

**Supporting Information**  
**for**  
**A practical way to synthesize chiral fluoro-containing**  
**polyhydro-2*H*-chromenes from monoterpenoids**

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**Detailed experimental procedures, compound characterization data, and copies**  
**of NMR spectra**

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## Experimental part

*General methods:* All the chemicals were of commercial reagent grade.  $\text{CH}_2\text{Cl}_2$  was passed through calcined  $\text{Al}_2\text{O}_3$ . (1*R*,2*R*,6*S*)-3-Methyl-6-(prop-1-en-2-yl)cyclohex-3-ene-1,2-diol 1 ( $[\alpha]_{\text{D}}^{31} = -49.1$  ( $c = 2.6$ ,  $\text{CHCl}_3$ )) was synthesized according to [1] from (-)-verbenone (*Aldrich*), the content of the main substance was not less than 98.0%. Column chromatography (CC): silica gel ( $\text{SiO}_2$ ; 60–200  $\mu$ ; Macherey-Nagel). GC/MS (purity control and products analysis): Agilent 7890A with a quadrupole mass spectrometer Agilent 5975C as a detector, HP-5MS quartz column, 30000x0.25 mm, He (1 atm) as carrier gas. Optical rotation: *polAAR 3005* spectrometer,  $\text{CHCl}_3$  soln. HR-MS: DFS-Thermo-Scientific spectrometer in a full scan mode (15–500  $m/z$ , 70 eV electron-impact ionization, direct sample introduction).  $^1\text{H}$  and  $^{13}\text{C}$  NMR: Bruker DRX-500 apparatus at 500.13 MHz ( $^1\text{H}$ ) and 125.76 MHz ( $^{13}\text{C}$ ) in  $\text{CDCl}_3$  or  $\text{CDCl}_3/\text{CD}_3\text{OD}$  (10:1 v/v); chemical shifts  $\delta$  in ppm rel. to residual  $\text{CHCl}_3$  ( $\delta(\text{H})$  7.24,  $\delta(\text{C})$  76.90 ppm),  $J$  in Hz; structure determinations by analyzing the  $^1\text{H}$  NMR spectra, including  $^1\text{H}$ – $^1\text{H}$  double resonance spectra and  $^1\text{H}$ – $^1\text{H}$  2D homonuclear correlation, J-modulated  $^{13}\text{C}$  NMR spectra (JMOD), and  $^{13}\text{C}$ – $^1\text{H}$  2D heteronuclear correlation with one-bond and long-range spin–spin coupling constants (C–H COSY,  $^1J(\text{C},\text{H}) = 160$  Hz, COLOC,  $^{2,3}J(\text{C},\text{H}) = 10$  Hz).

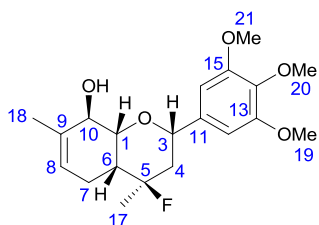
*General procedure:* Monoterpenoid (2.4 mmol) and aldehyde (2.9 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (5 ml) and cooled to 2 °C. Then water (17.8 mmol) was added to the  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (3.6 mmol) solution in  $\text{CH}_2\text{Cl}_2$  (5 ml) under vigorous stirring. Resulting cloudy solution of  $\text{BF}_3\cdot\text{Et}_2\text{O}$  was added dropwise to the mixture of aldehyde and monoterpenoid, and then the reaction mixture was stirred for 8 or 72 hours at 2 °C. Then 10 %  $\text{NaHCO}_3$  solution was added, the layers were separated and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (2 x 15 ml). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. Reaction mixture was separated on a  $\text{SiO}_2$  column (hexane/EtOAc 100:0–0:100 as eluent).

**Reaction of 1 with 3,4,5-trimethoxybenzaldehyde (6a):** The reaction of diol **1** and aldehyde **6a** for 8 hours at 2 °C gave products **2a** (*R:S* = 2:3, 7%), **8a** (*R:S* = 4:1, 69%). Spectral characteristics of compounds **2a** have coincided with those described in the work [2].

**(2*S*,4*R*,4*aR*,8*R*,8*aR*)-4-fluoro-4,7-dimethyl-2-(3,4,5-trimethoxyphenyl)**

**-3,4,4*a*,5,8,8*a*-**

**hexahydro-2*H*-chromen-8-ol ((*R*)-8a):** Yellow viscous oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.36 (d, <sup>3</sup>*J*(17, F) =



22.4 Hz, 3 H, 17-H); 1.78 (ddd, <sup>3</sup>*J*(4*a*,F) = 39.4 Hz, *J*(4*a*,4*e*) = 14.7 Hz,

*J*(4*a*,3*a*) = 11.7 Hz, 1H, 4-*H<sub>a</sub>*); 1.81 (m, all *J* ≤ 2.5 Hz, 3H, 18-H); 1.90

(dddd, *J*(4*e*,4*a*) = 14.7 Hz, <sup>3</sup>*J*(4*e*,F) = 11.3 Hz, *J*(4*e*, 3*a*) = 3.0 Hz,

*J*(4*e*,6*a*) = 1.1 Hz, 1H, 4-*H<sub>e</sub>*); 1.93-2.03 (m, *H<sub>a</sub>*-C(6), 2 H, 7-H); 3.78 (s, 3

H, 20-MeO); 3.82 (s, 6 H, 19-MeO, 21-MeO); 3.94 (br.s, 1 H, 10-*H<sub>e</sub>*);

4.14 (m, all *J* ≤ 3.0 Hz, 1 H, 1-*H<sub>e</sub>*); 4.67 (dd, *J*(3*a*,4*a*) = 11.7 Hz, *J*(3*a*,4*e*) = 3.0 Hz, 1 H, 3-*H<sub>a</sub>*); 5.55-

5.59 (m, 1 H, 8-H); 6.51 (s, 2 H, 12-H, 16-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 20.75 (C-18); 24.04 (d, <sup>3</sup>*J*(C-F) =

9.7 Hz, C-7); 24.77 (d, <sup>2</sup>*J*(C-F) = 24.3 Hz, C-17); 36.08 (d, <sup>2</sup>*J*(C-F) = 20.8 Hz, C-6); 40.13 (d, <sup>2</sup>*J*(C-F) =

21.7 Hz, C-4); 56.04 (C-19, C-21); 60.61 (C-20); 70.08 (C-10); 75.51 (C-1); 75.96 (C-3); 95.15 (d,

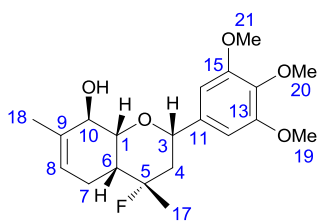
<sup>1</sup>*J*(C-F) = 168.5 Hz, C-5); 103.09 (C-12, C-16); 123.12 (C-8); 132.16 (C-9); 137.41, 137.46 (C-11, C-

14); 153.17 (C-13, C-15). HR-MS: 366.1833 (*M*<sup>+</sup> (C<sub>20</sub>H<sub>27</sub>O<sub>5</sub>F)<sup>+</sup>; calc. 366.1837).

**(2*S*,4*S*,4*aR*,8*R*,8*aR*)-4-fluoro-4,7-dimethyl-2-(3,4,5-trimethoxyphenyl)**

**-3,4,4*a*,5,8,8*a*-**

**hexahydro-2*H*-chromen-8-ol ((*S*)-8a):** Yellow viscous oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.61 (d, <sup>3</sup>*J*(17, F) =



23.5 Hz, 3 H, 17-H); 1.78 (m, all *J* ≤ 2.5 Hz, 3 H, 18-H); 1.79-1.83 (m, 1

H, 4-*H<sub>e</sub>*); 2.04 (br.dd, *J*(6*a*,7*a*) = 10.7 Hz, *J*(6*a*,7*e*) = 6.6 Hz, 1 H, 6-*H<sub>a</sub>*);

2.07-2.21 (m, 3 H, *H<sub>a</sub>*-4, 7-2H); 3.68 (m, all *J* ≤ 3.0 Hz, 1 H, 1-*H<sub>e</sub>*); 3.75

(s, 3 H, 20-MeO); 3.80 (s, 6 H, 19-MeO, 21-MeO); 3.87 (br.s, 1 H, 10-

*H<sub>e</sub>*); 4.27 (dd, *J*(3*a*,4*a*) = 12.1 Hz, *J*(3*a*,4*e*) = 2.6 Hz, 1 H, 3-*H<sub>a</sub>*); 5.59-

5.63 (m, 1H, 8-H); 6.49 (s, 2 H, 12-H, 16-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 20.53 (C-18); 22.39 (d, <sup>3</sup>*J*(C-F) =

6.2 Hz, C-7); 24.68 (d, <sup>2</sup>*J*(C-F) = 24.8 Hz, C-17); 37.65 (d, <sup>2</sup>*J*(C-F) = 18.7 Hz, C-6); 40.41 (d, <sup>2</sup>*J*(C-F) =

20.6 Hz, C-4); 55.97 (C-19, C-21); 60.55 (C-20); 69.74 (C-10); 77.73 (d, <sup>3</sup>*J*(C-F) = 11.5 Hz, C-3);

78.05 (d, <sup>3</sup>*J*(C-F) = 7.5 Hz, C-1); 95.09 (d, <sup>1</sup>*J*(C-F) = 176.1 Hz, C-5); 103.24 (C-12, C-16); 123.97 (C-

8); 131.24 (C-9); 137.34, 137.56 (C-11, C-14); 153.06 (C-13, C-15).

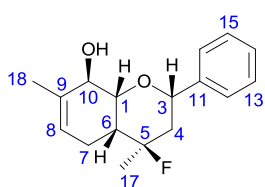
**Reaction of 1 with benzaldehyde (6b):** The reaction of diol **1** and aldehyde **6b** for 8 hours at

2 °C gave products **2b** (*R:S* = 1:3, 24%), **8b** (individual *R*-isomer, 10%) and **8b** (*R:S* = 5.5:1, 45%).

Spectral characteristics of compounds **2b** have coincided with those described in the work [2].

**(2*S*,4*R*,4*aR*,8*R*,8*aR*)-4-fluoro-4,7-dimethyl-2-phenyl-3,4,4*a*,5,8,8*a*-hexahydro-2*H*-chromen-8-ol**

**((*R*)-8*b*):** Yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.36 (d, <sup>3</sup>*J*(17, F) = 22.3 Hz, 3 H, 17-H); 1.80 (ddd, <sup>3</sup>*J*(4*a*,



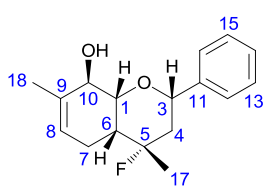
F) = 40.1 Hz, *J*(4*a*,4*e*) = 14.7 Hz, *J*(4*a*, 3*a*) = 11.6 Hz, 1 H, 4-*H<sub>a</sub>*); 1.84 (m, all *J* ≤ 3.0 Hz, 3 H, H-18); 1.92 (dddd, *J*(4*e*, 4*a*) = 14.7 Hz, <sup>3</sup>*J*(4*e*, F) = 10.6 Hz, *J*(4*e*,3*a*) = 3.0 Hz, *J*(4*e*,6*a*) = 1.2 Hz, 1 H, 4-*H<sub>e</sub>*); 1.94-2.07 (m, 3 H, 6-*H<sub>a</sub>*, 7-2*H*); 3.95 (br.s, 1 H, 10-*H<sub>e</sub>*); 4.16 (m, all *J* ≤ 3.0 Hz, 1 H, 1-*H<sub>e</sub>*); 4.76 (dd,

*J*(3*a*,4*a*) = 11.6 Hz, *J*(3*a*,4*e*) = 3.0 Hz, 1 H, 3-*H<sub>a</sub>*); 5.57-5.61 (m, 1 H, 8-H); 7.22-7.33 (m, 5 H, Ph-H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 20.79 (C-18); 24.06 (d, <sup>3</sup>*J*(C-F) = 9.3 Hz, C-7); 24.76 (d, <sup>2</sup>*J*(C-F) = 24.3 Hz, C-17); 36.05 (d, <sup>2</sup>*J*(C-F) = 20.8 Hz, C-6); 40.38 (d, <sup>2</sup>*J*(C-F) = 21.7 Hz, C-4); 70.08 (C(10)); 75.27 (d, <sup>3</sup>*J*(C-F) = 1.3 Hz, C-1); 75.66 (C-3); 95.09 (d, <sup>1</sup>*J*(C-F)=169.0 Hz, C-5); 123.14 (C-8); 125.67 (C-12, C-16); 127.43 (C-14); 128.27 (C-13, C-15); 132.19 (C-9); 141.95 (C-11). HR-MS: 276.1523 (*M*<sup>+</sup> (C<sub>17</sub>H<sub>21</sub>O<sub>2</sub>F)<sup>+</sup>; calc. 276.1520).

**(2*S*,4*S*,4*aR*,8*R*,8*aR*)-4-fluoro-4,7-dimethyl-2-phenyl-3,4,4*a*,5,8,8*a*-hexahydro-2*H*-chromen-8-ol**

**((*S*)-8*b*):** Yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.65 (dd, <sup>3</sup>*J*(17, F) = 23.5 Hz, *J*(17, 4*a*) = 0.8 Hz, 3 H, 17-



H); 1.82 (m, all *J* ≤ 2.5 Hz, 3H,18-H); 1.86 (br.dd, *J*(4*e*,4*a*) = 13.3 Hz, *J*(4*e*,3*a*) = 2.7 Hz, 1 H, 4-*H<sub>e</sub>*); 2.07 (br.dd, *J*(6*a*,7*a*) = 10.7 Hz, *J*(6*a*,7*e*) = 6.5 Hz, 1 H, 6-*H<sub>a</sub>*); 2.15 (dddq, <sup>3</sup>*J*(4*a*, F) = 14.1 Hz, *J*(4*a*,4*e*) = 13.3 Hz, *J*(4*a*,3*a*) = 12.1 Hz, *J*(4*a*, 17) = 0.8 Hz, 1 H, 4-*H<sub>a</sub>*); 2.16-2.29 (m, 2 H, 7-H); 3.73 (ddd,

*J*(1*e*,10*e*) = 2.3 Hz, *J*(1*e*,6*a*) = <sup>4</sup>*J*(1*e*,F) = 2.1 Hz, 1 H, 1-*H<sub>e</sub>*); 3.93 (m, all *J* ≤ 3.0 Hz, 1 H, 10-*H<sub>e</sub>*); 4.38

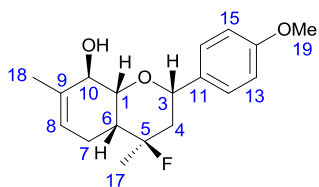
(dd, *J*(3*a*,4*a*) = 12.1 Hz, *J*(3*a*,4*e*) = 2.7 Hz, 1 H, 3-*H<sub>a</sub>*); 5.64-5.67 (m, 1 H, 8-H); 7.24-7.34 (m, 5 H,

Ph-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 20.68 (C-18); 22.54 (d, <sup>3</sup>*J*(C-F) = 6.3 Hz, C-7); 24.80 (d, <sup>2</sup>*J*(C-F) = 26.0 Hz, C-17); 37.74 (d, <sup>2</sup>*J*(C-F) = 18.6 Hz, C-6); 40.90 (d, <sup>2</sup>*J*(C-F) = 20.8 Hz, C-4); 70.20 (d, <sup>4</sup>*J*(C-F) = 2.3 Hz, C-10); 77.6 (d, <sup>3</sup>*J*(C-F) = 11.6 Hz, C-3); 77.8 (d, <sup>3</sup>*J*(C-F) = 7.6 Hz, C-1); 95.14 (d, <sup>1</sup>*J*(C-F)=176.6 Hz, C-5); 124.41 (C-8); 125.79 (C-12, C-16); 127.73 (C-14); 128.36 (C-13, C-15); 131.29 (C-9); 141.26 (C-11).

**Reaction of 1 with 4-methoxybenzaldehyde (6*c*):** The reaction of diol **1** and aldehyde **6c** for 8 hours at 2 °C gave products **2c** (*R*:*S* = 1:4, 24%), **8c** (*R*:*S* = 4:1, 34%). Spectral characteristics of compounds **2c** have coincided with those described in the work [3].

**(2*S*,4*R*,4*aR*,8*R*,8*aR*)-4-fluoro-2-(4-methoxyphenyl)-4,7-dimethyl-3,4,4*a*,5,8,8*a*-hexahydro-2*H*-**

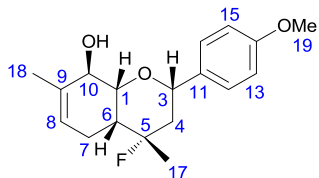
**chromen-8-ol ((*R*)-8*c*):** Yellow viscous oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.35 (d, <sup>3</sup>*J*(17, F) = 22.4 Hz, 3 H, 17-H); 1.80 (ddd, <sup>3</sup>*J*(4*a*, F) = 39.4 Hz, *J*(4*a*,4*e*) = 14.7 Hz, *J*(4*a*, 3*a*) = 11.5 Hz, 1 H, 4-*H<sub>a</sub>*); 1.82 (m,



all  $J \leq 3.0$  Hz, 3 H, 18-H); 1.84-1.91 (m, 1H, 4-H<sub>e</sub>); 1.91-2.06 (m, 3H, 6-H<sub>a</sub>, 7-2H); 3.76 (s, 3 H, 19-MeO); 3.93 (br.s, 1H, 10-H<sub>e</sub>); 4.14 (m, all  $J \leq 3.0$  Hz, 1 H, 1-H<sub>e</sub>); 4.70 (dd,  $J(3a,4a) = 11.5$  Hz,  $J(3a,4e) = 3.2$  Hz, 1 H, 3-H<sub>a</sub>); 5.55-5.59 (m, 1 H, 8-H); 6.84 (d,  $J(13,12) = J(15,16) = 8.8$  Hz, 2 H, 13-H, 15-H); 7.23 (d,  $J(12,13) = J(16,15) = 8.8$  Hz, 2 H, 12-H, 16-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 20.79 (C-18); 24.09 (d, <sup>3</sup> $J(C-F) = 9.3$  Hz, C-7); 24.79 (d, <sup>2</sup> $J(C-F) = 24.8$  Hz, C-17); 36.08 (d, <sup>2</sup> $J(C-F) = 20.8$  Hz, C-6); 40.23 (d, <sup>2</sup> $J(C-F) = 21.2$  Hz, C-4); 55.17 (C-19); 70.16 (C-10); 75.34 (d, <sup>3</sup> $J(C-F) = 1.3$  Hz, C-1); 75.36 (C-3); 95.15 (d, <sup>1</sup> $J(C-F) = 168.5$  Hz, C-5); 113.74 (C-13, C-15); 123.20 (C-8); 127.08 (C-12, C-16); 132.21 (C-9); 134.10 (C-11); 159.01 (C-14). HR-MS: 306.1623 ( $M^+$  (C<sub>17</sub>H<sub>23</sub>O<sub>3</sub>F)<sup>+</sup>; calc. 306.1626).

**(2S,4S,4aR,8R,8aR)-4-fluoro-2-(4-methoxyphenyl)-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-chromen-8-ol ((S)-8c):**

Yellow viscous oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.63 (dd, <sup>3</sup> $J(17, F) = 23.5$  Hz,  $J(17,4a) = 0.7$  Hz, 3 H, 17-H); 1.80 (m, all  $J \leq 2.5$  Hz, 3H, 18-H); 1.82

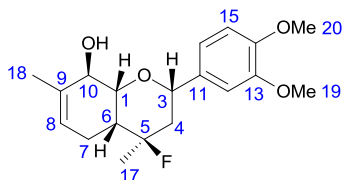


(br.dd,  $J(4e,4a) = 13.3$  Hz,  $J(4e, 3a) = 2.7$  Hz, 1 H, 4-H<sub>e</sub>); 2.05 (br.dd,  $J(6a,7a) = 10.8$  Hz,  $J(6a,7e) = 6.5$  Hz, 1 H, 6-H<sub>a</sub>); 2.16 (ddd, <sup>3</sup> $J(4a, F) = 14.1$  Hz,  $J(4a,4e) = 13.3$  Hz,  $J(4a, 3a) = 12.0$  Hz, 1 H, 4-H<sub>a</sub>); 2.17-2.27 (m, 2 H, 7-H); 3.71 ( $J(1e,10e) = 2.4$  Hz,  $J(1e,6a) = ^4J(1e,F) = 2.1$  Hz, 1 H, 1-H<sub>e</sub>); 3.76 (s, 3 H, 19-MeO); 3.90 (m, all  $J \leq 3.0$  Hz, 1 H, 10-H<sub>e</sub>); 4.32 (dd,  $J(3a,4a) = 12.0$  Hz,  $J(3a,4e) = 2.7$  Hz, 1 H, 3-H<sub>a</sub>); 5.62-5.66 (m, 1 H, 8-H); 6.84 (d,  $J(13,12) = J(15,16) = 8.8$  Hz, 2 H, 13-H, 15-H); 7.23 (d,  $J(12,13) = J(16,15) = 8.8$  Hz, 2 H, 12-H, 16-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 20.65 (C-18); 22.50 (d, <sup>3</sup> $J(C-F) = 6.2$  Hz, C-7); 24.77 (d, <sup>2</sup> $J(C-F) = 25.7$  Hz, C-17); 37.71 (d, <sup>2</sup> $J(C-F) = 19.0$  Hz, C-6); 40.70 (d, <sup>2</sup> $J(C-F) = 20.4$  Hz, C-4); 55.15 (C-19); 70.12 (d, <sup>4</sup> $J(C-F) = 2.2$  Hz, C-10); 77.26 (d, <sup>3</sup> $J(C-F) = 11.5$  Hz, C-3); 77.83 (d, <sup>3</sup> $J(C-F) = 7.5$  Hz, C-1); 95.18 (d, <sup>1</sup> $J(C-F) = 176.0$  Hz, C-5); 113.74 (C-13, C-15); 124.35 (C-8); 127.16 (C-12, C-16); 131.25 (C-9); 133.41 (C-11); 159.15 (C-14).

**Reaction of 1 with 3,4-dimethoxybenzaldehyde (6d):** The reaction of diol **1** and aldehyde **6d** for 8 hours at 2 °C gave products **2d** ( $R:S = 1:5$ , 20%), **8d** ( $R:S = 3:1$ , 35%). Spectral characteristics of compounds **2d** have coincided with those described in the work [3].

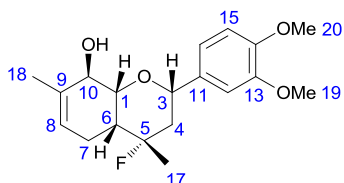
**(2S,4R,4aR,8R,8aR)-2-(3,4-dimethoxyphenyl)-4-fluoro-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-chromen-8-ol ((R)-8d):**

Yellow viscous oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.35 (d, <sup>3</sup> $J(17, F) = 22.4$  Hz, 3 H, 17-H); 1.81 (ddd, <sup>3</sup> $J(4a, F) = 39.2$  Hz,  $J(4a,4e) = 14.6$  Hz,  $J(4a, 3a) = 11.3$  Hz, 1 H, 4-H<sub>a</sub>); 1.81 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.89 (dddd,  $J(4e, 4a) = 14.6$  Hz, <sup>3</sup> $J(4e, F) = 11.2$  Hz,  $J(4e,3a) = 3.2$  Hz,



$J(4e,6a) = 1.0$  Hz, 1 H, 4- $H_e$ ); 1.91-2.06 (m, 3 H, 6- $H_a$ , 7-2H); 3.82 (s, 3 H, 20-MeO); 3.85 (s, 3 H, 19-MeO); 3.93 (br.s, 1 H, 10- $H_e$ ); 4.14 (m, all  $J < 3.0$  Hz, 1 H, 1- $H_e$ ); 4.68 (dd,  $J(3a,4a) = 11.3$  Hz,  $J(3a,4e) = 3.2$  Hz, 1 H, 3- $H_a$ ); 5.55-5.60 (m, 1 H, 8-H); 6.80 (d,  $J(15,16) = 8.2$  Hz, 1 H, 15-H); 6.82 (d,  $J(12,16) = 2.0$  Hz, 1 H, 12-H); 6.85 (dd,  $J(16,15) = 8.2$  Hz,  $J(16,12) = 2.0$  Hz, 1 H, 16-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 20.76$  (C-18); 24.07 (d,  $^3J(\text{C-F}) = 9.7$  Hz, C-7); 24.79 (d,  $^2J(\text{C-F}) = 24.8$  Hz, C-17); 36.10 (d,  $^2J(\text{C-F}) = 20.8$  Hz, C-6); 40.11 (d,  $^2J(\text{C-F}) = 21.2$  Hz, C-4); 55.78 (C-19); 55.83 (C-20); 70.12 (C-10); 75.44 (d,  $^3J(\text{C-F}) = 1.2$  Hz, C-1); 75.58 (C-3); 95.18 (d,  $^1J(\text{C-F}) = 169.0$  Hz, C-5); 109.54 (C-12); 111.13 (C-15); 118.06 (C-16); 123.13 (C-8); 132.20 (C-9); 134.47 (C-11); 148.48 (C-14); 148.85 (C-13). HR-MS: 336.1728 ( $M^+$  ( $\text{C}_{19}\text{H}_{25}\text{O}_4\text{F}$ ) $^+$ ); calc. 336.1731).

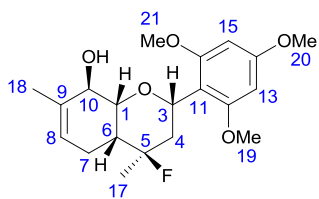
**(2S,4S,4aR,8R,8aR)-2-(3,4-dimethoxyphenyl)-4-fluoro-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-chromen-8-ol ((S)-8d):** Yellow viscous oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.63$  (dd,  $^3J(17, \text{F}) = 23.5$  Hz,



$J(17, 4a) = 0.7$  Hz, 3 H, 17-H); 1.79 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.83 (br.dd,  $J(4e, 4a) = 13.3$  Hz,  $J(4e,3a) = 2.6$  Hz, 1 H, 4- $H_e$ ); 2.04 (br.dd,  $J(6a, 7a) = 10.6$  Hz,  $J(6a,7e) = 6.5$ , 1 H, 6- $H_a$ ); 2.17 (ddd,  $^3J(4a, \text{F}) = 14.0$  Hz,  $J(4a,4e) = 13.3$  Hz,  $J(4a,3a) = 12.1$  Hz, 1 H, 4- $H_a$ ); 2.16-2.26 (m, 2 H, 7-H); 3.70 (m, all  $J \leq 3.0$  Hz, 1 H, 1- $H_e$ ); 3.82 (s, 3 H, 20-MeO); 3.85 (s, 3 H, 19-MeO); 3.89 (br.s, 1 H, 10- $H_e$ ); 4.31 (dd,  $J(3a,4a) = 12.1$  Hz,  $J(3a,4e) = 2.6$  Hz, 1 H, 3- $H_a$ ); 5.60-5.65 (m, 1 H, 8-H); 6.80 (d,  $J(15,16) = 8.2$  Hz, 1 H, 15-H); 6.81 (d,  $J(12,16) = 2.0$  Hz, 1 H, 12-H); 6.85 (dd,  $J(16,15) = 8.2$  Hz,  $J(16,12) = 2.0$  Hz, 1 H, 16-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 20.60$  (C-18); 22.46 (d,  $^3J(\text{C-F}) = 6.2$  Hz, C-7); 24.76 (d,  $^2J(\text{C-F}) = 26.0$  Hz, C-17); 37.71 (d,  $^2J(\text{C-F}) = 19.0$  Hz, C-6); 40.47 (d,  $^2J(\text{C-F}) = 20.3$  Hz, C-4); 55.76, 55.79 (C-19, C-20); 70.05 (d,  $^4J(\text{C-F}) = 1.8$  Hz, C-10); 77.43 (d,  $^3J(\text{C-F}) = 11.5$  Hz, C-3); 77.91 (d,  $^3J(\text{C-F}) = 7.5$  Hz, C-1); 95.13 (d,  $^1J(\text{C-F}) = 176.0$  Hz, C-5); 109.57 (C-12); 111.06 (C-15); 118.25 (C-16); 124.26 (C-8); 131.22 (C-9); 133.71 (C-11); 148.65 (C-14); 148.84 (C-13).

**Reaction of 1 with 2,4,6-trimethoxybenzaldehyde (6e):** The reaction of diol 1 and aldehyde 6e for 8 hours at 2 °C gave products 2e ( $R:S = 1:1$ , 35%), 8e ( $R:S = 10:1$ , 42%). Spectral characteristics of compounds 2e have coincided with those described in the work [4].

**(2S,4R,4aR,8R,8aR)-4-fluoro-4,7-dimethyl-2-(2,4,6-trimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-2H-chromen-8-ol ((R)-8e):** Brown viscous oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.34$  (d,  $^3J(17, \text{F}) = 22.2$  Hz, 3 H, 17-H); 1.54 (dddd,  $J(4e,4a) = 14.6$  Hz,  $^3J(4e,\text{F}) = 11.5$  Hz,  $J(4e, 3a) = 3.2$  Hz,  $J(4e,6a) = 1.3$  Hz, 1 H, 4- $H_e$ ); 1.77 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.87-2.00 (m, 2 H, 6- $H_a$ , 7- $H_e$ ); 2.14-2.23

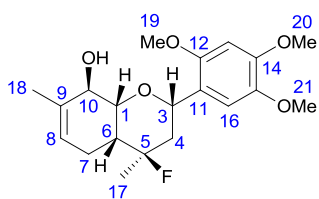


(m, 1 H, 7-H<sub>a</sub>); 2.60 (ddd,  $^3J(4a,F) = 42.0$  Hz,  $J(4a,4e) = 14.6$  Hz,  $J(4a,3a) = 12.1$  Hz, 1 H, 4-H<sub>a</sub>); 3.73 (s, 6 H, 19-MeO, 21-MeO); 3.75 (s, 3H, 20-MeO); 3.90 (br.s, 1 H, 10-H<sub>e</sub>); 4.09 (m, all  $J \leq 3.0$  Hz, 1 H, 1-H<sub>e</sub>); 5.31 (dd,  $J(3a,4a) = 12.1$  Hz,  $J(3a,4e) = 3.2$  Hz, 1H, 3-H<sub>a</sub>); 5.56-5.60 (m, 1 H, 8-H); 6.09 (s, 2 H, 13-H, 15-H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>)  $\delta = 20.71$  (C-18); 24.00 (d,  $^3J(\text{C-F}) = 9.3$  Hz, C-7); 25.06 (d,  $^2J(\text{C-F}) = 24.8$  Hz, C-17); 35.52 (d,  $^2J(\text{C-F}) = 20.8$  Hz, C-4); 36.62 (d,  $^2J(\text{C-F}) = 20.8$  Hz, C-6); 55.16 (C-20); 56.10 (C-19, C-21); 67.65 (C-3); 70.34 (C-10); 75.20 (d,  $^3J(\text{C-F}) = 1.8$  Hz, C-1); 91.97 (C-13, C-15); 95.84 (d,  $^1J(\text{C-F}) = 167.6$  Hz, C-5); 110.45 (C-11); 123.66 (C-8); 132.02 (C-9); 159.74 (C-14); 160.78 (C-12, C-16). HR-MS: 366.1836 ( $M^+$  (C<sub>20</sub>H<sub>27</sub>O<sub>5</sub>F)<sup>+</sup>; calc. 366.1837).

**Reaction of 1 with 2,4,5-trimethoxybenzaldehyde (6f):** The reaction of diol **1** and aldehyde **6f** for 8 hours at 2 °C gave products **2f** (*R:S* = 1:3, 8%), **8f** (*R:S* = 7:1, 20%) and **9f** (14%). Spectral characteristics of compounds **2f** and **9f** have coincided with those described in the work [4].

**(2*S*,4*R*,4*aR*,8*R*,8*aR*)-4-fluoro-4,7-dimethyl-2-(2,4,5-trimethoxyphenyl) -3,4,4*a*,5,8,8*a*-**

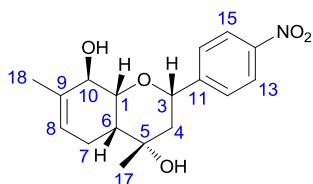
**hexahydro-2*H*-chromen-8-ol ((*R*)-8f):** Brown viscous oil.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta = 1.34$  (d,  $^3J(17, F) =$



22.3 Hz, 3 H, 17-H); 1.72 (ddd,  $J(4a,F) = 40.7$  Hz,  $J(4a,4e) = 14.7$  Hz,  $J(4a,3a) = 11.6$  Hz, 1 H, 4-H<sub>a</sub>); 1.83 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.92 (ddd,  $J(4e,4a) = 14.7$  Hz,  $J(4e,F) = 10.8$  Hz,  $J(4e,3a) = 2.8$  Hz, 1 H, 4-H<sub>e</sub>); 1.93-2.05 (m, 3 H, 6-H, 7-2H); 3.78 (s, 3 H, 19-MeO); 3.80 (s, 3 H, 21-MeO); 3.84 (s, 3 H, 20-MeO); 3.93 (br.s, 1 H, 10-H<sub>e</sub>); 4.16 (m, all  $J \leq 3.0$  Hz, 1 H, 1-H<sub>e</sub>); 5.05 (dd,  $J(3a,4a) = 11.6$  Hz,  $J(3a,4e) = 2.8$  Hz, 1 H, 3-H<sub>a</sub>); 5.57-5.61 (m, 1 H, 8-H); 6.48 (s, 1 H, 13-H); 6.88 (s, 1 H, 16-H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>)  $\delta = 20.81$  (C-18); 24.13 (d,  $^3J(\text{C-F}) = 9.3$  Hz, C-7); 24.81 (d,  $^2J(\text{C-F}) = 24.3$  Hz, C-17); 36.25 (d,  $^2J(\text{C-F}) = 20.8$  Hz, C-6); 38.89 (d,  $^2J(\text{C-F}) = 21.7$  Hz, C-4); 56.09, 56.49, 56.88 (C-19, C-20, C-21); 70.24 (C-10); 70.27 (C-3); 75.35 (d,  $^3J(\text{C-F}) = 1.3$  Hz, C-1); 95.28 (d,  $^1J(\text{C-F}) = 168.5$  Hz, C-5); 97.83 (C-13); 111.33 (C-16); 122.23 (C-11); 123.23 (C-8); 132.23 (C-9); 143.30 (C-15); 149.08 (C-14); 150.50 (C-12). HR-MS: 366.1842 ( $M^+$  (C<sub>20</sub>H<sub>27</sub>O<sub>5</sub>F)<sup>+</sup>; calc. 366.1837).

**Reaction of 1 with 4-nitrobenzaldehyde (6g):** The reaction of diol **1** and aldehyde **6g** for 72 hours at 2 °C gave products **2g** (*R:S* = 1:1, 17%), **8g** (*R:S* = 12:1, 53%).

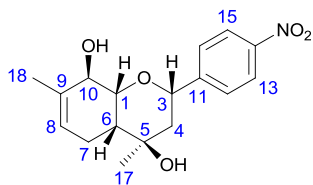
**(2*S*,4*S*,4*aR*,8*R*,8*aR*)-4,7-dimethyl-2-(4-nitrophenyl)-3,4,4*a*,5,8,8*a*-hexahydro-2*H*-chromene-4,8-diol ((*S*)-2g):** Yellow oil.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta = 1.53$  (s, 3 H, 17-H); 1.70 (ddd,  $J(4e,4a) = 13.3$



Hz,  $J(4e,3a) = 3.0$  Hz,  $J(4e,6a) = 1.1$  Hz, 1 H, 4- $H_e$ ); 1.75-1.81 (1H, m, 4- $H_a$ ); 1.81 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.86 (br.dd,  $J(6a,7a) = 10.7$  Hz,  $J(6a,7e) = 6.7$  Hz, 1 H, 6- $H_a$ ); 2.05-2.22 (m, 2 H, 7-H); 3.82 (br.dd, both  $J \sim 2.2$  Hz, 1 H, 1- $H_e$ ); 3.90 (br.s, 1 H, 10- $H_e$ ); 4.51 (dd,  $J(3a,4a) = 11.8$  Hz,  $J(3a,4e) = 3.0$  Hz, 1 H, 3- $H_a$ ); 5.62-5.65 (m, 1 H, 8-H); 7.43 (br.d,  $J = 8.9$  Hz, 2 H, 12-H, 16-H); 8.13 (br.d,  $J = 8.9$  Hz, 2 H, 13-H, 15-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 20.65$  (C-18); 22.58 (C-7); 26.93 (C-17); 38.13 (C-6); 42.96 (C-4); 70.35 (C-10); 70.83 (C-5); 76.34 (C-3); 77.64 (C-1); 123.47 (C-13, C-15); 124.43 (C-8); 126.29 (C-12, C-16); 131.34 (C-9); 147.12 (C-14); 149.24 (C-11). HR-MS: 319.1421 ( $M^+$  ( $\text{C}_{17}\text{H}_{21}\text{O}_5\text{N}$ ) $^+$ ); calc. 319.1414).

**(2S,4R,4aR,8R,8aR)-4,7-dimethyl-2-(4-nitrophenyl)-3,4,4a,5,8,8a-hexahydro-2H-chromene-**

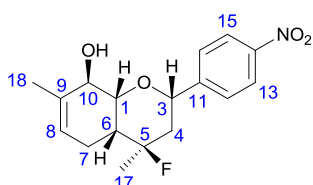
**4,8-diol ((R)-2g):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.22$  (s, 3 H, 17-H); 1.61 (dd,  $J(4a,4e) = 14.0$  Hz,  $J(4a,3a) =$



11.3 Hz, 1 H, 4- $H_a$ ); 1.67 (ddd,  $J(4e,4a) = 14.0$  Hz,  $J(4e,3a) = 3.2$  Hz,  $J(4e,6a) = 1.2$  Hz, 1 H, 4- $H_e$ ); 1.73 (br.dd,  $J(6a,7a) = 10.8$  Hz,  $J(6a,7e) = 6.7$  Hz, 1 H, 6- $H_a$ ); 1.81 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.88-2.04 (m, 2 H, 7-H); 3.92 (br.s, 1 H, 10- $H_e$ ); 4.26 (br.dd, both  $J \sim 2.2$  Hz, 1 H, 1- $H_e$ ); 4.88 (dd,  $J(3a,4a) = 11.3$  Hz,  $J(3a,4e) = 3.2$  Hz, 1 H, 3- $H_a$ ); 5.56-5.59 (m, 1 H, 8-H); 7.43 (br.d,  $J = 8.9$  Hz, 2 H, 12-H, 16-H); 8.10 (br.d,  $J = 8.9$  Hz, 2 H, 13-H, 15-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 20.74$  (C-18); 24.43 (C-7); 28.16 (C-17); 37.84 (C-6); 41.93 (C-4); 70.36 (C-10); 70.60 (C-5); 74.73 (C-3); 75.10 (C-1); 123.39 (C-13, C-15); 123.81 (C-8); 126.24 (C-12, C-16); 131.81 (C-9); 146.95 (C-14); 150.13 (C-11).

**(2S,4R,4aR,8R,8aR)-4-fluoro-4,7-dimethyl-2-(4-nitrophenyl)-3,4,4a,5,8,8a-hexahydro-2H-**

**chromen-8-ol ((R)-8g):** Yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.35$  (d,  $^3J(17, \text{F}) = 22.4$  Hz, 3 H, 17-H);



1.69 (ddd,  $^3J(4a, \text{F}) = 39.5$  Hz,  $J(4a,4e) = 14.5$  Hz,  $J(4a,3a) = 11.8$  Hz, 1 H, 4- $H_a$ ); 1.83 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.84-1.92 (m, 1 H, 7- $H_a$ ); 1.95 (dddd,  $J(4e,4a) = 14.5$  Hz,  $^3J(4e, \text{F}) = 10.0$  Hz,  $J(4e,3a) = 2.9$  Hz,  $J(4e,6a) = 1.2$  Hz, 1 H, 4- $H_e$ ); 1.99-2.07 (m, 2 H, 6- $H_a$ , 7- $H_e$ ); 3.93 (br.s, 1 H, 10- $H_e$ ); 4.16 (m, all  $J \leq 3.0$  Hz, 1 H, 1- $H_e$ ); 4.84 (dd,  $J(3a,4a) = 11.8$  Hz,  $J(3a,4e) = 2.9$  Hz, 1 H, 3- $H_a$ ); 5.56-5.60 (m, 1 H, 8-H); 7.45 (dd,  $J(12,13) = J(16,15) = 8.8$  Hz,  $J(12,3a) = J(16,3a) = 0.6$  Hz, 2 H, 12-H, 16-H); 8.14 (d,  $J(13,12) = J(15,16) = 8.8$  Hz, 2 H, 13-H, 15-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 20.76$  (C-18); 23.94 (d,  $^3J(\text{C-F}) = 9.3$  Hz, C-7); 24.65 (d,  $^2J(\text{C-F}) = 24.3$  Hz, C-17); 35.84 (d,  $^2J(\text{C-F}) = 20.8$  Hz, C-6); 40.17 (d,  $^2J(\text{C-F}) = 21.7$  Hz, C-4); 69.91 (C-10); 74.60 (C-3); 75.27 (d,  $^3J(\text{C-F}) = 1.3$  Hz, C-1); 94.81 (d,  $^1J(\text{C-F}) = 169.8$  Hz, C-5); 123.0 (C-8); 123.48 (C-13, C-15);

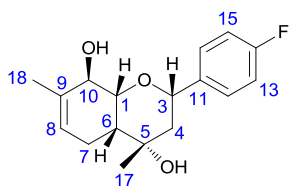


126.23 (C-12, C-16); 132.17 (C-9); 147.11 (C-14); 149.31 (C-11). HR-MS: 321.1369 ( $M^+$  ( $C_{17}H_{20}O_4NF$ ) $^+$ ; calc. 321.1371).

**Reaction of 1 with 4-fluorobenzaldehyde (6h):** The reaction of diol **1** and aldehyde **6h** for 72 hours at 2 °C gave products **2h** ( $R:S = 1:2$ , 17%), **8h** ( $R:S = 6:1$ , 47%).

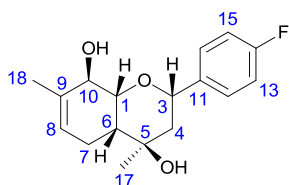
**(2S,4S,4aR,8R,8aR)-2-(4-fluorophenyl)-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-chromene-**

**4,8-diol ((S)-2h):** Yellow oil.  $^1H$  NMR ( $CDCl_3+CD_3OD$ ):  $\delta = 1.41$  (s, 3 H, 17-H); 1.54 (br. dd,  $J(4e,4a) = 13.3$  Hz,  $J(4e,3a) = 2.5$  Hz, 1 H, 4- $H_e$ ); 1.71 (br.s, 3 H, 18-H); 1.74 (br.t,  $J(6a,7) = 8.7$  Hz, 1 H, 6- $H_a$ ); 1.78 (dd,  $J(4a,4e) = 13.3$  Hz,  $J(4a,3a) = 12.1$  Hz, 1 H, 4- $H_a$ ); 2.03-2.11 (m, 2 H, 7-H); 3.70 (dd,  $J(1e,6a) \approx J(1e,10e) \approx 2.2$  Hz, 1 H, 1- $H_e$ ); 3.76 (br.s, 1 H, 10- $H_e$ ); 4.32 (dd,  $J(3a,4a) = 12.1$  Hz,  $J(3a,4e) = 2.5$  Hz, 1 H, 3- $H_a$ ); 5.53-5.57 (m, 1 H, 8-H); 6.89 (dd,  $J(13,12) = {}^3J(13,F) = J(15,16) = {}^3J(15,F) = 8.8$  Hz, 2 H, 13-H, 15-H); 7.18 (dd,  $J(12,13) = J(16,15) = 8.8$  Hz,  ${}^4J(12,F) = {}^4J(16,F) = 5.5$  Hz, 2 H, 12-H, 16-H).  $^{13}C$  NMR ( $CDCl_3+CD_3OD$ )  $\delta = 20.37$  (C-18); 22.50 (C-7); 26.39 (C-17); 38.02 (C-6); 42.50 (C-4); 69.90 (C-10); 70.38 (C-5); 76.76 (C-3); 77.79 (C-1); 114.84 (d,  ${}^2J(C-F) = 21.6$  Hz, C-13, C-15); 124.13 (C-8); 127.38 (d,  ${}^3J(C-F) = 8.3$  Hz, C-12, C-16); 131.07 (C-9); 137.67 (d,  ${}^4J(C-F) = 3.3$  Hz, C-11); 161.94 (d,  ${}^1J(C-F) = 245.1$  Hz, C-14); HR-MS: 275.1440 ( $[M-OH]^+$  ( $C_{17}H_{20}O_2F$ ) $^+$ ; calc. 275.1442).



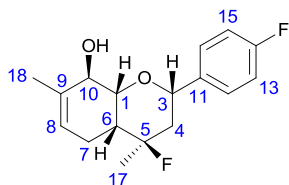
**(2S,4R,4aR,8R,8aR)-2-(4-fluorophenyl)-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-chromene-**

**4,8-diol ((R)-2h):** Yellow oil.  $^1H$  NMR ( $CDCl_3+CD_3OD$ ):  $\delta = 1.12$  (s, 3 H, 17-H); 1.51 (ddd,  $J(4e,4a) = 14.1$  Hz,  $J(4e,3a) = 3.0$  Hz,  $J(4e,6a) = 1.3$  Hz, 1 H, 4- $H_e$ ); 1.60 (dd,  $J(4a,4e) = 14.1$  Hz,  $J(4a,3a) = 11.5$  Hz, 1 H, 4- $H_a$ ); 1.58-1.63 (m, 1 H, 6- $H_a$ ); 1.71 (br.s, 3 H, 18-H); 1.86-1.96 (m, 2 H, 7-H); 3.77 (br.s, 1 H, 10- $H_e$ ); 4.12 (dd,  $J(1e,6a) \approx J(1e,10e) \approx 2.2$  Hz, 1 H, 1- $H_e$ ); 4.67 (dd,  $J(3a,4a) = 11.5$  Hz,  $J(3a,4e) = 3.0$  Hz, 1 H, 3- $H_a$ ); 5.47-5.51 (m, 1 H, 8-H); 6.88 (dd,  $J(13,12) = {}^3J(13,F) = J(15,16) = {}^3J(15,F) = 8.8$  Hz, 2 H, 13-H, 15-H); 7.18 (dd,  $J(12,13) = J(16,15) = 8.8$  Hz,  ${}^4J(12,F) = {}^4J(16,F) = 5.5$  Hz, 2 H, 12-H, 16-H).  $^{13}C$  NMR ( $CDCl_3+CD_3OD$ )  $\delta = 20.44$  (C-18); 24.32 (C-7); 27.61 (C-17); 37.47 (C-6); 41.75 (C-4); 69.90 (C-10); 70.05 (C-5); 75.12 (C-3); 75.24 (C-1); 114.76 (d,  ${}^2J(C-F) = 21.3$  Hz, C-13, C-15); 123.51 (C-8); 127.32 (d,  ${}^3J(C-F) = 8.3$  Hz, C-12, C-16); 131.66 (C-9); 138.31 (d,  ${}^4J(C-F) = 3.3$  Hz, C-11); 161.82 (d,  ${}^1J(C-F) = 245.0$  Hz, C-14).



**(2S,4R,4aR,8R,8aR)-4-fluoro-2-(4-fluorophenyl)-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-**

**chromen-8-ol ((R)-8h):** Yellow oil.  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 1.35$  (d,  ${}^3J(17, F) = 22.4$  Hz, 3 H, 17-H);

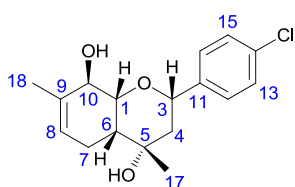


1.75 (ddd,  $^3J(4a, F) = 39.9$  Hz,  $J(4a,4e) = 14.6$  Hz,  $J(4a, 3a) = 11.7$  Hz, 1 H, 4- $H_a$ ); 1.82 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.89 (dddd,  $J(4e,4a) = 14.6$  Hz,  $^3J(4e,F) = 10.4$  Hz,  $J(4e,3a) = 2.9$  Hz,  $J(4e,6a) = 1.2$  Hz, 1 H, 4- $H_e$ ); 1.88-1.96 (m, 1 H, 7- $H_a$ ); 1.97-2.06 (m, 2 H, 6- $H_a$ , 7- $H_e$ ); 3.92 (br.s, 1 H, 10- $H_e$ ); 4.14 (m, all  $J \leq 3.0$  Hz, 1 H, 1- $H_e$ ); 4.73 (dd,  $J(3a,4a) = 11.7$  Hz,  $J(3a,4e) = 2.9$  Hz, 1 H, 3- $H_a$ ); 5.56-5.60 (m, 1 H, 8-H); 6.98 (dd,  $J(13,12) = J(15,16) = 8.8$  Hz,  $^3J(13,F) = ^3J(15,F) = 8.8$  Hz, 2 H, 13-H, 15-H); 7.26 (dd,  $J(12,13) = J(16,15) = 8.8$  Hz,  $^4J(12,F) = ^4J(16,F) = 5.4$  Hz, 2 H, 12-H, 16-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 20.78$  (C-18); 24.04 (d,  $^3J(\text{C-F}) = 9.4$  Hz, C-7); 24.73 (d,  $^2J(\text{C-F}) = 24.4$  Hz, C-17); 35.98 (d,  $^2J(\text{C-F}) = 20.8$  Hz, C-6); 40.38 (d,  $^2J(\text{C-F}) = 21.5$  Hz, C-4); 70.05 (C-10); 75.04 (C-3); 75.33 (d,  $^3J(\text{C-F}) = 1.2$  Hz, C-1); 95.05 (d,  $^1J(\text{C-F}) = 168.8$  Hz, C-5); 115.07 (d,  $^2J(\text{C-F}) = 21.3$  Hz, C-13, C-15); 123.12 (C-8); 127.37 (d,  $^3J(\text{C-F}) = 8.1$  Hz, C-12, C-16); 132.19 (C-9); 137.73 (d,  $^4J(\text{C-F}) = 3.1$  Hz, C-11); 162.06 (d,  $^1J(\text{C-F}) = 245.4$  Hz, C-14). HR-MS: 294.1424 ( $M^+$  ( $\text{C}_{17}\text{H}_{20}\text{O}_2\text{F}_2$ ) $^+$ ; calc. 294.1426).

**Reaction of 1 with 4-chlorobenzaldehyde (6i):** The reaction of diol **1** and aldehyde **6i** for 72 hours at 2 °C gave products **2i** ( $R:S = 1:3$ , 17%), **8i** ( $R:S = 6:1$ , 58%).

**(2S,4S,4aR,8R,8aR)-2-(4-chlorophenyl)-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-chromene-**

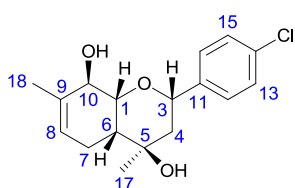
**4,8-diol ((S)-2i):** Transparent viscous oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{CD}_3\text{OD}$ ):  $\delta = 1.16$  (s, 3 H, 17-H); 1.29



(ddd,  $J(4e,4a) = 13.4$  Hz,  $J(4e,3a) = 2.7$  Hz,  $J(4e,6a) = 1.1$  Hz, 1 H, 4- $H_e$ ); 1.45 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.48-1.54 (m, 2 H, 4- $H_a$ , 6- $H_a$ ); 1.77-1.89 (m, 2 H, 7-H); 3.45 (dd,  $J(1e,10e) = 2.4$  Hz,  $J(1e,6a) = 2.2$  Hz, 1 H, 1- $H_e$ ); 3.48 (br.s, 1 H, 10- $H_e$ ); 4.10 (dd,  $J(3a,4a) = 12.1$  Hz,  $J(3a,4e) = 2.7$  Hz, 1 H, 3- $H_a$ ); 5.27-5.31 (m, 1 H, 8-H); 6.90-6.94 (m, 4 H, 12-H, 13-H, 15-H, 16-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{CD}_3\text{OD}$ )  $\delta = 19.67$  (C-18); 22.09 (C-7); 25.59 (C-17); 37.63 (C-6); 41.90 (C-4); 69.37 (C-10); 69.72 (C-5); 76.27 (C-3); 77.53 (C-1); 123.65 (C-8); 126.66 (C-12, C-16); 127.63 (C-13, C-15); 130.59 (C-9); 132.41 (C-14); 140.27 (C-11). HR-MS: 308.1178 ( $M^+$  ( $\text{C}_{17}\text{H}_{21}\text{O}_3\text{Cl}$ ) $^+$ ; calc. 308.1174).

**(2S,4R,4aR,8R,8aR)-2-(4-chlorophenyl)-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-chromene-**

**4,8-diol ((R)-2i):** Transparent viscous oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{CD}_3\text{OD}$ ):  $\delta = 1.05$  (s, 3 H, 17-H); 1.46

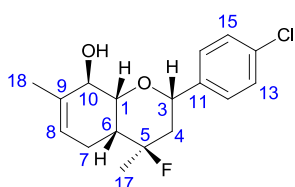


(ddd,  $J(4e,4a) = 14.1$  Hz,  $J(4e,3a) = 3.2$  Hz,  $J(4e,6a) = 1.1$  Hz, 1 H, 4- $H_e$ ); 1.51 (dd,  $J(4a,4e) = 14.1$  Hz,  $J(4a,3a) = 11.4$  Hz, 1 H, 4- $H_a$ ); 1.53 (dddd,  $J(6a,7a) = 10.8$  Hz,  $J(6a,7e) = 6.7$  Hz,  $J(6a,1e) = 2.1$  Hz,  $J(6a,4e) = 1.1$  Hz, 1 H, 6- $H_a$ ); 1.64 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.75-1.91 (m, 2 H, 7-H);

3.69 (br.s, 1 H, 10-H<sub>e</sub>); 4.04 (dd,  $J(1e,10e) = 2.3$  Hz,  $J(1e,6a) = 2.1$  Hz, 1 H, 1-H<sub>e</sub>); 4.60 (dd,  $J(3a,4a) = 11.4$  Hz,  $J(3a,4e) = 3.2$  Hz, 1 H, 3-H<sub>a</sub>); 5.45-5.50 (m, 1 H, 8-H); 7.06-7.13 (m, 4 H, 12-H, 13-H, 15-H, 16-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>+CD<sub>3</sub>OD)  $\delta = 20.18$  (C-18); 24.18 (C-7); 27.34 (C-17); 37.26 (C-6); 41.54 (C-4); 69.83 (C-10); 70.13 (C-5); 75.17 (C-3); 76.64 (C-1); 123.33 (C-8); 126.92 (C-12, C-16); 127.98 (C-13, C-15); 131.54 (C-9); 132.53 (C-14); 141.01 (C-11).

**(2S,4R,4aR,8R,8aR)-2-(4-chlorophenyl)-4-fluoro-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-**

**chromen-8-ol ((R)-8i):** Yellow viscous oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.35$  (d,  $^3J(17, F) = 22.4$  Hz, 3 H,

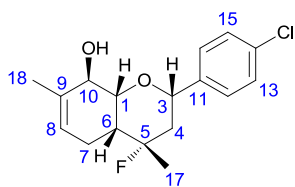


17-H); 1.73 (ddd,  $^3J(4a,F) = 39.9$  Hz,  $J(4a,4e) = 14.5$  Hz,  $J(4a,3a) = 11.7$  Hz, 1 H, 4-H<sub>a</sub>); 1.83 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.89 (dddd,  $J(4e,4a) = 14.5$  Hz,  $^3J(4e,F) = 10.2$  Hz,  $J(4e,3a) = 2.9$  Hz,  $J(4e,6a) = 1.1$  Hz, 1 H, 4-H<sub>e</sub>); 1.87-1.95 (m, 1 H, 7-H<sub>a</sub>); 1.97-2.06 (m, 2 H, 6-H<sub>a</sub>, 7-H<sub>e</sub>); 3.93 (br.s, 1

H, 10-H<sub>e</sub>); 4.14 (m, all  $J \leq 3.0$  Hz, 1 H, 1-H<sub>e</sub>); 4.72 (dd,  $J(3a,4a) = 11.7$  Hz,  $J(3a,4e) = 2.9$  Hz, 1 H, 3-H<sub>a</sub>); 5.56-5.60 (m, 1 H, 8-H); 7.23 (d,  $J(12,13) = J(16,15) = 8.5$  Hz, 2 H, 12-H, 16-H); 7.27 (d,  $J(13,12) = J(15,16) = 8.5$  Hz, 2 H, 13-H, 15-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta = 20.78$  (C-18); 24.03 (d,  $^3J(C-F) = 9.3$  Hz, C-7); 24.74 (d,  $^2J(C-F) = 24.3$  Hz, C-17); 35.98 (d,  $^2J(C-F) = 20.8$  Hz, C-6); 40.29 (d,  $^2J(C-F) = 21.23$  Hz, C-4); 70.07 (C-10); 74.97 (C-3); 75.30 (d,  $^3J(C-F) = 1.1$  Hz, C-1); 94.94 (d,  $^1J(C-F) = 168.5$  Hz, C-5); 123.13 (C-8); 127.05 (C-12, C-16); 128.41 (C-13, C-15); 132.19 (C-9); 133.10 (C-14); 140.47 (C-11). HR-MS: 310.1133 ( $M^+$  (C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>FCI)<sup>+</sup>; calc. 310.1130).

**(2S,4S,4aR,8R,8aR)-2-(4-chlorophenyl)-4-fluoro-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-**

**chromen-8-ol ((S)-8i):** Yellow viscous oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.64$  (d,  $^3J(17, F) = 23.4$  Hz, 3 H,



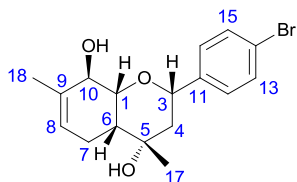
17-H); 1.81 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.82 (br.dd,  $J(4e,4a) = 13.3$  Hz,  $J(4e,3a) = 2.6$  Hz, 1 H, 4-H<sub>e</sub>); 1.98-2.12 (m, 2 H, 4-H<sub>a</sub>, 6-H<sub>a</sub>); 2.16-2.22 (m, 2 H, 7-H); 3.71 (m, all  $J \leq 3.0$  Hz, 1 H, 1-H<sub>e</sub>); 3.90 (br.s, 1 H, 10-H<sub>e</sub>); 4.35 (dd,  $J(3a,4a) = 12.1$  Hz,  $J(3a,4e) = 2.6$  Hz, 1 H, 3-H<sub>a</sub>); 5.63-5.67 (m,

1 H, 8-H); 7.23 (d,  $J(12,13) = J(16,15) = 8.5$  Hz, 2 H, 12-H, 16-H); 7.28 (d,  $J(13,12) = J(15,16) = 8.5$  Hz, 2 H, 13-H, 15-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta = 20.65$  (C-18); 22.46 (d,  $^3J(C-F) = 6.2$  Hz, C-7); 24.73 (d,  $^2J(C-F) = 26.1$  Hz, C-17); 37.62 (d,  $^2J(C-F) = 19.0$  Hz, C-6); 40.82 (d,  $^2J(C-F) = 20.8$  Hz, C-4); 70.07 (d,  $^4J(C-F) = 1.8$  Hz, C-10); 76.82 (d,  $^3J(C-F) = 11.5$  Hz, C-3); 77.81 (d,  $^3J(C-F) = 7.5$  Hz, C-1); 94.88 (d,  $^1J(C-F) = 176.9$  Hz, C-5); 124.32 (C-8); 127.11 (C-12, C-16); 128.47 (C-13, C-15); 131.23 (C-9); 133.38 (C-14); 139.76 (C-11).

**Reaction of 1 with 4-bromobenzaldehyde(6j):** The reaction of diol **1** and aldehyde **6j** for 72 hours at 2 °C gave products **2j** (*R:S* = 1:2, 13%), **8j** (*R:S* = 10:1, 60%).

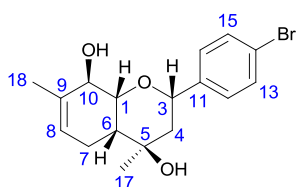
**(2*S*,4*S*,4*aR*,8*R*,8*aR*)-2-(4-bromophenyl)-4,7-dimethyl-3,4,4*a*,5,8,8*a*-hexahydro-2*H*-chromene-**

**4,8-diol ((*S*)-**2j**):** Yellow viscous oil. <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ = 1.54 (s, 3 H, 17-H); 1.67 (ddd, *J*(4*e*,4*a*) = 13.4 Hz, *J*(4*e*,3*a*) = 2.8 Hz, *J*(4*e*,6*a*) = 1.2 Hz, 1 H, 4-H<sub>e</sub>); 1.83 (m, all *J* ≤ 2.5 Hz, 3 H, 18-H); 1.85 (dd, *J*(4*a*,4*e*) = 13.4 Hz, *J*(4*a*,3*a*) = 12.0 Hz, 1 H, 4-H<sub>a</sub>); 1.88-1.93 (m, 1 H, 6-H<sub>a</sub>); 2.15-2.21 (m, 2 H, 7-H); 3.82-3.85 (m, 2 H, 1-H<sub>e</sub>, 10-H<sub>e</sub>); 4.51 (dd, *J*(3*a*,4*a*) = 12.0 Hz, *J*(3*a*,4*e*) = 2.8 Hz, 1 H, 3-H<sub>a</sub>); 5.65-5.69 (m, 1 H, 8-H); 7.26 (d, *J*(12,13) = *J*(16,15) = 8.5 Hz, 2 H, 12-H, 16-H); 7.48 (d, *J*(13,12) = *J*(15,16) = 8.5 Hz, 2 H, 13-H, 15-H). <sup>13</sup>C NMR (CD<sub>3</sub>OD) δ = 21.13 (C-18); 24.02 (C-7); 27.09 (C-17); 39.67 (C-6); 43.97 (C-4); 71.38 (C-10); 71.53 (C-5); 78.12 (C-3); 79.49 (C-1); 122.04 (C-14); 125.40 (C-8); 128.86 (C-12, C-16); 132.37 (C-13, C-15); 132.62 (C-9); 143.25 (C-11). HR-MS: 334.0569 ([*M*-H<sub>2</sub>O]<sup>+</sup> (C<sub>17</sub>H<sub>19</sub>O<sub>2</sub>Br)<sup>+</sup>; calc. 334.0563).



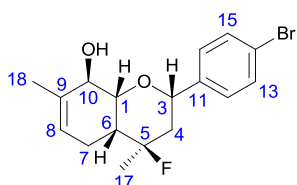
**(2*S*,4*R*,4*aR*,8*R*,8*aR*)-2-(4-bromophenyl)-4,7-dimethyl-3,4,4*a*,5,8,8*a*-hexahydro-2*H*-chromene-**

**4,8-diol ((*R*)-**2j**):** Yellow viscous oil. <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ = 1.24 (s, 3 H, 17-H); 1.63 (ddd, *J*(4*e*,4*a*) = 14.1 Hz, *J*(4*e*,3*a*) = 3.0 Hz, *J*(4*e*,6*a*) = 1.2 Hz, 1 H, 4-H<sub>e</sub>); 1.73 (dd, *J*(4*a*,4*e*) = 14.1 Hz, *J*(4*a*,3*a*) = 11.6 Hz, 1 H, 4-H<sub>a</sub>); 1.77-1.82 (m, 1 H, 6-H<sub>a</sub>); 1.83 (m, all *J* ≤ 2.5 Hz, 3 H, 18-H); 1.96-2.10 (m, 2 H, 7-H); 3.83 (br.s, 1 H, 10-H<sub>e</sub>); 4.26 (dd, *J*(1*e*,10*e*) = 2.3 Hz, *J*(1*e*,6*a*) = 2.1 Hz, 1 H, 1-H<sub>e</sub>); 4.77 (dd, *J*(3*a*,4*a*) = 11.6 Hz, *J*(3*a*,4*e*) = 3.0 Hz, 1 H, 3-H<sub>a</sub>); 5.60-5.64 (m, 1 H, 8-H); 7.25 (d, *J*(12,13) = *J*(16,15) = 8.5 Hz, 2 H, 12-H, 16-H); 7.47 (d, *J*(13,12) = *J*(15,16) = 8.5 Hz, 2 H, 13-H, 15-H). <sup>13</sup>C NMR (CD<sub>3</sub>OD) δ = 22.22 (C-18); 25.64 (C-7); 28.23 (C-17); 38.71 (C-6); 43.15 (C-4); 71.19 (C-5); 71.35 (C-10); 76.61 (C-3); 77.08 (C-1); 121.85 (C-14); 124.83 (C-8); 128.88 (C-12, C-16); 132.33 (C-13, C-15); 133.10 (C-9); 143.70 (C-11).



**(2*S*,4*R*,4*aR*,8*R*,8*aR*)-2-(4-bromophenyl)-4-fluoro-4,7-dimethyl-3,4,4*a*,5,8,8*a*-hexahydro-2*H*-**

**chromen-8-ol ((*R*)-**8j**):** Yellow viscous oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.35 (d, <sup>3</sup>*J*(17, F) = 22.3 Hz, 3 H, 17-H); 1.72 (ddd, <sup>3</sup>*J*(4*a*,F) = 39.8 Hz, *J*(4*a*,4*e*) = 14.6 Hz, *J*(4*a*,3*a*) = 11.7 Hz, 1 H, 4-H<sub>a</sub>); 1.83 (m, all *J* ≤ 2.5 Hz, 3 H, 18-H); 1.89 (dddd, *J*(4*e*,4*a*) = 14.6 Hz, <sup>3</sup>*J*(4*e*,F) = 10.2 Hz, *J*(4*e*,3*a*) = 3.0 Hz, *J*(4*e*,6*a*) = 1.1 Hz, 1 H, 4-H<sub>e</sub>); 1.87-1.95 (m, 1 H, 7-H<sub>a</sub>); 1.97-2.07 (m, 2 H, 6-H<sub>a</sub>, 7-H<sub>e</sub>); 3.93 (br.s, 1 H, 10-H<sub>e</sub>); 4.14 (m, all *J* ≤ 3.0 Hz, 1 H, 1-H<sub>e</sub>); 4.71 (dd, *J*(3*a*,4*a*) = 11.7

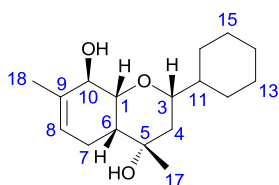


Hz,  $J(3a,4e) = 2.9$  Hz, 1 H, 3- $H_a$ ); 5.56-5.60 (m, 1 H, 8-H); 7.17 (d,  $J(12,13) = J(16,15) = 8.5$  Hz, 2 H, 12-H, 16-H); 7.42 (d,  $J(13,12) = J(15,16) = 8.5$  Hz, 2 H, 13-H, 15-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 20.79$  (C-18); 24.04 (d,  $^3J(\text{C-F}) = 9.3$  Hz, C-7); 24.74 (d,  $^2J(\text{C-F}) = 24.3$  Hz, C-17); 35.99 (d,  $^2J(\text{C-F}) = 20.8$  Hz, C-6); 40.26 (d,  $^2J(\text{C-F}) = 21.2$  Hz, C-4); 70.09 (C-10); 75.01 (C-3); 75.30 (d,  $^3J(\text{C-F}) = 1.3$  Hz, C-1); 94.98 (d,  $^1J(\text{C-F}) = 169.4$  Hz, C-5); 121.21 (C-14); 123.15 (C-8); 127.40 (C-12, C-16); 131.38 (C-13, C-15); 132.21 (C-9); 141.00 (C-11). HR-MS: 354.0620 ( $M^+$  ( $\text{C}_{17}\text{H}_{20}\text{O}_2\text{FBr}$ ) $^+$ ; calc. 354.0625).

**Reaction of 1 with cyclohexanecarbaldehyde (6k):** The reaction of diol **1** and aldehyde **6k** for 8 hours at 2 °C gave products **2k** ( $R:S = 1:3$ , 27%), **8k** ( $R:S = 3:1$ , 61%).

**(2S,4S,4aR,8R,8aR)-2-cyclohexyl-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-chromene-4,8-diol**

**((S)-2k):** Transparent oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3+\text{CD}_3\text{OD}$ ):  $\delta = 0.74$ - $0.87$  (m, 2 H, 12- $H_a$ , 16- $H_a$ );  $0.93$ - $1.10$

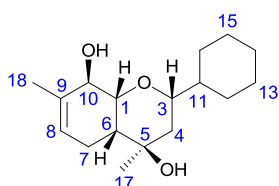


(m, 3 H, 13-H, 14-H, 15-H); 1.15-1.25 (m, 1 H, 11-H); 1.24 (d,  $J(17,4a) = 0.6$  Hz, 3 H, 17-H); 1.29 (ddd,  $J(4e,4a) = 13.2$  Hz,  $J(4e,3a) = 2.6$  Hz,  $J(4e,6a) = 1.0$  Hz, 1 H, 4- $H_e$ ); 1.44 (dd,  $J(4a,4e) = 13.2$  Hz,  $J(4a,3a) = 11.8$  Hz, 1 H, 4- $H_a$ ); 1.46-1.59 (m, 4 H, 12- $H_e$  or 16- $H_e$ , 13- $H'$ , 14- $H'$ , 15- $H'$ ); 1.58 (br.dd,  $J(6a,7a) = 10.8$  Hz,  $J(6a,7e) = 6.6$  Hz, 1 H, 6- $H_a$ ); 1.65 (m, all  $J$

$\leq 2.5$  Hz, 3 H, 18-H); 1.74-1.81 (m, 1 H, 16- $H_e$  or 12- $H_e$ ); 1.86 (dddq,  $J(7a,7e) = 18.0$  Hz,  $J(7a,6a) = 10.8$  Hz,  $J(7a,8) = 2.5$  Hz,  $J(7a,18) = 2.5$  Hz, 1 H, 7- $H_a$ ); 1.94 (dddq,  $J(7e,7a) = 18.0$  Hz,  $J(7e,6a) = 6.6$  Hz,  $J(7e,8) = 5.2$  Hz,  $J(7e,18) = 1.6$  Hz, 1 H, 7- $H_e$ ); 2.95 (ddd,  $J(3a,4a) = 11.8$  Hz,  $J(3a,11) = 6.7$  Hz,  $J(3a,4e) = 2.6$  Hz, 1 H, 3- $H_a$ ); 3.41 (dd,  $J(1e,10e) = 2.3$  Hz,  $J(1e,6a) = 2.1$  Hz, 1 H, 1- $H_e$ ); 3.63 (br.s, 1 H, 10- $H_e$ ); 5.44-5.47 (m, 1 H, 8-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3+\text{CD}_3\text{OD}$ )  $\delta = 20.32$  (C-18); 22.36 (C-7); 25.62, 25.77, 26.18 (C-13, C-14, C-15); 26.54 (C-17); 28.06, 28.91 (C-12, C-16); 37.29 (C-4); 38.40 (C-6); 42.27 (C-11); 70.02 (C-10); 70.53 (C-5); 77.32 (C-1); 79.66 (C-3); 124.30 (C-8); 131.02 (C-9). HR-MS: 262.1923 ( $[M-H_2O]^+$  ( $\text{C}_{17}\text{H}_{26}\text{O}_2$ ) $^+$ ; calc. 262.1927).

**(2S,4R,4aR,8R,8aR)-2-cyclohexyl-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-chromene-4,8-diol**

**((R)-2k):** Transparent oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3+\text{CD}_3\text{OD}$ ):  $\delta = 0.74$ - $0.87$  (m, 2 H, 12- $H_a$ , 16- $H_a$ );  $0.94$ - $1.11$



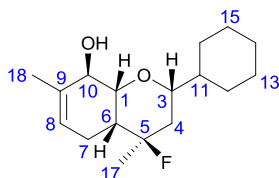
(m, 3 H, 13-H, 14-H, 15-H); 1.04 (s, 3 H, 17-H); 1.15-1.23 (m, 1 H, 11-H); 1.25-1.31 (m, 2 H, 4-H); 1.44-1.59 (m, 5 H, 6- $H_a$ , 12- $H_e$  or 16- $H_e$ , 13- $H'$ , 14- $H'$ , 15- $H'$ ); 1.65 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.74-1.79 (m, 2 H, 7-H); 3.25-3.30 (m, 1 H, 3- $H_a$ ); 3.65 (br.s, 1 H, 10- $H_e$ ); 3.81 (dd,  $J(1e,10e) = 2.4$

Hz,  $J(1e,6a) = 2.2$  Hz, 1 H, 1- $H_e$ ); 5.38-5.41 (m, 1 H, 8-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3+\text{CD}_3\text{OD}$ )  $\delta = 20.39$  (C-18); 24.14 (C-7); 25.65, 25.79, 26.21 (C-13, C-14, C-15); 27.81 (C-17); 27.93, 28.94 (C-12, C-16);

36.36 (C-4); 37.83 (C-6); 42.14 (C-11); 70.02 (C-10); 70.53 (C-5); 74.85 (C-1); 77.87 (C-3); 123.66 (C-8); 131.61 (C-9).

**(2S,4R,4aR,8R,8aR)-2-cyclohexyl-4-fluoro-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-chromen-**

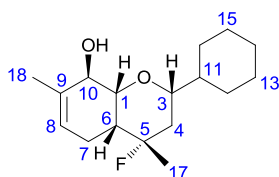
**8-ol ((R)-8k):** Yellow oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 0.85-0.98 (m, 2 H, 12- $\text{H}_a$ , 16- $\text{H}_a$ ); 1.04-1.23 (m, 3 H, 13-H, 14-H, 15-H); 1.29 (d,  $^3J(17, \text{F}) = 22.3$  Hz, 3 H, 17-H); 1.24-1.34 (m, 1 H, 11-H); 1.45 (ddd,  $^3J(4a, \text{F}) = 40.7$  Hz,  $J(4a, 4e) = 14.3$  Hz,  $J(4a, 3a) = 11.7$  Hz, 1 H, 4- $\text{H}_a$ ); 1.55-1.71 (m, 5 H, 4- $\text{H}_e$ , 13- $\text{H}'$ , 14- $\text{H}'$ , 15- $\text{H}'$ , 16- $\text{H}_e$  or 12- $\text{H}_e$ ); 1.78 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.72-1.80 (m, 1 H, 7-H); 1.82-1.95



(m, 3 H, 6-H, 7- $\text{H}'$ , 12- $\text{H}_e$  or 16- $\text{H}_e$ ); 3.36 (ddd,  $J(3a, 4a) = 11.7$  Hz,  $J(3a, 11) = 7.1$  Hz,  $J(3a, 4e) = 2.6$  Hz, 1 H, 3- $\text{H}_a$ ); 3.80 (br.s, 1 H, 10- $\text{H}_e$ ); 3.86 (m, all  $J \leq 3.0$  Hz, 1 H, 1- $\text{H}_e$ ); 5.48-5.52 (m, 1 H, 8-H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 20.80 (C-18); 23.91 (d,  $^3J(\text{C-F}) = 9.6$  Hz, C-7); 25.01 (d,  $^2J(\text{C-F}) = 24.5$  Hz, C-17); 25.73, 25.92, 26.36 (C-13, C-14, C-15); 28.11, 28.92 (C-12, C-16); 35.33 (d,  $^2J(\text{C-F}) = 21.6$  Hz, C-4); 36.40 (d,  $^2J(\text{C-F}) = 21.0$  Hz, C-6); 42.19 (C-11); 70.09 (C-10); 74.97 (C-1); 77.85 (C-3); 95.19 (d,  $^1J(\text{C-F}) = 167.8$  Hz, C-5); 123.24 (C-8); 132.17 (C-9). HR-MS: 263.2005 ( $[\text{M-F}]^+$  (C<sub>17</sub>H<sub>27</sub>O<sub>2</sub>)<sup>+</sup>; calc. 263.2006).

**(2S,4S,4aR,8R,8aR)-2-cyclohexyl-4-fluoro-4,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2H-chromen-**

**8-ol ((S)-8k):** Yellow oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 1.49 (d,  $^3J(17, \text{F}) = 23.7$  Hz, 3 H, 17-H); 1.78 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 2.02-2.08 (m, 2 H, 7-H); 3.00 (ddd,  $J(3a, 4a) = 12.0$  Hz,  $J(3a, 11) = 6.7$  Hz,  $J(3a, 4e) = 2.4$  Hz, 1 H, 3- $\text{H}_a$ ); 3.44 (m, all  $J \leq 3.0$  Hz, 1 H, 1- $\text{H}_e$ ); 3.78 (m, 1 H, 10- $\text{H}_e$ ); 5.55-5.59 (m, 1 H, 8-H). The signals of the others protons are overlapped by those of the main isomer (R)-7k in

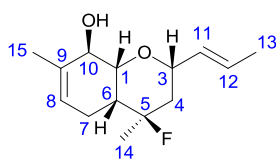


the areas 0.86-0.98, 1.05-1.23, 1.28-1.36, 1.56-1.71 and 1.87-1.95 ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 20.67 (C-18); 22.36 (d,  $^3J(\text{C-F}) = 6.2$  Hz, C-7); 24.93 (d,  $^2J(\text{C-F}) = 25.9$  Hz, C-17); 25.75, 25.91, 26.32 (C-13, C-14, C-15); 28.28, 28.94 (C-12, C-16); 36.01 (d,  $^2J(\text{C-F}) = 20.0$  Hz, C-4); 38.01 (d,  $^2J(\text{C-F}) = 18.5$  Hz, C-6); 42.35 (C-11); 70.09 (C-10); 77.43 (d,  $^3J(\text{C-F}) = 7.3$  Hz, C-1); 79.92 (d,  $^3J(\text{C-F}) = 10.7$  Hz, C-3); 95.67 (d,  $^1J(\text{C-F}) = 175.2$  Hz, C-5); 124.39 (C-8); 131.22 (C-9).

**Reaction of 1 with (E)-but-2-enal 6l:** The reaction of diol **1** and aldehyde **6l** for 8 hours at 2°C gave products **2l** ( $R:S = 1:2$ , 20%), **8l** ( $R:S = 3:1$ , 57%). Spectral characteristics of compounds **2l** have coincided with those described in the work [1].

**(2S,4R,4aR,8R,8aR)-4-fluoro-4,7-dimethyl-2-((E)-prop-1-en-1-yl)-3,4,4a,5,8,8a-hexahydro-2H-**

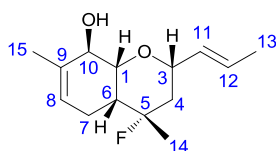
**chromen-8-ol ((R)-8l):** Yellow oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 1.29 (d,  $^3J(14, \text{F}) = 22.3$  Hz, 3 H, 14-H);



1.58 (ddd,  $^3J(4a,F) = 39.7$  Hz,  $J(4a,4e) = 14.6$  Hz,  $J(4a,3a) = 11.4$  Hz, 1 H, 4- $H_a$ ); 1.64 (dd,  $J(13,12) = 6.5$  Hz,  $J(13,11) = 1.7$  Hz, 3 H, 13-H); 1.60-1.70 (m, 1 H, 4- $H_e$ ); 1.77 (m, all  $J \leq 2.5$  Hz, 3 H, 15-H); 1.76-1.84 (m, 1 H, 7- $H_a$ ); 1.86-1.96 (m, 2 H, 6- $H_a$ , 7- $H_e$ ); 3.85 (m, 1 H, 10- $H_e$ ); 3.96 (m, all  $J \leq 3.0$  Hz, 1 H, 1- $H_e$ ); 4.12 (ddd,  $J(3a,4a) = 11.2$  Hz,  $J(3a,11) = 7.0$  Hz,  $J(3a,4e) = 3.1$  Hz, 1 H, 3- $H_a$ ); 5.42 (ddq,  $J(11,12) = 15.4$  Hz,  $J(11,3a) = 7.0$  Hz,  $J(11,13) = 1.7$  Hz, 1 H, 11-H); 5.48-5.52 (m, 1 H, 8-H); 5.68 (dq,  $J(12,11) = 15.4$  Hz,  $J(12,13) = 6.5$  Hz,  $J(12,3a) = 1.0$  Hz, 1 H, 12-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 17.57$  (C-13); 20.75 (C-15); 23.89 (d,  $^3J(\text{C-F}) = 9.6$  Hz, C-7); 24.71 (d,  $^2J(\text{C-F}) = 24.5$  Hz, C-14); 35.95 (d,  $^2J(\text{C-F}) = 20.9$  Hz, C-6); 38.26 (d,  $^2J(\text{C-F}) = 21.8$  Hz, C-4); 69.94 (C-10); 74.48 (C-3); 74.79 (C-1); 94.85 (d,  $^1J(\text{C-F}) = 168.1$  Hz, C-5); 123.22 (C-8); 127.99 (C-12); 131.08 (C-11); 132.02 (C-9). HR-MS: 240.1524 ( $M^+$  ( $\text{C}_{14}\text{H}_{21}\text{O}_2\text{F}$ ) $^+$ ); calc. 240.1520).

**(2S,4S,4aR,8R,8aR)-4-fluoro-4,7-dimethyl-2-((E)-prop-1-en-1-yl)-3,4,4a,5,8,8a-hexahydro-2H-**

**chromen-8-ol ((S)-8l):** Yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.53$  (dd,  $^3J(14, F) = 22.3$  Hz,  $J(14, 4a) = 0.8$

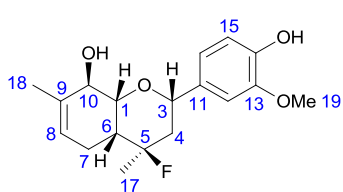


Hz, 3 H, 14-H); 1.59-1.70 (m, 5 H, 4-2H, 13-3H); 1.77 (m, 3 H, 15-H); 1.93-1.98 (m, 1 H, 6- $H_a$ ); 2.05-2.12 (m, 2 H, 7-H); 3.54 (m, all  $J \leq 3.0$  Hz, 1 H, 1- $H_e$ ); 3.76 (br.ddd,  $J(3a,4a) = 12.0$  Hz,  $J(3a,11) = 6.7$  Hz,  $J(3a,4e) = 2.5$  Hz, 1 H, 3- $H_a$ ); 3.83 (m, 1 H, 10- $H_e$ ); 5.45 (ddq,  $J(11,12) = 15.3$  Hz,  $J(11,3a) = 6.7$  Hz,  $J(11,13) = 1.6$  Hz, 1 H, 11-H); 5.56-5.60 (m, 1 H, 8-H); 5.64-5.72 (m, 1 H, 12-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 17.51$  (C-13); 20.62 (C-15); 22.35 (d,  $^3J(\text{C-F}) = 6.2$  Hz, C-7); 24.74 (d,  $^2J(\text{C-F}) = 25.9$  Hz, C-14); 37.57 (d,  $^2J(\text{C-F}) = 18.7$  Hz, C-6); 38.95 (d,  $^2J(\text{C-F}) = 20.1$  Hz, C-4); 69.97 (C-10); 76.33 (d,  $^3J(\text{C-F}) = 11.6$  Hz, C-3); 77.36 (d,  $^3J(\text{C-F}) = 7.5$  Hz, C-1); 94.91 (d,  $^1J(\text{C-F}) = 175.9$  Hz, C-5); 124.40 (C-8); 128.22 (C-12); 130.68 (C-11); 131.08 (C-9).

**Reaction of 1 with 4-hydroxy-3-methoxybenzaldehyde (6m):** The reaction of diol **1** and aldehyde **6m** for 8 hours at 2 °C gave products **2m** ( $R:S = 1:3$ , 35%), **8m** ( $R:S = 3:1$ , 60%). Spectral characteristics of compounds **2m** have coincided with those described in the work [2].

**(2S,4R,4aR,8R,8aR)-4-fluoro-2-(4-hydroxy-3-methoxyphenyl)-4,7-dimethyl-3,4,4a,5,8,8a-**

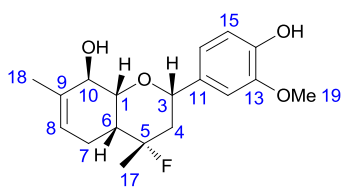
**hexahydro-2H-chromen-8-ol ((R)-8m):** Yellow viscous oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.36$  (d,  $^3J(17, F) = 22.4$  Hz, 3 H, 17-H); 1.81 (ddd,  $^3J(4a, F) = 39.2$  Hz,  $J(4a,4e) = 14.6$  Hz,  $J(4a, 3a) = 11.5$  Hz, 1 H, 4- $H_a$ ); 1.82 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.85-1.92 (m, 1 H, 4- $H_e$ ); 1.92-2.06 (m, 3 H, 6- $H_a$ , 7-2H); 3.86 (s, 3 H, 19-MeO); 3.94 (br.s, 1 H, 10- $H_e$ ); 4.15 (m, all  $J < 3.0$  Hz, 1 H, 1- $H_e$ ); 4.67 (dd,  $J(3a,4a) = 11.5$  Hz,  $J(3a,4e) = 3.3$  Hz, 1 H, 3- $H_a$ ); 5.56 (br.s, 1 H, 14-HO); 5.56-5.60 (m, 1 H, 8-H); 6.79-6.82



(m, 2 H, 12-H, 16-H); 6.85 (d,  $J(15,16) = 8.5$  Hz, 1 H, 15-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 20.77$  (C-18); 24.10 (d,  $^3J(\text{C-F}) = 9.7$  Hz, C-7); 24.81 (d,  $^2J(\text{C-F}) = 24.5$  Hz, C-17); 36.14 (d,  $^2J(\text{C-F}) = 20.9$  Hz, C-6); 40.17 (d,  $^2J(\text{C-F}) = 21.6$  Hz, C-4); 55.84 (C-19); 70.20 (C-10); 75.47 (d,  $^3J(\text{C-F}) = 1.0$  Hz, C-1); 75.72 (C-3); 95.21 (d,  $^1J(\text{C-F}) = 168.8$  Hz, C-5); 108.82 (C-12); 114.21 (C-15); 118.79 (C-16); 123.22 (C-8); 132.23 (C-9); 133.81 (C-11); 145.10 (C-14); 146.34 (C-13). HR-MS: 322.1573 ( $M^+$  ( $\text{C}_{18}\text{H}_{23}\text{O}_4\text{F}$ ) $^+$ ; calc. 322.1575).

**(2S,4S,4aR,8R,8aR)-4-fluoro-2-(4-hydroxy-3-methoxyphenyl)-4,7-dimethyl-3,4,4a,5,8,8a-**

**hexahydro-2H-chromen-8-ol ((S)-8m):** Yellow viscous oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.64$  (dd,  $^3J(17, \text{F})$

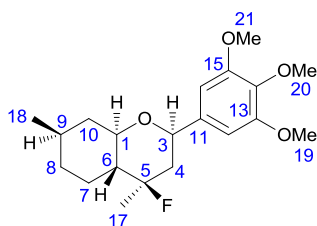


$= 23.5$  Hz,  $J(17, 4a) = 0.8$  Hz, 3 H, 17-H); 1.81 (m, all  $J \leq 2.5$  Hz, 3 H, 18-H); 1.83 (br.dd,  $J(4e, 4a) = 13.3$  Hz,  $J(4e, 3a) = 2.6$  Hz, 1 H, 4- $\text{H}_e$ ); 2.05 (br.dd,  $J(6a, 7a) = 10.6$  Hz,  $J(6a, 7e) = 6.5$ , 1 H, 6- $\text{H}_a$ ); 2.17 (dddq,  $^3J(4a, \text{F}) \sim 14.0$  Hz,  $J(4a, 4e) = 13.3$  Hz,  $J(4a, 3a) = 12.1$  Hz,  $J(4a, 17) = 0.8$  Hz, 1 H, 4- $\text{H}_a$ ); 2.15-2.28 (m, 2 H, 7-H); 3.72 (m, all  $J \leq 2.5$  Hz, 1 H, 1- $\text{H}_e$ ); 3.87 (s, 3 H, 19-MeO); 3.92 (br.s, 1 H, 10- $\text{H}_e$ ); 4.30 (dd,  $J(3a, 4a) = 12.1$  Hz,  $J(3a, 4e) = 2.6$  Hz, 1 H, 3- $\text{H}_a$ ); 5.58 (br.s, 1 H, 14-HO); 5.63-5.66 (m, 1 H, 8-H); 6.79-8.82 (m, 2 H, 12-H, 16-H); 6.85 (d,  $J(15,16) = 8.5$  Hz, 1 H, 15-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 20.64$  (C-18); 22.54 (d,  $^3J(\text{C-F}) = 6.4$  Hz, C-7); 24.84 (d,  $^2J(\text{C-F}) = 25.9$  Hz, C-17); 37.80 (d,  $^2J(\text{C-F}) = 18.9$  Hz, C-6); 40.62 (d,  $^2J(\text{C-F}) = 20.4$  Hz, C-4); 55.85 (C-19); 70.23 (d,  $^4J(\text{C-F}) = 2.1$  Hz, C-10); 77.65 (d,  $^3J(\text{C-F}) = 11.6$  Hz, C-3); 77.93 (d,  $^3J(\text{C-F}) = 7.9$  Hz, C-1); 95.18 (d,  $^1J(\text{C-F}) = 176.2$  Hz, C-5); 108.77 (C-12); 114.19 (C-15); 119.09 (C-16); 124.46 (C-8); 131.27 (C-9); 133.09 (C-11); 145.35 (C-14); 146.40 (C-13).

**Reaction of isopulegol 4 with 3,4,5-trimethoxybenzaldehyde (6a):** The reaction of isopulegol 4 and aldehyde 6a for 8 hours at 2 °C gave products 11 ( $R:S = 7:2$ , 76%), 12 ( $R:S = 1:5$ , 15%). Spectral characteristics of compound 12 have coincided with those described in the work [5].

**(2R,4R,4aR,7R,8aR)-4-fluoro-4,7-dimethyl-2-(3,4,5-trimethoxyphenyl)octahydro-2H-chromene**

**((R)-11):** Yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 0.85$ -1.00 (m, 1 H, 8- $\text{H}_a$ ); 0.93 (d,  $J(18, 9) = 6.6$  Hz, 3 H,



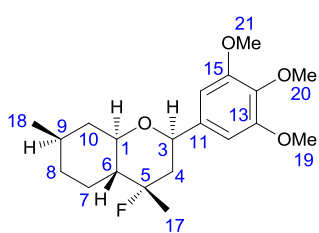
18-H); 1.09 (ddd,  $J(10a, 10e) = J(10a, 9a) = 12.2$  Hz,  $J(10a, 1a) = 11.2$  Hz, 1 H, 10- $\text{H}_a$ ); 1.18-1.34 (m, 2 H, 6- $\text{H}_a$ , 7- $\text{H}_a$ ); 1.34 (d,  $^3J(17, \text{F}) = 21.4$  Hz, 3 H, 17-H); 1.45-1.54 (m, 1 H, 9- $\text{H}_a$ ); 1.71 (ddd,  $^3J(4a, \text{F}) = 39.3$  Hz,  $J(4a, 4e) = 14.2$  Hz,  $J(4a, 3a) = 11.7$  Hz, 1 H, 4- $\text{H}_a$ ); 1.70-1.78 (m, 1 H, 8- $\text{H}_e$ ); 1.89 (dm,  $J(7e, 7a) = 13.1$  Hz, 1 H, 7- $\text{H}_e$ ); 1.98-2.04 (m, 2 H, 4- $\text{H}_e$ ,



10-H<sub>e</sub>); 3.56 (dddd,  $J(1a,10a) = 11.2$  Hz,  $J(1a,6a) = 9.8$  Hz,  $J(1a,10e) = 4.2$  Hz,  $^4J(1a,F) = 1.5$  Hz, 1 H, 1-H<sub>a</sub>); 3.79 (s, 3 H, 20-MeO); 3.84 (s, 6 H, 19-MeO, 21-MeO); 4.68 (dd,  $J(3a,4a) = 11.7$  Hz,  $J(3a,4e) = 2.3$  Hz, 1 H, 3-H<sub>a</sub>); 6.56 (s, 2 H, 12-H, 16-H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>)  $\delta = 22.10$  (C-18); 23.17 (C-7); 24.18 (d,  $^2J(\text{C-F}) = 24.8$  Hz, C-17); 31.10 (C-9); 34.32 (C-8); 41.11 (C-10); 45.76 (d,  $^2J(\text{C-F}) = 21.7$  Hz, C-4); 48.43 (d,  $^2J(\text{C-F}) = 20.3$  Hz, C-6); 55.99 (C-19, C-21); 60.63 (C-20); 74.87 (C-3); 75.84 (C-1); 93.40 (d,  $^1J(\text{C-F}) = 171.7$  Hz, C-5); 103.01 (C-12, C-16); 137.27 (C-14); 137.92 (C-11); 153.15 (C-13, C-15).

**(2*R*,4*S*,4*aR*,7*R*,8*aR*)-4-fluoro-4,7-dimethyl-2-(3,4,5-trimethoxyphenyl)octahydro-2*H*-chromene**

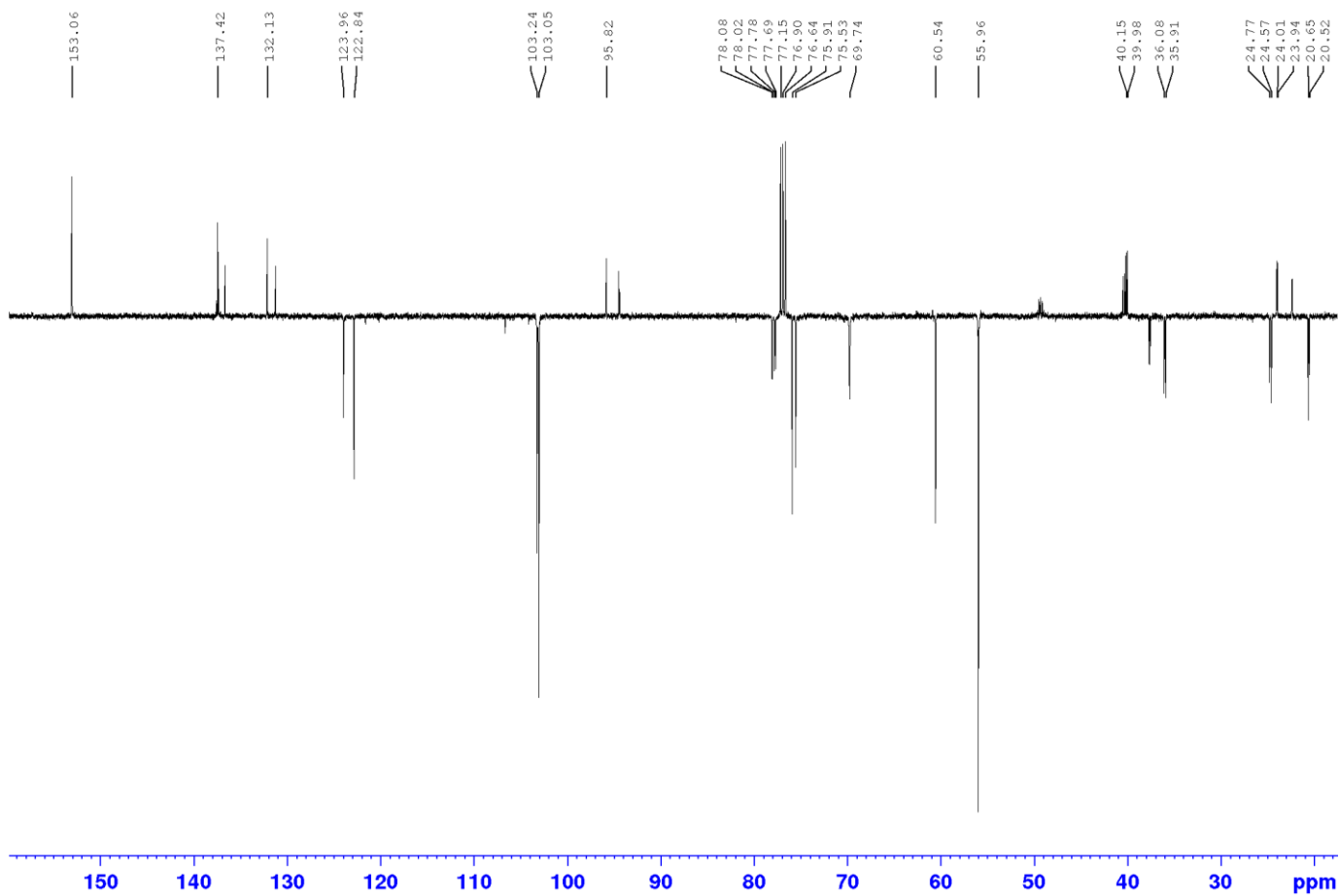
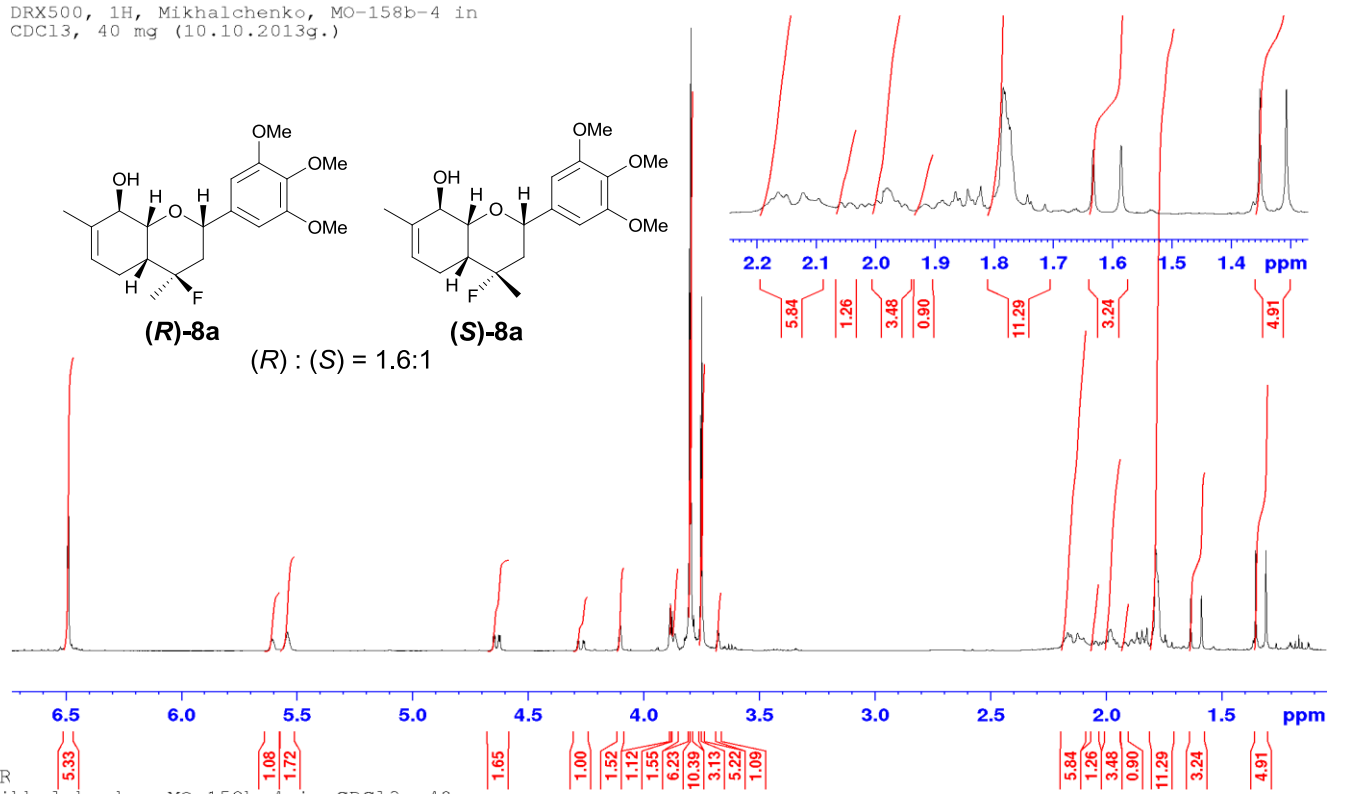
**((*S*)-11)**: Yellow oil.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta = 0.85$ -1.00 (m, 1 H, 8-H<sub>a</sub>); 0.94 (d,  $J(18, 9) = 6.5$  Hz, 3 H,



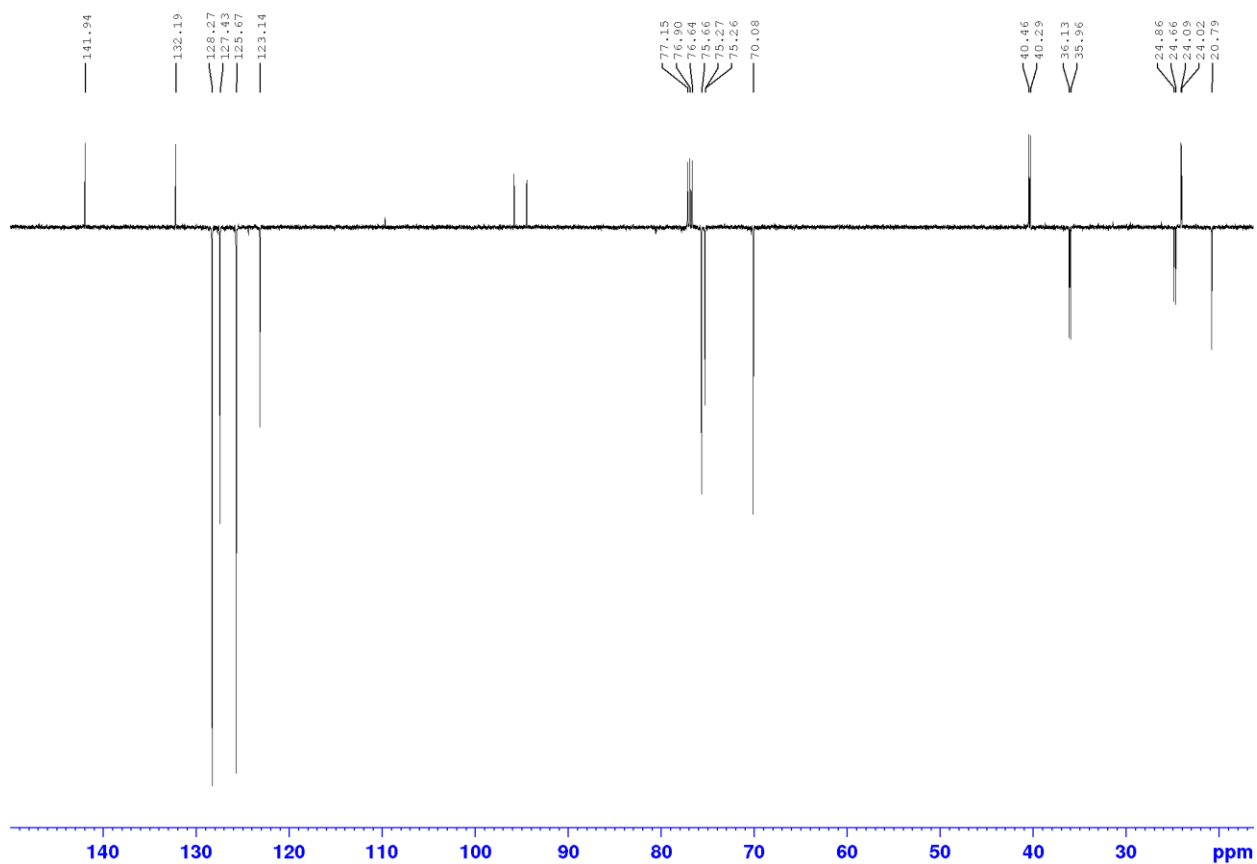
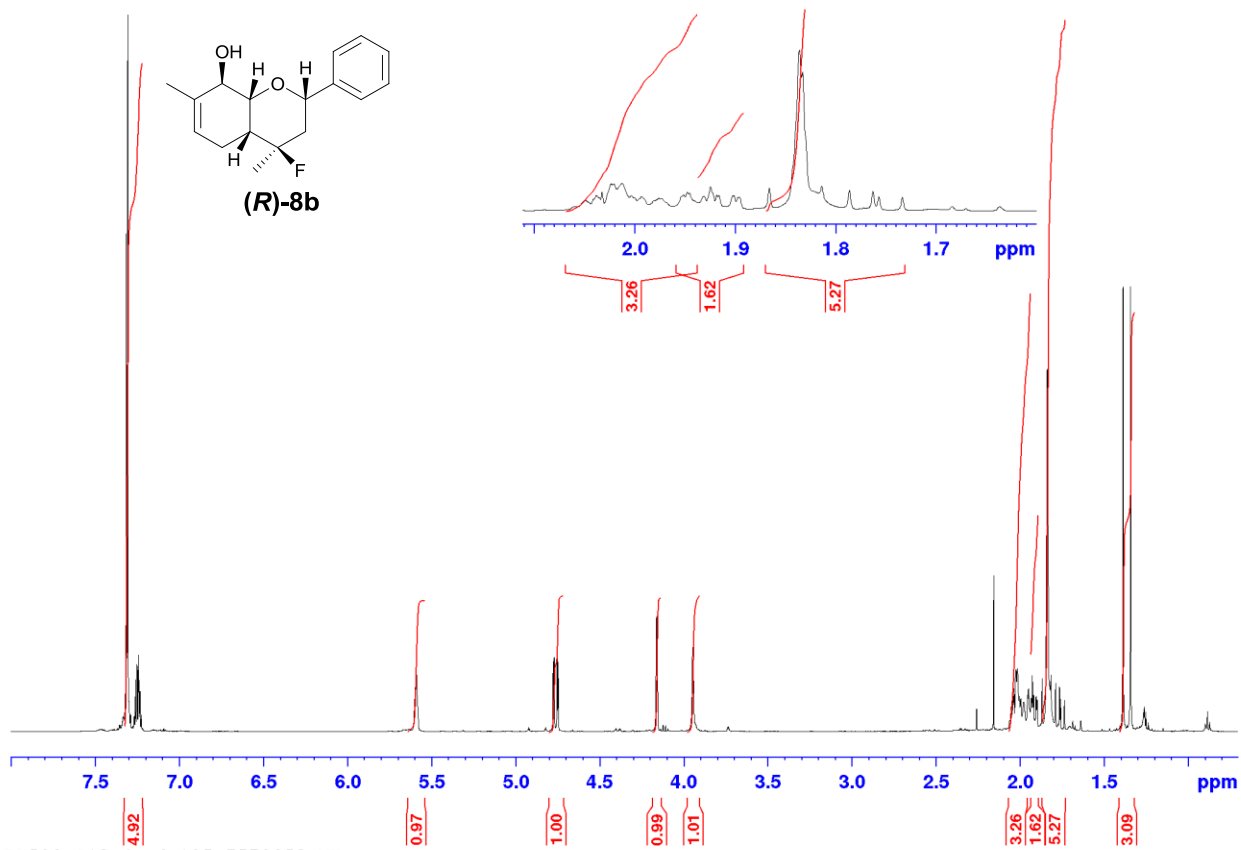
18-H); 1.05-1.13 (m, 1 H, 7-H<sub>a</sub>); 1.12-1.21 (m, 1 H, 10-H<sub>a</sub>); 1.43 (d,  $^3J(17,F) = 23.1$  Hz, 3 H, 17-H); 1.41-1.49 (m, 1 H, 9-H<sub>a</sub>); 1.59 (dddd,  $J(6a,7a) = J(6a,F) = 12.2$  Hz,  $J(6a,1a) = 10.2$  Hz,  $J(6a,7e) = 3.3$  Hz, 1 H, 6-H<sub>a</sub>); 1.70-1.78 (m, 1 H, 8-H<sub>e</sub>); 1.94 (dm,  $J(7e,7a) = 13.1$  Hz, 1 H, 7-H<sub>e</sub>); 1.96-2.08 (m, 3 H, 4-2H, 10-H<sub>e</sub>); 3.21 (ddd,  $J(1a,10a) = 10.8$  Hz,

$J(1a,6a) = 10.2$  Hz,  $J(1a,10e) = 4.3$  Hz, 1 H, 1-H<sub>a</sub>); 3.79 (s, 3 H, 20-MeO); 3.85 (s, 6 H, 19-MeO, 21-MeO); 4.30 (dd,  $J(3a,4a) = 11.4$  Hz,  $J(3a,4e) = 2.6$  Hz, 1 H, 3-H<sub>a</sub>); 6.55 (s, 2 H, 12-H, 16-H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>)  $\delta = 19.44$  (d,  $^2J(\text{C-F}) = 26.5$  Hz, C-17); 22.04 (C-18); 22.40 (d,  $^3J(\text{C-F}) = 2.7$  Hz, C-7); 31.26 (C-9); 33.92 (C-8); 41.23 (C-10); 47.13 (d,  $^2J(\text{C-F}) = 19.5$  Hz, C-4); 49.88 (d,  $^2J(\text{C-F}) = 19.5$  Hz, C-6); 56.02 (C-19, C-21); 60.63 (C-20); 76.91 (d,  $^3J(\text{C-F}) = 11.9$  Hz, C-3); 77.54 (C-1); 94.88 (d,  $^1J(\text{C-F}) = 173.3$  Hz, C-5); 103.24 (C-12, C-16); 137.12 (C-11); 137.54 (C-14); 153.17 (C-13, C-15). HR-MS: 352.2047 ( $M^+$  (C<sub>20</sub>H<sub>29</sub>O<sub>4</sub>F)<sup>+</sup>; calc. 352.2044).

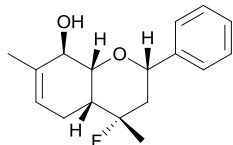
DRX500, 1H, Mikhalchenko, MO-158b-4 in CDC13, 40 mg (10.10.2013g.)



DRX500, 1H, Mikhalchenko, MO-150-1-3 in  
CDCl3, 60mg (23.10.2013g.)

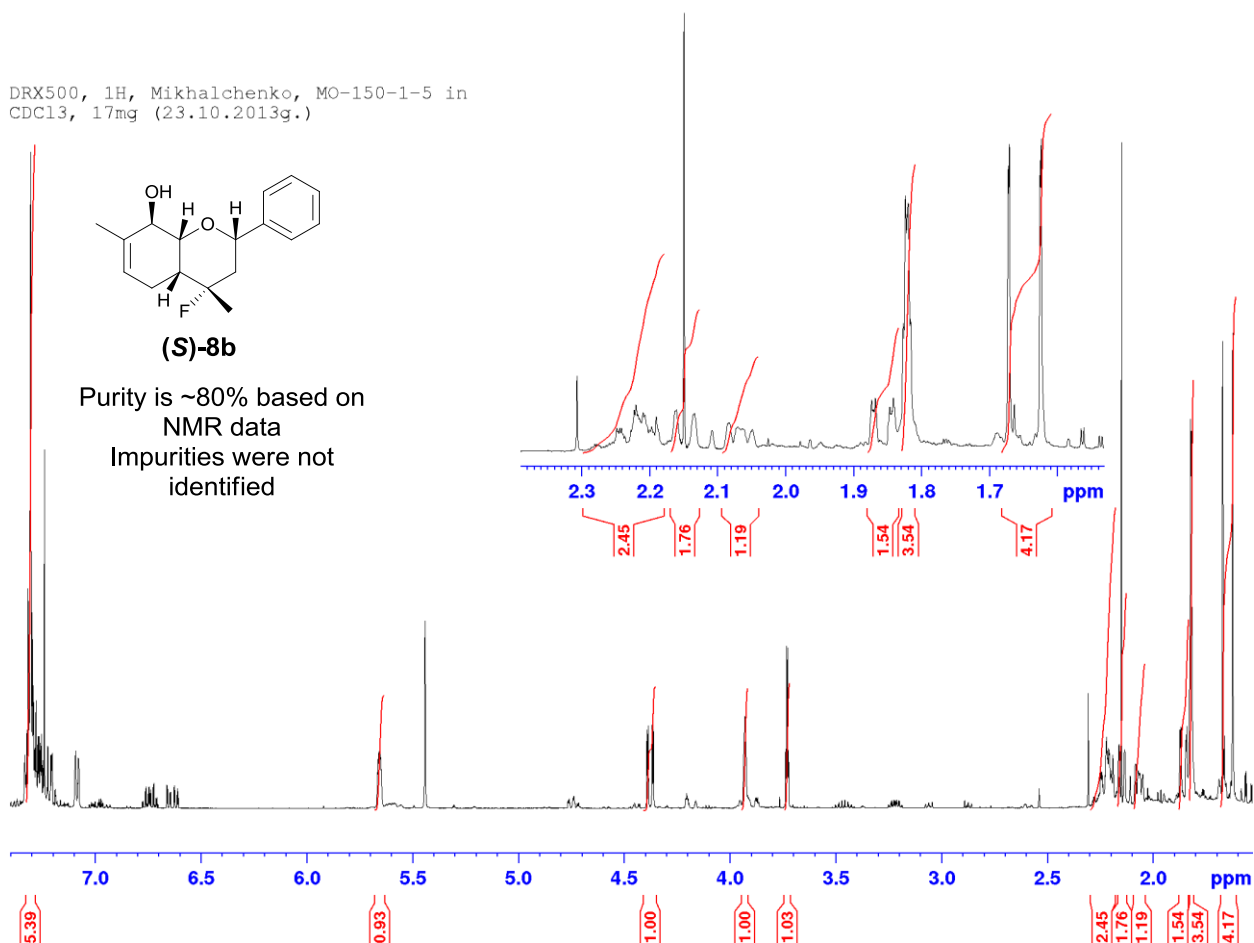


DRX500, 1H, Mikhalchenko, MO-150-1-5 in  
CDCl3, 17mg (23.10.2013g.)

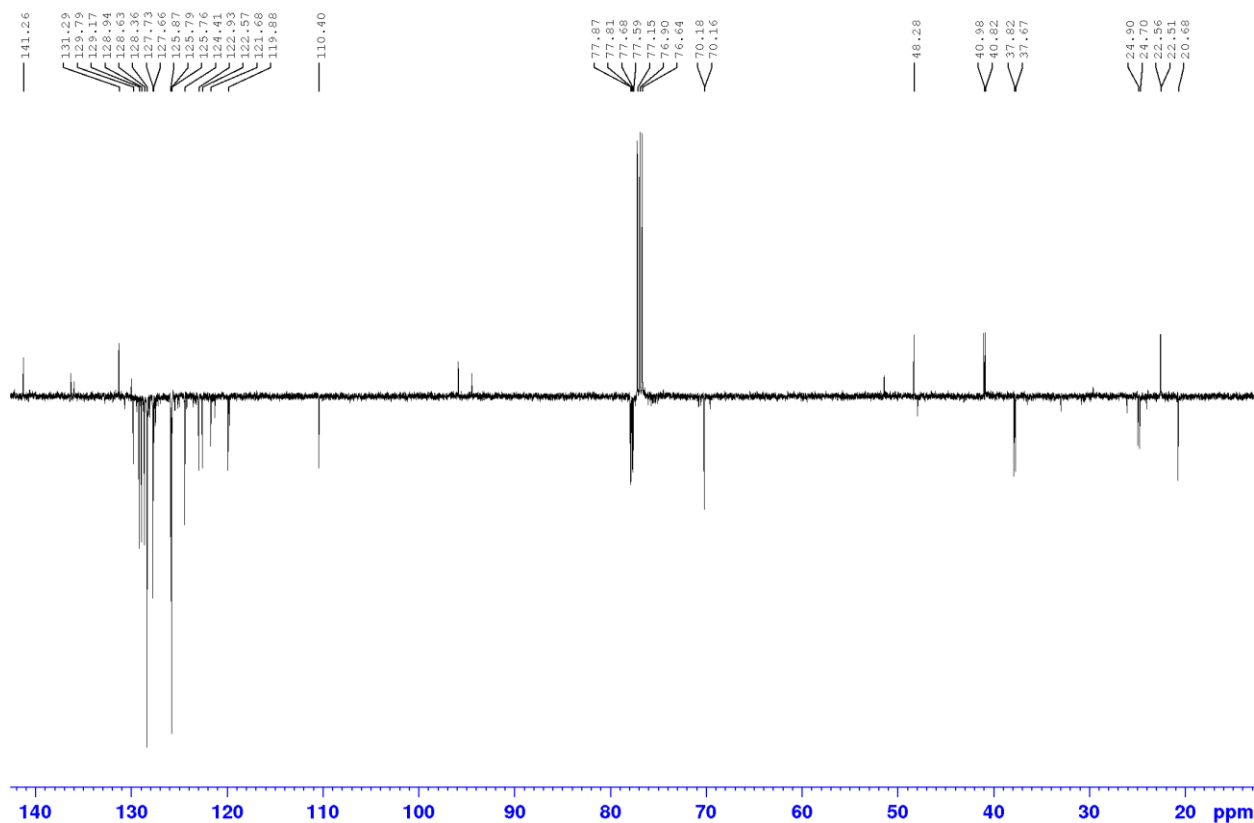


**(S)-8b**

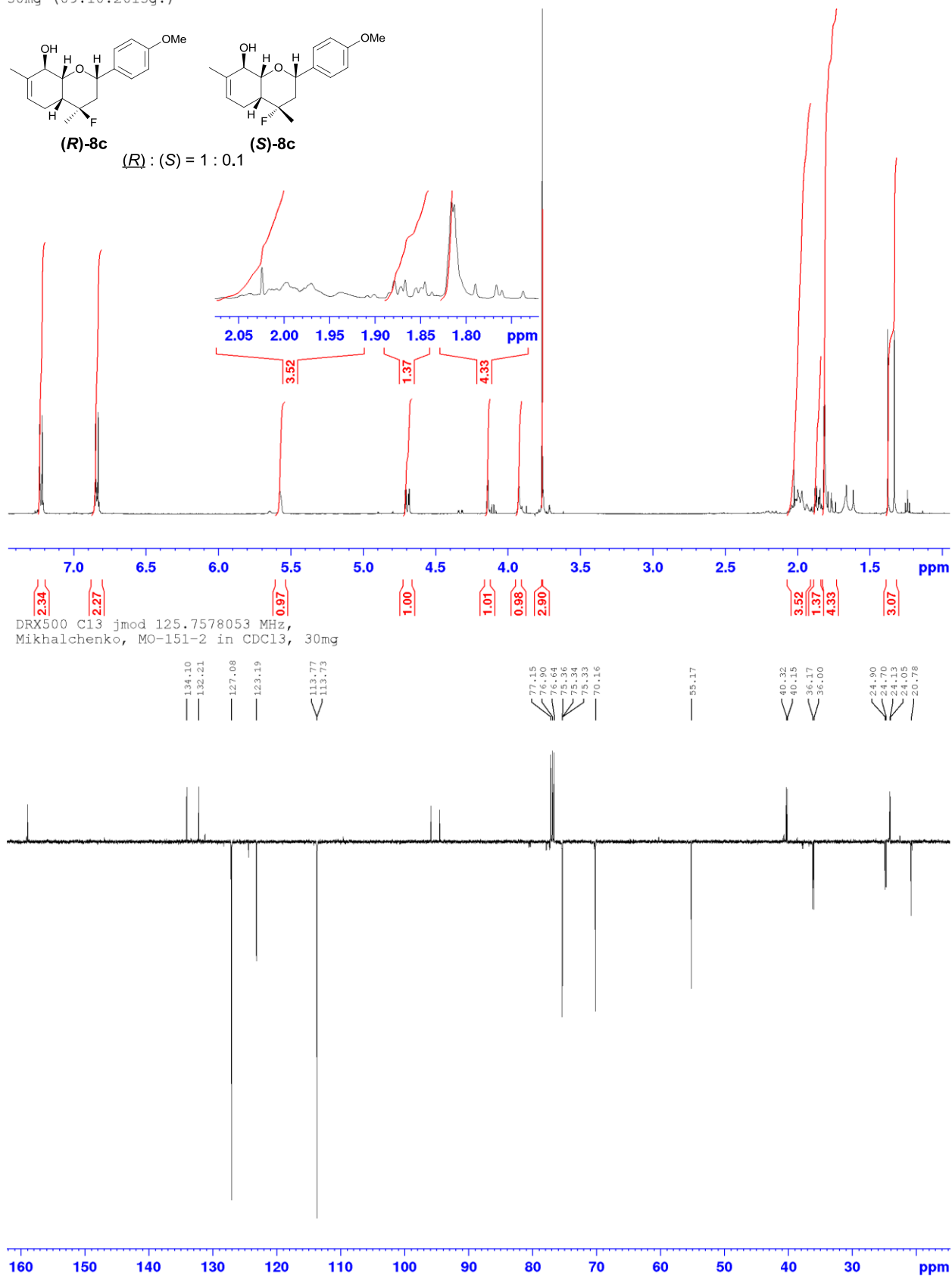
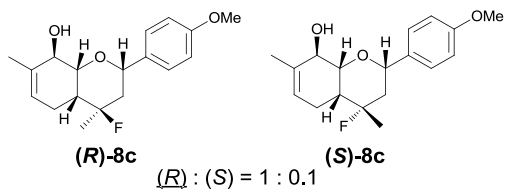
Purity is ~80% based on  
NMR data  
Impurities were not  
identified

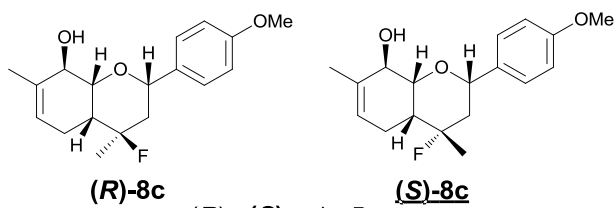


DRX500 C13 jmod 125.7578053 MHz,  
Mikhalchenko, MO-150-1-5 in CDCl3, 17mg

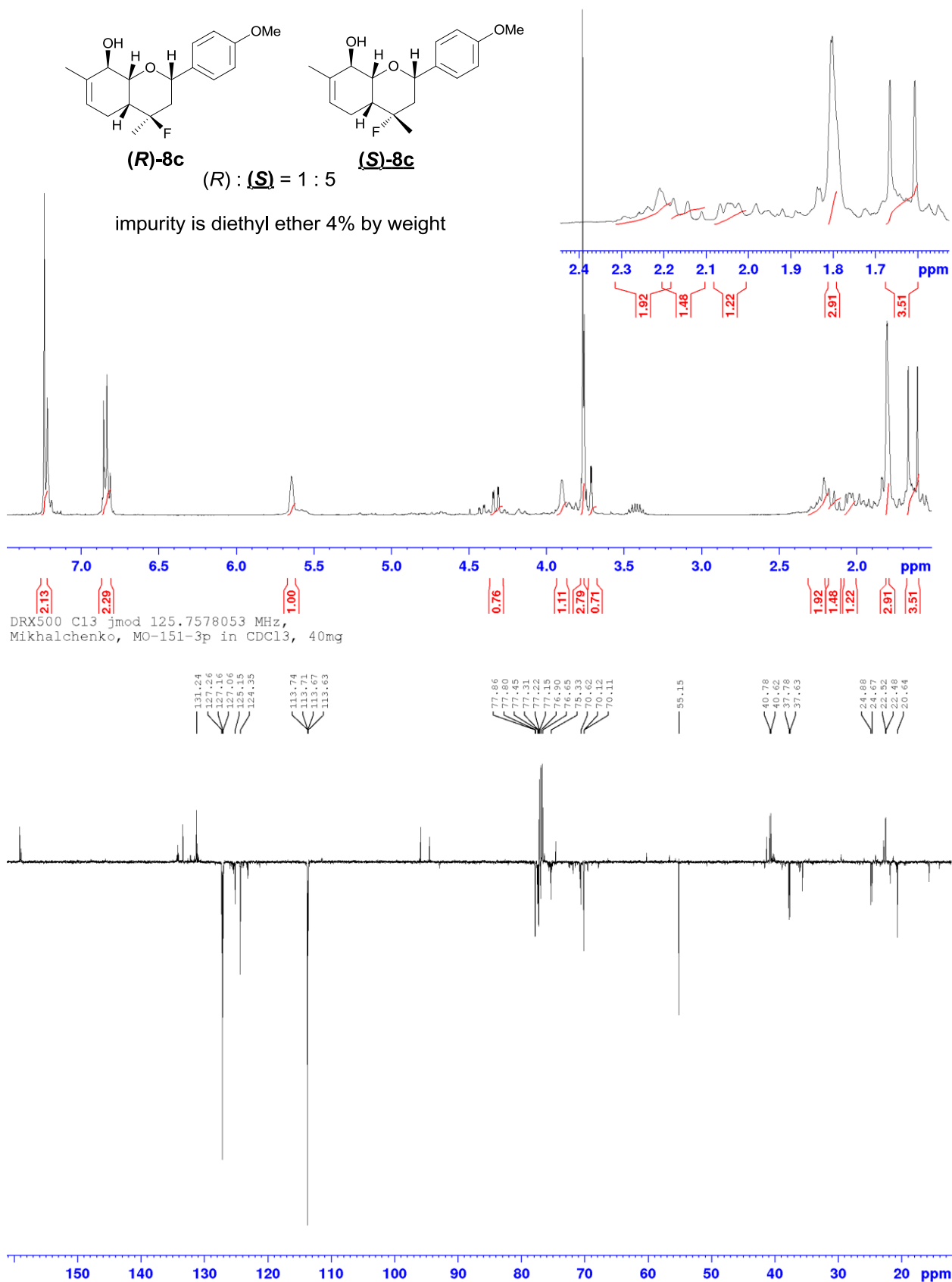


DRX500, 1H, Mikhalchenko, MO-151-2 in CDCl3, 30mg (09.10.2013g.)

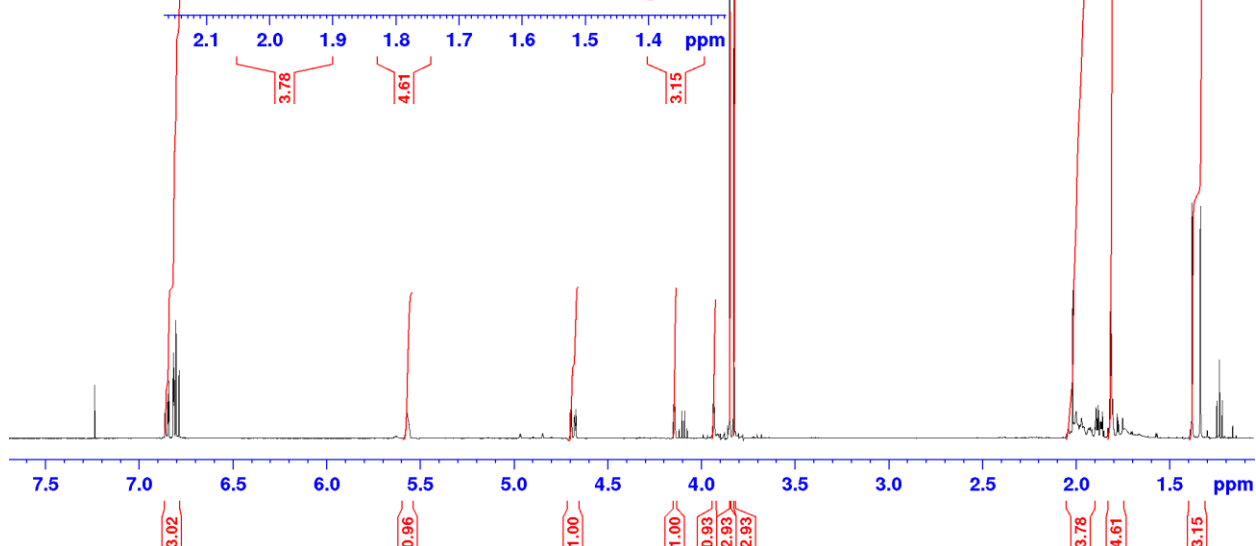
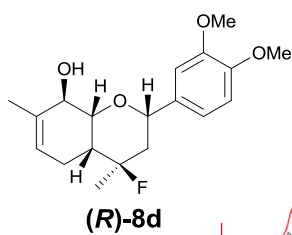




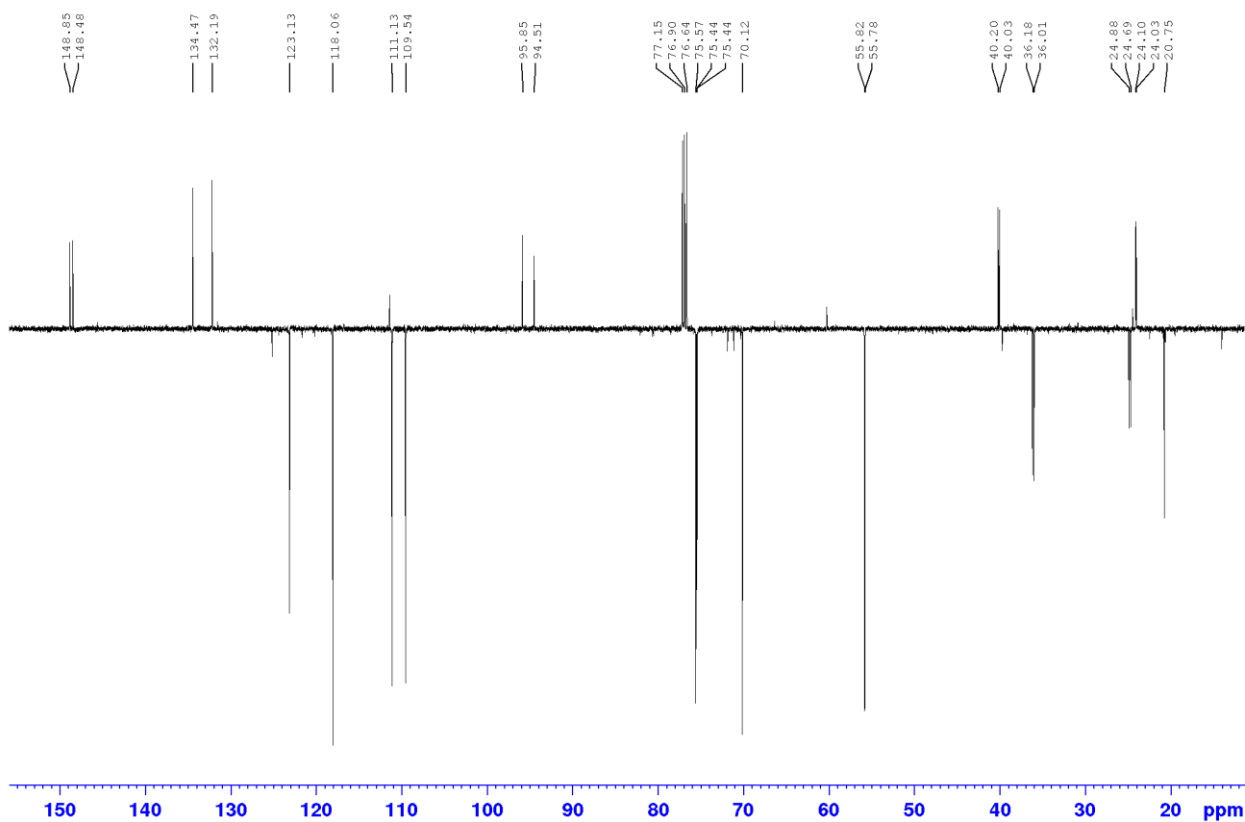
impurity is diethyl ether 4% by weight



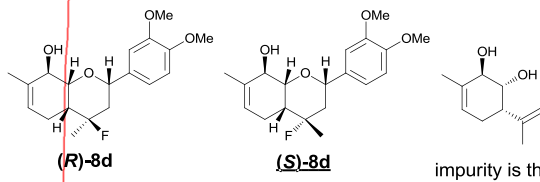
DRX500, 1H, Mikhalchenko, MO-152-2-2 in CDC13, 40mg (16.10.2013g.)



DRX500 C13 jmod 125.7578053 MHz, Mikhalchenko, MO-152-2-2 in CDCl3, 40mg

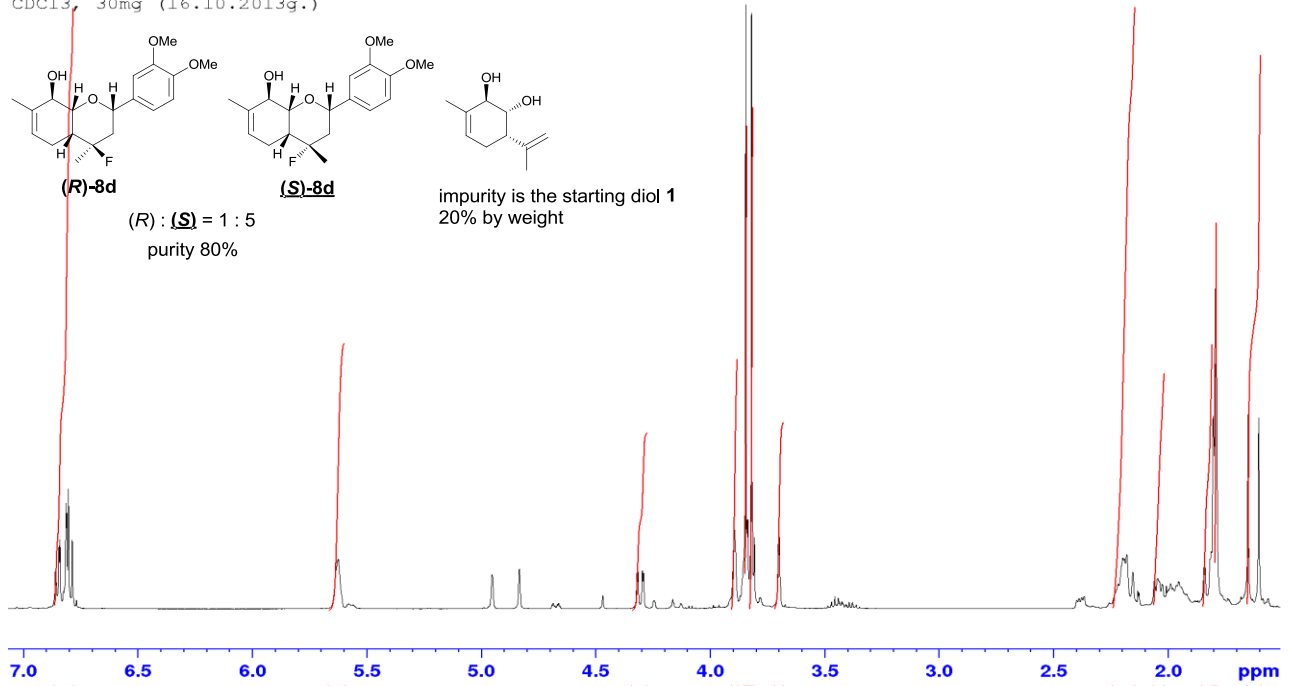


DRX500, 1H, Mikhalchenko, MO-152-2-3b in CDCl3, 30mg (16.10.2013g.)

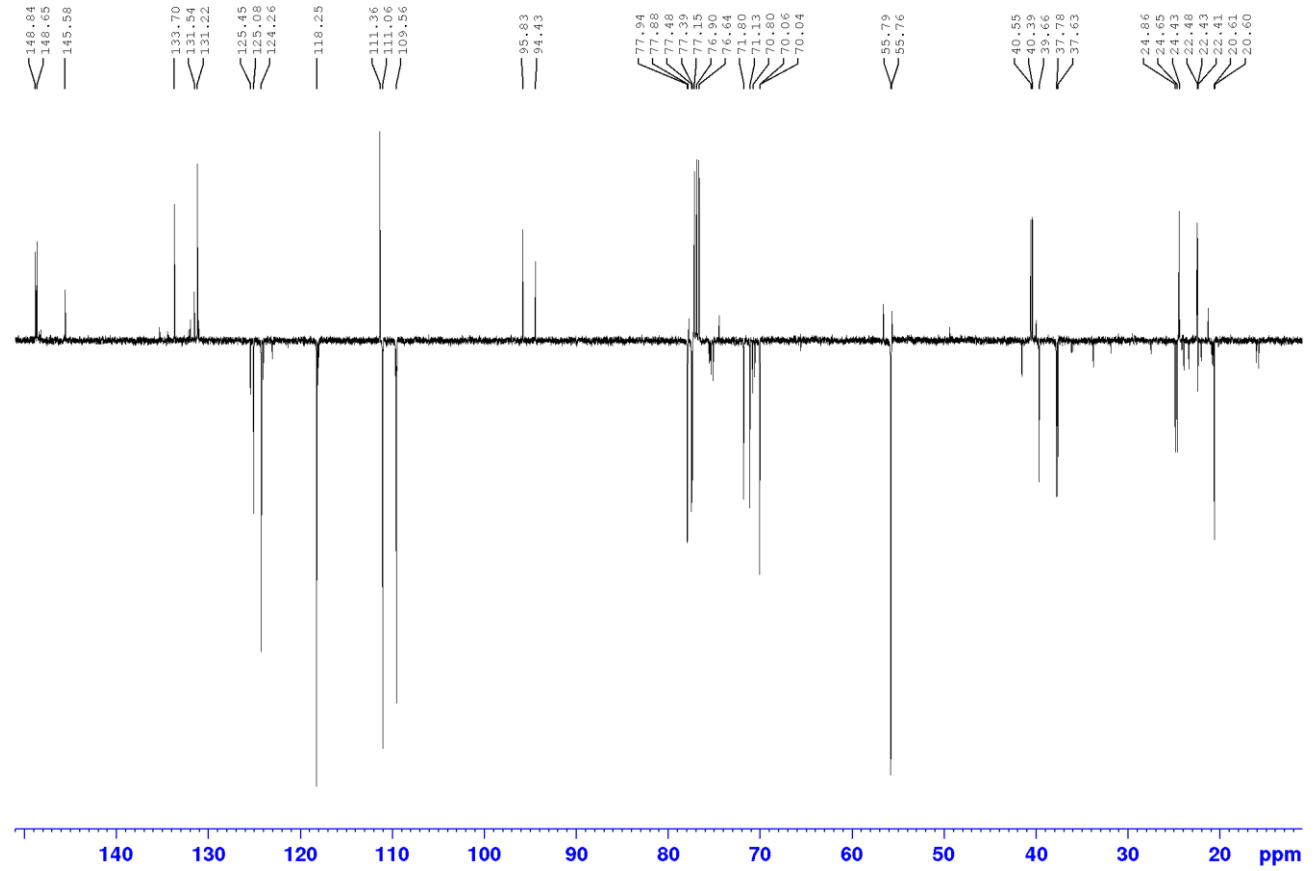


(R) : (S) = 1 : 5  
purity 80%

impurity is the starting diol 1  
20% by weight

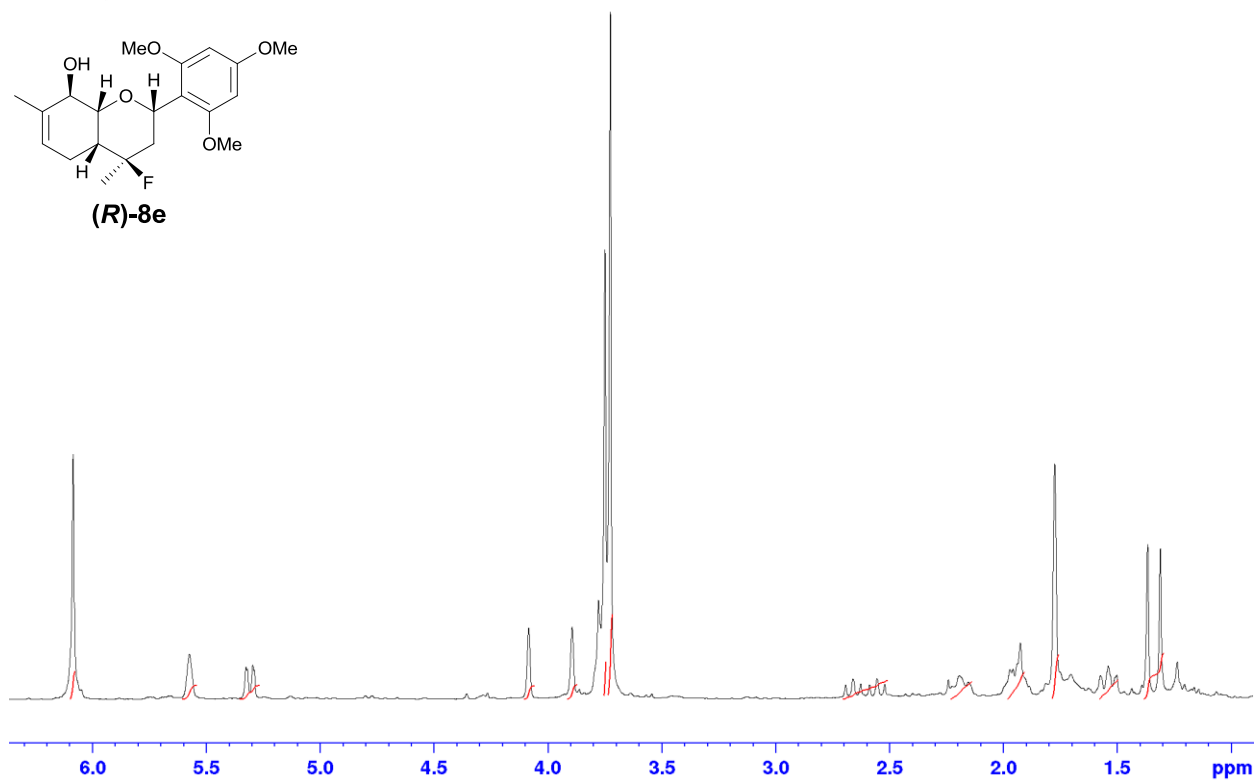
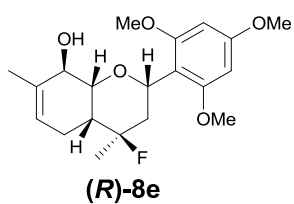


DRX500 C13 jmod 125.7578053 MHz,  
Mikhalchenko, MO-152-2-3b in CDCl3, 30mg

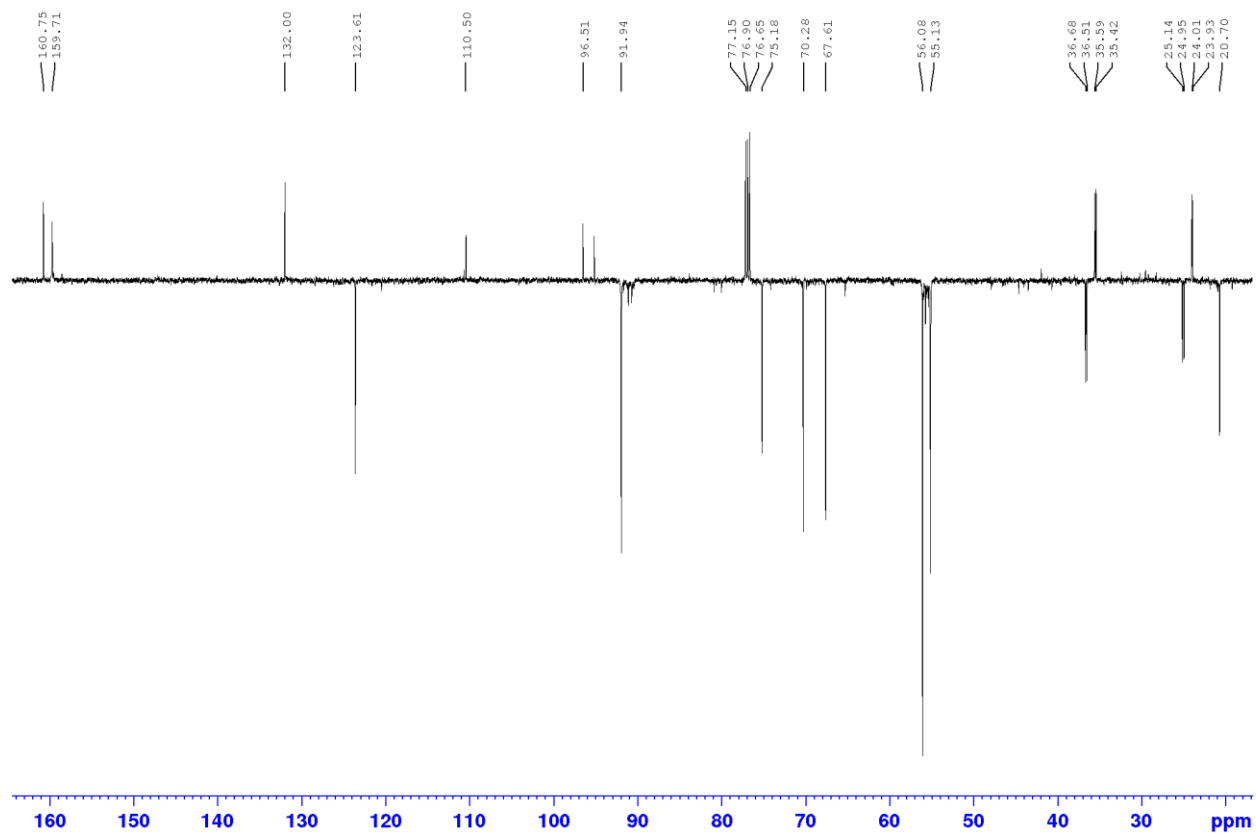




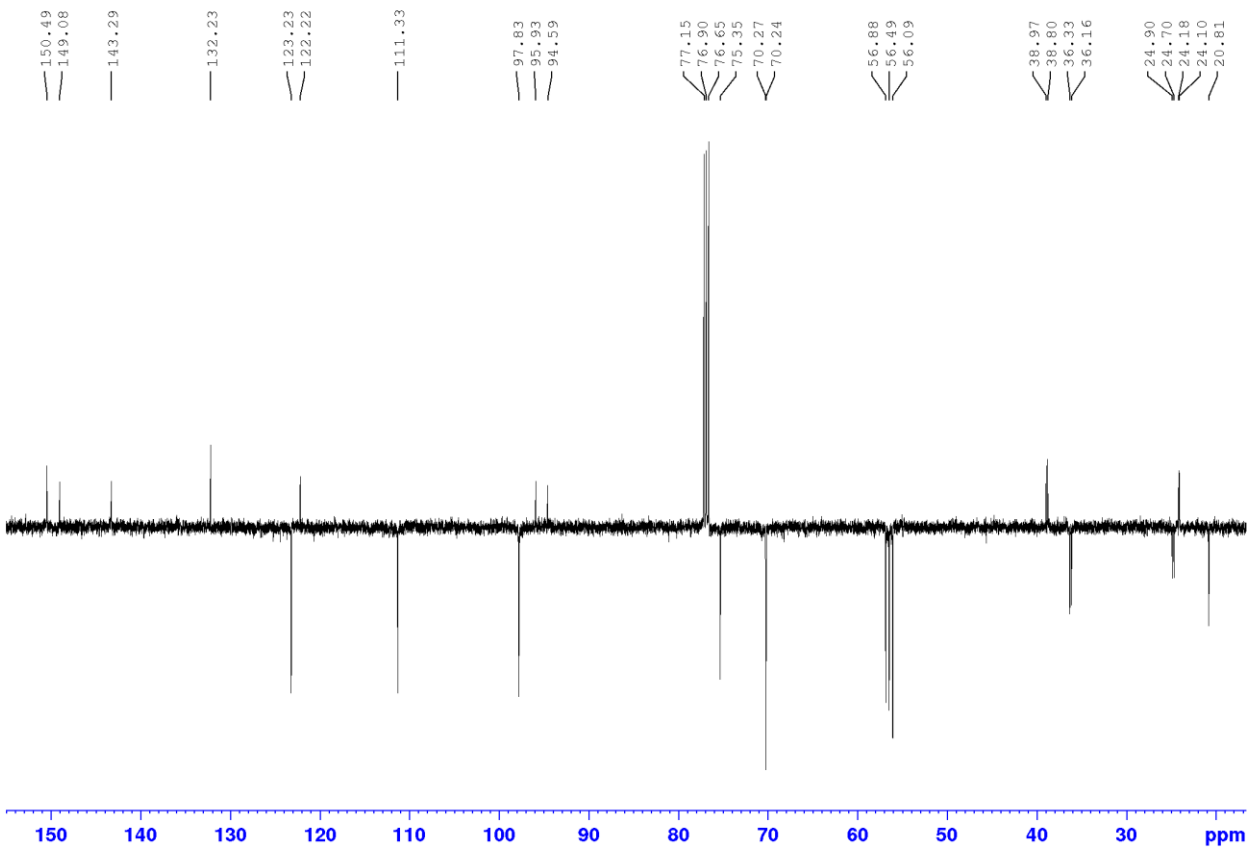
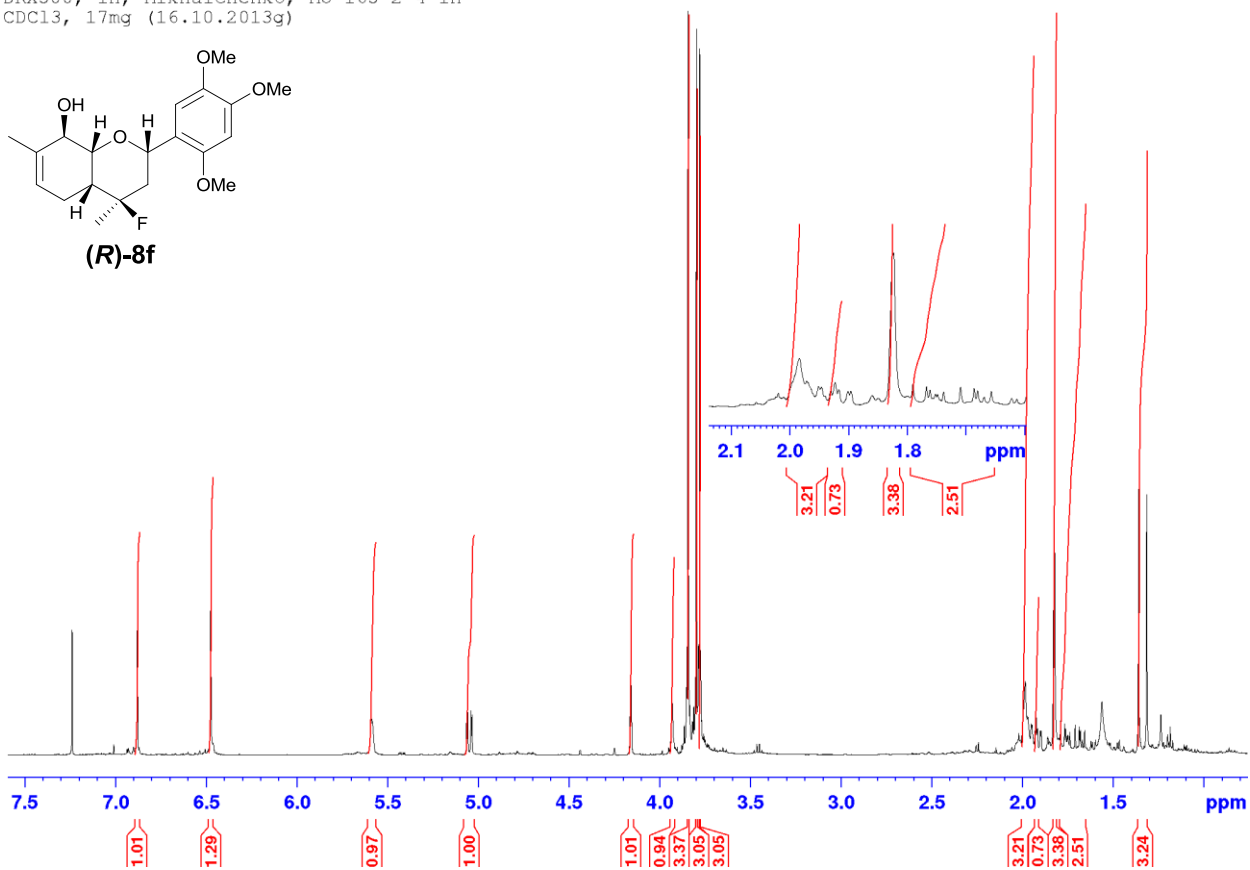
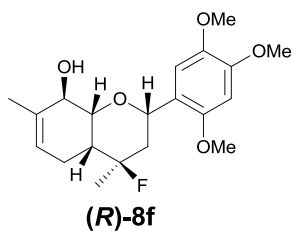
MO-164-2; CDC13

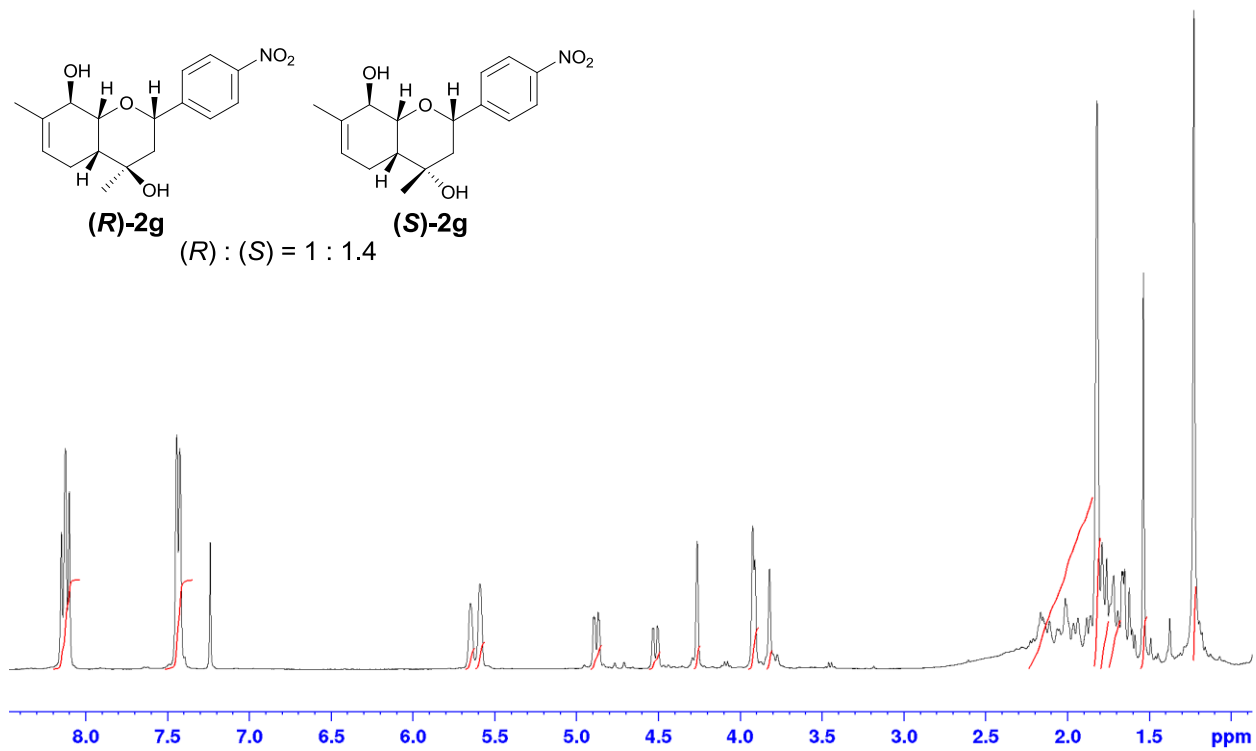
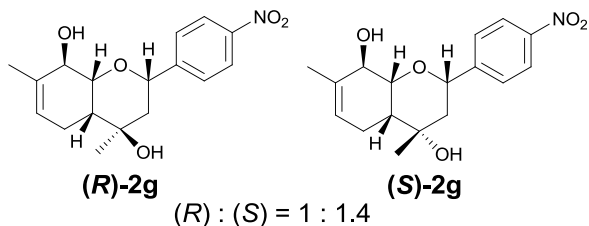


DRX500, 13 C-jmod, Mikhalchenko,  
MO-164-2 in CDCl3, 20mg

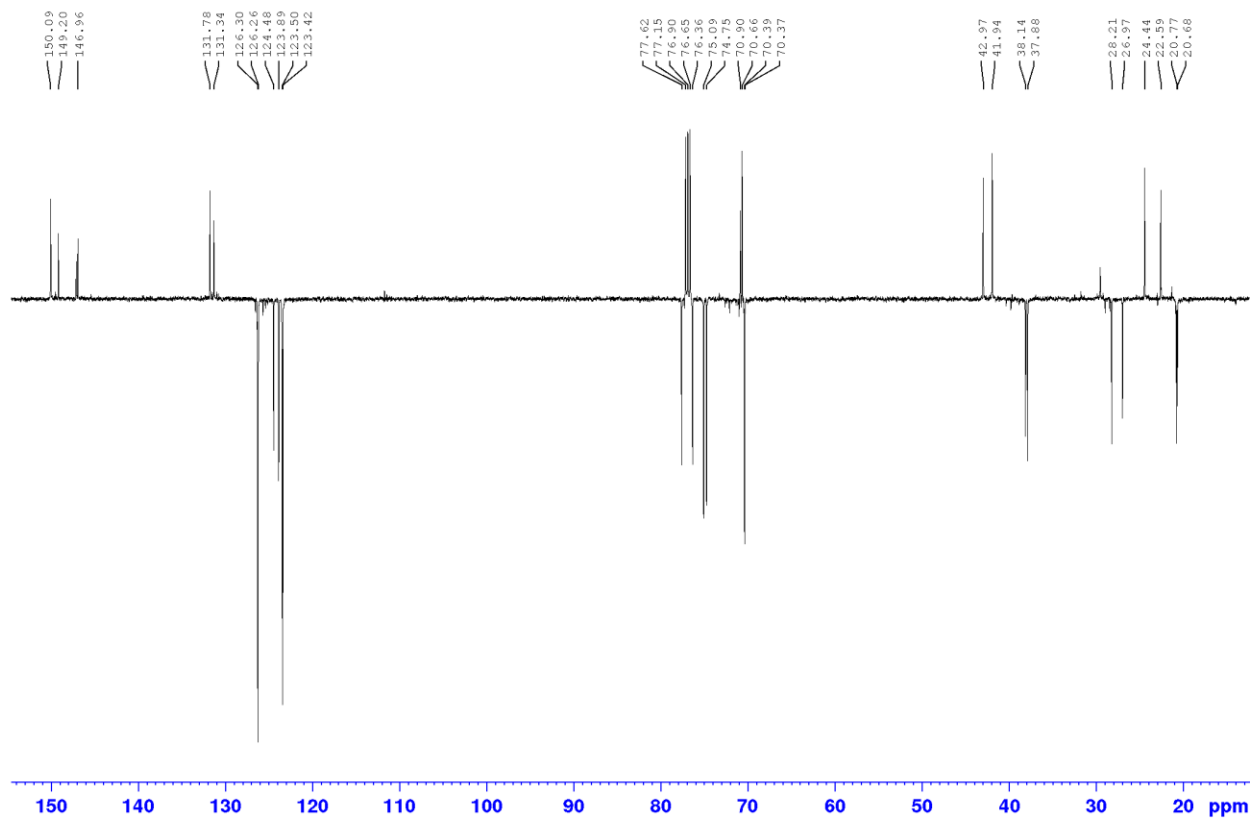


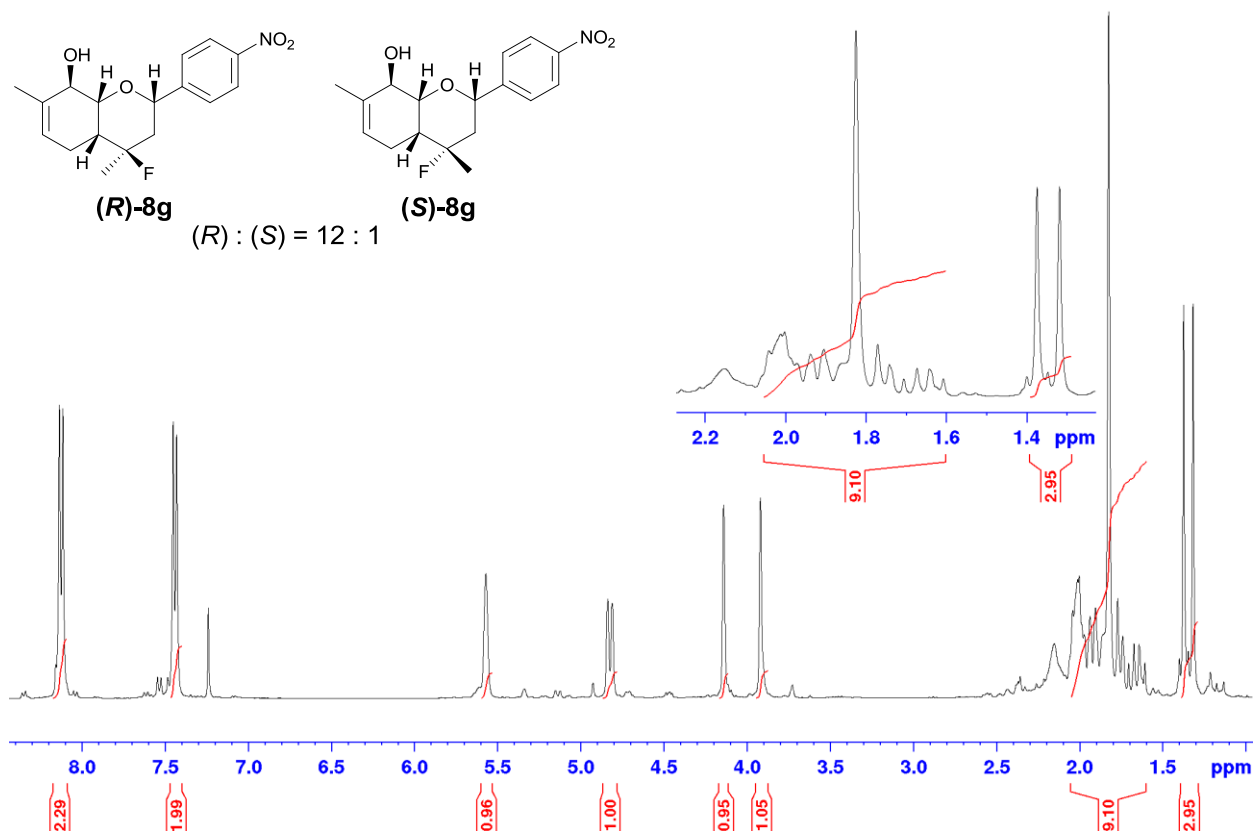
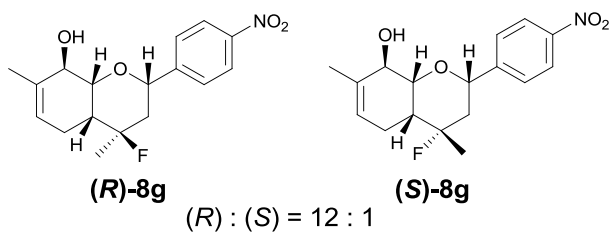
DRX500, 1H, Mikhalchenko, MO-165-2-4 in  
CDCl3, 17mg (16.10.2013g)



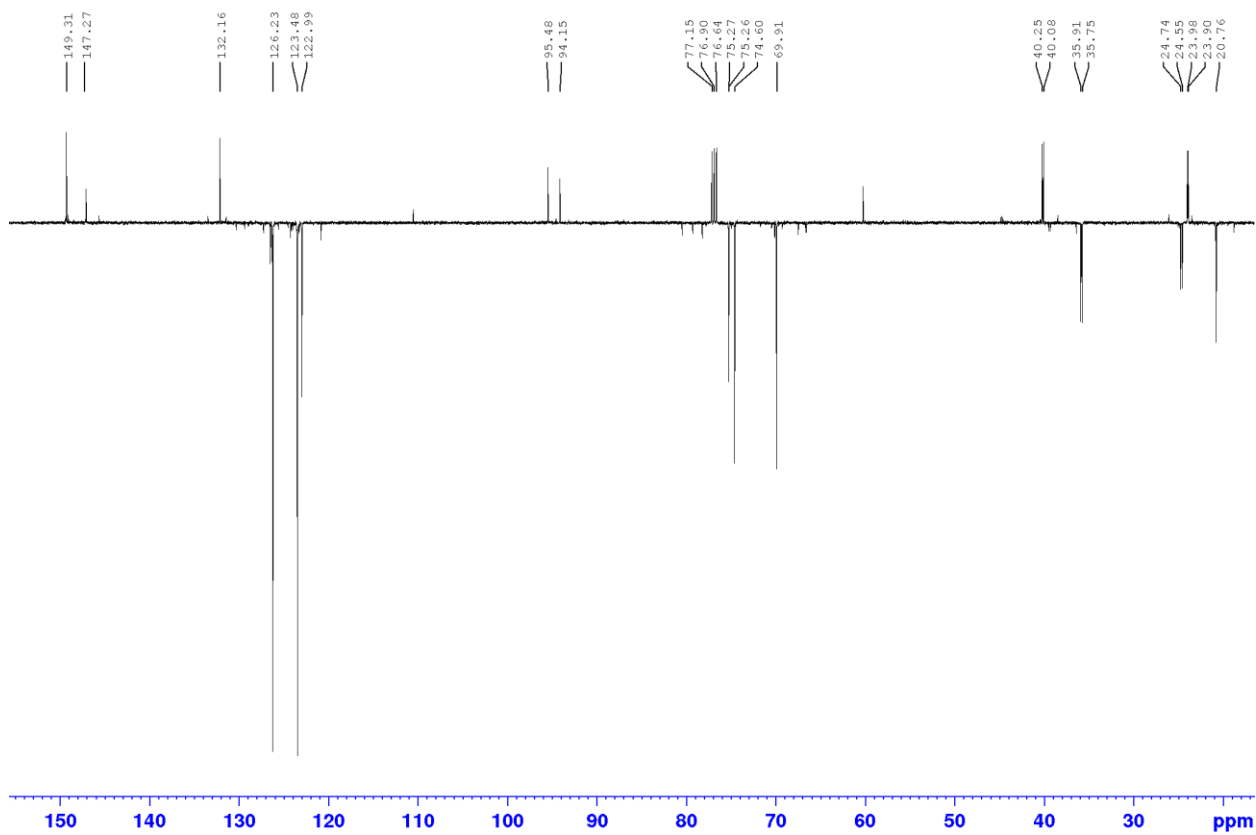


DRX500, 13 C-jmod, Mikhalchenko,  
 MO-174-7-1 in CDCl<sub>3</sub>, 20mg

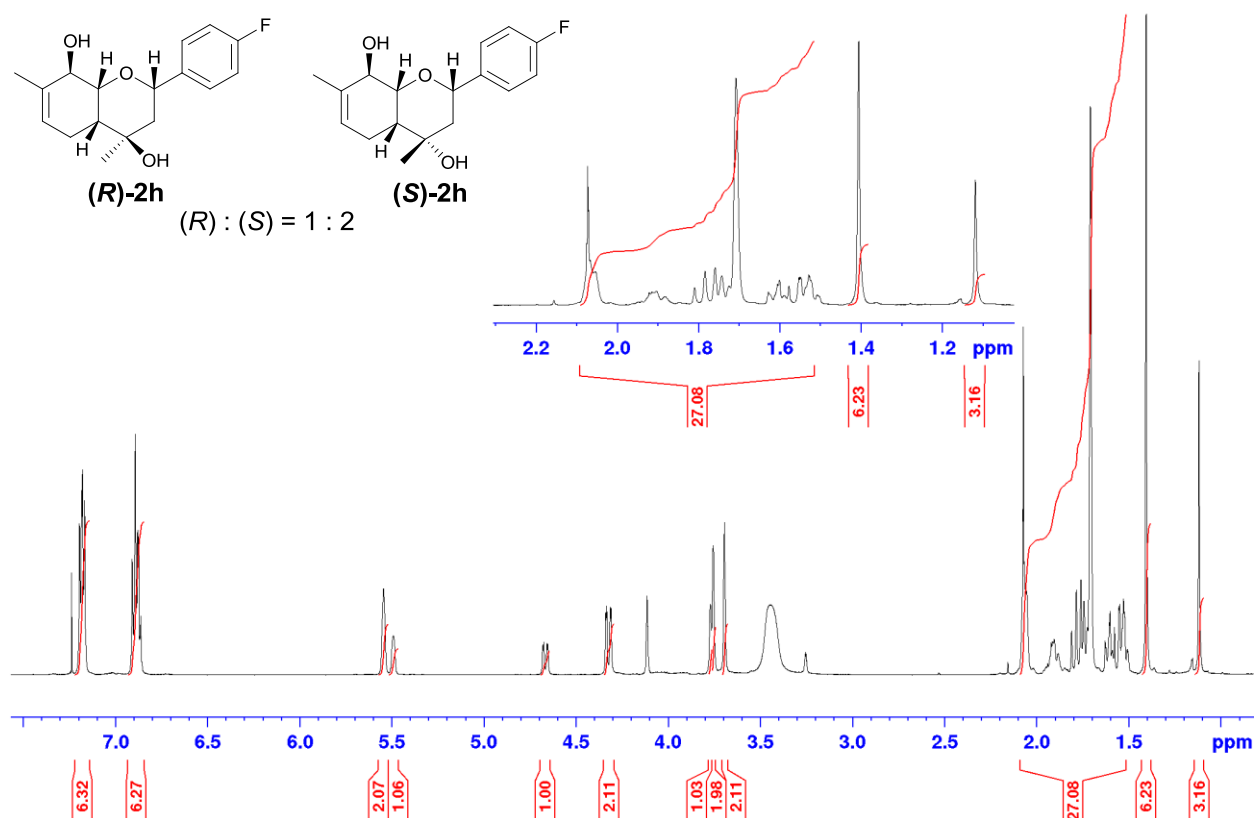
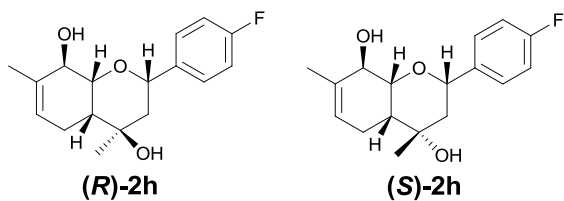




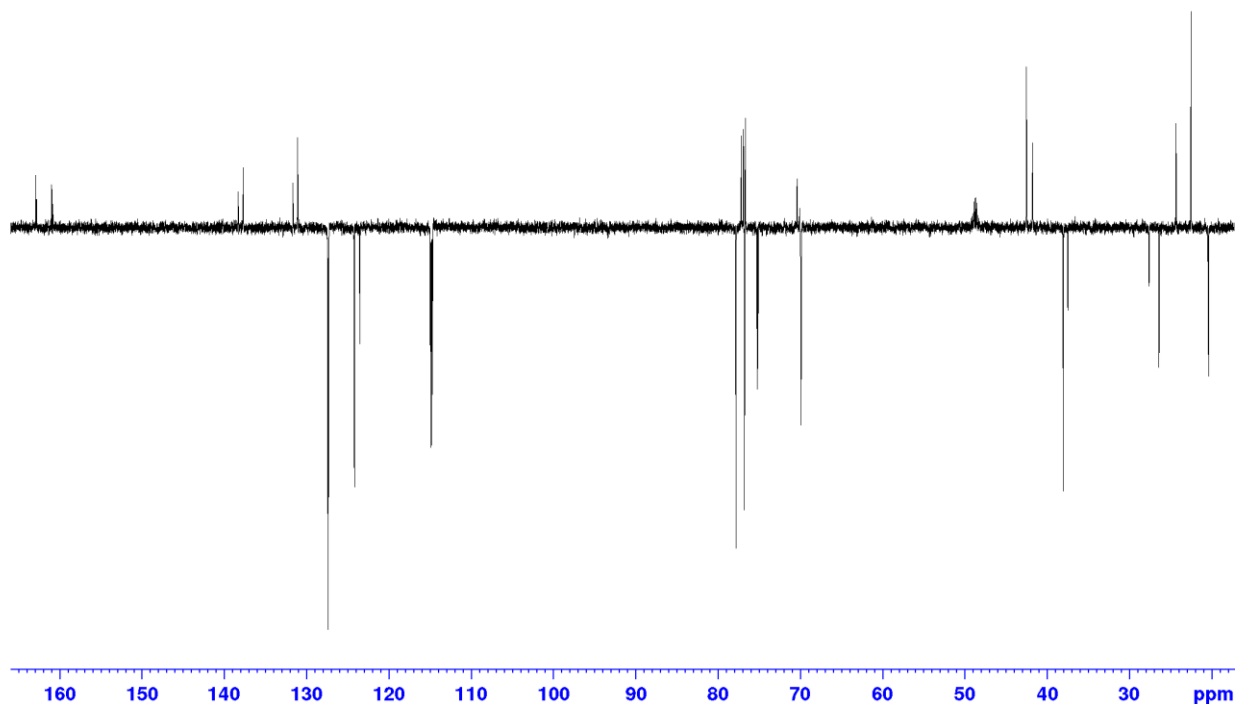
DRX500 C13 jmod 125.7578053 MHz,  
Mikhailchenko, MO-174-4 in CDCl<sub>3</sub>, 55mg

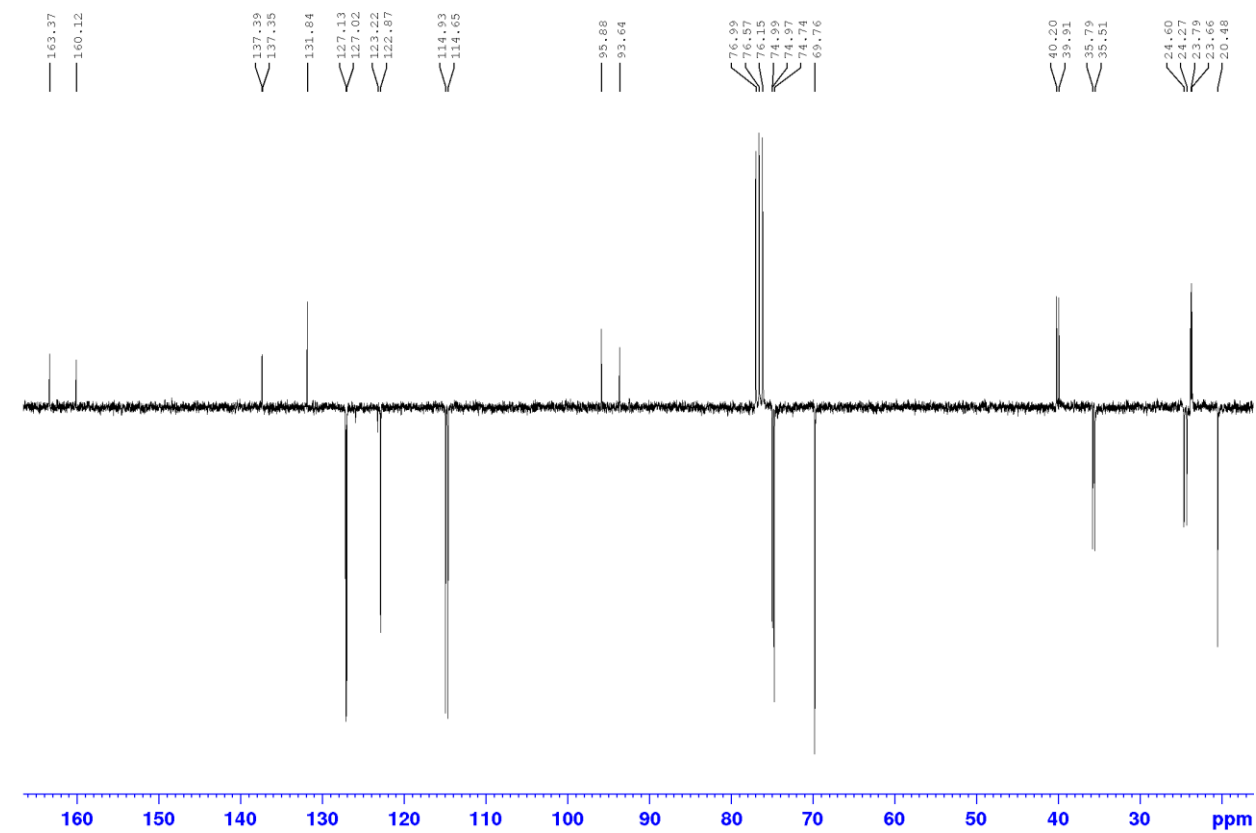
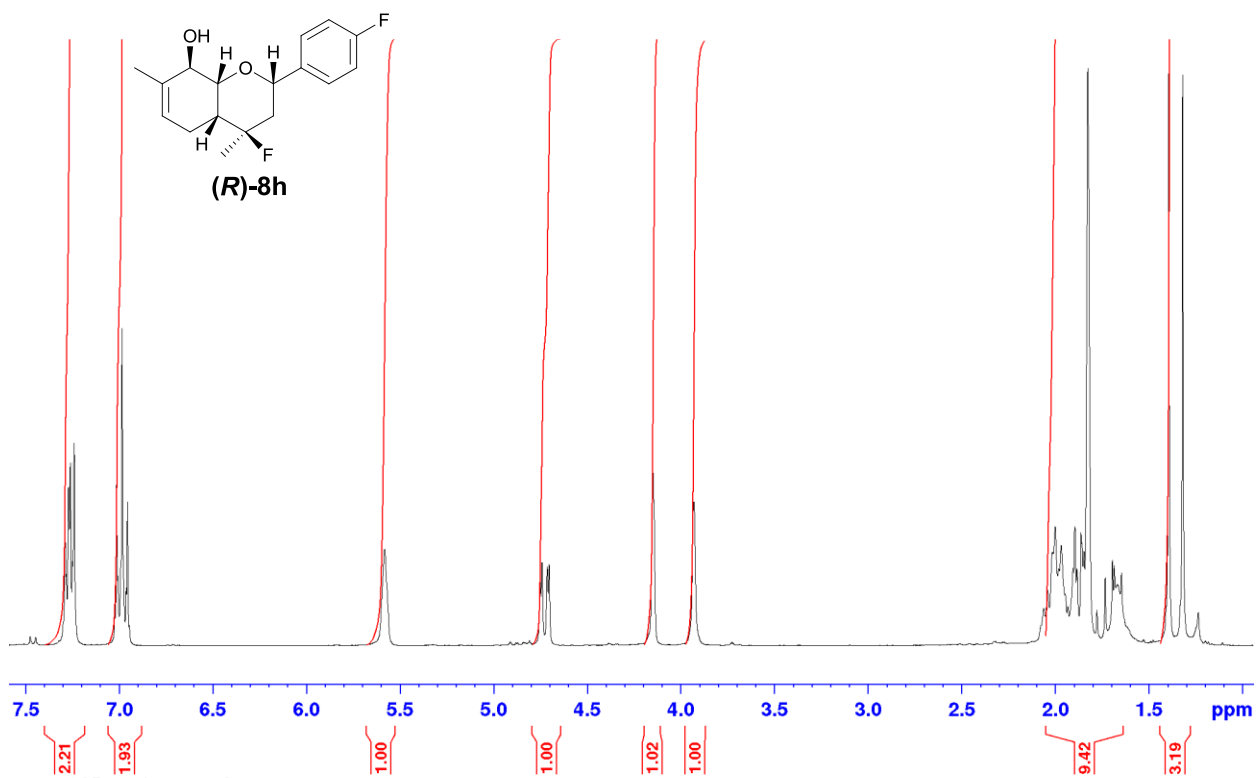


DRX500, 1H, Mikhalchenko, MO-187-6  
in CDCl3+CD3OD, 60mg (26.05.2015g.)

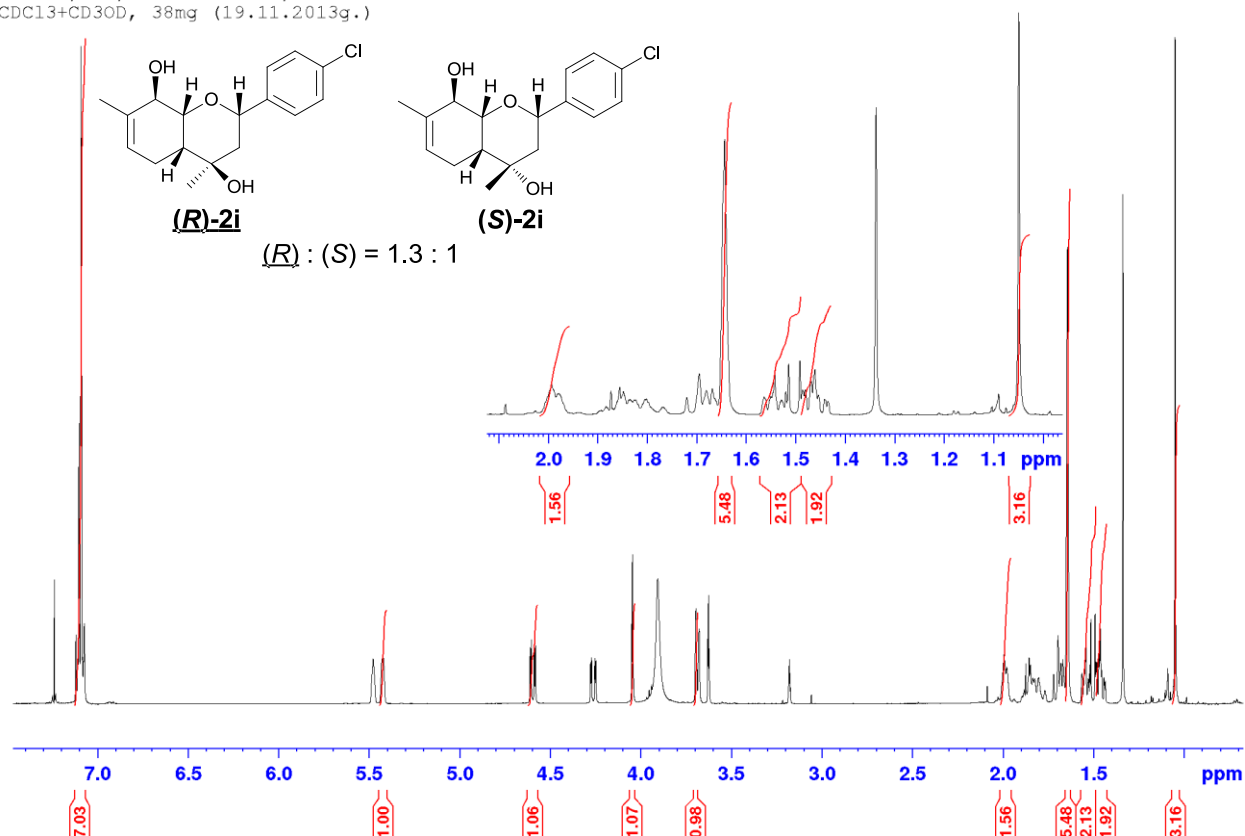


DRX500, 13 C-jmod, Mikhalchenko,  
MO-187-6 in CDCl3+CD3OD, 60mg

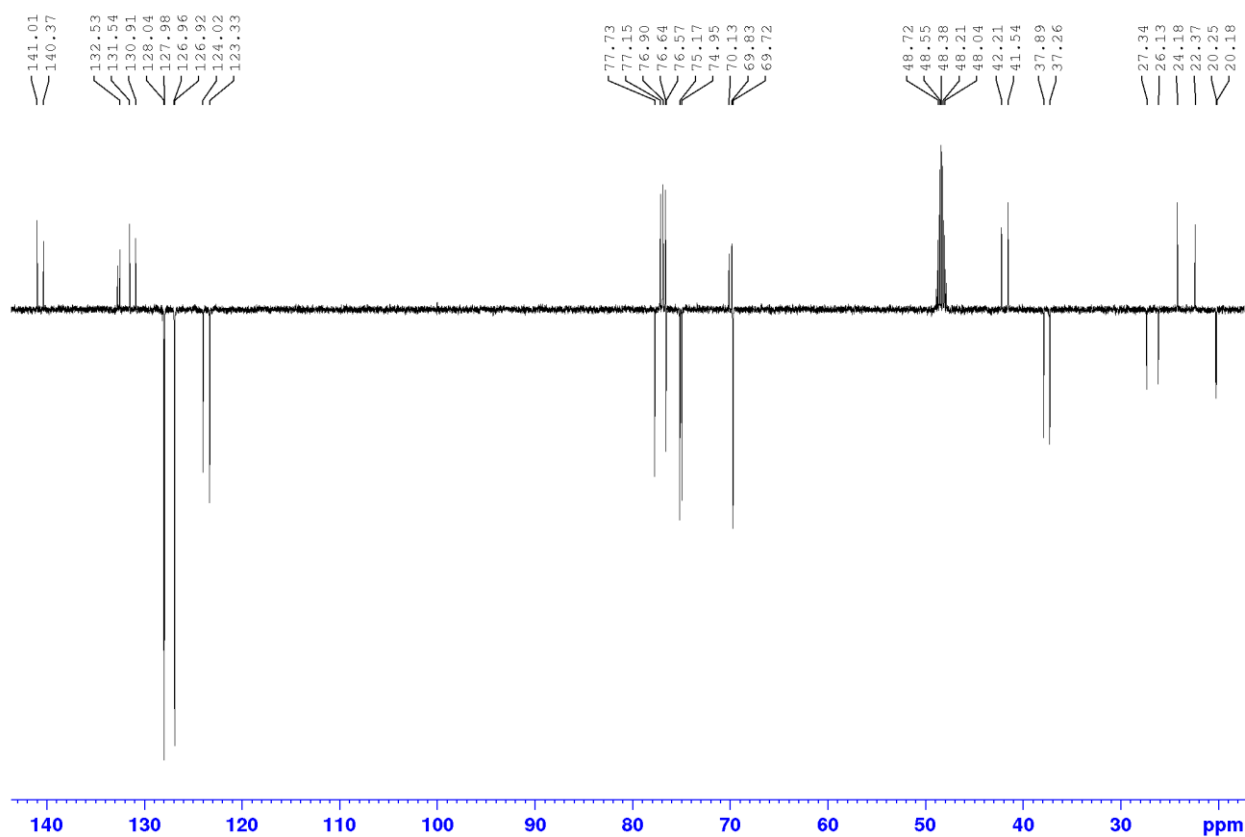




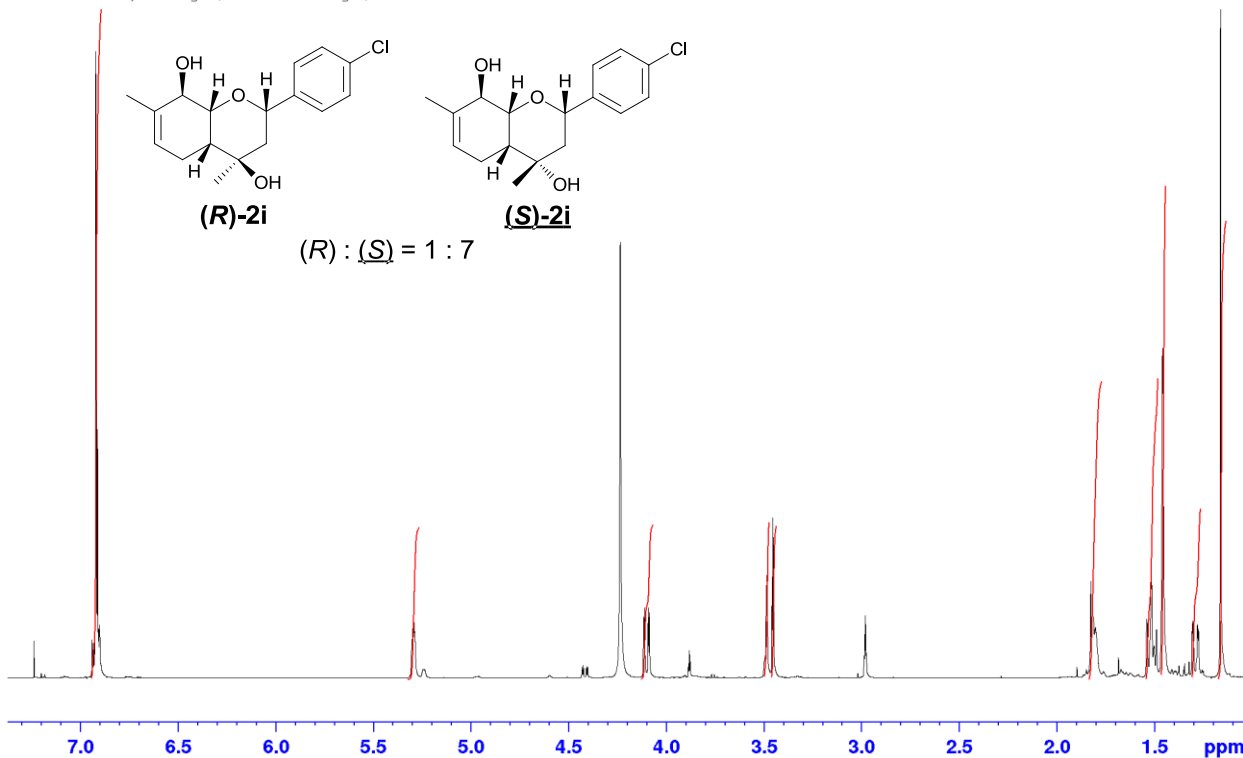
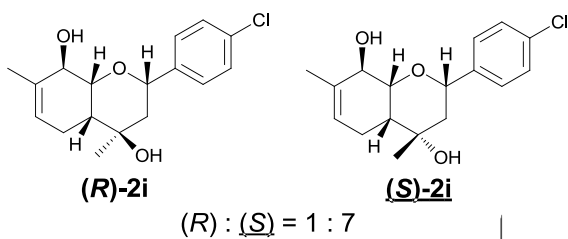
DRX500, 1H, Mikhalchenko, MO-173-7 in  
 CDCl3+CD3OD, 38mg (19.11.2013g.)



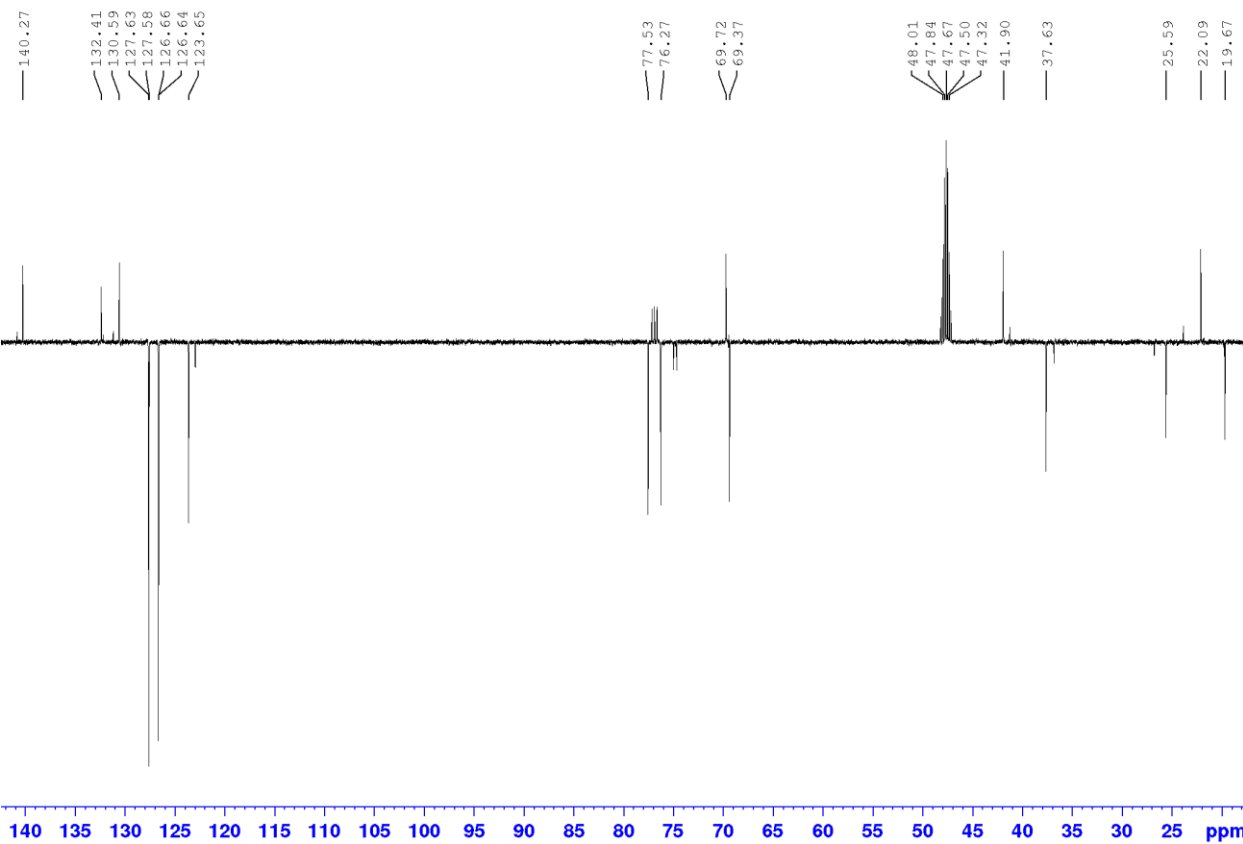
DRX500 C13 jmod 125.7578053 MHz,  
 Mikhalchenko, MO-173-7 in CDCl3+CD3OD, 38mg



DRX500, 1H, Mikhalchenko, MO-173-8 in CDC13+CD3OD, 60mg (19.11.2013g.)

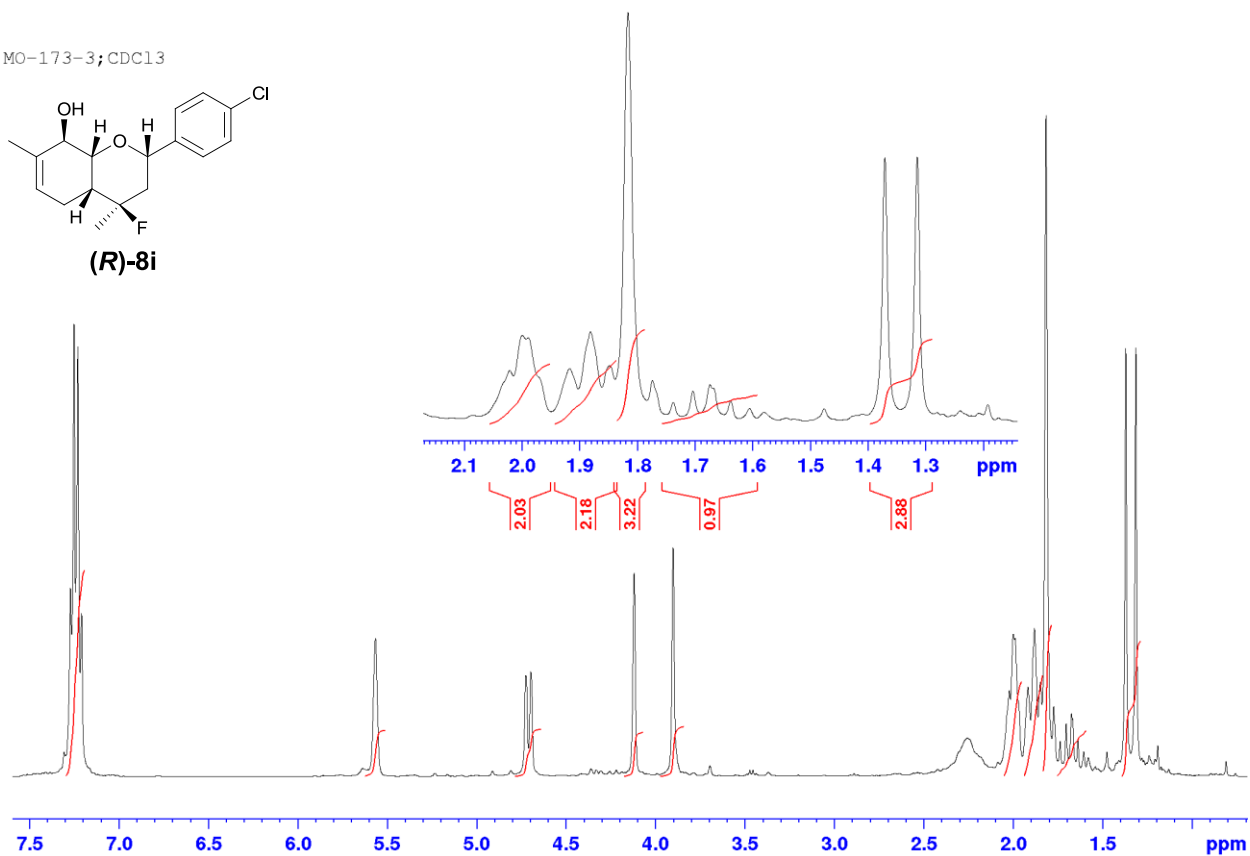
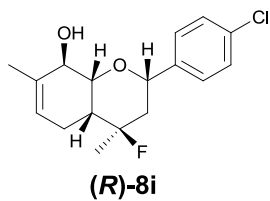


DRX500 C13 jmod 125.7578053 MHz,  
Mikhalchenko, MO-173-8 in CDC13+CD3OD, 60mg

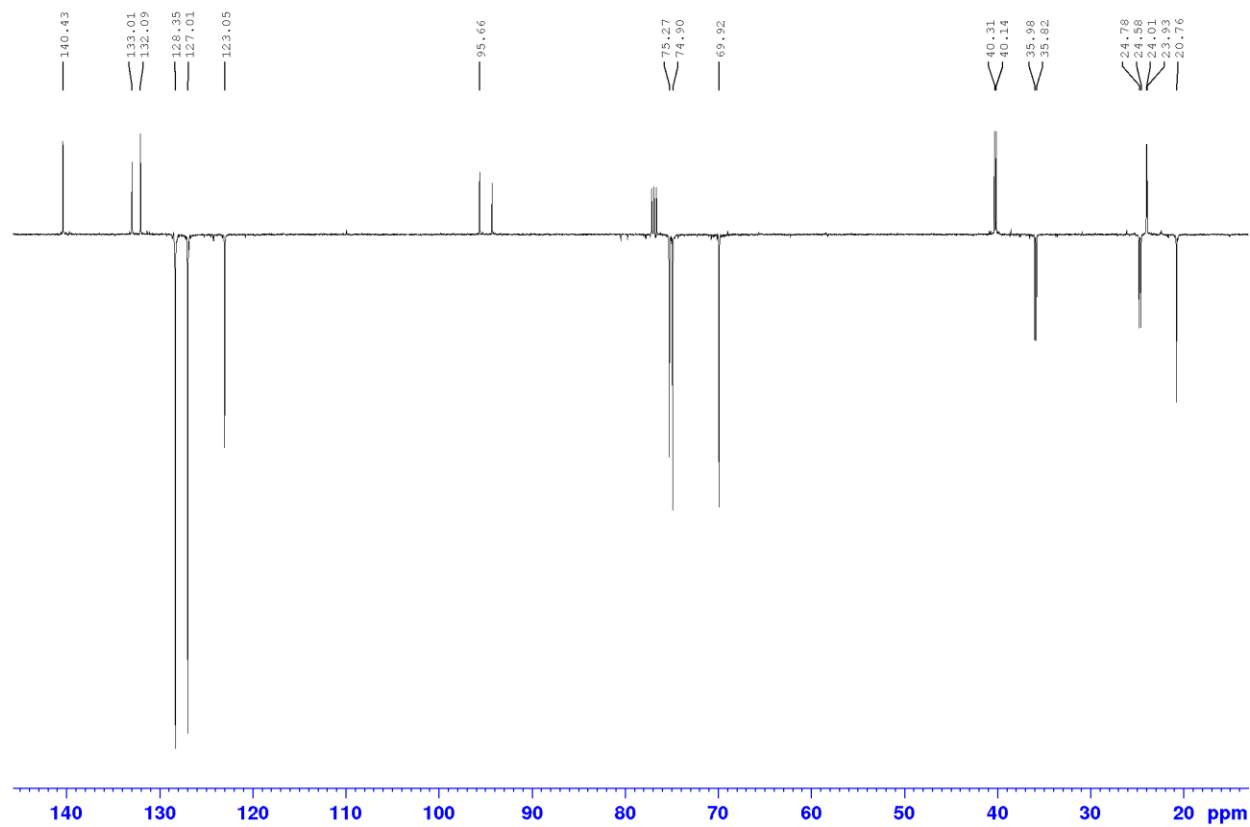




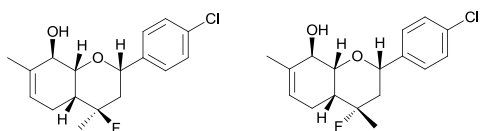
MO-173-3; CDC13



DRX500, 13 C-jmod, Mikhalchenko,  
MO-173-3 in CDCl<sub>3</sub>, 20mg



mo-173-4; CDCL3

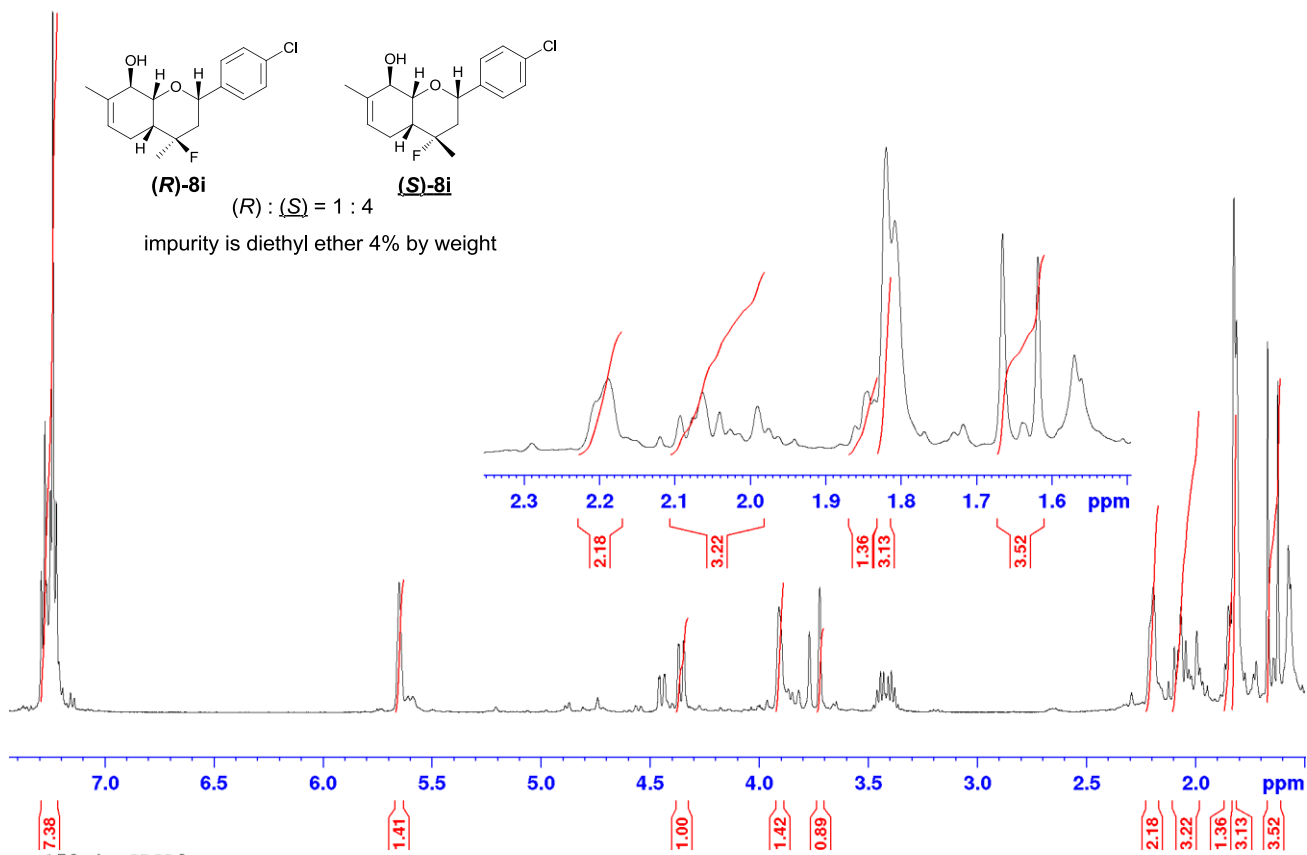


**(R)-8i**

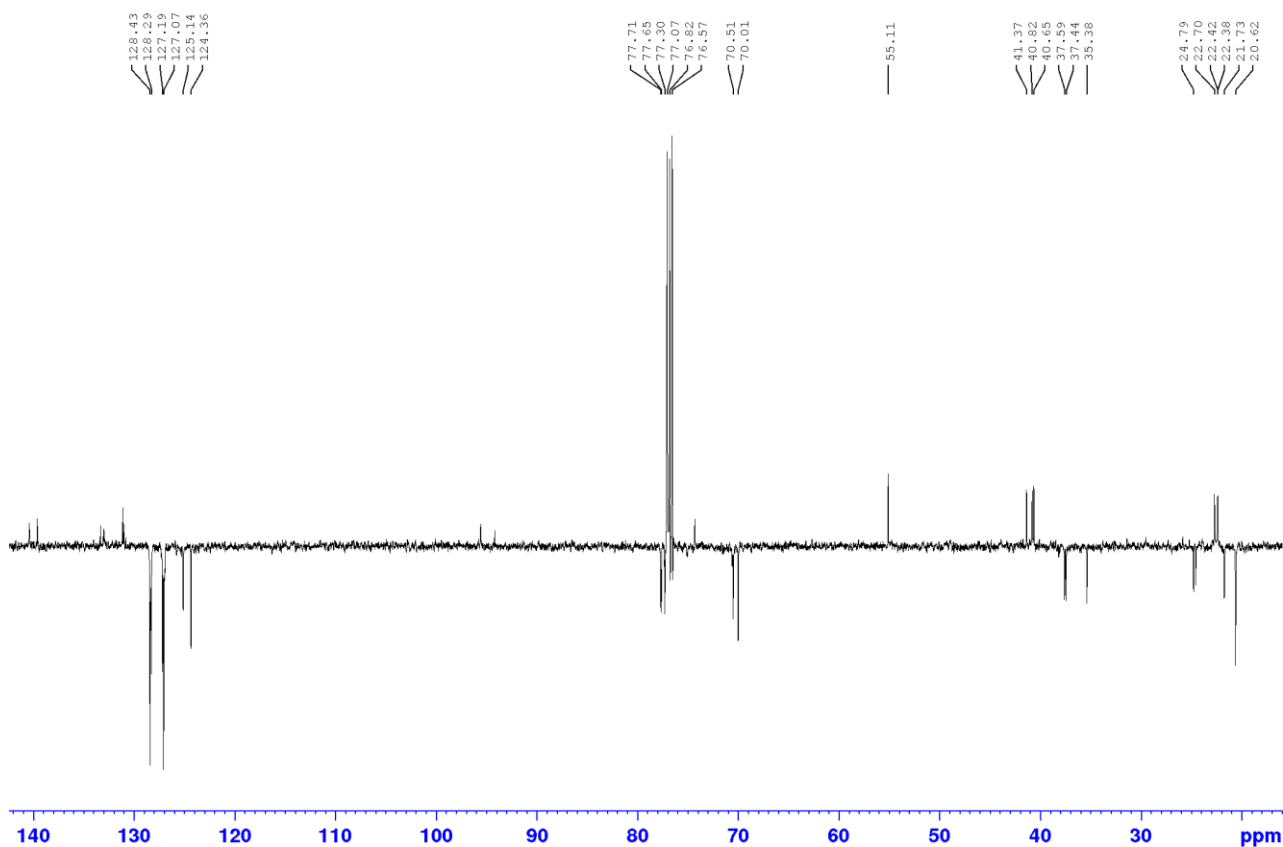
(R) : (S) = 1 : 4

**(S)-8i**

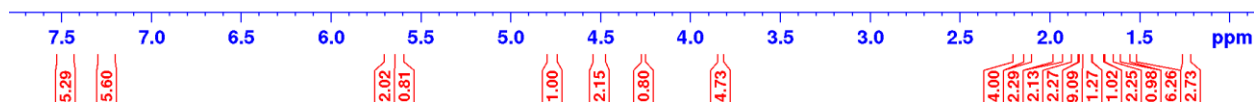
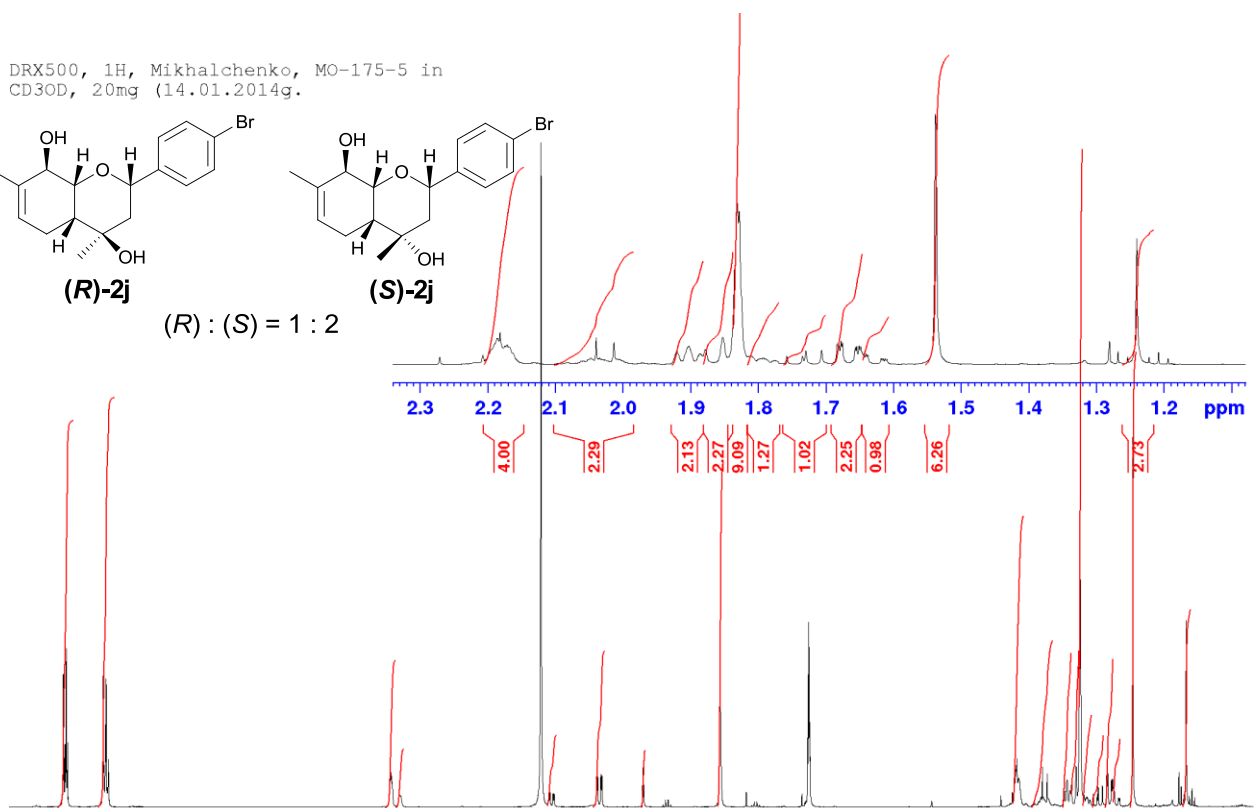
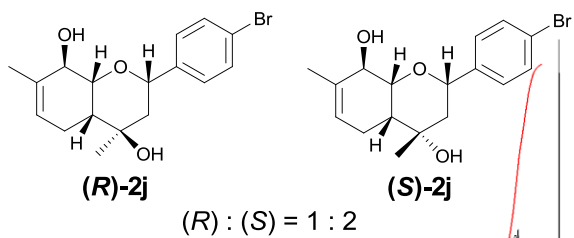
impurity is diethyl ether 4% by weight



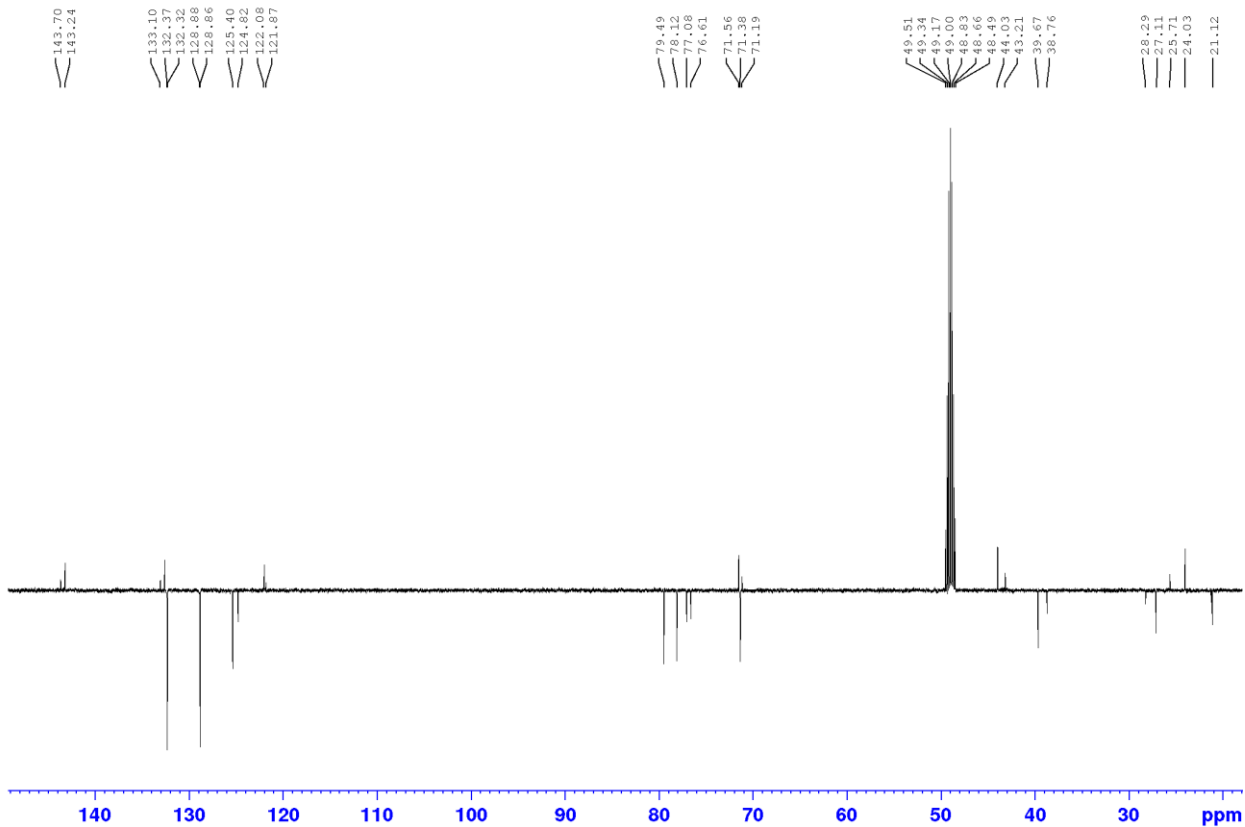
mo-173-4; CDCL3

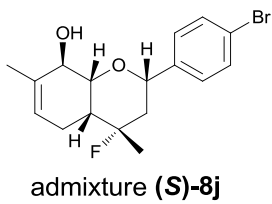
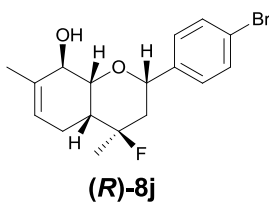


DRX500, 1H, Mikhalchenko, MO-175-5 in CD3OD, 20mg (14.01.2014g.

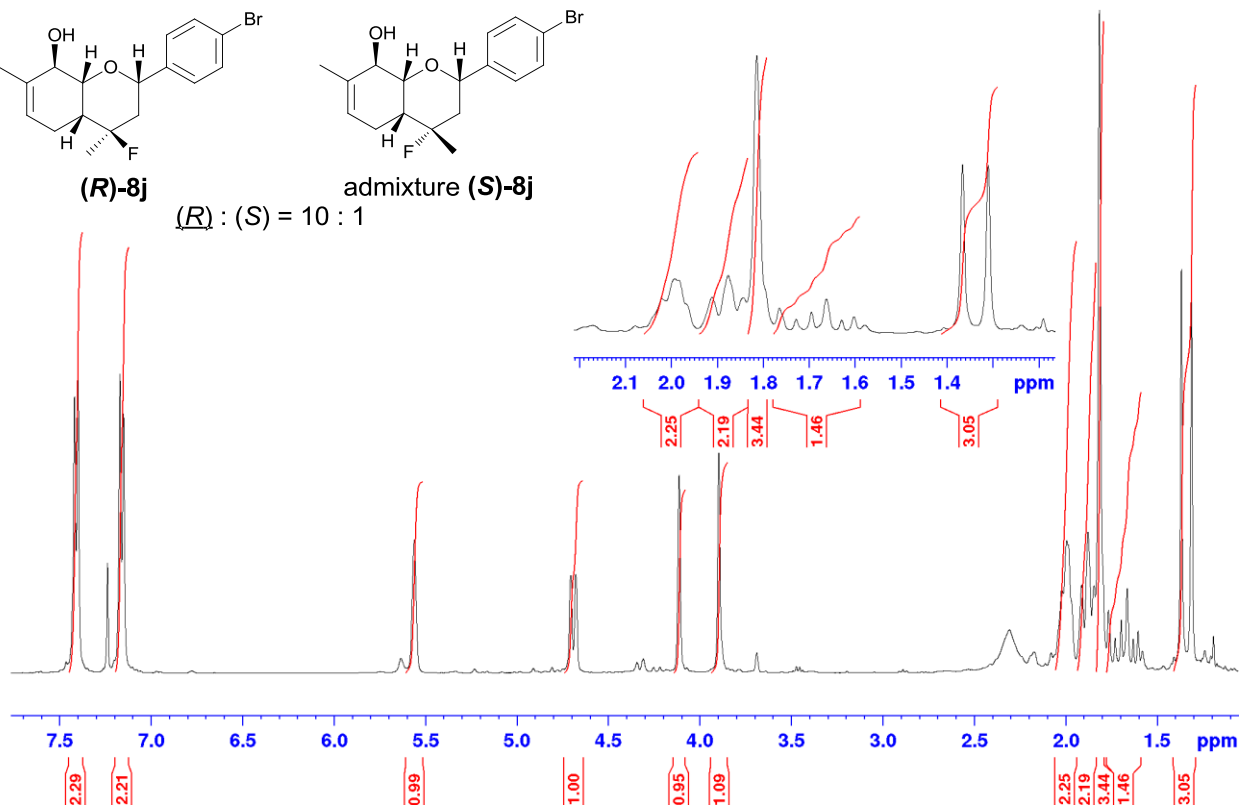


DRX500 C13 jmod 125.7578053 MHz, Mikhalchenko, MO-175-5 in CD3OD, 20mg

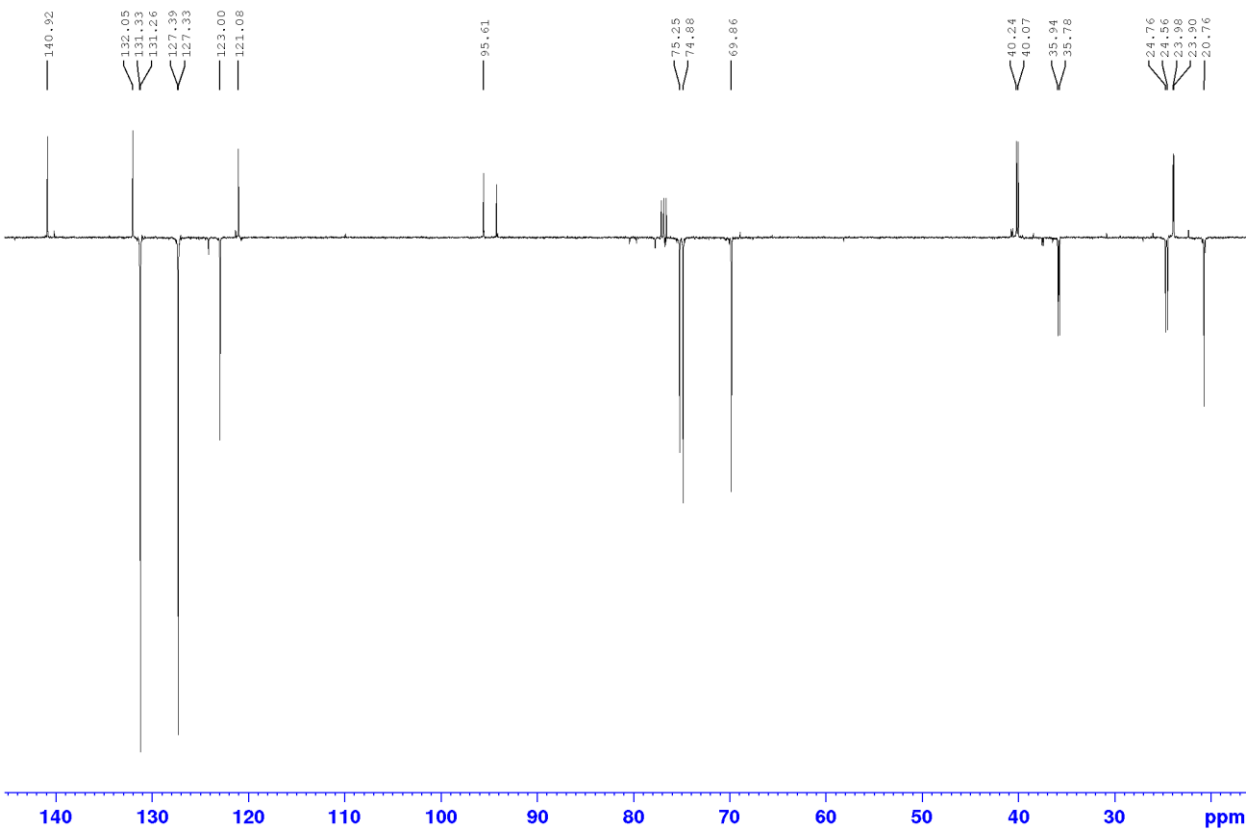




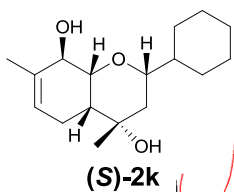
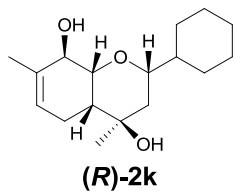
(R) : (S) = 10 : 1



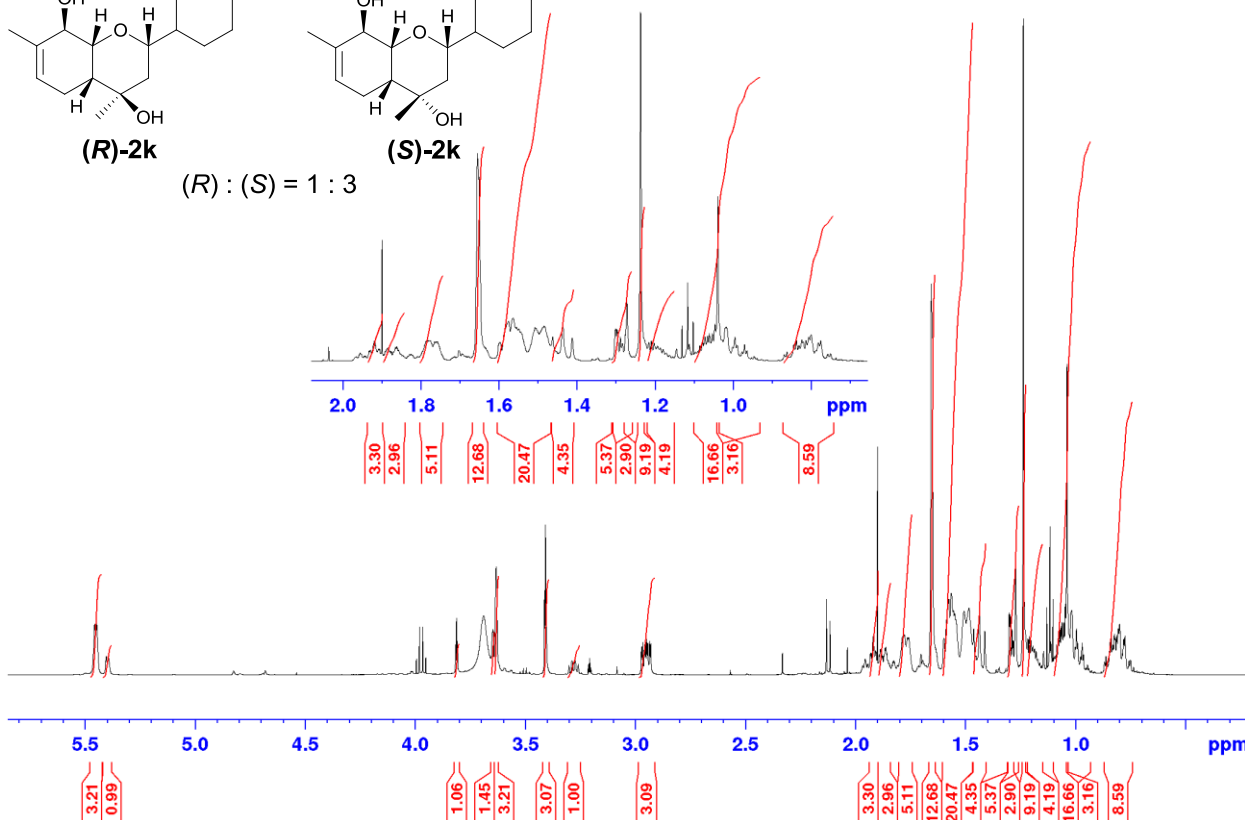
DRX500, <sup>13</sup>C-jmod, Mikhalchenko,  
MO-175-3 in CDCl<sub>3</sub>, 20mg



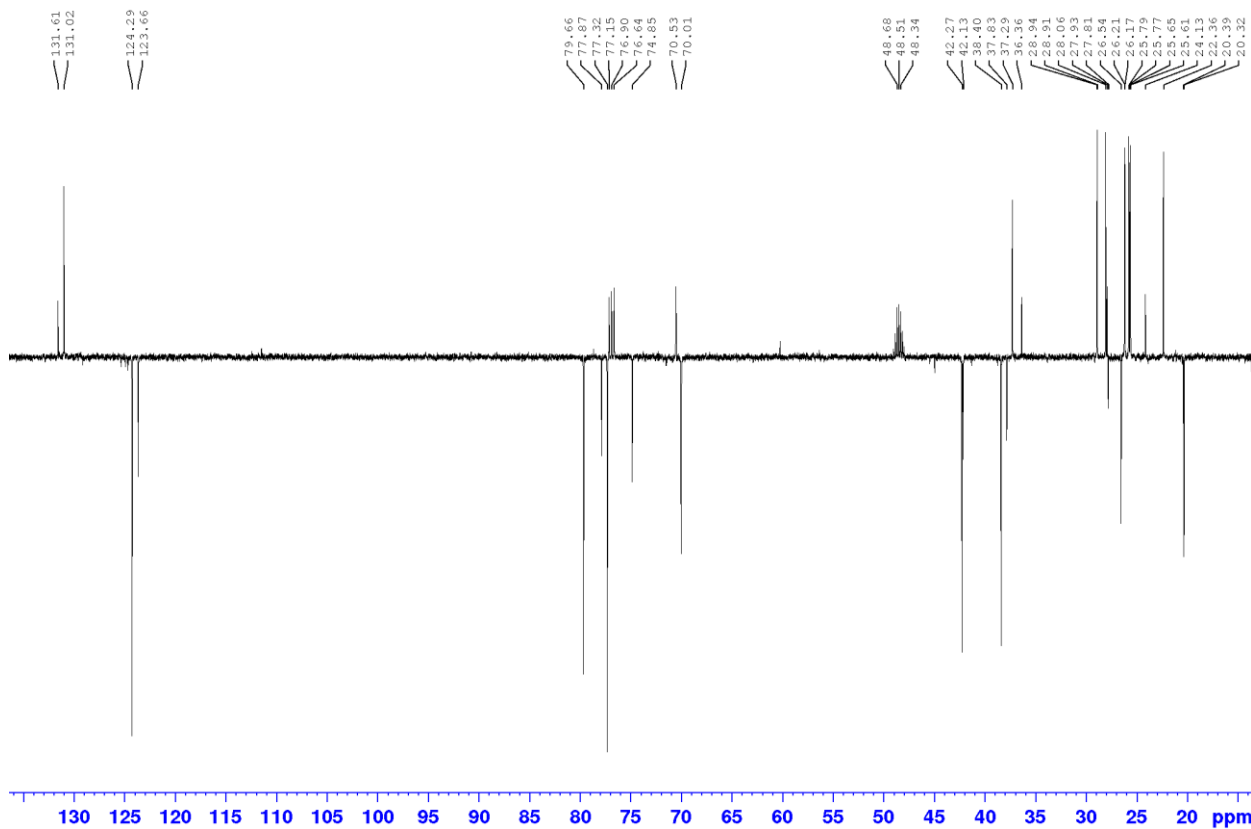
DRX500, 1H, Mikhalchenko, MO-234-3 in  
 CDCl3+CD3OD, 60mg (27.05.2014g.)



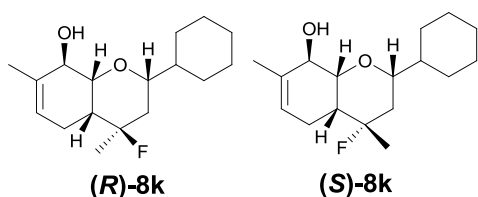
(R) : (S) = 1 : 3



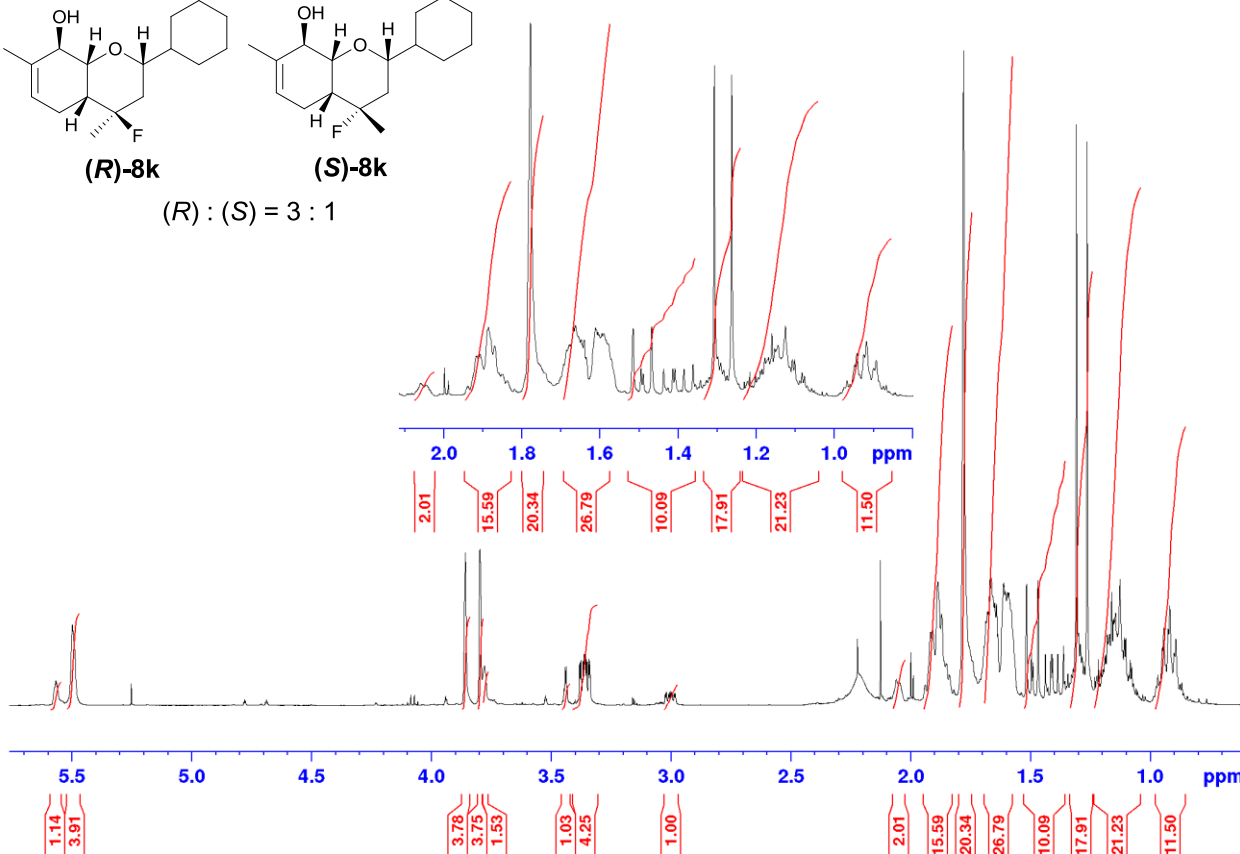
DRX500 C13 jmod 125.7578053 MHz,  
 Mikhalchenko, MO-234-3 in CDCl3+CD3OD, 60mg



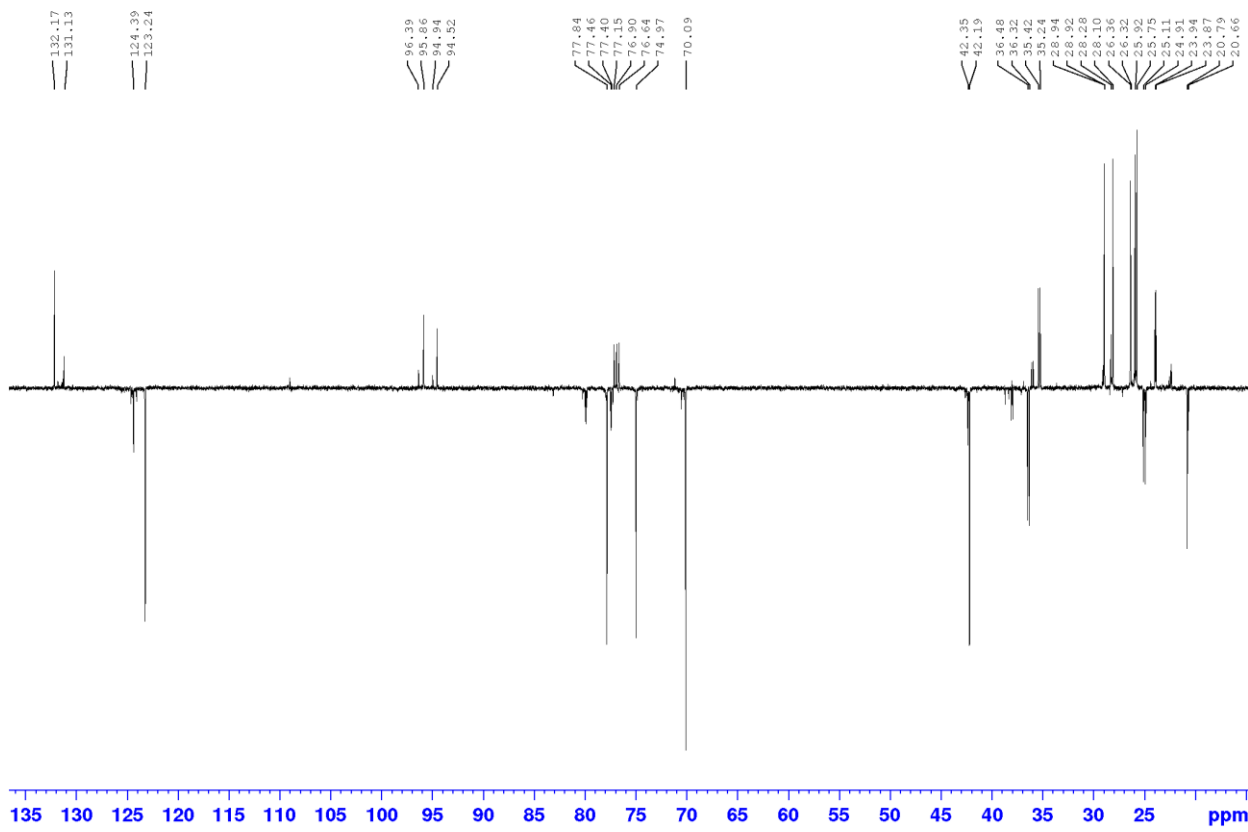
DRX500, 1H, Mikhalchenko, MO-234-1 in CDCl3, 60mg (27.05.2014g.)



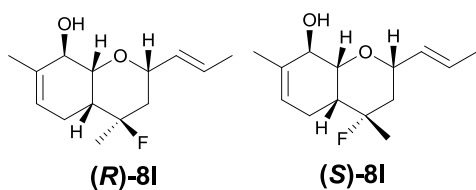
(R) : (S) = 3 : 1



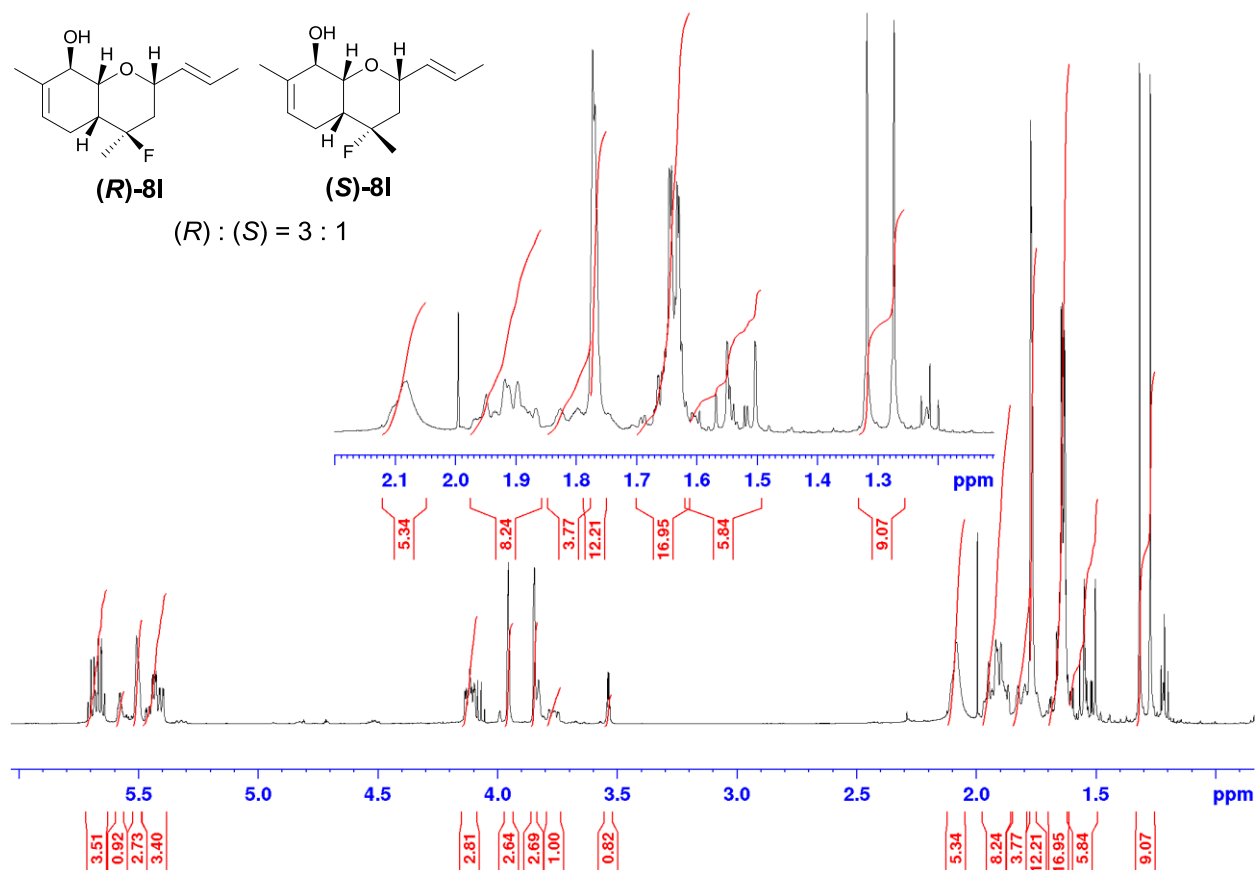
DRX500 C13 jmod 125.7578053 MHz, Mikhalchenko, MO-234-1 in CDCl3, 60mg



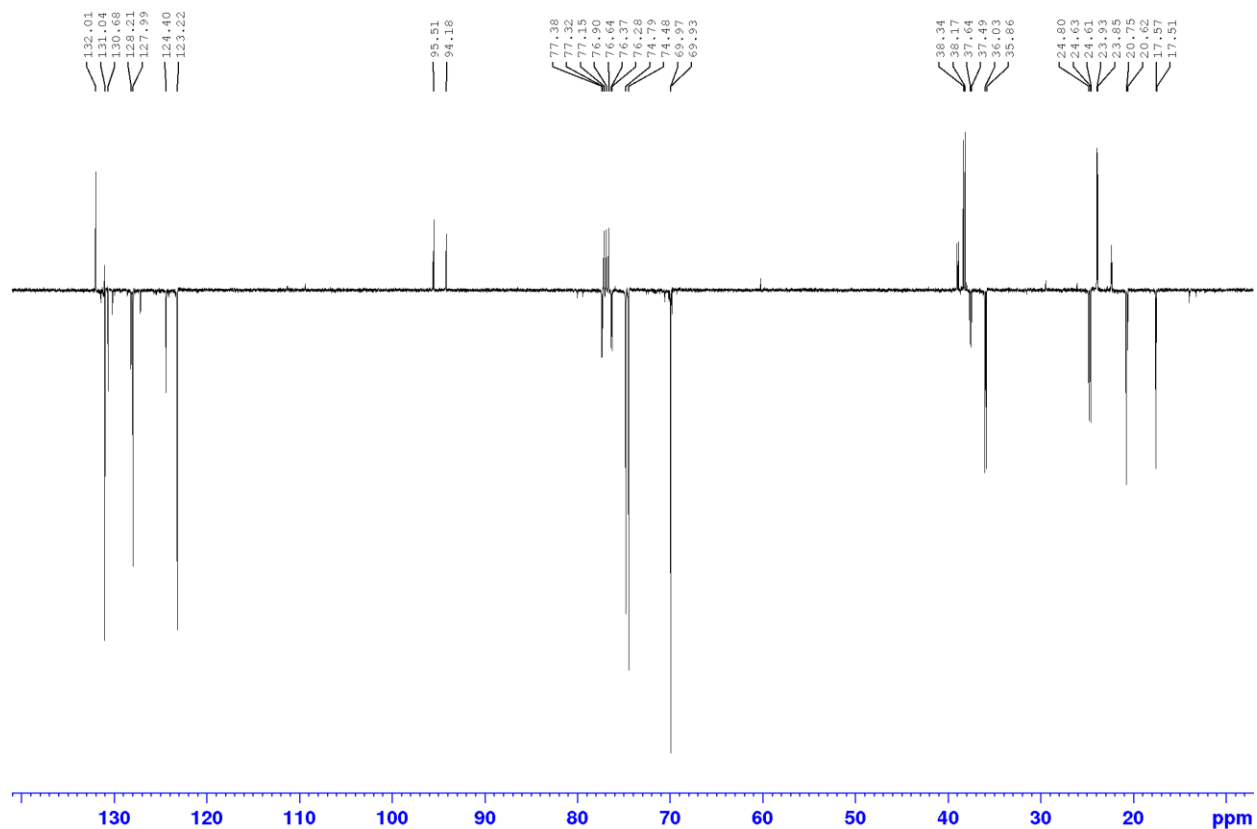
DRX500, 1H, Mikhalchenko, MO-230-1 in CDCl3, 60mg (04.06.2014g.)



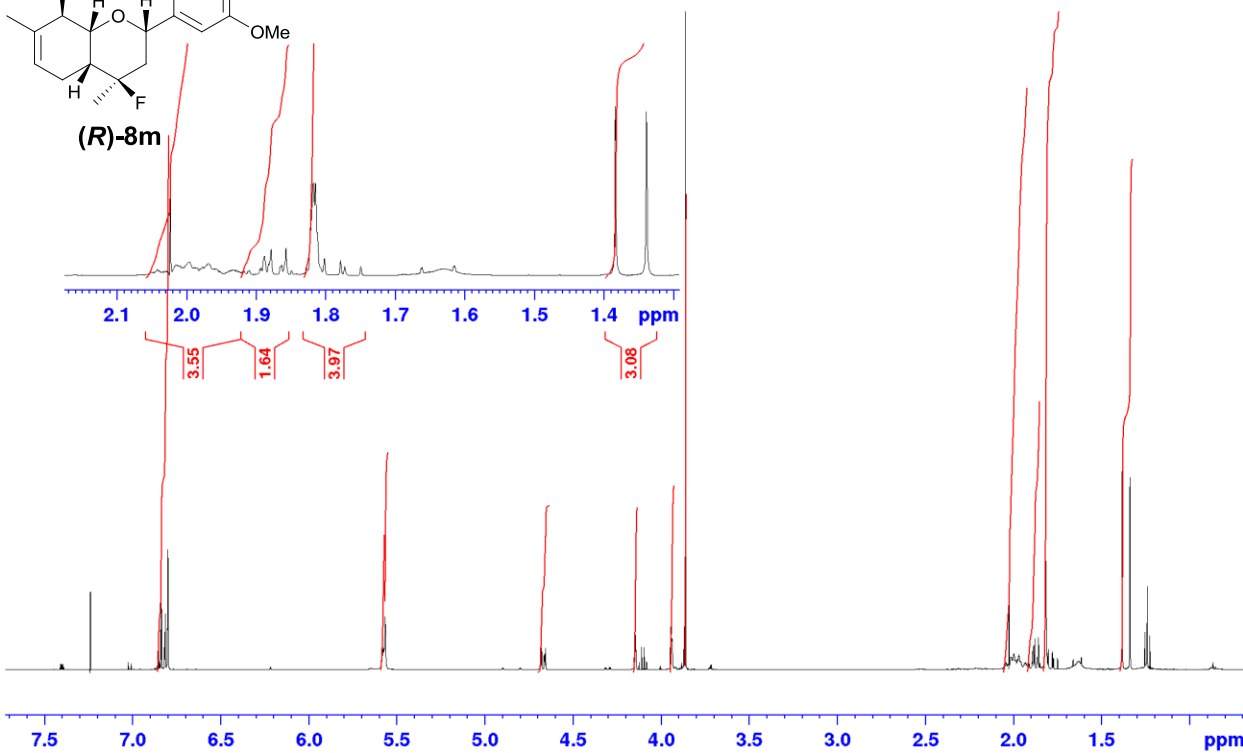
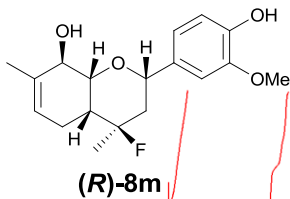
(R) : (S) = 3 : 1



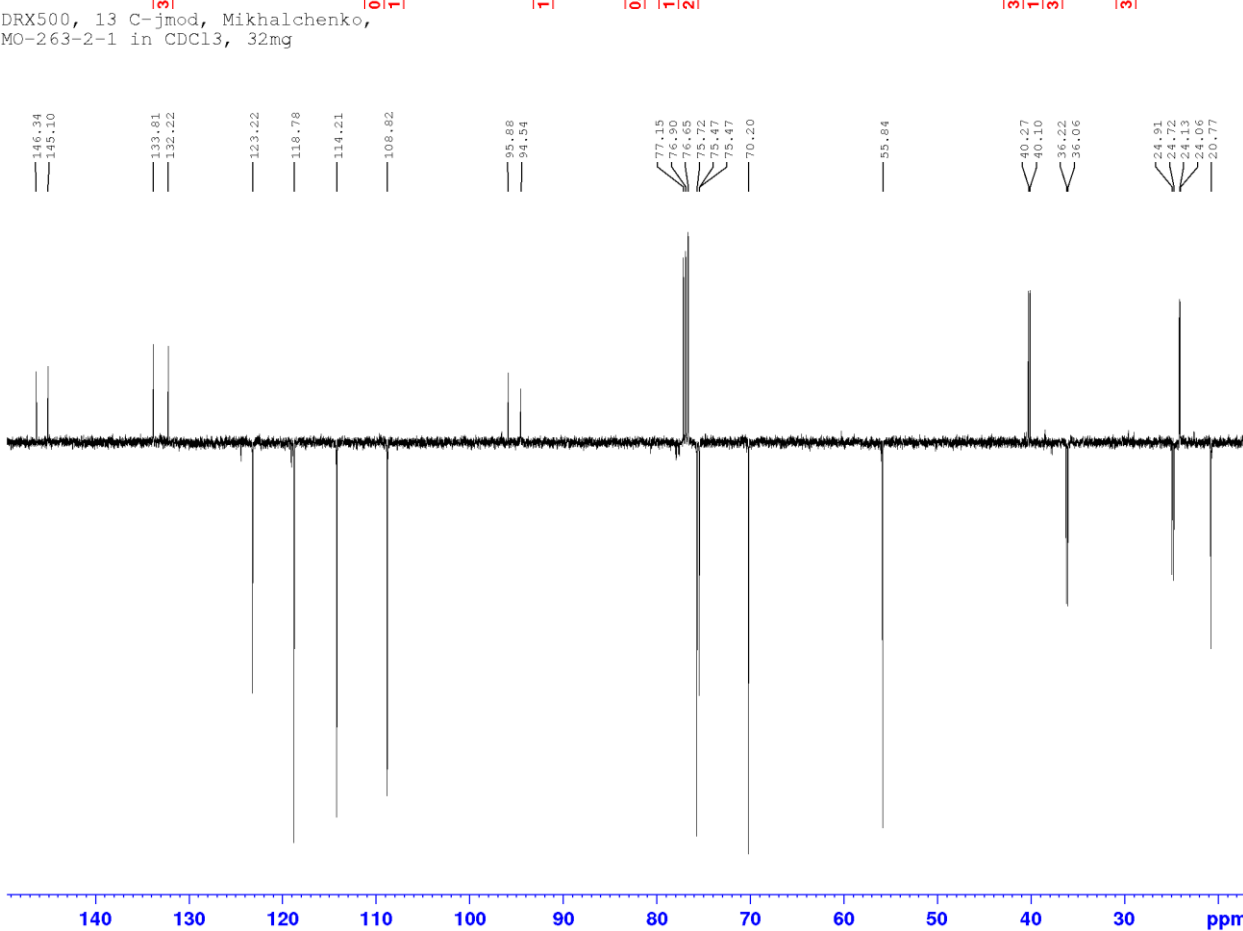
DRX500 C13 jmod 125.7578053 MHz, Mikhalchenko, MO-230-1 in CDCl<sub>3</sub>, 60mg



DRX500, 1H, Mikhalchenko,  
MO-263-2-1 in CDCl3, 32mg (07.04.2015g.)



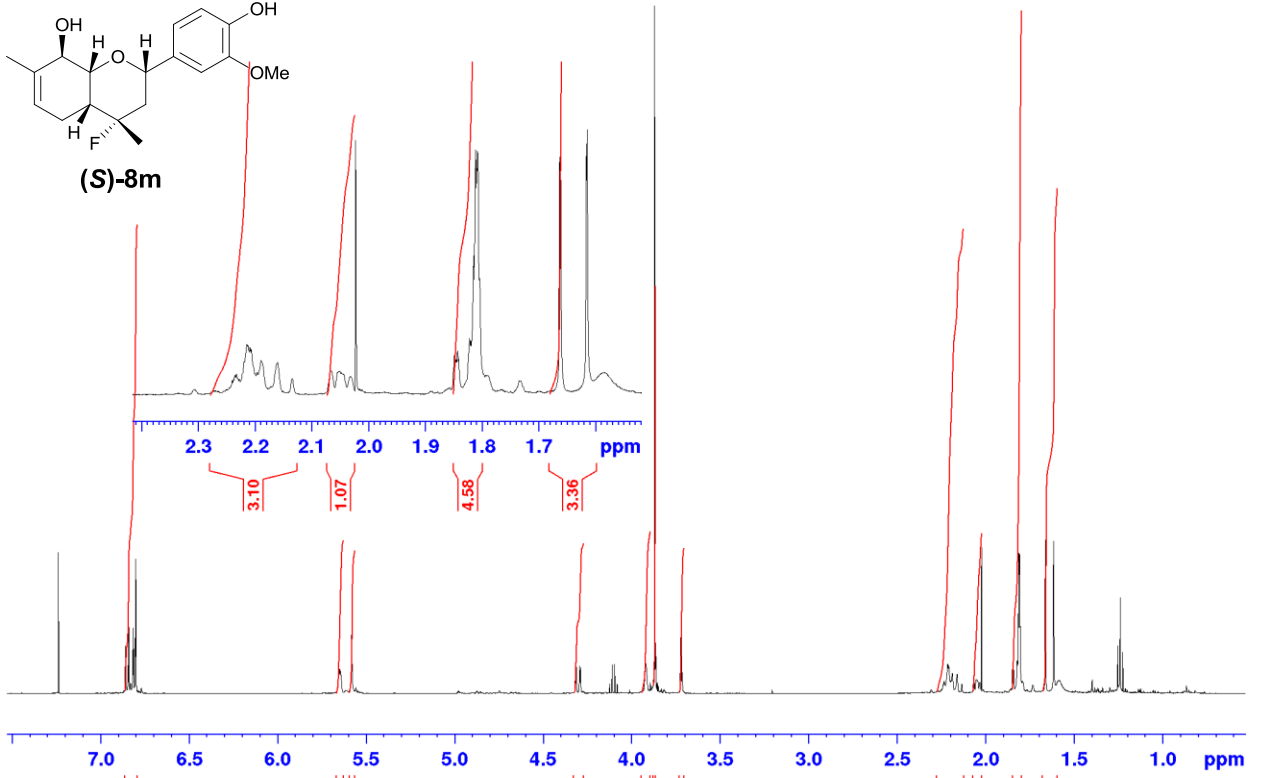
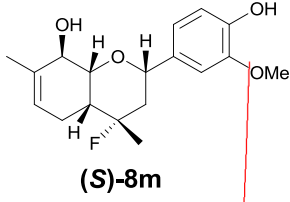
DRX500, 13 C-jmod, Mikhalchenko,  
MO-263-2-1 in CDCl3, 32mg



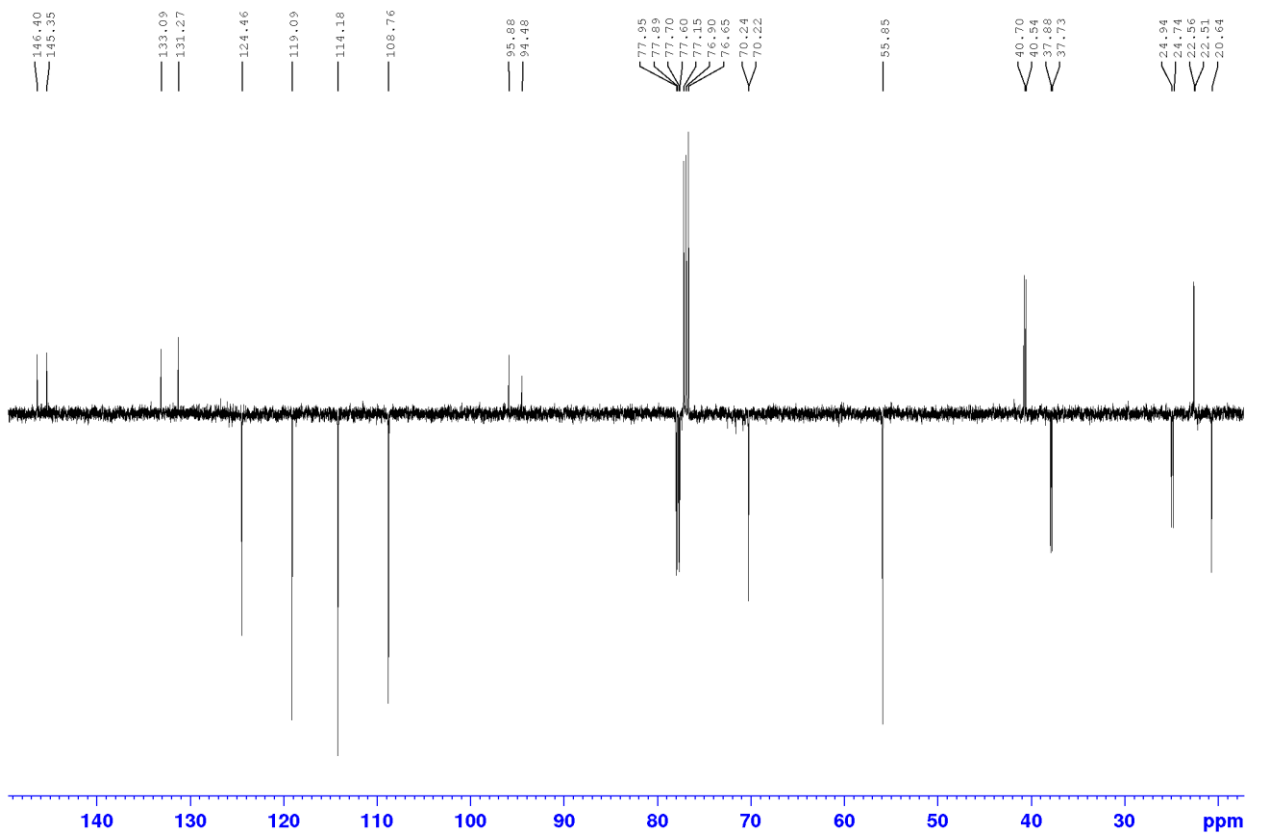
146.34  
145.10  
133.81  
132.22  
123.22  
118.78  
114.21  
108.82  
95.88  
94.54  
77.15  
76.90  
76.65  
75.72  
75.47  
75.47  
70.20  
55.84  
40.27  
40.10  
36.22  
36.06  
24.31  
24.22  
24.13  
24.06  
20.77



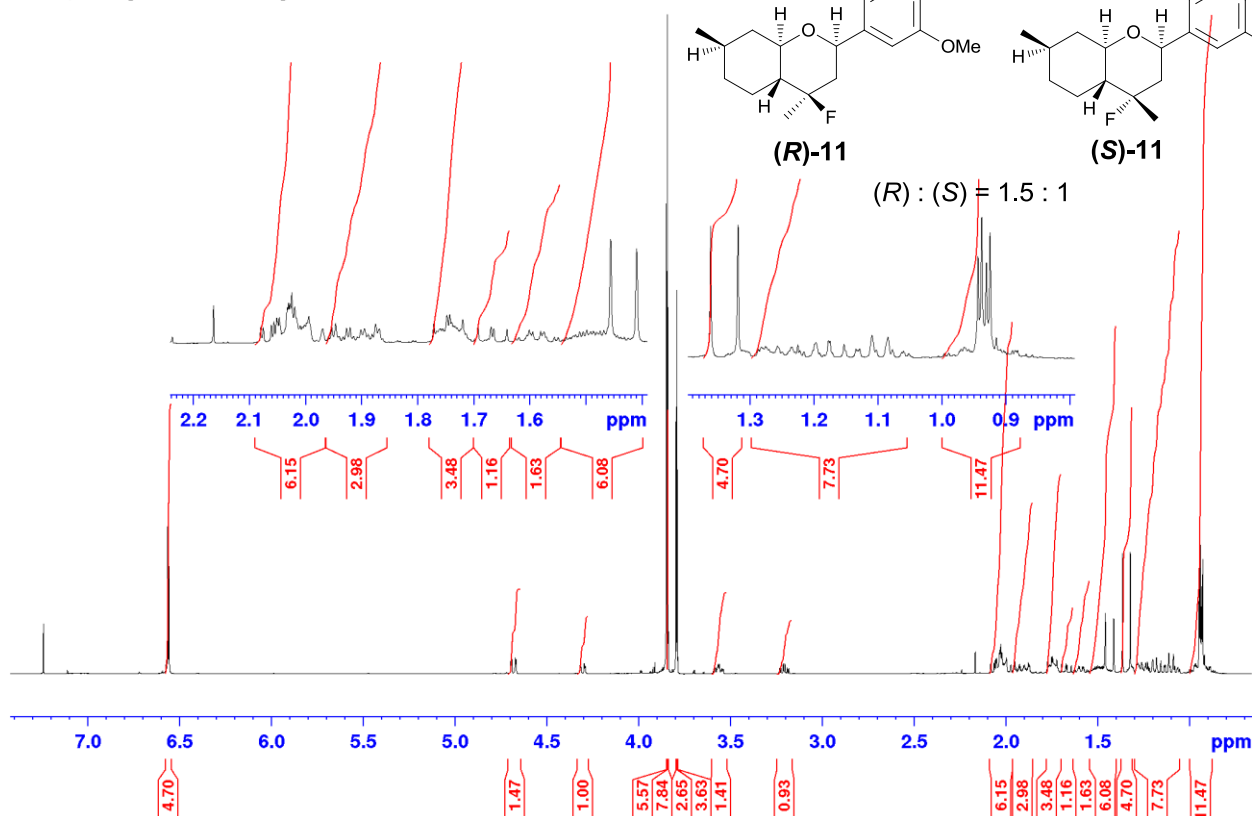
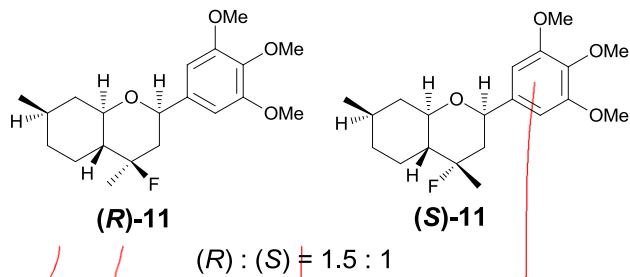
DRX500, 1H, Mikhalchenko,  
MO-263-2-2 in CDCl3, 22mg (08.04.2015g.)



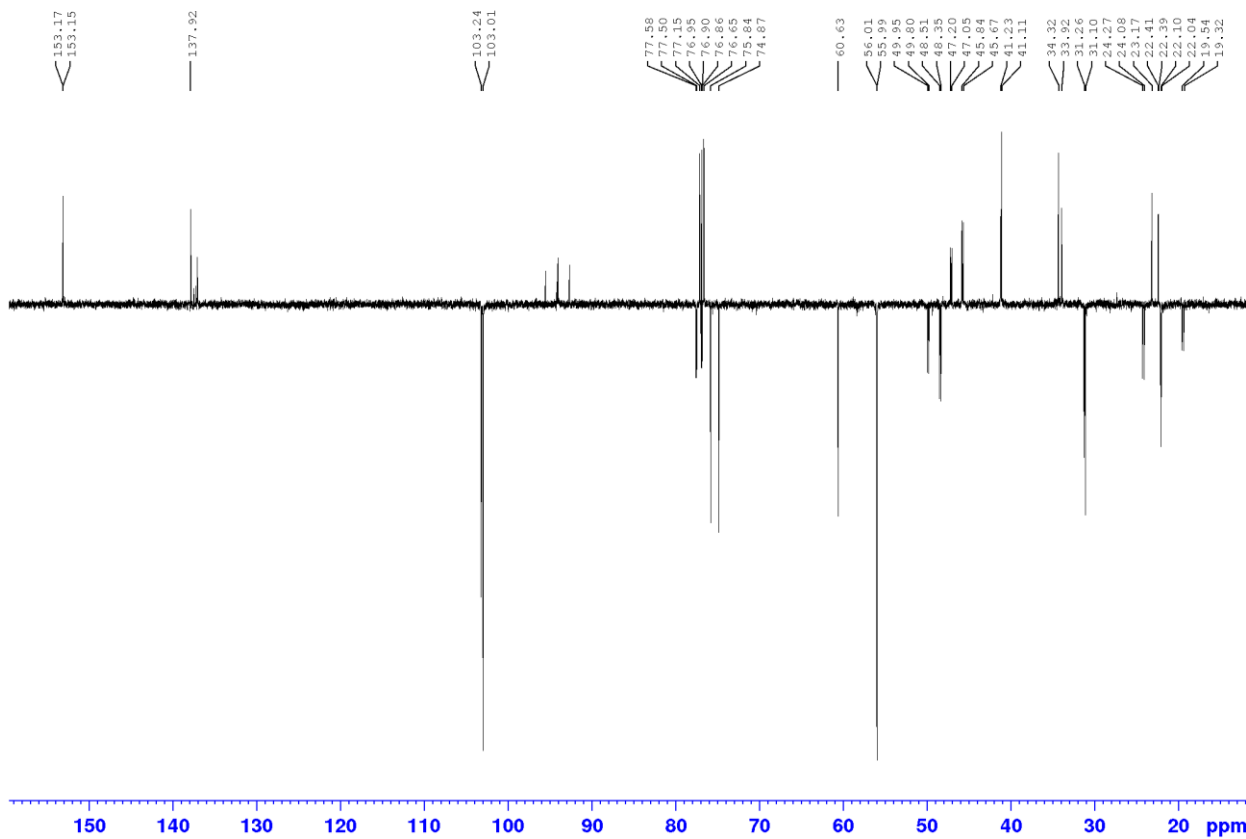
DRX500, 13 C-jmod, Mikhalchenko,  
MO-263-2-2 in CDCl3, 22mg



DRX500, 1H, Mikhalchenko, MO-227-3 in CDCl3, 30mg (25.03.2014g.)



DRX500 C13 jmod 125.7578053 MHz, Mikhalchenko, MO-227-3 in CDCl3, 30mg



## References

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