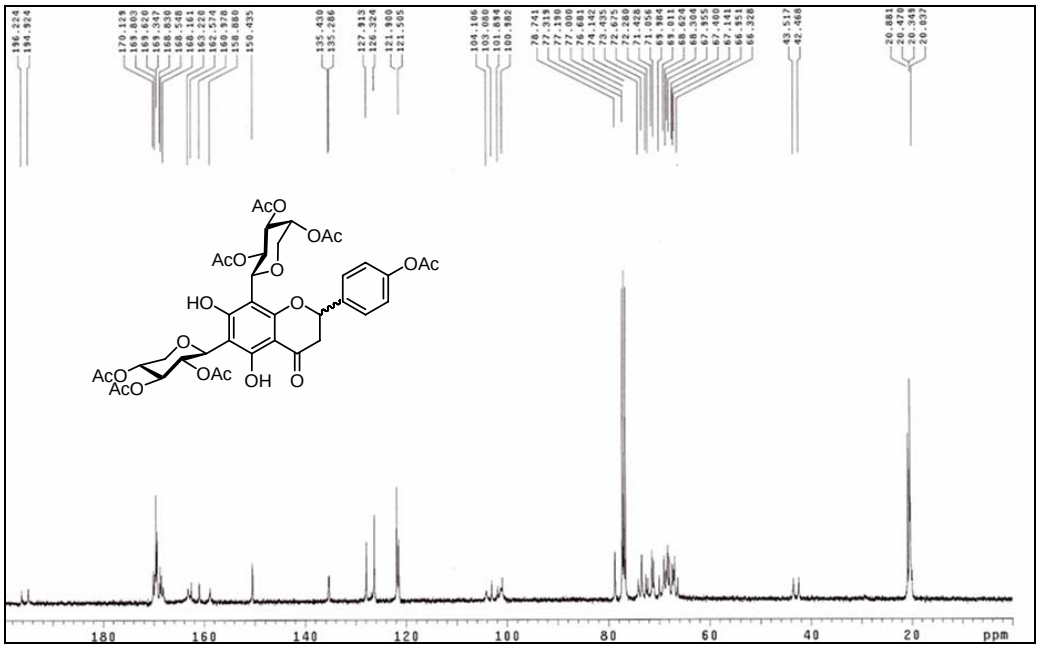
^{1}H NMR spectrum of compound **15dbBn** (400 MHz, $CDCl_3$)



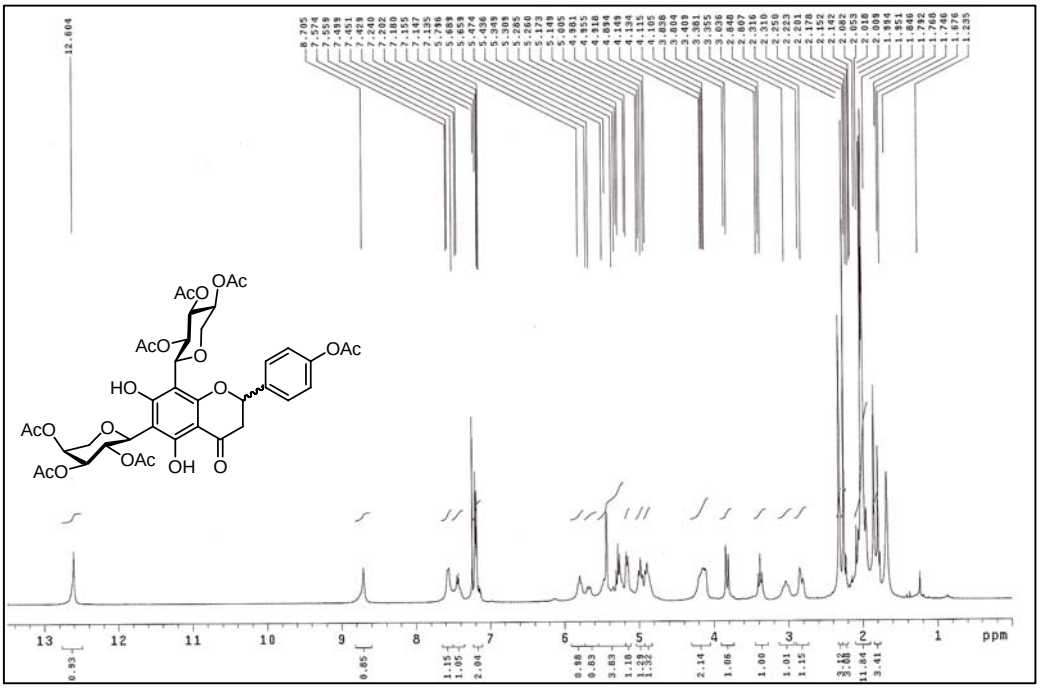
^{13}C NMR spectrum of compound **15dbBn** (100 MHz, $CDCl_3$)



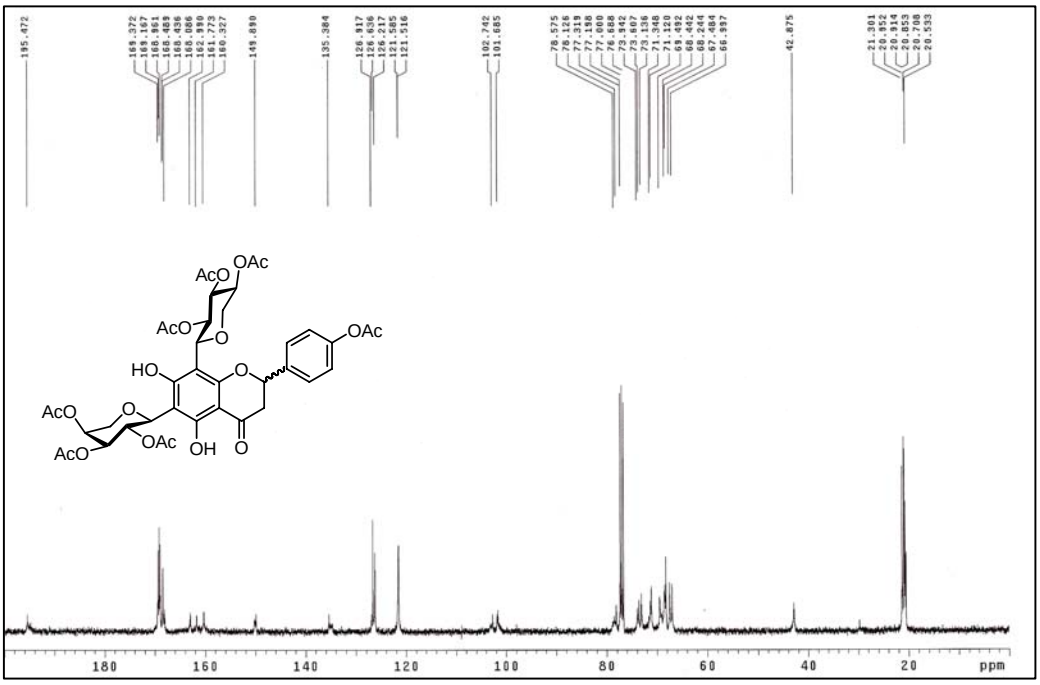
^{1}H NMR spectrum of compound **15bd** (400 MHz, $CDCl_3$)



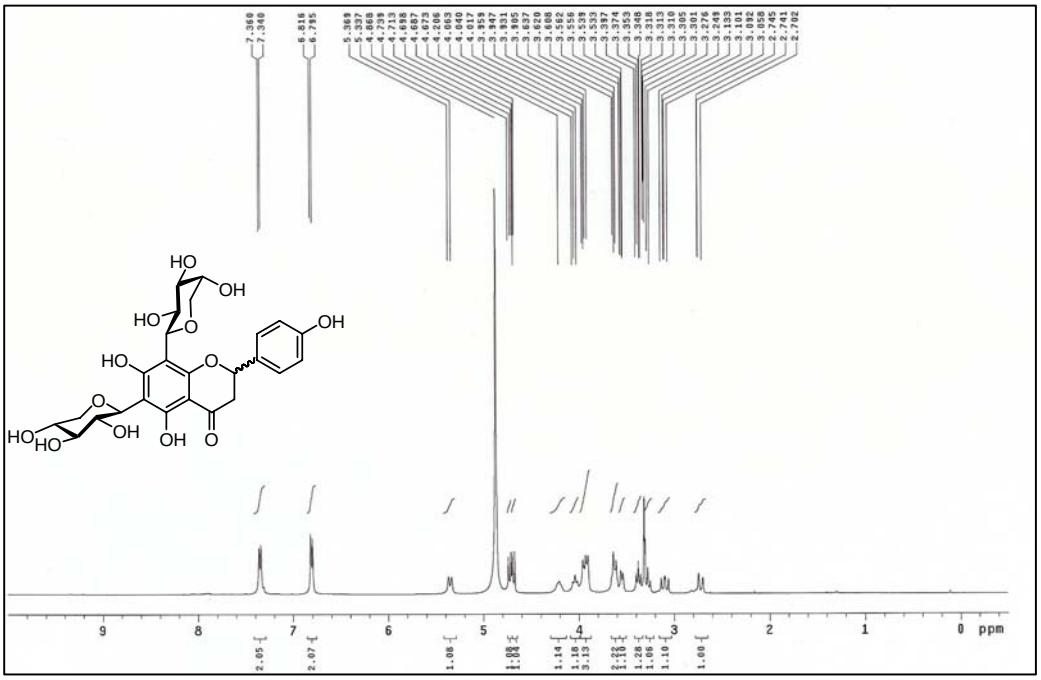
^{13}C NMR spectrum of compound **15bd** (100 MHz, $CDCl_3$)



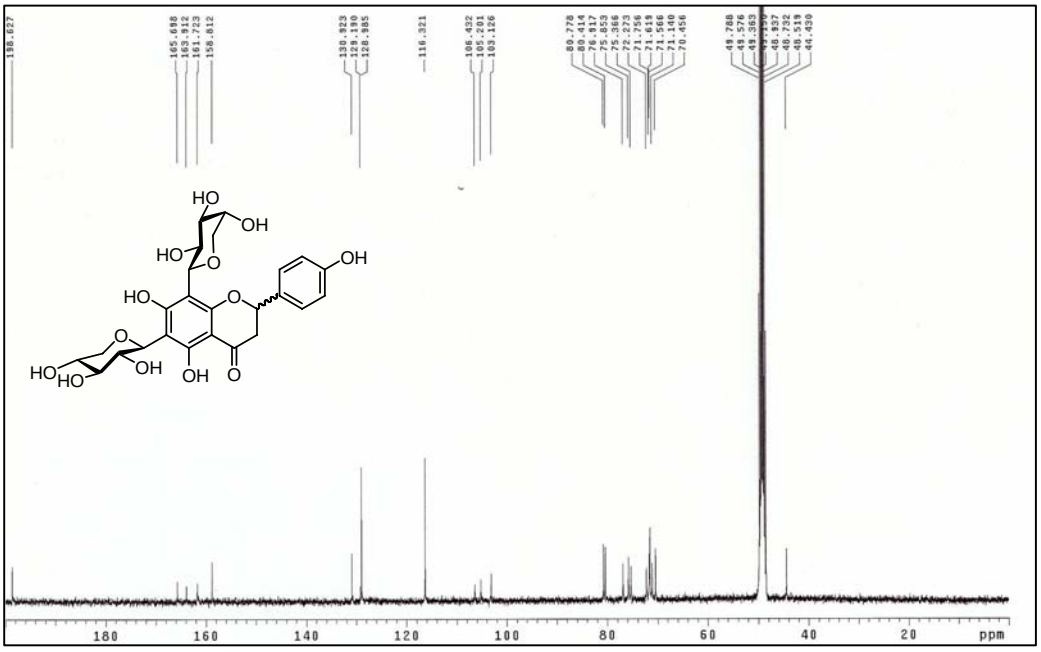
^{1}H NMR spectrum of compound **15db** (400 MHz, $CDCl_3$)



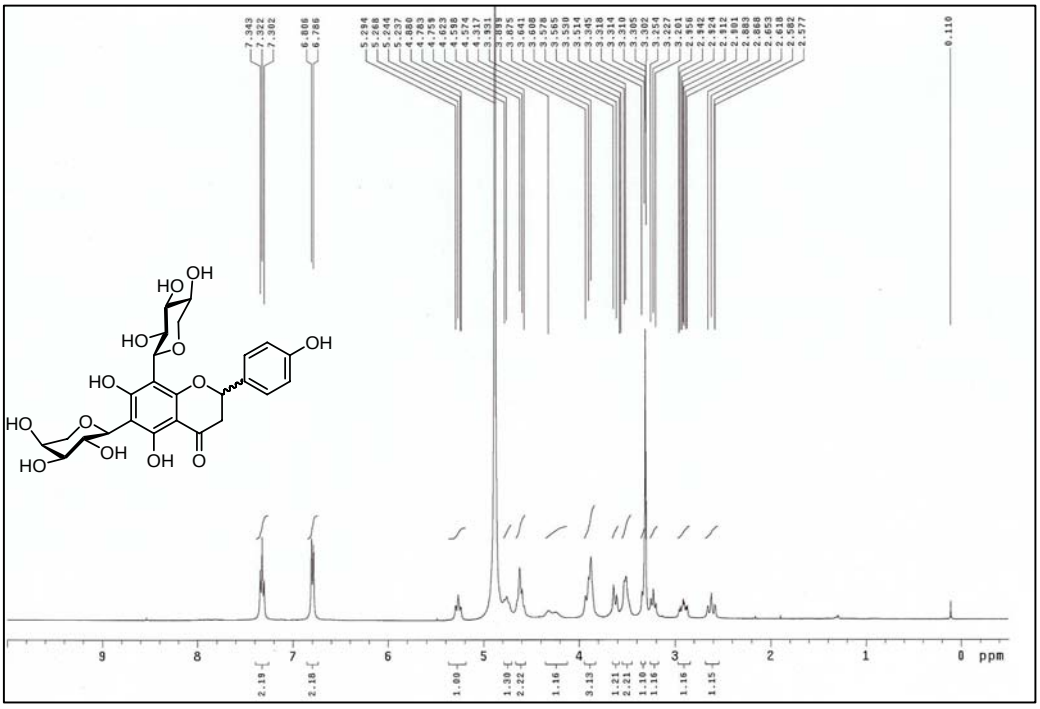
^{13}C NMR spectrum of compound **15db** (100 MHz, $CDCl_3$)



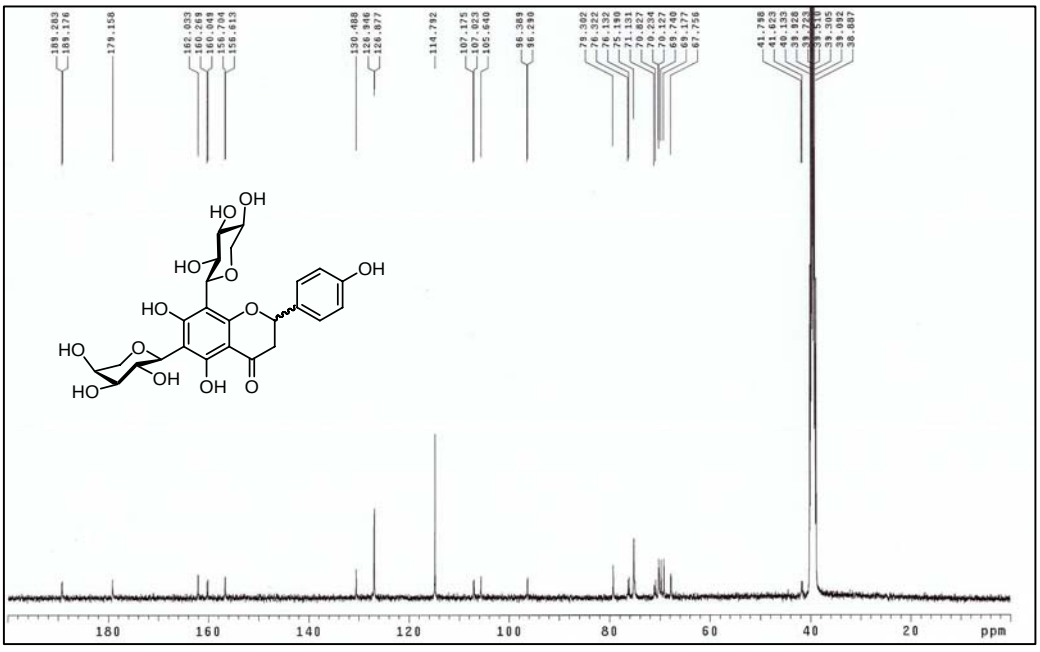
^{1}H NMR spectrum of compound **2bd** (400 MHz, CD_3OD)



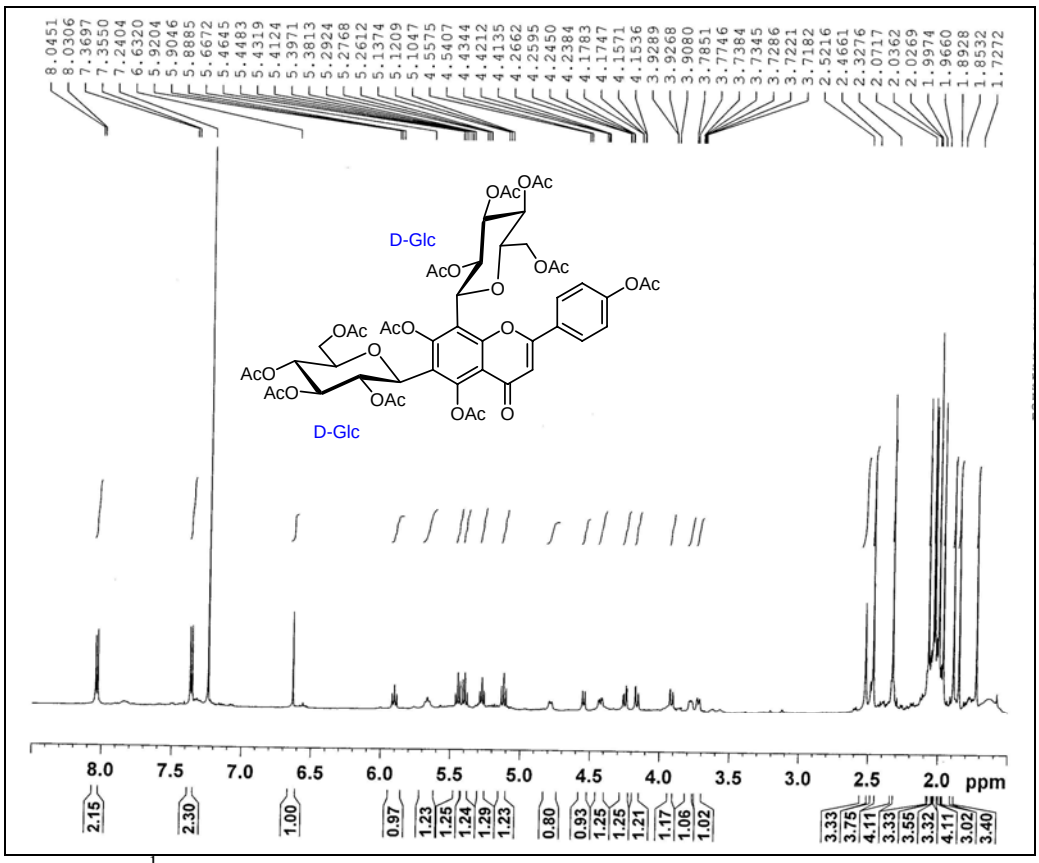
^{13}C NMR spectrum of compound **2bd** (100 MHz, CD_3OD)



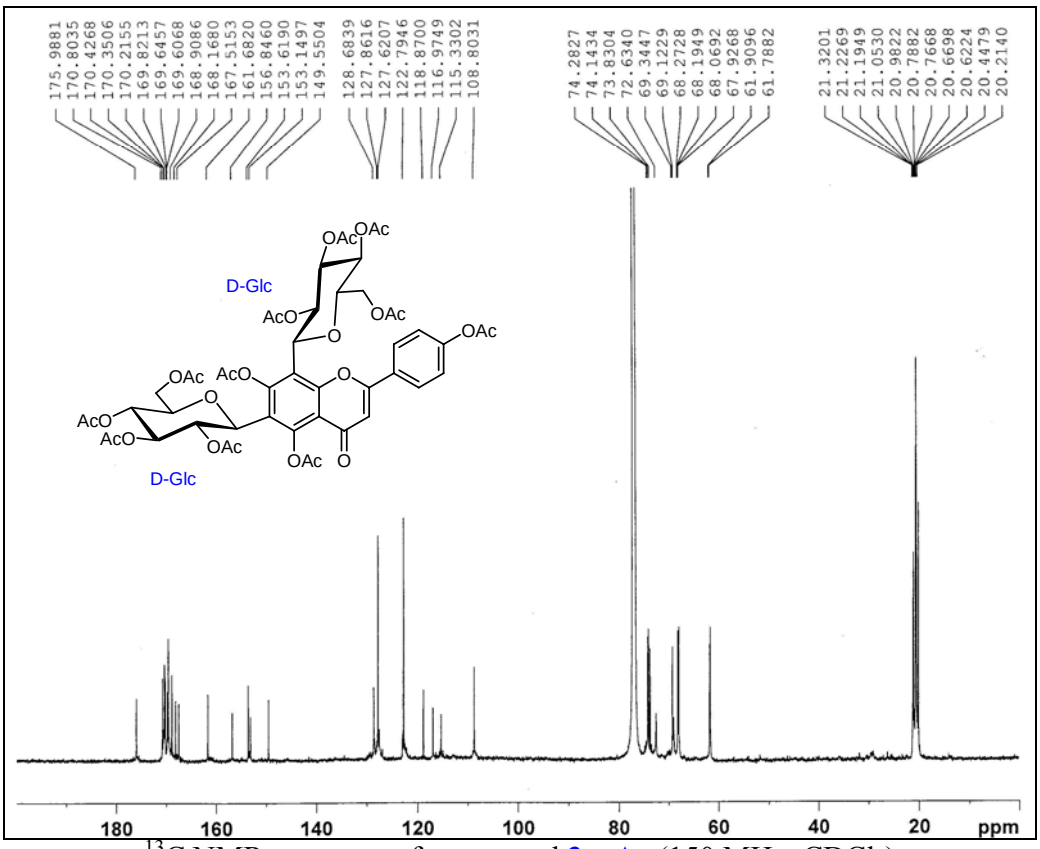
^{1}H NMR spectrum of compound **2db** (400 MHz, CD_3OD)



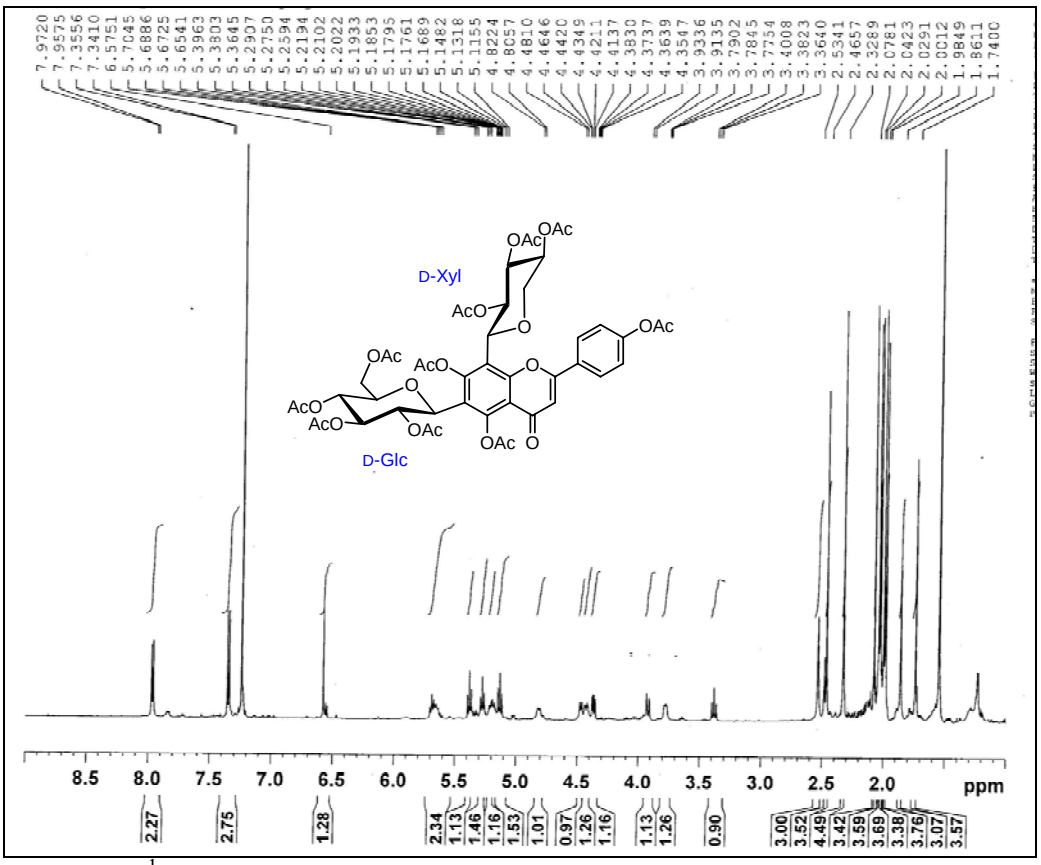
^{13}C NMR spectrum of compound **2db** (100 MHz, DMSO-d_6)



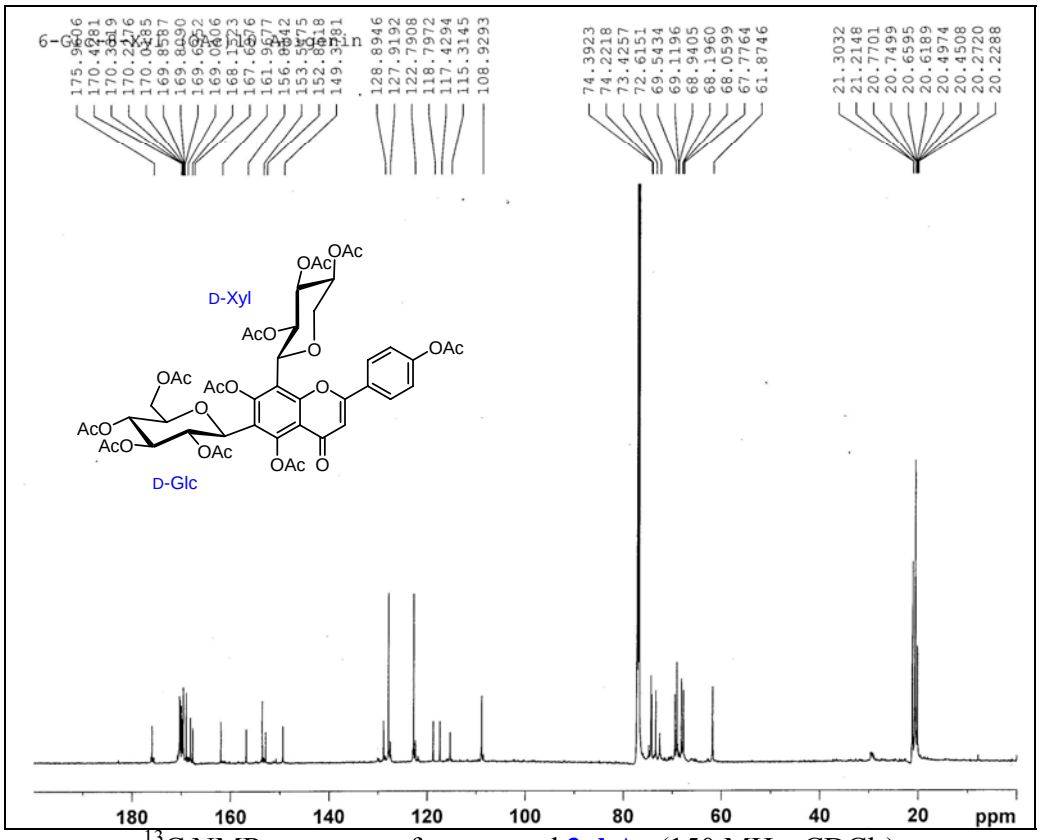
^{1}H NMR spectrum of compound **3aaAc** (600 MHz, $CDCl_3$)



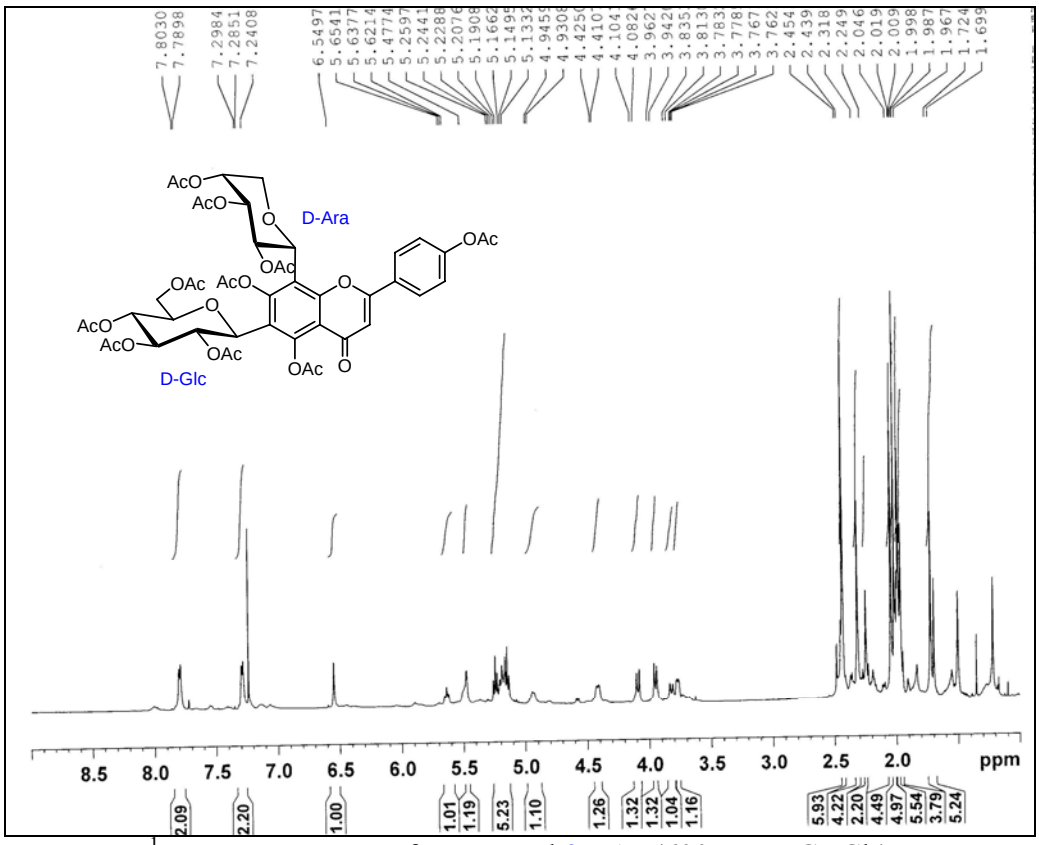
^{13}C NMR spectrum of compound **3aaAc** (150 MHz, $CDCl_3$)



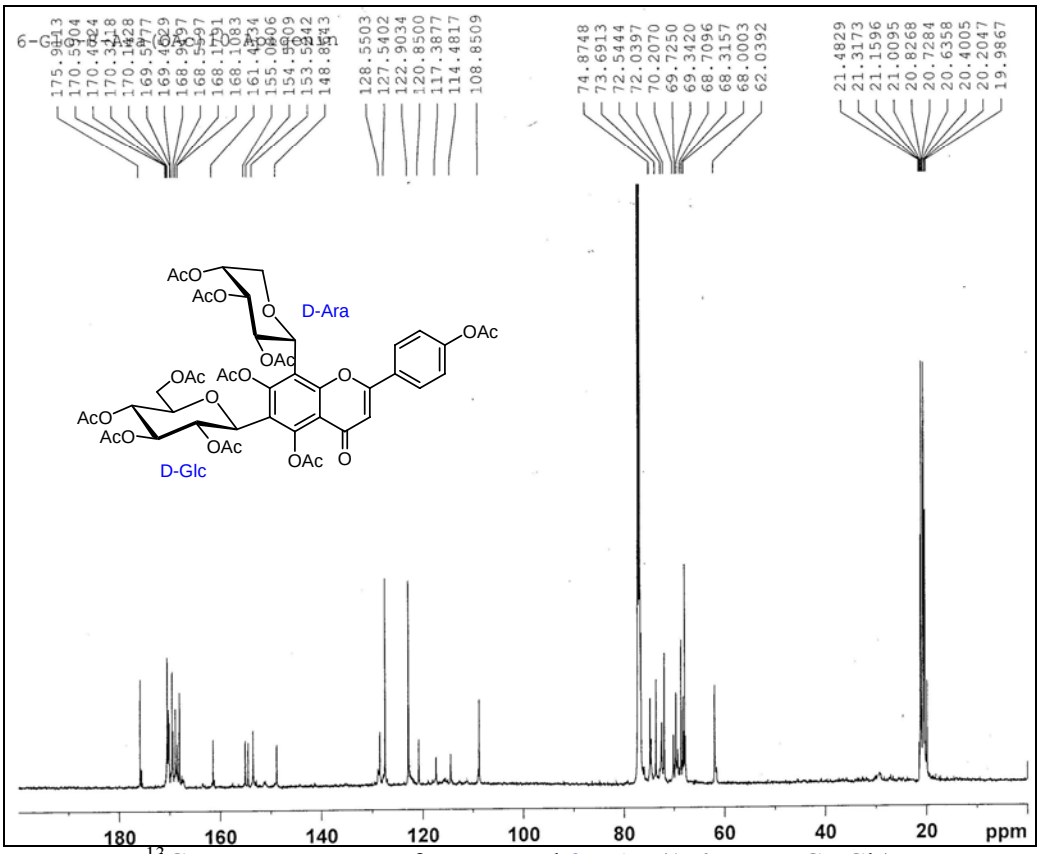
^{1}H NMR spectrum of compound **3abAc** (600 MHz, $CDCl_3$)



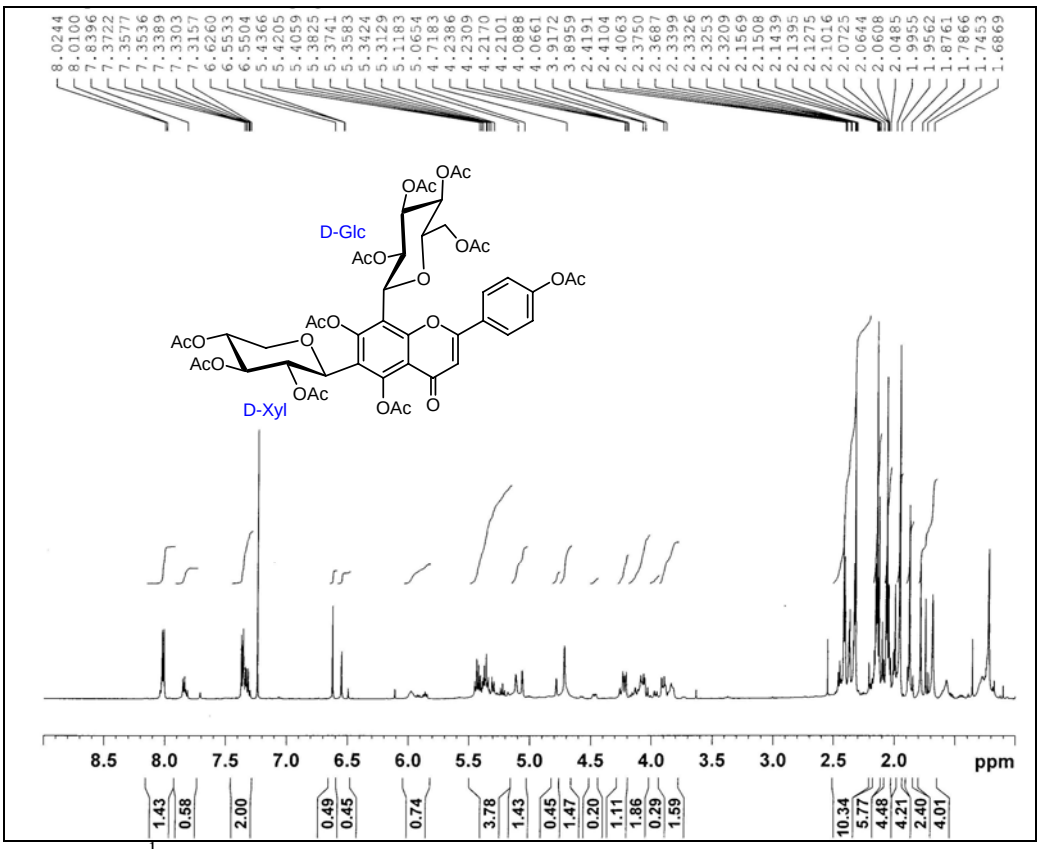
^{13}C NMR spectrum of compound **3abAc** (150 MHz, $CDCl_3$)



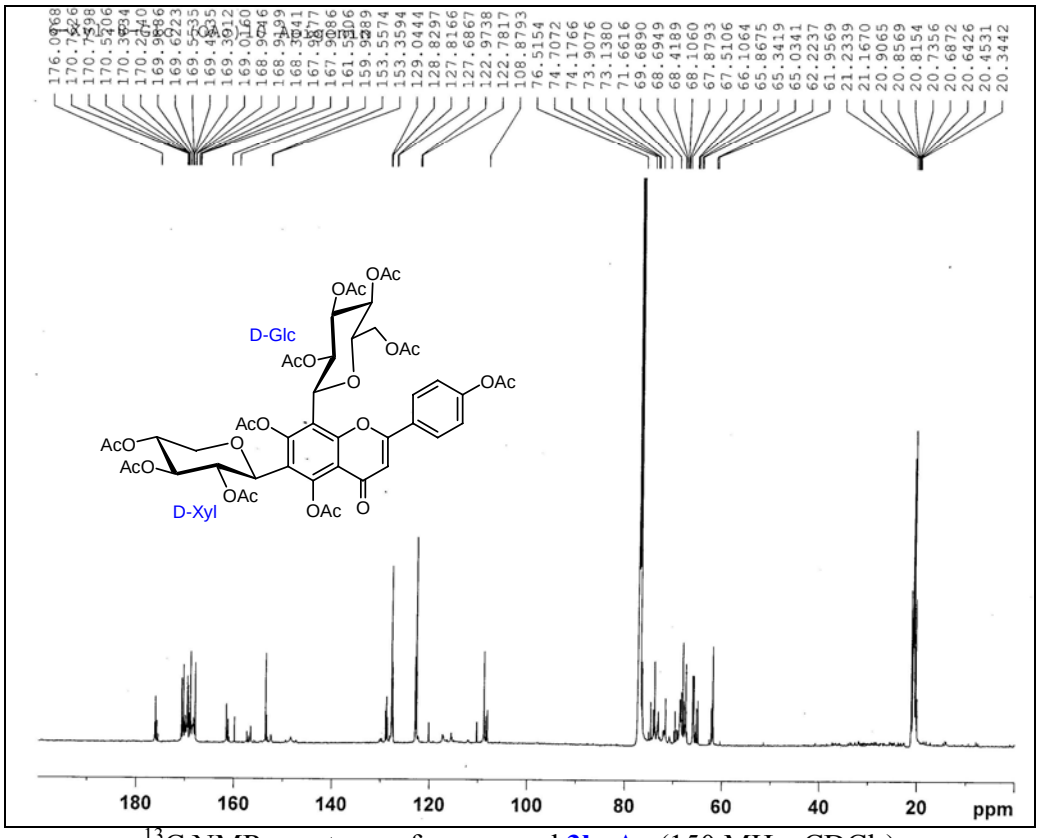
^{1}H NMR spectrum of compound **3acAc** (600 MHz, $CDCl_3$)



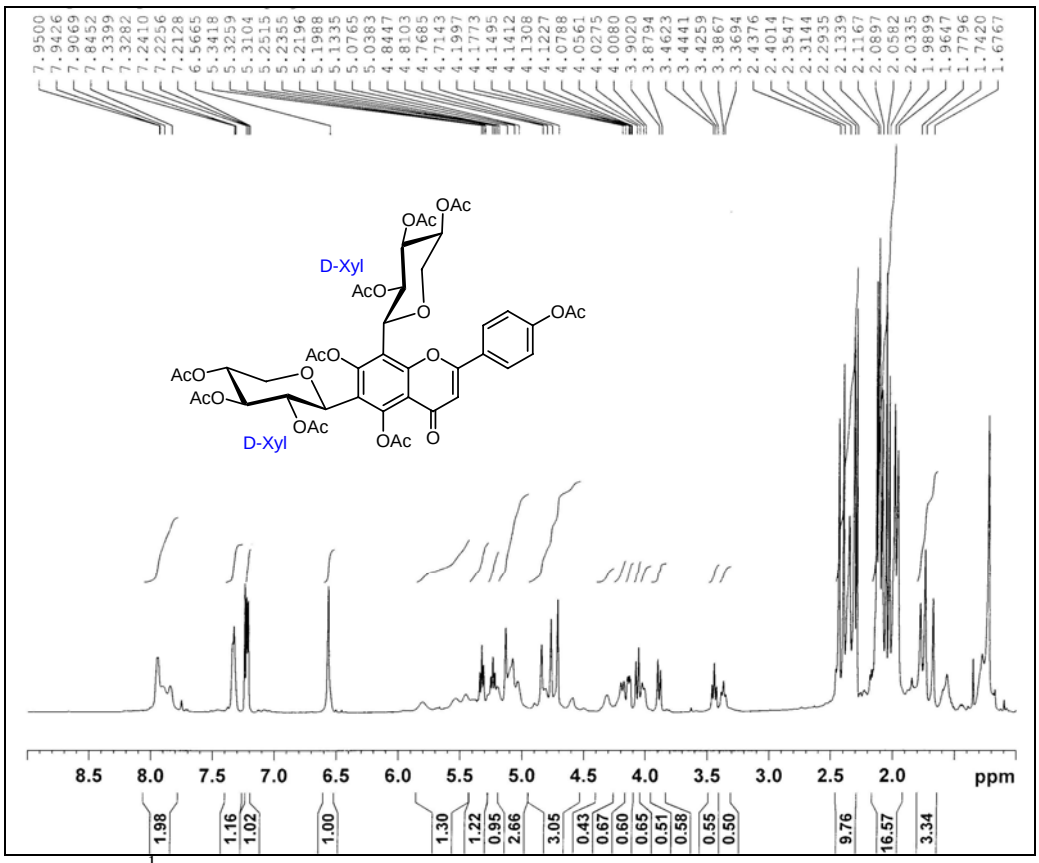
^{13}C NMR spectrum of compound **3acAc** (150 MHz, $CDCl_3$)



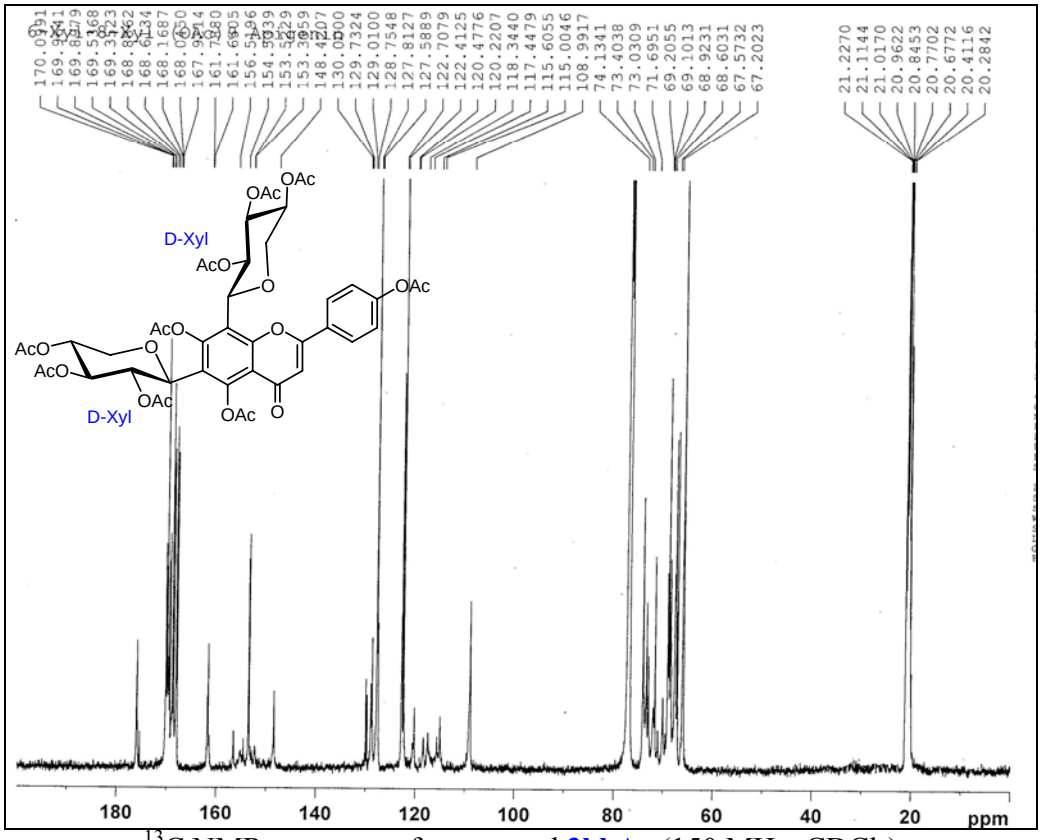
^{1}H NMR spectrum of compound **3baAc** (600 MHz, $CDCl_3$)



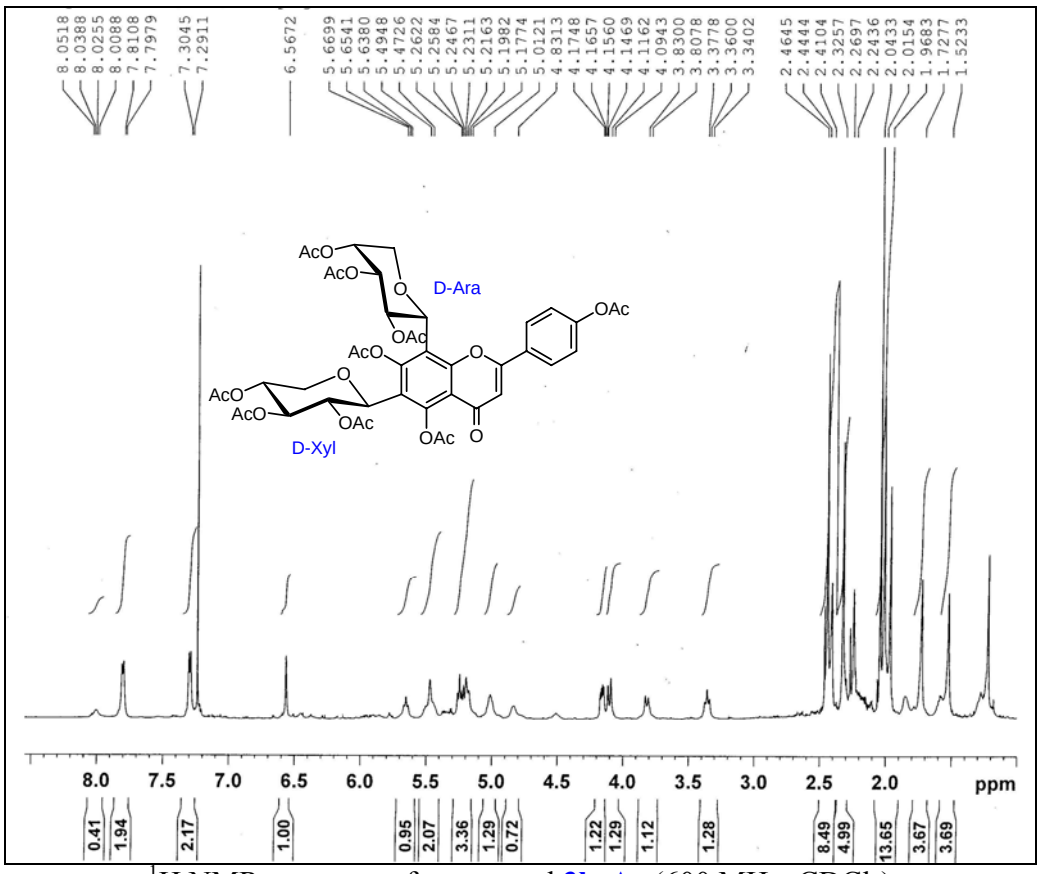
^{13}C NMR spectrum of compound **3baAc** (150 MHz, $CDCl_3$)



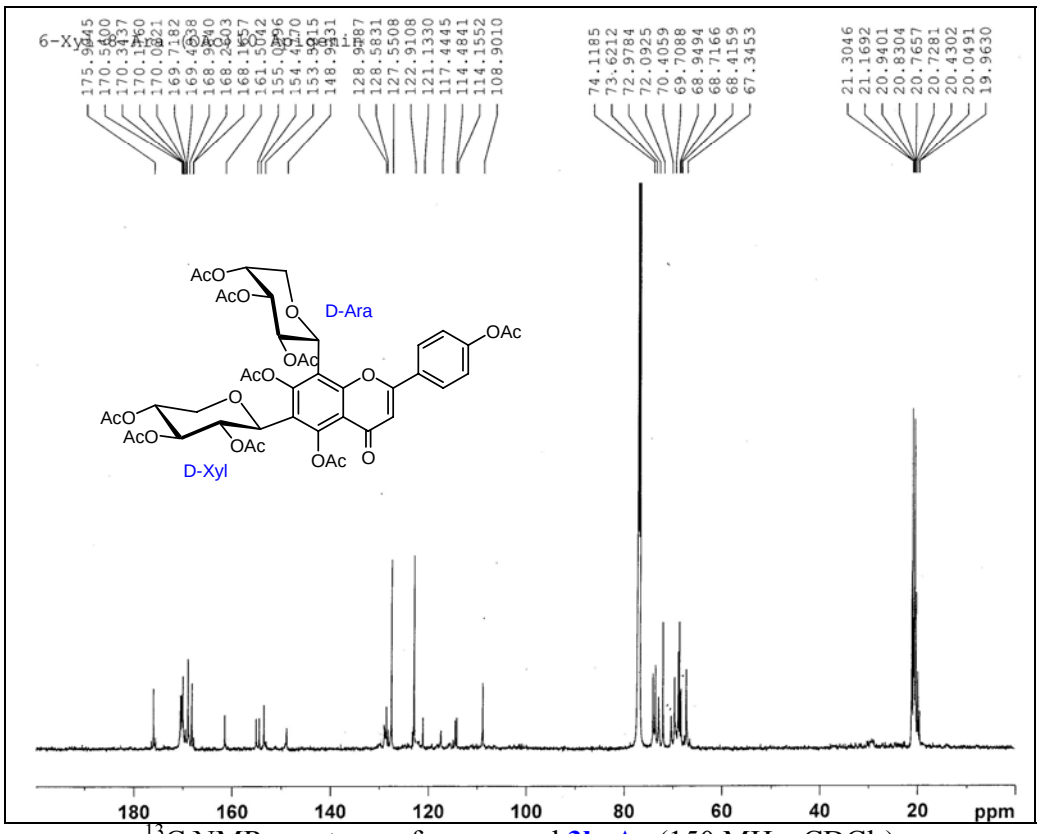
^{1}H NMR spectrum of compound **3bbAc** (600 MHz, $CDCl_3$)



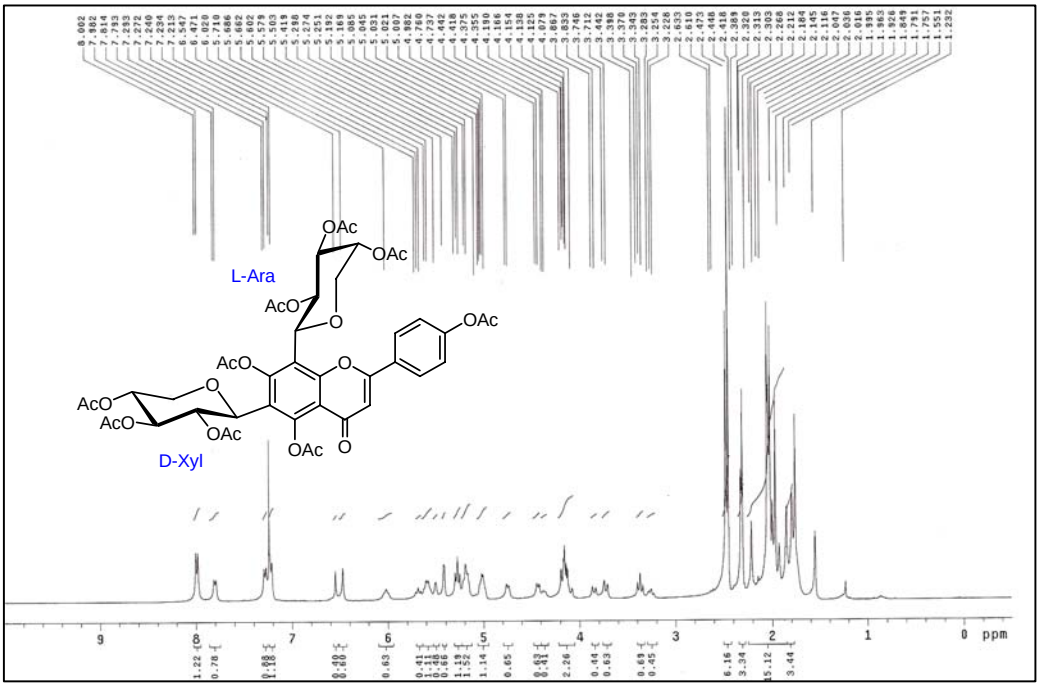
^{13}C NMR spectrum of compound **3bbAc** (150 MHz, $CDCl_3$)



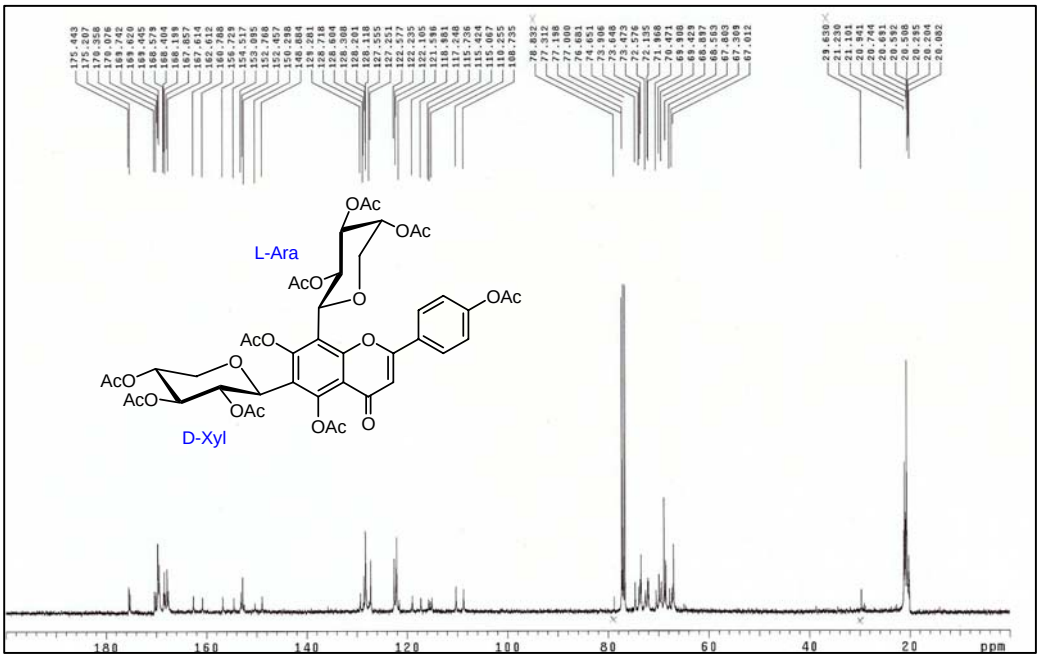
^{1}H NMR spectrum of compound **3bcAc** (600 MHz, $CDCl_3$)



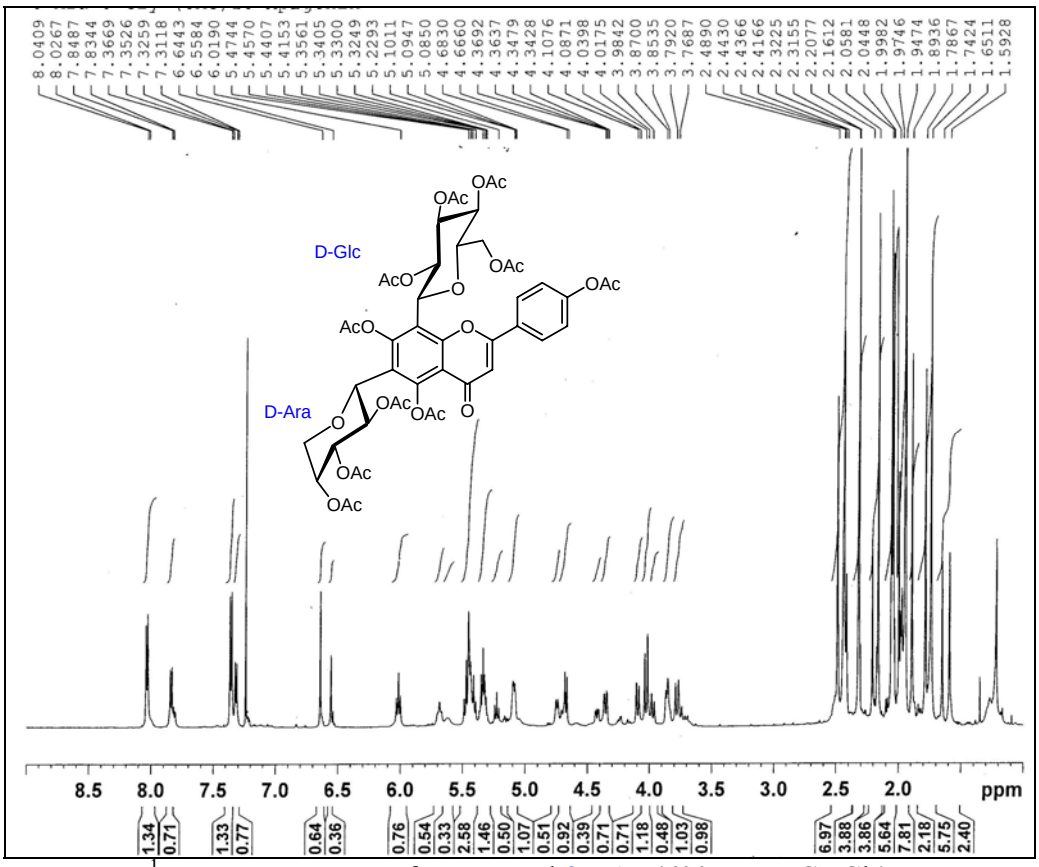
^{13}C NMR spectrum of compound **3bcAc** (150 MHz, $CDCl_3$)



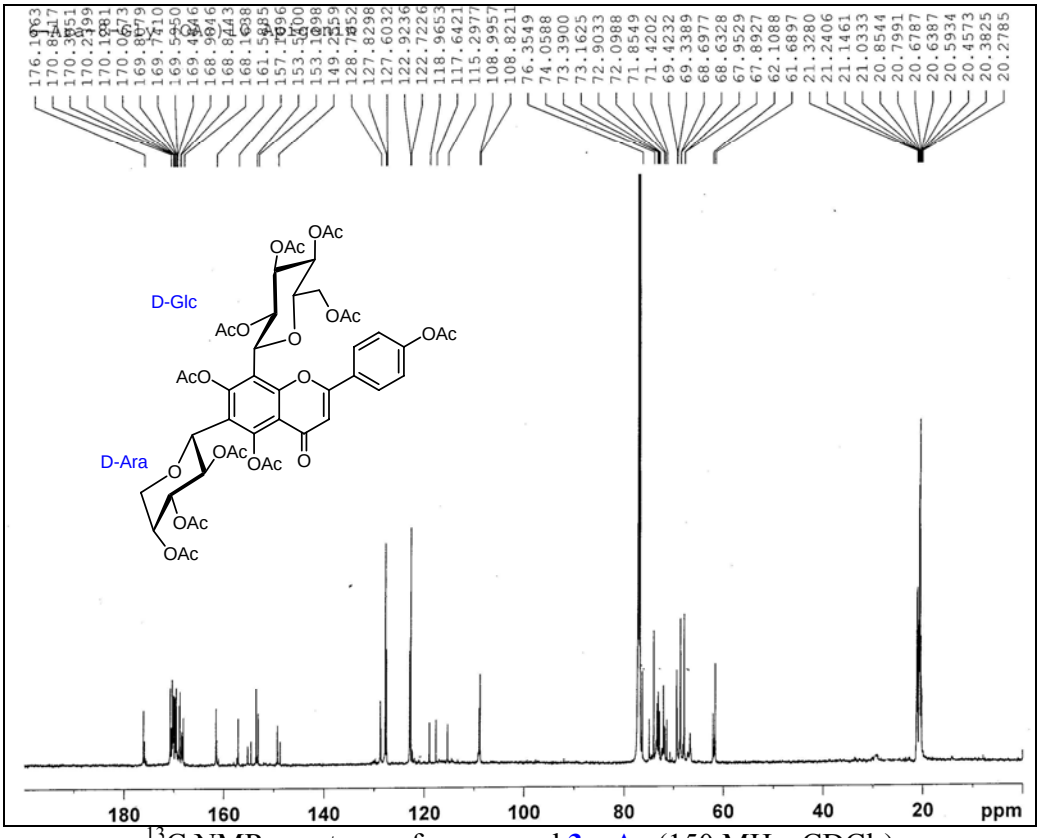
^{1}H NMR spectrum of compound **3bdAc** (400 MHz, $CDCl_3$)



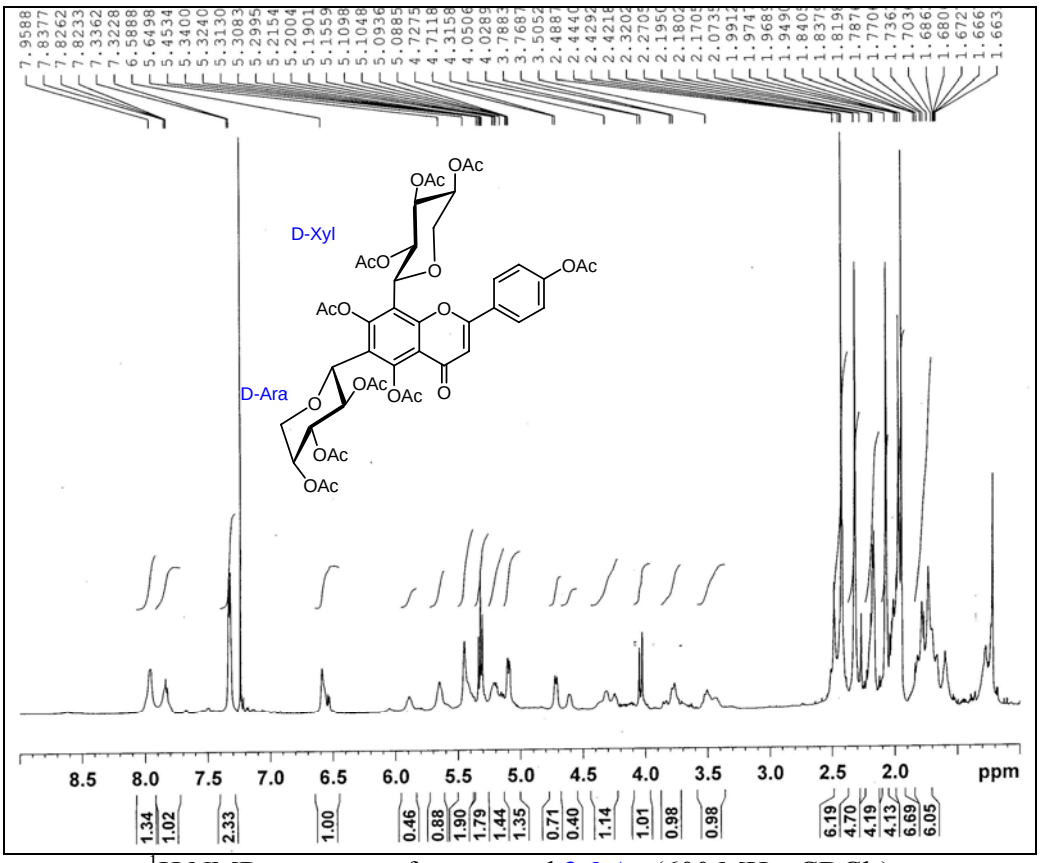
^{13}C NMR spectrum of compound **3bdAc** (100 MHz, $CDCl_3$)



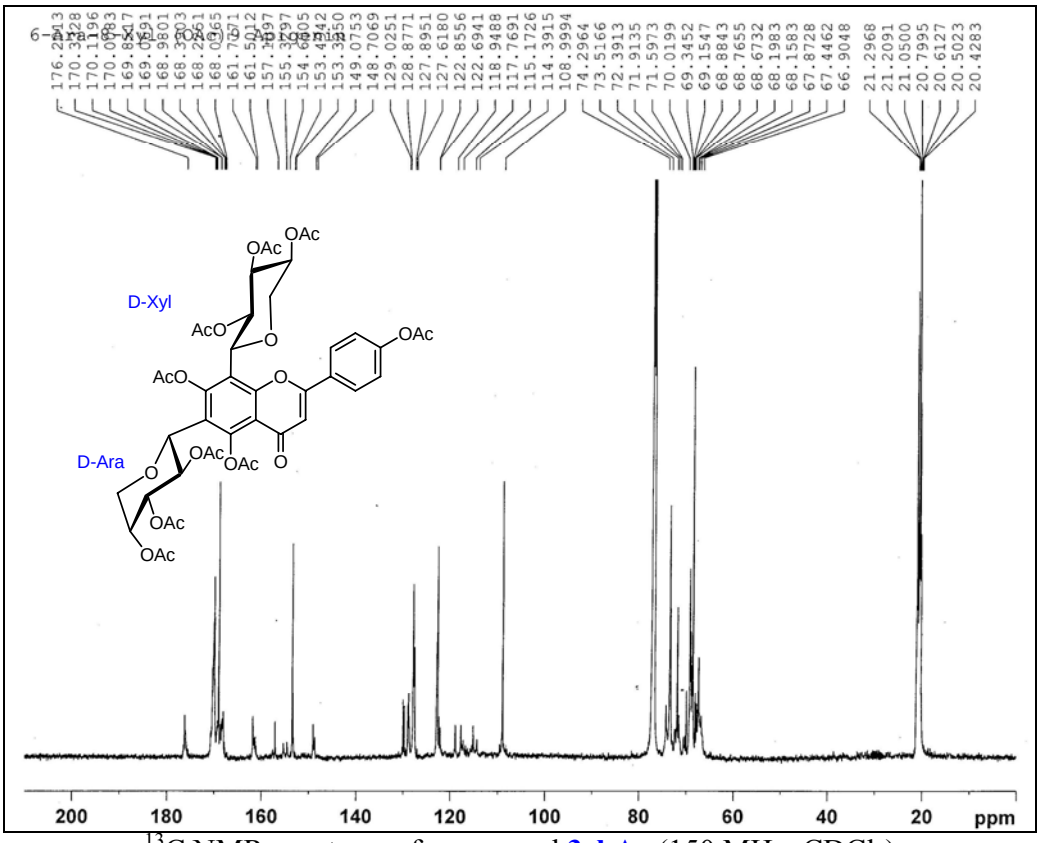
^{1}H NMR spectrum of compound **3caAc** (600 MHz, $CDCl_3$)



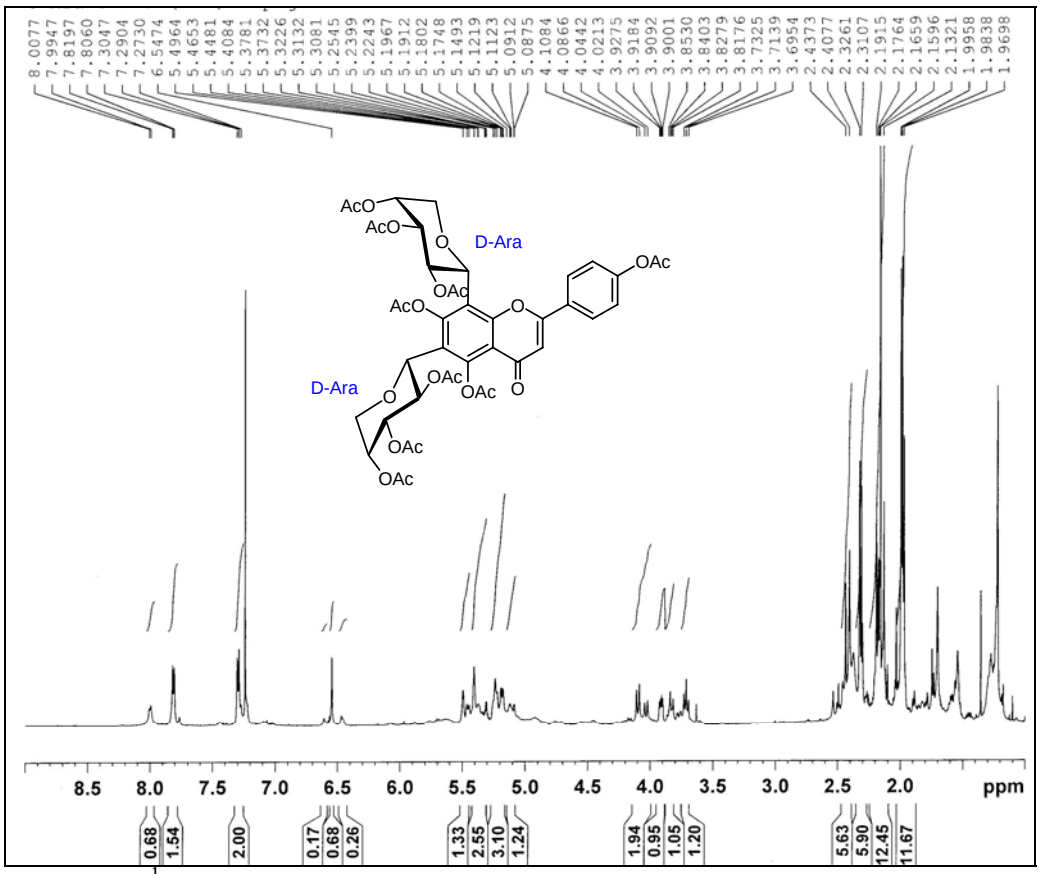
^{13}C NMR spectrum of compound **3caAc** (150 MHz, $CDCl_3$)



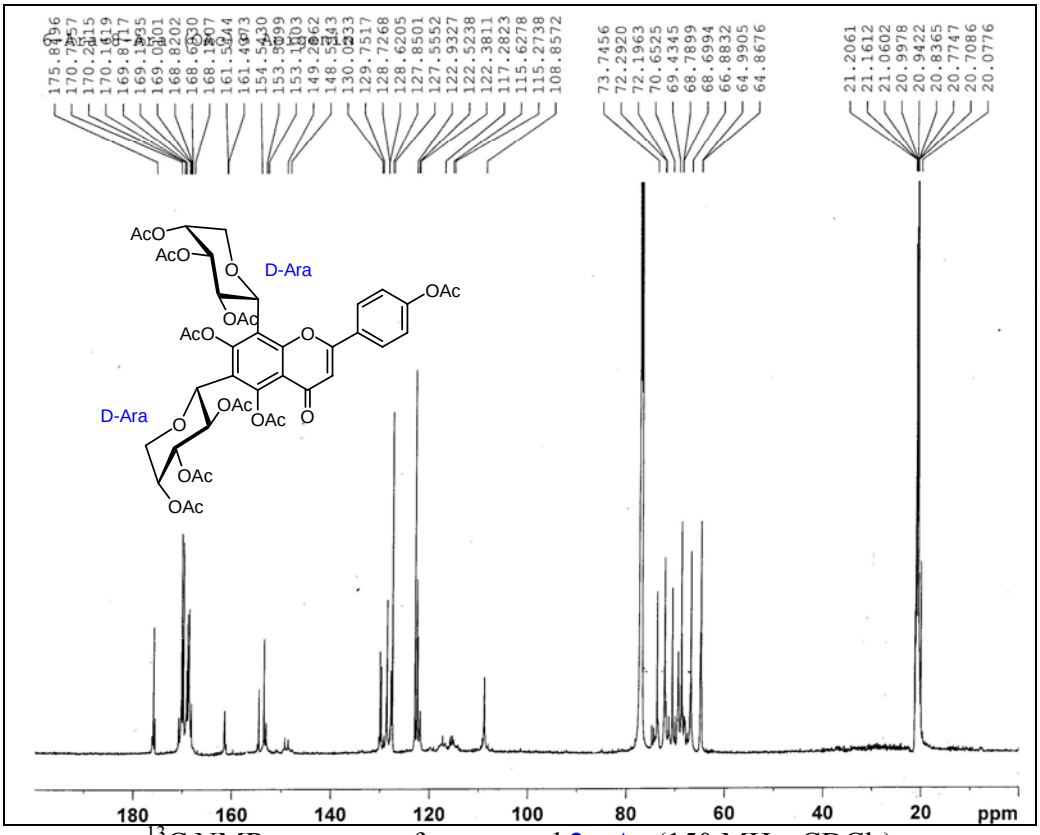
^{1}H NMR spectrum of compound **3cbAc** (600 MHz, $CDCl_3$)



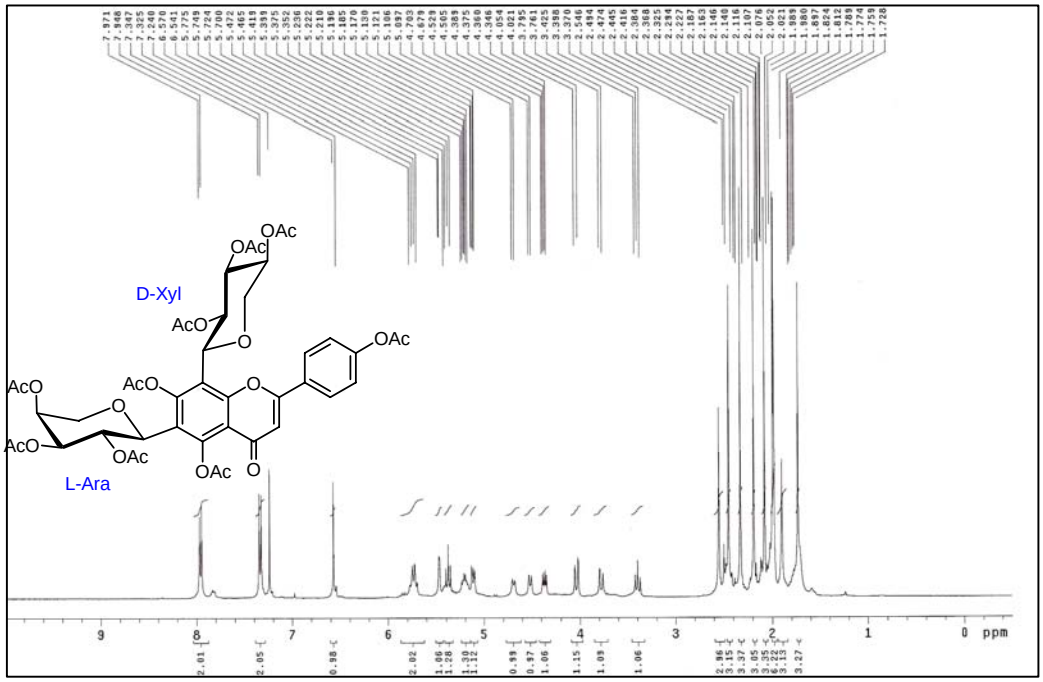
^{13}C NMR spectrum of compound **3cbAc** (150 MHz, $CDCl_3$)



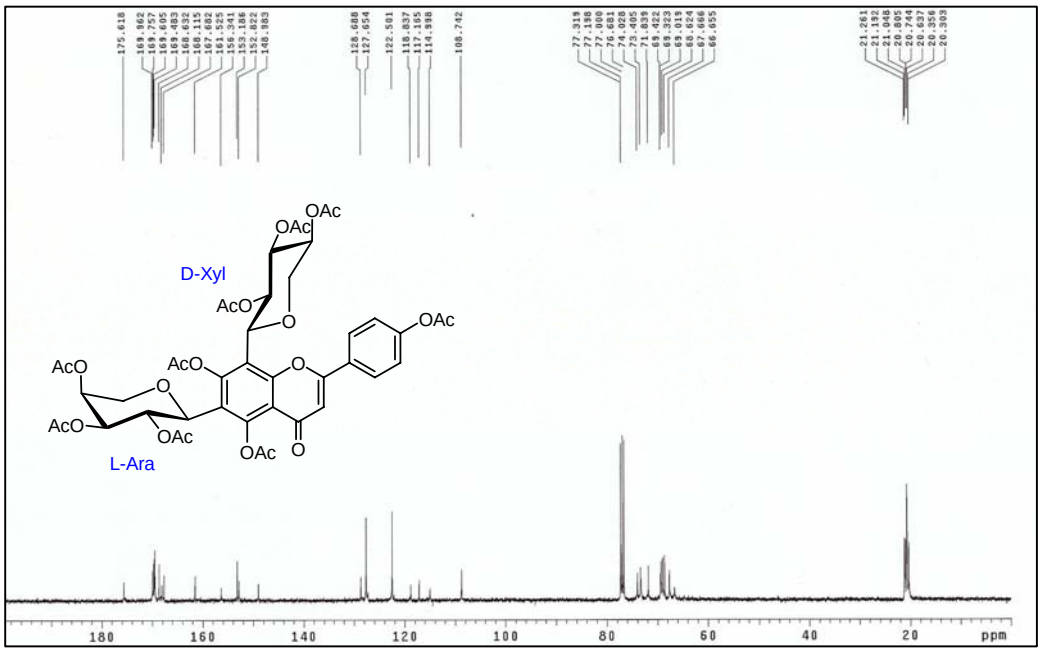
^{1}H NMR spectrum of compound **3ccAc** (600 MHz, $CDCl_3$)



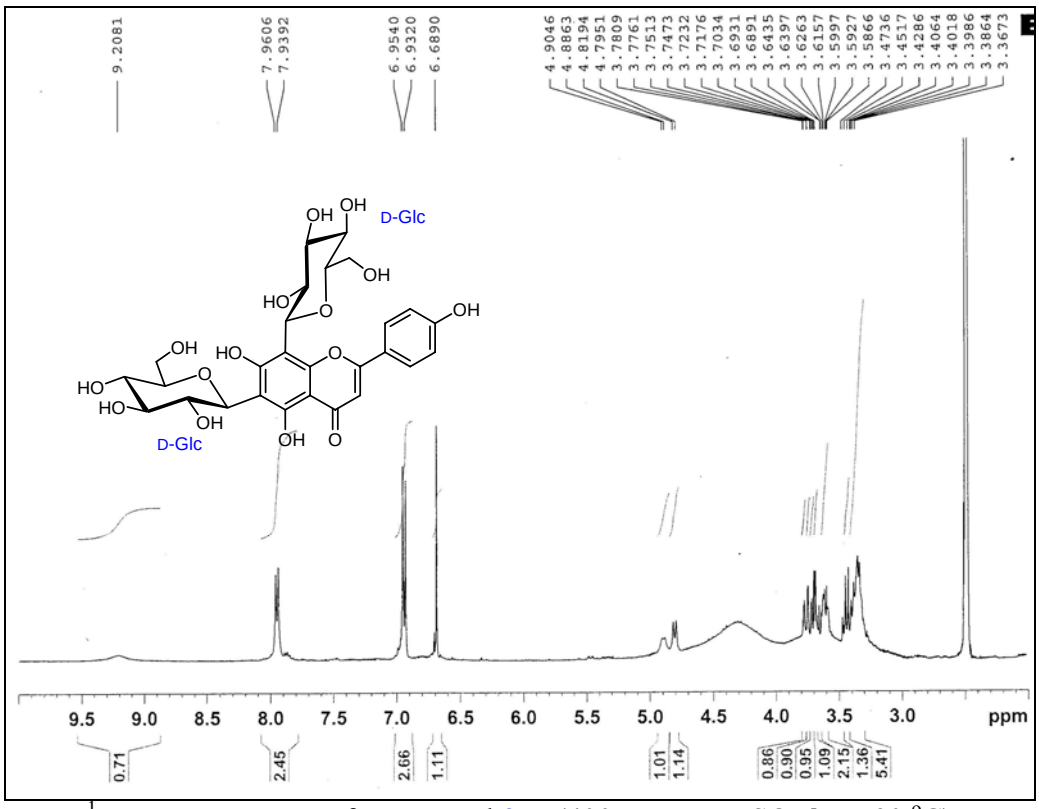
^{13}C NMR spectrum of compound **3ccAc** (150 MHz, $CDCl_3$)



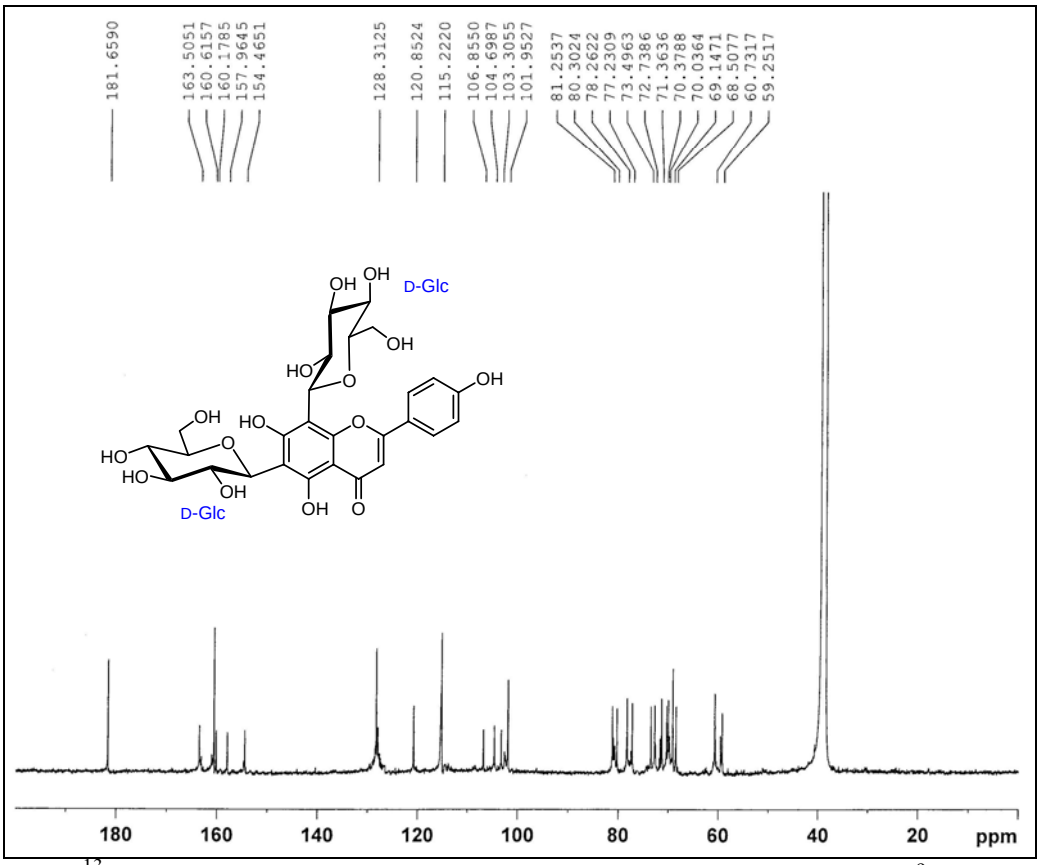
^{1}H NMR spectrum of compound **3dbAc** (400 MHz, $CDCl_3$)



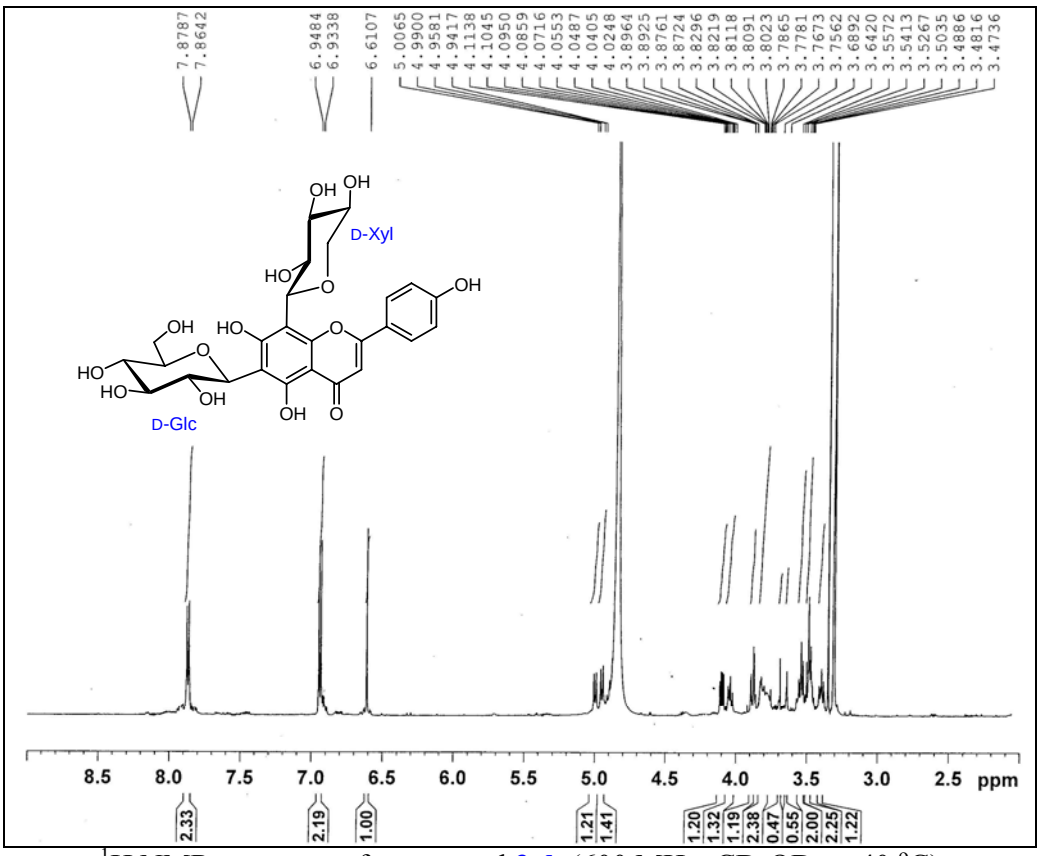
^{13}C NMR spectrum of compound **3dbAc** (100 MHz, $CDCl_3$)



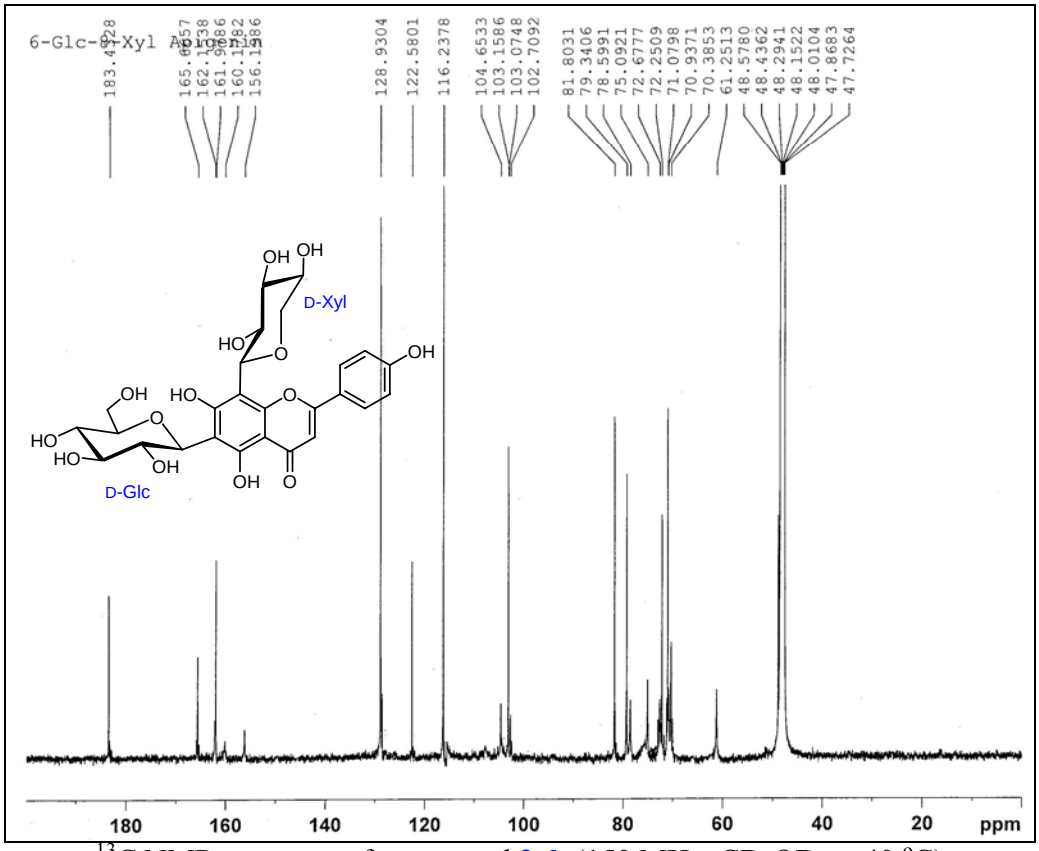
^{1}H NMR spectrum of compound **3aa** (400 MHz, DMSO-d_6, at 90 ^{o}C)



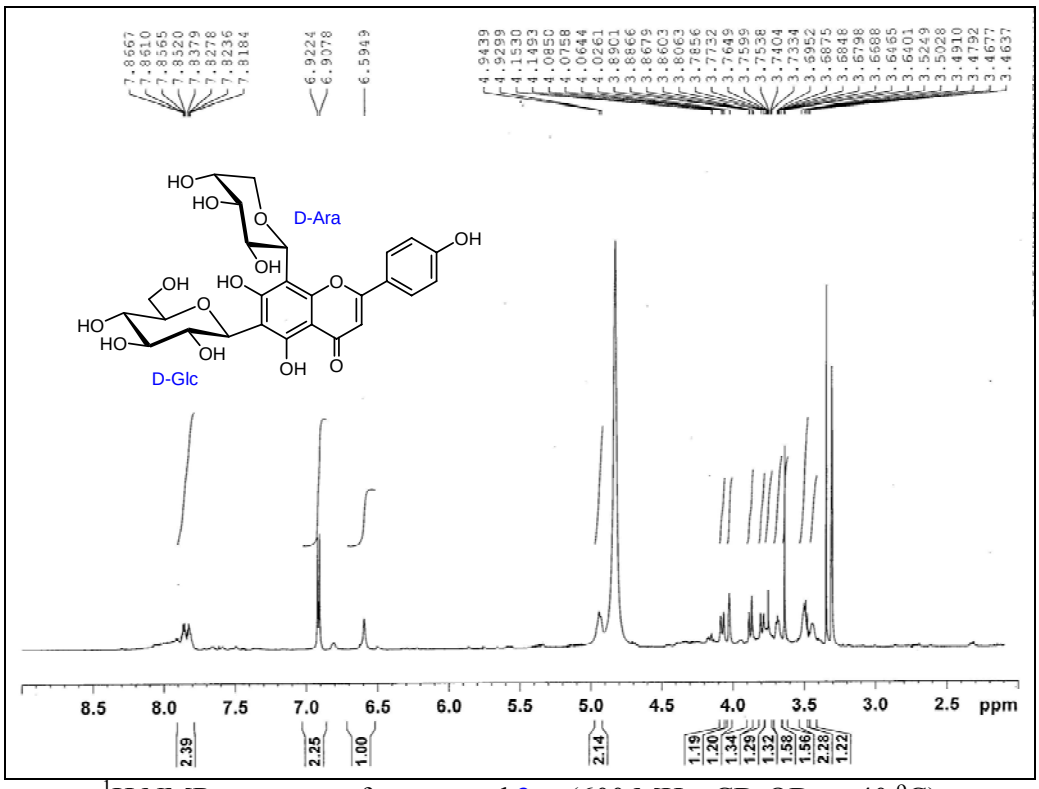
^{13}C NMR spectrum of compound **3aa** (150 MHz, DMSO-d_6, at 50 ^{o}C)



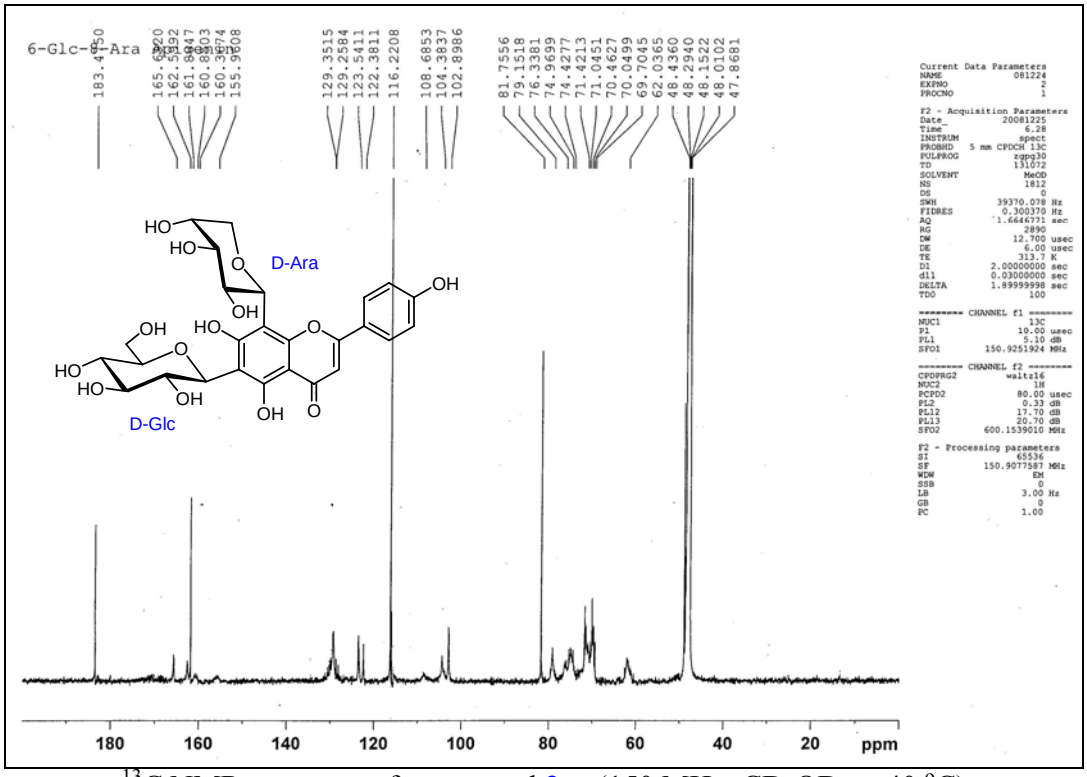
^{1}H NMR spectrum of compound **3ab** (600 MHz, CD_3OD, at 40 ^{o}C)



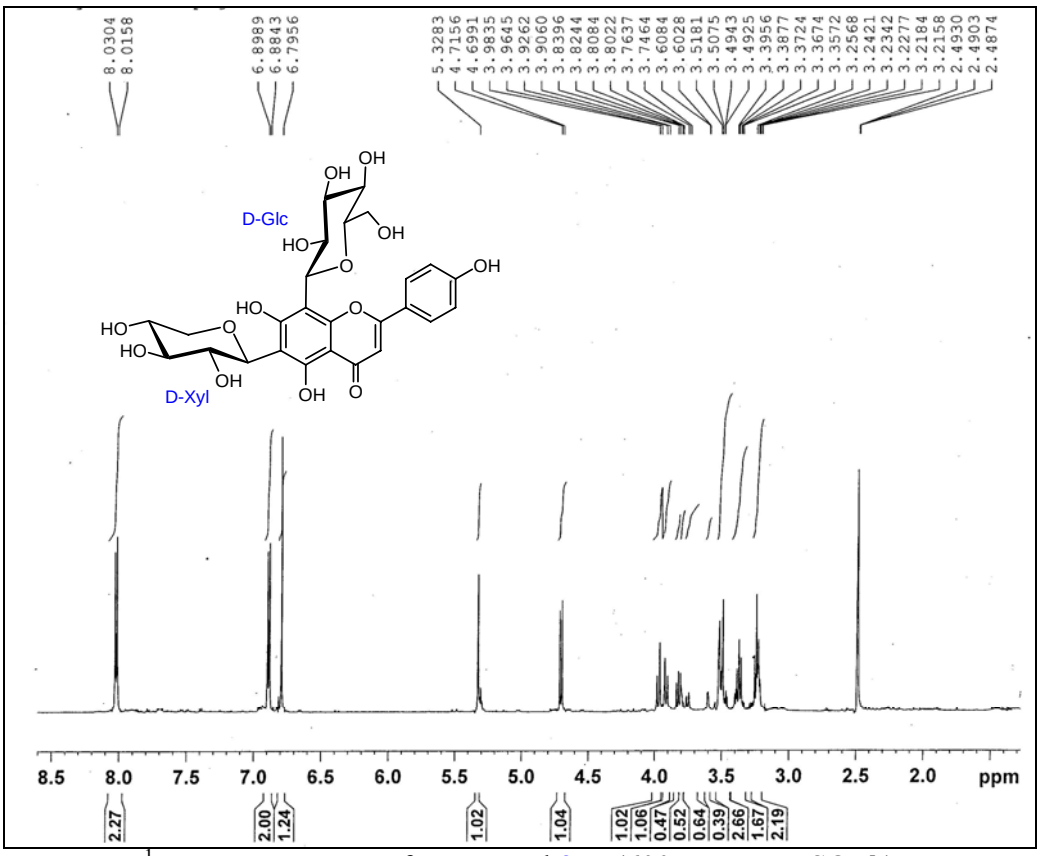
^{13}C NMR spectrum of compound **3ab** (150 MHz, CD_3OD, at 40 ^{o}C)



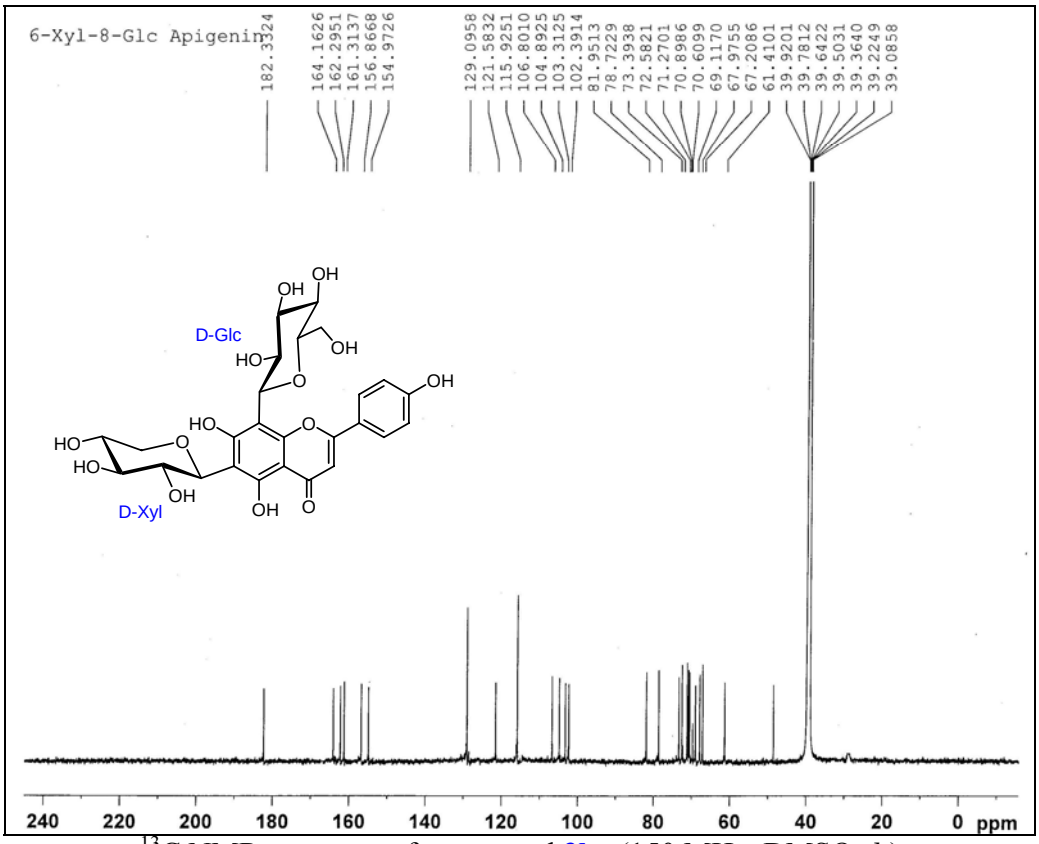
^{1}H NMR spectrum of compound **3ac** (600 MHz, CD_3OD, at 40 ^{o}C)



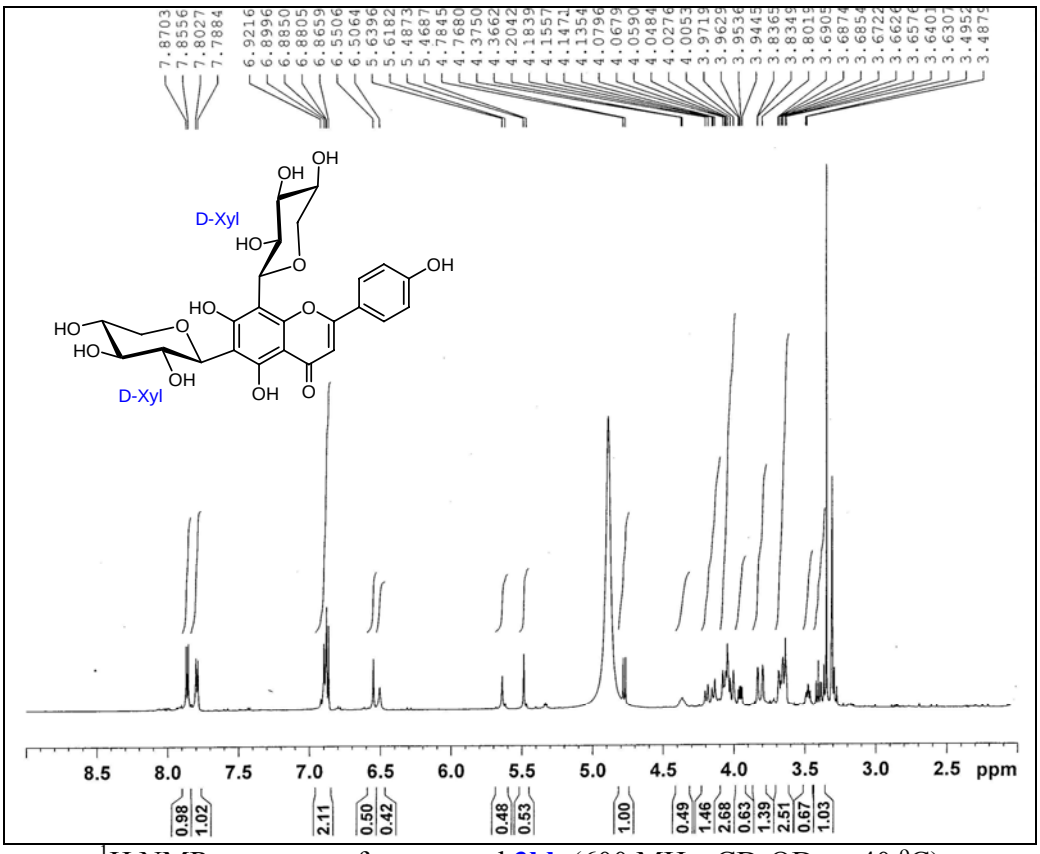
^{13}C NMR spectrum of compound **3ac** (150 MHz, CD_3OD, at 40 ^{o}C)



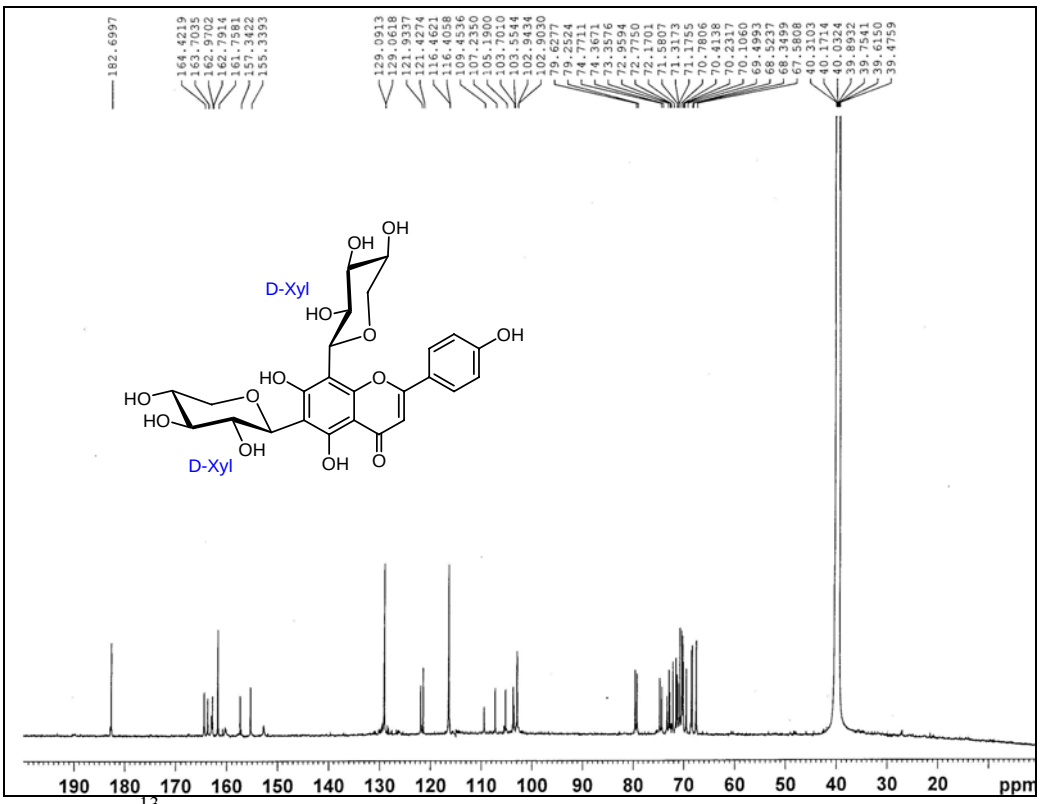
^{1}H NMR spectrum of compound **3ba** (600 MHz, DMSO-d_6)



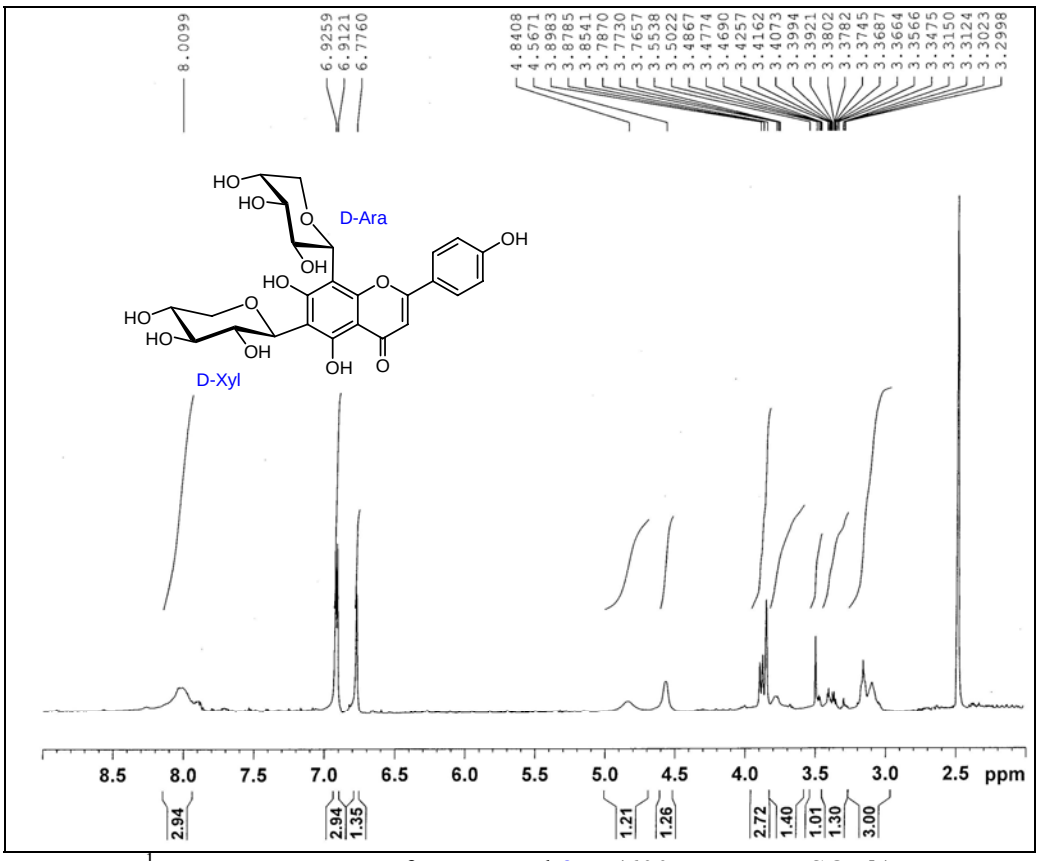
^{13}C NMR spectrum of compound **3ba** (150 MHz, DMSO-d_4)



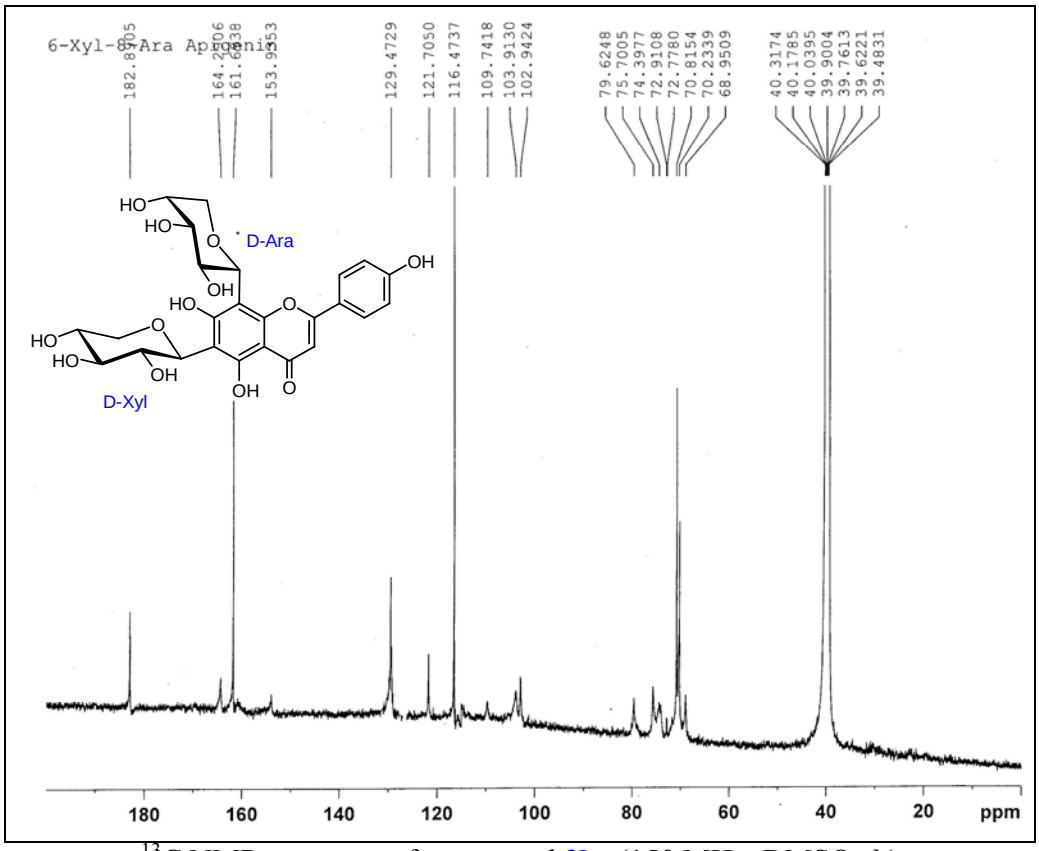
^{1}H NMR spectrum of compound **3bb** (600 MHz, CD_3OD, at 40 ^{o}C)



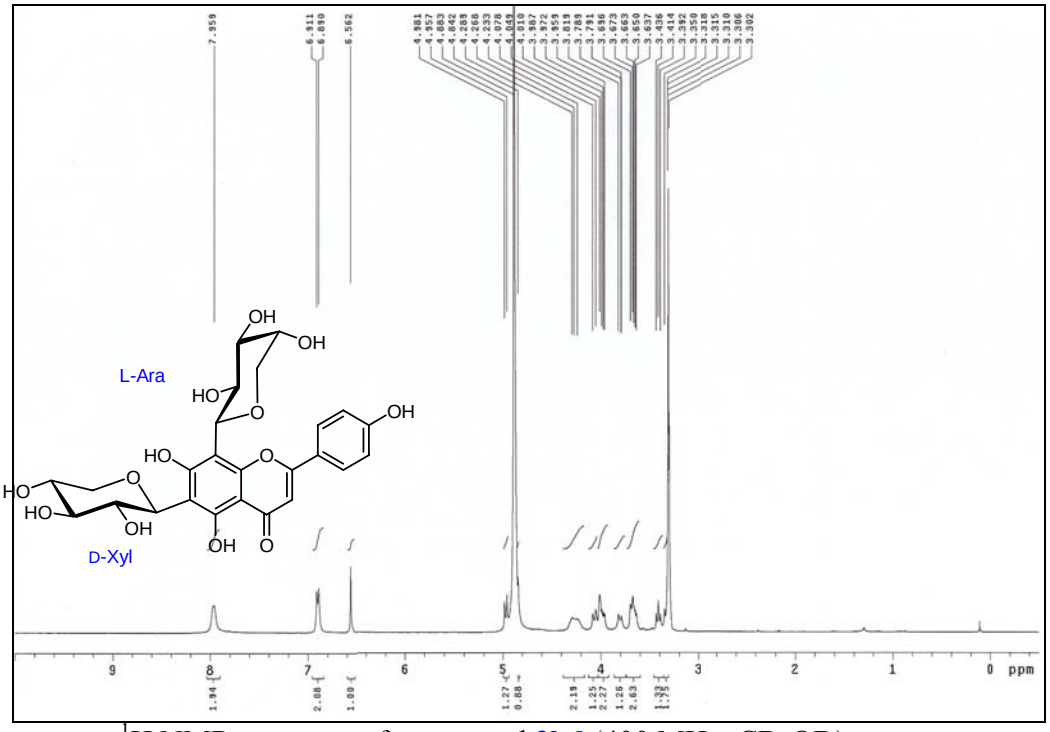
^{13}C NMR spectrum of compound **3bb** (150 MHz, DMSO-d_6)



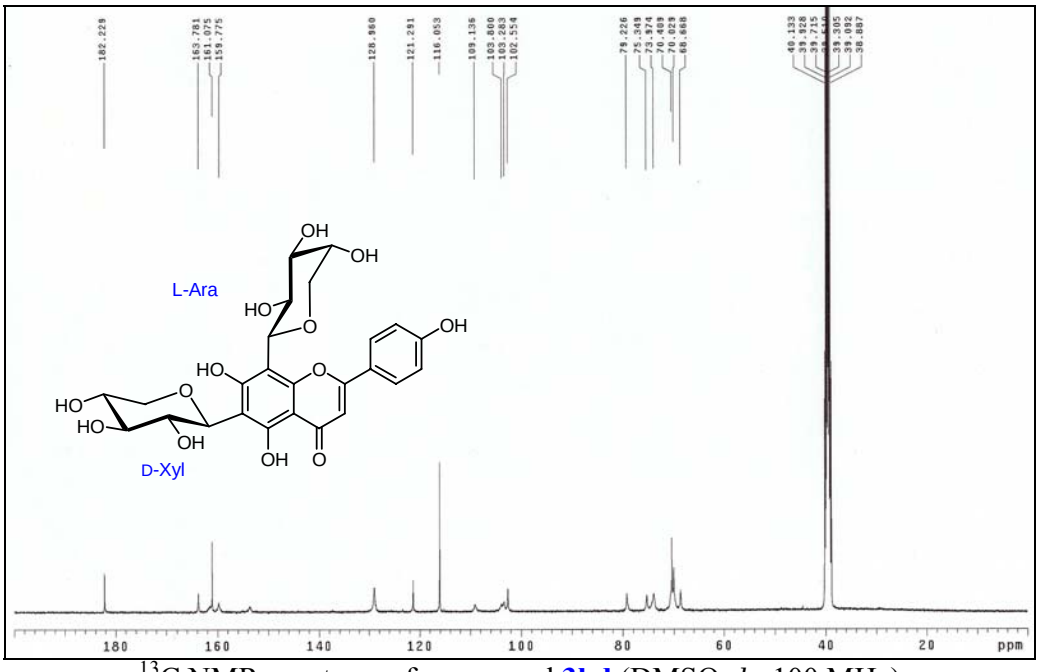
^{1}H NMR spectrum of compound **3bc** (600 MHz, DMSO-d_6)



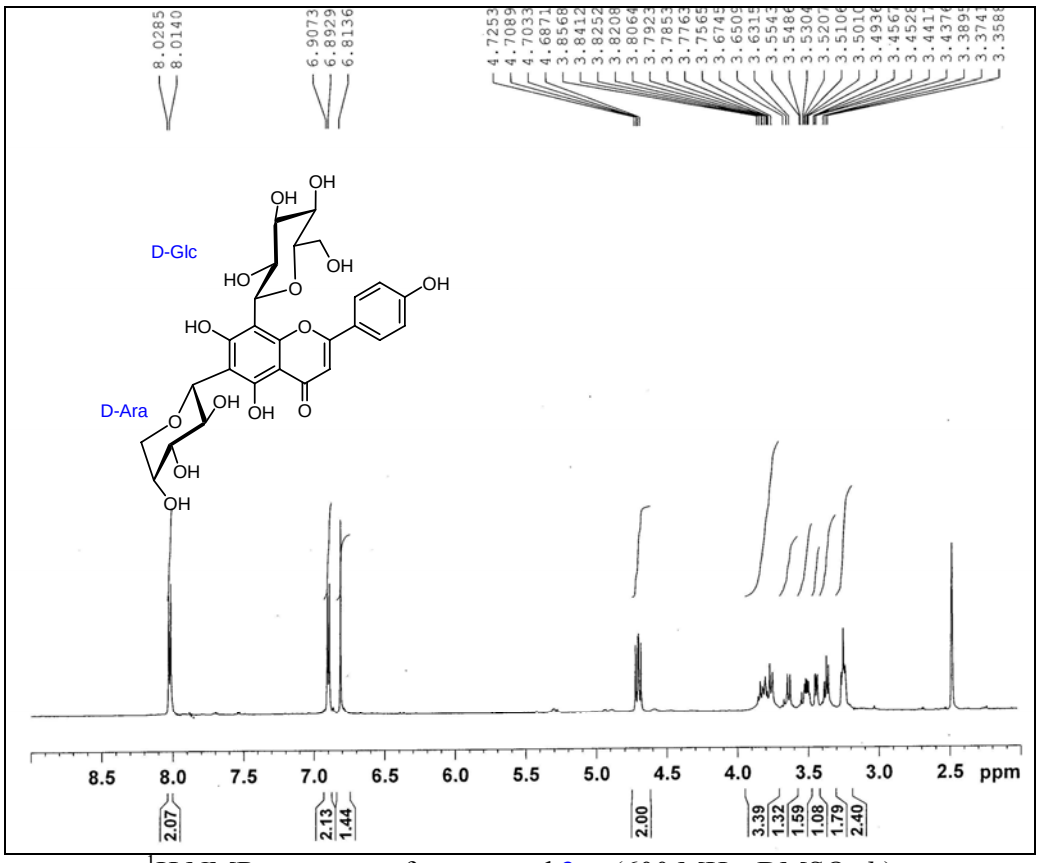
^{13}C NMR spectrum of compound **3bc** (150 MHz, DMSO-d_6)



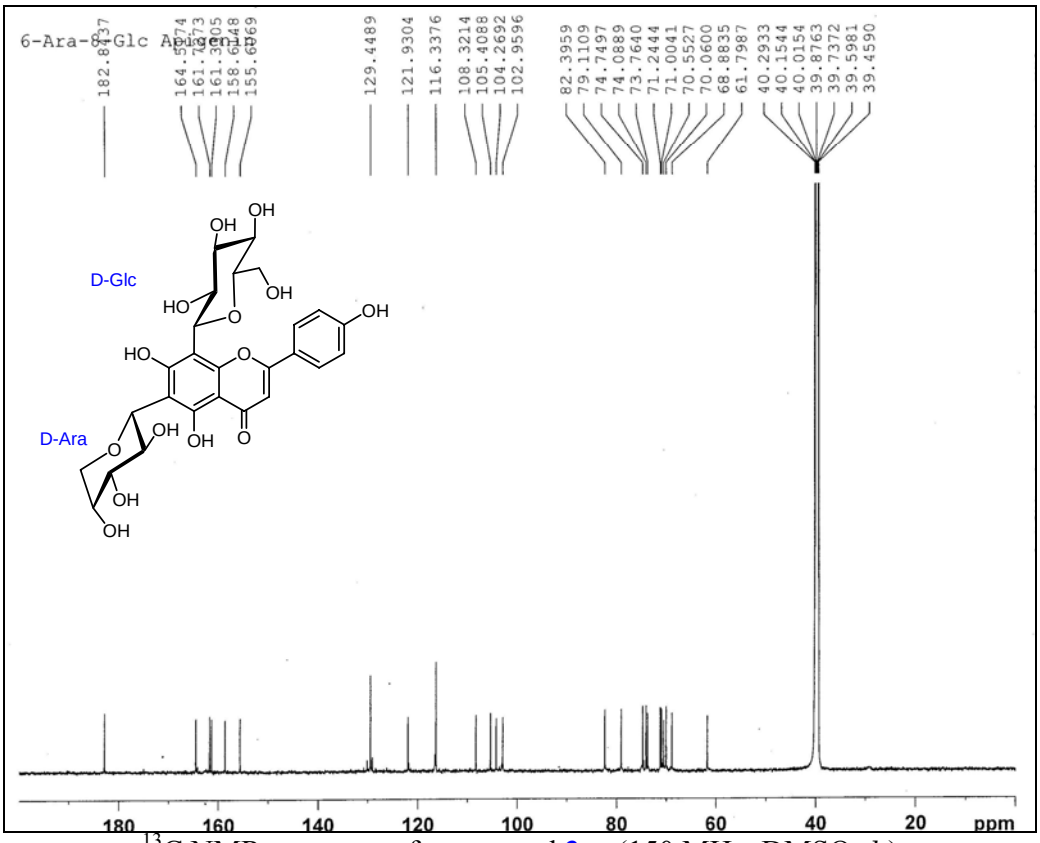
^{1}H NMR spectrum of compound **3bd** (400 MHz, CD_3OD)



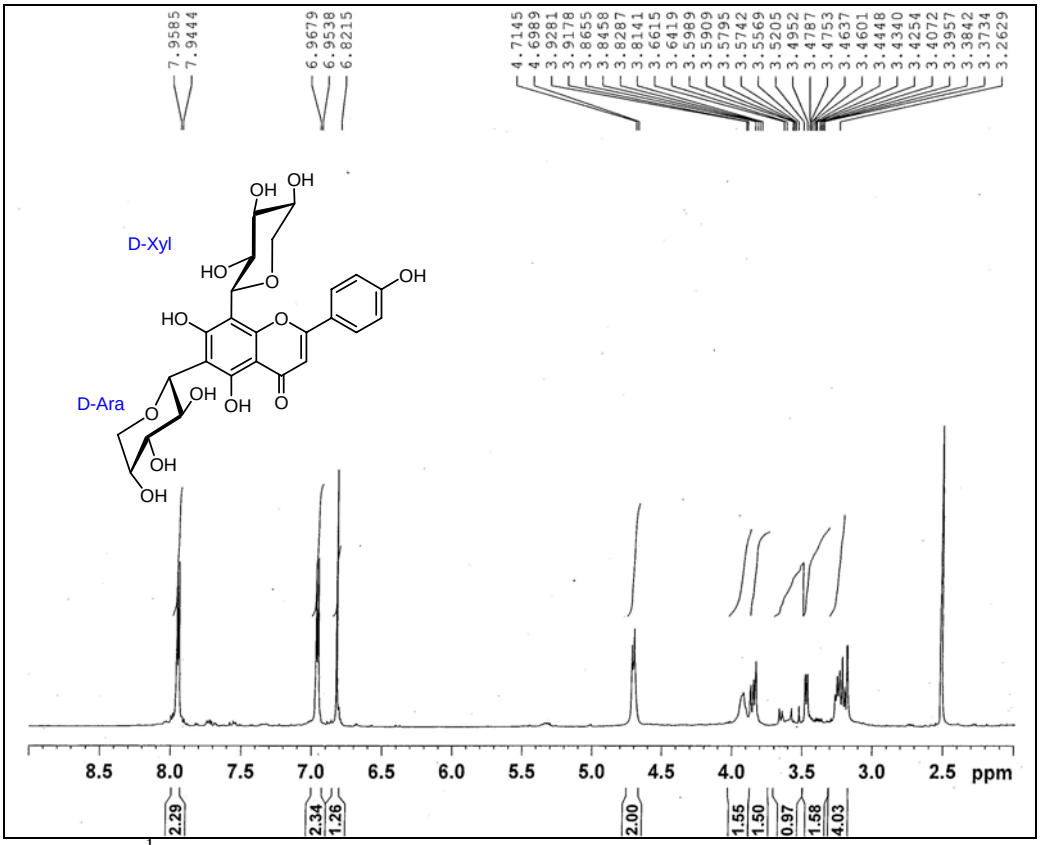
^{13}C NMR spectrum of compound **3bd** (DMSO-d_6, 100 MHz)



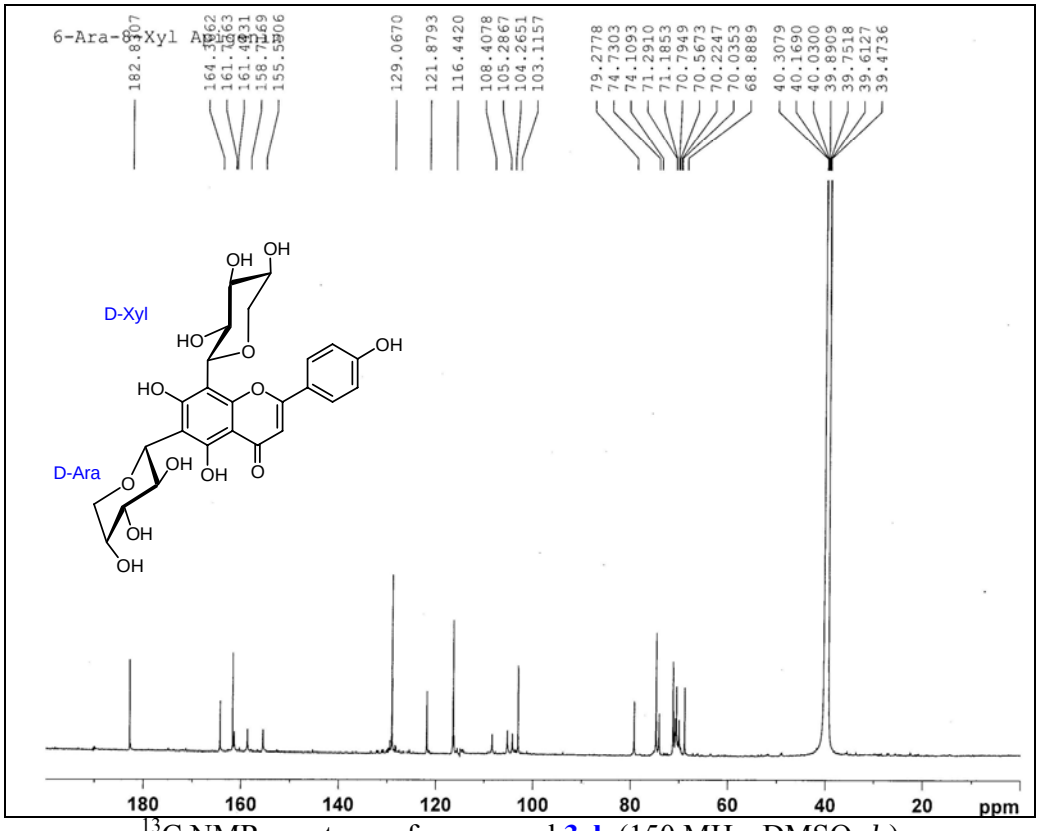
^{1}H NMR spectrum of compound **3ca** (600 MHz, DMSO-d_6)



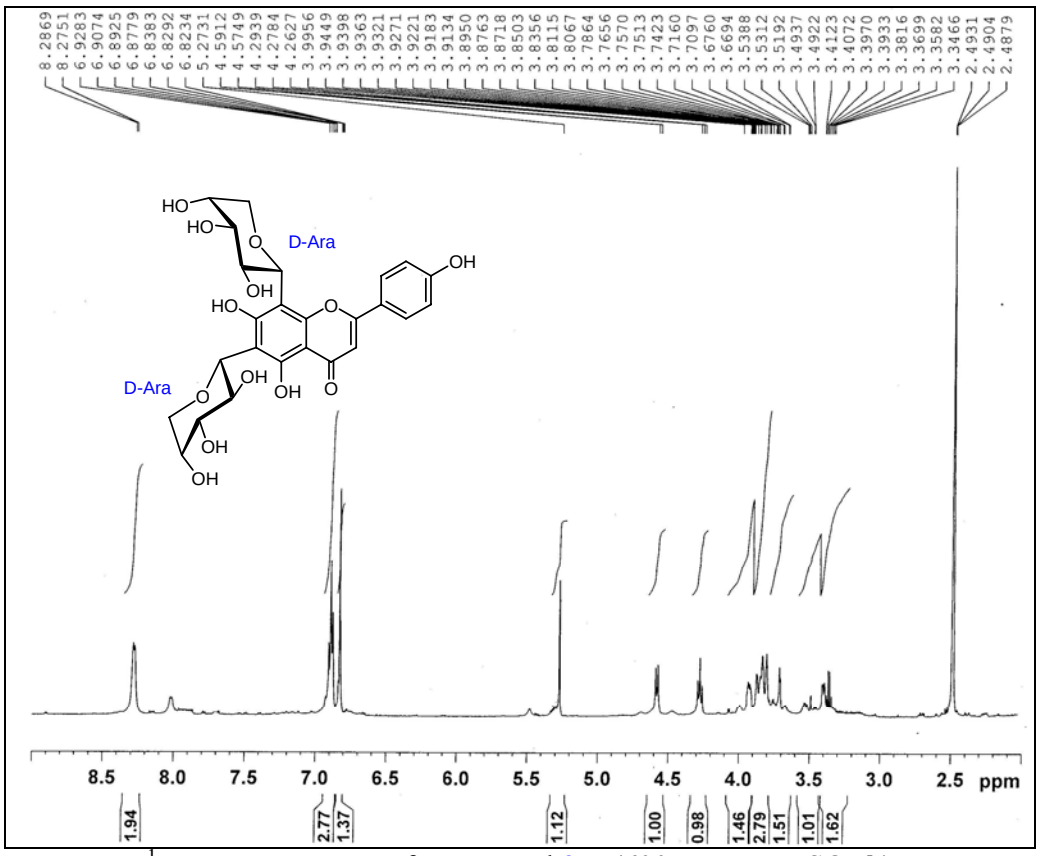
^{13}C NMR spectrum of compound **3ca** (150 MHz, DMSO-d_6)



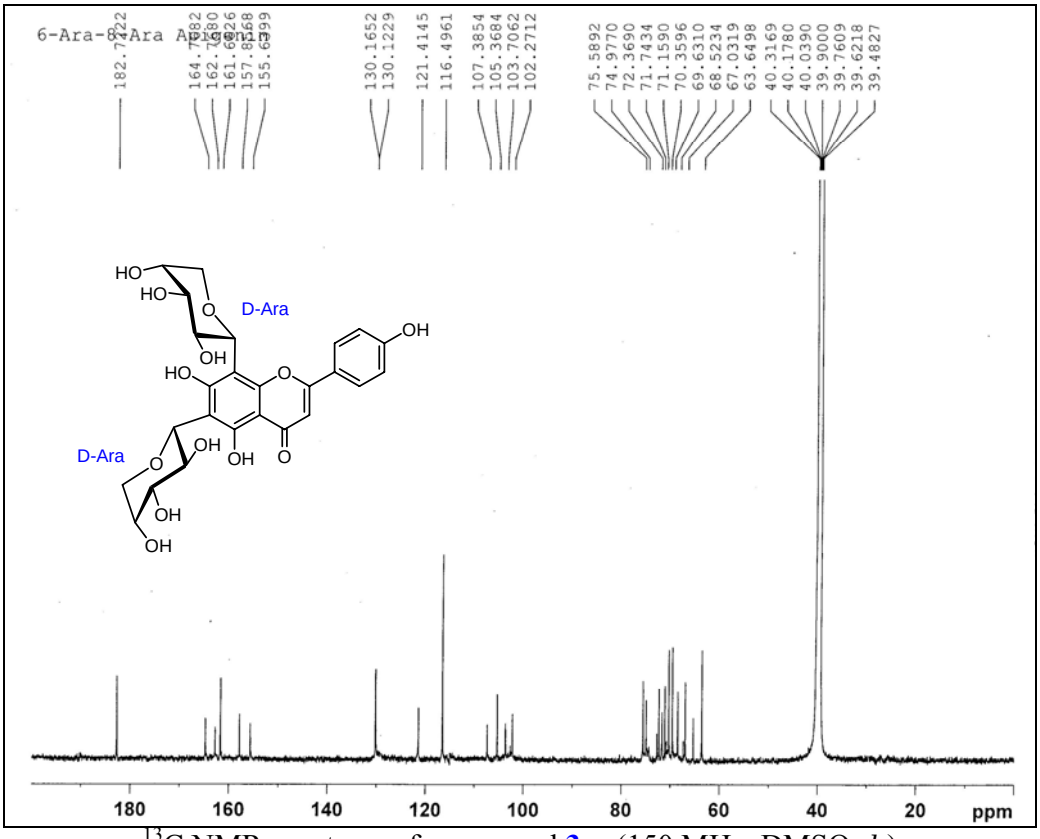
^{1}H NMR spectrum of compound **3cb** (600 MHz, DMSO-d_6)



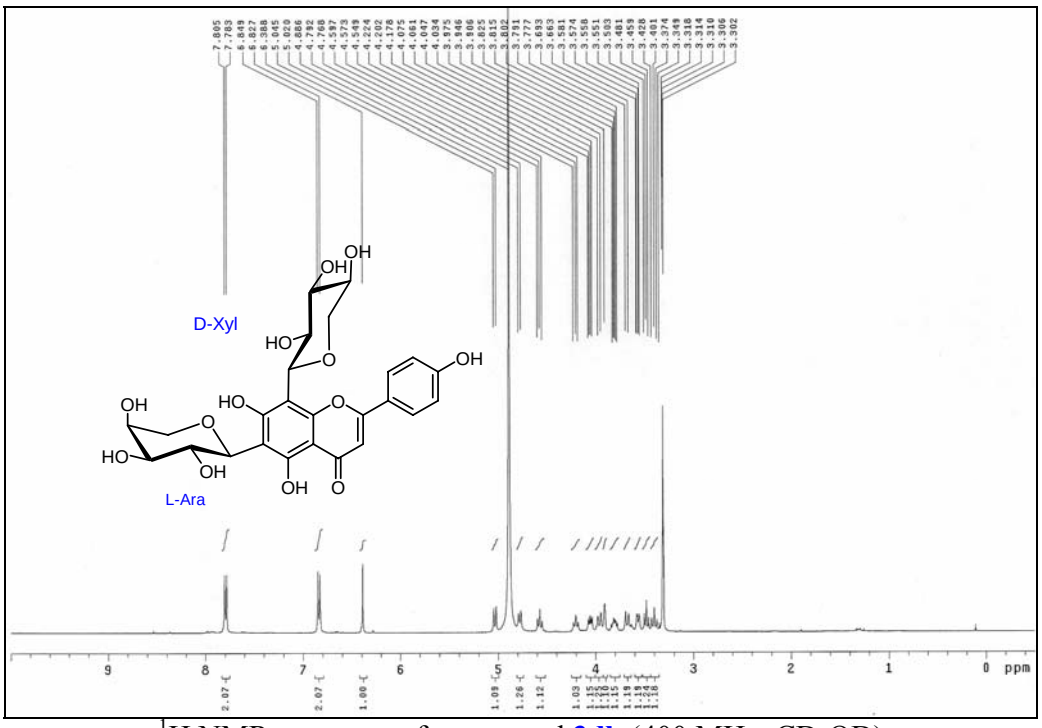
^{13}C NMR spectrum of compound **3cb** (150 MHz, DMSO-d_6)



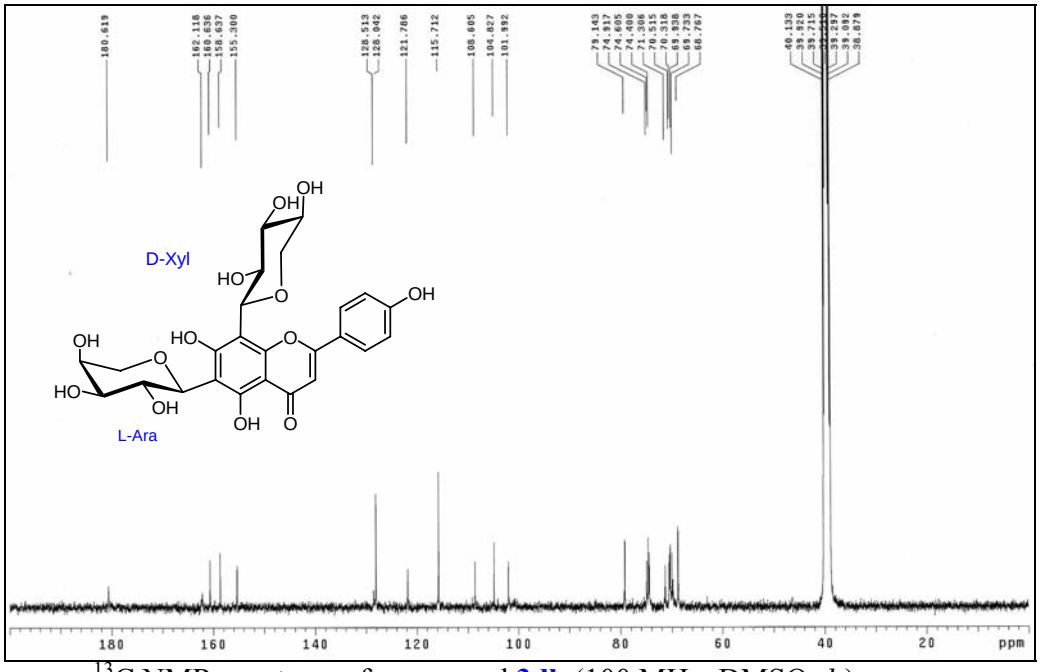
^{1}H NMR spectrum of compound **3cc** (600 MHz, DMSO-d_6)



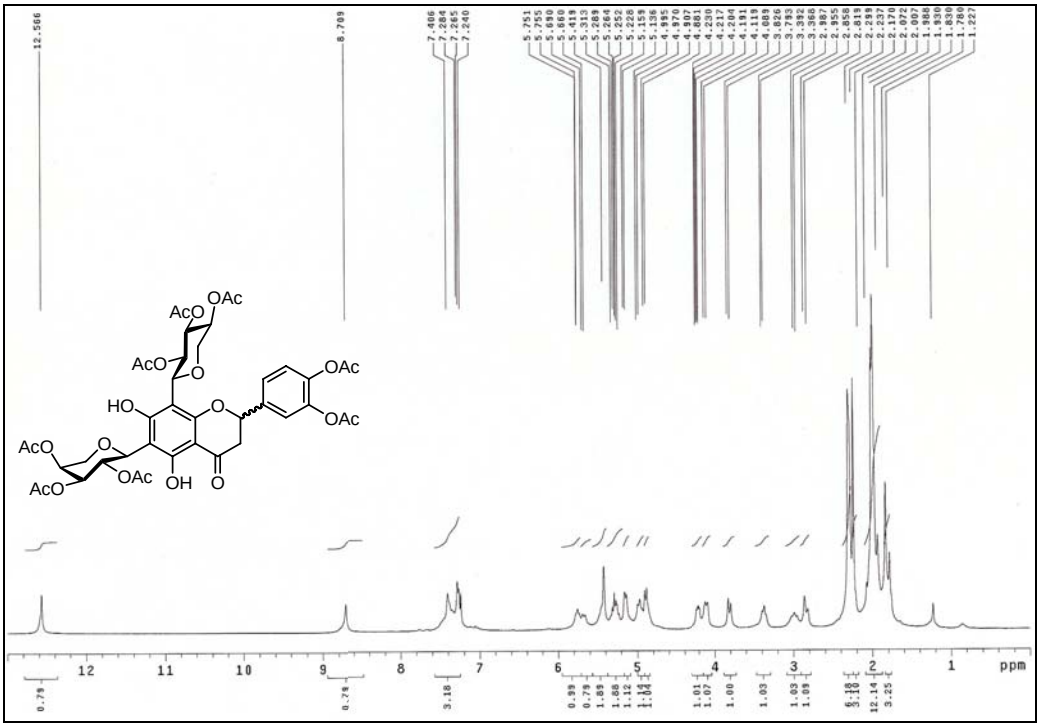
^{13}C NMR spectrum of compound **3cc** (150 MHz, DMSO-d_6)



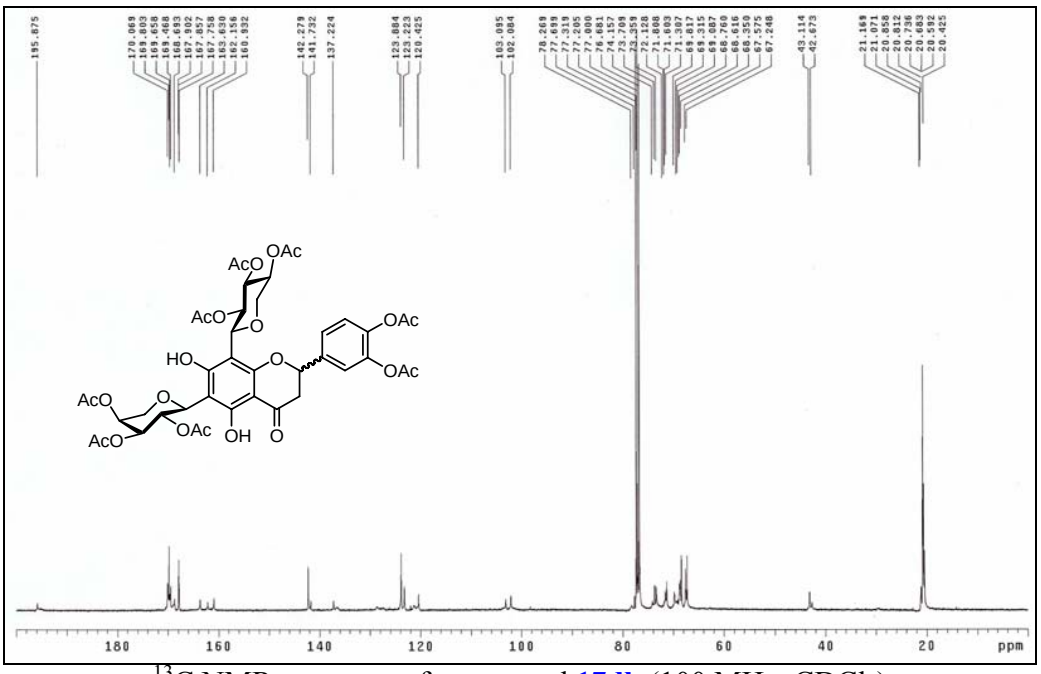
^{1}H NMR spectrum of compound **3db** (400 MHz, CD_3OD)



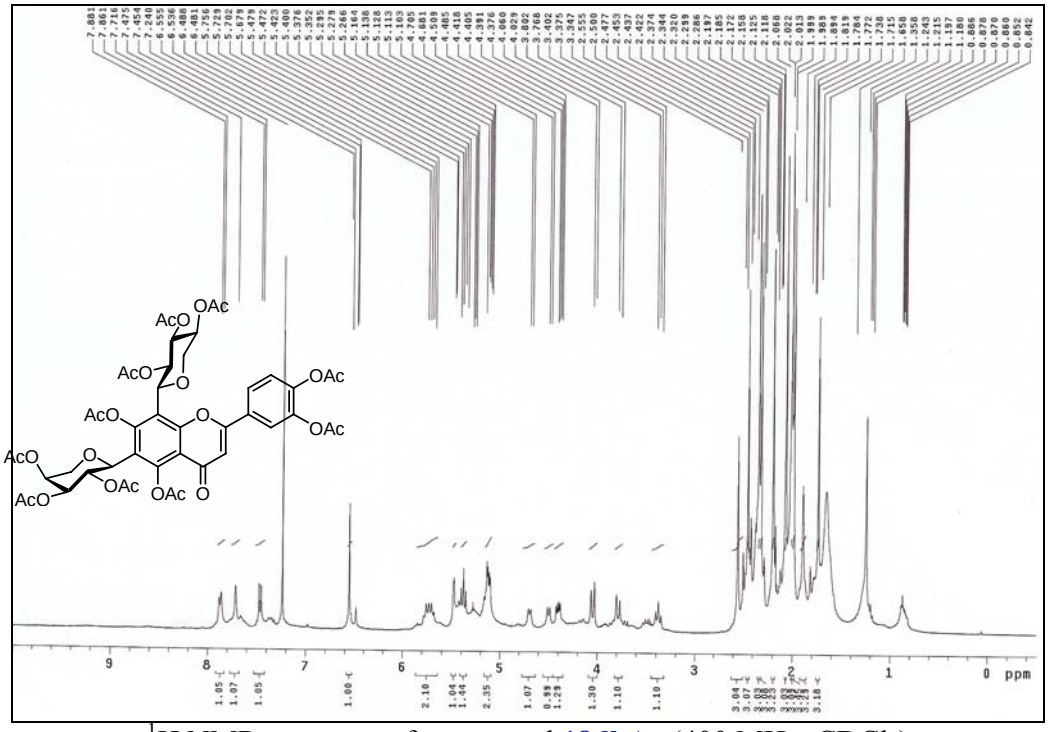
^{13}C NMR spectrum of compound **3db** (100 MHz, DMSO-d_6)



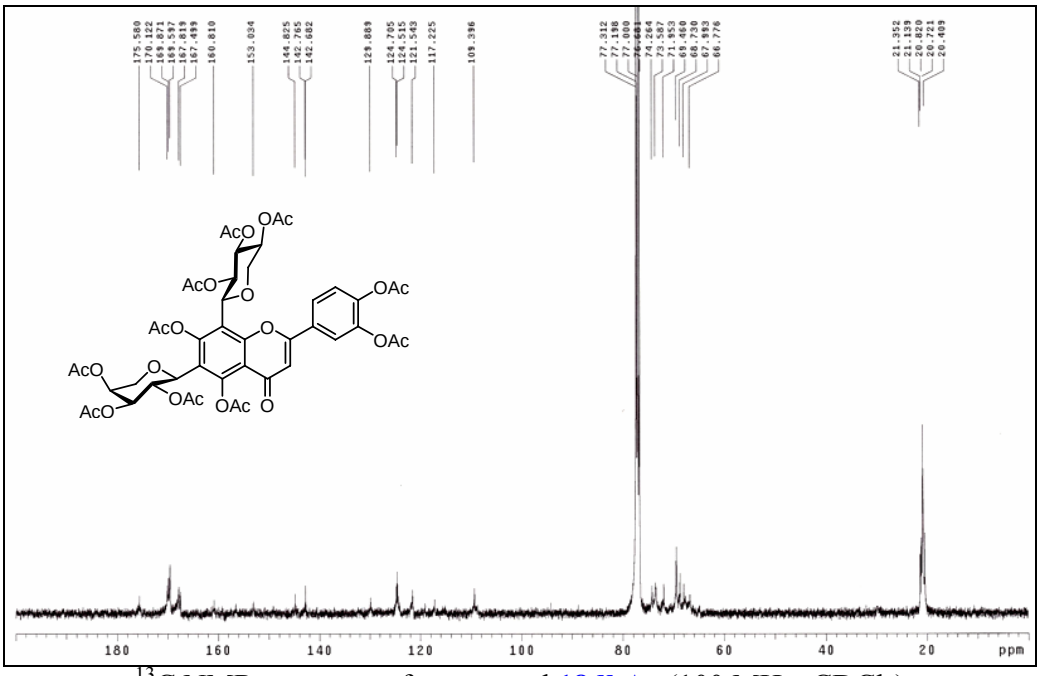
^{1}H NMR spectrum of compound **17db** (400 MHz, $CDCl_3$)



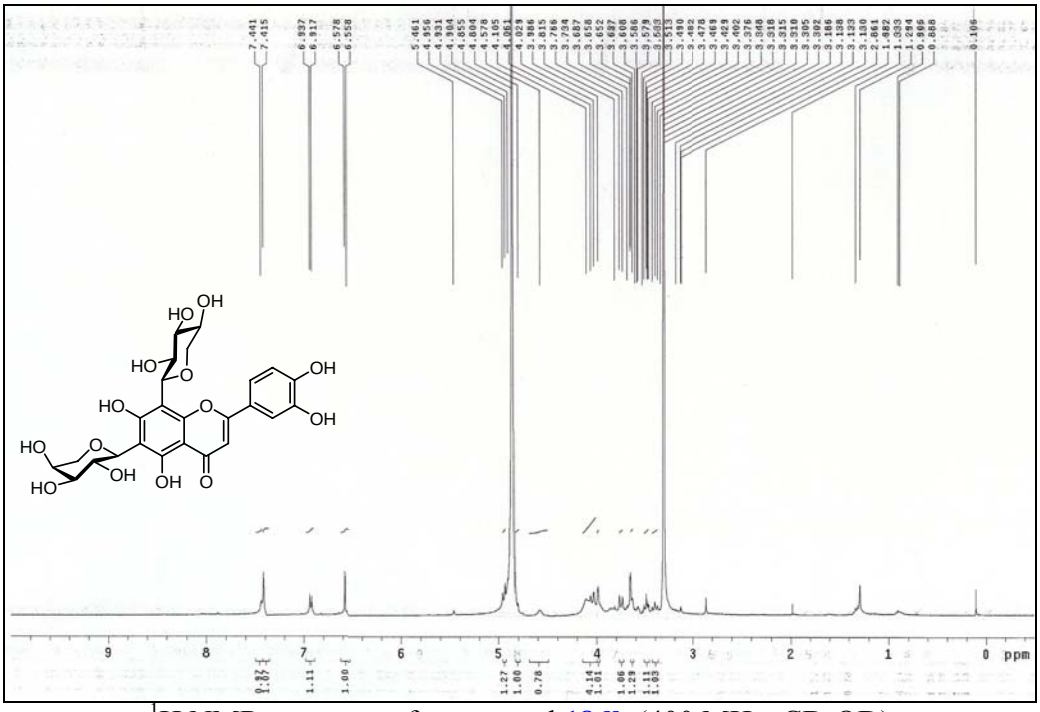
^{13}C NMR spectrum of compound **17db** (100 MHz, $CDCl_3$)



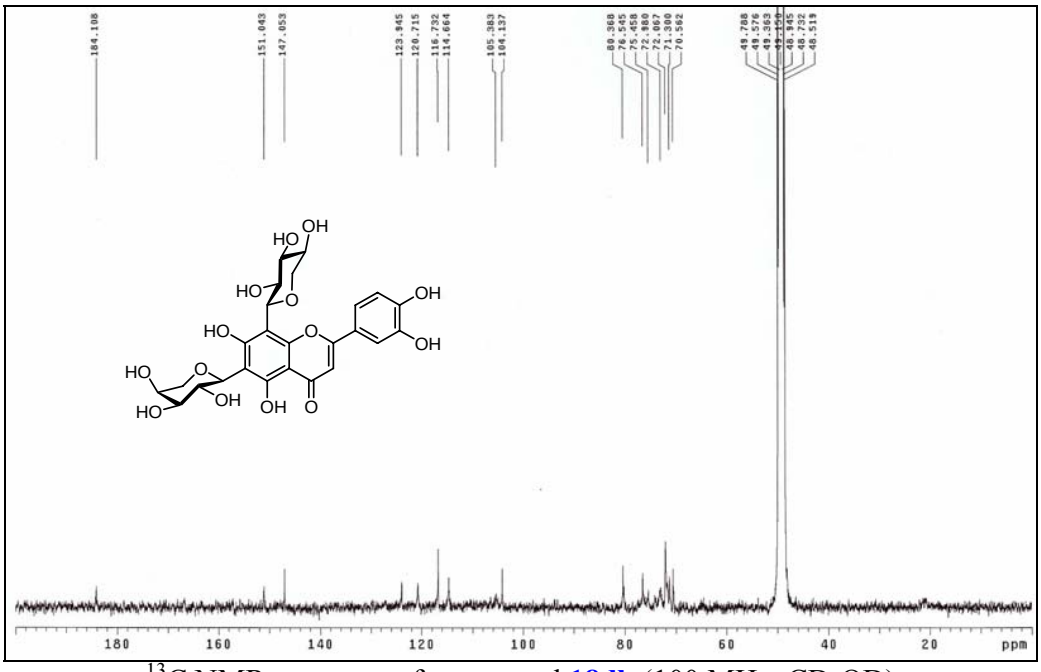
^{1}H NMR spectrum of compound **18dbAc** (400 MHz, $CDCl_3$)



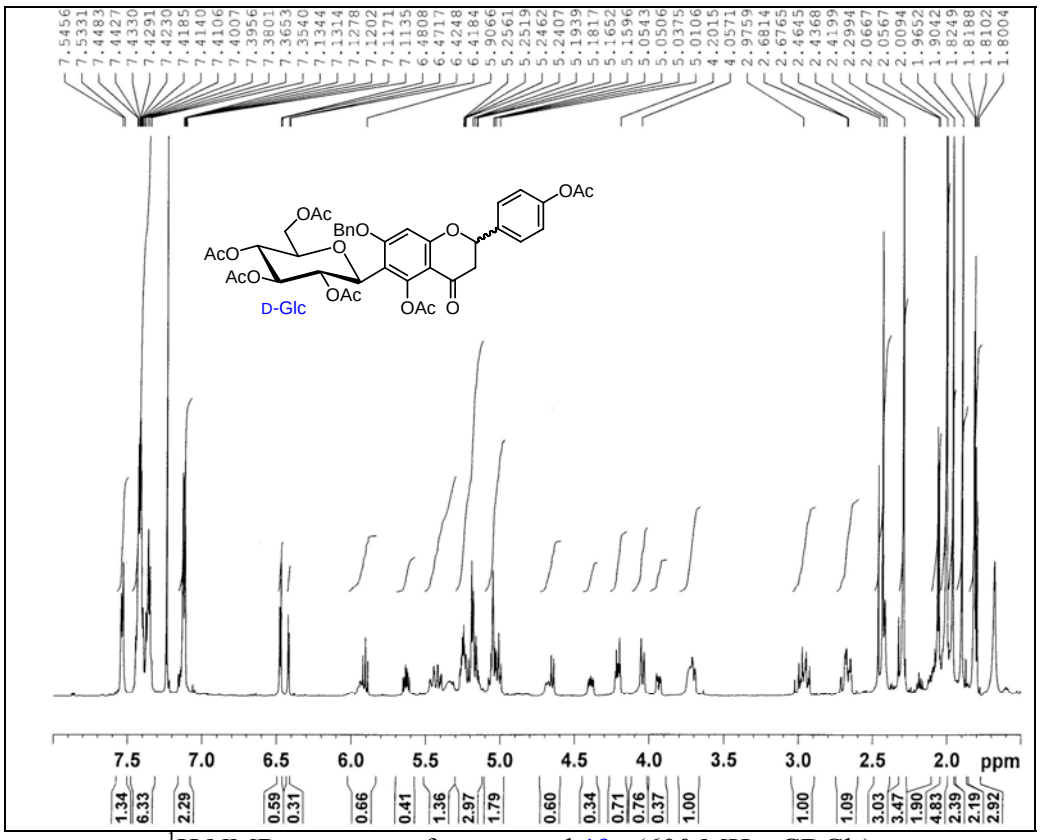
^{13}C NMR spectrum of compound **18dbAc** (100 MHz, $CDCl_3$)



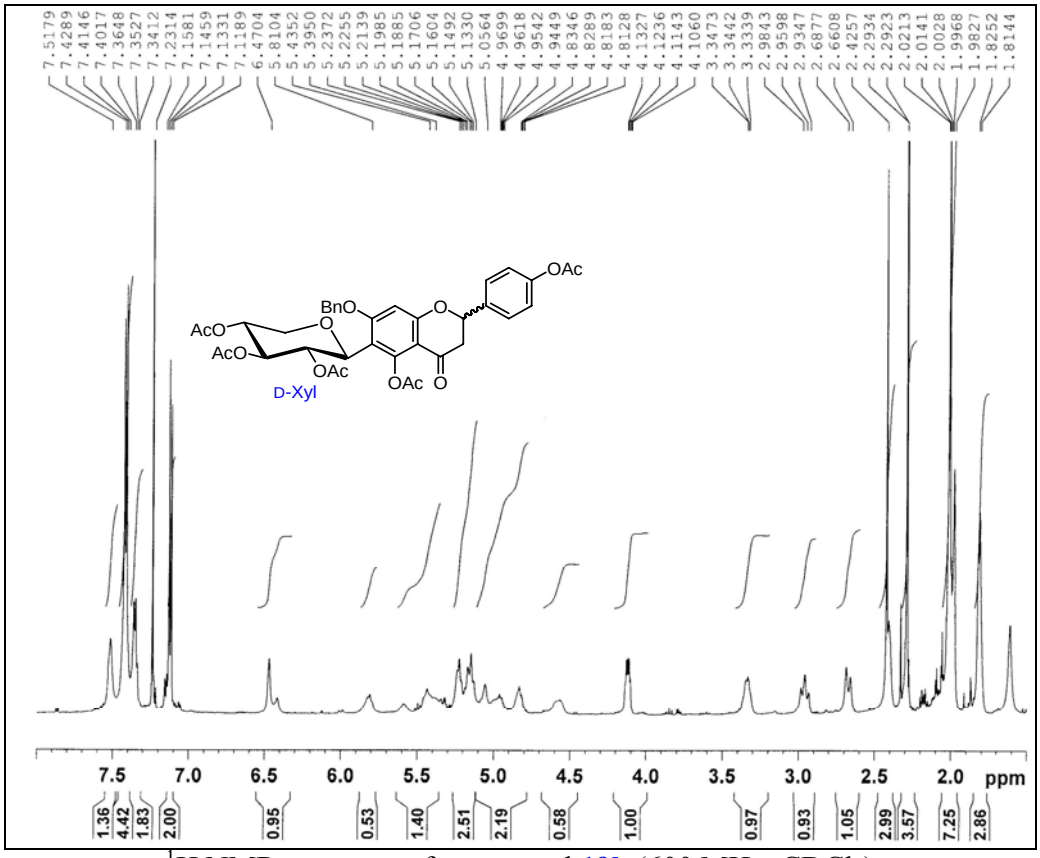
^{1}H NMR spectrum of compound **18db** (400 MHz, CD_3OD)



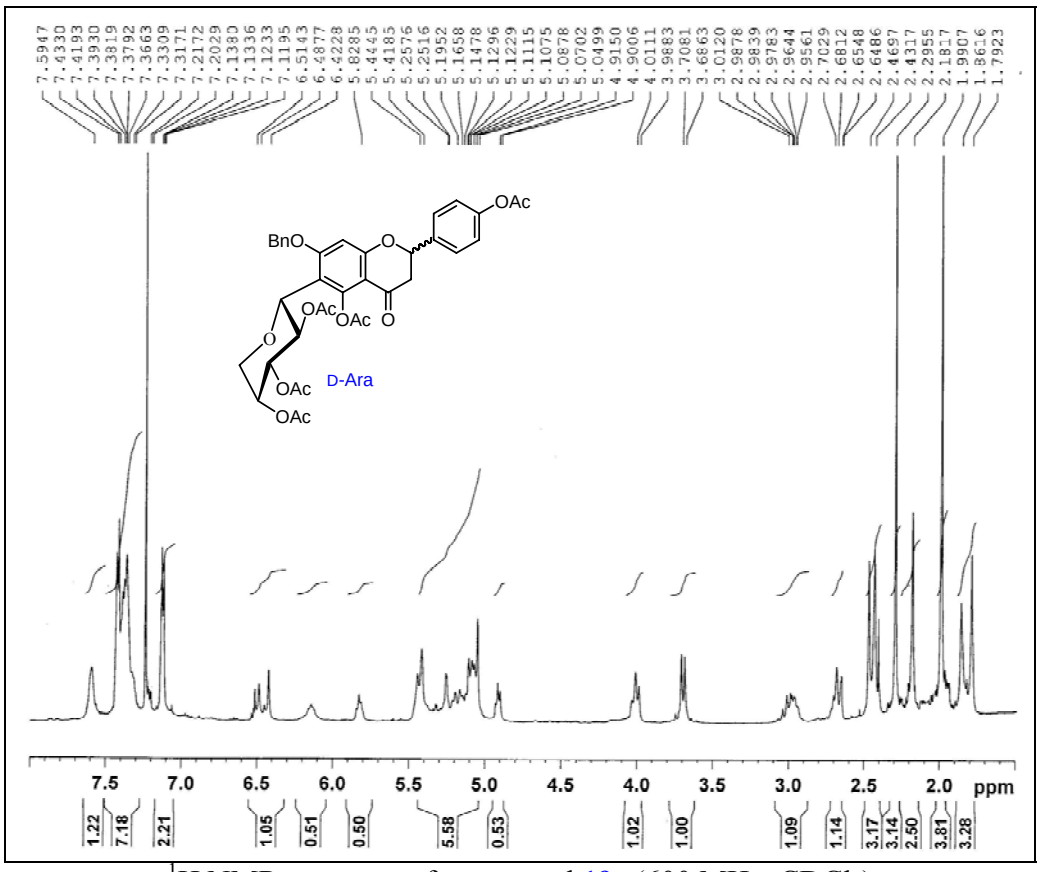
^{13}C NMR spectrum of compound **18db** (100 MHz, CD_3OD)



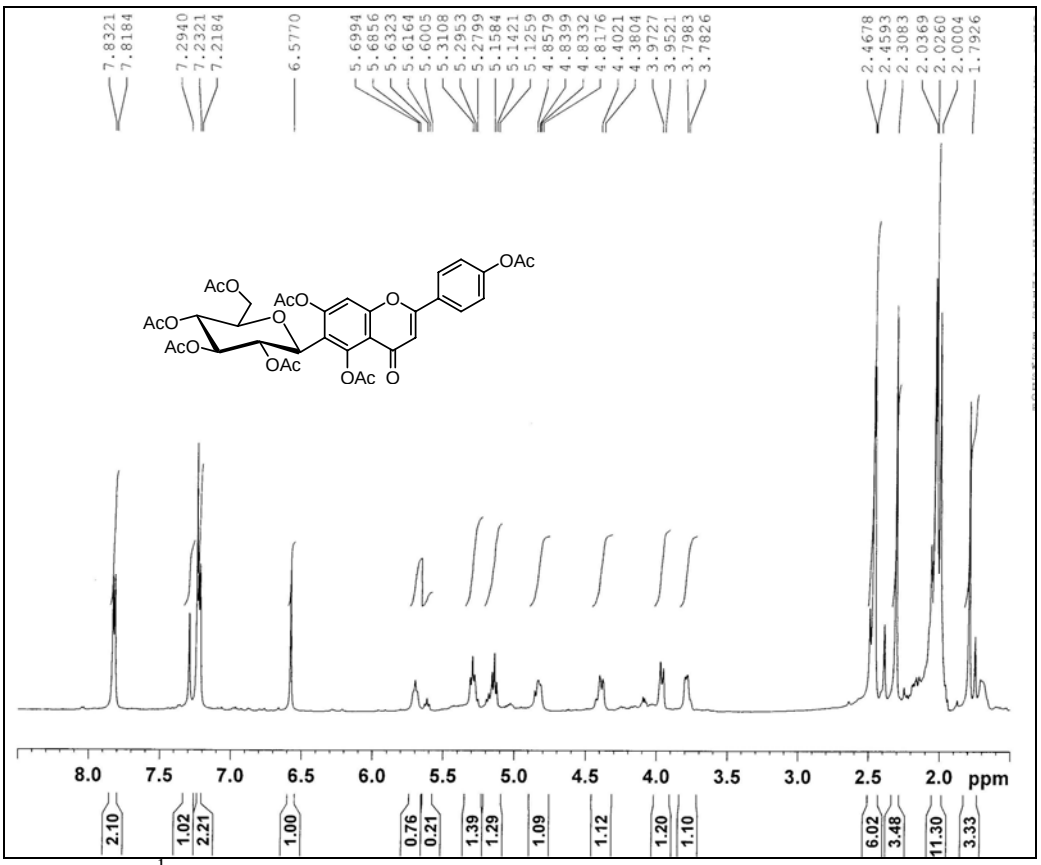
^{1}H NMR spectrum of compound **19a** (600 MHz, $CDCl_3$)



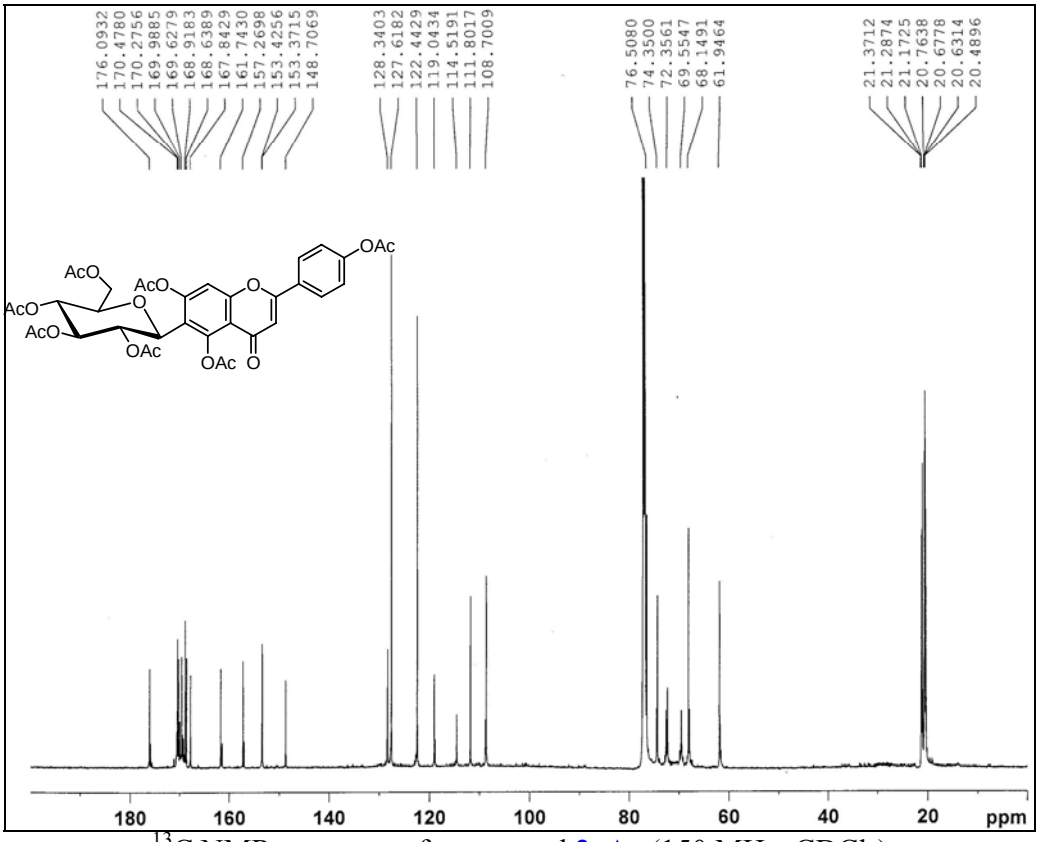
^{1}H NMR spectrum of compound **19b** (600 MHz, $CDCl_3$)



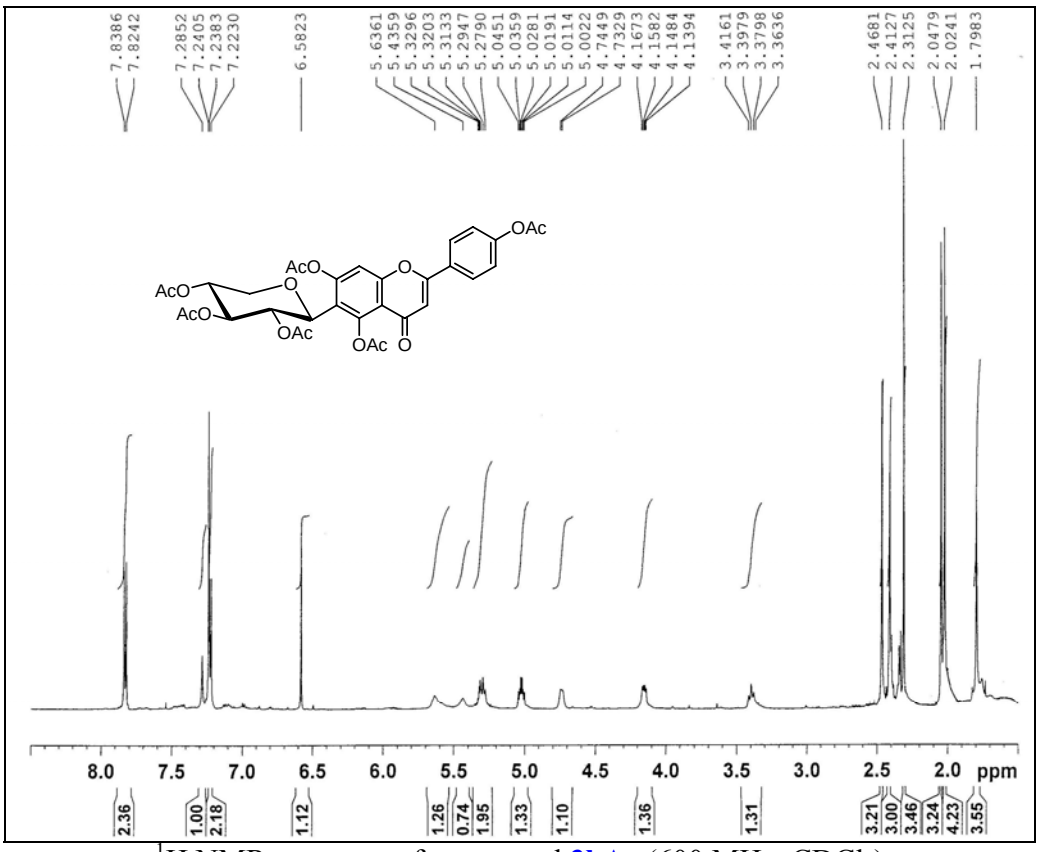
^{1}H NMR spectrum of compound **19c** (600 MHz, $CDCl_3$)



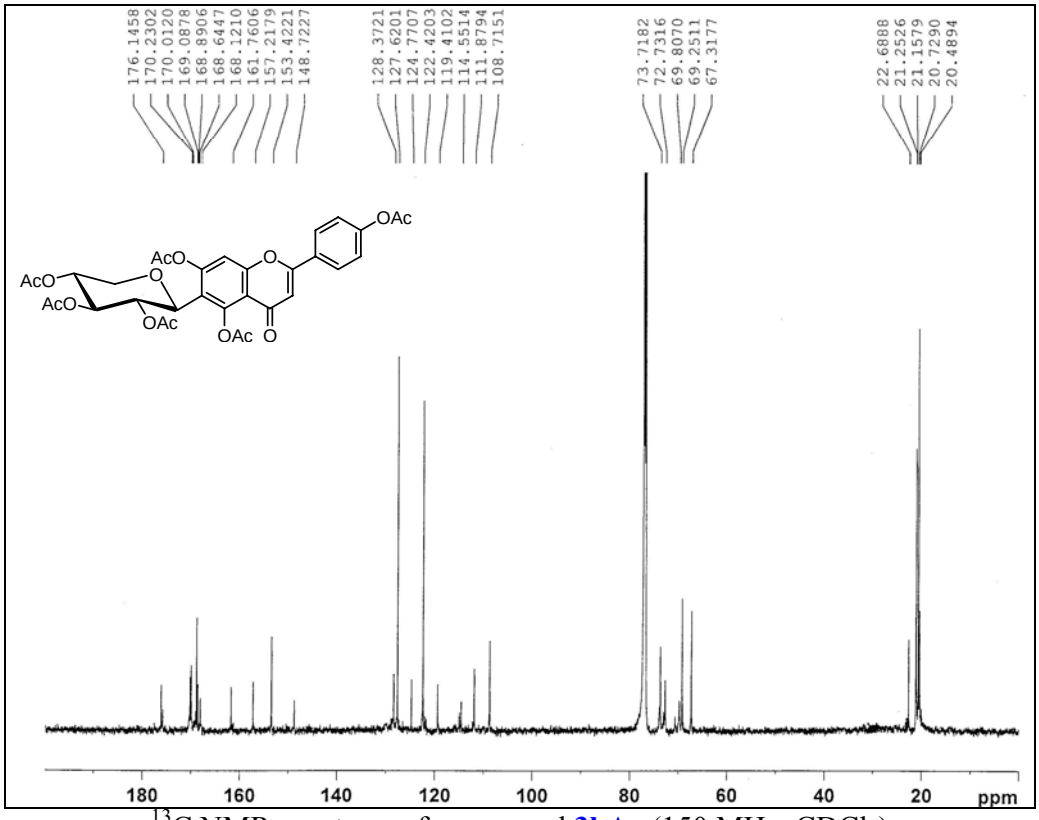
^{1}H NMR spectrum of compound **3aAc** (600 MHz, $CDCl_3$)



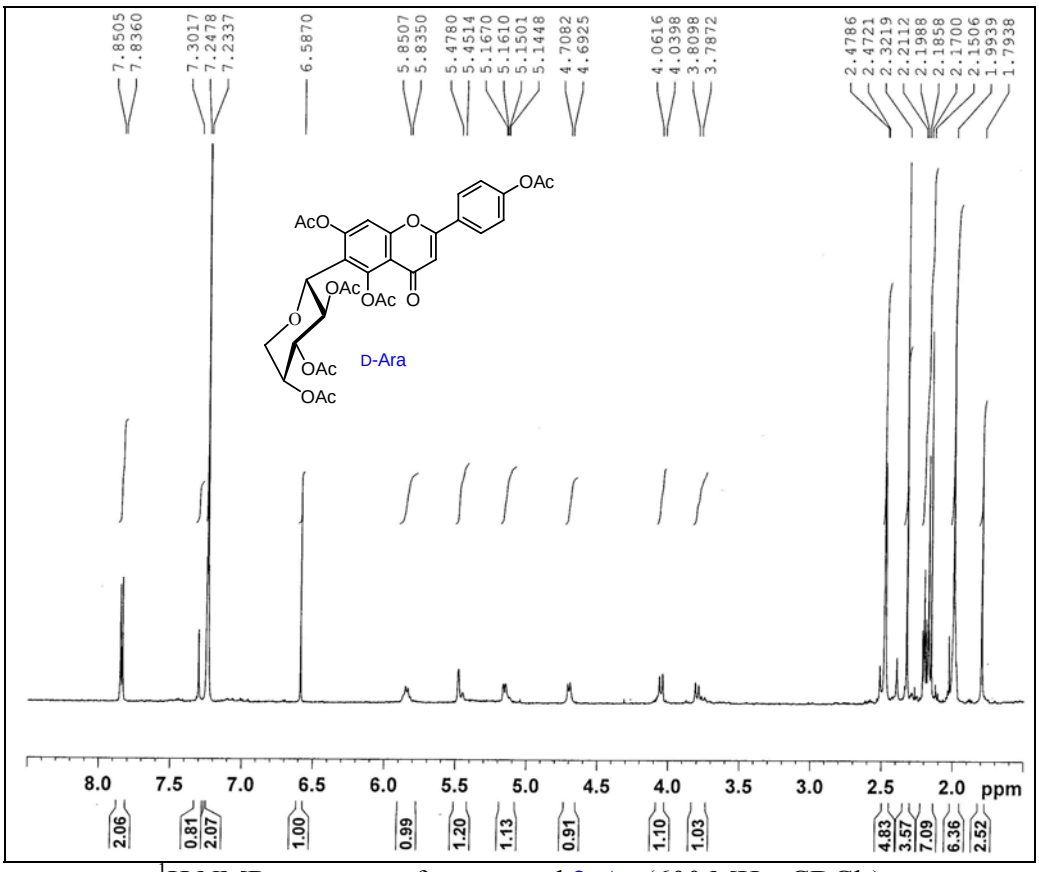
^{13}C NMR spectrum of compound **3aAc** (150 MHz, $CDCl_3$)



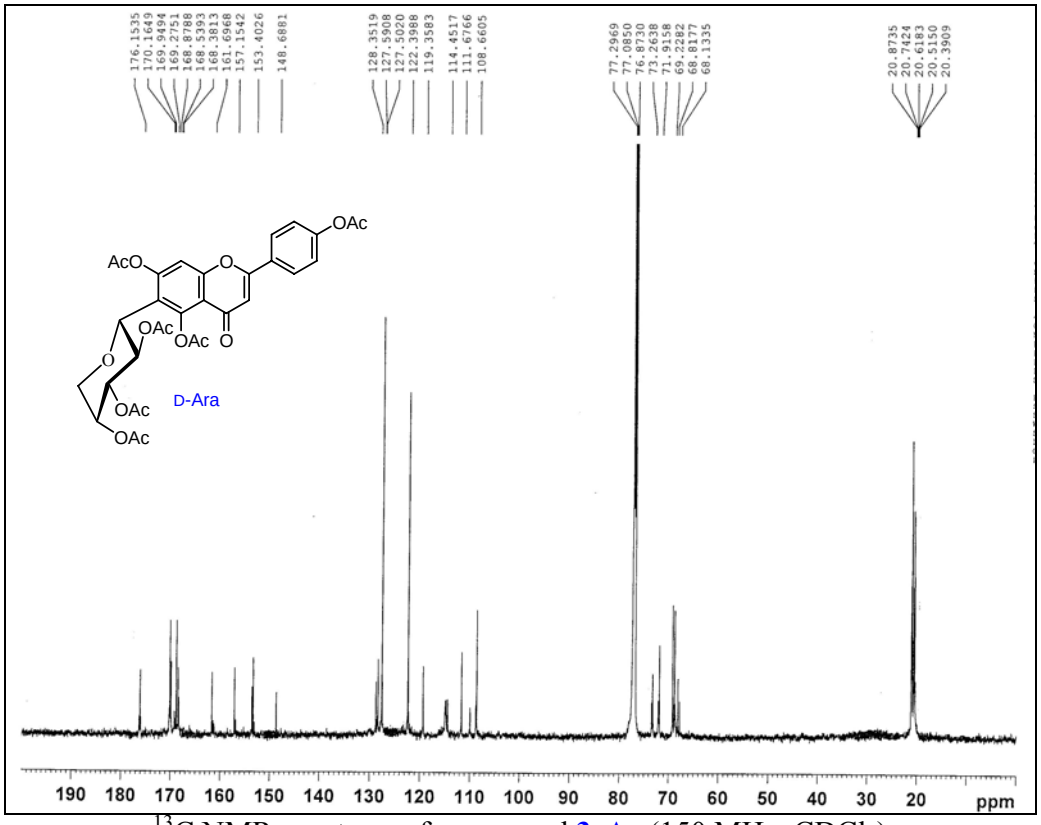
^{1}H NMR spectrum of compound **3bAc** (600 MHz, $CDCl_3$)



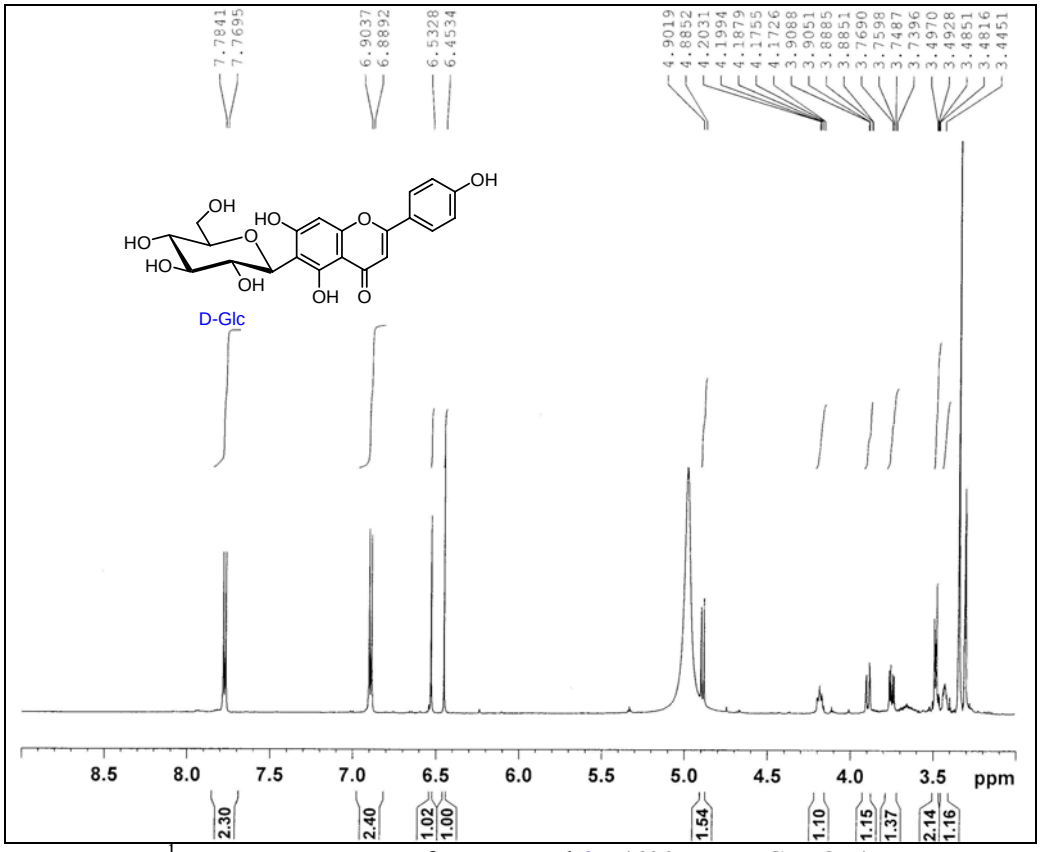
^{13}C NMR spectrum of compound **3bAc** (150 MHz, $CDCl_3$)



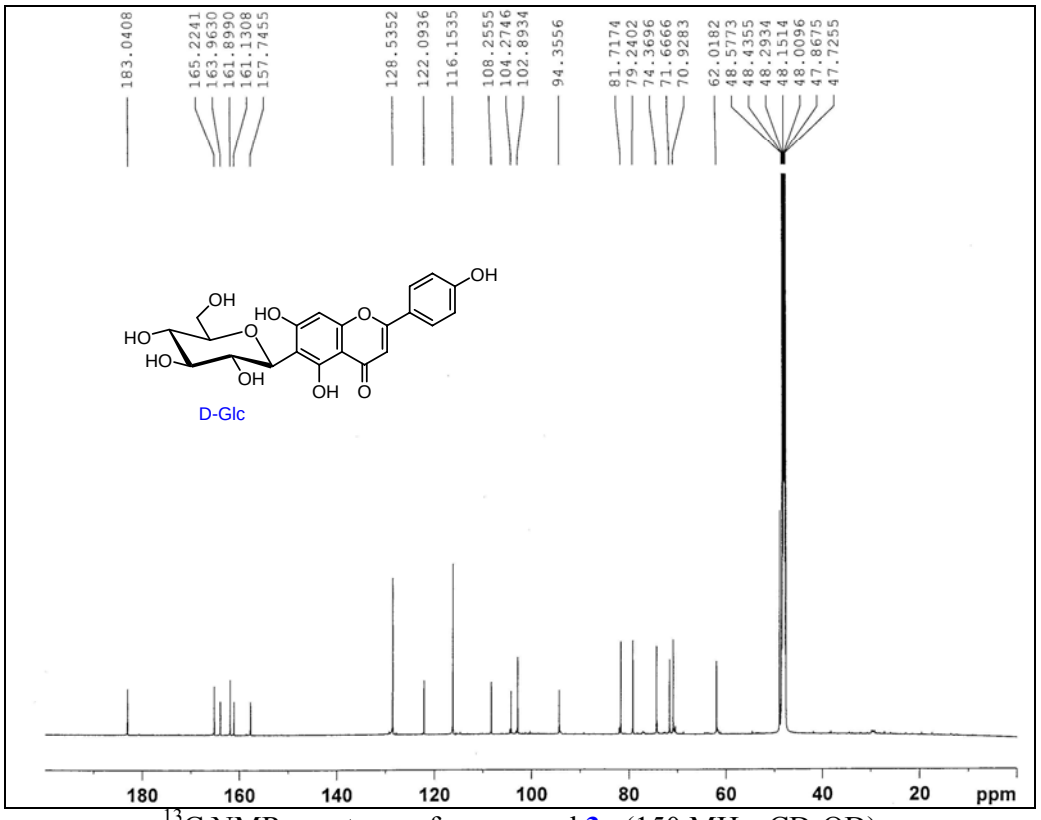
^{1}H NMR spectrum of compound **3cAc** (600 MHz, $CDCl_3$)



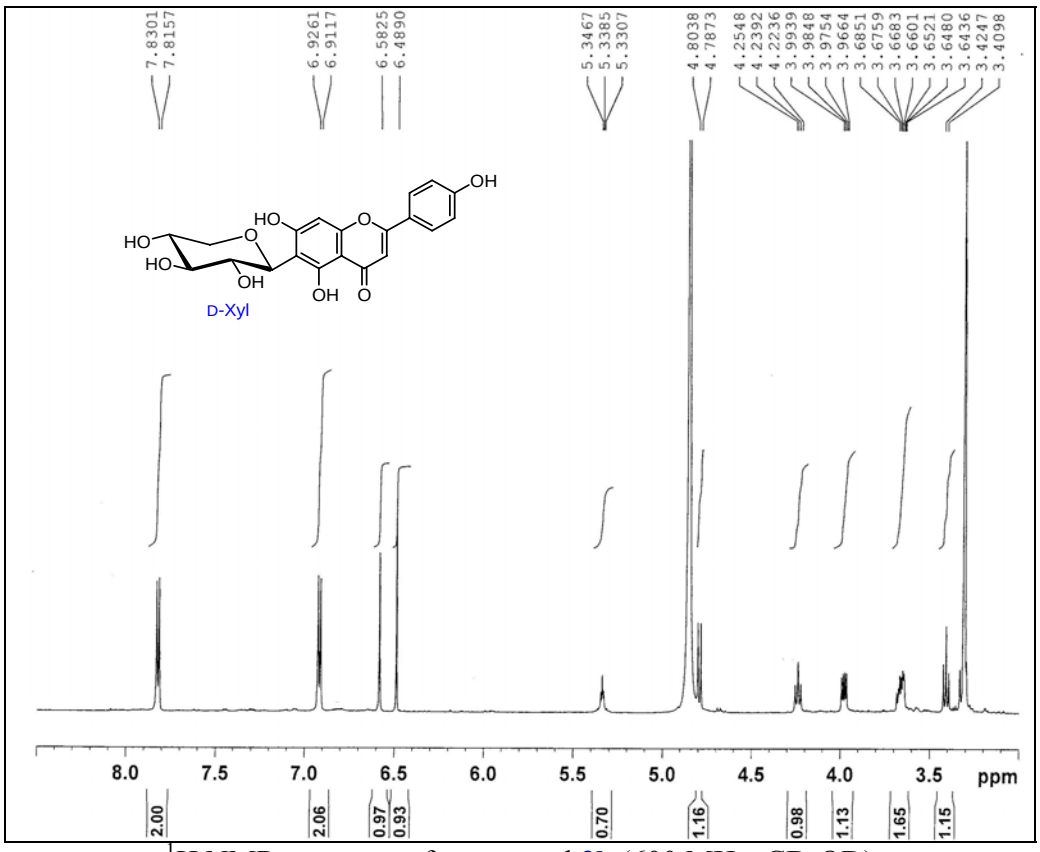
^{13}C NMR spectrum of compound **3cAc** (150 MHz, $CDCl_3$)



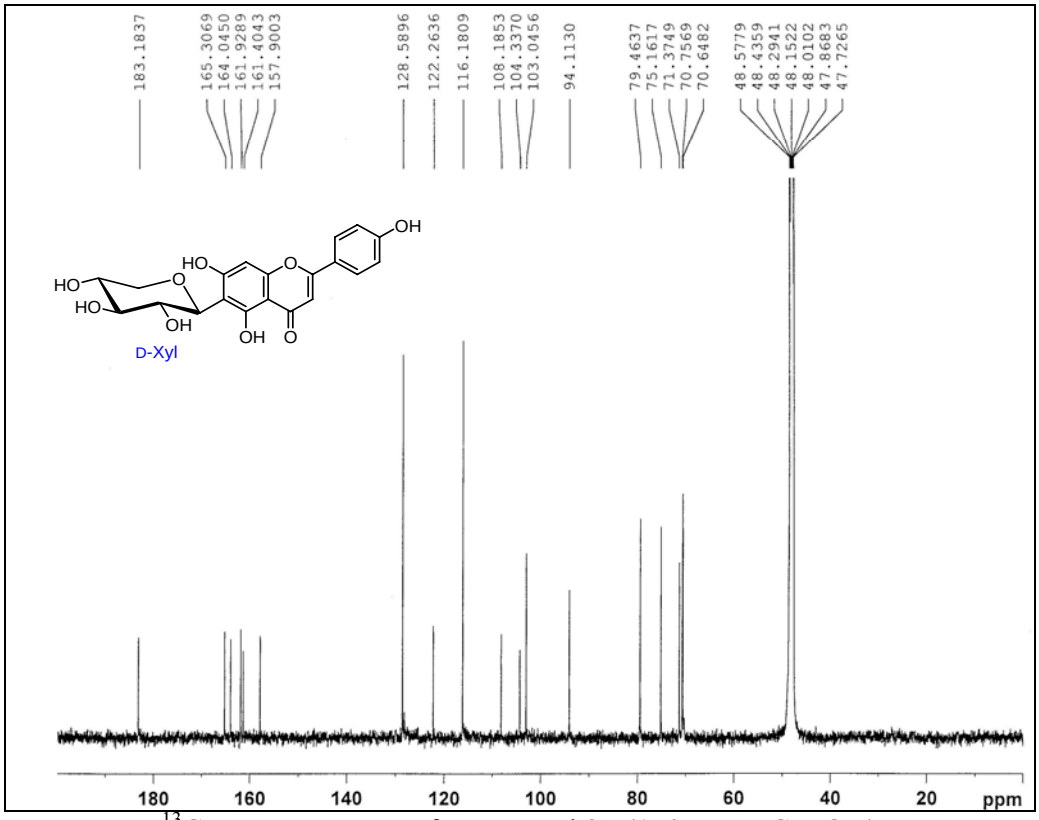
^{1}H NMR spectrum of compound **3a** (600 MHz, CD_3OD)



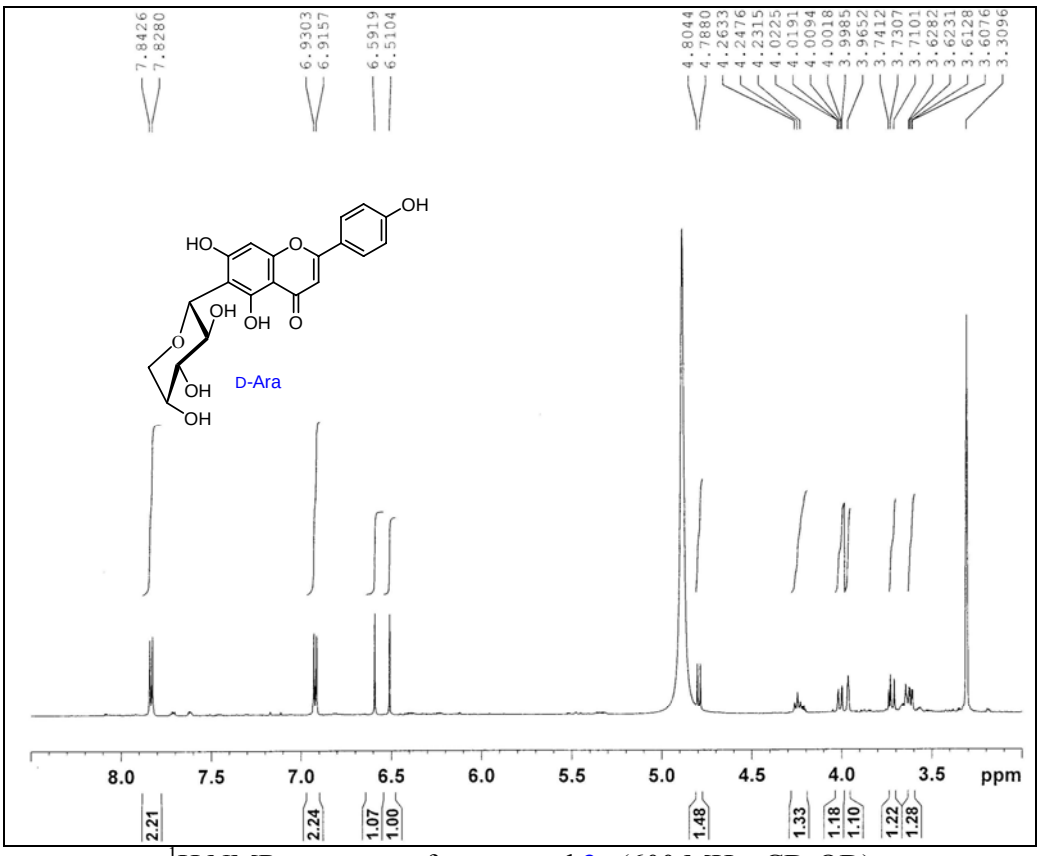
^{13}C NMR spectrum of compound **3a** (150 MHz, CD_3OD)



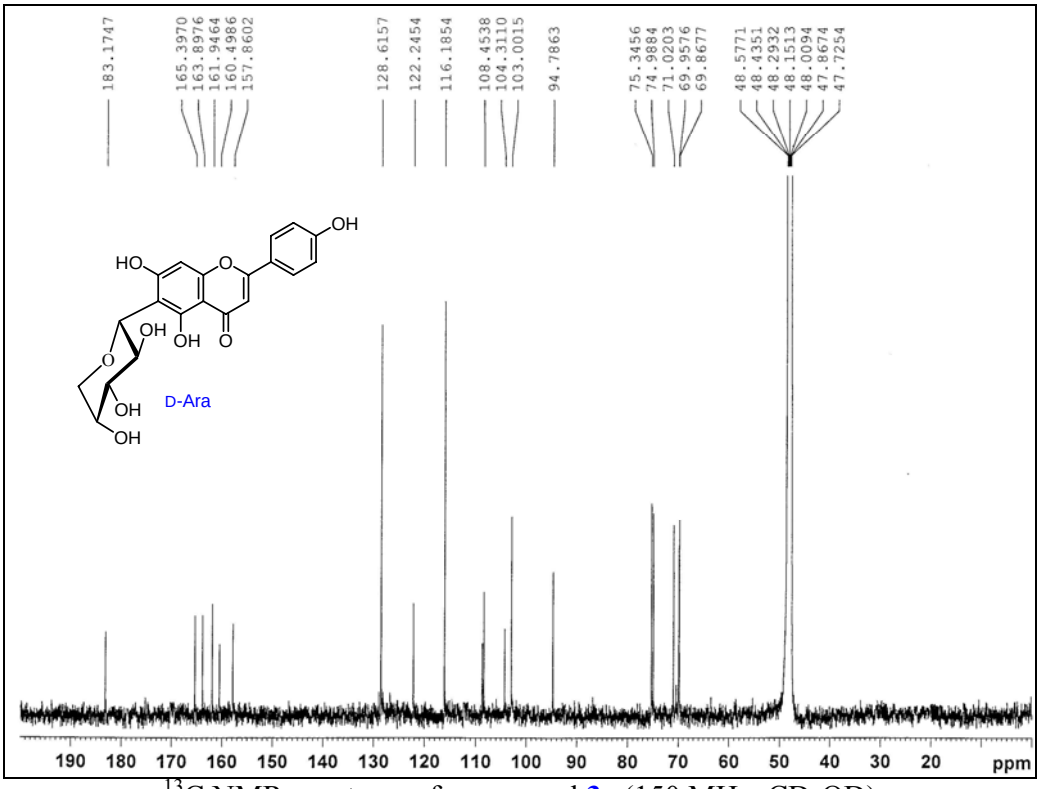
^{1}H NMR spectrum of compound **3b** (600 MHz, CD_3OD)



^{13}C NMR spectrum of compound **3b** (150 MHz, CD_3OD)



^{1}H NMR spectrum of compound **3c** (600 MHz, CD_3OD)



^{13}C NMR spectrum of compound **3c** (150 MHz, CD_3OD)