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Tandem [4+2]/[4+2] cycloaddition of bis-furyl dienes with fumaric and maleic esters at ultra-high pressure

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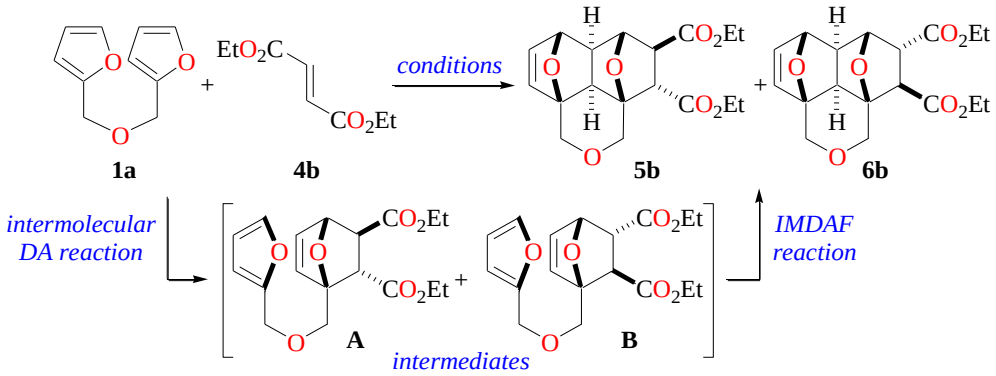


Scheme S1

1. Experimental section

Starting reagents were purchased from commercial sources and were used without any additional purification. The routine ^{1}H and ^{13}C NMR spectra were acquired on JEOL JNM-ECA 600 or Bruker Avance NEO 700 spectrometers with operating frequencies of 600/700 and 150/175 MHz for ^{1}H and ^{13}C, respectively) at r.t. and referenced to the residual signals of $CDCl_3$. Chemical shifts are reported in parts per million (δ/ppm) referenced to an internal solvent signal. Coupling constants are reported in Hertz (*J*/Hz). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; dd, doublet of doublets; ddd, doublet of doublet of doublets; tt, triplet of triplets, and br s, broad singlet. Infrared spectra were measured on an Infralum FT-801 FTIR instrument. The wavelengths are reported in reciprocal centimeters (ν_{max}/cm^{-1}). HRMS spectra were recorded on a tandem quadrupole time-of-flight (QTOF) accurate mass detector (Agilent 6545 Q-TOF LC/MS; Agilent Technologies, USA). Melting points were determined on SMP 10 or 30 apparatus and not corrected. Solvents were distilled and dried according to standard procedures, silica gel 5−40 μ was used for filtration. Microanalyses were performed for C, H, N and S on an Eurovector EA 3000 (CHNS) elemental analysis system and were within ±0.4 % of theoretical values (the data were obtained in Center for Collective Use of RUDN University − CCUPCMR PFUR).

Synthesis

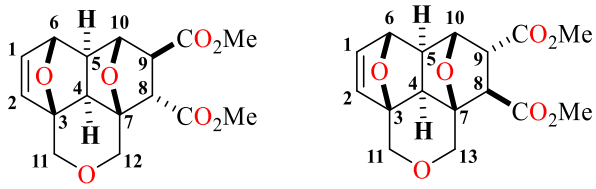
*General procedure for preparation **5a−p**, **6a−p**, **7a**,**b** and **8a**,**b***

Regularly, a solution of diene **1** (4.5 mmol) and corresponding dienophile **4** (4.95 mmol, 1.1 equiv) in methanol (21 mL) was transferred in a polytetrafluoroethylene (PTFE) vial and then held at 15 kbar and at temperature indicated in Table 2 for two days in a piston-cylinder type steel pressure chamber. For the reactions between **1a**+**4a**, **1b**+**4b**, **1b**+**4e** and all cases with sulfone bis-furan **1c**, $MeOH/CH_2Cl_2$ (1:1) mixtures as solvents and heating to 40-45 °C were applied.

The resulting mixture was concentrated *in vacuo* and treated with hexane (~ 10 mL). The resulting light-yellow solid was purified by column chromatography on silica gel using a mixture of $CHCl_3$/MeOH (10:1) as an eluent. Purified fractions were concentrated *in vacuo* and dried under reduced pressure in a vacuum desiccator to constant weight, yielding the target products as white powders.

NOTE. The atom numbering in the structures below does not correspond to the systematic one and is given for assignment in the NMR spectra.

5a+6a



White powder, yield 0.64 g (40%). R_f = 0.41, "Sorbfil" plates, eluent $CHCl_3$. M. p. 152−154 °C. Anal. calcd for $C_{16}H_{18}O_7$: C, 59.62%; H, 5.63%; O, 34.75%. found: C, 59.58%; H, 5.65%; O, 34.77%. IR νmax/cm^{-1} (tablet KBr): 3089, 3052, 3003, 2950, 2950, 2903, 2857, 1737, 1438, 1338, 1309, 1294, 1214, 1078, 988, 920, 827, 700, 586. HRMS (ESI-TOF): calculated for $C_{16}H_{19}O_7$ [M + H]: 323.1130, found: 323.1132 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

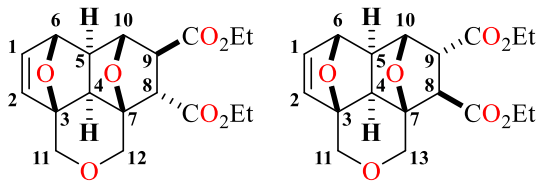
Dimethyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate (**5a**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.39 (d, J = 5.8 Hz, 1H, 1-H overlap **5a** and **6a**), 6.19 (d, J = 5.8 Hz, 1H, 2-H overlap **5a** and **6a**), 5.01 (s, 1H, 6-H overlap **5a** and **6a**), 4.84 (s, 1H, 10-H overlap **5a** and **5a**), 4.37 (d, J = 12.8 Hz, 1H, 11A-H overlap **5a** and **6a**), 4.25 (d, J = 12.9 Hz, 1H, 12A-H), 4.01 (d, J = 12.9 Hz, 1H, 12B-H), 3.91 (d, J = 12.8 Hz, 1H, 11B-H overlap **5a** and **6a**), 3.73 (d, J = 6.3 Hz, 6H, 2CH_3), 3.20 (d, J = 5.3 Hz, 1H, 8-H), 3.13 (d, J = 5.3 Hz, 1H, 9-H), 2.12 (d, J = 6.3 Hz, 1H, 5-H), 1.75 (d, J = 6.3 Hz, 1H, 4-H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 172.1, 170.9, 138.1, 136.6, 84.1, 82.7, 82.1, 81.6, 66.6, 66.3, 53.1, 52.7, 52.6, 52.5, 49.9, 43.2 ppm.

Dimethyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate (**6a**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.40 (d, J = 5.9 Hz, 1H, 1-H overlap **5a** and **6a**), 6.18 (d, J = 5.9 Hz, 1H, 2-H overlap **5a** and **6a**), 5.01 (s, 1H, 6-H overlap **5a** and **6a**), 4.85 (s, 1H, 10-H overlap **5a** and **6a**), 4.38 (d, J = 12.8 Hz, 1H, 11A-H overlap **5a** and **6a**), 4.06 (d, J = 12.9 Hz, 1H, 13A-H), 3.95 (d, J = 12.9 Hz, 1H, 13B-H overlap with 8-H), 3.93 (s, 1H, 9-H), 3.91 (d, J = 12.8 Hz, 1H, 11B-H overlap **5a** and **6a**), 3.70 (d, J = 7.8 Hz, 6H, 2CH_3), 3.01 (d, J = 4.9 Hz, 1H, 8-H), 1.94 (d, J = 6.4 Hz, 1H, 5-H), 1.79 (d, J = 6.4 Hz, 1H, 4-H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.2, 170.7, 138.4, 136.2, 84.2, 83.6, 81.6, 79.7, 66.3, 66.2, 52.4, 52.4, 52.3, 51.9, 47.9, 46.6 ppm.

5b+6b



White powder, yield 1.4 g (80%). R_f = 0.47, "Sorbfil" plates, eluent $CHCl_3$. M. p. 133−135 °C. Anal. calcd for $C_{18}H_{22}O_7$: C, 61.71%; H, 6.33%; O, 31.96%. found: C, 61.67%; H, 6.36%; O, 31.97%. IR νmax/cm^{-1} (tablet KBr): 3440, 2982, 2950, 2910, 2859, 1728, 1473, 1311, 1211, 1174, 1093, 1029, 973, 912, 856, 697. HRMS (ESI-TOF): calculated for $C_{18}H_{23}O_7$ [M + H] 351.1443; found 351.1440 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

Diethyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate (**5b**)

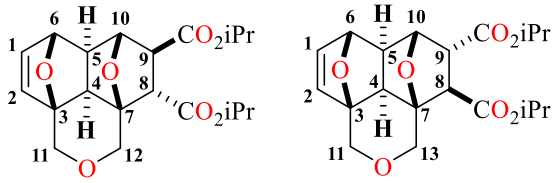
^{1}H NMR (700 MHz, $CDCl_3$) δ 6.38 (d, J = 5.7 Hz, 1H, 1-H overlap **5b** and **6b**), 6.19 (d, J = 5.7 Hz, 1H, 2-H overlap **5b** and **6b**), 5.01 (s, 1H, 6-H overlap **5b** and **6b**), 4.82 (s, 1H, 10-H overlap **5b** and **6b**), 4.36 (d,

J = 12.7 Hz, 1H, 11A-H overlap **5b** and **6b**), 4.25 (d, J = 12.9 Hz, 1H, 12A-H), 4.21 – 4.12 (m, 4H, $2CH_2$, overlap **5b** and **6b**), 4.01 (d, J = 12.9 Hz, 1H, 12B-H), 3.88 (d, J = 12.7 Hz, 1H, 11B-H), 3.18 (d, J = 5.2 Hz, 1H, 8-H), 3.10 (d, J = 5.2 Hz, 1H, 9-H), 2.12 (d, J = 6.4 Hz, 1H, 5-H), 1.74 (d, J = 6.4 Hz, 1H, 4-H), 1.26 (q, J = 14.4, 7.1 Hz, 6H, $2CH_3$) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.7, 170.5, 138.0, 136.6, 84.0, 82.6, 82.2, 81.6, 66.7, 66.3, 61.5, 61.4, 53.1, 52.7, 49.9, 43.1, 14.3, 14.2 ppm.

Diethyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate (**6b**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.39 (d, J = 5.6 Hz, 1H, 1-H overlap **5b** and **6b**), 6.18 (d, J = 7.2 Hz, 1H, 2-H overlap **5b** and **6b**), 5.00 (s, 1H, 6-H overlap **5b** and **6b**), 4.83 (d, J = 5.8 Hz, 1H, 10-H overlap **5b** and **6b**), 4.37 (d, J = 12.7 Hz, 1H, 11A-H overlap **5b** and **6b**), 4.21 – 4.13 (m, 4H, $2CH_2$, overlap **5b** and **6b**), 4.07 (d, J = 13.2 Hz, 1H, 13A-H), 3.95 (d, J = 8.2 Hz, 1H, 13B-H), 3.93 (d, J = 8.7 Hz, 1H, 11B-H), 3.71 (d, J = 5.2 Hz, 1H, 9-H), 2.98 (d, J = 4.9 Hz, 1H, 8-H), 1.94 (d, J = 6.4 Hz, 1H, 5-H), 1.79 (d, J = 6.4 Hz, 1H, 4-H), 1.26 (q, J = 14.4, 7.1 Hz, 6H, $2CH_3$) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.8, 170.3, 138.4, 136.2, 84.1, 83.5, 81.6, 79.7, 66.3, 66.2, 61.5, 61.3, 52.4, 51.9, 47.8, 46.6, 14.3, 14.2 ppm.

5c+6c



White powder, yield 1.46 g (78%). R_f = 0.46, "Sorbfil" plates, eluent $CHCl_3$. M. p. 131−133 °C. Anal. calcd for $C_{20}H_{26}O_7$: C, 63.48%; H, 6.93%; O, 29.59%. found: C, 63.42%; H, 6.97%; O, 29.61%. IR νmax/cm^{-1} (tablet KBr): 3049, 3013, 2982, 2860, 1725, 1374, 1308, 1197, 1108, 973, 915, 847, 702. HRMS (ESI-TOF): calculated for $C_{20}H_{27}O_7$ [M + H]: 379.1756, found: 379.1752 $[M + H]^+$.

Some ^{1}H and ^{13}C signals might overlap

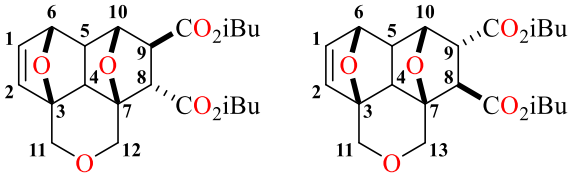
Diisopropyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate (**5c**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.39 (d, J = 5.7 Hz, 1H, 1-H overlap **5c** and **6c**), 6.19 (d, J = 5.7 Hz, 1H, 2-H overlap **5c** and **6c**), 5.05 – 4.98 (m, 3H, 6-H and 2CH from 2*i*Pr, overlap **5c** and **6c**), 4.80 (s, 1H, 10-H), 4.37 (d, J = 12.8 Hz, 1H, 11A-H, overlap **5c** and **6c**), 4.26 (d, J = 12.9 Hz, 1H, 12A-H), 4.00 (d, J = 12.9 Hz, 1H, 12B-H), 3.86 (d, J = 12.8 Hz, 1H, 11B-H), 3.16 (d, J = 5.1 Hz, 1H, 8-H), 3.08 (d, J = 5.1 Hz, 1H, 9-H), 2.12 (d, J = 6.4 Hz, 1H, 5-H), 1.73 (d, J = 6.4 Hz, 1H, 4-H), 1.29 – 1.19 (m, 12H, $4CH_3$ from 2*i*Pr) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.3, 170.1, 138.1, 136.6, 84.1, 82.6, 82.4, 81.7, 69.1, 68.9, 66.8, 66.4, 53.2, 52.8, 49.8, 43.2, 22.0, 21.9 ppm.

Diisopropyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate (**6c**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.39 (d, J = 5.7 Hz, 1H, 1-H, overlap **5c** and **6c**), 6.18 (d, J = 5.7 Hz, 1H, 2-H overlap **5c** and **6c**), 5.05 – 4.97 (m, 3H, 6-H and 2CH from 2*i*Pr, overlap **5c** and **6c**), 4.82 (d, J = 5.8 Hz, 1H, 10-H), 4.38 (d, J = 12.6 Hz, 1H, 11A-H, overlap **5c** and **6c**), 4.09 (d, J = 13.1 Hz, 1H, 13A-H), 3.97 – 3.92 (m, 2H, 13B-H and 11B-H), 3.72 – 3.67 (m, 1H, 9-H), 2.95 (d, J = 4.9 Hz, 1H, 8-H), 1.94 (d, J = 6.4 Hz, 1H, 5-H), 1.79 (d, J = 6.4 Hz, 1H, 4-H), 1.29 – 1.19 (m, 12H, $4CH_3$ from 2*i*Pr) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.4, 169.8, 138.4, 136.3, 84.1, 83.6, 81.6, 79.7, 69.2, 68.9, 66.3, 66.2, 52.5, 52.0, 47.8, 46.5, 22.0, 21.9 ppm.

5d+6d



Light brown powder, yield 1.93 g (76%). R_f = 0.51, "Sorbfil" plates, eluent $CHCl_3$. M. p. 133−136 °C. Anal. calcd for $C_{22}H_{30}O_7$: C, 65.01%; H, 7.44%; O, 27.55%. found: C, 64.93%; H, 7.49%; O, 27.58%. IR νmax/cm^{-1} (tablet KBr): 3053, 3033, 2960, 2895, 1730, 1470, 1454, 1395, 1370, 1206, 1178, 1073, 985, 828, 699. HRMS (ESI-TOF): calculated for $C_{22}H_{31}O_7$ [M + H]: 407.2069, found: 407.2064 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

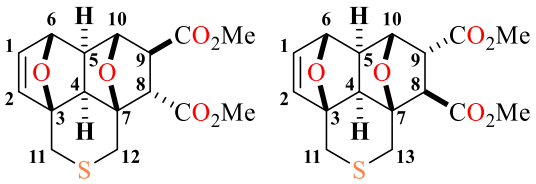
Diisobutyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate (**5d**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.40 (d, J = 5.3 Hz, 1H, 1-H, overlap **5d** and **6d**), 6.19 (d, J = 5.7 Hz, 1H, 2-H, overlap **5d** and **6d**), 5.04 (s, 1H, 6-H), 4.86 (d, J = 5.4 Hz, 1H, 10-H, overlap **5d** and **6d**), 4.56 (d, J = 12.9 Hz, 1H, 11A-H), 4.39 (d, J = 12.8 Hz, 1H, 12A-H overlap **5d** and **6d**), 4.28 (d, J = 12.8 Hz, 1H, 12B-H), 4.04 (d, J = 12.9 Hz, 1H, 11B-H), 4.00 – 3.80 (m, 4H, 2CH_2 from *i*Bu, overlap **5d** and **6d**), 3.22 (d, J = 5.1 Hz, 1H, 8-H), 3.15 (d, J = 5.1 Hz, 1H, 9-H), 2.14 (d, J = 6.4 Hz, 1H, 5-H), 1.96 – 1.88 (m, 2H, 2CH from iBu, overlap **5d** and **6d**), 1.78 (d, J = 6.4 Hz, 1H, 4-H), 0.99 – 0.80 (m, 12H, 4CH_3 from *i*Bu, overlap **5d** and **6d**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.8, 170.6, 138.1, 136.6, 84.1, 82.7, 82.2, 81.7, 71.9, 71.6, 66.7, 53.3, 52.9, 49.9, 43.2, 27.8, 27.7, 19.3, 19.1 ppm.

Diisobutyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate (**6d**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.40 (d, J = 5.3 Hz, 1H, 1-H, overlap **5d** and **6d**), 6.19 (d, J = 5.7 Hz, 1H, 2-H, overlap **5d** and **6d**), 5.01 (s, 1H, 6-H), 4.86 (d, J = 5.4 Hz, 1H, 10-H, overlap **5d** and **6d**), 4.39 (d, J = 12.7 Hz, 1H, 11A-H, overlap **5d** and **6d**), 4.10 (d, J = 13.1 Hz, 1H, 13A-H), 4.00 – 3.80 (m, 6H, 13B-H, 11B-H and 2CH_2 from *i*Bu, overlap **5d** and **6d**), 3.76 (t, J = 5.2 Hz, 1H, 9-H), 3.01 (d, J = 5.2 Hz, 1H, 8-H), 1.97 (d, J = 6.4 Hz, 1H, 5-H), 1.93 (m, 2H, 2CH from *i*Bu, overlap **5d** and **6d**), 1.81 (d, J = 6.4 Hz, 1H, 4-H), 0.99 – 0.80 (m, 12H, 4CH_3 from *i*Bu, overlap **5d** and **6d**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.9, 170.5, 138.4, 136.3, 84.2, 83.6, 81.6, 79.8, 71.8, 71.5, 66.4, 52.6, 52.1, 47.9, 46.6, 27.8, 27.7, 19.3, 19.2 ppm.

5e+6e



Yellow oil, yield 0.70 g (35%). R_f = 0.76, "Sorbfil" plates, eluent $CHCl_3$/MeOH (10:1). Anal. calcd for $C_{16}H_{18}O_6S$: C, 56.79%; H, 5.36%; O, 28.37%% S, 9.47%. found: C, 56.72%; H, 5.45%; O, 28.40%% S, 9.43%. IR νmax/cm^{-1} (tablet KBr): 2963, 1729, 1643, 1435, 1302, 1254, 1207, 1032, 977. HRMS (ESI-TOF): calculated for $C_{16}H_{19}O_6S$ [M + H]: 339.0902, found: 339.0900 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

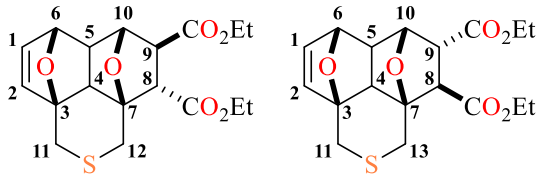
Dimethyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**5e**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.48 – 6.36 (m, 1H, 1-H overlap **5e** and **6e**), 6.16 – 6.08 (m, 1H, 2-H overlap **5e** and **6e**), 5.01 (s, 1H, 6-H, overlap **5e** and **6e**), 4.85 (s, 1H, 10-H overlap **5e** and **6e**), 3.75 – 3.63 (m, 6H, $2CH_3$ overlap **5e** and **6e**), 3.51 – 3.44 (m, 1H, 11A-H overlap **5e** and **6e**), 3.29 (d, J = 13.9 Hz, 1H, 12A-H), 3.04 (d, J = 4.9 Hz, 1H, 8-H), 3.00 (d, J = 4.9 Hz, 1H, 9-H), 2.88 (d, J = 13.9 Hz, 1H, 12B-H), 2.60 (d, J = 14.5 Hz, 1H, 11B-H), 2.14 (d, J = 6.4 Hz, 1H, 5-H), 1.60 (d, J = 6.4 Hz, 1H, 4-H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 172.1, 171.0, 138.9, 138.6, 83.7, 82.6, 81.8, 81.4, 56.4, 54.4, 52.7, 51.2, 49.4, 44.5, 29.4, 28.7 ppm.

Dimethyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**6e**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.48 – 6.36 (m, 1H, 1-H overlap **5e** and **6e**), 6.16 – 6.08 (m, 1H, 2-H overlap **5e** and **6e**), 5.01 (s, 1H, 6-H, overlap **5e** and **6e**), 4.85 (s, 1H, 10-H overlap **5e** and **6e**), 3.75 – 3.63 (m, 6H, $2CH_3$ overlap **5e** and **6e**), 3.51 – 3.44 (m, 1H, 9-H overlap **5e** and **6e**), 3.28 – 3.14 (m, 4H, 11A-H, 13A-H, 13B-H and 11B-H, overlap **5e** and **6e**), 2.94 (d, J = 5.7 Hz, 1H, 8-H), 2.01 (d, J = 6.4 Hz, 1H, 5-H), 1.69 (d, J = 6.4 Hz, 1H, 4-H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.3, 171.1, 138.8, 138.6, 83.7, 82.6, 81.8, 81.3, 79.3, 53.4, 53.1, 52.7, 49.4, 47.9, 28.6, 28.3 ppm.

5f+6f



Light brown oil, yield 0.87 g (70%). R_f = 0.69, "Sorbfil" plates, $CHCl_3$/MeOH (10:1). Anal. calcd for $C_{18}H_{22}O_6S$: C, 59.00%; H, 6.05%; O, 26.20%; S, 8.75% found: C, 58.96%; H, 6.11%; O, 26.23%; S, 8.70%. IR νmax/cm^{-1} (tablet KBr): 3165, 3066, 2977, 2925, 1727, 1633, 1469, 1370, 1324, 1296, 1253, 1185, 1032, 976, 845, 827, 739, 704, 592. HRMS (ESI-TOF): calculated for $C_{18}H_{23}O_6S$ [M + H]: 367.1215, found: 367.1210 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

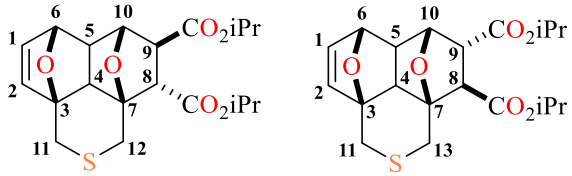
Diethyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**5f**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.43 – 6.41 (m, 1H, 1-H, overlap **5f** and **6f**), 6.12 (d, J = 5.6 Hz, 1H, 2-H, overlap **5f** and **6f**), 5.01 (s, 1H, 6-H, overlap **5f** and **6f**), 4.84 (s, 2H, 10-H, overlap **5f** and **6f**), 4.21 – 4.11 (m, 4H, $2CH_2$ from *i*Pr, overlap **5f** and **6f**), 3.47 (d, J = 14.6 Hz, 1H, 11A-H), 3.24 (d, J = 14.6 Hz, 1H, 12A-H), 3.19 (d, J = 4.9 Hz, 1H, 8-H), 3.14 (d, J = 4.9 Hz, 1H, 9-H), 3.02 (d, J = 14.6 Hz, 1H, 12B-H, overlap **5f** and **6f**), 2.89 (d, J = 14.6 Hz, 1H, 11B-H), 2.14 (d, J = 6.4 Hz, 1H, 5-H), 1.60 (d, J = 6.4 Hz, 1H, 4-H), 1.32 – 1.21 (m, 6H, $2CH_3$ from *i*Pr, overlap **5f** and **6f**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.7, 170.6, 138.8, 138.6, 83.6, 82.6, 81.9, 81.4, 61.5, 56.3, 53.4, 51.1, 44.5, 29.5, 28.7, 14.4, 14.3 ppm.

Diethyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**6f**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.44 – 6.41 (m, 1H, 1-H, overlap **5f** and **6f**), 6.12 (d, J = 5.6 Hz, 1H, 2-H, overlap **5f** and **6f**), 5.01 (s, 1H, 6-H, overlap **5f** and **6f**), 4.82 (d, J = 7.7 Hz, 1H, 10-H, overlap **5f** and **6f**), 4.22 – 4.09 (m, 4H, $2CH_2$ from *i*Pr, overlap **5f** and **6f**), 3.68 (t, J = 5.6 Hz, 1H, 9-H), 3.29 (d, J = 14.7 Hz, 1H, 11A-H), 3.24 (d, J = 14.4 Hz, 1H, 13A-H), 3.02 (d, J = 14.4 Hz, 1H, 13B-H), 2.91 (d, J = 5.6 Hz, 1H, 8-H), 2.62 (d, J = 14.7 Hz, 1H, 11B-H), 2.01 (d, J = 6.4 Hz, 1H, 5-H), 1.69 (d, J = 6.4 Hz, 1H, 4-H), 1.33 – 1.17 (m, 6H, $2CH_3$ from *i*Pr, overlap **5f** and **6f**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.9, 170.7, 138.9, 138.6, 83.7, 83.6, 81.3, 79.3, 61.4, 61.3, 54.4, 53.2, 49.4, 47.9, 31.0, 28.3, 14.4, 14.3 ppm.

5g+6g



White powder, yield 1.43 g (79%). R_f = 0.72, "Sorbfil" plates, eluent $CHCl_3$/MeOH (10:1). M. p. 135−137 °C. Anal. calcd for $C_{20}H_{26}O_6S$: C, 60.90%; H, 6.64%; O, 24.33%; S, 8.13%. found: C, 60.85%; H, 6.67%; O, 24.37%; S, 8.11%. IR νmax/cm^{-1} (tablet KBr): 3057, 2979, 2938, 2880, 1724, 1633, 1468, 1419, 1321, 1374, 1291, 1252, 1107, 1018, 972, 834, 738, 701, 686, 570. HRMS (ESI-TOF): calculated for $C_{20}H_{27}O_6S$ [M + H]: 395.1528, found: 395.1522 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

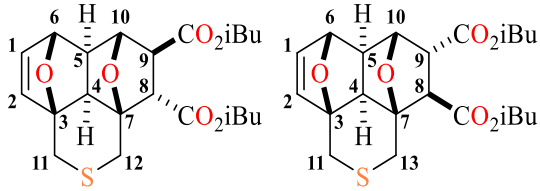
Diisopropyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**5g**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.43 (d, J = 5.6, 1H, 1-H overlap **5g** and **6g**), 6.12 (d, J = 5.6 Hz, 1H, 2-H overlap **5g** and **6g**), 5.05 – 4.98 (m, 3H, 6-H and 2CH from 2*i*Pr overlap **5g** and **6g**), 4.82 (s, 1H, 10-H), 3.46 (d, J = 14.6 Hz, 1H, 11A-H), 3.21 (d, J = 14.4 Hz, 1H, 12A-H), 3.17 (d, J = 4.8 Hz, 1H, 9-H), 3.12 (d, J = 4.8 Hz, 1H, 8-H), 3.03 (d, J = 14.4 Hz, 1H, 12B-H overlap **5g** and **6g**), 2.89 (d, J = 14.6 Hz, 1H, 11B-H), 2.15 (d, J = 6.4 Hz, 1H, 5-H), 1.58 (d, J = 6.4 Hz, 1H, 4-H), 1.28 – 1.21 (m, 12H, 4CH_3) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.3, 170.2, 138.8, 138.6, 83.6, 82.6, 82.1, 81.5, 69.1, 68.9, 56.3, 53.5, 51.0, 44.5, 29.7, 28.9, 22.1, 21.9 ppm.

Diisopropyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**6g**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.43 (d, J = 5.6, 1H, 1-H overlap **5g** and **6g**), 6.12 (d, J = 5.6 Hz, 1H, 2-H overlap **5g** and **6g**), 5.05 – 4.98 (m, 3H, 6-H and 2CH from 2*i*Pr overlap **5g** and **6g**), 4.80 (s, 1H, 10-H), 3.64 (t, J = 5.6 Hz, 1H, 9-H), 3.30 (d, J = 14.4 Hz, 1H, 11A-H), 3.24 (d, J = 14.6 Hz, 1H, 13A-H), 3.03 (d, J = 14.6 Hz, 1H, 13B-H overlap **5g** and **6g**), 2.86 (d, J = 5.7 Hz, 1H, 8-H), 2.65 (d, J = 14.4 Hz, 1H, 11B-H), 2.01 (d, J = 6.4 Hz, 1H, 5-H), 1.69 (d, J = 6.4 Hz, 1H, 4-H), 1.28 – 1.21 (m, 12H, 4CH_3) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.4, 170.3, 138.9, 138.6, 83.7, 82.6, 81.3, 79.3, 68.9, 68.8, 54.4, 53.3, 49.4, 47.9, 28.9, 28.3, 22.0, 21.9 ppm.

5h+6h



Light yellow oil, yield 1.49 g (77%). R_f = 0.74, "Sorbfil" plates, eluent $CHCl_3$/MeOH (10:1). Anal. calcd for $C_{22}H_{30}O_6S$: C, 62.54%; H, 7.16%; O, 22.72%; S, 7.59%. found: C, 62.49%; H, 7.18%; O, 22.79%; S, 7.54%. IR νmax/cm^{-1} (tablet KBr): 3107, 2907, 2876, 1729, 1639, 1470, 1379, 1179, 1023, 977, 826, 738, 703, 583. HRMS (ESI-TOF): calculated for $C_{22}H_{31}O_6S$ [M + H]: 423.1841, found: 423.1838 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

Diisobutyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**5h**)

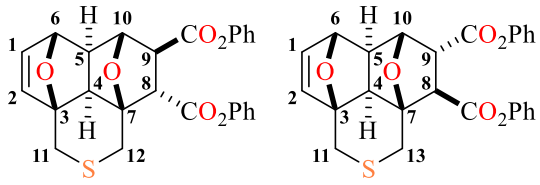
^{1}H NMR (700 MHz, $CDCl_3$) δ 6.43 (d, J = 5.6 Hz, 1H, 1-H overlap **5h** and **6h**), 6.13 – 6.11 (m, 1H, 2-H overlap **5h** and **6h**), 5.03 (s, 1H, 6-H), 4.87 (s, 1H, 10-H), 3.99 – 3.82 (m, 4H, 2CH_2 from *i*Bu, overlap **5h** and **6h**), 3.50 (d, J = 14.6 Hz, 1H, 11A-H), 3.22 (d, J = 4.9 Hz, 1H, 12A-H), 3.18 (d, J = 4.9 Hz, 1H, 12B-H overlap **5h** and **6h**), 3.04 (d, J = 4.8 Hz, 1H, 9-H), 3.02 (d, J = 5.1 Hz, 1H, 8-H), 2.90 (d, J = 14.6 Hz, 1H, 11B-H), 2.16 (d, J = 6.4 Hz, 1H, 5-H), 1.99 – 1.87 (m, 2H, CH from 2*i*Bu, overlap **5h** and **6h**), 1.63 (d, J = 6.4 Hz, 1H, 4-H), 0.99 – 0.85 (m, 12H, 4CH_3 from *i*Bu, overlap **5h** and **6h**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.8, 170.7, 138.8, 138.6, 83.7, 82.6, 81.8, 81.5, 71.7, 71.6, 56.5, 53.6, 51.2, 44.5, 29.5, 28.7, 27.8, 27.7, 19.3, 19.1 ppm.

Diisobutyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**6h**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.43 (d, J = 5.6 Hz, 1H, 1-H overlap **5h** and **6h**), 6.12 (m, 1H, 2-H overlap **5h** and **6h**), 5.00 (s, 1H, 6-H), 4.84 (d, J = 5.6 Hz, 1H, 10-H), 3.98 – 3.80 (m, 4H, 2CH_2 from *i*Bu, overlap

5h and **6h**), 3.71 (t, J = 5.7 Hz, 1H, 9-H), 3.30 (d, J = 14.5 Hz, 1H, 12A-H), 3.24 (d, J = 10.2 Hz, 1H, 13A-H, overlap **5h** and **6h**), 3.21 (d, J = 5.6 Hz, 1H, 13B-H, overlap **5h** and **6h**), 2.93 (d, J = 5.7 Hz, 1H, 8-H), 2.64 (d, J = 11.5 Hz, 1H, 11B-H), 2.05 (d, J = 6.4 Hz, 1H, 5-H), 1.98 – 1.89 (m, 2H, CH from 2*i*Bu, overlap **5h** and **6h**), 1.70 (d, J = 6.4 Hz, 1H, 4-H), 0.99 – 0.87 (m, 12H, $4CH_3$ from iBu, overlap **5h** and **6h**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.0, 170.7, 138.9, 138.6, 83.6, 81.8, 81.3, 79.4, 71.7, 71.4, 54.5, 53.3, 49.4, 47.9, 29.5, 28.4, 27.8, 27.7, 19.3, 19.1 ppm.

5i+6i



White powder, yield 1.09 g (39%). R_f = 0.61, "Sorbfil" plates, eluent $CHCl_3$/MeOH (10:1). M. p. 105−108 °C. Anal. calcd for $C_{26}H_{22}O_6S$: C, 67.52%; H, 4.79%; O, 20.75%; S, 6.93%. found: C, 67.49%; H, 4.86%; O, 20.76%; S, 6.89%. IR νmax/cm^{-1} (tablet KBr): 2972, 1747, 1592, 1493, 1416, 1294, 1198, 1166, 1058, 1020, 974, 823, 737, 687. HRMS (ESI-TOF): calculated for $C_{26}H_{23}O_6S$ [M + H]: 463.1215, found: 463.1210 $[M + H]^+$.

Some ^1H and ^{13}C signals might overlap

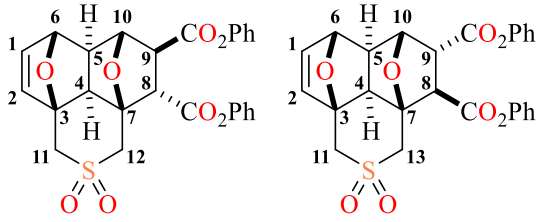
Diphenyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**5i**)

^1H NMR (700 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 4H, $4CH_{arom}$ overlap **5i** and **6i**), 7.31 – 7.24 (m, 2H, $2CH_{arom}$ overlap **5i** and **6i**), 7.09 (d, J = 8.5 Hz, 4H, $4CH_{arom}$ overlap **5i** and **6i**), 6.49 (d, J = 7.3 Hz, 1H, 1-H), 6.20 (d, J = 5.7 Hz, 1H, 2-H), 5.14 (s, 1H, 6-H), 5.11 (d, J = 1.4 Hz, 1H, 10-H), 3.68 (d, J = 15.0 Hz, 1H, 11A-H), 3.61 (d, J = 4.8 Hz, 1H, 8-H), 3.56 (d, J = 4.8 Hz, 1H, 9-H), 3.33 (d, J = 14.5 Hz, 1H, 12A-H), 3.11 (d, J = 14.5 Hz, 1H, 12B-H), 3.07 (d, J = 15.0 Hz, 1H, 11B-H), 2.32 (d, J = 6.4 Hz, 1H, 5-H), 1.85 (d, J = 6.4 Hz, 1H, 4-H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.3, 169.2, 150.7, 150.3, 139.0, 138.7, 129.8, 129.7, 126.6, 126.3, 121.4, 121.3, 83.8, 83.3, 82.3, 81.5, 56.3, 53.8, 51.2, 44.9, 29.7, 28.9 ppm.

Diphenyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**6i**)

^1H NMR (700 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 4H, $4CH_{arom}$ overlap **5i** and **6i**), 7.32 – 7.24 (m, 2H, $2CH_{arom}$ overlap **5i** and **6i**), 7.11 (d, J = 8.6 Hz, 4H, $4CH_{arom}$ overlap **5i** and **6i**), 6.51 (d, J = 5.7 Hz, 1H, 1-H), 6.19 (d, J = 5.7 Hz, 1H, 2-H), 5.13 (d, J = 1.5 Hz, 1H, 6-H), 5.10 (d, J = 5.7 Hz, 1H, 10-H), 4.08 (t, J = 5.7 Hz, 1H, 9-H), 3.51 (d, J = 14.8 Hz, 1H, 11A-H), 3.38 (d, J = 14.5 Hz, 1H, 13A-H), 3.30 (d, J = 5.7 Hz, 1H, 8-H), 3.11 (d, J = 14.5 Hz, 1H, 13B-H), 2.92 (d, J = 14.8 Hz, 1H, 11B-H), 2.27 (d, J = 6.4 Hz, 1H, 5-H), 1.85 (d, J = 6.4 Hz, 1H, 4-H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.4, 169.3, 150.5, 150.3, 139.0, 138.7, 129.8, 129.7, 126.6, 126.3, 121.4, 121.3, 84.4, 83.8, 81.3, 79.5, 54.5, 53.4, 49.6, 48.2, 28.8, 28.6 ppm.

5j+6j



White powder, yield 1.22 g (45%). R_f = 0.66, "Sorbfil" plates, eluent $CHCl_3$/MeOH (10:1). M. p. 189−191 °C. Anal. calcd for $C_{26}H_{22}O_8S$: C, 63.15%; H, 4.48%; O, 25.88%; S, 6.48% found: C, 63.09%; H, 4.54%; O, 25.95%; S, 6.42%. IR νmax/cm^{-1} (tablet KBr): 2982, 1748, 1592, 1493, 1322, 1191, 1071, 1019, 976, 829, 742, 689. HRMS (ESI-TOF): calculated for $C_{26}H_{23}O_8S$ [M + H]: 495.1113 found: 495.1108 $[M + H]^+$.

Some ^1H and ^{13}C signals might overlap

Diphenyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate 2,2-dioxide (**5j**)

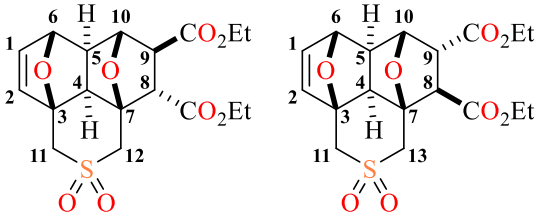
^1H NMR (700 MHz, $CDCl_3$) δ 7.52 – 7.36 (m, overlap **5j** and **6j**), 7.35 – 7.19 (m, 2H, $2CH_{arom}$ overlap **5j** and **6j**), 7.19 – 6.98 (m, 4H, $4CH_{arom}$ overlap **5j** and **6j**), 6.57 – 6.46 (m, 1H, 1-H overlap **5j** and **6j**), 6.33 – 6.12 (m, 1H, 2-H overlap **5j** and **6j**), 5.26 (s, 1H, 6-H), 5.22 (s, 1H, 10-H), 4.14 (d, J = 14.8 Hz, 1H, 11A-H), 3.84 – 3.68 (m, 3H, 12A-H, 12B-H and 11B-H), 3.68 (d, J = 4.3 Hz, 1H, 8-H), 3.55 (d, J = 4.3 Hz, 1H,

9-H overlap **5j** and **6j**), 2.43 (d, J = 6.1 Hz, 1H, 5-H), 2.20 (d, J = 6.1 Hz, 1H, 4-H) ppm.^{13}C NMR (175 MHz, $CDCl_3$) δ 169.6, 168.4, 150.6, 150.1, 138.7, 138.2, 129.9, 129.7, 126.8, 126.5, 121.4, 121.3, 85.3, 84.4, 82.8, 82.1, 56.6, 53.2, 52.5, 52.3, 51.1, 44.8, 44.7 ppm.

Diphenyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate 2,2-dioxide (**6j**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.52 – 7.36 (m, 4H, $4CH_{arom}$ overlap **5j** and **6j**), 7.35 – 7.19 (m, 2H, $2CH_{arom}$ overlap **5j** and **6j**), 7.19 – 6.98 (m, 4H, $4CH_{arom}$ overlap **5j** and **6j**), 6.57 – 6.46 (m, 1H, 1-H overlap **5j** and **6j**), 6.33 – 6.12 (m, 1H, 2-H overlap **5j** and **6j**), 5.15 (s, 1H, 6-H), 5.04 (s, 1H, 10-H), 4.08 (s, 1H, 9-H), 3.84 – 3.68 (m, 3H, 11A-H, 13A-H and 13B-H, overlap **5j** and **6j**), 3.58 – 3.56 (m, 1H, 11B-H overlap **5j** and **6j**), 3.30 – 3.24 (m, 1H, 8-H), 2.33 (d, J = 5.9 Hz, 1H, 5-H), 2.14 (d, J = 5.9 Hz, 1H, 4-H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.3, 168.5, 150.6, 150.1, 138.7, 138.2, 129.9, 126.8, 126.5, 129.8, 121.4, 121.3, 85.2, 84.1, 82.6, 82.1, 56.7, 53.0, 52.53, 52.3, 51.1, 44.8, 44.7 ppm.

5k+6k



White powder, yield 0.99 g (61%). R_f = 0.68, "Sorbfil" plates, eluent $CHCl_3$/MeOH (10:1). M. p. 158−161 °C. Anal. calcd for $C_{18}H_{22}O_8S$: C, 54.26%; H, 5.57%; O, 32.12%; S, 8.05%. found: C, 54.21%; H, 5.60%; O, 32.17%; S, 8.02%. IR νmax/cm^{-1} (tablet KBr): 3041, 2986, 1725, 1643, 1395, 1372, 1308, 1218, 1131, 974, 868, 829, 809, 765, 590. HRMS (ESI-TOF): calculated for $C_{18}H_{23}O_8S$ [M + H]: 399.1113, found: 399.1109 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

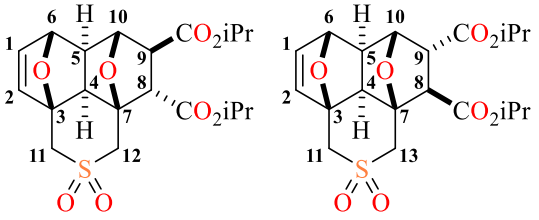
Diethyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate 2,2-dioxide (**5k**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.53 – 6.47 (m, 1H, 1-H, overlap **5k** and **6k**), 6.18 (d, J = 5.6 Hz, 1H, 2-H, overlap **5k** and **6k**), 5.13 (d, J = 11.7 Hz, 1H, 6-H overlap **5k** and **6k**), 5.01 (s, 1H, 10-H), 4.35 – 4.10 (m, 4H, $2CH_2$ from Et, overlap **5k** and **6k**), 3.98 (d, J = 15.0 Hz, 1H, 11A-H), 3.83 – 3.63 (m, 3H, 12A-H, 12B-H and 11B-H, overlap **5k** and **6k**), 3.27 (d, J = 4.9 Hz, 1H, 8-H), 3.21 (d, J = 4.9 Hz, 1H, 9-H), 2.28 (d, J = 6.5 Hz, 1H, 5-H), 1.96 (d, J = 6.5 Hz, 1H, 4-H), 1.39 – 1.10 (m, 6H, $2CH_3$ from Et, overlap **5k** and **6k**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 174.0, 169.9, 138.7, 137.9, 85.2, 84.0, 82.6, 82.1, 62.3, 62.1, 56.5, 53.2, 52.3, 51.7, 51.2, 44.5, 14.4 ppm.

Diethyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate 2,2-dioxide (**6k**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.53 – 6.47 (m, 1H, 1-H, overlap **5k** and **6k**), 6.18 (d, J = 5.6 Hz, 1H, 2-H, overlap **5k** and **6k**), 5.13 (d, J = 11.7 Hz, 1H, 6-H overlap **5k** and **6k**), 4.93 (d, J = 5.6 Hz, 1H, 10-H), 4.35 – 4.10 (m, 5H, 9-H and $2CH_2$ from Et, overlap **5k** and **6k**), 3.83 – 3.63 (m, 4H, 11A-H, 13A-H, 13B-H and 11B-H, overlap **5k** and **6k**), 3.10 (d, J = 5.8 Hz, 1H, 8-H), 2.16 (d, J = 7.3 Hz, 1H, 5-H), 2.04 (m, 1H, 4-H), 1.39 – 1.10 (m, 6H, $2CH_3$ from Et, overlap **5k** and **6k**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.0, 170.3, 139.1, 137.6, 85.1, 83.9, 82.6, 79.9, 62.0, 61.8, 56.6, 55.2, 53.3, 52.2, 49.3, 48.3, 14.4 ppm.

5l+6l



White powder, yield 0.98 g (58%). R_f = 0.72, "Sorbfil" plates, eluent $CHCl_3$/MeOH (10:1). M. p. 112−115 °C. Anal. calcd for $C_{20}H_{26}O_8S$: C, 56.33%; H, 6.15%; O, 30.01%; S, 7.52%. found: C, 56.29%; H, 6.19%; O, 30.02%; S, 7.50%. IR νmax/cm^{-1} (tablet KBr): 3106, 3088, 3057, 2981, 2935, 2884, 1725, 1631, 1468, 1376, 1297, 1213, 1132, 1018, 977, 866, 830, 771, 699. HRMS (ESI-TOF): calculated for $C_{20}H_{27}O_8S$ [M + H]: 427.1426, found: 427.1421 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

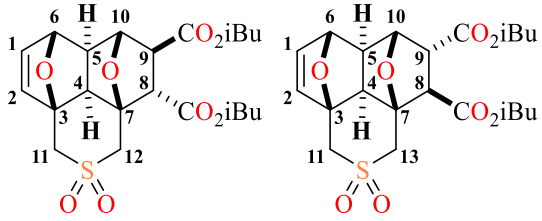
Diisopropyl (3a*RS*,3a^{1}*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^{1},5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate 2,2-dioxide (**5l**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.49 – 6.47 (m, 1H, 1-H, overlap **5l** and **6l**), 6.17 (d, J = 5.6 Hz, 1H, 2-H), 5.12 (s, 1H, 6-H), 5.07 – 4.99 (m, 2H, 2CH from 2*i*Pr, overlap **5l** and **6l**), 4.94 (s, 1H, 10-H), 3.95 (d, J = 15.1 Hz, 1H, 11A-H), 3.78 – 3.63 (m, 3H, 12A-H, 12B-H and 11B-H overlap **5l** and **6l**), 3.25 (d, J = 4.8 Hz, 1H, 8-H), 3.10 (d, J = 4.8 Hz, 1H, 9-H), 2.27 (d, J = 6.3 Hz, 1H, 5-H), 1.92 (d, J = 6.3 Hz, 1H, 4-H), 1.32 – 1.19 (m, 12H, 2CH_3 from 2*i*Pr, overlap **5l** and **6l**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.5, 169.3, 138.6, 138.0, 85.1, 83.8, 82.6, 82.0, 69.8, 69.4, 56.5, 53.3, 52.2, 51.1, 44.4, 21.9, 21.8 ppm.

Diisopropyl (3a*RS*,3a^{1}*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^{1},5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate 2,2-dioxide (**6l**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.50 – 6.46 (m, 1H, 1-H overlap **5l** and **6l**), 6.15 (d, J = 5.6 Hz, 1H, 2-H), 5.10 (d, J = 1.7 Hz, 1H, 6-H), 5.08 – 4.98 (m, 2H, 2CH from 2*i*Pr, overlap **5l** and **6l**), 4.89 (d, J = 5.6 Hz, 1H, 10-H), 3.81 – 3.69 (m, 4H, 11A-H, 13A-H, 13B-H and 11B-H overlap **5l** and **6l**), 3.63 (t, J = 5.7 Hz, 1H, 9-H), 3.04 (d, J = 5.7 Hz, 1H, 8-H), 2.15 (d, J = 6.3 Hz, 1H, 5-H), 2.03 (d, J = 6.3 Hz, 1H, 4-H), 1.31 – 1.13 (m, 12H, 2CH_3 from 2*i*Pr, overlap **5l** and **6l**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.7, 169.1, 138.8, 137.6, 85.1, 82.6, 81.9, 79.8, 69.8, 69.3, 55.1, 52.4, 52.2, 49.1, 48.1, 22.0, 21.9 ppm.

5m+6m



White powder, yield 1.02 g (53%). R_f = 0.78, “Sorbfil” plates, eluent $CHCl_3$/MeOH (10:1). M. p. 170−173 °C. Anal. calcd for $C_{22}H_{30}O_8S$: C, 58.13%; H, 6.65%; O, 28.16%; S, 7.05%. found: C, 58.09%; H, 6.71%; O, 28.18%; S, 7.02%. IR νmax/cm^{-1} (tablet KBr): 3106, 3094, 2966, 2915, 2876, 1729, 1637, 1560, 1473, 1385, 1300, 1199, 1135, 1028, 982, 839, 703, 605. HRMS (ESI-TOF): calculated for $C_{22}H_{31}O_8S$ [M + H]: 455.1739, found: 455.1734 [M + H]$^{+}$.

Some ^{1}H and ^{13}C signals might overlap

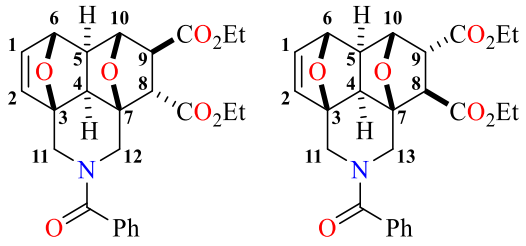
Diisobutyl (3a*RS*,3a^{1}*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^{1},5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate 2,2-dioxide (**5m**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.49 (d, J = 5.5 Hz, 1H, 1-H, overlap **5m** and **6m**), 6.19 – 6.14 (m, 1H, 2-H, overlap **5m** and **6m**), 5.13 (s, 1H, 6-H), 4.98 (s, 1H, 10-H), 4.02 – 3.84 (m, 4H, 2CH_2 from 2*i*Bu, overlap **5m** and **6m**), 3.81 – 3.66 (m, 3H, 11A-H, 12A-H and 12B-H, overlap **5m** and **6m**), 3.48 (d, J = 12.6 Hz, 1H, 11B-H), 3.31 (d, J = 4.9 Hz, 1H, 8-H), 3.16 (d, J = 4.9 Hz, 1H, 9-H), 2.28 (d, J = 6.3 Hz, 1H, 5-H), 2.00 – 1.91 (m, 3H, 4-H and 2CH from 2*i*Bu, overlap **5m** and **6m**), 0.93 (dd, J = 11.8, 6.7 Hz, 6H, 2CH_3 from 2*i*Bu, overlap **5m** and **6m**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.0, 169.7, 139.0, 137.7, 85.1, 83.9, 82.5, 82.1, 72.1, 71.7, 56.7, 52.4, 52.3, 51.3, 44.5, 27.8, 27.7, 19.3, 19.2, 19.1, 19.0 ppm.

Diisobutyl (3a*RS*,3a^{1}*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^{1},5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate 2,2-dioxide (**6m**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.49 (d, J = 5.5 Hz, 1H, 1-H, overlap **5m** and **6m**), 6.19 – 6.14 (m, 1H, 2-H, overlap **5m** and **6m**), 5.10 (s, 1H, 6-H), 4.92 (d, J = 5.6 Hz, 1H, 10-H), 4.02 – 3.84 (m, 5H, 9-H and 2CH_2 from 2iBu, overlap **5m** and **6m**), 3.81 – 3.66 (m, 4H, 11A-H, 13A-H, 13B-H and 11B-H, overlap **5m** and **6m**), 3.11 (d, J = 5.8 Hz, 1H, 8-H), 2.19 (d, J = 6.3 Hz, 1H, 5-H), 2.05 (d, J = 6.3 Hz, 1H, 4-H), 2.00 – 1.91 (m, 2H, 2CH from 2*i*Bu, overlap **5m** and **6m**), 0.93 (dd, J = 11.8, 6.7 Hz, 6H, 2CH_3 from 2*i*Bu, overlap **5m** and **6m**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.2, 169.8, 138.7, 138.0, 85.0, 82.5, 82.0, 79.9, 72.1, 71.9, 55.3, 53.4, 52.3, 49.2, 48.3, 27.8, 27.7, 19.3, 19.2, 19.1, 19.10 ppm.

5n+6n



White powder, yield 0.93 g (66%). R_f = 0.47, "Sorbfil" plates, eluent $CHCl_3$. M. p. 163−165 °C. Anal. calcd for $C_{25}H_{27}NO_7$: C, 66.21%; H, 6.00%; N, 3.09%; O, 24.70%. found: C, 66.15%; H, 6.05%; N, 3.23%; O, 24.67%. IR νmax/cm^{-1} (tablet KBr): 3053, 3005, 2979, 2912, 1732, 1626, 1444, 1369, 1304, 1198, 1086, 1032, 986, 848, 791, 700, 654. HRMS (ESI-TOF): calculated for $C_{25}H_{28}NO_7$ [M + H]: 454.1865, found: 454.1860 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

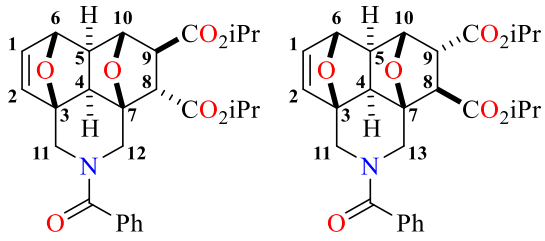
Diethyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-2-benzoyl-2,3,3a^1,5,6,6a-hexahydro-1*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isoquinoline-4,5-dicarboxylate (**5n**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.53 (s, 2H, $2CH_{arom}$ overlap **5n** and **6n**), 7.36 (s, 3H, $3CH_{arom}$ overlap **5n** and **6n**), 6.40 (s, 1H, 1-H), 6.21 (m, 1H, 2-H), 5.41 – 5.23 (m, 1H, 6-H), 5.03 (s, 1H, 10-H), 4.87 (m, 1H, 11A-H), 4.44 – 4.24 (m, 1H, 12A-H), 4.23 – 4.10 (m, 4H, $2CH_2$ from 2Et), 3.75 – 3.52 (m, 2H, 8-H and 12B-H), 3.33 (m, 1H, 11B-H), 3.11 (m, 1H, 9-H), 2.15 (d, J = 6.4 Hz, 1H, 5-H), 1.80 (d, J = 6.4 Hz, 1H, 4-H), 1.26 (t, J = 7.1 Hz, 6H, $2CH_3$ from Et) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 172.0, 171.9, 170.6, 138.5, 135.7, 129.7, 128.4, 128.3, 127.9, 83.7, 83.1, 81.6, 80.2, 61.6, 61.4, 53.1, 52.5, 49.7, 46.7, 44.9, 42.4, 14.4, 14.3 ppm.

Diethyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-2-benzoyl-2,3,3a^1,5,6,6a-hexahydro-1*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isoquinoline-4,5-dicarboxylate (**6n**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 2H, $2CH_{arom}$ overlap **5n** and **6n**), 7.41 – 7.32 (m, s, 3H, $3CH_{arom}$ overlap **5n** and **6n**), 6.39 (s, 1H, 1-H overlap **5n** and **6n**), 6.32 – 6.07 (m, 1H, 2-H overlap **5n** and **6n**), 5.42 – 5.24 (m, 1H, 6-H overlap **5n** and **6n**), 5.02 (s, 1H, 10-H overlap **5n** and **6n**), 4.92 – 4.80 (m, 1H, 9-H overlap **5n** and **6n**), 4.43 – 4.23 (m, 1H, 11A-H, overlap **5n** and **6n**), 4.21 – 4.09 (m, 4H, $2CH_2$ from 2Et overlap **5n** and **6n**), 3.99 – 2.92 (m, 4H, 8-H, 13A-H, 13B-H and 11A-H overlap **5n** and **6n**), 1.98 (d, J = 6.2 Hz, 1H, 5-H), 1.85 (d, J = 6.2 Hz, 2H, 4-H), 1.35 – 1.22 (m, 6H, $2CH_3$ from Et overlap **5n** and **6n**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.9,171.5, 170.6, 137.3, 136.8, 129.7, 128.4, 128.3, 127.9, 83.7, 82.9, 81.5, 79.6, 61.6, 61.4, 53.7, 52.5, 49.7, 47.8, 46.7, 43.2, 14.3, 14.2 ppm.

5o+6o



White powder, yield 0.52 g (46%). R_f = 0.53, "Sorbfil" plates, eluent $CHCl_3$. M. p. 76−78 °C. Anal. calcd for $C_{27}H_{31}NO_7$: C, 67.35%; H, 6.49%; N, 2.91%; O, 23.26%. found: C, 67.29%; H, 6.51%; N, 2.96%; O, 23.24%. IR νmax/cm^{-1} (tablet KBr): 3952, 2980, 2943, 1726, 1633, 1434, 1376, 1272, 1208, 1180, 1105, 988, 830, 700, 651. HRMS (ESI-TOF): calculated for $C_{27}H_{32}NO_7$ [M + H]: 482.2178, found: 482.2175 [M + H]$^+$.

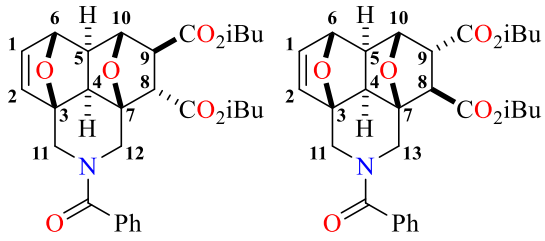
Some ^{1}H and ^{13}C signals might overlap

Diisopropyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-2-benzoyl-2,3,3a^1,5,6,6a-hexahydro-1*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isoquinoline-4,5-dicarboxylate (**5o**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 2H, $2CH_{arom}$ overlap **5o** and **6o**), 7.40 – 7.32 (m, 3H, $3CH_{arom}$ overlap **5o** and **6o**), 6.40 (s, 1H overlap **5o** and **6o,** 1-H), 6.32 – 6.08 (m, 1H, overlap **5o** and **6o**, 2-H), 5.43 – 5.23 (m, 1H, 6-H overlap **5o** and **6o**), 5.01 (m, 2H, CH from 2*i*Pr), 4.90 – 4.79 (m, 1H, 10-H overlap **5o** and **6o**), 3.76 – 2.88 (m, 6H, 8-H, 9-H, 11A-H, 12A-H, 12B-H and 11B-H overlap **5o** and **6o**), 2.15 (d, J = 6.4 Hz, 1H, 5-H), 1.79 (d, J = 6.4 Hz, 1H, 4-H), 1.28 – 1.20 (m, 12H, $4CH_3$ from 2*i*Pr) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 172.0, 171.0, 169.9, 138.6, 136.7, 135.6, 129.8, 128.4, 128.0, 84.2, 82.9, 82.0, 81.7, 69.2, 69.1, 53.8, 53.3, 50.1, 49.6, 47.9, 44.9, 22.1, 21.9 ppm.

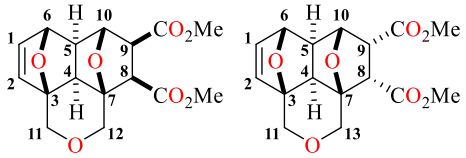
Diisopropyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-2-benzoyl-2,3,3a^1,5,6,6a-hexahydro-1*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isoquinoline-4,5-dicarboxylate (**6o**)
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 2H, $2CH_{arom}$ overlap **5o** and **6o**), 7.40 – 7.32 (m, 3H, $2CH_{arom}$ overlap **5o** and **6o**), 6.40 (s, 1H, overlap **5o** and **6o**, 1-H), 6.32 – 6.08 (m, 1H, overlap **5o** and **6o**, 2-H), 5.43 – 5.23 (m, 1H, 6-H overlap **5o** and **6o**), 5.06 – 4.96 (m, 2H, CH from 2*i*Pr), 4.90 – 4.79 (m, 1H, 10-H overlap **5o** and **6o**), 4.62 – 4.05 (m, 5H, 8-H, 11A-H, 12A-H, 12B-H and 11B-H overlap **5o** and **6o**), 3.76 – 2.88 (m, 1H, 9-H overlap **5o** and **6o**), 1.97 (d, J = 6.4 Hz, 1H, 5-H), 1.84 (d, J = 6.4 Hz, 1H, 4-H), 1.28 – 1.20 (m, 12H, $4CH_3$ from 2*i*Pr) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 172.0, 171.6, 170.2, 138.2, 137.3, 135.6, 129.7, 128.4, 128.0, 84.3, 82.2, 81.6, 79.9, 69.4, 69.0, 53.5, 53.3, 51.2, 50.1, 46.7, 45.5, 22.1, 21.9 ppm.

5p+6p



White powder, yield 0.8 g (52%). R_f = 0.49, "Sorbfil" plates, eluent $CHCl_3$. M. p. 72−74 °C. Anal. calcd for $C_{29}H_{35}NO_7$: C, 68.35%; H, 6.92%; N, 2.75%; O, 21.98%. found: C, 68.31%; H, 6.95%; N, 2.79%; O, 21.95%. IR νmax/cm^{-1} (tablet KBr): 3069, 2964, 1730, 1637, 1434, 1205, 1070, 987, 830, 794, 701, 652. HRMS (ESI-TOF): calculated for $C_{29}H_{36}NO_7$ [M + H]: 510.2491, found: 510.2487 [M + H]$^+$.
Some ^{1}H and ^{13}C signals might overlap
Diisobutyl (3a*RS*,3a^1*SR*,4*RS*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-2-benzoyl-2,3,3a^1,5,6,6a-hexahydro-1*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isoquinoline-4,5-dicarboxylate (**5p**)
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H, $2CH_{arom}$ overlap **5p** and **6p**), 7.40 – 7.33 (m, 3H, $2CH_{arom}$ overlap **5p** and **6p**), 6.40 (s, 1H, overlap **5p** and **6p**), 6.32 – 6.09 (m, 1H overlap **5p** and **6p**), 5.43 – 5.25 (m, 1H overlap **5p** and **6p**), 5.02 (m, 1H, overlap **5p** and **6p**), 3.96 – 3.81 (m, 4H, $4CH_2$ from 2*i*Bu overlap **5p** and **6p**), 3.77 – 2.97 (m, 6H, 11A-H, 12A-H, 12B-H, 11B-H, 8-H and 9-H overlap **5p** and **6p**), 2.19 – 2.15 (m, 1H, 5-H), 1.99 – 1.90 (m, 2H, 4CH from 2*i*Bu overlap **5p** and **6p**), 1.86 (d, J = 6.4 Hz, 1H, 4-H), 1.05 – 0.80 (m, 12H, $4CH_3$ from 2*i*Bu overlap **5p** and **6p**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 172.0, 172.0, 170.4, 138.5, 135.6, 135.3, 129.8, 128.4, 127.9, 84.2, 82.9, 81.9, 81.4, 71.8, 71.5, 53.3, 53.1, 52.6, 52.2, 51.2, 45.6, 27.8, 27.7, 19.2, 19.1 ppm.
Diisobutyl (3a*RS*,3a^1*SR*,4*SR*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-2-benzoyl-2,3,3a^1,5,6,6a-hexahydro-1*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isoquinoline-4,5-dicarboxylate (**6p**)
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H, $2CH_{arom}$ overlap **5p** and **6p**), 7.40 – 7.33 (m, 3H, $2CH_{arom}$ overlap **5p** and **6p**), 6.40 (s, 1H, overlap **5p** and **6p**), 6.32 – 6.09 (m, 1H overlap **5p** and **6p**), 5.43 – 5.25 (m, 1H, overlap **5p** and **6p**), 5.06 – 4.89 (m, 1H, overlap **5p** and **6p**), 4.85 (d, J = 5.8 Hz, 1H, 9-H), 4.56 (m, 1H, 11A-H), 4.46 – 3.99 (m, 4H, 12A-H, 12B-H, 11B-H and 8-H overlap **5p** and **6p**), 3.96 – 3.81 (m, 4H, $4CH_2$ from 2*i*Bu overlap **5p** and **6p**), 2.31 (d, J = 6.7 Hz, 1H, 5-H), 2.01 (d, J = 6.4 Hz, 1H, 4-H), 1.99 – 1.90 (m, 2H, 4CH from 2*i*Bu overlap **5p** and **6p**), 1.05 – 0.80 (m, 12H, $4CH_3$ from 2*i*Bu overlap **5p** and **6p**) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 172.0, 171.5, 170.7, 137.3, 136.8, 135.3, 129.9, 128.5, 128.3, 84.4, 81.9, 81.4, 79.9, 71.9, 71.6, 53.9, 52.2, 51.2, 49.7, 45.0, 43.2, 27.9, 27.7, 19.2, 19.1 ppm.

7a+8a



Light brown powder, yield 1.1 g (51%). R_f = 0.56, "Sorbfil" plates, eluent $CHCl_3$. M. p. 164−166 °C. Anal. calcd for $C_{16}H_{18}O_7$: C, 59.62%; H, 5.63%; O, 34.75%. found: C, 59.58%; H, 5.66%; O, 34.76%. IR νmax/cm^{-1} (tablet KBr): 3069, 2968, 2995, 2863, 1747, 1436, 1305, 1202, 1082, 1031, 983, 937, 916, 879, 843, 818, 733, 593. HRMS (ESI-TOF): calculated for $C_{16}H_{19}O_7$ [M + H]: 323.1130, found: 323.1137 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

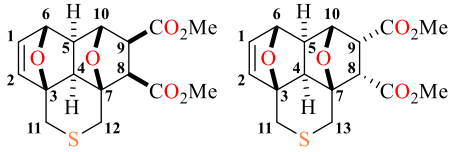
Dimethyl (3a*RS*,3a^1*SR*,4*SR*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate (**7a**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.38 (d, J = 5.9 Hz, 1H, 1-H), 6.15 (d, J = 5.9 Hz, 1H, 2-H), 5.03 (s, 1H, 6-H), 4.97 (s, 1H, 10-H), 4.33 (d, J = 12.6 Hz, 1H, 11A-H overlap **10a** and **11a**), 4.13 (d, J = 12.8 Hz, 1H, 12A-H), 3.91 (d, J = 12.8 Hz, 1H, 12B-H overlap **10a** and **11a**), 3.73 (m, 1H, 11B-H), 3.60 (d, J = 7.2 Hz, 6H, 2CH_3 overlap **10a** and **11a**), 2.94 (d, J = 9.1 Hz, 1H, 9-H), 2.88 (d, J = 9.1 Hz, 1H, 8-H), 1.94 (d, J = 6.0 Hz, 1H, 5-H), 1.70 (d, J = 6.0 Hz, 1H, 4-H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.6, 169.6, 138.4, 136.1, 83.9, 82.1, 81.3, 79.6, 66.1, 65.5, 53.5, 53.3, 52.0, 51.8, 49.7, 47.5 ppm.

Dimethyl (3a*RS*,3a^1*SR*,4*RS*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate (**8a**)

^{1}H NMR (700 MHz, $CDCl_3$) δ 6.34 (d, J = 5.7 Hz, 1H, 1-H), 6.17 (d, J = 5.7 Hz, 1H, 2-H), 4.95 (s, 1H, 6-H), 4.73 (d, J = 5.2 Hz, 1H, 10-H), 4.33 (d, J = 12.7 Hz, 1H, 11A-H overlap **10a** and **11a**), 4.04 (d, J = 12.6 Hz, 1H, 13A-H), 3.97 (d, J = 12.6 Hz, 1H, 13B-H), 3.91 (d, J = 12.7 Hz, 1H, 11B-H overlap **10a** and **11a**), 3.60 (d, J = 7.2 Hz, 6H, 2CH_3 overlap **10a** and **11a**), 3.47 (dd, J = 11.5, 5.4 Hz, 1H, 9-H), 2.78 (d, J = 11.5 Hz, 1H, 8-H), 2.47 (d, J = 6.2 Hz, 1H, 5-H), 2.21 (d, J = 6.2 Hz, 1H, 4-H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.5, 170.4, 137.9, 136.3, 84.2, 83.2, 81.6, 80.3, 66.4, 66.2, 52.0, 51.8, 50.2, 49.5, 45.9, 41.6 ppm.

7b+8b



Light brown powder, yield 0.89 g (40%). R_f = 0.73, "Sorbfil" plates, eluent $CHCl_3$/MeOH (10:1). M. p. 177−179 °C. Anal. calcd for $C_{16}H_{18}O_6S$: C, 56.79%; H, 5.36%; O, 28.37%; S, 9.47%. found: C, 56.75%; H, 5.41%; O, 28.42%; S, 9.42%. IR νmax/cm^{-1} (tablet KBr): 3085, 3030, 2994, 2970, 2853, 1729, 1437, 1359, 1208, 1093, 1058, 1019, 991, 835, 818, 739, 714, 577. HRMS (ESI-TOF): calculated for $C_{16}H_{19}O_6S$ [M + H]: 339.0902, found: 339.0898 [M + H]$^+$.

Some ^{1}H and ^{13}C signals might overlap

Dimethyl (3a*RS*,3a^1*SR*,4*SR*,5*RS*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**7b**)

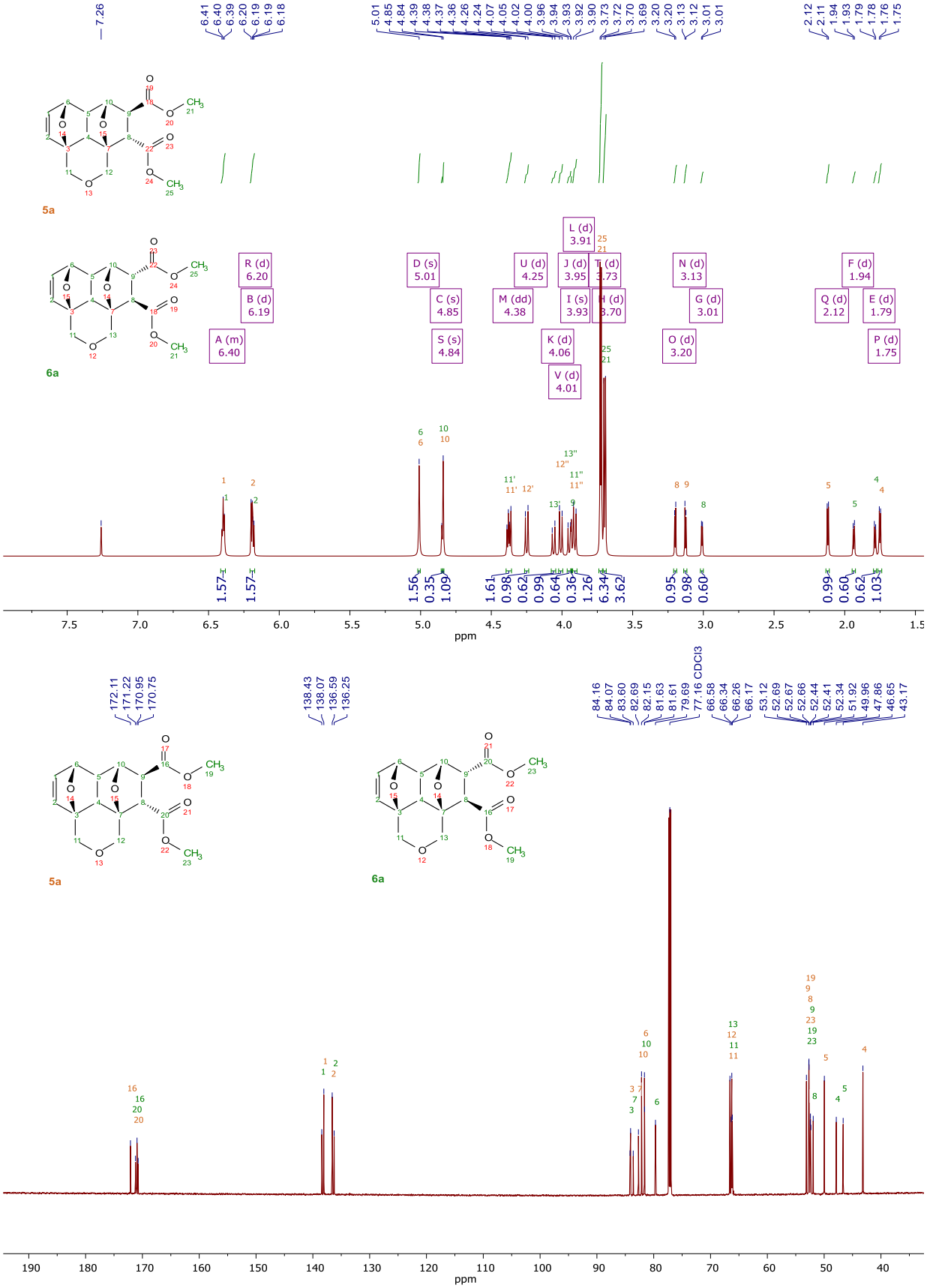
^{1}H NMR (700 MHz, $CDCl_3$) δ 6.45 (d, J = 5.6 Hz, 1H, 1-H), 6.12 (d, J = 5.6 Hz, 1H, 2-H), 5.09 (s, 1H, 6-H), 5.01 (s, 1H, 10-H), 3.63 (d, J = 6.5 Hz, 6H, 2CH_3), 3.26 (d, J = 14.4 Hz, 1H, 11A-H), 3.07 (d, J = 14.4 Hz, 1H, 12A-H), 3.03 (d, J = 14.4 Hz, 1H, 12B-H), 2.97 (d, J = 9.5 Hz, 1H, 9-H), 2.92 (d, J = 9.5 Hz, 1H, 8-H), 2.79 (d, J = 14.4 Hz, 1H, 11B-H), 1.98 (d, J = 6.3 Hz, 1H, 5-H), 1.64 (d, J = 6.3 Hz, 1H, 4-H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.8, 170.2, 139.1, 138.5, 83.7, 82.1, 81.1, 79.2, 56.4, 54.0, 52.2, 52.0, 51.2, 49.1, 28.8, 27.7 ppm.

Dimethyl (3a*RS*,3a^1*SR*,4*RS*,5*SR*,6*SR*,6a*RS*,7*SR*,9a*RS*)-3a^1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isothiochromene-4,5-dicarboxylate (**8b**)

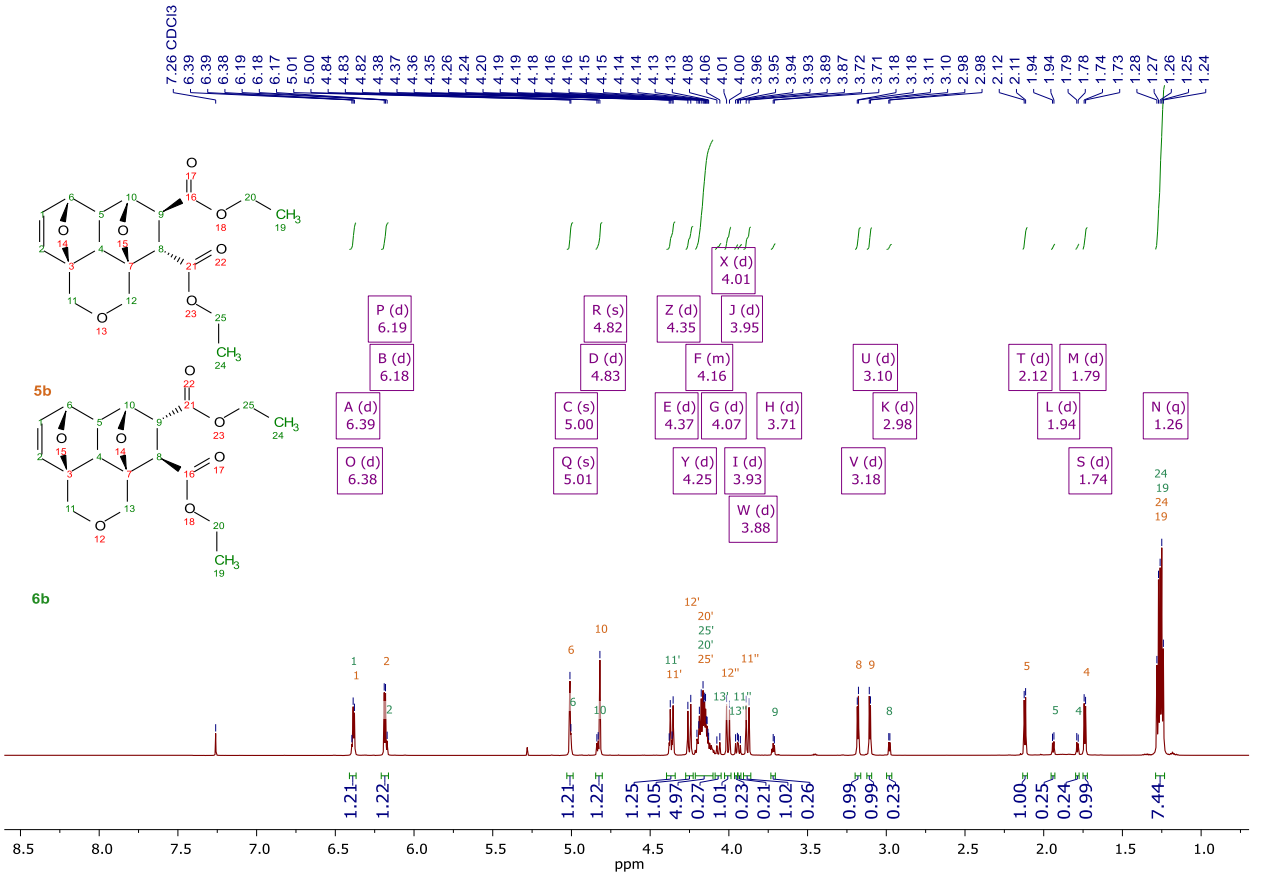
^{1}H NMR (700 MHz, $CDCl_3$) δ 6.43 (d, J = 5.6 Hz, 1H, 1-H), 6.13 (d, J = 5.6 Hz, 1H, 2-H), 5.00 (s, 1H, 6-H), 4.75 (d, J = 5.4 Hz, 1H, 10-H), 3.65 (d, J = 9.1 Hz, 2CH_3), 3.45 (dd, J = 11.7, 5.4 Hz, 1H, 9-H), 3.34 (d, J = 14.4 Hz, 1H, 11A-H), 3.32 (d, J = 14.4 Hz, 1H, 13A-H), 3.02 (d, J = 14.4 Hz, 1H, 13B-H), 2.88 (d, J = 11.7 Hz, 1H, 8-H), 2.71 (d, J = 14.4 Hz, 1H, 11B-H), 2.45 (d, J = 6.5 Hz, 1H, 5-H), 2.24 (d, J = 6.5 Hz, 1H, 4-H) ppm.^{13}C NMR (175 MHz, $CDCl_3$) δ 170.6, 138.7, 138.6, 83.8, 83.2, 81.6, 80.2, 53.9, 52.0, 52.0, 50.7, 47.0, 43.4, 29.5, 28.7 ppm

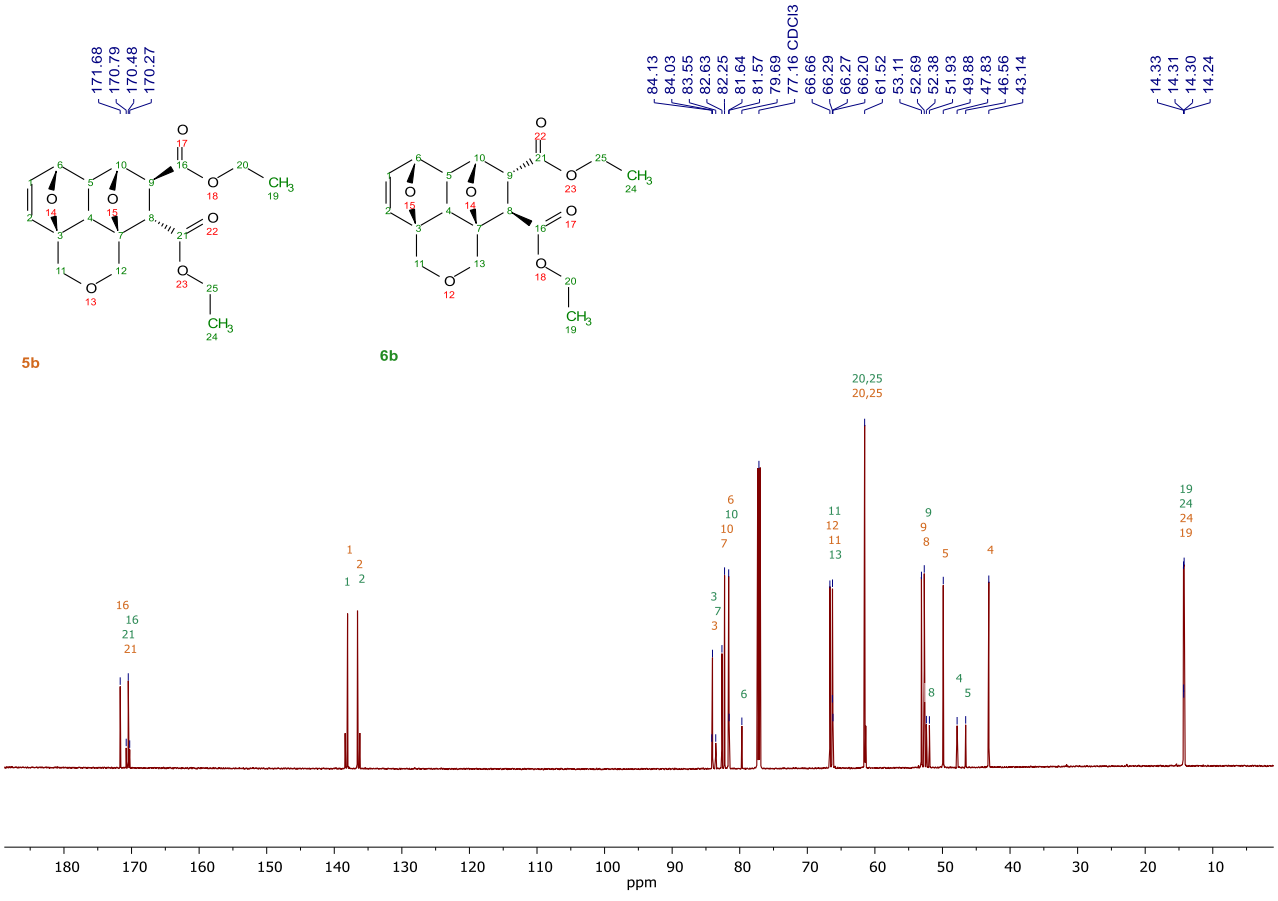
2. ^{1}H and ^{13}C NMR spectra of the synthesized compounds

Mixture of **5a** and **6a**

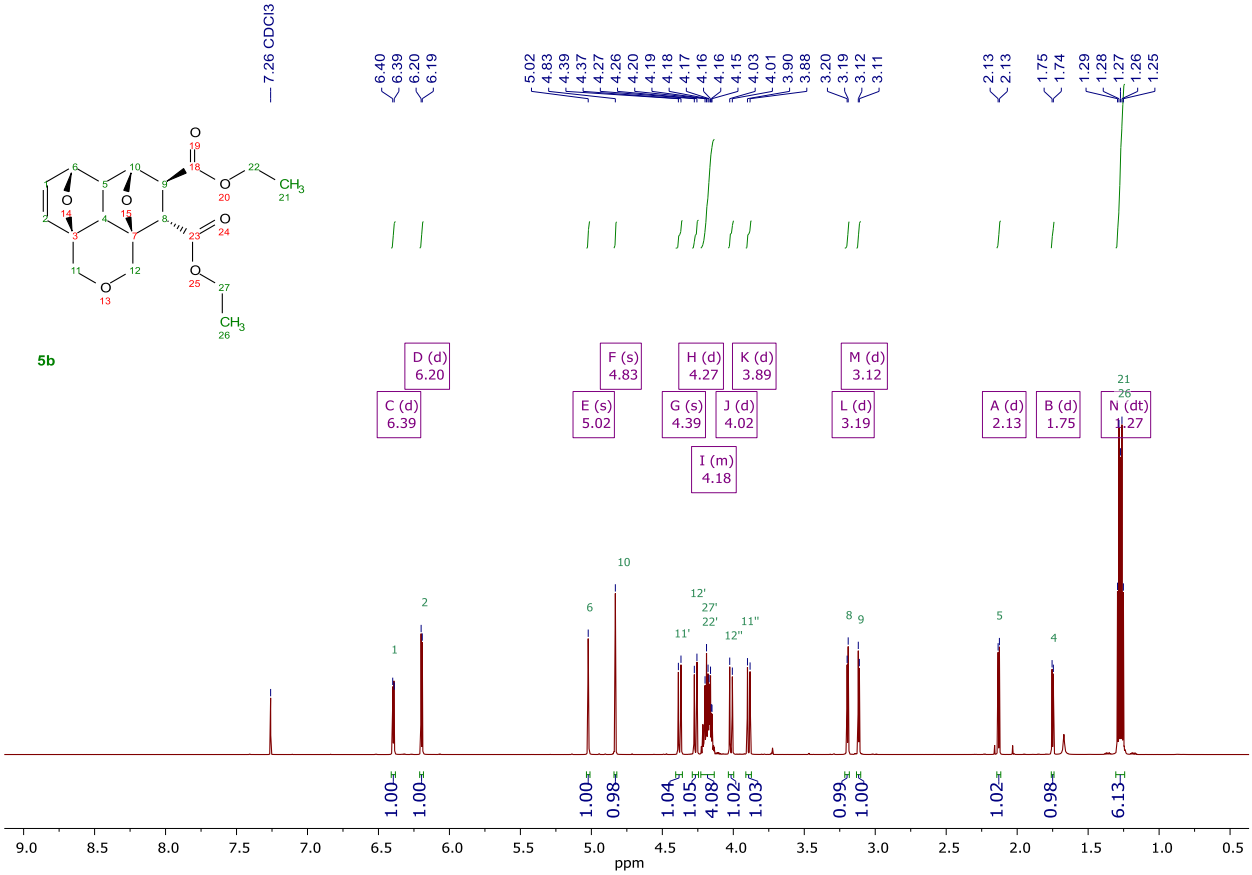


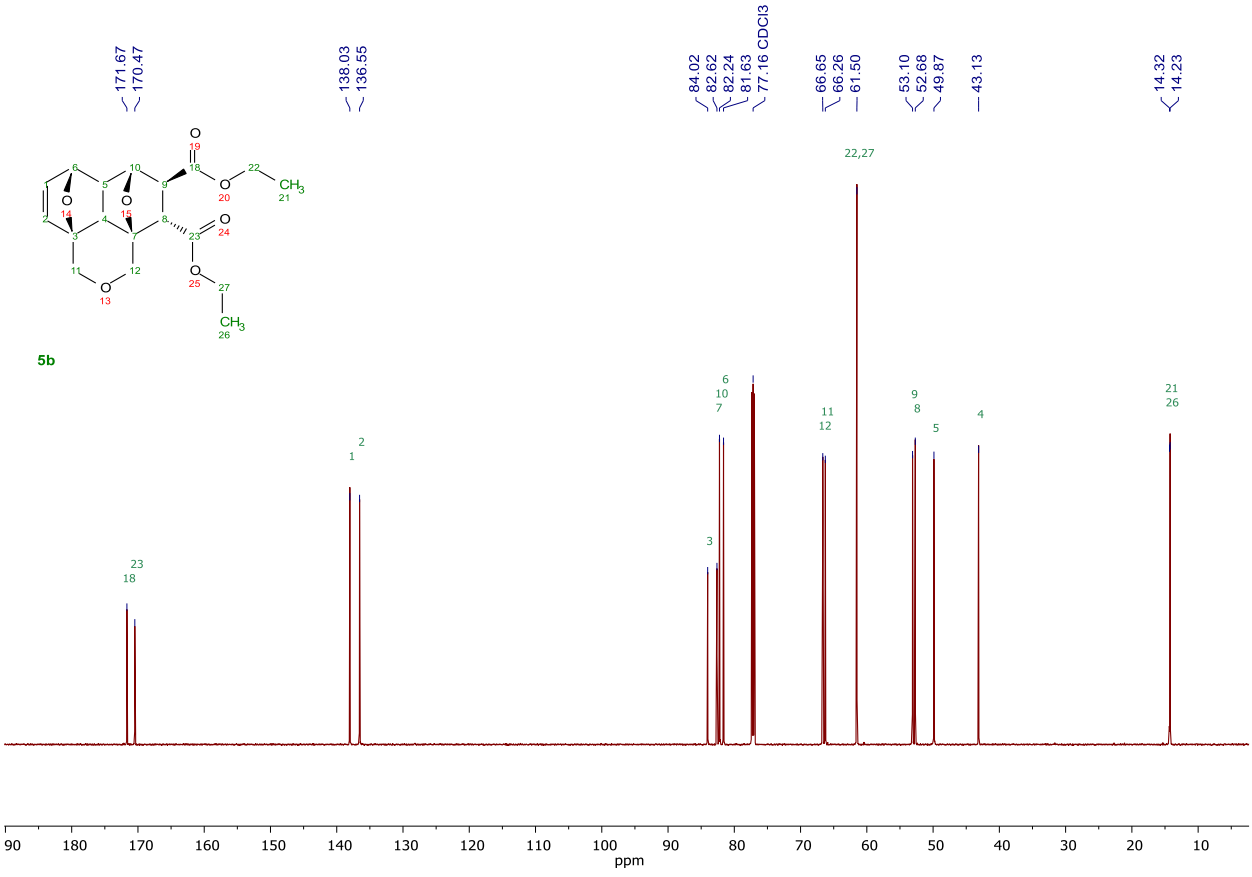
Mixture of **5b** and **6b**



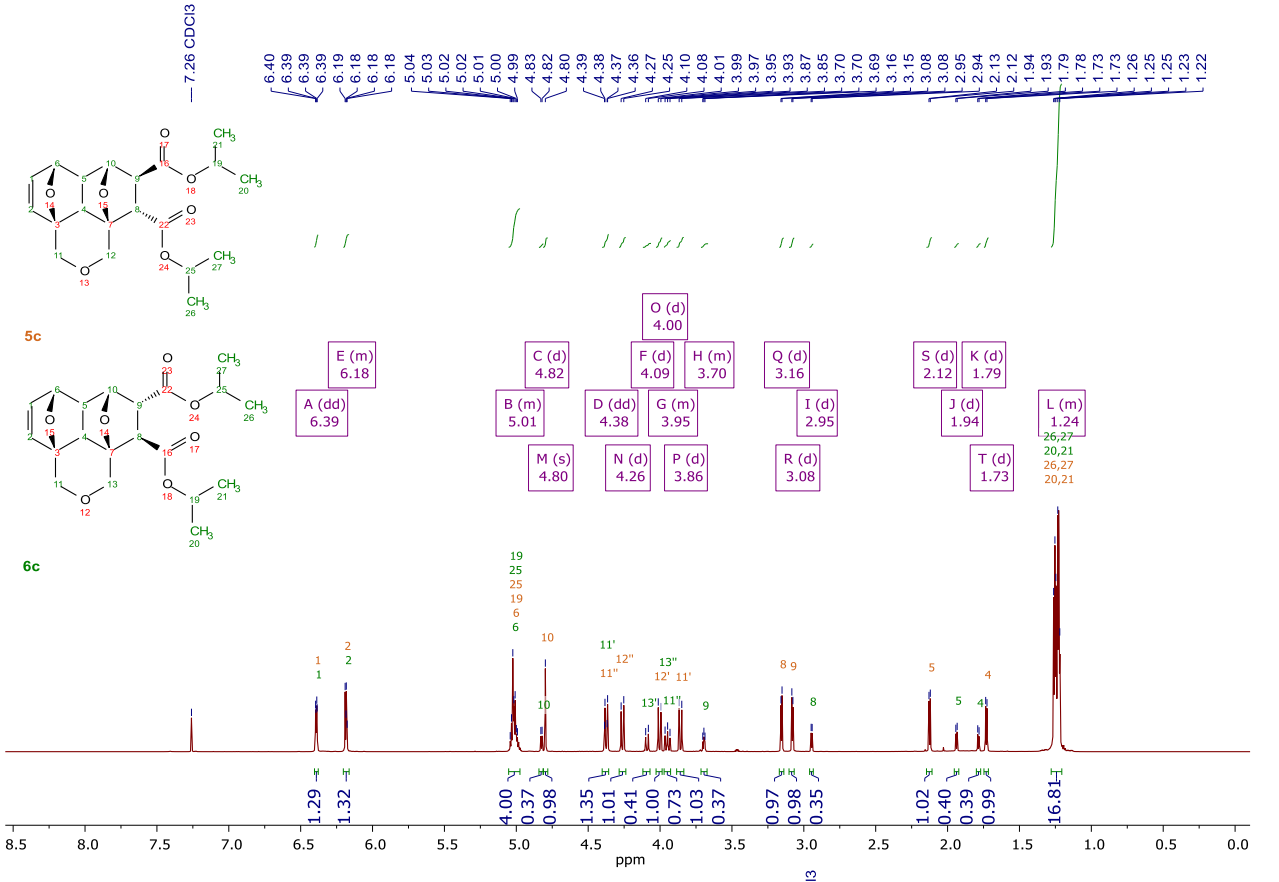


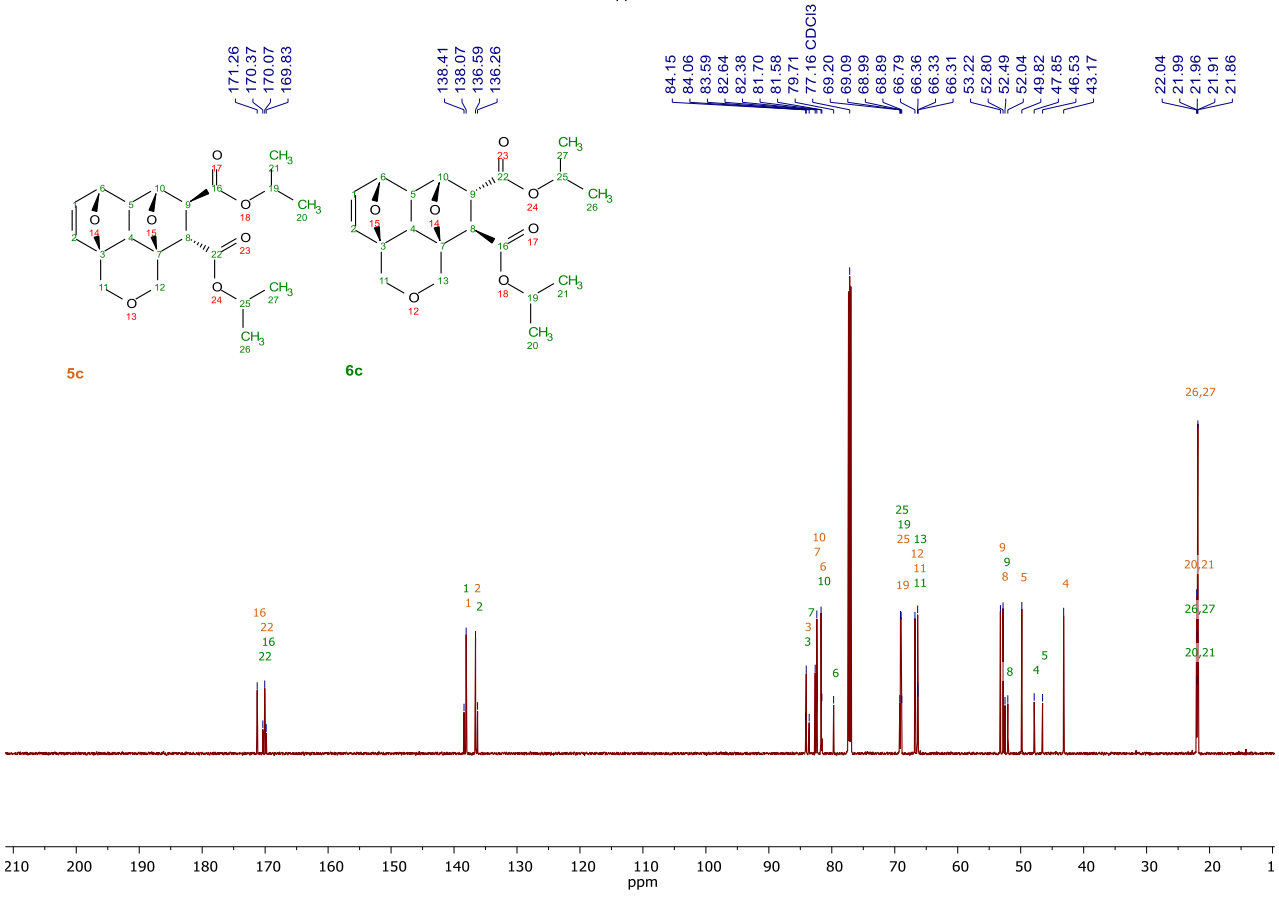
Individual compound **5b**



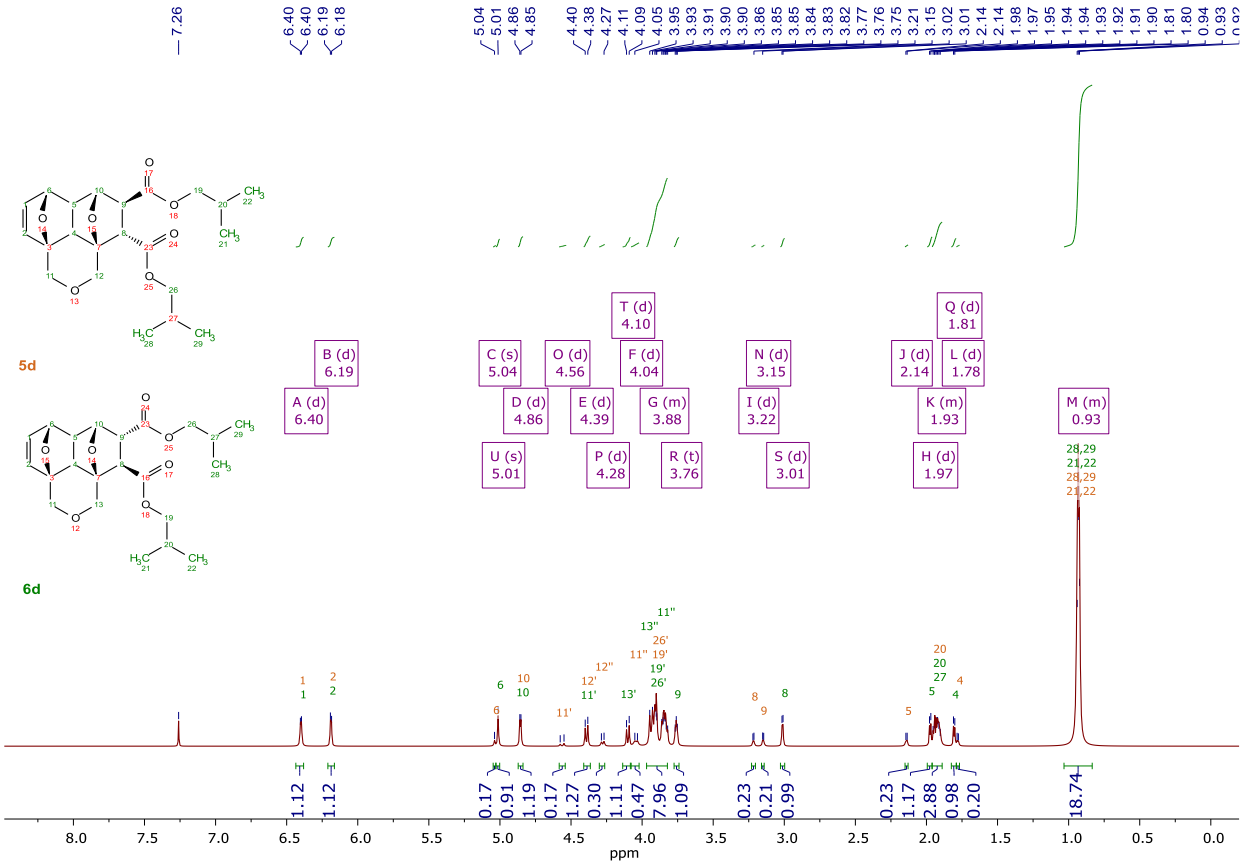


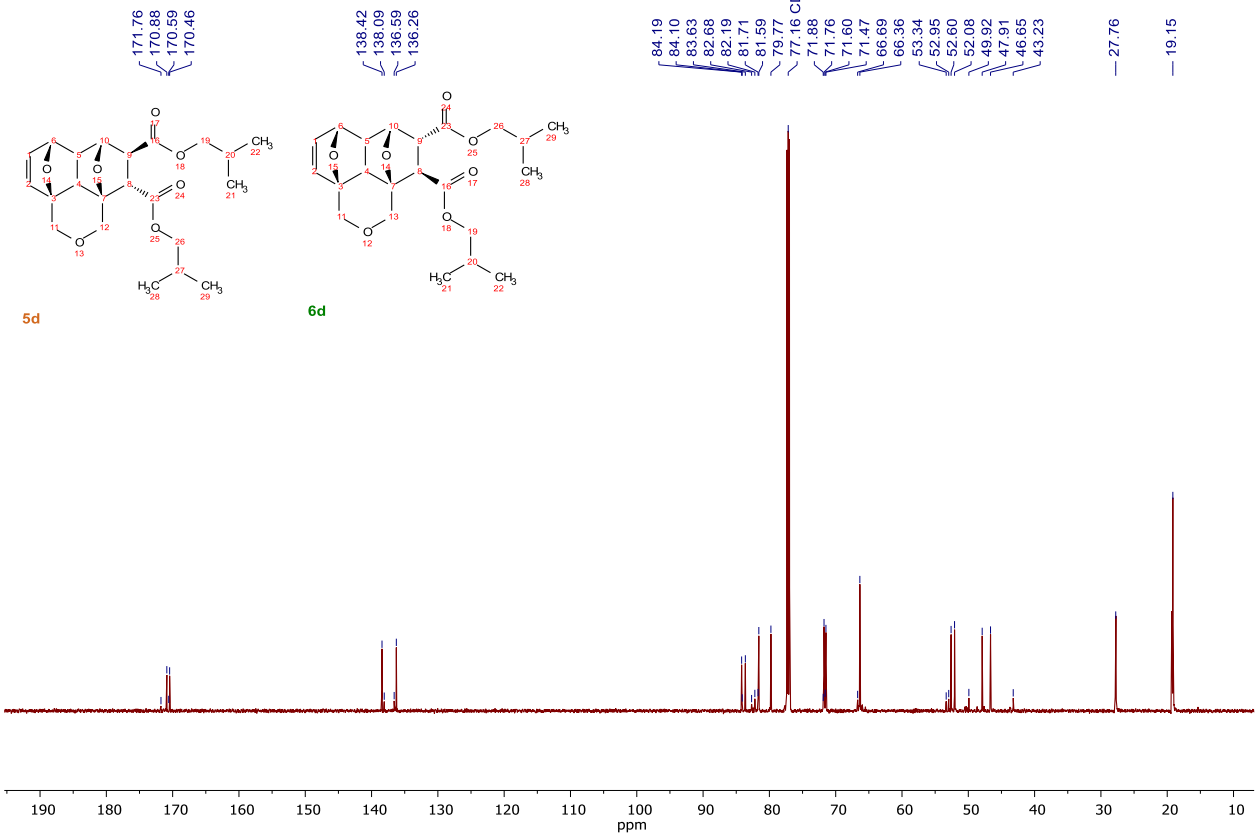
Mixture of **5c** and **6c**



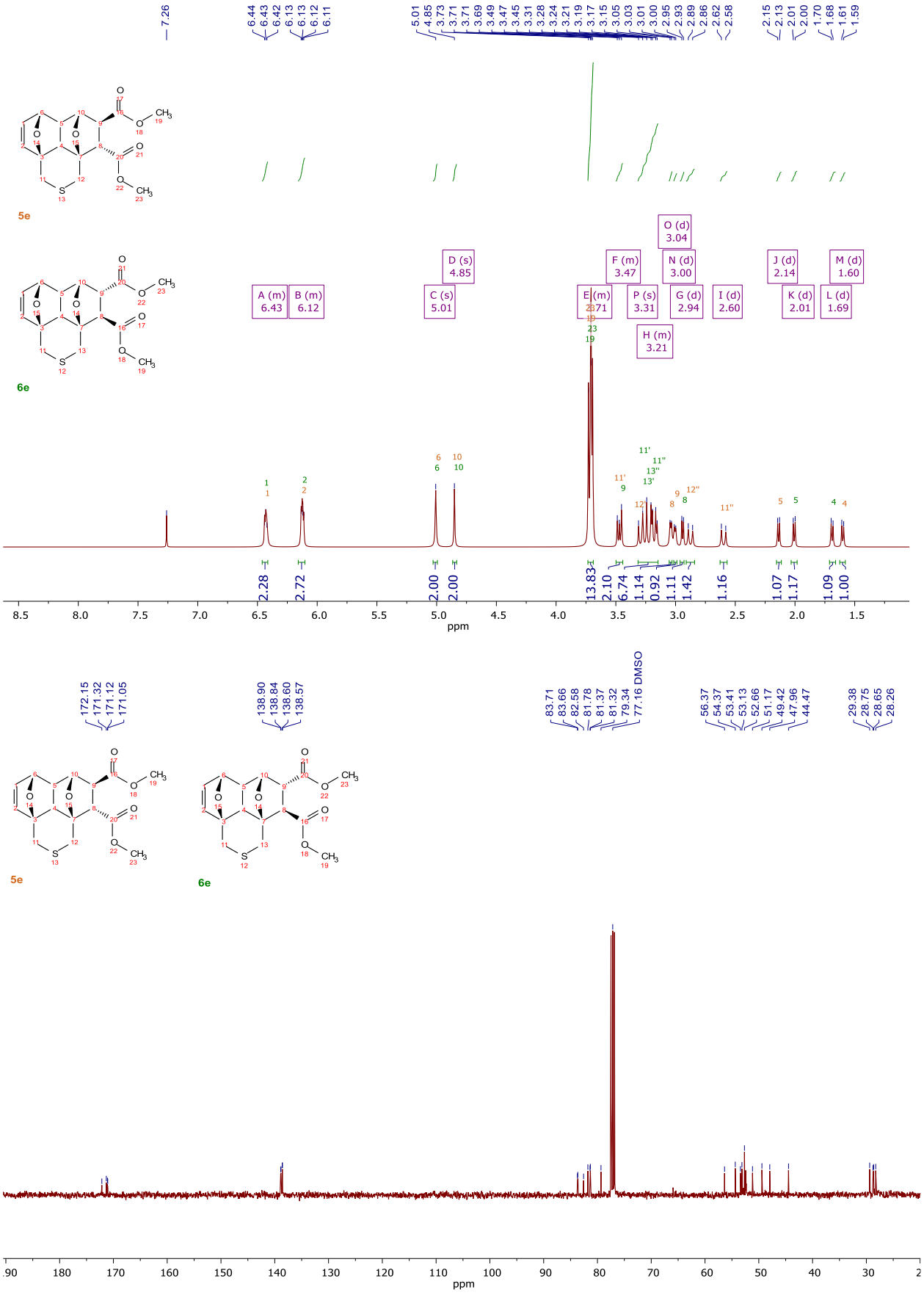


Mixture of **5d** and **6d**

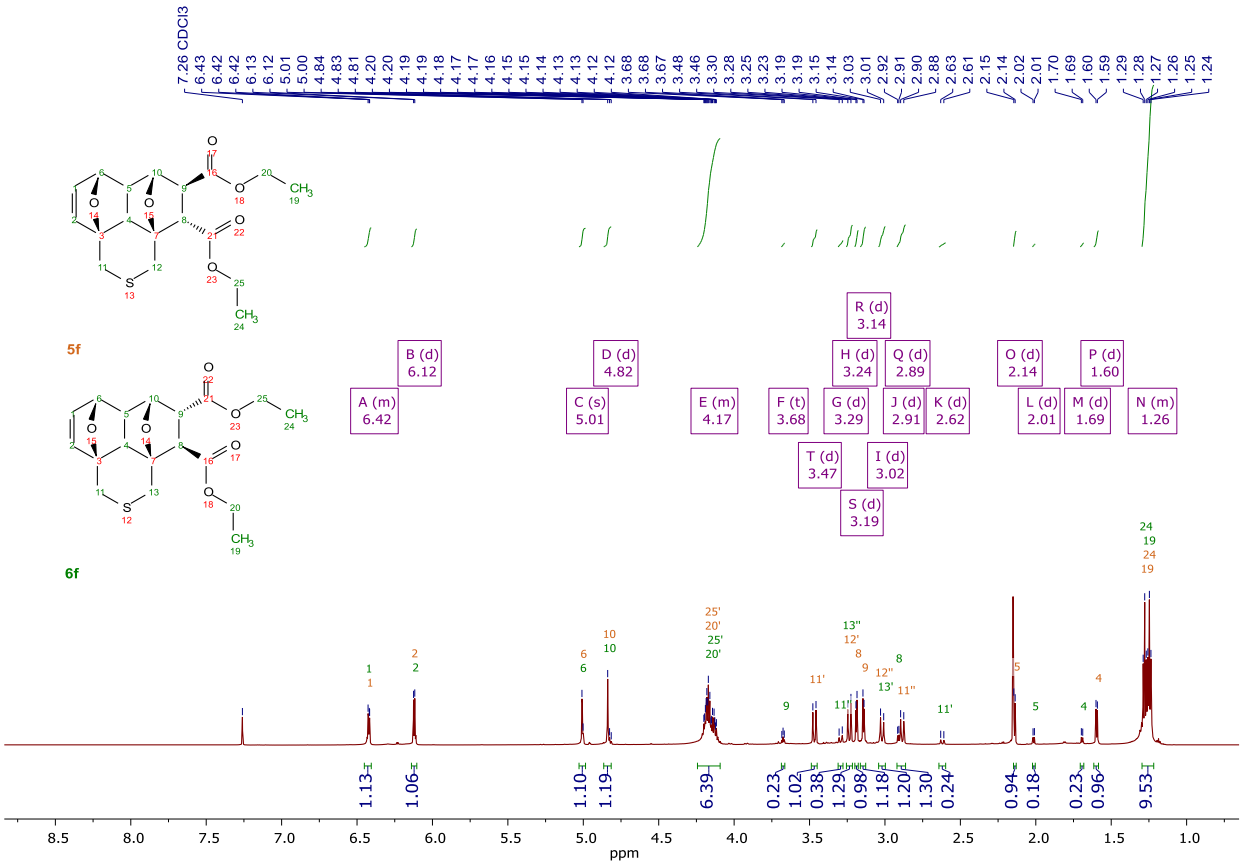


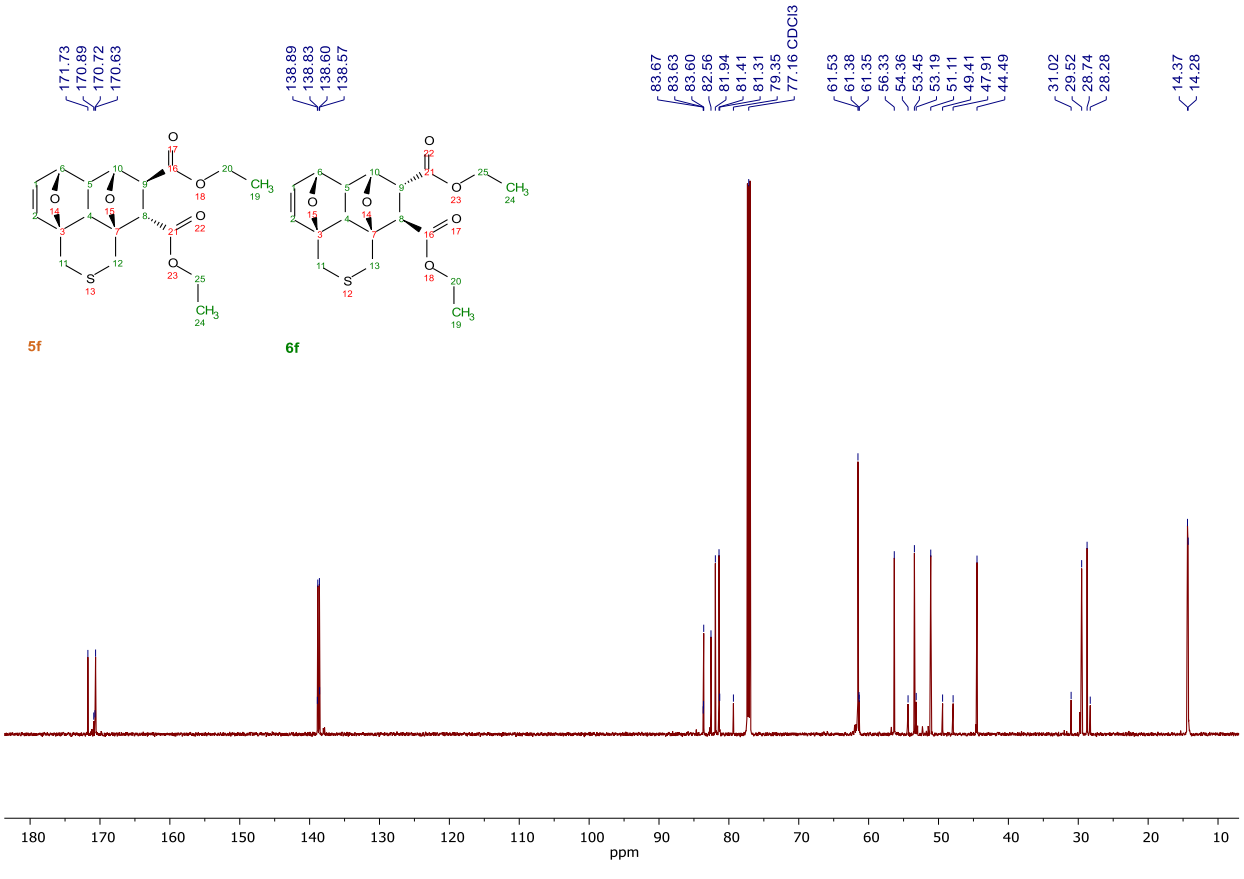


Mixture of **5e** and **6e**

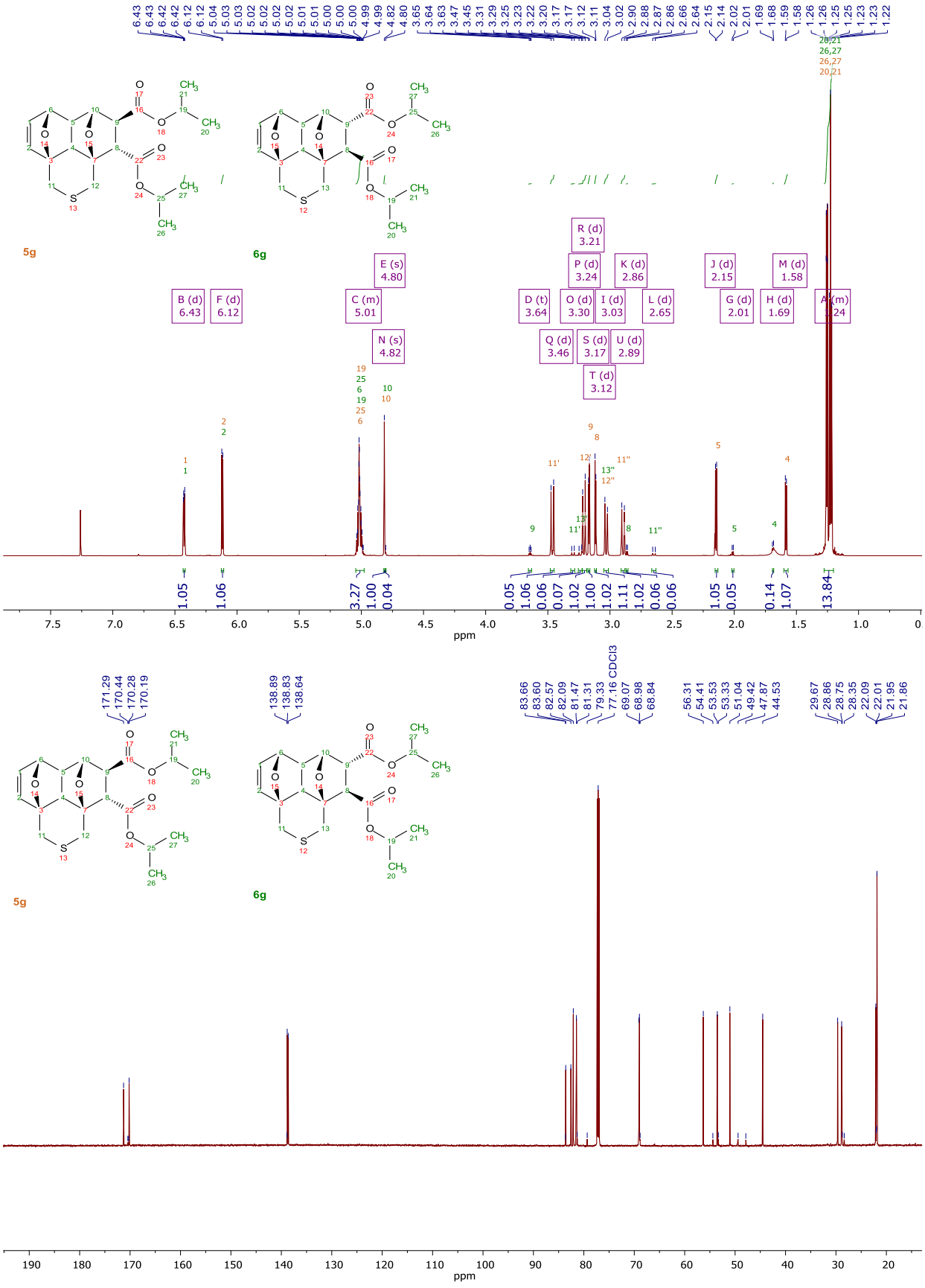


Mixture of **5f** and **6f**

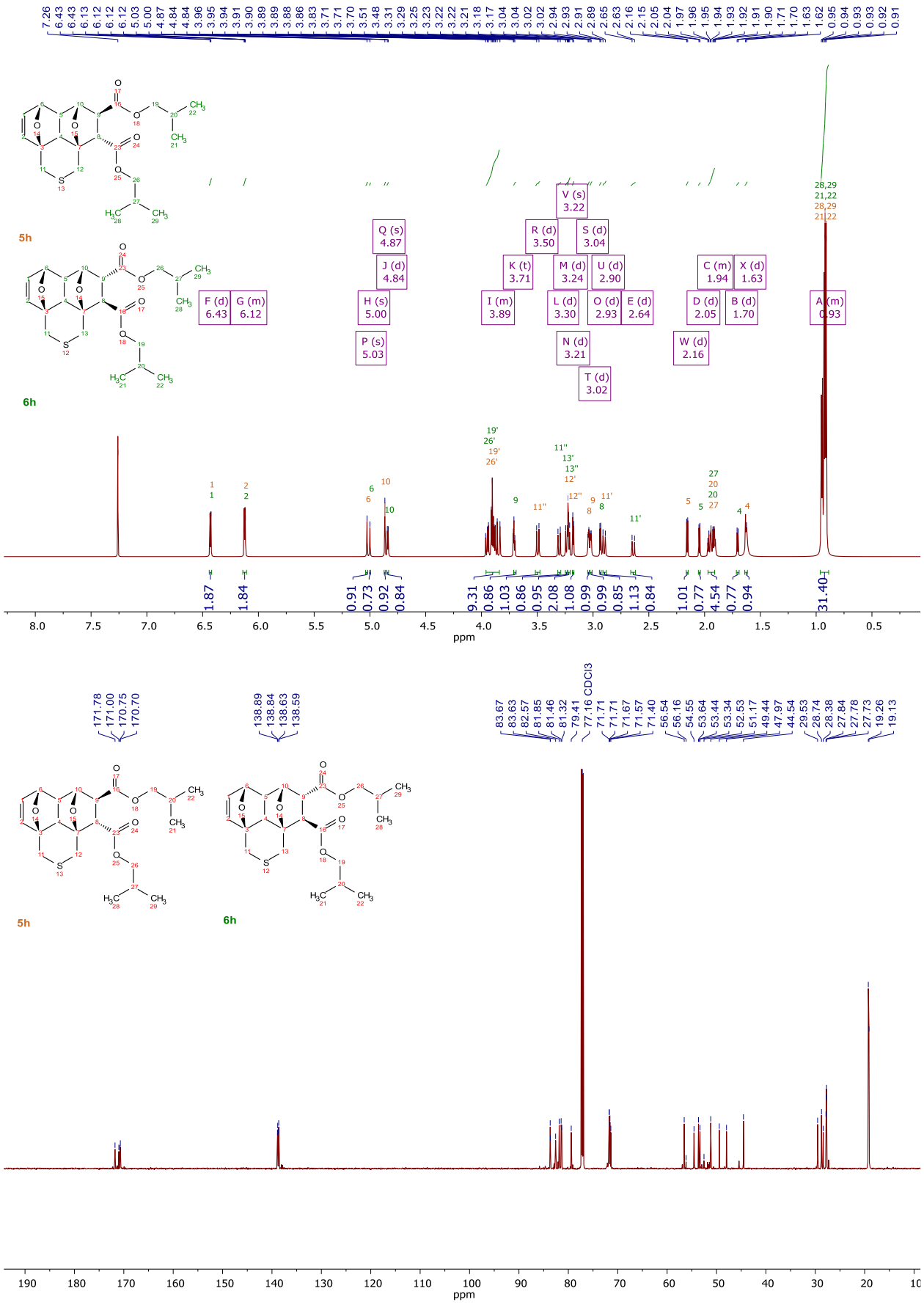




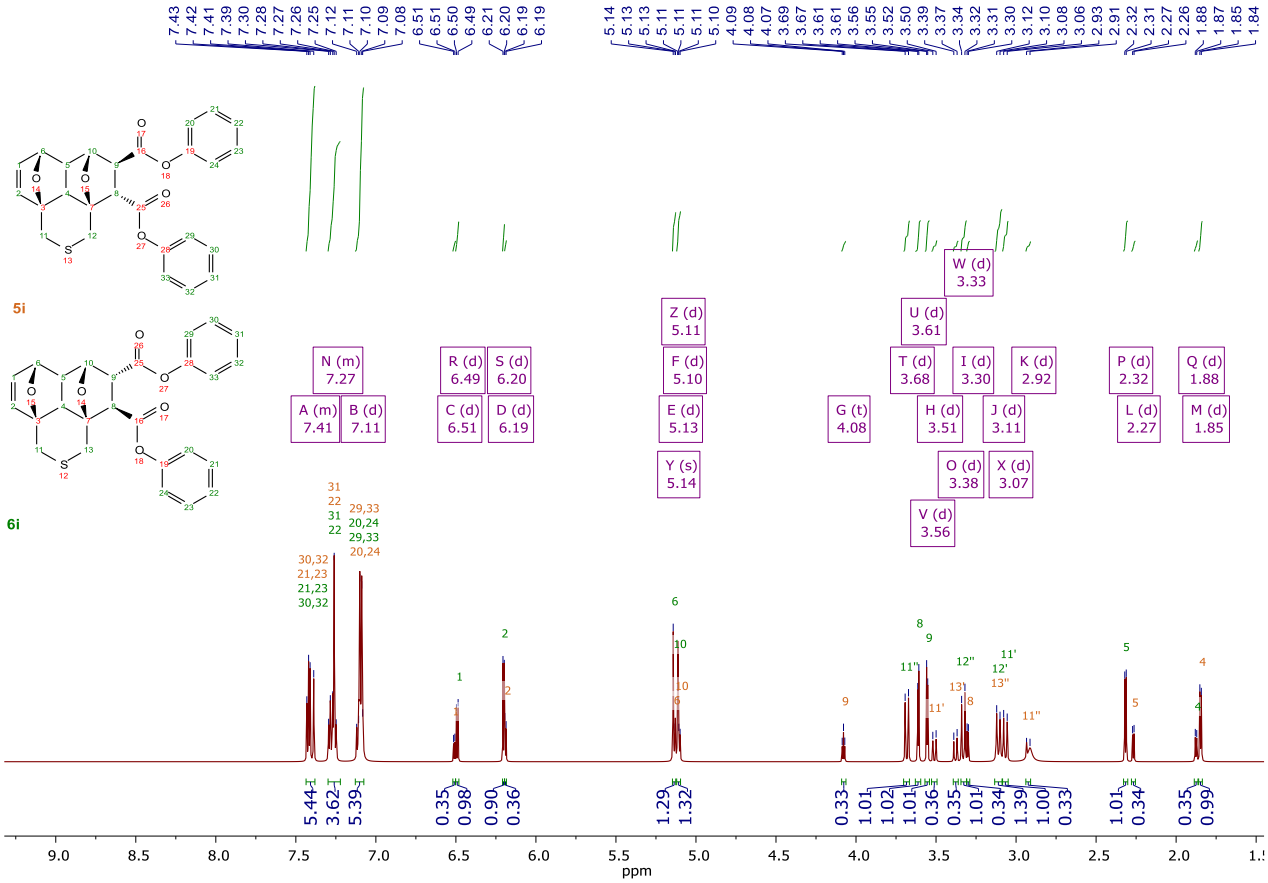
Mixture of **5g** and **6g**

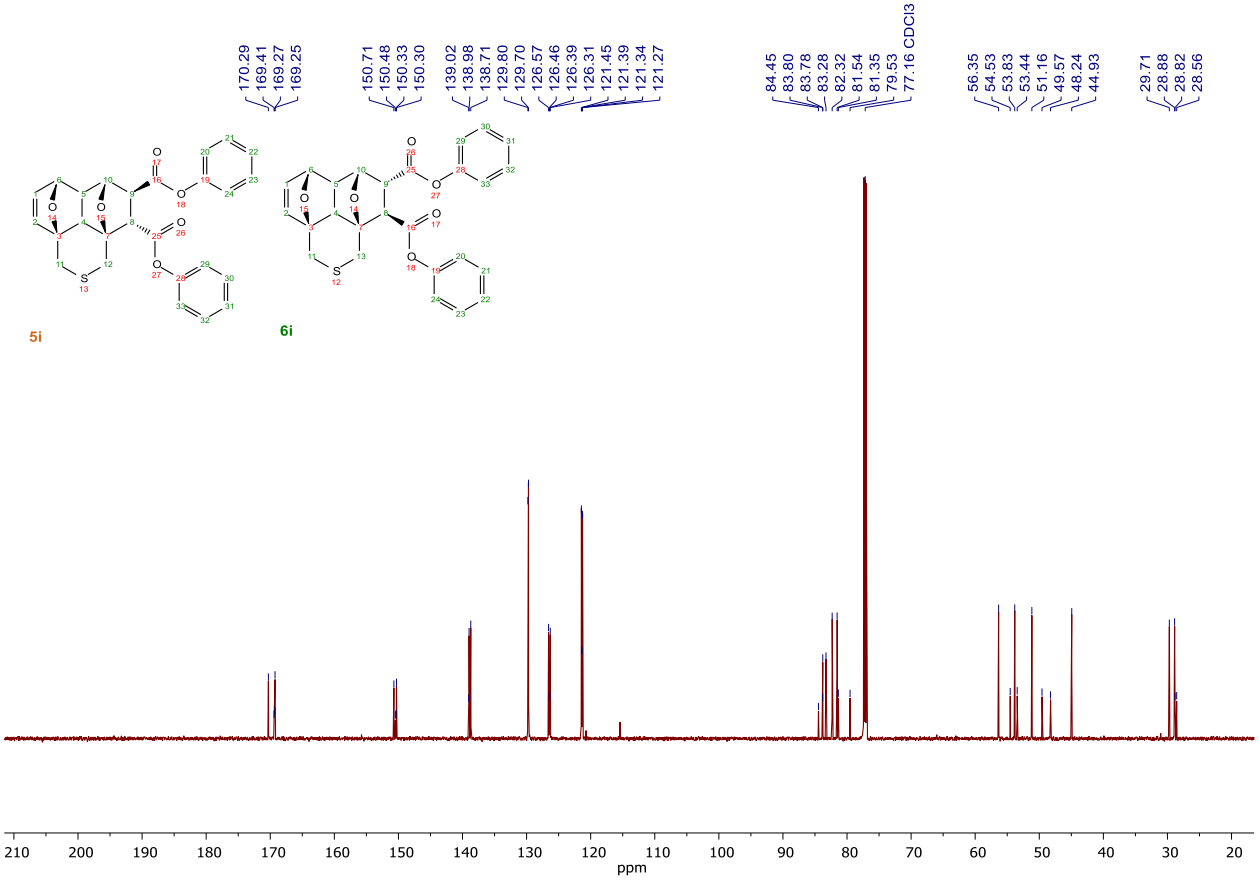


Mixture of **5h** and **6h**

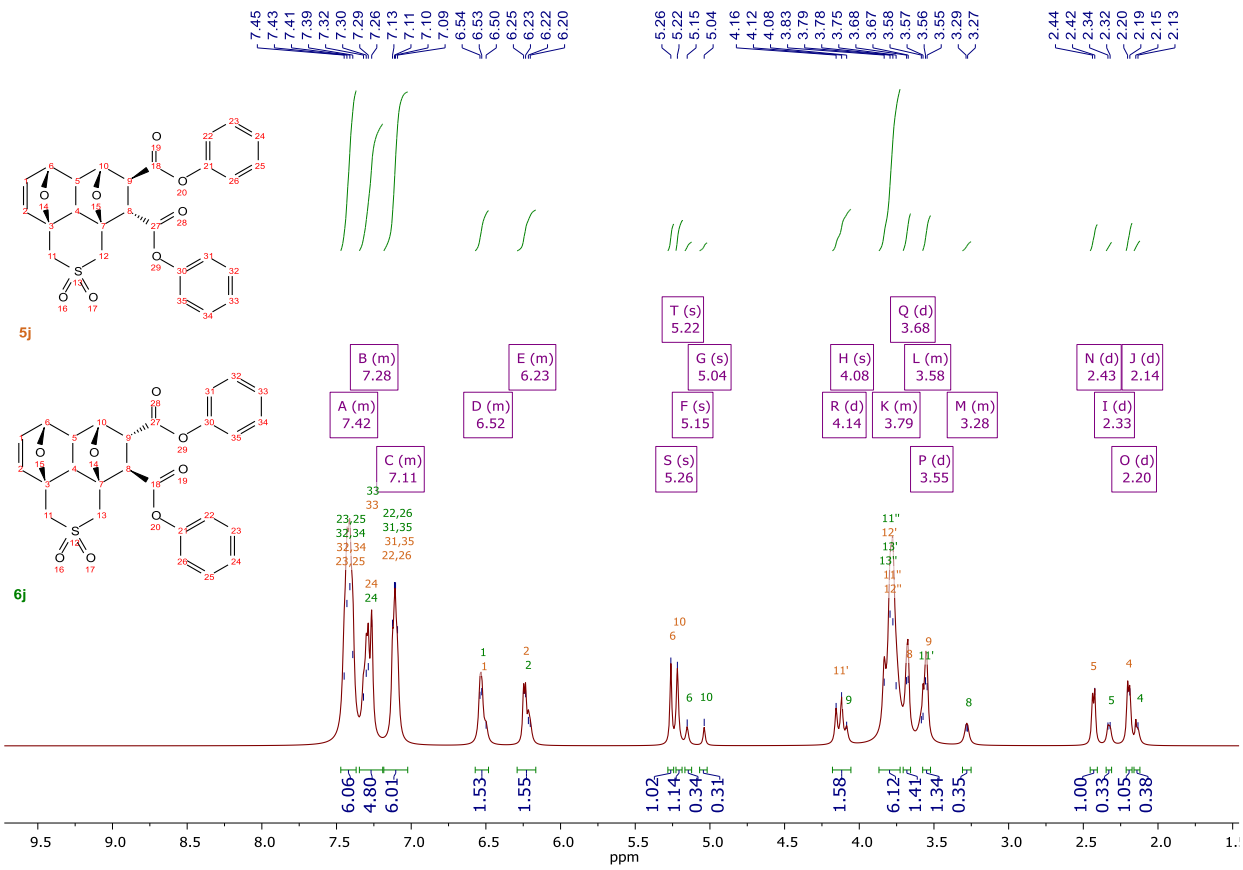


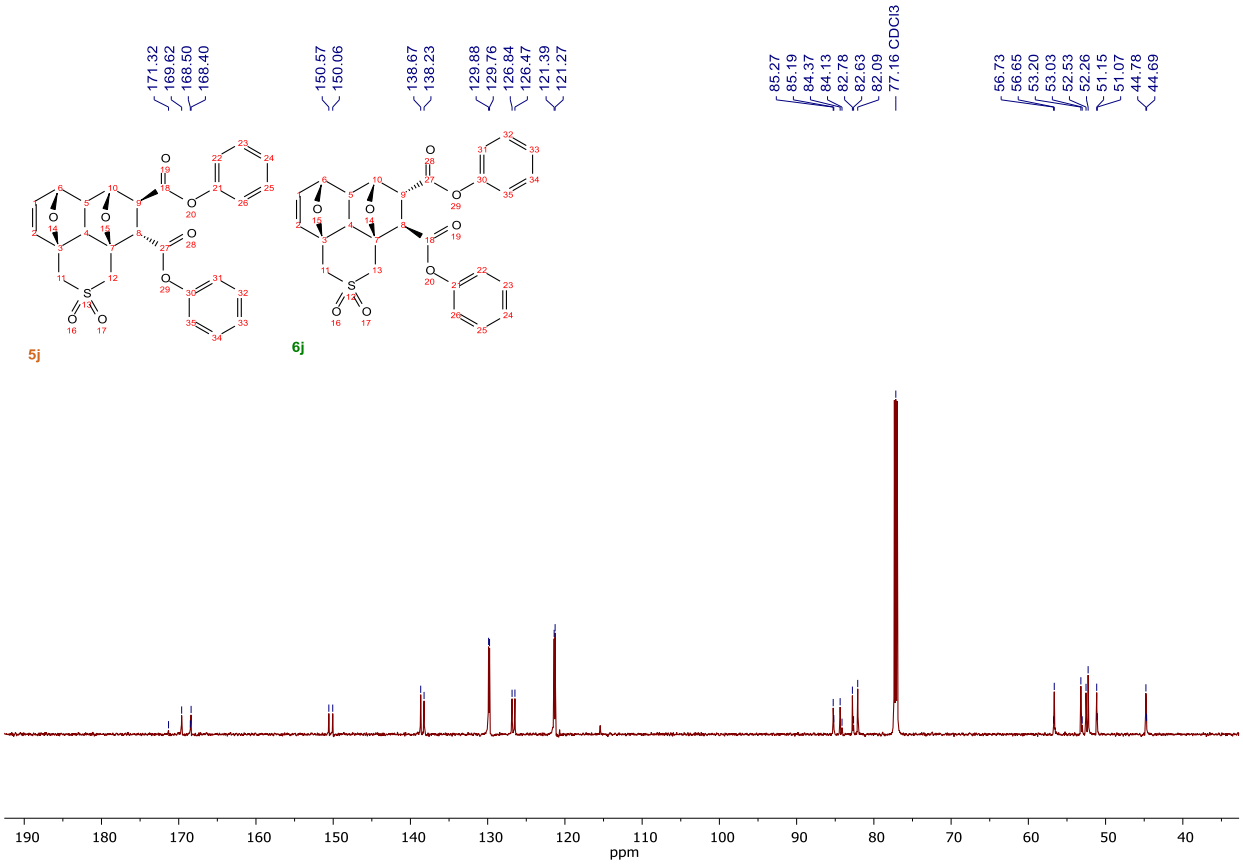
Mixture of **5i** and **6i**



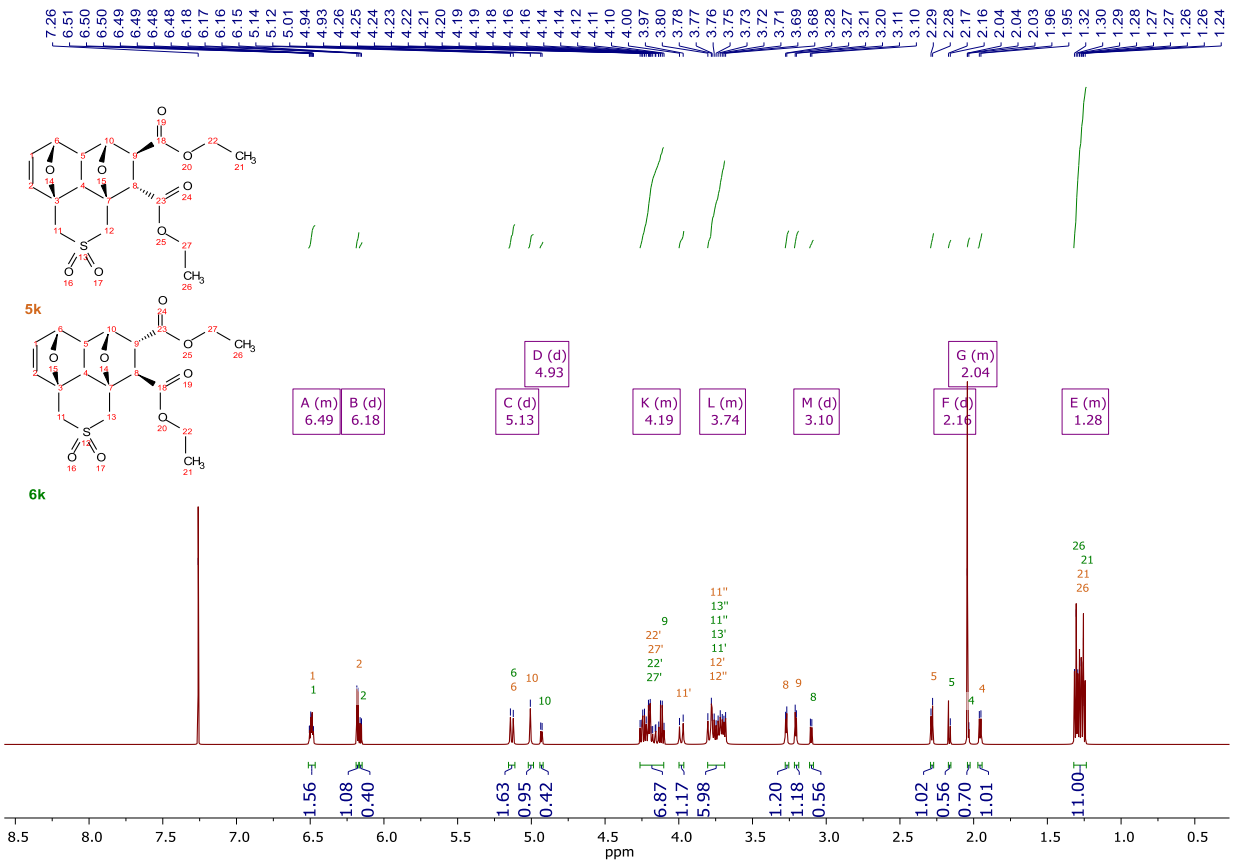


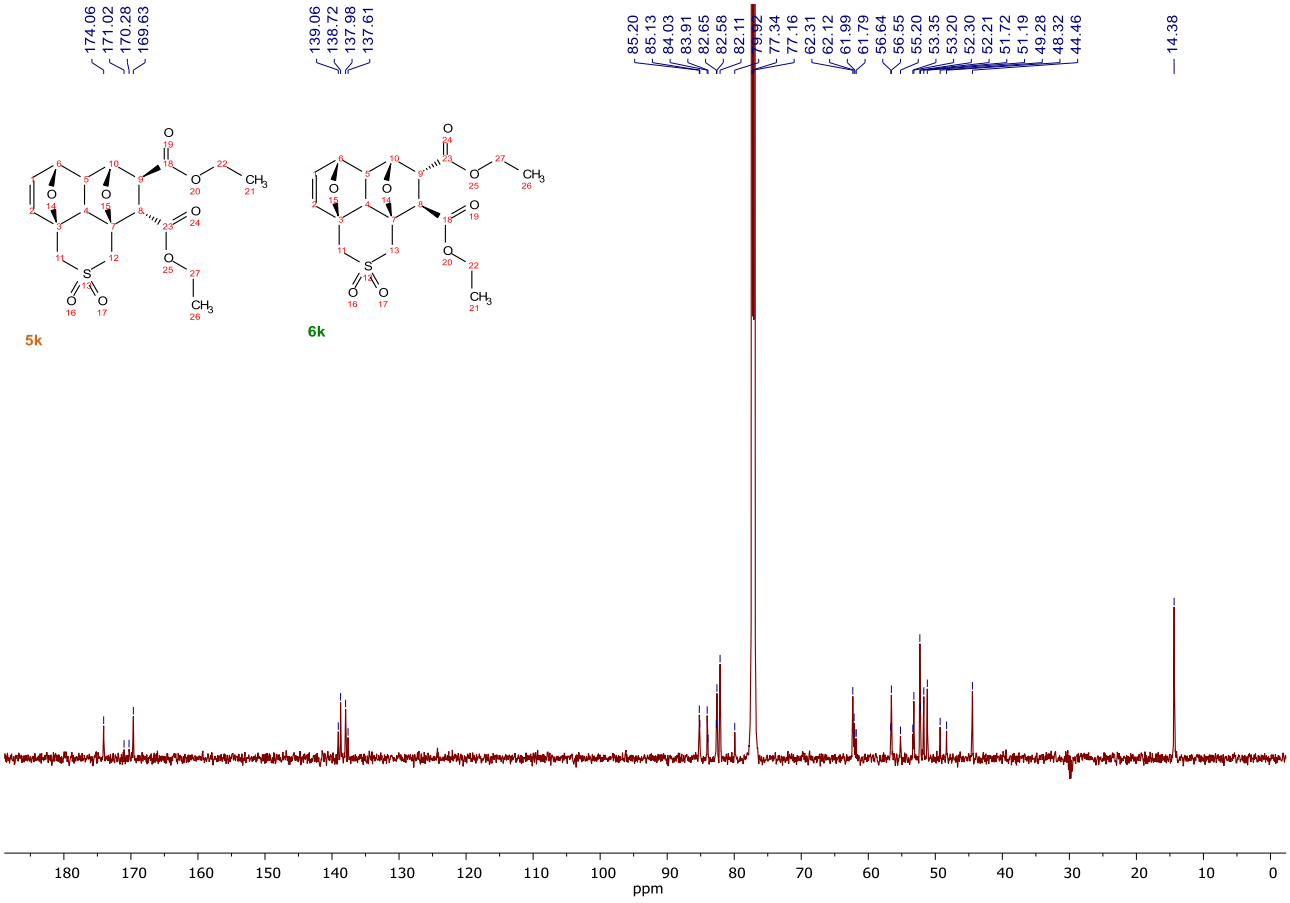
Mixture of **5j** and **6j**



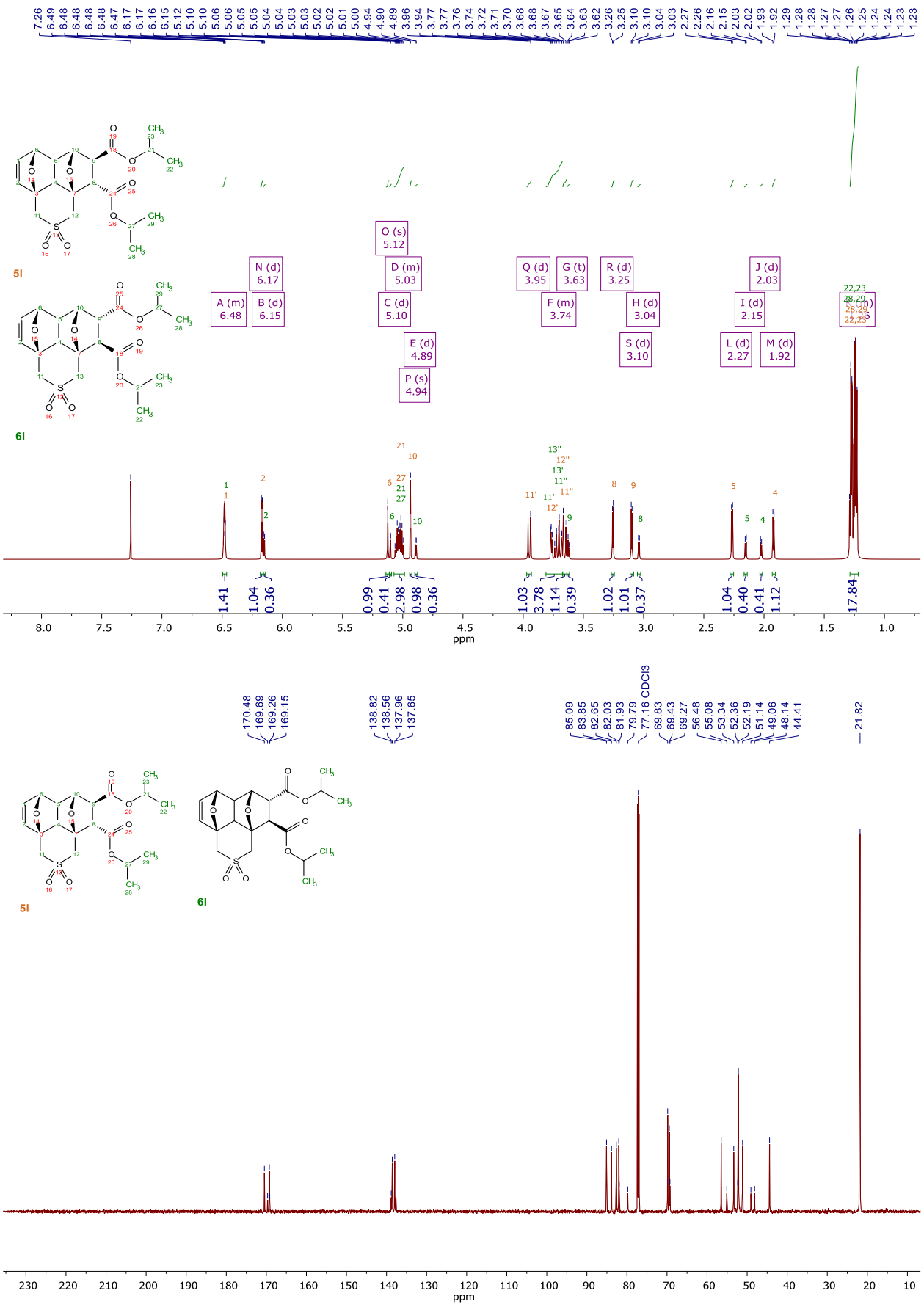


Mixture of **5k** and **6k**

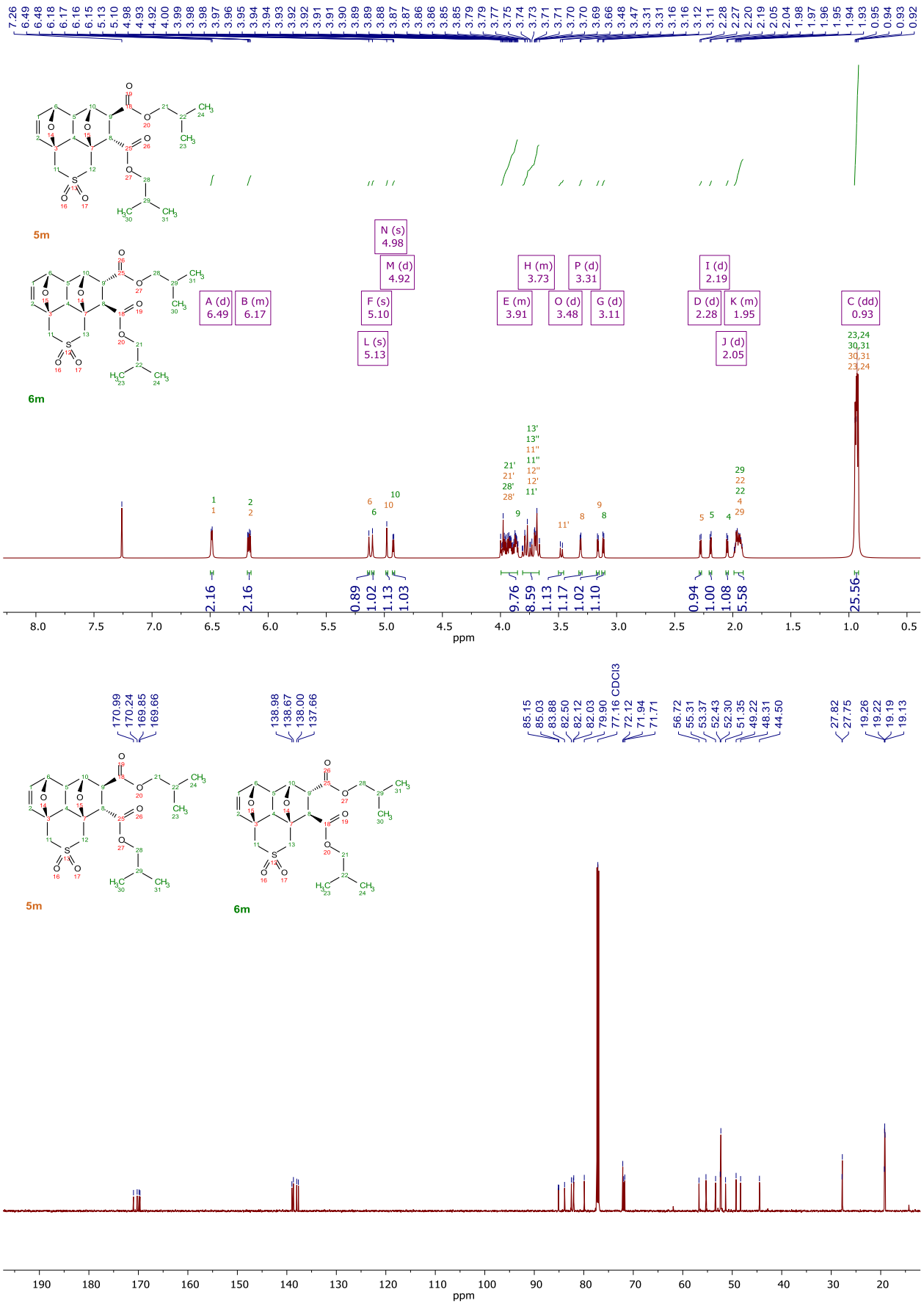




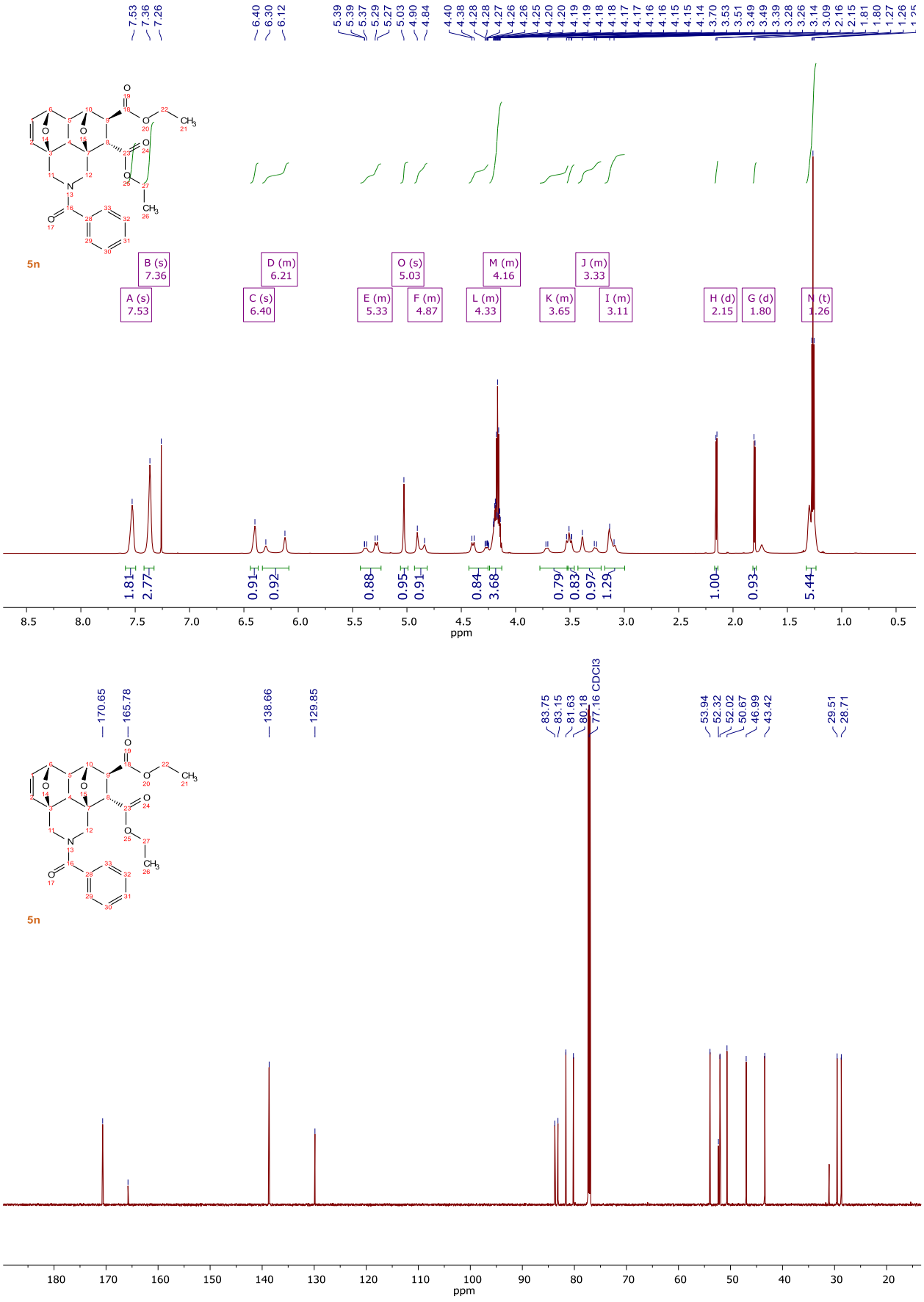
Mixture of **5l** and **6l**



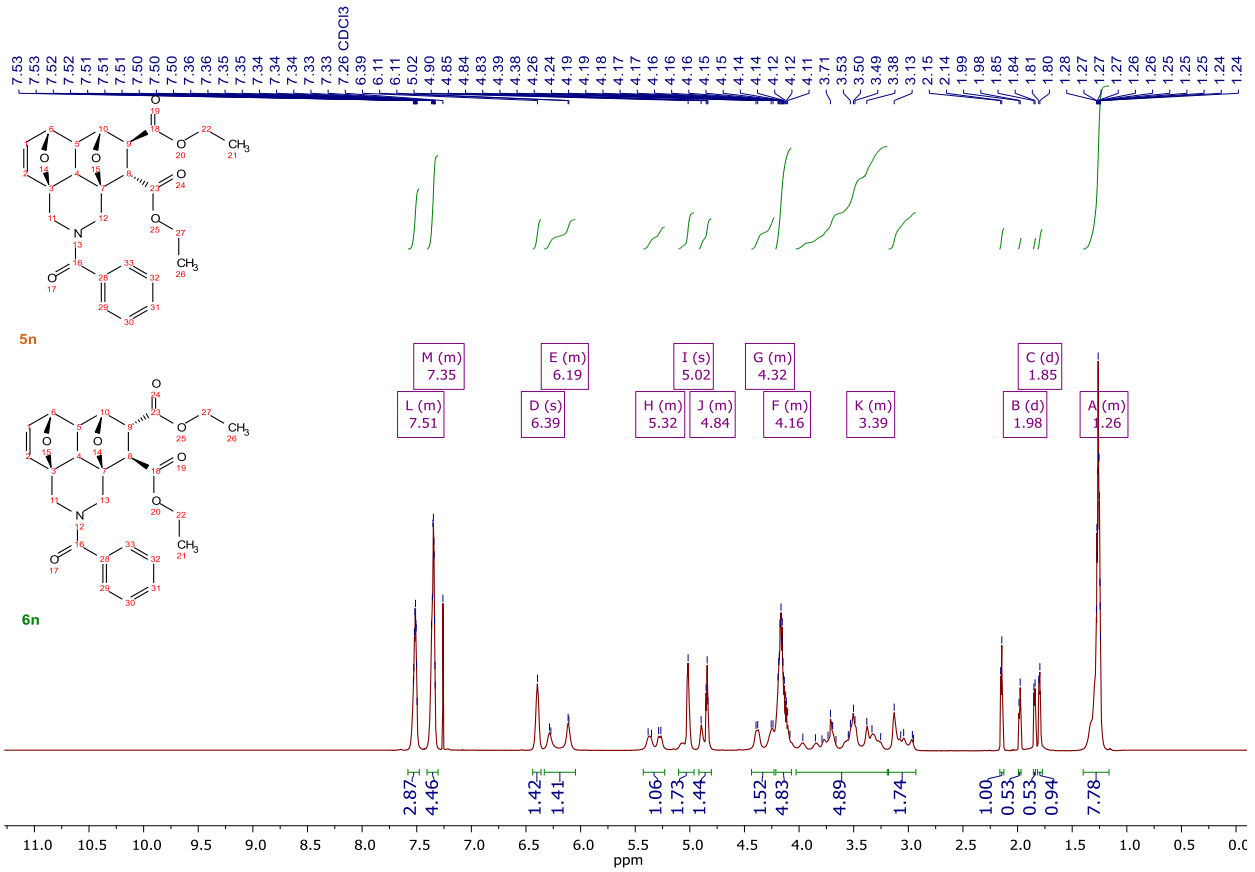
Mixture of **5m** and **6m**

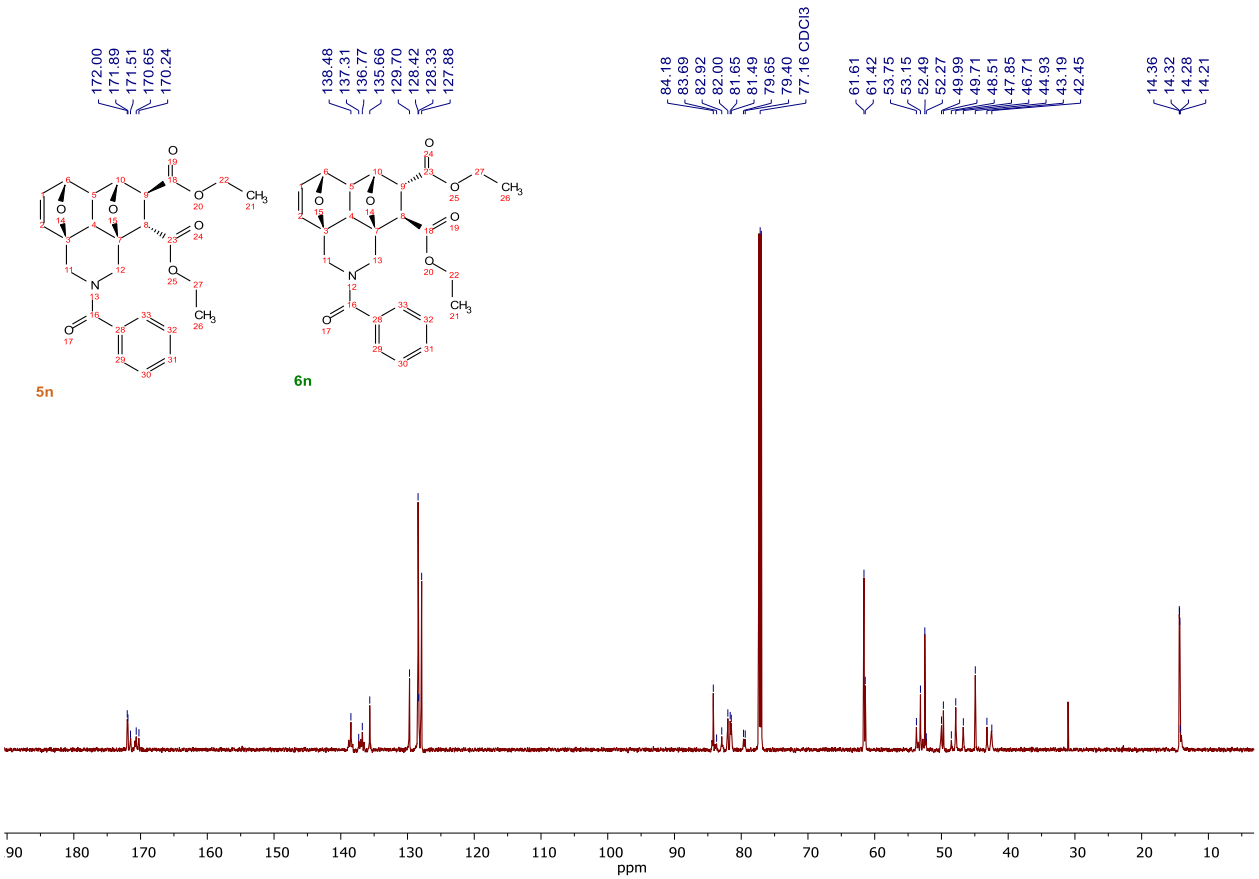


Individual compound **5n**

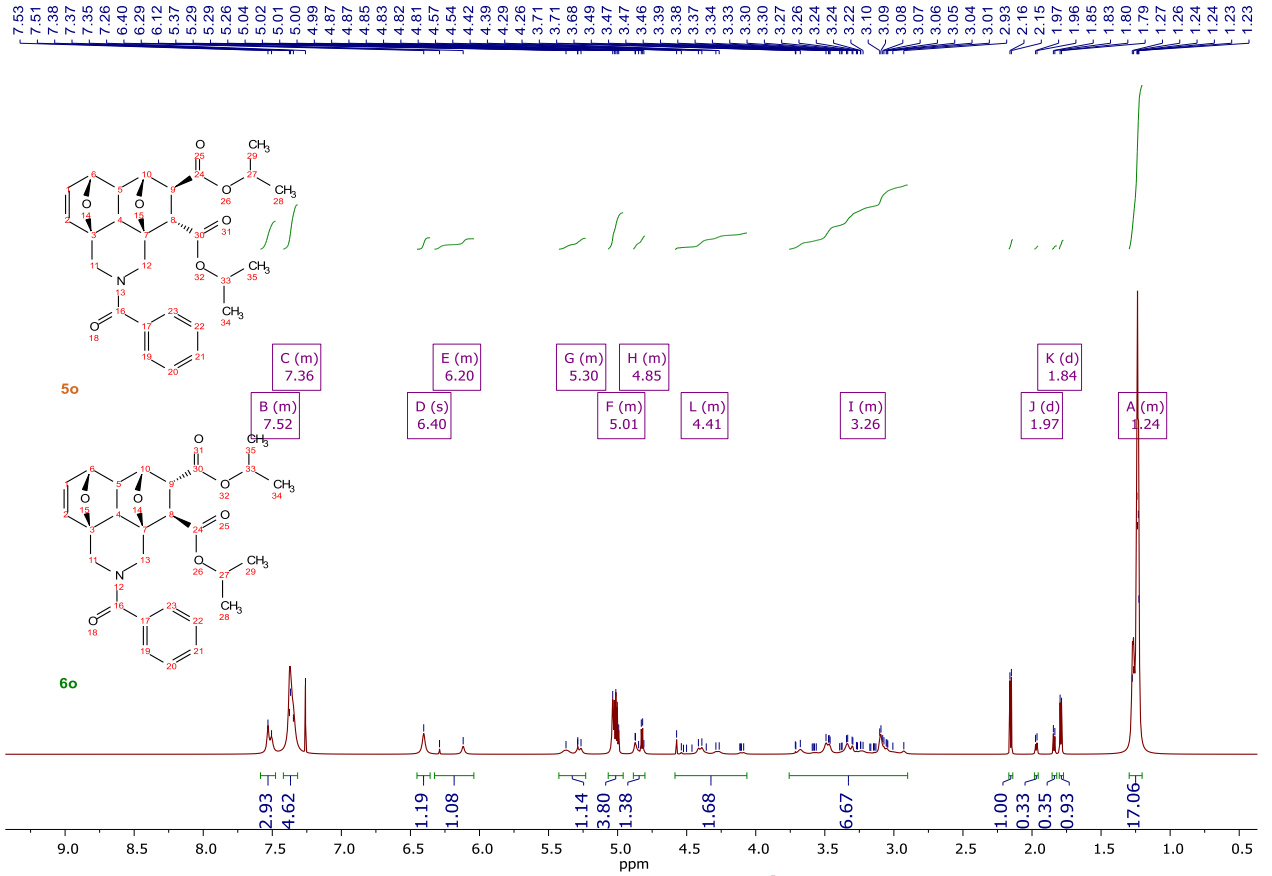


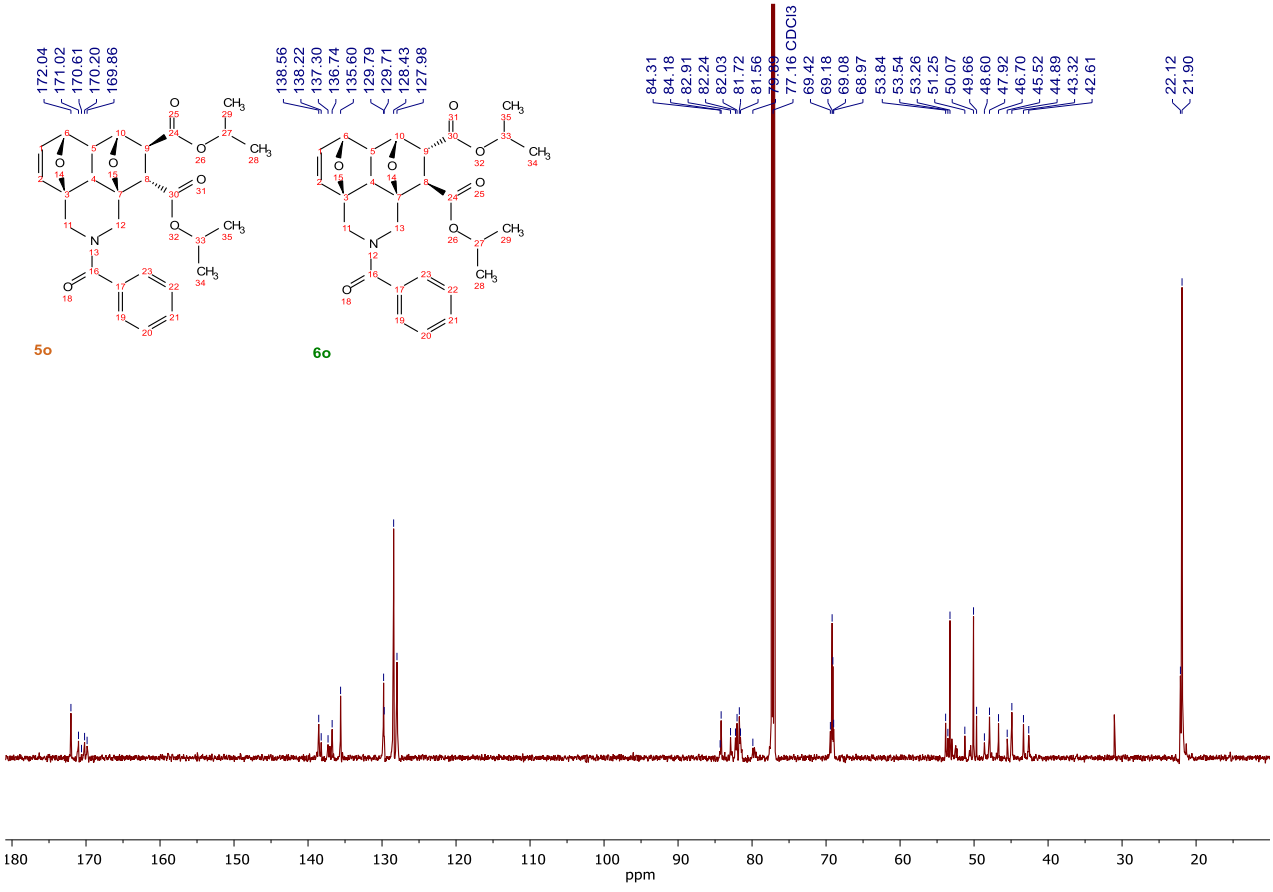
Mixture of **5n** and **6n**



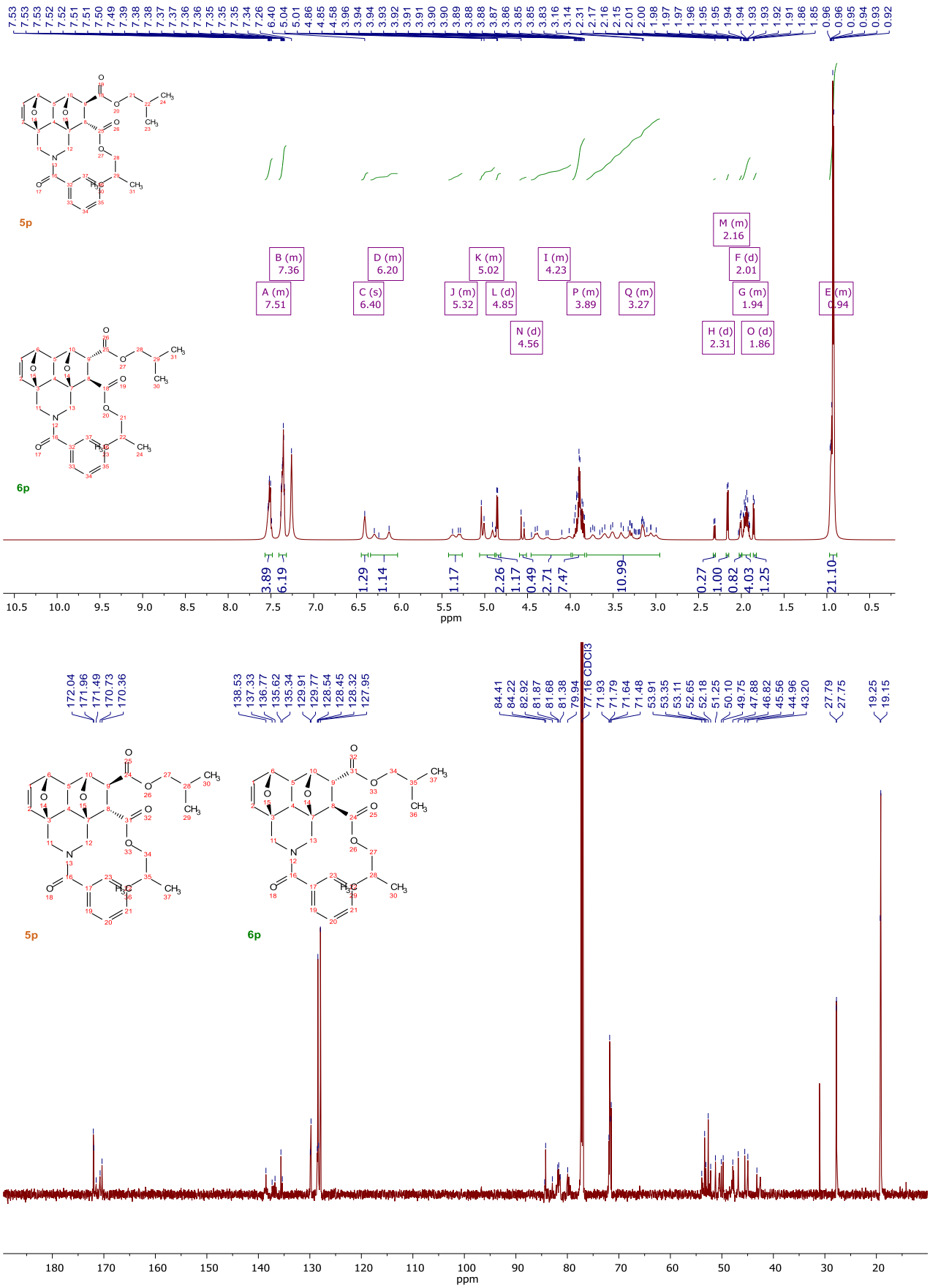


Mixture of **5o** and **6o**

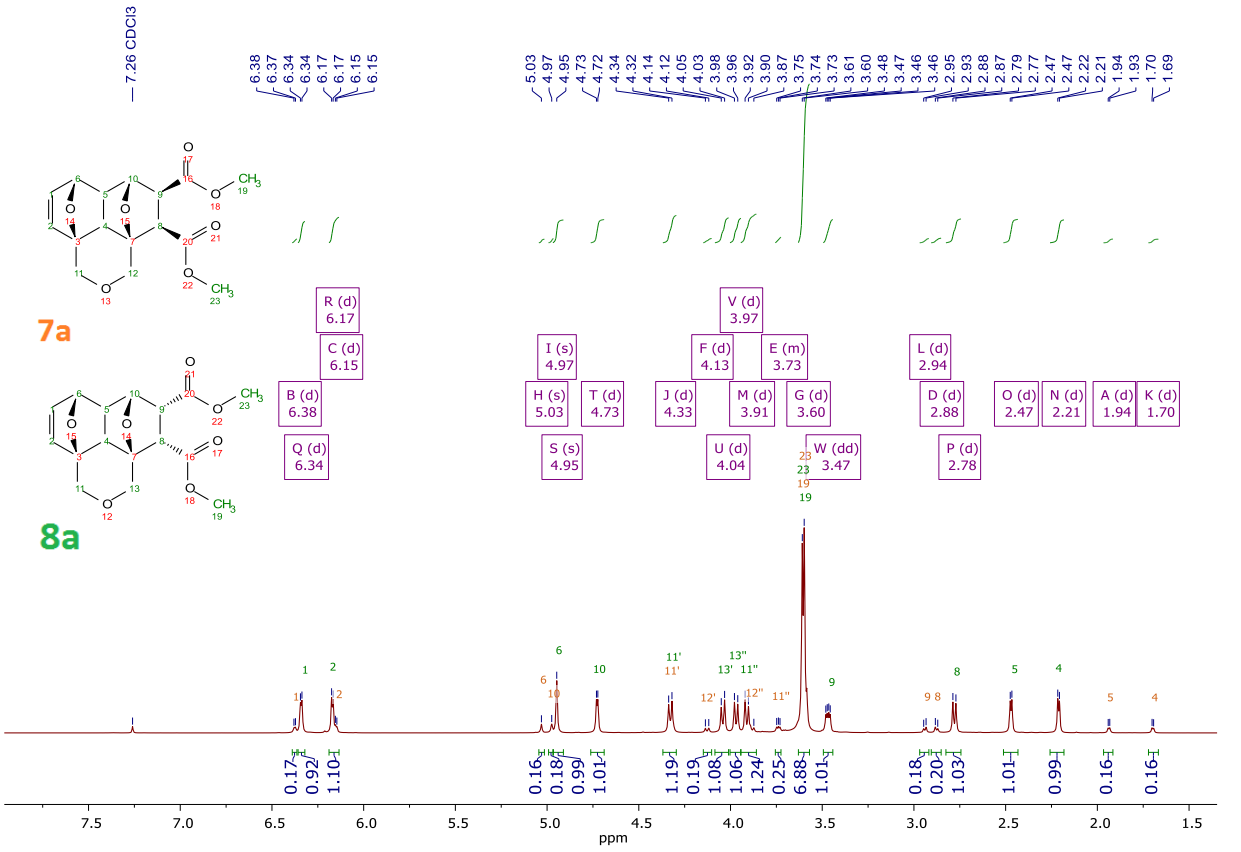


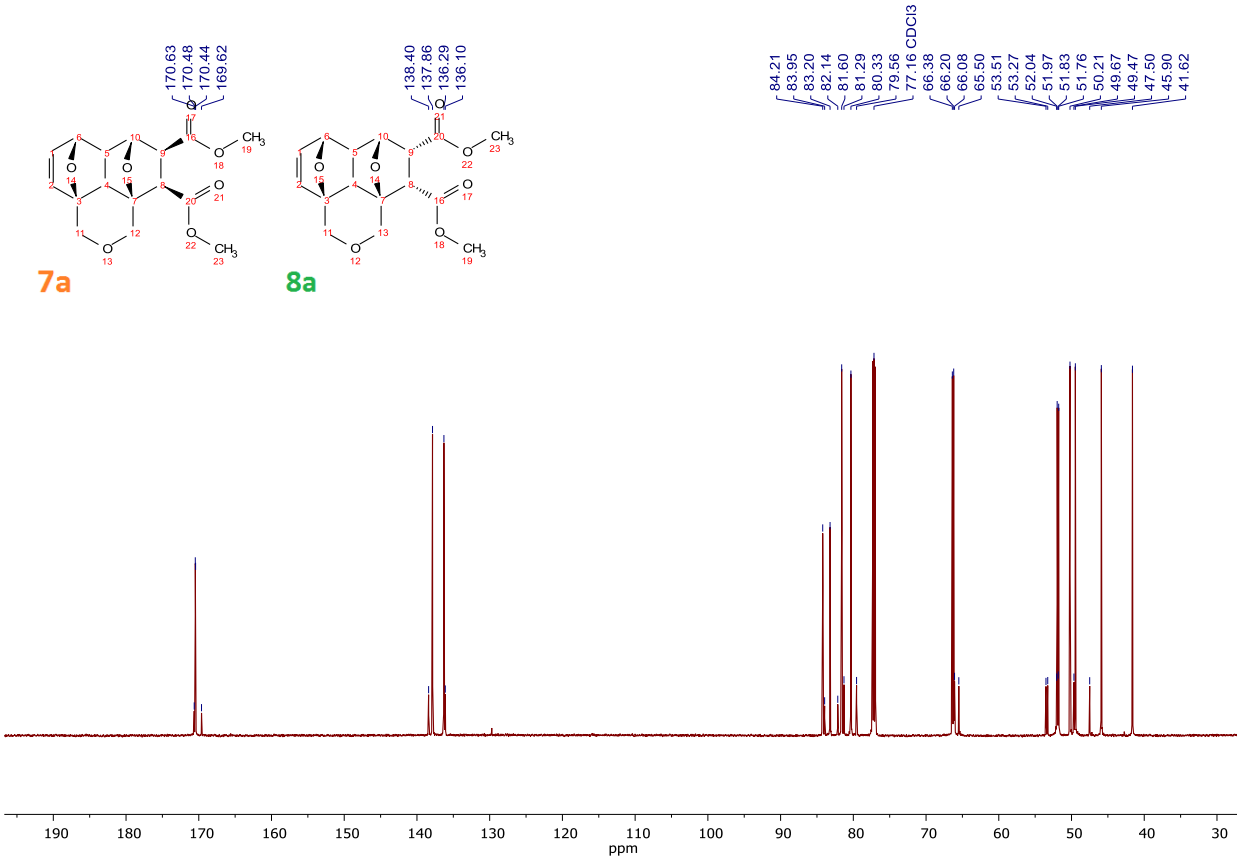


Mixture of **5p** and **6p**

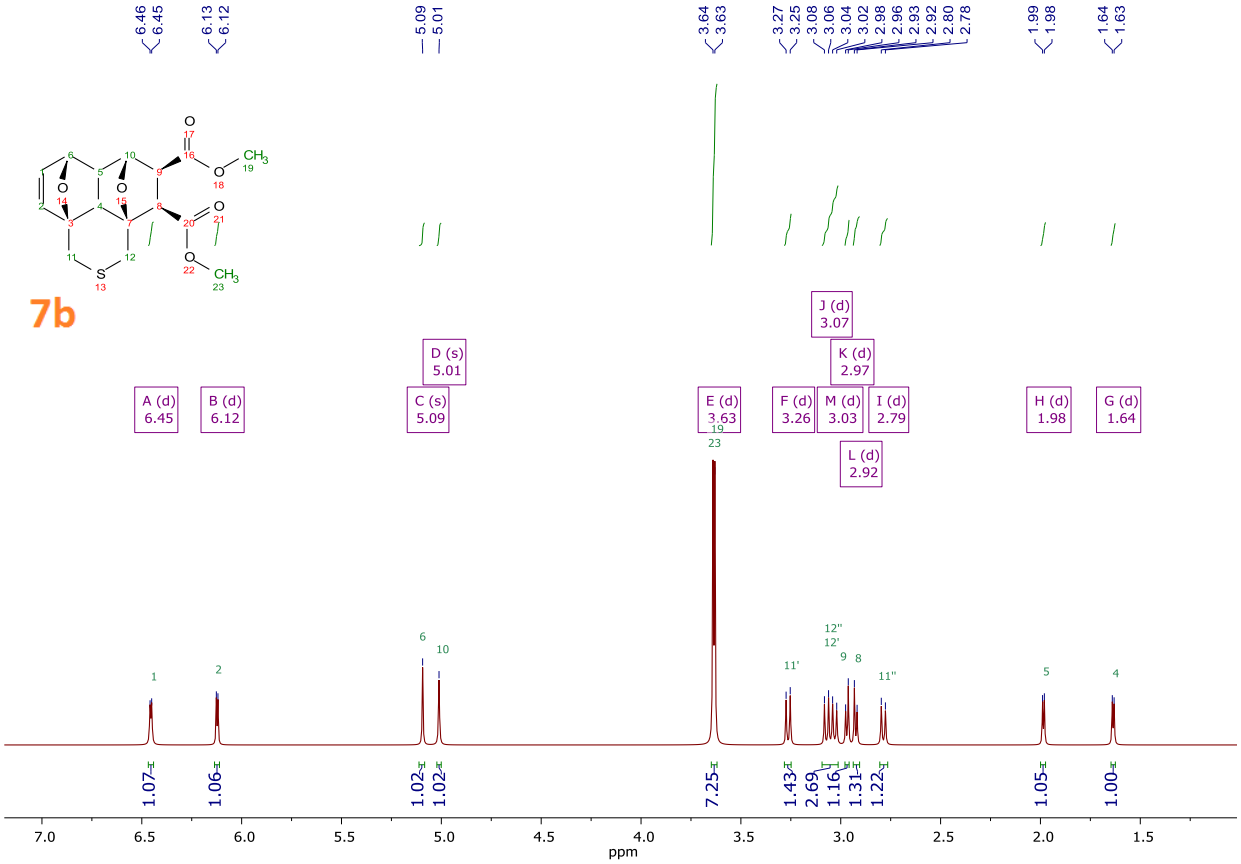


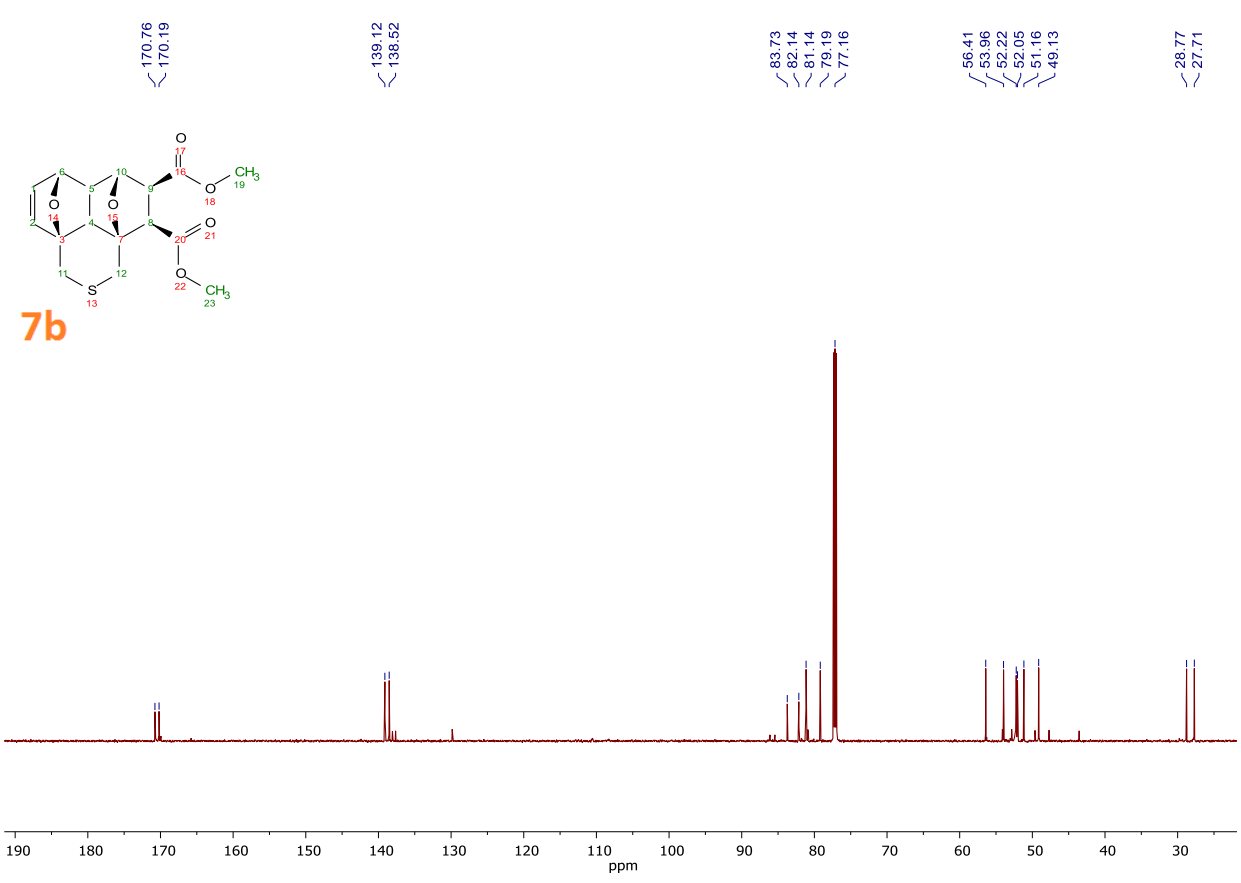
Mixture of **7a** and **8a**



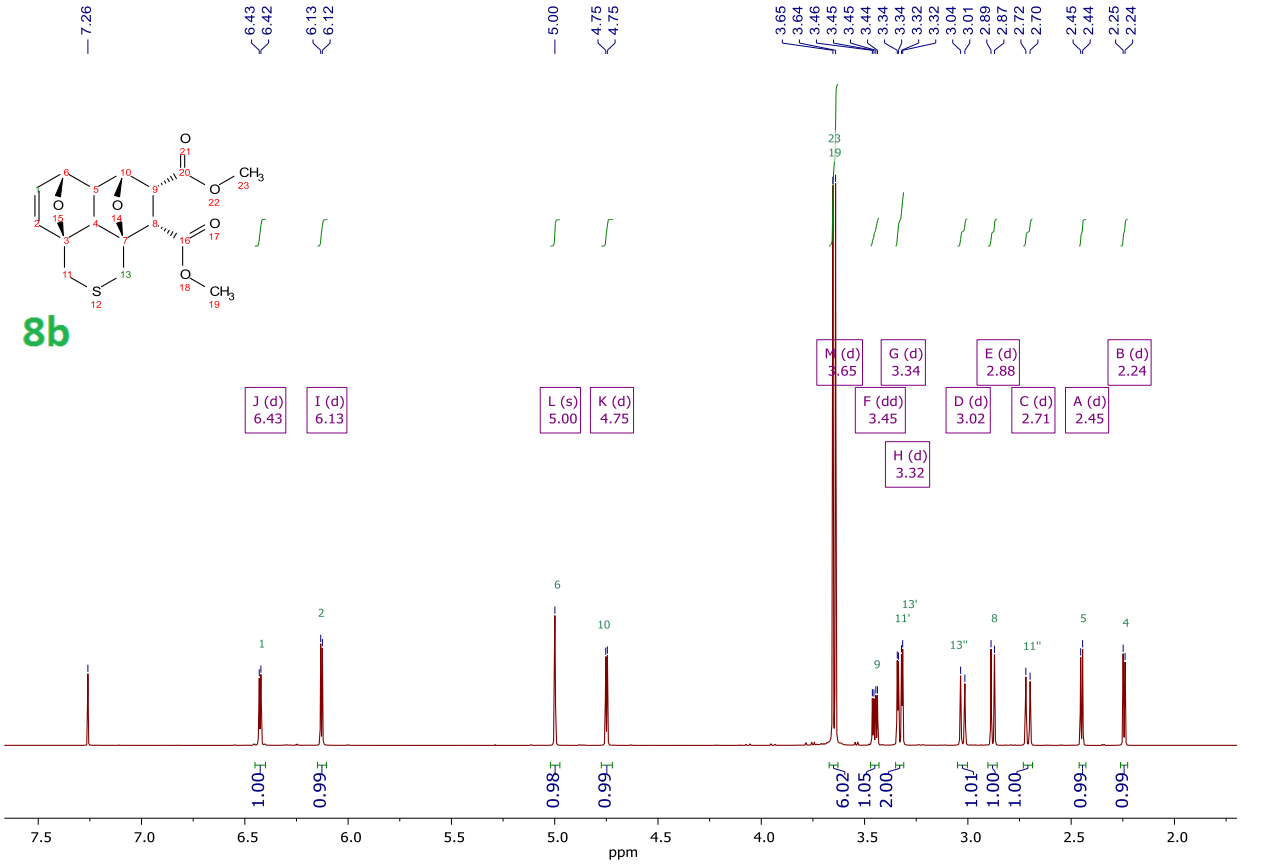


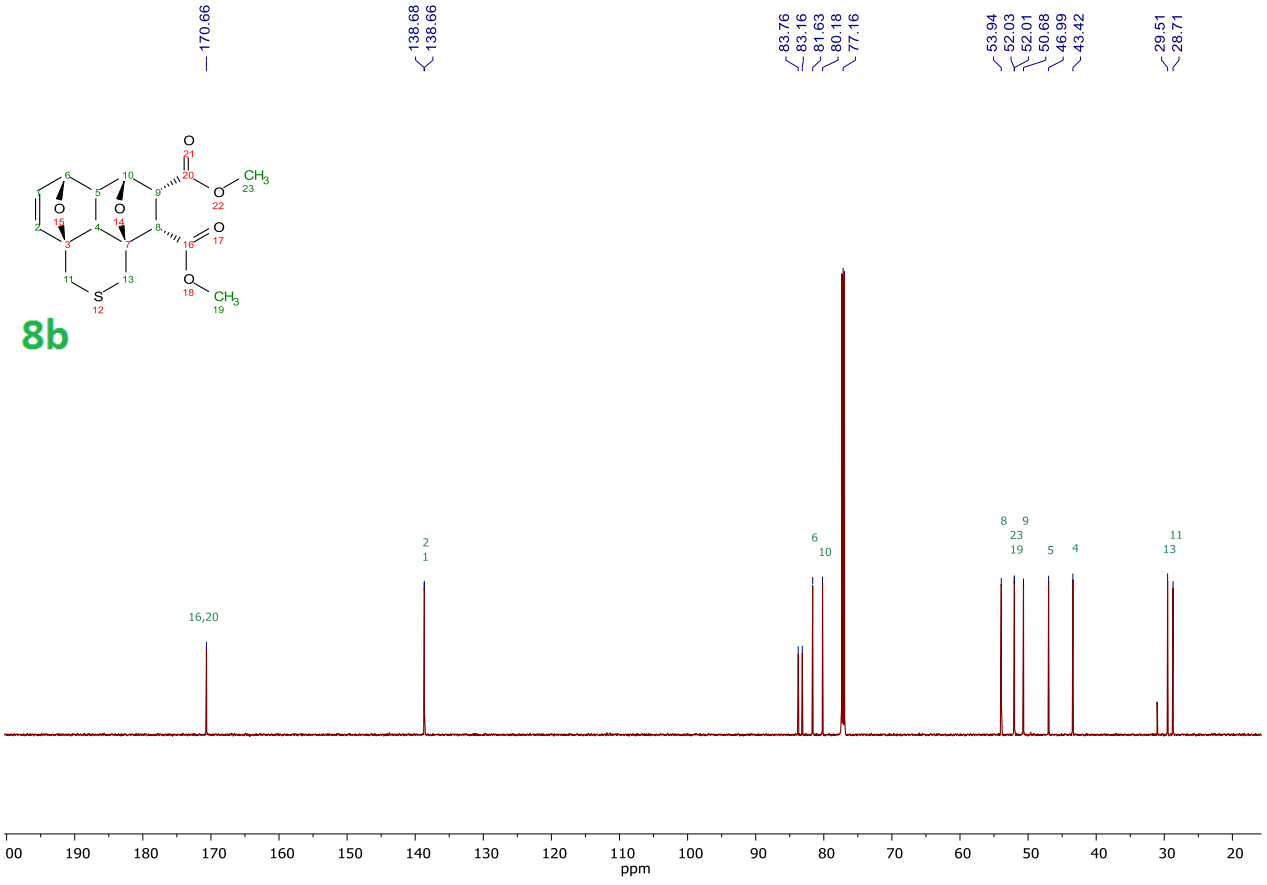
Individual compound **7b**





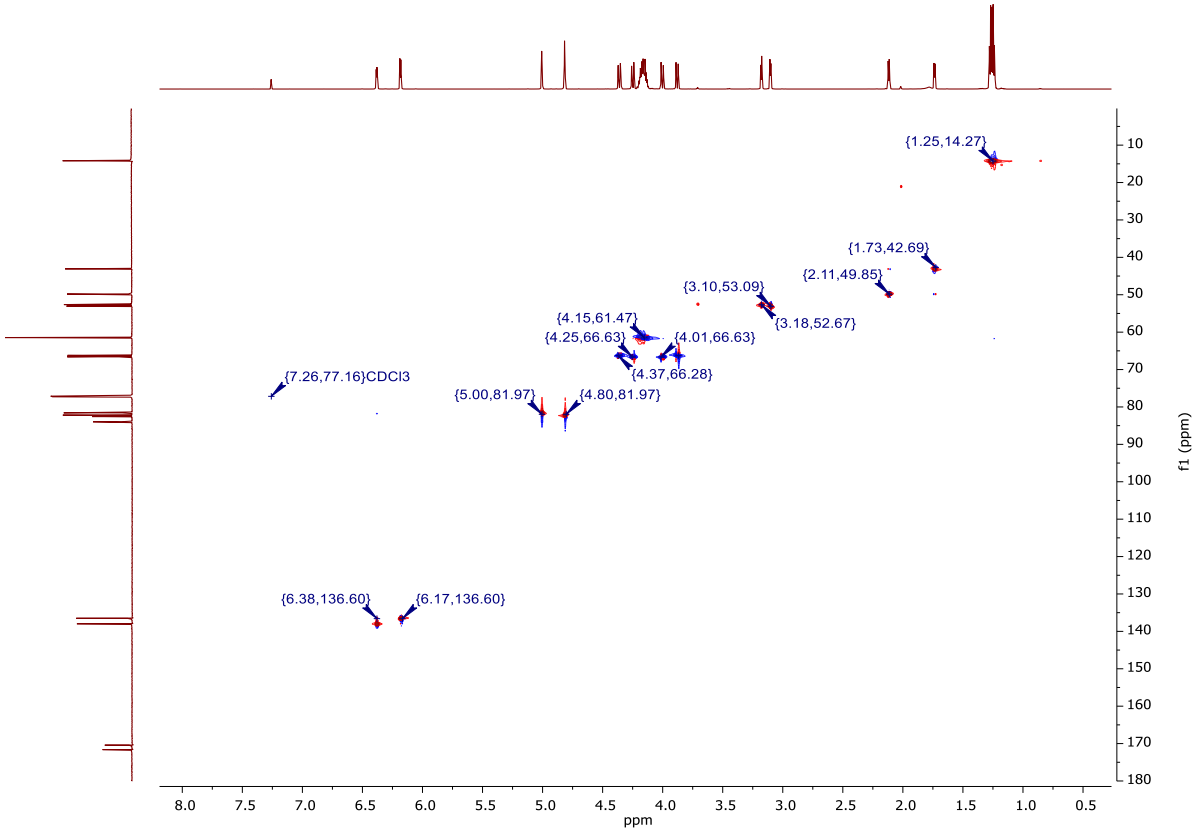
Individual compound **8b**



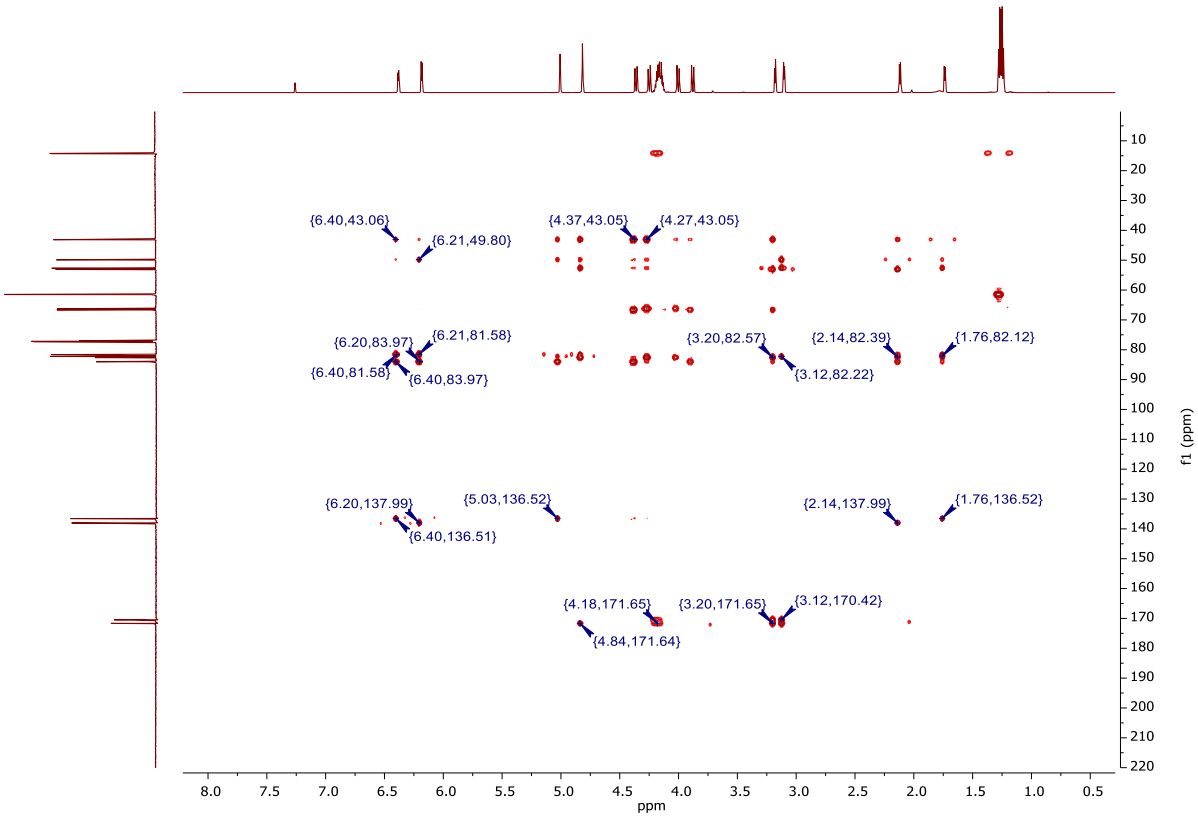


3. 2D NMR

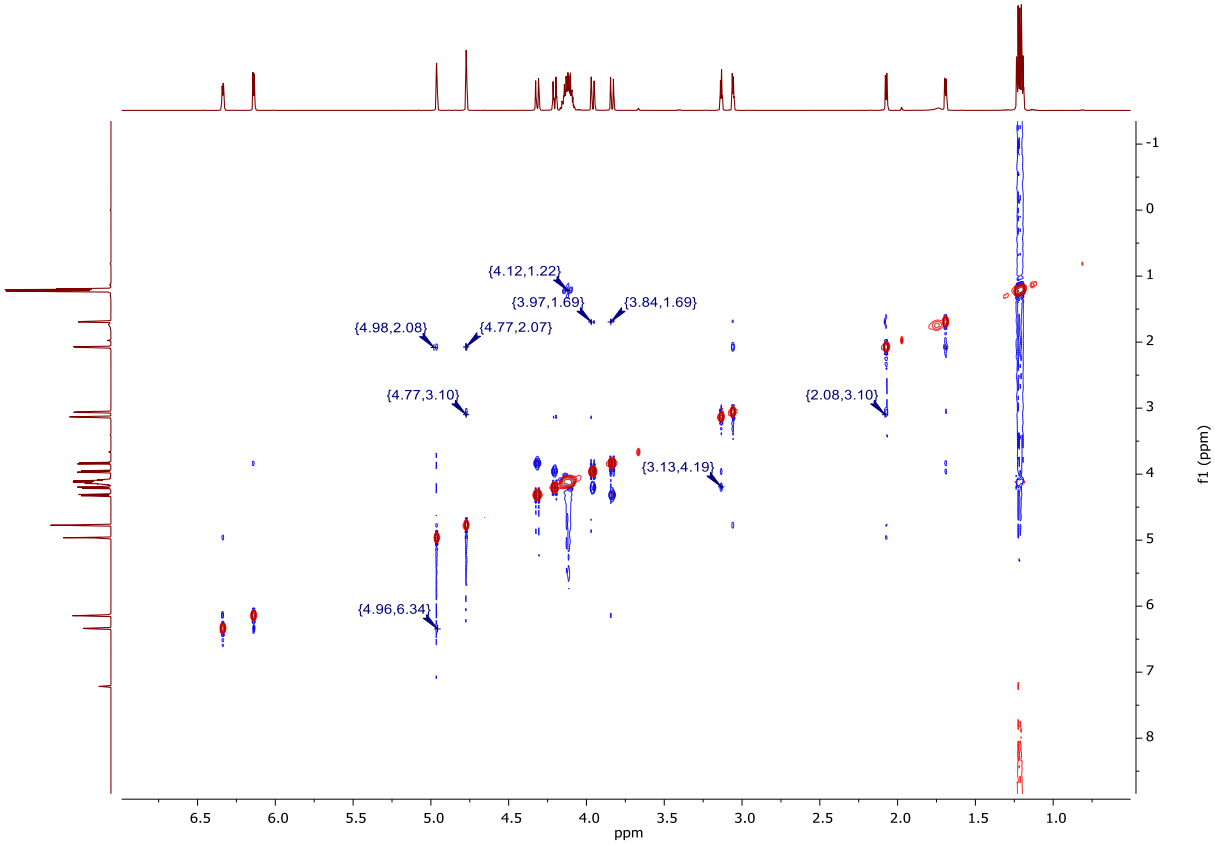
5b HSQC (^{1}H-^{13}C)



5b HMBC (^{1}H-^{13}C)

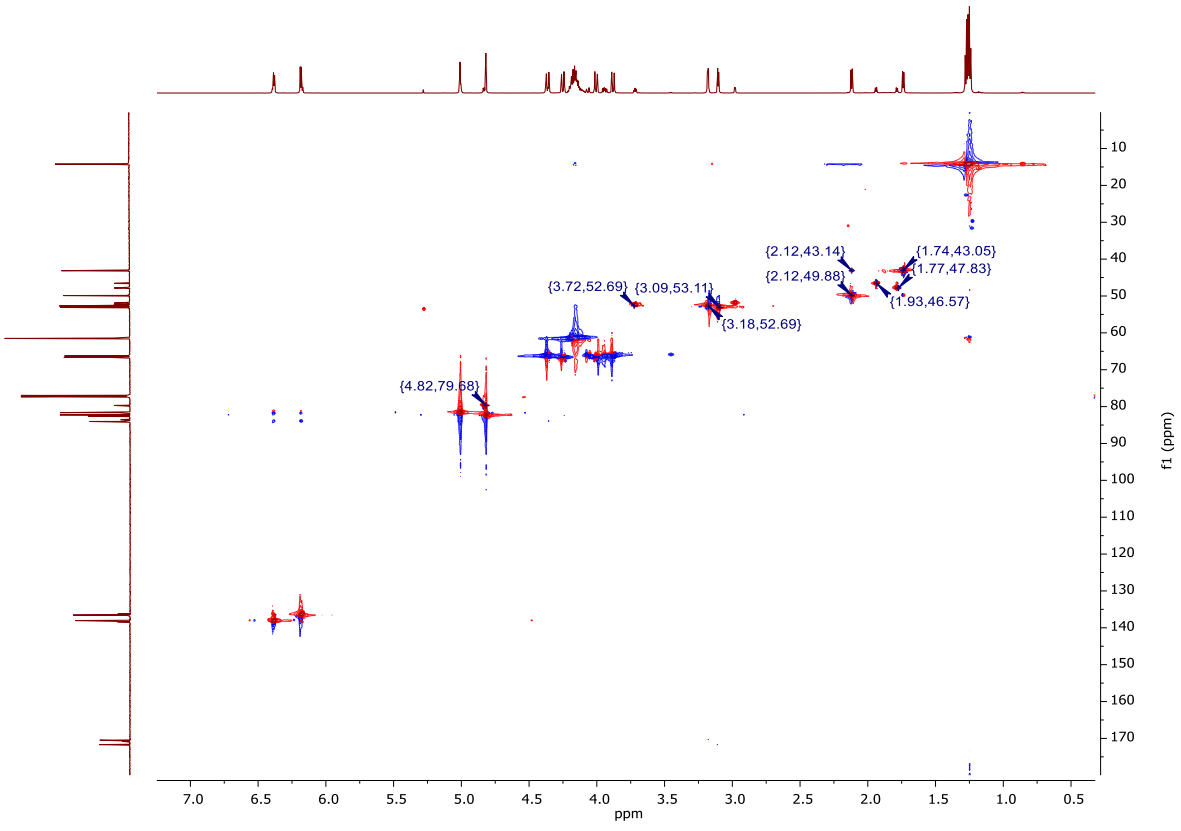


5b NOESY (^{1}H-^{1}H)

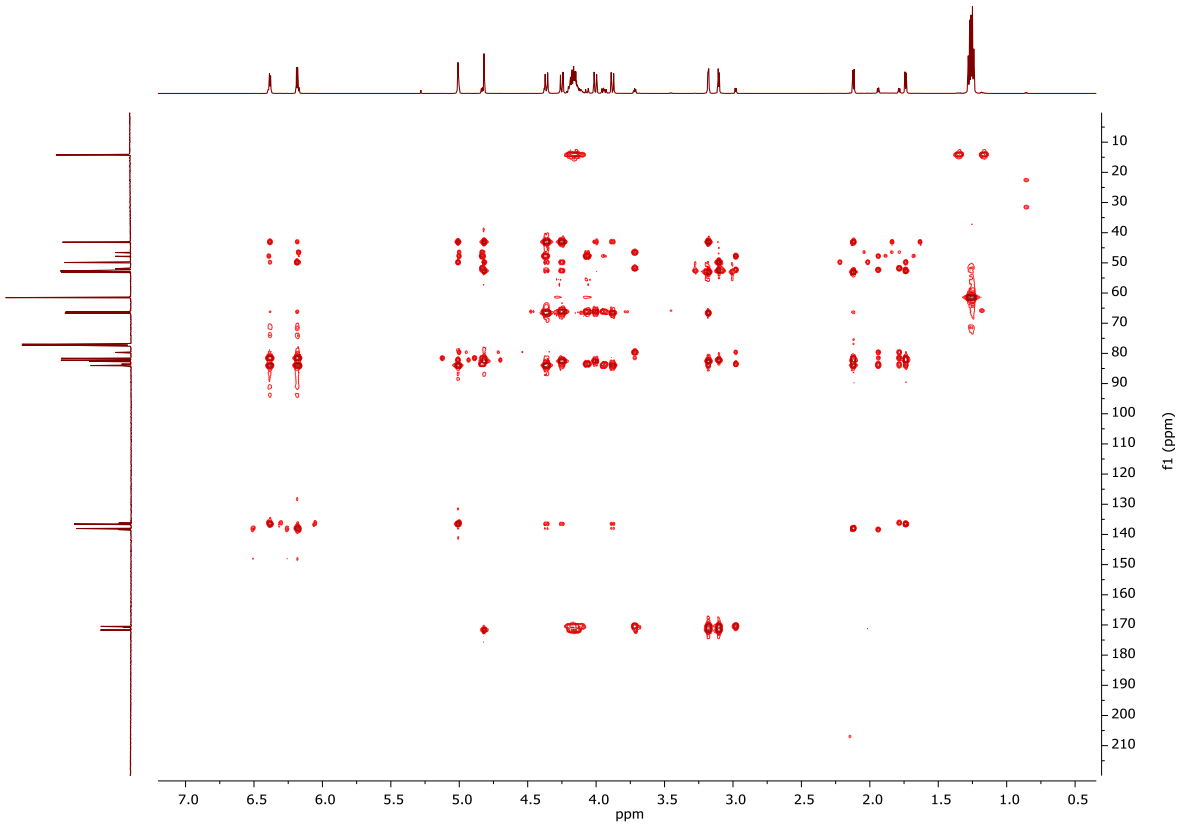


Mixture of **5b** and **6b**

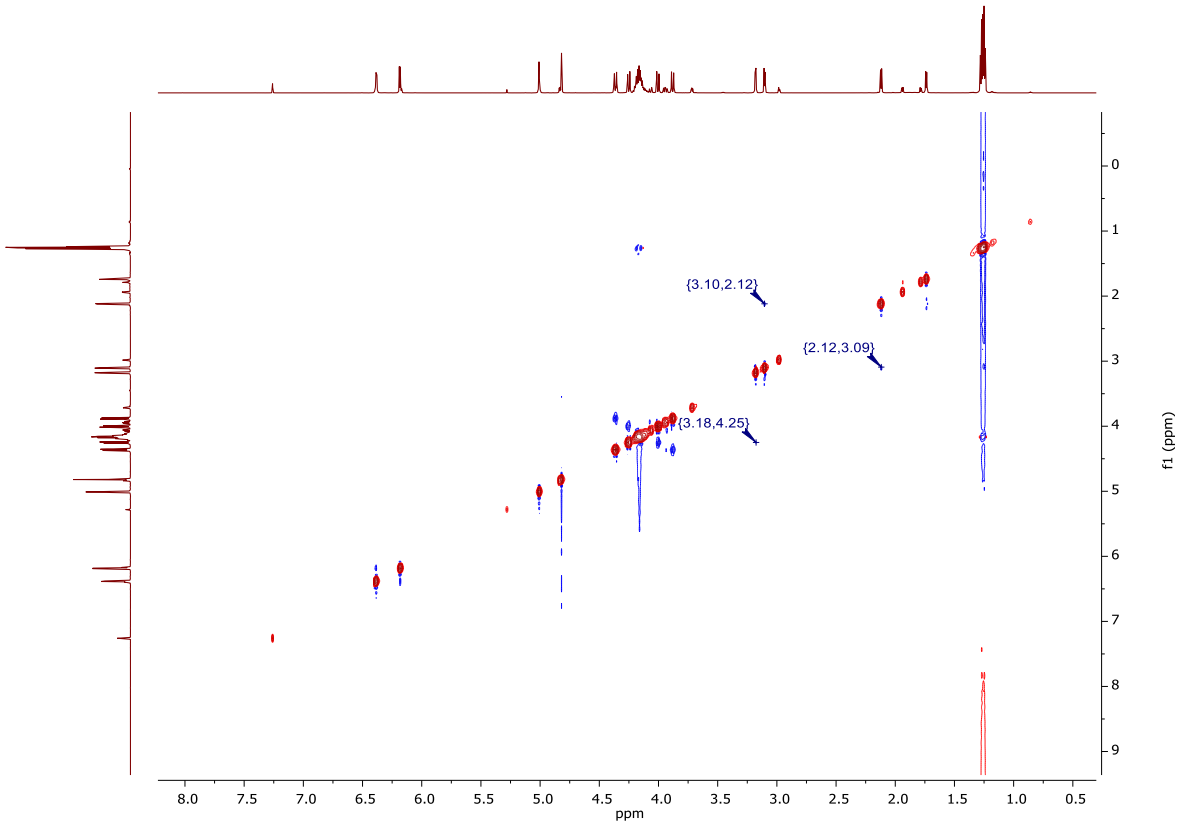
5b + 6b HSQC (^{1}H-^{13}C)



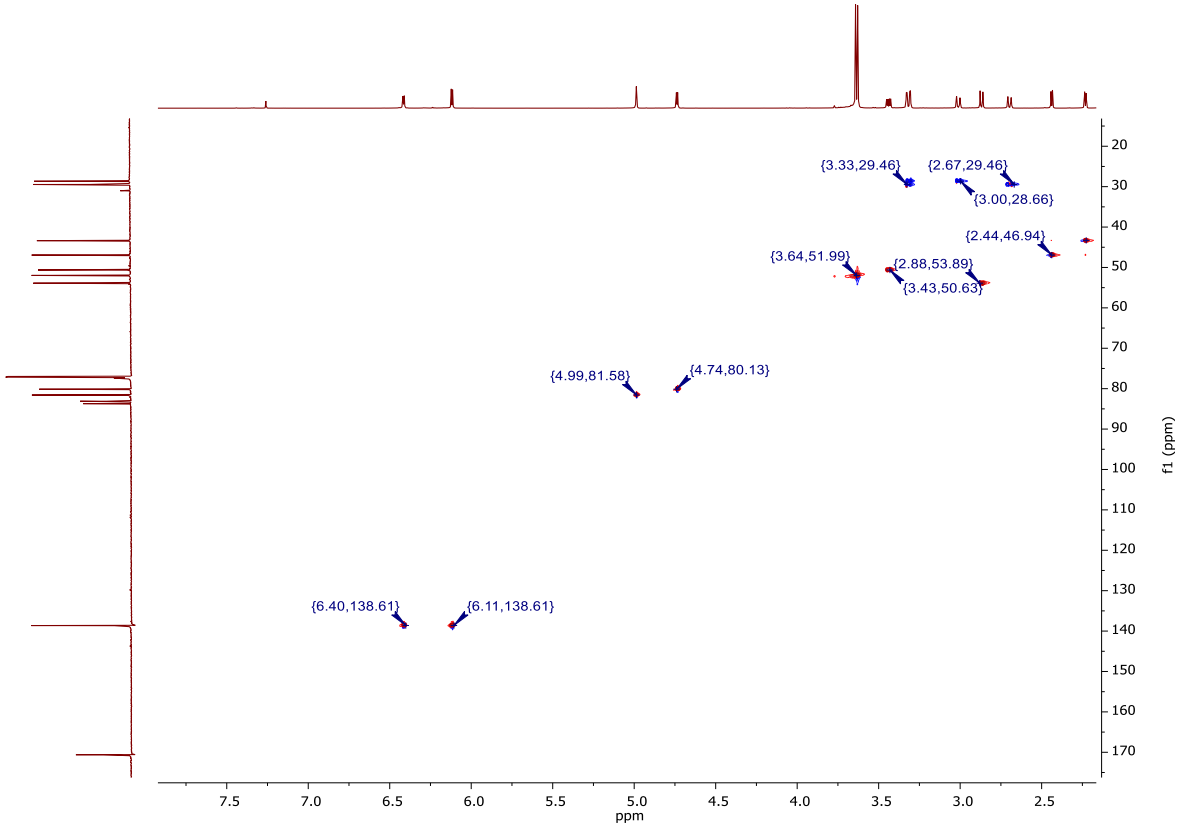
5b + 6b HMBC (^{1}H-^{13}C)



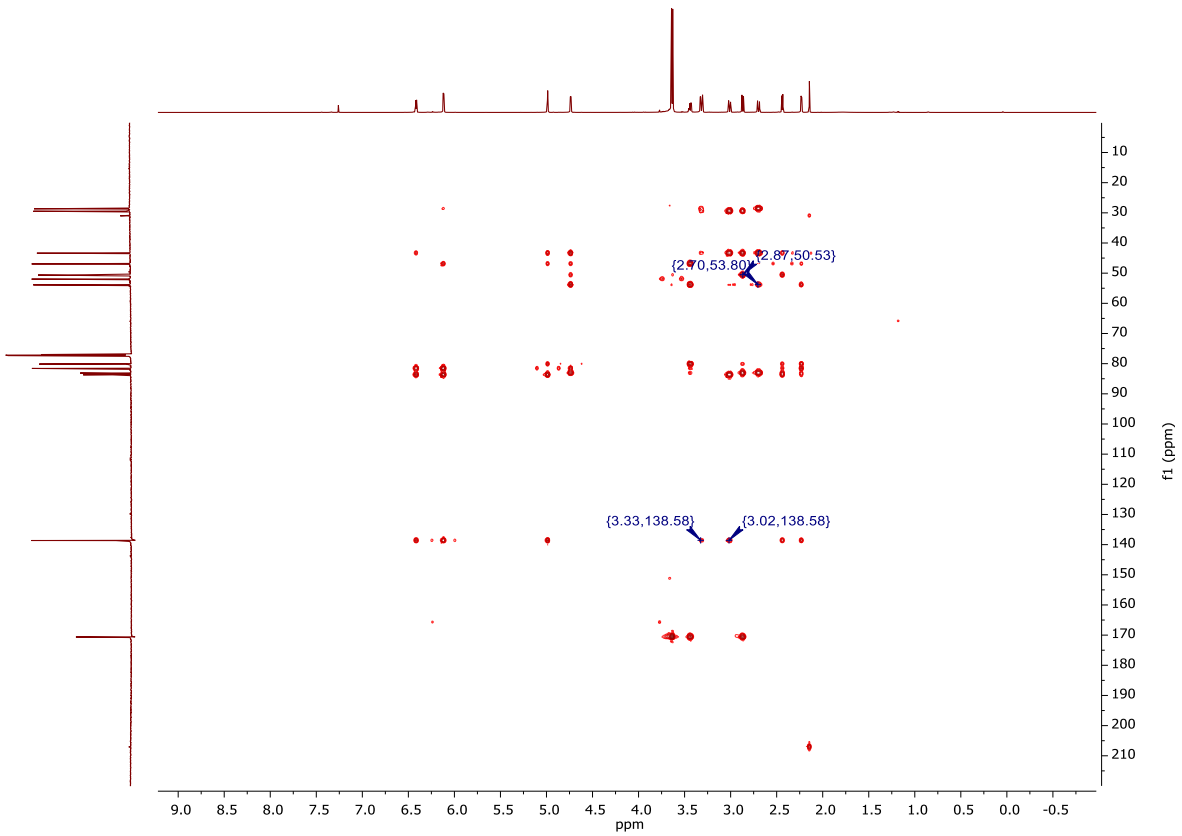
5b + 6b NOESY (^{1}H-^{1}H)



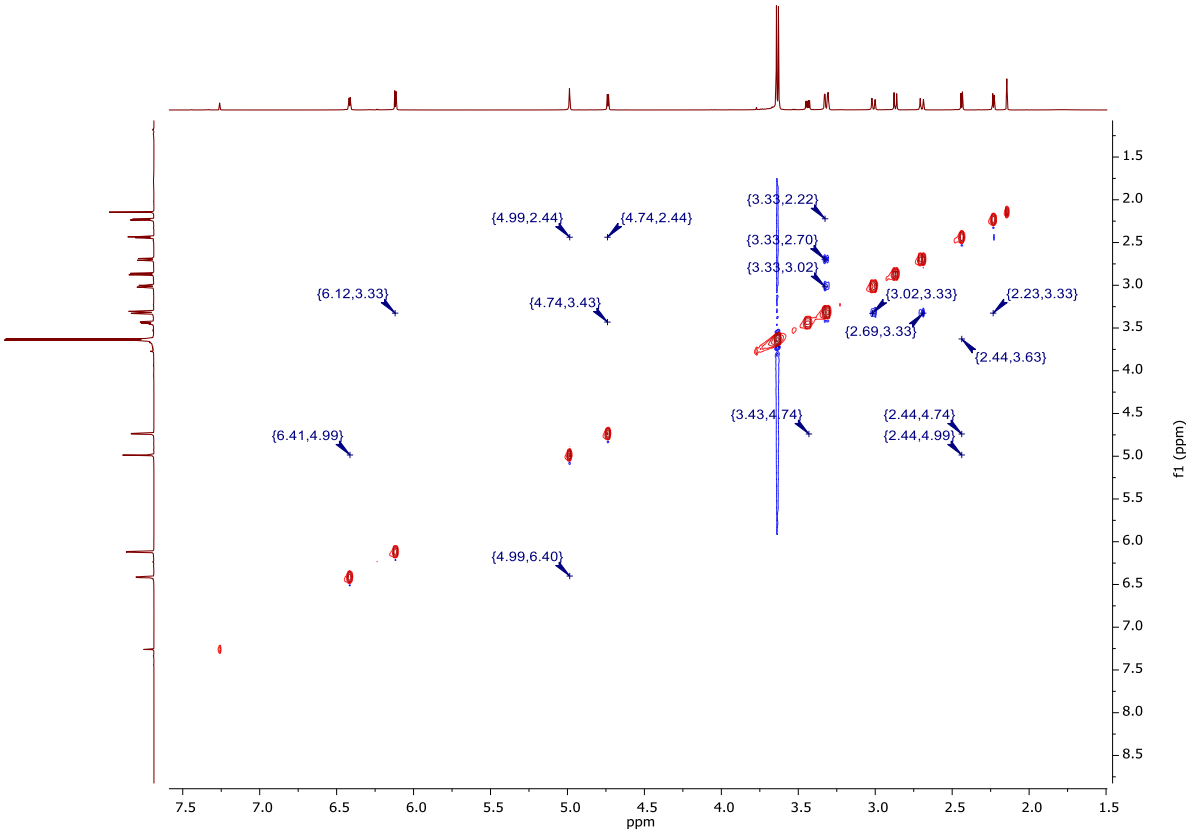
8b HSQC (^{1}H-^{13}C)



8b HMBC (^{1}H-^{13}C)



8b NOESY (^{1}H-^{1}H)



4. Piston-cylinder high-pressure apparatus

All reactions were carried out in a piston-cylinder ultrahigh pressure apparatus at a pressure of about 15 kbar. The initial working volume was 21 mL. The main parts of this apparatus are shown in the (Figure S1). The high-pressure vessel consisted of two outer steel rings, into which an inner cylindrical PTFE vessel with a cap was placed. The inner vessel was pressed into the support rings by a hydraulic press piston in a well-controlled manner depending on the internal pressure. The cylindrical high-pressure volume was closed at the bottom with a steel plug. Sealing of the mobile piston and the stopper were attained by using brass O-rings. For the reactions performed at the elevated temperatures external heating jacket was employed.

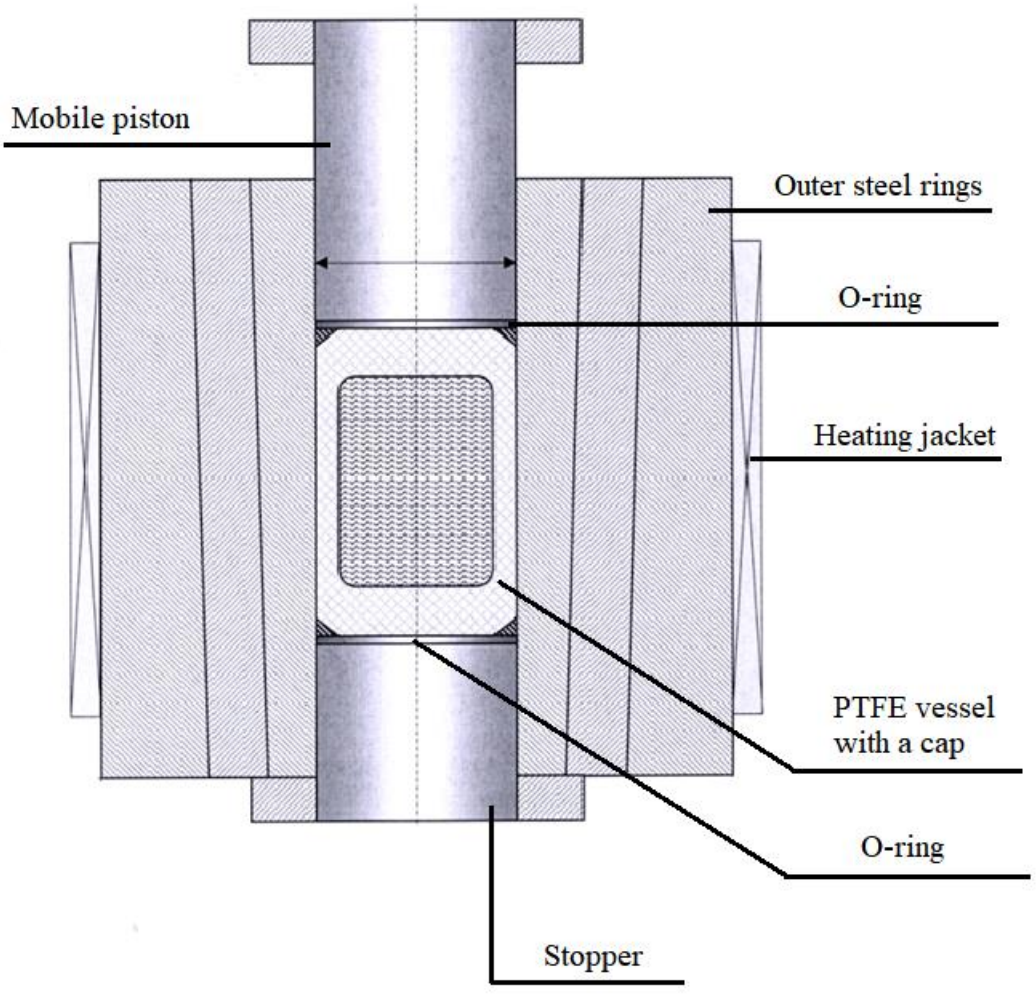


Figure S1. Piston-cylinder high-pressure apparatus

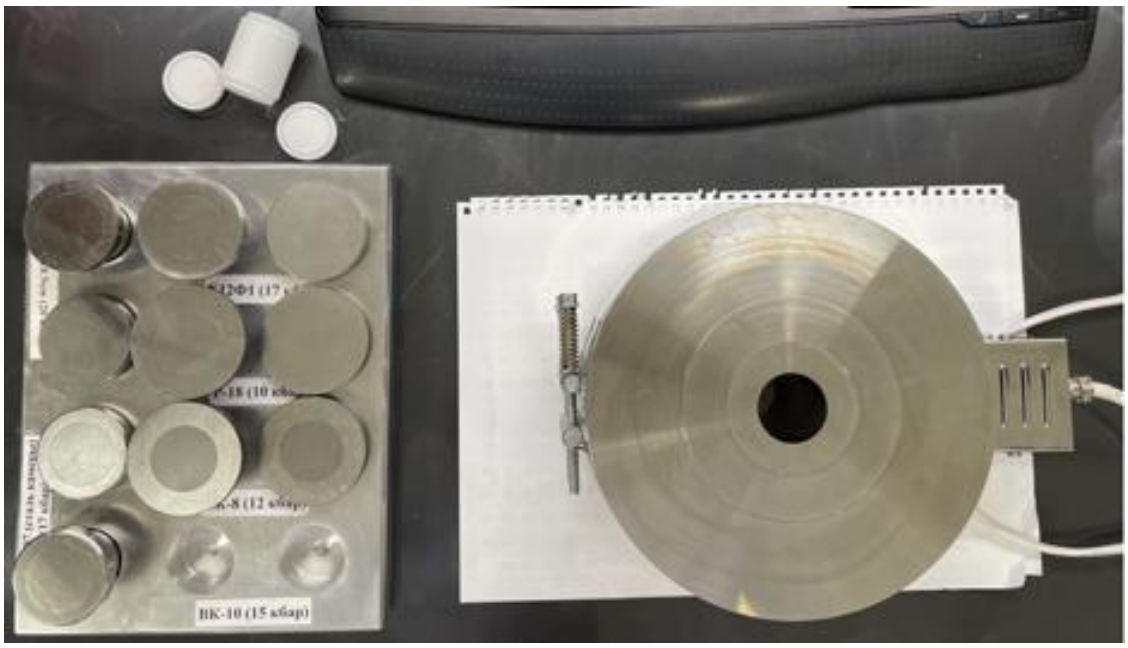


Figure S2. PTFE ampoule, set of pistons and piston-cylinder chamber.

Figure S3. Cell with a piston-cylinder chamber.

5. X-ray structural analysis (Figure S4)

For details see[S1] (CCDC number 2319519)

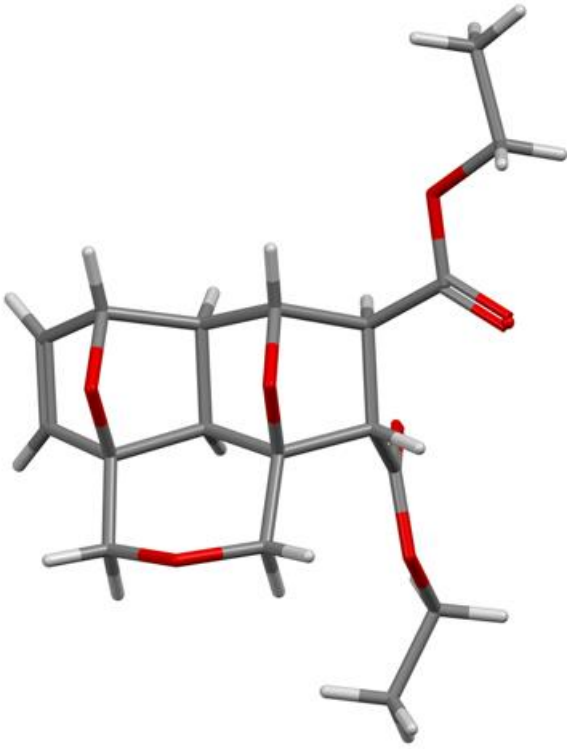


Figure S4. Structure of compound **5b**.

S1 N. D. Sadikhova, Z. Atioğlu, N. A. Guliyeva, A. G. Podrezova, E. V. Nikitina, M. Akkurt and A. Bhattarai, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2024, **80**, 83; https://doi.org/10.1107/S2056989023010794.