Supporting Information

Total Synthesis of Solandelactone I

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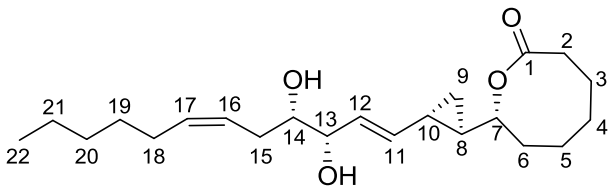
1. General numbering



2. Procedures

1-Iodohept-1-yne (11). In a flame-dried Schlenk flask equipped with a magnetic stirring bar under N_2 atmosphere 51.1 mL of 2.5 M *n*-butyl lithium solution in hexanes (124.7 mmol, 1.00 eq) were added to a solution of 1-heptyne (**7**) (16.4 mL, 12.0 g, 124.8 mmol) in 60 mL Et_2O at -50 °C over 30 min. Stirring was continued for 30 min at the same temperature. The solution was cooled to -70 °C (formation of white solid was observed), then a solution of iodine (31.70 g, 124.7 mmol, 1.00 eq) in 170 mL of Et_2O performed under inert conditions was added dropwise over 1 h. Upon completion of addition the cooling bath was removed and the reaction was allowed to reach room temperature (rt) while stirring. The reaction mixture was washed three times with 150 mL H_2O, then dried over $MgSO_4$ and filtered. After evaporation of the solvent the product **11** (22.40 g, 100.8 mmol, 81%) was isolated as colorless oil (under storage it turned into slight red) by vacuum distillation (bp 69-70 °C; 7 mbar). Analytical data are in agreement with those previously reported (Ravid, U.; Silverstein, R. M.; Smith, L. R. *Tetrahedron* **1978**, *34*, 1449-1452). R_f (80/20 PE/EtOAc): 0.74; FT IR ν_{max} 2956, 2927, 2859, 1466, 1428, 1378, 1326, 1107, 729 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 0.90 (3H, t, $^3J_{7,6}$ = 7.1 Hz, H-7), 1.28-1.38 (4H, m, H-5, H-6), 1.51 (2H, m_c, H-4), 2.35 (2H, t, $^3J_{3,4}$ = 7.2 Hz, H-3). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: -7.6 (C-1), 14.1 (C-7), 20.9 (C-5), 22.3 (C-6), 28.3 (C-4), 31.1 (C-3), 95.0 (C-2). GC/MS *m/z* 222 (79) [M^+], 207 (2), 165 (94), 127 (53), 95 (100).

(*Z*)-1-Iodohept-1-ene (12). A solution of 10 M BH_3*Me_2S (9.00 mL, 90.1 mmol, 1.00 eq) in 90 mL Et_2O at 0 °C was place in a flame-dried Schlenk flask. Freshly distilled cyclohexene (18.24 mL, 180.1 mmol, 2.00 eq) was added while stirring with a magnetic stirring bar. After 10 min the ice bath was removed and the reaction mixture was stirred for further 50 min at rt (formation of precipitate). Then the mixture was cooled to 0 °C again and 1-iodoheptyne (**11**) (20.00 g, 90.06 mmol, 1.00 eq) was added within 10 min and the mixture was stirred for further 30 min at this temperature. Upon

removal of the cooling bath the reaction mixture was stirred for another hour, leading to full consumption of the previously observed precipitate. The solution was cooled to 0 °C again and 45 mL glacial acetic acid were added within 15 min. After 2 h of stirring, 50 mL Et_2O were added and the solution was washed four times with 40 mL H_2O and dried over $MgSO_4$. After evaporation of the solvents, alkene **12** (13.32 g, 59.5 mmol, 66%) was obtained by distillation under reduced pressure (bp.: 63-64 °C, 6-7 mbar). Analytical data are in agreement with those previously reported (Ravid, U.; Silverstein, R. M.; Smith, L. R. *Tetrahedron* **1978**, *34*, 1449-1452).

R_f (80/20 PE/EtOAc): 0.86; FT IR ν_{max} 2956, 2926, 2856, 1608, 1458, 1378, 1334, 1296, 1276, 1233, 1174, 1097, 989, 729, 686 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz) δ 0.90 (3H, t, $^3J_{7,6}$ = 7.2 Hz, H-7), 1.28-1.36 (4H, m, H-5, H-6), 1.43 (2H, m_c, H-4), 2.13 (2H, m_c, H-3), 6.15-6.19 (2H, m, H-1, H-2); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 14.2 (C-7), 22.6 (C-6), 27.8 (C-4), 31.4 (C-5), 34.8 (C-3), 82.2 (C-1), 141.7 (C-2). GC/MS *m/z*: 224 (86) [M^+], 127 (30), 97 (68).

(*S*)-(−)-2-Bromo-3-hydroxypropanoic acid (16). L-Serine (24.00 g, 228.0 mmol, 1.00 eq) and KBr (92.40 g, 776.5 mmol, 3.40 eq) were dissolved in 185 mL of H_2O in a three-necked-flask equipped with a magnetic stirring bar, gas inlet tube and a washing bottle (KOH solution). At room temperature, 56.3 mL of 48 % hydrobromic acid were added and the reaction was cooled to -15 °C afterwards. Subsequently seven portions of sodium nitrite (19.70 g, 285.5 mmol, 1.25 eq; ~2.80 g every 15 min) were added to the reaction mixture while bubbling N_2 gently. After addition of sodium nitrite was complete, N_2 bubbling was stopped after 1.5 h and the reaction was stirred for further 6 h at 0 °C. The reaction was then stirred while bubbling N_2 for 40 min before it was extracted six times with 200 mL Et_2O and dried over $MgSO_4$. Solvent was removed at 25 °C under reduced pressure using a rotary evaporator. The obtained almost pure product **16** (31.00 g, 183.5 mmol, 80%) was used without further purification in the next step.

R_f (EtOAc): 0.58; ^1H NMR ($CDCl_3$, 600 MHz) δ 4.00 (2H, d, $^3J_{3,2}$ = 6.01 Hz, H-3), 4.52 (1H, t, $^3J_{2,3}$ = 6.03 Hz, H-2); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 47.4 (C-2), 63.6 (C-3), 173.0 (C-1); GC/MS *m/z* 169 (<1) [M^+], 122 (42) [M^+-COOH], 89 (15) [M^+-Br].

Potassium (*R*)-(+)-2,3-epoxypropanoate (17). Crude **16** was dissolved in 120 mL freshly distilled abs. EtOH and cooled to -20 °C. A solution of KOH (<86%, 25.40 g, 452.70 mmol, 2.46 eq) in 130 mL freshly distilled abs. EtOH was filtered and added to previously formed solution of **16**. After 1.5 h the temperature was set to 0 °C and the reaction mixture was stirred for 17 h. The formed precipitate was collected by filtration; the filtrate was reduced to half of its volume and cooled to 0 °C. The precipitate was filtered off again and the combined solids were dried under vacuum. The obtained solids were split into three portions. Each portion was dissolved in 224 mL of EtOH and 6 mL H_2O and heated to reflux for 30 min, then the solution was directly filtered hot. The precipitate formed upon cooling down of the filtrate was collected, and the mother liquor was used for the next extraction. After extraction of all three portions the filtration residues of all three approaches were also extracted using the mother liquor a fourth time. All collected precipitates of the cooled filtrates were combined and dried under vacuum. The fluffy solid (12.30 g, max. 97.50 mmol, max. 53%) was applied in the next reaction step without titrimetric determination of residual KBr content. ^{1}H NMR (D_2O, 600 MHz) δ 2.81 (1H, dd, $^2J_{3a,3b}$ = 5.8 Hz, $^3J_{3a,2}$ = 2.8 Hz, H-3a), 2.97 (1H, dd, $^2J_{3b,3a}$ = 5.8 Hz, $^3J_{3b,2}$ = 4.9 Hz, H-3b), 3.39 (1H, dd, $^3J_{2,3b}$ = 4.8 Hz, $^3J_{2,3a}$ = 2.8 Hz, H-2). ^{13}C NMR (D_2O, 151 MHz) δ 46.0 (C-3), 49.4 (C-2), 176.8 (C-1). Analytical data are in agreement to those previously reported (Petit, Y.; Larchevêque, M. *Org. Synth., Coll. Vol*. **1998**, *10*, 401).

Ethyl (*R*)-(+)-2,3-epoxypropanoate (8). In a round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser with drying tube potassium salt **17** (12.3 g, max. 97.5 mmol, 1.00 eq), benzyltriethylammonium chloride (22.2 g, 97.5 mmol, 1.00 eq) and bromoethane (27.3 mL, 365.6 mmol, 3.75 eq) were dissolved in 150 mL CH_2Cl_2. The reaction mixture was heated to reflux for 5 h, and then it was stirred at rt for 17 h and finally heated to reflux for 6 h. The solvent and excess of bromoethane were removed on rotary evaporator (22 °C; 560-120 mbar). The remaining solid was triturated with 4 x 60 mL Et_2O. The ethereal solution was then dried over $MgSO_4$ and filtered. After evaporation (22 °C), the obtained crude **8** was purified *via* vacuum distillation (44-47 °C; 3.8 mbar). Compound **8** (7.58 g, 65.30 mmol, 67%; 28% over three steps) was obtained as analytically pure and clear liquid and stored in a refrigerator. Analytical data are in agreement to those reported (Petit, Y.; Larchevêque, M. *Org. Synth., Coll. Vol*. **1998**, *10*, 401). R_f (80/20 PE/EtOAc): 0.42; $[\alpha]_D^{25} + 31.4$ (*c*

1.26, $CHCl_3$); FT IR ν_{max} 2987, 1746, 1469, 1411, 1387, 1288, 1251, 1199, 1145, 1096, 1080, 1030, 915, 858, 821, 751, 674 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.30 (3H, t, $^3J_{2',1'}$ = 7.2 Hz, H-2'), 2.93 (1H, dd, $^2J_{3a,3b}$ = 6.5 Hz, $^3J_{3a,2}$ = 4.2 Hz, H-3a), 2.96 (1H, dd, $^2J_{3b,3a}$ = 6.5 Hz, $^3J_{3b,2}$ = 2.4 Hz, H-3b), 3.43 (1H, dd, $^3J_{2,3a}$ = 4.2 Hz, $^3J_{2,3b}$ = 2.4 Hz, H-2), 4.24 (2H, m_c, H-1'); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 14.2 (C-2'), 46.4 (C-3), 47.5 (C-2), 61.8 (C-1'), 169.4 (C-1); GC/MS *m/z* 115 (2), 71 (100).

Ethyl (*S*)-(-)-2,3-epoxypropanoate (*ent*-8): *Ent*-**8** (10.05 g, 86.50 mmol, 38% over three steps) has been synthesized in full analogy to compound **8**.

$[\alpha]_D^{25} - 29.4$ (*c* 1.02, $CHCl_3$). The remaining data correspond to those of compound **8**.

Ethyl (*R,Z*)-2-hydroxydec-4-enoate (**13**):

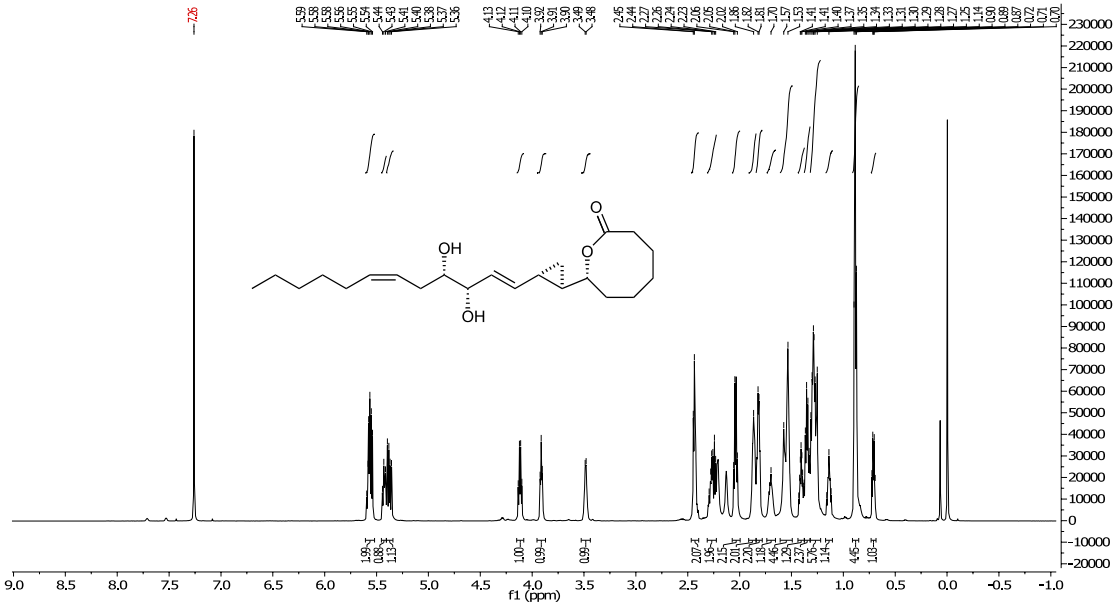
i) Preparation of organolithium reagent solution: In analogy to a procedure by Whitesides and coworkers (Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc*. **1971**, 1379-1389) lithium beads (846 mg, 106 mmol, 4.50 eq) and 28 mL Et_2O were cooled to -30 °C in a flame-dried and argon-purged Schlenk flask while stirring. (*Z*)-iodoheptene (**12**) (5.30 g, 23.7 mmol, 1.00 eq) was dissolved in 7 mL Et_2O and added to the lithium beads *via* cannula through a septum. The reaction mixture was stirred vigorously for 1.5 h. The completion of conversion was determined by hydrolysis of an aliquot using 0.5 M aq HCl solution and extraction with EtOAc followed by GC/MS analysis. Thus obtained solution of organolithium reagent was titrated according to a procedure by Duhamel and Plaquevent (Duhamel, L.; Plaquevent, J.-C. *J. Organomet. Chem.* **1993**, *448*, 1-3) and found to be 0.59 M. Stirring was stopped and the solids were allowed to settle, enabling withdrawal of the formed solution by syringe needle.

ii) Preparation of cyano diorganocopper reagent solution/ring-opening reaction: In a separate Schlenk flask CuCN (866.00 mg, 9.67 mmol, 1.00 eq) was dried for 2 h at 120 °C under high vacuum. In analogy to a procedure by Lipshutz and Barton (Lipshutz, B. H.; Barton, J. C. *J. Org. Chem*. **1988**, *53*, 4495-4499) the Cu(I) salt was suspended in 12 mL THF and cooled to -78 °C. Previously prepared 0.59 M heptenyl lithium solution in Et_2O (33.0 mL, 19.3 mmol, 2.00 eq) was added to the CuCN suspension, then the acetone/dry ice cooling bath was removed. The stirred reaction mixture was allowed to warm up while stirring until the mixture became clear, then it was immediately cooled

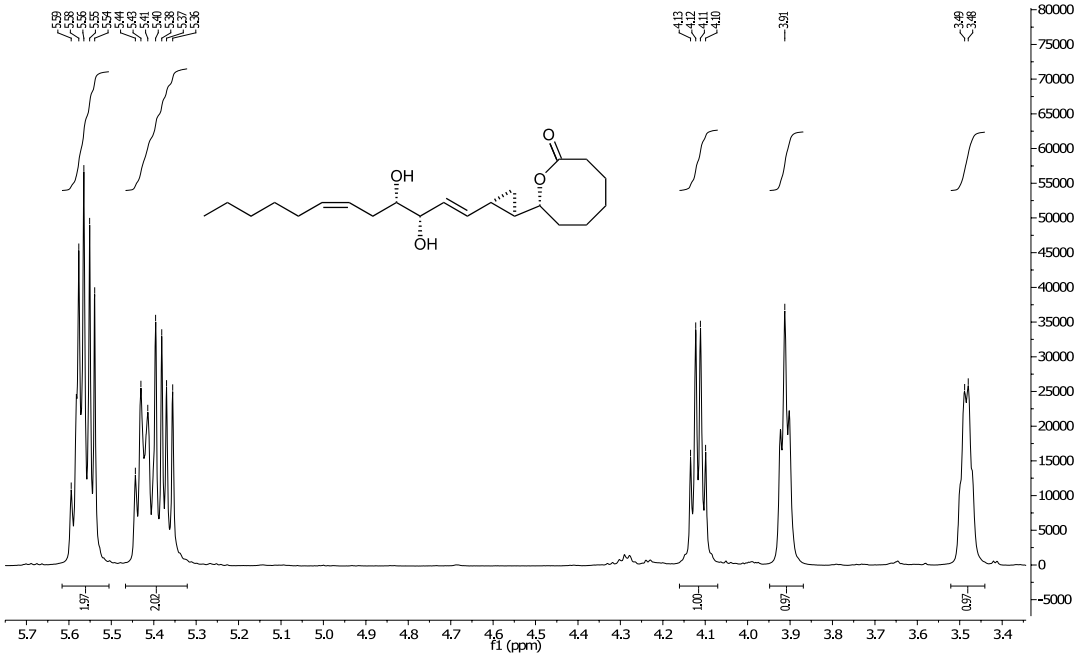
again to -78 °C again. In the next step, a solution of oxirane **8** (1.20 g, 10.6 mmol, 1.10 eq) in 8 mL THF was added via syringe. The cooling bath was removed and the reaction was allowed to reach room temperature. The reaction mixture was hydrolyzed by addition of 20 mL sat aq NH_4Cl and 2 mL 25 % aq NH_3 solution. The aqueous layer was extracted with 3 x 50 mL Et_2O. The combined organic layers were washed with 50 mL H_2O and 50 mL brine. The organic layer was dried over $MgSO_4$ and filtered, then the solvent was evaporated under reduced pressure. The desired product **13** (1.80 g, 8.30 mmol, 86%) was isolated by column chromatography on silica (85/15 PE/EtOAc) as colorless oil. Analytical data are in agreement to those previously reported (Larchevêque, M.; Petit, Y. *Bull. Soc. Chim. Fr.* **1989**, 130). R_f (80/20 PE/EtOAc): 0.35. $[\alpha]_D^{20}$ -12.5 (*c* 1.16, $CHCl_3$); FT IR ν_{max} 3476, 2958, 2928, 2858, 1735, 1466, 1369, 1267, 1206, 1094, 1029, 862, 726 cm^{-1};^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.30 (3H, t, $^3J_{2',1'}$ = 7.25 Hz, H-2'), 1.24-1.37 (6H, m, H-7, H-8, H-9), 2.04 (2H, m_c, H-6), 2.44-2.50 (1H, m, H-3a), 2.52-2.58 (1H, m, H-3b), 2.75 (1H, s_b, *OH*), 4.24 (1H, m, H-1'), 4.20-4.28 (1H m, H-2), 5.38 (1H, dtt, $^3J_{4,5}$ = 10.8 Hz, $^3J_{4,3}$ = 7.3 Hz, $^4J_{4,6}$ = 1.6 Hz, H-4), 5.57 (1H, dtt, $^3J_{5,4}$ = 10.8 Hz, $^3J_{5,6}$ = 7.3 Hz, $^4J_{5,3}$ = 1.6 Hz, H-5); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 14.2 (C-10), 14.4 (C-2'), 22.7 (C-9), 27.5 (C-6), 29.4 (C-7), 31.7 (C-8), 32.4 (C-3), 61.8 (C-1'), 70.4 (C-2), 122.8 (C-4), 134.2 (C-5), 174.8 (C-1). HRMS (ESI) *m/z* 237.1458 (calcd for $C_{12}H_{22}O_3Na$, 237.1461); HPLC [Chiralpak IC, 250*10 mm, Fa. Diacel; heptane/isopropanol 95/5; 0.5 mL/ min, 205 nm]: 17.5 min; *ee* = 98 %.

Ethyl (*S*,*Z*)-2-hydroxydec-4-enoate (***ent*-13)**: Compound *ent*-**13** was prepared in full analogy to the synthesis of the enantiomeric compound **13** using a 0.55 M (*Z*)-hept-1-en-1-yllithium solution (35.00 mL, 19.14 mmol, 2.00 eq), 857.00 mg of CuCN (9.57 mmol, 1.00 eq) and oxirane *ent*-**8** (1.22 g, 10.5 mmol, 1.10 eq). The desired product could be isolated as pure and colorless oil in 81% yield (1.67 g, 7.79 mmol). $[\alpha]_D^{20}$ $+11.8$ (*c* 1.00, $CHCl_3$); HPLC [Chiralpak IC, 250*10 mm, Fa. Diacel; heptane/isopropanol 95/5; 0.5 mL/ min, 205 nm]: 19.1 min; *ee* = >99%. The remaining analytical data correspond to the enantiomeric compound **13**.

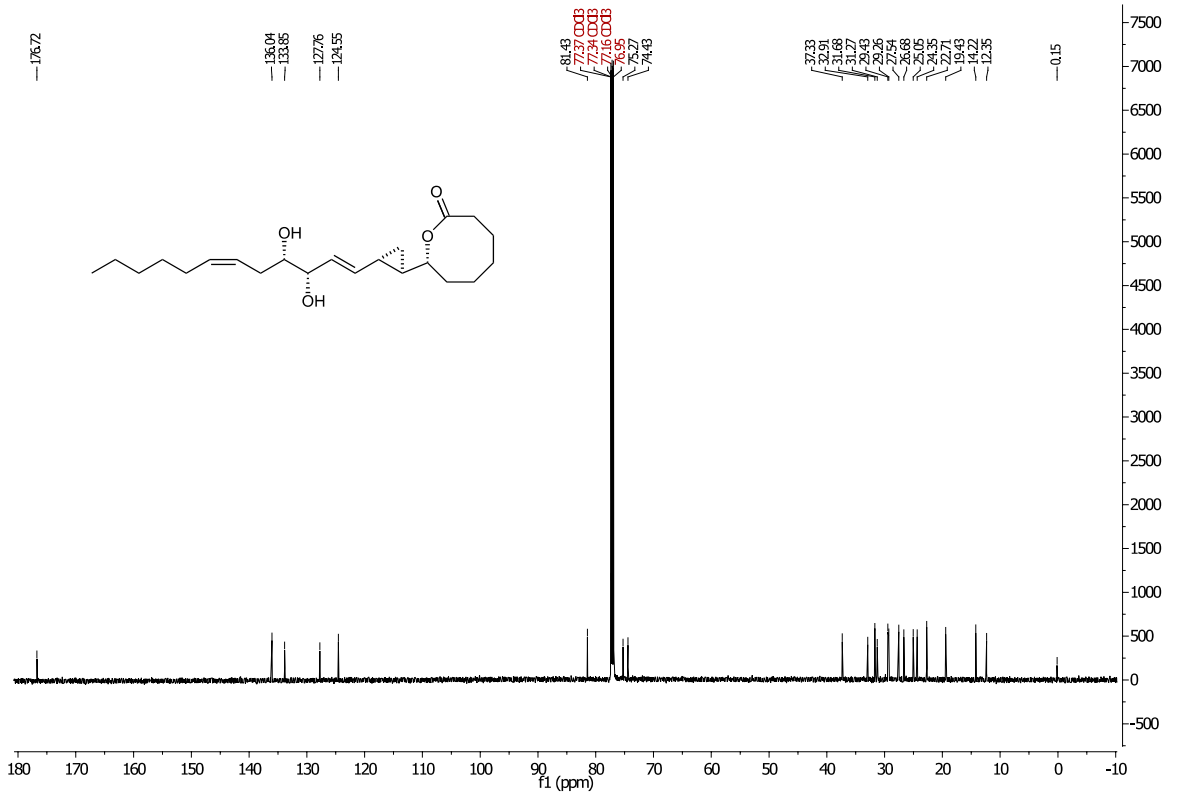
3. NMR Spectra



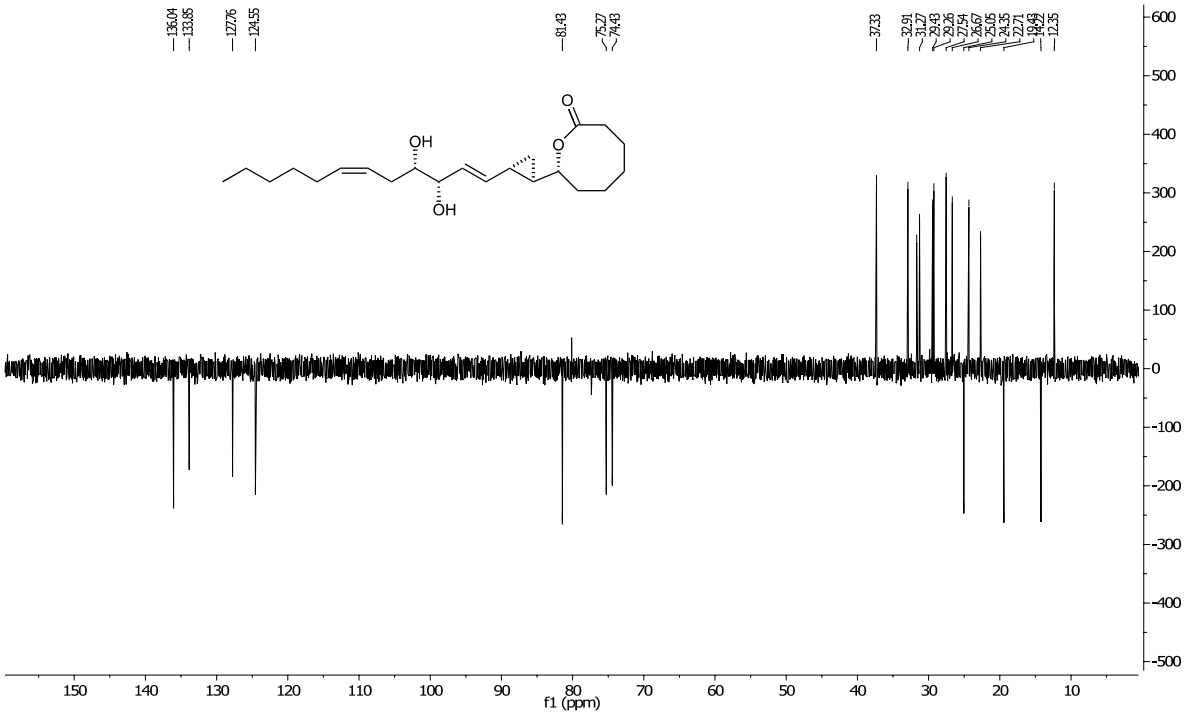
S 1: ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3**.



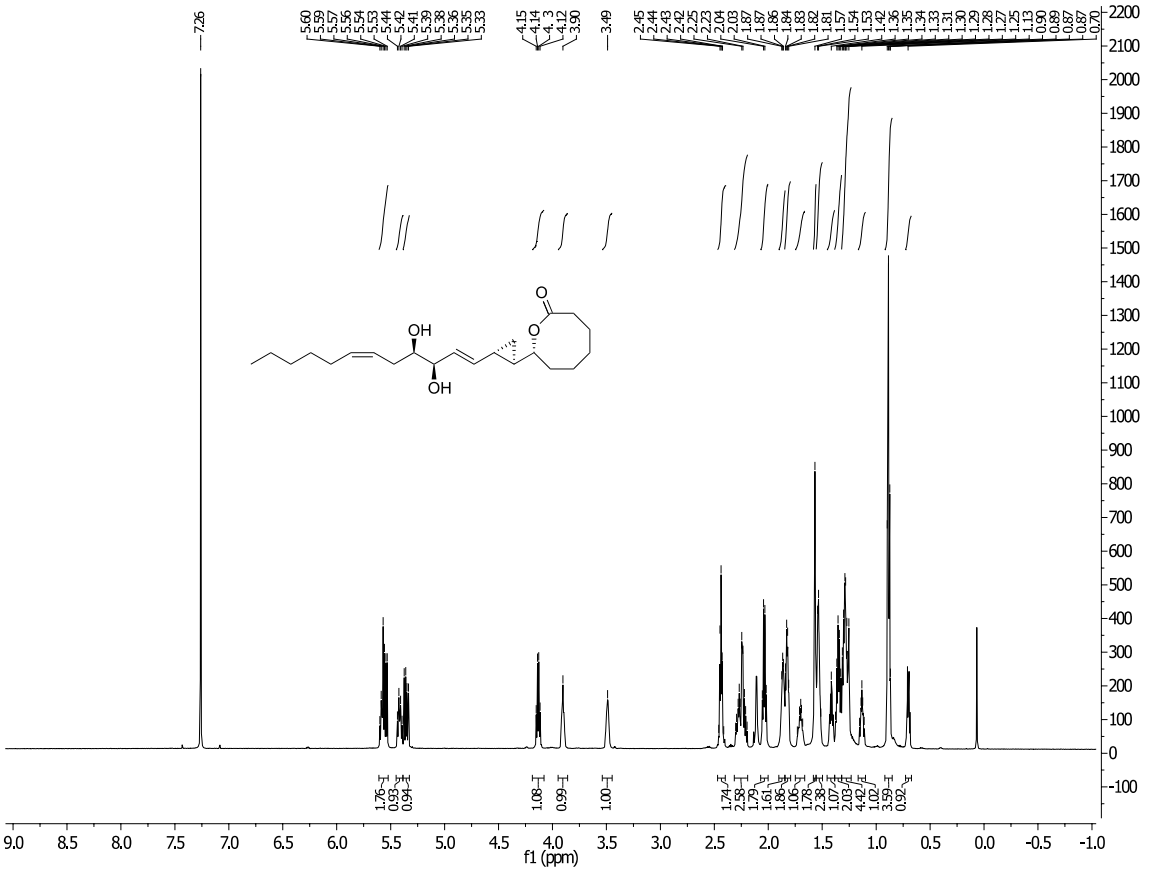
S 2: ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3**.



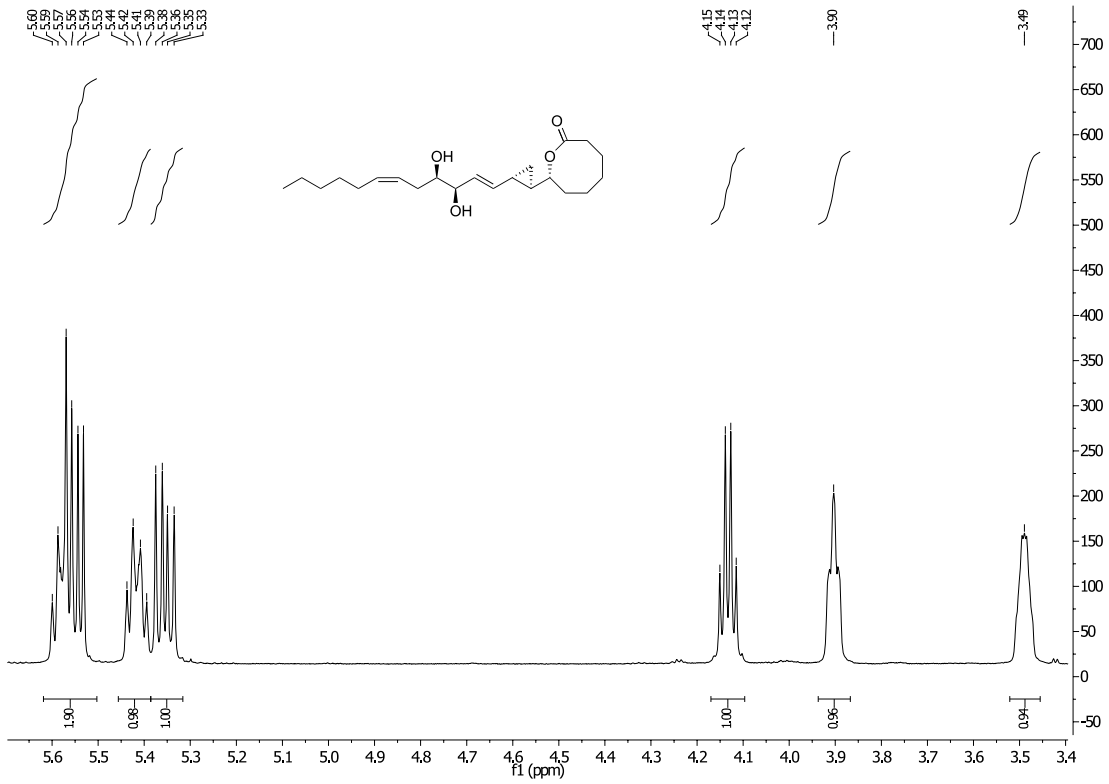
S 3: ^{13}C-NMR (151 MHz, $CDCl_3$) of compound **3**.



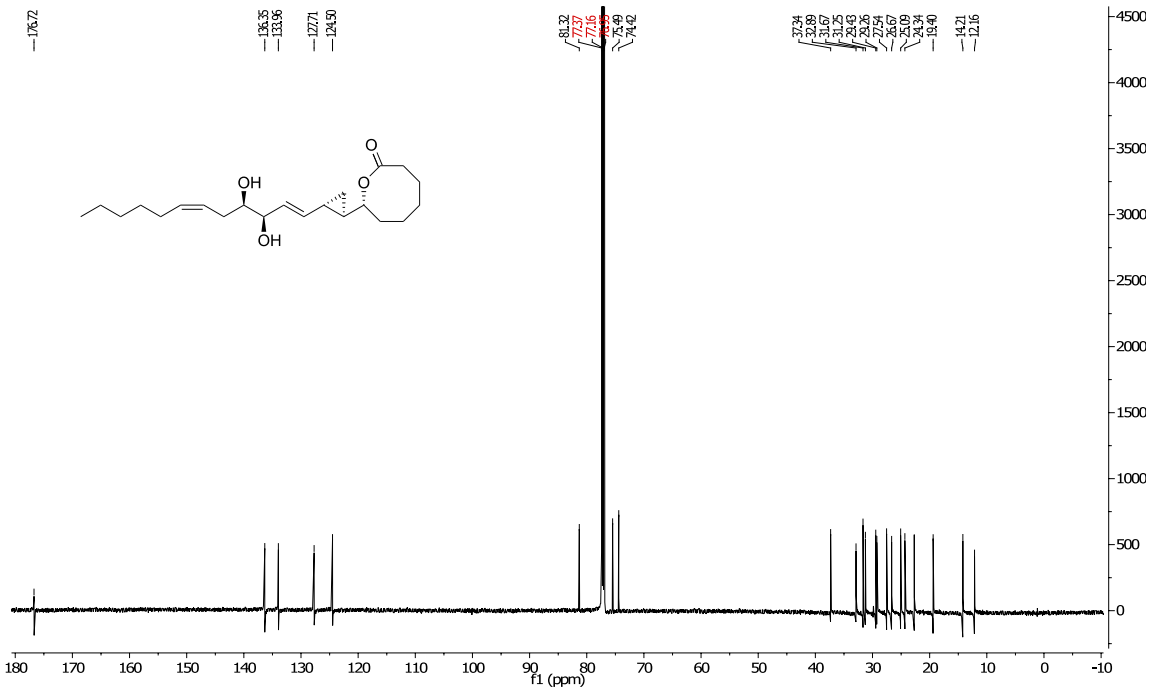
S 4: DEPT 135 NMR (600 MHz, $CDCl_3$) of compound **3**.



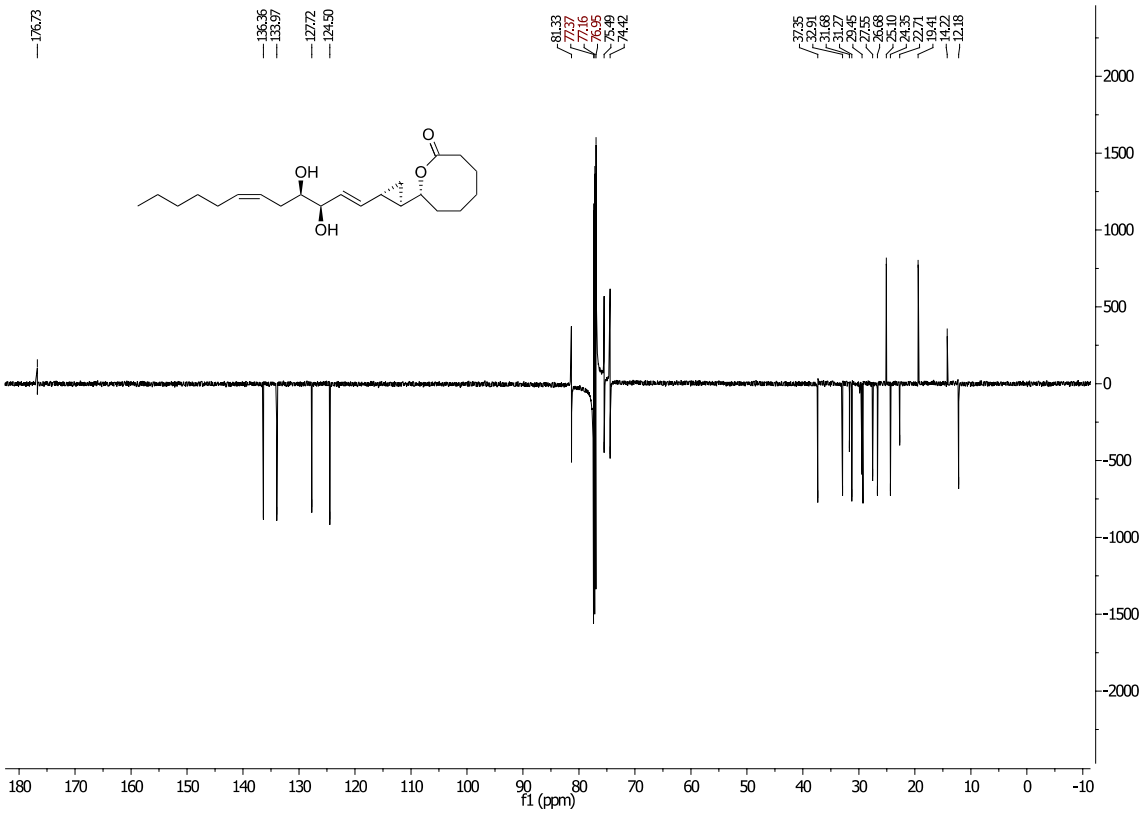
S 5: ^{1}H NMR (600 MHz, $CDCl_3$) of compound **1**.



S 6: ^{1}H NMR (600 MHz, $CDCl_3$) of compound **1**.



S 7: ^{13}C NMR (151 MHz, $CDCl_3$) of compound **1**.

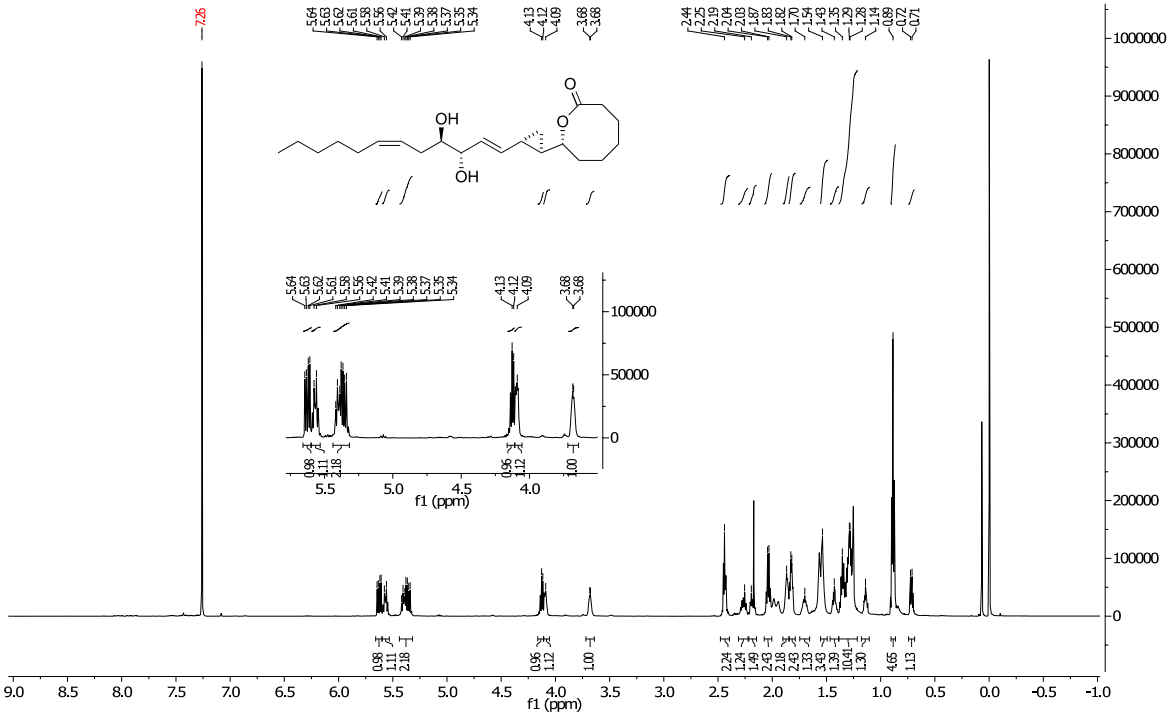


S 8*:* DEPT 135 (151 MHz, $CDCl_3$) of compound **1**.

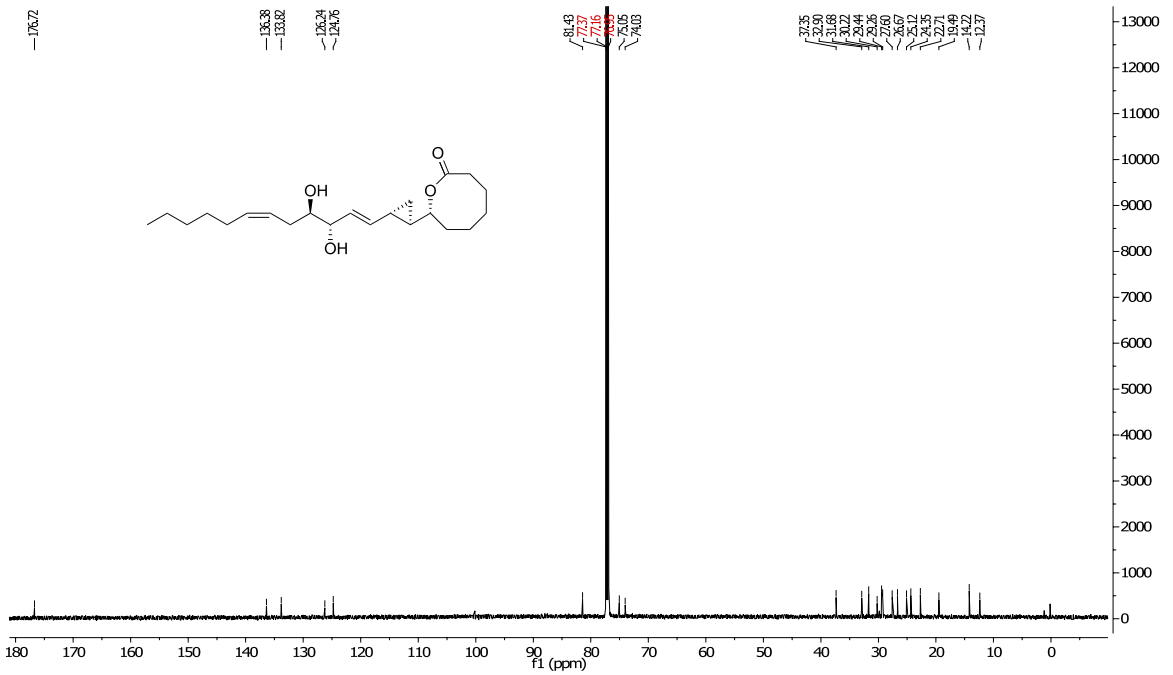
Table 1. Comparison of the NMR data of compound **1** and **3** with the literature known one

	Diastereomer **3***		Diastereomer **1***		**Solandelactone I**** (according to *Seo et al.*)	
position	δ_C [ppm], structural moiety; $\Delta\delta$ [ppm]	δ_H(*J* in Hz)	δ_C [ppm], structural moiety; $\Delta\delta$ [ppm]	δ_H(*J* in Hz)	δ_C [ppm], structural moiety;	δ_H(*J* in Hz)
1	176.72, CO +0.10	-	176.72, CO +0.10	-	176.62, CO	-
2	32.91, CH_2 +0.22	2.40-2.47, m	32.89, CH_2 +0.20	2.40-2.47, m	32.69, CH_2	2.44, m
3	29.43, CH_2 +0.19	1.84-1.89, m	29.43, CH_2 +0.19	1.84-1.91, m	29.24, CH_2	1.87, m
4	26.68, CH_2 +0.22	1.66-1.75, m H-4_a, 1.55-1.62, m, H-4_a	26.67, CH_2 +0.21	1.66-1.73, m H-4_a, 1.55-1.60, m, H-4_a	26.46, CH_2	1.70, m, H-4_a 1.56, m, H-4_b
5	24.35, CH_2 +0.20	1.48-1.55, m	24.34, CH_2 +0.19	1.50-1.55, m	24.15, CH_2	1.54, m
6	37.33, CH_2 +0.20	1.79-1.84, m	37.34, CH_2 +0.19	1.79-1.84, m	37.13, CH_2	1.82, m
7	81.43, CH +0.14	4.12, m_c	81.32, CH +0.03	4.13, m_c	81.29, CH	4.12, dt (6.3, 7.6)
8	25.05, CH +0.19	1.14, m_c	25.09, CH +0.23	1.13, m_c	24.86, CH	1.14, m
9	12.35, CH_2 +0.19	0.71, m_c, H-9_a 0.87-0.90, m, H-9_b	12.16, CH_2 +0.00	0.71, m_c, H-9_a 0.87-0.90, m, H-9_b	12.16, CH_2	0.90, ddd,(8.3, 5.4, 5.4), H-9a; 0.71, ddd, (8.3, 5.4, 5.4), H-9b
10	19.43, CH +0.19	1.41, m_c	19.40, CH +0.16	1.42, m_c	19.24, CH	1.41, m
11	136.04, CH +0.42	5.38, dd (8.7, 15.4)	136.35, CH +0.73	5.37, dd (8.7, 15.4)	135.62, CH	5.37, dd (15.1, 8.3)
12	127.76, CH +0.16	5.56, dd (7.0, 15.3)	127.71, CH +0.11	5.56, dd (7.1, 15.4)	127.60, CH	5.56, dd (15.1, 6.3)
13	75.27, CH +0.17	3.91, m_c	75.49, CH +0.39	3.91, m_c	75.10, CH	3.92, dd (6.3, 6.3)
14	74.43, CH +0.14	3.48, m_c	74.42, CH +0.13	3.49, m_c	74.29, CH	3.49, ddd (7.8, 6.3, 4.8)
15	31.27, CH +0.20	2.21-2.30, m	31.25, CH +0.18	2.21-2.30, m	31.07, CH	2.25, m
16	124.55, CH +0.13	5.42, m_c	124.50, CH +0.08	5.42, m_c	124.42, CH	5.42, dtt (9.8, 7.8, 1.5)
17	133.85, CH +0.30	5.54-5.60, m (overlapped)	133.96, CH +0.41	5.53-5.60, m (overlapped)	133.55, CH	5.57, dtt (9.8, 7.3, 1.5)
18	27.54, CH_2 +0.19	2.04, m_c	27.54, CH_2 +0.18	2.04, m_c	27.36, CH_2	2.04, dt (6.8, 7.1)
19	29.27, CH_2 +0.02	1.32-1.38, m_c	29.26, CH_2 +0.01	1.33-1.38, m_c	29.25, CH_2	1.35, m
20	31.68, CH_2 +0.18	1.20-1.32, m	31.67, CH_2 +0.17	1.20-1.32, m	31.50, CH_2	1.30, m
21	22.71, CH_2 +0.09	1.20-1.32, m	22.70, CH_2 +0.08	1.20-1.32, m	22.62, CH_2	1.27, m
22	14.22, CH_3 +0.19	0.89, t (7.1)	14.21, CH_3 +0.18	0.89, t (7.0)	14.03, CH_3	0.89, t (6.8)

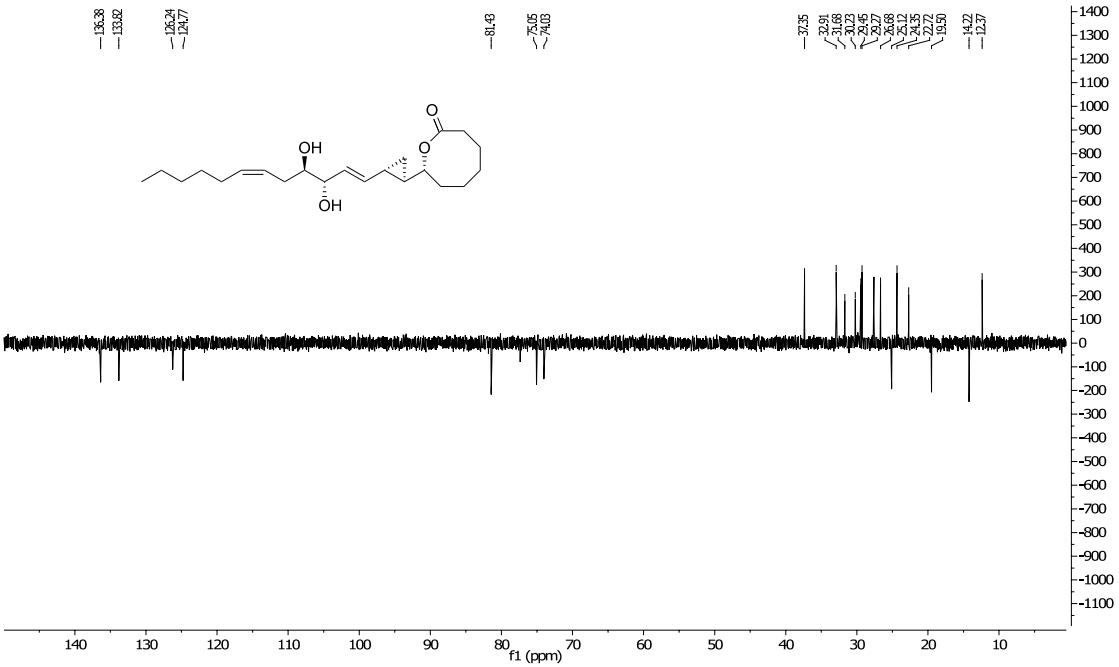
*NMR measured in $CDCl_3$ (600 MHz); **NMR measured in $CDCl_3$ (500 MHz)



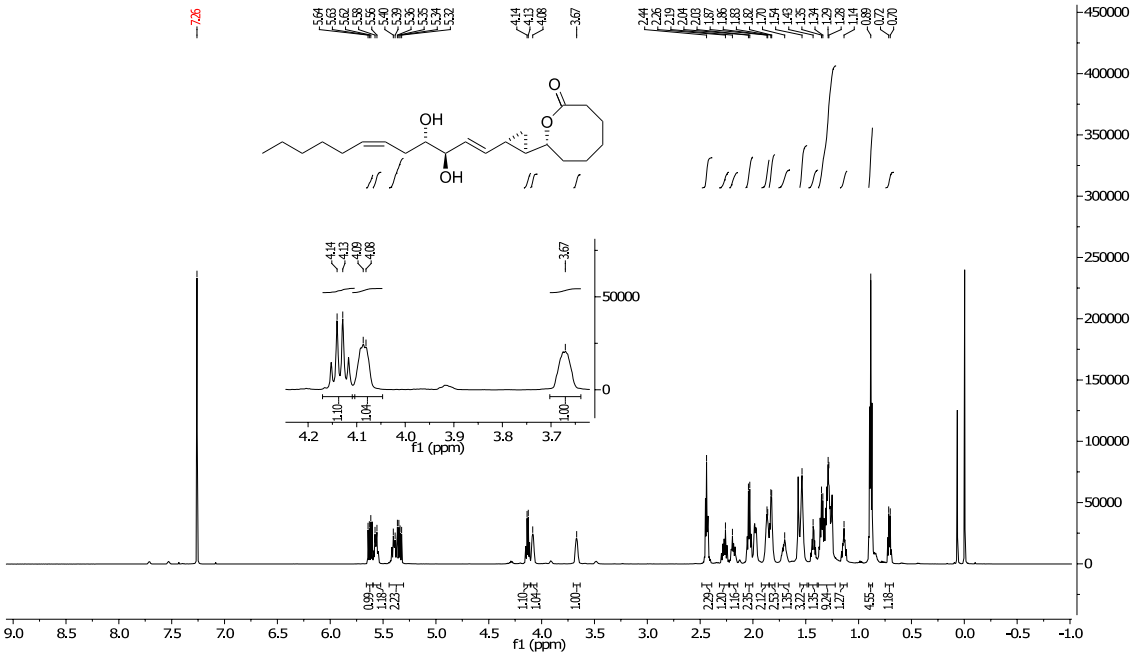
S 9: ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2** [contains impurities of water and acetone resulting in higher integrals in the alkyl region].



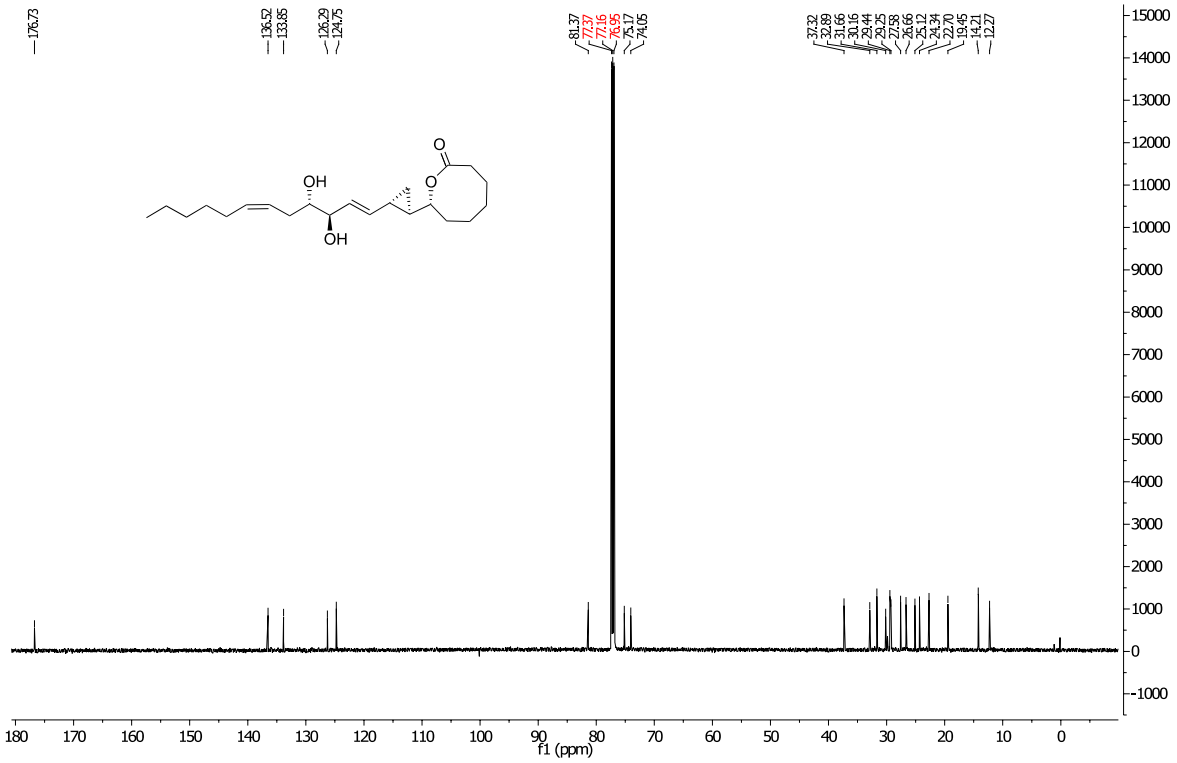
S 10: ^{13}C NMR (151 MHz, $CDCl_3$) of compound **2**.



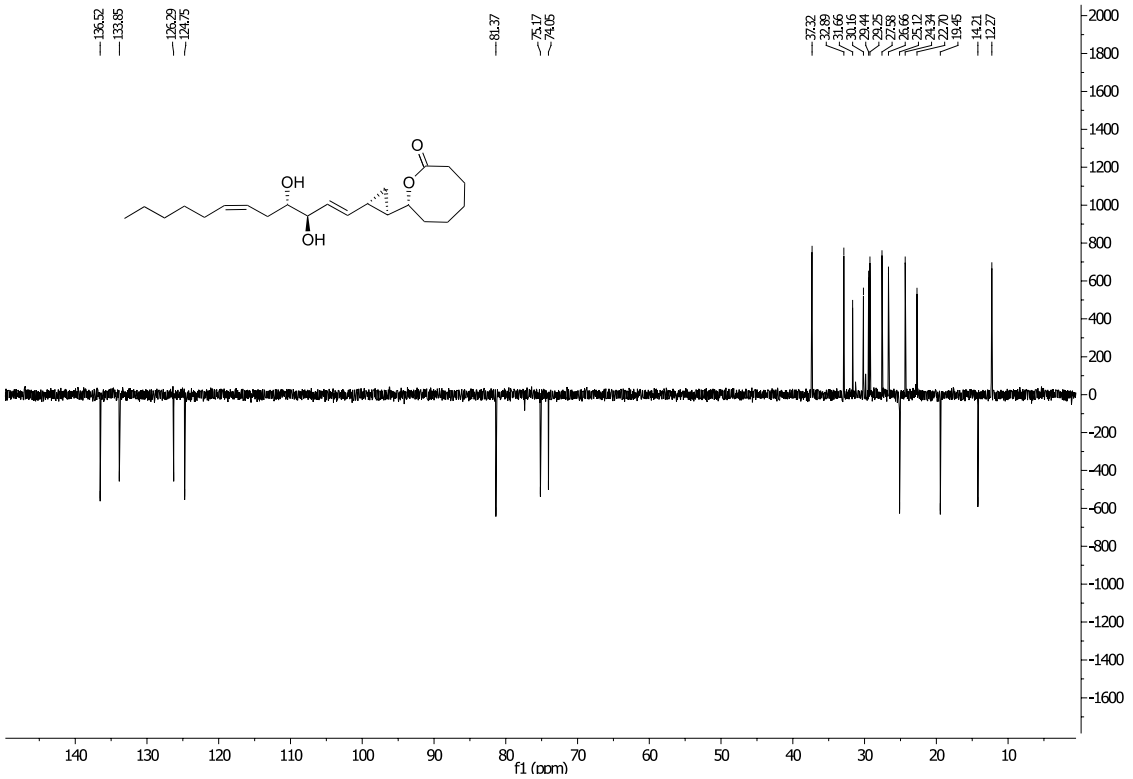
S 11: DEPT 135 (151 MHz, $CDCl_3$) of compound **2**.



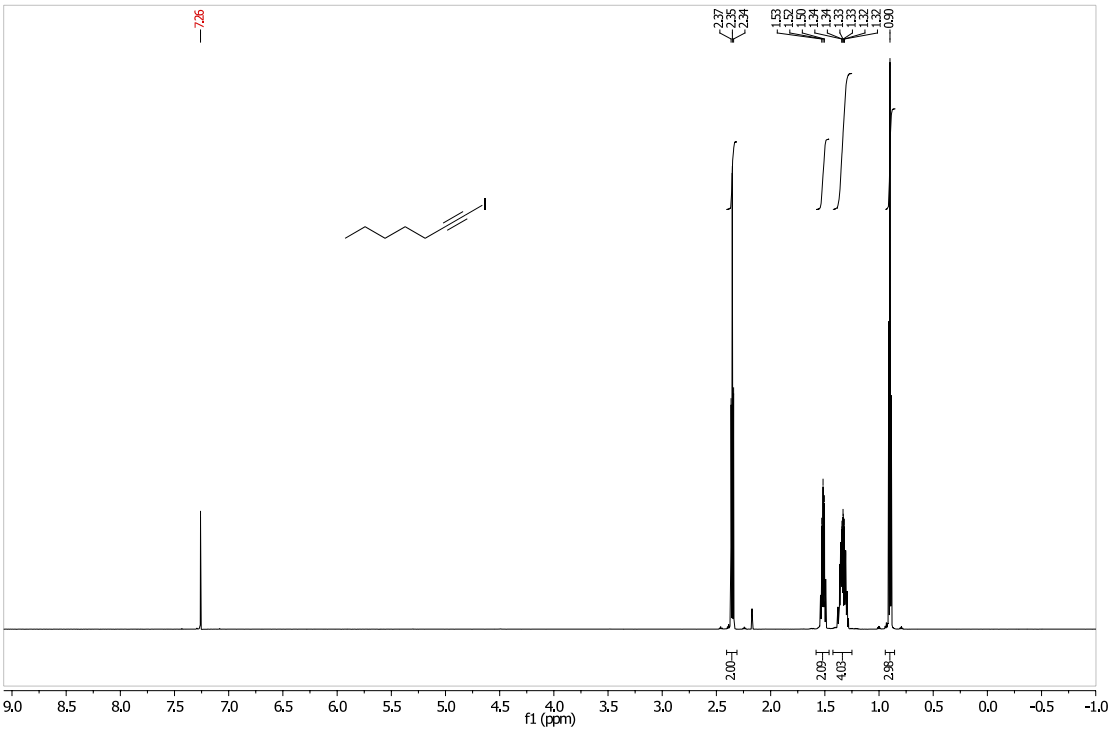
S 12: ^{1}H NMR (600 MHz, $CDCl_3$) of compound **4** [contains signals of remaining water]



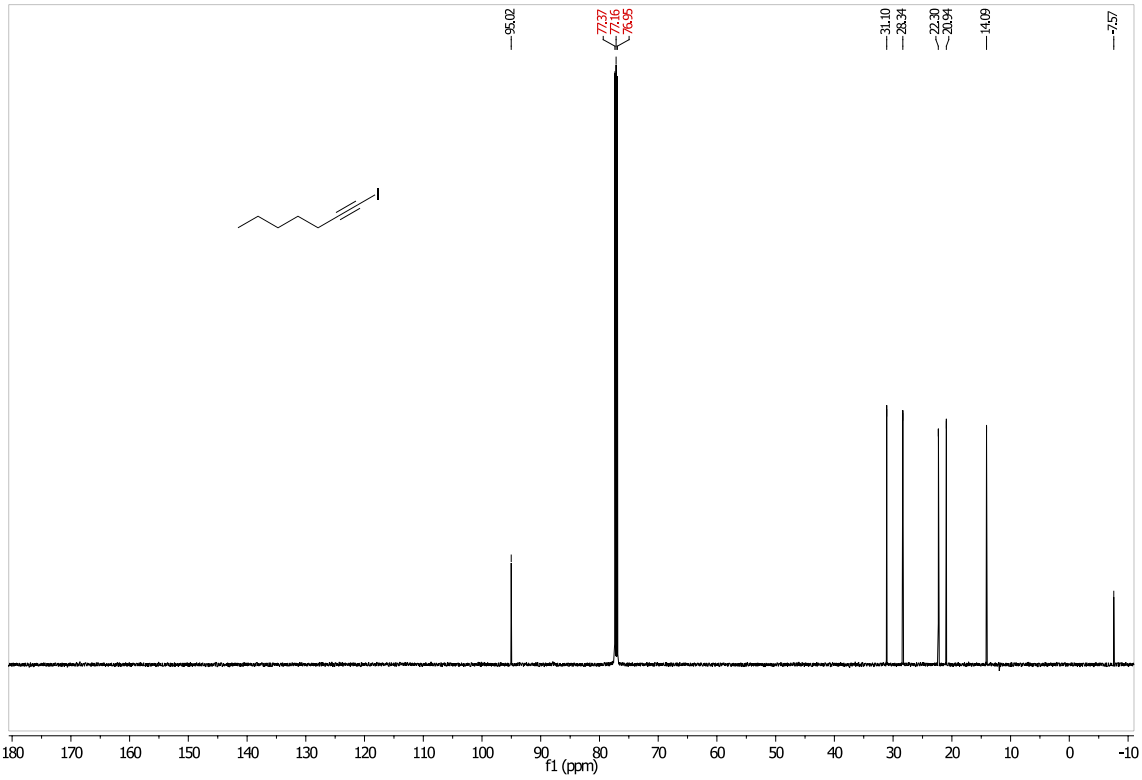
S 13: ^{13}C NMR (151 MHz, $CDCl_3$) of compound **4**.



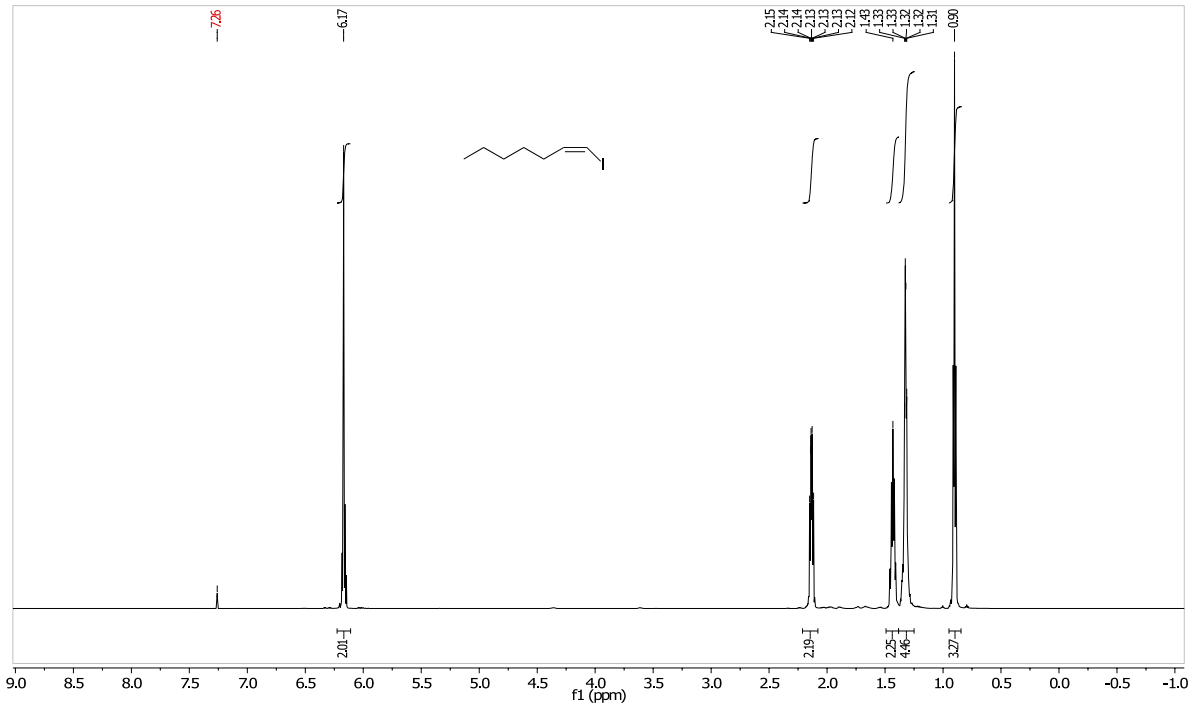
S 14: DEPT 135 (151 MHz, $CDCl_3$) of compound **4**.



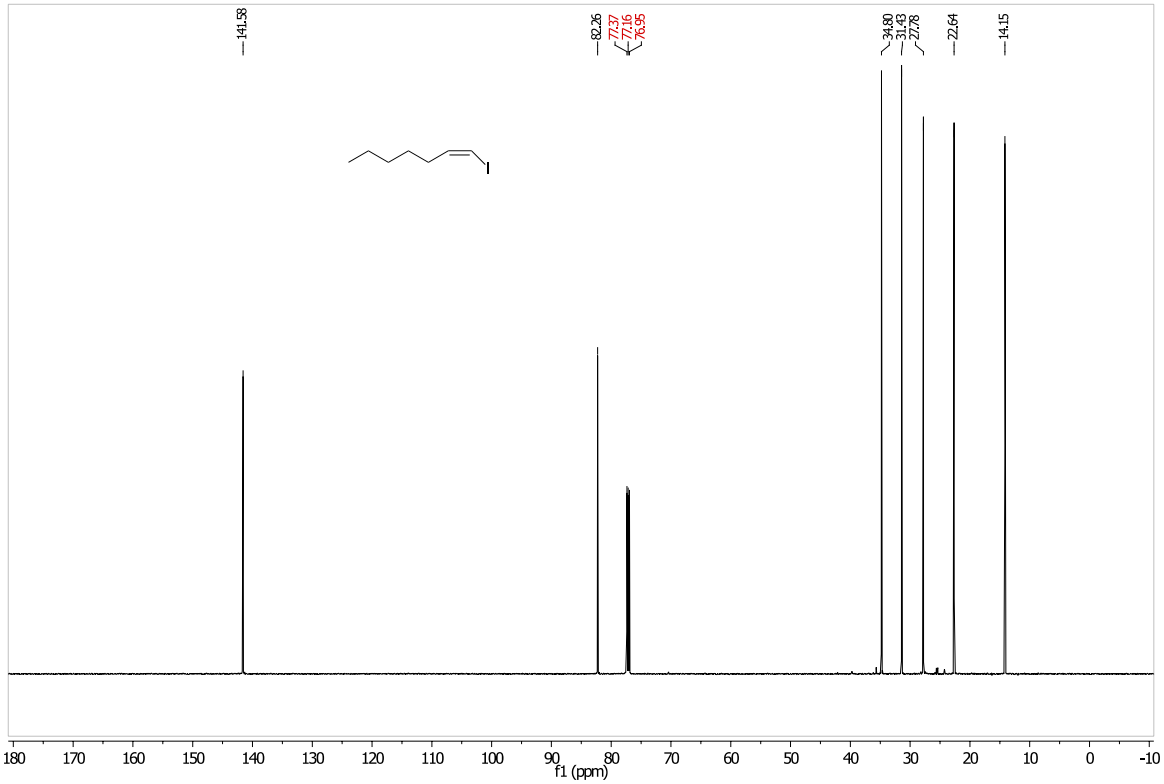
S 15*:* ^{1}H NMR (600 MHz, $CDCl_3$) of compound **11**.



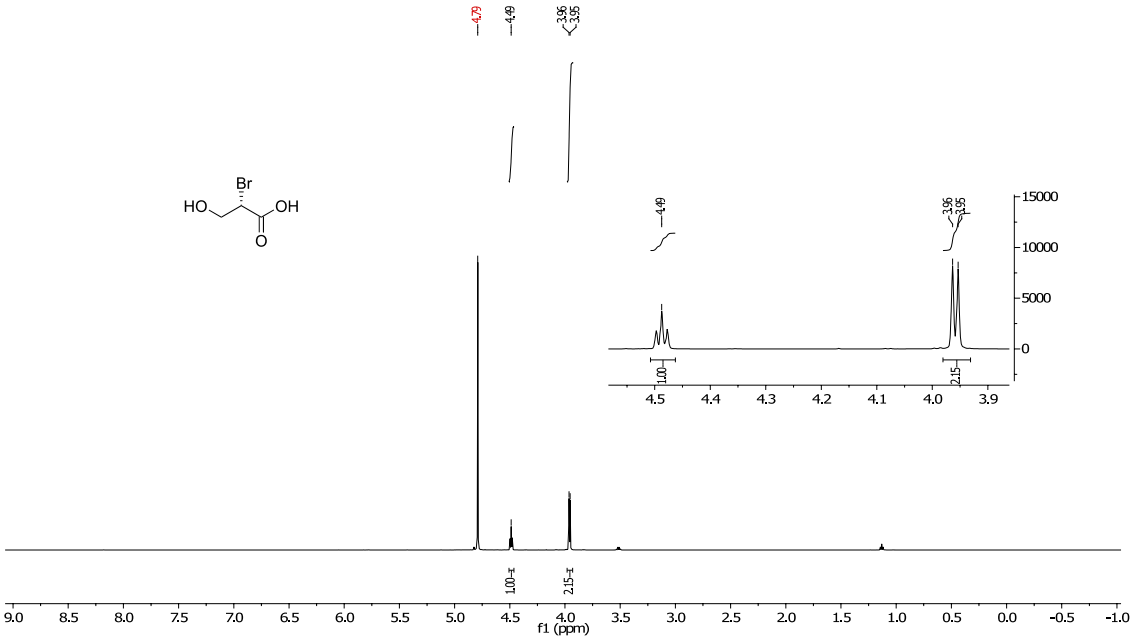
S 16: ^{13}C NMR (MHz, $CDCl_3$) of compound **11**.



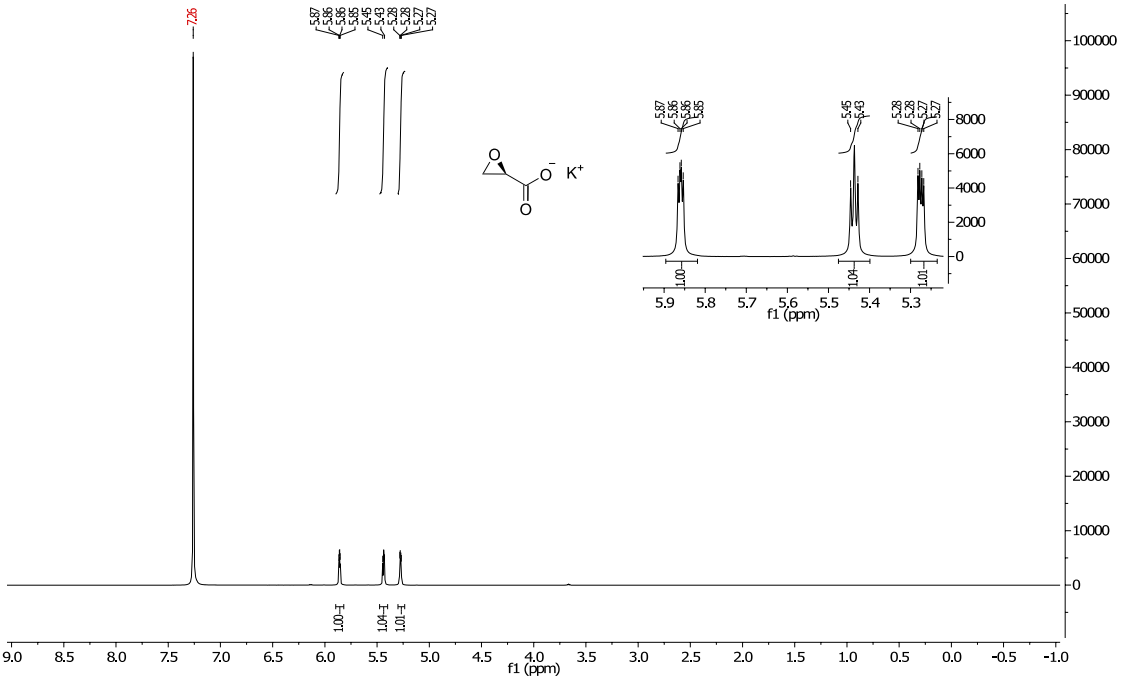
S 17: ^{1}H NMR (600 MHz, $CDCl_3$) of compound **12**.



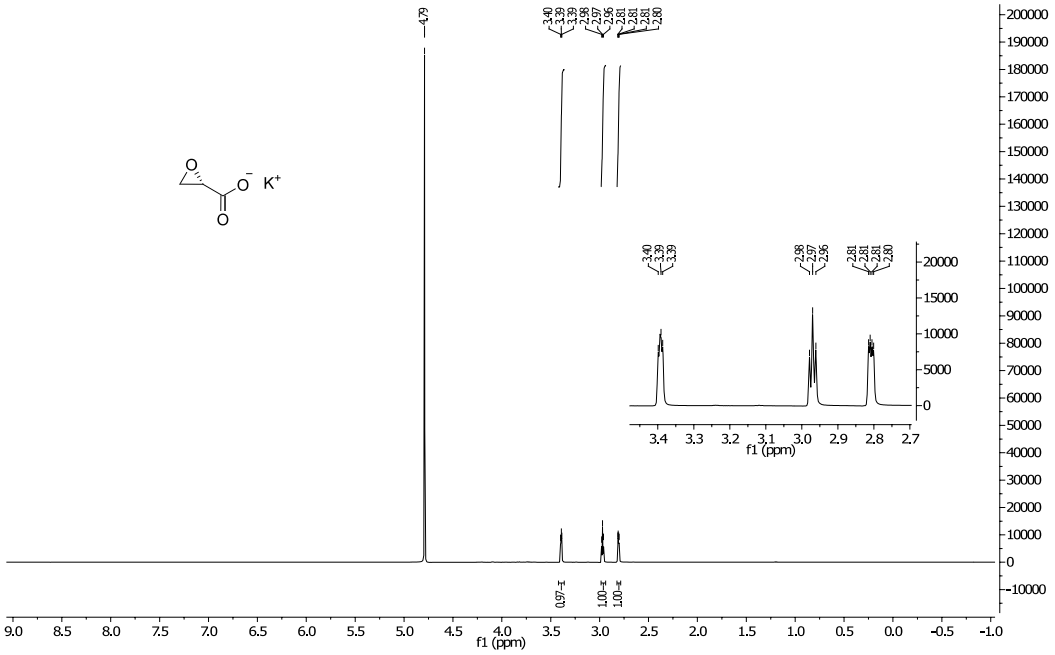
S 18: ^{13}C NMR (151 MHz, $CDCl_3$) of compound **12**.



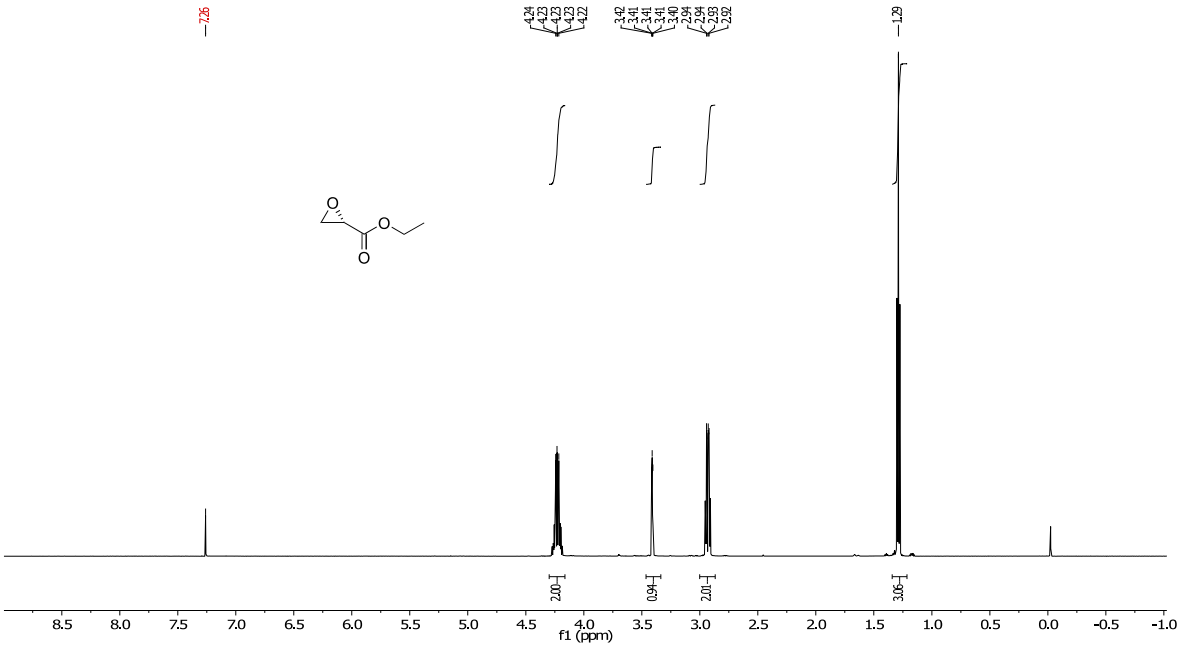
S 19: ^{1}H NMR (600 MHz, D_2O) of compound **16**.



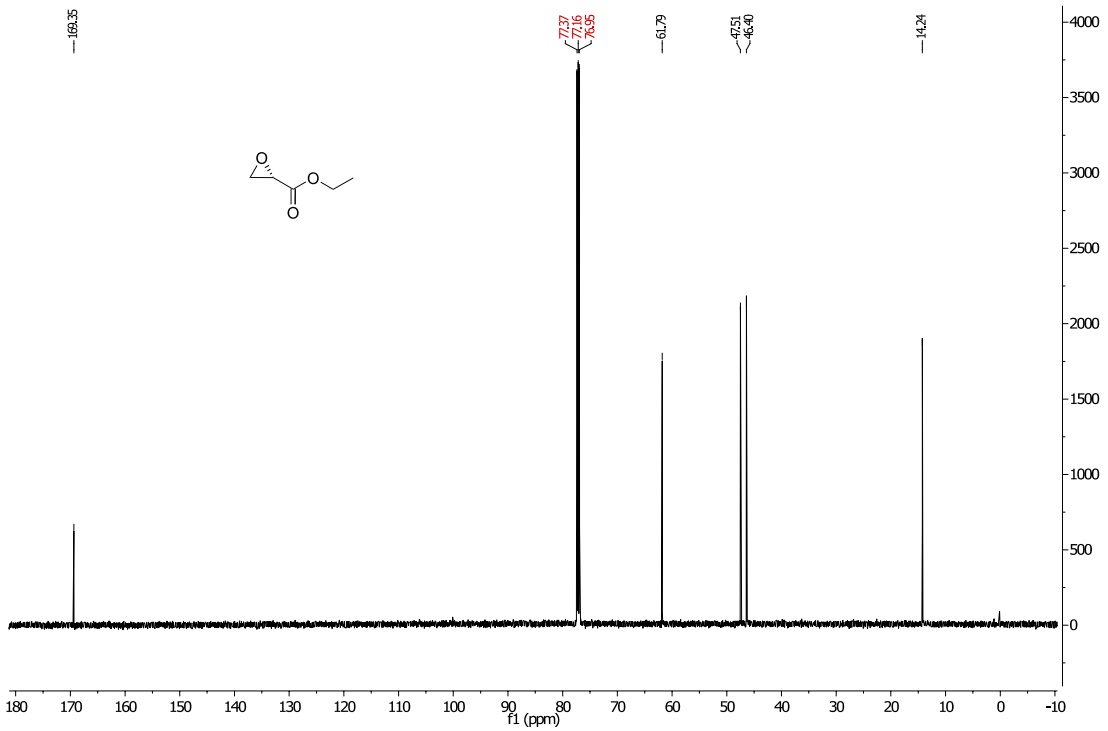
S 20*:* ^{1}H NMR (600 MHz, $CDCl_3$) of compound **17**.



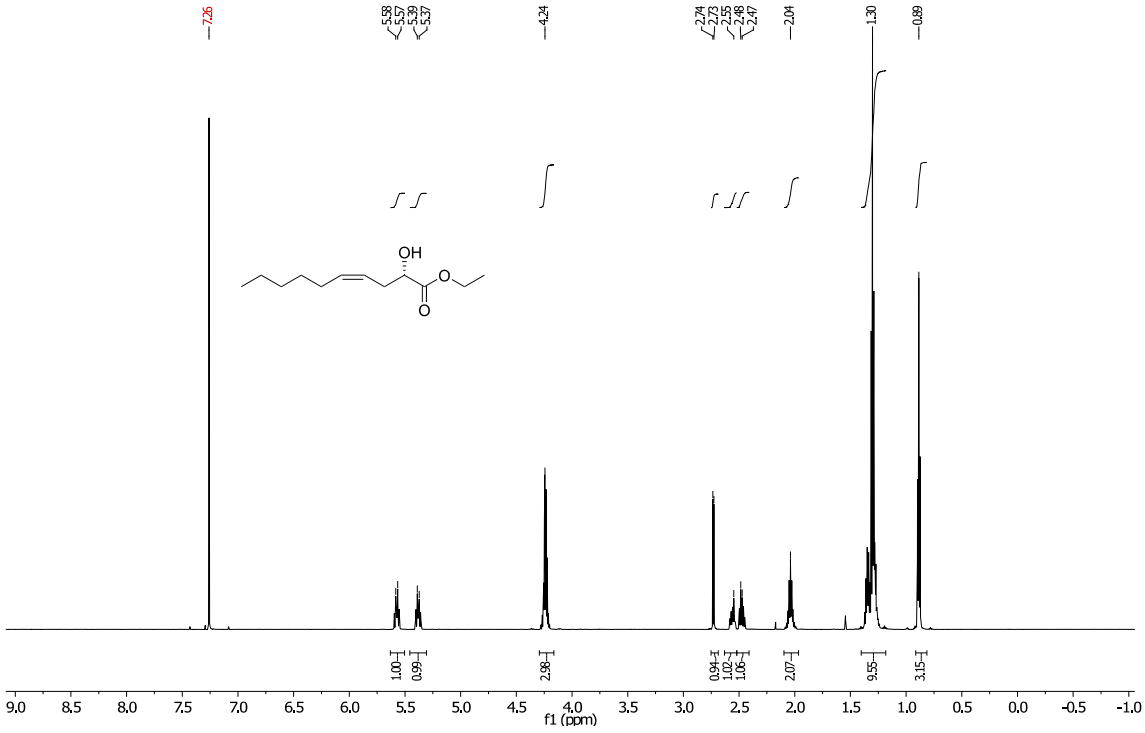
S 21: ^{1}H NMR (600 MHz, D_2O) of compound ***ent*-17**.



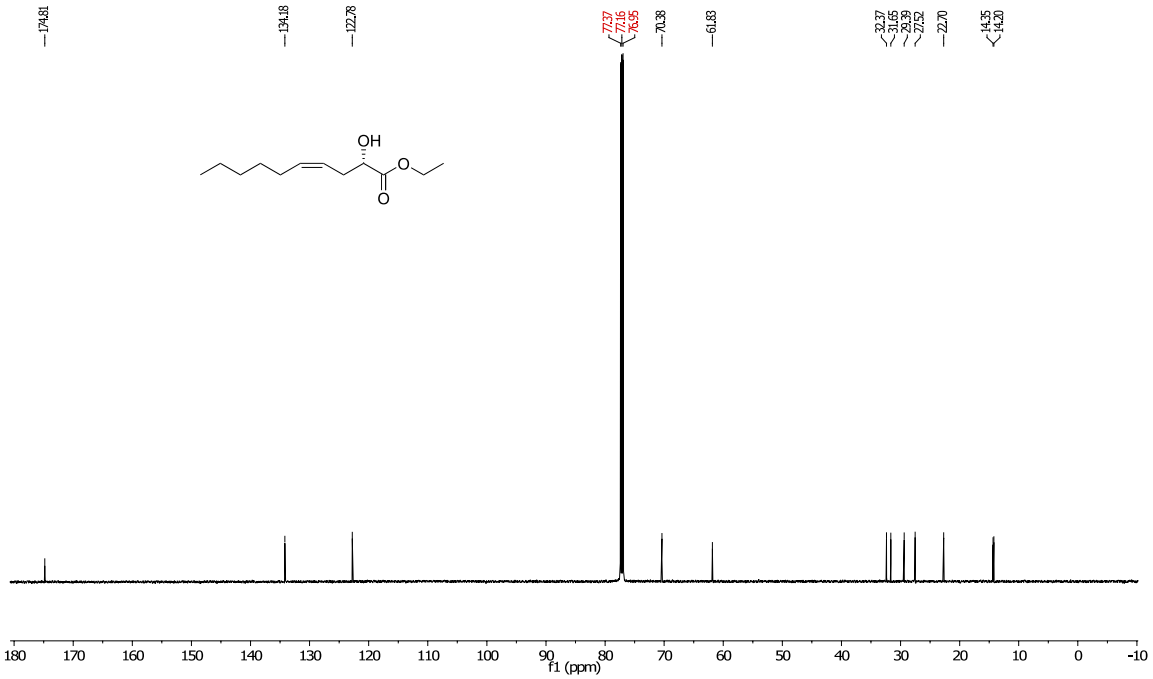
S 22: ^{1}H NMR (600 MHz, $CDCl_3$) of compound ***ent*-8**.



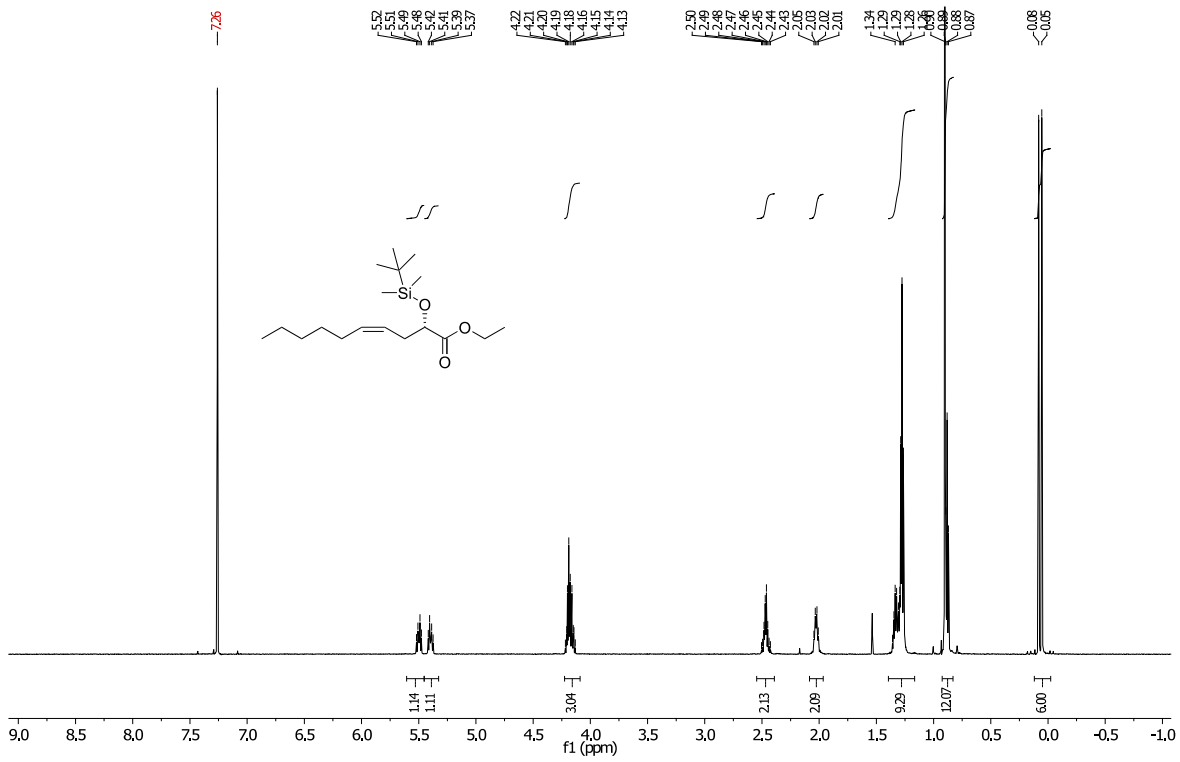
S 23: ^{13}C NMR (151 MHz, $CDCl_3$) of compound ***ent*-8**.



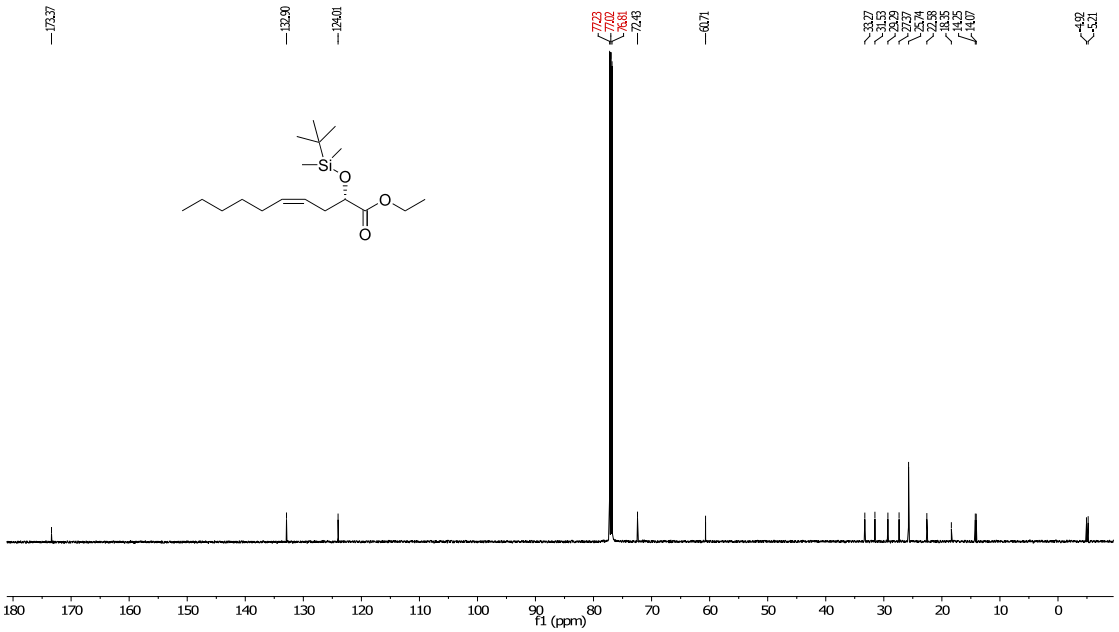
S 24: ^{1}H NMR (600 MHz, $CDCl_3$) of compound ***ent*-13**.



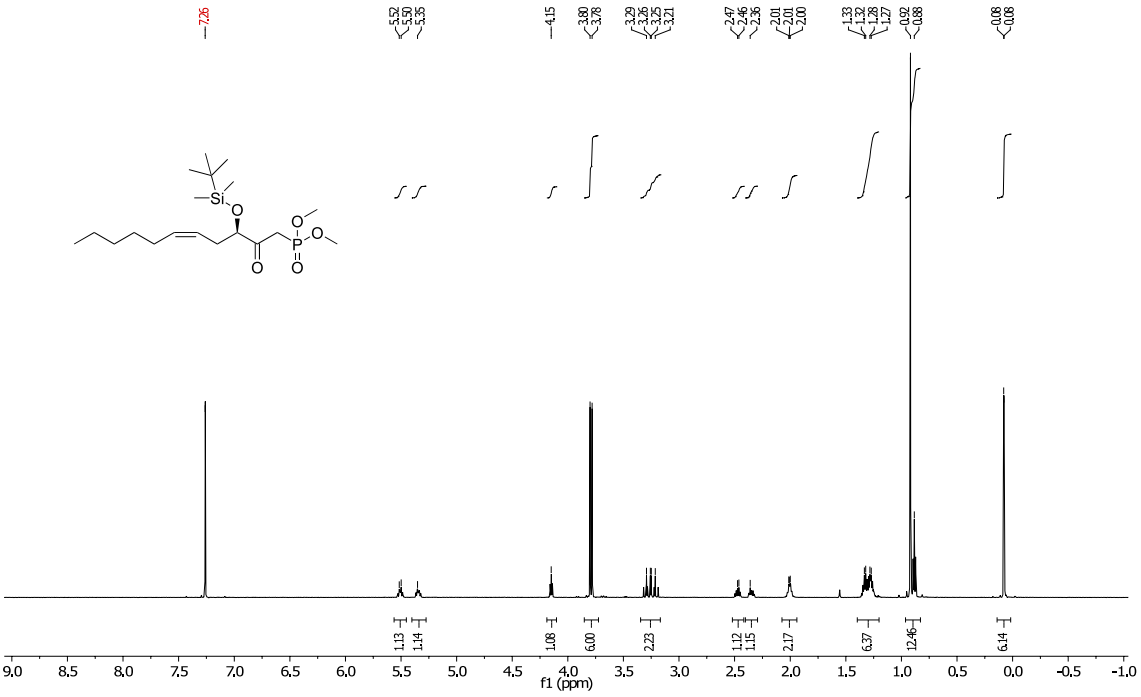
S 25: ^{13}C NMR (151 MHz, $CDCl_3$) of compound ***ent*-13**.



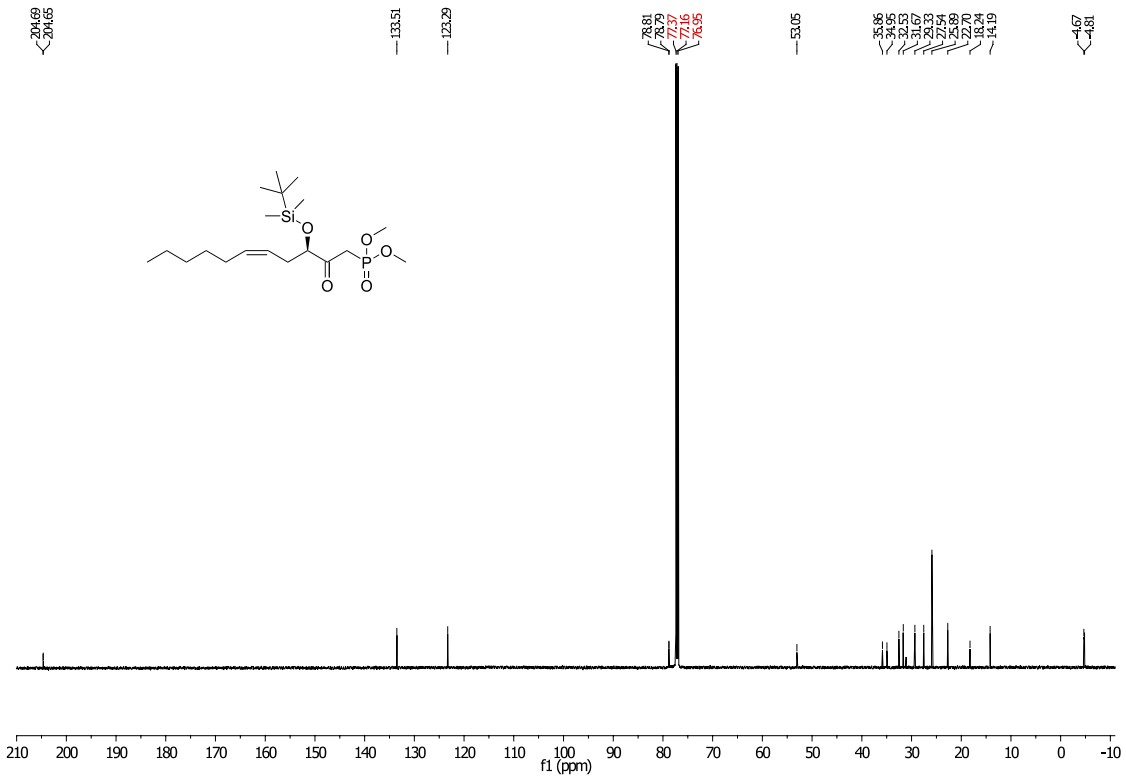
S 26: ^{1}H NMR (600 MHz, $CDCl_3$) of compound ***ent*-14**.



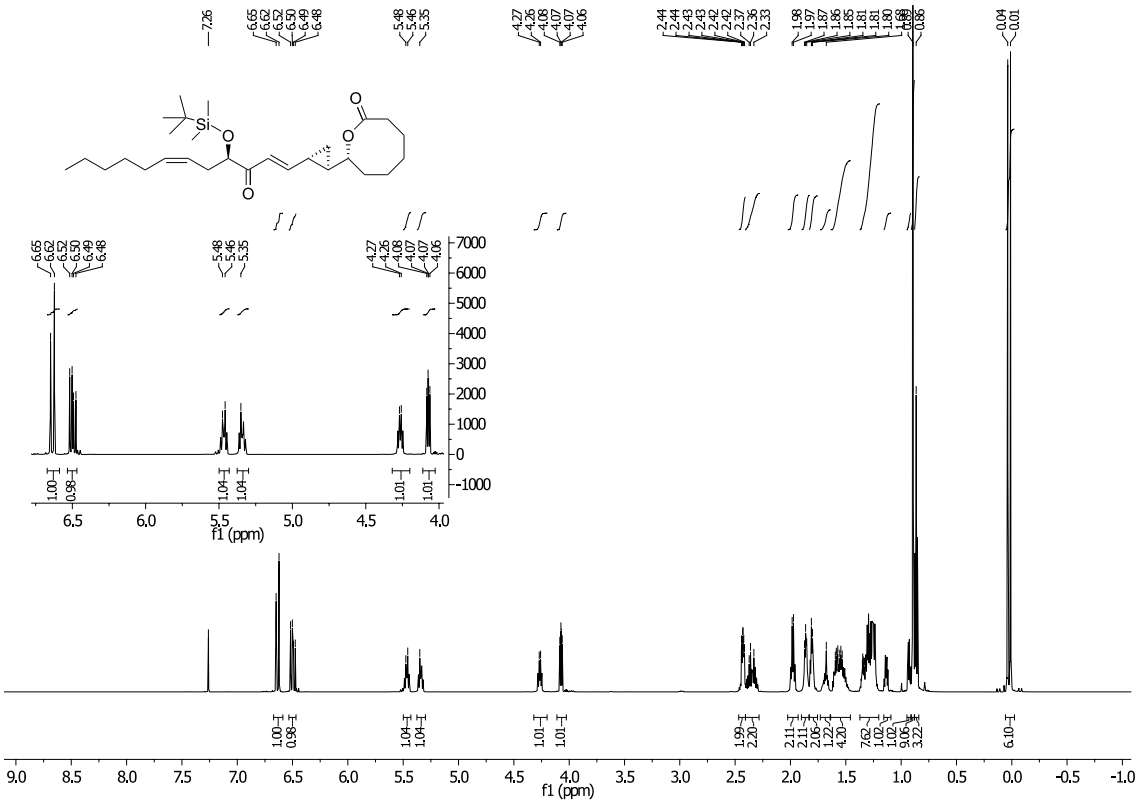
S 27: ^{13}C NMR (151 MHz, $CDCl_3$) of compound ***ent*-14**.



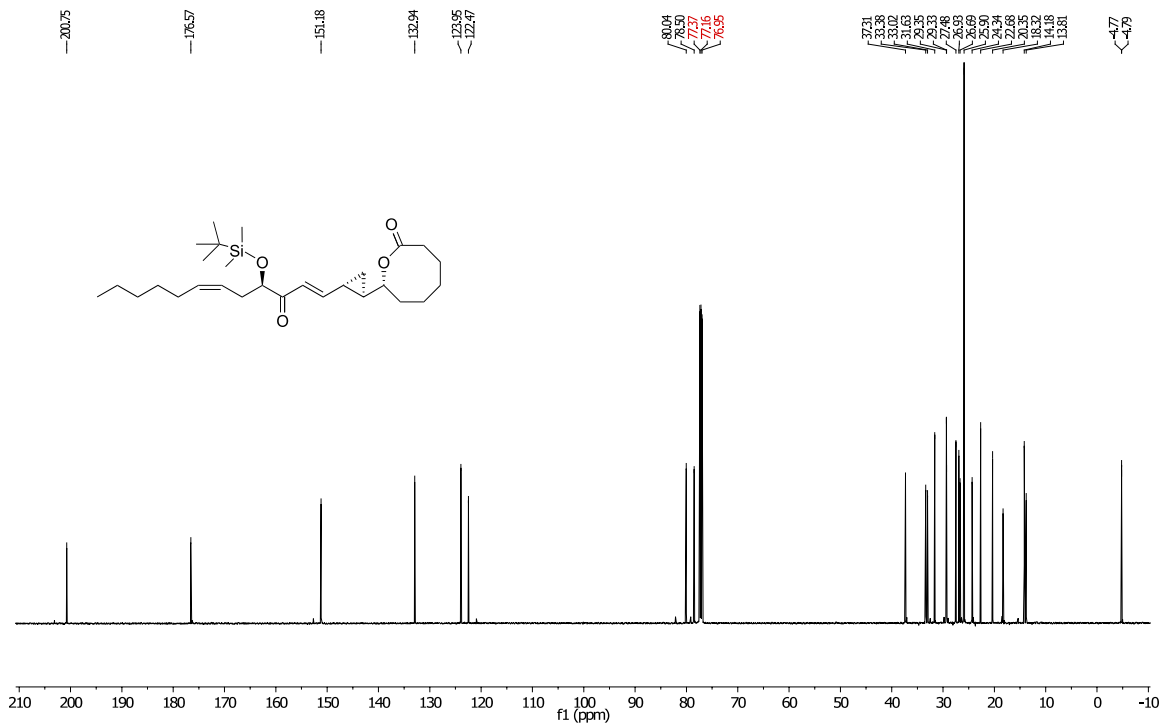
S 28: ^{1}H NMR (600 MHz, $CDCl_3$) of compound **5**.



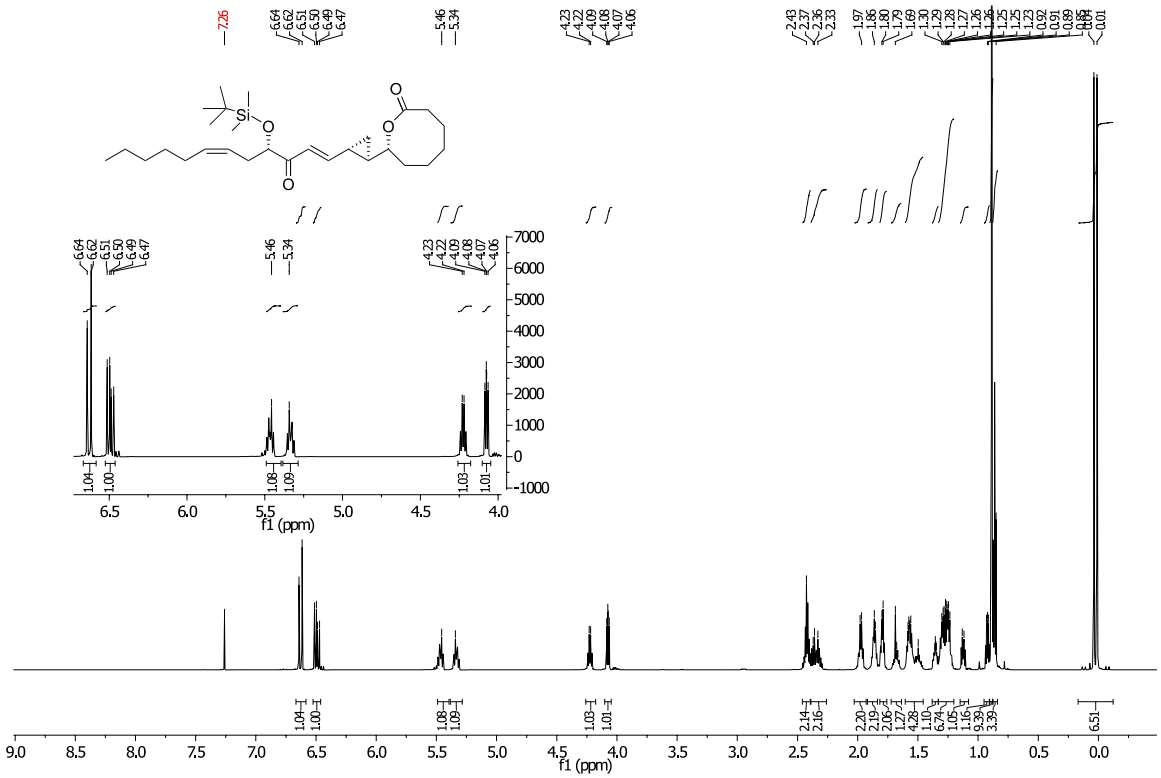
S 29: ^{13}C NMR (151 MHz, $CDCl_3$) of compound **5**.



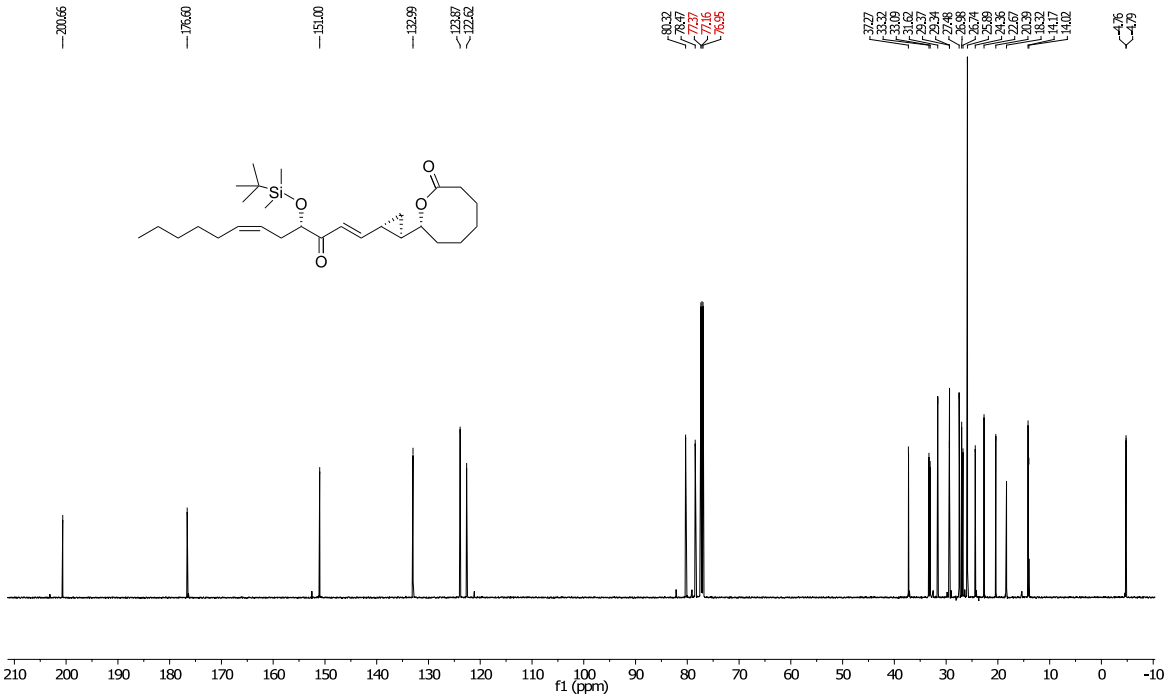
S 30: ^{1}H NMR (600 MHz, $CDCl_3$) of compound **10**.



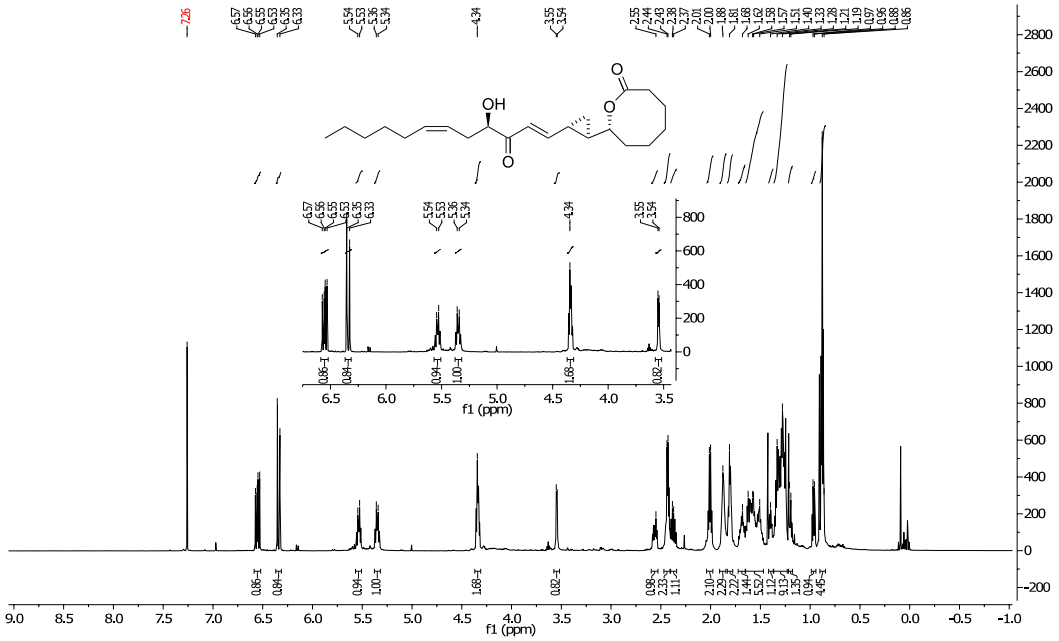
S 31: ^{13}C NMR (151 MHz, $CDCl_3$) of compound **10**.



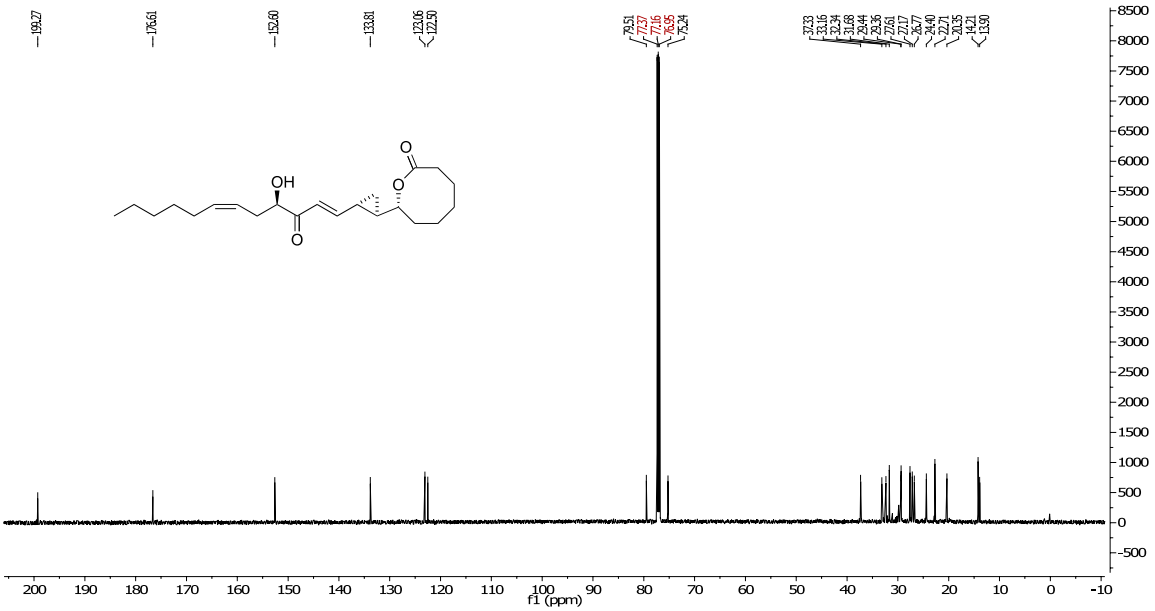
S 32: ^{1}H NMR (600 MHz, $CDCl_3$) of compound *dia*-**10**.



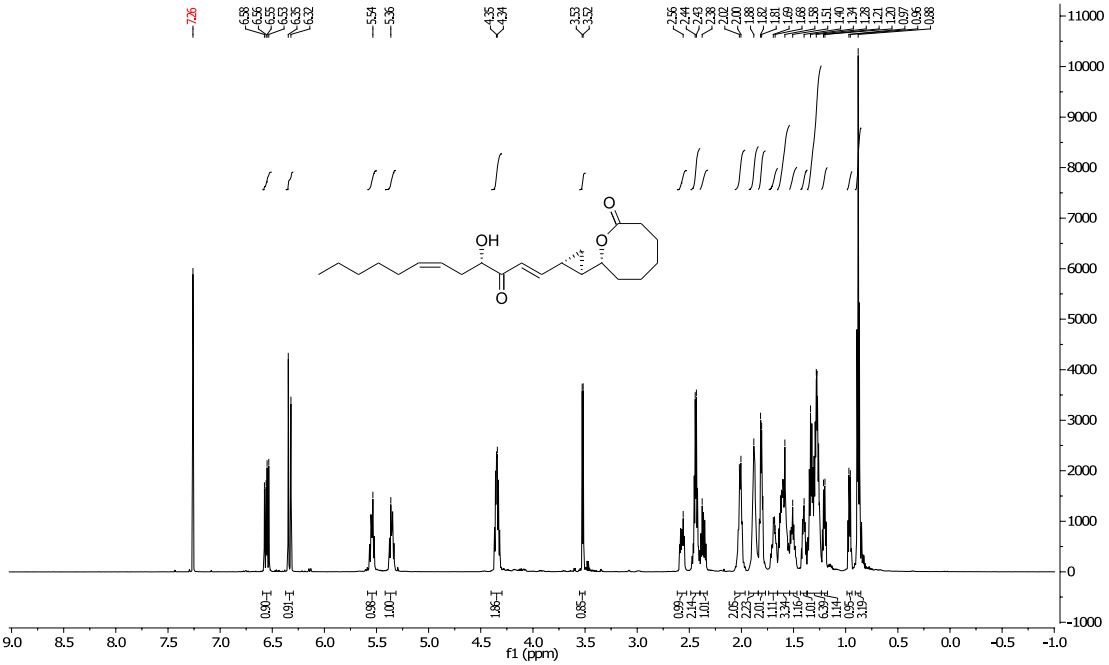
S 33: ^{13}C NMR (151 MHz, $CDCl_3$) of compound *dia*-**10**.



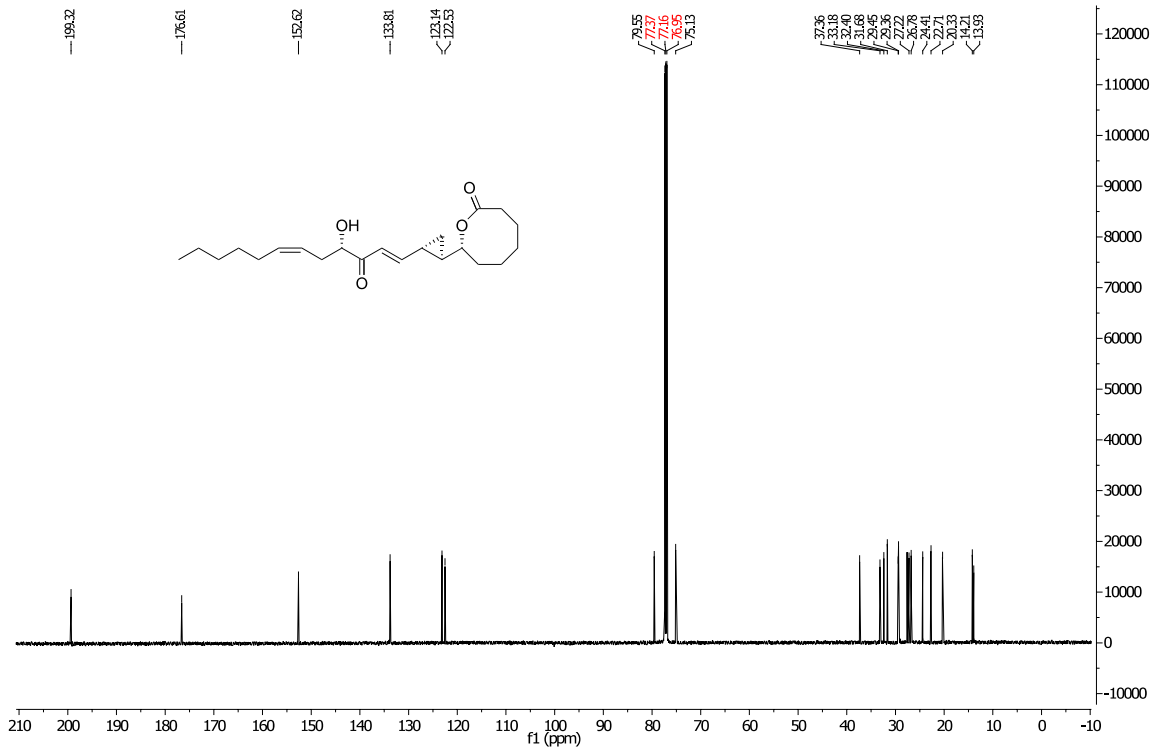
S 34: ^{1}H NMR (600 MHz, $CDCl_3$) of compound **18**.



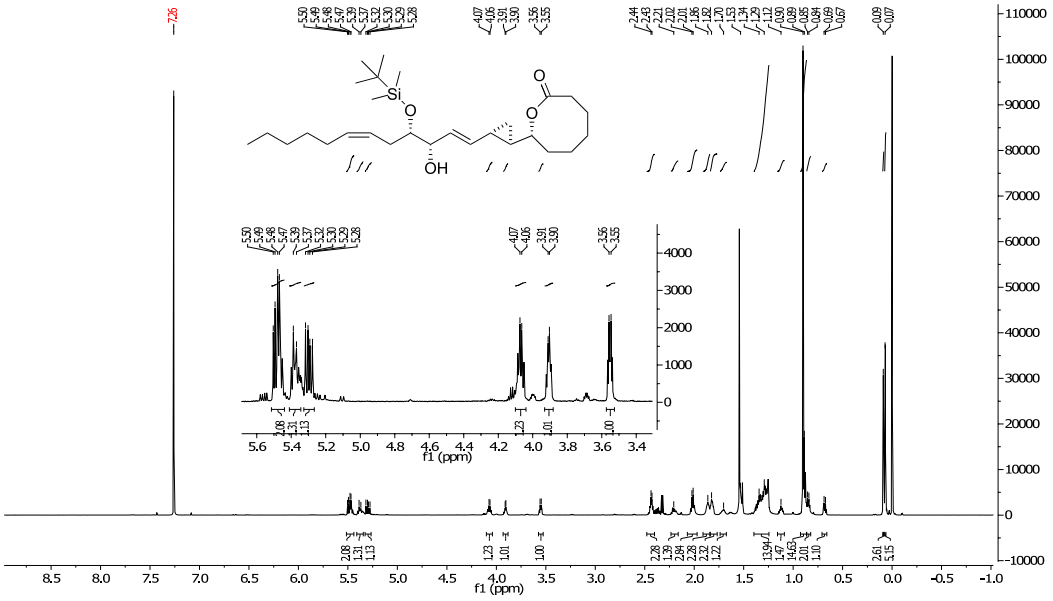
S 35: ^{13}C NMR (151 MHz, $CDCl_3$) of compound **18**.



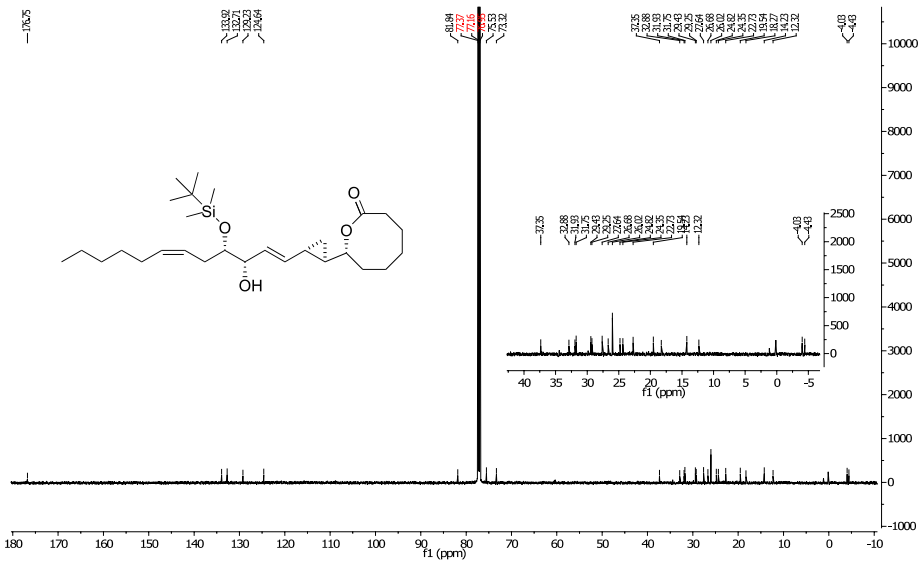
S 36: ^{1}H NMR (600 MHz, $CDCl_3$) of compound *dia*-**18**.



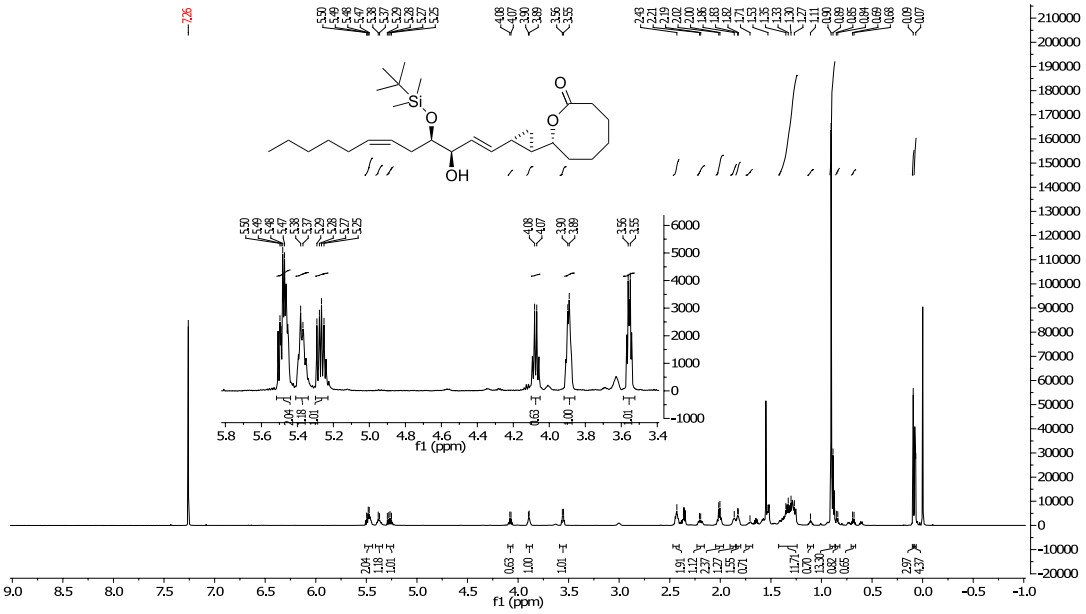
S 37: ^{13}C NMR (151 MHz, $CDCl_3$) of compound *dia*-**18**.



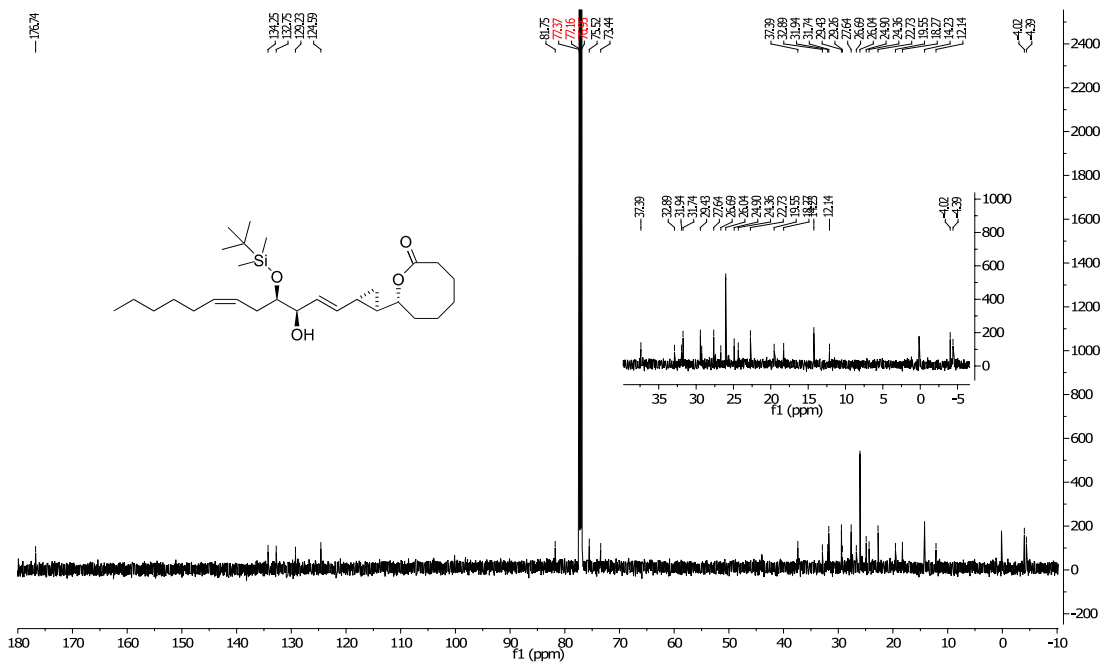
S 38: ^{1}H NMR (600 MHz, $CDCl_3$) of compound *dia*-**19** [impurities may cause slight differences in the chemical shifts].



S 39: ^{13}C NMR (151 MHz, $CDCl_3$) of compound *dia*-**19** [impurities may cause slight differences in the chemical shifts].



S 40: ^{1}H NMR (600 MHz, $CDCl_3$) of compound **19** [impurities may cause slight differences in the chemical shifts].



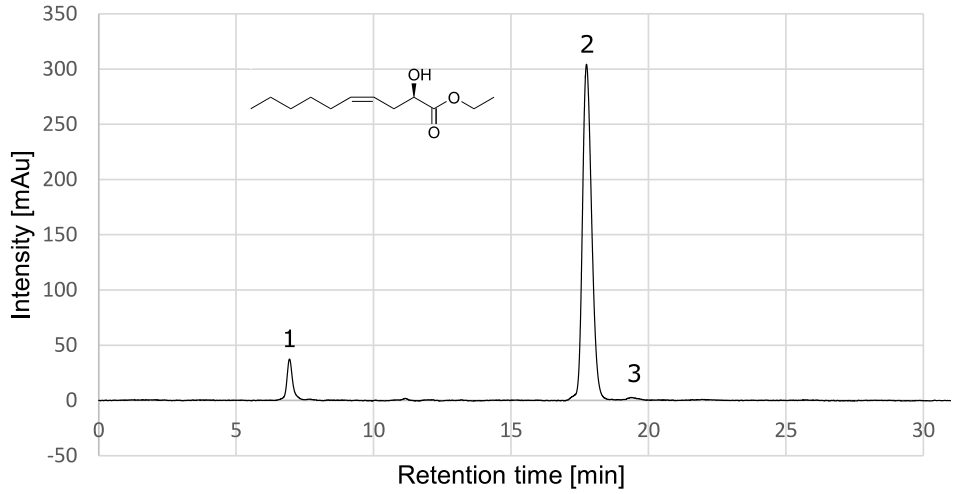
S 41: ^{13}C NMR (151 MHz, $CDCl_3$) of compound **19** [impurities may cause slight differences in the chemical shifts].

4. HPLC data

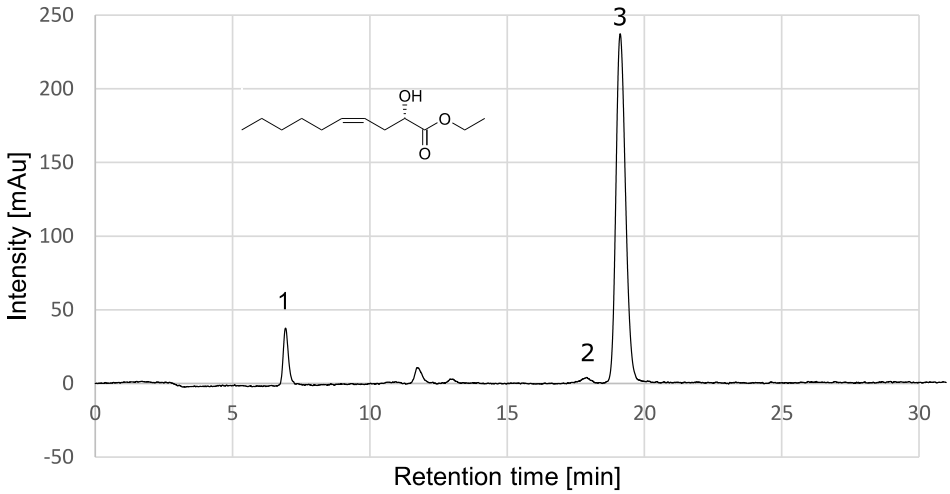
4.1 General procedure

All compounds were measured on chiral HPLC columns (250*4,6 mm). For the analytical HPLC (to determine the enantiomeric excess of the single compounds), all samples were diluted to 1 mg/mL in the appropriate heptane/isopropanol ratio. 300 µL of this solution were transferred into vials (with inlet) for the measurement. In case of the preparative HPLC the column Chiralpak IC (10 mm*250 mm; 5 µm pore size; DIACEL Chemical Industries, LTD) was used for the purification of the natural products **1** and **3**. Therefore 25 mg of the crude reaction mixture was diluted in 500 µL of the solvent system (100 µL isopropanol and 400 µL heptane to get a 20/80 ratio). In case of any particulate material, the solution was filtered over 0.45 µm (pore size). In several runs (100 µL per HPLC run), the desired fractions were collected manually in glas vessels. The single collected fractions were again measured on the analytical HPLC to test the grade of purity.

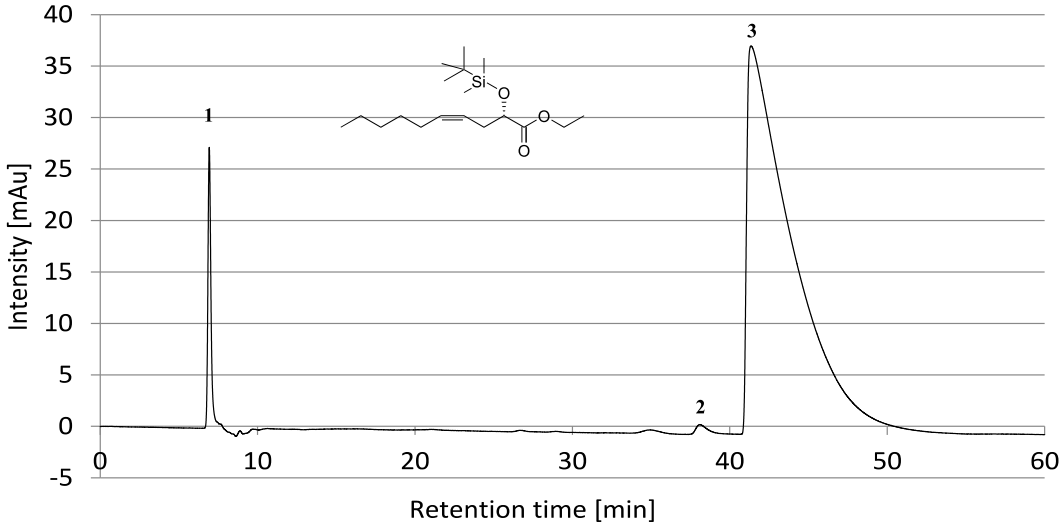
4.2 Chromatograms



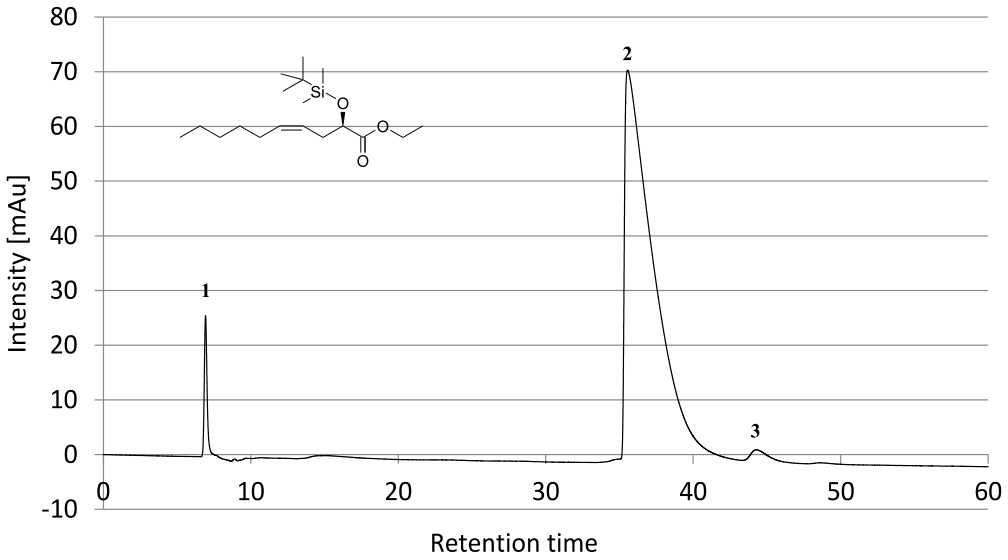
S 42: Chromatogram of compound **13**. [Analytical HPLC, Chiralpak IC; 250*4.6 mm, 95:5 heptane: isopropanol, 0.5 mL/min, 200 nm; signals: **1** injection peak (7.6 min), **2** compound **13** (17.7 min, area: 118.1 mAU*min), **3** compound *ent*-**13** (19.4 min, area: 0.5 mAU*min)]



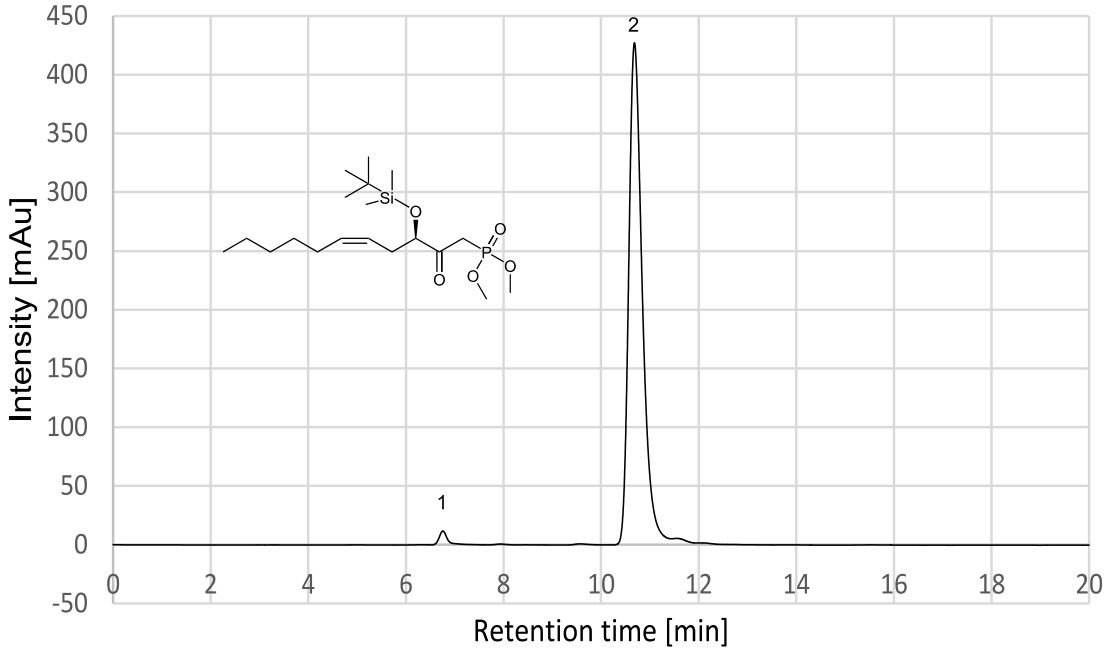
S 43: Chromatogram of compound *ent*-**13**. [Analytical HPLC, Chiralpak IC; 250*4.6 mm, 95:5 heptane: isopropanol, 0.5 mL/min, 200 nm; signals: **1** injection peak (6.9 min), **2** compound **13** (17.9 min), **3** compound *ent*-**13** (19.1 min)]



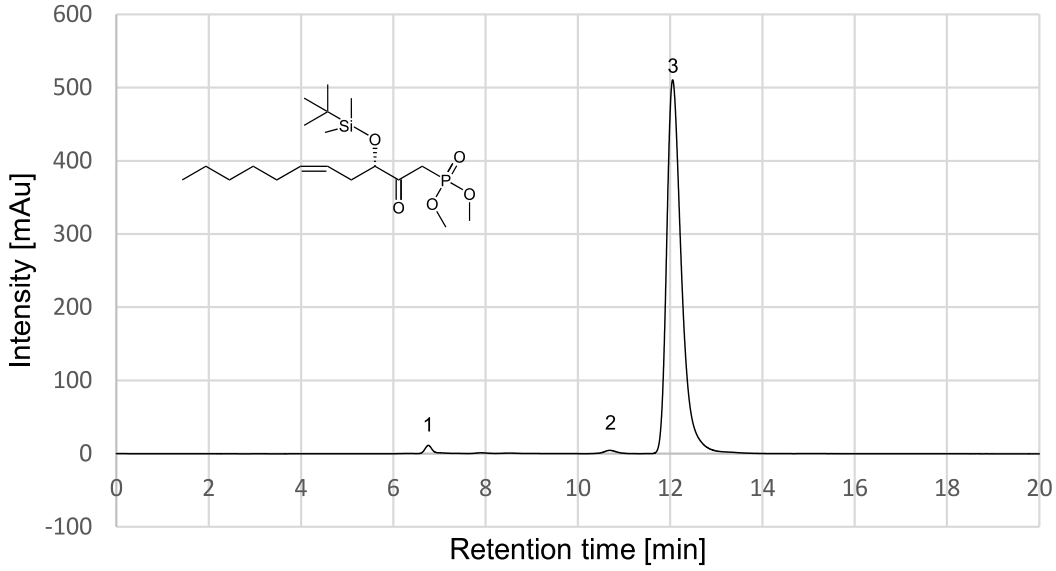
S 44: Chromatogram of compound *ent*-**14**. [Analytical HPLC, Chiralpak OD-H; 250*4.6 mm, 95:5 heptane: isopropanol, 0.5 mL/min, 225 nm; signals: **1** injection peak (6.9 min), **2** impurity (38.1 min), **3** compound *ent*-**14** (41.4 min)]



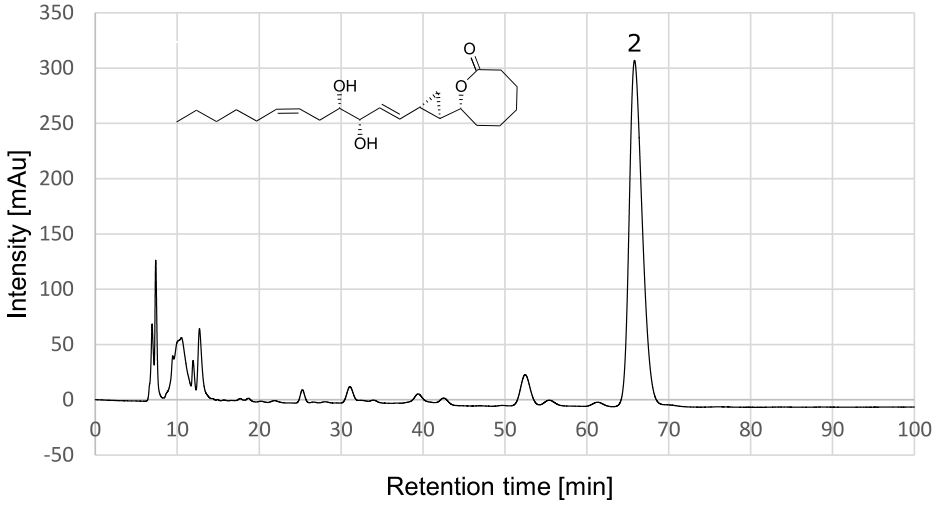
S 45: Chromatogram of compound **14**. [Analytical HPLC, Chiralpak OD-H; 250*4.6 mm, 95:5 heptane: isopropanol, 0.5 mL/min, 225 nm; signals: **1** injection peak (6.9 min), **2** compound **14** (35.6 min), **3** impurity (44.3 min)]



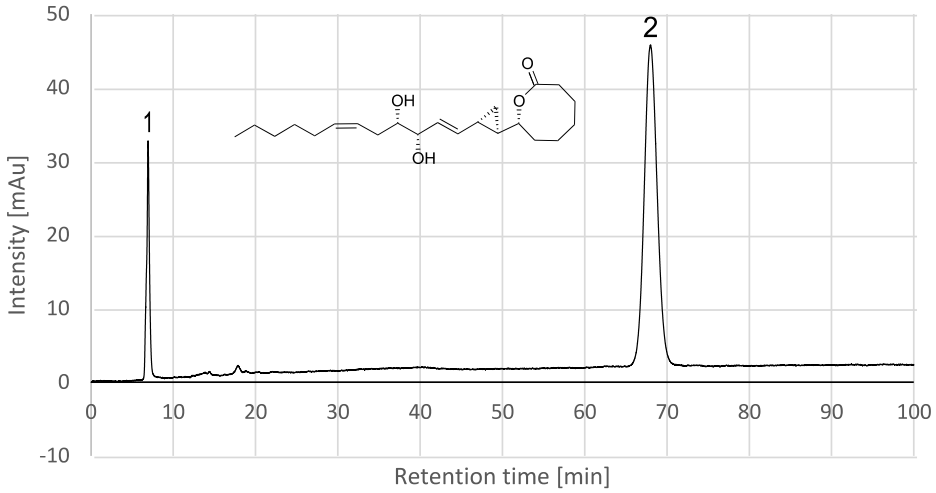
S 46: Chromatogram of compound **5**. [Analytical HPLC, Chiralpak OD-H; 250*4.6 mm, 95:5 heptane: isopropanol, 0.5 mL/min, 202 nm; signals: **1** injection peak (6.7 min), **2** compound **5** (10.7 min); >99% *ee*]



S 47: Chromatogram of compound *ent*-**5**. [Analytical HPLC, Chiralpak OD-H; 250*4.6 mm, 95:5 heptane: isopropanol, 0.5 mL/min, 202 nm; signals: **1** injection peak (6.7 min), **2** compound **5** (10.69 min), **3** compound *ent*-**5** (12.0 min); 98% *ee*]



S 48: Chromatogram of compound **3**. [Preparative HPLC, Chiralpak IC, 10 mm*250 mm, 80:20 heptane: isopropanol, 0.5 mL/min, 205 nm; signals: **2** compound **3**]



S 49: Chromatogram of compound **3**. [Analytical HPLC, Chiralpak IC; 250*4,6 mm, 80:20 heptane: isopropanol, 0.5 mL/min, 205 nm; signals: **1** injection peak (6.9 min), **2** compound **3** (68.0 min)]