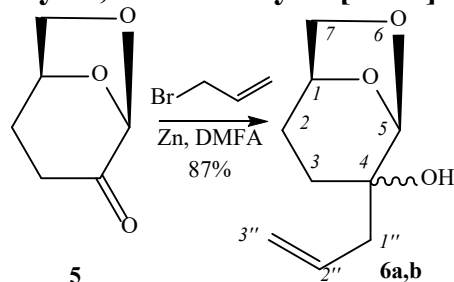


Synthesis of functional allyl- α -tetrahydropyrones from cyrene

Yuliya A. Khalilova, Liliya Kh. Faizullina, Shamil M. Salikhov and Farid A. Valeev

The spectral and analytical data were obtained using the equipment of the *Khimiya* Joint Center at the Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences. ^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance III, (500.13 MHz for ^1H and 125.47 MHz for ^{13}C). Mass spectra were recorded on a Shimadzu LCMS-2010 EV LC-MS system with one quadrupole in the positive and negative ion detection mode at a capillary potential of 4.5 and -3.5 kV, respectively, electrospray ionization, eluent MeCN– H_2O . Optical rotation was determined on a polarimeter Perkin Elmer-341. Analytic TLC was carried out on Sorbfil plates of the grade PTSKh-AF-A ("Sorbpolymer" Co., Krasnodar). The melting points were measured on a Boëtius 05 heating block.

6,8-Dioxabicyclo[3.2.1]octan-4-one (**5**) (Cyrene) were obtained from Circa, Melbourne, Australia. The authors are grateful to Circa Group for providing industrial grade Cyrene.

(1*S*,4*RS*,5*R*)-4-Allyl-6,8-dioxabicyclo[3.2.1]octan-4-ol (**6a,b**).

To a suspension of 0.200 g (0.002 mol) of cyrene **5** in 4.0 ml of DMF and 0.400 g (0.006 mol) Zn (dust) in an argon atmosphere at 0°C and stirring was added 0.6 ml (0.006 mol) of allyl bromide. The resulting was stirred at room temperature until the initial mixture disappeared (TLC control) ~ 30 min. Then the reaction mixture was treated with 3% HCl solution, the reaction products was extracted with ethyl acetate (3×5.0 ml), the combined organic layers were dried over MgSO_4 , the solvent was distilled off, the residue was chromatographed on SiO_2 . Oil. Yield 0.231 g (87%) in ratio $R:S=2.5:1$. $[\alpha]_D^{25} = -68.7^\circ$ (c 1.0, CHCl_3). R_f 0.50 (petroleum ether–EtOAc, 3:1). ^1H NMR (CDCl_3), δ : 1.44–1.57 [1.41–1.53] (m, 2H, $\text{C}^{2\text{B}}\text{H}_2$, $\text{C}^{3\text{B}}\text{H}_2$); 1.76–1.85 (m, 2H, $\text{C}^{2\text{A}}\text{H}_2$, $\text{C}^{3\text{B}}\text{H}_2$) [1.65 (dt, 1H, $^2J_{3\text{A},3\text{B}}$ 13.5, $^3J_{3\text{A},2\text{B}}$ 13.5, $^3J_{3\text{A},2\text{A}}$ 6.1, $\text{C}^{3\text{A}}\text{H}_2$); 1.95–2.03 (m, 1H, $\text{C}^{2\text{A}}\text{H}_2$)¹; 2.22 [2.60] (br.s, 1H, OH); 2.27–2.34 [2.14–2.20] (m, 2H, $\text{C}^{1\text{A}}\text{H}_2$, $\text{C}^{1\text{B}}\text{H}_2$); 3.74 [3.73] (dd, 1H, $^2J_{7\text{B},7\text{A}}$ 7.1, $^3J_{7\text{B},1}$ 4.6, $\text{C}^{7\text{B}}\text{H}_2$); 3.81 [3.82] (d, 1H, $^2J_{7\text{A},7\text{B}}$ 7.1, $\text{C}^{7\text{A}}\text{H}_2$); 4.45–4.48 [4.44–4.47] (m, 1H, C^1H); 4.99 [4.98] (s, 1H, C^5H); 5.06–5.11 [5.04–5.10] (m, 2H, $\text{C}^{3\text{A}}\text{H}_2$, $\text{C}^{3\text{B}}\text{H}_2$); 5.82–5.91 [5.80–5.8] (m, 1H, C^2H).

¹ In square brackets are signals of minor diastereomers

^{13}C NMR (CDCl_3), δ : 26.98 [25.46] (C^2), 29.52 [27.74] (C^3), 39.13 [41.83] ($\text{C}^{1'}$), 67.68 [67.09] (C^7), 71.73 [71.05] (C^4), 73.19 [72.92] ($\text{C}^{1'}$), 105.02 [104.26] (C^5), 118.44 [118.36] (C^3 '), 133.09 [132.56] (C^2 ').

Mass spectrum, m/z : 171.1 [MH] $^+$. Calcd for $\text{C}_9\text{H}_{14}\text{O}_3$. 170.2.

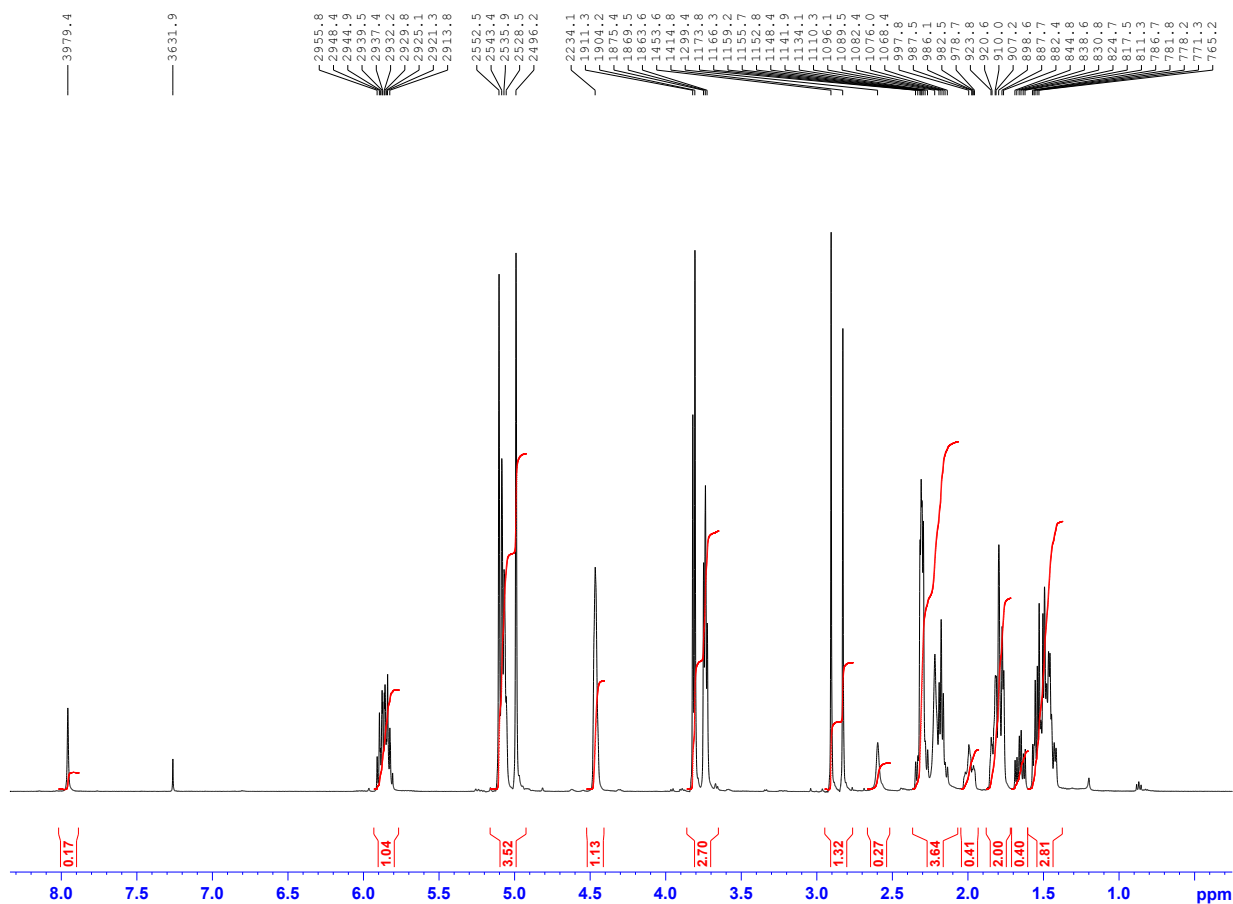


Fig. S6.1. Complete ^1H NMR (500 MHz) spectrum in CDCl_3

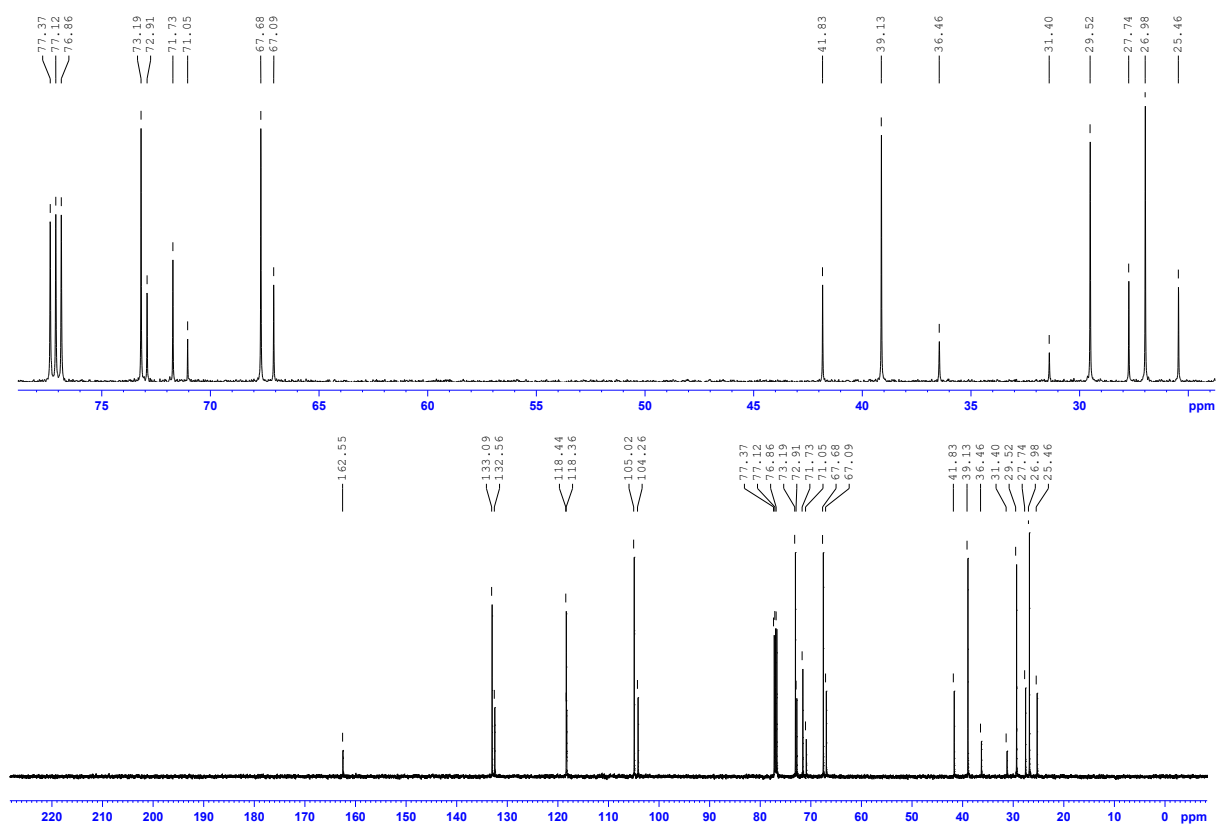


Fig. S6.2. Complete $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CDCl_3

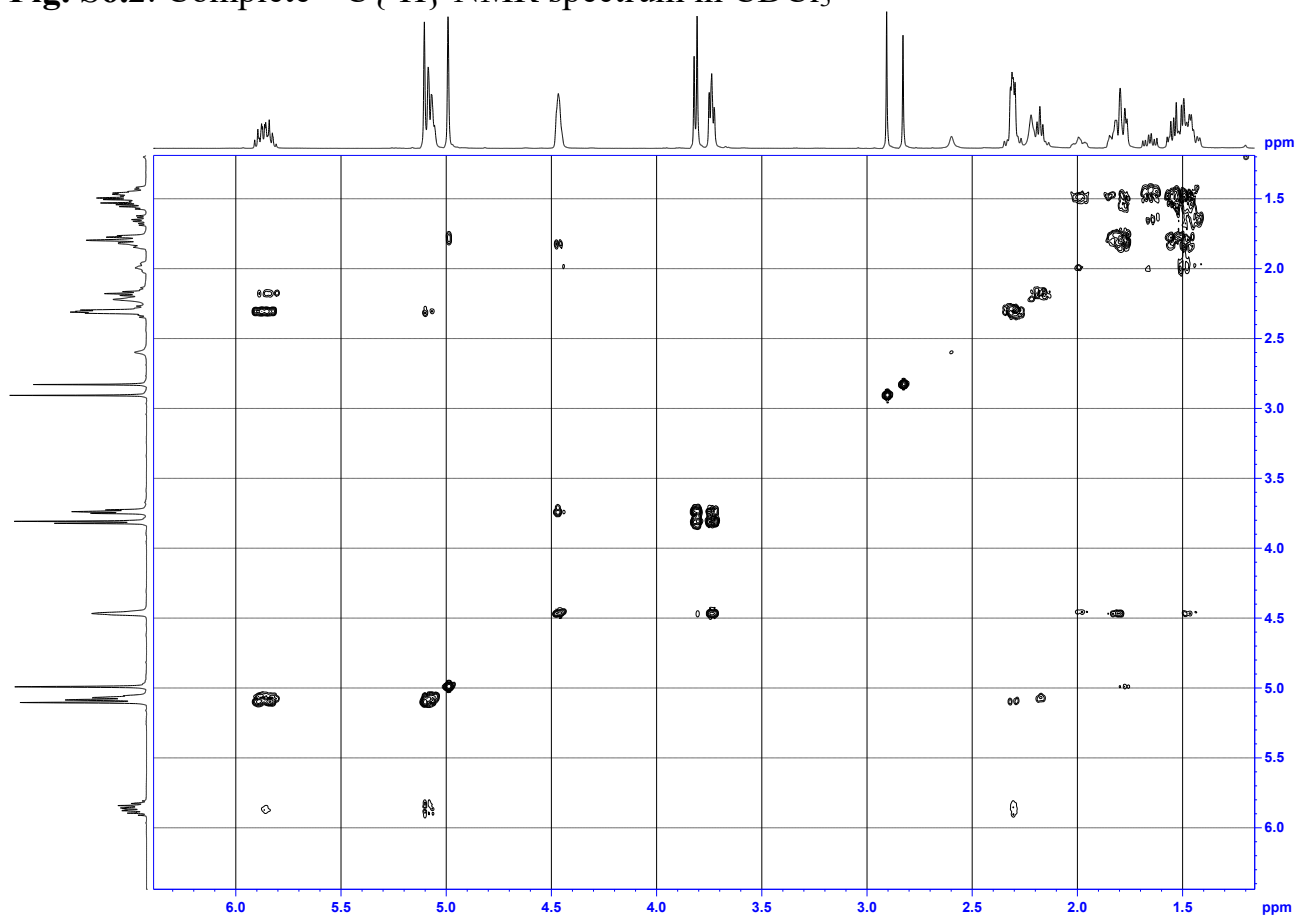


Fig. S6.3. Complete $\{^1\text{H},^1\text{H}\}$ COSY NMR spectrum in CDCl_3

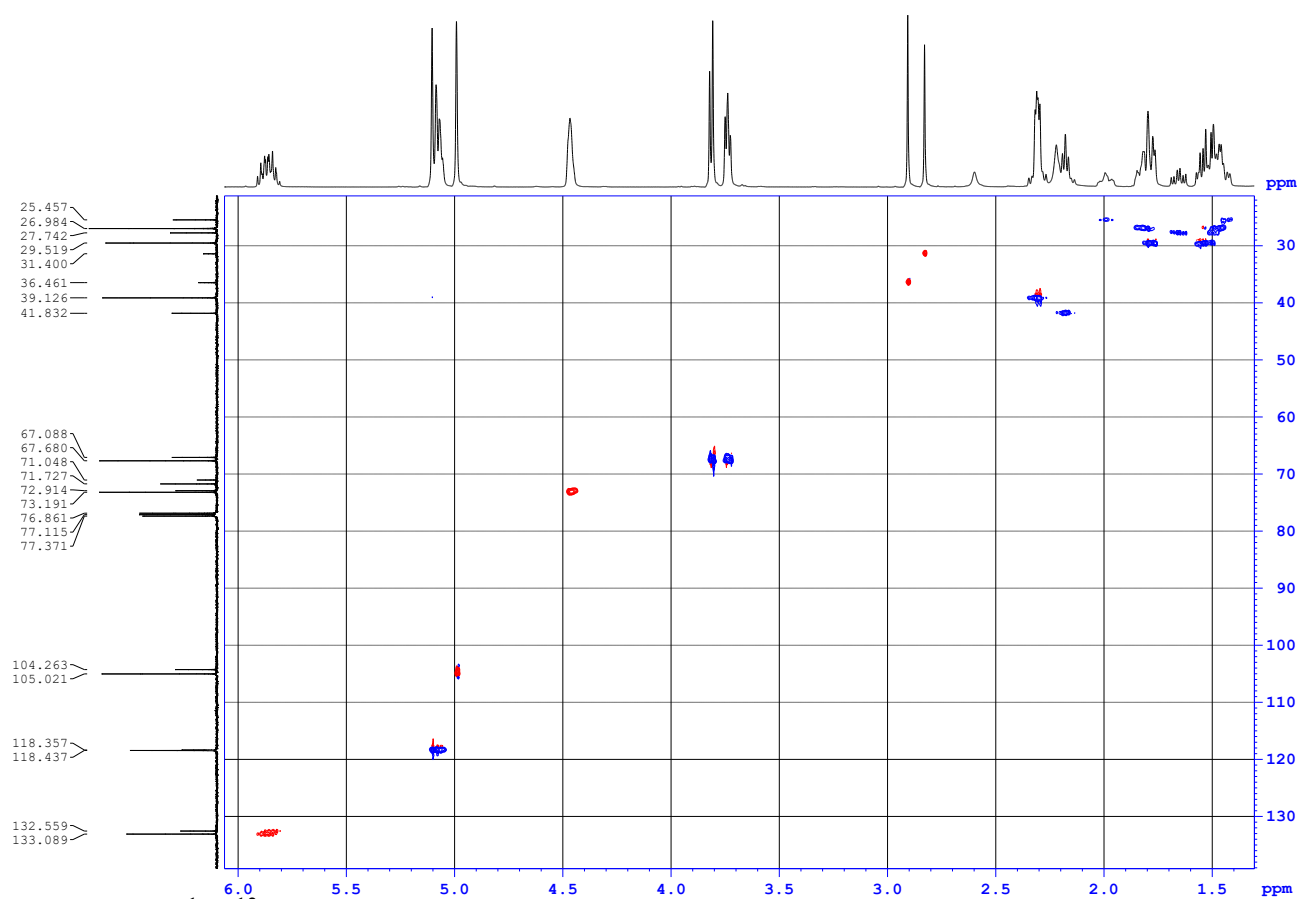


Fig. S6.4. $\{^1\text{H}, ^{13}\text{C}\}$ HSQCED NMR spectrum in CDCl_3

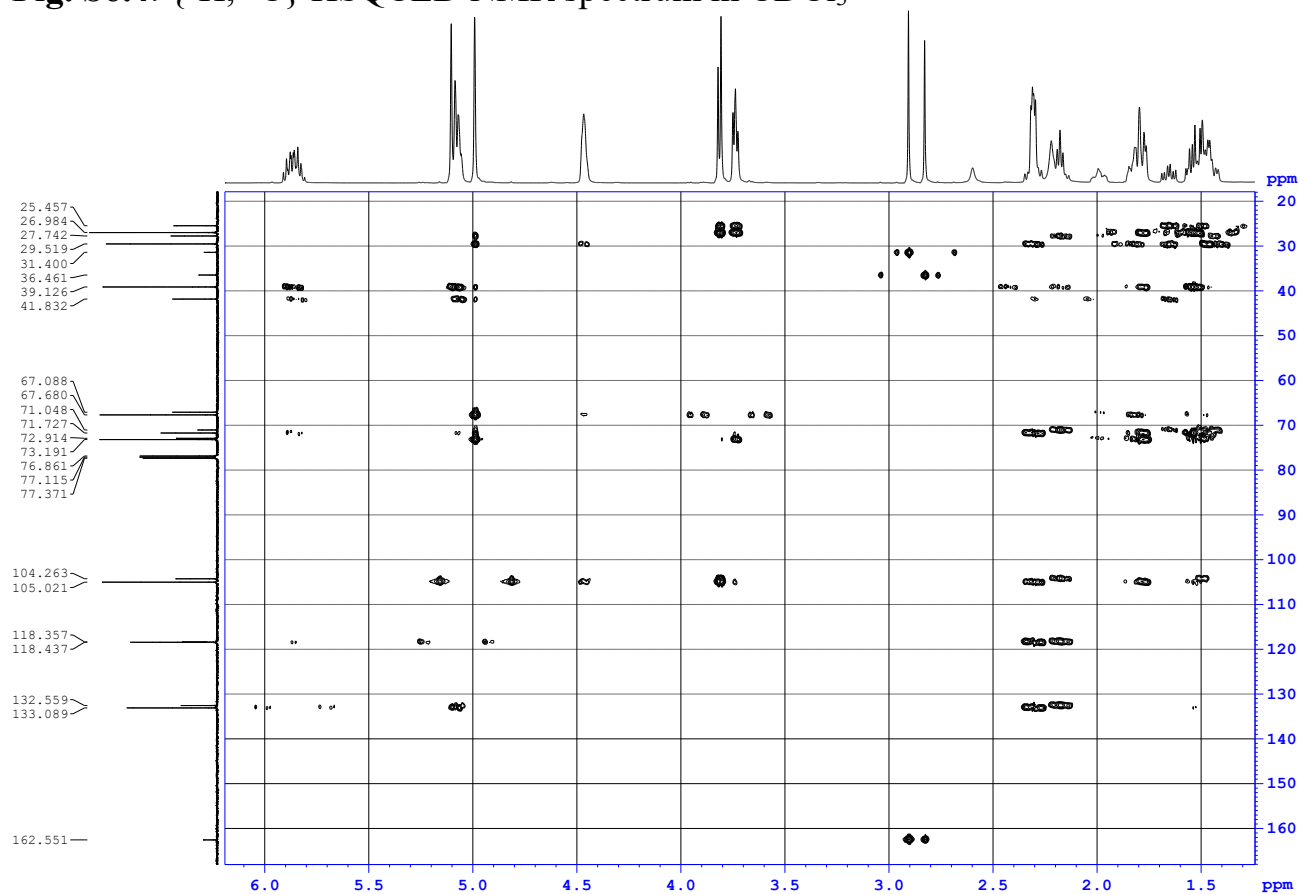


Fig. S6.5. $\{^1\text{H}, ^{13}\text{C}\}$ HMBC NMR spectrum in CDCl_3

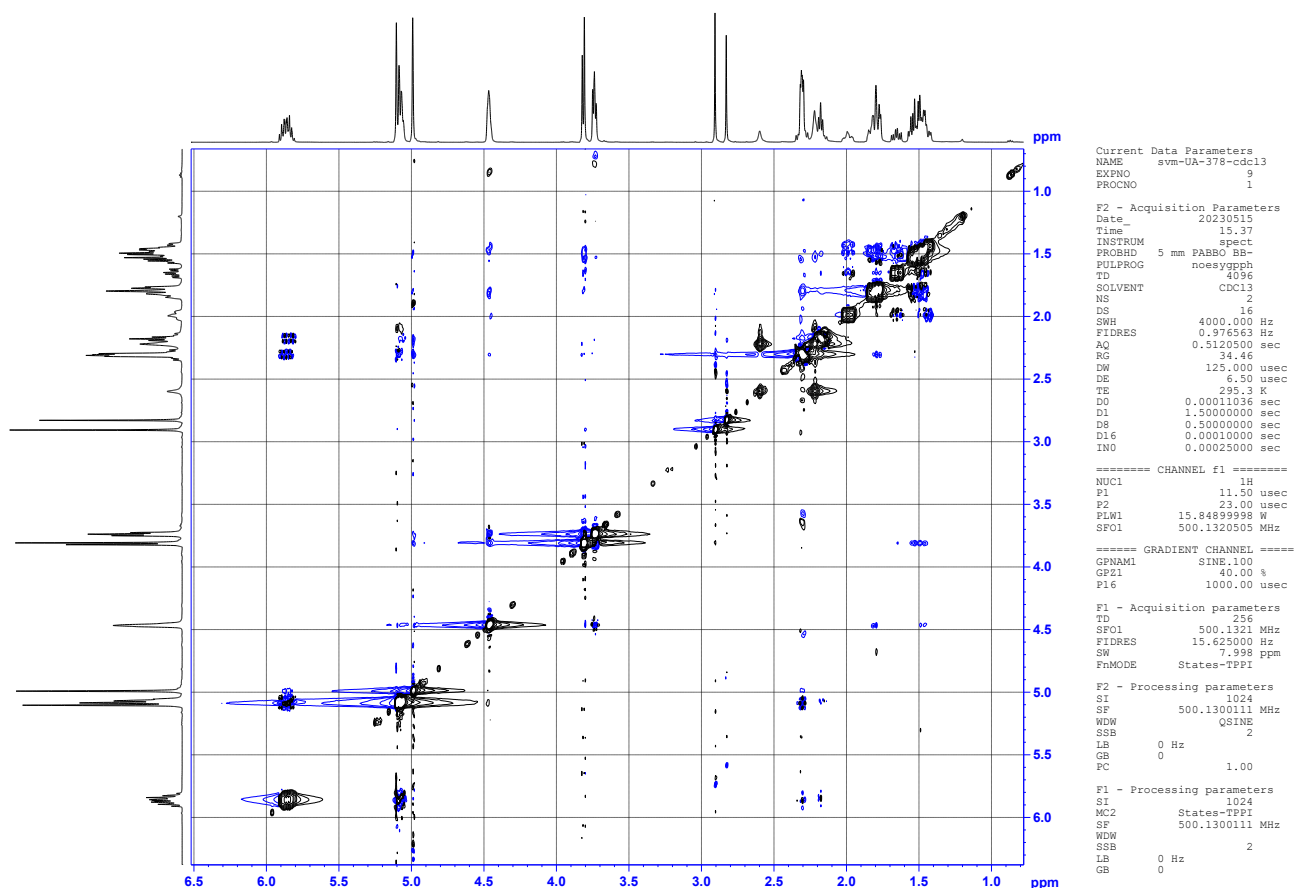
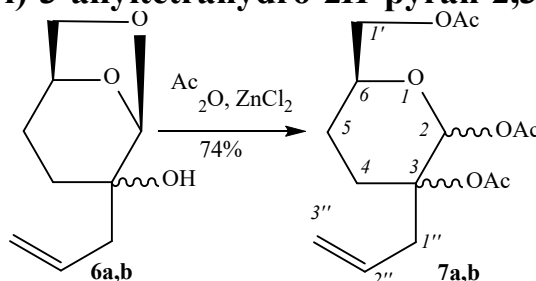


Fig. S6.6. Complete $\{^1\text{H}, ^1\text{H}\}$ NOESY NMR spectrum in CDCl_3

(S)-6-(Acetoxymethyl)-3-allyltetrahydro-2H-pyran-2,3-diyl diacetate (7a,b).



To a solution of 0.500 g (0.003 mol) of adducts **6a,b** in 7.0 ml Ac_2O at 0 °C was added 0.400 g (0.003 mol) ZnCl_2 . The reaction mixture was stirred for 3 hours at room temperature (control by TLC). Then the reaction mixture was treated with a saturated aqueous solution of NaHCO_3 (pH=6) and the reaction products were extracted with ethyl acetate (3×15.0 ml), the combined organic layers were dried over MgSO_4 , the solvent was distilled off, the residue was chromatographed on SiO_2 . Oil. Yield 0.686 g (74%) in ratio 20.8:7.7:1.2:1.0 in favor of the 2*R*,3*R*-diastereomer, $[\alpha]_D^{25} = +57.2^\circ$ (*c* 1.0, CHCl_3). R_f 0.6 (petroleum ether– EtOAc , 3:1). ^1H NMR (CDCl_3), δ : ^1H NMR (CDCl_3), δ : 1.42–1.47 [1.49–1.60; 1.43–1.45; 1.44–1.46] (m, 1H, $\text{C}^3\text{B}_\text{H}_2$); 1.54–1.62 [1.50–1.59; 1.64–1.68; 1.68–1.72] (m, 1H, $\text{C}^3\text{A}_\text{H}_2$); 1.72 [1.92; 1.60; 2.11] (dt, 1H, $^2J_{4\text{B},4\text{A}}$ 13.8, $^3J_{4\text{B},5\text{A}}$ 13.8, $^3J_{4\text{B},5\text{B}}$ 4.2, $\text{C}^4\text{B}_\text{H}_2$); 1.96 [1.88; 1.90; 1.95] (s, 3H, Ac); 1.97 [1.98; 1.96; 2.02] (s, 3H, Ac); 2.05 [2.03; 2.04; 2.06] (s, 3H, Ac); 2.38 [2.16; 2.29; 2.80] (td, 1H, $^2J_{4\text{A},4\text{B}}$ 13.8, $^3J_{4\text{A},5\text{A}}$ 3.7, $^3J_{4\text{A},5\text{B}}$ 3.7, $\text{C}^4\text{A}_\text{H}_2$); 2.53 [2.71; 2.63;

2.66] (dd, 1H, $^2J_{I'B, I'A}$ 14.9, $^3J_{I'B, 2'}$ 7.7, $C^{I'B}H_2$); 2.59 [2.93; 2.92; 2.7] (dd, 1H, $^2J_{I'A, I'B}$ 14.9, $^3J_{I'A, 2'}$ 7.7, $C^{I'A}H_2$); 3.92-4.00 [3.91-3.99; 3.90-3.98; 3.93-3.99] (m, 3H, C^6H , $C^{7A}H_2$, $C^{7B}H_2$); 4.94-5.08 [4.93-5.08; 4.95-5.09; 4.93-5.09] (m, 2H, $C^{3'A}H_2$, $C^{3'B}H_2$); 5.54-5.62 [5.53-5.61; 5.55-5.64; 5.57-5.68] (m, 1H, C^2H); 6.22 [6.33; 6.01; 5.51] (s, 1H, C^2H). ^{13}C NMR ($CDCl_3$), δ : 20.70 [20.81, 20.83, 20.71] (Ac), 20.90 [20.69, 20.99, 21.03] (Ac), 21.80 [21.54, 21.90, 21.95] (Ac), 22.24 [24.03, 22.70, 23.39] (C^3), 26.65 [26.46, 27.56, 28.03] (C^4), 37.45 [35.30, 35.45, 38.17] ($C^{I'}$), 66.18 [65.80, 65.38, 65.69] (C^7), 67.91 [67.83, 73.16, 73.98] (C^6), 79.11 [79.93, 79.39, 80.19] (C^3), 90.80 [91.64, 93.33, 94.65] (C^2), 119.19 [119.38, 118.57, 118.89] (C^3), 130.89 [131.13, 131.62, 132.39] (C^2).

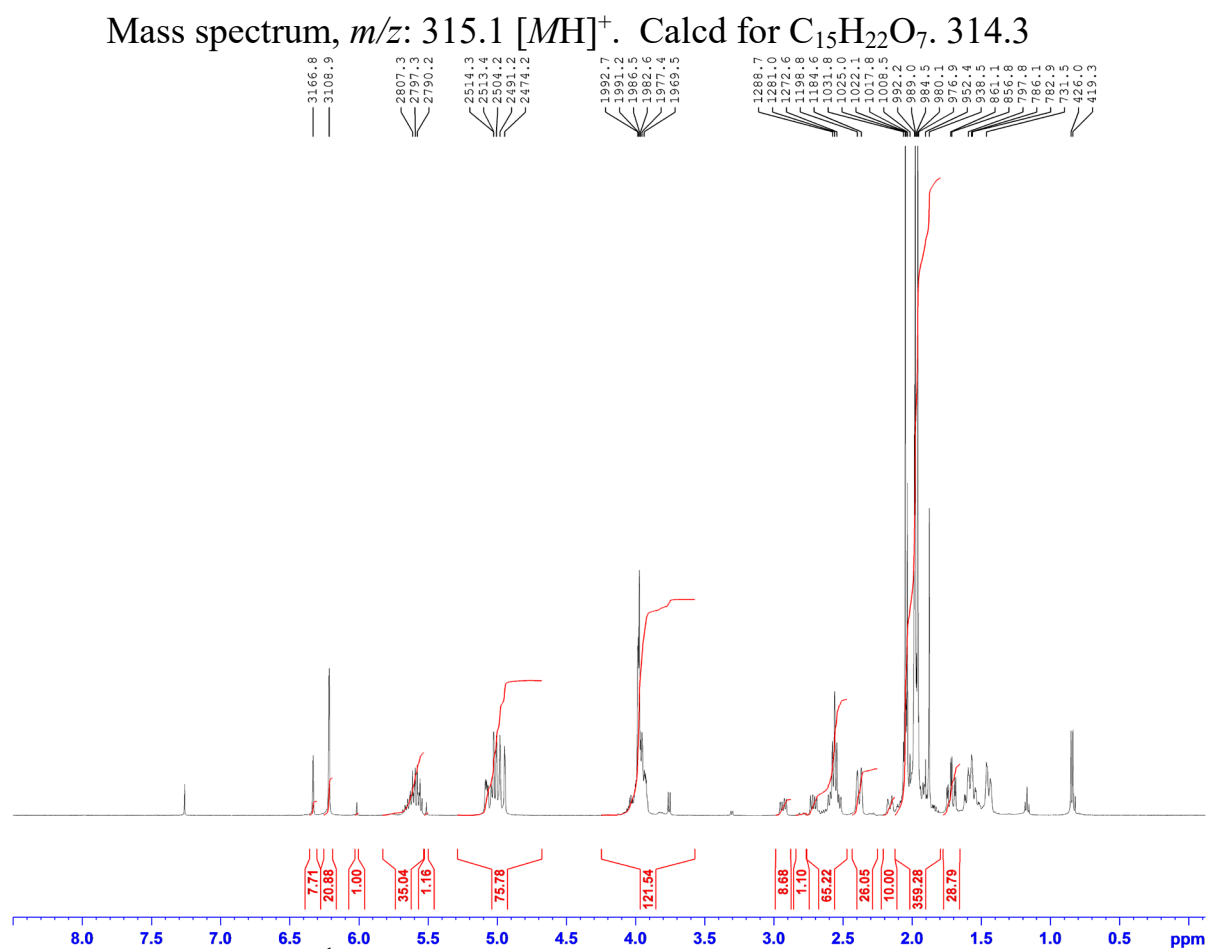


Fig. S7.1. Complete 1H NMR (500 MHz) spectrum in $CDCl_3$

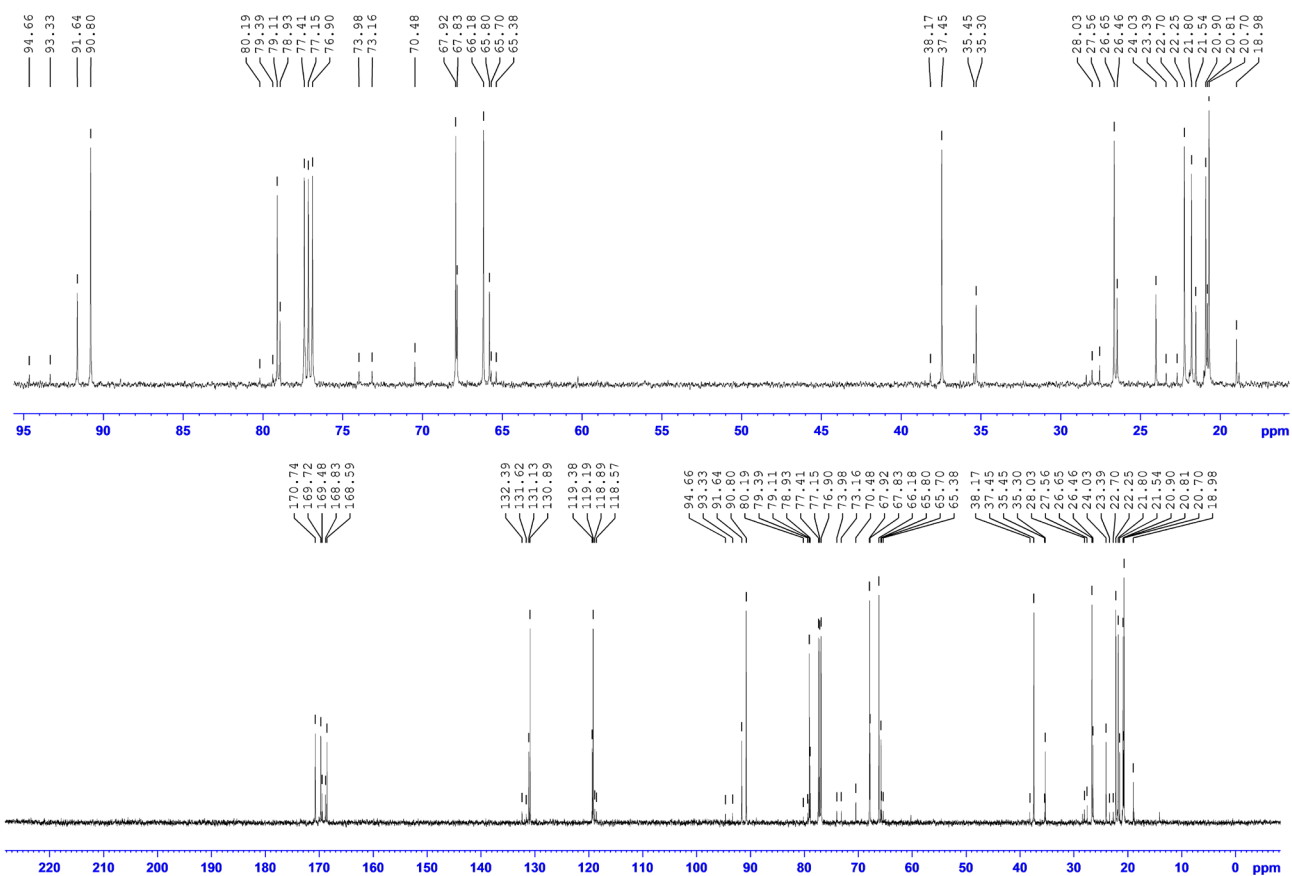


Fig. S7.2. Complete $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CDCl_3

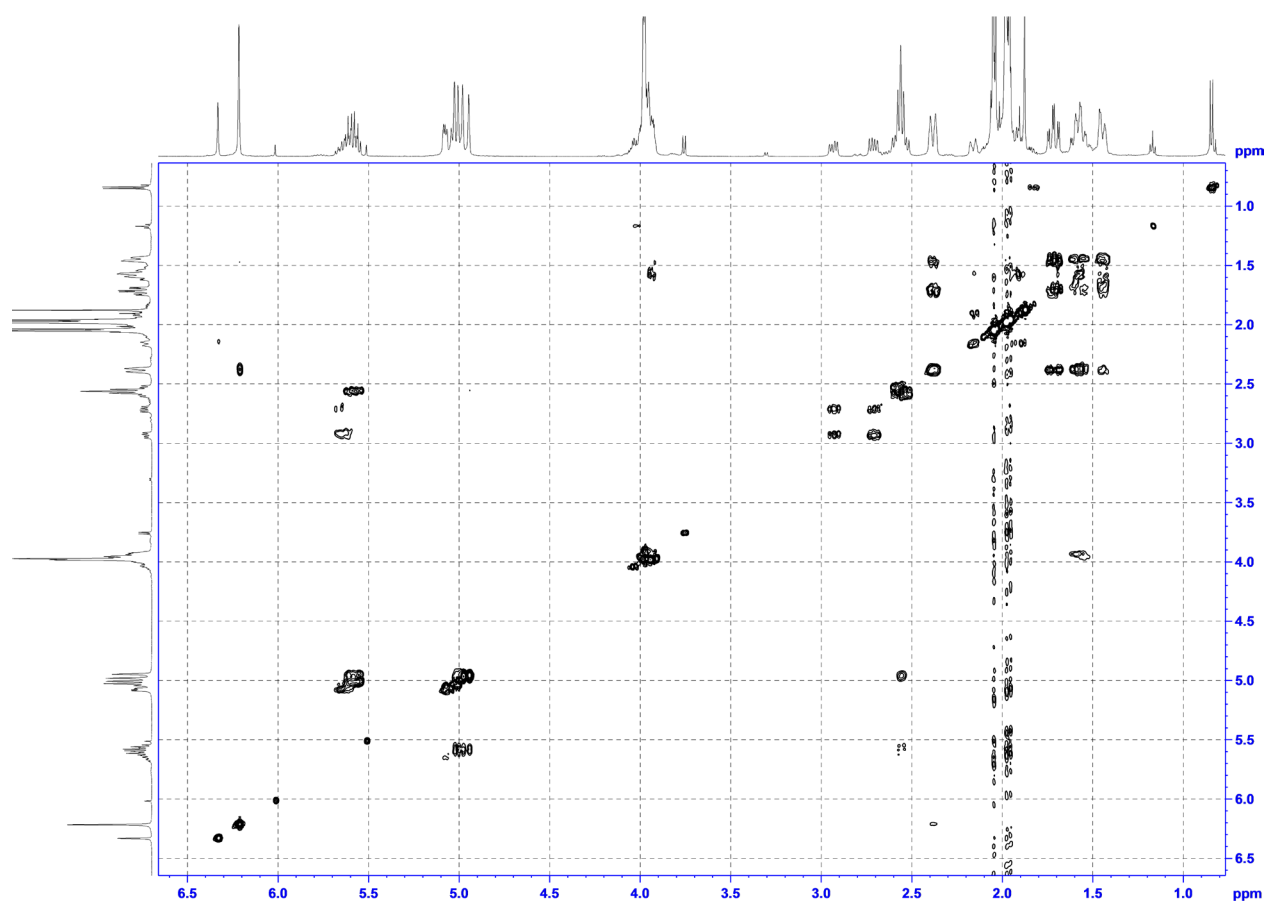


Fig. S7.3. Complete $\{^1\text{H},^1\text{H}\}$ COSY NMR spectrum in CDCl_3

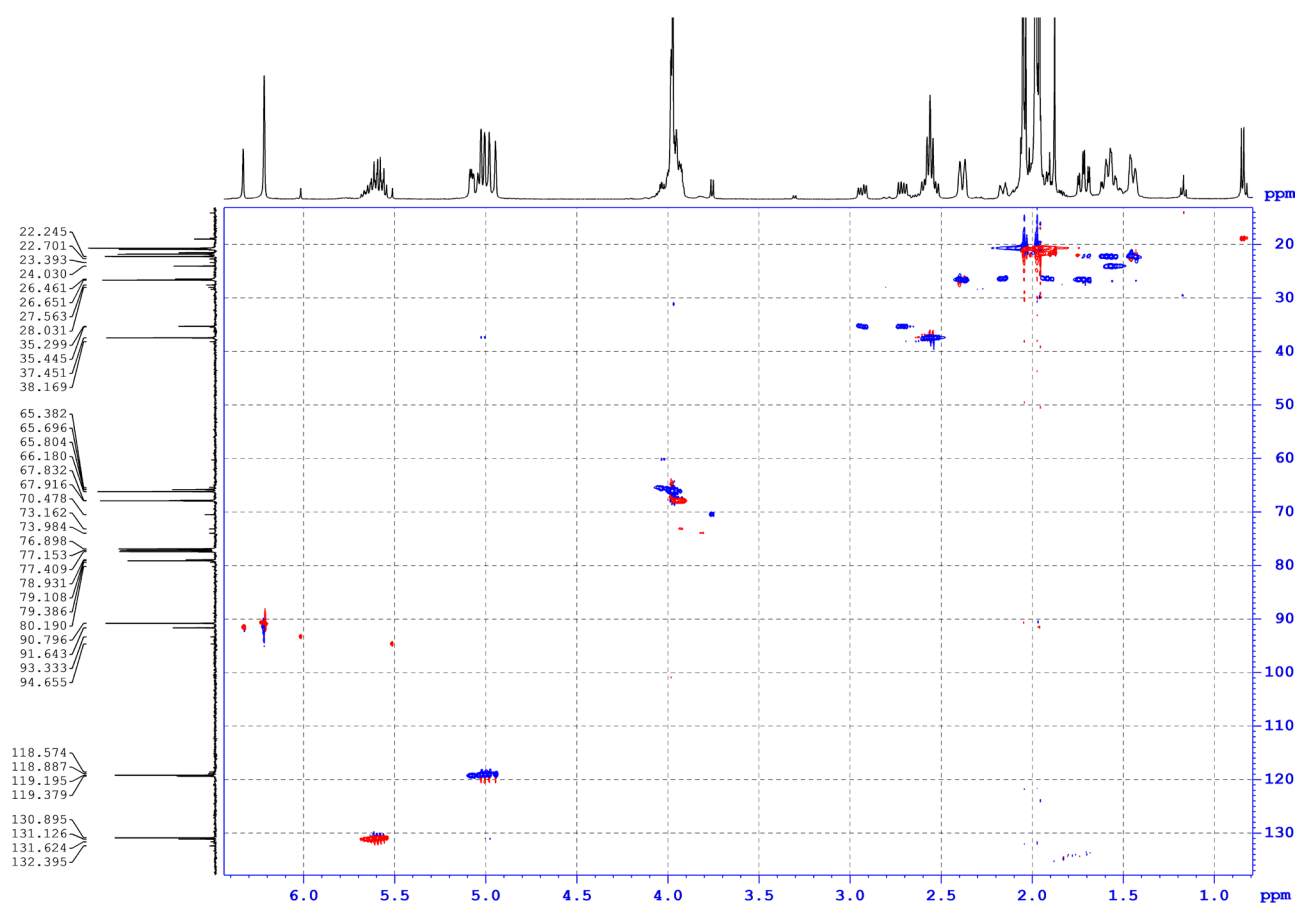


Fig. S7.4. Complete $\{^1\text{H}, ^{13}\text{C}\}$ HSQC NMR spectrum in CDCl_3

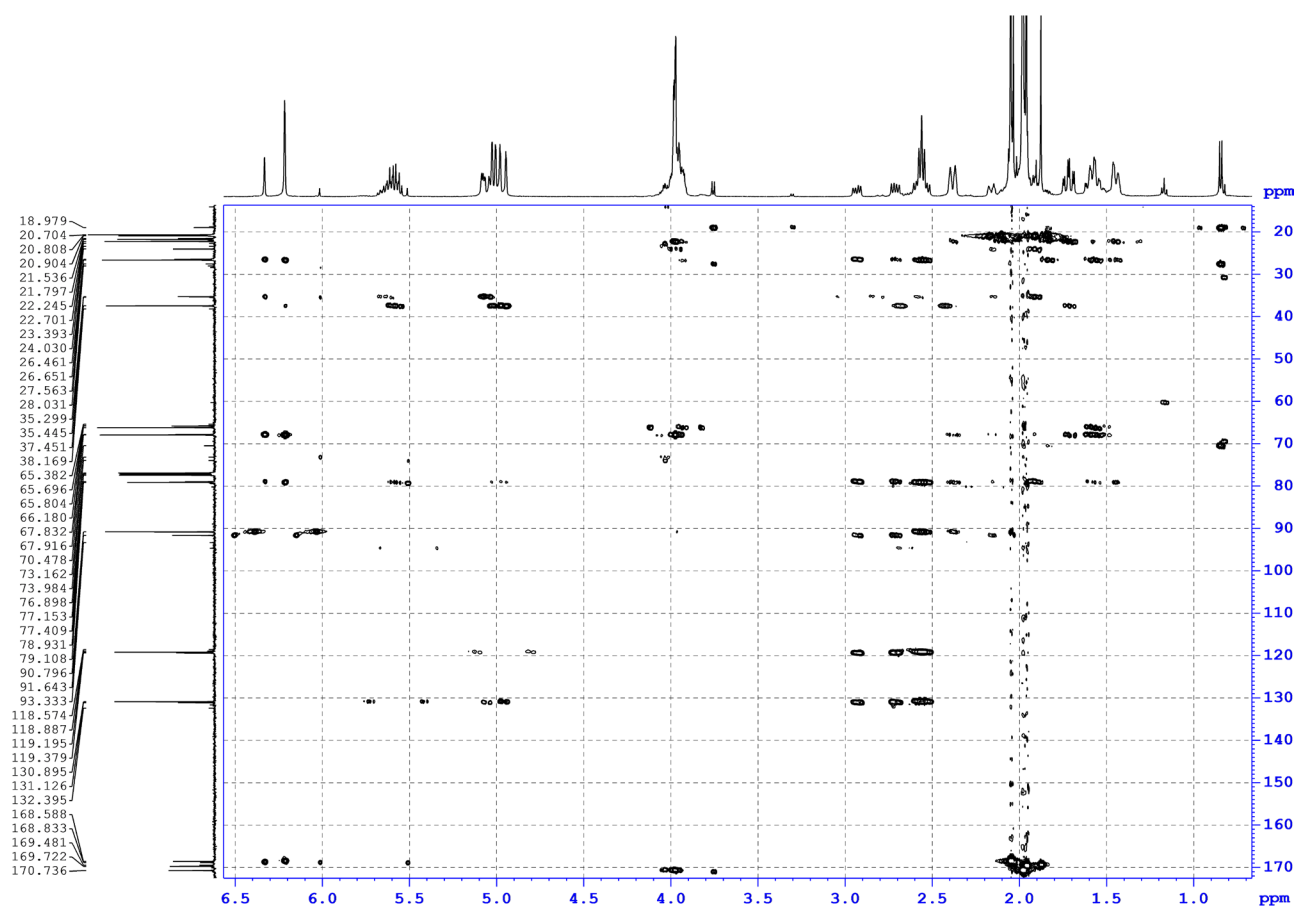


Fig. S7.5. Complete $\{^1\text{H}, ^{13}\text{C}\}$ HMBC NMR spectrum in CDCl_3

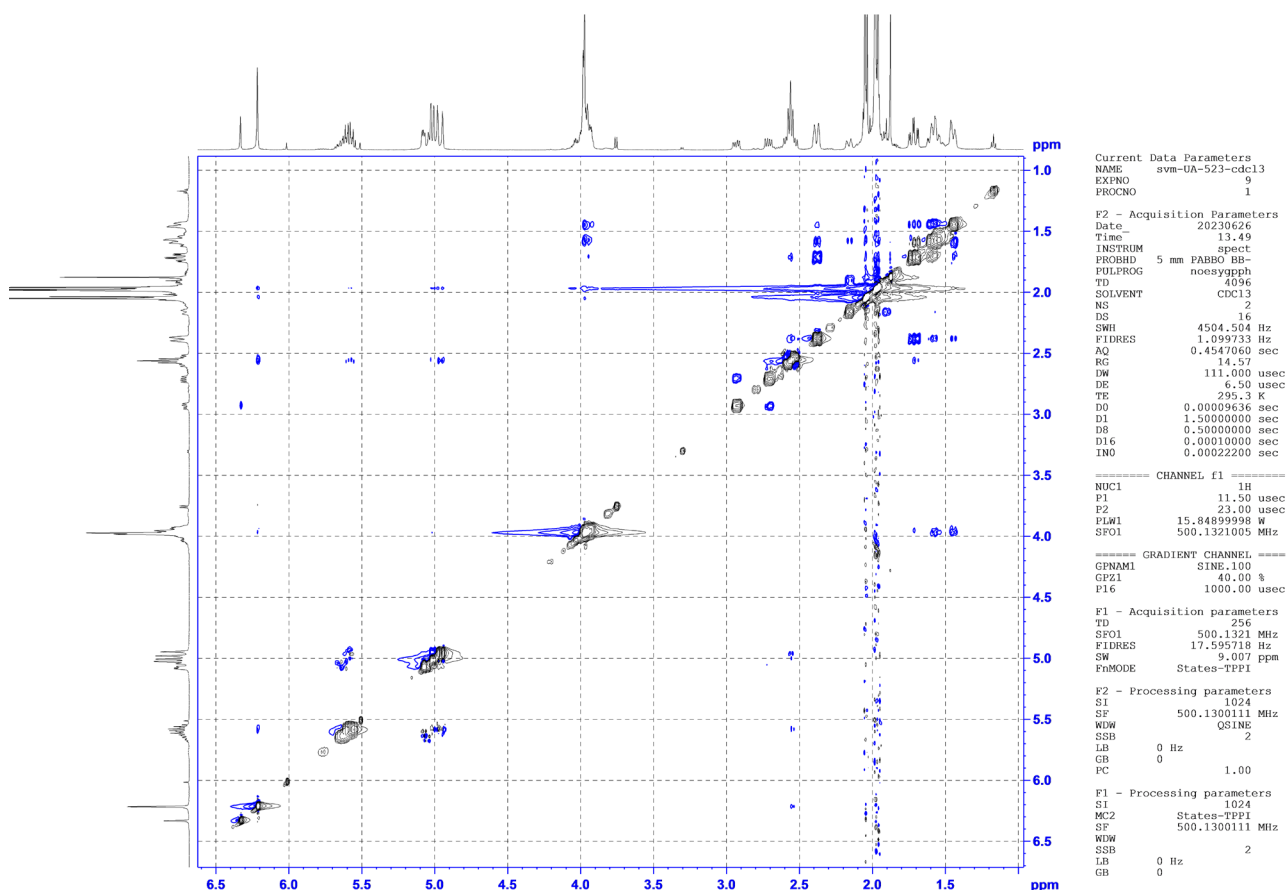
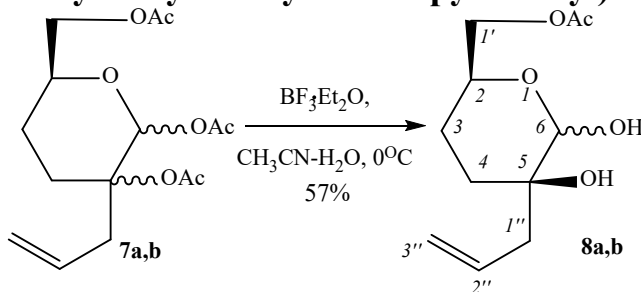


Fig. S7.6. Complete $\{^1\text{H}, ^1\text{H}\}$ NOESY NMR spectrum in CDCl_3

(2*S*,5*R*)-(5-Allyl-5,6-dihydroxytetrahydro-2*H*-pyran-2-yl)methyl acetate (**8a,b**).



To a solution of 0.100 g (0.003 mol) of acetates **7a,b** in 11.0 ml CH_3CN and 2 drops of H_2O at 0°C was added 0.060 ml (0.0005 mol) $\text{BF}_3 \cdot \text{Et}_2\text{O}$. The reaction mixture was stirred for 8 hours at room temperature (control by TLC). Then the reaction mixture was treated with a saturated aqueous solution of NaHCO_3 (pH=6) and the reaction products was extracted with ethyl acetate (3×10.0 ml), the combined organic layers were dried over MgSO_4 , the solvent was distilled off, the residue was chromatographed on SiO_2 . Oil. Yield 0.044 g (65%) in ratio 6*R*:6*S* = 1.7:1.0. $[\alpha]_D^{25} = +28.3^\circ$ (c 1.0, CHCl_3). R_f 0.20 (petroleum ether– EtOAc , 3:1). ^1H NMR (CDCl_3), δ : 1.45–1.51 [1.59–1.66] (m, 1H, C^3BH_2); 1.52–1.60 [1.59–1.72] (m, 2H, C^3AH_2 , C^4BH_2); 1.88–1.92 [1.81–1.87] (m, 1H, C^4AH); 2.07 [2.08] (s, 3H, Ac); 2.18 [2.22] (dd, 1H, $^2J_{1''\text{B},1''\text{A}}$ 13.8, $^3J_{1''\text{B},2''}$ 7.2, $\text{C}^{1''}\text{BH}_2$); 2.37 [2.30] (dd, 1H, $^2J_{1''\text{A},1''\text{B}}$ 13.8, $^3J_{1''\text{A},2''}$ 7.2, $\text{C}^{1''}\text{AH}_2$); 2.43 [2.27] (br.s, 1H, $\text{C}^5\text{-OH}$); 3.68–3.73 [4.17–4.21] (m, 1H, C^2H); 3.81 (d, 1H, $^3J_{\text{OH},6}$ 8.7, $\text{C}^6\text{-OH}$) [3.32 (d, 1H, $^3J_{\text{OH},6}$ 3.0, $\text{C}^6\text{-OH}$); 4.08–4.11 [4.04–4.09] (m, 2H, $\text{C}^{1'\text{A}}\text{H}_2$, $\text{C}^{1'\text{B}}\text{H}_2$); 4.52 (d, 1H, $^3J_{6,\text{OH}}$ 8.7, C^6H) [4.83 (d, 1H, $^3J_{6,\text{OH}}$ 3.0, C^6H); 5.10–

5.16 [5.09-5.15] (m, 2H, C^{3''}AH₂, C^{3''}BH₂), 5.79-5.87 [5.85-5.93] (m, 1H, C^{2''}H). ¹³C NMR (CDCl₃), δ: 20.90 [20.91] (Ac), 22.85 [22.74] (C³), 31.87 [28.62] (C⁴), 41.86 [42.31] (C^{1'}), 66.30 [66.18] (C^{1'}), 70.24 [69.75] (C⁵), 73.78 [66.75] (C²), 97.45 [96.07] (C⁶), 119.30 [119.01] (C^{3''}), 132.34 [132.64] (C^{2''}), 171.07 [171.06] (Ac). Mass spectrum, *m/z*: 231.0 [MH]⁺. Calcd for C₁₁H₁₈O₅. 230.2

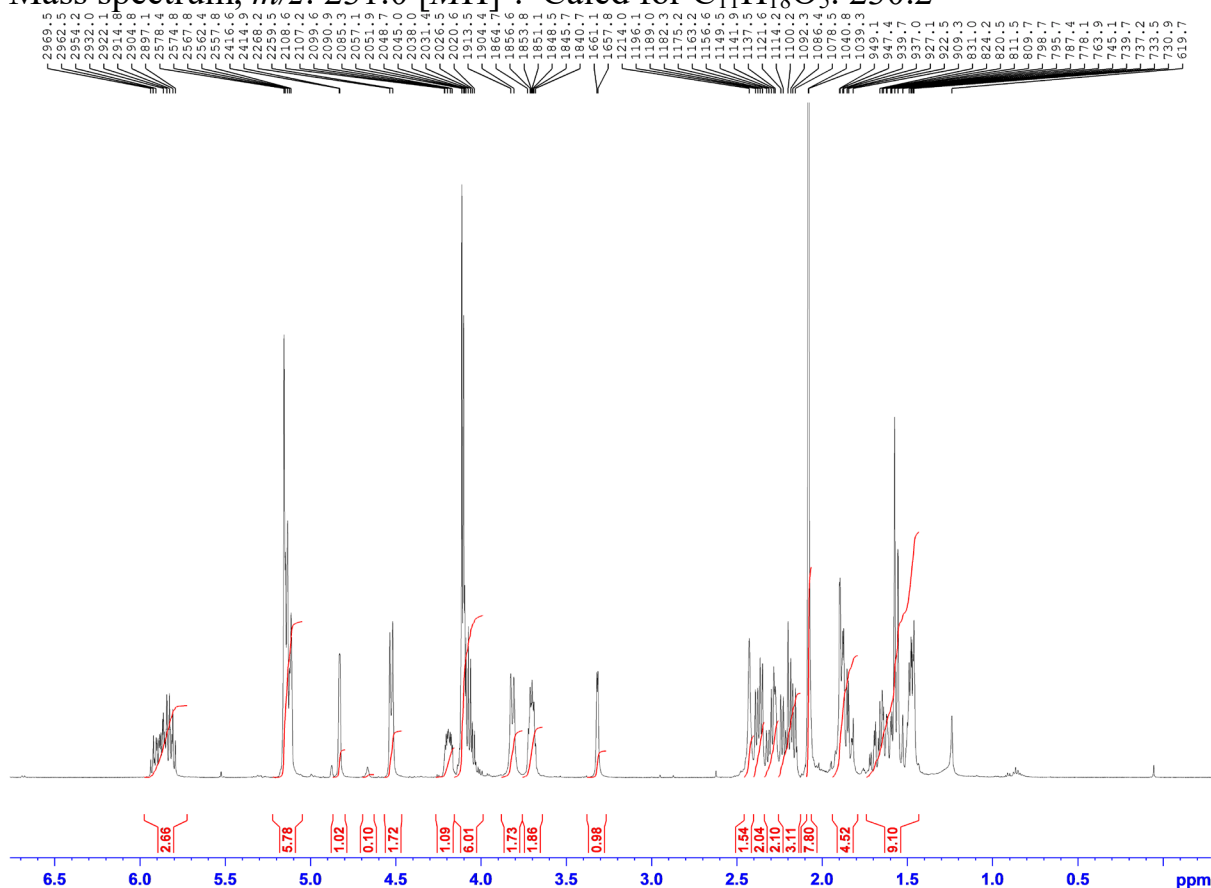


Fig. S8.1. Complete ¹H NMR (500 MHz) spectrum in CDCl₃

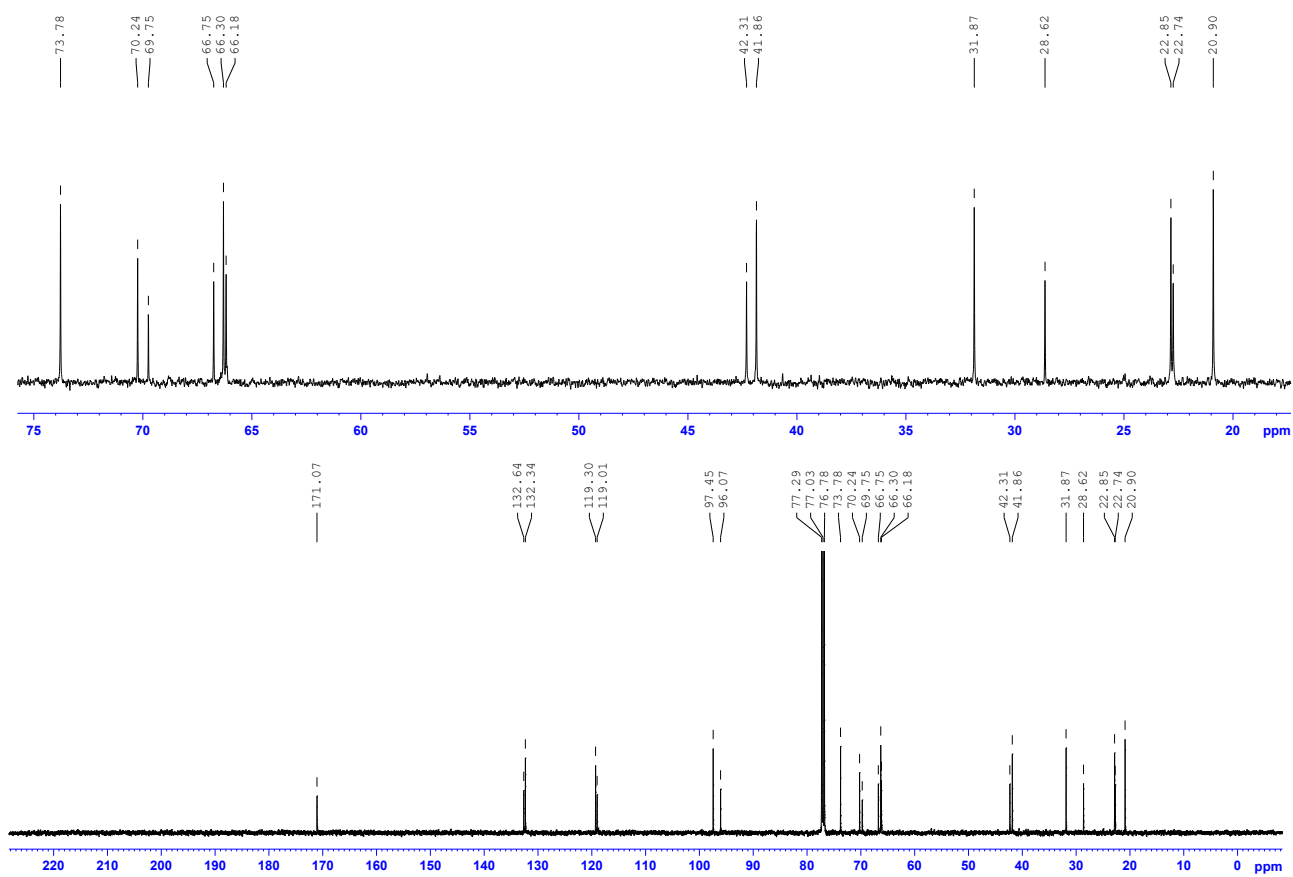


Fig. S8.2. Complete $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CDCl_3

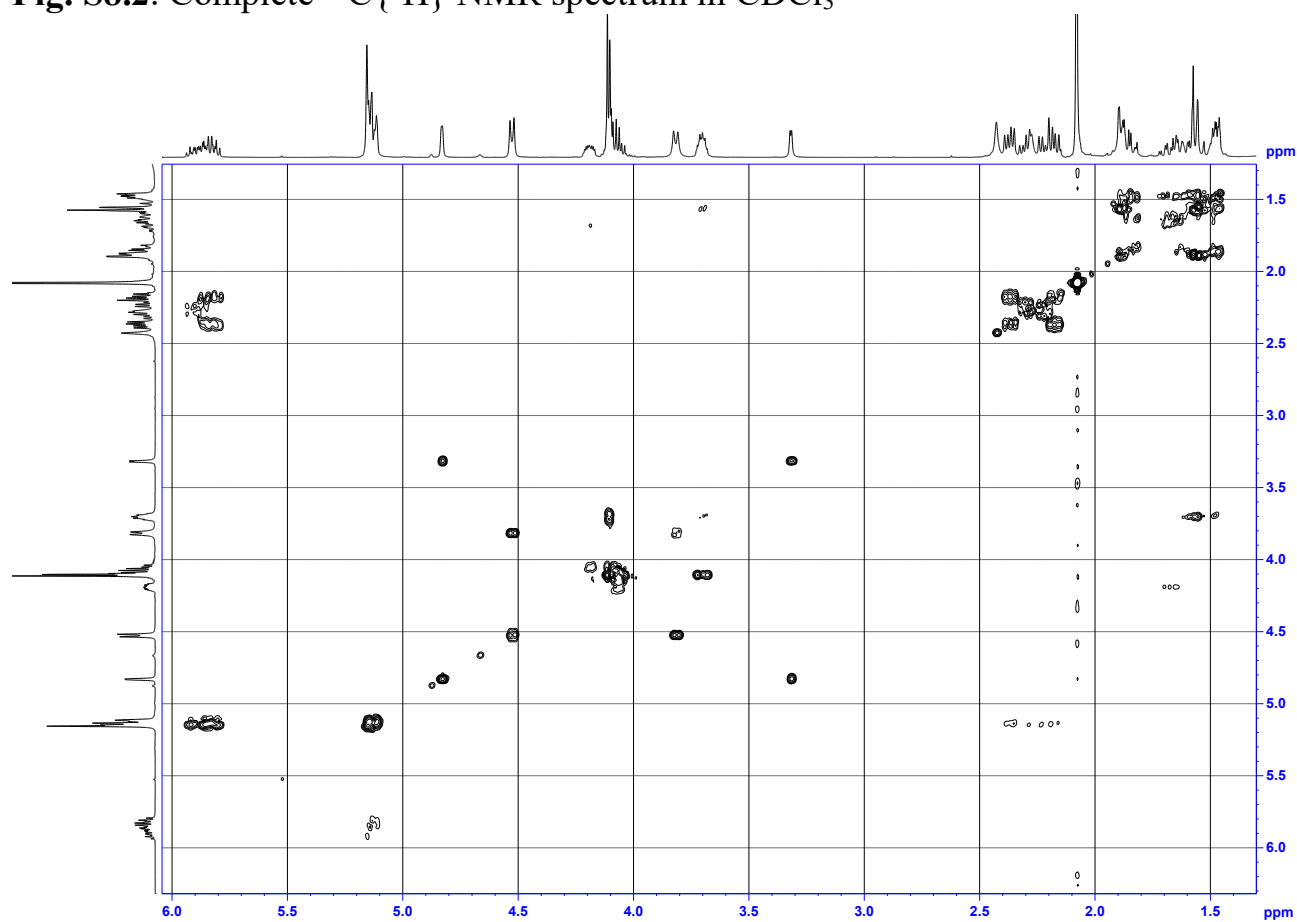


Fig. S8.3. Complete $\{^1\text{H}, ^1\text{H}\}$ COSY NMR spectrum in CDCl_3

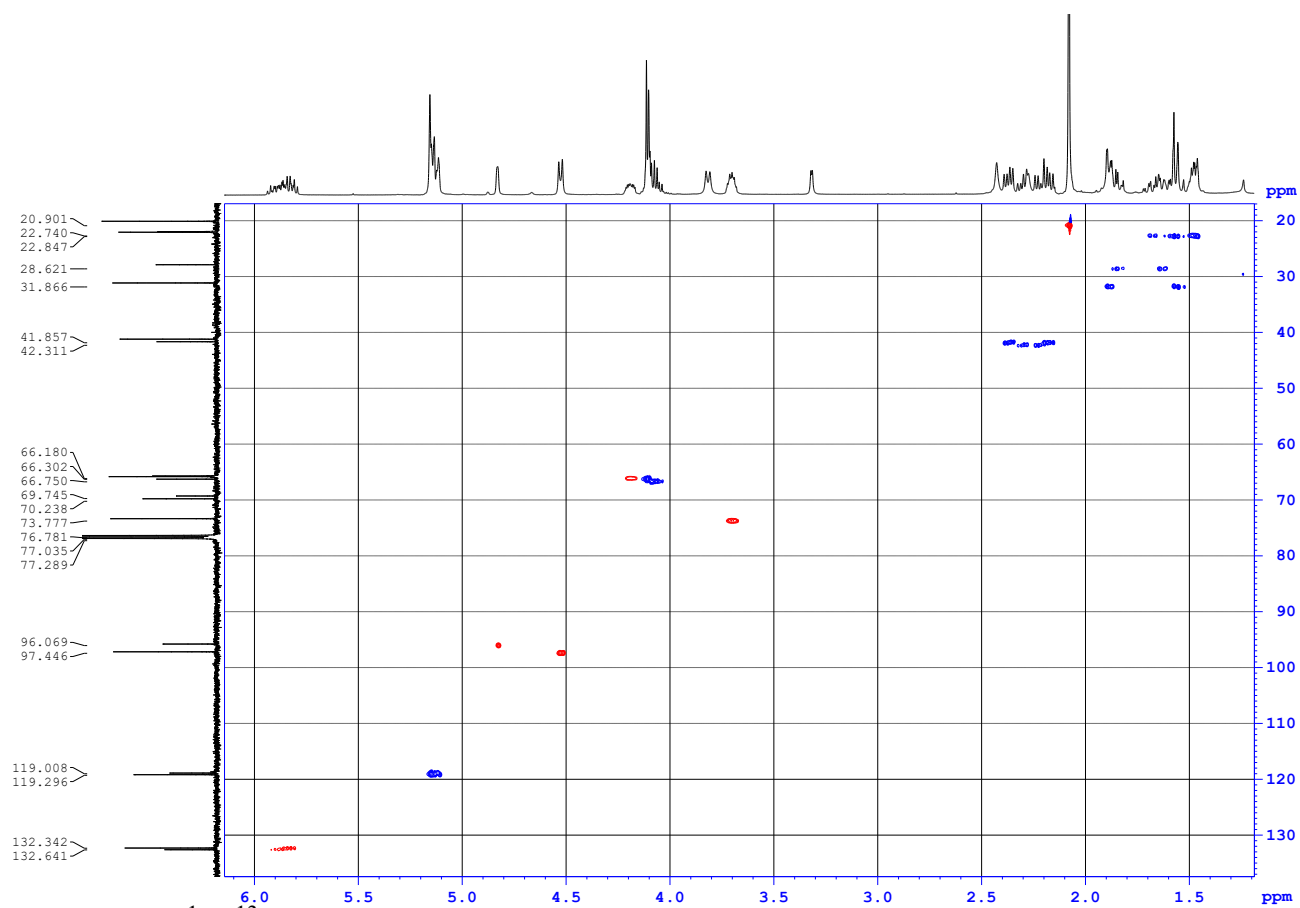


Fig. S8.4. $\{^1\text{H}, ^{13}\text{C}\}$ HSQCED NMR spectrum in CDCl_3

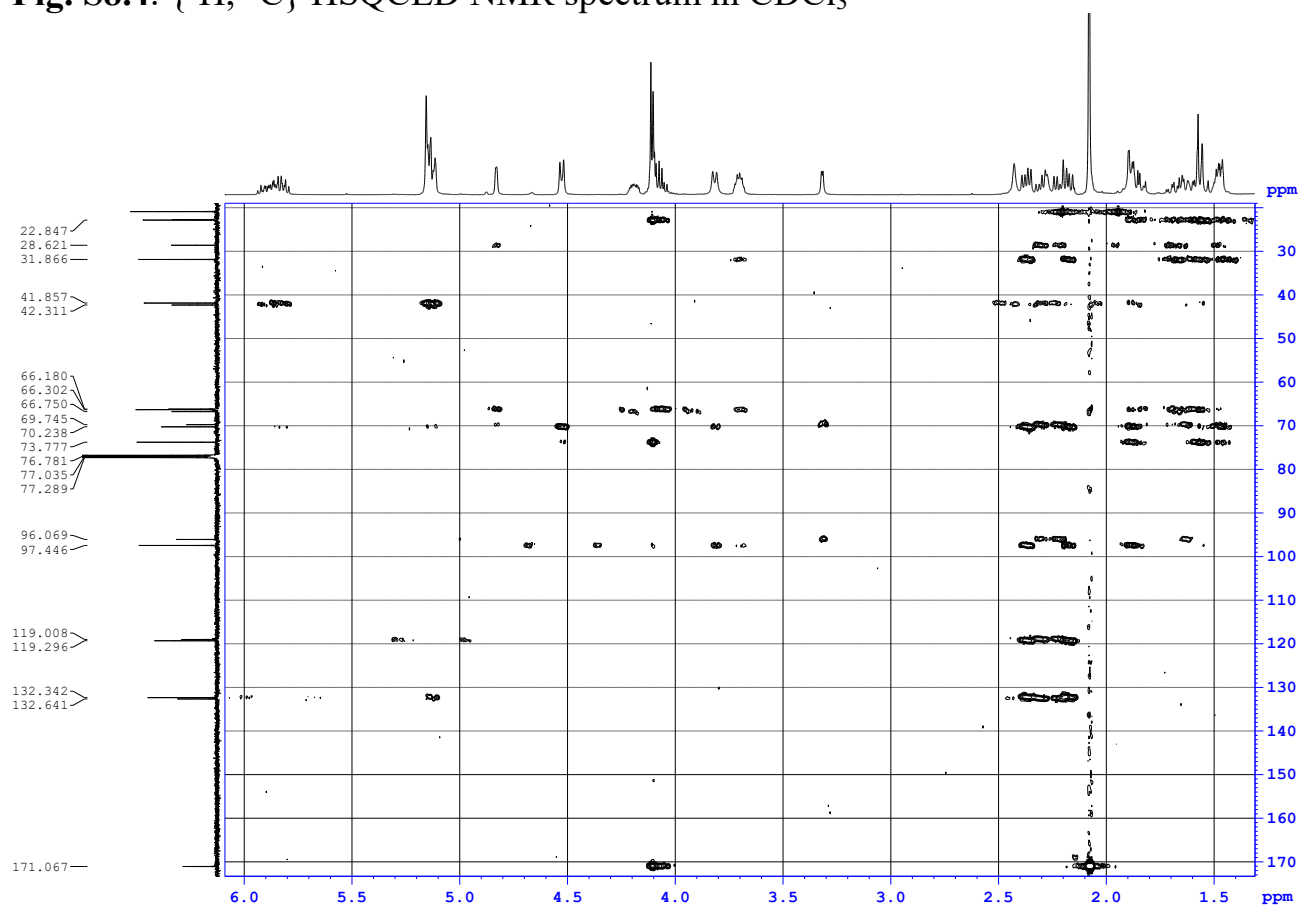


Fig. S8.5. $\{^1\text{H}, ^{13}\text{C}\}$ HMBC NMR spectrum in CDCl_3

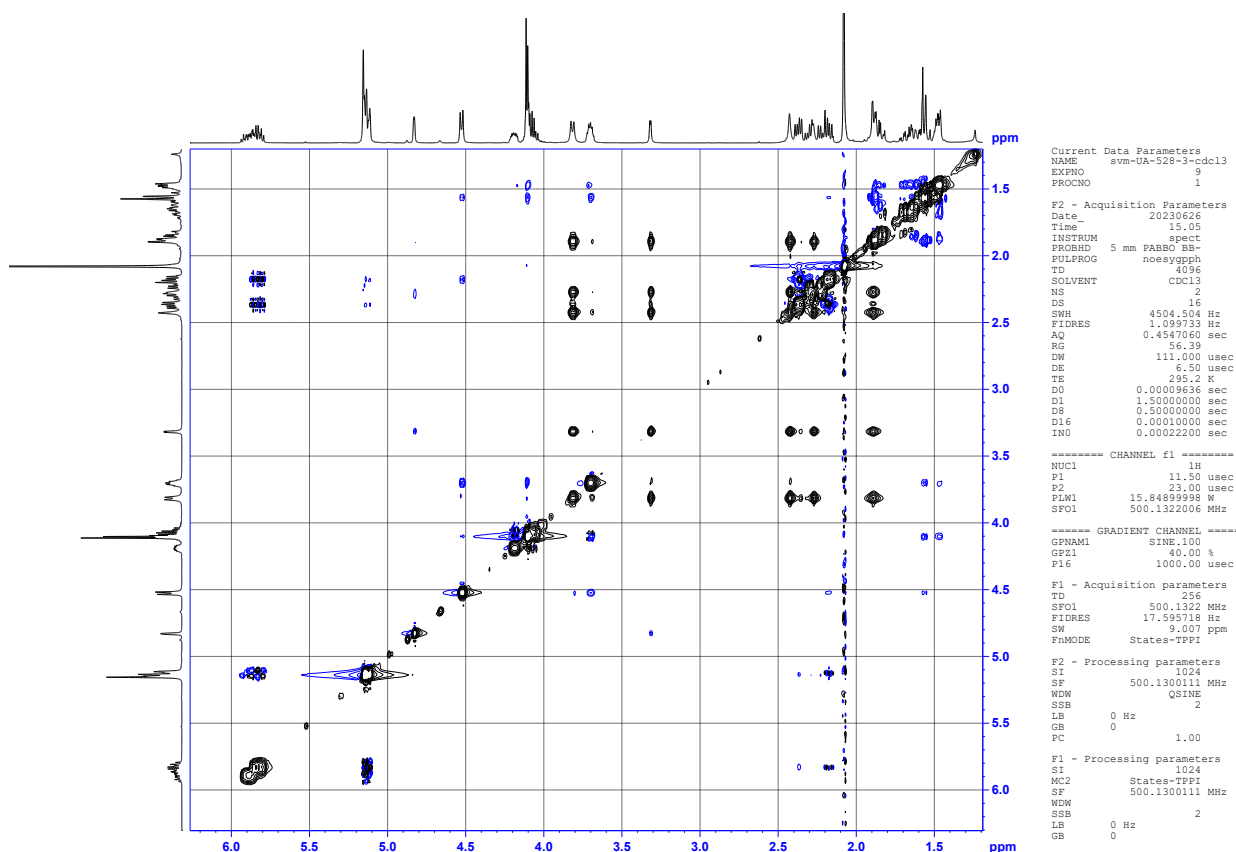
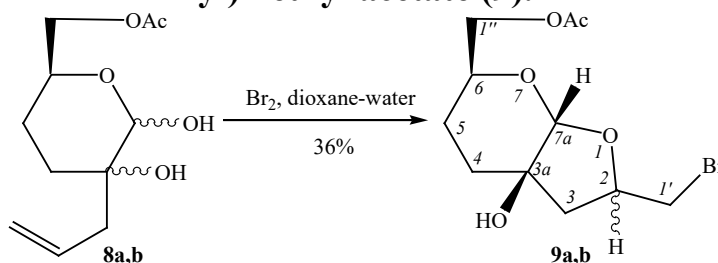


Fig. S8.6. Complete $\{^1\text{H}, ^1\text{H}\}$ NOESY NMR spectrum in CDCl_3

((3*aR*,6*S*,7*aR*)-2-Bromomethyl-3*a*-hydroxyhexahydro-2*H*-furo[2,3-*b*]pyran-6-yl)methyl acetate (9).



To a solution of 0.037 g (0.00019 mol) of lactols **8a,b** in 1.2 ml 1,4-dioxane and 1.2 ml of H_2O at room temperature was added 0.010 ml (0.00019 mol) Br_2 . The reaction mixture was stirred for 30 min at room temperature (control by TLC). Then the reaction mixture was treated with a saturated aqueous solution of NaHCO_3 (pH=6) and the reaction products was extracted with ethyl acetate (2×3.0 ml), the combined organic layers were dried over MgSO_4 , the solvent was distilled off, the residue was chromatographed on SiO_2 . Oil. Yield 0.019 g (36%) in ratio 2R:2S =4:1. $[\alpha]_D^{25} = + 8.6^\circ$ (c 1.0, CHCl_3). R_f 0.30 (petroleum ether– EtOAc , 2:1). ^1H NMR (CDCl_3), δ : 1.56-1.68 [1.65-1.78] (m, 2H, C^5AH_2 , C^5BH_2); 1.88-1.96 [1.85-1.93] (m, 2H, C^4AH_2 , C^4BH_2); 1.99 [2.01] (dd, 1H, $^2J_{3B,3A}$ 12.8, $^3J_{3B,2}$ 8.3, C^3BH_2); 2.08 [2.09] (s, 3H, Ac); 2.21 [2.11] (dd, 1H, $^2J_{3A,3B}$ 12.8, $^3J_{3A,2}$ 7.0, C^3AH_2); 3.48-3.52 [3.43-3.55] (m, 2H, $\text{C}^{1'A}\text{H}_2$, $\text{C}^{1'B}\text{H}_2$); 4.02-4.07 [3.88-3.92] (m, 1H, C^6H); 4.11-4.16 [4.13-4.21] (m, 2H, $\text{C}^{1''A}\text{H}_2$, $\text{C}^{1''B}\text{H}_2$), 4.34-4.39 [4.39-4.44] (m, 1H, C^2H); 5.18 [5.06] (s, 1H, C^7aH). ^{13}C NMR (CDCl_3), δ : 20.89 [20.81] (Ac), 22.01 [22.21] (C^5), 30.89 [30.36] (C^4),

Fig. S9.1. Complete ^1H NMR (500 MHz) spectrum in CDCl_3

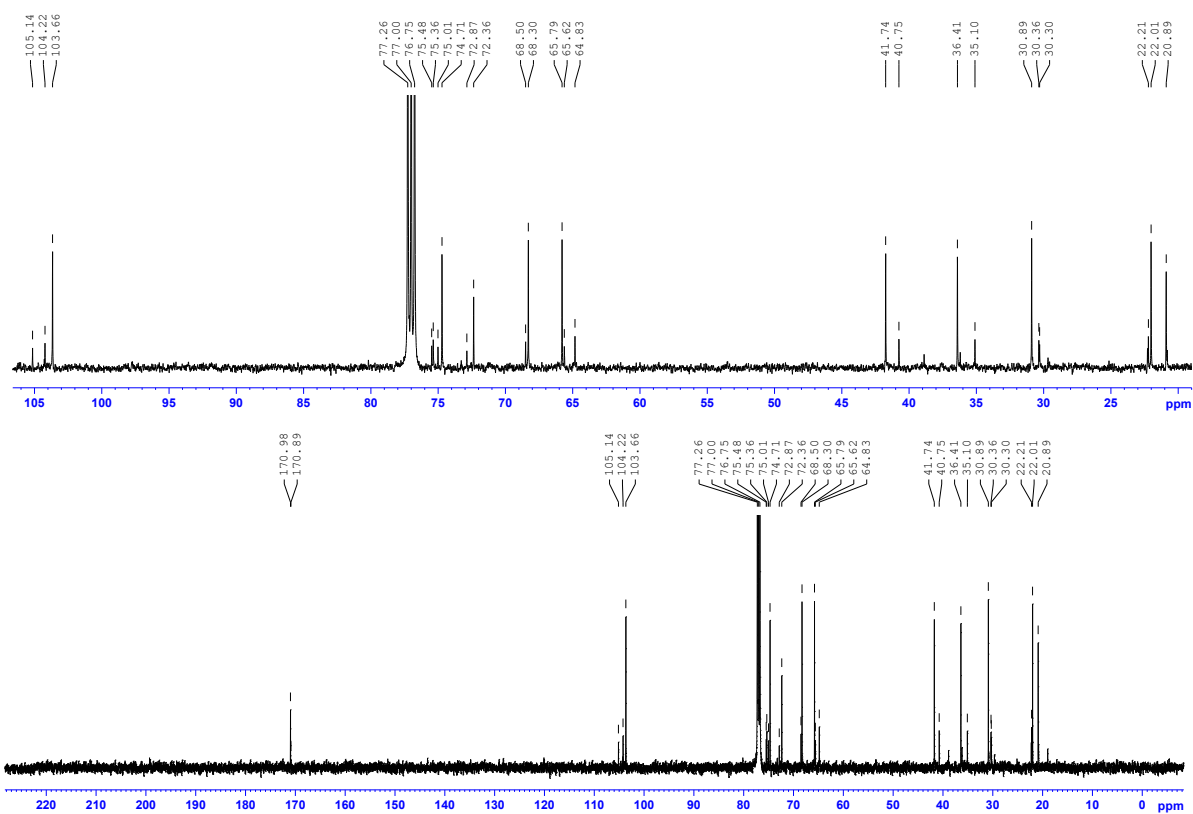


Fig. S9.2. Complete $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CDCl_3

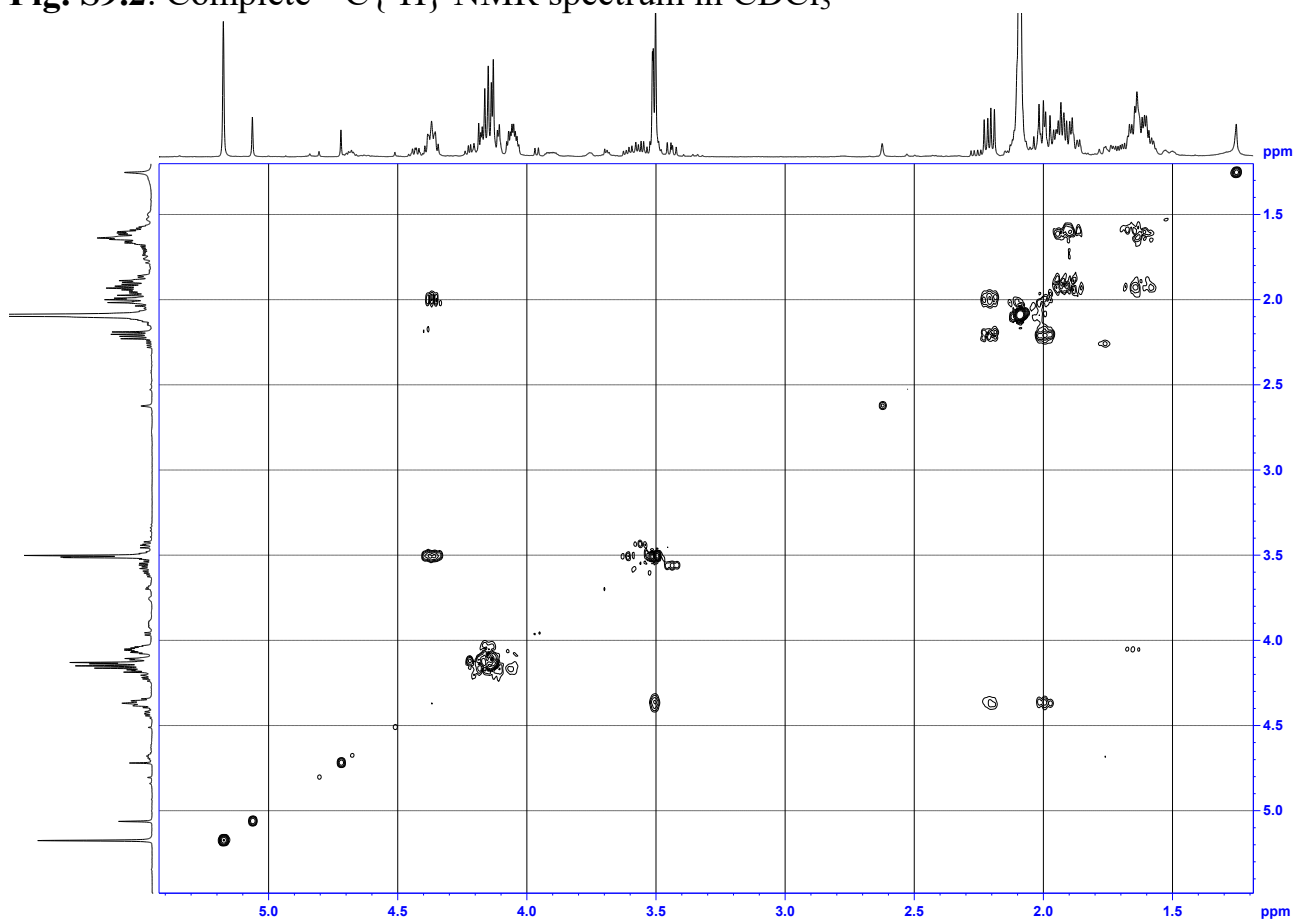


Fig. S9.3. Complete $\{^1\text{H}, ^1\text{H}\}$ COSY NMR spectrum in CDCl_3

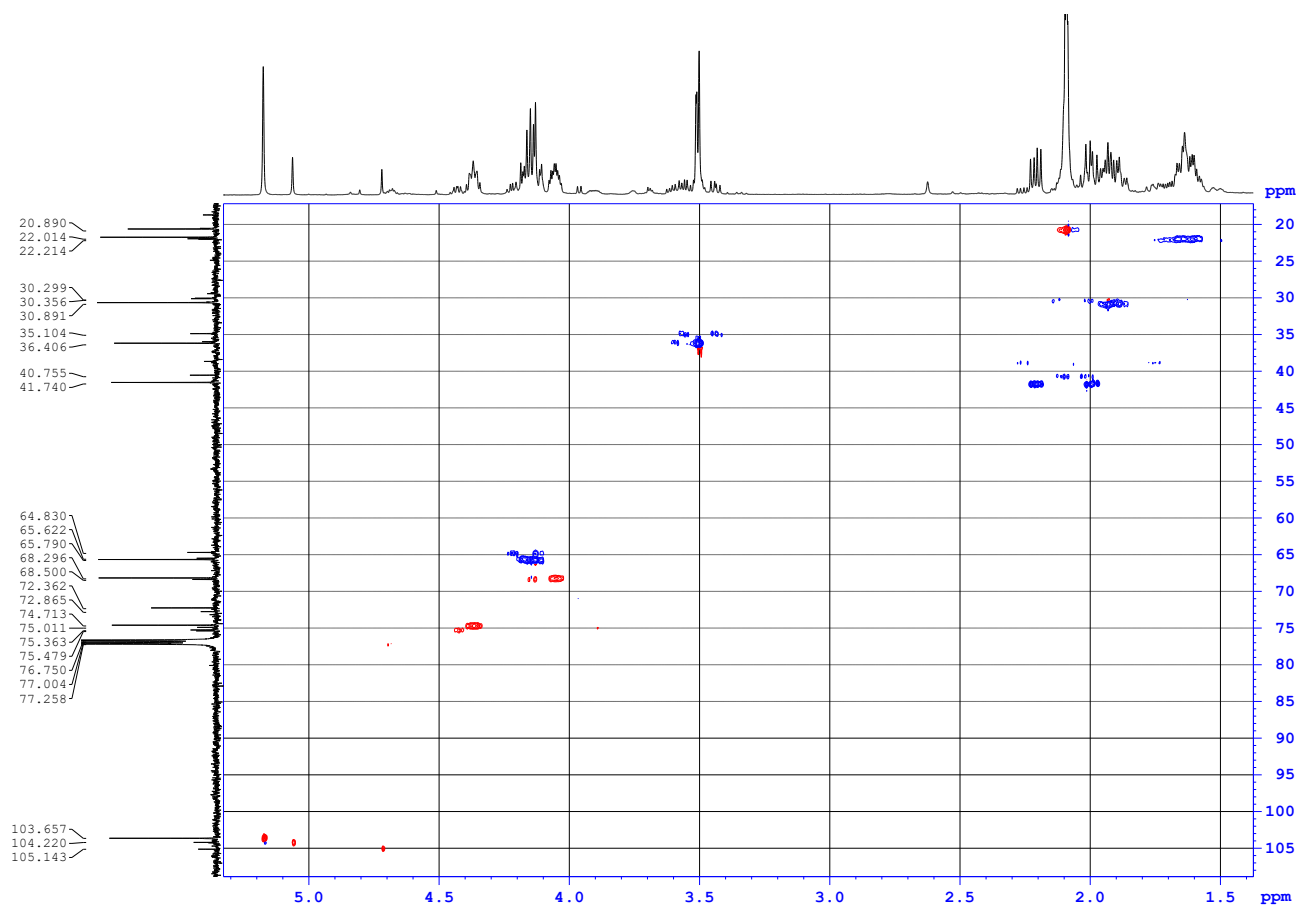


Fig. S9.4. $\{^1\text{H}, ^{13}\text{C}\}$ HSQCED NMR spectrum in CDCl_3

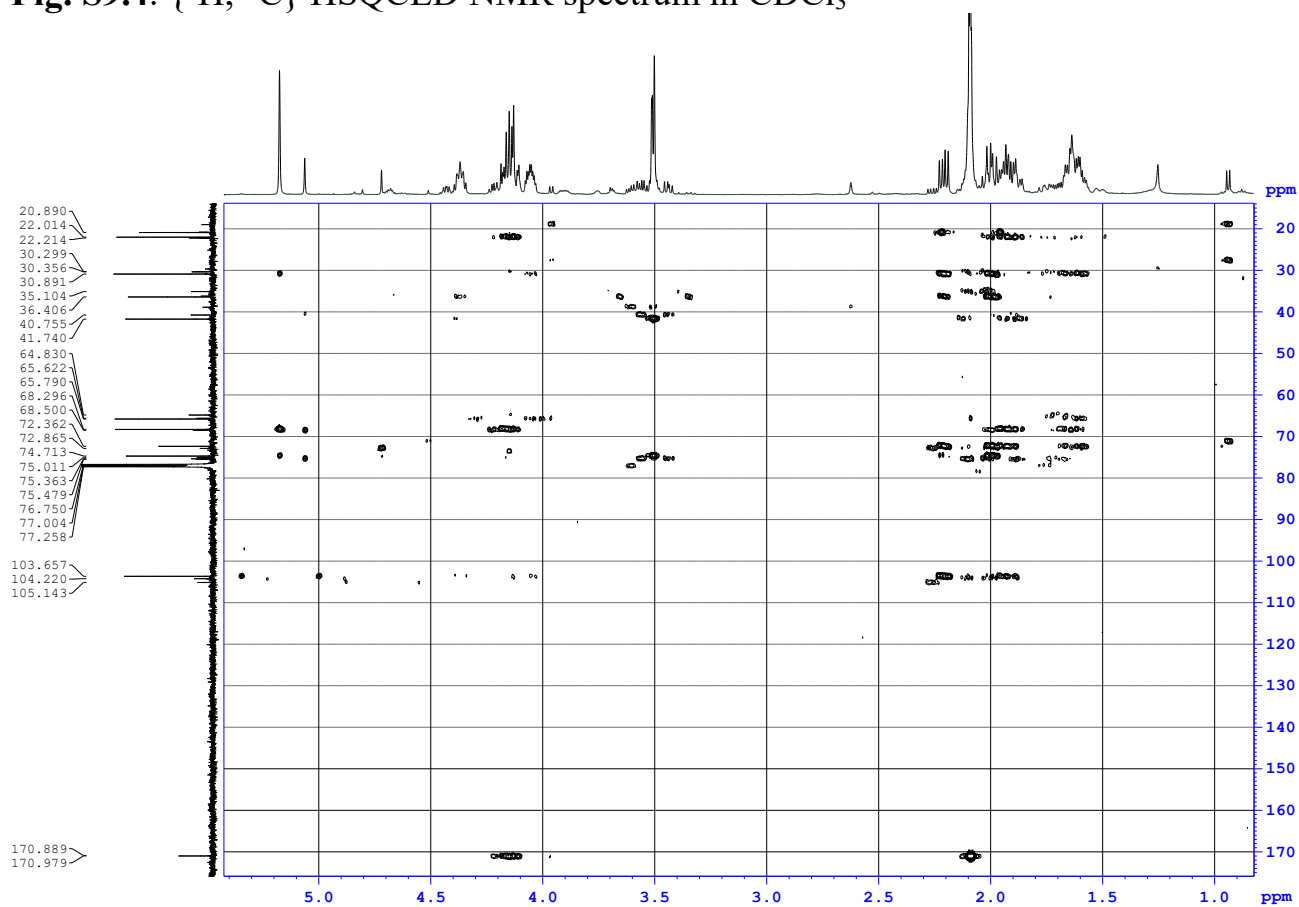


Fig. S9.5. $\{^1\text{H}, ^{13}\text{C}\}$ HMBC NMR spectrum in CDCl_3

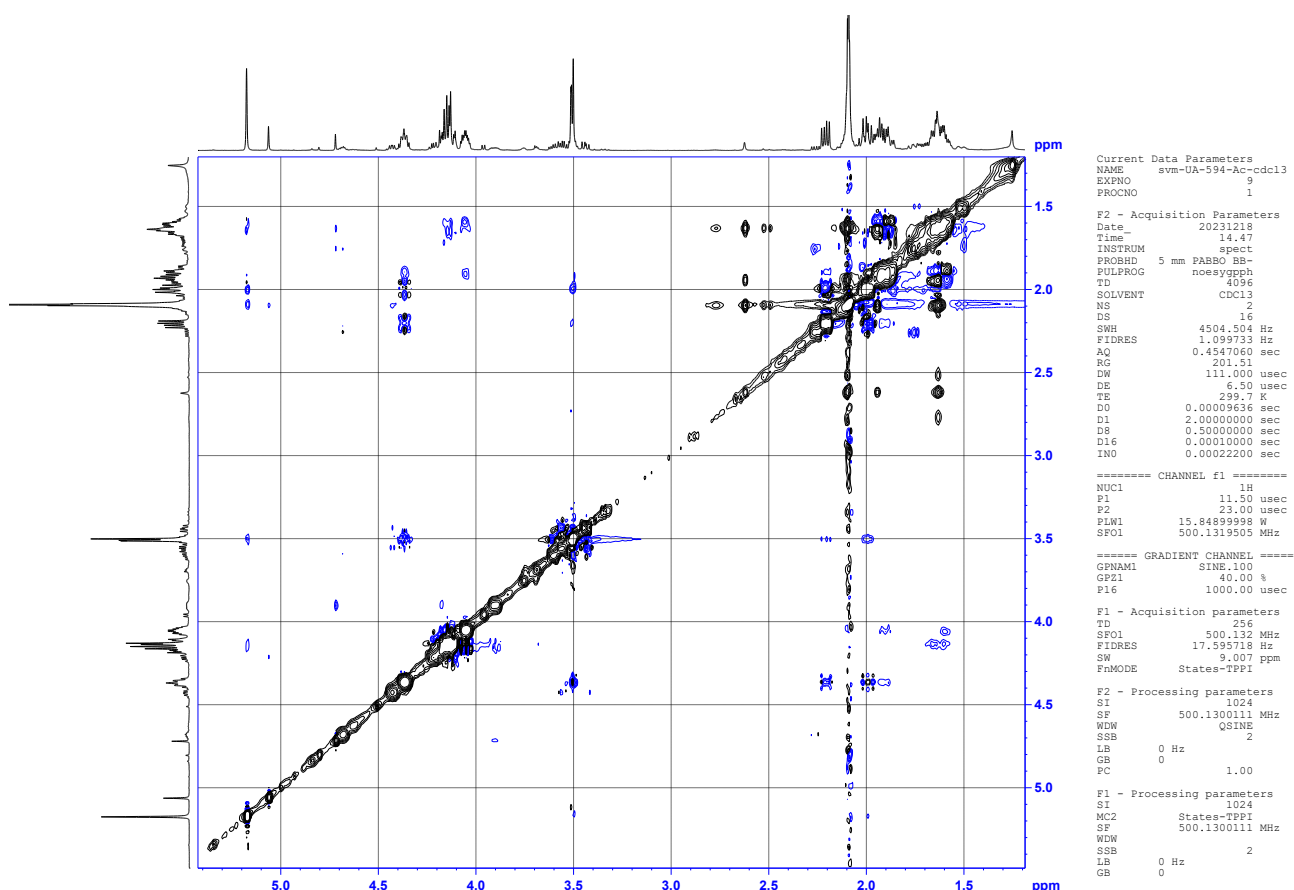
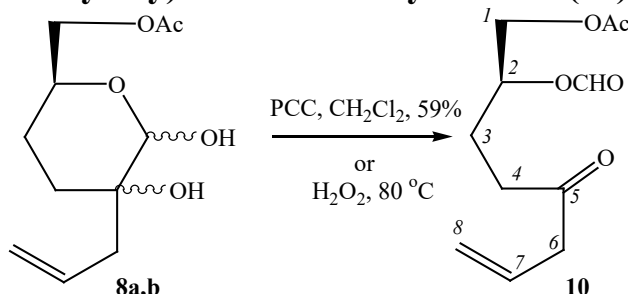


Fig. S9.6. Complete $\{^1\text{H}, ^1\text{H}\}$ NOESY NMR spectrum in CDCl_3

(S)-2-Formyloxy)-5-oxooct-7-enyl acetate (10).



Method I. A solution of compounds **8a,b** (0.080 g, 0.0004 mol) in 5.0 ml CH_2Cl_2 was thoroughly stirred and treated by adding small portions of 0.180 g (0.0008 mol) PCC. After 2 h (control by TLC), the reaction mixture was treated with 3.0 ml Et_2O , the precipitate was removed by filtration through a SiO_2 layer on a Schott sintered glass filter, the filtrate was evaporated, and the residue was separated by chromatography. Yield 0.050 g (59%).

Method II. To a solution of 7.0 ml CH_2Cl_2 and 1.2 ml pyridine in an argon atmosphere at room temperature was added 0.500 g (0.005 mol) CrO_3 under stirring. After 1 h (control by TLC) was added 0.113 g (0.0005 mol) compounds **8a,b**. The reaction mixture was stirred for 30 min at room temperature (control by TLC). Then the reaction mixture was treated with a saturated aqueous solution of NaHCO_3 (pH=6) and the reaction products was extracted with Et_2O (2×10.0 ml), the combined organic layers were dried over MgSO_4 , the solvent was distilled off, the residue was chromatographed on SiO_2 . Oil. Yield 0.280 g (23%). $[\alpha]_D^{25} = -4.5^\circ$ (c 1.0, CHCl_3).

R_f 0.57 (petroleum ether–EtOAc, 3:1). ^1H NMR (CDCl_3), δ : 1.79-1.87 (m, 1H, $\text{C}^{3\text{B}}\text{H}_2$); 1.89-1.96 (m, 1H, $\text{C}^{3\text{A}}\text{H}_2$); 2.02 (s, 3H, Ac); 2.50 (t, 2H, $^3J_{4,3\text{A}}$ 7.3, $^3J_{4,3\text{B}}$ 7.3, $\text{C}^{4\text{A}}\text{H}_2$, $\text{C}^{4\text{B}}\text{H}_2$); 3.14 (d, 2H, $^3J_{6,7}$ 6.9, $\text{C}^{6\text{A}}\text{H}_2$, $\text{C}^{6\text{B}}\text{H}_2$); 4.03 (dd, 1H, $^2J_{1\text{B},1\text{A}}$ 12.1, $^3J_{1\text{B},2}$ 6.7, $\text{C}^{1\text{B}}\text{H}_2$); 4.20 (dd, 1H, $^2J_{1\text{A},1\text{B}}$ 12.1, $^3J_{1\text{A},2}$ 3.4, $\text{C}^{1\text{A}}\text{H}_2$); 5.07-5.18 (m, 3H, $\text{C}^{8\text{A}}\text{H}_2$, $\text{C}^{8\text{B}}\text{H}_2$, C^2H); 5.82-5.90 (m, 1H, C^7H); 8.05 (s, 1H, CHO). ^{13}C NMR (CDCl_3), δ : 20.64 (Ac), 24.32 (C^3), 37.34 (C^4), 47.68 (C^6), 64.64 (C^1), 70.54 (C^2), 119.11 (C^8), 130.19 (C^7), 160.43 (CHO), 170.54 (Ac); 206.86 ($\text{C}=\text{O}$). Mass spectrum, m/z : 229.1 $[\text{MH}]^+$. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_5$. 228.2.

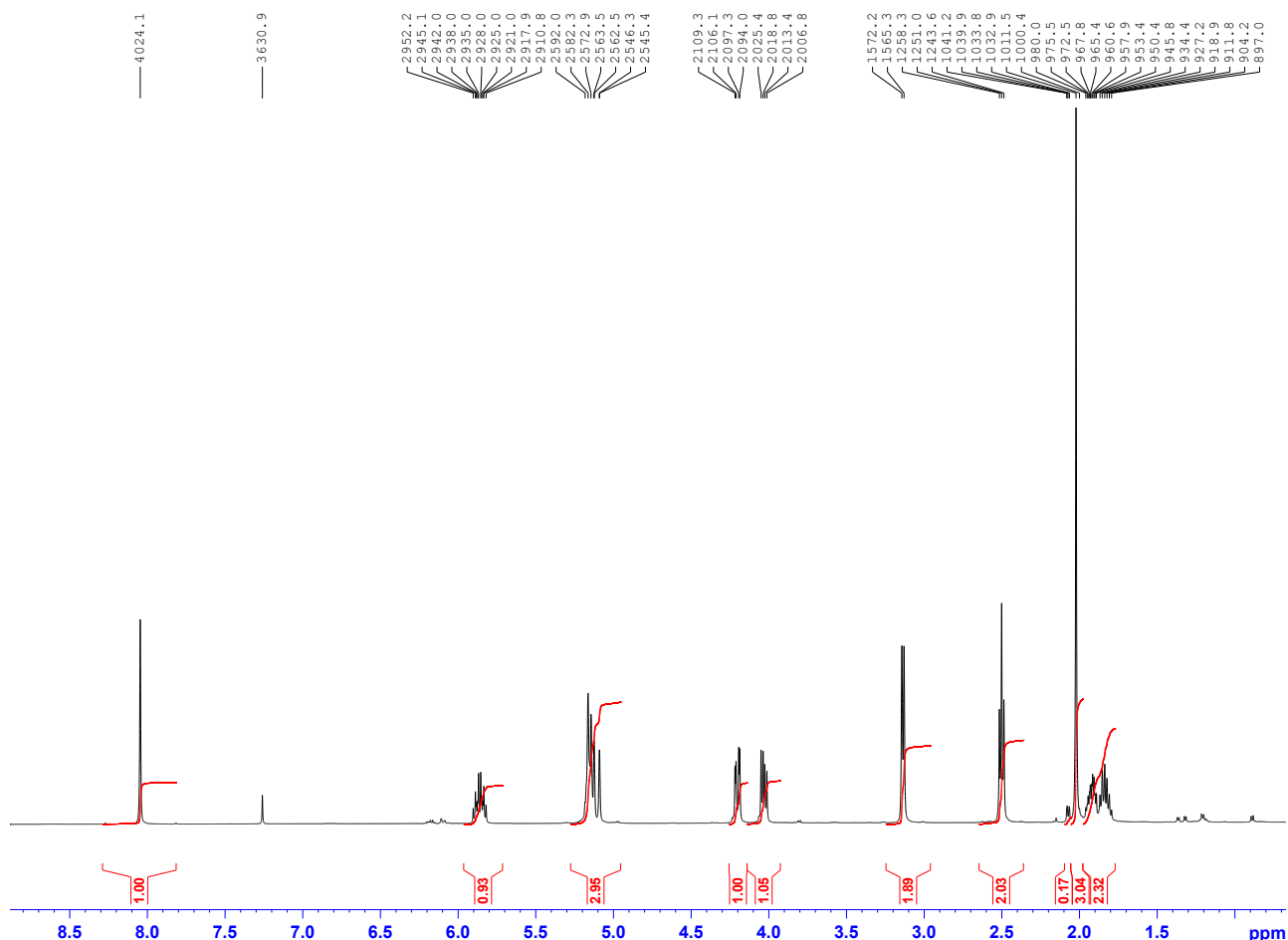


Fig. S10.1. Complete ^1H NMR (500 MHz) spectrum in CDCl_3

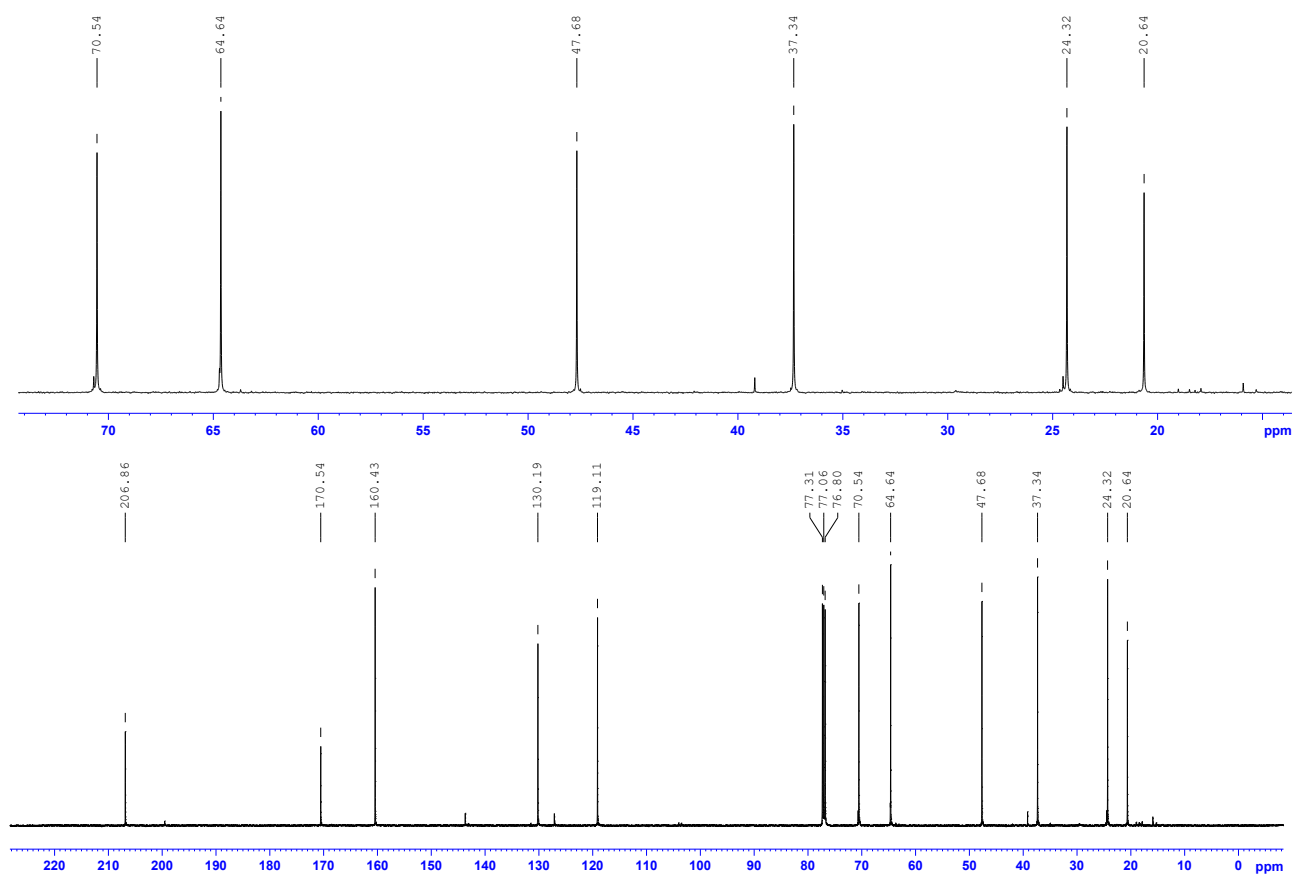


Fig. S10.2. Complete $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CDCl_3

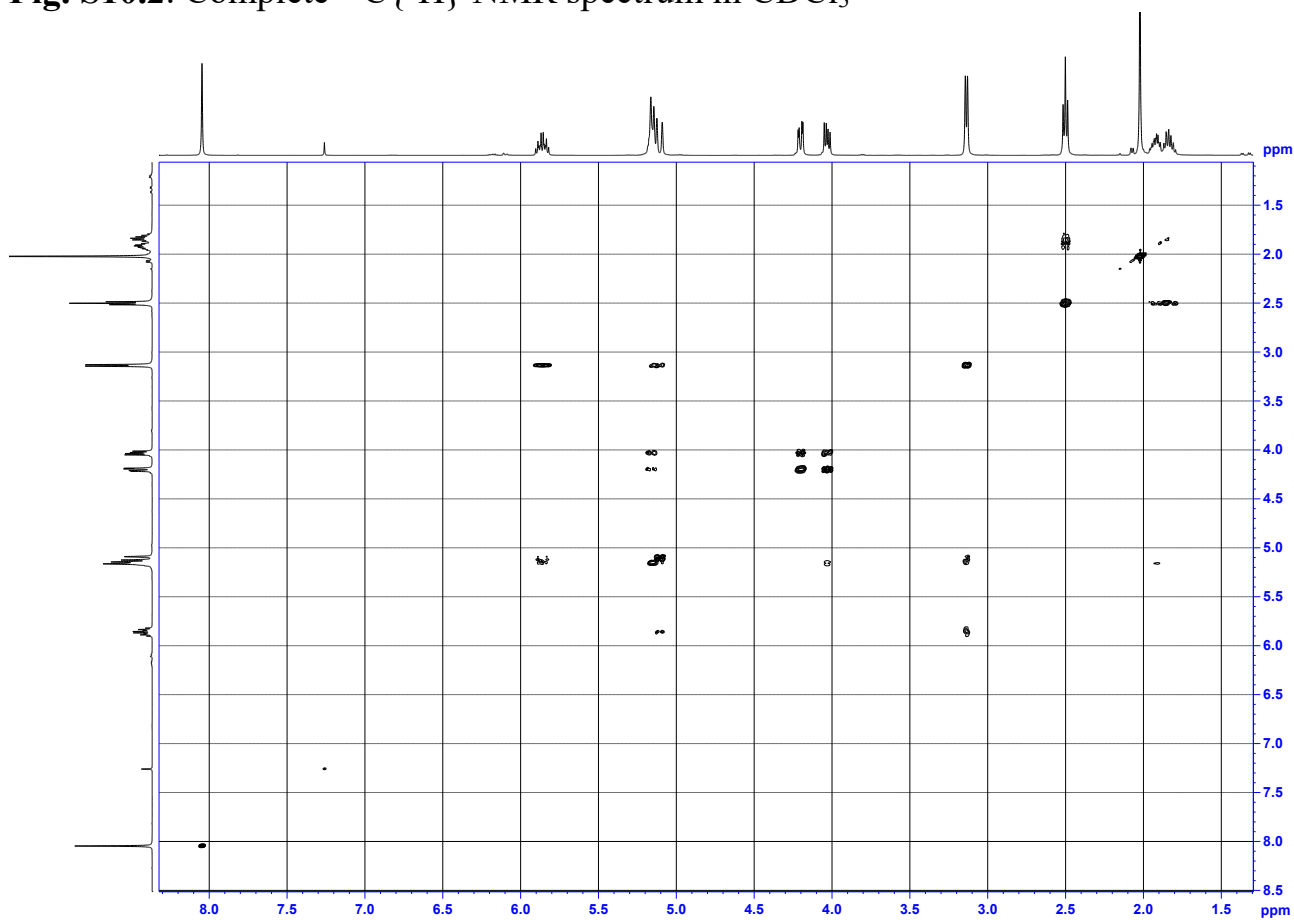


Fig. S10.3. Complete $\{^1\text{H}, ^1\text{H}\}$ COSY NMR spectrum in CDCl_3

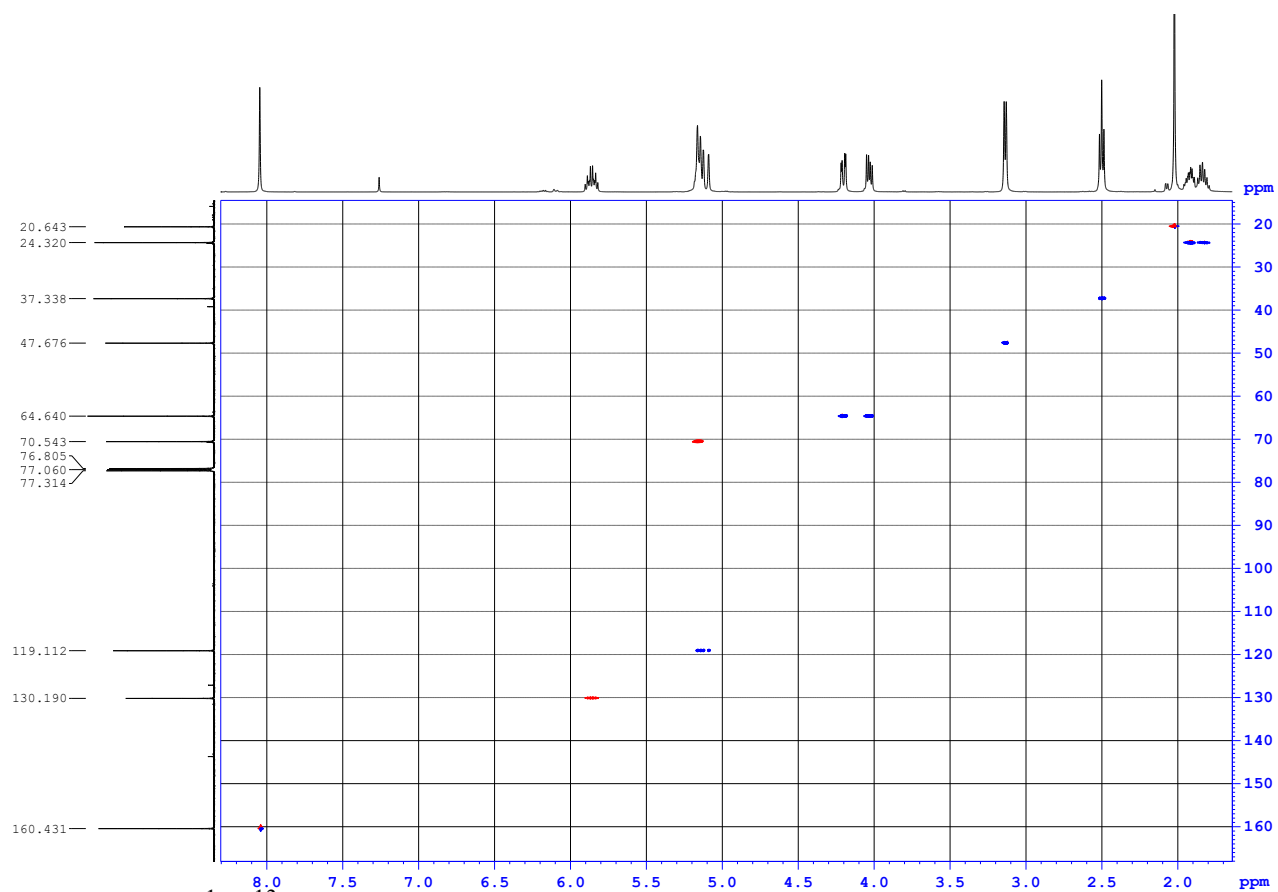


Fig. S10.4. $\{^1\text{H}, ^{13}\text{C}\}$ HSQCED NMR spectrum in CDCl_3

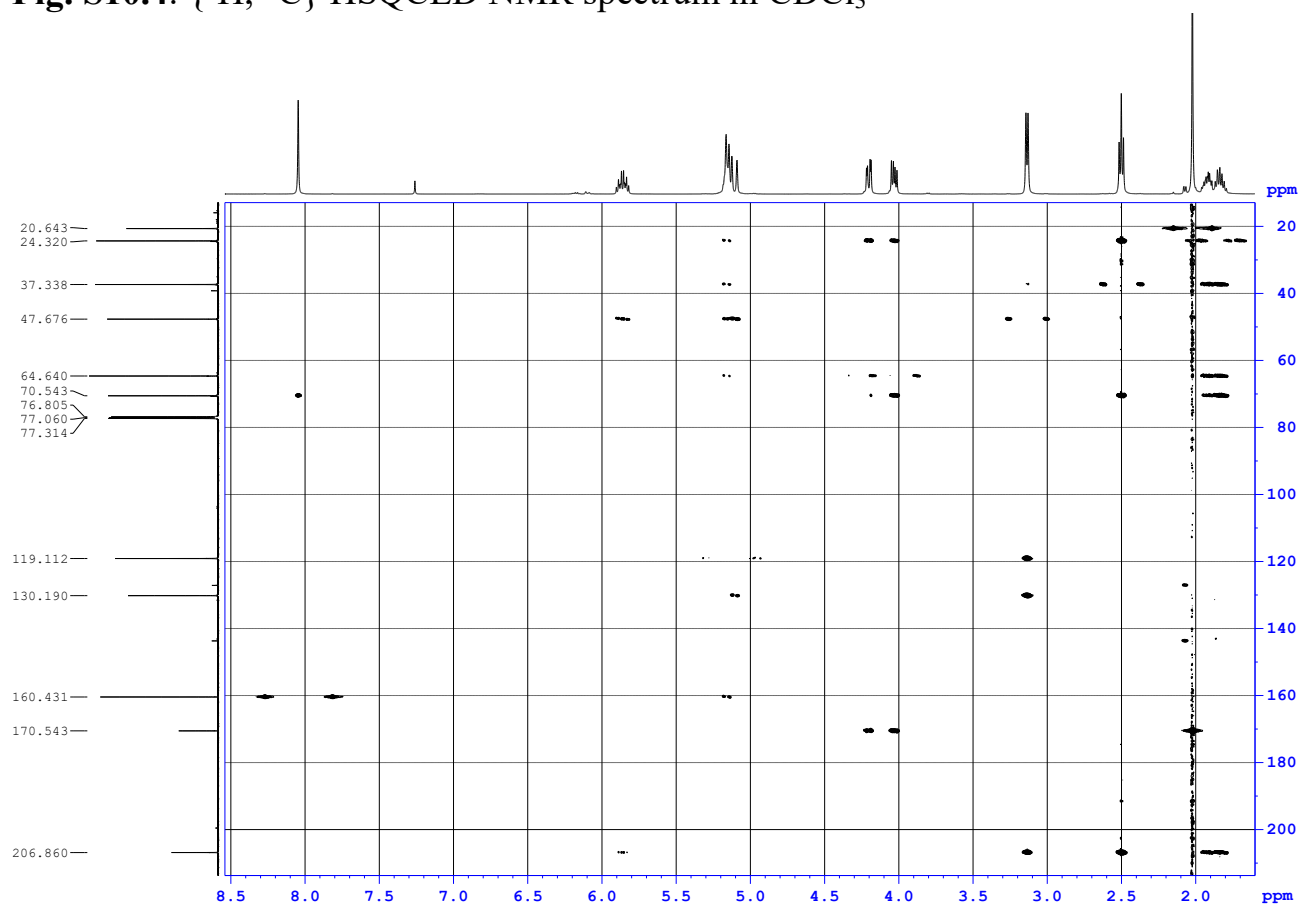


Fig. S10.5. $\{^1\text{H}, ^{13}\text{C}\}$ HMBC NMR spectrum in CDCl_3

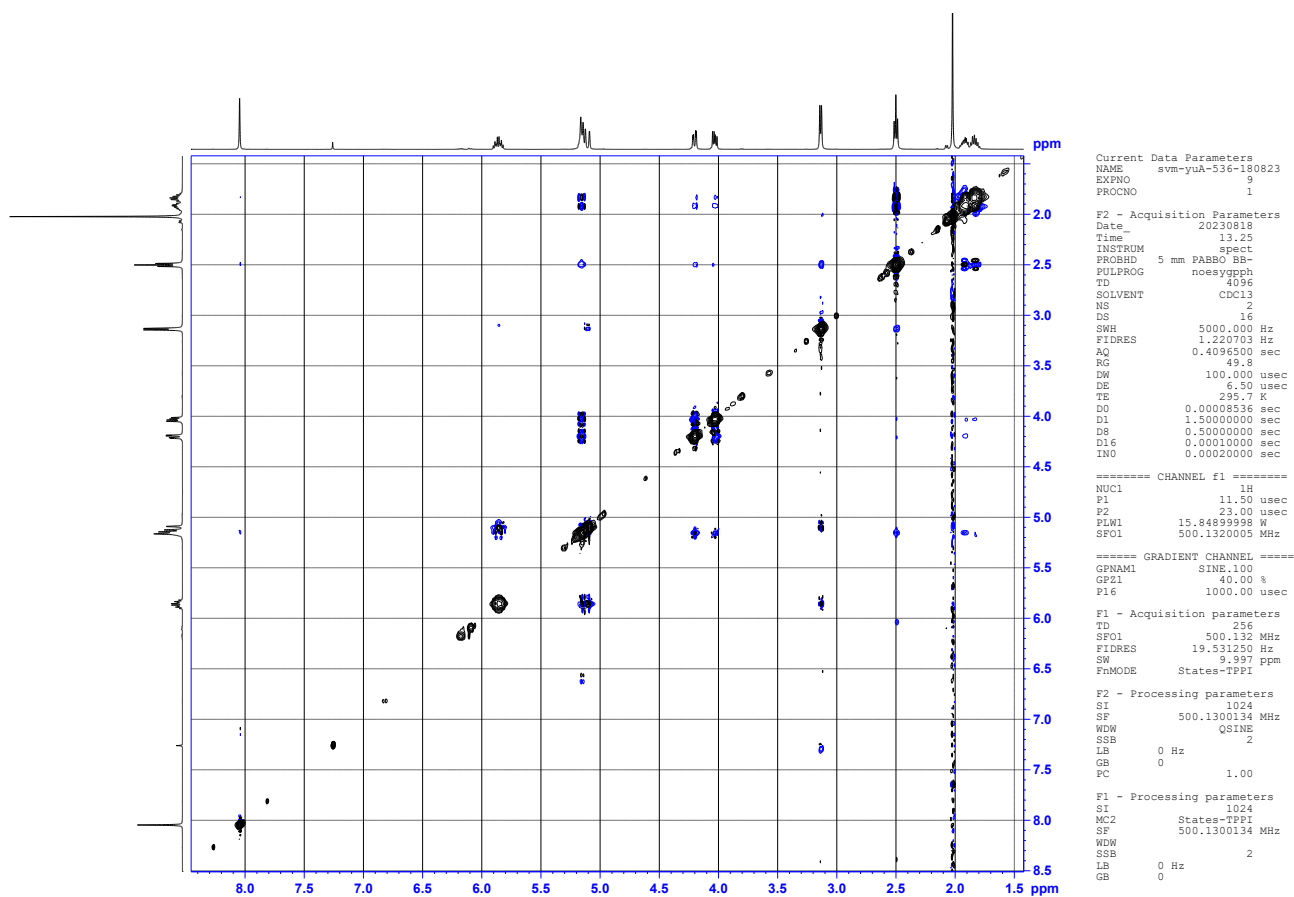
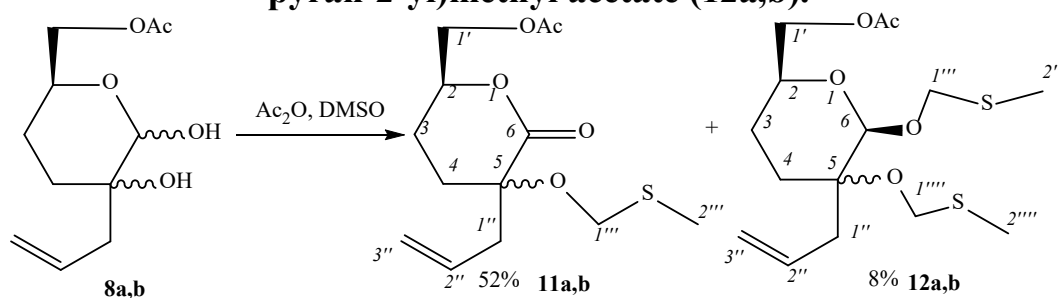


Fig. S10.6. Complete $\{^1\text{H}, ^1\text{H}\}$ NOESY NMR spectrum in CDCl_3

(*S*)-(5-Allyl-5-(methylthiomethoxy)-6-oxotetrahydro-2*H*-pyran-2-yl)methyl acetate (11a,b**) and ((2*S*)-5-allyl-5,6-bis(methylthiomethoxy)tetrahydro-2*H*-pyran-2-yl)methyl acetate (**12a,b**).**



To a solution of 0.141 g (0.0007 mol) lactols **8a,b** in 2.2 ml DMSO was added 1.5 ml Ac_2O under stirring at room temperature. The reaction mixture was stirred for 7 day at room temperature (control by TLC). Then the reaction mixture was treated with a saturated aqueous solution of NaHCO_3 (pH=6) and the reaction products was extracted with ethyl acetate (3×5.0 ml), the combined organic layers were dried over MgSO_4 , the solvent was distilled off, the residue was chromatographed on SiO_2 .

Lactone **11a,b** in ratio 5*R*/5*S*=4:1. Yield 0.098 g (52 %). Oil. R_f 0.3 (light petroleum– EtOAc , 3:1). $[\alpha]_D^{25} = +39.2^\circ$ (c 2.0, CHCl_3). ^1H NMR (CDCl_3), δ : 1.71–1.76 [1.40–1.45] (m, 1H, C^3BH_2); 1.87 [1.85] (dd, 1H, $^2J_{4B,4A}$ 14.8, $^3J_{4B,3B}$ 3.2, C^4BH_2);

2.04-2.17 [2.03-2.15] (m, 2H, C^{3A}H₂, C^{4A}H₂); 2.07 [2.03] (s, 3H, Ac); 2.16 [2.22] (s, 3H, S-Me); 2.56-2.65 [2.23-2.28] (m, 2H, C^{1''A}H₂, C^{1''B}H₂); 4.14 (dd, 1H, ²J_{I'B,I'A} 12.1, ³J_{I'B,2} 5.8, C^{I'B}H₂) [4.02-4.06 (m, 2H, C^{1'A}H₂, C^{1'B}H₂); 4.21 (dd, 1H, ²J_{I'A,I'B} 12.1, ³J_{I'A,2} 3.4, C^{I'A}H₂); 4.48-4.53 [3.93-3.99] (m, 1H, C²H); 4.61 [4.55] (d, 1H, ²J_{I'''B,I'''A} 10.7, C^{I'''B}H₂); 4.66 [4.60] (d, 1H, ²J_{I'''A,I'''B} 10.7, C^{I'''A}H₂); 5.13-5.18 [5.01-5.09] (m, 2H, C^{3''A}H₂, C^{3''B}H₂), 5.63-5.72 [5.73-5.81] (m, 1H, C^{2''}H). ¹³C NMR (CDCl₃), δ: 14.65 [14.62] (S-Me), 20.77 [20.81] (Ac), 21.10 [22.24] (C³), 30.73 [30.72] (C⁴), 39.05 [37.74] (C^{I'}), 65.78 [66.27] (C^{I'}), 69.12 [66.44] (C^{I'''}), 76.46 [74.60] (C⁵), 79.18 [68.22] (C²), 120.17 [118.63] (C^{3''}), 131.29 [131.60] (C^{2''}), 168.77 [168.94] (C¹), 170.62 [170.87] (Ac).

Mass spectrum, *m/z*: 289.1 [MH]⁺. Calcd for C₁₃H₂₀O₅S. 288.4

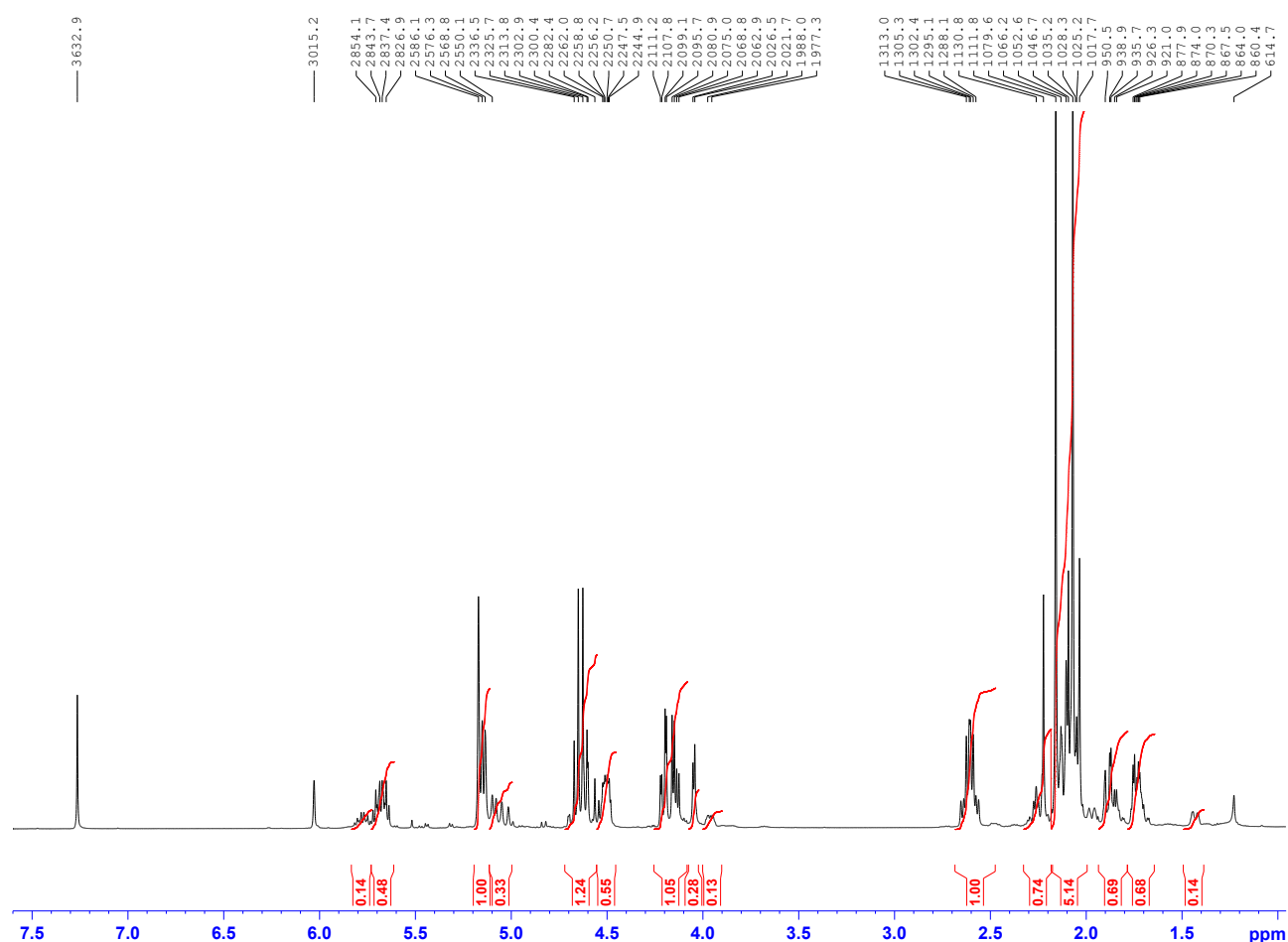


Fig. S11.1. Complete ¹H NMR (500 MHz) spectrum in CDCl₃

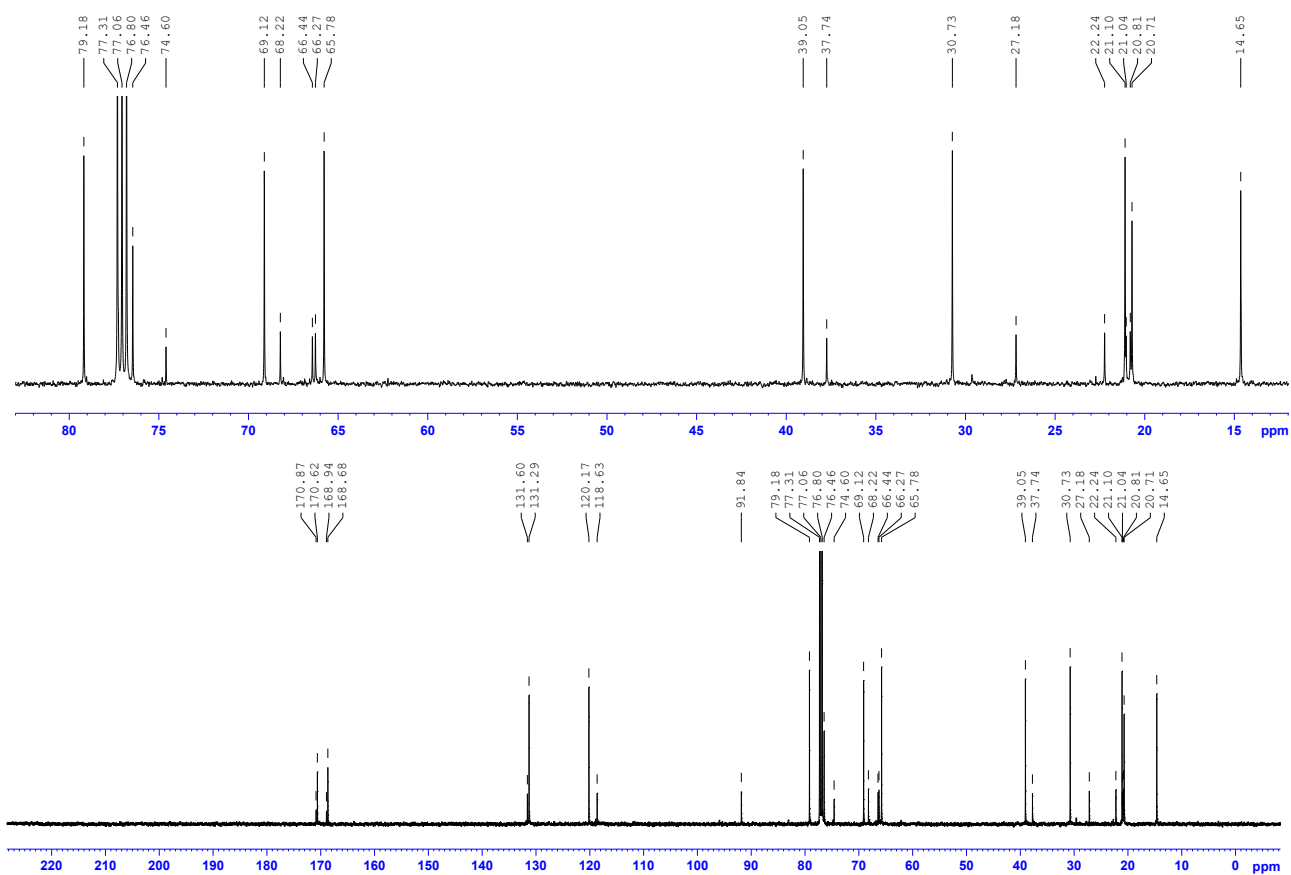


Fig. S11.2. Complete $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CDCl_3

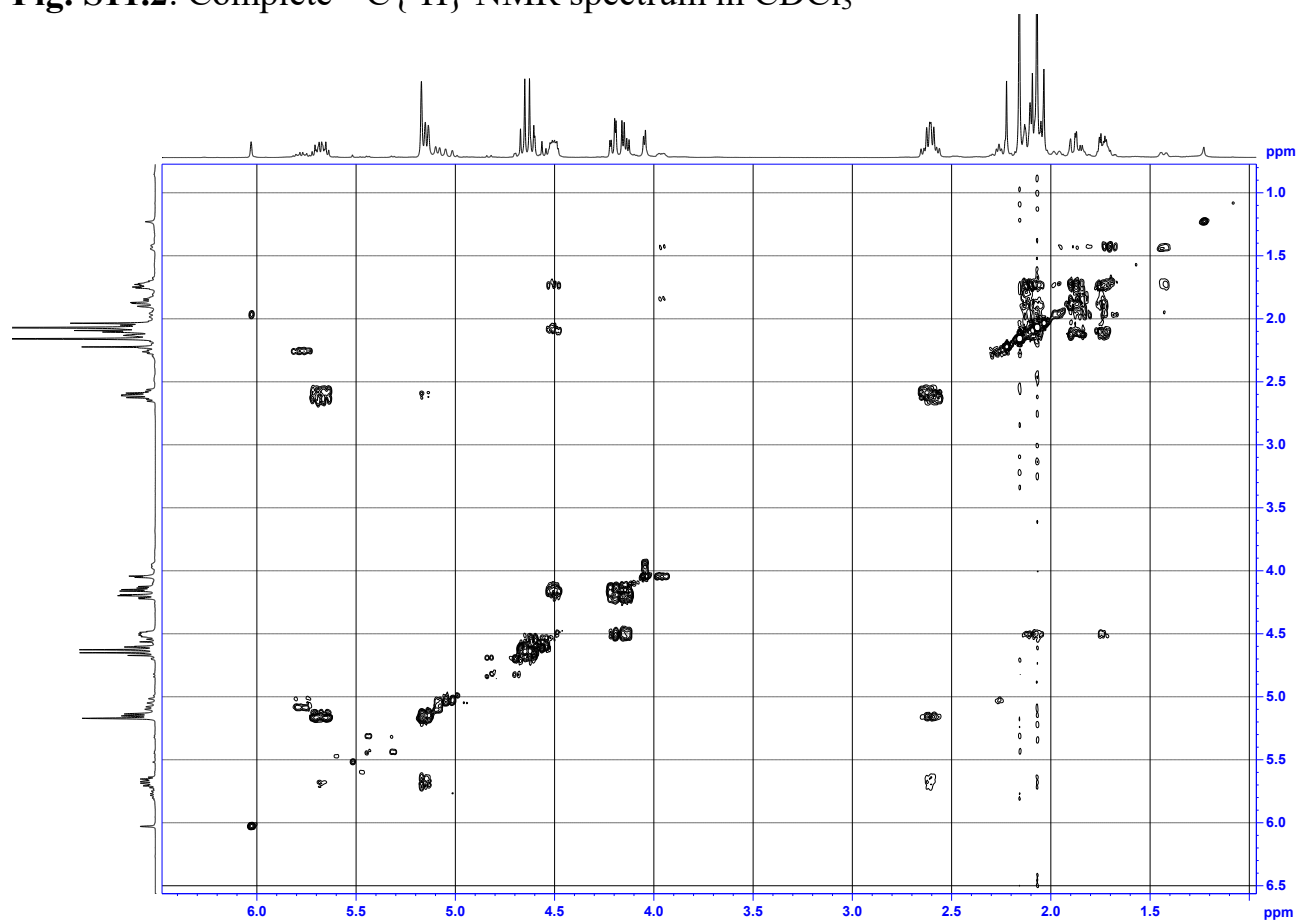


Fig. S11.3. Complete $\{^1\text{H}, ^1\text{H}\}$ COSY NMR spectrum in CDCl_3

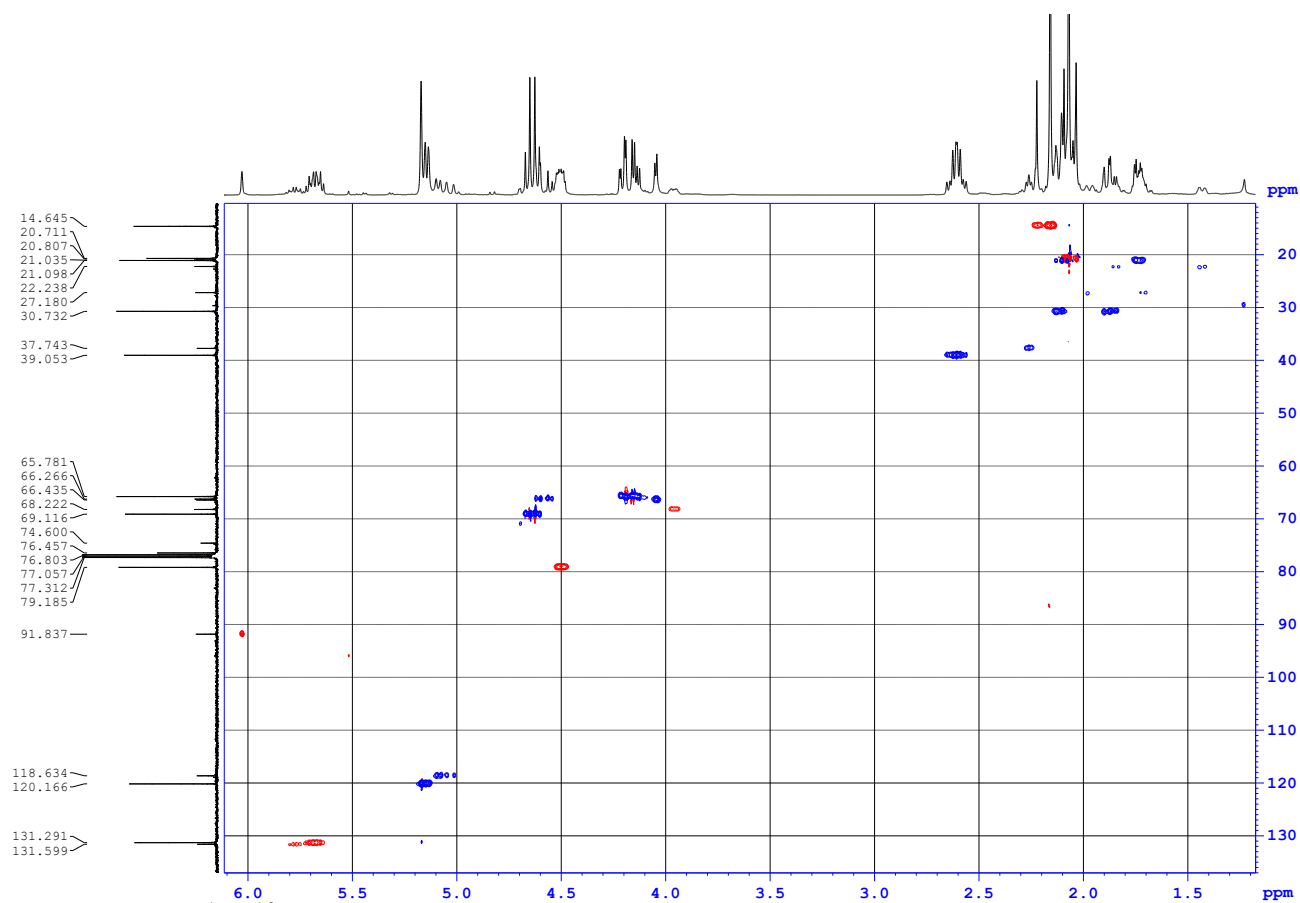


Fig. S11.4. $\{^1\text{H}, ^{13}\text{C}\}$ HSQCED NMR spectrum in CDCl_3

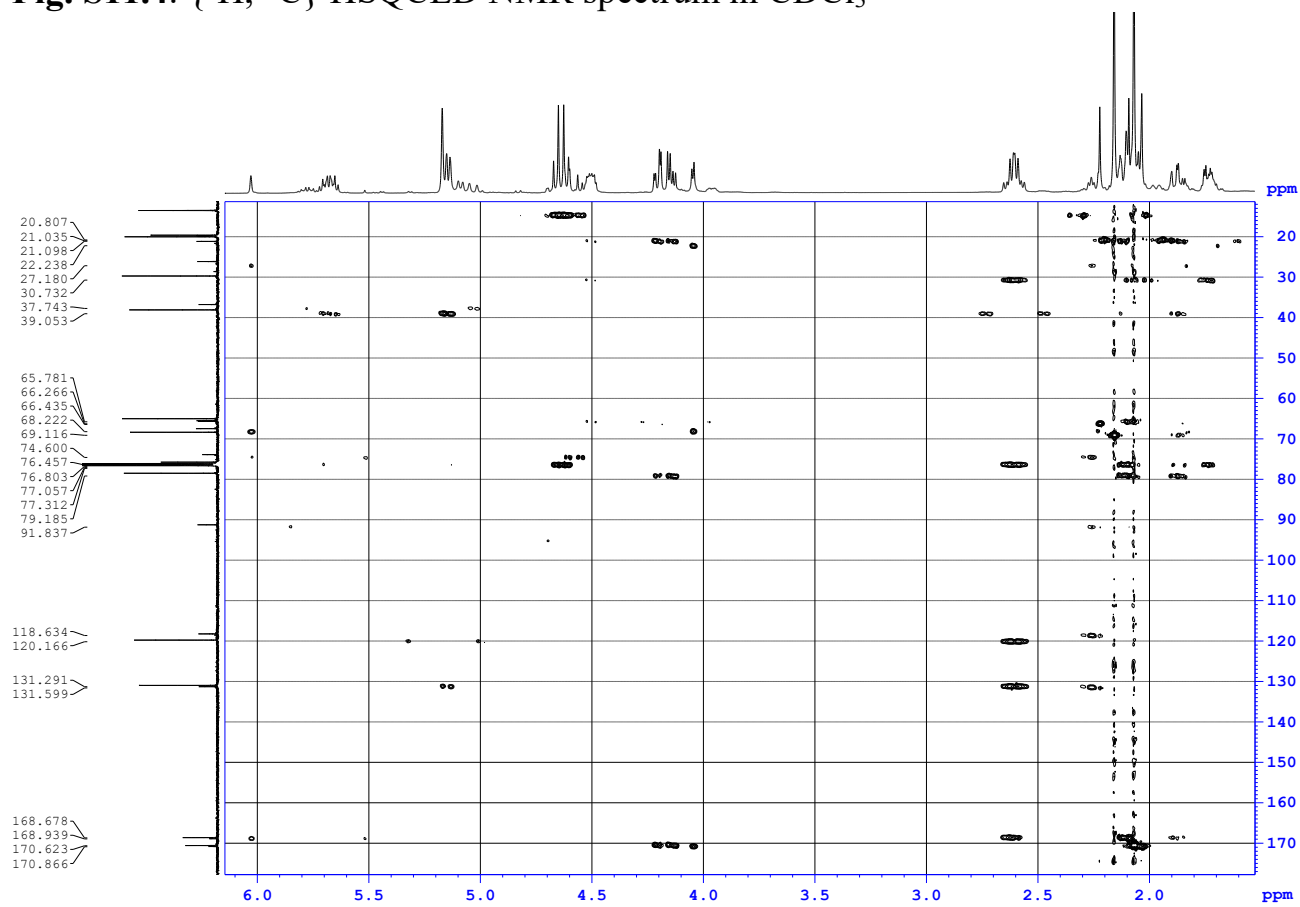


Fig. S11.5. $\{^1\text{H}, ^{13}\text{C}\}$ HMBC NMR spectrum in CDCl_3

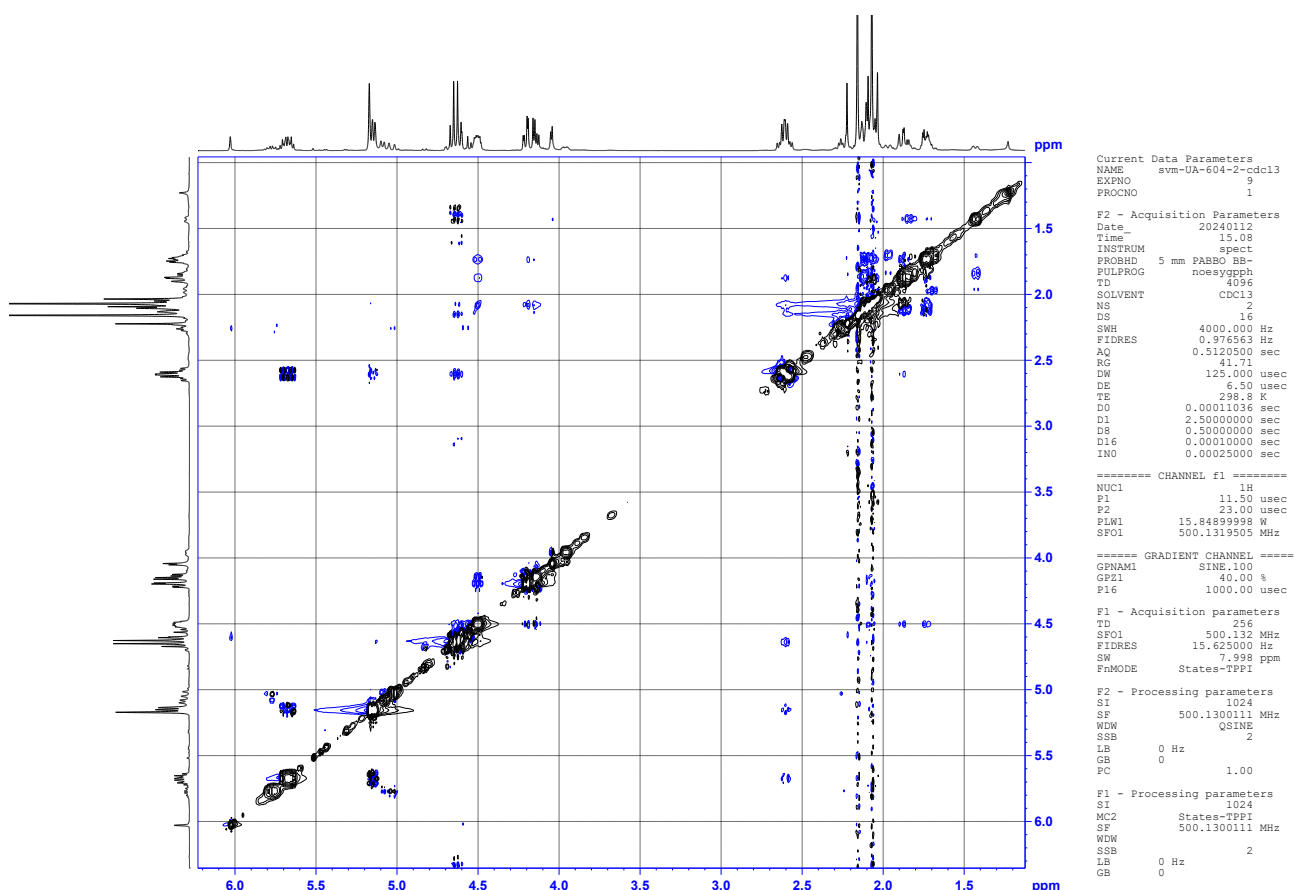


Fig. S11.6. Complete $\{^1\text{H}, ^1\text{H}\}$ NOESY NMR spectrum in CDCl_3

Compounds **12a,b**: Yield 0.019 g (8%) in ratio 8.0:1.0 in favor of the 5*R*-diastereomer. Oil. $[\alpha]_D^{25} = +40.8^\circ$ (*c* 0.5, CHCl_3). R_f 0.5 (petroleum ether–EtOAc, 3:1). ^1H NMR (CDCl_3), δ : 1.37–1.42 [1.38–1.43] (m, 1H, $\text{C}^3\text{B}_2\text{H}_2$); 1.70 [1.53] (dt, 1H, $^2J_{4B,4A}$ 12.5, $^3J_{4B,3A}$ 12.5, $^3J_{4B,3B}$ 3.8, $\text{C}^4\text{B}_2\text{H}_2$); 1.80 [1.82] (dt, 1H, $^2J_{3A,3B}$ 12.5, $^3J_{3A,4B}$ 12.5, $^3J_{3A,4A}$ 3.6, $\text{C}^3\text{A}_2\text{H}_2$); 1.91 [1.92] (td, 1H, $^2J_{4A,4B}$ 12.5, $^3J_{4A,3B}$ 3.6, $^3J_{4A,3A}$ 3.6, $\text{C}^4\text{A}_2\text{H}_2$); 2.07 [2.05] (s, 3H, Ac); 2.18 [2.19] (s, 3H, S-Me); 2.25 [2.23] (s, 3H, S-Me); 3.91–3.96 [3.69–3.75] (m, 1H, C^2H); 4.05 [4.07] (dd, 1H, $^2J_{1'B,1'A}$ 11.4, $^3J_{1'B,2}$ 6.3, $\text{C}^{1'B}_2\text{H}_2$); 4.11 [4.12] (dd, 1H, $^2J_{1'A,1'B}$ 11.4, $^3J_{1'A,2}$ 3.7, $\text{C}^{1'A}_2\text{H}_2$); 4.57 [4.71] (d, 1H, $^2J_{1''''B,1''''A}$ 10.1, $\text{C}^{1''''B}_2\text{H}_2$); 4.62 [4.93] (d, 1H, $^2J_{1''''A,1''''B}$ 10.1, $\text{C}^{1''''A}_2\text{H}_2$); 4.72 [4.82] (d, 1H, $^2J_{1''''B,1''''A}$ 11.7, $\text{C}^{1''''B}_2\text{H}_2$); 4.74 [4.85] (d, 1H, $^2J_{1''''A,1''''B}$ 11.7, $\text{C}^{1''''A}_2\text{H}_2$); 5.07 [4.66] (s, 1H, C^6H); 5.08–5.15 [5.09–5.16] (m, 2H, $\text{C}^{3''}\text{AH}_2$, $\text{C}^{3''}\text{BH}_2$); 5.83–5.91 [5.84–5.92] (m, 1H, $\text{C}^{2''}\text{H}$). ^{13}C NMR (CDCl_3), δ : 14.68 [14.55] (S-Me), 14.78 [14.64] (S-Me), 20.84 [20.85] (Ac), 22.54 [23.18] (C^3), 27.31 [31.97] (C^4), 37.86 [37.44] ($\text{C}^{1''}$), 66.14 [66.43] ($\text{C}^{1''''}$), 66.79 [74.38] (C^2), 66.88 [66.43] ($\text{C}^{1'}$), 70.94 [72.05] ($\text{C}^{1''}$), 75.31 [74.94] (C^5), 94.99 [99.88] (C^2), 118.27 [118.67] ($\text{C}^{3''}$), 132.26 [132.59] ($\text{C}^{2''}$), 170.88 [170.87] (Ac). Mass spectrum, m/z : 351.0 $[\text{MH}]^+$. Calcd. for $\text{C}_{15}\text{H}_{26}\text{O}_5\text{S}_2$. 350.5

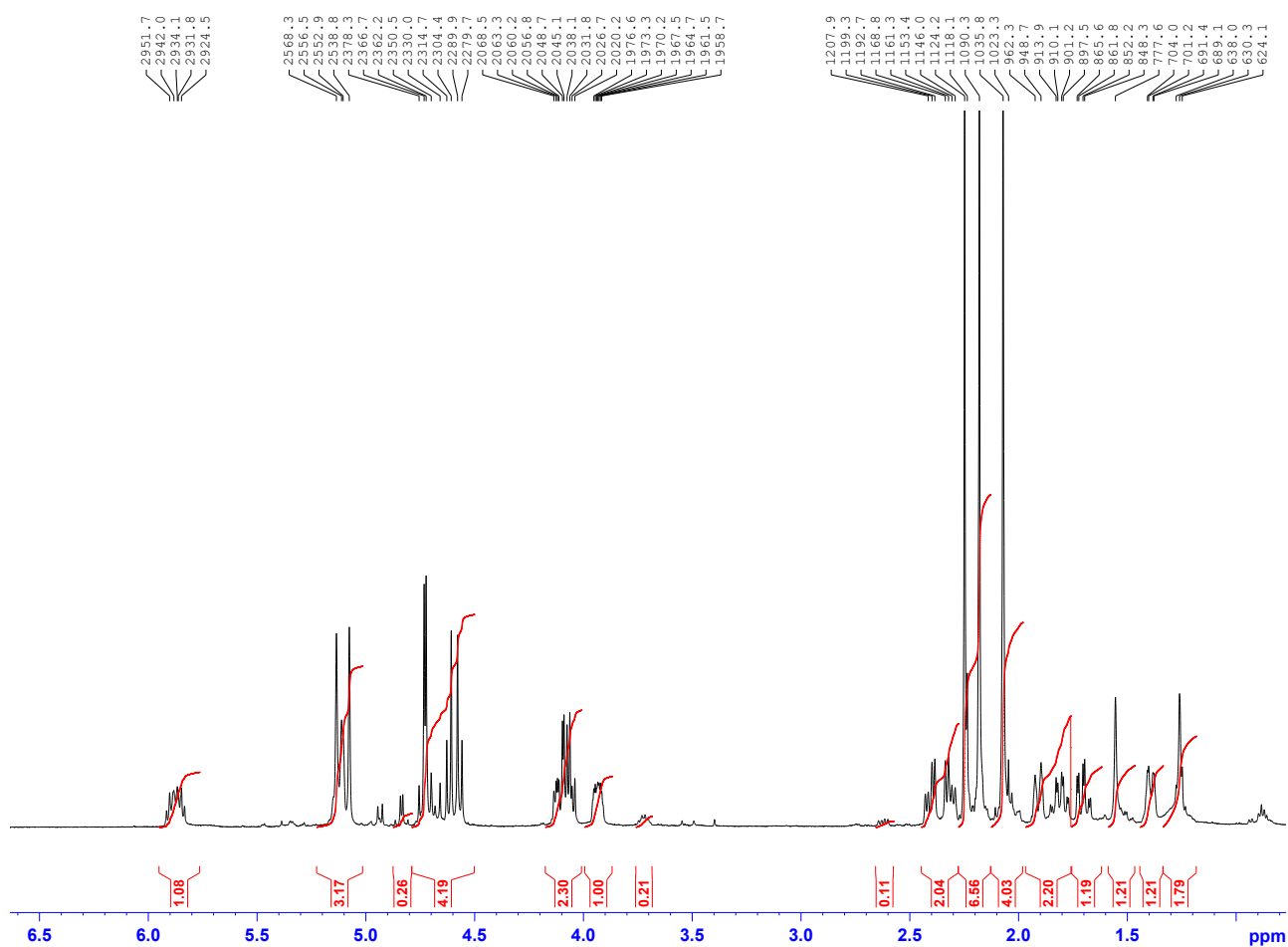


Fig. S12.1. Complete ^1H NMR (500 MHz) spectrum in CDCl_3

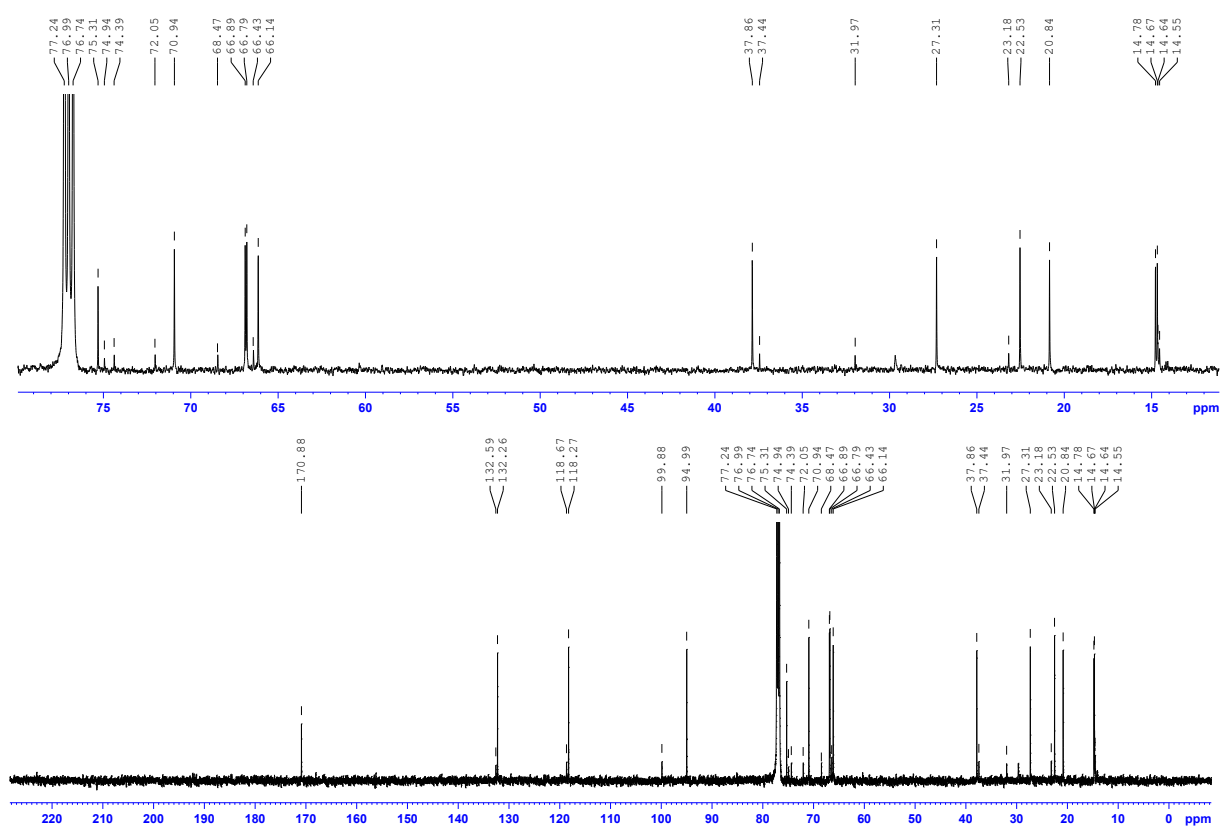


Fig. S12.2. Complete $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CDCl_3

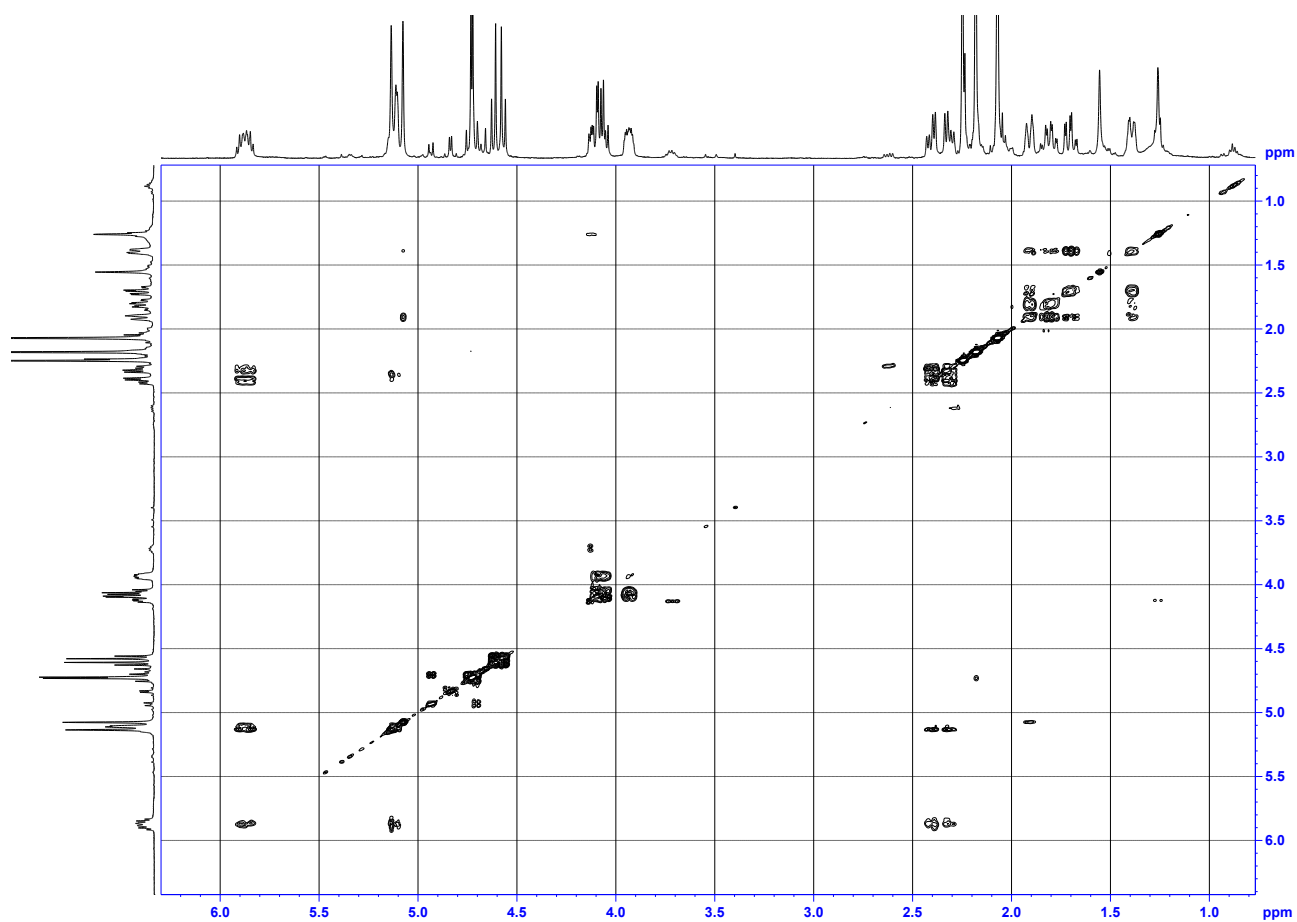


Fig. S12.3. Complete $\{^1\text{H}, ^1\text{H}\}$ COSY NMR spectrum in CDCl_3

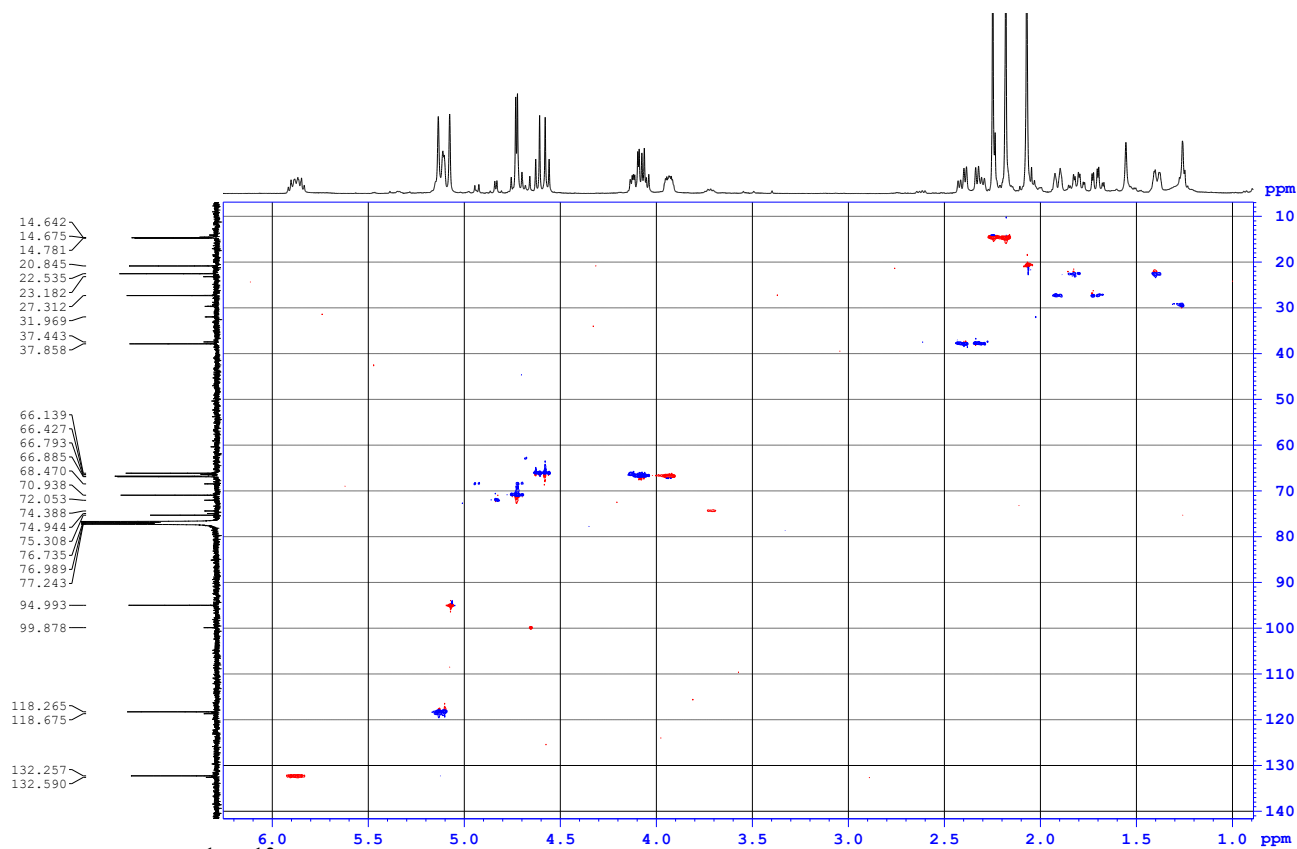


Fig. S12.4. $\{^1\text{H}, ^{13}\text{C}\}$ HSQCED NMR spectrum in CDCl_3

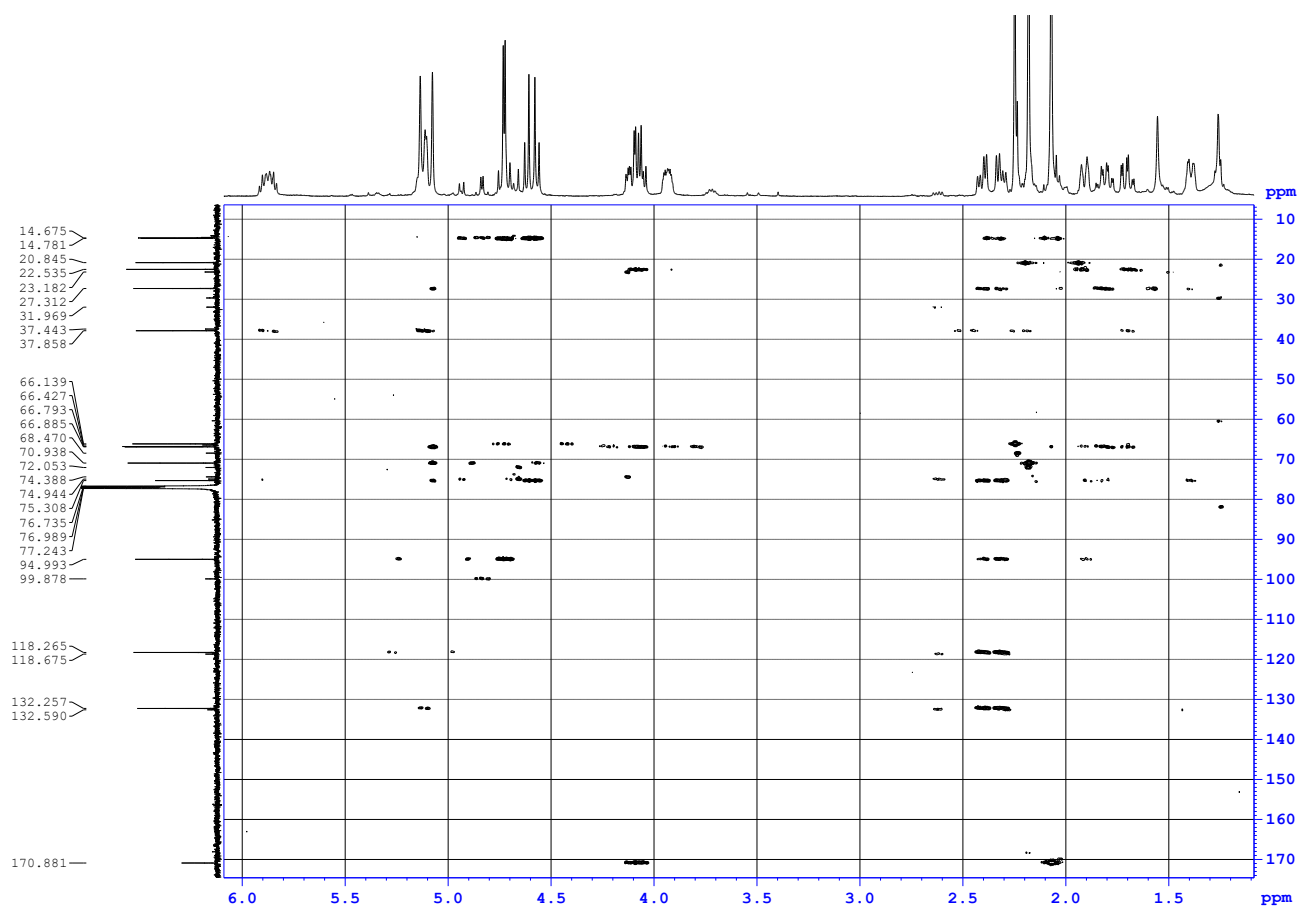


Fig. S12.5. $\{^1\text{H}, ^{13}\text{C}\}$ HMBC NMR spectrum in CDCl_3

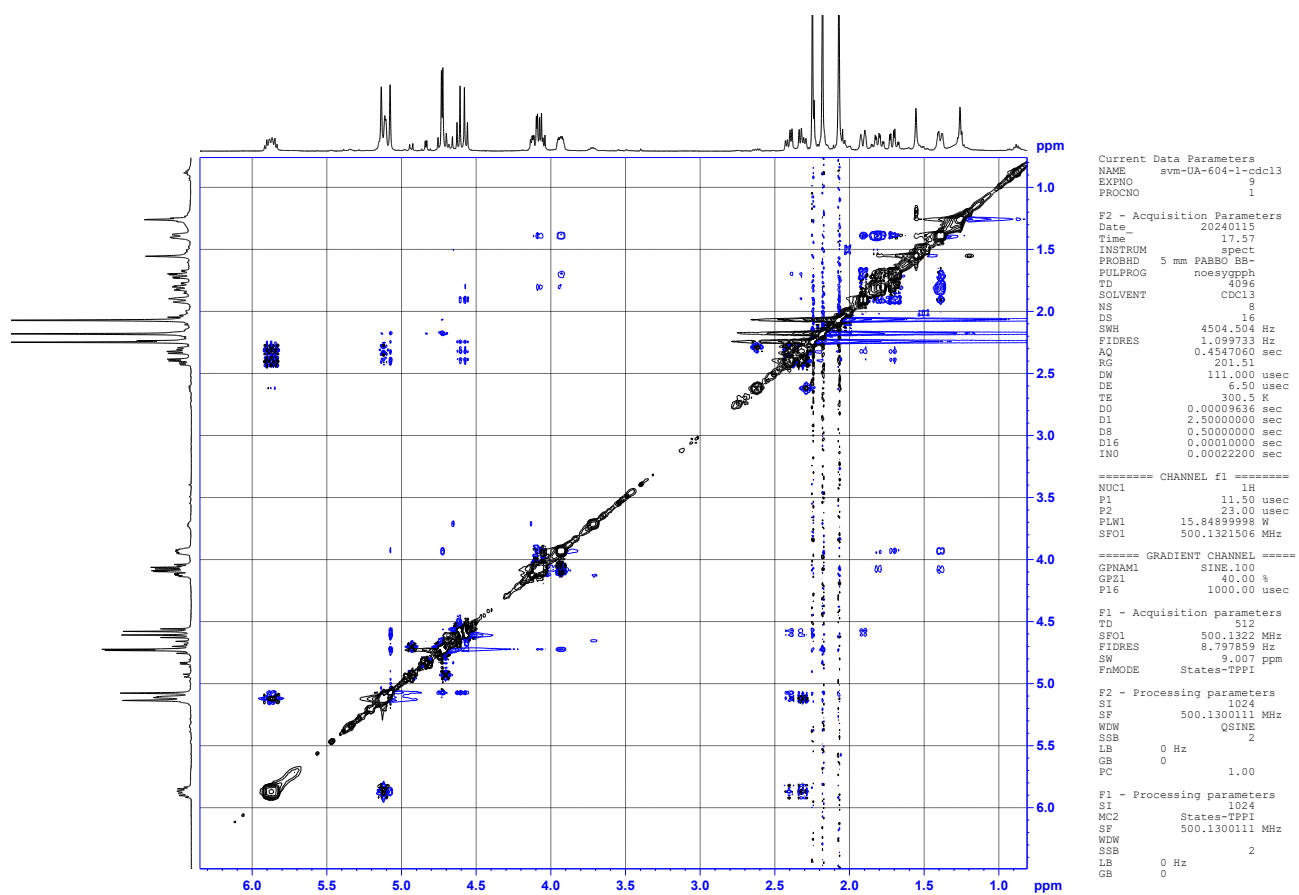
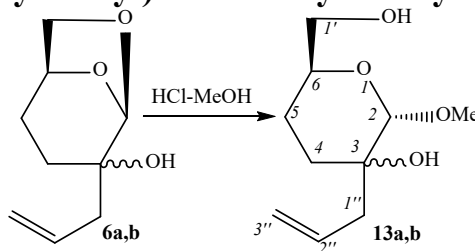


Fig. S12.6. Complete $\{^1\text{H}, ^1\text{H}\}$ NOESY NMR spectrum in CDCl_3

(2*S*,6*S*)-3-Allyl-6-(hydroxymethyl)-2-methoxytetrahydro-2*H*-pyran-3-ol (13a,b).



To a solution of 0.600 g (0.004 mol) adducts **6a,b** in 2.0 ml methanol at 0°C was added 10.0 ml 16% solution HCl in methanol. The reaction mixture was stirred for 60 hour at room temperature (control by TLC). Then the reaction mixture was treated with a saturated aqueous solution of NaHCO₃ (pH=6) and the reaction products was extracted with ethyl acetate (3×10.0 ml), the combined organic layers were dried over MgSO₄, the solvent was distilled off, the residue was chromatographed on SiO₂. Yield 0.629 g (88%) in ratio 3*R*:3*S*=2.5:1.

3*S*-Diastereomer **13b** Oil. [α]_D²⁵ = + 97.1° (*c* 1.0, CHCl₃). *R*_f 0.3 (petroleum ether–EtOAc, 3:1). ¹H NMR (CDCl₃), δ : 1.45-1.55 (m, 2H, C^{5B}H₂, C^{5A}H₂); 1.73-1.80 (m, 2H, C^{4A}H₂, C^{4B}H₂); 2.29 (br.s, 1H, C³-OH); 2.35 (dd, 1H, ²*J*_{1'B,1'A} 14.2, ²*J*_{1'B,2'} 6.9, C^{1'B}H₂); 2.43 (dd, 1H, ²*J*_{1'A,1'B} 14.2, ²*J*_{1'A,2'} 6.9, C^{1'A}H₂); 3.49 (s, 3H, OMe); 3.53 (dd, 1H, ²*J*_{7B,7A} 11.5, ³*J*_{7B,1} 6.7, C^{7B}H₂); 3.62 (dd, 1H, ²*J*_{7A,7B} 11.5, ³*J*_{7B,1} 2.9, C^{7A}H₂); 3.76-3.81 (m, 1H, C⁶H); 4.34 (s, 1H, C⁵H); 5.10-5.15 (m, 2H, C^{3'A}H₂, C^{3'B}H₂); 5.86-5.95 (m, 1H, C²H). ¹³C NMR (CDCl₃), δ : 24.53 (C⁵), 30.24 (C⁴), 39.30 (C^{1'}), 55.15 (OMe), 65.40 (C⁷), 68.70 (C⁶), 70.22 (C³), 102.16 (C²), 118.27 (C^{3'}), 132.93 (C^{2'}).

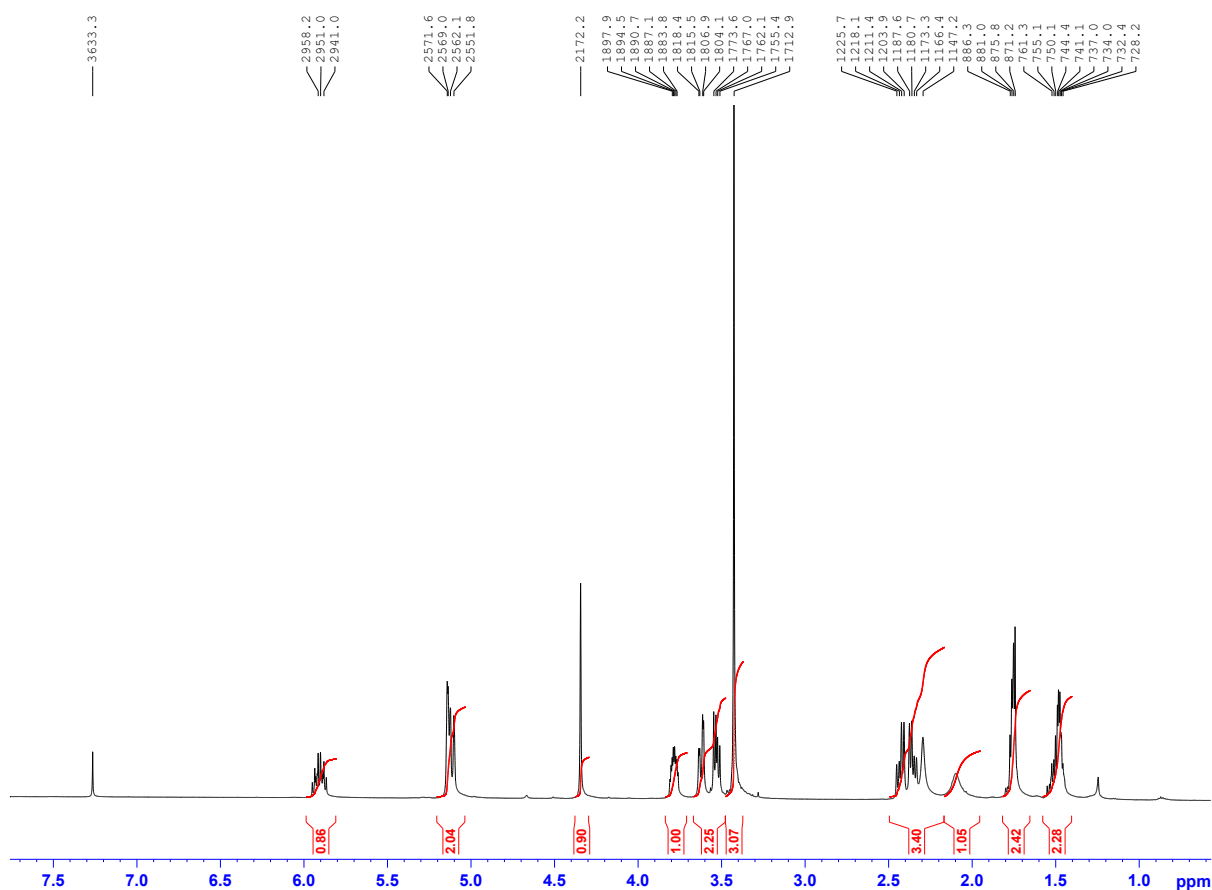


Fig. S13b.1. Complete ^1H NMR (500 MHz) spectrum in CDCl_3

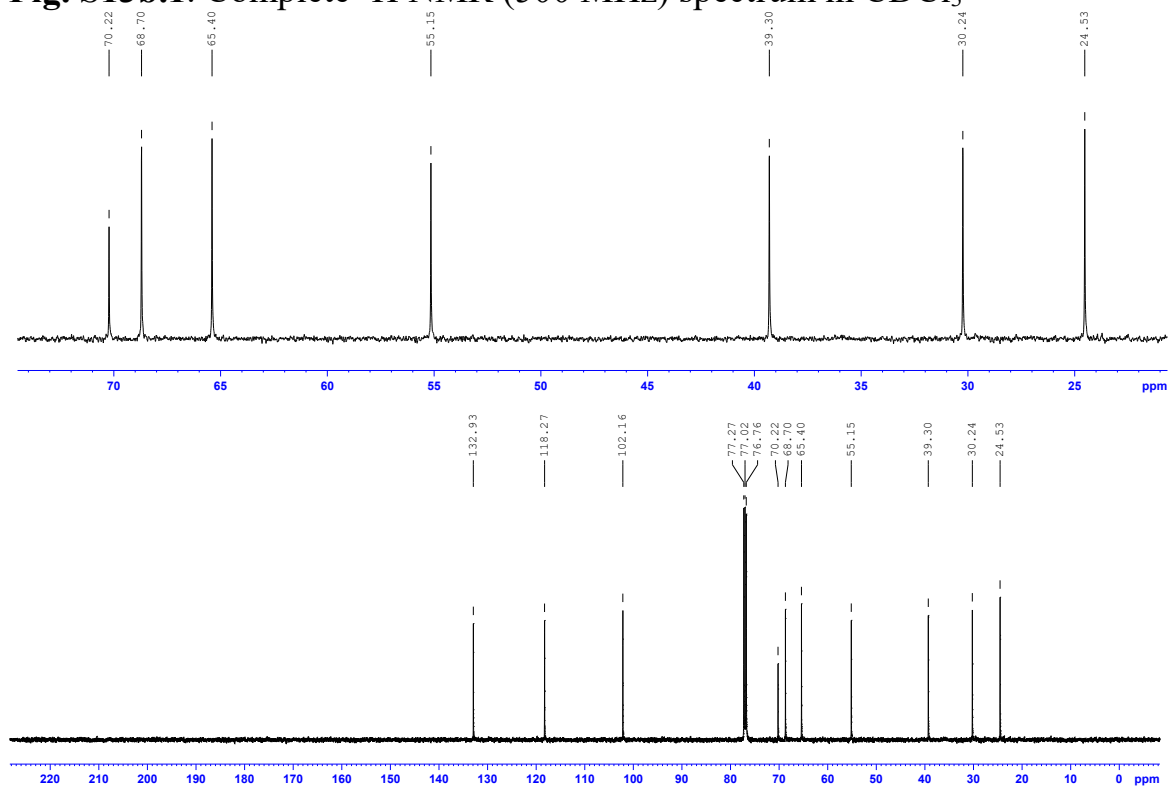


Fig. S13b.2. Complete $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CDCl_3

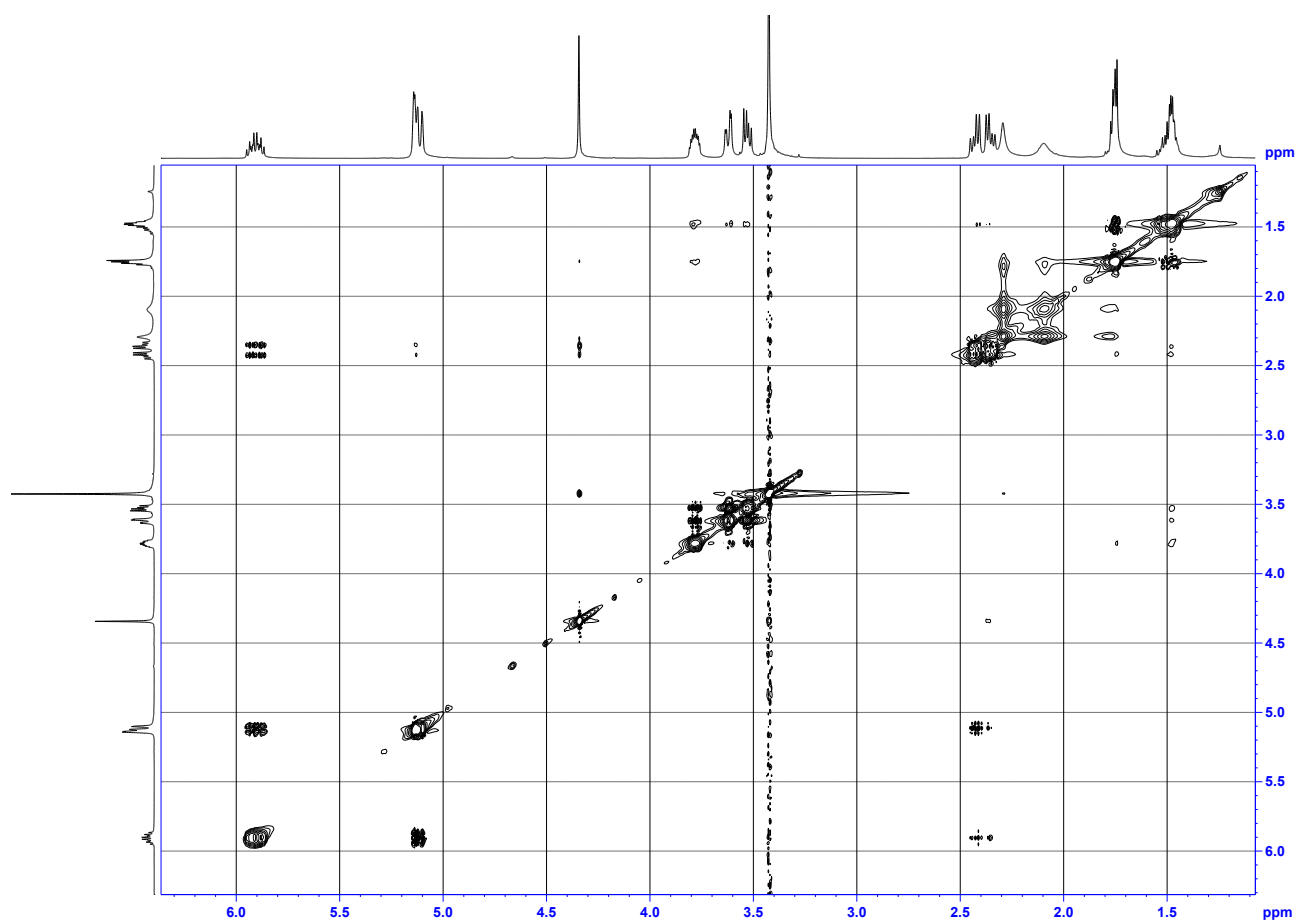


Fig. S13b.3. Complete $\{^1\text{H}, ^1\text{H}\}$ COSY NMR spectrum in CDCl_3

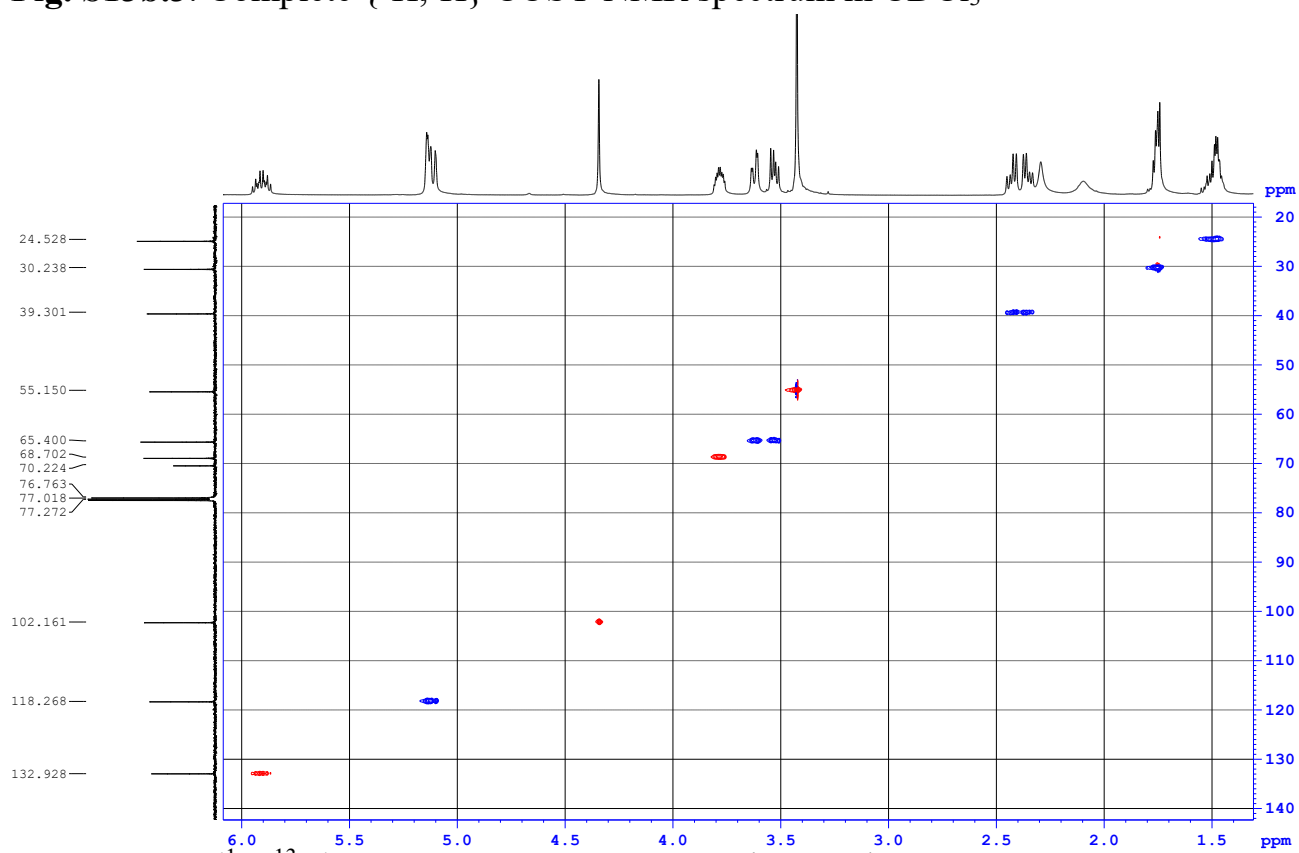


Fig. S13b.4. $\{^1\text{H}, ^{13}\text{C}\}$ HSQC NMR spectrum in CDCl_3

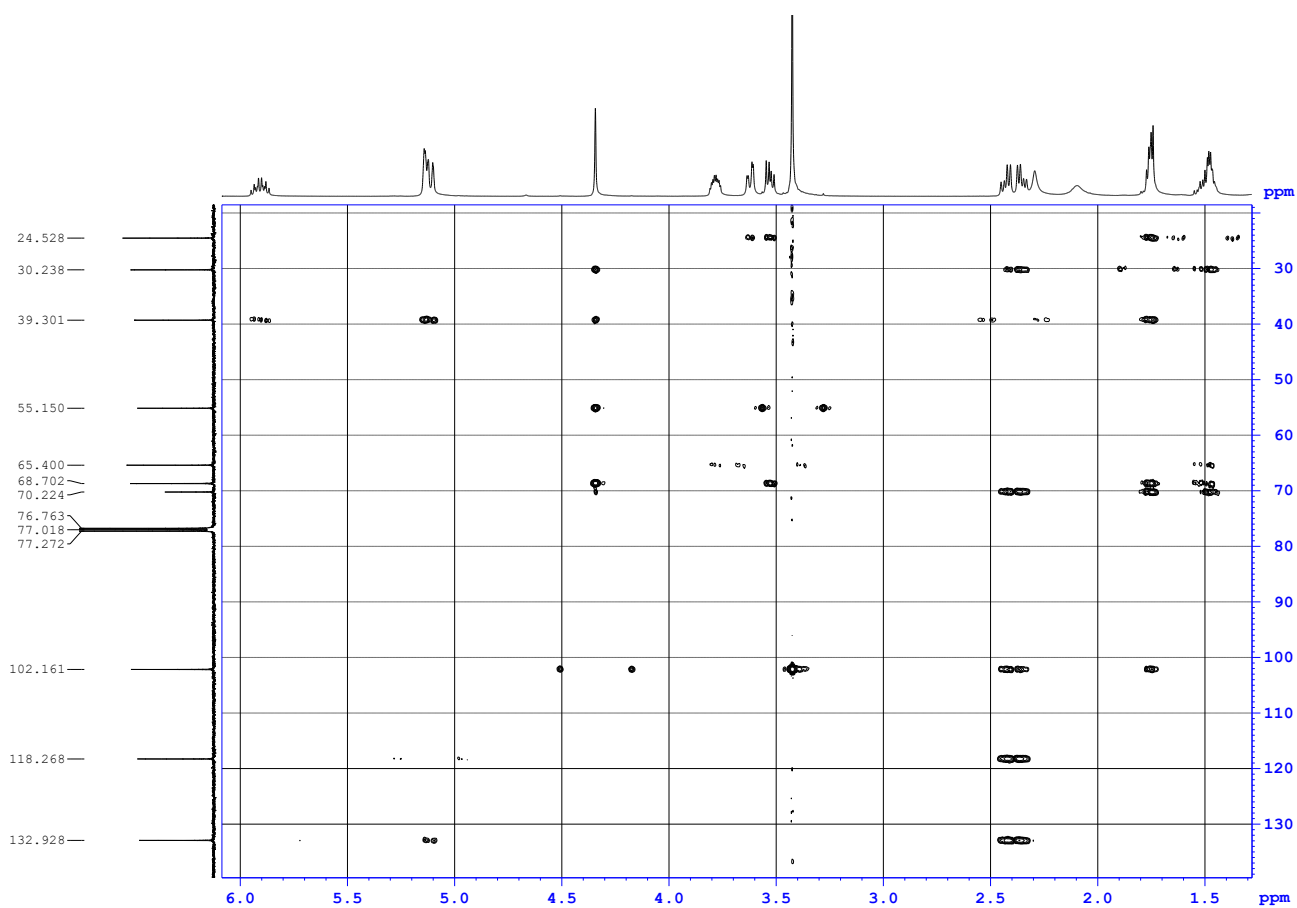


Fig. S13b.5. $\{^1\text{H}, ^{13}\text{C}\}$ HMBC NMR spectrum in CDCl_3

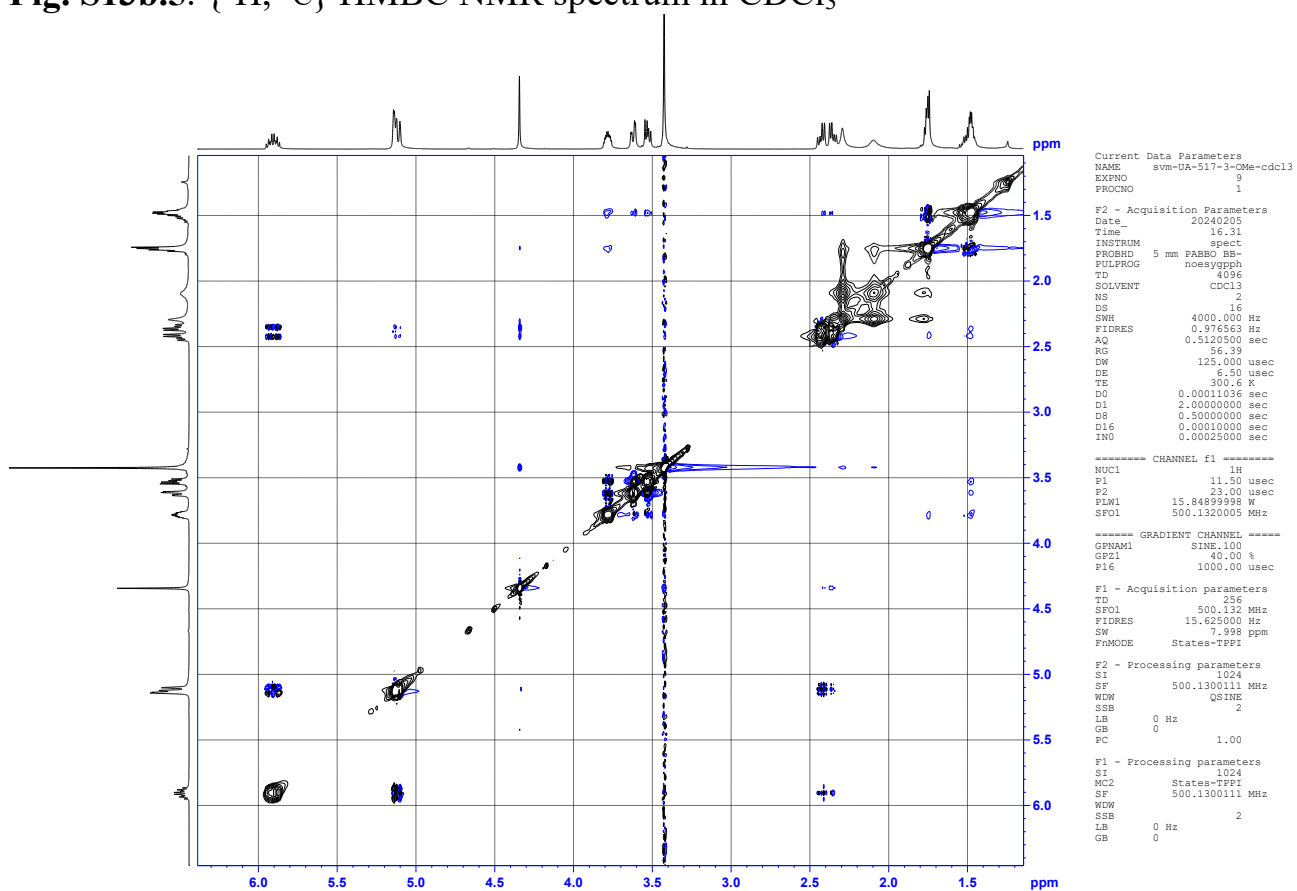


Fig. S13b.6. Complete $\{^1\text{H}, ^1\text{H}\}$ NOESY NMR spectrum in CDCl_3

3*R*-Diastereomer **13a** Oil. $[\alpha]_D^{25} = +60.0^\circ$ (c 1.0, CHCl_3). R_f 0.2 (petroleum ether–EtOAc, 3:1). ^1H NMR (CDCl_3), δ : 1.36–1.41 (m, 1H, C^5H_2); 1.58–1.63 (m, 1H, C^4H_2); 1.65–1.72 (m, 1H, C^5A_2); 1.74–1.81 (m, 1H, C^4A_2); 2.19 (dd, 1H, $^2J_{I'B, I'A}$ 14.2, $^2J_{I'B, 2}$ 6.9, $\text{C}^{I'B}\text{H}_2$); 2.72 (dd, 1H, $^2J_{I'A, I'B}$ 14.2, $^2J_{I'A, 2}$ 6.9, $\text{C}^{I'A}\text{H}_2$); 2.34 (br.s, 1H, $\text{C}^3\text{-OH}$); 3.38 (s, 3H, OMe); 3.56 (dd, 1H, $^2J_{7B, 7A}$ 11.5, $^3J_{7B, I}$ 6.7, C^{7B}H_2); 3.63 (dd, 1H, $^2J_{7A, 7B}$ 11.5, $^3J_{7B, I}$ 2.9, C^{7A}H_2); 3.78–3.82 (m, 1H, C^6H); 4.30 (s, 1H, C^5H); 5.07–5.16 (m, 2H, $\text{C}^{3'A}\text{H}_2$, $\text{C}^{3'B}\text{H}_2$); 5.82–5.90 (m, 1H, C^2H). ^{13}C NMR (CDCl_3), δ : 22.10 (C^5), 29.53 (C^4), 42.25 (C^I), 55.00 (OMe), 65.59 (C^7), 68.72 (C^6), 69.81 (C^3), 102.74 (C^2), 118.75 (C^3), 132.78 (C^2).

Mass spectrum, m/z : 203.0 $[\text{MH}]^+$. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_4$. 202.2.

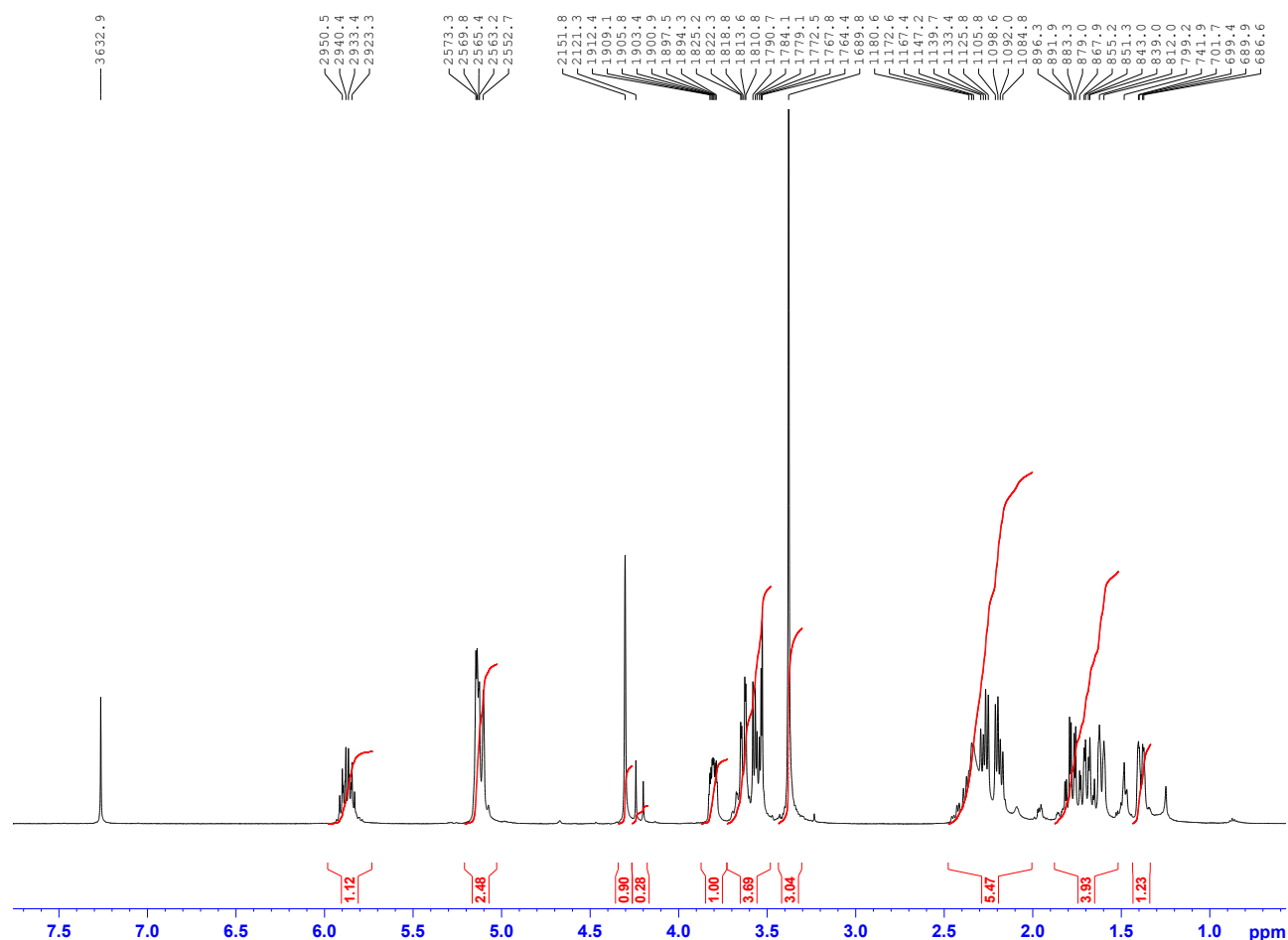


Fig. S13a.1. Complete ^1H NMR (500 MHz) spectrum in CDCl_3

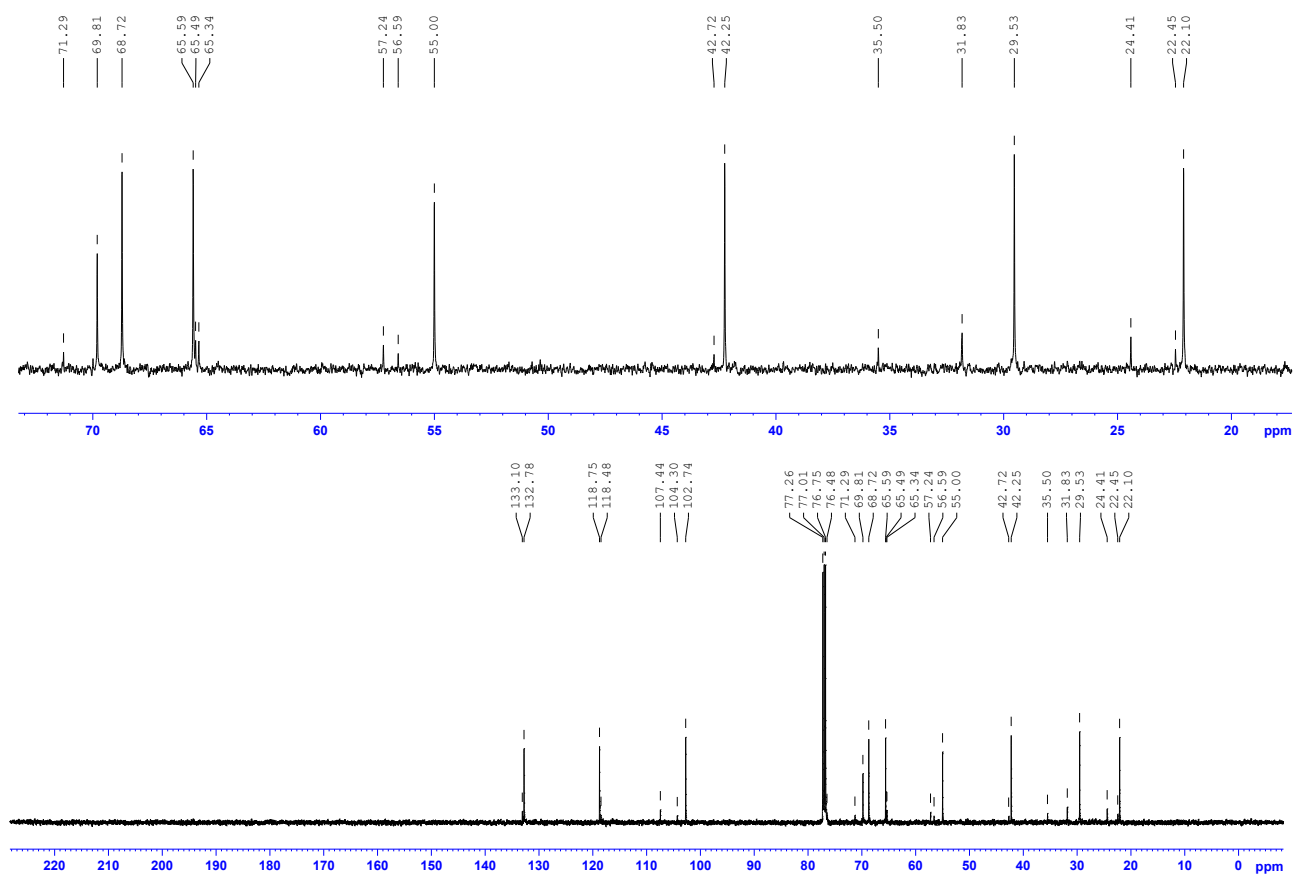


Fig. S13a.2. Complete $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CDCl_3

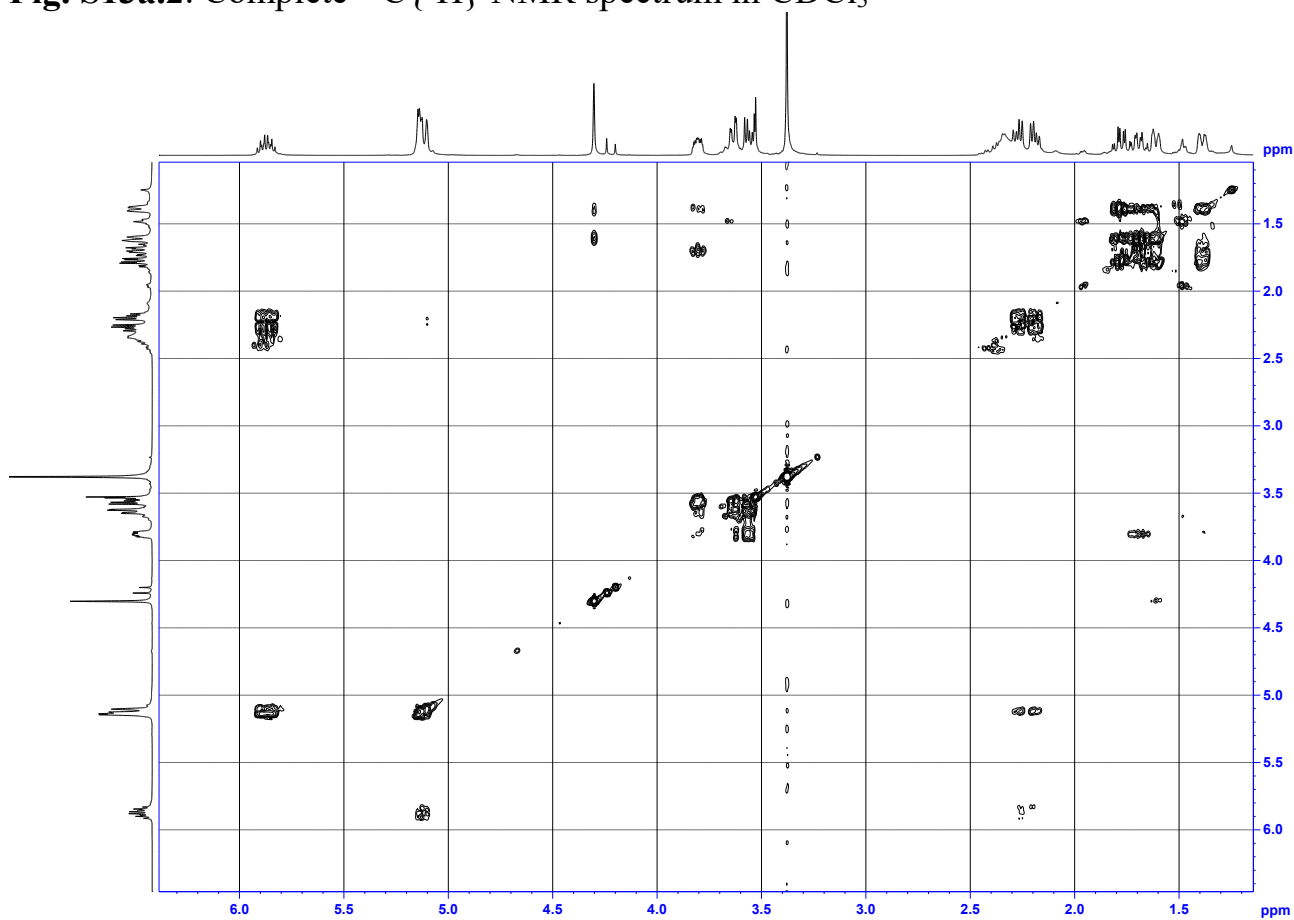


Fig. S13a.3. Complete $\{^1\text{H}, ^1\text{H}\}$ COSY NMR spectrum in CDCl_3

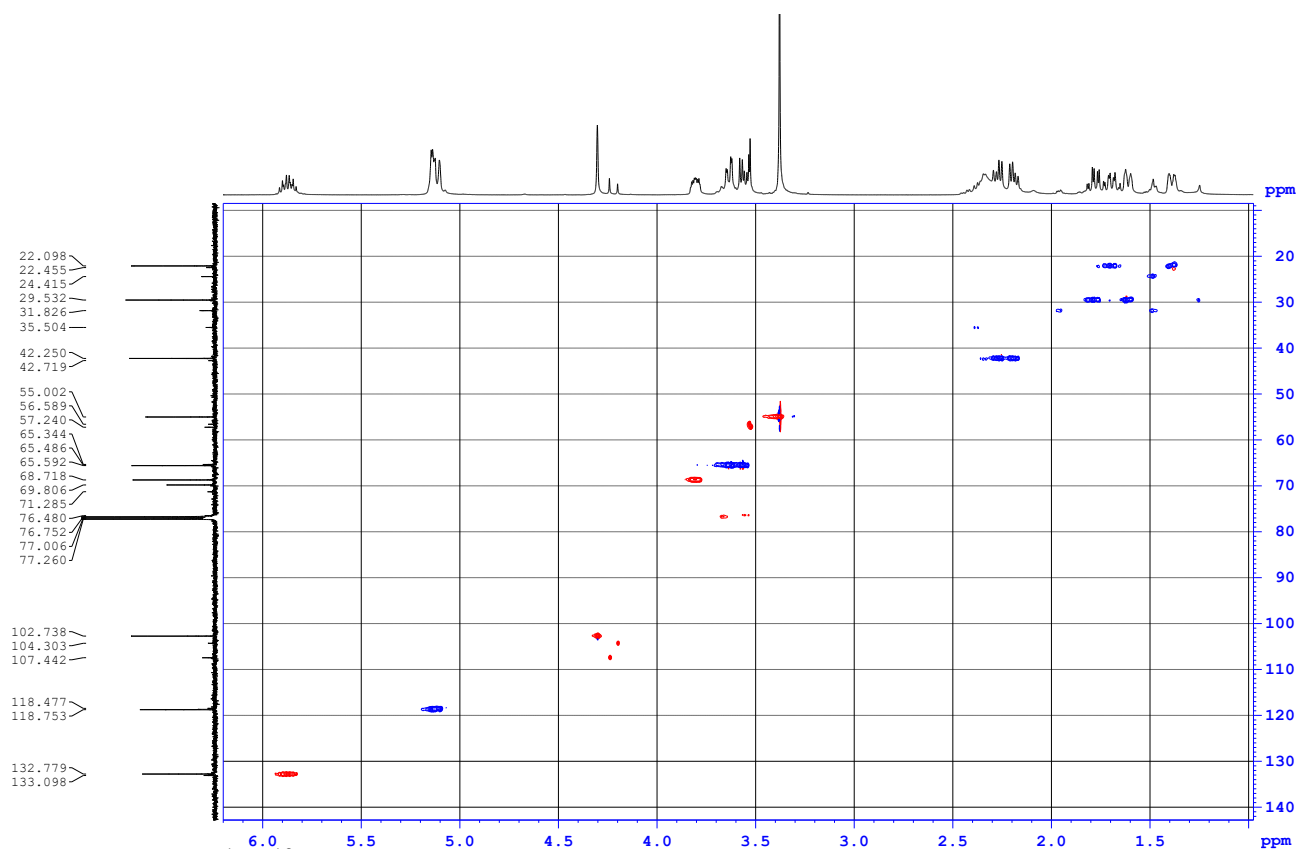


Fig. S13a.4. $\{^1\text{H}, ^{13}\text{C}\}$ HSQCED NMR spectrum in CDCl_3

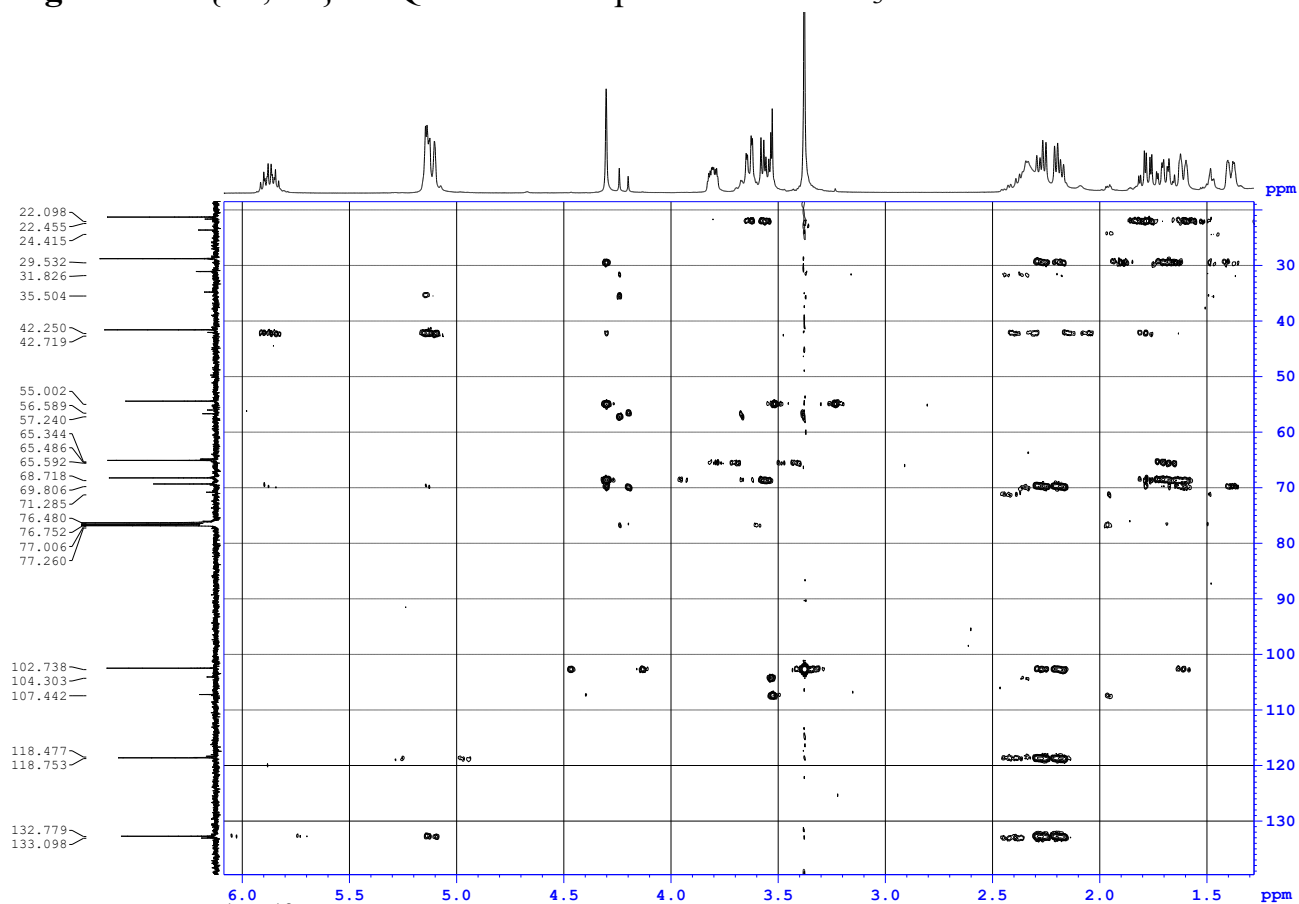


Fig. S13a.5. $\{^1\text{H}, ^{13}\text{C}\}$ HMBC NMR spectrum in CDCl_3

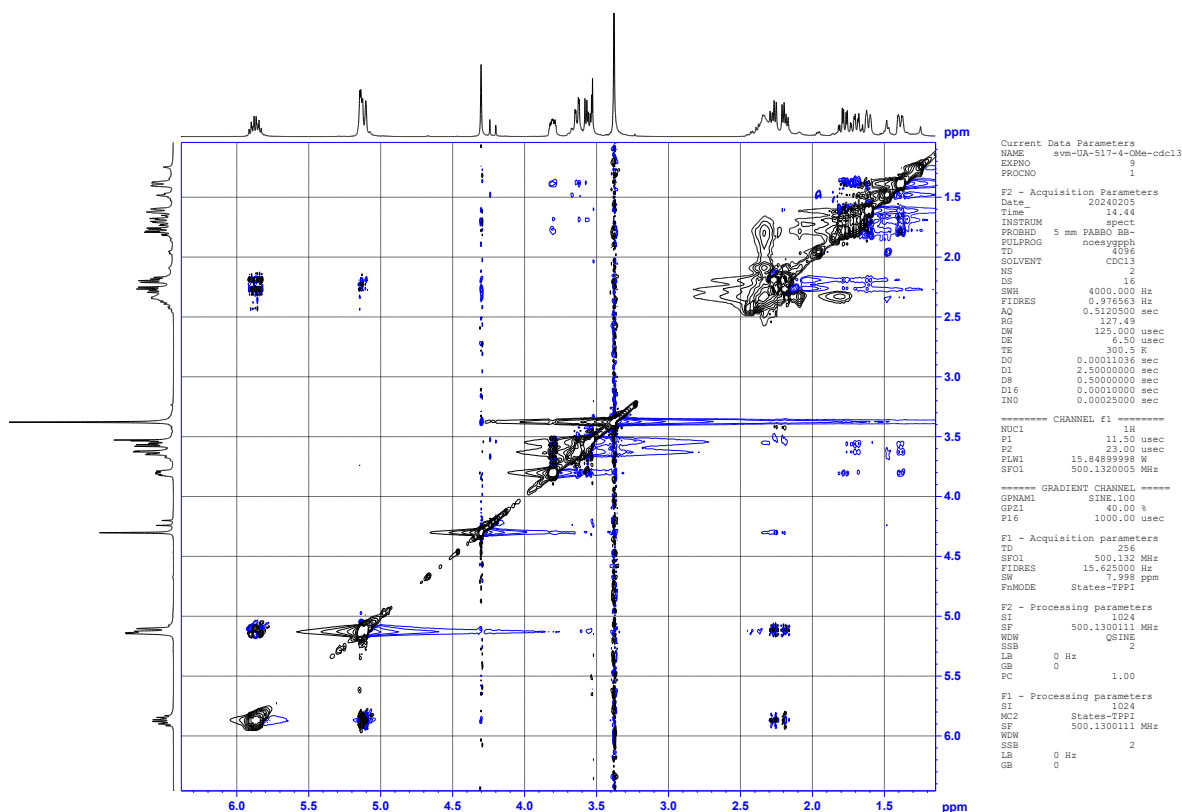
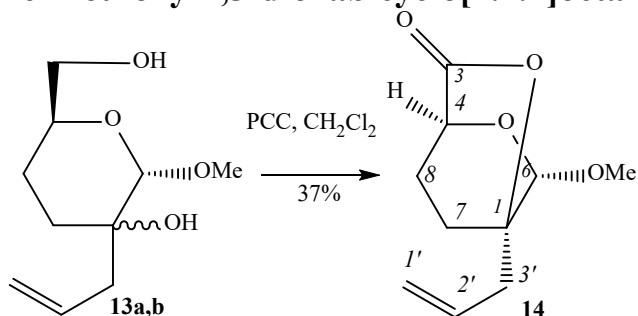


Fig. S13a.6. Complete $\{^1\text{H}, ^1\text{H}\}$ NOESY NMR spectrum in CDCl_3

(4*S*,6*S*)-1-Allyl-6-methoxy-2,5-dioxabicyclo[2.2.2]octan-3-one (14).



A solution of compounds **13a,b** 0.115 g (0.0007 mol) in 5.0 ml CH_2Cl_2 was thoroughly stirred and treated by adding small portions of 0.291 g (0.0014 mol) PCC. After 3 h (control by TLC), the reaction mixture was treated with 5.0 ml Et_2O , the precipitate was removed by filtration through a SiO_2 layer on a Schott sintered glass filter, the filtrate was evaporated, and the residue was separated by chromatography. Yield 0.050 g (37%). Oil. $[\alpha]_D^{25} = +99.6^\circ$ (c 1.0, CHCl_3). R_f 0.56 (petroleum ether– EtOAc , 3:1). ^1H NMR (CDCl_3), δ : 1.63–1.70 (m, 1H, $\text{C}^{\text{B}}\text{H}_2$); 1.79–1.85 (m, 1H, $\text{C}^{\text{B}}\text{H}_2$); 2.05 (dt, 1H, $^2J_{7\text{A},7\text{B}}$ 11.1, $^3J_{7\text{A},8\text{B}}$ 11.1, $^3J_{7\text{A},8\text{A}}$ 2.5, C^7H_2); 2.19–2.26 (m, 1H, C^8H_2); 2.40–2.44 (m, 2H, $\text{C}^{1'\text{A}}\text{H}_2$, $\text{C}^{1'\text{B}}\text{H}_2$); 3.45 (s, 3H, OMe); 4.26 (dd, 1H, $^3J_{4,8\text{B}}$ 2.6, $^3J_{4,8\text{A}}$ 2.6, C^4H); 4.67 (s, 1H, C^6H); 5.09–5.16 (m, 2H, $\text{C}^{3'\text{A}}\text{H}_2$, $\text{C}^{3'\text{B}}\text{H}_2$); 5.78–5.86 (m, 1H, C^2H). ^{13}C NMR (CDCl_3), δ : 22.84 (C^8), 23.54 (C^7), 38.71 ($\text{C}^{1'}$), 56.10 (OMe), 68.96 (C^4), 82.26 (C^1), 100.25 (C^6), 119.59 (C^3), 130.86 (C^2), 171.25 ($\text{C}=\text{O}$).

Mass spectrum, m/z : 199.1 $[MH]^+$. Calcd for $C_{10}H_{14}O_4$. 198.2.

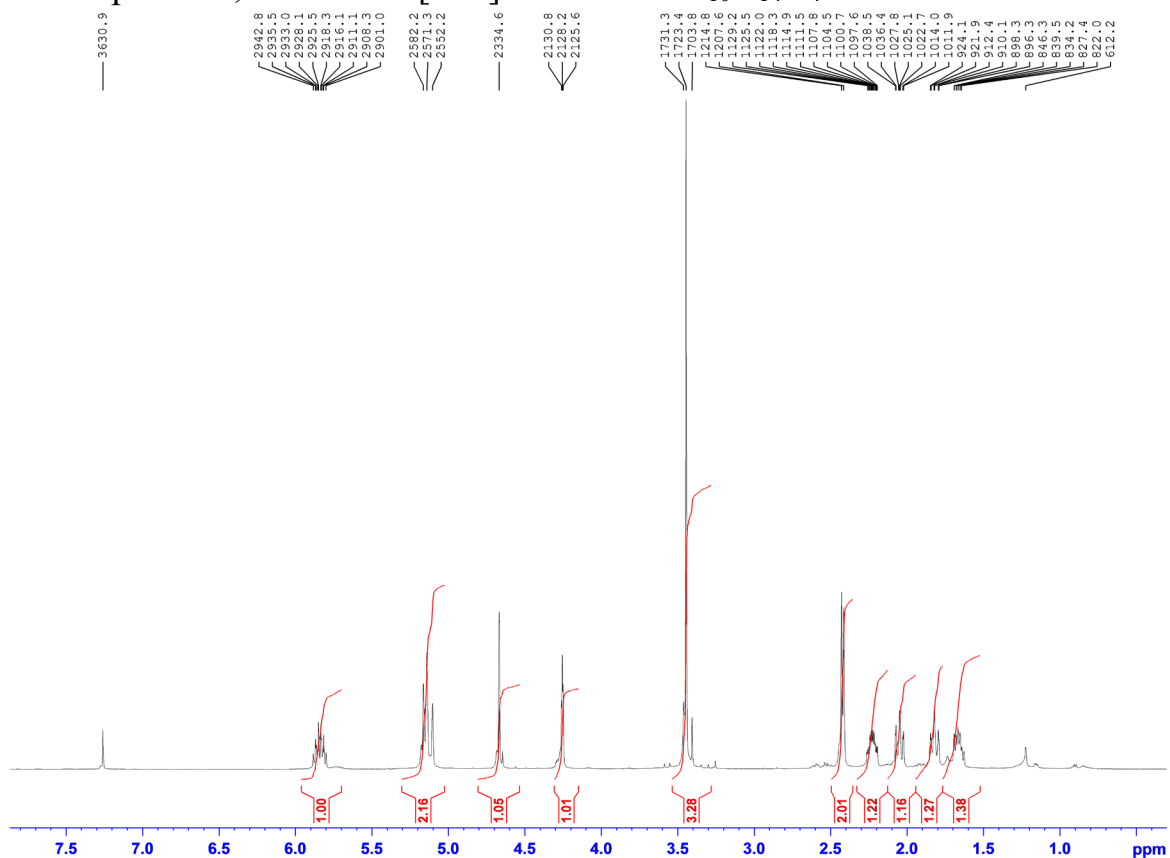


Fig. S14.1. Complete 1H NMR (500 MHz) spectrum in $CDCl_3$

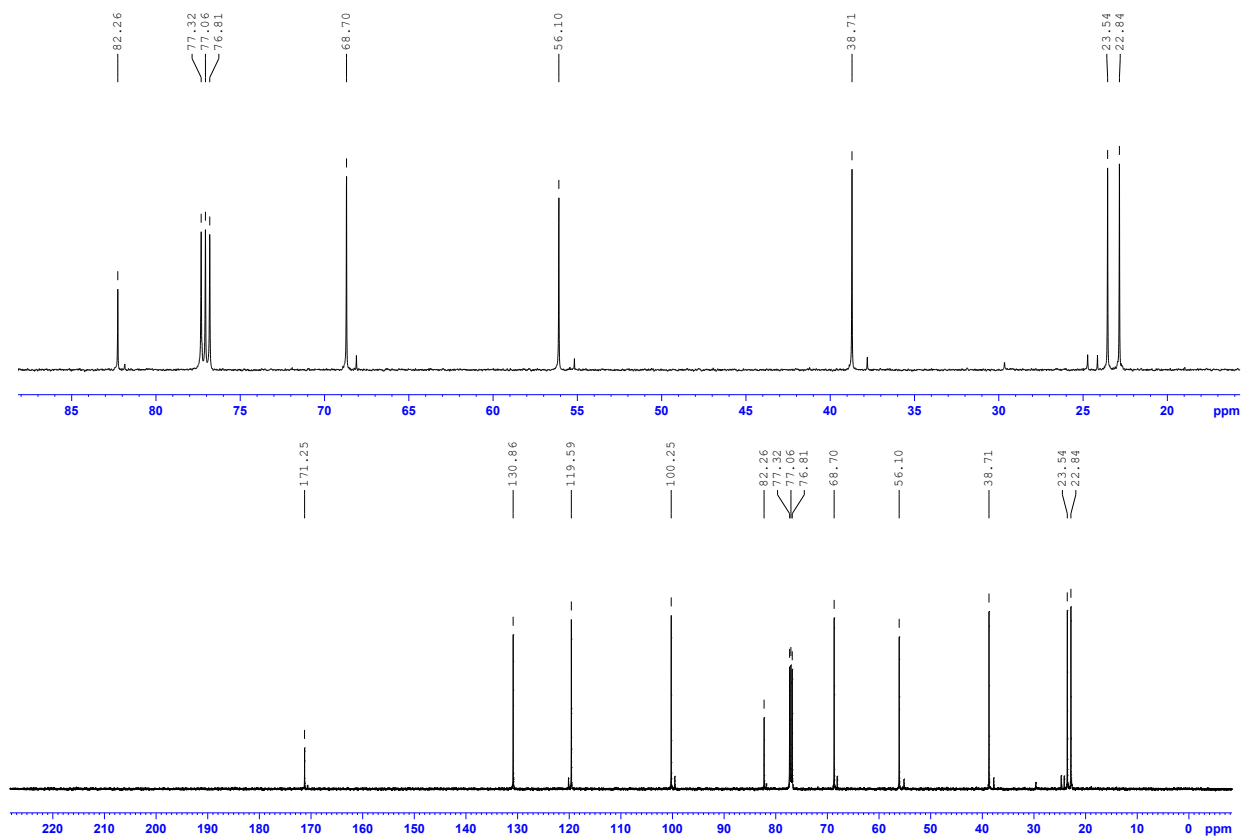


Fig. S14.2. Complete $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$

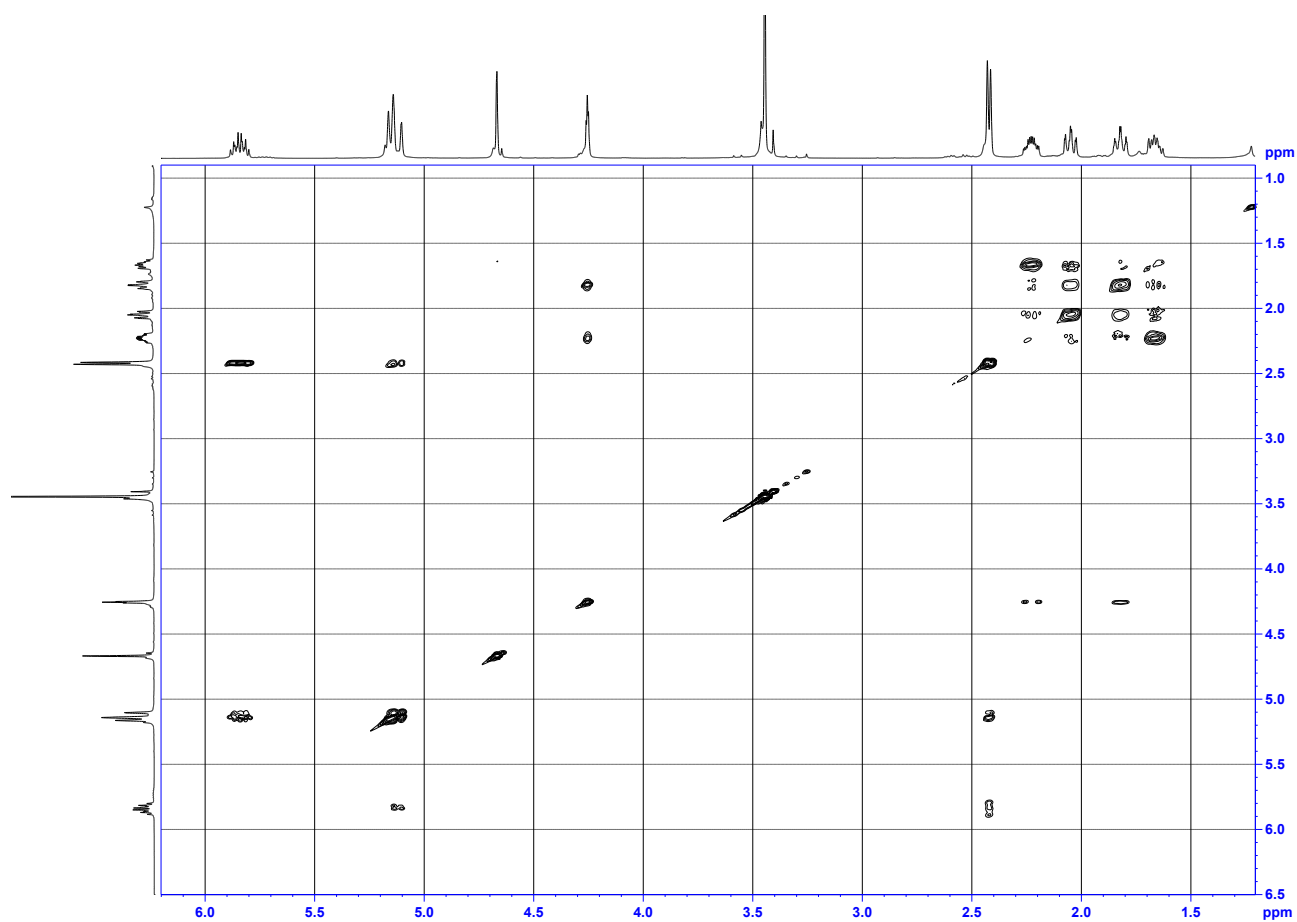


Fig. S14.3. Complete $\{^1\text{H}, ^1\text{H}\}$ COSY NMR spectrum in CDCl_3

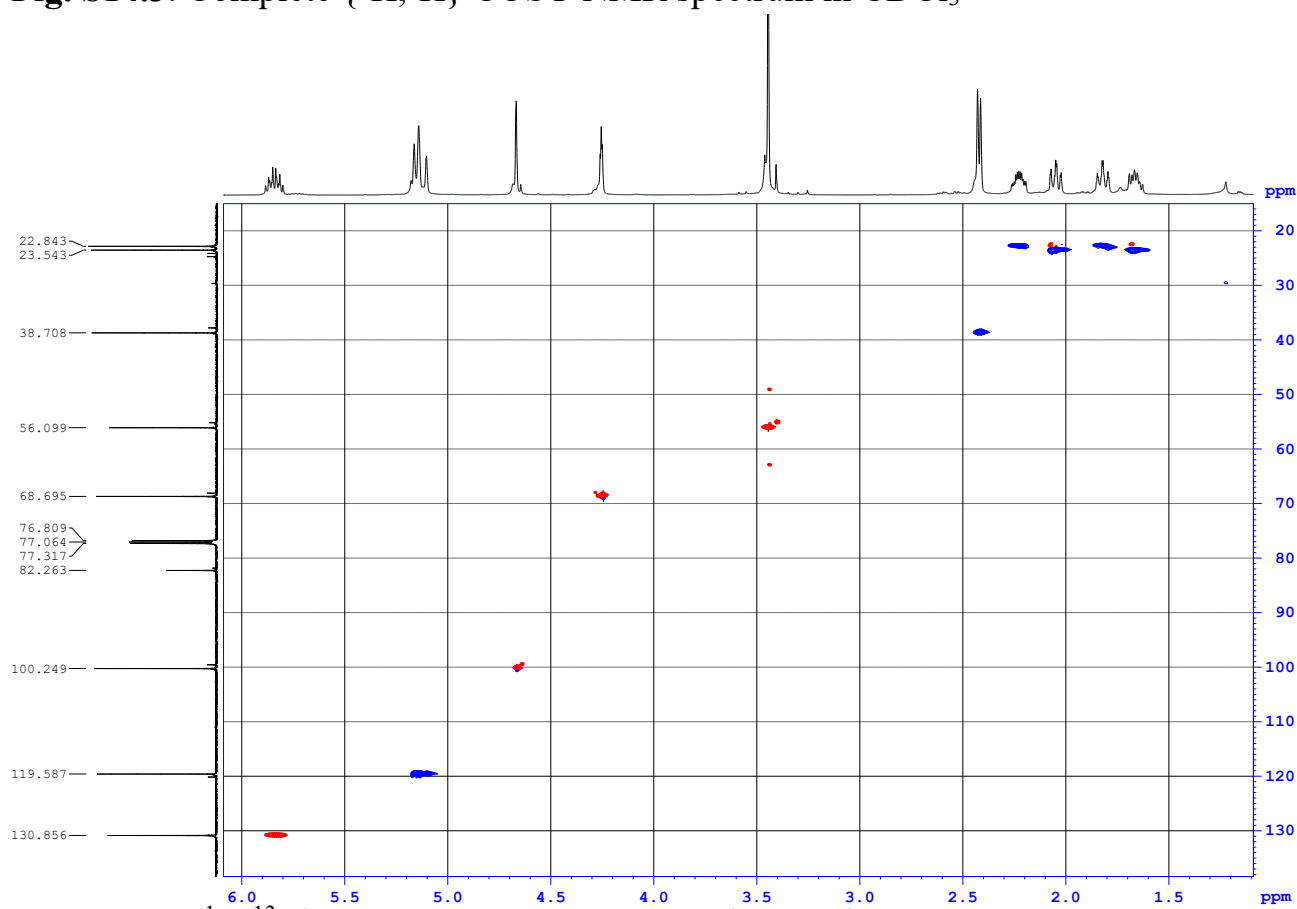


Fig. S14.4. $\{^1\text{H}, ^{13}\text{C}\}$ HSQCED NMR spectrum in CDCl_3

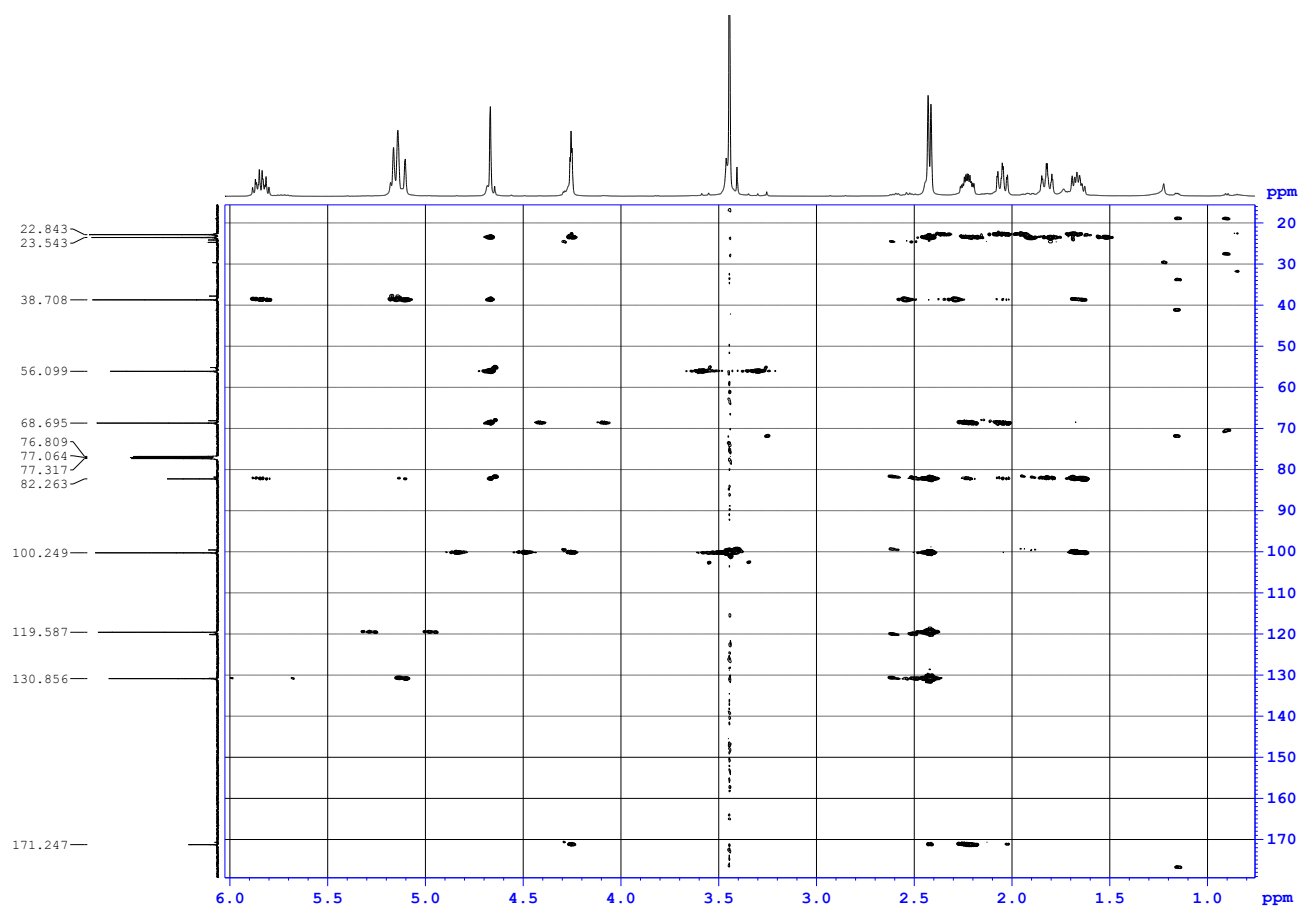


Fig. S14.5. $\{^1\text{H}, ^{13}\text{C}\}$ HMBC NMR spectrum in CDCl_3

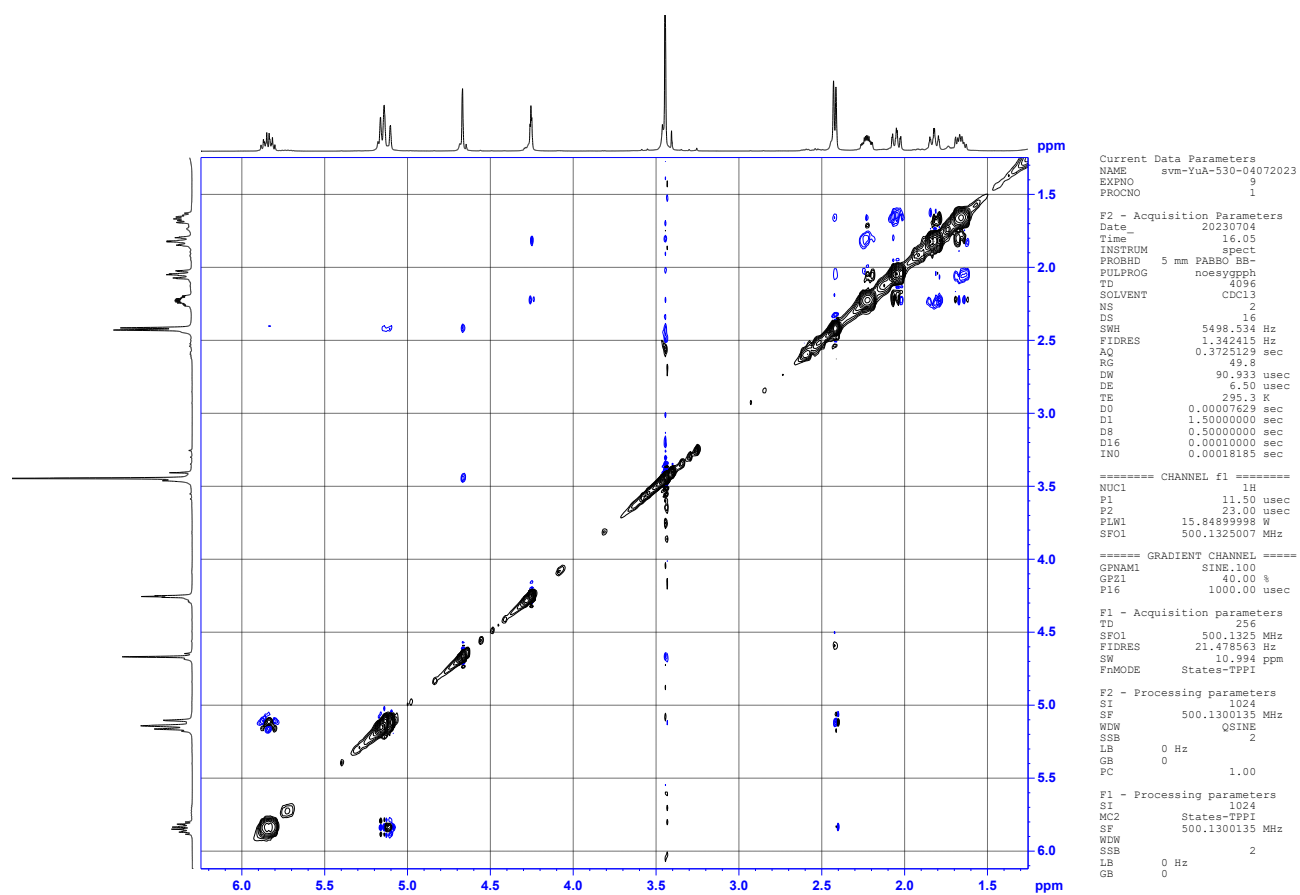


Fig. S14.6. Complete $\{^1\text{H}, ^1\text{H}\}$ NOESY NMR spectrum in CDCl_3