Palladium(0)-Catalyzed Synthesis of Cyclic Glucosides

Xin Huang,[a] Chunling Fu,[a] and Shengming Ma[a,*]

[a] Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, Hangzhou 310027, Zhejiang, P. R. China

Fax: (+86)21-6260-9305; E-mail: masm@ sioc.ac.cn

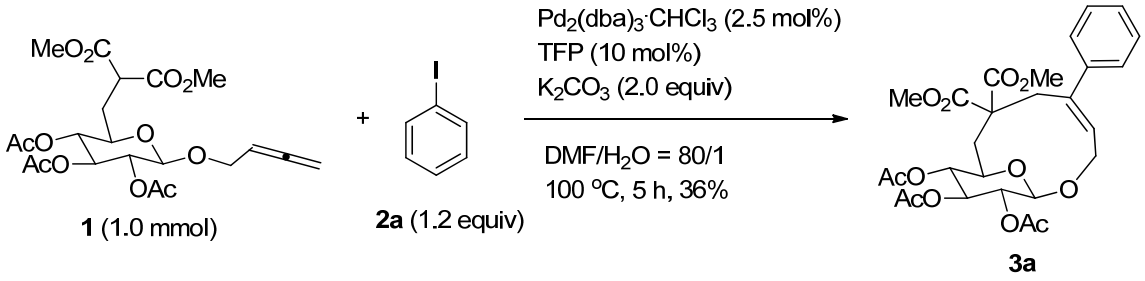
Supporting Information

General Experimental Methods:

^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on an instrument operated at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. Deuterochloroform ($CDCl_3$) and dimethyl sulfoxide-d6 (d_6-DMSO) were used as solvent in NMR experiments. Chemical shifts (δ) are given in parts per million (ppm). Infrared spectra were recorded from the films of pure samples on sodium chloride plates for liquid or in the form of KBr discs for the solid samples. Mass and HRMS spectra were carried out in ESI mode. Thin layer chromatography was performed on pre-coated glass-back plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel. DMF used was stirred with CaH_2 for 12 hours at 80 ^{o}C and distilled in vacuo before use. K_2CO_3 was bought from Sinopharm Chemical Reagent Co., Ltd. $Pd_2(dba)_3 \cdot CHCl_3$ was bought from Alfa Aesar and TFP was bought from Aldrich.

1. Pd(0)-Catalyzed Coupling-Cyclization of 1 with Different Organic iodides 2 under Standard Conditions.

(1) Preparation of **3a**. (hx-5-144)

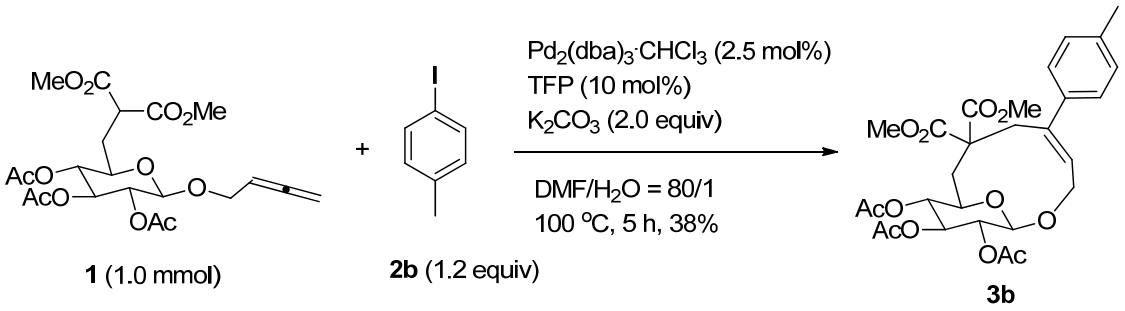


Typical Procedure I**:** To a flame-dried three-necked flask (100 mL) equipped with a reflux condenser containing K_2CO_3 (278.1 mg, 2.0 mmol) were added $Pd_2(dba)_3{\cdot}CHCl_3$ (25.5 mg, 0.025 mmol), TFP (23.5 mg, 0.1 mmol), **1** (477.6 mg, 1.0 mmol), **2a** (251.2 mg, 1.2 mmol), and DMF/H_2O (*V*/*V* = 80/1, 40.0 mL) sequentially under nitrogen atmosphere. The reaction was complete after being stirred at 100 °C for 5 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 2.5/1). After evaporation of the solvent, the residue was diluted with 60 mL of EtOAc, washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2.5/1) afforded **3a** (197.4 mg, 36%) as a solid: M.P. 185-186 °C (*n*-hexane/DCM); $[\alpha]^{20}_D$ = + 111.4 (*c* = 0.475, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5 H, ArH), 5.99 (t, *J* = 8.1 Hz, 1 H, CH=), 5.22-5.08 (m, 2 H), 5.03-4.93 (m, 1 H), 4.86 (s, 1 H), 4.41-4.27 (m, 2 H), 3.88 (d, *J* = 13.8 Hz, 1 H), 3.83-3.67 (m, 1 H), 3.74 (s, 3 H, Me), 3.29 (d, *J* = 13.8 Hz, 1 H), 2.89 (s, 3 H, Me), 2.70 (dd, J_1 = 14.7 Hz, J_2 = 12.3 Hz, 1 H), 2.13-1.96 (m, 1 H), 2.08 (s, 3 H, Me), 2.06 (s, 3 H, Me), 2.04 (s, 3 H, Me); ^{13}C NMR (75 Hz, $CDCl_3$) δ 170.8, 170.4, 169.7, 169.5, 169.3, 145.0,

141.4, 128.2, 127.8, 127.5, 127.0, 102.0, 73.7, 70.8, 69.7, 64.5, 55.6, 52.5, 51.7, 33.6, 32.9, 20.6, 20.5; IR (KBr) ν (cm^{-1}) 2957, 1754, 1730, 1439, 1370, 1243, 1221, 1117, 1080, 1067, 1041; MS (ESI, m/z) 1119 ($2M+Na^+$), 587 ($M+K^+$), 571 ($M+Na^+$), 566 ($M+NH_4^+$), 549 ($M+H^+$); Anal. Calcd. for $C_{27}H_{32}O_{12}$ (%): C 59.12, H 5.88; Found: C 59.13, H 5.92.

The following compounds were prepared according to **Typical Procedure I.**

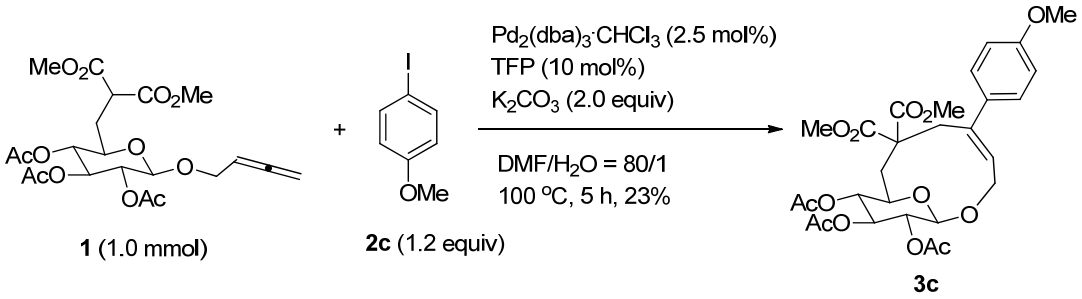
(2) Preparation of **3b**. (hx-8-140, hx-4-119)



The reaction of K_2CO_3 (276.4 mg, 2.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (25.9 mg, 0.025 mmol), TFP (23.2 mg, 0.1 mmol), **1** (471.7 mg, 1.0 mmol), and **2b** (262.3 mg, 1.2 mmol) in DMF/H_2O (*V*/*V* = 80/1, 40.0 mL) at 100 °C for 5 h afforded **3b** (212.6 mg, 38%) as a solid after chromatography on silica gel (eluent: petroleum ether/ethyl acetate (2.5/1): M.P. 171-172 °C (*n*-hexane/DCM); $[\alpha]^{20}_D$ = + 105.5 (*c* = 0.685, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.1 Hz, 2 H, ArH), 7.08 (d, *J* = 8.1 Hz, 2 H, ArH), 5.96 (t, *J* = 7.8 Hz, 1 H, CH=), 5.22-5.08 (m, 2 H), 5.05-4.92 (m, 1 H), 4.85 (s, 1 H), 4.40-4.24 (m, 2 H), 3.93-3.66 (m, 2 H), 3.74 (s, 3 H, Me), 3.27 (d, *J* = 13.8 Hz, 1 H), 2.93 (s, 3 H, Me), 2.77-2.60 (m, 1 H), 2.31 (s, 3 H), 2.13-1.95 (m, 1 H), 2.08 (s, 3 H, Me), 2.05 (s, 3 H, Me), 2.04 (s, 3 H, Me); ^{13}C NMR (75 Hz, $CDCl_3$) δ 170.7, 170.4, 169.7, 169.4, 169.2, 144.9, 138.5, 137.1, 128.4, 127.5, 126.9, 102.0,

73.8, 73.7, 70.8, 69.7, 64.6, 55.6, 52.4, 51.7, 33.6, 32.9, 20.8, 20.51, 20.47; IR (KBr) ν (cm^{-1}) 2964, 1754, 1731, 1437, 1369, 1239, 1220, 1114, 1079, 1067, 1042; MS (ESI, m/z) 585 ($M+Na^+$); Anal. Calcd. for $C_{28}H_{34}O_{12}$ (%): C 59.78, H 6.09; Found: C 59.43, H 5.93.

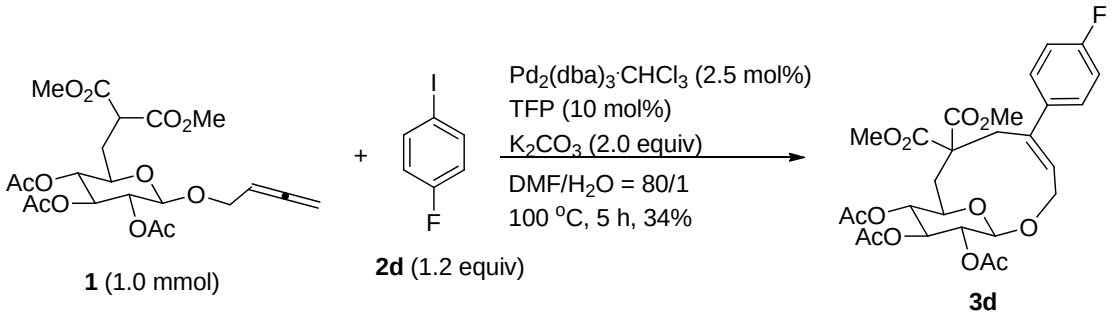
(3) Preparation of **3c**. (hx-5-172)



The reaction of K_2CO_3 (277.4 mg, 2.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (25.7 mg, 0.025 mmol), TFP (23.5 mg, 0.1 mmol), **1** (474.4 mg, 1.0 mmol), and **2c** (280.9 mg, 1.2 mmol) in DMF/H_2O (*V/V* = 80/1, 40.0 mL) at 100 °C for 5 h afforded **3c** (133.0 mg, 23%) as a solid after chromatography on silica gel (eluent: petroleum ether/ethyl acetate (2.5/1): M.P. 101-102 °C (*n*-hexane/EtOAc); $[\alpha]^{20}_D$ = + 117.9 (*c* = 0.895, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.7 Hz, 2 H, ArH), 6.82 (d, *J* = 8.4 Hz, 2 H, ArH), 5.93 (t, *J* = 8.0 Hz, 1 H, CH=), 5.22-5.07 (m, 2 H), 5.04-4.94 (m, 1 H), 4.86 (s, 1 H), 4.40-4.24 (m, 2 H), 3.93-3.67 (m, 2 H), 3.78 (s, 3 H, Me), 3.75 (s, 3 H, Me), 3.25 (d, *J* = 13.8 Hz, 1 H), 2.99 (s, 3 H, Me), 2.68 (dd, J_1 = 14.6 Hz, J_2 = 12.5 Hz, 1 H), 2.14-1.95 (m, 1 H), 2.09 (s, 3 H, Me), 2.06 (s, 3 H, Me), 2.04 (s, 3 H, Me); ^{13}C NMR (75 Hz, $CDCl_3$) δ 170.8, 170.5, 169.8, 169.5, 169.4, 159.0, 144.5, 133.8, 128.1, 127.1, 113.1, 102.0, 73.9, 73.7, 70.7, 69.7, 64.7, 55.5, 55.0, 52.5, 51.9, 33.5, 32.9, 20.6, 20.5; IR (KBr) ν (cm^{-1}) 2954, 1755, 1739, 1607, 1152, 1438, 1371, 1247,

1221, 1181, 1036; MS (ESI, m/z) 617 ($M+K^+$), 601 ($M+Na^+$), 596 ($M+NH_4^+$), 579 ($M+H^+$); Anal. Calcd. for $C_{28}H_{34}O_{13}$ (%): C 58.13, H 5.92; Found: C 57.99, H 5.94.

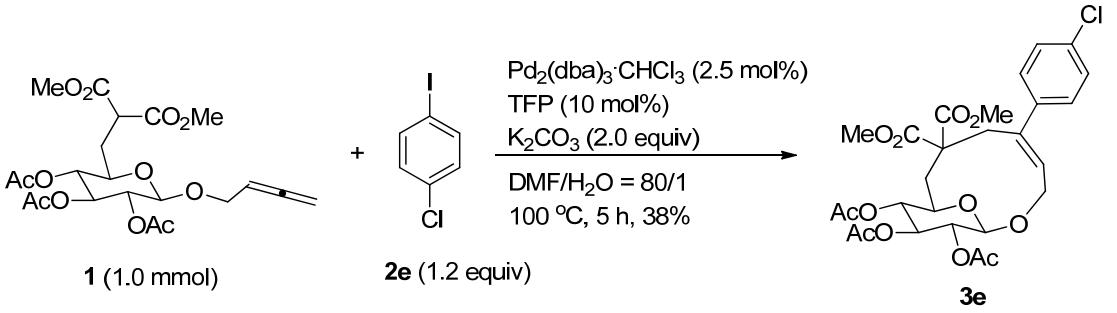
(4) Preparation of **3d**. (hx-6-10)



The reaction of K_2CO_3 (277.2 mg, 2.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (26.0 mg, 0.025 mmol), TFP (23.4 mg, 0.1 mmol), **1** (471.1 mg, 1.0 mmol), and **2d** (266.8 mg, 1.2 mmol) in DMF/H_2O (*V*/*V* = 80/1, 40.0 mL) at 100 °C for 5 h afforded **3d** (193.8 mg, 34%) as a solid after chromatography on silica gel (eluent: petroleum ether/ethyl acetate (2.5/1): M.P. 185-186 °C (*i*-PrOH); $[\alpha]^{20}_D$ = + 88.9 (*c* = 1.025, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.28-7.16 (m, 2 H, ArH), 6.98 (t, *J* = 8.4 Hz, 2 H, ArH), 5.96 (t, *J* = 8.0 Hz, 1 H, CH=), 5.22-5.08 (m, 2 H), 4.98 (d, *J* = 5.1 Hz, 1 H), 4.86 (s, 1 H), 4.42-4.24 (m, 2 H), 3.88 (d, *J* = 14.1 Hz, 1 H), 3.83-3.65 (m, 1 H), 3.75 (s, 3 H, Me), 3.24 (d, *J* = 13.8 Hz, 1 H), 2.99 (s, 3 H, Me), 2.67 (dd, J_1 = 14.7 Hz, J_2 = 12.3 Hz, 1 H), 2.17-1.95 (m, 1 H), 2.09 (s, 3 H, Me), 2.06 (s, 3 H, Me), 2.04 (s, 3 H, Me); ^{13}C NMR (75 Hz, $CDCl_3$) δ 170.7, 170.4, 169.8, 169.5, 169.4, 162.2 (d, *J* = 245.5 Hz), 144.0, 137.5 (d, *J* = 2.8 Hz), 128.8 (d, *J* = 8.3 Hz), 128.5, 114.7 (d, *J* = 21.4 Hz), 102.1, 73.85, 73.77, 70.8, 69.7, 64.5, 55.6, 52.6, 51.8, 33.6, 33.1, 20.6, 20.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.8 (s, 1 F); IR (KBr) ν (cm^{-1}) 2956, 1755, 1728, 1599, 1508, 1438, 1370, 1239, 1220, 1080, 1067, 1042; MS (ESI, m/z) 584 ($M+NH_4^+$); Anal.

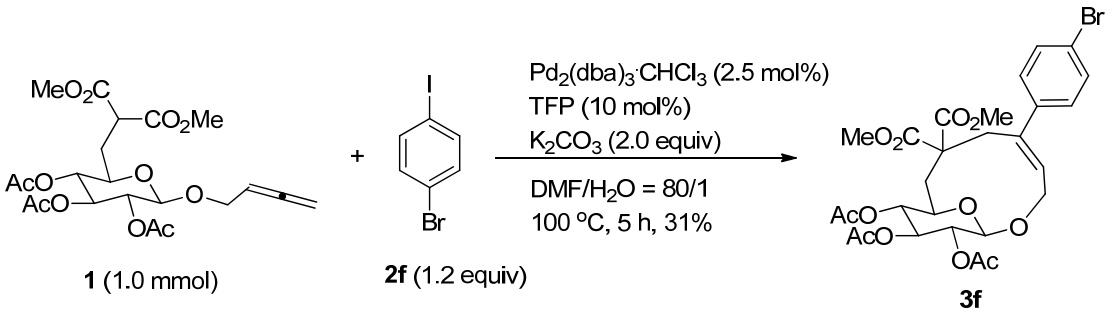
Calcd. for $C_{27}H_{31}FO_{12}$ (%): C 57.24, H 5.52; Found: C 56.88, H 5.55.

(5) Preparation of **3e**. (hx-5-198, hx-4-118)

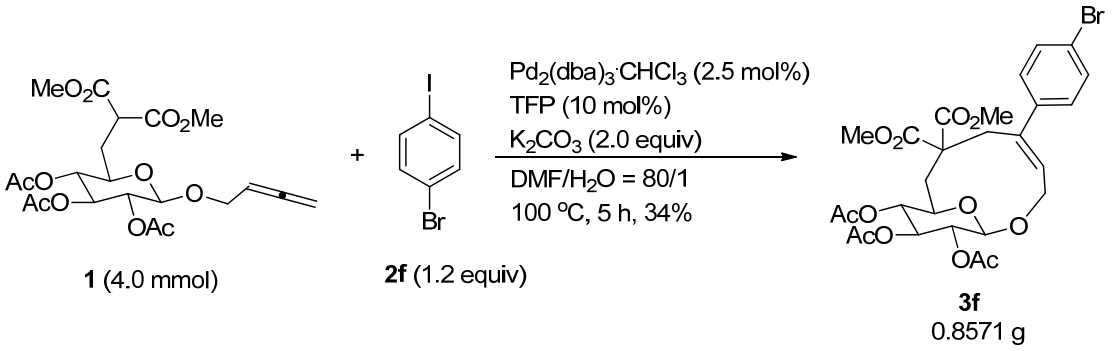


The reaction of K_2CO_3 (278.1 mg, 2.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (25.7 mg, 0.025 mmol), TFP (23.8 mg, 0.1 mmol), **1** (473.2 mg, 1.0 mmol), and **2e** (287.3 mg, 1.2 mmol) in DMF/H_2O (*V/V* = 80/1, 40.0 mL) at 100 °C for 5 h afforded **3e** (222.6 mg, 38%) as a solid after chromatography on silica gel (eluent: petroleum ether/ethyl acetate (2.5/1): M.P. 181-182 °C (*n*-hexane/DCM); $[\alpha]^{20}_D$ = + 107.5 (*c* = 1.055, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.1 Hz, 2 H, ArH), 7.18 (d, *J* = 8.4 Hz, 2 H, ArH), 5.98 (t, *J* = 7.8 Hz, 1 H, CH=), 5.23-5.05 (m, 2 H), 4.98 (d, *J* = 5.4 Hz, 1 H), 4.86 (s, 1 H), 4.45-4.22 (m, 2 H), 3.88 (d, *J* = 14.1 Hz, 1 H), 3.82-3.65 (m, 1 H), 3.75 (s, 3 H, Me), 3.23 (d, *J* = 14.1 Hz, 1 H), 2.98 (s, 3 H, Me), 2.66 (dd, J_1 = 14.7 Hz, J_2 = 12.3 Hz, 1 H), 2.14-1.94 (m, 1 H), 2.08 (s, 3 H, Me), 2.06 (s, 3 H, Me), 2.04 (s, 3 H, Me); ^{13}C NMR (75 Hz, $CDCl_3$) δ 170.7, 170.4, 169.8, 169.5, 169.4, 144.0, 140.0, 133.4, 128.9, 128.5, 128.0, 102.2, 73.8, 70.9, 69.8, 64.5, 55.7, 52.6, 51.9, 33.7, 33.0, 20.62, 20.59; IR (KBr) ν (cm^{-1}) 2961, 1728, 1490, 1467, 1436, 1368, 1241, 1219, 1111, 1080, 1067, 1044, 1015; MS (ESI, m/z) 607 (M (^{37}Cl)+Na^+), 605 (M (^{35}Cl)+Na^+), 585 (M (^{37}Cl)+H^+), 583 (M (^{35}Cl)+H^+); Anal. Calcd. for $C_{27}H_{31}ClO_{12}$ (%): C 55.63, H 5.36; Found: C 55.35, H 5.24.

(6) Preparation of **3f**. (hx-5-42 hx-7-88 (4.0 mmol))



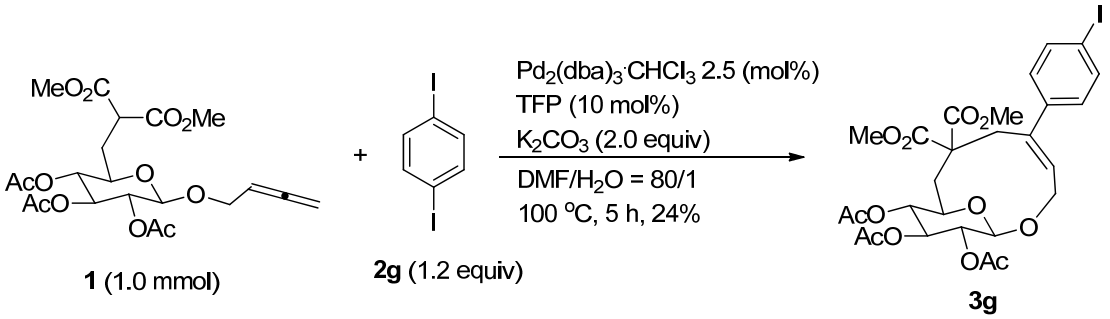
The reaction of K_2CO_3 (276.4 mg, 2.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (26.2 mg, 0.025 mmol), TFP (23.5 mg, 0.1 mmol), **1** (472.3 mg, 1.0 mmol), and **2f** (340.1 mg, 1.2 mmol) in DMF/H_2O (*V*/*V* = 80/1, 40.0 mL) at 100 °C for 5 h afforded **3f** (193.5 mg, 31%) as a solid after chromatography on silica gel (eluent: petroleum ether/ethyl acetate (3/1) to petroleum ether/ethyl acetate (2/1)): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2 H, ArH), 7.08 (d, *J* = 8.4 Hz, 2 H, ArH), 5.93 (t, *J* = 7.8 Hz, 1 H, CH=), 5.19-5.03 (m, 2 H), 4.92 (d, *J* = 5.7 Hz, 1 H), 4.81 (s, 1 H), 4.37-4.18 (m, 2 H), 3.82 (d, *J* = 14.1 Hz, 1 H), 3.78-3.63 (m, 1 H), 3.70 (s, 3 H, Me), 3.18 (d, *J* = 13.8 Hz, 1 H), 2.93 (s, 3 H, Me), 2.67-2.53 (m, 1 H), 2.10-1.90 (m, 1 H), 2.04 (s, 3 H, Me), 2.01 (s, 3 H, Me), 2.00 (s, 3 H).



A 4.0 mmol scale reaction: The reaction of K_2CO_3 (1174.2 mg, 8.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (103.6 mg, 0.1 mmol), TFP (92.8 mg, 0.4 mmol), **1** (1889.0 mg, 4.0 mmol), and **2f** (1358.2 mg, 1.2 mmol) in DMF/H_2O (*V*/*V* = 80/1, 160.0 mL) at 100 °C

for 5 h afforded **3f** (857.1 mg, 34%) as a solid after chromatography on silica gel (eluent: petroleum ether/ethyl acetate (2.5/1)): M.P. 172-174 ^{o}C (*n*-hexane/EtOAc); $[\alpha]^{20}_{D}$ = + 105.2 (*c* = 1.080, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2 H, ArH), 7.13 (d, *J* = 8.4 Hz, 2 H, ArH), 5.98 (t, *J* = 8.1 Hz, 1 H, CH=), 5.23-5.05 (m, 2 H), 4.97 (d, *J* = 5.7 Hz, 1 H), 4.86 (s, 1 H), 4.42-4.23 (m, 2 H), 3.87 (d, *J* = 13.8 Hz, 1 H), 3.82-3.65 (m, 1 H), 3.75 (s, 3 H, Me), 3.23 (d, *J* = 14.1 Hz, 1 H), 2.97 (s, 3 H, Me), 2.72-2.56 (m, 1 H), 2.14-1.94 (m, 1 H), 2.09 (s, 3 H, Me), 2.06 (s, 3 H, Me), 2.04 (s, 3 H, Me); ^{13}C NMR (75 Hz, $CDCl_3$) δ 170.7, 170.5, 169.9, 169.6, 169.5, 144.1, 140.5, 131.0, 129.0, 128.9, 121.6, 102.3, 73.9, 70.9, 69.8, 64.5, 55.8, 52.7, 52.0, 33.7, 33.0, 20.71, 20.66; IR (KBr) ν (cm^{-1}) 2953, 1755, 1728, 1486, 1467, 1436, 1369, 1242, 1217, 1111, 1079, 1066, 1042, 1011; MS (ESI, m/z) 667 (M (^{81}Br)+K^+), 665 (M (^{79}Br)+K^+), 646 (M (^{81}Br)+NH_4^+), 644 (M (^{79}Br)+ NH_4^+), 629 (M (^{81}Br)+H^+), 627 (M (^{79}Br)+H^+); Anal. Calcd. for $C_{27}H_{31}BrO_{12}$ (%): C 51.69, H 4.98; Found: C 52.09, H 5.03.

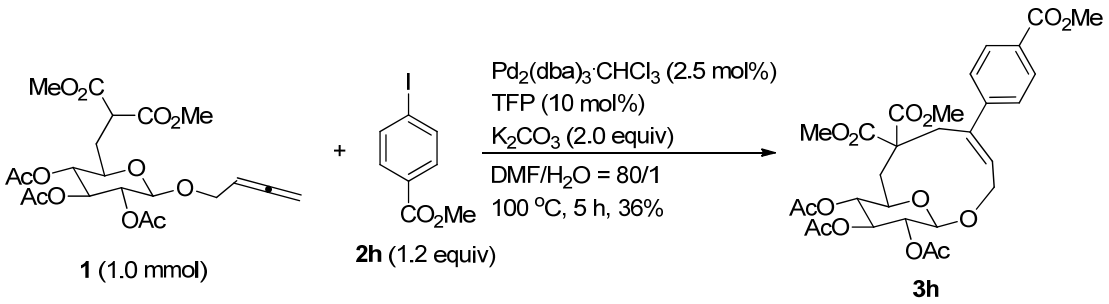
(7) Preparation of **3g**. (hx-6-7, hx-4-134)



The reaction of K_2CO_3 (276.8 mg, 2.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (25.9 mg, 0.025 mmol), TFP (23.2 mg, 0.1 mmol), **1** (473.5 mg, 1.0 mmol), and **2g** (396.3 mg, 1.2 mmol) in DMF/H_2O (*V*/*V* = 80/1, 40.0 mL) at 100 ^{o}C for 5 h afforded **3g** (164.2 mg,

24%) as a solid after chromatography on silica gel (eluent: petroleum ether/ethyl acetate (2.5/1)): M.P. 115-116 ^{o}C (*n*-hexane/EtOAc); $[\alpha]^{20}_{D}$ = + 92.4 (*c* = 0.94, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2 H, ArH), 6.93 (d, *J* = 8.1 Hz, 2 H, ArH), 5.91 (t, *J* = 8.0 Hz, 1 H, CH=), 5.17-4.99 (m, 2 H), 4.90 (d, *J* = 5.7 Hz, 1 H), 4.79 (s, 1 H), 4.35-4.16 (m, 2 H), 3.79 (d, *J* = 14.1 Hz, 1 H), 3.74-3.60 (m, 1 H), 3.68 (s, 3 H, Me), 3.15 (d, *J* = 14.1 Hz, 1 H), 2.89 (s, 3 H, Me), 2.58 (dd, J_1 = 14.9 Hz, J_2 = 12.5 Hz, 1 H), 2.10-1.90 (m, 1 H), 2.01 (s, 3 H, Me), 2.00 (s, 3 H, Me), 1.97 (s, 3 H, Me); ^{13}C NMR (75 Hz, $CDCl_3$) δ 170.6, 170.4, 169.8, 169.5, 169.4, 144.0, 141.0, 136.9, 129.0, 128.8, 102.1, 93.0, 73.7, 70.8, 69.6, 64.4, 55.6, 52.7, 51.9, 33.6, 32.8, 20.65, 20.60; IR (neat, cm^{-1}) 2953, 1747, 1485, 1435, 1371, 1251, 1221, 1132, 1109, 1038, 1006; MS (ESI, m/z) 697 ($M+Na^+$), 692 ($M+NH_4^+$), 675 ($M+H^+$); Anal. Calcd. for $C_{27}H_{31}IO_{12}$ (%): C 48.08, H 4.63; Found: C 47.81, H 4.59.

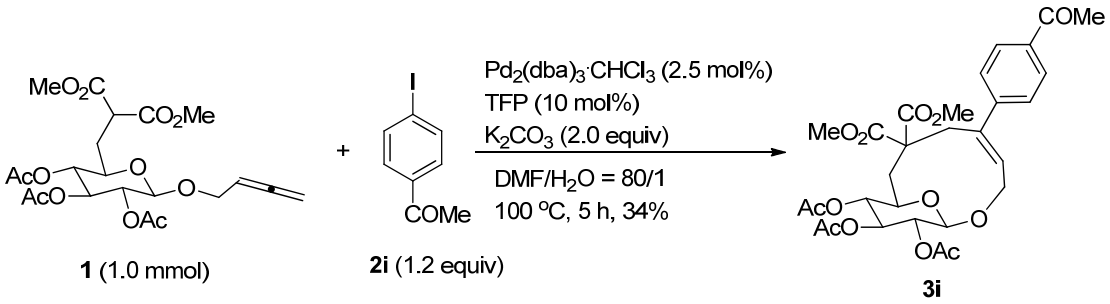
(8) Preparation of **3h**. (hx-5-163, hx-4-106)



The reaction of K_2CO_3 (277.8 mg, 2.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (25.6 mg, 0.025 mmol), TFP (23.1 mg, 0.1 mmol), **1** (474.3 mg, 1.0 mmol), and **2h** (314.6 mg, 1.2 mmol) in DMF/H_2O (*V*/*V* = 80/1, 40.0 mL) at 100 ^{o}C for 5 h afforded **3h** (219.9 mg, 36%) as a solid after chromatography on silica gel (eluent: petroleum ether/ethyl acetate (2.5/1)): M.P. 109-111 ^{o}C (*n*-hexane/EtOAc); $[\alpha]^{20}_{D}$ = + 116.1 (*c* = 0.89,

$CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2 H, ArH), 7.34 (d, *J* = 8.4 Hz, 2 H, ArH), 6.06 (t, *J* = 8.0 Hz, 1 H, CH=), 5.23-5.08 (m, 2 H), 4.99 (d, *J* = 5.7 Hz, 1 H), 4.89 (s, 1 H), 4.43-4.25 (m, 2 H), 4.00-3.68 (m, 2 H), 3.91 (s, 3 H, Me), 3.76 (s, 3 H, Me), 3.31 (d, *J* = 14.1 Hz, 1 H), 2.90 (s, 3 H, Me), 2.69 (dd, J_1 = 14.9 Hz, J_2 = 12.2 Hz, 1 H), 2.20-1.94 (m, 1 H), 2.10 (s, 3 H, Me), 2.07 (s, 3 H, Me), 2.05 (s, 3 H, Me); ^{13}C NMR (75 Hz, $CDCl_3$) δ 170.5, 170.2, 169.7, 169.4, 169.3, 166.4, 146.1, 144.1, 129.6, 129.0, 127.0, 102.1, 73.7, 73.6, 70.7, 69.5, 64.3, 55.5, 52.6, 51.9, 51.7, 33.6, 32.7, 20.53, 20.48; IR (neat, cm^{-1}) 2954, 1732, 1607, 1435, 1372, 1281, 1223, 1107, 1038; MS (ESI, m/z) 645 ($M+K^+$), 629 ($M+Na^+$), 624 ($M+NH_4^+$), 607 ($M+H^+$); Anal. Calcd. for $C_{29}H_{34}O_{14}$ (%): C 57.42, H 5.65; Found: C 57.39, H 5.61.

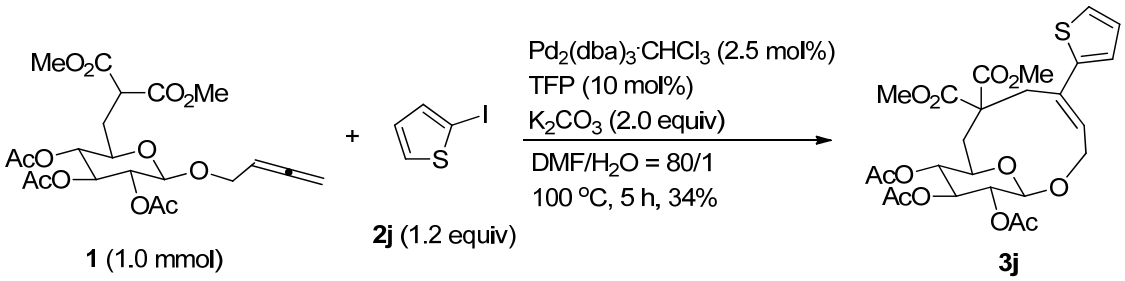
(9) Preparation of **3i**. (hx-6-11)



The reaction of K_2CO_3 (276.3 mg, 2.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (25.6 mg, 0.025 mmol), TFP (23.3 mg, 0.1 mmol), **1** (470.7 mg, 1.0 mmol), and **2i** (295.4 mg, 1.2 mmol) in DMF/H_2O (*V*/*V* = 80/1, 40.0 mL) at 100 °C for 5 h afforded **3i** (201.4 mg, 34%) as a solid after chromatography on silica gel (eluent: petroleum ether/ethyl acetate (2/1)): M.P. 108-109 °C (*n*-hexane/EtOAc); $[\alpha]^{20}_D$ = + 111.5 (*c* = 1.105, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2 H, ArH), 7.36 (d, *J* = 7.8 Hz, 2 H, ArH), 6.07 (t, *J* = 8.0 Hz, 1 H, CH=), 5.23-5.08 (m, 2 H), 4.99 (d, *J* = 6.0 Hz,

1 H), 4.89 (s, 1 H), 4.45-4.25 (m, 2 H), 3.92 (d, *J* = 13.8 Hz, 1 H), 3.84-3.69 (m, 1 H), 3.76 (s, 3 H, Me), 3.31 (d, *J* = 14.1 Hz, 1 H), 2.90 (s, 3 H, Me), 2.75-2.55 (m, 1 H), 2.59 (s, 3 H, Me), 2.18-1.96 (m, 1 H), 2.09 (s, 3 H, Me), 2.07 (s, 3 H, Me), 2.05 (s, 3 H, Me); ^{13}C NMR (75 Hz, $CDCl_3$) δ 197.3, 170.5, 170.3, 169.7, 169.5, 169.3, 146.3, 144.1, 136.0, 129.8, 127.8, 127.2, 102.1, 73.71, 73.67, 70.8, 69.6, 64.3, 55.6, 52.6, 51.7, 33.6, 32.7, 26.4, 20.54, 20.49; IR (KBr) ν (cm^{-1}) 2954, 1753, 1736, 1685, 1603, 1437, 1370, 1247, 1221, 1134, 1107, 1039; MS (ESI, m/z) 608 ($M+NH_4^+$); Anal. Calcd. for $C_{29}H_{34}O_{13}$ (%): C 58.98, H 5.80; Found: C 58.69, H 5.80.

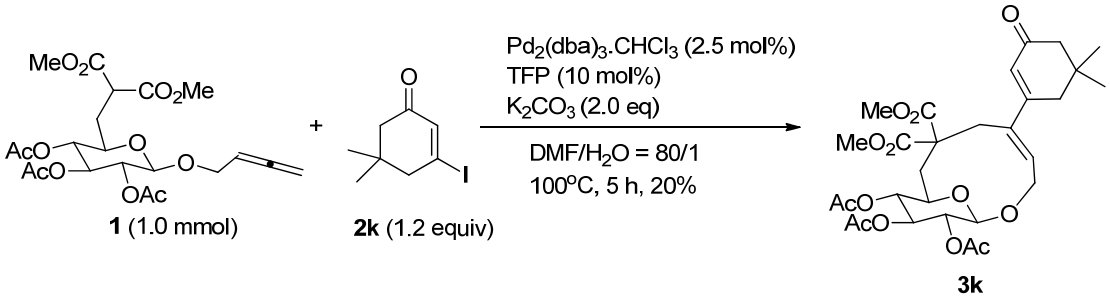
(10) Preparation of **3j**. (hx-5-164, hx-5-72)



The reaction of K_2CO_3 (277.3 mg, 2.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (25.8 mg, 0.025 mmol), TFP (23.4 mg, 0.1 mmol), **1** (472.0 mg, 1.0 mmol), and **2j** (253.1 mg, 1.2 mmol) in DMF/H_2O (*V/V* = 80/1, 40.0 mL) at 100 °C for 5 h afforded **3j** (188.8 mg, 34%) as a solid after chromatography on silica gel (eluent: petroleum ether/ethyl acetate (2/1)): M.P. 96-97 °C (*n*-hexane/EtOAc); $[\alpha]^{20}_D$ = + 116.4 (*c* = 1.085, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 3.6 Hz, 1 H, ArH), 6.88-6.75 (m, 2 H, ArH), 6.08 (t, *J* = 7.5 Hz, 1 H, CH=), 5.12-4.95 (m, 2 H), 4.86 (d, *J* = 5.1 Hz, 1 H), 4.74 (s, 1 H), 4.31-4.11 (m, 2 H), 3.83-3.59 (m, 2 H), 3.66 (s, 3 H, Me), 3.20-3.00 (m, 1 H), 3.09 (s, 3 H, Me), 2.63 (t, *J* = 13.5 Hz, 1 H), 2.11-1.86 (m, 1 H), 1.98 (s, 3 H, Me), 1.94 (s, 6 H, Me × 2); ^{13}C NMR (75 Hz, $CDCl_3$) δ 170.7, 170.6, 169.6, 169.3,

169.2, 144.1, 137.8, 127.3, 126.6, 124.7, 124.3, 101.8, 73.7, 73.5, 70.6, 69.4, 64.1, 55.7, 52.4, 51.9, 33.6, 20.42, 20.39, 20.36; IR (KBr) ν (cm^{-1}) 3104, 3030, 2953, 2843, 1755, 1736, 1437, 1371, 1245, 1221, 1120, 1102, 1039; MS (ESI, m/z) 593 ($M+K^+$), 577 ($M+Na^+$), 572 ($M+NH_4^+$), 555 ($M+H^+$); Anal. Calcd. for $C_{25}H_{30}O_{12}S$ (%): C 54.14, H 5.45; Found: C 53.80, H 5.37.

(11) Preparation of **3k**. (hx-6-78)

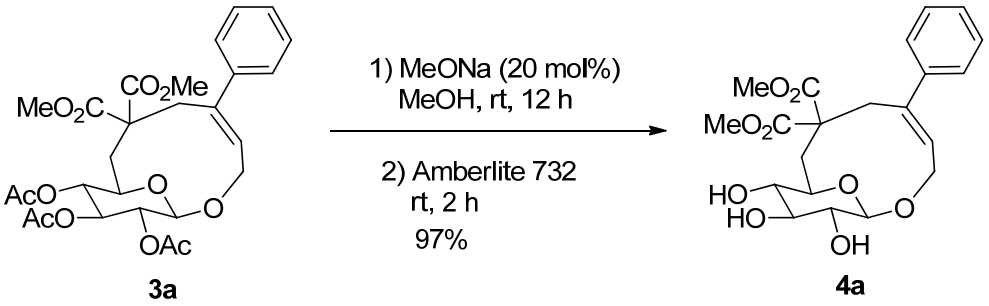


The reaction of K_2CO_3 (276.2 mg, 2.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (25.7 mg, 0.025 mmol), TFP (22.8 mg, 0.1 mmol), **1** (472.4 mg, 1.0 mmol), and **2k** (300.5 mg, 1.2 mmol) in DMF/H_2O (*V*/*V* = 80/1, 40.0 mL) at 100 °C for 5 h afforded **3k** (120.3 mg, 20%) as a solid after chromatography on silica gel (eluent: petroleum ether/ethyl acetate (2/1)): M.P. 104-106 °C (*n*-hexane/EtOAc); $[\alpha]^{20}_D$ = + 96.0 (*c* = 0.95, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.26 (t, *J* = 7.7 Hz, 1 H, CH=), 5.95 (s, 1 H, CH=), 5.23-5.00 (m, 2 H), 5.10-4.90 (m, 1 H), 4.83 (s, 1 H), 4.42-4.18 (m, 2 H), 3.90-3.68 (m, 2 H), 3.79 (s, 3 H, Me), 3.55 (s, 3 H, Me), 3.09 (d, *J* = 14.4 Hz, 1 H), 2.60-2.33 (m, 2 H), 2.32-2.17 (m, 3 H), 2.15-1.93 (m, 1 H), 2.08 (s, 3 H, Me), 2.05 (s, 6 H, Me × 2), 1.07 (s, 3 H), 1.04 (s, 3 H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 200.1, 171.2, 170.5, 169.8, 169.6, 169.4, 158.2, 143.7, 128.9, 124.1, 102.2, 74.2, 73.4, 70.5, 70.1, 64.2, 55.2, 52.7, 52.4, 50.8, 42.1, 33.6, 33.3, 31.3, 28.6, 27.5, 20.64, 20.59, 20.57; IR (KBr)

ν (cm^{-1}) 2956, 1755, 1736, 1664, 1438, 1370, 1304, 1245, 1223, 1112, 1039; MS (ESI, m/z) 617 ($M+Na^+$), 595 ($M+H^+$); Anal. Calcd. for $C_{29}H_{38}O_{13}$ (%): C 58.58, H 6.44; Found: C 58.45, H 6.56.

2. **Synthesis of cyclic glucosides 4 by deacetylation of 3.**[1]

(1) Preparation of **4a**. (hx-8-143)

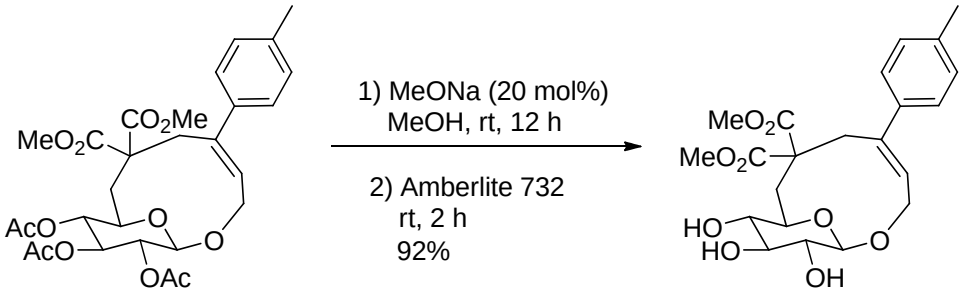


Typical Procedure II: To a 50-mL round-bottom flask were added **3a** (304.7 mg, 0.556 mmol), MeOH (30.0 mL), and MeONa (5.9 mg, 0.111 mmol) sequentially. The reaction was complete after being stirred at room temperature for 12 h as monitored by TLC (eluent: ethyl acetate /methanol = 6/1). Then Amberlite 732 was added to quench the reaction, which was filtered after the result mixture stirring at rt for 2 h. After evaporation of the solvent, chromatography on silica gel (eluent: ethyl acetate/methanol = 6/1) afforded **4a** (228.0 mg, 97%) as a syrup: $[\alpha]^{20}_D$ = + 132.0 (*c* = 0.38, MeOH); ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.38-7.20 (m, 5 H, ArH), 5.94 (t, *J* = 8.3 Hz, 1 H, CH=), 5.42 (d, *J* = 5.1 Hz, 1 H), 5.23 (d, *J* = 3.9 Hz, 1 H), 5.02 (s, 1 H), 4.67 (s, 1 H), 4.30-4.16 (m, 2 H), 3.91 (d, *J* = 13.8 Hz, 1 H), 3.68 (s, 3 H, Me), 3.34-3.08 (m, 5 H), 2.87 (s, 3 H, Me), 2.30 (dd, J_1 = 14.9 Hz, J_2 = 11.6 Hz, 1 H), 2.16 (d, *J* = 13.2 Hz, 1 H); ^{13}C NMR (75 Hz, d_6-DMSO) δ 171.7, 145.0, 142.5, 130.0,

128.9, 128.4, 128.0, 108.0, 78.1, 77.7, 74.4, 73.7, 64.5, 56.4, 53.5, 52.6, 35.4, 33.6; IR (neat) ν (cm^{-1}) 3406, 3023, 2951, 2921, 1735, 1635, 1461, 1439, 1308, 1251, 1208, 1178, 1097, 1029; MS (ESI, m/z) 467 ($M+COOH^-$); HRMS calcd. for $C_{21}H_{26}O_9Na$ ($M+Na^+$): 445.1469; Found: 445.1478.

The following compounds were prepared according to **Typical Procedure II.**

(2) Preparation of **4b**. (hx-8-141)

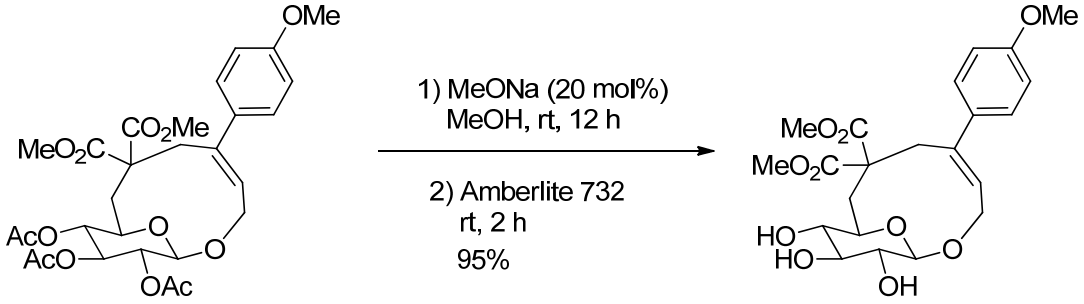


3b **4b**

The reaction of **3b** (159.7 mg, 0.284 mmol), and MeONa (3.0 mg, 0.0568 mmol) in MeOH (30.0 mL) at room temperature for 12 h afforded **4b** (114.3 mg, 92%) after filtration of Amberlite 732 (added to quench the reaction with stirring for another 2 h) and chromatography on silica gel (eluent: ethyl acetate/methanol = 6/1) as a syrup: $[\alpha]^{20}_D$ = + 141.7 (*c* = 0.52, MeOH); ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.20-7.05 (m, 4 H, ArH), 5.90 (t, *J* = 7.8 Hz, 1 H, CH=), 5.42 (d, *J* = 5.1 Hz, 1 H), 5.23 (d, *J* = 4.8 Hz, 1 H), 5.02 (d, *J* = 2.7 Hz, 1 H), 4.66 (s, 1 H), 4.30-4.15 (m, 2 H), 3.88 (d, *J* = 13.5 Hz, 1 H), 3.67 (s, 3 H, Me), 3.35-3.07 (m, 5 H), 2.90 (s, 3 H, Me), 2.38-2.10 (m, 2 H), 2.29 (s, 3 H, Me); ^{13}C NMR (75 Hz, d_6-DMSO) δ 171.8, 144.9, 139.6, 137.7, 129.5, 129.3, 127.9, 108.0, 78.1, 77.7, 74.4, 73.6, 64.5, 56.3, 53.5, 52.7, 35.4, 33.5, 21.7; IR (neat) ν (cm^{-1}) 3439, 3024, 2950, 2920, 1732, 1636, 1512, 1439, 1371, 1349, 1309, 1256, 1204, 1177, 1141, 1092, 1032; MS (ESI, m/z) 481 ($M+COOH^-$); HRMS calcd.

for $C_{22}H_{28}O_9Na$ ($M+Na^+$): 459.1626; Found: 459.1631.

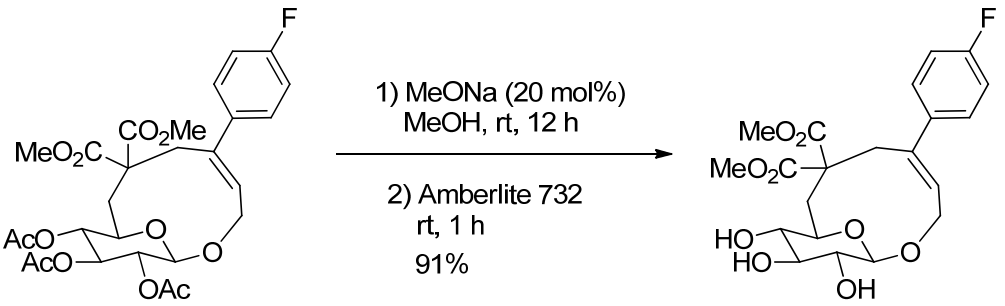
(3) Preparation of **3c**. (hx-8-138)



3c **4c**

The reaction of **3c** (141.2 mg, 0.244 mmol) and MeONa (2.6 mg, 0.05 mmol) in MeOH (30.0 mL) at room temperature for 12 h afforded **4c** (104.8 mg, 95%) after filtration of Amberlite 732 (added to quench the reaction with stirring for another 2 h) and chromatography on silica gel (eluent: ethyl acetate/methanol = 6/1) as a syrup: $[\alpha]^{20}_D$ = + 142.5 (*c* = 0.53, MeOH); ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.17 (d, *J* = 8.4 Hz, 2 H, ArH), 6.87 (d, *J* = 8.4 Hz, 2 H, ArH), 5.87 (t, *J* = 8.1 Hz, 1 H, CH=), 5.40 (d, *J* = 5.1 Hz, 1 H), 5.21 (d, *J* = 4.2 Hz, 1 H), 5.00 (s, 1 H), 4.65 (s, 1 H), 4.30-4.14 (m, 2 H), 3.88 (d, *J* = 13.5 Hz, 1 H), 3.76 (s, 3 H, Me), 3.68 (s, 3 H, Me), 3.34-3.07 (m, 5 H), 2.97 (s, 3 H, Me), 2.34-2.10 (m, 2 H); ^{13}C NMR (75 Hz, d_6-DMSO) δ 171.81, 171.76, 159.7, 144.5, 134.7, 129.1, 128.7, 114.3, 108.0, 78.1, 77.7, 74.4, 73.6, 64.5, 56.3, 56.1, 53.5, 52.8, 35.3, 33.6; IR (neat) ν (cm^{-1}) 3436, 2950, 2926, 2838, 1732, 1607, 1572, 1511, 1441, 1376, 1309, 1289, 1250, 1205, 1183, 1142, 1092, 1032; MS (ESI, m/z) 497 ($M+COOH^-$); HRMS calcd. for $C_{22}H_{28}O_{10}Na$ ($M+Na^+$): 475.1575; Found: 475.1581.

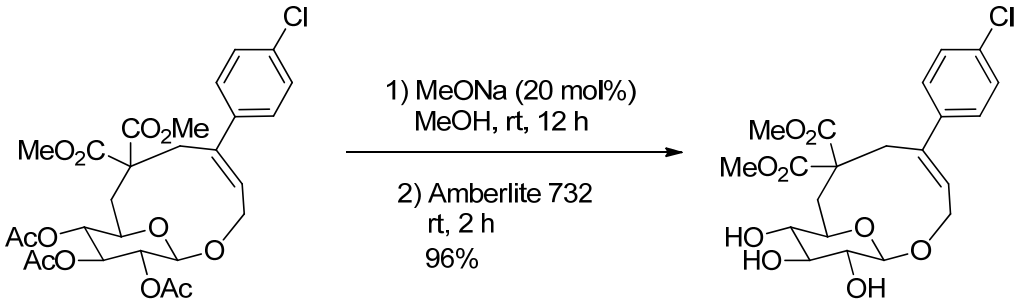
(4) Preparation of **4d**. (hx-8-124)



3d **4d**

The reaction of **3d** (231.2 mg, 0.41 mmol) and MeONa (4.5 mg, 0.082 mmol) in MeOH (30.0 mL) at room temperature for 12 h afforded **4d** (163.0 mg, 91%) after filtration of Amberlite 732 (added to quench the reaction with stirring for another 1 h) and chromatography on silica gel (eluent: ethyl acetate/methanol = 6/1) as a syrup: $[\alpha]^{20}_{D}$ = + 125.4 (*c* = 0.32, MeOH); ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.40-7.06 (m, 4 H, ArH), 5.92 (t, *J* = 7.4 Hz, 1 H, CH=), 5.42 (d, *J* = 3.9 Hz, 1 H), 5.23 (d, *J* = 3.3 Hz, 1 H), 5.03 (s, 1 H), 4.66 (s, 1 H), 4.33-4.12 (m, 2 H), 3.90 (d, *J* = 13.8 Hz, 1 H), 3.68 (s, 3 H, Me), 3.36-3.05 (m, 5 H), 2.96 (s, 3 H, Me), 2.36-2.09 (m, 2 H); ^{13}C NMR (75 Hz, d_6-DMSO) δ 171.8, 171.7, 162.6 (d, *J* = 242.6 Hz), 143.9, 138.9, 130.2, 130.1 (d, *J* = 8.3 Hz), 115.7 (d, *J* = 21.4 Hz), 108.0, 78.0, 77.7, 74.5, 73.7, 64.5, 56.3, 53.6, 52.8, 35.4, 33.7; ^{19}F NMR (282 MHz, d_6-DMSO) δ -114.3 (s, 1 F); IR (neat) ν (cm^{-1}) 3433, 3319, 2953, 2931, 2891, 1732, 1628, 1601, 1508, 1475, 1444, 1378, 1321, 1262, 1221, 1205, 1184, 1091, 1033; MS (ESI, m/z) 485 ($M+COOH^-$); HRMS calcd. for $C_{21}H_{25}FO_9Cl^{35}$ ($M+(^{35}Cl)^-$): 475.1177; Found: 475.1173.

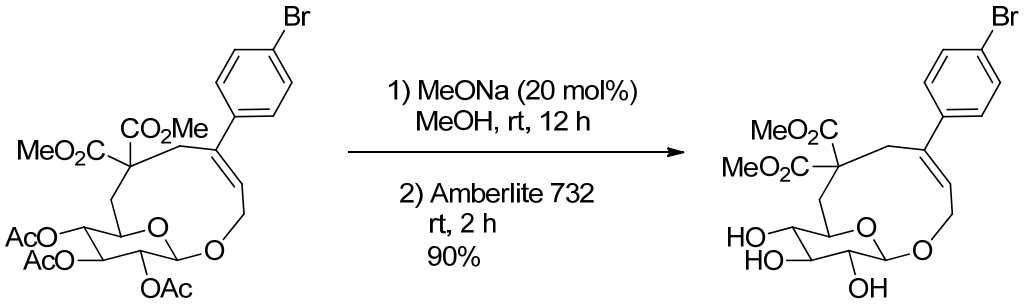
(5) Preparation of **4e** (hx-8-142)



3e **4e**

The reaction of **3e** (171.0 mg, 0.294 mmol) and MeONa (3.3 mg, 0.059 mmol) in MeOH (30.0 mL) at room temperature for 12 h afforded **4e** (128.8 mg, 96%) after filteration of Amberlite 732 (added to quench the reaction with stirring for another 2 h) and chromatography on silica gel (eluent: ethyl acetate/methanol = 6/1) as a syrup: $[\alpha]^{20}_{D}$ = + 140.4 (*c* = 0.43, MeOH); ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.38 (d, *J* = 8.4 Hz, 2 H, ArH), 7.27 (d, *J* = 7.8 Hz, 2 H, ArH), 5.96 (t, *J* = 8.0 Hz, 1 H), 5.41 (d, *J* = 4.2 Hz, 1 H), 5.22 (s, 1 H), 5.01 (s, 1 H), 4.66 (s, 1 H), 4.30-4.14 (m, 2 H), 3.91 (d, *J* = 14.1 Hz, 1 H), 3.68 (s, 3 H, Me), 3.35-3.06 (m, 5 H), 2.96 (s, 3 H, Me), 2.32-2.10 (m, 2 H); ^{13}C NMR (75 Hz, d_6-DMSO) δ 171.8, 171.6, 143.8, 141.4, 133.1, 130.6, 129.9, 128.9, 108.0, 78.0, 77.6, 74.4, 73.7, 64.4, 56.4, 53.6, 52.7, 35.4, 33.5; IR (neat) ν (cm^{-1}) 3435, 2951, 2890, 1732, 1629, 1491, 1475, 1439, 1401, 1377, 1349, 1310, 1257, 1207, 1139, 1092, 1032; MS (ESI, m/z) 503 (M(^{37}Cl)+$COOH^-$), 501 (M(^{35}Cl)+$COOH^-$); HRMS calcd. for $C_{21}H_{25}{}^{35}ClO_9Na$ (M(^{35}Cl) +Na^+): 479.1079; Found: 479.1083.

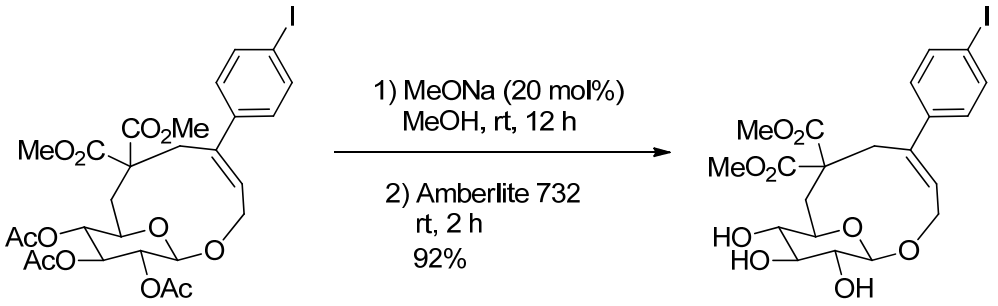
(6) Preparation of **4f**. (hx-8-123)



3f **4f**

The reaction of **3f** (848.5 mg, 1.35 mmol) and MeONa (14.7 mg, 0.27 mmol) in MeOH (50.0 mL) at room temperature for 12 h afforded **4f** (608.7 mg, 90%) after filtration of Amberlite 732 (added to quench the reaction with stirring for another 2 h) and chromatography on silica gel (eluent: ethyl acetate/methanol = 6/1) as a syrup: $[\alpha]^{20}_{D}$ = + 131.2 (*c* = 0.72, MeOH); ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.51 (d, *J* = 8.7 Hz, 2 H, ArH), 7.21 (d, *J* = 8.4 Hz, 2 H, ArH), 5.96 (t, *J* = 8.3 Hz, 1 H, CH=), 5.42 (d, *J* = 5.4 Hz, 1 H), 5.24 (d, *J* = 5.1 Hz, 1 H), 5.03 (d, *J* = 3.9 Hz, 1 H), 4.66 (d, *J* = 1.2 Hz, 1 H), 4.30-4.15 (m, 2 H), 3.90 (d, *J* = 13.8 Hz, 1 H), 3.68 (s, 3 H, Me), 3.33-3.07 (m, 5 H), 2.96 (s, 3 H, Me), 2.33-2.10 (m, 2 H); ^{13}C NMR (75 Hz, d_6-DMSO) δ 171.7, 171.6, 143.8, 141.7, 131.8, 130.6, 130.2, 121.6, 108.0, 78.0, 77.6, 74.4, 73.6, 64.3, 56.3, 53.5, 52.7, 35.4, 33.4; IR (neat) ν (cm^{-1}) 3435, 2951, 2917, 1734, 1486, 1438, 1352, 1310, 1252, 1207, 1180, 1091, 1031, 1010; MS (ESI, m/z) 547 (M(^{81}Br)+$COOH^-$), 545 (M(^{79}Br)+$COOH^-$); HRMS calcd. for $C_{21}H_{25}{}^{79}BrO_9{}^{35}Cl$ (M(^{79}Br)+($^{35}Cl)^-$): 535.0376; Found: 535.0358.

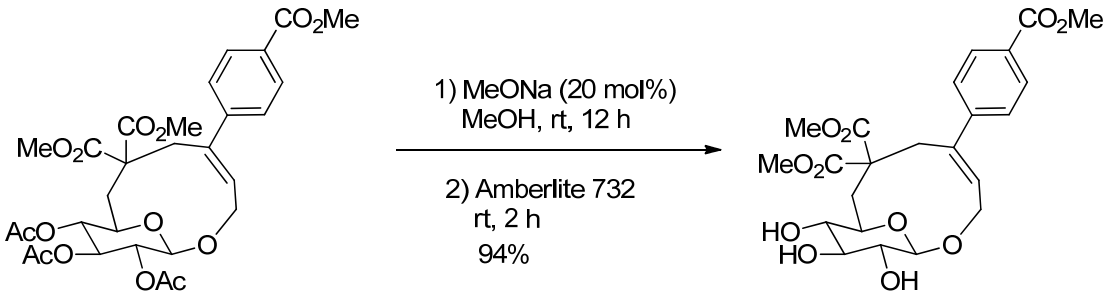
(7) Preparation of **4g**. (Hx-8-127)



3g **4g**

The reaction of **3g** (441.7 mg, 0.655 mmol) and MeONa (7.0 mg, 0.13 mmol) in MeOH (40.0 mL) at room temperature for 12 h afforded **4g** (331.3 mg, 92%) after filtration of Amberlite 732 (added to quench the reaction with stirring for another 2 h) and chromatography on silica gel (eluent: ethyl acetate/methanol = 6/1) as a syrup: $[\alpha]^{20}_{D}$ = + 129.9 (*c* = 0.50, MeOH); ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.68 (d, *J* = 8.4 Hz, 2 H, ArH), 7.05 (d, *J* = 8.1 Hz, 2 H, ArH), 5.95 (t, *J* = 8.1 Hz, 1 H, CH=), 5.40 (d, *J* = 4.5 Hz, 1 H), 5.21 (d, *J* = 3.6 Hz, 1 H), 5.01 (s, 1 H), 4.66 (s, 1 H), 4.30-4.15 (m, 2 H), 3.89 (d, *J* = 14.1 Hz, 1 H), 3.68 (s, 3 H, Me), 3.34-3.06 (m, 5 H), 2.95 (s, 3 H, Me), 2.33-2.10 (m, 2 H); ^{13}C NMR (75 Hz, d_6-DMSO) δ 171.8, 171.6, 144.0, 142.1, 137.7, 130.5, 130.3, 108.0, 94.5, 78.0, 77.6, 74.4, 73.6, 64.4, 56.3, 53.6, 52.7, 35.4, 33.4; IR (neat) ν (cm^{-1}) 3524, 3472, 3429, 2950, 2925, 1735, 1720, 1437, 1382, 1309, 1259, 1204, 1128, 1091, 1028, 1005; MS (ESI, m/z) 593 ($M+COOH^-$); HRMS calcd. for $C_{21}H_{25}IO_9{}^{35}Cl$ ($M+(^{35}Cl)^-$): 583.0237; Found: 583.0245.

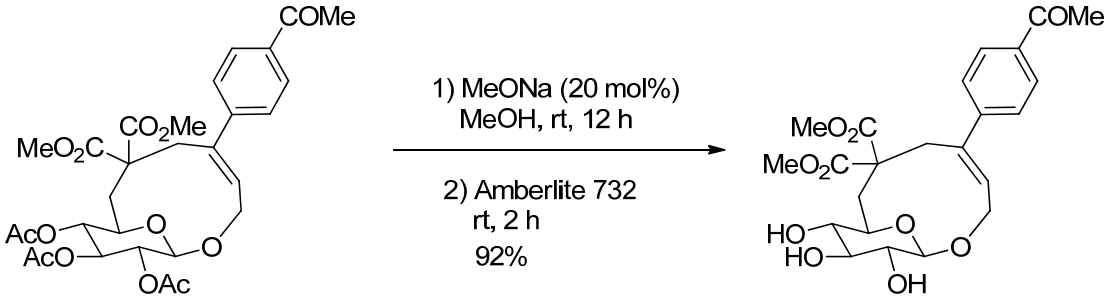
(8) Preparation of **4h**. (Hx-8-137)



3h **4h**

The reaction of **3h** (319.6 mg, 0.527 mmol) and MeONa (5.7 mg, 0.105 mmol) in MeOH (30.0 mL) at room temperature for 12 h afforded **4h** (238.8 mg, 94%) after filtration of Amberlite 732 (added to quench the reaction with stirring for another 2 h) and chromatography on silica gel (eluent: ethyl acetate/methanol = 6/1) as a syrup: $[\alpha]^{20}_{D}$ = + 160.6 (*c* = 0.325, MeOH); ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.91 (d, *J* = 8.1 Hz, 2 H, ArH), 7.40 (d, *J* = 8.1 Hz, 2 H, ArH), 6.04 (t, *J* = 7.8 Hz, 1 H, CH=), 5.42 (d, *J* = 4.8 Hz, 1 H), 5.23 (d, *J* = 4.5 Hz, 1 H), 5.03 (s, 1 H), 4.68 (s, 1 H), 4.33-4.14 (m, 2 H), 3.94 (d, *J* = 14.1 Hz, 1 H), 3.87 (s, 3 H, Me), 3.68 (s, 3 H, Me), 3.36-3.08 (m, 5 H), 2.88 (s, 3 H, Me), 2.34-2.09 (m, 2 H); ^{13}C NMR (75 Hz, d_6-DMSO) δ 164.04, 163.95, 159.7, 139.9, 136.6, 123.2, 121.8, 121.7, 120.2, 99.6, 70.0, 69.4, 66.4, 66.3, 56.4, 48.9, 44.6, 44.1, 43.9, 27.5, 25.3; IR (neat) ν (cm^{-1}) 3524, 3488, 3427, 3003, 2953, 2921, 2887, 1720, 1608, 1437, 1407, 1353, 1310, 1278, 1203, 1184, 1106, 1027; MS (ESI, m/z) 525 ($M+COOH^-$); HRMS calcd. for $C_{23}H_{28}O_{11}Na$ ($M+Na^+$): 503.1524; Found: 503.1535.

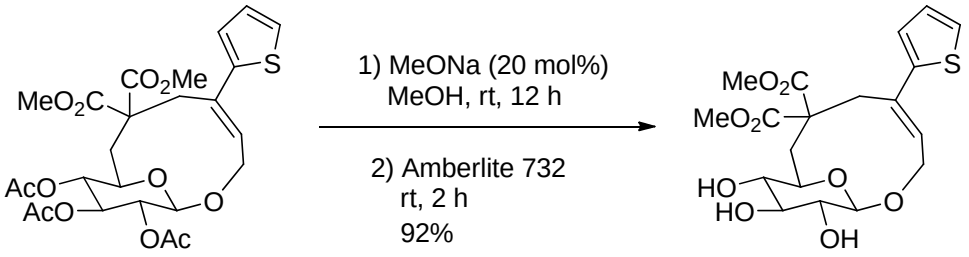
(9) Preparation of **4i**. (hx-8-128)



3i **4i**

The reaction of **3i** (360.2 mg, 0.61 mmol) and MeONa (6.5 mg, 0.122 mmol) in MeOH (30.0 mL) at room temperature for 12 h afforded **4i** (260.1 mg, 92%) after filtration of Amberlite 732 (added to quench the reaction with stirring for another 2 h) and chromatography on silica gel (eluent: ethyl acetate/methanol = 6/1) as a syrup: $[\alpha]^{20}_{D}$ = + 149.4 (*c* = 0.345, MeOH); ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.91 (d, *J* = 8.4 Hz, 2 H, ArH), 7.40 (d, *J* = 8.1 Hz, 2 H, ArH), 6.04 (t, *J* = 8.1 Hz, 1 H, CH=), 5.45 (s, 1 H), 5.26 (s, 1 H), 5.08 (s, 1 H), 4.68 (s, 1 H), 4.33-4.16 (m, 2 H), 3.94 (d, *J* = 14.1 Hz, 1 H), 3.68 (s, 3 H, Me), 3.36-3.05 (m, 5 H), 2.88 (s, 3 H, Me), 2.59 (s, 3 H, Me), 2.34-2.10 (m, 2 H); ^{13}C NMR (75 Hz, d_6-DMSO) δ 198.6, 171.8, 171.6, 147.3, 144.2, 136.7, 131.5, 128.9, 128.3, 108.1, 78.0, 77.6, 74.4, 73.6, 64.3, 56.3, 53.6, 52.7, 35.4, 33.4, 27.8; IR (neat) ν (cm^{-1}) 3436, 3315, 2930, 2888, 1729, 1681, 1625, 1602, 1560, 1476, 1444, 1402, 1382, 1366, 1319, 1307, 1268, 1243, 1224, 1204, 1182, 1140, 1118, 1093, 1033; MS (ESI, m/z) 509 ($M+COOH^-$); HRMS calcd. for $C_{23}H_{28}O_{10}{}^{35}Cl$ ($M+(^{35}Cl)^-$): 499.1376; Found: 499.1378.

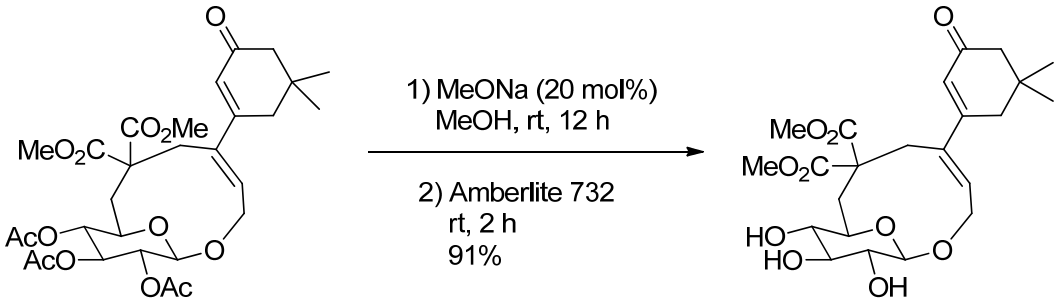
(10) Preparation of **4j**. (Hx-8-129)



3j **4j**

The reaction of **3j** (360.3 mg, 0.66 mmol) and MeONa (7.0 mg, 0.132 mmol) in MeOH (30.0 mL) at room temperature for 12 h afforded **4j** (256.8 mg, 92%) after filtration of Amberlite 732 (added to quench the reaction with stirring for another 2 h) and chromatography on silica gel (eluent: ethyl acetate/methanol = 6/1) as a syrup: $[\alpha]^{20}_{D}$ = + 161.3 (*c* = 0.395, MeOH); ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.42 (d, *J* = 4.8 Hz, 1 H, ArH), 7.05-6.95 (m, 2 H, ArH), 6.12 (t, *J* = 8.3 Hz, 1 H, CH=), 5.41 (d, *J* = 5.1 Hz, 1 H), 5.23 (d, *J* = 4.5 Hz, 1 H), 5.01 (d, *J* = 1.8 Hz, 1 H), 4.64 (s, 1 H), 4.30-4.15 (m, 2 H), 3.91 (d, *J* = 13.8 Hz, 1 H), 3.70 (s, 3 H, Me), 3.38-3.05 (m, 5 H), 3.19 (s, 3 H, Me), 2.30 (dd, J_1 = 14.7 Hz, J_2 = 11.7 Hz, 1 H), 2.17 (d, *J* = 13.5 Hz, 1 H); ^{13}C NMR (75 Hz, d_6-DMSO) δ 172.2, 171.7, 145.0, 138.1, 129.2, 128.2, 126.3, 125.7, 108.0, 78.1, 77.6, 74.3, 73.5, 64.2, 56.5, 53.5, 52.9, 35.5, 34.4; IR (neat) ν (cm^{-1}) 3482, 3387, 2950, 2922, 1735, 1629, 1462, 1437, 1370, 1346, 1306, 1247, 1197, 1176, 1096, 1030; MS (ESI, m/z) 473 ($M+COOH^-$); HRMS calcd. for $C_{19}H_{24}O_9SNa$ ($M+Na^+$):451.1033; Found: 451.1034.

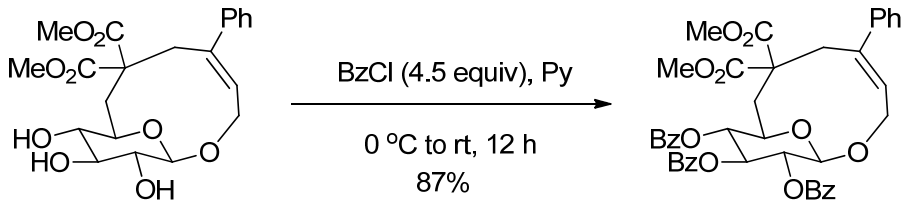
(11) Preparation of **4k**. (Hx-8-136)



3k **4k**

The reaction of **3k** (165.8 mg, 0.28 mmol) and MeONa (3.1 mg, 0.056 mmol) in MeOH (30.0 mL) at room temperature for 12 h afforded **4k** (119.2 mg, 91%) after filtration of Amberlite 732 (added to quench the reaction with stirring for another 2 h) and chromatography on silica gel (eluent: ethyl acetate/methanol = 6/1) as a syrup: $[\alpha]^{20}_{D}$ = + 133.0 (*c* = 0.345, MeOH); ^{1}H NMR (300 MHz, d_6-DMSO) δ 6.32 (t, *J* = 8.4 Hz, 1 H, CH=), 5.84 (s, 1 H, CH=), 5.41 (d, *J* = 5.1 Hz, 1 H), 5.24 (d, *J* = 5.1 Hz, 1 H), 5.02 (d, *J* = 3.3 Hz, 1 H), 4.63 (s, 1 H), 4.19 (d, *J* = 8.1 Hz, 2 H), 3.78 (d, *J* = 14.1 Hz, 1 H), 3.72 (s, 3 H, Me), 3.48 (s, 3 H, Me), 3.33-3.04 (m, 4 H), 2.94 (d, *J* = 14.1 Hz, 1 H), 2.59 (d, *J* = 18.0 Hz, 1 H), 2.28-2.05 (m, 5 H), 1.03 (s, 3 H, Me), 0.98 (s, 3 H, Me); ^{13}C NMR (75 Hz, d_6-DMSO) δ 200.2, 172.6, 171.5, 159.4, 143.4, 131.3, 124.3, 108.0, 77.8, 77.6, 74.5, 73.4, 64.1, 56.1, 53.6, 53.2, 51.5, 42.5, 35.5, 34.1, 31.8, 29.3, 28.3; IR (neat) ν (cm^{-1}) 3431, 2955, 1734, 1655, 1593, 1438, 1369, 1307, 1249, 1202, 1178, 1145, 1093, 1031; MS (ESI, m/z) 513 ($M+COOH^-$); HRMS calcd. for $C_{23}H_{32}O_{10}Na$ ($M+Na^+$): 491.1888; Found: 491.1901.

3. Synthesis of 5.[2] (hx-7-45)



4a **5**

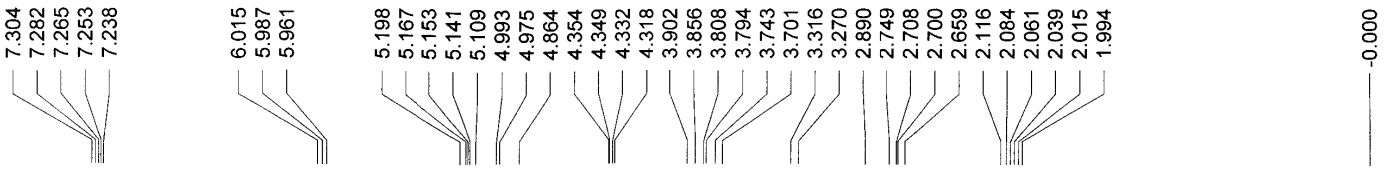
To a flame-dried Schlenk tube were added **4a** (169.6 mg, 0.4 mmol) and pyridine (2.0 mL). After BzCl (0.21 mL, d = 1.212 g/mL, 1.8 mmol) was injected by a springe at 0 ^{o}C, the resulting solution was allowed to warm up to room temperature and stirred for 12 hours as monitored by TLC. Then it was diluted with DCM (30 mL) and washed by 10 mL of diluted hydrochloric acid (3 M). The organic layer was separated and the aqueous layer was extracted with DCM (20 mL × 2). The combined organic layer was then washed with brine and dried over with anhydrous Na_2SO_4. After filtration and concentration, chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1) afforded **5** (256.1 mg, 87%) as a solid: M.P. 184-185 ^{o}C (*n*-hexane/EtOAc); $[\alpha]^{20}_{D}$ = + 60.7 (*c* = 1.215, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13-8.00 (m, 4 H, ArH), 7.93 (d, *J* = 7.5 Hz, 2 H, ArH), 7.60-7.20 (m, 15 H, ArH), 6.06 (t, *J* = 8.0 Hz, 1 H, CH=), 5.79 (t, *J* = 6.0 Hz, 1 H), 5.49-5.37 (m, 2 H), 5.17 (s, 1 H), 4.58-4.32 (m, 2 H), 4.07 (dd, J_1 = 11.4 Hz, J_2 = 3.0 Hz, 1 H), 3.95 (d, *J* = 13.8 Hz, 1 H), 3.73 (s, 3 H, Me), 3.36 (d, *J* = 14.1 Hz, 1 H), 3.26 (dd, J_1 = 14.9 Hz, J_2 = 12.5 Hz, 1 H), 2.82 (s, 3 H, Me), 2.32 (d, *J* = 15.0 Hz, 1 H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 171.1, 170.4, 165.32, 165.26, 165.1, 145.0, 141.7, 133.3, 133.2, 129.93, 129.88, 129.7, 129.15, 129.11, 129.0, 128.5, 128.3, 128.2, 127.8, 127.5, 127.3, 100.4, 73.9, 71.4, 71.3, 68.1, 63.8, 56.4, 52.5, 51.7, 34.1, 32.8; IR (KBr) ν (cm^{-1}) 2953, 1736, 1720, 1602, 1584, 1492, 1452, 1308, 1264, 1201, 1181, 1164, 1114, 1090, 1070, 1028; MS

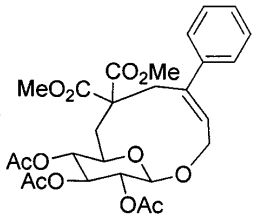
(ESI, m/z) 757 ($M+Na^+$), 752 ($M+NH_4^+$); Anal. Calcd. for $C_{42}H_{38}O_{12}$ (%): C 68.66, H 5.21; Found: C 68.77, H 5.27.

References

[1] Pietrzik, N.; Schmollinger, D.; Ziegler, T. *Beilstein J. Org. Chem.* **2008**, *4*, No. 30.

[2] P. Verma, B. Mukhopadhyay, *Carbohydrate Research* **2009**, *344*, 2554.

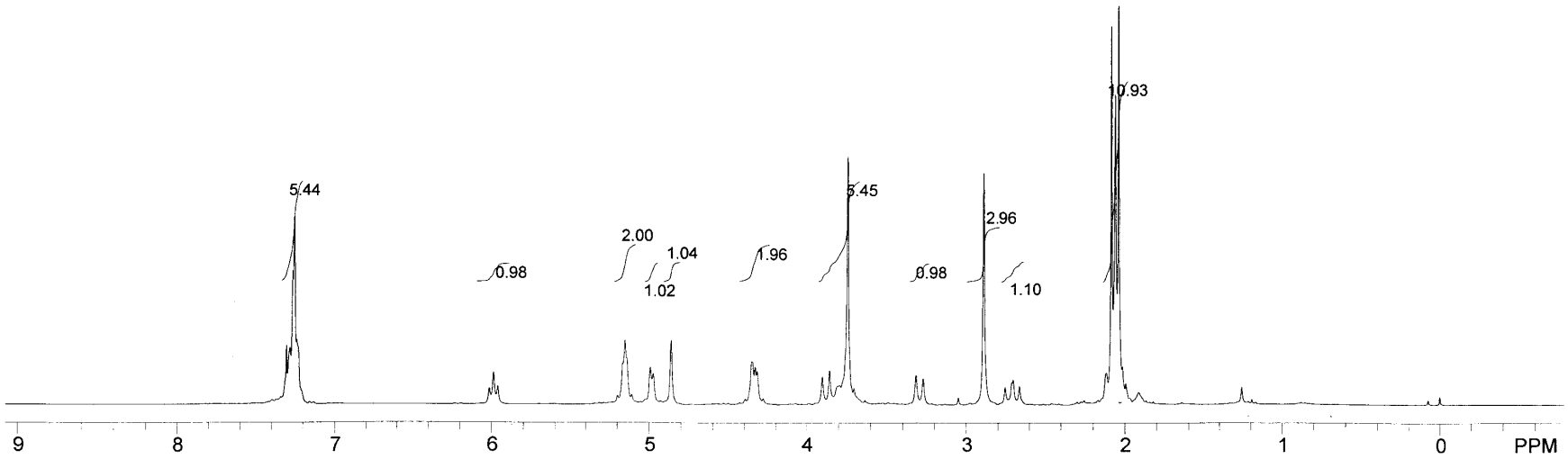


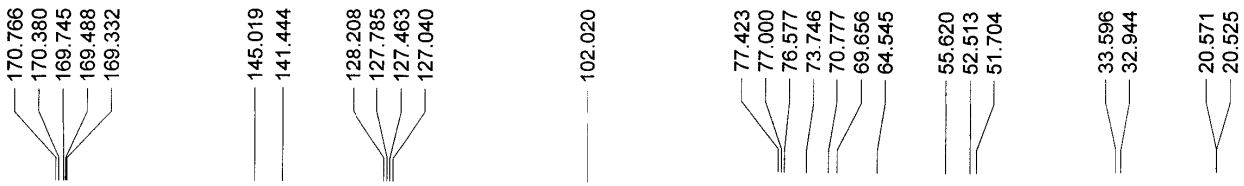


3a

hx-5-144

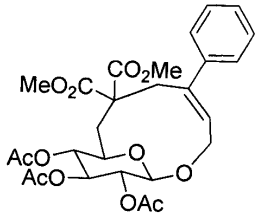
2012-05-22 20:41:23.937
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8



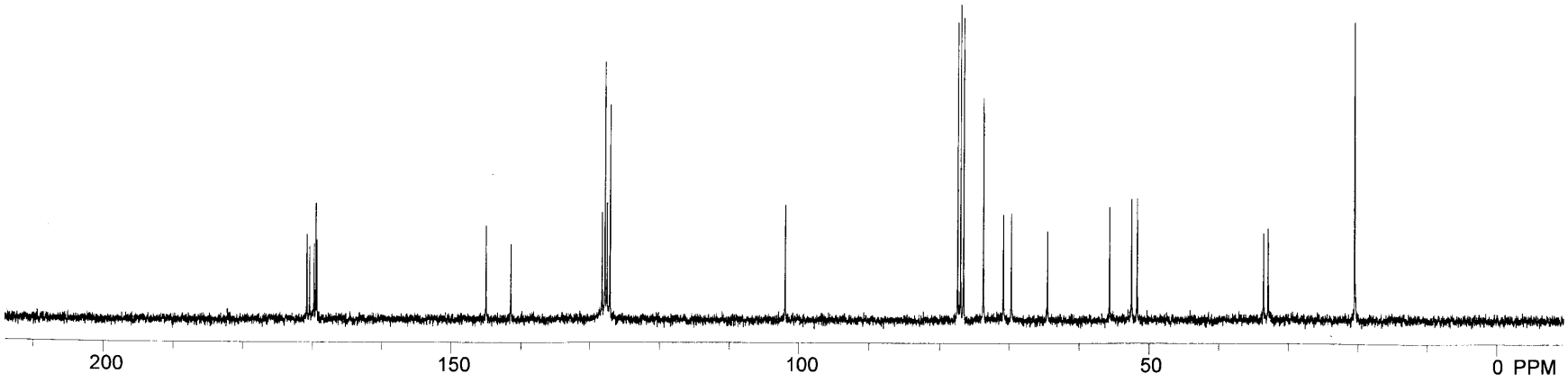


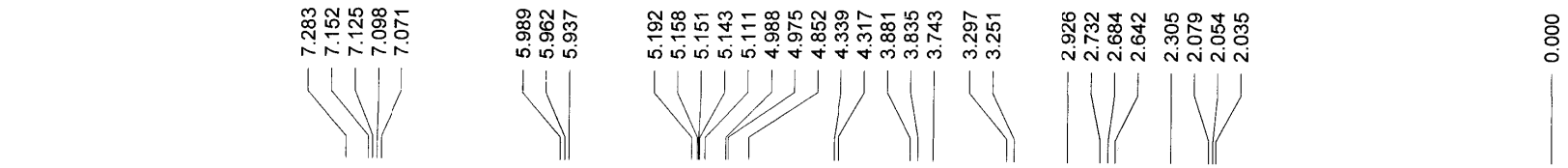
hx-5-144

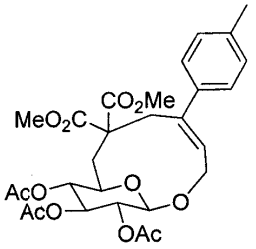
2012-05-22 20:49:37.734
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 110



3a



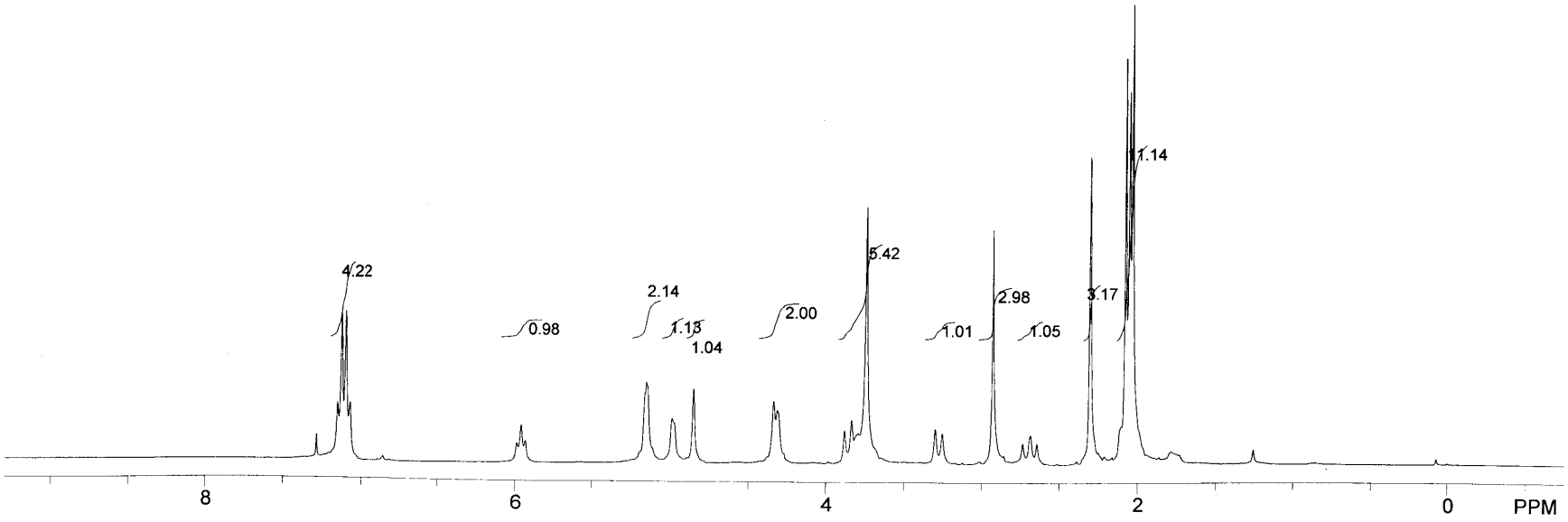


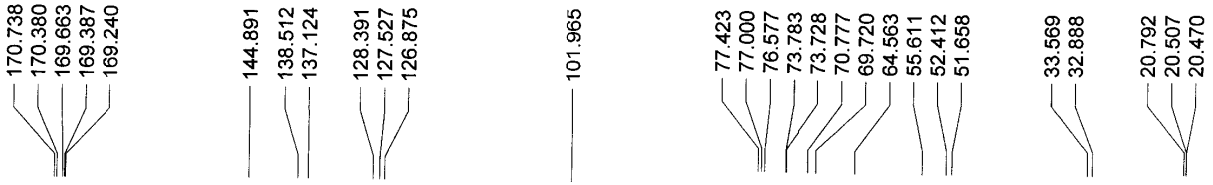


3b

hx-8-140

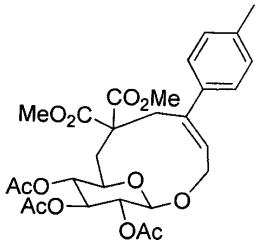
2013-07-17 18:51:05.453
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8



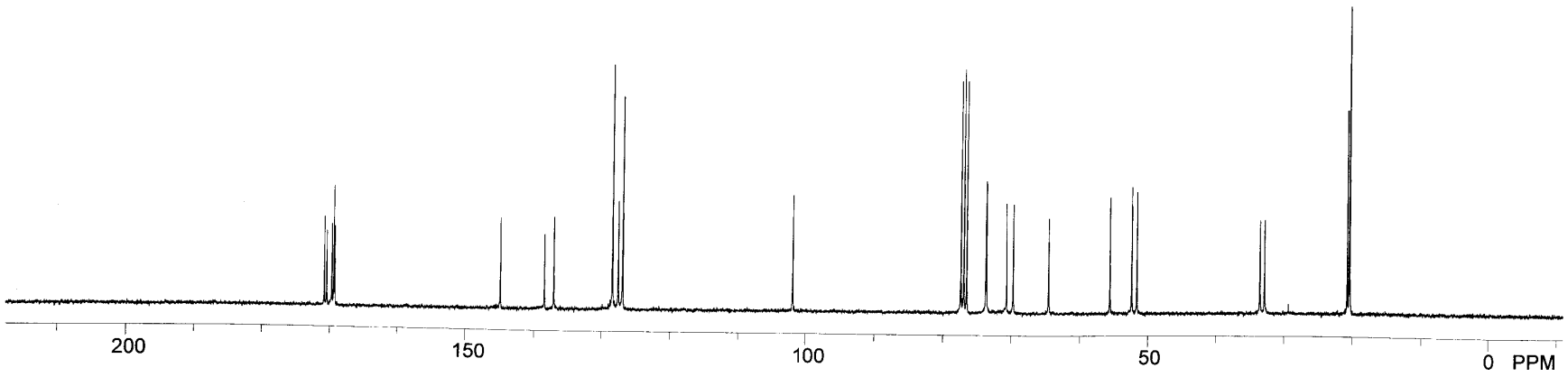


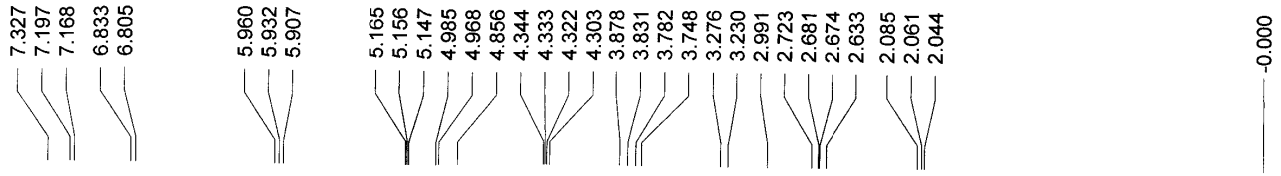
hx-8-140

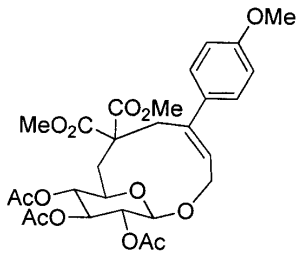
2013-07-17 14:27:17.265
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 535



3b

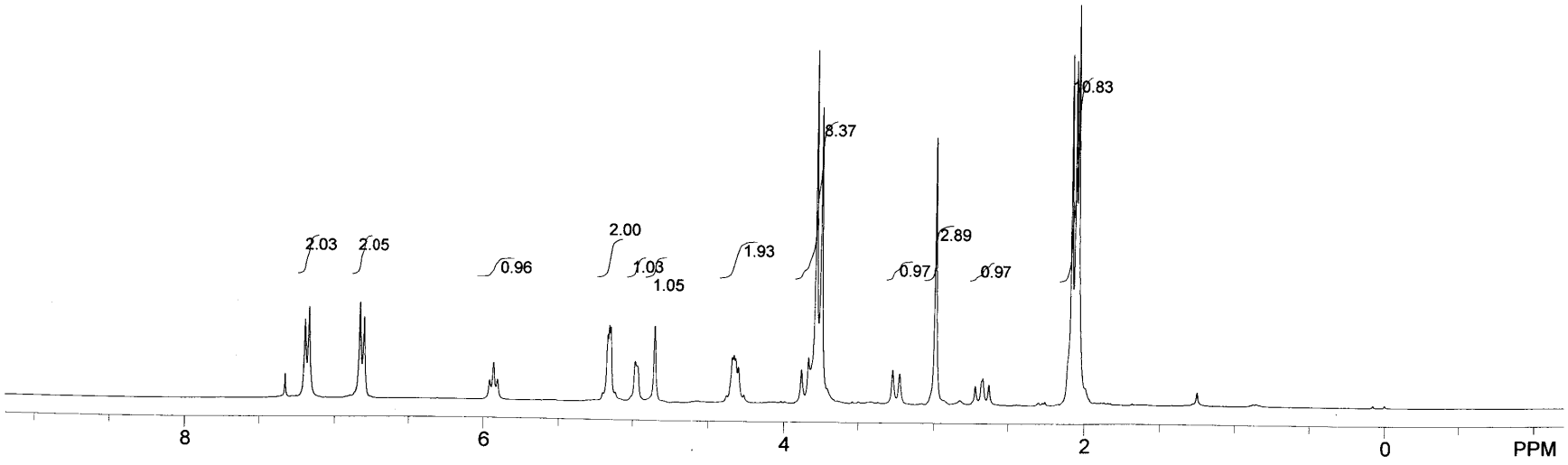


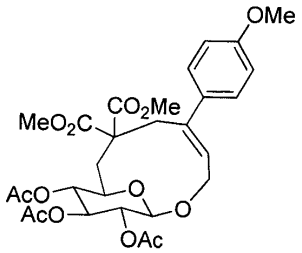




3c

hx-5-172
2012-07-07 08:57:41.359
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8

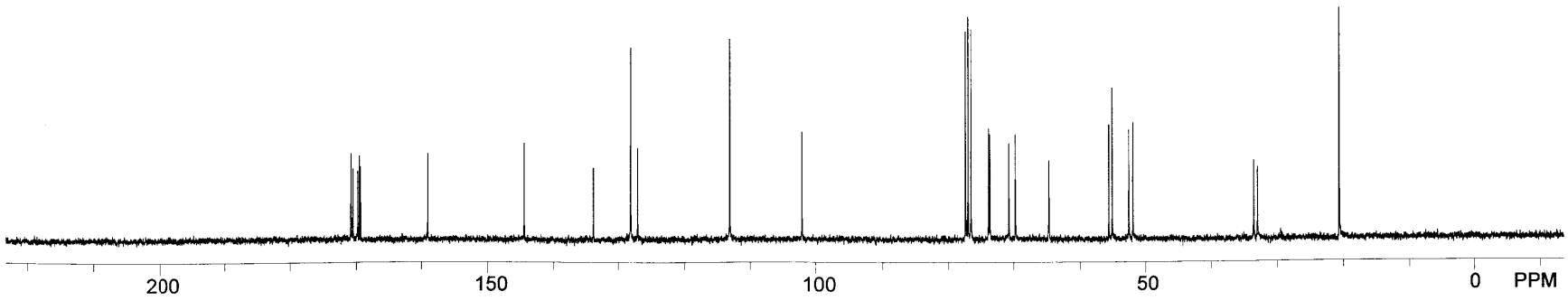


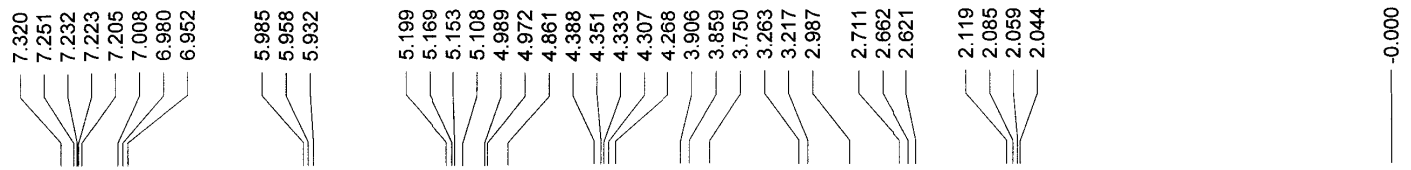


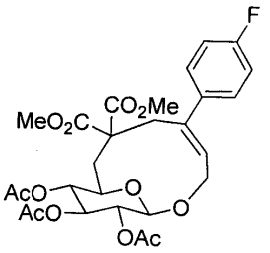
3c

hx-5-172

2012-07-07 09:05:44.828
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 116



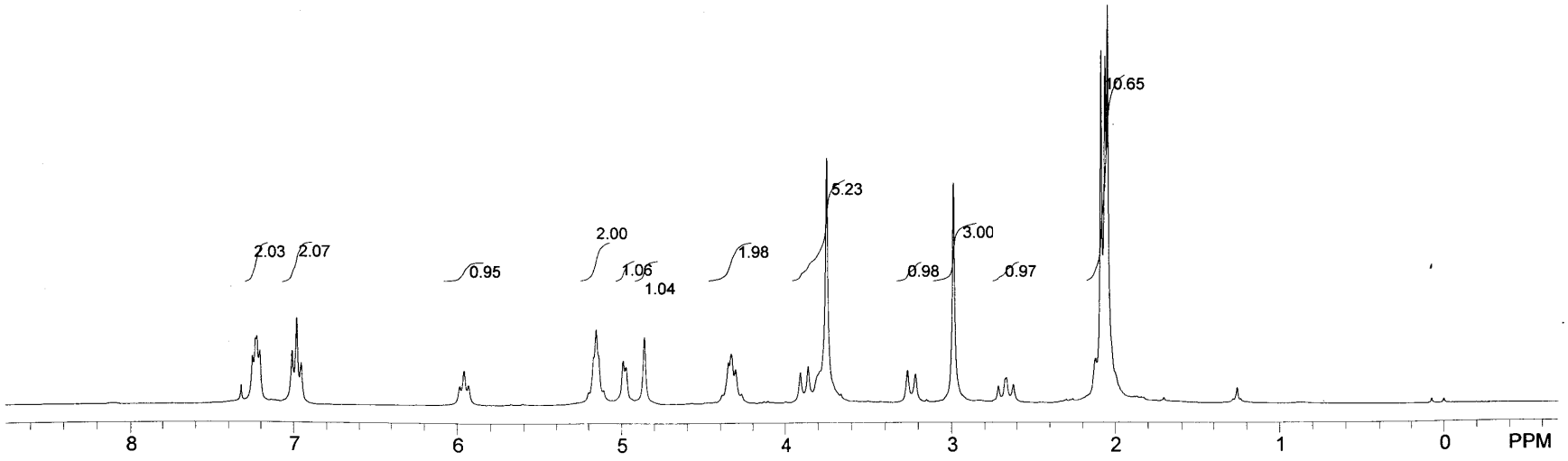




3d

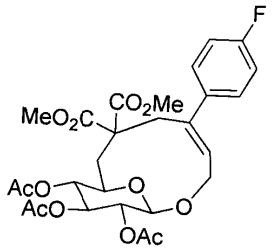
hx-6-10

2012-07-05 19:36:14.343
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8

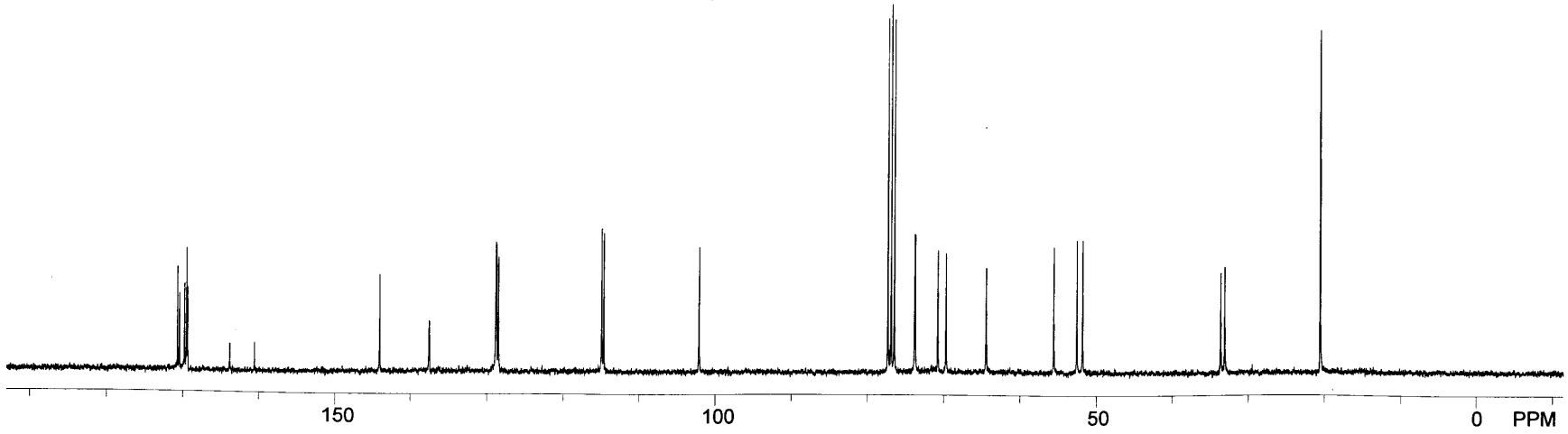


hx-6-10

2012-07-05 20:04:52.765
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 461



3d

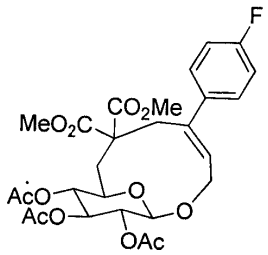


0.000

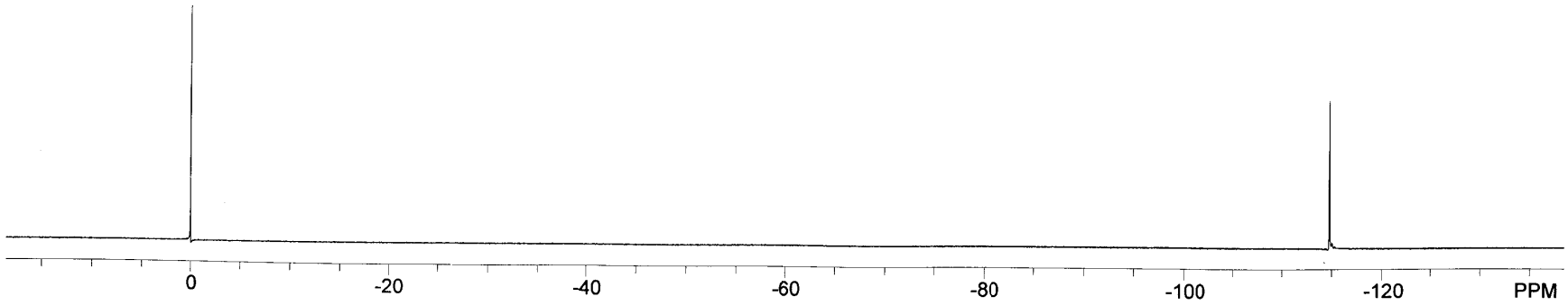
-114.796

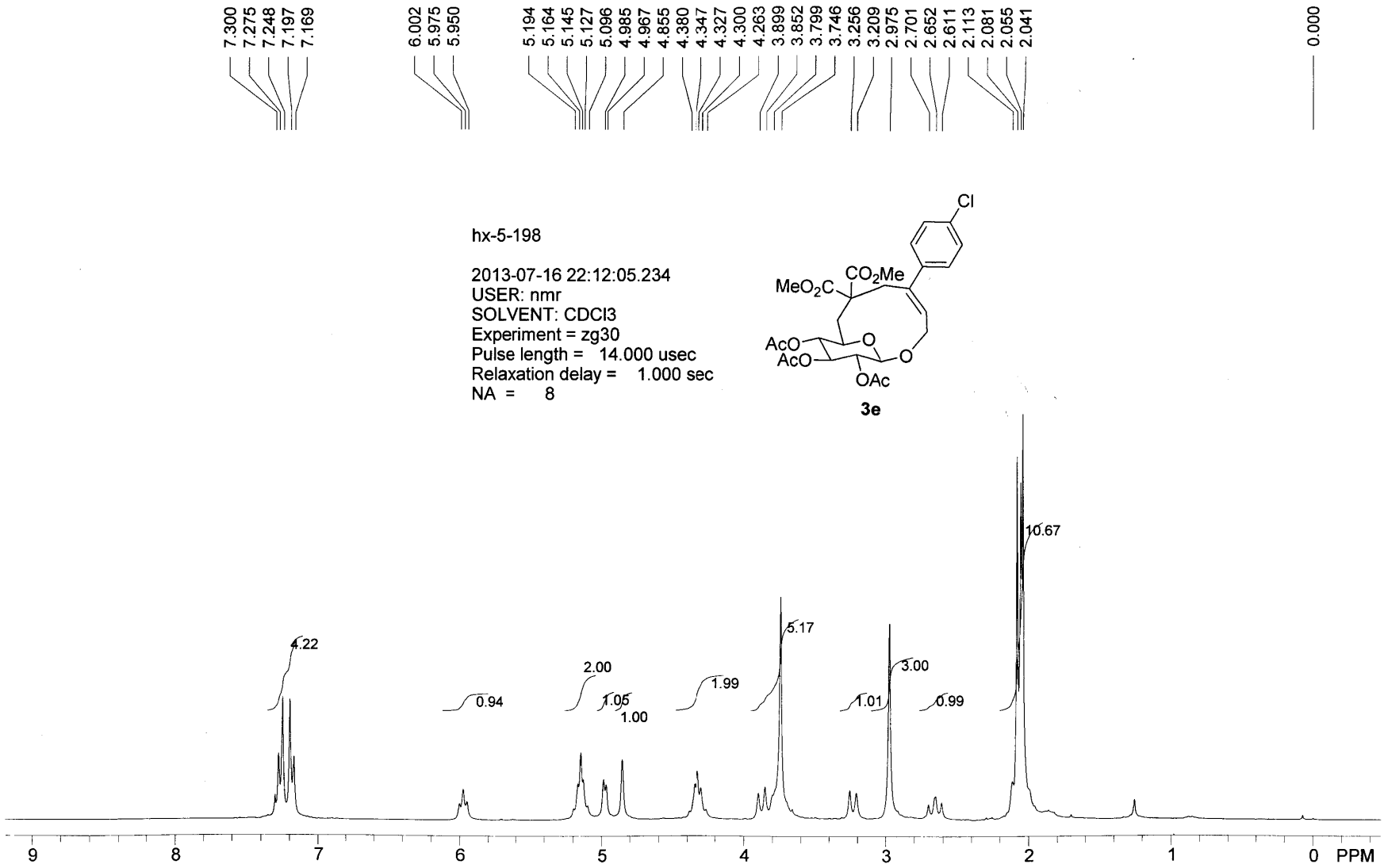
hx-6-10

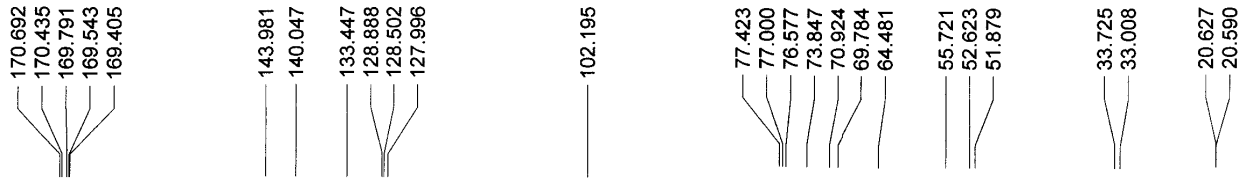
2012-11-05 13:38:47.015
USER: nmr
SOLVENT: CDCl3
Experiment = zgflqn
Pulse length = 13.500 usec
Relaxation delay = 1.000 sec
NA = 16



3d

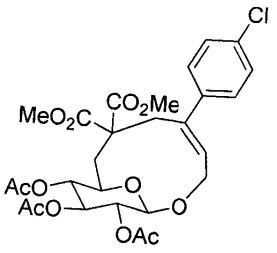



7.300
7.275
7.248
7.197
7.169
6.002
5.975
5.950
5.194
5.164
5.145
5.127
5.096
4.985
4.967
4.855
4.380
4.347
4.327
4.300
4.263
3.899
3.852
3.799
3.746
3.256
3.209
2.975
2.701
2.652
2.611
2.113
2.081
2.055
2.041
0.000
hx-5-198
2013-07-16 22:12:05.234
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Cl
CO2Me
MeO2C
AcO
AcO
O
O
OAc
3e
4.22
0.94
2.00
1.05
1.00
1.99
5.17
1.01
3.00
0.99
10.67
9
8
7
6
5
4
3
2
1
0
PPM

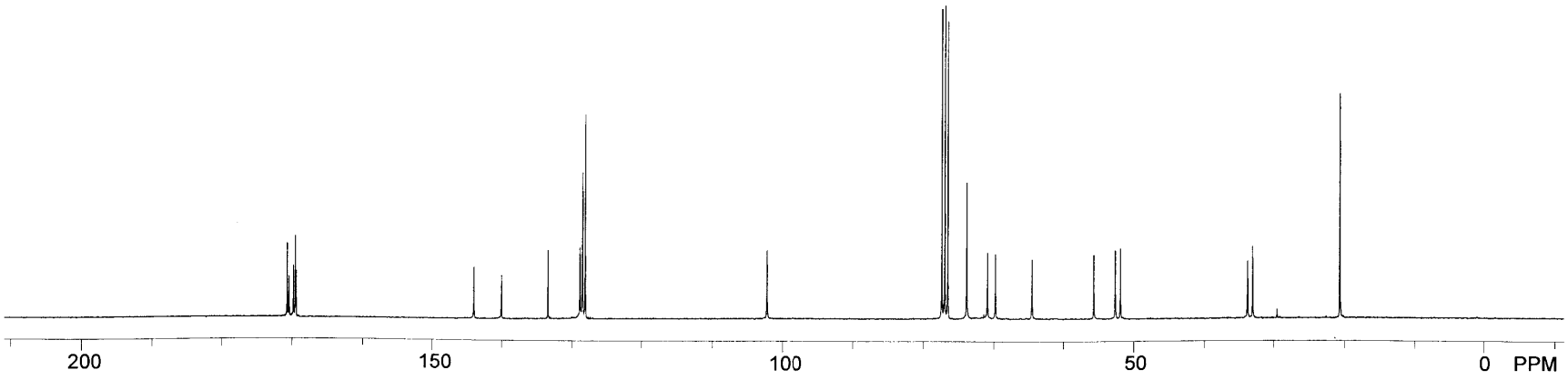


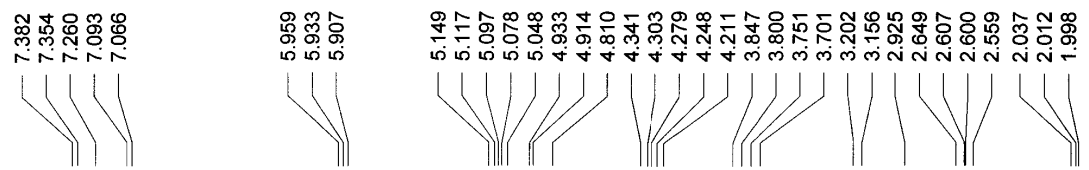
hx-5-198

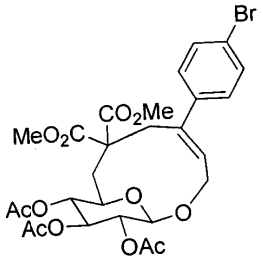
2013-07-17 08:38:42.015
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 10676



3e





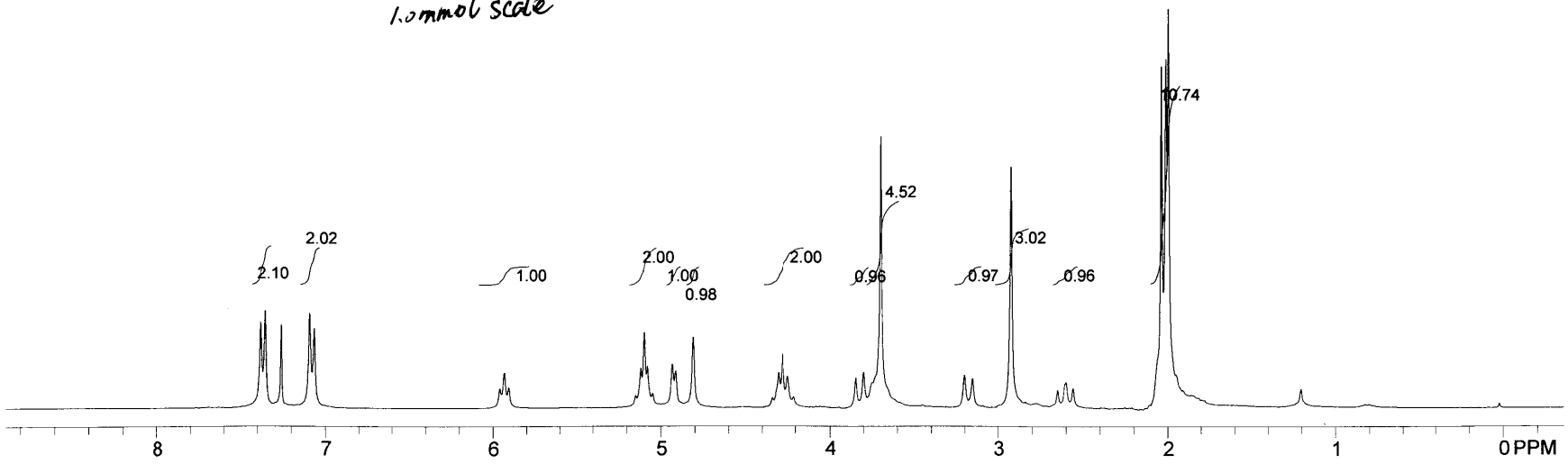


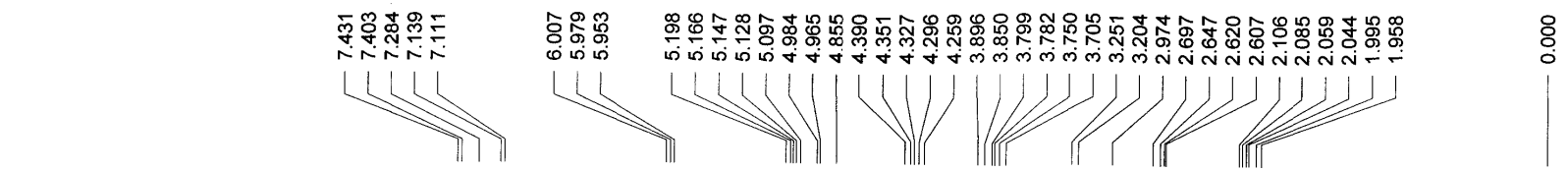
3f

1.0 mmol scale

hx-5-42

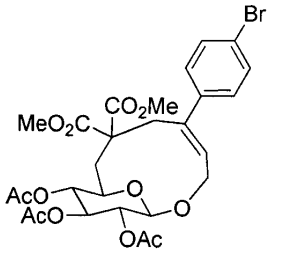
2012-03-29 15:47:01.406
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8





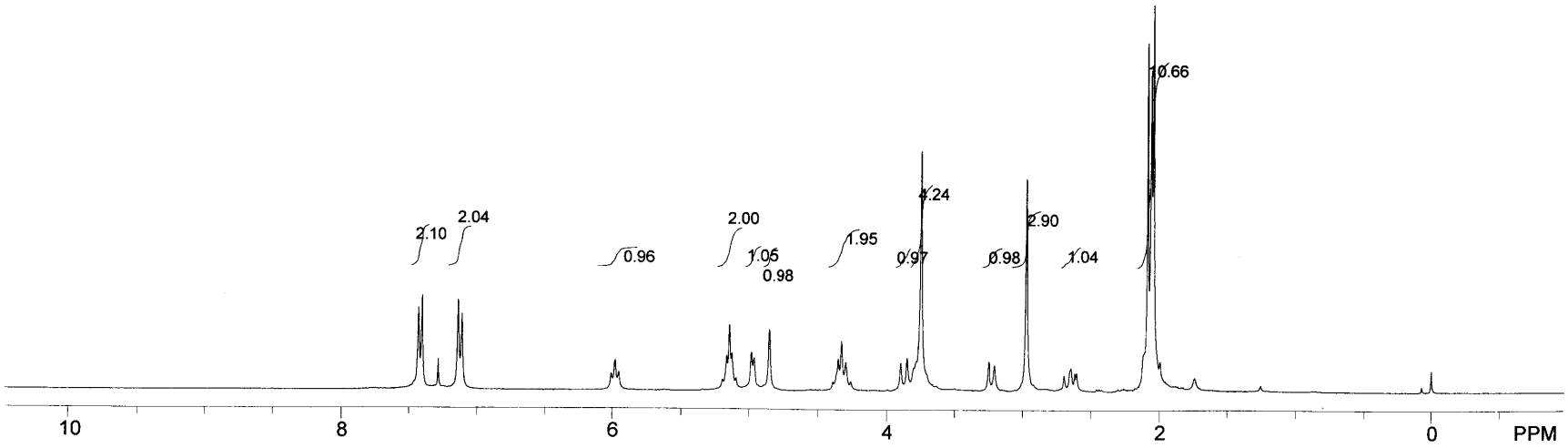
hx-7-88

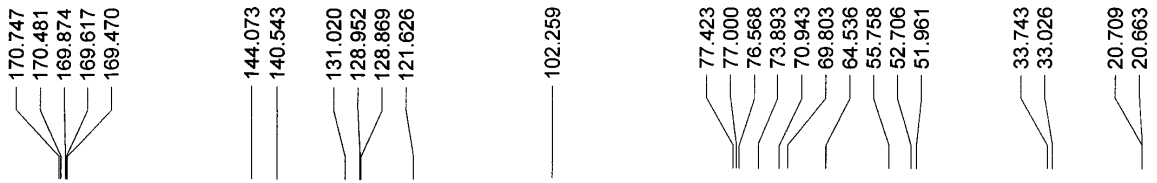
2013-03-05 21:04:05.687
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8

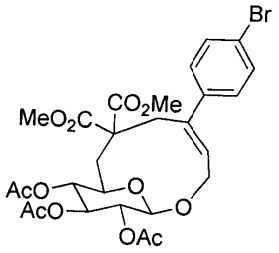


3f

4.0 mmol scale





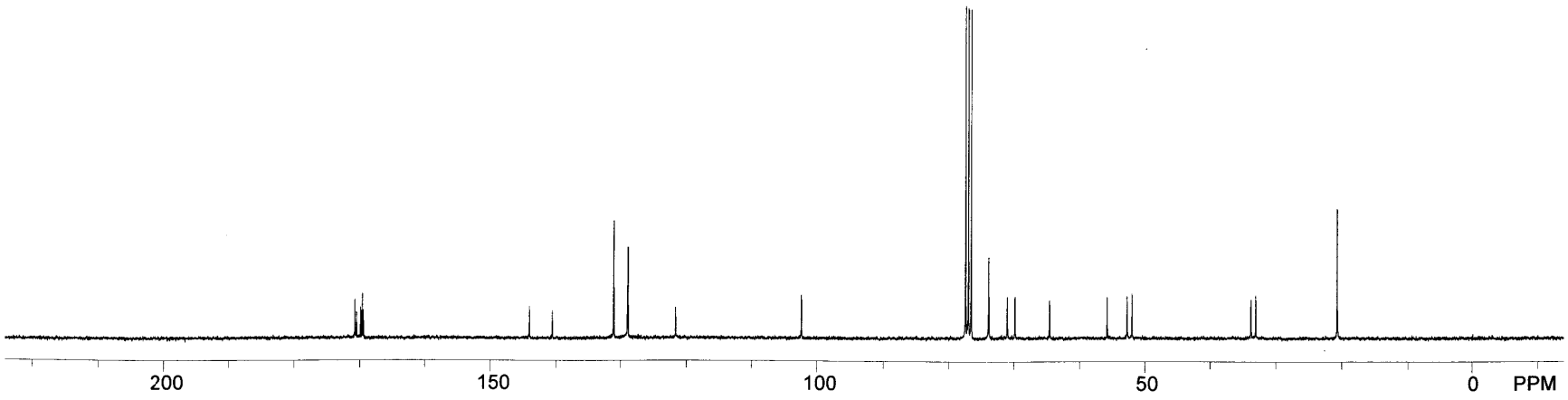


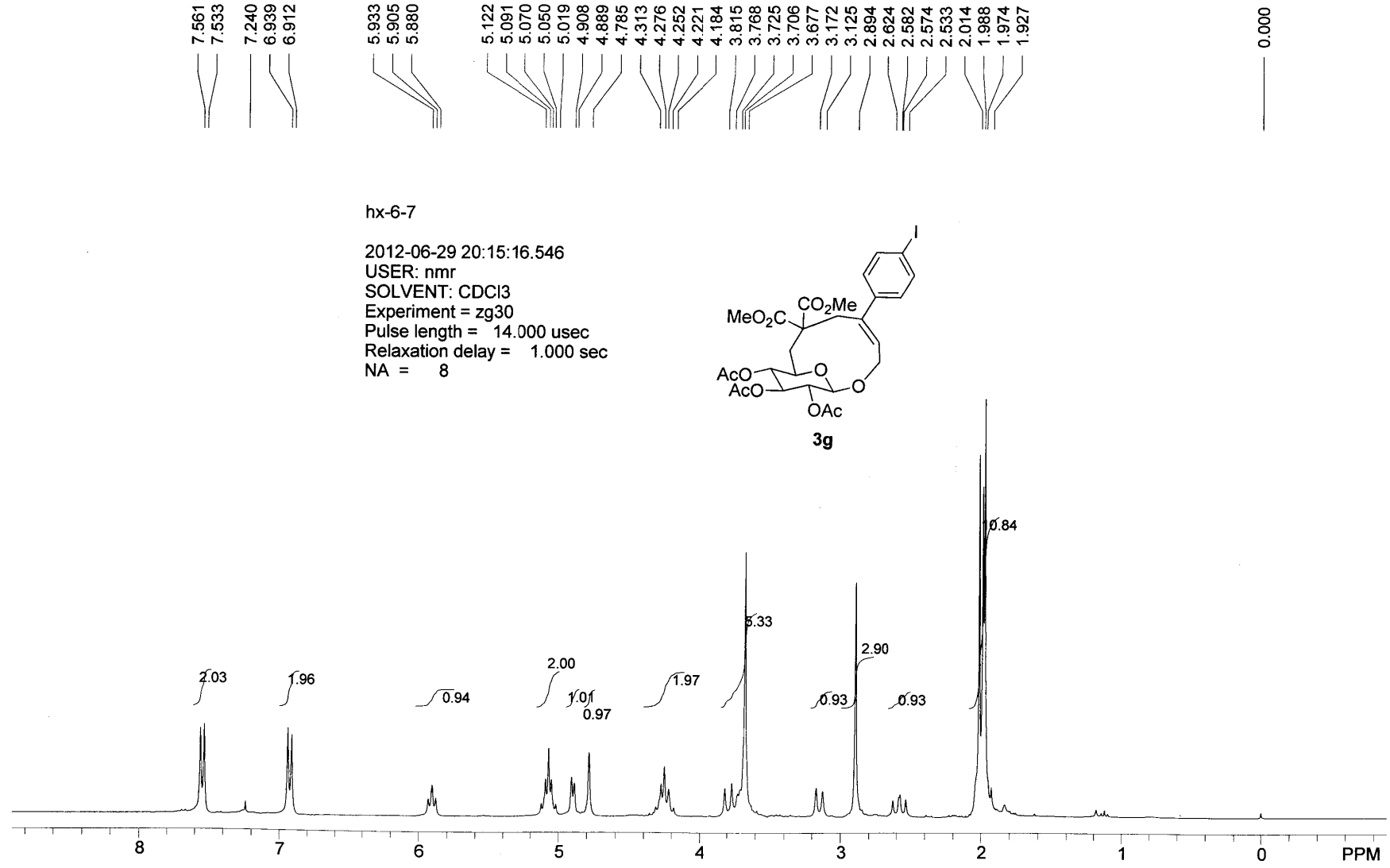
3f

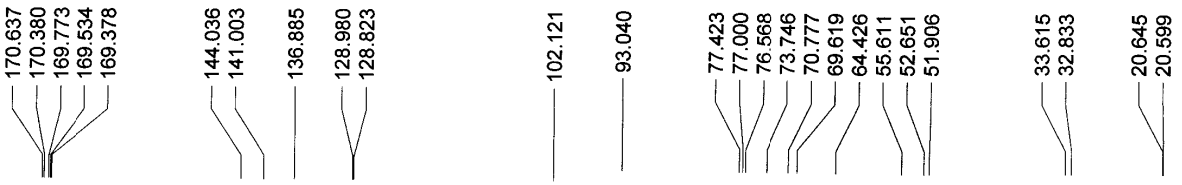
4.0mmol scale

hx-7-88

2013-03-06 00:10:24.296
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 1024

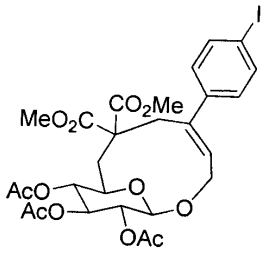



7.561
7.533
7.240
6.939
6.912
5.933
5.905
5.880
5.122
5.091
5.070
5.050
5.019
4.908
4.889
4.785
4.313
4.276
4.252
4.221
4.184
3.815
3.768
3.725
3.706
3.677
3.172
3.125
2.894
2.624
2.582
2.574
2.533
2.014
1.988
1.974
1.927
0.000
hx-6-7
2012-06-29 20:15:16.546
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
I
CO2Me
MeO2C
AcO
AcO
O
O
OAc
3g
2.03
1.96
0.94
2.00
1.01
0.97
1.97
5.33
0.93
2.90
0.93
0.84
8
7
6
5
4
3
2
1
0
PPM

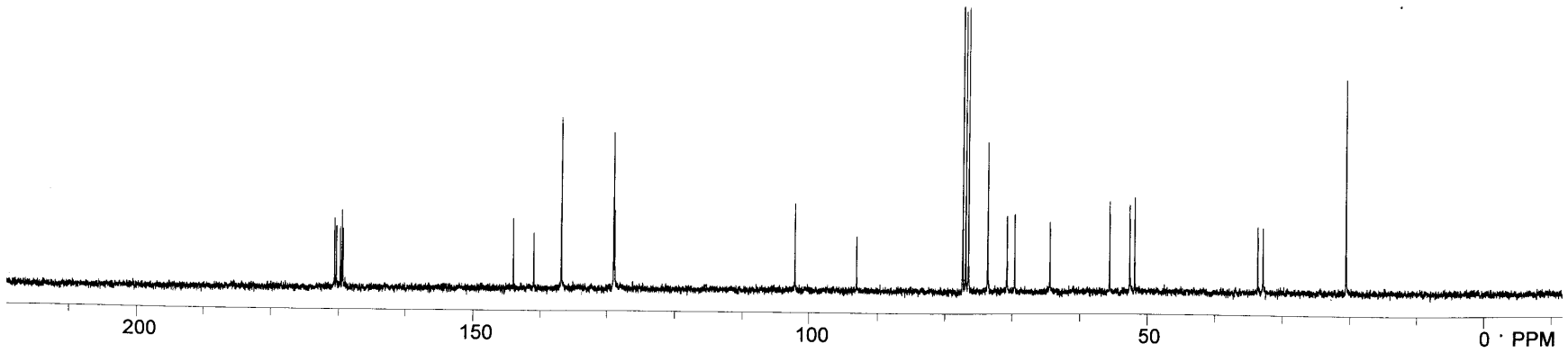


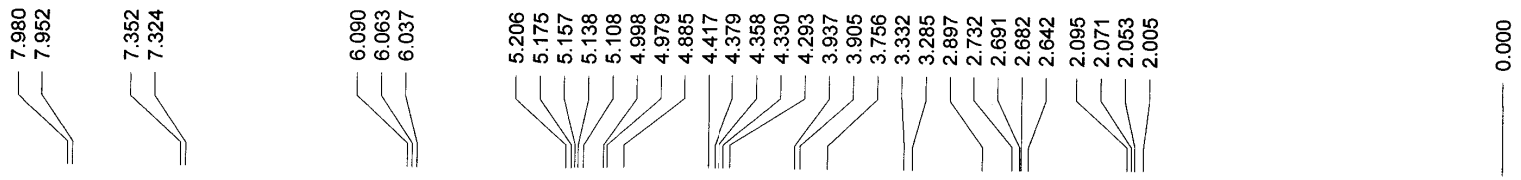
hx-6-7

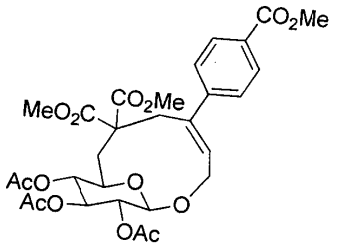
2012-06-29 20:26:45.250
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 125



3g



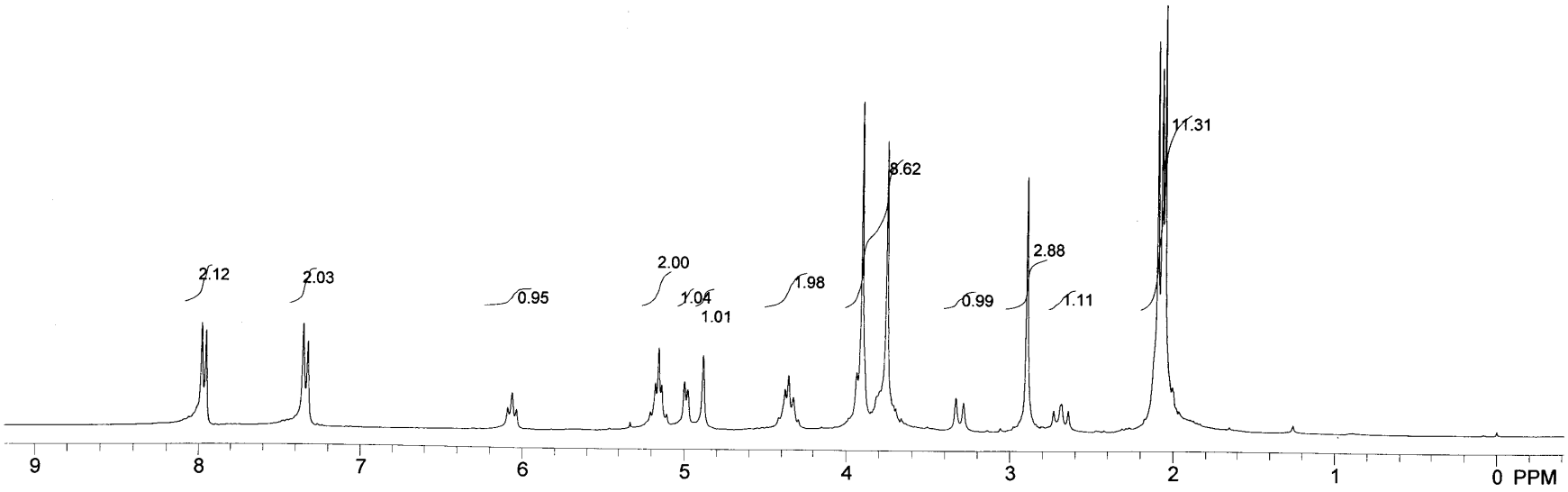


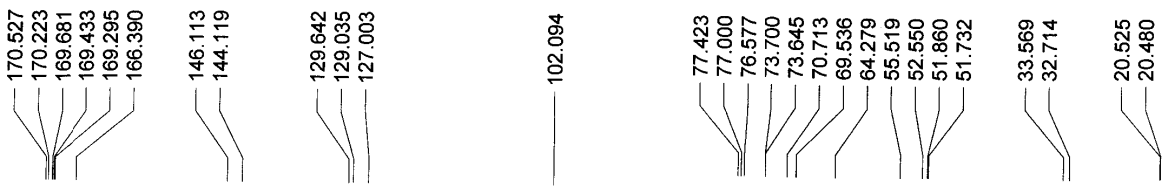


3h

hx-5-163

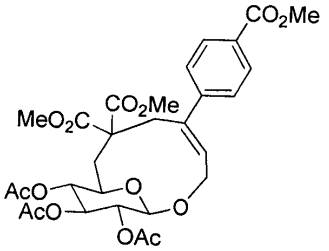
2012-05-31 21:02:56.937
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8



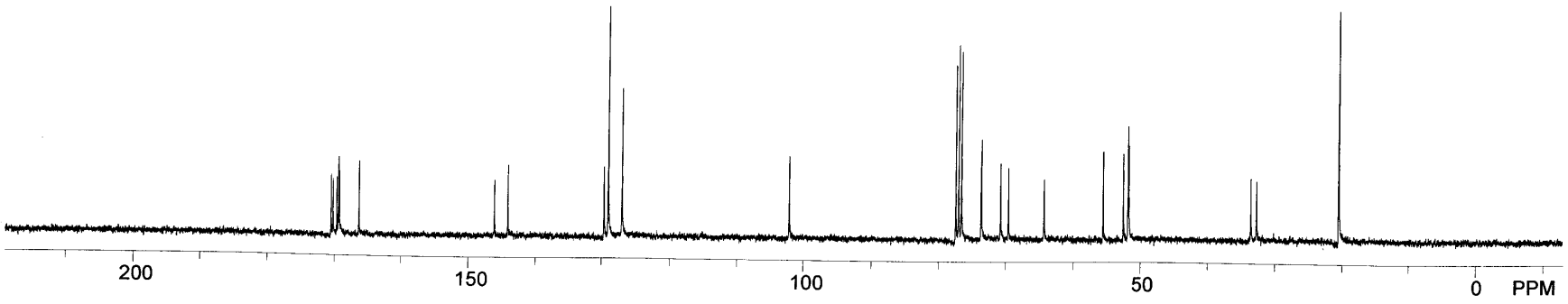


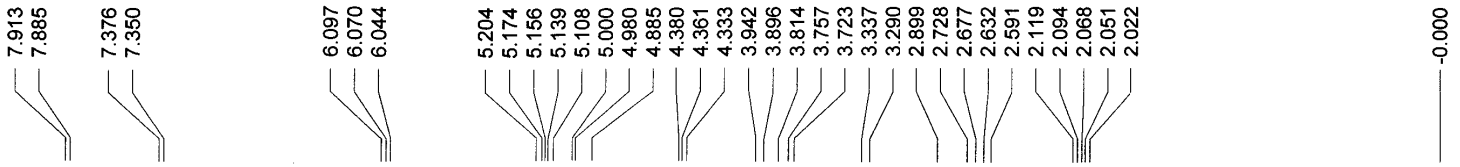
hx-5-163

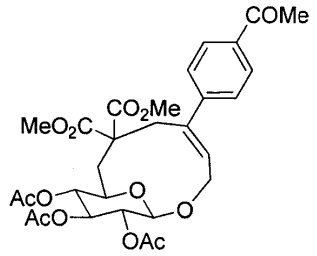
2012-05-31 21:12:49.156
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 148



3h



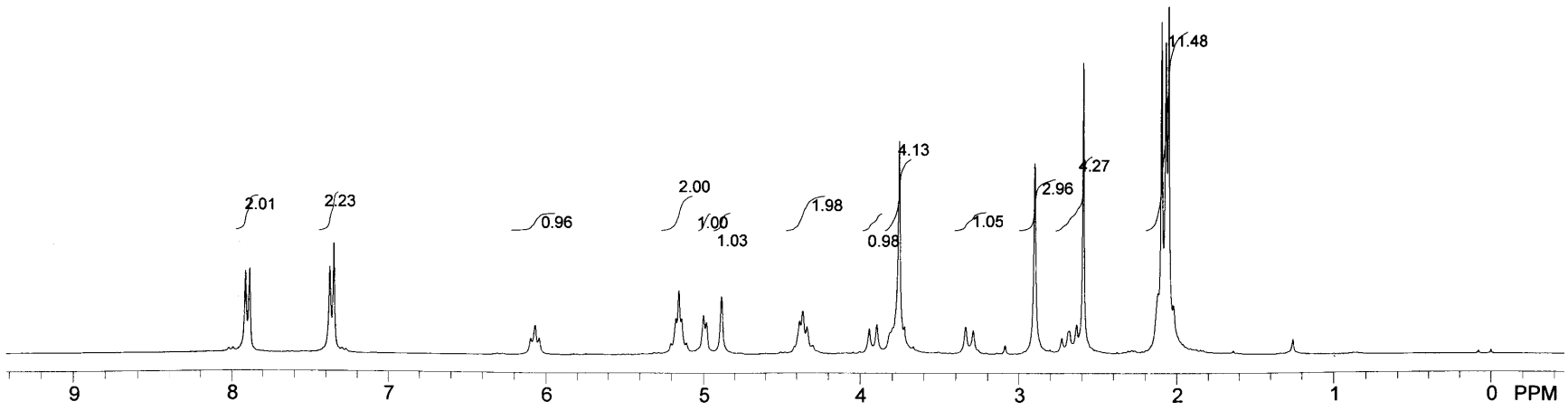


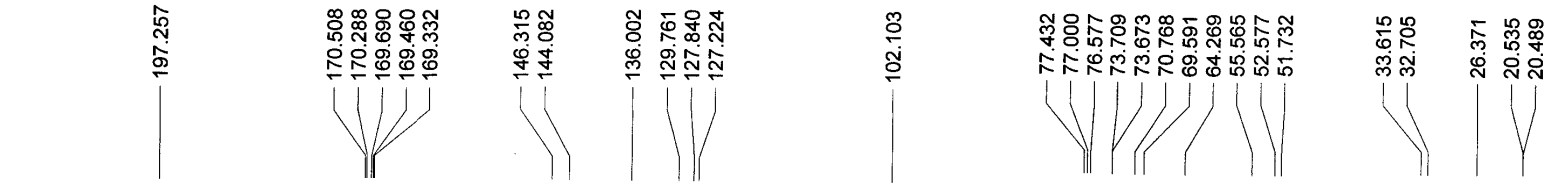


3i

hx-6-11

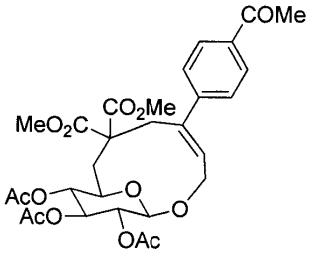
2012-07-05 20:08:43.671
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8



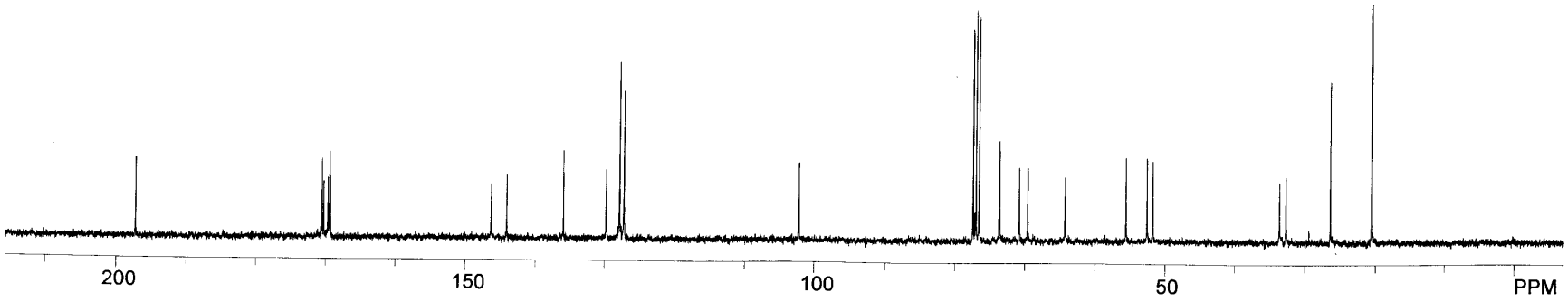


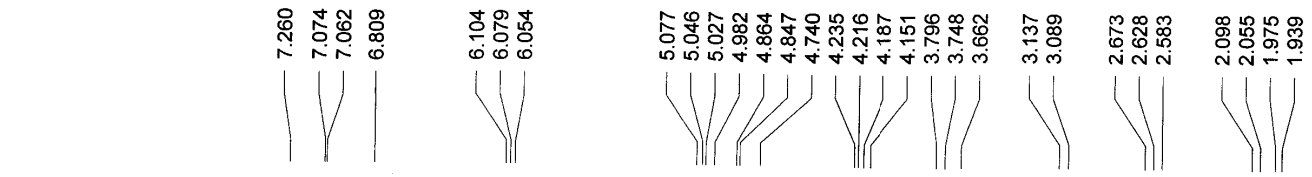
hx-6-11

2012-07-05 20:17:42.437
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 132



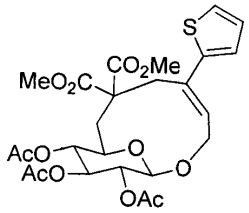
3i



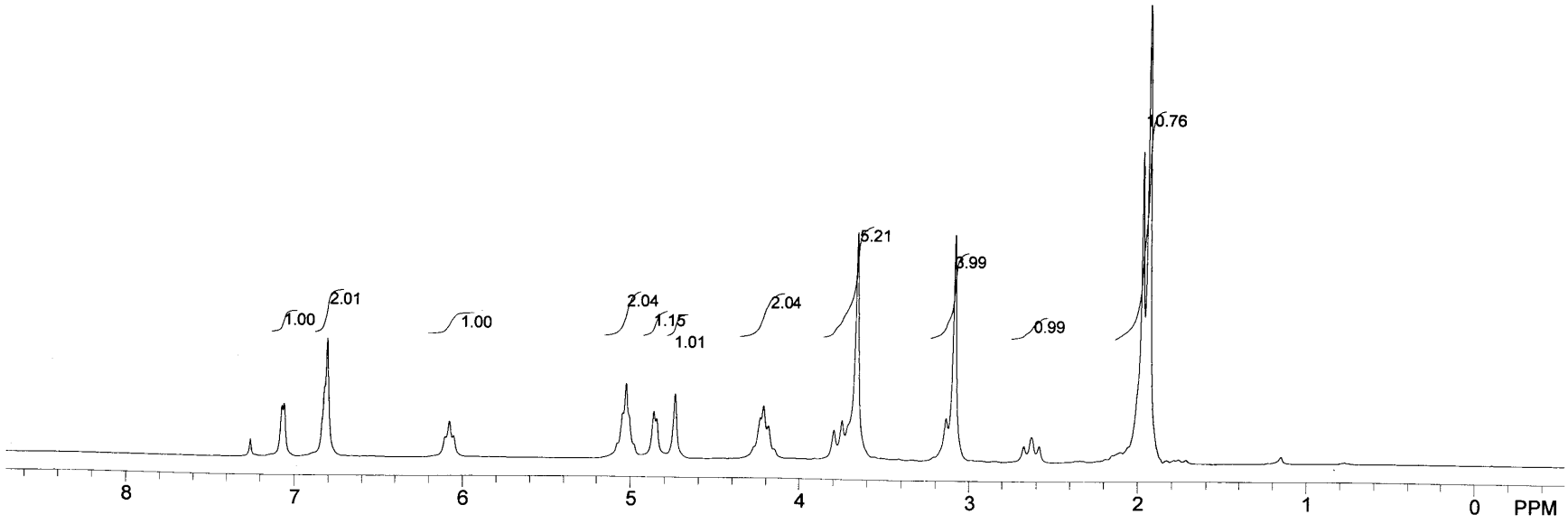


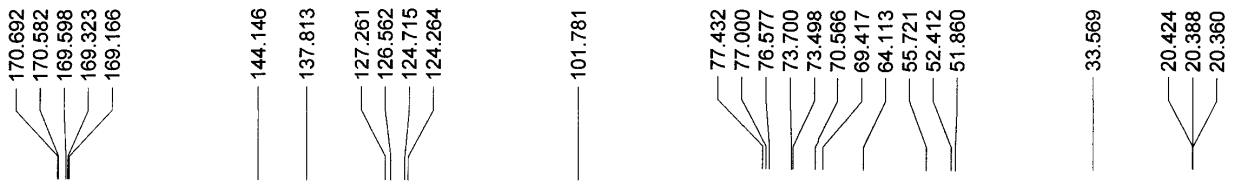
hx-5-164

2012-07-07 08:37:54.875
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8



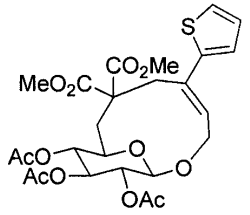
3j



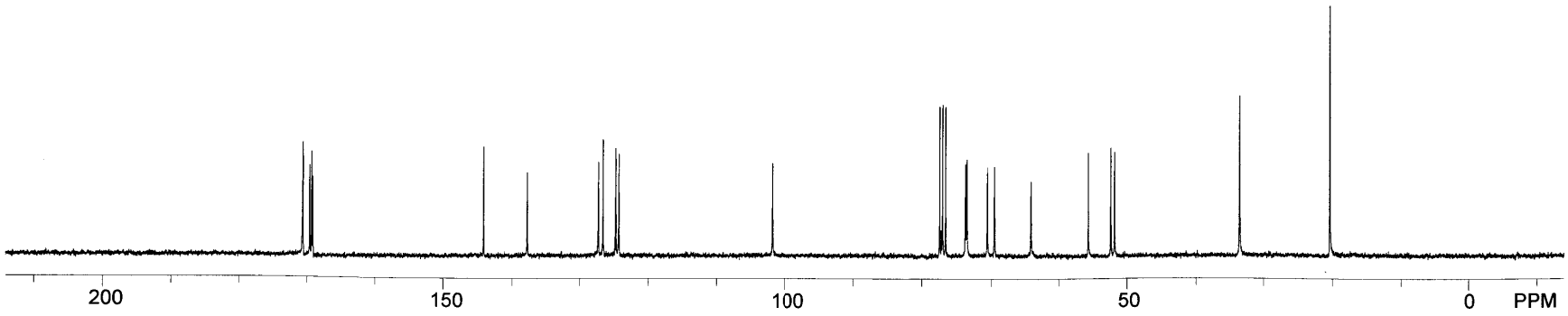


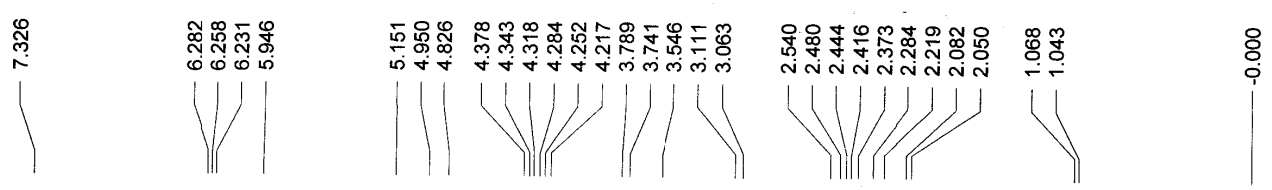
hx-5-164

2012-07-07 08:52:43.156
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 202



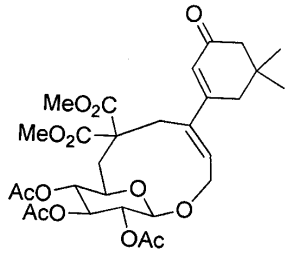
3j



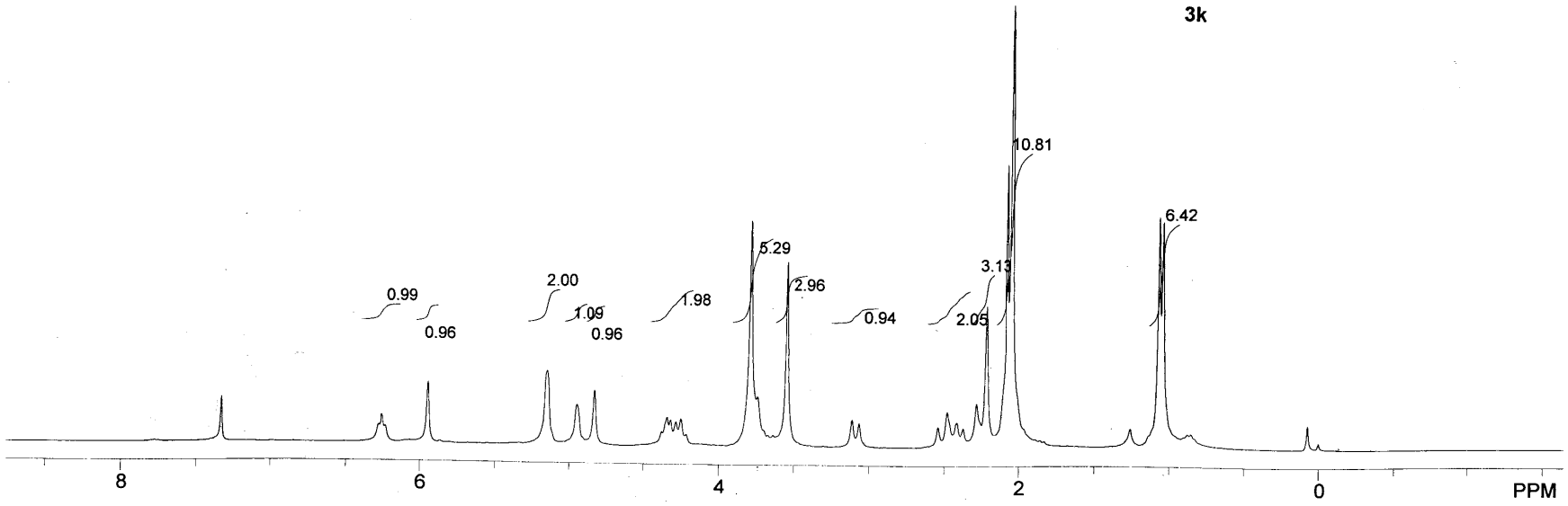


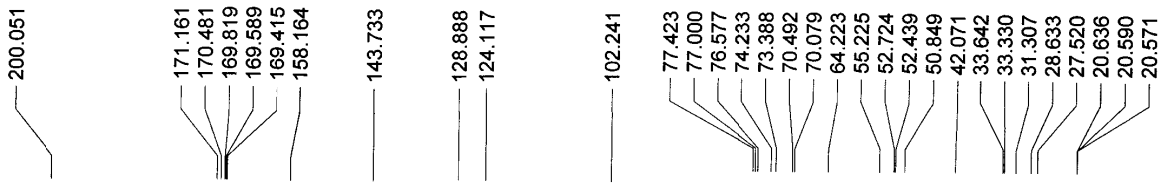
hx-6-78

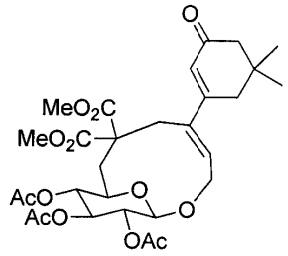
2012-10-18 21:40:16.093
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8



3k



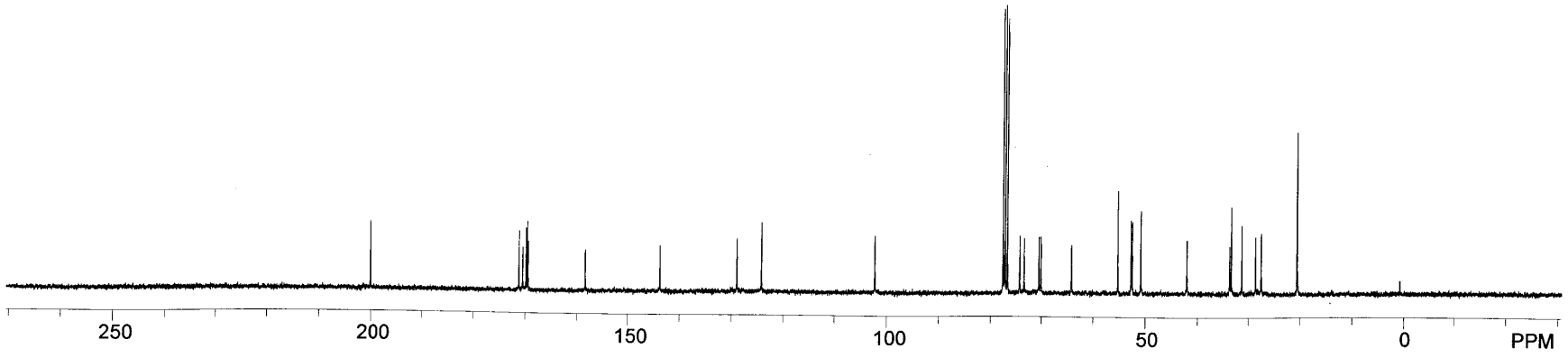


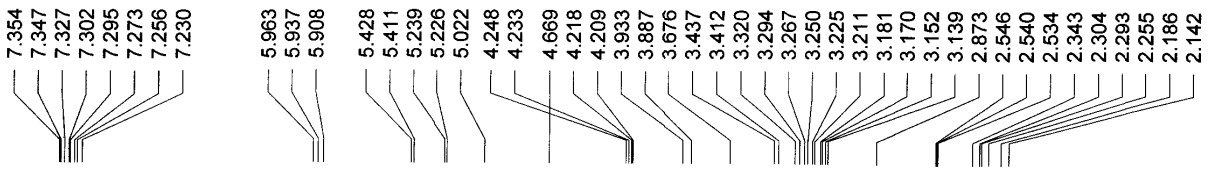


3k

hx-6-78

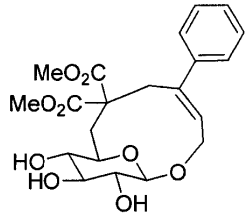
2012-10-18 22:03:33.406
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 377



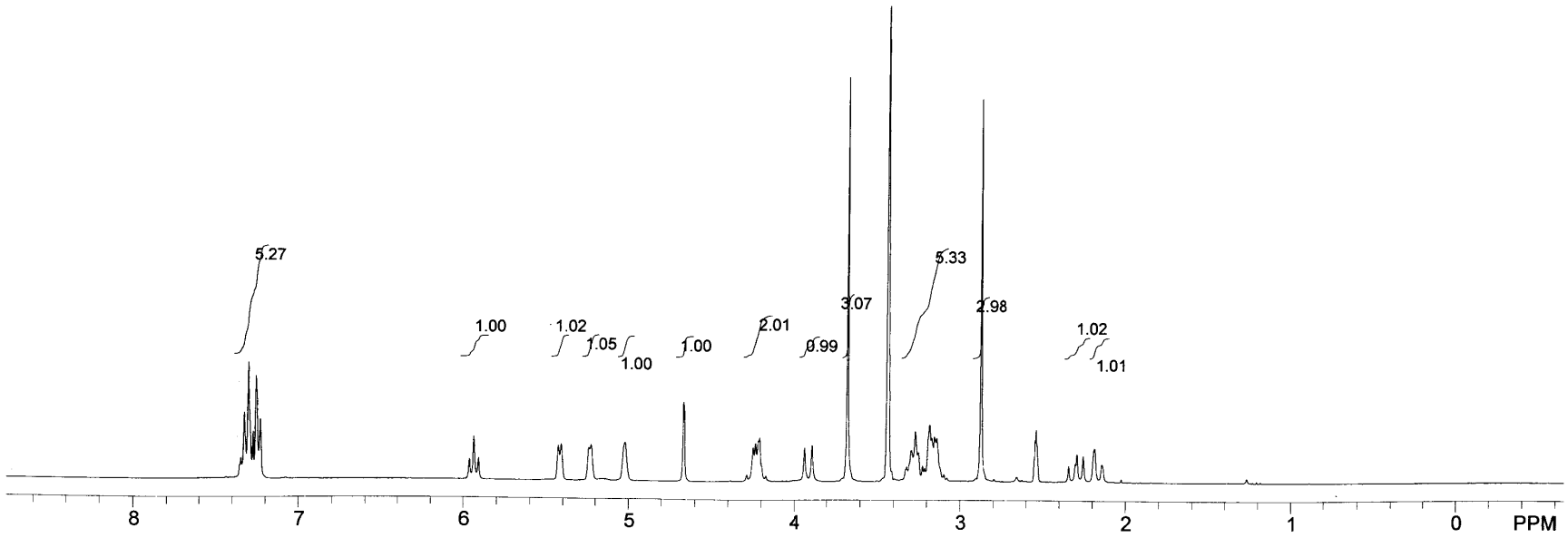


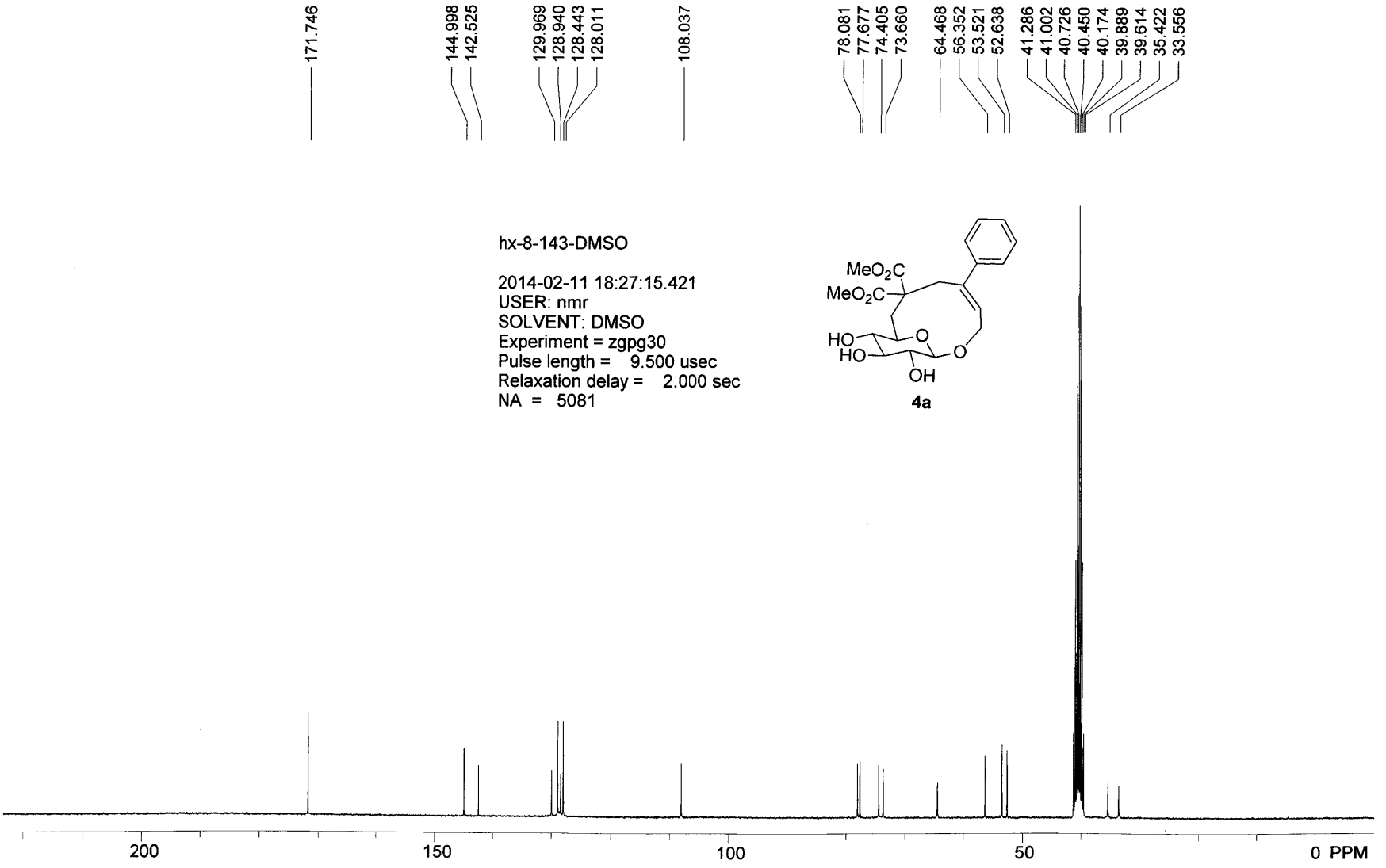
hx-8-143-DMSO

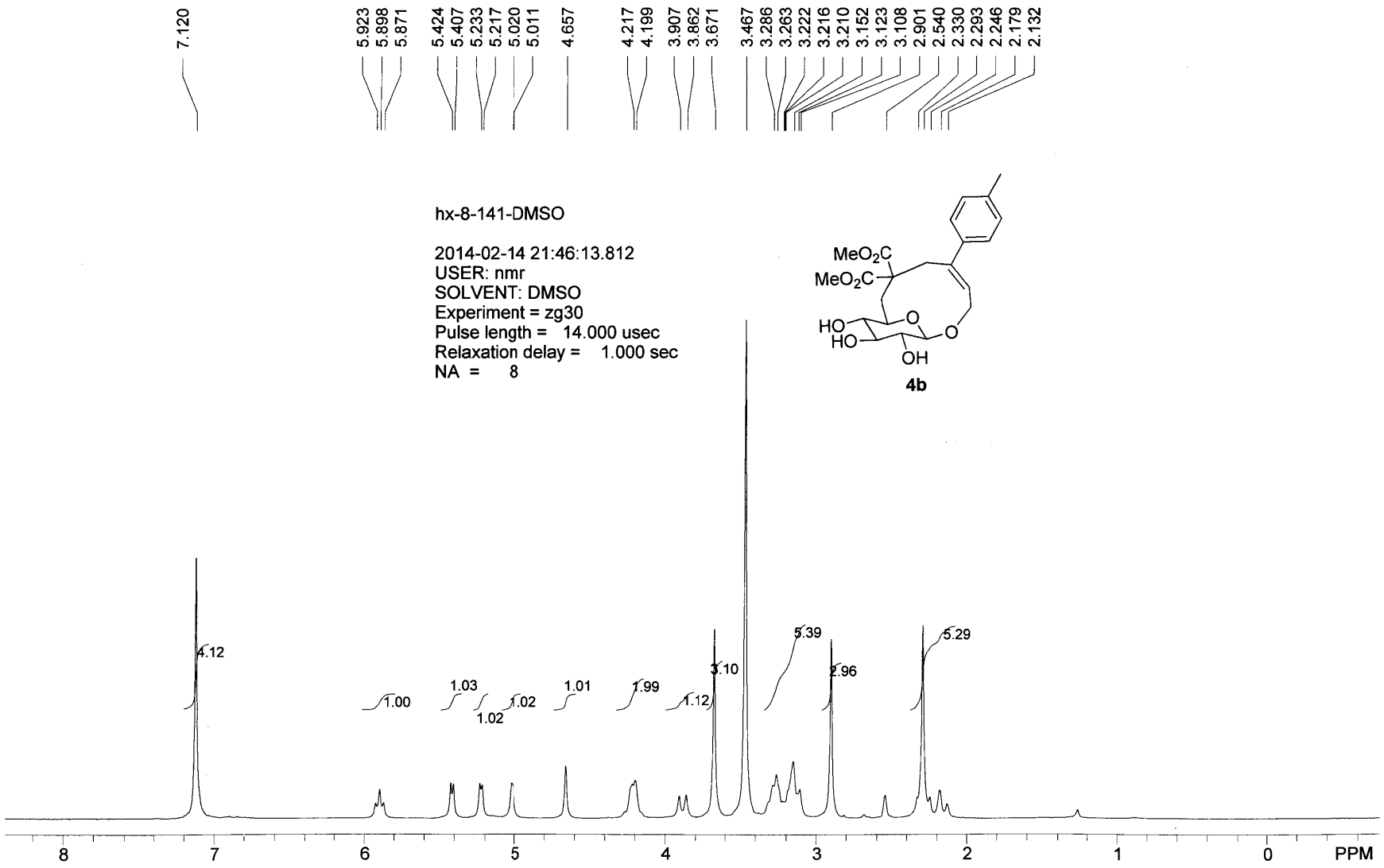
2014-02-12 11:55:30.859
USER: nmr
SOLVENT: DMSO
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8



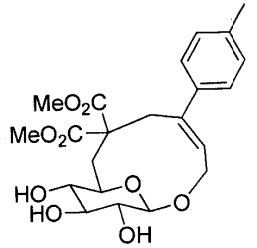
4a




171.746
144.998
142.525
129.969
128.940
128.443
128.011
108.037
78.081
77.677
74.405
73.660
64.468
56.352
53.521
52.638
41.286
41.002
40.726
40.450
40.174
39.889
39.614
35.422
33.556
hx-8-143-DMSO
2014-02-11 18:27:15.421
USER: nmr
SOLVENT: DMSO
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 5081
MeO2C
MeO2C
HO
HO
OH
O
O
4a
200
150
100
50
0 PPM


7.120
5.923
5.898
5.871
5.424
5.407
5.233
5.217
5.020
5.011
4.657
4.217
4.199
3.907
3.862
3.671
3.467
3.286
3.263
3.222
3.216
3.210
3.152
3.123
3.108
2.901
2.540
2.330
2.293
2.246
2.179
2.132
hx-8-141-DMSO
2014-02-14 21:46:13.812
USER: nmr
SOLVENT: DMSO
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
MeO2C
MeO2C
HO
HO
O
O
OH
4b
4.12
1.00
1.03
1.02
1.02
1.01
1.99
1.12
3.10
5.39
2.96
5.29
8
7
6
5
4
3
2
1
0
PPM

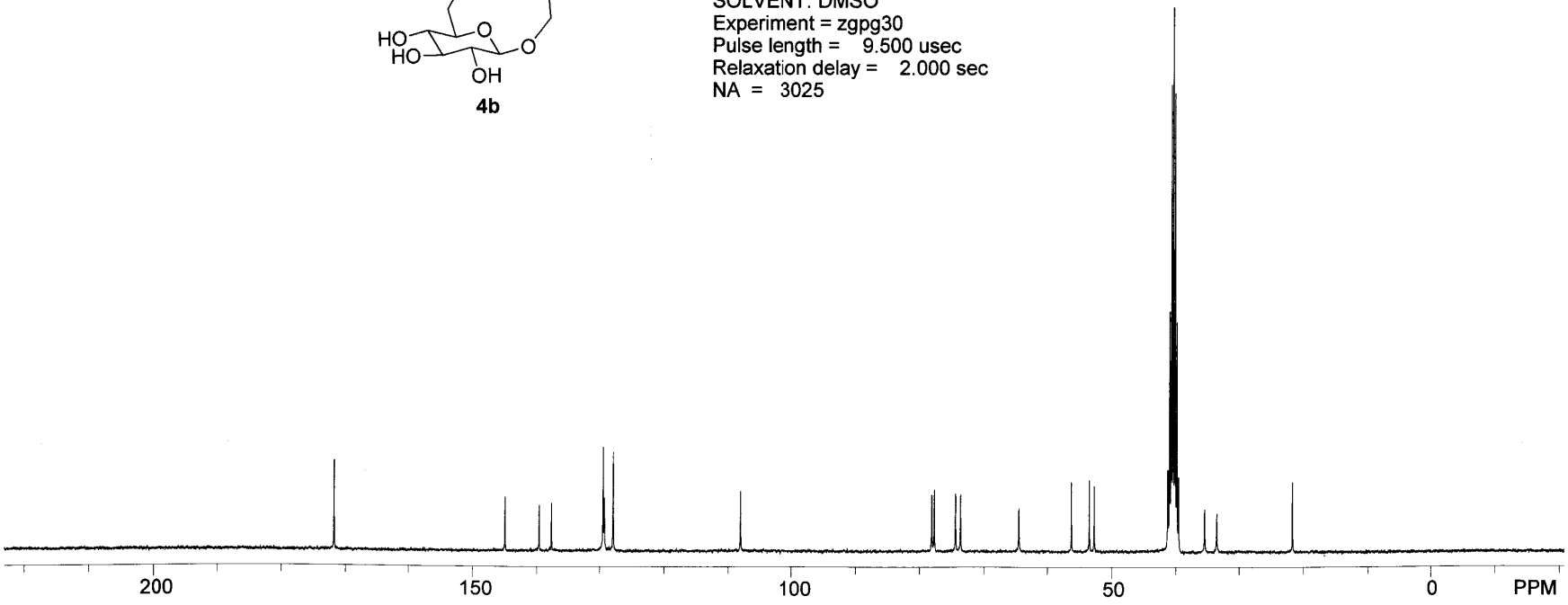
171.783
144.897
139.611
137.681
129.473
129.271
127.873
108.037
78.109
77.723
74.414
73.632
64.523
56.343
53.502
52.721
41.286
41.002
40.726
40.450
40.174
39.889
39.614
35.404
33.538
21.717

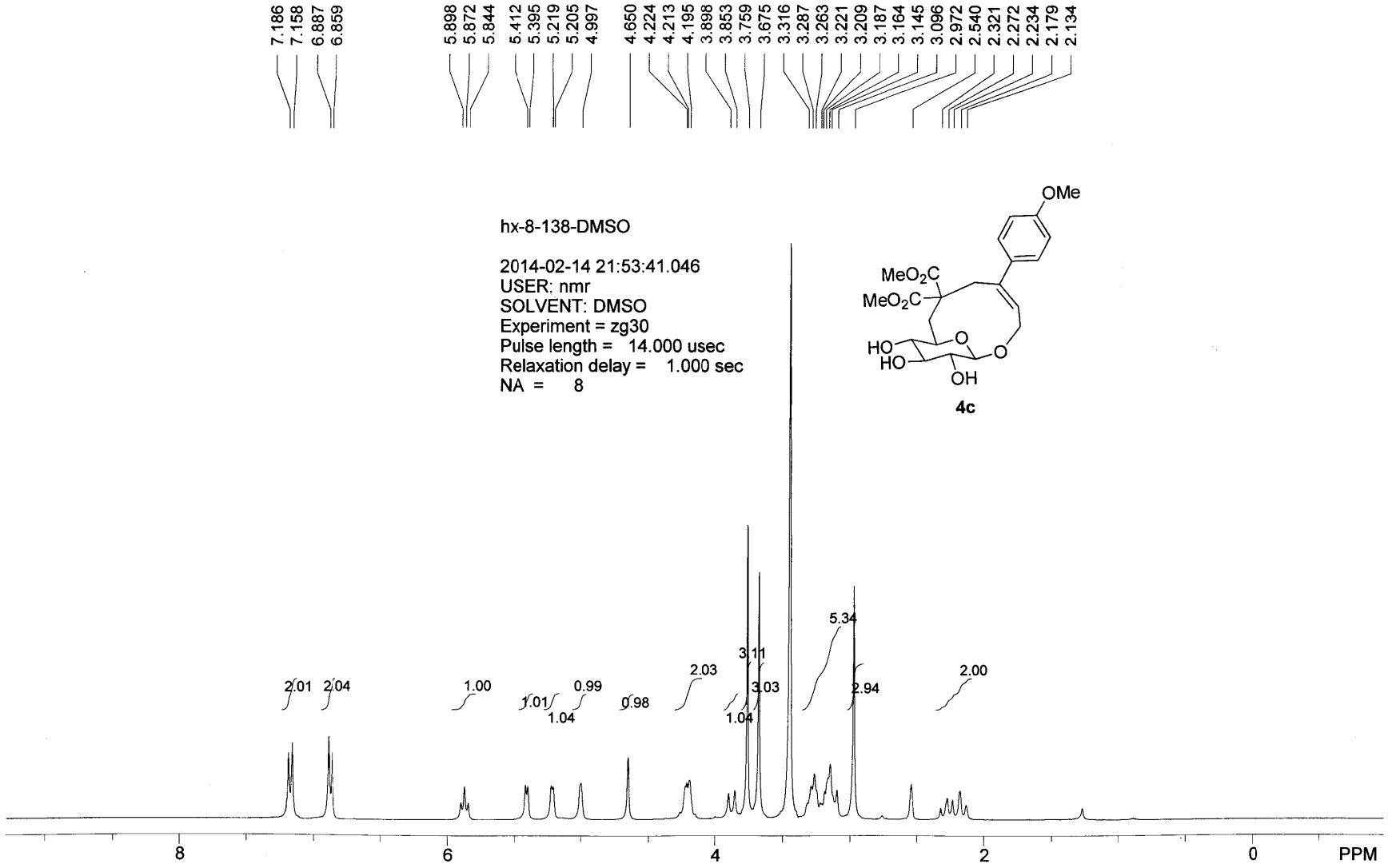


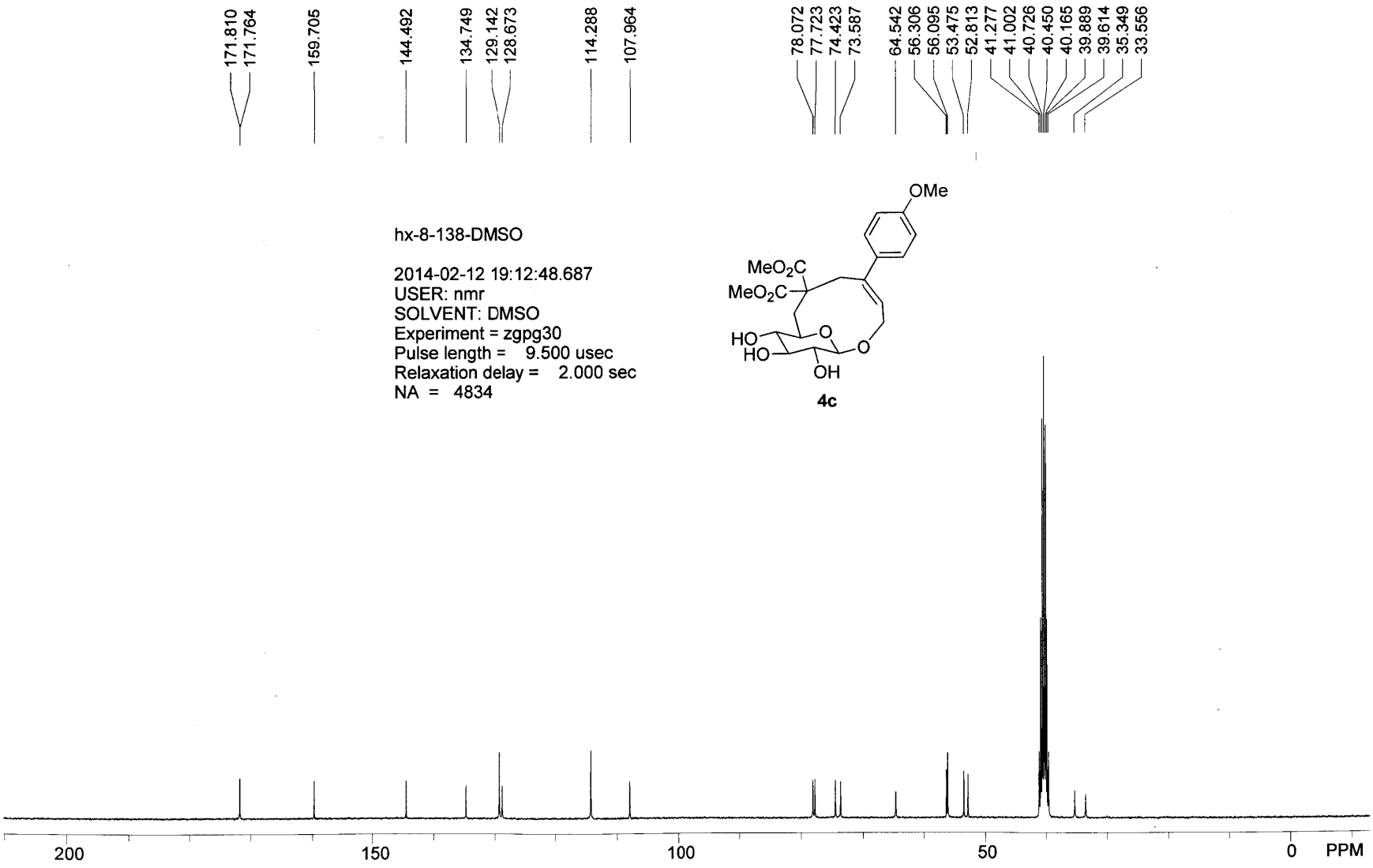
4b

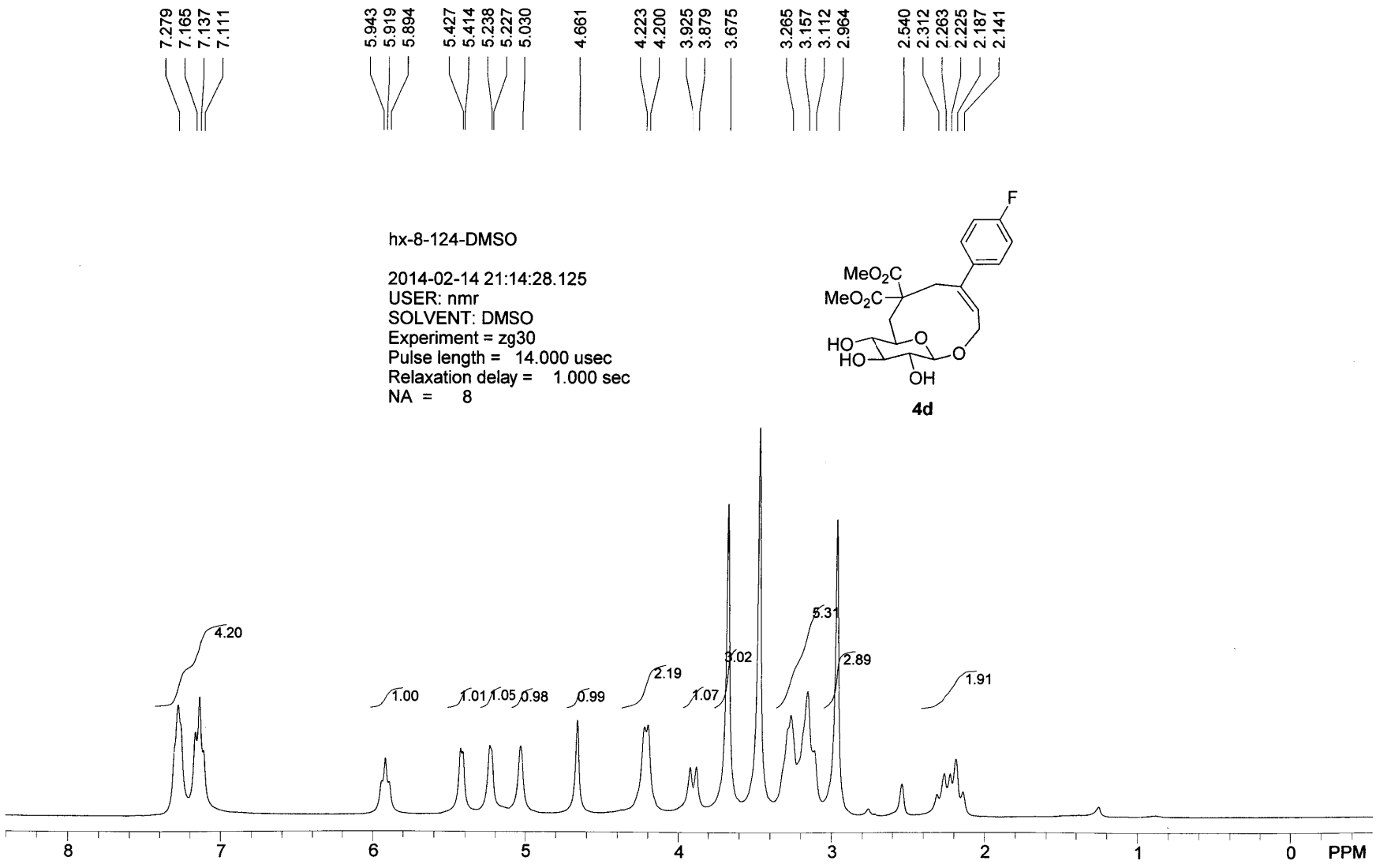
hx-8-141-DMSO

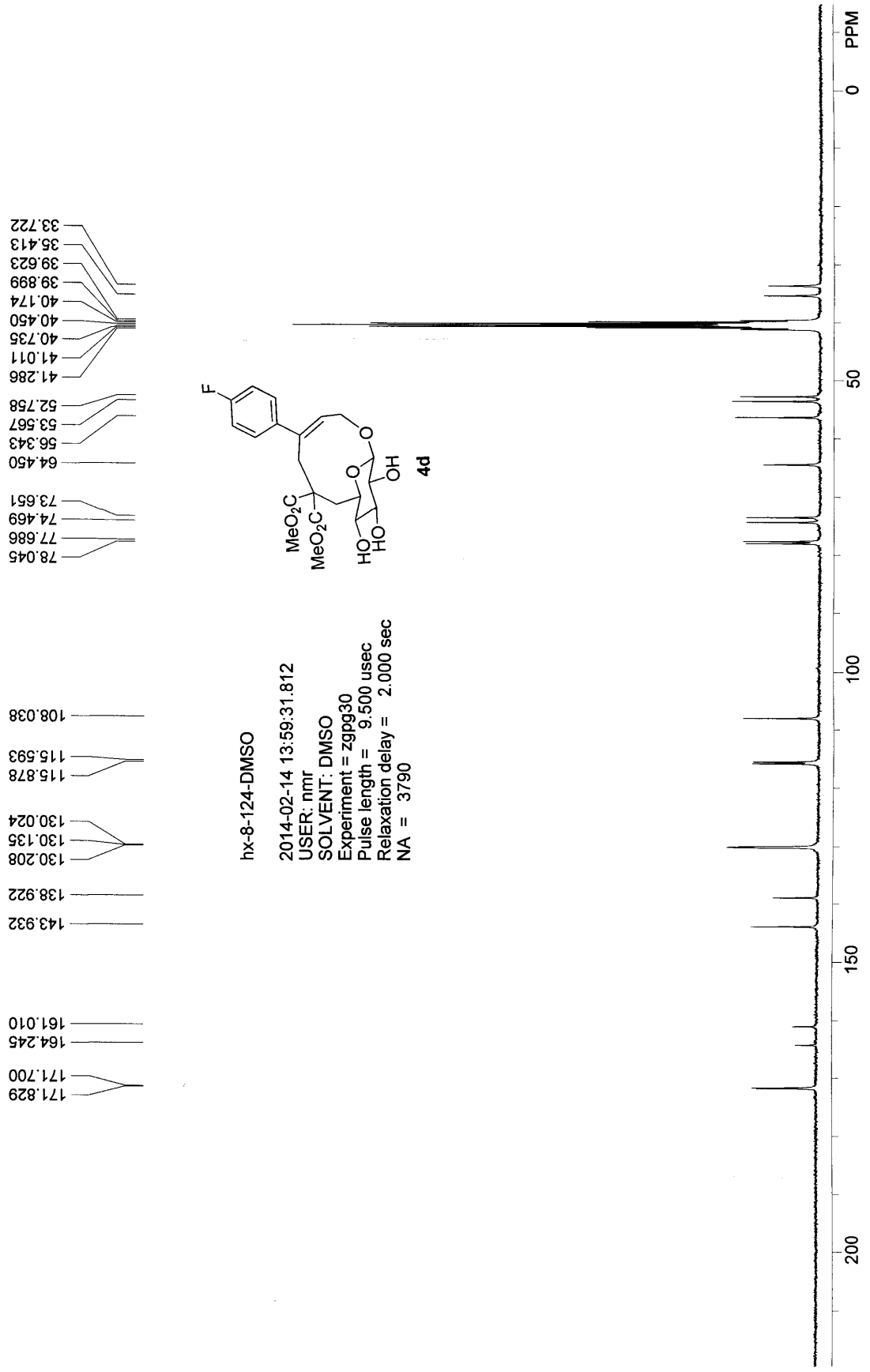
2014-02-12 22:15:35.375
USER: nmr
SOLVENT: DMSO
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 3025




7.186
7.158
6.887
6.859
5.898
5.872
5.844
5.412
5.395
5.219
5.205
4.997
4.650
4.224
4.213
4.195
3.898
3.853
3.759
3.675
3.316
3.287
3.263
3.221
3.209
3.187
3.164
3.145
3.096
2.972
2.540
2.321
2.272
2.234
2.179
2.134
hx-8-138-DMSO
2014-02-14 21:53:41.046
USER: nmr
SOLVENT: DMSO
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
OMe
MeO2C
MeO2C
HO
HO
O
O
OH
4c
2.01
2.04
1.00
1.01
1.04
0.99
0.98
2.03
1.04
3.11
3.03
5.34
2.94
2.00
8
6
4
2
0
PPM


171.810
171.764
159.705
144.492
134.749
129.142
128.673
114.288
107.964
78.072
77.723
74.423
73.587
64.542
56.306
56.095
53.475
52.813
41.277
41.002
40.726
40.450
40.165
39.889
39.614
35.349
33.556
hx-8-138-DMSO
2014-02-12 19:12:48.687
USER: nmr
SOLVENT: DMSO
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 4834
OMe
MeO2C
MeO2C
HO
HO
O
O
OH
4c
200
150
100
50
0
PPM


7.279
7.165
7.137
7.111
5.943
5.919
5.894
5.427
5.414
5.238
5.227
5.030
4.661
4.223
4.200
3.925
3.879
3.675
3.265
3.157
3.112
2.964
2.540
2.312
2.263
2.225
2.187
2.141
hx-8-124-DMSO
2014-02-14 21:14:28.125
USER: nmr
SOLVENT: DMSO
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
F
MeO2C
MeO2C
HO
HO
O
O
OH
4d
4.20
1.00
1.01
1.05
0.98
0.99
2.19
1.07
3.02
5.31
2.89
1.91
8
7
6
5
4
3
2
1
0
PPM

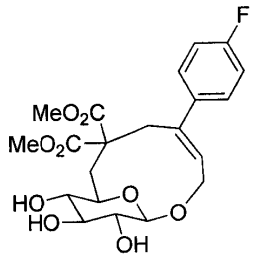

33.722
35.413
39.623
39.899
40.174
40.450
40.735
41.011
41.286
52.758
53.567
56.343
64.450
73.651
74.469
77.686
78.045
108.038
115.593
115.878
130.024
130.135
130.208
138.922
143.932
161.010
164.245
171.700
171.829
hx-8-124-DMSO
2014-02-14 13:59:31.812
USER: nmr
SOLVENT: DMSO
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 3790
F
MeO2C
MeO2C
HO
HO
OH
O
O
O
4d
200
150
100
50
0
PPM

-0.000

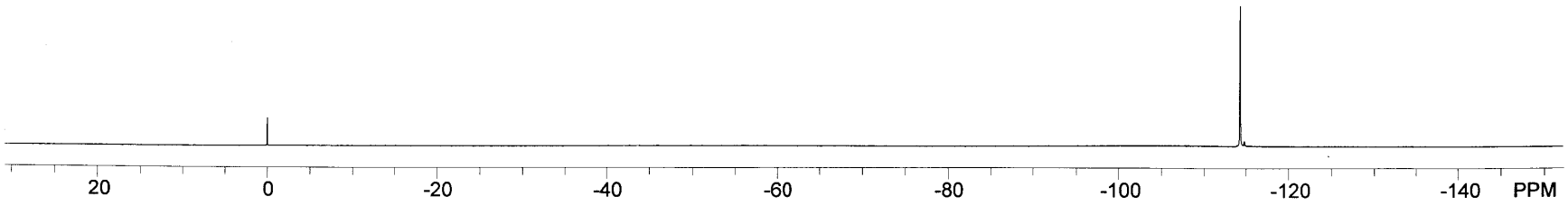
-114.339

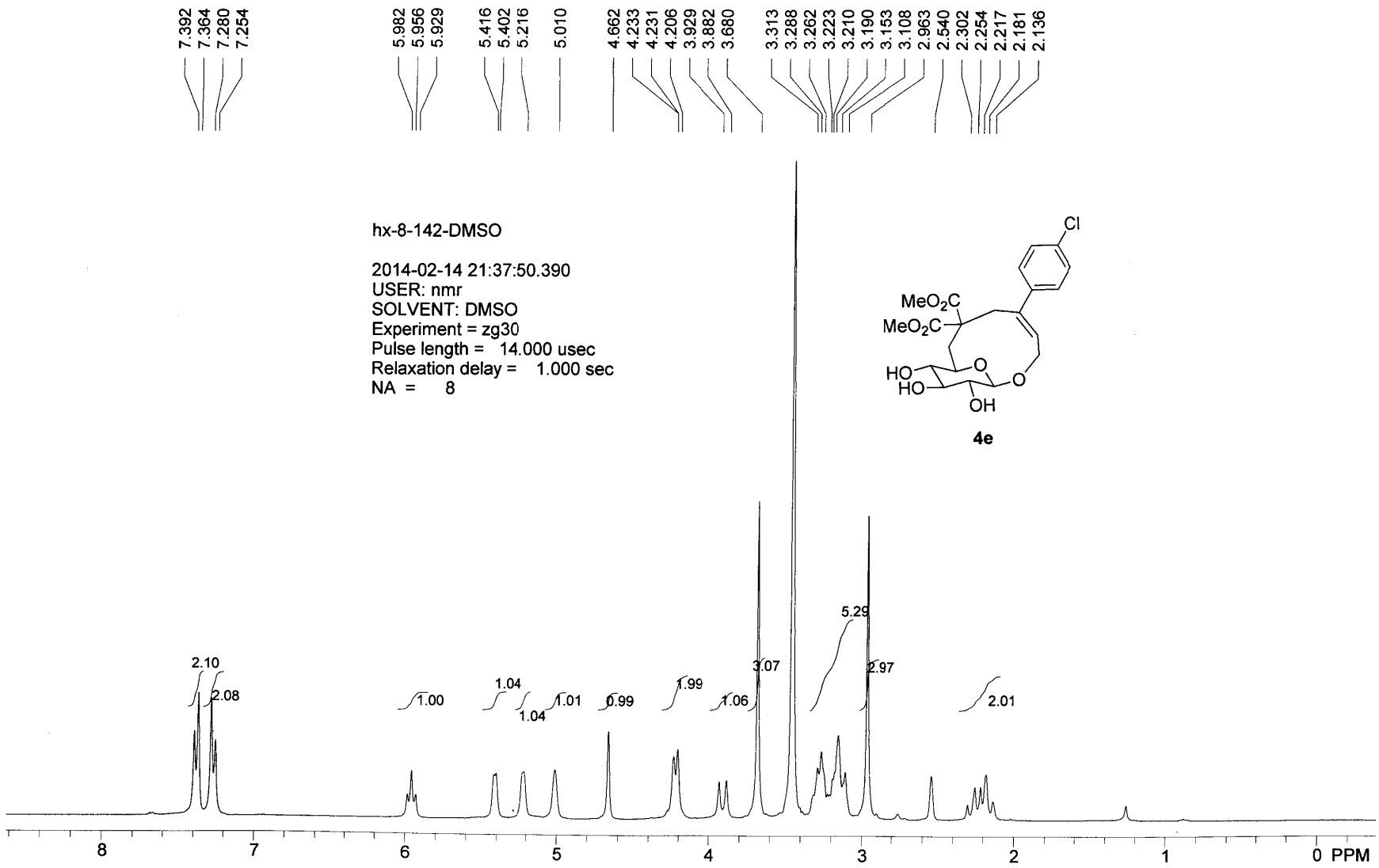
hx-8-124-DMSO

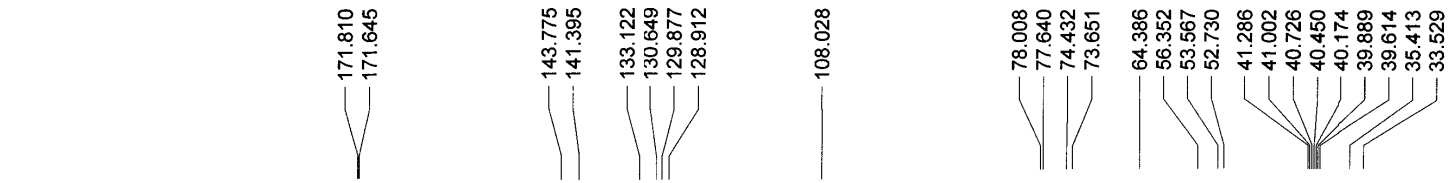
2014-02-15 14:19:53.968
USER: nmr
SOLVENT: DMSO
Experiment = zgflqn
Pulse length = 13.500 usec
Relaxation delay = 1.000 sec
NA = 16



4d

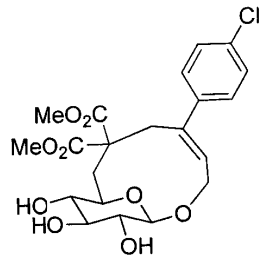



7.392
7.364
7.280
7.254
5.982
5.956
5.929
5.416
5.402
5.216
5.010
4.662
4.233
4.231
4.206
3.929
3.882
3.680
3.313
3.288
3.262
3.223
3.210
3.190
3.153
3.108
2.963
2.540
2.302
2.254
2.217
2.181
2.136
hx-8-142-DMSO
2014-02-14 21:37:50.390
USER: nmr
SOLVENT: DMSO
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Cl
MeO2C
MeO2C
HO
HO
O
O
OH
4e
2.10
2.08
1.00
1.04
1.04
1.01
0.99
1.99
1.06
3.07
5.29
2.97
2.01
8
7
6
5
4
3
2
1
0 PPM

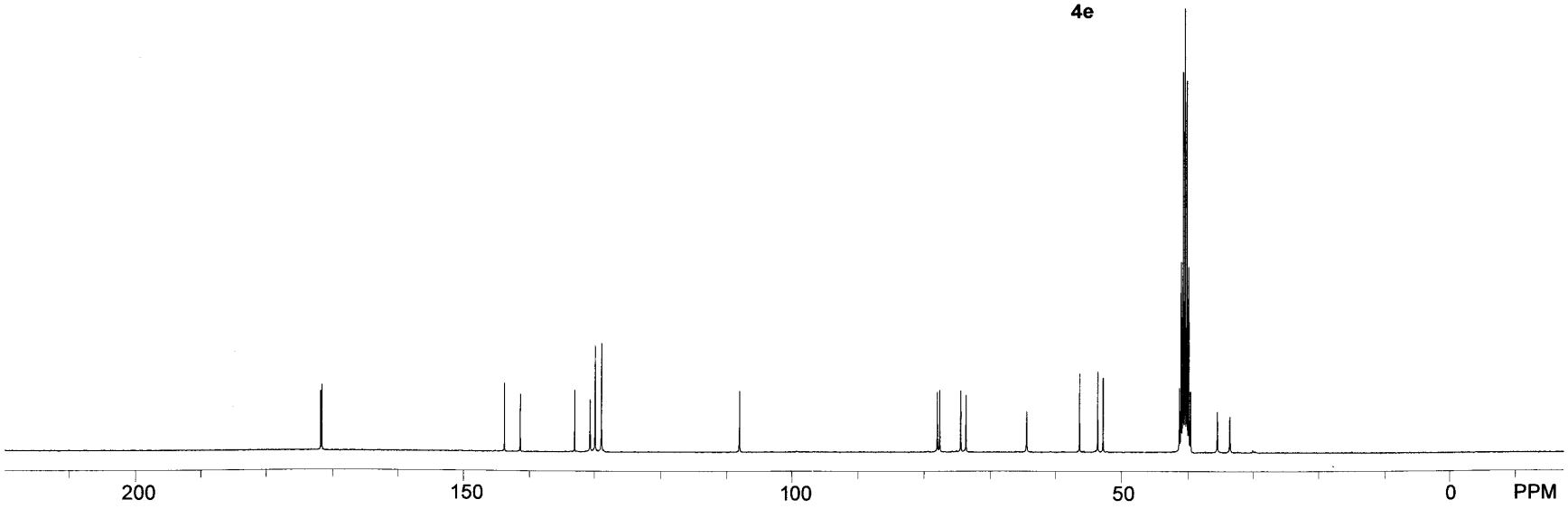


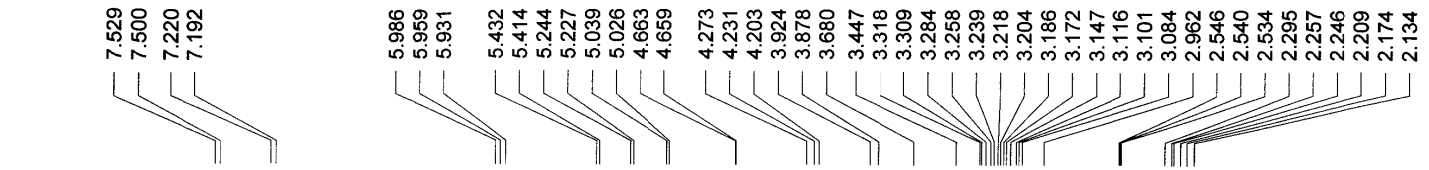
hx-8-142-DMSO

2014-02-12 10:22:23.015
USER: nmr
SOLVENT: DMSO
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 14504



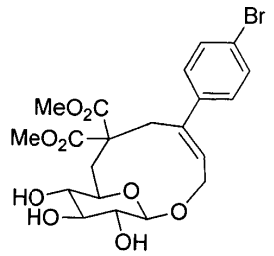
4e



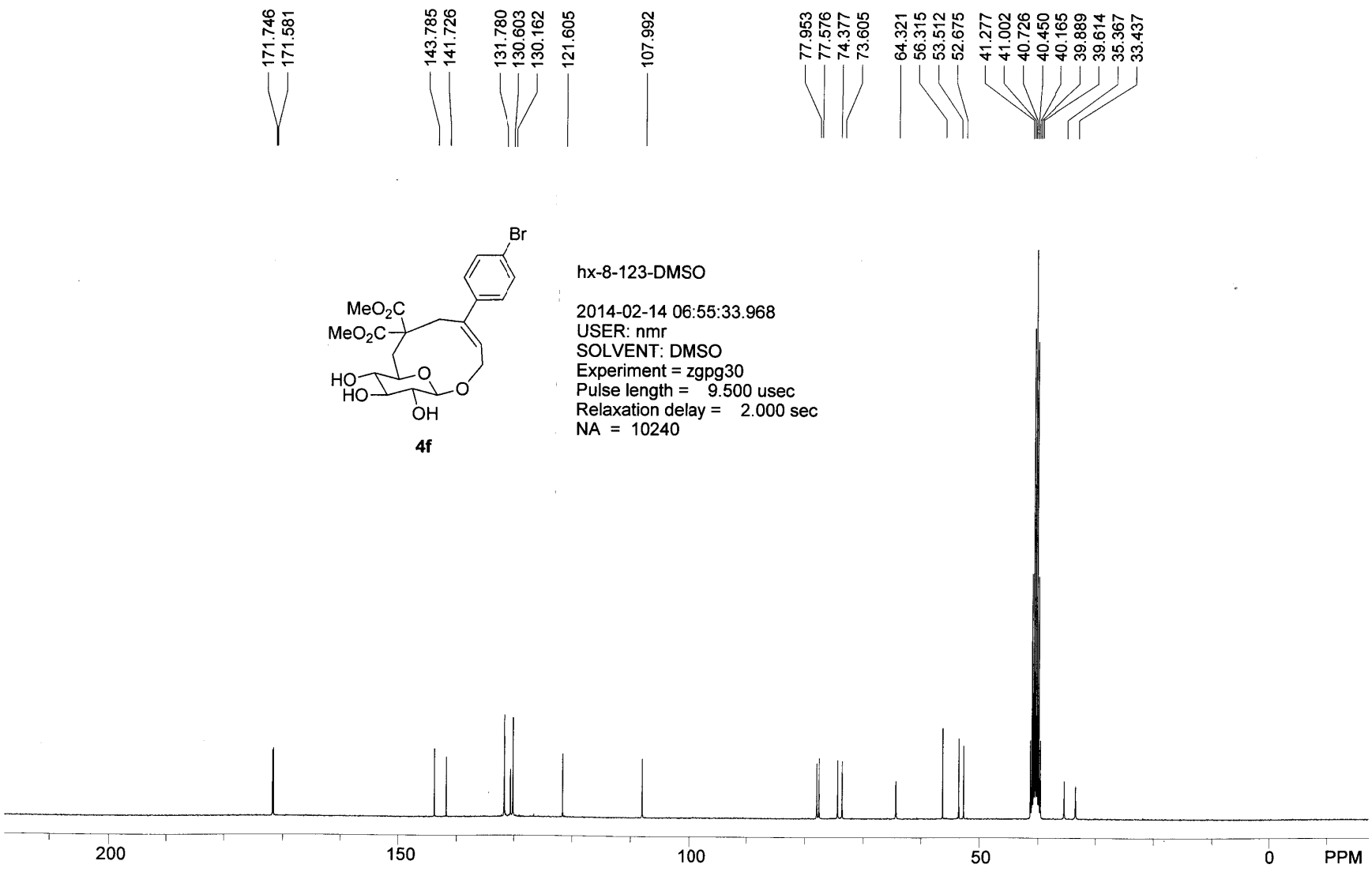


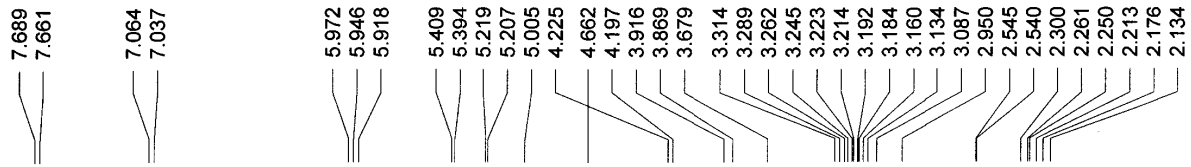
hx-8-123-DMSO

2014-02-14 10:11:37.796
USER: nmr
SOLVENT: DMSO
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8



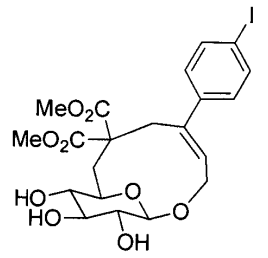
4f


171.746
171.581
143.785
141.726
131.780
130.603
130.162
121.605
107.992
77.953
77.576
74.377
73.605
64.321
56.315
53.512
52.675
41.277
41.002
40.726
40.450
40.165
39.889
39.614
35.367
33.437
Br
MeO2C
MeO2C
HO
HO
O
O
OH
4f
hx-8-123-DMSO
2014-02-14 06:55:33.968
USER: nmr
SOLVENT: DMSO
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 10240
200
150
100
50
0
PPM

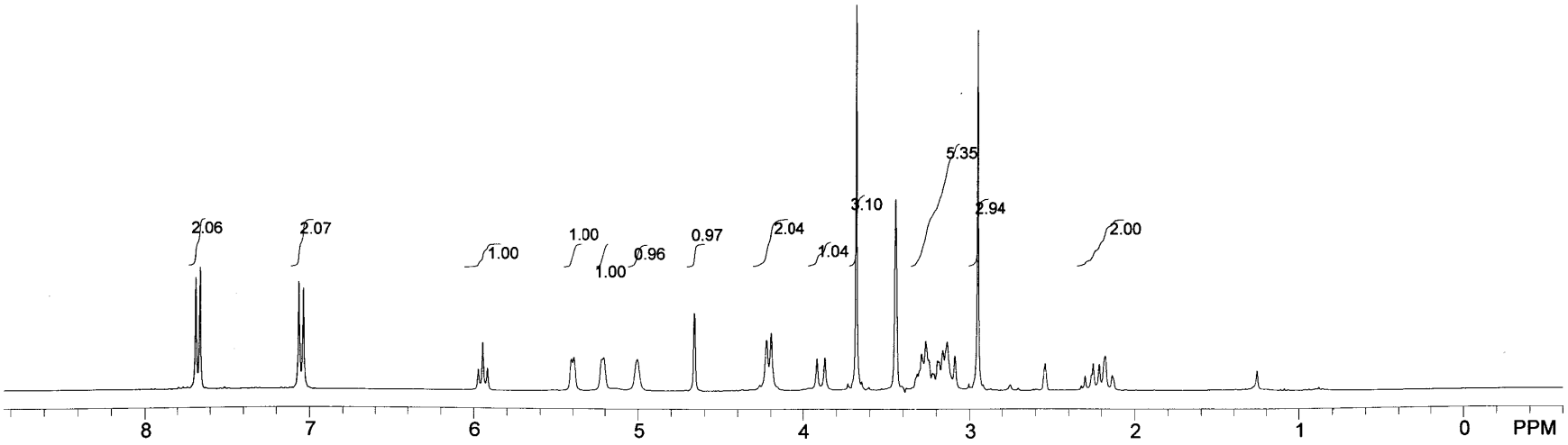


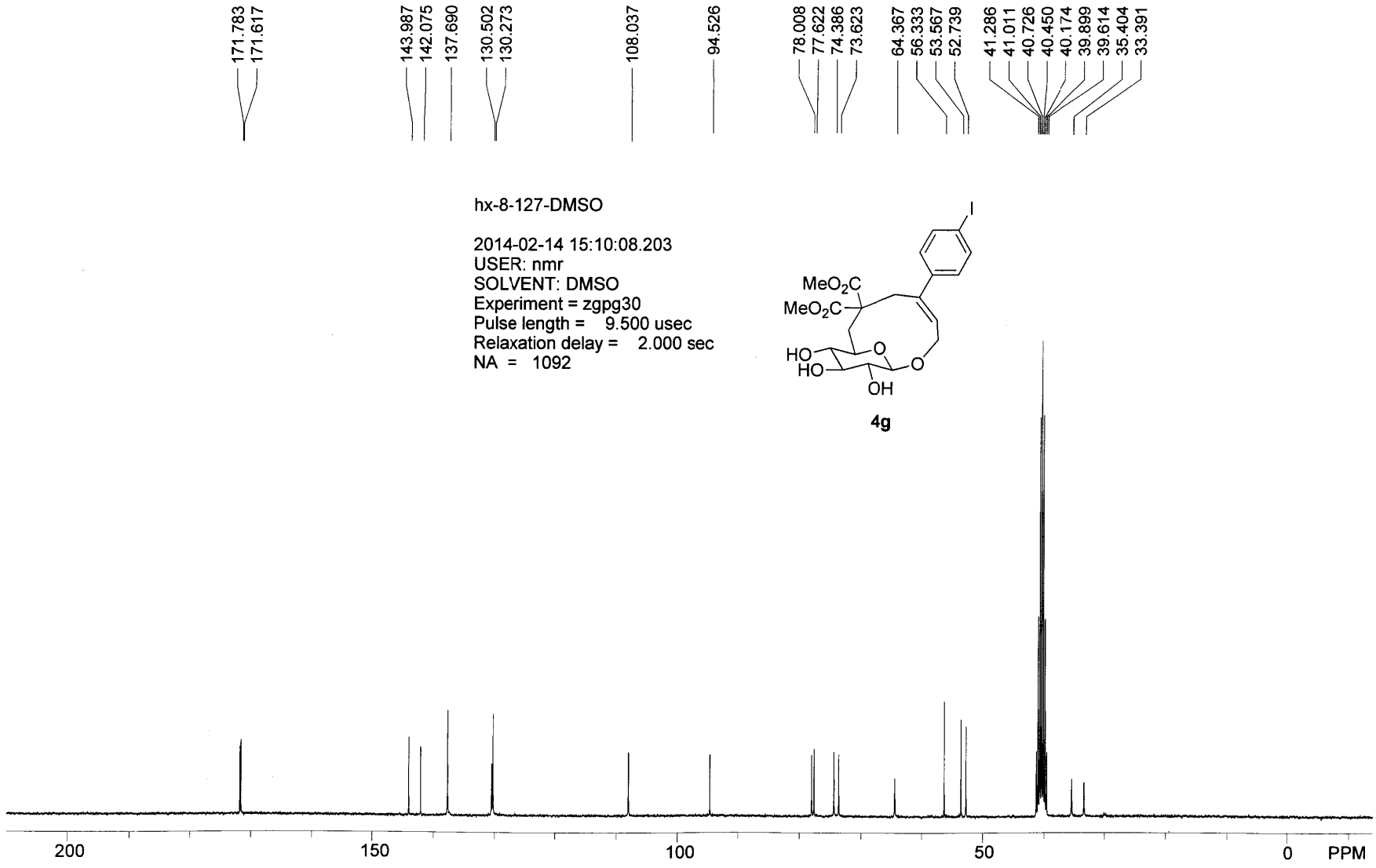
hx-8-127-DMSO

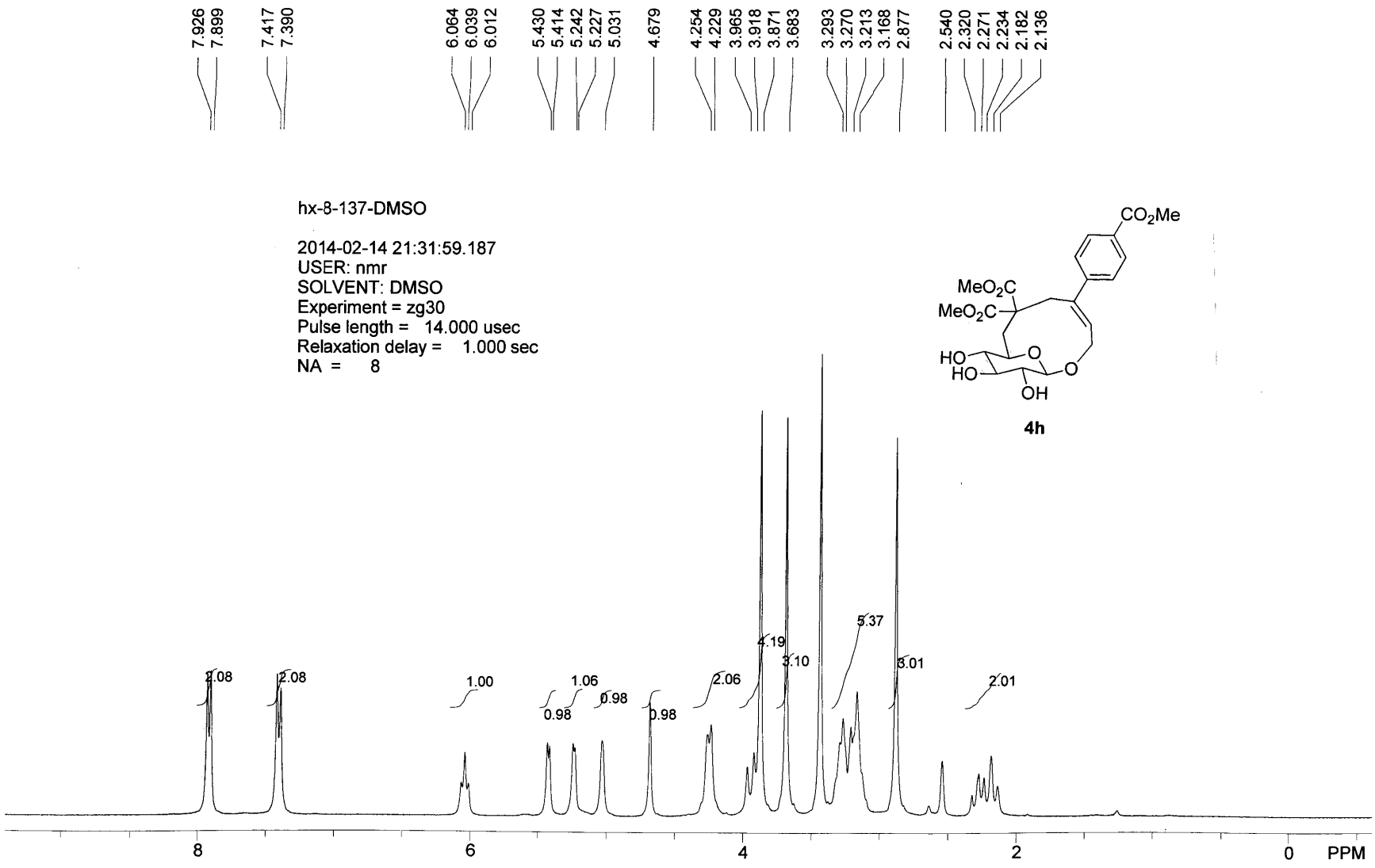
2014-02-14 14:05:02.312
USER: nmr
SOLVENT: DMSO
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8



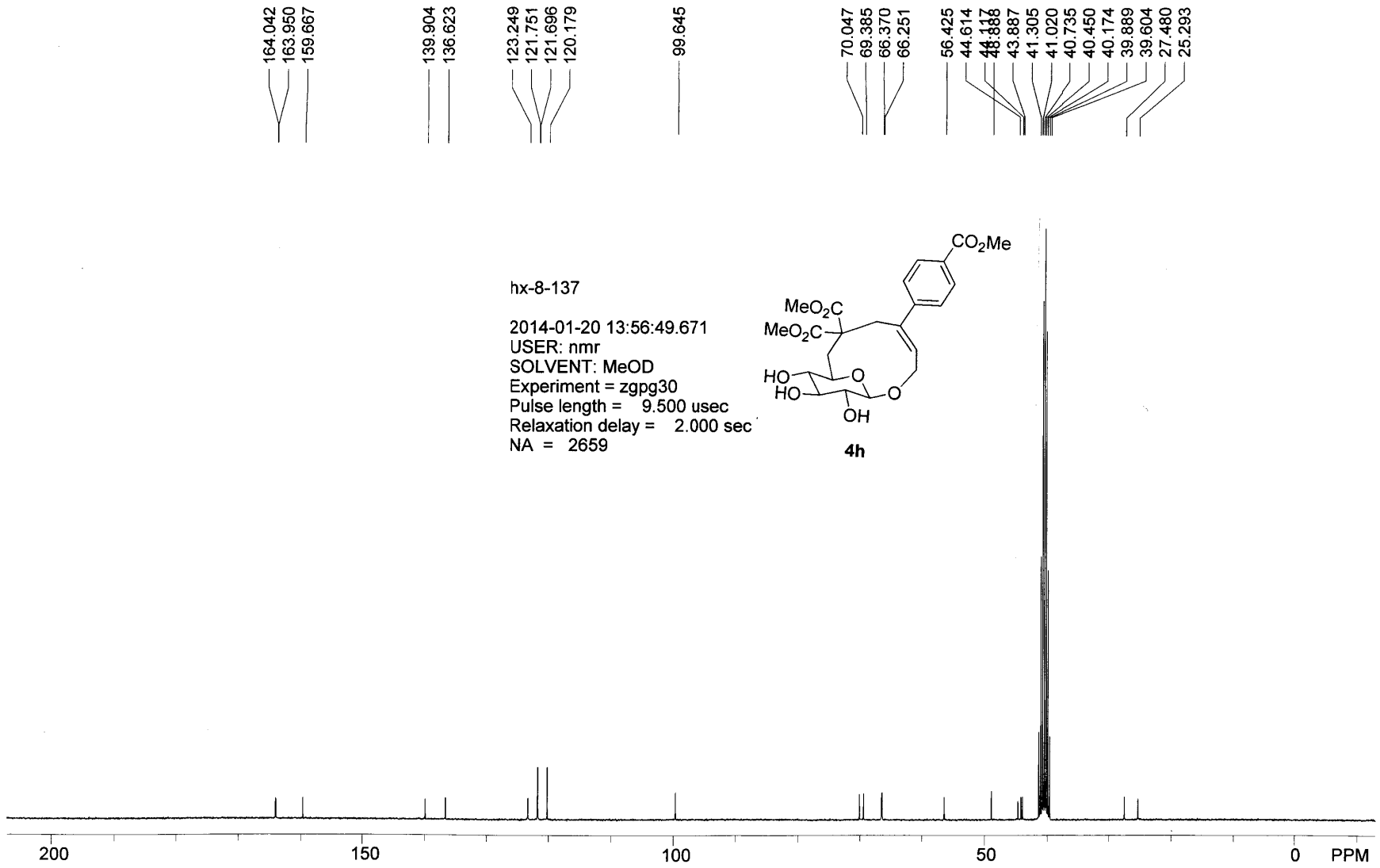
4g

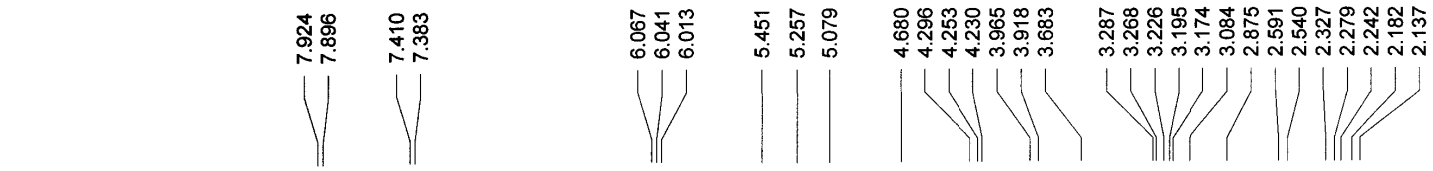



171.783
171.617
143.987
142.075
137.690
130.502
130.273
108.037
94.526
78.008
77.622
74.386
73.623
64.367
56.333
53.567
52.739
41.286
41.011
40.726
40.450
40.174
39.899
39.614
35.404
33.391
hx-8-127-DMSO
2014-02-14 15:10:08.203
USER: nmr
SOLVENT: DMSO
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 1092
I
MeO2C
MeO2C
HO
HO
O
O
OH
4g
200
150
100
50
0
PPM


7.926
7.899
7.417
7.390
6.064
6.039
6.012
5.430
5.414
5.242
5.227
5.031
4.679
4.254
4.229
3.965
3.918
3.871
3.683
3.293
3.270
3.213
3.168
2.877
2.540
2.320
2.271
2.234
2.182
2.136
hx-8-137-DMSO
2014-02-14 21:31:59.187
USER: nmr
SOLVENT: DMSO
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
CO2Me
MeO2C
MeO2C
HO
HO
OH
O
O
2.08
2.08
1.00
0.98
1.06
0.98
0.98
2.06
4.19
3.10
5.37
5.01
2.01
8
6
4
2
0
PPM

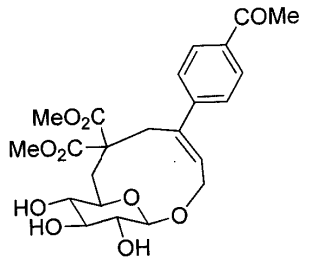
4h


164.042
163.950
159.667
139.904
136.623
123.249
121.751
121.696
120.179
99.645
70.047
69.385
66.370
66.251
56.425
44.614
43.887
41.305
41.020
40.735
40.450
40.174
39.889
39.604
27.480
25.293
hx-8-137
2014-01-20 13:56:49.671
USER: nmr
SOLVENT: MeOD
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 2659
CO2Me
MeO2C
MeO2C
HO
HO
O
O
OH
4h
200
150
100
50
0
PPM

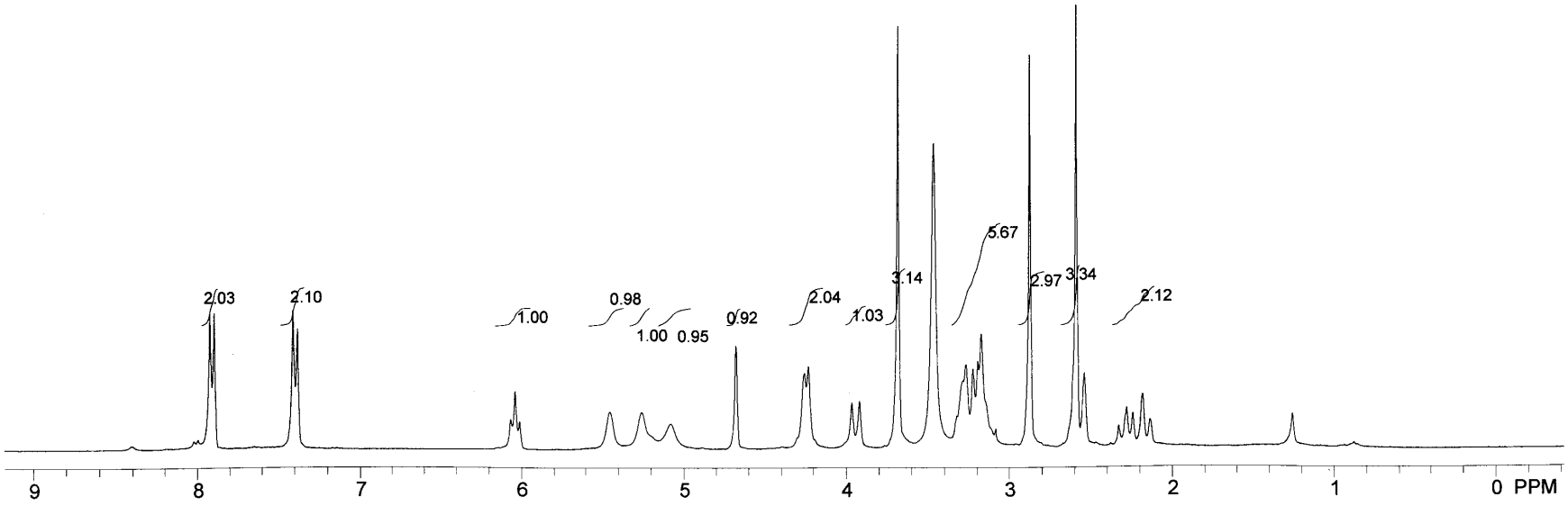


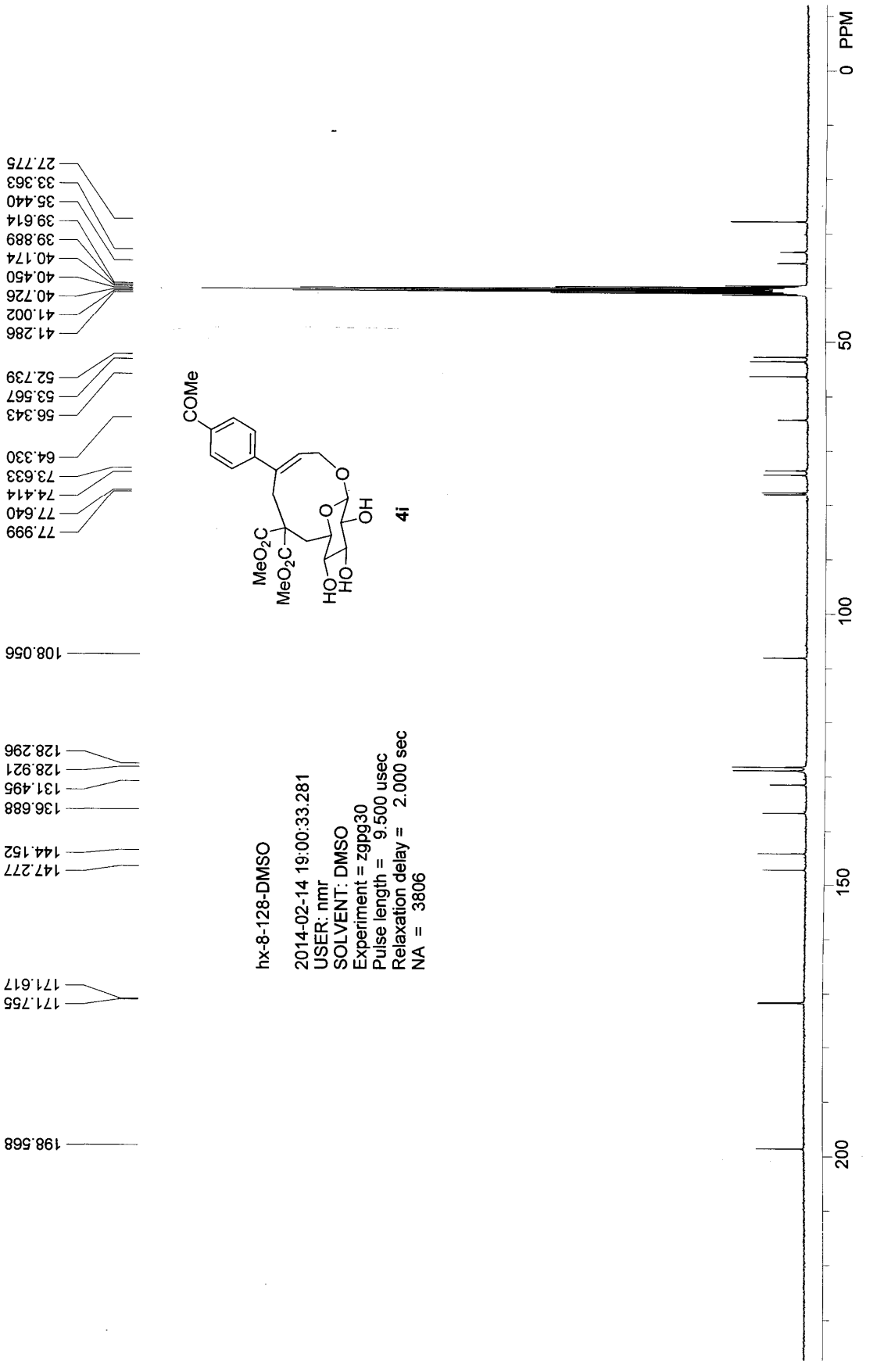
hx-8-128-DMSO

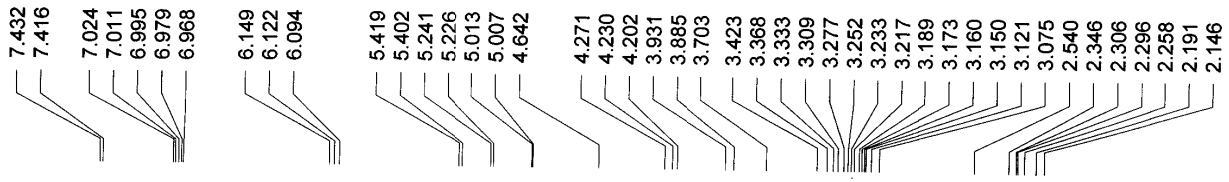
2014-02-14 21:57:05.296
USER: nmr
SOLVENT: DMSO
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8



4i

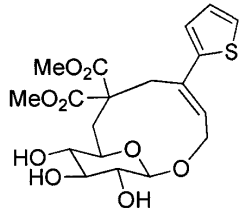



27.775
33.363
35.440
39.614
39.889
40.174
40.450
40.726
41.002
41.286
52.739
53.567
56.343
64.330
73.633
74.414
77.640
77.999
108.056
128.296
128.921
131.495
136.688
144.152
147.277
171.617
171.755
198.568
hx-8-128-DMSO
2014-02-14 19:00:33.281
USER: nmr
SOLVENT: DMSO
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 3806
COMe
MeO2C
MeO2C
HO
HO
OH
O
O
4i
200
150
100
50
0 PPM

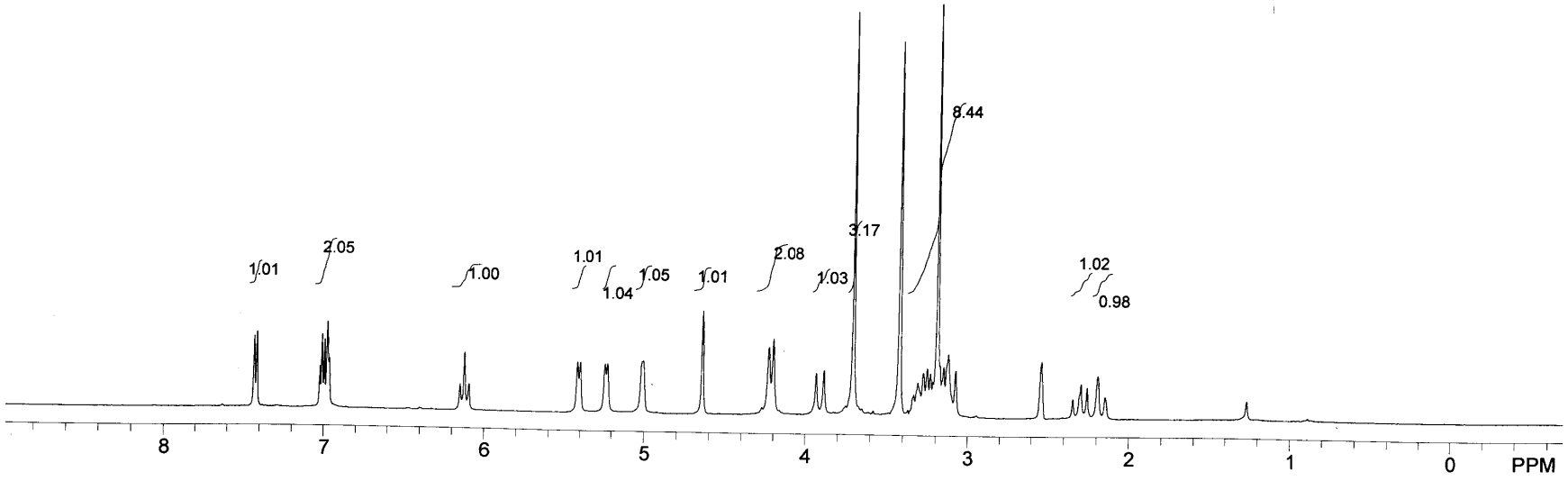


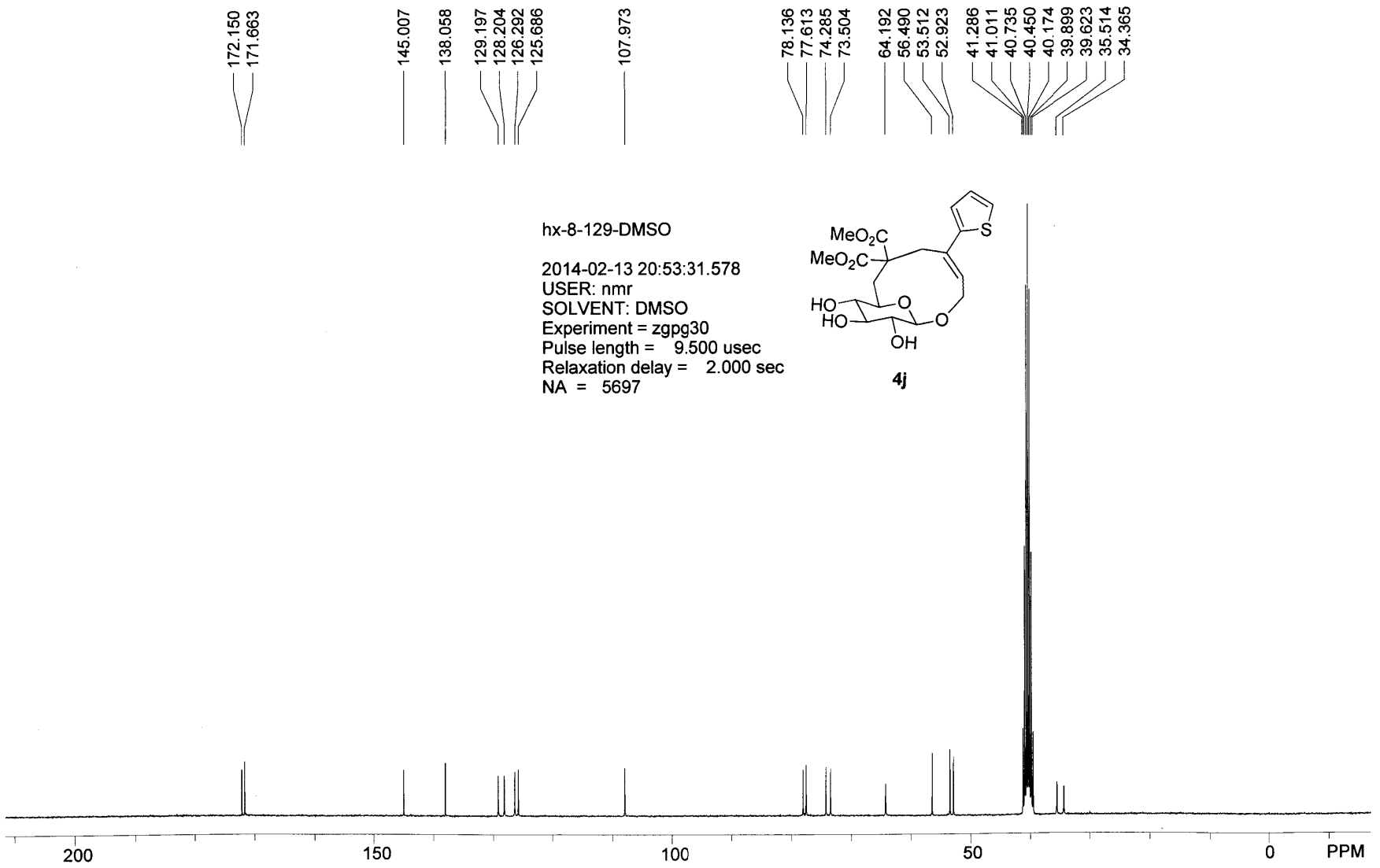
hx-8-129-DMSO

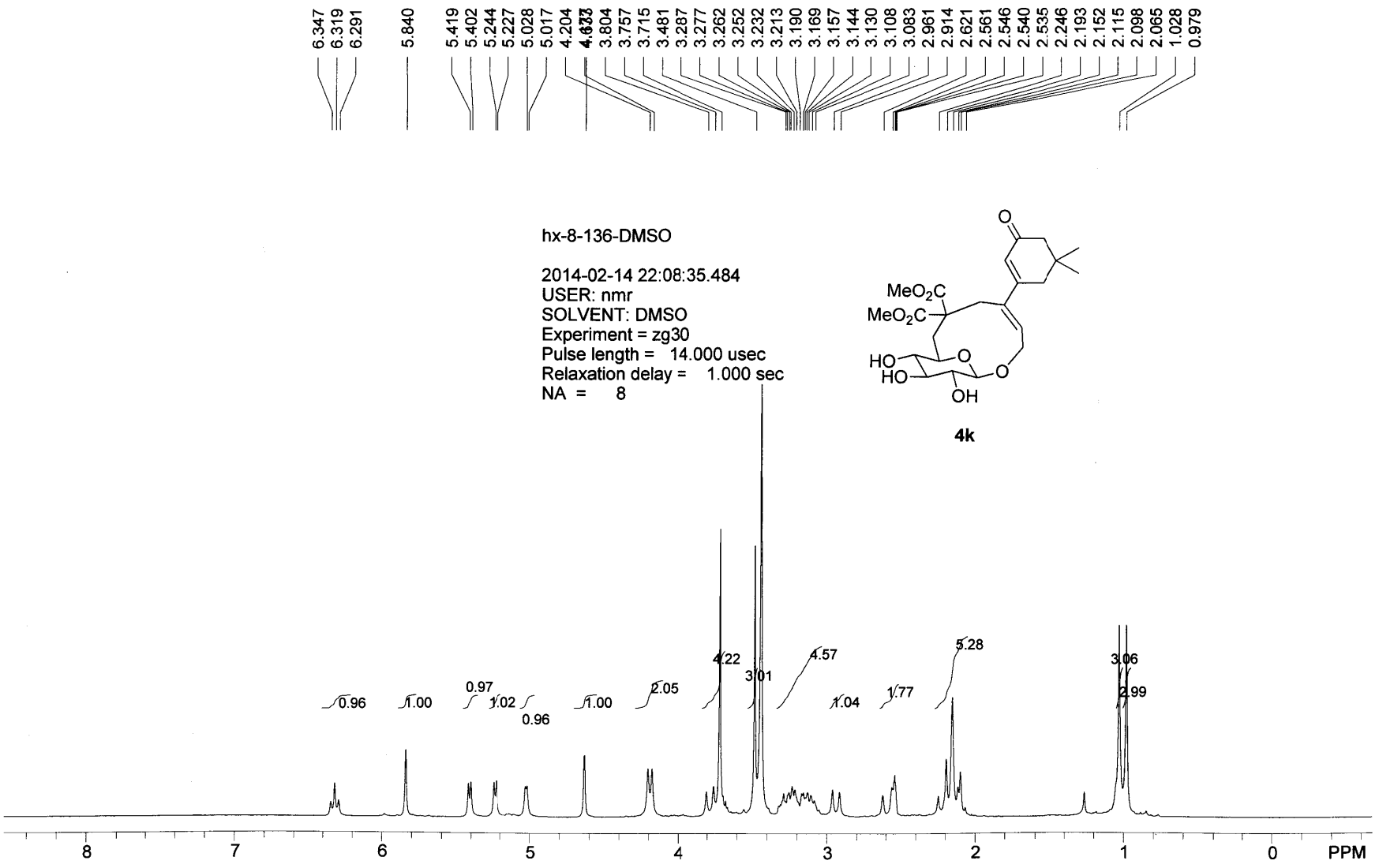
2014-02-14 21:50:07.625
USER: nmr
SOLVENT: DMSO
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8

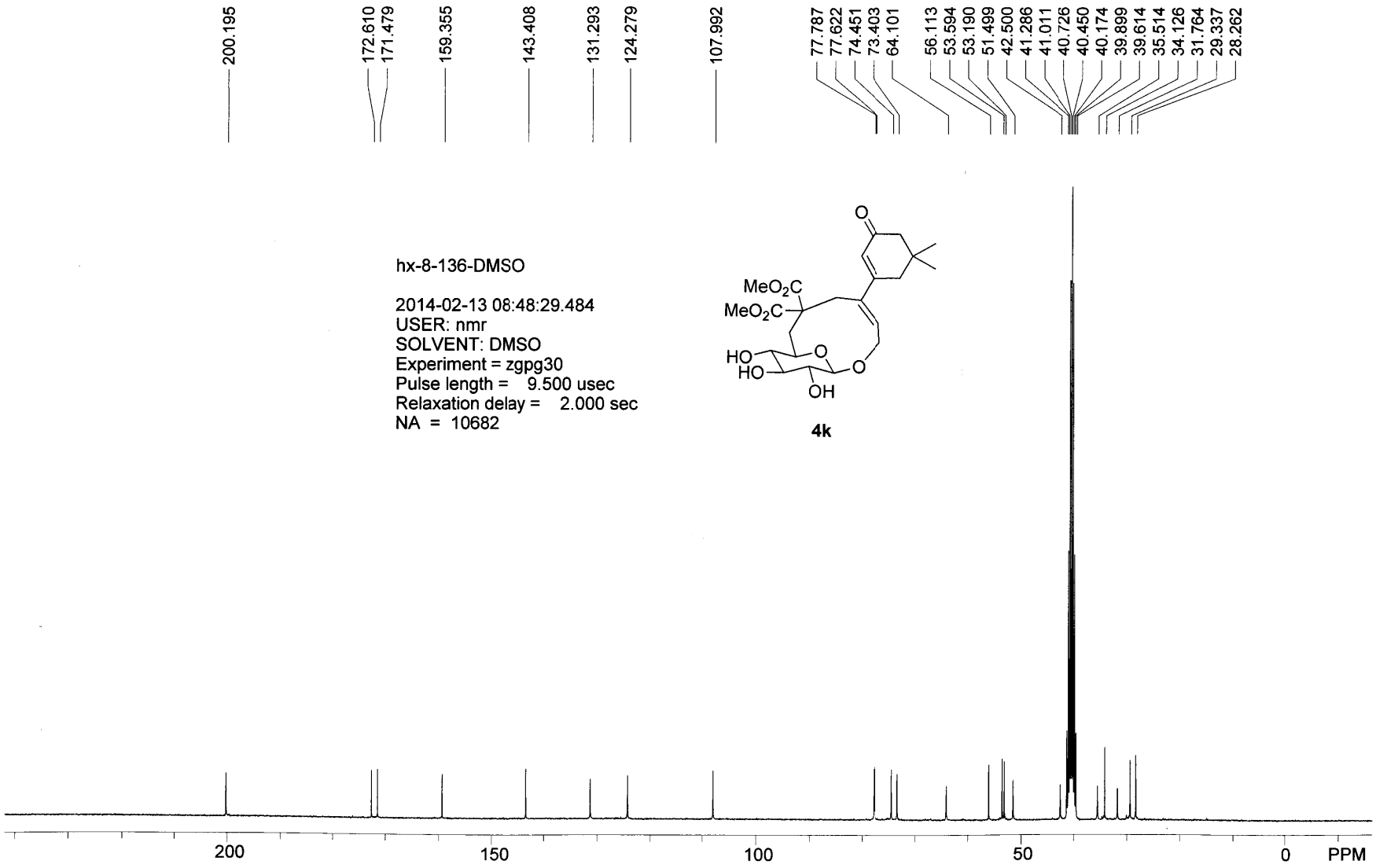


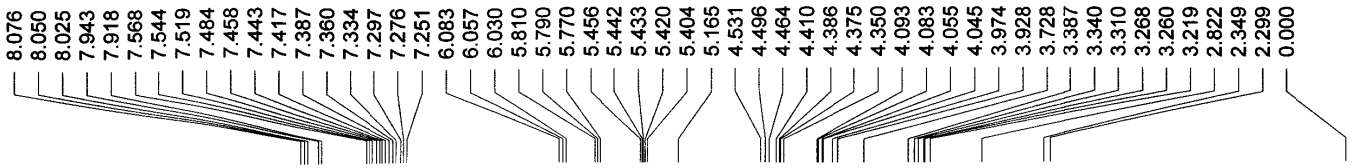
4j

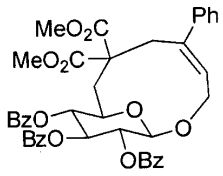



172.150
171.663
145.007
138.058
129.197
128.204
126.292
125.686
107.973
78.136
77.613
74.285
73.504
64.192
56.490
53.512
52.923
41.286
41.011
40.735
40.450
40.174
39.899
39.623
35.514
34.365
hx-8-129-DMSO
2014-02-13 20:53:31.578
USER: nmr
SOLVENT: DMSO
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 5697
MeO2C
MeO2C
HO
HO
O
O
OH
S
4j
200
150
100
50
0
PPM


6.347
6.319
6.291
5.840
5.419
5.402
5.244
5.227
5.028
5.017
4.204
3.804
3.757
3.715
3.481
3.287
3.277
3.262
3.252
3.232
3.213
3.190
3.169
3.157
3.144
3.130
3.108
3.083
2.961
2.914
2.621
2.561
2.546
2.540
2.535
2.246
2.193
2.152
2.115
2.098
2.065
1.028
0.979
hx-8-136-DMSO
2014-02-14 22:08:35.484
USER: nmr
SOLVENT: DMSO
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
MeO2C
MeO2C
HO
HO
O
O
OH
4k
0.96
1.00
0.97
1.02
0.96
1.00
2.05
4.22
3.01
4.57
1.04
1.77
5.28
3.06
2.99
8
7
6
5
4
3
2
1
0
PPM


200.195
172.610
171.479
159.355
143.408
131.293
124.279
107.992
77.787
77.622
74.451
73.403
64.101
56.113
53.594
53.190
51.499
42.500
41.286
41.011
40.726
40.450
40.174
39.899
39.614
35.514
34.126
31.764
29.337
28.262
hx-8-136-DMSO
2014-02-13 08:48:29.484
USER: nmr
SOLVENT: DMSO
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 10682
MeO2C
MeO2C
HO
HO
O
O
OH
O
4k
200
150
100
50
0
PPM

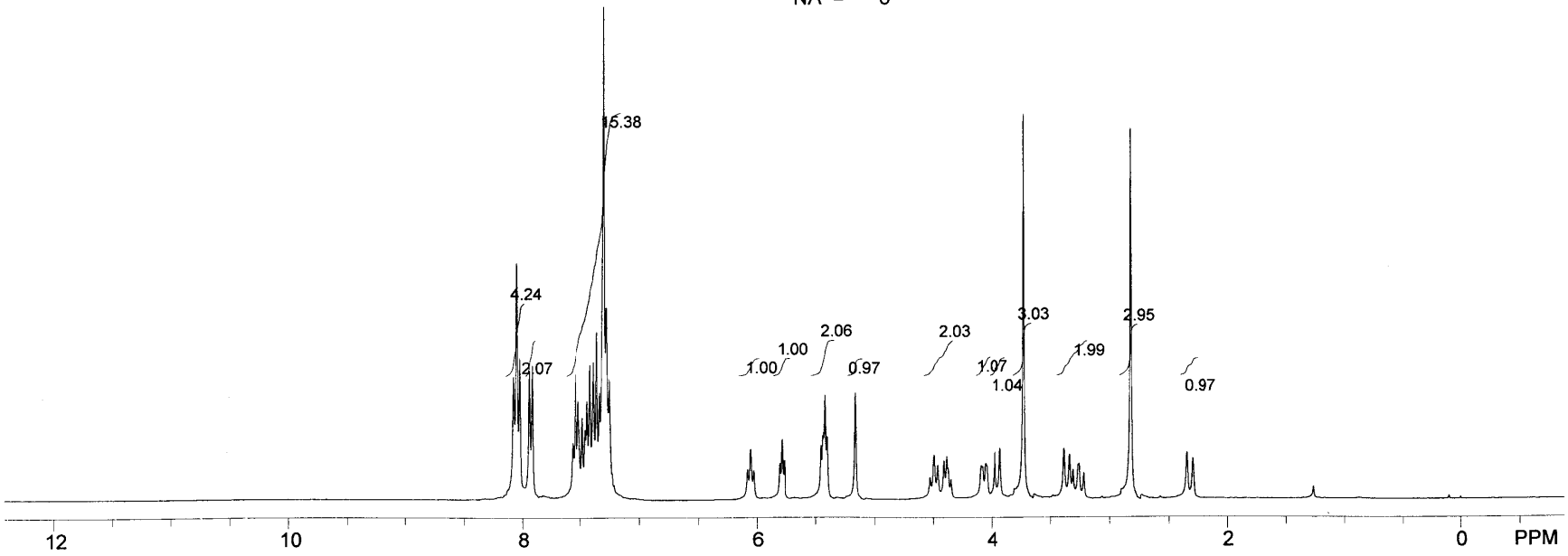


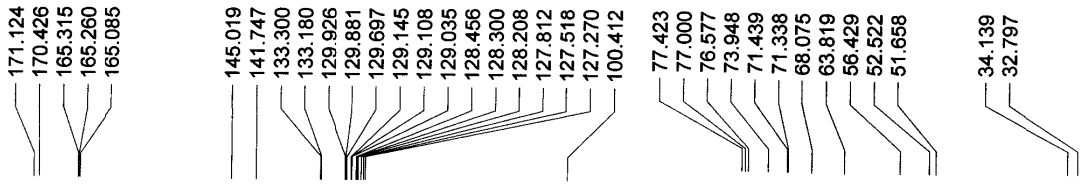


5

hx-7-45

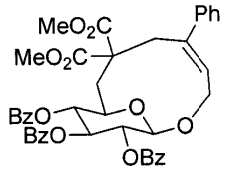
2013-07-17 10:02:21.609
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8





hx-7-45

2013-07-17 11:31:05.000
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 1480



5