Supporting Information

for

Synthesis of C-Acyl Furanosides via the Cross-Coupling of Glycosyl Esters with Carboxylic Acids

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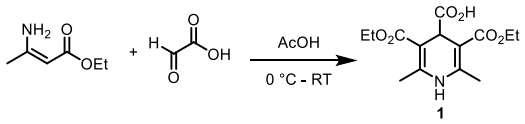
Contents

Materials and Methods

All reactions were conducted in oven dried glassware under an atmosphere of nitrogen unless otherwise noted. THF, DCM, EtOH were dried and deoxygenated by passing through alumina in a solvent purification system. 1,4-dioxane was dried by refluxing over Na with benzophenone as an indicator. ^{1}H NMR spectra were recorded on on a Bruker 400 MHz Avance spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent resonance ($CDCl_3$, δ = 7.26 ppm; CD_3CN, δ = 1.94 ppm) as the internal reference. Spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded on Bruker 400 (101 MHz). Chemical shifts were reported in ppm relative to tetramethylsilane with the solvent resonance used as the internal reference ($CDCl_3$, δ = 77.16 ppm; CD_3CN, δ = 118.26 ppm). ^{19}F NMR spectra were recorded on Bruker 400 (377 MHz). High resolution mass spectra (HRMS) were recorded on an Agilent 6224 TOF LC/MS (APCI source and ESI source). Reactions were monitored by thin-layer chromatography (TLC) on Merck TLC silica gel 60 F254 plates and compounds were visualized by UV light (254 nm) or staining with $KMnO_4$ or phosphomolybdic acid. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer.

Synthesis of the Substrates

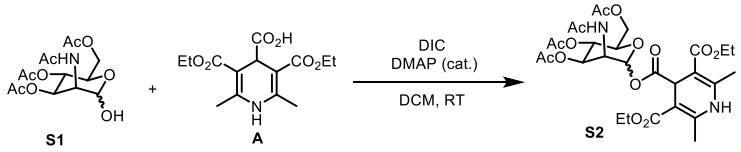
1. Synthesis of 3,5-Diethoxycarbonyl-3,6-dimethyl-1,4-dihydroisonicotinic Acid (1)



In accordance to a procedure reported in the literature,[1,2] glyoxylic acid (10 g, 108 mmol, 1 equiv.) was added to a solution of ethyl-3-aminocrotonate (27.4 mL, 218 mmol, 2.0 equiv.) in 50 mL of glacial acetic acid at 0 °C. The reaction mixture slowly turned yellow and formed a precipitate. After stirring overnight at room temperature, the resulting solid was collected by filtration and washed with acetic acid (3*15 ml) and water (2*15 ml). The solid was dried overnight under reduced pressure to afford the pure acid **1** (12.3 g, 38%) as a white powder.

2. Preparation of Glycosyl 4-Formate-1,4-dihydropyridine

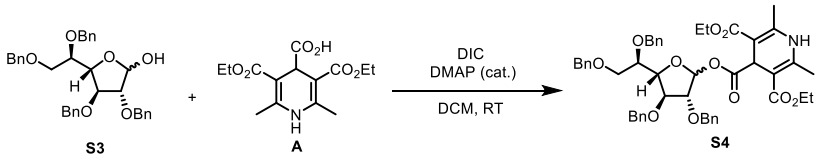
Sugar DHP ester substrates were synthesized according to literature procedures. [2]



In a round bottom flask, carboxylic acid **A** (180 mg, 0.605 mmol, 1.0 equiv.), DIC (DIC = N, N'-diisopropylcarbodiimide) (0.1 mL, 0.67 mmol, 1.1 equiv.) and DMAP (DMAP = 4-

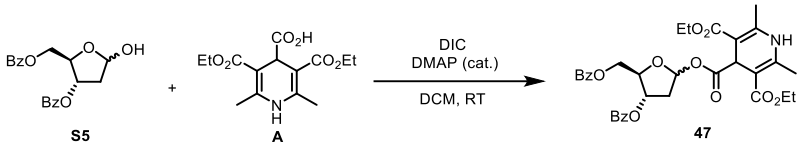
dimethylaminopyridine) (7.0 mg, 0.0605 mmol, 0.1 equiv.) were added to a solution of 2-(acetylamino)-3,4,6-tri-*O*-acetyl- 2-deoxy-α/β-D-mannopyranose [3] **S1**(210 mg, 0,0605 mmol, 1.0 equiv.) in DCM (3 mL) at room temperature. After stirring for 2 h, 3 mL Et_2O was added, then the reaction mixture was filtered through a pad of Celite® and washed with DCM/Et_2O (1:1). After the removal of solvent under vacuum, the crude material was purified by flash column chromatography (*n*-hexane/EA gradient 1:2 to 0:1) to afford the corresponding product **S2** (310 mg, α and β mixture, 82% yield) as a white solid.

Major β isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (d, *J* = 3.9 Hz, 1H), 6.03 (d, *J* = 8.9 Hz, 1H), 5.81 (d, *J* = 2.3 Hz, 1H), 5.09 (t, *J* = 8.1 Hz, 1H), 5.01 (dd, *J* = 8.4, 4.0 Hz, 1H), 4.87 (s, 1H), 4.69 (ddd, *J* = 9.1, 4.0, 2.4 Hz, 1H), 4.29 – 4.07 (m, 6H), 3.84 – 3.75 (m, 1H), 2.26 (d, *J* = 4.0 Hz, 6H), 2.09 – 2.01 (m, 12H), 1.30 – 1.23 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.06, 170.82, 170.62, 170.26, 169.74, 167.37, 167.12, 146.44, 146.27, 97.84, 97.80, 91.07, 73.19, 70.48, 65.78, 62.41, 60.30, 60.28, 48.25, 40.66, 23.31, 20.85, 20.83, 19.35, 19.22, 14.47, 14.46. HRMS: m/z (ESI) Calcd for $C_{28}H_{39}N_2O_{14}$ $[M+H]^+$: 627.2396, found: 627.2383. IR (cm^{-1}): 3345, 2981, 1745, 1684, 1489, 1366, 1203, 1097, 1047, 907, 731.



In a round bottom flask, carboxylic acid **A** (275 mg, 0.925 mmol, 1.0 equiv.), DIC (0.172 mL, 1.11 mmol, 1.2 equiv.) and DMAP (11.3 mg, 0.0925 mmol, 0.1 equiv.) were added to a solution of 2,3,5,6-tetra-*O*-benzyl-α/β-D-galactofuranose **S3** (500 mg, 0.925 mmol, 1.0 equiv.) in DCM (4.6 mL) at room temperature. After stirring for 12 to 18 h, 5 mL Et_2O was added, then the reaction mixture was filtered through a pad of Celite® and washed with DCM/Et_2O (1:1). After the removal of solvent under vacuum, the crude material was purified by flash column chromatography (*n*-hexane/EA gradient 1:2 to 1:1) to afford the corresponding product **S4** (635 mg, α and β mixture, 87% yield) as a colorless oil.

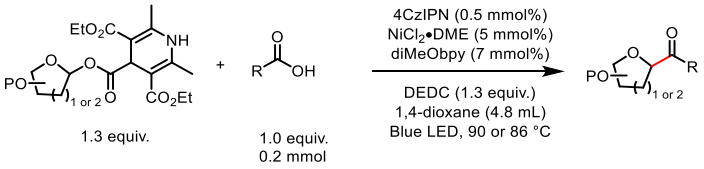
Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.25 (m, 20H), 6.31 (d, *J* = 3.7 Hz, 1H), 5.85 (s, 1H), 5.04 (s, 1H), 4.76 (d, *J* = 11.6 Hz, 2H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.60-4.47 (m, 4H), 4.42 (d, *J* = 11.5 Hz, 1H), 4.19-4.04 (m, 7H), 3.76-3.71 (m, 1H), 3.64 (dd, *J* = 10.5, 3.6 Hz, 1H), 3.56 (dd, *J* = 10.5, 6.2 Hz, 1H), 2.21 (s, 3H), 2.19 (s, 3H), 1.22-1.17 (m, 6H). 13C NMR (101 MHz, $CDCl_3$) δ 172.00, 167.11, 167.08, 145.76, 145.71, 139.20, 138.35, 137.91, 137.49, 128.46, 128.40, 128.36, 128.24, 128.10, 127.97, 127.90, 127.78, 127.73, 127.68, 127.60, 127.33, 98.27, 98.23, 94.65, 84.10, 82.64, 81.83, 80.68, 73.79, 73.46, 72.84, 72.07, 70.32, 60.09, 60.07, 40.35, 19.23, 19.03, 14.41, 14.34. HRMS: m/z (ESI) Calcd for $C_{48}H_{53}NO_{11}$ $[M+Na]^+$: 842.3511, found: 842.3543. IR (cm^{-1}): 3345, 3031, 2981, 2930, 1729, 1698, 1494, 1454, 1206, 1097, 1027, 930, 736.



In a round bottom flask, carboxylic acid **A** (1.3 g, 4.4 mmol, 1.0 equiv.), DIC (0.81 mL, 5.3 mmol, 1.2 equiv.) and DMAP (54 mg, 0.44 mmol, 0.1 equiv.) were added to a solution of 3,5-di-*O*-benzoyl-2-deoxy-α/β-D-ribofuranose[4] **S5** (1.5 g, 4.4 mmol, 1.0 equiv.) in DCM (22 mL) at room temperature. After stirring for 12 to 18 h, 22 mL Et_2O was added, then the reaction mixture was filtered through a pad of Celite® and washed with DCM/Et_2O (1:1). After the removal of solvent under vacuum, the crude material was purified by flash column chromatography (*n*-hexane/EA gradient 1:2 to 1:1) to afford the corresponding product **47** (2.0 g, α and β mixture, 70% yield) as a white solid.

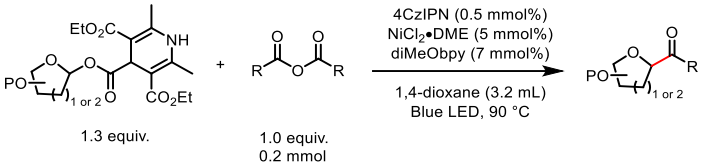
Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (ddd, *J* = 13.7, 8.3, 1.4 Hz, 4H), 7.64 – 7.48 (m, 2H), 7.40 (dt, *J* = 15.9, 7.7 Hz, 4H), 6.44 (dd, *J* = 5.5, 1.8 Hz, 1H), 6.39 (s, 1H), 5.56 (ddd, *J* = 6.9, 5.4, 3.5 Hz, 1H), 4.90 (s, 1H), 4.59 (td, *J* = 6.7, 3.5 Hz, 1H), 4.46 (dd, *J* = 11.3, 6.7 Hz, 1H), 4.40 (dd, *J* = 11.4, 6.8 Hz, 1H), 4.28 – 4.15 (m, 4H), 2.61 (ddd, *J* = 14.4, 7.2, 1.9 Hz, 1H), 2.45 (dt, *J* = 14.3, 5.5 Hz, 1H), 2.32 (s, 3H), 2.28 (s, 3H), 1.32 – 1.22 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.39, 167.21, 167.17, 166.30, 165.97, 146.15, 146.06, 133.51, 133.27, 129.83, 129.77, 129.67, 129.38, 128.54, 128.48, 98.76, 98.17, 98.11, 82.51, 75.07, 65.27, 60.22, 40.67, 38.72, 19.24, 19.21, 14.54, 14.49. HRMS: m/z (ESI) Calcd for $C_{33}H_{35}NO_{11}$ $[M+Na]^+$: 644.2102, found: 644.2089. IR (cm^{-1}): 3344, 2980, 1720, 1697, 1487, 1267, 1201, 1093, 1070, 978, 765.

3. General Procedure for the Coupling of Glycosyl Esters with Carboxylic Acid

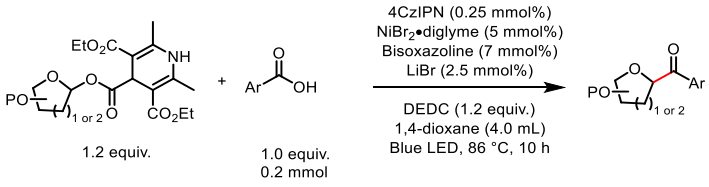


General procedure A for alkyl carboxylic acids as the coupling partner: in a nitrogen-filled glove box, a 8 mL vial was charged with diMeObpy (diMeObpy = 4,4'-dimethoxy-2,2'-bipyridine) (0.014 mmol, 3.0 mg, 7.0 mol%), $NiCl_2$•DME (2.2 mg, 0.010 m mol, 5.0 mol%), 4CzIPN (0.8 mg, 0.001 mmol, 0.5 mol%) (4CzIPN = 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile), the glycosyl ester (1.3 equiv., 0.26 mmol), the carboxylic acid (1.0 equiv., 0.20 mmol) and DEDC (diethyl dicarbonate) (42.2 mg, 0.26 mmol, 1.3 equiv.). After addition of the stir bar and 1,4-dioxane (4.8 mL), the vial was sealed and removed from the glove box. The mixture was sonicated to solubilize $NiCl_2$•DME. Then the vial was immersed in a preheated oil bath with the oil submerges up to 1/3 of the reaction mixture. In the beginning, the temperature of the oil bath was set to a value 2 °C below the desired temperature to avoid overheating once light source was applied. After stirring for 2 minutes, the vial was irradiated with one kessil pro160 - 467 nm LED lights (about 5 cm between the vial and the light), and the

temperature of the oil bath was set to the desired value. The reaction mixture was allowed to stir for 10 h. After cooling to room temperature, the reaction mixture was filtered through a short plug of silica gel (2 cm) and flushed with ethyl acetate. After removal of the solvent under vacuum, the residue was purified by flash column chromatography to afford the corresponding coupling product.



General procedure B for alkyl carboxylic anhydrides as the coupling partner: in a nitrogen-filled glove box, a 4 mL vial was charged with diMeObpy (0.014 mmol, 3.0 mg, 7.0 mol%), $NiCl_2$•DME (2.2 mg, 0.010 mmol, 5.0 mol%), 4CzIPN (0.8 mg, 0.001 mmol, 0.5 mol%), the glycosyl ester (1.3 equiv., 0.26 mmol) and the carboxylic anhydride (1.0 equiv., 0.20 mmol). After addition of the stir bar and 1,4-dioxane (3.2 mL), the vial was sealed and removed from the glove box. The mixture was sonicated to solubilize $NiCl_2$•DME. Then the vial was immersed in a preheated oil bath with the oil submerges up to 1/3 of the reaction mixture. In the beginning, the temperature of the oil bath was set to a value 2 ℃ below the desired temperature to avoid overheating once light source was applied. After stirring for 2 minutes, the vial was irradiated with one kessil pro160 - 467 nm LED lights (about 5 cm between the vial and the light), and the temperature of the oil bath was set to the desired value. The reaction mixture was allowed to stir for 10 h. After cooling to room temperature, the reaction mixture was filtered through a short plug of silica gel (2 cm) and flushed with ethyl acetate. After removal of the solvent under vacuum, the residue was purified by flash column chromatography to afford the corresponding coupling product.



General procedure C for aryl acid as the coupling partner: in a nitrogen-filled glove box, a 8 mL vial was charged with 4,4',5,5'-tetrahydro-2,2'-bioxazole (0.014 mmol, 2.0 mg, 7.0 mol%), $NiBr_2$•diglyme (3.5 mg, 0.010 mmol, 5.0 mol%), 4CzIPN (0.4 mg, 0.001 mmol, 0.5 mol%), ground LiBr (0.4 mg, 0.005 mmol, 0.025 equiv.), aryl acid (1.0 equiv., 0.20 mmol), the glycosyl ester (1.2 equiv., 0.24 mmol) and DEDC (38.9 mg, 0.24 mmol, 1.2 equiv.). After addition of the stir bar and 1,4-dioxane (4.0 mL), the vial was sealed and removed from the glove box. The mixture was sonicated to solubilize $NiBr_2$•DME. Then the vial was immersed in a preheated oil bath with the oil submerges up to 1/3 of the reaction mixture. In the beginning, the temperature of the oil bath was set to a value 2 ℃ below the desired temperature to avoid overheating once light source was applied. After stirring for 2 minutes, the vial was irradiated with one kessil pro160 - 467 nm LED lights (about 5 cm between the vial and

the light), and the temperature of the oil bath was set to the desired value. The reaction mixture was allowed to stir for 10 h. After cooling to room temperature, the reaction mixture was filtered through a short plug of silica gel (2 cm) and flushed with ethyl acetate. After removal of the solvent under vacuum, the residue was purified by flash column chromatography to afford the corresponding coupling product.

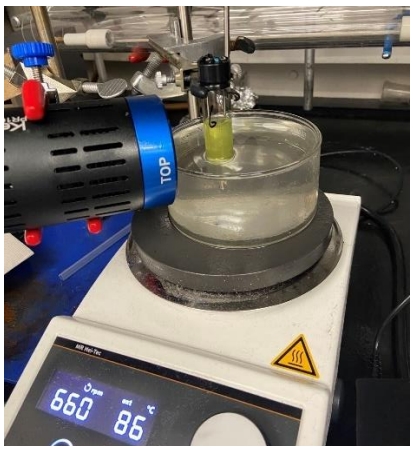
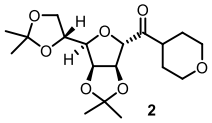


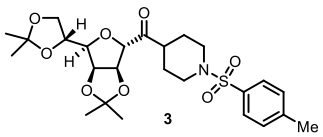
Figure S1: Standard reaction setup with one kessil pro160 - 467 nm LED lights (34 W).



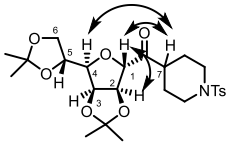
2

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/Acetone gradient 15:1 to 10:1) to afford **2** (60 mg, 84% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.71 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.55 (s, 1H), 4.42 – 4.33 (m, 1H), 4.12 – 4.01 (m, 2H), 3.99 – 3.92 (m, 2H), 3.68 (dd, *J* = 7.0, 3.6 Hz, 1H), 3.41 (tt, *J* = 11.5, 2.3 Hz, 2H), 2.84 (tt, *J* = 11.2, 4.0 Hz, 1H), 1.89 – 1.80 (m, 1H), 1.78 – 1.58 (m, 3H), 1.47 (s, 3H), 1.41 (s, 4H), 1.35 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.87, 113.19, 109.33, 86.54, 82.81, 81.89, 80.68, 73.28, 67.24, 67.07, 66.72, 44.33, 28.37, 27.38, 26.86, 26.18, 25.25, 24.78. HRMS: m/z (ESI) Calcd for $C_{18}H_{29}O_7$ $[M+H]^+$: 357.1908, found: 357.1920. IR (cm^{-1}): 2985, 2936, 1713, 1372, 1209, 1067, 848.



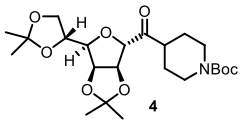
3



Key NOE interactions presented in **3**

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/EA gradient 10:1 to 3:1) to afford **3** (90 mg, 88% yield) as a colorless oil.

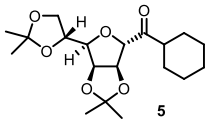
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.01 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.70 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.49 (s, 1H), 4.36 (td, *J* = 6.6, 4.5 Hz, 1H), 4.08 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.75 – 3.65 (m, 2H), 3.61 (dd, *J* = 7.1, 3.6 Hz, 1H), 2.60 – 2.48 (m, 1H), 2.46 – 2.35 (m, 5H), 2.07 – 1.98 (m, 1H), 1.85 – 1.63 (m, 3H), 1.47 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.57, 143.83, 133.17, 129.87, 127.82, 113.31, 109.40, 86.74, 82.84, 81.86, 80.64, 73.26, 66.74, 45.72, 45.39, 44.24, 27.32, 26.91, 26.31, 26.22, 25.25, 24.79, 21.68. HRMS: m/z (ESI) Calcd for $C_{25}H_{36}NO_8S$ $[M+H]^+$: 510.2156, found: 510.2168. IR (cm^{-1}): 2985, 2934, 1712, 1210, 1162, 1067, 929, 723.



4

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/EA gradient 15:1 to 10:1) to afford **4** (64 mg, 70% yield) as a colorless oil.

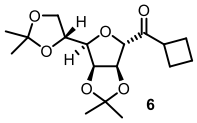
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (dd, *J* = 6.1, 1.0 Hz, 1H), 4.72 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.56 (s, 1H), 4.39 (td, *J* = 6.6, 4.7 Hz, 1H), 4.20 – 4.00 (m, 4H), 3.70 (dd, *J* = 7.0, 3.6 Hz, 1H), 2.77 (ddq, *J* = 11.2, 7.4, 4.5, 3.7 Hz, 3H), 1.90 (d, *J* = 13.2 Hz, 1H), 1.71 (d, *J* = 14.4 Hz, 1H), 1.61 – 1.48 (m, 5H), 1.45 – 1.41 (m, 12H), 1.36 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.22, 154.72, 113.27, 109.39, 86.74, 82.86, 81.93, 80.73, 79.83, 73.33, 66.75, 45.35, 28.54, 27.76, 26.90, 26.85, 26.23, 25.30, 24.82. HRMS: m/z (ESI) Calcd for $C_{23}H_{38}NO_8$ $[M+H]^+$: 456.2594, found: 456.2592. IR (cm^{-1}): 2981, 2935, 1693, 1367, 1162, 1066, 848.



5

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (DCM/EA gradient 60:1 to 50:1) to afford **5** (41 mg, 58% yield) as a colorless oil.

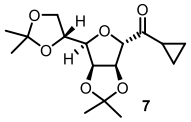
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00 (dd, *J* = 6.1, 1.1 Hz, 1H), 4.72 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.56 (s, 1H), 4.38 (ddd, *J* = 7.3, 6.2, 4.7 Hz, 1H), 4.09 (qd, *J* = 8.7, 5.5 Hz, 2H), 3.72 (dd, *J* = 7.4, 3.6 Hz, 1H), 2.69 – 2.57 (m, 1H), 1.93 – 1.86 (m, 1H), 1.82 – 1.62 (m, 4H), 1.49 (s, 3H), 1.42 (s, 3H), 1.41 – 1.12 (m, 11H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.78, 113.14, 109.39, 86.75, 82.83, 82.08, 80.81, 73.32, 66.94, 47.29, 28.67, 27.88, 26.90, 26.24, 25.83, 25.44, 25.33, 24.86. HRMS: m/z (ESI) Calcd for $C_{19}H_{31}O_6$ $[M+H]^+$: 355.2115, found: 355.2126. IR (cm^{-1}): 2986, 2932, 2855, 1709, 1371, 1209, 1065, 845.



6

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (DCM/EA gradient 60:1 to 50:1) to afford **6** (41 mg, 63% yield) as a colorless oil.

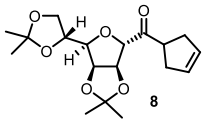
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (dd, *J* = 6.0, 1.0 Hz, 1H), 4.72 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.46 (s, 1H), 4.39 (ddd, *J* = 7.5, 6.0, 4.6 Hz, 1H), 4.17 – 4.05 (m, 2H), 3.66 (dd, *J* = 7.5, 3.6 Hz, 1H), 3.54 (pd, *J* = 8.5, 1.1 Hz, 1H), 2.33 – 1.94 (m, 5H), 1.91 – 1.78 (m, 1H), 1.57 (s, 1H), 1.49 (s, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.05, 113.15, 109.46, 87.08, 82.74, 82.32, 80.67, 73.32, 66.94, 42.39, 27.02, 26.25, 25.35, 24.86, 24.80, 24.36, 18.14. HRMS: m/z (ESI) Calcd for $C_{27}H_{26}NaO_6$ $[M+Na]^+$: 469.1622, found: 469.1641. IR (cm^{-1}): 2985, 2937, 1707, 1371, 1208, 1065, 847.



7

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 15:1 to 6:1) to afford **7** (43 mg, 69% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (dd, *J* = 6.1, 1.0 Hz, 1H), 4.73 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.58 (s, 1H), 4.43 (ddd, *J* = 7.5, 6.0, 4.9 Hz, 1H), 4.21 – 4.07 (m, 2H), 3.76 (dd, *J* = 7.5, 3.6 Hz, 1H), 2.32 (tt, *J* = 7.8, 4.6 Hz, 1H), 1.51 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H), 1.13 – 0.92 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.13, 113.22, 109.45, 88.93, 82.88, 82.75, 80.59, 73.30, 67.09, 26.99, 26.24, 25.34, 24.89, 17.21, 12.15, 12.07. HRMS: m/z (ESI) Calcd for $C_{16}H_{25}O_6$ $[M+H]^+$: 313.1646, found: 313.1655. IR (cm^{-1}): 2987, 2937, 1698, 1371, 1208, 1053, 846.

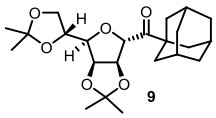


8

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/Acetone gradient 15:1 to 10:1) to afford **8** (60 mg, 84% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 – 5.56 (m, 2H), 5.05 (dd, *J* = 6.0, 1.0 Hz, 1H), 4.73 (dd, *J* = 6.1, 3.7 Hz, 1H), 4.55 (s, 1H), 4.39 (ddd, *J* = 7.3, 6.1, 4.6 Hz, 1H), 4.09 (qd, *J* = 8.8, 5.4 Hz, 2H), 3.73 (dd, *J* = 7.3, 3.6 Hz, 1H), 3.49 (tt, *J* = 9.6, 6.8 Hz, 1H), 2.76 – 2.44 (m, 4H), 1.49 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.43, 129.20, 128.37, 113.15, 109.40, 87.53,

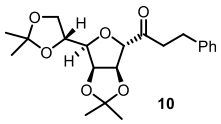
82.73, 82.35, 80.70, 73.30, 66.88, 45.70, 35.81, 34.56, 26.95, 26.22, 25.30, 24.81. HRMS: m/z (ESI) Calcd for $C_{18}H_{26}NaO_6$ $[M+Na]^+$: 361.2622, found: 361.2626. IR (cm^{-1}): 2986, 2936, 1712, 1372, 1209, 1066, 845.



9

Prepared according to the **general procedure A**. Temperature: 86 ℃. The crude material was purified by flash column chromatography (DCM/EA gradient 60:1 to 50:1) to afford **9** (20 mg, 25% yield) as a colorless oil. Using the **general procedure C** afforded **9** (54 mg, 66% yield).

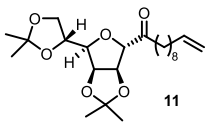
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88 (d, *J* = 5.9 Hz, 2H), 4.80 (dd, *J* = 5.8, 3.7 Hz, 1H), 4.35 (ddd, *J* = 7.7, 6.2, 4.7 Hz, 1H), 4.09 (dd, *J* = 8.7, 6.2 Hz, 1H), 4.02 (dd, *J* = 8.7, 4.7 Hz, 1H), 3.95 (dd, *J* = 7.7, 3.7 Hz, 1H), 2.06 (p, *J* = 3.0 Hz, 3H), 1.86 (d, *J* = 2.9 Hz, 6H), 1.77 – 1.66 (m, 6H), 1.51 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.96, 113.01, 109.40, 82.66, 82.63, 82.56, 81.34, 73.49, 67.04, 46.29, 37.84, 36.54, 27.84, 26.97, 26.31, 25.45, 24.78. HRMS: m/z (ESI) Calcd for $C_{23}H_{34}NaO_6$ $[M+Na]^+$: 429.2248, found: 429.2262. IR (cm^{-1}): 2985, 2904, 2851, 1696, 1370, 1208, 1065, 847.



10

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (DCM/EA gradient 60:1 to 50:1) to afford **10** (57 mg, 76% yield) as a colorless oil.

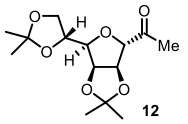
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 4.96 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.65 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.42 – 4.33 (m, 2H), 4.11 (dd, *J* = 8.7, 6.3 Hz, 1H), 4.04 (dd, *J* = 8.8, 4.6 Hz, 1H), 3.61 (dd, *J* = 7.4, 3.6 Hz, 1H), 2.98 – 2.81 (m, 4H), 1.48 (s, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.54, 140.70, 128.73, 128.47, 126.45, 113.20, 109.45, 88.48, 82.78, 81.94, 80.62, 73.23, 66.95, 40.68, 29.41, 26.98, 26.21, 25.31, 24.81. HRMS: m/z (APCI) Calcd for $C_{21}H_{29}O_6$ $[M+H]^+$: 377.1959, found: 377.1967. IR (cm^{-1}): 2987, 2936, 1716, 1371, 1210, 1066, 847.



11

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (DCM/EA gradient 60:1 to 50:1) to afford **11** (35 mg, 43% yield) as a colorless oil.

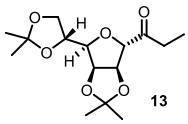
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.04 (dd, *J* = 6.1, 1.0 Hz, 1H), 5.01 – 4.88 (m, 2H), 4.71 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.43 – 4.35 (m, 2H), 4.10 (qd, *J* = 8.7, 5.4 Hz, 2H), 3.68 (dd, *J* = 7.4, 3.6 Hz, 1H), 2.63 – 2.39 (m, 2H), 2.07 – 1.97 (m, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.49 (s, 3H), 1.43 (s, 3H), 1.40 – 1.20 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.59, 139.27, 114.28, 113.18, 109.43, 88.32, 82.73, 82.14, 80.66, 73.27, 66.93, 39.28, 33.89, 29.43, 29.38, 29.29, 29.15, 29.00, 26.96, 26.23, 25.29, 24.85, 23.38. HRMS: m/z (ESI) Calcd for $C_{23}H_{39}O_6$ $[M+H]^+$: 411.2741, found: 411.2746. IR (cm^{-1}): 2986, 2926, 2855, 1715, 1371, 1209, 1066, 847.



12

Prepared according to the **general procedure B**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/EA gradient 10:1 to 5:1) to afford **12** (44 mg, 77% yield) as a solid.

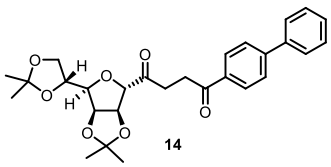
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.72 (dd, *J* = 6.0, 3.6 Hz, 1H), 4.44 – 4.39 (m, 2H), 4.16 – 4.07 (m, 2H), 3.68 (ddd, *J* = 7.3, 3.7, 0.8 Hz, 1H), 2.23 (s, 3H), 1.50 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 207.54, 113.27, 109.47, 88.88, 82.71, 82.10, 80.60, 73.27, 66.91, 26.99, 26.75, 26.24, 25.29, 24.87. HRMS: m/z (APCI) Calcd for $C_{14}H_{23}O_6$ $[M+H]^+$: 287.1489, found: 287.1491. IR (cm^{-1}): 2987, 2935, 1717, 1372, 1211, 1068, 847.



13

Prepared according to the **general procedure B**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/EA gradient 12:1 to 5:1) to afford **13** (43 mg, 72% yield) as a colorless oil.

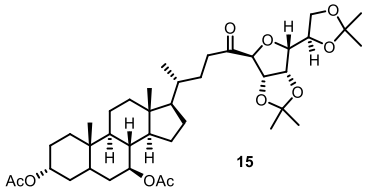
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.72 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.45 – 4.36 (m, 2H), 4.17 – 4.05 (m, 2H), 3.68 (ddd, *J* = 7.4, 3.7, 0.8 Hz, 1H), 2.69 – 2.47 (m, 2H), 1.49 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H), 1.06 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.05, 113.20, 109.45, 88.33, 82.74, 82.29, 80.66, 73.30, 66.92, 32.61, 26.99, 26.24, 25.29, 24.86, 7.34. HRMS: m/z (ESI) Calcd for $C_{15}H_{24}NaO_6$ $[M+Na]^+$: 323.1465, found: 323.1471. IR (cm^{-1}): 2985, 2940, 1717, 1373, 1209, 1067, 847.



14

Prepared according to the **general procedure A**. Temperature: 90 ℃. Notice: due to the bad solubility of the acid fenbufen in 1,4-dioxane, the solution of fenbufen and DEDC in 1,4-dioxane was stirred for 30 min before the solution was added into the 8 mL vial. The crude material was purified by flash column chromatography (hexane/EA gradient 10:1 to 3:1) to afford **14** (42 mg, 44% yield) as a solid.

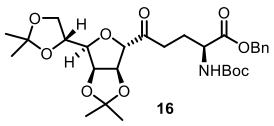
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.72 – 7.60 (m, 4H), 7.50 – 7.38 (m, 3H), 5.21 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.84 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.58 (d, *J* = 1.1 Hz, 1H), 4.45 (dt, *J* = 7.3, 5.5 Hz, 1H), 4.16 (d, *J* = 5.5 Hz, 2H), 4.02 – 3.95 (m, 1H), 3.38 (t, *J* = 5.9 Hz, 2H), 3.07 – 2.85 (m, 2H), 1.53 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.48, 197.65, 146.01, 139.85, 135.08, 128.97, 128.94, 128.66, 128.28, 127.29, 113.09, 109.32, 88.72, 82.79, 82.77, 80.64, 73.29, 66.89, 32.52, 32.44, 26.84, 26.19, 25.27, 24.84. HRMS: m/z (ESI) Calcd for $C_{22}H_{33}O_7$ $[M+H]^+$: 481.2221, found: 481.2227. IR (cm^{-1}): 2986, 2930, 1717, 1680, 1604, 1371, 1210, 1066, 844, 763.



15

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 10:1 to 2:1) to afford **15** (85 mg, 60% yield) as a solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 (dd, *J* = 6.1, 1.0 Hz, 1H), 4.71 (ttd, *J* = 21.1, 10.8, 5.3 Hz, 3H), 4.45 – 4.36 (m, 2H), 4.11 (qd, *J* = 8.7, 5.3 Hz, 2H), 3.67 (dd, *J* = 7.4, 3.6 Hz, 1H), 2.58 (ddd, *J* = 16.8, 9.8, 5.0 Hz, 1H), 2.44 (ddd, *J* = 16.8, 9.3, 6.2 Hz, 1H), 2.00 (d, *J* = 16.8 Hz, 7H), 1.87 – 1.00 (m, 35H), 0.96 (s, 3H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.93, 170.73, 170.71, 113.20, 109.45, 88.23, 82.74, 82.12, 80.67, 73.71, 73.68, 73.28, 66.95, 55.36, 55.24, 43.74, 42.18, 40.09, 40.05, 39.50, 36.23, 35.37, 34.64, 34.11, 33.01, 29.45, 28.62, 27.01, 26.52, 26.24, 25.74, 25.30, 24.86, 23.36, 21.96, 21.53, 21.34, 18.60, 12.23. HRMS: m/z (ESI) Calcd for $C_{40}H_{63}O_{10}$ $[M+H]^+$: 703.4416, found: 703.4428. IR (cm^{-1}): 2942, 2873, 1732, 1369, 1238, 1069, 1043, 1028, 847.

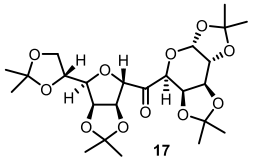


16

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/acetone gradient 15:1 to 8:1) to afford **16** (80 mg, 71% yield) as a solid.

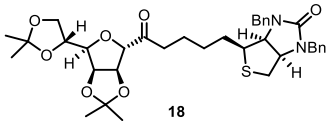
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 5H), 5.21 – 5.06 (m, 3H), 5.03 (d, *J* = 6.0 Hz, 1H), 4.71 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.42 – 4.31 (m, 3H), 4.15 – 4.03 (m, 2H), 3.70 (dd, *J* = 7.5, 3.6 Hz, 1H), 2.70 (dt, *J* = 18.7, 7.3 Hz, 1H), 2.55 (dt, *J* = 18.8, 6.5 Hz, 1H), 2.28 – 2.10 (m, 1H), 1.92 – 1.76 (m, 1H),

1.49 (s, 3H), 1.46 – 1.39 (m, 12H), 1.37 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.02, 172.27, 155.59, 135.35, 128.78, 128.64, 128.46, 113.23, 109.43, 88.44, 82.82, 82.27, 80.67, 80.25, 73.26, 67.41, 66.94, 52.73, 34.80, 28.42, 26.96, 26.33, 26.26, 25.34, 24.90. HRMS: m/z (ESI) Calcd for $C_{29}H_{42}NO_{10}$ $[M+H]^+$: 564.2803, found: 564.2821. IR (cm^{-1}): 3359, 2982, 2934, 1713, 1500, 1369, 1162, 1066, 846.



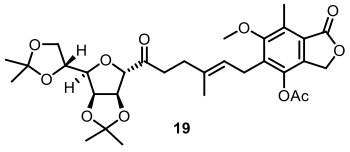
Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 15:1 to 5:1) to afford **17** (55 mg, 55% yield) as a solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 (d, *J* = 4.9 Hz, 1H), 5.28 (dd, *J* = 6.1, 1.2 Hz, 1H), 5.00 (d, *J* = 1.0 Hz, 1H), 4.69 (dd, *J* = 6.1, 3.8 Hz, 1H), 4.63 (t, *J* = 1.5 Hz, 2H), 4.42 – 4.32 (m, 3H), 4.12 (d, *J* = 5.5 Hz, 2H), 4.04 (dd, *J* = 8.0, 3.7 Hz, 1H), 1.51 (s, 3H), 1.48 (s, 3H), 1.47 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.33 (d, *J* = 3.3 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.66, 112.85, 109.74, 109.40, 109.10, 96.61, 86.27, 83.23, 80.95, 80.58, 73.50, 73.41, 72.08, 70.66, 70.52, 67.28, 27.00, 26.26, 26.10, 25.77, 25.43, 24.91, 24.07. HRMS: m/z (ESI) Calcd for $C_{24}H_{37}O_{11}$ $[M+H]^+$: 501.2330, found: 501.2348. IR (cm^{-1}): 2986, 2936, 1732, 1371, 1209, 1063, 1004, 848.



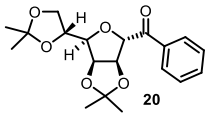
Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 6:1 to1.5:1) to afford **18** (43 mg, 33% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 10H), 5.12 – 5.03 (m, 2H), 4.80 – 4.71 (m, 2H), 4.46 – 4.38 (m, 2H), 4.19 – 4.07 (m, 3H), 4.02 – 3.93 (m, 2H), 3.86 (dd, *J* = 9.5, 5.6 Hz, 1H), 3.72 (dd, *J* = 7.4, 3.6 Hz, 1H), 2.80 – 2.45 (m, 4H), 1.69 – 1.32 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.15, 161.13, 137.08, 136.94, 128.84, 128.78, 128.37, 127.77, 127.74, 113.22, 109.41, 88.40, 82.75, 82.14, 80.64, 73.25, 66.89, 62.75, 61.24, 54.30, 48.09, 46.71, 39.07, 34.88, 28.79, 26.98, 26.23, 25.27, 24.86, 23.04. HRMS: m/z (ESI) Calcd for $C_{36}H_{47}N_2O_7S$ $[M+H]^+$: 651.3098, found: 651.3118. IR (cm^{-1}): 2985, 2931, 1693, 1448, 1370, 1233, 1209, 1067, 846.



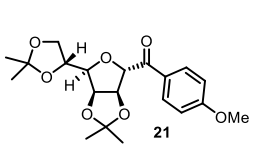
Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 6:1 to 2:1) to afford **19** (93 mg, 79% yield) as a solid.

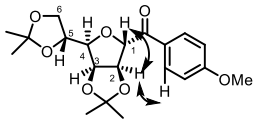
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (s, 2H), 5.11 – 5.03 (m, 1H), 5.00 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.68 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.37 (d, *J* = 7.2 Hz, 2H), 4.07 (qd, *J* = 8.8, 5.4 Hz, 2H), 3.78 (d, *J* = 0.9 Hz, 3H), 3.66 (dd, *J* = 7.3, 3.6 Hz, 1H), 3.33 (d, *J* = 6.9 Hz, 2H), 2.72 – 2.48 (m, 2H), 2.39 (d, *J* = 0.9 Hz, 3H), 2.22 (d, *J* = 6.8 Hz, 5H), 1.76 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.83, 169.07, 168.37, 162.74, 146.32, 146.01, 134.53, 129.20, 123.07, 122.40, 113.63, 113.18, 109.35, 88.36, 82.74, 82.13, 80.62, 73.24, 68.46, 66.84, 61.29, 37.62, 32.75, 26.91, 26.21, 25.25, 24.84, 23.63, 20.66, 16.49, 11.90. HRMS: m/z (ESI) Calcd for $C_{31}H_{41}O_{11}$ $[M+H]^+$: 589.2643, found: 589.2665. IR (cm^{-1}): 2985, 2937, 1760, 1711, 1368, 1187, 1066, 967, 845.



Prepared according to the **general procedure C**. Temperature: 86 ℃. The crude material was purified by flash column chromatography (DCM/EA gradient 60:1 to 50:1) to afford **20** (39 mg, 56% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.65 – 7.57 (m, 1H), 7.54 – 7.45 (m, 2H), 5.32 (d, *J* = 1.0 Hz, 1H), 5.16 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.82 (dd, *J* = 6.0, 3.6 Hz, 1H), 4.42 (ddd, *J* = 7.9, 6.2, 4.5 Hz, 1H), 4.16 – 4.01 (m, 2H), 3.91 (dd, *J* = 7.9, 3.6 Hz, 1H), 1.58 (s, 3H), 1.41 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.50, 134.37, 134.04, 129.05, 128.94, 113.31, 109.49, 85.48, 82.96, 82.94, 81.09, 73.32, 67.19, 26.99, 26.38, 25.40, 24.94. HRMS: m/z (ESI) Calcd for $C_{19}H_{25}O_6$ $[M+H]^+$: 349.2646, found: 349.2656. IR (cm^{-1}): 2985, 2936, 1697, 1679, 1370, 1206, 1063, 844.



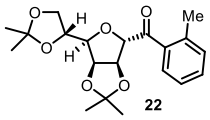


Key NOE interactions presented in **21**

Prepared according to the **general procedure C**. Temperature: 86 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 10:1 to 6:1) to afford **21** (48 mg, 63% yield) as a solid.

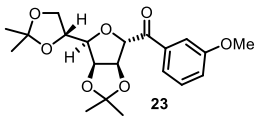
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 6.99 – 6.92 (m, 2H), 5.27 (d, *J* = 1.0 Hz, 1H), 5.15 (dd, *J* = 6.0, 1.0 Hz, 1H), 4.81 (dd, *J* = 6.0, 3.6 Hz, 1H), 4.41 (ddd, *J* = 8.0, 6.2, 4.6 Hz, 1H), 4.11 (dd, *J* = 8.7, 6.2 Hz, 1H), 4.04 (dd, *J* = 8.7, 4.6 Hz, 1H), 3.88 (s, 4H), 1.57 (s, 3H), 1.40 (s, 3H), 1.37 (d, *J* = 5.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.95, 164.22, 131.44, 127.46, 114.11, 113.16, 109.45,

85.19, 83.08, 82.86, 81.09, 73.33, 67.20, 55.67, 26.97, 26.35, 25.39, 24.90. HRMS: m/z (ESI) Calcd for $C_{20}H_{27}O_7$ $[M+H]^+$: 379.1751, found: 379.1760. IR (cm^{-1}): 2986, 2933, 1600, 1258, 1065, 846.



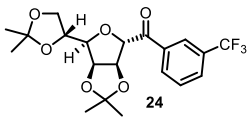
Prepared according to the **general procedure C**. Temperature: 86 ℃. The crude material was purified by flash column chromatography (DCM/EA gradient 60:1 to 50:1) to afford **22** (36 mg, 50% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.42 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33 – 7.26 (m, 2H), 5.21 (s, 1H), 5.10 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.82 (dd, *J* = 6.0, 3.6 Hz, 1H), 4.39 (ddd, *J* = 7.9, 6.3, 4.6 Hz, 1H), 4.09 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.96 (dd, *J* = 8.7, 4.5 Hz, 1H), 3.85 (dd, *J* = 7.9, 3.6 Hz, 1H), 2.51 (s, 3H), 1.55 (s, 3H), 1.41 – 1.32 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.53, 139.61, 134.53, 132.41, 132.37, 129.80, 125.93, 113.25, 109.45, 86.70, 83.14, 82.95, 81.05, 73.25, 67.18, 26.95, 26.33, 25.38, 24.90, 21.68. HRMS: m/z (ESI) Calcd for $C_{20}H_{27}O_6$ $[M+H]^+$: 363.1802, found: 363.1811. IR (cm^{-1}): 2986, 2936, 1694, 1371, 1209, 1067, 847.



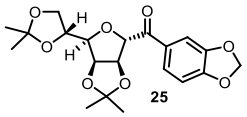
Prepared according to the **general procedure C**. Temperature: 86 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 10:1 to 5:1) to afford **23** (45 mg, 59% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 7.52 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.15 (ddd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 5.30 (t, *J* = 0.9 Hz, 1H), 5.13 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.82 (ddd, *J* = 6.0, 3.6, 0.5 Hz, 1H), 4.42 (ddd, *J* = 7.9, 6.2, 4.6 Hz, 1H), 4.12 (dd, *J* = 8.7, 6.2 Hz, 1H), 4.06 (dd, *J* = 8.7, 4.6 Hz, 1H), 3.92 (ddd, *J* = 7.9, 3.7, 0.7 Hz, 1H), 3.86 (s, 3H), 1.59 – 1.55 (m, 3H), 1.41 (d, *J* = 0.7 Hz, 3H), 1.39 – 1.36 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.33, 160.06, 135.66, 129.94, 121.73, 120.69, 113.31, 112.96, 109.48, 85.55, 83.04, 82.97, 81.08, 73.31, 67.20, 55.61, 26.98, 26.38, 25.40, 24.94. HRMS: m/z (ESI) Calcd for $C_{20}H_{27}O_7$ $[M+H]^+$: 379.1751, found: 379.1738. IR (cm^{-1}): 2986, 2937, 1698, 1372, 1265, 1067, 846.



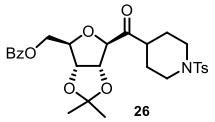
Prepared according to the **general procedure C**. Temperature: 86 ℃. The crude material was purified by flash column chromatography (DCM/EA gradient 60:1 to 50:1) to afford **24** (25 mg, 30% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.9 Hz, 1H), 8.22 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 5.27 (s, 1H), 5.24 (dd, *J* = 6.0, 1.0 Hz, 1H), 4.83 (dd, *J* = 6.0, 3.6 Hz, 1H), 4.42 (ddd, *J* = 7.6, 6.3, 4.5 Hz, 1H), 4.10 (dd, *J* = 8.8, 6.3 Hz, 1H), 3.99 (dd, *J* = 8.8, 4.5 Hz, 1H), 1.57 (s, 3H), 1.39 (s, 6H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.44, 134.95, 132.33, 131.60 (q, *J* = 33.0 Hz), 130.38 (q, *J* = 3.7 Hz), 129.55, 126.18, 123.69 (q, *J* = 272.4 Hz), 113.37, 109.47, 85.44, 82.83, 82.38, 80.91, 73.24, 66.94, 26.91, 26.31, 25.34, 24.82. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.88. HRMS: m/z (ESI) Calcd for $C_{20}H_{24}F_3O_6$ $[M+H]^+$: 417.1519, found: 417.1519. IR (cm^{-1}): 2988, 2937, 1690, 1331, 1130, 1072, 848.



Prepared according to the **general procedure C**. Temperature: 86 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 12:1 to 6:1) to afford **25** (46 mg, 58% yield) as a colorless oil.

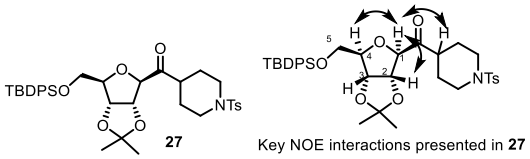
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.46 (d, *J* = 1.7 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.07 – 6.05 (m, 2H), 5.22 (d, *J* = 0.9 Hz, 1H), 5.14 (dd, *J* = 6.0, 1.0 Hz, 1H), 4.81 (dd, *J* = 6.0, 3.6 Hz, 1H), 4.40 (ddd, *J* = 7.9, 6.2, 4.6 Hz, 1H), 4.11 (dd, *J* = 8.7, 6.2 Hz, 1H), 4.04 (dd, *J* = 8.7, 4.6 Hz, 1H), 3.89 (ddd, *J* = 7.9, 3.6, 0.7 Hz, 1H), 1.56 (s, 3H), 1.41 (s, 3H), 1.38 – 1.35 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.54, 152.58, 148.45, 129.19, 125.81, 113.21, 109.46, 108.58, 108.26, 102.12, 85.24, 83.07, 82.88, 81.07, 73.32, 67.16, 26.97, 26.35, 25.38, 24.90. HRMS: m/z (ESI) Calcd for $C_{20}H_{24}NaO_8$ $[M+Na]^+$: 415.1363, found: 415.1369. IR (cm^{-1}): 2986, 2936, 1674, 1603, 1445, 1371, 1253, 1066, 1038, 846.



Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 6:1 to 3:1) to afford **26** (92 mg, 85% yield) as a colorless oil.

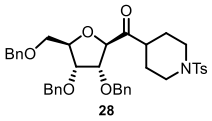
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.62 – 7.54 (m, 3H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.94 (dd, *J* = 6.5, 3.5 Hz, 1H), 4.69 (dd, *J* = 6.5, 2.4 Hz, 1H), 4.50 – 4.37 (m, 3H), 4.35 – 4.26 (m, 1H), 3.68 – 3.51 (m, 2H), 2.69 – 2.57 (m, 1H), 2.44 (s, 3H), 2.38 (td, *J* = 11.5, 2.9 Hz, 1H), 2.21 (td, *J* = 11.5, 3.2 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.72 – 1.49 (m, 6H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.11, 166.19, 143.71, 133.66, 133.20, 129.81, 129.69, 129.27, 128.68, 127.78, 114.50, 88.55, 83.25, 82.28, 81.85, 64.75, 45.71, 45.26, 43.54, 27.29, 27.23, 25.98, 25.43, 21.67.

HRMS: m/z (ESI) Calcd for $C_{28}H_{34}NO_8S$ $[M+H]^+$: 544.2000, found: 544.2010. IR (cm^{-1}): 2932, 1717, 1450, 1268, 1162, 1091, 1069, 929, 862.



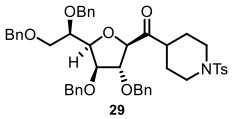
Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/acetone gradient 12:1 to 8:1) to afford **27** (110 mg, 81% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 6H), 7.43 – 7.27 (m, 8H), 4.80 (dd, *J* = 6.5, 4.1 Hz, 1H), 4.62 (dd, *J* = 6.5, 2.9 Hz, 1H), 4.37 (d, *J* = 4.1 Hz, 1H), 4.15 (q, *J* = 3.7 Hz, 1H), 3.72 (dd, *J* = 11.4, 3.7 Hz, 1H), 3.68 – 3.52 (m, 3H), 2.74 (tt, *J* = 10.6, 3.9 Hz, 1H), 2.43 (s, 4H), 2.23 (td, *J* = 11.3, 3.4 Hz, 1H), 2.11 – 2.02 (m, 1H), 1.77 – 1.57 (m, 3H), 1.52 (s, 3H), 1.33 (s, 3H), 0.97 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.58, 143.61, 135.64, 135.54, 133.07, 133.05, 132.86, 130.09, 130.00, 129.79, 129.77, 127.96, 127.87, 127.85, 127.82, 114.28, 88.34, 85.48, 82.20, 81.34, 63.86, 45.85, 45.33, 43.33, 27.39, 27.27, 26.92, 25.94, 25.44, 21.67, 19.30. HRMS: m/z (ESI) Calcd for $C_{37}H_{48}NO_7SSi$ $[M+H]^+$: 678.2915, found: 678.2925. IR (cm^{-1}): 2931, 2857, 1711, 1354, 1162, 1104, 927, 820.



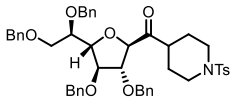
Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 10:1 to 4:1) to afford **28** (95 mg, 71% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.39 – 7.20 (m, 15H), 7.16 – 7.08 (m, 2H), 4.60 (d, *J* = 14.5 Hz, 3H), 4.49 (d, *J* = 3.9 Hz, 1H), 4.43 (d, *J* = 18.6 Hz, 3H), 4.26 (dt, *J* = 6.4, 3.2 Hz, 1H), 4.12 (dd, *J* = 5.1, 3.8 Hz, 1H), 3.83 (dd, *J* = 6.6, 5.0 Hz, 1H), 3.71 – 3.63 (m, 2H), 3.59 – 3.47 (m, 2H), 2.78 (tt, *J* = 11.1, 4.0 Hz, 1H), 2.46 (s, 3H), 2.32 (td, *J* = 11.6, 2.9 Hz, 1H), 2.15 – 2.04 (m, 1H), 1.91 (dq, *J* = 13.1, 3.6 Hz, 1H), 1.65 – 1.52 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.02, 143.58, 137.89, 137.57, 137.45, 133.35, 129.76, 129.71, 128.55, 128.52, 128.48, 128.44, 128.42, 128.37, 128.08, 128.05, 127.83, 127.78, 127.73, 127.55, 85.84, 81.24, 78.79, 73.37, 72.22, 72.05, 69.12, 45.72, 45.29, 43.11, 27.05, 26.21, 21.63. HRMS: m/z (ESI) Calcd for $C_{39}H_{44}NO_7S$ $[M+H]^+$: 670.2833, found: 670.2853. IR (cm^{-1}): 3030, 2857, 1709, 1352, 1336, 1161, 1091, 926, 722.



Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/acetone gradient 20:1 to 6:1) to afford **29** (95 mg, 60% yield) as a colorless oil.

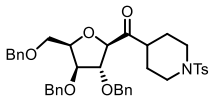
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.41 – 7.17 (m, 20H), 7.07 – 7.01 (m, 2H), 4.79 (d, *J* = 11.4 Hz, 1H), 4.66 – 4.47 (m, 5H), 4.40 (s, 1H), 4.32 – 4.19 (m, 4H), 4.04 – 3.94 (m, 2H), 3.86 (dd, *J* = 10.6, 2.1 Hz, 1H), 3.66 – 3.49 (m, 2H), 2.74 (tt, *J* = 10.8, 3.7 Hz, 1H), 2.43 (s, 3H), 2.33 (td, *J* = 11.5, 2.9 Hz, 1H), 2.20 (td, *J* = 11.6, 3.0 Hz, 1H), 2.01 – 1.93 (m, 1H), 1.65 – 1.40 (m, 2H), 1.28 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.06, 143.55, 138.71, 138.28, 137.38, 137.00, 133.69, 129.77, 128.60, 128.46, 128.43, 128.13, 128.11, 128.06, 127.87, 127.83, 127.78, 127.73, 127.66, 127.53, 87.76, 84.77, 81.35, 80.06, 75.89, 73.68, 72.78, 71.66, 71.63, 71.21, 45.72, 45.11, 42.36, 27.51, 25.60, 21.64. HRMS: m/z (ESI) Calcd for $C_{47}H_{52}NO_8S$ $[M+H]^+$: 790.3408, found: 790.3426. IR (cm^{-1}): 3029, 2923, 2856, 1709, 1453, 1352, 1162, 1091, 1026, 926, 815.



30

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/acetone gradient 15:1 to 6:1) to afford **30** (114 mg, 72% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 2H), 7.40 – 7.23 (m, 20H), 7.17 – 7.10 (m, 2H), 4.74 – 4.60 (m, 2H), 4.56 (d, *J* = 11.8 Hz, 1H), 4.52 – 4.42 (m, 4H), 4.36 – 4.19 (m, 4H), 4.07 (t, *J* = 2.6 Hz, 1H), 3.80 – 3.50 (m, 5H), 2.74 (tt, *J* = 11.2, 3.7 Hz, 1H), 2.46 (s, 3H), 2.35 (td, *J* = 11.6, 2.8 Hz, 1H), 2.18 (td, *J* = 11.7, 2.9 Hz, 1H), 2.05 (dq, *J* = 12.4, 3.5 Hz, 1H), 1.76 – 1.63 (m, 1H), 1.59 – 1.45 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.50, 143.65, 138.53, 138.05, 137.47, 137.34, 133.16, 129.77, 128.57, 128.50, 128.39, 128.21, 128.05, 128.00, 127.98, 127.84, 127.81, 127.79, 127.72, 87.20, 85.79, 85.55, 82.70, 77.24, 73.50, 73.32, 71.81, 71.60, 70.32, 45.97, 45.45, 42.84, 27.68, 25.98, 21.66. HRMS: m/z (ESI) Calcd for $C_{47}H_{52}NO_8S$ $[M+H]^+$: 790.3408, found: 790.3428. IR (cm^{-1}): 3030, 2923, 2855, 1710, 1453, 1352, 1162, 1091, 1069, 927, 721.

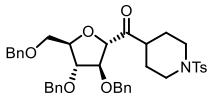


31

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/EA gradient 10:1 to 4:1) to afford **31** (99 mg, 74% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.39 – 7.24 (m, 15H), 7.09 (dd, *J* = 6.5, 3.0 Hz, 2H), 4.63 (d, *J* = 11.8 Hz, 1H), 4.57 – 4.48 (m, 3H), 4.45 – 4.38 (m, 2H), 4.37 – 4.22 (m, 3H), 3.89 (dd,

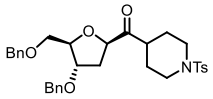
J = 3.1, 1.1 Hz, 1H), 3.78 – 3.62 (m, 3H), 3.61 – 3.54 (m, 1H), 2.84 (tt, *J* = 11.0, 3.7 Hz, 1H), 2.45 (s, 3H), 2.36 (td, *J* = 11.5, 2.9 Hz, 1H), 2.18 (td, *J* = 11.6, 3.0 Hz, 1H), 2.02 (ddd, *J* = 12.8, 5.6, 3.1 Hz, 1H), 1.67 – 1.45 (m, 2H), 1.39 – 1.32 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.25, 143.55, 138.11, 137.38, 137.13, 133.54, 129.74, 128.60, 128.48, 128.12, 128.07, 127.90, 127.88, 127.78, 127.71, 87.65, 85.00, 81.26, 80.60, 73.42, 71.62, 71.60, 68.11, 45.81, 45.26, 42.26, 27.50, 25.85, 21.65. HRMS: m/z (ESI) Calcd for $C_{39}H_{44}NO_7S$ $[M+H]^+$: 670.2833, found: 670.2840. IR (cm^{-1}): 3031, 2924, 2858, 1709, 1452, 1352, 1336, 1162, 1091, 926, 816.



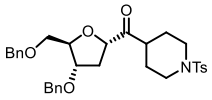
32

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/EA gradient 12:1 to 5:1) to afford **32** (96 mg, 72% yield) as a colorless oil.

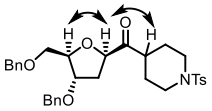
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.36 – 7.24 (m, 15H), 7.18 – 7.11 (m, 2H), 4.60 – 4.44 (m, 5H), 4.41 – 4.25 (m, 4H), 3.93 (t, *J* = 1.6 Hz, 1H), 3.72 – 3.48 (m, 4H), 2.75 (tt, *J* = 11.2, 3.6 Hz, 1H), 2.45 (s, 3H), 2.35 (td, *J* = 11.6, 2.9 Hz, 1H), 2.17 (td, *J* = 11.7, 2.9 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.72 – 1.45 (m, 2H), 1.44 – 1.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.57, 143.64, 138.08, 137.36, 137.07, 133.17, 129.76, 128.62, 128.53, 128.15, 128.11, 128.07, 127.90, 127.86, 87.68, 85.39, 84.32, 82.89, 73.50, 71.83, 71.53, 70.07, 45.97, 45.45, 42.67, 27.68, 25.90, 21.67. HRMS: m/z (ESI) Calcd for $C_{39}H_{44}NO_7S$ $[M+H]^+$: 670.2833, found: 670.2857. IR (cm^{-1}): 3031, 2925, 2858, 1710, 1453, 1352, 1336, 1162, 1091, 926, 816, 720.



33β



33α

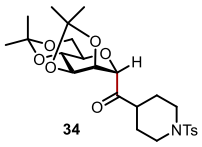


Key NOE interactions presented in **33**β

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/EA gradient 8:1 to 4:1) to afford **33** (96 mg, β/α = 1:1.2, 85% yield) as a colorless oil.

β isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.35 – 7.27 (m, 10H), 7.19 (dd, *J* = 7.1, 2.9 Hz, 2H), 4.60 – 4.40 (m, 5H), 4.22 – 4.17 (m, 1H), 4.06 – 4.00 (m, 1H), 3.70 – 3.58 (m, 2H), 3.47 (d, *J* = 4.2 Hz, 2H), 2.83 – 2.71 (m, 1H), 2.44 (s, 4H), 2.34 – 2.19 (m, 2H), 2.07 – 1.94 (m, 2H), 1.76 – 1.57 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.87, 143.65, 137.92, 137.84, 133.40, 129.78, 128.63, 128.54, 127.98, 127.92, 127.86, 127.82, 127.59, 84.47, 82.56, 80.21, 73.53, 71.38, 70.73, 45.80, 45.44, 43.26, 35.16, 27.23, 26.46, 21.69. HRMS: m/z (ESI) Calcd for $C_{32}H_{38}NO_6$ $[M+H]^+$: 564.2414, found: 564.2414. IR (cm^{-1}): 2844, 2855, 1709, 1452, 1352, 1161, 1090, 925, 816, 721.

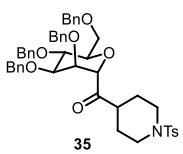
α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.36 – 7.24 (m, 10H), 7.18 (dd, *J* = 6.8, 2.9 Hz, 2H), 4.54 – 4.43 (m, 3H), 4.36 (d, *J* = 11.3 Hz, 1H), 4.30 – 4.22 (m, 2H), 4.04 – 3.98 (m, 1H), 3.70 – 3.58 (m, 2H), 3.46 (dd, *J* = 10.3, 4.6 Hz, 1H), 3.38 (dd, *J* = 10.2, 5.3 Hz, 1H), 2.83 (tt, *J* = 11.1, 3.7 Hz, 1H), 2.47 – 2.34 (m, 6H), 2.26 – 2.16 (m, 2H), 2.10 – 2.01 (m, 1H), 1.74 – 1.40 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.85, 143.59, 137.96, 137.48, 133.27, 129.74, 128.58, 128.54, 128.49, 128.05, 127.97, 127.93, 127.91, 127.86, 127.82, 127.71, 84.50, 83.00, 79.89, 73.65, 70.81, 70.71, 46.02, 45.48, 42.30, 34.89, 27.80, 26.07, 21.67. HRMS: m/z (ESI) Calcd for $C_{32}H_{38}NO_6$ $[M+H]^+$: 564.2414, found: 564.2435.



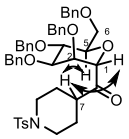
34

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/acetone gradient 15:1 to 4:1) to afford **34** (81 mg, 79% yield) as a solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.66 – 4.59 (m, 2H), 4.02 (dd, *J* = 7.9, 5.6 Hz, 1H), 3.82 – 3.62 (m, 5H), 2.92 (td, *J* = 10.0, 5.6 Hz, 1H), 2.70 – 2.58 (m, 1H), 2.44 – 2.30 (m, 5H), 2.06 – 1.96 (m, 1H), 1.89 – 1.71 (m, 2H), 1.70 – 1.56 (m, 1H), 1.51 (s, 3H), 1.47 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.89, 143.79, 133.06, 129.81, 127.76, 109.31, 99.84, 77.68, 74.46, 72.54, 72.44, 66.95, 61.93, 45.79, 45.34, 43.63, 28.96, 28.18, 27.81, 26.13, 26.00, 21.62, 18.78. HRMS: m/z (ESI) Calcd for $C_{25}H_{38}NO_8S$ $[M+H]^+$: 510.2156, found: 510.2164. IR (cm^{-1}): 2989, 2934, 1710, 1353, 1161, 1090, 1061, 926, 859, 722.



35

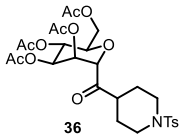


Key NOE interactions presented in **35**

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/EA gradient 12:1 to 4:1) to afford **35** (98 mg, 65% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.34 – 7.23 (m, 20H), 7.18 – 7.11 (m, 2H), 4.78 (d, *J* = 11.0 Hz, 1H), 4.72 – 4.56 (m, 4H), 4.54 – 4.41 (m, 3H), 4.38 (d, *J* = 3.2 Hz, 1H), 4.21 (t, *J* = 3.1 Hz, 1H), 3.78 (t, *J* = 8.6 Hz, 1H), 3.74 – 3.61 (m, 4H), 3.55 (dd, *J* = 8.4, 3.1 Hz, 1H), 3.48 – 3.39 (m, 1H), 2.68 – 2.56 (m, 1H), 2.43 (s, 3H), 2.31 – 2.14 (m, 2H), 1.95 – 1.87 (m, 1H), 1.76 – 1.44 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.52, 143.64, 138.23, 138.20, 138.11, 133.44, 129.78, 128.54, 128.51, 128.45, 128.40, 128.14, 128.06, 128.04, 127.94, 127.90, 127.88, 127.78, 127.70, 127.62, 79.65, 78.46, 74.78, 74.66, 73.43, 73.11, 72.83, 72.43, 69.68, 45.78, 45.32, 43.69, 28.10, 25.99, 21.66.

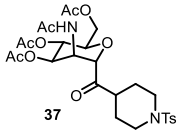
HRMS: m/z (ESI) Calcd for $C_{47}H_{52}NO_8S$ $[M+H]^+$: 790.3408, found: 790.3413. IR (cm^{-1}): 3029, 2856, 1709, 1453, 1353, 1162, 1091, 1026, 927, 816. 735, 721.



36

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/acetone gradient 12:1 to 4:1) to afford **36** (27 mg, 23% yield) as a solid.

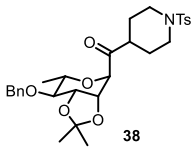
^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.58 (dd, *J* = 3.4, 2.5 Hz, 1H), 5.21 (t, *J* = 9.5 Hz, 1H), 5.01 (dd, *J* = 9.6, 3.4 Hz, 1H), 4.51 (d, *J* = 2.5 Hz, 1H), 4.23 (dd, *J* = 12.4, 6.2 Hz, 1H), 4.08 (dd, *J* = 12.3, 2.5 Hz, 1H), 3.88 – 3.81 (m, 1H), 3.79 – 3.68 (m, 2H), 2.65 – 2.54 (m, 1H), 2.43 (s, 3H), 2.36 (tdd, *J* = 11.9, 9.2, 3.7 Hz, 2H), 2.13 (s, 3H), 2.01 (s, 3H), 1.99 (d, *J* = 4.5 Hz, 7H), 1.86 – 1.78 (m, 2H), 1.75 – 1.58 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.80, 170.49, 170.35, 169.87, 169.68, 143.87, 132.94, 129.84, 127.82, 127.77, 78.64, 74.01, 69.27, 67.90, 66.03, 62.68, 45.70, 45.46, 44.12, 27.38, 26.49, 21.64, 21.00, 20.76, 20.74, 20.71. HRMS: m/z (ESI) Calcd for $C_{27}H_{36}NO_{12}S$ $[M+H]^+$: 598.1953, found: 598.1963. IR (cm^{-1}): 2932, 1743, 1710, 1365, 1216, 1162, 1046, 923, 722.



37

Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/acetone gradient 4:1 to 1:1) to afford **37** (72 mg, 60% yield) as a solid.

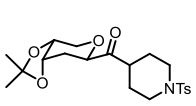
^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.92 (d, *J* = 8.4 Hz, 1H), 5.03 (t, *J* = 8.5 Hz, 1H), 4.94 (dd, *J* = 8.9, 4.2 Hz, 1H), 4.86 – 4.78 (m, 1H), 4.42 (d, *J* = 3.4 Hz, 1H), 4.25 (dd, *J* = 12.2, 6.0 Hz, 1H), 4.12 – 3.97 (m, 2H), 3.79 – 3.70 (m, 2H), 2.70 – 2.58 (m, 1H), 2.43 (s, 3H), 2.35 (tt, *J* = 11.4, 3.6 Hz, 2H), 2.05 – 1.97 (m, 13H), 1.91 – 1.63 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.11, 170.53, 170.42, 169.86, 169.79, 143.87, 132.90, 129.85, 127.84, 79.09, 73.46, 69.55, 65.86, 62.26, 47.15, 45.68, 45.54, 43.75, 27.26, 26.89, 23.40, 21.65, 20.82, 20.81. HRMS: m/z (ESI) Calcd for $C_{27}H_{37}N2O_{11}S$ $[M+H]^+$: 597.2113, found: 597.2110. IR (cm^{-1}): 3374, 2929, 1744, 1662, 1533, 1367, 1228, 1050, 921, 725.



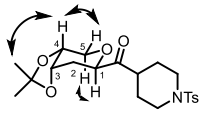
38

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 12:1 to 4:1) to afford **38** (94 mg, 86% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.35 – 7.23 (m, 7H), 4.84 (d, *J* = 11.5 Hz, 1H), 4.62 – 4.55 (m, 2H), 4.54 (d, *J* = 2.1 Hz, 1H), 4.17 (t, *J* = 6.3 Hz, 1H), 3.78 – 3.67 (m, 2H), 3.21 (dd, *J* = 9.0, 6.8 Hz, 1H), 3.10 (dq, *J* = 9.0, 6.1 Hz, 1H), 2.69 (tt, *J* = 10.9, 4.5 Hz, 1H), 2.48 – 2.33 (m, 5H), 2.07 – 1.99 (m, 1H), 1.89 – 1.57 (m, 3H), 1.50 (s, 3H), 1.37 (s, 3H), 1.24 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.85, 143.72, 138.08, 133.19, 129.80, 128.39, 128.07, 127.82, 127.76, 109.01, 80.36, 77.69, 76.88, 72.93, 72.55, 71.06, 45.82, 45.35, 43.41, 28.01, 27.91, 26.16, 26.03, 21.62, 18.21. HRMS: m/z (ESI) Calcd for $C_{29}H_{38}NO_7S$ $[M+H]^+$: 544.2363, found: 544.2365. IR (cm^{-1}): 2984, 2933, 1710, 1353, 1219, 1219, 1262, 1091, 1070, 924, 859, 724.



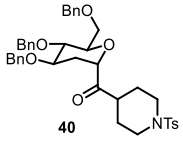
39β



Key NOE interactions presented in **39**β

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 12:1 to 4:1) to afford **39** (68 mg, β/α = 4.3:1, 80% yield) as a colorless oil.

β isomer: ^{1}H NMR (400 MHz, CD_3CN) δ 4.39 (dt, *J* = 6.0, 3.0 Hz, 1H), 4.18 – 4.02 (m, 2H), 3.78 (dd, *J* = 11.9, 5.3 Hz, 1H), 3.62 (dtd, *J* = 11.5, 3.8, 1.9 Hz, 2H), 3.42 (dd, *J* = 11.9, 7.3 Hz, 1H), 2.73 (tt, *J* = 11.2, 3.7 Hz, 1H), 2.42 (s, 3H), 2.40 – 2.29 (m, 2H), 2.09 (dt, *J* = 15.1, 3.0 Hz, 1H), 1.92 – 1.70 (m, 3H), 1.63 – 1.48 (m, 2H), 1.42 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 212.21, 144.88, 134.07, 130.65, 128.59, 109.50, 75.95, 71.42, 71.18, 67.06, 46.55, 46.44, 43.75, 28.89, 27.93, 27.75, 27.54, 25.91, 21.50. HRMS: m/z (ESI) Calcd for $C_{21}H_{30}NO_6S$ $[M+H]^+$: 424.1788, found: 424.1793. IR (cm^{-1}): 2932, 1711, 1243, 1162, 1060, 928, 853, 723.

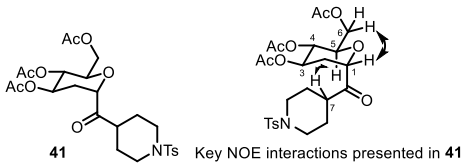


40

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/acetone gradient 15:1 to 5:1) to afford **40** (90 mg, β/α < 1:10, 66% yield) as a colorless oil.

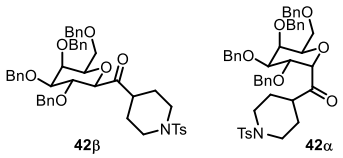
α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.33 – 7.26 (m, 15H), 7.20 – 7.13 (m, 2H), 4.77 (d, *J* = 11.2 Hz, 1H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.56 (d, *J* = 11.7 Hz, 1H), 4.53 – 4.42 (m, 3H), 4.40 (dd, *J* = 5.4, 4.0 Hz, 1H), 3.76 – 3.60 (m, 5H), 3.51 – 3.35 (m, 2H), 2.78 (tt, *J* = 10.6, 4.1 Hz, 1H), 2.43 (s, 4H), 2.30 (dtd, *J* = 22.5, 11.4, 3.4 Hz, 2H), 2.05 – 1.96 (m, 1H), 1.82 – 1.65 (m, 3H),

1.57 (dtd, *J* = 12.9, 11.5, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.15, 143.63, 138.37, 138.16, 138.03, 133.40, 129.78, 128.60, 128.56, 128.53, 128.48, 128.00, 127.91, 127.86, 127.84, 127.81, 127.76, 76.69, 76.67, 76.52, 75.21, 74.34, 73.50, 71.73, 69.07, 45.90, 45.43, 42.91, 28.86, 28.21, 26.11, 21.66. HRMS: m/z (ESI) Calcd for $C_{40}H_{46}NO_7S$ $[M+H]^+$: 684.2989, found: 684.3018. IR (cm^{-1}): 3029, 2925, 2854, 1713, 1453, 1353, 1334, 1163, 1093, 930, 816, 723.



Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/acetone gradient 15:1 to 5:1) to afford **41** (54 mg, 50% yield) as a colorless oil.

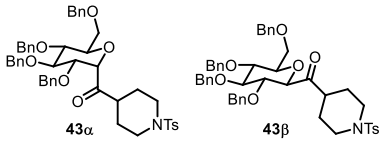
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.98 (ddd, *J* = 9.2, 7.8, 4.6 Hz, 1H), 4.86 (t, *J* = 7.8 Hz, 1H), 4.48 (dd, *J* = 5.5, 4.3 Hz, 1H), 4.32 (dd, *J* = 12.2, 6.5 Hz, 1H), 4.07 (dd, *J* = 12.2, 2.9 Hz, 1H), 3.82 – 3.69 (m, 3H), 2.68 (ddt, *J* = 11.2, 8.8, 4.1 Hz, 1H), 2.49 – 2.32 (m, 6H), 2.08 – 2.01 (m, 7H), 1.99 (s, 3H), 1.96 – 1.87 (m, 1H), 1.87 – 1.78 (m, 2H), 1.76 – 1.65 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.09, 170.55, 169.90, 169.79, 143.82, 133.05, 129.84, 129.81, 127.86, 127.81, 74.42, 73.69, 68.54, 68.42, 62.10, 45.88, 45.54, 43.32, 28.67, 27.73, 26.38, 21.66, 21.06, 20.85, 20.77. HRMS: m/z (ESI) Calcd for $C_{25}H_{34}NO_{10}S$ $[M+H]^+$: 540.1898, found: 540.1920. IR (cm^{-1}): 2931, 1740, 1712, 1365, 1222, 1162, 1052, 925, 818, 724.



Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/acetone gradient 15:1 to 5:1) to afford **42** (30 mg, β/α = 1:1, 19% yield) as a colorless oil. **42β** and **42α** were separated by prep-HPLC.

β isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.16 (m, 20H), 7.11 (dd, *J* = 6.3, 3.0 Hz, 2H), 4.58 – 4.24 (m, 10H), 4.05 (t, *J* = 10.4 Hz, 1H), 3.99 – 3.93 (m, 2H), 3.70 – 3.56 (m, 4H), 2.83 – 2.73 (m, 1H), 2.44 (s, 3H), 2.25 (qd, *J* = 11.3, 3.0 Hz, 2H), 1.99 (d, *J* = 13.1 Hz, 1H), 1.80 – 1.46 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.75, 143.60, 138.34, 138.15, 138.13, 137.71, 133.07, 129.71, 128.57, 128.56, 128.52, 128.25, 128.19, 127.95, 127.88, 127.86, 127.71, 77.05, 74.63, 74.00, 73.89, 73.66, 73.25, 73.22, 71.88, 65.43, 45.93, 45.65, 43.86, 27.00, 25.93, 21.66. HRMS: m/z (ESI) Calcd for $C_{47}H_{51}NNaO_8S$ $[M+Na]^+$: 812.3228, found: 812.3264. IR (cm^{-1}): 3030, 2925, 2857, 1711, 1453, 1352, 1163, 1092, 1027, 927, 723.

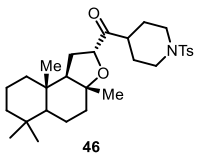
α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (d, *J* = 11.9 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.47 – 4.43 (m, 2H), 4.41 (s, 2H), 4.04 (dd, *J* = 3.1, 2.0 Hz, 1H), 3.77 – 3.47 (m, 5H), 2.71 (tt, *J* = 11.2, 3.7 Hz, 1H), 2.43 (s, 3H), 2.32 (td, *J* = 11.6, 2.8 Hz, 1H), 2.15 (td, *J* = 11.7, 2.9 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.72 – 1.41 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.51, 143.66, 138.54, 138.06, 137.49, 137.35, 133.18, 129.78, 128.58, 128.56, 128.51, 128.41, 128.25, 128.23, 128.07, 128.02, 127.99, 127.89, 127.85, 127.83, 127.80, 127.73, 87.22, 85.80, 85.56, 82.71, 77.25, 73.51, 73.34, 71.82, 71.61, 70.33, 45.98, 45.46, 42.85, 27.69, 25.99, 21.67. HRMS: m/z (ESI) Calcd for $C_{47}H_{51}NNaO_8S$ $[M+Na]^+$: 812.3228, found: 812.3266.



Prepared according to the **general procedure A**. Temperature: 90 °C. The crude material was purified by flash column chromatography (hexane/acetone gradient 15:1 to 5:1) to afford **43** (36 mg, β/α = 1:2, 23% yield) as a colorless oil.

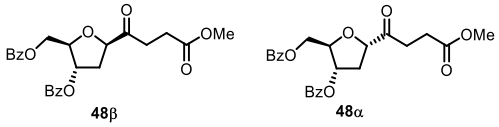
β isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.32 – 7.24 (m, 18H), 7.20 – 7.14 (m, 4H), 4.86 (s, 2H), 4.76 (dd, *J* = 24.1, 10.7 Hz, 2H), 4.58 – 4.53 (m, 2H), 4.50 (d, *J* = 5.0 Hz, 2H), 3.89 – 3.83 (m, 1H), 3.78 – 3.43 (m, 8H), 2.58 (ddt, *J* = 11.1, 7.5, 3.8 Hz, 1H), 2.43 (s, 3H), 2.33 (qd, *J* = 11.5, 2.9 Hz, 2H), 1.91 – 1.82 (m, 2H), 1.80 – 1.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.56, 143.68, 138.39, 138.13, 137.95, 137.84, 133.27, 129.78, 128.64, 128.62, 128.58, 128.53, 128.23, 128.13, 128.06, 127.91, 127.85, 127.83, 127.73, 86.63, 80.67, 79.53, 78.80, 77.91, 75.71, 75.17, 75.06, 73.50, 69.11, 45.64, 45.61, 45.47, 26.92, 26.74, 21.67. HRMS: m/z (ESI) Calcd for $C_{47}H_{52}NO_8S$ $[M+H]^+$: 790.3408, found: 790.3425. IR (cm^{-1}): 3030, 2921, 2861, 1721, 1353, 1163, 1093, 1070, 931, 724.

α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.22 (m, 18H), 7.22 – 7.12 (m, 4H), 4.63 (dt, *J* = 21.4, 11.0 Hz, 4H), 4.51 – 4.39 (m, 5H), 4.37 (d, *J* = 4.1 Hz, 1H), 4.01 (ddd, *J* = 8.2, 5.1, 2.8 Hz, 1H), 3.90 (dd, *J* = 5.0, 3.4 Hz, 2H), 3.65 – 3.49 (m, 3H), 2.60 (ddt, *J* = 10.7, 8.0, 4.0 Hz, 1H), 2.43 (s, 3H), 2.23 (td, *J* = 11.5, 2.9 Hz, 2H), 1.89 – 1.81 (m, 1H), 1.76 – 1.55 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.46, 143.59, 138.12, 137.83, 129.74, 128.63, 128.58, 128.52, 128.32, 128.18, 128.01, 127.91, 127.88, 127.85, 79.07, 77.96, 76.57, 76.19, 74.45, 74.14, 73.87, 73.60, 73.46, 69.01, 45.65, 45.55, 45.20, 26.90, 26.38, 21.68. HRMS: m/z (ESI) Calcd for $C_{47}H_{52}NO_8S$ $[M+H]^+$: 790.3408, found: 790.3422.



Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/acetone gradient 20:1 to 10:1) to afford **46** (60 mg, d.r. > 10:1, 60% yield) as a colorless oil.

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.45 – 4.38 (m, 1H), 3.76 – 3.65 (m, 2H), 2.74 (tt, *J* = 10.9, 3.8 Hz, 1H), 2.47 – 2.35 (m, 5H), 2.03 – 1.49 (m, 9H), 1.44 – 1.08 (m, 10H), 1.00 – 0.83 (m, 5H), 0.80 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.97, 143.65, 133.29, 129.77, 127.87, 82.70, 79.98, 59.50, 57.22, 45.81, 45.60, 43.37, 42.43, 39.92, 39.87, 36.39, 33.63, 33.19, 27.26, 26.88, 26.52, 21.67, 21.54, 21.20, 20.71, 18.40, 15.07. HRMS: m/z (ESI) Calcd for $C_{29}H_{44}NO_4S$ $[M+H]^+$: 502.2986, found: 502.3009. IR (cm^{-1}): 2925, 2866, 1772, 1710, 1354, 1161, 1092, 927, 815, 719.

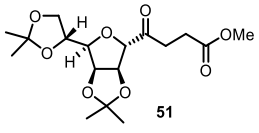


48β **48**α

Prepared according to the **general procedure A**. Temperature: 86 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 8:1 to 4:1) to afford **48** (48 mg, β/α = 1:1.2, 55% yield) as a colorless oil.

β isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 4H), 7.64 – 7.51 (m, 2H), 7.49 – 7.40 (m, 4H), 5.55 (dt, *J* = 5.6, 2.0 Hz, 1H), 4.71 (dd, *J* = 10.2, 6.6 Hz, 1H), 4.64 – 4.52 (m, 3H), 3.64 (s, 3H), 3.01 (ddd, *J* = 19.1, 8.0, 5.4 Hz, 1H), 2.82 (ddd, *J* = 19.0, 7.0, 5.1 Hz, 1H), 2.68 – 2.37 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.77, 173.05, 166.34, 166.07, 133.63, 133.41, 129.84, 129.83, 129.73, 129.56, 128.67, 128.66, 83.88, 83.67, 76.34, 64.65, 51.92, 35.76, 33.03, 27.20. HRMS: m/z (ESI) Calcd for $C_{24}H_{25}O_8$ $[M+H]^+$: 441.1544, found: 441.1548. IR (cm^{-1}): 1791, 1720, 1270, 1110, 1070, 1026.

α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.99 (m, 2H), 7.97 – 7.91 (m, 2H), 7.63 – 7.53 (m, 2H), 7.50 – 7.39 (m, 4H), 5.52 (dt, *J* = 6.0, 2.0 Hz, 1H), 4.72 (dd, *J* = 9.2, 3.5 Hz, 1H), 4.66 (td, *J* = 4.5, 1.8 Hz, 1H), 4.56 – 4.48 (m, 2H), 3.61 (s, 3H), 3.11 – 2.91 (m, 2H), 2.77 – 2.51 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.38, 173.11, 166.34, 165.96, 133.60, 133.44, 129.83, 129.81, 129.76, 129.47, 128.68, 128.66, 83.84, 83.38, 76.02, 64.59, 51.91, 35.33, 33.32, 27.46. HRMS: m/z (ESI) Calcd for $C_{24}H_{25}O_8$ $[M+H]^+$: 441.1544, found: 441.1552. IR (cm^{-1}): 1719, 1268, 1110, 1070, 1025.

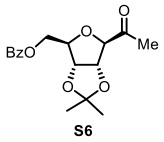


51

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/Acetone gradient 15:1 to 8:1) to afford **51** (43 mg, 60% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.75 (dd, *J* = 6.0, 3.6 Hz, 1H), 4.47 (d, *J* = 1.0 Hz, 1H), 4.45 – 4.37 (m, 1H), 4.16 – 4.08 (m, 2H), 3.80 (ddd, *J* = 7.3, 3.6, 0.7 Hz, 1H), 3.67 (s, 3H), 2.83 (q, *J* = 6.0 Hz, 2H), 2.64 (q, *J* = 7.0, 6.3 Hz, 2H), 1.50 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.04, 173.05, 113.26, 109.45, 88.60, 82.82, 82.48, 80.64, 73.32, 66.93, 52.04, 33.54, 27.47, 26.95, 26.27, 25.34, 24.91. HRMS: m/z (ESI) Calcd for $C_{17}H_{27}O_8$ $[M+H]^+$: 359.1700, found: 359.1708. IR (cm^{-1}): 2987, 2937, 1731, 1371, 1206, 1064, 844.

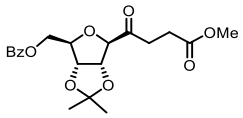
Below are unlisted compounds in the paper.



S6

Prepared according to the **general procedure B**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/acetone gradient 20:1 to 15:1) to afford **S6** (48 mg, 75% yield) as a colorless oil.

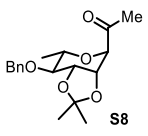
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.63 – 7.54 (m, 1H), 7.52 – 7.42 (m, 2H), 4.95 (dd, *J* = 6.4, 3.6 Hz, 1H), 4.70 (dd, *J* = 6.4, 2.6 Hz, 1H), 4.55 – 4.36 (m, 4H), 2.21 (s, 3H), 1.57 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.90, 166.32, 133.54, 129.80, 129.51, 128.67, 114.49, 90.16, 83.31, 82.25, 82.06, 64.94, 27.33, 26.59, 25.49. HRMS: m/z (ESI) Calcd for $C_{17}H_{20}NaO_6$ $[M+Na]^+$: 343.1152, found: 343.1160. IR (cm^{-1}): 2985, 2936, 1713, 1372, 1209, 1067, 848.



S7

Prepared according to the **general procedure A**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (hexane/EA gradient 10:1 to 4:1) to afford **S7** (58 mg, 74% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.61 – 7.53 (m, 1H), 7.45 (dd, *J* = 8.4, 7.1 Hz, 2H), 5.00 (dd, *J* = 6.4, 3.6 Hz, 1H), 4.70 (dd, *J* = 6.5, 2.8 Hz, 1H), 4.53 – 4.39 (m, 4H), 3.62 (s, 3H), 2.95 – 2.75 (m, 2H), 2.53 (td, *J* = 6.5, 1.6 Hz, 2H), 1.57 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.11, 173.03, 166.31, 133.45, 129.82, 129.59, 128.62, 114.52, 89.69, 83.38, 82.43, 81.96, 64.79, 51.94, 33.69, 27.37, 27.33, 25.55. HRMS: m/z (ESI) Calcd for $C_{20}H_{24}NaO_8$ $[M+Na]^+$: 415.1363, found: 415.1378. IR (cm^{-1}): 2990, 1793, 1723, 1271, 1096, 1071, 1026, 867.

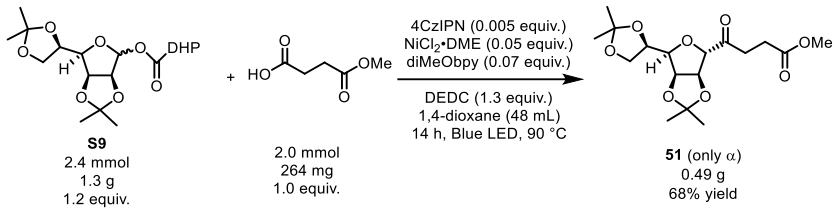


S8

Prepared according to the **general procedure B**. Temperature: 90 ℃. The crude material was purified by flash column chromatography (DCM/EA gradient 60:1 to 50:1) to afford **S8** (50 mg, 81% yield) as a colorless oil.

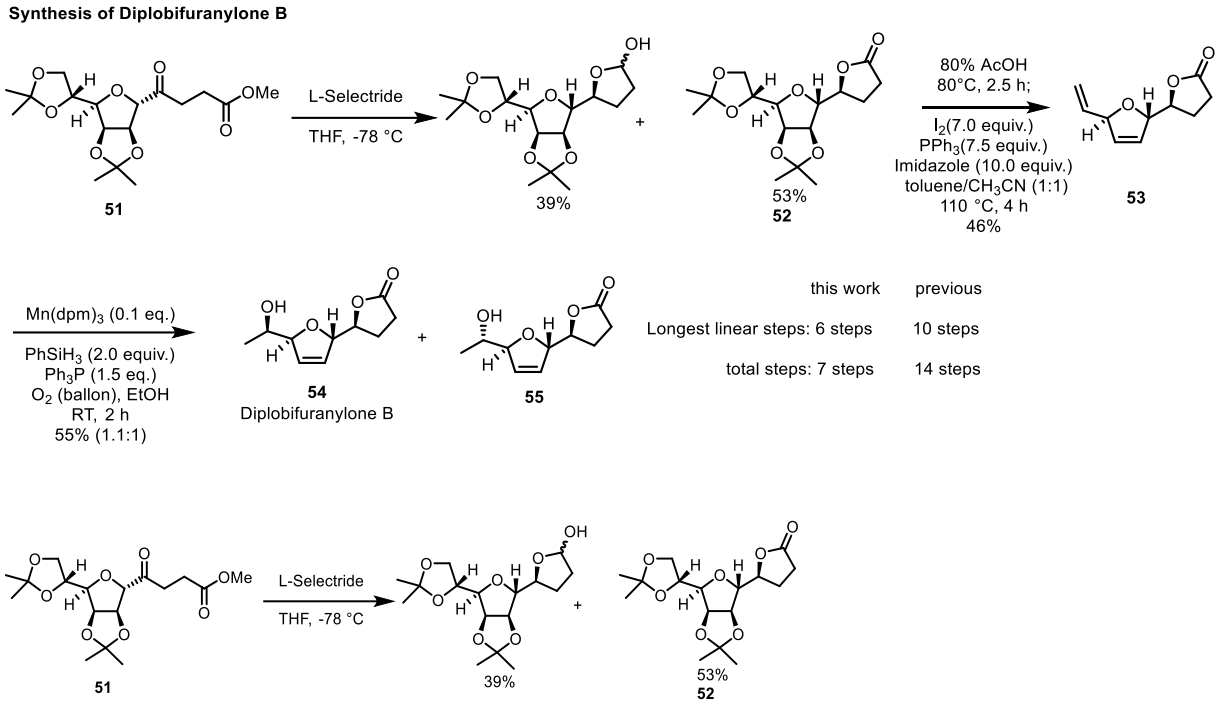
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 5H), 4.87 (d, *J* = 11.6 Hz, 1H), 4.70 (dd, *J* = 5.8, 2.0 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.43 (d, *J* = 2.0 Hz, 1H), 4.16 (t, *J* = 6.1 Hz, 1H), 3.29 – 3.15 (m, 2H), 2.28 (s, 3H), 1.53 (s, 3H), 1.40 (s, 3H), 1.33 (d, *J* = 5.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.74, 138.25, 128.42, 128.11, 127.81, 109.03, 80.48, 79.71, 77.94, 72.98, 72.66, 70.91, 28.09, 26.48, 26.25, 18.27. HRMS: m/z (ESI) Calcd for $C_{18}H_{24}NaO_5$ $[M+Na]^+$: 343.1516, found: 343.1523. IR (cm^{-1}): 2984, 2932, 1713, 1368, 1246, 1095, 1072, 1019, 856, 738.

Reaction on Scale



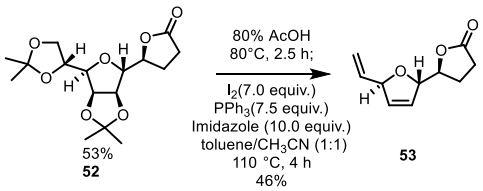
In a nitrogen-filled glove box, a 100 mL seal tube was charged with diMeObpy (30.0 mg, 0.14 mmol, 7.0 mol%), $NiCl_2$•DME (22.0 mg, 0.10 mmol, 5.0 mol%), 4CzIPN (8.0 mg, 0.01 mmol, 0.5 mol%) , DEDC (422 mg, 2.6 mmol, 1.3 equiv.), **S9** (1.3 g, 2.4 mmol, 1.2 equiv.) and 4-methoxy-4-oxobutanoic acid (0.264 g, 2.0 mmol, 1.0 equiv.). After addition of the stir bar and 1,4-dioxane (48.0 mL), the seal tube was capped and removed from the glove box. The mixture was sonicated to solubilize $NiCl_2$•DME. Then the tube was immersed in a preheated oil bath with the oil submerged up to 1/3 of the reaction mixture. In the beginning, the temperature of the oil bath was set to a value of 88 ℃. After stirring for 2 minutes, the tube was irradiated with one kessil pro160 - 467 nm LED lights (34 W), approximately 5 cm away from the tube, and the temperature of the oil bath was set to 90 ℃. The reaction mixture was allowed to stir vigorously for 14 h. After cooling to room temperature, the reaction mixture was filtered through a short plug of silica gel (2 cm) and flushed with ethyl acetate. After removal of the solvent under vacuum, the residue was purified by flash column chromatography (hexane/acetone gradient 15:1 to 8:1) to afford **51** (0.49 g, 68% yield).

Synthesis of Diplobifuranylone B



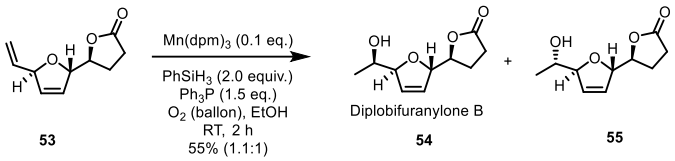
L-Selectride (1.0 M in THF, 0.64 mL, 0.640 mmol, 1.05 equiv.) was dropwise added into the solution of **51** (220 mg, 0.614 mmol, 1.0 equiv.) in dry THF (15 mL) at -78 ℃ (dry ice and acetone bath) over 5 min. After being stirred at -78 ℃ for 2 h, the reaction was quenched by sat. $NaHCO_3$ aqueous. After it warmed to room temperature, the mixture was extracted by EA (3*15 mL). The combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was dissolved in dry THF (5 mL). Then NaH (60% in mineral oil, 23 mg, 1.0 equiv.) was added. After being stirred for 10 mins, the solution was concentrated *in vacuo.* The residue was purified by flash column chromatography (hexanes/ethyl acetate 2.5:1 to 1:1) to afford the desired product **52** (106 mg, *d.r.* > 20:1, 53%) as a solid and the over-reduced product (80 mg, mixture, 39 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 – 4.82 (m, 2H), 4.61 (td, *J* = 7.1, 2.1 Hz, 1H), 4.32 (td, *J* = 6.7, 5.0 Hz, 1H), 4.12 – 4.03 (m, 2H), 4.02 – 3.94 (m, 2H), 2.68 – 2.44 (m, 2H), 2.36 – 2.17 (m, 2H), 1.50 (s, 3H), 1.41 (s, 3H), 1.38 – 1.32 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.64, 113.21, 109.34, 85.71, 83.90, 83.36, 81.47, 81.25, 73.82, 66.79, 28.48, 26.84, 26.43, 25.39, 24.75, 23.91. HRMS: m/z (ESI) Calcd for $C_{16}H_{25}O_7$ $[M+H]^+$: 329.1595, found: 329.1595. IR (cm^{-1}): 2986, 2936, 1777, 1372, 1160, 1066, 847.

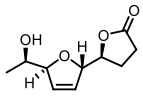


The lactone **52** (44 mg, 0.134 mmol) was dissolved in 80 % acetic acid aqueous. After being stirred at 80 ℃ for 2.5 h, the mixture was concentrated *in vacuo*. The residue was dissolved in toluene (2 mL) and acetonitrile (2 mL). PPh_3 (228.5 mg, 0.871 mmol, 6.5 equiv.), imidazole (91.0 mg, 1.340 mmol, 10.equiv.), and I_2 (204.0 mg, 0.804 mmol, 6.0 equiv.) were successively added into the solution. The mixture was stirred at 110 ℃ for 4 h. After cooled down to room temperature, the reaction was quenched by saturated $Na_2S_2O_3$ aqueous. The mixture was extracted by EA (3*5 mL). The combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexanes/ethyl acetate 2.5:1 to 1.5:1) to afford the desired product **53** (11 mg, 46%) as a colorless oil.

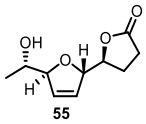
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (ddd, *J* = 6.2, 2.3, 1.6 Hz, 1H), 5.81 – 5.70 (m, 2H), 5.28 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.22 (tdt, *J* = 5.8, 2.4, 1.3 Hz, 1H), 5.14 (dt, *J* = 10.2, 1.2 Hz, 1H), 4.99 (dtd, *J* = 6.0, 2.3, 1.5 Hz, 1H), 4.57 (ddd, *J* = 7.8, 5.4, 2.5 Hz, 1H), 2.68 (ddd, *J* = 17.5, 10.0, 7.4 Hz, 1H), 2.46 (ddd, *J* = 17.7, 9.7, 6.7 Hz, 1H), 2.34 – 2.20 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.59, 137.46, 132.30, 125.56, 116.81, 88.15, 87.59, 80.15, 28.12, 23.88. HRMS: m/z (ESI) Calcd for $C_{10}H_{13}O_3$ $[M+H]^+$: 181.0859, found: 181.0861. IR (cm^{-1}): 2964, 1769, 1175, 1023, 917, 799.



To a solution of **53** (15 mg, 0.0833 mmol, 1.00 equiv) in anhydrous EtOH (4.5 ml, bubbled with O_2 for 5 min prior to use) was added Mn(dpm)3 (Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) manganese(III)) (5.00 mg, 0.00833 mmol, 0.10 equiv) and PPh_3 (32.8 mg, 0.125 mmol, 1.50 eq.) at room temperature. The reaction flask was purged with oxygen and charged with an oxygen balloon, before phenylsilane (20.5 µl, 0.1666 mmol, 2.00 equiv) was added dropwise by syringe-pump (2.0 µl / 30 min). After the addition was complete, stirring was continued for 1 h. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel (^{i}PrOH/CCl_3H 1:30) to obtain diplobifuranylone B **54** and **55** (total 9 mg, *d.r.* =1.09 :1 (H NMR), 55 %) as a colorless oil and recover **53** (4 mg, 27%). The spectrum of **54** is consistent with the reported. [5]


Diplobifuranylone B

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (dt, *J* = 6.6, 1.7 Hz, 1H), 5.91 (dt, *J* = 6.5, 1.9 Hz, 1H), 4.98 (tt, *J* = 4.3, 2.0 Hz, 1H), 4.82 – 4.77 (m, 1H), 4.55 (ddd, *J* = 8.0, 5.3, 2.7 Hz, 1H), 3.90 (qd, *J* = 6.5, 3.4 Hz, 1H), 1.18 (d, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.42, 128.92, 127.52, 91.17, 88.13, 80.27, 69.24, 28.13, 23.92, 18.09. HRMS: m/z (ESI) Calcd for $C_{10}H_{15}O_4$ $[M+H]^+$: 199.0965, found: 199.0958. IR (cm^{-1}): 3381, 2923, 2853, 1761, 1179, 1056, 918, 825.

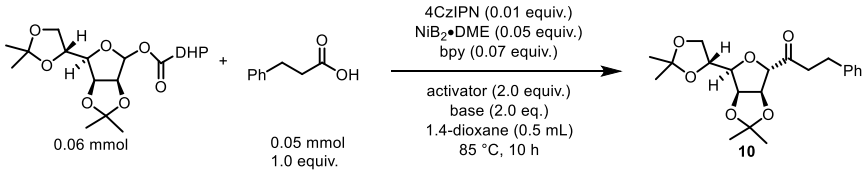


55

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 – 5.91 (m, 1H), 5.87 (dt, *J* = 6.4, 1.8 Hz, 1H), 4.96 (tt, *J* = 3.9, 2.2 Hz, 1H), 4.63 (tt, *J* = 6.2, 1.9 Hz, 1H), 4.56 (ddd, *J* = 8.0, 5.3, 2.8 Hz, 1H), 2.65 (ddd, *J* = 17.3, 10.1, 7.0 Hz, 1H), 2.53 – 2.42 (m, 1H), 2.35 – 2.17 (m, 2H), 1.19 (d, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.37, 130.07, 127.22, 91.62, 87.65, 80.13, 70.33, 28.13, 23.80, 18.71. HRMS: m/z (ESI) Calcd for $C_{10}H_{15}O_4$ $[M+H]^+$: 199.0965, found: 199.0965. IR (cm^{-1}): 3420, 2924, 2853, 1770, 1157, 1059, 916, 823.

Coupling Reaction Optimization

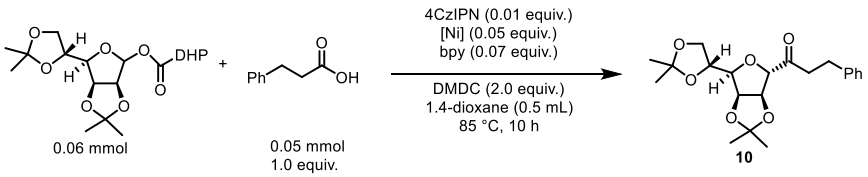
Table S1. The Effect of Activators for 3-Phenylpropionic acid



Entry	activator	Base	**10** (yield)[a]
1	EtOCOCl	No base	ND
2	MeOCOCl	No base	ND
3	PhOCOCl	No base	ND
4	Ac_2O	No base	yes
5	EtOCOCl	Na_2CO_3	yes
6	MeOCOCl	Na_2CO_3	yes
7	PhOCOCl	Na_2CO_3	ND
8	Boc_2O	Na_2CO_3	ND
9	DMDC[b]	No base	42%

a. Crude H NMR yield with the mesitylene as the internal standard
b. DMDC: dimethyl dicarbonate

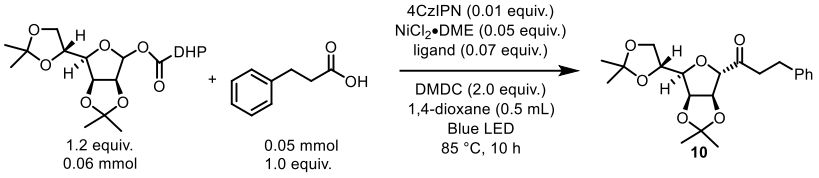
Table S2. The Effect of Nickel Catalysts



Entry	[Ni]	**10** (yield)[a]
1	$Ni(acac)_2$	trace
2	$Ni(NO_3)_2$	trace
3	$Ni(cod)_2$	trace
4	$Ni(OAc)_2$	trace
5	$Ni(OTf)_2$	15%
6	$NiBr_2$•DME	42%
7	$NiCl_2$•DME	63%

a. Crude H NMR yield with the mesitylene as the internal standard

Table S3. The Effect of Ligands with DMDC as the activator



Entry	Ligand	**10** (yield)[a]
1	bpy	63%
2	diMeObpy	42%
3	**L1**	60%
4	bpy and $MgCl_2$(1.5 equiv.)	3%
5	**L2**	30%
6	Phen	12%
7	**L3**	27%

a. Crude H NMR yield with the mesitylene as the internal standard

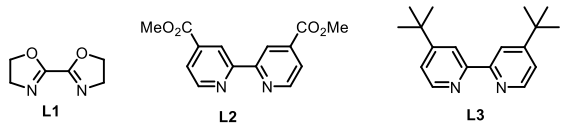
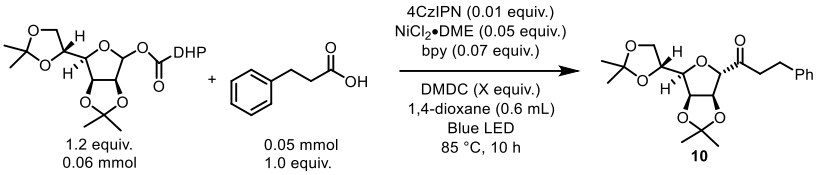


Table S4. The Effect of the equivalence of DMDC

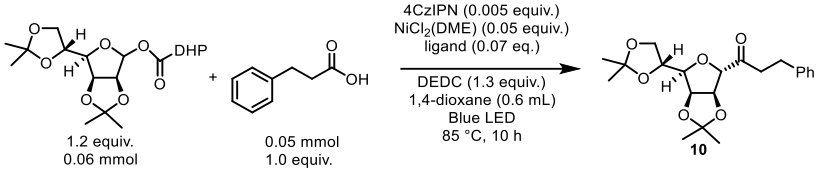


Entry	DMDC(X equiv.)	**10** (yield)[a]
1	1.0	63%
2	1.1	63%
3	1.2	63%
4	1.3	69%
5	2.0	63%

a. Crude H NMR yield with the mesitylene as the internal standard

During the screen, we found that in the reaction DEDC was more reproducible than DMDC and gave higher yield, so DEDC was chosen to be the activator of carboxylic acids.

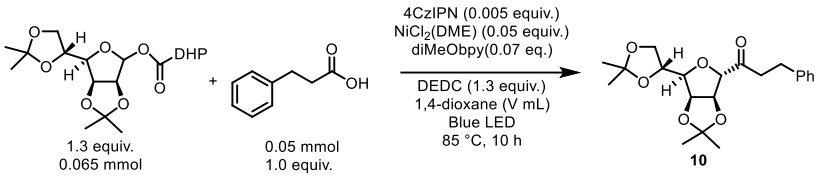
Table S5. The Effect of Ligands with DEDC as the Activator



Entry	Ligand	**10** (yield)[a]
1	bpy	63%
2	dtbbpy	45%
3	diMeObpy	66%
4	diMebpy[b]	42%
5	**L1**	54%

a. Crude H NMR yield with the mesitylene as the internal standard
b. diMebpy: 4,4'-dimethyl-2,2'-bipyridine

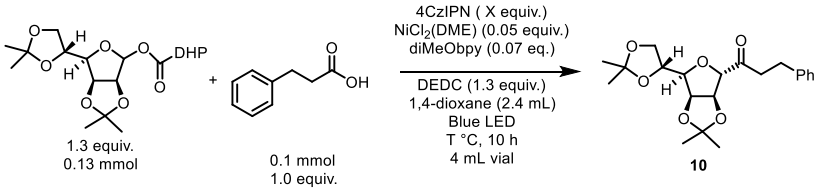
Table S6. The Effect of concentration with DEDC as the Activator



Entry	V	**10** (yield)[a]
1	0.4	66%
2	0.6	66%
3	0.8	57%
4	1.0	72%
5	1.2	78%
6	1.4	72%

a. Crude H NMR yield with the mesitylene as the internal standard

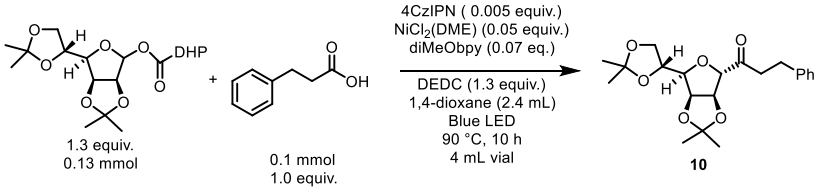
Table S7. The Effect of Temperature with Oil Bath and 4 mL Vial



Entry	4CzIPN	T	Number of Light	**10** (yield)[a]
1	0.01	85	2	39%
2	0.01	90	2	57%
3	0.0075	95	2	66%
4	0.005	90	1	78%
5[b]	0.005	90	1	66%

a. Crude H NMR yield with the mesitylene as the internal standard;
b. with a deflated ballon.

Table S8. Control experiments



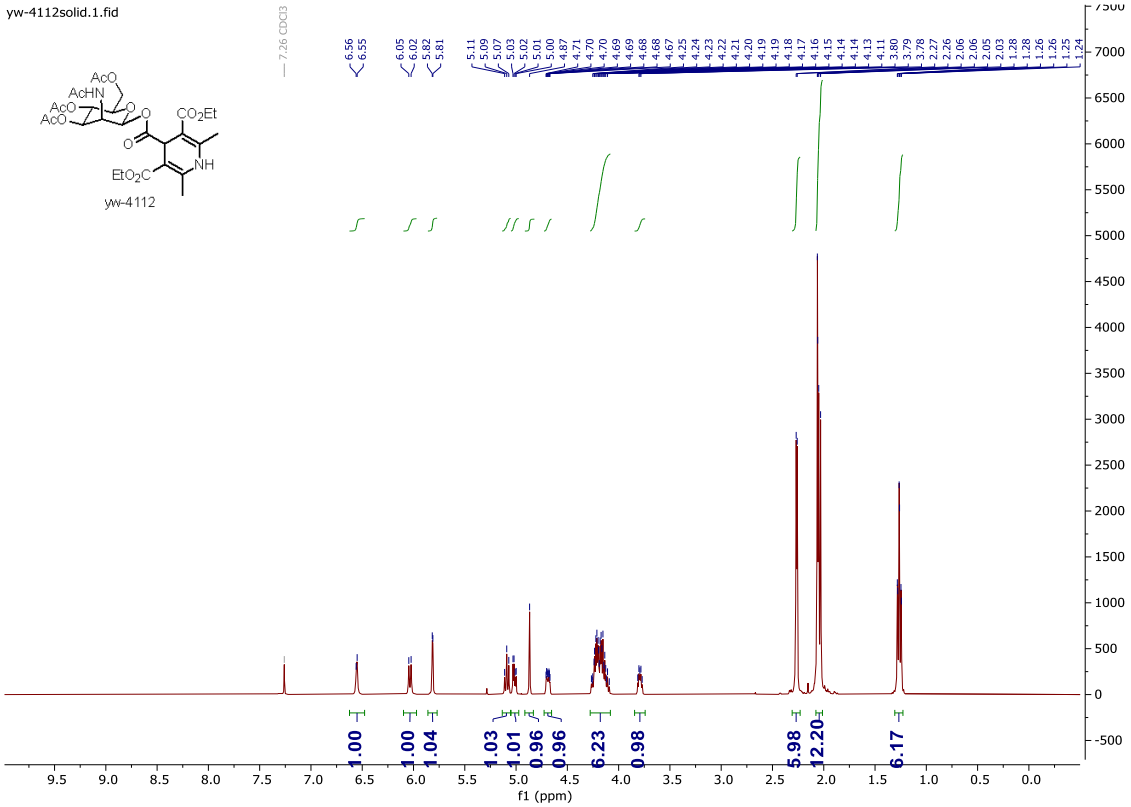
Entry	condition variants	**10** (yield)[a]
1	as shown	78%
2	without 4CzIPN	0
3	without $NiCl_2$(DME)	0
4	without irradition	0
5	without DEDC	0
6	room temperature	0

a. Crude H NMR yield with the mesitylene as the internal standard

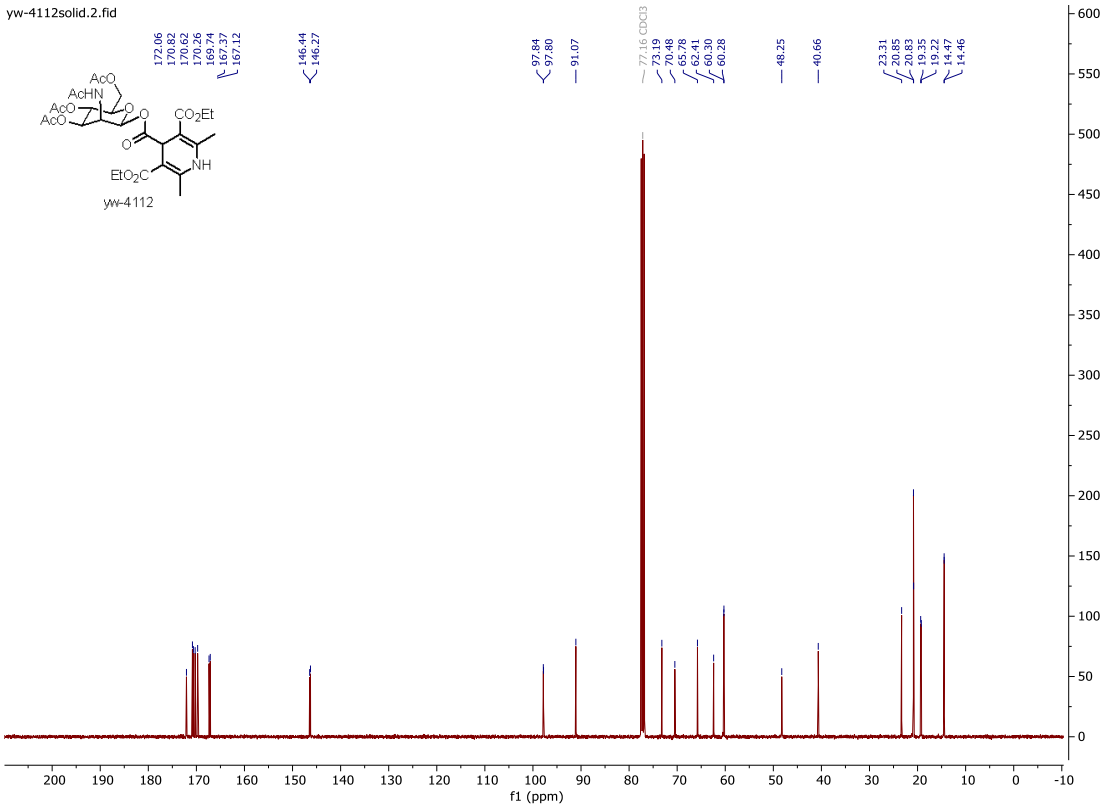
Reference

1. a) G. Ya. Dubur, Ya. R. Uldrikis, *Chem. Heterocycl. Compd.* 1972, **5**, 762–763; b) N. Alandini, L. Buzzetti, G. Favi, T. Schulte, L. Candish, K. D. Collins, P. Melchiorre, *Angew. Chem. Int. Ed.* 2020, **59**, 5248–5253.
2. Y. Wei, B. Ben-zvi, T. Diao, *Angew. Chem., Int. Ed.* 2021, **60**, 9433-9438.
3. C. Morozzi, J. Sedlakova, M. Serpi, M. Avigliano, R. Carbajo, L. Sandoval, Y. Valles-Ayoub, P. Crutcher, S. Thomas, F. Pertusati, *J. Med. Chem*. 2019, **62**, 8178–8193.
4. Y. Shiozaki, S. Sakurai, R. Sakamoto, A. Matsumoto, K. Maruoka, *Chem. - Asian J.*, 2020, **15**, 573-576.
5. a) X. P. Cheng, C. D. Quintanilla, L. M. Zhang, *J. Org. Chem.* 2019, **84**, 11054−11060; b) A. Evidente, A. Andolfi, M. Fiore, E. Spanu, L. Maddau, A. Franceschini, F. Marras, A. Motta, *J. Nat. Prod*. **2006**, **69**, 671-674.

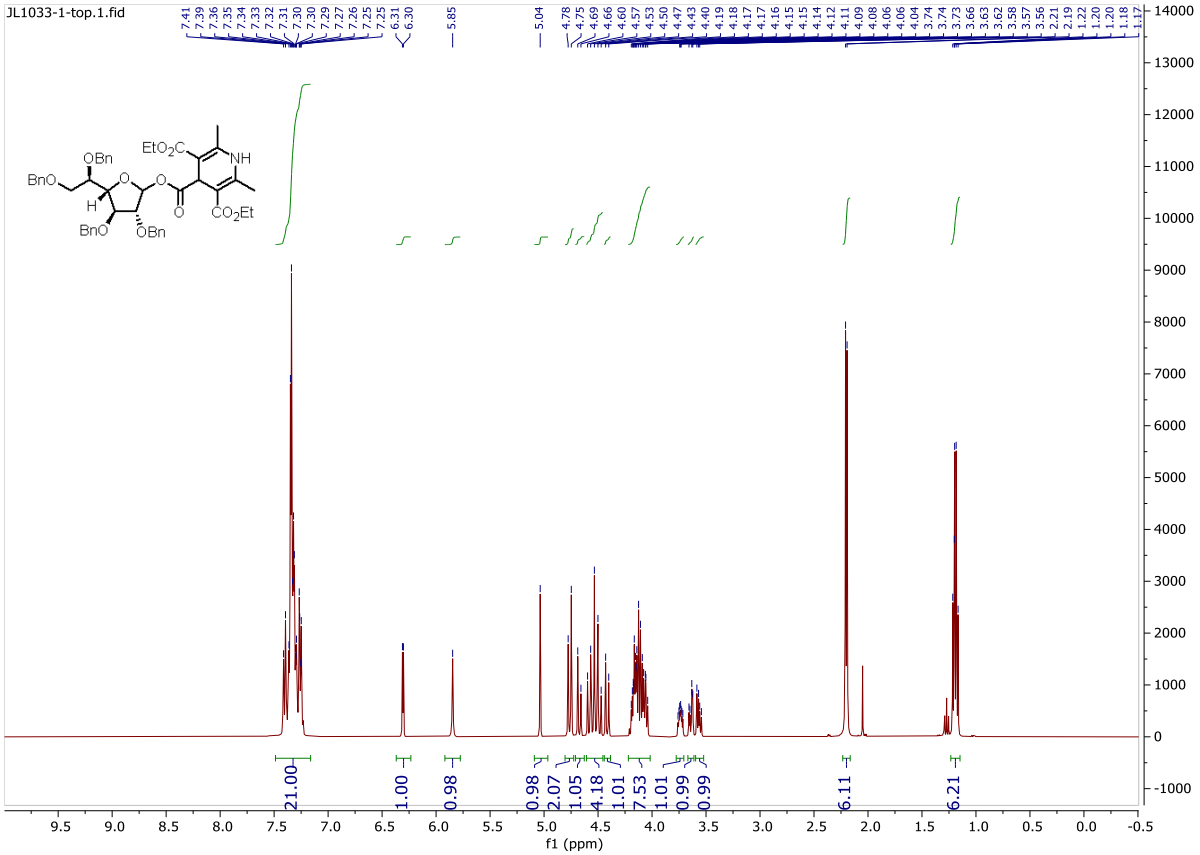
NMR Spectra



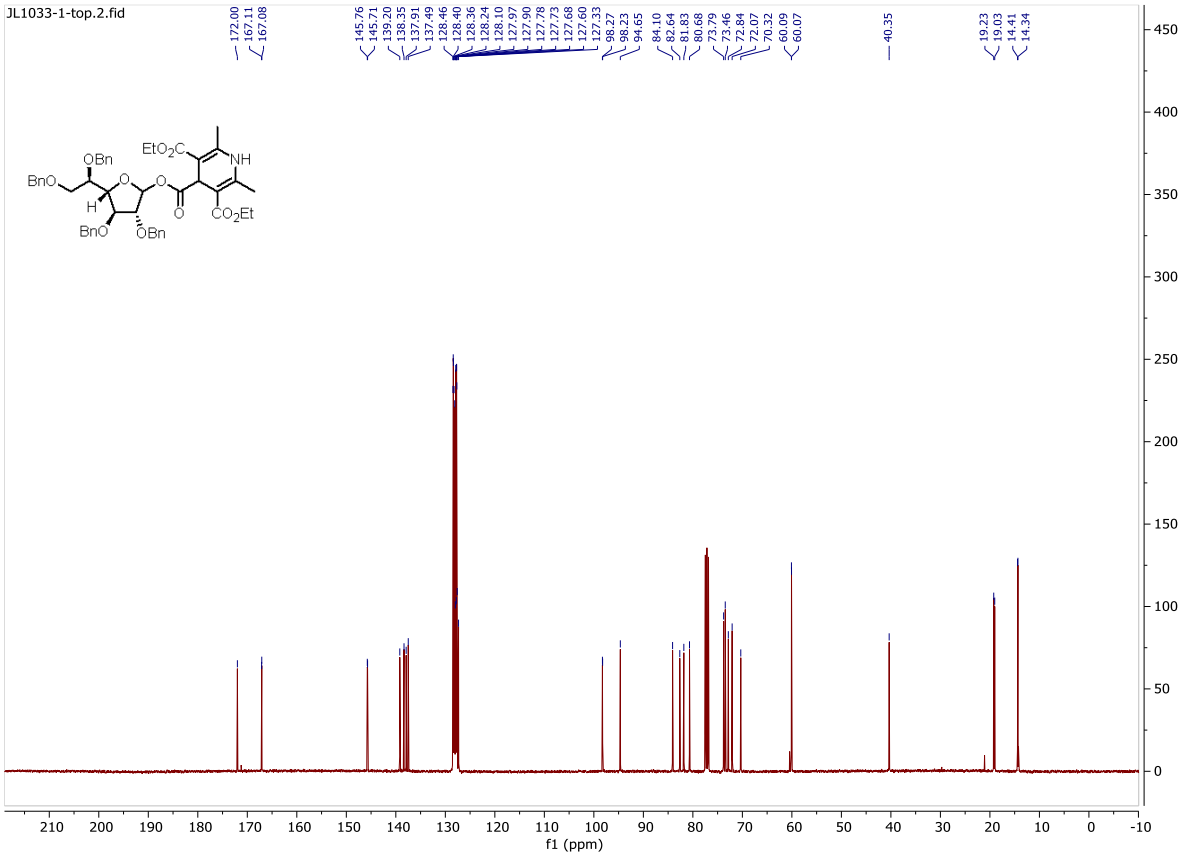
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S2**



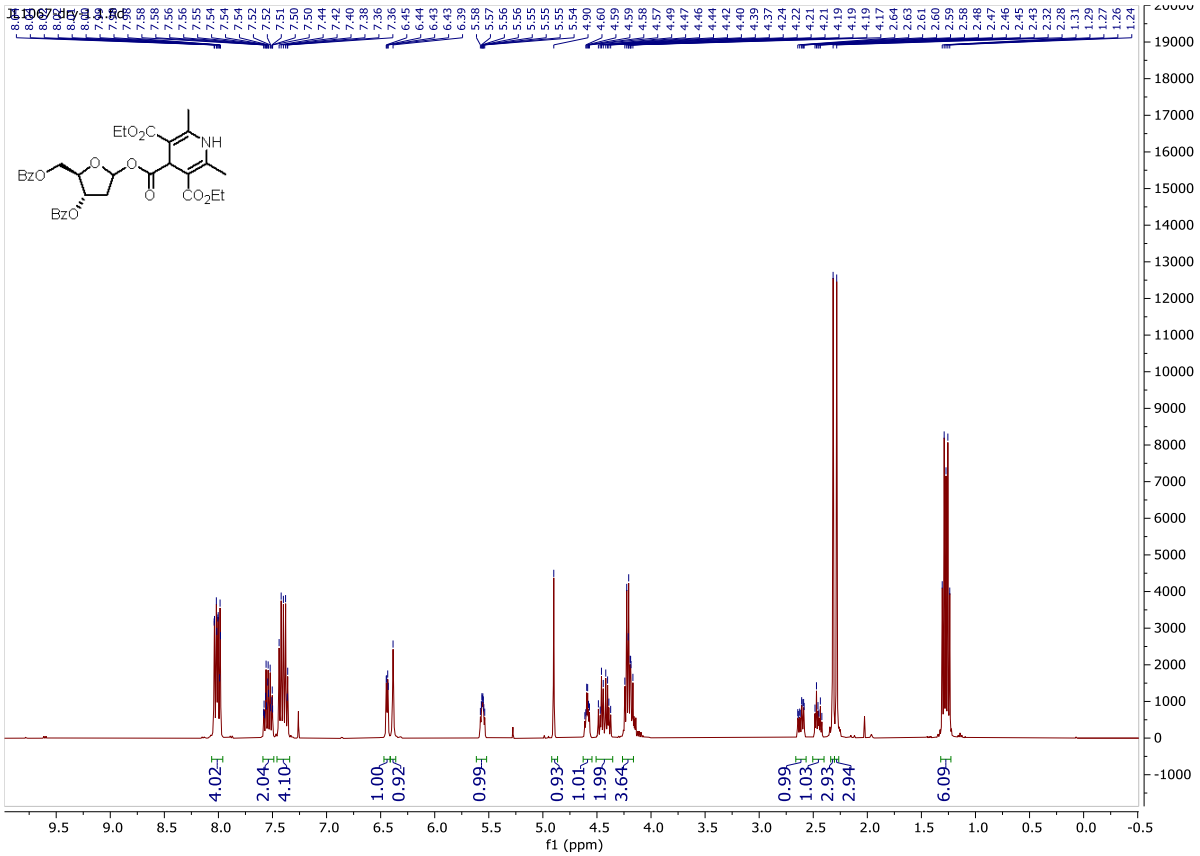
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S2**



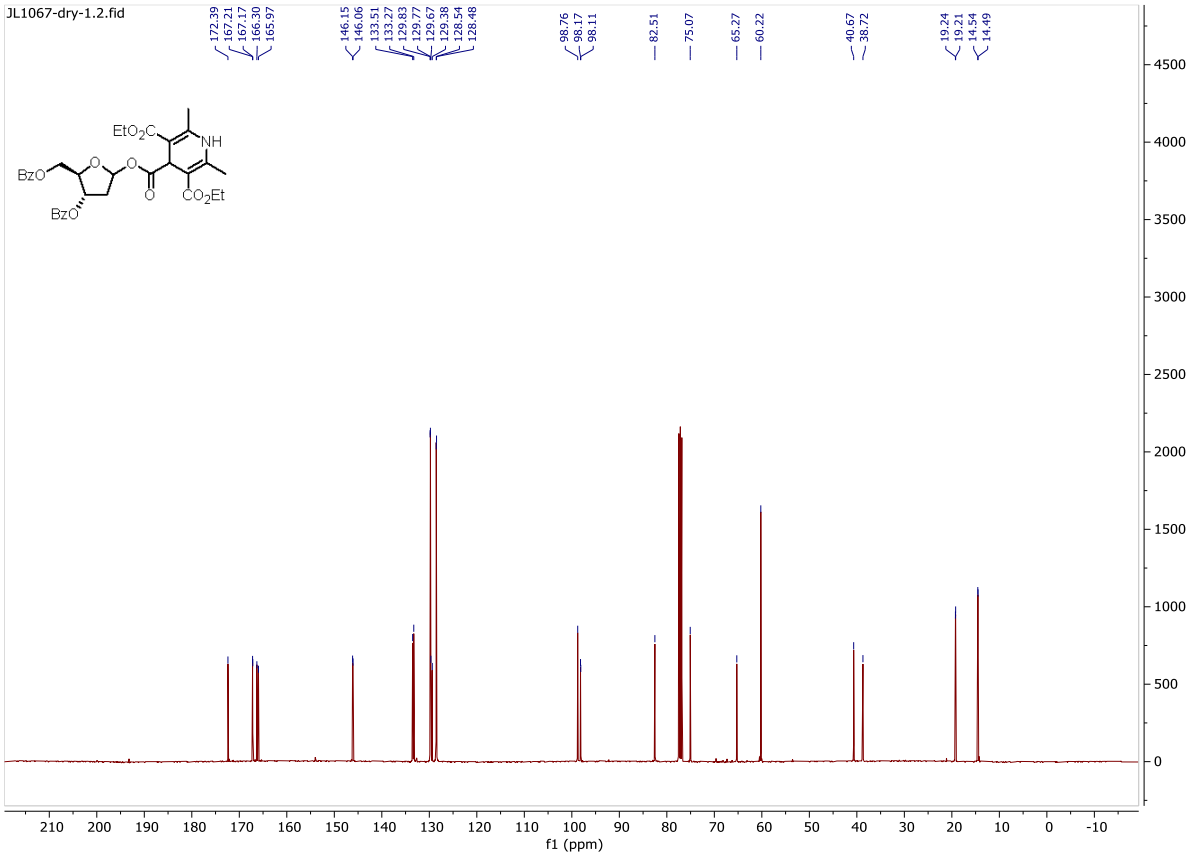
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S4**



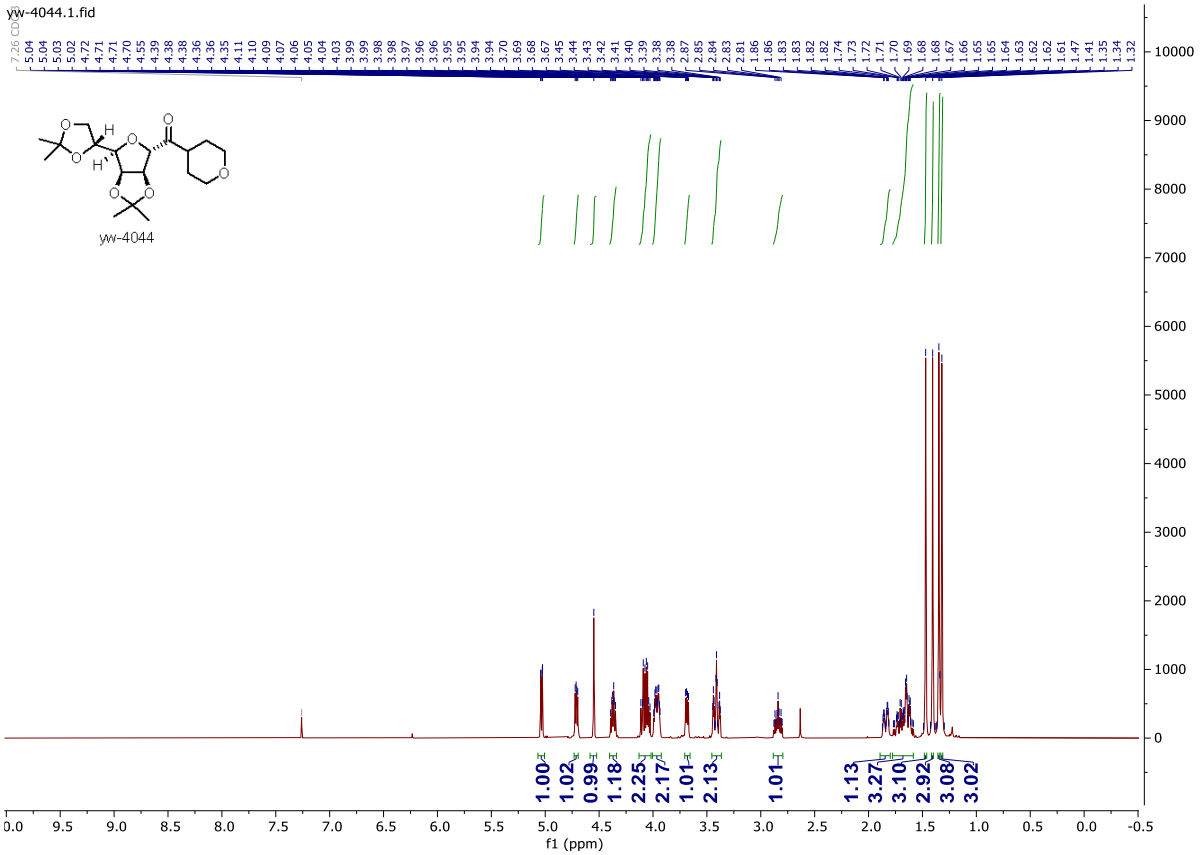
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S4**



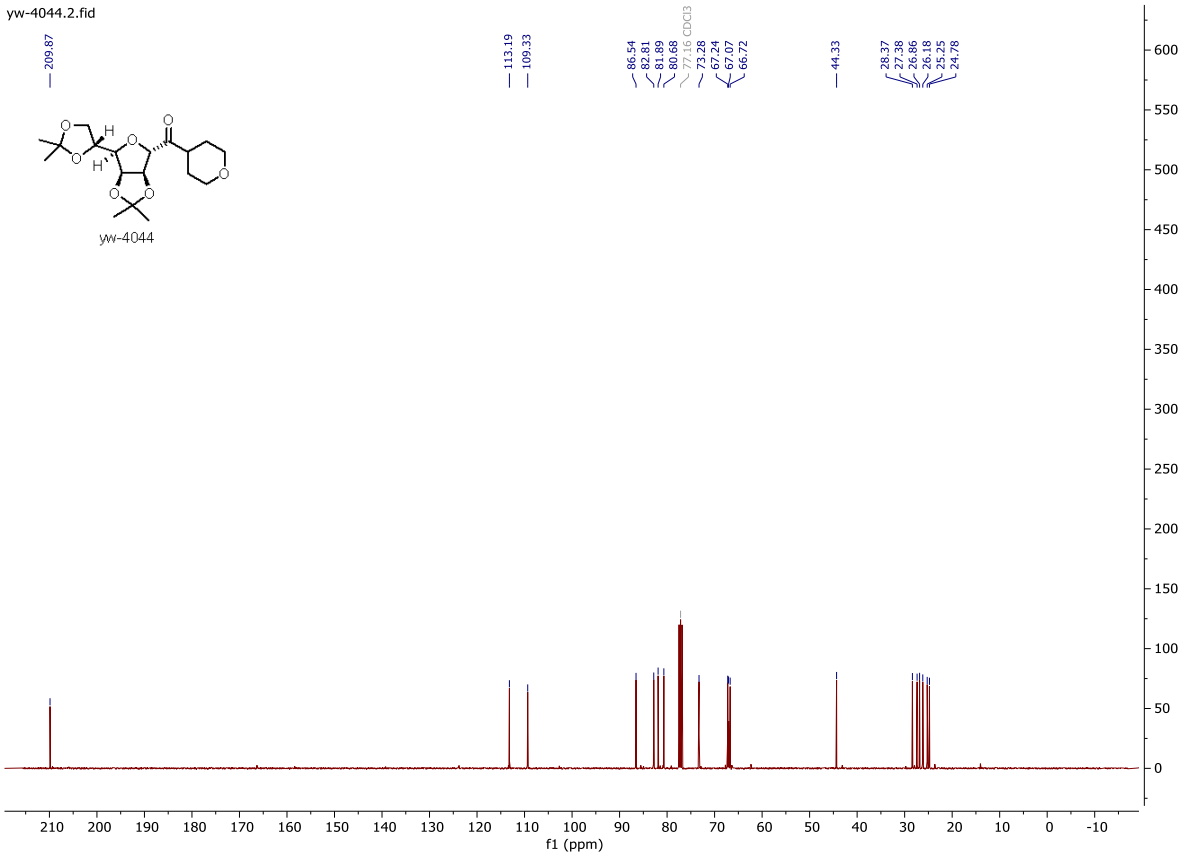
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **47**



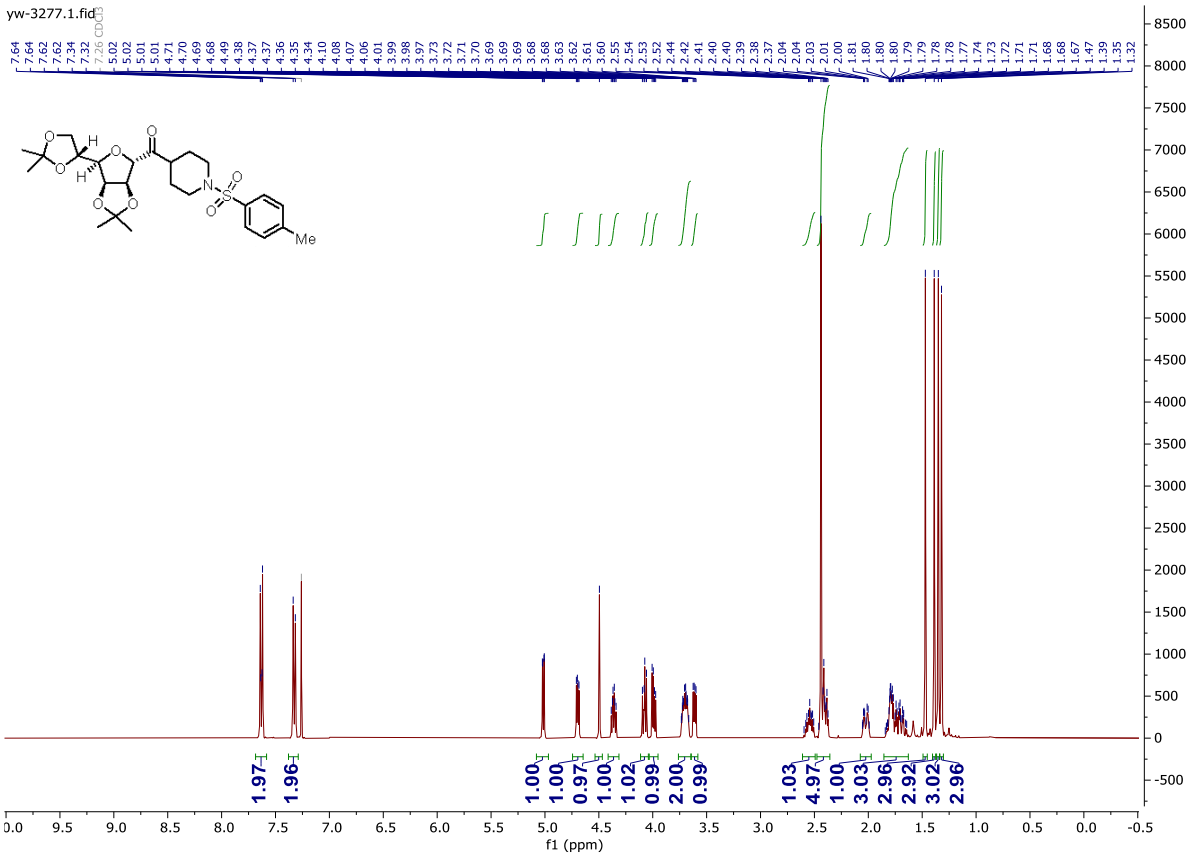
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **47**



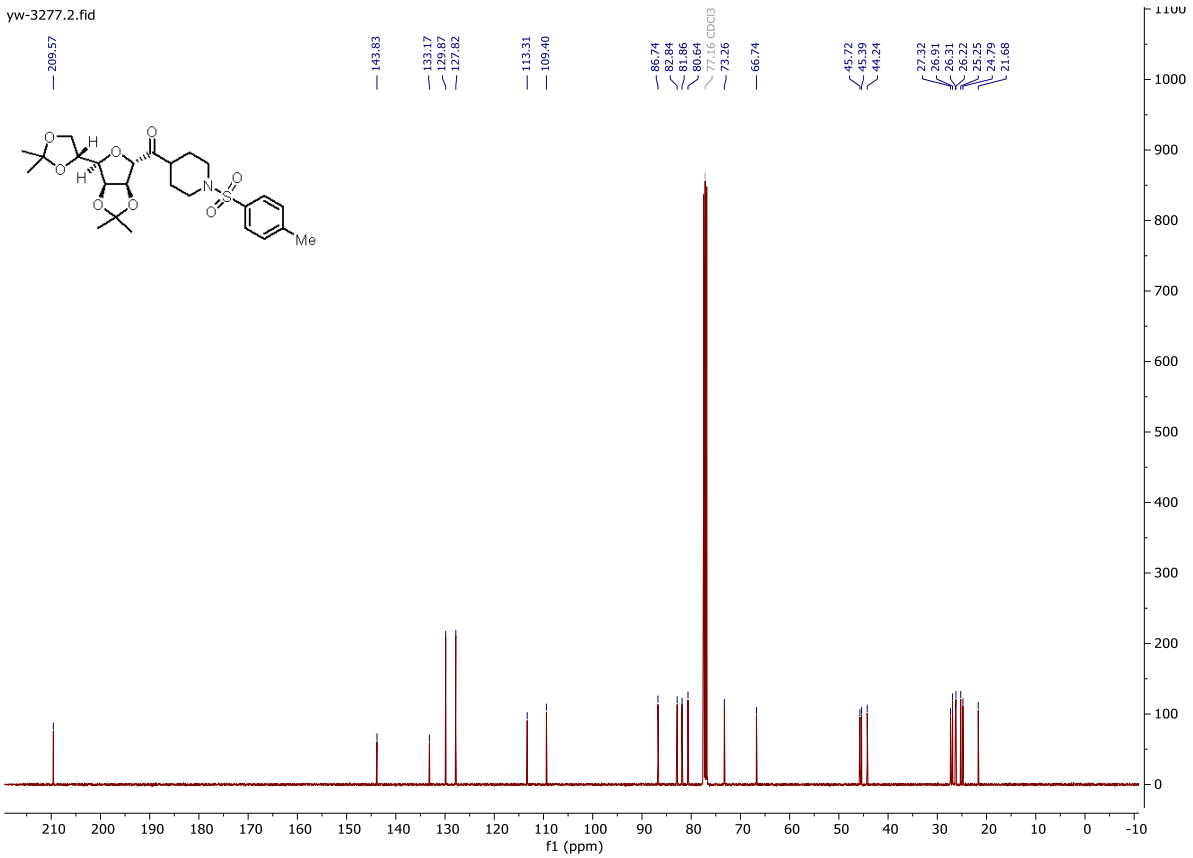
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2**



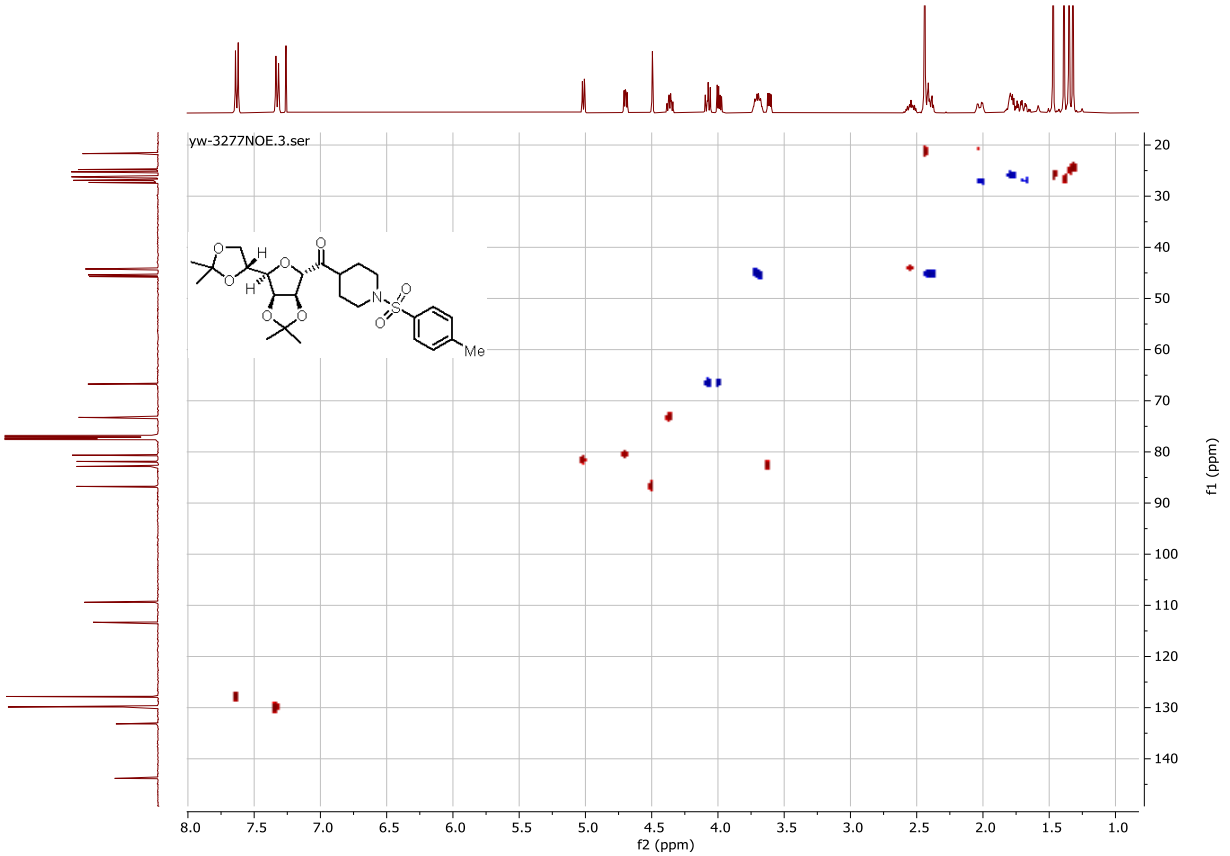
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2**



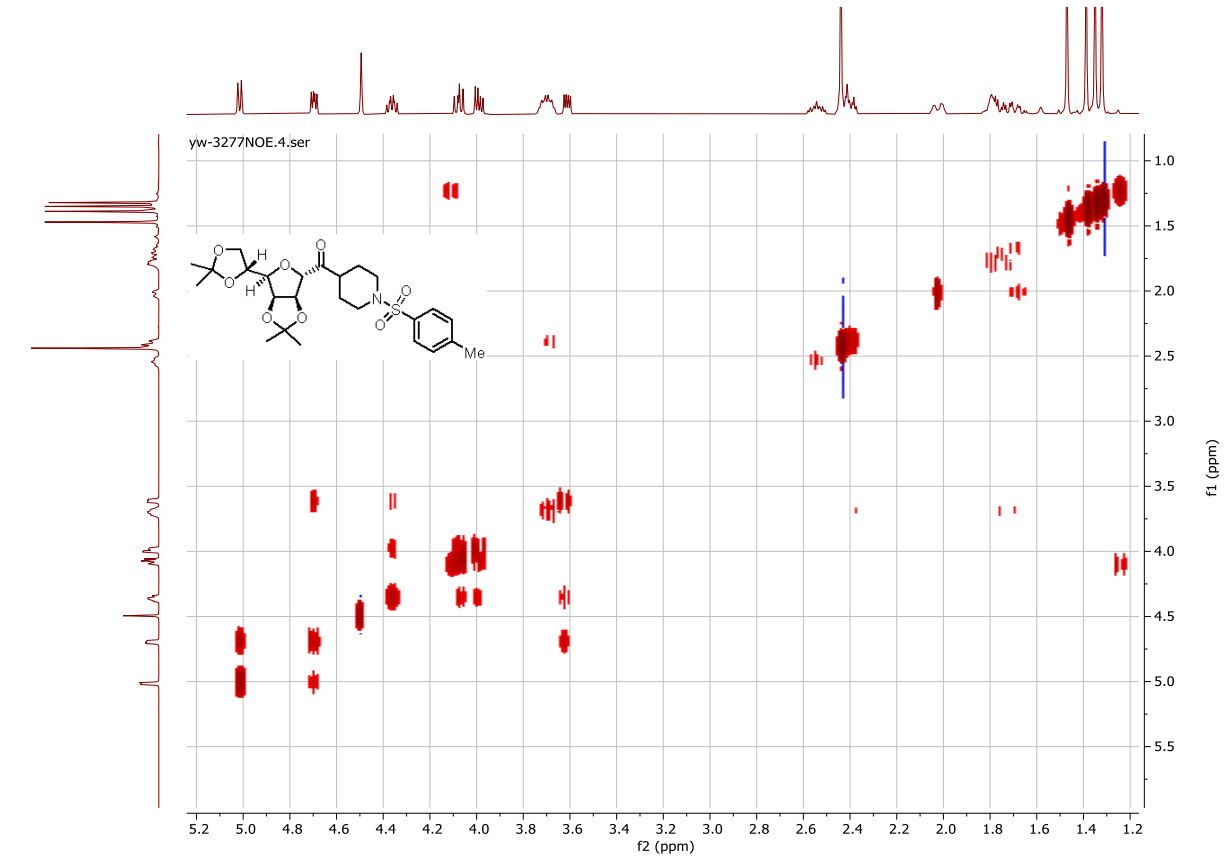
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**



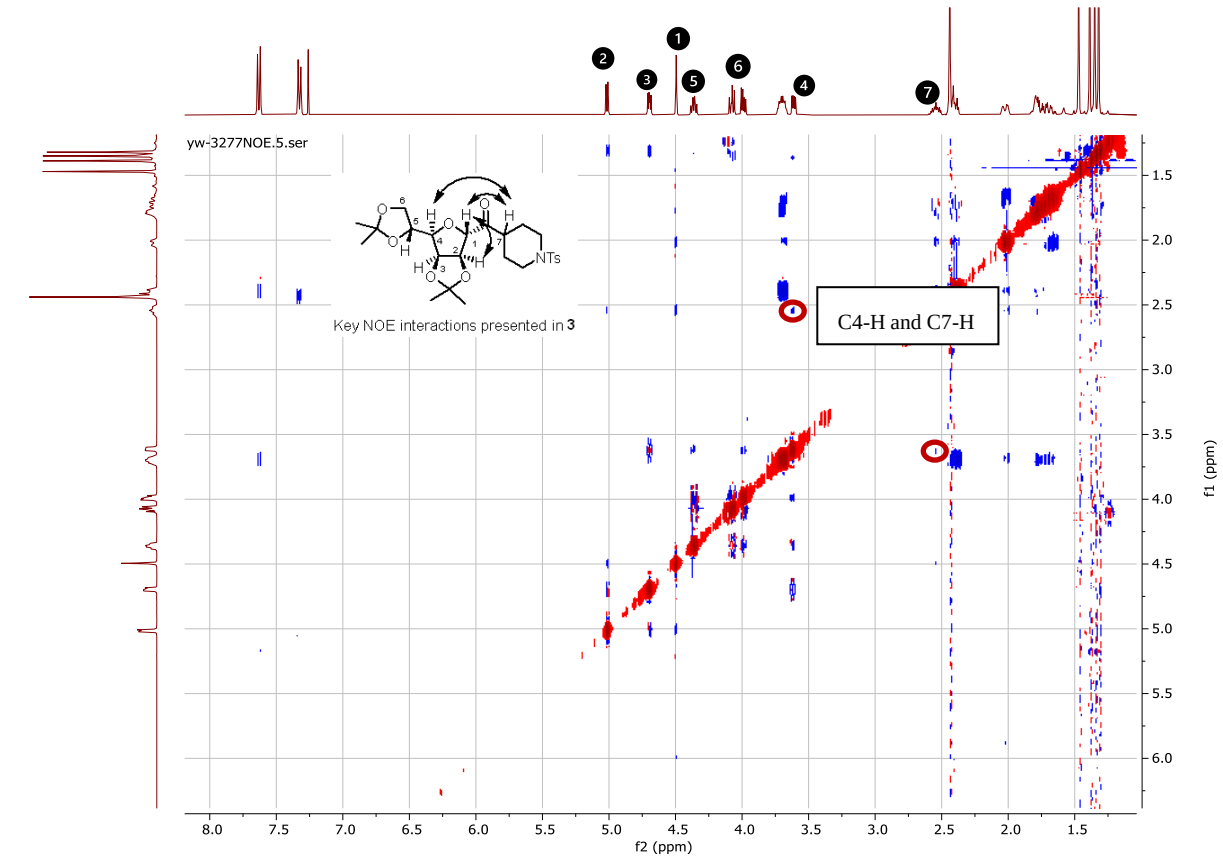
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3**



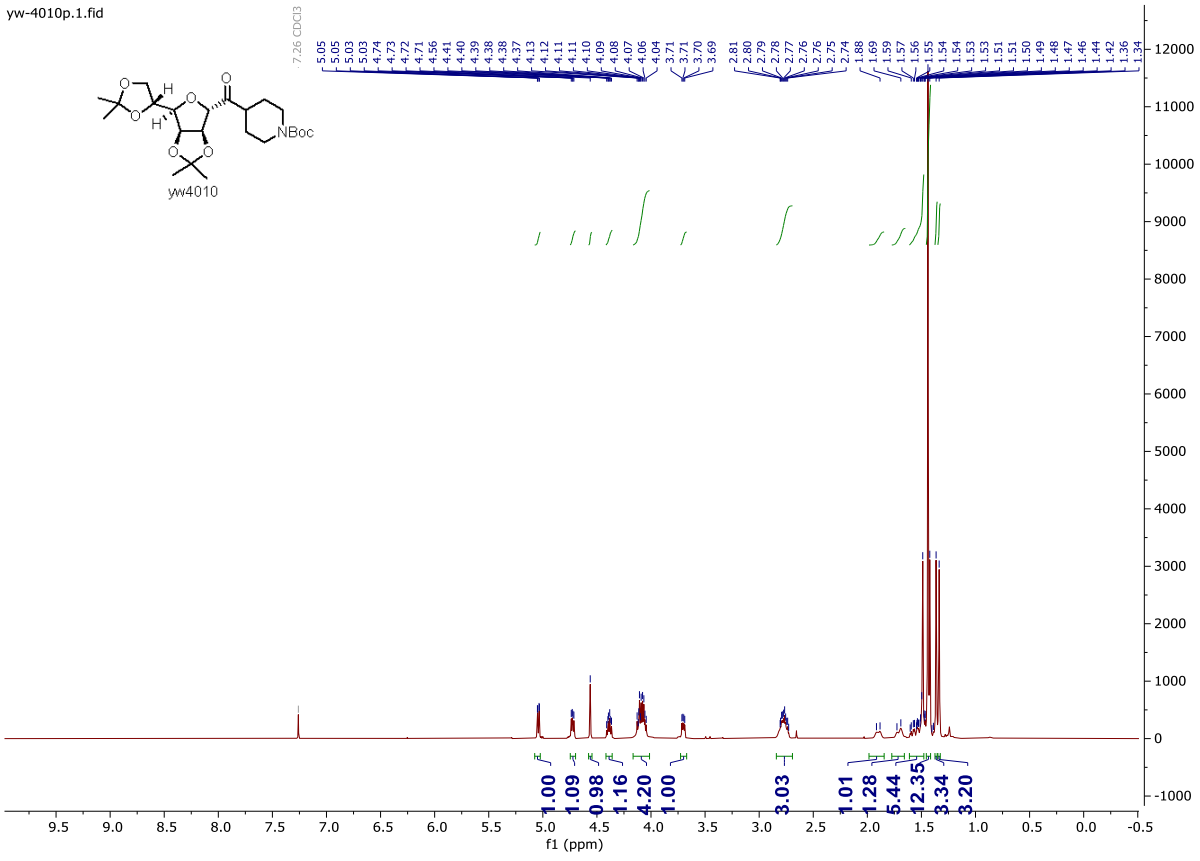
HSQCED of **3**



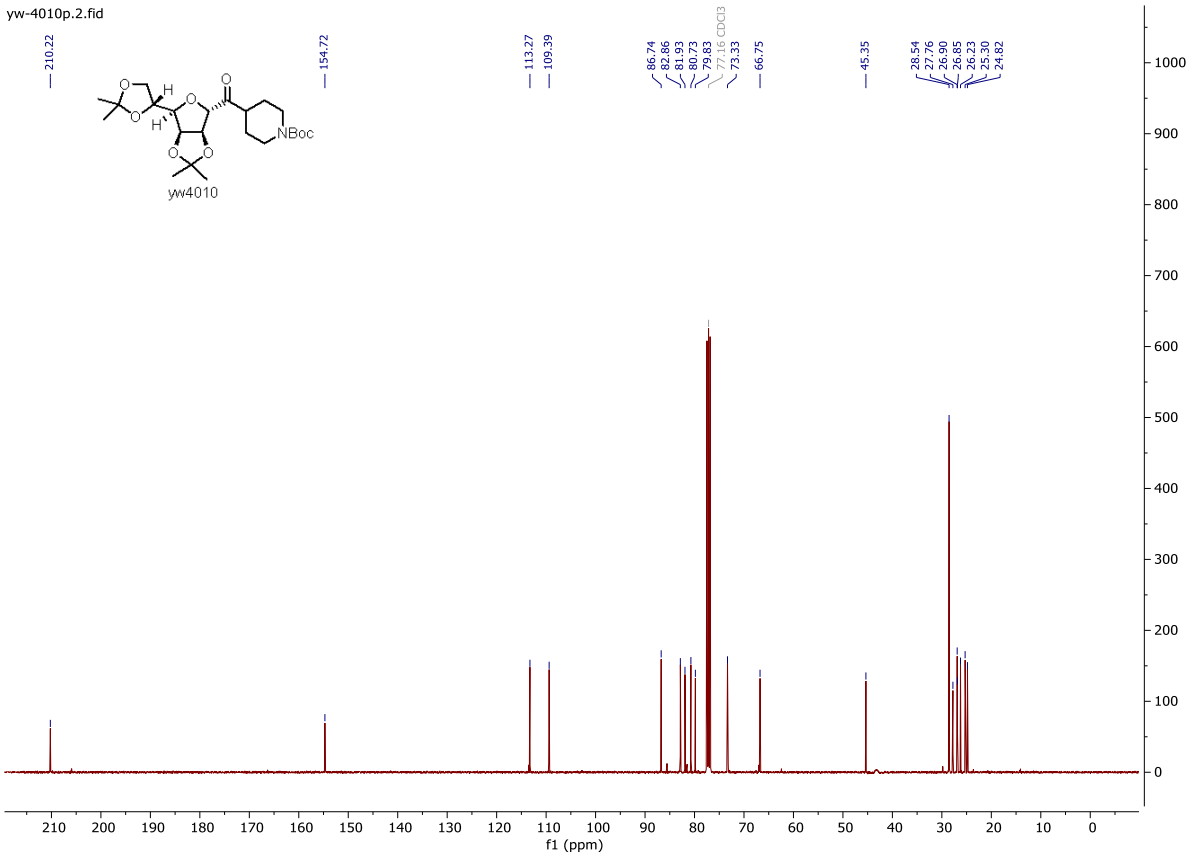
H-H COSY of **3**



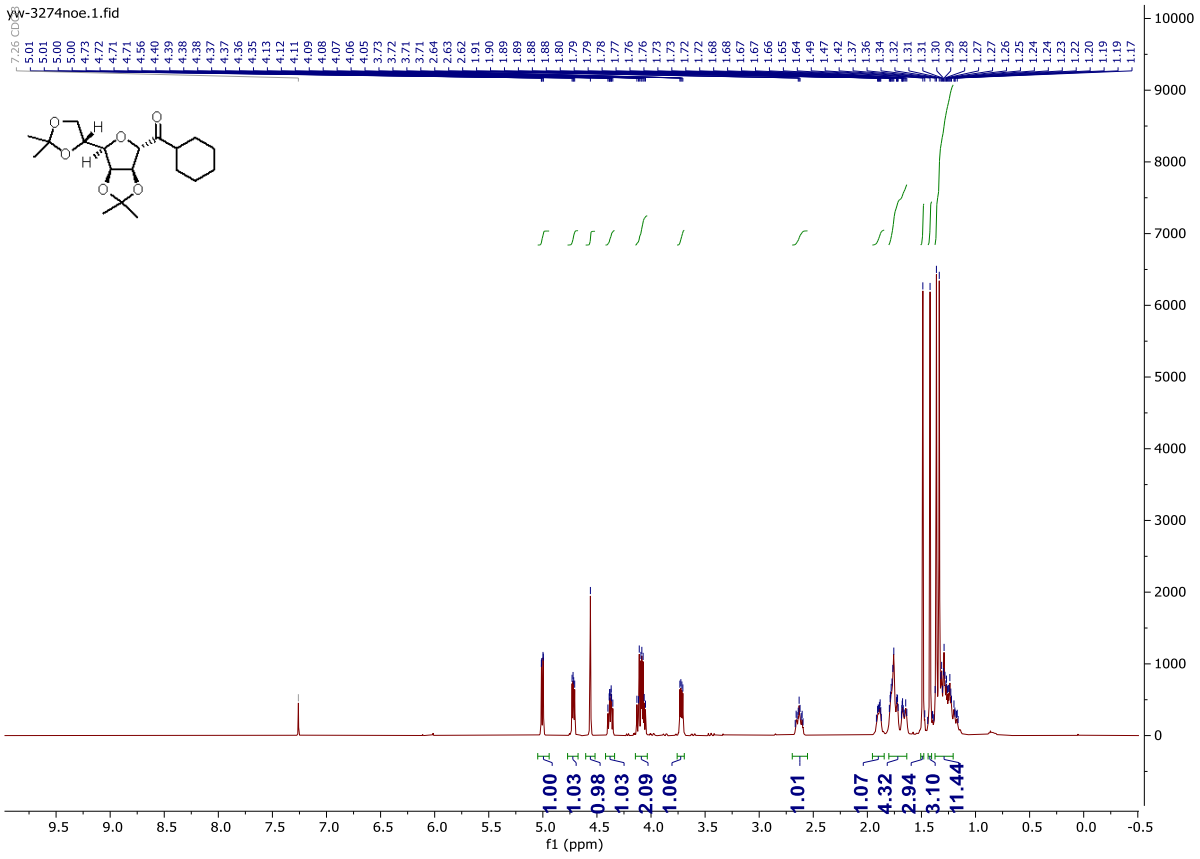
NOESY of **3**



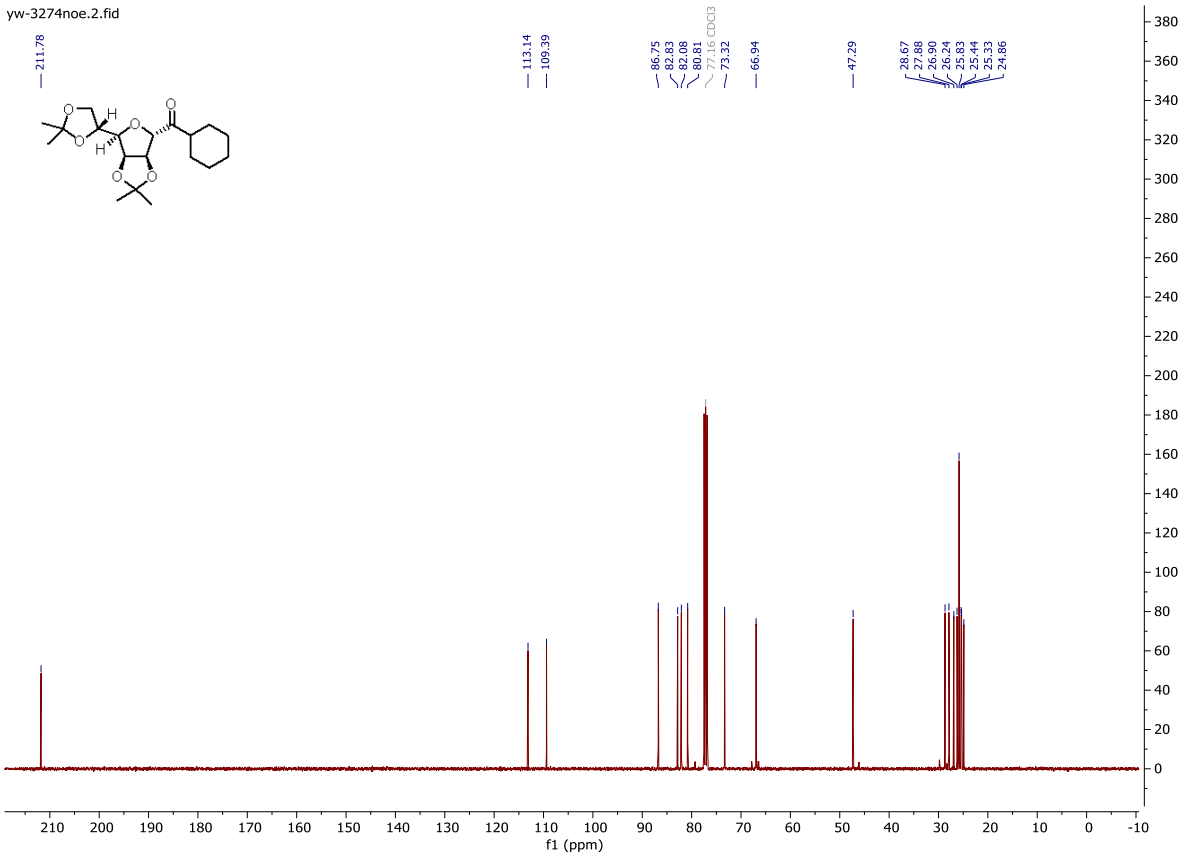
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**



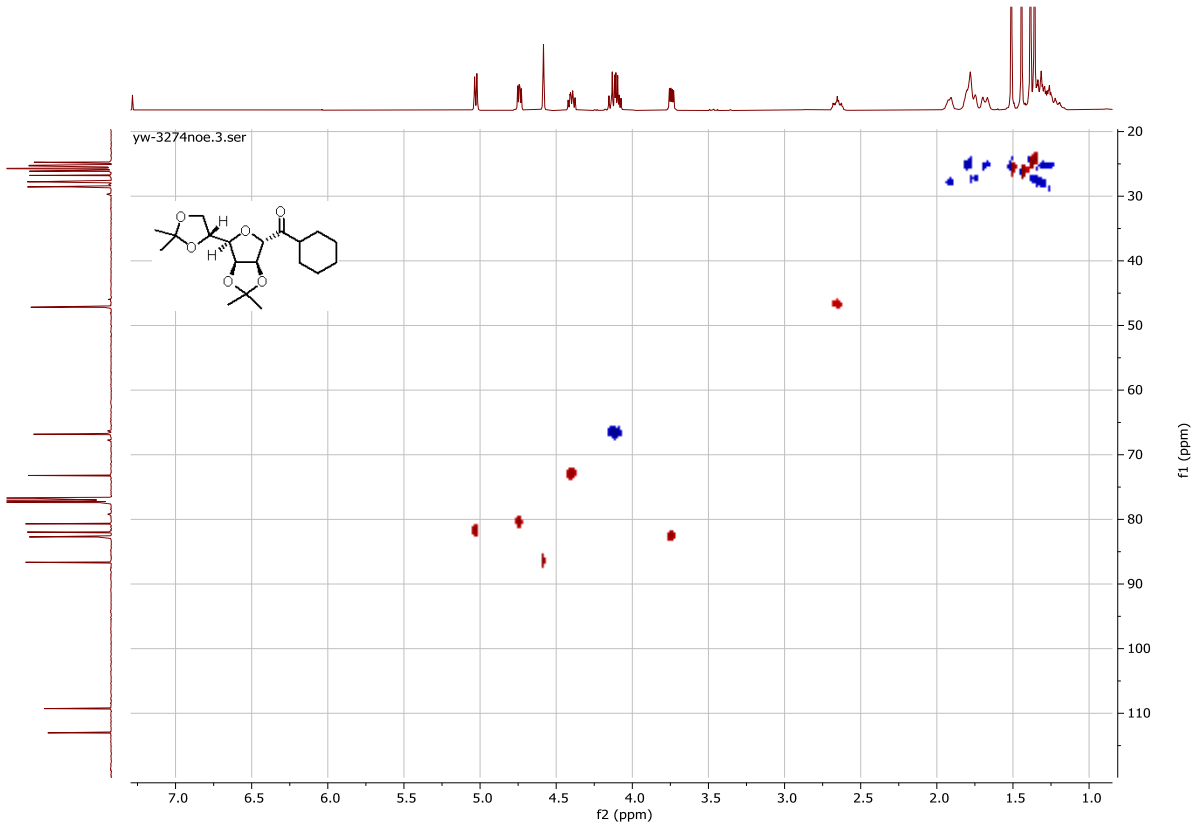
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4**



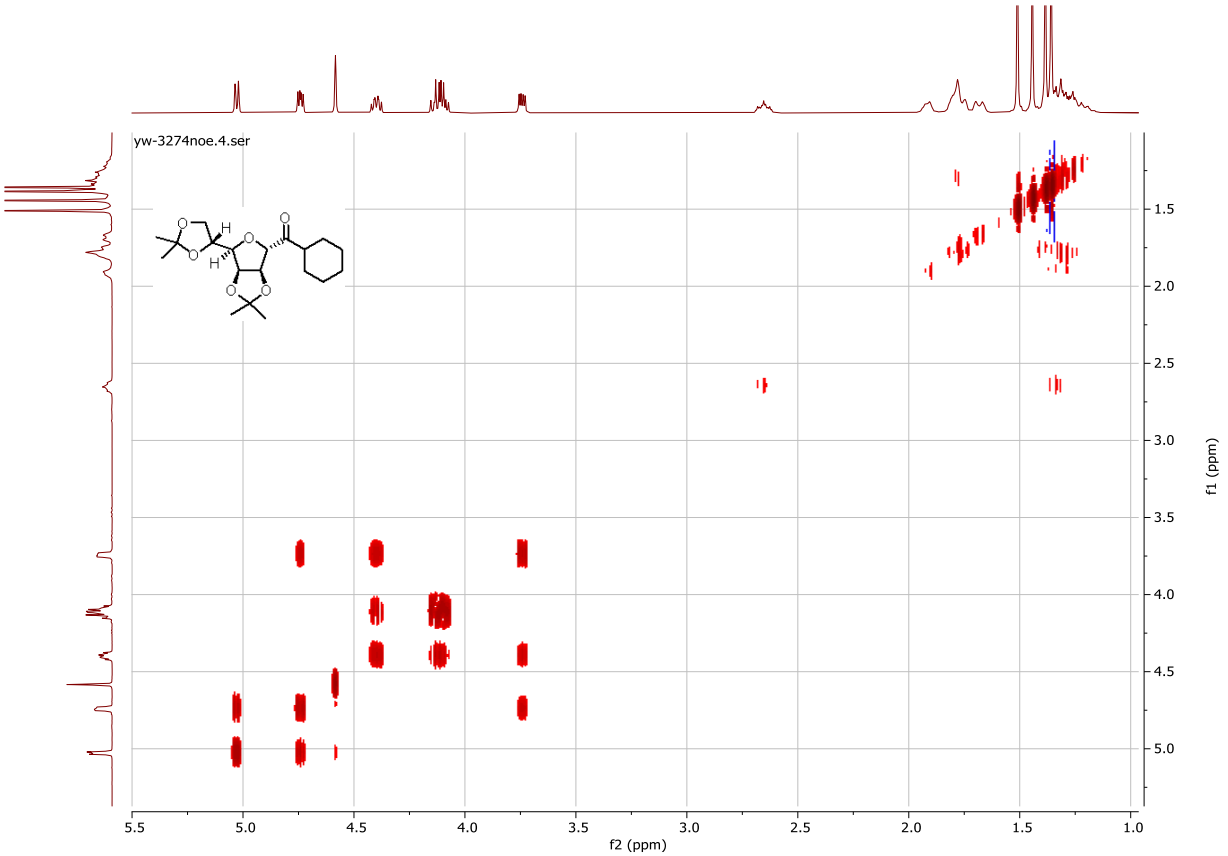
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5**



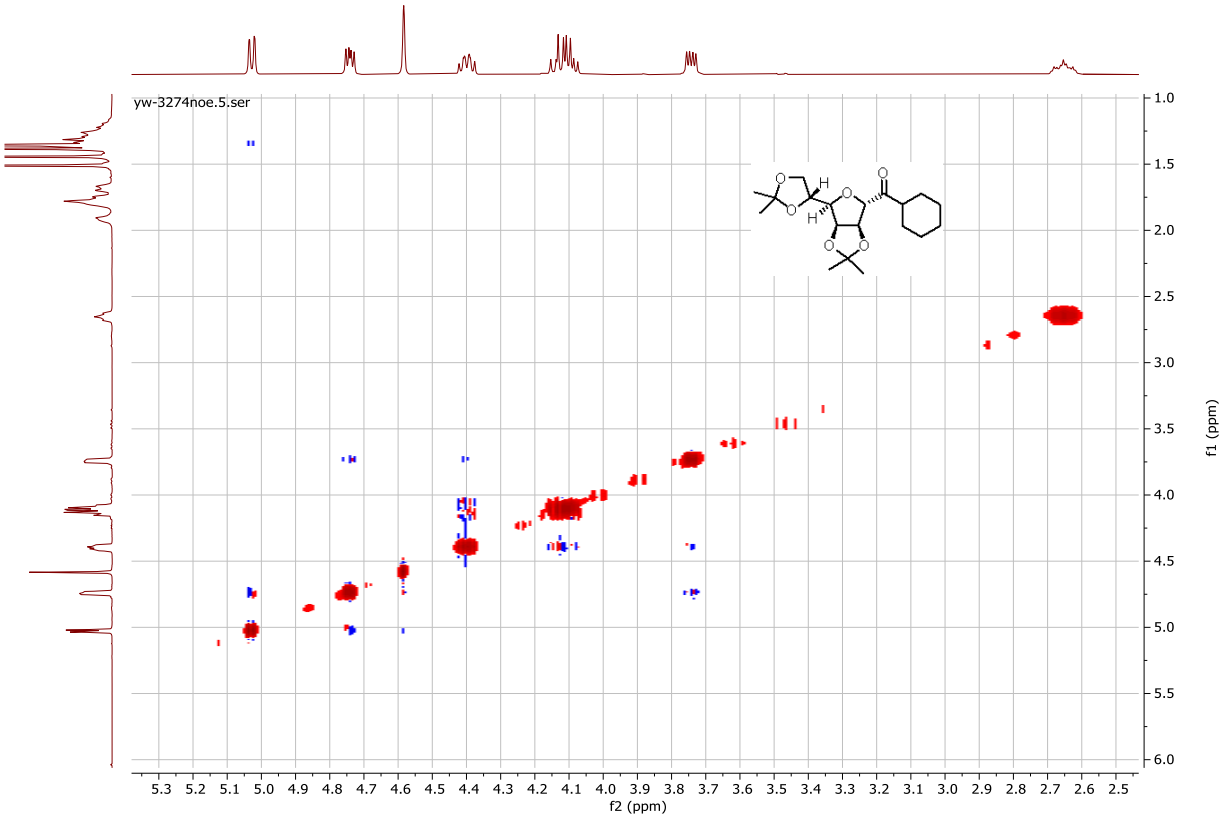
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5**



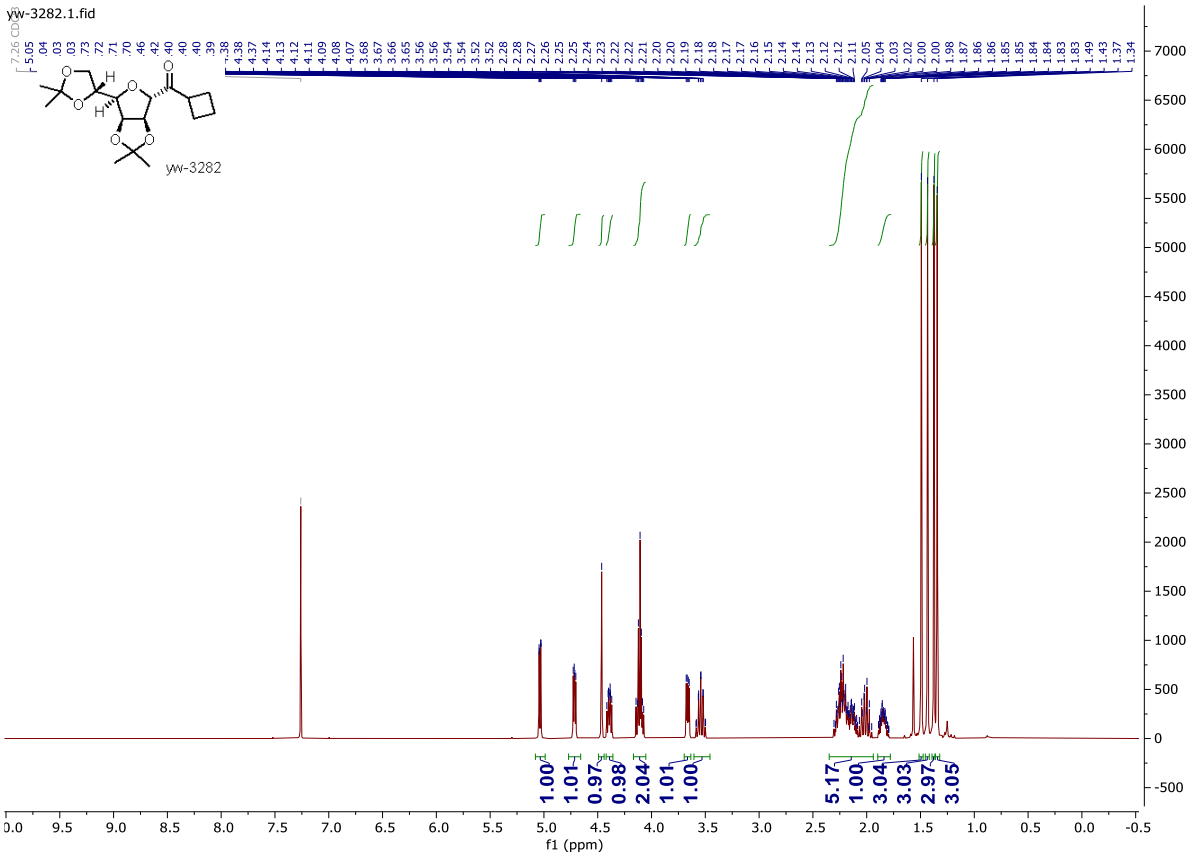
HSQCED of **5**



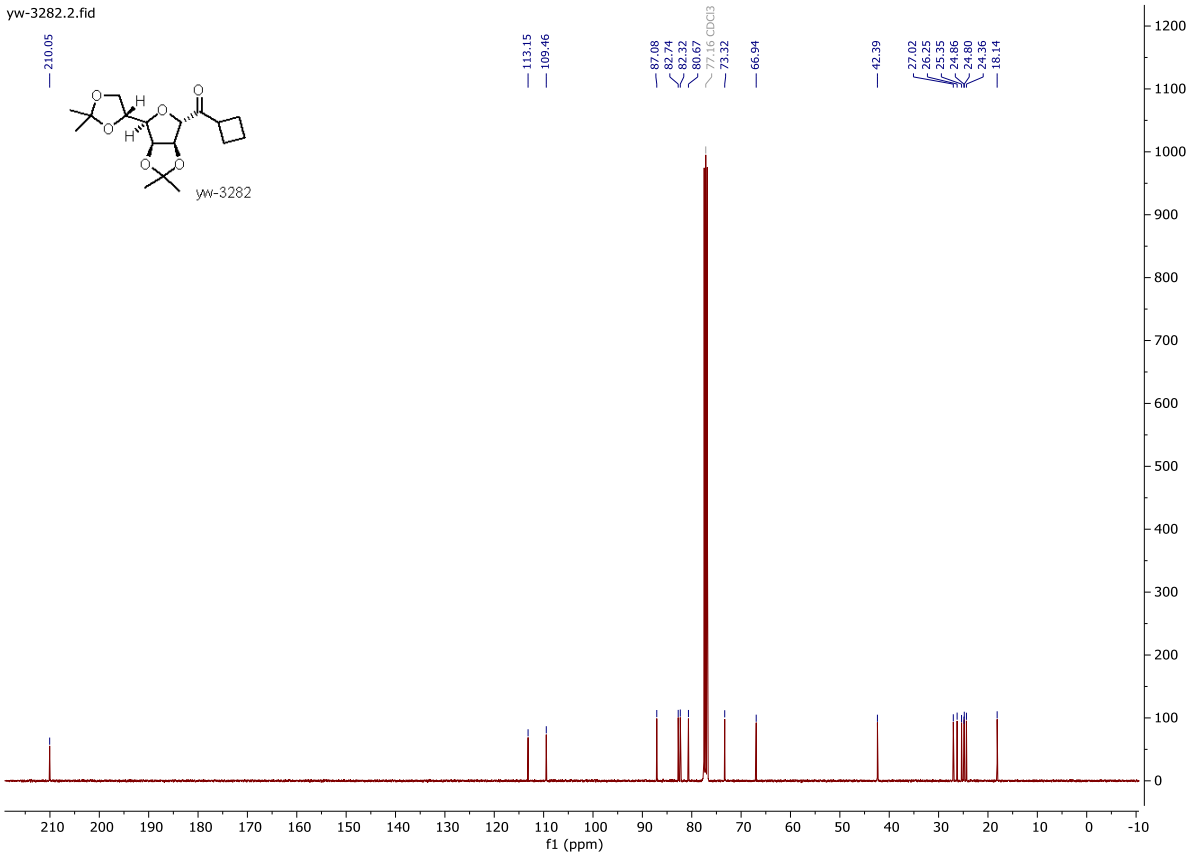
H-H COSY of **5**



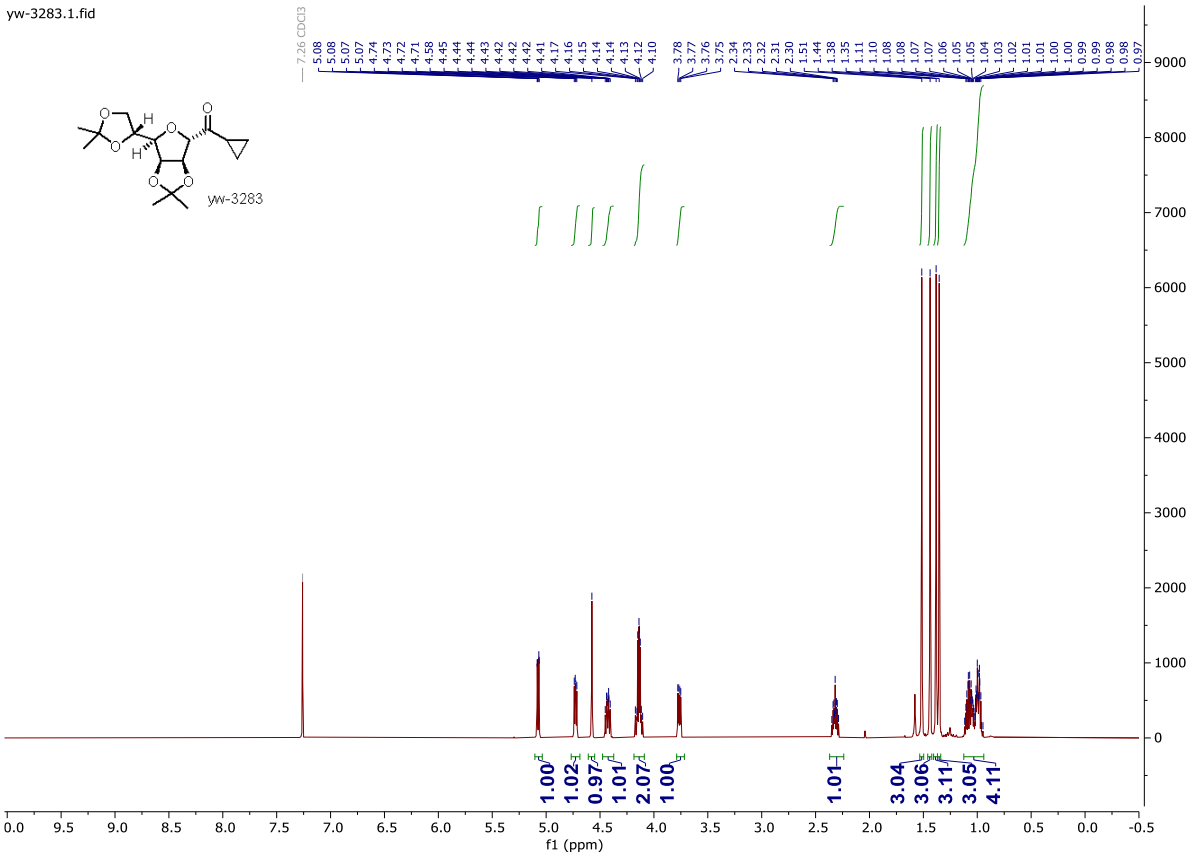
NOESY of **5**



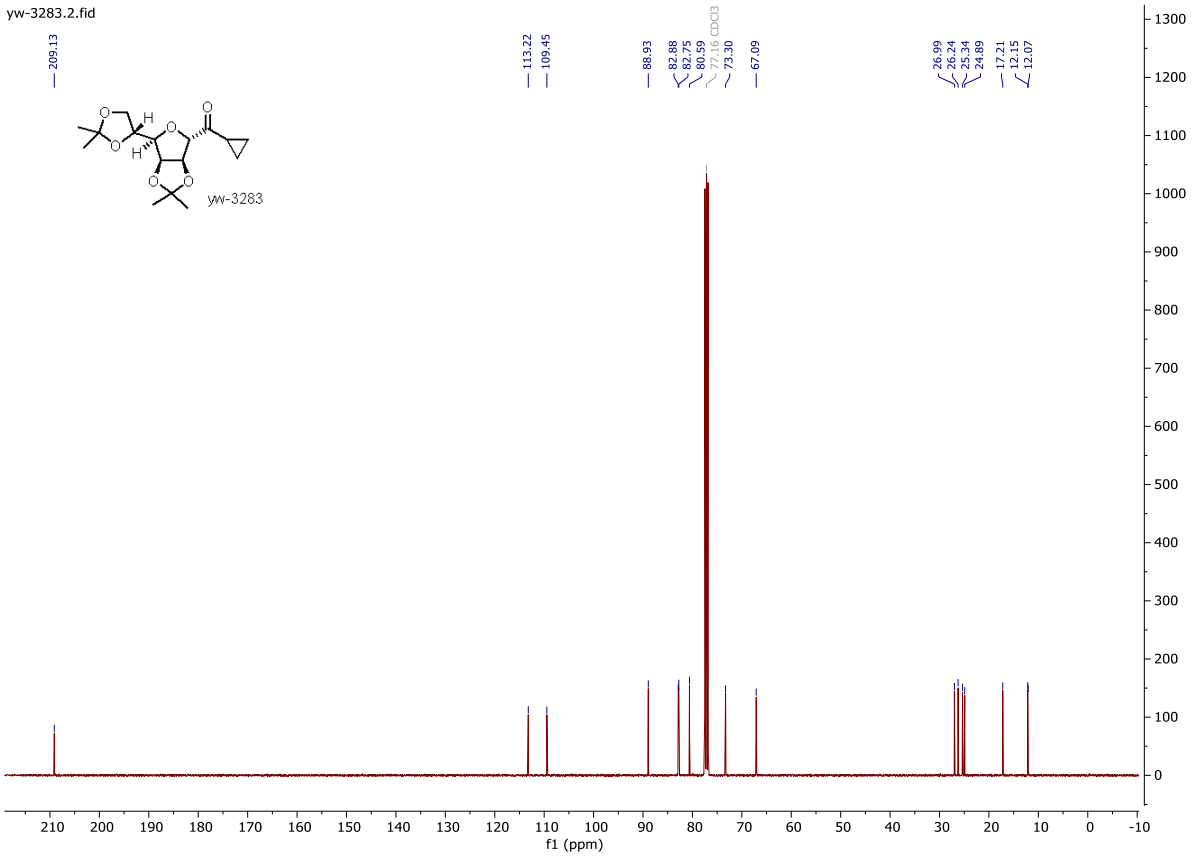
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6**



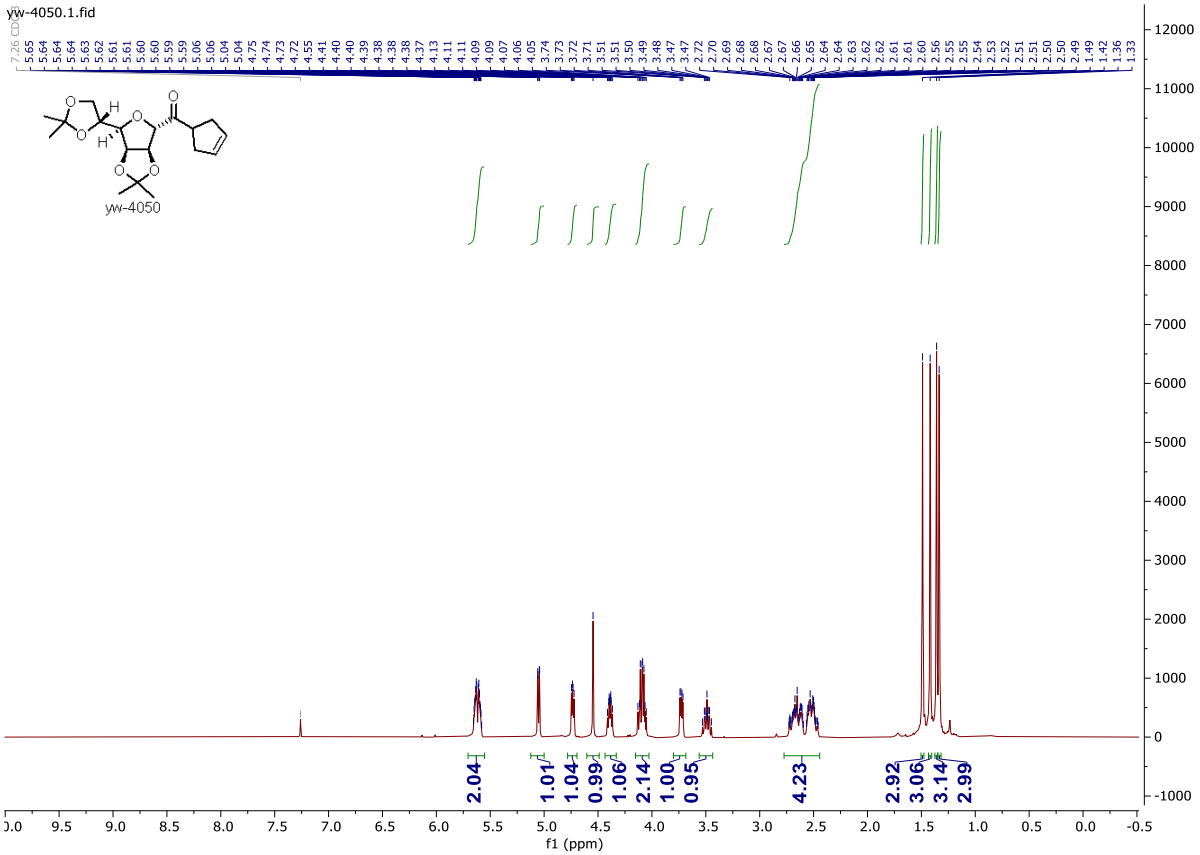
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6**



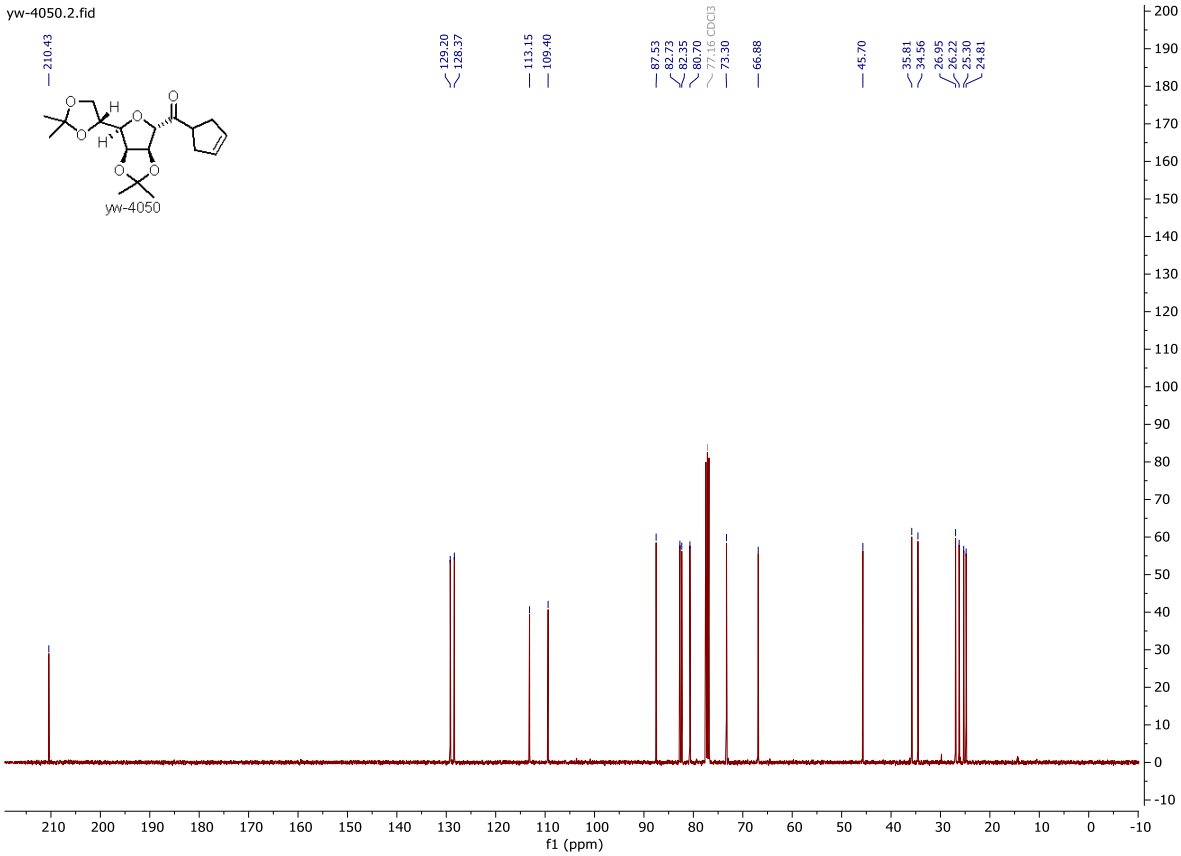
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7**



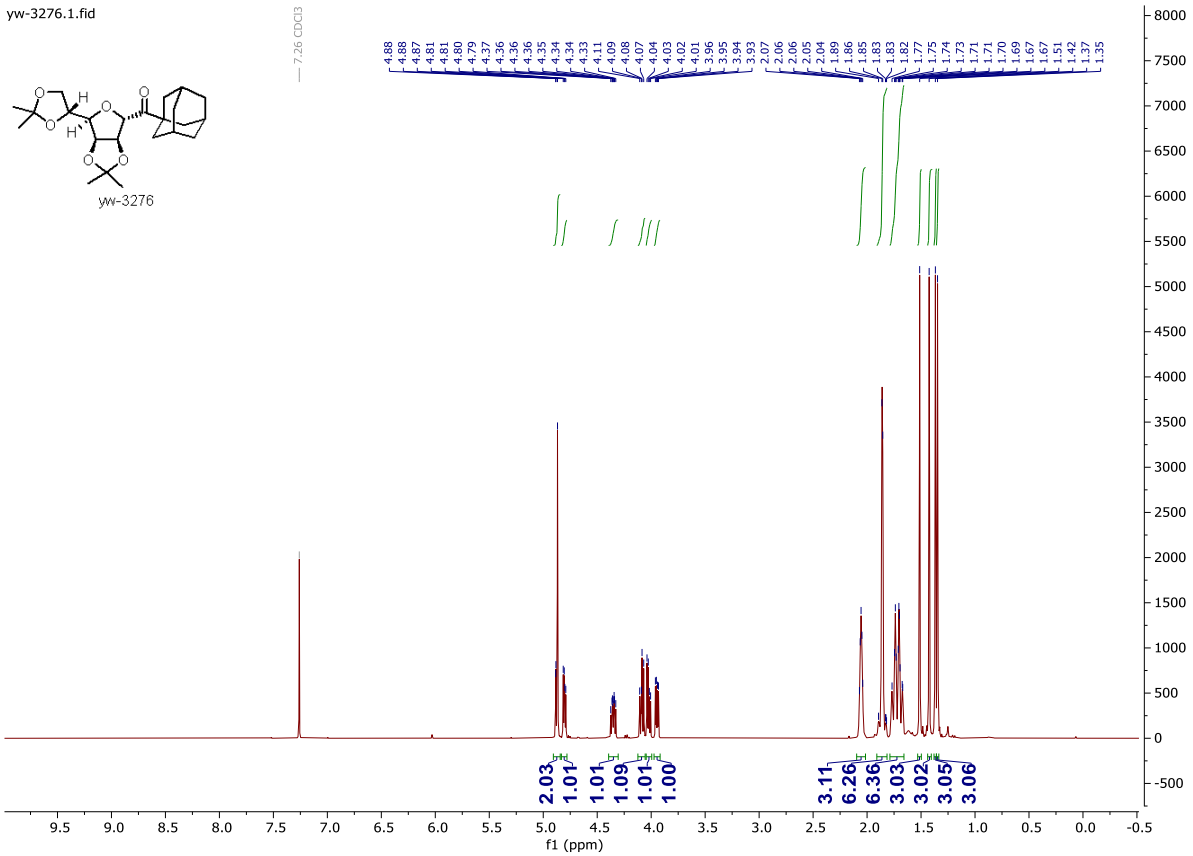
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7**



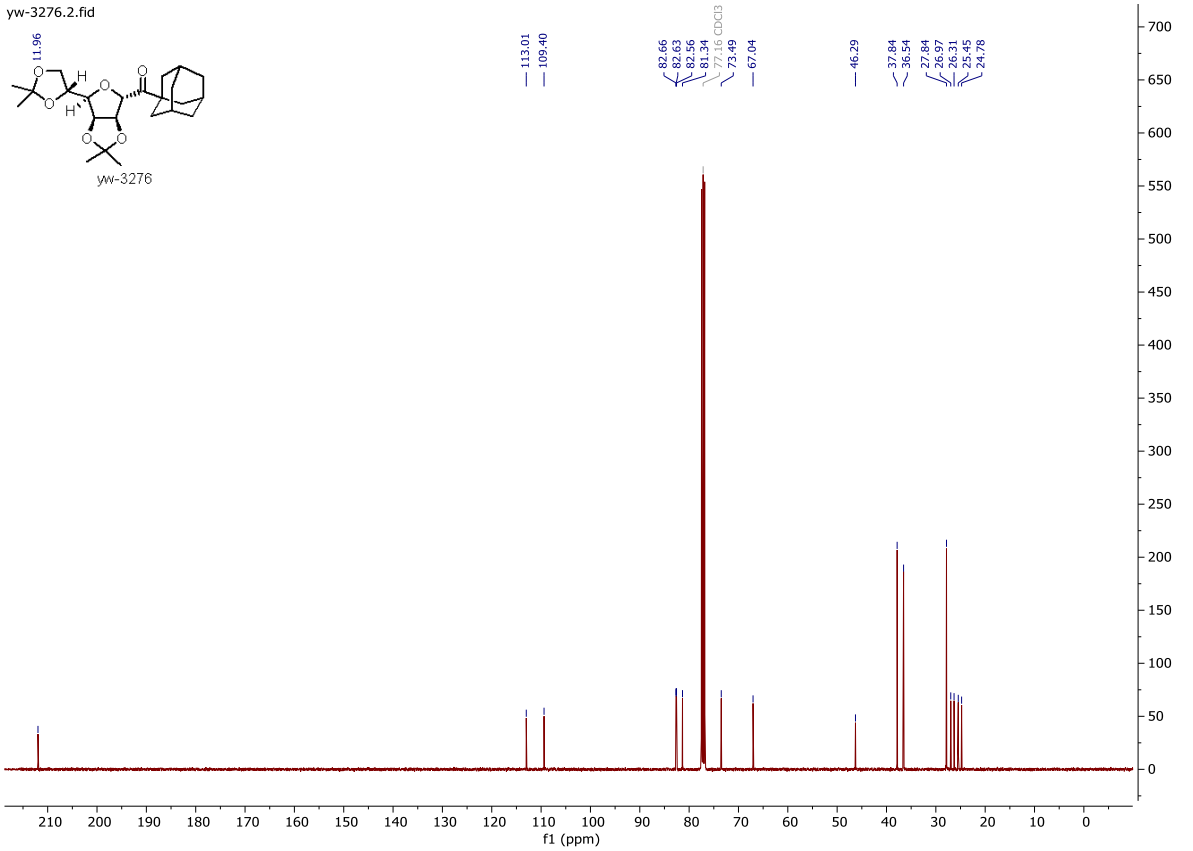
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8**



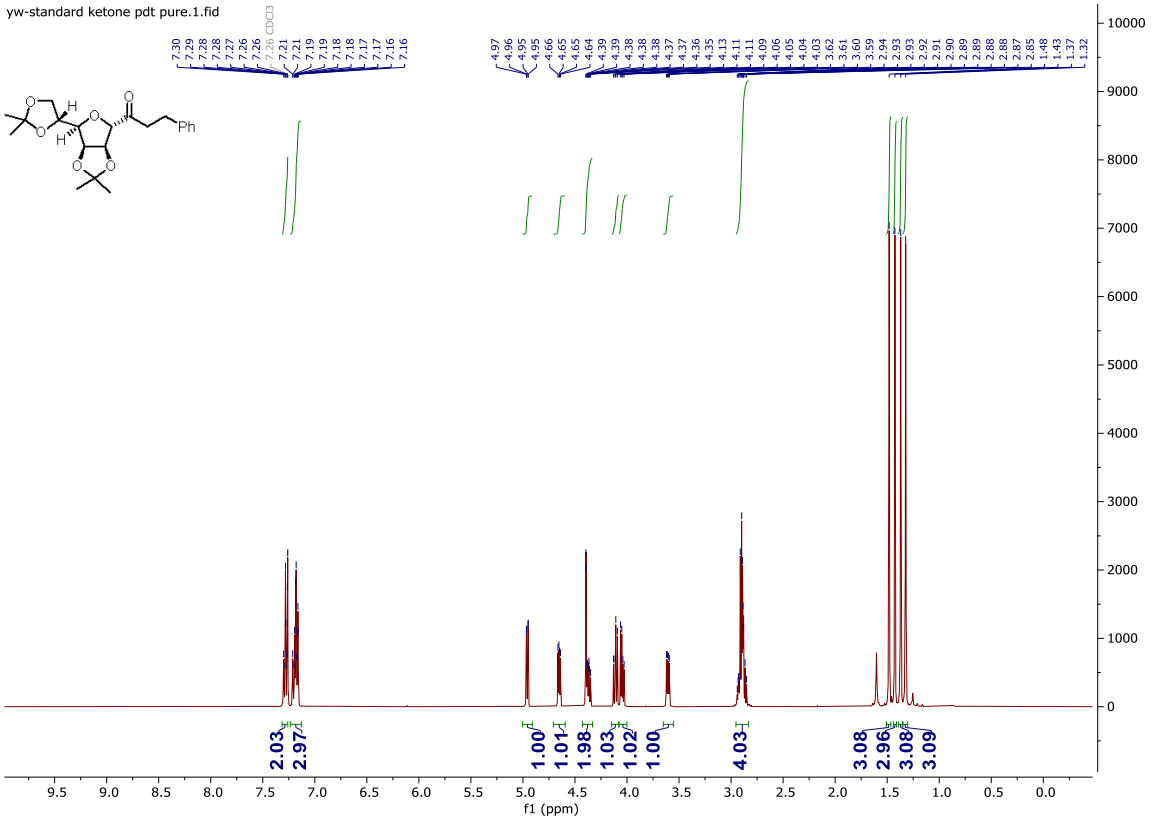
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **8**



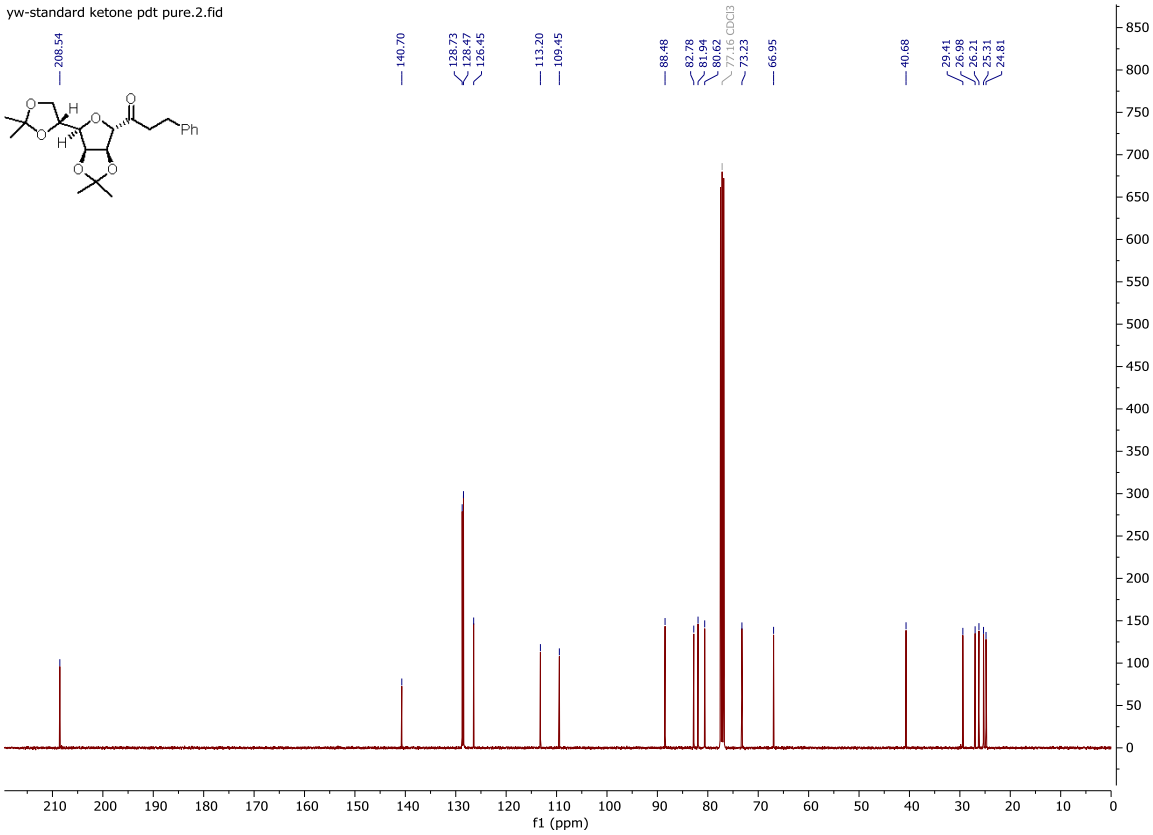
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9**



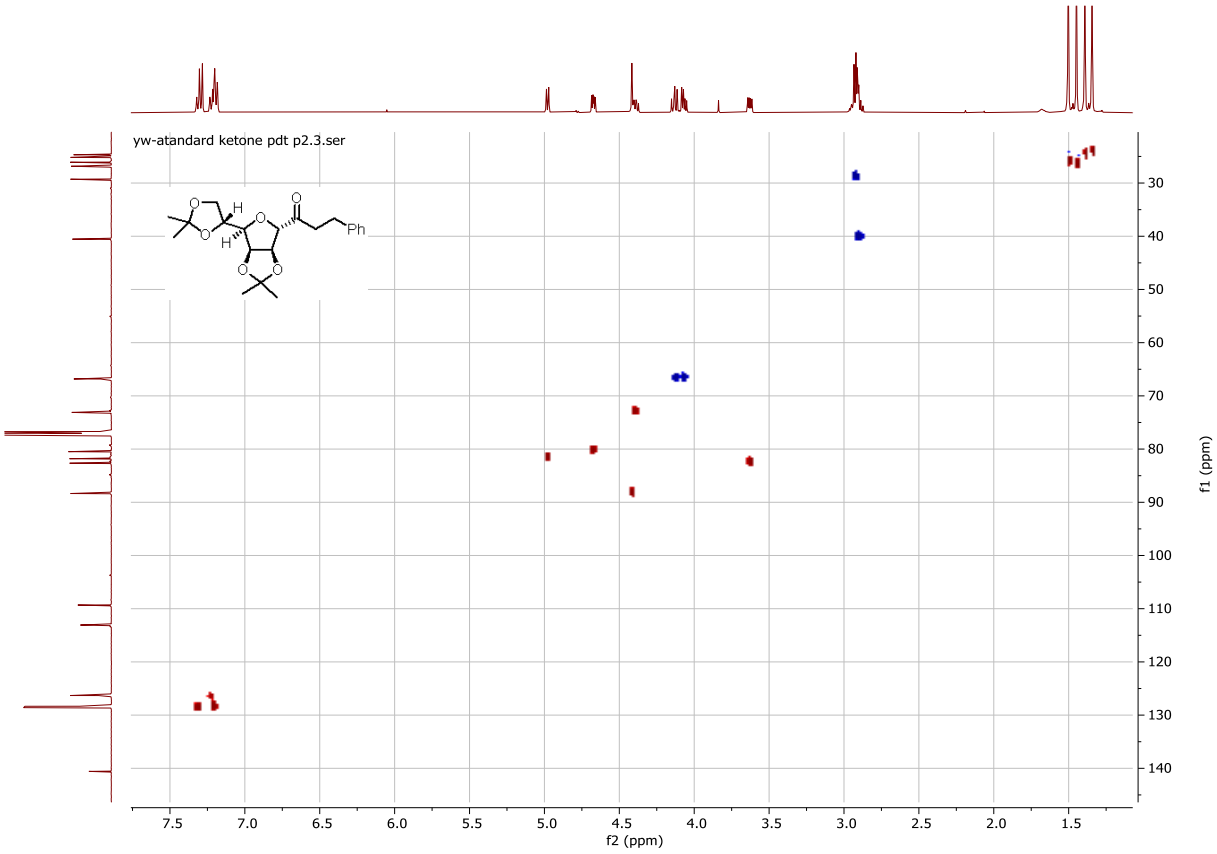
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **9**



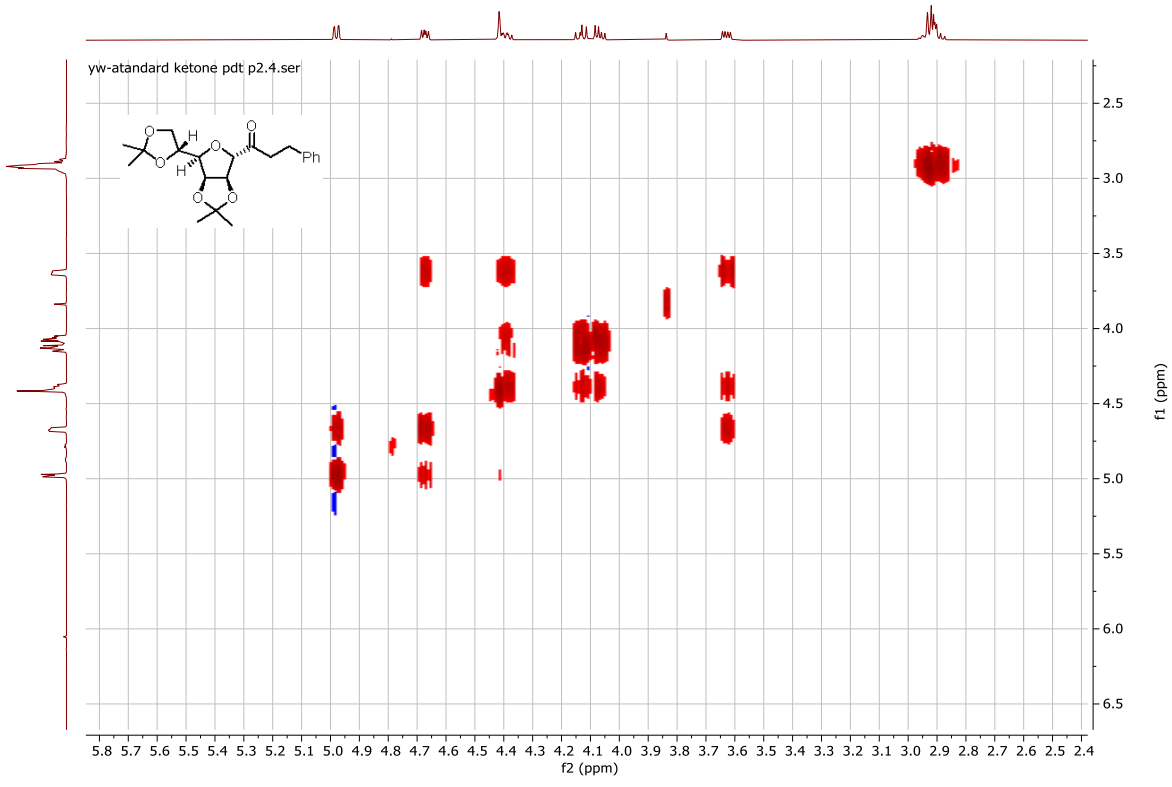
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **10**



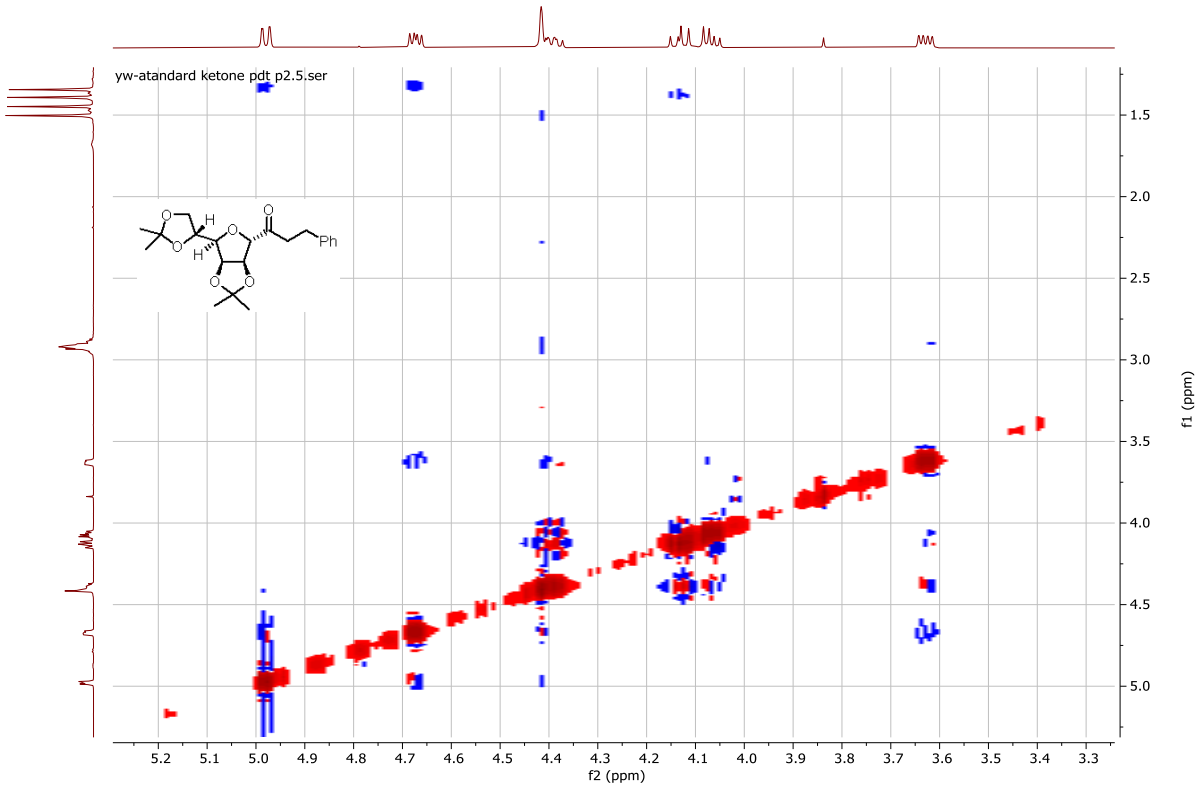
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **10**



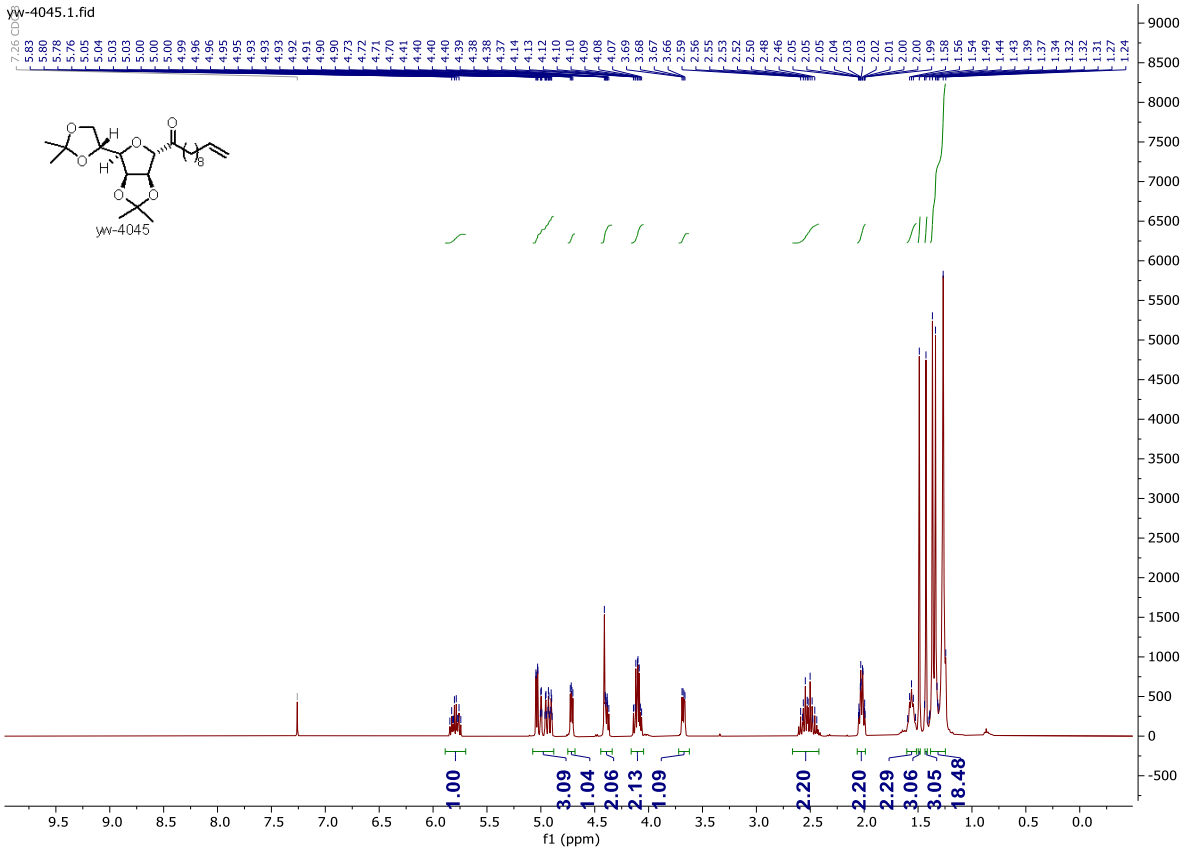
HSQCED of **10**



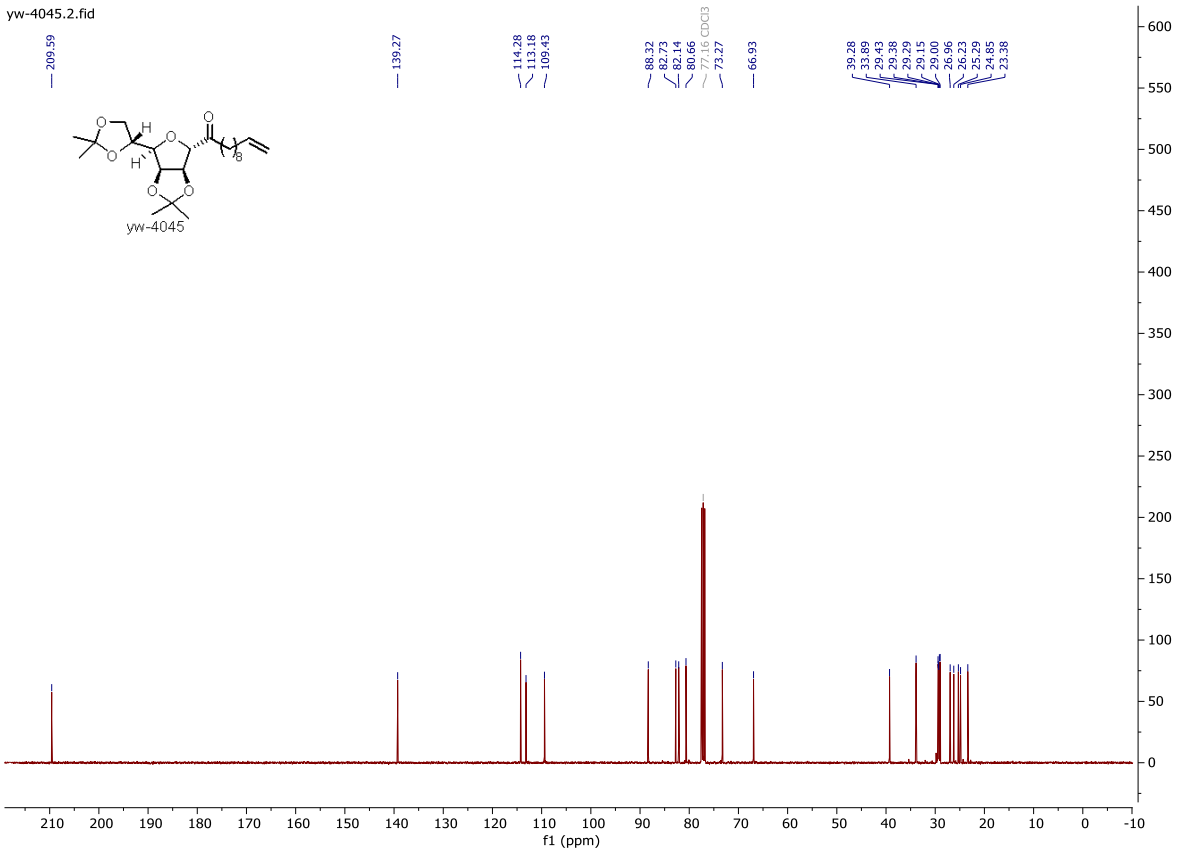
H-H COSY of **10**



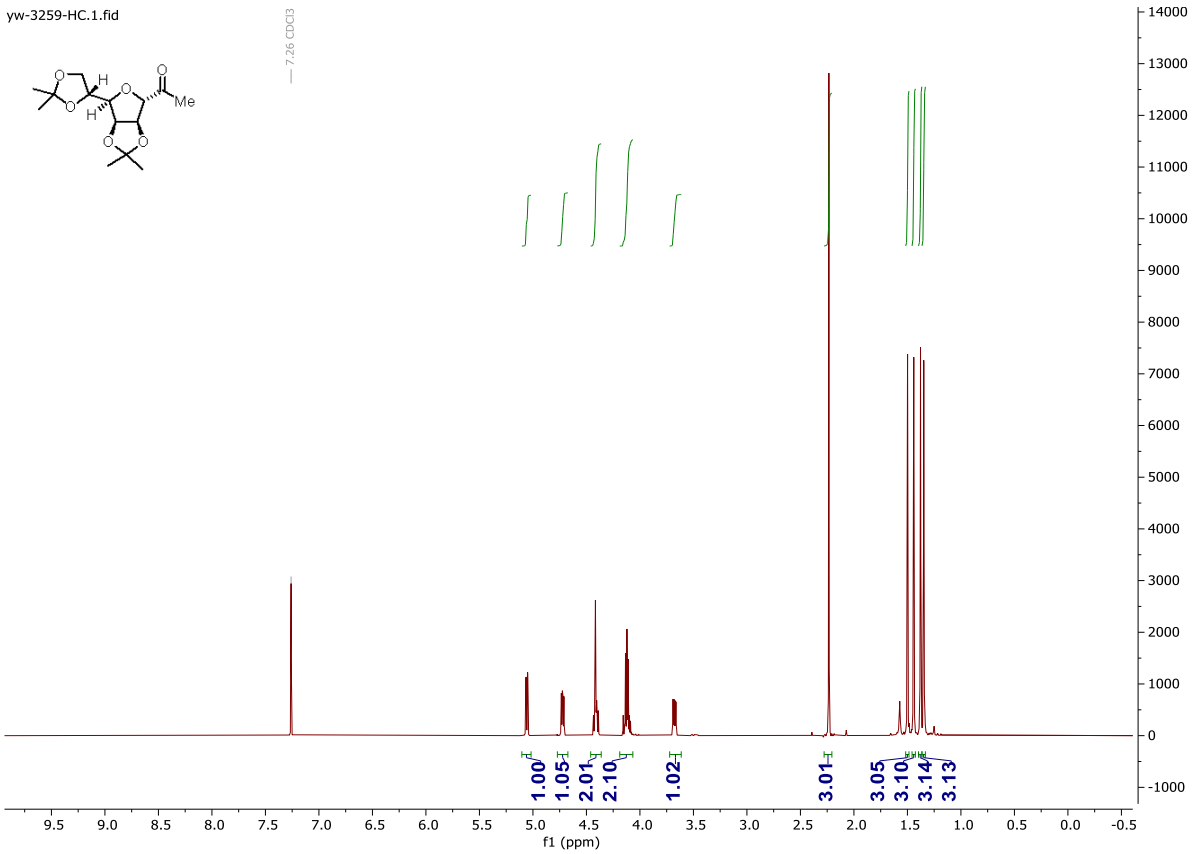
NOESY of **10**



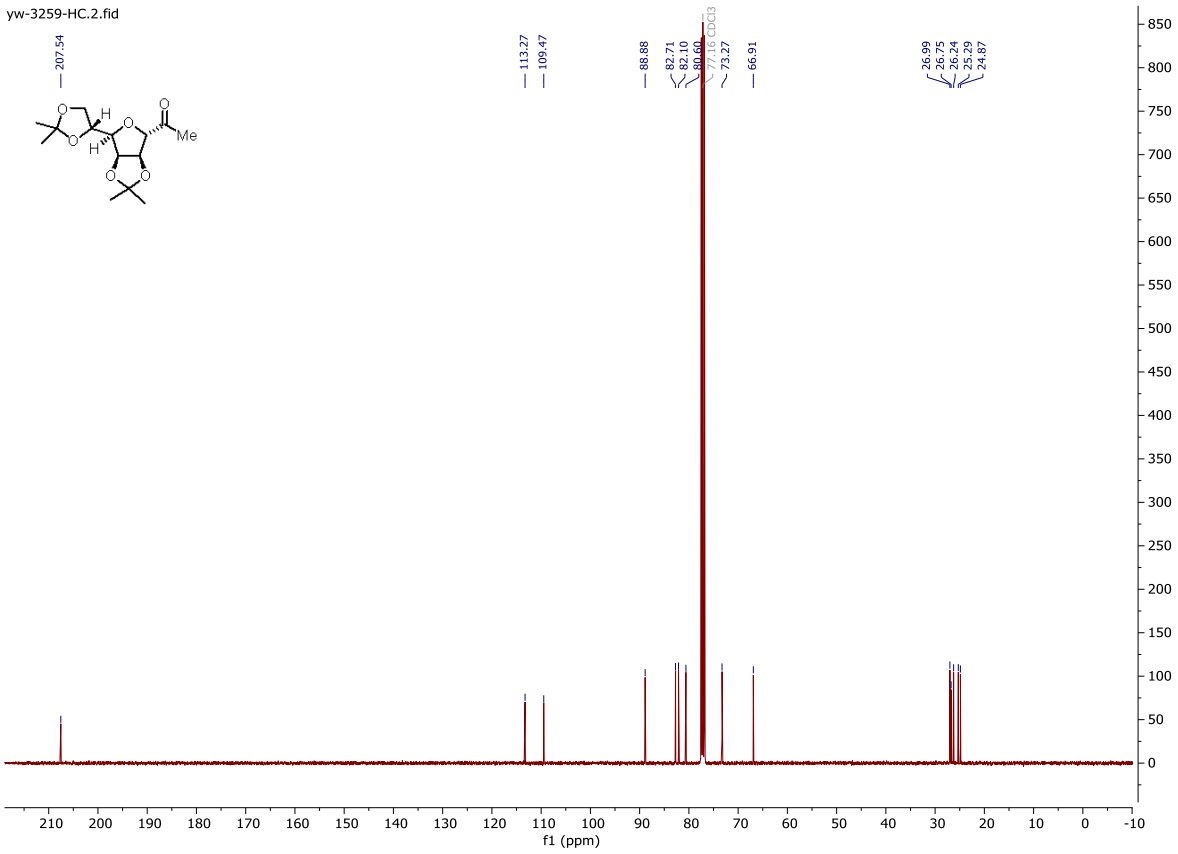
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **11**



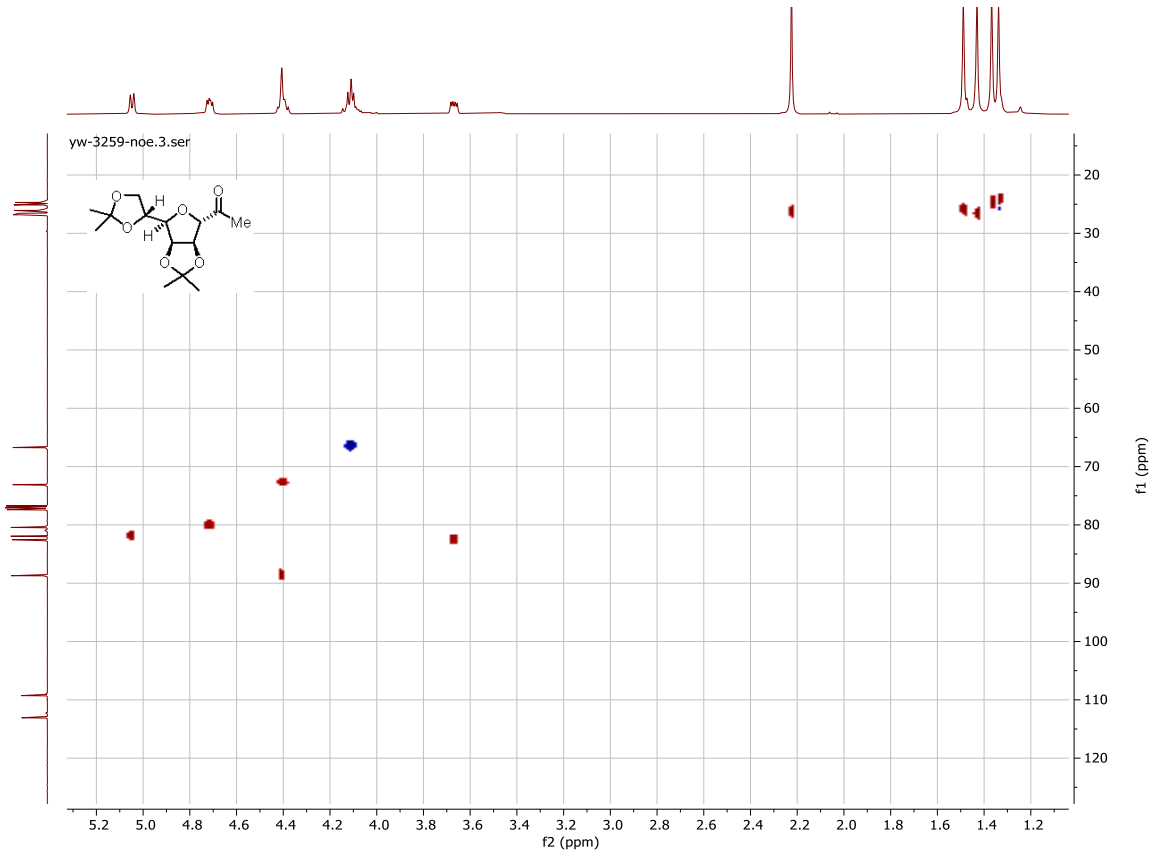
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **11**



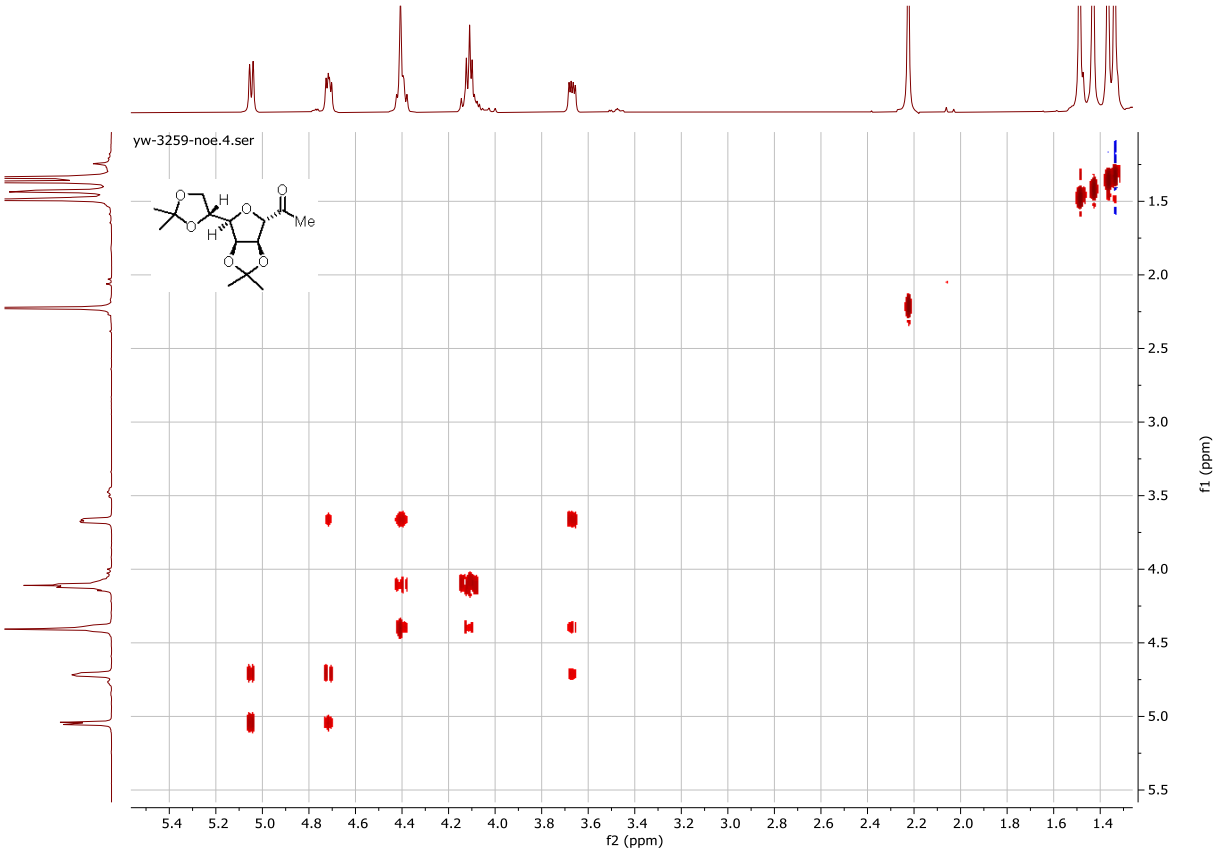
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **12**



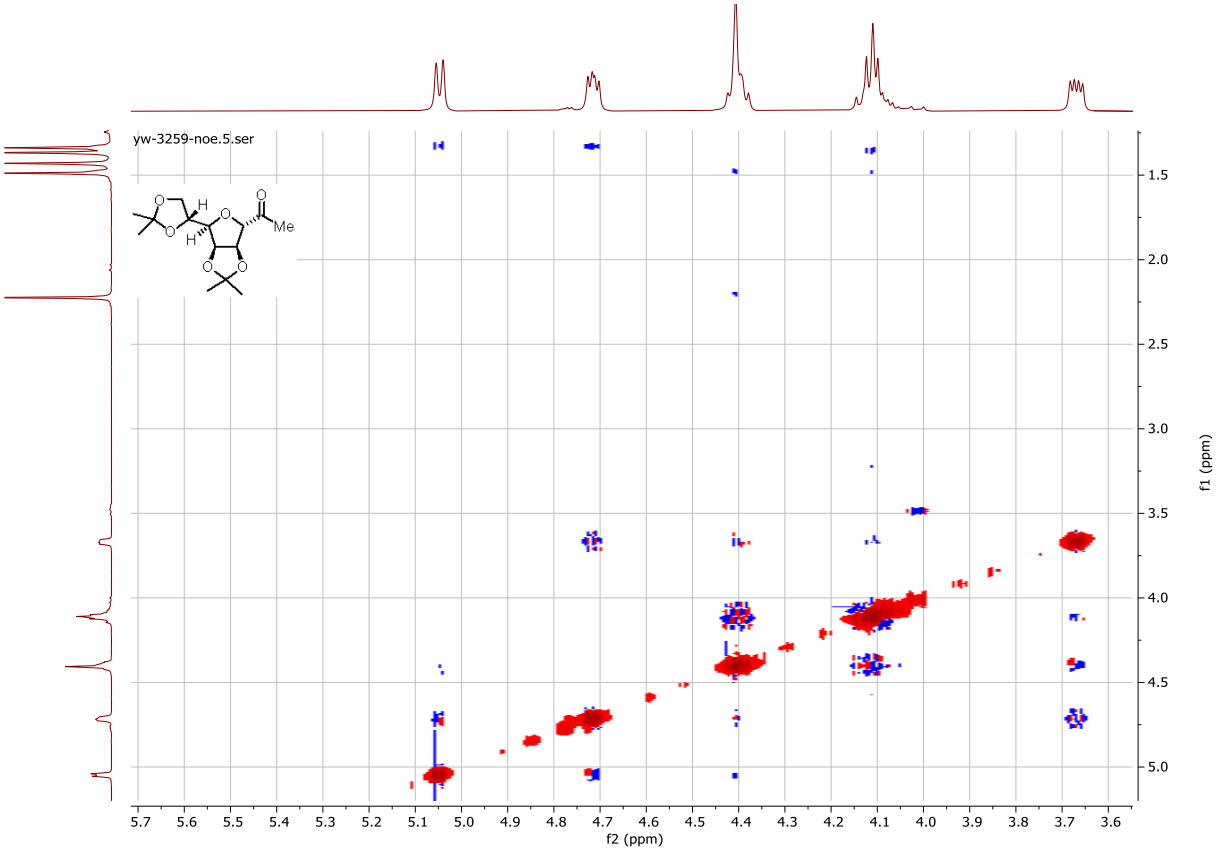
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **12**



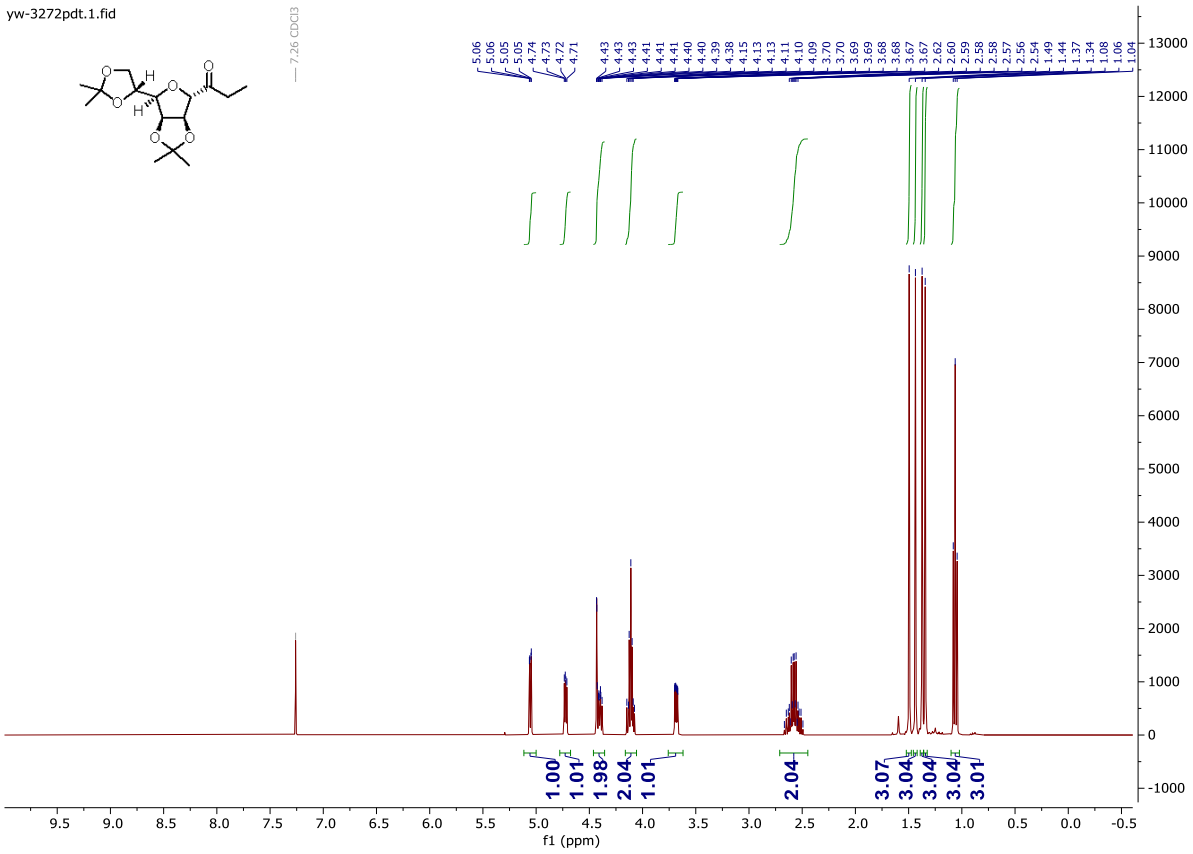
HSQCED of **12**



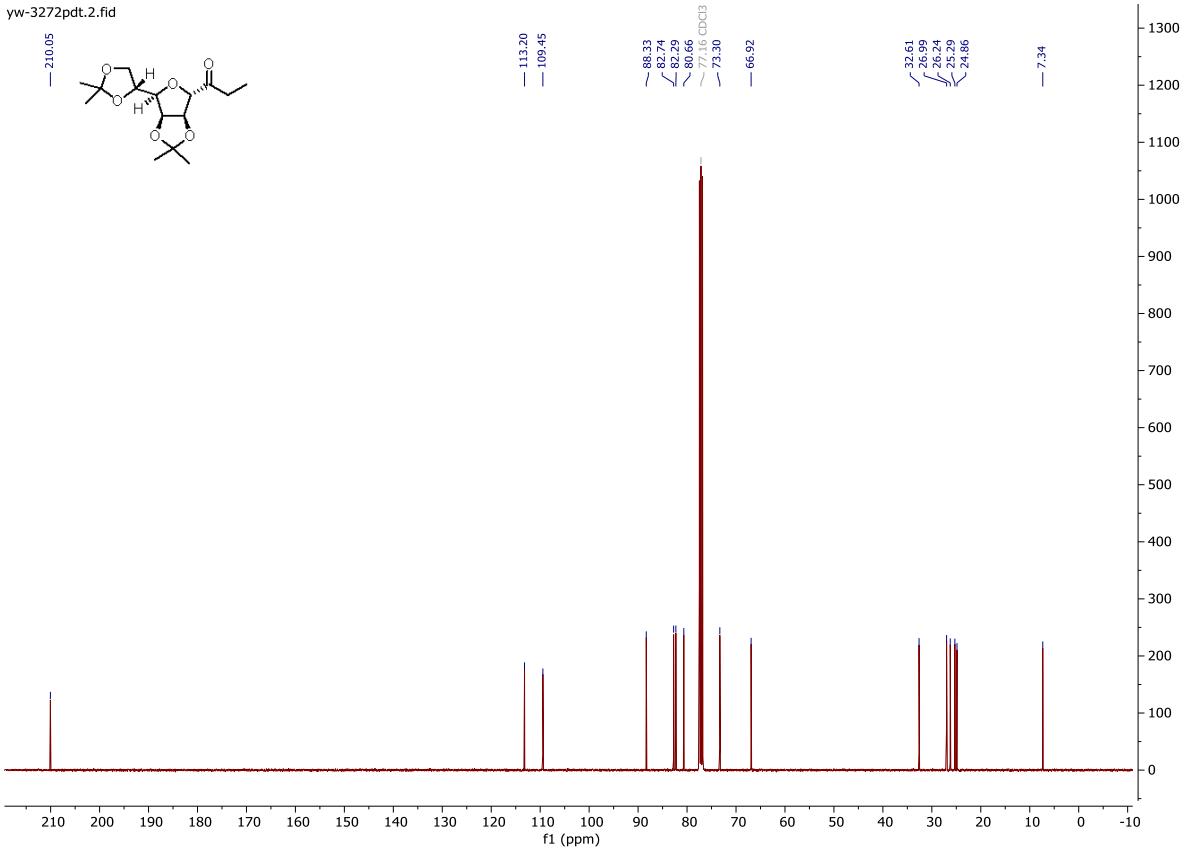
H-H COSY of **12**



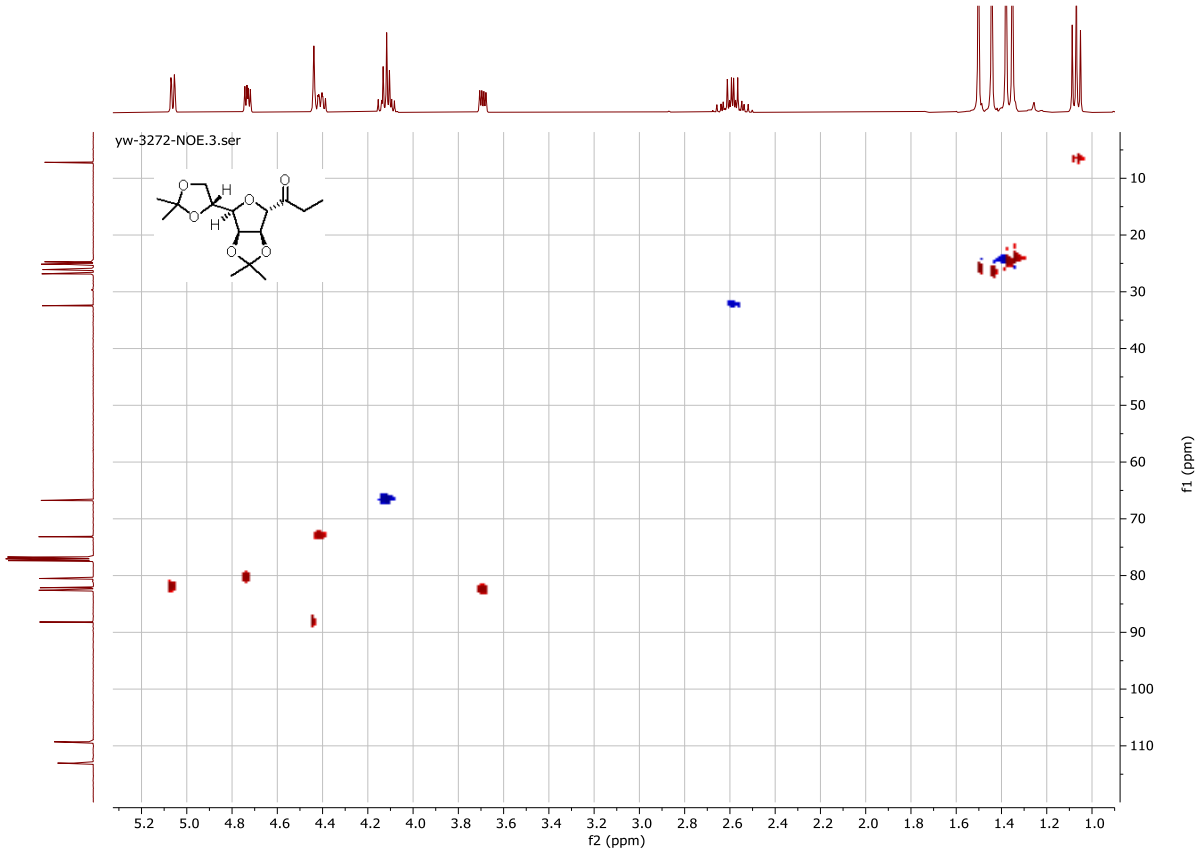
NOESY of **12**



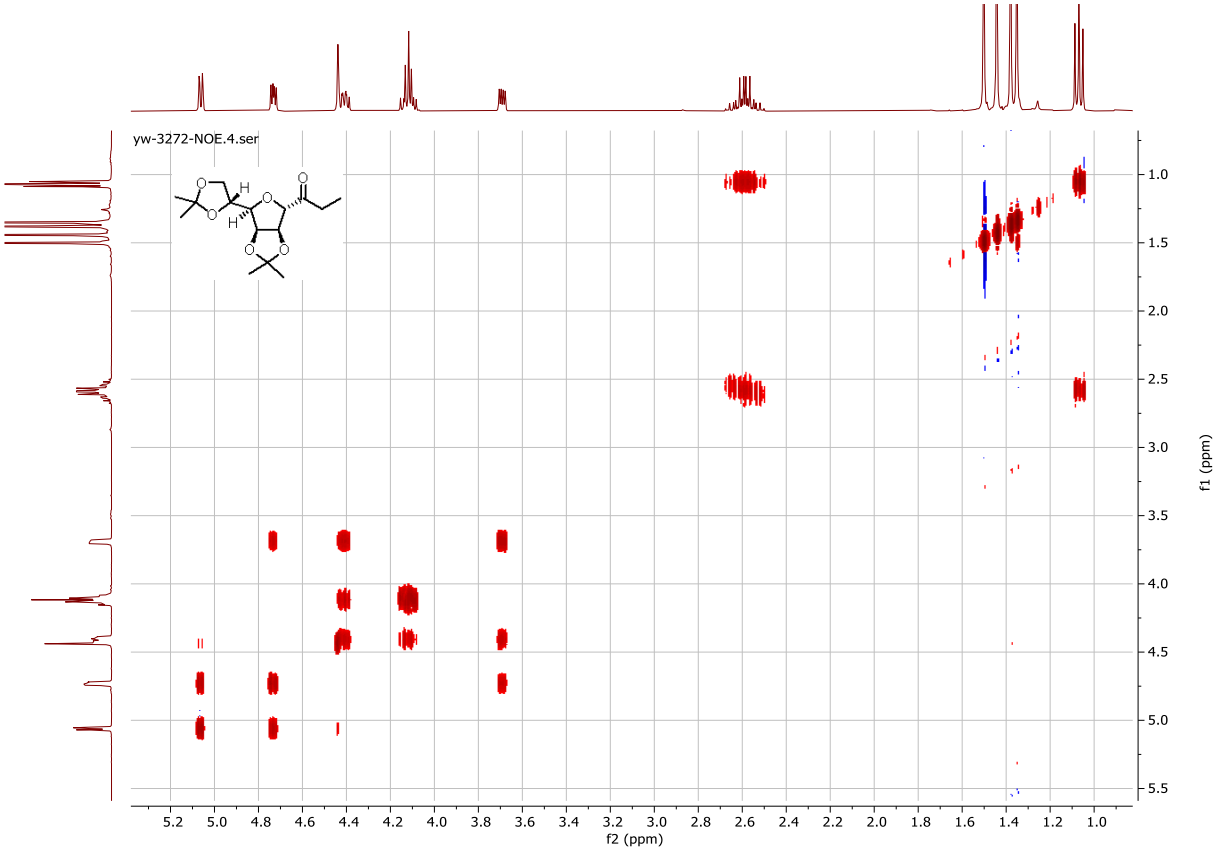
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **13**



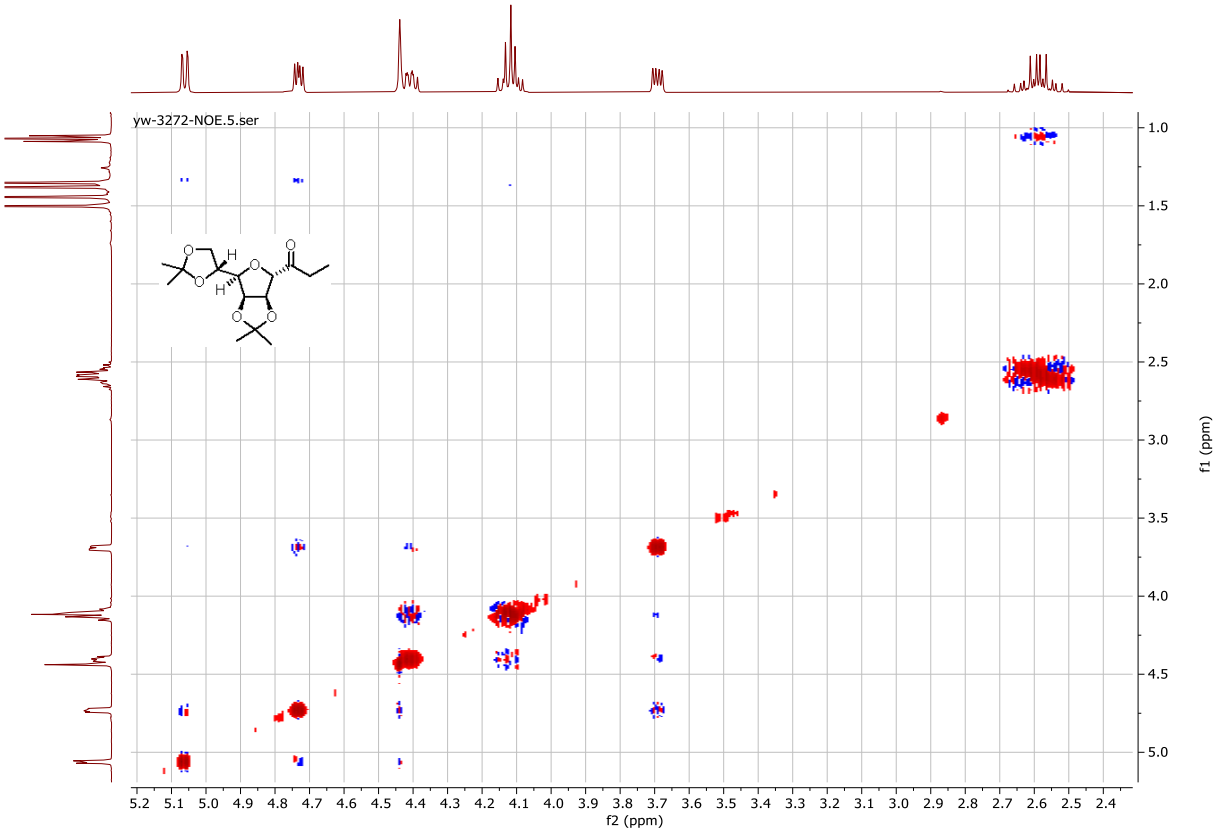
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **13**



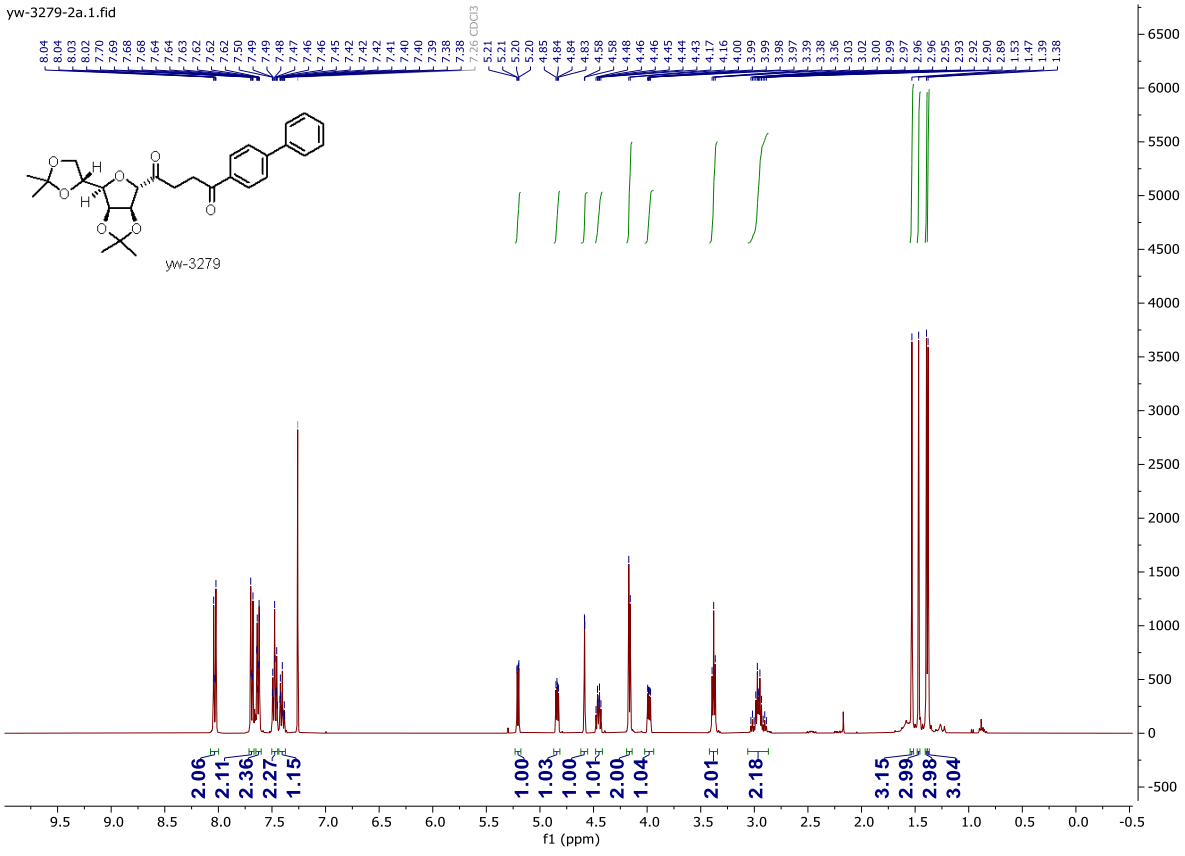
HSQCED of **13**



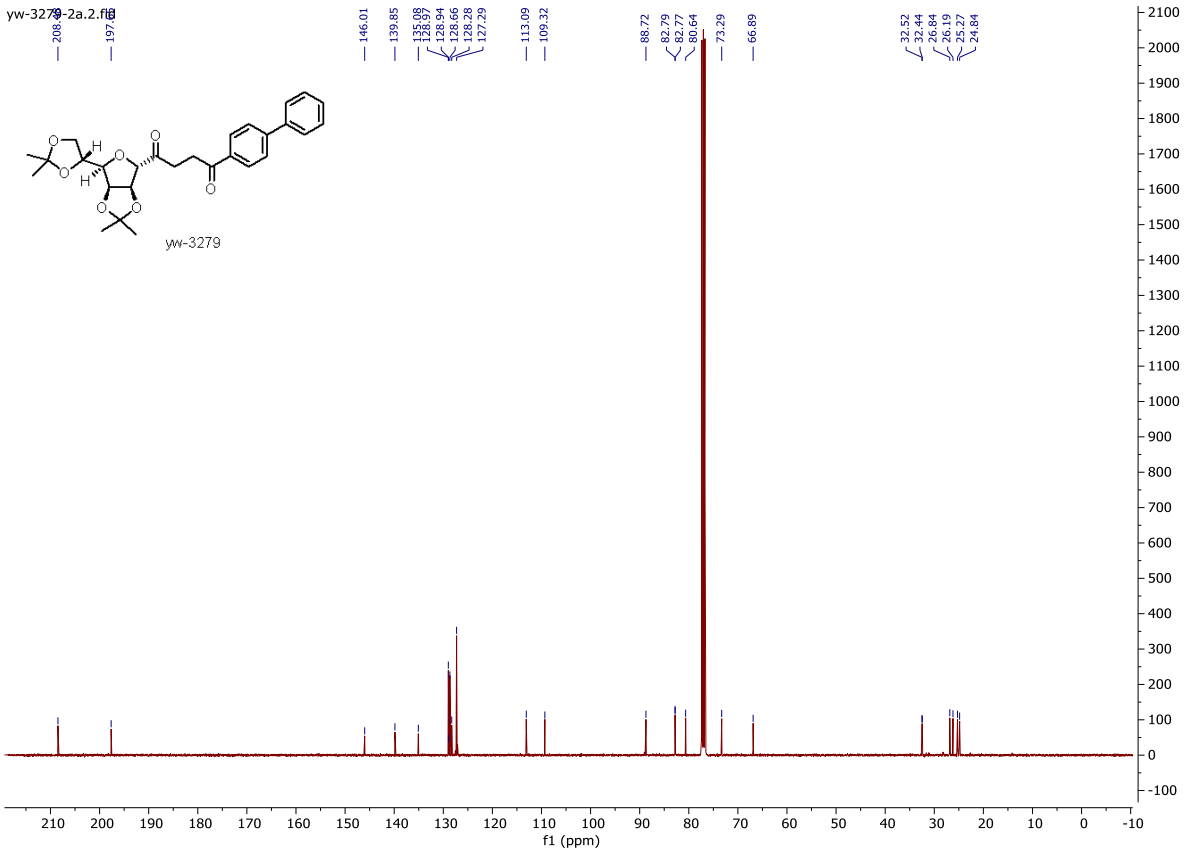
H-H COSY of **13**



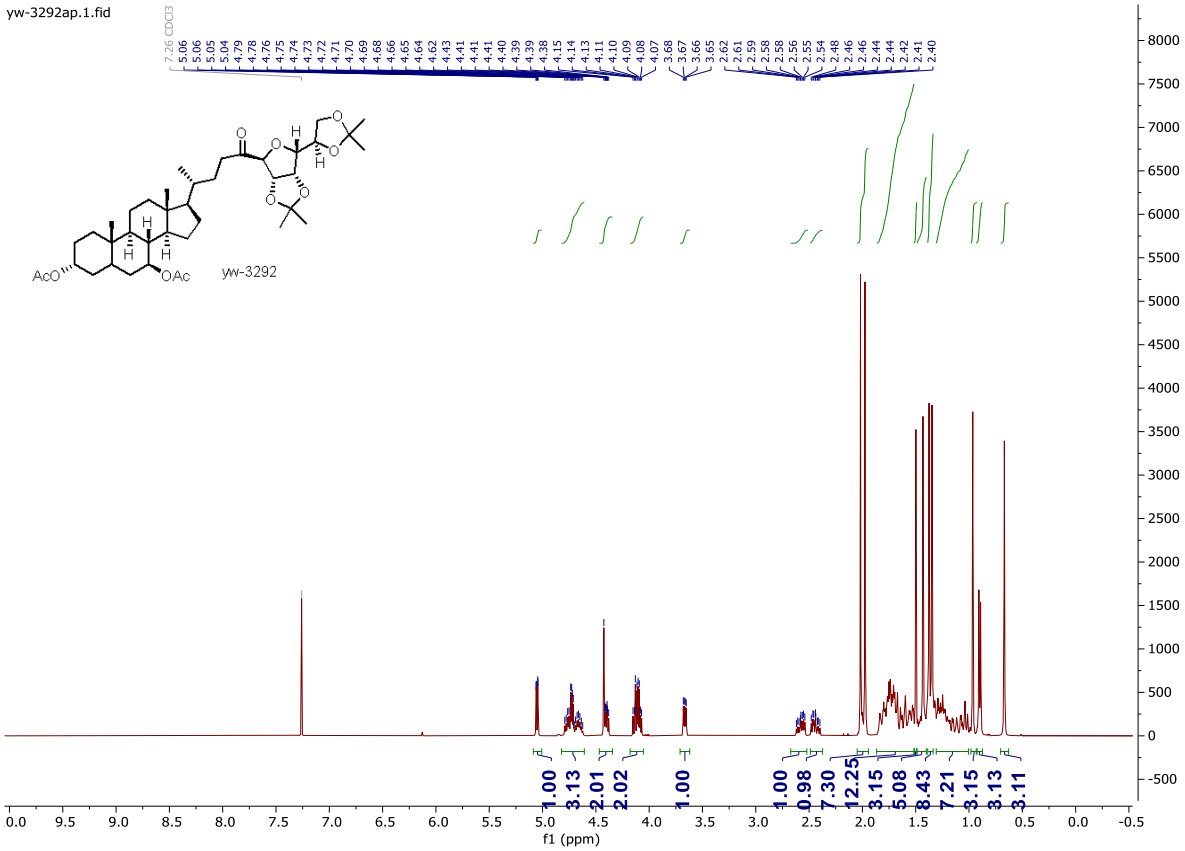
NOE of **13**



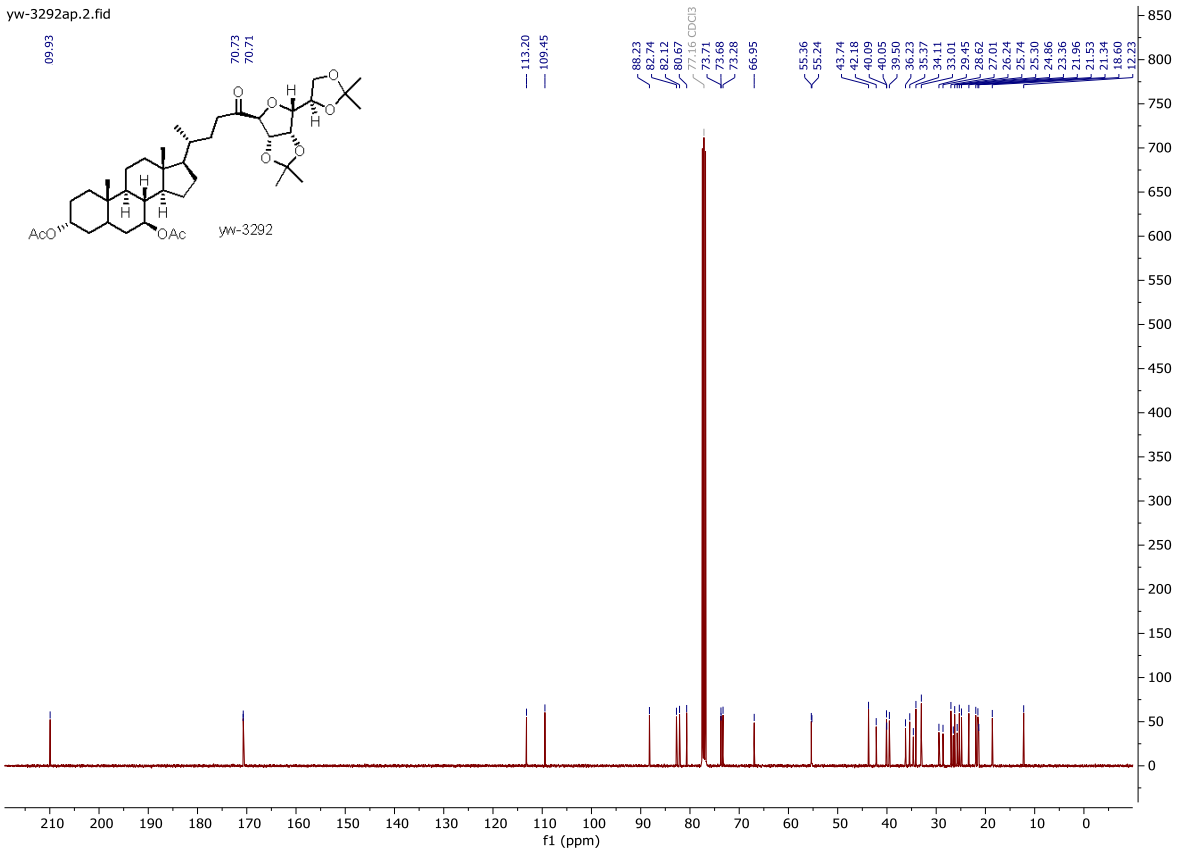
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14**



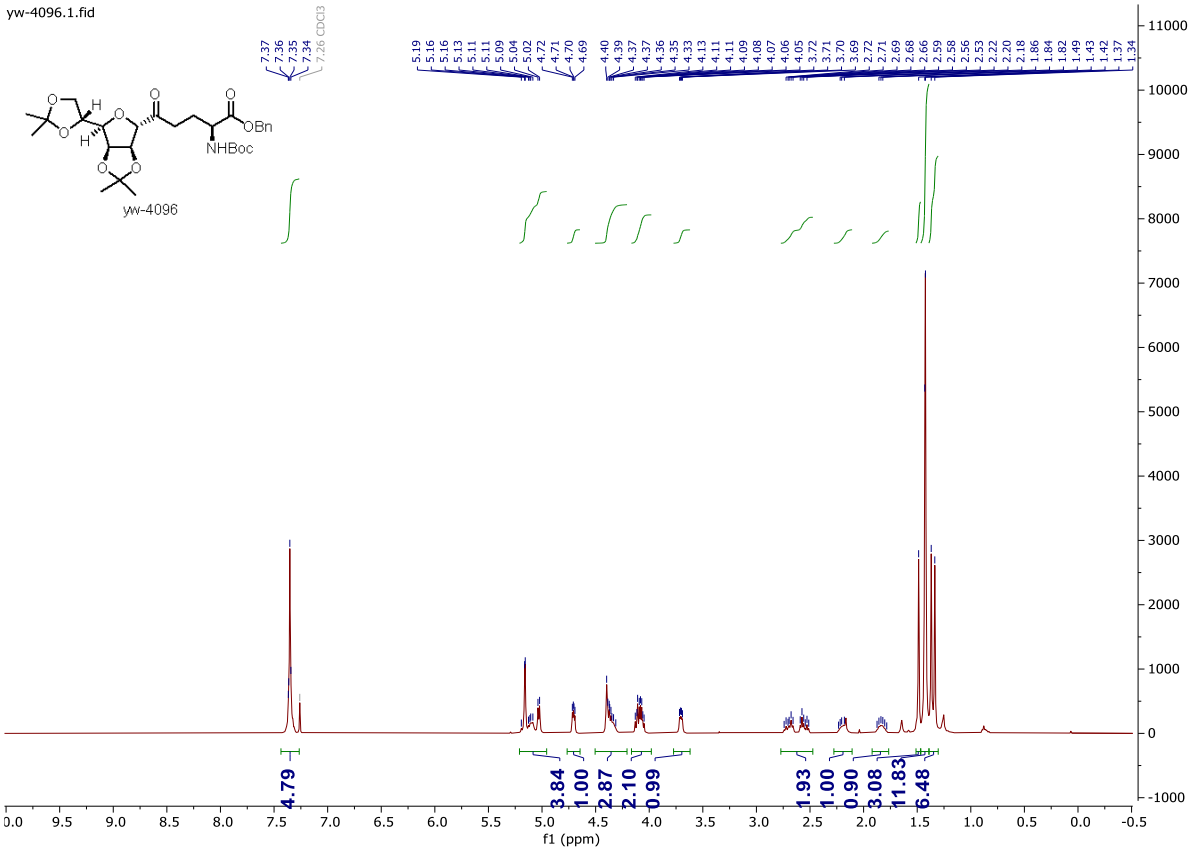
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **14**



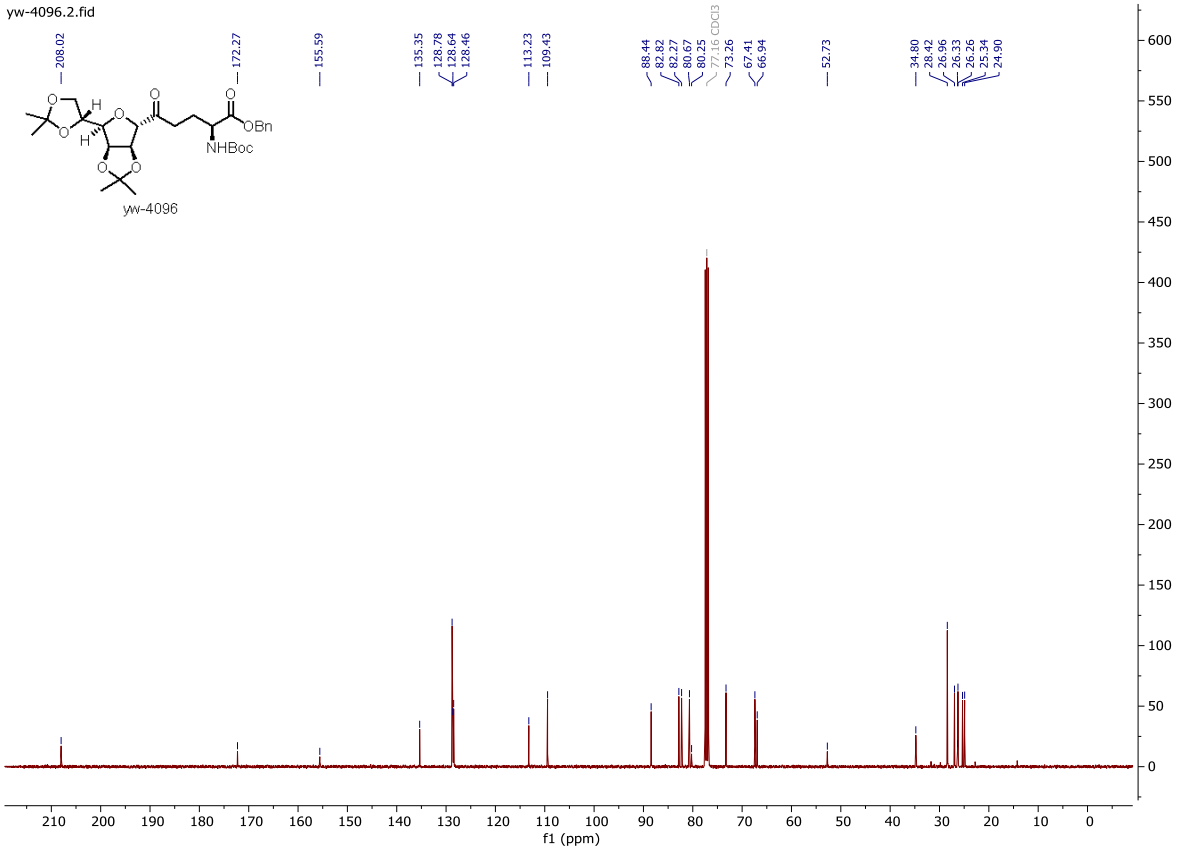
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **15**



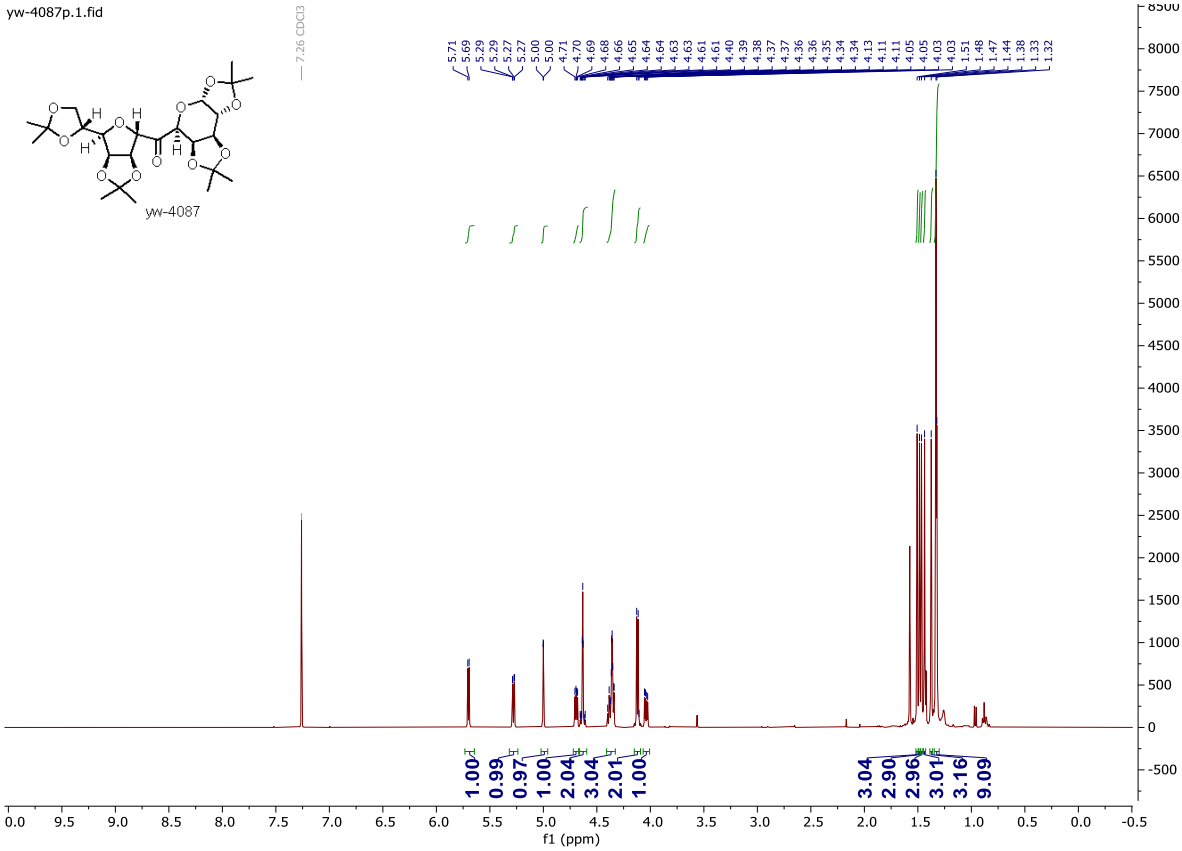
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **15**



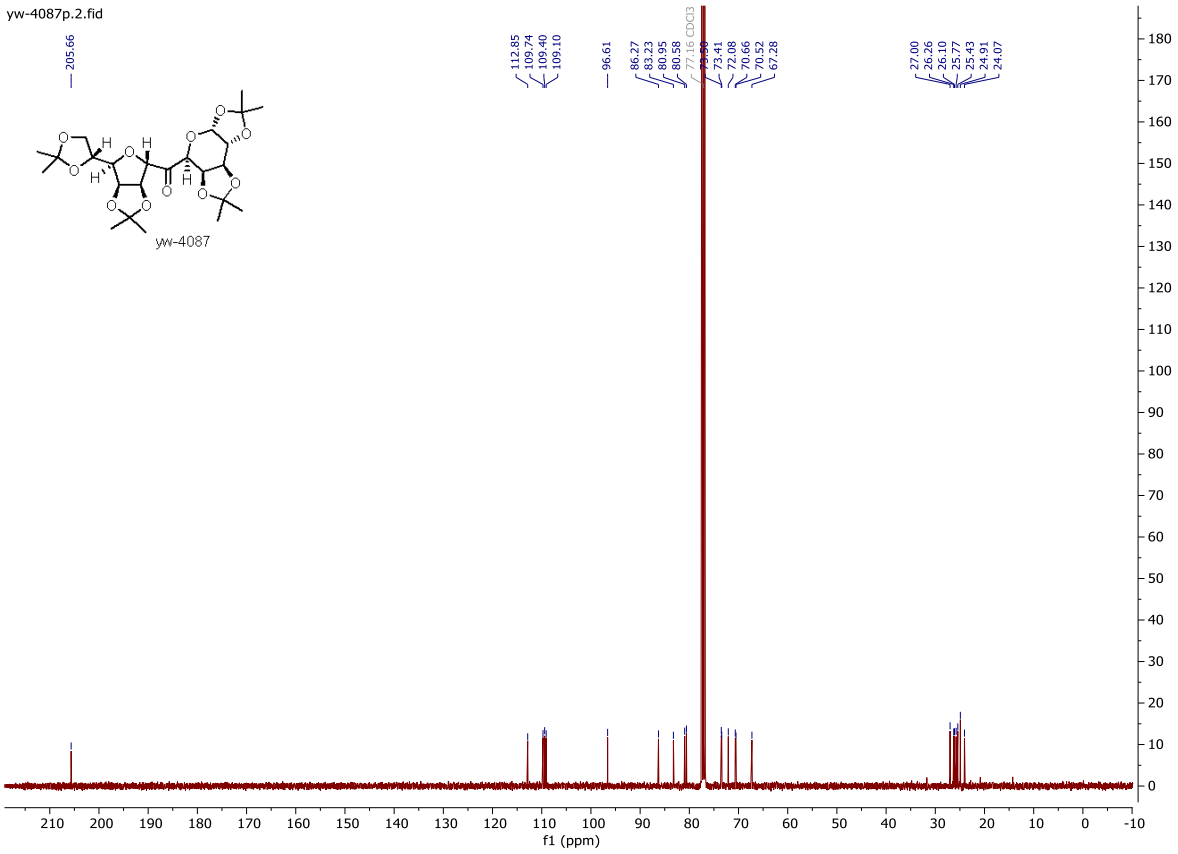
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **16**



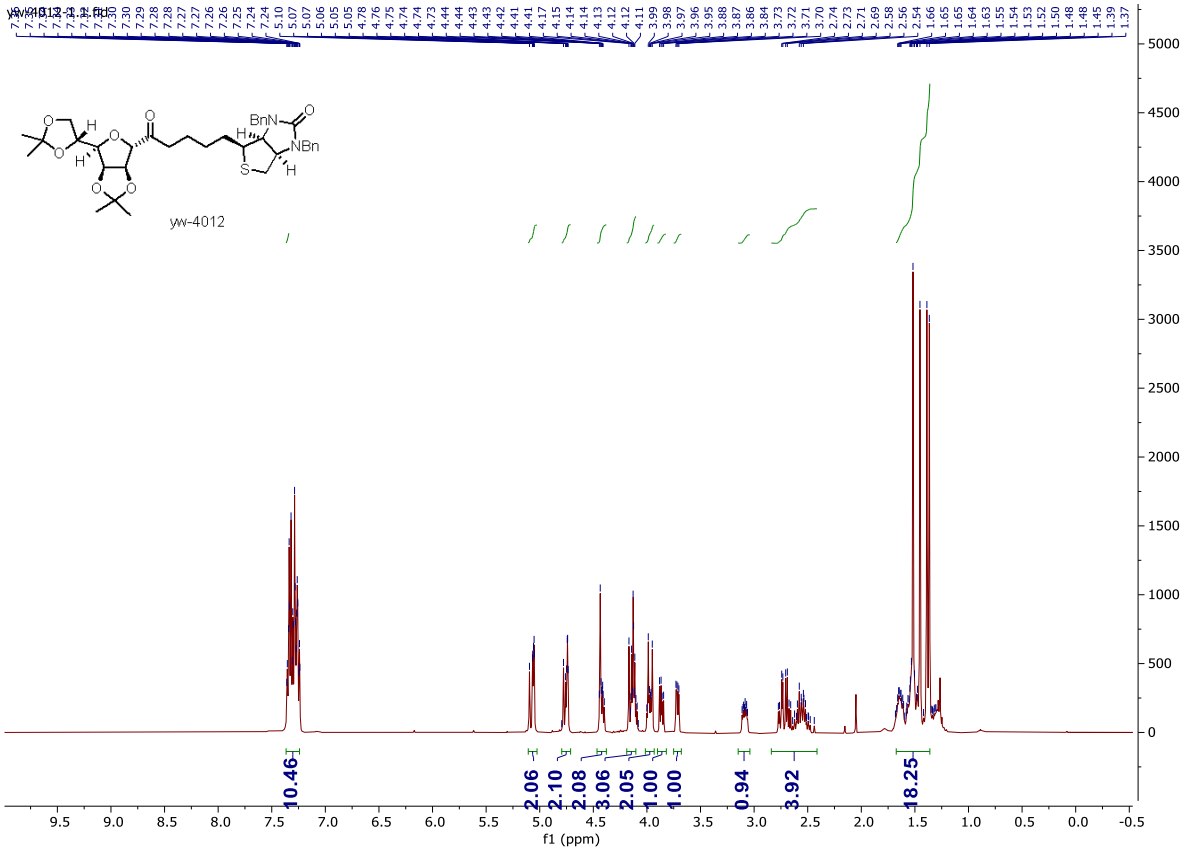
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **16**



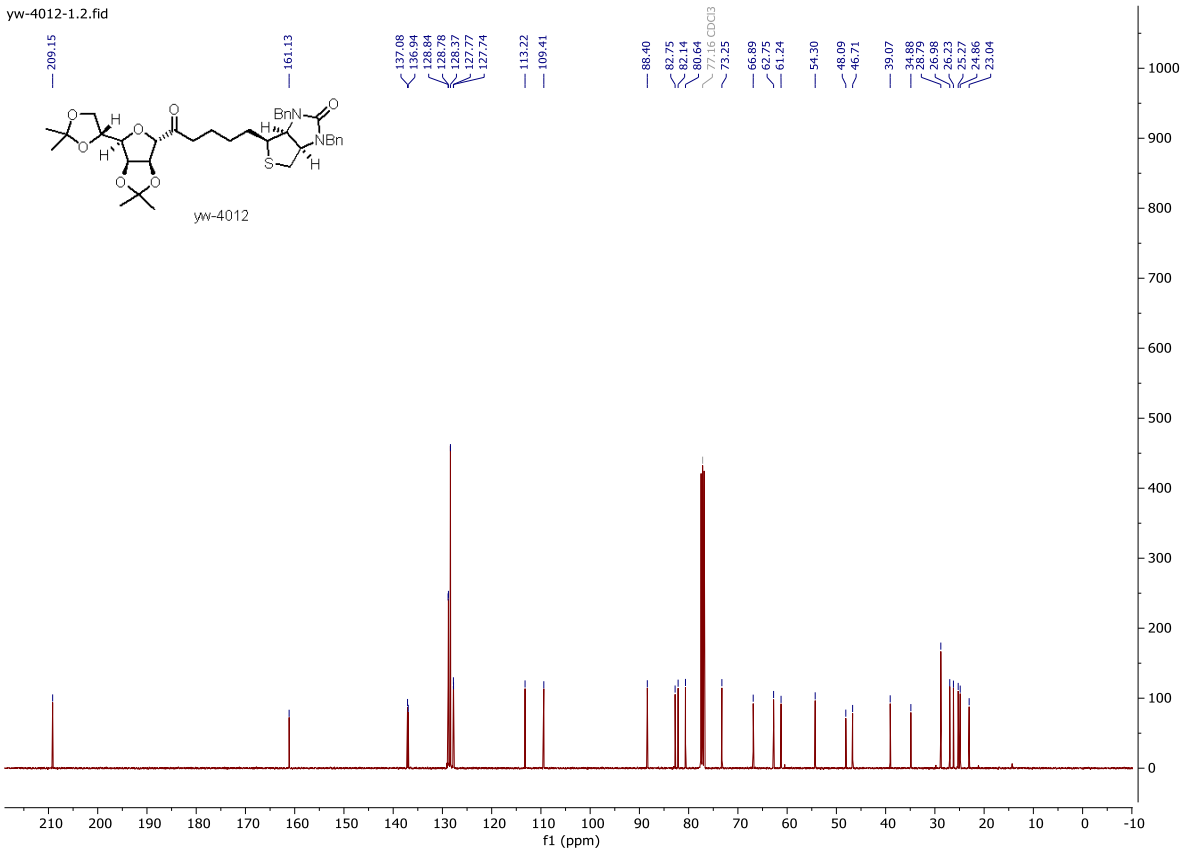
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **17**



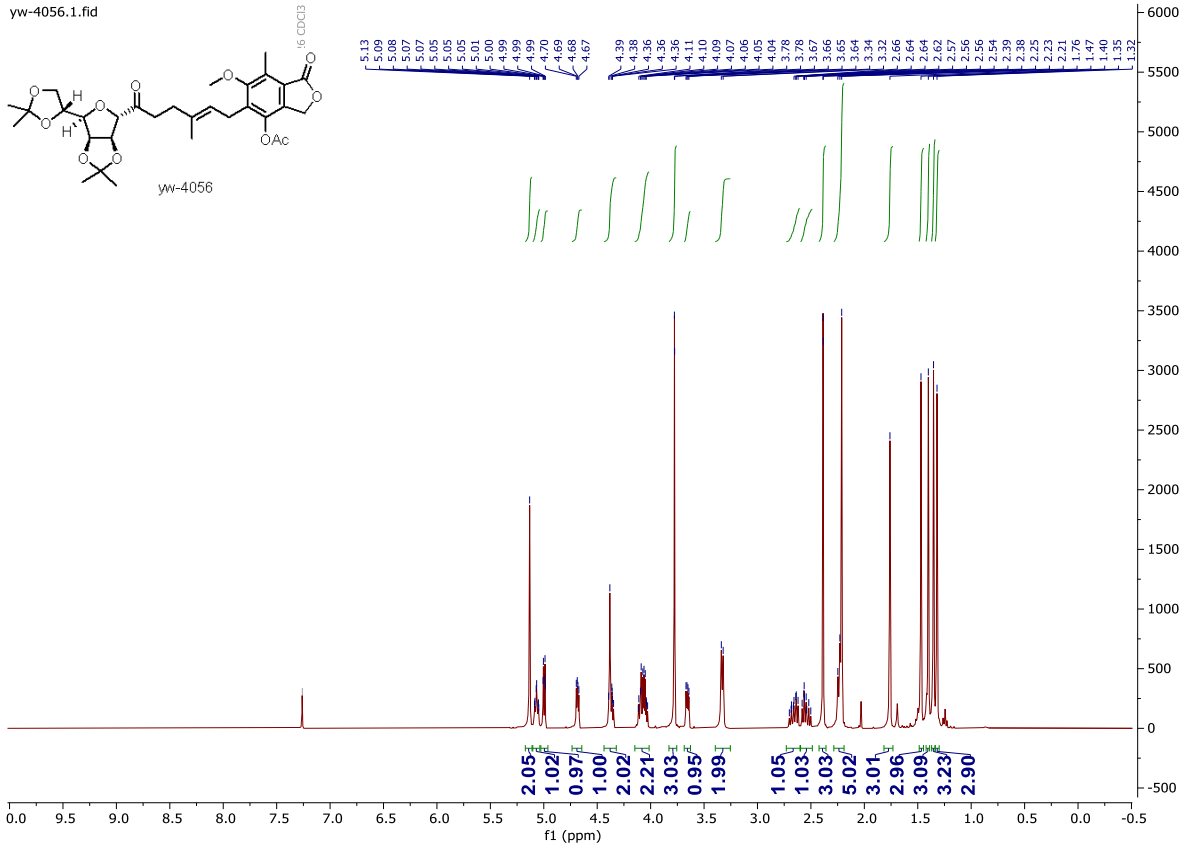
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **17**



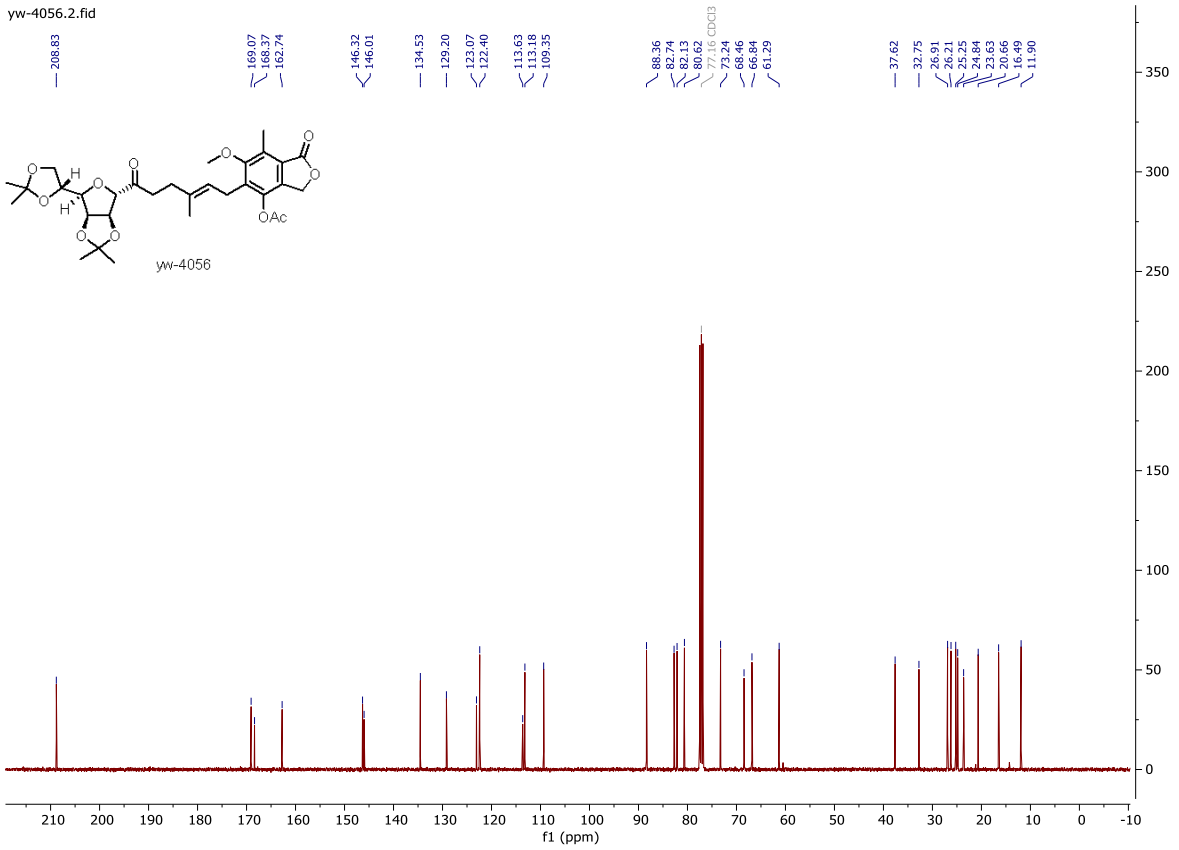
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **18**



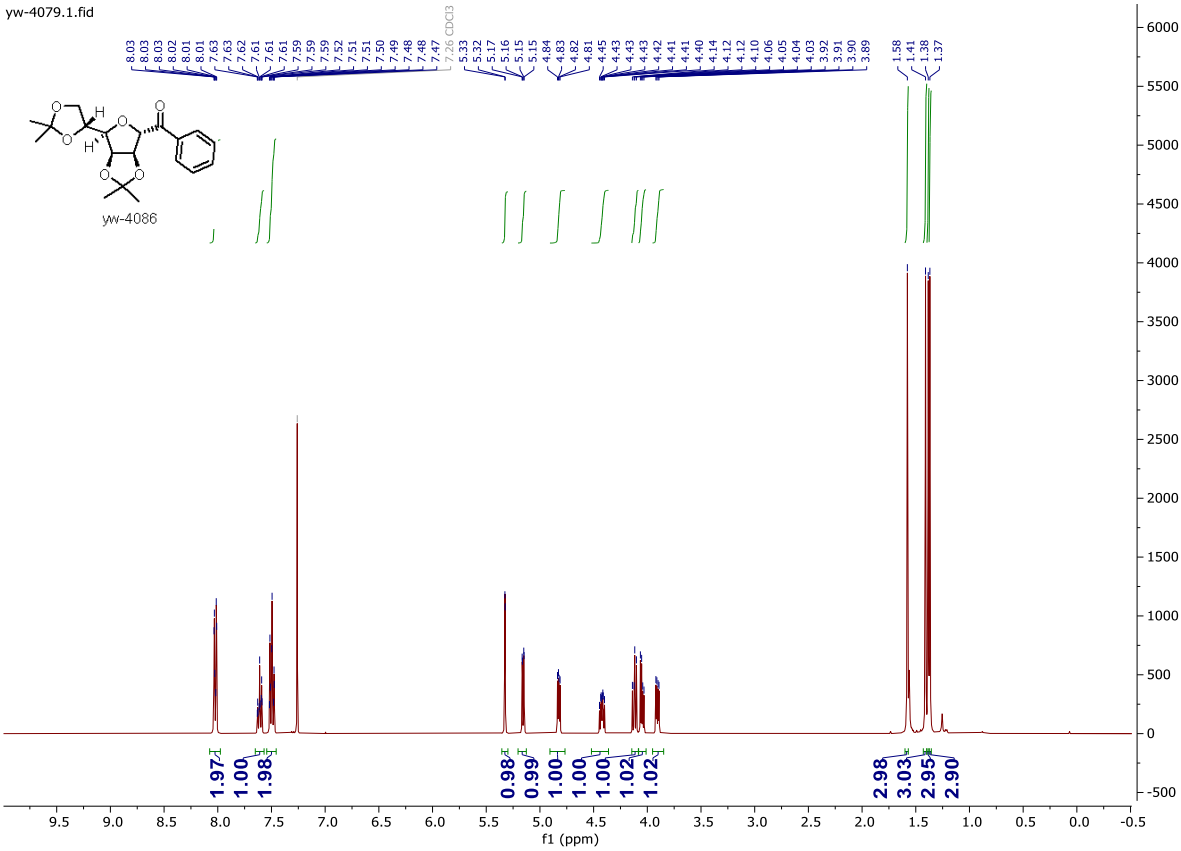
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **18**



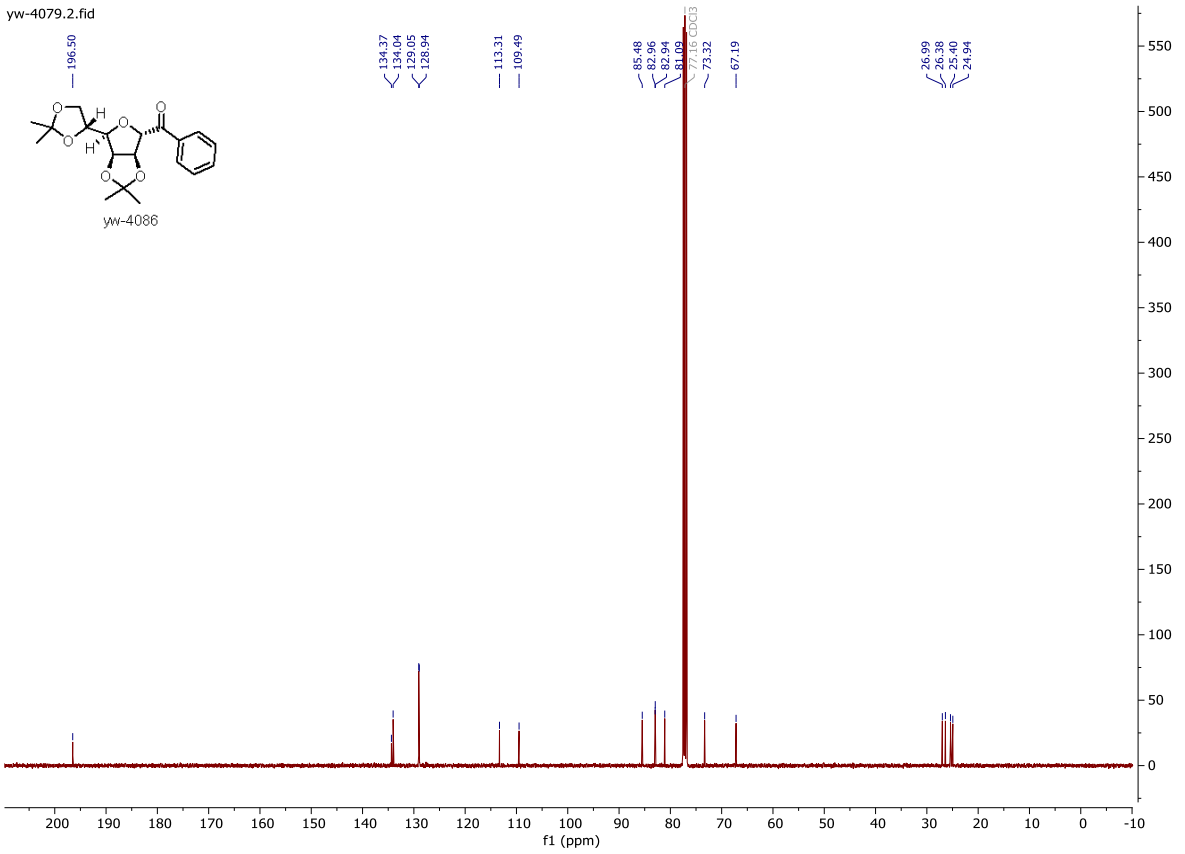
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **19**



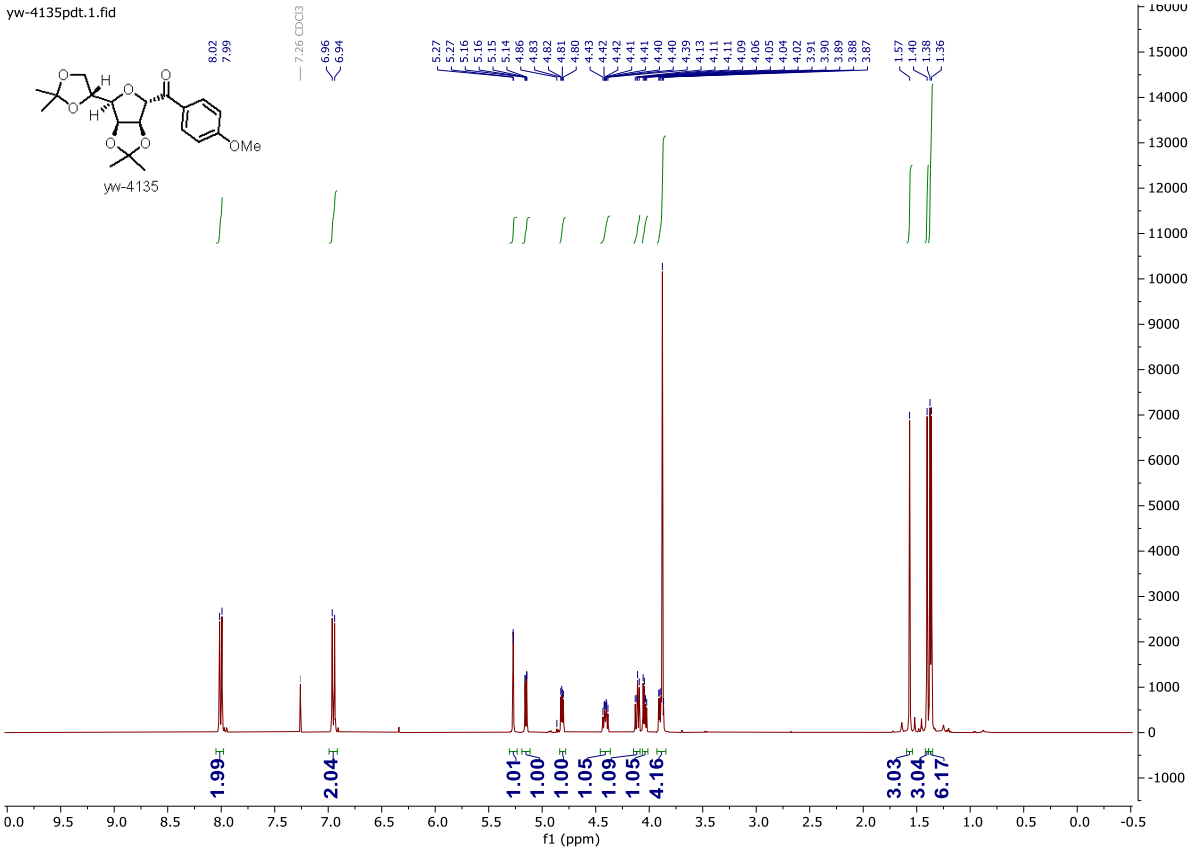
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **19**



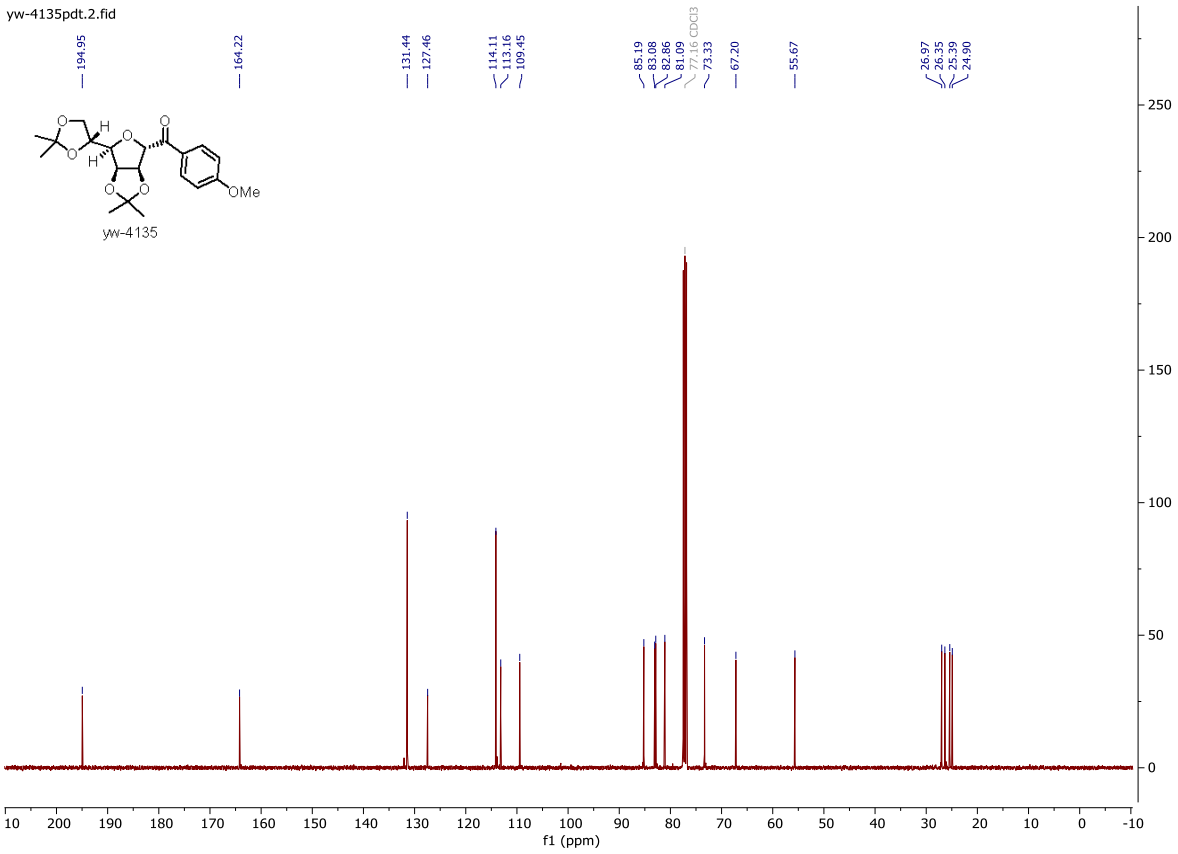
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **20**



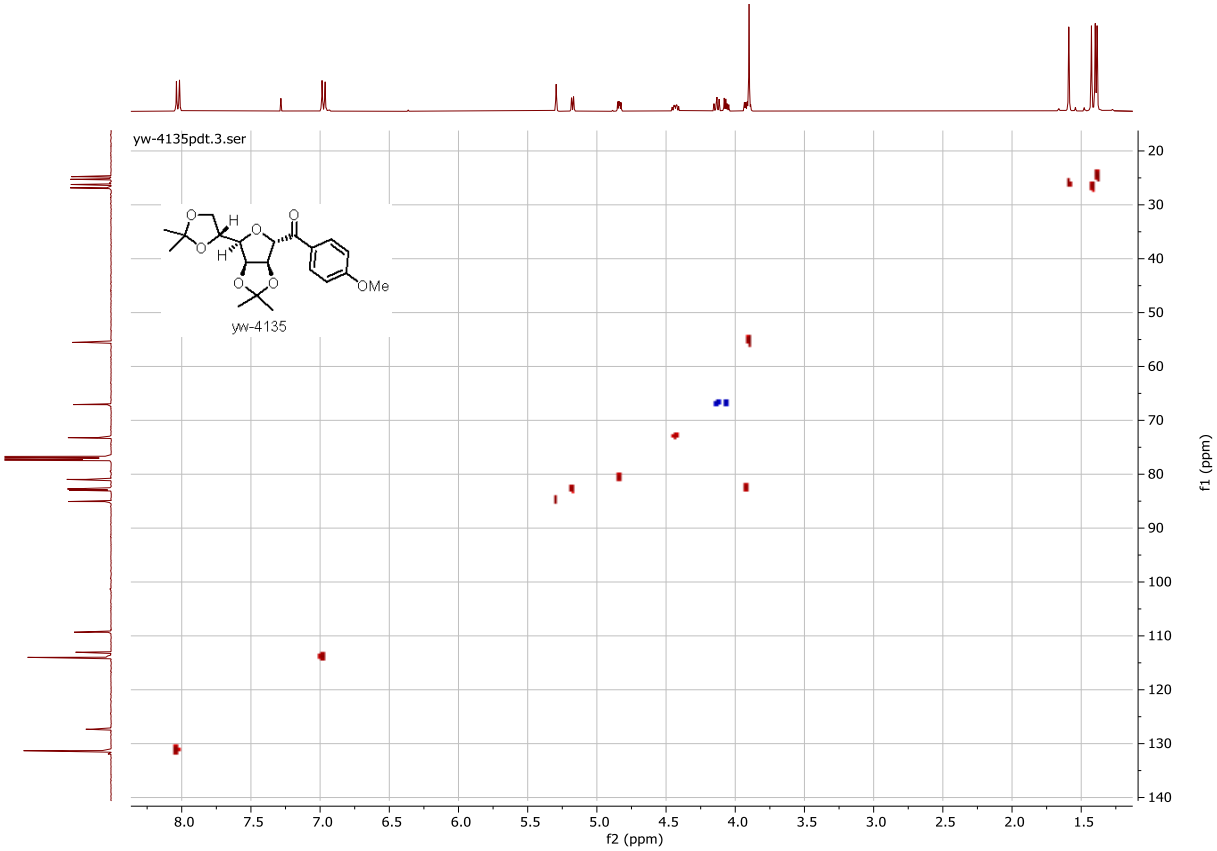
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **20**



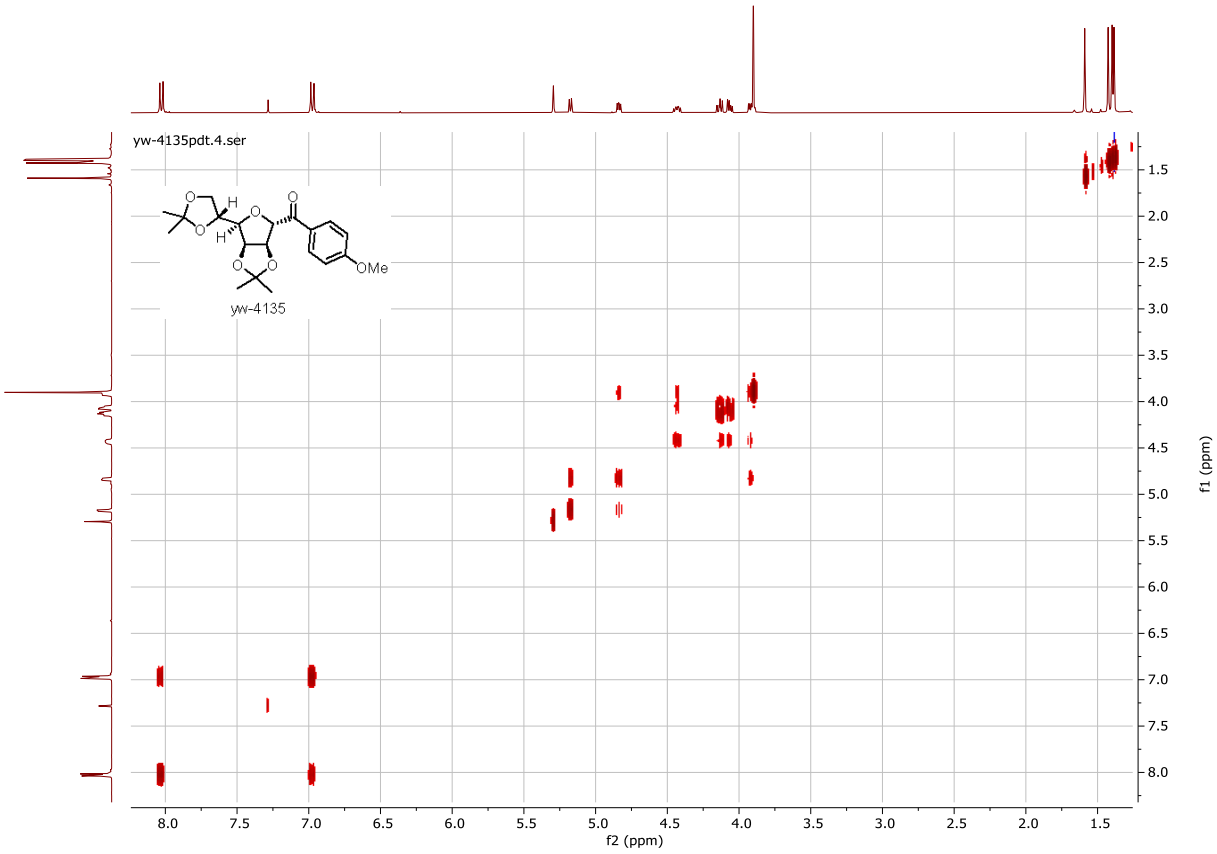
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **21**



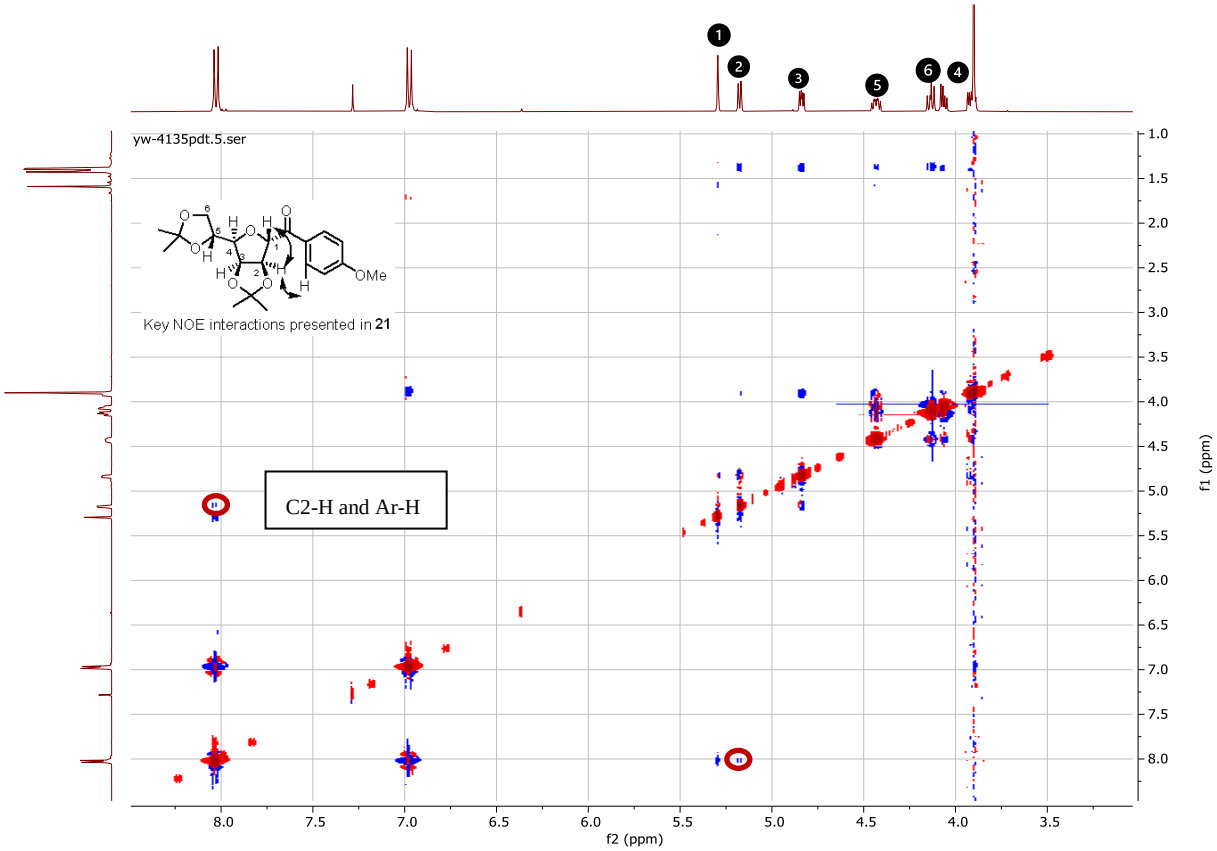
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **21**



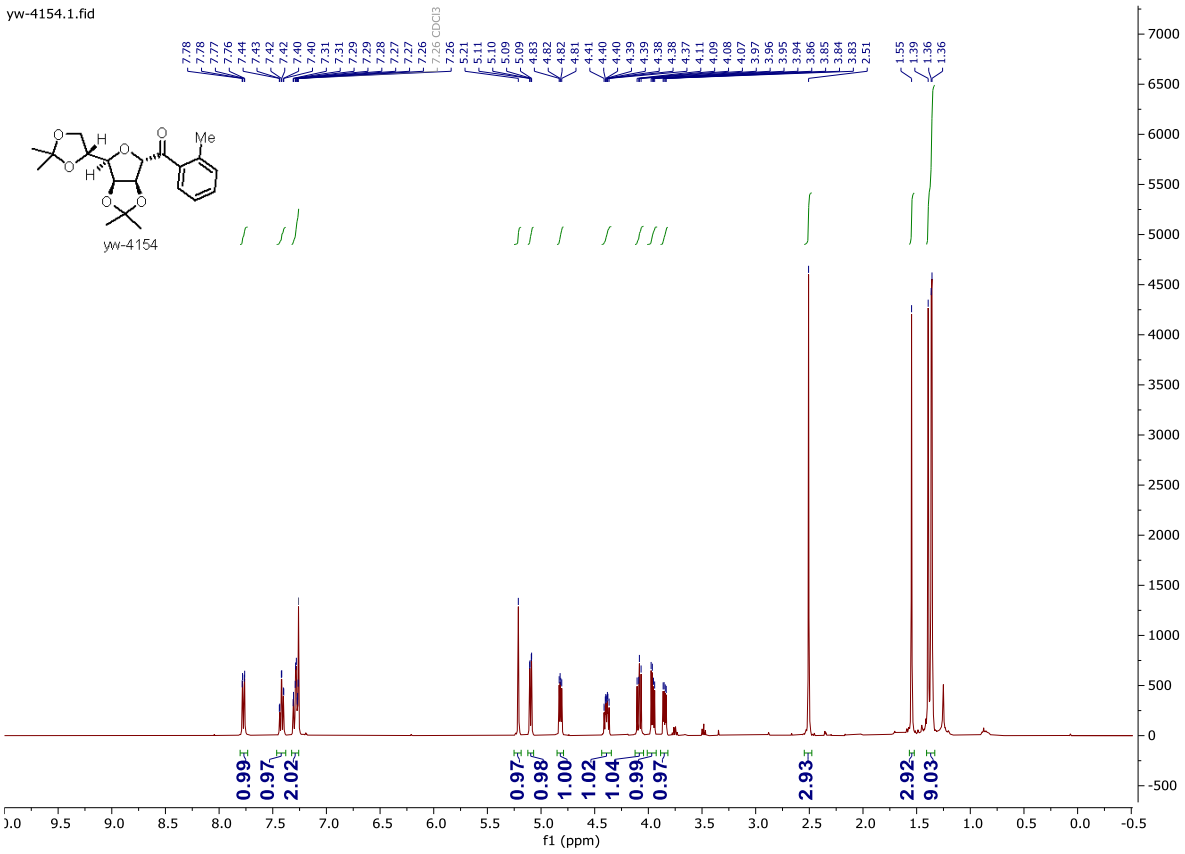
H-H COSY of **21**



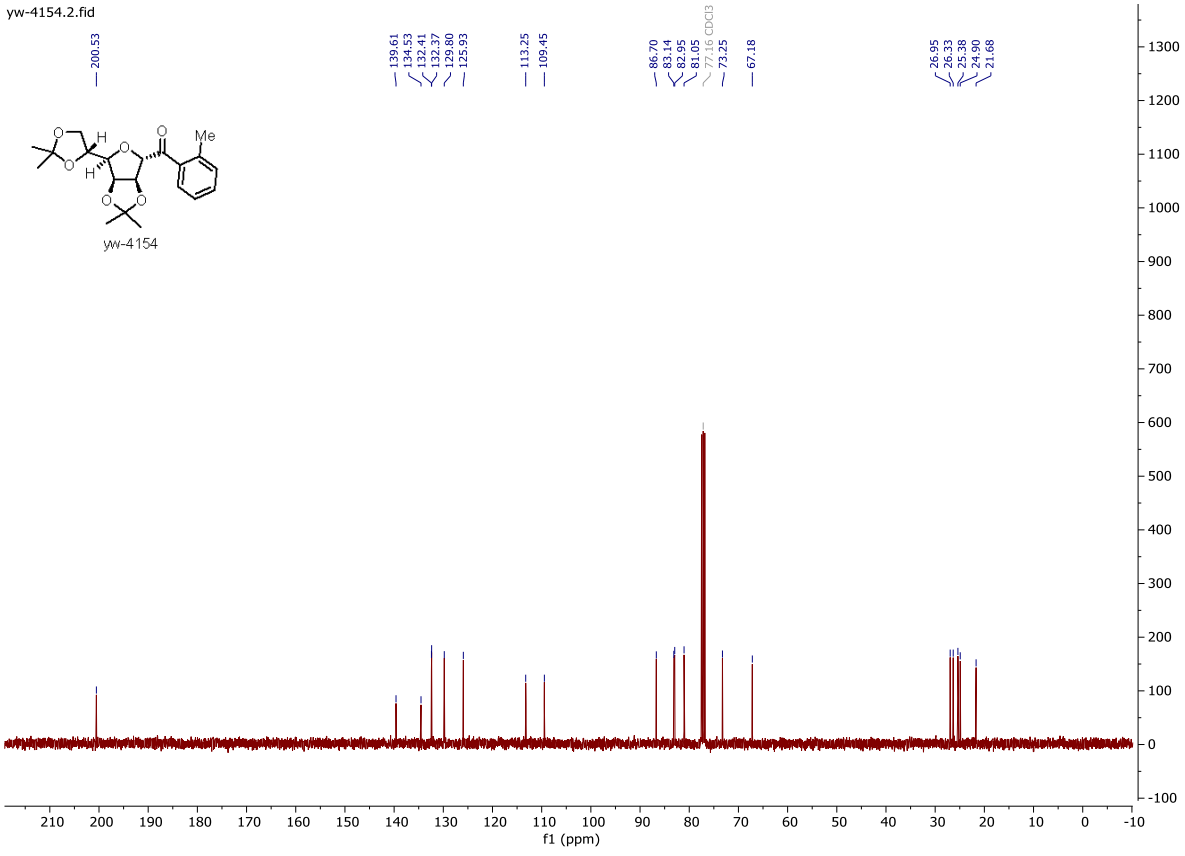
H-H COSY of **21**



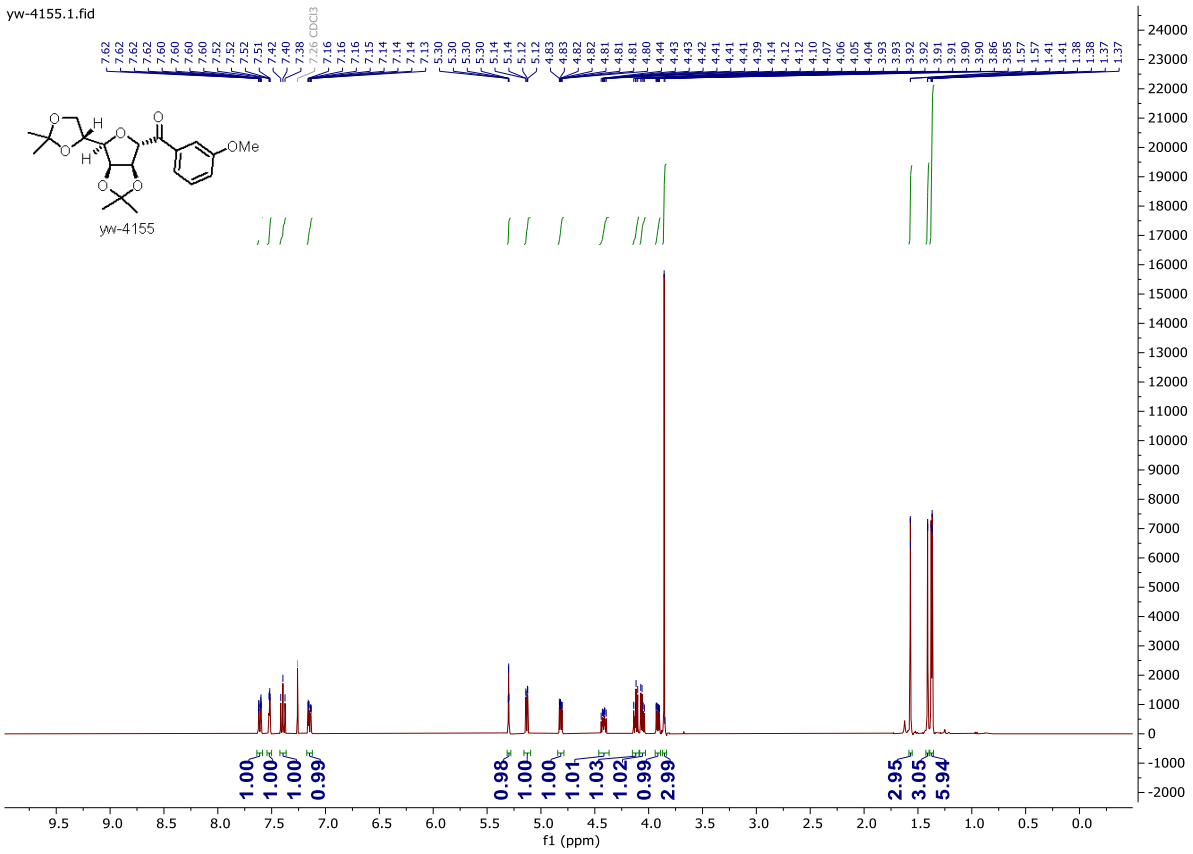
NOESY of **21**



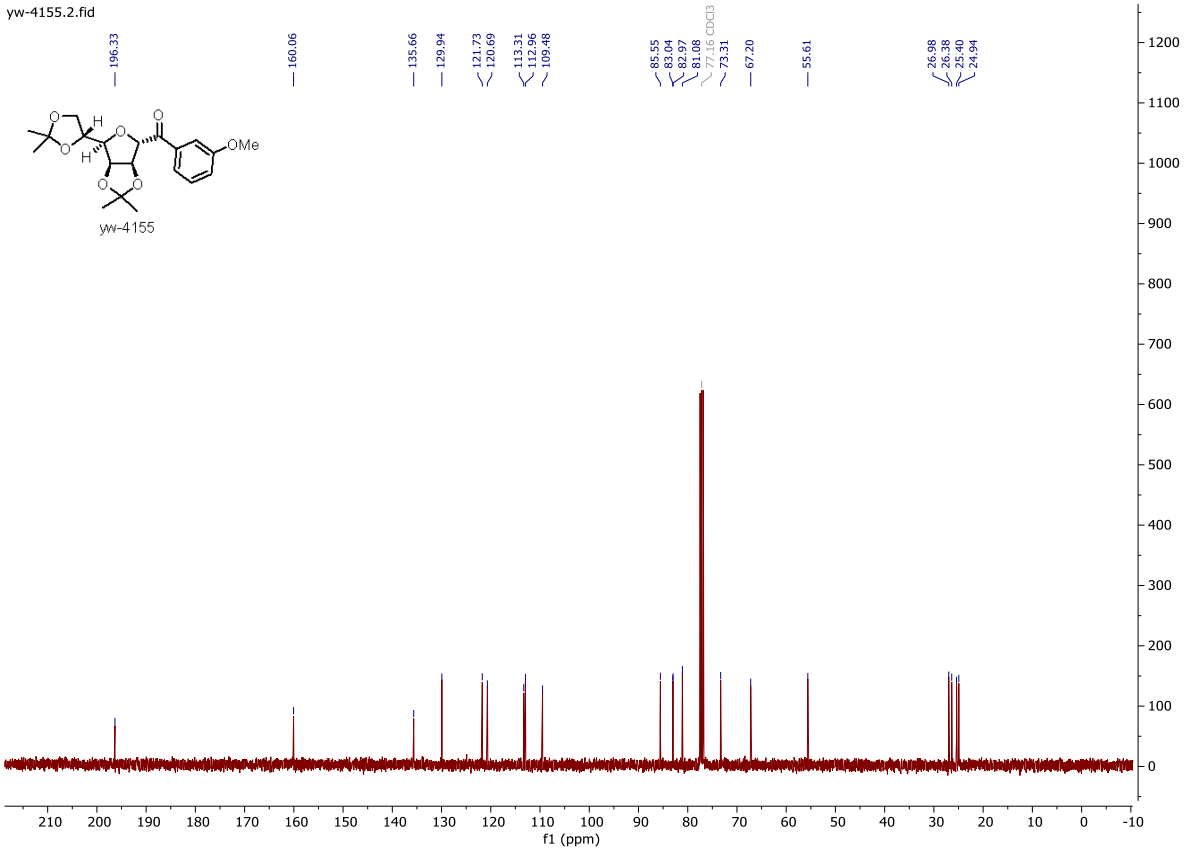
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **22**



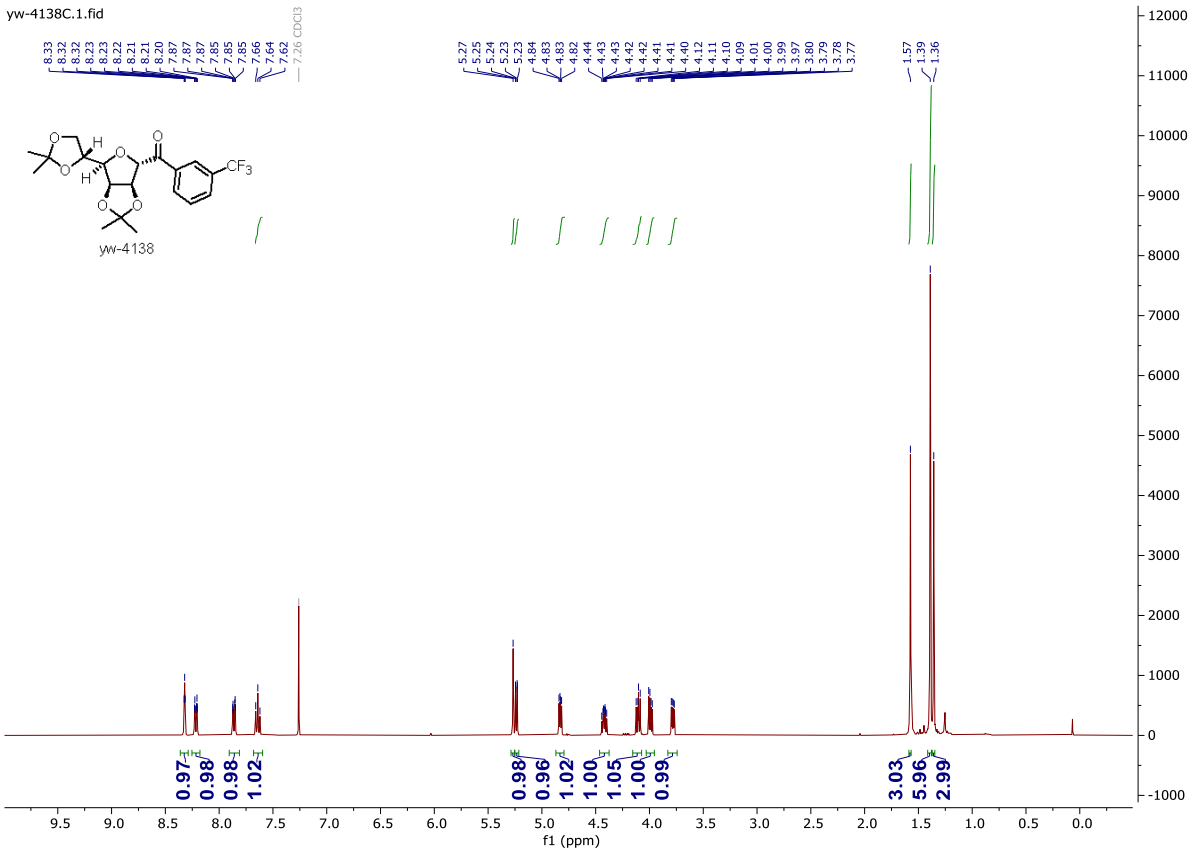
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **22**



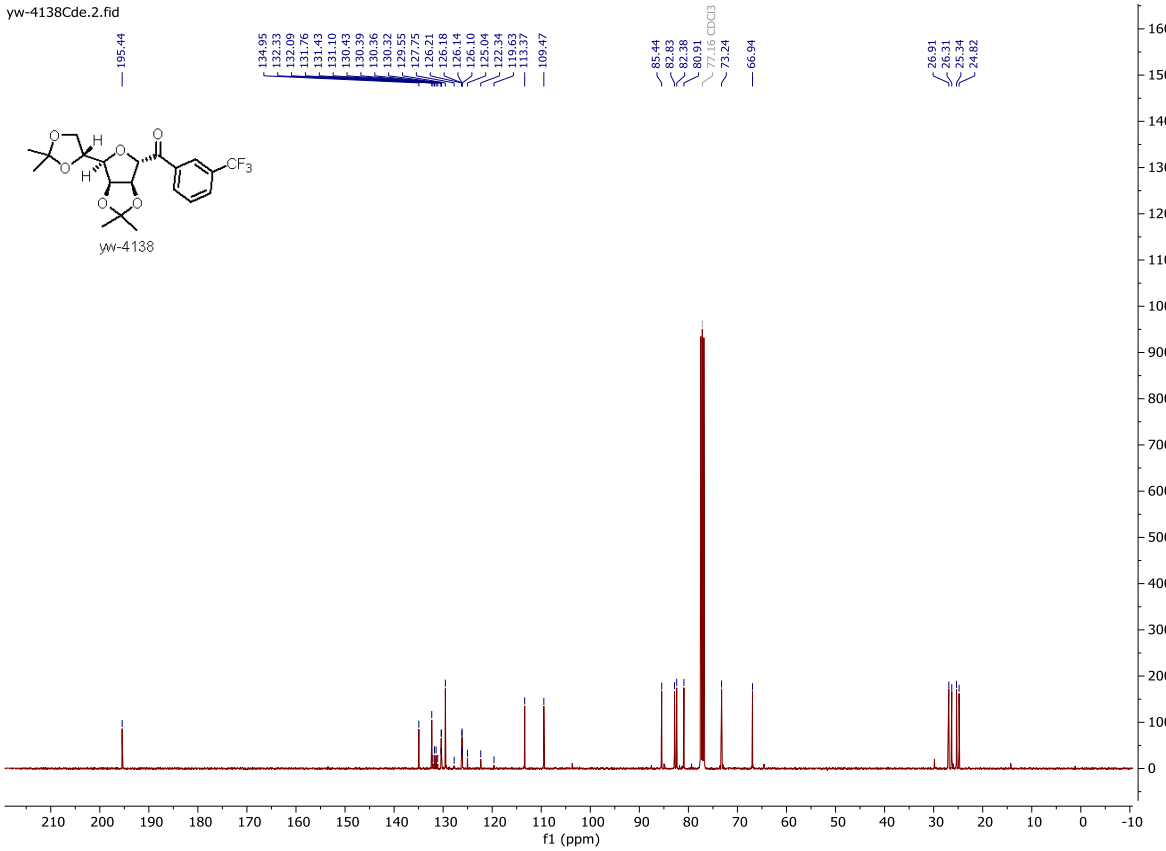
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **23**



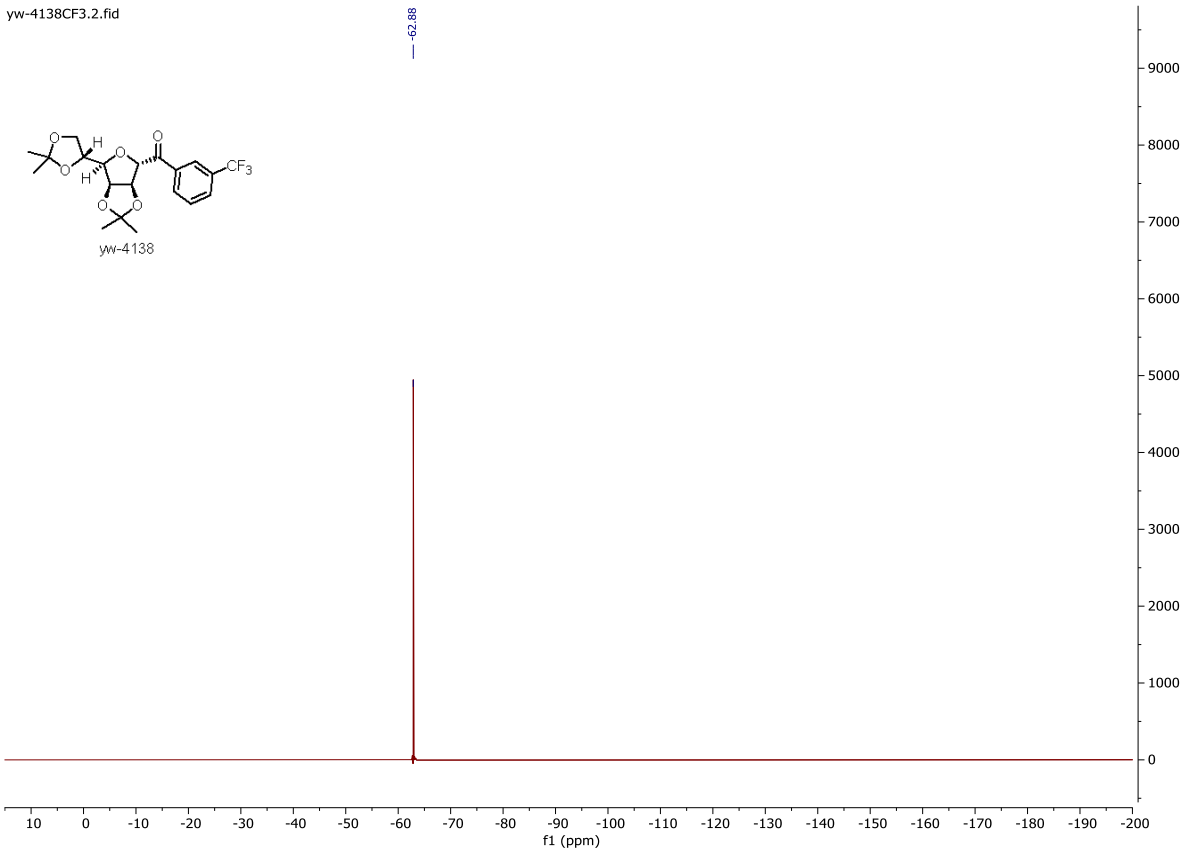
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **23**



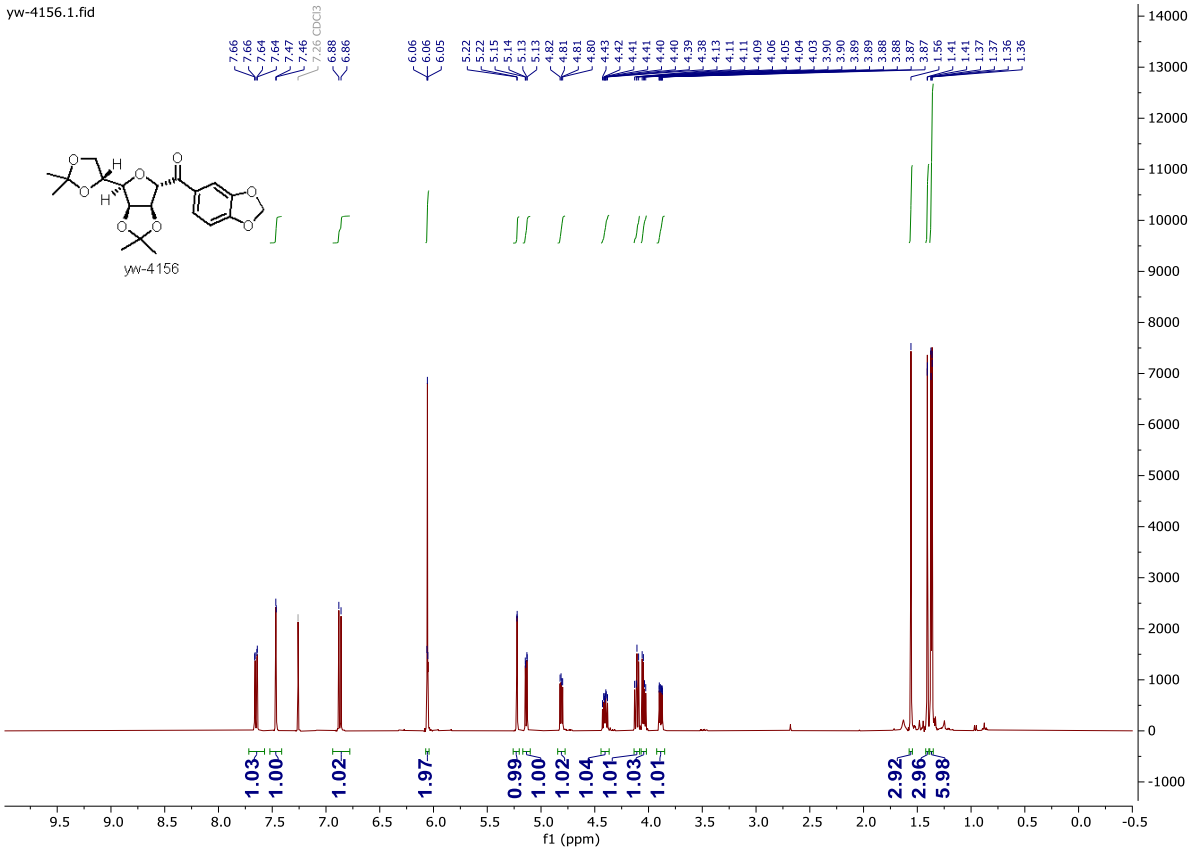
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **24**



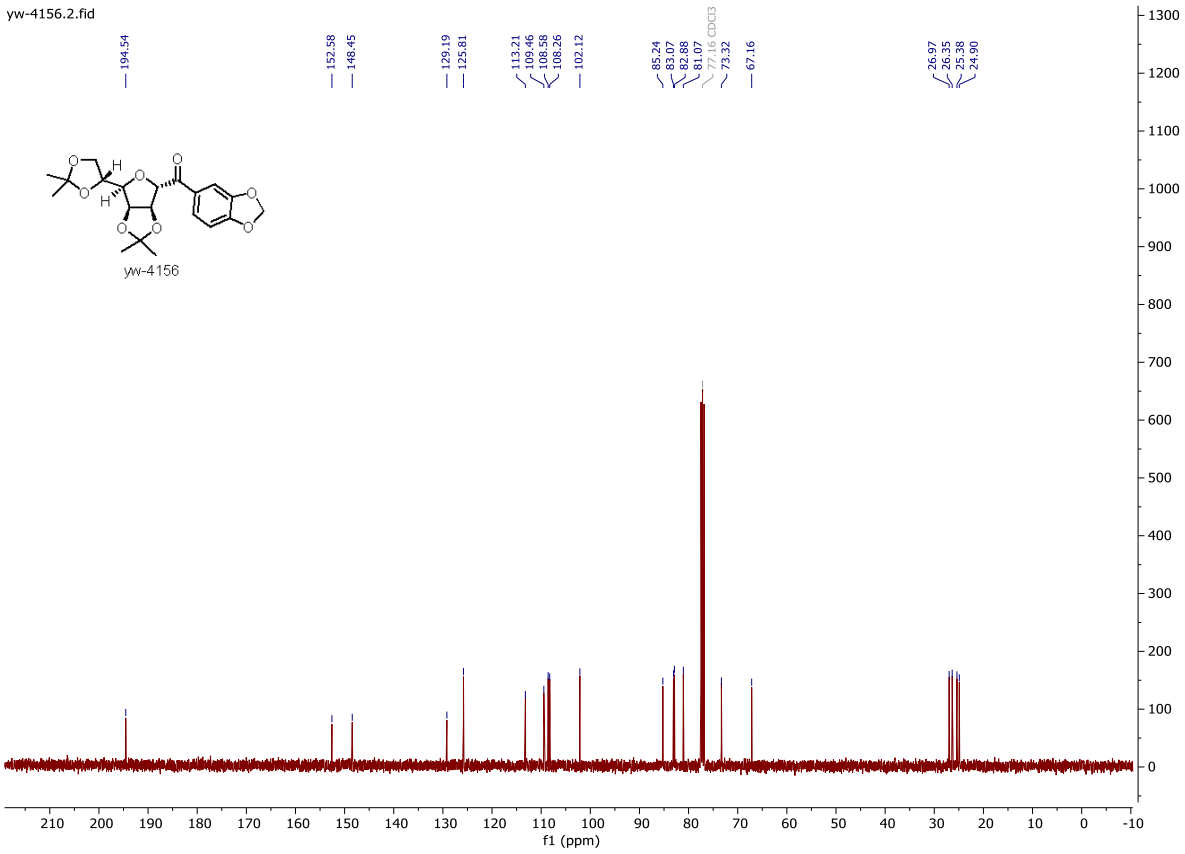
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **24**



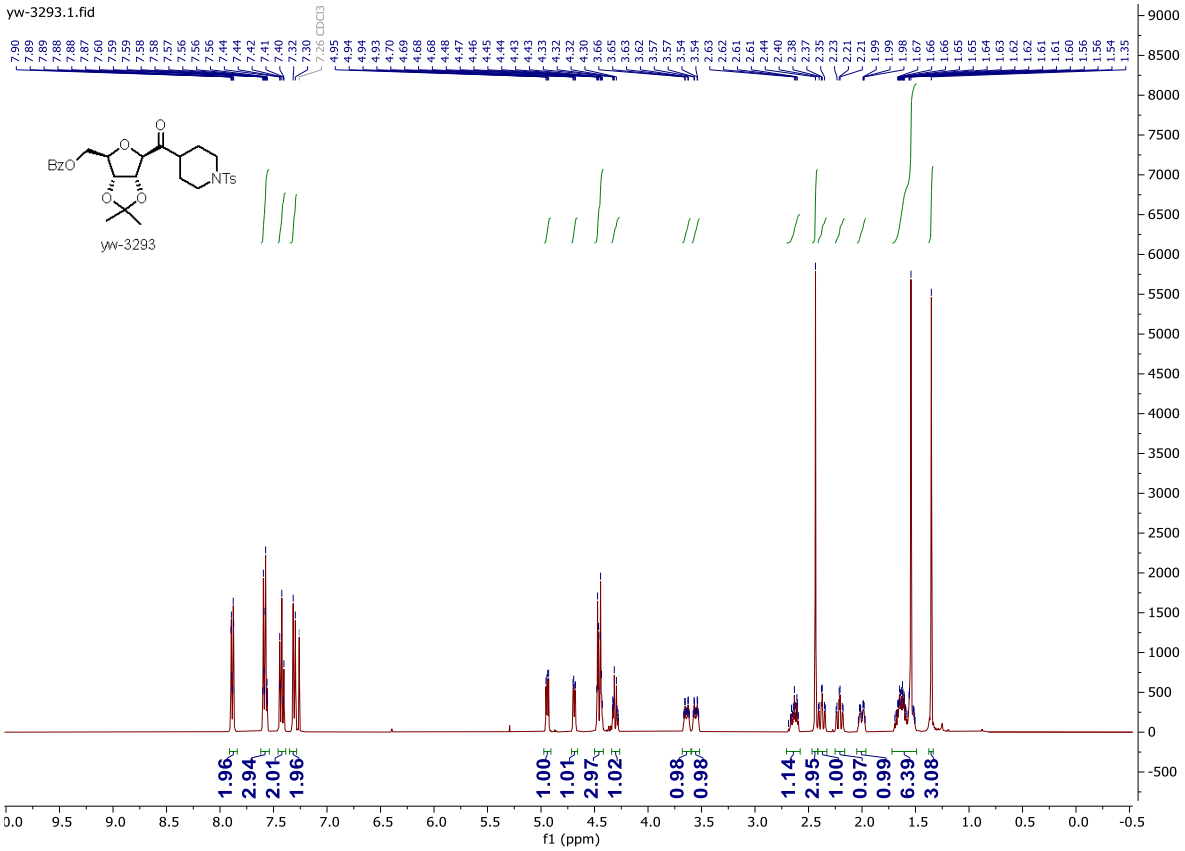
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of **24**



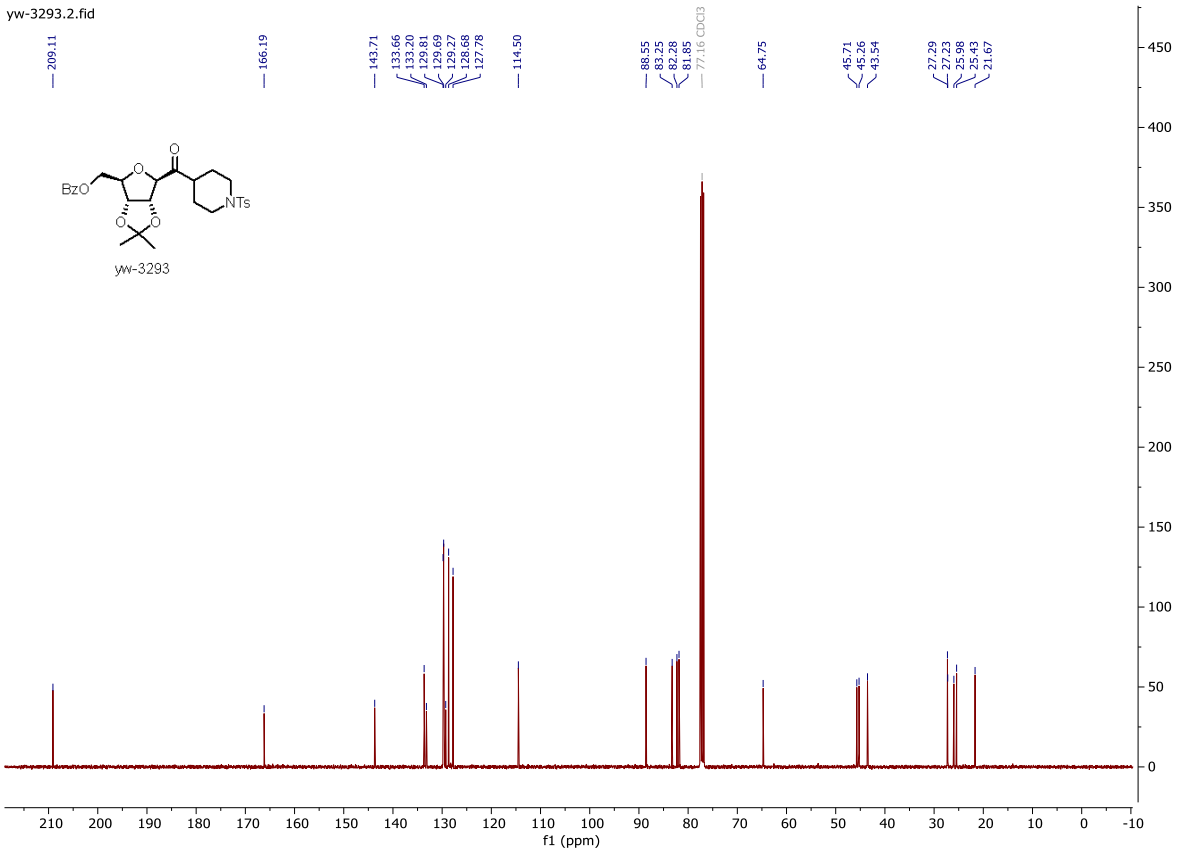
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **25**



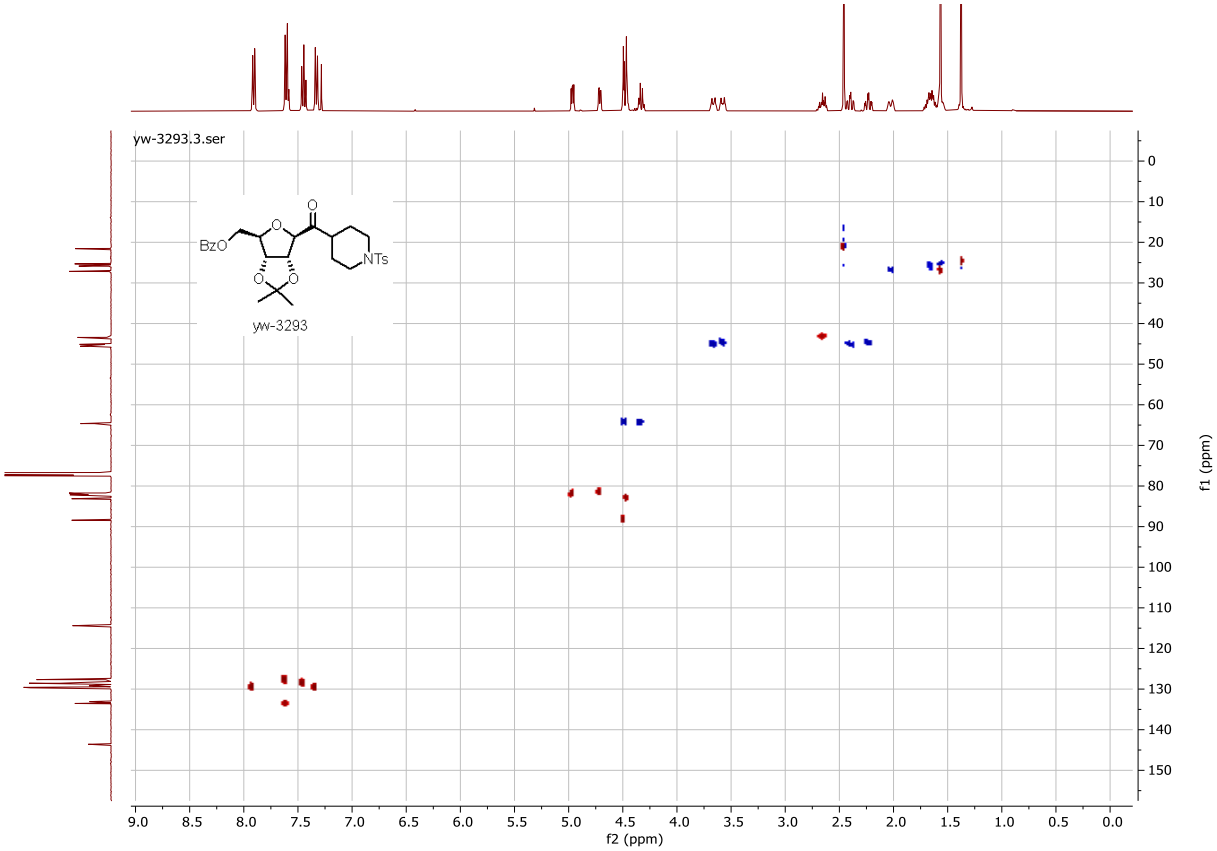
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **25**



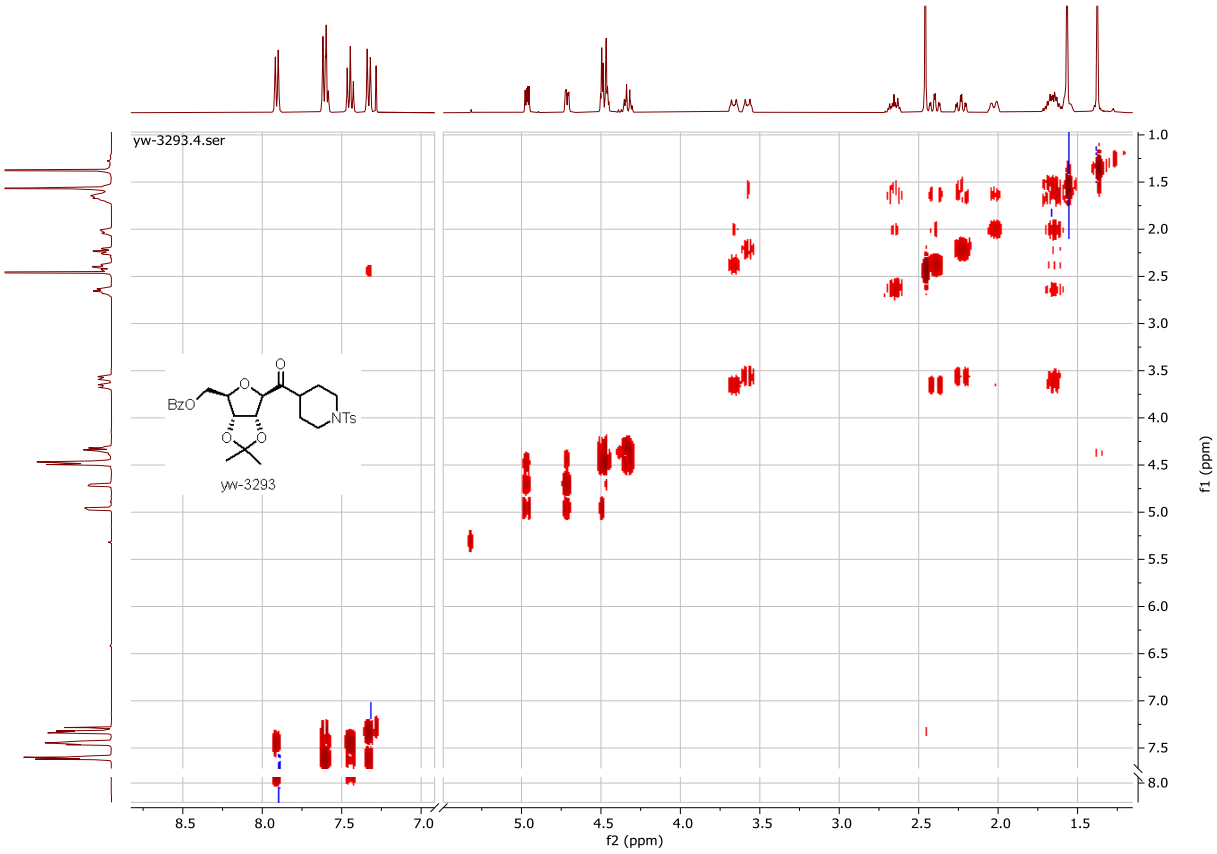
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **26**



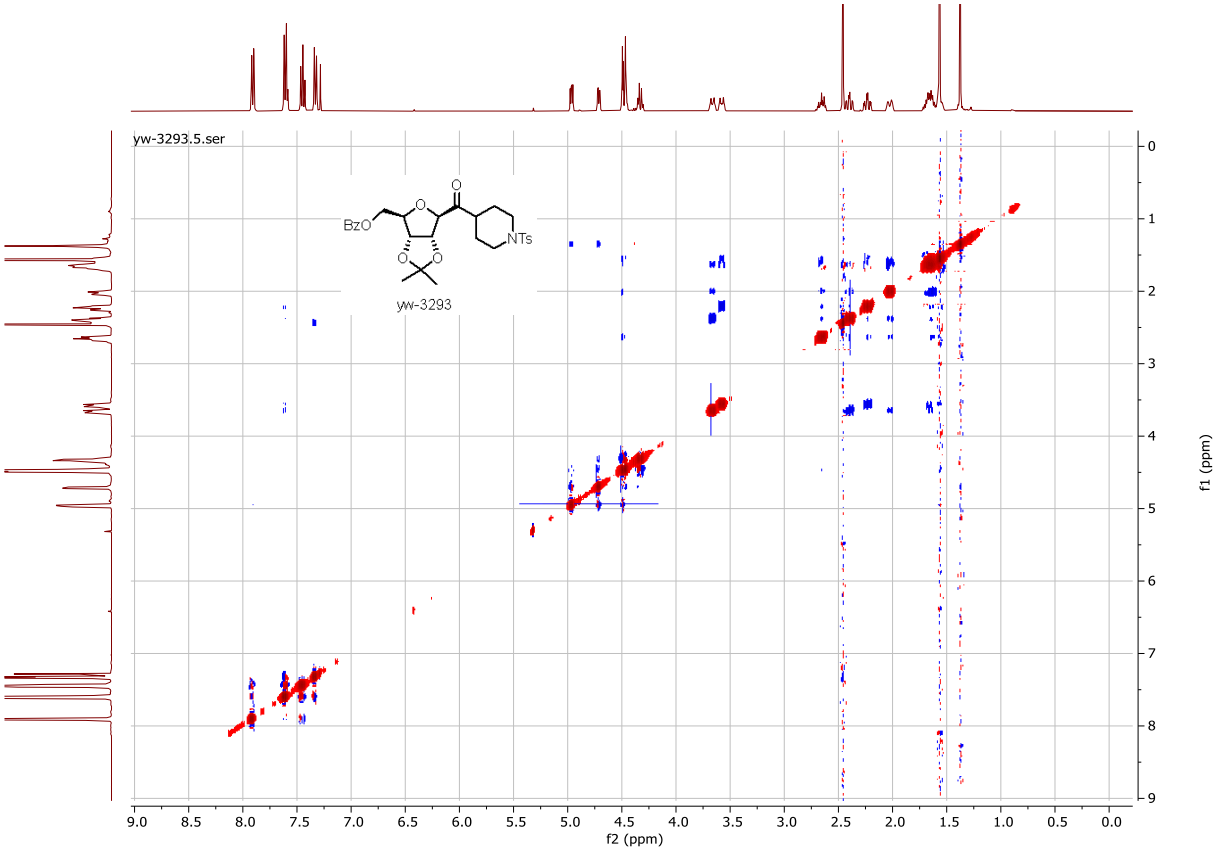
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **26**



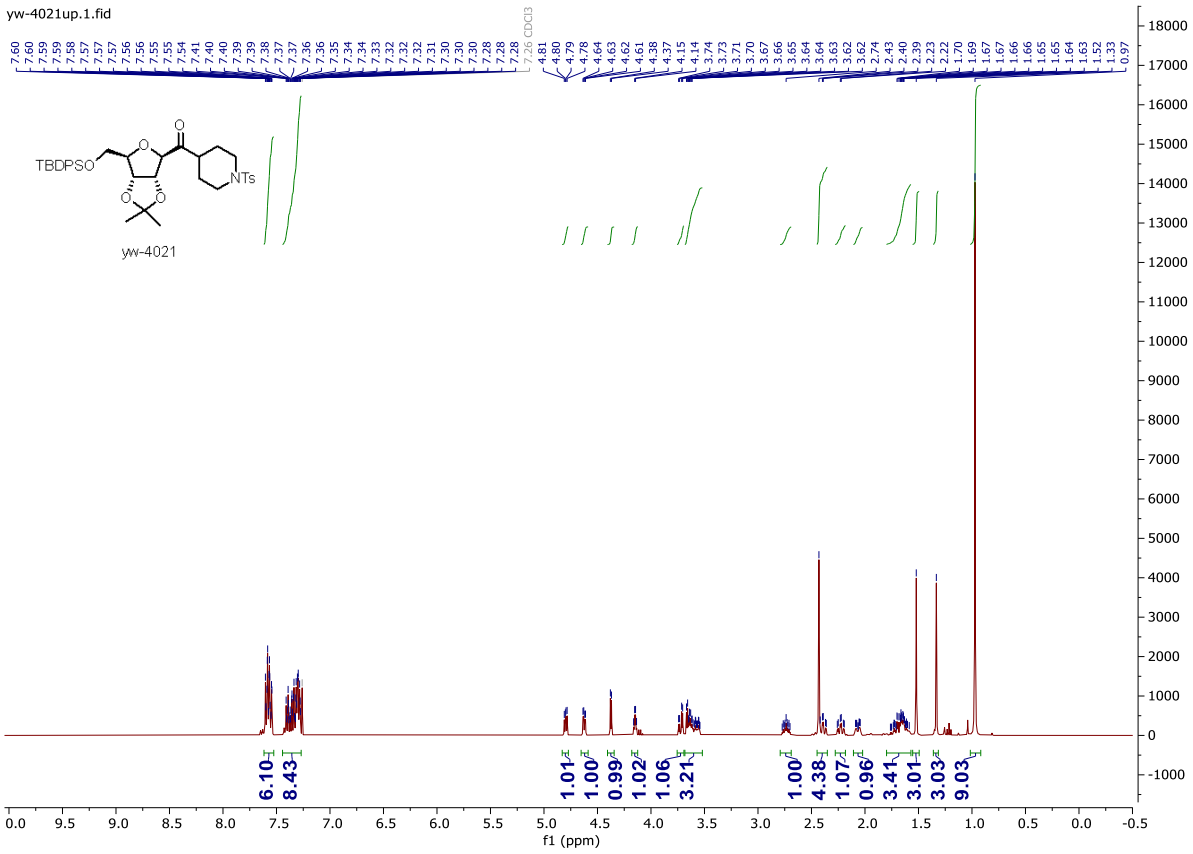
HSQCED of **26**



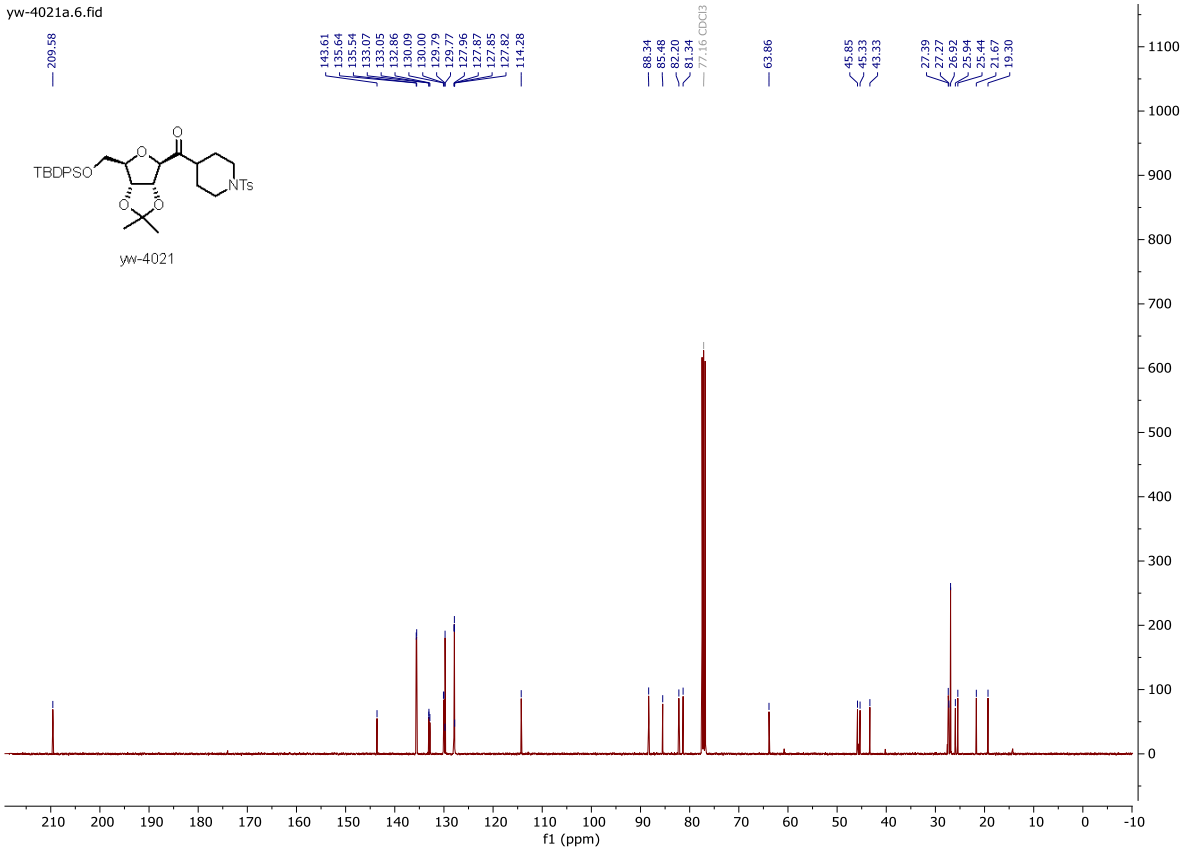
H-H COSY of **26**



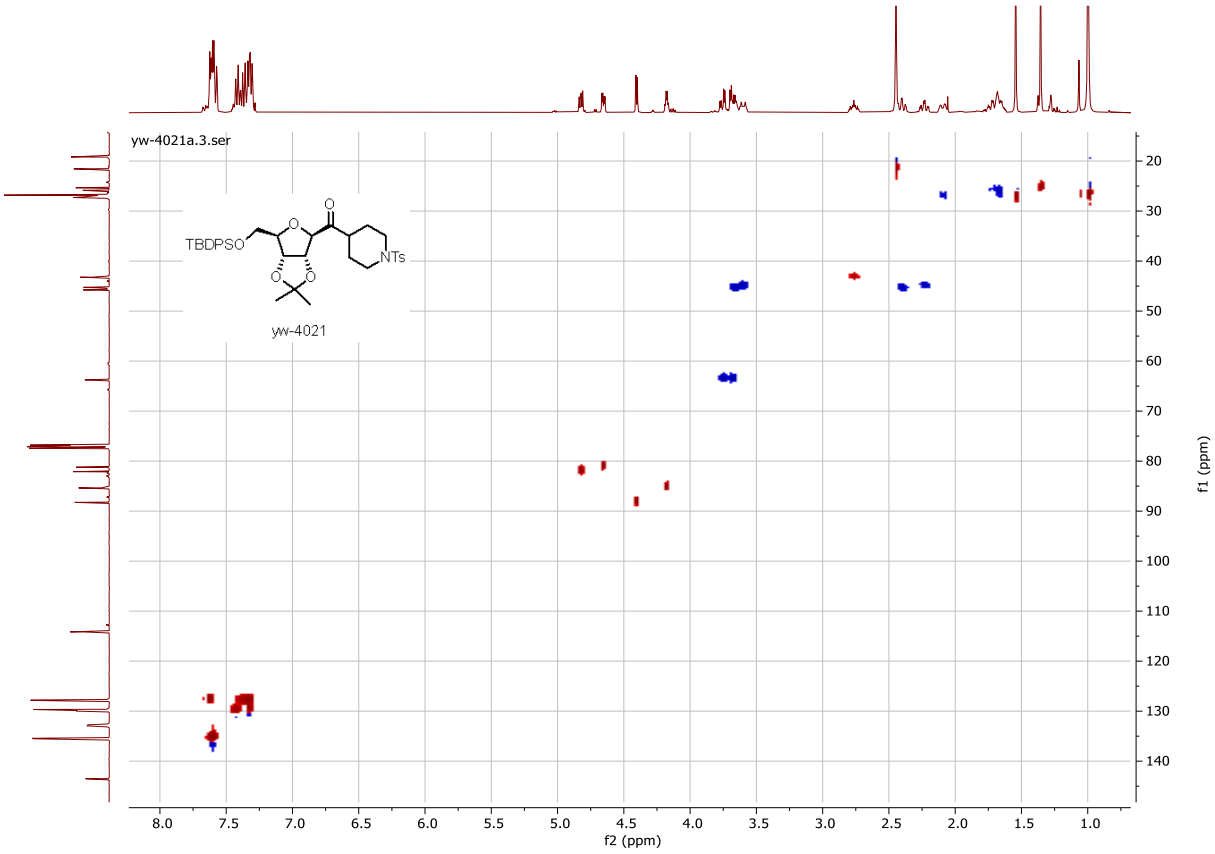
NOESY of **26**



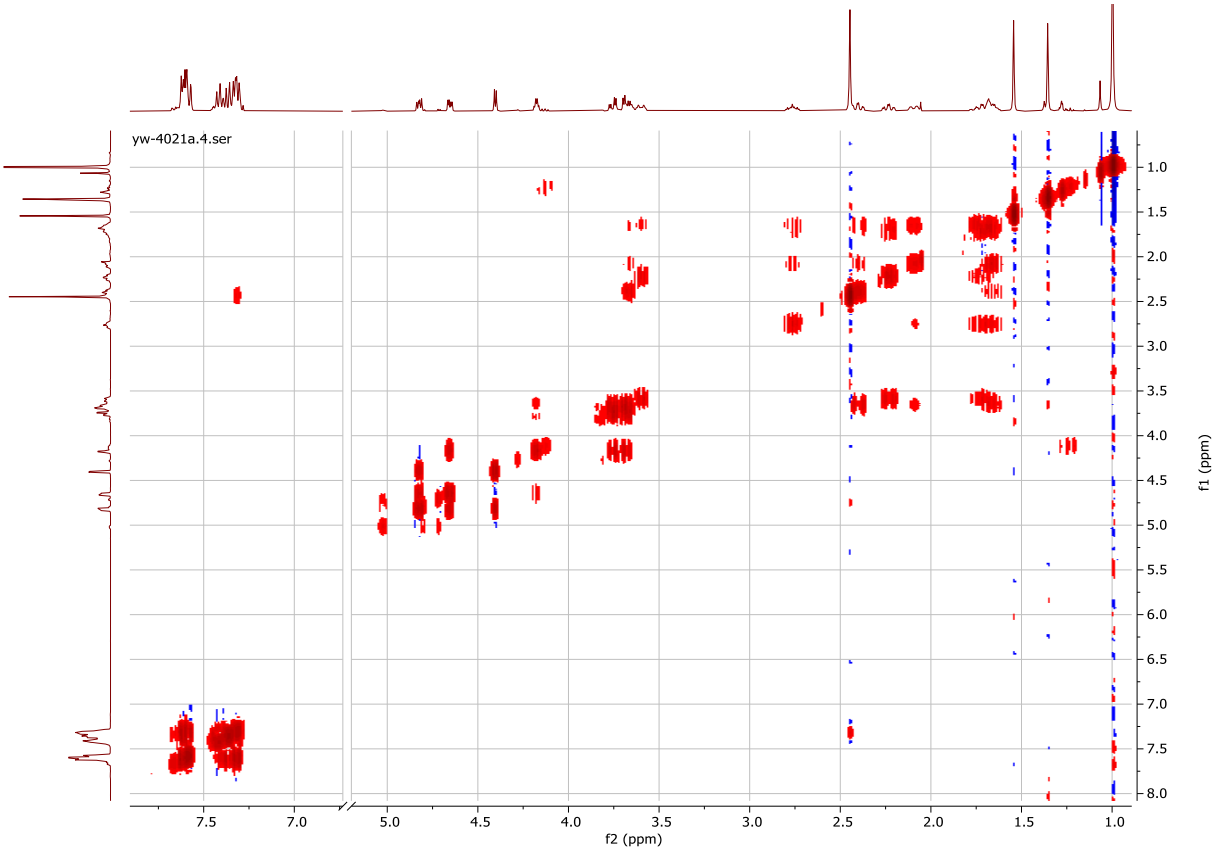
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **27**



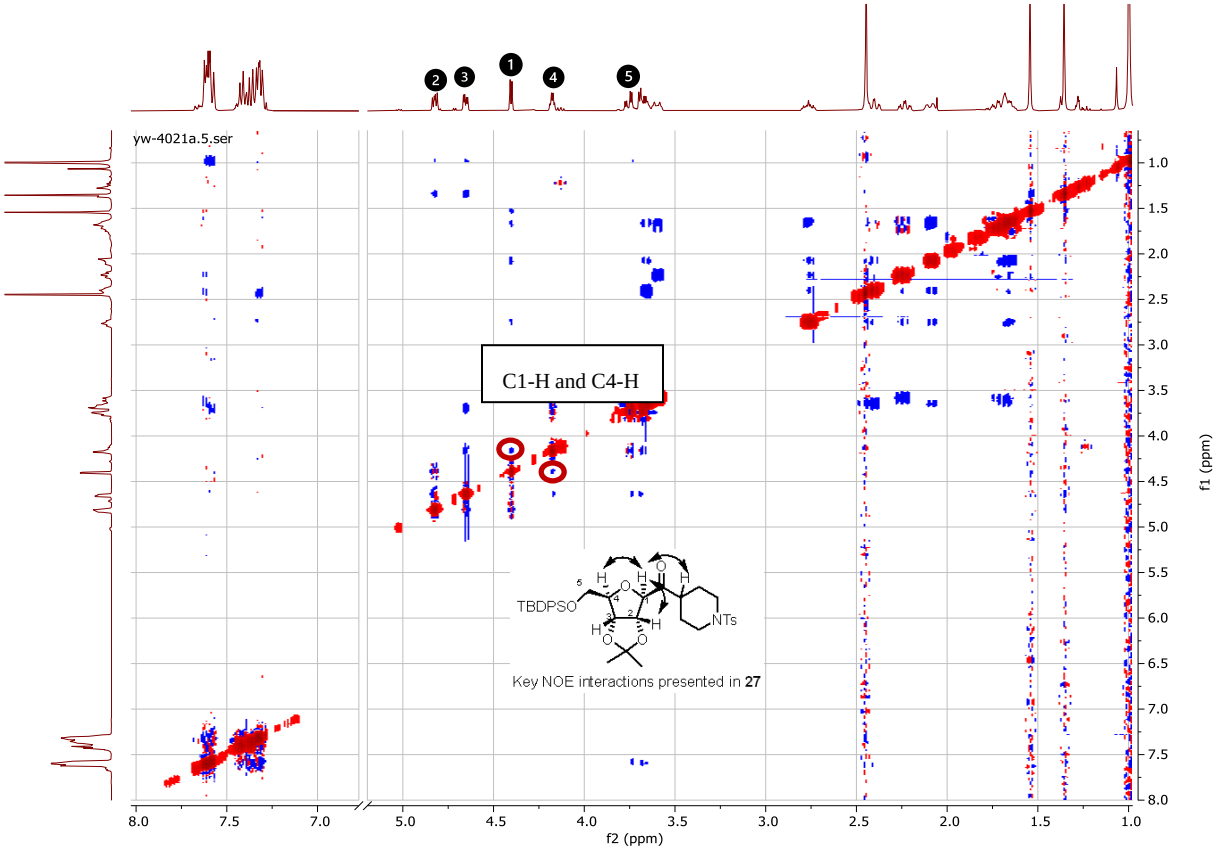
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **27**



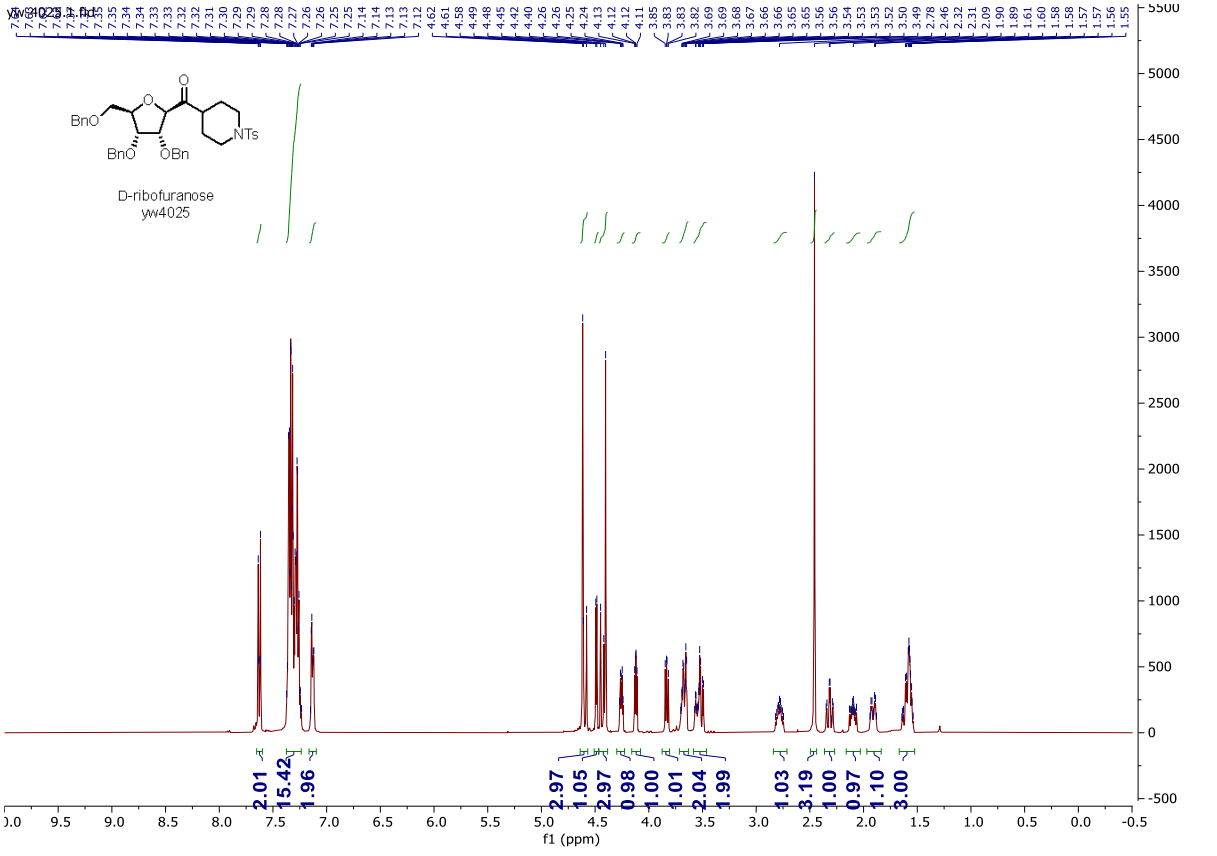
HSQCED of **27**



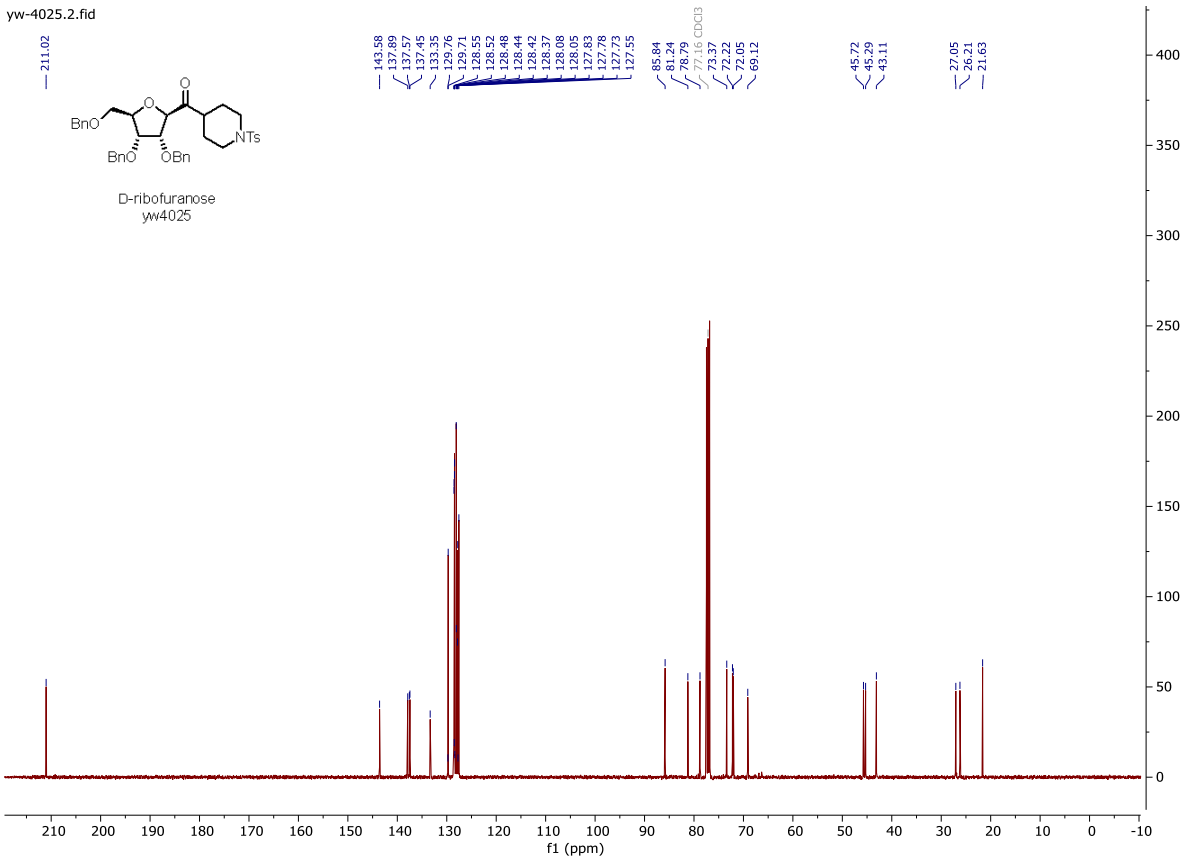
H-H COSY of **27**



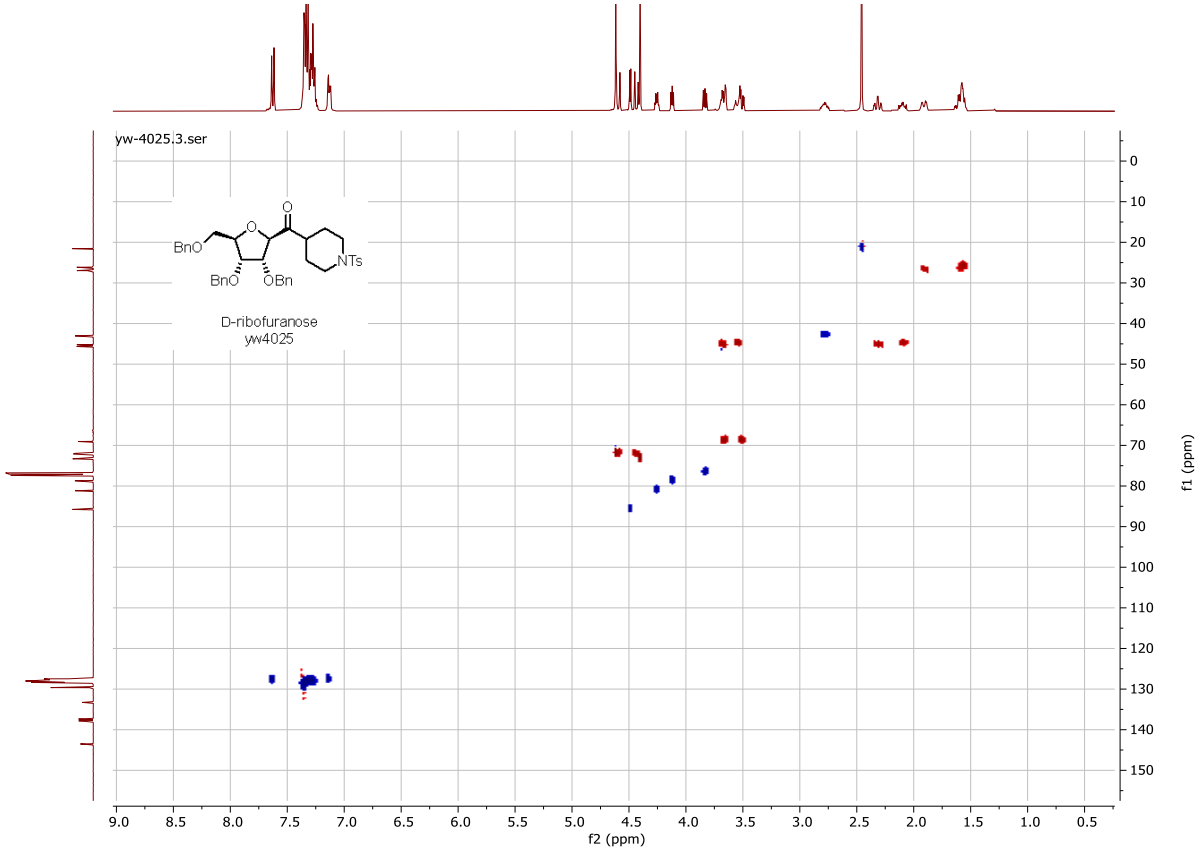
NOESY of **27**



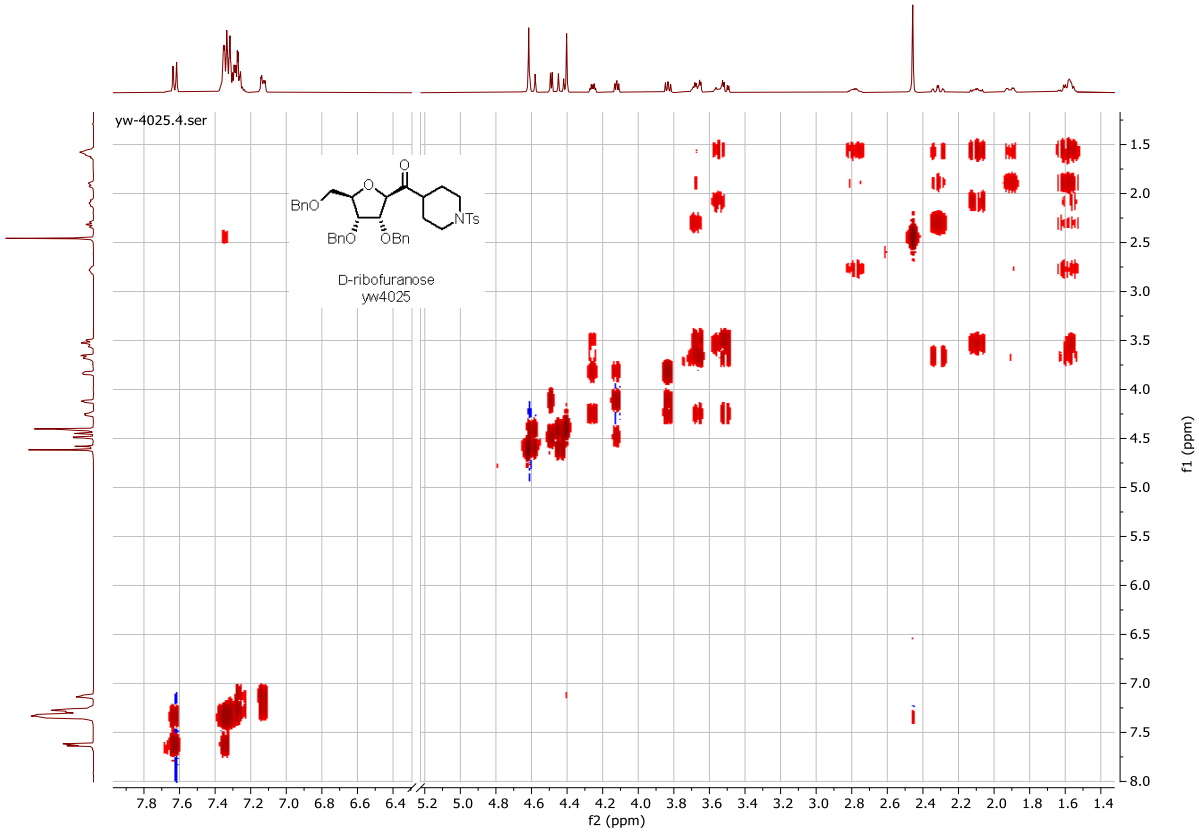
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **28**



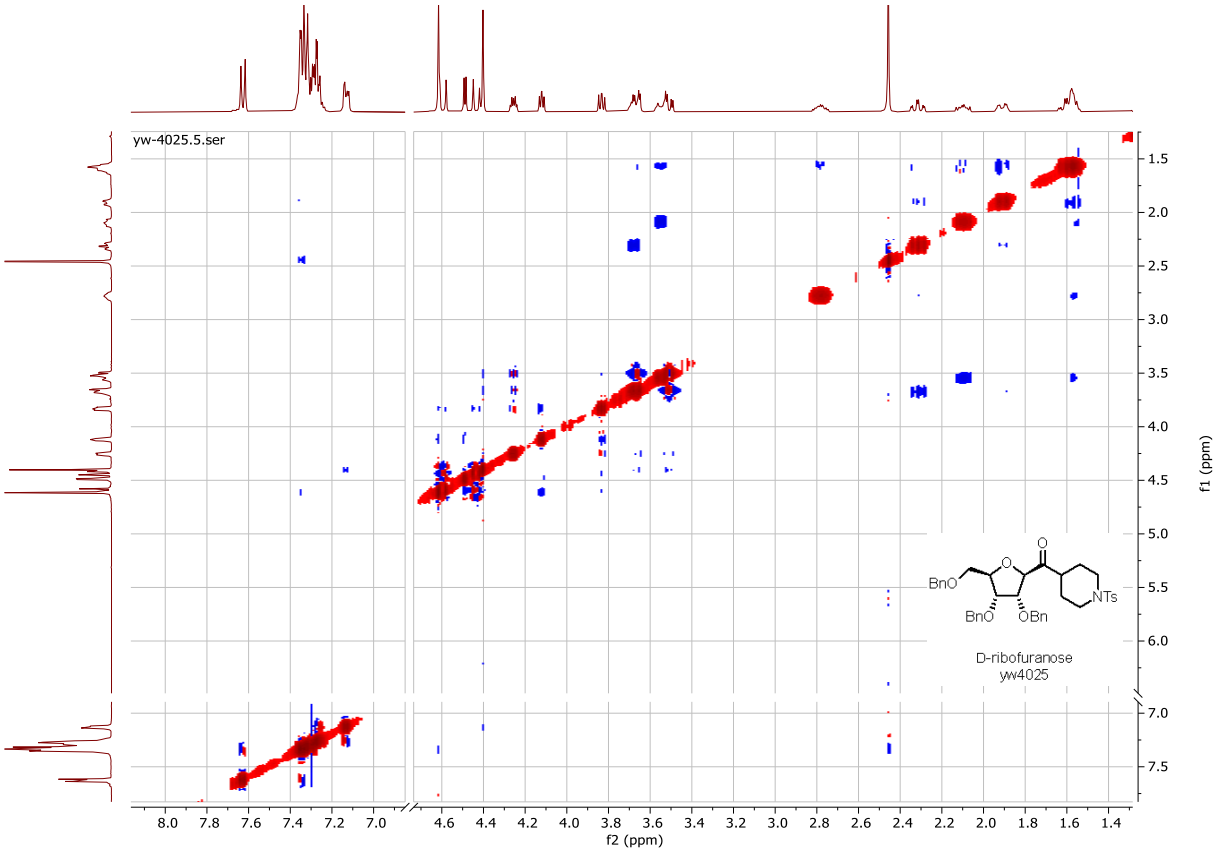
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **28**



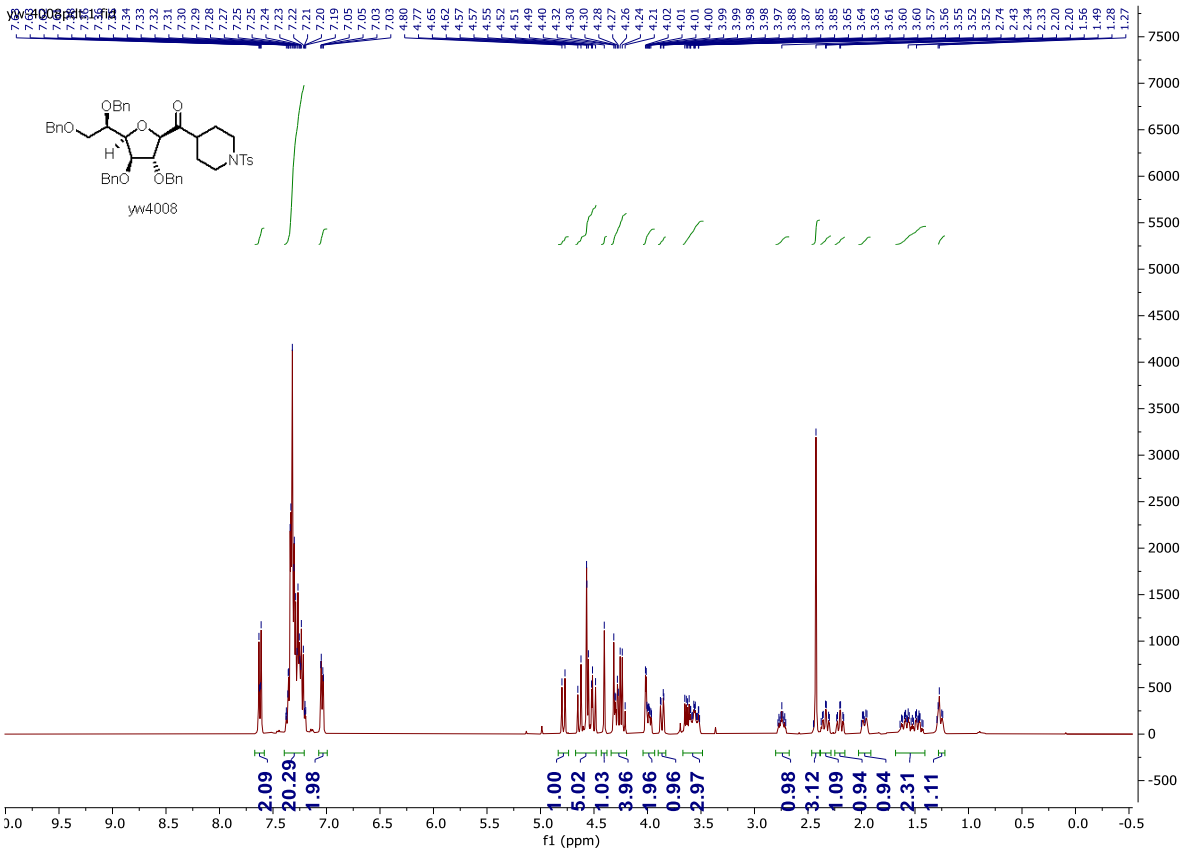
HSQCED of **28**



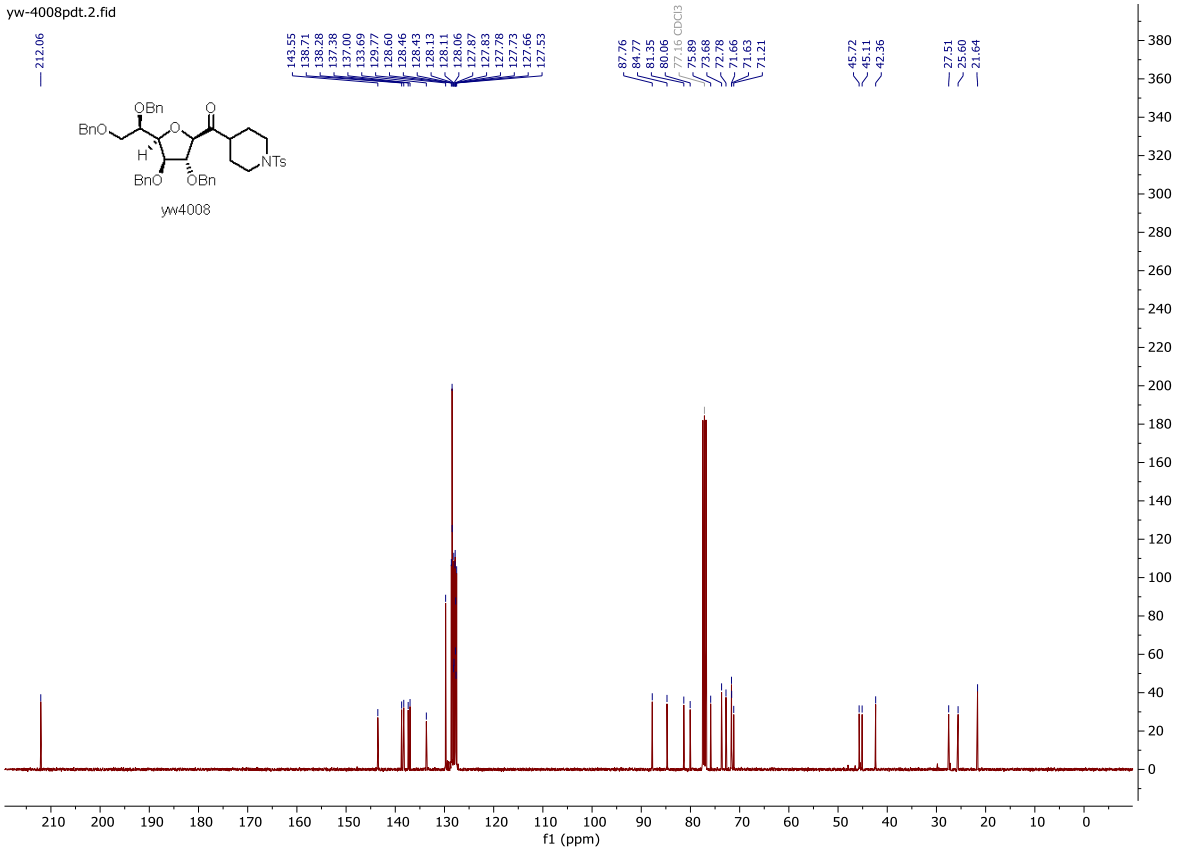
H-H COSY of **28**



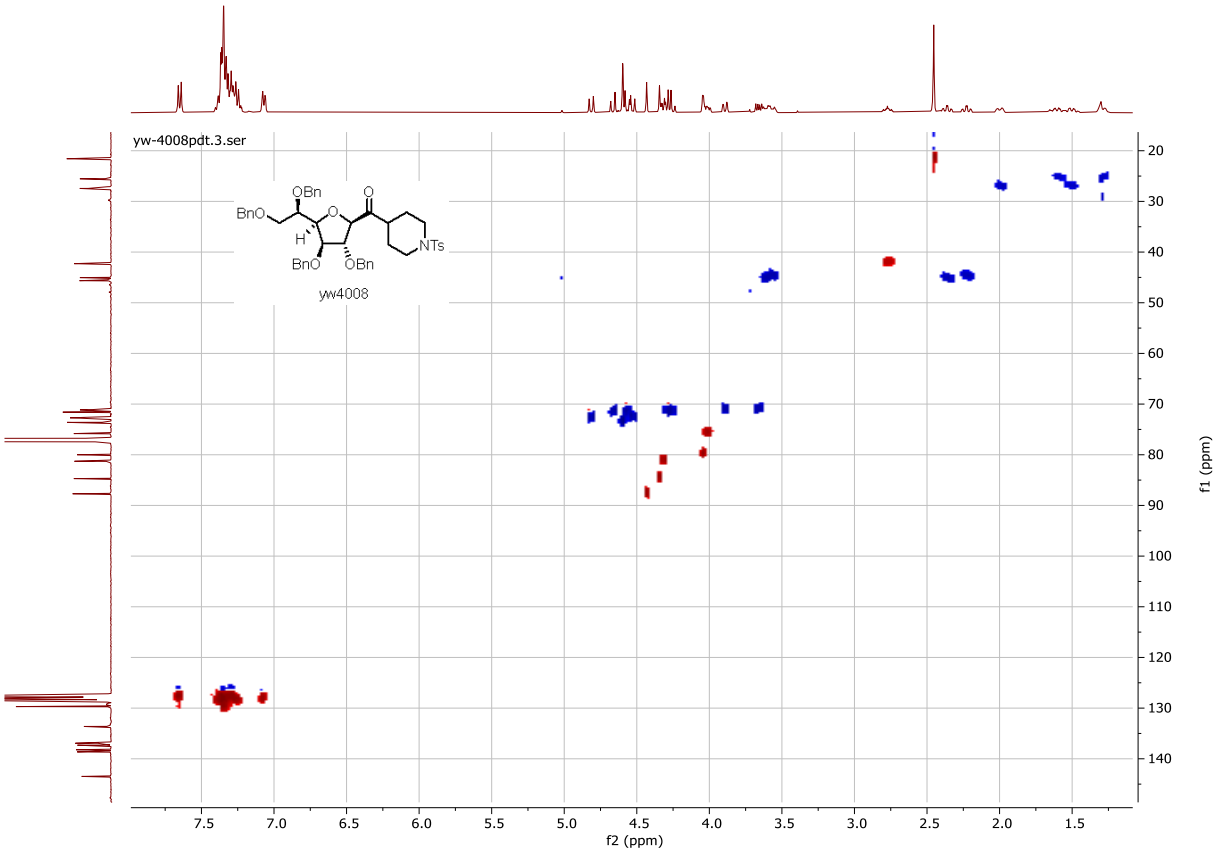
NOESY of **28**



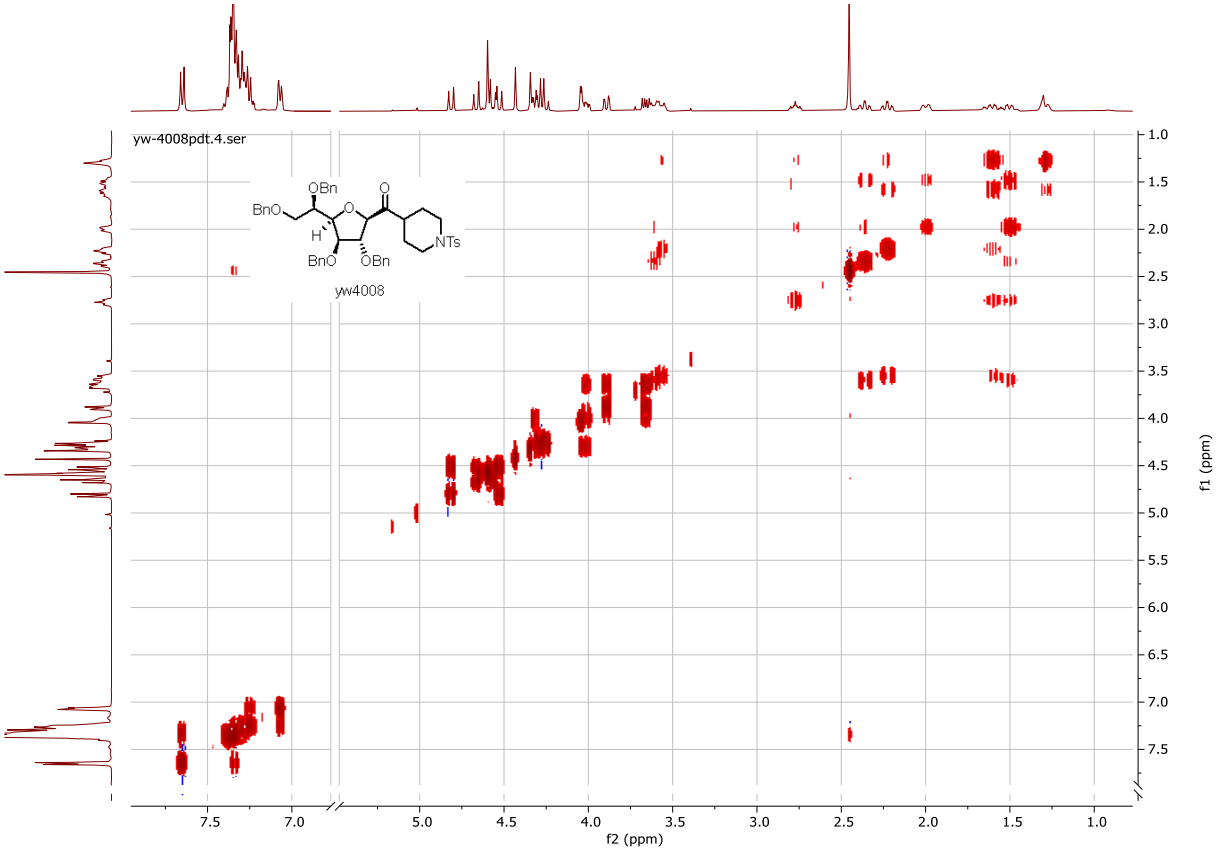
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **29**



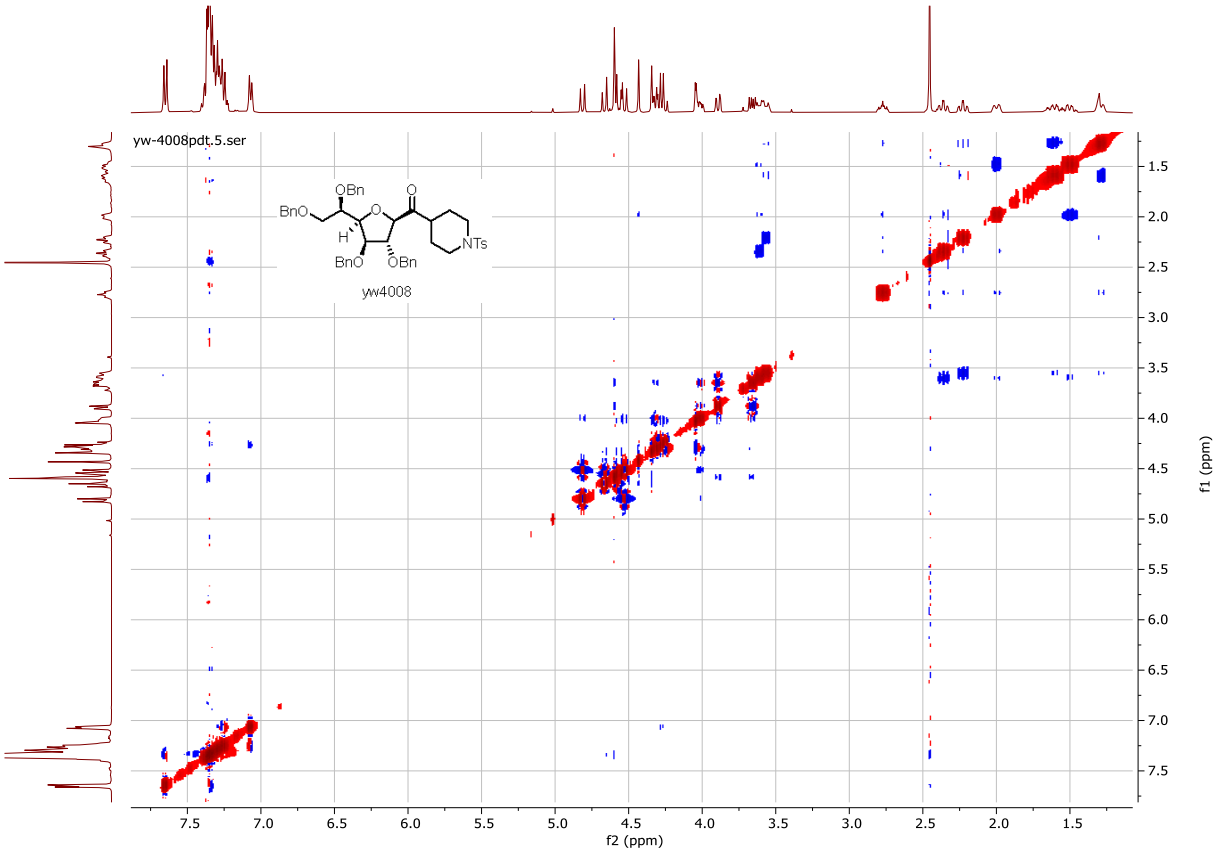
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **29**



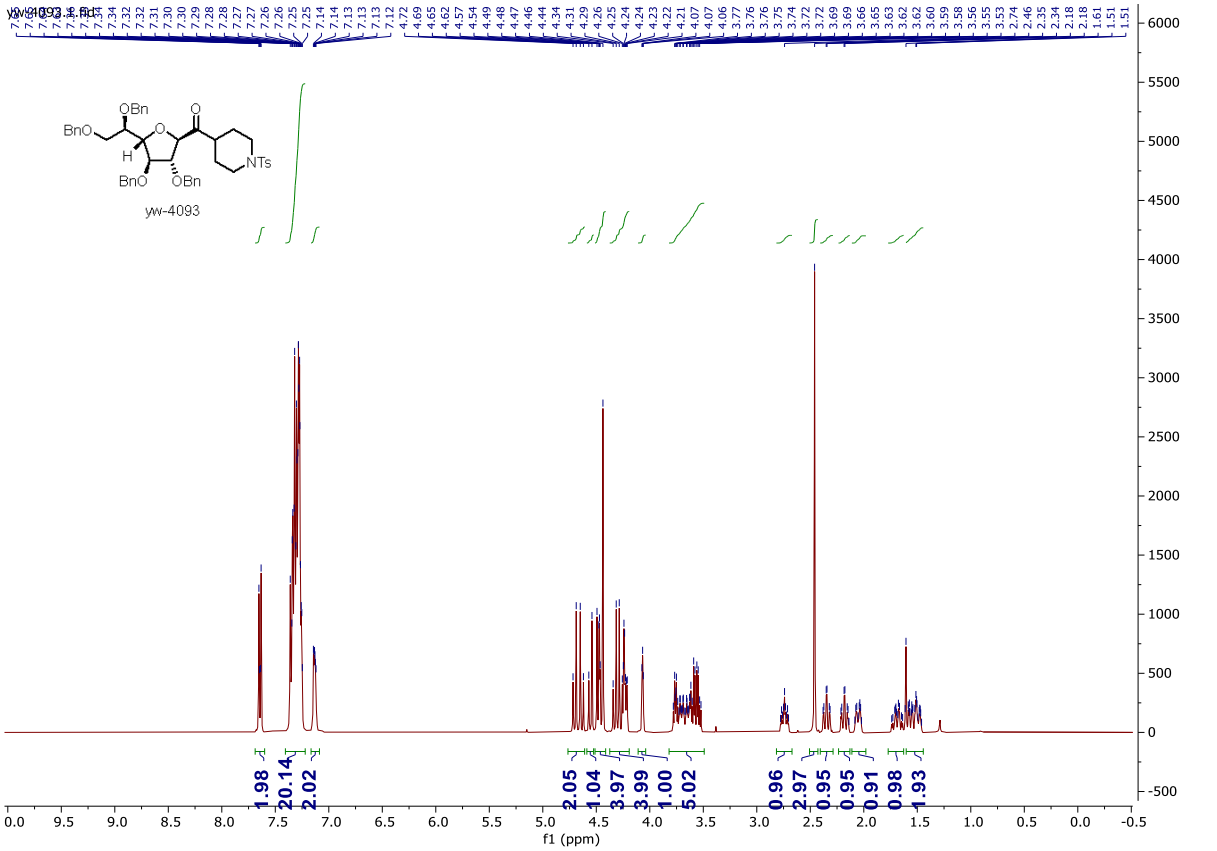
HSQCED of **29**



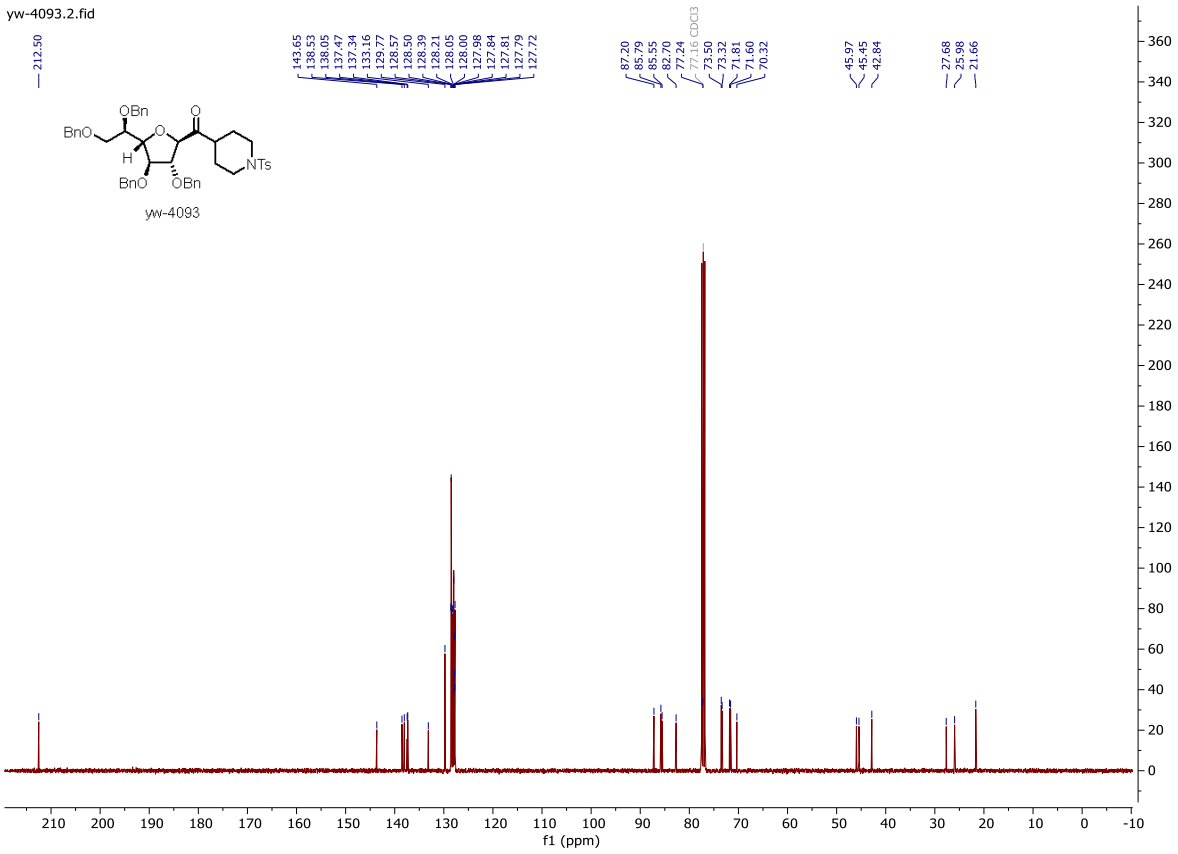
H-H-COSY of **29**



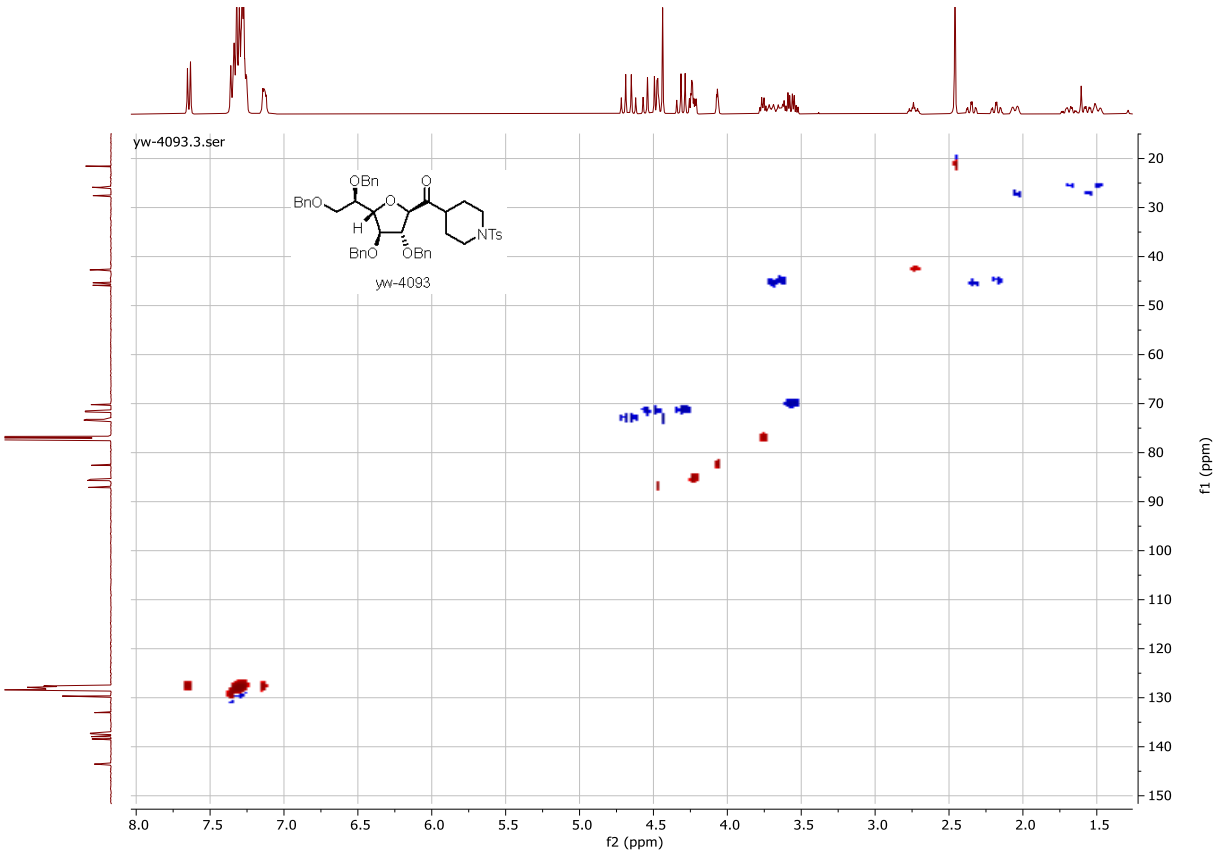
NOESY of **29**



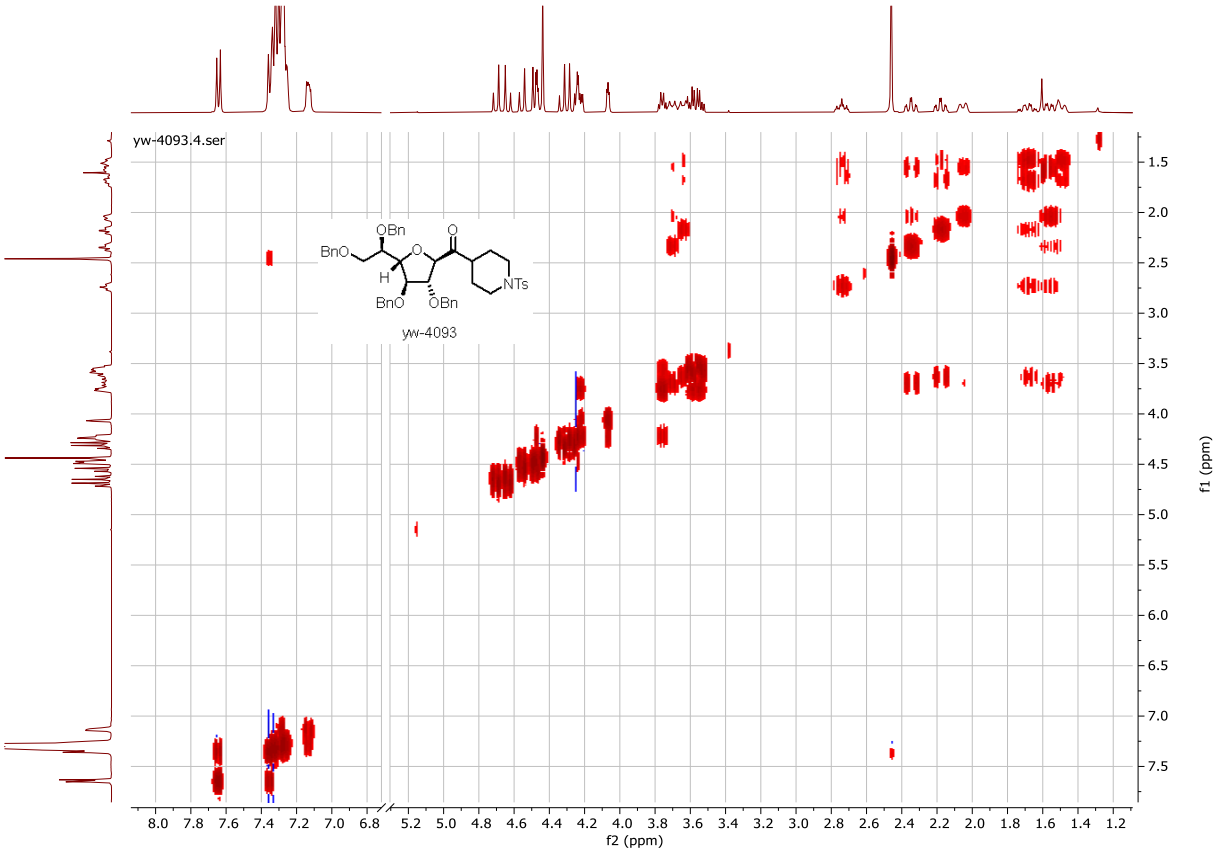
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **30**



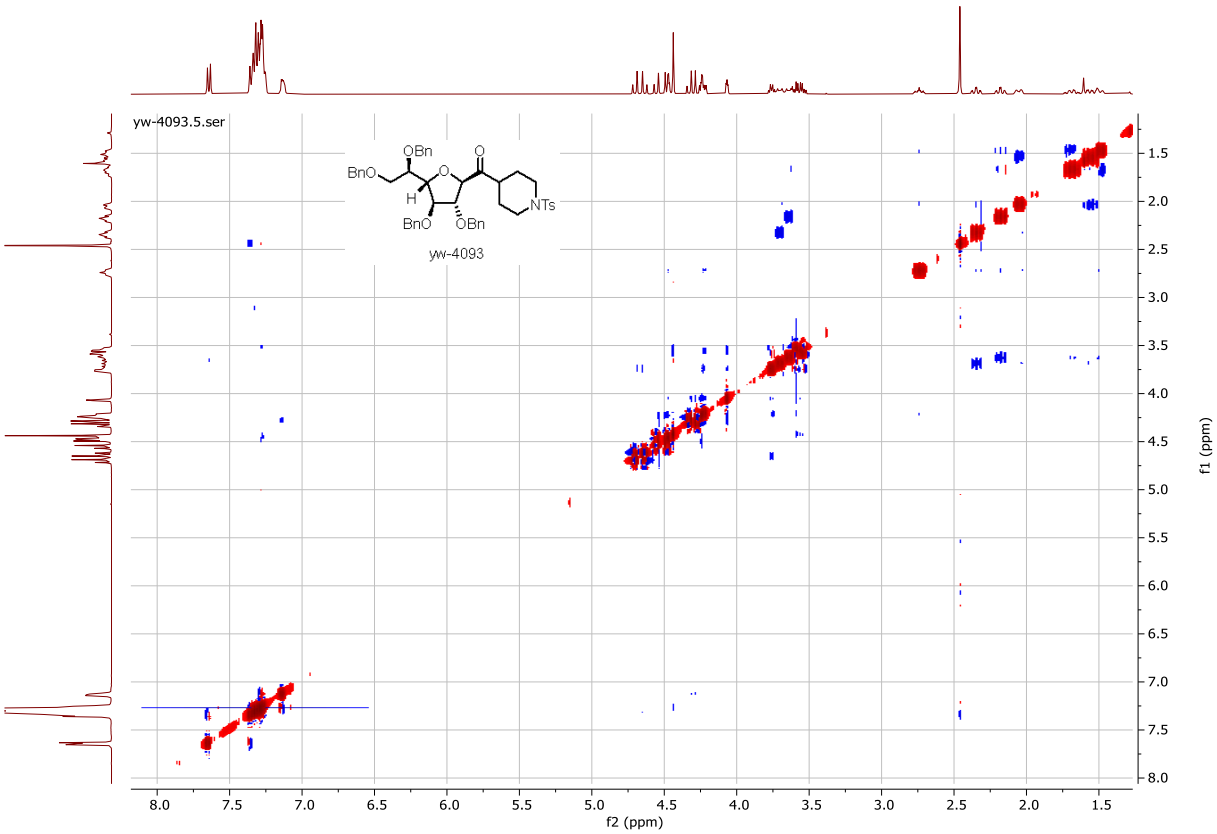
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **30**



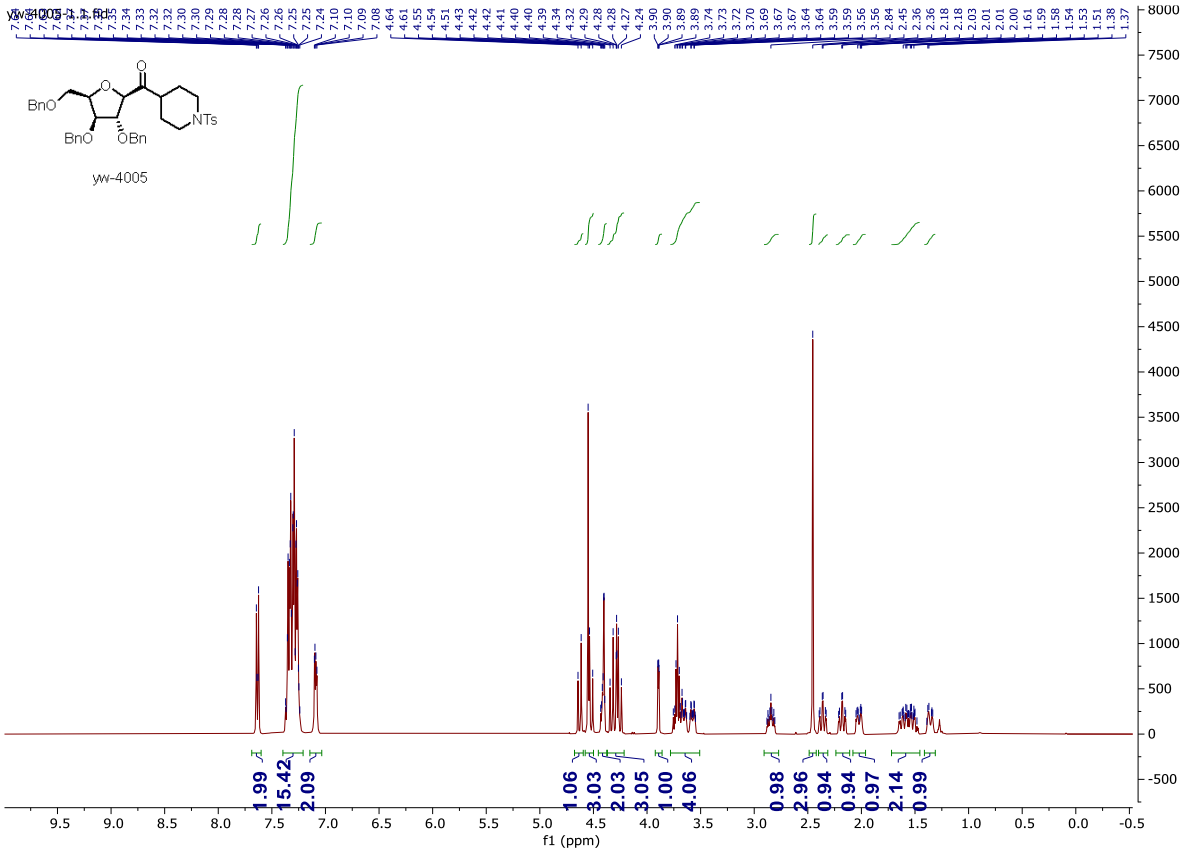
HSQCED of **30**



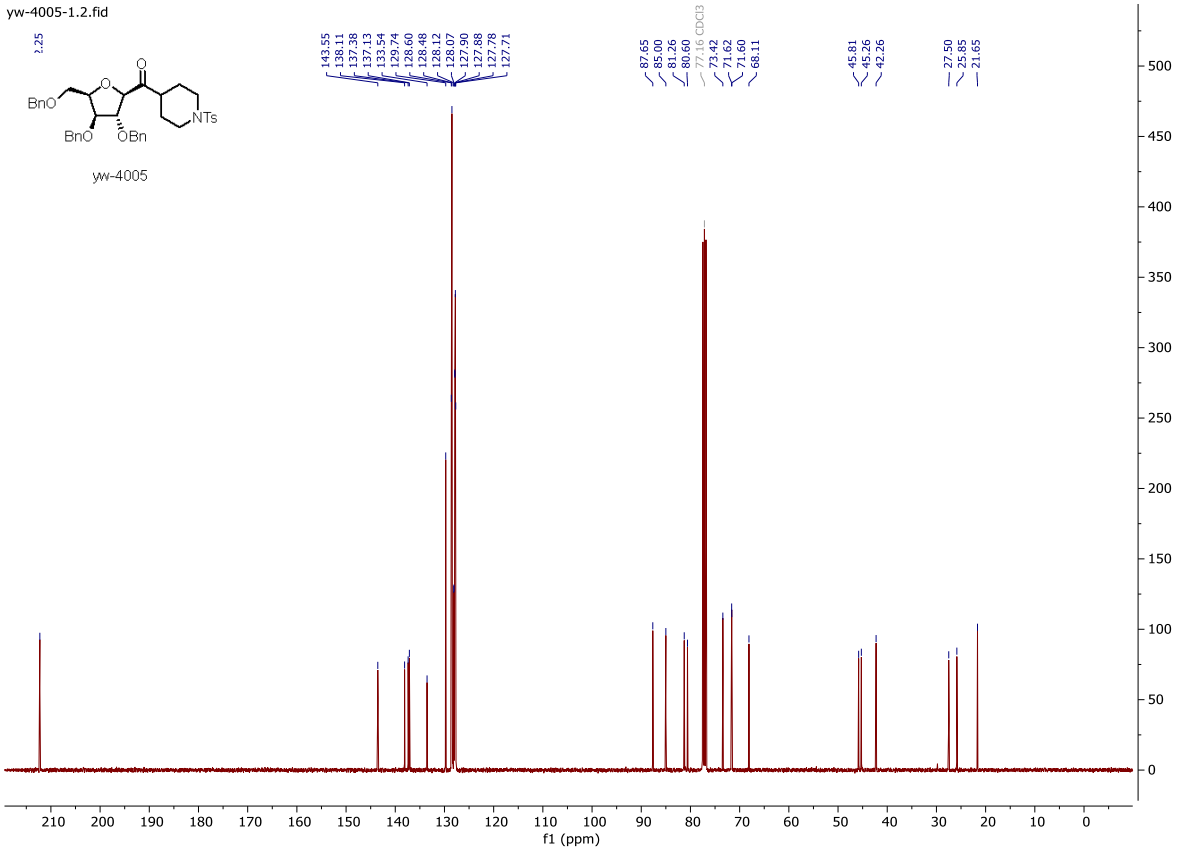
H-H COSY of **30**



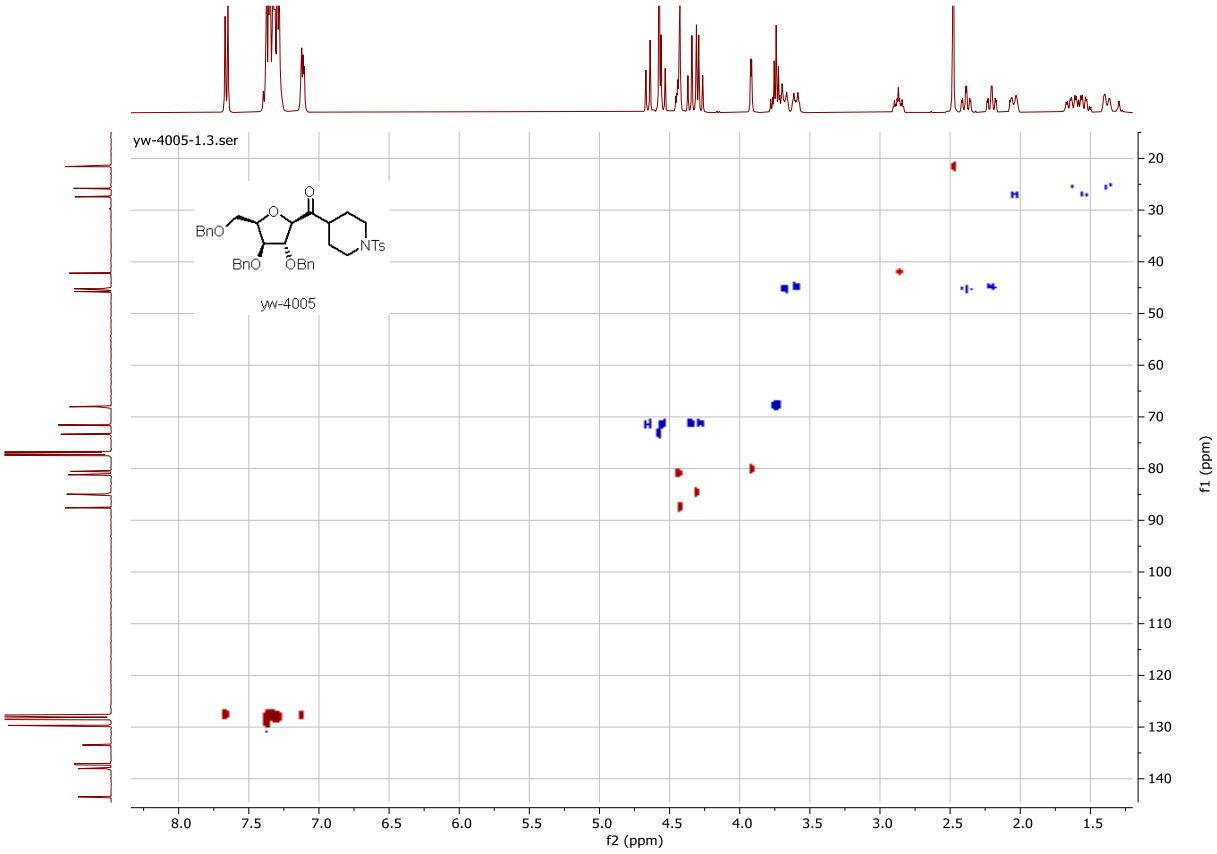
NOESY of **30**



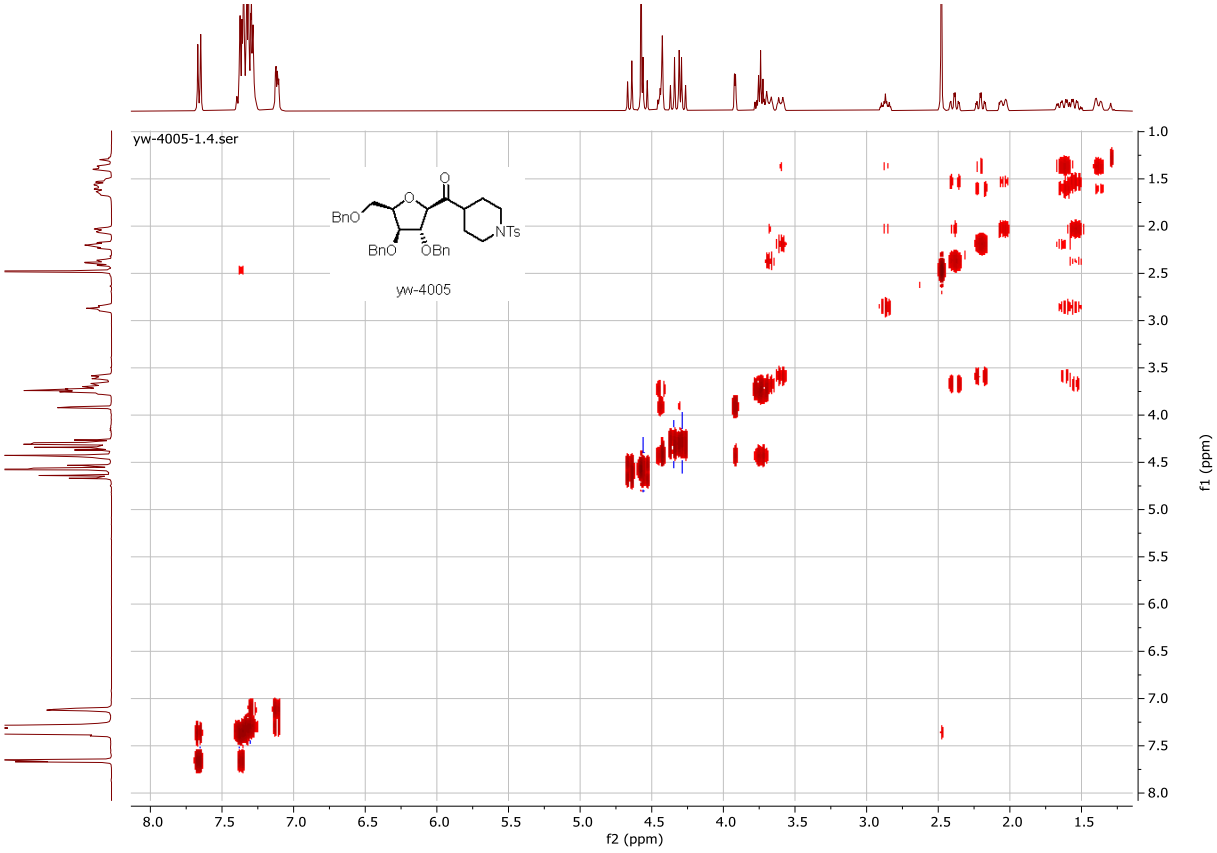
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **31**



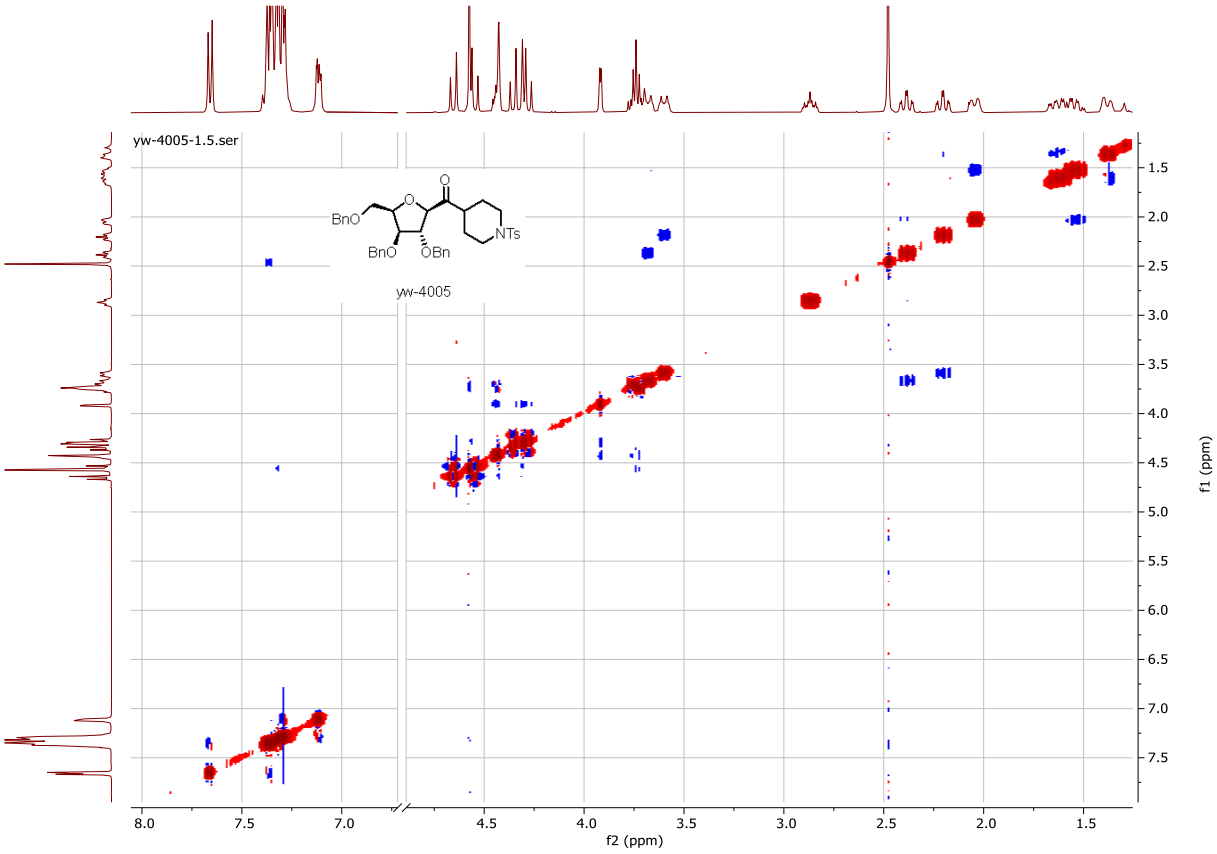
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **31**



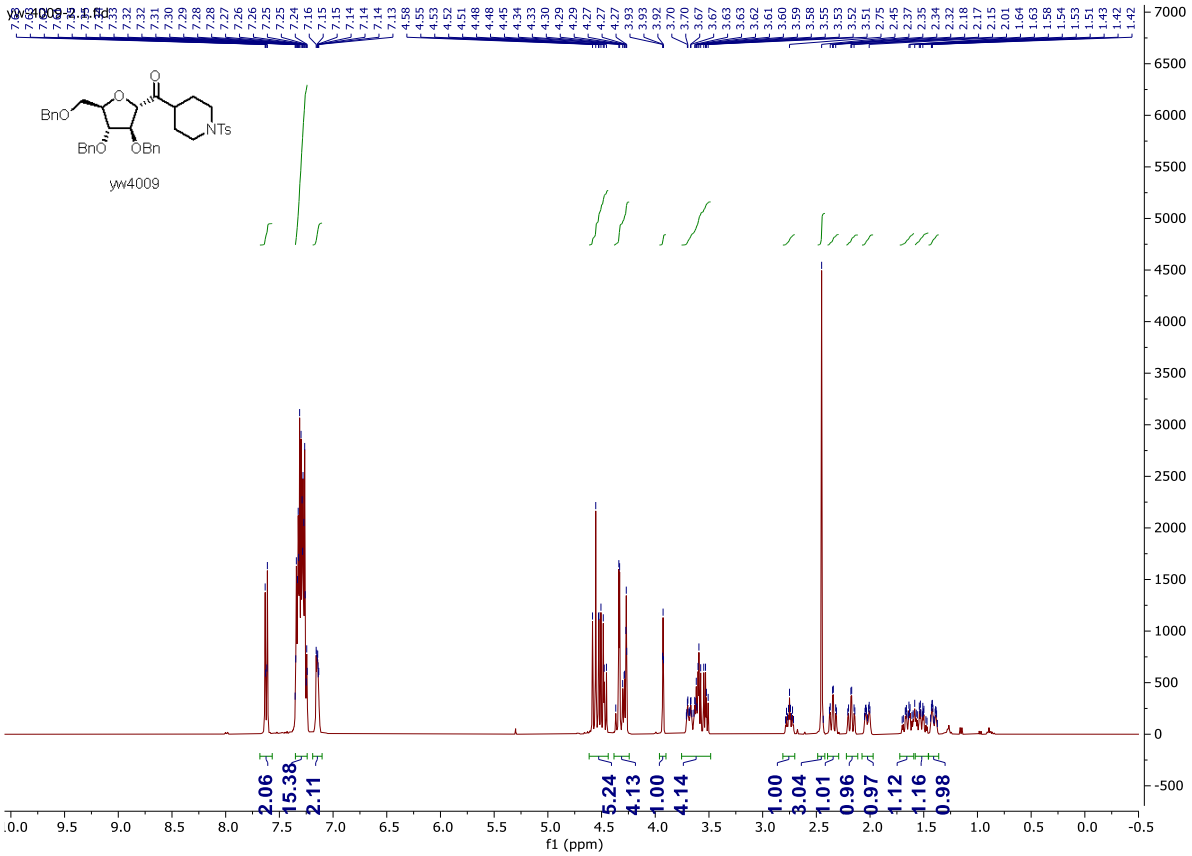
HSQCED of **31**



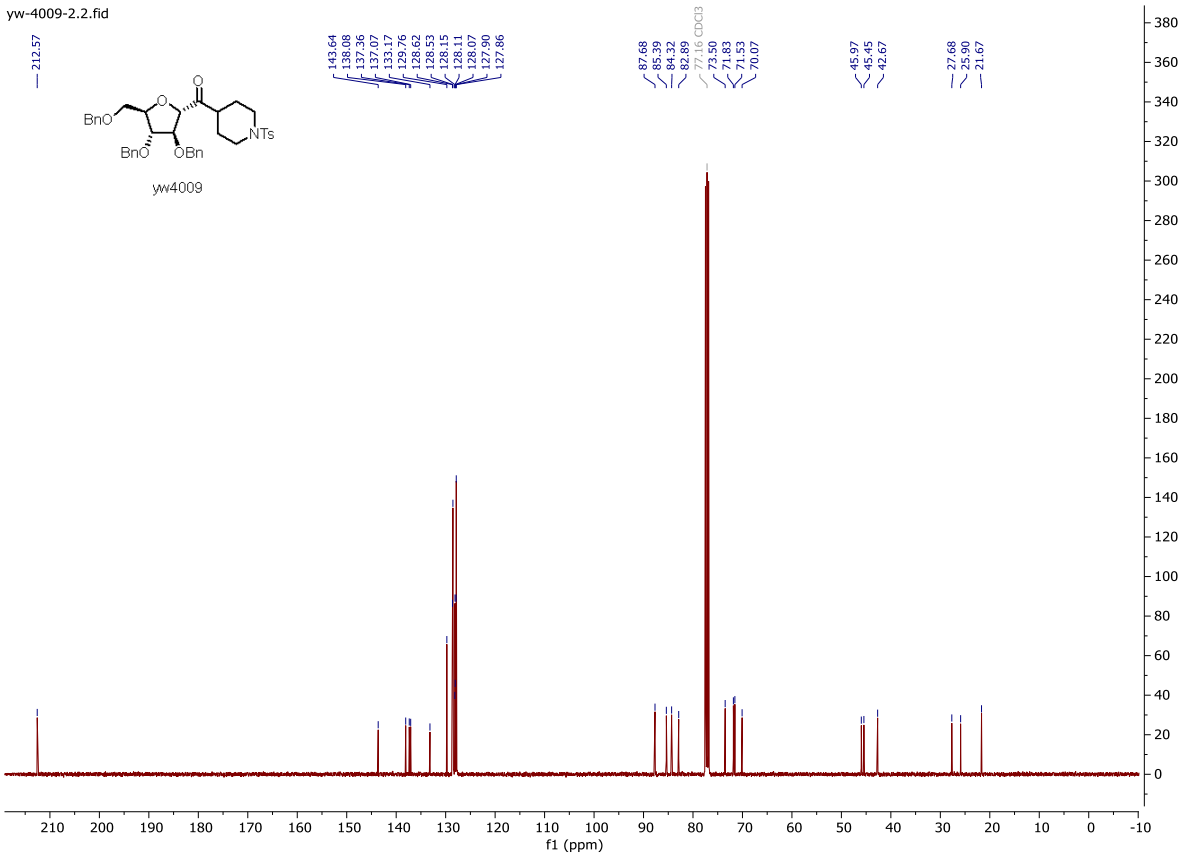
H-H COSY of **31**



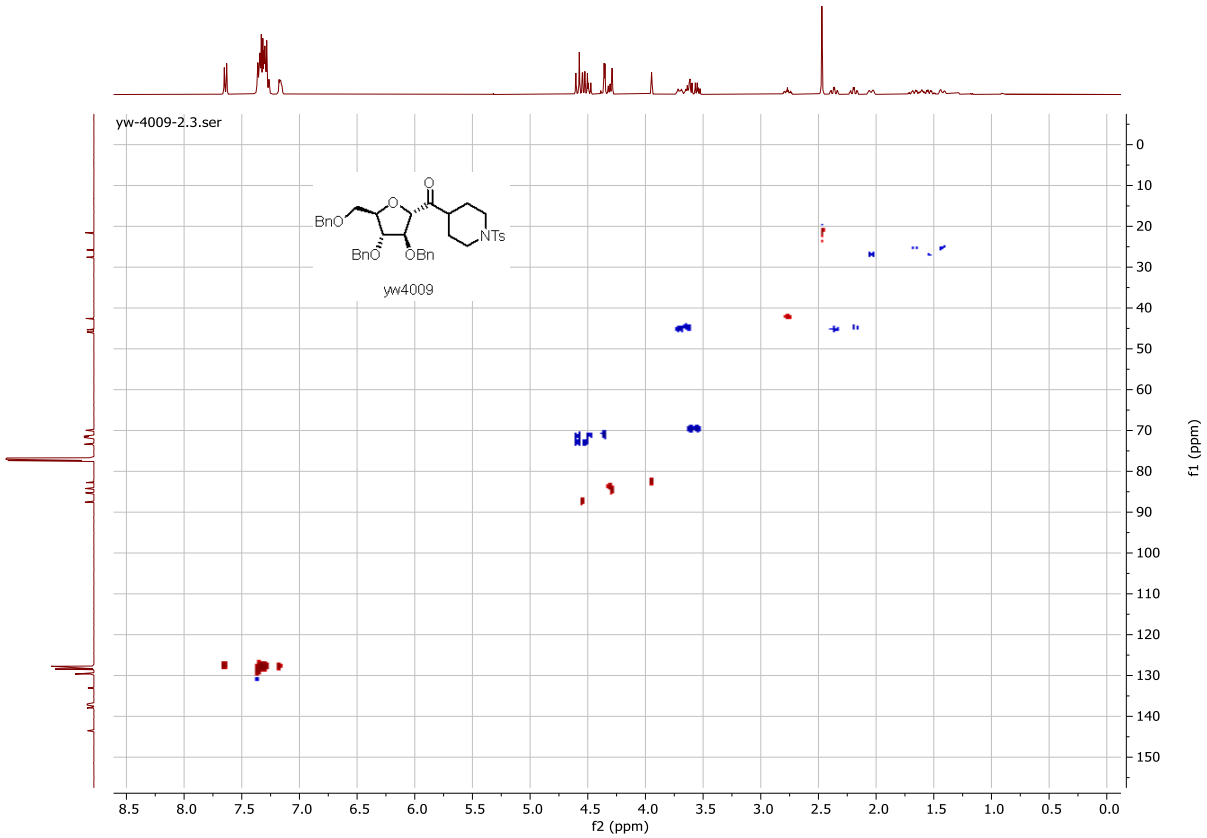
NOESY of **31**



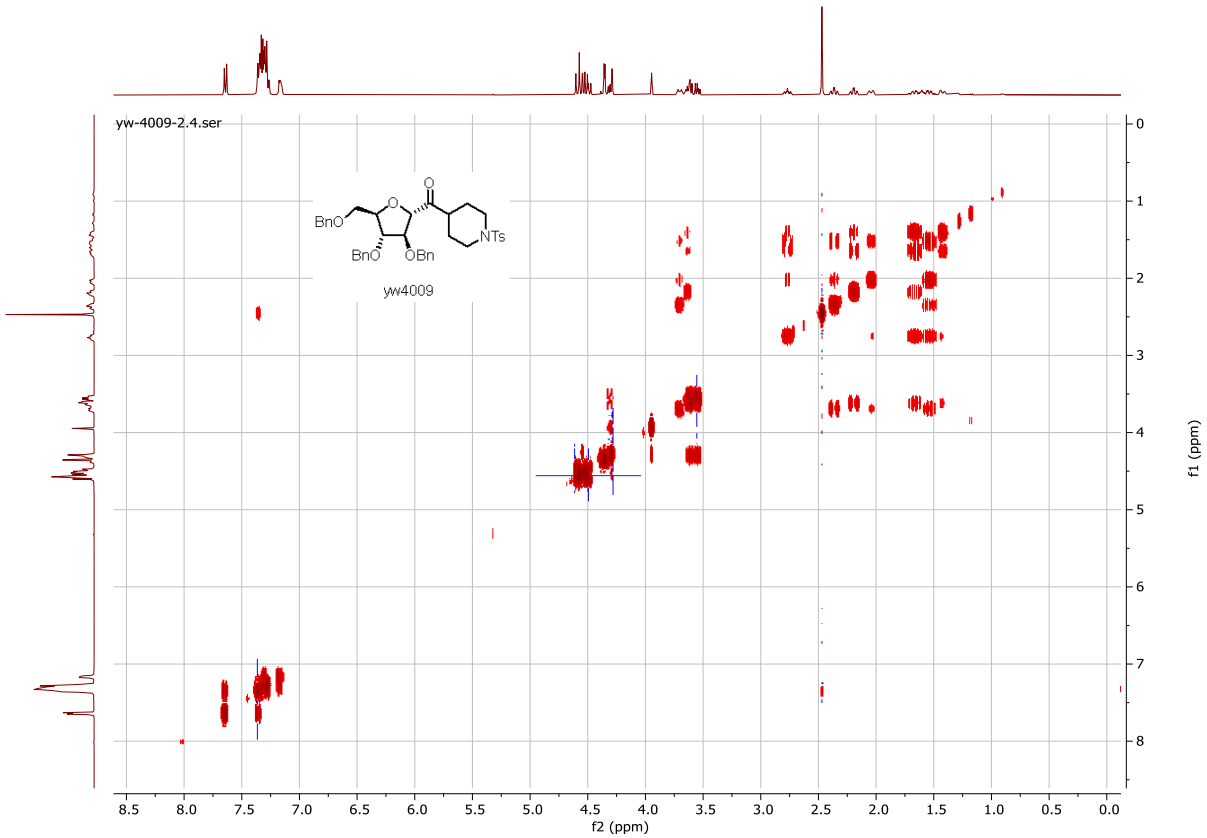
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **32**



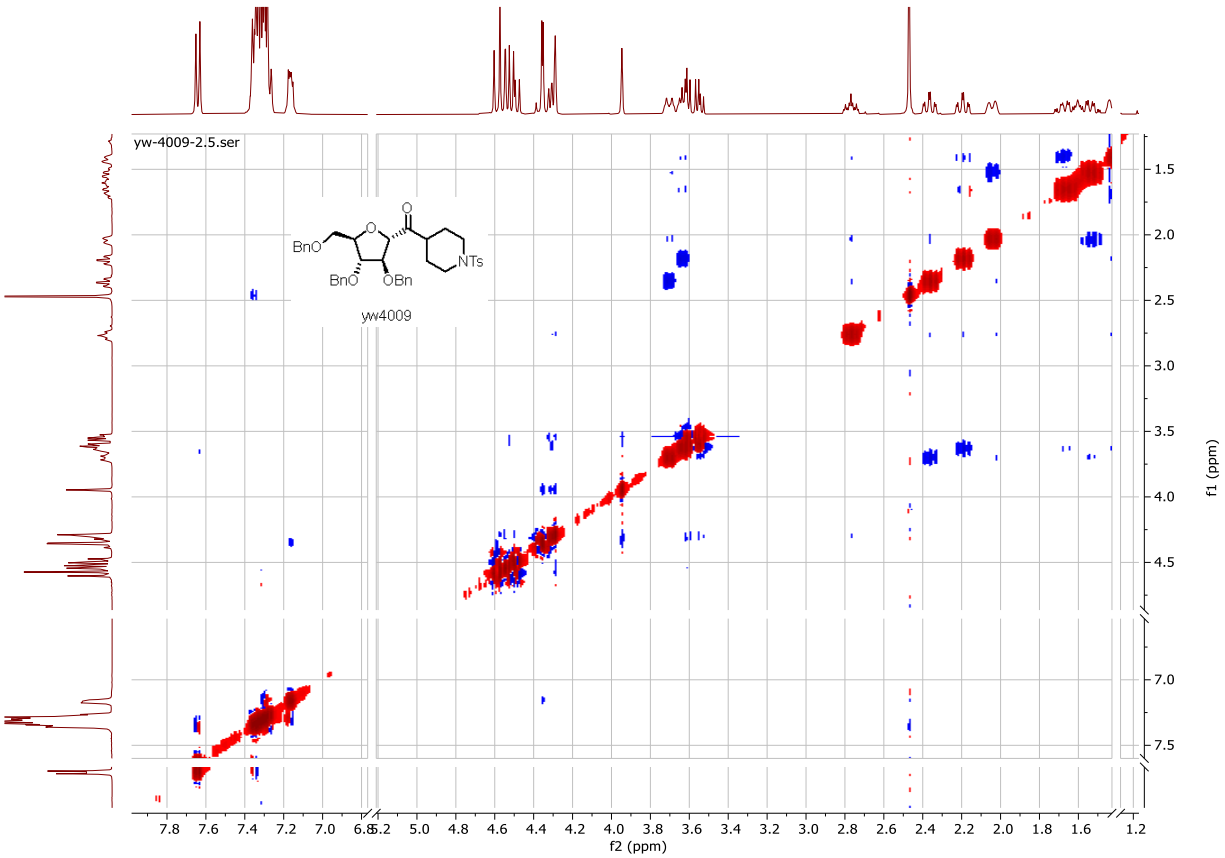
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **32**



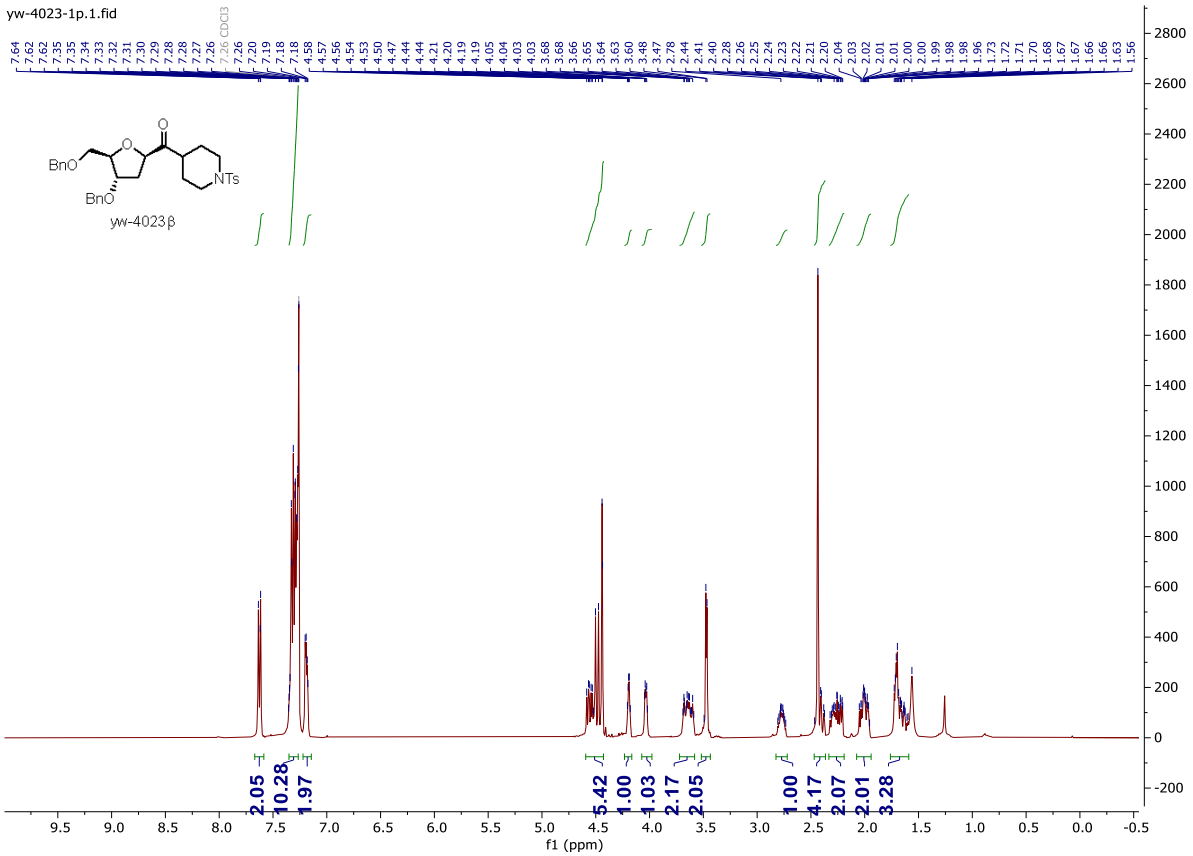
HSQCED of **32**



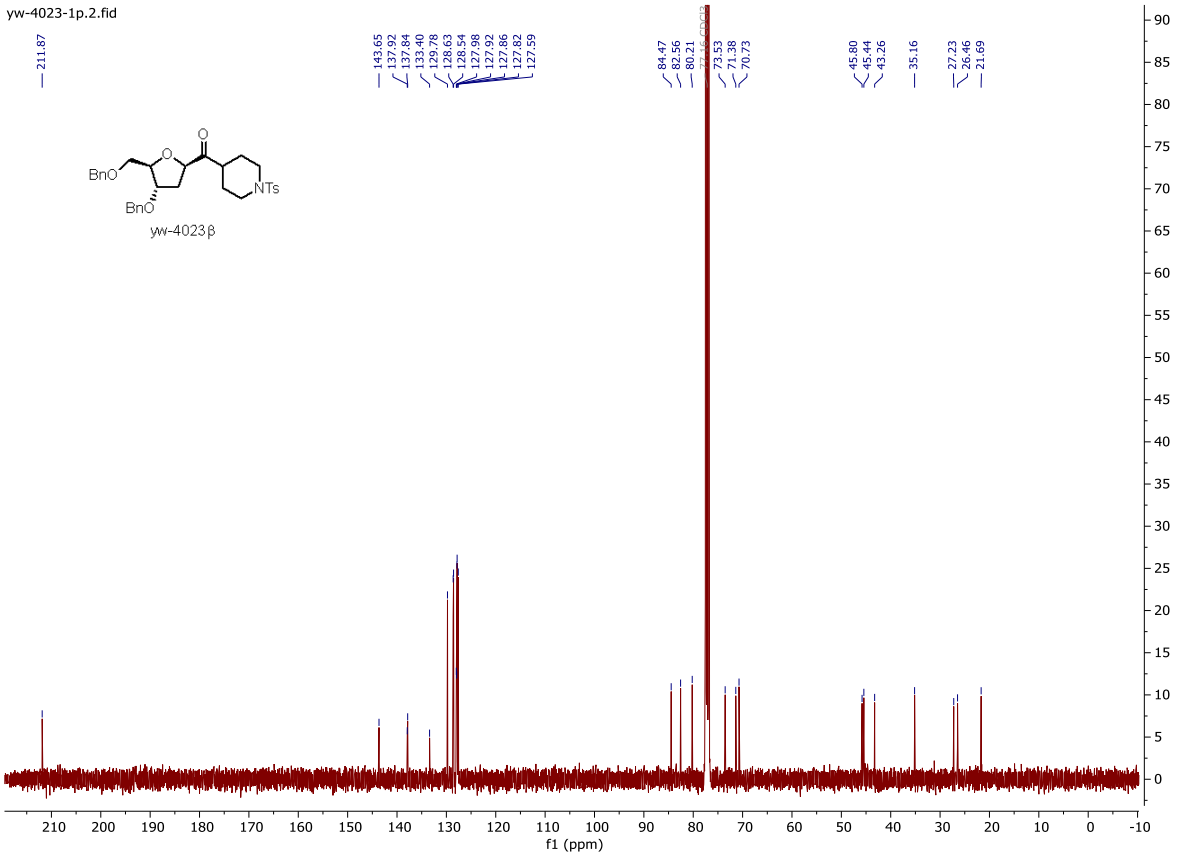
H-H COSY of **32**



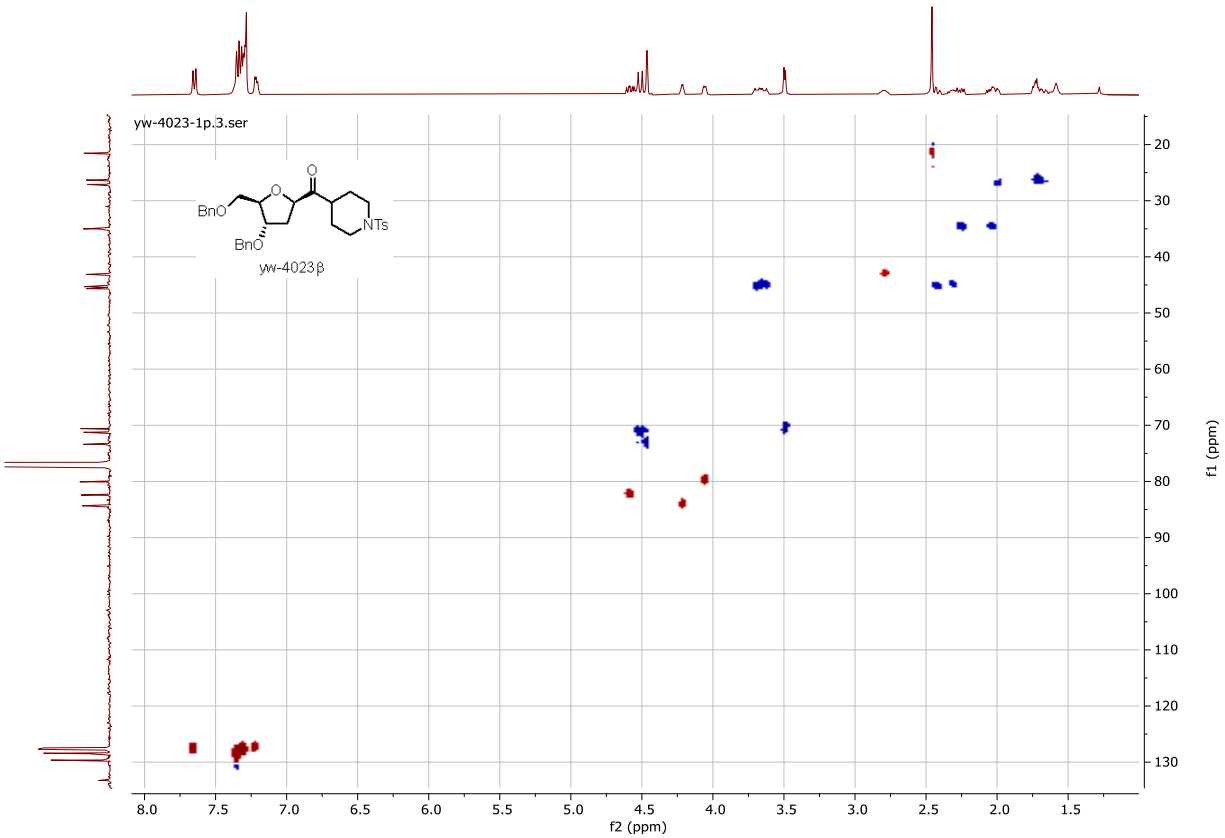
NOESY of **32**



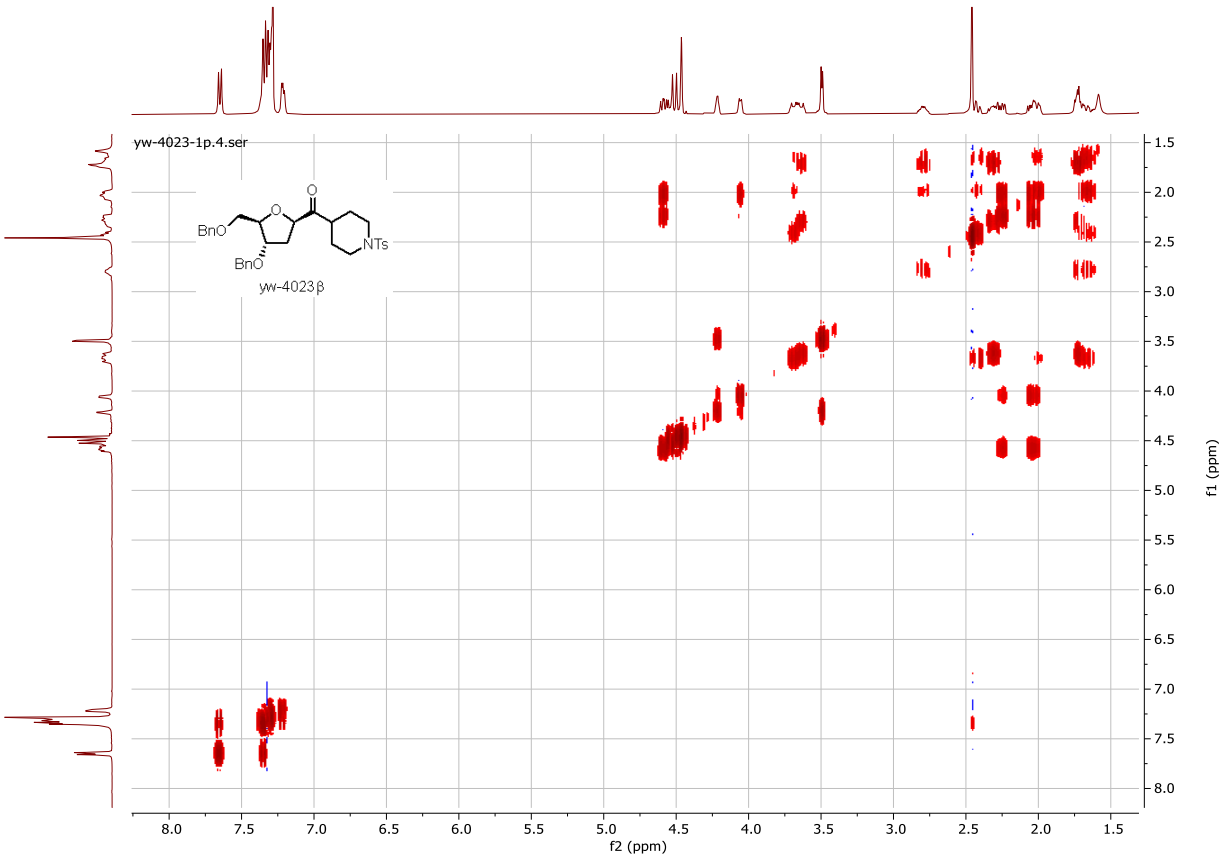
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **33β**



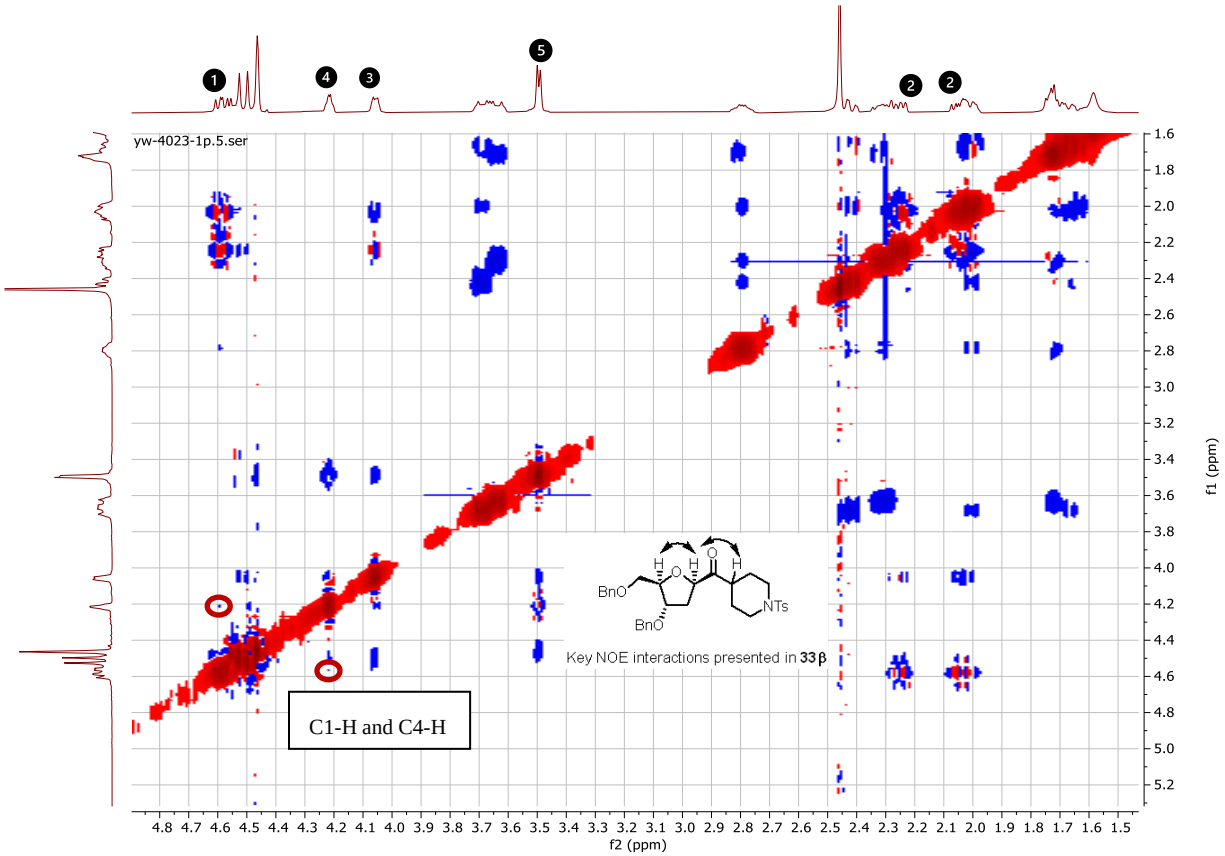
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **33β**



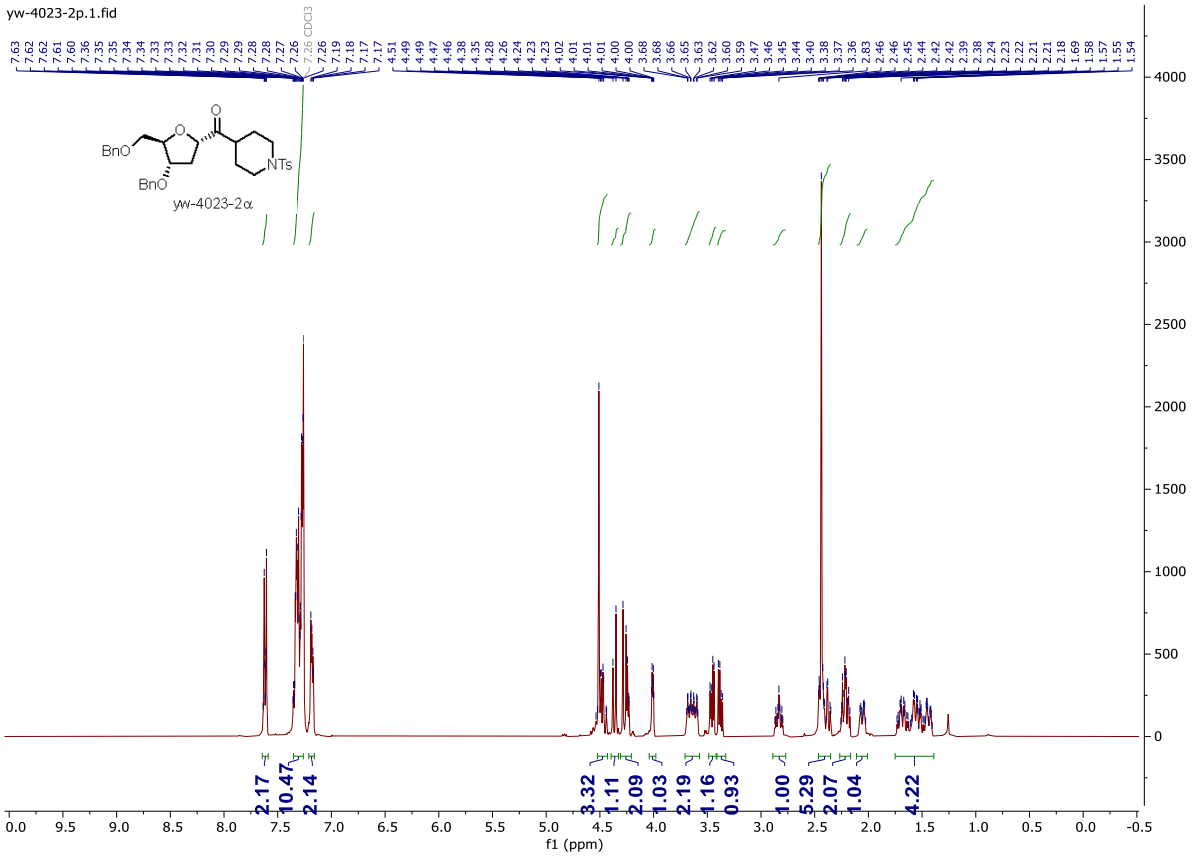
HSQCED of **33β**



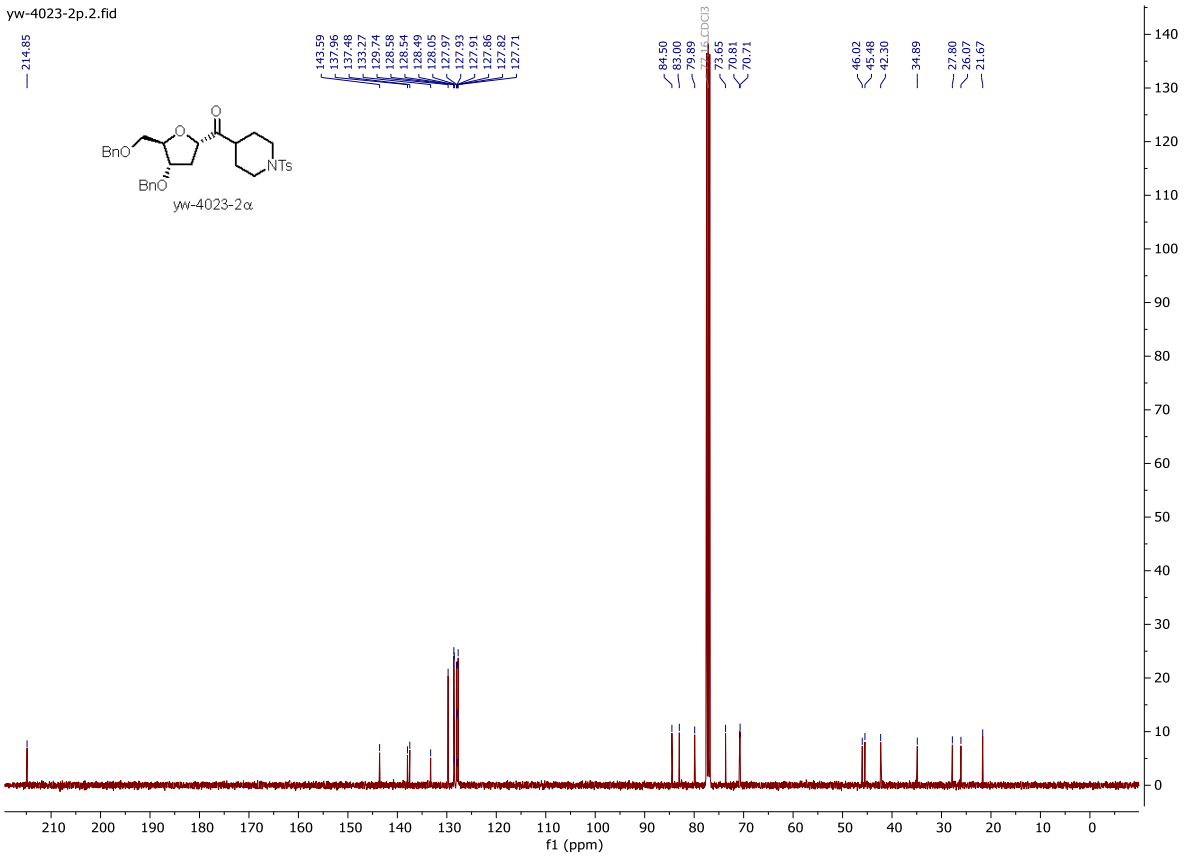
H-H COSY of **33β**



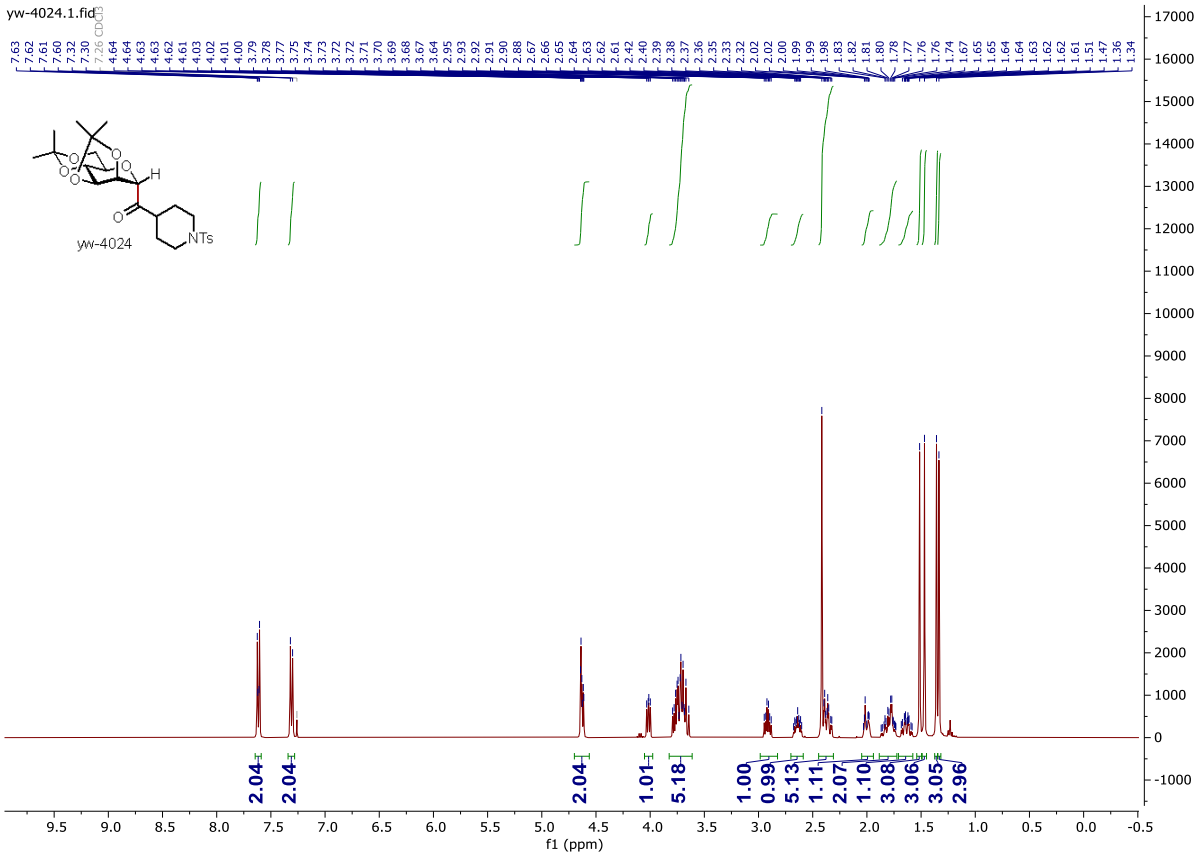
NOESY of **33β**



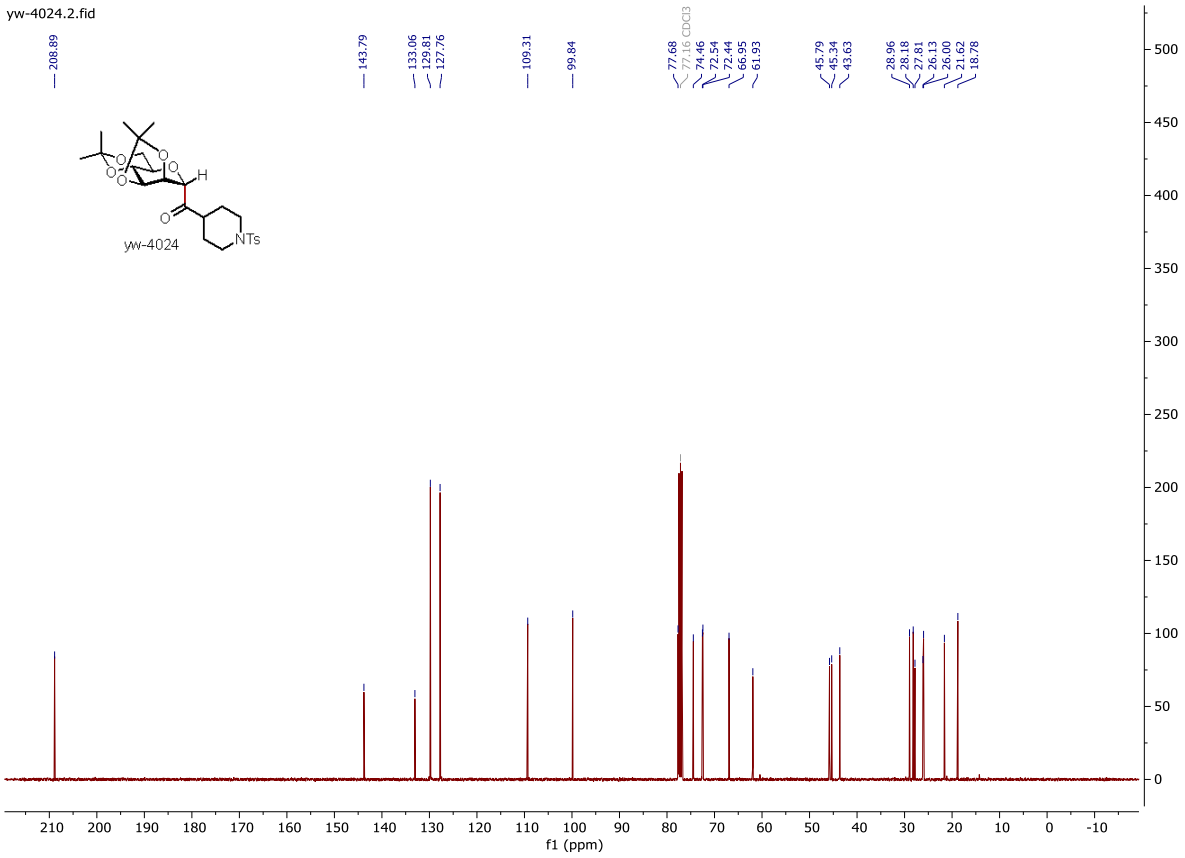
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **33α**



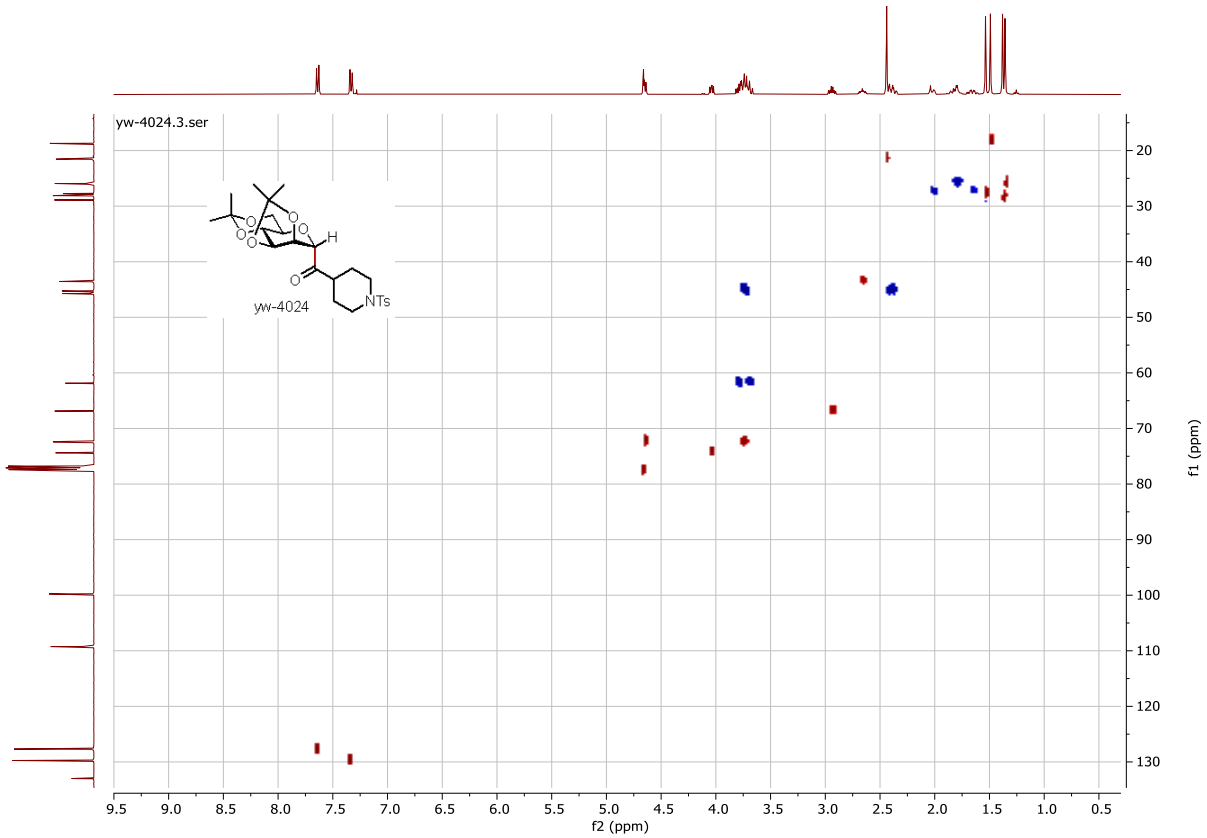
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **33α**



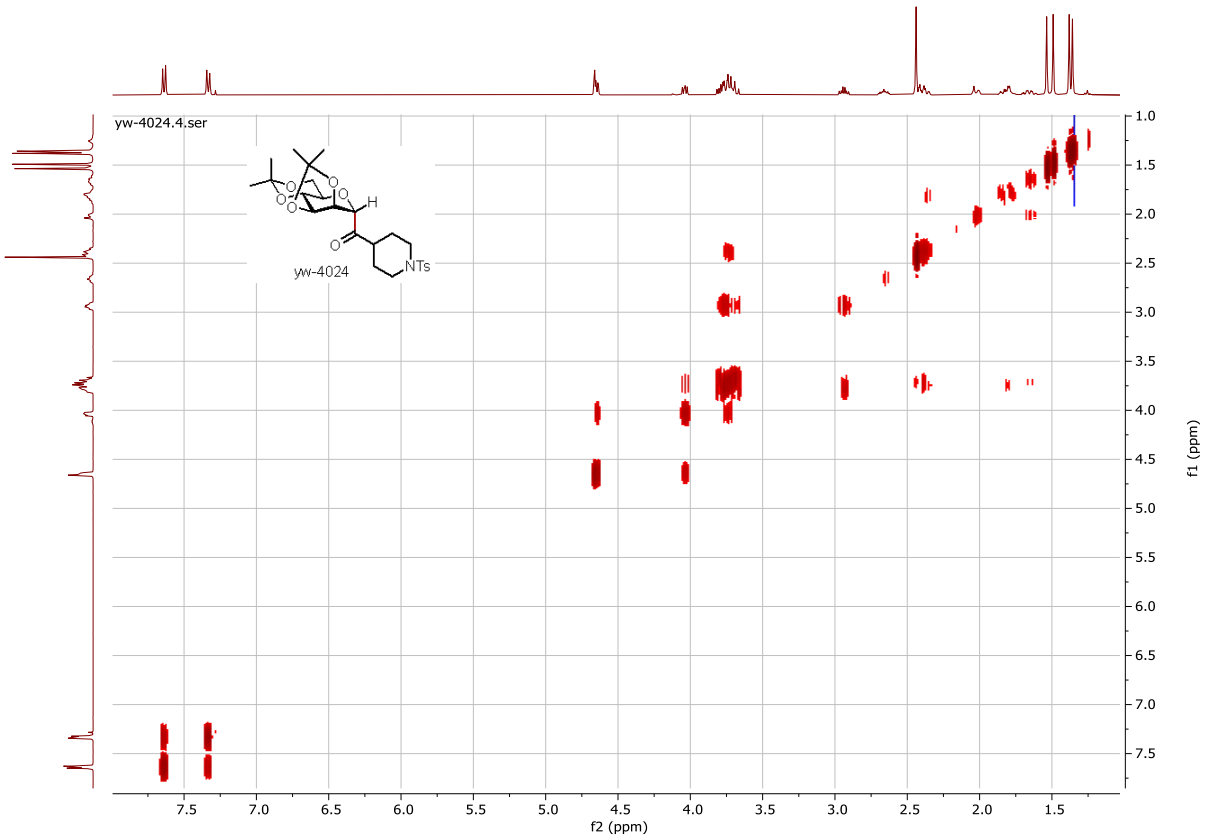
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **34**



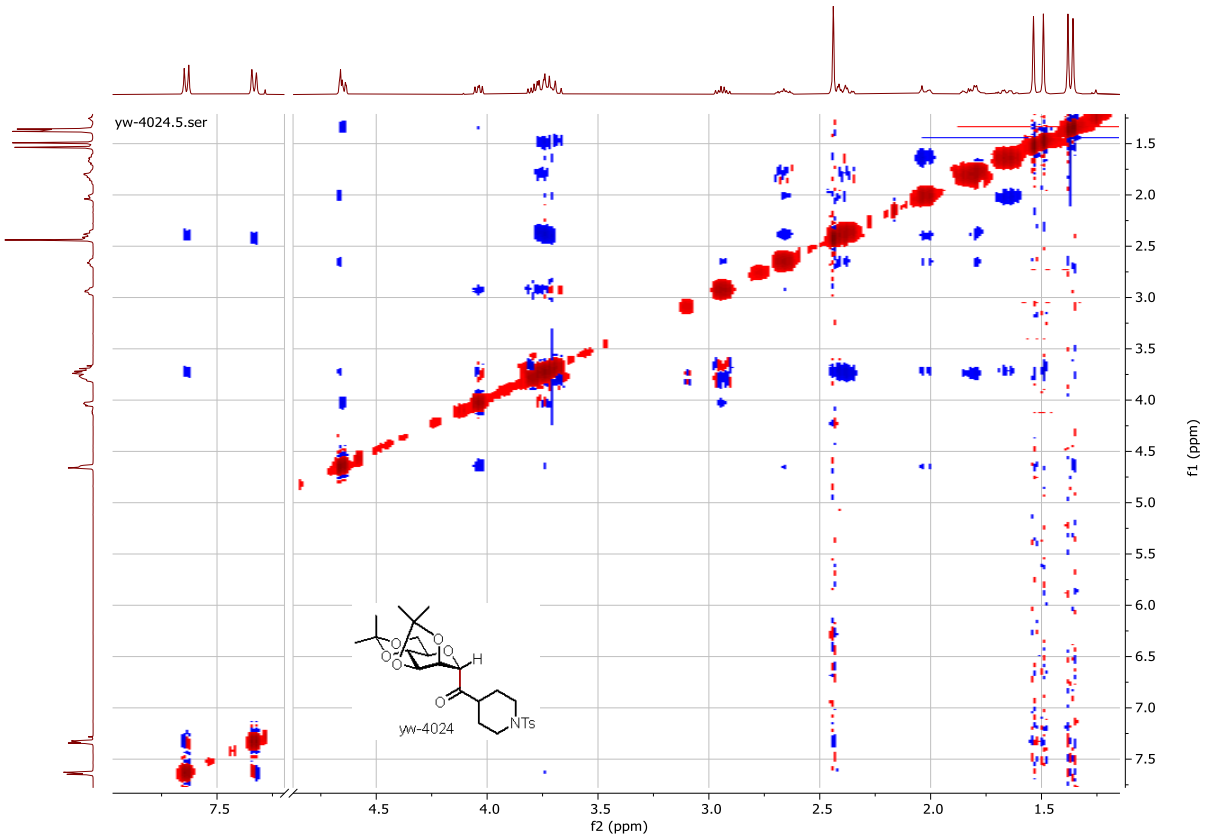
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **34**



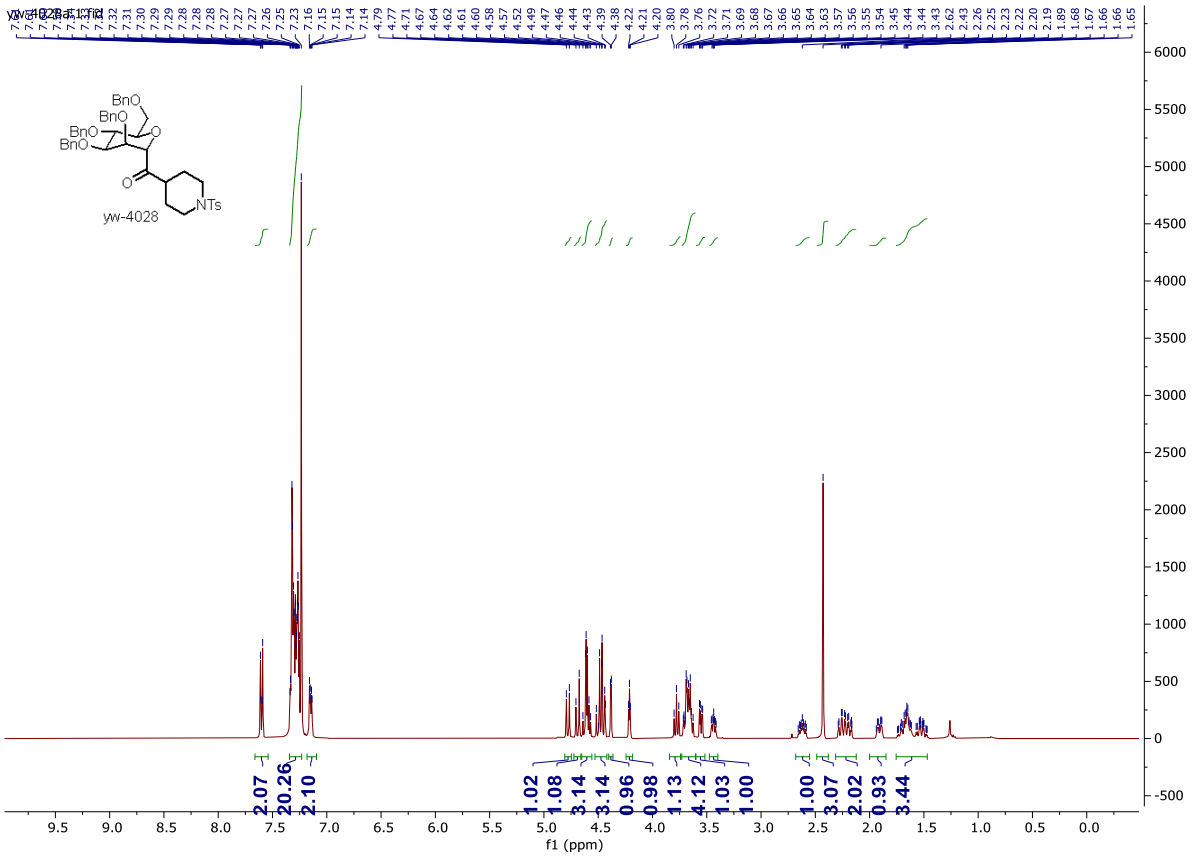
HSQCED of **34**



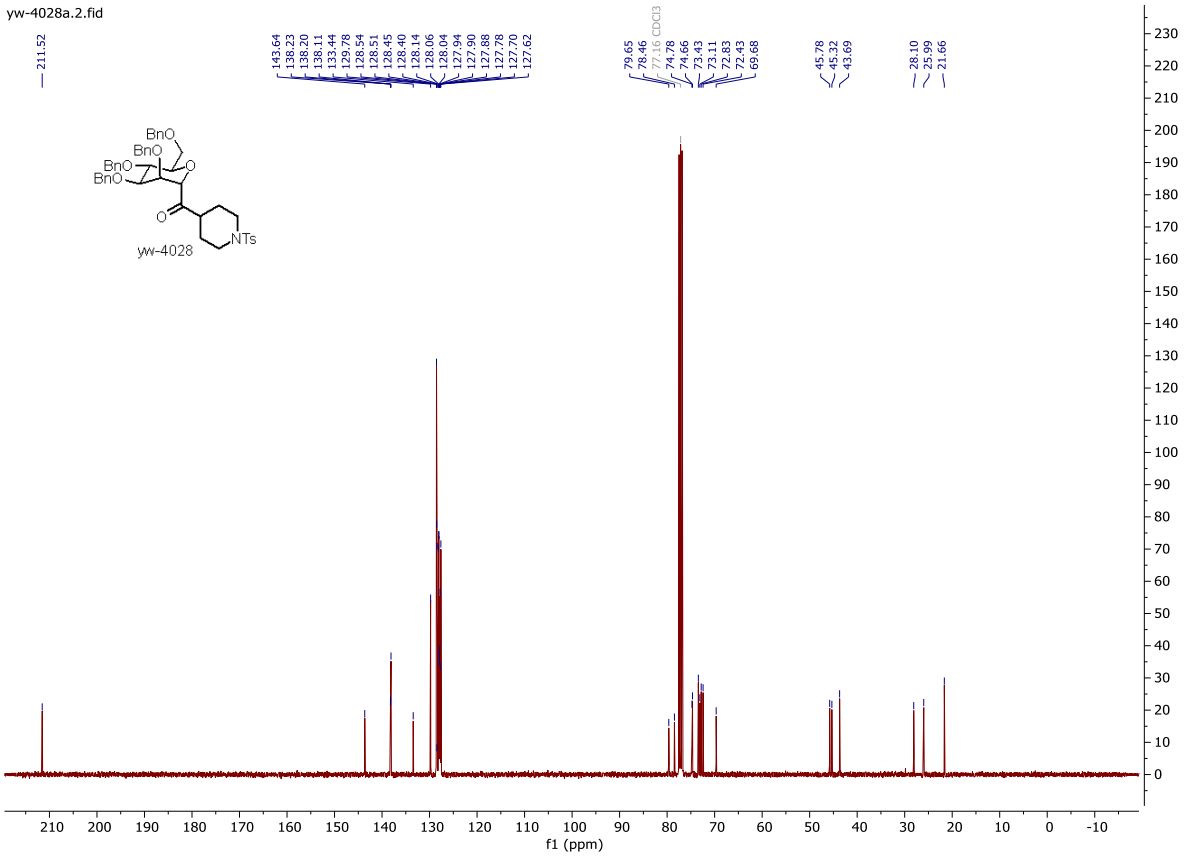
H-H COSY of **34**



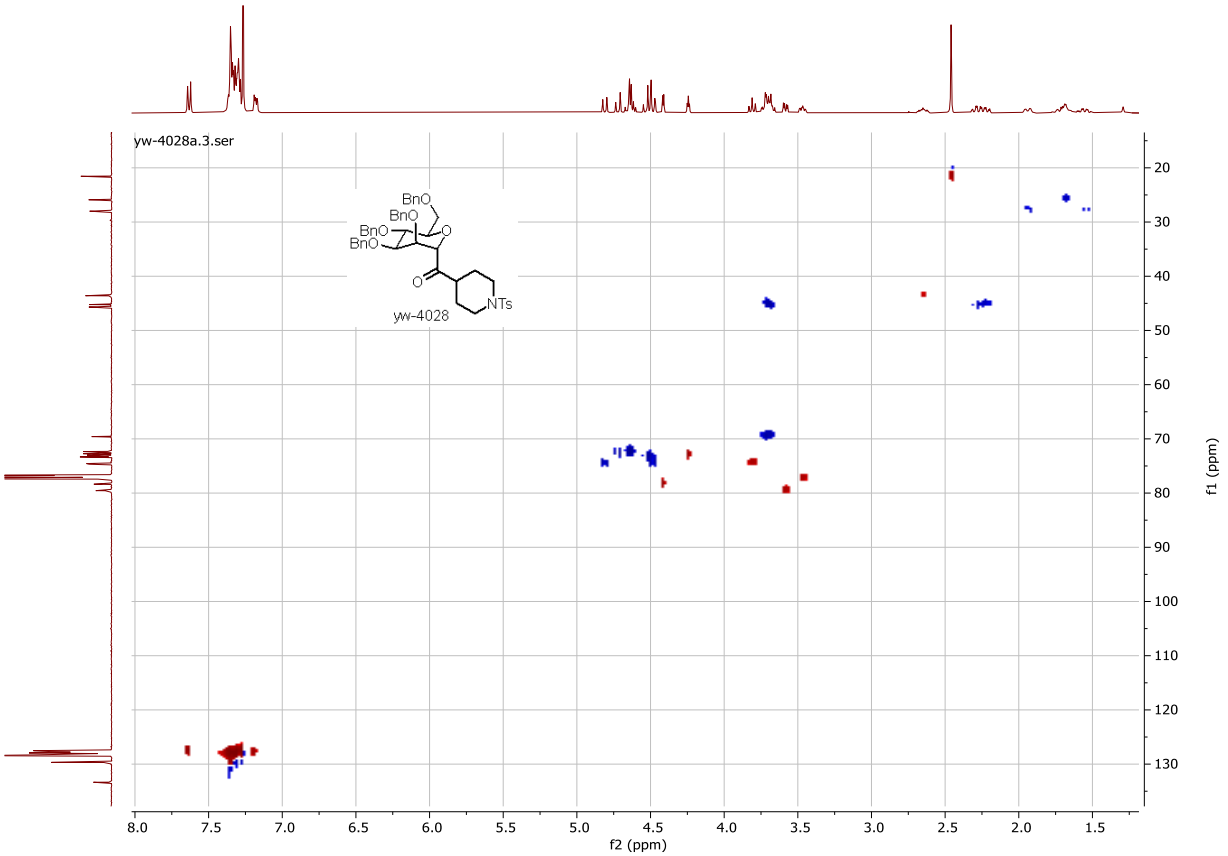
NOESY of **34**



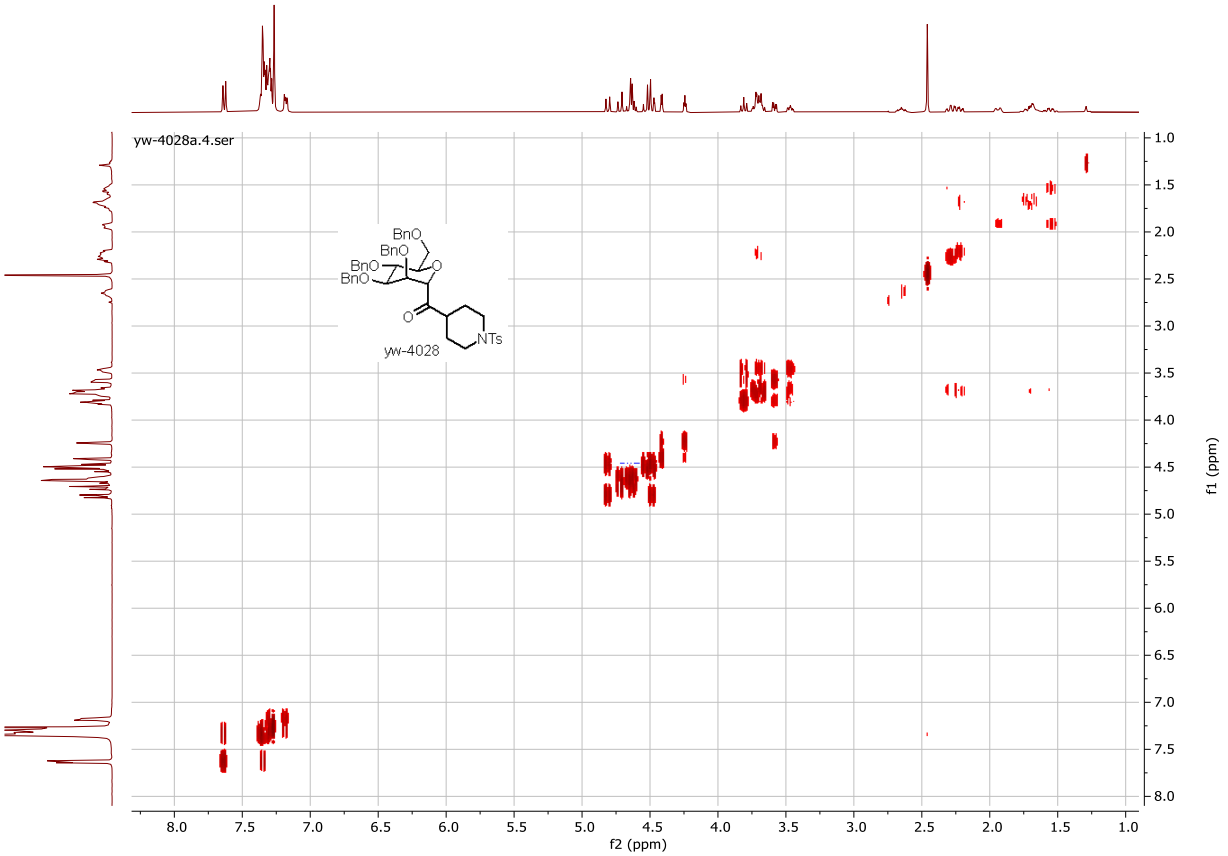
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **35**



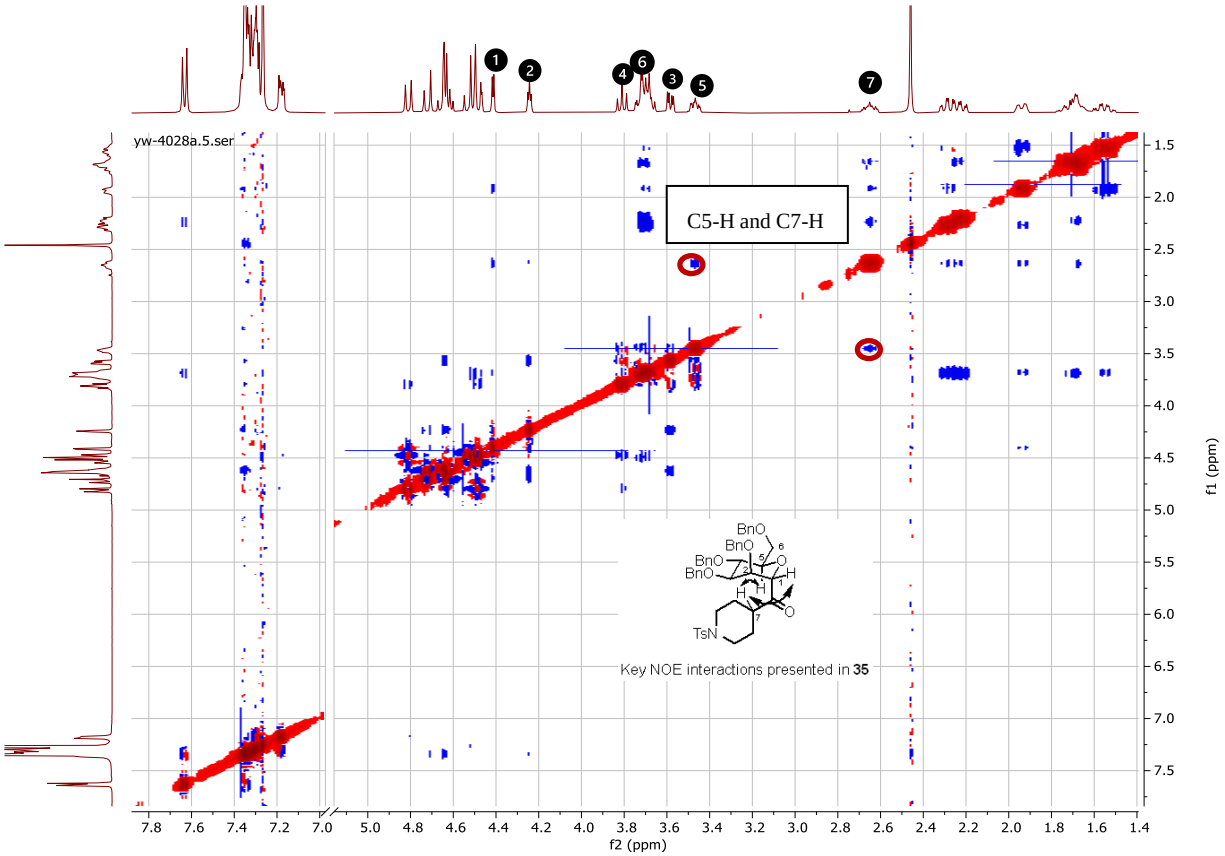
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **35**



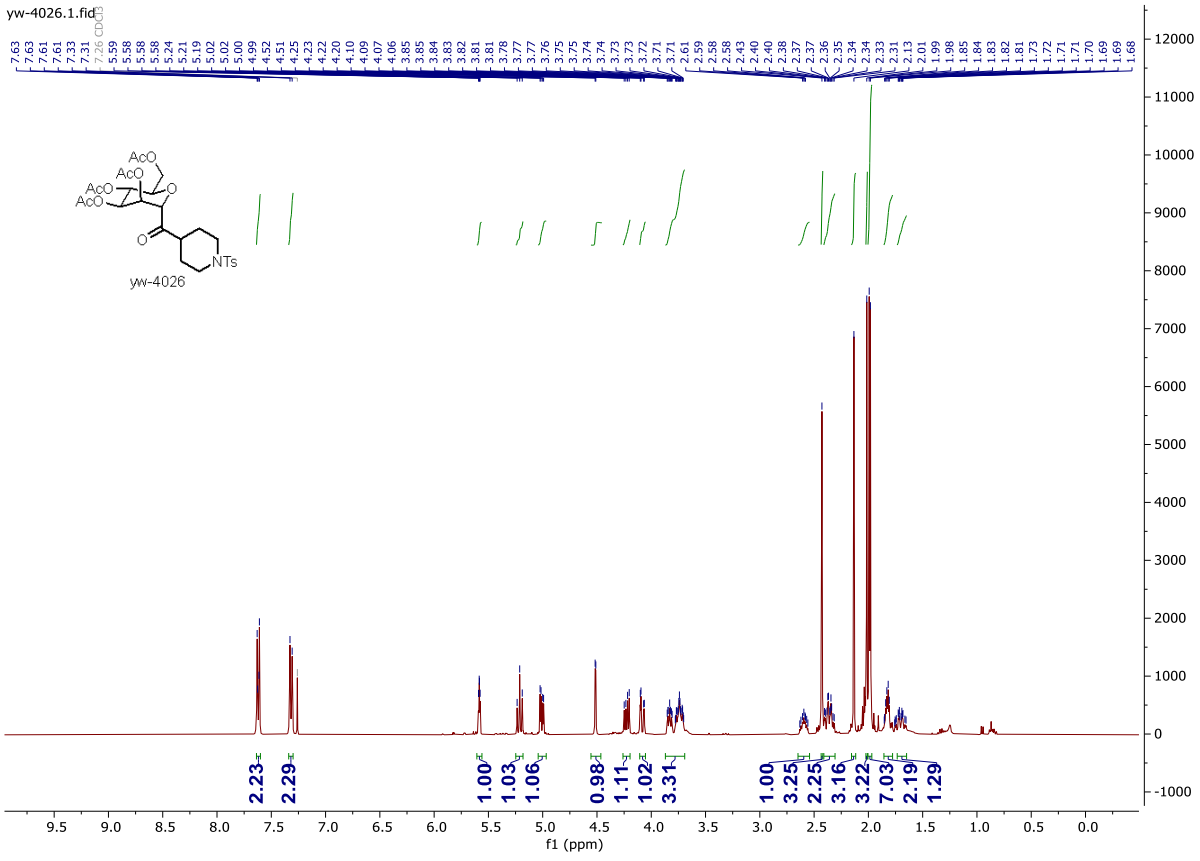
HSQCED of **35**



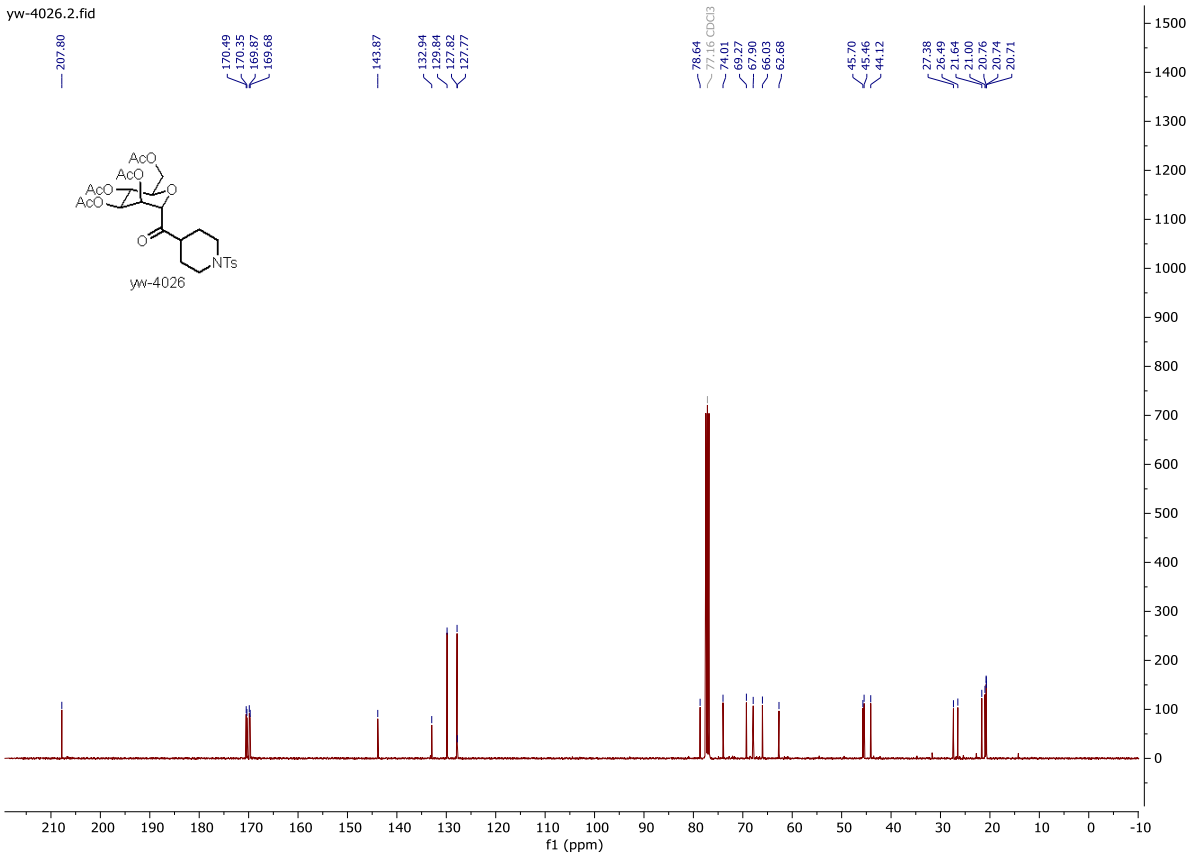
H-H COSY of **35**



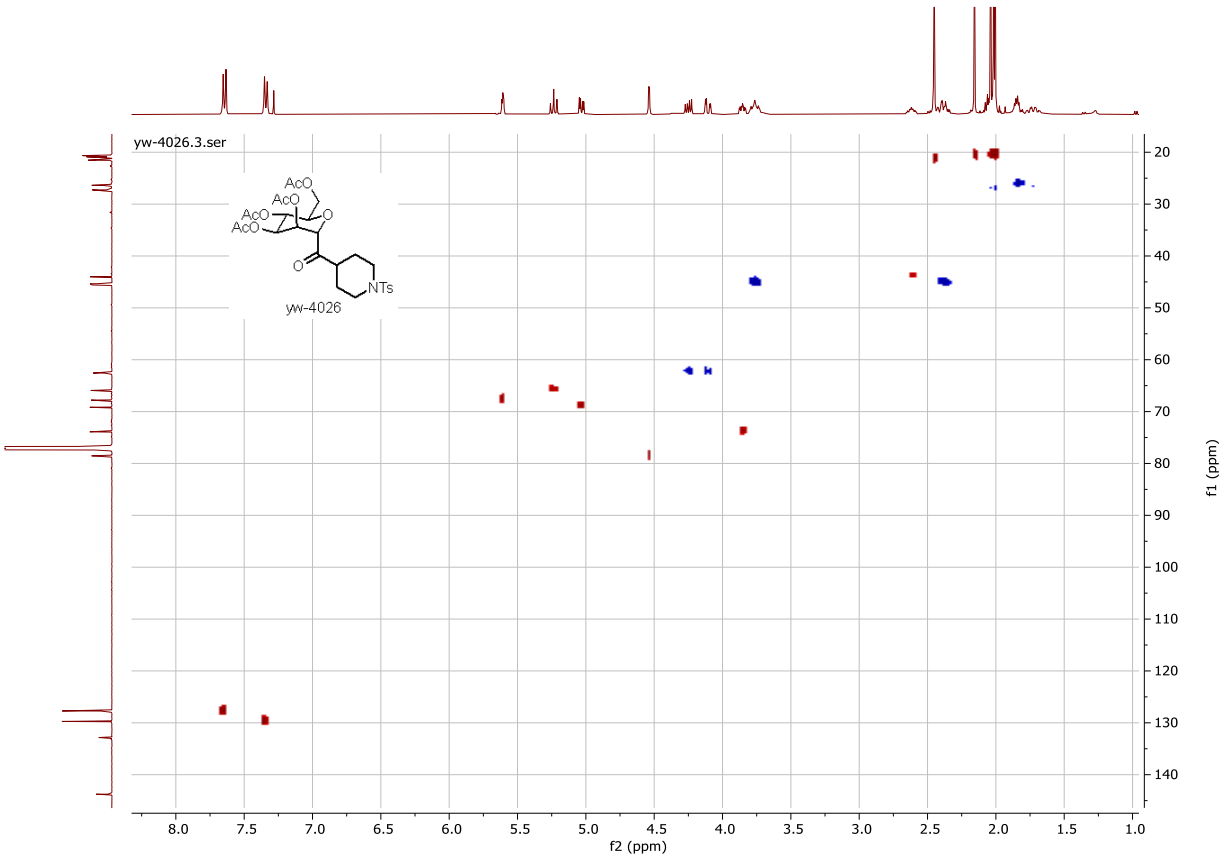
NOESY of **35**



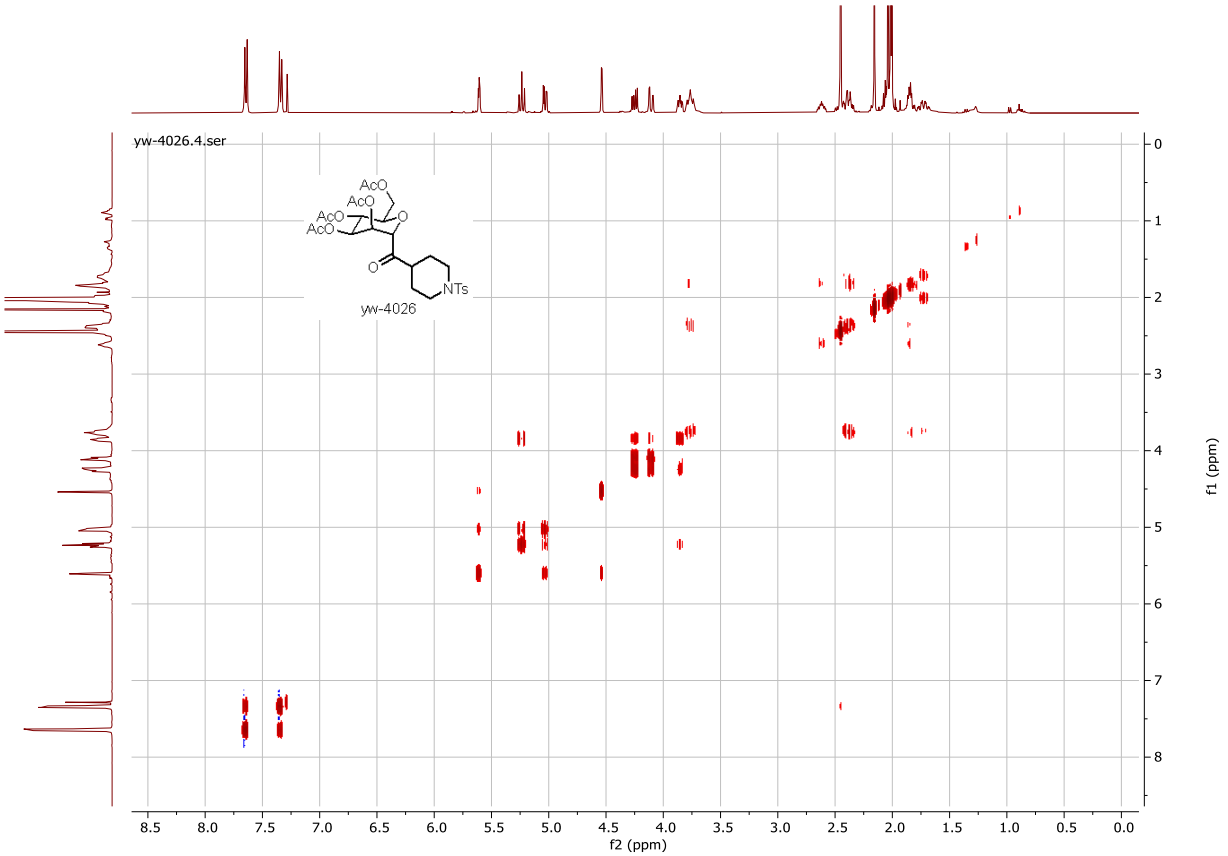
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **36**



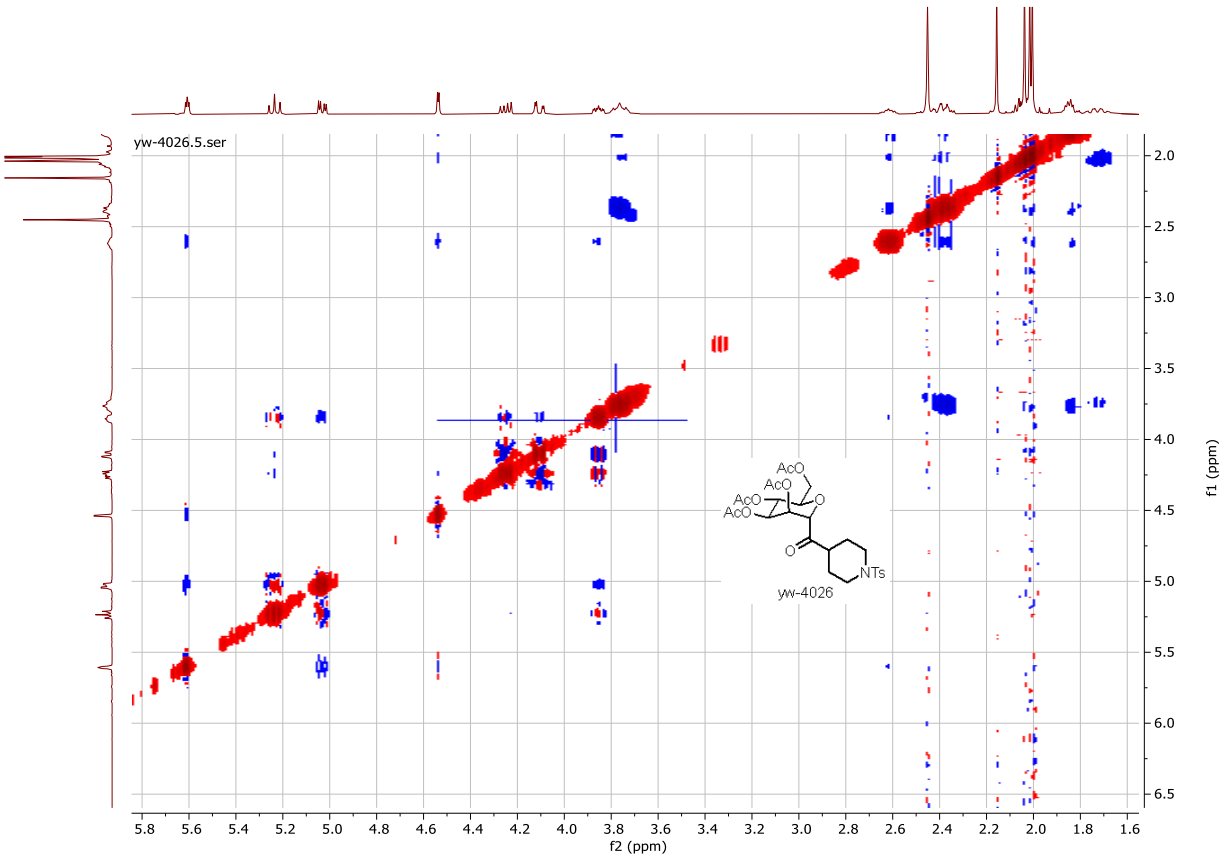
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **36**



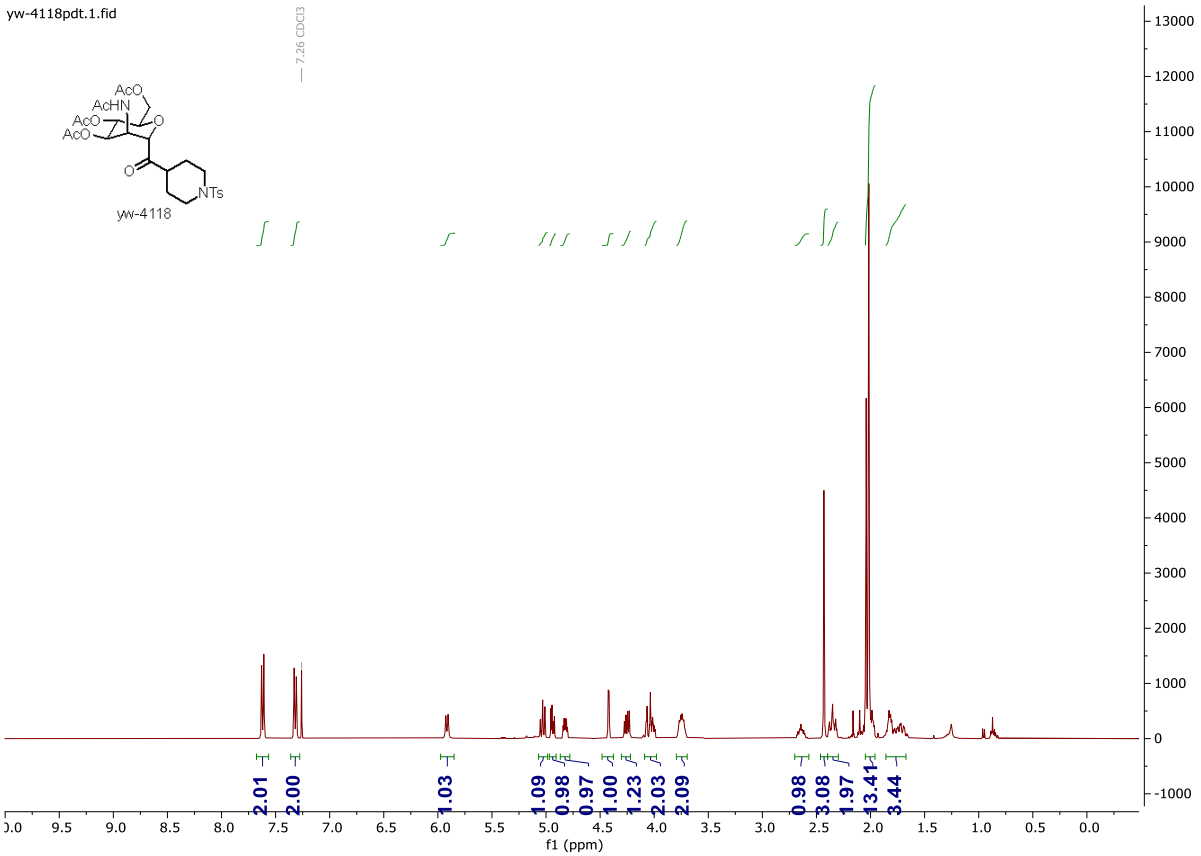
HSQCED of **36**



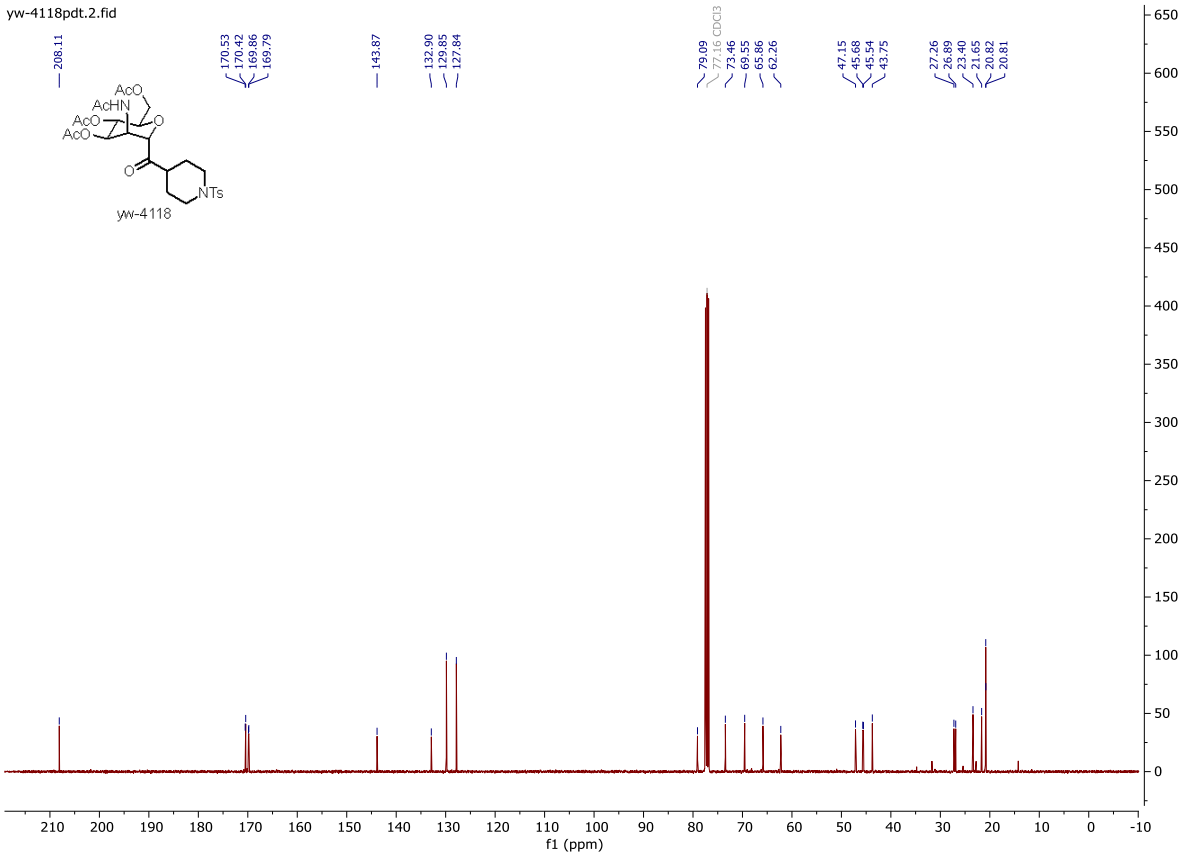
H-H COSY of **36**



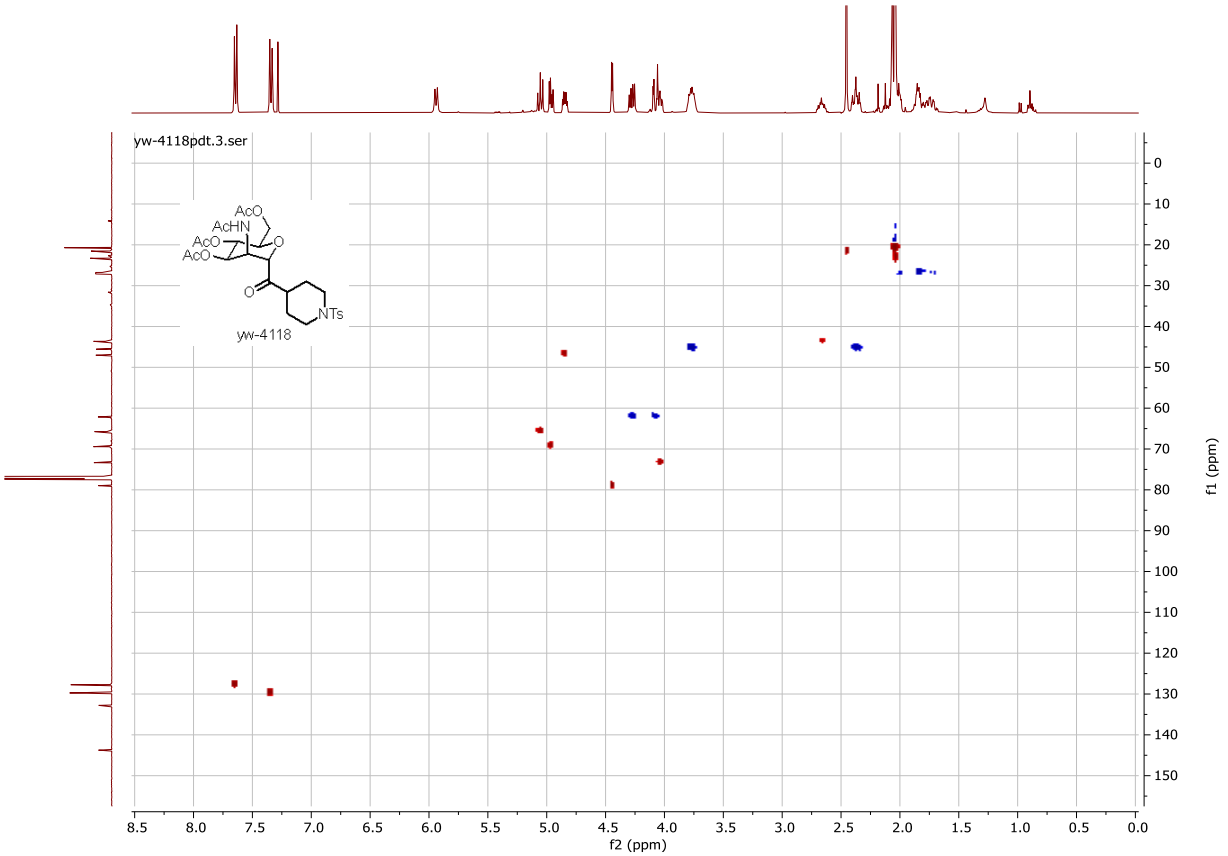
NOESY of **36**



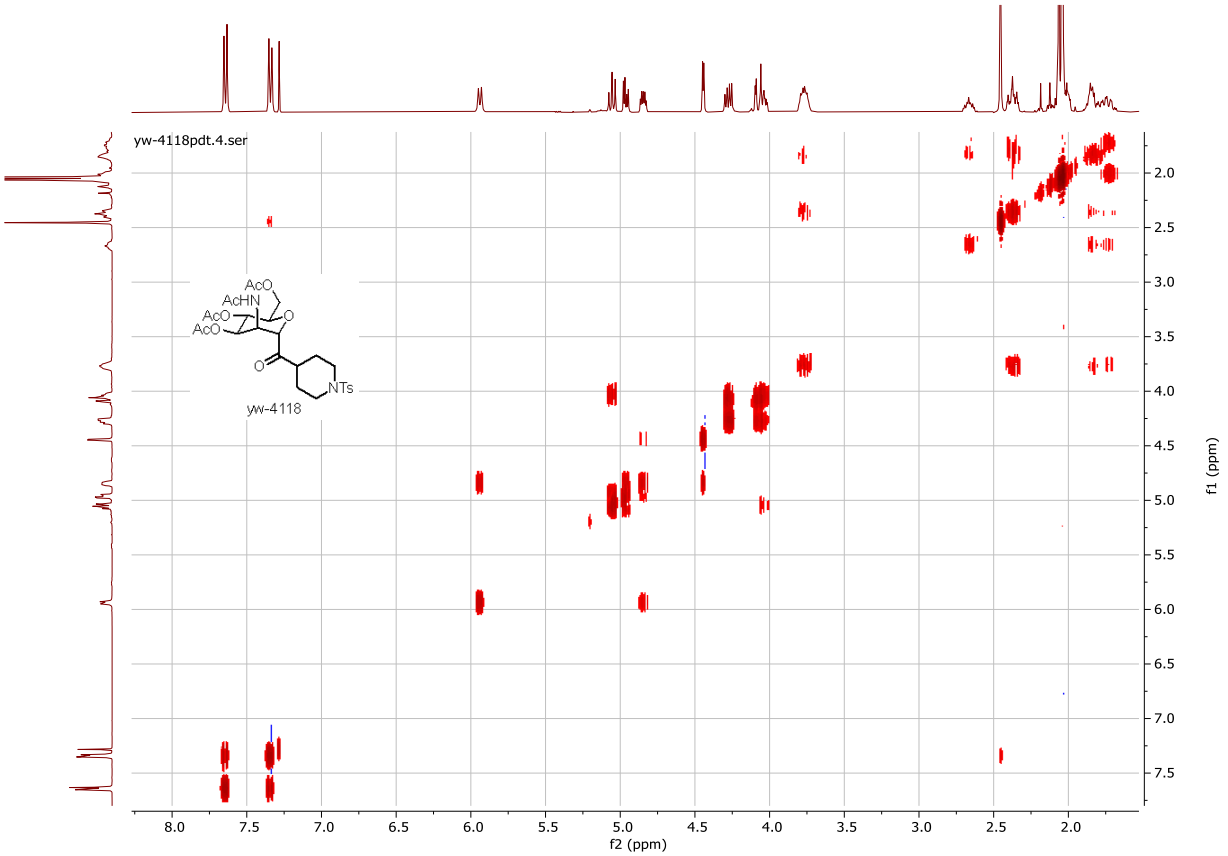
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **37**



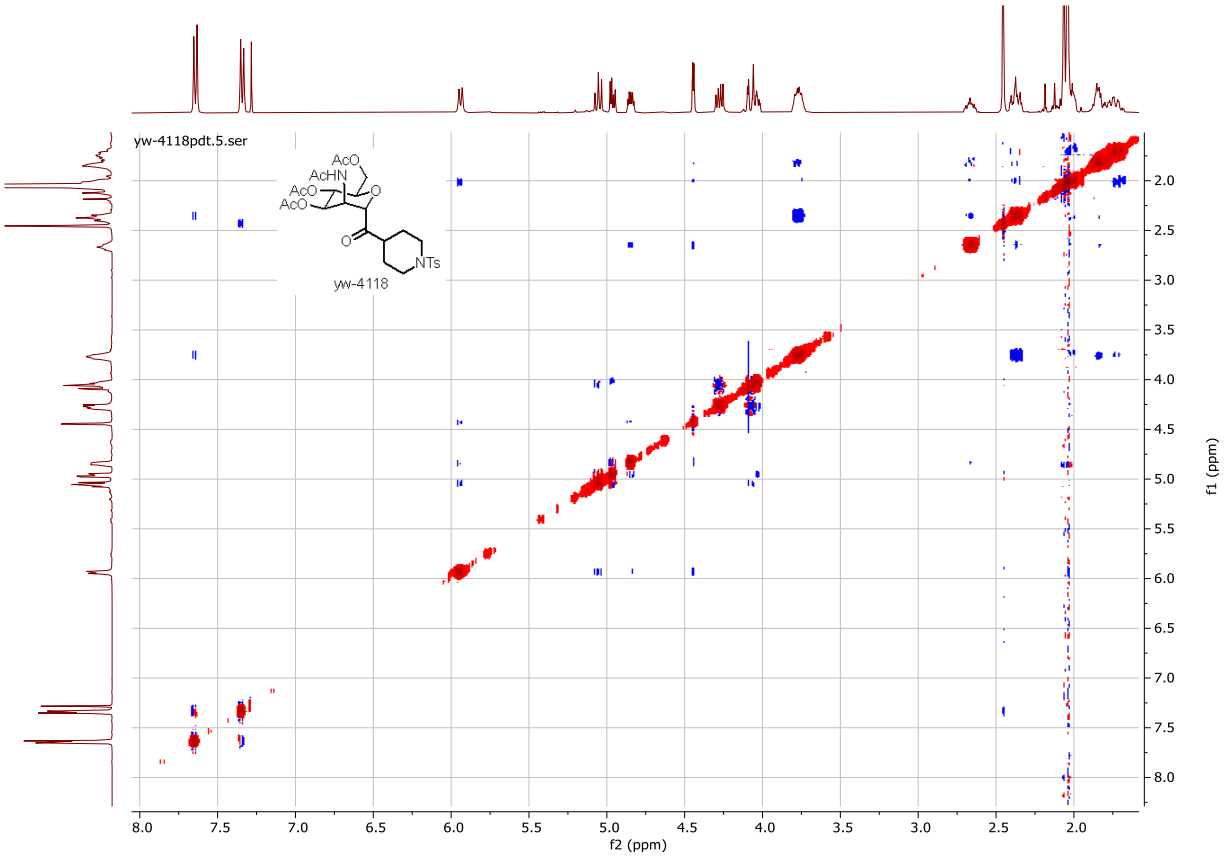
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **37**



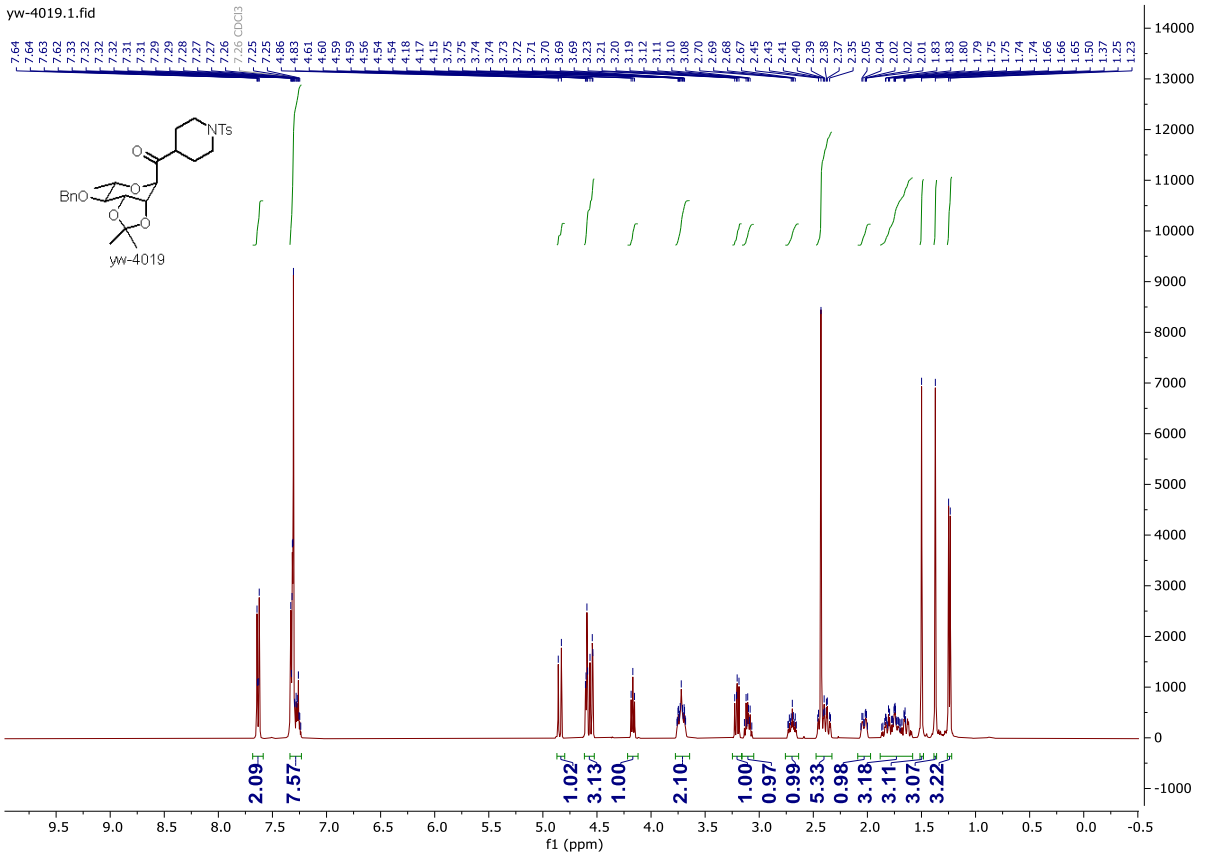
HSQCED of **37**



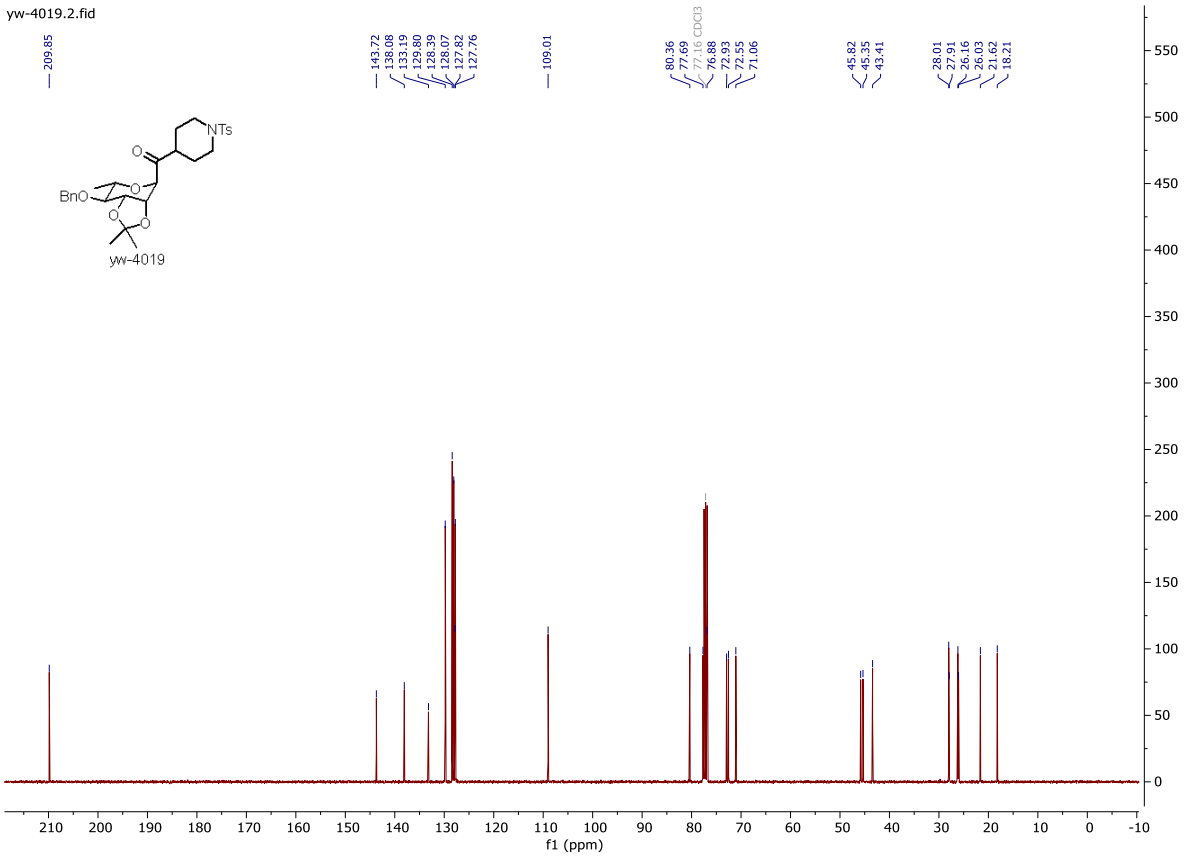
H-H COSY of **37**



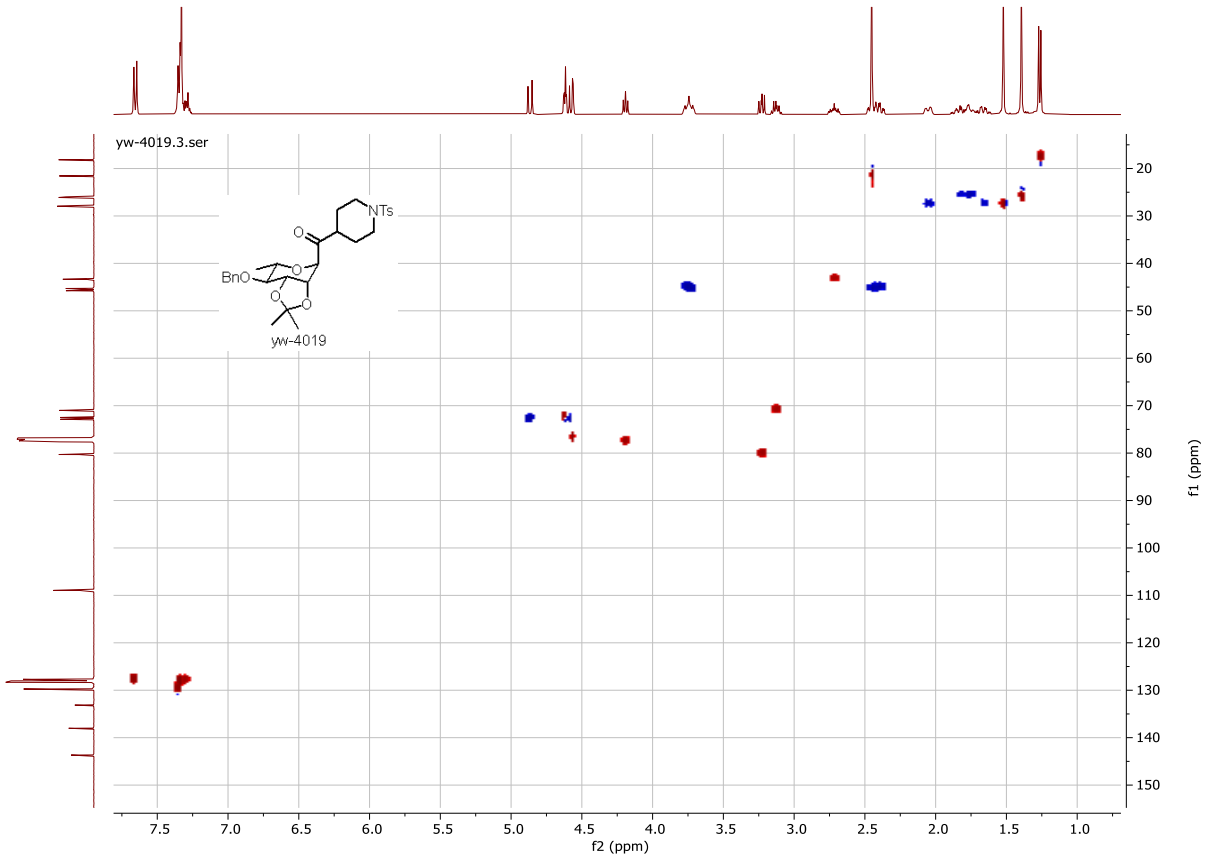
NOE of **37**



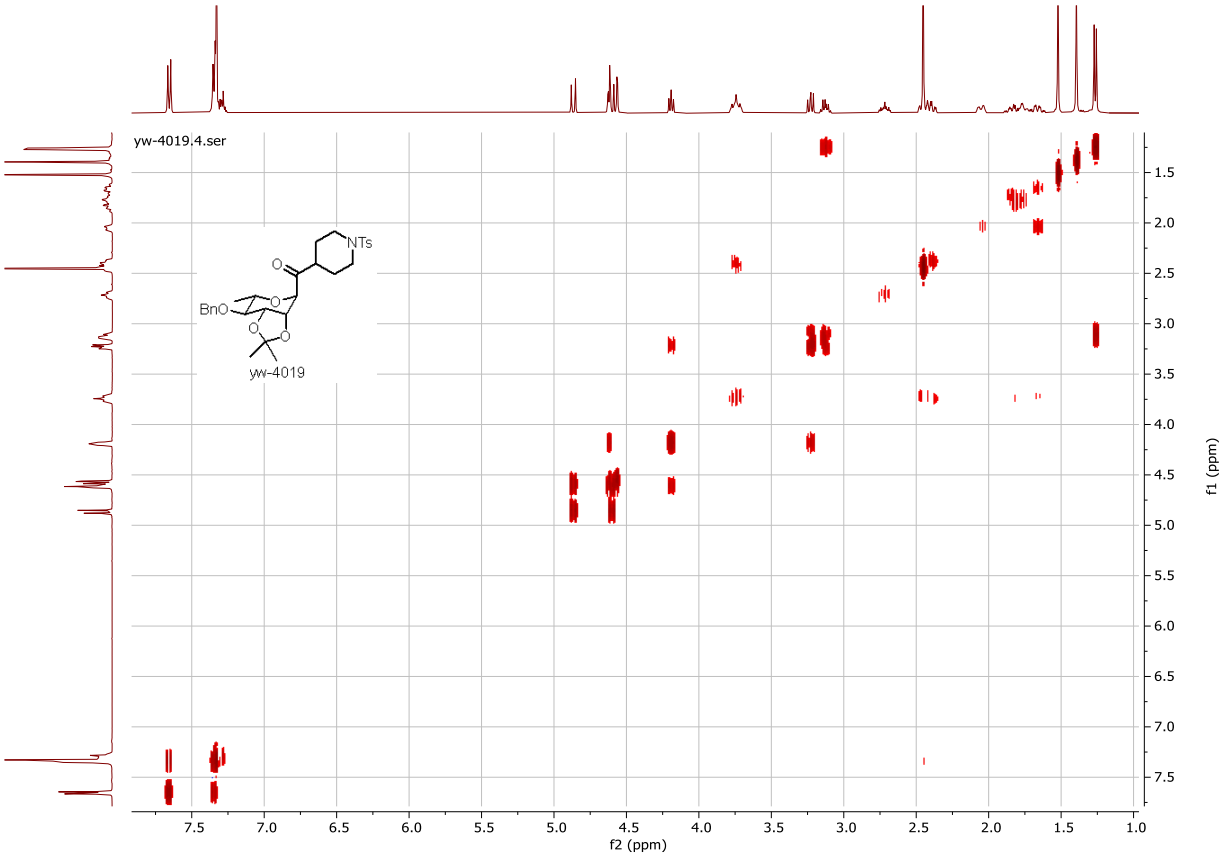
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **38**



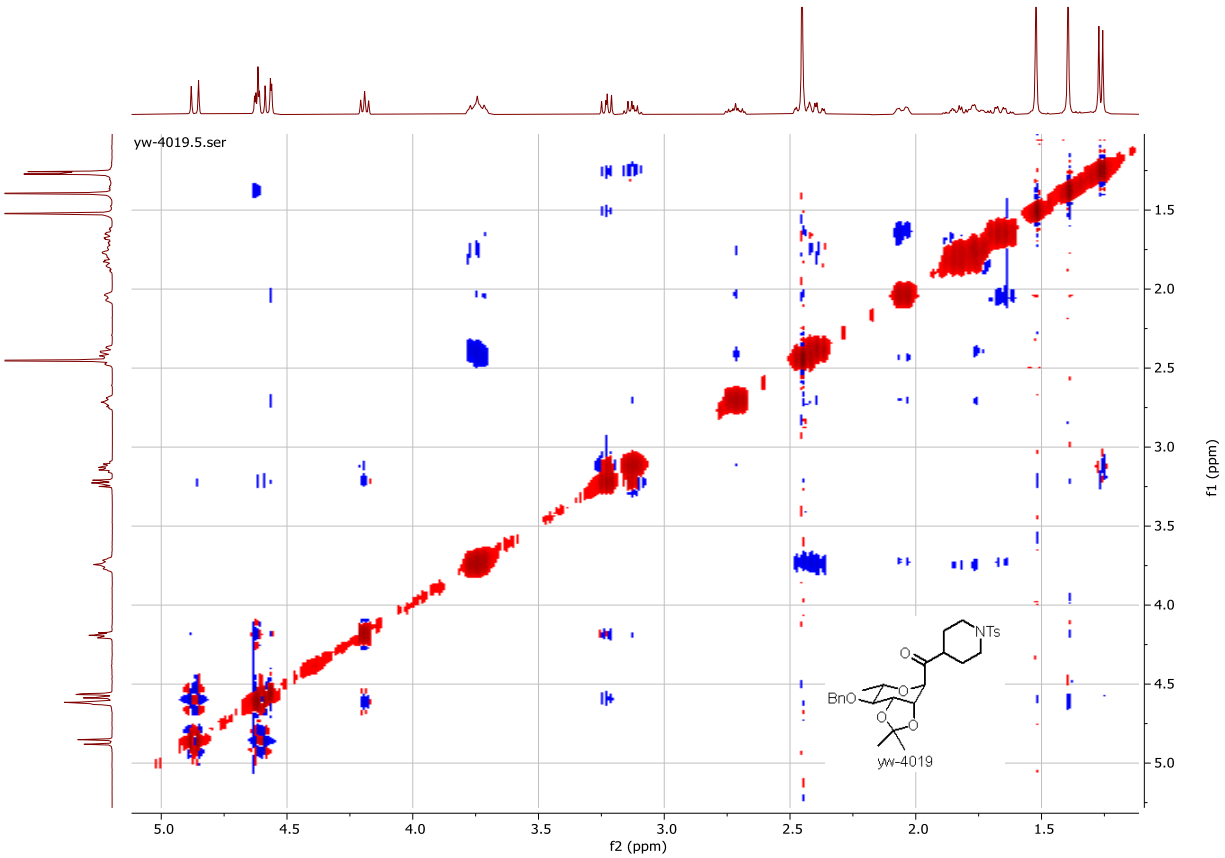
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **38**



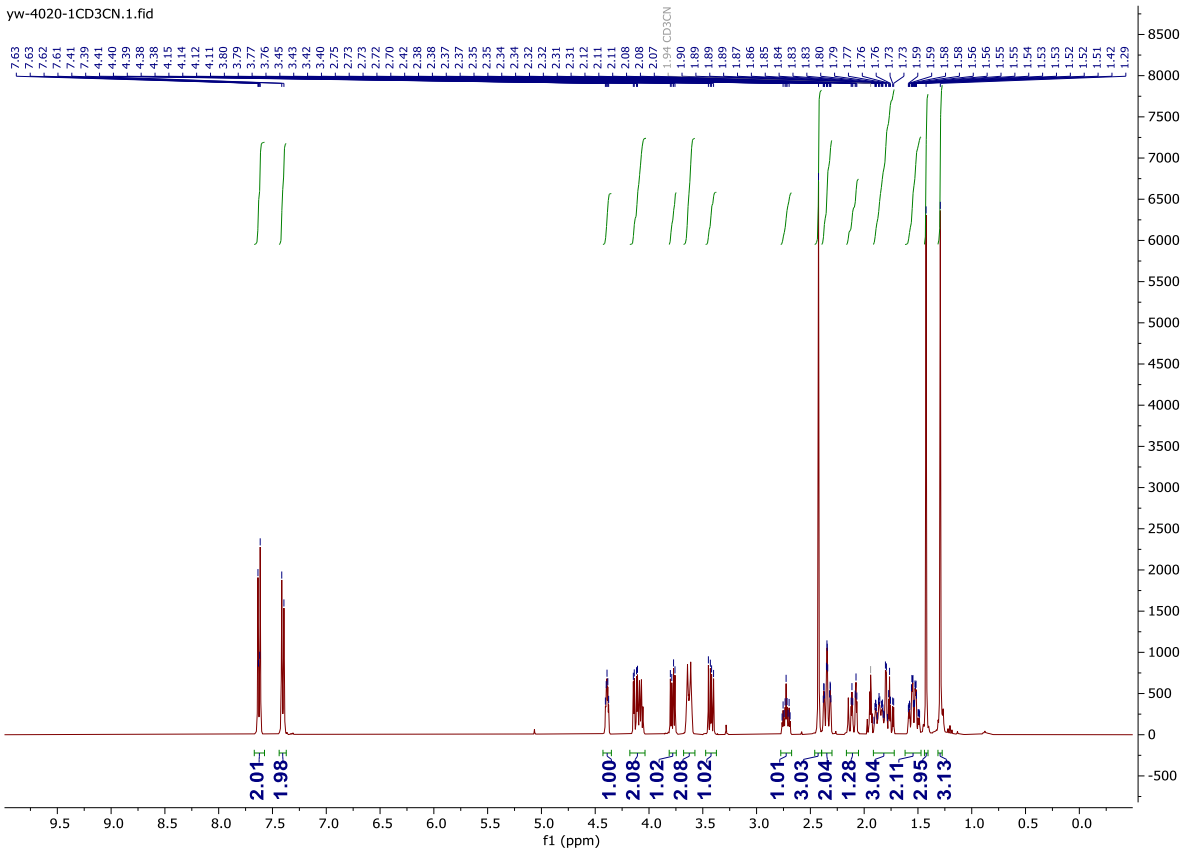
HSQCED of **38**



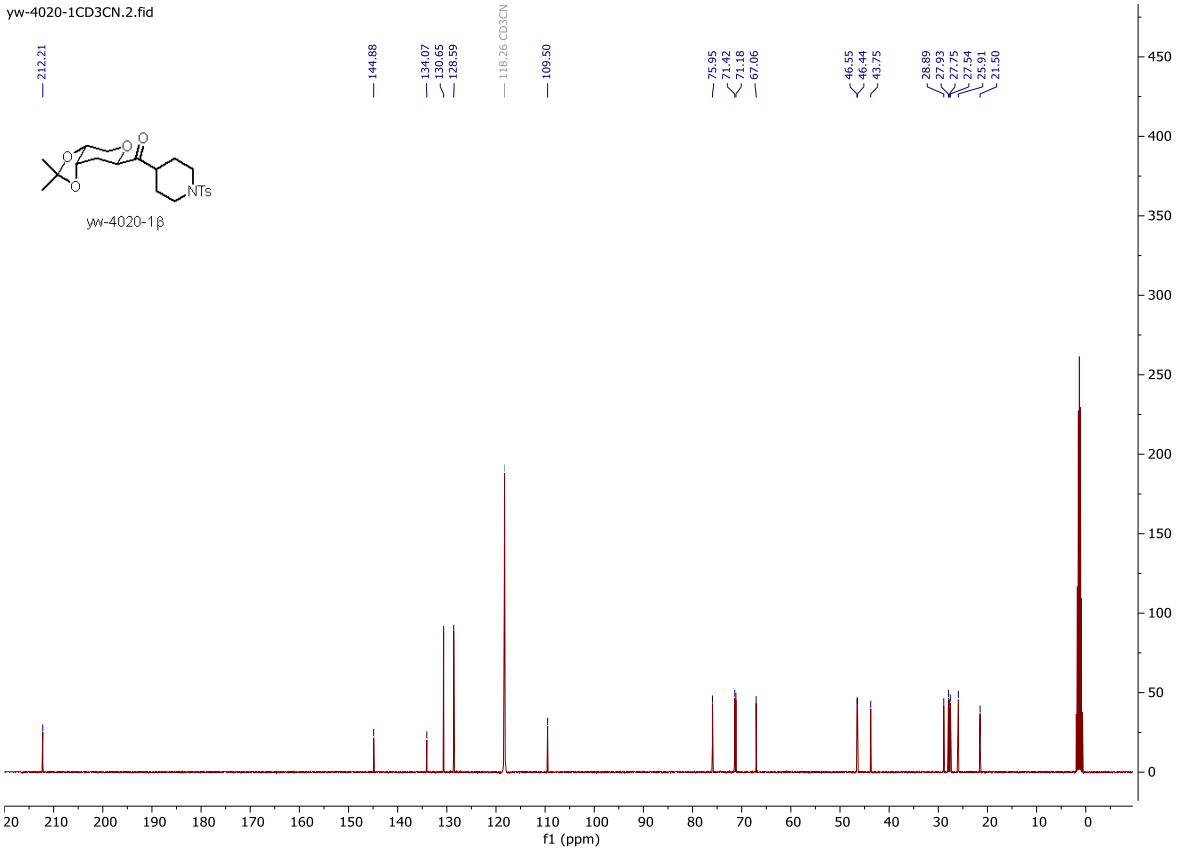
H-H COSY of **38**



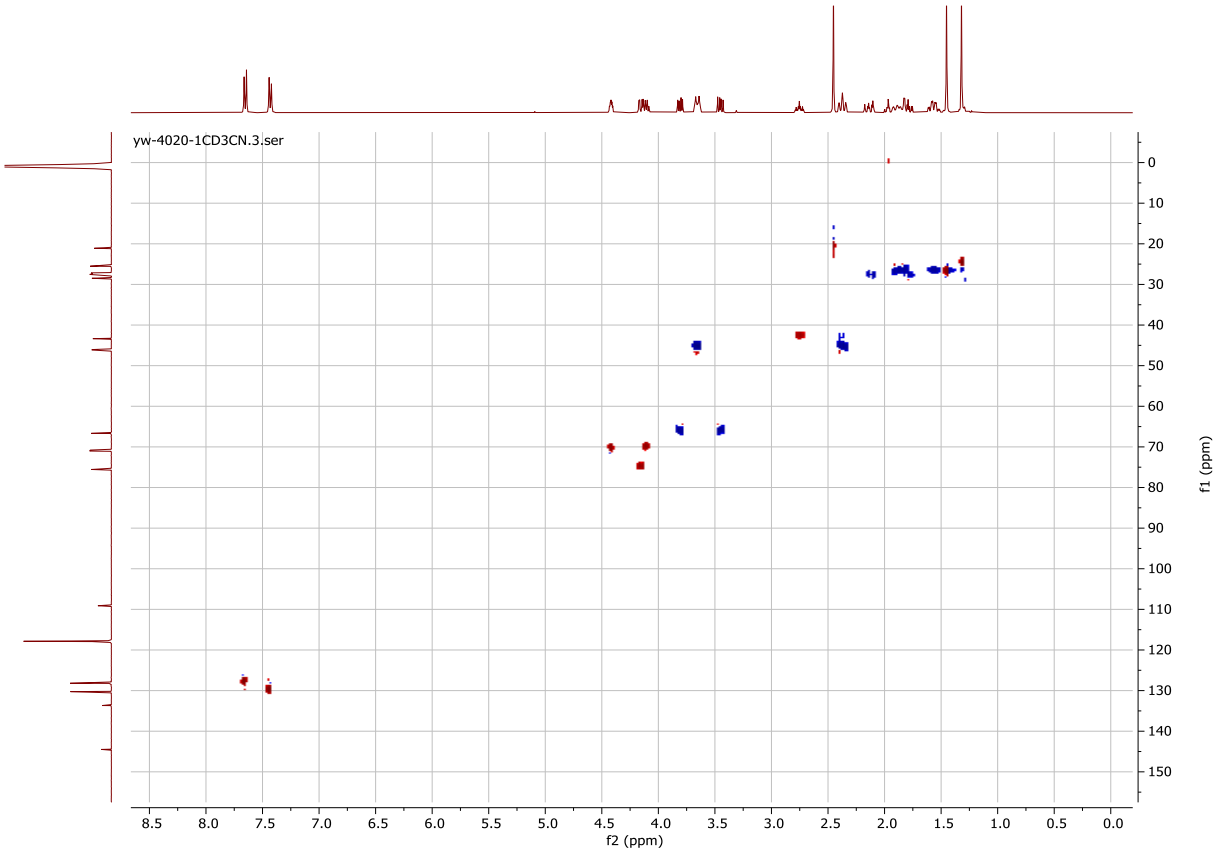
NOE of **38**



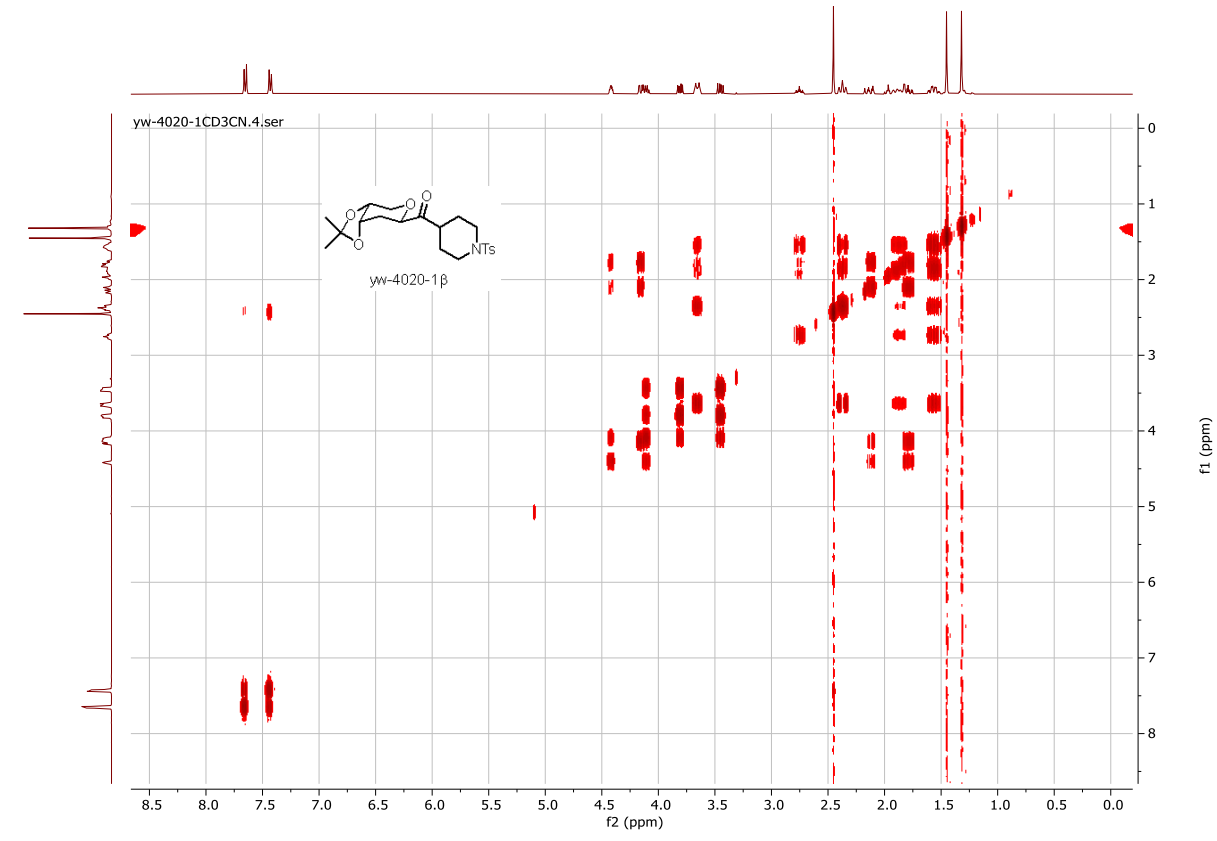
^{1}H NMR spectrum (400 MHz, CD_3CN) of **39β**



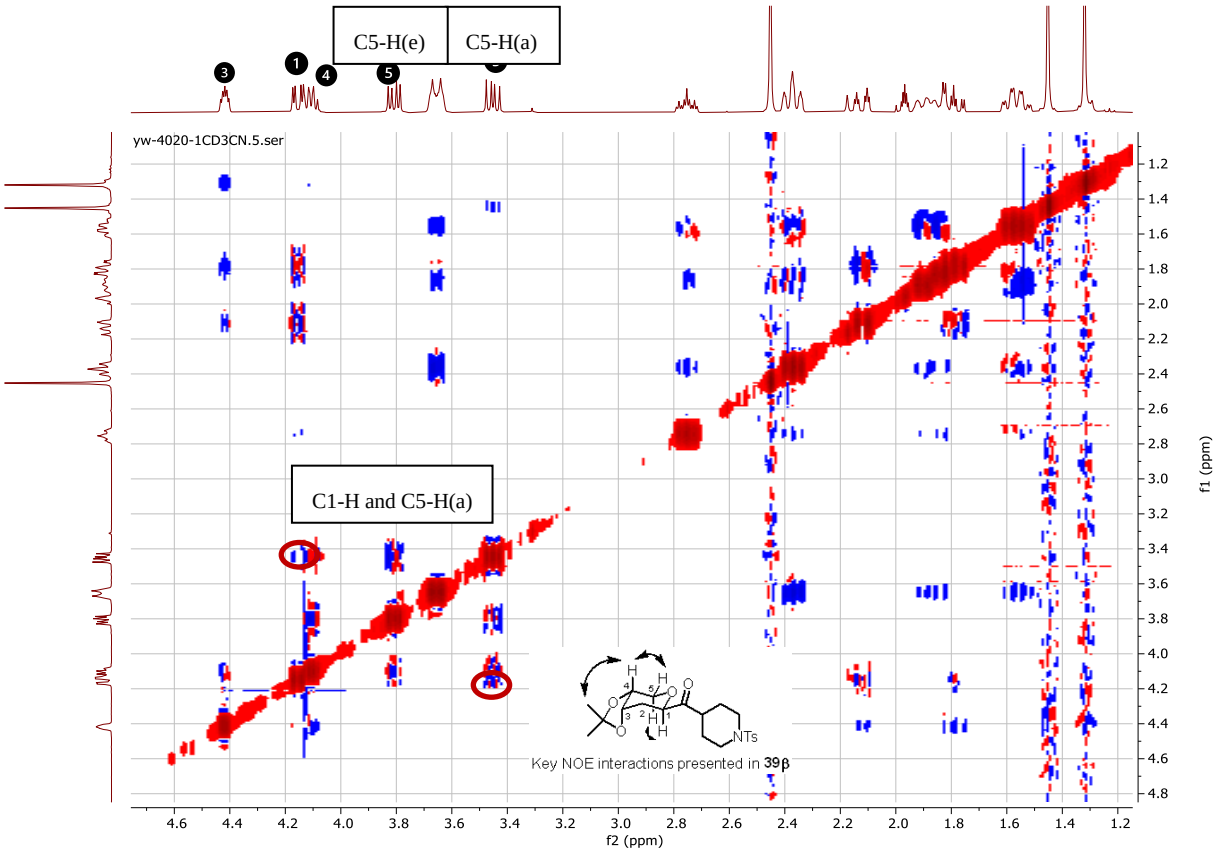
^{13}C NMR spectrum (101 MHz, CD_3CN) of **39β**



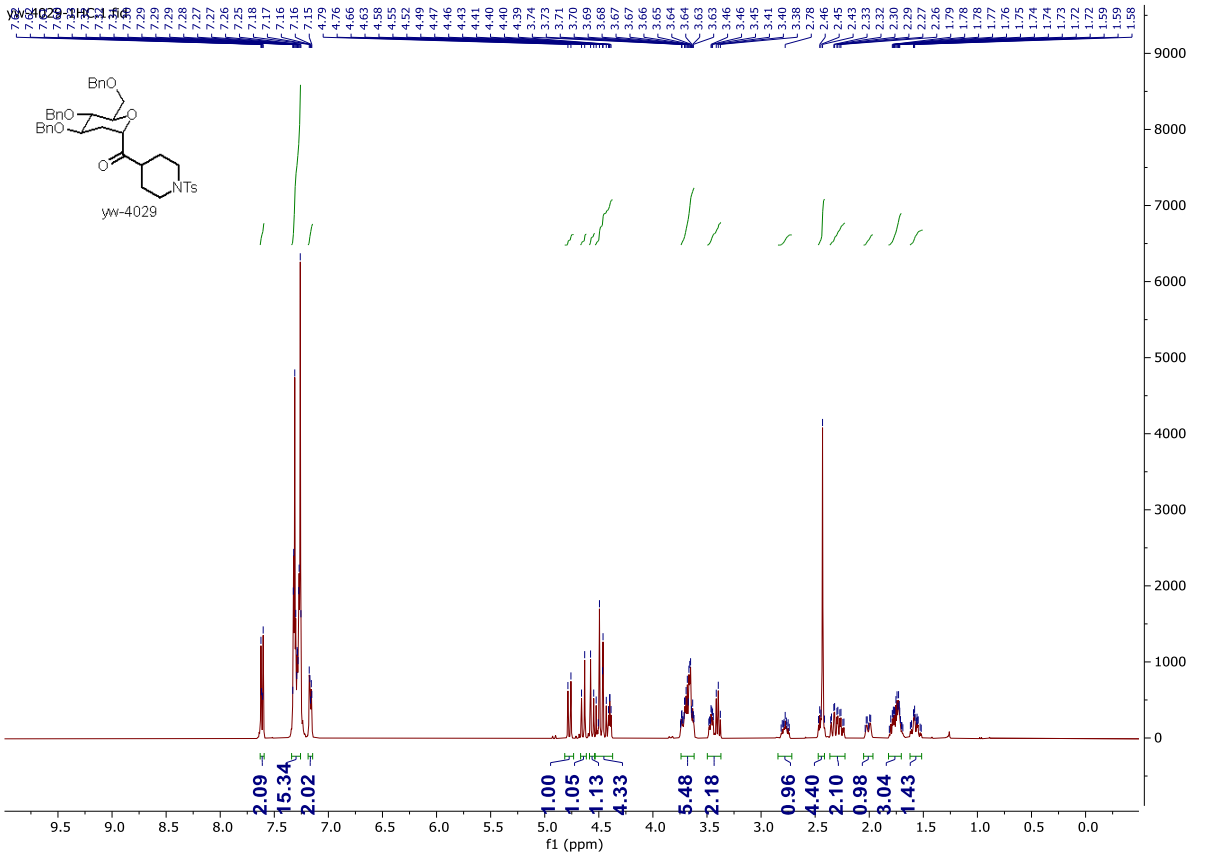
HSQCED of **39β**



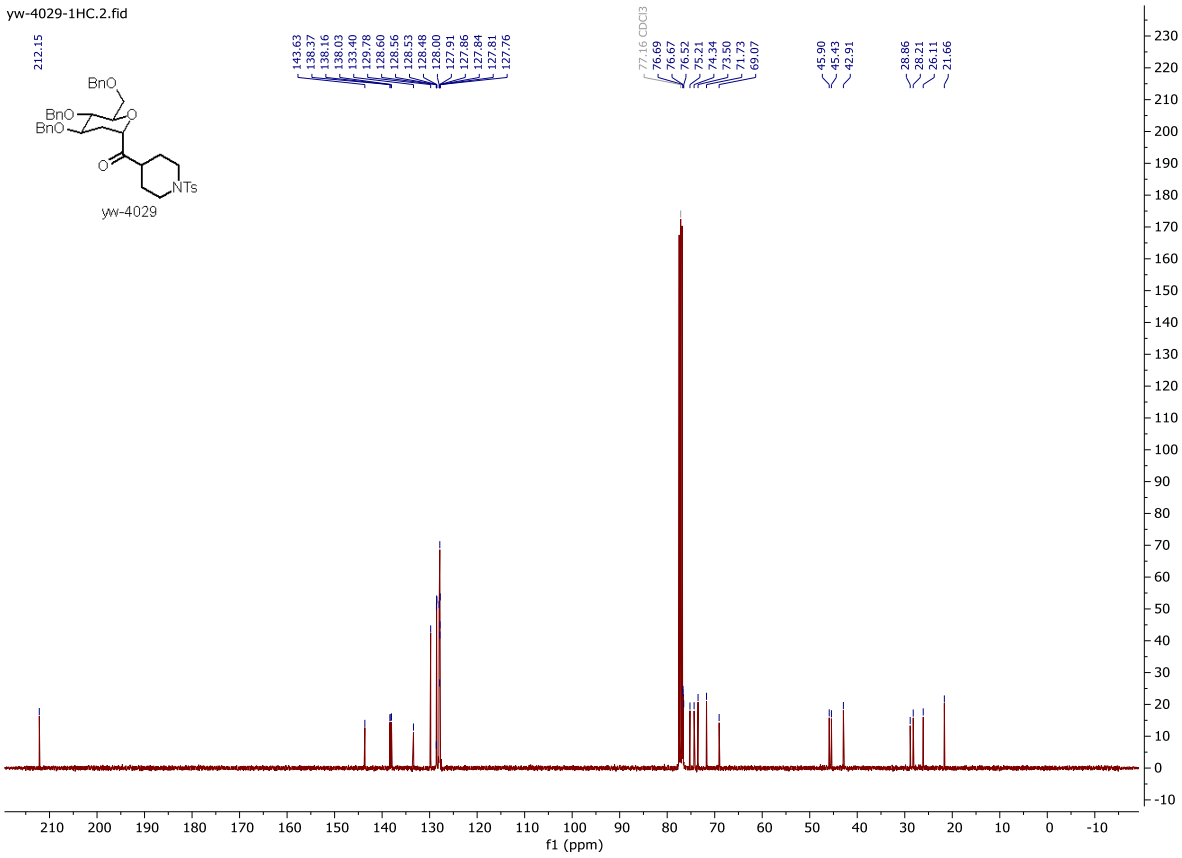
H-H COSY of **39β**



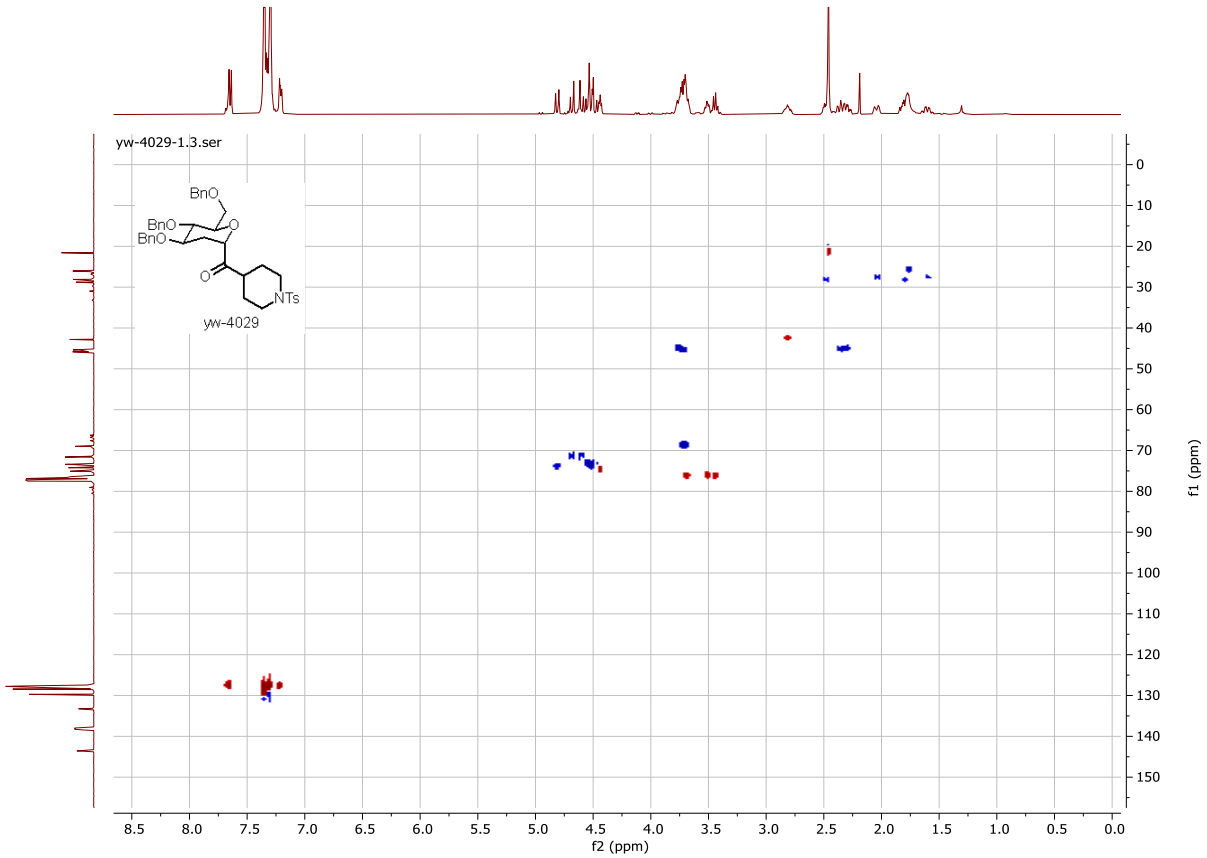
NOESY of **39β**



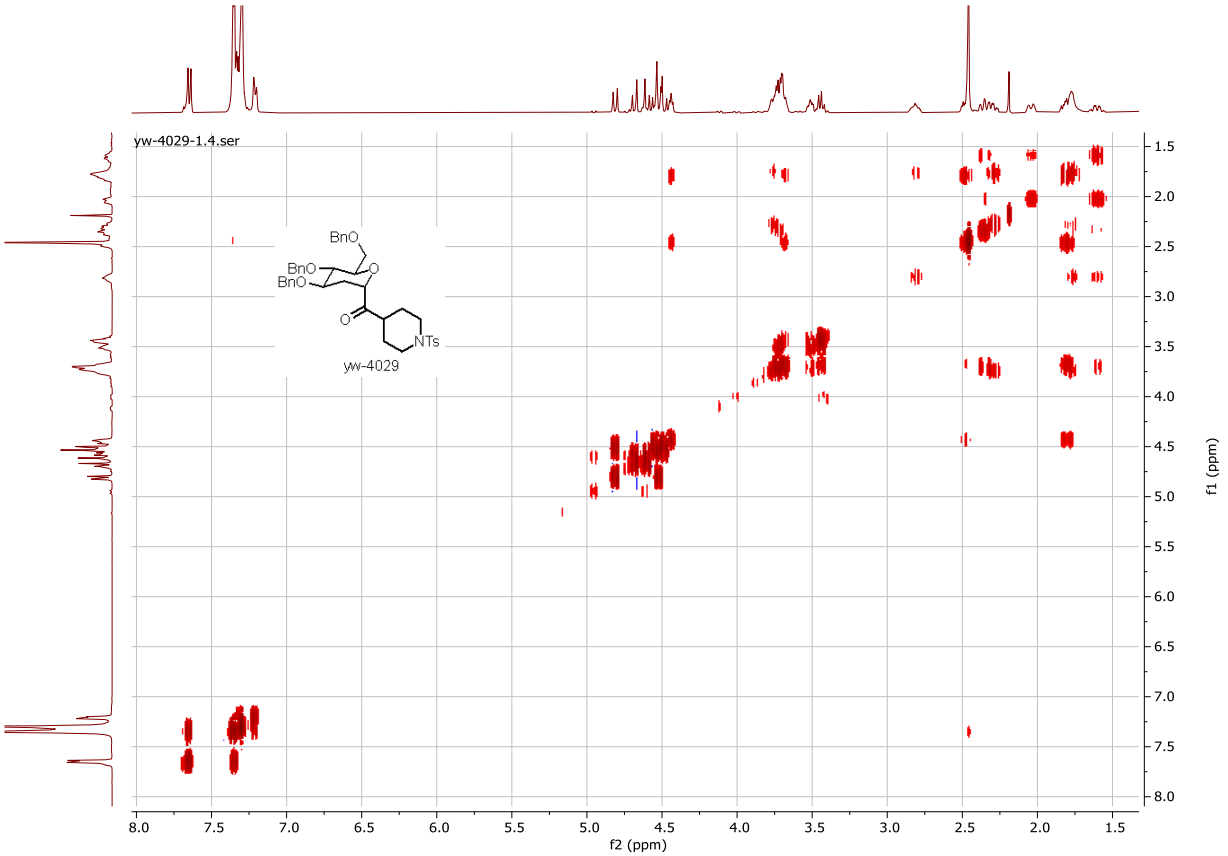
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **40**



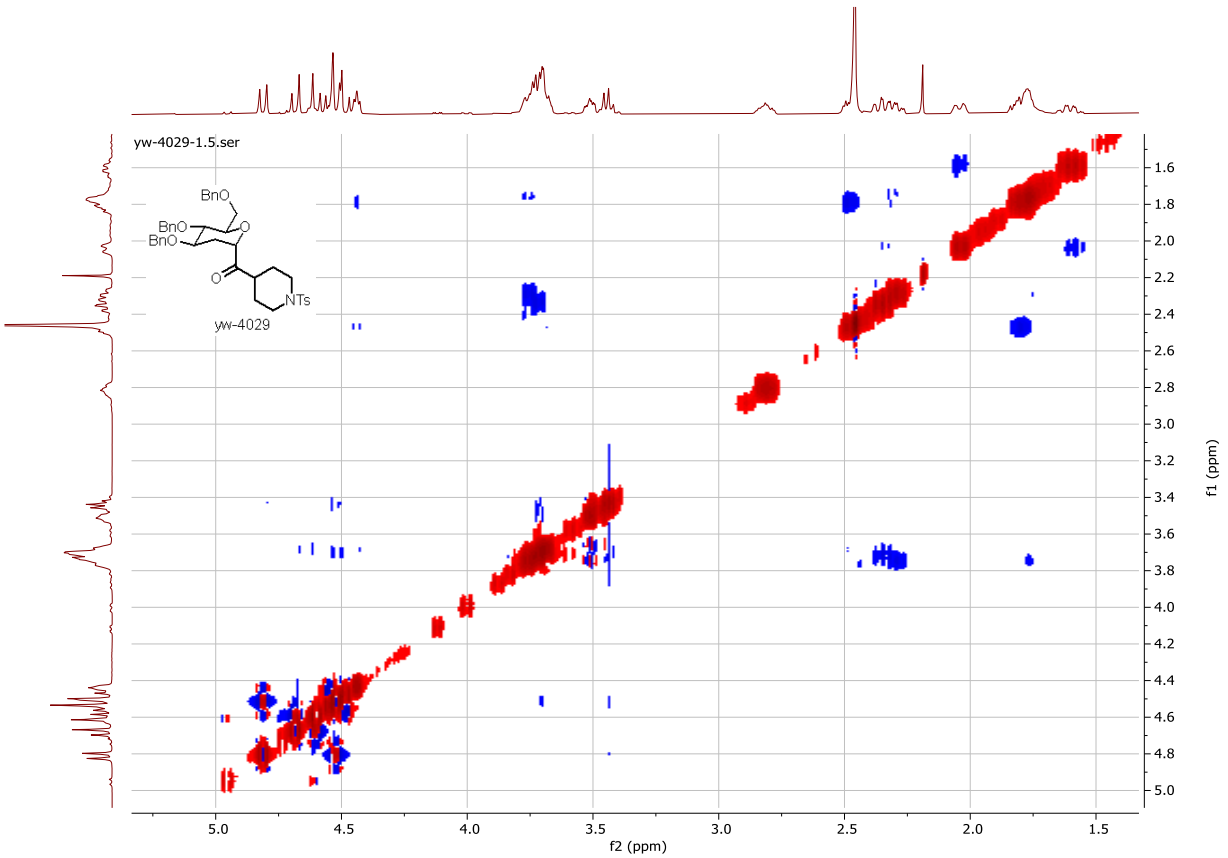
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **40**



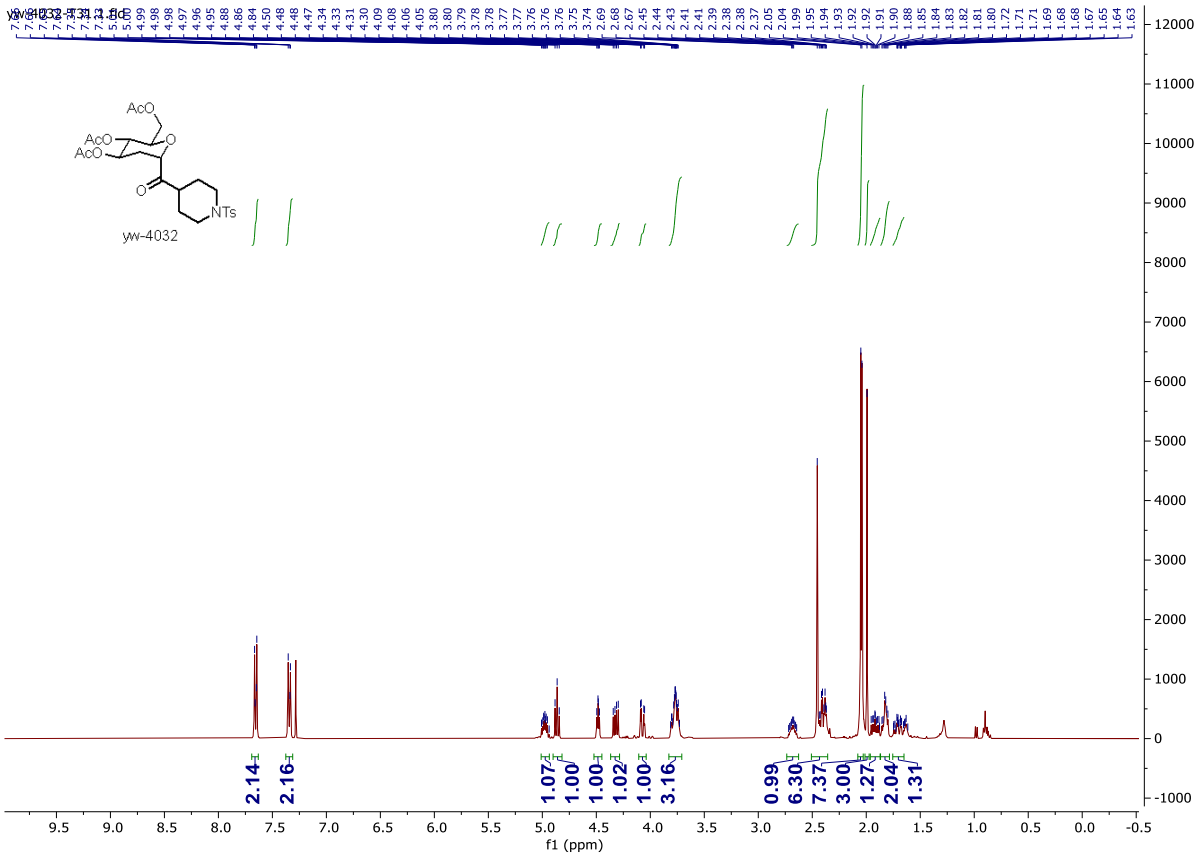
HSQCED of **40**



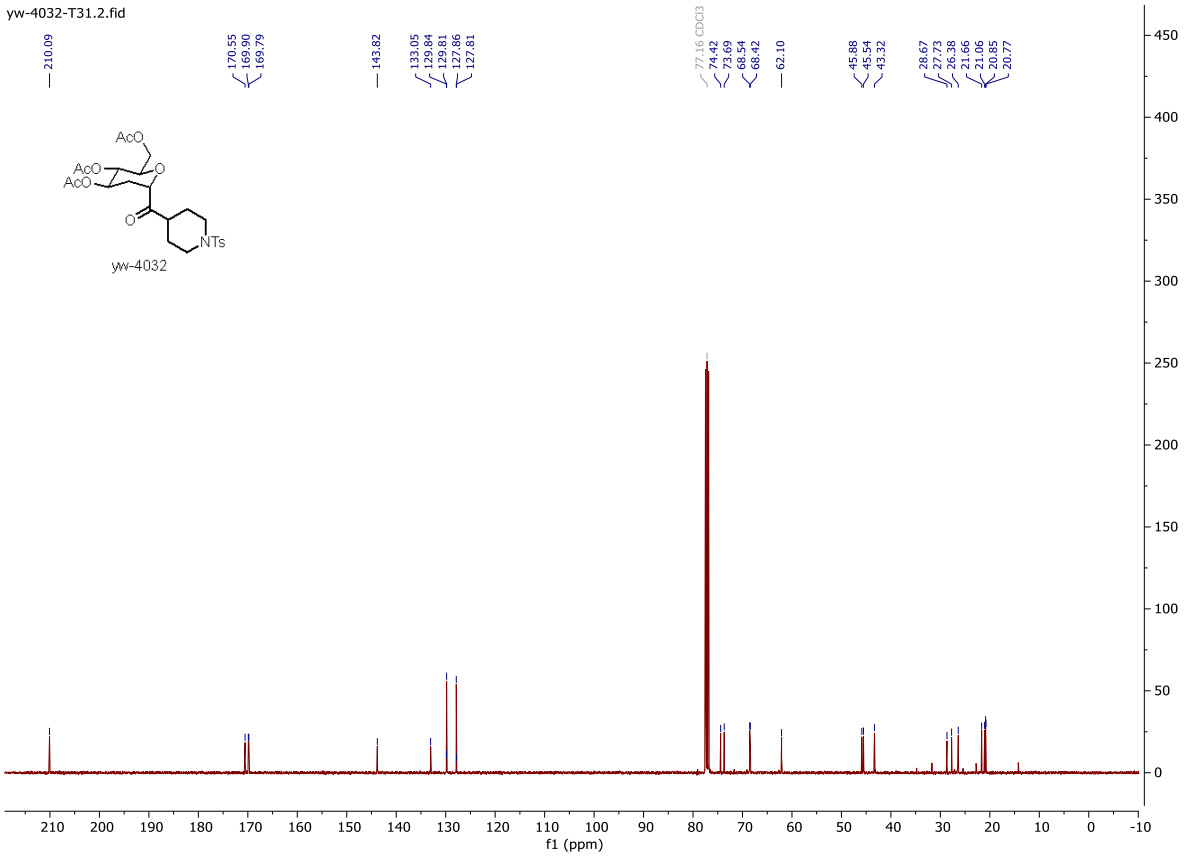
H-H COSY of **40**



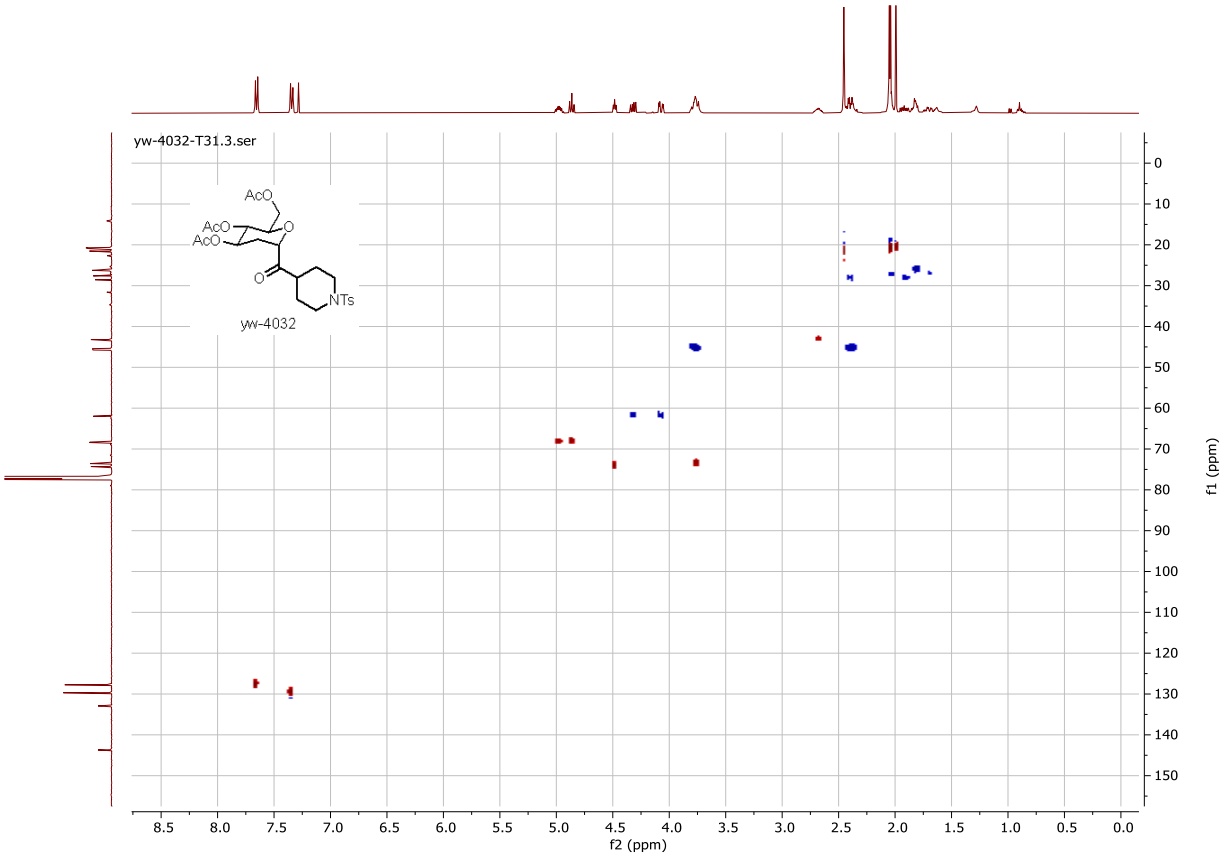
NOESY of **40**



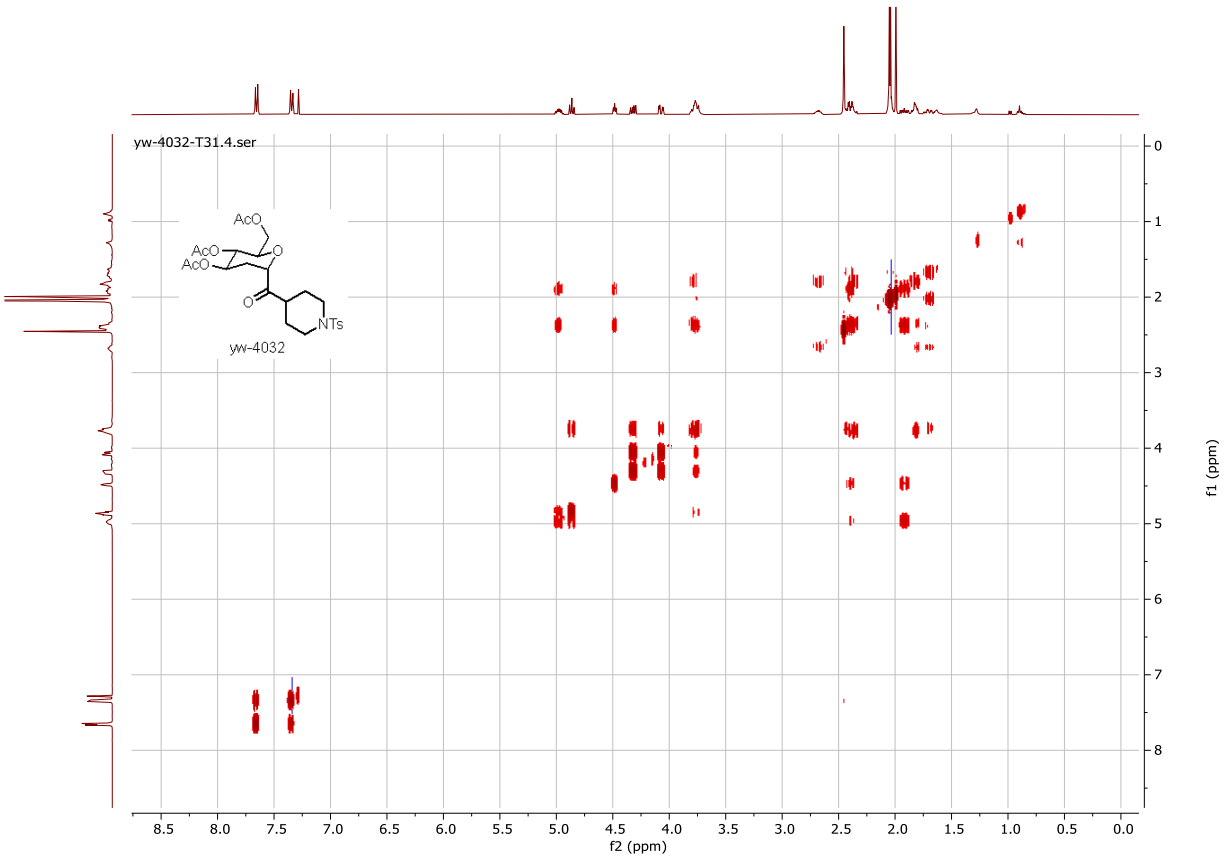
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **41**



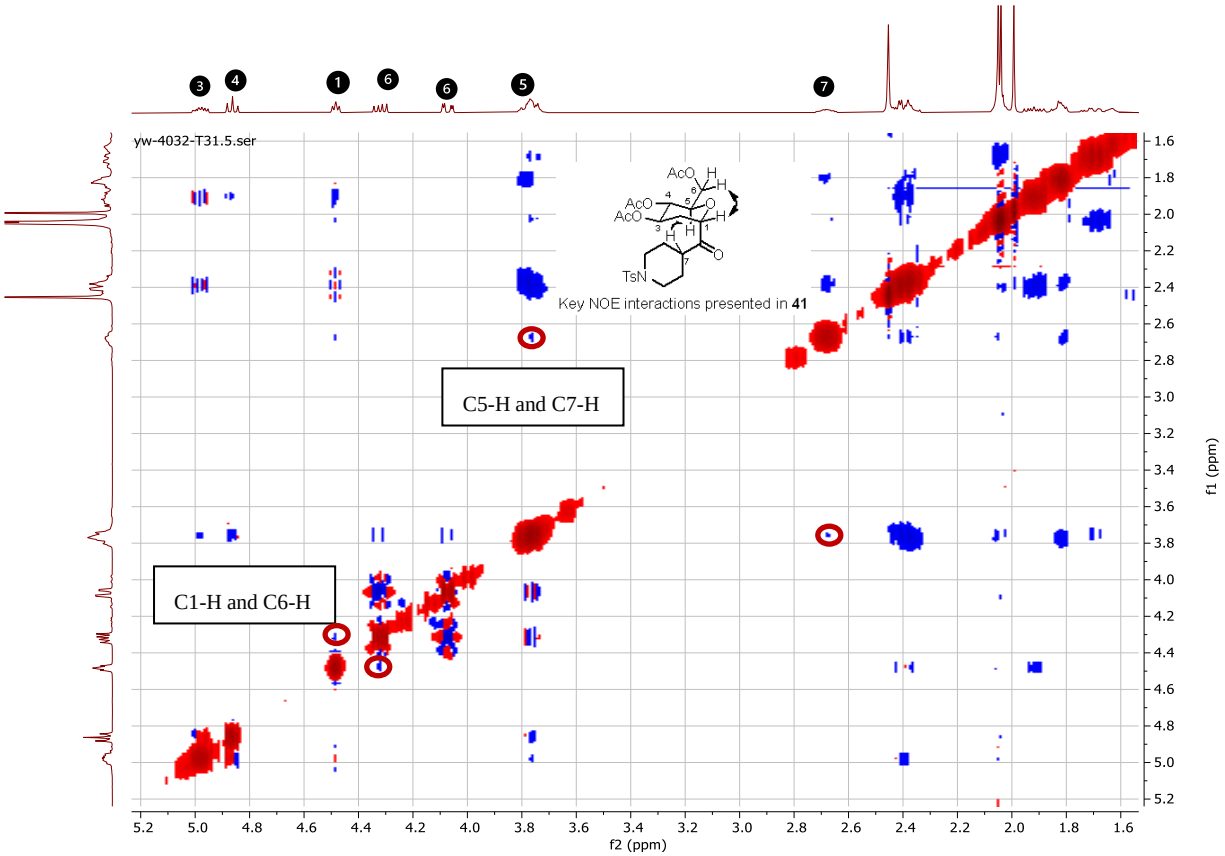
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **41**



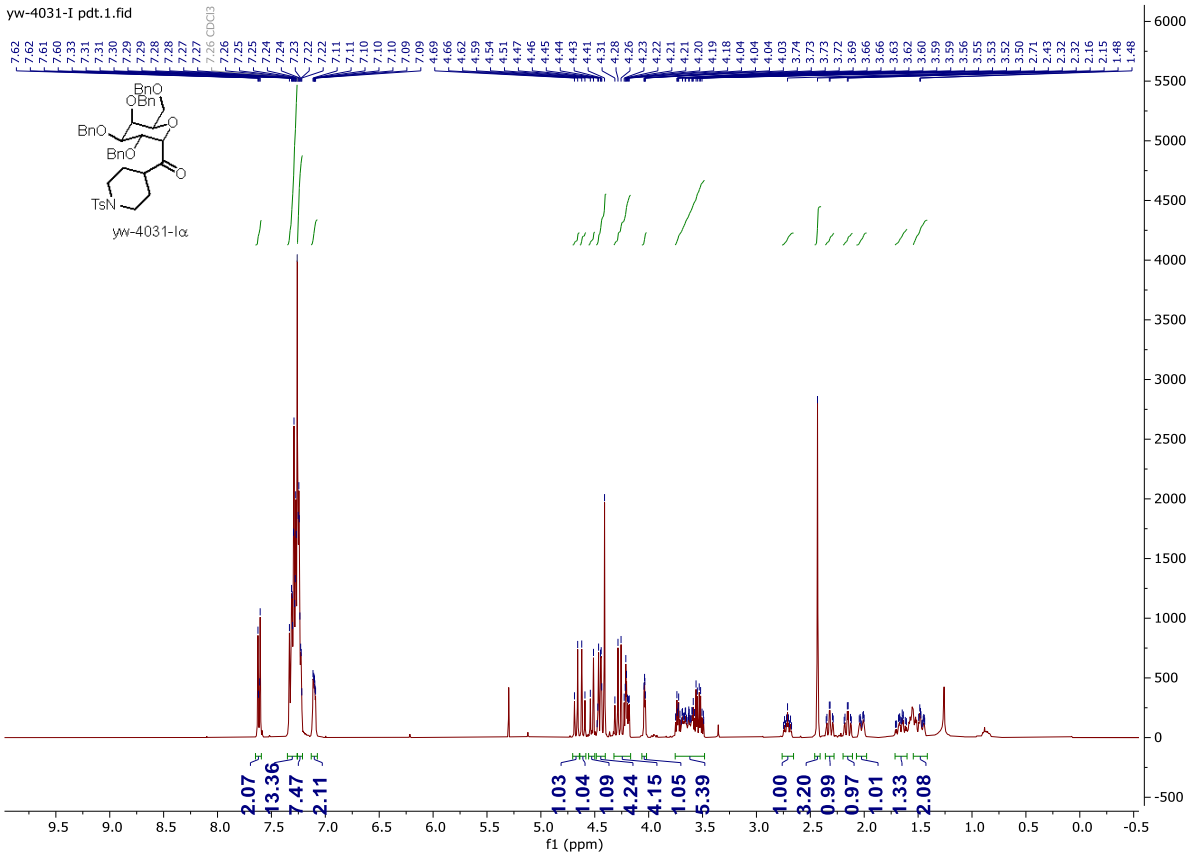
HSQCED of **41**



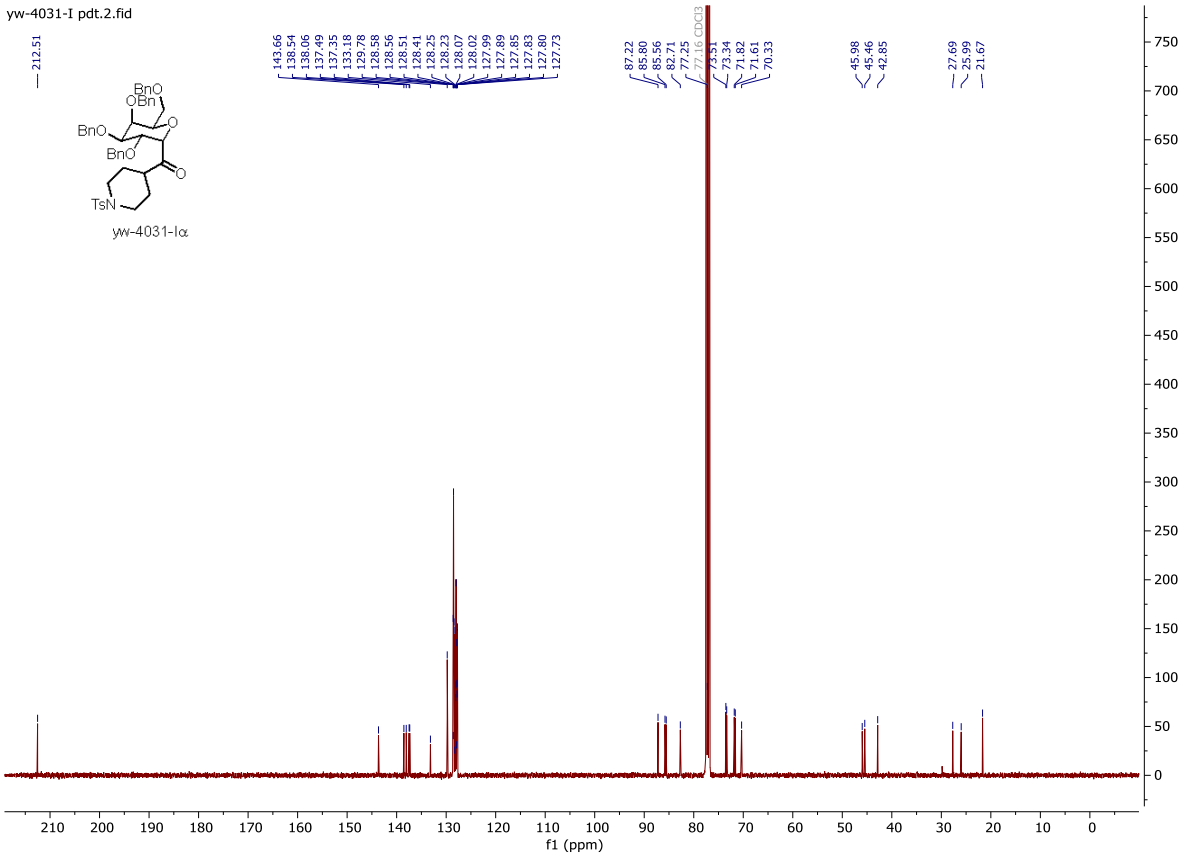
H-H COSY of **41**



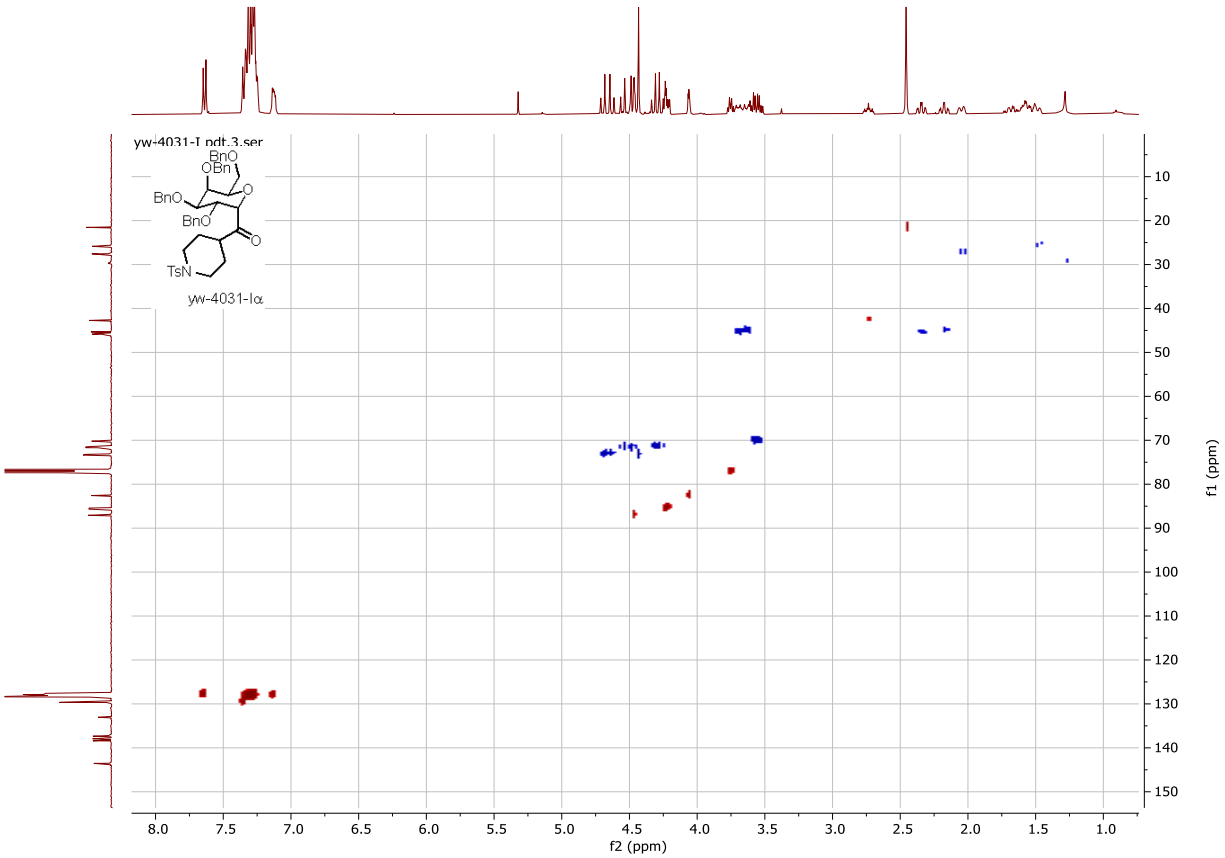
NOESY of **41**



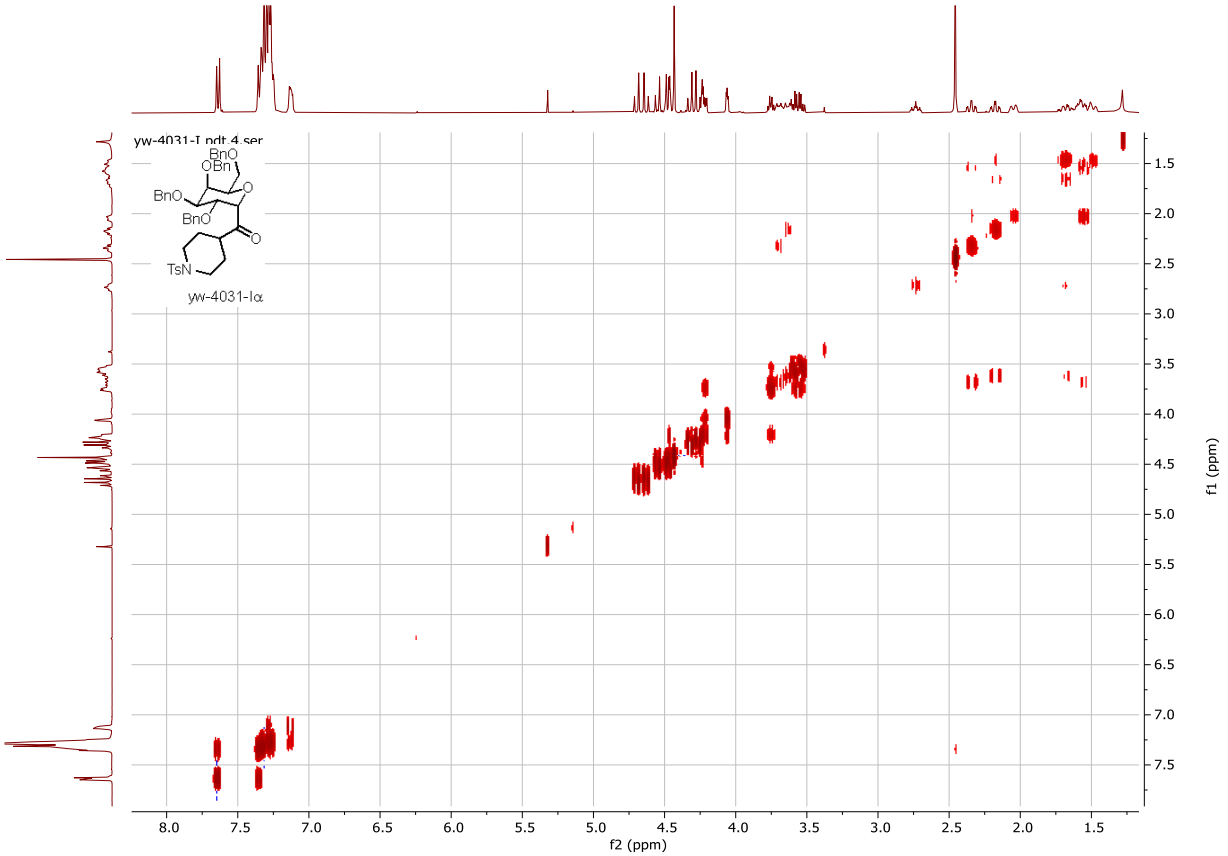
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **42α**



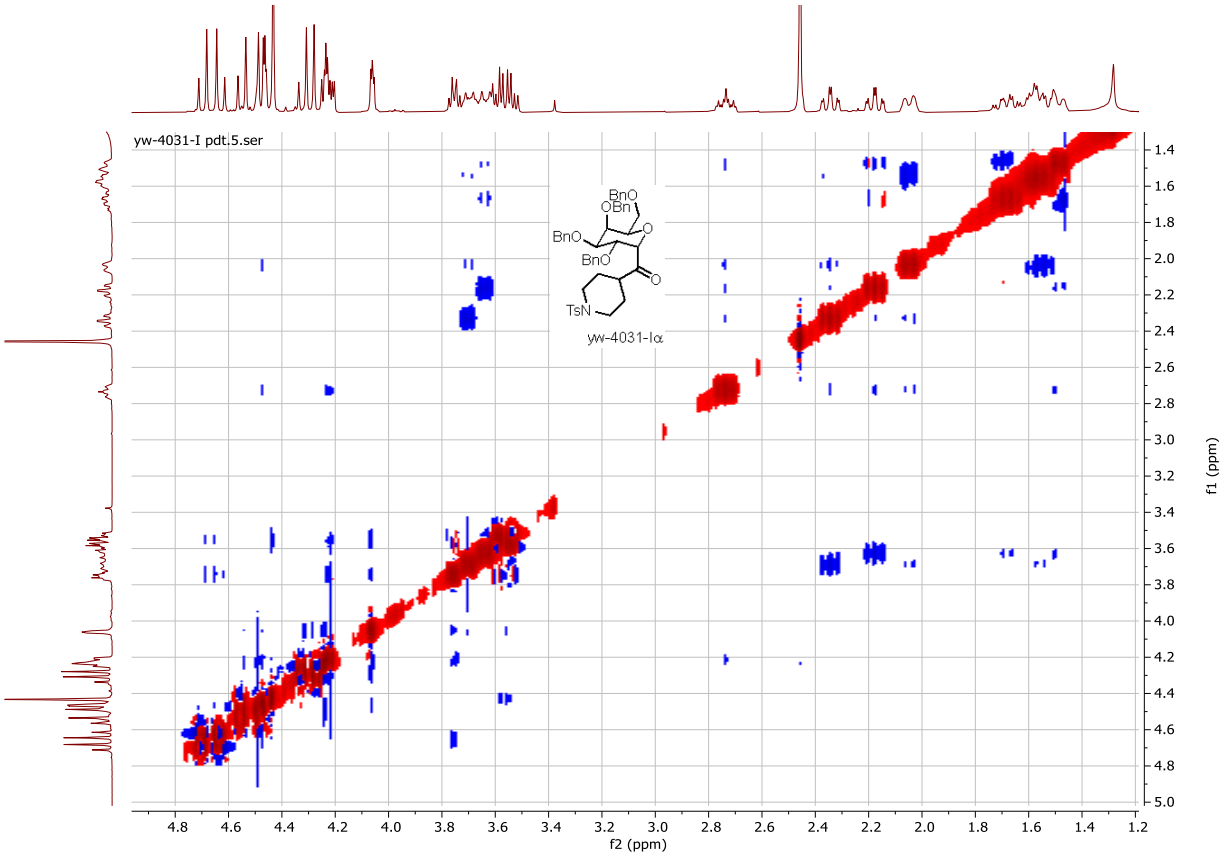
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **42α**



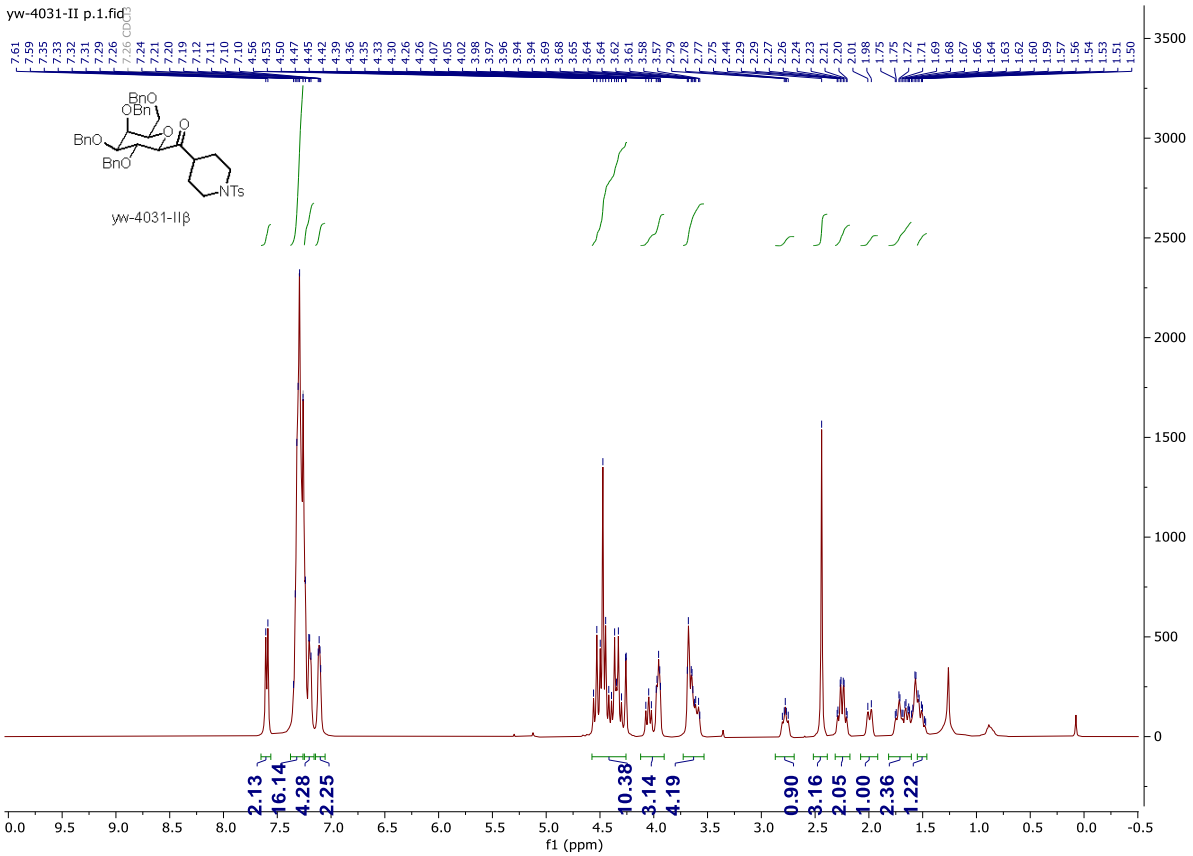
HSQCED of **42α**



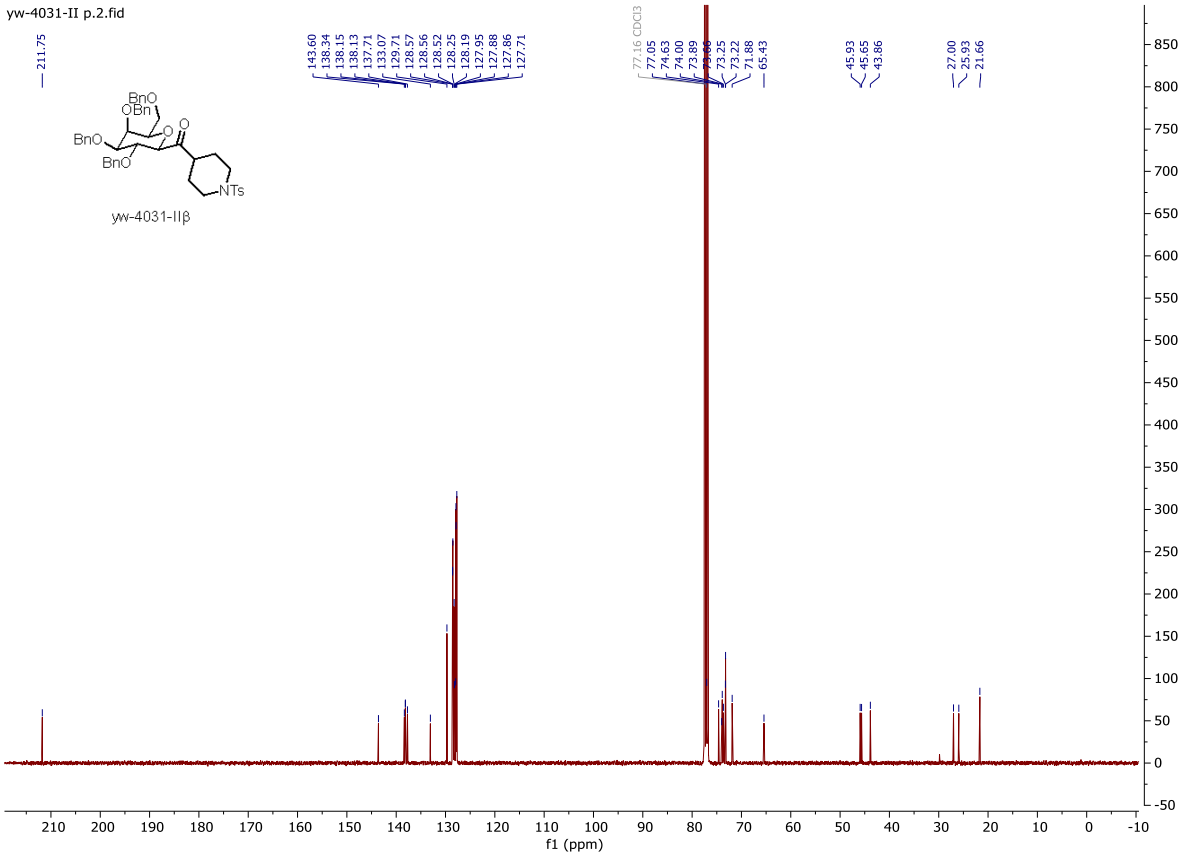
H-H COSY of **42α**



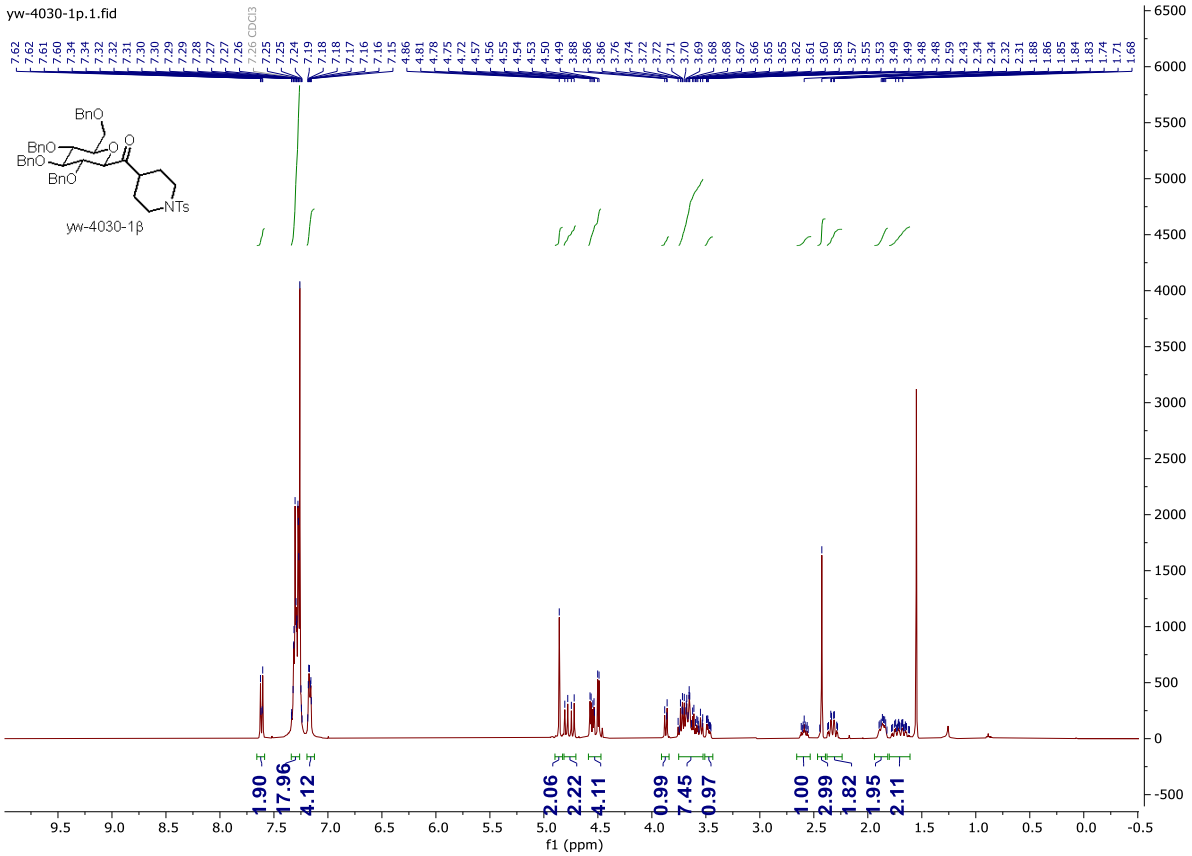
NOESY of **42α**



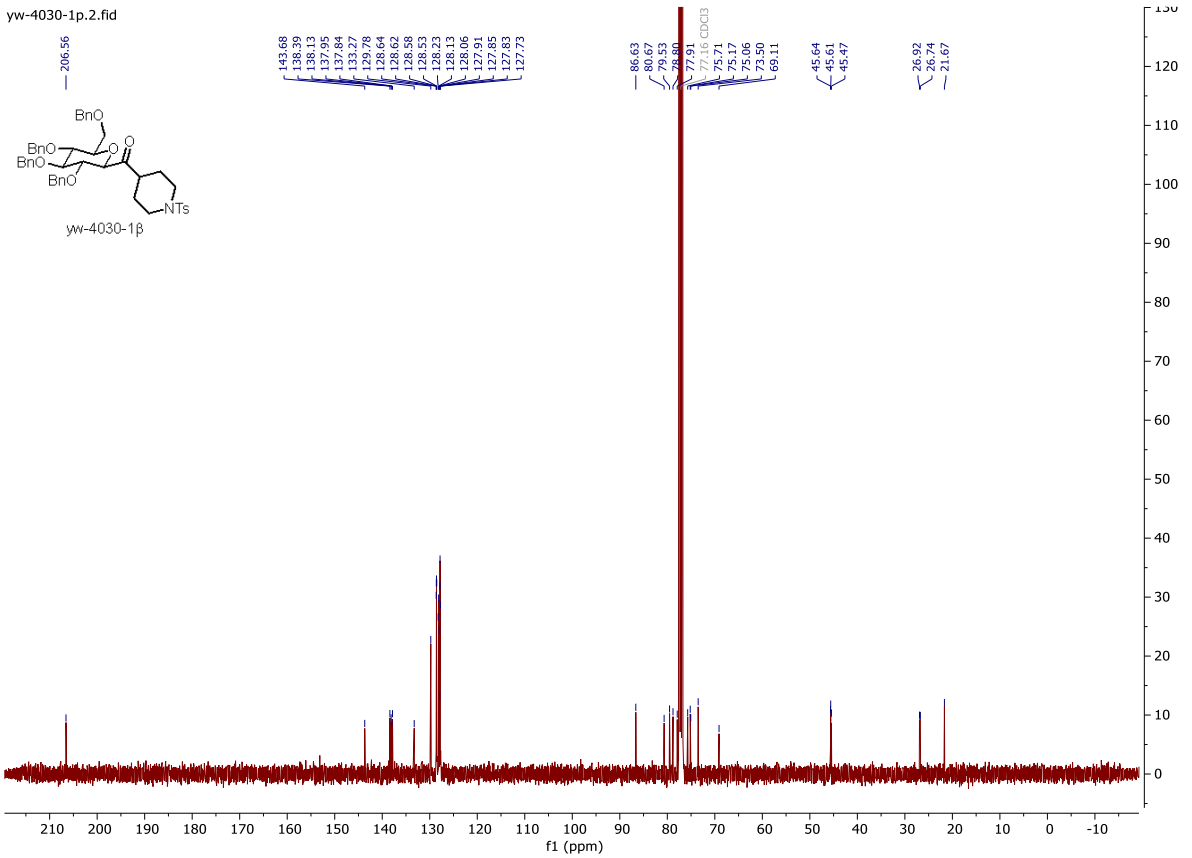
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **42β**



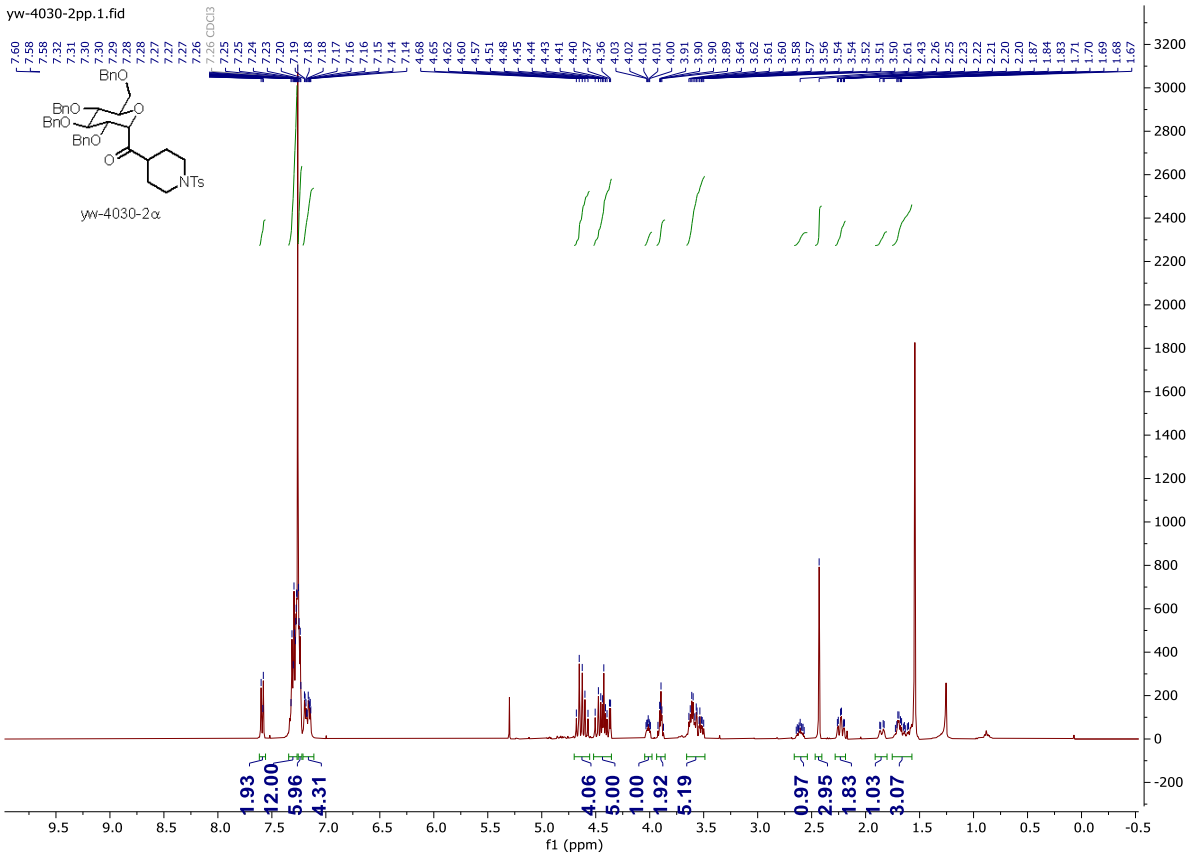
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **42β**



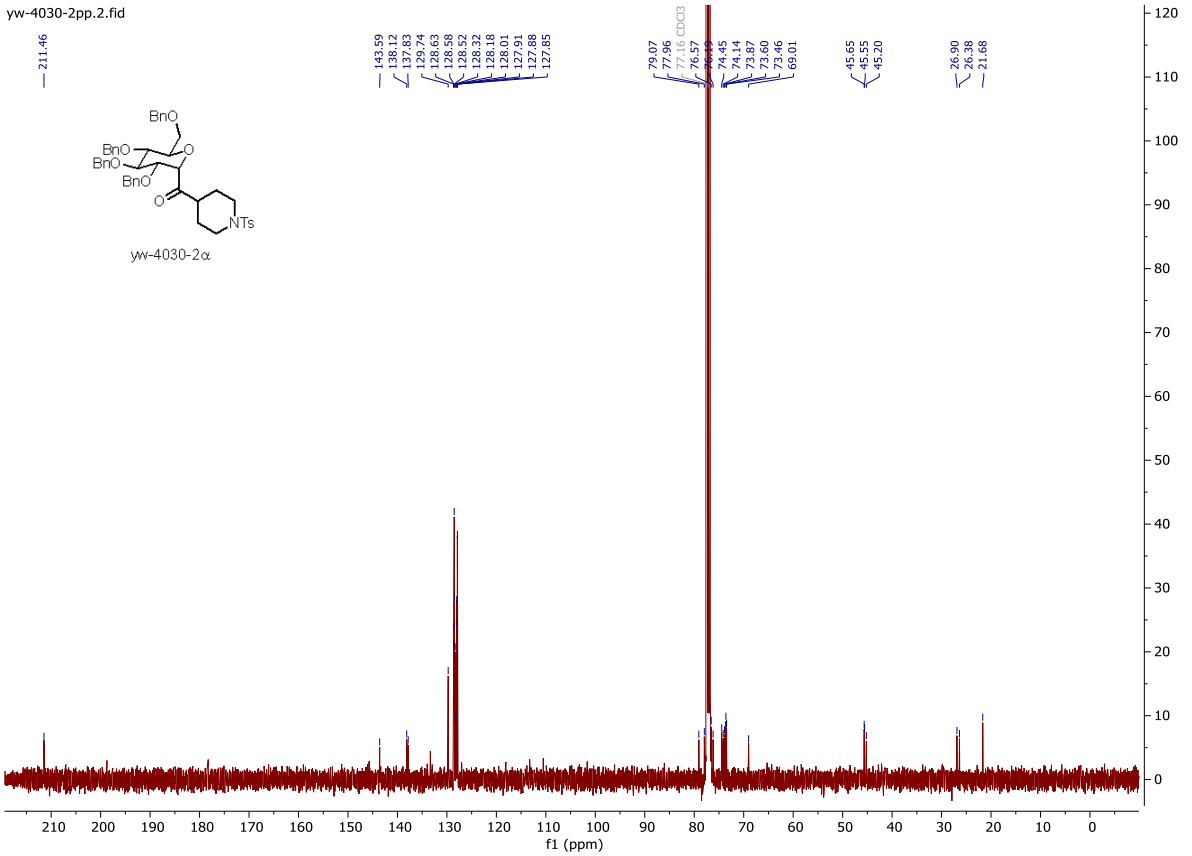
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **43β**



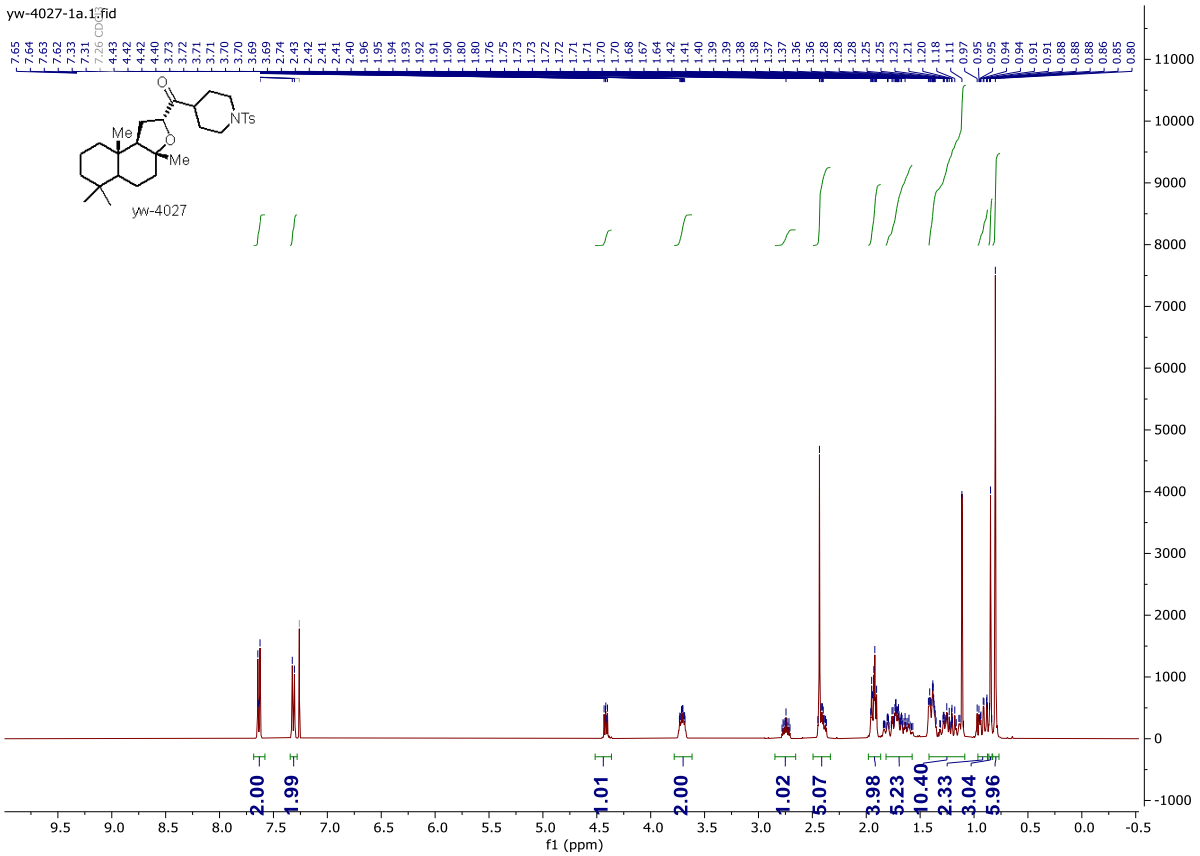
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **43β**



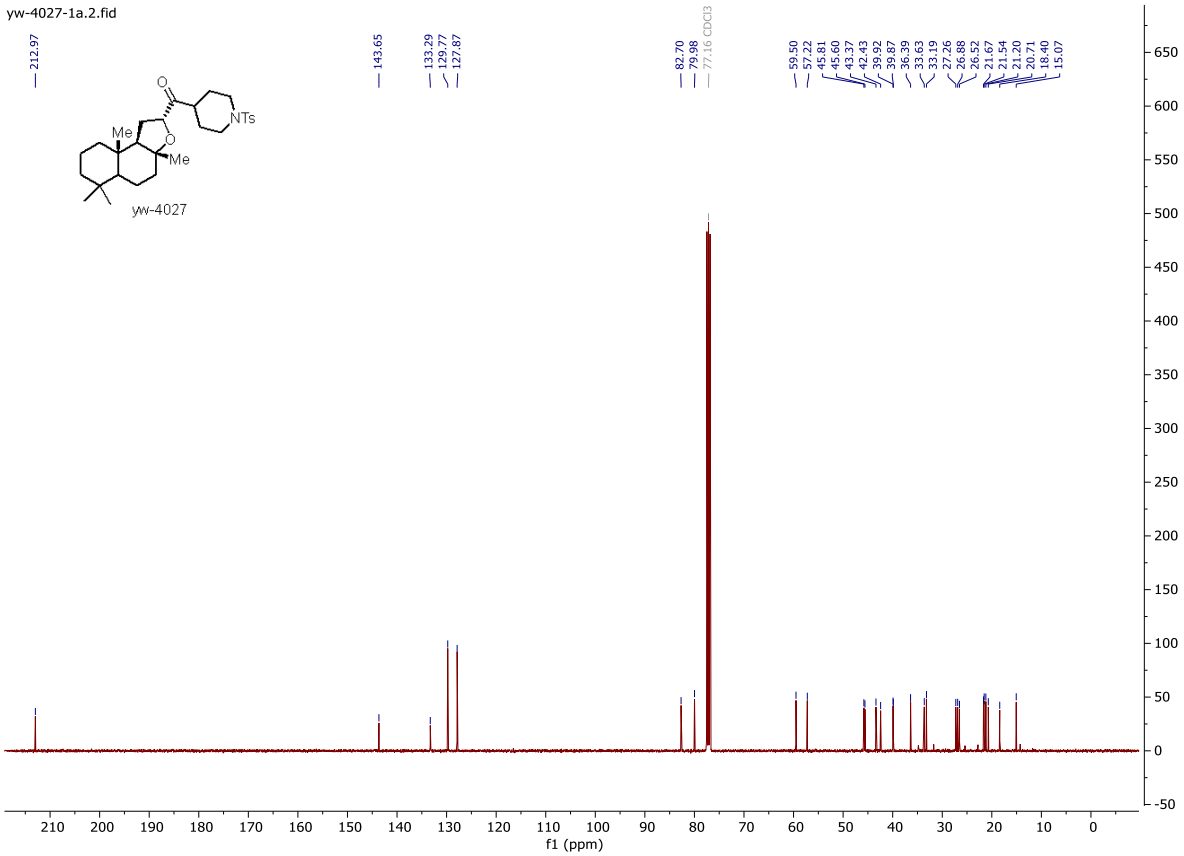
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **43α**



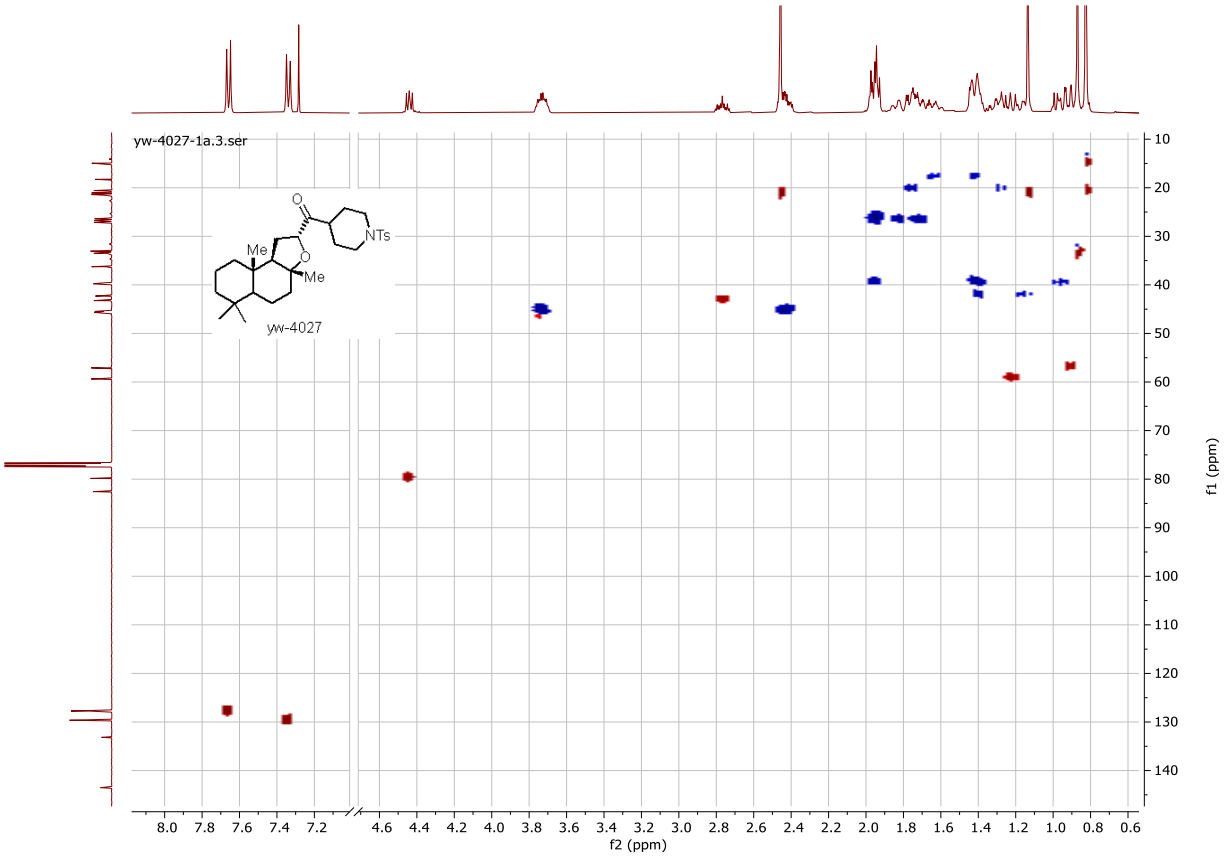
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **43α**



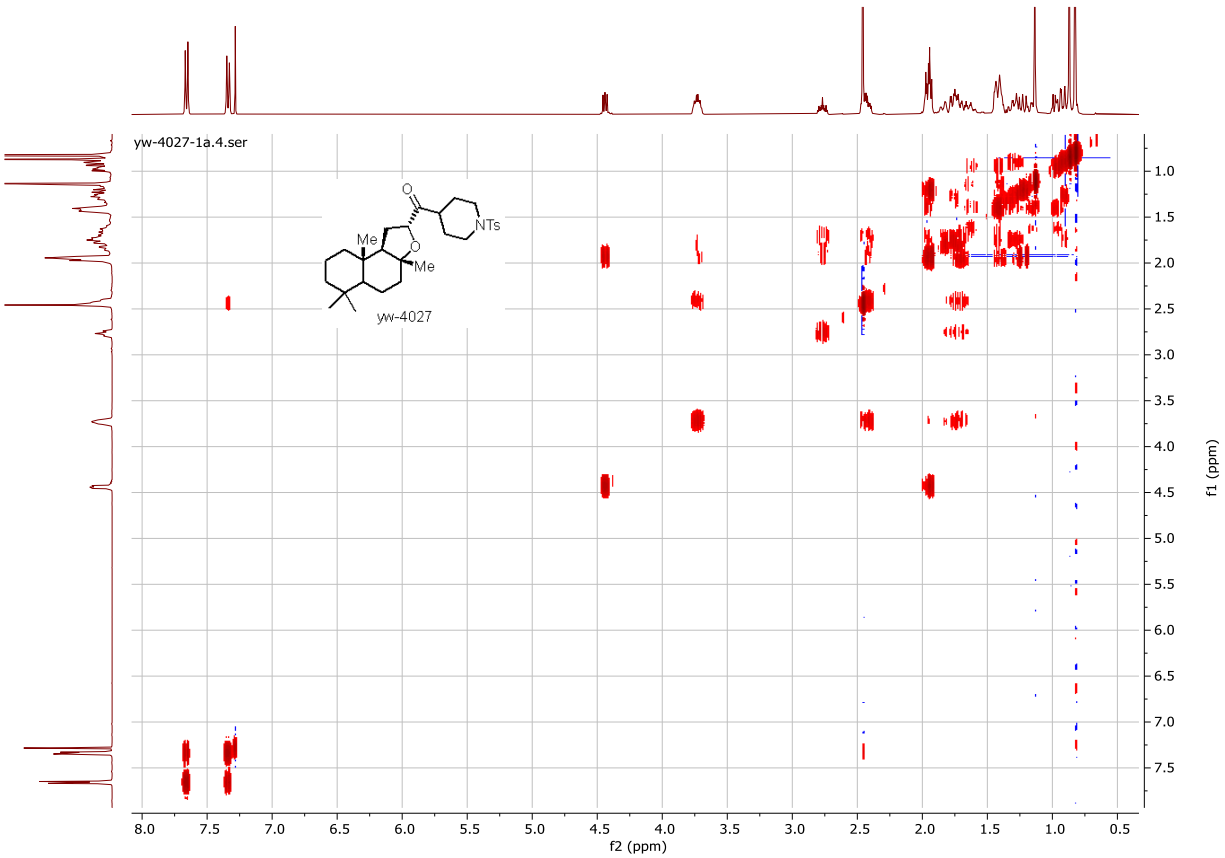
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **46**



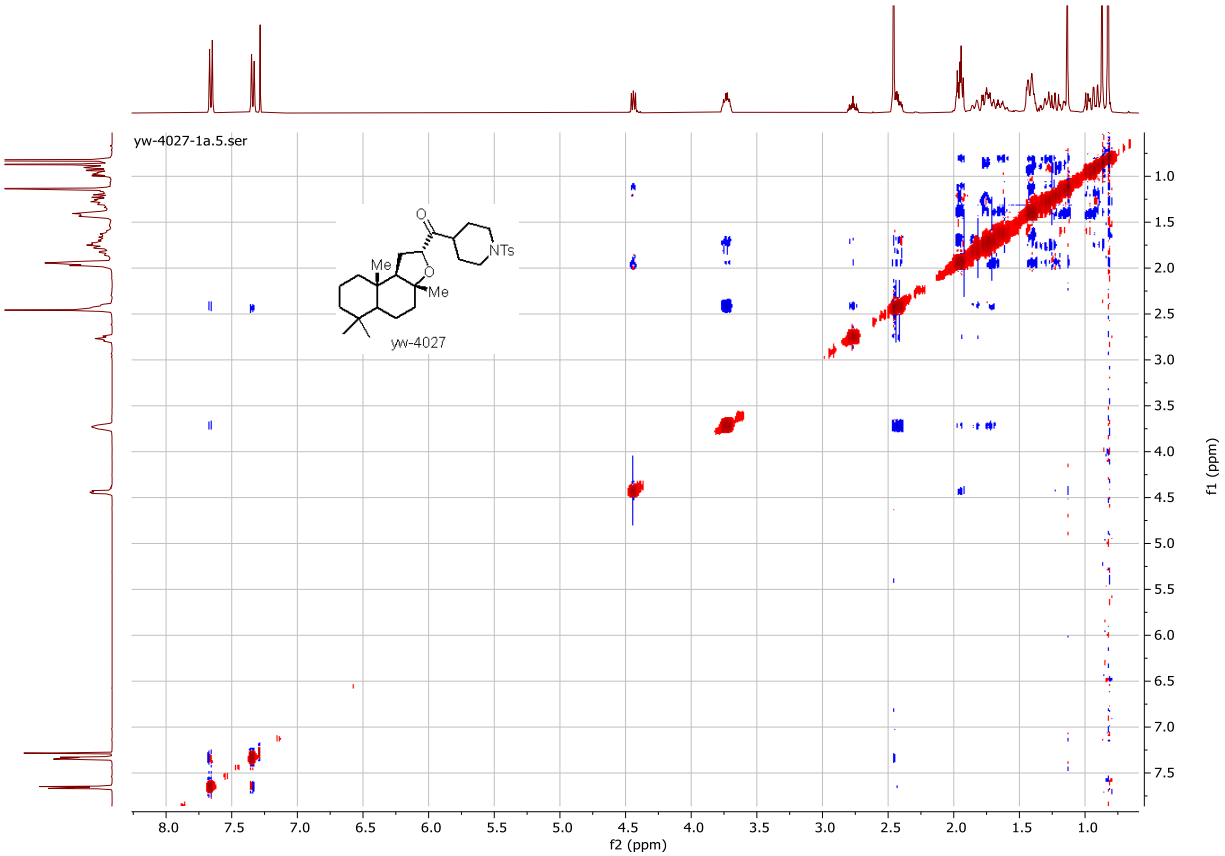
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **46**



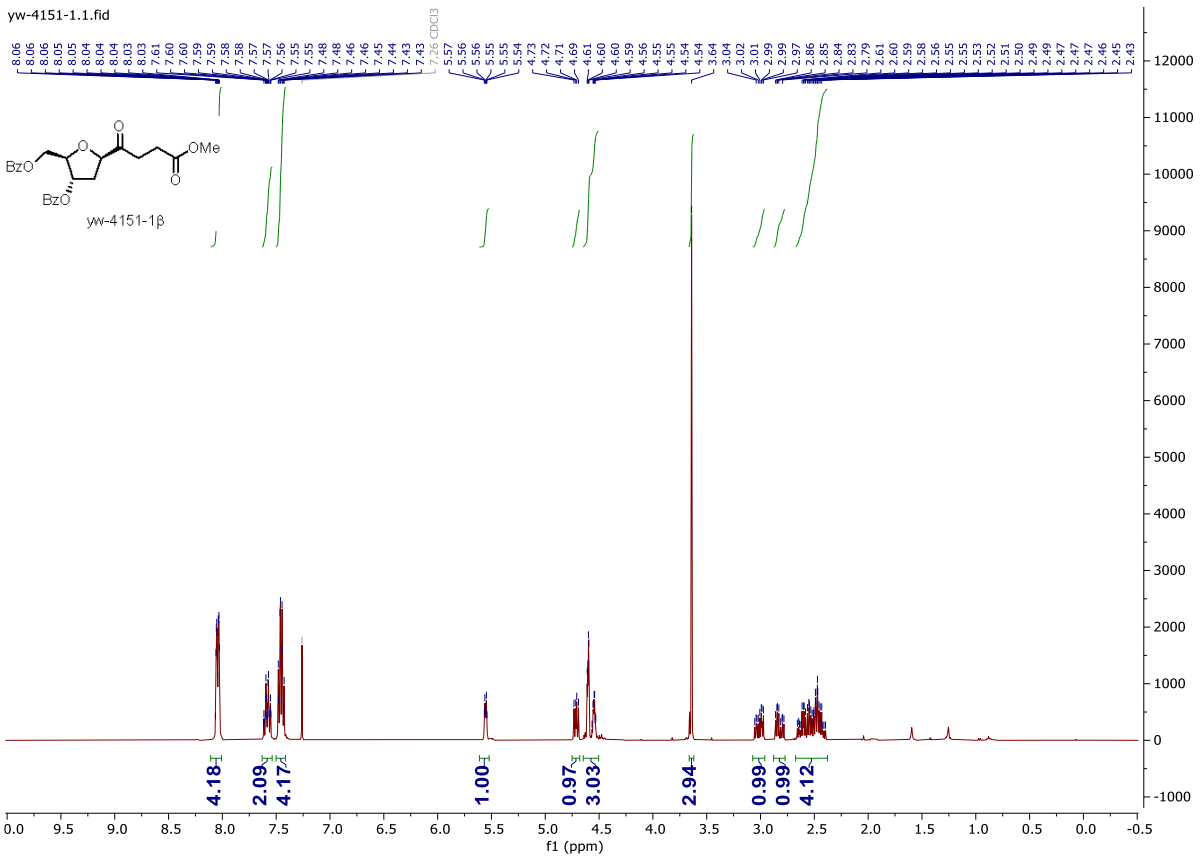
HSQCED of **46**



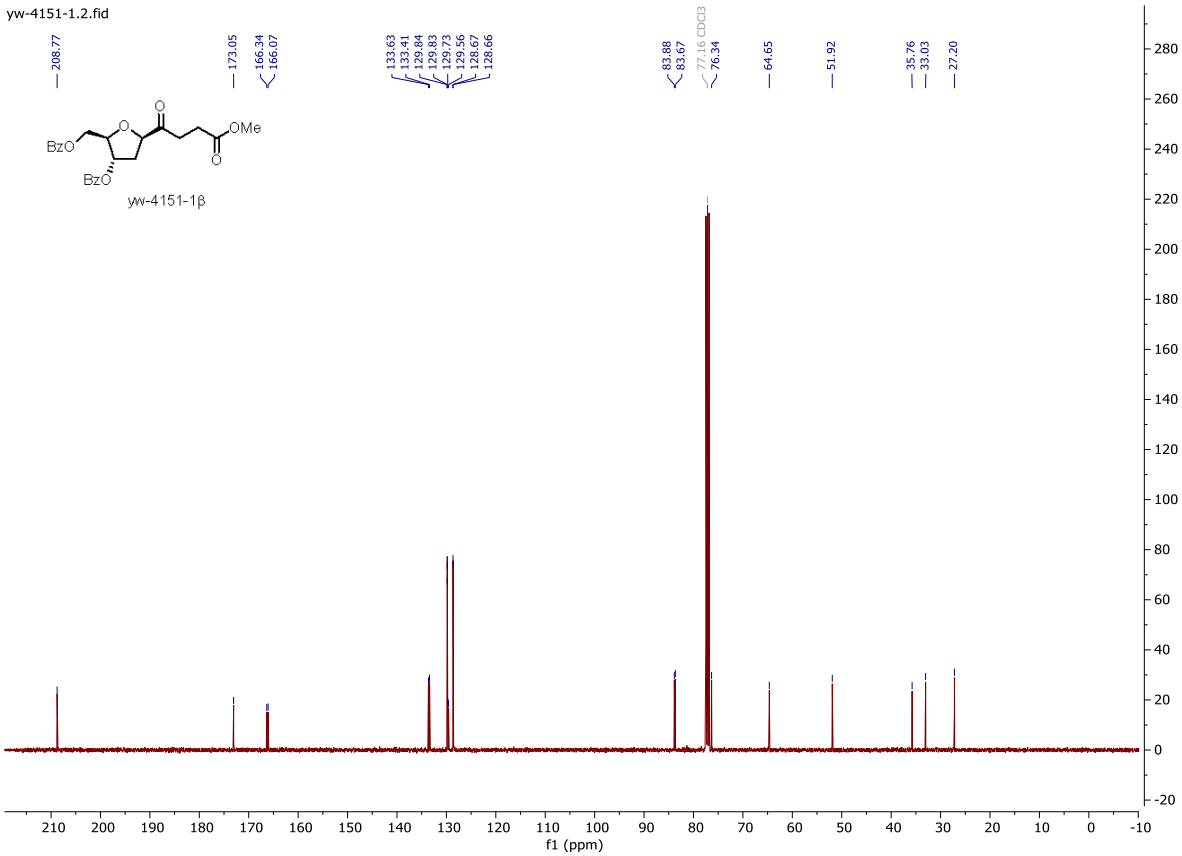
H-H COSY of **46**



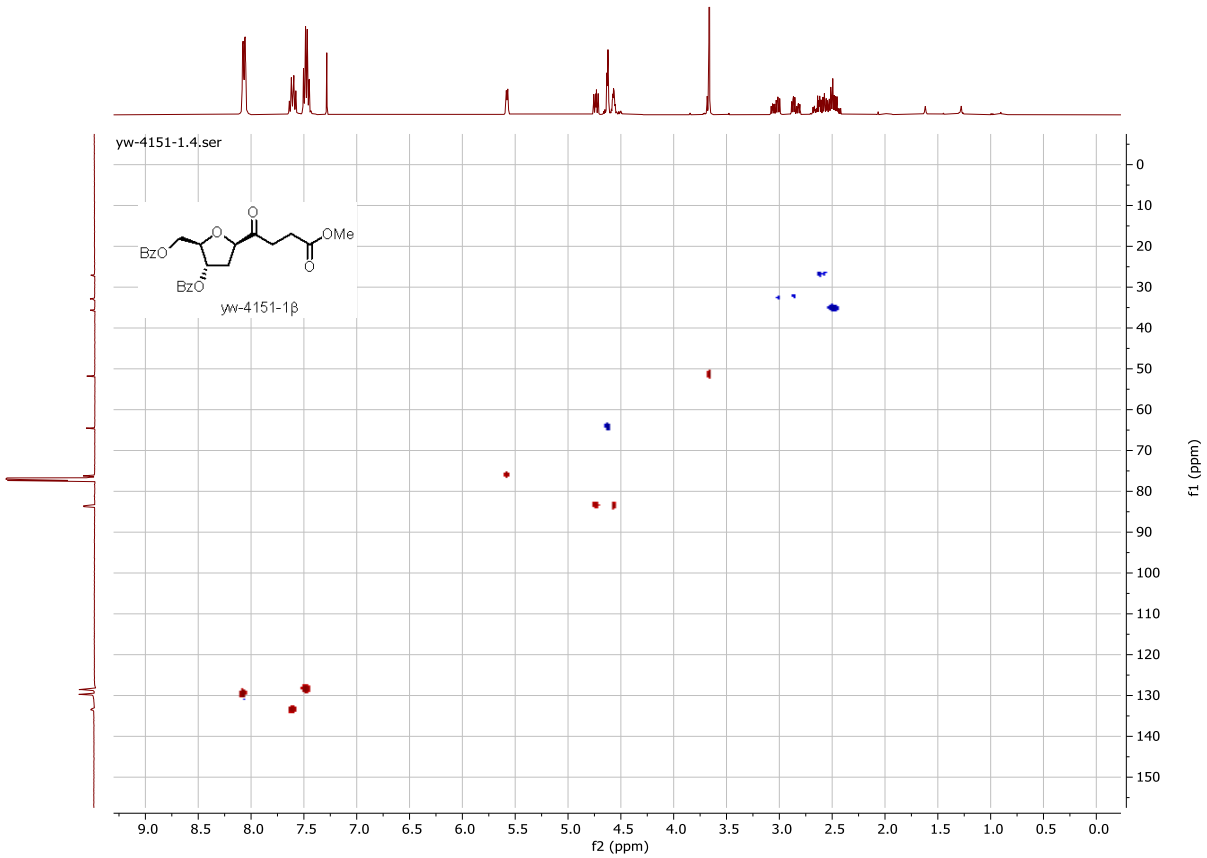
NOESY of **46**



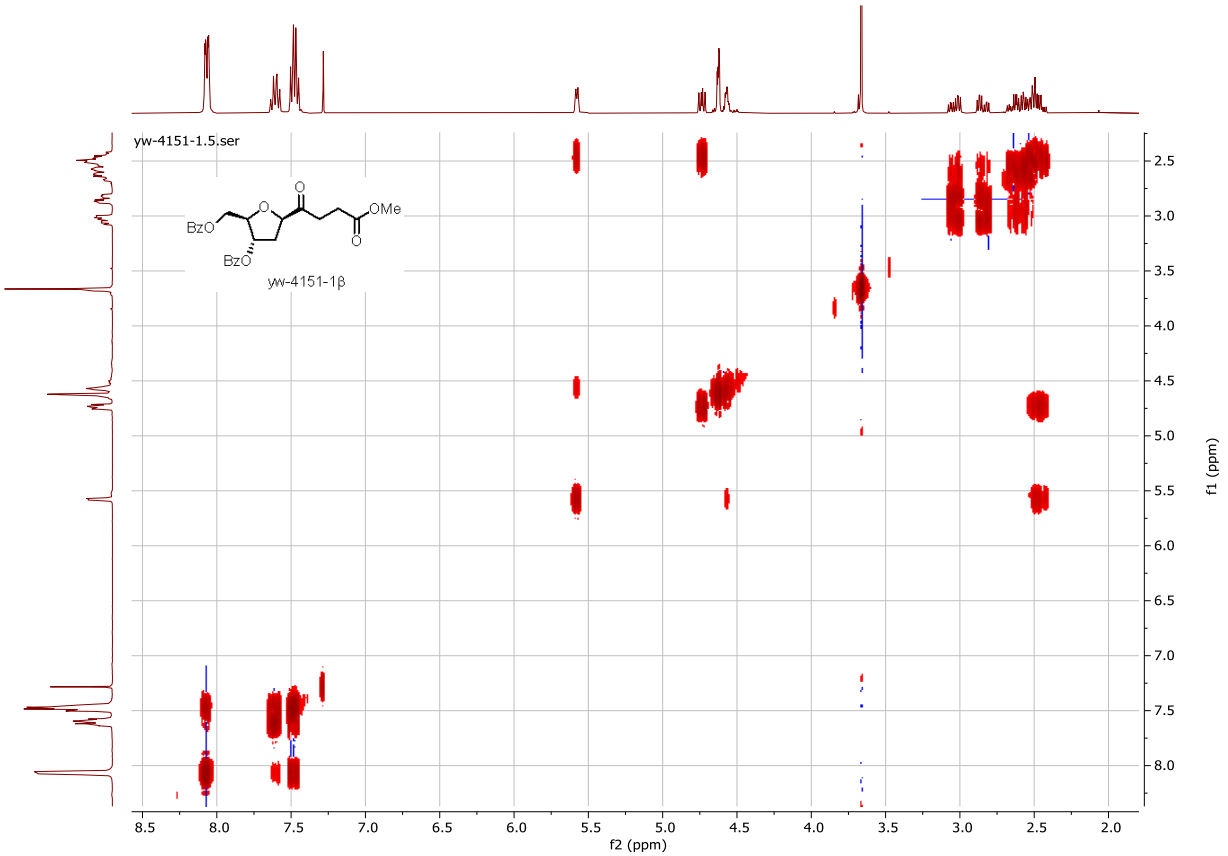
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **48β**



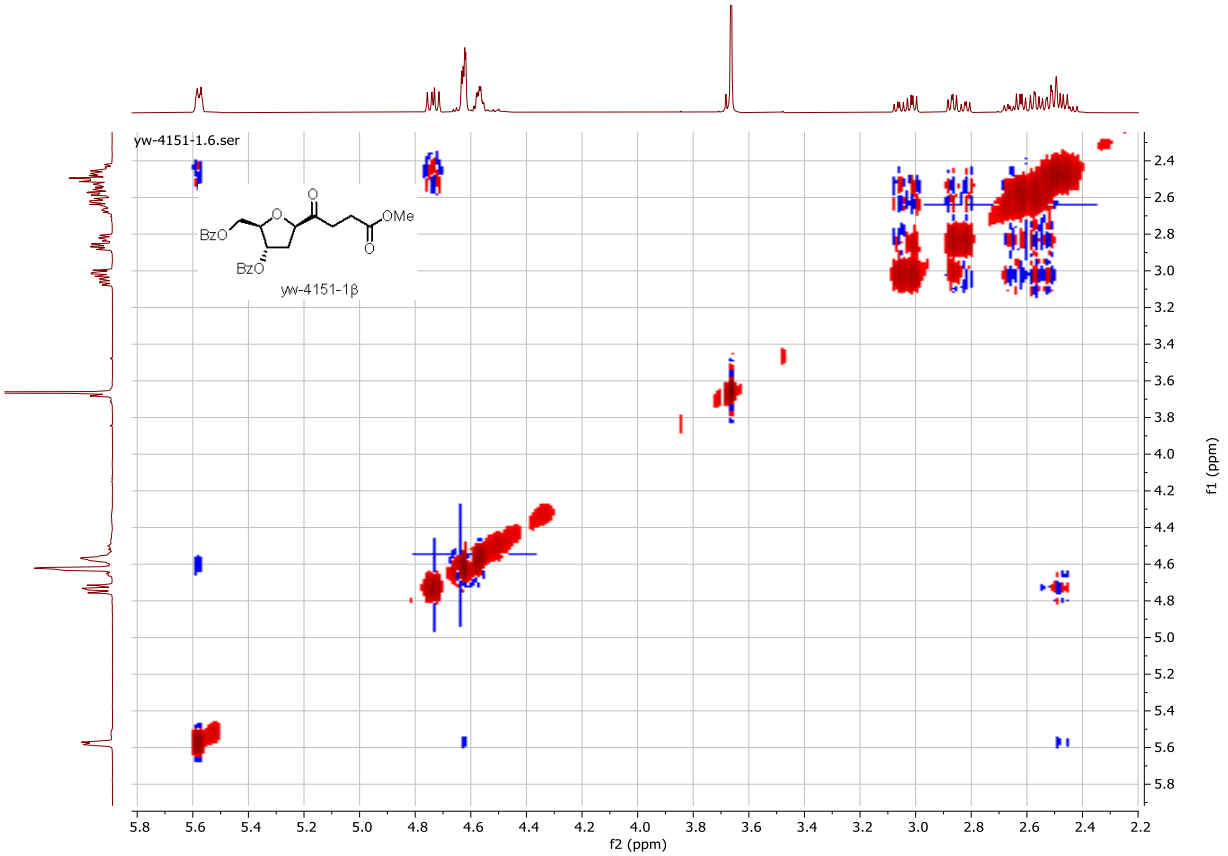
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **48β**



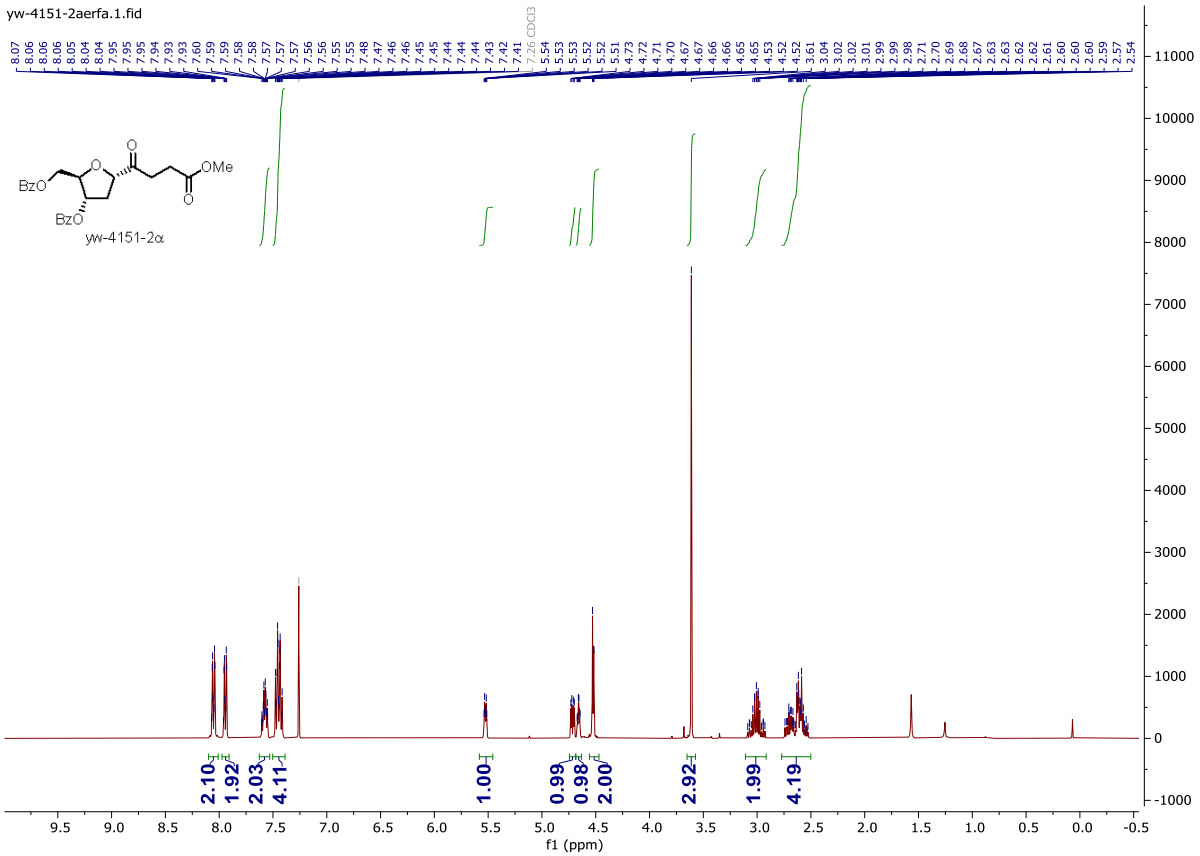
HSQCED of **48β**



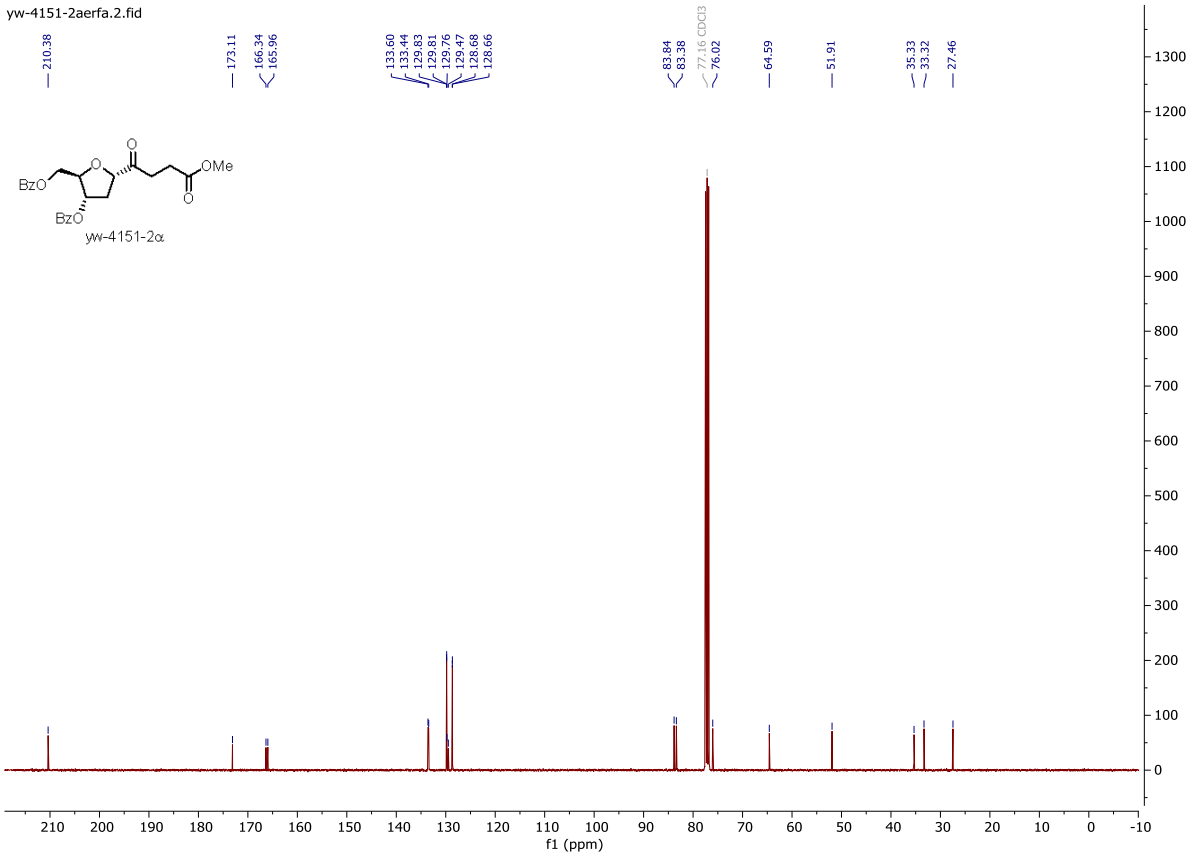
H-H COSY of **48β**



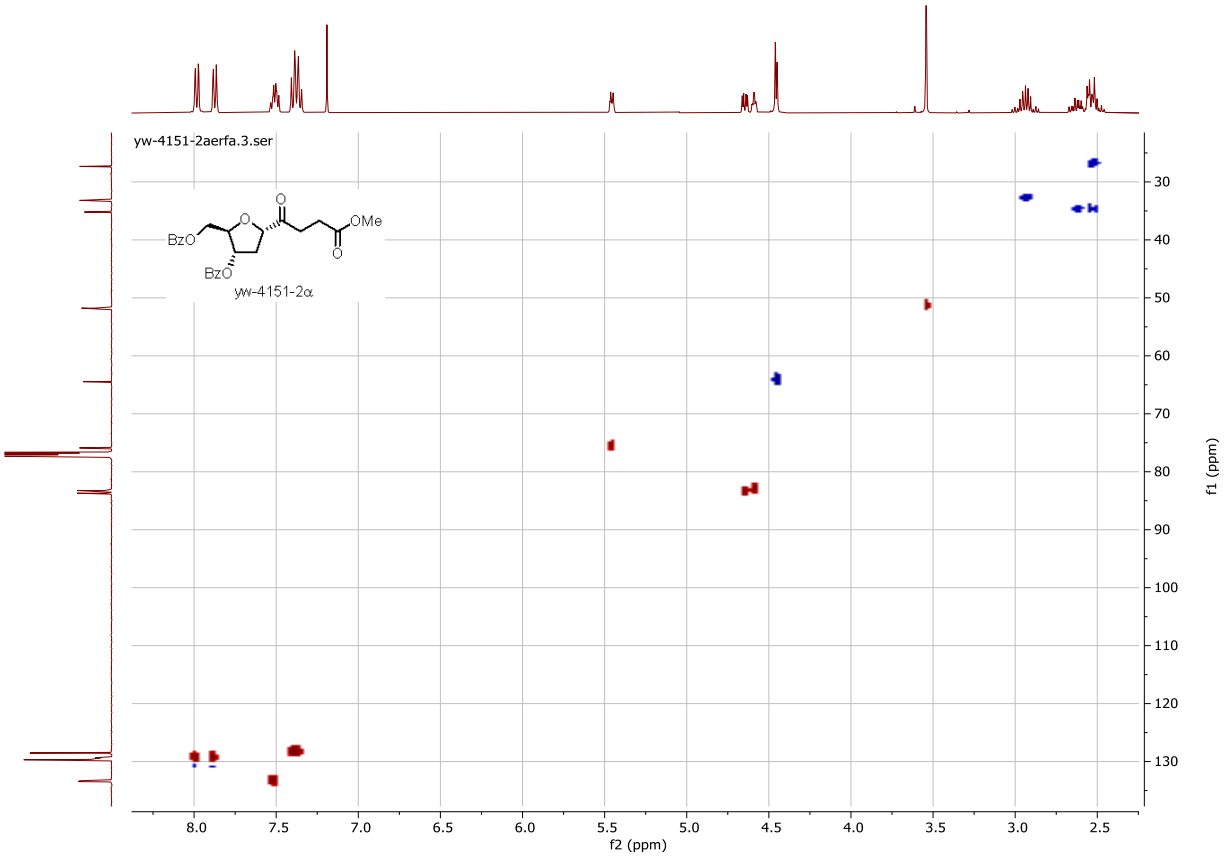
NOESY of **48β**



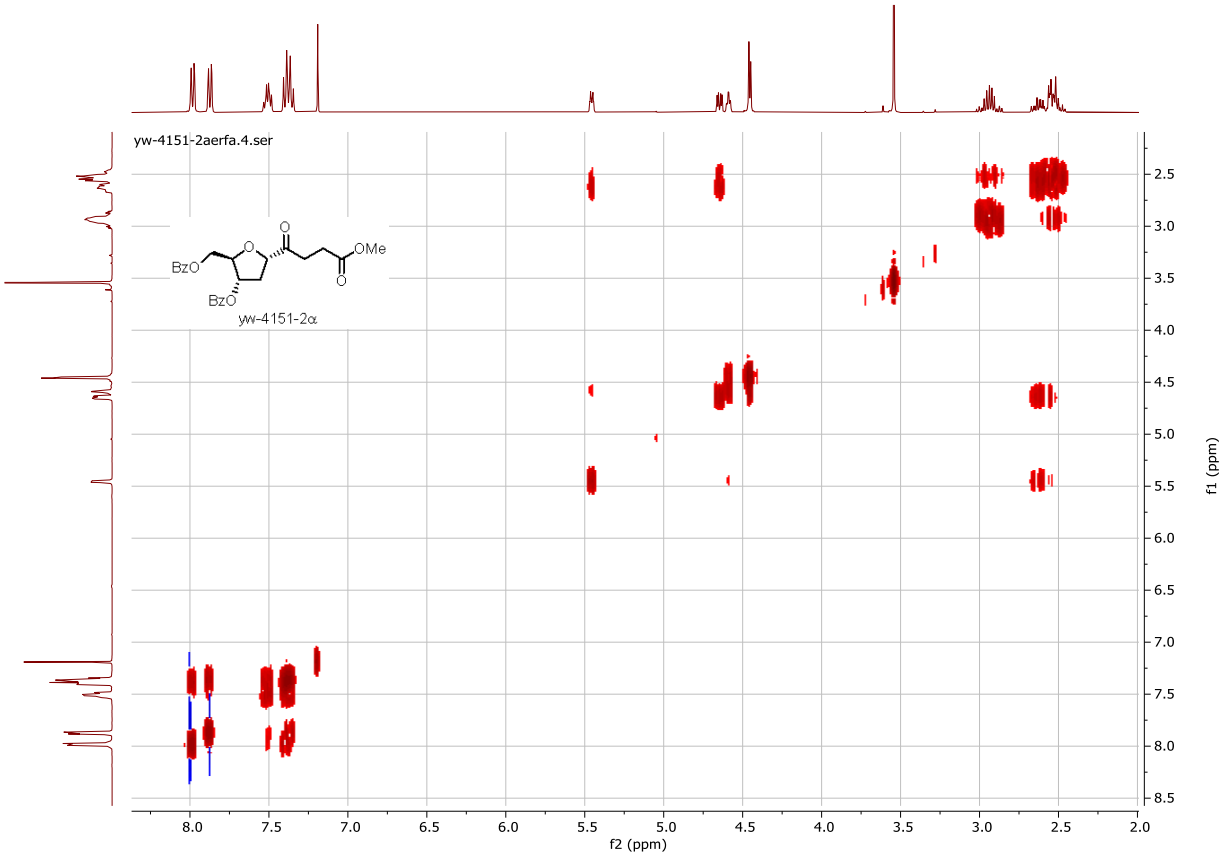
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **48α**



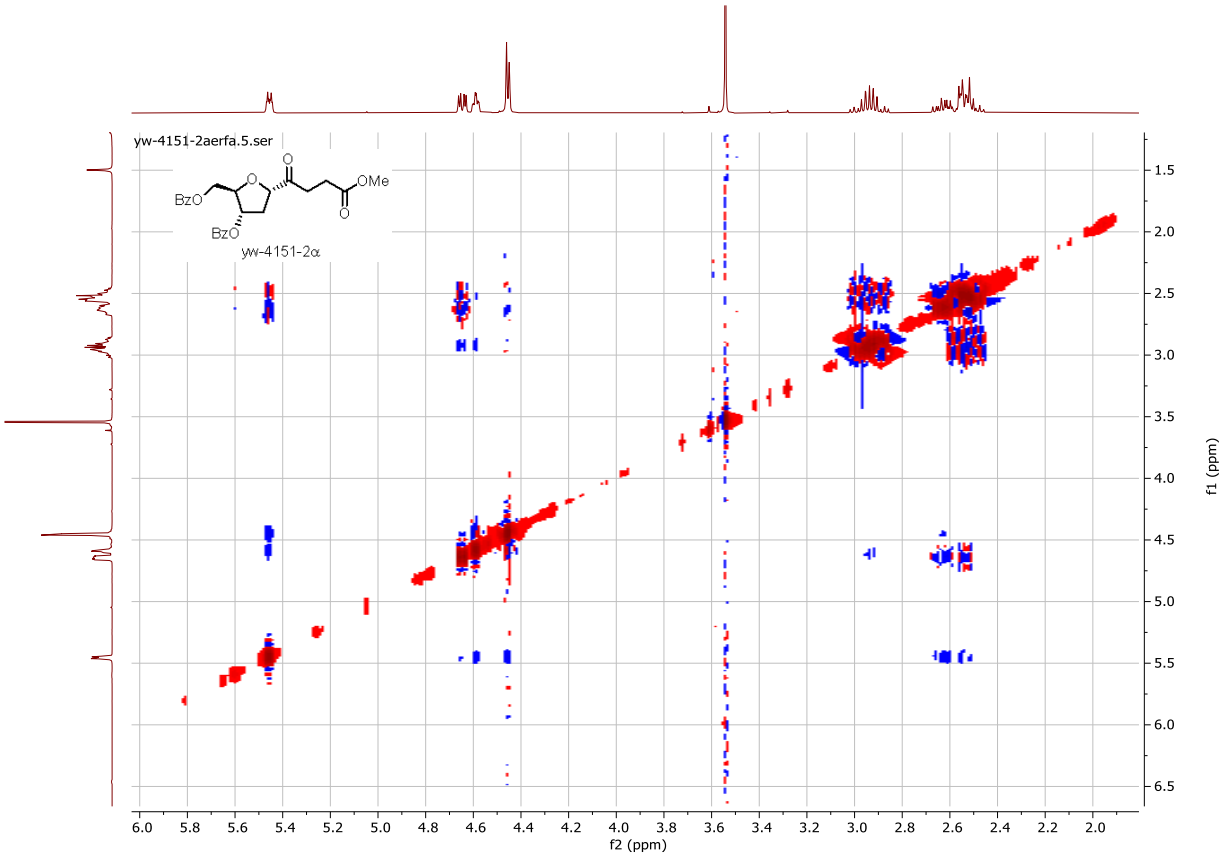
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **48α**



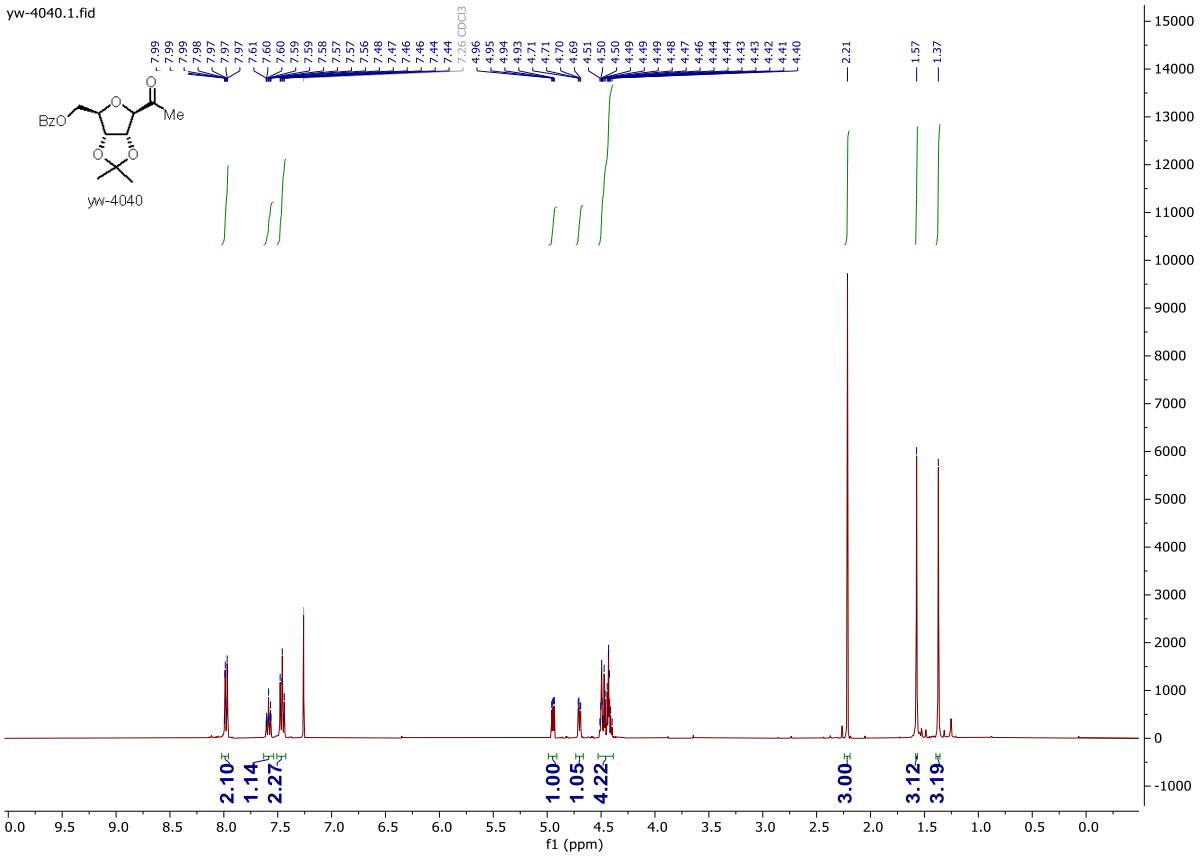
HSQCED of **48α**



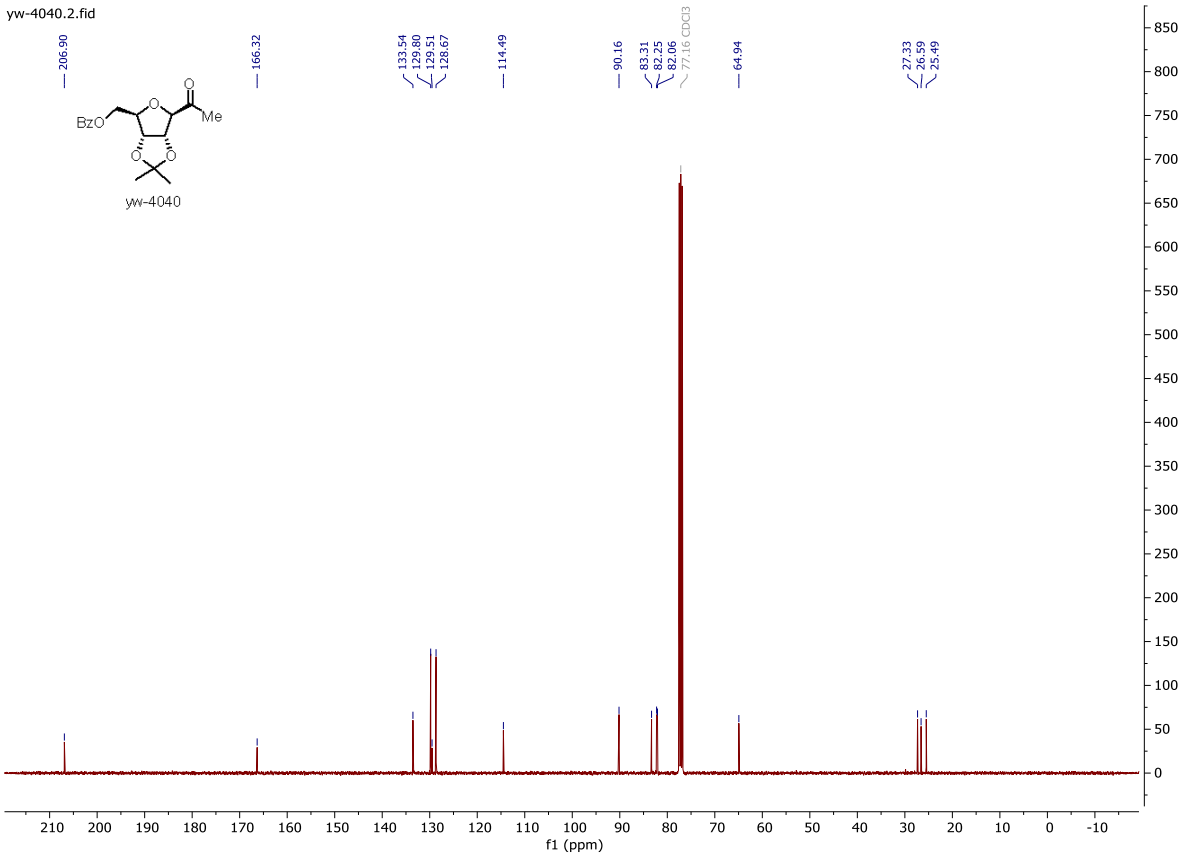
H-H COSY of **48α**



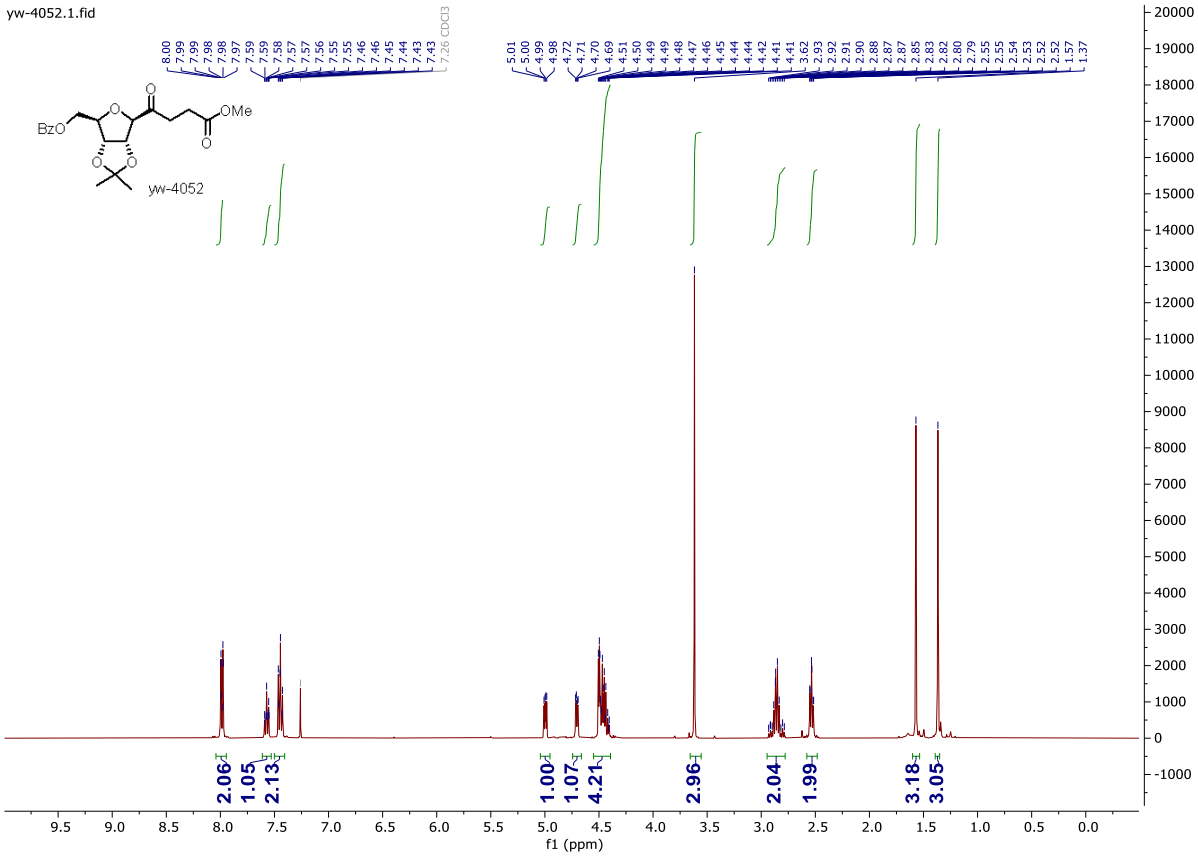
NOESY of **48α**



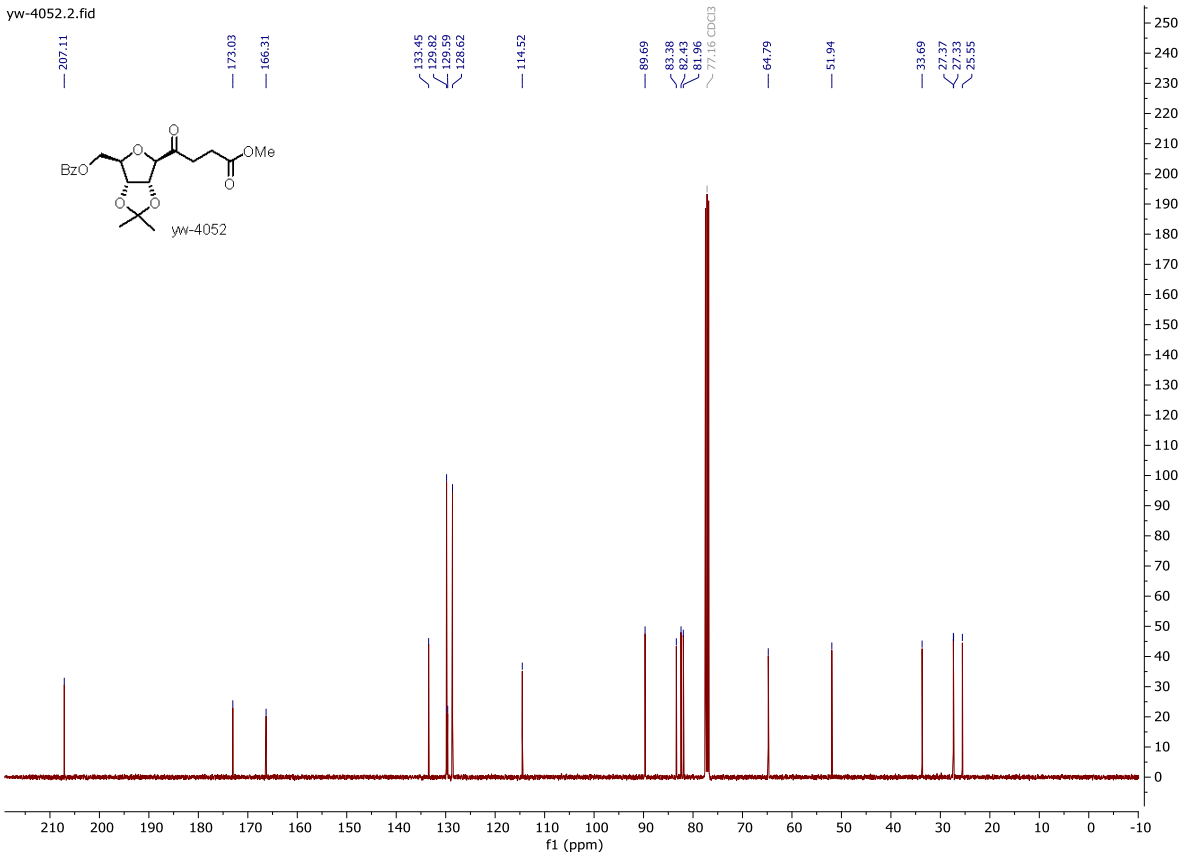
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S6**



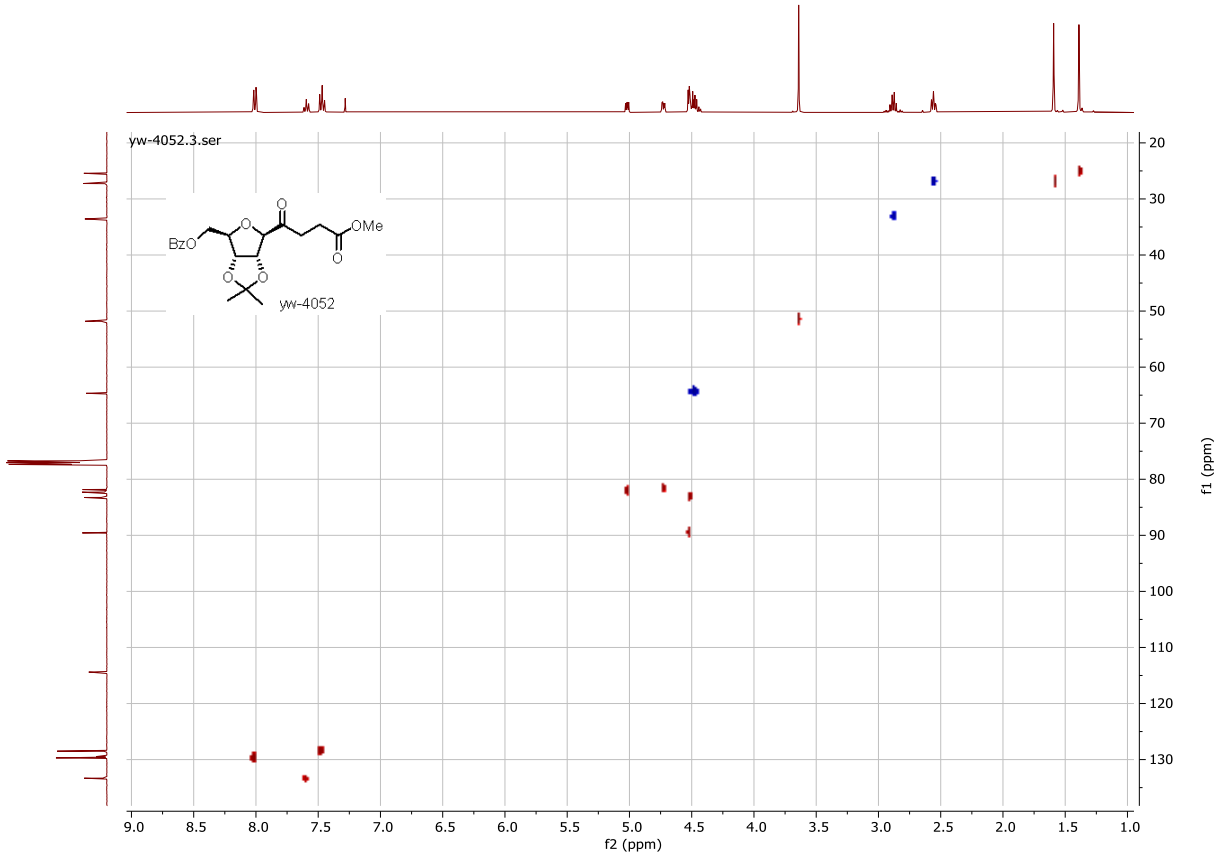
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S6**



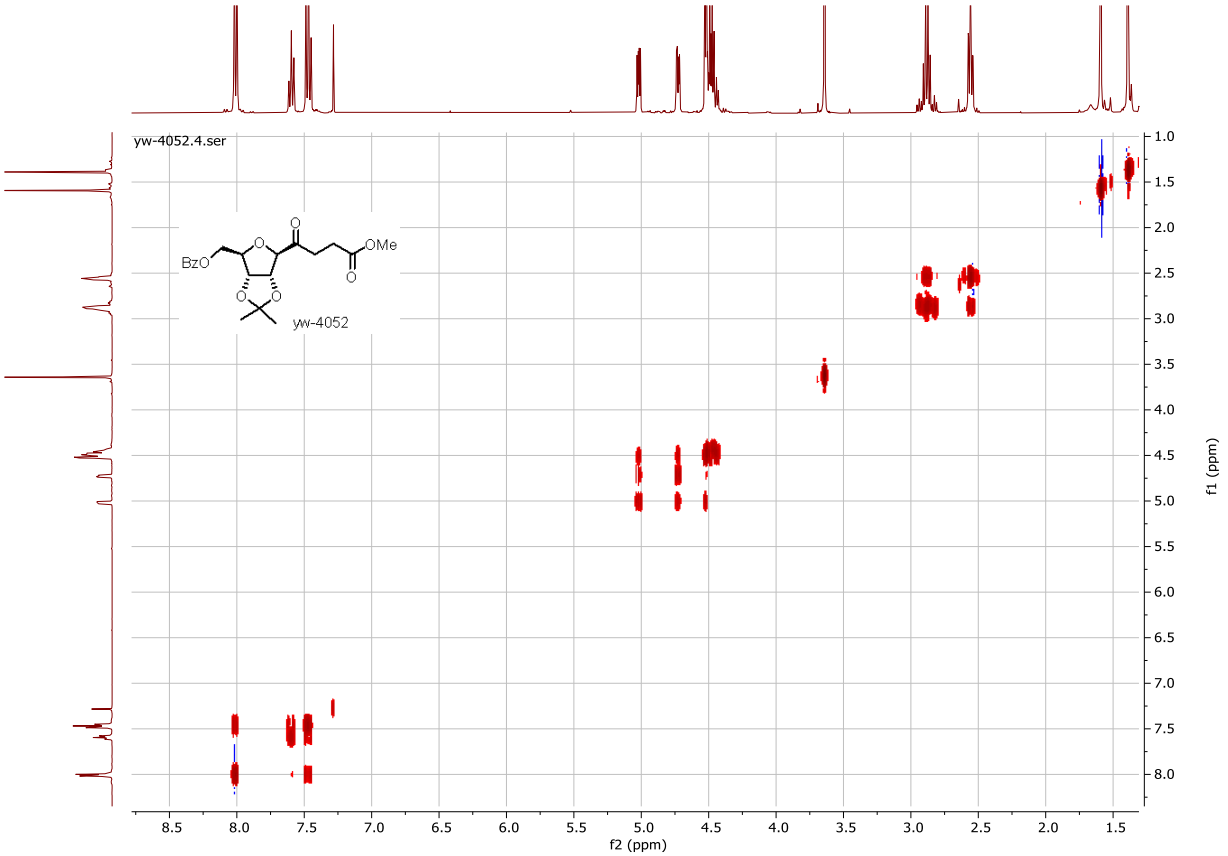
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S7**



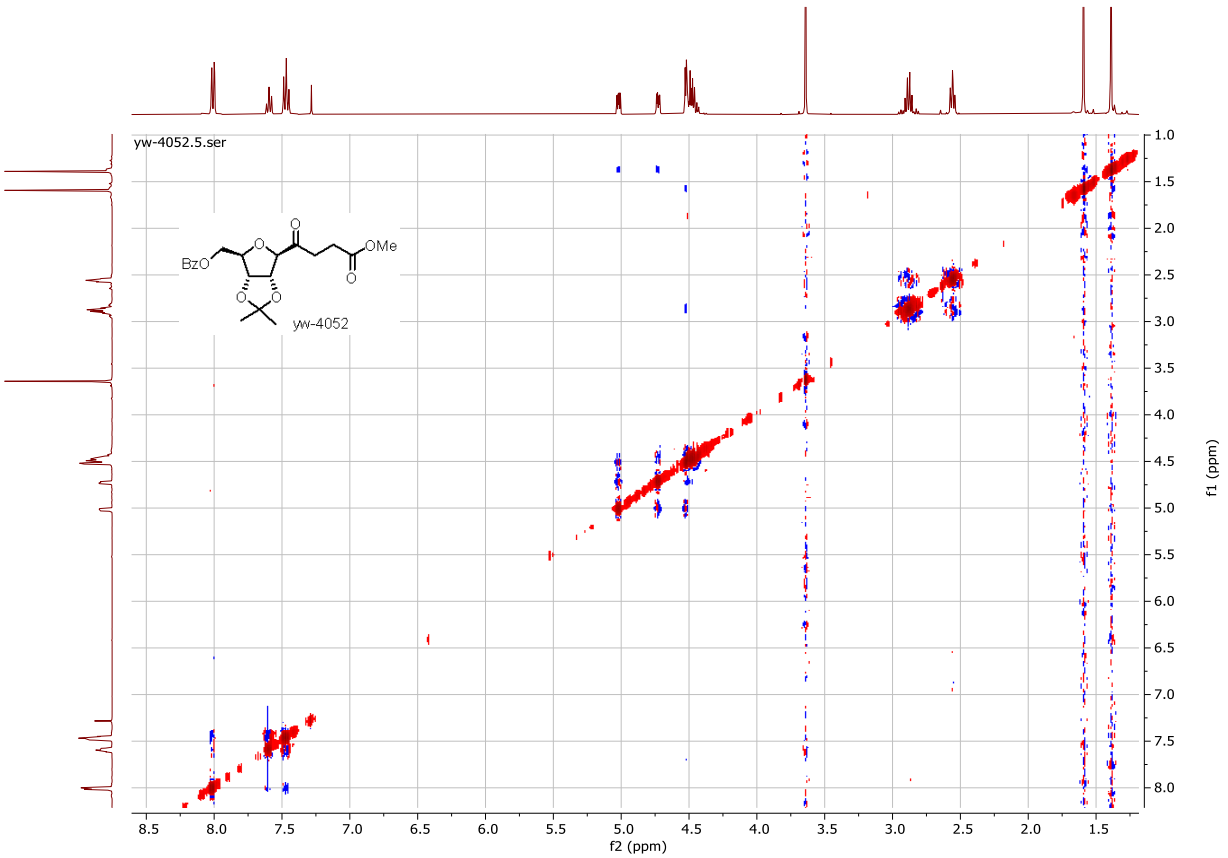
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S7**



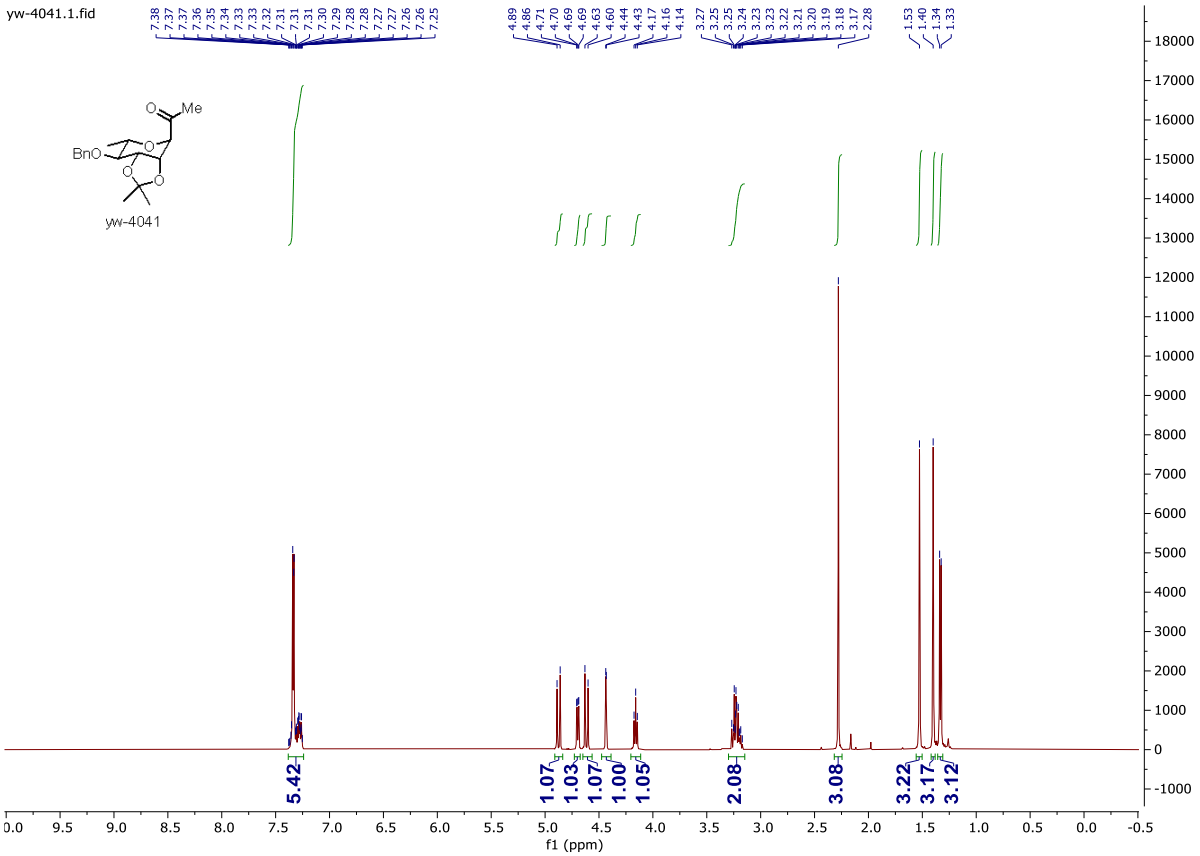
HSQCED of **S7**



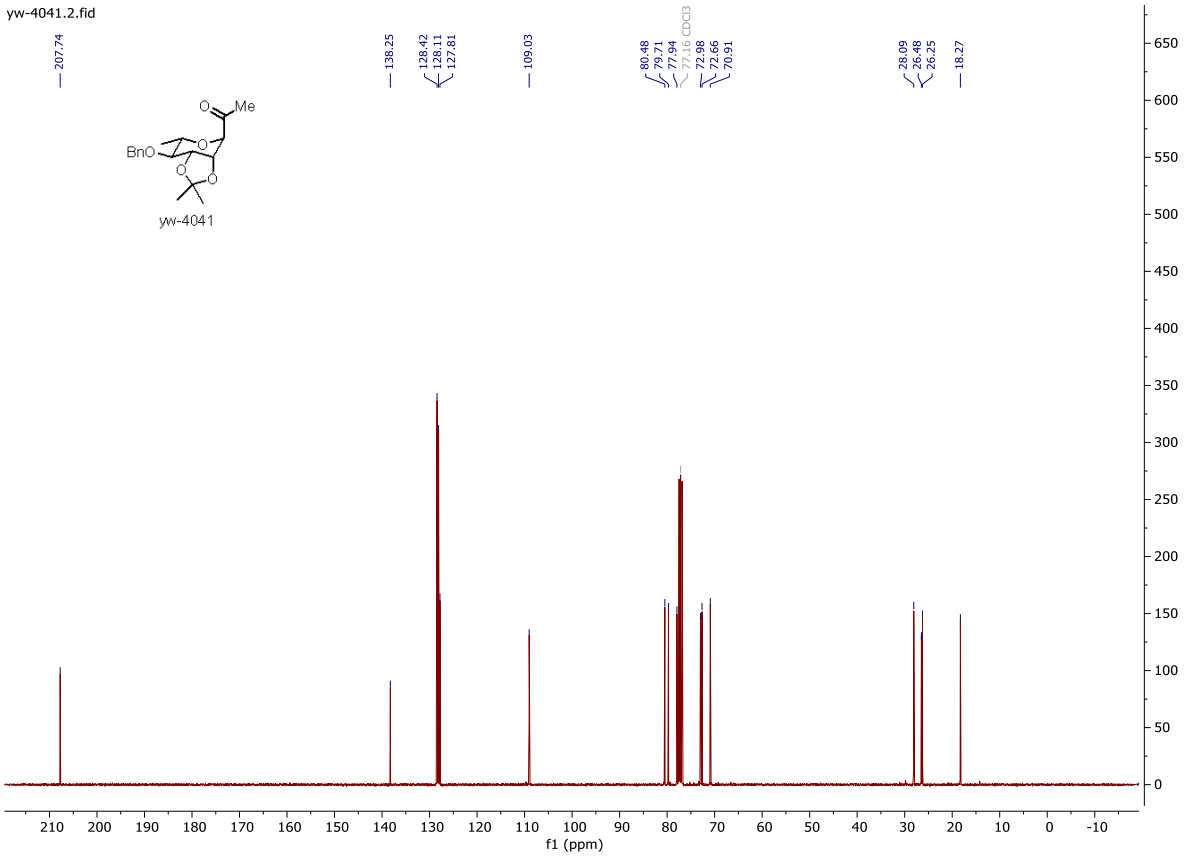
H-H COSY of **S7**



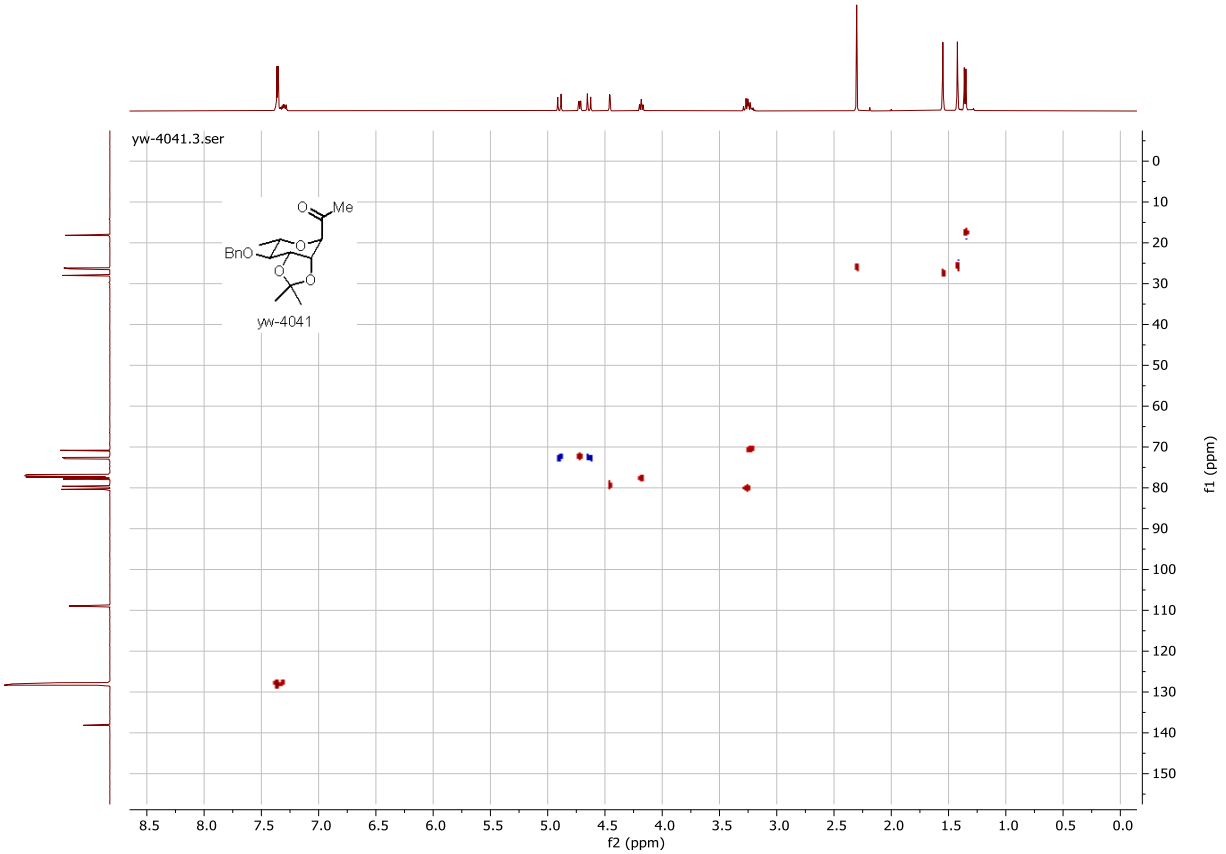
NOESY of **S7**



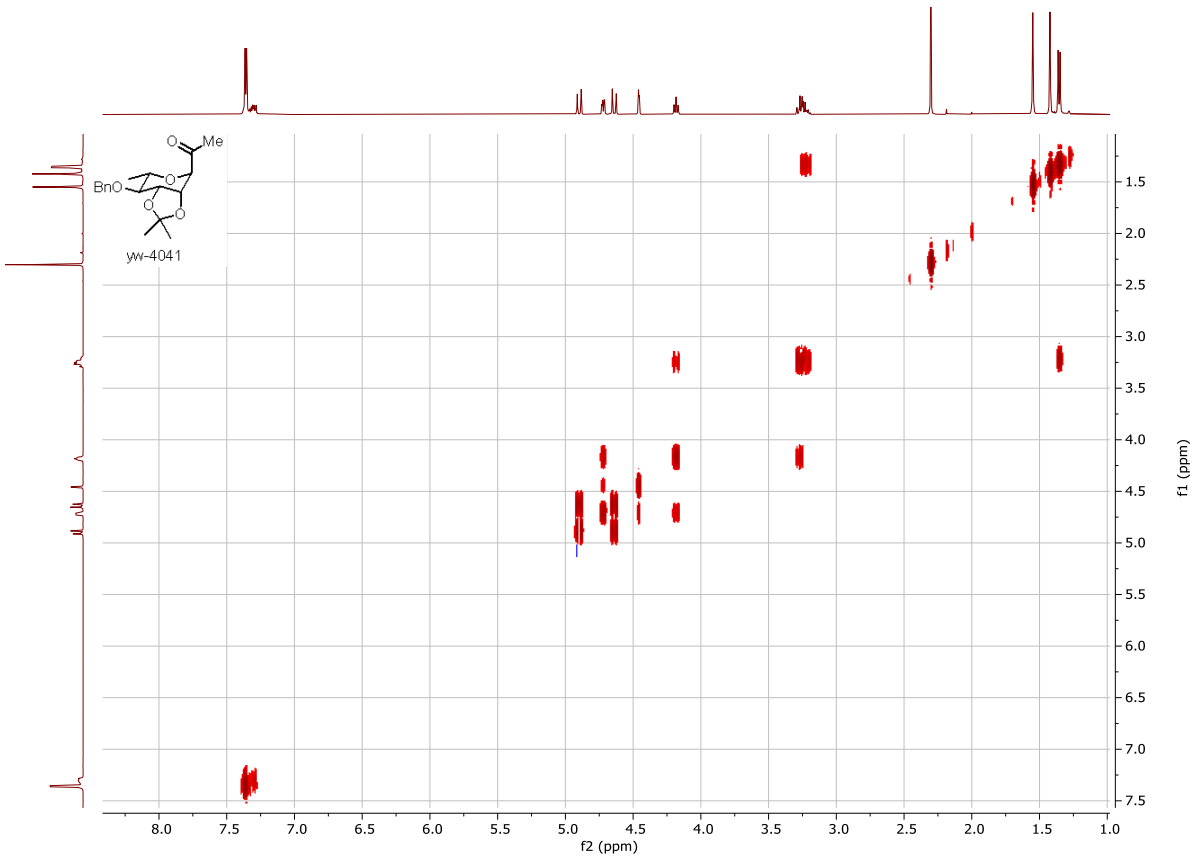
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S8**



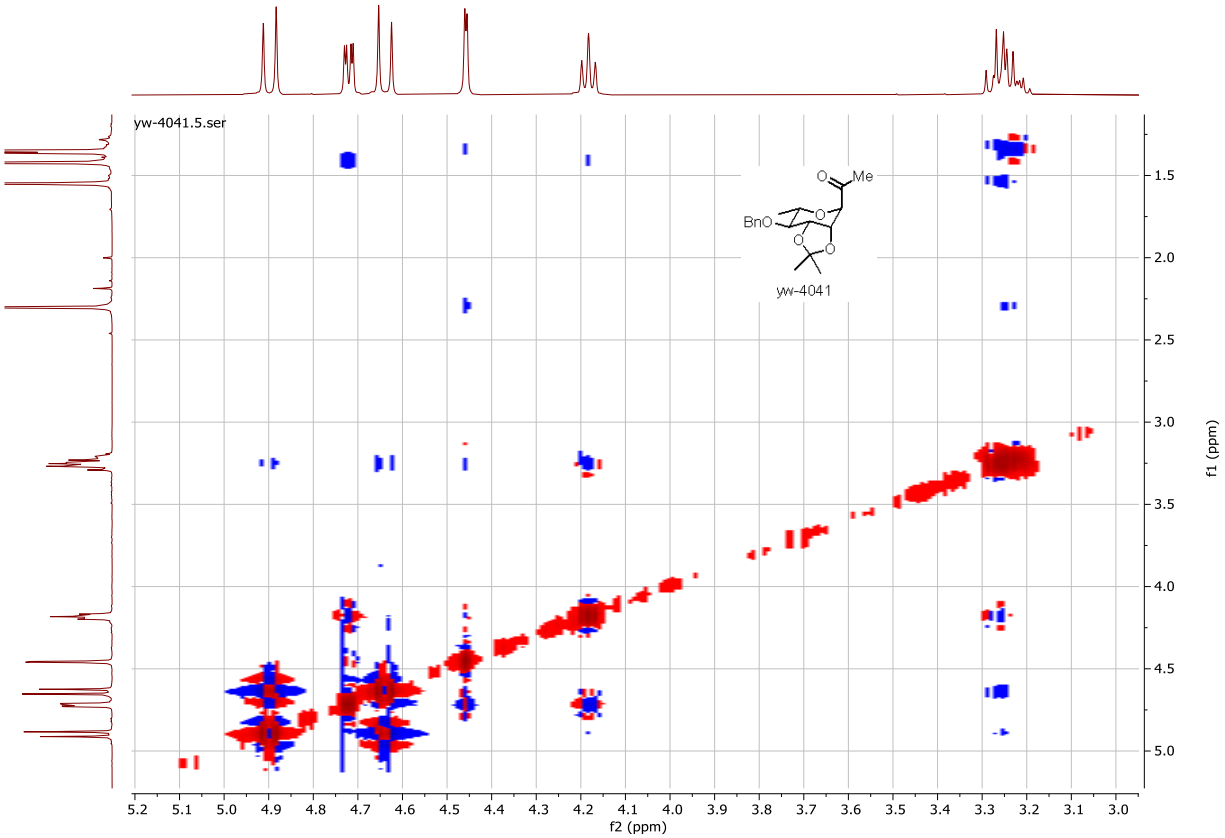
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S8**



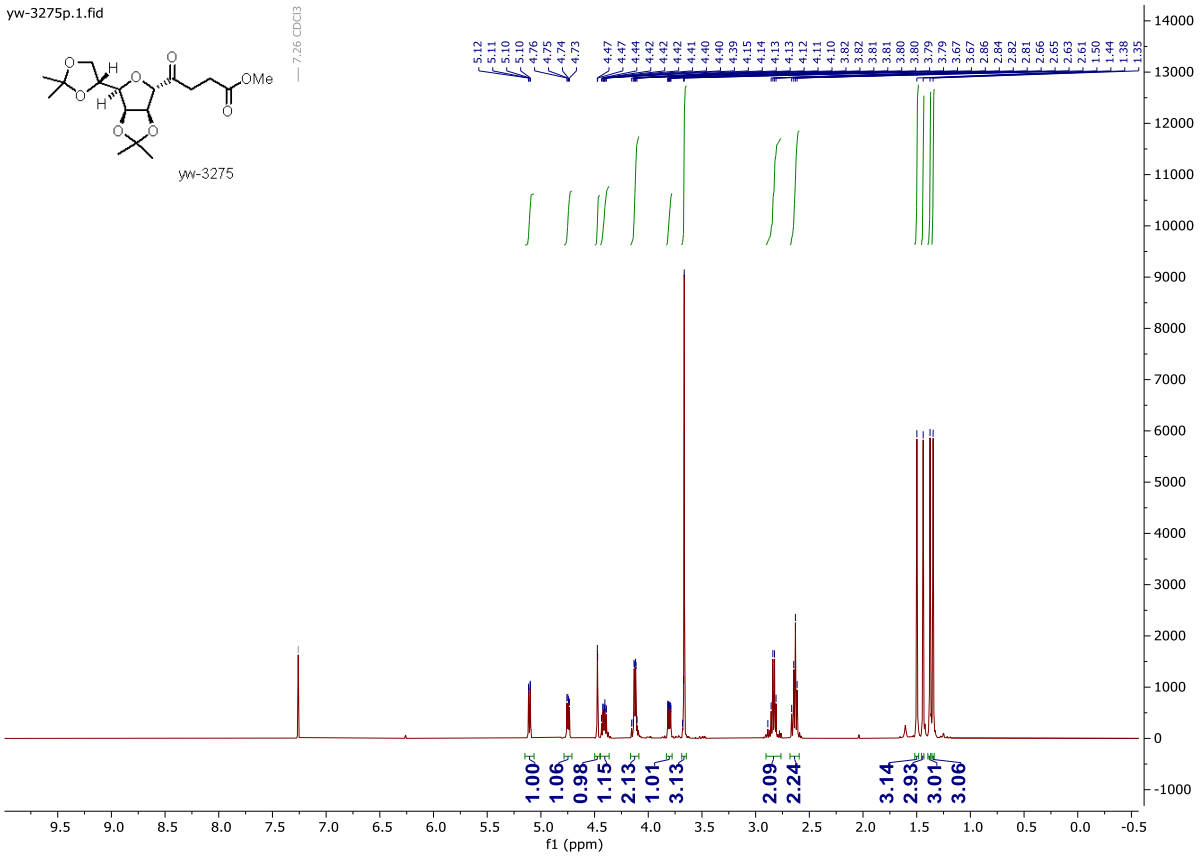
HSQCED of **S8**



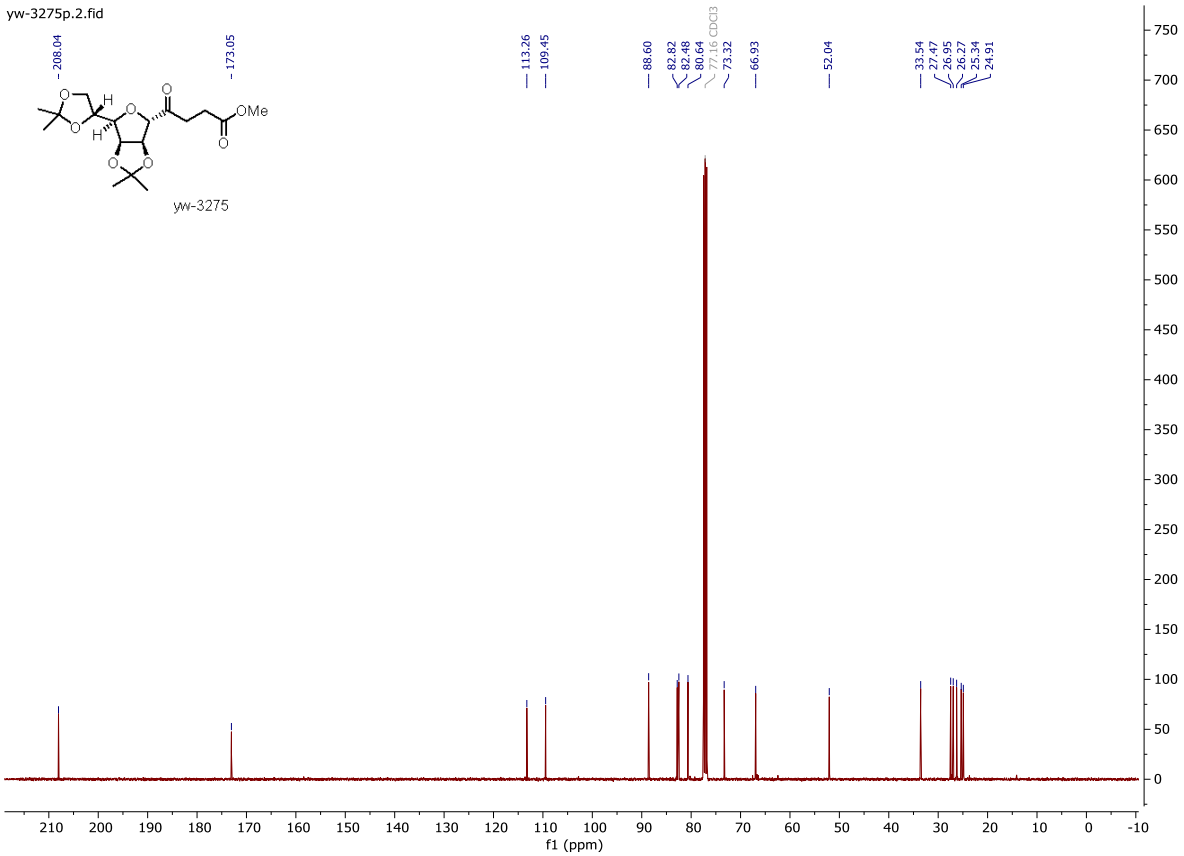
H-H COSY of **S8**



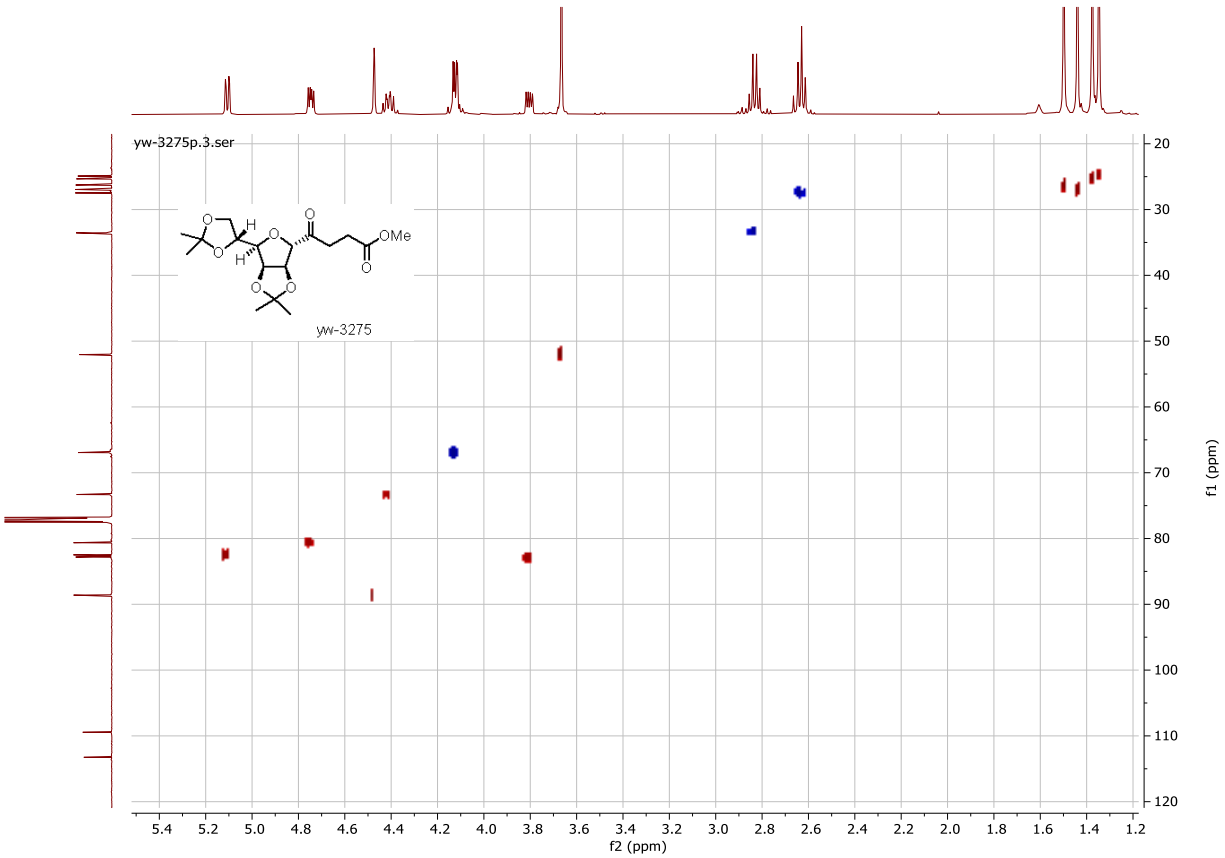
NOESY of **S8**



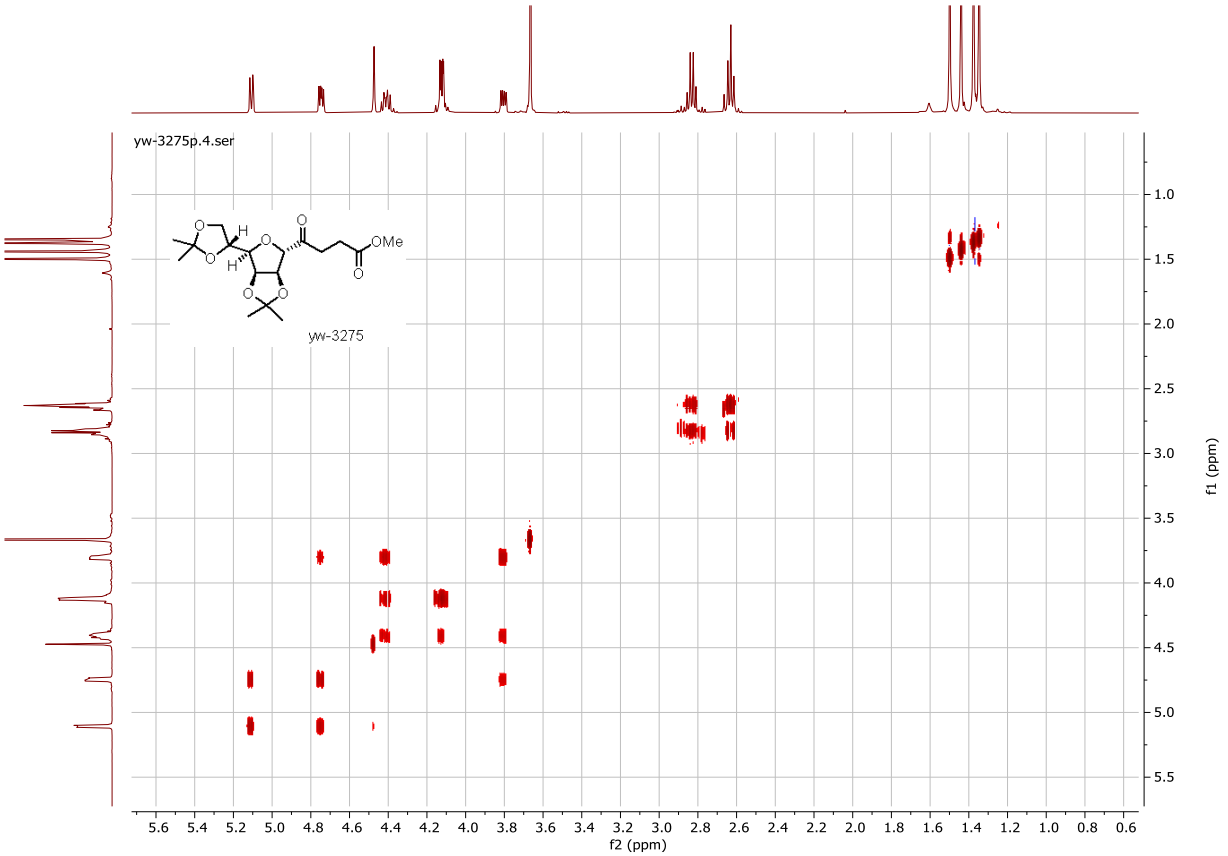
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **51**



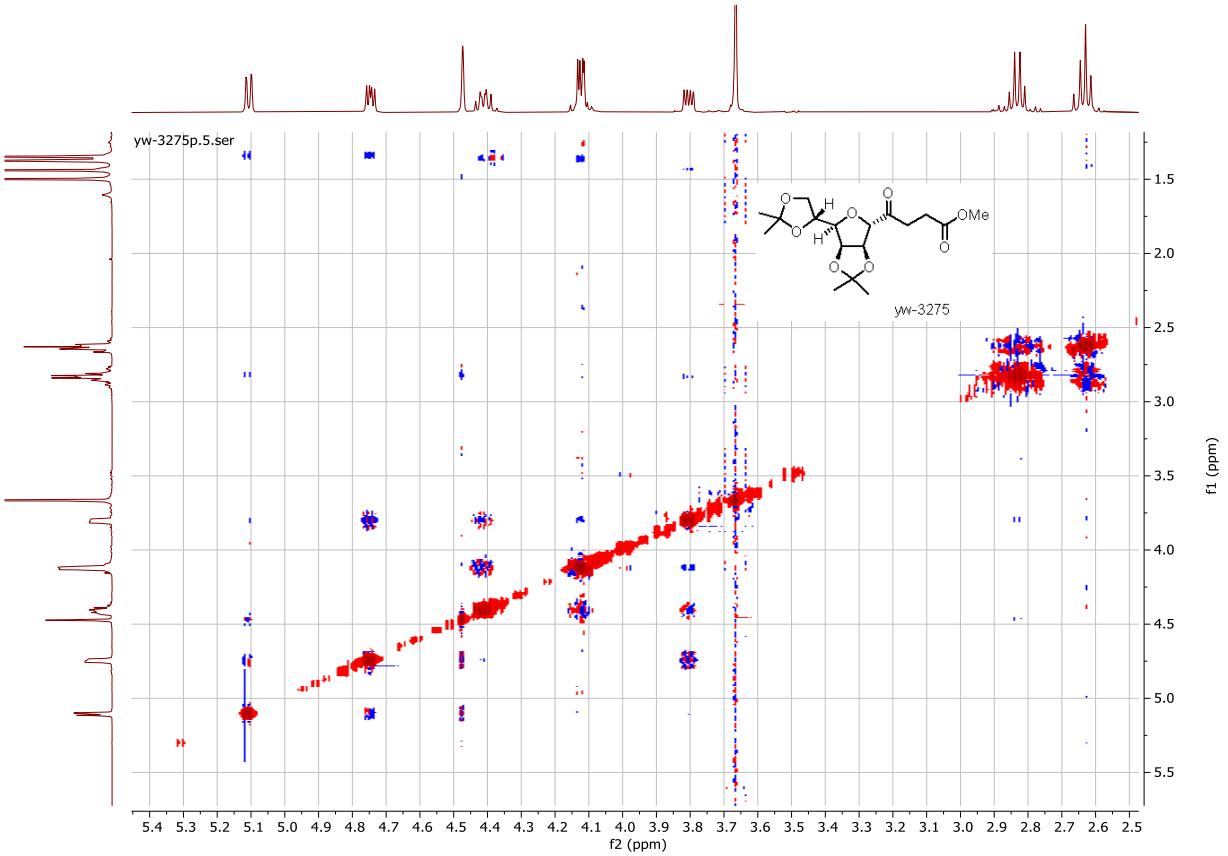
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **51**



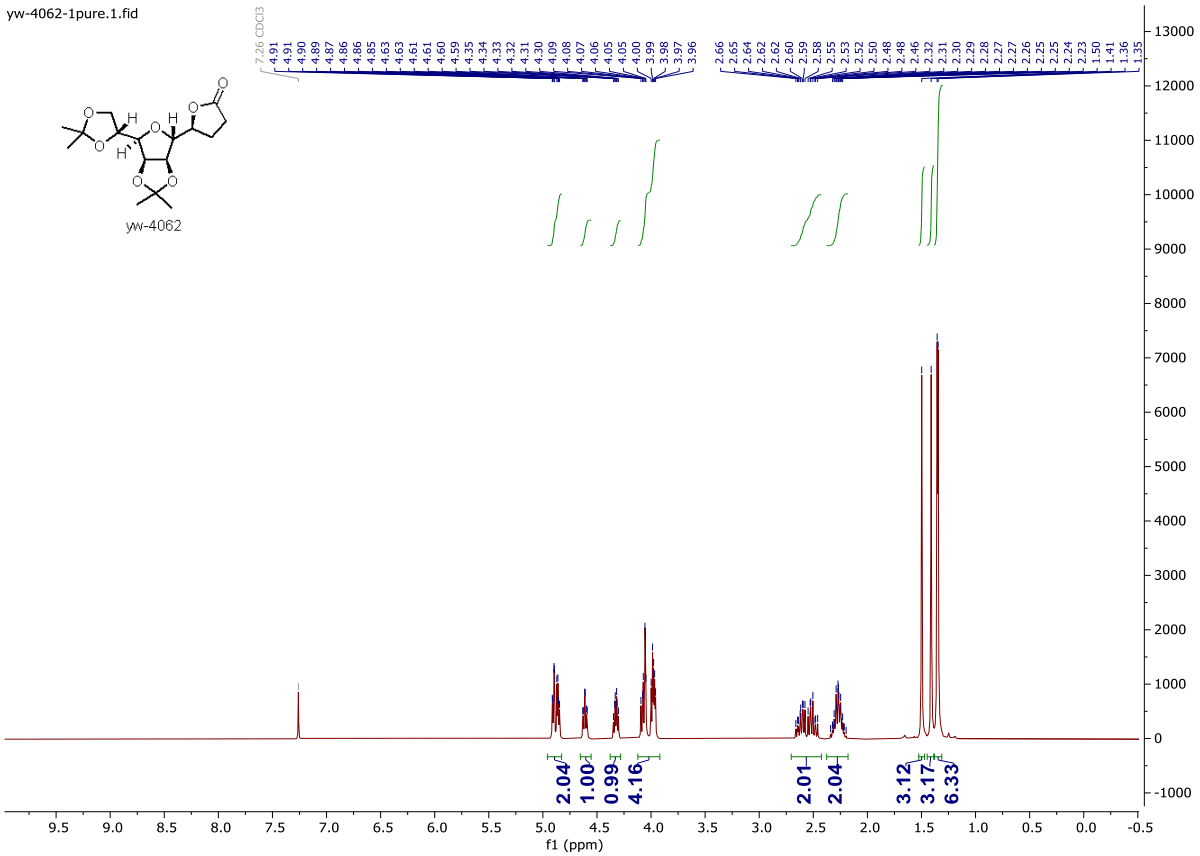
HSQCED of **51**



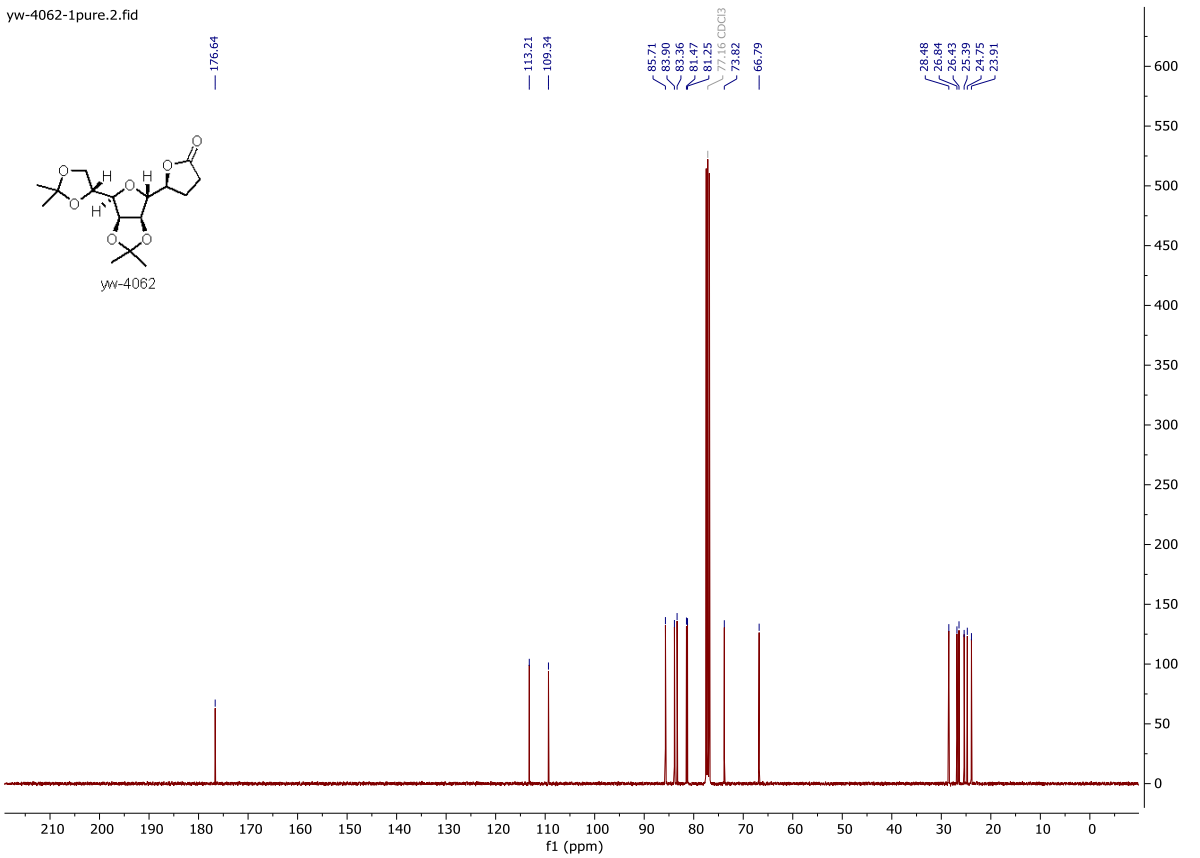
H-H COSY of **51**



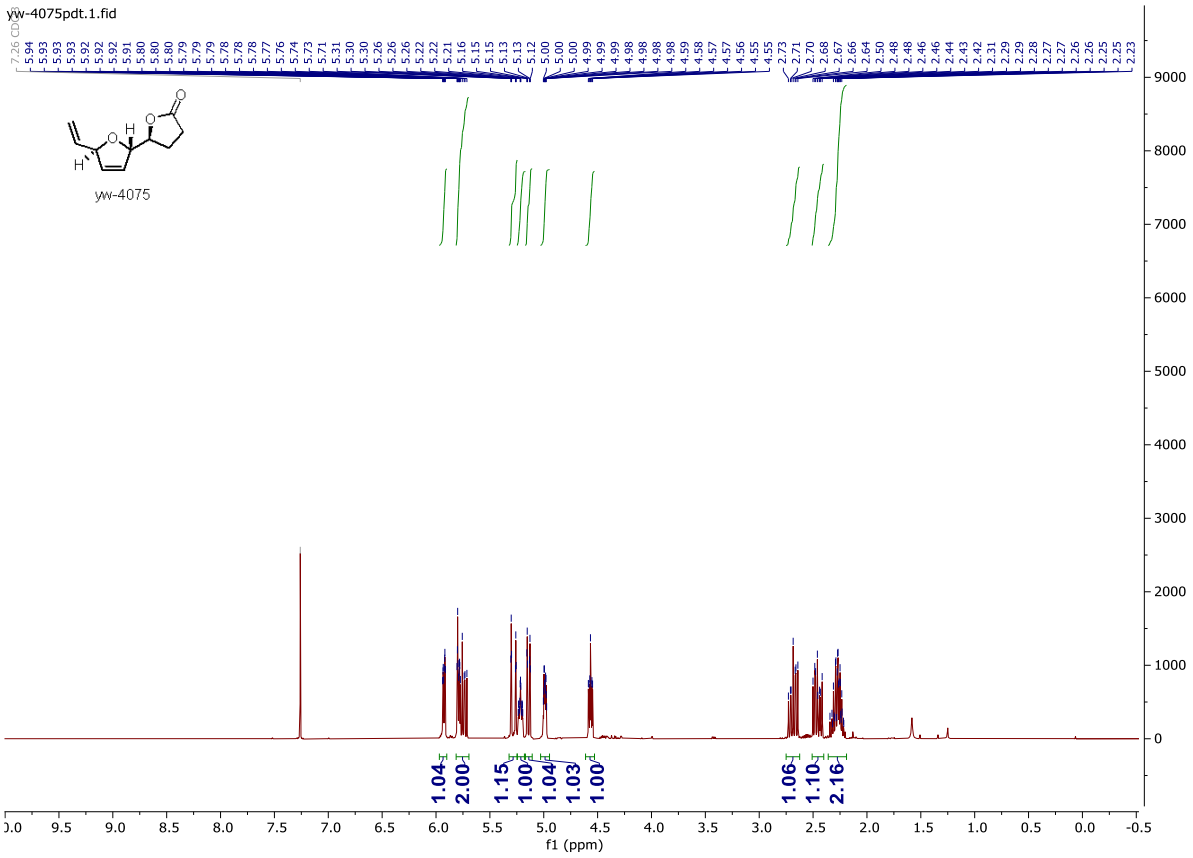
NOESY of **51**



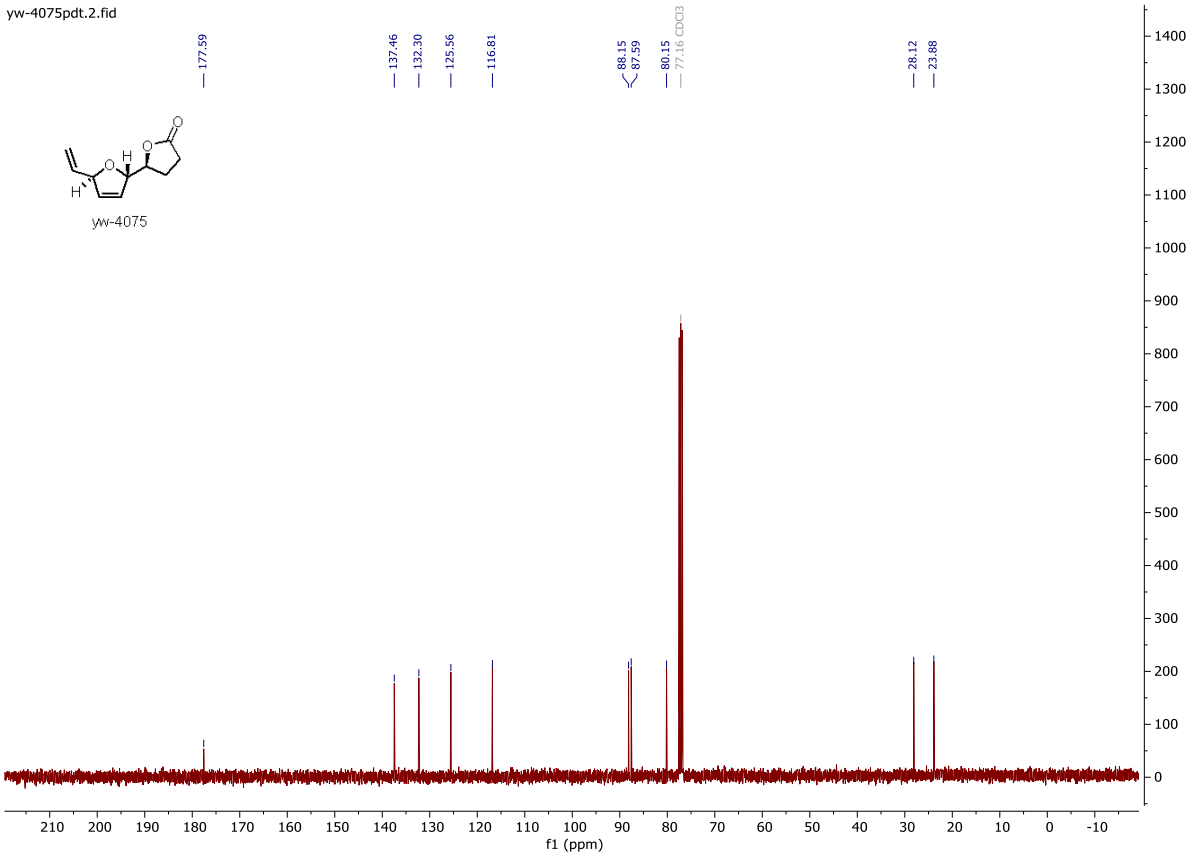
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **52**



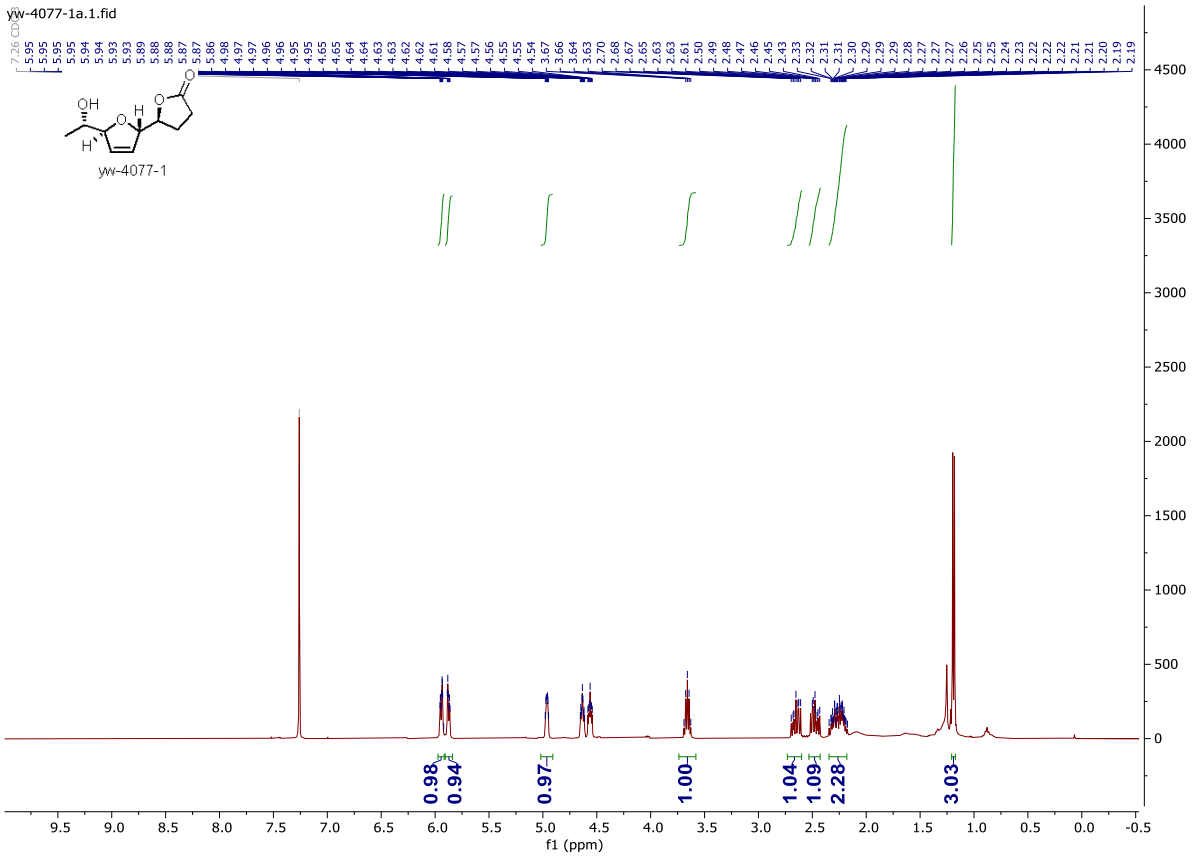
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **52**



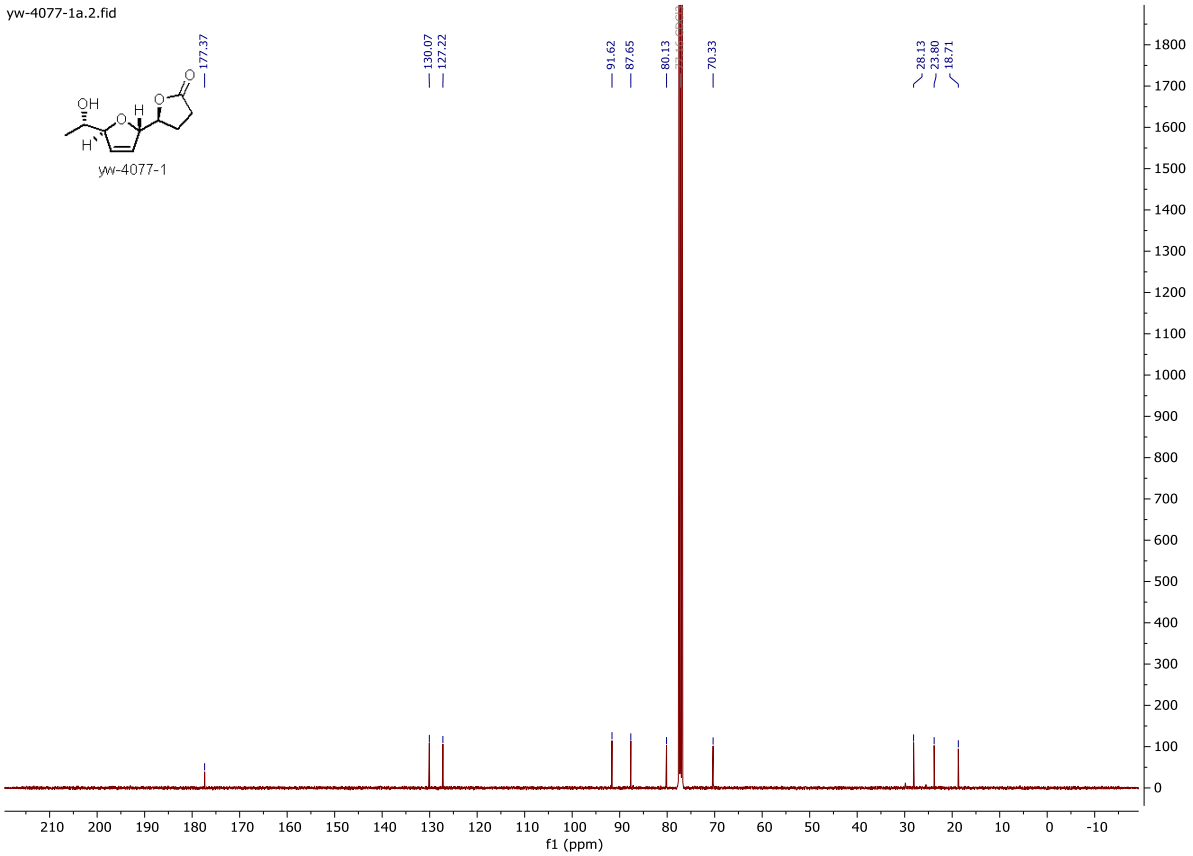
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **53**



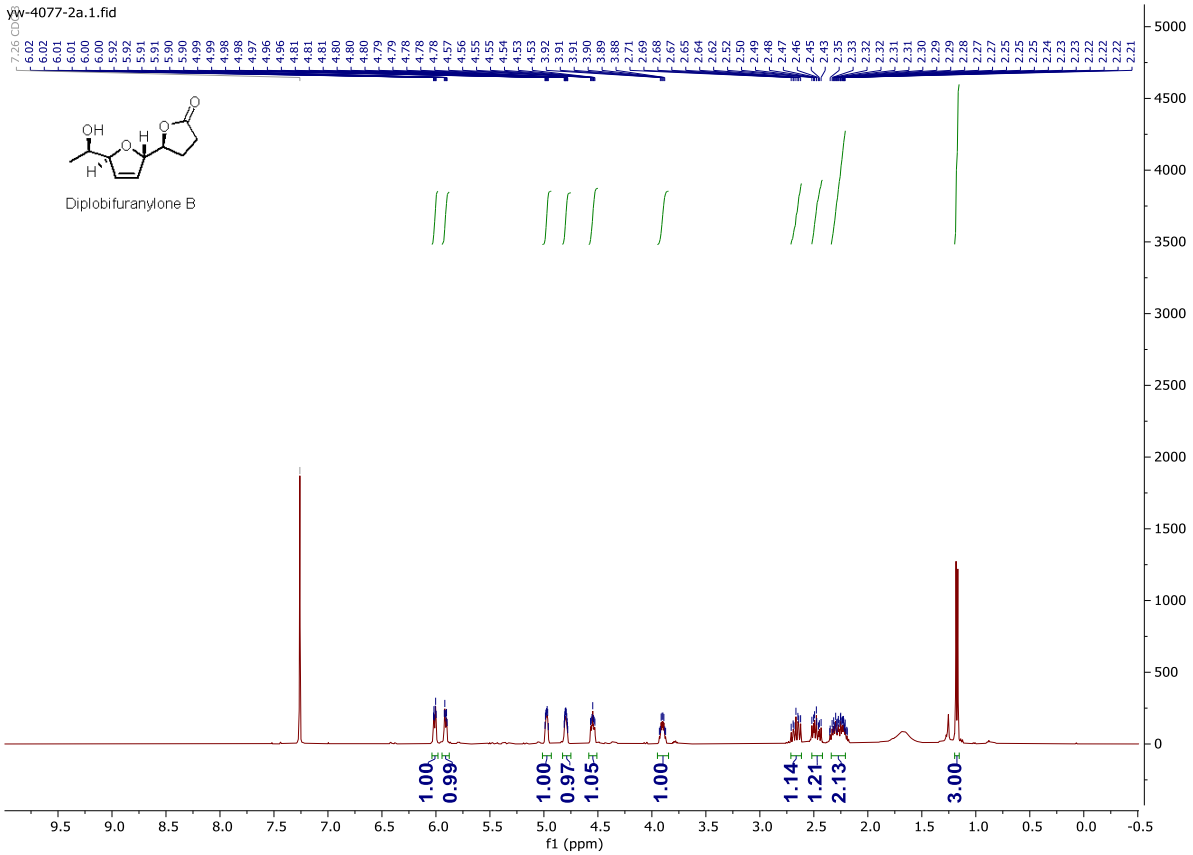
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **53**



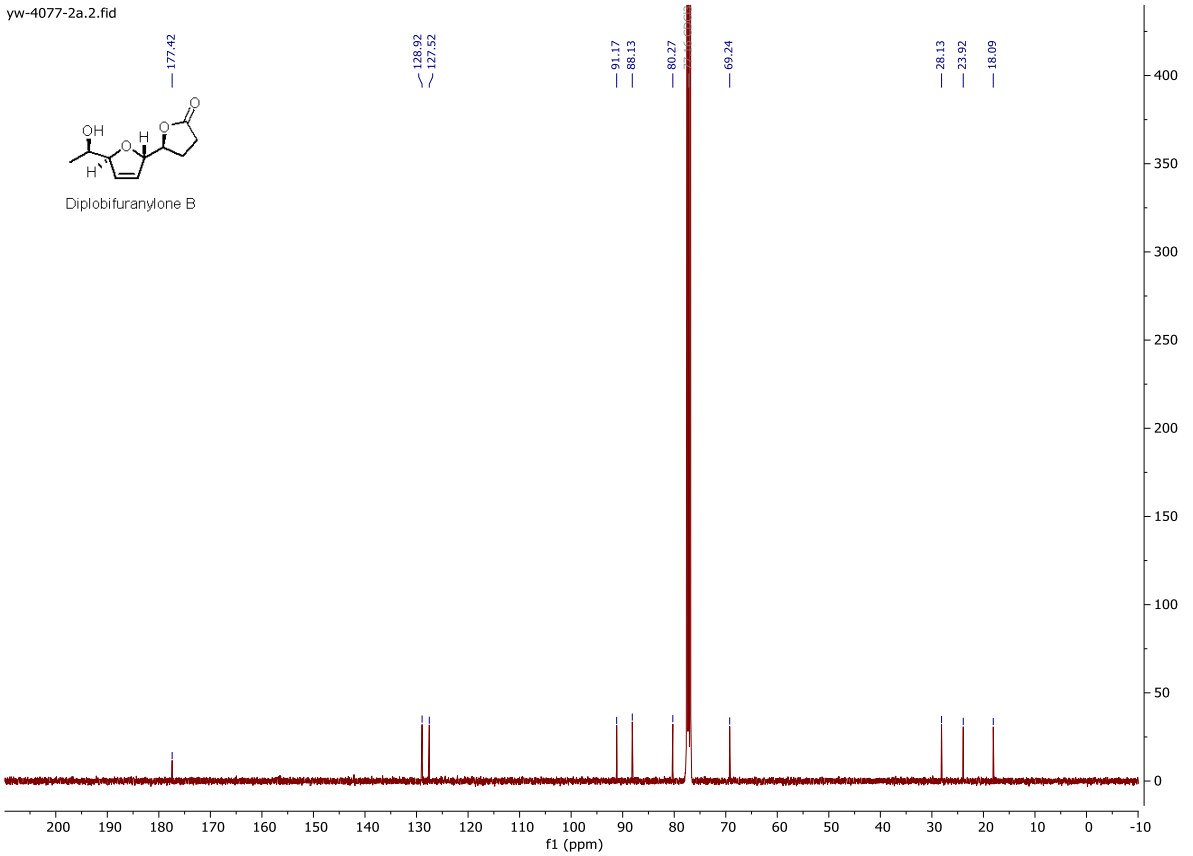
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **55**



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **55**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of diplobifuranylone B **54**



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of diplobifuranylone B **54**