Supporting Information

Total Synthesis of (-)- Preussochromone D

Eric Kerste†, Klaus Harms†, Ulrich Koert†*

†Department of chemistry, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, D-35043 Marburg, Germany

koert@chemie.uni-marburg.de

Experimental procedures, spectroscopic and analytical data

of all new compounds

1 General Methods and Materials

All non-aqueous reactions were carried out using flame-dried glassware under argon atmosphere. All solvents were distilled by rotary evaporation. Solvents for non-aqueous reactions were dried as follows prior to use: THF was dried with KOH and subsequently distilled from Solvona®. CH_2Cl_2 was distilled from CaH_2. MeOH was dried by refluxing with Mg-turnings (5g/L) and subsequent distillation. Toluene was distilled from Solvona®. MeCN All commercially available reagents and reactants were used without purification unless otherwise noted.

Reactions were monitored by thin layer chromatography (TLC) using Merck Silica Gel 60 F_{254}-plates and visualized by fluorescence quenching under UV-light. In addition, TLC-plates were stained using a ceric sulfate/phosphomolybdic acid stain. Chromatographic purification of products was performed on Merck Silica Gel 60 (230-400 mesh) unless otherwise noted using a forced flow of eluents. Concentration under reduced pressure was performed by rotary evaporation at 40 °C and appropriate pressure and by exposing to fine vacuum at room temperature if necessary.

NMR spectra were recorded on a Bruker AV 300 MHz, AV III 500 MHz, AV III HD 500 MHz spectrometer at room temperature. Chemical shifts are reported in ppm with the solvent resonance as internal standard. Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet.

Mass spectra were recorded by the mass service department of the Philipps-Universität Marburg. HR-ESI mass spectra were acquired with an LTQ-FT mass spectrometer (Thermo Fischer Scientific). The resolution was set to 100 000.

IR spectra were recorded on a Bruker IFS 200 spectrometer. The absorption bands are given in wave numbers (cm^{-1}), intensities are reported as follows: s = strong, m = medium, w = weak, br = broad band.

Melting points were determined on a Mettler Toledo MP70 using one end closed capillary tubes.

Optical rotations were determined at 20 ^{o}C with a Krüss P8000-T polarimeter.

Diastereomeric ratios were accurately determined by integration of ^{1}H-NMR spectra.

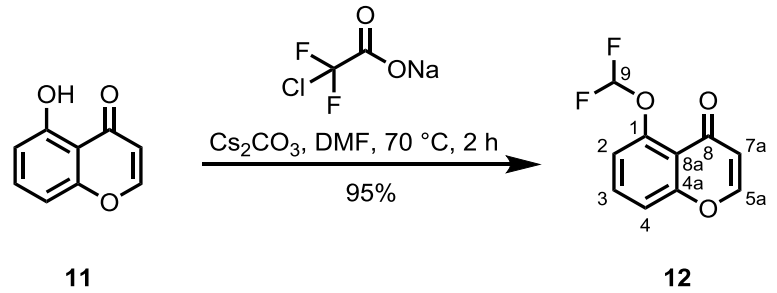
Optical rotations were determined at 20 °C for the Na-D wavelength (589 nm) with a Krüss P8000 T polarimeter.

Emission and UV/Vis spectra were recorded on a SpectraMax M5 (Molecular Devices). Spectral bandwidth: 9 nm (excitation) 15 nm (emission).

Room temperature was 21 – 24 °C.

2 Synthetic Procedures for the Preparation of Preussochromone D (3)

2.1 5-(difluoromethoxy)-4*H*-chromen-4-one 12

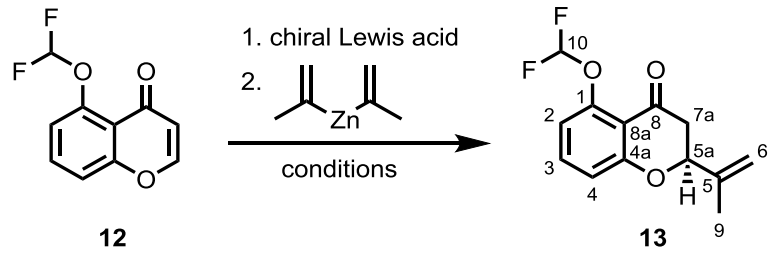


11 **12**

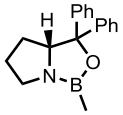
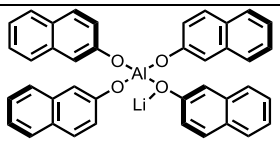
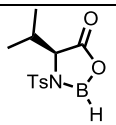
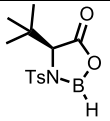
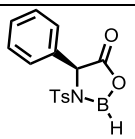
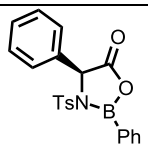
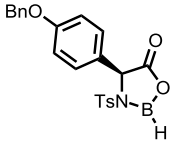
Hydroxy chromenone **11** (2.76 g, 17.0 mmol, 1.00 equiv), sodium chlorodifluoroacetate (6.48 g, 42.5, 2.50 equiv) and cesium carbonate (27.7 g, 85.0 mmol, 5.00 equiv) were suspended in dry DMF (200 mL) and heated to 70 °C for 2 h. H_2O (300 mL) was added and the mixture was stirred until all solids were dissolved, then EtOAc (150 mL) was added. The reaction was transferred to a separation funnel, the layers were separated and the aqueous layer was further extracted with EtOAc (4x100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (silica, *n*-pentane/EtOAc 2:1) to obtain difluoromethyl ether **12** (3.43 g, 16.2 mmol, 95%) as pale yellow powder.

TLC: R_f = 0.55 (*n*-pentane/EtOAc 1:1). **^{1}H-NMR:** 500 MHz, $CDCl_3$; δ=7.77 (d, 1H, *J*=6.0 Hz, 5a-H), 7.62 (t, 1H, *J*=8.3 Hz, 3-H), 7.38 (dd, 1H, *J*=1.0 Hz, 8.6 Hz, 4-H), 7.19 (dd, 1H, *J*=0.5 Hz, 8.0 Hz, 2-H), 6.68 (t, 1H, *J*=75.4 Hz, 9-H), 6.28 (d, 1H, *J*=6.0 Hz, 7a-H) ppm. **^{13}C-NMR:** 125 MHz, $CDCl_3$; δ=125 MHz, $CDCl_3$; δ = 176.4 (8-C), 157.9 (4a-C), 154.2 (5a-C), 149.1 (1-C), 133.7 (3-C), 119.7 (2-C), 118.6 (8a-C), 116.8 (4-C), 116.5 (t, *J*=261.7 Hz, 9-C), 114.5 (7a-C) ppm. **^{19}F-NMR:** 282 MHz, $CDCl_3$; δ=–84.13 (s, 2F, 9-F_2) ppm. **HR-MS:** (ESI+): m/z calc. for $C_{14}H_{19}O_3$ $[M-H]^+$: 235.0177, found: 235.0177. **FT-IR:** (neat): $\tilde{\nu}$ = 3089 (w), 1663 (w), 1642 (s), 1619 (w), 1566 (w), 1472 (m), 1394 (w), 1350 (m), 1295 (w), 1234 (w), 1214 (w), 1116 (s), 1046 (w), 1028 (m), 996 (m), 903 (w), 838 (m), 809 (w), 767 (w), 680 (w), 640 (w), 512 (w), 475 (w) cm^{-1}. **m.p.:** 109 °C (Et_2O).

2.2 Screening of chiral Lewis acids for the asymmetric conjugate addition

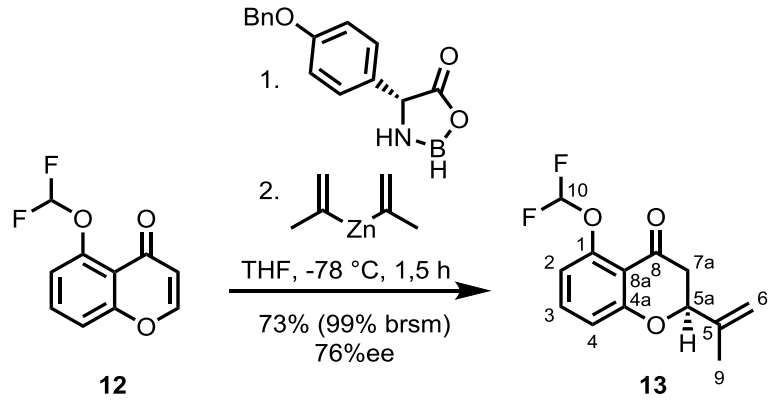


12 13

Chiral Lewis acid	conditions	Yield (ee)
 (*R*)-Me-CBS	THF, -78 °C, 1 h	decomposition
 (*R*)-ALB[1]	THF, 0 °C, 1 h	decomposition
	THF, -78 °C, 1 h	48% (56%ee)
	THF, -78 °C, 1 h	67% (68%ee)
	THF, -78 °C, 1 h	50% (73%ee)
	THF, -78 °C, 1 h	87% (45%ee)
	THF, -78 °C, 1 h	70% (78%ee) 73% (76%ee) (gram-scale)

All tested amino acids were tosylated according to the protocol of DeRuiter *et. al.*[2] Benzylation of *para*-hydroxy-phenylglycine was performed according to the protocol of Behnam *et al.*[3] The in situ preparation of the chiral borane reagents followed a protocol of Kiyooka *et al.*[4]

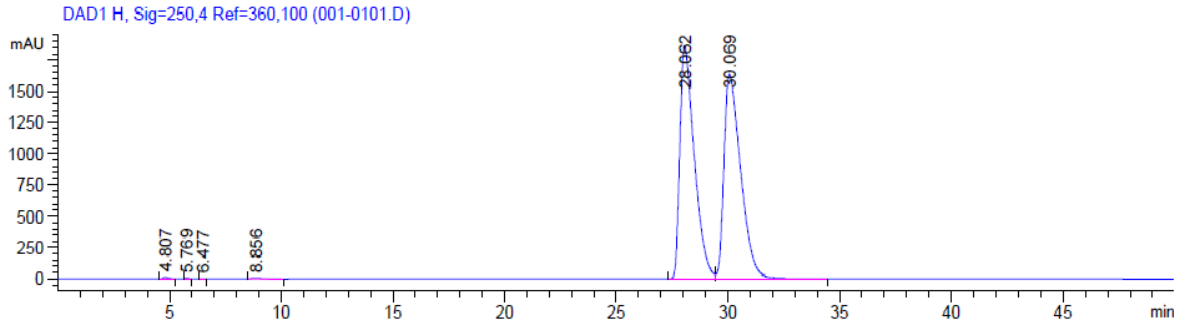
2.3 (*S*)-5-(difluoromethoxy)-2-(prop-1-en-2-yl)chroman-4-one 13



(*S*)-*N*-Ts-*para*-benzyloxy phenylglycine[2,3] (4.27 g, 10.4 mmol, 1.10 equiv) was dissolved in THF (260 mL) and BH_3·THF-solution (1M in THF, 11.3 mL, 11.3 mmol, 1.20 equiv) was added dropwise at room temperature. After evolution of gas had ceased (~45 min), the solution was cooled to -78 °C and a solution of difluoromethyl ether **12** (2.00 g, 9.43 mmol, 1.00 equiv) in THF (170 mL) was added. The reaction was stirred for 15 min and then freshly prepared diisopropenyl zinc-solution[5] (11.3 mmol in 170 mL THF, 1.20 equiv) was added dropwise over a period of 1 h. After complete addition, aqueous HCl (2M, 100 mL) was added at -78 °C and the resulting suspension was stirred for further 5 min before warming to room temperature. H_2O (100 mL) and Et_2O (100 mL) were added and the reaction was transferred into a separation funnel. The aqueous layer was extracted with Et_2O (2x100 mL), the combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Column chromatography (silica, *n*-pentane/EtOAc 4:1) gave alkenyl chromanone **13** (1.75 g, 6.88 mmol, 73%) as pale yellow oil.

TLC: R_f = 0.76 (*n*-pentane/EtOAc 2:1). **^{1}H-NMR**: 500 MHz, $CDCl_3$; δ=7.43 (t, 1H, *J*=8.3 Hz, 3-H), 6.94 (dd, 1H, *J*=1.0 Hz, 8.5 Hz, 4-H), 6.81 (dd, 1H, *J*=0.9 Hz, 8.1 Hz, 2-H), 6.57 (dd, 1H, *J*=74.4 Hz, 75.5 Hz, 10-H), 5.15 (dd, 1H, *J*=1.0 Hz, 1.9 Hz, 6-H_a), 5.07 (s, 1H, 6-H_b), 4.87 (dd, 1H, *J*=3.1 Hz, 12.3 Hz, 5a-H), 2.90 (dd, 1H, *J*=12.4 Hz, 16.3 Hz, 7a-H_a), 2.74 (dd, 1H, *J*=3.1 Hz, 16.3 Hz, 7a-H_b), 1.87 (s, 3H, 9-H_3) ppm. **^{13}C-NMR**: 126 MHz, $CDCl_3$; δ=190.4 (8-C), 162.7 (1-C), 150.1 (4a-C), 141.7 (5-C), 135.8 (3-C), 116.2 (4-C), 116.2 (dd, *J*=260.9 Hz, 10-C), 115.2 (2-C), 114.5 (6-C), 114.1 (8a-C), 80.4 (5a-C), 42.8 (7a-C), 18.3 (9-C) ppm. **^{19}F-NMR:** 282 MHz, $CDCl_3$; δ=–83.52 (dd, *J*=164.0 Hz, 219.9 Hz, 2F, 10-F_2) ppm. **HR-MS:** (ESI+): m/z calc. for $C_{13}H_{12}O_3F_2Na$ $[M\text{-}Na]^+$: 277.0647, found: 277.0643. **FT-IR:** (neat): $\tilde{\nu}$ = 2978 (w), 1694 (m), 1657 (w), 1609 (s), 1574 (w), 1469 (m), 1381 (w), 1349 (w), 1319 (w), 1275 (w), 1218 (w), 1173 (w), 1124 (s), 1038 (m), 977 (w), 912 (w), 797 (w), 765 (w), 743 (w) cm^{-1}. **[α]:** -34.9 (c 1.0, $CHCl_3$, for a sample with 76%ee).

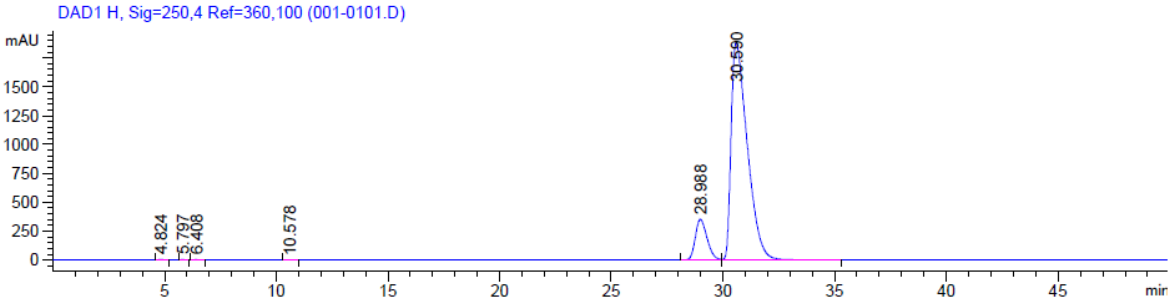
Racemic sample



Signal 8: DAD1 H, Sig=250,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.807	BB	0.1942	177.35933	13.24793	0.1052
2	5.769	BB	0.1402	29.75374	3.20819	0.0177
3	6.477	BB	0.1563	10.74800	1.17938	6.377e-3
4	8.856	BB	0.8425	265.86951	4.37805	0.1577
5	28.062	BV	0.6666	8.33199e4	1859.99731	49.4323
6	30.069	VB	0.7940	8.47499e4	1636.92615	50.2807

Enantiomerically enriched sample



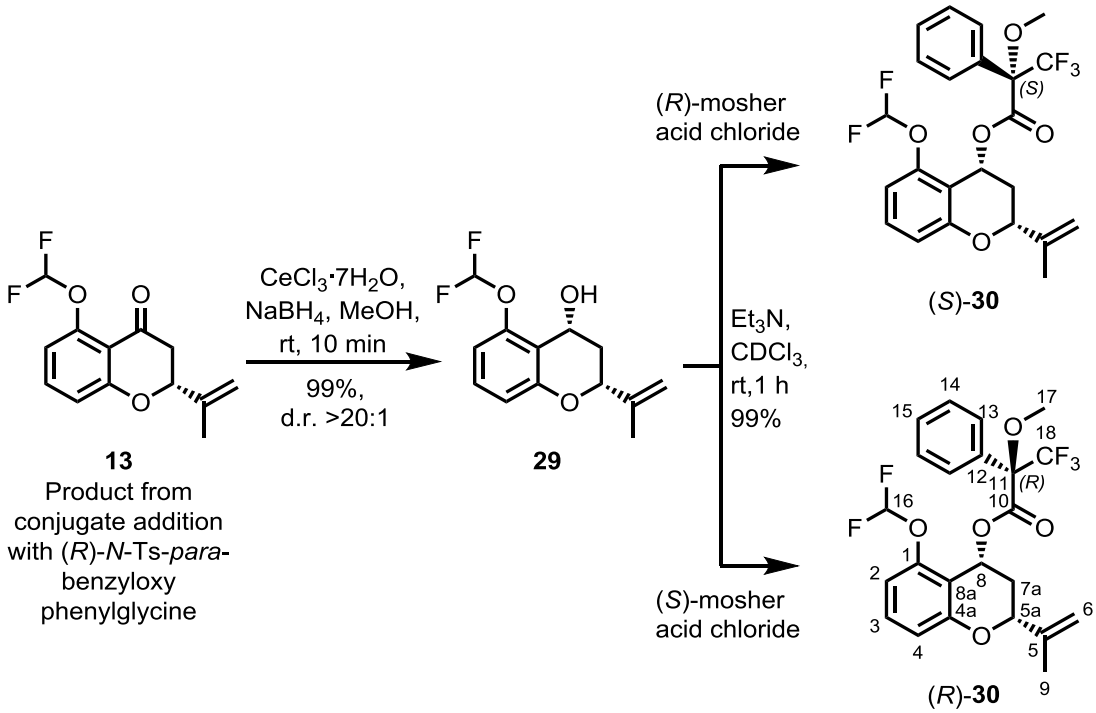
Signal 8: DAD1 H, Sig=250,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.824	BB	0.1427	58.19304	5.91969	0.0541
2	5.797	BB	0.1579	28.91702	2.67972	0.0269
3	6.408	BB	0.1909	29.34975	2.18230	0.0273
4	10.578	BB	0.2624	22.36465	1.32823	0.0208
5	28.988	BV	0.5684	1.28427e4	351.37961	11.9335
6	30.590	VB	0.7617	9.46367e4	1885.12781	87.9375

HPLC conditions for the determination of the *ee* of **13**: CHIRALPAK IC® (Diacel Chemical Industries) column; *n*-hexane/iPrOH 99:1, flow 0.7 mL/min, ϑ=25 °C.

2.4 Determination of absolute stereoconfiguration by Mosher ester analysis of 13

Mosher ester Synthesis:[6,7]

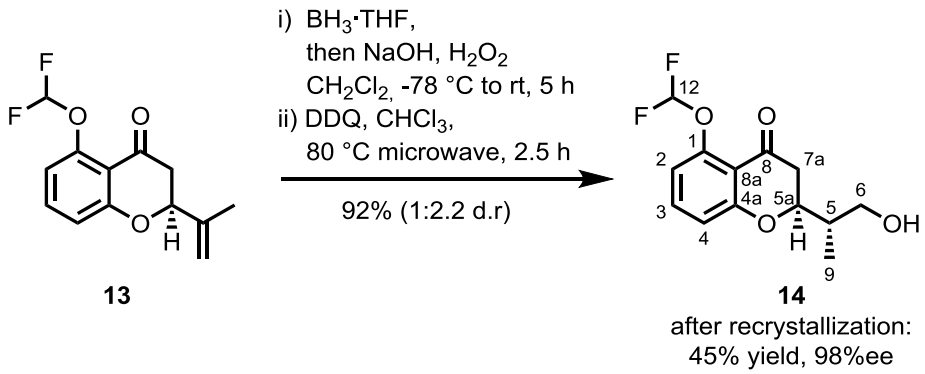


Mosher ester analysis:[7]

C-Atom	δ (*S*)-ester in $CDCl_3$ [ppm]	δ (*R*)-ester in $CDCl_3$ [ppm]	δ(*S*)-δ(*R*)
2	6.68	6.62	+0.06
3	7.23	7.21	+0.02
4	6.78	6.79	-0.01
5a	4.51	4.55	-0.04
6	4.93	5.01	-0.08
7a-α	2.54	2.63	-0.07
7a-β	2.04	2.21	-0.17
9	1.63	1.79	-0.16
16	6.48	6.32	+0.16

Result: The use of D-Amino acids leads to (*R*)-configuration on C-5a (and (*R*)-configuration at C-8 after substrate controlled Luche reduction[6]). Thus, the synthesis of (-)-preussochromone D (**3**) needed to be performed with L-amino acids.

2.5 (*S*)-5-(difluoromethoxy)-2-((*S*)-1-hydroxypropan-2-yl)chroman-4-one 14

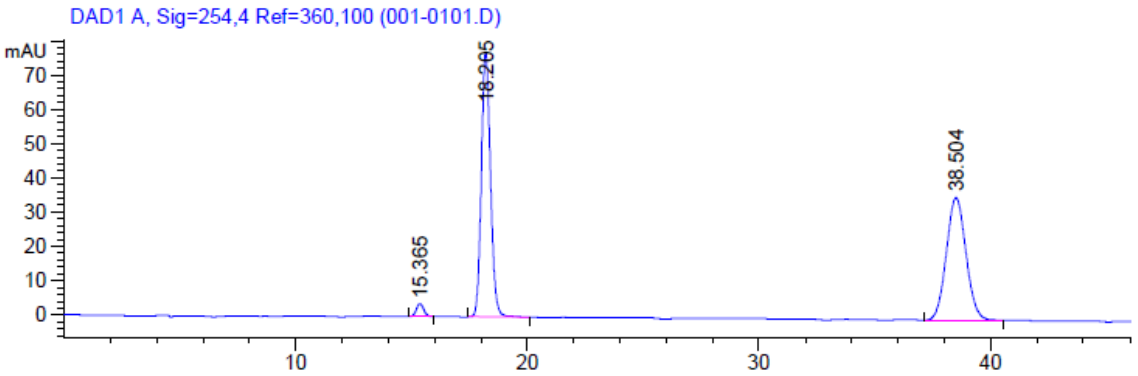


Alkene **13** (1.44 g, 5.66 mmol, 1.00 equiv) was dissolved in CH_2Cl_2 (170 mL) and cooled to -78 °C. BH_3·THF-solution was added dropwise and the solution was allowed to warm up to rt over a period of 5 h. NaOH (3M, 5.66 mL, 17.0 mmol, 3.00 equiv) was added dropwise at 0 °C followed by H_2O_2-solution (30%, 5.66 mL). The mixture was stirred vigorously over night, then H_2O was added until all solids went into solution. The reaction was transferred into a separation funnel and the aqueous layer was extracted with CH_2Cl_2 (3x50 mL), the combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica, *n*-pentane/EtOAc 2:1) to obtain diol **14** (1.55 g, 5.66 mmol, quant, 1:2.2 d.r.) as colourless oil. The diastereomers were separated by recrystallization from Et_2O and *n*-pentane. Therefore diol **14** was solved in a minimal amount of Et_2O and pentane was added until the solution went slightly cloudly, then Et_2O was added dropwise until the solution became clear again. The cloudy solution was cooled to -25 °C for 18 h during which a colourless precipitate formed. The solid was filtered off, washed with ice-cold Et_2O and dried to give diastereomer **14** as single diastereomer in 98%ee (693 mg, 2.55 mmol, 45%).

TLC: R_f = 0.22 (*n*-pentane/EtOAc 2:1). **^{1}H-NMR:** 500 MHz, $CDCl_3$; δ=7.42 (t, 1H, *J*=8.3 Hz, 3-H), 6.90 (dd, 1H, *J*=1.0 Hz, 8.5 Hz, 4-H), 6.81 (dd, 1H, *J*=0.8 Hz, 8.1 Hz, 2-H), 6.58 (dd, 1H, *J*=73.9 Hz, 76.0 Hz, 12-H), 4.62 (ddd, 1H, *J*=2.5 Hz, 4.1 Hz, 14.0 Hz, 5a-H), 3.80 (dd, 1H, *J*=7.3 Hz, 10.6 Hz, 6-Ha), 3.73 (dd, 1H, *J*=5.2 Hz, 10.7 Hz, 6-Hb), 2.89 (dd, 1H, *J*=13.9 Hz, 16.3 Hz, 7a-Ha), 2.60 (dd, 1H, *J*=2.5 Hz, 16.3 Hz, 7a-Hb), 2.00-2.07 (m, 1H, 5-H), 1.09 (d, 3H, *J*=7.0 Hz, 9-H_3) ppm. **^{13}C-NMR:** 126 MHz, $CDCl_3$; δ = 191.0 (8-C), 163.0 (1-C), 150.2 (4a-C), 135.6 (3-C), 116.3 (dd, *J*=263.7 Hz, 12-C), 116.1 (4-C), 115.2 (2-C), 114.2 (8a-C), 78.4 (5a-C), 64.4 (6-C), 41.7 (7a-C), 39.4 (5-C), 11.3 (9-C) ppm. **^{19}F-NMR:** 282 MHz, $CDCl_3$; δ=–82.71 (q, 2F, *J*=163.9 Hz, 12-F_2) ppm. **HR-MS:** (ESI-)**:** m/*z* calc. for $C_{13}H_{14}F_2O_4Na$ $[M\text{-}Na]^+$: 295.0752, found 295.0750. **FT-IR:** (neat): $\tilde{\nu}$ = 3438 (w), 2971 (w),

2887 (w), 1691 (s), 1610 (s), 1574 (w), 1470 (m), 1383 (w), 1324 (w), 1278 (w), 1224 (w), 1177 (w), 1125 (s), 1033 (s), 963 (w), 887 (w), 796 (w), 742 (w) cm^{-1}. **m.p.:** 98 °C (Et_2O). **[α]:** -80.1 (c 1.0, $CHCl_3$, for a sample with 98%ee).

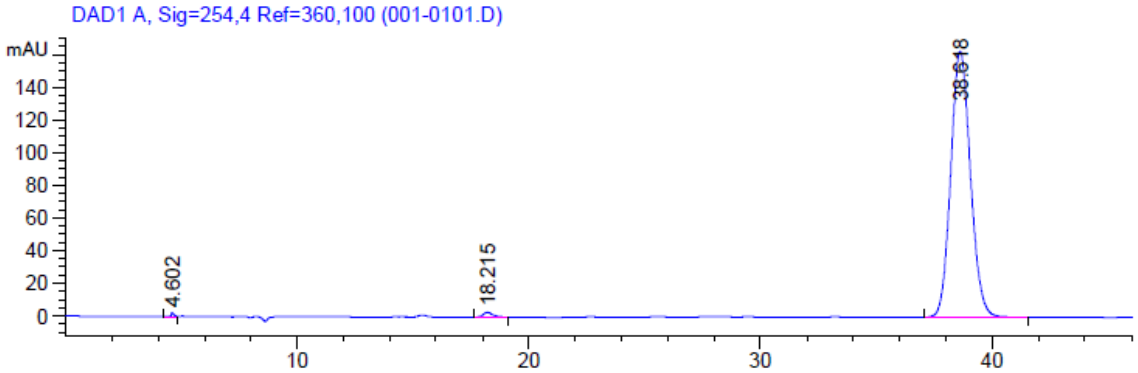
Racemic sample



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.365	BB	0.3462	82.31128	3.74838	1.9067
2	18.205	BB	0.4233	2122.62256	77.07831	49.1696
3	38.504	BB	0.9056	2112.00317	35.83540	48.9237

Enantiomerically enriched sample

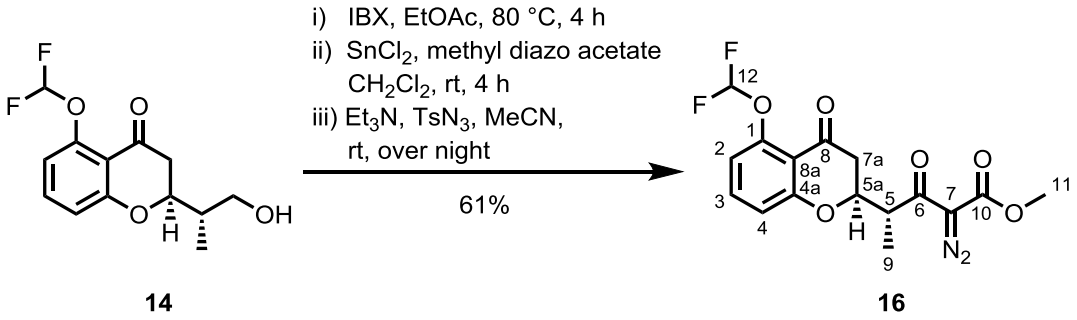


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.602	BB	0.1101	16.65333	2.15697	0.1720
2	18.215	BB	0.4306	79.92821	2.85490	0.8254
3	38.618	BB	0.9135	9587.46484	162.70660	99.0027

HPLC conditions for the determination of the *ee* of **14**: CHIRALPAK IC® (Diacel Chemical Industries) column; *n*-hexane/iPrOH 80:20, flow 0.7 mL/min, ϑ=25 °C.

2.6 methyl (*R*)-2-diazo-4-((*S*)-5-(difluoromethoxy)-4-oxochroman-2-yl)-3-oxopentanoate 16

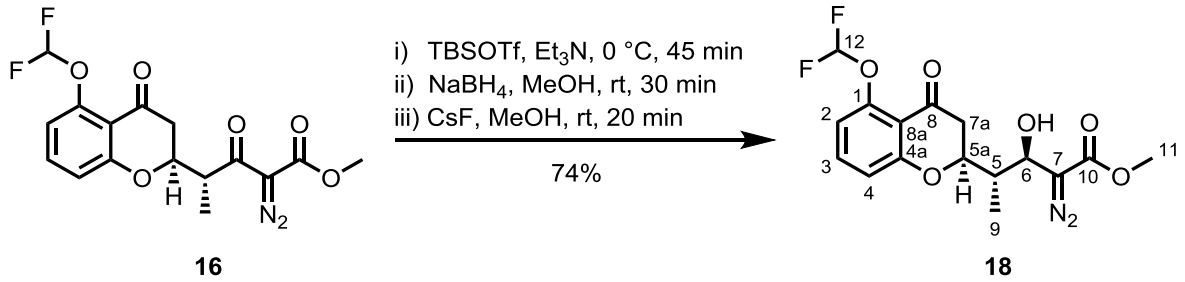


Alcohol **14** (1.18 g, 4.99 mmol, 1.00 equiv) was dissolved in EtOAc (60 mL), IBX (2.10 g, 7.49 mmol, 1.50 equiv) was added and the suspension was heated under reflux for 4 h. After cooling to room temperature, the reaction was concentrated under reduced pressure and the remnants were suspended in Et_2O (50 mL) and stirred for 5 min. The suspension was filtered over a pad of Na_2SO_4 and washed with Et_2O (50 mL). The filtrate was concentrated under reduced pressure and redissolved in CH_2Cl_2 (55 mL). $SnCl_2$ (95.0 mg, 0.449 mmol, 0.10 equiv.) was added and the reaction was stirred for 5 min, then methyl diazoacetate-solution[8] (9.61 M in CH_2Cl_2, 0.68 mL, 6.49 mmol, 1.30 equiv.) was added dropwise. The orange solution was stirred for 4 h and then concentrated under reduced pressure. The resulting slurry was taken up in MeCN (10 mL) and filtered over a syringe filter. The filter was washed with MeCN (2x20 ml) and the filtrate was cooled to 0 °C. TsN_3 (1.15 mL, 7.49 mmol, 1.50 equiv) and Et_3N (0.76 mL, 5.50 mmol, 1.10 equiv) were added and the reaction was stirred over night at room temperature. The reaction was concentrated under reduced pressure and the crude product was purified by column chromatography (silica, *n*-pentane/EtOAc 4:1) to obtain α-diazo-β-ketoester **16** (1.01 g, 3.04 mmol, 61%) as pale yellow crystals.

TLC: R_f = 0.68 (*n*-pentane/EtOAc 2:1). **^{1}H-NMR:** 500 MHz, $CDCl_3$; δ=7.42 (t, 1H, *J*=8.3 Hz 3-H), 6.90 (dd, 1H, *J*=1.0 Hz, 8.5 Hz, 4-H), 6.81 (dd, 1H, *J*=0.9 Hz, 8.1 Hz, 2-H), 6.57 (t, 1H, *J*=75.0 Hz, 12-H), 4.70 (ddd, 1H, *J*=4.1 Hz, 7.1 Hz, 11.0 Hz, 5a-H), 4.04 (p, 1H, *J*=6.9 Hz, 5-H), 3.84 (s, 3H, 11-H_3), 2.71-2.84 (m, 2H, 7a-H_2), 1.33 (d, 3H, *J*=6.9 Hz, 9-H_3) ppm. **^{13}C-NMR:** 126 MHz, $CDCl_3$; δ=192.7 (6-C), 190.0 (8-C), 162.5 (4a-C), 161.4 (10-C), 150.2 (1-C), 135.7 (3-C), 116.3 (t, *J*=260.4 Hz, 12-C), 116.3 (4-C), 115.5 (2-C), 114.2 (8a-C), 78.1 (5a-C), 76.6 (7-C), 52.6 (11-C), 45.2 (5-C), 42.0 (7a-C), 12.9 (9-C) ppm. **^{19}F-NMR:** 282 MHz, $CDCl_3$; δ=–82.8 (d, 2F, *J*=5.0 Hz, 12-F_2) ppm. **HR-MS:** (ESI+)**:** m/*z* calc. for $C_{16}H_{14}F_2N_2O_6Na$ $[M\text{-}Na]^+$: 391.0712, found 391.0702. **FT-IR:** (neat): $\tilde{\nu}$ =2958 (w), 2149

(m), 1697 (s), 1648 (m), 1610 (s), 1575 (w), 1469 (m), 1440 (m), 1381 (m), 1308 (s), 1210 (m), 1125 (s), 1040 (m), 997 (m), 878 (w), 804 (w), 741 (w) cm^{-1}. **m.p.:** 120 °C (Et_2O). **[α]:** -65.2 (c 1.0, $CHCl_3$, for a sample with 98%ee).

2.7 methyl (3*R*,4*S*)-2-diazo-4-((*S*)-5-(difluoromethoxy)-4-oxochroman-2-yl)-3-hydroxypentanoate 18

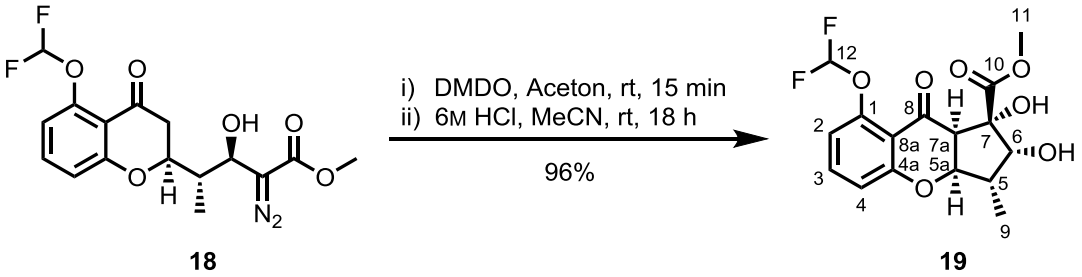


16 **18**

α-Diazo-β-ketoester **16** (1.29 g, 3.50 mmol, 1.00 equiv) was dissolved in CH_2Cl_2 (65 mL) and TBSOTf (0.89 mL, 3.85 mmol, 1.10 equiv) and Et_3N (0.53 mL, 3.85 mmol, 1.10 equiv) were added at 0 °C. The reaction was stirred for 45 min, then MeOH (5 mL) was added and all volatile components were removed under reduced pressure. The resulting slurry was redissolved in MeOH (65 mL) and $NaBH_4$ (2.65 g, 70.0 mmol, 20.0 equiv) was added in 4 portions over 30 min. Water (100 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3x100 mL). The organic extracts were combined and a saturated solution of CsF in MeOH (100 mL) was added. After stirring for 20 min, the solution was washed with water (50 mL) and brine (20 mL) and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, *n*-pentane/EtOAc 8:1, no dryload since the crude product is acid labile and eliminates the diazo moiety under dryload conditions) and recrystallized from CH_2Cl_2 and *n*-pentane to obtain α-diazo-β-hydroxyester **18** (956 mg, 2.58 mmol, 74%) as pale yellow crystals.

TLC: R_f = 0.49 (*n*-pentane/EtOAc 2:1). **^{1}H-NMR:** 500 MHz, $CDCl_3$; δ=7.41 (t, 1H, *J*=8.3 Hz, 3-H), 6.90 (dd, 1H, *J*=0.9 Hz, 8.5 Hz, 4-H), 6.79 (d, 1H, *J*=8.0 Hz, 2-H), 6.56 (dd, 1H, *J*=73.7 Hz, 76.1 Hz, 12-H), 4.95 (dt, 1H, *J*=2.3 Hz, 14.5 Hz, 5a-H), 4.76 (dd, 1H, *J*=1.9 Hz, 9.6 Hz, 6-H), 3.79 (s, 3H, 11-H_3), 2.92 (dd, 2H, *J*=14.6 Hz, 16.2 Hz, 7a-H_2), 2.48 (dd, 1H, *J*=2.3 Hz, 16.2 Hz, 6-OH), 1.95-2.09 (m, 1H, 5-H), 1.07 (s, 3H, J=7.0 Hz, 9-H_3) ppm. **^{13}C-NMR:** 75 MHz, $CDCl_3$; δ=190.7 (8-C), 166.8 (4a-C), 162.9 (10-C), 150.2 (1-C), 135.6 (3-C), 116.2 (dd, *J*=260.3 Hz, 261.7 Hz, 12-C), 116.1 (4-C), 115.3 (2-C), 114.2 (8a-C), 112.8 (7-C), 76.4 (5a-C), 68.7 (6-C), 52.3 (11-C), 41.9 (7a-C), 41.3 (5-C), 10.1 (9-C) ppm. **^{19}F-NMR:** 282 MHz, $CDCl_3$; δ=–82.8 (q, 2F, *J*=164.0 Hz, 12-F_2) ppm. **HR-MS:** (ESI+)**:** m/z calc. for $C_{16}H_{16}F_2N_2O_6Na$ $[M\text{-}Na]^+$: 393.0869, found 393.0878. **FT-IR:** (neat): $\tilde{\nu}$ =3468 (w), 2955 (w), 2097 (m), 1747 (w), 1689 (s), 1609 (m), 1574 (w), 1470 (m), 1441 (m), 1383 (m), 1358 (m), 1323 (m), 1278 (m), 1228 (m), 1190 (m), 1120 (s), 1028 (s), 962 (w), 797 (w), 768 (w), 744 (w) cm^{-1}. **m.p.:** 132 °C (Et_2O). **[α]:** -56.8 (c 1.0, $CHCl_3$, for a sample with 98%ee).

2.8 methyl (1*S*,2*R*,3*S*,3a*R*,9a*R*)-8-(difluoromethoxy)-1,2-dihydroxy-3-methyl-9-oxo-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-1-carboxylate 19

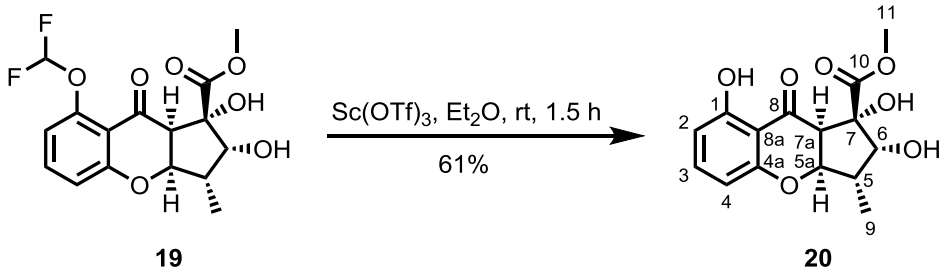


18 **19**

α-Diazo-β-hydroxyester **18** (66.0 mg, 0.184 mmol, 1.00 equiv) was dissolved in DMDO-solution[9] (0.055M in acetone, 6.7 mL, 2.00 equiv) and stirred at room temperature for 15 min. All volatiles were removed under reduced pressure and the remaining slurry was dried under vacuum for 1 h at 50 °C. The resulting yellow oil was dissolved in MeCN (5 mL) and HCl (6M, 0.05 mL, 0.30 mmol, 1.63 equiv) was added. The solution was stirred for 24 h, then diluted with H_2O (10 mL), extracted with EtOAc (3x10 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography (silica, *n*-pentane/EtOAc 2:1) to obtain diol **19** (63.0 mg, 0.177 mmol, 96%) as white solid.

TLC: R_f = 0.38 (*n*-pentane/EtOAc 1:1). **^{1}H-NMR:** 500 MHz, $CDCl_3$; δ=7.44 (t, 1H, *J*=8.3 Hz, 3-H), 6.90 (dd, 1H, *J*=0.9 Hz, 8.4 Hz, 4-H), 6.84 (dd, 1H, *J*=0.8 Hz, 8.1 Hz, 2-H), 6.55 (dd, 1H, *J*=73.6 Hz, 75.6 Hz, 12-H), 4.74 (dd, 1H, *J*=3.6 Hz, 7.7 Hz, 5a-H), 4.38 (s, br, 1H, 6-OH), 4.27 (s, 1H, 7-OH), 3.57 (s, 3H, 11-H_3), 3.46 (d, 1H, *J*=7.7 Hz, 7a-H), 2.92 (d, 1H, *J*=4.5 Hz, 6-H), 2.75 (ttd, 1H, *J*=3.7 Hz, 7.4 Hz, 11.0 Hz, 5-H), 1.17 (d, 3H, *J*=7.4 Hz, 9-H_3) ppm. **^{13}C-NMR:** 125 MHz, $CDCl_3$; δ=189.8 (8-C), 173.4 (4a-C), 162.5 (10-C), 149.6 (1-C), 135.9 (3-C), 116.5 (8a-C), 116.0 (dd, *J*=261.4 Hz, 262.4 Hz, 12-C), 115.7 (4-C), 115.6 (2-C), 83.8 (7a-C), 83.6 (7-C), 76.4 (5a-C), 59.9 (6-C), 53.3 (11-C), 43.9 (5-C), 10.7 (9-C) ppm. **^{19}F-NMR:** 282 MHz, $CDCl_3$; δ=–82.5 (d, 2F, *J*=17.1 Hz, 12-F_2) ppm. **HR-MS:** (ESI+)**:** m/z calc. for $C_{16}H_{16}F_2O_7Na$ $[M\text{-}Na]^+$: 381.0756, found 381.0767. **FT-IR:** (neat): $\tilde{\nu}$ =3466 (w), 2955 (w), 1737 (m), 1680 (m), 1609 (s), 1576 (w), 1471 (m), 1383 (w), 1325 (w), 1278 (w), 1244 (w), 1212 (w), 1119 (s), 1039 (m), 966 (w), 914 (w), 826 (w), 763 (w), 738 (w) cm^{-1}. **m.p.:** 128 °C (Et_2O). **[α]:** -8.7 (c 0.25, $CHCl_3$, for a sample with 98%ee).

2.9 methyl (1*S*,2*R*,3*S*,3a*R*,9a*R*)-1,2,8-trihydroxy-3-methyl-9-oxo-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-1-carboxylate 20

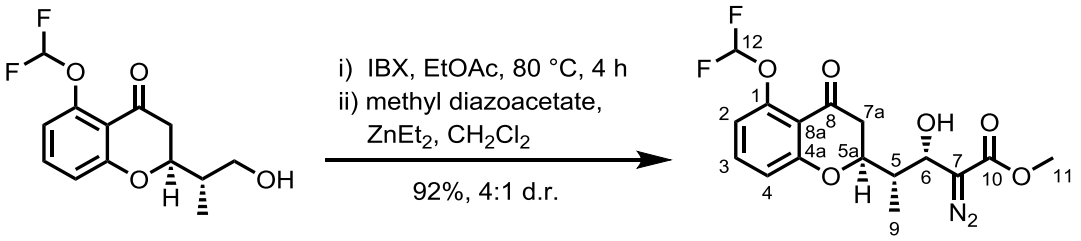


19 **20**

Difluoromethyl ether **19** (23.0 mg, 0.0642 mmol, 1.00 equiv) was solved in Et_2O (3 mL) and $Sc(OTf)_3$ (32.0 mg, 0.0642 mmol, 1.00 equiv) was added in one portion. The yellow solution was stirred for 1.5 h at room temperature, then water was added (5 mL). The aqueous layer was extracted with Et_2O (3x5 mL) and the combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, *n*-pentane/EtOAc 2:1) 7-*epi*-preussochromone D (12.0 mg, 0.0389 mmol, 61%).

TLC: R_f = 0.36 (*n*-pentane/EtOAc 1:1). **^{1}H-NMR:** 500 MHz, $CDCl_3$; δ=11.58 (s, 1H, 1-OH), 7.37 (t, 1H, *J*=8.3 Hz, 3-H), 6.50 (dd, 1H, *J*=0.9 Hz, 8.4 Hz, 4-H), 6.42 (dd, 1H, *J*=0.9 Hz, 8.2 Hz, 2-H), 4.75 (dd, 1H, *J*=3.2 Hz, 7.1 Hz, 5a-H), 4.49 (dd, 1H, *J*=6.2 Hz, 7.8 Hz, 6-H), 4.28 (s, 1H, 7-OH), 3.54 (s, 3H, 11-H_3), 3.42 (d, 1H, *J*=7.1 Hz, 7a-H), 2.81 (d, 1H, *J*=8.0 Hz, 6-OH), 2.77 (tdd, 1H, *J*=3.3 Hz, 7.5 Hz, 13.4 Hz, 5-H), 1.15 (s, 3H, *J*=7.5 Hz, 9-H_3) ppm. **^{13}C-NMR:** 125 MHz, $CDCl_3$; δ=196.4 (8-C), 173.2 (4a-C), 162.1 (1-C), 160.8 (10-C), 139.1 (3-C), 109.8 (4-C), 108.3 (8a-C), 107.8 (2-C), 83.5 (5a-C), 82.7 (7-C), 76.2 (7a-C), 57.7 (6-C), 53.4 (11-C), 44.2 (5-C), 10.4 (9-C) ppm. **HR-MS:** (ESI+)**:** m/*z* calc. for $C_{15}H_{16}O_7Na$ [M-Na]$^+$: 331.0797, found 331.0788. **FT-IR:** (neat): $\tilde{\nu}$ =3466 (w), 2926 (w), 2854 (w), 1740 (m), 1636 (s), 1577 (w), 1462 (s), 1366 (m), 1295 (w), 1222 (s), 1160 (w), 1114 (m), 1078 (w), 1057 (w), 995 (w), 825 (w), 798 (w), 726 (w) cm^{-1}. **m.p.:** 156 °C (Et_2O). **[α]:** -16.3 (c 0.1, $CHCl_3$, for a sample with 98%ee).

2.10 methyl (3*S*,4*S*)-2-diazo-4-((*S*)-5-(difluoromethoxy)-4-oxochroman-2-yl)-3-hydroxypentanoate 21



14 **21**

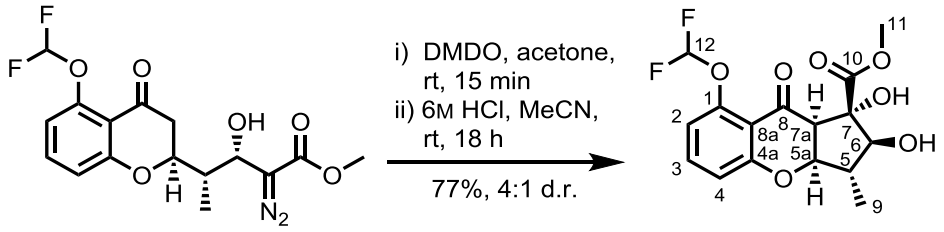
65% after recrystallization

Alcohol **14** (1.66 g, 6.10 mmol, 1.00 equiv) was dissolved in EtOAc (100 mL), IBX (3.42 g, 12.2 mmol, 2.00 equiv) was added and the suspension was heated under reflux for 4 h. After cooling to room temperature, the reaction was concentrated under reduced pressure and the remnants were suspended in Et_2O (100 mL) and stirred for 5 min. The suspension was filtered over a pad of Na_2SO_4 and washed with Et_2O (50 mL). The solvent was removed under reduced pressure and the remnants were dissolved in CH_2Cl_2 (30 mL) and cooled to -78 °C. In another flask, methyl diazoacetate[8] (11.55M in CH_2Cl_2, 0.63 mL, 7.32 mmol, 1.20 equiv) was dissolved in CH_2Cl_2 and cooled to -78 °C before diethylzinc-solution (1M in heptane, 7.32 mL, 7.32 mmol, 1.20 equiv.) was added dropwise. The solution was allowed to warm to -50 °C, then the previously prepared aldehyde-solution was added via a cannula. The reaction mixture was allowed to warm to room temperature and stirred for further 2 h. Then, the whole mixture was directly poured onto a wide column and purified by column chromatography (silica, *n*-pentane/EtOAc 4:1) to obtain α-diazo-β-hydroxyester **21** (2.08 g, 5.63 mmol, 92%, 4:1 d.r.) as yellow powder. The diastereomers were separated via recrystallization from small amounts of Et_2O at room temperature to give **21** as single diastereomer (1.47 g, 3.97 mmol, 65%).

TLC: R_f = 0.44 (*n*-pentane/EtOAc 2:1). **^{1}H-NMR:** 300 MHz, $CDCl_3$; δ=7.43 (t, 1H, *J*=8.3 Hz, 3-H), 6.87 (dd, 1H, *J*=1.0 Hz, 8.5 Hz, 4-H), 6.83 (dd, 1H, *J*=0.9 Hz, 8.1 Hz, 2-H), 6.56 (dd, 1H, *J*=65.8 Hz, 67.5 Hz, 12-H), 4.78 (dd, 1H, *J*=5.9 Hz, 6.5 Hz, 6-H), 4.61 (dt, 1H, *J*=2.9 Hz, 14.1 Hz, 5a-H), 3.77 (s, 3H, 11-H_3), 2.95 (dd, 1H, *J*=14.1 Hz, 16.3 Hz, 7a-H_a), 2.75 (d, 1H, *J*=5.3 Hz, 6-OH), 2.55 (dd, 1H, *J*=2.4 Hz, 16.3 Hz, 7a-H_b), 2.18 (pd, 1H, *J*=3.1 Hz, 6.9 Hz, 5-H), 1.23 (d, 3H, *J*=7.0 Hz, 9-H_3) ppm. **^{13}C-NMR:** 75 MHz, $CDCl_3$; δ=190.5 (8-C), 166.7 (4a-C), 162.6 (10-C), 150.2 (1-C), 150.2 (7-C), 135.8 (3-C), 116.2 (t, *J*=261.2, 12-C), 116.0 (4-C), 115.4 (2-C), 114.2 (8a-C), 78.7 (5a-C), 68.4 (6-C), 52.2 (11-C), 41.8 (7a-C), 41.8 (5-C), 9.6 (9-C) ppm. **^{19}F-NMR:** 282 MHz, $CDCl_3$; δ=–82.7 (q, 2F, *J*=163.8 Hz, 12-F_2) ppm.

HR-MS: (ESI+)**:** m/z calc. for $C_{16}H_{16}F_2N_2O_6Na$ $[M\text{-}Na]^+$: 393.0869, found 393.0868. **FT-IR:** (neat): $\tilde{\nu}$ =3472 (w), 2957 (w), 1730 (m), 1690 (m), 1608 (m), 1575 (w), 1469 (m), 1384 (w), 1321 (m), 1275 (m), 1222 (m), 1180 (m), 1118 (s), 1032 (s), 963 (m), 911 (m), 795 (m), 731 (s), 648 (w), 581 (w), 555 (w), 521 (w) cm^{-1}. **m.p.:** 130 °C (Et_2O). **[α]:** -102.6 (c 1.0, $CHCl_3$, for a sample with 98%ee).

2.11 methyl (1S,2S,3S,3aR,9aR)-8-(difluoromethoxy)-1,2-dihydroxy-3-methyl-9-oxo-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-1-carboxylate 22

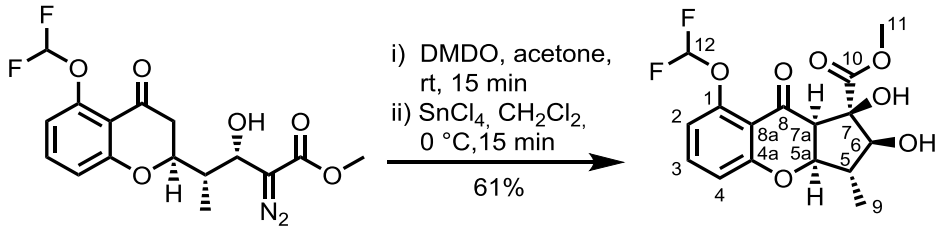


21 **22**

α-Diazo-β-hydroxyester **21** (180 mg, 0.486 mmol, 1.00 equiv) was dissolved in DMDO-solution[9] (0.055M in acetone, 20.0 mL, 2.26 equiv.) and stirred at room temperature for 15 min. All volatile components were removed under reduced pressure and the remaining slurry was dried at 50 °C under vacuum for 1 h. The oily remnants were dissolved in MeCN (20 mL) and HCl (6M, 1.0 mL) was added. The aqueous solution was stirred over night and then water (10 mL) and CH_2Cl_2 (10 mL) were added. The aqueous layer was extracted with CH_2Cl_2 (2x20 mL) and the combined organic extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, *n*-pentane/EtOAc 2:1) to obtain *trans*-diol **22** (134 mg, 0.374 mmol, 77%, 4:1 d.r.) as colourless oil.

TLC: R_f = 0.28 (*n*-pentane/EtOAc 1:1). **^{1}H-NMR:** 500 MHz, $CDCl_3$; δ=7.42 (t, 1H, *J*=8.3 Hz, 3-H), 6.89 (dd, 1H, *J*=0.9 Hz, 8.5 Hz, 4-H), 6.81 (d, 1H, *J*=7.7 Hz, 2-H), 6.55 (dd, 1H, *J*=72.9 Hz, 76.5 Hz, 12-H), 4.64 (dd, 1H, *J*=6.9 Hz, 10.4 Hz, 5a-H), 4.31 (s, br, 1H, 7-OH), 3.82 (d, 1H, *J*=10.5 Hz, 6-H), 3.67 (s, 3H, 11-H_3), 3.39 (d, 1H, *J*=10.4 Hz, 7a-H), 3.24 (s, br, 1H, 6-OH), 2.65 (dp, 1H, *J*=6.8 Hz, 10.6 Hz, 5-H), 1.32 (d, 3H, *J*=6.8 Hz, 9-H_3) ppm. **^{13}C-NMR:** 126 MHz, $CDCl_3$; δ=189.8 (8-C), 172.3 (4a-C), 161.9 (10-C), 149.5 (1-C), 135.8 (3-C), 116.5 (8a-C), 116.2 (dd, *J*=260.0 Hz, 262.8 Hz, 12-C), 115.9 (4-C), 115.3 (2-C), 86.6 (7a-C), 83.0 (7-C), 81.5 (5a-C), 57.8 (6-C), 53.0 (11-C), 44.5 (5-C), 16.0 (9-C) ppm. **^{19}F-NMR:** 282 MHz, $CDCl_3$; δ=–82.6 (dd, 2F, *J*=164.5 Hz, 411.2 Hz, 12-F_2) ppm. **HR-MS:** (ESI-)**:** m/z calc. for $C_{16}H_{15}F_2O_7Na$ [M-H]: 357.0791, found 357.0796. **FT-IR:** (neat): $\tilde{\nu}$ =3473 (w), 2961 (w), 1738 (m), 1681 (m), 1610 (s), 1577 (w), 1472 (m), 1378 (w), 1327 (w), 1284 (w), 1257 (w), 1220 (m), 1123 (s), 1048 (m), 972 (w), 912 (w), 827 (w), 795 (w), 734 (w) cm^{-1}. **[α]:** -21.3 (c 1.0, $CHCl_3$, for a sample with 98%ee).

2.12 methyl (1*R*,2*S*,3*S*,3a*R*,9a*R*)-8-(difluoromethoxy)-1,2-dihydroxy-3-methyl-9-oxo-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-1-carboxylate 23

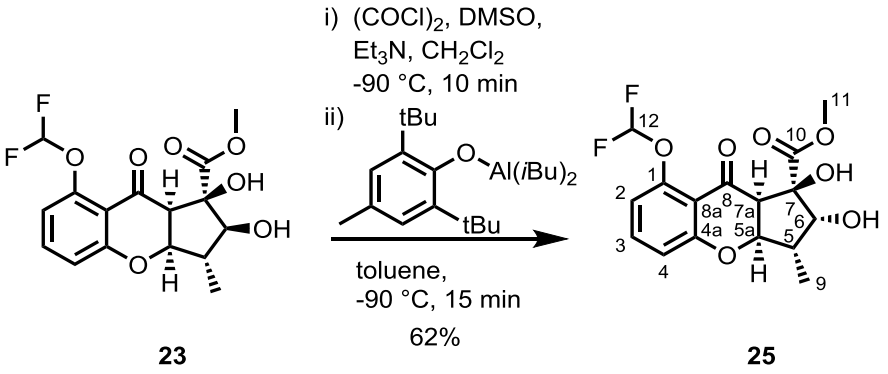


21 **23**

α-Diazo-β-hydroxyester **21** (290 mg, 0.783 mmol, 1.00 equiv) was dissolved in DMDO-solution[9] (0.055M in acetone, 30.0 mL, 2.10 equiv) and stirred at room temperature for 15 min. All volatile components were removed under reduced pressure and the remaining slurry was dried at 50 °C under vacuum for 1 h. The oily remnants were dissolved in CH_2Cl_2 (60 mL) and $SnCl_4$ (0.37 mL, 3.13 mmol, 4.00 equiv.) was added dropwise at 0 °C. The yellow solution was stirred for 15 min and then water was added (20 mL) at 0 °C. The aqueous layer was extracted with CH_2Cl_2 (2x20 mL) and the combined organic extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, *n*-pentane/EtOAc 2:1) to obtain *cis*-diol **23** (170 mg, 0.475 mmol, 61%) as colourless powder.

TLC: R_f = 0.32 (*n*-pentane/EtOAc 2:1). **^{1}H-NMR:** 500 MHz, $CDCl_3$; δ=7.42 (t, 1H, *J*=8.3 Hz, 3-H), 6.88 (dd, 1H, *J*=0.9 Hz, 8.5 Hz, 4-H), 6.81 (d, 1H, *J*=8.1 Hz, 2-H), 6.57 (dd, 1H, *J*=71.8 Hz, 77.5 Hz, 12-H), 4.57 (dd, 1H, *J*=4.1 Hz, 8.0 Hz, 5a-H), 3.92 (s, 3H, 11-H_3), 3.87 (dd, 1H, *J*=9.0 Hz, 11.5 Hz, 6-H), 3.86 (s, 1H, 7-OH), 3.52 (d, 1H, *J*=8.0 Hz, 7a-H), 2.47 (dqd, 1H, *J*=4.1 Hz, 7.2 Hz, 14.3 Hz, 5-H), 2.38 (d, 1H, *J*=11.6 Hz, 6-OH), 1.38 (d, 3H, *J*=7.2 Hz, 9-H_3) ppm. **^{13}C-NMR:** 126 MHz, $CDCl_3$; δ=187.9 (8-C), 173.2 (4a-C), 162.3 (10-C), 149.8 (1-C), 136.1 (3-C), 116.5 (8a-C), 116.1 (dd, *J*=259.0 Hz, 263.4 Hz, 12-C), 115.7 (4-C), 115.2 (2-C), 83.5 (7a-C), 82.7 (7-C), 81.4 (5a-C), 55.5 (6-C), 54.0 (11-C), 48.7 (5-C), 16.5 (9-C) ppm. **^{19}F-NMR:** 282 MHz, $CDCl_3$; δ=–82.6 (d, 2F, *J*=164.4 Hz, 398.7 Hz, 12-F_2) ppm. **HR-MS:** (ESI+)**:** m/z calc. for $C_{16}H_{16}F_2O_7Na$ $[M\text{-}Na]^+$: 381.0756, found 381.0747. **FT-IR:** (neat): $\tilde{\nu}$ =3481 (w), 2961 (w), 1735 (m), 1682 (m), 1610 (s), 1575 (w), 1472 (m), 1378 (w), 1328 (w), 1268 (m), 1239 (w), 1124 (s), 1042 (m), 962 (w), 796 (w), 738 (w) cm^{-1}. **m.p.:** 159 °C ($CHCl_3$). **[α]:** -34.8 (c 1.0, $CHCl_3$, for a sample with 98%ee).

2.13 methyl (1*R*,2*R*,3*S*,3a*R*,9a*R*)-8-(difluoromethoxy)-1,2-dihydroxy-3-methyl-9-oxo-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-1-carboxylate 24



DMSO (0.06 mL, 0.846 mmol, 11.6 equiv) was added dropwise at -90 °C to a solution of $(COCl)_2$ (0.03 mL, 0.350 mmol 4.82 equiv) in CH_2Cl_2. The solution was stirred for 20 min and then *trans*-diol **23** (26.0 mg, 0.0726 mmol, 1.00 equiv) in CH_2Cl_2 (1 mL) was added via canula. The reaction was stirred for 5 min before Et_3N (0.12 mL, 87.6 mmol, 11.9 equiv) was added dropwise. After stirring for further 5 min the reaction was stopped by addition of HOAc (0.2 mL) and allowed to warm to room temperature. Water (5 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The combined organic extracts were dried over Na_2SO_4, then the solvent was removed under reduced pressure. The crude ketone was dissolved in toluene (1.5 mL) and cooled to -90 °C. In another flask, DIBAH-solution (1M in toluene, 0.14 mL, 0.140 mmol, 1.93 equiv) was added dropwise at 0 °C to a solution of 2,6-di-tert-butyl-4-methylphenol (32.0 mg, 0.145 mmol, 2.00 equiv) in toluene (2 mL). The solution was stirred for 1 h and then cooled to -90 °C. The previously prepared ketone-solution was added via cannula and stirred for 15 min at -90 °C. Then HCl (1M, 1 mL) was added and the reaction was warmed to room temperature. The aqueous layer was extracted with Et_2O (2x5 mL) and the combined organic extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, *n*-pentane/EtOAc 2:1) to obtain *trans*-diol **25** (16.0 mg, 0.0447 mmol, 62%) as colourless oil.

TLC: R_f = 0.34 (*n*-pentane/EtOAc 2:1). **^{1}H-NMR:** 500 MHz, $CDCl_3$; δ=7.41 (t, 1H, *J*=8.3 Hz, 3-H), 6.88 (dd, 1H, *J*=1.0 Hz, 8.5 Hz, 4-H), 6.80 (dd, 1H, *J*=0.8 Hz, 8.1 Hz, 2-H), 6.57 (dd, 1H, *J*=72.1 Hz, 77.2 Hz, 12-H), 4.74 (dd, 1H, *J*=5.1 Hz, 8.6 Hz, 5a-H), 4.11 (d, 1H, *J*=3.0 Hz, 6-H), 3.96 (s, 3H, 11-H_3), 3.85 (d, 1H, *J*=8.6 Hz, 7a-H), 3.56 (s, 1H, 7-OH), 2.90 (qt, 1H, *J*=4.6 Hz, 7.2 Hz, 5-H), 2.73 (s, 1H, 6-OH), 1.30 (d, 3H, *J*=7.3 Hz, 9-H_3) ppm. **^{13}C-NMR:** 126 MHz, $CDCl_3$; δ=189.6 (8-C), 173.2 (4a-C), 162.5 (10-C), 149.7 (1-C), 136.0 (3-

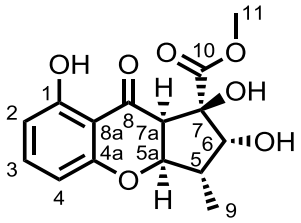
C), 116.5 (8a-C), 116.2 (dd, *J*=259.1 Hz, 262.9 Hz, 12-C), 115.9 (4-C), 115.0 (2-C), 84.9 (7a-C), 80.1 (7-C), 77.4 (5a-C), 57.0 (6-C), 54.0 (11-C), 46.1 (5-C), 11.4 (9-C) ppm. **^{19}F-NMR:** 282 MHz, $CDCl_3$; δ=–82.1 (d, 2F, *J*=164.4 Hz, 595.5 Hz, 12-F_2) ppm. **HR-MS:** (ESI+)**:** m/z calc. for $C_{16}H_{16}F_2O_7Na$ $[M\text{-}Na]^+$: 381.0756, found 381.0754. **FT-IR:** (neat): $\tilde{\nu}$ =3458 (w), 2956 (w), 1766 (m), 1742 (w), 1641 (s), 1578 (w), 1462 (s), 1361 (m), 1262 (w), 1219 (s), 1151 (w), 1058 (m), 1019 (w), 968 (w), 922 (w), 793 (w), 729 (m), 670 (w) cm^{-1}. **[α]:** -37.7 (c 1.0, $CHCl_3$, for a sample with 98%ee).

2.14 (−)-Preussochromone D 3

25 (-)-preussochromone **3**

Trans-diol **25** (16.0 mg, 0.0447 mmol, 1.00 equiv) was dissolved in Et_2O (2 mL) and $Sc(OTf)_3$ (24.0 mg, 0.0492 mmol, 1.10 equiv) was added at room temperature. The reaction was stirred for 45 min, then water (5 mL) was added and the aqueous layer was extracted with Et_2O (3x5 mL). The combined organic extracts were dried over Na_2SO_4, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, *n*-pentane/EtOAc 2:1) to obtain (−)-preussochromone D (**3**) (8.00 mg, 0.0260 mmol, 58%) as pale yellow powder.

TLC: R_f = 0.30 (*n*-pentane/EtOAc 2:1). **^{1}H-NMR:** 500 MHz, $CDCl_3$; δ=11.93 (s, 1H, 1-OH), 7.37 (t, 1H, *J*=8.3 Hz, 3-H), 6.37 (dd, 2H, *J*=0.8 Hz, 8.3 Hz, 4-H, 2-H), 4.82 (dd, 1H, *J*=4.4 Hz, 7.9 Hz, 5a-H), 4.73 (s, 1H, 7-OH), 4.50 (d, 1H, *J*=5.2 Hz, 6-OH), 4.23 (t, 1H, *J*=5.4 Hz, 6-H), 3.98 (d, 1H, *J*=7.9 Hz, 7a-H), 3.79 (s, 3H, 11-H_3), 2.80-2.86 (m, 1H, 5-H), 1.20 (d, 3H, *J*=7.4 Hz, 9-H_3) ppm. **^{13}C-NMR:** 126 MHz, $CDCl_3$; δ=198.0 (8-C), 173.3 (10-C), 162.9 (1-C), 162.1 (4a-C), 139.3 (3-C), 109.5 (8a-C), 109.1 (2-C), 108.1 (4-C), 88.1 (7-C), 86.0 (5a-C), 82.3 (6-C), 52.9 (7a-C), 52.9 (11-C), 46.6 (5-C), 11.5 (9-C) ppm. **HR-MS:** (ESI+)**:** m/*z* calc. for $C_{15}H_{16}O_7Na$ $[M-Na]^+$: 331.0788, found 331.0790. **FT-IR:** (neat): $\tilde{\nu}$ =3478 (w), 2930 (w), 1728 (m), 1635 (s), 1577 (w), 1462 (s), 1368 (m), 1292 (w), 1219 (s), 1159 (w), 1129 (w), 1067 (m), 991 (w), 962 (w), 801 (w), 733 (w), 501 (w), 477 (w) cm^{-1}. **UV/VIS:** (MeOH, c=1.62·10^{-5} mol/L); λ_{max} (log ε): 227 (5.33), 258 (5.31), 282 (5.30), 355 (5.33) nm. **m.p.:** 162 °C (Et_2O). **[α]:** -21.1 (c 0.17, MeOH, for a sample with 98%ee).

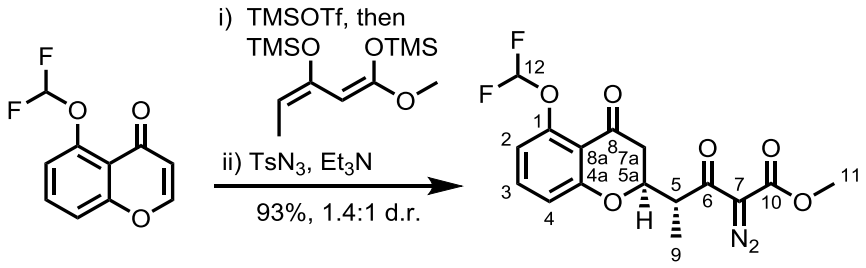


(-)-preussochromone **3**

No	Isolated product[10] acetone-d_6 (500 MHz) δH (J in Hz)	synthetic product acetone-d_6 (500 MHz) δH (J in Hz)	Isolated product[10] acetone-d_6 (100 MHz) δC	synthetic product acetone-d_6 (126 MHz) δC
1			162.8	162.9
2	6.37, d (8.5)	6.37, d (8.3)	109.0	109.1
3	7.38, t (8.5)	7.37, t (8.3)	139.2	139.3
4	6.37, d (8.5)	6.37, d (8.3)	108.1	108.1
4a			162.1	162.1
5	2.83, m	2.80-2.86, m	46.6	46.6
5a	4.82, dd (4.0, 8.0)	4.82, dd (4.4, 7.9)	86.0	86.0
6	4.23, d (5.5)	4.23, t (5.4)	82.3	82.3
7			88.0	88.1
7a	3.98, d (8.0)	3.98, d (7.9)	52.8	52.9
8			198.0	198.0
8a			109.4	109.5
9	1.20, d (7.5)	1.20, d (7.4)	11.4	11.5
10			173.2	173.3
11	3.79, s	3.79, s	52.8	52.9
OH-1	11.94, s	11.93, s		
OH-6[a]	4.77, s	4.50, d (5.2)		
OH-7[a]	4.54, s, br	4.73, s		

[a] The author assigned the duplet at 4.50 ppm to OH-6 instead of OH-7 (and vice versa) as described in the publication of Che *et al*. due to its multiplicity.

2.15 *rac*-methyl (*R*)-2-diazo-4-((*S*)-5-(difluoromethoxy)-2-methyl-4-oxochroman-2-yl)-3-oxopentanoate 16

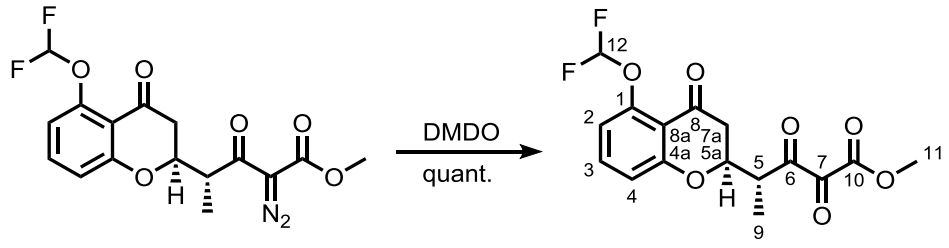


12 *rac*-**16**

TMSOTf (9.26 mL, 51.2 mmol, 1.50 equiv) was added to a solution of chromenone **12** (7.24 g, 31.1 mmol, 1.00 equiv) in CH_2Cl_2 (300 mL) at room temperature. The yellow solution was stirred for 30 min and then cooled to -78 °C. A solution of bissilylenolether[9] (15.6 g, 68.2 mmol, 2.00 equiv) in CH_2Cl_2 (150 mL) was added dropwise over a period of 2 h, then the reaction was stopped by addition of sat. NH_4Cl-solution (50 mL). The suspension was warmed to room temperature and the aqueous layer was extracted with CH_2Cl_2 (3x100 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The oily remnants were dissolved in MeCN (300 mL) and TsN_3 (7.84 mL, 51.2 mmol, 1.50 equiv) and Et_3N (5.23 mL, 37.5 mmol, 1.10 equiv) were added subsequently. The orange solution was stirred over night and then all volatile components were removed under reduced pressure. The crude product was purified by column chromatography (silica, *n*-pentane/EtOAc 4:1) to obtain *rac*-**16** (11.7 g, 31.7 mmol, 93 %) as yellow solid.

The analytical data of *rac*-**16** was in accordance with the chiral product **16** received from 2.6.

2.16 *rac*-methyl (*R*)-4-((*S*)-5-(difluoromethoxy)-4-oxochroman-2-yl)-2,3-dioxopentanoate 26

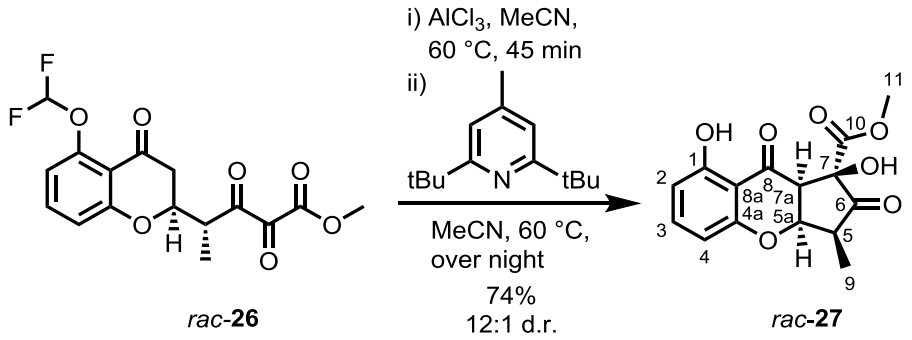


rac-**16** *rac*-**26**

α-Diazo-β-ketoester *rac*-**16** (3.17 g, 8.61 mmol, 1.00 equiv) was dissolved in DMDO-solution[9] (0.055M, 250 mL, 13.8 mmol, 1.60 equiv) and stirred over night at room temperature. The solution was concentrated under reduced pressure to obtain *rac*-**26** (3.22 g, 8.61 mmol, quant) as yellow oil. The crude product was used in the next step without further purification.

TLC: R_f = 0.12 (*n*-pentane/EtOAc 2:1). **^{1}H-NMR**: 500 MHz, $CDCl_3$; δ=7.43 (t, 1H, *J*=8.3 Hz, 3-H), 6.84 (d, 2H, *J*=8.5 Hz, 4-H, 2-H), 6.57 (t, 1H, *J*=74.6 Hz, 12-H), 4.82 (ddd, 1H, *J*=2.5 Hz, 5.4 Hz, 13.6 Hz, 5a-H), 3.89 (s, 3H, 11-H_3), 3.73-3.81 (m, 1H, 5-H), 2.85 (dd, 1H, *J*=14.0 Hz, 16.1 Hz, 7a-H_a), 2.67 (dd, 1H, *J*=2.4 Hz, 16.3 Hz, 7a-H_b), 1.33 (d, 3H, *J*=7.1Hz, 9-H_3) ppm. **^{13}C-NMR**: 126 MHz, $CDCl_3$; δ=198.9 (6-C), 188.9 (8-C), 181.9 (7-C), 161.8 (1-C), 161.0 (10-C), 150.2 (4a-C), 136.0 (3-C), 116.1 (t, *J*=262.8 Hz, 12-C), 115.9 (4-C), 115.8 (2-C), 114.2 (8a-C), 53.6 (5-C), 44.6 (11-C), 40.6 (7a-C), 10.0 (9-C) ppm. **^{19}F-NMR:** 282 MHz, $CDCl_3$; δ=–82.7 (dd, *J*=163.2 Hz, 234.9 Hz, 2F, 10-F_2) ppm. **HR-MS:** (ESI+): m/z calc. for $C_{16}H_{14}F_2O_7Na$ $[M\text{-}Na]^+$: 379.0611, found: 379.0594. **FT-IR:** (neat): $\tilde{\nu}$ = 3451 (w), 2959 (w), 1731 (w), 1692 (s), 1609 (m), 1575 (w), 1469 (m), 1382 (w), 1321 (w), 1273 (w), 1223 (w), 1118 (s), 1035 (m), 968 (w), 909 (m), 799 (w), 730 (s), 648 (w), 581 (w), 522 (w) cm^{-1}.

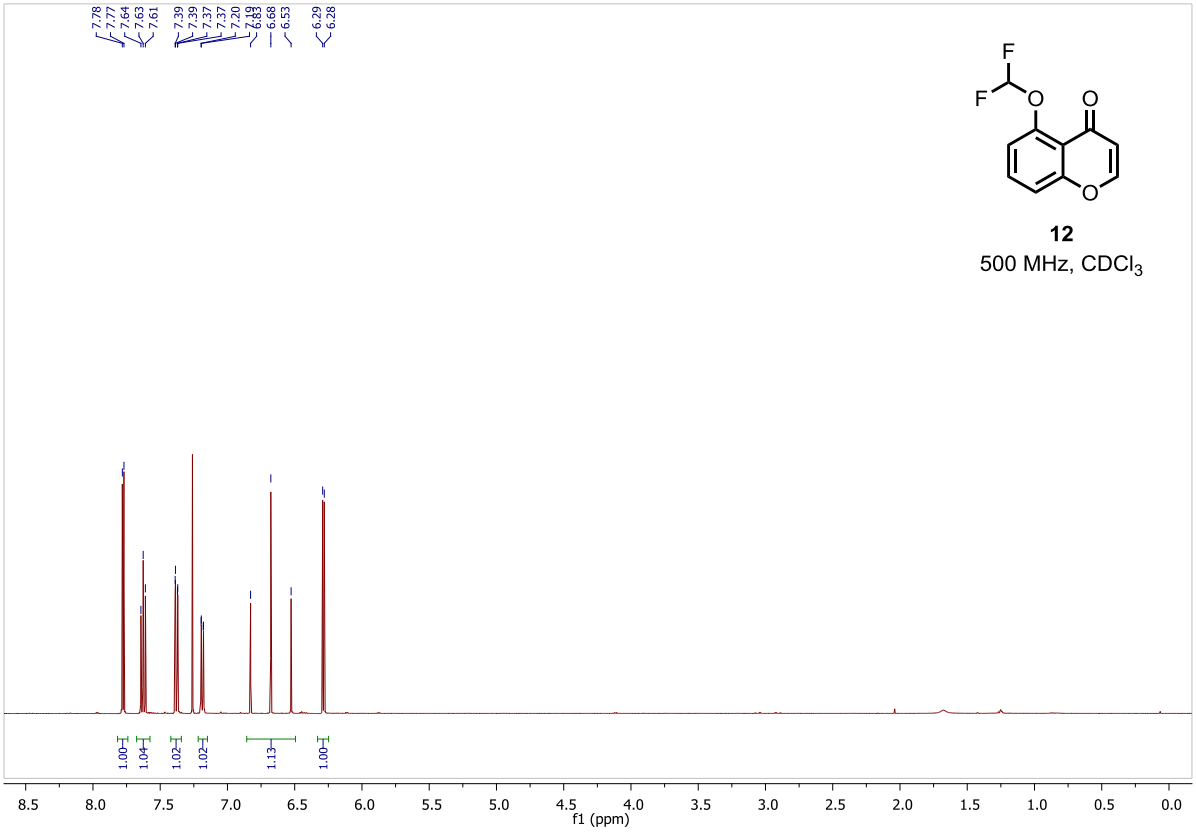
2.17 *rac*-methyl (1*R*,3*S*,3a*R*,9a*R*)-1,8-dihydroxy-3-methyl-2,9-dioxo-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-1-carboxylate 27

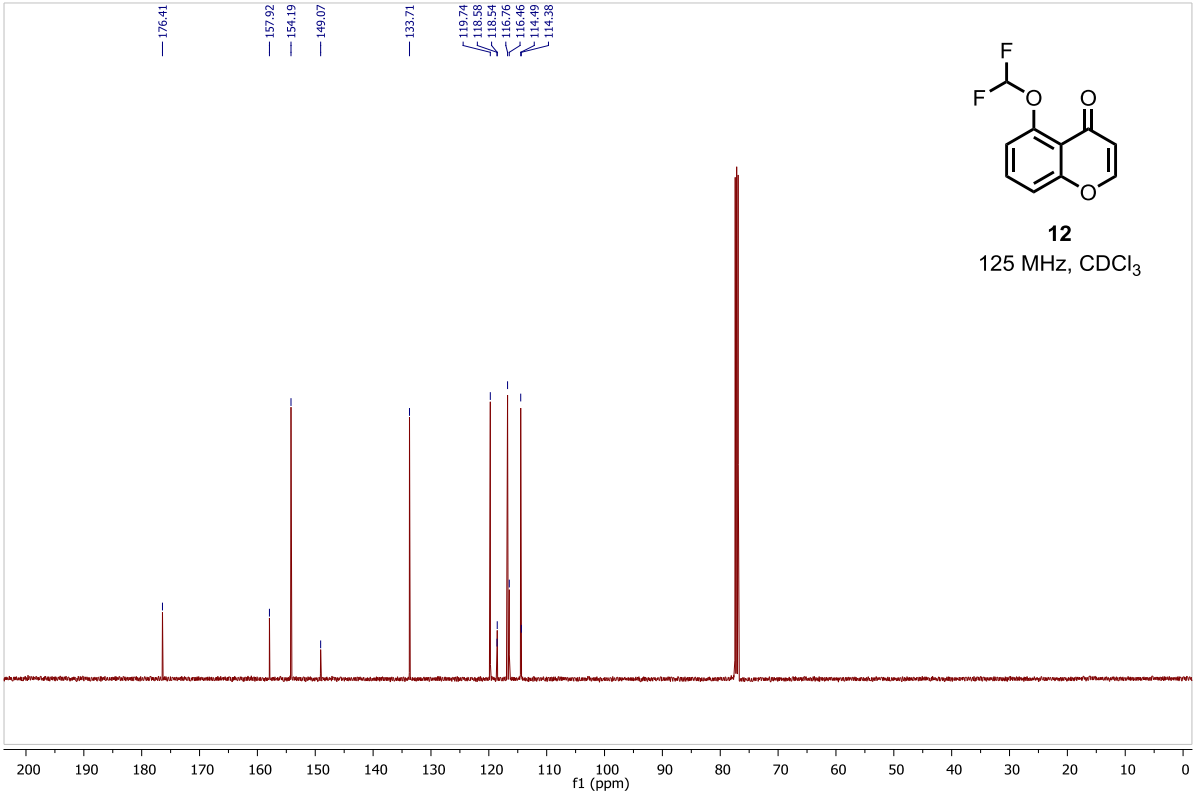


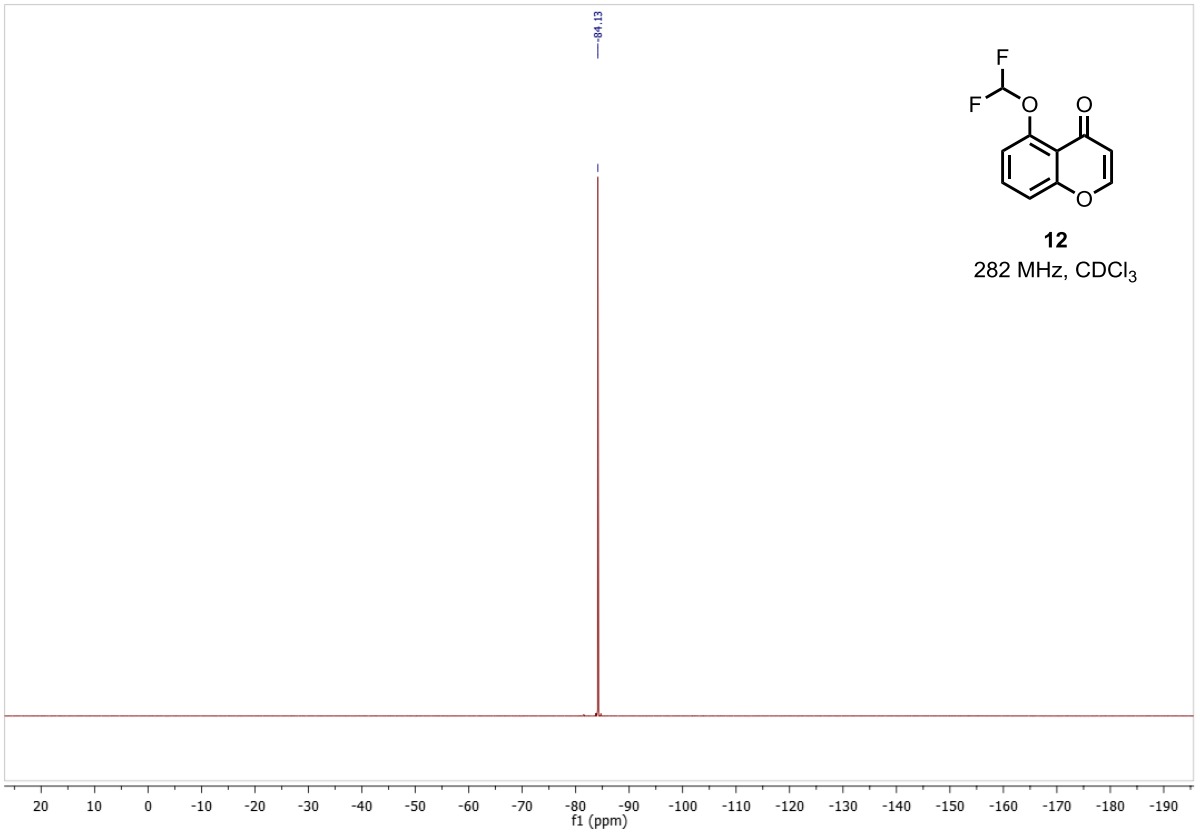
Vicinal tricarbonyle *rac*-**26** (1.04 g, 2.78 mmol, 1.00 equiv) was dissolved in MeCN (40 mL), $AlCl_3$ (556 mg, 4.17 mmol, 1.50 equiv) was added and the orange solution was heated to 60 °C for 45 min. The solution was cooled to room temperature and water (20 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (4x60 mL), the combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The oily remnants were dissolved in MeCN (100 mL), 2,6-di-tert-butyl-4-methylpyridine (571 mg, 2.78 mmol, 1.00 equiv) was added and the reaction was stirred over night at 60 °C. Silica was added and the solvent was removed under reduced pressure. Column chromatography (silica, *n*-pentane/EtOAc 2:1) gave *rac*-**27** (630 mg, 2.06 mmol, 74%, 12:1 d.r.) as pale yellow solid.

TLC: R_f = 0.69 (*n*-pentane/EtOAc 1:1). **^{1}H-NMR**: 500 MHz, $CDCl_3$; δ=11.53 (s, 1H, 1-OH), 7.37 (t, 1H, *J*=8.3 Hz, 3-H), 6.55 (dd, 1H, *J*=0.8 Hz, 8.4 Hz, 4-H), 6.44 (dd, 1H, *J*=0.8 Hz, 8.2 Hz, 2-H), 5.06 (t, 1H, *J*=4.1 Hz, 5a-H), 3.89 (s, 3H, 11-H_3), 3.84 (s, 1H, 7-OH), 3.68 (d, 1H, *J*=4.1 Hz, 7a-H), 2.90 (qd, 1H, *J*=4.1 Hz, 6.9 Hz, 5-H), 6.96 (d, 3H, *J*=7.0 Hz, 9-H_3) ppm. **^{13}C-NMR**: 126 MHz, $CDCl_3$; δ=208.7 (6-C), 194.0 (8-C), 170.6 (10-C), 162.1 (1-C), 160.6 (4a-C), 139.0 (3-C), 110.7 (2-C), 109.4 (8a-C), 108.0 (4-C), 78.4 (7-C), 78.2 (5a-C), 54.4 (7a-C), 52.8 (11-C), 49.5 (5-C), 7.6 (9-C) ppm. **HR-MS:** (ESI+): m/z calc. for $C_{15}H_{14}O_7Na$ $[M-Na]^+$: 329.0632, found: 329.0629. **FT-IR:** (neat): $\tilde{\nu}$ =3459 (w), 2956 (w), 1765 (m), 1744 (w), 1641 (s), 1578 (w), 1463 (s), 1362 (m), 1259 (w), 1220 (s), 1139 (w), 1060 (m), 968 (w), 819 (w), 795 (w), 727 (w) cm^{-1}. **m.p.:** 174 °C (Et_2O).

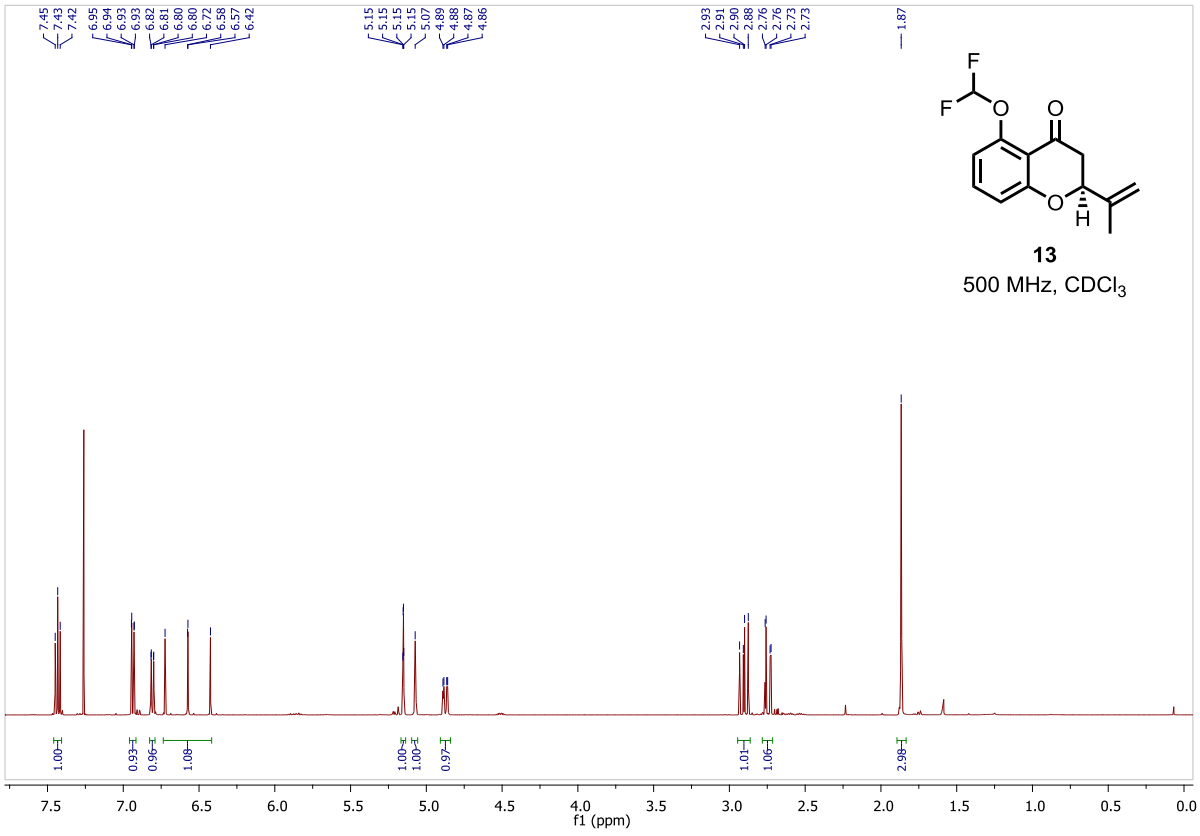
3 ^{1}H, ^{13}C, ^{19}F & NOESY-NMR



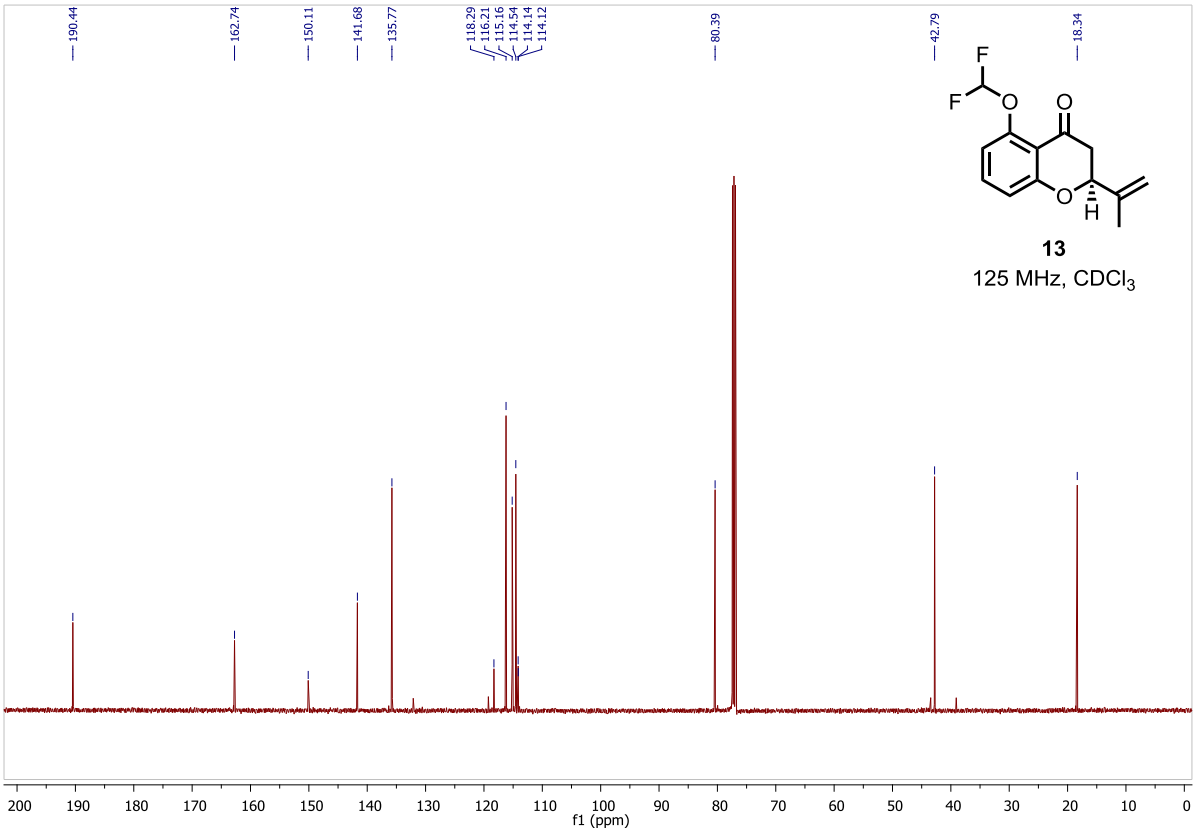




12
282 MHz, $CDCl_3$



13
500 MHz, $CDCl_3$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114.12
80.39
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18.34
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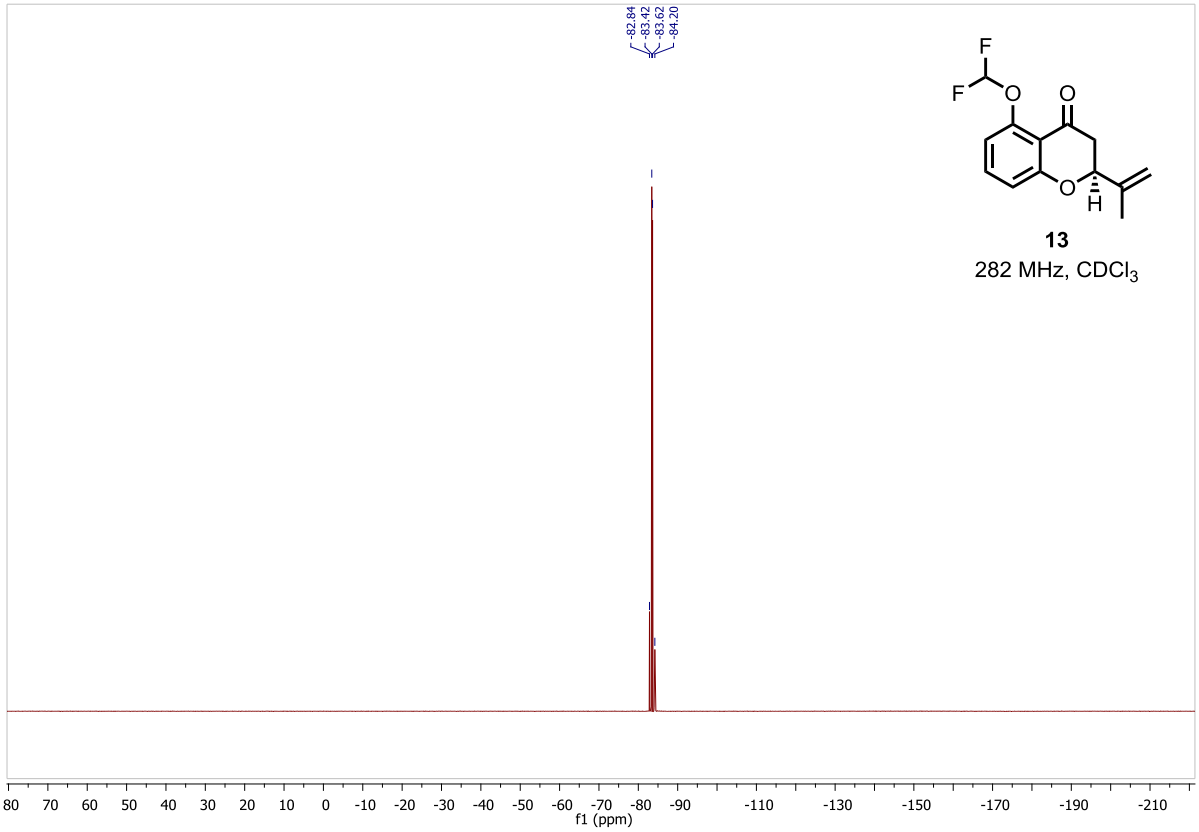
f1 (ppm)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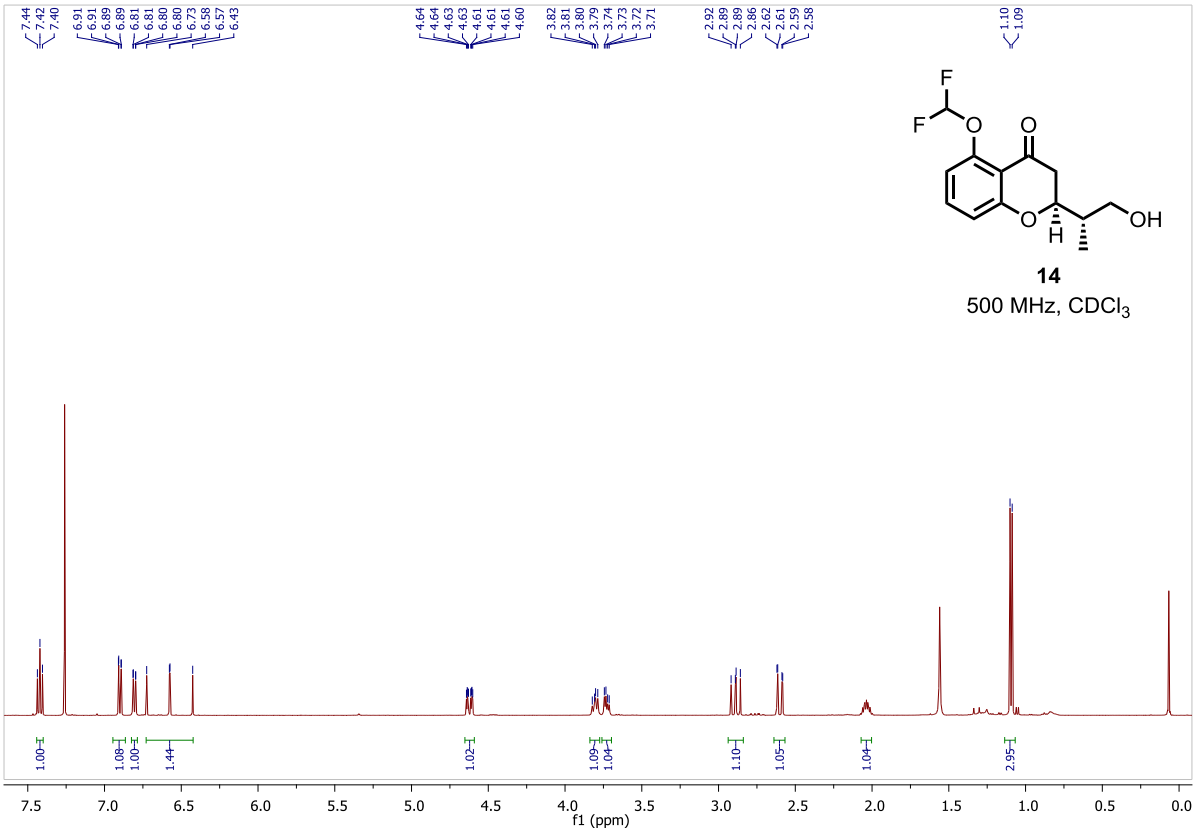
83.42
83.62
84.20
F
F
O
O
O
H
13
282 MHz, CDCl3
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)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7.40
6.91
6.91
6.89
6.89
6.81
6.81
6.80
6.80
6.73
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6.57
6.43
4.64
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4.61
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4.60
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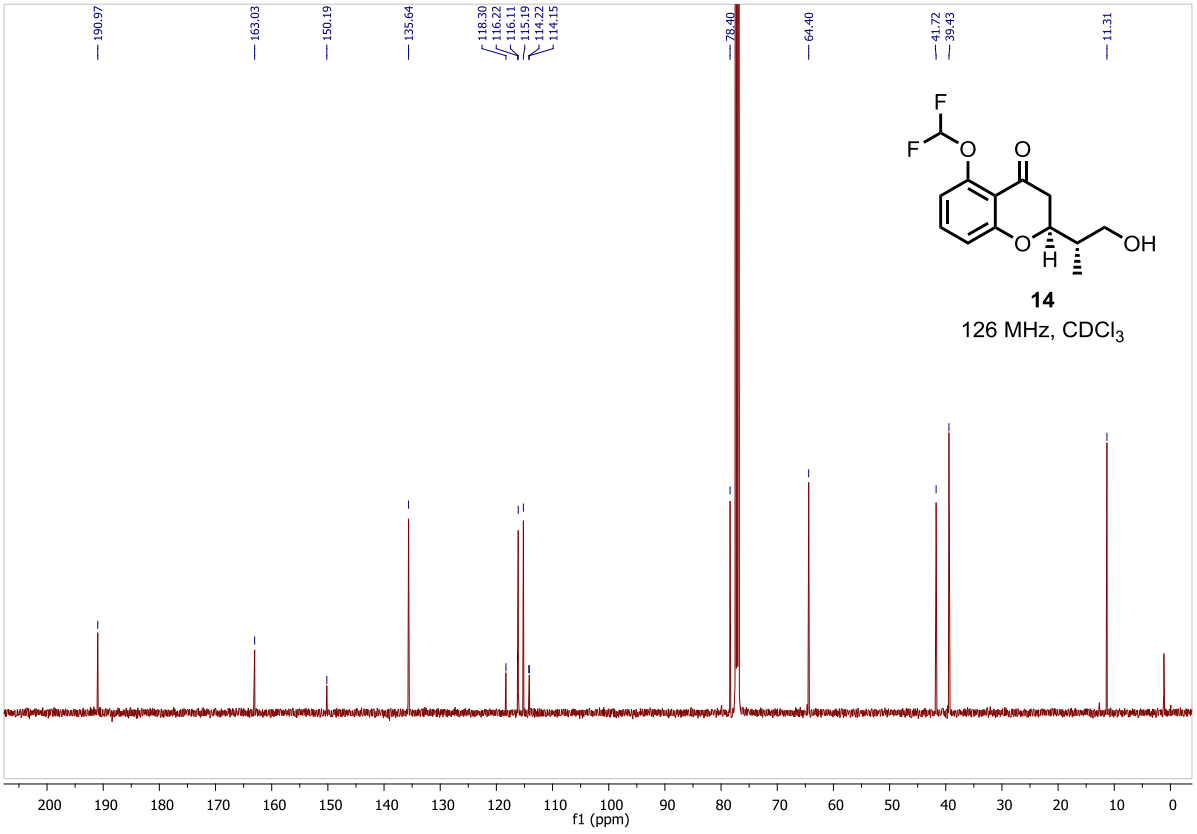
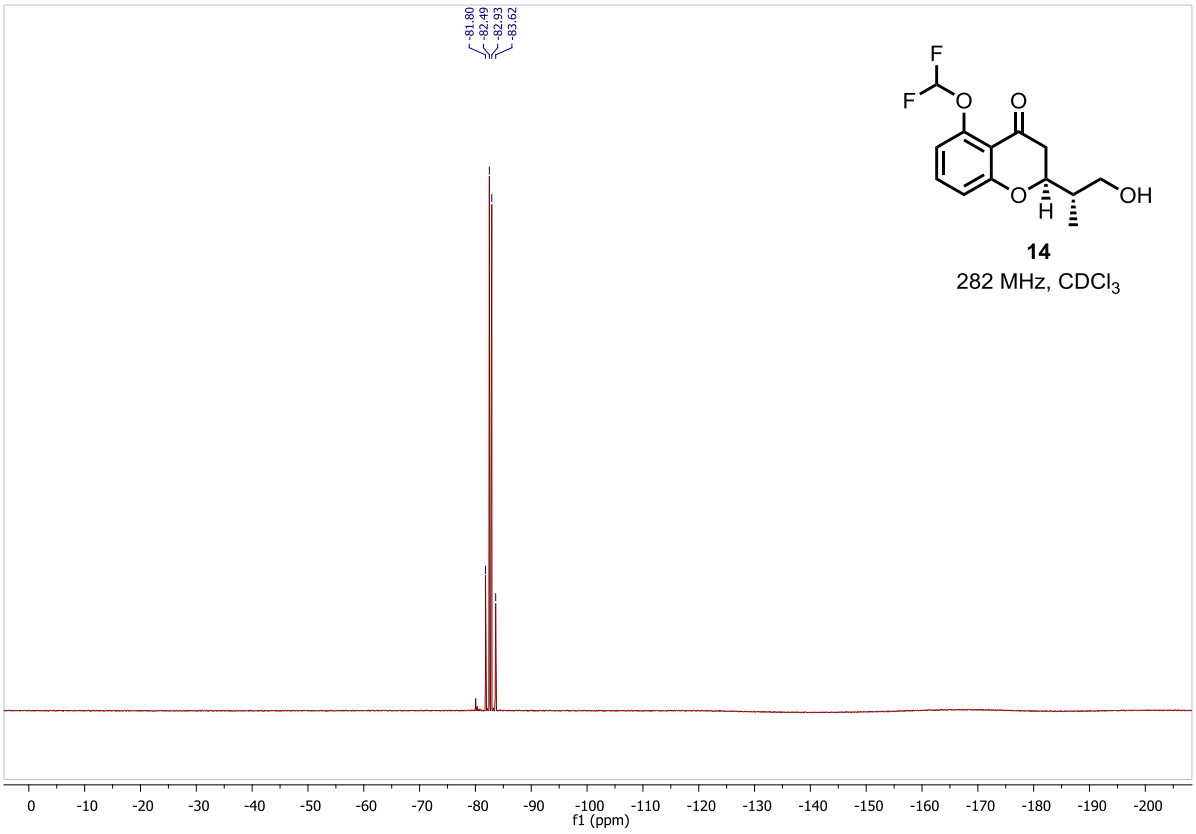
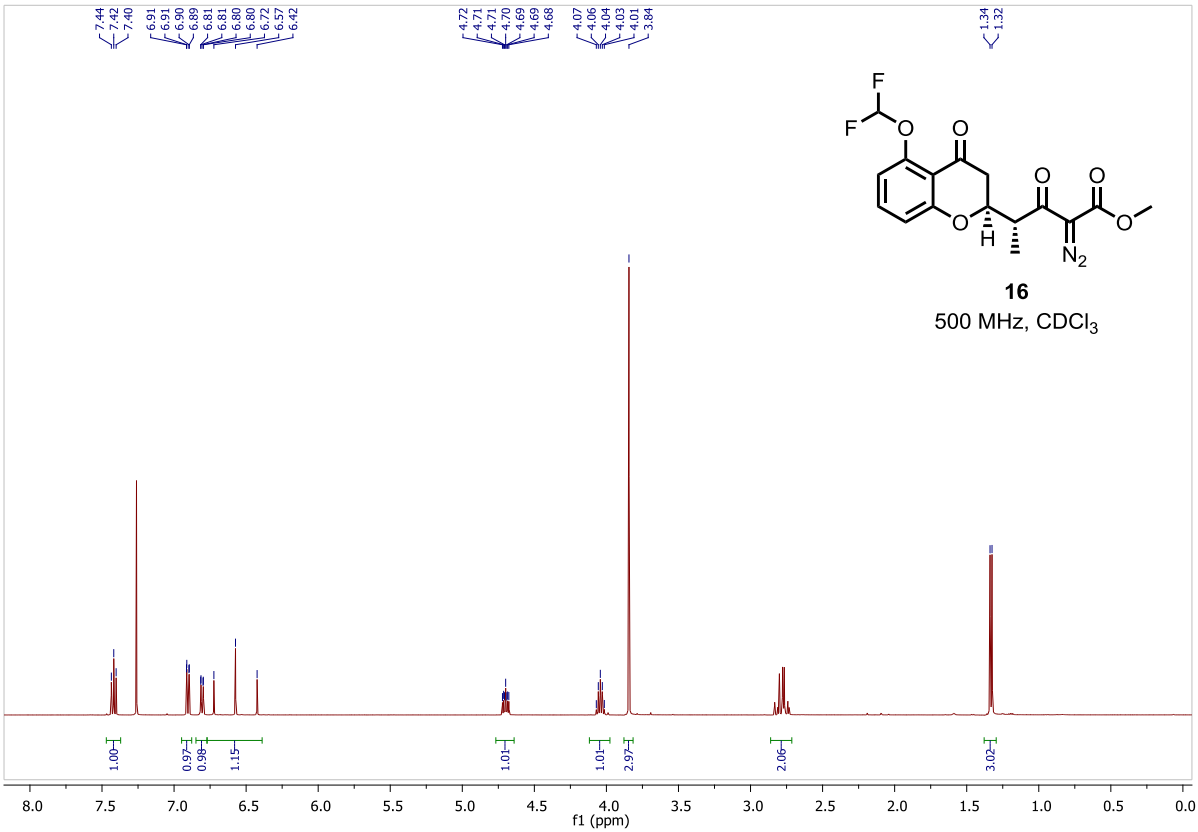
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


190.97
163.03
150.19
135.64
118.30
116.22
116.11
115.19
114.22
114.15
78.40
64.40
41.72
39.43
11.31
F
F
O
O
O
H
OH
14
126 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



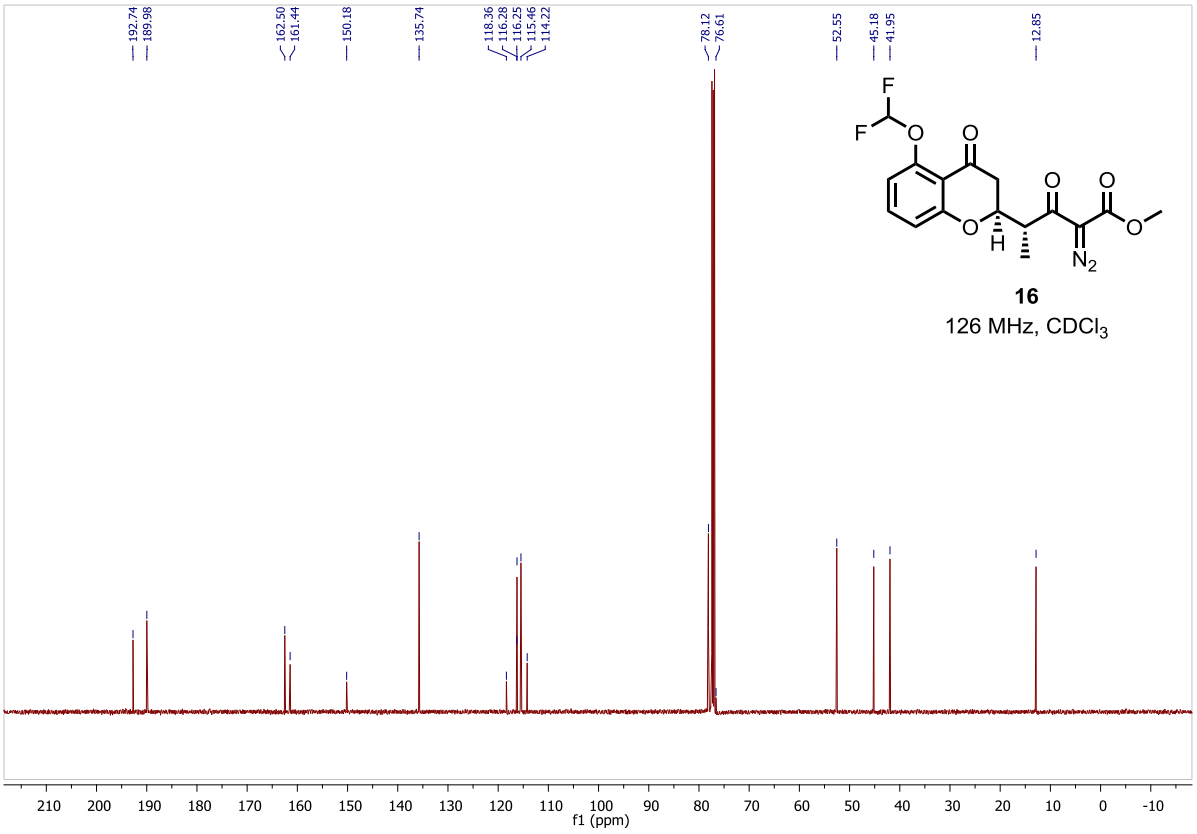
14

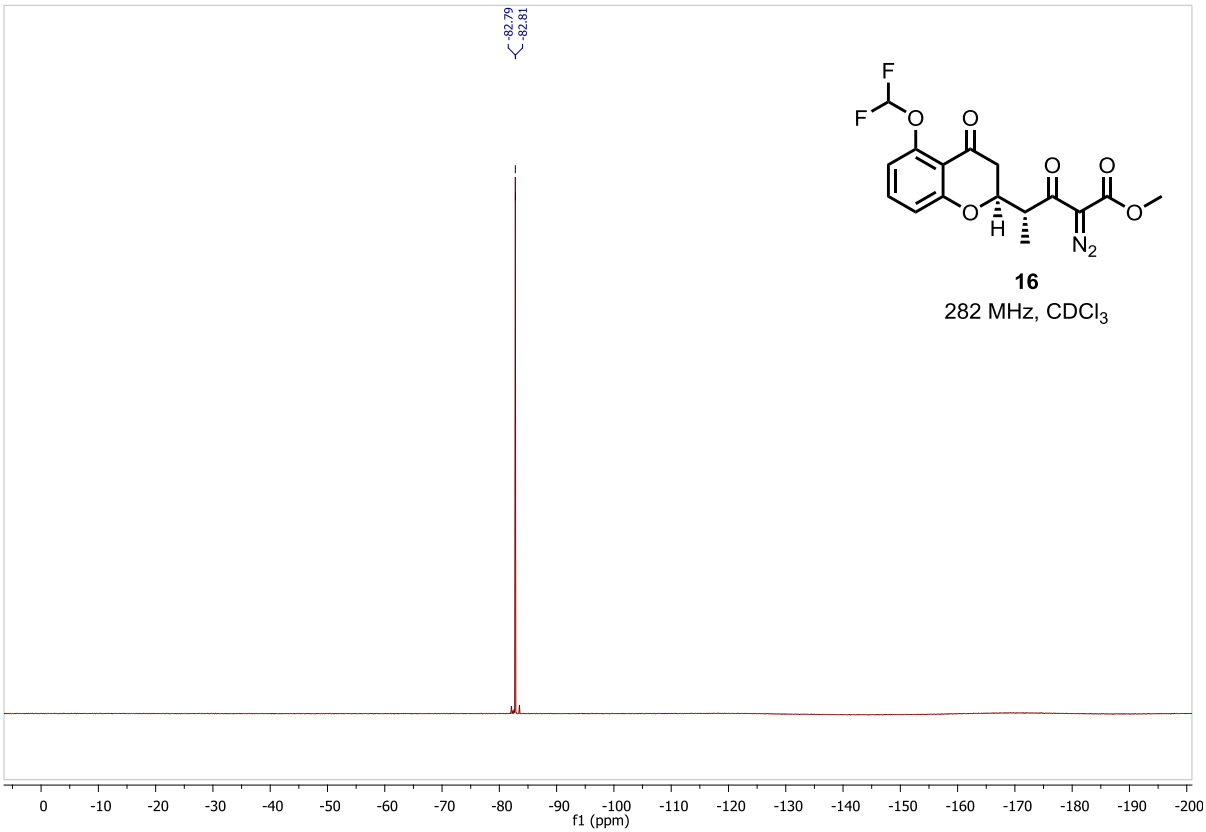
282 MHz, $CDCl_3$

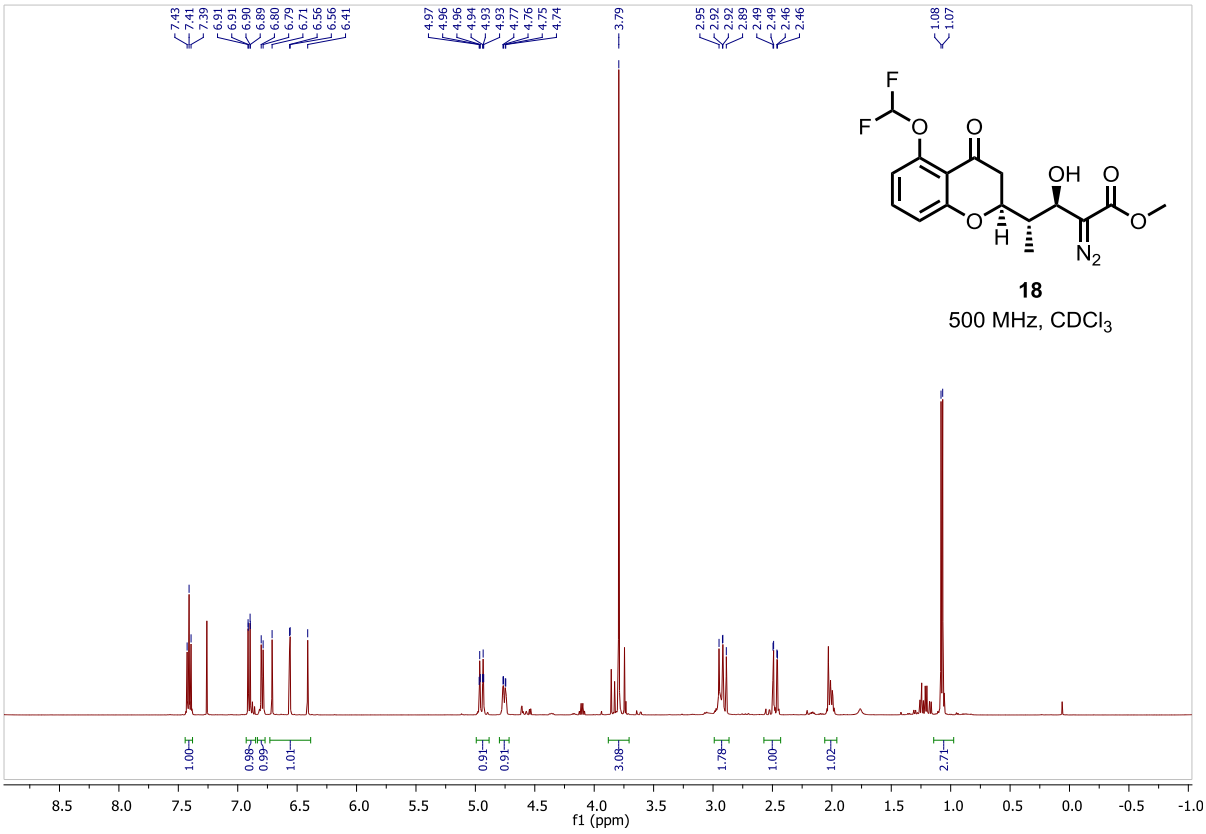


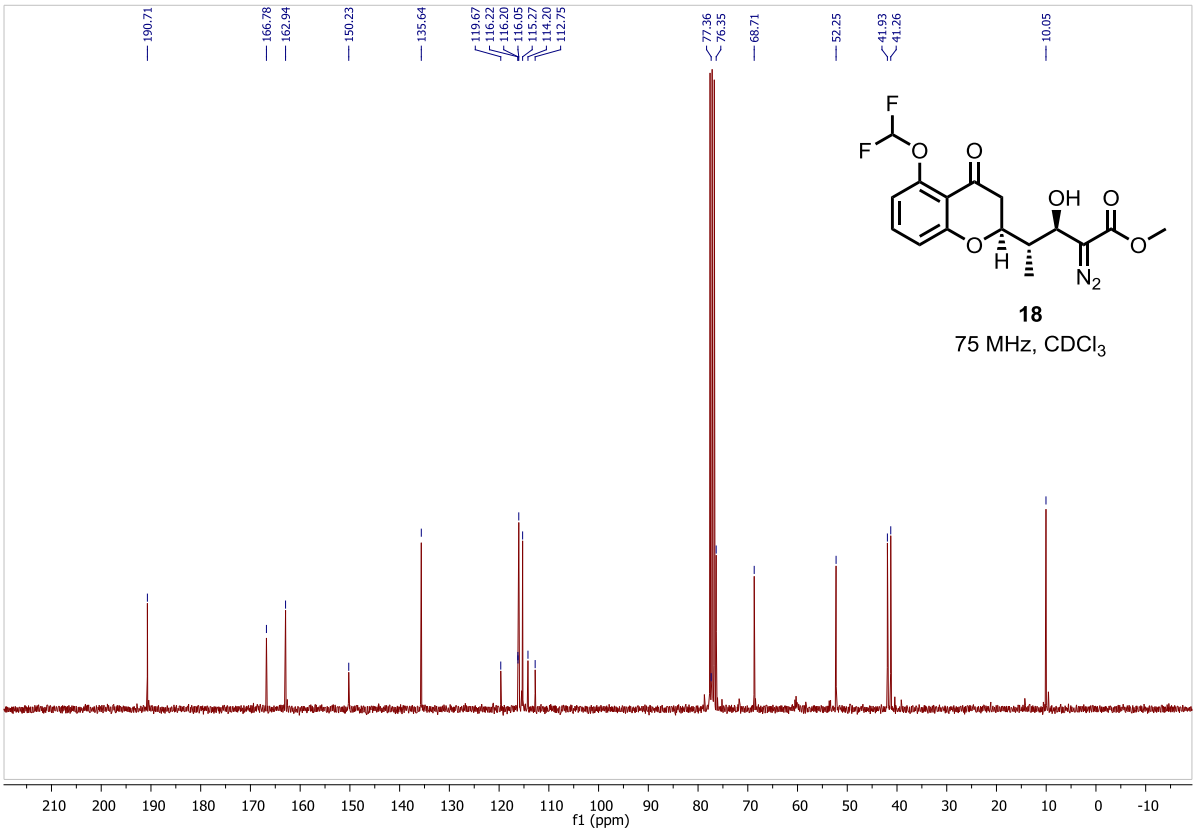
16

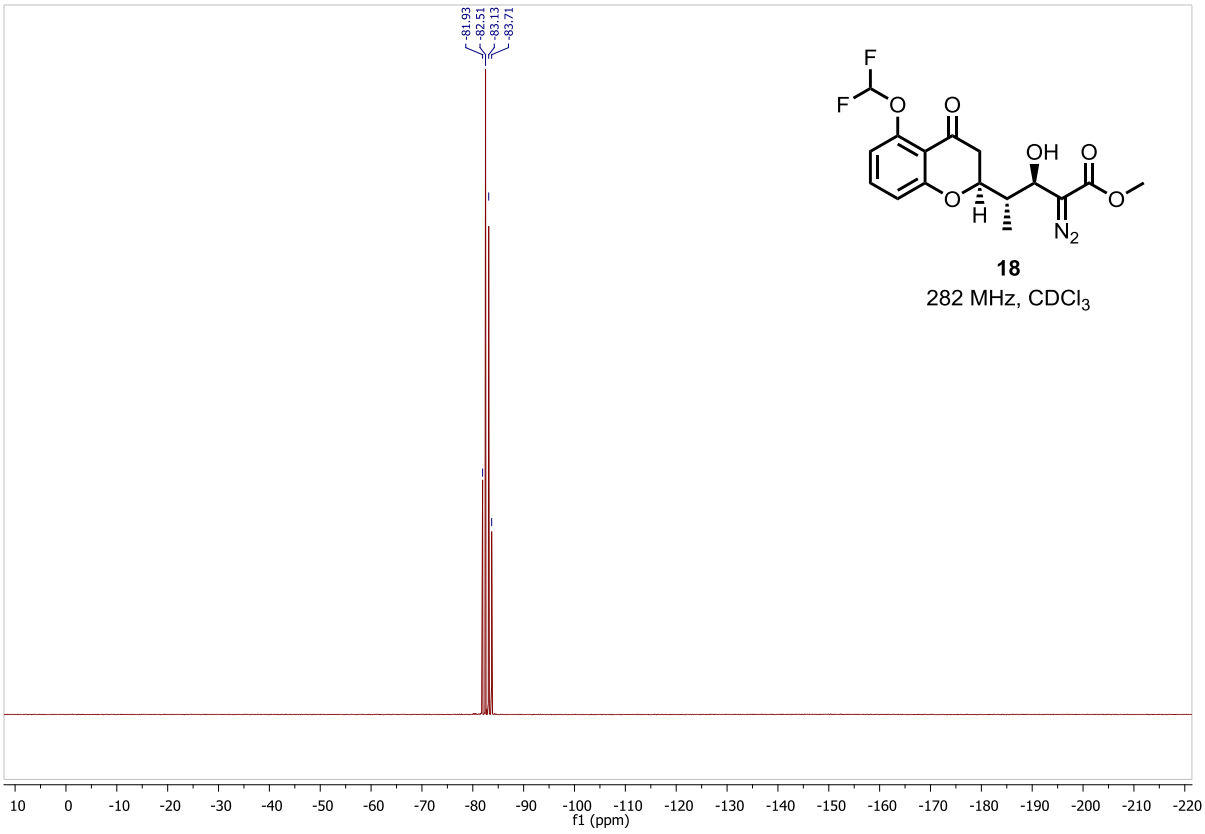
500 MHz, $CDCl_3$


192.74
189.98
162.50
161.44
150.18
135.74
118.36
116.28
116.25
115.46
114.22
78.12
76.61
52.55
45.18
41.95
12.85
F
F
O
O
O
O
O
O
H
N2
16
126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-82.79
-82.81
F
F
O
O
O
O
O
O
H
N2
16
282 MHz, CDCl3
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

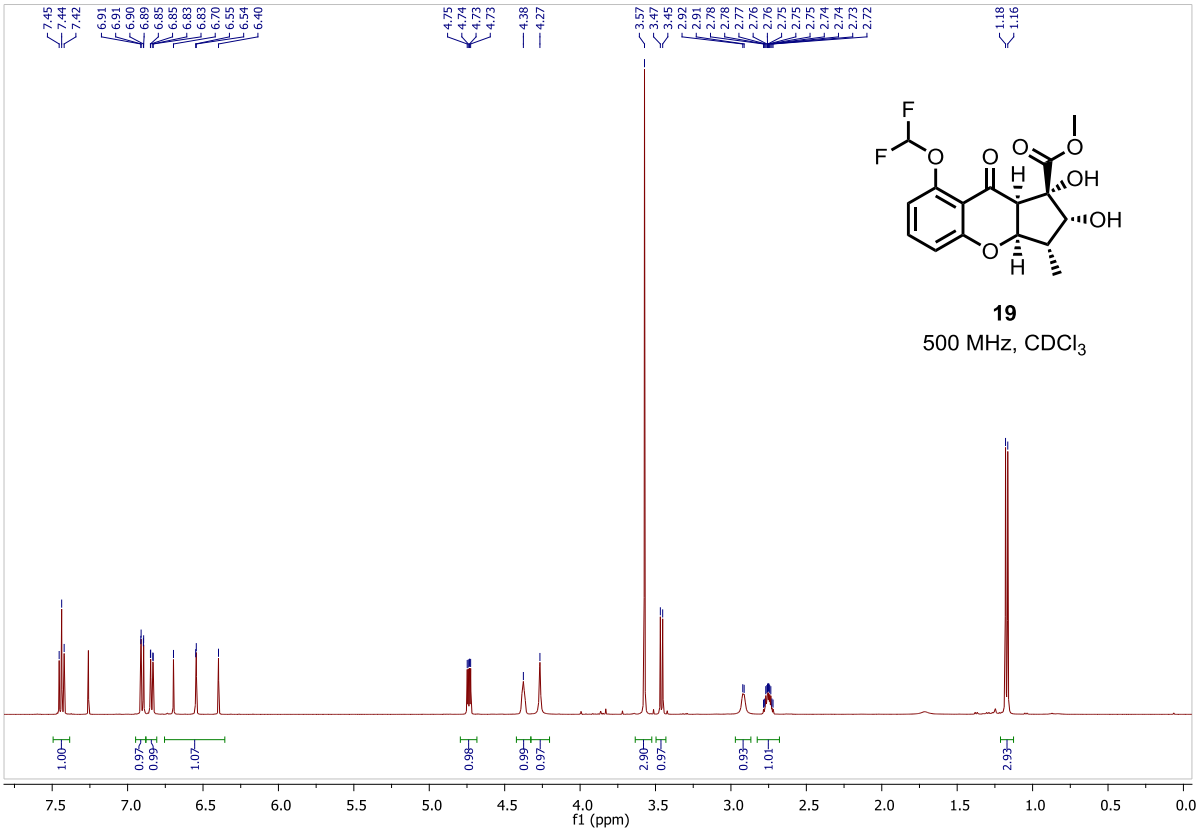

7.43
7.41
7.39
6.91
6.91
6.90
6.89
6.80
6.79
6.71
6.56
6.56
6.41
4.97
4.96
4.96
4.94
4.93
4.93
4.77
4.76
4.75
4.74
3.79
2.95
2.92
2.92
2.89
2.49
2.49
2.46
2.46
1.08
1.07
1.00
0.98
0.99
1.01
0.91
0.91
3.08
1.78
1.00
1.02
2.71
F
F
O
O
OH
O
O
H
O
N2
18
500 MHz, CDCl3
f1 (ppm)


190.71
166.78
162.94
150.23
135.64
119.67
116.22
116.20
116.05
115.27
114.20
112.75
77.36
76.35
68.71
52.25
41.93
41.26
10.05
F
F
O
O
OH
O
O
H
O
N2
18
75 MHz, CDCl3
f1 (ppm)



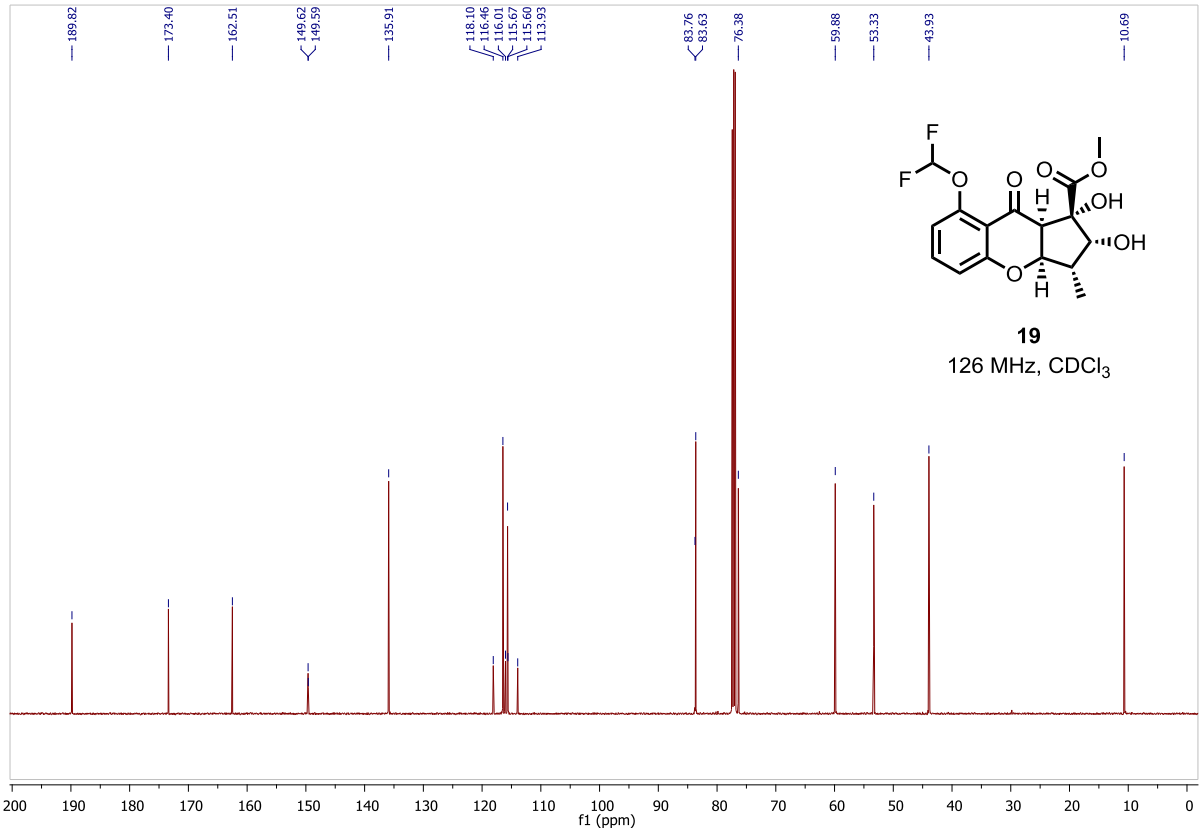
18

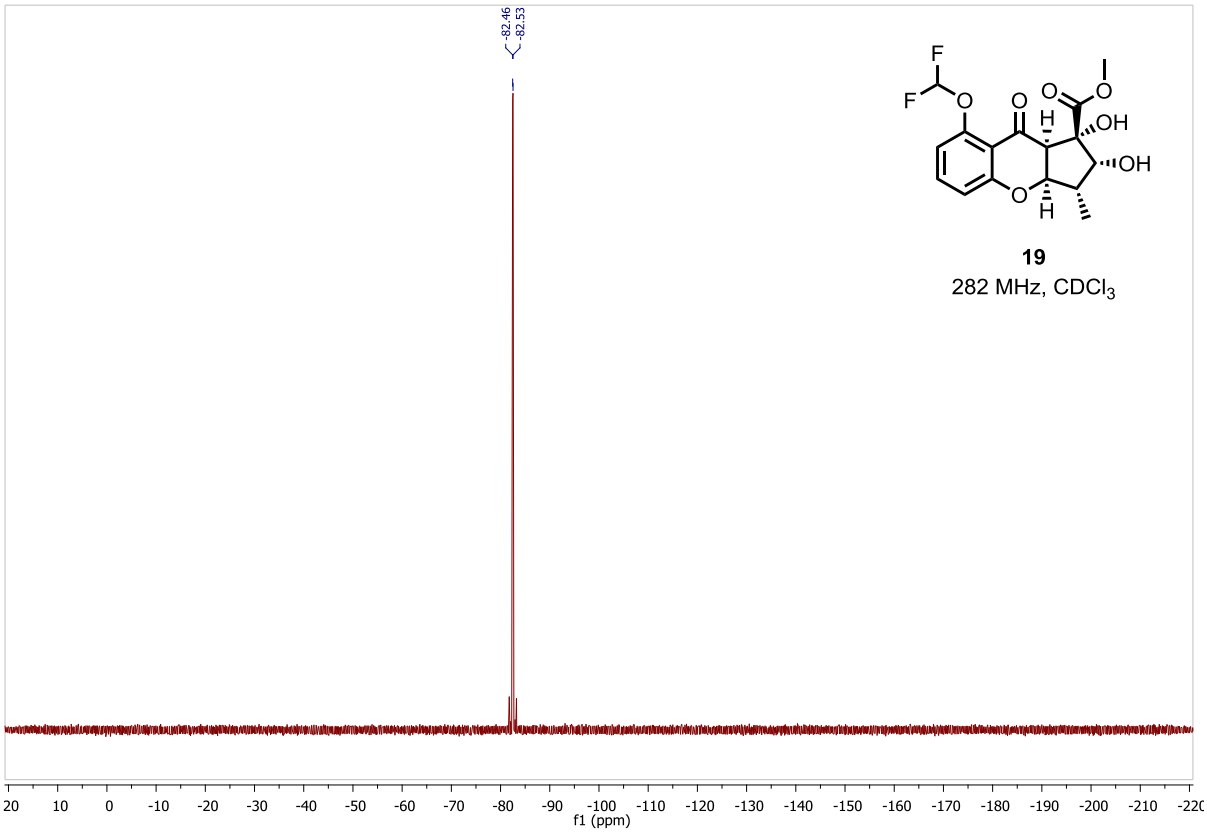
282 MHz, $CDCl_3$

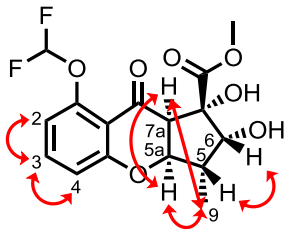


19

500 MHz, $CDCl_3$

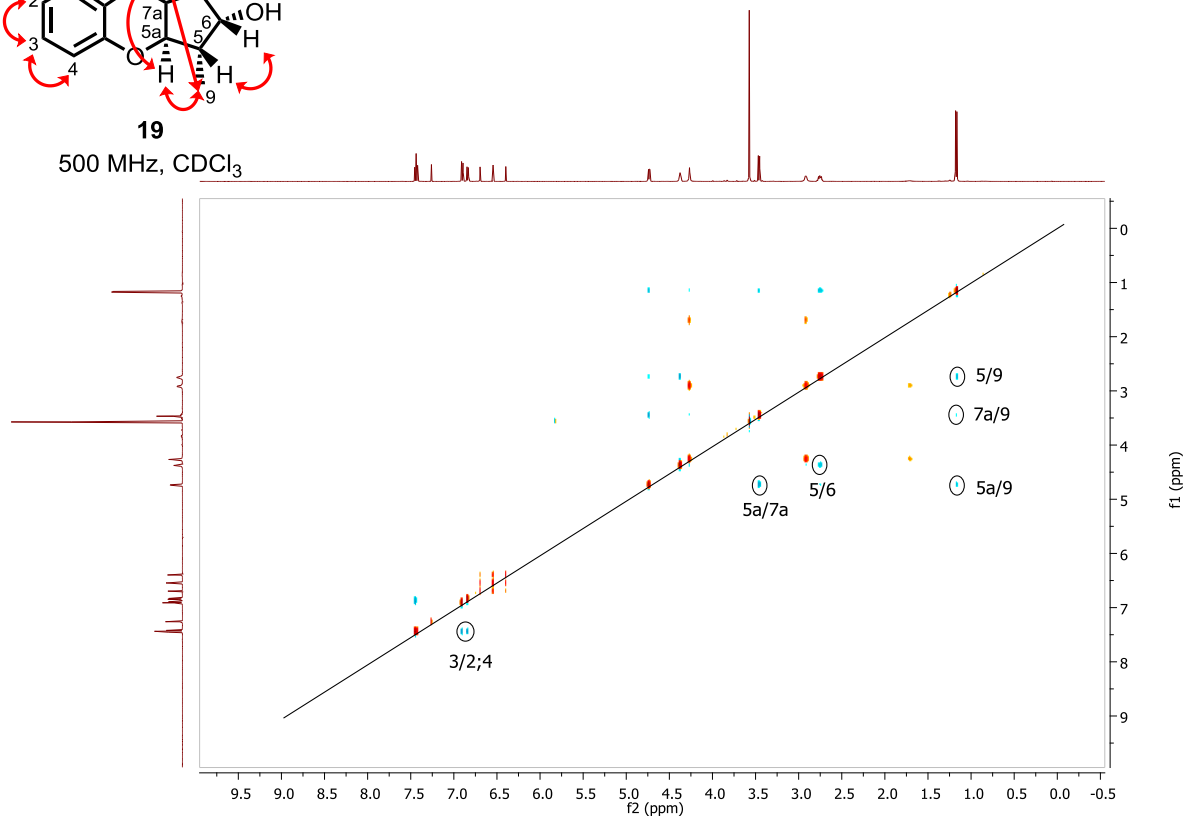

189.82
173.40
162.51
149.62
149.59
135.91
118.10
116.46
116.01
115.67
115.60
113.93
83.76
83.63
76.38
59.88
53.33
43.93
10.69
F
F
O
O
O
O
H
OH
OH
O
H
19
126 MHz, CDCl3
f1 (ppm)

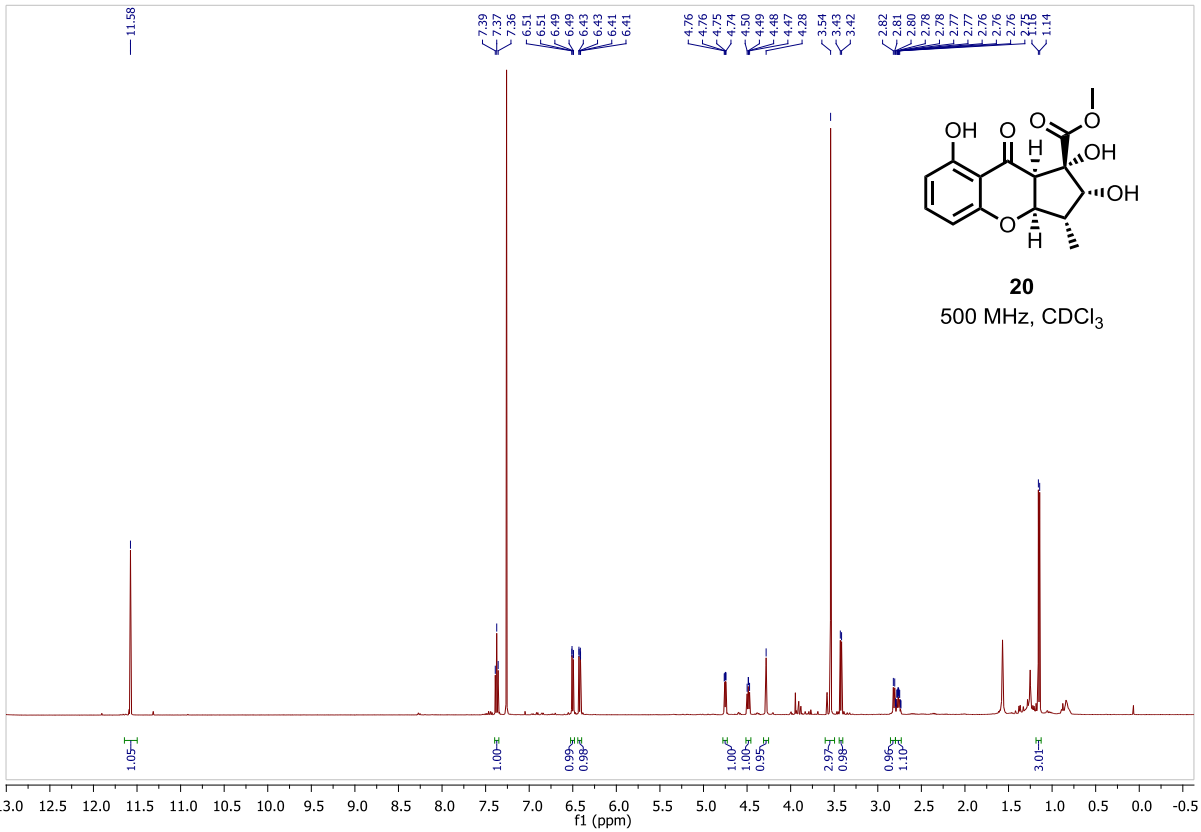

82.46
82.53
F
F
O
O
O
O
H
OH
OH
O
H
19
282 MHz, CDCl3
f1 (ppm)



19

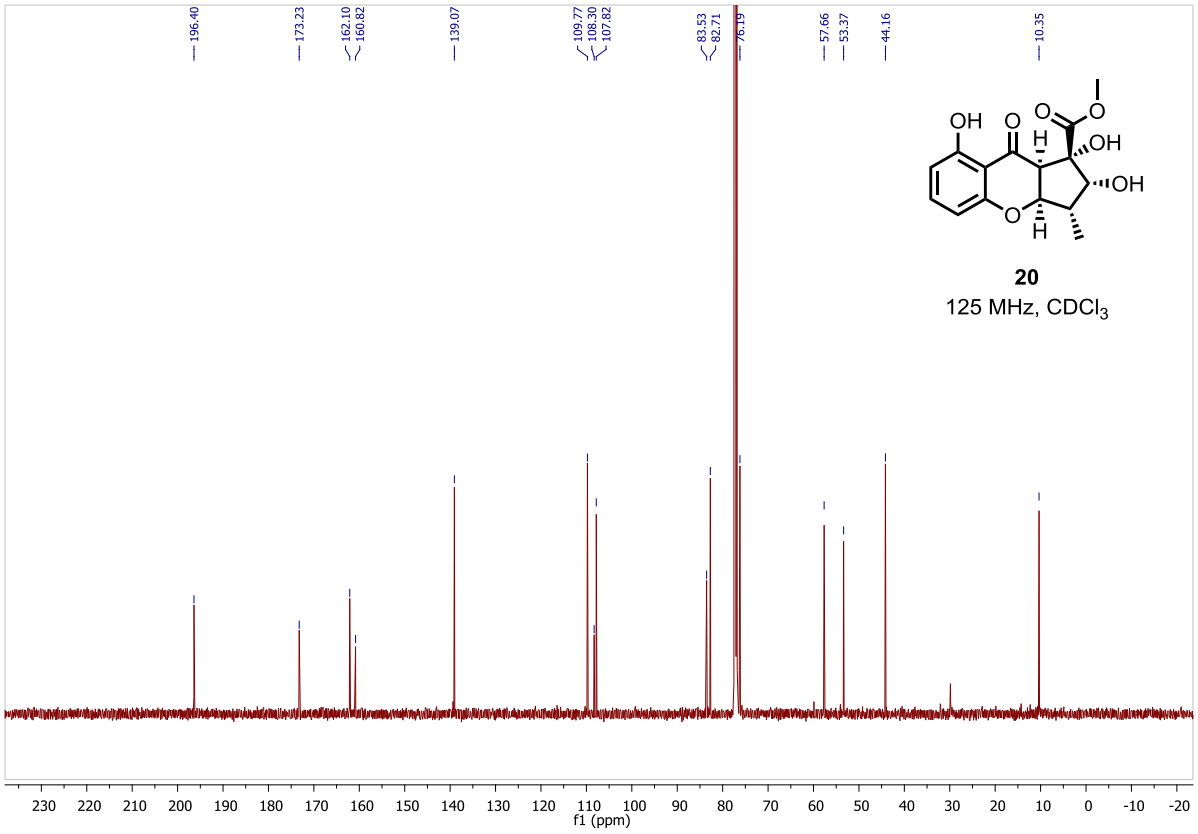
500 MHz, $CDCl_3$

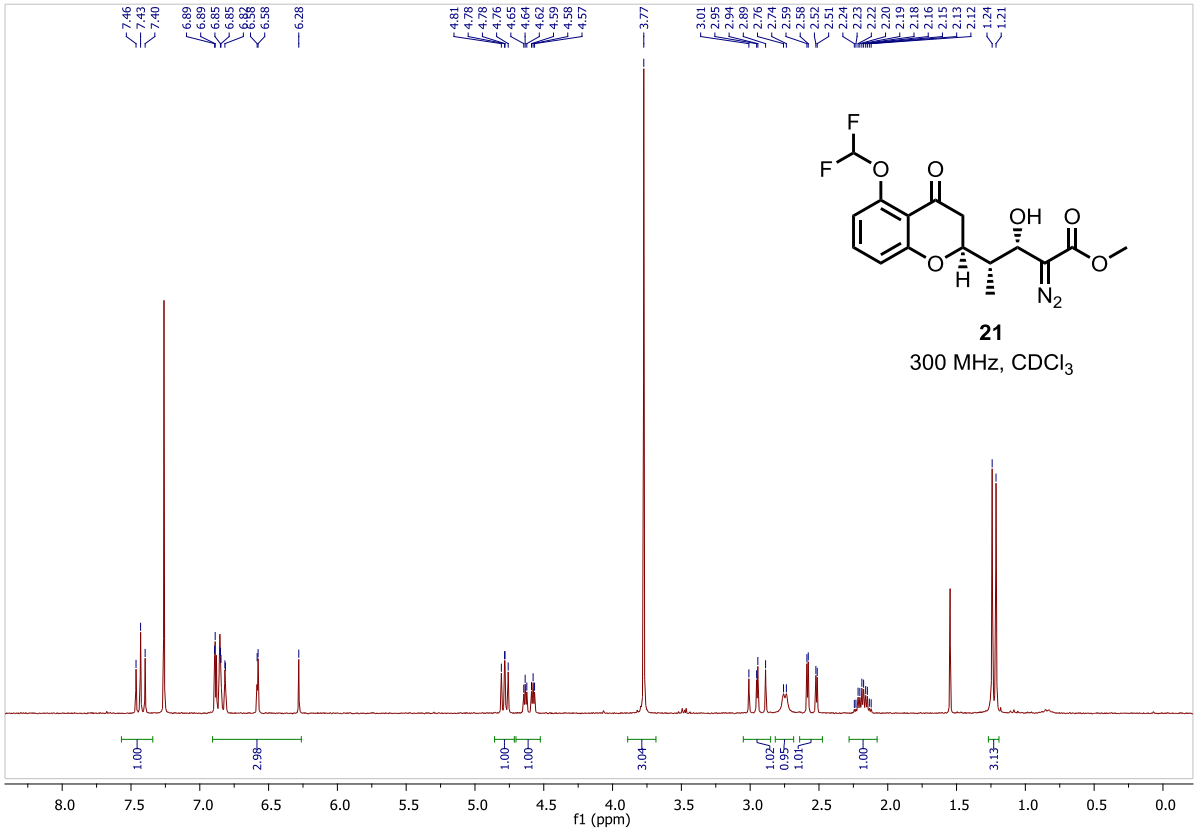


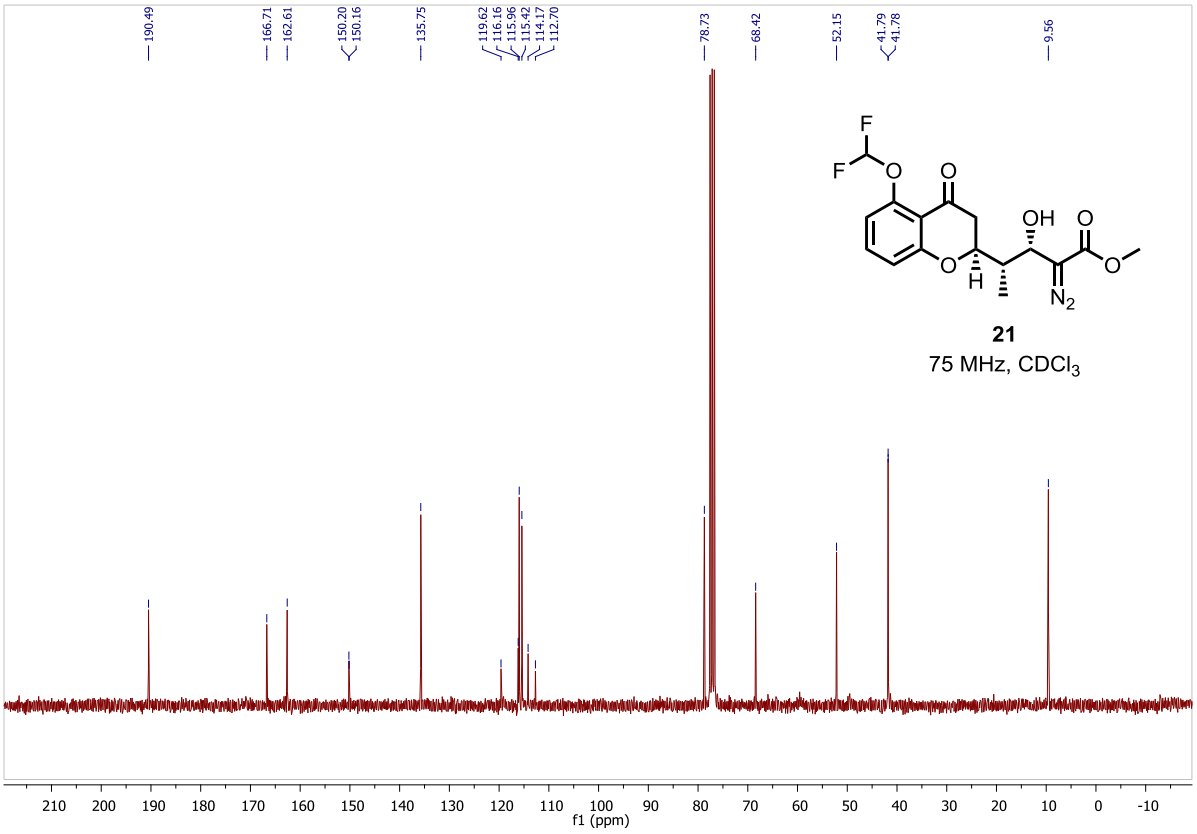


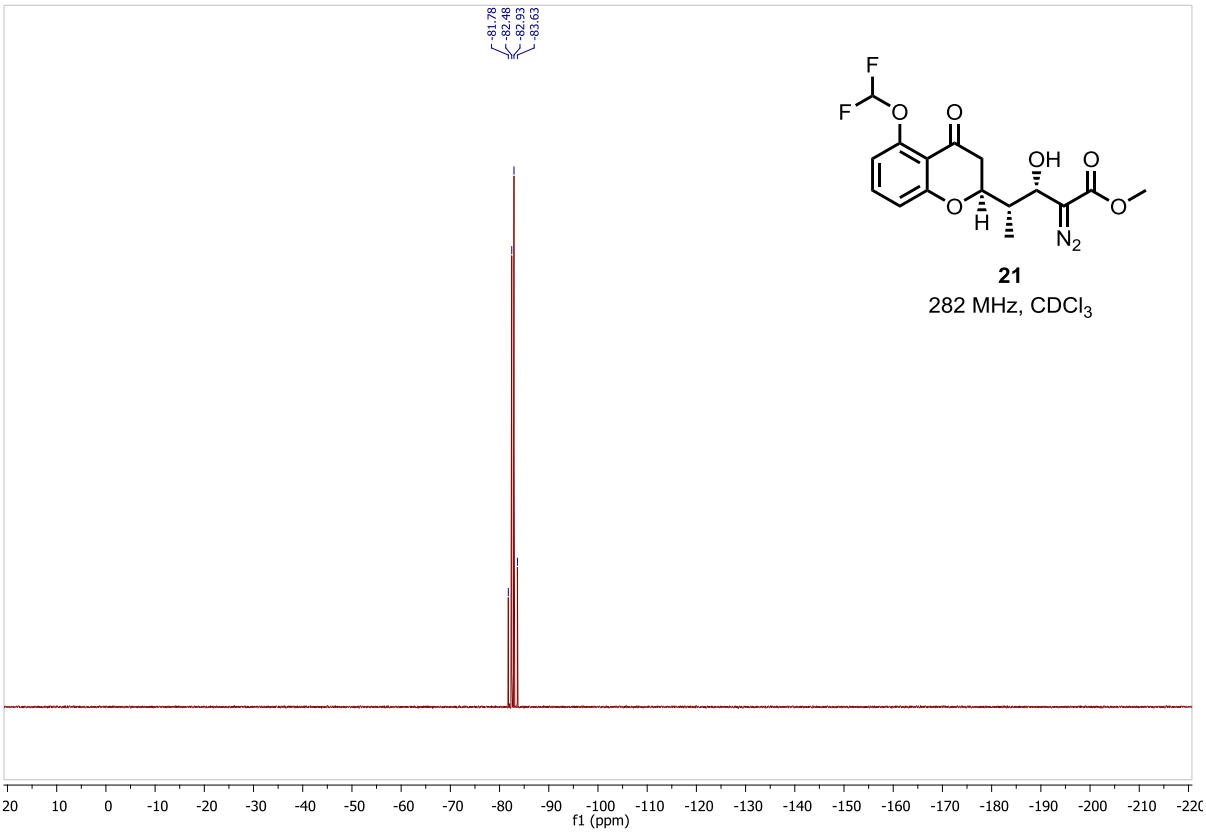
20

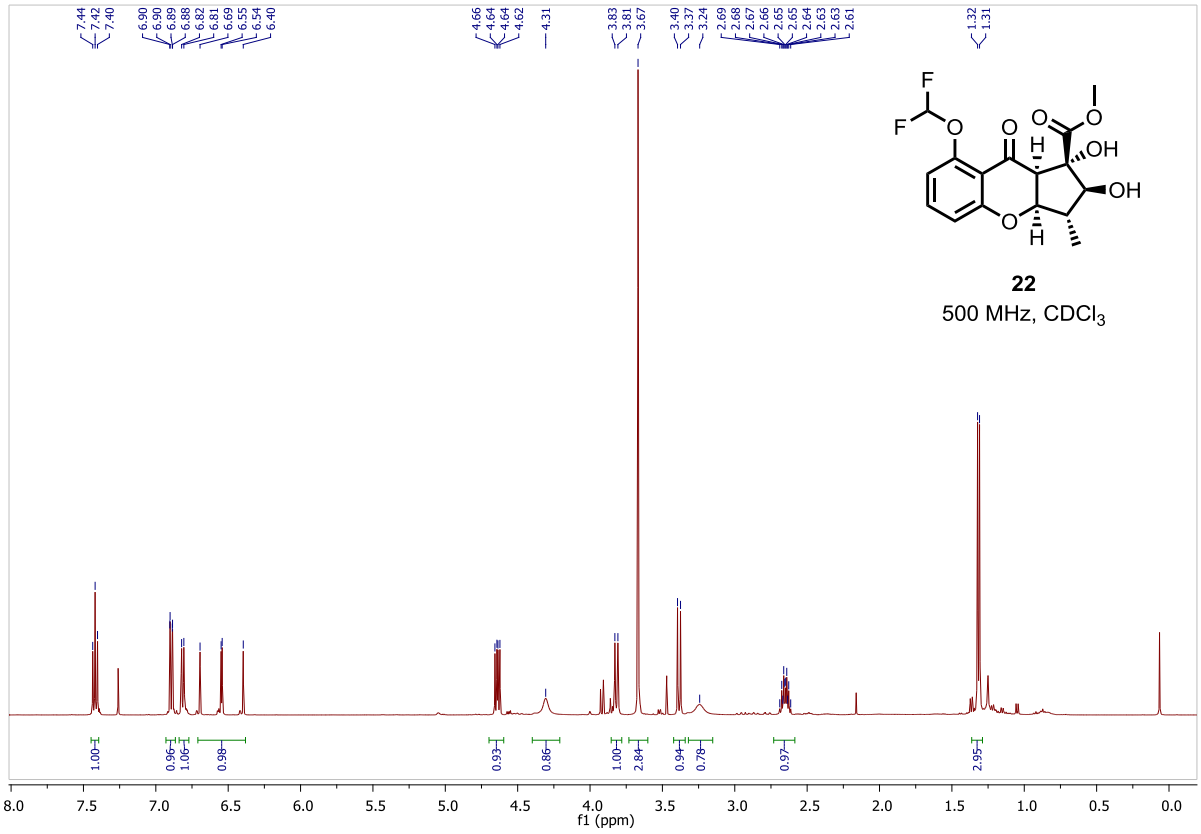
500 MHz, $CDCl_3$


196.40
173.23
162.10
160.82
139.07
109.77
108.30
107.82
83.53
82.71
76.19
57.66
53.37
44.16
10.35
OH
O
O
O
H
OH
OH
O
H
20
125 MHz, CDCl3
f1 (ppm)


7.46
7.43
7.40
6.89
6.89
6.85
6.85
6.58
6.28
4.81
4.78
4.78
4.76
4.65
4.64
4.62
4.59
4.58
4.57
3.77
3.01
2.95
2.94
2.89
2.76
2.74
2.59
2.58
2.52
2.51
2.24
2.23
2.22
2.20
2.19
2.18
2.16
2.15
2.13
2.12
1.24
1.21
F
F
O
O
OH
O
O
H
N2
21
300 MHz, CDCl3
1.00
2.98
1.00
1.00
3.04
1.02
0.95
1.01
1.00
3.13
f1 (ppm)

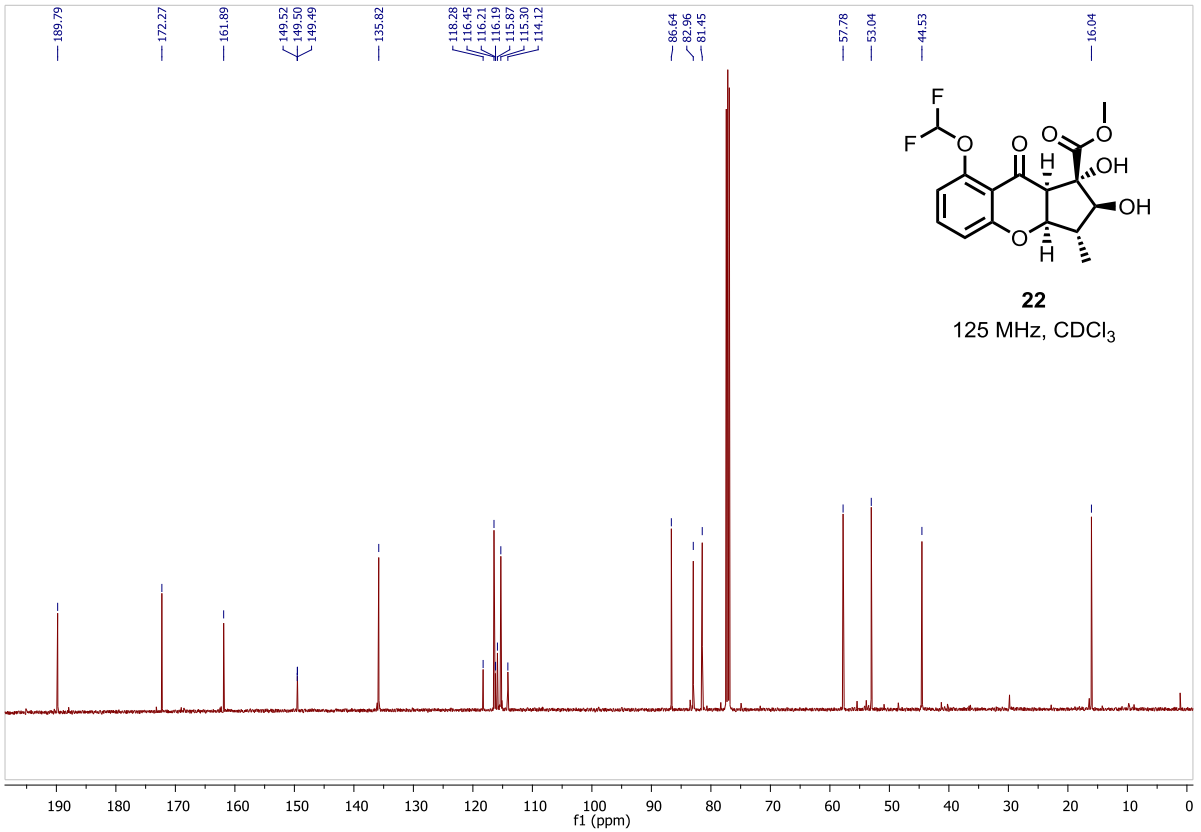

190.49
166.71
162.61
150.20
150.16
135.75
119.62
116.16
115.96
115.42
114.17
112.70
78.73
68.42
52.15
41.79
41.78
9.56
F
F
O
O
OH
O
O
H
O
N2
21
75 MHz, CDCl3
f1 (ppm)


-81.78
-82.48
-82.93
-83.63
F
F
O
O
OH
O
O
H
O
N2
21
282 MHz, CDCl3
f1 (ppm)



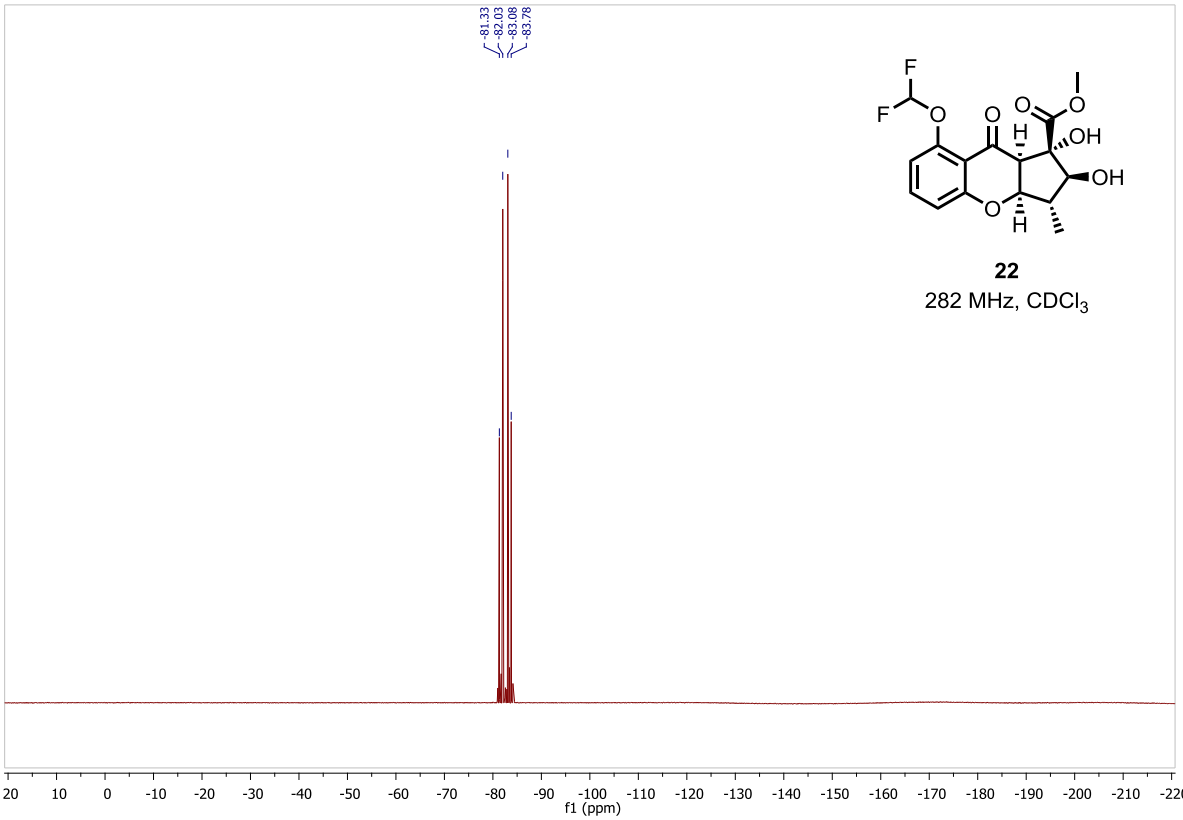
22

500 MHz, $CDCl_3$



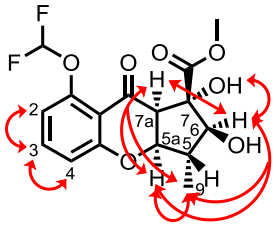
22

125 MHz, $CDCl_3$



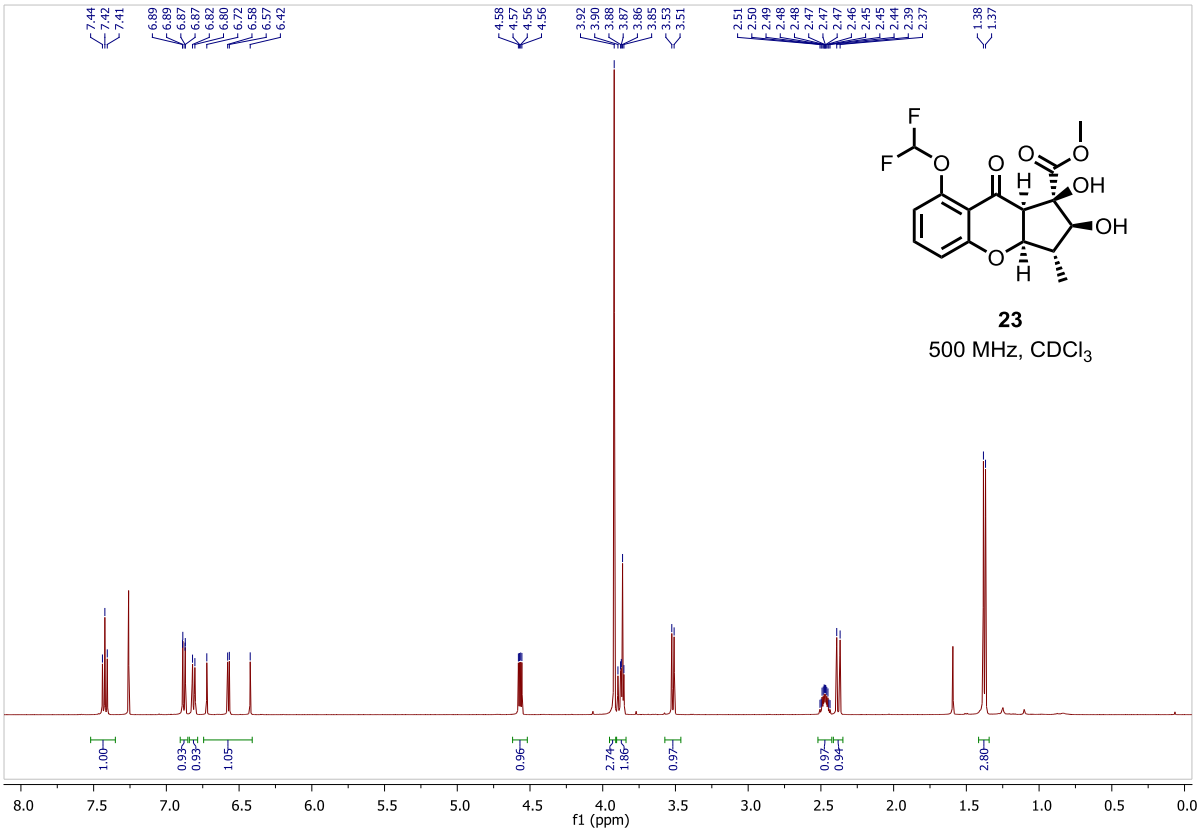
22

282 MHz, $CDCl_3$



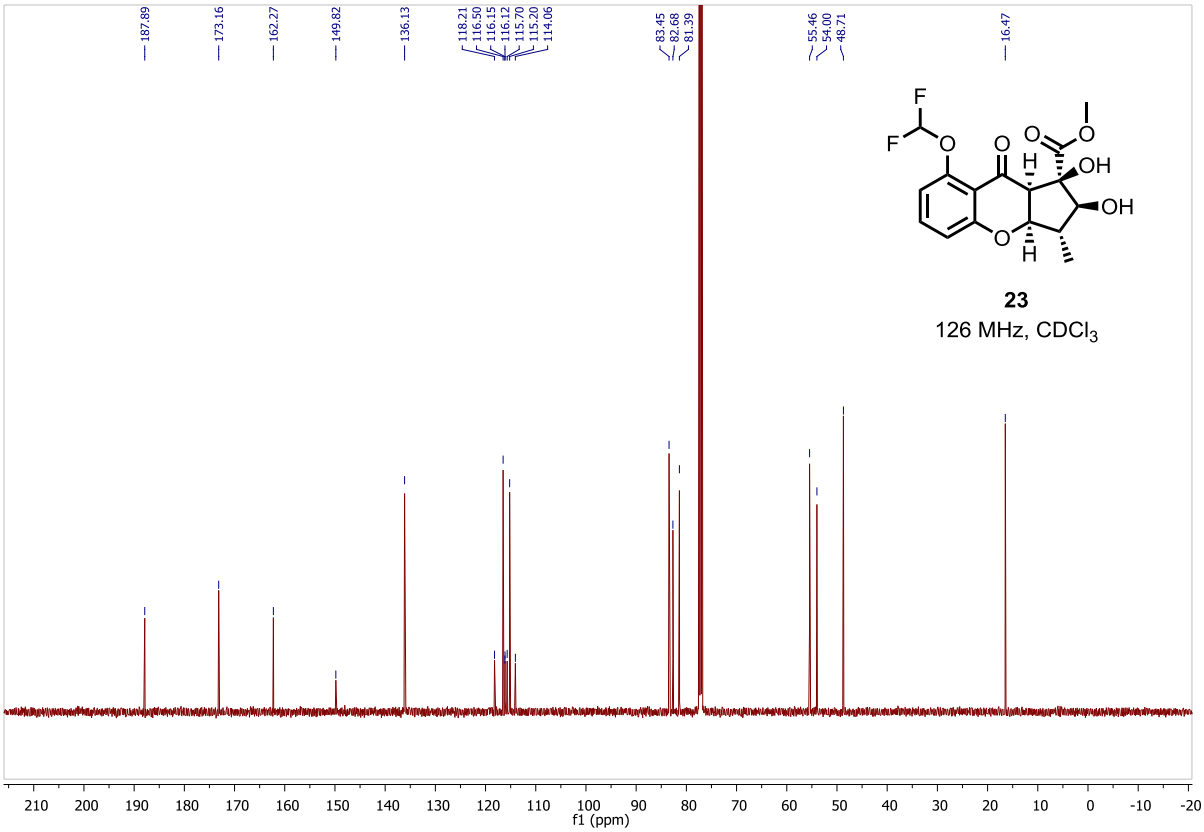
22

500 MHz, $CDCl_3$



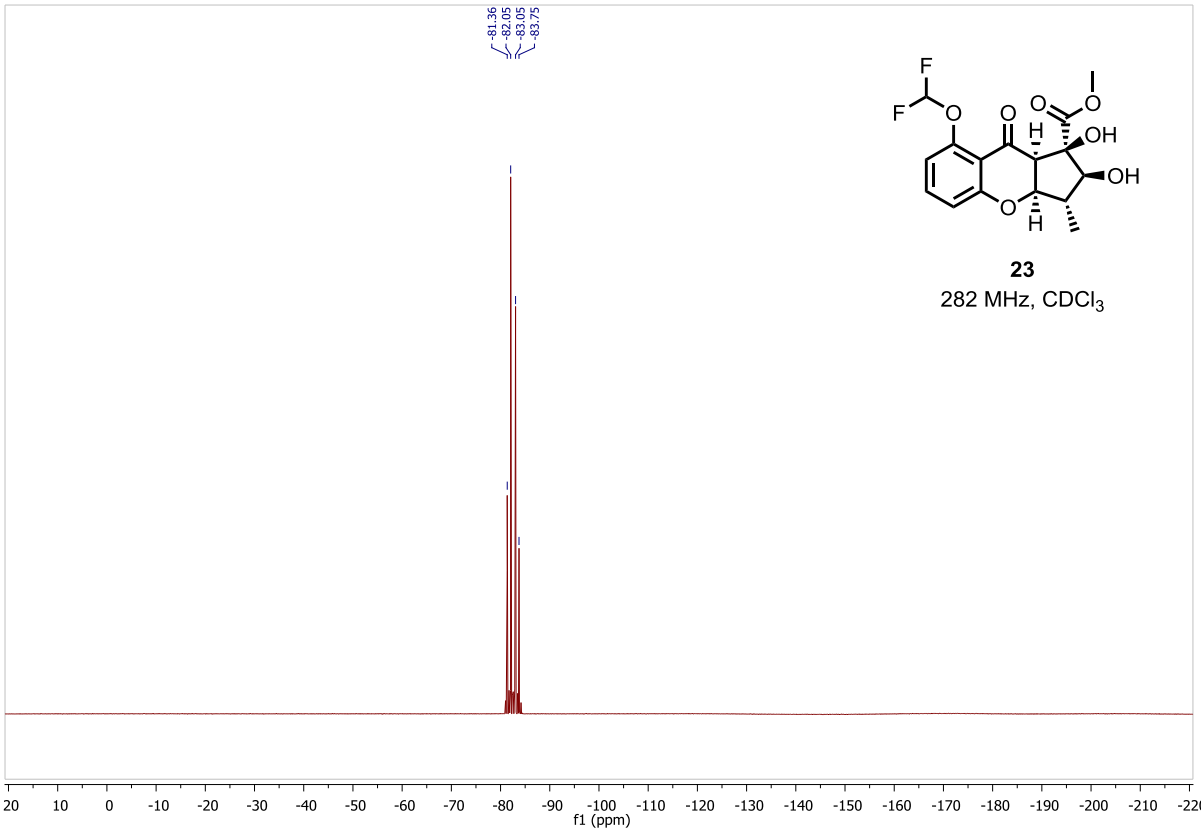
23

500 MHz, $CDCl_3$



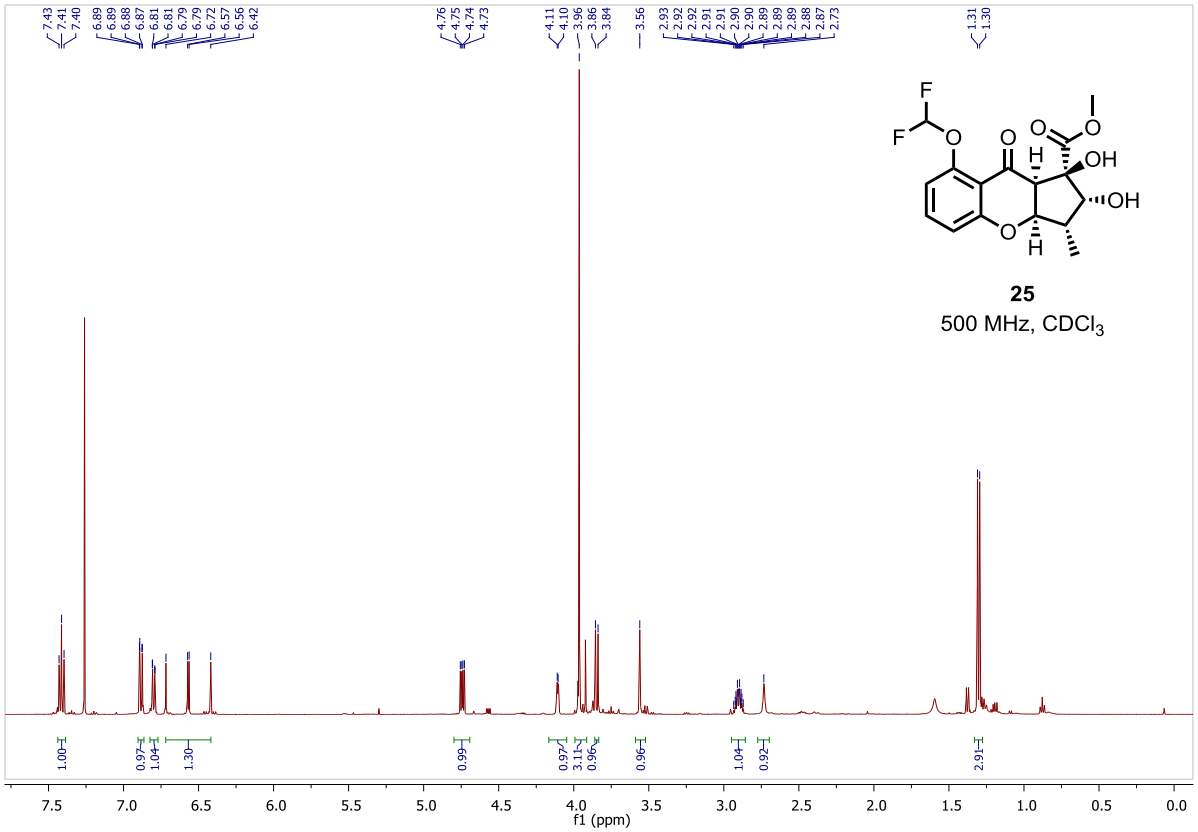
23

126 MHz, $CDCl_3$



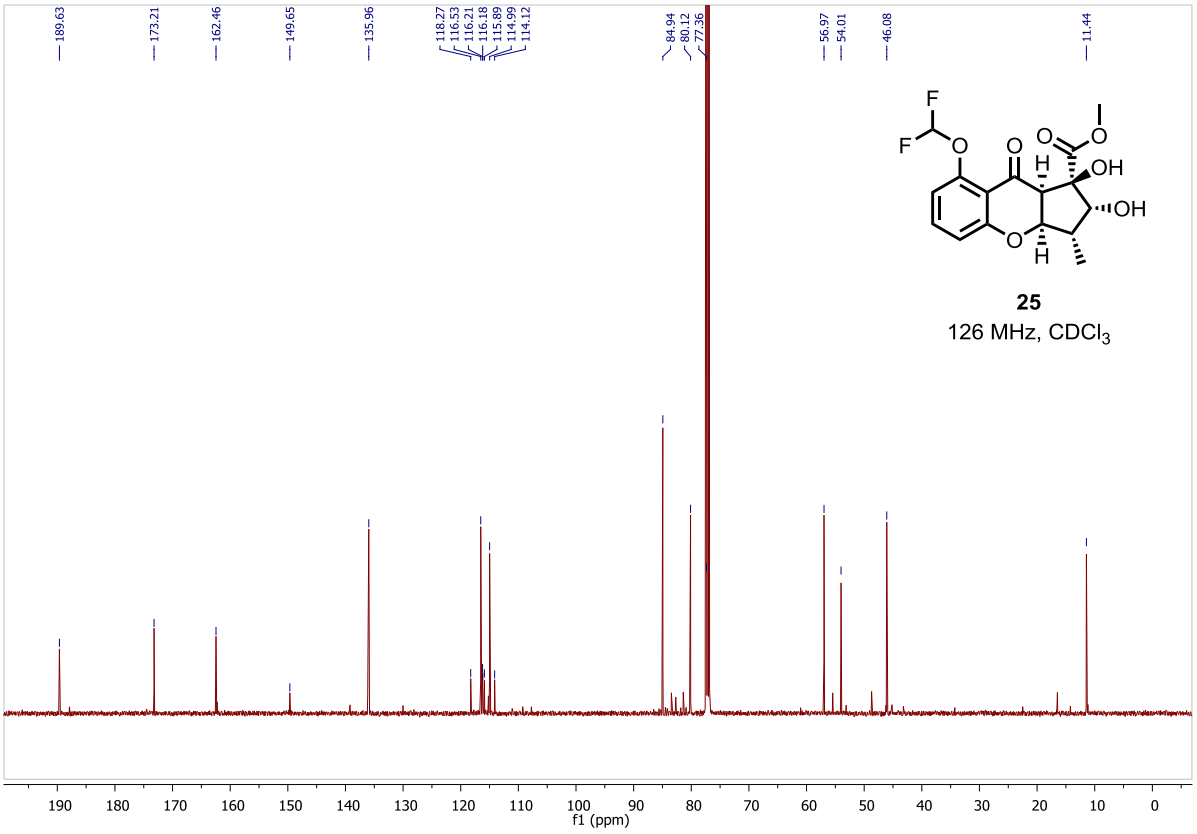
23

282 MHz, $CDCl_3$



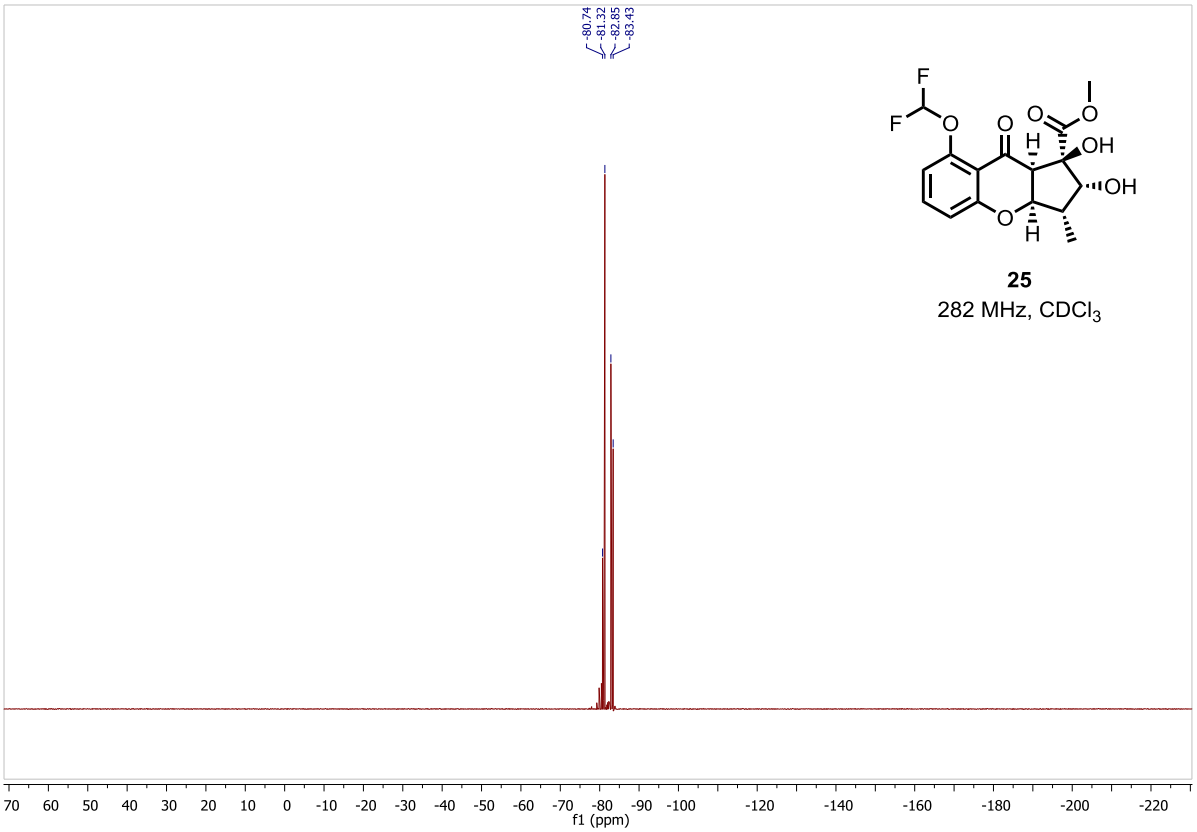
25

500 MHz, $CDCl_3$



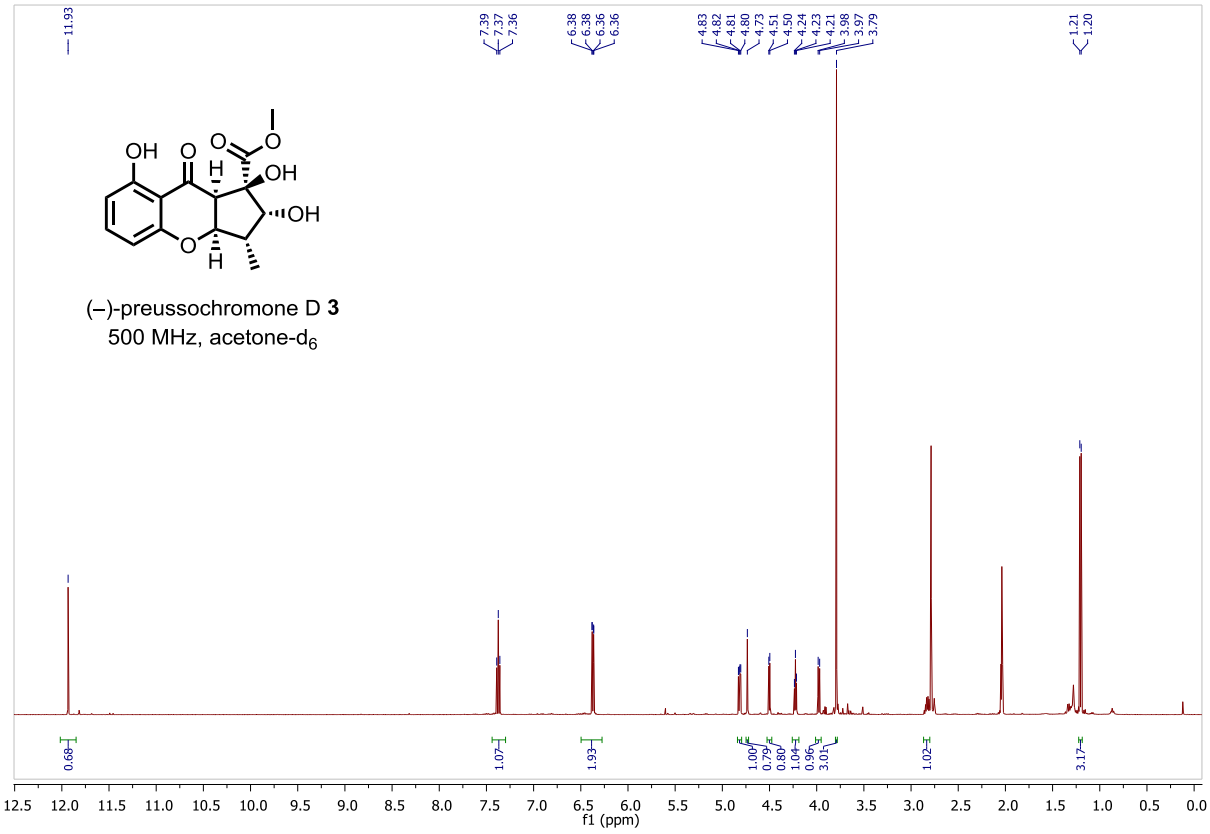
25

126 MHz, $CDCl_3$

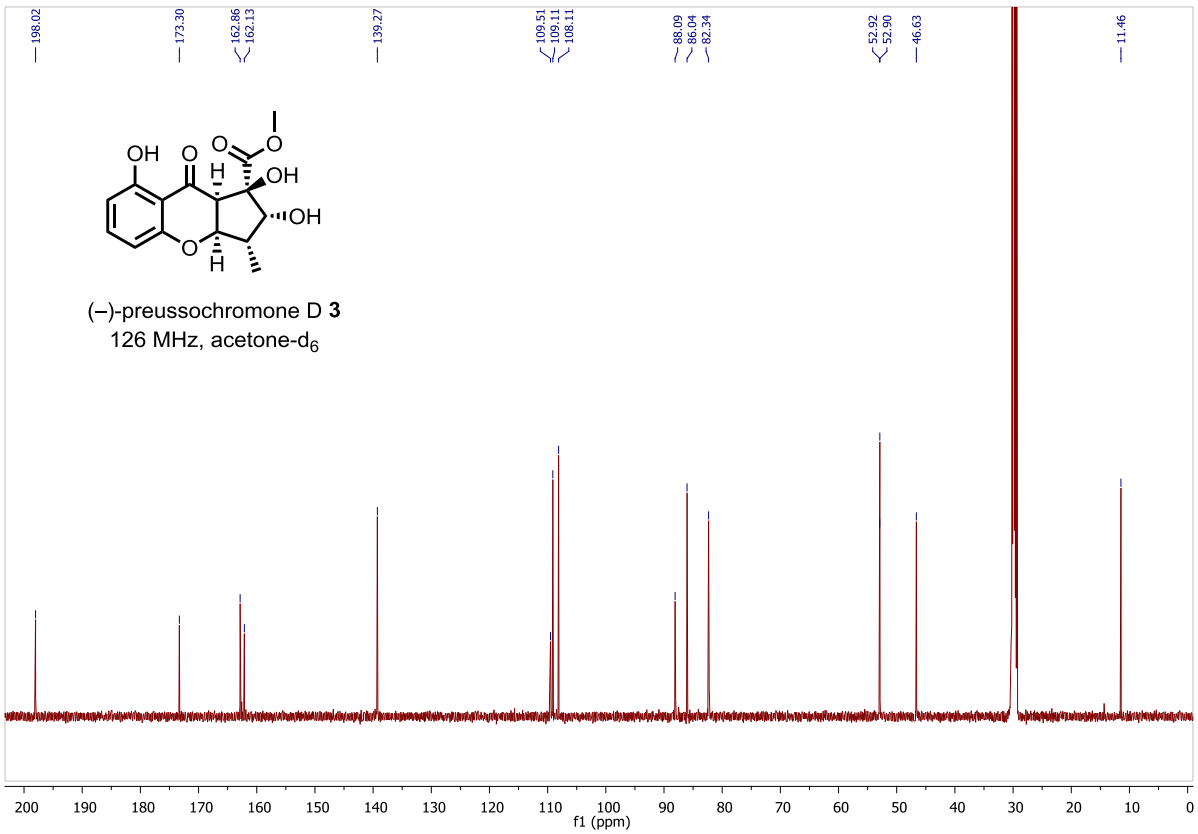


25

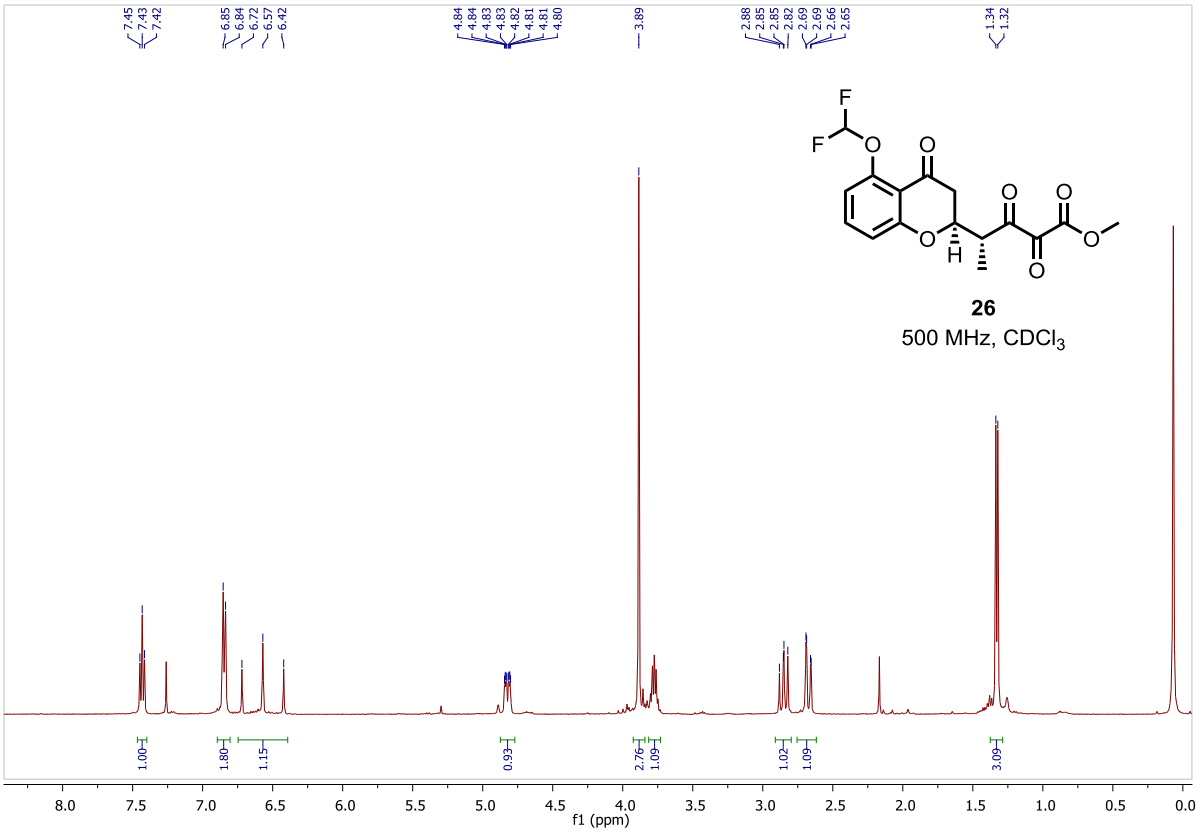
282 MHz, $CDCl_3$

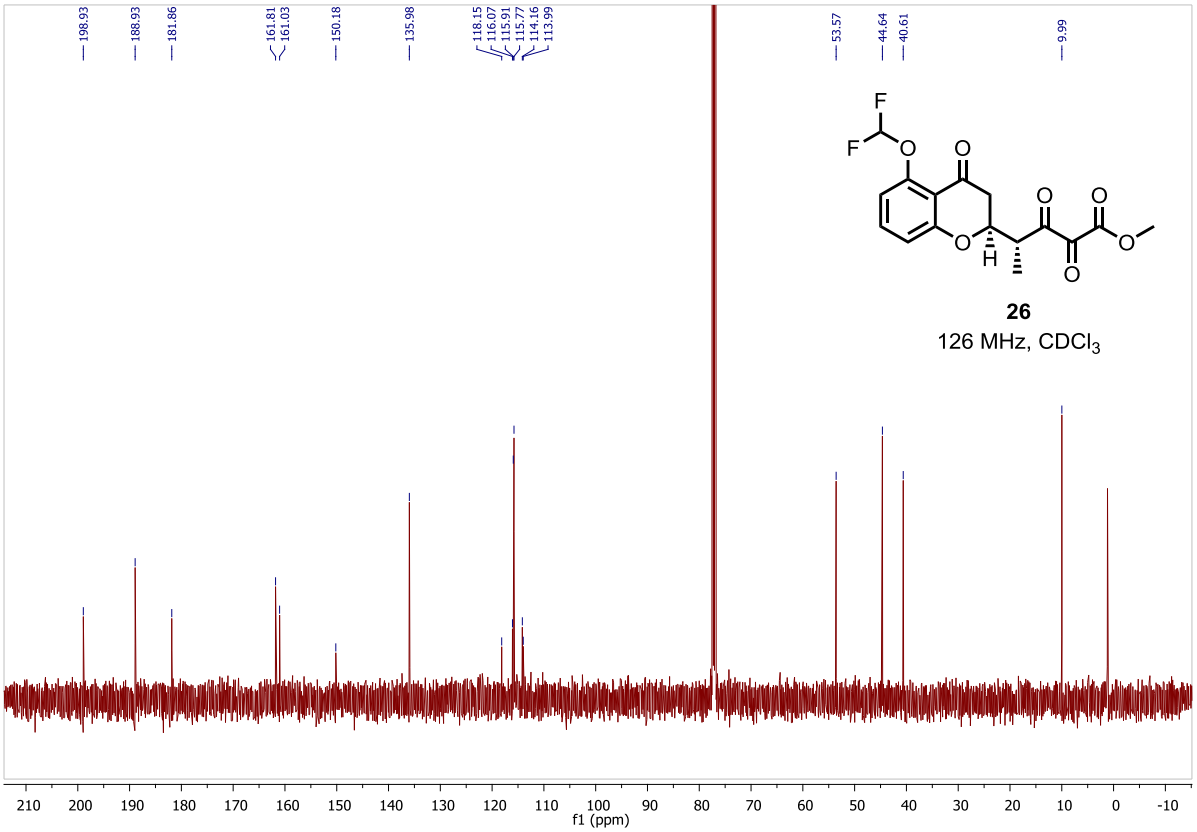


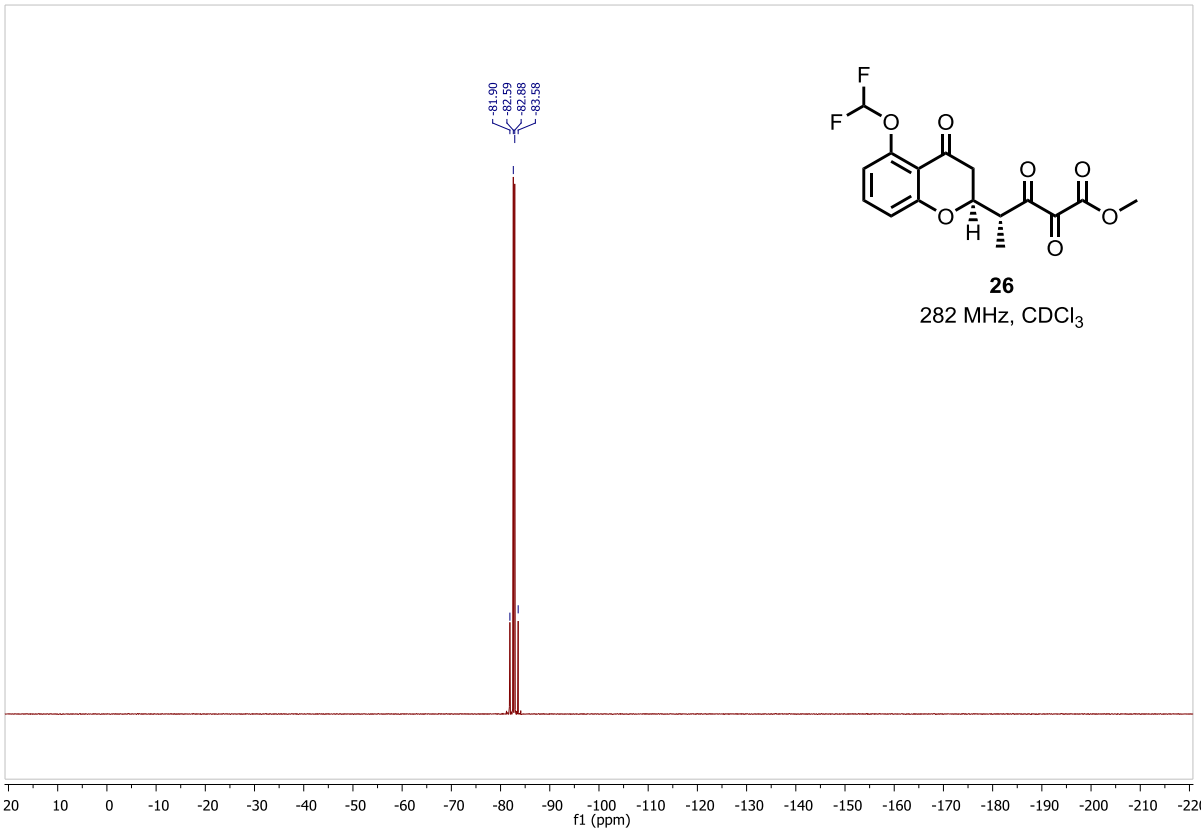
(–)-preussochromone D **3**
500 MHz, acetone-d_6



(–)-preussochromone D **3**
126 MHz, acetone-d_6

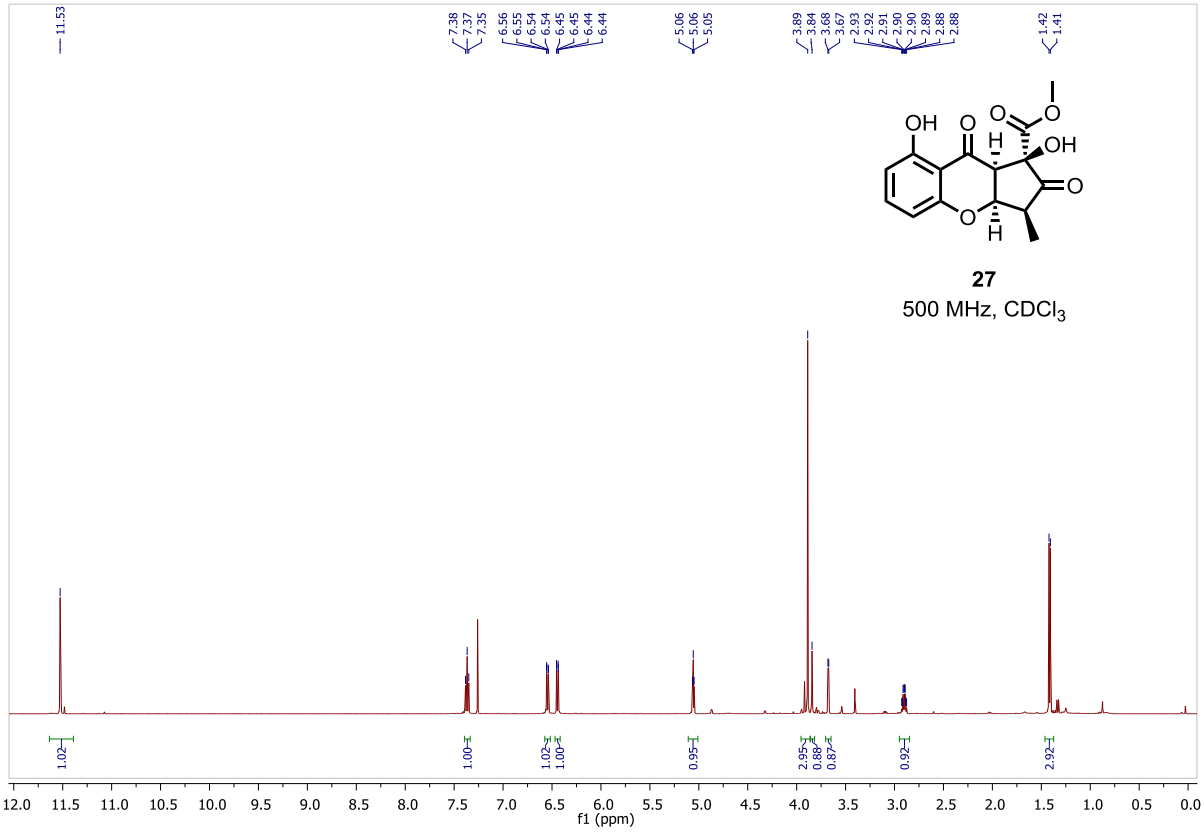

7.45
7.43
7.42
6.85
6.84
6.72
6.57
6.42
4.84
4.84
4.83
4.83
4.82
4.81
4.81
4.80
3.89
2.88
2.85
2.85
2.82
2.69
2.69
2.66
2.65
1.34
1.32
1.00
1.80
1.15
0.93
2.76
1.09
1.02
1.09
3.09
F
F
O
O
O
O
O
O
O
H
O
26
500 MHz, CDCl3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.93
188.93
181.86
161.81
161.03
150.18
135.98
118.15
116.07
115.91
115.77
114.16
113.99
53.57
44.64
40.61
9.99
F
F
O
O
O
O
O
O
O
H
O
26
126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



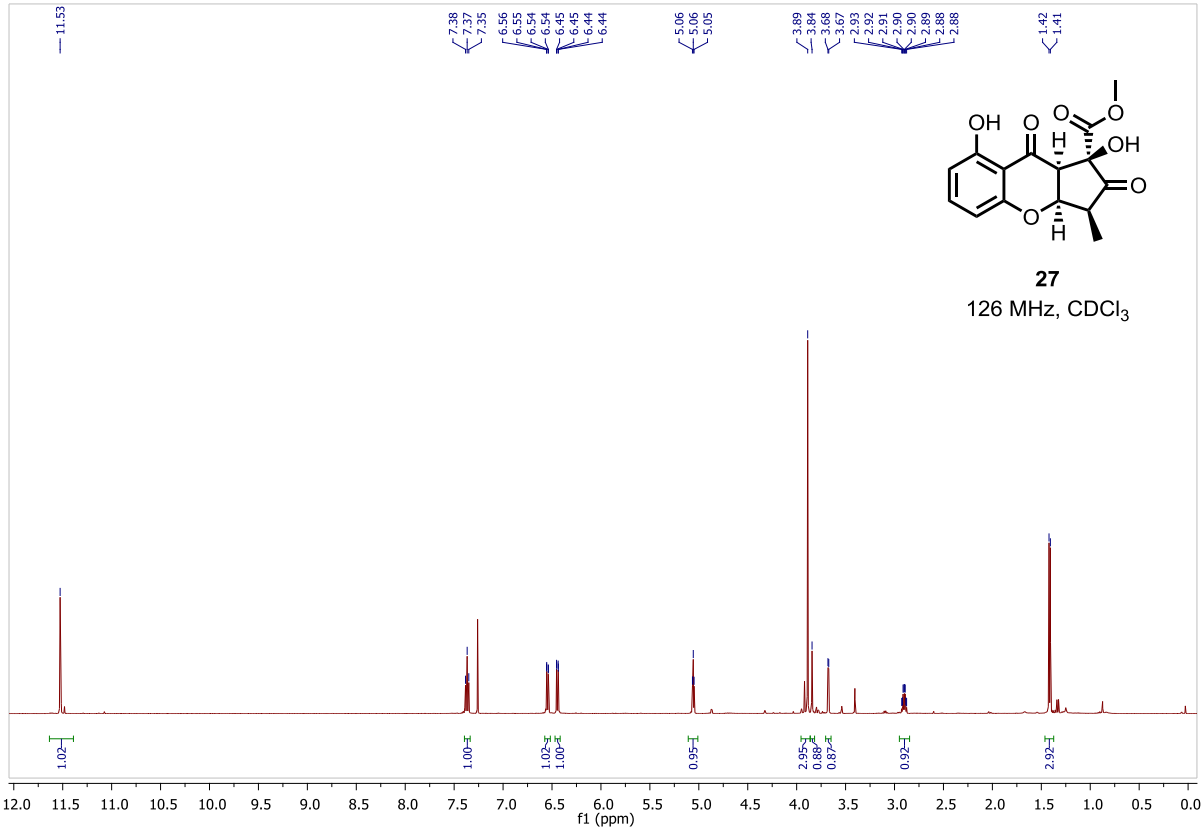
26

282 MHz, $CDCl_3$

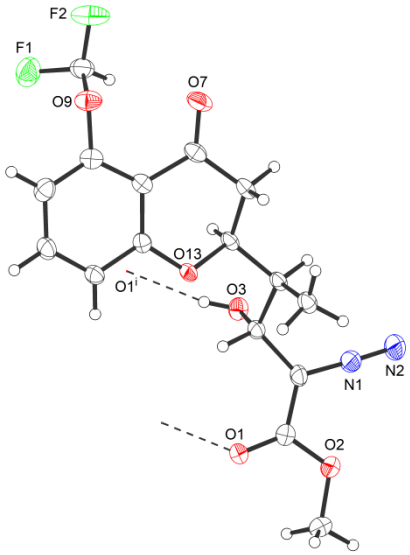


27

500 MHz, $CDCl_3$


11.53
7.38
7.37
7.35
6.56
6.55
6.54
6.54
6.45
6.45
6.44
6.44
5.06
5.06
5.05
3.89
3.84
3.68
3.67
2.93
2.92
2.91
2.90
2.90
2.89
2.88
2.88
1.42
1.41
OH
O
O
O
H
OH
O
O
H
27
126 MHz, CDCl3
1.02
1.00
1.02
1.08
0.95
2.95
0.88
0.87
0.92
2.92
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

4 X-Ray



Crystal data

Habitus, colour	plate, colourless	
Crystal size	0.32 x 0.13 x 0.03 mm^3	
Crystal system	Monoclinic	
Space group	$P2_1/c$	Z = 4
Unit cell dimensions	a = 14.9067(5) Å	α= 90°.
	b = 15.3584(4) Å	β= 90.112(3)°.
	c = 7.1490(2) Å	γ = 90°.
Volume	1636.71(8) $Å^3$	
Cell determination	11647 peaks with Theta 3.0 to 75.8°.	
Empirical formula	$C_{16}\ H_{16}\ F_2\ N_2\ O_6$	
Moiety formula	$C_{16}\ H_{16}\ F_2\ N_2\ O_6$	
Formula weight	370.31	
Density (calculated)	1.503 Mg/m^3	
Absorption coefficient	1.128 mm^{-1}	
F(000)	768	

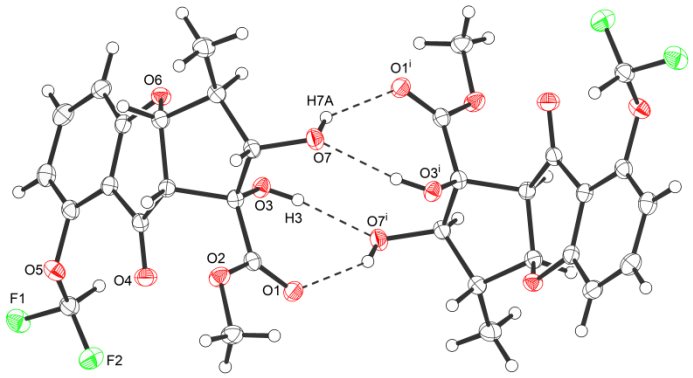
Data collection:

Diffractometer type	STOE STADIVARI
Wavelength	1.54186 Å
Temperature	100(2) K
Theta range for data collection	2.964 to 75.817°.
Index ranges	-18<=h<=18, -16<=k<=19, -8<=l<=6

Data collection software	X-Area Pilatus3_SV 1.31.127.0 (STOE, 2016) [12]
Cell refinement software	X-Area Recipe 1.33.0.0 (STOE, 2015)[13]
Data reduction software	X-Area Integrate 1.71.0.0 (STOE, 2016)[14]
	X-Area LANA 1.68.2.0 (STOE, 2016)[15]

Solution and refinement:

Reflections collected	18665
Independent reflections	3368 [R(int) = 0.0395]
Completeness to theta = 67.686°	99.9 %
Observed reflections	2638[I > 2σ(I)]
Reflections used for refinement	3368
Absorption correction	Semi-empirical from equivalents[15]
Max. and min. transmission	0.8468 and 0.3716
Largest diff. peak and hole	0.276 and -0.228 e.Å^{-3}
Solution	intrinsic phases[16]
Refinement	Full-matrix least-squares on F^2[17]
Treatment of hydrogen atoms	CH calculated, constr., OH located, isotr. ref.
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[16]
	SHELXL-2018/3 (Sheldrick, 2018)[17]
	DIAMOND (Crystal Impact)[18]
	ShelXle (Hübschle, Sheldrick, Dittrich, 2011)[19]
Data / restraints / parameters	3368 / 0 / 241
Goodness-of-fit on F^2	1.056
R index (all data)	wR2 = 0.1040
R index conventional [I>2sigma(I)]	R1 = 0.0373



Crystal data

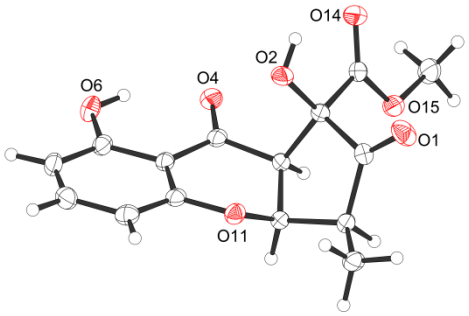
Habitus, colour	prism, colourless	
Crystal size	0.21 x 0.12 x 0.08 mm^3	
Crystal system	Monoclinic	
Space group	$P2_1/n$	Z = 4
Unit cell dimensions	a = 8.8431(3) Å	α= 90°.
	b = 8.7484(3) Å	β= 97.632(3)°.
	c = 19.8164(7) Å	γ = 90°.
Volume	1519.48(9) $Å^3$	
Cell determination	17360 peaks with Theta 4.5 to 76.1°.	
Empirical formula	$C_{16}\ H_{16}\ F_2\ O_7$	
Moiety formula	$C_{16}\ H_{16}\ F_2\ O_7$	
Formula weight	358.29	
Density (calculated)	1.566 Mg/m^3	
Absorption coefficient	1.204 mm^{-1}	
F(000)	744	

Data collection:

Diffractometer type	STOE STADIVARI
Wavelength	1.54186 Å
Temperature	100(2) K
Theta range for data collection	4.503 to 75.447°.
Index ranges	-10<=h<=11, -9<=k<=10, -24<=l<=16
Data collection software	X-Area Pilatus3_SV 1.31.127.0 (STOE, 2016) [12]
Cell refinement software	X-Area Recipe 1.33.0.0 (STOE, 2015)[13]
Data reduction software	X-Area Integrate 1.71.0.0 (STOE, 2016)[14]
	X-Area LANA 1.68.2.0 (STOE, 2016)[15]

Solution and refinement:

Reflections collected	15502
Independent reflections	3091 [R(int) = 0.0283]
Completeness to theta = 67.686°	99.7 %
Observed reflections	2659[I > 2σ(I)]
Reflections used for refinement	3091.
Absorption correction	Semi-empirical from equivalents[15]
Max. and min. transmission	0.8373 and 0.2650
Largest diff. peak and hole	0.331 and -0.231 e.Å^{-3}
Solution	intrinsic phases[16]
Refinement	Full-matrix least-squares on F^{2}[17]
Treatment of hydrogen atoms	CH calculated, constr., OH located, isotropic ref.
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[16]
	SHELXL-2018/3 (Sheldrick, 2018)[17]
	DIAMOND (Crystal Impact)[18]
	ShelXle (Hübschle, Sheldrick, Dittrich, 2011)[19]
Data / restraints / parameters	3091 / 0 / 236
Goodness-of-fit on F^{2}	1.053
R index (all data)	wR2 = 0.0888
R index conventional [I>2sigma(I)]	R1 = 0.0321



Crystal data

Habitus, colour	plate, colourless	
Crystal size	0.27 x 0.05 x 0.04 mm^3	
Crystal system	Monoclinic	
Space group	$P2_1/n$	Z = 4
Unit cell dimensions	a = 12.1155(3) Å	α= 90°.
	b = 10.1088(3) Å	β= 114.983(2)°.
	c = 12.2188(4) Å	γ = 90°.
Volume	1356.45(7) $Å^3$	
Cell determination	15585 peaks with Theta 4.3 to 76.2°.	
Empirical formula	$C_{15}\ H_{14}\ O_7$	
Moiety formula	$C_{15}\ H_{14}\ O_7$	
Formula weight	306.26	
Density (calculated)	1.500 Mg/m^3	
Absorption coefficient	1.028 mm^{-1}	
F(000)	640	

Data collection:

Diffractometer type	STOE STADIVARI
Wavelength	1.54178 Å
Temperature	100(2) K
Theta range for data collection	4.309 to 75.588°.
Index ranges	-15<=h<=11, -12<=k<=11, -7<=l<=15
Data collection software	X-Area Pilatus3_SV 1.31.127.0 (STOE, 2016) [12]
Cell refinement software	X-Area Recipe 1.33.0.0 (STOE, 2015)[13]
Data reduction software	X-Area Integrate 1.71.0.0 (STOE, 2016)[14]
	X-Area LANA 1.68.2.0 (STOE, 2016)[15]

Solution and refinement:

Reflections collected	14565

Independent reflections	2761 [R(int) = 0.0347]
Completeness to theta = 67.679°	99.2 %
Observed reflections	2394[I > 2σ(I)]
Reflections used for refinement	2761
Absorption correction	Semi-empirical from equivalents[15]
Max. and min. transmission	0.8582 and 0.5344
Largest diff. peak and hole	0.385 and -0.205 e.Å^{-3}
Solution	intrinsic phases[16]
Refinement	Full-matrix least-squares on F^2[17]
Treatment of hydrogen atoms	CH 'riding model'; OH located, isotropic refinement
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[16]
	SHELXL-2018/3 (Sheldrick, 2018)[17]
	DIAMOND (Crystal Impact)[18]
	ShelXle (Hübschle, Sheldrick, Dittrich, 2011)[19]
Data / restraints / parameters	2761 / 97 / 229
Goodness-of-fit on F^2	1.082
R index (all data)	wR2 = 0.1088
R index conventional [I>2sigma(I)]	R1 = 0.0386

5 Literature

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