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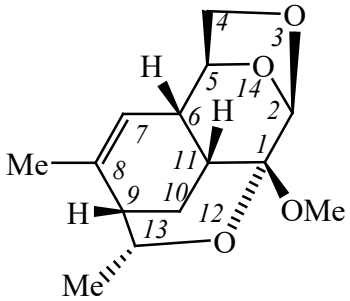
Diels–Alder adduct of levoglucosenone and isoprene in the syntheses of the key synthon for loganin

Liliya Kh. Faizullina, Yuliya A. Khalilova, Marsel G. Yalalov, Artur R. Tagirov, Shamil M. Salikhov, El'za M. Minnibaeva 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. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance III, (500.13 MHz for ^{1}H 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. 8,13-Dimethyl-3,12,14-trioxatetracyclo[7.2.2.1^{2,5}.0^{6,11}]tetradec-7-en-1-ol (**3**) was obtained as reproted[S1].

(1*R*,2*R*,5*S*,6*S*,9*S*,11*R*,13*R*)-1-Methoxy-8,13-dimethyl-3,12,14-trioxatetracyclo[7.2.2.1^{2,5}.0^{6,11}]tetradec-7-ene (4)



A solution of compound **3** (0.5 g, 2.10 mmol) in methanol (10.0 ml) was cooled to 0 °C and treated by the addition of 5% HCl solution in methanol (5.0 ml). The reaction mixture was stirred for 2 h at room temperature (control by TLC). The mixture was then neutralized with aqueous $NaHCO_3$ solution (pH 6), and the reaction products were extracted with EtOAc (3×20.0 ml). The extract was dried over anhydrous $MgSO_4$, the solvent was removed by distillation and the residue was chromatographed on SiO_2, eluent petroleum ether–EtOAc, 1:1. Yield 0.49 g (93%). White crystals, m.p. 82-83 °C, $[\alpha]_D^{20}$ -37.5° (*c* 1.0, $CHCl_3$). R_f 0.30 (petroleum ether–EtOAc, 1:1). ^{1}H NMR ($CDCl_3$), δ: 1.21 (d, 3H, $^{3}J_{14,13}$ 6.7 Hz, H^{14}), 1.51 (dt, 1H, $^{2}J_{10B,10A}$ 12.3, $^{3}J_{10B,9}$ 3.1, $^{3}J_{10B,11}$ 3.1 Hz, H^{10B}), 1.83 (s, 3H, CH_3), 1.93-1.95 (m, 1H,

H^{9}), 2.00-2.03 (m, 1H, H^{11}), 2.15 (dt, 1H, $^{2}J_{10A,10B}$ 12.3, $^{3}J_{10A,9}$ 3.1, $^{3}J_{10A,11}$ 3.1 Hz, H^{10A}), 2.24-2.27 (m, 1H, H^{6}), 3.30 (s, 3H, OCH_3), 3.83 (dd, 1H, $^{2}J_{4B,4A}$ 7.0, $^{3}J_{4B,5}$ 5.0 Hz, H^{4B}), 3.85-3.89 (m, 1H, H^{13}), 3.91 (d, 1H, $^{2}J_{4A,4B}$ 7.0 Hz, H^{4A}), 4.47 (d, 1H, $^{3}J_{5,4B}$ 5.0 Hz, H^{5}), 5.26 (s, 1H, H^{2}), 5.53 (s, 1H, H^{7}). ^{13}C NMR ($CDCl_3$), δ: 20.27 (CH_3), 25.52 (CH_3), 28.14 (C^{10}), 28.56 (C^{11}), 38.93 (C^{9}), 41.46 (C^{6}), 47.88 (OCH_3), 68.16 (C^{4}), 69.43 (C^{13}), 75.85 (C^{5}), 95.95 (C^{1}), 98.75 (C^{2}), 124.88 (C^{7}), 136.14 (C^{8}). Mass spectrum, *m/z*: 253 $[M+H]^+$, Calcd for $C_{14}H_{20}O_4$. 252.31.

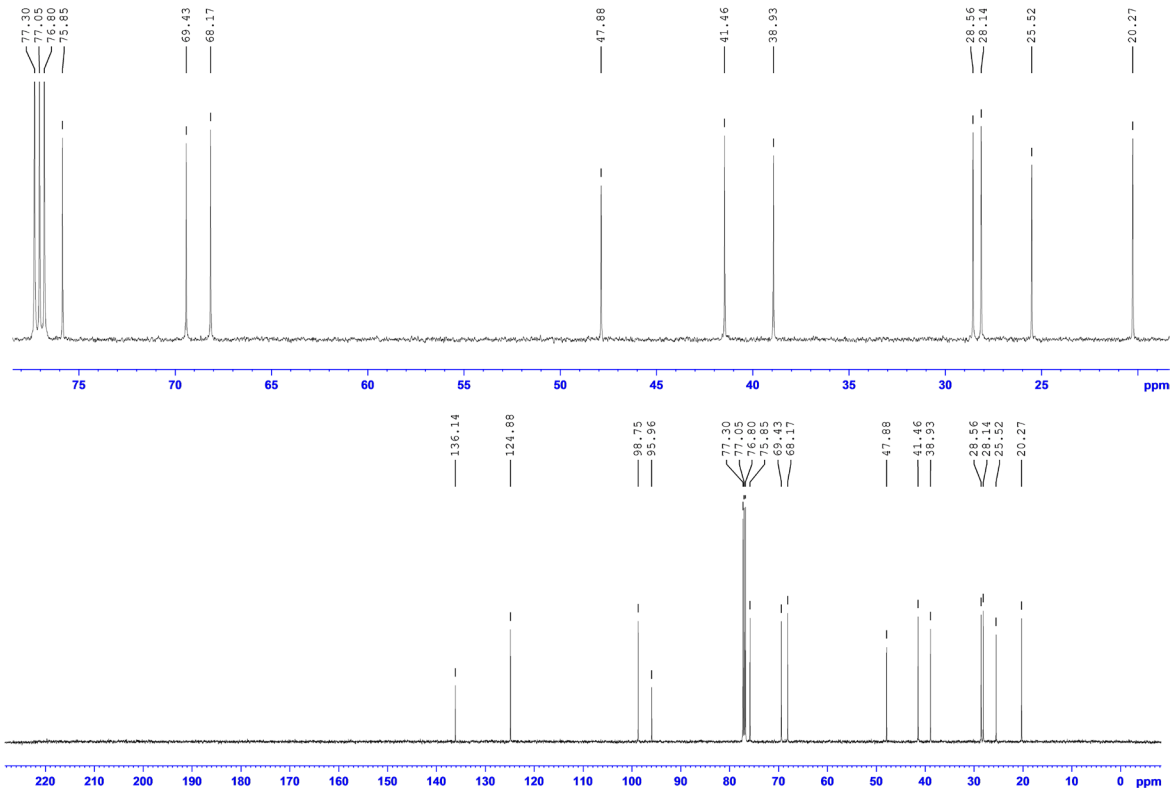


Fig. S4.1. Complete $^{13}C\{^{1}H\}$ NMR spectrum of compound **4** in $CDCl_3$

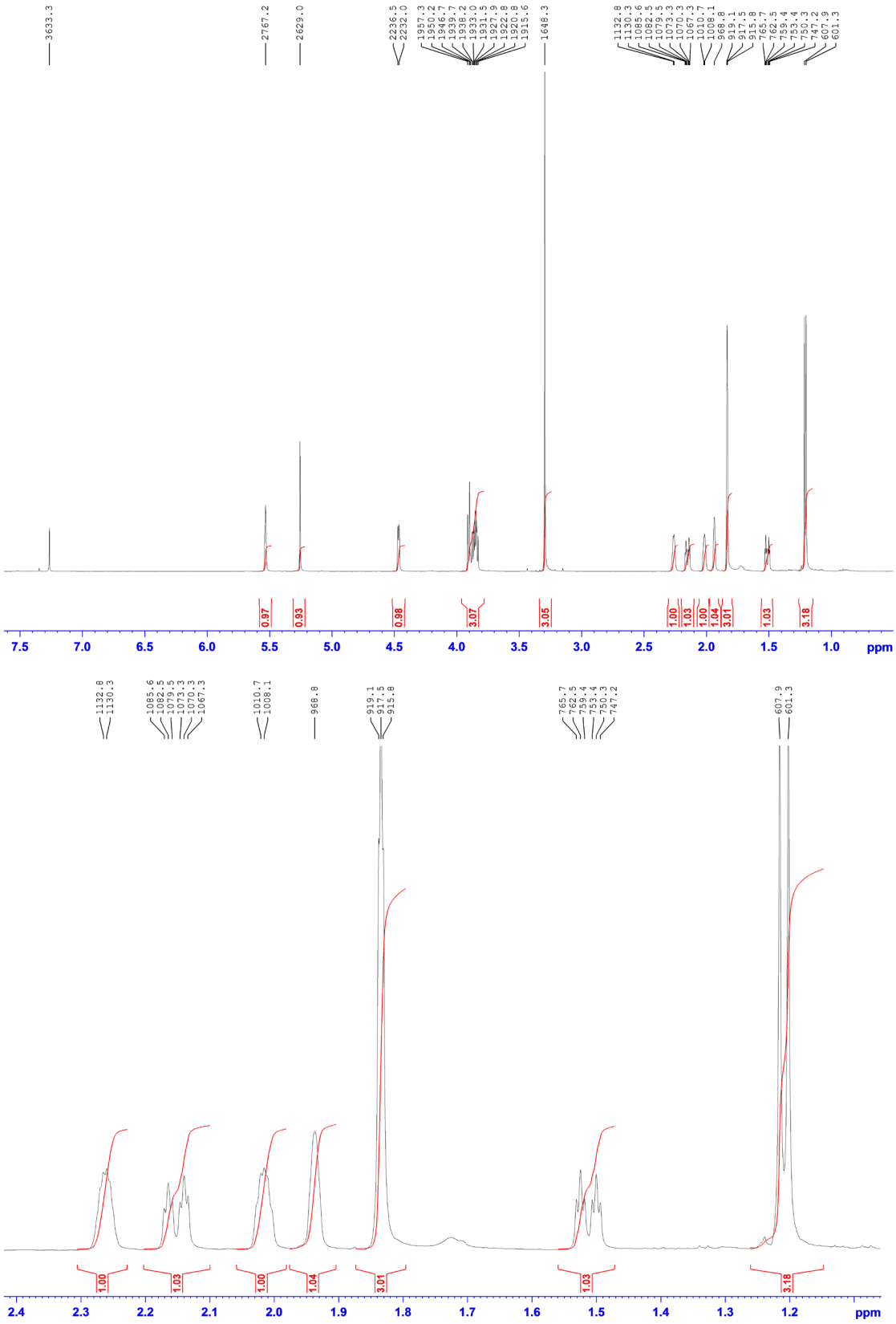


Fig. S4.2. Complete ^{1}H NMR (500 MHz) spectrum of compound **4** in $CDCl_3$

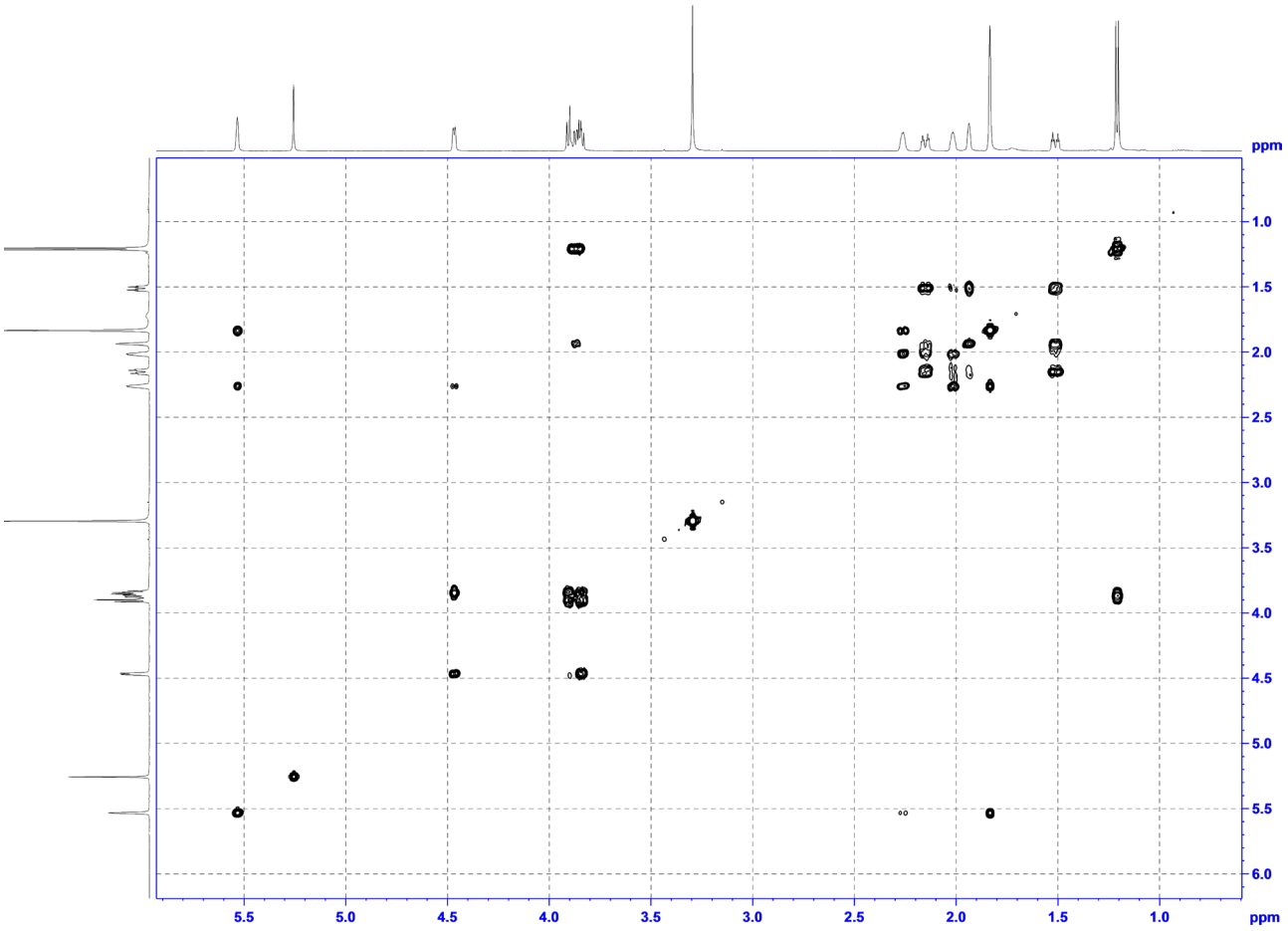


Fig. S4.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of compound **4** in $CDCl_3$

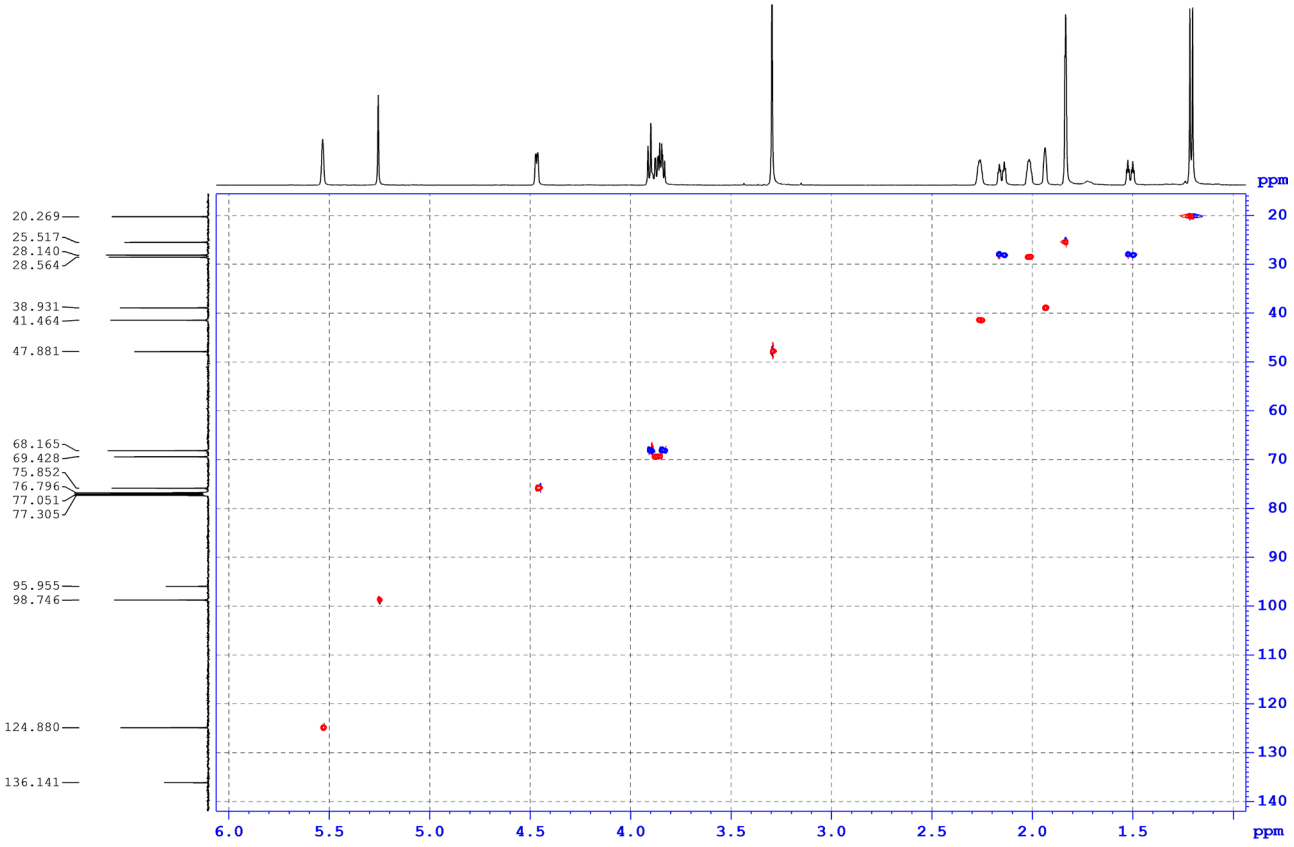


Fig. S4.4. Complete {^{1}H,^{13}C} HSQCED NMR spectrum of compound **4** in $CDCl_3$

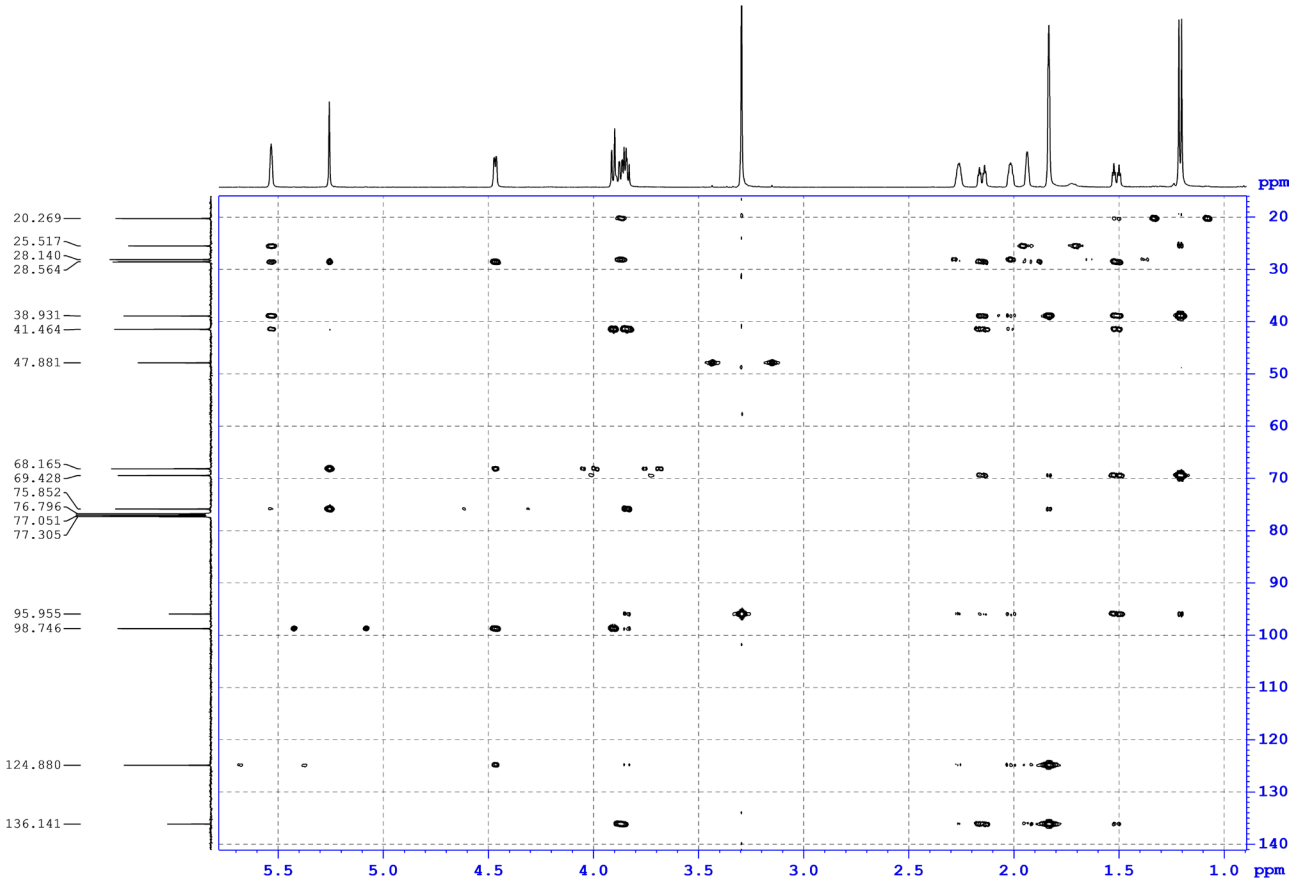


Fig. S4.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum of compound **4** in $CDCl_3$

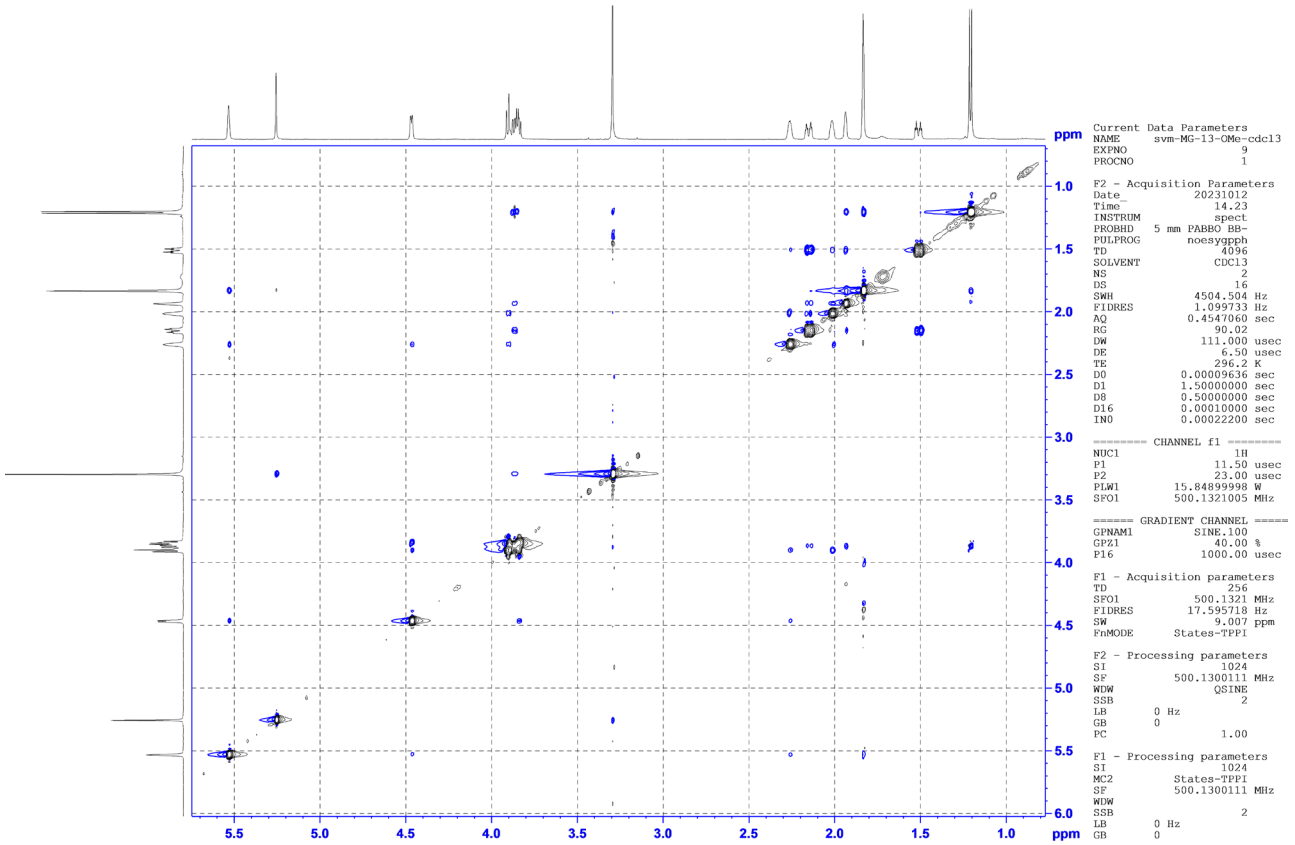
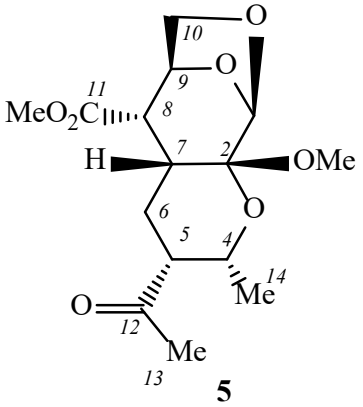
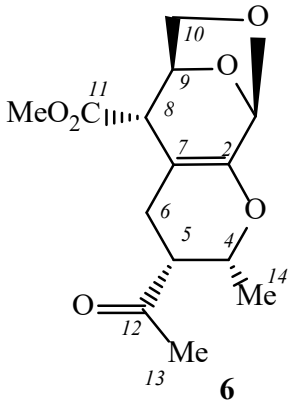


Fig. S4.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of compound **4** in $CDCl_3$

Methyl (1*R*,2*R*,4*R*,5*R*,7*R*,8*S*,9*S*)-5-acetyl-2-methoxy-4-methyl-3,11,12-trioxatricyclo[7.2.1.0^{2,7}]dodecane-8-carboxylate (5) and methyl (1*R*,4*R*,5*R*,8*S*,9*S*)-5-acetyl-4-methyl-3,11,12-trioxatricyclo[7.2.1.0^{2,7}]dodec-2(7)-ene-8-carboxylate (6)



5



6

a) Ozone-oxygen mixture was passed through a solution of 0.19 g (0.80 mmol) of compound **4** in 3.0 ml of absolute CH_2Cl_2 at -50 °C. At the end of the reaction (~15 min, monitored by TLC), an excess of ozone was removed by flushing with argon, and 2.0 ml of Me_2S was added at -78 °C, through ~15 min the temperature of the reaction mixture was brought to ambient. The solvent was distilled off. To a solution of the crude reaction mass in 5.0 ml of acetone was added at 0 °C dropwise of Jones reagent (CrO_3 0.15 g, H_2SO_4 0.05 g, H_2O 1.1 g) until the reaction mixture turns red-brown and stirred for 10 minutes. Then, isopropyl alcohol was added dropwise to the reaction mass until green color appears; then the reaction mass was treated by ether solution of CH_2N_2 (excess) (control by TLC). The reaction was then stirred for 10 minutes and the reaction products were extracted with Et_2O (3×5.0 ml). The extract was dried over anhydrous $MgSO_4$, the solvent was removed by distillation and the residue was chromatographed on SiO_2 eluente petroleum ether–EtOAc, 2:1. Yield 0.050 g (21%) of ester **5** and 0.080 g (38%) compound **6**.

b) Ozone-oxygen mixture was passed through a solution of 0.50 g (2.00 mmol) of compound **4** in 8.0 ml of absolute CH_2Cl_2 at -50 °C. At the end of the reaction (~15 min, monitored by TLC), an excess of ozone was removed by flushing with argon, and 5.0 ml of Me_2S was added at -78 °C, through ~15 min the temperature of the reaction mixture was brought to ambient. The solvent was distilled off. To a solution of the crude reaction mass in 10.0 ml of acetone was added at 0 °C dropwise Jones reagent (CrO_3 0.35 g, H_2SO_4 0.125 g, H_2O 2.5 g) (monitored by TLC) and stirred for 10 minutes the color of the reaction mass remained green; then the reaction mass was treated with ether solution of CH_2N_2 (excess) (control by TLC). The reaction mass was stirred for 10 minutes and the reaction products were extracted with Et_2O (3×10.0 ml).

The extract was dried over anhydrous $MgSO_4$, the solvent was removed by distillation and the residue was chromatographed on SiO_2, eluente petroleum ether–EtOAc, 2:1. Yield 0.220 g (35%) of ester **5** and 0.145 g (26%) compound **6**.

Ester **5**: White crystals, m.p. 87 °C, $[\alpha]_D^{25}$ −77.3° (*c* 1.0, $CHCl_3$). R_f 0.30 (petroleum ether–EtOAc, 2:1). ^{1}H NMR ($CDCl_3$), δ: 1.19 (d, 3H, $^3J_{14,4}$ 7.0 Hz, H^{14}), 1.44 (ddd, 1H, $^2J_{6A,6B}$ 10.3, $^3J_{6A,5}$ 7.0, $^3J_{6A,7}$ 4.1 Hz, H^{6A}), 1.97 (dt, 1H, $^2J_{6B,6A}$ 10.3, $^3J_{6B,7}$ 13.5, $^3J_{6B,5}$ 10.3 Hz, H^{6B}), 2.12 (ddd, 1H, $^3J_{7,6B}$ 13.5, $^3J_{7,8}$ 6.5, $^3J_{7,8A}$ 4.1 Hz, H^7), 2.19 (s, 3H, CH_3), 2.69 (dt, 1H, $^3J_{5,6B}$ 10.3, $^3J_{5,6A}$ 7.0, $^3J_{5,4}$ 7.0 Hz, H^5), 2.79 (dd, 1H, $^3J_{8,7}$ 6.5, $^3J_{8,9}$ 2.9 Hz, H^8), 3.34 (s, 3H, OCH_3), 3.62-3.67 (m, 2H, H^{10A}, H^{10B}), 3.73 (s, 3H, CO_2CH_3), 4.08 (pent, 1H, $^3J_{4,5}$ 7.0, $^3J_{4,14}$ 7.0 Hz, H^4), 5.10 (t, 1H, $^3J_{9,10B}$ 2.9, $^3J_{9,6}$ 2.9 Hz, H^9), 5.31 (s, 1H, H^1). ^{13}C NMR ($CDCl_3$), δ: 17.39 (CH_3), 24.47 (C^6), 28.95 (CH_3), 36.14 (C^7), 45.34 (C^8), 50.00 (OCH_3), 52.42 (CO_2CH_3), 53.48 (C^5), 63.38 (C^4), 71.09 (C^9), 71.14 (C^{10}), 100.10 (C^2), 101.74 (C^1), 172.43 (C=O), 210.68 (C=O). Mass spectrum, *m/z*: 315 $[M+H]^+$. Calcd for $C_{15}H_{22}O_7$. 314.33.

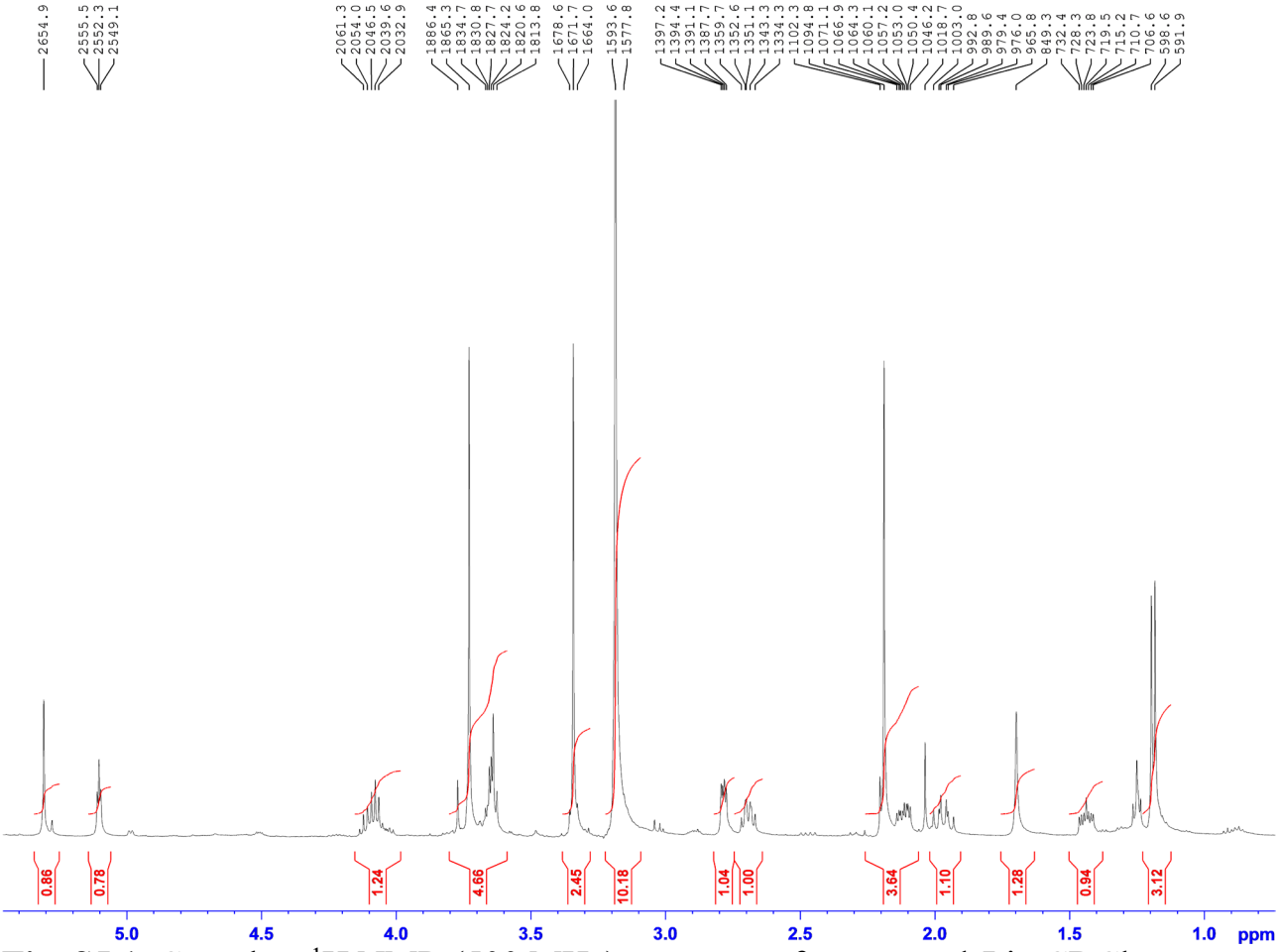


Fig. S5.1. Complete ^{1}H NMR (500 MHz) spectrum of compound **5** in $CDCl_3$

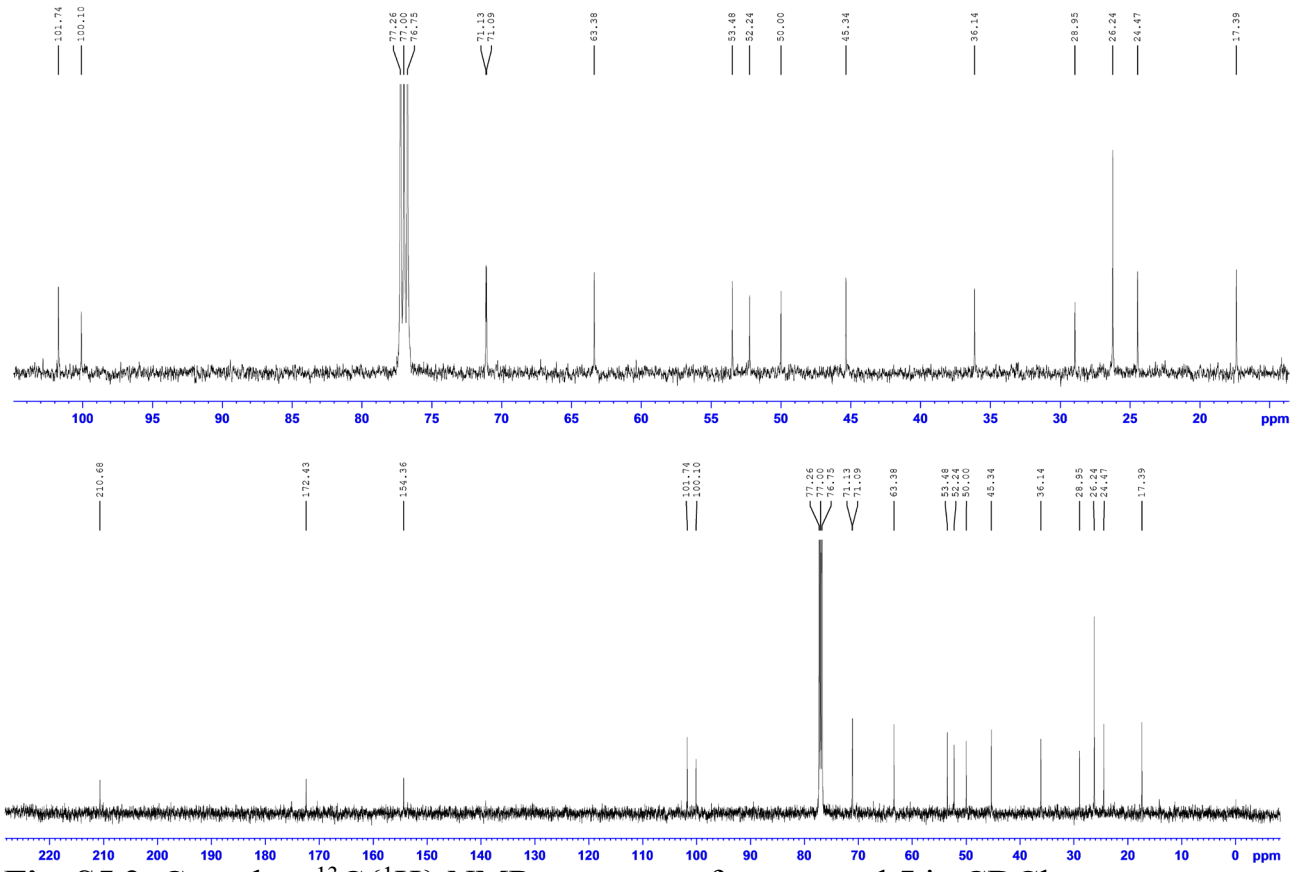


Fig. S5.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of compound **5** in $CDCl_3$

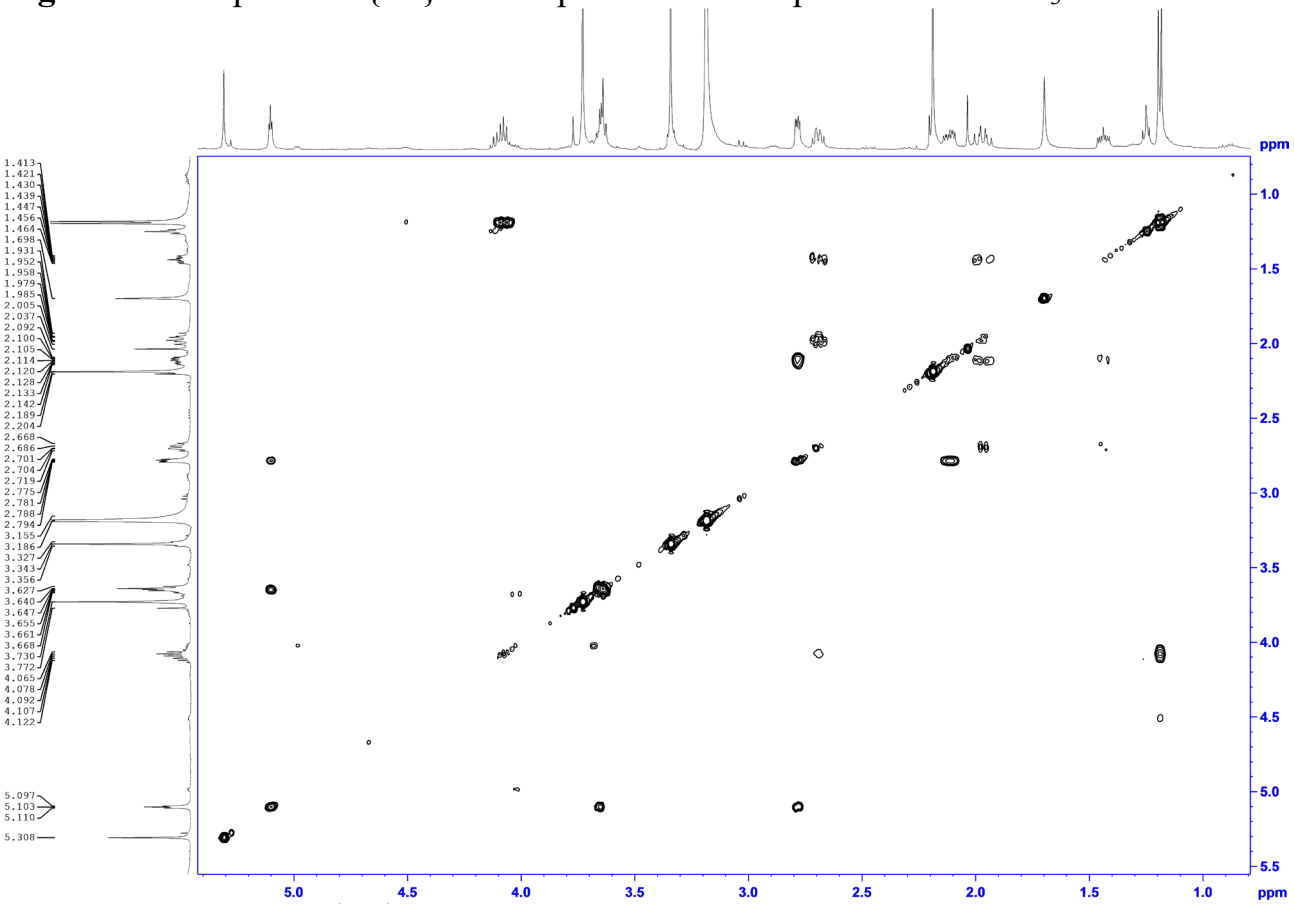


Fig. S5.3. Complete $\{^{1}H,^{1}H\}$ COSY NMR spectrum of compound **5** in $CDCl_3$

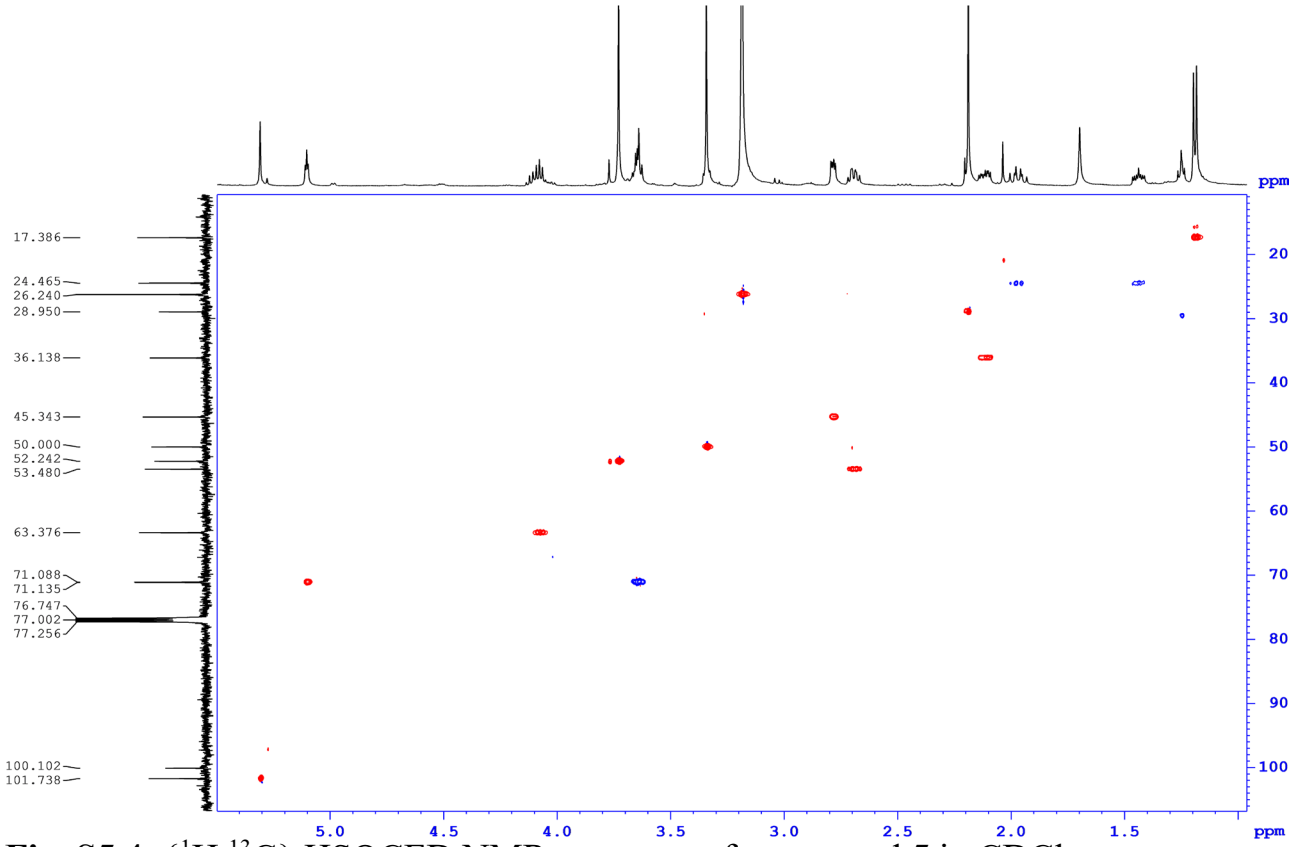


Fig. S5.4. {^{1}H,^{13}C} HSQCED NMR spectrum of compound **5** in $CDCl_3$

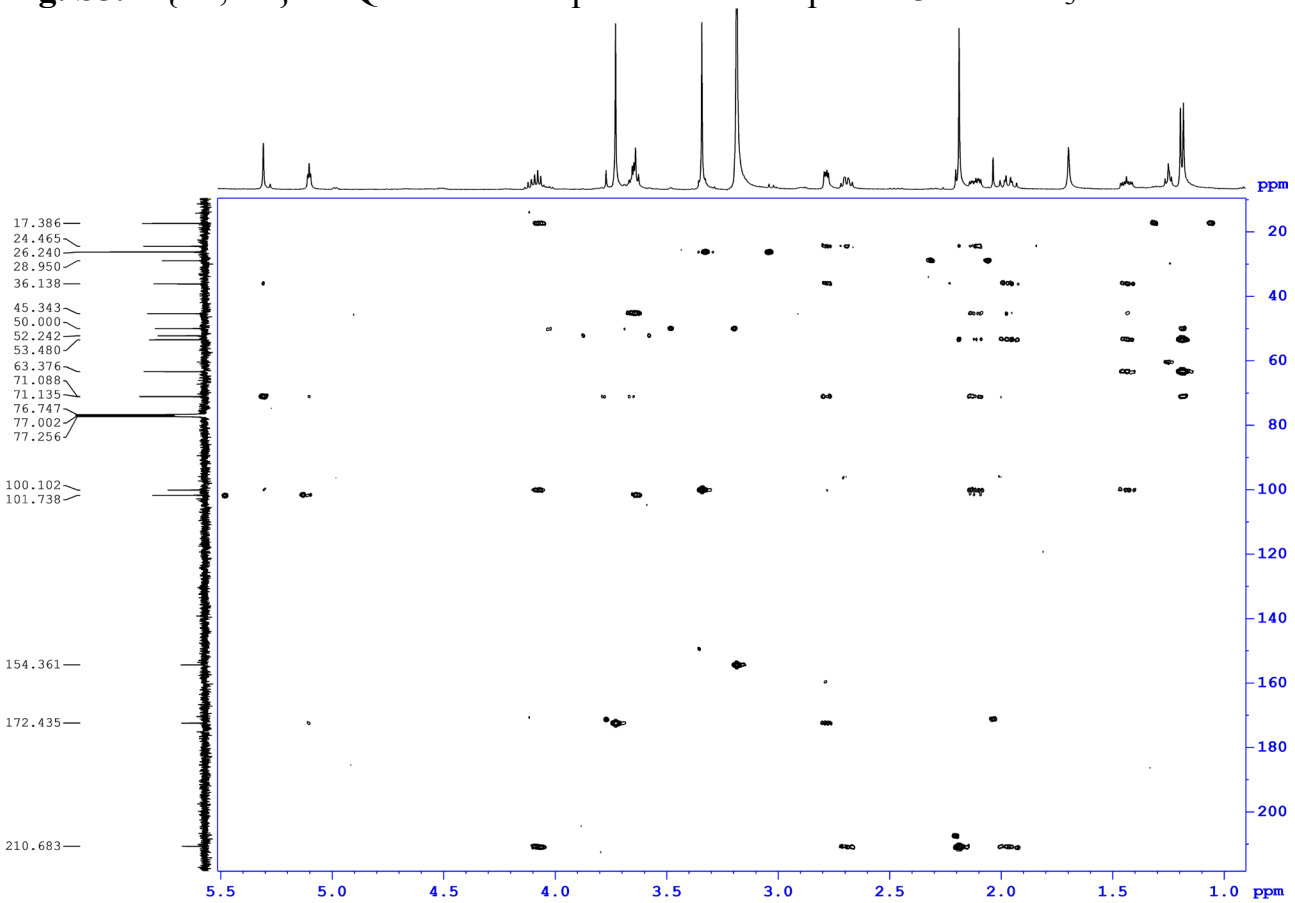


Fig. S5.5. {^{1}H,^{13}C} HMBC NMR spectrum of compound **5** in $CDCl_3$

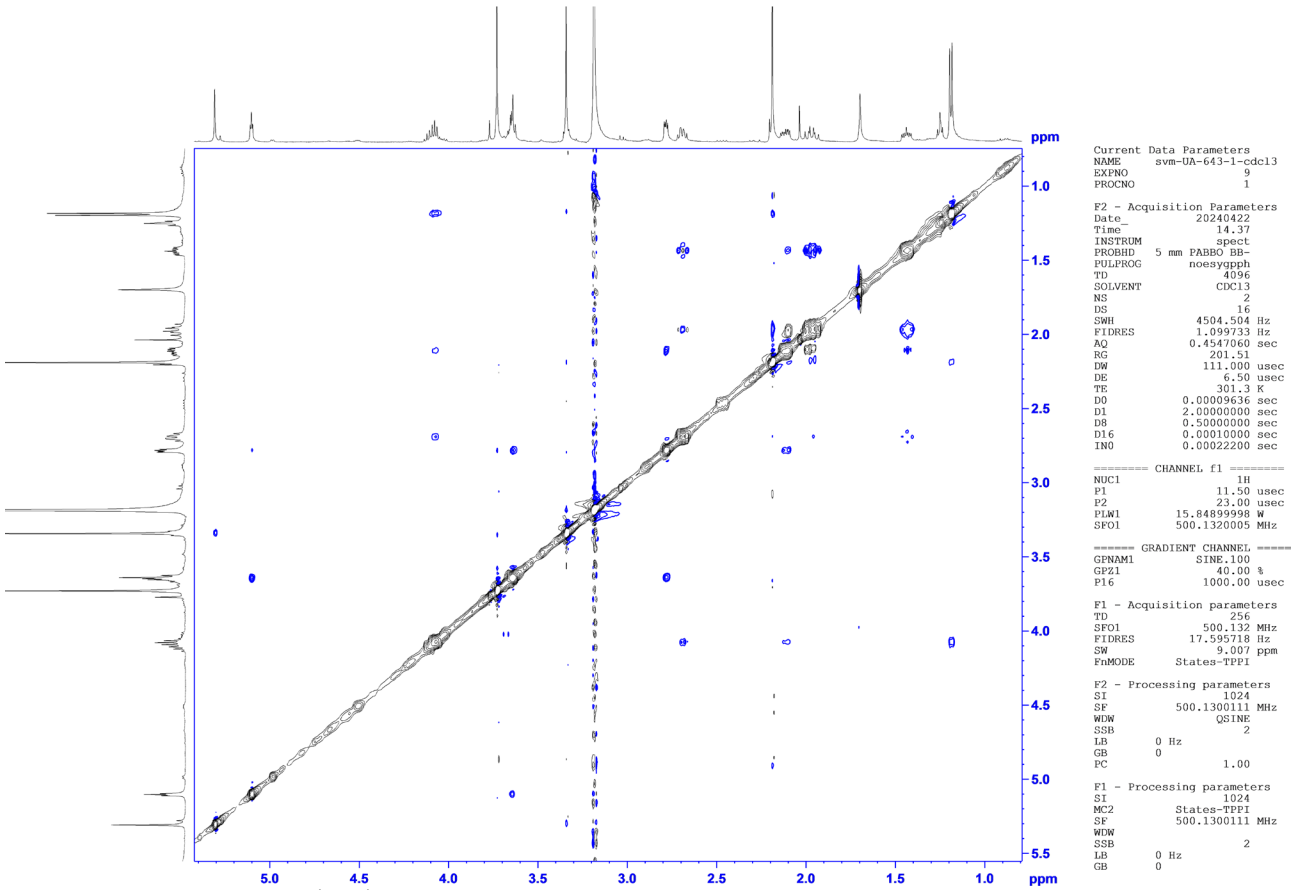


Fig. 5.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of compound **5** in $CDCl_3$

Compound **6**: Oil, $[\alpha]_D^{25}$ + 1.8° (*c* 1.0, $CHCl_3$). R_f 0.2 (petroleum ether–EtOAc, 2:1). ^{1}H NMR ($CDCl_3$), δ: 1.20 (d, 3H, $^{3}J_{14,4}$ 6.9 Hz, H^{14}), 1.99 (dd, 1H, $^{2}J_{6A,6B}$ 17.3, $^{3}J_{6A,5}$ 6.1 Hz, H^{6A}), 2.21 (s, 3H, CH_3), 2.48 (dd, 1H, $^{2}J_{6B,6A}$ 17.3, $^{3}J_{6B,5}$ 8.6 Hz, H^{6B}), 2.71 (s, 1H, H^{8}), 2.87-2.92 (m, 1H, H^{5}), 3.69 (d, 1H, $^{2}J_{10B,10A}$ 7.3 Hz, H^{10B}), 3.77 (s, 3H, CO_2CH_3), 4.03 (dd, 1H, $^{2}J_{10A,10B}$ 7.3, $^{3}J_{10A,9}$ 6.0 Hz, H^{10A}), 4.52 (pent, 1H, $^{3}J_{4,5}$ 6.9, $^{3}J_{4,14}$ 6.9 Hz, H^{4}), 4.99 (d, 1H, $^{3}J_{9,10A}$ 6.0 Hz, H^{9}), 5.28 (s, 1H, H^{1}). ^{13}C NMR ($CDCl_3$), δ: 15.69 (CH_3), 22.47 (C^{6}), 28.73 (CH_3), 50.06 (C^{5}), 50.19 (C^{8}), 52.38 (CO_2CH_3), 67.22 (C^{10}), 71.00 (C^{4}), 74.75 (C^{9}), 96.29 (C^{7}), 97.27 (C^{1}), 147.73 (C^{2}), 171.29 (C=O), 207.33 (C=O). Mass spectrum, *m/z*: 283 [*M*+H]$^{+}$, Calcd for $C_{14}H_{18}O_6$. 282.29.

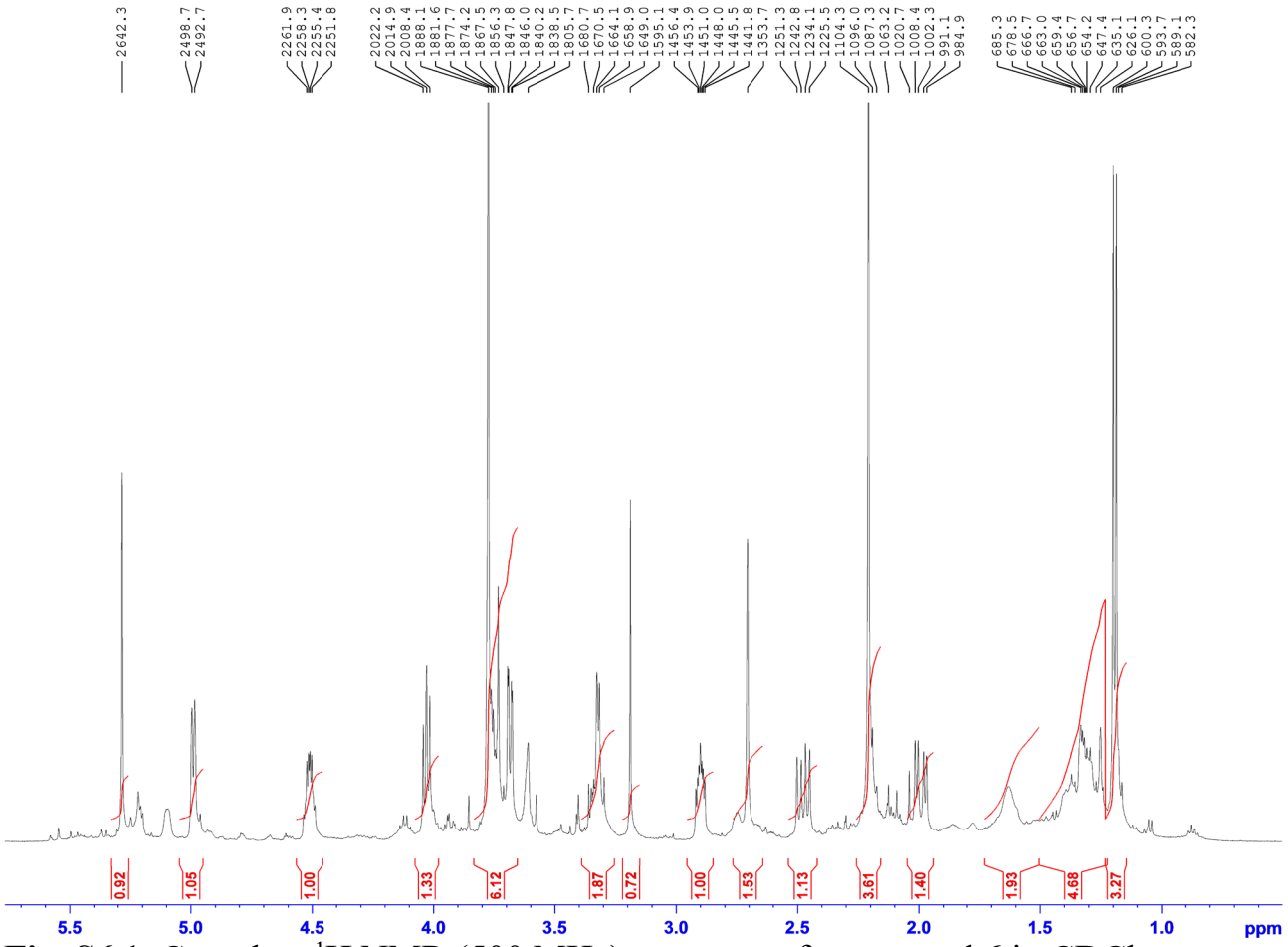


Fig. S6.1. Complete ^{1}H NMR (500 MHz) spectrum of compound **6** in $CDCl_3$

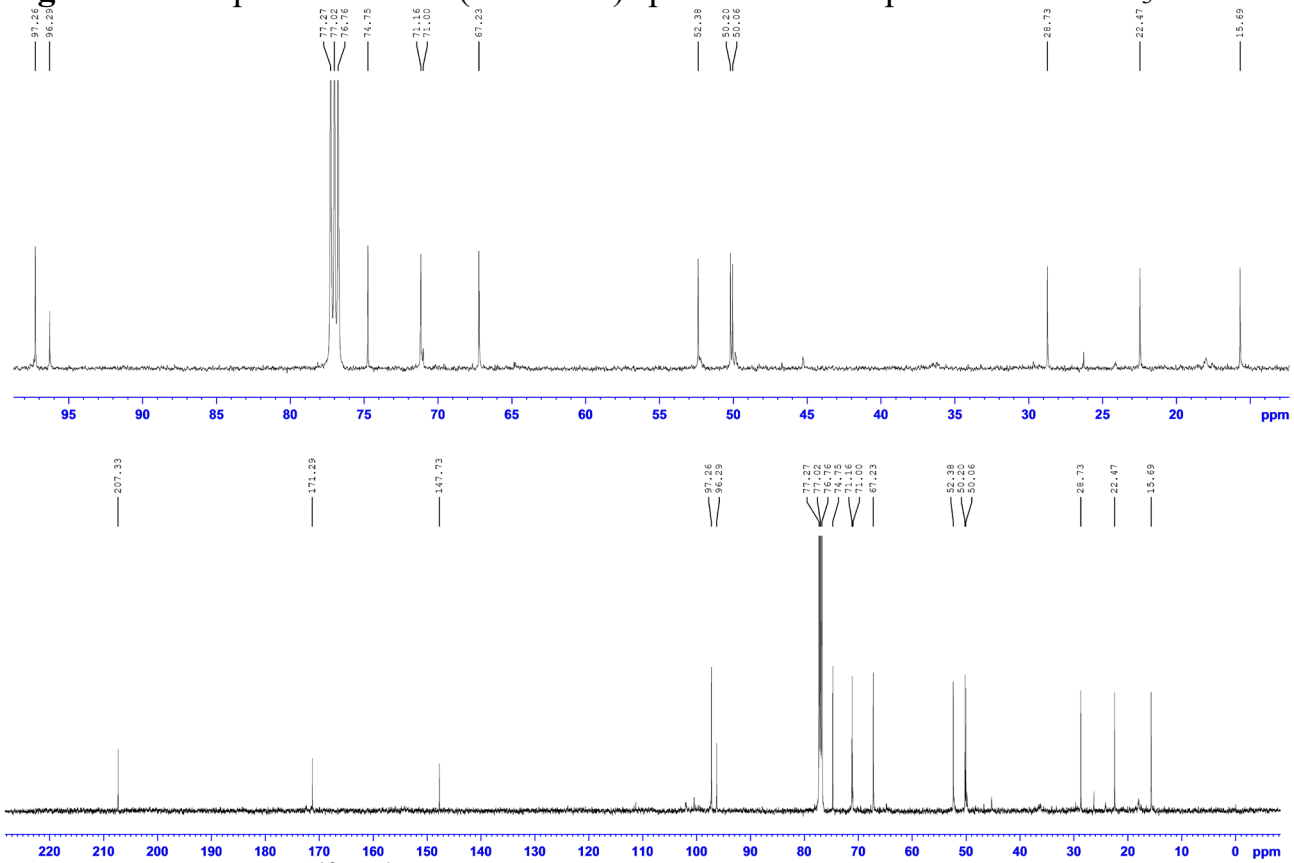


Fig. S6.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** in $CDCl_3$

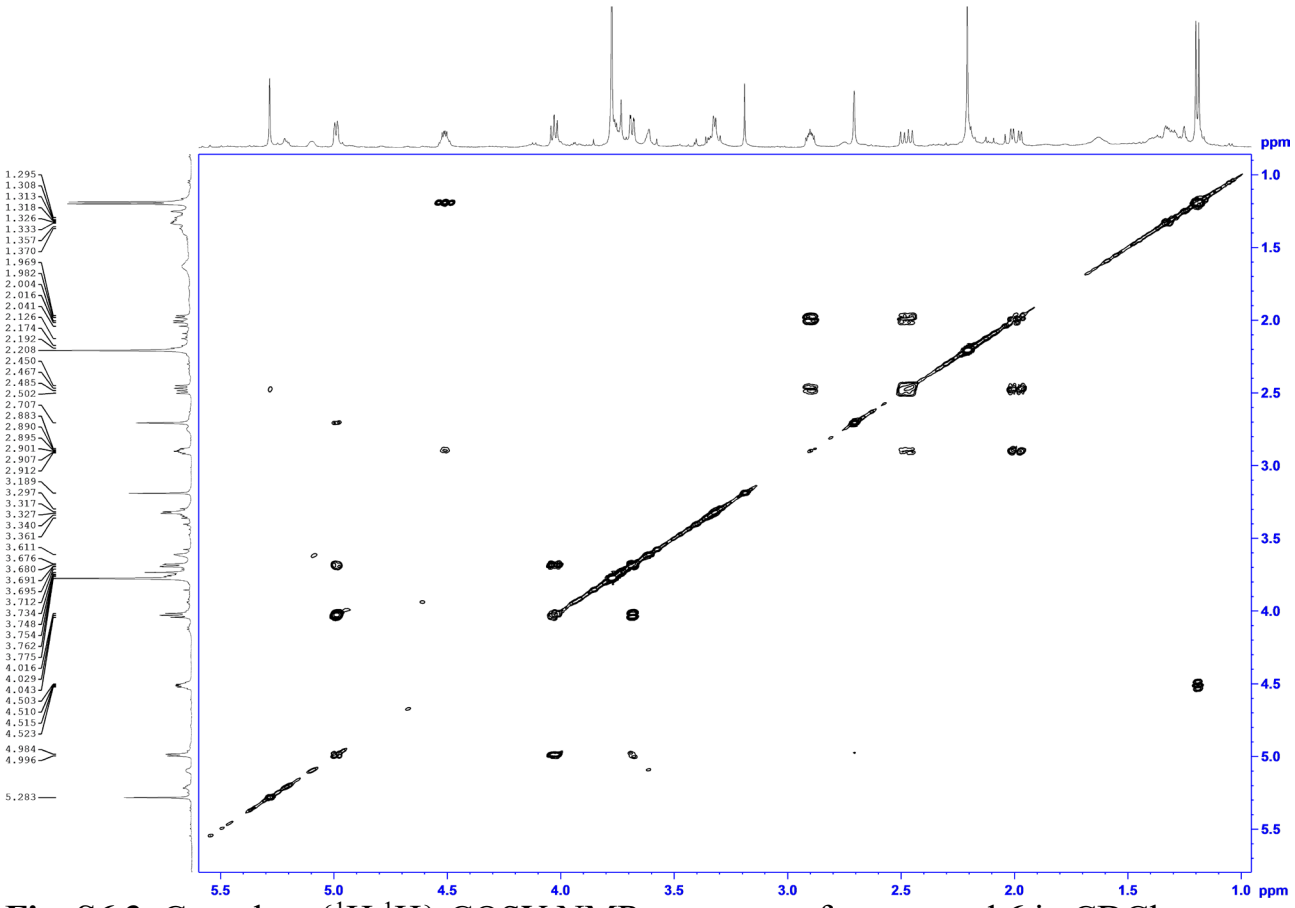


Fig. S6.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of compound **6** in $CDCl_3$

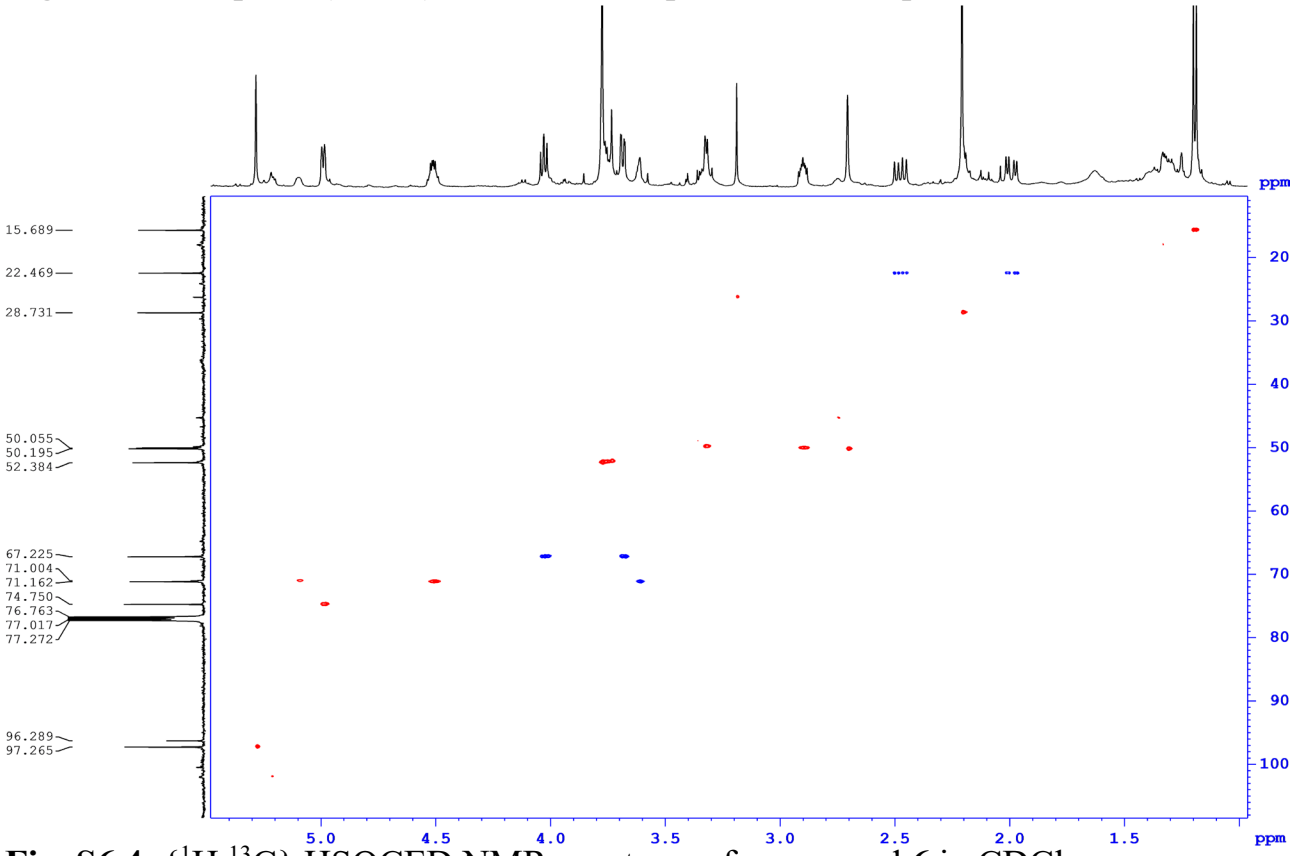


Fig. S6.4. {^{1}H,^{13}C} HSQCED NMR spectrum of compound **6** in $CDCl_3$

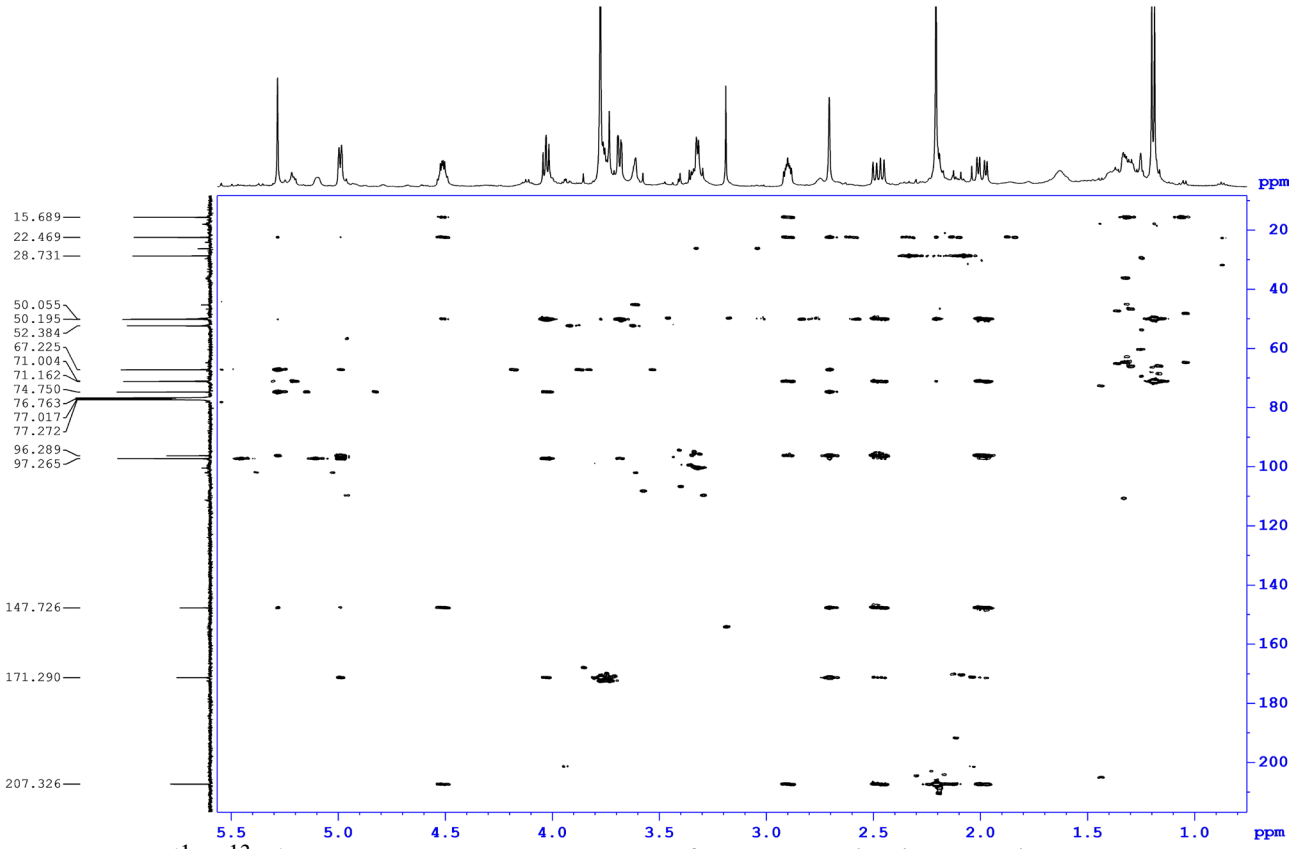


Fig. S6.5. {^{1}H,^{13}C} HMBC NMR spectrum of compound **6** in $CDCl_3$

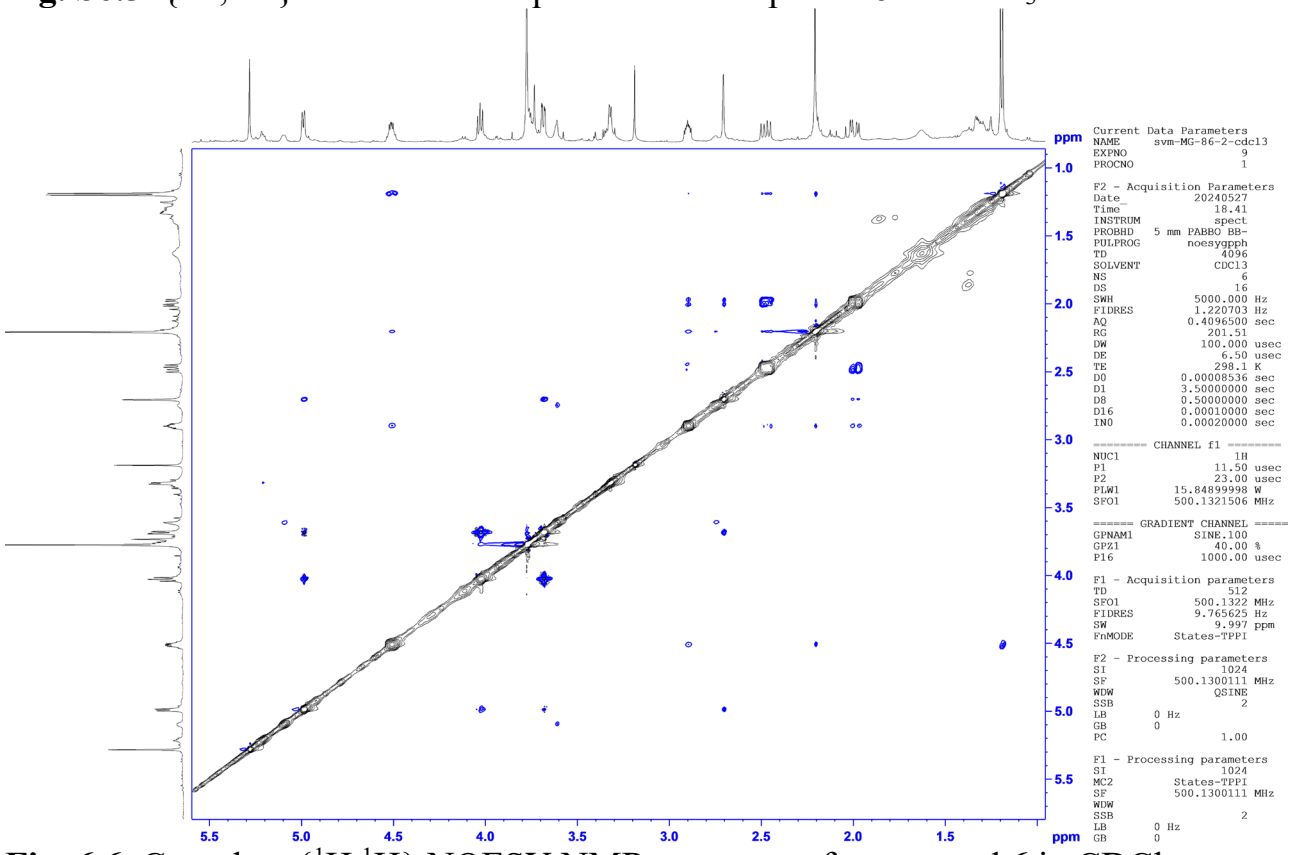
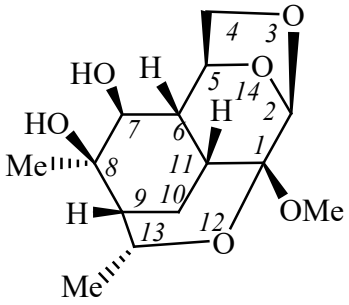


Fig. 6.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of compound **6** in $CDCl_3$

(1*R*,2*R*,5*S*,6*R*,7*S*,8*R*,9*R*,11*R*,13*R*)-1-Methoxy-8,13-dimethyl-3,12,14-trioxatetracyclo[7.2.2.1^{2,5}.0^{6,11}]tetradecane-7,8-diol (7)



A solution of 0.09 g (0.59 mmol) of potassium permanganate in 2.0 ml of water was added dropwise over a period of 15 min under vigorous stirring at 0 °C to a solution of 0.1 g (0.39 mmol) of compound **4** in 2.0 ml of ethanol, and the mixture was stirred for 30 min at room temperature until the initial compound disappeared (TLC). The precipitate of MnO_2 was filtered off and washed on a filter with ethanol (2 × 3.0 ml), the solvent was distilled off from the filtrate, and the residue was chromatographed on SiO_2 eluente petroleum ether–EtOAc, 3:1. Yield 0.11 g (98%). White crystals, m.p. 225-227 °C, $[\alpha]_D^{20}$ –50.8° (*c* 1.0, $CHCl_3$). R_f 0.43 (petroleum ether–EtOAc, 1:1). ^{1}H NMR ($CDCl_3$), δ: 1.32 (d, 3H, $^3J_{14,13}$ 7.0 Hz, H^{14}), 1.47 (s, 3H, CH_3), 1.61-1.64 (m, 1H, H^9), 1.68 (ddd, 1H, $^3J_{6,7}$ 9.3, $^3J_{6,11}$ 5.3, $^3J_{6,5}$ 1.3 Hz, H^6), 1.92 (dt, 1H, $^2J_{10B,10A}$ 13.0, $^3J_{10B,9}$ 2.7, $^3J_{10B,11}$ 2.7 Hz, H^{10B}), 2.00-2.07 (m, 1H, H^{11}), 2.17-2.25 (m, 2H, H^{10A}, OH), 3.28 (s, 3H, OCH_3), 3.84 (dd, 1H, $^2J_{4B,4A}$ 7.2, $^3J_{4B,5}$ 5.0 Hz, H^{4B}), 3.91 (d, 1H, $^2J_{4A,4B}$ 7.0 Hz, H^{4A}), 4.08 (qd, 1H, $^3J_{13,14}$ 7.0, $^3J_{13,9}$ 1.8 Hz, H^{13}), 4.40 (d, 1H, $^3J_{7,6}$ 9.3 Hz, H^7), 4.68 (dd, 1H, $^3J_{5,4B}$ 5.0, $^3J_{5,6}$ 1.3 Hz, H^5), 5.27 (s, 1H, H^2). ^{13}C NMR ($CDCl_3$), δ: 21.07 (CH_3), 23.86 (C^{10}), 28.29 (CH_3), 31.05 (C^{11}), 44.01 (C^6), 44.73 (C^9), 47.97 (OCH_3), 67.42 (C^4), 70.47 (C^{13}), 71.58 (C^7), 74.02 (C^8), 74.33 (C^5), 96.38 (C^1), 98.20 (C^2). Mass spectrum, *m/z*: 287 [*M*+H]$^+$, Calcd for $C_{14}H_{22}O_6$. 286.32.

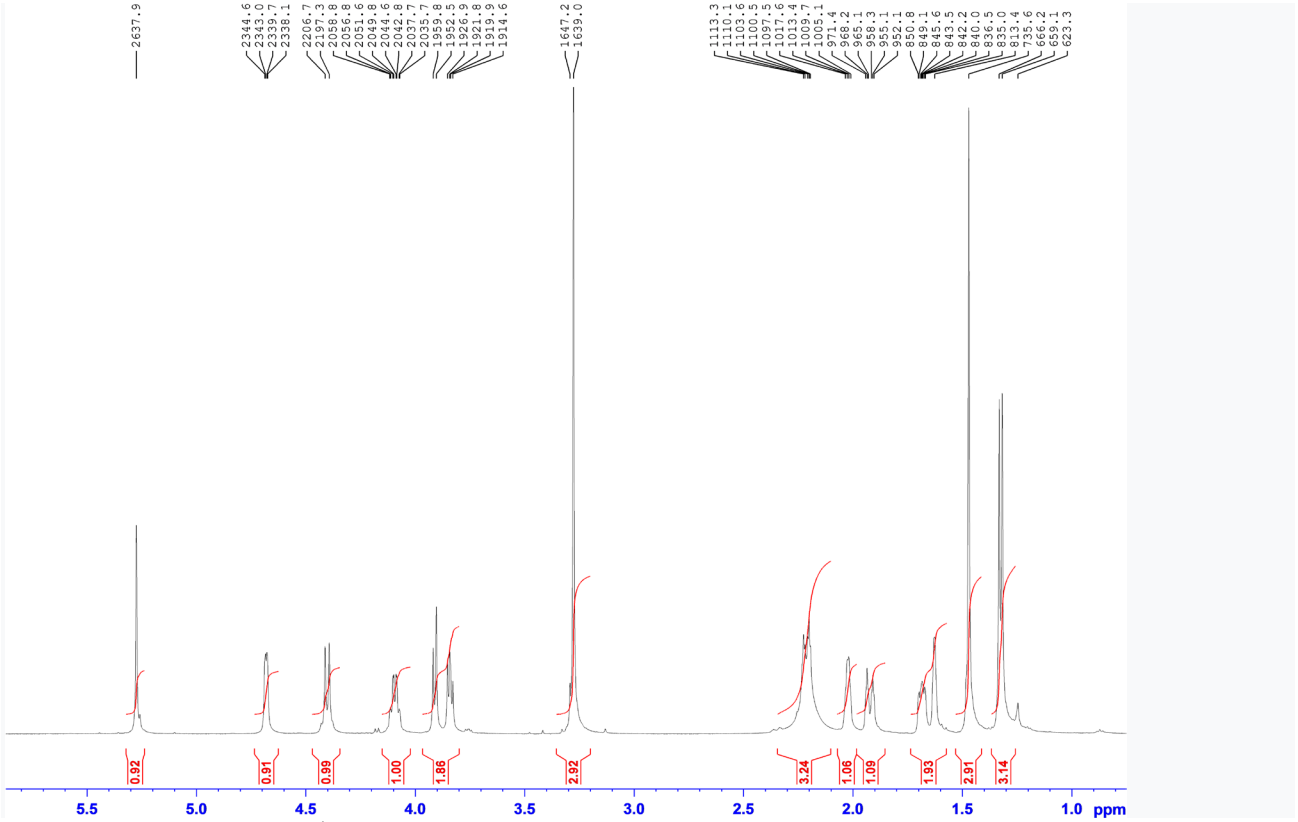


Fig. S7.1. Complete ^{1}H NMR (500 MHz) spectrum of compound **7** in $CDCl_3$

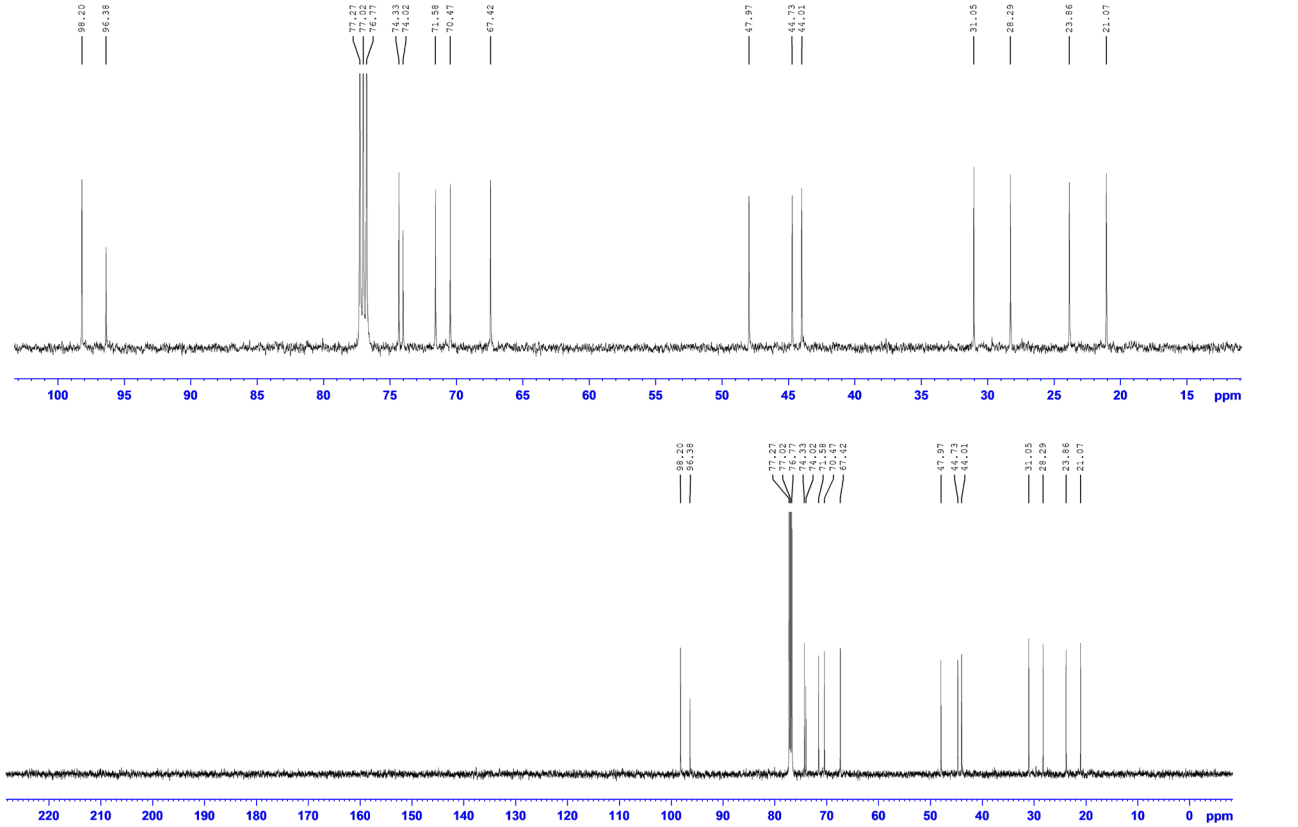


Fig. S7.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of compound **7** in $CDCl_3$

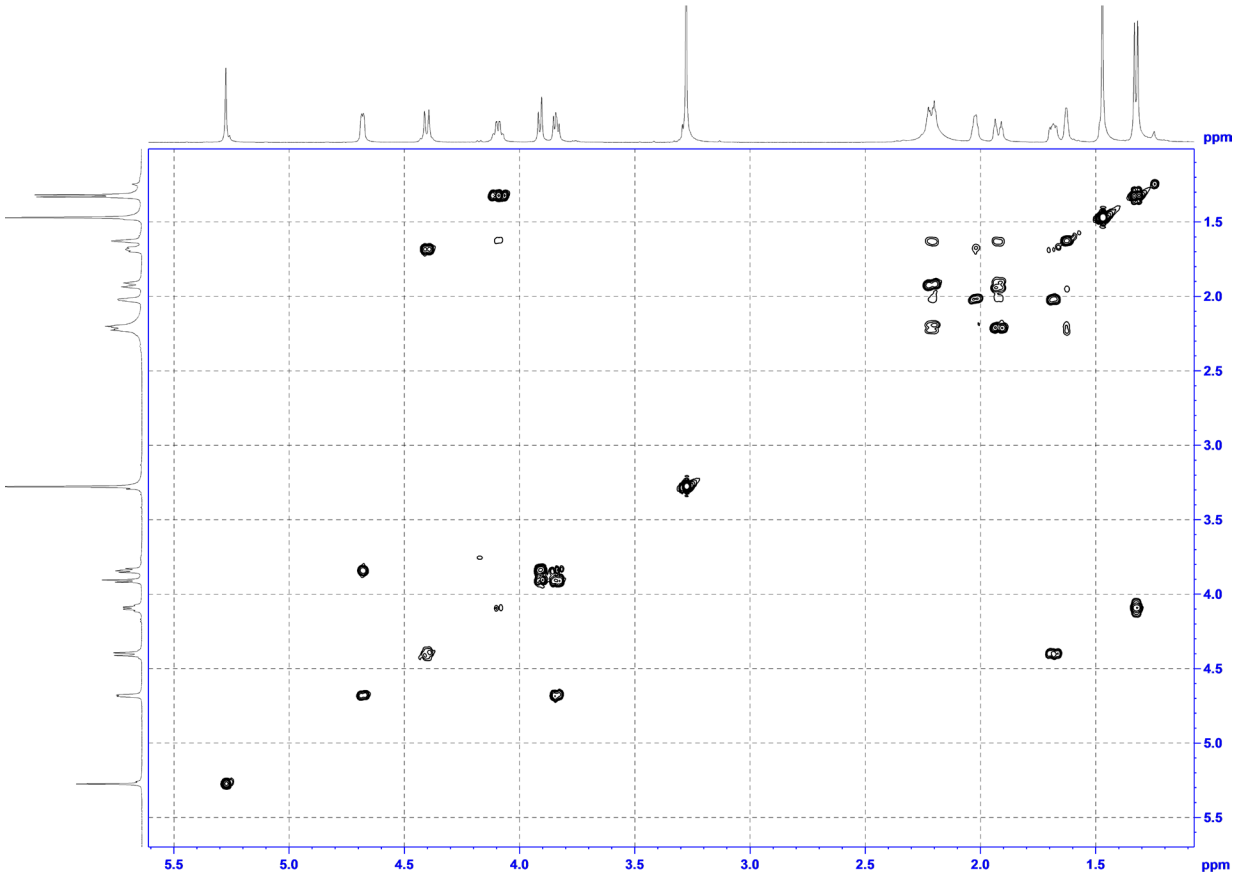


Fig. S7.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of compound **7** in $CDCl_3$

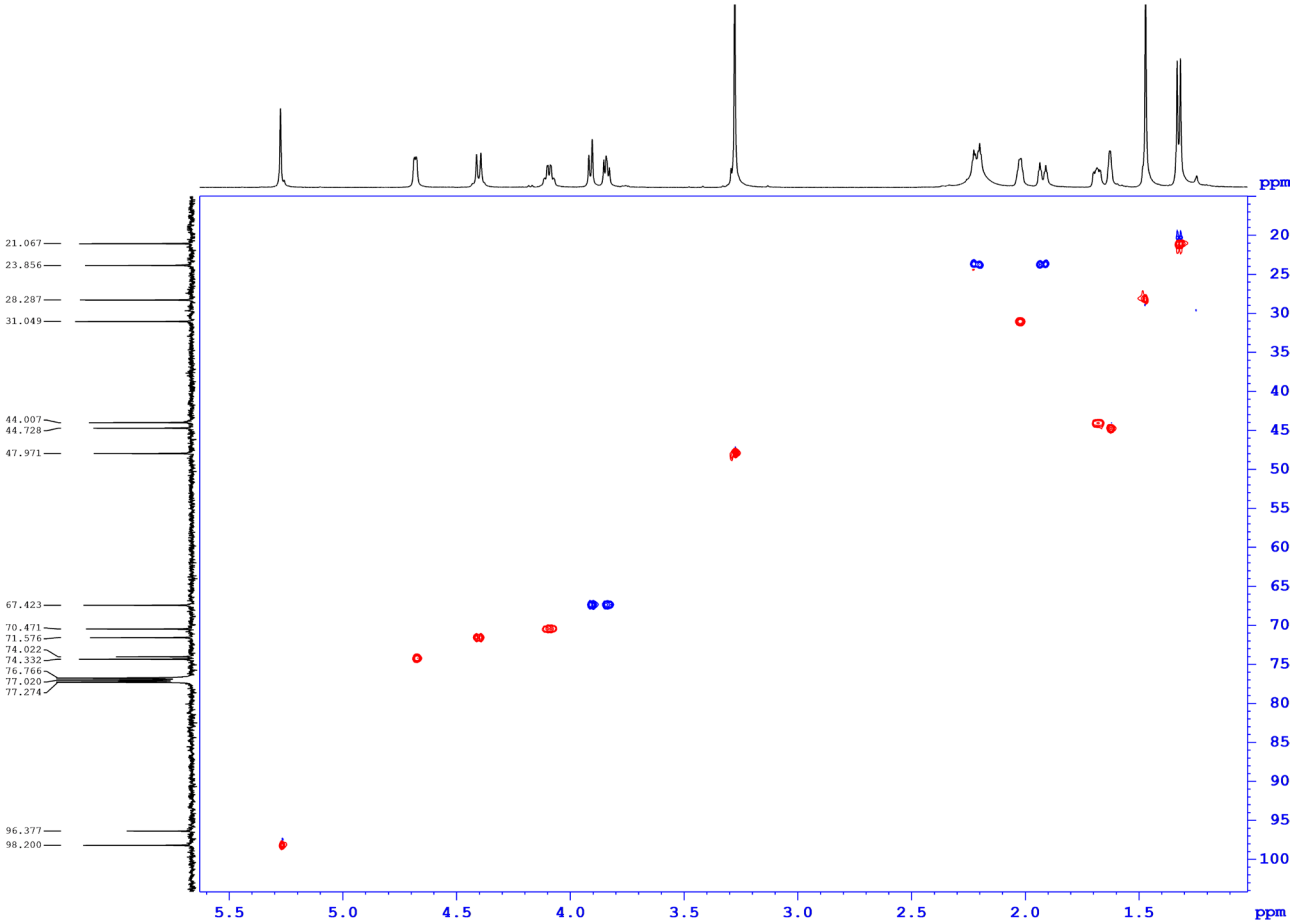


Fig. S7.4. Complete {^{1}H,^{13}C} HSQCED NMR spectrum of compound **7** in $CDCl_3$

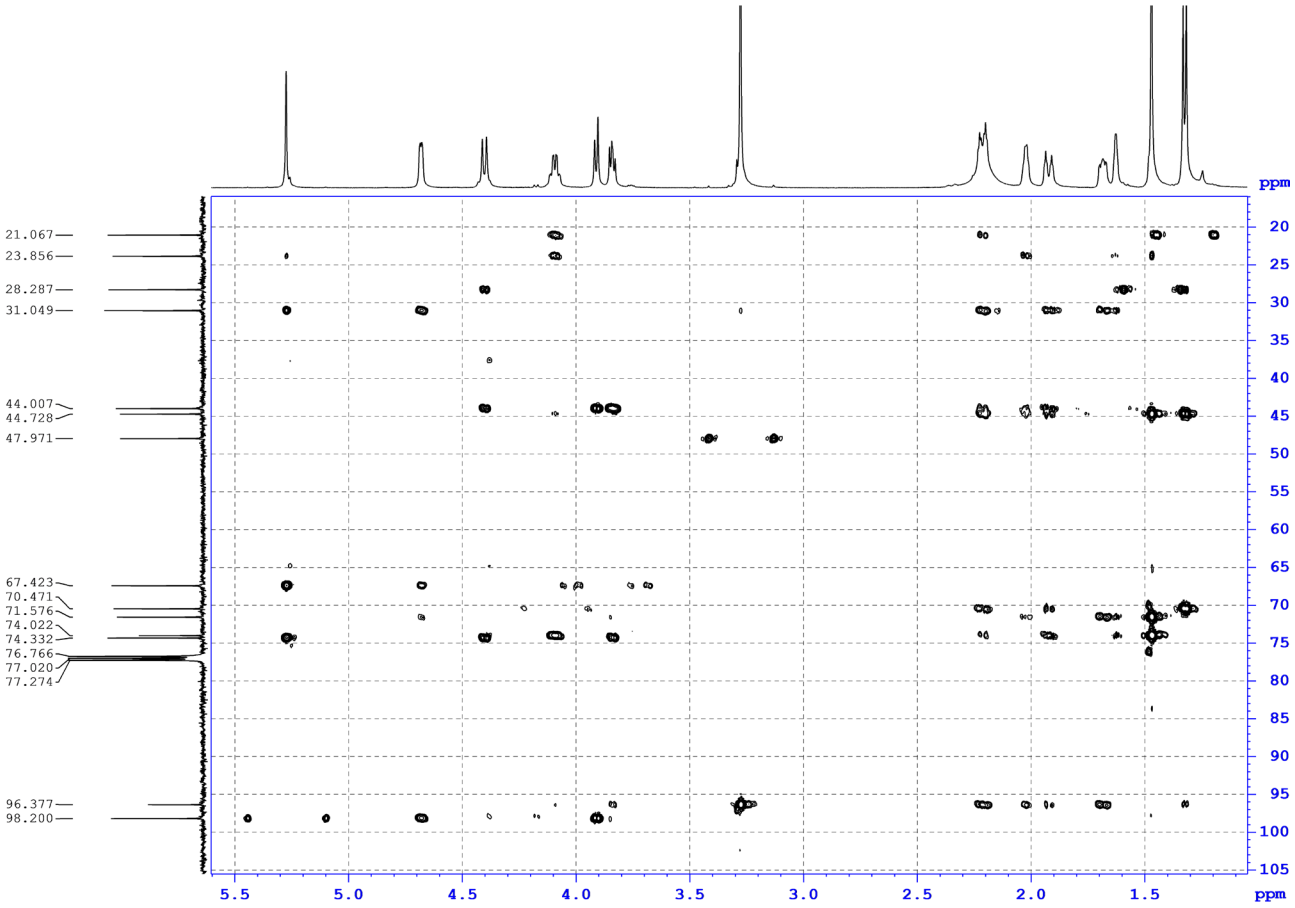


Fig. S7.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum of compound **7** in $CDCl_3$

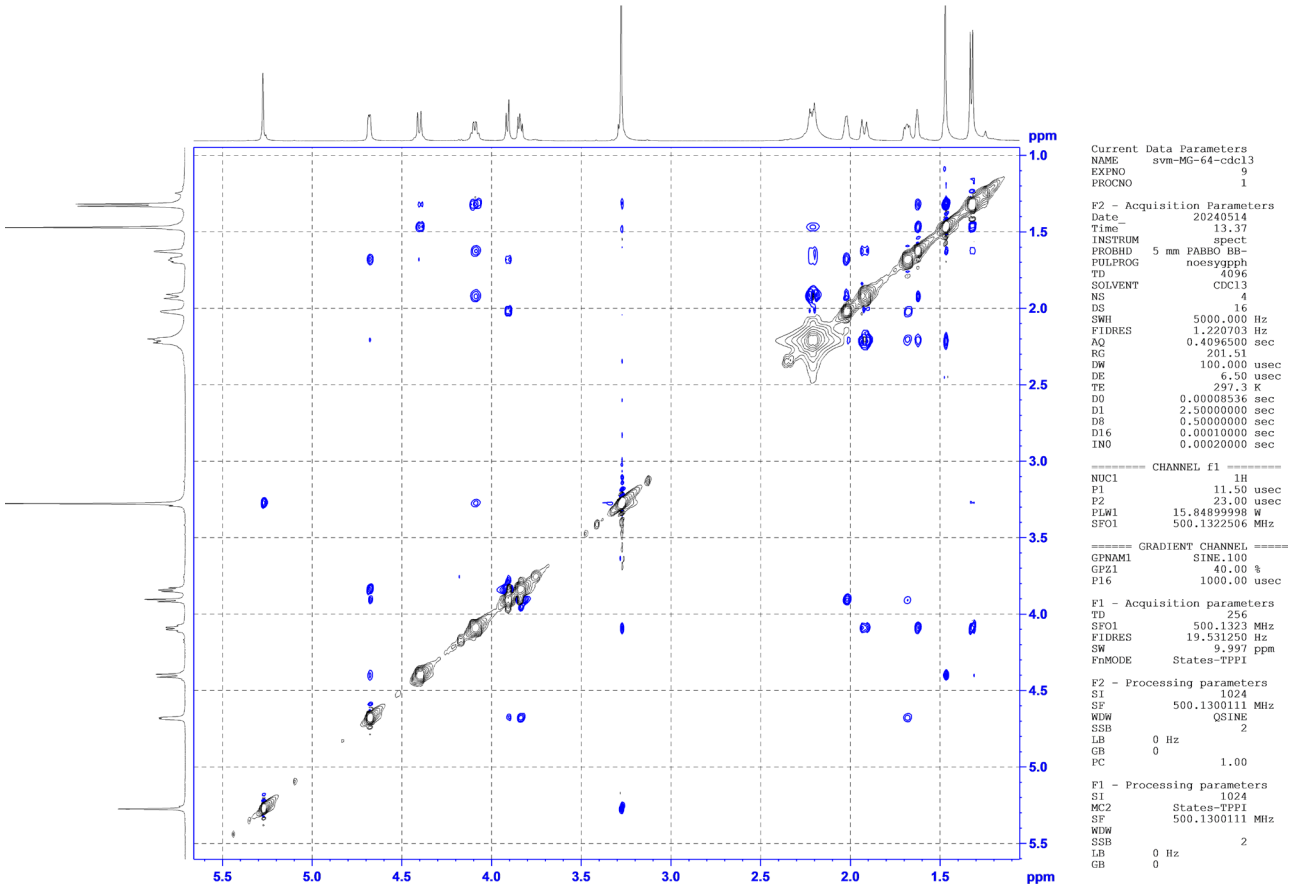


Fig. S7.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of compound **7** in $CDCl_3$

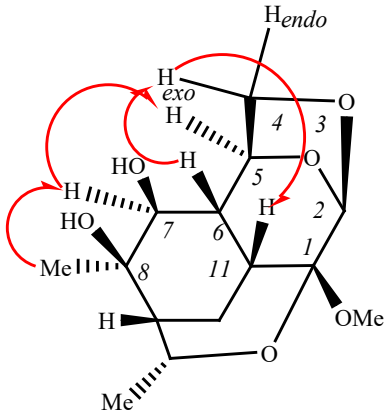
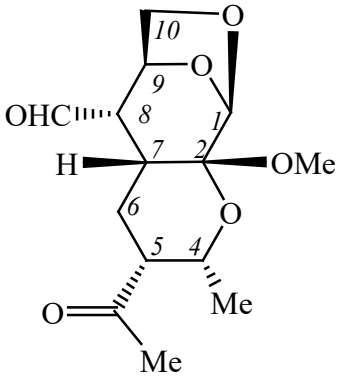


Figure S1. Proof of the *S*-configuration of the C^7 center and the *R*-configuration of the C^6 and C^8, C^{11} centers by the presence of the NOE effect between H^{4A}/H^6, H^{4A}/H^{11}, H^7/H^5 and H^7/H^{Me} in compound **7**

(1*R*,2*R*,4*R*,5*R*,7*R*,8*S*,9*S*)-5-Acetyl-2-methoxy-4-methyl-3,11,12-trioxatricyclo[7.2.1.$0^{2,7}$]dodecane-8-carbaldehyde (8)



A solution of 0.097 g (0.035 mmol) of diol **7** in 3.0 ml of THF was added at 0 °C to a solution of 0.074 g (0.035 mmol) of $NaIO_4$ in 0.6 ml of water. The reaction mixture was stirred for 1 hour at room temperature (control by TLC). The mixture was extracted with ethyl acetate (3 × 5.0 ml), the extract was dried over $MgSO_4$, the solvent was distilled off, and the residue was chromatographed on SiO_2 eluent petroleum ether–EtOAc, 1:1. Yield 0.095 g (99%). White crystals, m.p. 123-124 °C, $[\alpha]_D^{25}$ = -56.9° (*c* 1.0, $CHCl_3$). R_f 0.68 (EtOAc). ^{1}H NMR ($CDCl_3$), δ: 1.00 (d, 3H, $^3J_{14,4}$ 6.7 Hz, H^{14}), 1.50-1.57 (m, 2H, H^{6A}, H^{6B}), 2.07 (s, 3H, CH_3), 2.22 (dt, 1H, $^3J_{7,6B}$ 10.0, $^3J_{7,6A}$ 7.5, $^3J_{7,8}$ 7.5 Hz, H^8), 2.66 (dt, 1H, $^3J_{8,7}$ 7.5, $^3J_{8,5}$ 2.4, $^3J_{8,CHO}$ 2.4 Hz, H^8), 3.08 (dt, 1H, $^3J_{5,6B}$ 9.8, $^3J_{5,6A}$ 6.7, $^3J_{5,4}$ 6.7 Hz, H^5), 3.25 (s, 3H, OCH_3), 3.56 (dd, 1H, $^2J_{10B,10A}$ 7.1, $^3J_{10B,9}$ 4.6 Hz, H^{10B}), 3.68 (d, 1H, $^2J_{10A,10B}$ 7.1 Hz, H^{10A}), 4.18 (pent, 1H, $^3J_{4,5}$ 6.7, $^3J_{4,14}$ 6.7 Hz, H^4), 4.88 (dd, 1H, $^3J_{9,10B}$ 4.6, $^3J_{9,6}$ 2.8 Hz, H^9), 5.28 (s, 1H, H^1), 9.70 (d, 1H, $^3J_{CHO,8}$ 2.4 Hz, H^{CHO}). ^{13}C NMR ($CDCl_3$), δ: 17.32 (CH_3), 22.54 (C^6), 30.54 (CH_3), 33.41 (C^7), 49.54 (OCH_3), 49.84 (C^5), 52.41 (C^8), 64.81 (C^4), 68.93

(C^{10}), 69.94 (C^{9}), 98.17 (C^{2}), 100.56 (C^{1}), 203.62 (CHO), 209.25 (C=O). Mass spectrum, *m/z*: 285 $[M+H]^+$. Calcd for $C_{14}H_{20}O_6$. 284.31

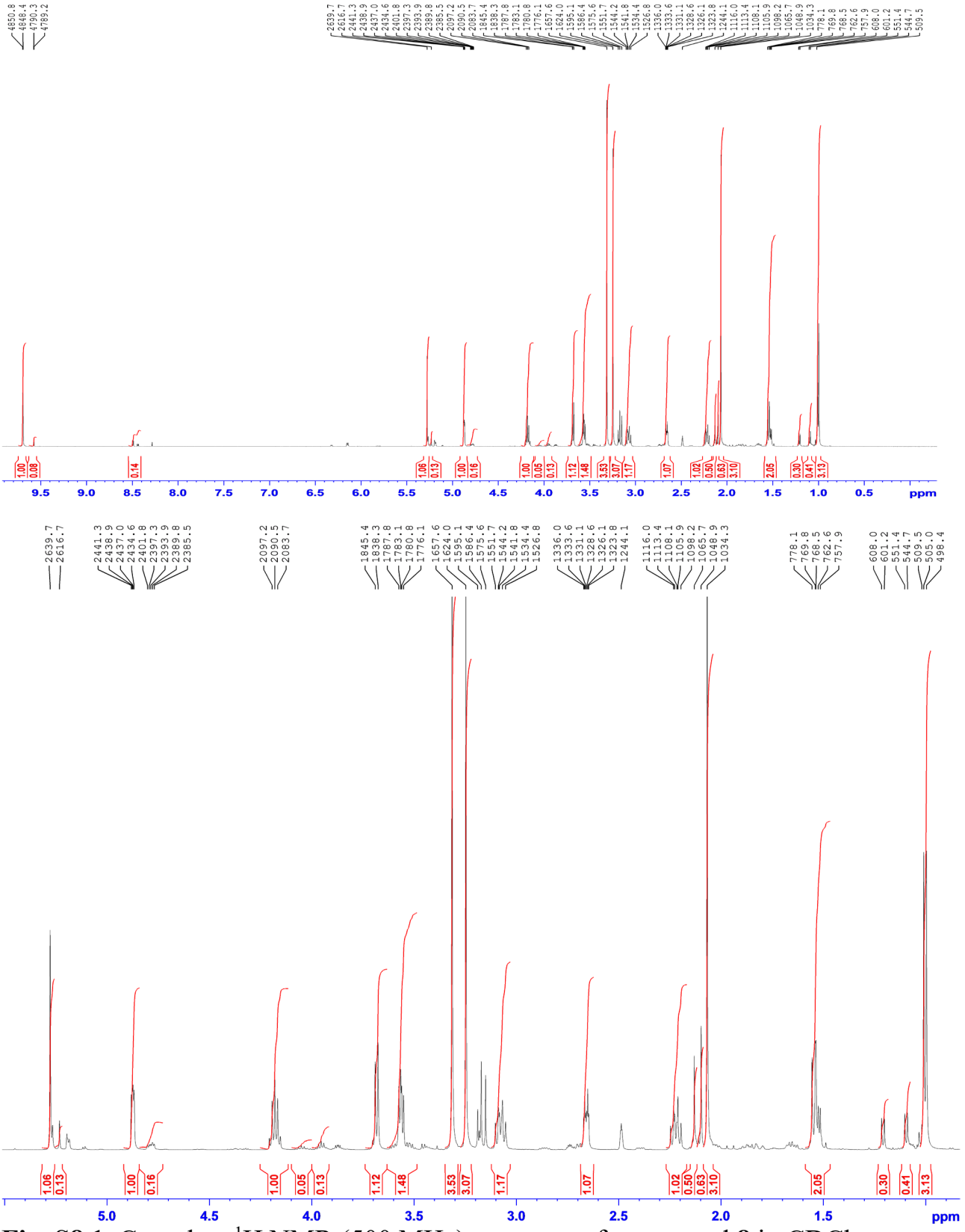


Fig. S8.1. Complete ^{1}H NMR (500 MHz) spectrum of compound **8** in $CDCl_3$

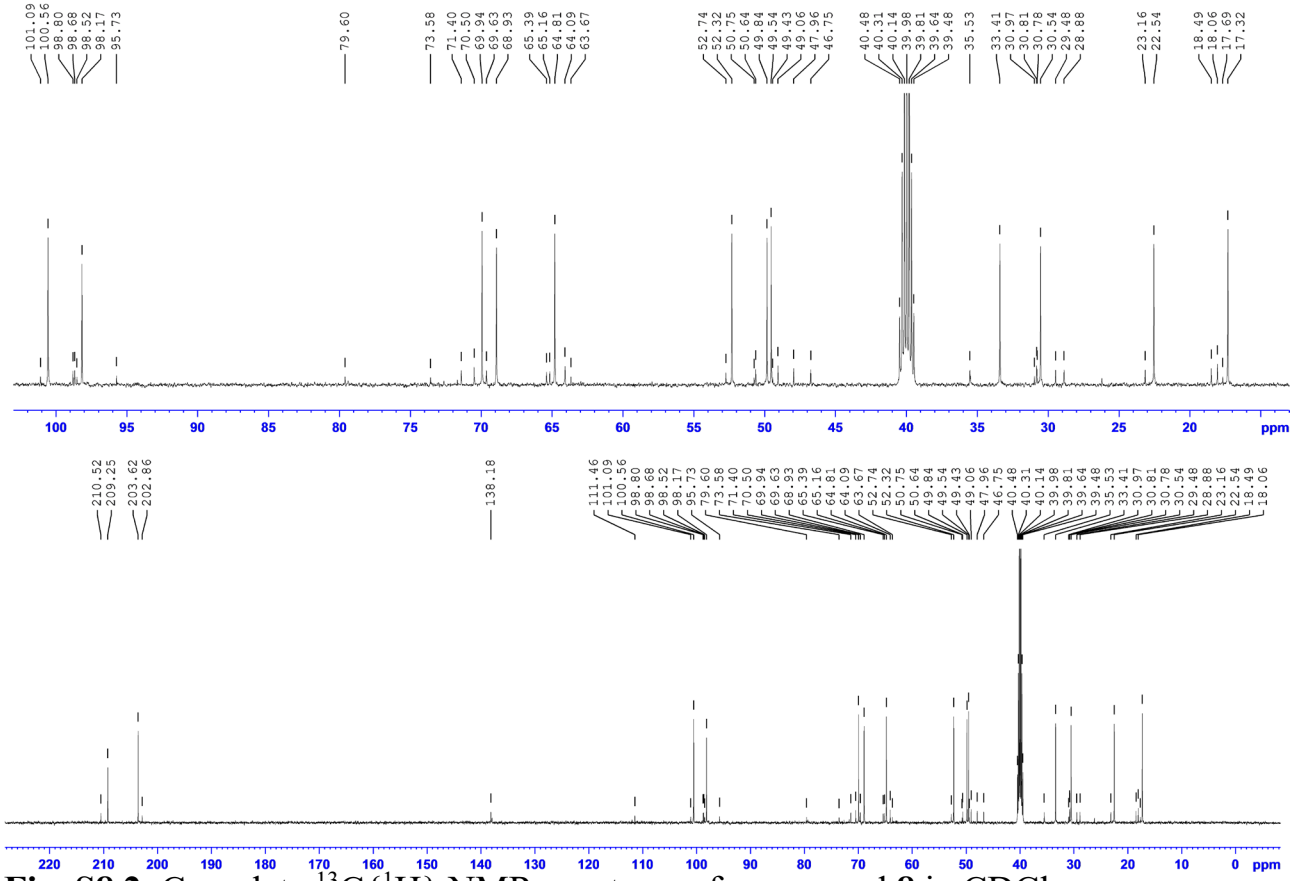


Fig. S8.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of compound **8** in $CDCl_3$

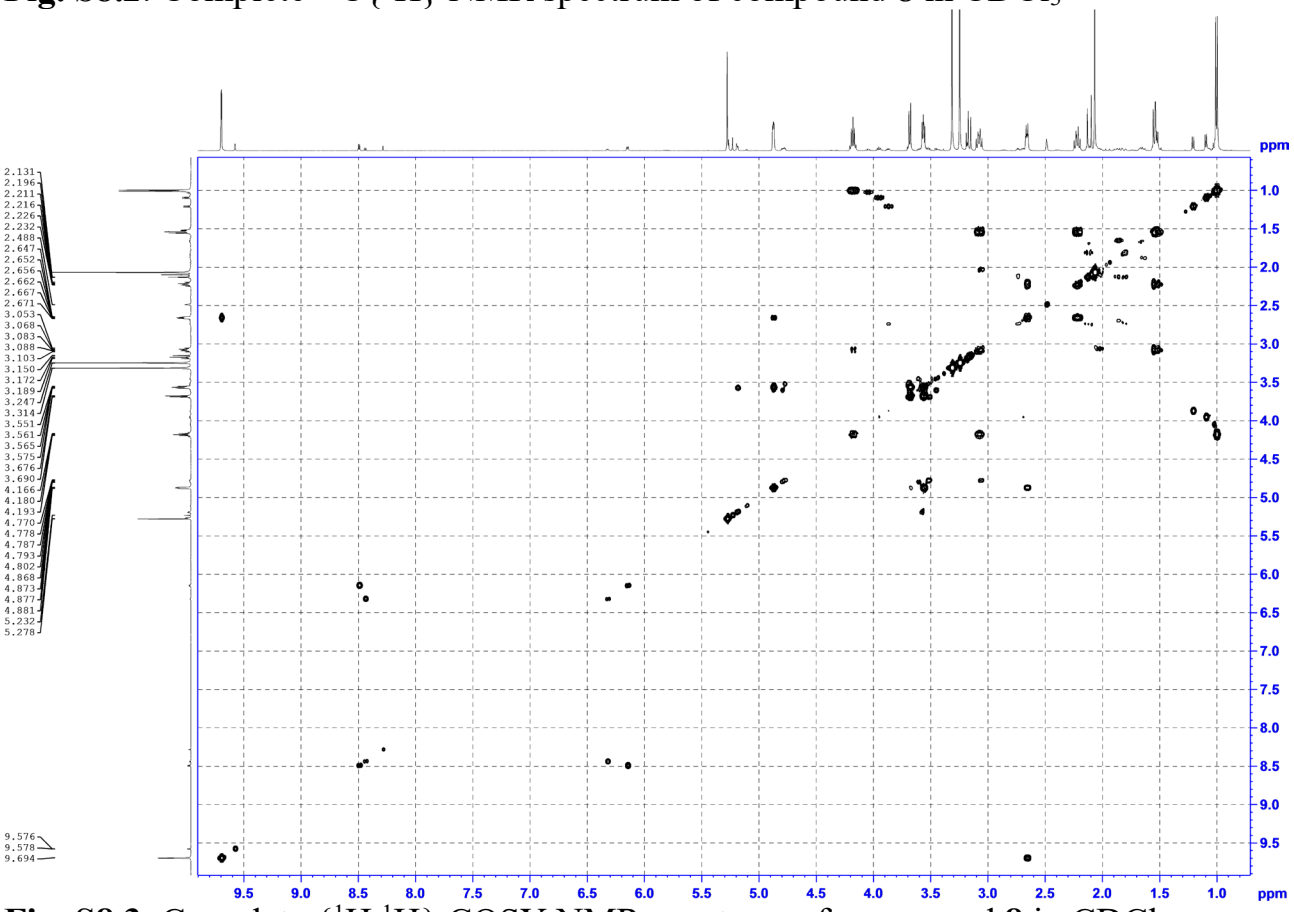


Fig. S8.3. Complete $\{^{1}H,^{1}H\}$ COSY NMR spectrum of compound **8** in $CDCl_3$

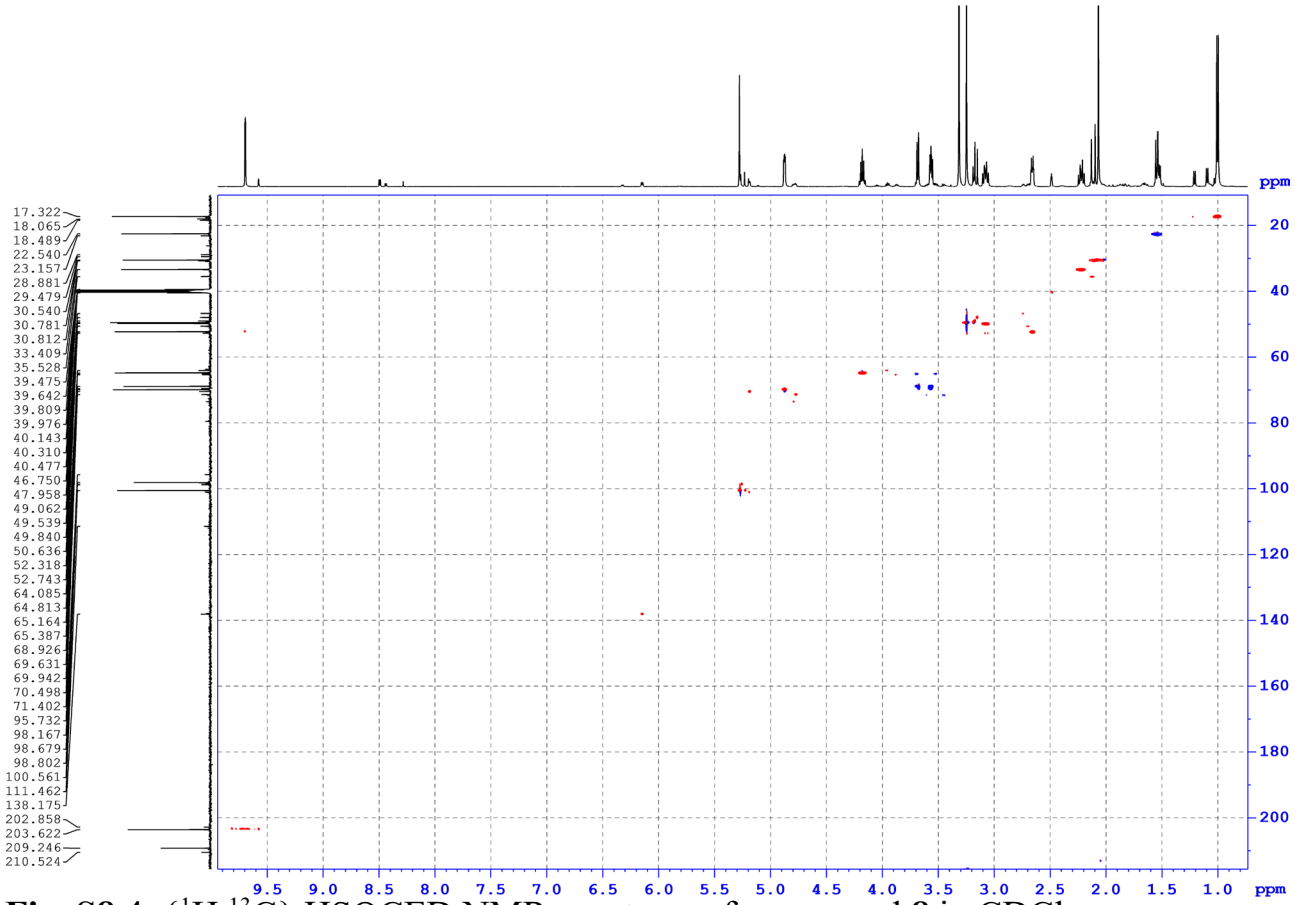


Fig. S8.4. {^{1}H,^{13}C} HSQCED NMR spectrum of compound **8** in $CDCl_3$

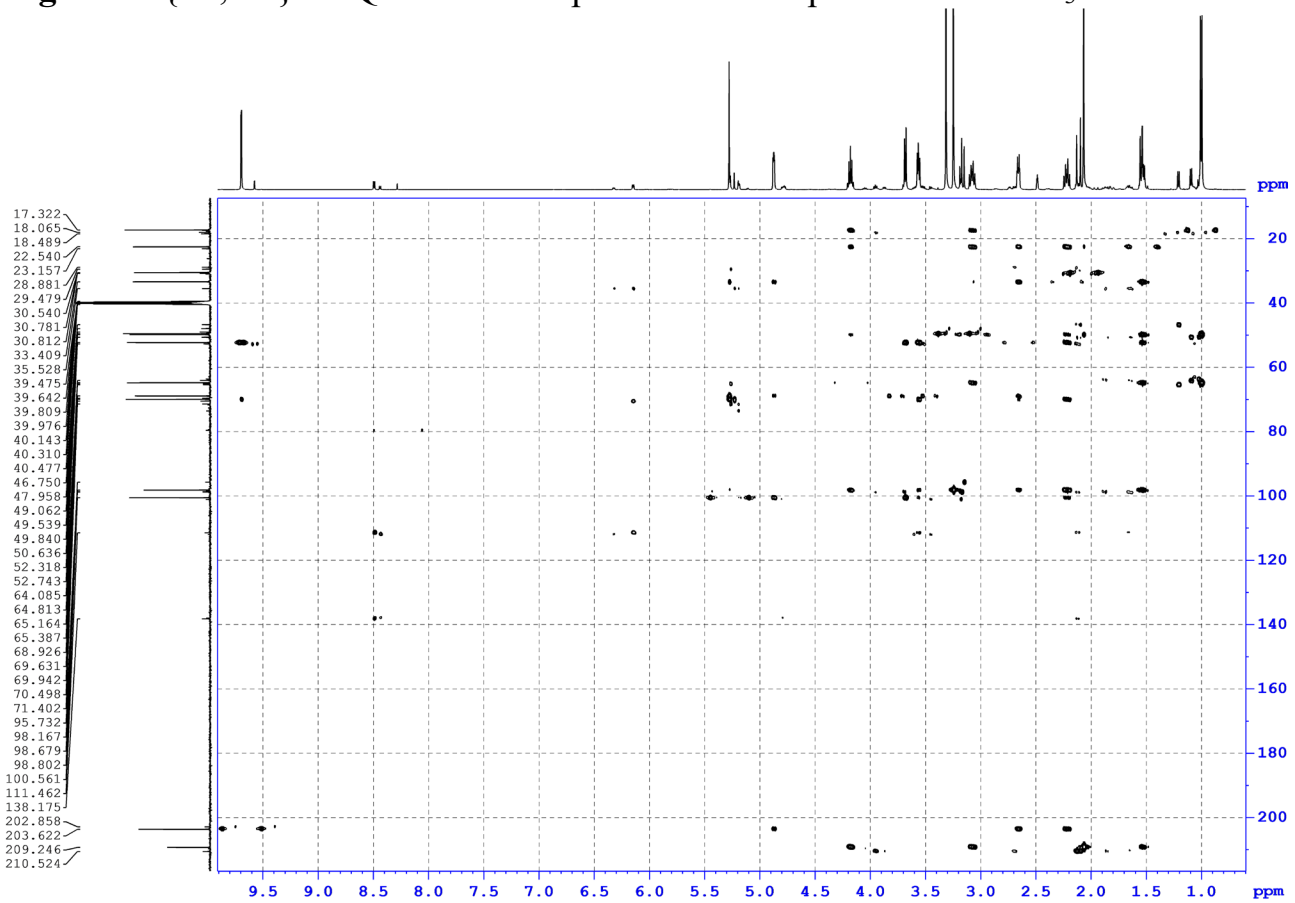


Fig. S8.5. {^{1}H,^{13}C} HMBC NMR spectrum of compound **8** in $CDCl_3$

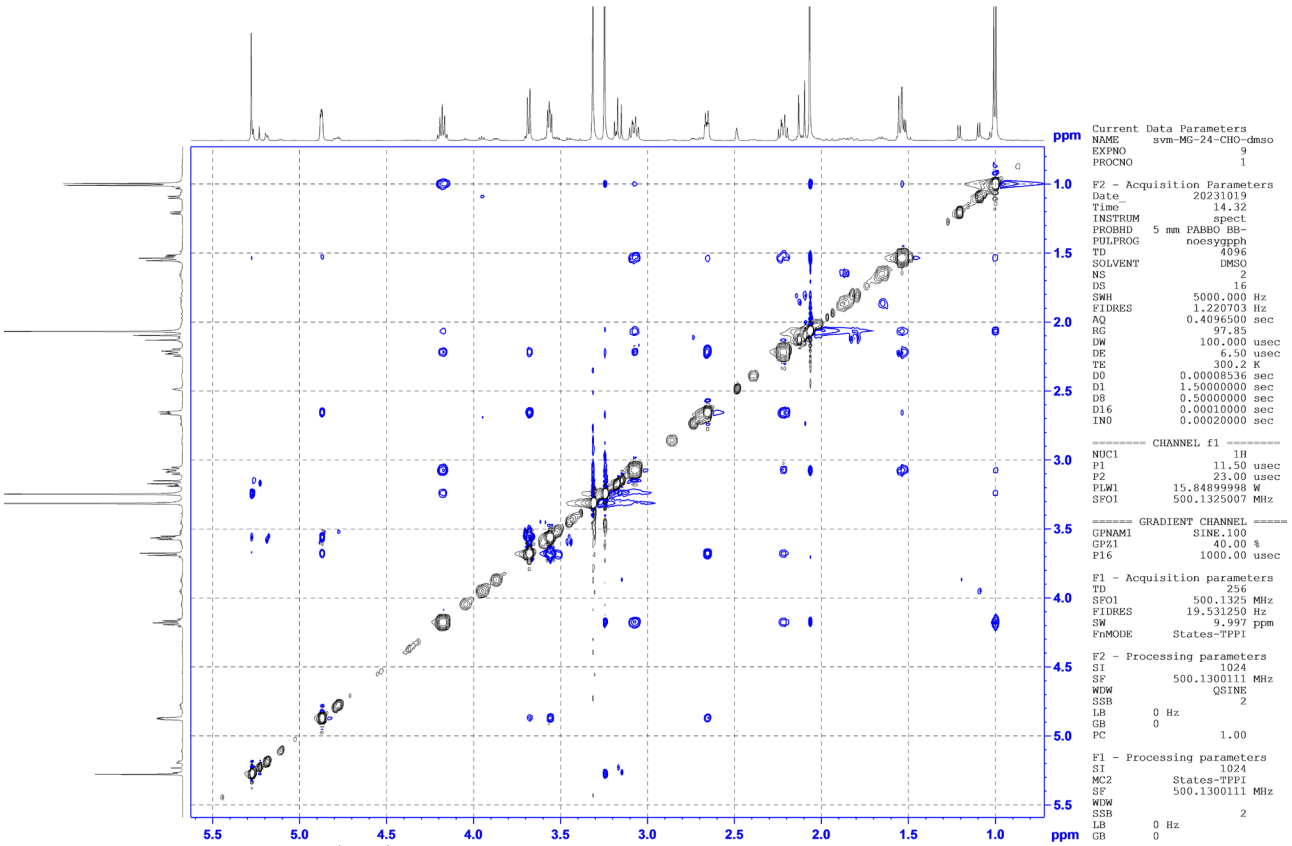


Fig. S8.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of compound **8** in $CDCl_3$

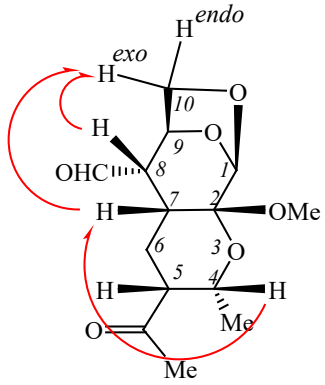


Figure S2. The presence of the NOE effect between H^{10A}/H^8, H^{10A}/H^7 and H^7/H^4 in compound **8**

Methyl (1*R*,2*R*,4*R*,5*R*,7*R*,8*S*,9*S*)-5-acetyl-2-methoxy-4-methyl-3,11,12-trioxatricyclo[7.2.1.0^{2,7}]dodecane-8-carboxylate (5) and methyl (1*R*,2*R*,4*R*,5*R*,7*R*,8*S*,9*S*)-5-acetyl-2-hydroxy-4-methyl-3,11,12-trioxatricyclo[7.2.1.0^{2,7}]dodecane-8-carboxylate (9)

To a solution of the mixture of compound **7** (0.195 g, 0.77 mmol) in 1,4-dioxane (4.2 ml) and H_2O (4.2 ml) was added Br_2 (0.04 ml, 0.77 mmol). The mixture was stirred at room temperature for 1 h until complete conversion of the starting material (TLC control). The reaction mass treated with a solution of diazomethane in Et_2O. The reaction mass was stirred for 15 minutes, and the product was extracted

with Et_2O (3×5.0 ml), the extract was dried over $MgSO_4$, the solvent was distilled off, and the residue was chromatographed on SiO_2. Yield 0.086 g (40%) of ester **5**, 0.043 g (21%) of 2-hydroxy ester **9**.

Compound **9** white crystals, m.p. 98-100 °C, $[\alpha]_D^{25}$ = -0.3° (*c* 1.0, $CHCl_3$). R_f 0.38 (petroleum ether–EtOAc, 1:1). ^{1}H NMR ($CDCl_3$), δ: 1.31 (d, 3H, $^3J_{14,4}$ 6.9 Hz, H^{14}), 1.44 (dt, 1H, $^2J_{6A,6B}$ 10.4, $^3J_{6A,5}$ 2.1, $^3J_{6A,7}$ 2.1 Hz, H^{6A}), 2.19 (s, 3H, CH_3), 2.25-2.36 (m, 2H, H^7, H^{6B}), 2.65 (d, 1H, $^3J_{8,7}$ 5.1 Hz, H^8), 3.12 (ddd, 1H, $^3J_{5,6B}$ 10.4, $^3J_{5,4}$ 6.9, $^3J_{5,6A}$ 2.1 Hz, H^5), 3.77 (s, 3H, CO_2CH_3), 3.93-3.95 (m, 2H, H^{10A}, H^{10B}), 4.63 (pent, 1H, $^3J_{4,5}$ 6.9, $^3J_{4,14}$ 6.9 Hz, H^4), 4.67 (dd, 1H, $^3J_{9,10A}$ 3.7, $^3J_{9,10B}$ 1.7 Hz, H^9), 5.07 (s, 1H, H^1), 5.57 (s, 1H, H^{OH}). ^{13}C NMR ($CDCl_3$), δ: 18.40 (C^6), 19.35 (CH_3), 28.61 (CH_3), 35.47 (C^7), 47.62 (C^8), 52.85 (CO_2CH_3), 55.32 (C^5), 68.98 (C^{10}), 70.51 (C^4), 74.52 (C^9), 94.21 (C^2), 103.84 (C^1), 173.56 (C=O), 206.73 (C=O). Mass spectrum, *m/z*: 301 $[M+H]^+$. Calcd for $C_{14}H_{20}O_7$. 300.30.

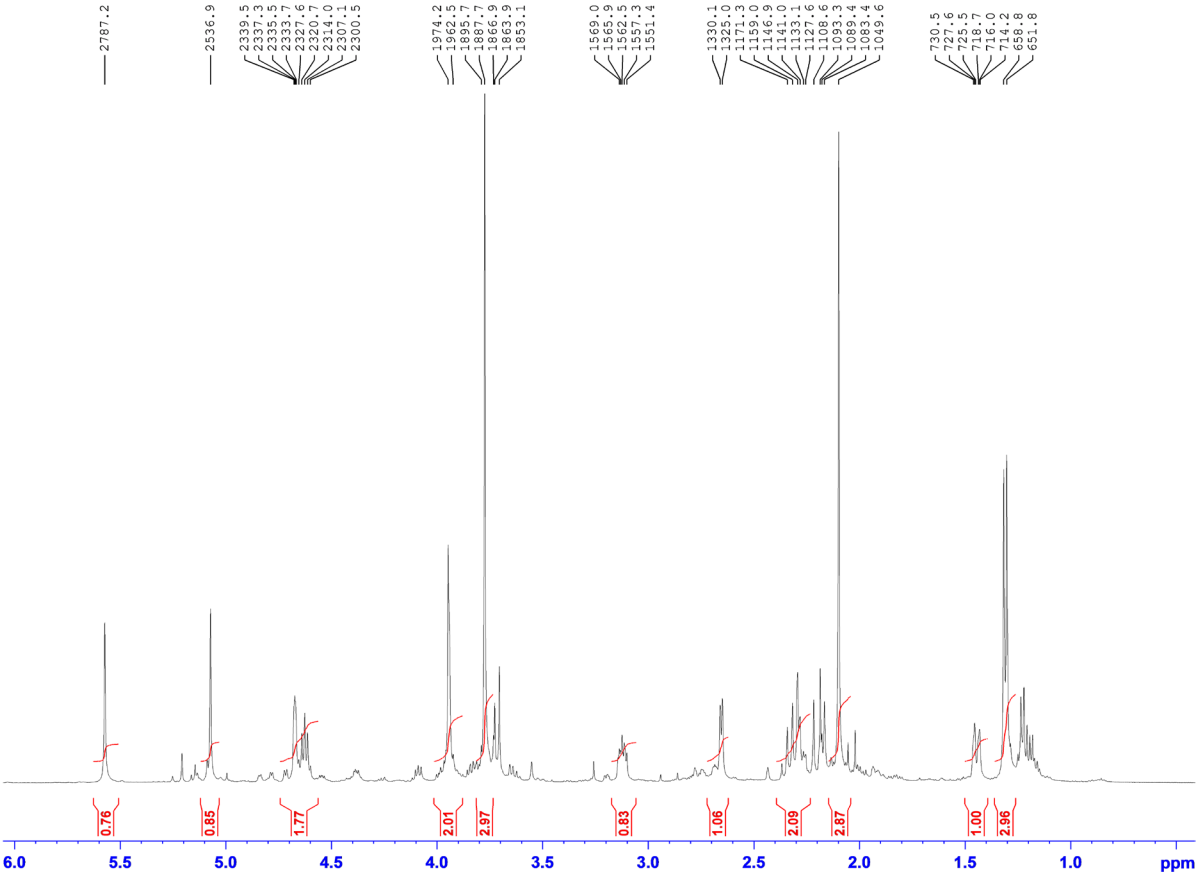


Fig. S9.1. Complete ^{1}H NMR (500 MHz) spectrum of compound **9** in $CDCl_3$

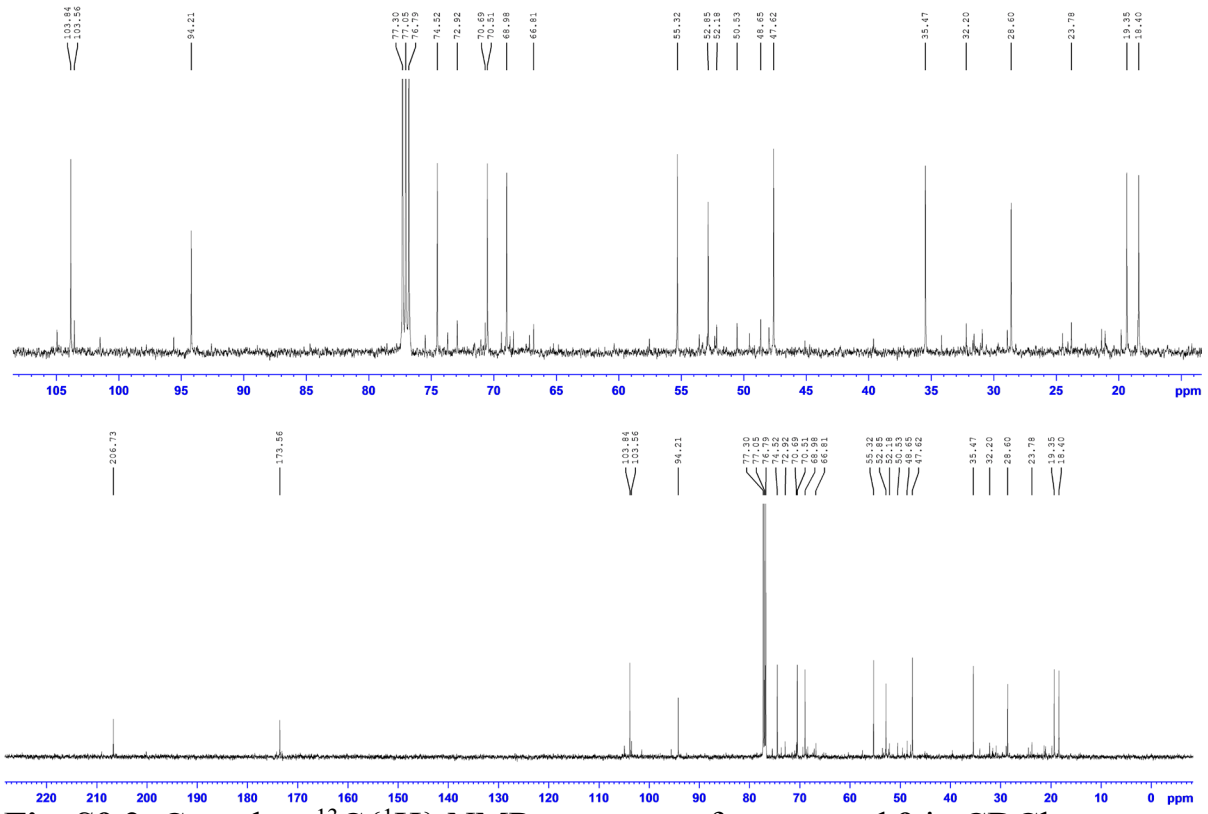


Fig. S9.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of compound **9** in $CDCl_3$

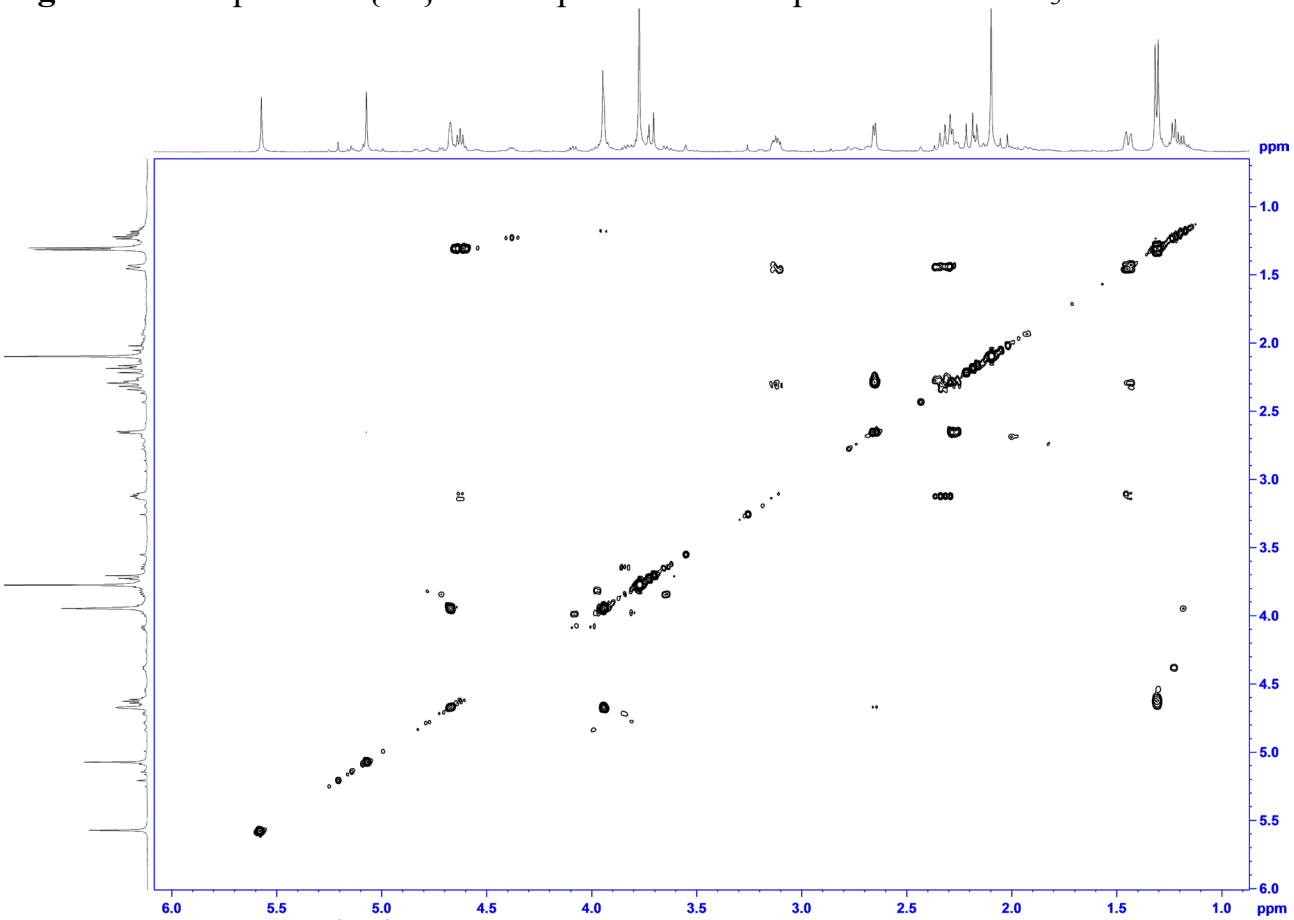


Fig. S9.3. Complete $\{^{1}H,^{1}H\}$ COSY NMR spectrum of compound **9** in $CDCl_3$

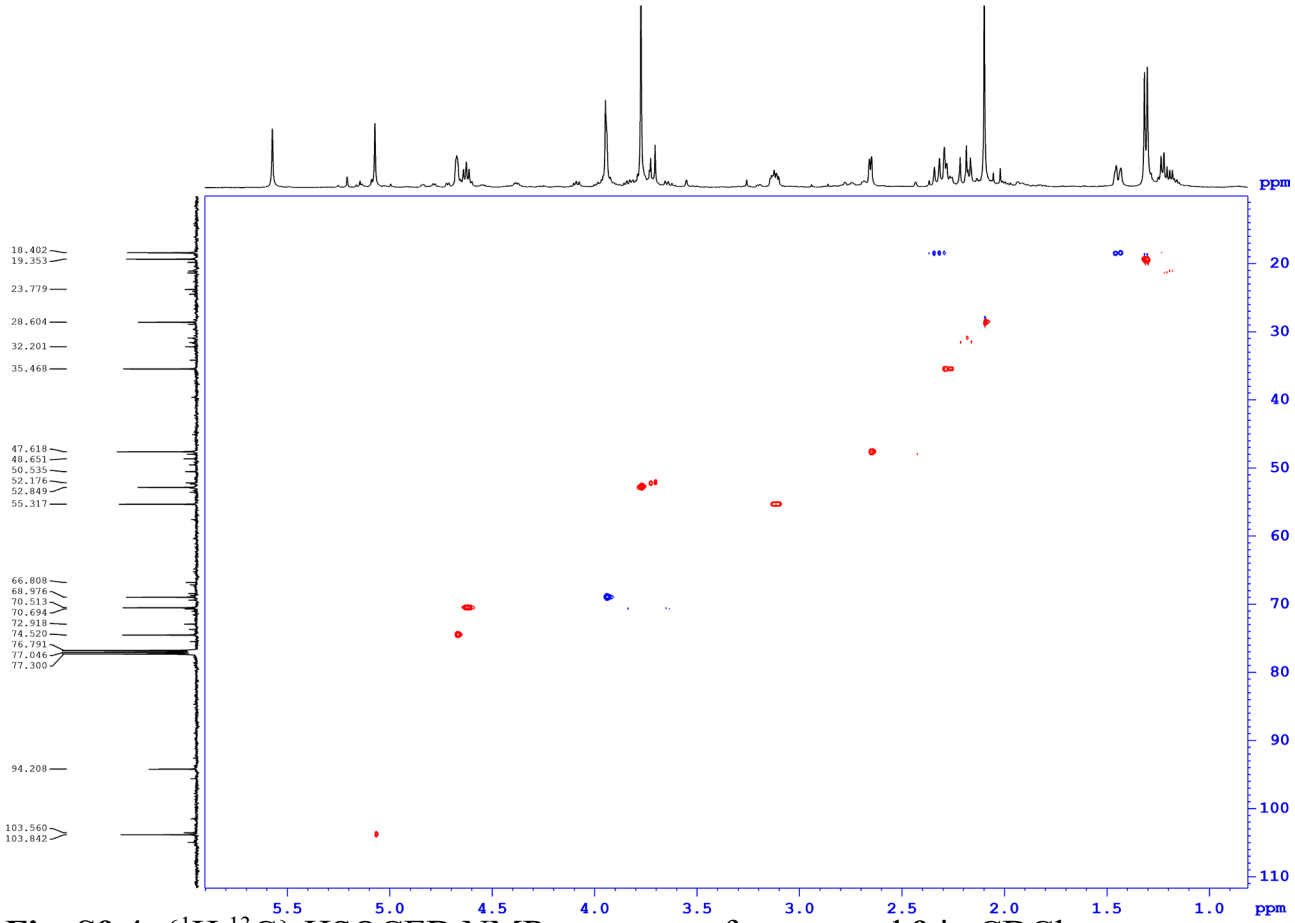


Fig. S9.4. {^{1}H,^{13}C} HSQCED NMR spectrum of compound **9** in $CDCl_3$

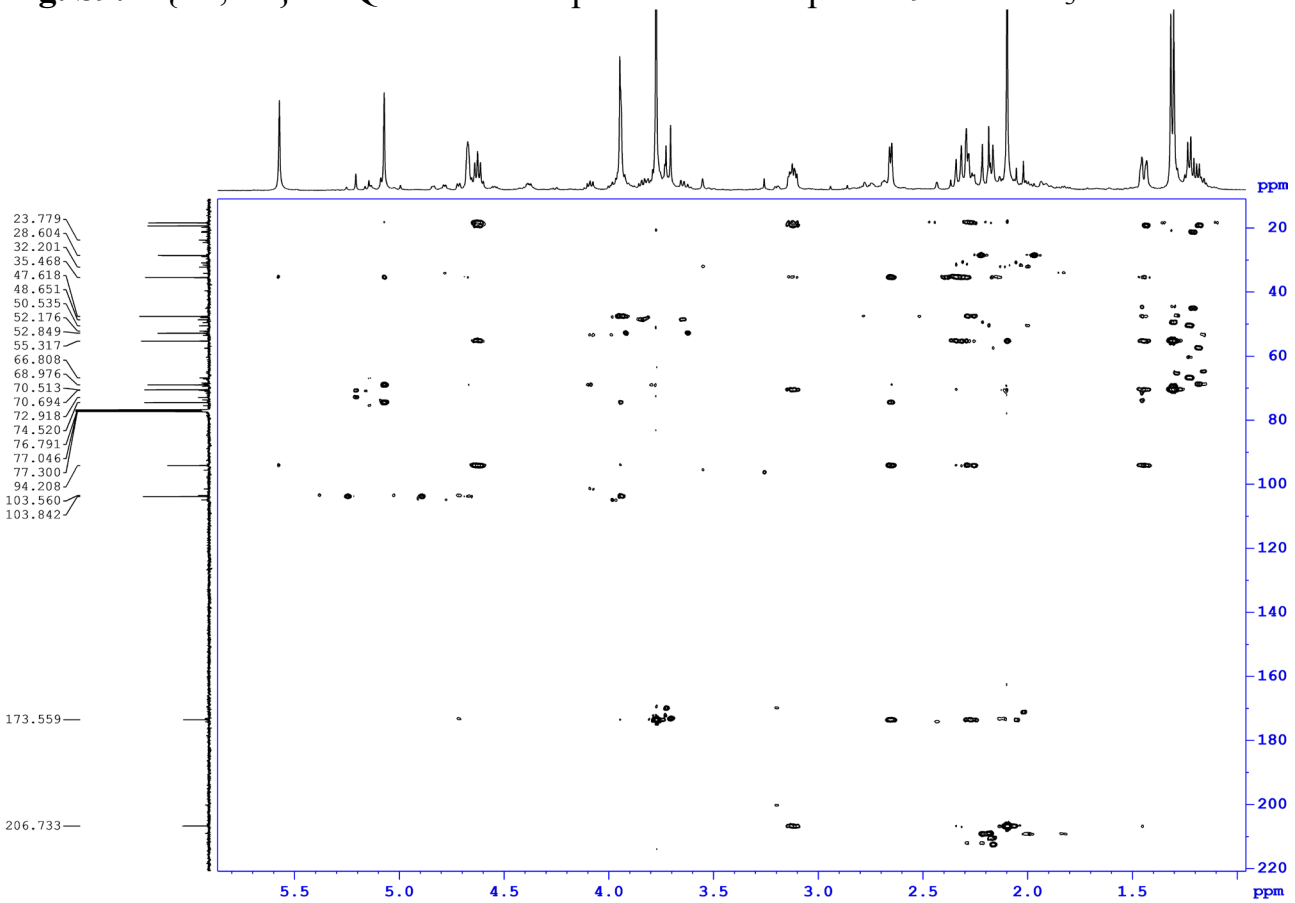


Fig. S9.5. {^{1}H,^{13}C} HMBC NMR spectrum of compound **9** in $CDCl_3$

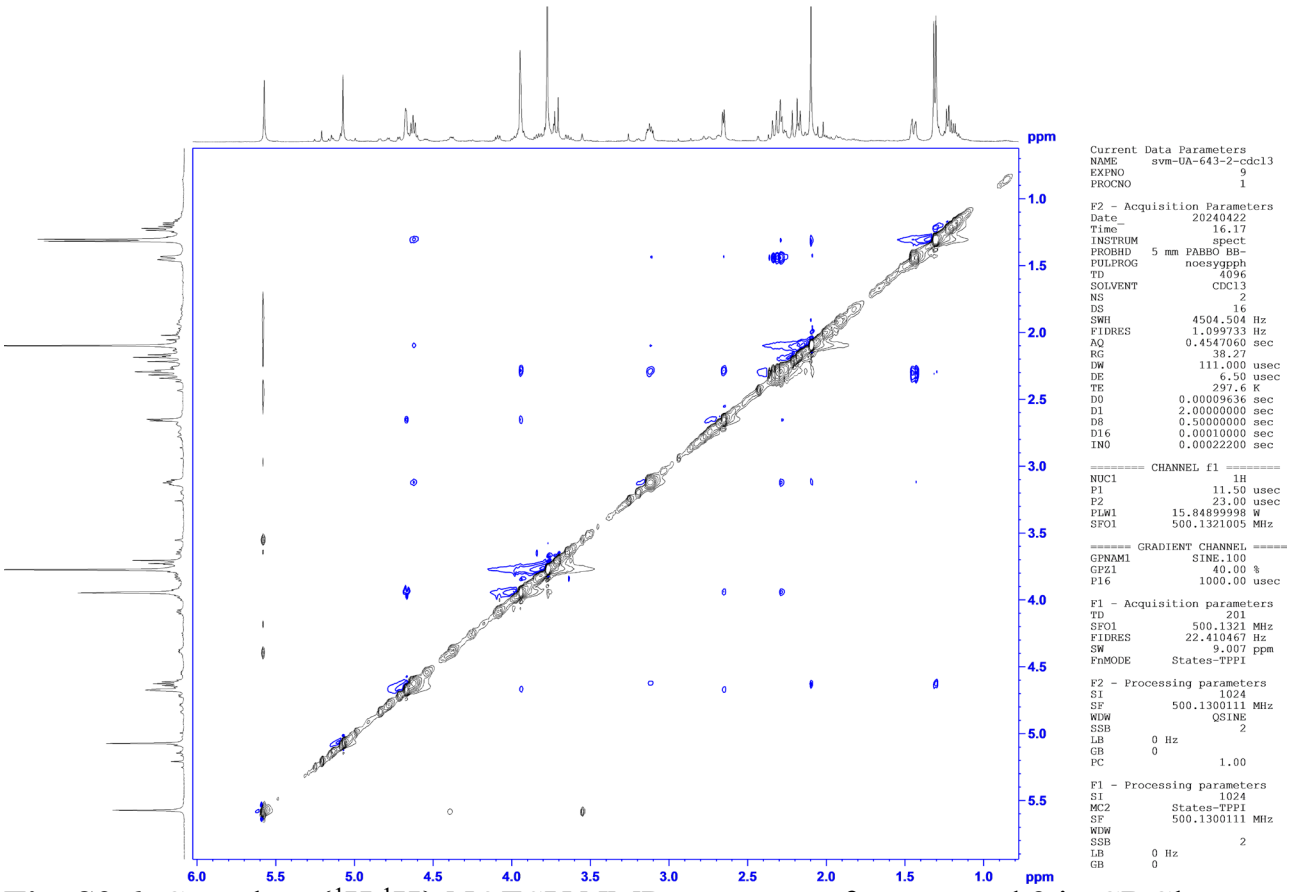


Fig. S9.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of compound **9** in $CDCl_3$

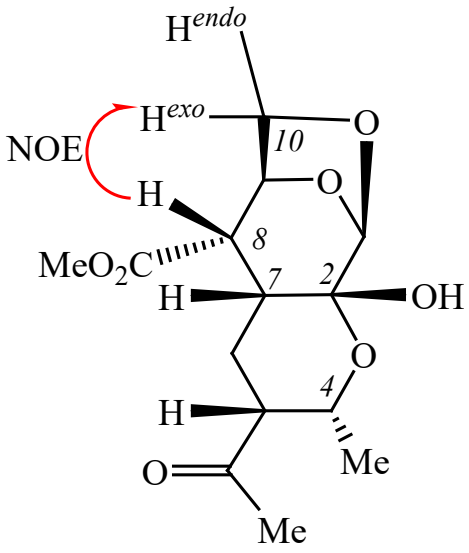


Figure S3. The presence of the NOE effect between H-8 and H-10 in compound **9**

References

S1. L. Kh. Faizullina, A. R. Tagirov, Sh. M. Salikhov and F. A.Valeev, *Mendeleev Commun*., 2022, **31**, 22. https://doi.org/10.1016/j.mencom.2022.01.032.