

Supporting Information

for

Synthesis of zearalenone-16- β ,D-glucoside and zearalenone-16-sulfate: A tale of protecting resorcylic acid lactones for regiocontrolled conjugation

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Experimental details (including remarks and general procedures), characterization data, copies of NMR spectra of new compounds, 2D NMR spectra of glucoside 7.

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1. Experimental

General remarks

All reactions were performed under an argon atmosphere. The progress of reactions was monitored by thin-layer chromatography (TLC) over silica gel 60 F254 (Merck). The chromatograms were visualized by irradiation with ultraviolet light or by heat staining with ceric ammonium molybdate in ethanol/sulfuric acid. LC–ESI–MS/MS was performed on an HCT ion trap mass spectrometer (Bruker, Germany) in full scan mode. Chromatographic separation was done on a 1200 series HPLC system (Agilent Technologies, Germany) using a Luna RP-C18 column (3.0 × 150 mm, 3 μm particle size, Phenomenex, Germany) and application of pure substances was achieved using a TLC–MS interface (Camag, Germany). Preparative column chromatography was performed on silica gel 60 (Merck, 40–63 μm) or RP-C18 silica gel (Merck, 40–63 μm) using a Büchi Sepacore™ Flash System. NMR spectra were recorded on a Bruker DPX-200 MHz or Avance DRX-400 MHz spectrometer. Data were recorded and evaluated using TOPSPIN 1.3 (Bruker Biospin). All chemical shifts are given in ppm relative to tetramethylsilane. The calibration was done using residual solvent signals. Multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), b (broad signal). Zearalenone was obtained from Fermentek (Israel) and all other chemicals were purchased from ABCR (Germany) or Sigma-Aldrich (Austria/Germany).

General procedure A: regioselective acetylation of RAL type compounds

To a solution of the RAL type compound (1.0 mmol) and DMAP (1.2 mg, 10 μmol) in dry toluene (5 mL) at 0 °C was slowly added a solution of Ac₂O (110 mg, 1.1 mmol) in dry toluene (1 mL). The reaction mixture was gradually warmed to room temperature and stirred for further 16 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (hexanes/EtOAc gradient elution) to yield the desired 4'-O-acetylated product.

4-Acetoxy-2-hydroxybenzoic acid isopropyl ester (10)

Following general procedure A, **10** was obtained as a white solid (203 mg, 85%); R_f 0.4 (hexanes/EtOAc, 9/1); ^1H NMR (200 MHz, CDCl_3) δ 11.07 (s, 1H, 2-OH), 7.84 (d, $J = 8.8$ Hz, 1H, H-6), 6.72 (d, $J = 2.3$ Hz, 1H, H-3), 6.62 (dd, $J = 8.8, 2.3$ Hz, 1H, H-5), 5.26 (sept., $J = 6.2$ Hz, 1H, COOCH), 2.27 (s, 3H, CH_3COO), 1.36 (d, $J = 6.2$ Hz, 6H, $(\text{CH}_3)_2\text{CH}$); ^{13}C NMR (50 MHz, CDCl_3) δ 169.2 (s), 168.5 (s), 162.9 (s), 156.1 (s), 131.0 (d), 112.9 (d), 110.7 (s), 110.4 (d), 69.3 (d), 21.8 (q), 21.1 (q); HRMS m/z calcd for $\text{C}_{12}\text{H}_{14}\text{NaO}_5^+$ $[\text{M}+\text{Na}]^+$ 261.0733, found 261.0750.

14-O-Acetylzearalenone (14)

Following general procedure A (reduced scale), **14** was obtained starting from ZEN (**1**, 32 mg, 0.1 mmol) as a white solid (27 mg, 75%); R_f 0.4 (hexanes/EtOAc, 2/1); ^1H NMR (200 MHz, CDCl_3) δ 11.88 (s, 1H, 16-OH), 7.00 (d, $J = 15.6$ Hz, 1H, H-12), 6.67-6.62 (m, 2H, H-13, H-15), 5.71 (ddd, $J = 15.4, 10.1, 4.3$ Hz, 1H, H-11), 5.11-4.93 (m, 1H, H-3), 2.81 (ddd, $J = 18.7, 12.1, 2.5$ Hz, 1H, H_a -8), 2.59 (m, 1H, H_a -6), 2.37-2.05 (m, 5H, H_a -5, H_b -6, H_b -8, H_{ab} -10), 2.29 (s, 3H, CH_3COO), 1.85-1.54 (m, 5H, H_{ab} -4, H_b -5, H_{ab} -9), 1.39 (d, $J = 6.1$ Hz, 3H, CH_3); ^{13}C NMR (50 MHz, CDCl_3) δ 211.0 (s, C-7), 171.1 (s, CH_3COO), 168.8 (s, C-1), 164.6 (s, C-14), 154.9 (s, C-16), 143.4 (s, C-12a), 133.5 (d, C-11), 132.6 (d, C-12), 113.7 (d, C-13), 109.6 (d, C-15), 108.3 (s, C-16a), 74.1 (d, C-3), 43.0 (t, C-6), 36.7 (t, C-8), 34.7 (t, C-4), 31.1 (t, C-10), 22.2 (t, C-5), 21.2 (q, CH_3COO), 21.0 (t, C-9), 20.8 (q, CH_3); NMR data matched that reported previously by Munoz et al.¹ HRMS m/z calcd for $\text{C}_{20}\text{H}_{24}\text{NaO}_6^+$ $[\text{M}+\text{Na}]^+$ 383.1465, found 383.1466.

General procedure B: regioselective *p*-methoxybenzylation of RAL type compounds

To a solution of the RAL type compound (1 mmol) and Cs_2CO_3 (433 mg, 1.5 mmol) in dry DMF (5 mL) was slowly added a solution of *p*-methoxybenzyl chloride (PMB-Cl, 172 mg, 1.1 mmol) in dry DMF (1 mL). The reaction mixture was stirred at room temperature for 24 h, diluted with water (20 mL) and extracted with EtOAc (3 \times 15 mL). The combined organic layer was washed with brine,

¹ Munoz, L.; Castro, J.L.; Cardelle, M.; Castedo, L.; Riguera, R. *Phytochemistry* **1989**, *28*, 83-85.

dried over Na₂SO₄ and concentrated. Column chromatography (hexane/EtOAc gradient elution) afforded the desired 4'-O-PMB protected compound.

2-Hydroxy-4-((*p*-methoxybenzyl)oxy)benzoic acid isopropyl ester (15)

Following general procedure B, **15** was obtained as a white solid (256 mg, 81%); R_f 0.8 (hexanes/EtOAc, 3/1); ¹H NMR (200 MHz, CDCl₃) δ 11.07 (s, 1H, 2-OH), 7.66 (d, *J* = 8.5 Hz, 1H, H-6), 7.26 (d, *J* = 8.5 Hz, 2H, PMB), 6.84 (d, *J* = 8.5 Hz, 2H, PMB), 6.46-6.36 (m, 2H, H-3, H-5), 5.17 (sept., *J* = 6.5 Hz, 1H, COOCH), 4.92 (s, 2H, OCH₂), 3.74 (s, 3H, OCH₃), 1.29 (d, *J* = 6.4 Hz, 6H, (CH₃)₂CH); ¹³C NMR (50 MHz, CDCl₃) δ 169.6 (s), 164.6 (s), 163.8 (s), 159.6 (s), 131.2 (d), 129.3 (d), 128.1 (s), 114.1 (d), 108.0 (d), 106.1 (s), 101.6 (d), 69.9 (t), 68.7 (q), 55.3 (q), 21.9 (q); HRMS *m/z* calcd for C₁₈H₂₀NaO₅⁺ [M+Na]⁺ 339.1203, found 339.1195.

14-*O*-(*p*-Methoxybenzyl)zearalenone (18)

Following general procedure B (reduced scale), **18** was obtained starting from ZEN (**1**, 32 mg, 0.1 mmol) as a white solid (31 mg, 71%); R_f 0.6 (hexanes/EtOAc, 2/1); ¹H NMR (200 MHz, CDCl₃) δ 12.01 (s, 1H, 16-OH), 7.27 (d, *J* = 8.6 Hz, 2H, PMB), 6.94 (d, *J* = 14.9 Hz, 1H, H-12), 6.84 (d, *J* = 8.8 Hz, 2H, PMB), 6.46 (d, *J* = 2.6 Hz, 1H, H-13), 6.39 (d, *J* = 2.6 Hz, 1H, H-15), 5.60 (ddd, *J* = 15.5, 10.3, 4.0 Hz, 1H, H-11), 5.03-4.83 (m, 3H, H-3, OCH₂), 3.74 (s, 3H, OCH₃), 2.77 (ddd, *J* = 18.2, 12.2, 2.9 Hz, 1H, H_a-8), 2.60-2.45 (m, 1H, H_a-6), 2.37-1.96 (m, 5H, H_a-5, H_b-6, H_b-8, H_{ab}-10), 1.78-1.45 (m, 5H, H_{ab}-4, H_b-5, H_{ab}-9), 1.31 (d, *J* = 6.1 Hz, 3H, CH₃); ¹³C NMR (50 MHz, CDCl₃) δ 211.0 (s, C-7), 171.4 (s, C-1), 165.6 (s, C-14), 163.2 (s, C-16), 159.6 (s, Ar-OCH₃), 143.3 (s, C-12a), 133.3 (d, C-11), 132.4 (d, C-12), 129.3 (d, PMB), 128.1 (s, PMB), 114.0 (d, PMB), 108.9 (d, C-13), 103.7 (s, C-16a), 100.8 (d, C-15), 73.4 (d, C-3), 69.9 (t, OCH₂), 55.4 (q, OCH₃), 42.9 (t, C-6), 36.6 (t, C-8), 34.7 (t, C-4), 31.0 (t, C-10), 22.3 (t, C-5), 21.0 (t, C-9), 20.9 (q, CH₃); HRMS *m/z* calcd for C₂₆H₃₀NaO₆⁺ [M+Na]⁺ 461.1935, found 461.1957.

General procedure C: regioselective TIPS-protection of RAL type compounds

To a solution of the RAL type compound (1 mmol) and imidazole (156 mg, 2.3 mmol) in dry CH₂Cl₂ (10 mL) was slowly added TIPS-Cl (216 mg, 1.1 mmol). The reaction mixture was stirred at room temperature for 16 h, diluted with CH₂Cl₂ (20 mL), washed with brine, dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography (hexanes/EtOAc gradient elution).

2-Hydroxy-4-(triisopropylsilyloxy)benzoic acid isopropyl ester (21)

Following general procedure C, **21** was obtained as a colorless viscous oil (350 mg, 99%); R_f 0.9 (hexanes/EtOAc, 12/1); ¹H NMR (200 MHz, CDCl₃) δ 11.0 (s, 1H, 2-OH), 7.70 (d, *J* = 8.7 Hz, 1H, H-6), 6.44 (d, *J* = 2.3 Hz, 1H, H-3), 6.39 (dd, *J* = 8.6, 2.3 Hz, 1H, H-5), 5.24 (sept., *J* = 6.2 Hz, 1H, COOCH), 1.35 (d, *J* = 6.3 Hz, 6H, (CH₃)₂CH), 1.31-1.16 (m, 3H, SiCH), 1.12-1.04 (m, 18H, SiCH(CH₃)₂); ¹³C NMR (50 MHz, CDCl₃) δ 169.6 (s), 163.5 (s), 162.5 (s), 131.2 (d), 112.1 (d), 107.5 (d), 106.6 (s), 68.6 (d), 21.9 (q), 17.8 (q), 12.9 (d); HRMS *m/z* calcd for C₁₉H₃₂NaO₄Si⁺ [M+Na]⁺ 375.1962, found 375.1960.

14-O-(Triisopropylsilyl)zearalenone (22)

Following general procedure C (reduced scale), **22** was obtained starting from ZEN (**1**, 100 mg, 0.31 mmol) as a white solid (145 mg, 99%); R_f 0.8 (hexanes/EtOAc, 2/1); ¹H NMR (200 MHz, CDCl₃) δ 11.85 (s, 1H, 16-OH), 6.90 (d, *J* = 15.2 Hz, 1H, H-12), 6.30 (d, *J* = 2.5 Hz, 1H, H-13), 6.25 (d, *J* = 2.5 Hz, 1H, H-15), 5.51 (ddd, *J* = 15.3, 10.2, 3.8 Hz, 1H, H-11), 4.97-4.79 (m, 1H, H-3), 2.75 (ddd, *J* = 18.4, 12.2, 3.0 Hz, 1H, H_a-8), 2.55-2.41 (m, 1H, H_a-6), 2.34-1.93 (m, 5H, H_a-5, H_b-6, H_b-8, H_{ab}-10), 1.76-1.35 (m, 5H, H_{ab}-4, H_b-5, H_{ab}-9), 1.26 (d, *J* = 6.1 Hz, 3H, CH₃), 1.21-1.09 (m, 3H, SiCH), 1.02-0.93 (m, 18H, SiCH(CH₃)₂); ¹³C NMR (50 MHz, CDCl₃) δ 211.1 (s, C-7), 171.4 (s, C-1), 165.3 (s, C-16), 161.2 (s, C-14), 143.4 (s, C-12a), 133.4 (d, C-11), 132.1 (d, C-12), 113.0 (s, C-13), 106.7 (d, C-15), 104.1 (d, C-16a), 73.3 (d, C-3), 43.0 (t, C-6), 36.7 (t, C-8), 34.8 (t, C-6), 31.1 (t,

C-10), 22.3 (t, C-5), 21.0 (t, C-9), 20.9 (q, CH₃), 17.9 (q, SiCH(CH₃)₂), 12.7 (d, SiCH); HRMS *m/z* calcd for C₂₇H₄₂NaO₅Si⁺ [M+Na]⁺ 497.6294, found 497.6299.

General procedure D: Königs–Knorr glucosylation

To a solution of the glucosyl acceptor (0.5 mmol) and bromoacetoglucose **13** (617 mg, 1.5 mmol) in dry MeCN (10 mL) was added molecular sieve 3 Å (1 g) and the resulting suspension was stirred at room temperature for 1 h. After addition of Ag₂O (174 mg, 0.75 mmol), the reaction mixture was stirred in the dark for 48 h. Since TLC analysis indicated remaining glucosyl acceptor, **13** (411 mg, 1 mmol) and Ag₂O (116 mg, 0.5 mmol) were added and stirring was continued in the dark for 24 h. The reaction mixture was diluted with CH₂Cl₂, filtered through Celite and concentrated under reduced pressure. Silica gel filtration (hexane/EtOAc gradient elution) was performed to remove most the carbohydrate byproducts. Since we were not able to fully purify the crude glucosylated products, these compounds were directly subjected to deprotection within subsequent steps.

5-Hydroxy-2-(isopropoxycarbonyl)phenyl-β,D-glucoside (17)

Following general procedure D, crude **16** was obtained starting from the PMB protected ZEN mimic **15** (95 mg, 0.3 mmol). This material was dissolved in CH₂Cl₂/H₂O (10/1, 6 mL) and cooled to 0 °C. After addition of DDQ (102 mg, 0.45 mmol) the reaction mixture was gradually warmed to room temperature. TLC/MS analysis indicated full conversion after stirring for 24 h. The reaction mixture was diluted with CH₂Cl₂ (20 mL), washed with satd. aq. NaHCO₃, dried over Na₂SO₄ and concentrated. The crude product was dissolved in THF/H₂O (4/1, 7 mL) and KOH (168 mg, 3 mmol) was added. After stirring for 2 h at room temperature, the solution was diluted with water (15 mL) and acidified to pH 6.5 by slow addition of 0.2 M aq. HCl followed by extraction with EtOAc (4 × 15 mL). The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (MPLC, RP-C18, MeCN/H₂O, gradient elution) to yield the desired product **17** as a white solid (32 mg, 30%); R_f 0.5 (CH₂Cl₂/MeOH, 5/1); ¹H NMR

(200 MHz, CD₃OD) δ 7.68 (d, J = 8.8 Hz, 1H, H-6), 6.80 (d, J = 2.3 Hz, 1H, H-3), 6.52 (dd, J = 8.8, 2.3 Hz, 1H, H-5), 5.16 (sept., J = 6.3 Hz, 1H, COOCH), 4.82 (d, J = 7.2 Hz, 1H, H-1'), 3.94 (dd, J = 11.8, 1.5 Hz, 1H, H_a-6'), 3.80-3.68 (m, 1H, H_b-6'), 3.56-3.39 (m, 4H, H-2', H-3', H-4', H-5'), 1.34 (d, J = 6.3 Hz, 6H, (CH₃)₂CH); ¹³C NMR (50 MHz, CD₃OD) δ 167.3 (s), 164.4 (s), 161.4 (s), 134.1 (d), 113.2 (s), 111.0 (d), 105.9 (d), 104.3 (d), 78.5 (d), 77.5 (d), 74.9 (d), 71.2 (d), 69.4 (d), 62.5 (t), 22.2 (q), 22.1 (q); HRMS m/z calcd for C₁₆H₂₂NaO₉⁺ [M+Na]⁺ 381.1156, found 381.1145.

Zearalenone-16- β ,D-glucoside (7)

Following general procedure D, crude protected ZEN-16-glucoside was obtained starting from **22** (47 mg, 0.1 mmol). This material was dissolved in dry THF (2 mL) and the resulting solution was cooled to -10 °C. After addition of AcOH (6 mg, 0.1 mmol) and TBAF (0.1 mL, 0.1 mmol, 1 M in THF), the reaction was stirred at -10 °C for 3 h. TLC/MS analysis indicated full conversion of the starting material to the desired product. The solvent was evaporated and the residue was dissolved in THF/H₂O (4/1, 6 mL). KOH (56 mg, 1 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. The solution was diluted with water (15 mL) and acidified to pH 6.5 by slow addition of 0.2 M aq. HCl followed by extraction with EtOAc (4 \times 15 mL). The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (MPLC, RP-C18, MeCN/H₂O, gradient elution) to yield the desired product **7** as a white solid (16 mg, 34%, 3 steps); R_f 0.4 (CH₂Cl₂/MeOH, 6/1); ¹H and ¹³C NMR data matched that reported² (for additional 2D NMR spectra see Figures S1, S2 and S3); HRMS m/z calcd for C₂₄H₃₂NaO₁₀⁺ [M+Na]⁺ 503.1888, found 503.1905.

16-*O*-((2,2,2-Trichloroethoxy)sulfonyl)-14-*O*-(triisopropylsilyl)zearalenone (24)

To a solution of **22** (47.5 mg, 0.1 mmol) in dry CH₂Cl₂ (2 mL) cooled to 0 °C was added 1,2-dimethylimidazole (28 mg, 0.5 mmol) and **23** (184 mg, 0.4 mmol). The reaction mixture was warmed

² Kovalsky Paris, M. P.; Schweiger, W.; Hametner, C.; Stückler, R.; Muehlbauer, G. J.; Varga, E.; Kraska, R.; Berthiller, F.; Adam, G. *J. Agric. Food Chem.* **2014**, *62*, 1181-1189.

to room temperature and stirred overnight. After dilution with CH₂Cl₂ (10 mL), the solution was washed with water, dried over Na₂SO₄ and concentrated. Column chromatography over silica gel (hexanes/EtOAc gradient elution) gave the desired product **24** as a colorless viscous oil (62 mg, 91%); R_f 0.4 (hexanes/EtOAc, 5/1); ¹H NMR (200 MHz, CDCl₃) δ 6.96 (d, *J* = 2.2 Hz, 1H, H-13), 6.92 (d, *J* = 2.2 Hz, 1H, H-15), 6.45 (d, *J* = 15.6 Hz, 1H, H-12), 5.93 (ddd, *J* = 15.5, 9.5, 4.7 Hz, 1H, H-11), 5.42-5.25 (m, 1H, H-3), 4.92 (d, *J* = 11.0 Hz, 1H, CH_{2a}), 4.84 (d, *J* = 11.0 Hz, 1H, CH_{2b}), 2.65 (ddd, *J* = 17.6, 10.9, 3.2 Hz, 1H, H_a-8), 2.45-2.18 (m, 4H, H_{ab}-6, H_b-8, H_a-10), 2.15-1.93 (m, 2H, H_a-5, H_b-10), 1.80-1.51 (m, 5H, H_{ab}-4, H_b-5, H_{ab}-9), 1.37 (d, *J* = 6.3 Hz, 3H, CH₃), 1.31-1.18 (m, 3H, SiCH), 1.14-1.05 (m, 18H, SiCH(CH₃)₂); ¹³C NMR (50 MHz, CDCl₃) δ 211.1 (s, C-7), 165.2 (s, C-1), 158.0 (s, C-16), 147.8 (s, C-14), 138.7 (s, C-12a), 134.8 (d, C-11), 128.4 (d, C-12), 118.6 (s, C-16a), 116.1 (d, C-13), 110.8 (d, C-15), 92.4 (s, CCl₃), 80.6 (t, OCH₂), 72.2 (d, C-3), 43.7 (t, C-6), 37.6 (t, C-8), 35.1 (t, C-4), 31.4 (t, C-10), 21.5 (t, C-5), 21.2 (t, C-9), 19.8 (q, CH₃), 17.9 (q, SiCH(CH₃)₂), 12.60 (d, SiCH); HRMS *m/z* calcd for C₂₉H₄₃Cl₃NaO₈SSi⁺ [M+Na]⁺ 707.1406, found 707.1433.

Zearalenone-16-sulfate, tetrabutylammonium salt (NBu₄-8)

To a solution of the **24** (55 mg, 0.08 mmol) in dry THF (1 mL), cooled to -10 °C, was added AcOH (5 mg, 0.083 mmol) and TBAF (83 μL, 0.083 mmol, 1 M in THF). The reaction mixture was stirred at -10 °C for 3 h and subsequently concentrated under reduced pressure. The residue was dissolved in dry MeOH (1 mL) and after addition of HCOONH₄ (44 mg, 0.7 mmol) and zinc dust (16 mg, 0.25 mmol), the reaction mixture was stirred for 16 h at room temperature. Filtration through Celite and evaporation of the solvent afforded the crude product, which was purified by column chromatography over silica gel (CH₂Cl₂/MeOH/NH₄OH = 10/4/1). **8** was obtained as tetrabutylammonium salt starting from **24** as a white solid (33 mg, 65%); R_f 0.5 (CH₂Cl₂/MeOH/NH₄OH, 20/5/1); ¹H NMR (400 MHz, CD₃OD) δ 7.01 (d, *J* = 1.9 Hz, 1H, Ar-H), 6.75 (d, *J* = 1.9 Hz, 1H, Ar-H), 6.39 (d, *J* = 15.7 Hz, 1H, H-12), 6.01 (ddd, *J* = 15.7, 10.0, 4.3 Hz,

1H, H-11), 5.33-5.24 (m, 1H, H-3), 3.26-3.19 (m, 8H, N⁺CH₂), 2.72 (ddd, *J* = 17.1, 11.1, 3.1 Hz, 1H, H_a-8), 2.50 (ddd, *J* = 13.2, 8.5, 4.5 Hz, 1H, H_a-6), 2.37-2.21 (m, 3H, H_b-6, H_b-8, H_a-10), 2.10-1.97 (m, 2H, H_a-5, H_b-10), 1.85-1.70 (m, 2H, H_a-4, H_a-9), 1.69-1.54 (m, 11H, N⁺CH₂CH₂, H_b-4, H_b-5, H_b-9), 1.47-1.35 (m, 11H, N⁺CH₂CH₂CH₂, CH₃), 1.02 (t, *J* = 7.4 Hz, 12H, N⁺CH₂CH₂CH₂CH₃); ¹³C NMR (100 MHz, CD₃OD) δ 212.7 (s, C-7), 167.6 (s, C-1), 159.0 (s, C-14), 150.8 (s, C-16), 136.7 (s, C-12a), 132.7 (d, C-11), 128.7 (d, C-12), 117.8 (s, C-16a), 107.5 (d, C-13), 106.8 (d, C-15), 71.2 (d, C-3), 58.05 (q_{NH}, ²J_{CN} = 2.1 Hz, N⁺CH₂, 4C), 43.4 (t, C-6), 37.1 (t, C-8), 34.8 (t, C-4), 31.0 (t, C-10), 23.4 (t, N⁺CH₂CH₂), 21.2 (t, C-5), 21.0 (t, C-9), 19.3 (t, N⁺CH₂CH₂CH₂), 18.9 (q, CH₃), 12.6 (q, N⁺CH₂CH₂CH₂CH₃); HRMS *m/z* calcd for C₁₈H₂₁O₈S⁻ [M-NBu₄]⁻ 397.0963, found 397.0961.

2. NMR spectra

Figure S1: COSY spectrum of 7

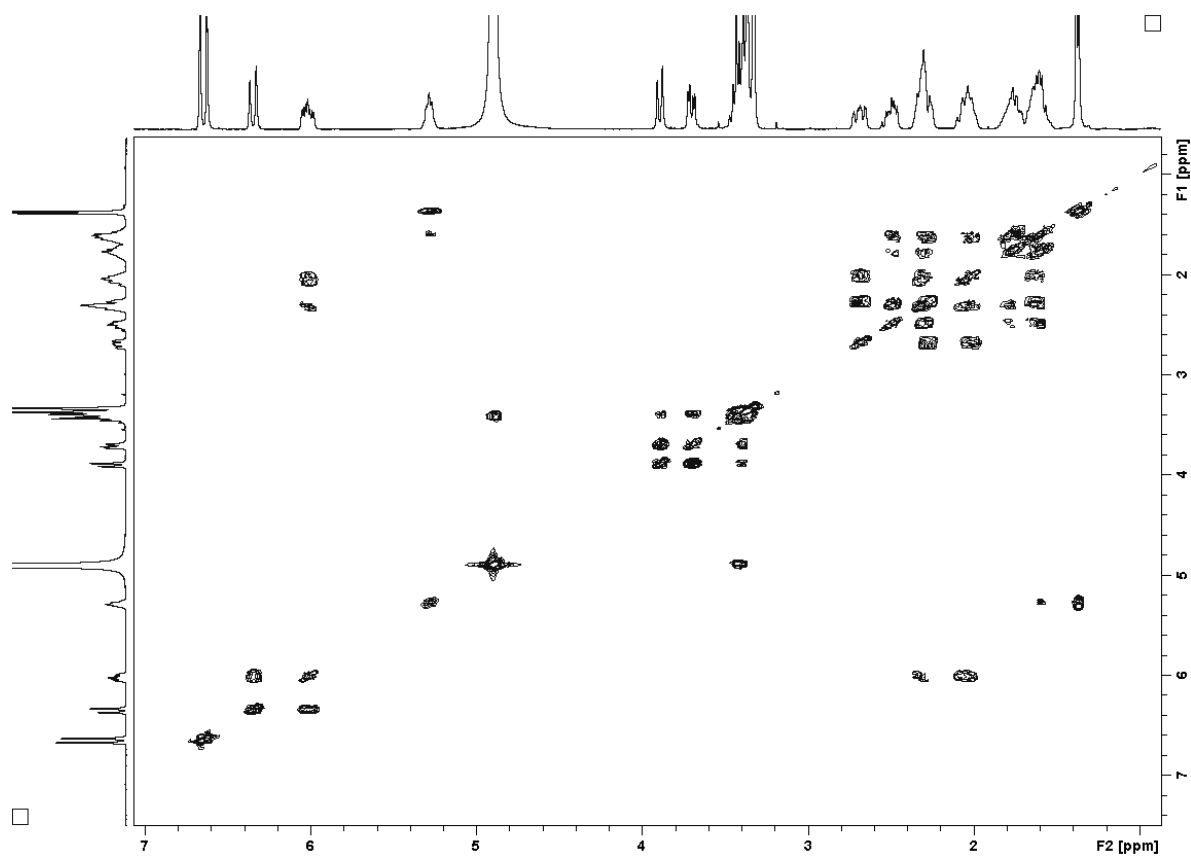


Figure S2: HSQC spectrum of 7

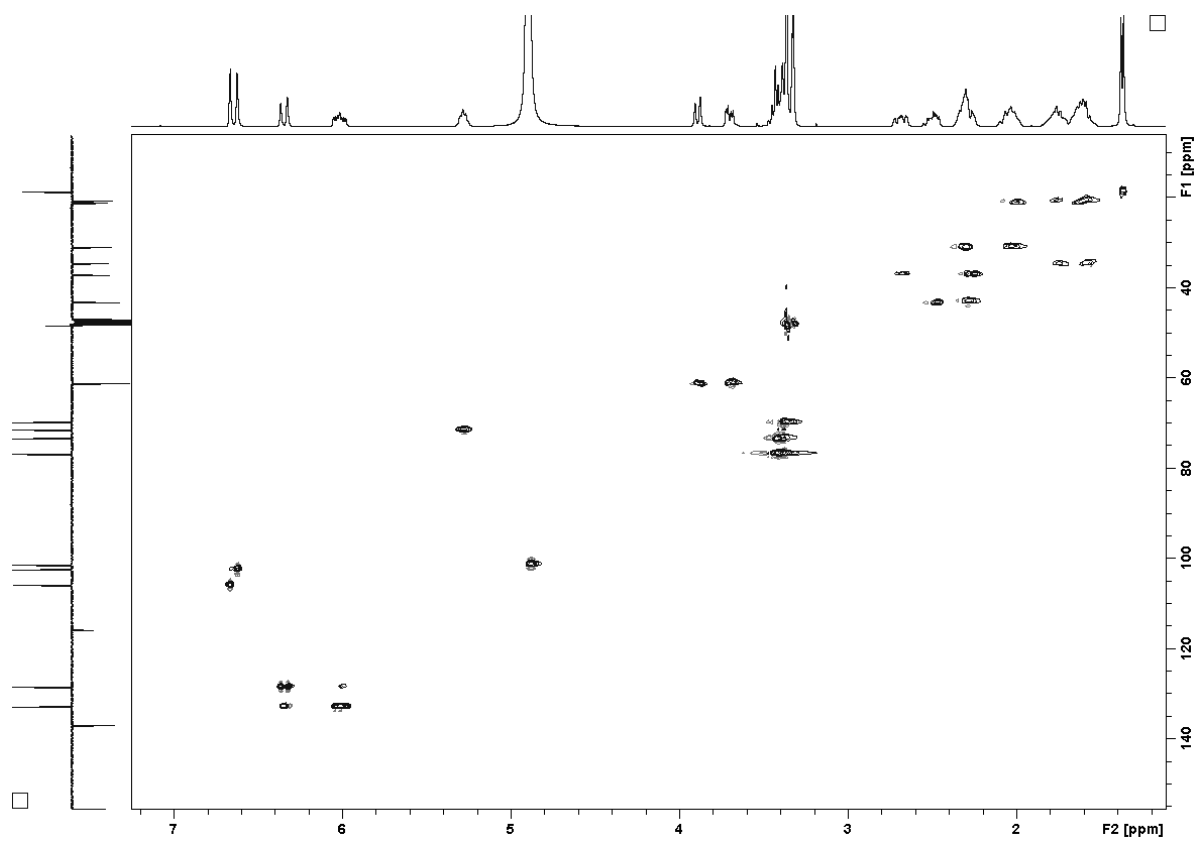


Figure S3: HMBC spectrum of 7

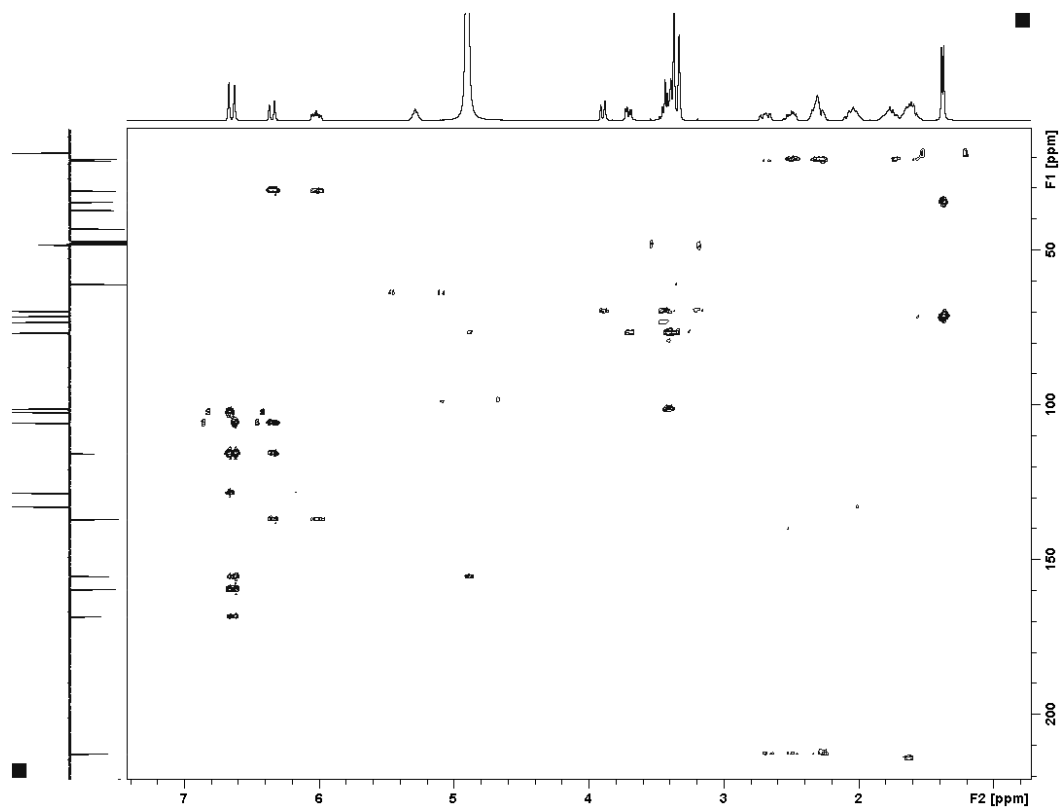


Figure S4: ¹H NMR spectrum of **8**

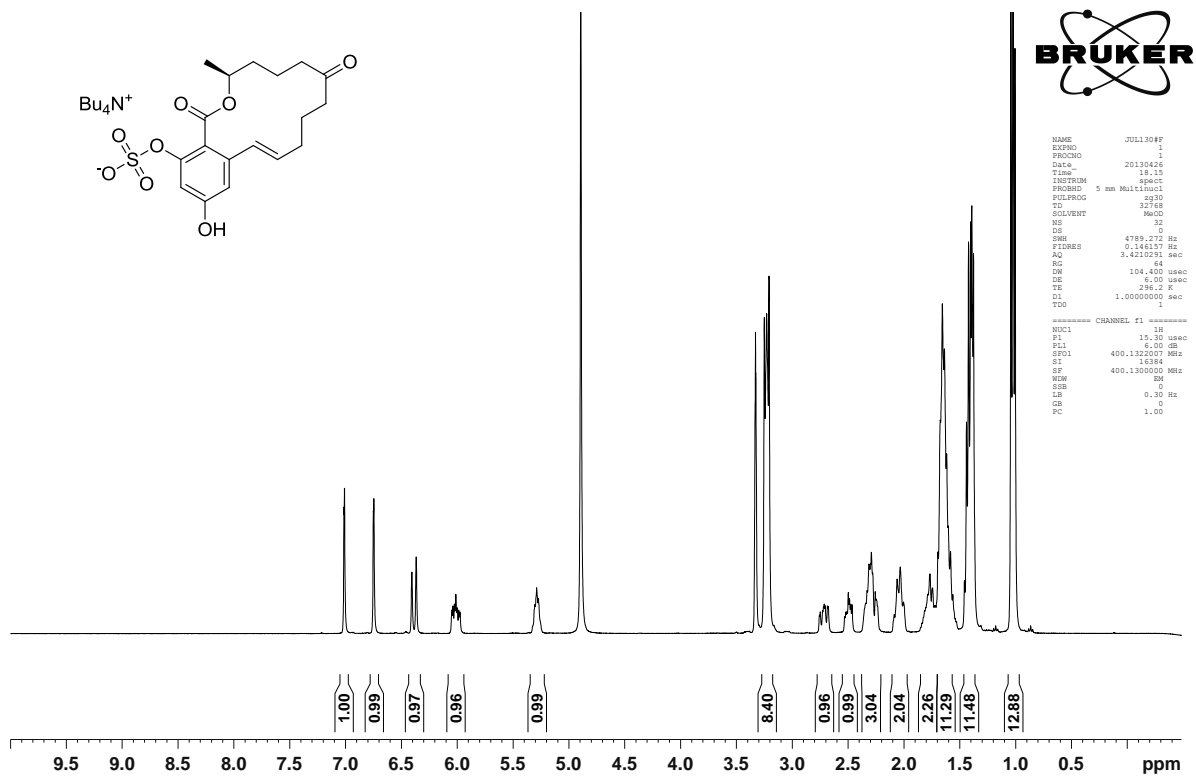


Figure S5: ¹³C NMR spectrum of **8**

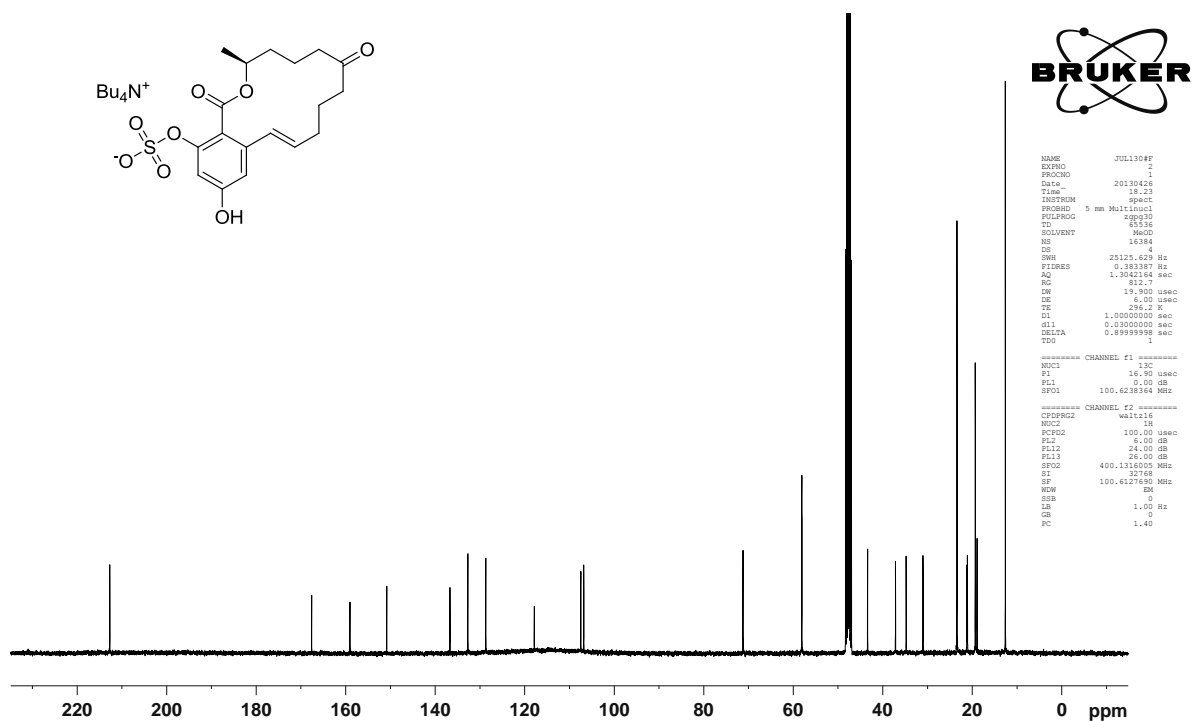


Figure S6: ¹H NMR spectrum of 10

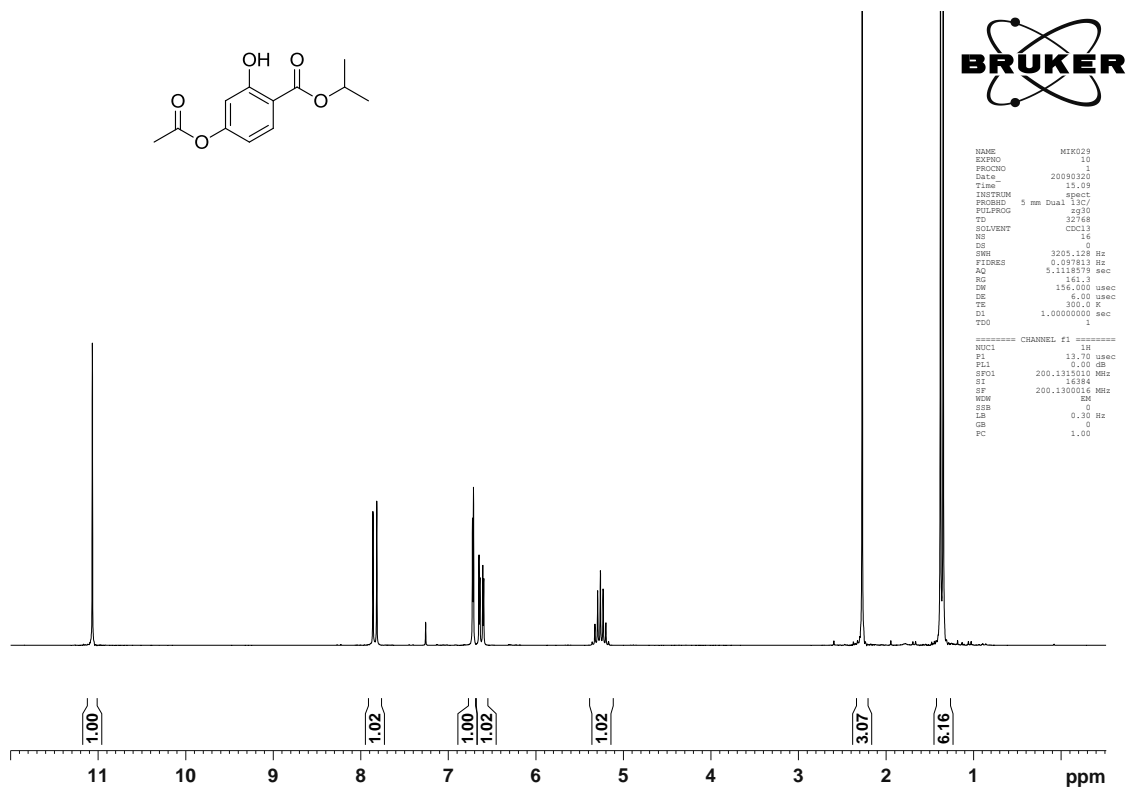


Figure S7: ¹³C NMR spectrum of 10

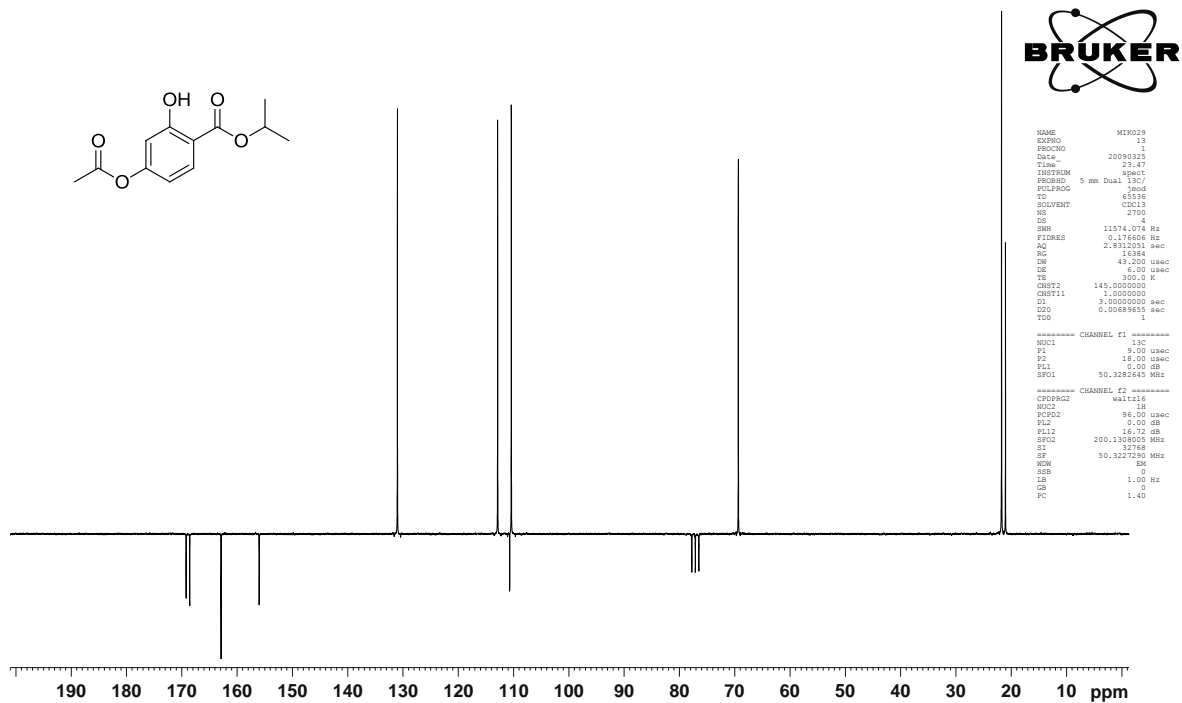


Figure S8: ¹H NMR spectrum of 14

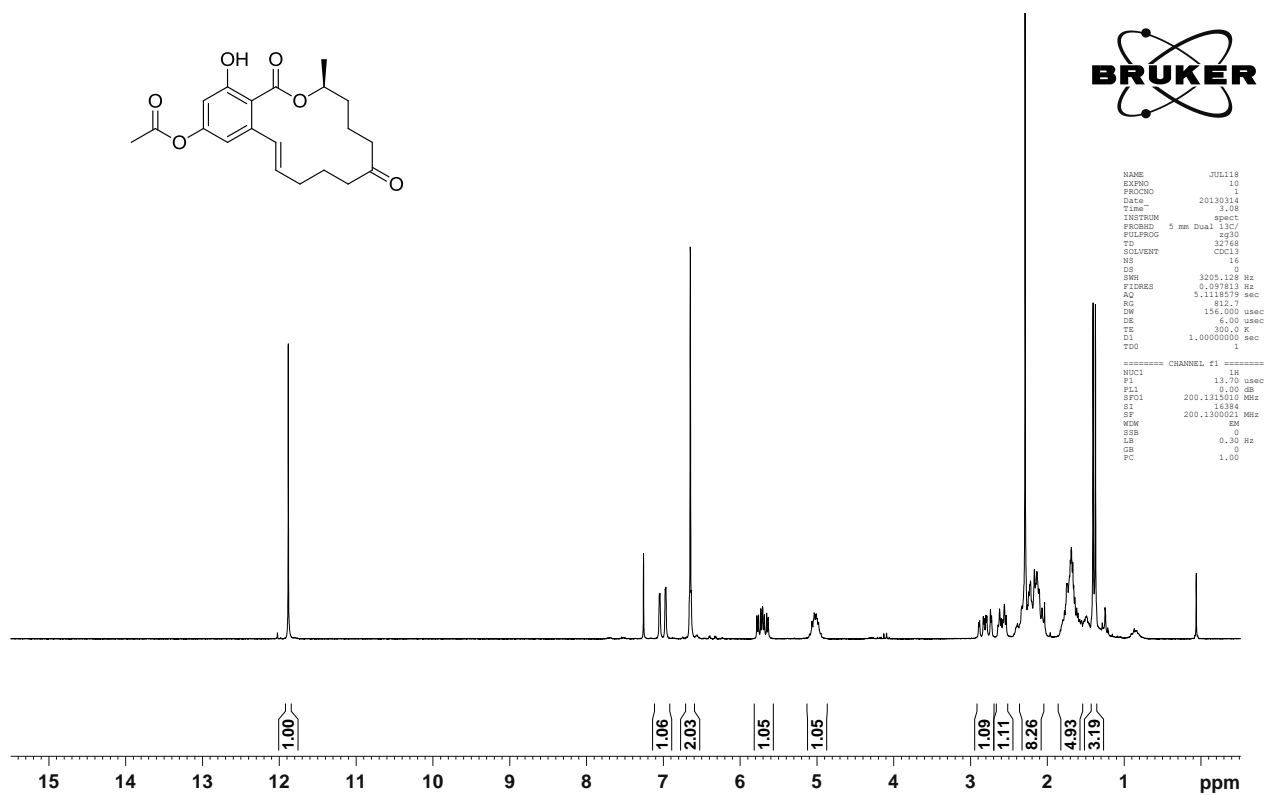


Figure S9: ¹³C NMR spectrum of 14

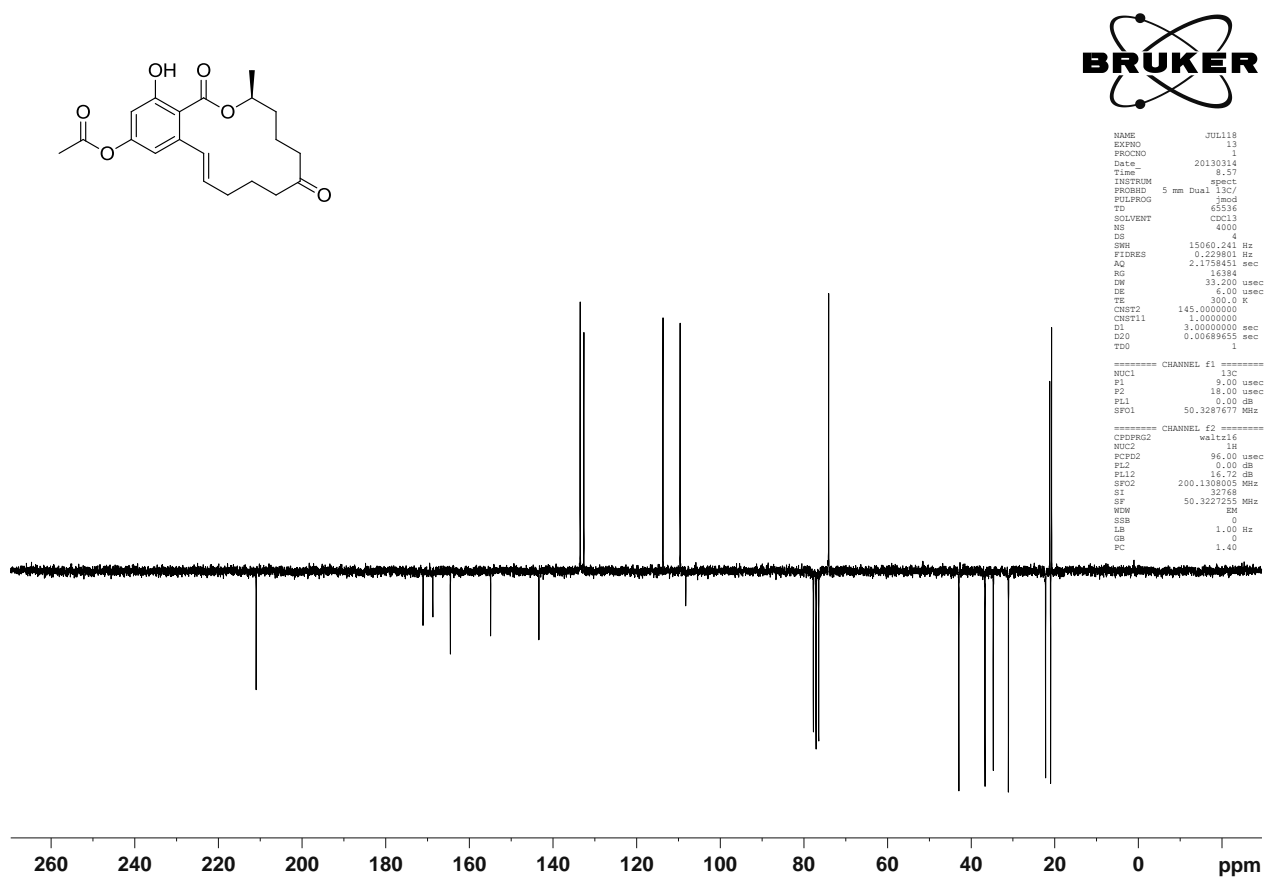


Figure S10: ^1H NMR spectrum of 15

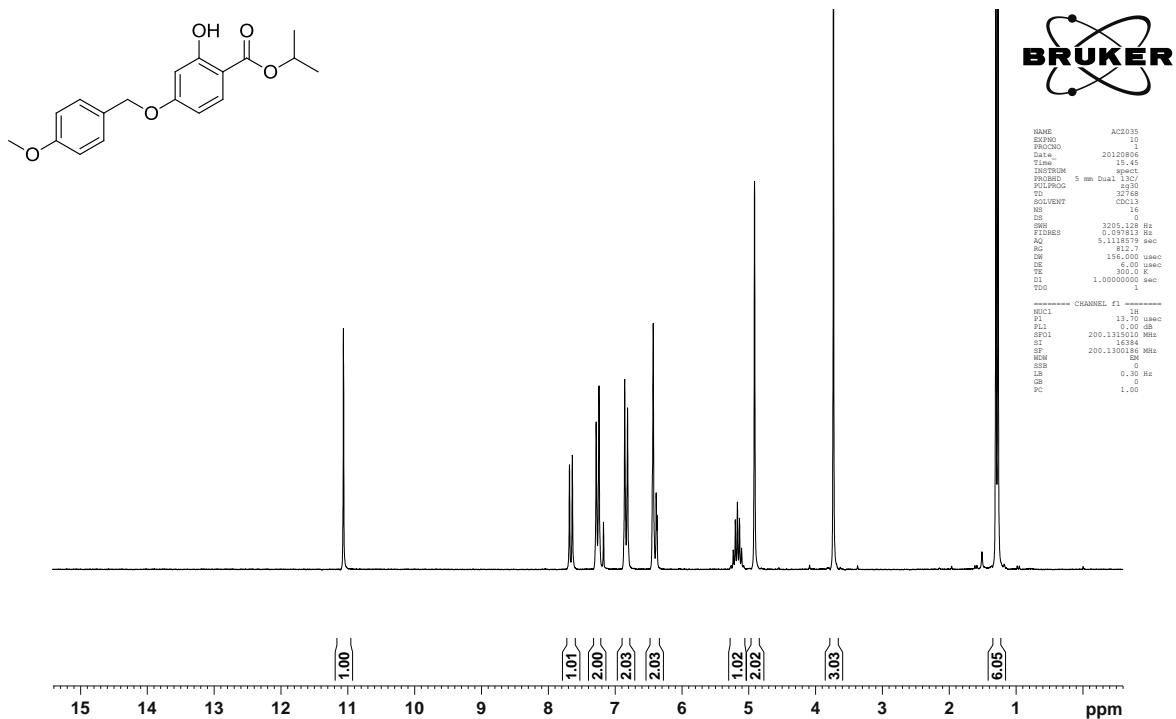


Figure S11: ^{13}C NMR spectrum of 15

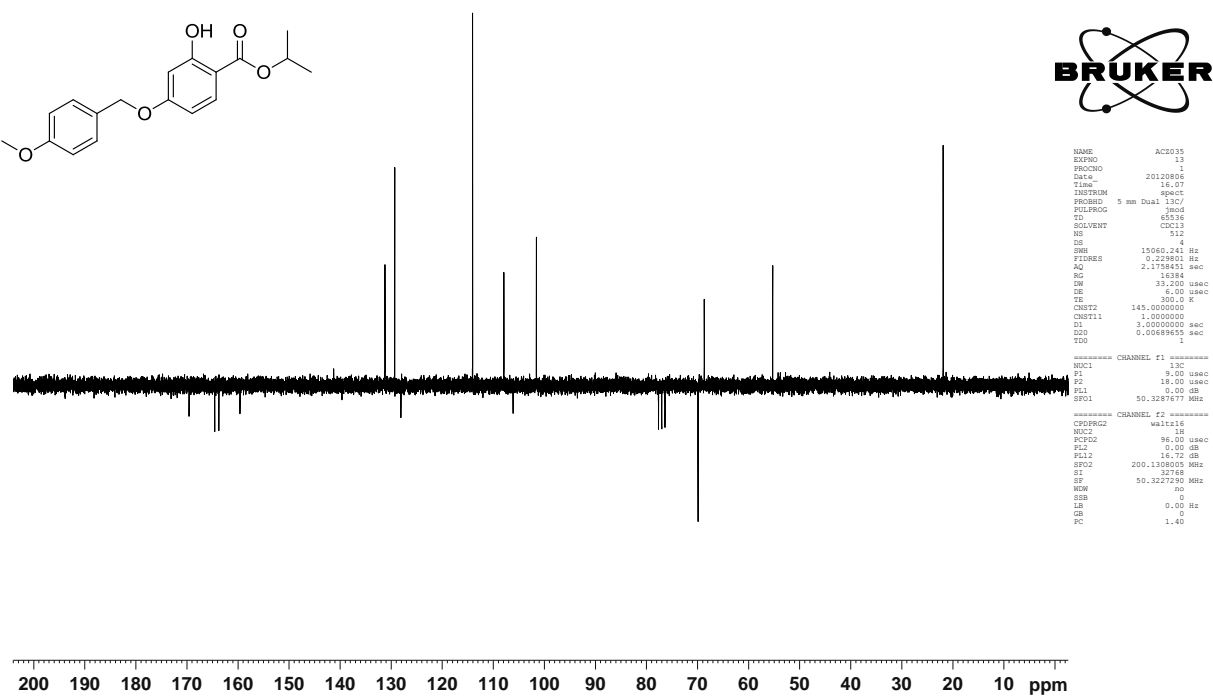


Figure S12: ¹H NMR spectrum of 17

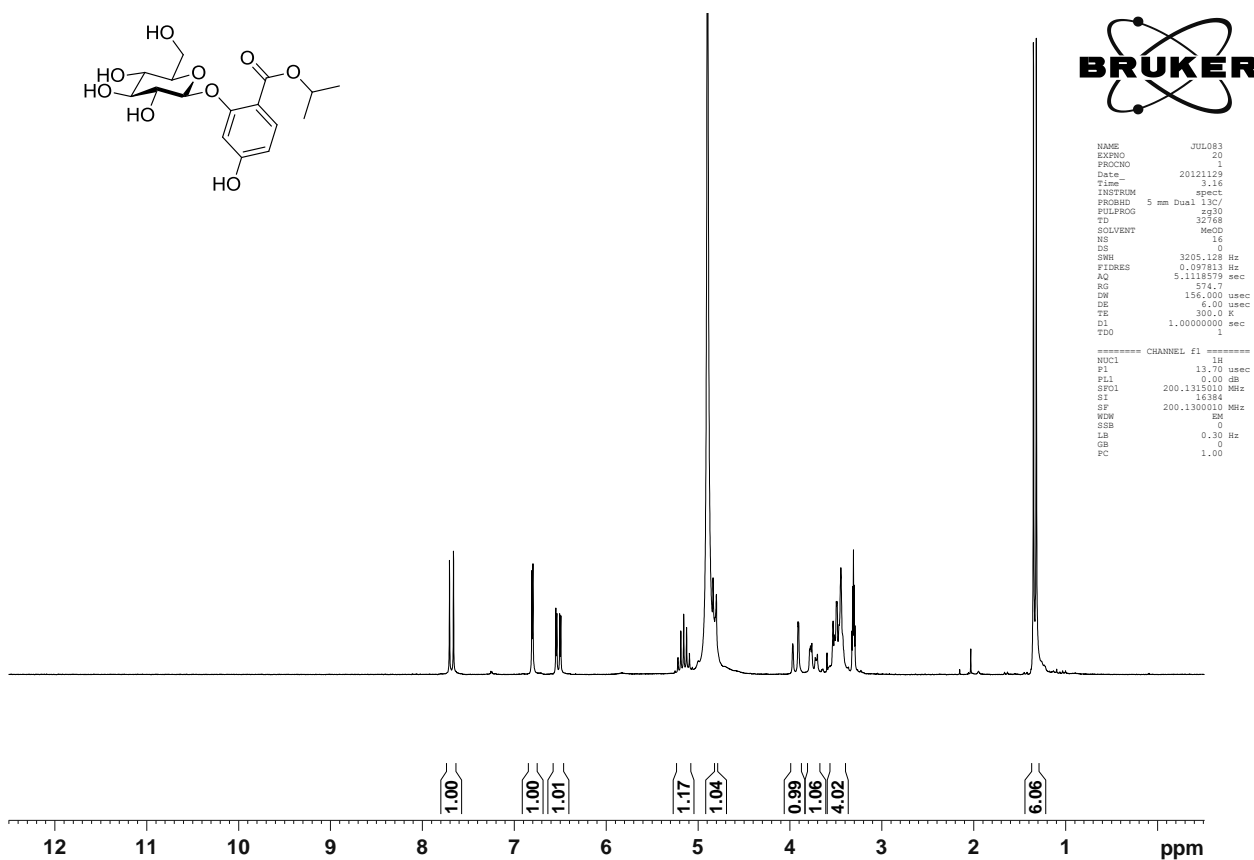


Figure S13: ¹³C NMR spectrum of 17

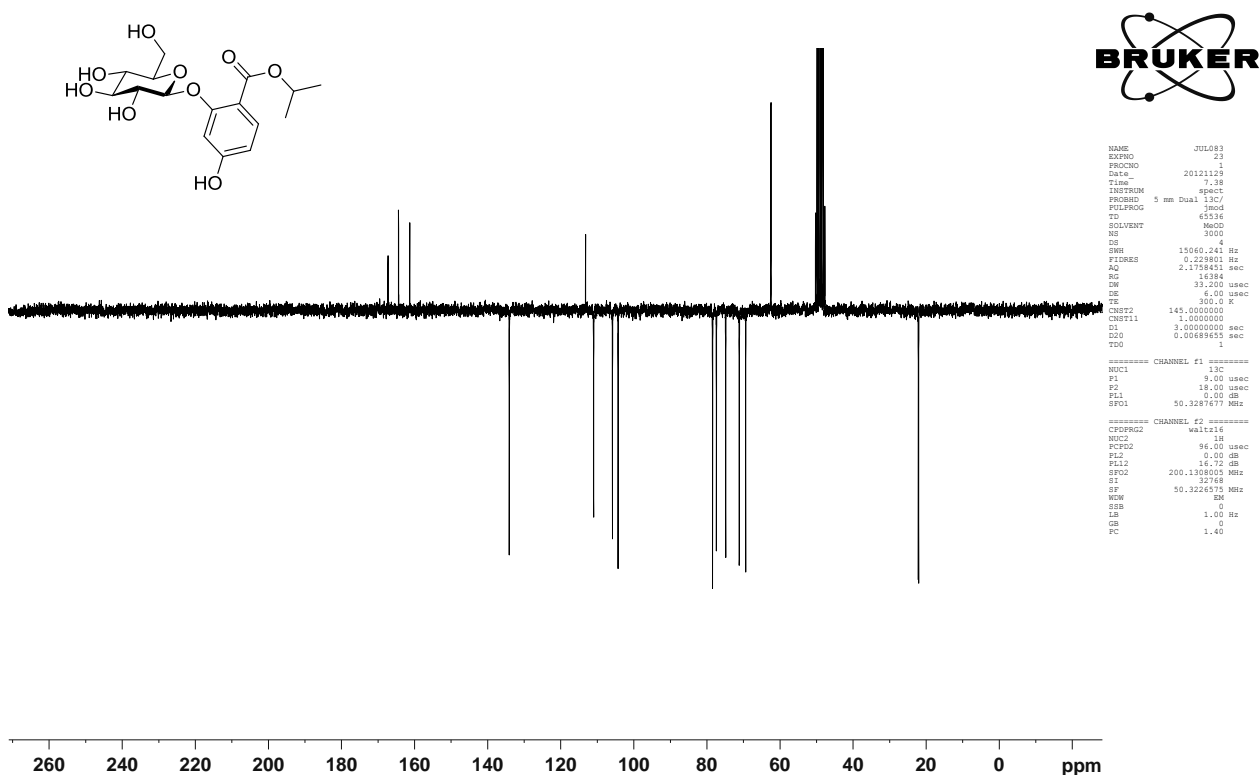


Figure S14: ¹H NMR spectrum of 18

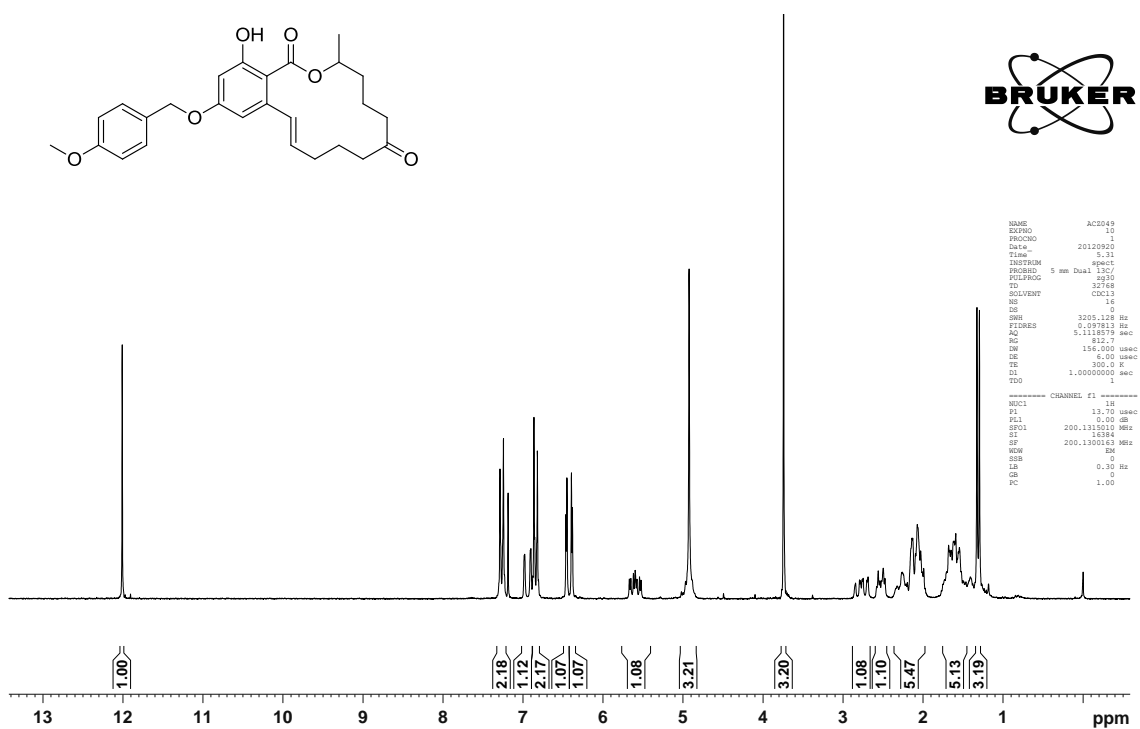


Figure S15: ¹³C NMR spectrum of 18

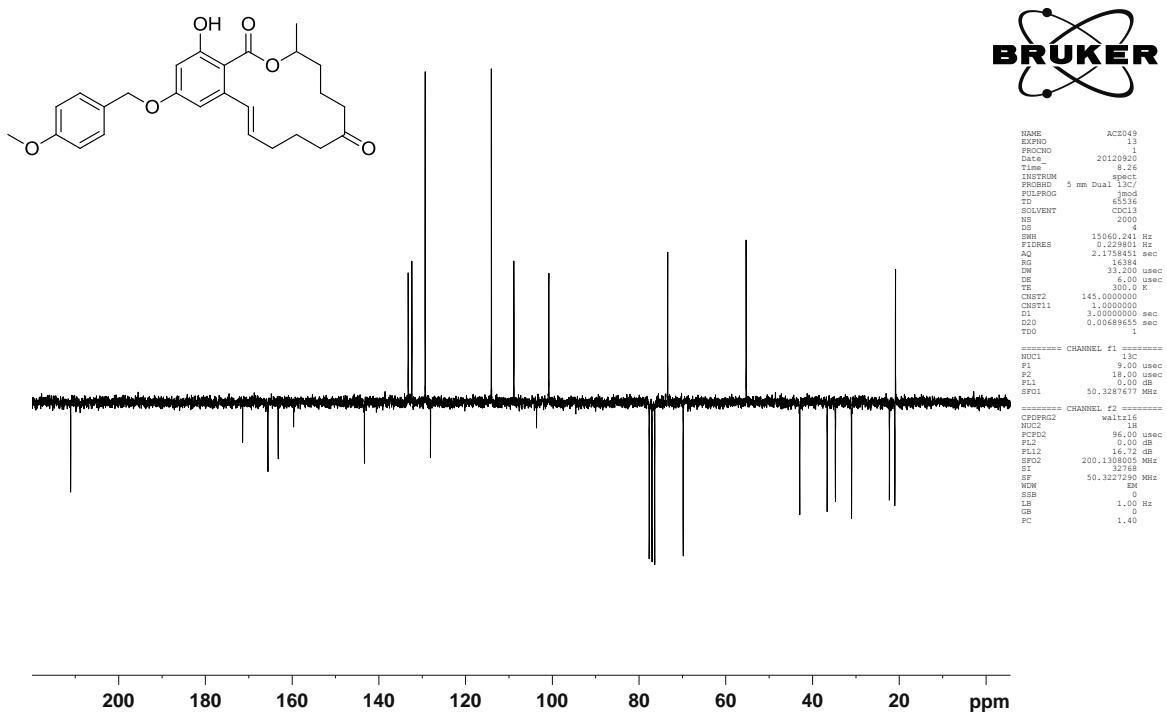


Figure S16: ¹H NMR spectrum of 21

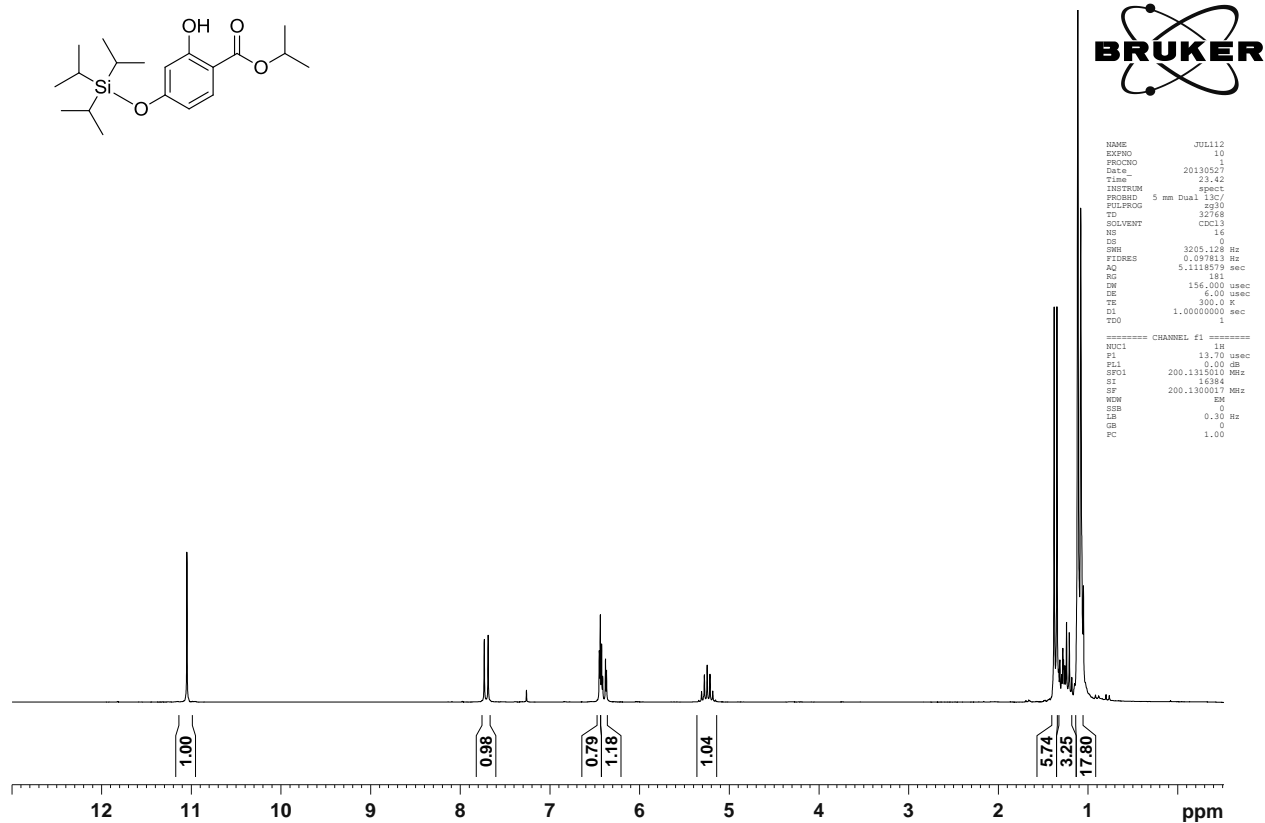


Figure S17: ¹³C NMR spectrum of 21

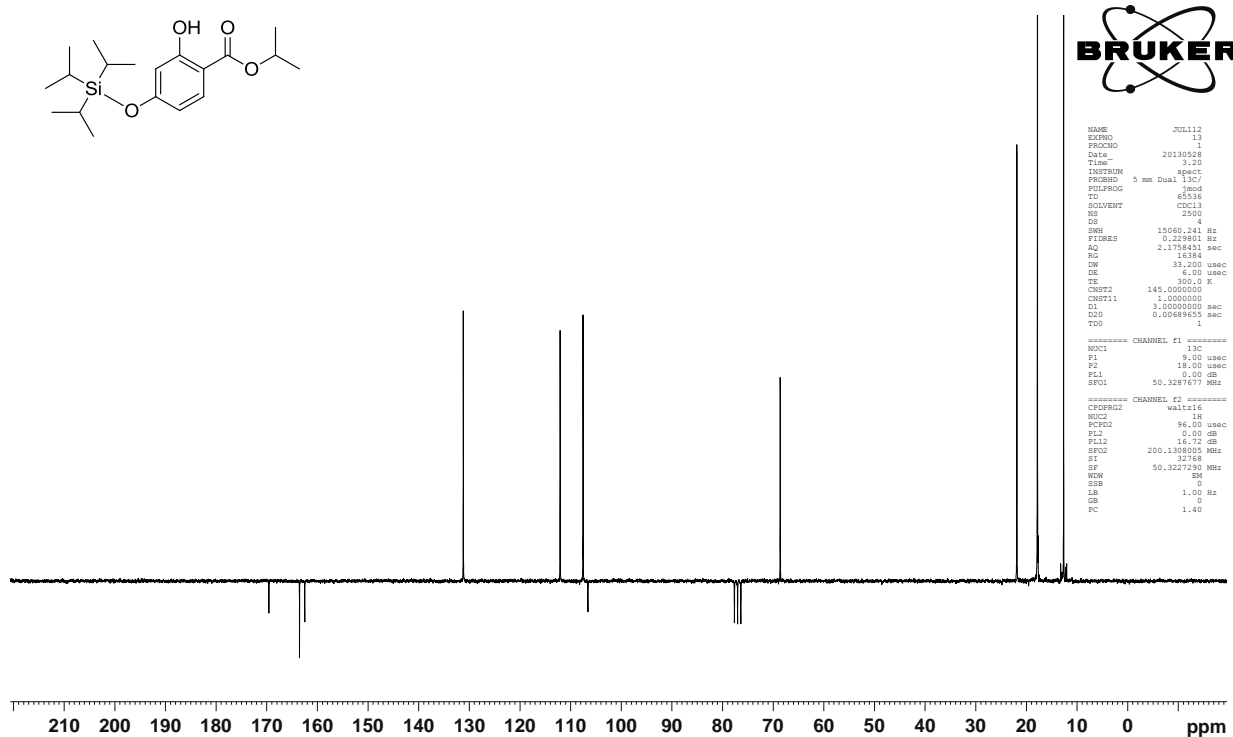


Figure S18: ^1H NMR spectrum of **22**

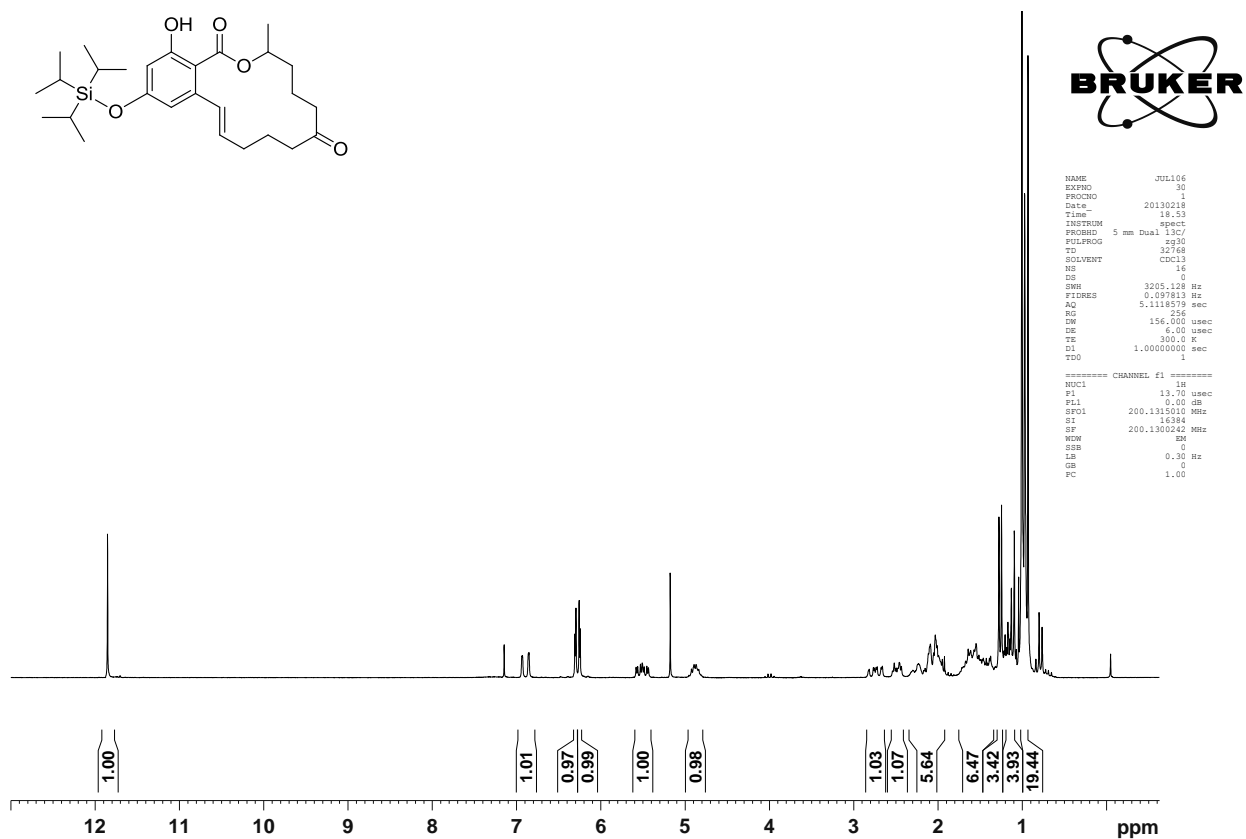


Figure S19: ^{13}C NMR spectrum of **22**

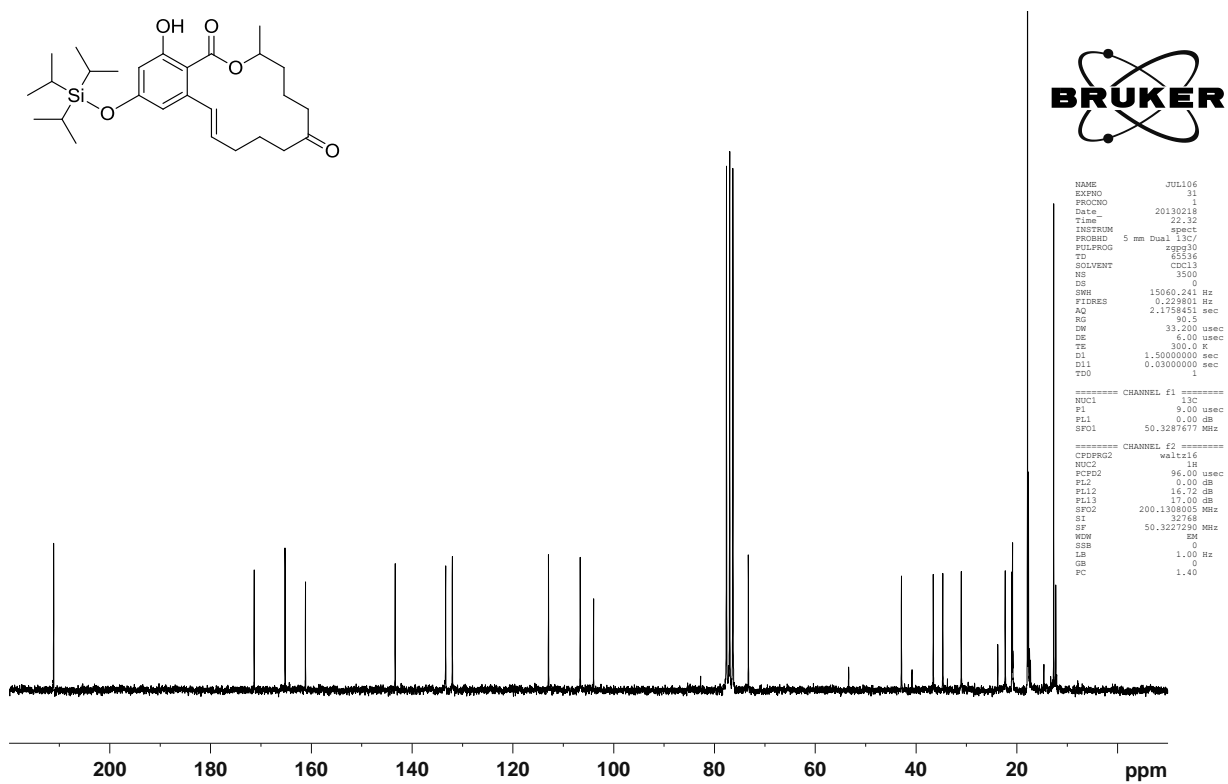


Figure S20: ¹H NMR spectrum of 24

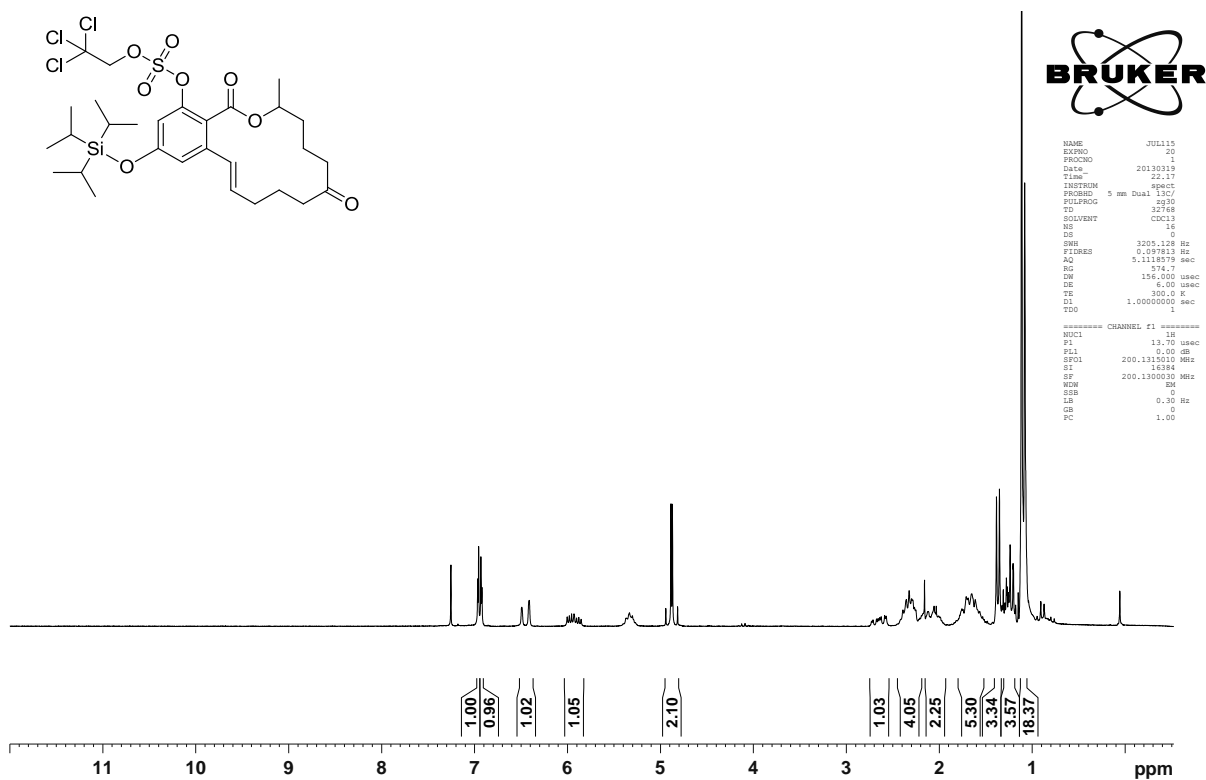


Figure S21: ¹³C NMR spectrum of 24

