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The synthetic potential of α,α-diallylcyrene

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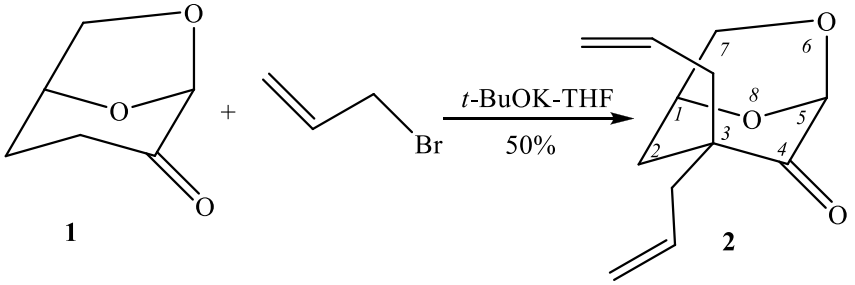
The spectral and analytical data were obtained using the equipment of the *Khimiya* Joint Center at the Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance III, (500.13 MHz for ^{1}H and 125.47 MHz for ^{13}C). IR spectra were recorded on spectrophotometers Shimadzu IRPrestige-21 or Bruker Tensor 27 (from films or mulls in mineral oil). Mass spectra were measured on a GC-MS instrument Hewlett Packard, chromatograph HP 6890 with a mass-selective detector HP 5973. 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. Cyrene (6,8-dioxabicyclo[3.2.1]octan-4-one) **1** was obtained from Circa, Melbourne, Australia.

(1*S*,5*R*)-3,3-Diallyl-6,8-dioxabicyclo[3.2.1]octan-4-one (2).



Cyrene **1** (1.00 g, 8 mmol) and allyl bromide (9.7 g, 80 mmol, 10 equiv.) were dissolved in THF (8 ml) under N_2, and then potassium *tert*-butoxide (1.9 g, 17 mmol) was added at 0°C. The solution was stirred at 25°C for 3 h (TLC control). The reaction mixture was then treated with 3% aqueous HCl to pH=7, the reaction products were extracted with EtOAc (3×10.0 ml), the extract was dried with $MgSO_4$, the solvent was distilled off on a rotary evaporator, the residue was subjected to silica gel column chromatography. Yield 0.798 g (50%). A colourless oil, $[\alpha]_D^{24}$ -79.2° (*c* 1.0, $CHCl_3$). R_f 0.47 (EtOAc–petroleum ether, 1:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.08-2.13 (m, 1H, H^{4B}), 2.24-2.29 (m, 2H, H^{1B}, H^{4A}), 2.42-2.48 (m, 2H, H^{1B}, H^{4A}), 3.78 (dt, 1H, H^{6B}, J =1.3, 1.6, 3.4, 5.1, 7.2 Hz), 3.92 (d, 1H, H^{6A}, J = 7.2 Hz), 4.71 (t,1H, H^{5}, J = 5.3, 5.7, 11.0 Hz), 5.03-5.13 (m, 5H, $C\underline{H}_2$=CH, H^{1}), 5.58-5.73 (m, 2H, CH_2=C$\underline{H}$).

^{13}C NMR (500 MHz, $CDCl_3$): δ 34.84 (C^4), 43.69 ($\underline{C}H_2$=CH), 44.20 (CH_2=$\underline{C}$H), 46.64 (C^3), 68.37 (C^6), 73.15 (C^5), 100.46 (C^1), 119.11 ($\underline{C}H_2$=CH), 119.18 ($\underline{C}H_2$=CH), 133.27 (CH_2=$\underline{C}$H), 133.38 (CH_2=$\underline{C}$H), 203.76 (C^4).

FT-IR (neat) 3432, 2978, 1715, 1697, 1437, 1364, 1230, 1115, 995, 917, 901, 825, 1100, 600 cm-1.

Mass spectrum, *m/z*: 209 [*M*H]$^+$. Calcd for $C_{12}H_{16}O_3$. 208.25.

The formation of diallyl derivative **2** is demonstrated by signals from the nodal quaternary carbon atom C^3 at δ 46.64 and two allyl moieties at δ 43.69, 44.20, 119.10, 119.17, 133.27 and 133.38.

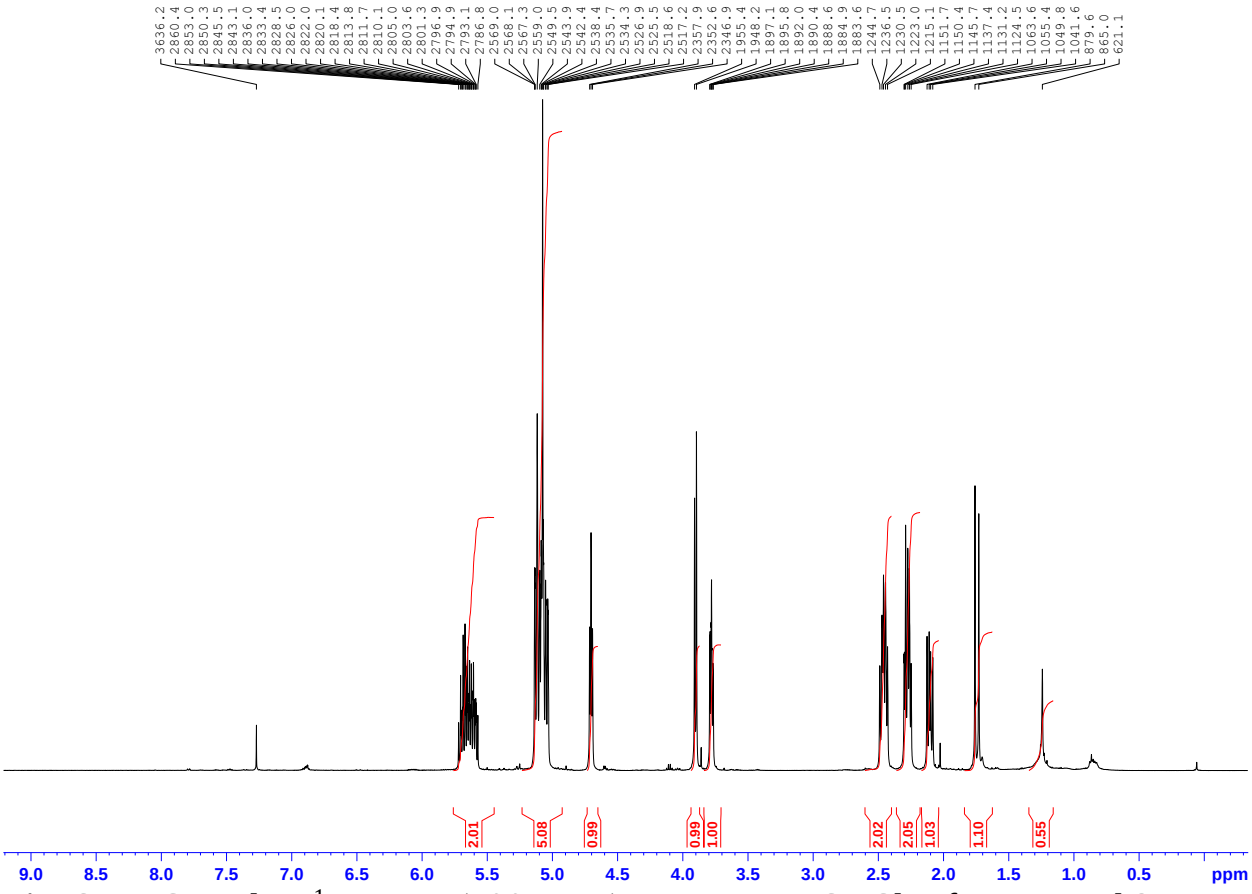


Fig. S1.1. Complete ^{1}H NMR (500 MHz) spectrum in $CDCl_3$ of compound **2**

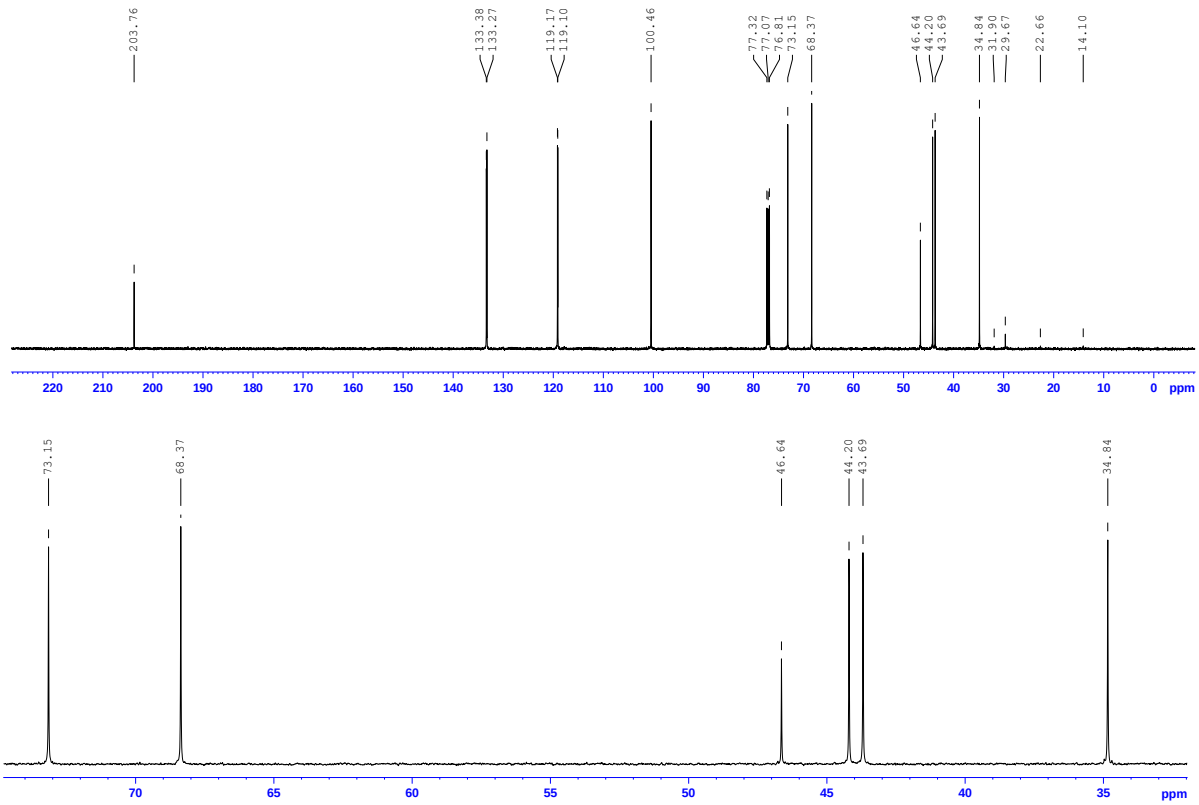


Fig. S1.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of compound **2**

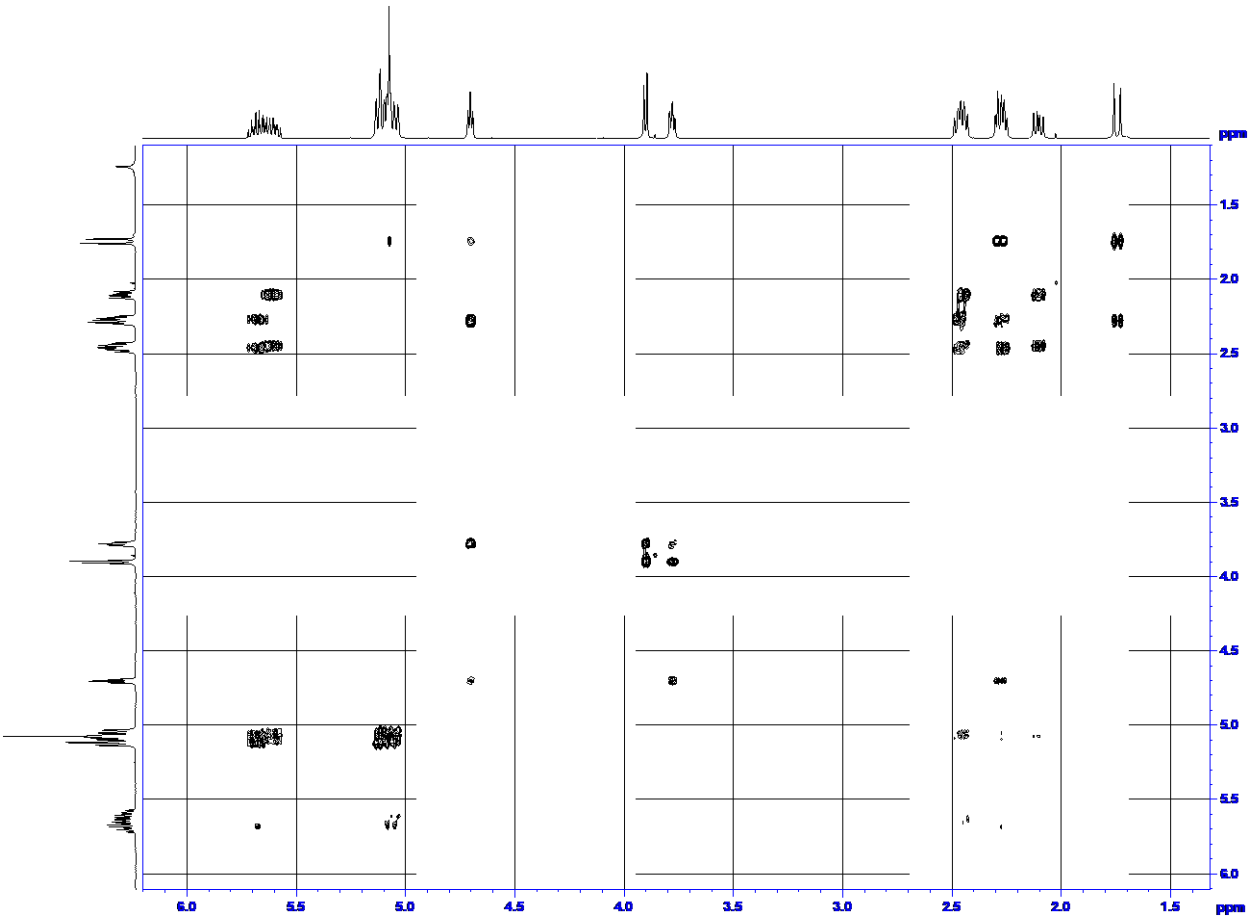


Fig. S1.3. Complete $\{^{1}H,^{1}H\}$ COSY NMR spectrum in $CDCl_3$ of compound **2**

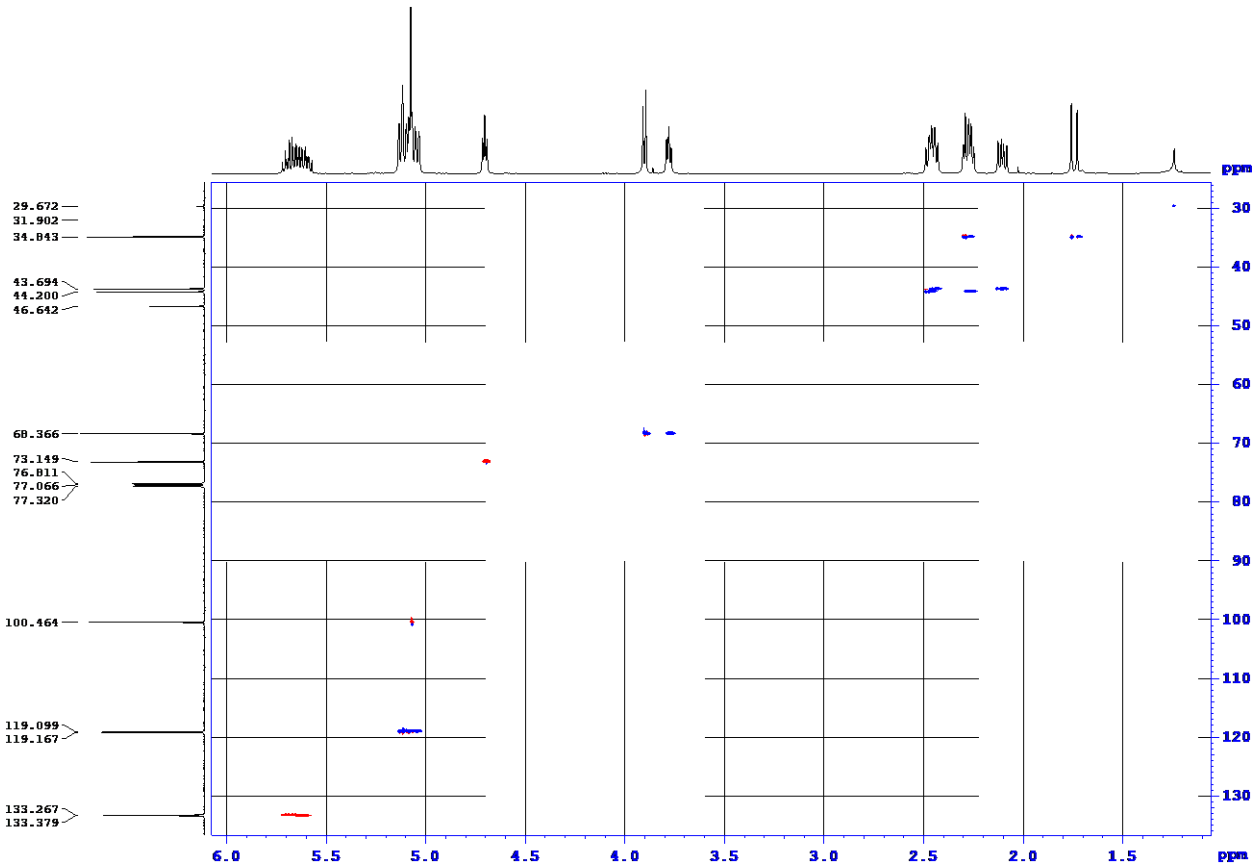


Fig. S1.4. Complete {^{1}H,^{13}C} HSQCED NMR spectrum in $CDCl_3$ of compound **2**

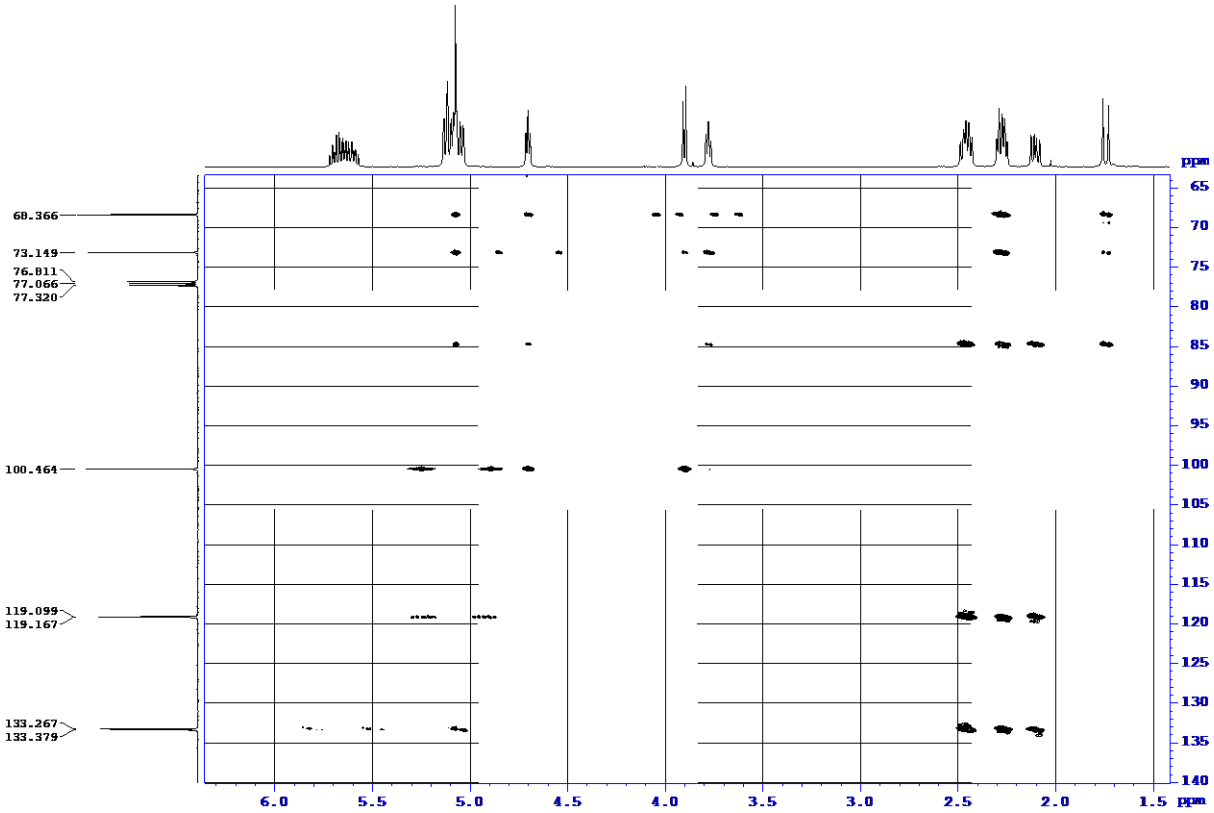


Fig. S1.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum in $CDCl_3$ of compound **2**

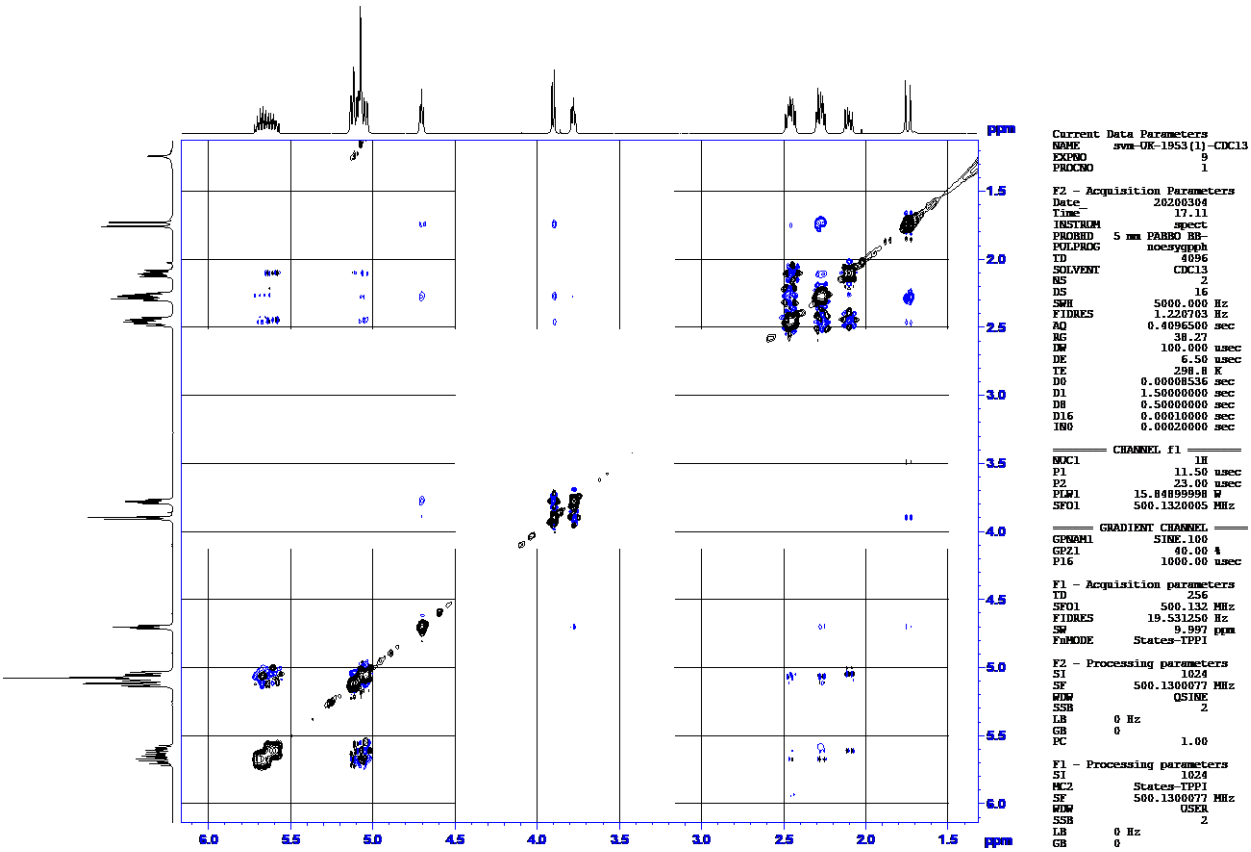
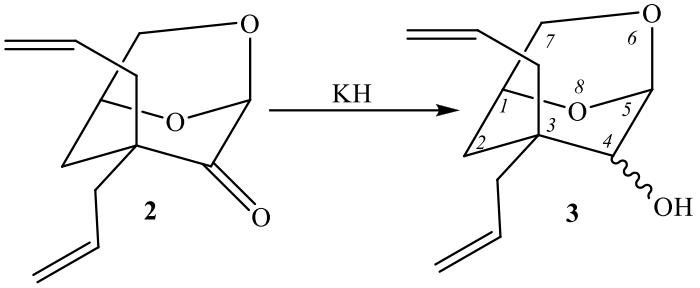


Fig. S1.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum in $CDCl_3$ of compound **2**

(1*S*,5*R*)-3,3-Diallyl-6,8-dioxabicyclo[3.2.1]octan-4-ol (3)



a) A dry Schlenk flask was charged with KH (0.07 g, washed from oil, 1.7 mmol) and THF (10 ml) under N_2. Compound **2** (0.3 g, 1.5 mmol) was added, and the resulting suspension was boiled for 15 hours. (TLC control). The reaction mixture was treated with 3% aqueous HCl to pH=7, the reaction products were extracted with EtOAc (3x10.0 ml), the extract was dried with $MgSO_4$, the solvent was distilled off on a rotary evaporator, the residue was subjected to silica gel column chromatography. Yield 0.100 g (33%).

b) Compound **2** (0.30 g, 1.4 mmol) was dissolved under argon in CH_2Cl_2 (7 ml), Et_2AlCl (0.3 ml, 2 mmol) was added, and the mixture was stirred at room temperature for 2 h until the reaction was complete (TLC). The mixture was treated with water and aqueous NH_4Cl and extracted with CH_2Cl_2 (3×10 ml). The extract was dried over $CaCl_2$, the solvent was distilled off, and the product was isolated by silica gel column chromatography. Yield 0.231 g (76%). A colourless oil, R_f 0.35 (EtOAc–petroleum ether, 1:2).

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.62 (dd, 1H, $H^{2B,}$ J = 14.6, 4.1 Hz) [1.61 (dd, 1H, $H^{2B,}$ J = 14.6, 4.1 Hz)], 1.79 (d, 1H, $H^{2A,}$ J = 14.6 Hz) [1.81 (d, 1H, $H^{2A,}$ J = 14.6 Hz)], 1.99 (dd, 1H, $H^{1''B,}$ J = 14.0, 7.0 Hz) [1.97 (dd, 1H, $H^{1''B,}$ J = 14.0, 7.0 Hz)], 2.18 (dd, 1H, $H^{1''A,}$ J = 14.0, 7.6 Hz) [1.97 (dd, 1H, $H^{1''A,}$ J = 14.0, 7.6 Hz)], 2.38-2.47 (m, 2H, $H^{1'A,}$ $H^{1'B)}$ [2.30-2.43 (m, 2H, $H^{1'A,}$ $H^{1'B)}$], 3.52 (d, 1H, $H^{4,}$ J = 1.8 Hz) [3.28 (d, 1H, $H^{4,}$ J = 2.4 Hz)], 3.70 (dd, 1H, $H^{7B,}$ J = 7.3, 5.3 Hz) [3.69 (dd, 1H, $H^{7B,}$ J = 7.3, 5.3 Hz)], 3.86 (d, 1H, $H^{7A,}$ J = 7.3 Hz) [3.87 (d, 1H, $H^{7A,}$ J = 7.3 Hz)], 4.43 (dd, 1H, $H^{1,}$ J = 5.3, 4.1 Hz) [4.42 (dd, 1H, $H^{1,}$ J = 5.3, 4.1 Hz)], 5.06-5.13 (m, 4H, $H^{3'A,}$ $H^{3'B,}$ $H^{3''A,}$ $H^{3''B)}$ [5.07-5.14 (m, 4H, $H^{3'A,}$ $H^{3'B,}$ $H^{3''A,}$ $H^{3''B)}$], 5.31 (d, 1H, $H^{5,}$ J = 1.8 Hz) [5.43 (d, 1H, $H^{5,}$ J = 2.4 Hz)], 5.78-5.96 (m, 2H, $H^{2',}$ $H^{2'')}$ [5.07-5.14 (m, 2H, $H^{2',}$ $H^{2'')}$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 34.84 [34.59] (C^2), 36.43 [39.43] ($C^{1'}$), 39.85 [37.34] (C^3), 45.78 [] ($C^{1''}$), 67.60 [67.26] (C^7), 73.47 [72.38] (C^1), 74.57 [71.12] (C^4), 102.39 [102.71] (C^5), 118.26 [118.11] ($C^{3'}$), 118.31 [118.42] ($C^{3''}$), 134.86 [134.02] ($C^{2'}$), 135.26 [134.57] ($C^{2''}$).

FT-IR (neat) 3448, 3074, 2975, 2948, 1637, 1152, 1067, 912, 595 cm-1. Mass spectrum, *m/z*: 211 $[MH]^+$. Calcd for $C_{12}H_{18}O_3$

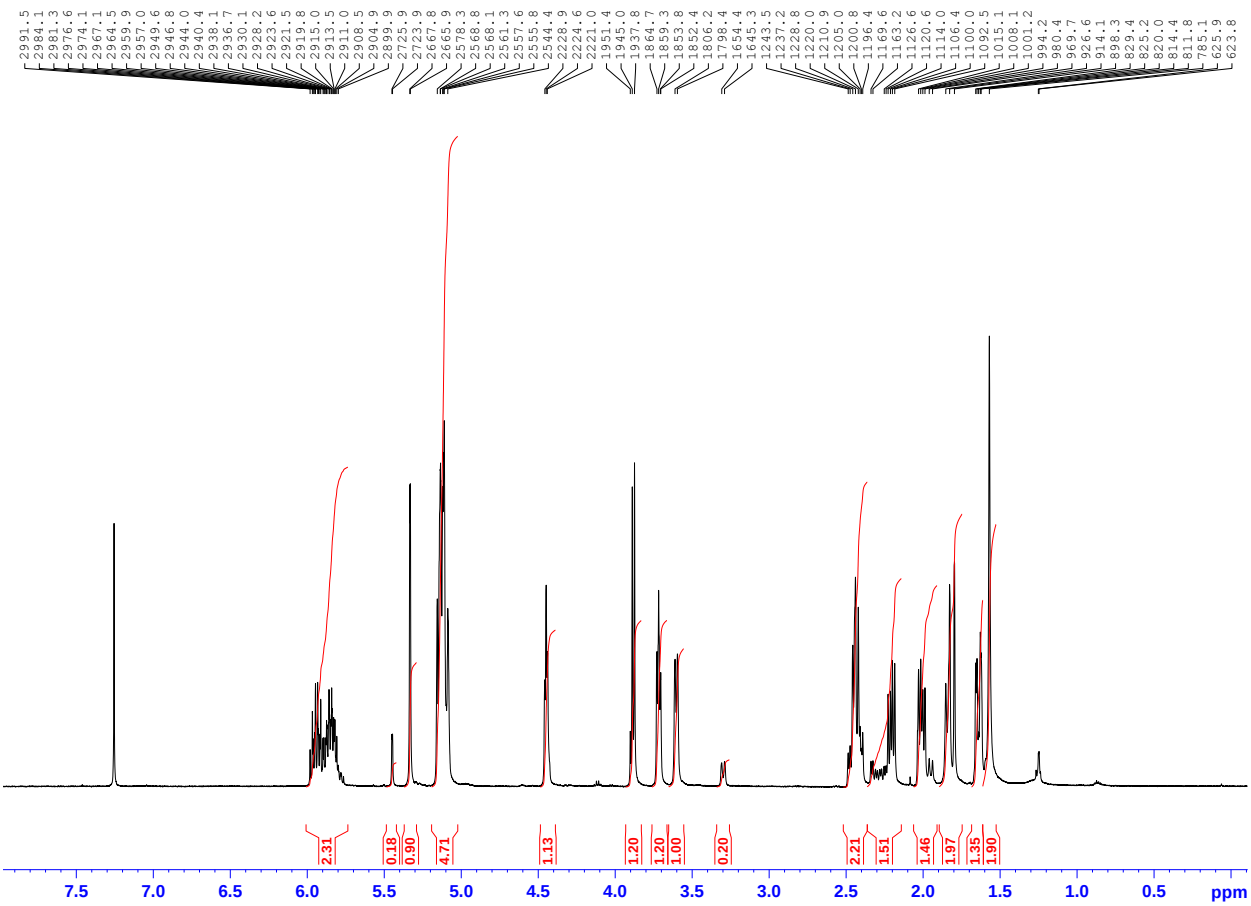


Fig. S2.1. Complete ^{1}H NMR (500 MHz) spectrum in $CDCl_3$ of compound **3**

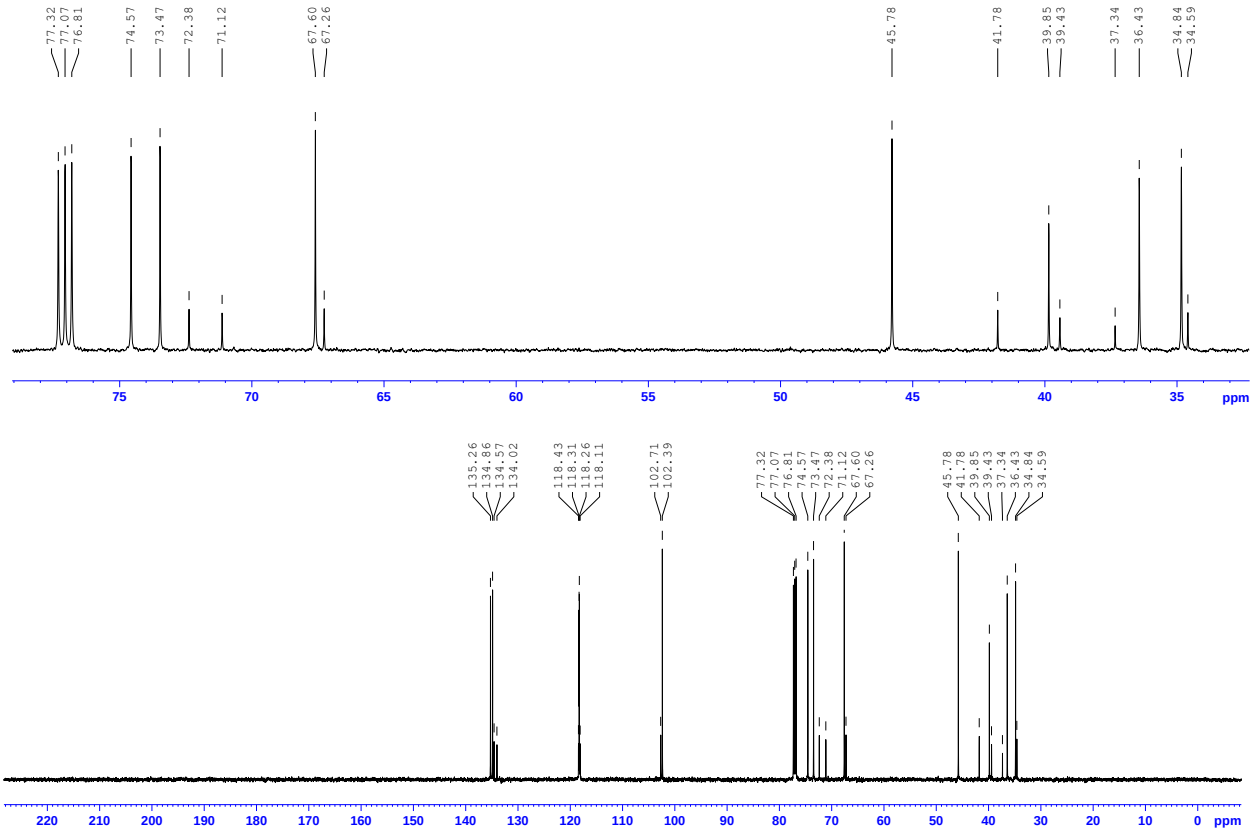


Fig. S2.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of compound **3**

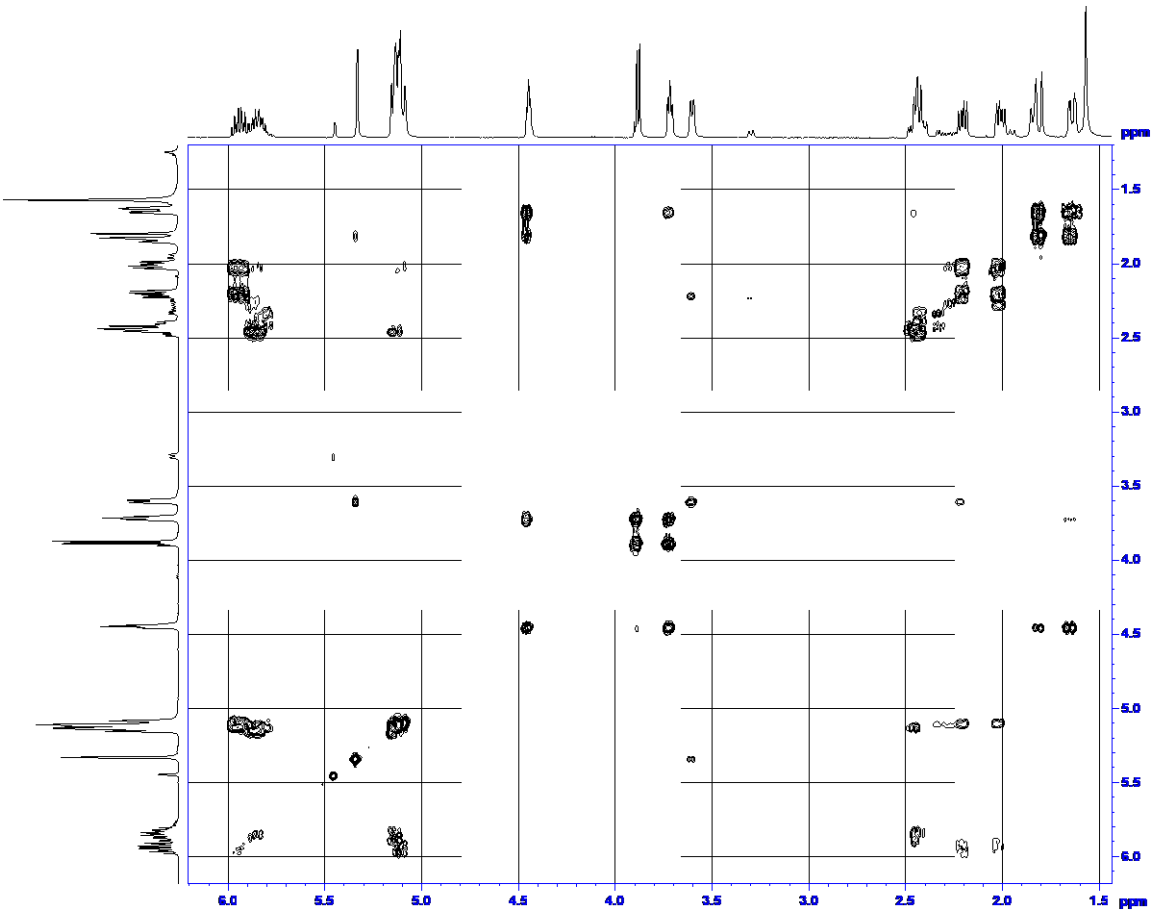


Fig. S2.3. Complete {^{1}H,^{1}H} COSY NMR spectrum in $CDCl_3$ of compound **3**

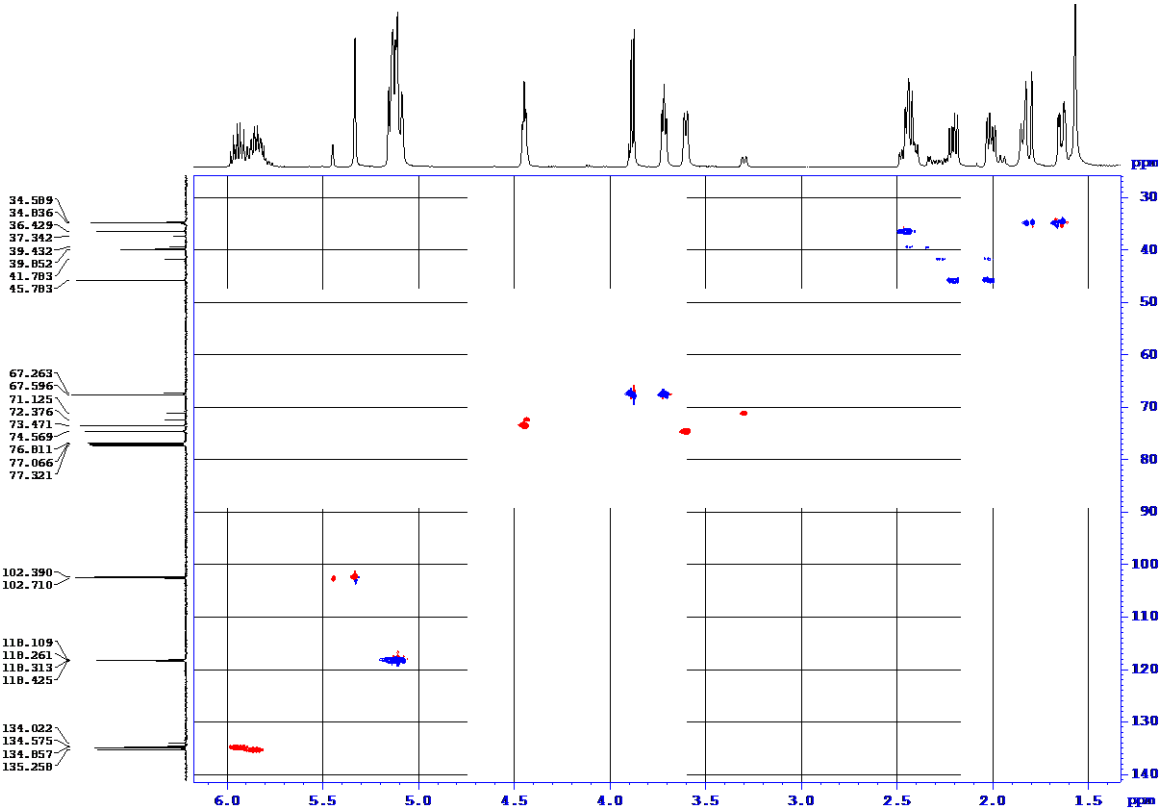


Fig. S2.4. Complete {^{1}H,^{13}C} HSQCED NMR spectrum in $CDCl_3$ of compound **3**

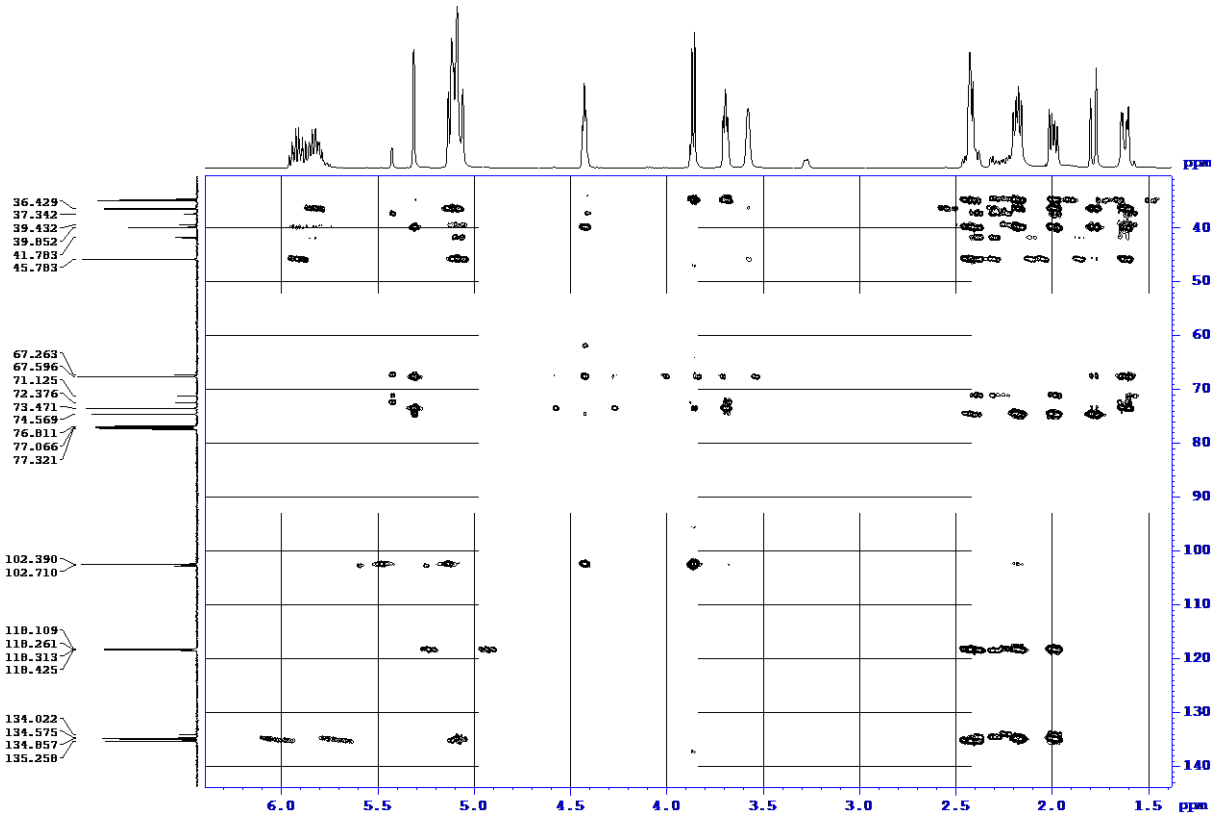


Fig. S2.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum in $CDCl_3$ of compound **3**

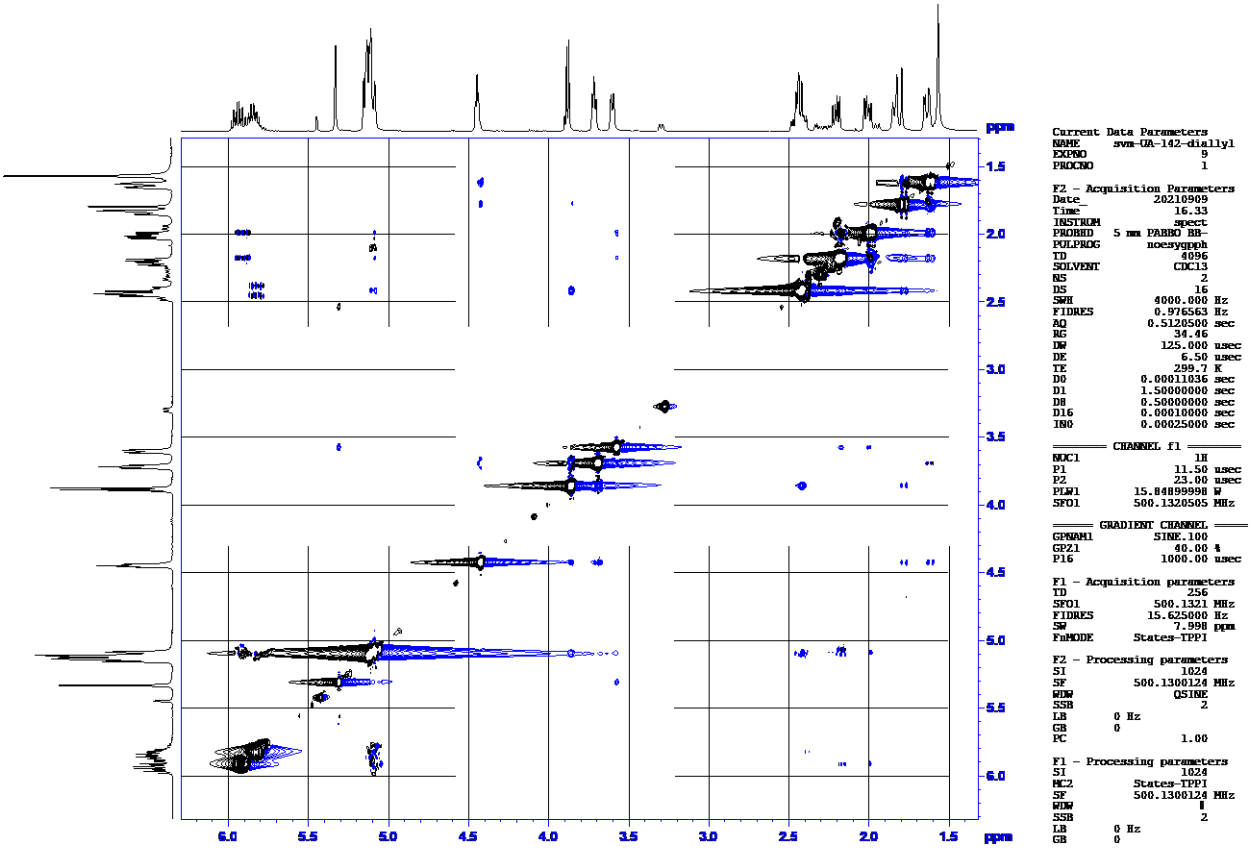
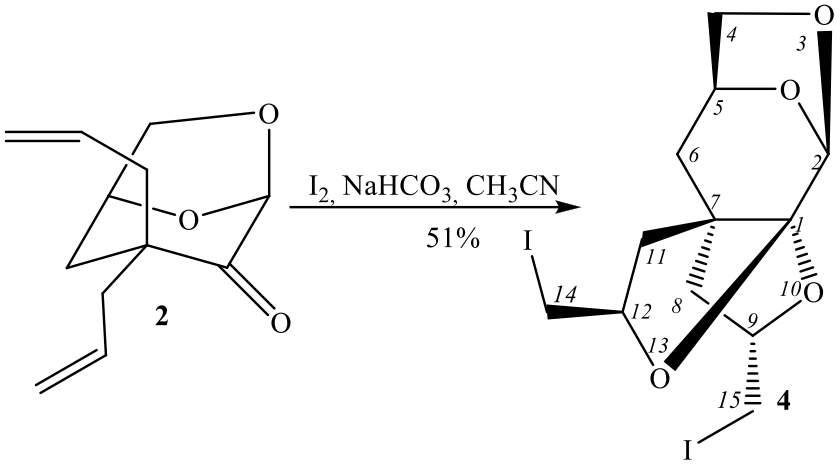


Fig. S2.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum in $CDCl_3$ of compound **3**

9,12-Bis(iodomethyl)-3,10,11,14-tetraoxatetracyclo[5.3.3.1^{2,5}.0^{1,7}]tetradecane (4)



A solution of compound **2** (0.112 g, 0.5 mmol) in MeCN (5.0 ml) was cooled to 0°C, $NaHCO_3$ (0.09 g, 1 mmol) and iodine (0.127 g, 1 mmol) were added, and the mixture was stirred at room temperature for 1 h (TLC). The mixture was treated with water (7 ml) and extracted with ethyl acetate (3×10 ml). The extract was washed with aqueous $Na_2S_2O_3$ and with water and dried over $MgSO_4$. The solvent was distilled off, and the residue was subjected to silica gel chromatography to isolate 0.13 g (51%) of diiodide **4**. A colourless oil.

$[\alpha]_D^{20}$ -10.4° (*c* 1.0, $CHCl_3$). R_f 0.15 (EtOAc–petroleum ether, 1:2).

^{1}H NMR (500 MHz, $CDCl_3$): 1.65 (dd, 1H, H^{11B}, *J* = 12.4, 11.0 Hz), 1.99 (dd, 1H, H^{8B}, *J* = 13.6, 5.8 Hz), 2.03 (d, 1H, H^{6B}, *J* = 14.8 Hz), 2.10 (dd, 1H, H^{6A}, *J* = 14.8, 5.0 Hz), 2.24 (dd, 1H, H^{8A}, *J* = 13.6, 8.2 Hz), 2.49 (dd, 1H, H^{11A}, *J* = 12.4, 5.1 Hz), 3.13 (t, 1H, H^{14B}, *J* = 9.1 Hz), 3.46 (t, 1H, H^{15B}, *J* = 9.1 Hz), 3.33-3.39 (m, 2H, H^{14A}, H^{15A}), 3.75 (dd, 1H, H^{4B}, *J* = 7.5, 5.0 Hz), 3.86 (d, 1H, H^{4A}, *J* = 7.5 Hz), 4.38-4.45 (m, 2H, H^9, H^{12}), 4.59 (t, 1H, H^5, *J* = 5.0 Hz), 5.32 (s, 1H, H^2).

^{13}C NMR (125 MHz, $CDCl_3$): δ 7.63 (C^{14}), 8.76 (C^{15}), 39.09 (C^6), 47.88 (C^8), 48.00 (C^{11}), 48.36 (C^7), 68.13 (C^4), 72.22 (C^5), 78.48 (C^{12}), 79.60 (C^9), 99.28 (C^2), 112.78 (C^1).

FT-IR (neat) 2955, 2893, 1155, 1080, 1038, 993, 920, 696 cm-1

Mass spectrum, *m/z*: 479 [*M*H]$^+$. Calcd for $C_{12}H_{16}I_2O_3$.

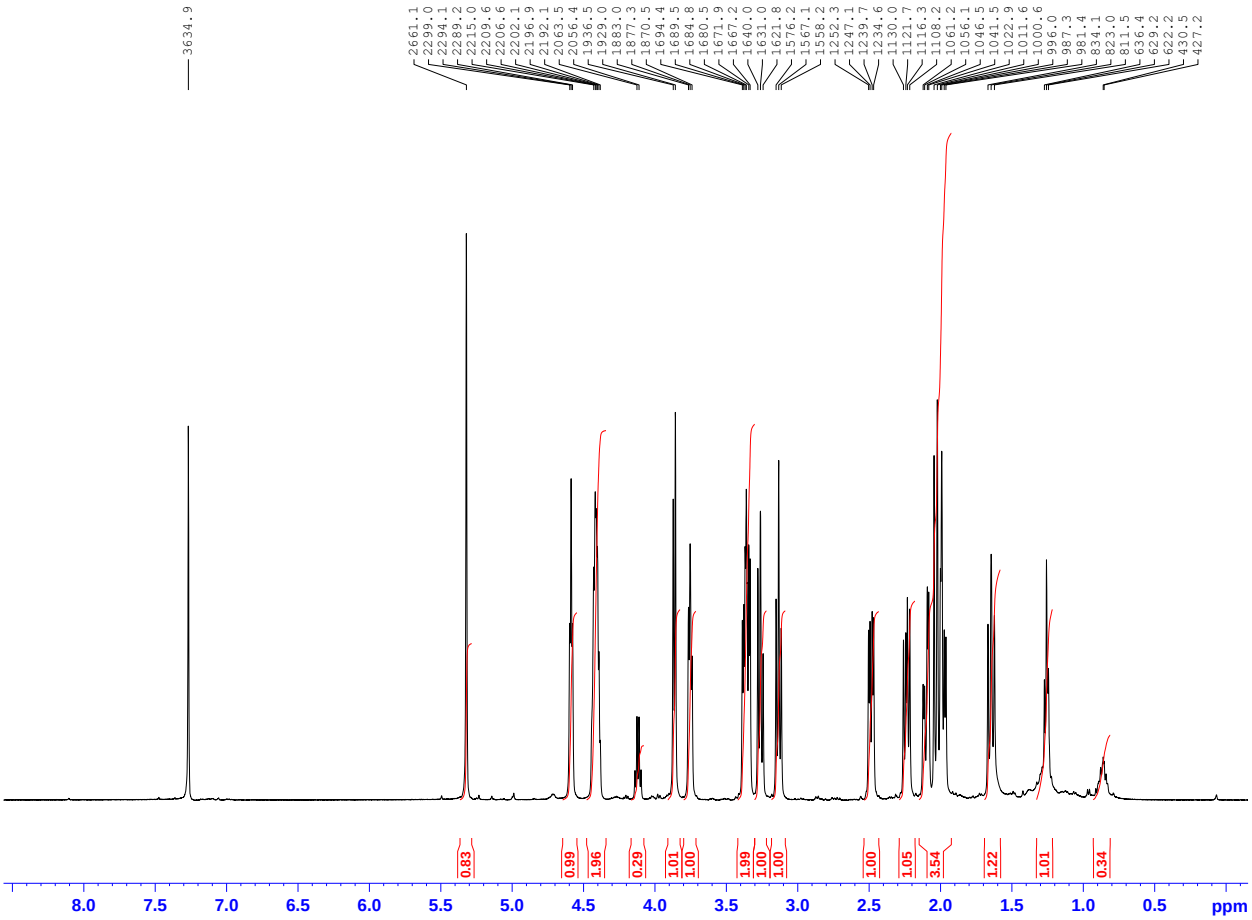


Fig. S3.1. Complete ^{1}H NMR (500 MHz) spectrum in $CDCl_3$ of compound **4**

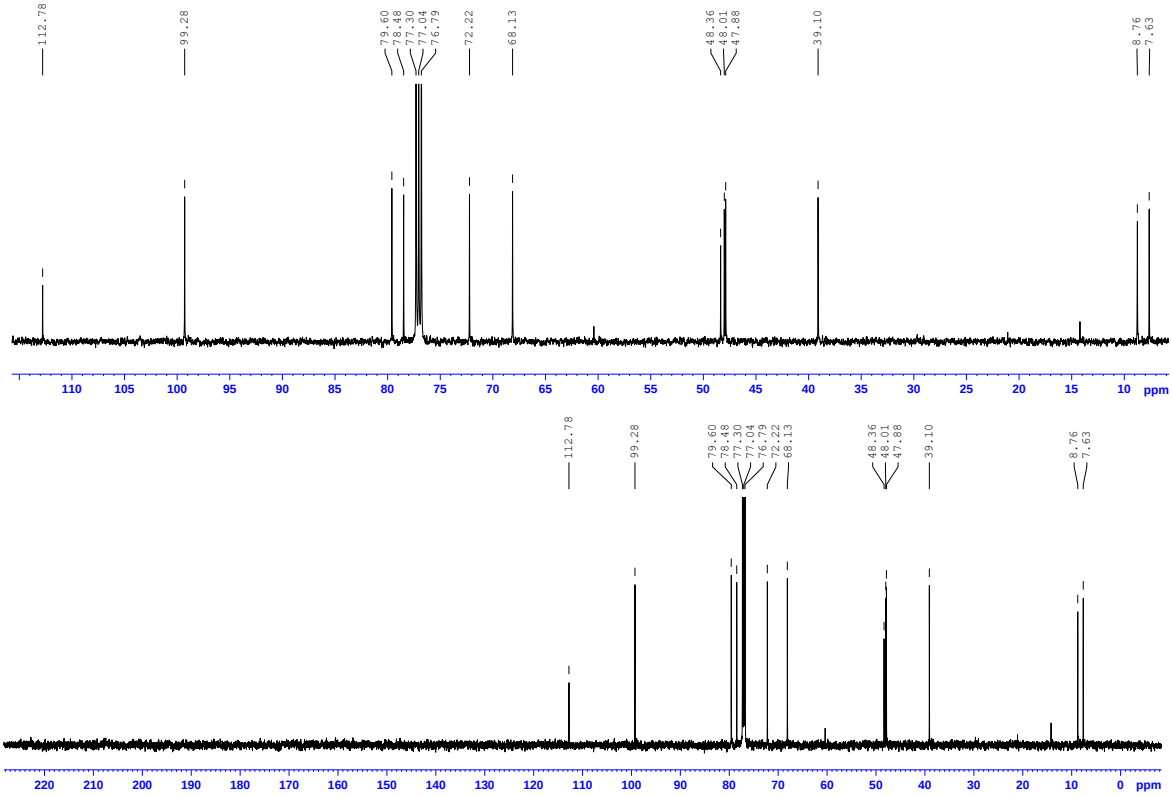


Fig. S3.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of compound **4**

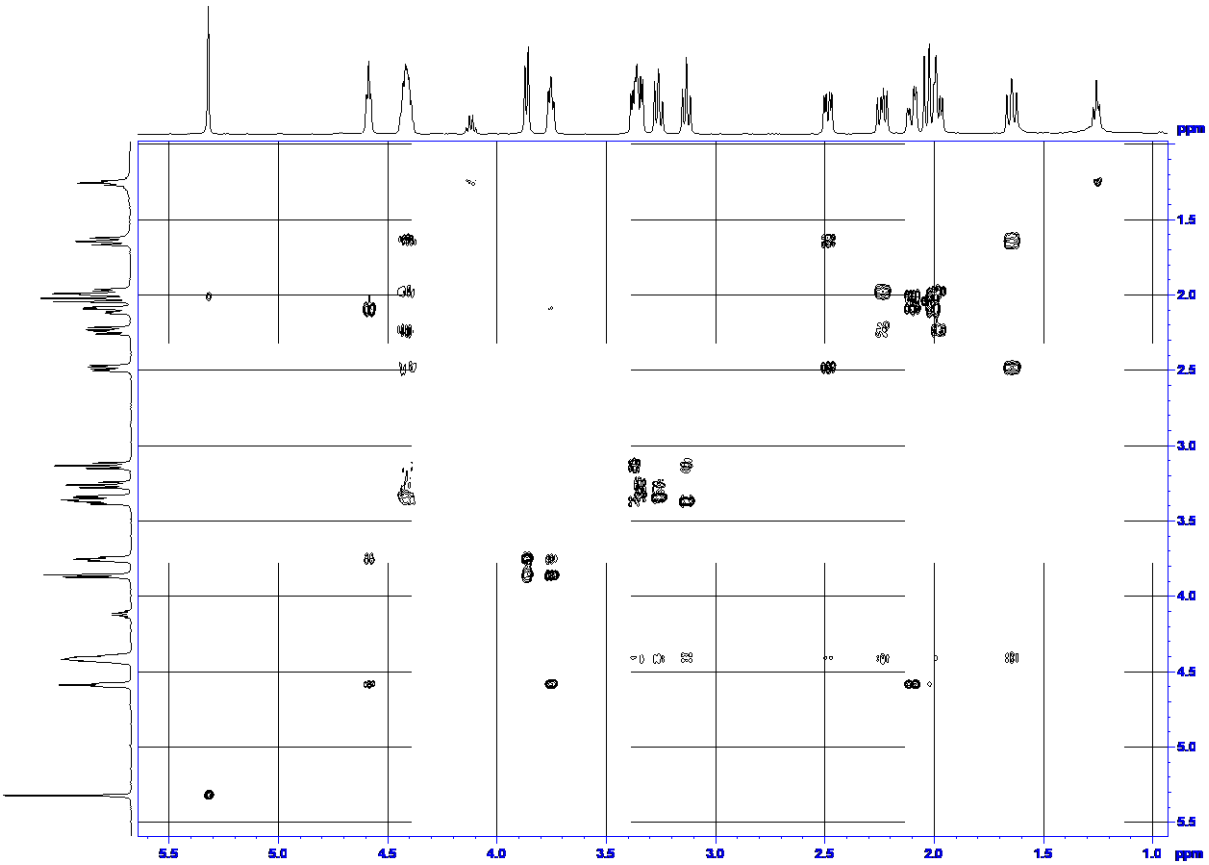


Fig. S3.3. Complete {^{1}H,^{1}H} COSY NMR spectrum in $CDCl_3$ of compound **4**

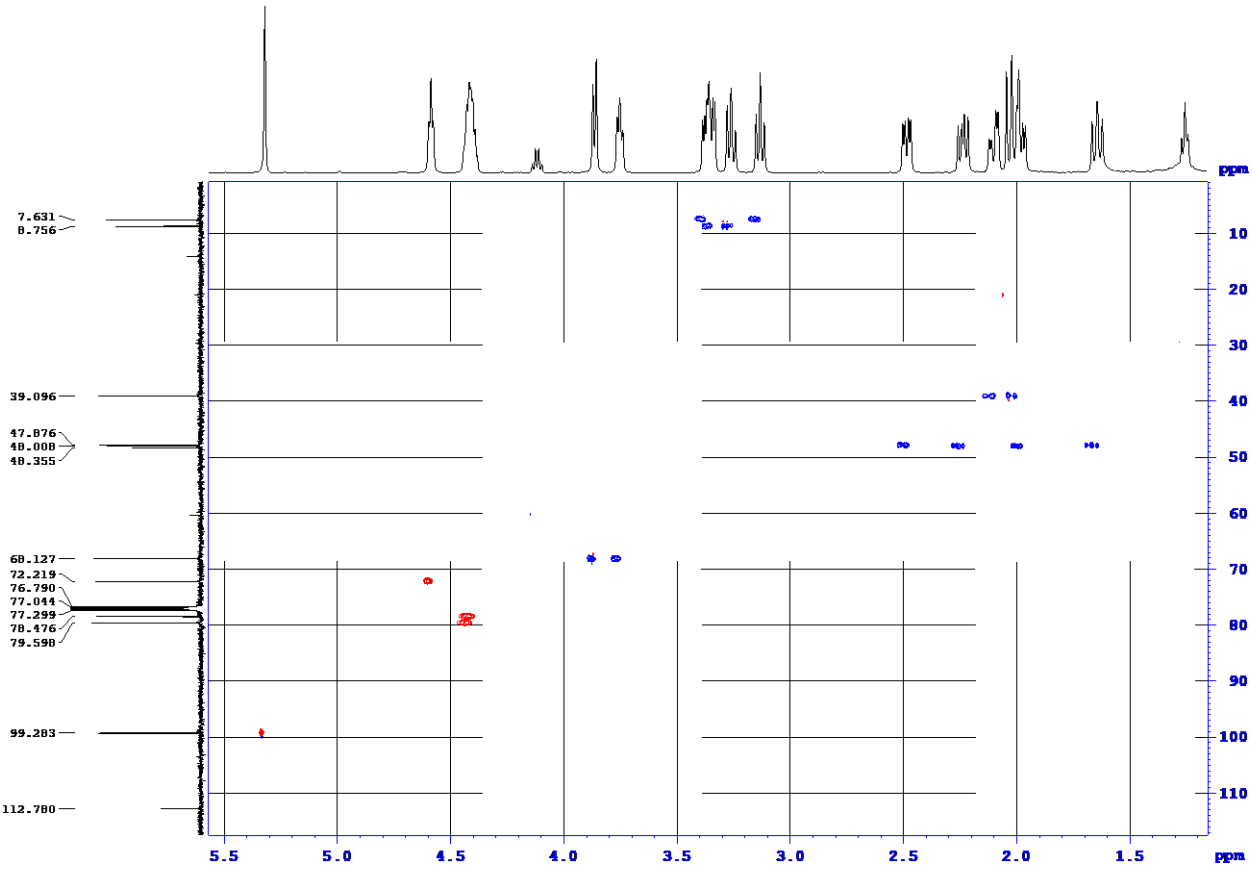


Fig. S3.4. Complete {^{1}H,^{13}C} HSQCED NMR spectrum in $CDCl_3$ of compound **4**

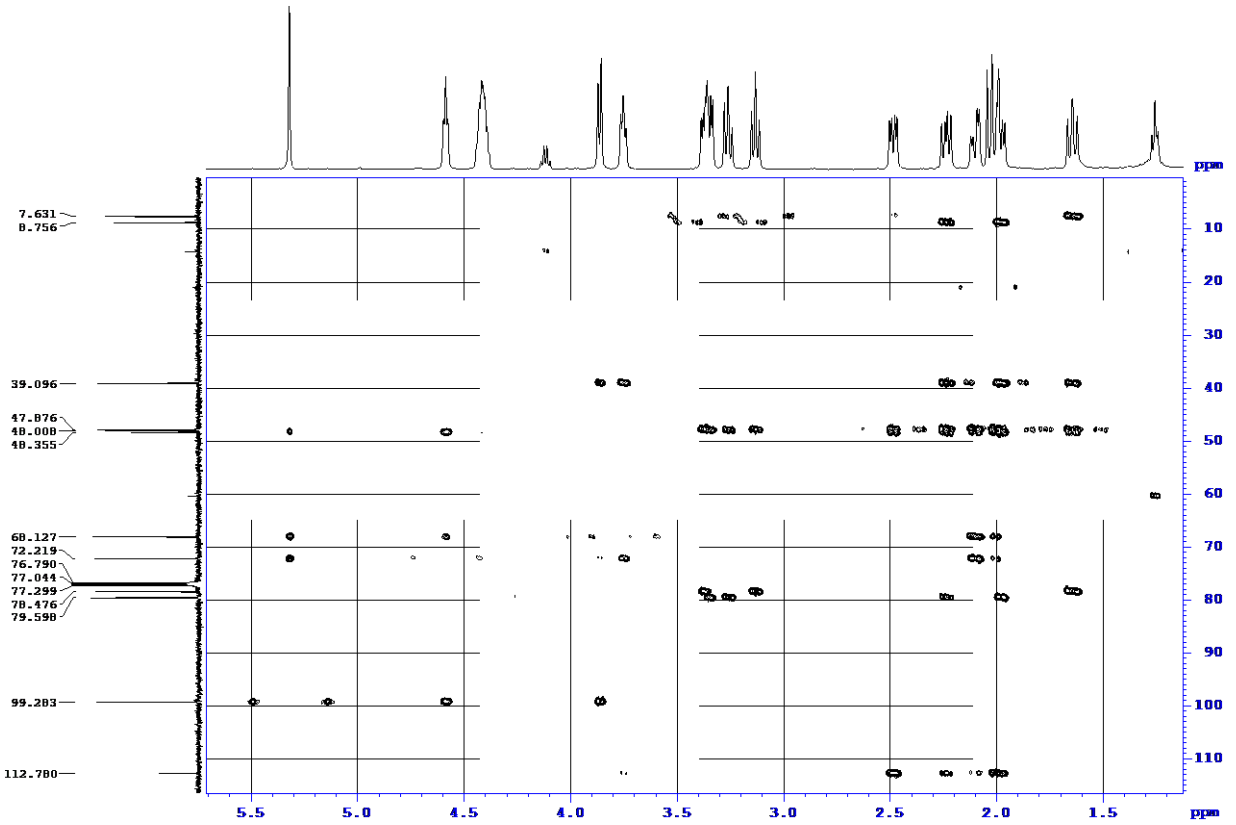


Fig. S3.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum in $CDCl_3$ of compound **4**

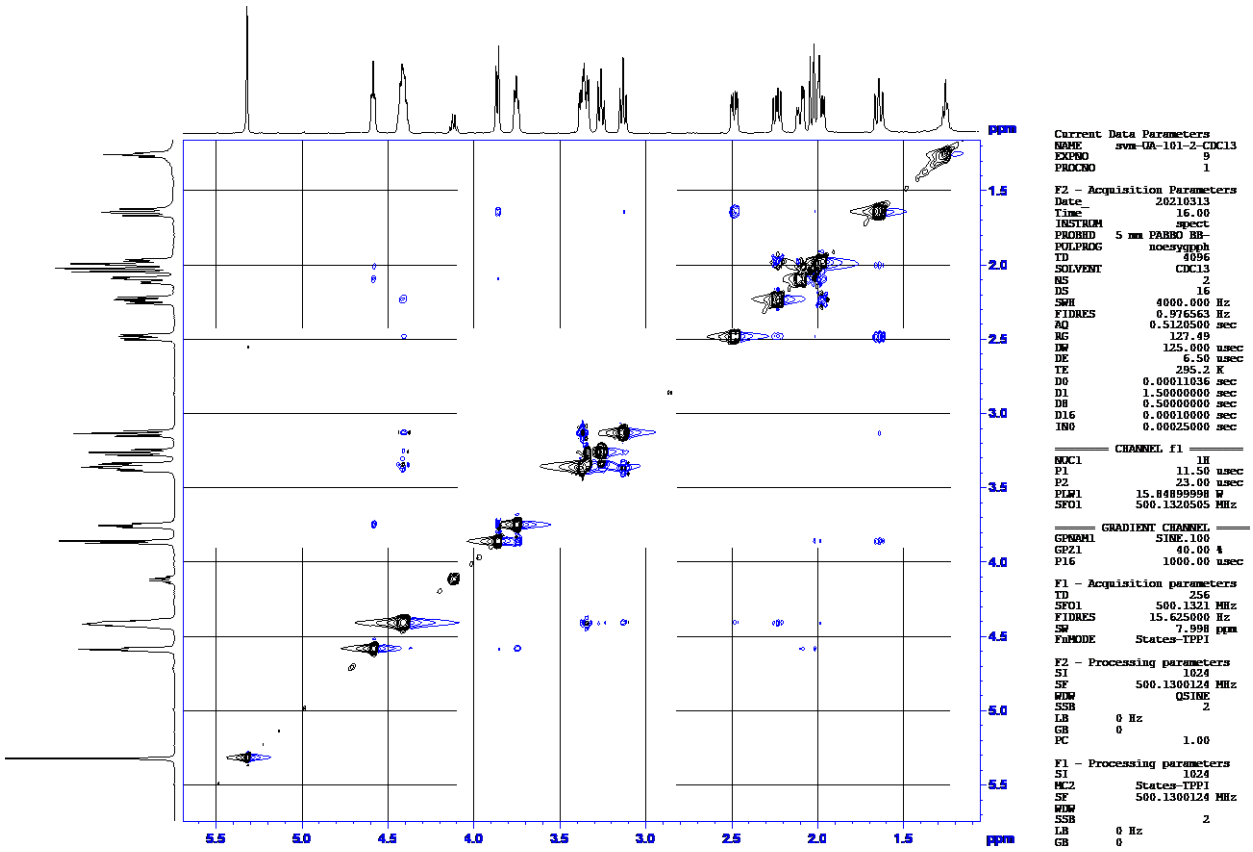
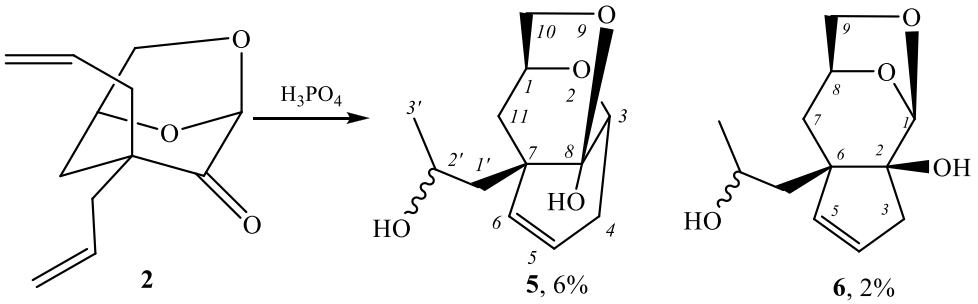


Fig. S3.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum in $CDCl_3$ of compound **4**

(1*S*,3*R*,7*S*,8*S*)-7-(2-Hydroxypropyl)-2,9-dioxatricyclo[5.3.1.0^{3,8}]undec-5-en-8-ol (5) and (1*R*,2*S*,6*S*,8*S*)-6-(2-hydroxypropyl)-10,11-dioxatricyclo[6.2.1.0^{2,6}]undec-4-en-2-ol (6).



Compound **2** (0.34 g, 2 mmol) was dissolved in concentrated H_3PO_4 (3 ml), and the solution was stirred at room temperature for 10 days (TLC control). The reaction mixture was treated with aqueous $NaHCO_3$ to pH=7, the reaction products were extracted with EtOAc (3×5.0 ml), the extract dried with $MgSO_4$, the solvent was distilled off on a rotary evaporator, the residue was subjected to silica gel column chromatography.

Product 5, a 4:1 mixture of (2'*R*)/(2'*S*) isomers. Yield 0.02 g (6%). White crystals, mp 94 °C. $[\alpha]_D^{20}$ +0.7° (*c* 1.0, $CHCl_3$), R_f 0.13 (EtOAc–petroleum ether, 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35 [1.18] (d, 3H, H$^{3'}$, $^3J_{3',2'}$ 6.3 Hz), 1.80 [1.79] (d, 1H, H^{11B}, $^2J_{11B,11A}$ 13.0 Hz), 1.88 (dd, 1H, H$^{1'B}$, $^2J_{1'B,1'A}$ 11.5, $^3J_{1'B,2'}$ 10.0 Hz) [1.66 (dd,1H, H$^{1'B}$, $^2J_{1'B,1'A}$ 11.8, $^3J_{1'B,2'}$ 2.2 Hz)], 2.00 (dd, 1H, H$^{1'A}$, $^2J_{1'A,1'B}$ 11.5, $^3J_{1'A,2'}$ 5.5 Hz) [2.38 (dd, 1H, H$^{1'A}$, $^2J_{1'A,1'B}$ 11.8, $^3J_{1'A,2'}$ 10.0 Hz)], 2.12 [2.14] (ddd, 1H, H^{11A}, $^2J_{11A,11B}$ 13.0, $^3J_{11A,1}$ 5.5, $^3J_{11A,10A}$ 2.2 Hz), 2.23-2.28 [2.24-2.30] (m, 1H, H^{4B}), 2.36-2.41 [2.37-2.42] (m, 1H, H^{4A}), 3.88-3.93 [3.89-3.94] (m, 2H, H^{10A}, H^{10B}), 4.17-4.21 [4.53-4.59] (m, 1H, H$^{2'}$), 4.50 [4.51] (t, 1H, H^3, $^3J_{3,4B}$ 2.2, $^3J_{3,4A}$ 2.2 Hz), 5.45-5.49 [5.37-5.52] (m, 1H, H^5, H^6). ^{13}C NMR (500 MHz, $CDCl_3$): δ 22.09 [22.08] (C$^{3'}$), 31.23 [31.14] (C^4), 36.97 [37.99] (C^{11}), 41.99 [41.55] (C$^{1'}$), 46.58 [45.42] (C^7), 65.99 [65.65] (C^1), 71.00 [71.02] (C^{10}), 73.75 [73.81] (C^3), 78.86 [77.63] (C$^{2'}$), 102.14 [102.44] (C^8), 121.61 [119.85] (C^5), 134.09 [136.16] (C^4). IR (neat) 2969, 2874, 1316, 1182, 1062, 1007, 979, 934, 810, 722 cm-1; Mass spectrum, *m/z*: 227 [*M*H]$^+$. Calcd for $C_{12}H_{18}O_4$ 226.12.

Product 6, a 8:1 mixture of (2'*R*)/(2'*S*) isomers. Yield 0.01 g (2%). White crystals, mp 64°C. $[\alpha]_D^{20}$ +275.7° (*c* 0.4, $CHCl_3$), R_f 0.34 (EtOAc–petroleum ether, 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 [1.14] (d, 3H, H$^{3'}$, $^3J_{3',2'}$ 6.0 Hz), 1.59 (t, 1H, H$^{1'B}$, $^2J_{1'B,1'A}$ 11.7, $^3J_{1'B,2'}$ 11.7 Hz) [1.82 (dd, 1H, H$^{1'B}$, $^2J_{1'B,1'A}$ 12.5, $^3J_{1'B,2'}$ 4.8 Hz)], 1.80 [1.79] (ddd, 1H, H^{7A}, $^2J_{7A,7B}$ 14.3, $^3J_{7A,8}$ 5.3, $^3J_{7A,9A}$ 1.5 Hz), 1.99 [2.00] (d, 1H, H^{7B}, $^2J_{7B,7A}$ 14.3 Hz), 2.08 (dd, 1H, H$^{1'A}$, $^2J_{1'A,\ 1'B}$ 11.7, $^3J_{1'A,2'}$ 4.8 Hz) [2.21 (dd, 1H, H$^{1'A}$, $^2J_{1'A,\ 1'B}$ 12.5, $^3J_{1'A,2'}$ 8.5 Hz)], 2.44 [2.45] (dt, 1H, H^{3B}, $^2J_{3B,3A}$ 17.3, $^3J_{3B,4}$ 2.3, $^4J_{3B,5}$ 2.3 Hz), 2.66 [2.58] (dt, 1H, H^{3A}, $^2J_{3A,3B}$ 17.3, $^3J_{3A,4}$ 2.3, $^4J_{3A,5}$ 2.3 Hz), 3.80 [3.81] (ddd, 1H, H^{9B}, $^2J_{9B,9A}$ 7.3, $^3J_{9B,8}$ 5.3, $^3J_{9B,7A}$ 1.5 Hz), 3.90 [3.93] (d,1H, H^{9A}, $^2J_{9A,9B}$ 7.3 Hz), 3.96-4.03 [4.46-4.51] (m, 1H, H$^{2'}$), 4.43 [4.45] (t, 1H, H^8, $^3J_{8,9B}$ 5.3, $^3J_{8,7A}$ 5.3 Hz), 5.35 [5.34] (s, 1H, H^1), 5.42 [5.49] (dt,1H, H^5, $^3J_{5,4}$ 5.7, $^4J_{5,3A}$ 2.3,

$^{4}J_{5,3B}$ 2.3 Hz), 5.65 [5.53] (dt, 1H, H^{4}, $^{3}J_{4,5}$5.7, $^{3}J_{4,3A}$ 2.3, $^{3}J_{4,3B}$ 2.3 Hz). ^{13}C NMR (500 MHz, $CDCl_3$): δ 20.29 [23.16] ($C^{3'}$), 37.99 [39.39] (C^{7}), 42.47 [41.67] (C^{3}), 46.18 [46.54] ($C^{1'}$), 54.75 [54.11] (C^{6}), 68.63 [68.56] (C^{9}), 70.48 [70.59] (C^{8}), 75.19 [75.27] ($C^{2'}$), 88.67 [90.25] (C^{2}), 101.49 [102.63] (C^{1}), 127.47 [124.78] (C^{4}), 137.67 [139.99] (C^{5}). IR (neat) 2923, 2850, 2375, 1217, 829 cm-1; Mass spectrum, *m/z*: 227 $[MH]^{+}$. Calcd for $C_{12}H_{18}O_4$ 226.27.

The HMBC spectrum of compounds **5** contains H^{3}/C^{8}, H^{3}/C^{7} and H^{4}/C^{3} correlation peaks, which indicates that the allyl moiety is closed on the C^{3} center. The H^{3} proton is recorded as a triplet at δ 4.50 with $^{3}J_{3\text{-}4A}$ 2.2 Hz and $^{3}J_{3\text{-}4B}$ 2.2 Hz. The presence of the H^{6}/H^{11A} correlation peaks in the NOESY spectra results from the *S* configuration of the C^{7} center.

The retention of the 1,6-anhydro bridge in compounds **6** was proved by the presence of the H^{9A}/C^{1} and H^{8}/C^{1} correlation peaks in the HMBC spectrum. Moreover, the HMBC spectra contain the H^{1}/C^{2} and H^{3B}/C^{2} correlation peaks that indicate that an axial allyl moiety has been added to the C^{2} center. The presence of an NOE effect between the $H^{9A}/H^{1'B}$, H^{9A}/H^{7B} and H^{5}/H^{7A} protons is due to the *S* - configuration of the C^{8} and C^{6} centers.

NMR spectrum of compound **5**:

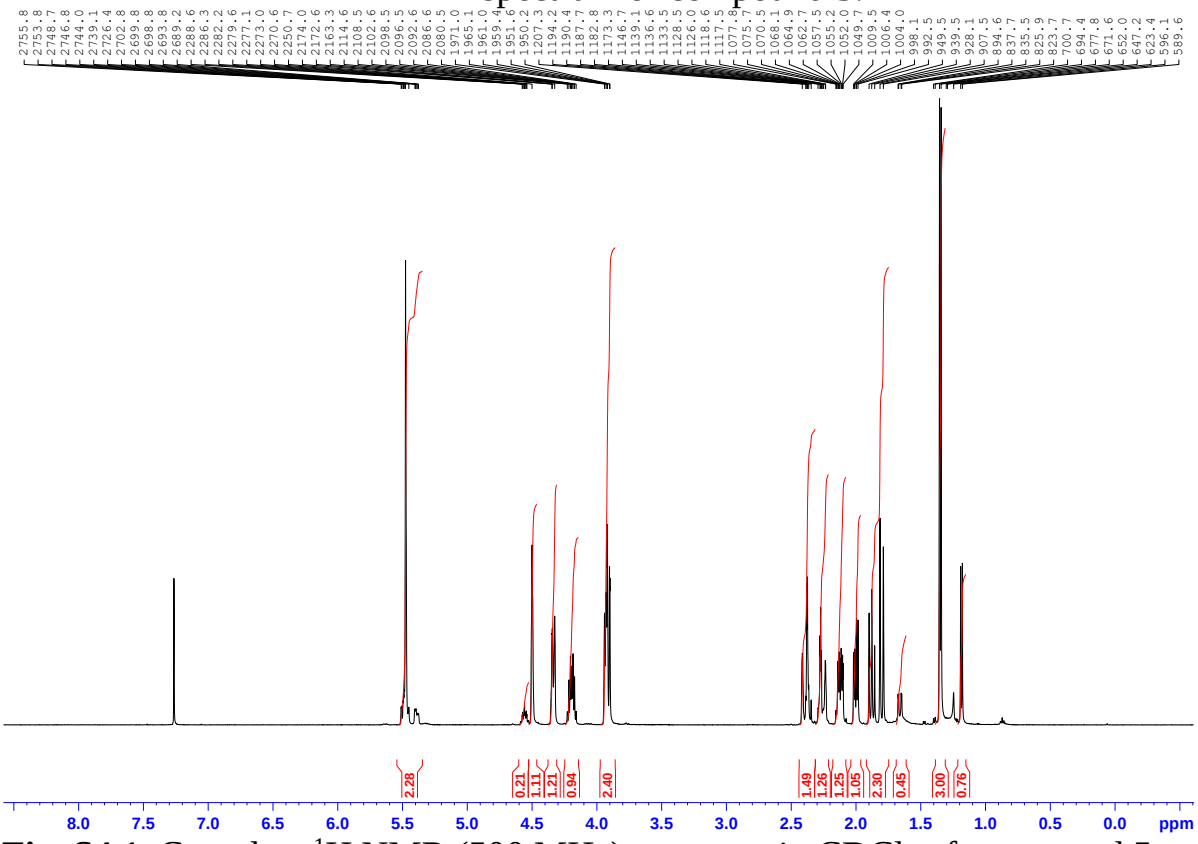


Fig. S4.1. Complete ^{1}H NMR (500 MHz) spectrum in $CDCl_3$ of compound **5**

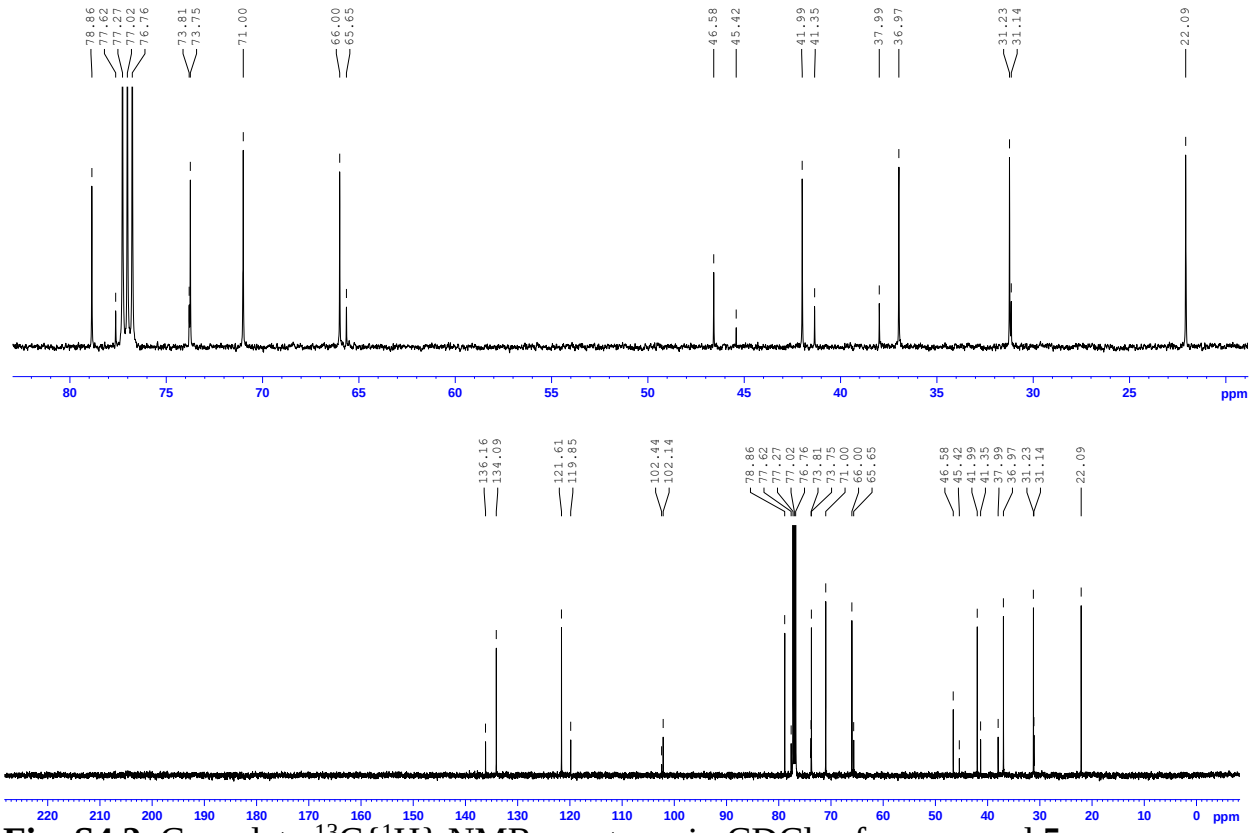


Fig. S4.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of compound **5**

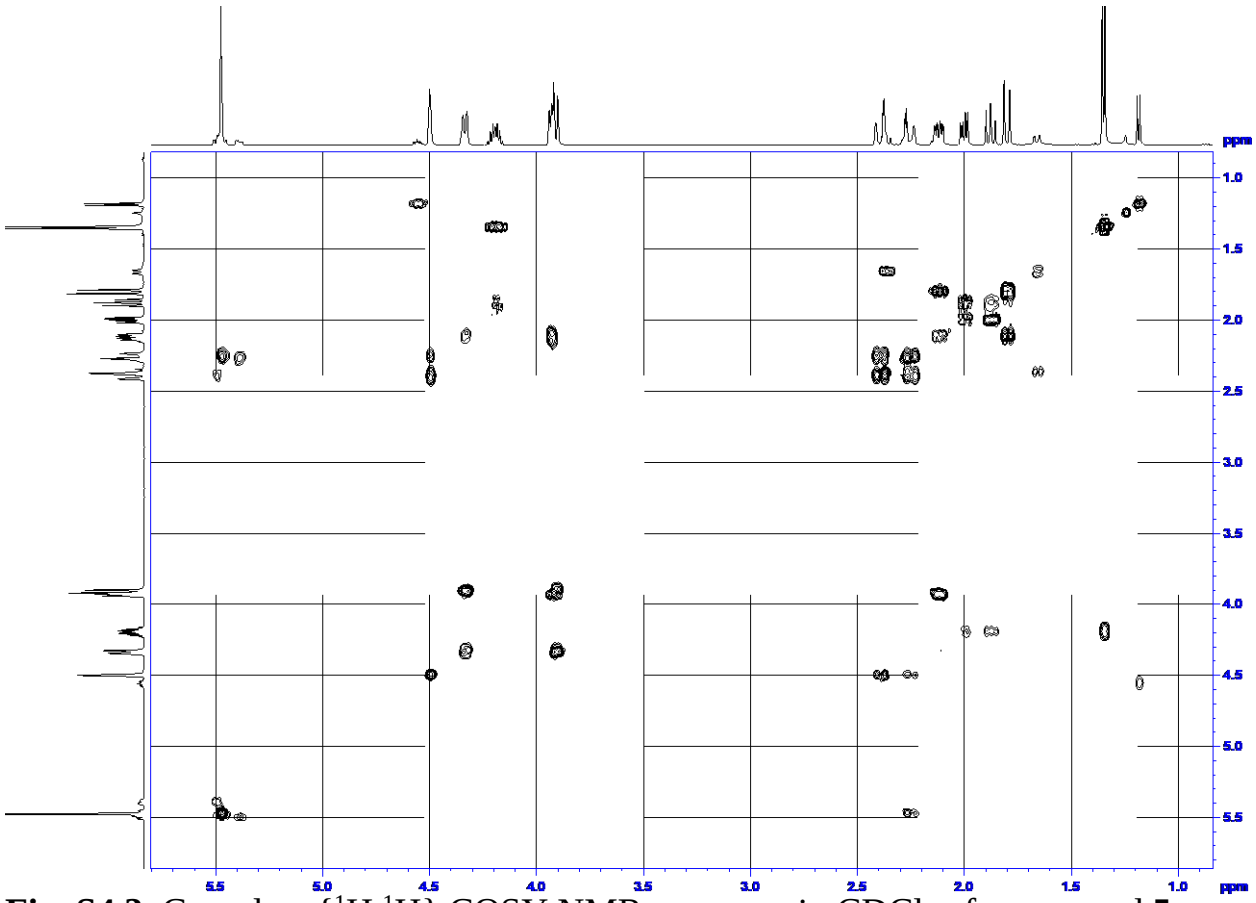


Fig. S4.3. Complete $\{^{1}H,^{1}H\}$ COSY NMR spectrum in $CDCl_3$ of compound **5**

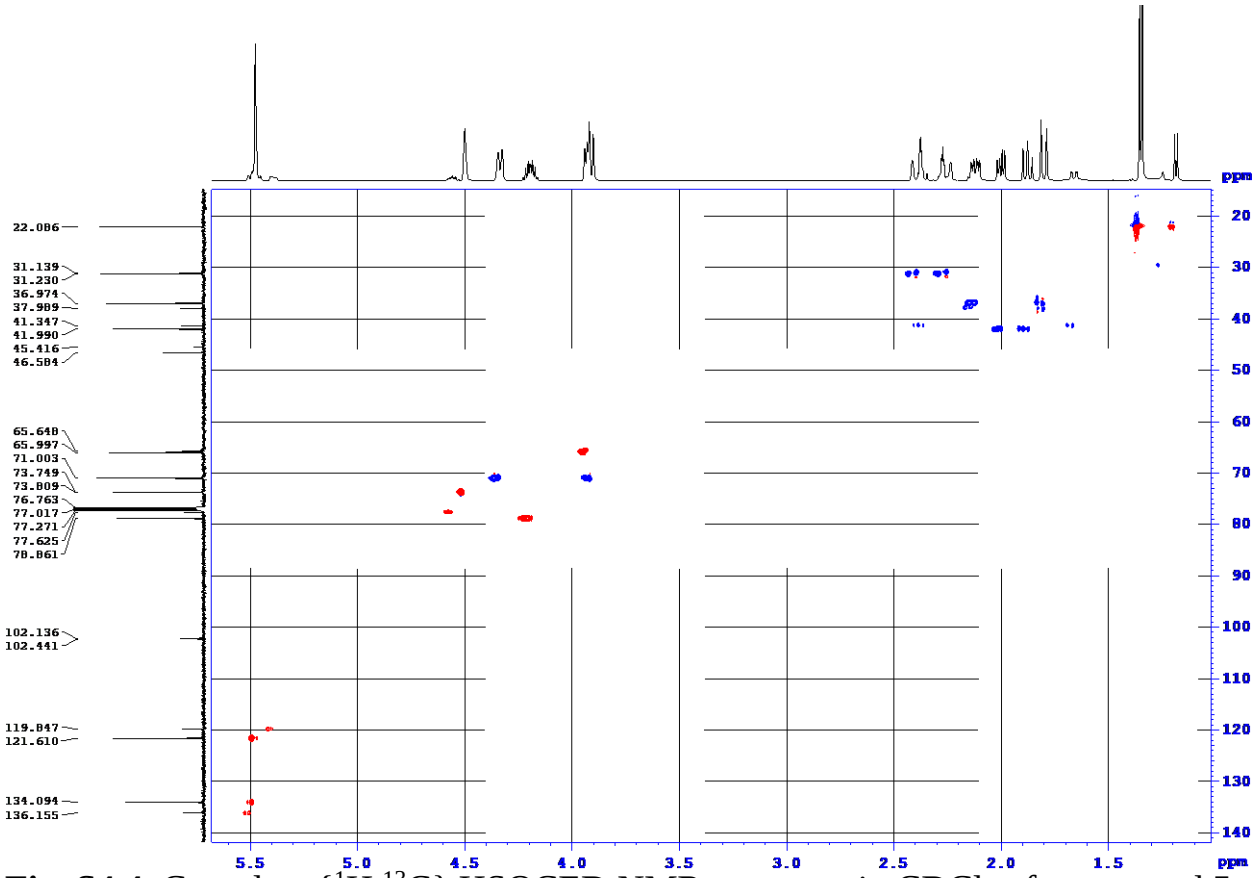


Fig. S4.4. Complete {^{1}H,^{13}C} HSQCED NMR spectrum in $CDCl_3$ of compound **5**

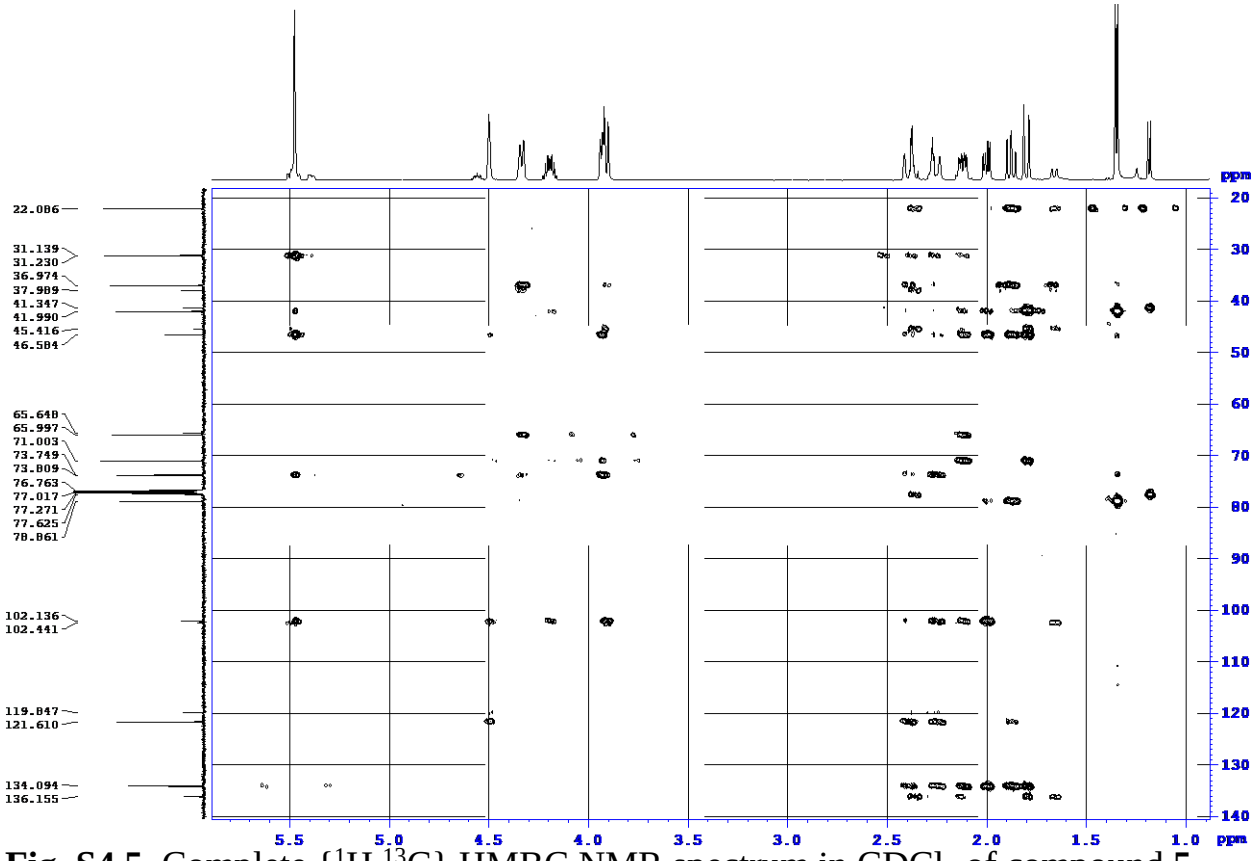


Fig. S4.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum in $CDCl_3$ of compound **5**

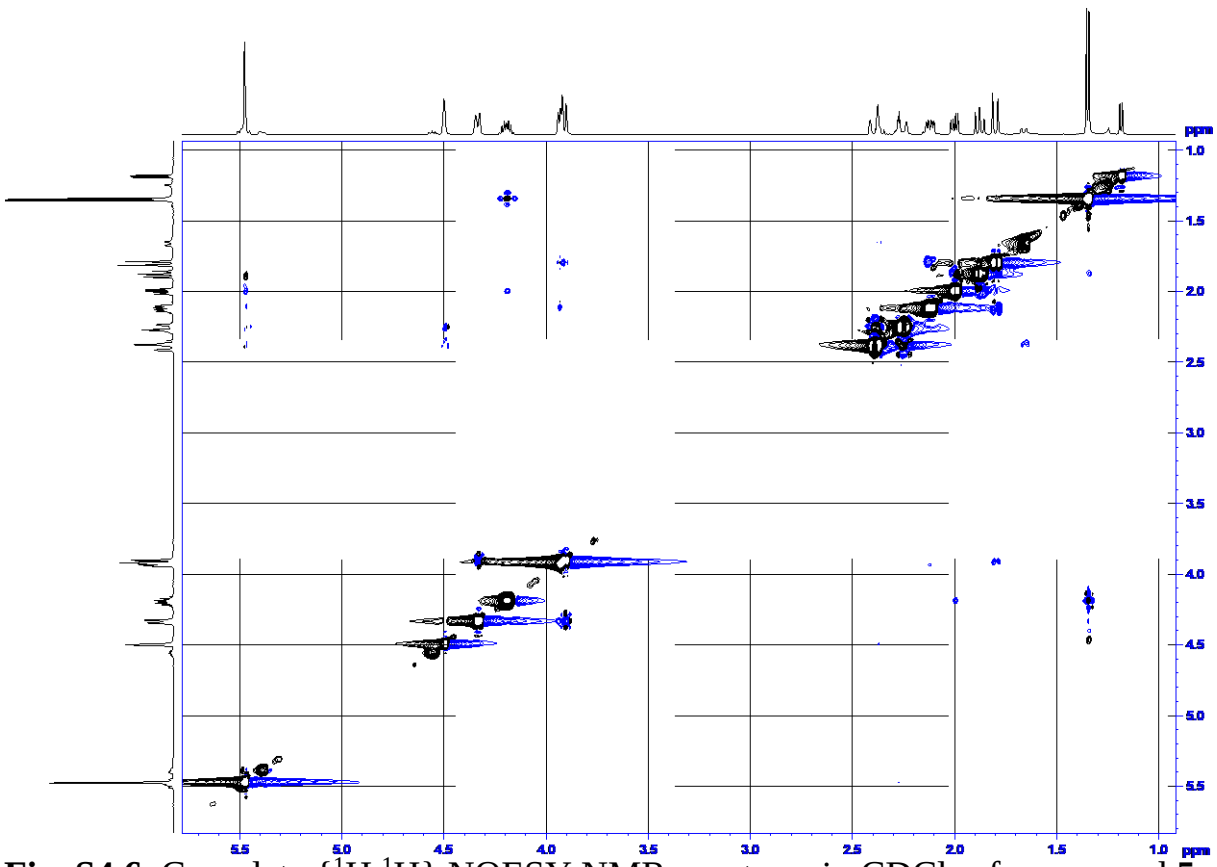


Fig. S4.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum in $CDCl_3$ of compound **5**

NMR spectrum of compound **6**:

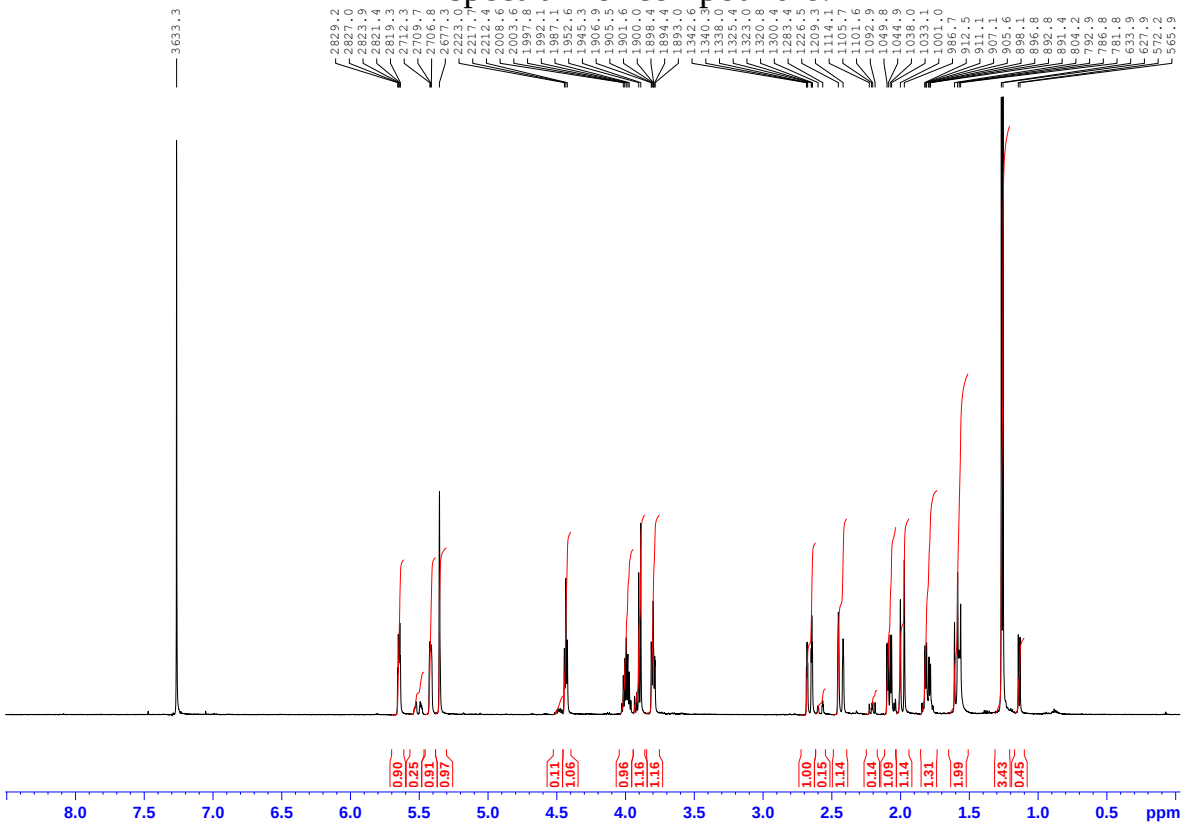


Fig. S5.1. Complete ^{1}H NMR (500 MHz) spectrum in $CDCl_3$ of compound **6**

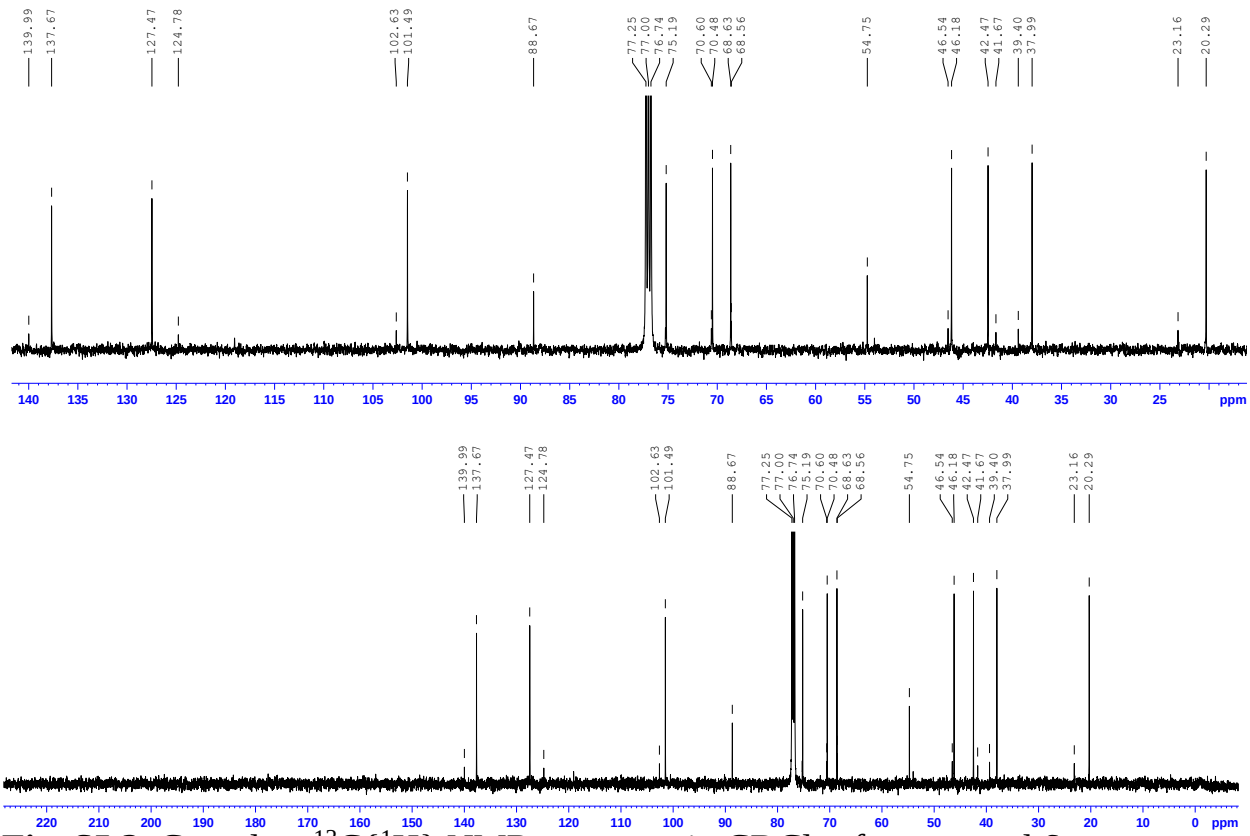


Fig. S5.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of compound **6**

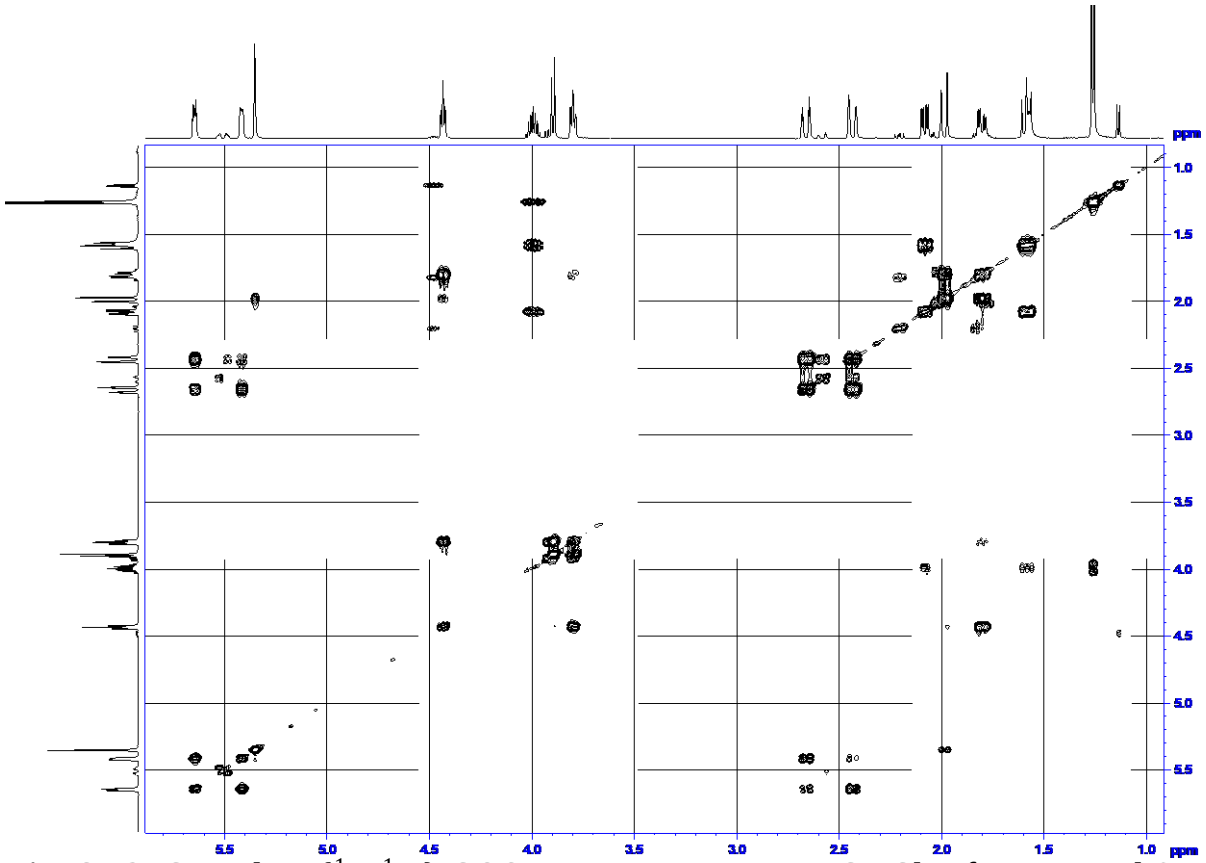


Fig. S5.3. Complete $\{^{1}H,^{1}H\}$ COSY NMR spectrum in $CDCl_3$ of compound **6**

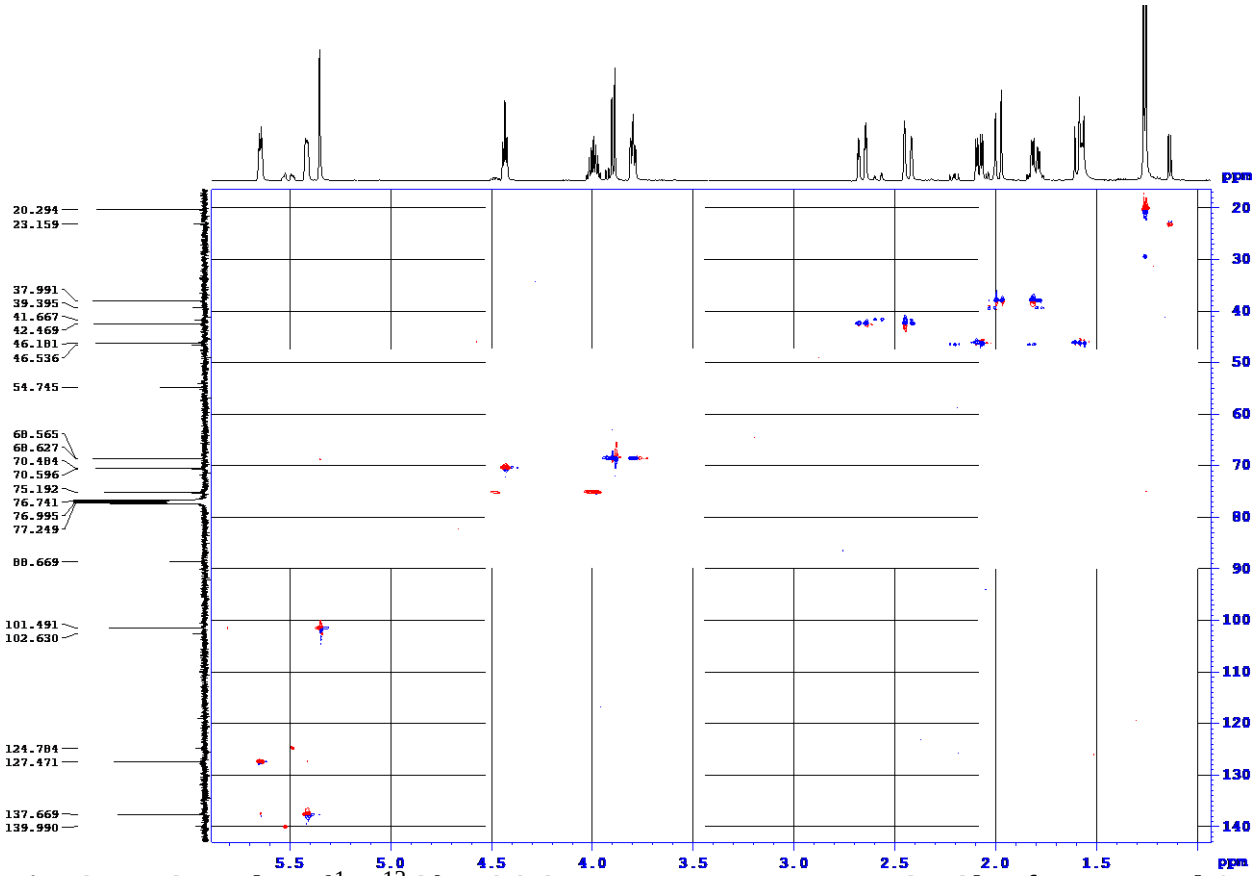


Fig. S5.4. Complete {^{1}H,^{13}C} HSQCED NMR spectrum in $CDCl_3$ of compound **6**

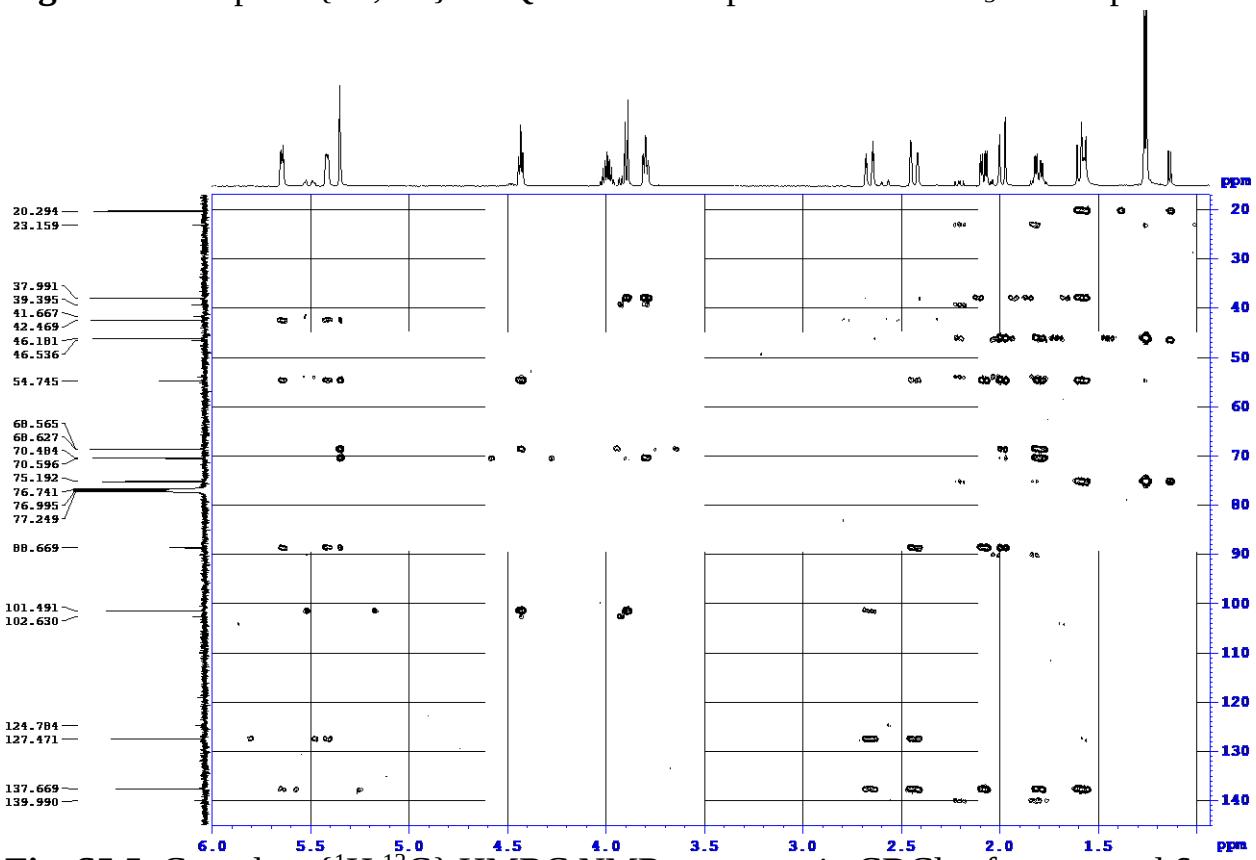


Fig. S5.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum in $CDCl_3$ of compound **6**

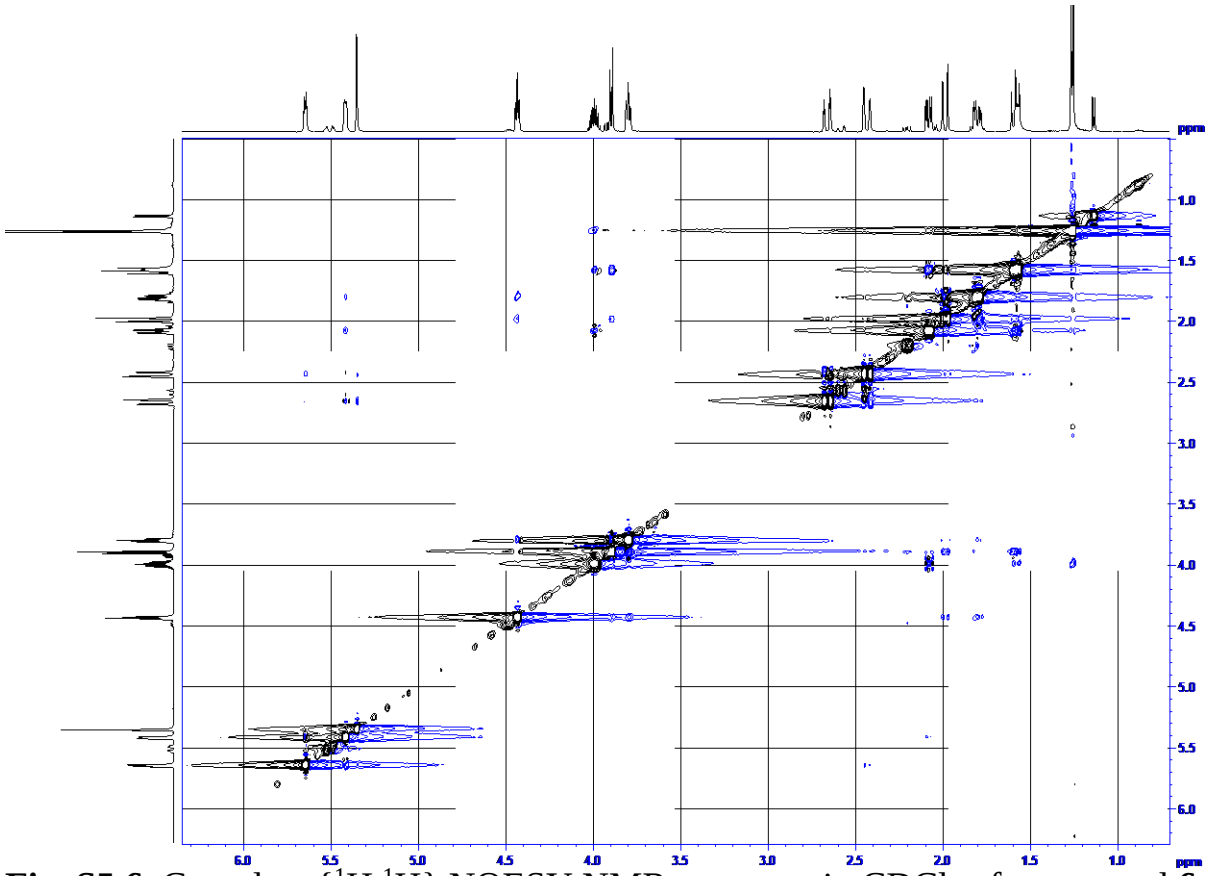
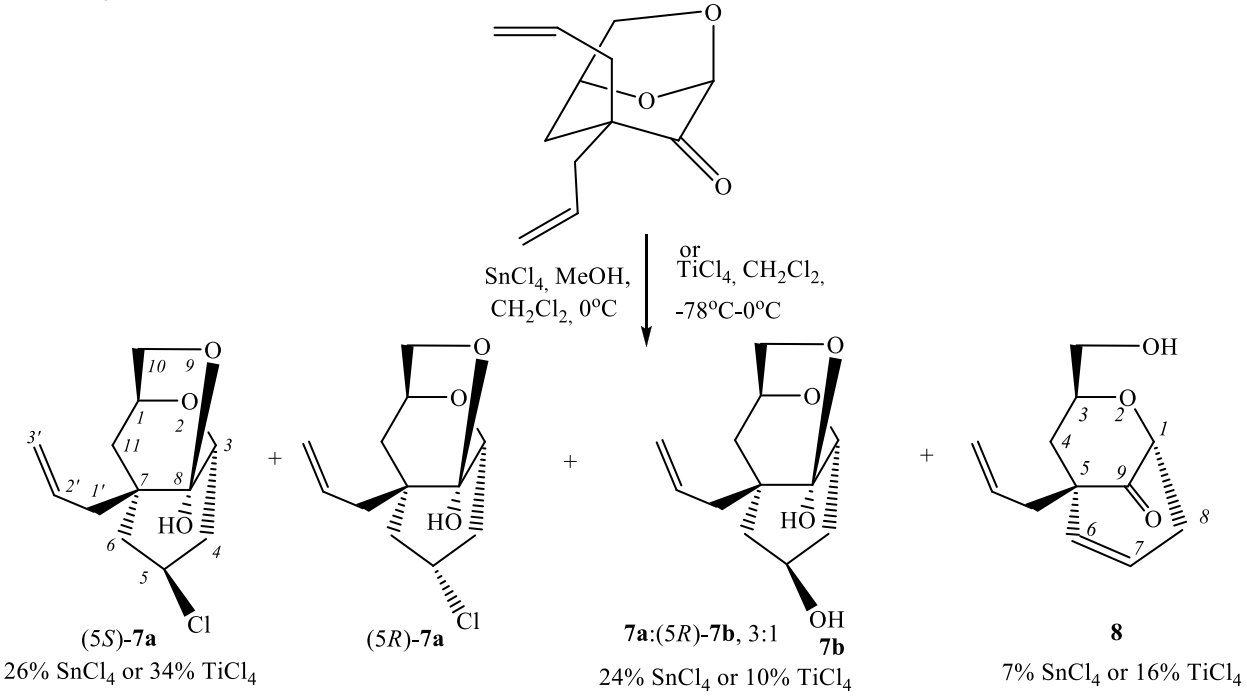


Fig. S5.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum in $CDCl_3$ of compound **6**

(1*S*,3*R*,5*S*,7*S*,8*S*)-7-Allyl-5-chloro-2,9-dioxatricyclo[5.3.1.0^{3,8}]undecan-8-ol (7a), (1*S*,3*R*,5*R*,7*S*,8*S*)-7-allyl-5-chloro-2,9-dioxatricyclo[5.3.1.0^{3,8}]undecan-8-ol (7a), (1*S*,3*R*,5*S*,7*R*,8*S*)-7-allyl-5-hydroxy-2,9-dioxatricyclo[5.3.1.0^{3,8}]-undecan-8-ol (7b) and (1*R*,3*S*,5*S*)-5-allyl-3-(hydroxymethyl)-2-oxabicyclo[3.3.1]non-6-en-9-one (8).



a. Compound **2** (0.20 g, 1 mmol) was dissolved under argon in CH_2Cl_2 (5 ml) and was cooled to –78°C. Titanium tetrachloride (0.13 ml, 1.2 mmol) was added, the mixture was allowed to warm up to room temperature and was stirred for 2 h at that temperature. Then it was treated with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3×7.0 ml). The extract was dried over $CaCl_2$, the solvent was distilled off, and the residue was purified by column chromatography on silica gel.

b. Compound **2** (0.271 g, 1 mmol) was dissolved under argon in CH_2Cl_2 (5 ml) and was cooled to 0°C. Tin tetrachloride (0.2 ml, 1.7 mmol) was added, and the mixture was stirred for 20 min at that temperature. Methanol (0.07 ml, 1.7 mmol) was added, and the mixture was stirred at room temperature for 2 h (TLC). The mixture was treated with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 7.0 ml). The extract was dried over $CaCl_2$, the solvent was distilled off, and the residue was purified by column chromatography on silica gel.

(5*S*)-**7a:** Yield 0.08 g (34%) (method *a*) or 0.08 g (26%) (method *b*). White crystals, mp 117°C. $[\alpha]_D^{20}$ +56.9 ° (*c* 1.0, $CHCl_3$). R_f 0.38 (EtOAc–petroleum ether, 1:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.72 (d, 1H, H^{11B}, $^2J_{11B,11A}$ 14.1 Hz), 1.85 (d,1H, H^{6B}, $^2J_{6B,6A}$ 12.5, $^3J_{6B,5}$ 12.5 Hz), 1.91-1.96 (m, 2H, H^{11A}, H^{6A}), 2.04 (dt, 1H, H^{4B}, $^2J_{4B,4A}$ 12.0, $^3J_{4B,5}$12.0, $^3J_{4B,3}$ 1.5 Hz), 2.26-2.30 (m, 2H, H$^{1'B}$, H^{4A}), 2.37 (dd, 1H, H$^{1'A}$, $^2J_{1'A,1'B}$ 13.8, $^3J_{1'A,2'}$ 7.0 Hz), 3.21 (br.s, 1H, OH), 3.86 (ddd, 1H, H^1, $^3J_{1,11A}$ 3.4, $^3J_{1,10A}$ 2.2, $^3J_{1,10B}$ 1.0 Hz), 3.92 (dd,1H, H^{10B}, $^2J_{10B,10A}$ 9.3, $^3J_{10B,1}$ 1.0 Hz),

4.02 (dd, 1H, H^{3}, $^{3}J_{3,4A}$ 3.8, $^{3}J_{3,4B}$ 1.5 Hz), 4.28 (dt,1H, H^{10A}, $^{2}J_{10A,10B}$ 9.3, $^{3}J_{10A,1}$ 2.2, $^{3}J_{10A,11A}$ 2.2 Hz), 4.31-4.38 (m,1H, H^{5}), 5.11-5.16 (m,2H, $H^{3'A}$, $H^{3'B}$), 5.82-5.90 (m,1H, $H^{2'}$). ^{13}C NMR (500 MHz, $CDCl_3$): δ 35.77 (C^{11}), 38.77 (C^{4}), 40.12 ($C^{1'}$), 41.29 (C^{7}), 43.62 (C^{6}), 52.64 (C^{5}), 65.37 (C^{1}), 71.32 (C^{10}), 78.04 (C^{3}), 93.85 (C^{8}), 118.92 ($C^{3'}$), 133.73 ($C^{2'}$). IR (neat) 3424, 2927, 1739, 1203, 1063, 1003, 920, 826, 696 cm-1; Mass spectrum, *m/z*: 245 $[MH]^{+}$. Calcd for $C_{12}H_{17}ClO_3$ 244.71.

The formation of a new 10,8-anhydro bridge in compound (5*S*)-**7a** was proved by the presence of the H^{10}/C^{8} correlation peak in the HMBC spectrum. Moreover, the HMBC spectrum exhibits H^{1}/C^{3}, H^{3}/C^{8} and H^{5}/C^{3} correlation peaks. The H^{3} proton is recorded as a dd at δ 4.02 with $^{3}J_{3\text{-}4A}$ 3.8 Hz and $^{3}J_{3\text{-}4B}$ 1.5 Hz, while the H^{4B} proton is recorded at δ 2.04 with $^{3}J_{4B,5}$ 12.0 Hz, indicating the *S*-configuration of the C^{5} center. The presence of the H^{1}/H^{11B} and $H^{11B}/H^{1'}$ correlation peaks in the NOESY spectra results from the *S*-configuration of the C^{1} and C^{7} centers.

The presence of chlorine in the product is indicated by H^{5} signals at δ 4.31-4.38 and those of its C^{5} carbon atom at δ 52.64. Moreover, elemental analysis and mass spectrometry data confirm the composition of the compound.

The formation of a cyclohexenone ring in compound **8** is indicated by the signals of the H^{6} and H^{7} protons at δ 5.51 and 5.98 in the ^{1}H NMR spectra and the corresponding carbons in the ^{13}C NMR spectrum at δ 131.06 and 128.78, respectively, as well as the carbonyl at δ 210.47. Moreover, the HMBC spectrum exhibits the H^{10}/C^{3}, $H^{10}/C{=}O$, $H^{1}/C{=}O$ and H^{1}/C^{8} correlation peaks.

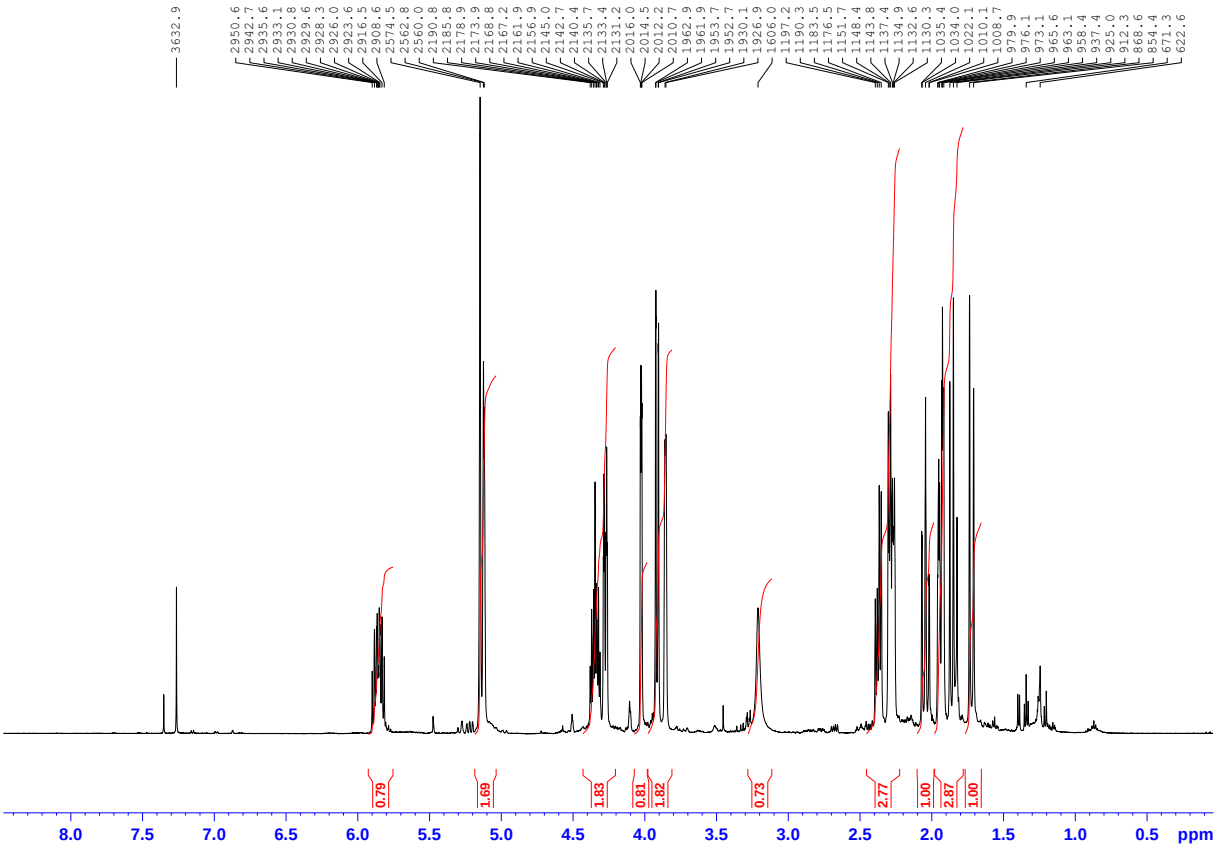


Fig. S6.1. Complete ^{1}H NMR (500 MHz) spectrum in $CDCl_3$ of (5*S*)-**7a**

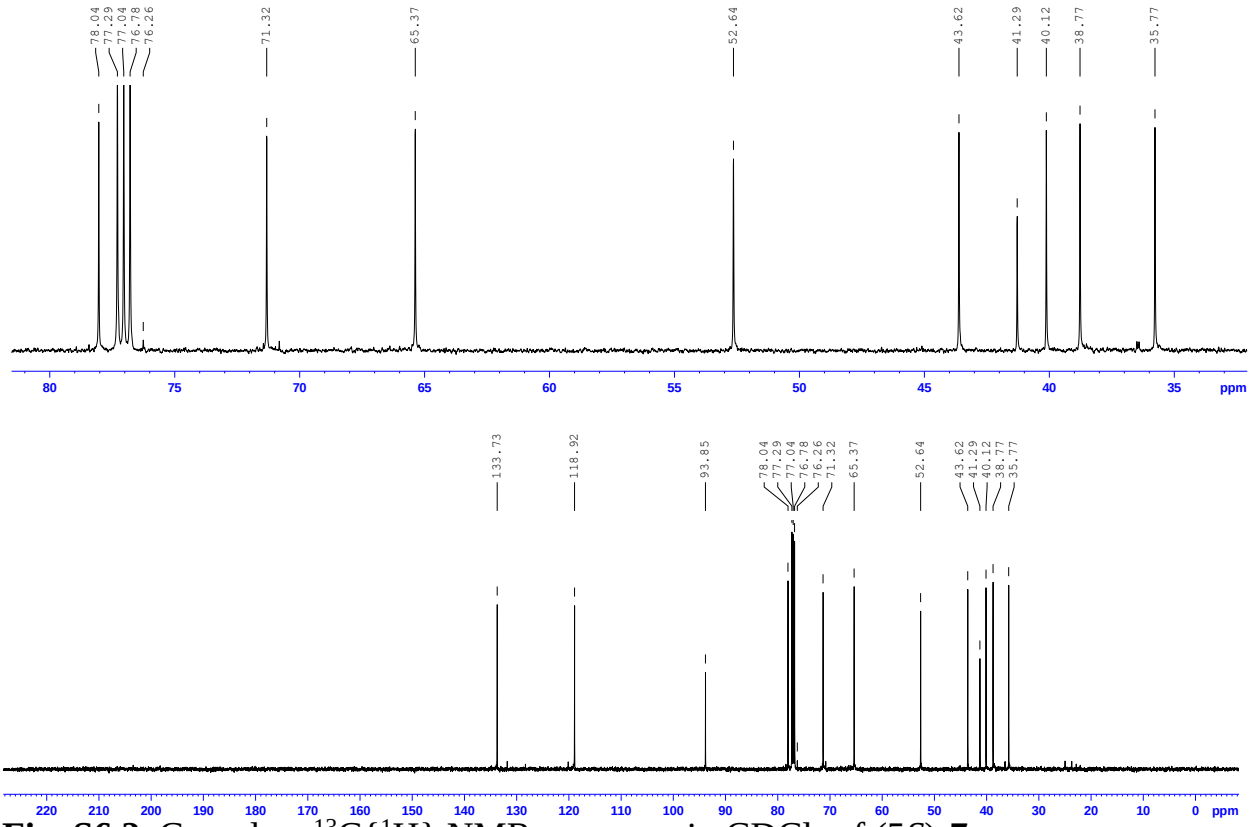


Fig. S6.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of (5*S*)-**7a**

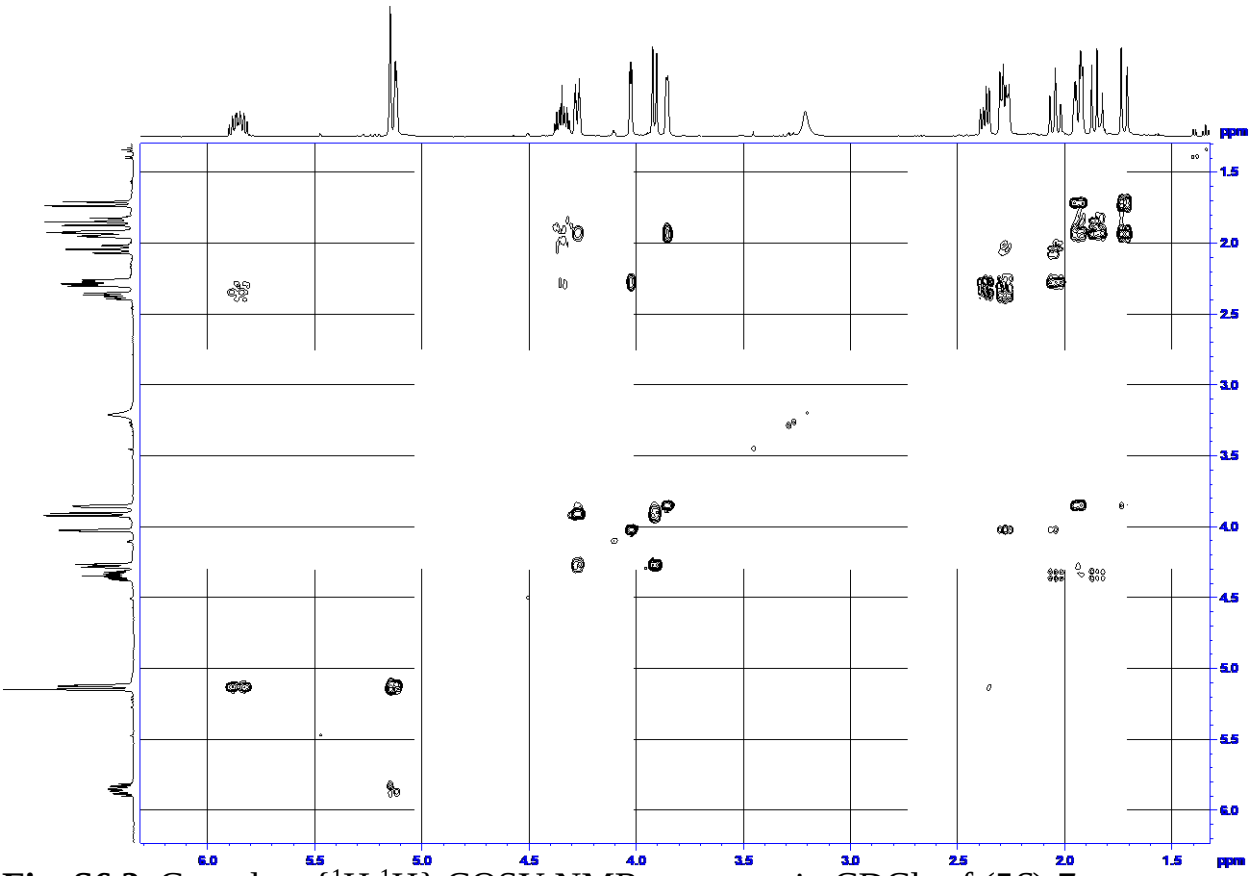


Fig. S6.3. Complete {^{1}H,^{1}H} COSY NMR spectrum in $CDCl_3$ of (5*S*)-**7a**

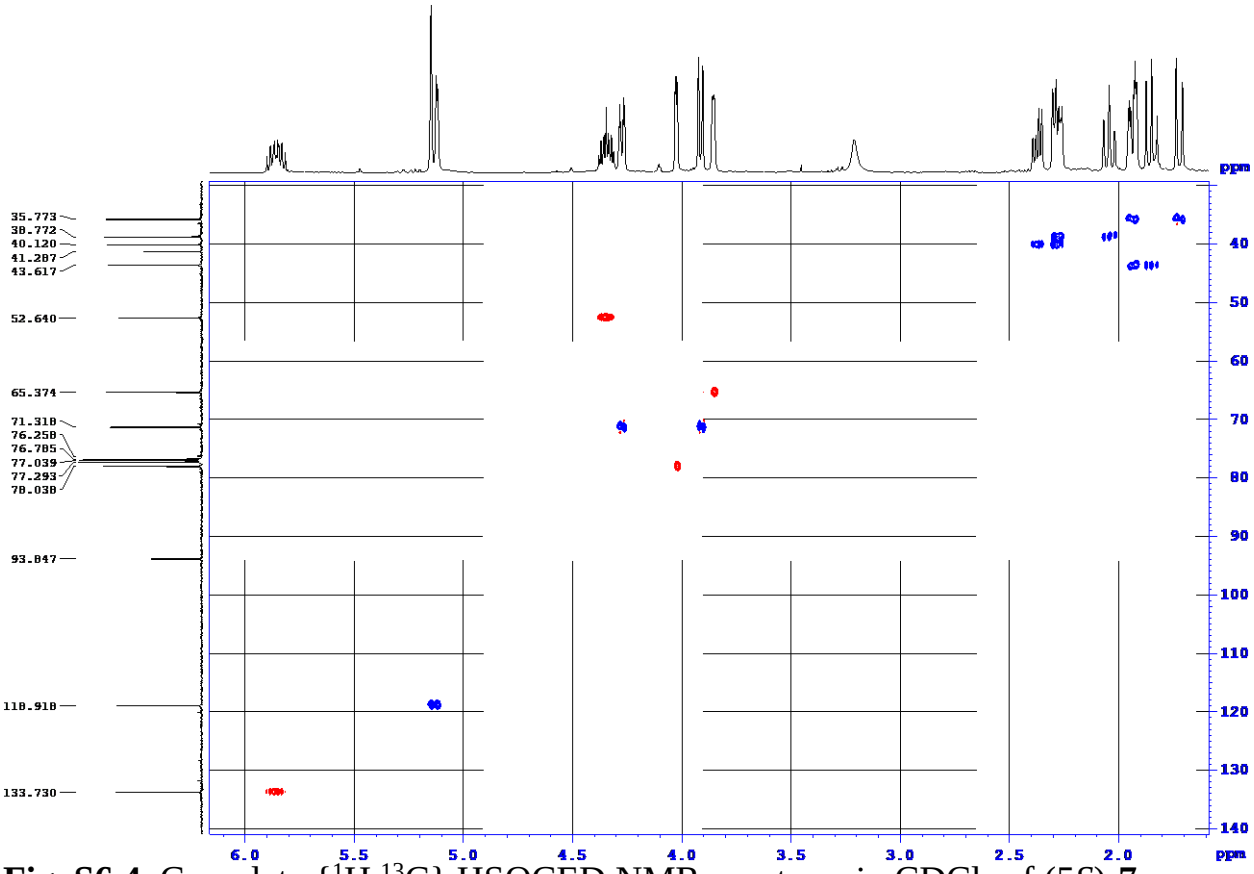


Fig. S6.4. Complete {^{1}H,^{13}C} HSQCED NMR spectrum in $CDCl_3$ of (5*S*)-**7a**

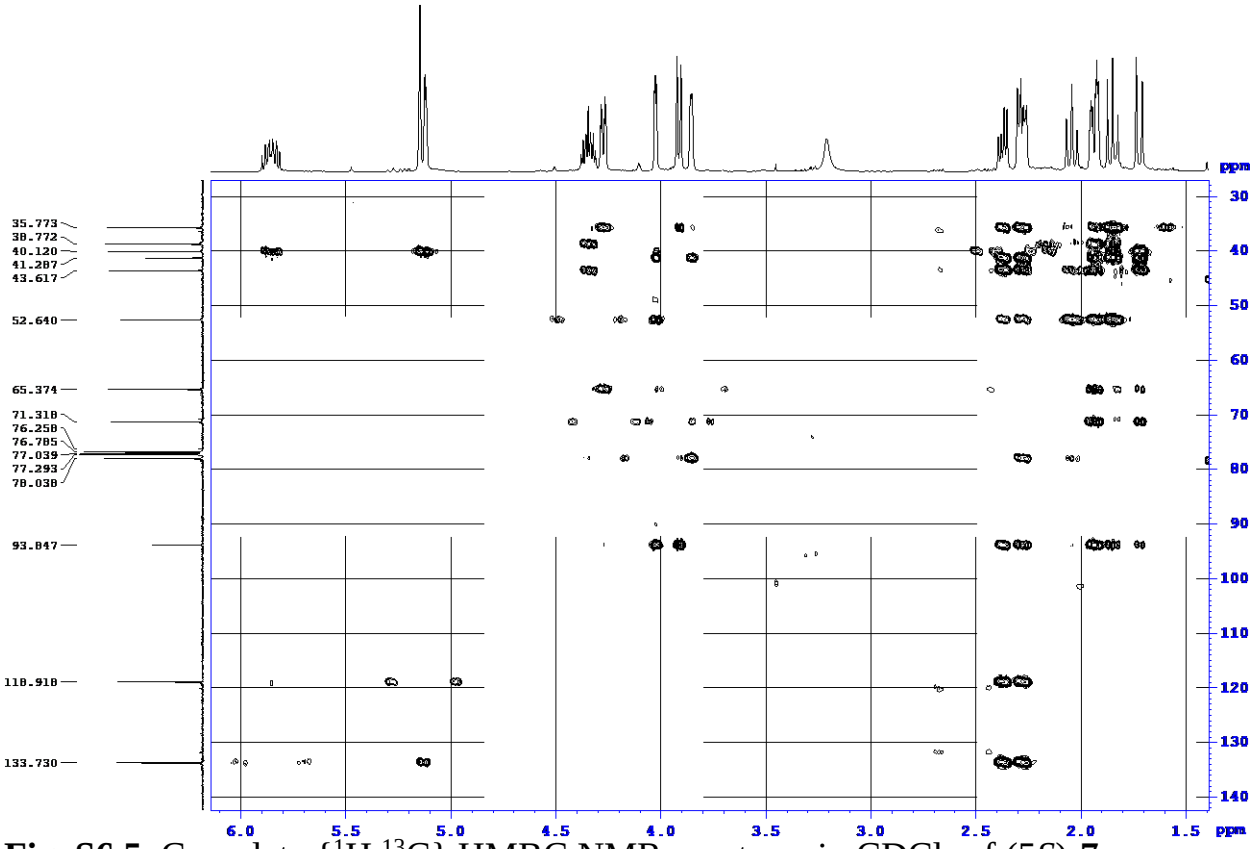


Fig. S6.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum in $CDCl_3$ of (5*S*)-**7a**

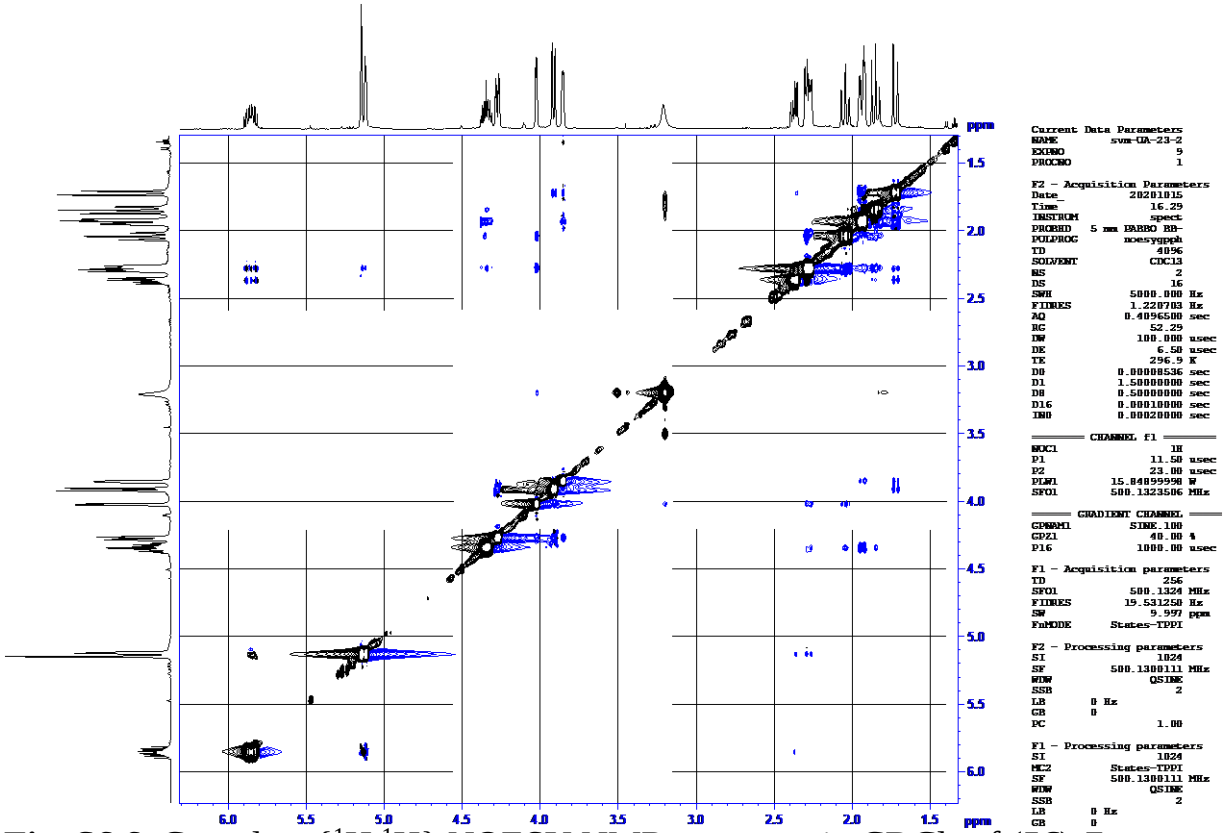


Fig. S6.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum in $CDCl_3$ of (5*S*)-**7a**

Mixtures of compounds (5*R*)-**7a** and (5*S*)-**7b** at a ratio of 3:1. Yield 0.023 g (10%) (method *a*), 0.076g (24%) (method *b*). White crystals, mp 70°C. R_f 0.3 (EtOAc–petroleum ether, 1:3).

(5*R*)-**7a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.65 (d, 1H, H^{11B}, J 13.9 Hz), 2.05-2.10 (m, 2H, H^{6A}, H^{6B}), 2.21 (dd, 1H, $H^{1'B}$, J = 13.8, 8.0 Hz), 2.29 (ddd, 1H, H^{4B}, J = 15.8, 5.6, 2.5 Hz), 2.35-2.43 (m, 2H, H^{4A}, $H^{1'A}$), 2.82 (br.s, 1H, OH), 2.96 (ddd, 1H, H^{11A}, J = 13.9, 4.6, 3.0 Hz), 3.92-3.94 (m, 1H, H^1), 3.97 (dd, 1H, H^{10B}, J = 7.6, 0.9 Hz), 4.13 (t, 1H, H^3, J = 2.5 Hz), 4.34 (dd, 1H, H^{10A}, J = 7.6, 2.5 Hz), 4.44 (tt, 1H, H^5, J = 5.6, 2.0 Hz), 5.10-5.15 (m, 2H, $H^{3'A}$, $H^{3'B}$), 5.82-5.92 (m, 1H, $H^{2'}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 35.33 (C^{11}), 36.15 (C^4), 38.89 (C^7), 40.81 ($C^{1'}$), 40.87 (C^6), 52.61 (C^5), 65.84 (C^1), 72.17 (C^{10}), 76.68 (C^3), 94.05 (C^8), 118.67 ($C^{3'}$), 133.97 ($C^{2'}$).

(5*S*)-**7b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.69-1.74 (m, 1H, H^{4B}), 1.85-1.89 (m, 1H, H^{6B}), 2.09-2.12 (m, 1H, H^{6B}), 2.16 (dt, 1H, H^{4A}, J = 14.3, 14.3, 4.0 Hz), 2.45 (dd, 1H, $H^{1'B}$, J = 13.8, 7.8 Hz), 2.47-2.54 (m, 2H, H^{6A}, H^{11A}), 2.68 (dd, 1H, $H^{1'A}$, J = 13.8, 7.4 Hz), 3.39 (br.s, 1H, OH), 3.90-3.93 (m, 2H, H^1, H^{10B}), 4.09-4.13 (m, 2H, H^3, H^5), 4.32 (dd, 1H, H^{10A}, J = 7.6, 2.5 Hz), 5.20-5.28 (m, 2H, $H^{3'A}$, $H^{3'B}$), 5.71-5.81 (m, 1H, $H^{2'}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.70 (C^4), 24.98 (C^6), 36.44 ($C^{1'}$), 36.49 (C^{11}), 43.58 (C^7), 65.38 (C^5), 65.49 (C^1), 70.83 (C^{10}), 76.22 (C^3), 93.90 (C^8), 120.12 ($C^{3'}$), 131.80 ($C^{2'}$).

NMR spectrum of mixture of compounds (5*R*)-**7a** and (5*S*)-**7b**:

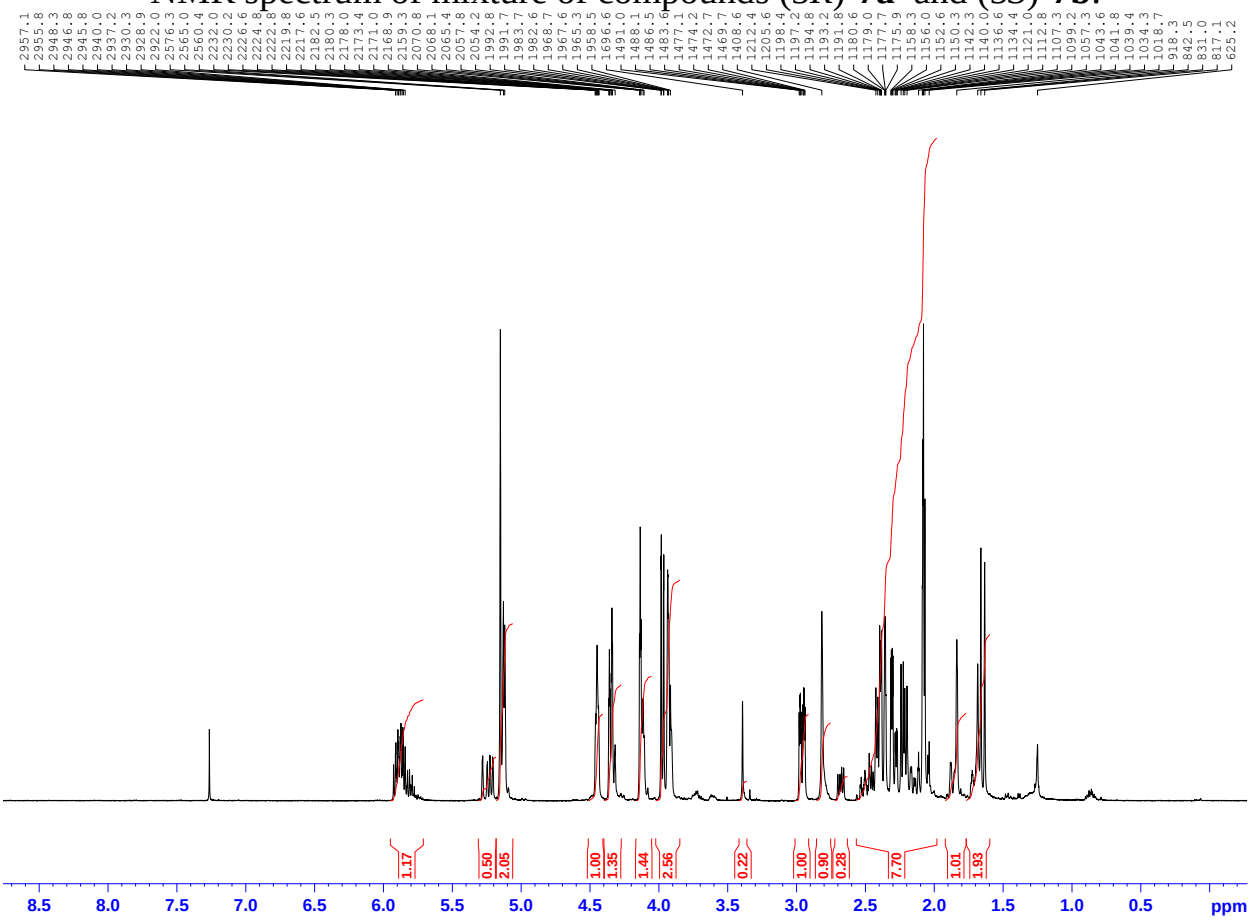


Fig. S7.1. Complete ^{1}H NMR (500 MHz, $CDCl_3$) of (5*R*)-**7a** and (5*S*)-**7b**

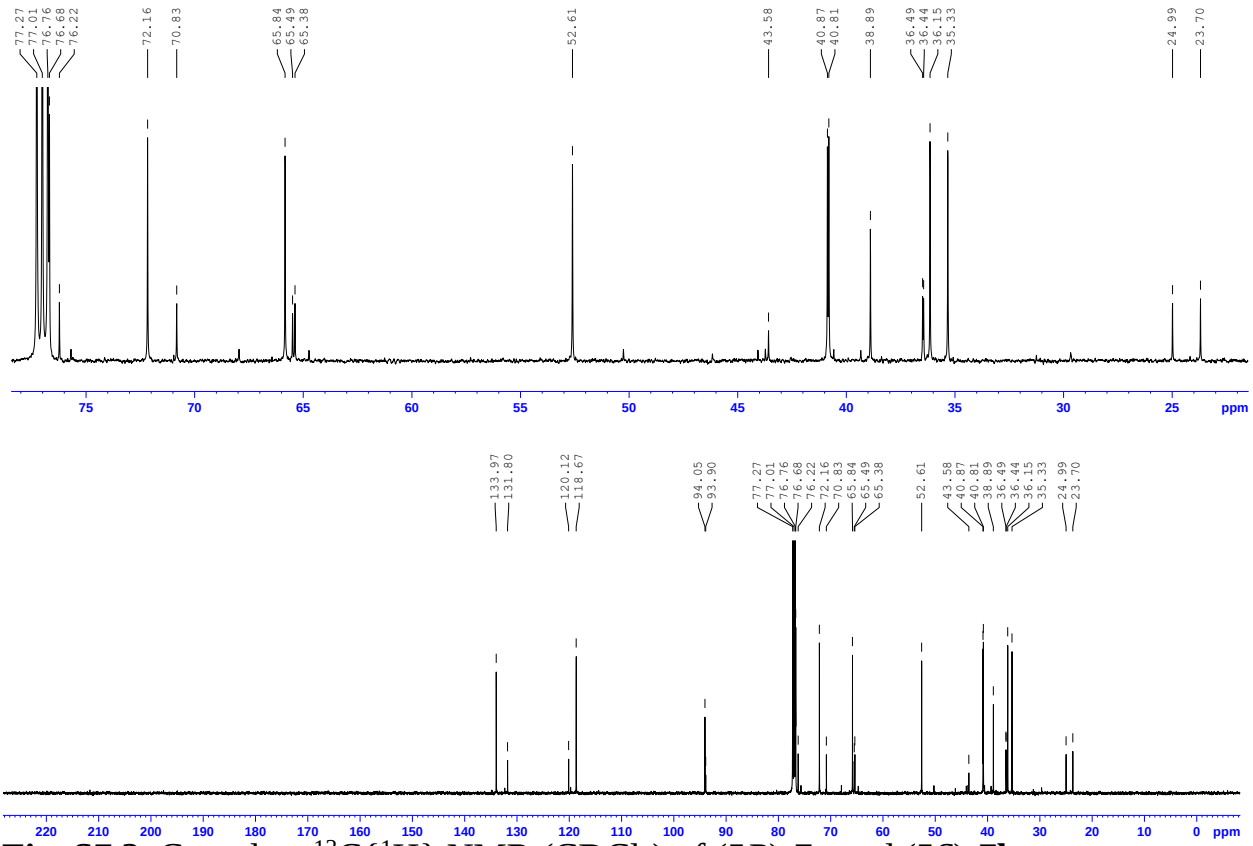


Fig. S7.2. Complete $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of (5*R*)-**7a** and (5*S*)-**7b**

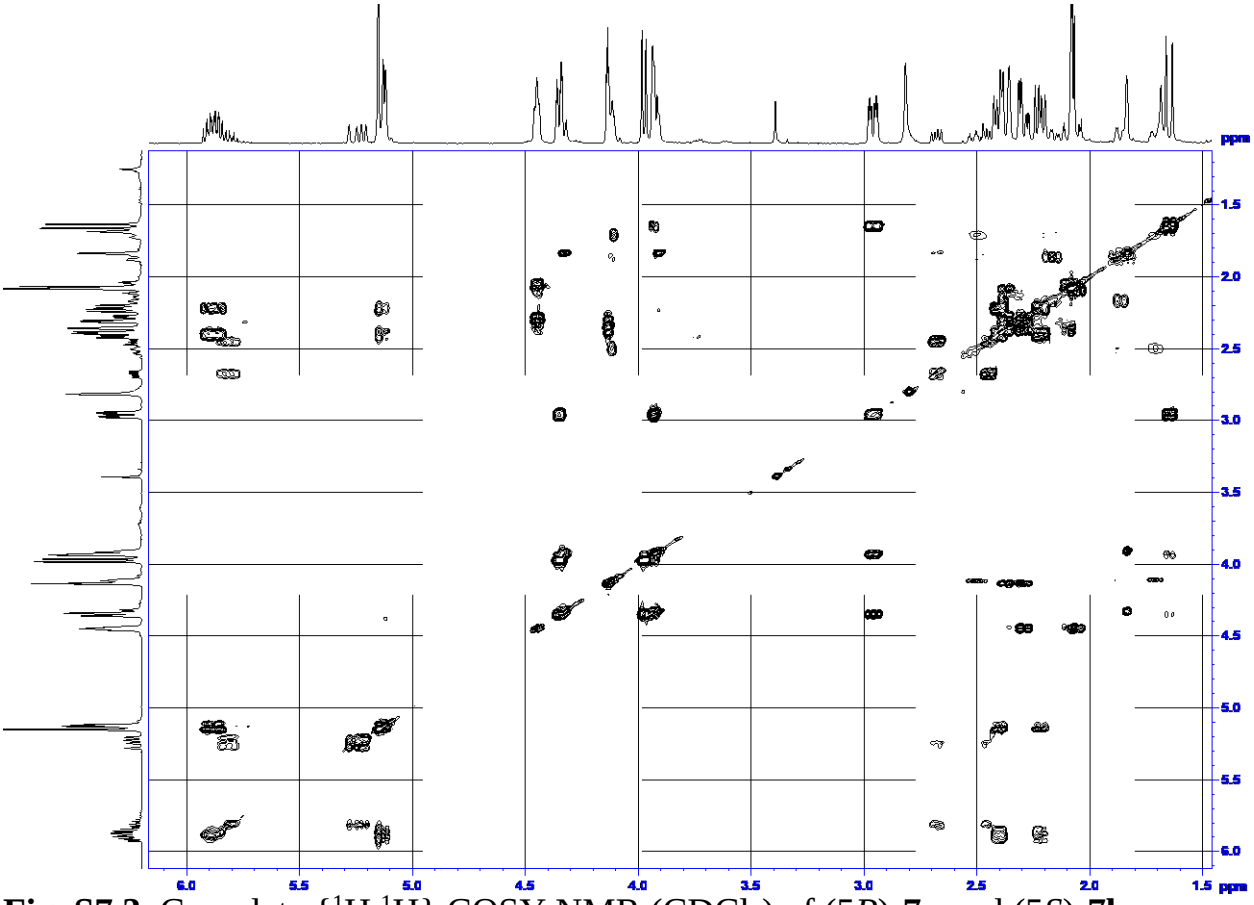


Fig. S7.3. Complete $\{^{1}H,^{1}H\}$ COSY NMR ($CDCl_3$) of (5*R*)-**7a** and (5*S*)-**7b**

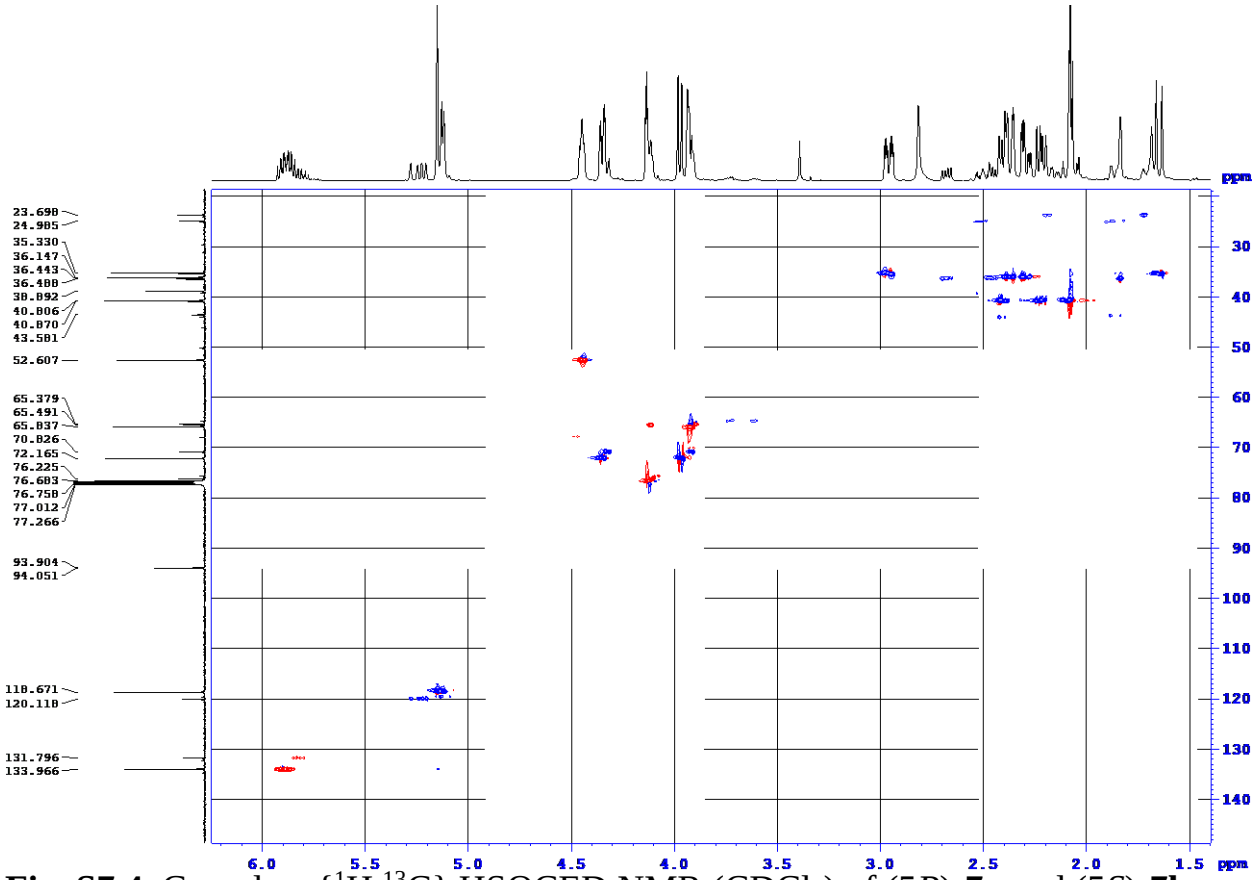


Fig. S7.4. Complete {^{1}H,^{13}C} HSQCED NMR ($CDCl_3$) of (5*R*)-**7a** and (5*S*)-**7b**

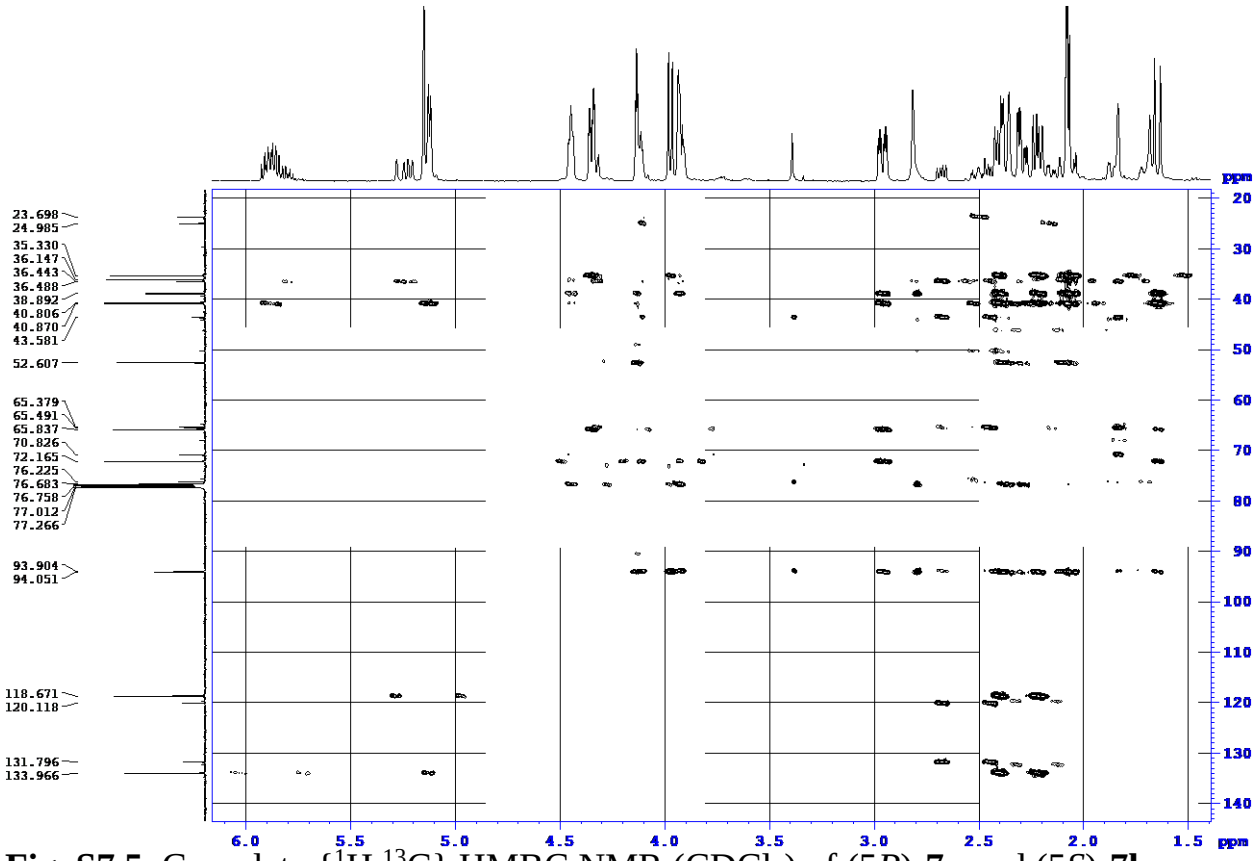


Fig. S7.5. Complete {^{1}H,^{13}C} HMBC NMR ($CDCl_3$) of (5*R*)-**7a** and (5*S*)-**7b**

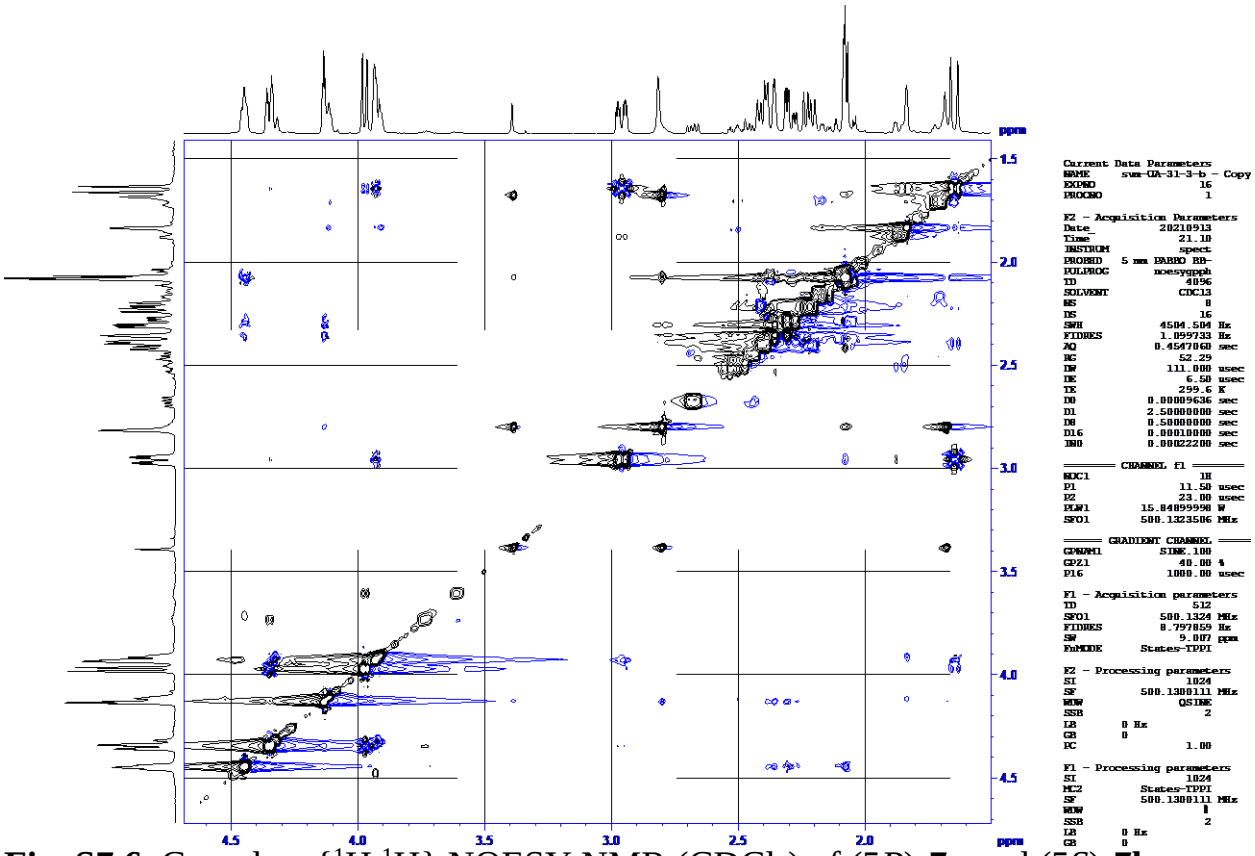
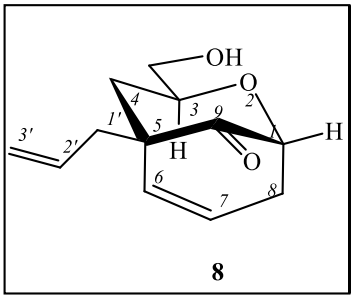


Fig. S7.6. Complete {^{1}H,^{1}H} NOESY NMR ($CDCl_3$) of (5*R*)-**7a** and (5*S*)-**7b**

Product 8: Yield 0.031 g (16%) (method *a*), 0.019 g (7%) (method *b*). Colourless oil. $[\alpha]_D^{20}$ -28.1° (*c* 1.0, $CHCl_3$). R_f 0.2 (EtOAc–petroleum ether, 1:3).

^{1}H NMR (500 MHz, $CDCl_3$): 1.74 (dd, 1H, H^{4B}, *J* = 12.9, 2.4 Hz), 1.89 (t, 1H, H^{4A}, *J* = 12.9 Hz), 2.29 (dd, 1H, $H^{1'B}$, *J* = 14.0, 7.3 Hz), 2.37 (dd, 1H, $H^{1'A}$, *J* = 14.0, 7.5 Hz), 2.76-2.79 (m, 2H, H^{8A}, H^{8B}), 3.56 (dd, 1H, $H^{1''B}$, *J* = 11.6, 6.2 Hz), 3.69 (dd, 1H, $H^{1''A}$, *J* = 11.6, 2.9 Hz), 4.88 (t, 1H, H^{1}, *J* = 2.7 Hz), 4.33-4.37 (m, 1H, H^{3}), 5.07-5.12 (m, 2H, $H^{3'A}$, $H^{3'B}$), 5.51 (dt, 1H, H^{6}, *J* = 9.6, 1.5, 1.5 Hz), 5.74-5.83 (m, 1H, $H^{2'}$), 5.98 (dt, 1H, $H^{3'}$, *J* = 9.6, 2.9, 2.9 Hz).



8

^{13}C NMR (125 MHz, $CDCl_3$): δ 36.61 (C^{8}), 38.15 ($C^{1'}$), 40.21 (C^{4}), 47.62 (C^{5}), 64.83 (C^{10}), 70.22 (C^{3}), 75.92 (C^{1}), 118.79 ($C^{3'}$), 128.78 (C^{7}), 131.06 (C^{6}), 133.05 ($C^{2'}$), 210.47 (C=O). Mass spectrum, *m/z*: 209 $[MH]^+$. Calcd for $C_{12}H_{16}O_3$.

NMR spectrum of compound **8**:

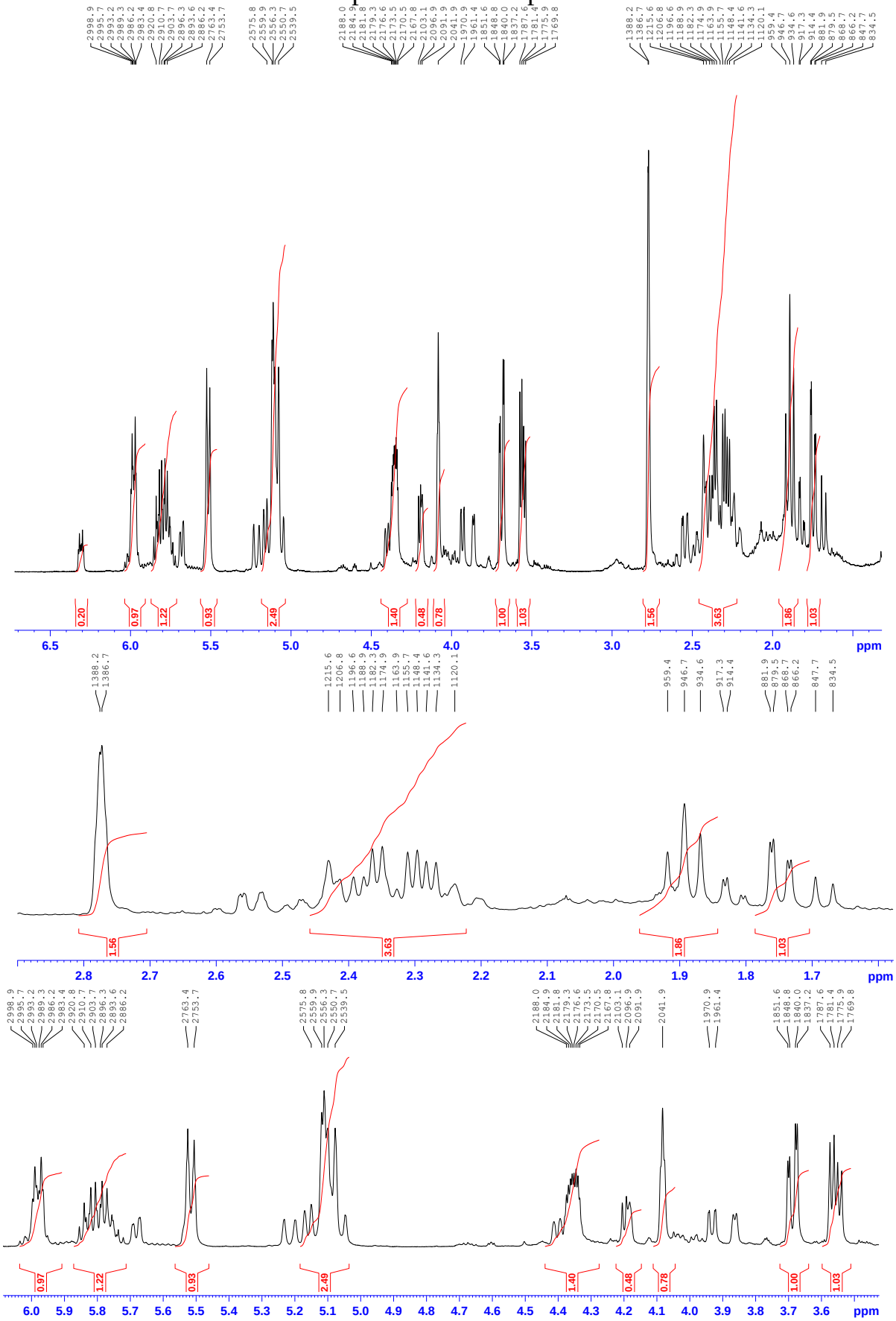


Fig. S8.1. Complete ^{1}H NMR (500 MHz) spectrum in $CDCl_3$ of compound **8**

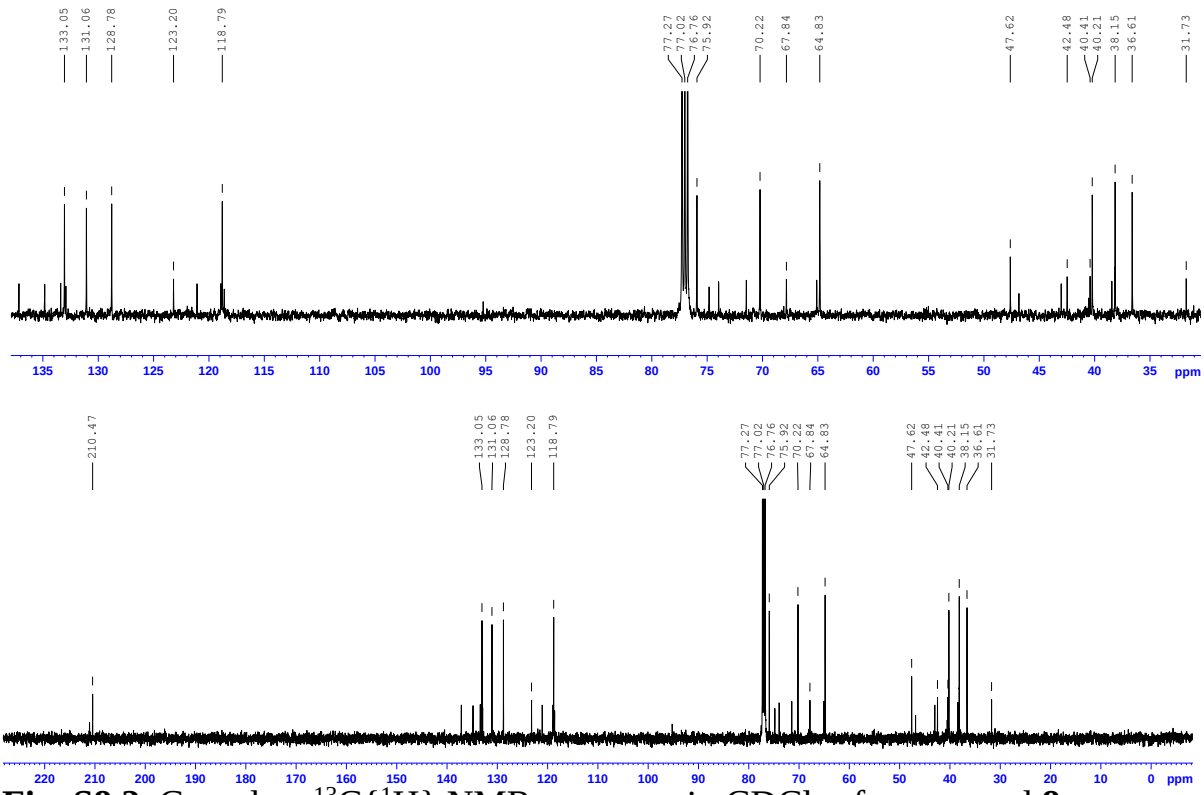


Fig. S8.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of compound **8**

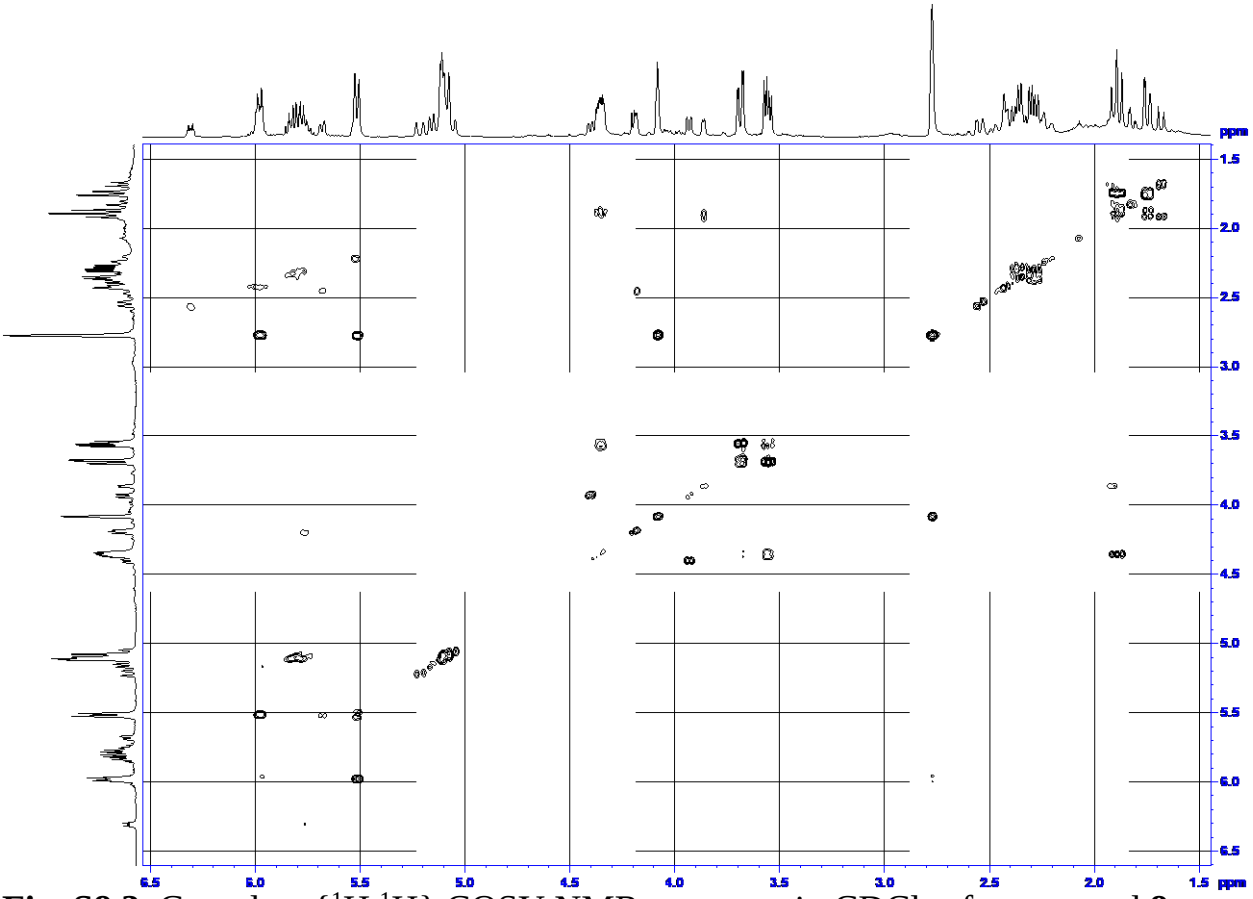


Fig. S8.3. Complete $\{^{1}H,^{1}H\}$ COSY NMR spectrum in $CDCl_3$ of compound **8**

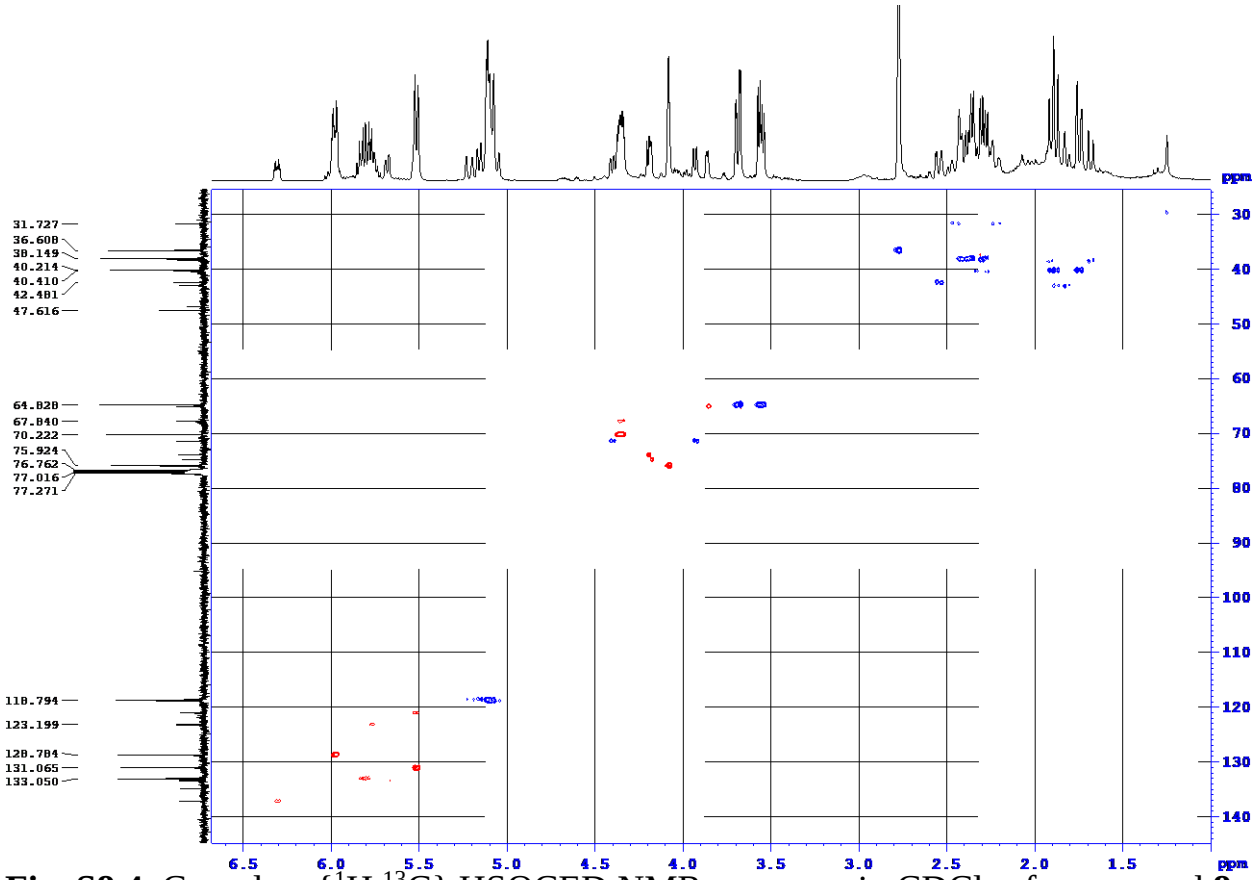


Fig. S8.4. Complete {^{1}H,^{13}C} HSQCED NMR spectrum in $CDCl_3$ of compound **8**

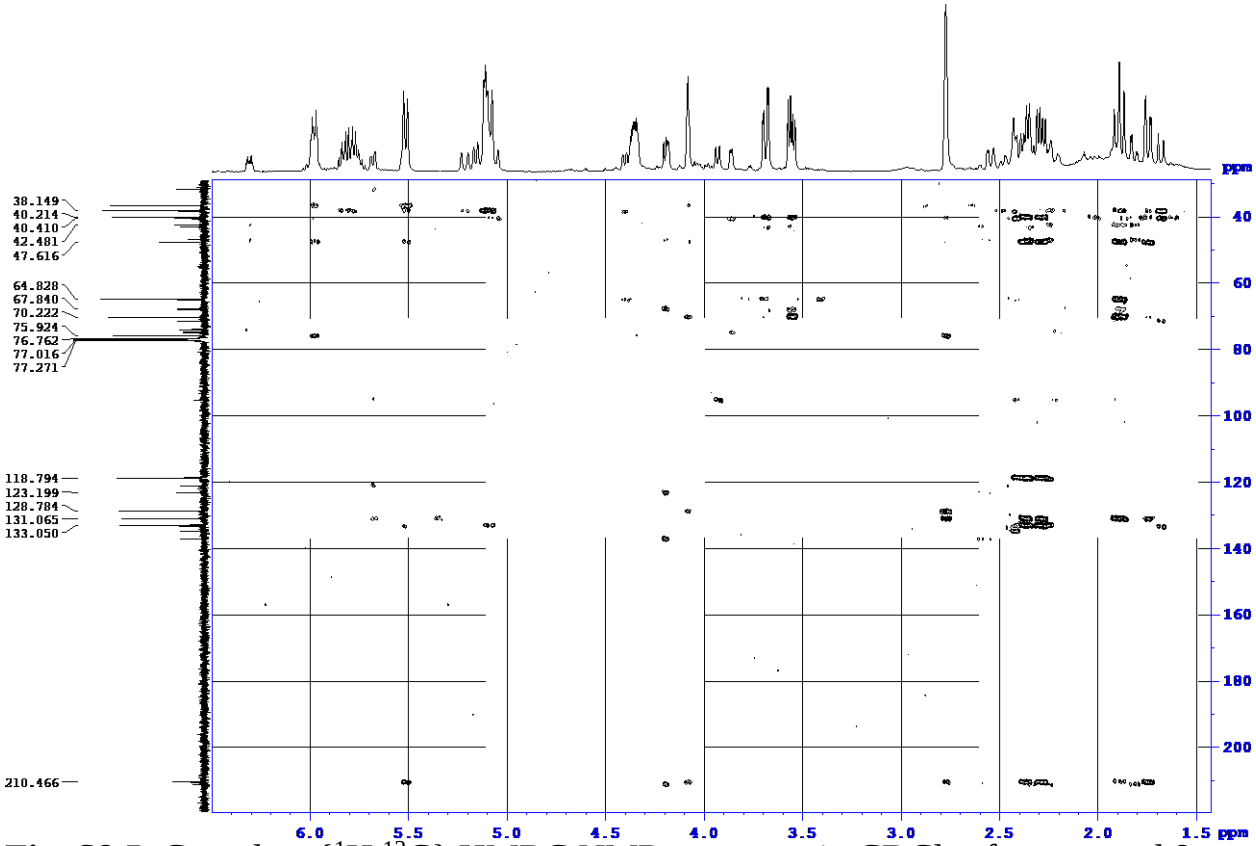


Fig. S8.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum in $CDCl_3$ of compound **8**

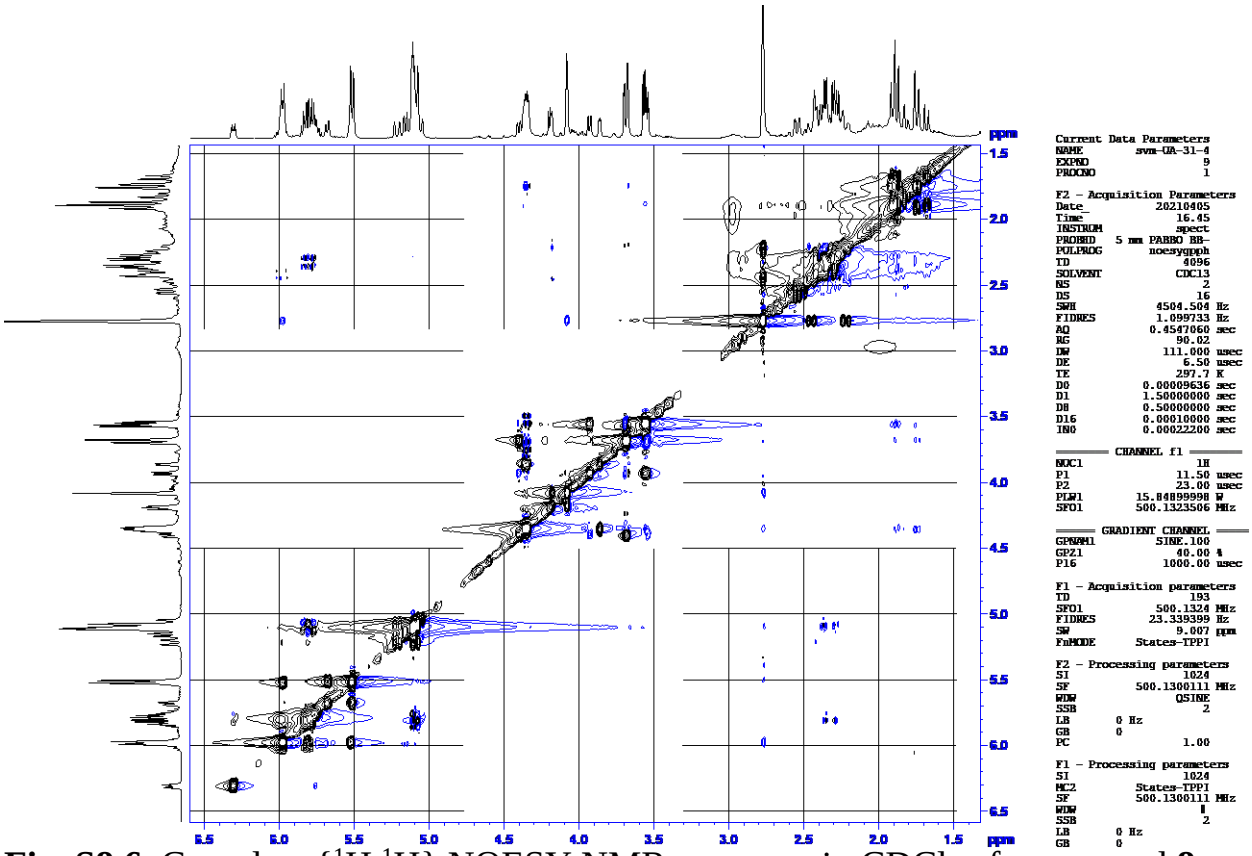
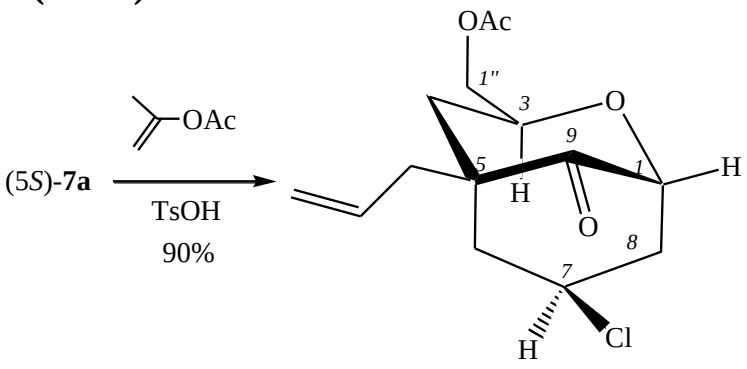


Fig. S8.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum in $CDCl_3$ of compound **8**

((1*R*,3*S*,5*S*,7*S*)-5-Allyl-7-chloro-9-oxo-2-oxabicyclo[3.3.1]nonan-3-yl)methyl acetate (7*S*-9a).



(7*S*)-**9a**

A catalytic amount of *p*-toluenesulfonic acid was added to a solution of compound (5*S*)-**7a** (0.017 g, 0.07 mmol) in isopropenyl acetate (3 ml). The mixture was stirred at room temperature for 15 h (TLC), then treated with a H_2O (2 ml) and extracted with EtOAc (3×5.0 ml). The extract was dried over $MgSO_4$, the solvent was distilled off, and the residue was purified by column chromatography on silica gel. Yield 0.018 g (90%). Colourless oil. $[\alpha]_D^{20}$ +30.5 ° (*c* 1.1, $CHCl_3$). R_f 0.6 (EtOAc–petroleum ether, 1:2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.89 (ddd, 1H, H^{4B}, $^2J_{4B,4A}$ 14.0, $^3J_{4B,3}$ 10.3, $^3J_{4B,6B}$ 1.5 Hz), 2.06 (ddd, 1H, H^{6B}, $^2J_{6B,6A}$ 14.0, $^3J_{6B,7}$ 11.6, $^3J_{6B,4B}$ 1.5 Hz), 2.09 (s, 3H, OAc), 2.15-2.32 (m, 4H, H^{4A}, $H^{1'A}$, $H^{1'B}$, H^{8B}), 2.57 (ddd, 1H, H^{6A}, $^2J_{6A6B}$ 14.0, $^3J_{6A,7}$ 6.0, $^3J_{6A,8A}$ 2.7 Hz), 2.89-2.95 (m, 1H, H^{8A}), 3.91 (dd, 1H, $H^{1''B}$, $^2J_{1''B,1''A}$ 11.7, $^3J_{1''B,3}$ 6.6 Hz), 4.04 (t, 1H, H^1, $^3J_{1,8A}$ 3.2, $^3J_{1,8B}$ 3.2 Hz), 4.07 (dd, 1H, $H^{1''A}$, $^2J_{1''A,1''B}$ 11.7, $^3J_{1''A,3}$ 3.6 Hz), 4.52-4.57 (m, 1H, H^3), 4.91-4.98 (m, 1H, H^7), 5.08 (dd, 1H, $H^{3'B}$, $^2J_{3'B,3'A}$ 1.2, $^3J_{3'B,2'}$ 16.9 Hz), 5.14 (dd, 1H, $H^{3'A}$, $^2J_{3'A,3'B}$ 1.2, $^3J_{3'A,2}$ 9.9 Hz), 5.71-5.79 (m, 1H, $H^{2'}$). ^{13}C NMR (500 MHz, $CDCl_3$): δ 20.84 (OAc), 40.03 (C^4), 40.78 ($C^{1'}$), 44.90 (C^8), 47.03 (C^5), 49.31 (C^6), 51.71 (C^7), 66.51 ($C^{1''}$), 69.92 (C^3), 76.91 (C^1), 119.65 ($C^{3'}$), 132.821 ($C^{2'}$), 170.69 (OAc), 211.36 (C=O). IR (neat) 3075, 2942, 1731, 1236, 1104, 1044, 922, 807, 702 cm-1; Mass spectrum, *m/z*: 287 $[M\text{H}]^+$. Calcd for $C_{14}H_{19}ClO_4$.

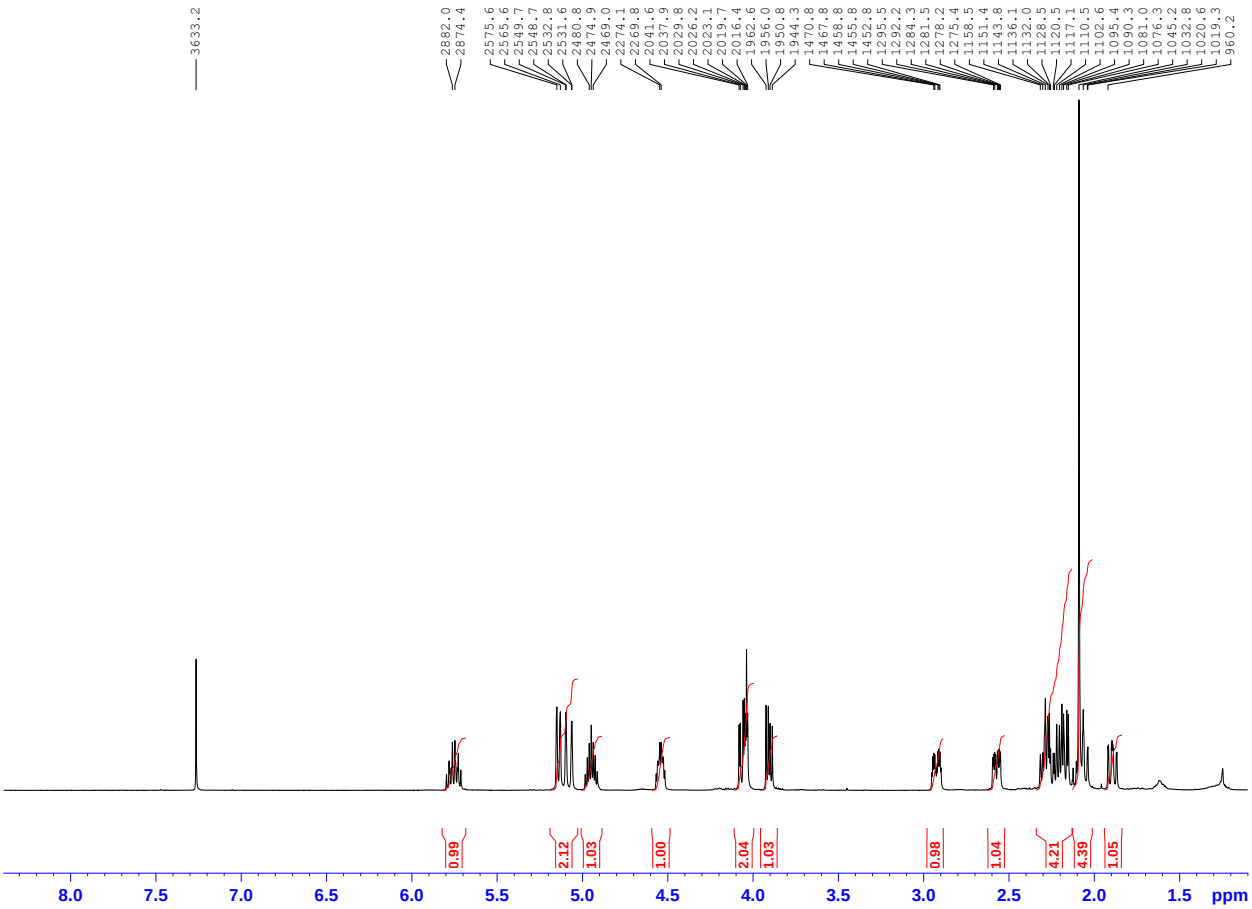


Fig. S9.1. Complete ^{1}H NMR (500 MHz) spectrum in $CDCl_3$ of (**7*S*)-9a**

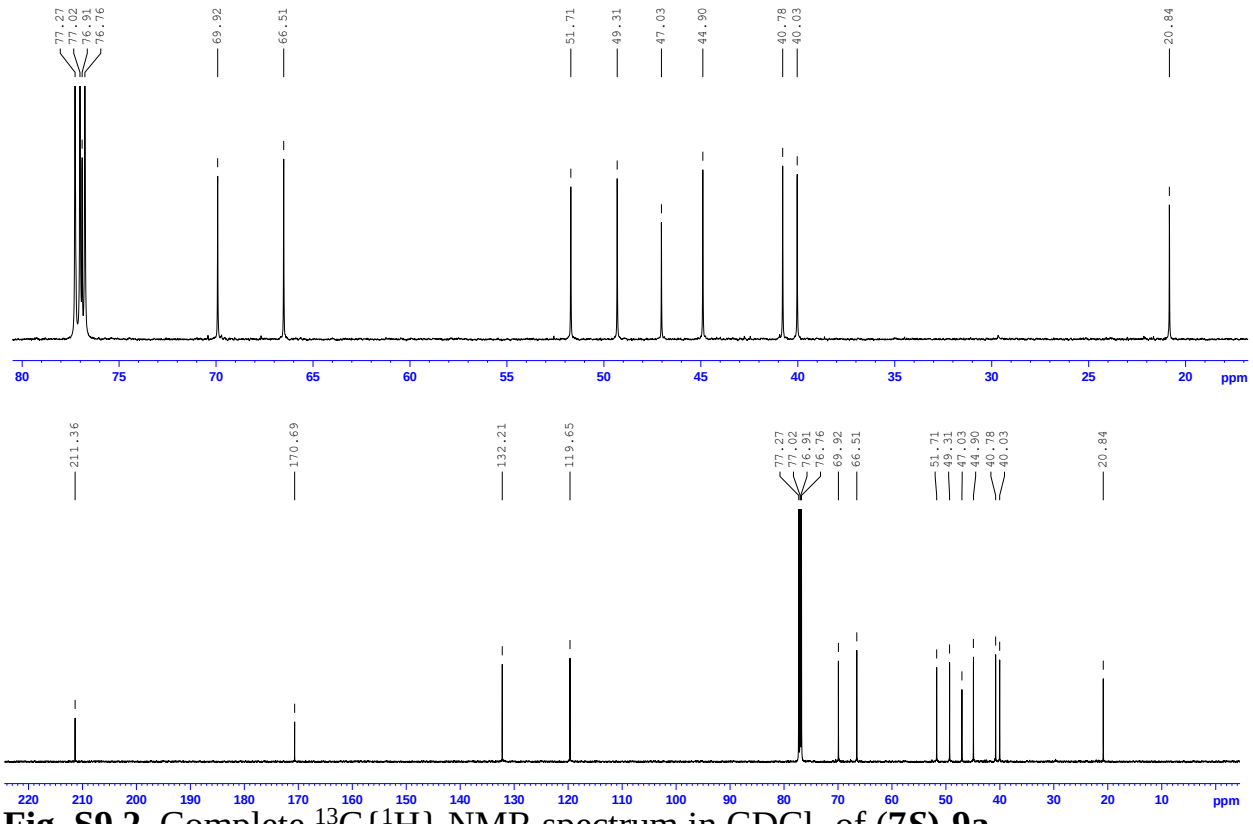


Fig. S9.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of (**7*S*)-9a**

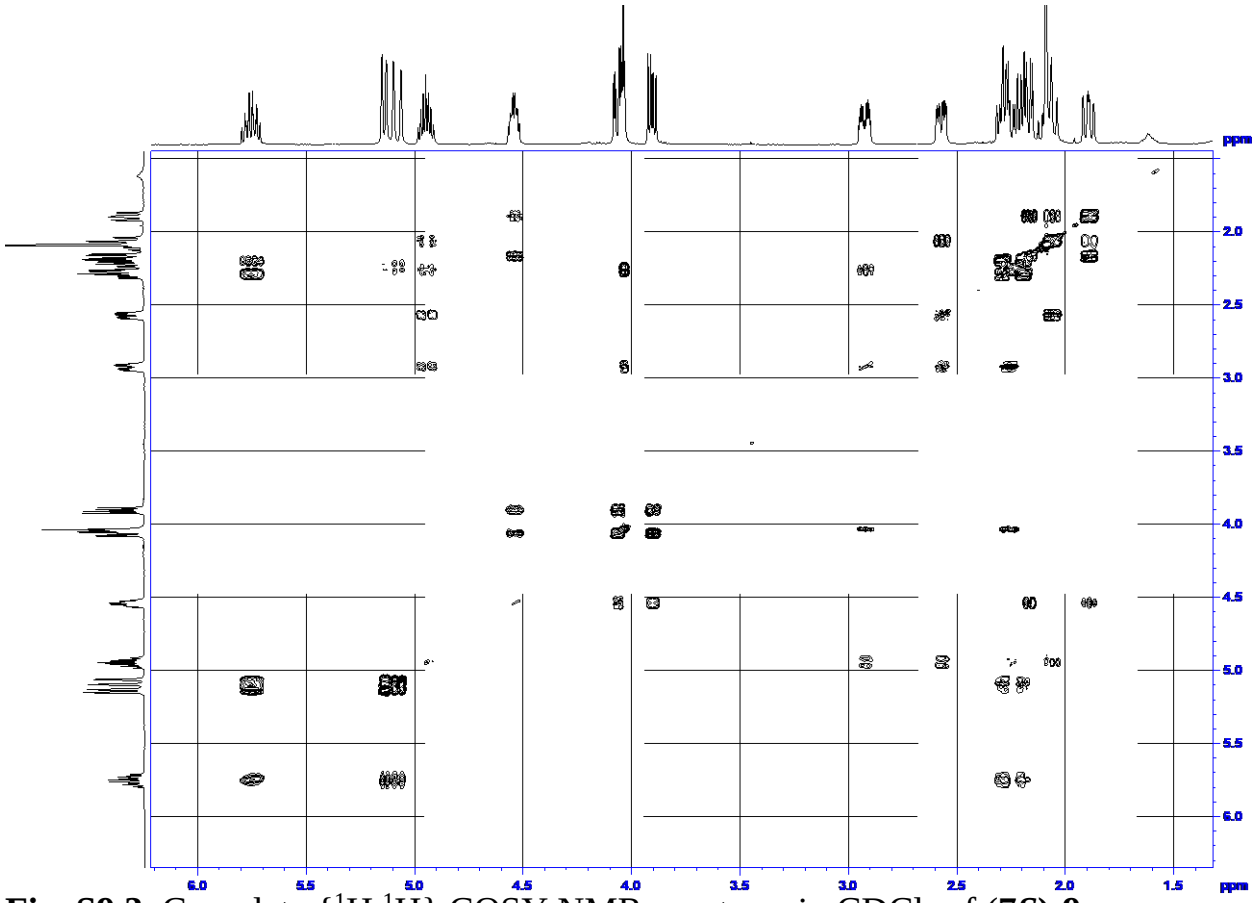


Fig. S9.3. Complete {^{1}H,^{1}H} COSY NMR spectrum in $CDCl_3$ of (7***S***)-9a

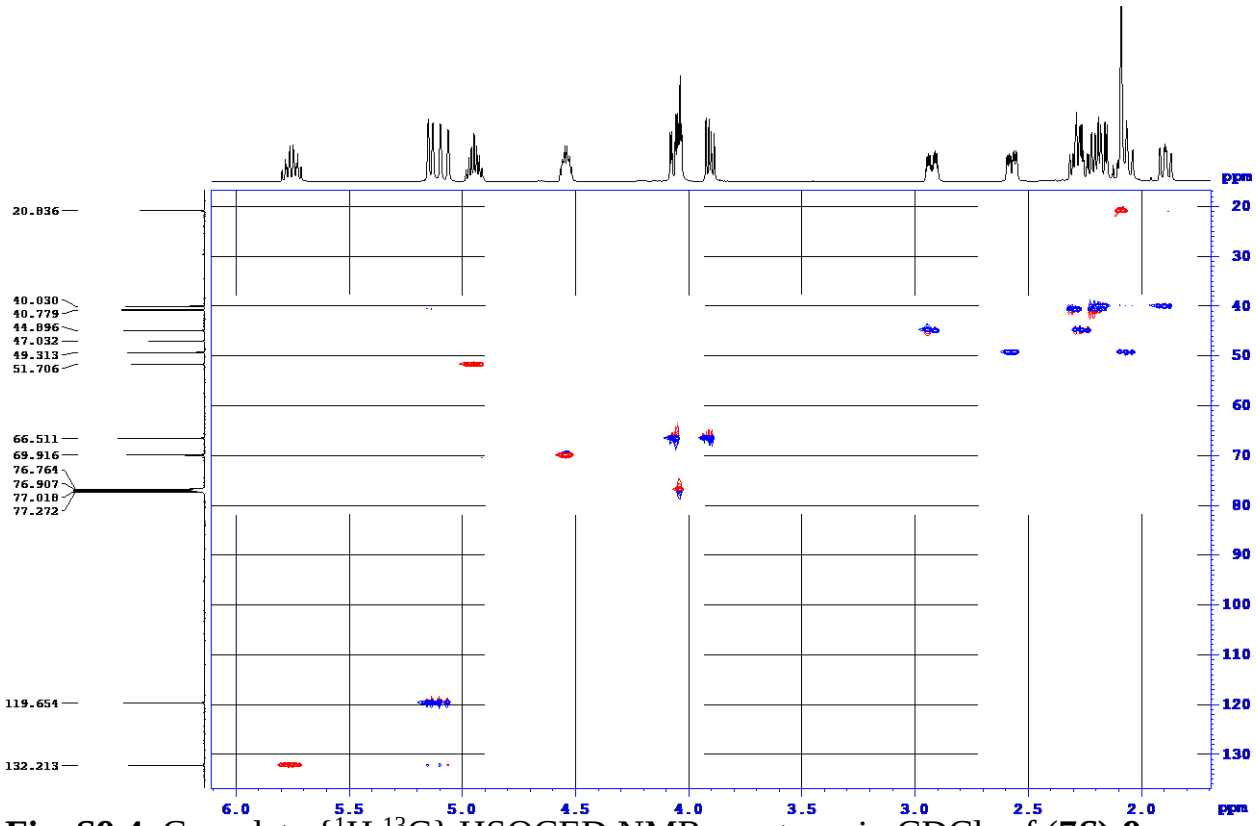


Fig. S9.4. Complete {^{1}H,^{13}C} HSQCED NMR spectrum in $CDCl_3$ of (7***S***)-9a

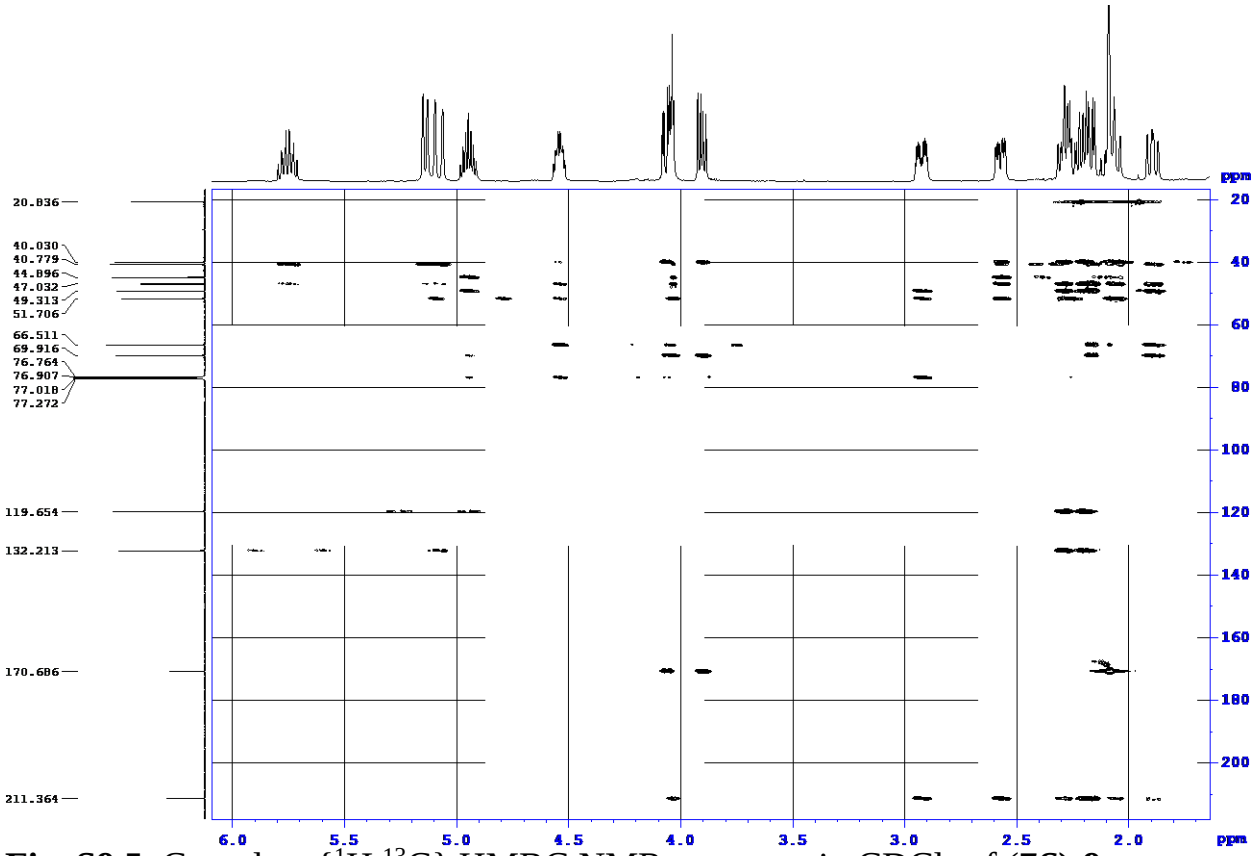


Fig. S9.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum in $CDCl_3$ of (**7*S*)-9a**

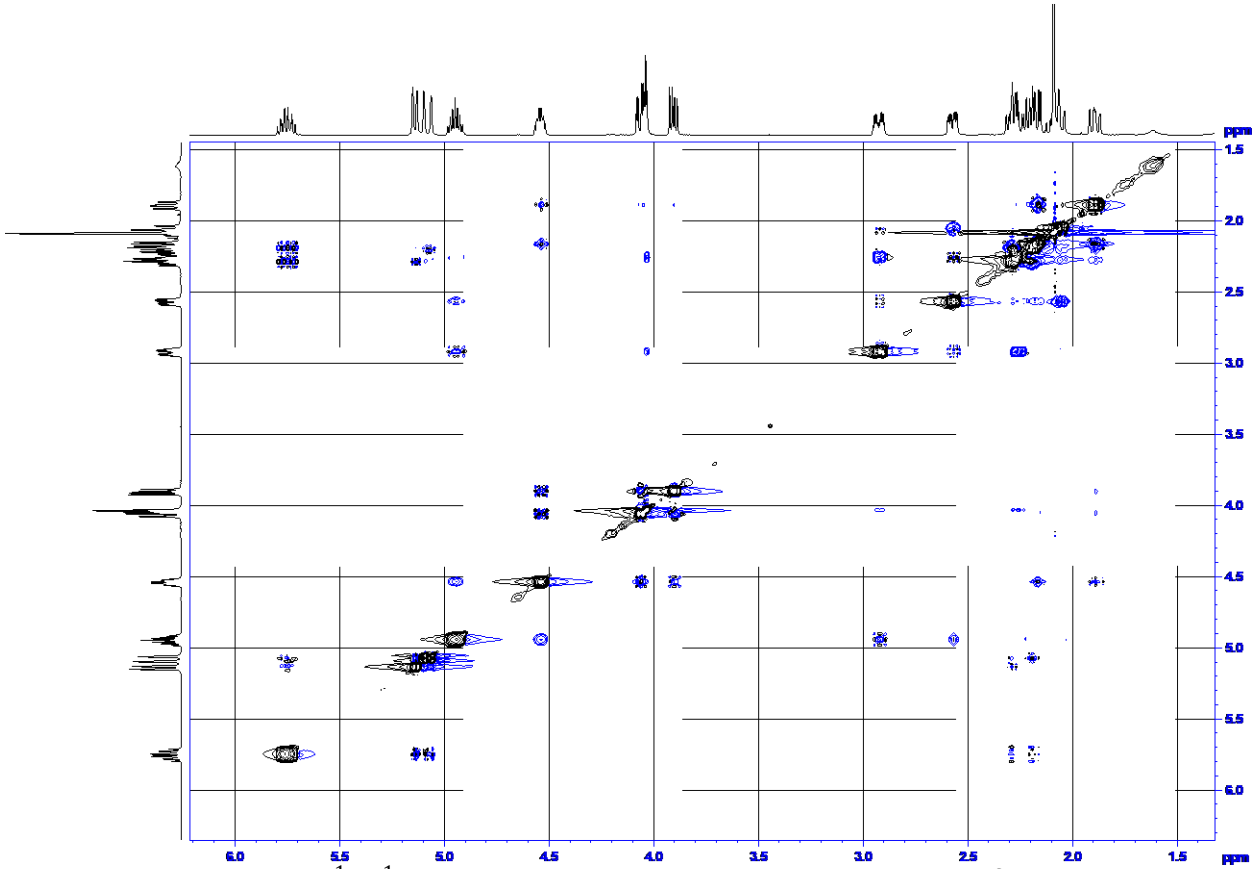
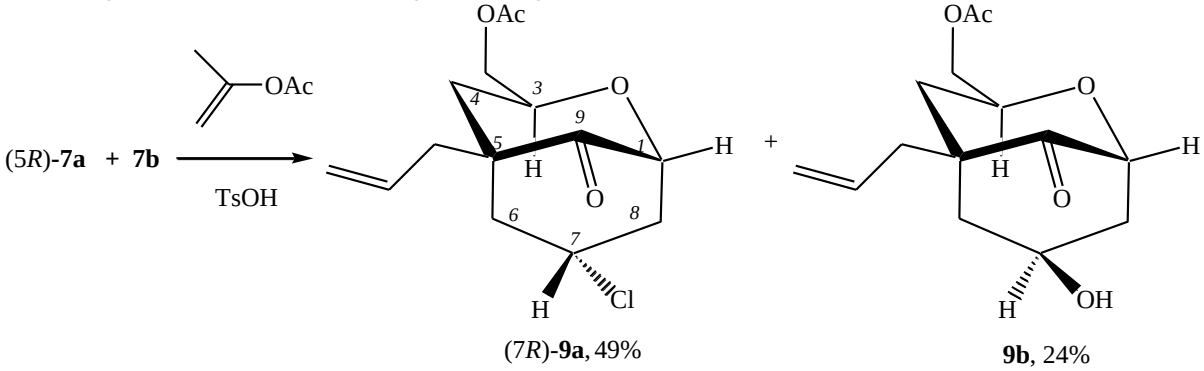


Fig. S9.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum in $CDCl_3$ of (**7*S*)-9a**

((1*R*,3*S*,5*S*,7*R*)-5-Allyl-7-chloro-9-oxo-2-oxabicyclo[3.3.1]nonan-3-yl)methyl acetate (9a) and ((1*R*,3*S*,5*R*,7*S*)-5-allyl-7-hydroxy-9-oxo-2-oxabicyclo[3.3.1]nonan-3-yl)methyl acetate (9b).



(7*R*)-**9a**, 49% **9b**, 24%

A catalytic amount of *p*-toluenesulfonic acid was added to a solution of a mixture of compounds (5*S*)-**7a** and **7b** (0.035 g) in isopropenyl acetate (5 ml). The solution was stirred at room temperature for 20 h (TLC) and then treated with H_2O (4 ml) and extracted with EtOAc (3×7.0 ml). The extract was dried over $MgSO_4$, the solvent was distilled off, and the residue was purified by column chromatography on silica gel.

9a: Yield 0.020 g (49%). Colourless oil. $[\alpha]_D^{20}$ +13.2 ° (*c* 1.35, $CHCl_3$). R_f 0.6 (EtOAc–petroleum ether, 1:2).

^{1}H NMR (500 MHz, $CDCl_3$): 1.76 (t, 1H, H^{4B}, *J* = 13.1 Hz), 1.95 (dd, 1H, H^{4A}, *J* = 13.1, 2.7 Hz), 2.11 (s, 3H, CH_3), 2.13 (dd, 1H, $H^{1'B}$, *J* = 14.2, 7.5 Hz), 2.32 (dd, 1H, $H^{1'A}$, *J* = 14.2, 6.8 Hz), 2.38-2.45 (m, 2H, H^{6A}, H^{6B}), 2.51 (t, 1H, H^{8B}, *J* = 14.5 Hz), 2.76-2.83 (m, 1H, H^{8A}), 3.67-3.75 (m, 1H, H^7), 4.07 (dd, 1H, $H^{1''B}$, *J* = 11.7, 6.2 Hz), 4.10 (d, 1H, H^1, *J* = 8.6 Hz), 4.21 (dd, 1H, $H^{1''A}$, *J* = 11.7, 3.4 Hz), 4.55-4.61 (m, 1H, H^3), 5.11 (d, 1H, $H^{3'B}$, *J* = 17.0 Hz), 5.15 (d, 1H, $H^{3'A}$, *J* = 10.0 Hz), 5.71-5.80 (m, 1H, $H^{2'}$).

^{13}C NMR (125 MHz, $CDCl_3$): δ 20.86 (CH_3), 39.26 (C^8), 40.54 ($C^{1'}$), 43.98 (C^6), 44.17 (C^4), 46.11 (C^5), 50.19 (C^7), 65.62 ($C^{1''}$), 65.66 (C^3), 75.68 (C^1), 119.86 ($C^{3'}$), 132.25 ($C^{2'}$), 170.77 (C=O) , 211.27 (C=O).

IR (neat) 3075, 2942, 1731, 1236, 1104, 1044, 922, 807, 702 cm-1; Mass spectrum, *m/z*: 287 $[MH]^+$. Calcd for $C_{14}H_{19}ClO_4$.

NMR spectrum of compound (**7*R*)-9a**:

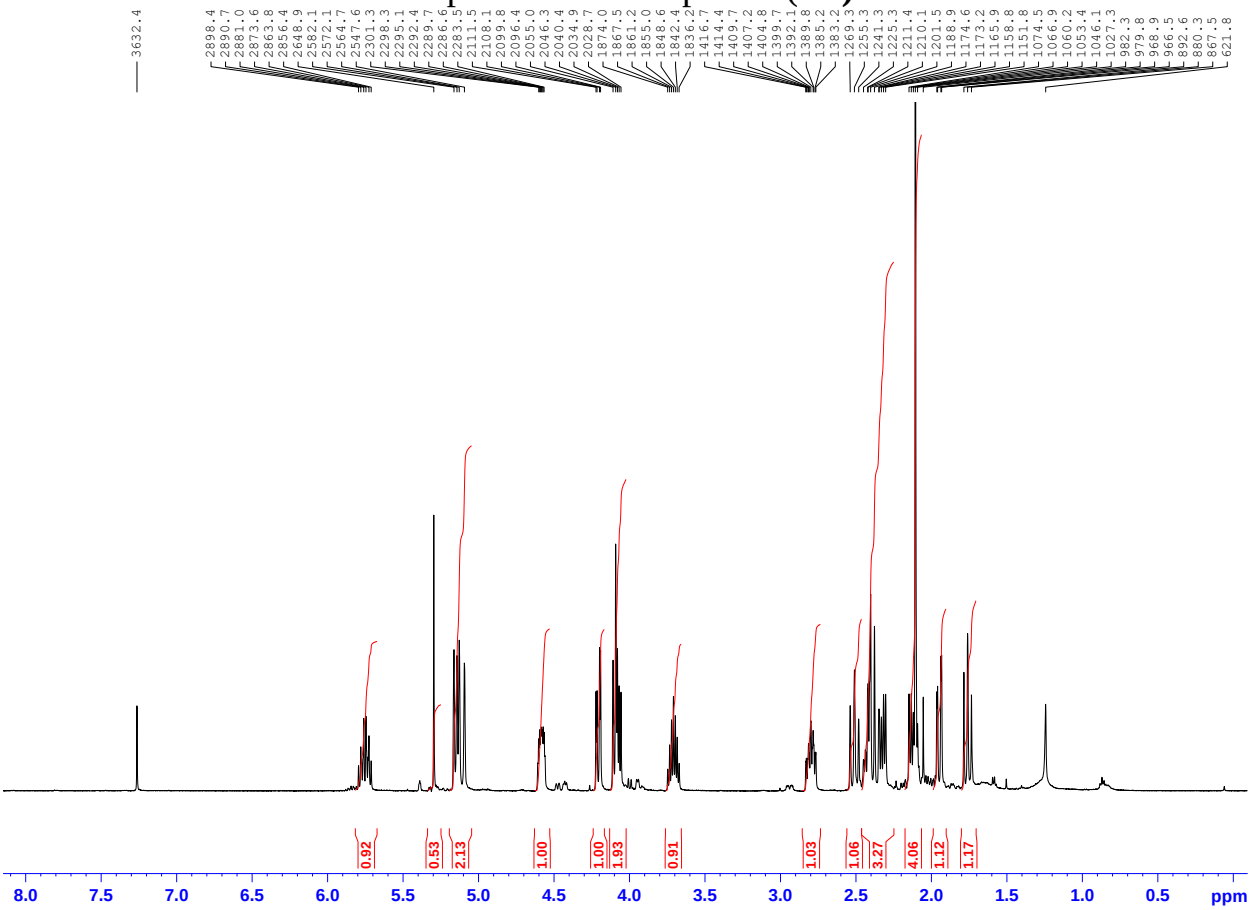


Fig. S10.1. Complete ^{1}H NMR (500 MHz) spectrum in $CDCl_3$ of (**7*R*)-9a**

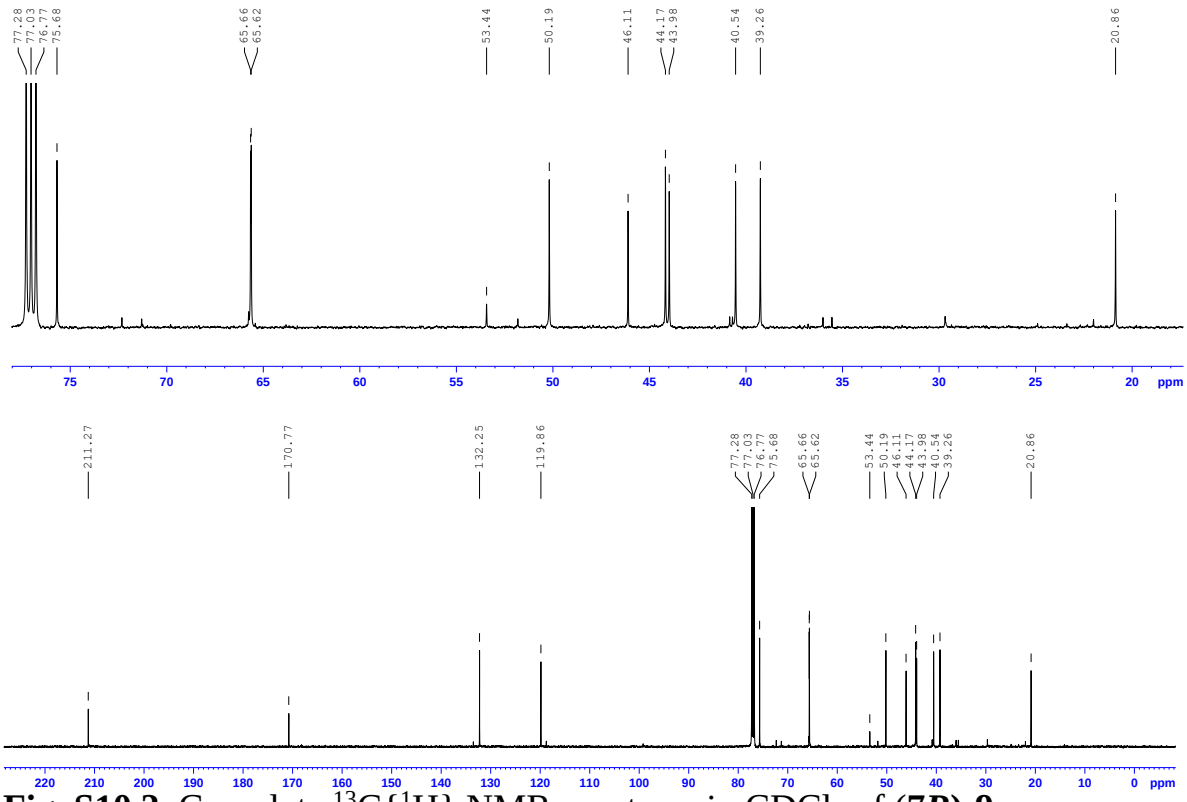


Fig. S10.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of (**7*R*)-9a**

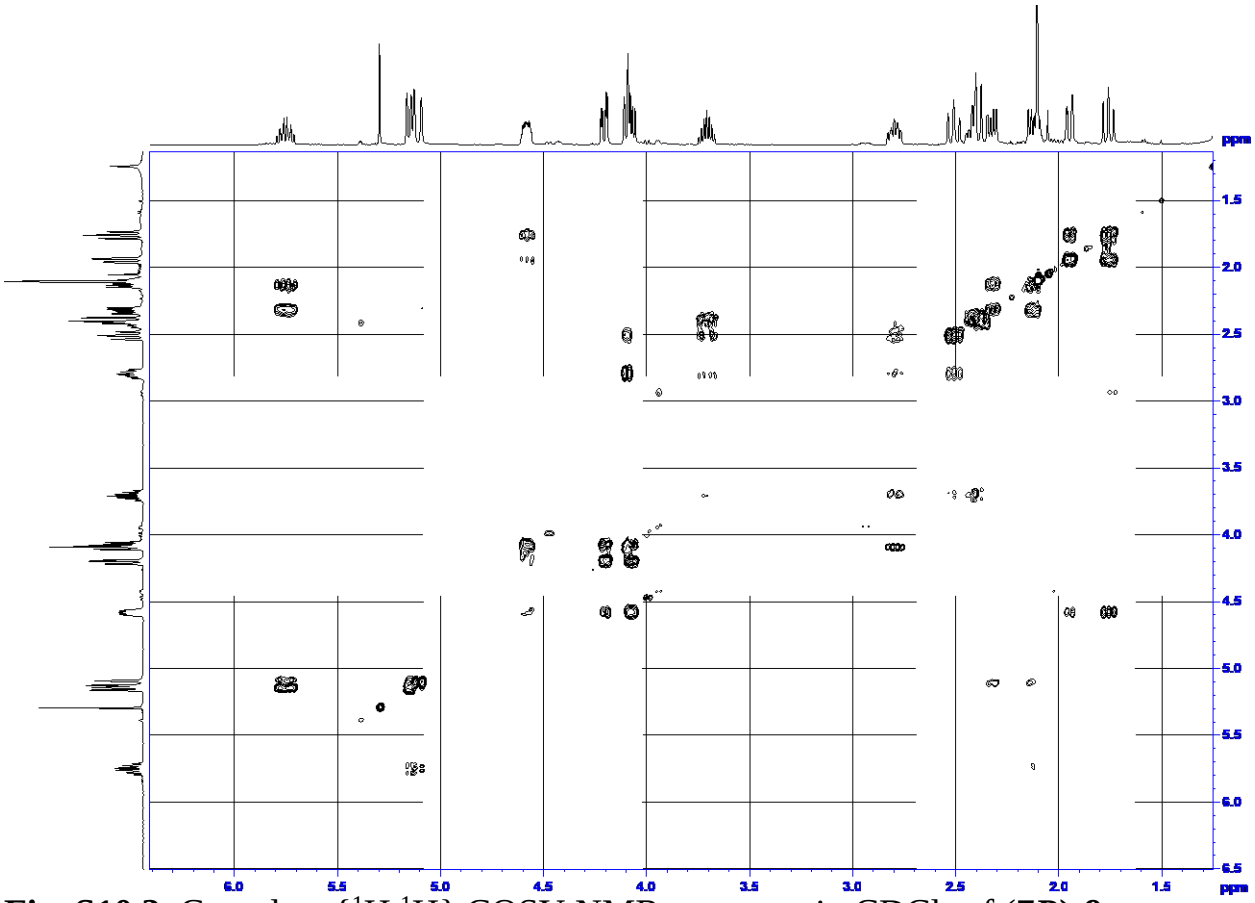


Fig. S10.3. Complete {^{1}H,^{1}H} COSY NMR spectrum in $CDCl_3$ of (7***R***)-9a

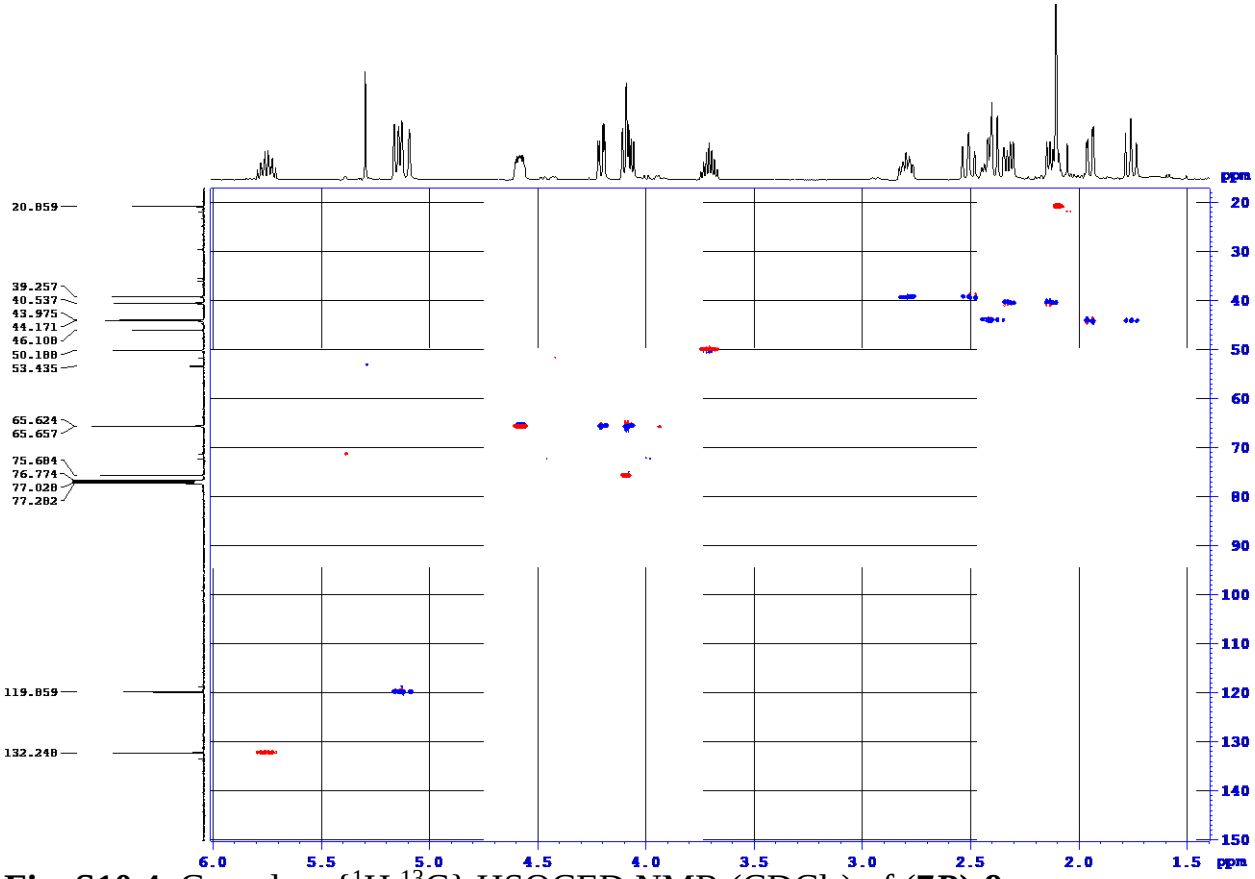


Fig. S10.4. Complete {^{1}H,^{13}C} HSQCED NMR ($CDCl_3$) of (7***R***)-9a

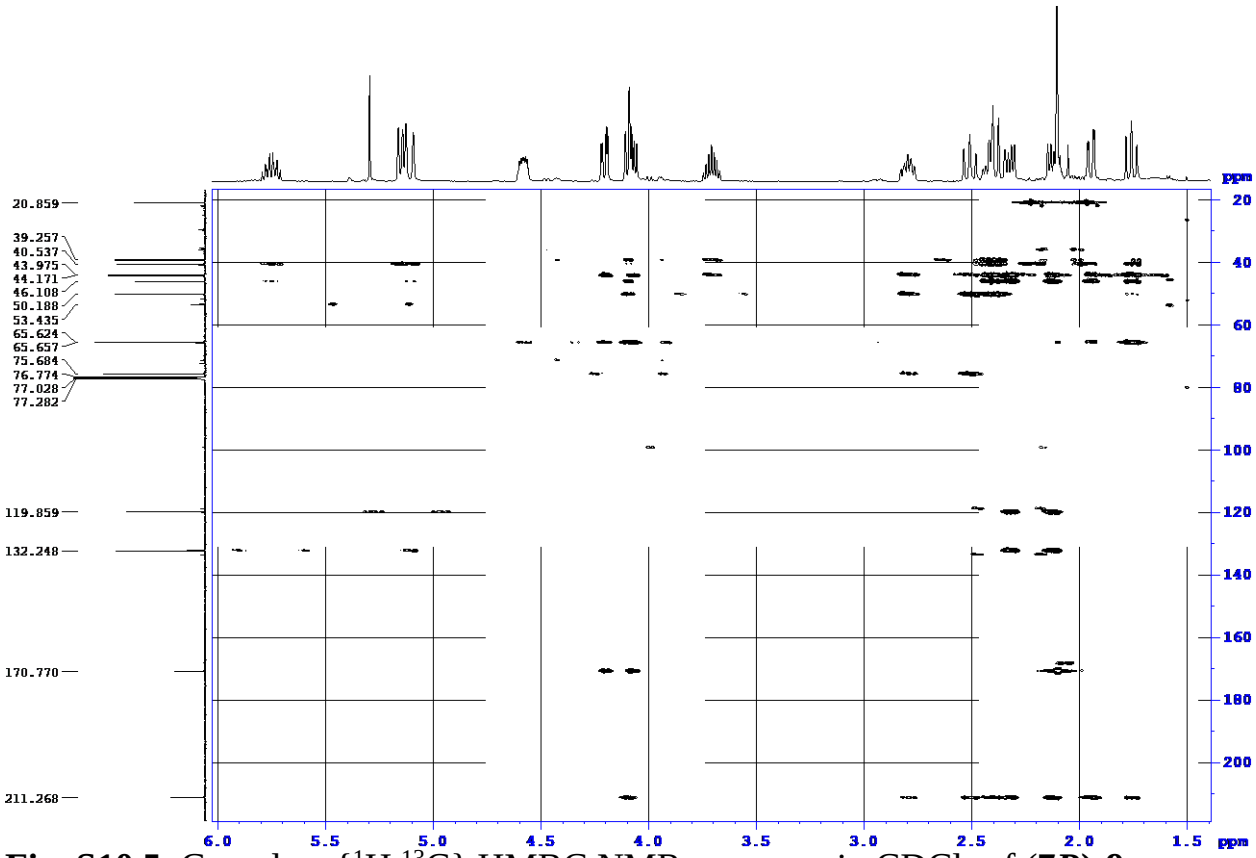


Fig. S10.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum in $CDCl_3$ of (**7*R*)-9a**

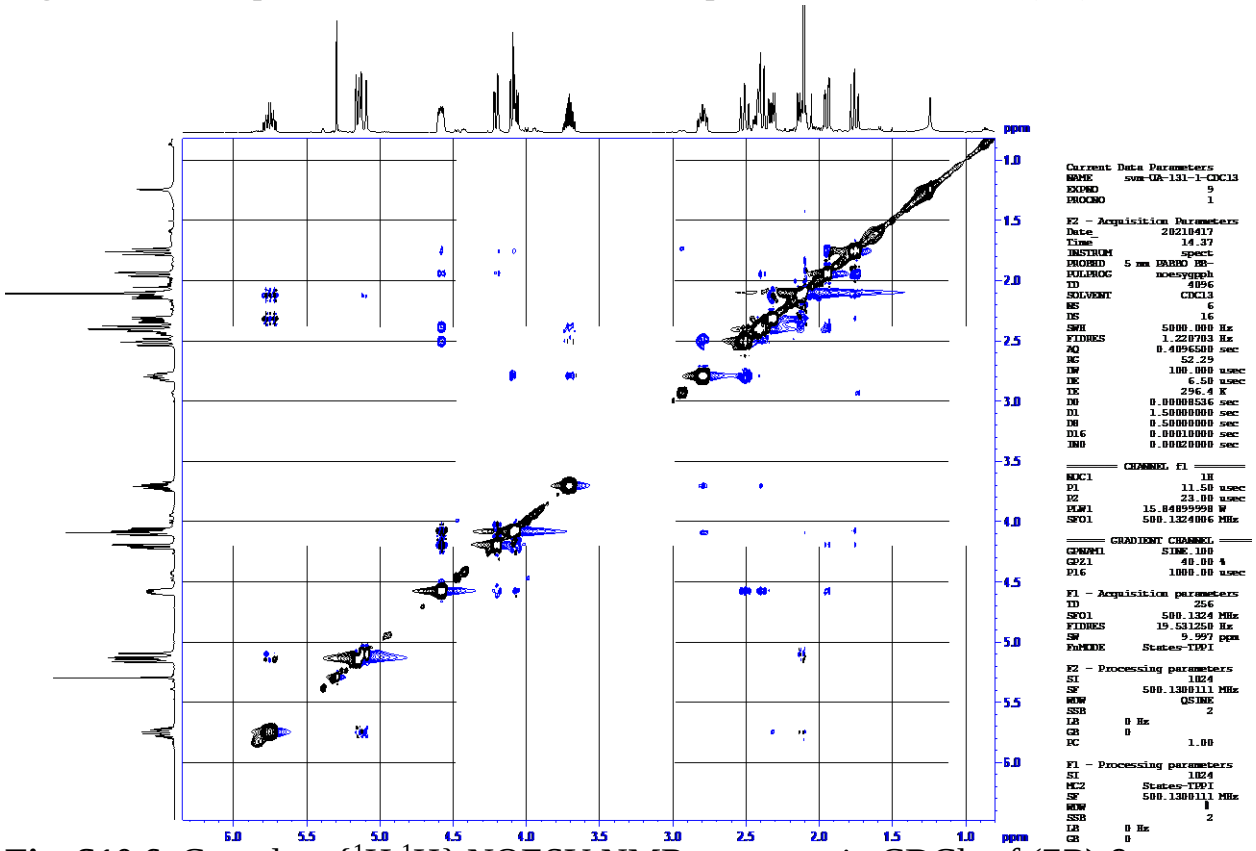


Fig. S10.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum in $CDCl_3$ of (**7*R*)-9a**

(**7*S*)-9b:** Yield 0.009 g (24%). Colourless oil. $[\alpha]_D^{20}$ +11.6° (*c* 1.0, $CHCl_3$). R_f 0.26 (EtOAc–petroleum ether, 1:2).

^{1}H NMR (500 MHz, $CDCl_3$): 2.04 (dd, 1H, H^{4B}, *J* = 14.7, 8.9 Hz), 2.09 (s, 3H, CH_3), 2.16 (dd, 1H, H^{6B}, *J* = 16.0, 5.7 Hz), 2.28 (dd, 1H, H^{4A}, *J* = 14.7, 5.5 Hz), 2.30-2.40 (m, 3H, $H^{1'A}$, H^{6A}, H^{8B}), 2.65 (dd, 1H, $H^{1'B}$, *J* = 14.2, 8.4 Hz), 2.77-2.85 (m, 1H, H^{8A}), 3.89 (dd, 1H, $H^{1''B}$, *J* = 11.7, 6.7 Hz), 4.03 (t, 1H, H^1, *J* = 3.0 Hz), 4.06 (dd, 1H, $H^{1''A}$, *J* = 11.7, 3.8 Hz), 4.49-4.52 (m, 1H, H^7), 4.60-4.66 (m, 1H, H^3), 5.16-5.21 (m, 2H, $H^{3'B}$, $H^{3'A}$), 5.66-5.74 (m, 1H, $H^{2'}$).

^{13}C NMR (125 MHz, $CDCl_3$): δ 20.83 (CH_3), 29.61 (C^8), 29.75 (C^6), 38.27 ($C^{1'}$), 39.29 (C^4), 51.58 (C^5), 66.55 (C^{10}), 68.25 (C^7), 69.34 (C^3), 76.04 (C^1), 120.33 ($C^{3'}$), 131.34 ($C^{2'}$), 170.69 (C=O) , 208.62 (C=O).

IR (neat) 3467, 2950, 1734, 1368, 1237, 1052, 958, 628 cm-1; Mass spectrum, *m/z*: 269 $[MH]^+$. Calcd for $C_{14}H_{20}O_5$.

NMR spectrum of compound (**7*S*)-9b**:

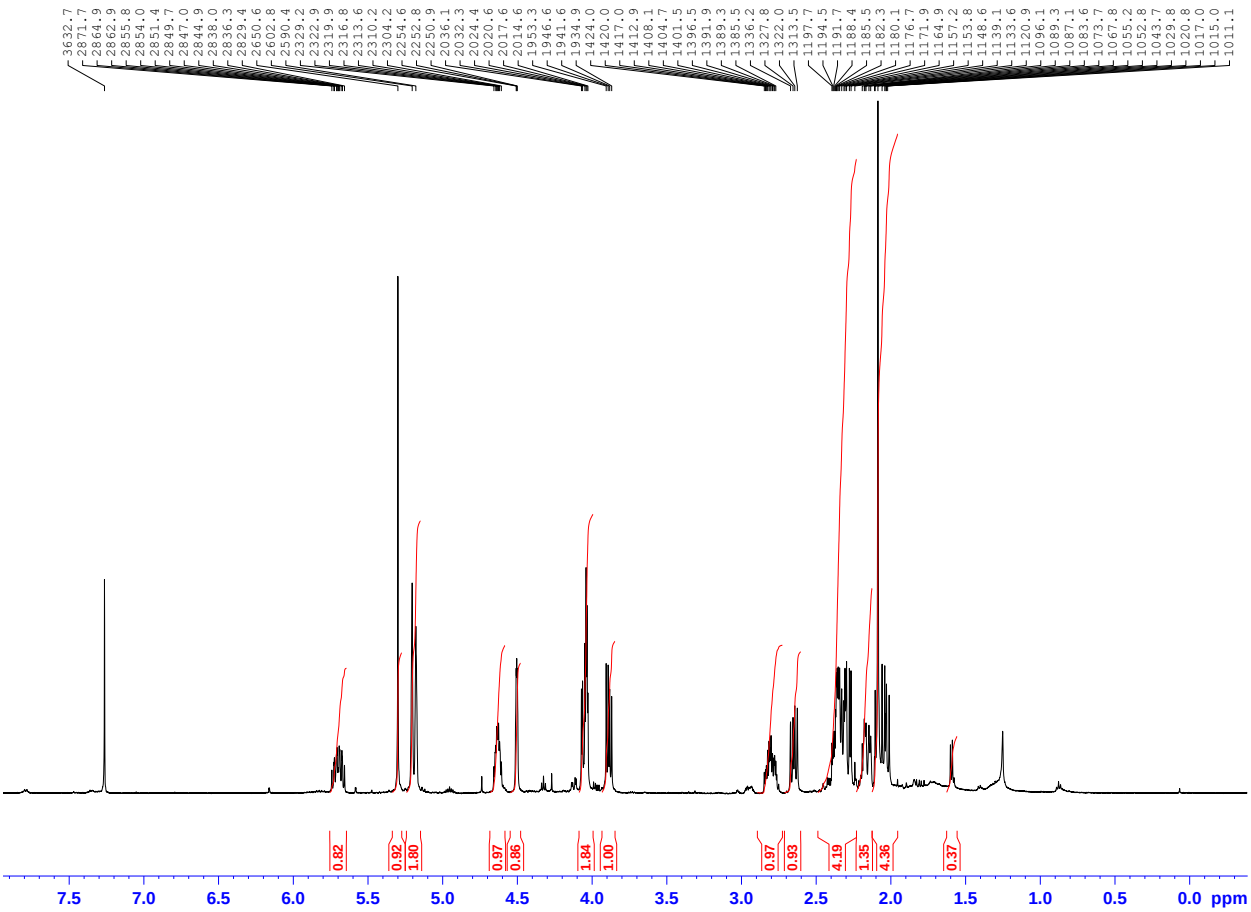


Fig. S11.1. Complete ^{1}H NMR (500 MHz) spectrum in $CDCl_3$ of (**7*S*)-9b**

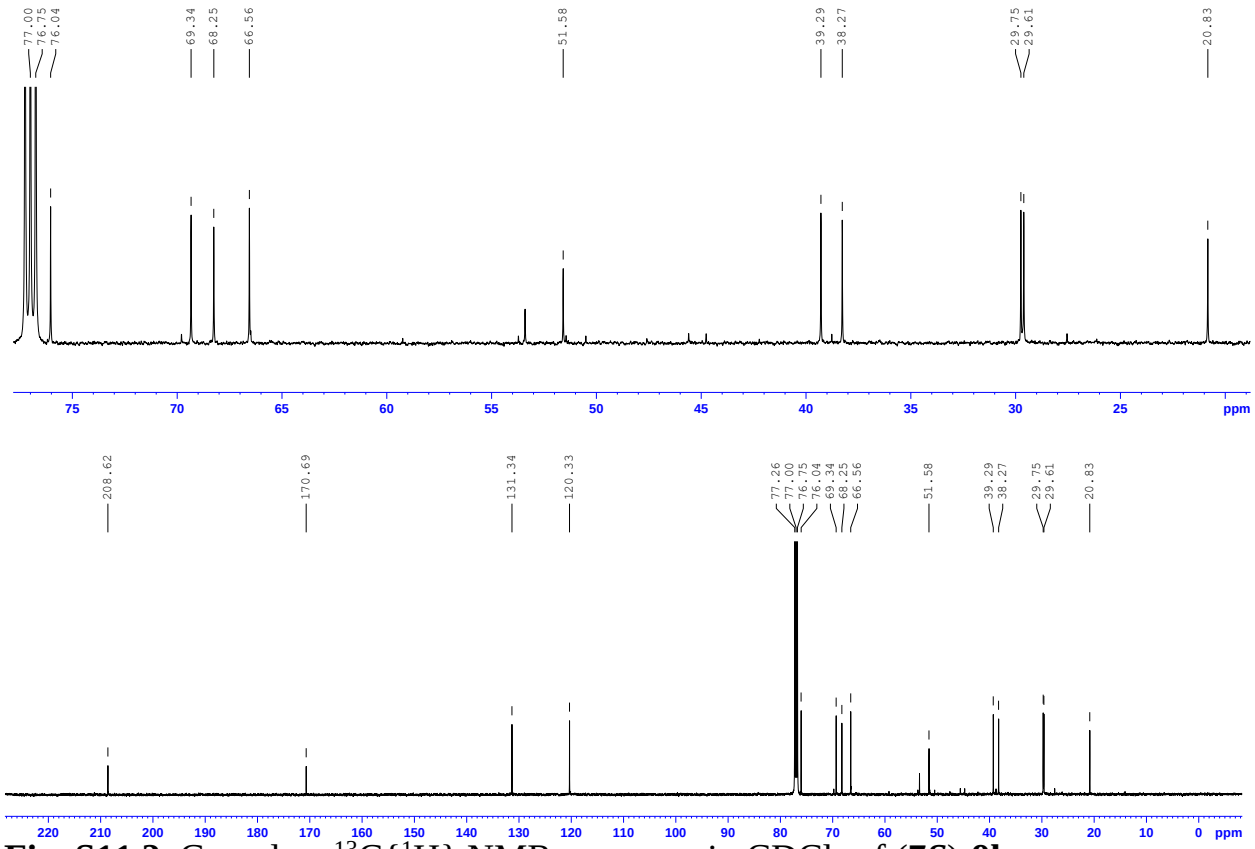


Fig. S11.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of (**7*S*)-9b**

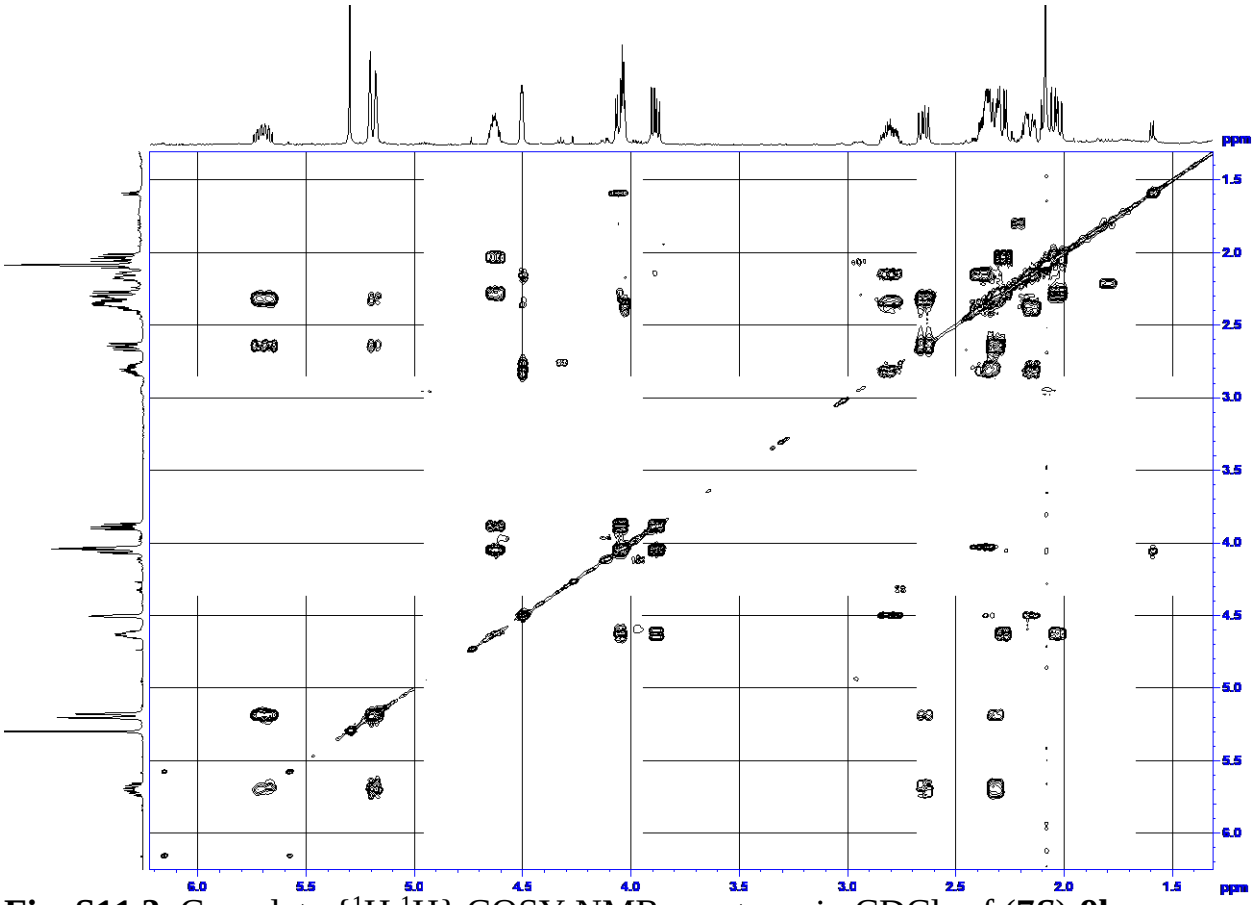


Fig. S11.3. Complete $\{^{1}H,^{1}H\}$ COSY NMR spectrum in $CDCl_3$ of (**7*S*)-9b**

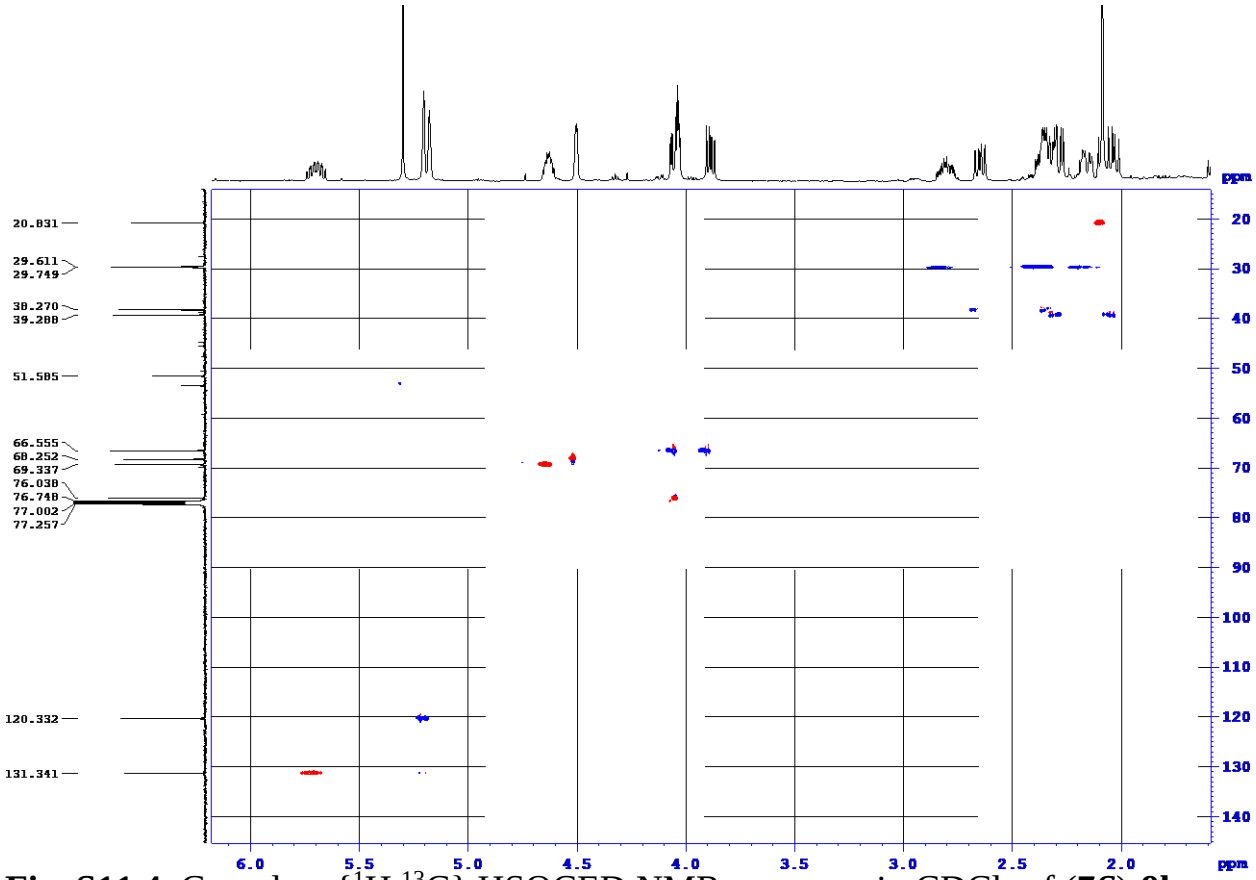


Fig. S11.4. Complete {^{1}H,^{13}C} HSQCED NMR spectrum in $CDCl_3$ of (7***S***)-**9b**

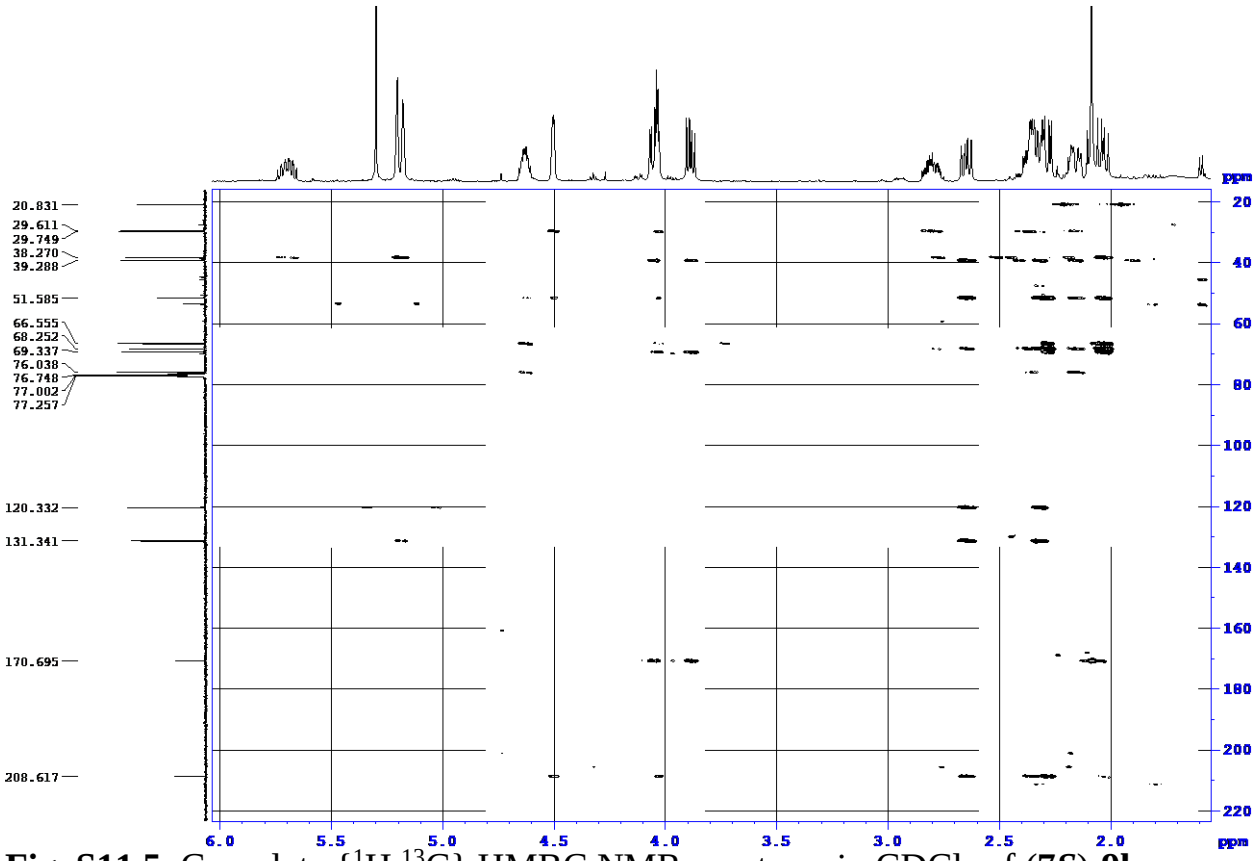


Fig. S11.5. Complete {^{1}H,^{13}C} HMBC NMR spectrum in $CDCl_3$ of (7***S***)-**9b**

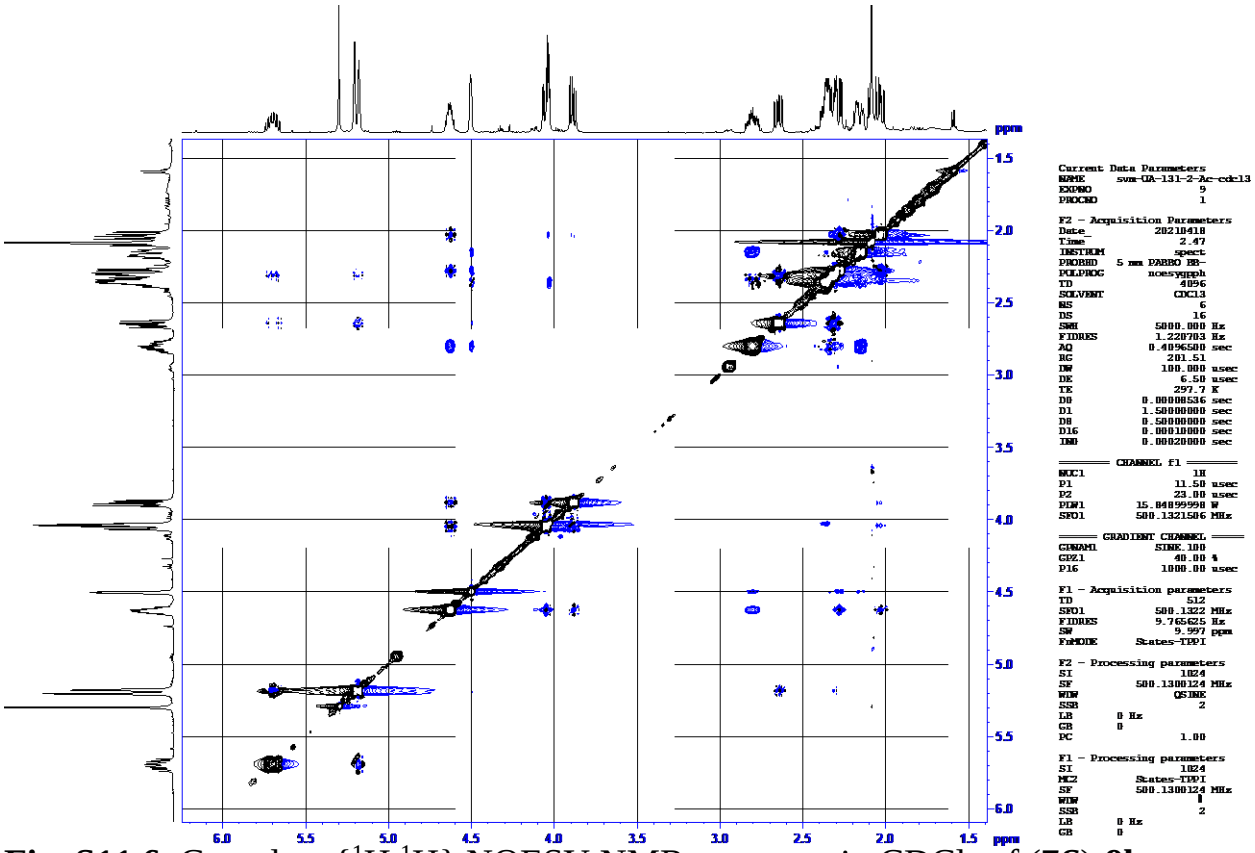


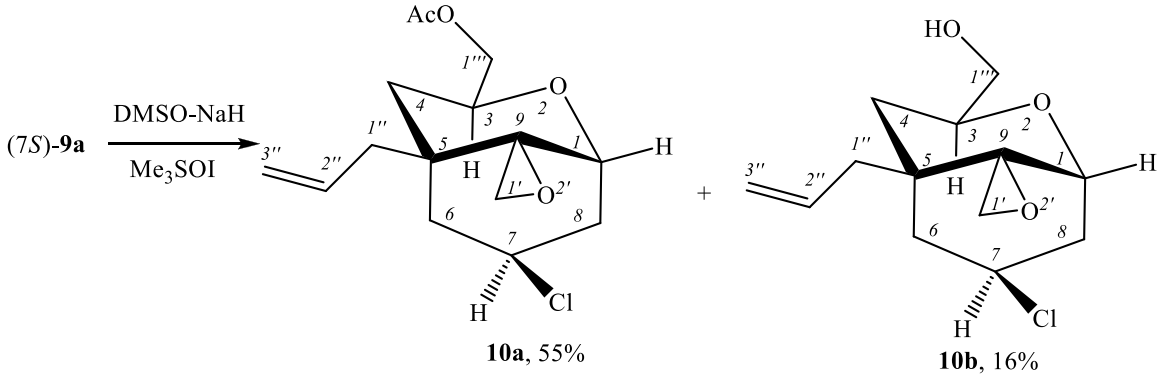
Fig. S11.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum in $CDCl_3$ of (7***S***)-**9b**

The formation of acetate **9a** is indicated by the $H^{1''}$/C=O correlation peak in the NMBC spectrum.

Opening the anhydro bridge with formation of an acetate group and a keto group at C^9 in compound (7*R*)-**9a** is indicated by the signals of a carboxyl carbon atom at δ 170.77 and of a keto group at δ 211.27 in the ^{13}C NMR spectrum. Moreover, the HMBC spectrum exhibits the $H^{1''}$/C=O^{Ac}, H^1/C^9 and H^1/C^3 correlation peaks. The *R*-configuration of the C^7 center was identified by the large coupling constant ($^3J_{8B\text{-}7}$ 14.5 Hz) between the H^7 and H^{8B} protons and the presence of the H^3/H^{8B} correlation peaks in the NOESY spectrum.

The existence of the NOE effect between the H^7 and H^{4A} protons in the NOESY spectrum of alcohol (7*S*)-**9b** indicates that the C^7 center has the *S*-configuration.

((1*R*,2'*R*,3*S*,5*S*,7*S*)-5-Allyl-7-chloro-2-oxaspiro[bicyclo[3.3.1]nonane-9,2'-oxirane]-3-yl)methyl acetate (10a) and ((1*R*,2'*R*,3*S*,5*S*,7*S*)-5-allyl-7-chloro-2-oxaspiro[bicyclo[3.3.1]nonane-9,2'-oxirane]-3-yl)methanol (10b)



A suspension of sodium hydride (7 mg, 0.4 mol, preliminarily washed with hexane) in DMSO (0.3 ml) was heated to 60–70°C. The solution turned yellow, it was cooled to 0°C, and a solution of trimethyloxosulfonium iodide (0.066 g, 0.3 mmol) of in DMSO (0.15 ml) and a solution of compound (7*S*)-**9a** (0.042 g, 0.2 mmol) in THF (0.2 ml) was added. The mixture was stirred at 0°C until the reaction was complete (TLC). The mixture was allowed to warm up to room temperature, treated with water (3 ml), and extracted with ethyl acetate (3×2.0 ml). The extract was dried over $MgSO_4$ and evaporated, and the residue was purified by silica gel column chromatography.

Product 10a: Yield 0.0024 g (55%). Colourless oil. $[\alpha]_D^{20}$ +13 ° (*c* 1.0, $CHCl_3$). R_f 0.5 (EtOAc–petroleum ether, 1:2).

10a: ^{1}H NMR (500 MHz, $CDCl_3$): 1.45 (dt, 1H, H^{4B}, *J* = 13.8, 13.8, 1.7 Hz), 1.74 (dd, 1H, $H^{1''B}$, *J* = 13.5, 7.6 Hz), 1.93 (dd, 1H, H^{4A}, *J* = 13.8, 4.0 Hz), 2.01 (dt, 1H, H^{6B}, *J* = 13.7, 13.7, 1.6 Hz), 2.04-2.08 (m, 1H, $H^{1''A}$), 2.09 (s, 3H, CH_3), 2.23 (ddd, 1H, H^{8B}, *J* = 14.6, 12.0, 3.2 Hz), 2.30 (ddd, 1H, H^{6A}, *J* = 13.7, 6.0, 1.9 Hz), 2.60 (tdd, 1H, H^{8A}, *J* = 14.6, 3.2, 1.9, 1.9 Hz), 2.75 (d, 1H, $H^{1'B}$, *J* = 4.1 Hz), 3.06 (d, 1H, $H^{1'A}$, *J* = 4.1 Hz), 3.39 (t, 1H, H^1, *J* = 3.2 Hz), 3.87 (dd, 1H, $H^{1'''B}$, *J* = 11.5, 6.6 Hz), 4.10 (dd, 1H, $H^{1'''A}$, *J* = 11.5, 3.2 Hz), 4.27-4.32 (m, 1H, H^3), 4.74-4.82 (m, 1H, H^7), 5.03 (dd, 1H, $H^{3''B}$, *J* = 17.0, 1.0 Hz), 5.11 (dd, 1H, $H^{3''A}$, *J* = 10.0, 1.0 Hz), 5.65-5.74 (m, 1H, $H^{2''}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.86 (CH_3), 36.26 (C^5), 38.21 (C^4), 40.37 (C^8), 40.44 ($C^{1''}$), 43.05 (C^6), 51.44 ($C^{1'}$), 54.13 (C^7), 60.57 (C^9), 67.69 ($C^{1'''}$), 70.73 (C^3), 75.83 (C^1), 119.28 ($C^{3''}$), 131.95 ($C^{2''}$), 170.79 (C=O). IR (neat) 2939, 1740, 1639, 1440, 1368, 1236, 1043, 988, 610, 378 cm-1; Mass spectrum, *m/z*: 301 $[MH]^+$. Calcd for $C_{15}H_{19}ClO_4$.

NMR spectrum of compound **10a**:

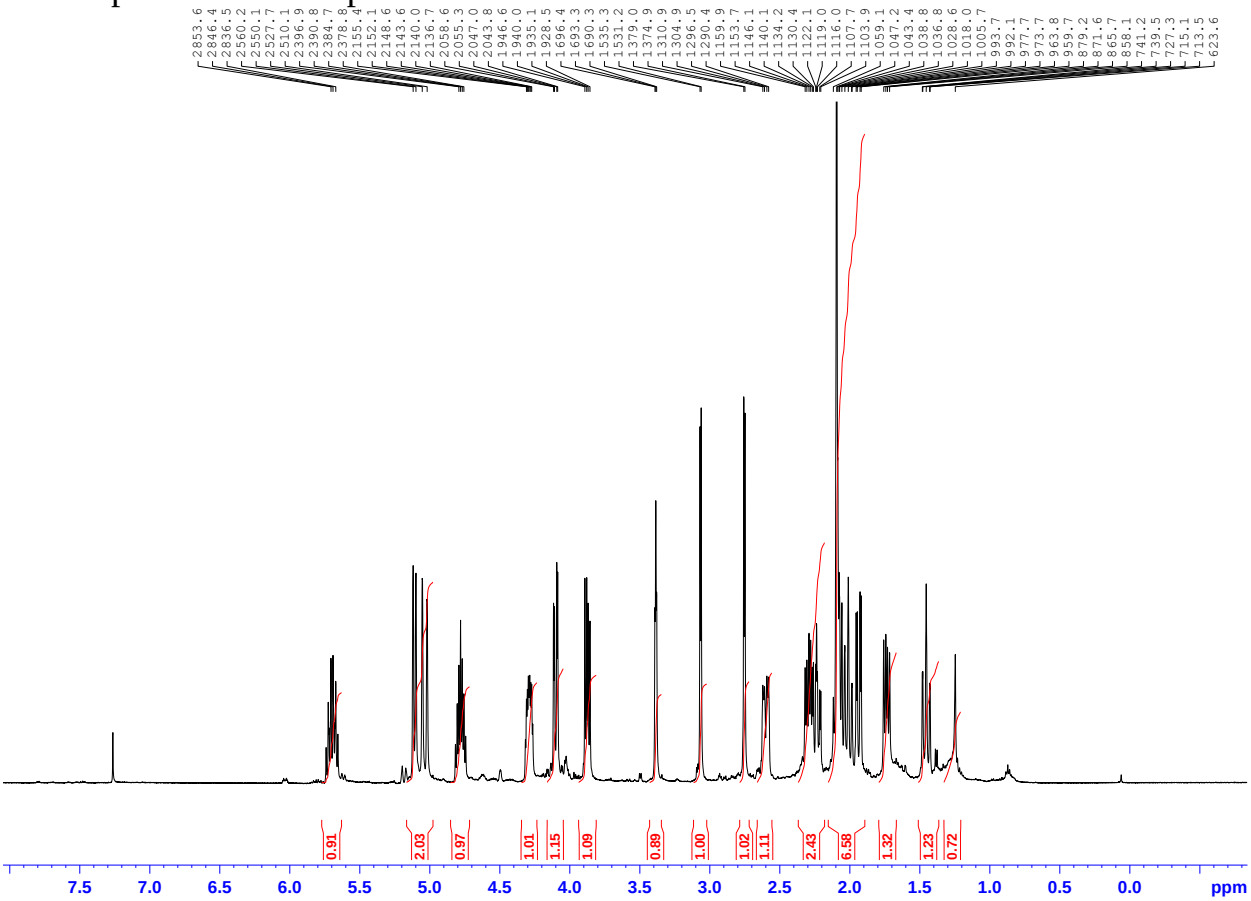


Fig. S12.1. Complete ^{1}H NMR (500 MHz, $CDCl_3$) of compound **10a**

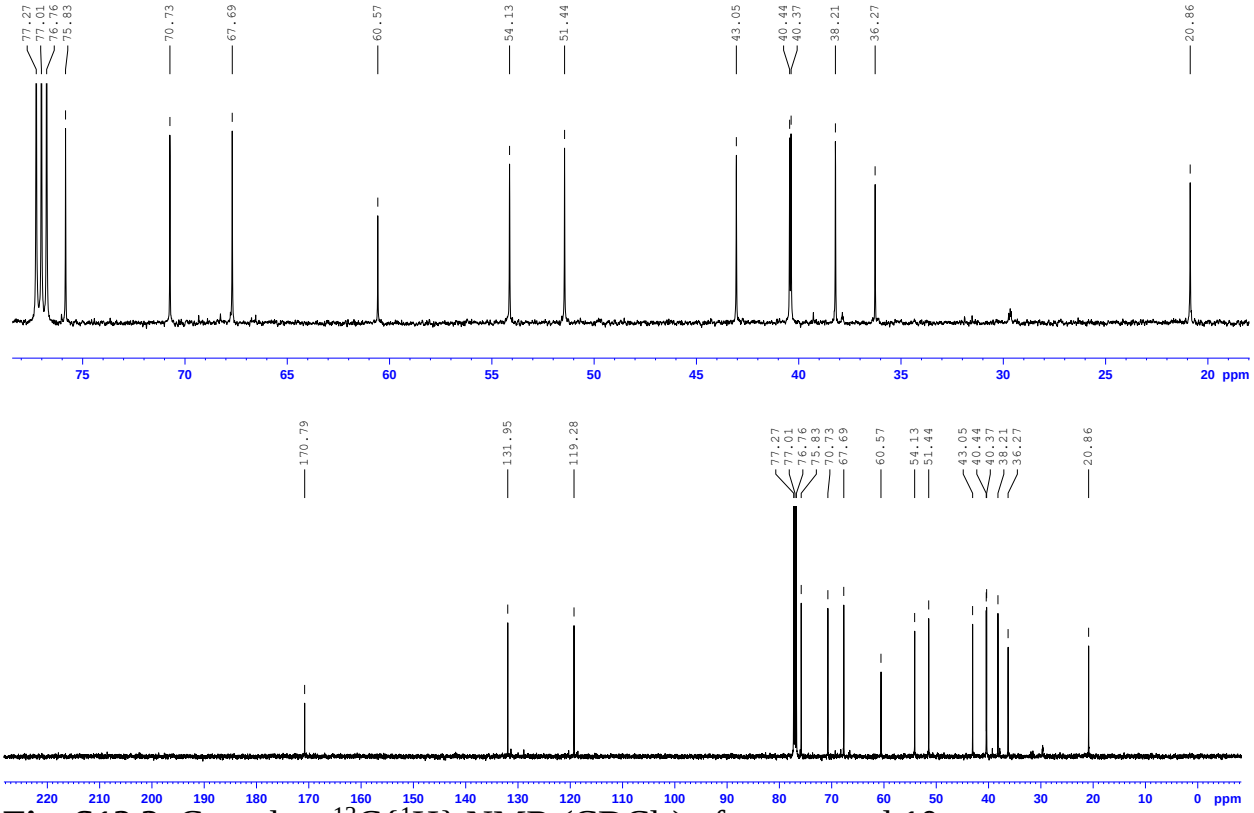


Fig. S12.2. Complete $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound **10a**

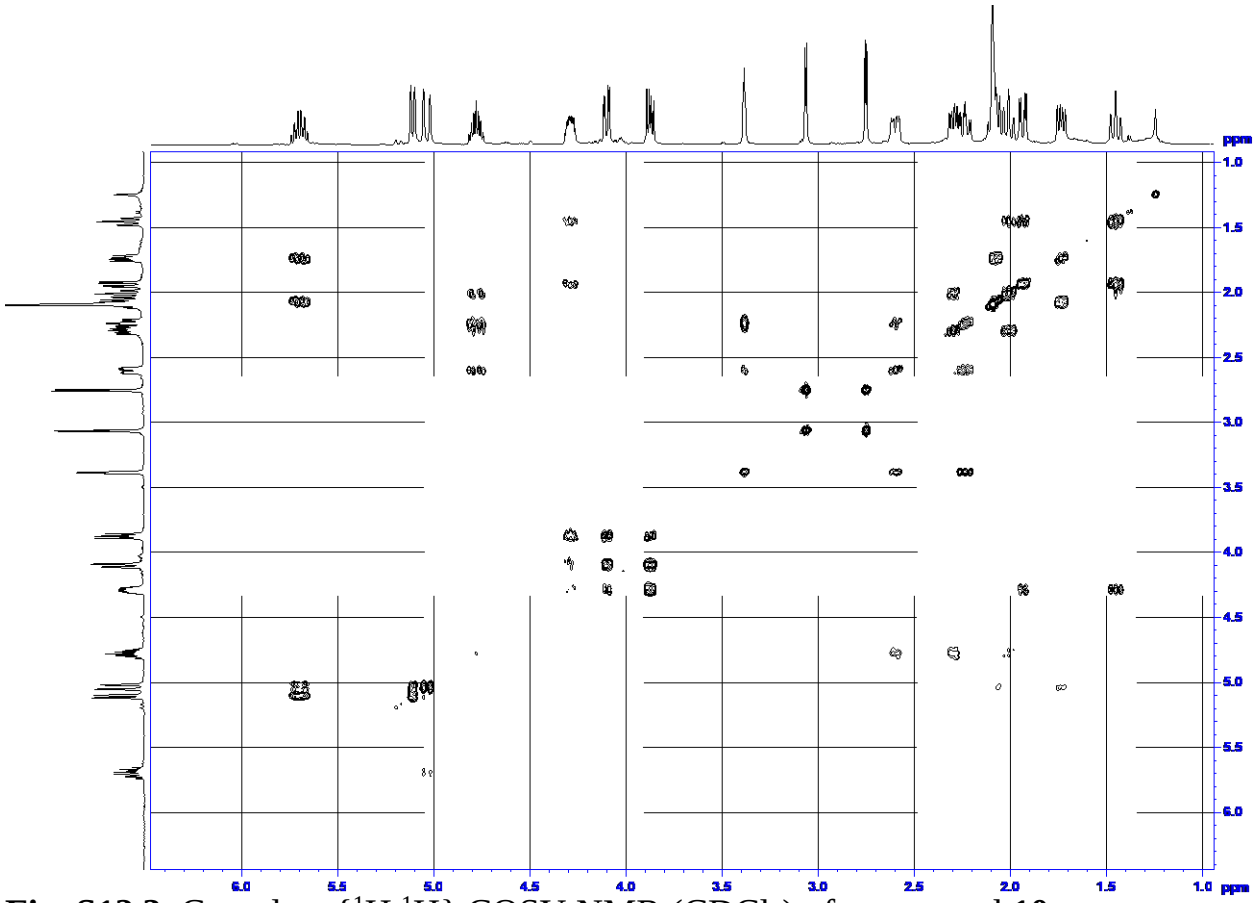


Fig. S12.3. Complete {^{1}H,^{1}H} COSY NMR ($CDCl_3$) of compound **10a**

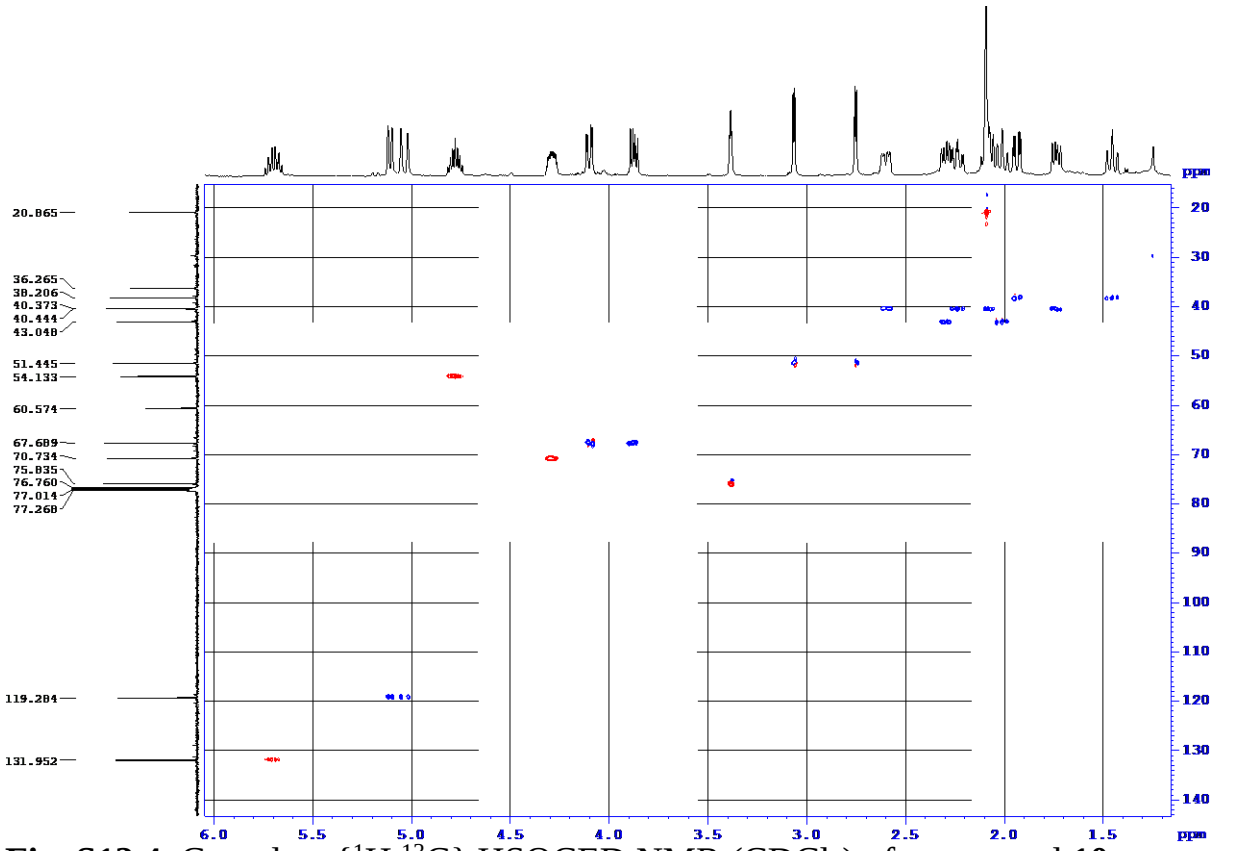


Fig. S12.4. Complete {^{1}H,^{13}C} HSQCED NMR ($CDCl_3$) of compound **10a**

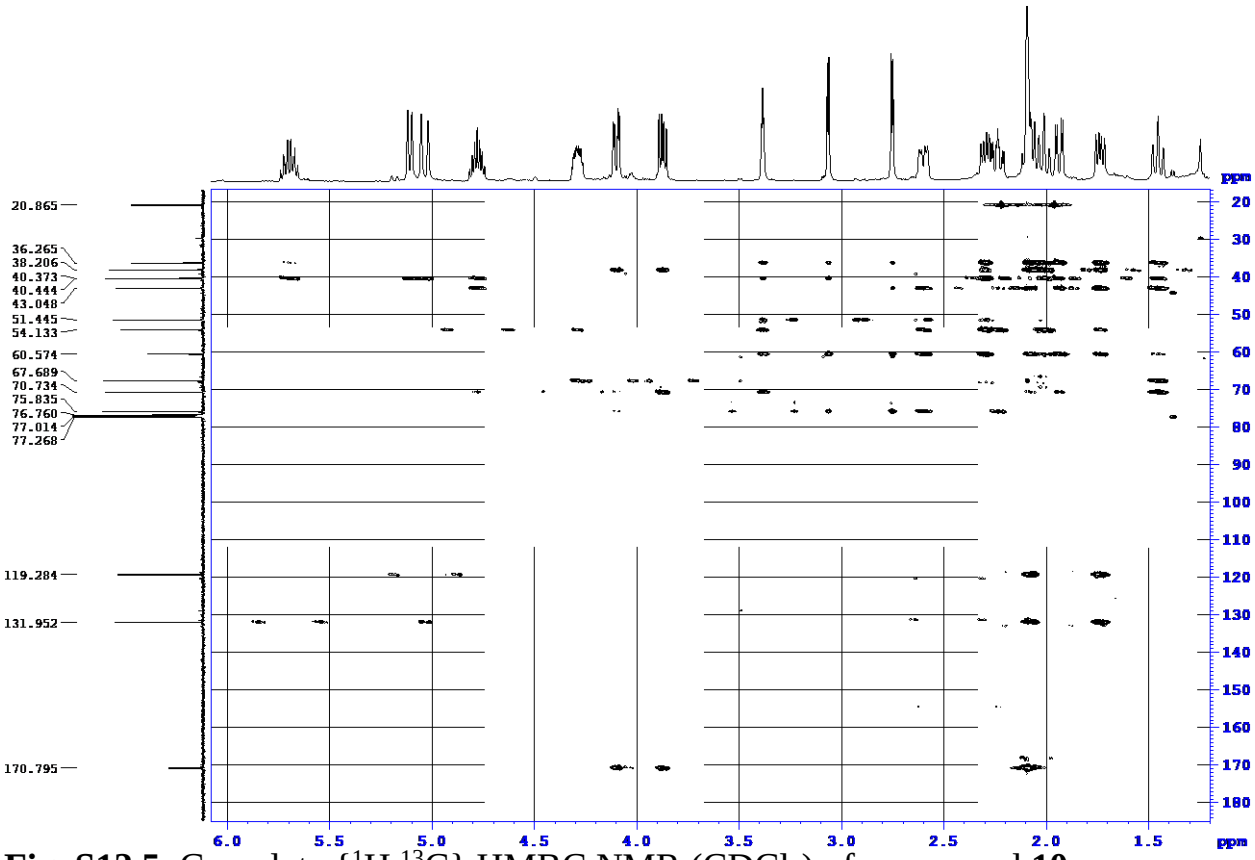


Fig. S12.5. Complete {^{1}H,^{13}C} HMBC NMR ($CDCl_3$) of compound **10a**

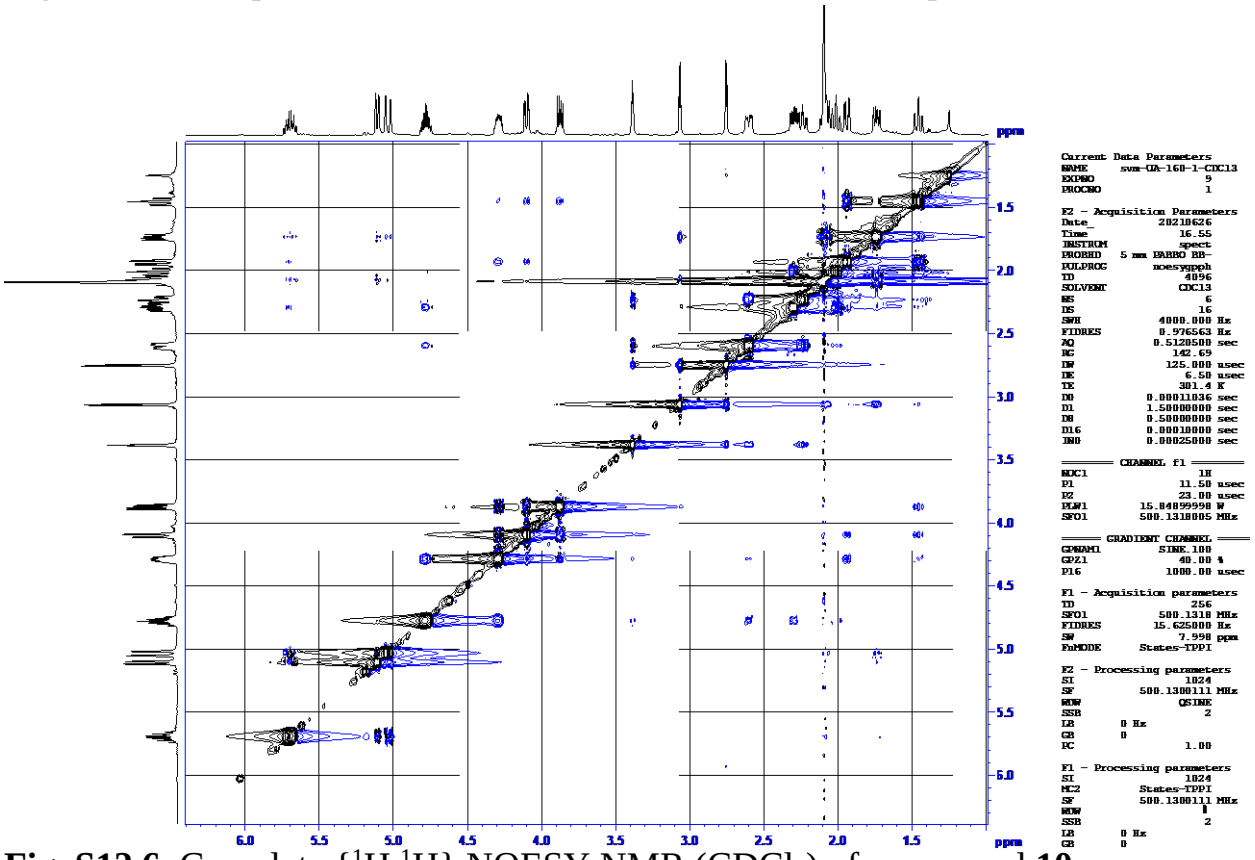


Fig. S12.6. Complete {^{1}H,^{1}H} NOESY NMR ($CDCl_3$) of compound **10a**

Product 10b: ^{1}H NMR (500 MHz, $CDCl_3$): 1.61 (dt, 1H, H^{4B}, J = 13.9, 13.9, 1.7 Hz), 1.74 (dd, 1H, $H^{1''B}$, J = 13.5, 7.6 Hz), 1.85 (dd, 1H, H^{4A}, J = 13.9, 4.2 Hz), 2.00 (dt, 1H, H^{6B}, J = 13.6, 13.6, 1.7 Hz), 2.05-2.08 (m, 1H, $H^{1''A}$), 2.25 (ddd, 1H, H^{8B}, J = 14.6, 12.0, 3.7 Hz), 2.31 (ddd, 1H, H^{6A}, J = 13.7, 6.0, 1.9 Hz), 2.59 (tdd, 1H, H^{8A}, J = 14.5, 6.2, 1.8, 1.8 Hz), 2.75 (d, 1H, $H^{1'B}$, J = 4.1 Hz), 3.07 (d, 1H, $H^{1'A}$, J = 4.1 Hz), 3.37 (dd, 1H, H^{1}, J = 6.2, 3.7 Hz), 3.40 (dd, 1H, $H^{1'''B}$, J = 11.4, 5.3 Hz), 3.65 (dd, 1H, $H^{1'''A}$, J = 11.4, 2.8 Hz), 4.14-4.19 (m, 1H, H^{3}), 4.77-4.85 (m, 1H, H^{7}), 5.04 (dd, 1H, $H^{3''B}$, J = 17.0, 1.0 Hz), 5.11 (dd, 1H, $H^{3''A}$, J = 10.0, 1.0 Hz), 5.66-5.75 (m, 1H, $H^{2''}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 36.22 (C^{5}), 37.19 (C^{4}), 40.44 (C^{8}), 40.57 ($C^{1''}$), 43.14 (C^{6}), 51.44 ($C^{1'}$), 54.28 (C^{7}), 60.77 (C^{9}), 66.28 ($C^{1'''}$), 73.16 (C^{3}), 75.82 (C^{1}), 119.24 ($C^{3''}$), 132.07 ($C^{2''}$). Yield 0.006 g (16%). Colourless oil. $[\alpha]_D^{20}$ +19.9 ° (c 0.7, $CHCl_3$). R_f 0.15 (EtOAc–petroleum ether, 1:2). IR (neat) 3458, 2931, 1719, 1447, 1340, 1072, 920, 609, 570 cm-1; Mass spectrum, m/z: 259 $[MH]^+$. Calcd for $C_{13}H_{19}ClO_3$.

NMR spectrum of compound **10b**:

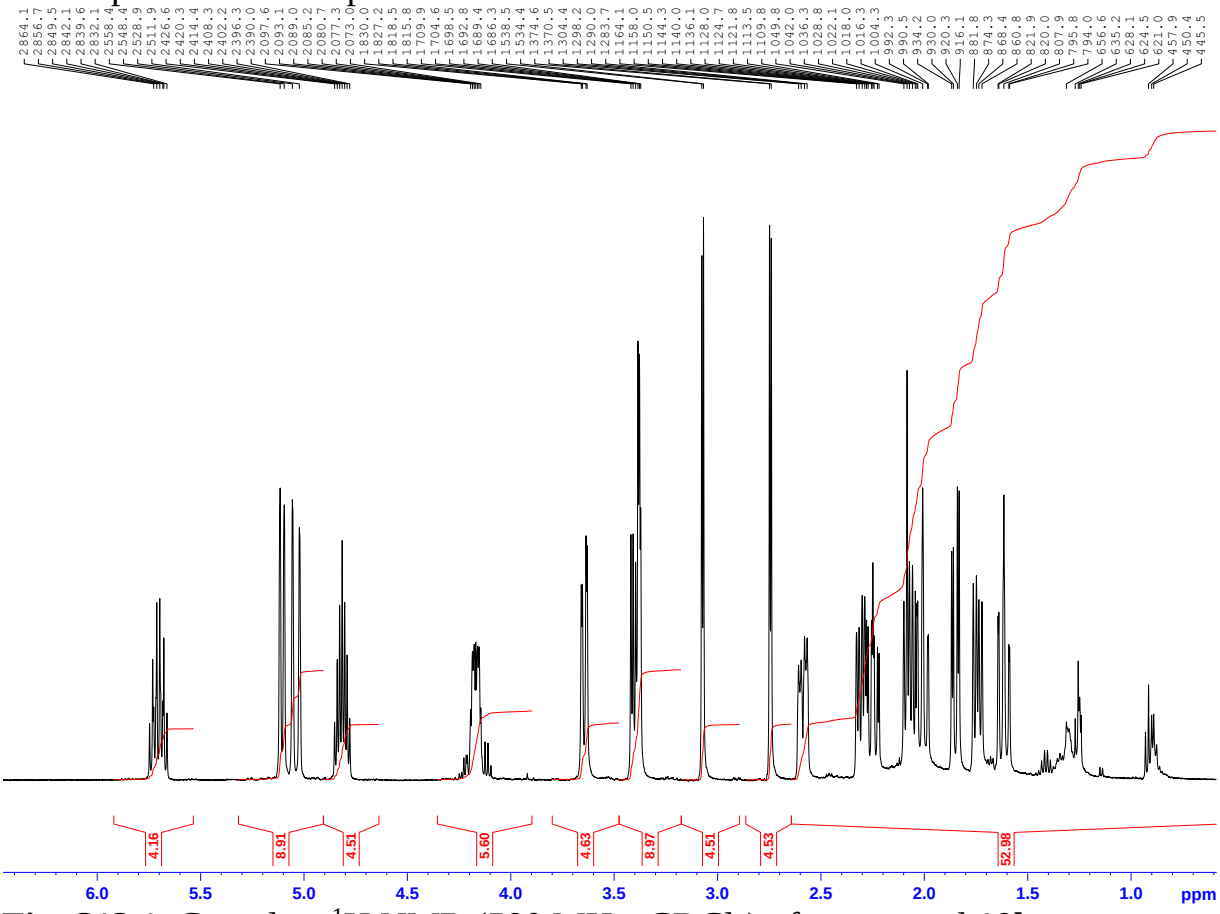


Fig. S13.1. Complete ^{1}H NMR (500 MHz, $CDCl_3$) of compound **10b**

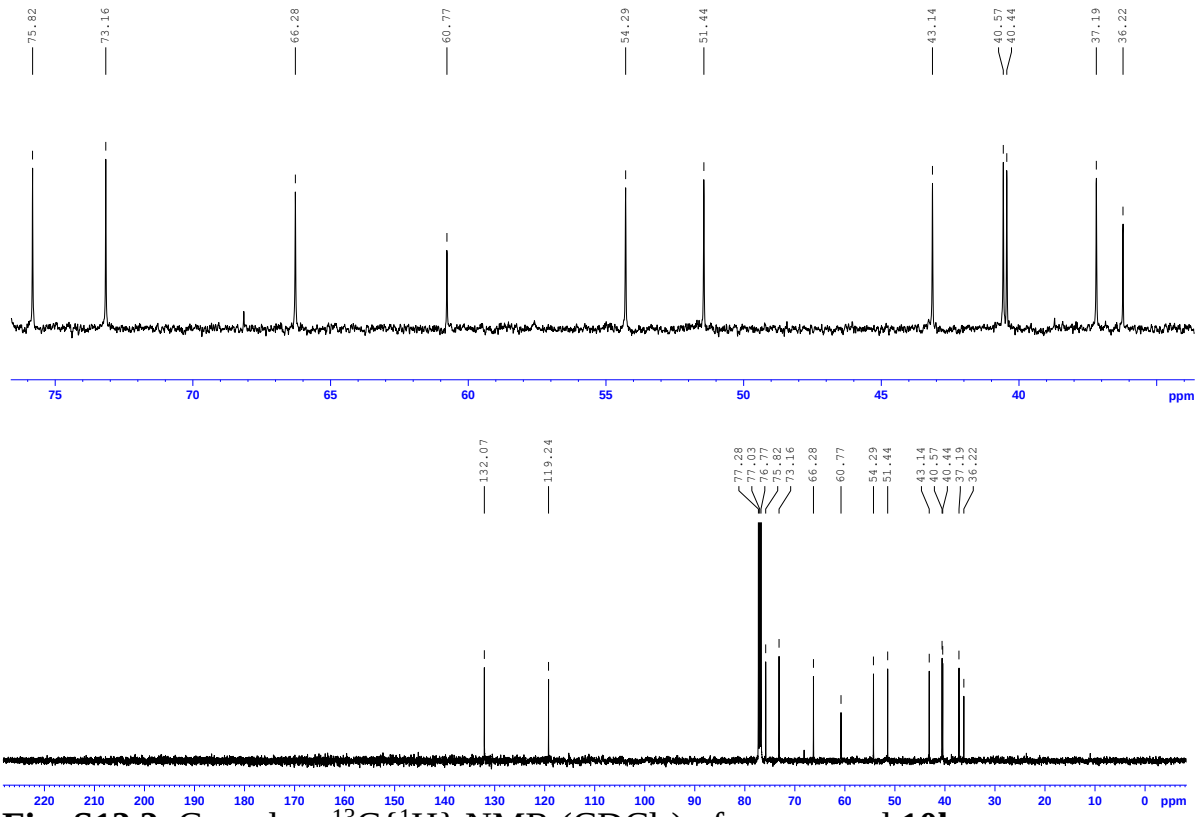


Fig. S13.2. Complete $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound **10b**

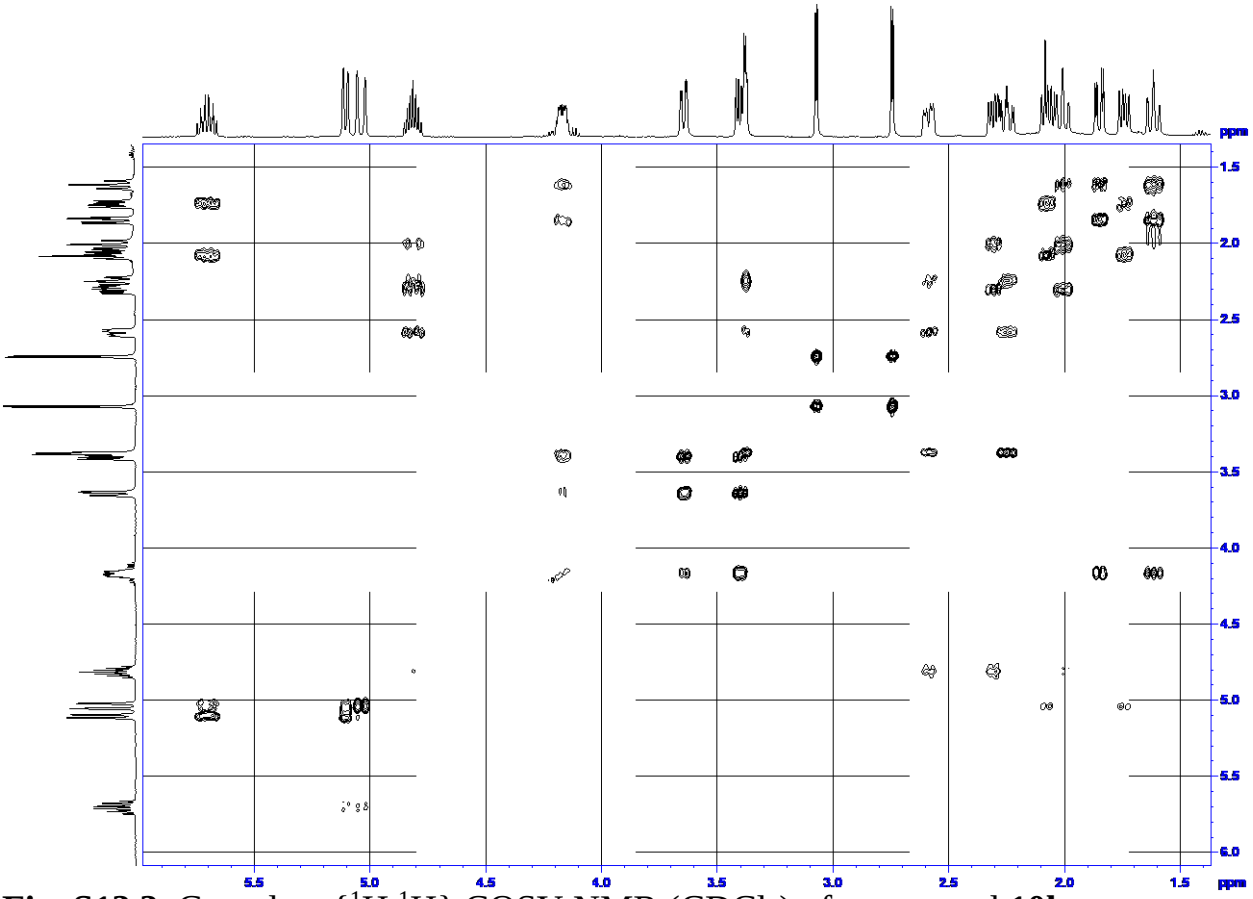


Fig. S13.3. Complete $\{^{1}H,^{1}H\}$ COSY NMR ($CDCl_3$) of compound **10b**

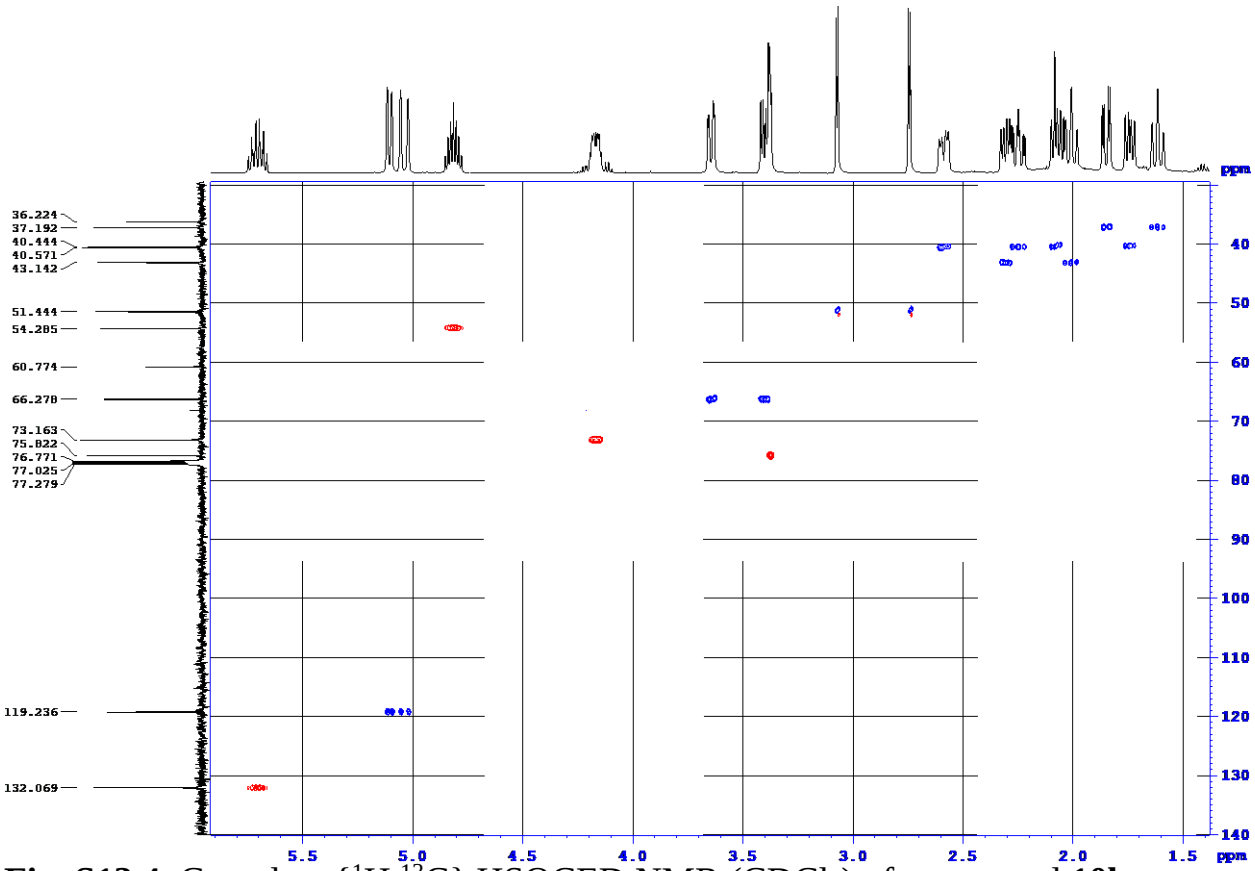


Fig. S13.4. Complete {^{1}H,^{13}C} HSQCED NMR ($CDCl_3$) of compound **10b**

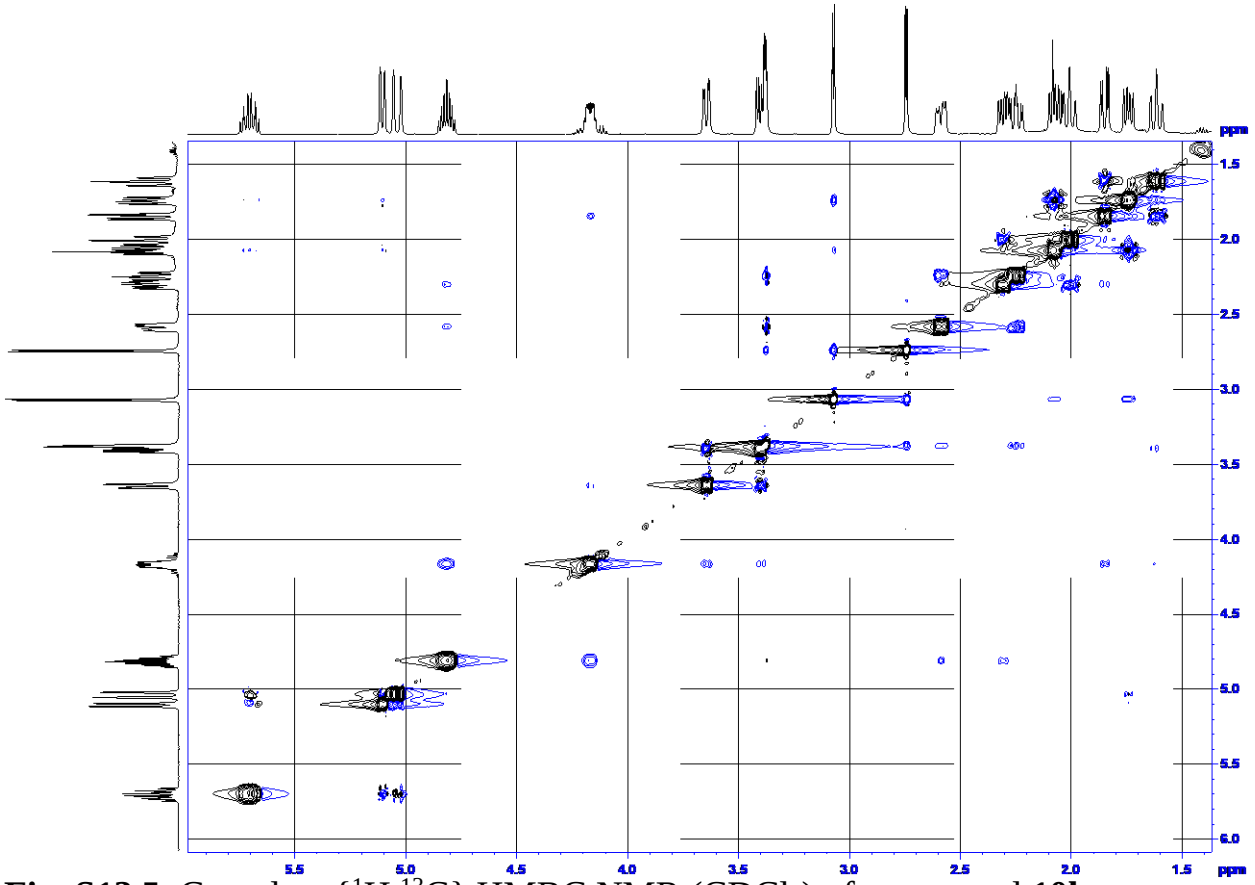


Fig. S13.5. Complete {^{1}H,^{13}C} HMBC NMR ($CDCl_3$) of compound **10b**

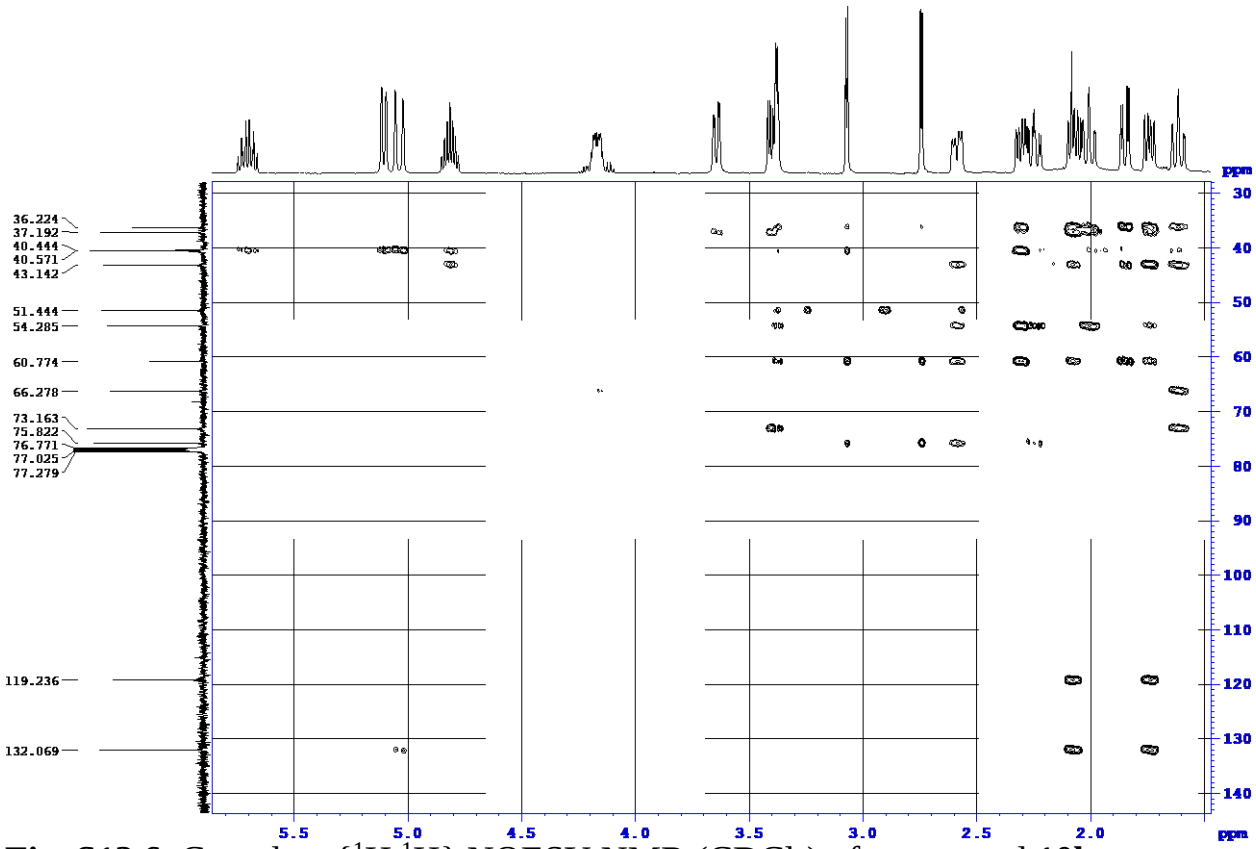


Fig. S13.6. Complete {^{1}H,^{1}H} NOESY NMR ($CDCl_3$) of compound **10b**

The formation of epoxide **10a** is indicated by the signals of tetra-substituted C^9 carbon atom (δ_c 60.57) and secondary $C^{1'}$ atom (δ_c 51.44) with geminal protons at δ 3.06 and 3.39 with a coupling constant of ^2J 4.1 Hz. Moreover, the HMBC spectrum exhibits the $H^{1'}/C^9$, $H^{1'}/C^5$ and $H^{1'}/C^1$ correlation peaks. The existence of the NOE effect between the H^7 and H^3 protons in the NOESY spectrum is evidence of the *S*-configuration of the C^7 center.