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Reaction of the levoglucosenone Diels–Alder adducts with acetaldehyde under the McMurry conditions

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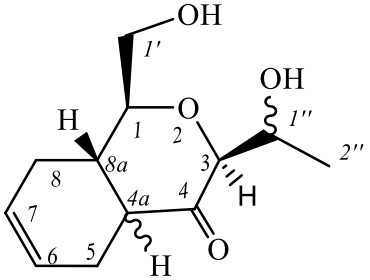
The spectral and analytical data were obtained using the equipment of the *Khimiya* Joint Center at the Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance III, (500.13 MHz for ^{1}H and 125.47 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.

General procedure. To a solution of the Diels-Alder adduct of levoglucosenone and 1,3-diene (1.0 mmol), acetaldehyde (1.5 mmol) in THF (3.0 ml) at -10°C, $TiCl_4$ (1.5 mmol) was added. Then at the same temperature with stirring, a suspension of zinc dust (3.0 mmol, preliminarily evacuated on a vacuum pump while heating, in order to remove residual water) in THF (2.0 ml) was added in portions. The reaction mixture was slowly brought to room temperature, and stirring was continued until the disappearance of the starting compound (from 12 hours to 3 days, TLC control). The mixture was treated with a saturated aqueous solution of $NaHCO_3$ (4.0 ml), and the products were extracted with $CHCl_3$ (2 × 5.0 ml). The combined organic layers were dried over $MgSO_4$, the solvent was distilled off, the residue was chromatographed on a silica gel column.

(1*S*,3*S*,4a*R*,8a*S*)-3-(1-Hydroxyethyl)-1-hydroxymethyl-4a,5,8,8a-tetrahydro-1*H*-isochromen-4(3*H*)-one (2a)



From 0.139 g (0.77 mmol) of adduct **1a**, the product yield was 0.027 g (30%), a mixture of four diastereomers, epimer 4a*R*/4a*S* is 2:1. (EtOAc – petroleum ether 1:1, R_f 0.06). Oil.

4*R*-isomer: (1"*R*/1"*S*, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$):1.23 [1.26] d (3H, $H^{2"}$, $^3J_{2",1"}$ 6.4 Hz), 1.71-1.76 [1.72-1.77] m (1H, H^{8B}), 2.02-2.18 [2.03-2.19] m (2H, H^{8A}, H^{5B}), 2.34-2.39 [2.40-2.49] m (1H, H^{8a}), 2.58-2.65 [2.59-2.66] m (1H, H^{5A}), 3.07 [3.11] dd (1H, H^{4a}, $^3J_{4a,8a}$ 6.5, $^3J_{4a,5A}$ 6.5 Hz), 3.55-3.58 [3.56-3.59] m (1H, H^{1}), 3.76-3.81 [3.77-3.82] m (3H, H^{3}, $H^{1'A}$, $H^{1'B}$), 4.08-4.13 [4.09-4.14] m (1H, $H^{1"}$), 5.53-5.55 [5.54-5.56] m (1H, H^{6}), 5.63-5.67 [5.64-5.68] m (1H, H^{7}). ^{13}C NMR (500 MHz, $CDCl_3$): δ 18.02 [19.56] ($C^{2"}$), 21.52 [21.62] (C^{5}), 29.50 [29.67] (C^{8}), 33.35 [33.23] (C^{8a}), 42.16 [42.50] (C^{4a}), 65.29 [65.41] ($C^{1'}$), 68.21 [67.94] ($C^{1"}$), 80.55 [80.38] (C^{1}), 83.63 [83.55] (C^{3}), 123.74 [123.73] (C^{6}), 125.57 [125.73] (C^{7}), 213.18 [213.16] (C^{4}).

4*S*-isomer: (1"*R*/1"*S*, 2:1). ^{1}H NMR (500 MHz, $CDCl_3$): 1.22 [1.25] d (3H, $H^{2"}$, $^3J_{2",1"}$ 6.4 Hz), 1.89-1.96 [1.90-1.97] m (1H, H^{8B}), 2.03-2.08 [2.10-2.16] m (1H, H^{8a}), 2.07-2.19 [2.08-2.20] m (2H, H^{8A}, H^{5B}), 2.27-2.33 [2.28-2.35] m (1H, H^{5A}), 2.38-2.43 [2.40-2.45] m (1H, H^{1}), 3.65-3.71 [3.66-3.72] m (2H, $H^{1'B}$, H^{1}), 3.80-3.88 [3.79-3.87] m (2H, H^{3}, $H^{1'A}$), 4.21-4.25 [4.20-4.24] m (1H, $H^{1"}$), 5.60-5.65 [5.61-5.66] m (1H, H^{6}), 5.63-5.67 [5.70-5.75] m (1H, H^{7}). ^{13}C NMR (500 MHz, $CDCl_3$): δ 18.39 [18.64] ($C^{2"}$), 23.55 [23.63] (C^{5}), 27.66 [27.72] (C^{8}), 40.59 [40.15] (C^{8a}), 48.09 [48.10] (C^{4a}), 62.78 [62.51] ($C^{1'}$), 66.76 [65.76] ($C^{1"}$), 81.77 [81.72] (C^{1}), 84.13 [84.01] (C^{3}), 124.39 [124.45] (C^{6}), 125.54 [125.51] (C^{7}), 208.83 [207.37] (C^{4}).

Mass spectrum, *m/z*: 227 [*M*H]+. Found, %: C 63.69, H 8.00. $C_{12}H_{18}O_4$. Calculation, %: C 63.70, H 8.02. IR: 3385, 2923, 1726, 1436, 1268, 1078, 1008, 943, 736 cm^{-1}.

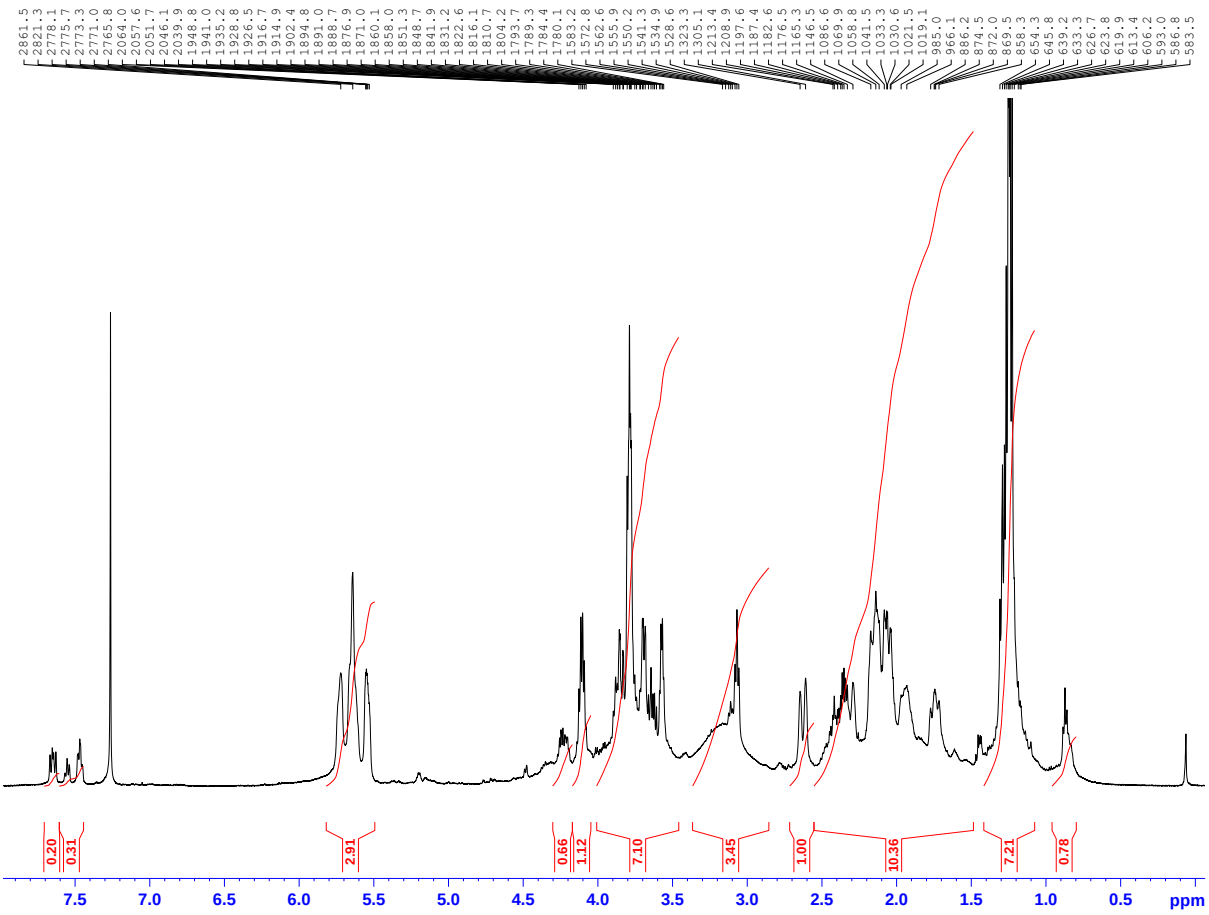


Figure S1.1 Complete ^{1}H NMR (500 MHz) spectrum of **2a** in $CDCl_3$.

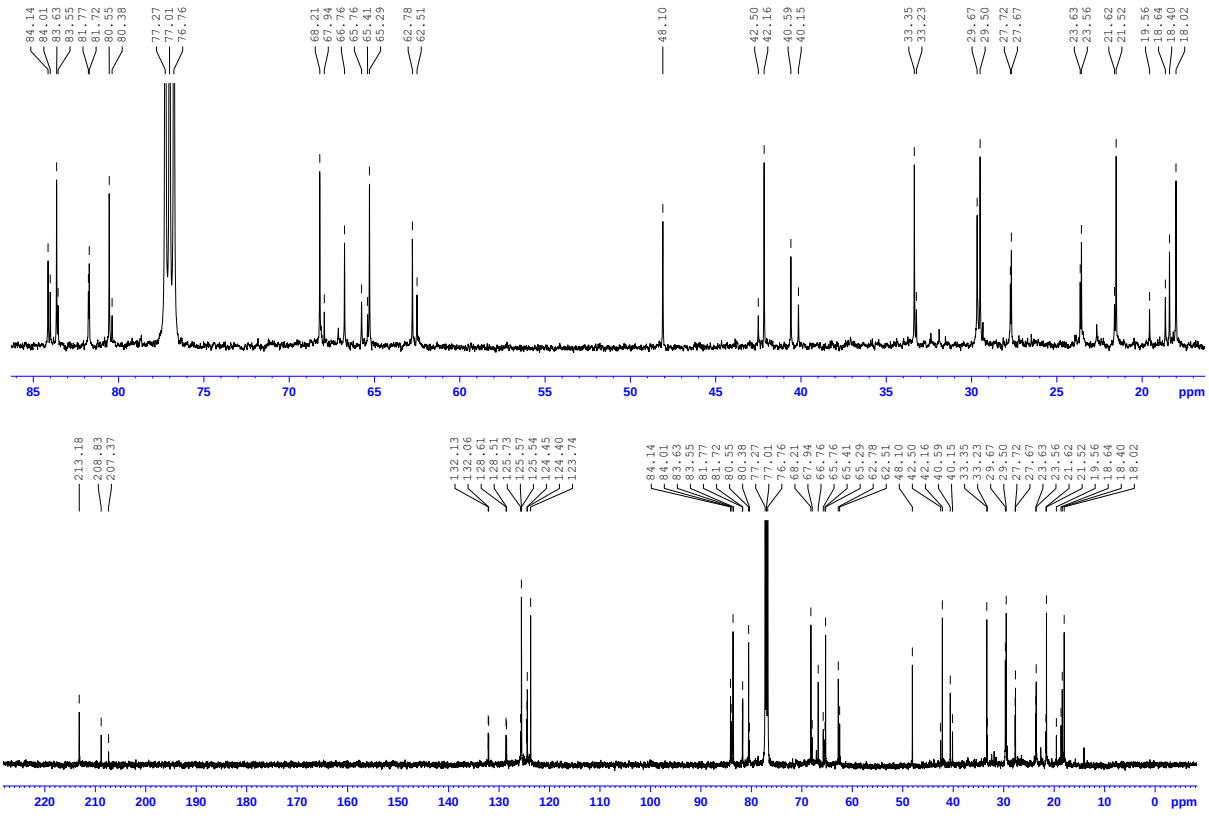


Figure S1.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in $CDCl_3$

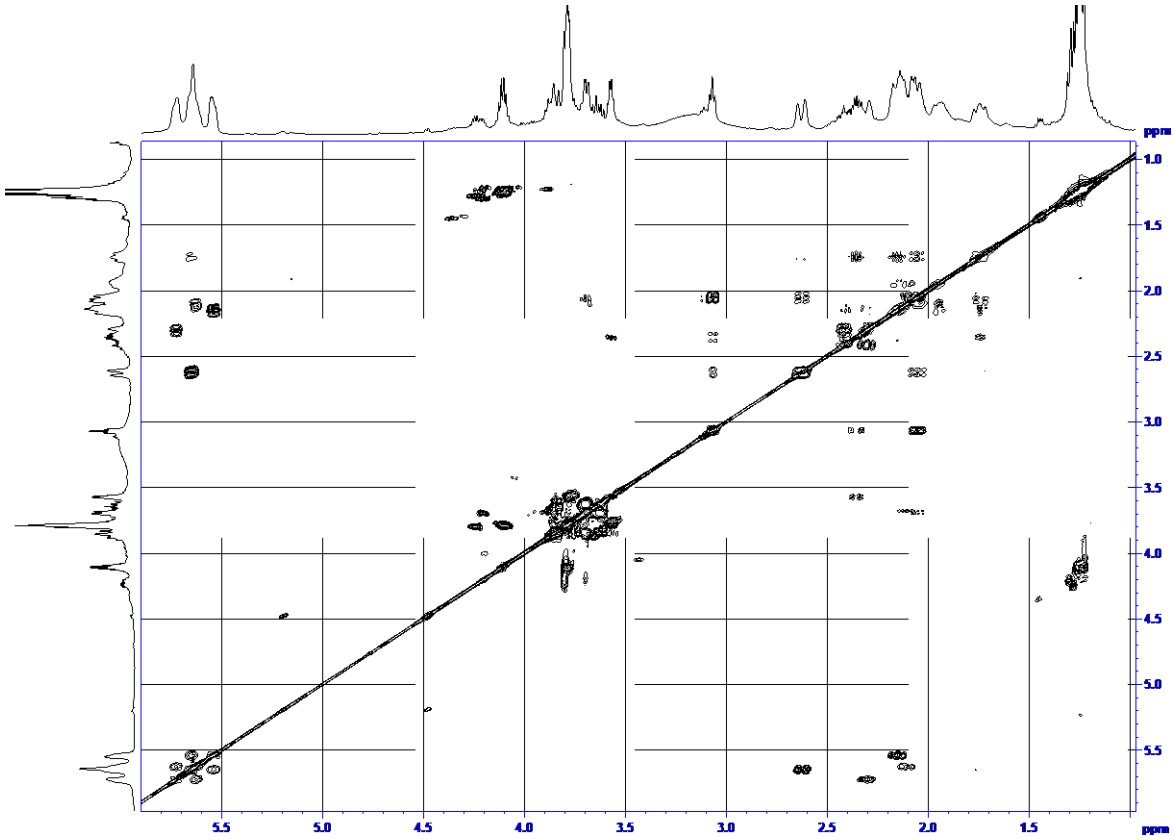


Figure S1.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of **2a** in $CDCl_3$

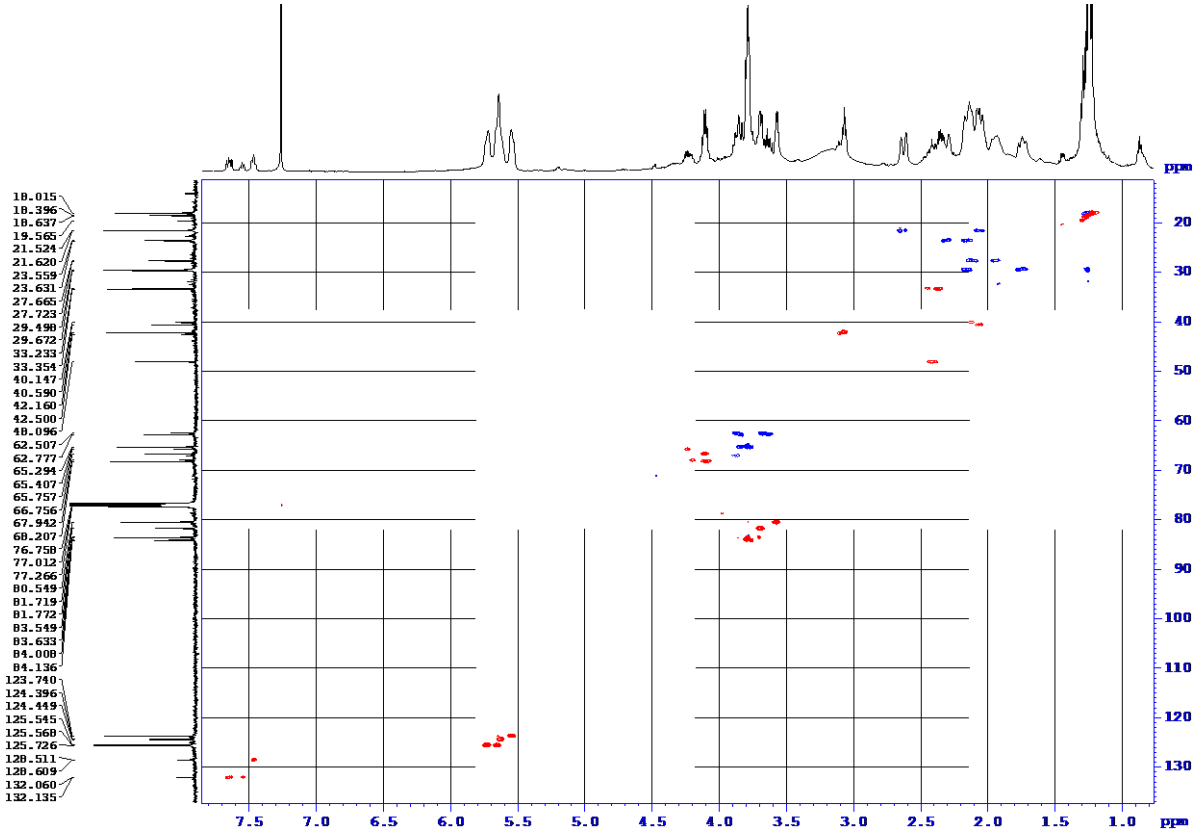


Figure S1.4. {^{1}H,^{13}C} HSQCED NMR spectrum of **2a** in $CDCl_3$.

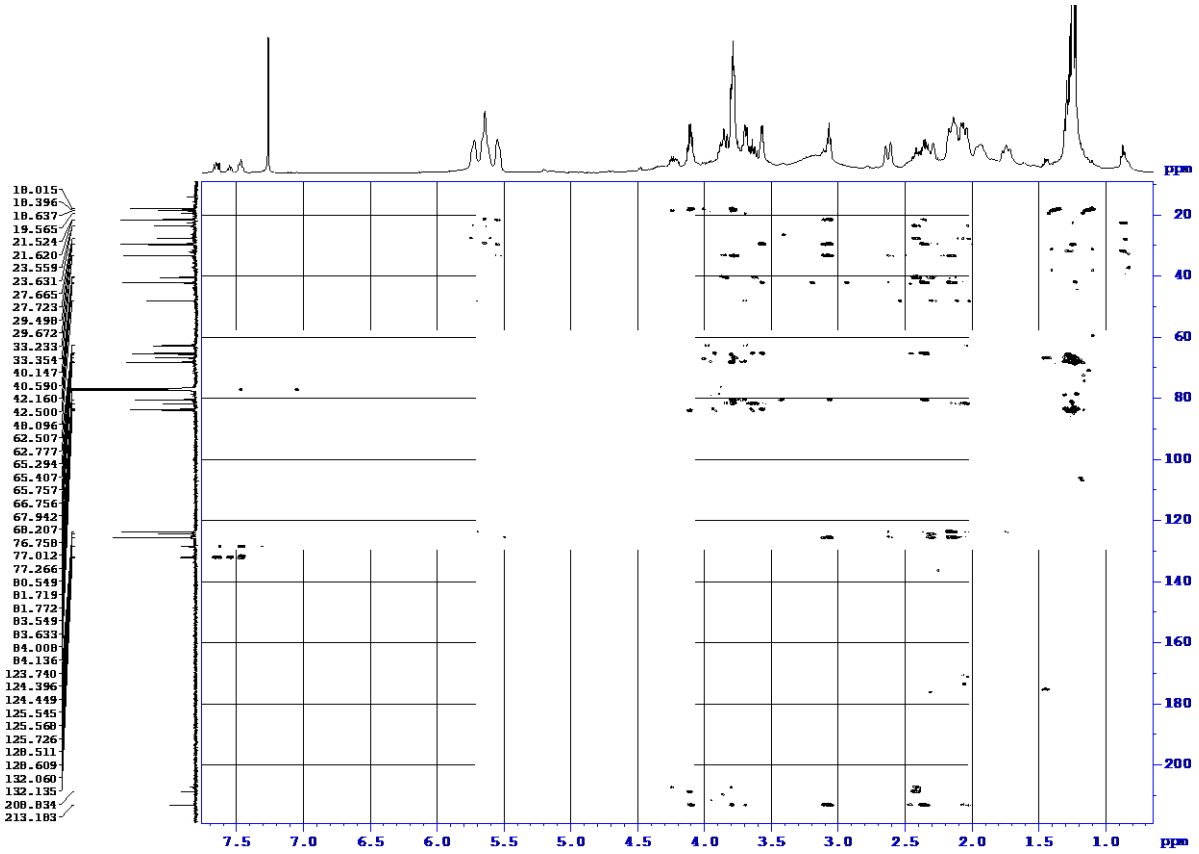


Figure S1.5. {^{1}H,^{13}C} HMBC NMR spectrum of **2a** in $CDCl_3$.

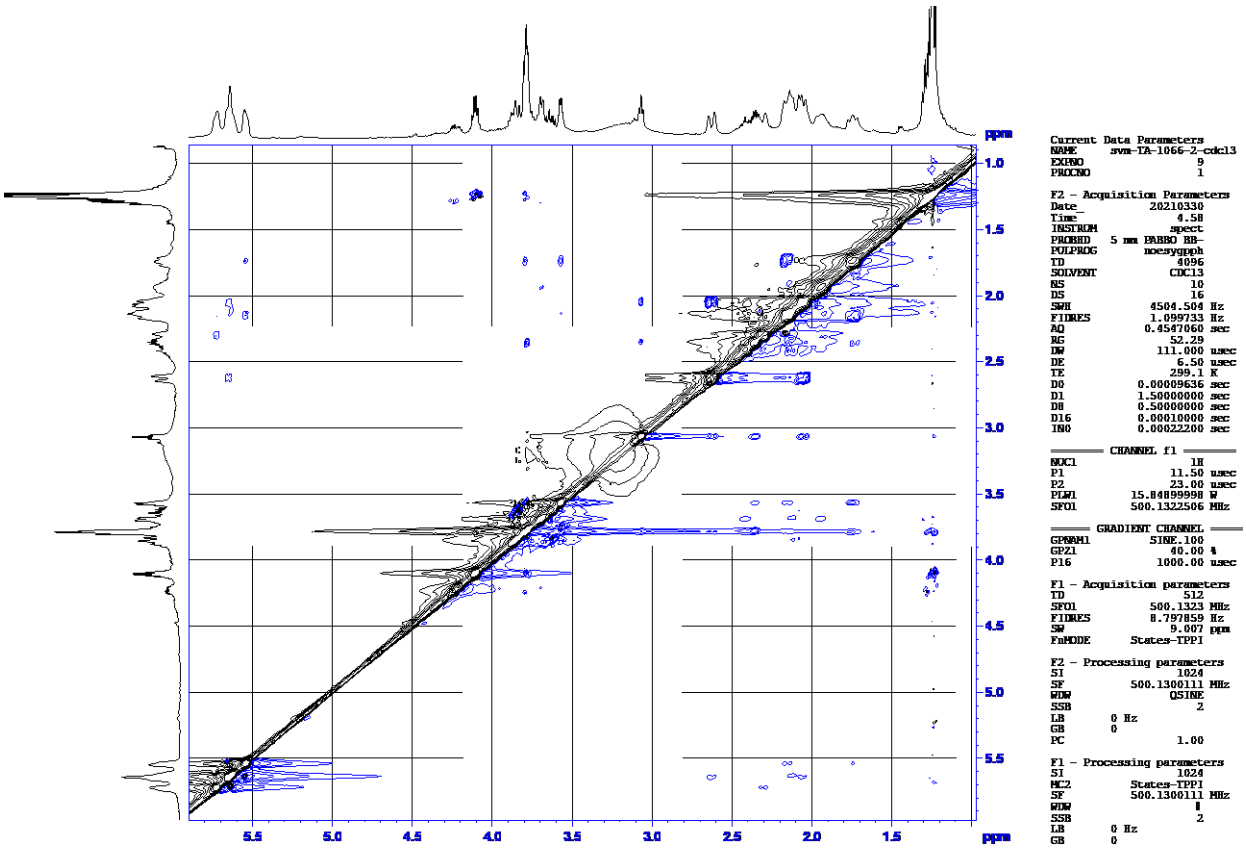
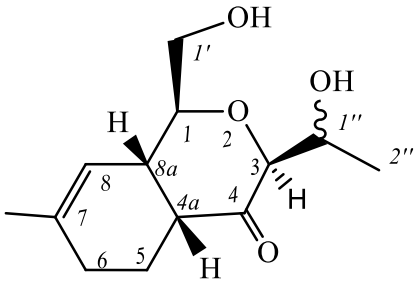


Figure S1.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of **2a** in $CDCl_3$

(1*S*,3*S*,4a*R*,8a*S*)-3-(1-Hydroxyethyl)-1-hydroxymethyl-7-methyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-4(3*H*)-one (2b)



From 0.15 g (7.73 mmol) of adduct **1b**, the product yield was 0.038 g (30%), a mixture of two 1"*R*/1"*S* diastereomers in the 3:1 ratio (EtOAc – petroleum ether 1:1, R_f 0.1). Oil. ^{1}H NMR (500 MHz, $CDCl_3$): 1.23 [1.30] d (3H, $H^{2''}$, $^3J_{2'',1''}$ 6.4 Hz), 1.59-1.63 [1.58-1.64] m (1H, H^{5B}), 1.65 [1.68] s (3H, CH_3), 1.90-1.95 [1.91-1.96] m (1H, H^{6B}), 2.07-2.13 [2.06-2.12] m (2H, H^{6A}, H^{5A}), 2.66-2.71 [2.71-2.74] m (1H, H^{4a}), 2.74-2.79 [2.85-2.89] m (1H, H^{8a}), 3.48-3.52 [3.49-3.53] m (1H, H^1), 3.72 [3.73] d.d (1H, $H^{1'B}$, $^2J_{1'B,1'A}$ 11.9, $^3J_{1'B,1}$ 6.8 Hz), 3.77 [3.70] d (1H, H^3, $^3J_{3,1''}$ 4.8 Hz), 3.85 [3.88] d.d (1H, H^{6A}, $^2J_{6A,6B}$ 11.9, $^3J_{6A,5}$ 2.3 Hz), 4.09-4.13 [4.16-4.20] m (1H, $H^{1''}$), 5.14-5.17 [5.15-5.18] m (1H, H^8). ^{13}C NMR (500 MHz, $CDCl_3$): δ 18.04 [19.31] ($C^{2''}$), 21.65 [21.47] (C^5), 23.70 [23.69] (CH_3), 27.63 [27.45] (C^6), 37.07 [36.60] (C^{8a}), 44.20 [43.98] (C^{4a}), 64.08 [64.00] ($C^{1'}$), 67.77 [67.38] ($C^{1''}$), 80.21 [80.27] (C^1), 84.25 [84.43] (C^3), 119.18 [119.54] (C^8), 136.74 [136.58] (C^7), 213.13 [212.69] (C^4). Mass spectrum, *m/z*: 241 [*M*H]+. Found, %: C 64.79, H 8.35. $C_{13}H_{20}O_4$. Calculation, %: C 64.98, H 8.39. IR: 3413, 2932, 2879, 1750, 1461, 1269, 1107, 1048, 736 cm^{-1}.

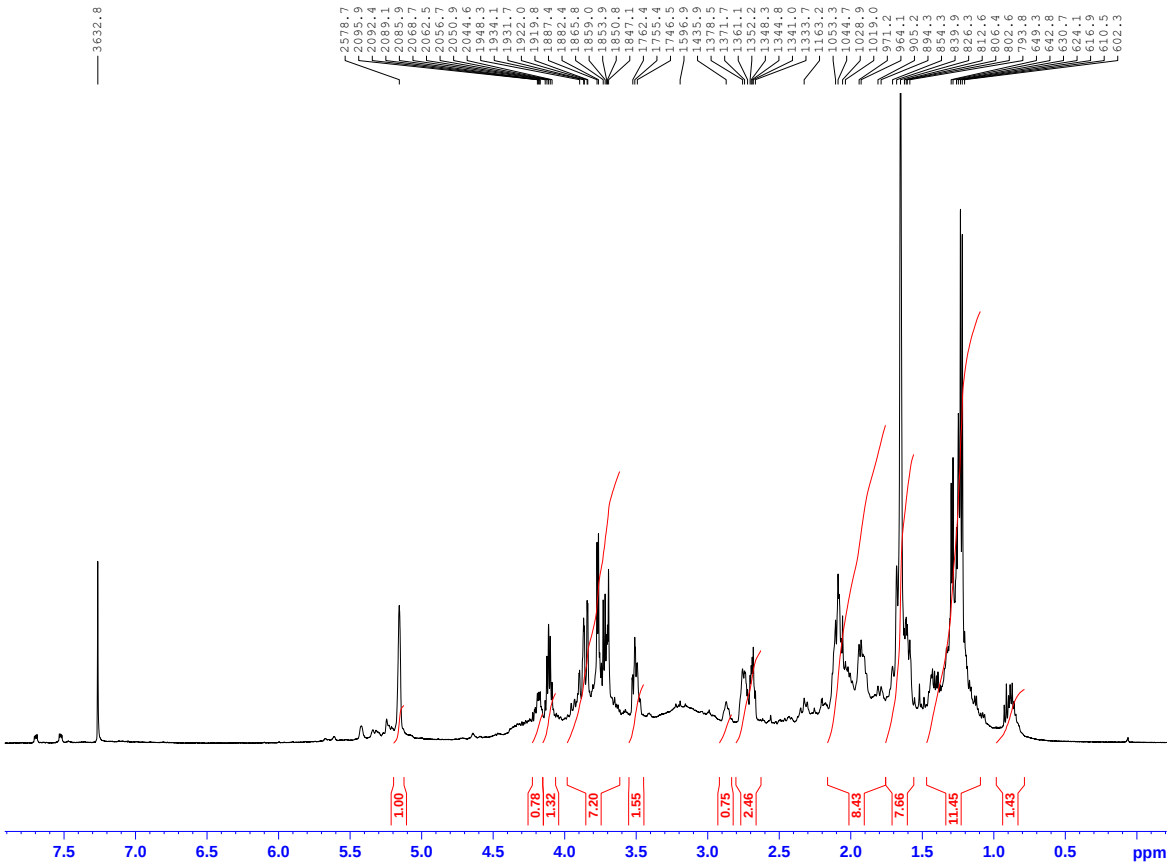


Figure S2.1. Complete ^{1}H NMR (500 MHz) spectrum of **2b** in $CDCl_3$.

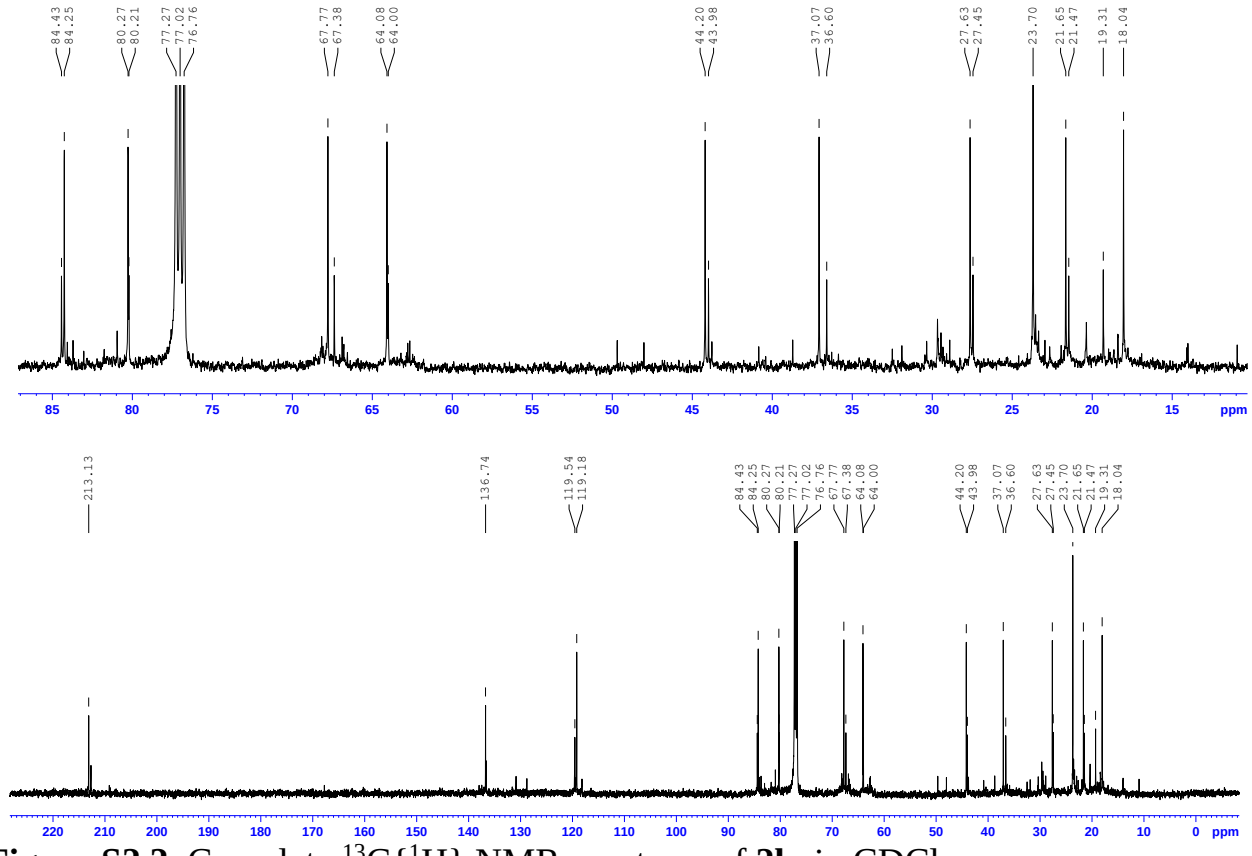


Figure S2.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in $CDCl_3$.

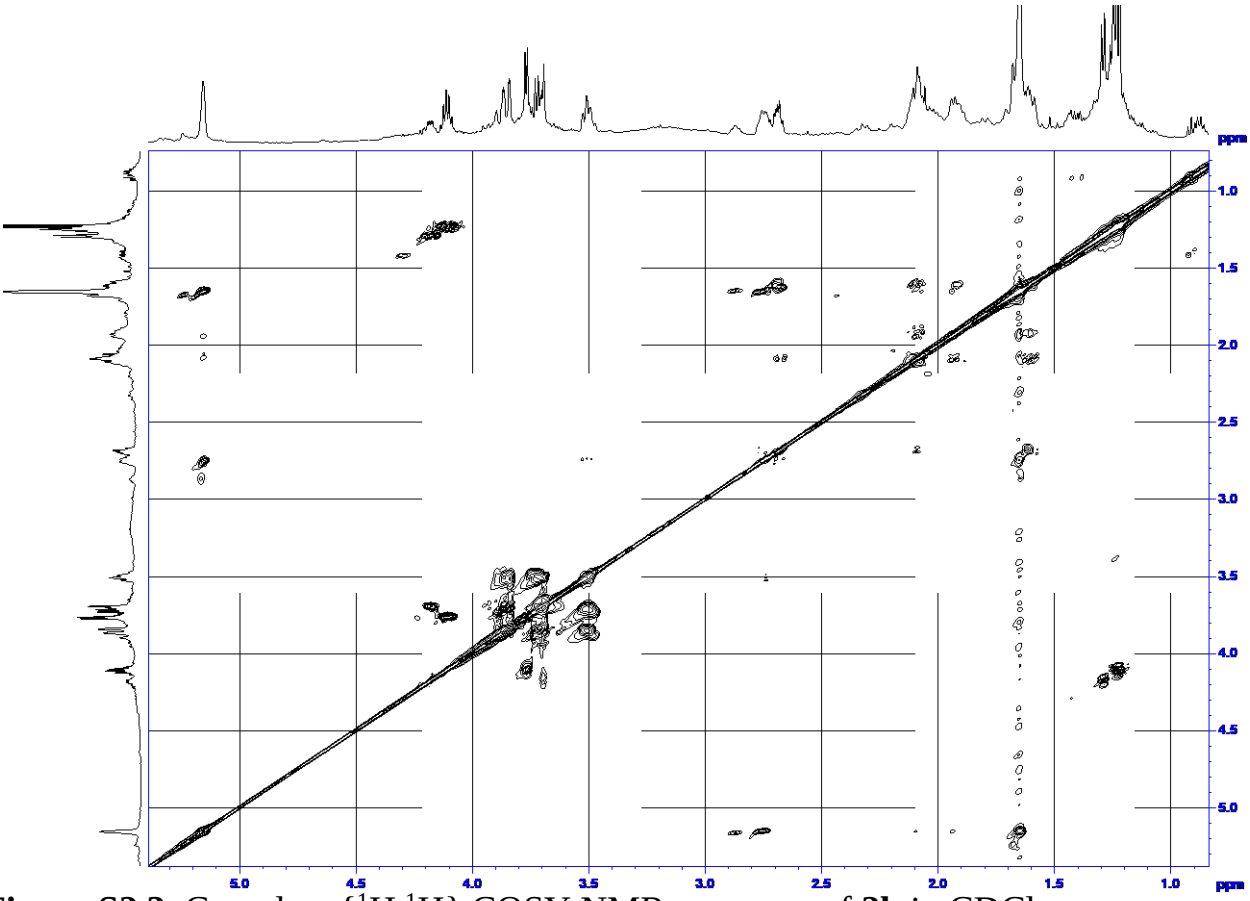


Figure S2.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of **2b** in $CDCl_3$

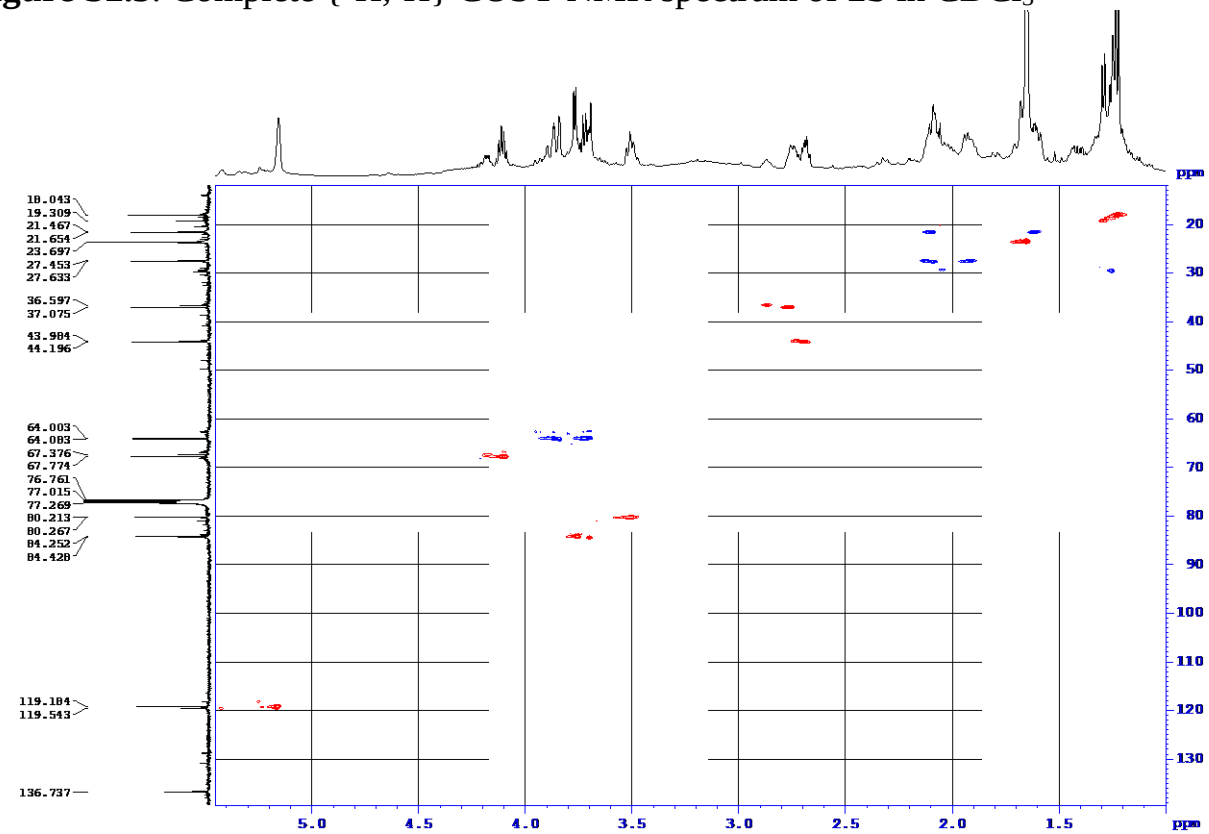


Figure S2.4. {^{1}H,^{13}C} HSQCED NMR spectrum of **2b** in $CDCl_3$.

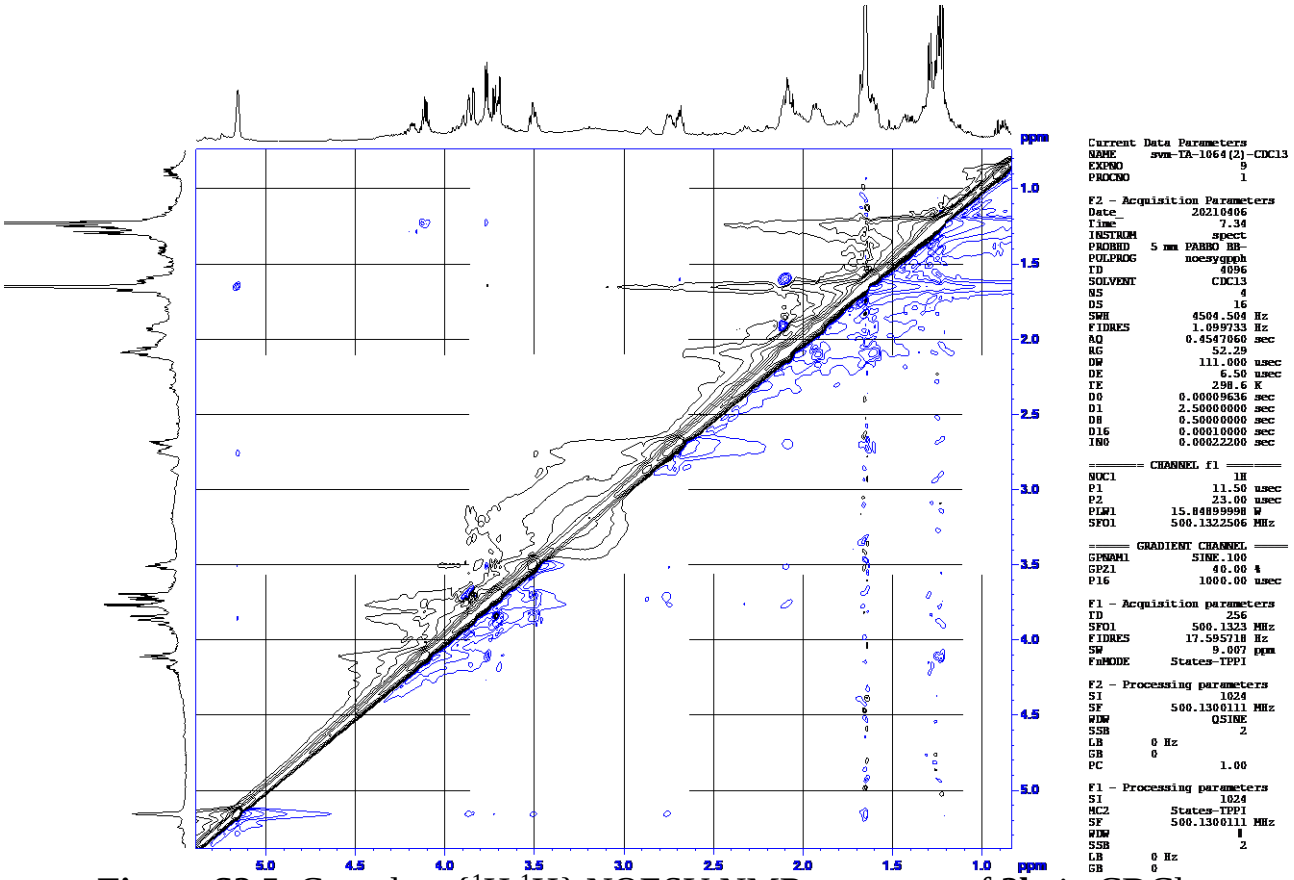
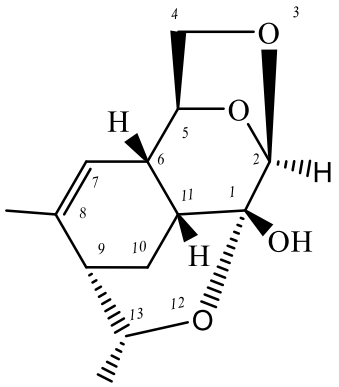


Figure S2.5. Complete {^{1}H,^{1}H} NOESY NMR spectrum of **2b** in $CDCl_3$

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



From 0.100 g (0.51 mmol) of adduct **1c**, the product yield was 0.057 g (75%). (EtOAc – petroleum ether 1:1, R_f 0.2). White crystals, m.p. 226°C, $[\alpha]_D^{20}$ -51° (*c* 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.16 d (3H, CH_3, $^3J_{CH3,13}$ 6.5 Hz), 1.52-1.56 [m 1H, H^{10B}), 1.81 s (3H, CH_3), 1.92-1.95 m (1H, H^9), 2.03-2.06 m (1H, H^{11}), 2.18-2.26 m (2H, H^6, H^{10A}), 2.74 br.s (1H, OH), 3.83 dd (1H, H^{4B}, $^2J_{4B,4A}$ 7.0, $^3J_{4B,5}$ 5.0 Hz), 3.88 d (1H, H^{4A}, $^2J_{4A,4B}$ 7.0 Hz), 4.08-4.11 m(1H, H^{13}), 4.46 d (1H, H^5, $^3J_{5,4B}$ 5.0 Hz), 4.95 s (1H, H^2), 5.51 s (1H, H^7). ^{13}C NMR (500 MHz, $CDCl_3$): δ 20.47 (CH_3), 25.49 (CH_3), 27.83 (C^{10}), 28.74 (C^{11}), 39.11 (C^9), 41.24 (C^6), 67.98 (C^4), 69.51 (C^{13}), 75.87 (C^5), 94.02 (C^1), 103.11 (C^2), 124.73 (C^7), 136.04 (C^8). Mass spectrum, *m/z*: 239 [*M*H]+. Found, %: C 65.50, H 7.59. $C_{13}H_{18}O_4$. Calculation, %: C 65.53, H 7.61. IR: 3420, 2946, 1712, 1455, 1088, 1043, 968, 881 cm^{-1}.

The HMBC spectrum of compound **3** contains H^{13}/C^1, 13-CH_3/C^9 and H^9/C^8 correlation peaks, which indicates that the hydroxyethyl moiety at the C^9 center is added to give a 1,13-ether bond.

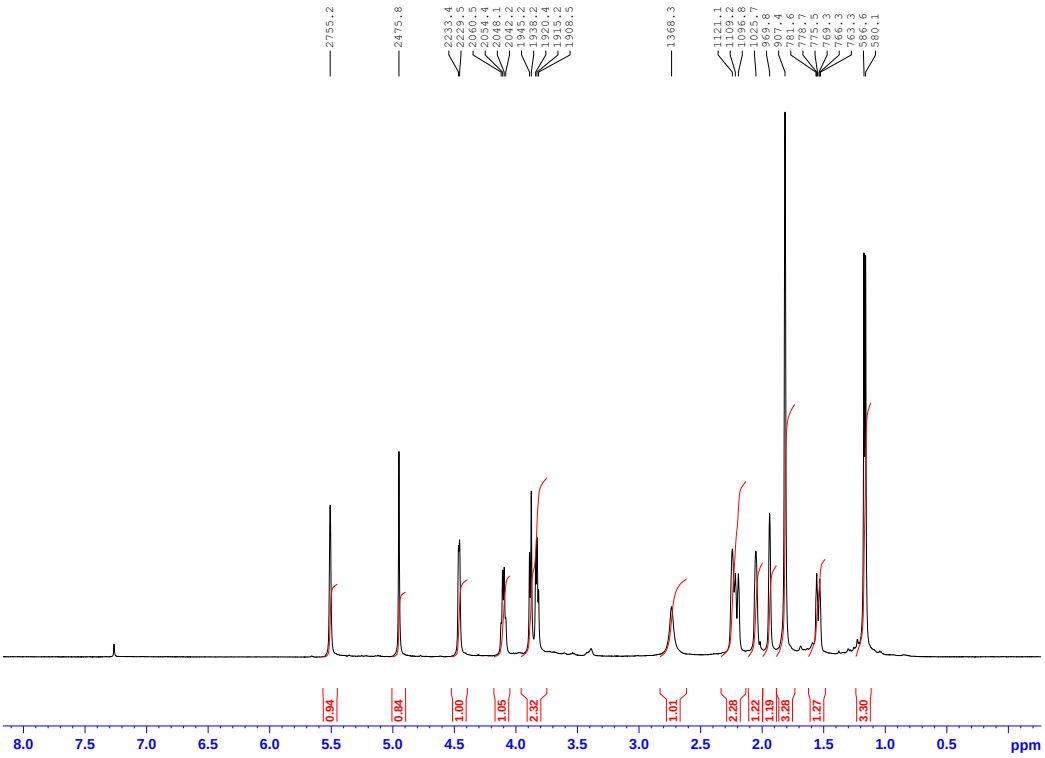


Figure S3.1. Complete ^{1}H NMR (500 MHz) spectrum of **3** in $CDCl_3$.

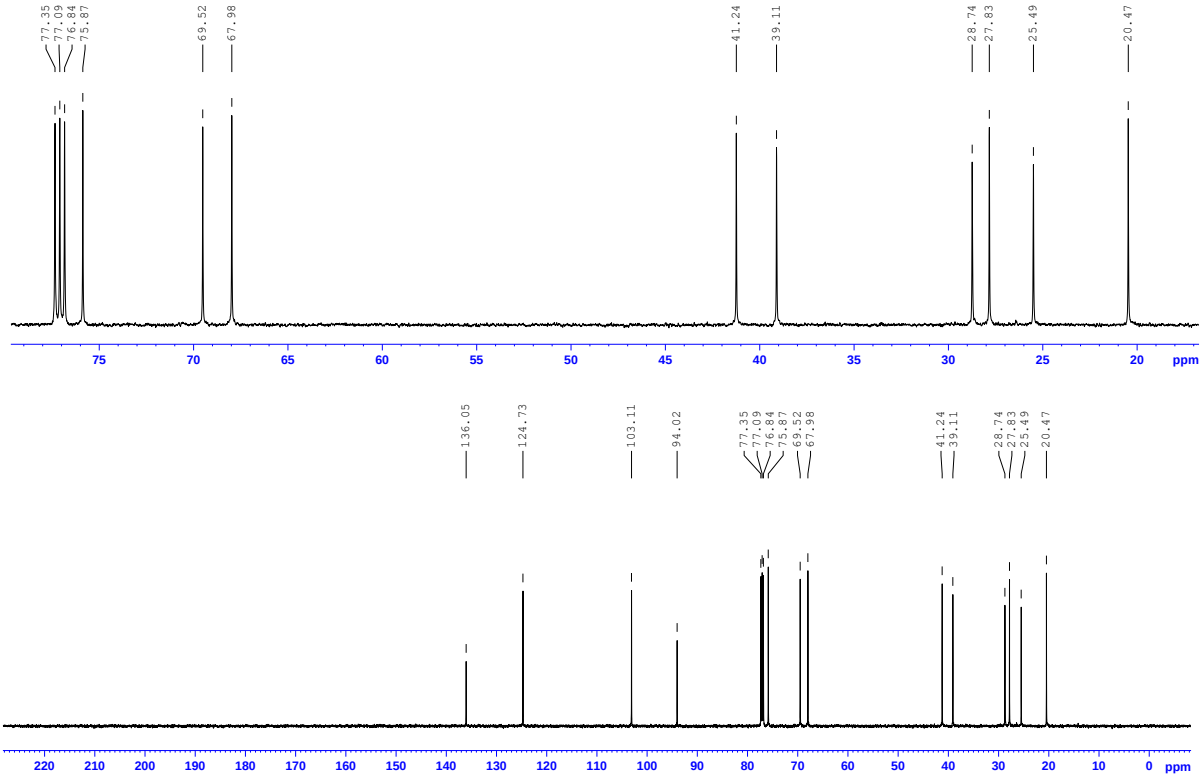


Figure S3.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

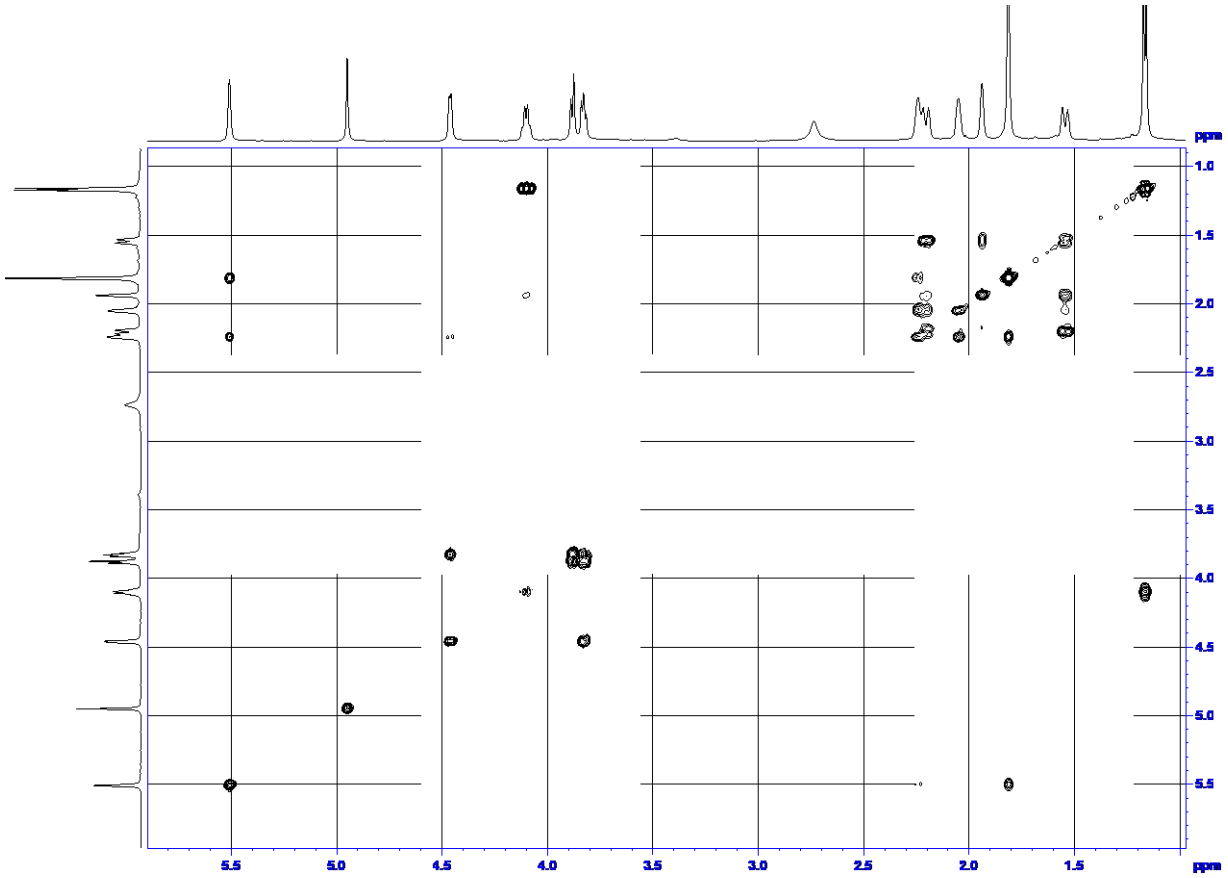


Figure S3.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of **3** in $CDCl_3$

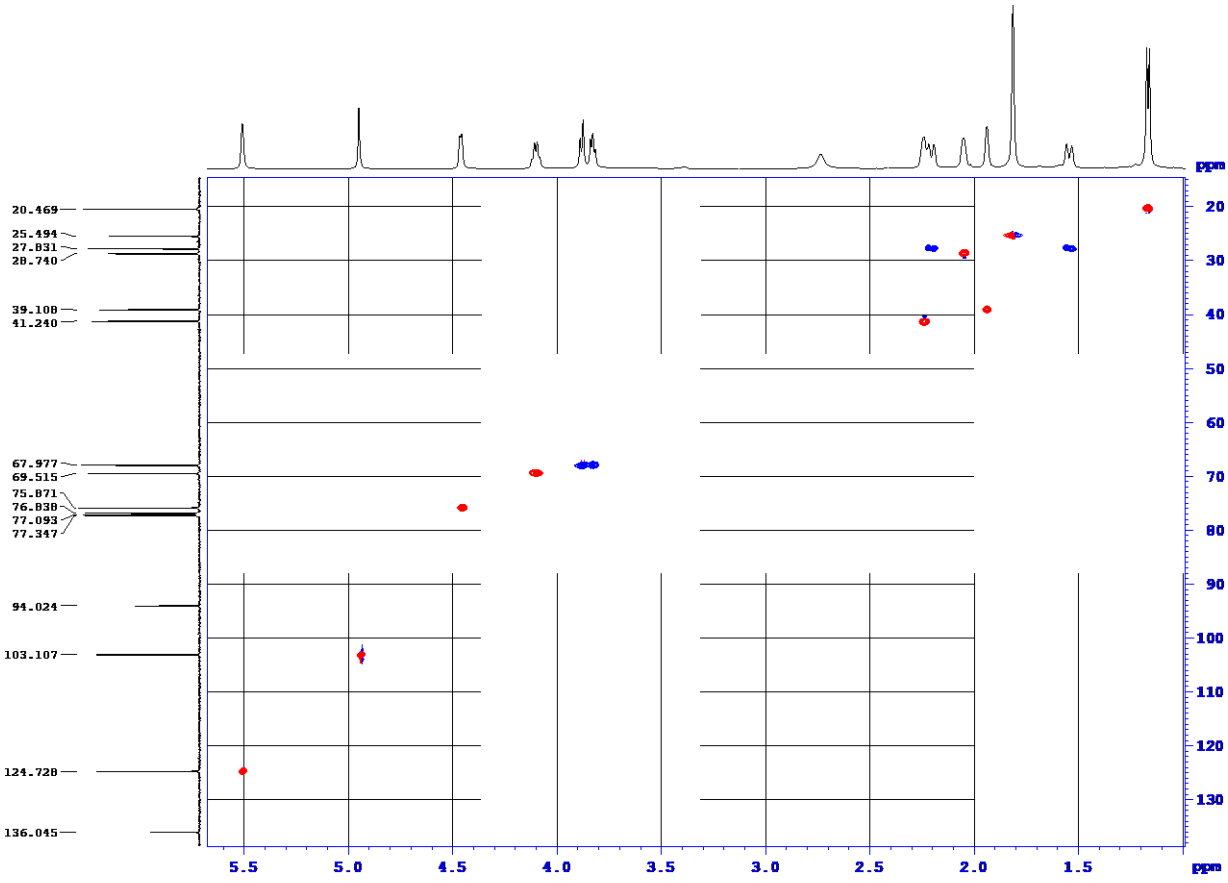


Figure S3.4. {^{1}H,^{13}C} HSQCED NMR spectrum of **3** in $CDCl_3$.

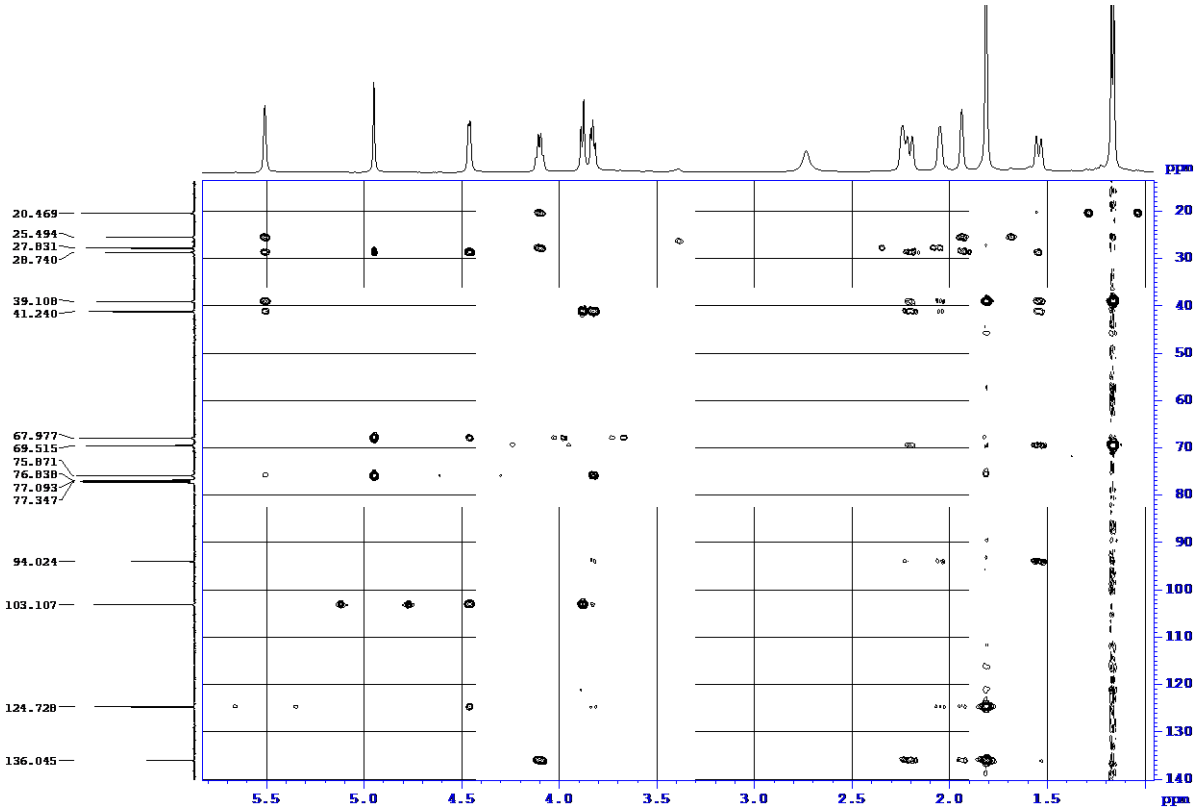


Figure S3.5. {^{1}H,^{13}C} HMBC NMR spectrum of **3** in $CDCl_3$.

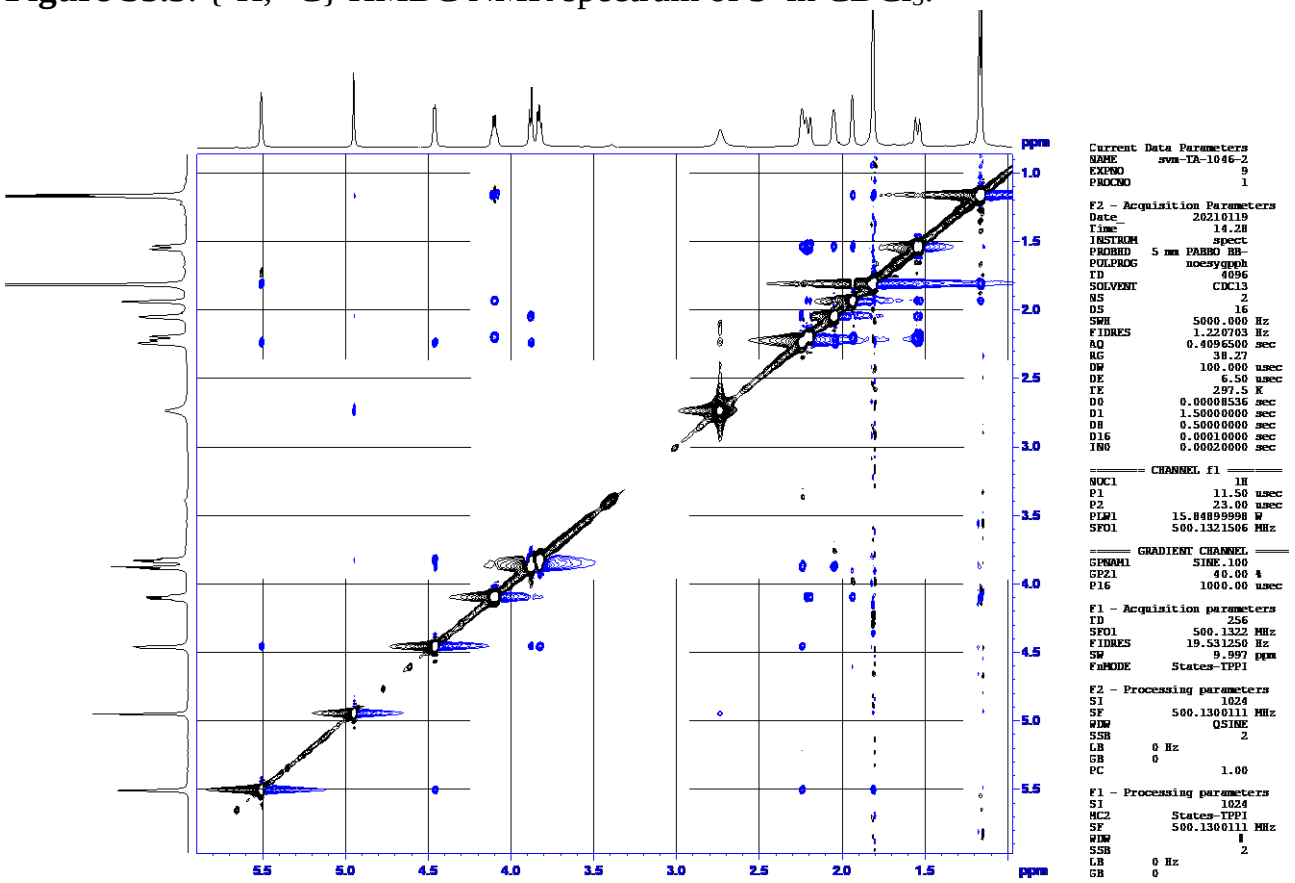
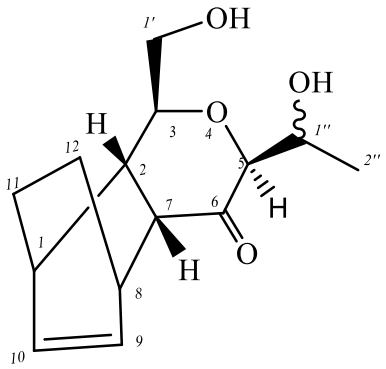


Figure S3.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of **3** in $CDCl_3$

(2*S*,3*S*,5*S*,7*R*)-5-(1-Hydroxyethyl)-3-hydroxymethyl-4-oxatricyclo-[6.2.2.0^{2,7}]dodec-9-en-6-one (5)



From 0.150 g (0.73 mmol) of adduct **4a**, the product yield was 0.098 g (56%), a 1"*R*/1"*S* diastereomer mixture in the 2:1 ratio (EtOAc – petroleum ether 1:1, R_f 0.06). Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.10 [1.21] d (3H, H$^{2''}$, $^3J_{2'',1''}$ 6.4 Hz), 1.22-1.30 [1.22-1.30] m (2H, H^{11B}, H^{12B}), 1.44-1.50 [1.43-1.49] m (1H, H^{11A}), 1.51-1.58 [1.50-1.57] m (1H, H^{12A}), 2.37-2.41 [2.36-2.42] m (1H, H^1), 2.47-2.55 [2.57-2.67] m (1H, H^2), 2.52-2.56 [2.53-2.57] m (1H, H^7), 2.96-3.01 [2.95-3.01] m (1H, H^3), 3.12-3.16 [3.11-3.15] m (1H, H^8), 3.62 [3.64] dd (1H, H$^{1'B}$, $^2J_{1'B,1'A}$ 11.9, $^3J_{1'B,3}$ 6.5 Hz), 3.69 [3.54] d (1H, H^5, $^3J_{5,1''}$ 3.1 Hz), 3.78 [3.81] dd (1H, H$^{1'A}$, $^2J_{1'A,1'B}$ 11.9, $^3J_{1'A,3}$ 1.7 Hz), 4.01-4.05 [3.95-3.99] m (1H, H$^{1''}$), 6.01-6.06 [6.02-6.07] m (1H, H^{10}), 6.24-6.28 [6.25-6.29] m (1H, H^9). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.35 [19.57] (C$^{2''}$), 22.84 [22.83] (C^{11}), 25.67 [25.66] (C^{12}), 30.41 [30.30] (C^8), 31.50 [31.43] (C^1), 42.02 [41.51] (C^2), 51.01 [50.92] (C^7), 63.78 [63.33] (C$^{1'}$), 68.32 [68.60] (C$^{1''}$), 79.45 [78.96] (C^3), 86.58 [86.44] (C^5), 131.99 [131.88] (C^{10}), 135.47 [135.57] (C^9), 211.84 [212.74] (C^6). Mass spectrum, *m/z*: 253 [*M*H]+. Found, %: C 66. 95, H 7.92. $C_{14}H_{20}O_4$. Calculation, %: C 66.65, H 7.99. IR: 3387, 2939, 1712, 1462, 1106, 1040, 736.

The existence of a hydroxyethyl substituent at C^5 in compound **5** was confirmed by the presence of an H^5/C$^{1''}$ correlation peak in the HMBC spectrum. Moreover, the HMBC spectrum exhibits H^5/C^6, H$^{1'}$/C^2 and H^5/C^3 correlation peaks that indicate the retention of the pyran ring and opening of the 1,6-anhydro bridge. The existence of the NOE effect between the H^5/H^3 protons in both isomers results from the *S*-configuration of the C^5 center.

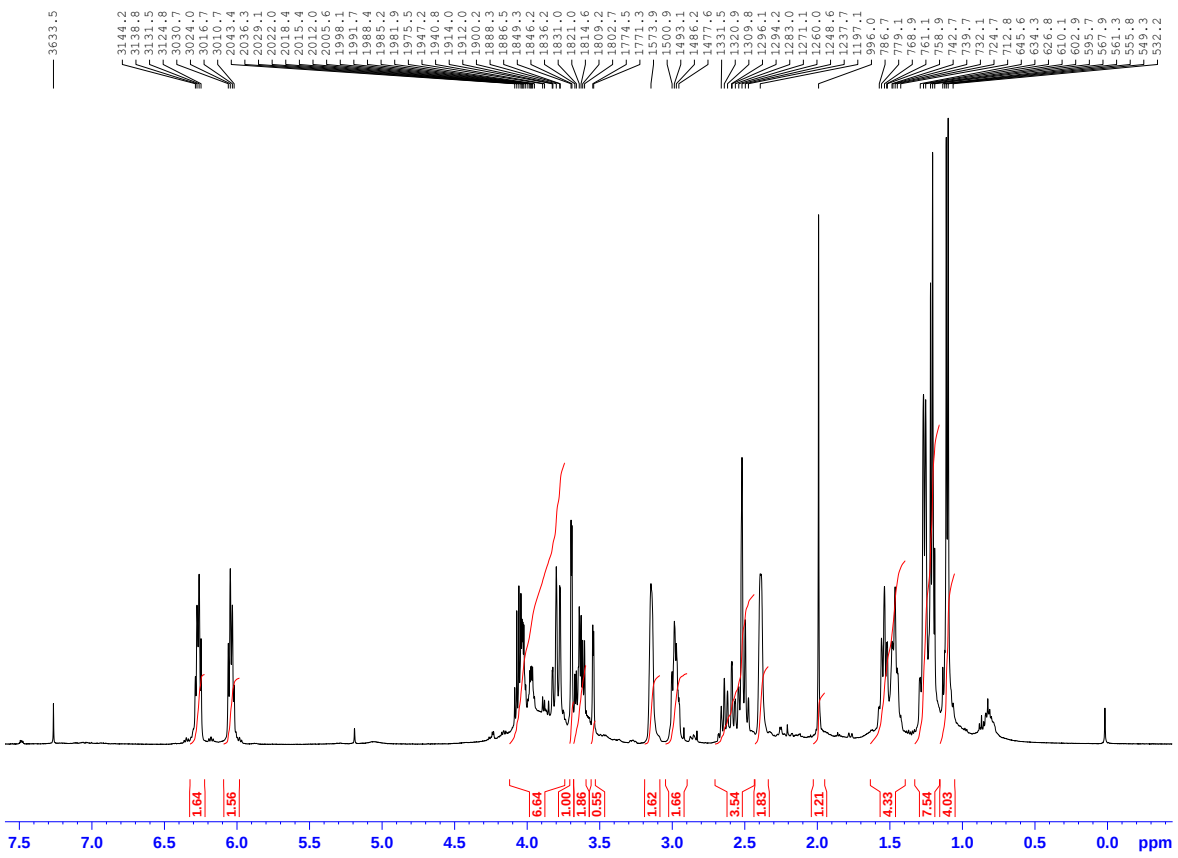


Figure S4.1. Complete ^{1}H NMR (500 MHz) spectrum of **5** in $CDCl_3$.

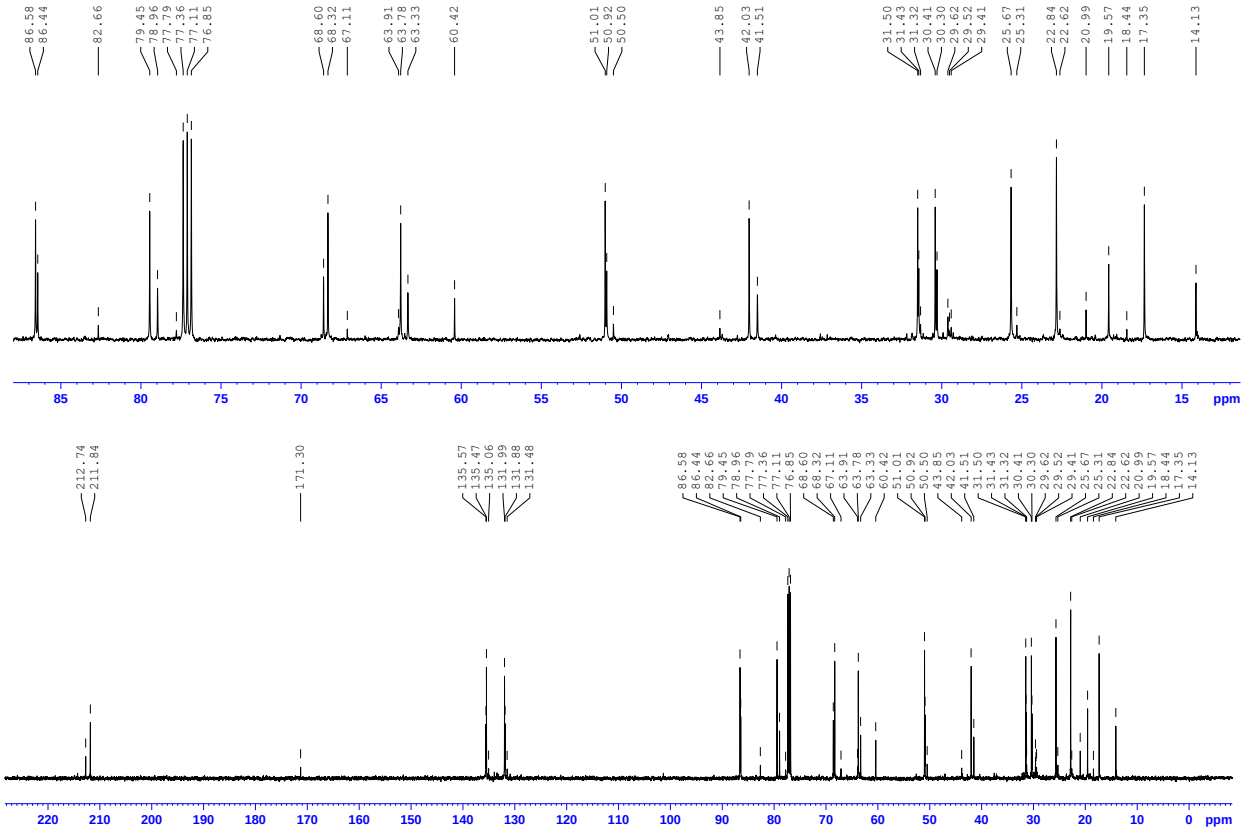


Figure S4.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

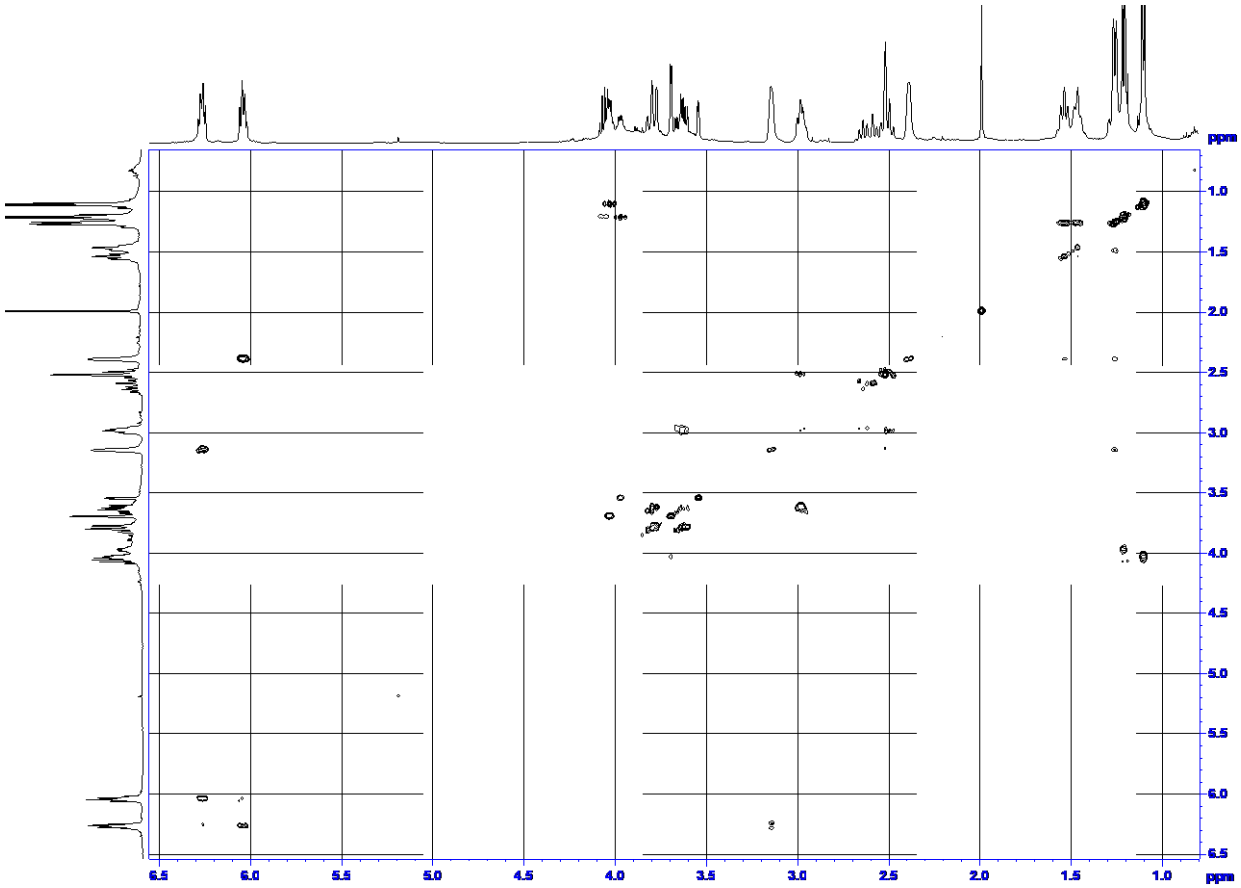


Figure S4.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of **5** in $CDCl_3$

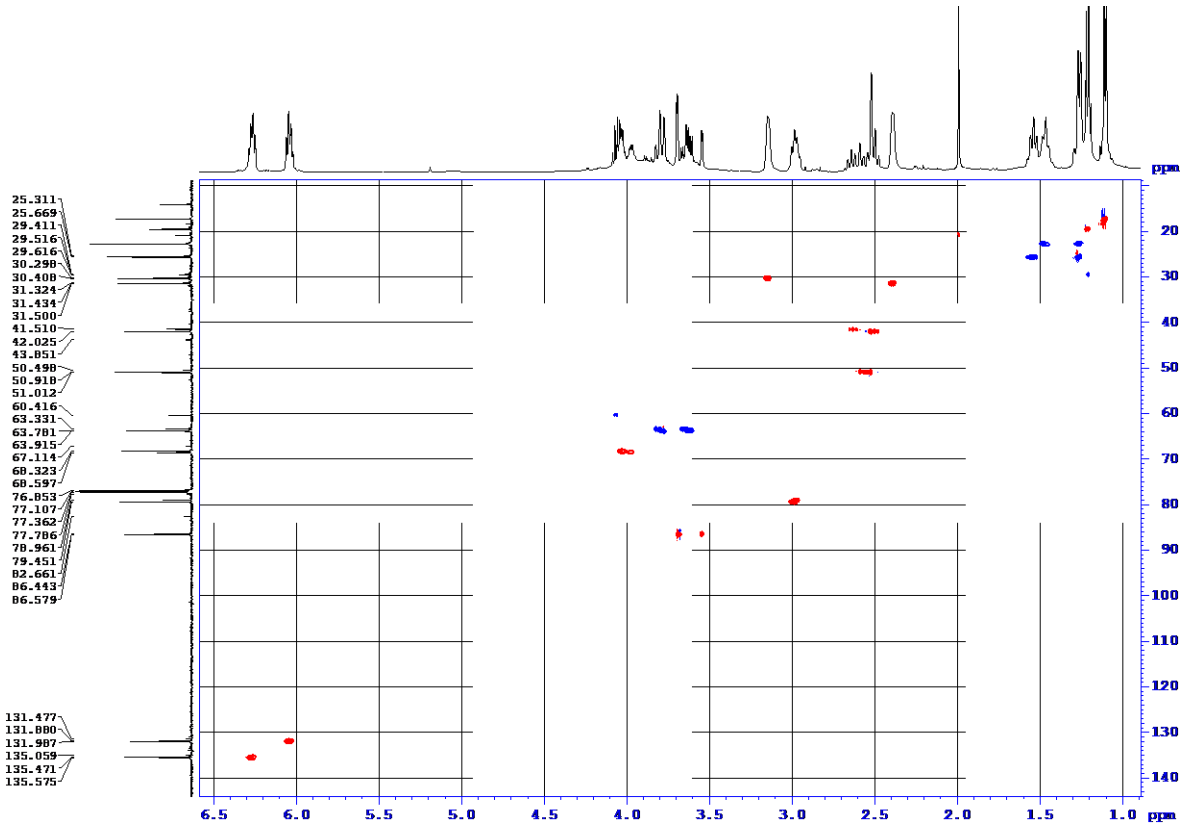


Figure S4.4. {^{1}H,^{13}C} HSQCED NMR spectrum of **5** in $CDCl_3$.

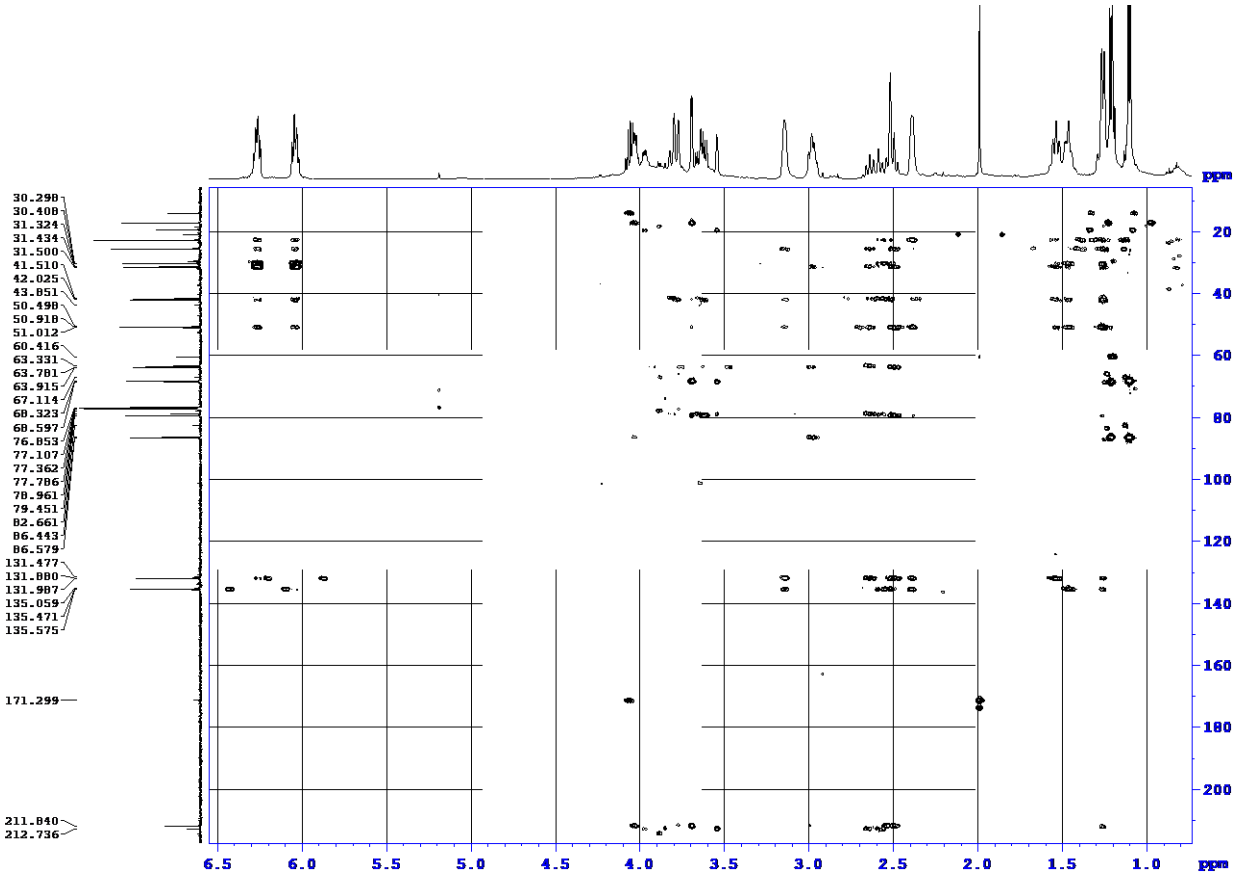


Figure S4.5. {^{1}H,^{13}C} HMBC NMR spectrum of **5** in $CDCl_3$.

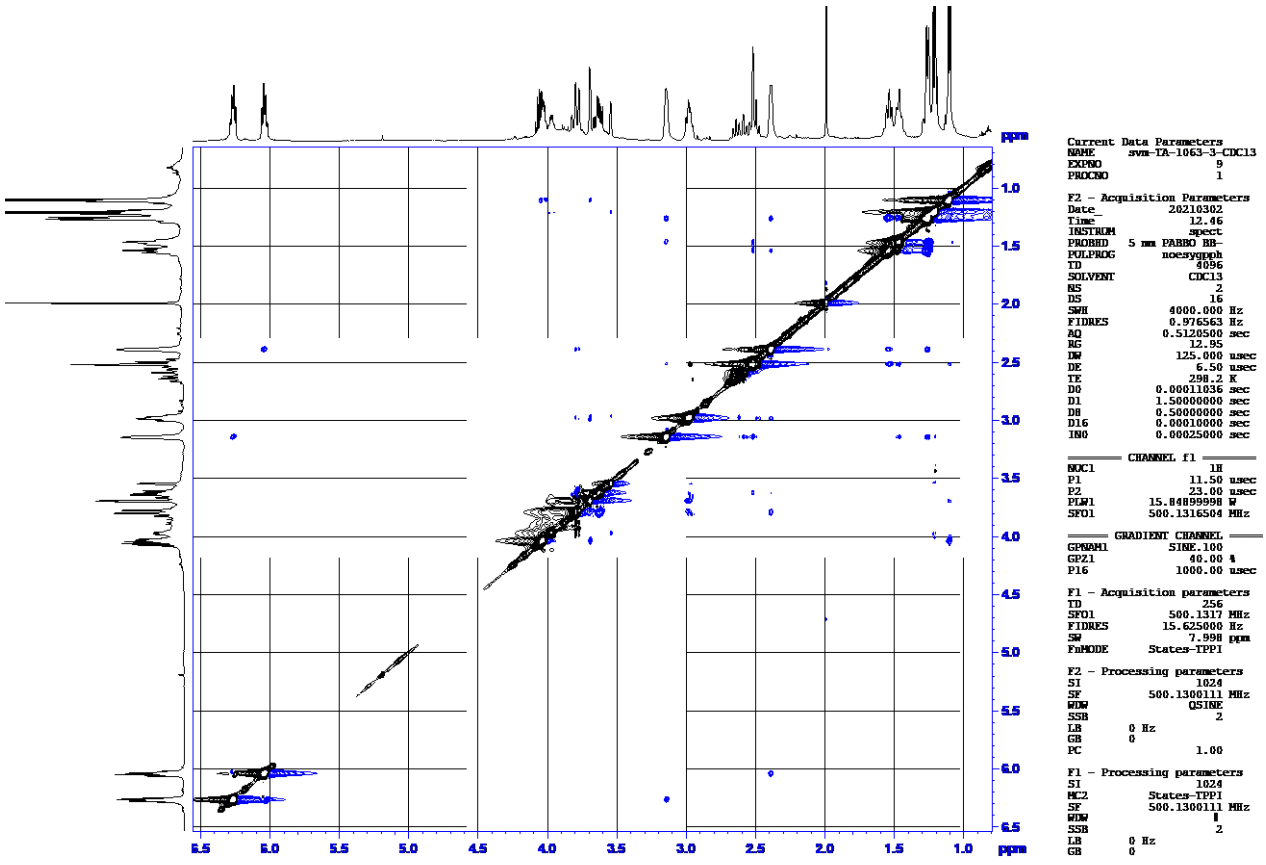
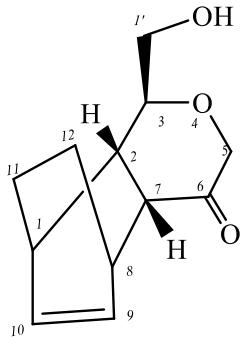


Figure S4.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of **5** in $CDCl_3$

(2*S*,3*S*,7*R*)-3-Hydroxymethyl-4-oxatricyclo[6.2.2.0^{2,7}]dodec-9-en-6-one (6)



From 0.150 g (0.73 mmol) of adduct **4a**, the product yield was 0.02 g (12%). (EtOAc – petroleum ether 1:5, R_f 0.3). Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27-1.35 m (2H, H^{11B}, H^{12B}), 1.52-1.62 m (2H, H^{11A}, H^{12A}), 2.43-2.46 m (1H, H^{1}), 2.51 t (1H, H^{2}, $^3J_{2,7}$ 11.0, $^3J_{2,1}$ 11.0 Hz), 2.62 dd (1H, H^{7}, $^3J_{7,2}$11.0, $^3J_{7,8}$ 1.8 Hz), 2.99-3.03 m (1H, H^{3}), 3.22-3.24 m (1H, H^{8}), 3.64 dd (1H, H$^{1'B}$, $^2J_{1'B,1'A}$ 11.8, $^3J_{1'B,3}$ 6.7 Hz), 3.79 d (1H, H^{5B}, $^2J_{5B,5A}$ 18.3 Hz), 3.85 д.д (1H, H$^{1'A}$, $^2J_{1'A,1'B}$ 11.8, $^3J_{1'A,3}$ 2.3 Hz), 4.22 д (1H, H^{5A}, $^2J_{5A,5B}$ 18.3 Hz), 6.13 t (1H, H^{10}, $^3J_{10,9}$ 7.5, $^3J_{10,1}$ 7.5 Hz), 6.31 t (1H, H^{9}, $^3J_{9,8}$ 7.5, $^3J_{9,10}$ 7.5 Hz). ^{13}C NMR (500 MHz, $CDCl_3$): δ 23.14 (C^{11}), 25.65 (C^{12}), 30.82 (C^{8}), 31.58 (C^{1}), 41.48 (C^{2}), 49.67 (C^{7}), 64.34 (C$^{1'}$), 74.10 (C^{5}), 80.32 (C^{3}), 132.43 (C^{10}), 135.34 (C^{9}), 211.18 (C^{6}). Mass spectrum, *m/z*: 209 [*M*H]+. Found, %: C 69. 19, H 7.70. $C_{12}H_{16}O_3$. Calculation, %: C 69.21, H 7.74. IR: 3443, 2948, 2869, 1725, 1696, 1458, 1178, 1069, 986, 835, 735 cm^{-1}.

In the ^{1}H NMR spectrum of compound **6**, the protons for the methylene group at C^{9} appear at δ 4.22 and 3.70 as doublets with ^2J = 18.3 Hz. In the HMBC spectra, they correlate with the C^{1} and C^{8} carbon atoms.

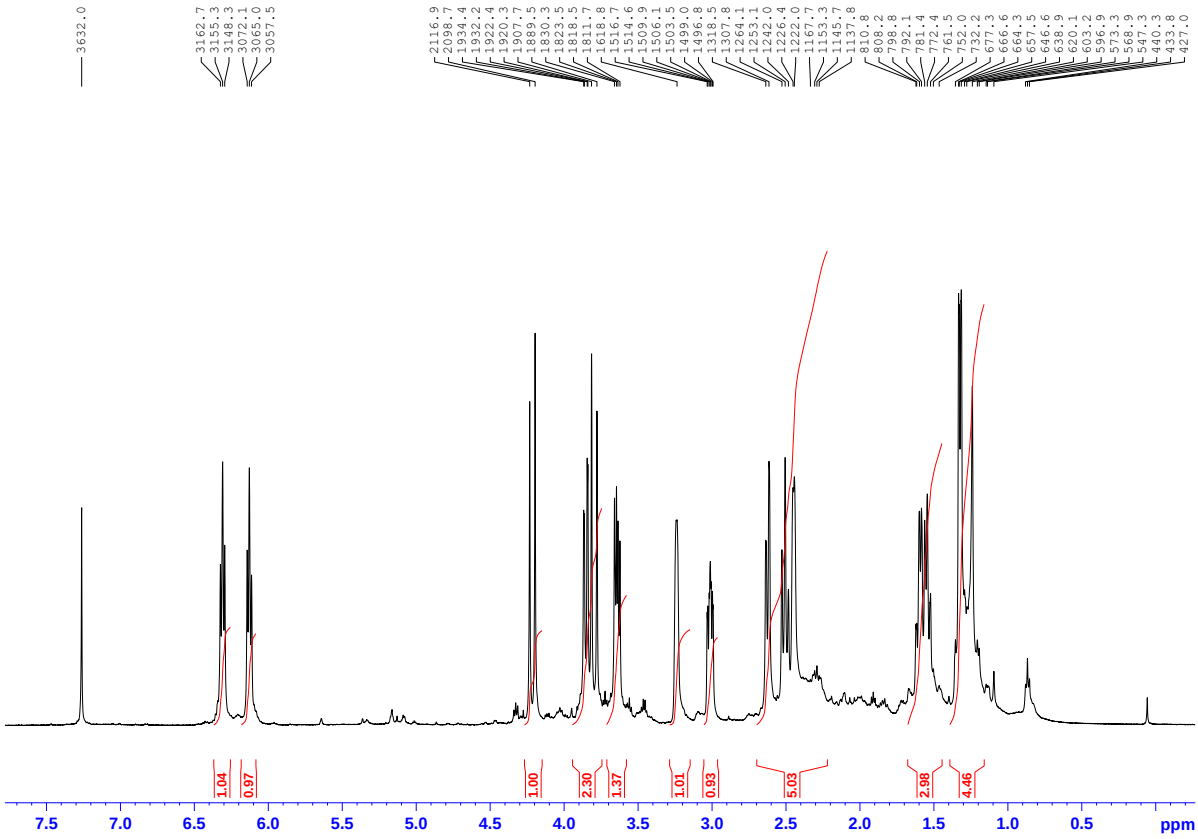


Figure S6.1. Complete ^{1}H NMR (500 MHz) spectrum of **6** in $CDCl_3$.

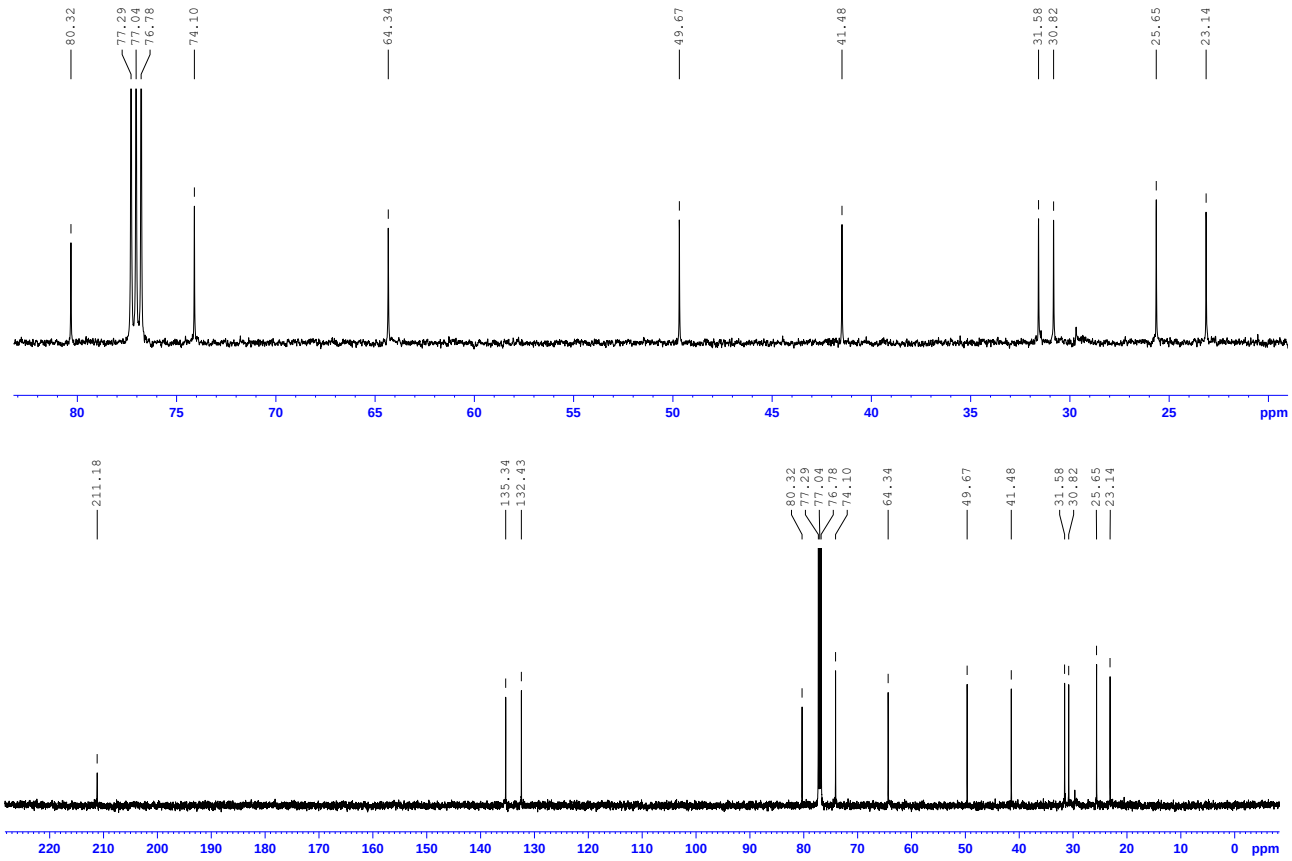


Figure S6.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

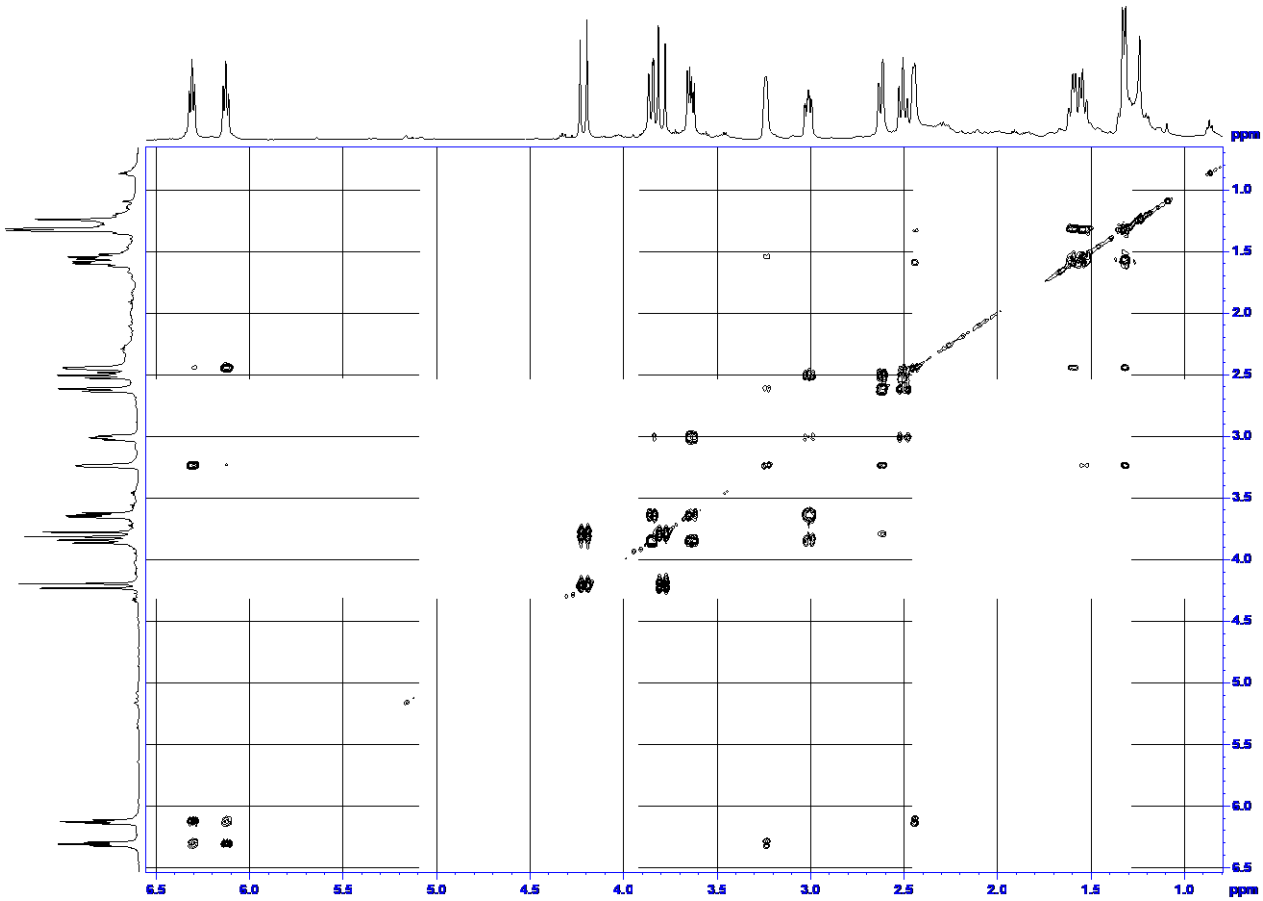


Figure S6.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of **6** in $CDCl_3$

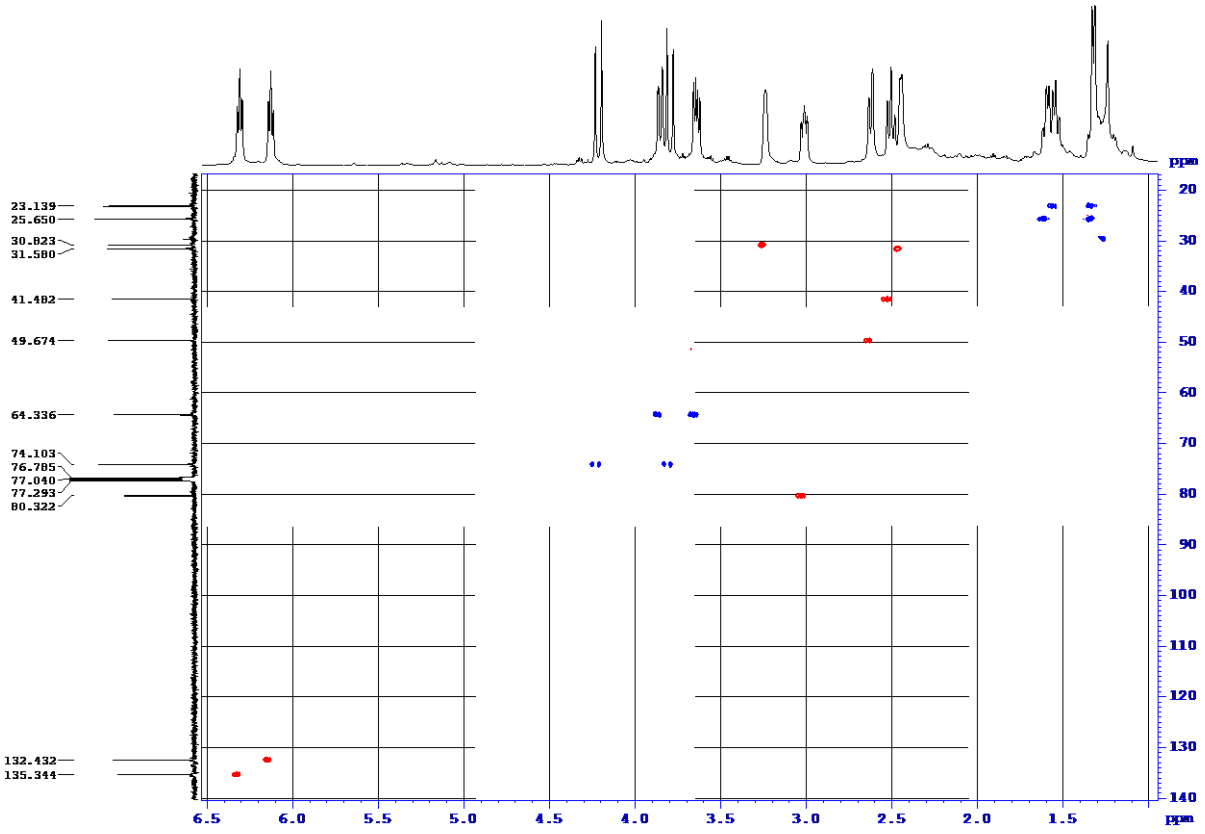


Figure S6.4. {^{1}H,^{13}C} HSQCED NMR spectrum of **6** in $CDCl_3$.

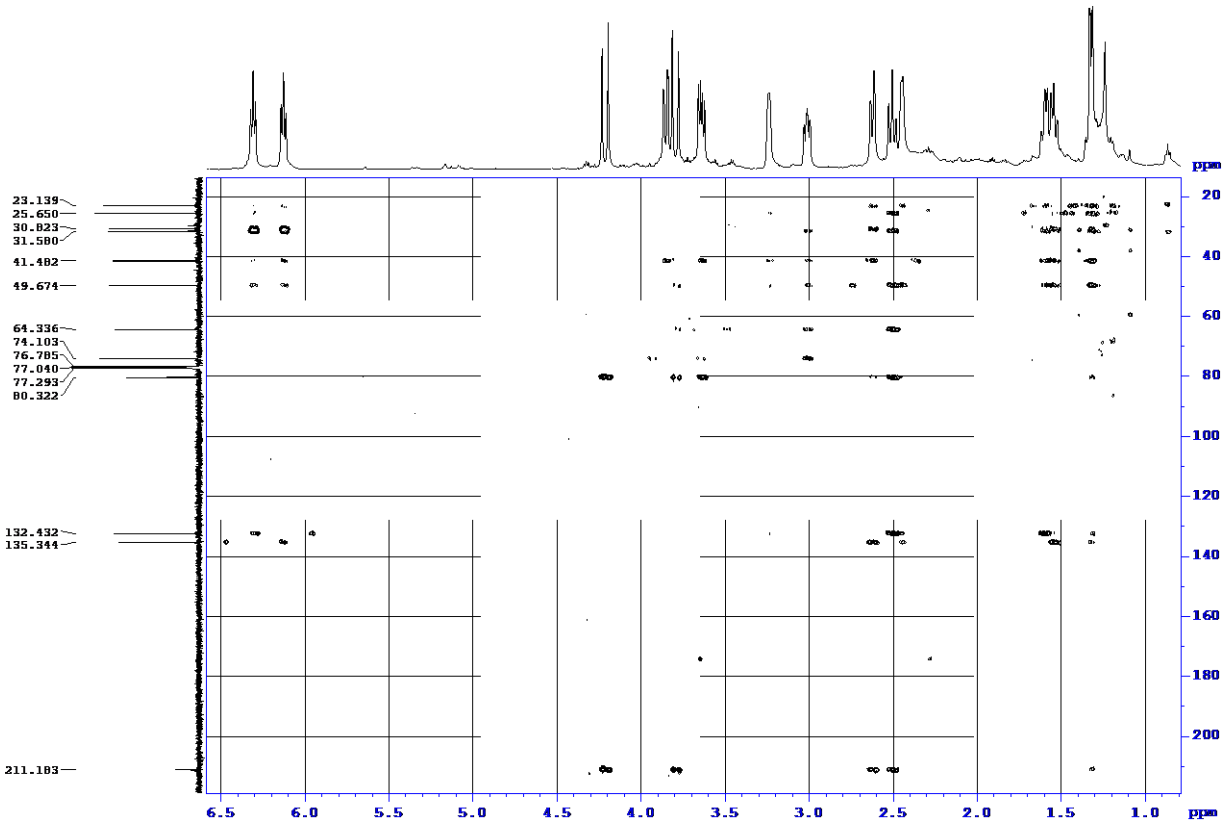


Figure S6.5. {^{1}H,^{13}C} HMBC NMR spectrum of **6** in $CDCl_3$.

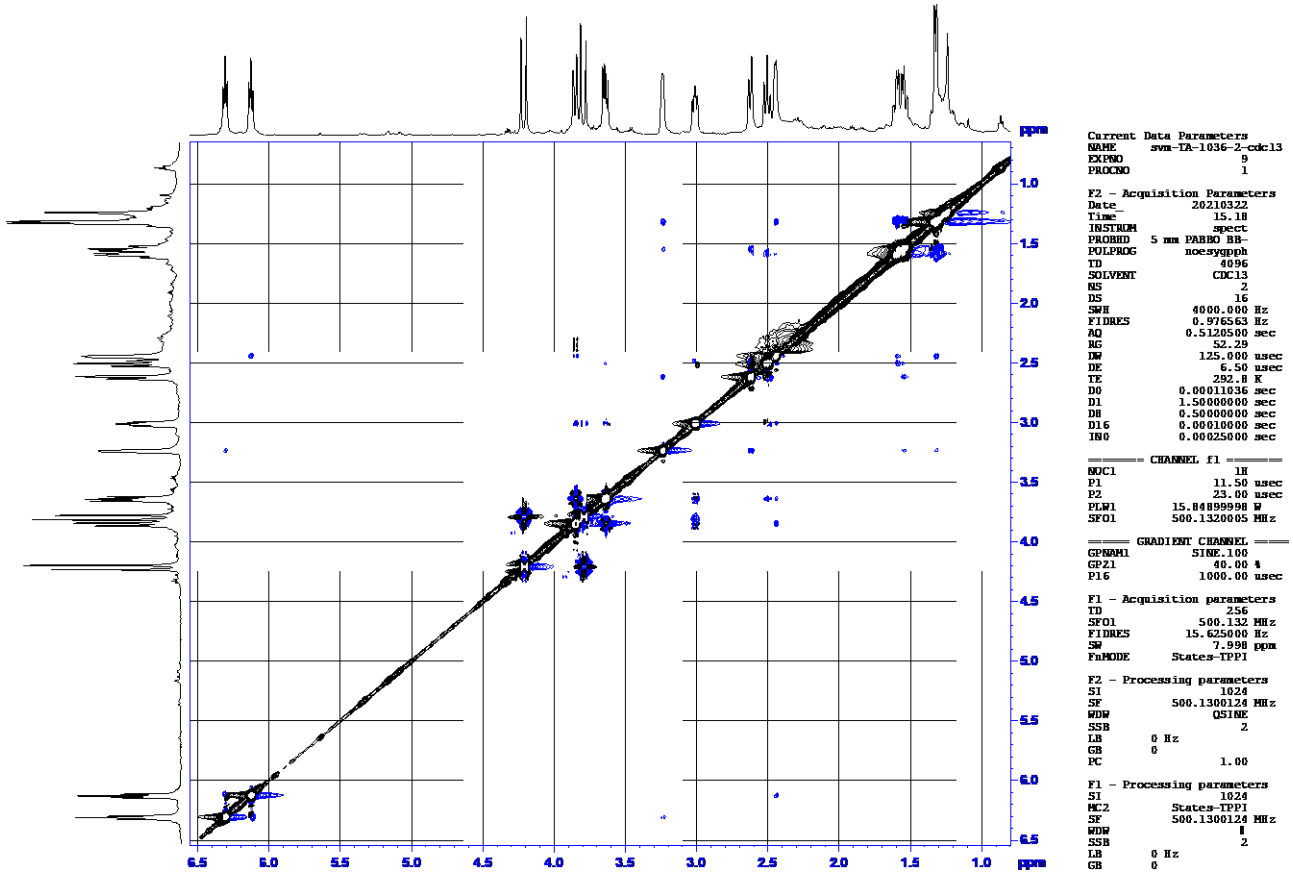
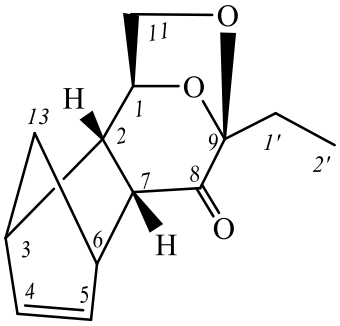


Figure S6.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of **6** in $CDCl_3$

(1*S*,2*S*,3*S*,6*R*,7*R*,9*R*)-)-9-Ethyl-10,12-dioxatetacyclo[7.2.1.1^{3,6}.0^{2,7}]tridec-4-en-8-one (7)



From 0.057 g (0.24 mmol) of adduct **4b**, the product yield was 0.026 g (43%). (EtOAc – petroleum ether 1:1, R_f 0.07). Oil. $[\alpha]_D^{20}$ -20° (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 t (3H, H$^{2'}$, $^3J_{2',1'}$ 7.5 Hz), 1.31 dt. (1H, H^{13B}, $^2J_{13B,13A}$ 8.4, $^3J_{13B,3}$ 1.7, $^3J_{13B,6}$1.7 Hz), 1.45 dt. (1H, H^{13A}, $^2J_{13A,13B}$ 8.4, $^3J_{13A,3}$ 1.7, $^3J_{13A,6}$ 1.7 Hz), 1.77 qur (2H, H$^{1'}$, $^3J_{1',2'}$ 7.5 Hz), 2.44 dd (1H, H^2, $^3J_{2,7}$ 9.0, $^3J_{2,3}$ 3.3 Hz), 3.01-3.06 m (2H, H^7, H^3), 3.39-3.42 m (1H, H^6), 3.82-3.88 m (2H, H^{11A}, H^{11B}), 4.61 d (1H, H^1, $^3J_{1,11A}$ 4.4 Hz), 6.00 dd (1H, H^4, $^3J_{4,5}$ 5.6, $^3J_{4,3}$ 2.9 Hz), 6.26 t (1H, H^5, $^3J_{5,4}$ 5.6, $^3J_{5,6}$ 2.9 Hz). ^{13}C NMR (500 MHz, $CDCl_3$): δ 6.43 (C$^{2'}$), 22.66 (C$^{1'}$), 43.34 (C^2), 46.91 (C^7), 47.12 (C^3), 47.56 (C^6), 49.66 (C^{13}), 71.28 (C^{11}), 75.73 (C^1), 105.20 (C^9), 134.49 (C^5), 135.22 (C^4), 200.79 (C^8). Mass spectrum, *m/z*: 221 [*M*H]+. Found, %: C 70.85, H 7.29. $C_{13}H_{16}O_3$. Calculation, %: C 70.89, H 7.32. IR: 3408, 2933, 1716, 1265, 1100, 737, 704 cm^{-1}.

The HMBC spectrum of compound **7** contains H$^{1'}$/C^{9}and H^{11}/C^9 correlation peaks which indicates that the ethyl moiety is added to the C^9 center to create the 1,6-anhydro bridge.

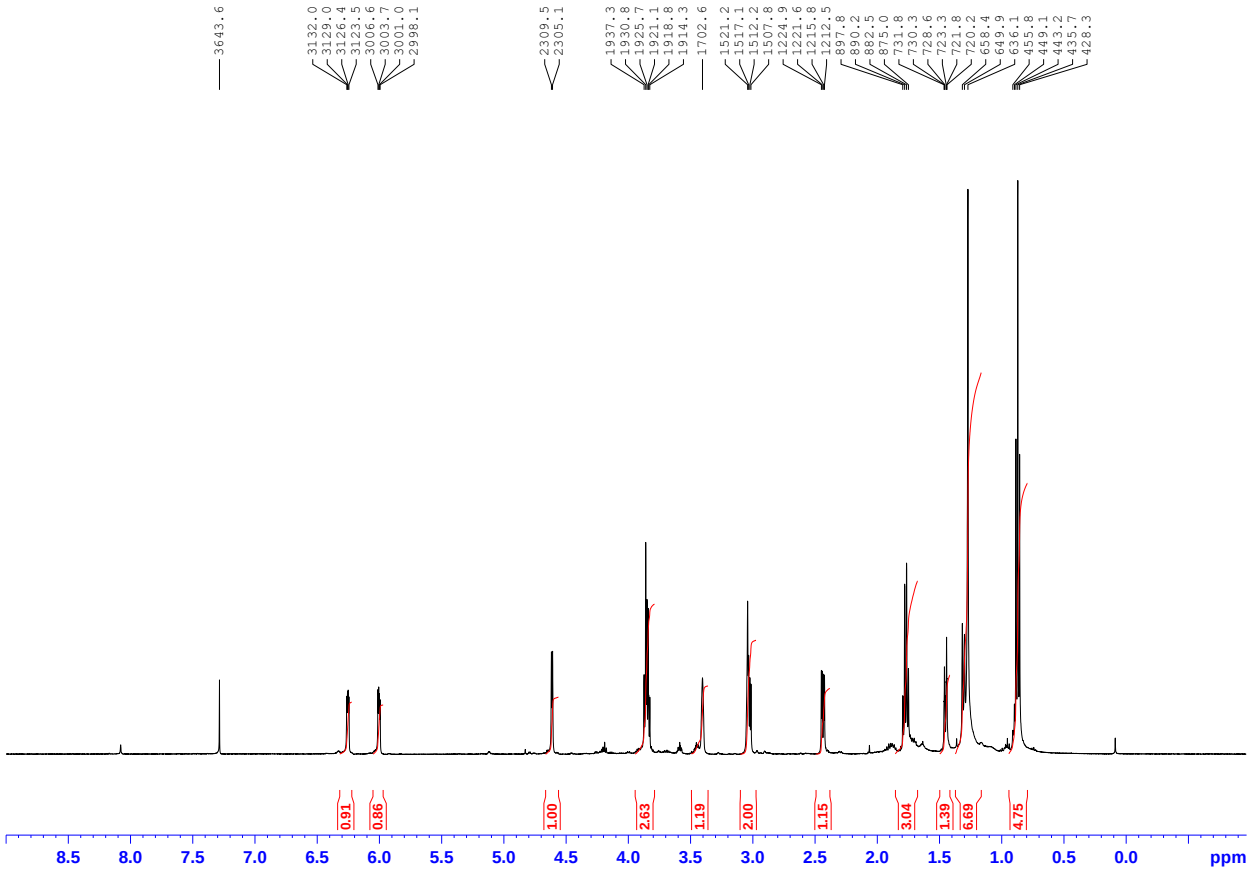


Figure S7.1. Complete ^{1}H NMR (500 MHz) spectrum of **7** in $CDCl_3$.

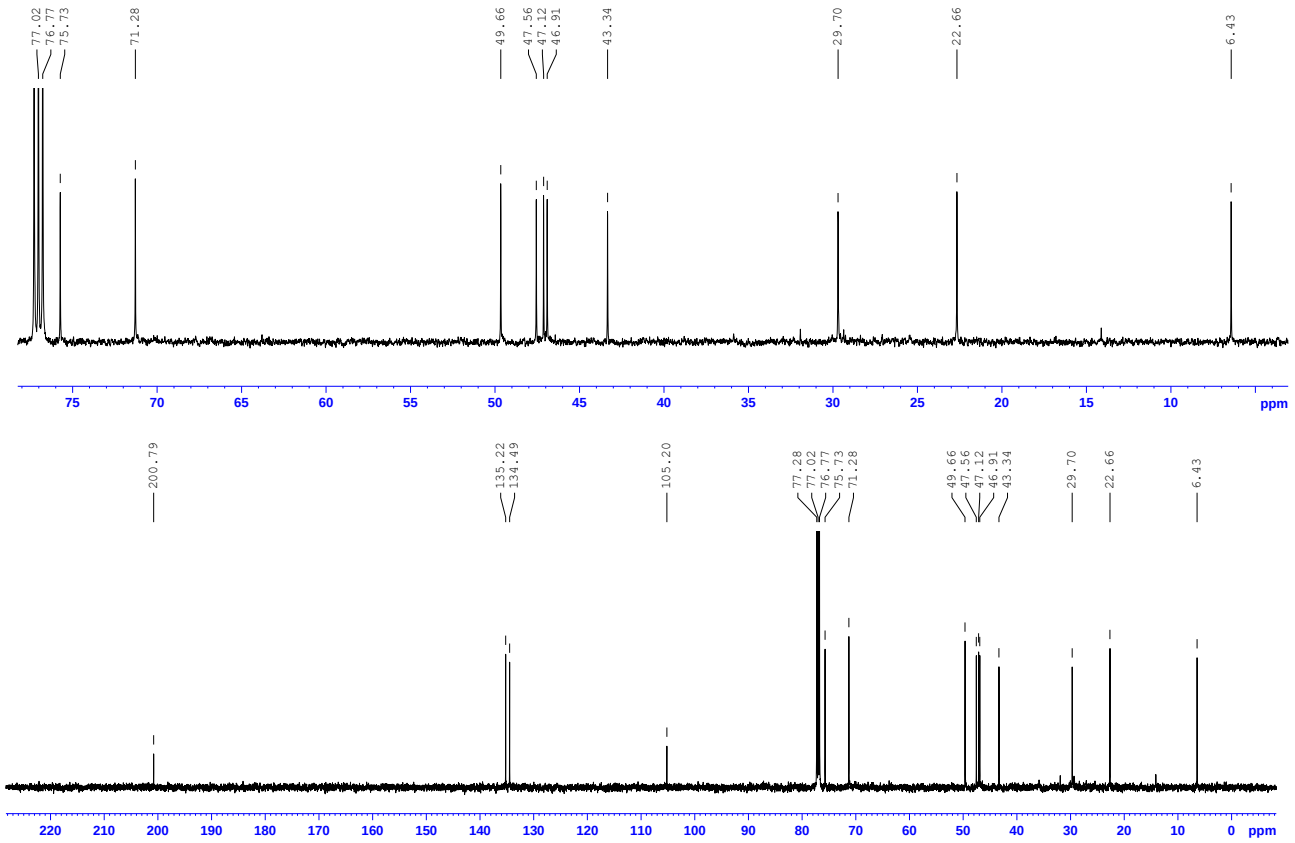


Figure S7.2. Complete ^{13}C{^{1}H} NMR spectrum of **7** in $CDCl_3$.

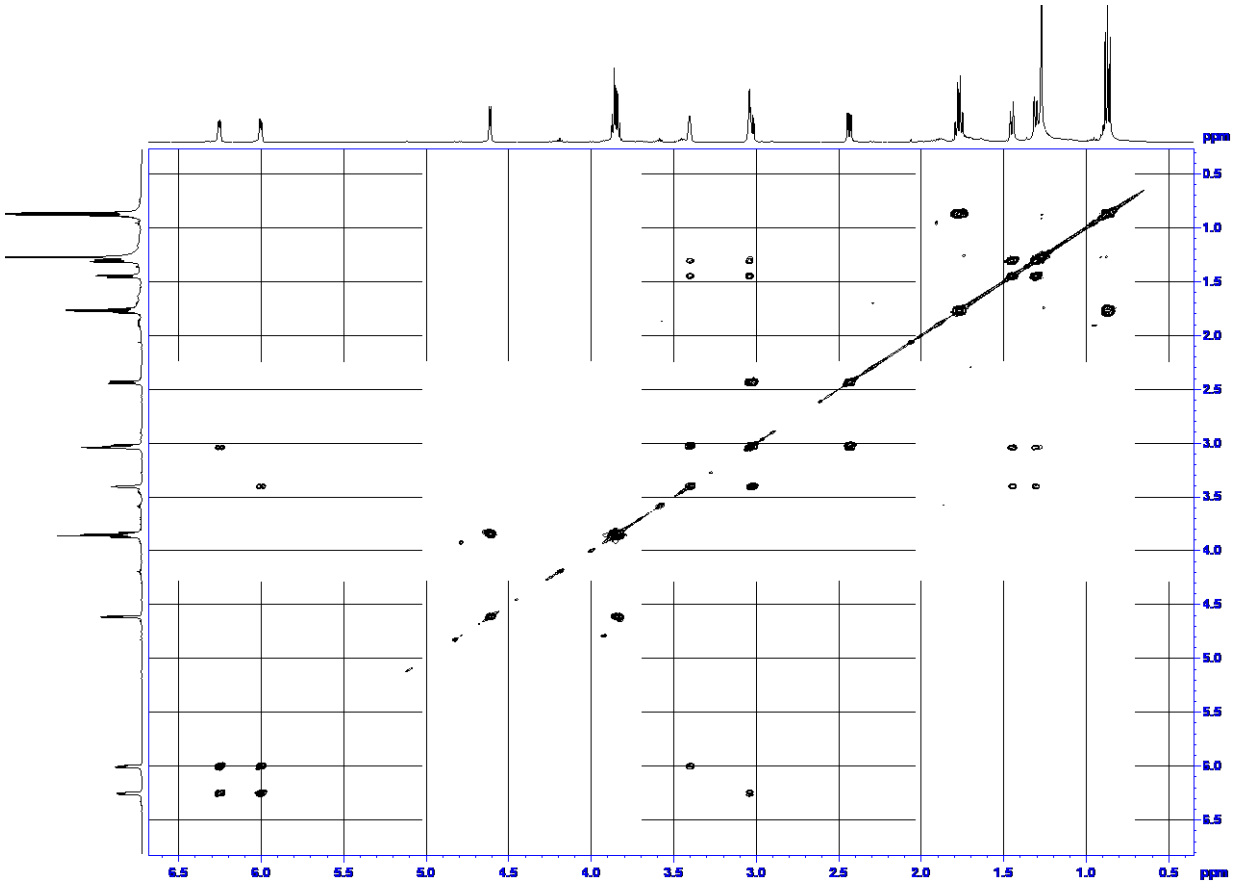


Figure S7.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of **7** in $CDCl_3$

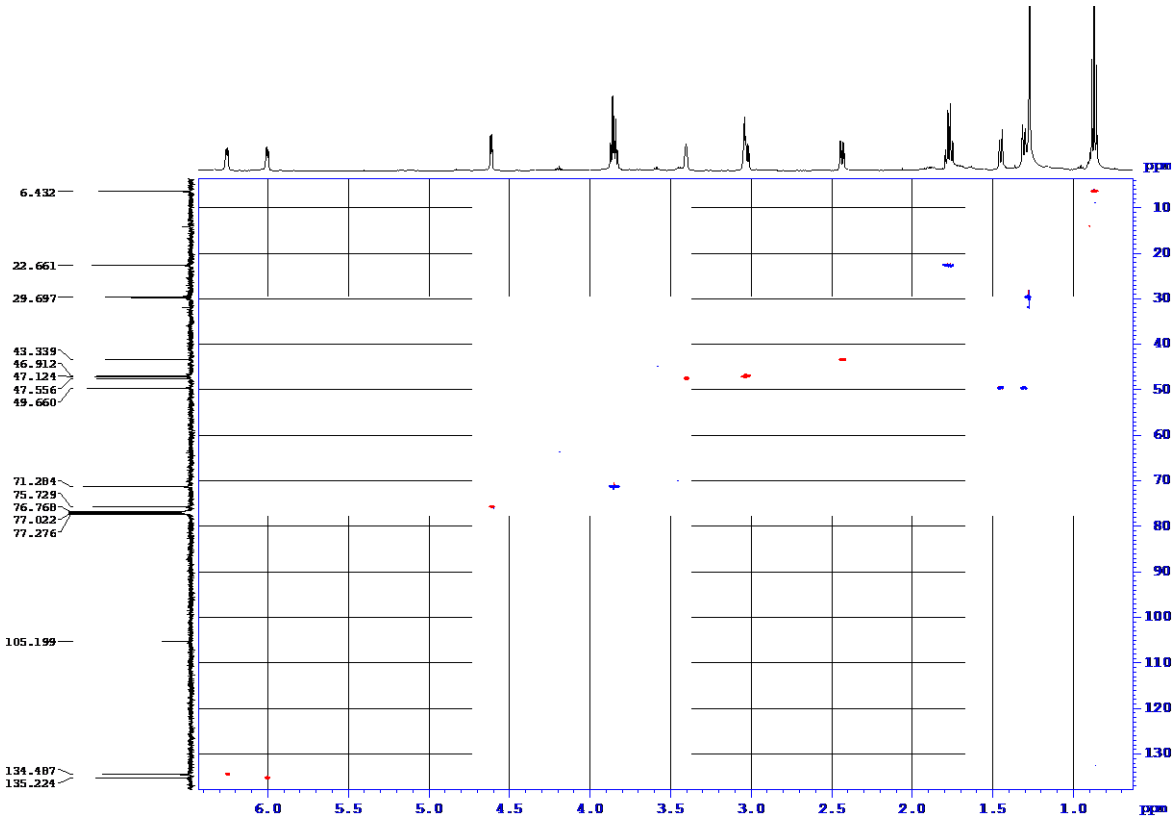


Figure S7.4. {^{1}H,^{13}C} HSQCED NMR spectrum of **7** in $CDCl_3$.

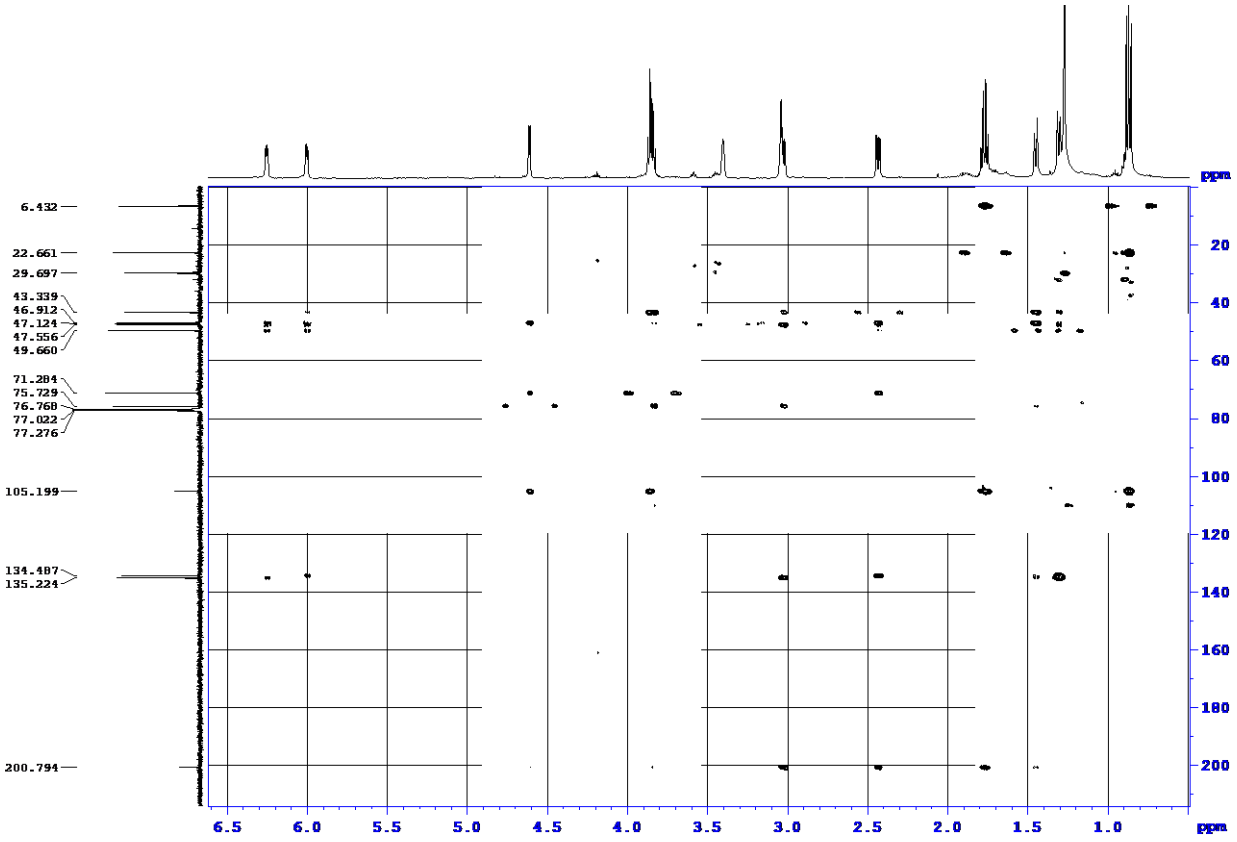


Figure S7.5. {^{1}H,^{13}C} HMBC NMR spectrum of **7** in $CDCl_3$.

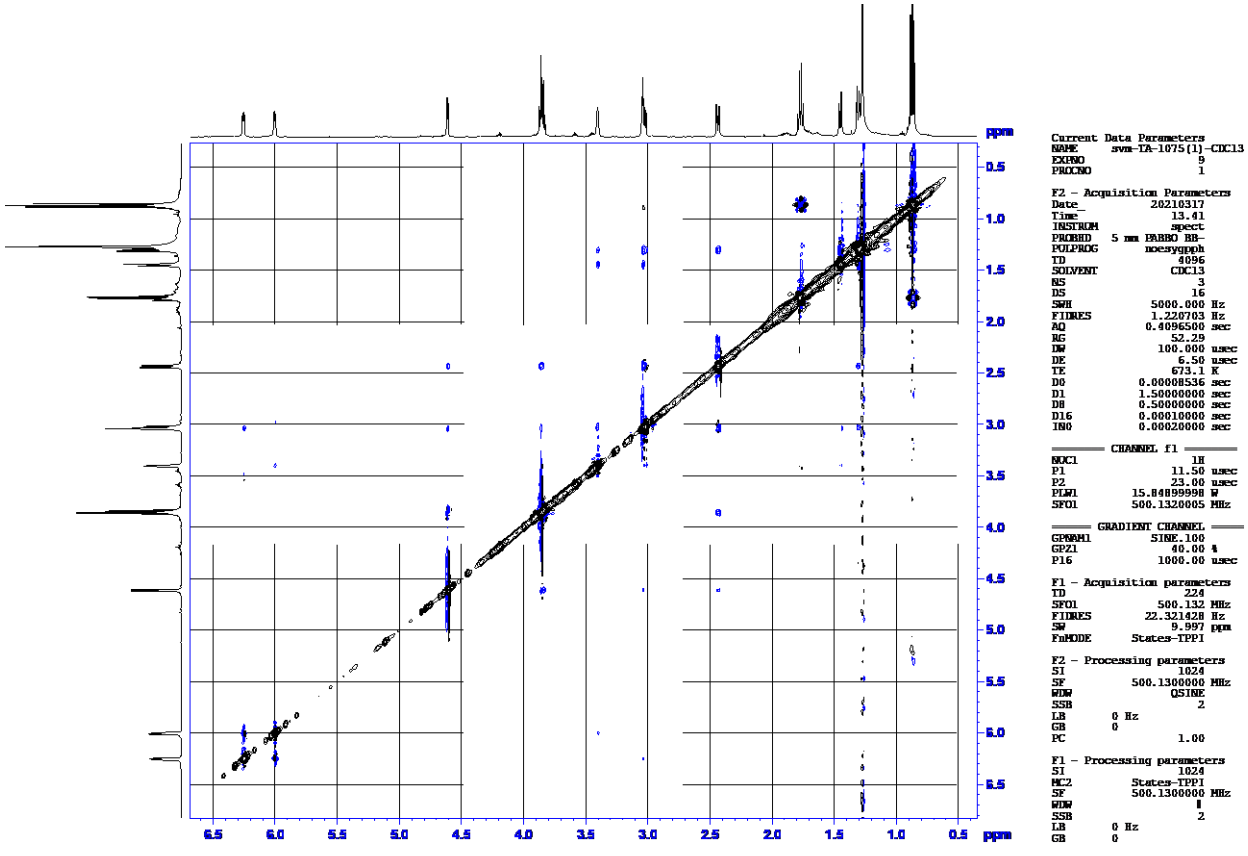
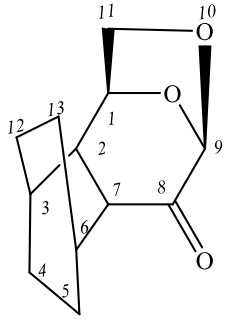


Figure S7.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of **7** in $CDCl_3$

(2*S*,3*S*,6*R*,8*R*)-5,14-Dioxatetracyclo[7.2.2.1^{3,6}.0^{2,8}]tetradecan-7-one (8)



To a solution of cyclohexadiene adduct **4a** (0.2 g, 1.03 mmol) of in EtOAc (15 ml) was added Pd/C (10%, 0.01 g). The reaction mixture was stirred in an atmosphere of H_2. After the disappearance of the starting compound (~ 3 h, TLC control), the reaction mixture was filtered, concentrated, the residue was chromatographed on SiO_2. Yield 0.202 g (99%). White crystals, m.p. 101°C, R_f 0.25 (petroleum ether – EtOAc, 1: 1). $[\alpha]_D^{20}$ -172.4° (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 1.30-1.36 m (1H, H^{12B}), 1.39-1.49 m (2H, H^{12A}, H^{13B}), 1.53-1.59 m (3H, H^{4A}, H^{4B}, H^{5B}), 1.65-1.70 m (2H, H^{3}, H^{5A}), 2.04-2.14 m (3H, H^{2}, H^{6}, H^{13A}), 2.56 dd (1H, H^{7}, $^3J_{7,2}$ 10.8, $^3J_{7,6}$ 2.2 Hz), 3.87 d (2H, H^{11A}, H^{11B}, $^3J_{11,1}$ 3.0 Hz), 4.57 t (1H, H^{1}, $^3J_{1,11A}$ 3.0, $^3J_{1,11B}$ 3.0 Hz), 5.07 s (1H, H^{9}). ^{13}C NMR (500 MHz, $CDCl_3$): δ 21.27 (C^{13}), 21.53 (C^{12}), 25.51 (C^{5}), 26.91 (C^{4}), 27.74 (C^{6}), 30.33 (C^{3}), 41.63 (C^{2}), 42.88 (C^{7}), 69.96 (C^{11}), 78.07 (C^{1}), 100.60 (C^{9}), 203.04 (C^{2}). Mass spectrum, *m/z*: 210 [*M*H]+. Found, %: C 69. 22, H 7.71. $C_{12}H_{16}O_3$. Calculation, %: C 69.21, H 7.74. IR: 3420, 2932, 2861, 2360, 1718, 1123, 999, 815.

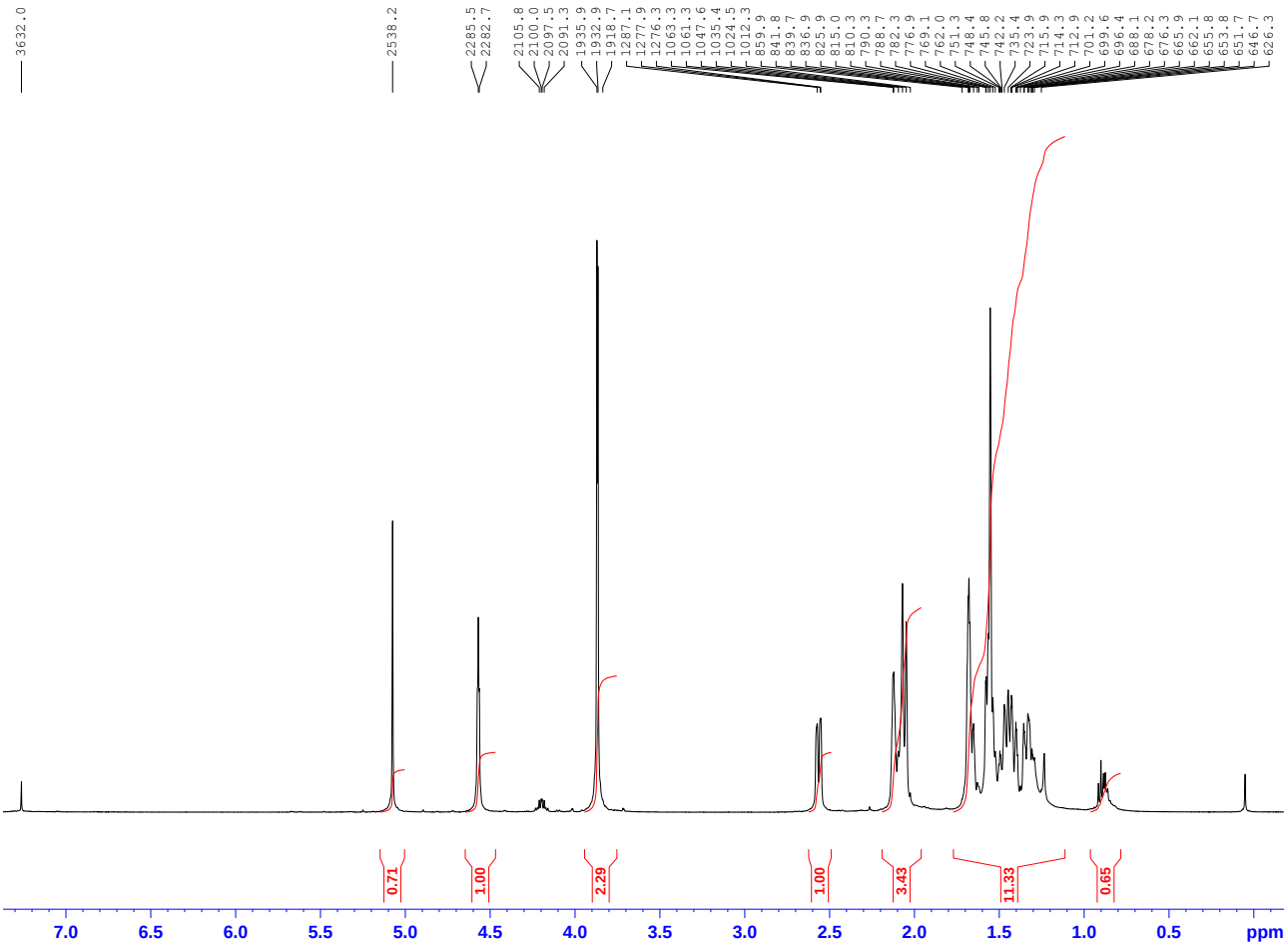


Figure S8.1. Complete ^{1}H NMR (500 MHz) spectrum of **8** in $CDCl_3$.

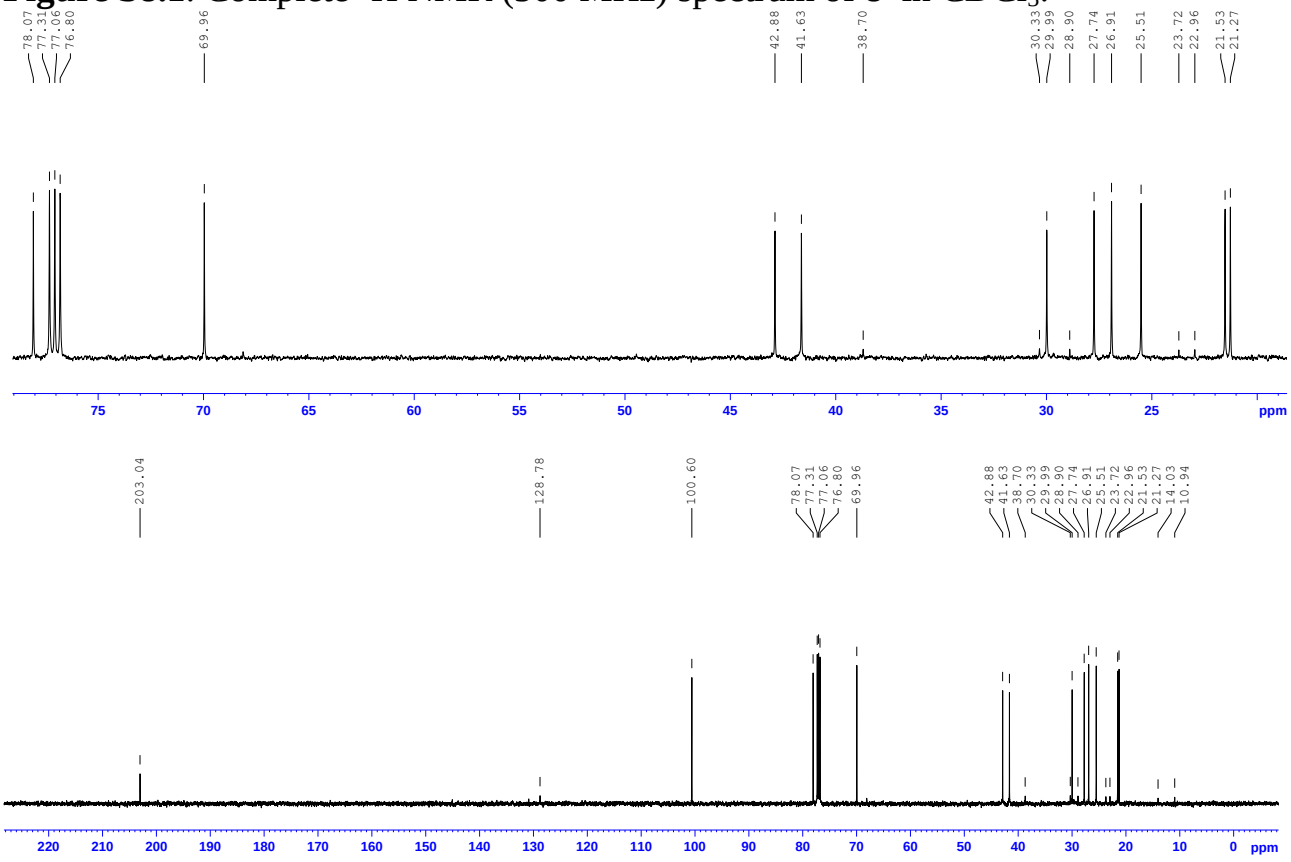


Figure S8.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$.

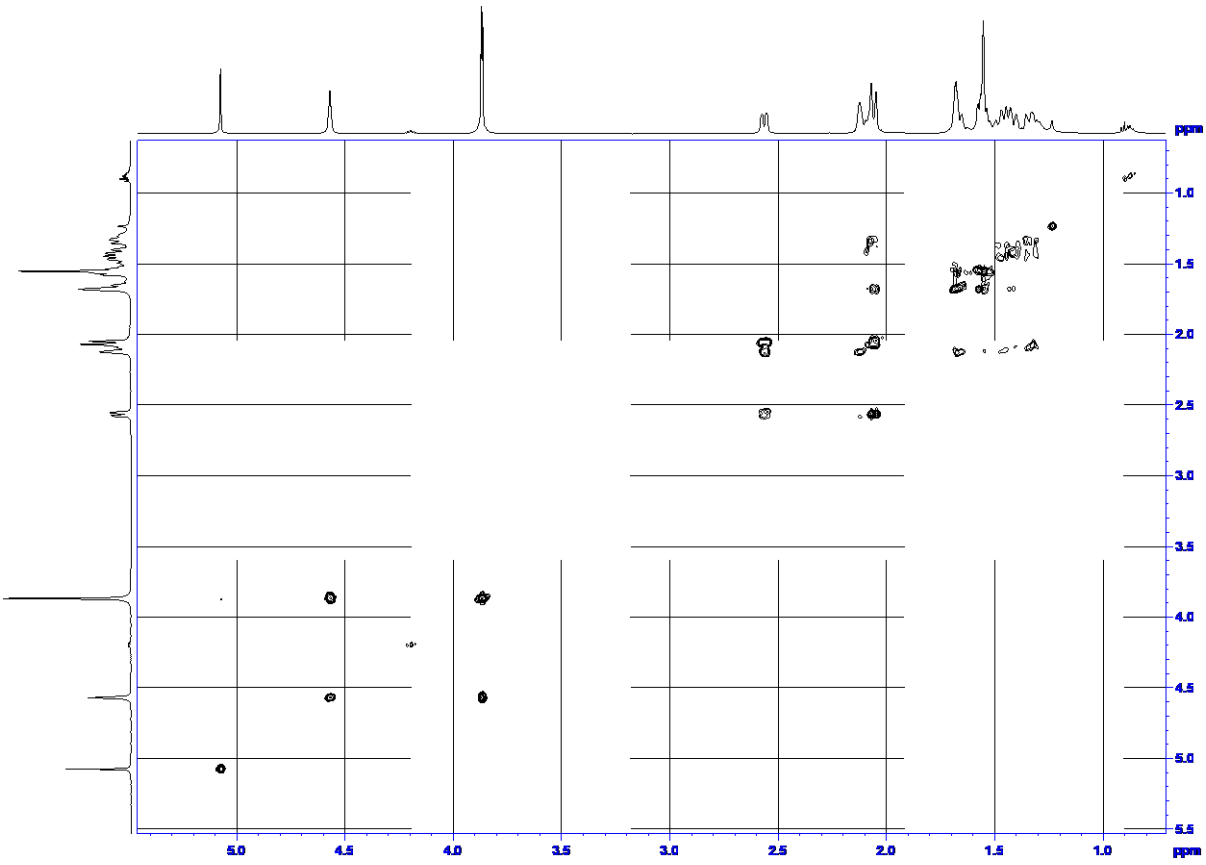


Figure S8.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of **8** in $CDCl_3$

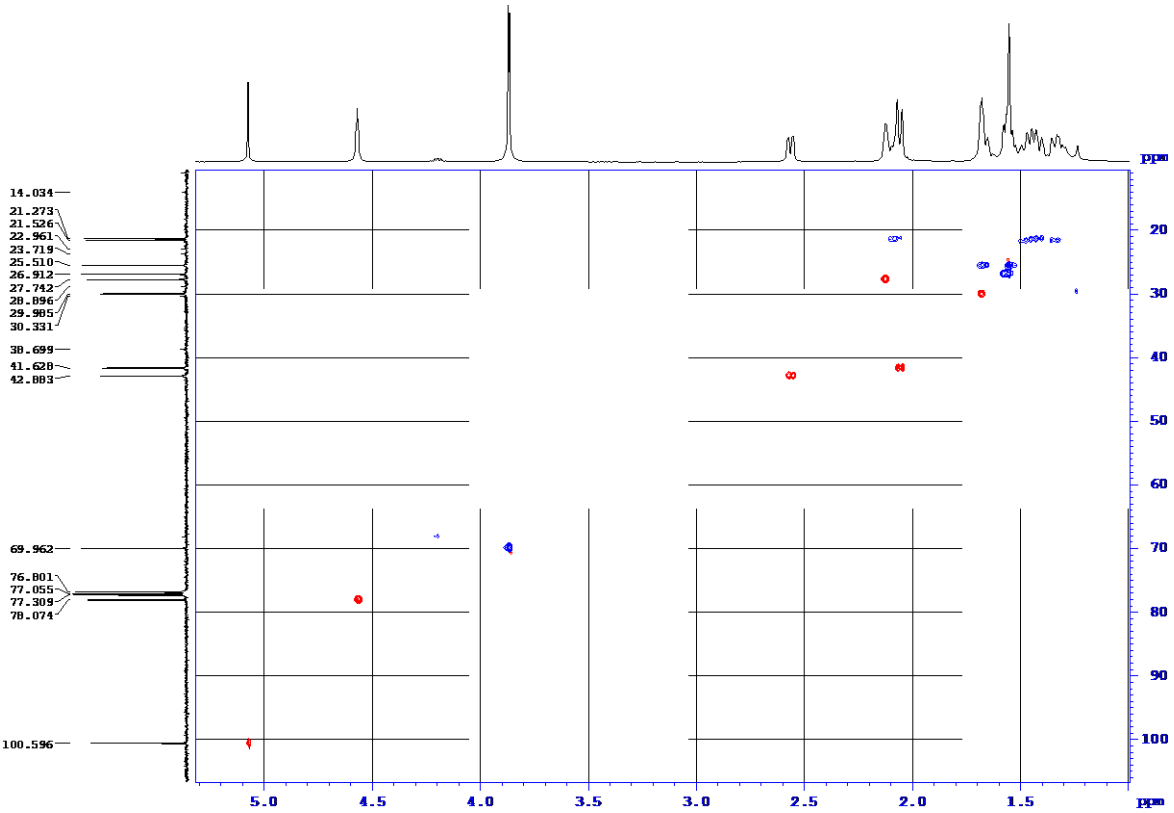


Figure S8.4. {^{1}H,^{13}C} HSQCED NMR spectrum of **8** in $CDCl_3$.

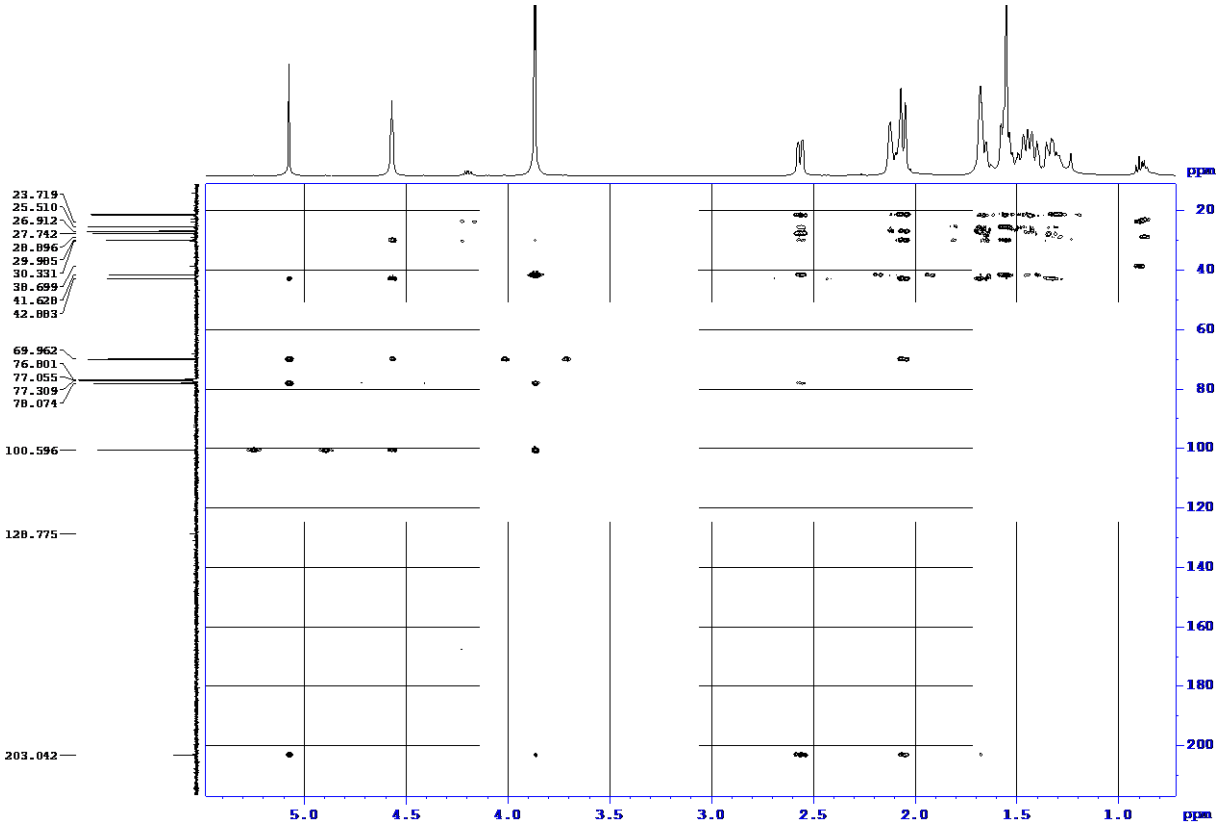


Figure S8.5. {^{1}H,^{13}C} HMBC NMR spectrum of **8** in $CDCl_3$.

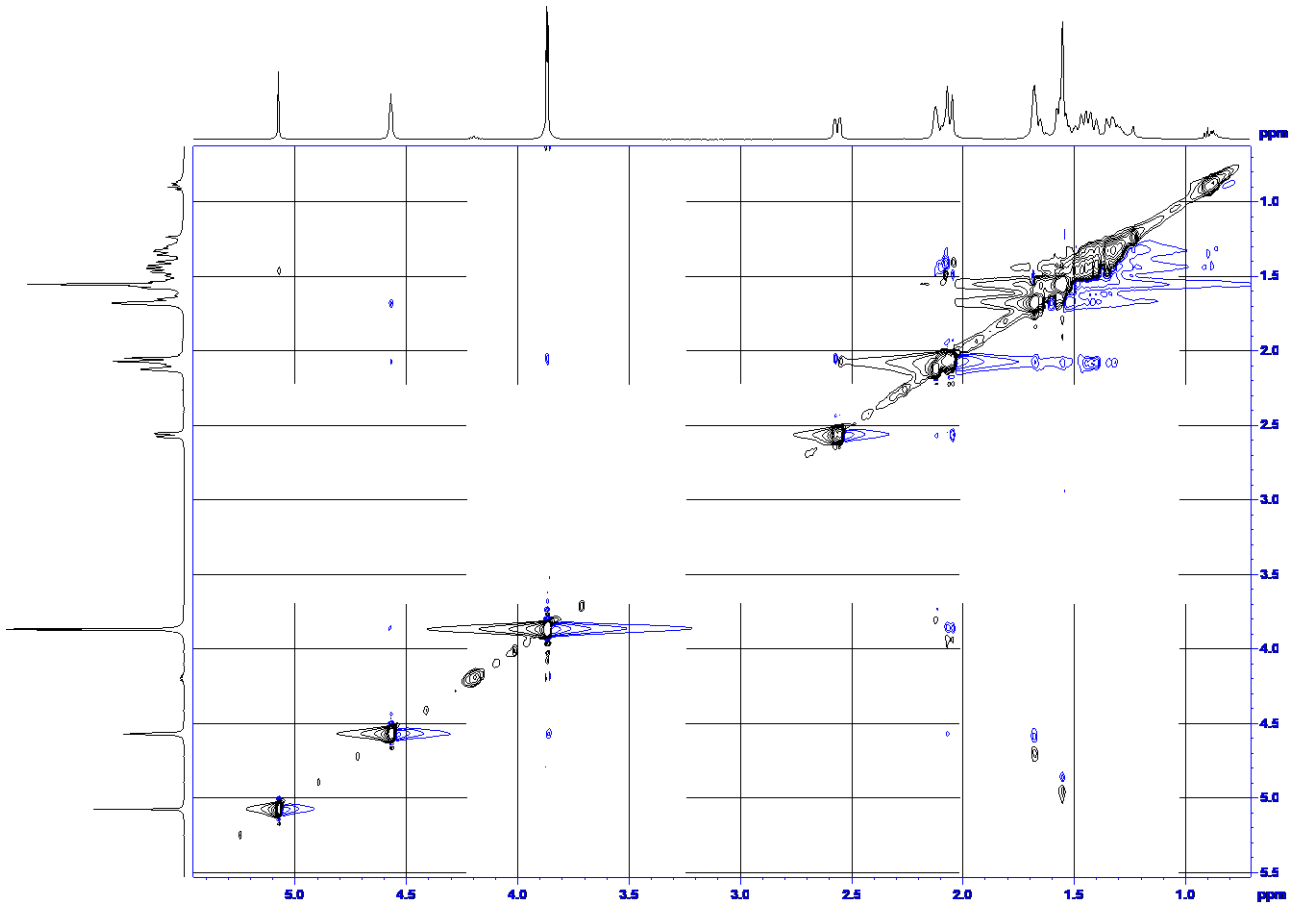
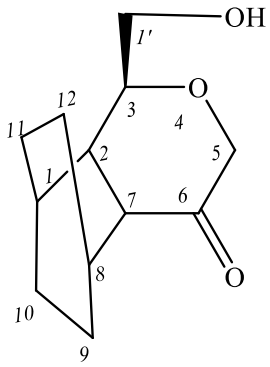


Figure S8.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of **8** in $CDCl_3$

(2*S*,3*S*,7*R*)-3-Hydroxymethyl-4-oxatricyclo[6.2.2.0^{2,7}]dodecan-6-one (9)



From 0.245 g (1.25 mmol) of compound **8**, general procedure, the product yield was 0.02 g (10%). (EtOAc – petroleum ether 1:1, R_f 0.2). $[\alpha]_D^{20}$ -99° (*c* 1.0, $CHCl_3$). Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ.: 1.36-1.66 m (9H, H^{1}, H^{9A}, H^{9B}, H^{10A}, H^{10B}, H^{11A}, H^{11B}, H^{12A}, H^{12B}), 2.17-2.20 m (1H, H^{8}), 2.36 t (1H, H^{2}, $^3J_{2,1}$ 11.6, $^3J_{2,7}$ 11.6 Hz), 2.57 dd (1H, H^{7}, $^3J_{7,2}$ 11.6, $^3J_{7,8}$ 2.3 Hz), 3.50-3.56 m (1H, H^{3}), 3.60 dd (1H, H$^{1'B}$, $^2J_{1'B,1'A}$ 11.7, $^3J_{1'B,3}$ 7.0 Hz), 3.78 dd (1H, H$^{1'A}$, $^2J_{1'A,1'B}$ 11.7, $^3J_{1'A,3}$ 2.4 Hz), 4.00 d (1H, H^{5B}, $^2J_{5B,5A}$ 18.3 Hz), 4.32 d (1H, H^{5A}, $^2J_{5A,5B}$ 18.3 Hz). ^{13}C NMR (500 MHz, $CDCl_3$): δ 20.45 (C^{11}), 21.32 (C^{12}), 25.20 (C^{8}), 25.21 (C^{1}), 25.44 (C^{9}), 26.20 (C^{10}), 38.08 (C^{2}), 46.77 (C^{7}), 64.58 (C$^{1'}$), 74.78 (C^{5}), 78.51 (C^{3}), 212.19 (C^{6}). Mass spectrum, *m/z*: 211 [*M*H]+. Found, %: C 68. 50, H 8.59. $C_{12}H_{18}O_3$. Calculation, %: C 68.54, H 8.63.

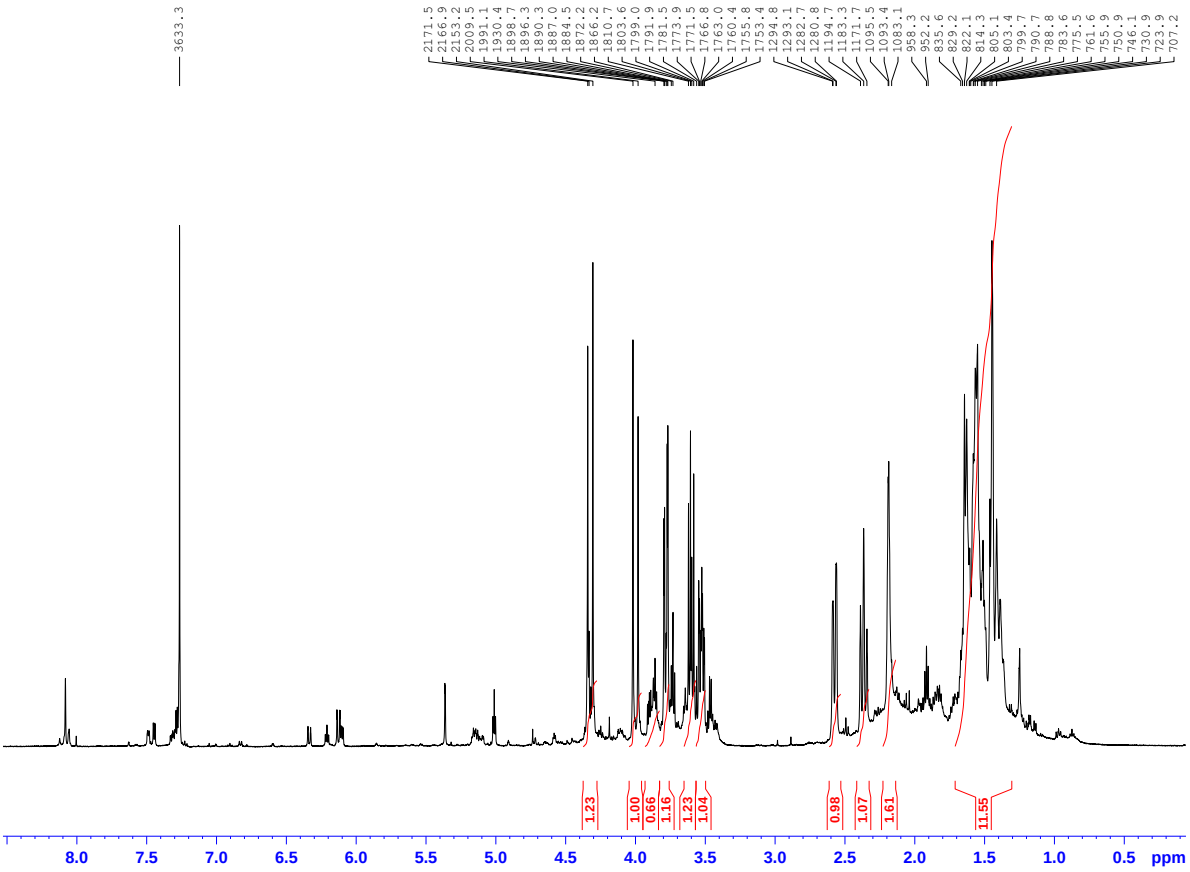


Figure S9.1. Complete ^{1}H NMR (500 MHz) spectrum of **9** in $CDCl_3$.

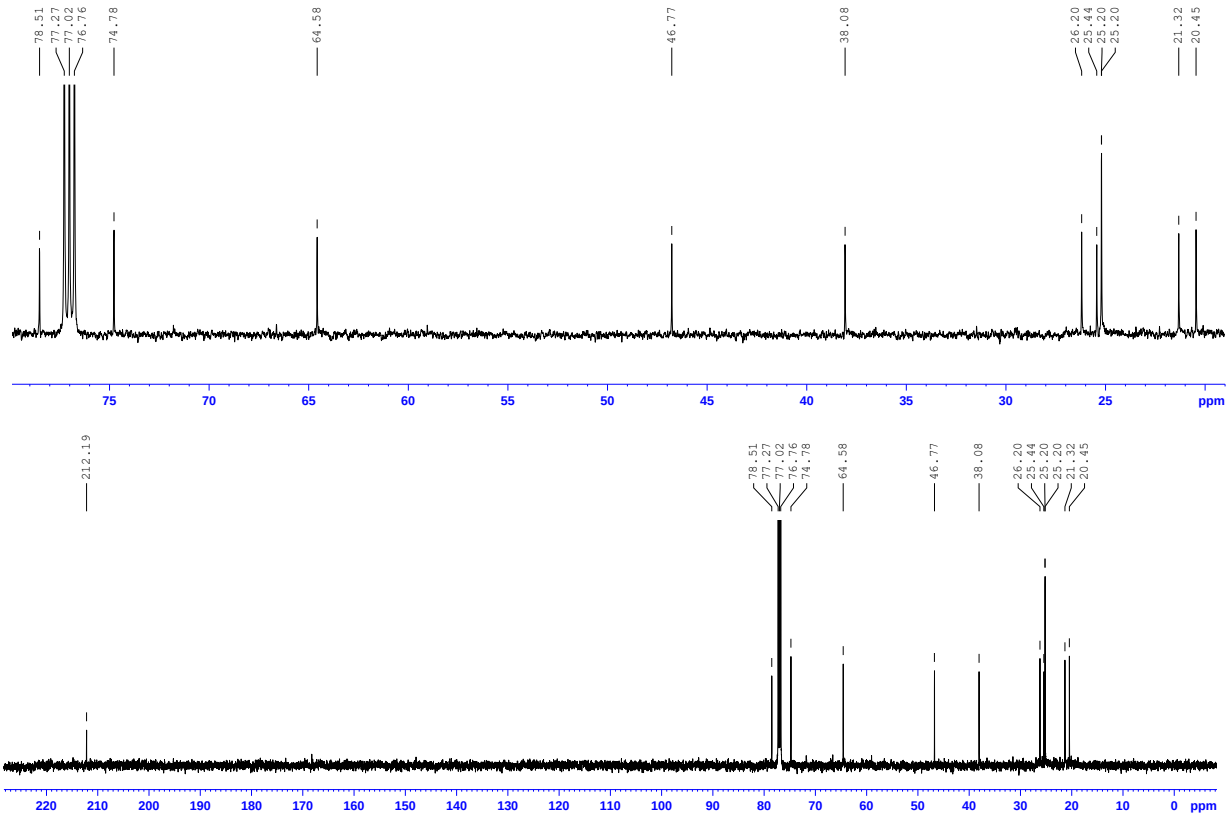


Figure S9.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of **9** in $CDCl_3$.

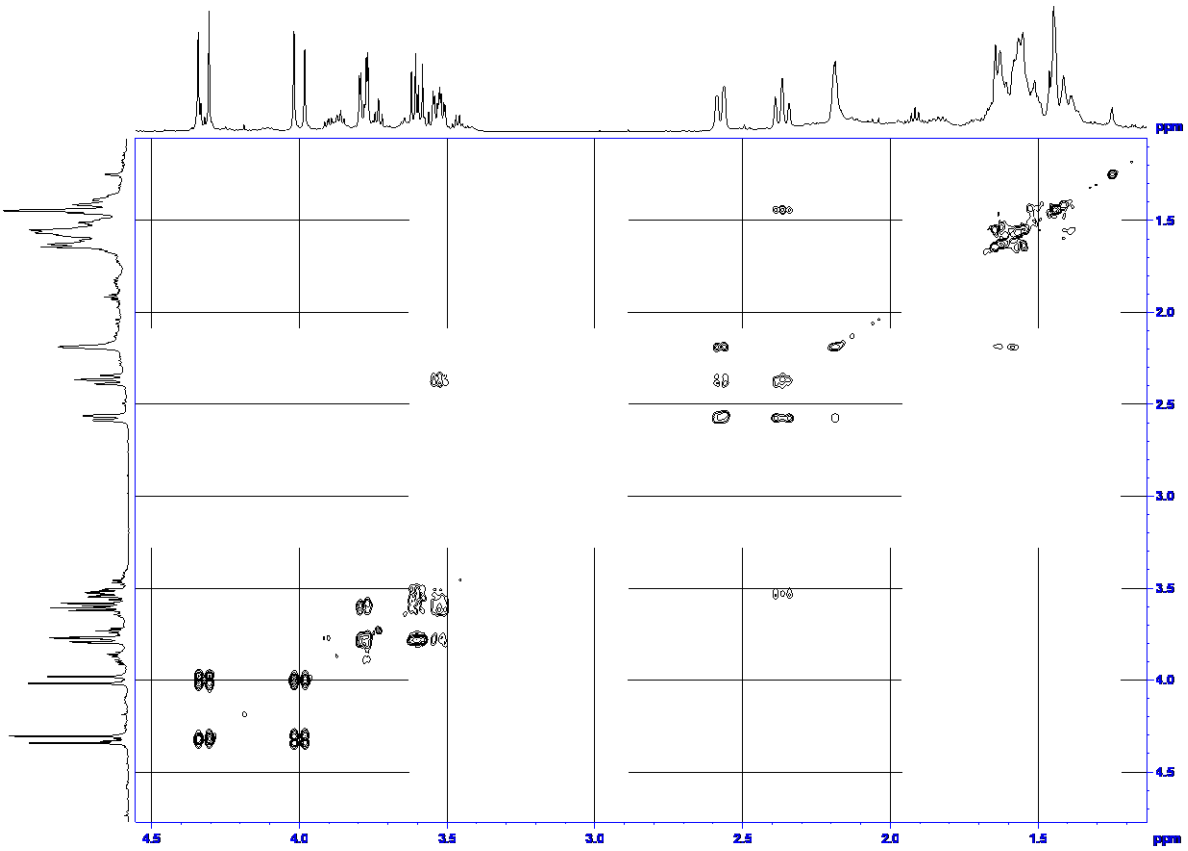


Figure S9.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of **9** in $CDCl_3$

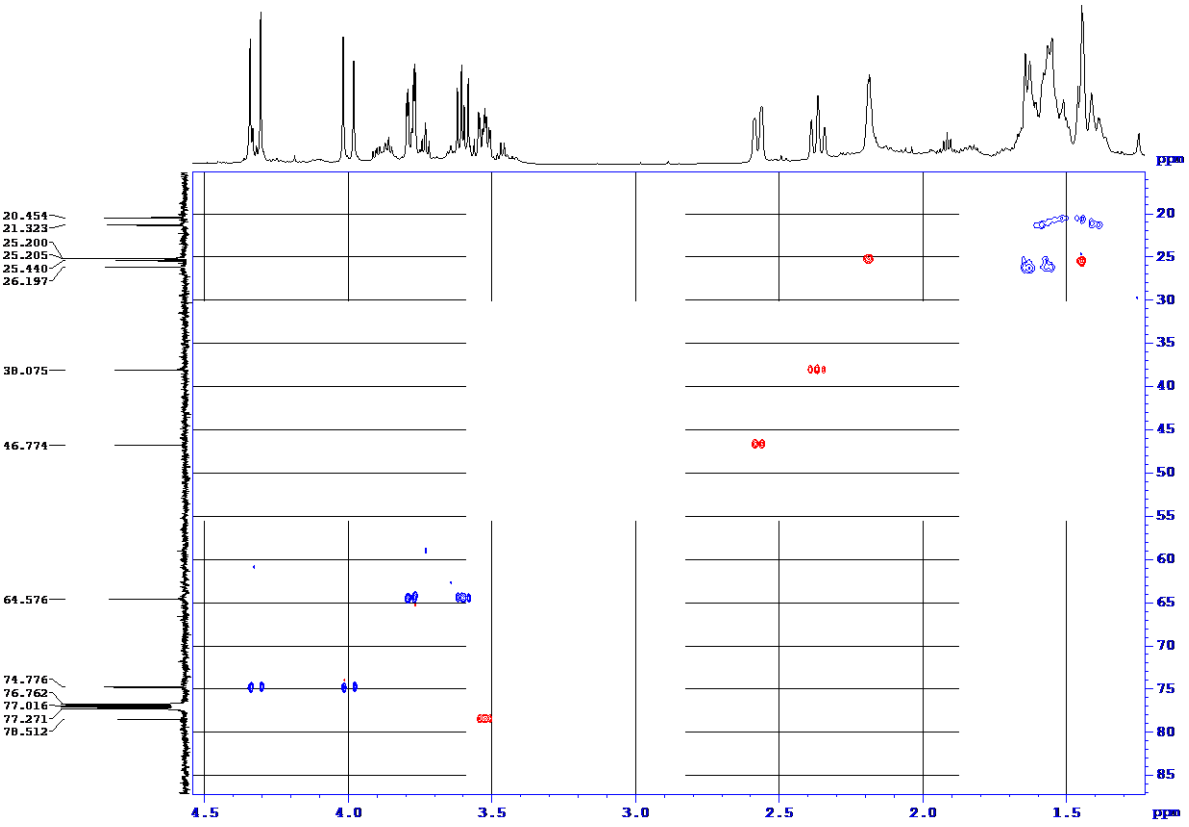


Figure S9.4. {^{1}H,^{13}C} HSQCED NMR spectrum of **9** in $CDCl_3$.

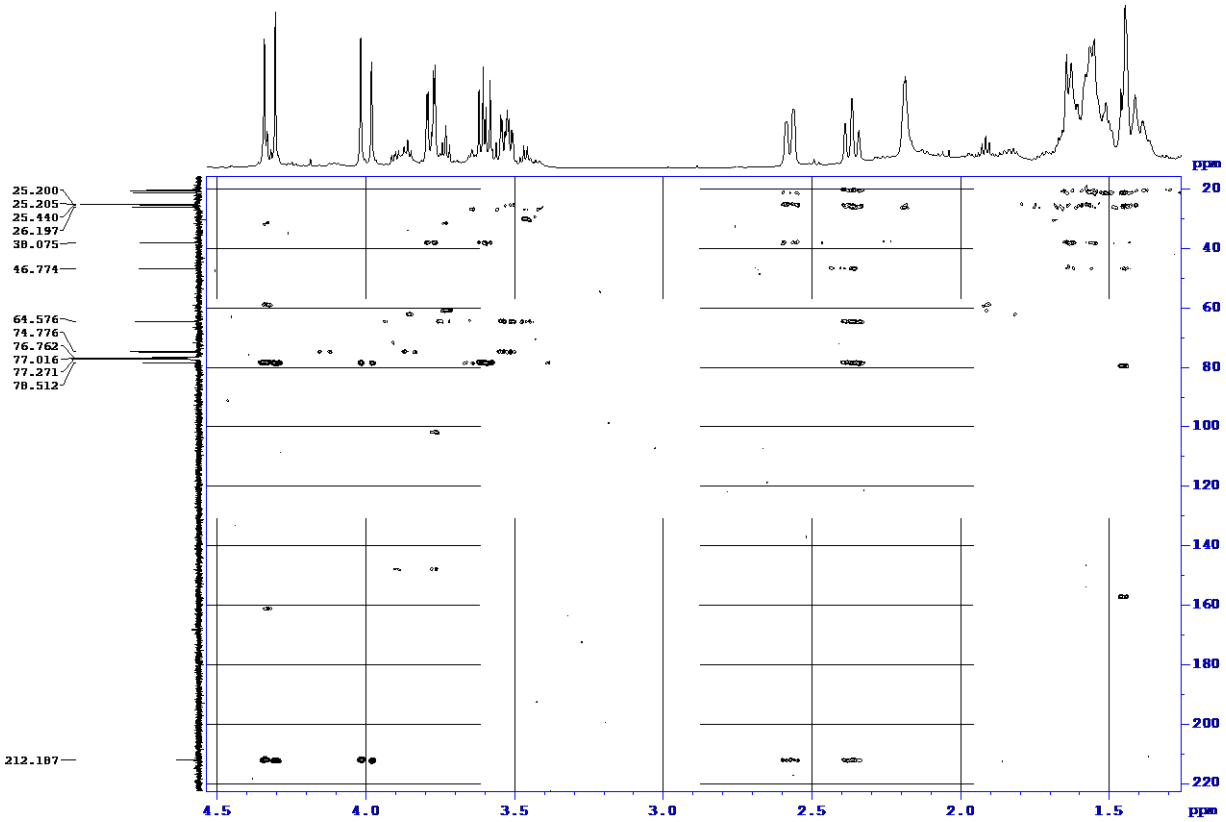


Figure S9.5. {^{1}H,^{13}C} HMBC NMR spectrum of **9** in $CDCl_3$.

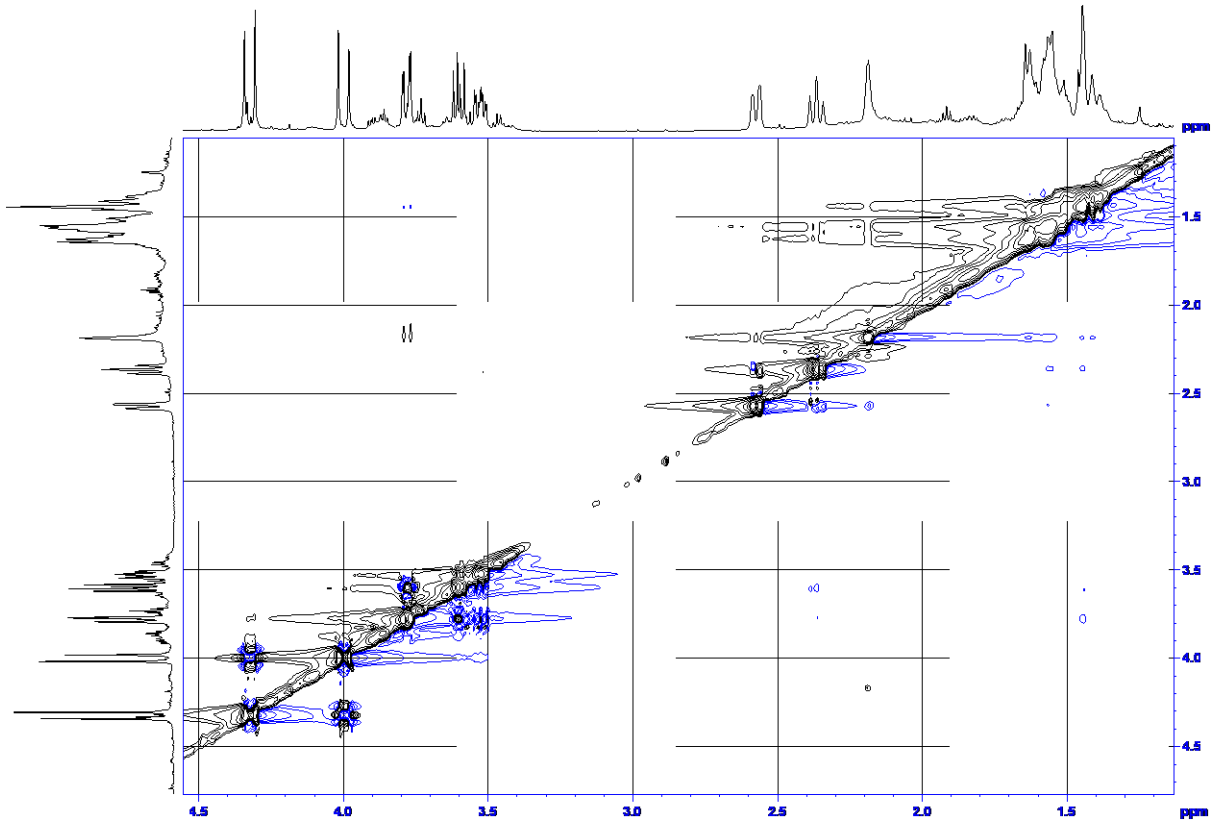
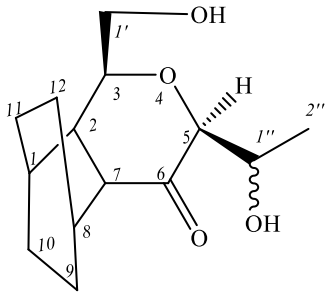


Figure S9.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of **9** in $CDCl_3$

(2*S*,3*S*,5*S*,7*R*)-5-(1-Hydroxyethyl)-3-hydroxymethyl-4-oxatricyclo[6.2.2.0^{2,7}]dodecan-6-one (10).



From 0.245 g (1.25 mmol) of compound **8**, the product yield was 0.045 g (20%), a 1"*R*/1"*S* diastereomer mixture in the ratio 2:1 (EtOAc – petroleum ether 2:1, R_f 0.1). Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30 [1.20] d (3H, H$^{2''}$, $^3J_{2'',1''}$ 6.5 Hz), 1.33-1.62 [1.34-1.63] m (9H, H^{1}, H^{9A}, H^{9B}, H^{10A}, H^{10B}, H^{11A}, H^{11B}, H^{12A}, H^{12B}), 2.11-2.15 [2.12-2.16] m (1H, H^{8}), 2.37 [2.46] t (1H, H^{2}, $^3J_{2,1}$ 11.6, $^3J_{2,7}$ 11.6 Hz), 2.54 [2.49] dd (1H, H^{7}, $^3J_{7,2}$ 11.6, $^3J_{7,8}$ 2.3 Hz), 3.54-3.58 [3.55-3.59] m (1H, H^{3}), 3.63 [3.61] т (1H, H$^{1'B}$, $^2J_{1'B,1'A}$ 11.8, $^3J_{1'B,3}$ 11.8 Hz), 3.79 [3.76] dd (1H, H$^{1'A}$, $^2J_{1'A,1'B}$ 11.8, $^3J_{1'A,3}$ 1.9 Hz), 3.81 [3.92] d (1H, H^{5}, $^3J_{5,1''}$ 3.8 Hz), 4.07-4.11 [4.09-4.15] m (1H, H$^{1''}$). ^{13}C NMR (500 MHz, $CDCl_3$): δ 19.67 [17.61] (C$^{2''}$), 20.43 [20.44] (C^{11}), 21.20 [21.24] (C^{12}), 24.78 [24.59] (C^{9}), 25.12 [25.13] (C^{8}), 25.38 [25.43] (C^{1}), 26.08 [26.09] (C^{10}), 38.83 [38.47] (C^{2}), 47.71 [47.82] (C^{7}), 64.29 [64.03] (C$^{1'}$), 68.82 [68.58] (C^{1}), 77.77 [77.45] (C^{3}), 87.07 [87.19] (C^{5}), 213.03 [213.61] (C^{6}). Mass spectrum, *m/z*: 255 [*M*H]+. Found, %: C 66. 09, H 8.69. $C_{14}H_{22}O_4$. Calculation,%: C 66.12, H 8.72. IR: 3397, 2933, 2868, 1710, 1458, 1076, 908, 734 cm^{-1}.

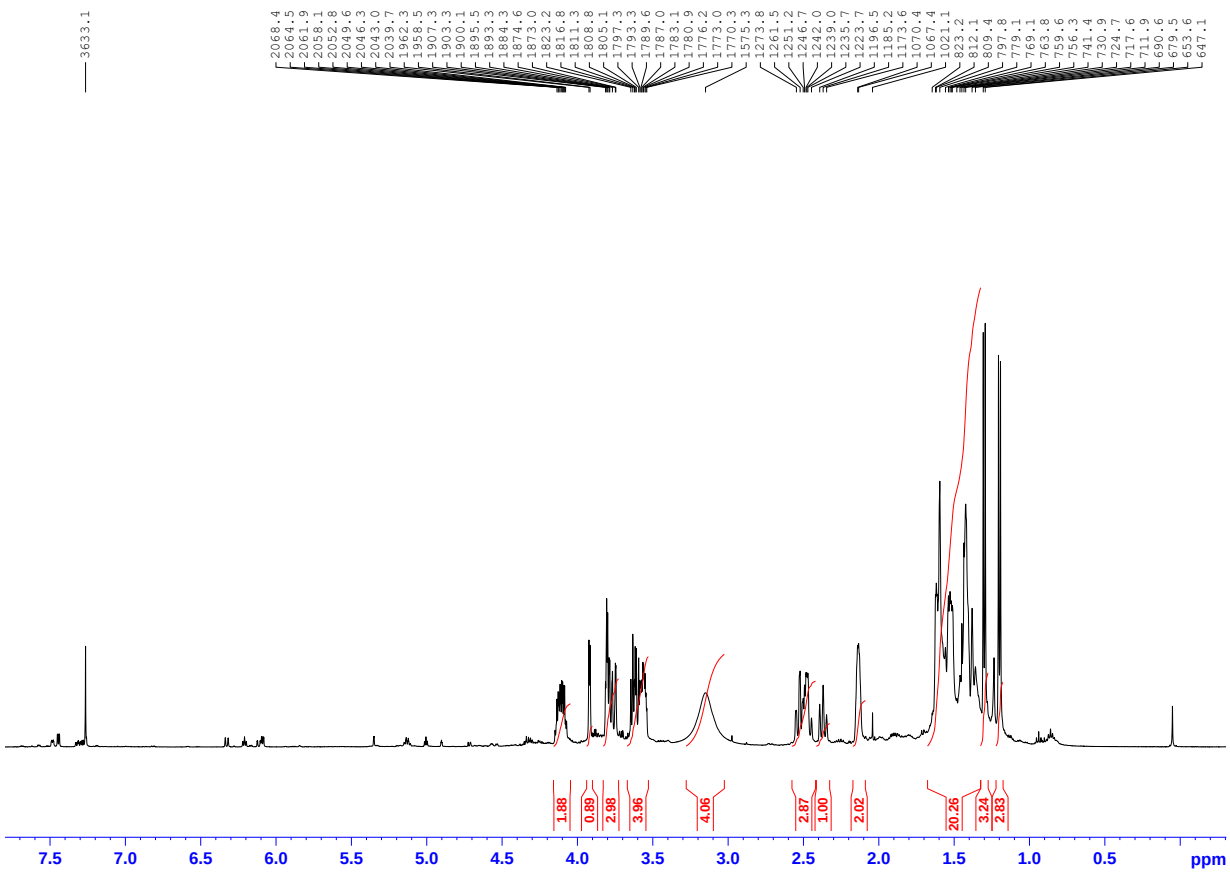


Figure S10.1. Complete ^{1}H NMR (500 MHz) spectrum of **10** in $CDCl_3$.

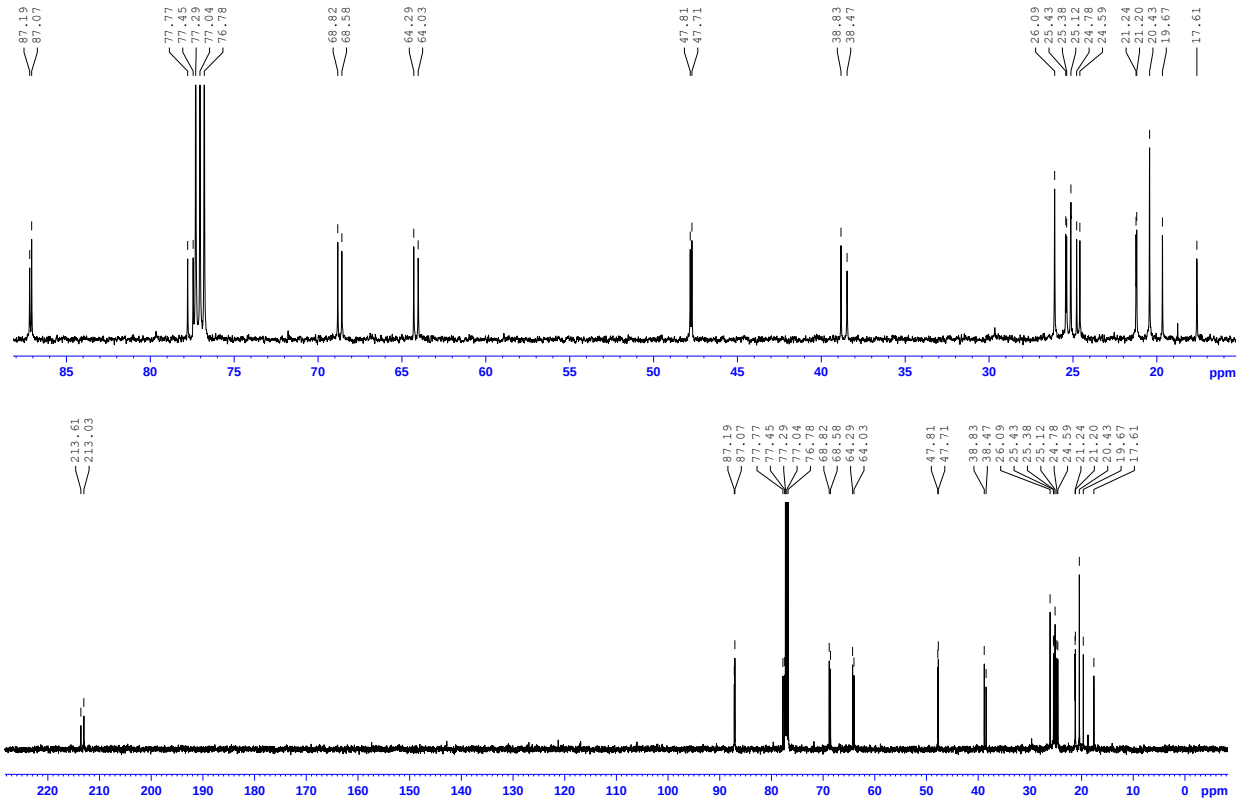


Figure S10.2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of **10** in $CDCl_3$.

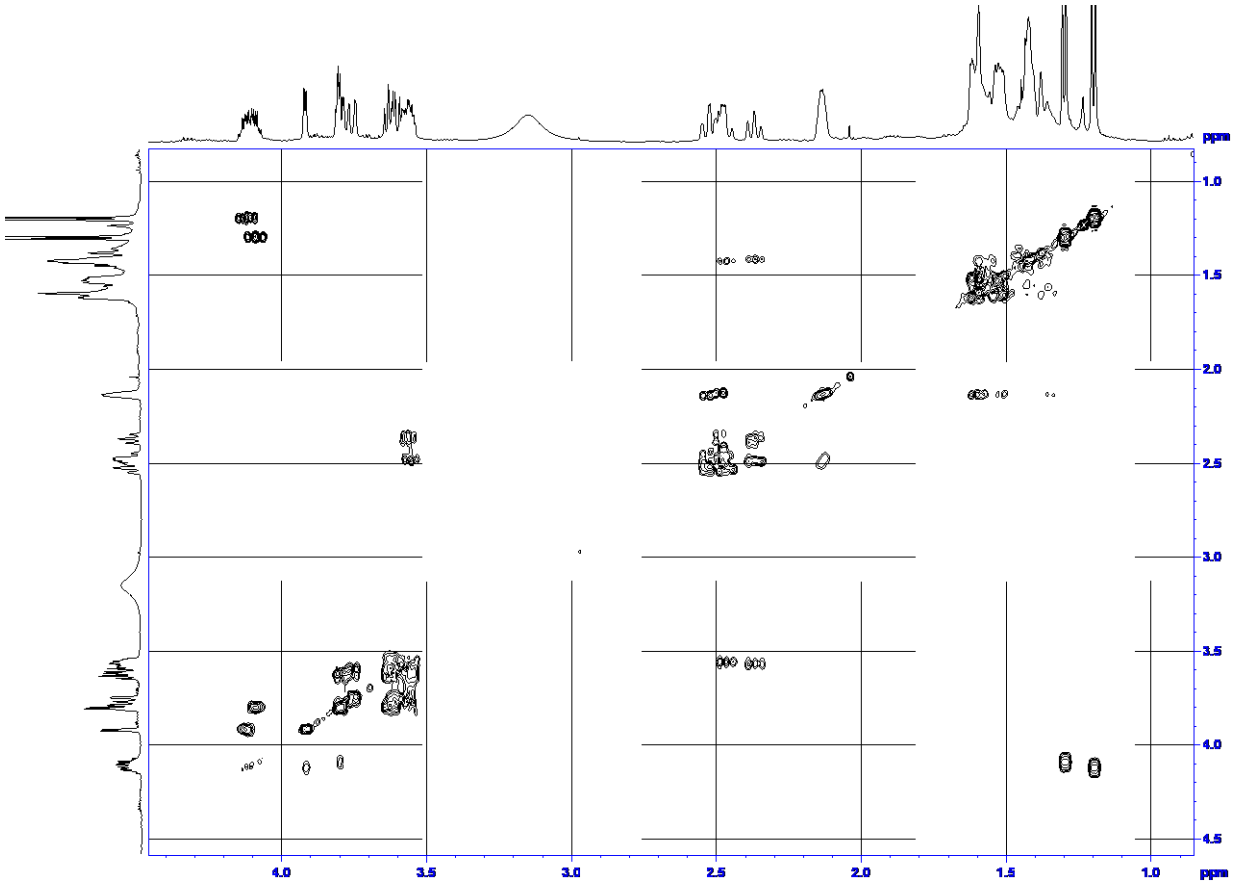


Figure S10.3. Complete {^{1}H,^{1}H} COSY NMR spectrum of **10** in $CDCl_3$

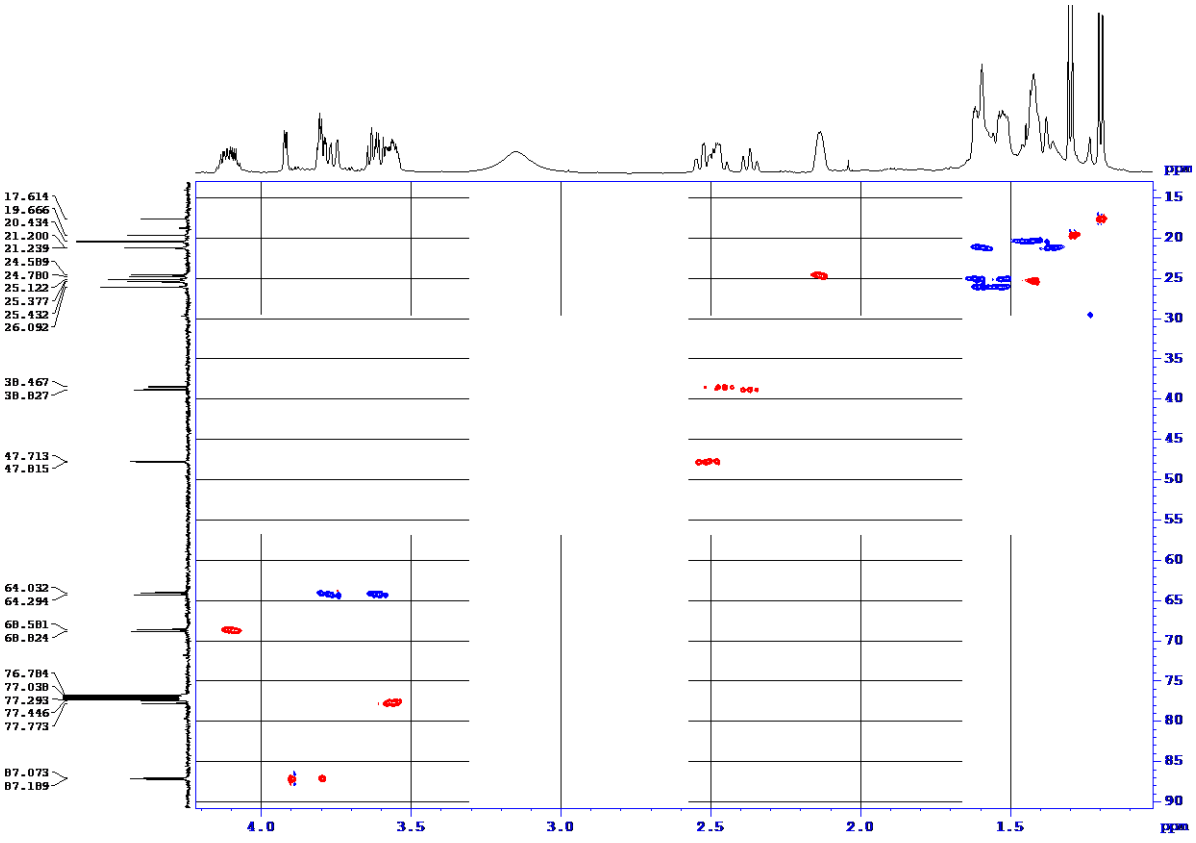


Figure S10.4. {^{1}H,^{13}C} HSQCED NMR spectrum of **10** in $CDCl_3$.

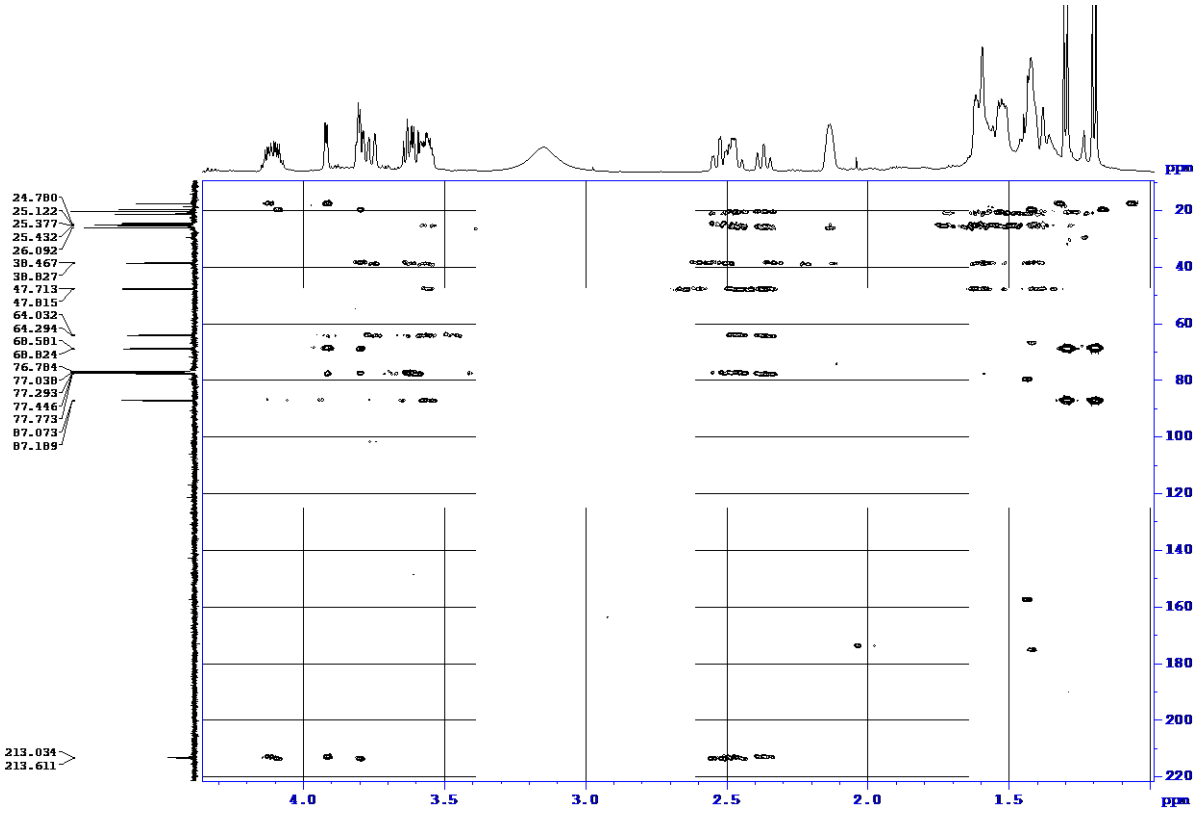


Figure S10.5. {^{1}H,^{13}C} HMBC NMR spectrum of **10** in $CDCl_3$.

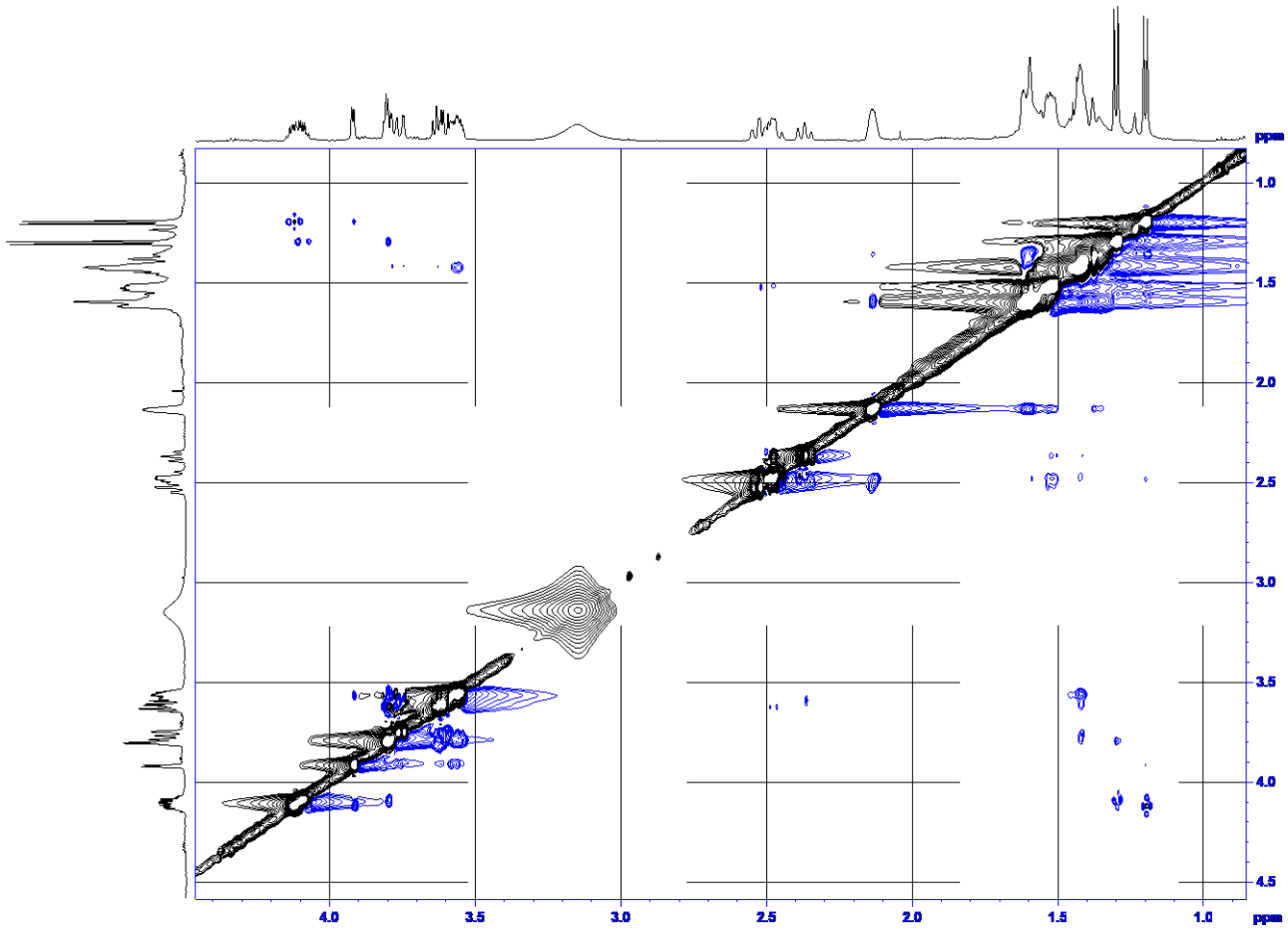
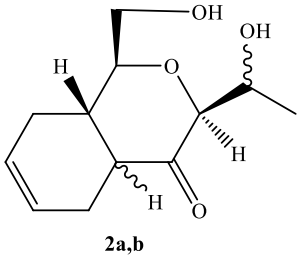


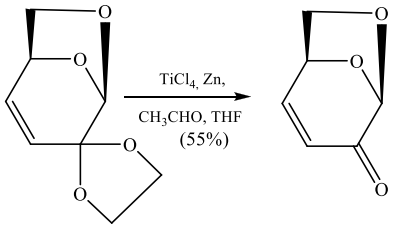
Figure S10.6. Complete {^{1}H,^{1}H} NOESY NMR spectrum of **10** in $CDCl_3$



2a,b

Figure S11 Diastereomeric mixture **2a,b**, products of the addition of acetaldehyde to the Diels-Alder adduct of levoglucosenone and 1,3-butadiene

The reaction of the dioxolane derivative of levoglucosenone resulted only in deprotection. Unfortunately, opening of the 1,6-anhydro bridge to give an intermediate semiketal did not occur.



Scheme S1