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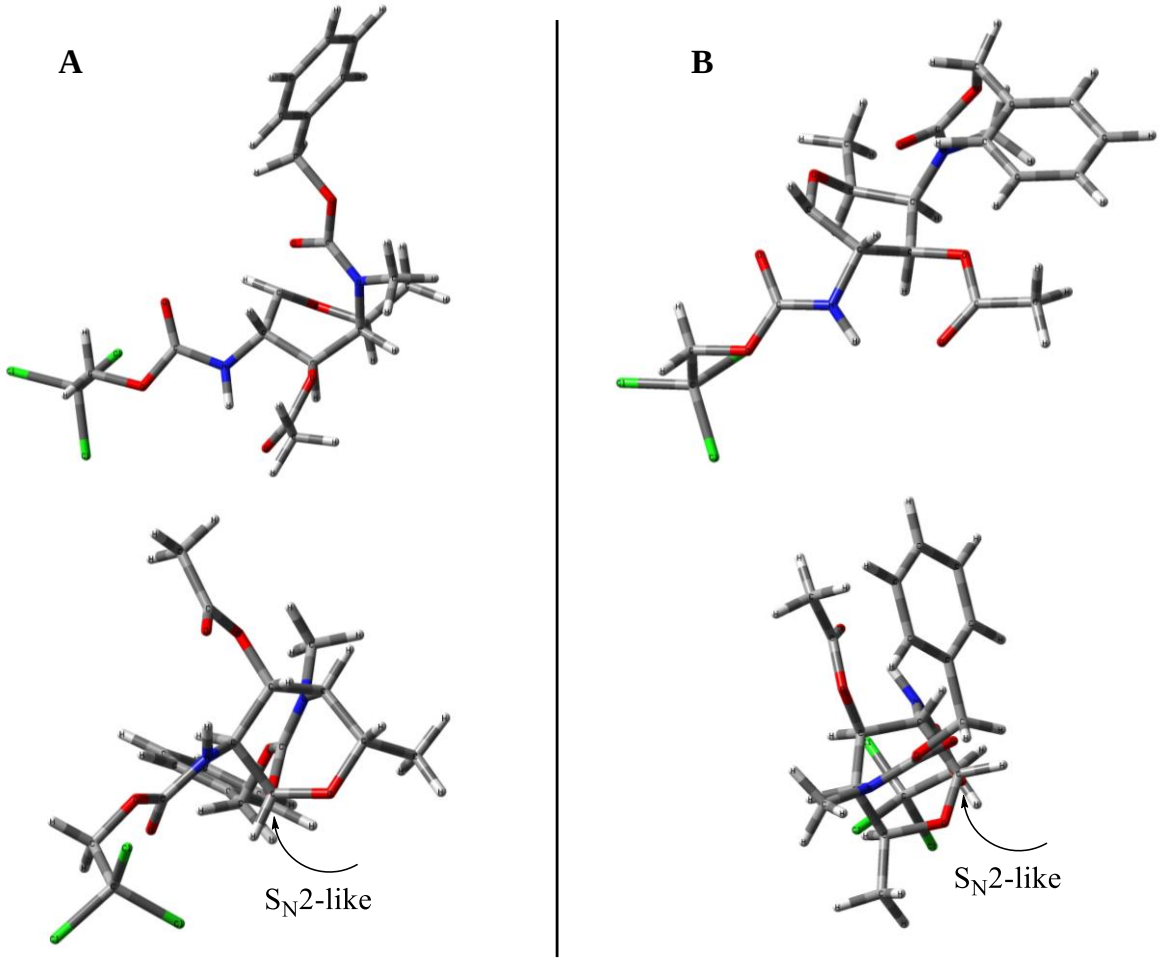
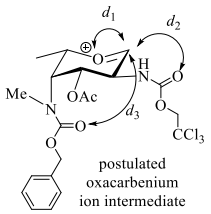


Figure S1. Two representative conformers of the postulated oxocarbenium intermediate. A) Remote group participation by the carbonyl oxygen of Cbz in conformer No. 4 from **table S1**. B) Neighboring group participation by the carbonyl oxygen of Troc in conformer No. 9. The greater participation of Cbz in conformer 4 provides a possible rationale to the lack of high 1,2-*trans* selectivity observed in the glycosylation reaction.

Table S1. The relative energies and geometry of the most stable 20 conformers of the postulated oxacarbenium ion intermediate upon activation of donor **31**.



Conformer No.	Relative E (kcal/mol)	d_1 (Å)	d_2 (Å)	d_3 (Å)
1	0.000	1.3625	3.0308	1.5152
2	0.000	1.3626	3.0307	1.5152
3	1.373	1.3606	3.0075	1.5226
4	1.746	1.3610	3.0115	1.5220
5	1.788	1.3569	2.8922	1.5363
6	1.834	1.3564	2.9113	1.5343
7	2.045	1.3626	3.2624	1.5132
8	2.056	1.3618	3.2151	1.5138
9	2.153	1.3333	1.5893	2.7571
10	2.153	1.3333	1.5893	2.7574
11	2.268	1.3584	2.9889	1.5325
12	2.382	1.3349	1.5848	2.7395
13	2.382	1.3350	1.5849	2.7393
14	2.404	1.3590	2.9811	1.5304
15	2.412	1.3618	3.2133	1.5259
16	2.441	1.3483	3.3137	1.5491
17	2.504	1.3597	2.9887	1.5302
18	2.504	1.3597	2.9888	1.5302
19	2.504	1.3598	2.9886	1.5301
20	2.504	1.3597	2.9887	1.5302

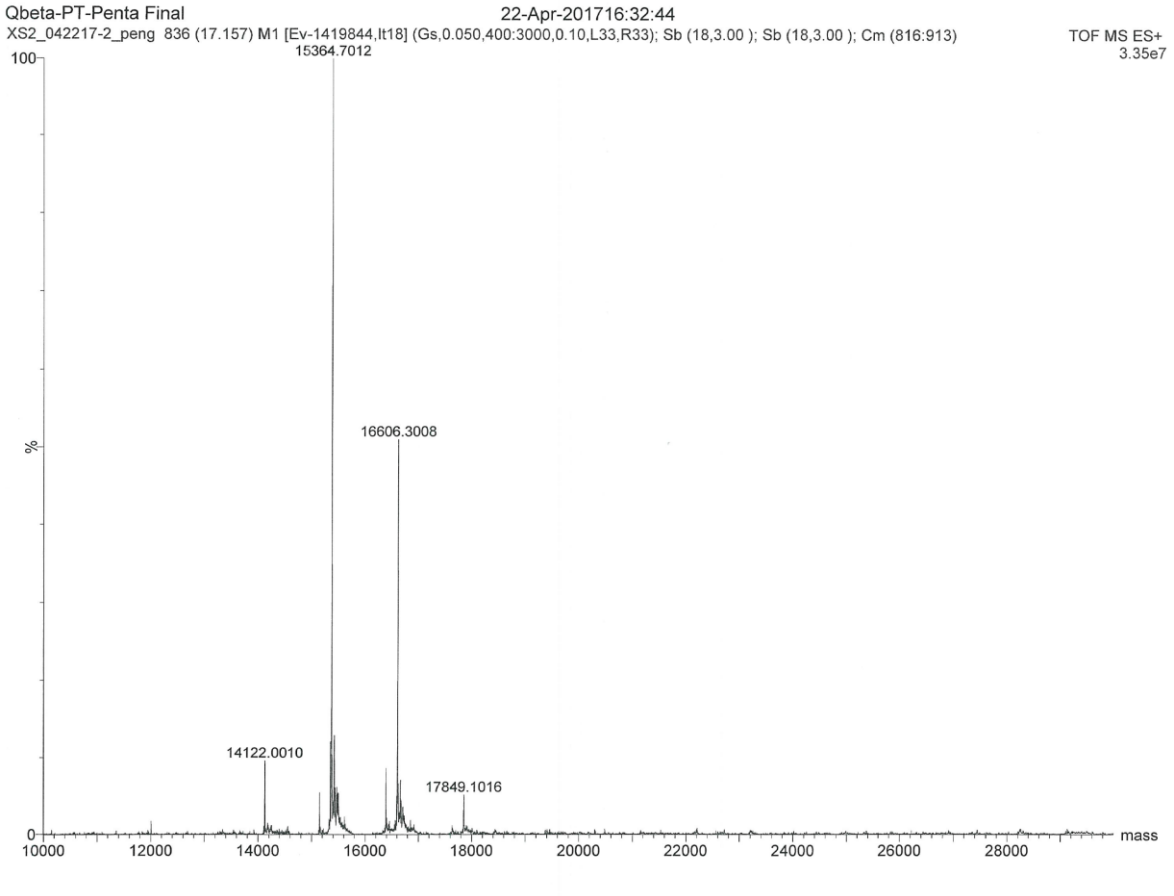


Figure S2. ESI-MS analysis of the Qβ-glycan conjugate **48**.

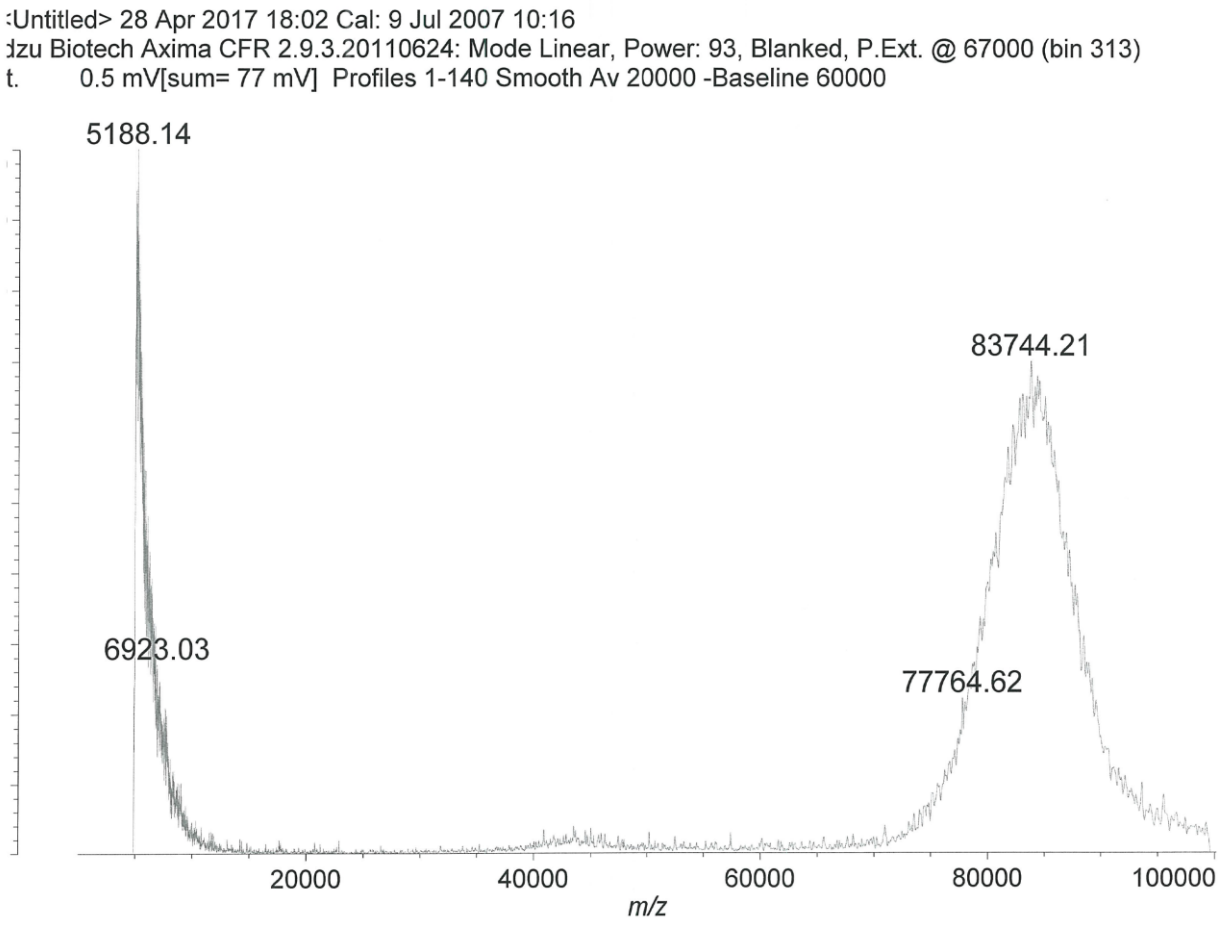


Figure S3. MALDI-TOF MS analysis of the BSA-glycan conjugate **52**.

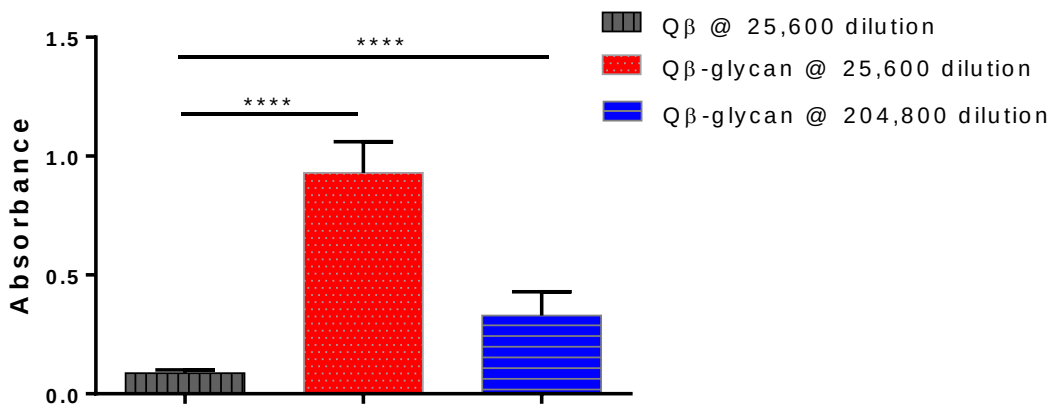


Figure S4. Sera from Qβ-glycan **48** immunized mice recognized with LPS isolated from *B. pertussis* bacteria (at 25,600- and 204,800-fold dilution) significantly stronger than those from Qβ immunized mice (25,600-fold dilution). Statistical analysis was performed using student t test. For each experiment, at least three samples were measured in duplicates. **** $p < 0.0001$.

Table S2. Sources of *Bordetella* pertussis strains utilized in the study.

Strain	**Description and year of isolation**	**Reference**
Bp536	Laboratory reference strain	[1]
Bp462	Isolated in Argentina in 2006	[2]
H973	Isolated in USA in 2012	[2-3]
GMT1	Isolated in USA in 1990	[4]
STO1-SEAT0004	Isolated in USA in 2011	[2-3]

Strains used in this work were grown on Bordet-Gengou agar (BGA) supplemented with 10% (vol/vol) defibrinated sheep blood. For liquid cultures, strains were grown in Stainer-Scholte (SS) broth with heptakis (2,6-di-*O*-methyl-β-cyclodextrin).[1,5-6]

Materials and Methods

All chemicals were reagent grade and were used as received from the manufacturer, unless otherwise noted. Solvents were dried using a solvent purification system. Glycosylation reactions were performed with 4Å molecular sieves that were flamed dried under high vacuum. Reactions were visualized by UV light (254 nm) and by staining with either $Ce(NH_4)_2(NO_3)_6$ (0.5 g) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (24.0 g) in 6% H_2SO_4 (500 mL), 5% H_2SO_4 in EtOH. Flash chromatography was performed on silica gel 601 (230–400 Mesh).

Centrifugal filter units of 10,000 and 100,000 molecular weight cut-off (MWCO) were purchased from EMD Millipore. Fast protein liquid chromatography (FPLC) was performed on a GE ÄKTA Explorer (Amersham Pharmacia) instrument equipped with a Superose-6 column. LCMS was performed on Waters Xevo G2-XS quadrupole/time-of-flight UPLC/MS/MS. The liquid chromatography was done on ACQUITY UPLC® Peptide BEH C18 column, 130Å, 1.7 μm, 2.1 mm × 150 mm, using gradient eluent from 95% 0.1% formic acid in water to 95% 0.1% formic acid in CHCN (0.3 mL/min flowrate) at column temperature 40 °C. The multiple charge mass spectra were transformed to single charge by using algorithm MaxEnd148a. MALDI-TOF analysis was performed by MALDI-TOF mass spectrometry (Applied Biosystems Voyager DE STR). Protein concentration was measured using the Coomassie Plus Protein Reagent (Bradford Assay, Pierce) with bovine serum albumin (BSA) as the standard.

Synthesis of the Glycan-Carrier Protein Conjugates

To the carrier protein (Qβ/BSA/KLH) suspended in potassium phosphate buffer (KPB, 0.1 M, pH 7.0, 1mL) was added compound **47** (4 eq per NH_2) in DMSO (0.1 mL). The reaction mixture was rotated on a rotating mixer at room temperature overnight. The solution was then subjected to ultracentrifugation in Millipore 100k MWCO centrifugal filter tube to remove excess glycan. The conjugates were purified by FPLC.

Quantification of Glycan Number on the Carrier Protein

For Qβ conjugate, the samples for LCMS were prepared as follows: 1:1 v/v of 40 μg/mL of stock solution and 100 mM DTT were mixed and incubated in a water bath at 37 °C for 30 min. One drop of 50% formic acid was added into the mixture. The average number of conjugated glycan on each viral capsid subunit was estimated from the intensity of peaks in the deconvoluted mass spectra from LC-MS analysis. Results are shown in **Figure S2**.

For BSA conjugate, the samples for MALDI-TOF were prepared as follows: 1:1 v/v of 2 mg/mL of conjugates and 100 mM DTT were mixed and incubated in a water bath at 37 °C for 30 min. After desalting using Cleanup C18 Pipette Tips (Agilent Technologies), the sample (2 μL) and matrix solution (2 μL, 10 mg/mL sinapic acid in 50/50/0.1 CH_3CN/H_2O/TFA) was mixed and spotted on a MALDI plate, air-dried (3 rounds) and then analyzed by MALDI-TOF. Results are shown in **Figure S3**.

For the KLH conjugate, the number of conjugated glycan was measured with a previously reported anthrone-sulfuric acid assay.[7] As KLH can exist as a didecamer (20-mer) with the molecular weight for each monomer at 390kDa,[8] an average molecular weight of 8MDa for KLH

was used to calculate the glycan loading levels of KLH.

Immunization Studies

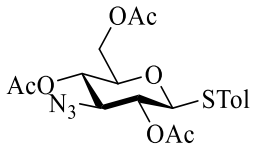
Pathogen-free C57BL/6 female mice age 6-10 weeks were obtained from Jackson Laboratory and maintained in the University Laboratory Animal Resources facility of Michigan State University. All animal care procedures and experimental protocols have been approved by the Institutional Animal Care and Use Committee (IACUC) of Michigan State University. Groups of 5 mice were injected subcutaneously under the scruff on day 0 with 0.2 mL of Qβ conjugate (contain 2 μg or 8 μg glycan) or KLH conjugate (contain 2 μg glycan) with monophosphoryl lipid A (MPLA, from *Salmonella enterica* serotype minnesota Re 595, Sigma-Aldrich, 20 μg) as the adjuvant. Boosters at the same dose were given subcutaneously under the scruff on day 14 and 28. Serum samples were collected on day 0 (before immunization), 7, 21 and 35.

Enzyme-linked Immunosorbent Assay (ELISA)

A Nunc MaxiSorp® flat-bottom 96 well plate was first coated with BSA-glycan (10ug/mL) in $NaHCO_3/Na_2CO_3$ buffer (0.05 M, pH = 9.6) overnight at 4 °C. The coated plate was then washed 4 times with PBS/0.5% Tween-20 (PBST), followed by the addition of 1% (w/v) BSA in PBS to each well and incubation at room temperature for one hour. The plate was washed again 4 times with PBST. 100 µl of the dilution of mouse sera in 0.1% BSA/PBS were added in each well. The plate was incubated for two hours at 37 °C and washed. A 1:2000 diluted horseradish peroxidase (HRP)-conjugated goat anti-mouse IgG, IgG1, IgG2b, IgG2c, or IgG3 antibody (Jackson ImmunoResearch Laboratory) in 0.1% BSA/PBS was added to each well, respectively. The plate was incubated for one hour at 37 ℃, washed, and a solution of 3,3',5,5'-tetramethylbenzidine (TMB) was added (200 μL). Color was allowed to develop for 15 min, and then a solution of 0.5 M H_2SO_4 (50 μL) was added to stop the reaction. The optical density was measured at 450 nm using a microplate autoreader (BioRad). Each experiment was repeated at least four times, and the average of the quadruplicate was used to calculate the titer. The titer was determined by linear regression analysis with reciprocal of dilution plotted with optical density (background subtracted). The titer was calculated as the highest dilution that gave OD = 0.1.

Binding ability of sera from Qβ-glycan immunized mice was determined by ELISA. Briefly, 96-well flat bottom plates (Corning #9018) were coated with 10^8 and 10^7 CFU of *B. pertussis* strains in sterile PBS overnight at 4°C. The next day, plates were washed with PBS containing 0.05% Tween-20 (PBS-T) followed by blocking for 1hr at room temperature with 1X ELISA diluent (Invitrogen #88-7044-88). Sera from Qβ- or Qβ-glycan immunize mice was used as the primary antibody at 1:2500 in 1X diluent for 2hrs at room temperature. Following washing, each well was treated with an HRP-conjugated anti-mouse secondary antibody at 1:1000 in 1X diluent for 1hr. Subsequently, plates were washed and developed with 1X 3,3',5,5'-tetramethylbenzidine (TMB, Invitrogen #00-4201-56) for 10 min. The reaction was stopped with addition of 1 M H_2SO_4 and absorbance values were read on a microtiter plate reader. OD_{450} values are reported.

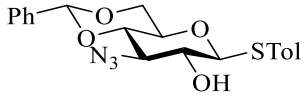
Product Preparation and Characterization Data



p-Tolyl 2, 4, 6-Tri-*O*-acetyl-3-azido-3-deoxy-1-thio-*β*-D-glucopyranoside (**8**)

10% HCl (25 mL) was added to 3-azido-1, 2:5, 6-Di-*O*-isopropylidene-3-deoxy-*α*-D-allofuranose (1.52 g, 5.3 mmol) and the mixture was stirred at r.t. for 16 hours. The solution was then concentrated, dissolved with pyridine (10 mL) and cooled to 0℃. Acetic anhydride (Ac_2O, 12 mL) and DMAP (100 mg, 0.8 mmol) were added. The solution was allowed to warm up slowly to r.t. and continued to stir overnight. Upon completion, excess Ac_2O was quenched by slow addition of MeOH. The reaction mixture was concentrated under vacuum, diluted with EtOAc and washed successively with 1M HCl, saturated Na_2CO_3 solution and saturated brine. The organic layer was then dried over anhydrous Na_2SO_4, filtered and concentrated. The product was mixed with *p*-toluenethiol (1.02 g, 8.2 mmol), dissolved in DCM and cooed to 0℃. Then $BF_3 \cdot Et_2O$ (3.0 mL, 24.6 mmol) was added and the reaction was stirred for 6 hours. The mixture was washed with saturated $NaHCO_3$ solution, dried and concentrated. Compound **9** was obtained through column chromatography (Hexanes/EtOAc = 3/1) as a white powder in 54% yield.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 2.08 (s, 3H), 2.11 (s, 3H), 2.18 (s, 3H), 2.35 (s, 3H), 3.62-3.66 (m, 2H), 4.16-4.17 (m, 2H), 4.58 (d, 1H, J = 10 Hz), 4.87 (t, 1H, J = 10 Hz), 4.92 (t, 1H, J = 10 Hz), 7.11-7.13 (m, 2H), 7.38-7.40 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 20.85, 20.96, 21.06, 21.38, 62.37, 65.99, 68.44, 70.19, 76.52, 86.59, 128.02, 129.86, 133.79, 138.93, 169.25, 169.37, 170.81. HRMS: m/z calc. for $C_{19}H_{27}N_4O_7S$: 455.1600; found: 455.1614 $[M + NH_4]^+$

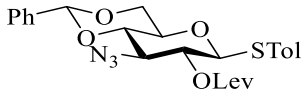


p-Tolyl 3-azido-4, 6-*O*-benzylidene-3-deoxy-1-thio-*β*-D-glucopyranoside (**9**)

Compound **8** (1.5 g, 3.4 mmol) was dissolved in a mixture of DCM/MeOH (7/7 mL) and the pH was adjusted to 11 with 30% NaOMe. The reaction was stirred for 1 h and then neutralized with H^+ resin. The mixture was then filtered through celite and concentrated. The residue was diluted with MeCN (40 mL) and then benzaldehyde dimethyl acetal (0.77 mL, 5.1 mmol) and (1*S*)-(+)-10-camphorsulfonic acid (CSA, 230 mg, 1.0 mmol) was added to the solution, which was allowed to stir at r.t. overnight. Upon completion by TLC, the reaction was quenched with Et_3N and concentrated. The residue was diluted with DCM and washed with brine. Compound **9** was obtained through recrystallization in Hexanes/EtOAc (4/1) as a white powder in 81% yield.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 2.62 (d, 1H, J = 2.5 Hz), 3.35 (dt, 1H, J = 2.5, 9.5 Hz), 3.47 (t, 1H, J = 9.5 Hz), 3.54 (dt, 1H, J = 5, 9.5 Hz), 3.72 (t, 1H, J = 9.5 Hz), 3.76 (t, 1H, J = 9.5 Hz), 4.39 (dd, 1H, J = 5, 10.5 Hz), 4.56 (d, 1H, J = 10 Hz), 5.55 (s, 1H), 7.15-7.17 (m, 2H),

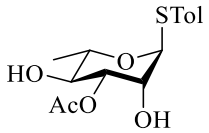
7.35-7.39 (m, 3H), 7.41-7.43 (m, 2H), 7.46-7.49 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 21.41, 65.97, 68.74, 71.64, 71.7, 79.33, 89.34, 101.71, 126.17, 126.71, 128.52, 129.37, 130.2, 134.12, 136.78, 139.41. HRMS: m/z calc. for $C_{20}H_{22}N_3O_4S$: 400.1331; found: 400.1323 $[M + H]^+$



p-Tolyl 3-azido-4, 6-*O*-benzylidene-3-deoxy-2-levulinoyl-1-thio-*β*-D-glucopyranoside (**5**)

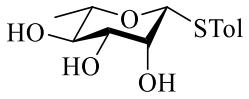
Compound **9** (1.0 g, 2.5 mmol) was dissolved in DCM (40 mL) followed by the addition of levulinic acid (0.77 mL, 7.5 mmol), EDC·HCl (1.58 g, 8.3 mmol) and DMAP (31 mg, 0.25 mmol). The reaction was stirred at r.t. overnight and then washed with saturated $NaHCO_3$ solution. Compound **5** was obtained through column chromatography (Hexanes/EtOAc = 2/1) as a white solid in 91% yield.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 2.35 (s, 3H), 2.67-2.74 (m, 2H), 2.80-2.90 (m, 2H), 3.52 (dt, 1H, *J* = 5.0, 9.5 Hz), 3.57 (t, 1H, *J* = 9.5 Hz), 3.76-3.81(m, 2H), 4.39 (dd, 1H, *J* = 4.5, 10.5 Hz), 4.66 (d, 1H, *J* = 9.5 Hz), 4.85 (t, 1H, *J* = 9.5 Hz), 5.57 (s, 1H), 7.12-7.16 (m, 2H), 7.34-7.41 (m, 5H), 7.45-7.49 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 21.33, 28.09, 30.0, 37.94, 64.74, 68.58, 70.69, 71.34, 79.17, 87.3, 101.54, 126.07, 127.91, 128.44, 129.3, 129.9, 133.79, 136.63, 138.92, 171.3, 206.12. HRMS: m/z calc. for $C_{25}H_{27}N_3NaO_6S$: 520.1518; found: 520.1517 $[M + Na]^+$



p-Tolyl 3-*O*-acetyl-1-thio-*α*-L-rhamnopyranoside (**10**)

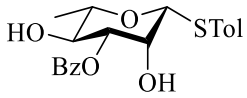
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.35 (d, 3H, *J* = 6.0 Hz), 2.18 (s, 3H), 2.33 (s, 3H), 2.42 (br, 2H), 3.71 (t, 1H, *J* = 9.5 Hz), 4.23 (dq, 1H, *J* = 6.5, 9.5 Hz), 4.29 (dd, 1H, *J* = 1.5, 3.0 Hz), 5.05 (dd, 1H, *J* = 3.0, 9.5 Hz), 5.38 (d, 1H, *J* = 1.5 Hz), 7.12 (d, 2H, *J* = 8.0 Hz), 7.35 (d, 2H, *J* = 8.5 Hz). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 17.58, 21.25, 21.27, 70.0, 71.21, 71.69, 75.02, 88.11, 129.94, 130.04, 132.33, 138.04, 171.6. HRMS: m/z calc. for $C_{15}H_{20}NaO_5S$: 335.0929; found 335.0937 $[M + Na]^+$



p-Tolyl 1-thio-*α*-L-rhamnopyranoside (**11**)

Compound **11** was prepared by following the previously reported protocol.[9]
^{1}HNMR (500 MHz, CD_3OD): δ = 1.31 (d, 3H, *J* = 6.0 Hz), 2.31 (s, 3H), 3.25 (dq, 1H, *J* = 6.0, 9.0

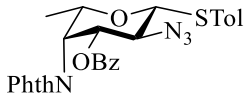
Hz), 3.37 (t, 1H, J = 9.0 Hz), 3.44 (dd, 1H, J = 3.5, 9.5 Hz), 4.04 (dd, 1H, J = 1.0, 3.5 Hz), 4.86 (d, 1H, J = 1.0 Hz), 7.12 (d, 2H, J = 7.5 Hz), 7.36 (d, 2H, J = 8.0 Hz). ^{13}CNMR (125 MHz, CD_3OD): δ = 18.24, 21.05, 73.64, 74.19, 75.91, 77.88, 89.04, 130.62, 131.87, 133.3, 138.2. HRMS: m/z calc. for $C_{13}H_{18}NaO_4S$: 293.0823; found 293.0833 $[M + Na]^+$



p-Tolyl 3-*O*-benzoyl-1-thio-*β*-L-rhamnopyranoside (**12**)

Compound **12** was prepared by following the previously reported protocol. [10]

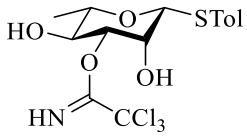
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.44 (d, 3H, J = 6.0 Hz), 2.28 (br, 1H), 2.35 (s, 3H), 2.43 (br, 1H), 3.46 (dq, 1H, J = 6.0, 9.0 Hz), 3.89 (t, 1H, J = 9.5 Hz), 4.39 (s, 1H), 4.89 (d, 1H, J = 1.0 Hz), 4.98 (dd, 1H, J = 3.0, 10.0 Hz), 7.12-7.16 (m, 2H), 7.40-7.49 (m, 4H), 7.56-7.62 (m, 1H), 8.06-8.11 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 18.08, 21.29, 70.83, 70.98, 77.13, 77.8, 87.46, 128.69, 129.44, 129.84, 130.02, 130.04, 132.6, 133.77, 138.3, 166.83. HRMS: m/z calc. for $C_{20}H_{22}NaO_5S$: 397.1086; found 397.1089 $[M + Na]^+$



p-Tolyl 2-azido-3-*O*-benzoyl-2, 4-dideoxy-4-phthalimido-1-thio-*β*-L-rhamnopyranoside (**13**)

Compound **13** was prepared by following the previously reported protocol. [11]

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.18 (d, 3H, J = 6.5 Hz), 2.37 (s, 3H), 3.94-4.00 (m, 1H), 4.65 (d, 1H, J = 10.5 Hz), 4.89 (t, 1H, J = 10.0 Hz), 5.02 (dd, 1H, J = 3.0, 7.0 Hz), 5.36 (dd, 1H, J = 7.0, 9.5 Hz), 7.14-7.19 (m, 2H), 7.27-7.33 (m, 2H), 7.43-7.51 (m, 2H), 7.52-7.57 (m, 2H), 7.66-7.79 (m, 3H), 7.82-7.87 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 17.07, 21.37, 51.7, 62.15, 73.19, 73.59, 89.45, 123.78, 128.58, 128.72, 128.8, 129.77, 129.84, 129.91, 130.03, 130.07, 133.12, 133.66, 134.24, 138.4, 165.19. HRMS: m/z calc. for $C_{28}H_{25}N_4O_5S$: 529.1546; found: 529.1548 $[M + H]^+$

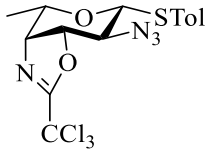


p-Tolyl 1-thio-3-trichloroacetimidate-*β*-L-rhamnopyranoside (**15**)

p-Tolyl 1-thio-*β*-L-rhamnopyranoside **11** (11.5 g, 42.7 mmol) was dissolved in THF (150 mL) followed by the addition of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 1.3 mL, 8.5 mmol). To the

mixture trichloroacetonitrile (5.1 mL, 51 mmol) in THF (30 mL) was added over a period of 1 h at 0 ℃. The reaction was allowed to warm up and stirred at r.t. overnight. It was concentrated and purified through column (DCM/EtOAc = 3/1). The impurity was dissolved in DCM/MeOH/AcOH (40/40/5 mL) and purified with the same condition, which gave compound **15** as a white solid in a combined yield of 90%.

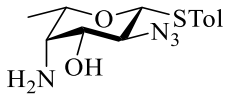
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.43 (d, 3H, J = 6.5 Hz), 2.34 (s, 3H), 2.81 (br, 3H), 3.46 (dq, 1H, J = 1.0, 6.5 Hz), 4.18 (dd, 1H, J = 1.0, 6.5 Hz), 4.54 (t, 1H, J = 6.5 Hz), 4.90-4.94 (m, 2H), 7.13 (d, 2H, J = 7.5 Hz), 7.44 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 18.89, 21.28, 71.91, 76.28, 80.19, 82.7, 84.66, 103.51, 117.13, 129.92, 130.95, 131.91, 138.01. HRMS: m/z calc. for $C_{15}H_{18}Cl_3NNaO_4S$: 435.9920; found: 435.9928 $[M + Na]^+$



p-Tolyl 2-azido-2, 4-dideoxy-1-thio-3, 4-trichlorooxazoline-*β*-L-fucopyranoside (**16**)

Compound **15** (16.0 g, 38.5 mmol) was dissolved in anhydrous DCM (200 mL) and cooled to -30 ℃. Pyridine (31.0 mL, 0.38 mol) and trifluoromethanesulfonic anhydride (19.4 mL, 0.12 mol) were added and the solution was allowed to warm up to r.t. over 3 h. Upon completion by TLC, the reaction was quenched and washed with saturated $NaHCO_3$ solution. The organic layer was dried with Na_2SO_4, concentrated and diluted in DMF (60 mL). NaN_3 (7.5 g, 0.12 mol) was added and the reaction was stirred at 50 ℃ overnight. The mixture was diluted with EtOAc, washed with brine, dried and concentrated. Compound **16** was obtained through column chromatography (Hexanes/DCM/EtOAc = 3/1/1) as a colorless solid in a yield of 85%.

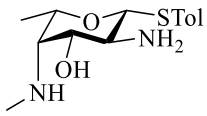
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.58 (d, 3H, J = 6.0 Hz), 2.33 (s, 3H), 3.29 (dd, 1H, J = 7.0, 10.0 Hz), 3.89 (dq, 1H, J = 3.0, 6.5 Hz), 4.10 (dd, 1H, J = 3.0, 8.0 Hz), 4.34 (d, 1H, J = 10.5 Hz), 4.88 (dd, 1H, J = 6.5, 8.0 Hz), 7.14 (m, 2H), 7.46 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 18.16, 21.16, 62.31, 68.78, 73.03, 84.86, 85.37, 86.31, 126.71, 129.83, 134.12, 138.9, 162.64. HRMS: m/z calc. for $C_{15}H_{16}Cl_3N_4O_2S$: 421.0060; found: 421.0072 $[M + H]^+$



p-Tolyl 4-amino-2-azido-2, 4-dideoxy-1-thio-*β*-L-fucopyranoside (**14**)

Compound **16** (13.9 g, 33.0 mmol) was dissolved in DCM/MeOH/H_2O/conc. HCl (40/50/20/30 mL) and the mixture was refluxed at 90 ℃ overnight. The reaction was then concentrated, diluted with DCM and washed with saturated $NaHCO_3$ solution. The organic layer was collected and dried with Na_2SO_4. Compound **14** was obtained through column chromatography (DCM/MeOH = 10/1) as a colorless syrup in a yield of 89%.

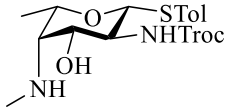
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.28 (d, 3H, J = 6.5 Hz), 2.35 (s, 3H), 2.82 (d, 1H, J = 4.0 Hz), 3.04 (t, 1H, J = 10.0 Hz), 3.51 (dd, 1H, J = 4.5, 9.5 Hz), 3.61 (q, 1H, J = 6.5 Hz), 4.28 (d, 1H, J = 10.5 Hz), 7.15 (d, 2H, J = 8.5 Hz), 7.48 (d, 2H, J = 8.0 Hz). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 17.16, 21.21, 54.31, 63.35, 73.61, 75.07, 86.04, 127.56, 129.77, 133.98, 138.72. HRMS: m/z calc. for $C_{13}H_{19}N_4O_2S$: 295.1229; found: 295.1242 $[M + H]^+$



p-Tolyl 2-amino-2, 4-dideoxy-4-methylamino-1-thio-β-L-fucopyranoside (**17**)

Compound **14** (6.1 g, 20.7 mmol) was dissolved in ethyl formate (50 mL) and Et_3N (3 mL) was added. The mixture was refluxed overnight and concentrated. The obtained syrup was diluted in anhydrous THF (60 mL) and cooled to -30 ℃. To the solution was added $LiAlH_4$ in THF (37.2 mL, 2M). The mixture was refluxed overnight and quenched with 15% NaOH, followed by filtration through celite and concentration. Compound **17** was obtained through column chromatography (DCM/MeOH = 8/1 with 1% Et_3N) as a colorless oil in a yield of 70%.

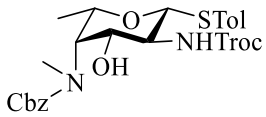
^{1}HNMR (500 MHz, CD_3OD): δ = 1.31 (d, 3H, J = 6.5 Hz), 2.32 (s, 3H), 2.51 (s, 3H), 2.54 (dd, 1H, J = 1.0, 4.0 Hz), 2.61 (t, 1H, J = 10.0 Hz), 3.43 (dd, 1H, J = 4.5, 9.5 Hz), 3.68 (dq, 1H, J = 1.0, 6.5 Hz), 4.37 (d, 1H, J = 10.0 Hz), 7.14 (d, 2H, J = 8.0 Hz), 7.43 (d, 2H, J = 8.5 Hz). ^{13}CNMR (125 MHz, CD_3OD): δ = 16.85, 19.73, 37.59, 52.36, 63.5, 74.1, 75.2, 89.15, 129.26, 129.45, 132.15, 137.68. HRMS: m/z calc. for $C_{28}H_{44}N_4NaO_4S_2$: 587.2702; found: 587.2707 $[2M + Na]^+$



p-Tolyl 2,4-dideoxy-4-methylamino-1-thio-2- (2,2,2-trichloroethyloxycarbonylamino)-β-L-fucopyranoside (**18**)

Compound **17** (3.7 g, 13.1 mmol) was dissolved in THF (100 mL) and pyridine (3.2 mL, 39.2 mmol) was added. The mixture was cooled in ice bath and trichloroethyl chloroformate (1.7 mL, 12.4 mmol) in THF (50 mL) was added slowly over 1 h. The reaction was concentrated, diluted with DCM and washed with saturated $NaHCO_3$ solution. Compound **18** was obtained through column chromatography (DCM/MeOH = 6/1 with 1% Et_3N) as a white solid in a yield of 88%.

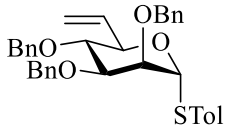
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.37 (d, 3H, J = 6.5 Hz), 2.32 (s, 3H), 2.60 (s, 3H), 2.64 (dd, 1H, J = 1.5, 4.5 Hz), 3.20 (q, 1H, J = 10.0 Hz), 3.57 (dd, 1H, J = 4.0, 9.5 Hz), 3.70 (q, 1H, J = 6.5 Hz), 4.61 (d, 1H, J = 10.5 Hz), 4.68 (d, 1H, J = 12.0 Hz), 4.81 (d, 1H, J = 12.0 Hz), 5.29 (br, 1H), 7.10 (d, 2H, J = 8.0 Hz), 7.37 (d, 2H, J = 7.5 Hz). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 17.93, 21.13, 38.39, 55.43, 63.07, 71.52, 74.55, 75.68, 87.3, 95.54, 129.63, 129.67, 132.55, 137.95, 154.51. HRMS: m/z calc. for $C_{17}H_{24}Cl_3N_2O_4S$: 457.0522; found: 457.0523 $[M + H]^+$



p-Tolyl 4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-1-thio-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranoside (**4**)

Compound **18** (3.0 g, 6.55 mmol) was dissolved in THF/H_2O (40/10 mL) and cooled to 0℃. To the solution was added benzyl chloroformate (1.1 mL, 7.86 mmol) and sodium carbonate (1.39 g, 13.1 mmol). The reaction was allowed to warm up to room temperature and stirred overnight. The reaction was concentrated, diluted with DCM and washed with saturated $NaHCO_3$ solution. Compound **4** was obtained through column chromatography (Hexanes/EtOAc = 1/1) as a white solid in a yield of 75%.

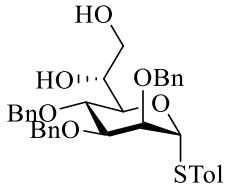
^{1}HNMR (500 MHz, d^6-DMSO): δ = 1.05&1.07 (d, 3H, J = 6.0 Hz, H-6), 2.27&2.28 (s, 3H, STol-Me), 2.82&2.88 (s, 3H, N-Me), 3.64-3.73 (m, 1H, H-2), 3.75-3.88 (m, 2H, H-3, H-5), 4.27&4.35 (dd, 1H, J = 2.5, 6.0 Hz, H-4), 4.66&4.69 (d, 1H, J = 10.0 Hz, H-1), 4.76 (d, 1H, J = 12.5 Hz, Troc-CH_2), 4.91&4.92 (d, 1H, J = 12.5 Hz, Troc-CH_2), 4.98&5.10 (d, 1H, J = 13.0 Hz, Cbz-CH_2), 5.08 (s, 1H, Cbz-CH_2), 5.45&5.53 (d, 1H, J = 6.0 Hz, OH), 7.12-7.17 (m, 2H), 7.27-7.39 (m, 7H), 7.73 (d, 1H, J = 9.5 Hz, Troc-NH). ^{13}CNMR (125 MHz, d^6-DMSO): δ = 16.8, 16.95, 20.64, 32.56, 32.98, 54.01, 54.11, 56.87, 56.92, 66.17, 66.29, 69.66, 69.74, 73.49, 73.51, 73.9, 74.04, 86.32, 96.26, 127.16, 127.27, 127.61, 127.68, 128.31, 128.4, 129.46, 129.49, 129.52, 129.59, 131.63, 131.8, 136.9, 136.99, 137.13, 137.2, 154.46, 156.97, 157.19. HRMS: m/z calc. for $C_{25}H_{30}Cl_3N_2O_6S$: 591.0890; found: 591.0878 $[M + H]^+$



p-Tolyl 2, 3, 4-Tri-*O*-benzyl-6,7-dideoxy-1-thio-*α*-D-mannohept-6-enopyranoside (**20**)

To a solution of oxalyl chloride (202 μL, 2.36 mmol) in DCM (4 mL) was added a solution of DMSO (200 μL, 2.83 mmol) in DCM (6 mL) at -65℃. After 15 min, a solution of *p*-Tolyl 2, 3, 4-Tri-*O*-benzyl-1-thio-*α*-D-mannopyranoside **19** (875 mg, 1.57 mmol) in DCM (5 mL) was added to the above solution via syringe. The reaction was allowed to stir at -50 ℃ for 2 h. Et_3N was added and the above mixture was warmed up to r.t. over a period of 4 h before it was quenched with water and extracted with DCM. The organic layer was washed with brine, dried and concentrated to give the crude aldehyde which was used without further purification. To a suspension of methyl triphenylphosphonium bromide (843 mg, 2.36 mmol) in THF (6 mL) at -40 ℃ was added n-BuLi (0.94 mL, 2.36 mmol, 2.5 M solution in hexane) and after 0.5 h, the above aldehyde in THF (5 mL) was added and the mixture was stirred at the same temperature for 1 h. The reaction was slowly warmed up to r.t. over 4 h before quenched with saturated NH_4Cl solution and extracted with EtOAc. The organic layer was washed with brine, dried and concentrated. Compound **20** was obtained through column chromatography (Hexanes/EtOAc = 10/1) as a yellow syrup in a yield of 83%.

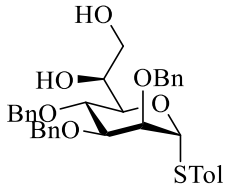
^{1}HNMR (500 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 3.81 (t, 1H, J = 9.5 Hz), 3.88 (dd, 1H, J = 3.0, 9.5 Hz), 4.00 (dd, 1H, J = 1.5, 3.0 Hz), 4.56 (dd, 1H, J = 6.5, 9.5 Hz), 4.60-4.68 (m, 4H), 4.73 (d, 1H, J = 12.5 Hz), 4.88 (d, 1H, J = 11.0 Hz), 5.28-5.31 (m, 1H), 5.43-5.49 (m, 2H), 6.04 (ddd, 1H, J = 6.0, 10.5, 17.0 Hz), 7.10 (d, 2H, J = 8.0 Hz), 7.26-7.38 (m, 17H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 21.25, 72.19, 72.47, 73.87, 75.4, 76.57, 78.97, 79.86, 86.26, 118.43, 127.8, 127.81, 127.87, 127.94, 128.11, 128.19, 128.46, 128.51, 128.53, 129.93, 130.72, 132.29, 135.13, 137.77, 138.04, 138.38, 138.54. HRMS: m/z calc. for $C_{35}H_{40}NO_4S$: 570.2678; found: 570.2681 $[M + NH_4]^+$



p-Tolyl 2, 3, 4-Tri-*O*-benzyl-D-glycero-1-thio-α-D-mannoheptopyranoside (**21**)

To a solution of compound **20** (2.57 g, 4.65 mmol) in Acetone/water (27/3 mL) at 0 ℃ were added 4-methylmorpholine *N*-oxide (NMO, 1.09 g, 9.3 mmol) and OsO_4 (2.3 mL, 0.18 mmol, 2.5%wt in *t*-BuOH). The reaction was allowed to stir at r.t. for 6 h before it was quenched with saturated $NaHSO_3$ solution. After 15 min, the mixture was concentrated and extracted with EtOAc. The organic layer was washed with brine, dried and concentrated. Column chromatography (Hexanes/EtOAc = 2/1) afforded compound **21** (1.3 g, 48%) and compound **22** (0.52 g, 20 %).

^{1}HNMR (500 MHz, $CDCl_3$): δ = 2.04 (br, 1H), 2.33 (s, 3H), 3.06 (br, 1H), 3.57 (dd, 1H, J = 4.0, 11.5 Hz), 3.65 (dd, 1H, J = 5.0, 12.0 Hz), 3.90 (dd, 1H, J = 3.0, 9.0 Hz), 3.93 (q, 1H, J = 4.5 Hz), 3.99 (dd, 1H, J = 2.0, 3.0 Hz), 4.05 (t, 1H, J = 9.5 Hz), 4.22 (dd, 1H, J = 5.0, 9.5 Hz), 4.58 (d, 1H, J = 11.5 Hz), 4.61 (d, 1H, J = 11.5 Hz), 4.63-4.69 (m, 3H), 5.04 (d, 1H, J = 11.0 Hz), 5.39 (d, 1H, J = 1.5 Hz), 7.12 (d, 2H, J = 8.0 Hz), 7.27-7.38 (m, 17H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 21.14, 63.09, 71.93, 72.24, 72.3, 72.66, 75.08, 75.87, 76.63, 80.25, 86.25, 127.86, 127.9, 127.93, 128.05, 128.18, 128.47, 128.52, 128.57, 129.57, 129.96, 132.75, 137.57, 137.68, 137.72, 138.25. HRMS: m/z calc. for $C_{35}H_{38}NaO_6S$: 609.2287; found: 609.2278 $[M + Na]^+$

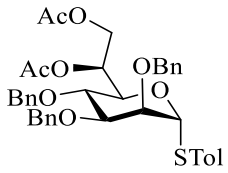


p-Tolyl 2, 3, 4-Tri-*O*-benzyl-L-glycero-1-thio-α-D-mannoheptopyranoside (**22**)

Compound **21** (1.28 g, 2.18 mmol) was dissolved in pyridine (8 mL) and *t*-butyldiphenylsilyl chloride (TBDPSCl, 1.13 mL, 4.26 mmol) was added. The reaction was stirred at r.t. overnight before it was diluted with DCM and washed with brine. The organic layer was dried and concentrated to give the crude silyl ether which was taken forward without purification. A solution of the silyl ether, PPh_3 (1.14 g, 4.26 mmol) and *p*-nitrobenzoic acid (0.73 g, 4.36 mmol) in THF (30 mL) was treated with DIAD (858 μL, 4.36 mmol) at r.t. and stirred for 5 h. The reaction was the

concentrated, diluted with DCM and washed with brine. The organic layer was concentrated and diluted with DCM/MeOH (10/30 mL) and K_2CO_3 (0.5 g, 3.57 mmol) was added. The reaction was stirred at r.t. for 3 h before concentrated, diluted with EtOAc and washed with brine. The organic layer was concentrated, dissolved in THF (30 mL) and treated with TBAF (3.5 mL, 3.5 mmol, 1 M in THF) overnight. The mixture was then concentrated, diluted with EtOAc and washed with brine. Column chromatography (Hexanes/EtOAc = 2/1) gave compound **22** in an 84% yield over 4 steps.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 3.56 (m, 2H), 3.88 (dd, 1H, J = 3.0, 9.0 Hz), 3.97 (m, 2H), 4.05 (dd, 1H, J = 1.0, 9.5 Hz), 4.20 (t, 1H, J = 9.5 Hz), 4.62 (d, 1H, J = 12.0 Hz), 4.65 (d, 1H, J = 12.0 Hz), 4.69 (s, 2H), 4.71 (d, 1H, J = 10.5 Hz), 4.98 (d, 1H, J = 10.5 Hz), 5.47 (d, 1H, J = 1.5 Hz), 7.12 (d, 2H, J = 8.5 Hz), 7.24 (d, 2H, J = 8.0 Hz), 7.27-7.37 (m, 15H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 21.29, 65.21, 69.25, 72.37, 72.52, 74.0, 74.51, 75.56, 76.05, 80.08, 86.36, 127.93, 127.97, 127.99, 128.0, 128.05, 128.26, 128.61, 129.54, 130.21, 132.47, 137.96, 138.18, 138.37, 138.41. HRMS: m/z calc. for $C_{35}H_{42}NO_6S$: 604.2733; found: 604.2745 $[M + NH_4]^+$

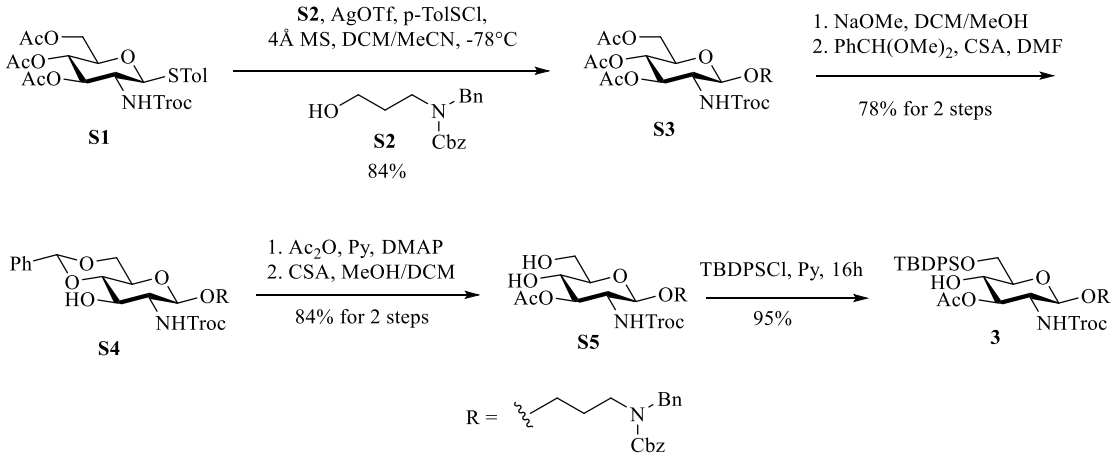


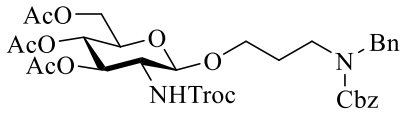
p-Tolyl 6, 7-Di-*O*-acetyl-2, 3, 4-Tri-*O*-benzyl-L-glycero-1-thio-α-D-mannoheptopyranoside (**2**)

Compound **22** (1.64 g, 2.80 mmol) was dissolved in pyridine (10 mL) and treated with Ac_2O (1.1 mL, 11.2 mmol) and DMAP (17 mg, 0.14 mmol) at 0 °C. The reaction was allowed to warm up to r.t. and stirred overnight. It was then concentrated, diluted with EtOAc and washed with 1 M HCl, brine, saturated $NaHCO_3$ and brine in order. The organic layer was dried and concentrated. Column chromatography (Hexanes/EtOAc = 3/1) gave compound **2** as a colorless syrup in a yield of 91%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.92 (s, 3H), 2.12 (s, 3H), 2.32 (s, 3H), 3.86-3.92 (m, 2H), 3.99 (dd, 1H, J = 1.5, 3.0 Hz), 4.04-4.13 (m, 2H), 4.24 (d, 1H, J = 13.0 Hz), 4.47 (d, 1H, J = 9.5 Hz), 4.58 (s, 2H), 4.64 (d, 1H, J = 12.5 Hz), 4.76 (d, 1H, J = 12.5 Hz), 4.90 (d, 1H, J = 10.0 Hz), 5.63 (d, 1H, J = 1.5 Hz), 5.66 (ddd, 1H, J = 1.5, 6.0, 7.5 Hz), 7.09 (d, 2H, J = 8.5 Hz), 7.23 (d, 2H, J = 8.5 Hz), 7.27-7.39 (m, 15H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 20.65, 20.95, 21.07, 62.29, 68.24, 70.77, 71.77, 72.0, 73.67, 75.36, 75.47, 80.36, 85.54, 127.8, 127.85, 127.91, 127.96, 128.38, 128.45, 128.48, 128.57, 129.91, 130.0, 131.25, 137.72, 137.79, 137.88, 170.31, 170.41. HRMS: m/z calc. for $C_{39}H_{46}NO_8S$: 688.2944; found: 688.2937 $[M + NH_4]^+$

Scheme **S1**. Preparation of building block **3**

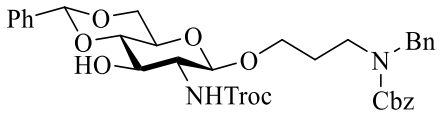




N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2- (2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**S3**)

A solution of *p*-Tolyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2- (2,2,2-trichloroethyloxycarbonylamino) -1-thio-β-D-glucopyranoside **S1** (2.12 g, 3.61 mmol), *N*-(Benzyl)-benzyloxycarbonyl- 3-aminopropanol **S2** (1.0 g, 3.33 mmol) and freshly activated 4 Å molecular sieves (1.5 g) in DCM (50 mL) was stirred at r.t. for 20 min and then cooled to -78 °C. To the above solution was added silver trifluoromethanesulfonate (AgOTf, 2.23 g, 8.68 mmol) in MeCN (2.5 mL). The mixture was stirred for 10 min and *p*-TolSCl (480 μL, 3.61 mmol) was added directly into it via microsyringe. The reaction was allowed to stir at the same temperature for 2 h before quenched with Et_3N (0.5 mL). The mixture was then filtered through celite and concentrated. Column chromatography gave compound **S3** in a yield of 84%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.73 (m, 2H), 2.04 (s, 3H), 2.05 (s, 3H), 2.08 (s, 3H), 2.98 (m, 1H), 3.20-3.50 (m, 2H), 3.56 (m, 1H), 3.75 (q, 1H, J = 9.5 Hz), 3.83 (m, 1H), 3.92 (m, 1H), 4.10 (d, 1H, J = 12.0 Hz), 4.24 (d, 0.5H, J = 4.5 Hz), 4.27 (d, 0.5H, J = 5.0 Hz), 4.34 (d, 1H, J = 9.0 Hz), 4.52-4.78 (m, 3H), 5.07 (m, 1H), 5.13-5.22 (m, 3H), 6.29 (d, 1H, J = 9.0 Hz), 7.17 (d, 1H, J = 7.0 Hz), 7.27-7.44 (m, 9H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 20.66, 20.75, 20.77, 27.31, 43.03, 50.08, 56.13, 61.99, 67.07, 67.49, 68.64, 71.74, 73.09, 74.31, 101.19, 127.2, 127.47, 127.95, 128.03, 128.53, 128.64, 136.76, 137.45, 154.79, 156.5, 169.46, 170.64, 170.75. HRMS: m/z calc. for $C_{33}H_{39}Cl_3N_2NaO_{12}$: 783.1466; found: 783.1440 $[M + Na]^+$

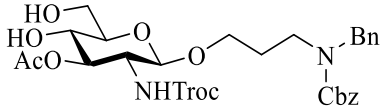


N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 4,6-*O*-benzylidene-2-deoxy-2- (2,2,2-

trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**S4**)

Compoud **S3** (2.13 g, 2.80 mmol) was dissolved in DCM/MeOH (10/10 mL) and the solution was cooled to -10 ℃. NaOMe was added to adjust the pH to 11 and the solution was stirred at the same temperature for 2 h. After neutralizing with H^+ resin, the solution was filtered, concentrated and diluted in DMF (10 mL). Benzaldehyde dimethyl acetal (611μL, 4.07 mmol) and CSA (166 mg, 0.72 mmol) were added and the mixture was heated at 50 ℃ overnight. Upon completion by TLC the reaction was quenched with Et_3N, diluted with EtOAc and washed with brine. The organic layer was dried and concentrated. Column chromatography (Hexanes/EtOAc = 1/1) gave compound **S4** in a 78% yield over 2 steps.

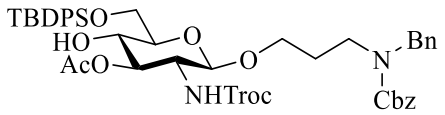
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.69-1.77 (m, 2H), 2.94 (d, 1H, J = 14.0 Hz), 3.27-3.39 (m, 2H), 3.46-3.61 (m, 2H), 3.69-3.82 (m, 2H), 3.83-3.94 (m, 2H), 4.21-4.32 (m, 2H), 4.34 (d, 1H, J = 8.5 Hz), 4.42-4.66 (m, 2H), 4.70 (d, 1H, J = 16.0 Hz), 4.81 (d, 1H, J = 12.0 Hz), 5.13-5.27 (m, 2H), 5.54 (s, 1H), 6.93 (br, 1H), 7.17 (d, 2H, J = 7.5 Hz), 7.26-7.43 (m, 11H), 7.46-7.54 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 27.45, 42.92, 43.34, 50.05, 50.76, 59.02, 59.04, 66.03, 66.13, 66.91, 67.38, 67.56, 68.6, 72.98, 74.61, 81.43, 95.6, 101.32, 101.89, 126.38, 127.2, 127.5, 127.89, 128.15, 128.23, 128.34, 128.37, 128.53, 128.62, 128.67, 129.25, 136.65, 137.1, 137.37, 156.38, 156.65. HRMS: m/z calc. for $C_{34}H_{38}Cl_3N_2O_9$: 723.1643; found: 723.1631 $[M + H]^+$



N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 3-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**S5**)

To a solution of **S4** (1.66 g, 2.30 mmol) in pyridine (6 mL) was added acetic anhydride (1 mL, 10 mmol)) and DMAP (20 mg, 0.16 mmol) at 0 ℃. The solution was stirred at r.t. overnight before it was quenched with MeOH, concentrated, diluted with EtOAc and washed with brine. The organic layer was dried, concentrated and dissolved in DCM/MeOH (8/8 mL). CSA (150 mg, 0.65 mmol) was added and the solution was stirred at r.t. overnight, followed by quenching with Et_3N. The mixture was concentrated, diluted with EtOAc, washed with brine, dried and concentrated again. Column chromatography (DCM/EtOAc = 1/2) gave compound **S5** in an 84% yield over 2 steps.

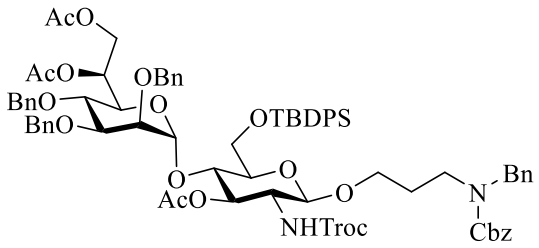
^{1}HNMR (500 MHz, $CDCl_3$): δ =1.71-1.77 (m, 2H), 2.10 (s, 3H), 2.64 (br, 1H), 3.05-3.16 (m, 2H), 3.21-3.37 (m, 2H), 3.39-3.45 (m, 1H), 3.60-3.74 (m, 2H), 3.76-3.93 (m, 3H), 4.27-4.35 (m, 1H), 4.37 (d, 1H, J = 8.5 Hz), 4.48-4.63 (m, 2H), 4.64-4.68 (m, 1H), 4.95-4.99 (m, 1H), 5.13-5.22 (m, 2H), 6.18 (d, 1H, J = 8.5 Hz), 7.11-7.20 (m, 2H), 7.25-7.42 (m, 8H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 21.14, 27.65, 28.16, 43.38, 43.63, 50.31, 56.12, 62.26, 67.42, 67.65, 69.71, 74.44, 75.73, 76.27, 95.83, 101.41, 127.34, 127.60, 128.04, 128.21, 128.66, 128.78, 136.70, 137.59, 154.99, 156.65, 172.24. HRMS: m/z calc. for $C_{29}H_{35}Cl_3N_2NaO_{10}$: 699.1255; found: 699.1227 $[M + Na]^+$



N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 3-*O*-acetyl-6-*tert*-butyldiphenylsilyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**3**)

To a solution of **S5** (0.86 g, 1.27 mmol) in pyridine (6 mL) was added TBDPSCl (0.65 mL, 2.5 mmol) and the mixture was allowed to stir at r.t. overnight. Then it was concentrated, diluted with EtOAc and washed with brine. The organic layer was dried, concentrated and purified through column chromatography to afford compound **3** in a 95% yield.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.07 (s, 9H), 1.70-1.75 (m, 2H), 2.12 (s, 3H), 2.97-3.05 (m, 1H), 3.09-3.16 (m, 1H), 3.18-3.41 (m, 3H), 3.65-3.85 (m, 4H), 3.86-3.95 (m, 2H), 4.22-4.33 (m, 1H), 4.40-4.57 (m, 1H), 4.59-4.72 (m, 2H), 4.91-5.02 (m, 1H), 5.10-5.24 (m, 2H), 6.14 (d, 1H, J = 9.0 Hz), 7.12-7.19 (m, 2H), 7.26-7.48 (m, 14H), 7.63-7.73 (m, 4H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 19.32, 21.16, 22.78, 25.4, 26.91, 27.03, 27.49, 28.33, 31.71, 34.79, 43.46, 50.32, 50.97, 55.99, 64.79, 66.66, 67.4, 67.54, 71.28, 74.4, 74.61, 74.86, 74.98, 76.08, 95.87, 100.64, 101.14, 127.33, 127.53, 127.91, 127.95, 128.0, 128.06, 128.16, 128.63, 128.73, 130.04, 132.74, 132.93, 135.67, 135.76, 136.83, 137.7, 137.91, 154.28, 155.01, 156.51, 156.82, 171.92. HRMS: m/z calc. for $C_{45}H_{57}Cl_3N_3O_{10}Si$: 932.2879; found: 932.2835 $[M + NH_4]^+$

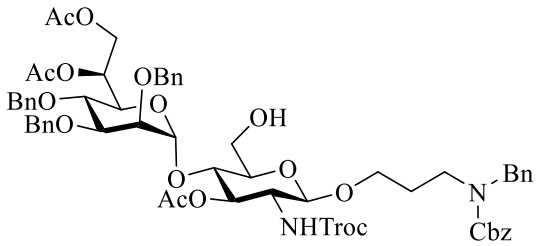


N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 6, 7-Di-*O*-acetyl-2, 3, 4-Tri-*O*-benzyl-L-glycero -*α*-D-mannoheptopyranosyl-(1→4)-3-*O*-acetyl-6-*tert*-butyldiphenylsilyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**23**)

A solution of compound **2** (160 mg, 0.24 mmol), **3** (197 mg, 0.21 mmol) and freshly activated 4 Å molecular sieves (300 mg) in DCM (5 mL) was stirred at r.t. for 20 min and then cooled to -78 ℃. To the above solution was added AgOTf (153 mg, 0.60 mmol) in Et_2O/DCM (6/1 mL). The mixture was stirred for 10 min and *p*-TolSCl (31.5 μL, 0.24 mmol) was added directly into it via microsyringe. The reaction was allowed to warm up to r.t. over a period of 2 h before quenched with Et_3N. The mixture was then filtered through celite and concentrated. Column chromatography gave compound **23** in a yield of 80%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.03 (s, 9H), 1.71-1.76 (m, 2H), 1.88 (s, 3H), 1.92 (s, 3H), 2.07 (s, 3H), 2.95-3.00 (m, 1H), 3.24-3.36 (m, 3H), 3.55-3.68 (m, 3H), 3.72-3.80 (m, 4H), 3.82-3.92 (m, 3H), 4.06 (dd, 1H, J = 7.5, 11.5 Hz), 4.23 (d, 1H, J = 8.0 Hz), 4.28 (d, 1H, J = 15.0 Hz), 4.43 (d, 1H, J = 10.5 Hz), 4.46-4.54 (m, 1H), 4.55-4.58 (m, 2H), 4.62-4.69 (m, 4H), 4.77-4.84 (m, 1H), 5.04-

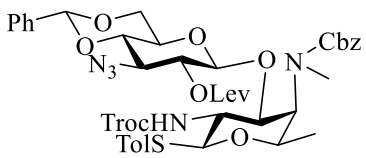
5.10 (m, 1H), 5.14-5.22 (m, 3H), 5.43-5.46 (m, 1H), 6.16 (d, 1H, J = 8.5 Hz), 7.14-7.19 (m, 2H), 7.22-7.41 (m, 29H), 7.62-7.71 (m, 4H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 19.42, 20.86, 21.07, 26.93, 27.04, 27.46, 43.34, 50.31, 50.99, 56.68, 63.11, 63.29, 66.53, 67.62, 68.7, 72.02, 72.29, 72.43, 73.82, 74.42, 74.72, 75.19, 75.50, 75.58, 75.86, 79.8, 99.21, 100.75, 127.34, 127.58, 127.64, 127.79, 127.85, 127.87, 127.98, 128.14, 128.44, 128.51, 128.57, 128.61, 128.65, 128.77, 129.8, 129.91, 133.02, 133.42, 135.68, 135.89, 136.85, 137.71, 138.13, 138.22, 155.06, 156.55, 170.28, 170.48, 170.54. Two C1-H1 coupling constants (171.0, 159.5 Hz) confirmed the stereochemistry.
HRMS: m/z calc. for $C_{77}H_{91}Cl_3N_3O_{18}Si$: 1478.5132; found: 1478.5088 $[M + NH_4]^+$



N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 6, 7-Di-*O*-acetyl-2, 3, 4-Tri-*O*-benzyl-L-glycero -*α*-D-mannoheptopyranosyl-(1→4)-3-*O*-acetyl-2-deoxy-2- (2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**24**)

To a solution of **23** (190 mg, 0.13 mmol) in pyridine (4 mL) in a plastic centrifuge tube, HF pyridine complex (2 mL) was added at 0 °C. The mixture was allowed to warm up to r.t. and stirred overnight. It was then diluted with DCM, washed with saturated $CuSO_4$ solution, 1M HCl and brine. The organic layer was dried and concentrated. Column chromatography (Hexanes/EtOAc = 1/1) gave **24** in a yield of 85%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.72-1.76 (m, 2H), 1.94 (s, 3H), 2.05 (s, 3H), 2.11 (s, 3H), 2.44 (br, 1H), 3.06-3.14 (m, 1H), 3.23-3.31 (m, 2H), 3.35-3.42 (m, 1H), 3.60-3.77 (m, 4H), 3.77-3.90 (m, 6H), 4.26-4.36 (m, 3H), 4.37-4.43 (dd, 1H, J = 4.5, 11.5 Hz), 4.47 (d, 1H, J = 11.5 Hz), 4.57-4.72 (m, 6H), 4.77-4.84 (m, 1H), 5.14-5.23 (m, 4H), 5.60-5.65 (m, 1H), 6.12 (m, 1H), 7.14-7.18 (m, 2H), 7.24-7.44 (m, 23H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 20.92, 21.02, 21.15, 27.58, 29.77, 43.41, 50.21, 56.59, 61.33, 63.06, 67.32, 67.58, 68.85, 72.0, 72.2, 72.78, 73.75, 74.09, 74.36, 74.88, 74.99, 75.11, 75.64, 79.56, 95.73, 99.22, 101.17, 127.26, 127.52, 127.57, 127.64, 127.79, 127.95, 128.09, 128.45, 128.49, 128.52, 128.57, 128.71, 136.73, 137.57, 137.91, 138.09, 138.14, 154.87, 156.56, 170.49, 170.59, 170.76. HRMS: m/z calc. for $C_{61}H_{70}Cl_3N_2O_{18}$: 1223.3689; found: 1223.3668 $[M + H]^+$

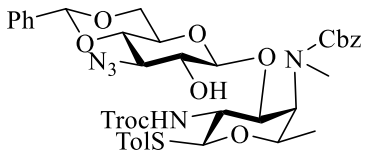


p-Tolyl 3-azido-4, 6-*O*-benzylidene-3-deoxy-2-levulinoyl-*β*-D-glucopyranosyl-(1→3)-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-

fucopyranoside (**25**)

A solution of compound **5** (788 mg, 1.58 mmol) and freshly activated 4 Å molecular sieves (1.6 g) in DCM (20 mL) was stirred at r.t. for 20 min and then cooled to -78 ℃. To the above solution was added AgOTf (1.02 g, 3.96 mmol) in Et_2O/DCM (20/2 mL). The mixture was stirred for 10 min and *p*-TolSCl (209 μL, 1.58 mmol) was added directly into it via microsyringe. After activation completed as indicated by disappearance of orange color and by TLC, acceptor **4** (797 mg, 1.35 mmol) in DCM (5 mL) was added slowly along the wall of the flask. Another 3 mL of DCM was used to rinse once. The reaction was allowed to warm up to r.t. over a period of 2 h before quenched with Et_3N. The mixture was then filtered through celite and concentrated. Column chromatography gave compound **25** in a yield of 70%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.20-1.28 (m, 3H), 2.13&2.21 (s, 3H), 2.33&2.34 (s, 3H), 2.40-2.82 (m, 4H), 2.86&2.94 (s, 3H), 3.03 (t, 1H, *J* = 10.0 Hz), 3.37-3.73 (m, 5H), 3.77-3.88 (m, 1.5H), 4.22 (dd, 0.5H, *J* = 5.0, 10.5 Hz), 4.32 (d, 1H, *J* = 8.0 Hz), 4.37-4.47 (m, 1H), 4.53 (0.5H, dd, *J* = 2.5, 7.0 Hz), 4.59 (d, 0.5H, *J* = 12.0 Hz), 4.64&4.66 (d, 0.5H, *J* = 10.0 Hz), 4.68 (d, 0.5H, *J* = 7.5 Hz), 4.71-4.84 (m, 3H), 5.01 (d, 1H, *J* = 12.0 Hz), 5.14 (d, 0.5 H, *J* = 12.0 Hz), 5.23 (d, 1H, *J* = 12.5 Hz), 5.35 (d, 0.5H, *J* = 12.0 Hz), 5.49&5.54 (s, 1H), 7.07-7.13 (m, 2H), 7.28-7.44 (m, 10H), 7.45-7.52 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 21.1, 27.61, 29.82, 32.73, 37.59, 37.82, 51.55, 53.18, 62.78, 63.06, 67.22, 67.68, 71.25, 71.56, 85.48, 96.84, 99.94, 101.57, 125.95, 126.01, 127.92, 128.19, 128.38, 128.55, 128.9, 128.95, 129.23, 129.26, 129.67, 129.7, 133.85, 134.16, 136.44, 138.49, 138.69, 156.49, 157.6. Two C1-H1 coupling constants (163.0, 161.0 Hz) confirmed the stereochemistry. Most peaks were split due to the secondary amides on the fucose.
HRMS: m/z calc. for $C_{43}H_{49}Cl_3N_5O_{12}S$: 964.2164; found: 964.2117 $[M + H]^+$

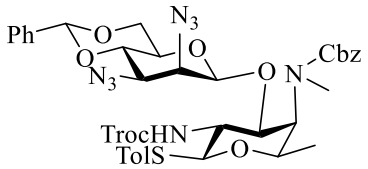


p-Tolyl 3-azido-4, 6-*O*-benzylidene-3-deoxy-*β*-D-glucopyranosyl-(1→3)-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranoside (**26**)

Compound **25** (366 mg, 0.379 mmol) was dissolved in DCM/Pyridine (10/0.05 mL) followed by addition of N_2H_4 • AcOH (50 mg, 0.543 mmol). The mixture was stirred at r.t. for 4 h before it was diluted with DCM and washed with brine. The organic layer was dried and concentrated. Column chromatography (Hexanes/DCM/EtOAc = 1/1/1) gave **26** as white solid in a yield of 93%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.31 (d, 3H, *J* = 6.5 Hz), 2.33 (s, 3H), 2.98 (s, 3H), 3.40 (t, 1H, *J* = 9.5 Hz), 3.42-3.52 (m, 2H), 3.61 (t, 1H, *J* = 9.5 Hz), 3.76 (t, 1H, *J* = 9.5 Hz), 3.88 (dd, 1H, *J* = 3.0, 6.5 Hz), 4.14 (dd, 1H, *J* = 5.5, 11.5 Hz), 4.32 (dd, 1H, *J* = 5.0, 10.5 Hz), 4.40 (d, 1H, *J* = 7.5 Hz), 4.59 (dd, 1H, *J* = 3.0, 5.5 Hz), 4.76 (d, 1H, *J* = 12.5 Hz), 4.81 (d, 1H, *J* = 12.0 Hz), 4.86 (d, 1H, *J* = 2.0 Hz), 4.91 (d, 1H, *J* = 10.5 Hz), 5.09 (d, 1H, *J* = 12.5 Hz), 5.20 (d, 1H, *J* = 12.5 Hz), 5.34

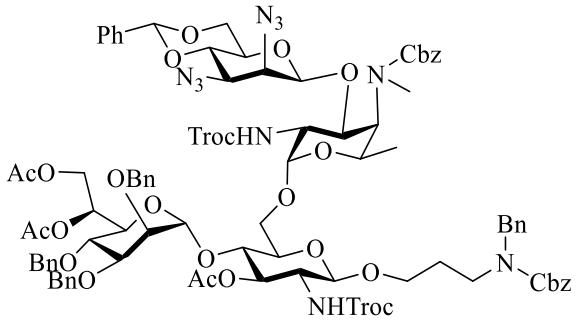
(d, 1H, J = 7.5 Hz), 5.52 (s, 1H), 7.08-7.13 (m, 2H), 7.32-7.45 (m, 10H), 7.46-7.52 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 17.3, 21.33, 33.2, 53.4, 56.21, 64.49, 67.58, 68.27, 68.58, 73.32, 74.35, 74.63, 79.02, 81.7, 86.27, 95.62, 101.73, 106.53, 125.42, 126.18, 127.75, 128.15, 128.35, 128.46, 128.49, 128.78, 129.16, 129.37, 129.8, 134.42, 136.23, 136.67, 138.92, 154.22, 159.87. Two C1-H1 coupling constants (161.0, 156.5 Hz) confirmed the stereochemistry.
HRMS: m/z calc. for $C_{38}H_{43}Cl_3N_5O_{10}S$: 866.1796; found: 866.1745 $[M + H]^+$



p-Tolyl 2, 3-diazido-4, 6-*O*-benzylidene-2, 3-dideoxy-*β*-D-mannopyranosyl-(1→3)-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranoside (**27**)

Compound **26** (307 mg, 0.35 mmol) was dissolved in anhydrous DCM (10 mL) and cooled to -30 °C. Pyridine (285 µL, 3.54 mmol) and Tf_2O (179 µL, 1.06 mmol) were added and the mixture was allowed to warm up to r.t. over a period over 4 h. It was then quenched with MeOH, diluted with DCM and washed with brine. The organic layer was dried, concentrated and dissolved with DMF (10 mL). NaN_3 (140 mg, 2.17 mmol) was added and the mixture was heated at 50 °C overnight. After diluting with EtOAc and washing with brine, compound **27** was purified through column chromatography (Hexanes/DCM/EtOAc = 3/2/1) in a yield of 84% over 2 steps.

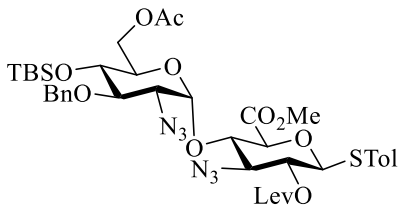
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.31 (d, 3H, J = 6.5 Hz), 2.33 (s, 3H), 2.96 (s, 3H), 3.26 (d, 1H, J = 3.5 Hz), 3.32 (dt, 1H, J = 5.0, 9.5 Hz), 3.46 (dd, 1H, J = 4.0, 10.0 Hz), 3.60-3.69 (m, 1H), 3.74-3.89 (m, 3H), 4.12-4.20 (m, 1H), 4.26 (dd, 1H, J = 4.5, 10.5 Hz), 4.56-4.62 (m, 2H), 4.72 (d, 1H, J = 1.5 Hz), 4.80 (d, 1H, J = 10.5 Hz), 4.95 (d, 1H, J = 12.0 Hz), 5.06 (d, 1H, J = 12.5 Hz), 5.14 (d, 1H, J = 6.5 Hz), 5.20 (d, 1H, J = 12.5 Hz), 5.56 (s, 1H), 7.08-7.14 (m, 2H), 7.32-7.51 (m, 12H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 17.3, 21.32, 32.88, 52.83, 54.13, 59.96, 62.38, 67.74, 67.94, 68.37, 74.39, 74.64, 76.07, 76.73, 86.75, 95.69, 98.6, 101.61, 101.76, 125.92, 125.99, 128.05, 128.43, 128.61, 128.72, 128.98, 129.26, 129.3, 129.74, 129.77, 134.19, 134.53, 136.63, 136.67, 138.74, 154.22, 158.48. Two C1-H1 coupling constants (163.5, 163.0 Hz) confirmed the stereochemistry. Most peaks were split due to the secondary amides on the fucose.
HRMS: m/z calc. for $C_{38}H_{42}Cl_3N_8O_9S$: 891.1861; found: 891.1813 $[M + H]^+$



N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 2, 3-diazido-4, 6-*O*-benzylidene-2, 3-dideoxy -*β*-D-mannopyranosyl-(1→3)-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*α*-L-fucopyranosyl-(1→6)-[6, 7-Di-*O*-acetyl-2, 3, 4-Tri-*O*-benzyl-L-glycero-*α*-D-mannoheptopyranosyl-(1→4)]-3-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**28**)

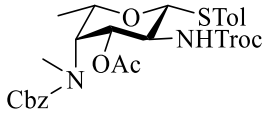
A solution of compound **27** (50 mg, 0.0561 mmol), **24** (55 mg, 0.0449 mmol) and freshly activated 4 Å molecular sieves (100 mg) in DCM (5 mL) was stirred at r.t. for 20 min and then cooled to -78 ℃. To the above solution was added AgOTf (36 mg, 0.14 mmol) in Et_2O/DCM (3/0.5 mL). The mixture was stirred for 10 min and *p*-TolSCl (7.4 μL, 0.0561 mmol) was added directly into it via microsyringe. The reaction was allowed to warm up to r.t. over a period of 2 h before quenched with Et_3N. The mixture was then filtered through celite and concentrated. Column chromatography (Hexanes/DCM/EtOAc = 2/2/1) gave compound **28** in a yield of 73%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.20 (d, 3H, J = 7.0 Hz), 1.65-1.77 (m, 2H), 1.86 (s, 3H), 2.06 (s, 3H), 2.12 (s, 3H), 2.85-2.94 (m, 1H), 3.19 (s, 3H), 3.25-3.31 (m, 1H), 3.34-3.49 (m, 4H), 3.53 (dd, 1H, J = 4.0, 10.0 Hz), 3.60-3.72 (m, 3H), 3.73-3.91 (m, 8H), 4.00-4.08 (m, 1H), 4.12 (dd, 1H, J = 4.0, 11.0 Hz), 4.15-4.32 (m, 5H), 4.33-4.41 (m, 1H), 4.47 (d, 2H, J = 10.0 Hz), 4.55-4.65 (m, 5H), 4.67-4.77 (m, 4H), 4.77-4.88 (m, 3H), 5.01-5.09 (m, 2H), 5.11 (d, 1H, J = 12.5 Hz), 5.14-5.23 (m, 3H), 5.35 (d, 1H, J = 4.0 Hz), 5.40 (d, 1H, J = 7.5 Hz), 5.58 (s, 1H), 5.60-5.65 (m, 1H), 6.46 (d, 1H, J = 8.5 Hz), 7.12-7.19 (m, 2H), 7.26-7.52 (m, 33H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 16.69, 16.74, 20.95, 21.0, 21.06, 27.37, 29.81, 33.21, 42.84, 50.05, 51.12, 54.54, 56.33, 59.92, 62.56, 63.17, 65.0, 65.82, 66.86, 67.69, 67.88, 68.25, 68.42, 68.64, 72.08, 72.23, 72.67, 73.78, 74.02, 74.39, 74.44, 74.6, 75.27, 75.42, 75.52, 76.69, 77.36, 77.63, 79.58, 95.92, 97.66, 99.08, 100.75, 101.75, 125.95, 126.03, 127.26, 127.58, 127.61, 127.66, 127.89, 127.96, 128.02, 128.1, 128.12, 128.39, 128.47, 128.58, 128.6, 128.68, 128.76, 129.1, 129.16, 129.21, 136.62, 136.76, 137.38, 137.76, 137.98, 138.04, 154.41, 155.17, 156.65, 158.49, 170.37, 170.42, 170.55. Four C1-H1 coupling constants (177.0, 171.0, 166.0, 163.5 Hz) confirmed the stereochemistry. Most peaks were split due to the secondary amides on the fucose and the linker.
HRMS: m/z calc. for $C_{92}H_{106}Cl_6N_{11}O_{27}$: 2006.5391; found: 2006.5326 $[M + NH_4]^+$



p-Tolyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-*tert*-butyldimethylsilyl-*α*-D-glucopyranosyl -(1→4)-methyl 3-azido-3-deoxy-2-*O*-levuniloyl-1-thio-*β*-D-glucopyranosyluronate (**29**)

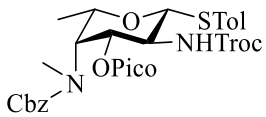
^{1}HNMR (500 MHz, $CDCl_3$): δ = -0.012 (s, 3H), -0.009 (s, 3H), 0.88(s, 9H), 2.08 (s, 3H), 2.22 (s, 3H), 2.34 (s, 3H), 2.65-2.75 (m, 2H), 2.80-2.88 (m, 2H), 3.38 (dd, 1H, *J* = 3.5, 10.5 Hz), 3.51 (dt, 1H, *J* = 2.5, 9.5 Hz), 3.59 (dd, 1H, *J* = 8.5, 10.0 Hz), 3.66 (t, 1H, *J* = 9.0 Hz), 3.76 (t, 1H, *J* = 9.5 Hz), 3.80 (s, 3H), 3.87 (t, 1H, *J* = 9.5 Hz), 3.98 (d, 1H, *J* = 9.5 Hz), 4.03 (dd, 1H, *J* = 8.5, 12.0 Hz), 4.35 (dd, 1H, *J* = 2.5, 12.0 Hz), 4.62 (d, 1H, *J* = 10.0 Hz), 4.76 (d, 1H, *J* = 11.5 Hz), 4.84-4.90 (m, 2H), 5.39 (d, 1H, *J* = 3.5 Hz), 7.10-7.14 (m, 2H), 7.27-7.30 (m, 1H), 7.31-7.38 (m, 6H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = -4.99, -3.57, 18.10, 20.99, 21.33, 25.98, 28.05, 29.99, 37.88, 52.99, 62.29, 64.11, 67.93, 70.45, 70.58, 71.50, 75.26, 75.30, 77.36, 78.54, 80.08, 87.10, 98.38, 127.41, 127,67, 128.40, 129.90, 133.71, 137.96, 138.96, 167.52, 170.86, 171.24, 206.05. HRMS: m/z calc. for $C_{40}H_{58}N_7O_{12}SSi$: 888.3633; found: 888.3687 $[M + NH_4]^+$



p-Tolyl 3-*O*-acetyl-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-1-thio-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranoside (**31**)

Compound **5** (102 mg, 0.172 mmol) was dissolved in pyridine (3 mL) followed by addition of DMAP (10 mg) and acetic anhydride (200 μL) at 0 °C. The reaction was stirred at room temperature overnight. Upon completion by TLC, the reaction was diluted with EtOAc, washed with 1 M HCl, sat. $NaHCO_3$ solution and brine. Column chromatography (Hexanes/DCM/EtOAc = 1/1/1) gave compound **31** in a yield of 85%.

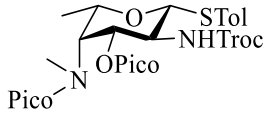
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.22&1.27 (d, 3H, *J* = 6.5 Hz, H-6), 1.76 (s, 3H, Ac), 2.32 (s, 3H, STol-Me), 2.87&2.92 (s, 3H, N-Me), 3.83-3.92 (m, 1H, H-5), 3.92-4.01 (m, 1H, H-2), 4.48-4.52&4.56-4.60 (m, 1H, H-4), 4.59&4.64 (d, 1H, *J* = 10.5 Hz, H-1), 4.73 (d, 1H, *J* = 11.5 Hz, Troc-CH_2), 4.80 (d, 1H, *J* = 12.0 Hz Troc-CH_2), 5.02&5.04 (d, 1H, *J* = 12.5 Hz, Cbz-CH_2), 5.08&5.17 (d, 1H, *J* = 12.5 Hz, Cbz-CH_2), 5.12 (dd, 1H, *J* = 5.5, 11.0 Hz, H-3), 5.20-5.30 (m, 1H, Troc-NH), 7.08-7.14 (m, 2H), 7.27-7.38 (m, 5H), 7.41-7.47 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 17.07, 17.08, 20.45, 20.55, 21.3, 32.78, 33.17, 51.74, 51.86, 54.64, 54.78, 67.47, 67.73, 71.71, 71.83, 74.59, 74.64, 86.48, 86.95, 95.65, 127.55, 127.9, 128.13, 128.33, 128.35, 128.6, 128.64, 129.7, 129.74, 134.4, 134.74, 136.37, 136.82, 138.81, 154.14, 154.35, 157.31, 158.07, 170.51. HRMS: m/z calc. for $C_{27}H_{32}Cl_3N_2O_7S$: 633.0996; found: 633.1012 $[M + H]^+$



p-Tolyl 4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-3-*O*-picoloyl-1-thio-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranoside (**32**)

Compound **5** (134 mg, 0.226 mmol) was dissolved in DCM (5 mL), followed by addition of picolinic acid (84 mg, 0.678 mmol), EDC·HCl (143 mg, 0.747 mmol) and DMAP (5.5 mg, 0.045 mmol). The reaction was stirred at room temperature overnight before concentrated and washed with sat. $NaHCO_3$ solution. The organic phase was dried over Na_2SO_4, concentrated and purified through column (Hexanes/DCM/EtOAc = 2/2/3) to obtain compound **32** in a yield of 94%.

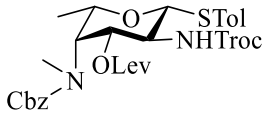
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.26&1.29 (d, 3H, J = 6.5 Hz, H-6), 2.30&2.33 (s, 3H, STol-Me), 2.96&3.00 (s, 3H, N-Me), 3.96-4.02&4.10-4.15 (m, 1H, H-5), 4.15-4.24 (m, 1H, H-2), 4.53&4.90 (d, 1H, J = 12.5 Hz, Cbz-CH_2), 4.58&4.69 (d, 1H, J = 12.0 Hz, Troc-CH_2), 4.62 (s, 1H, Troc-CH_2), 4.65&4.84 (dd, 1H, J = 3.0, 6.5 Hz, H-4), 4.80&4.93 (d, 1H, J = 10.5 Hz, H-1), 4.82&4.86 (d, 1H, J = 12.5 Hz, Cbz-CH_2), 5.56&5.77 (dd, 1H, J = 6.0, 11.0 Hz, H-3), 5.96&4.82 (d, 1H, J = 9.0 Hz, Troc-NH), 7.03-7.30 (m, 6H), 7.35-7.90 (m, 5H), 8.69-8.79 (m, 1H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 17.12, 17.15, 21.3, 32.94, 33.28, 51.67, 51.74, 54.97, 55.02, 67.28, 67.72, 73.44, 73.8, 74.34, 74.51, 74.54, 86.0, 86.14, 95.54, 95.65, 125.17, 125.46, 126.91, 126.99, 127.21, 127.32, 127.7, 127.96, 128.09, 128.13, 128.39, 128.49, 129.6, 129.71, 134.83, 135.0, 135.96, 136.65, 137.14, 137.51, 138.77, 139.07, 146.81, 147.11, 150.17, 150.36, 154.49, 154.68, 157.39, 157.98, 163.63, 163.85. HRMS: m/z calc. for $C_{31}H_{33}Cl_3N_3O_7S$: 696.1105; found: 696.1123 $[M + H]^+$



p-Tolyl 4-[*N*-(methyl)-*N*-(picoloyl)-amino]-2,4-dideoxy-3-*O*-picoloyl-1-thio-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranoside (**33**)

Compound **19** (157 mg, 0.343 mmol) was dissolved in DCM (5 mL), followed by addition of picolinic acid (127 mg, 1.03 mmol), EDC·HCl (237 mg, 1.24 mmol) and DMAP (8.4 mg, 0.069 mmol). The reaction was stirred at room temperature overnight before concentrated and washed with sat. $NaHCO_3$ solution. The organic phase was dried over Na_2SO_4, concentrated and purified through column (DCM/MeOH = 8/1) to obtain compound **33** in a yield of 99%.

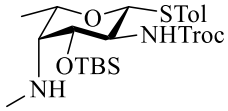
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.21&1.39&1.43 (d, 3H, J = 6.5 Hz, H-6), 2.29&2.32&2.35 (s, 3H, STol-Me), 3.08&3.12 (s, 3H, N-Me), 3.73-3.79&3.92-3.96&4.07-4.14 (m, 1H, H-5), 4.18-4.31&5.33-5.38 (m, 1H, H-2), 4.62&4.74&4.80 (d, 1H, J = 12.0 Hz, Troc-CH_2), 4.61-4.67 (m, 1H, Troc-CH_2), 4.68&3.91 (dd, 1H, J = 3.0, 6.5 Hz, H-4), 4.73&4.85 (d, 1H, J = 10.0 Hz, H-1), 5.42&5.75 (dd, 1H, J = 6.5, 11.0 Hz, H-3), 5.58-5.67&5.91-6.01 (m, 1H, Troc-NH), 7.04-7.19 (m, 3H), 7.26-7.53 (m, 4H), 7.65-8.01 (m, 2H), 8.20-8.77 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 16.99, 17.13, 17.41, 21.29, 21.35, 32.47, 36.32, 51.94, 52.41, 52.57, 57.4, 60.24, 72.59, 72.62, 74.07, 74.39, 74.93, 86.09, 86.8, 95.47, 95.56, 123.16, 123.84, 124.33, 124.43, 125.07, 125.32, 125.68, 126.13, 126.62, 127.19, 127.28, 127.44, 129.69, 129.74, 129.77, 134.56, 134.73, 135.25, 136.92, 137.06, 137.12, 137.44, 138.71, 138.8, 139.29, 147.09, 147.14, 147.16, 148.1, 148.61, 150.03, 150.27, 153.8, 153.94, 154.37, 154.59, 163.73, 164.12, 169.94, 171.18, 171.33. HRMS: m/z calc. for $C_{29}H_{30}Cl_3N_4O_6S$: 667.0952; found: 667.0966 $[M + H]^+$



p-Tolyl 4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-3-*O*-levuniloyl-1-thio-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranoside (**34**)

Compound **5** (1.81 g, 3.06 mmol) was dissolved in DCM (40 mL), followed by addition of levulinic acid (626 μL, 6.12 mmol), EDC·HCl (1.46 g, 7.64 mmol) and DMAP (38 mg, 0.31 mmol). The reaction was stirred at room temperature overnight before concentrated and washed with sat. $NaHCO_3$ solution. The organic phase was dried over Na_2SO_4, concentrated and purified through column (Hexanes/DCM/EtOAc =1/1/1) to obtain compound **34** in a yield of 93%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.21&1.25 (d, 3H, J = 6.5 Hz, H-6), 2.06&2.08 (s, 3H, Lev-Me), 2.10-2.60 (m, 4H, Lev-CH_2), 2.31 (s, 3H, STol-Me), 2.87&2.92 (s, 3H, N-Me), 3.87-3.99 (m, 2H, H-2, H-5), 4.50&4.57 (dd, 1H, J = 3.0, 6.0 Hz, H-4), 4.64&4.69 (d, 1H, J = 10.5 Hz, H-1), 4.68&4.87&4.90 (d, 2H, J = 12.0 Hz, Troc-CH_2), 5.02&5.05&5.16 (d, 2H, J = 12.5 Hz, Cbz-CH_2), 5.11 (dd, 1H, J = 6.0, 10.0 Hz, H-3), 5.51&5.61 (d, 1H, J = 9.5 Hz, Troc-NH), 7.07-7.12 (m, 2H), 7.27-7.37 (m, 5H), 7.38-7.45 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 17.04, 17.09, 21.27, 27.83, 29.75, 29.76, 32.81, 33.19, 37.76, 37.84, 51.63, 51.89, 54.61, 54.78, 67.44, 67.68, 71.88, 72.15, 74.43, 74.56, 86.27, 86.79, 95.73, 127.87, 128.09, 128.19, 128.23, 128.56, 128.58, 129.66, 129.69, 134.13, 134.53, 136.51, 136.87, 138.62, 138.87, 154.43, 157.27, 158.01, 171.86, 172.15, 206.52. HRMS: m/z calc. for $C_{30}H_{36}Cl_3N_2O_8S$: 689.1258; found: 689.1236 $[M + H]^+$

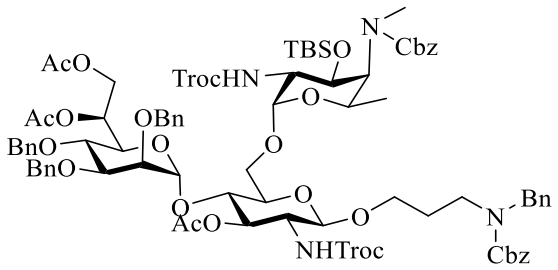


p-Tolyl 3-*O*-*tert*-butyldimethylsilyl-2,4-dideoxy-4-methylamino-1-thio-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranoside (**35**)

Compound **19** (1.2 g, 2.62 mmol) was dissolved in DCM (50 mL) followed by the addition of *t*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf, 0.9 mL, 3.93 mmol) and 2, 6-lutidine (0.61 mL, 5.24 mmol) at -40°C. The mixture was allowed to warm up to r.t. and stirred overnight. Compound **35** was obtained through column chromatography (DCM/EtOAc = 3/1) as a white solid in a yield of 87%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 0.06 (s, 3H), 0.08 (s, 3H), 0.88 (s, 9H), 1.33 (d, 3H, J = 6.5 Hz), 2.31 (s, 3H), 2.51 (dd, 1H, J = 1.5, 4.5 Hz), 2.53 (s, 3H), 3.46 (q, 1H, J = 9.5 Hz), 3.59 (q, 1H, J = 6.5 Hz), 3.94 (dd, 1H, J = 3.5, 10.0 Hz), 4.64 (d, 1H, J = 11.5 Hz), 4.70 (d, 1H, J = 12.0 Hz), 4.82 (d, 1H, J = 10.5 Hz), 4.99 (d, 1H, J = 8.5 Hz), 7.07 (d, 2H, J = 8.0 Hz), 7.39 (d, 2H, J = 8.0 Hz). ^{13}CNMR (125 MHz, $CDCl_3$): δ = -4.83, -4.31, 18.01, 18.23, 21.19, 25.75, 39.01, 54.54, 64.93, 73.81, 74.75, 75.68, 86.87, 95.34, 129.62, 130.2, 132.48, 137.57, 153.78. HRMS: m/z calc. for

$C_{23}H_{38}Cl_3N_2O_4SSi$: 571.1387; found: 571.1378 $[M + H]^+$

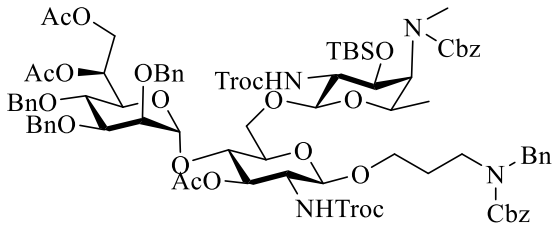


N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 4-[*N*-(methyl)-benzyloxycarbonylamino]-3-*O*-*tert*-butyldimethylsilyl-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*α*-L-fucopyranosyl-(1→6)-[6, 7-di-*O*-acetyl-2, 3, 4-tri-*O*-benzyl-L-glycero -*α*-D-mannoheptopyranosyl-(1→4)]-3-*O*-acetyl-2-deoxy-2- (2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**36α**)

A solution of compound **35** (0.89 g, 1.56 mmol), compound **24** (1.53 g, 1.25 mmol) and freshly activated 4 Å molecular sieves (1.6 g) in DCM (35 mL) was stirred at r.t. for 20 min and then cooled to -78 ℃. To the above solution was added AgOTf (1.0 g, 3.91 mmol) in DCM/MeCN (5/1 mL). The mixture was stirred for 10 min and *p*-TolSCl (207 μL, 1.56 mmol) was added directly into it via microsyringe. The reaction was allowed to warm up to r.t. over a period of 2 h. TLC indicated that acceptor was not completely consumed yet. The reaction was cooled to -78 ℃ followed by addition of **35** (0.53 g, 0.94 mmol), AgOTf (0.60 g, 2.35 mmol) and *p*-TolSCl (124 μL, 0.94 mmol) in order. After warming up over another period of 2 h, the mixture was quenched with Et_3N, filtered through celite and concentrated. Column chromatography gave inseparable *α* and *β* mixtures, which was dissolved in THF/water (40/10 mL) and treated with benzyl chloroformate (535 μL, 3.75 mmol) and sodium carbonate (0.66 g, 6.25 mmol). The reaction was stirred at r.t. for 4 h followed by concentration, dilution with EtOAc and wash with saturated $NaHCO_3$ and brine. The organic layer was dried, concentrated and purified through column chromatography (Hexanses/DCM/EtOAc = 3/2/2) to give compound **36α** (225 mg, 10%) and **36β** (1.46 g, 73%) over 2 steps.

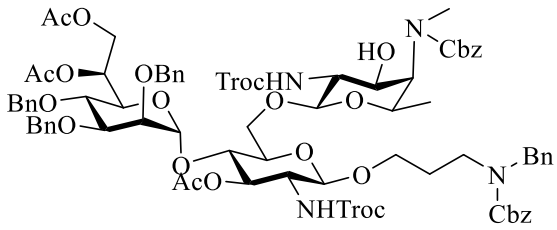
^{1}HNMR (500 MHz, $CDCl_3$): δ = -0.07-0.14 (m, 6H, TBS), 0.83 (s, 9H), 1.06&1.13 (d, 3H, J = 6.5Hz, Fuc-6-Me), 1.66-1.74 (m, 2H), 1.89 (s, 3H), 1.98 (s, 1H) + 2.05 (s, 2H, Ac), 2.10 (s, 3H), 2.85-2.91 (m, 1H), 3.15-3.29 (m, 5H), 3.40-3.57 (m, 2H), 3.62-3.74 (m, 3H), 3.76-3.92 (m, 6H), 4.00 (dd, 1H, J = 6.5, 11.0 Hz), 4.14-4.22 (m, 2H), 4.22-4.32 (m, 3H), 4.40-4.50 (m, 2H), 4.51-4.56 (m, 1H), 4.57-4.66 (m, 4H), 4.66-4.84 (m, 6H), 5.01-5.12 (m, 4H), 5.13-5.23 (m, 3H), 5.58-5.64 (m, 1H), 6.45-6.57 (m, 1H), 7.13-7.17 (m, 2H), 7.24-7.45 (m, 28H).. ^{13}CNMR (125 MHz, $CDCl_3$): δ = -4.93, -4.85, -4.83, -4.73, 16.5, 16.55, 17.77, 17.78, 17.8, 20.81, 20.91, 20.98, 21.05, 25.59, 25.6, 27.41, 33.1, 33.31, 33.71, 42.75, 50.02, 52.99, 53.04, 53.56, 56.25, 56.32, 57.44, 57.54, 63.34, 65.92, 66.78, 66.83, 67.42, 67.64, 67.68, 68.17, 68.28, 68.66, 68.75, 72.17, 72.21, 72.75, 73.86, 74.37, 74.75, 74.9, 75.02, 75.09, 75.19, 75.52, 95.47, 95.77, 98.63, 100.62, 100.91, 127.27, 127.58, 127.68, 127.87, 127.9, 127.92, 127.98, 128.01, 128.15, 128.42, 128.49, 128.54, 128.55, 128.58, 128.75, 136.53, 136.77, 136.87, 137.38, 137.83, 138.01, 138.05, 154.23, 154.27, 155.16, 156.67, 157.21, 157.72, 170.42, 170.57. Three C1-H1 coupling constants (175.5, 172.0, 160.0 Hz) confirmed the stereochemistry. Most peaks were split due to the secondary amides on the fucose and the linker.

HRMS: m/z calc. for $C_{85}H_{105}Cl_6N_4O_{24}Si$: 1803.5019; found: 1803.5009 $[M + H]^+$



N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 4-[*N*-(methyl)-benzyloxycarbonylamino]-3-*O*-*tert*-butyldimethylsilyl-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranosyl-(1→6)-[6, 7-di-*O*-acetyl-2, 3, 4-tri-*O*-benzyl-L-glycero -*α*-D-mannoheptopyranosyl-(1→4)]-3-*O*-acetyl-2-deoxy-2- (2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**36β**)

^{1}HNMR (500 MHz, $CDCl_3$): δ = -0.09-0.12 (m, 6H), 0.83 (s, 9H), 1.09-1.22 (m, 3H), 1.67-1.77 (m, 2H), 1.84 (s, 3H), 2.04 (s, 3H), 2.10-2.12(m, 3H), 2.97-3.07 (m, 1H), 3.14-3.18 (m, 3H), 3.24-3.42 (m, 3H), 3.56-3.77 (m, 5H), 3.77-3.90 (m, 5H), 3.92-4.05 (m, 2H), 4.16-4.25 (m, 1H), 4.26-4.40 (m, 3H), 4.42-4.51 (m, 2H), 4.53-4.80 (m, 10H), 4.91 (d, 1H, J = 12.0 Hz), 4.96-5.08 (m, 2H), 5.10-5.21 (m, 3H), 5.64-5.85 (m, 3H), 6.11-6.18 (m, 1H), 7.10-7.19 (m, 2H), 7.23-7.47 (m, 28H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = -4.99, -4.93, -4.81, -4.77, 16.58, 17.8, 17.83, 20.94, 21.04, 25.62, 27.51, 29.79, 33.29, 33.72, 43.28, 50.15, 56.2, 56.92, 57.23, 57.39, 64.06, 65.31, 66.94, 67.41, 67.57, 67.63, 68.47, 68.54, 70.15, 70.42, 70.96, 71.93, 72.02, 72.12, 73.65, 74.34, 74.68, 74.89, 75.31, 76.17, 79.74, 95.76, 99.82, 100.9, 102.16, 127.07, 127.27, 127.56, 127.61, 127.66, 127.78, 127.93, 127.97, 128.1, 128.21, 128.47, 128.51, 128.53, 128.57, 128.61, 128.74, 136.53, 136.75, 136.87, 137.59, 138.02, 138.13, 141.07, 154.14, 154.25, 154.84, 156.54, 157.16, 157.78, 170.38, 170.52, 171.25, 171.39. Three C1-H1 coupling constants (173.0, 160.5, 160.5 Hz) confirmed the stereochemistry. Most peaks were split due to the secondary amides on the fucose and the linker.
HRMS: m/z calc. for $C_{85}H_{105}Cl_6N_4O_{24}Si$: 1803.5019; found: 1803.4955 $[M + H]^+$

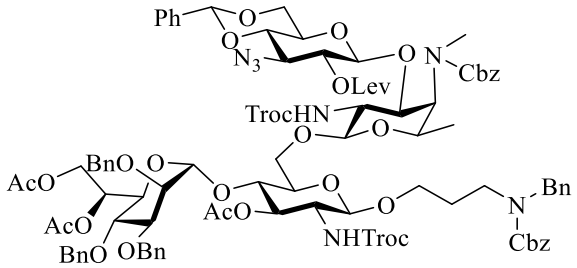


N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 4-[*N*-(methyl)-benzyloxycarbonylamino]- 2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranosyl-(1→6)-[6, 7-di-*O*-acetyl-2, 3,4-tri-*O*-benzyl-L-glycero-*α*-D-mannoheptopyranosyl-(1→4)]-3-*O*-acetyl-2-deoxy-2- (2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**37**)

Compound **36β** (1.80 g, 1.0 mmol) was dissolved with pyridine (10 mL) in a plastic centrifuge tube. After cooling to 0 ℃, HF pyridine complex (5 mL) was added and the reaction was allowed to warm up to r.t. and continued to stir for 3 days. The reaction was then diluted with DCM, washed with

saturated $CuSO_4$ solution, 1 M HCl and saturated $NaHCO_3$ solution successively. The organic layer was dried, concentrated and purified through column chromatography (Hexanes/DCM/EtOAc = 1/1/2) to give **37** as white foam in a yield of 85%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.19&1.24 (d, 3H, J = 6.5 Hz, Fuc-6-Me), 1.70-1.76 (m, 2H), 1.85 (s, 3H), 2.03&2.05 (s, 3H), 2.10&2.11 (s, 3H), 3.00-3.09 (m, 1H), 3.16 (s, 3H), 3.29 (d, 1H, J = 9.5 Hz), 3.34-3.48 (m, 2H), 3.57-3.93 (m, 11 Hz), 3.94-4.13 (m, 2H), 4.29-4.37 (m, 4H), 4.40-4.53 (m, 3H), 4.56-4.75 (m, 7H), 4.76-4.88 (m, 3H), 5.06-5.27 (m, 6H), 5.60-5.69 (m, 1H), 5.93-6.04 (m, 1H), 6.06-6.20 (m, 1H), 7.13-7.20 (m, 2H), 7.24-7.44 (m, 28H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 16.75, 16.76, 20.95, 21.02, 27.63, 29.78, 33.27, 33.7, 43.31, 50.15, 56.26, 56.44, 56.55, 56.81, 63.51, 67.06, 67.4, 67.58, 68.64, 70.58, 70.81, 71.87, 71.95, 72.07, 72.25, 72.42, 73.69, 74.32, 74.45, 74.59, 75.21, 75.35, 75.6, 79.66, 95.72, 95.82, 99.78, 100.94, 102.84, 127.23, 127.57, 127.68, 127.78, 127.86, 127.95, 128.0, 128.08, 128.48, 128.52, 128.56, 128.59, 128.76, 136.73, 136.87, 137.49, 137.9, 138.07, 138.13, 154.7, 156.58, 157.85, 158.97, 170.35, 170.57, 170.84, 170.94. Most peaks were split due to the secondary amides on the fucose and the linker.
HRMS: m/z calc. for $C_{79}H_{90}Cl_6FeN_4O_{24}$: 872.1713; found: 872.1685 $[M + Fe]^{2+}$

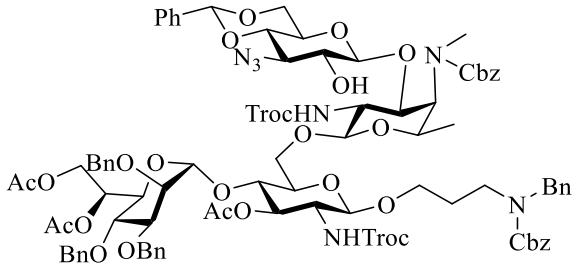


N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 3-azido-4, 6-*O*-benzylidene-3-deoxy-2-levulinoyl -*β*-D-glucopyranosyl-(1→3)-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranosyl-(1→6)-[6,7-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-L-glycero-*α*-D-mannoheptopyranosyl-(1→4)]-3-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**38**)

A solution of compound **5** (756 mg, 1.52 mmol), **37** (1.54 g, 0.91 mmol) and freshly activated 4 Å molecular sieves (1.2 g) in DCM (20 mL) was stirred at r.t. for 20 min and then cooled to -78 °C. To the above solution was added AgOTf (974 mg, 3.79 mmol) in DCM/MeCN (5/0.5 mL). The mixture was stirred for 10 min and *p*-TolSCl (201 μL, 1.52 mmol) was added directly into it via microsyringe. The reaction was allowed to warm up to r.t. over a period of 2 h before quenched with Et_3N. The mixture was then filtered through celite and concentrated. Column chromatography (Hexanes/DCM/EtOAc = 2/2/3) gave compound **38** in a yield of 65%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.18 (d, 3H, J = 6.0 Hz), 1.68-1.75 (m, 2H), 1.86 (s, 3H), 2.04&2.05 (s, 3H), 2.09-2.13 (m, 4H), 2.17-2.22 (m, 2H), 2.40-2.58 (m, 2H), 2.58-2.76 (3H), 2.76-2.87 (m, 1H), 2.95-3.05 (m, 1H), 3.08 + 3.11 (s, 3H), 3.21-3.44 (m, 4H), 3.47-3.58 (m, 2H), 3.58-3.73 (m, 5H), 3.74-3.90 (m, 6H), 3.92-4.03 (m, 1H), 4.16-4.23 (m, 1H), 4.24-4.39 (m, 4H), 4.40-4.52 (m, 2H), 4.53-4.63 (m, 3H), 4.63-4.90 (m, 9H), 5.01 (d, 1H, J = 11.5 Hz), 5.12-5.30 (m, 4H), 5.38 (d,

1H, J = 12.0 Hz), 5.45-5.57 (m, 1H), 5.58-5.73 (m, 2H), 6.08-6.19 (m, 1H), 7.12-7.20 (m, 2H), 7.22-7.55 (m, 33H).. ^{13}CNMR (125 MHz, $CDCl_3$): δ = 16.33, 16.58, 20.9, 20.95, 20.99, 21.02, 27.48, 27.69, 29.74, 29.83, 29.89, 33.02, 33.32, 37.73, 37.91, 43.21, 50.09, 50.87, 52.86, 53.02, 54.71, 54.91, 56.06, 62.91, 63.16, 63.39, 63.56, 66.7, 67.03, 67.14, 67.35, 67.54, 67.63, 67.71, 68.49, 68.56, 70.48, 70.63, 70.7, 71.35, 71.72, 71.8, 71.85, 72.07, 72.22, 73.64, 74.25, 74.31, 74.79, 75.31, 77.36, 79.12, 79.33, 79.72, 89.09, 95.79, 96.08, 96.9, 97.2, 99.53, 100.28, 100.9, 101.41, 101.51, 126.01, 126.08, 127.24, 127.53, 127.58, 127.74, 127.89, 128.02, 128.07, 128.21, 128.36, 128.4, 128.44, 128.45, 128.49, 128.53, 128.59, 128.65, 128.7, 128.71, 128.99, 129.22, 129.26, 136.55, 136.59, 136.67, 136.7, 136.76, 137.52, 137.95, 138.11, 153.93, 154.79, 156.52, 157.68, 170.39, 170.45, 170.48, 170.8, 170.92, 171.24, 171.55, 205.95, 206.37. Most peaks were split due to the secondary amides on the fucose and the linker.
HRMS: m/z calc. for $C_{97}H_{117}Cl_6N_9O_{30}$: 1048.8018; found: 1048.7975 $[M + Na + NH_4]^{2+}$

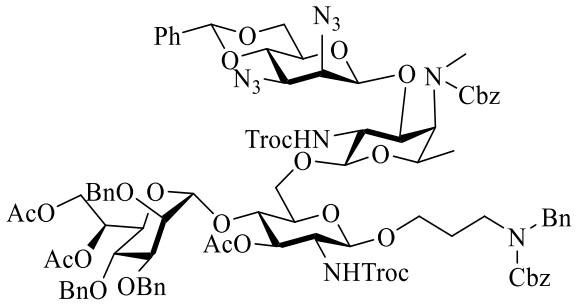


N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 3-azido-4, 6-*O*-benzylidene-3-deoxy -*β*-D-glucopyranosyl-(1→3)-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranosyl-(1→6)-[6, 7-di-*O*-acetyl-2, 3, 4-tri-*O*-benzyl-L-glycero-*α*-D-mannoheptopyranosyl-(1→4)]-3-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**39**)

Compound **38** (1.22 g, 0.59 mmol) was dissolved in DCM/AcOH/Pyridine (15/1/1.5 mL) followed by addition of $N_2H_4 \cdot H_2O$ (200 μL, 64%). The mixture was stirred at r.t. for 4 h before it was diluted with DCM and washed with brine. The organic layer was dried and concentrated. Column chromatography (Hexanes/DCM/EtOAc = 2/2/3) gave **39** as white foam in a yield of 84%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.26 (d, 3H, J = 5.5 Hz), 1.68-1.76 (m, 2H), 1.84 (s, 3H), 2.05 (s, 3H), 2.11 (s, 3H), 3.00-3.14 (m, 2H), 3.20 (s, 3H), 3.24-3.32 (d, 1H, J = 9.5 Hz), 3.34-3.51 (m, 4H), 3.53-3.72 (m, 5H), 3.72-3.91 (m, 8H), 3.94-4.09 (m, 2H), 4.18-4.26 (m, 1H), 4.26-4.44 (m, 5H), 4.44-4.50 (d, 1H, J = 10.0 Hz), 4.50-4.80 (m, 10H), 4.95-5.08 (m, 2H), 5.10-5.28 (m, 6H), 5.53 (s, 1H), 5.65 (t, 1H, J = 6.5 Hz), 5.79 (d, 1H, J = 8.5 Hz), 6.10 (d, 1H, J = 8.5 Hz), 7.14-7.21 (m, 2H), 7.23-7.47 (m, 31 H), 7.48-7.54 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 16.85, 20.93, 21.01, 21.03, 27.58, 29.78, 33.45, 43.36, 50.22, 54.78, 55.9, 56.16, 60.49, 63.65, 64.52, 66.83, 67.26, 67.47, 67.56, 68.14, 68.56, 68.65, 69.83, 71.84, 72.1, 73.28, 73.65, 74.18, 74.32, 74.44, 74.75, 75.12, 75.3, 76.01, 77.36, 79.04, 79.71, 95.77, 95.95, 99.8, 100.88, 101.6, 102.24, 106.29, 126.15, 127.28, 127.58, 127.77, 127.81, 127.92, 128.05, 128.1, 128.35, 128.39, 128.47, 128.49, 128.52, 128.53, 128.62, 128.7, 128.75, 129.24, 136.25, 136.71, 136.77, 137.56, 137.97, 138.06, 138.12, 154.44, 154.81, 156.54, 159.85, 170.36, 170.46, 170.99. Four C1-H1 coupling constants (174.5, 163.0, 163.0, 160.0

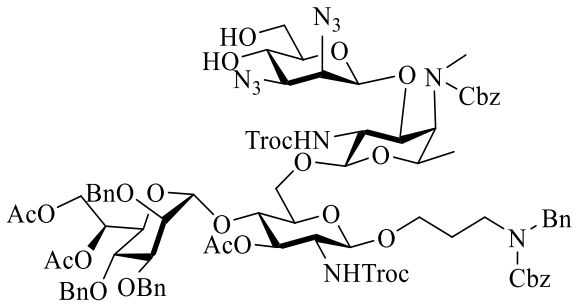
Hz) confirmed the stereochemistry. Most peaks were split due to the secondary amides on the fucose and the linker.
HRMS: m/z calc. for $C_{92}H_{103}Cl_6FeN_7O_{28}$: 1009.7166; found: 1009.7142 $[M + Fe]^{2+}$



N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 2, 3-diazido-4, 6-*O*-benzylidene-2, 3-dideoxy -*β*-D-mannopyranosyl-(1→3)-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranosyl-(1→6)-[6, 7-di-*O*-acetyl-2, 3, 4-tri-*O*-benzyl-L-glycero-*α*-D-mannoheptopyranosyl-(1→4)]-3-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**40**)

Compound **39** (974 mg, 0.50 mmol) was dissolved in anhydrous DCM (10 mL) and cooled to -30 °C. Pyridine (400 µL, 4.95 mmol) and Tf_2O (333 µL, 1.98 mmol) were added and the mixture was allowed to warm up to r.t. over a period over 4 h. It was then quenched with MeOH, diluted with DCM and washed with brine. The organic layer was dried, concentrated and dissolved with DMF (10 mL). NaN_3 (200 mg, 3.1 mmol) was added and the mixture was heated at 50 °C overnight. After diluting with EtOAc and washing with brine, compound **40** was purified through column chromatography in a yield of 86% over 2 steps.

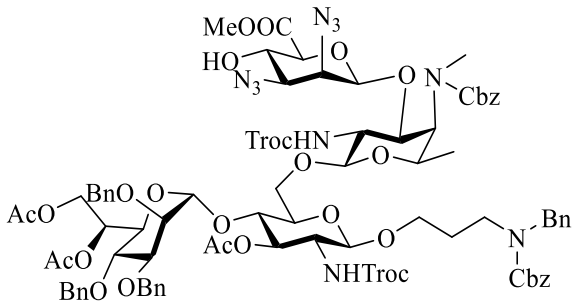
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.25 (d, 3H, J = 6.5 Hz), 1.68-1.77 (m, 2H), 1.82 (s, 3H), 2.04 (s, 3H), 2.11 (s, 3H), 2.98-3.08 (m, 1H), 3,19 (s, 3H), 3.24-3.48 (m 6H), 3.57-3.89 (m, 12H), 3.98-4.08 (m, 1H), 4.20 (d, 1H, J = 8.0 Hz), 4.27 (dd, 1H, J = 5.5, 10.5 Hz), 4.29-4.37 (m, 3H), 4.46 (d, 1H, J = 9.5 Hz), 4.51 (dd, 1H, J = 3.0, 6.0 Hz), 4.53-4.78 (m, 10H), 4.80-4.92 (m, 2H), 4.95 (d, 1H, J = 12.0 Hz), 5.00-5.07 (m, 1H), 5.08 (d, 1H, J = 12.5 Hz), 5.14-5.21 (m, 3H), 5.23 (d, 1H, J = 12.5 Hz), 5.44-5.52 (m, 1H), 5.55 (s, 1H), 5.64 (t, 1H, J = 6.5 Hz), 6.09 (d, 1H, J = 9.0 Hz), 7.17 (d, 2H, J = 7.5 Hz), 7.25-7.46 (m, 31H), 7.46-7.50 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 16.79, 16.84, 20.94, 20.99, 21.06, 21.08, 27.54, 29.8, 33.19, 43.36, 50.22, 53.86, 54.29, 56.13, 59.89, 60.51, 62.36, 63.58, 66.89, 67.11, 67.57, 67.62, 67.9, 68.46, 68.63, 69.98, 71.83, 72.0, 72.1, 73.68, 74.21, 74.34, 74.47, 74.92, 75.2, 75.35, 76.1, 76.57, 76.69, 77.36, 79.75, 95.81, 96.07, 98.45, 99.78, 100.97, 101.67, 102.28, 125.92, 125.98, 127.29, 127.58, 127.61, 127.67, 127.77, 127.97, 128.12, 128.39, 128.49, 128.53, 128.59, 128.63, 128.69, 128.76, 128.98, 129.19, 129.23, 136.51, 136.7, 136.77, 137.59, 138.01, 138.15, 138.18, 154.4, 154.81, 156.55, 156.84, 158.46, 170.43, 170.53, 170.88. Most peaks were split due to the secondary amides on the fucose and the linker.
HRMS: m/z calc. for $C_{92}H_{102}Cl_6FeN_{10}O_{27}$: 1022.2198; found: 1022.2167 $[M + Fe]^{2+}$



N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 2, 3-diazido-2, 3-dideoxy -*β*-D-mannopyranosyl-(1→3)-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranosyl-(1→6)-[6, 7-di-*O*-acetyl-2, 3, 4-tri-*O*-benzyl-L-glycero-*α*-D-mannoheptopyranosyl-(1→4)]-3-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**41**)

Compound **40** (850 mg, 0.43 mmol) was dissolved in DCM/TFA/water (15/1.5/0.5 mL) and stirred at r.t. for 30 min. The reaction was then washed with brine, dried and concentrated. Column chromatography gave compound **41** as white foam in a yield of 86%.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.24 (d, 3H, J = 6.5 Hz), 1.70-1.77 (m, 2H), 1.79-1.93 (m, 3H, Ac), 2.05 (s, 3H), 2.10 (s, 3H), 3.00-3.50 (m, 11H), 3.51-3.93 (m, 14H), 3.93-4.09 (m, 2H), 4.17-4.37 (m, 4H), 4.43-4.52 (m, 2H), 4.54-4.71 (m, 7H), 4.71-4.77 (m, 2H), 4.79-4.93 (m, 2H), 4.93-5.30 (m, 7H), 5.64 (t, 1H, J = 6.5 Hz), 6.01-6.27 (m, 2H), 7.13-7.22 (m, 2H), 7.24-7.47 (m, 28H). ^{13}CNMR (125 MHz, $CDCl_3$): δ = 16.78, 20.93, 21.0, 27.44, 33.26, 43.38, 50.17, 50.86, 54.14, 54.38, 56.05, 62.04, 62.23, 63.23, 63.69, 66.92, 67.55, 68.57, 70.02, 71.82, 72.06, 73.64, 74.32, 74.97, 75.34, 77.36, 79.71, 95.74, 95.92, 97.9, 99.61, 100.95, 102.12, 127.26, 127.56, 127.58, 127.73, 127.91, 128.09, 128.46, 128.5, 128.58, 128.65, 128.73, 136.5, 136.7, 137.53, 137.96, 138.12, 138.15, 154.63, 154.84, 156.58, 158.58, 170.41, 170.52, 171.17. Most peaks were split due to the secondary amides on the fucose and the linker.
HRMS: m/z calc. for $C_{85}H_{98}Cl_6FeN_{10}O_{27}$: 978.2041; found: 978.2010 $[M + Fe]^{2+}$

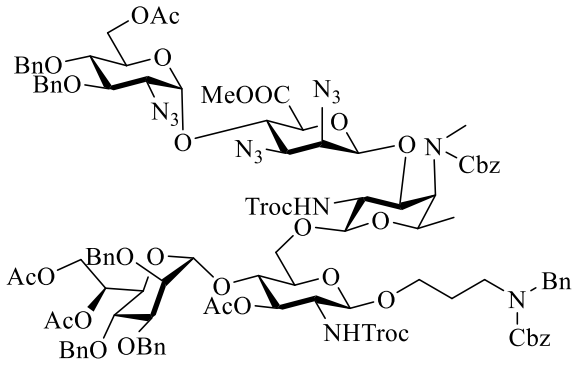


N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl methyl 2, 3-diazido-2, 3-dideoxy -*β*-D-mannopyranosyluronate-(1→3)-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranosyl-(1→6)-[6, 7-di-*O*-acetyl-2, 3, 4-tri-*O*-benzyl-L-glycero-*α*-D-mannoheptopyranosyl-(1→4)]-3-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**42**)

Compound **41** (700 mg, 0.37 mmol) was dissolved in DCM/t-BuOH/water (4/4/1 mL) followed by addition of BAIB (473 mg, 1.47 mmol) and TEMPO (23 mg, 0.15 mmol). The reaction was stirred at r.t. overnight. It was then diluted with DCM, washed with brine, dried and concentrated. The crude product was dissolved in DMF (10 mL) and treated with MeI (228 μL, 3.67 mmol) and K_2CO_3 (507 mg, 3.67 mmol). Upon completion by TLC, the mixture was diluted with EtOAc and washed with brine. The organic layer was dried, concentrated and purified through column chromatography to afford compound **42** in a yield of 66% over 2 steps.

^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.27 (d, 3H, J = 6.5 Hz), 1.62-1.78 (m, 2H), 1.71&1.91 (s, 3H, Ac), 2.04 (s, 3H), 2.12 (s, 3H), 2.93-3.04 (m, 1H), 3.10-3.17 (m, 1H), 3.20 (s, 3H), 3.23-3.27 (dd, 1H, J = 3.5, 9.5 Hz), 3.28-3.48 (m, 3H), 3.52-3.68 (m, 3H), 3.68-3.78 (m, 4H), 3.81 (s, 3H), 3.83-3.88 (m, 3H), 3.89-4.07 (m, 3H), 4.07-4.19 (m, 2H), 4.21-4.42 (m, 4H), 4.42-4.58 (m, 6H), 4.60-4.80 (m, 6H), 4.86 (d, 1H, J = 10.0 Hz), 4.92-5.02 (m, 1H), 5.05 (d, 1H, J = 12.0 Hz), 5.17 (d, 1H, J = 7.0 Hz), 5.22 (d, 1H, J = 12.0 Hz), 5.24-5.30 (m, 1H), 5.59-5.75 (m, 2H), 6.16 (d, 1H, J = 7.5 Hz), 7.10-7.20 (m, 2H), 7.22-7.51 (m, 28H), . ^{13}CNMR (125 MHz, $CDCl_3$): δ = 16.84, 20.76, 20.99, 21.11, 27.59, 29.81, 33.25, 43.29, 50.24, 53.41, 54.1, 56.14, 60.98, 62.1, 63.31, 66.99, 67.13, 67.61, 67.64, 68.67, 69.90, 71.49, 71.7, 72.11, 73.63, 74.22, 75.13, 75.38, 76.11, 77.36, 79.80, 95.92, 96.27, 98.32, 99.59, 101.17, 103.82, 127.25, 127.61, 127.63, 127.71, 127.91, 128.02, 128.05, 128.15, 128.48, 128.50, 128.57, 128.63, 128.68, 128.78, 136.74, 137.57, 138.06, 138.21, 138.26, 154.75, 154.95, 156.58, 158.67, 169.83, 170.32, 170.58, 170.70. Most peaks were split due to the tertiary amides on the fucose and the linker.

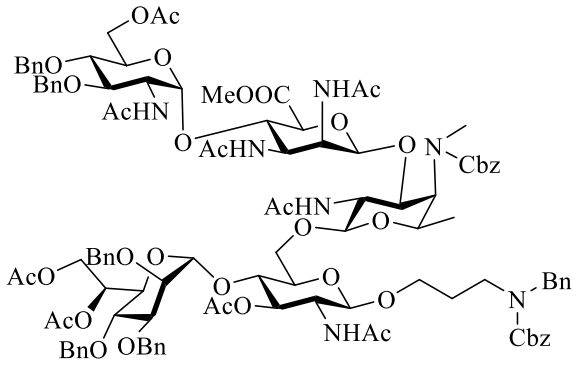
HRMS: m/z calc. for $C_{86}H_{98}Cl_6FeN_{10}O_{28}$: 992.2016; found: 992.1984 $[M + Fe]^{2+}$



N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 6-*O*-acetyl-2-azido-3, 4-Di-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-(1→4)-methyl 2, 3-diazido-2, 3-dideoxy -*β*-D-mannopyranosyluronate-(1→3)-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-L-fucopyranosyl-(1→6)-[6, 7-di-*O*-acetyl-2, 3, 4-tri-*O*-benzyl-L-glycero-*α*-D-mannoheptopyranosyl-(1→4)]-3-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-*β*-D-glucopyranoside (**43**)

A solution of compound **6** (258 mg, 0.48 mmol), **42** (467 mg, 0.24 mmol) and freshly activated 4 Å molecular sieves (400 mg) in DCM (5 mL) was stirred at r.t. for 20 min and then cooled to -78 °C. To the above solution was added AgOTf (310 mg, 1.21 mmol) in Et_2O/DCM (6/1 mL). The mixture was stirred for 10 min and *p*-TolSCl (64 μL, 0.48 mmol) was added directly into it via microsyringe. The reaction was allowed to warm up to r.t. over a period of 3 h before quenched with Et_3N. The mixture was then filtered through celite and concentrated. Column chromatography (Hexanes/DCM/EtOAc = 2/2/3) gave compound **43** in a yield of 63%.

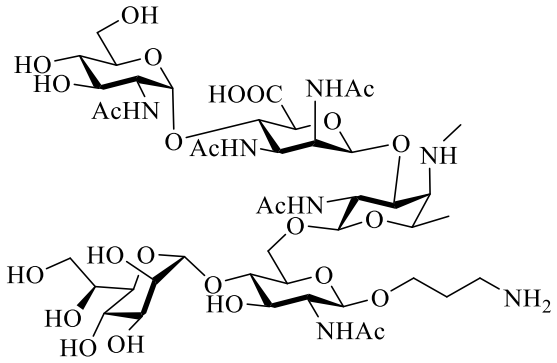
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.26 (d, 3H, J = 6.5 Hz), 1.69-1.77 (m, 2H), 1.82 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.11 (s, 3H), 2.98-3.08 (m, 1H), 3.22 (s, 3H), 3.26-3.44 (m, 4 H), 3.44-3.50 (m, 1H), 3.53-3.62 (m, 2H), 3.63-3.93 (m, 15H), 3.95-4.10 (m, 3H), 4.18-4.25 (m, 2H), 4.25-4.38 (m, 4H), 4.40-4.52 (m, 3H), 4.52-4.65 (m, 5H), 4.65-4.81 (m, 7H), 4.82-4.89 (m, 3H), 4.90-4.94 (m, 1H), 4.99-5.06 (m, 1H), 5.09 (d, 1H, J = 13.0 Hz), 5.14-5.23 (m, 3H), 5.26 (d, 1H, J = 12.5 Hz), 5.36-5.52 (m, 2H), 5.60-5.68 (m, 1H), 6.06-6.16 (m, 1H), 7.15-7.22 (m, 2H), 7.26-7.48 (m, 38H).
^{13}CNMR (125 MHz, $CDCl_3$): δ = 16.75, 20.86, 20.95, 20.99, 27.47, 29.71, 33.2, 43.27, 50.16, 53.03, 53.65, 54.04, 56.14, 61.41, 62.06, 62.71, 63.32, 63.82, 66.85, 67.09, 67.42, 67.47, 68.57, 69.89, 70.26, 71.67, 71.81, 72.0, 73.59, 74.04, 74.22, 74.28, 74.39, 74.77, 75.08, 75.16, 75.22, 75.65, 75.68, 75.76, 75.93, 76.05, 77.19, 77.3, 79.63, 80.19, 80.23, 95.75, 95.98, 97.67, 98.89, 99.59, 100.91, 102.18, 127.22, 127.47, 127.53, 127.63, 127.68, 127.82, 127.9, 127.98, 128.05, 128.08, 128.19, 128.4, 128.43, 128.5, 128.52, 128.56, 128.62, 128.66, 129.17, 136.73, 136.76, 137.48, 137.56, 137.97, 138.07, 138.13, 154.35, 154.65, 156.46, 156.68, 158.33, 167.28, 170.3, 170.44, 170.58, 170.74. Most peaks were split due to the secondary amides on the fucose and the linker.
HRMS: m/z calc. for $C_{108}H_{129}Cl_6N_{15}O_{33}$: 1186.8504; found: 1186.8445 $[M + 2NH_4]^{2+}$



N-(Benzyl)-benzyloxycarbonyl-3-aminopropyl 2-acetamido-6-*O*-acetyl-3, 4-Di-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-(1→4)-methyl 2, 3-diacetamido-2, 3-dideoxy -*β*-D-mannopyranosyluronate-(1→3)-2-acetamido-4-[*N*-(methyl)-benzyloxycarbonylamino]-2,4-dideoxy-*β*-L-fucopyranosyl-(1→6)-[6, 7-di-*O*-acetyl-2, 3, 4-Tri-*O*-benzyl-L-glycero-*α*-D-mannoheptopyranosyl-(1→4)]-2-acetamido-3-*O*-acetyl-2-deoxy-*β*-D-glucopyranoside (**44**)

Compound **43** (357 mg, 0.15 mmol) was dissolved in THF (10 mL) followed by addition of Ac_2O (1.73 mL, 18.3 mmol), AcOH (1.04 mL, 18.3 mmol) and Zn (1.48 g, 22.9 mmol). The reaction was stirred at r.t. overnight before it was quenched with MeOH and filtered through celite to remove the insoluble impurities. The filtrate was concentrated, diluted with EtOAc and washed with saturated $NaHCO_3$ solution. The organic layer was dried, concentrated and purified through column chromatography (DCM/MeOH = 10/1) to give compound **44** in a yield of 65%.

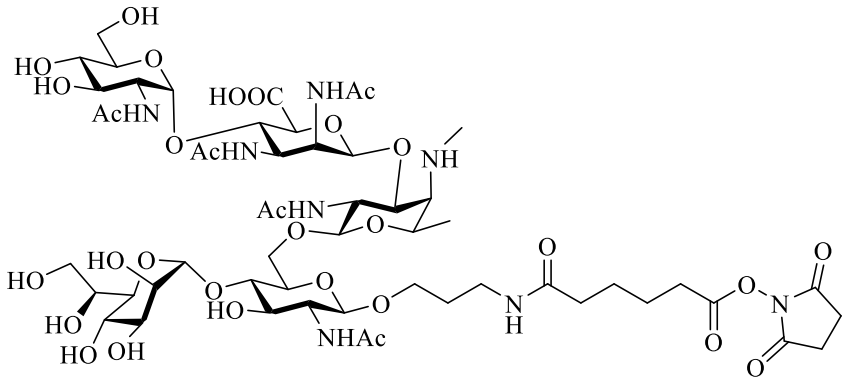
^{1}HNMR (500 MHz, $CDCl_3$): δ = 1.08&1.16 (d, 2H, J = 6.5 Hz, Fuc-6-Me), 1.64-1.72 (m, 2H), 1.81 (s, 3H), 1.89 (s, 3H), 1.98-2.01 (m, 6H), 2.03 (s, 9H), 2.04 (s, 3H), 2.08 (s, 3H), 2.90-2.98 (m, 1H), 3.03-3.10 (m, 1H), 3.15 + 3.18 (s, 3H, Fuc-4-N-Me), 3.19-3.33 (m, 3H), 3.60-3.73 (m, 6H), 3.76-3.92 (m, 8H), 4.01-4.12 (m, 2H), 4.20-4.35 (m, 6H), 4.38 (dd, 1H, J = 5.5, 12.0 Hz), 4.40-4.47 (m, 3H), 4.47-4.60 (m, 5H), 4.60-4.65 (m, 1H), 4.65-4.74 (m, 4H), 4.75-4.80 (m, 1H), 4.80-4.88 (m, 4H), 4.94 (d, 1H, J = 12.0 Hz), 4.97 (dd, 1H, J = 3.5, 7.0 Hz), 5.01 (d, 1H, J = 3.5 Hz), 5.04 (d, 1H, J = 3.5 Hz), 5.10-5.22 (m, 4H), 5.29 (d, 1H, J = 12.5 Hz), 5.57-5.63 (m, 1H), 6.42 (d, 1H, J = 9.5 Hz), 6.85 (m, 2H), 7.13-7.21 (m, 2H), 7.21-7.42 (m, 38H) . ^{13}CNMR (125 MHz, $CDCl_3$): δ = 16.36, 16.43, 20.81, 20.88, 20.91, 20.94, 20.97, 22.73, 22.8, 22.86, 22.92, 23.0, 23.06, 23.17, 24.03, 24.06, 26.97, 33.0, 33.42, 42.66, 49.74, 52.49, 52.71, 52.8, 53.81, 54.1, 62.14, 62.42, 62.66, 63.4, 63.67, 64.35, 66.37, 67.43, 67.62, 68.09, 68.29, 68.68, 69.98, 70.17, 71.67, 71.9, 71.97, 72.16, 73.54, 73.73, 74.24, 74.42, 75.1, 75.3, 75.33, 75.38, 75.49, 75.98, 76.35, 77.36, 79.72, 80.49, 99.55, 99.76, 99.85, 100.8, 102.39, 103.05, 127.3, 127.47, 127.51, 127.54, 127.57, 127.61, 127.65, 127.69, 127.71, 127.74, 127.78, 127.8, 127.85, 127.88, 127.92, 127.98, 128.01, 128.09, 128.15, 128.26, 128.37, 128.41, 128.46, 128.48, 128.5, 128.57, 128.62, 128.72, 136.0, 136.08, 136.7, 137.28, 137.67, 137.72, 137.91, 138.04, 138.1, 138.18, 138.28, 156.59, 158.27, 170.45, 170.59, 170.69, 170.79, 170.8, 170.82, 170.84, 171.02, 171.22, 171.44, 171.53, 171.61, 171.67, 172.0, 172.24, 175.36. Five C1-H1 coupling constants (174.5, 171.0, 163.0, 164.0, 160.5 Hz) confirmed the stereochemistry. Most peaks were split due to the secondary amides on the fucose and the linker.
HRMS: m/z calc. for $C_{112}H_{137}N_7O_{34}$: 1061.9603; found: 1061.9554 $[M + 2H]^{2+}$



3-Aminopropyl 2-acetamido-2-deoxy-α-D-glucopyranosyl-(1→4)-2, 3-diacetamido-2, 3-dideoxy -β-D-mannopyranosyluronate-(1→3)-2-acetamido-2,4-dideoxy-4-methylamino-β-L-fucopyranosyl-(1→6)-[L-glycero-α-D-mannoheptopyranosyl-(1→4)]-2-acetamido-2-deoxy-β-D-glucopyranoside (**1**)

Compound **44** (210 mg, 0.099 mmol) was dissolved in THF/water (20/5 mL) followed by addition of 1M LiOH solution (2.5 mL) at 0 ℃. The reaction was allowed to warm up to r.t. and stirred overnight. H^+ resin was added to neutralize the solution and filtered off through sintered glass funnel. The filtrate was concentrated and purified through column chromatography (DCM/MeOH = 4/1). To a solution of the product in THF/water/AcOH (2/2/2 mL) was added $Pd(OH)_2/C$ (100 mg) and it was stirred at r.t. overnight under H_2 atmosphere. $Pd(OH)_2/C$ was filtered off and the filtrate was concentrated and purified through a G10 column followed by Na^+ ion exchange column. The final aqueous solution was lyophilized to afford compound **1** in a yield of 68%.

^{1}HNMR (500 MHz, D_2O): δ = 1.25 (d, 3H, J = 6.5 Hz), 1.74 (s, 3H), 1.75 (s, 3H), 1.76-1.80 (m, 2H), 1.83 (s, 3H), 1.88 (s, 3H), 1.89 (s, 3H), 1.92 (s, 3H), 2.61 (s, 3H), 2.90 (t, 2H, J = 7.5 Hz), 3.32 (t, 1H, J = 10.0 Hz), 3.36-3.43 (m, 4H), 3.45-3.60 (m, 8H), 3.60-3.69 (m, 5H), 3.69-3.75 (m, 2H), 3.76-3.92 (m, 6H), 4.06 (dd, 1H, J = 4.0, 11.0 Hz), 4.11 (dd, 1H, J = 4.0, 10.5 Hz), 4.18 (d, 1H, J = 4.0 Hz), 4.26 (m, 1H), 4.43 (d, 1H, J = 8.0 Hz), 4.82 (s, 1H), 4.95 (d, 1H, J = 4.0 Hz), 5.11 (s, 1H). ^{13}CNMR (125 MHz, D_2O): δ = 15.98, 21.65, 21.73, 21.81, 21.97, 22.42, 23.19, 26.57, 36.21, 37.3, 50.89, 51.47, 53.22, 53.37, 55.66, 59.67, 60.97, 63.05, 65.75, 67.67, 68.29, 68.46, 68.89, 69.28, 70.06, 70.19, 70.24, 71.57, 72.48, 73.48, 73.78, 75.15, 75.75, 78.71, 96.5, 96.66, 101.07, 101.1, 101.88, 173.62, 173.93, 174.17, 174.63, 174.81, 175.07, 181.34. HRMS: m/z calc. for $C_{45}H_{79}N_7O_{26}$: 566.7537; found: 566.7537 $[M + 2H]^{2+}$



N-(5-(succinimidyloxycarbonyl)pentanoyl)-3-aminopropyl 2-acetamido-2-deoxy-α-D-glucopyranosyl-(1→4)-2, 3-diacetamido-2, 3-dideoxy -β-D-mannopyranosyluronate-(1→3)-2-acetamido-2,4-dideoxy-4-methylamino-β-L-fucopyranosyl-(1→6)-[L-glycero-α-D-mannoheptopyranosyl-(1→4)]-2-acetamido-2-deoxy-β-D-glucopyranoside (**46**)

Compound **1** (15 mg, 0.01324 mmol) together with compound **45** (22.5 mg, 0.066 mmol) was dissolved in dry DMF (2.5 mL) followed by addition of DIPEA (2 µL). The reaction was stirred at r.t. for 3 h and then DMF was removed by vacuum. The residue was washed with DCM and **46** was used for Qβ coupling without further purification.

^{1}HNMR (500 MHz, CD_3OD): δ = 1.35 (d, 3H, J = 6.5 Hz), 1.63-1.79 (m, 5H), 1.89 (s, 3H), 1.97 (s, 3H), 1.98 (s, 3H), 2.03 (s, 3H), 2.09 (s, 3H), 2.20-2.29 (m, 2H), 2.50-2.72 (m, 6H), 2.84 (s, 3H), 3.02-3.22 (m, 3H), 3.35 (s, 4H), 3.45-4.10 (m, 24H), 4.27 (dd, 1H, J = 4.0, 9.5 Hz), 4.32-4.38 (m, 2H), 4.40 (d, 1H, J = 8.0 Hz), 5.11 (d, 1H, J = 3.5 Hz), 5.41 (s, 1H). MS: m/z calc. for $C_{55}H_{89}N_8O_{31}$: 1357.56; found: 1357.56 $[M + H]^+$

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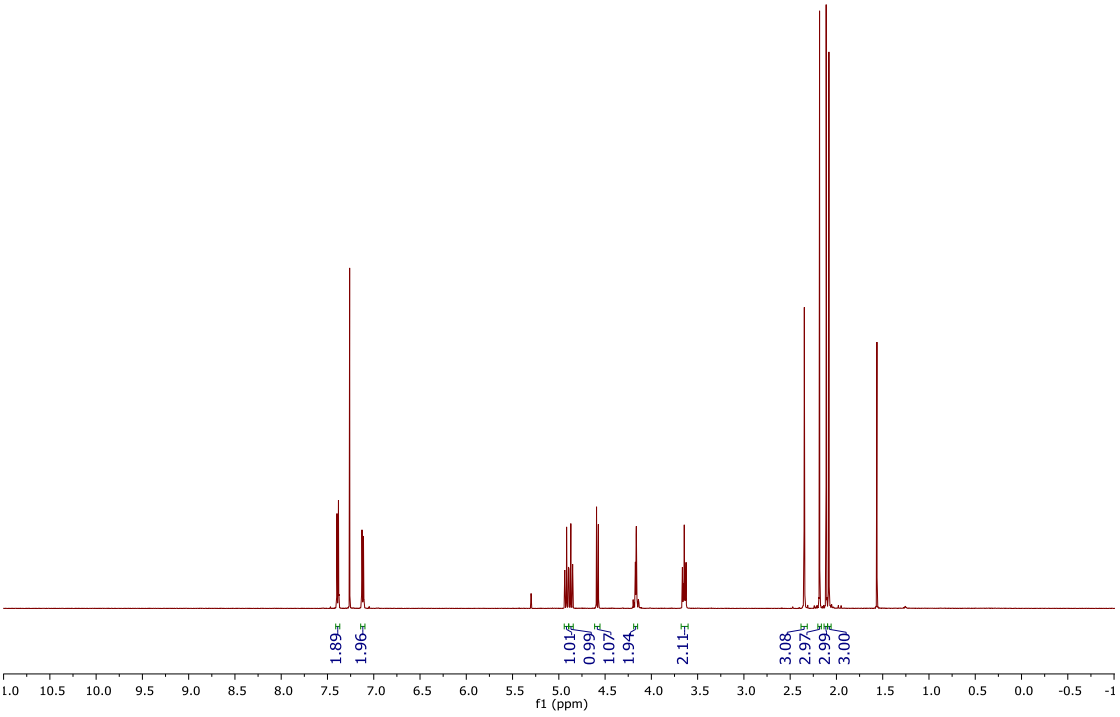
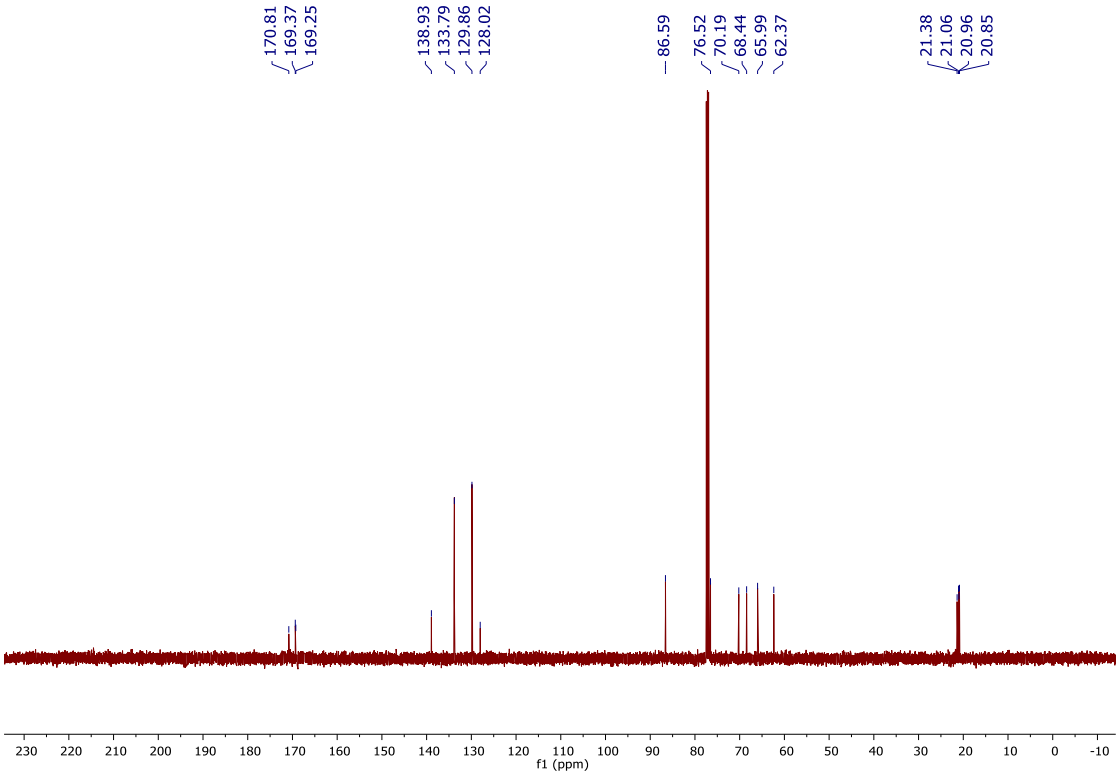
Product Characterization Spectra

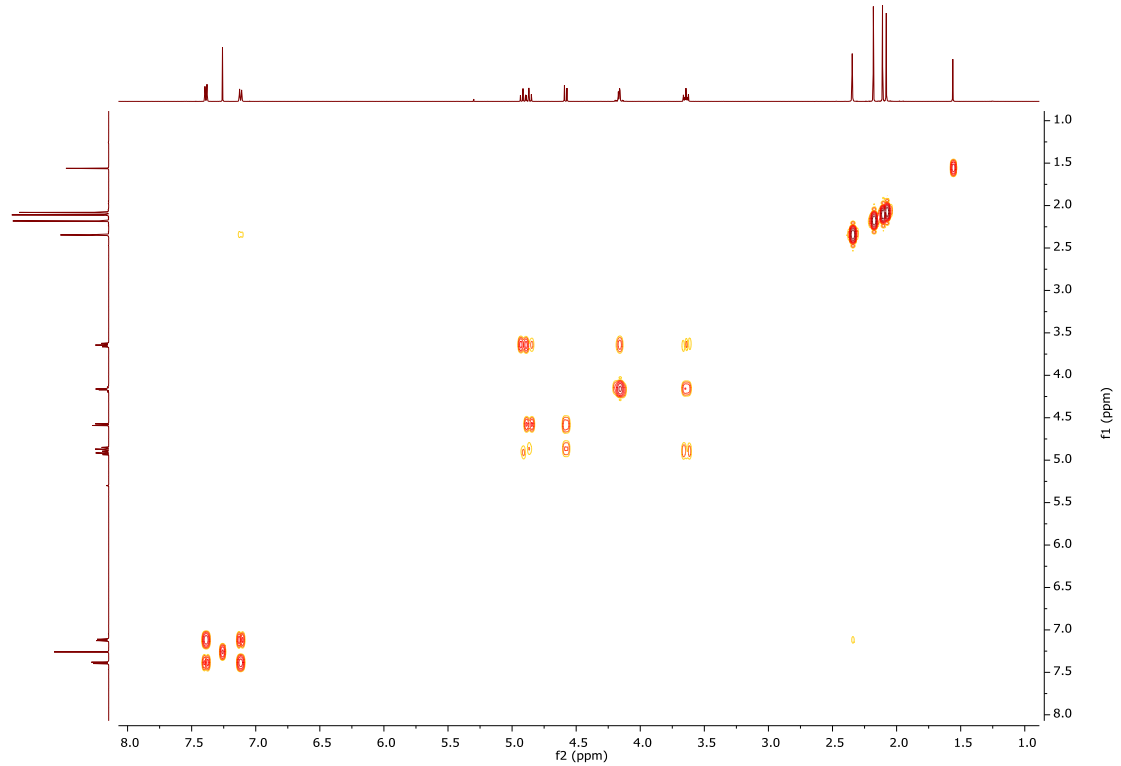
^{1}H-NMR of **8** (500 MHz $CDCl_3$)



^{13}C-NMR of **8** (125 MHz $CDCl_3$)



^{1}H-^{1}H gCOSY of **8** (500 MHz $CDCl_3$)



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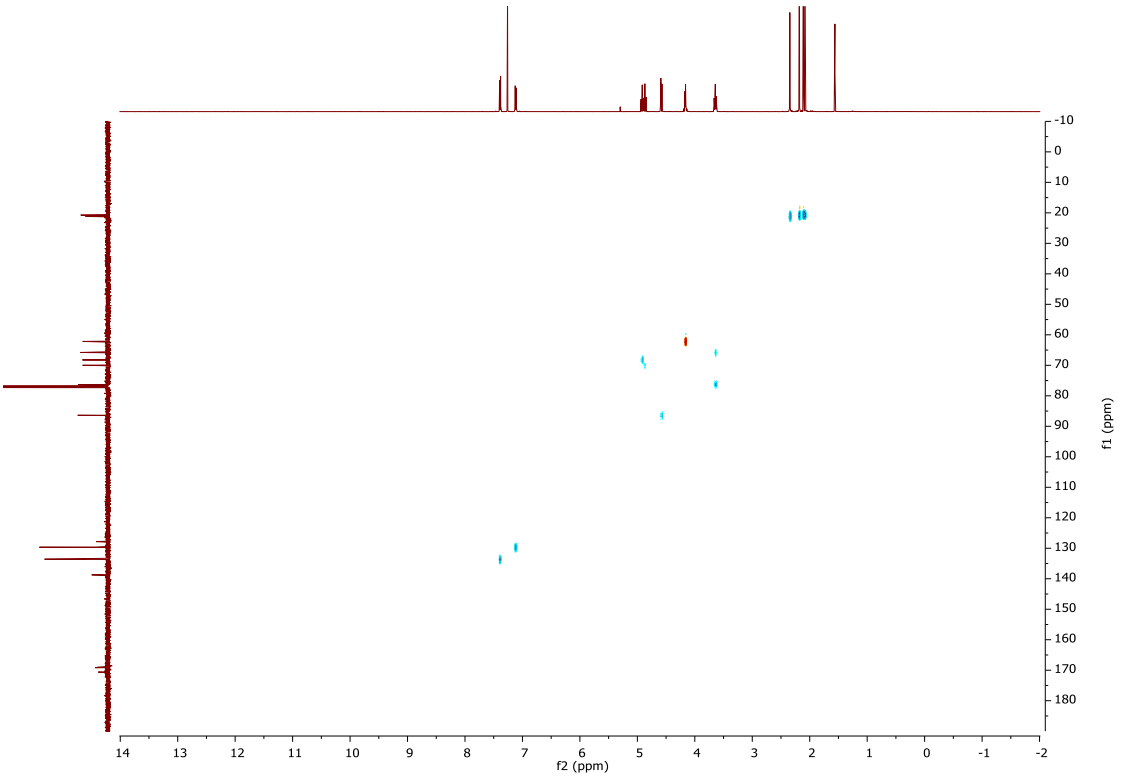
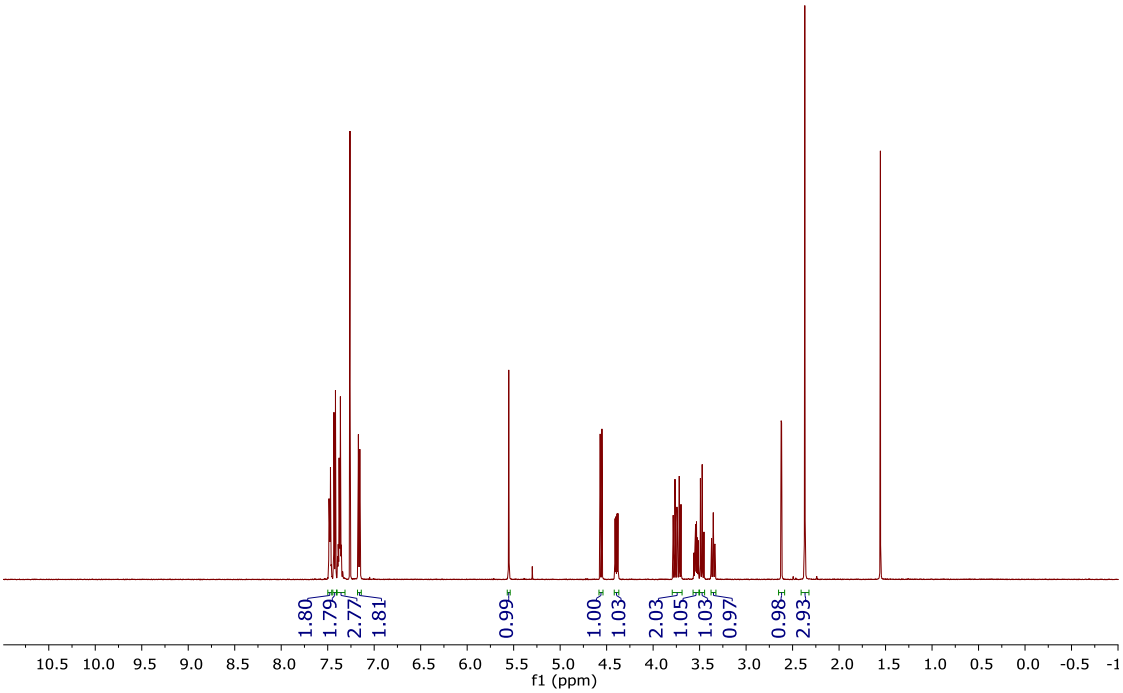
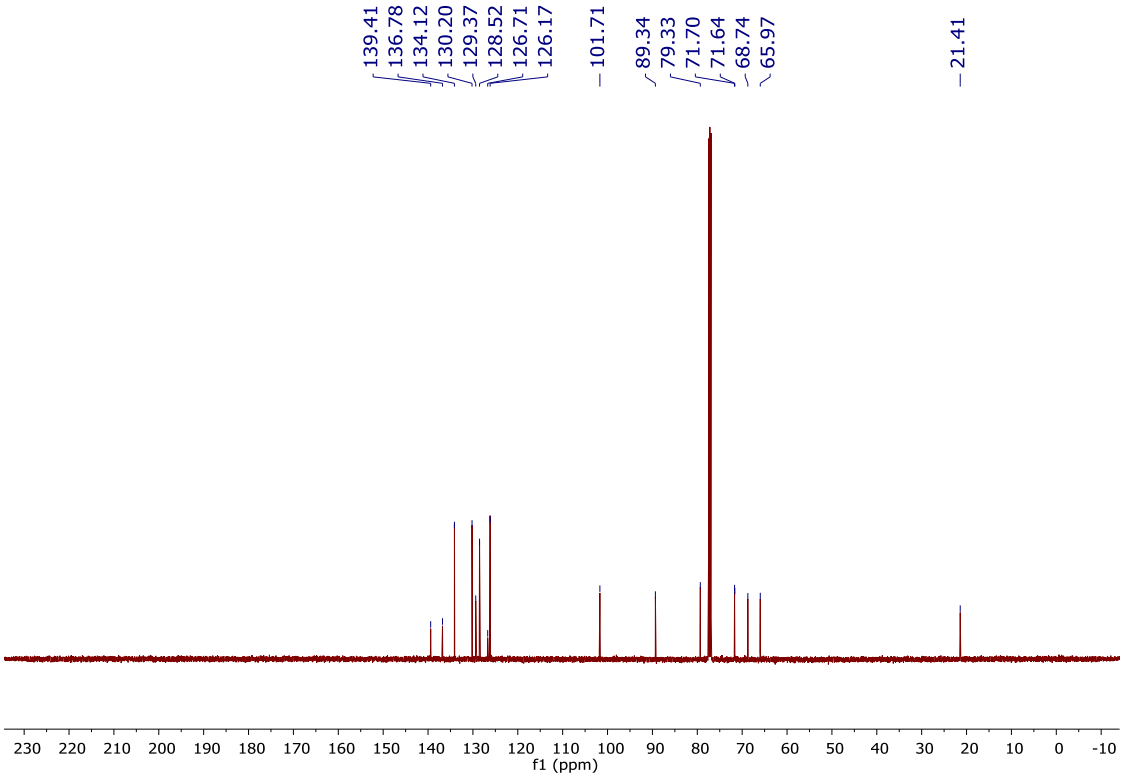


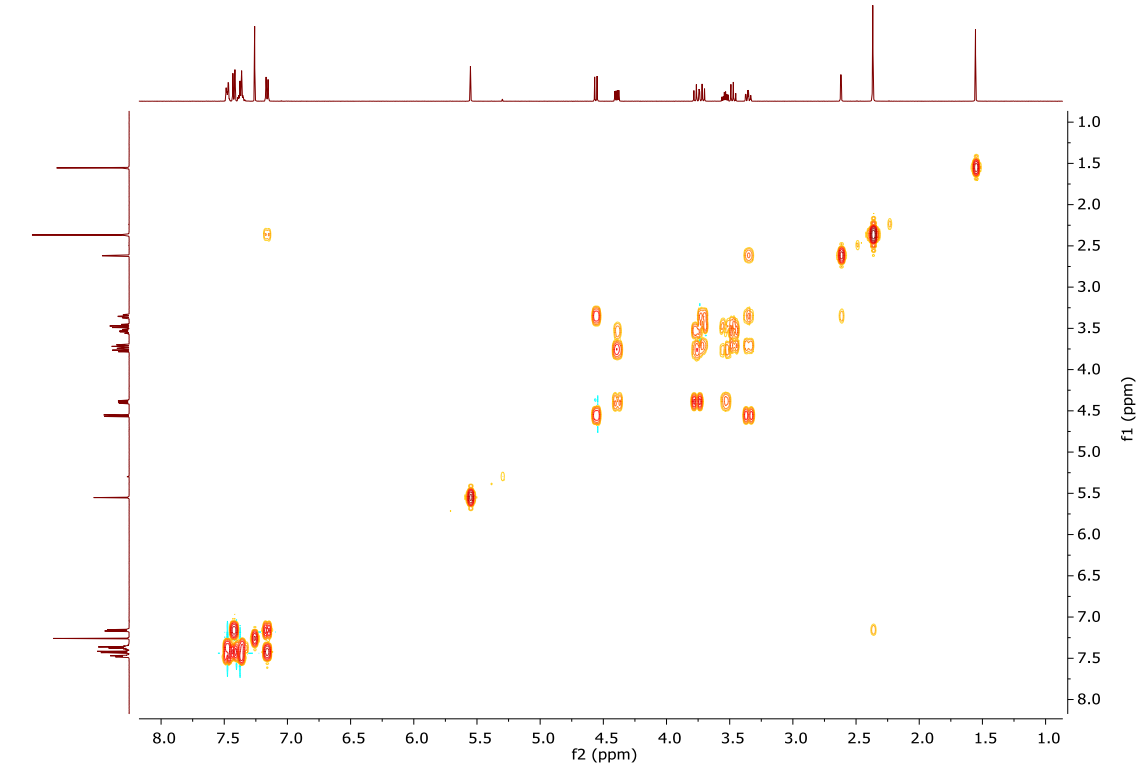
^{1}H-NMR of **9** (500 MHz $CDCl_3$)



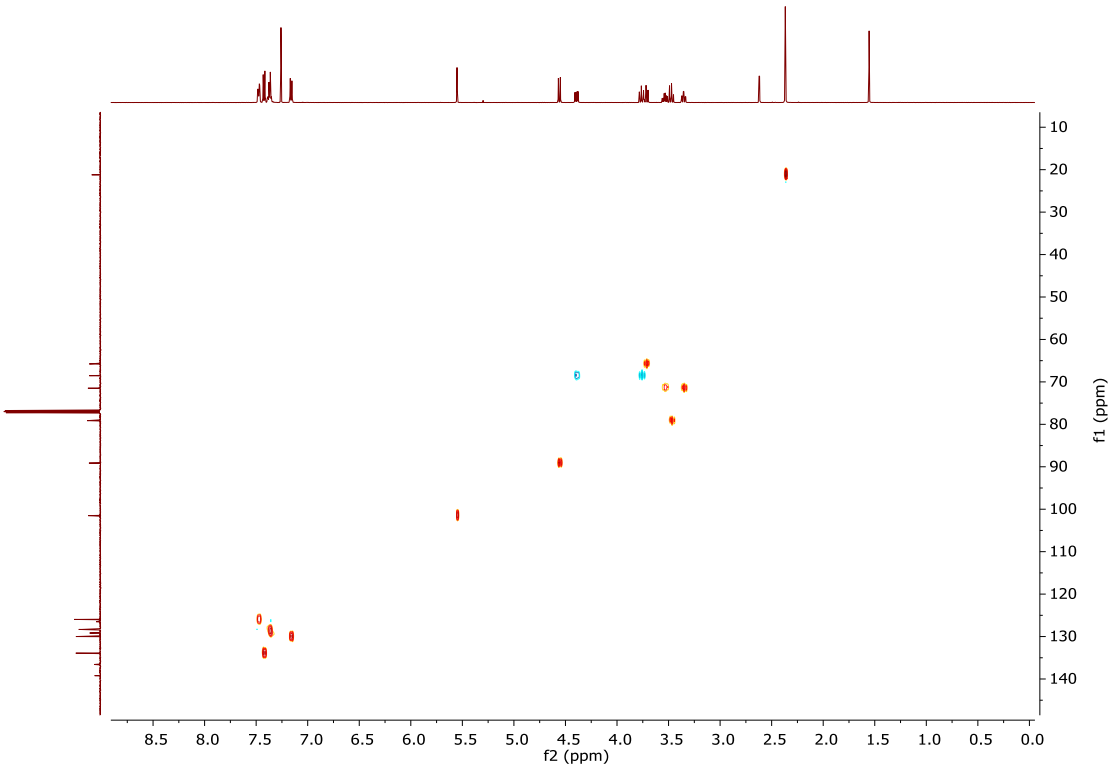
^{13}C-NMR of **9** (125 MHz $CDCl_3$)



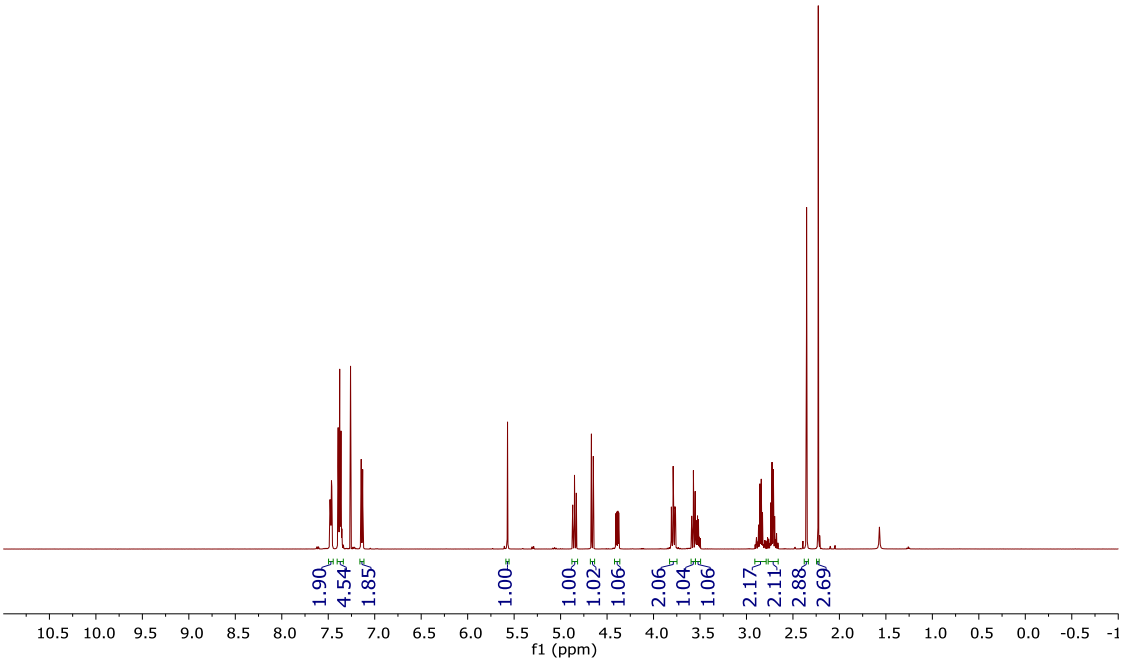
^{1}H-^{1}H gCOSY of **9** (500 MHz $CDCl_3$)



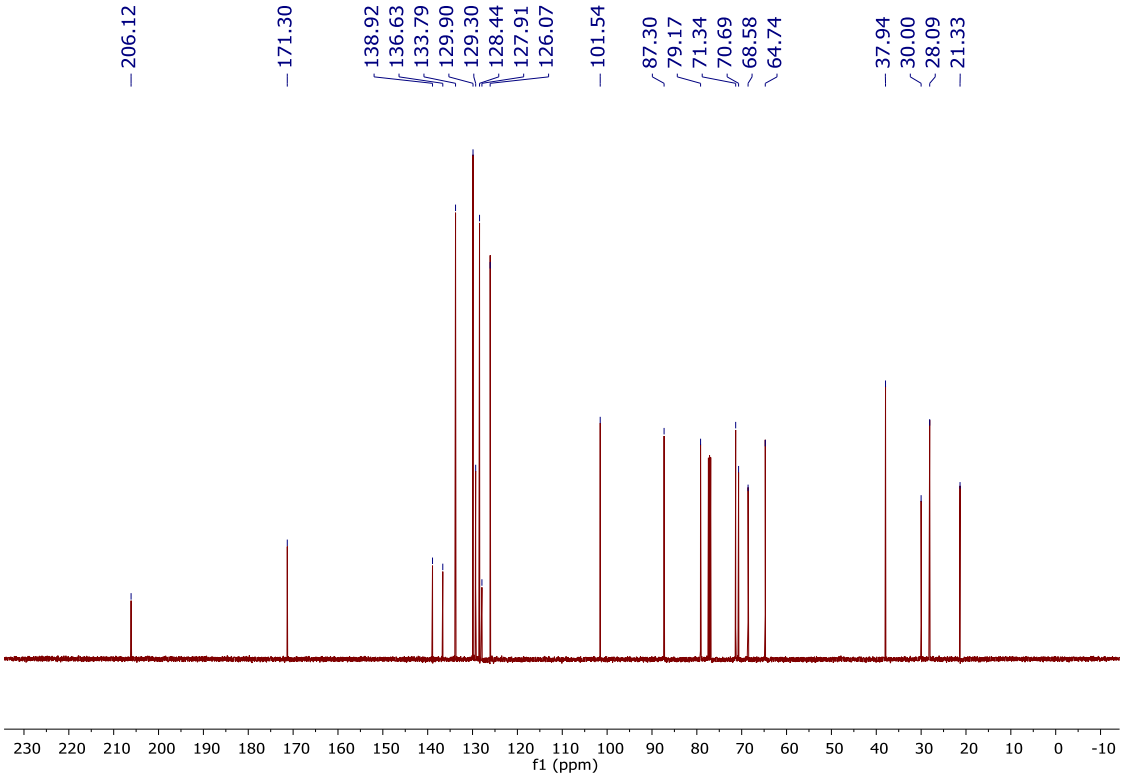
^{1}H-^{13}C gHSQCAD of **9** (500 MHz $CDCl_3$)



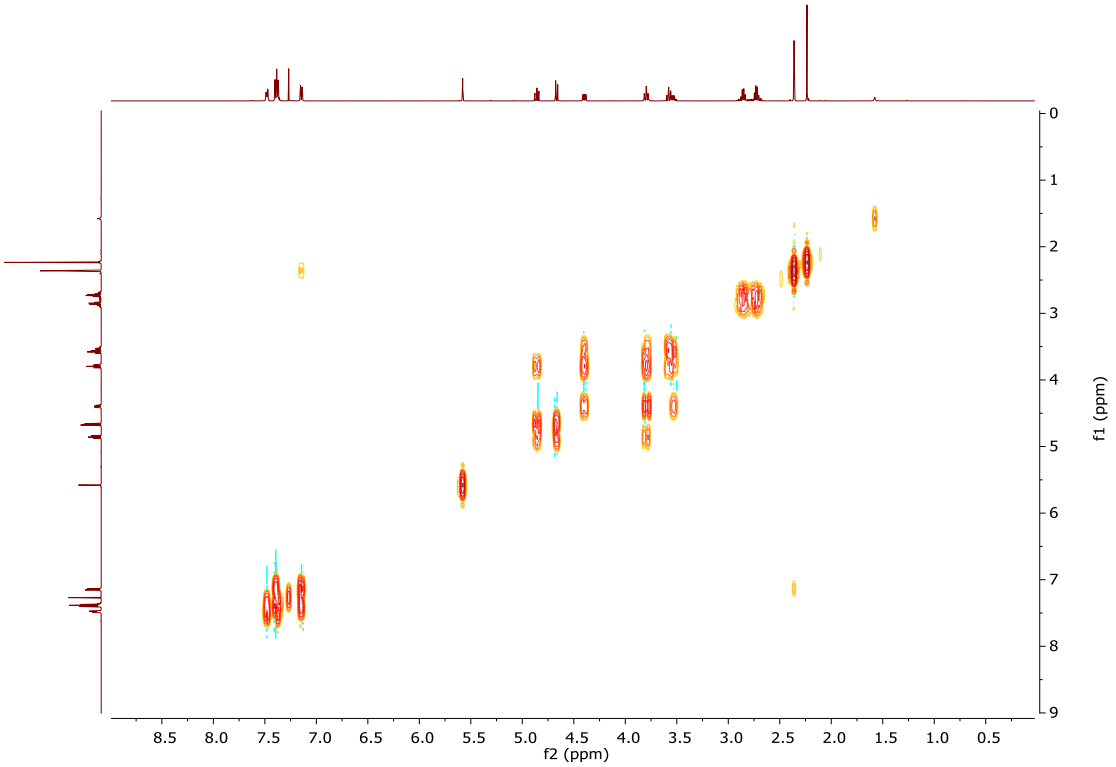
^{1}H-NMR of **5** (500 MHz $CDCl_3$)



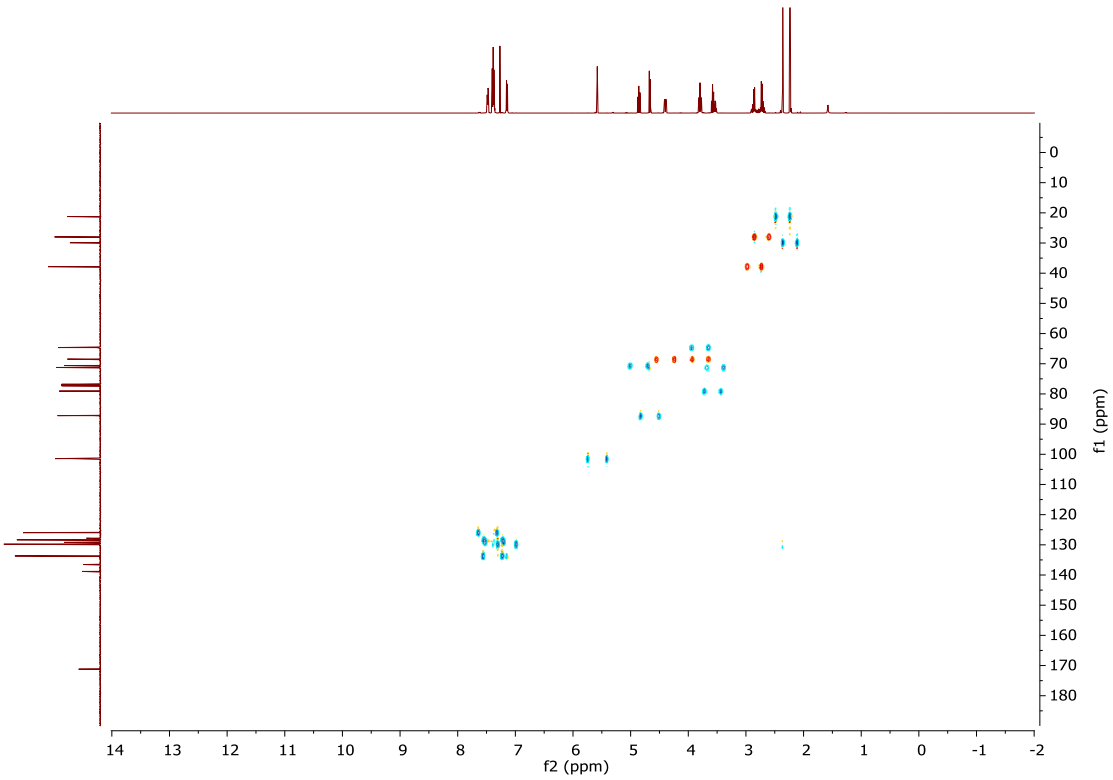
^{13}C-NMR of **5** (125 MHz $CDCl_3$)



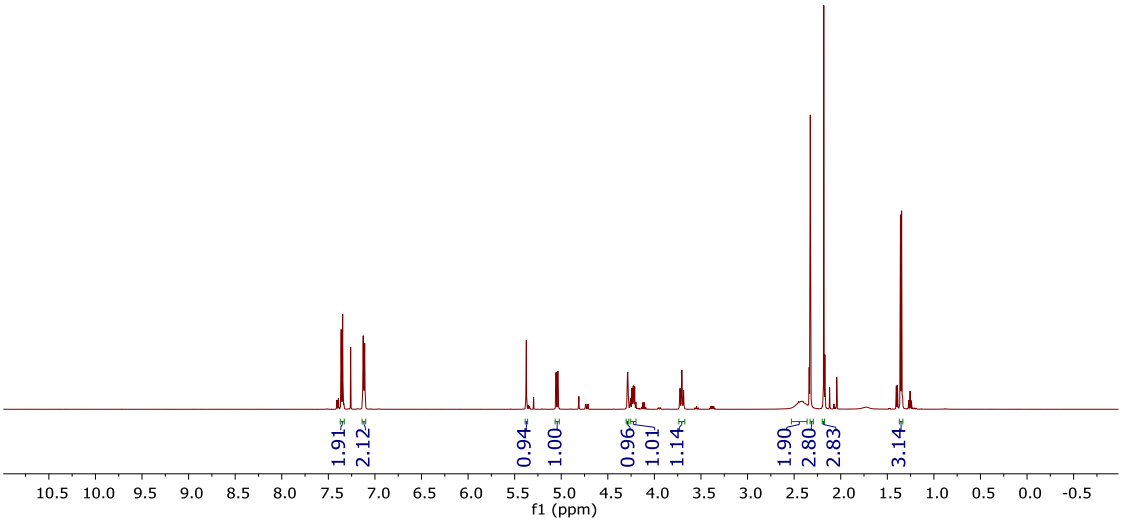
^{1}H-^{1}H gCOSY of **5** (500 MHz $CDCl_3$)



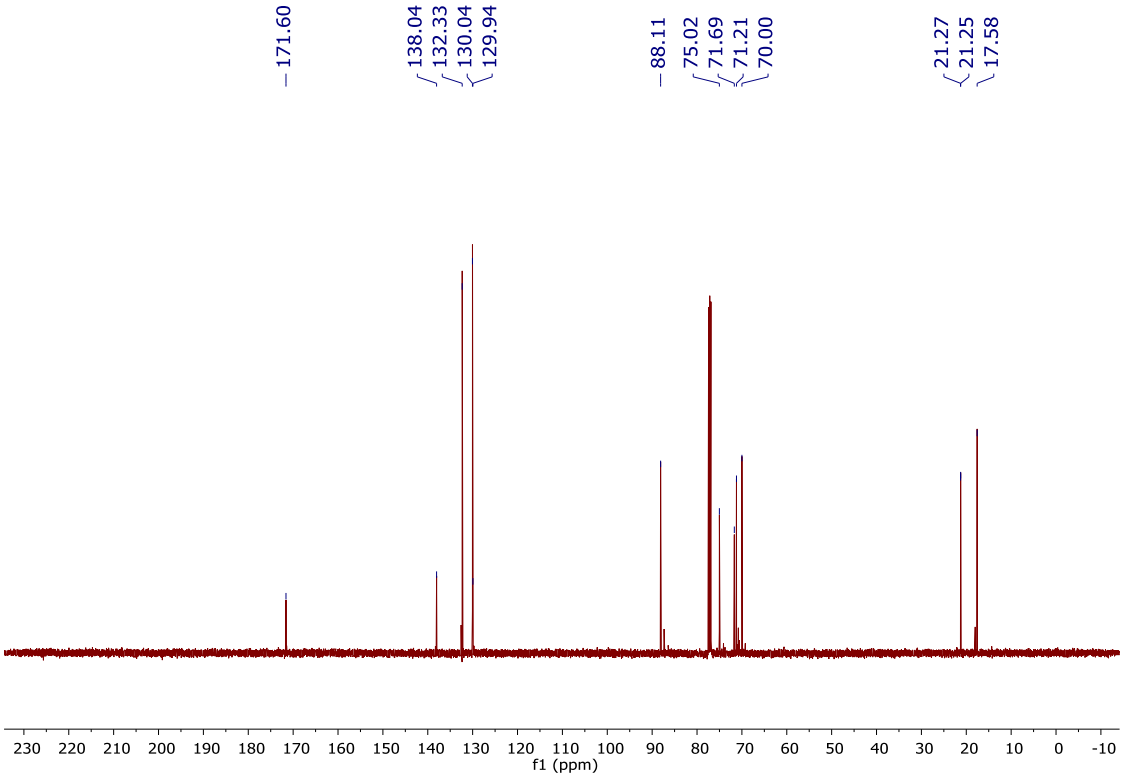
^{1}H-^{13}C gHSQCAD of **5** (500 MHz $CDCl_3$)



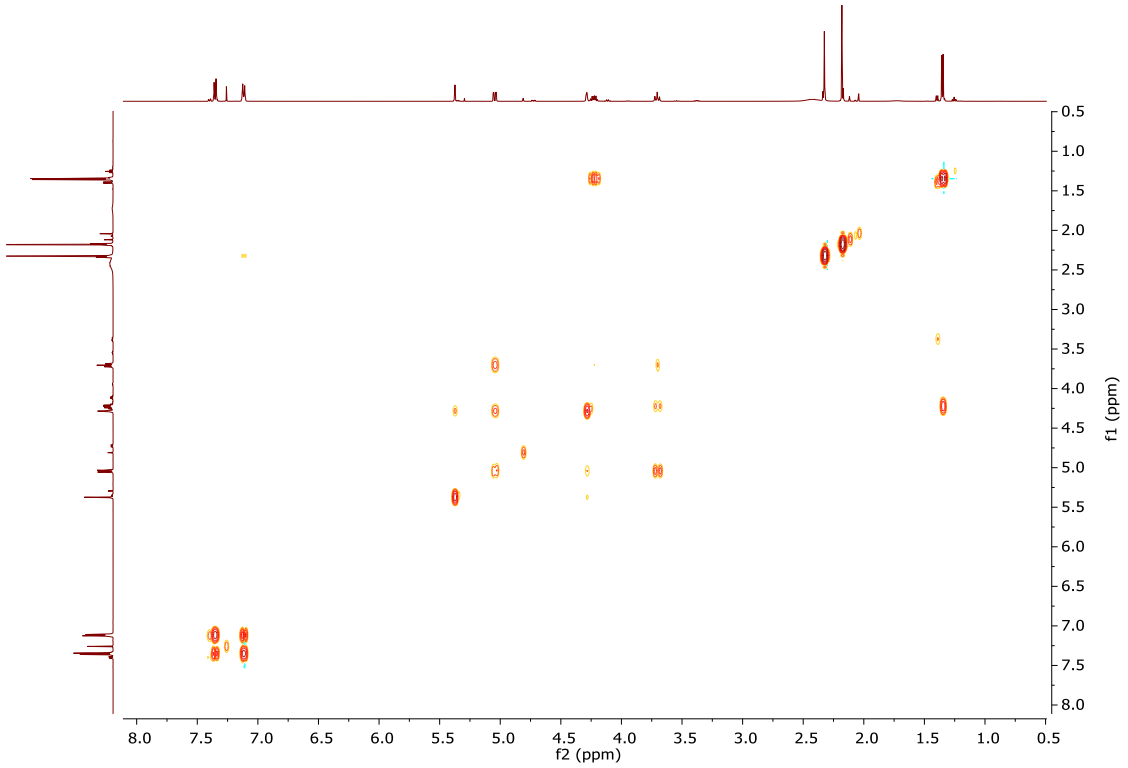
^{1}H-NMR of **10** (500 MHz $CDCl_3$)



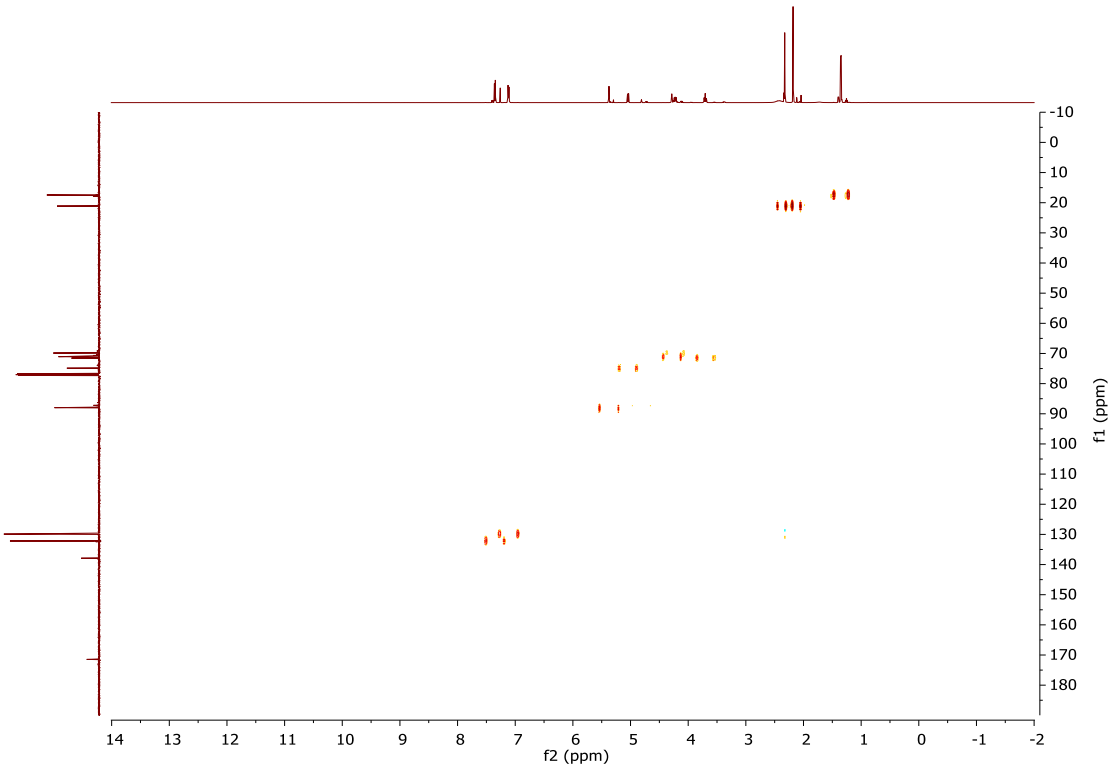
^{13}C-NMR of **10** (125 MHz $CDCl_3$)



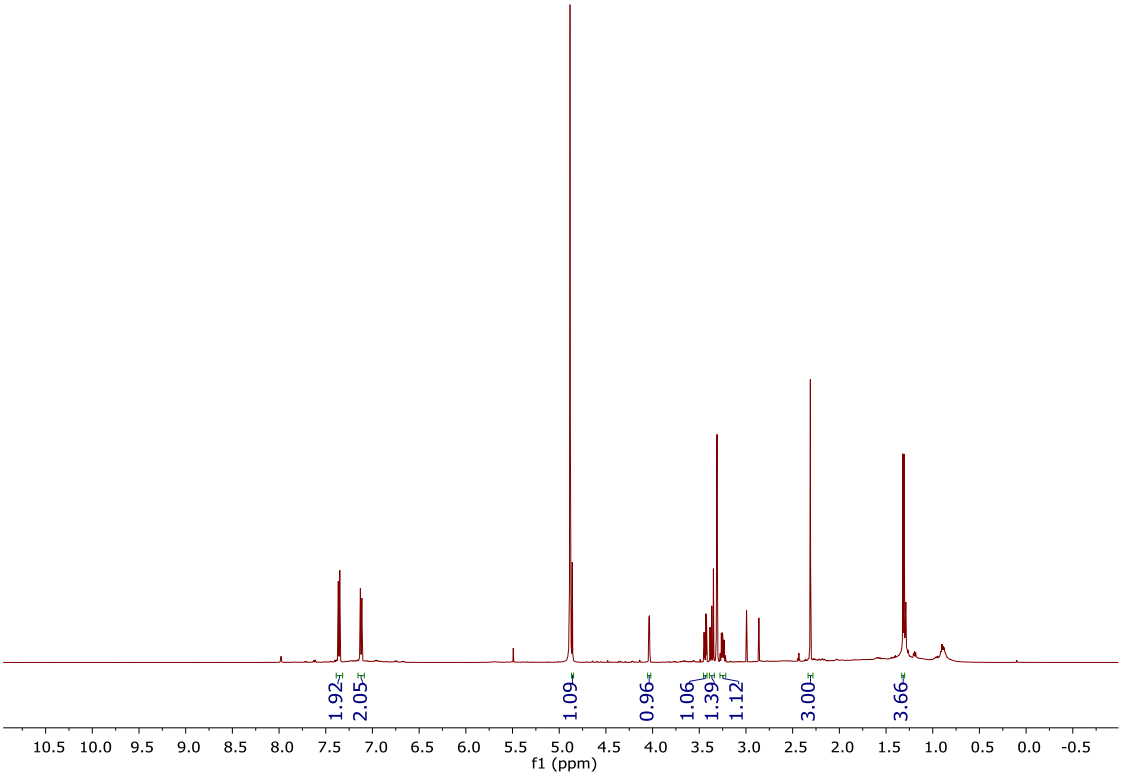
^{1}H-^{1}H gCOSY of **10** (500 MHz $CDCl_3$)



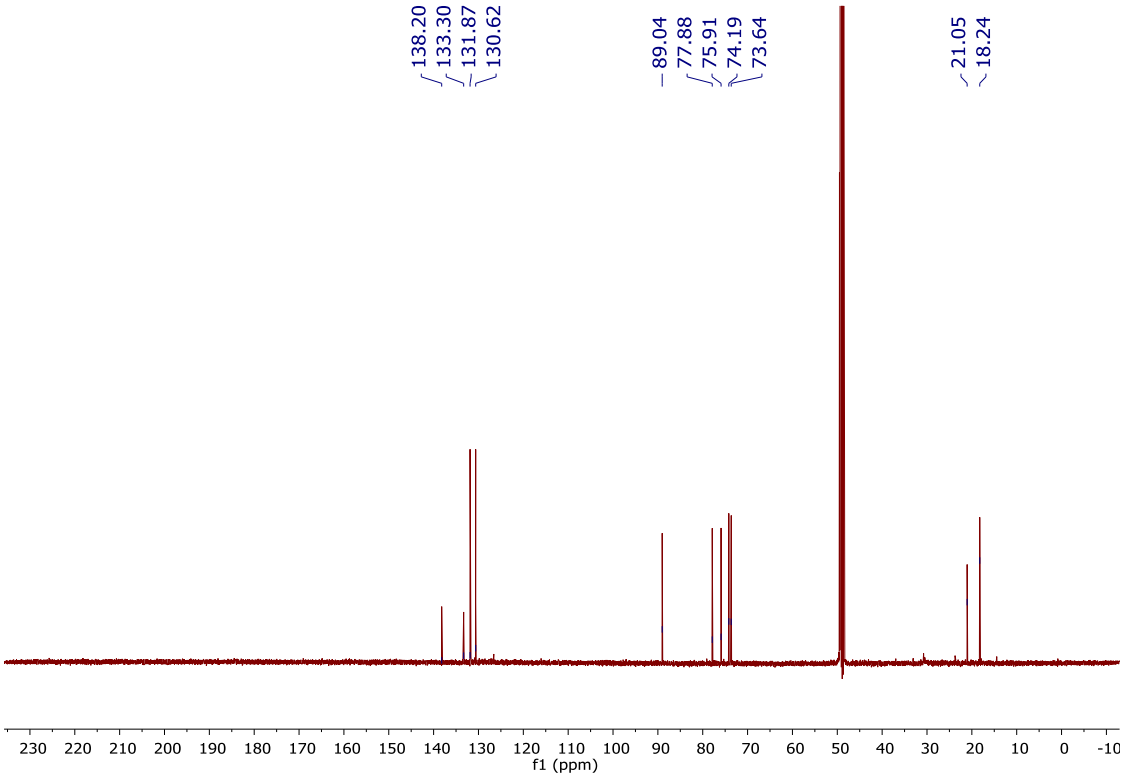
^{1}H-^{13}C gHSQCAD of **10** (500 MHz $CDCl_3$)



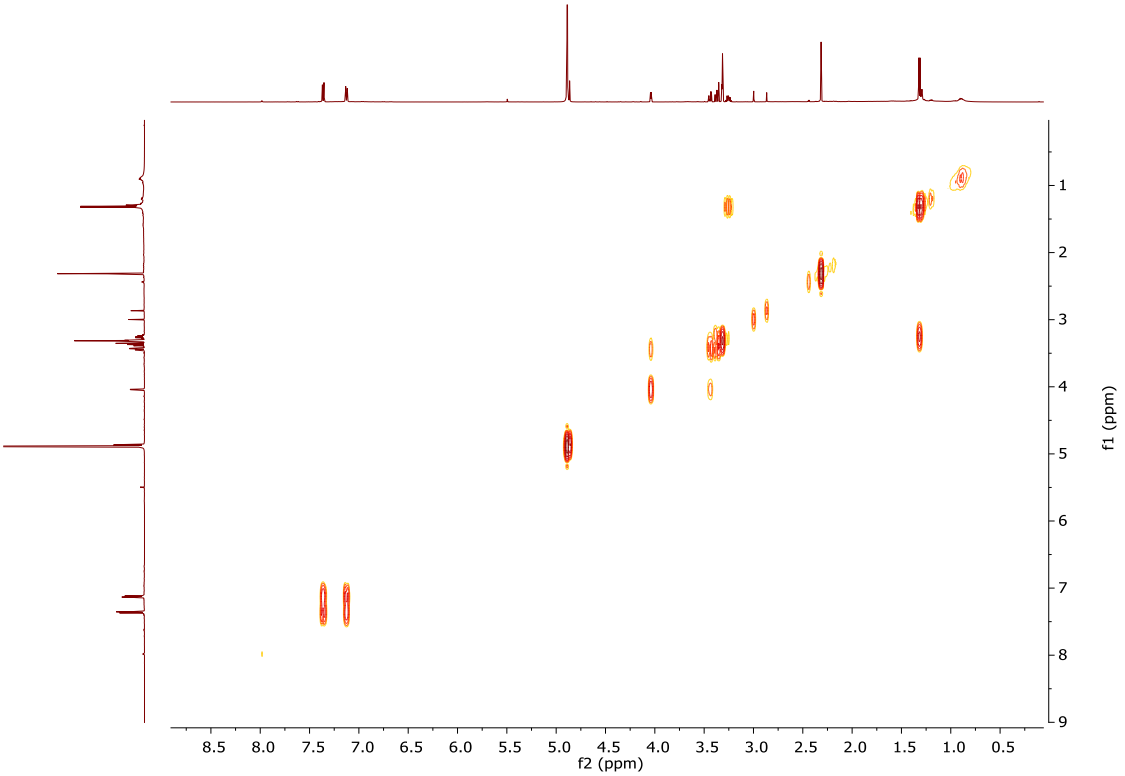
^{1}H-NMR of **11** (500 MHz CD_3OD)



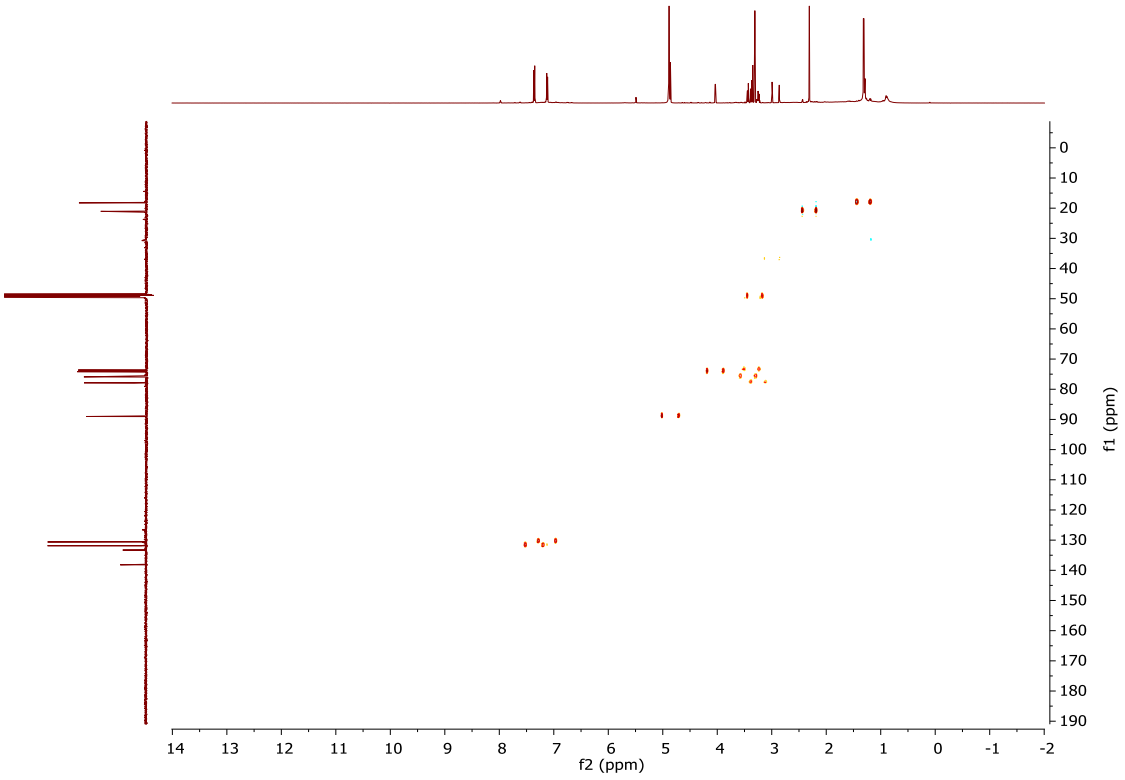
^{13}C-NMR of **11** (125 MHz CD_3OD)



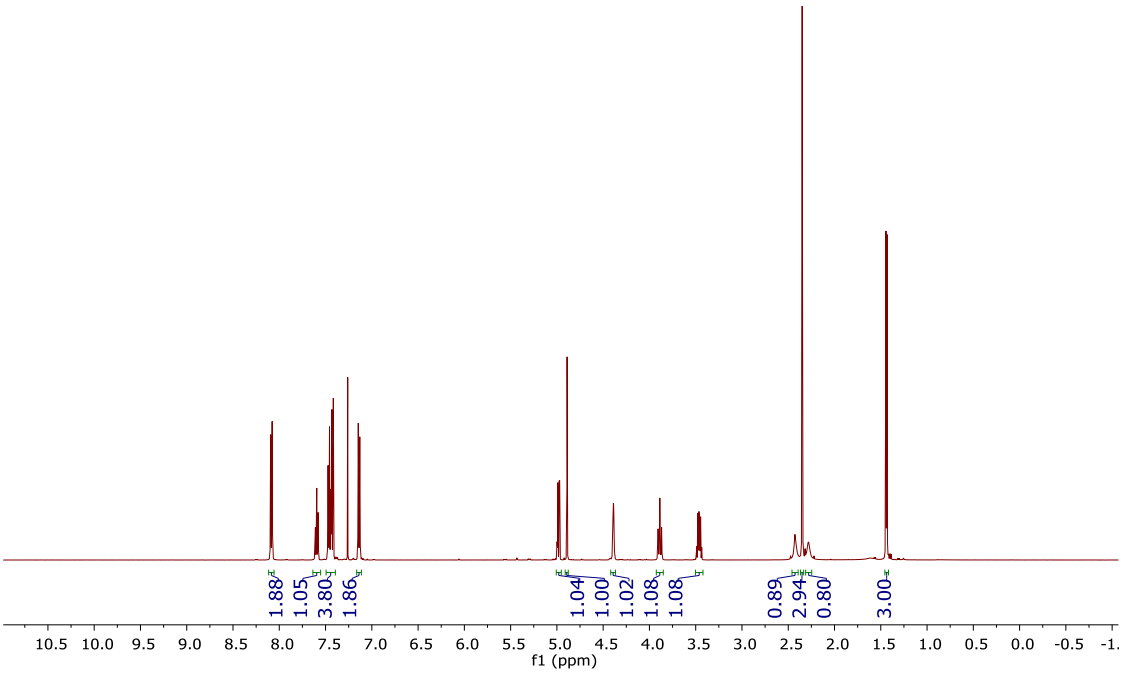
^{1}H-^{1}H gCOSY of **11** (500 MHz CD_3OD)



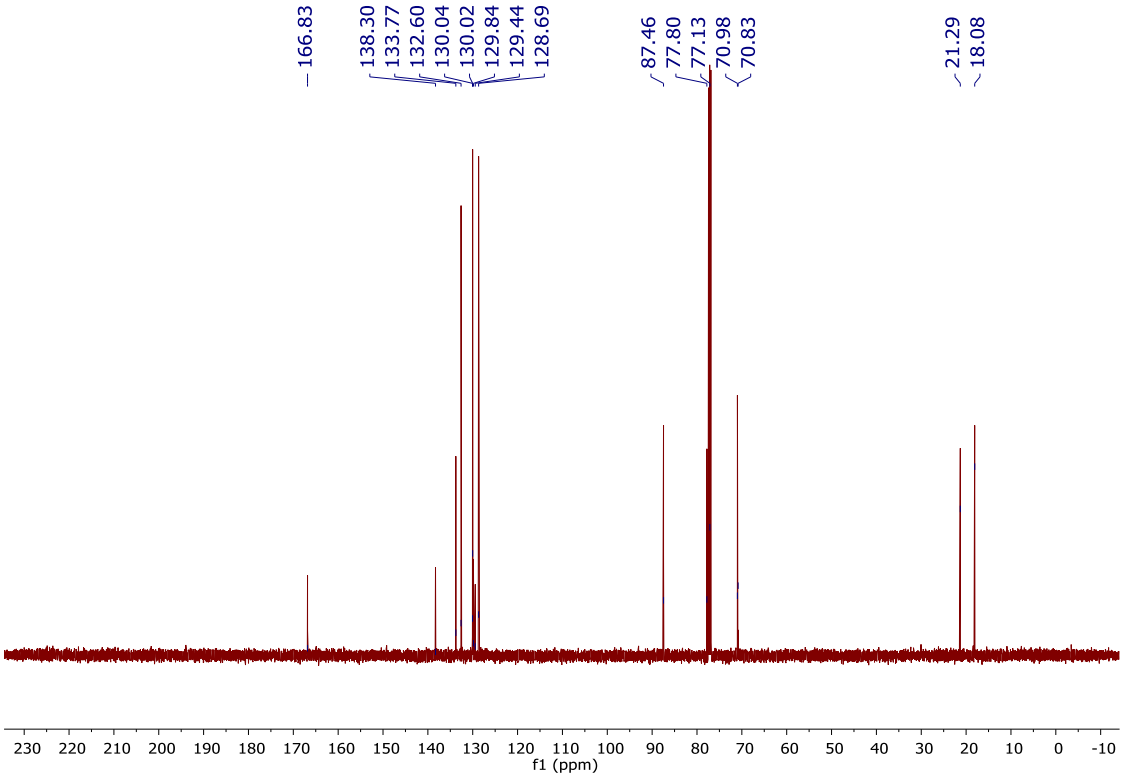
^{1}H-^{13}C gHSQCAD of **11** (500 MHz CD_3OD)



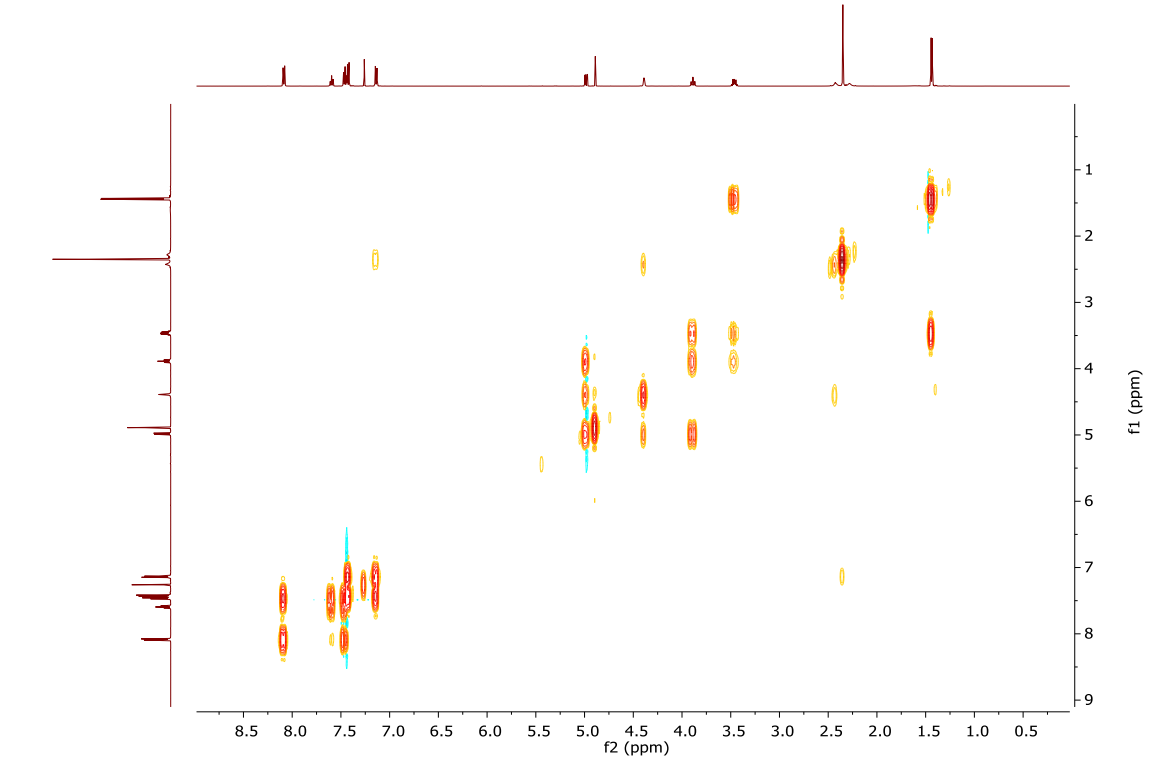
^{1}H-NMR of **12** (500 MHz $CDCl_3$)



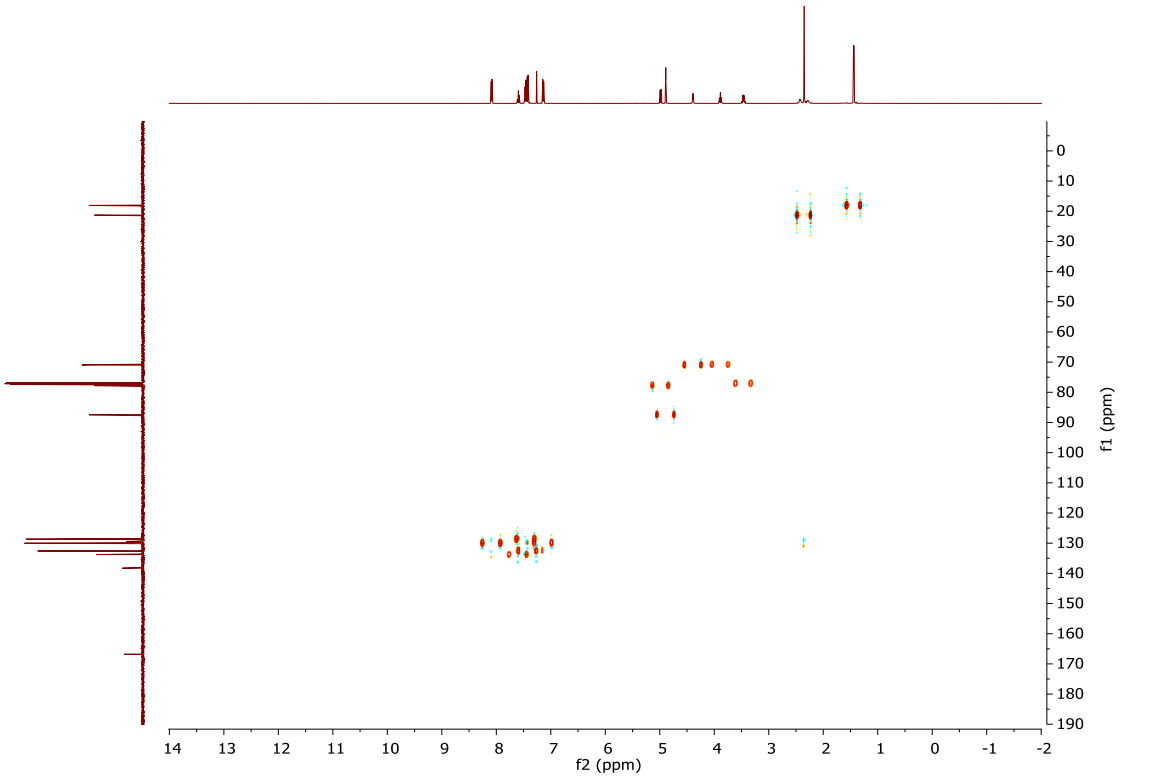
^{13}C-NMR of **12** (125 MHz $CDCl_3$)



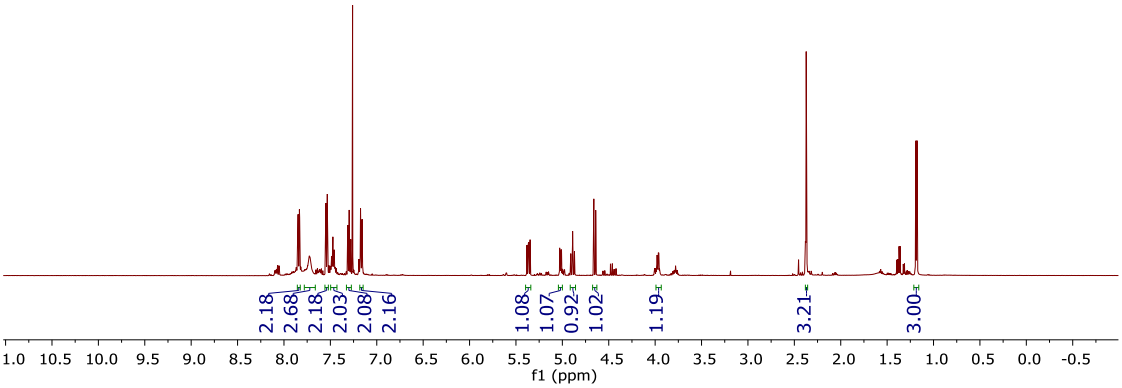
^{1}H-^{1}H gCOSY of **12** (500 MHz $CDCl_3$)



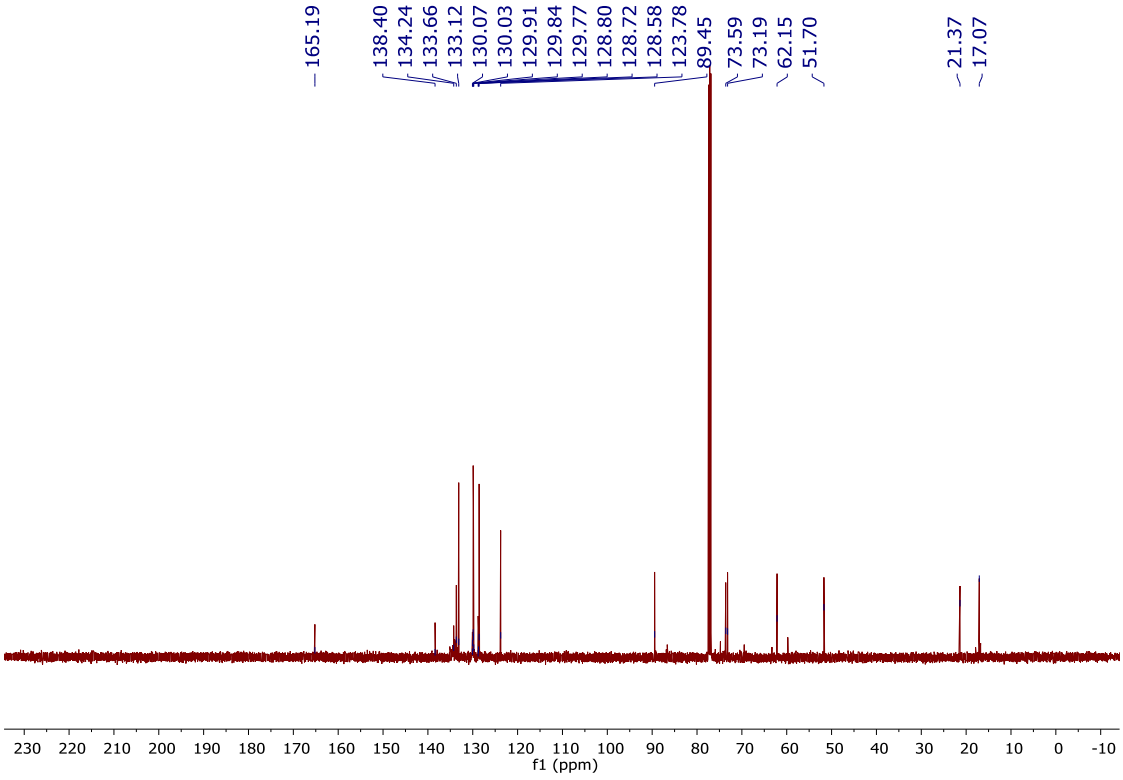
^{1}H-^{13}C gHSQCAD of **12** (500 MHz $CDCl_3$)



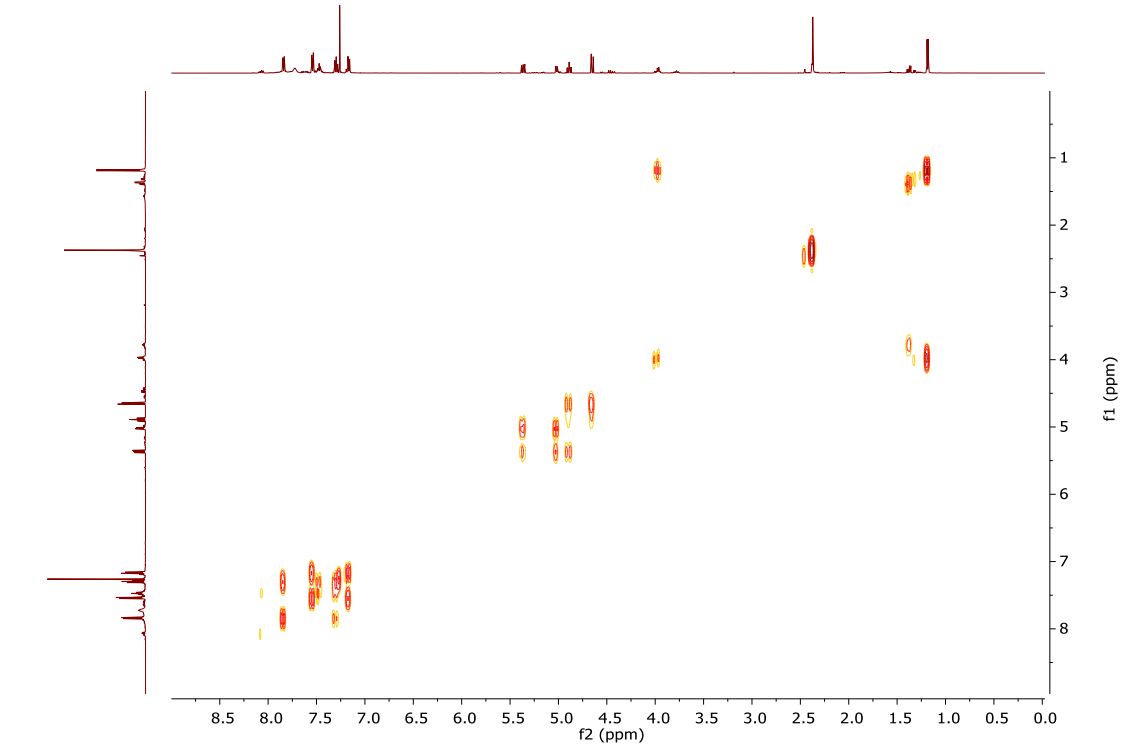
^{1}H-NMR of **13** (500 MHz $CDCl_3$)



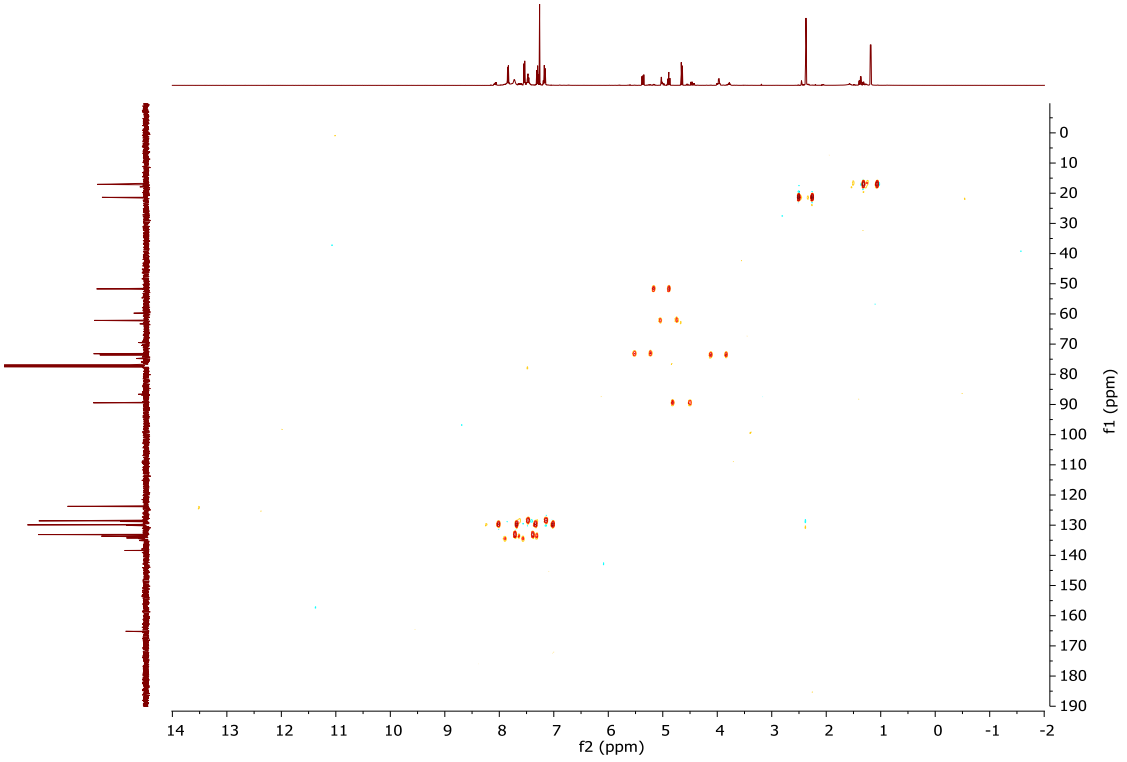
^{13}C-NMR of **13** (125 MHz $CDCl_3$)



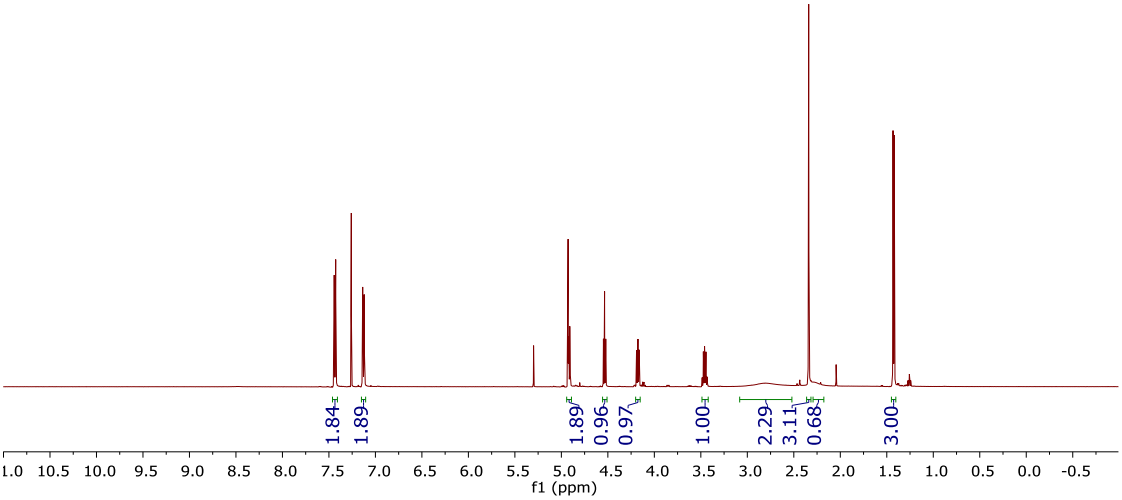
^{1}H-^{1}H gCOSY of **13** (500 MHz $CDCl_3$)



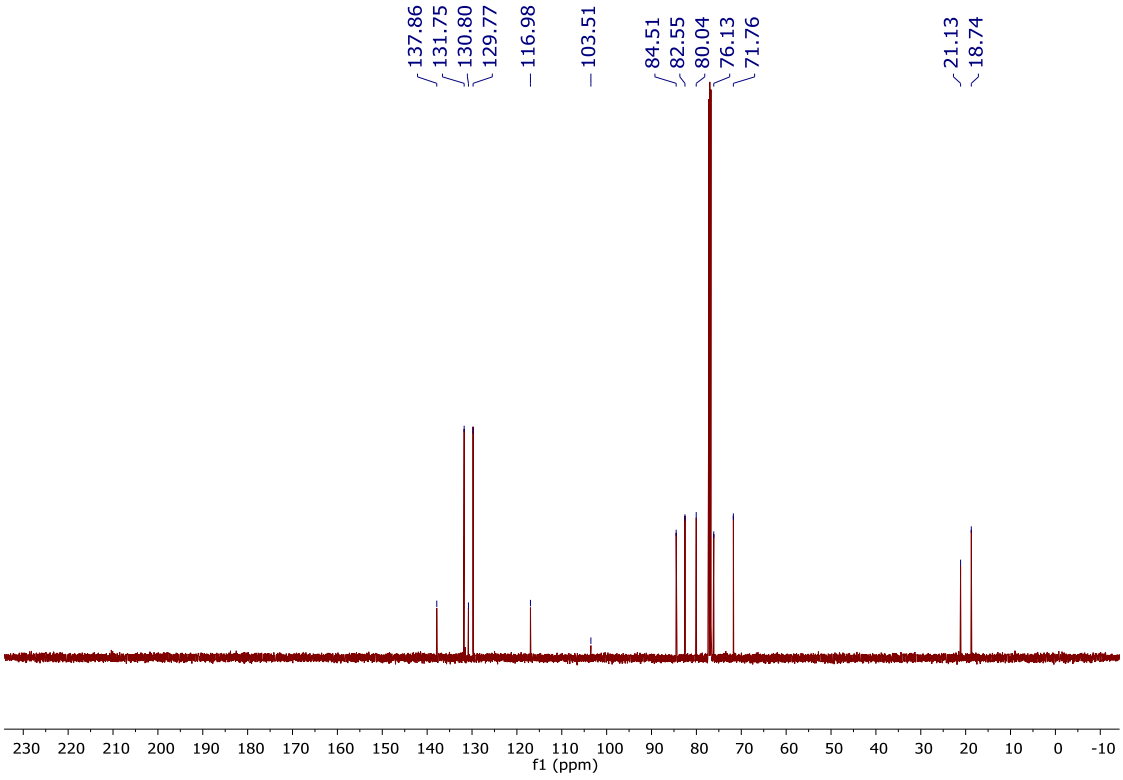
^{1}H-^{13}C gHSQCAD of **13** (500 MHz $CDCl_3$)



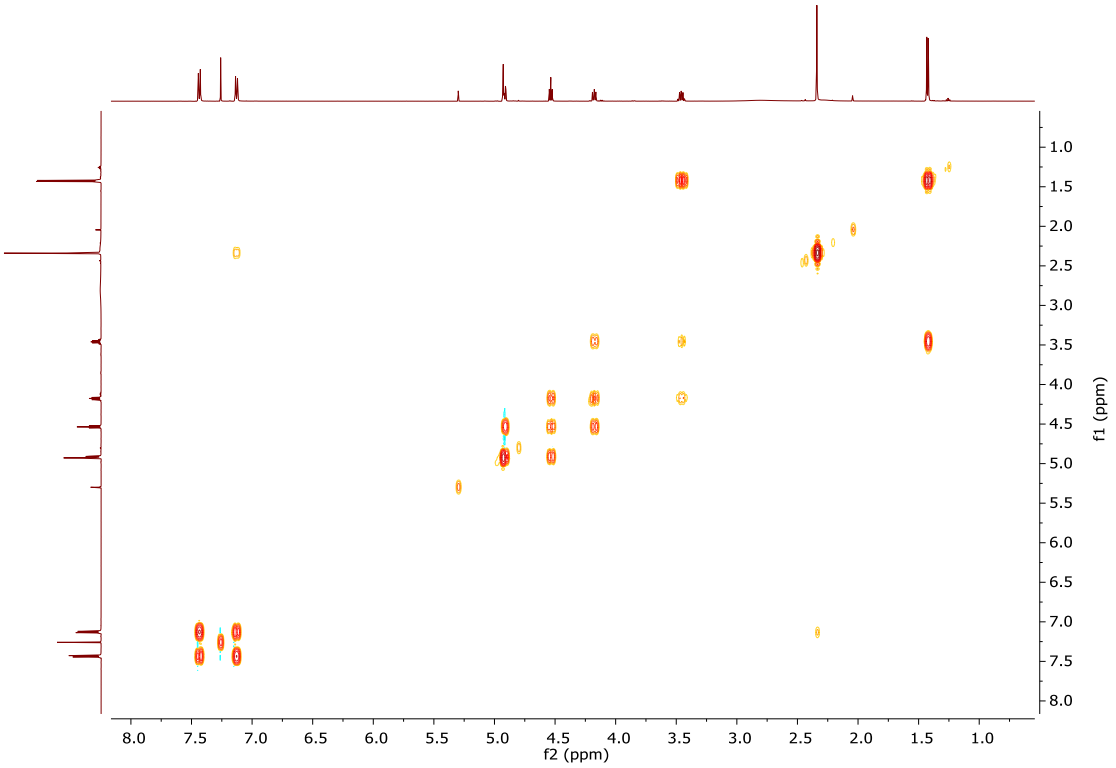
^{1}H-NMR of **15** (500 MHz $CDCl_3$)



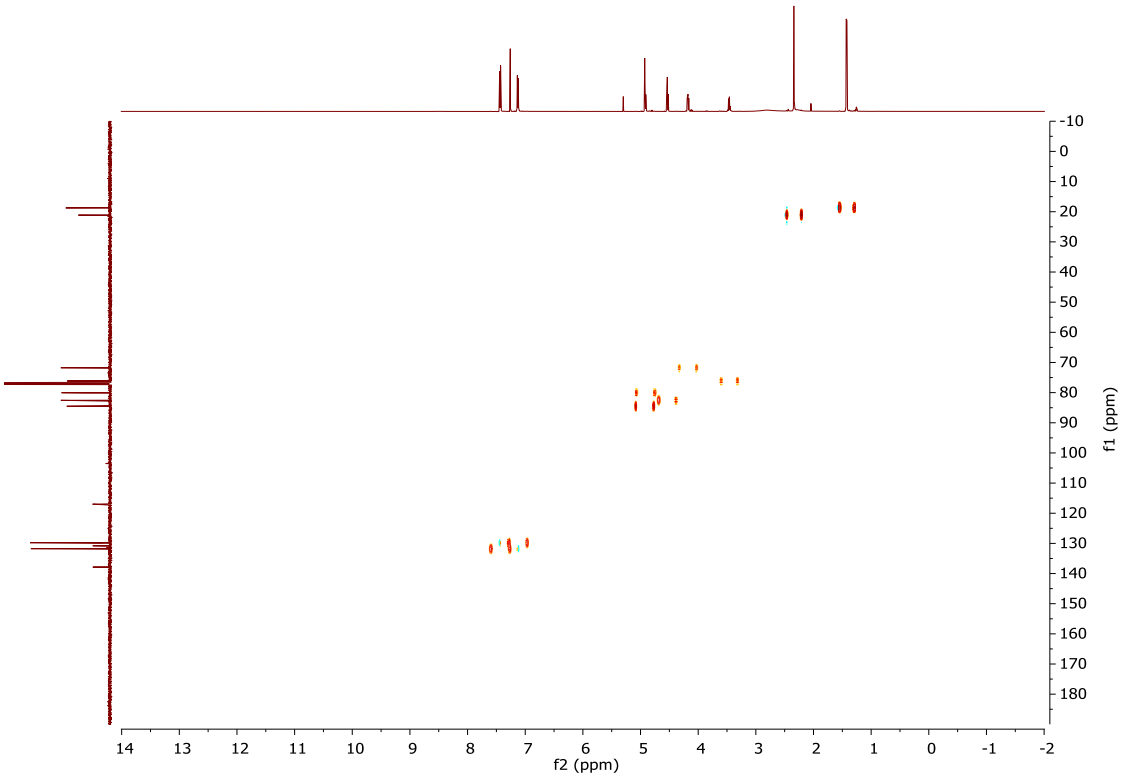
^{13}C-NMR of **15** (125 MHz $CDCl_3$)



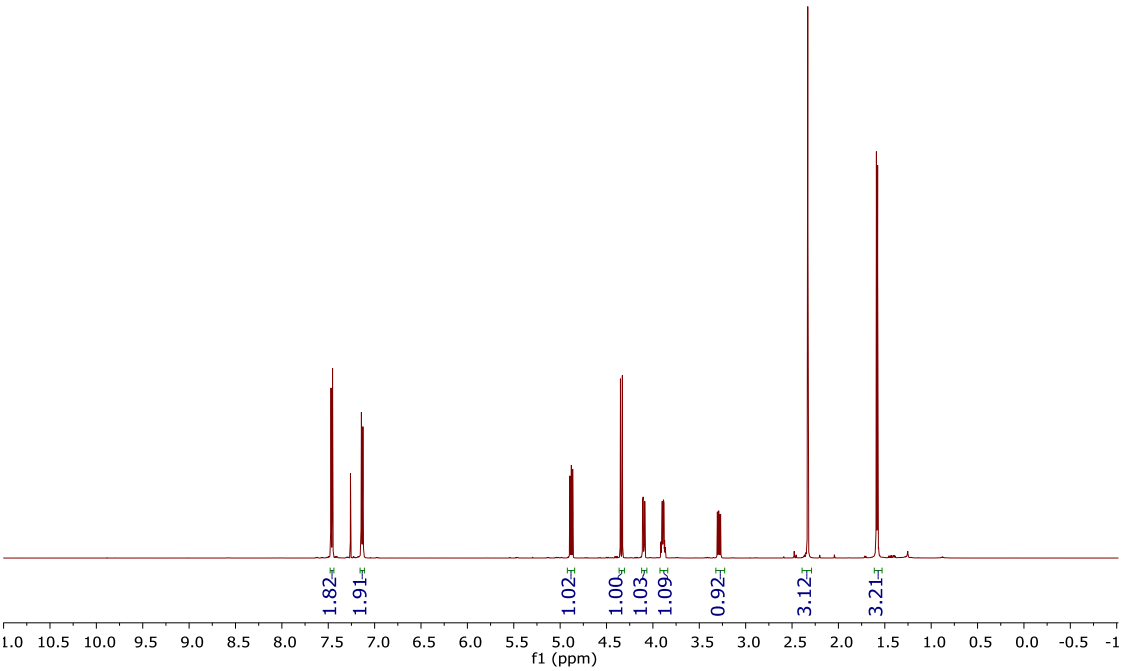
^{1}H-^{1}H gCOSY of **15** (500 MHz $CDCl_3$)



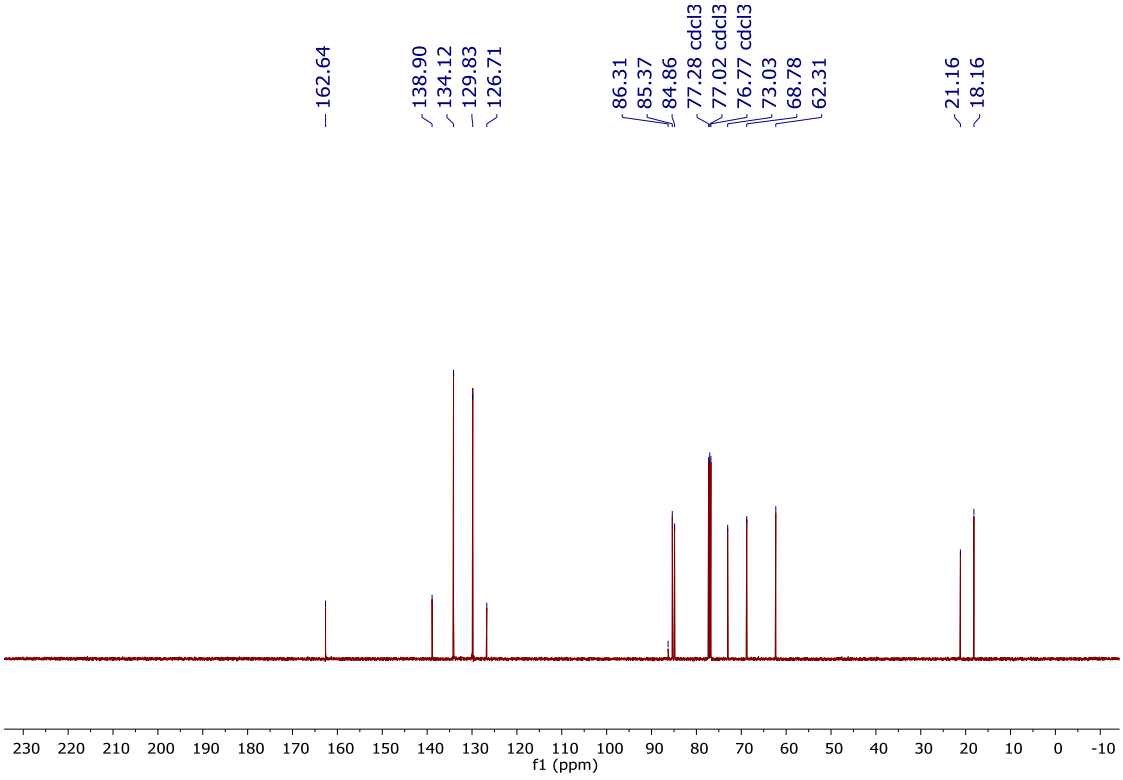
^{1}H-^{13}C gHSQCAD of **15** (500 MHz $CDCl_3$)



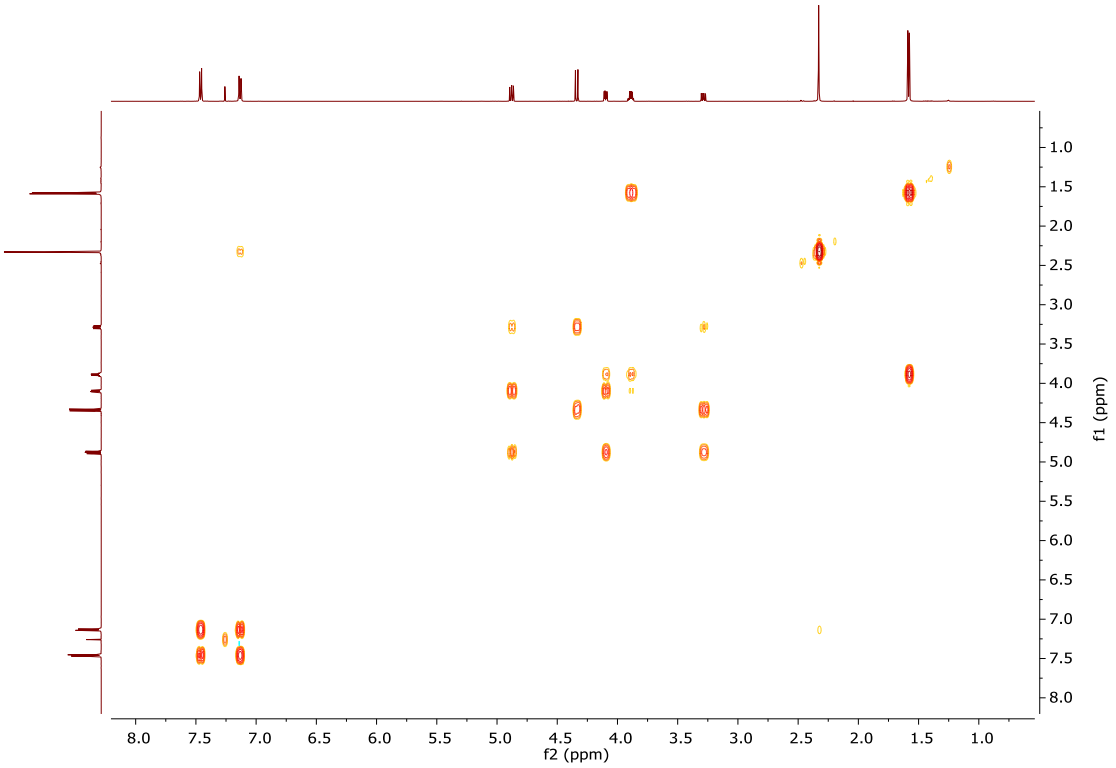
^{1}H-NMR of **16** (500 MHz $CDCl_3$)



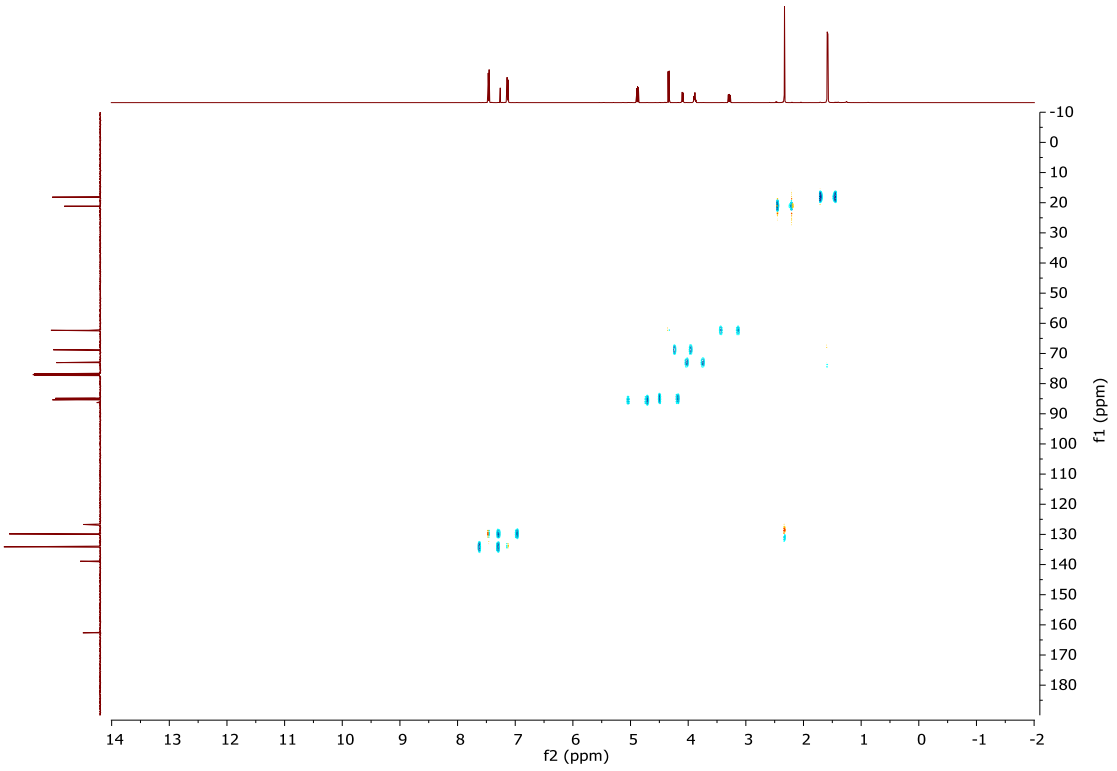
^{13}C-NMR of **16** (125 MHz $CDCl_3$)



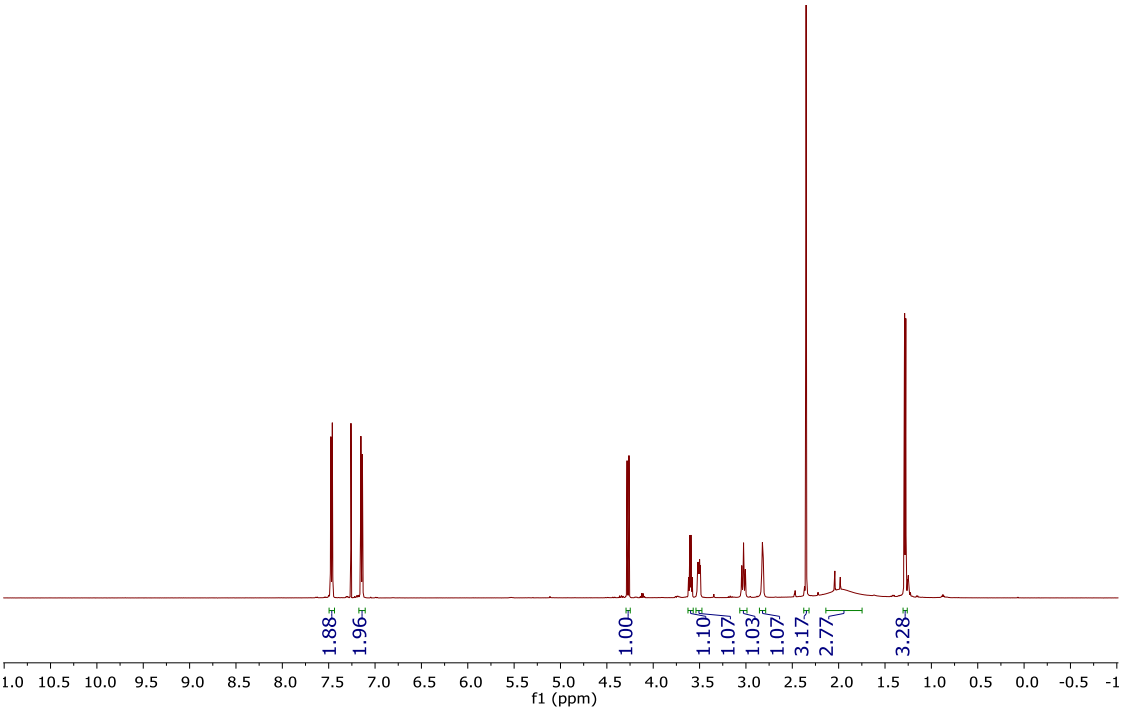
^{1}H-^{1}H gCOSY of **16** (500 MHz $CDCl_3$)



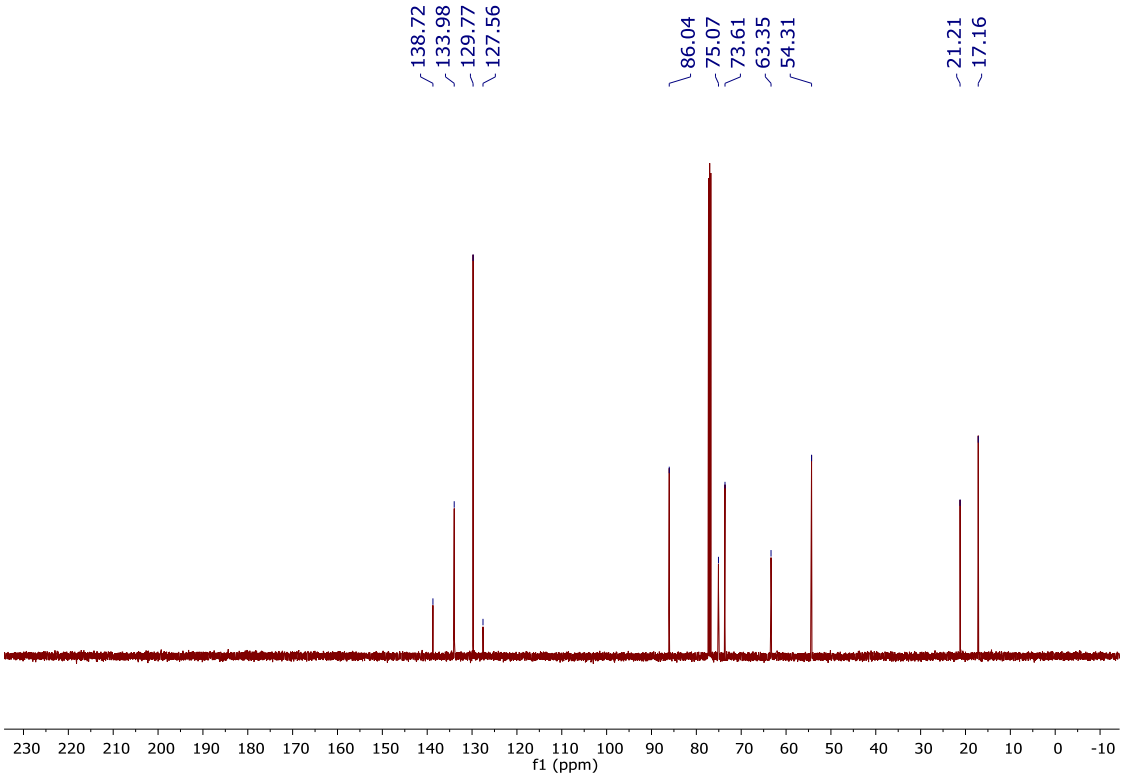
^{1}H-^{13}C gHSQCAD of **16** (500 MHz $CDCl_3$)



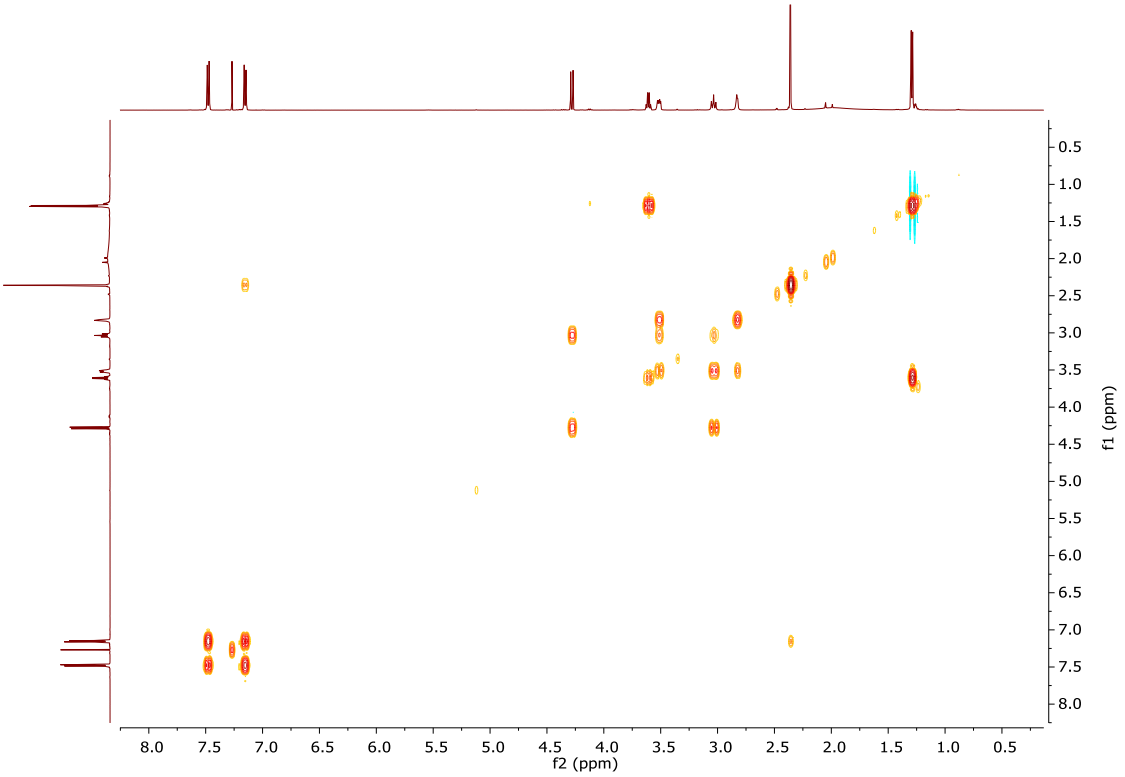
^{1}H-NMR of **14** (500 MHz $CDCl_3$)



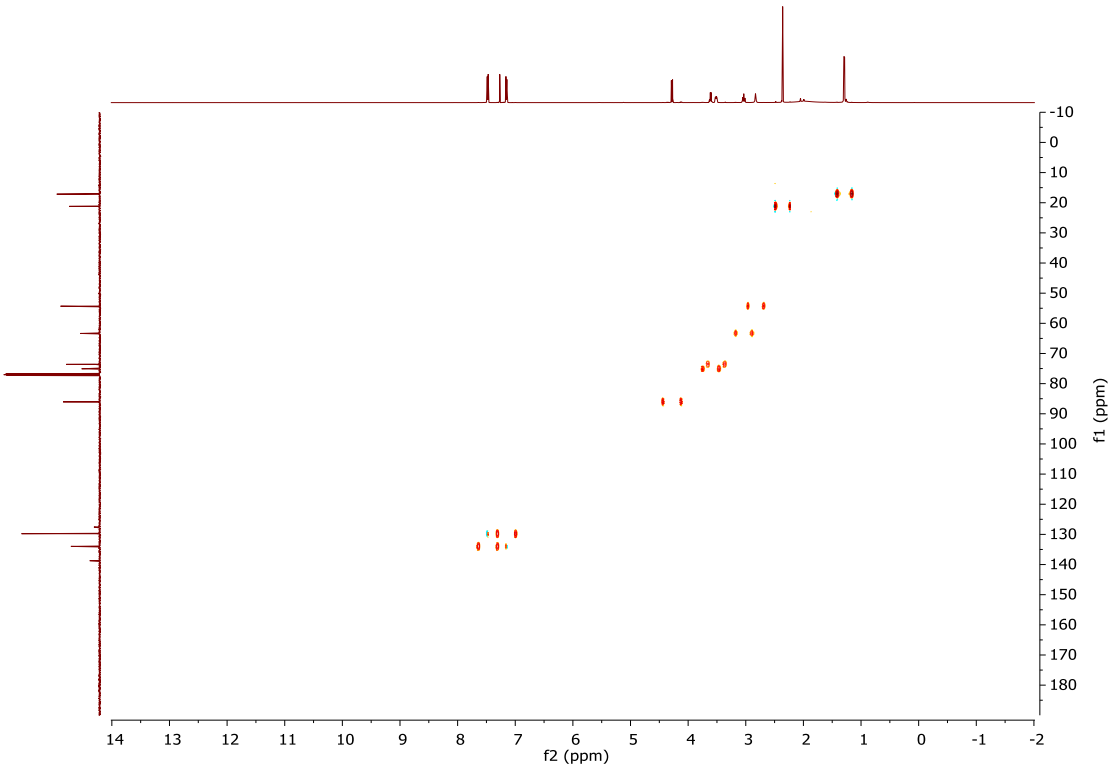
^{13}C-NMR of **14** (125 MHz $CDCl_3$)



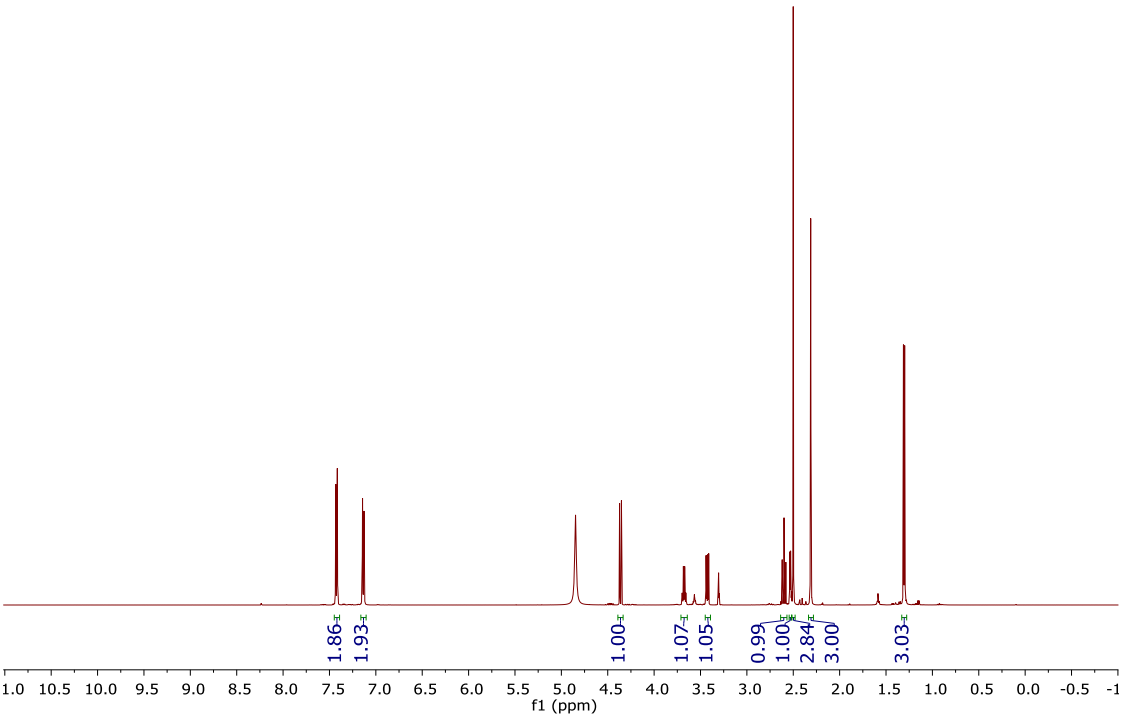
^{1}H-^{1}H gCOSY of **14** (500 MHz $CDCl_3$)



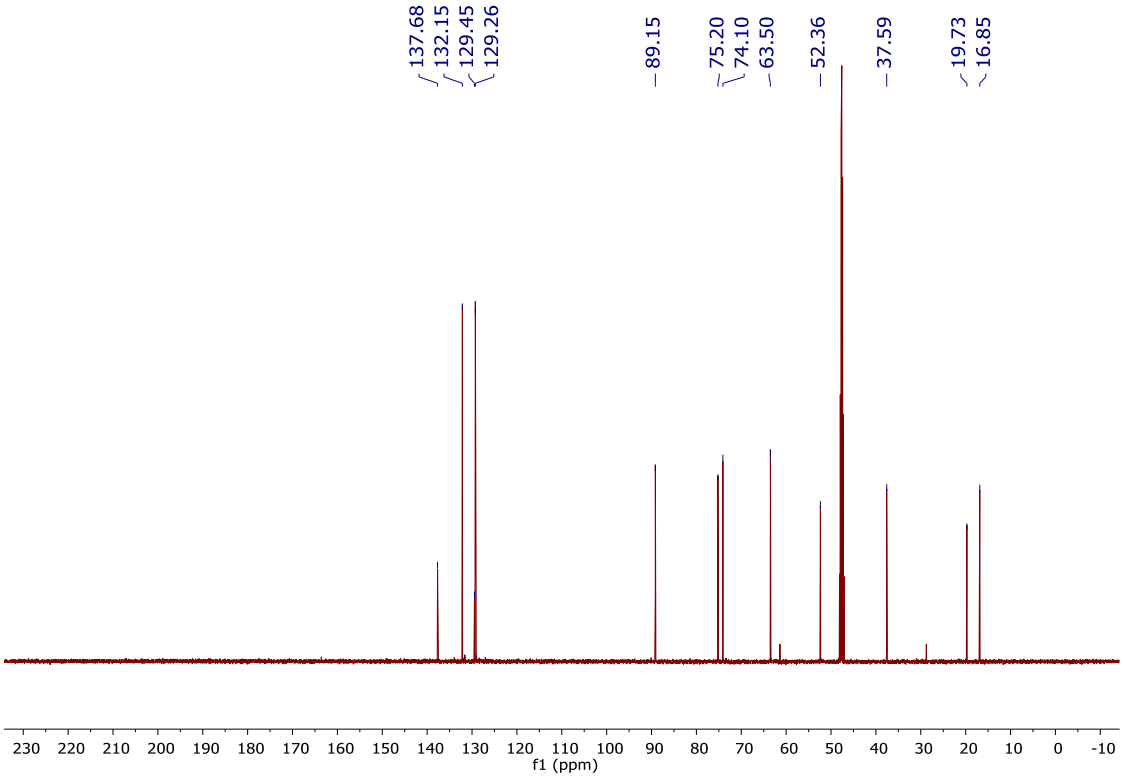
^{1}H-^{13}C gHSQCAD of **14** (500 MHz $CDCl_3$)



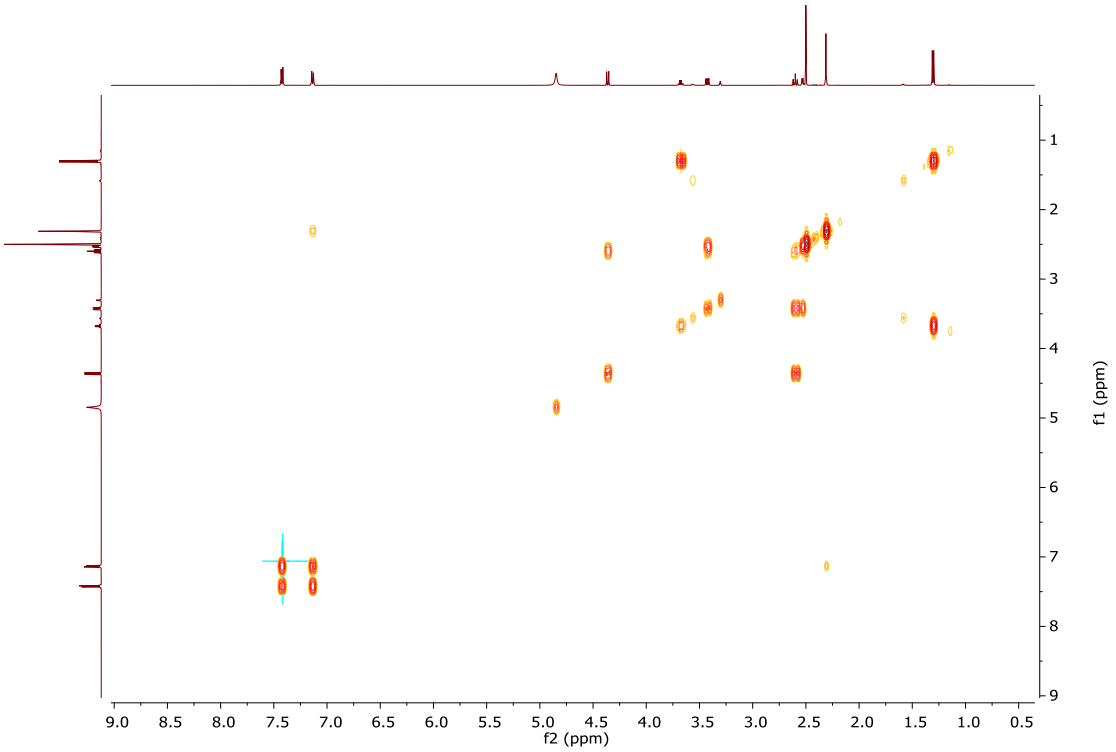
^{1}H-NMR of **17** (500 MHz CD_3OD)



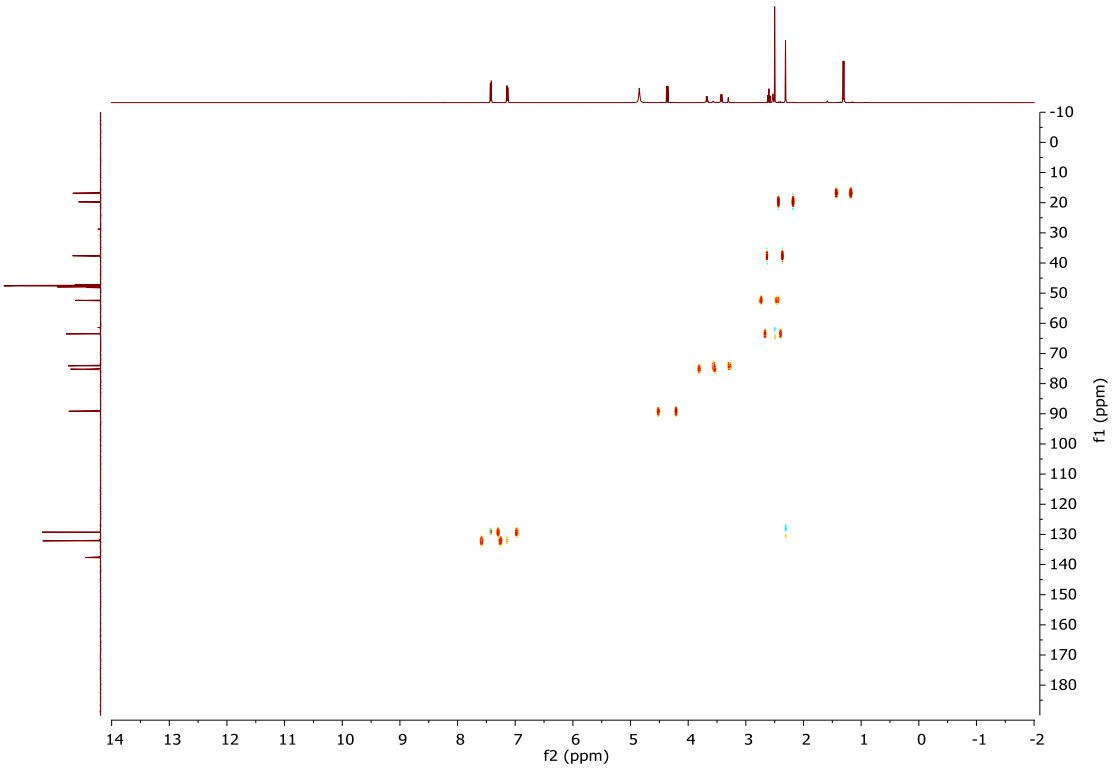
^{13}C-NMR of **17** (125 MHz CD_3OD)



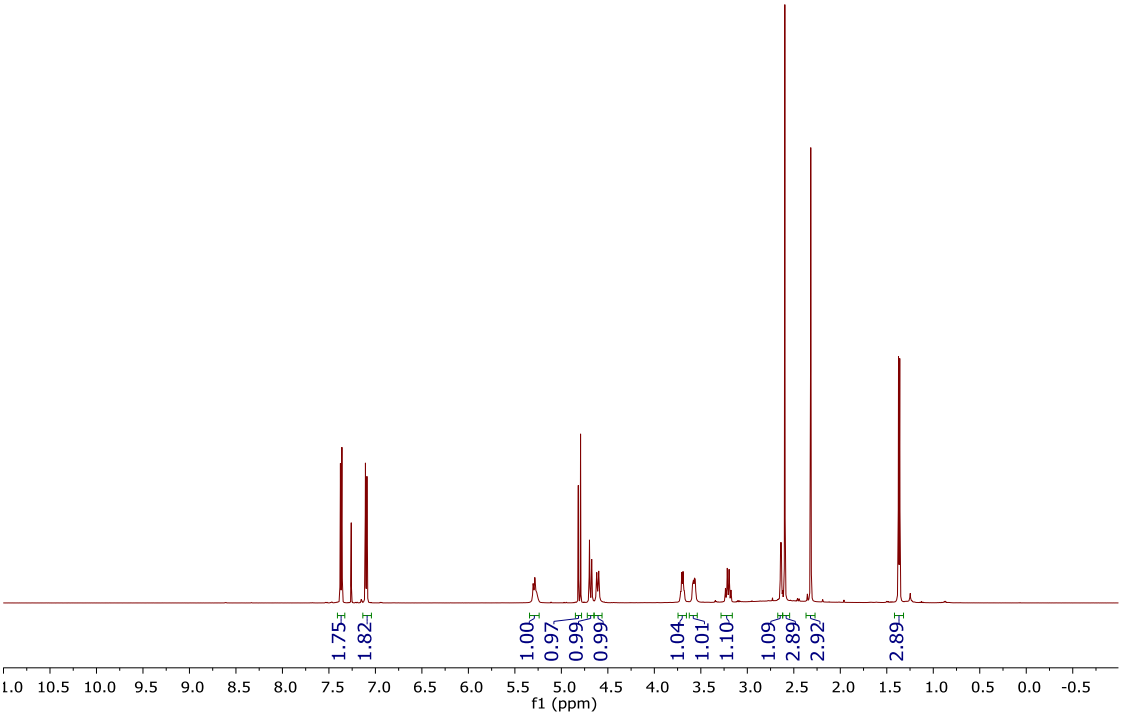
^{1}H-^{1}H gCOSY of **17** (500 MHz CD_3OD)



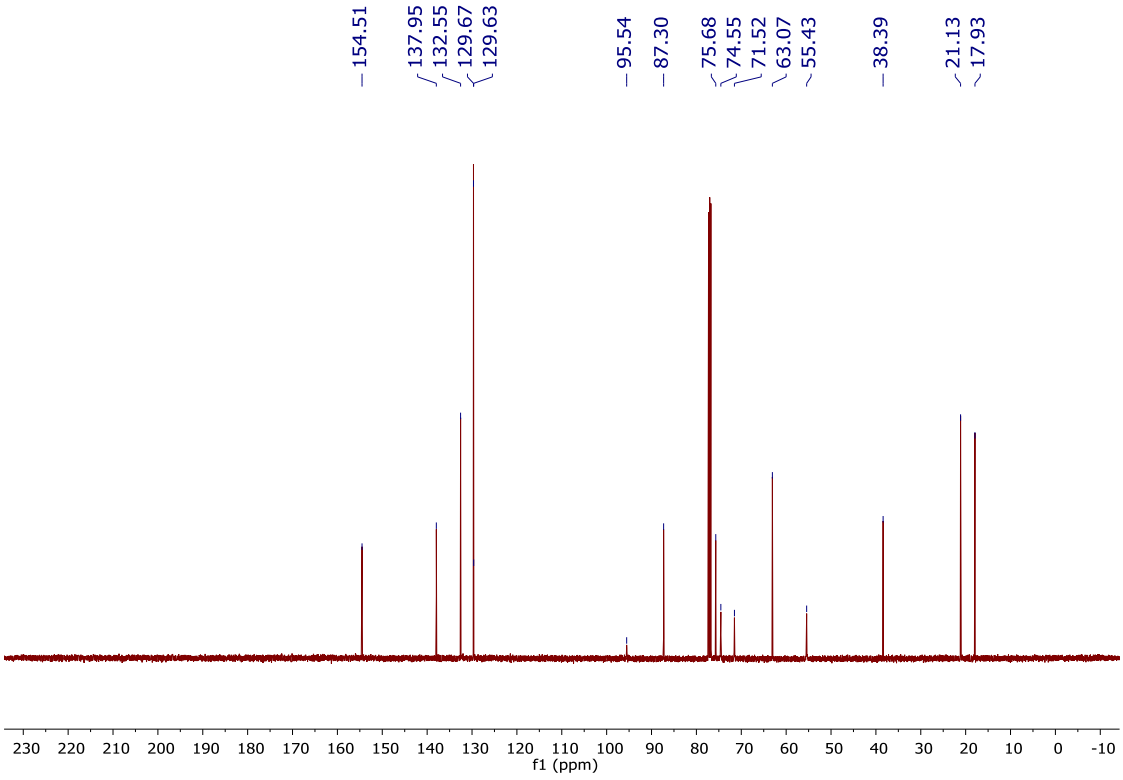
^{1}H-^{13}C gHSQCAD of **17** (500 MHz CD_3OD)



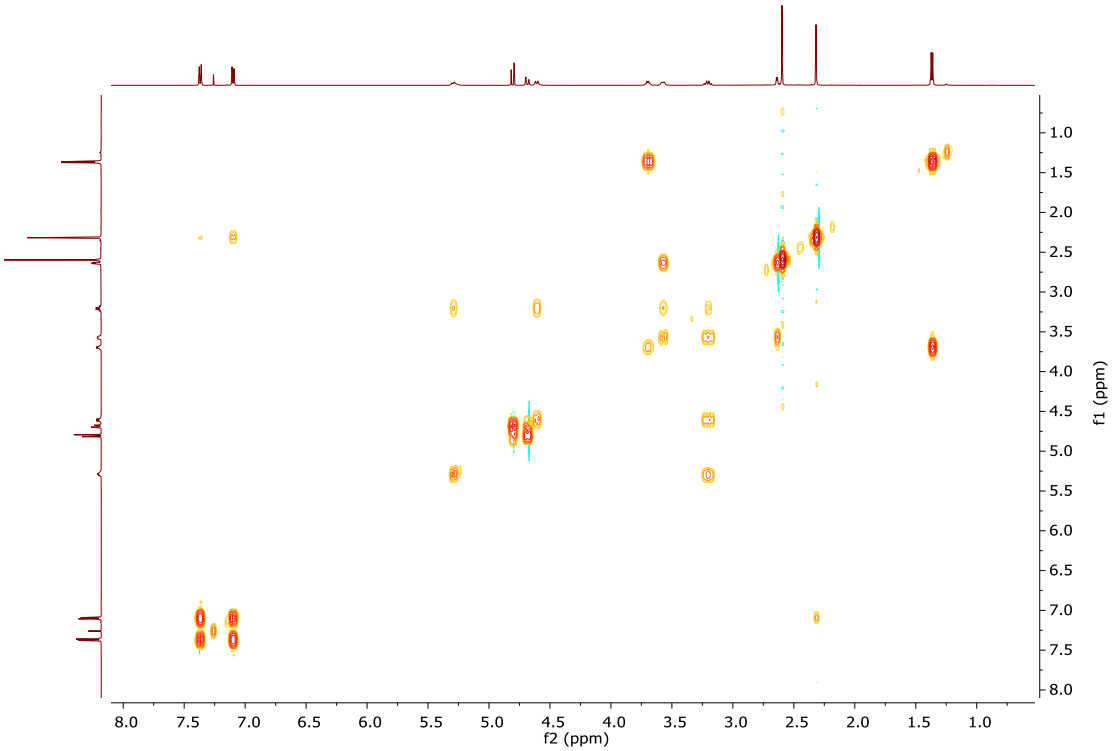
^{1}H-NMR of **18** (500 MHz $CDCl_3$)



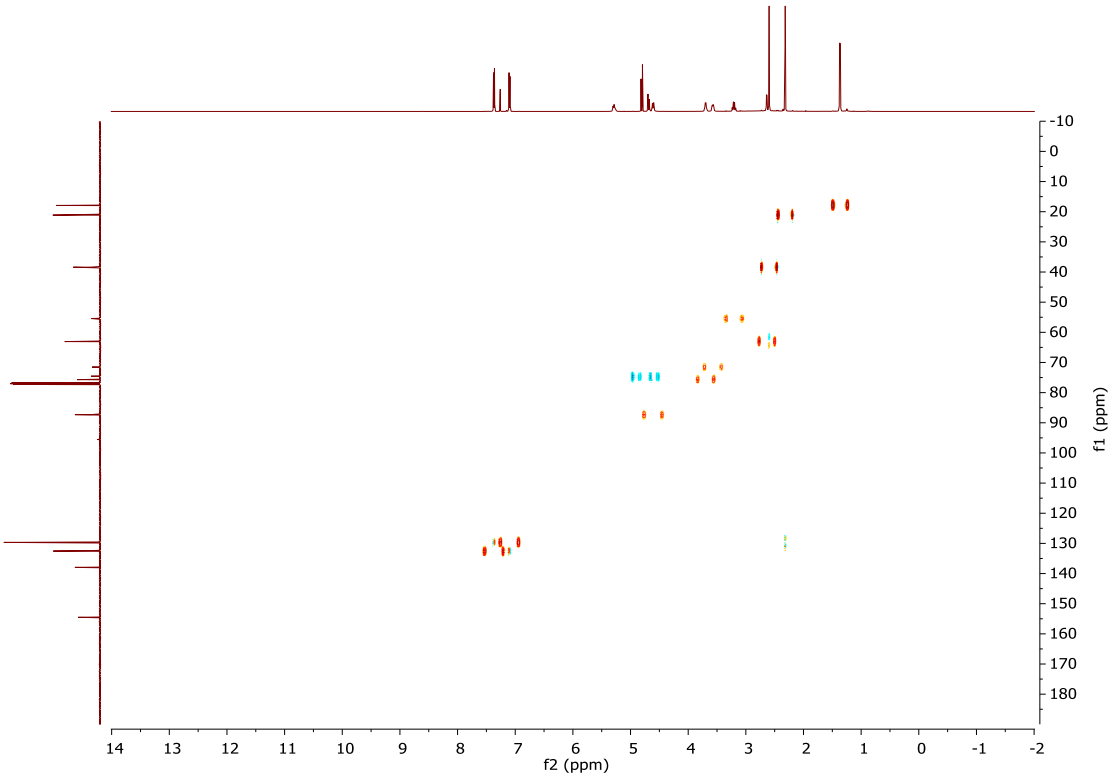
^{13}C-NMR of **18** (125 MHz $CDCl_3$)



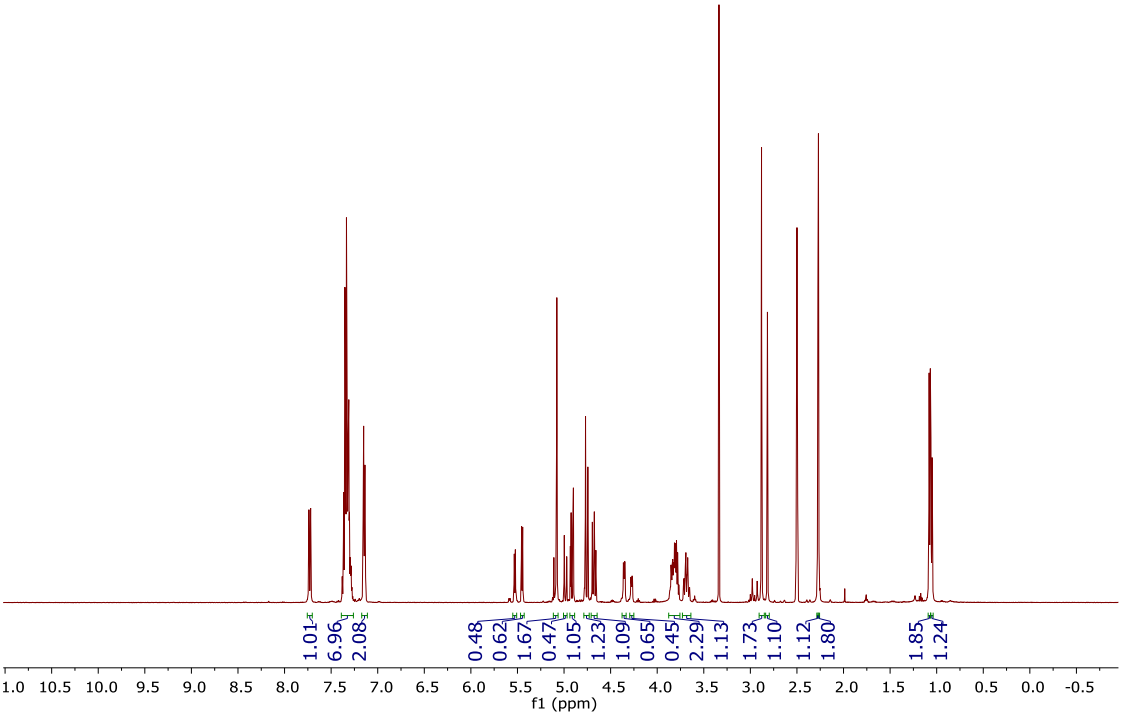
^{1}H-^{1}H gCOSY of **18** (500 MHz $CDCl_3$)



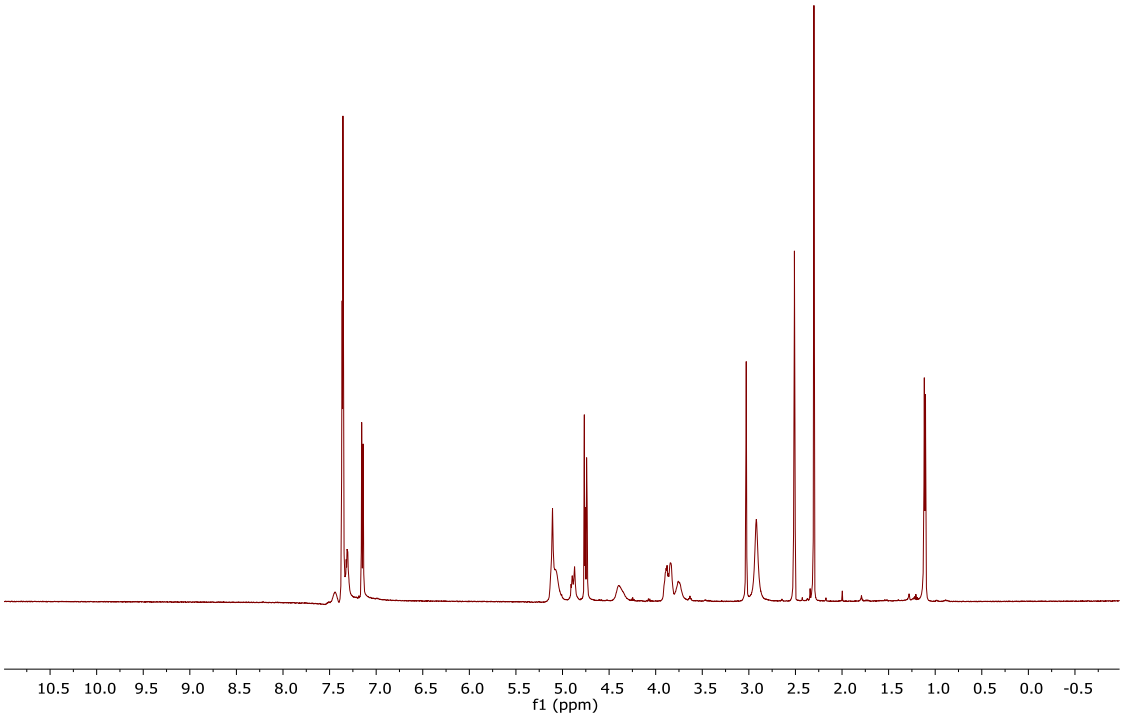
^{1}H-^{13}C gHSQCAD of **18** (500 MHz $CDCl_3$)



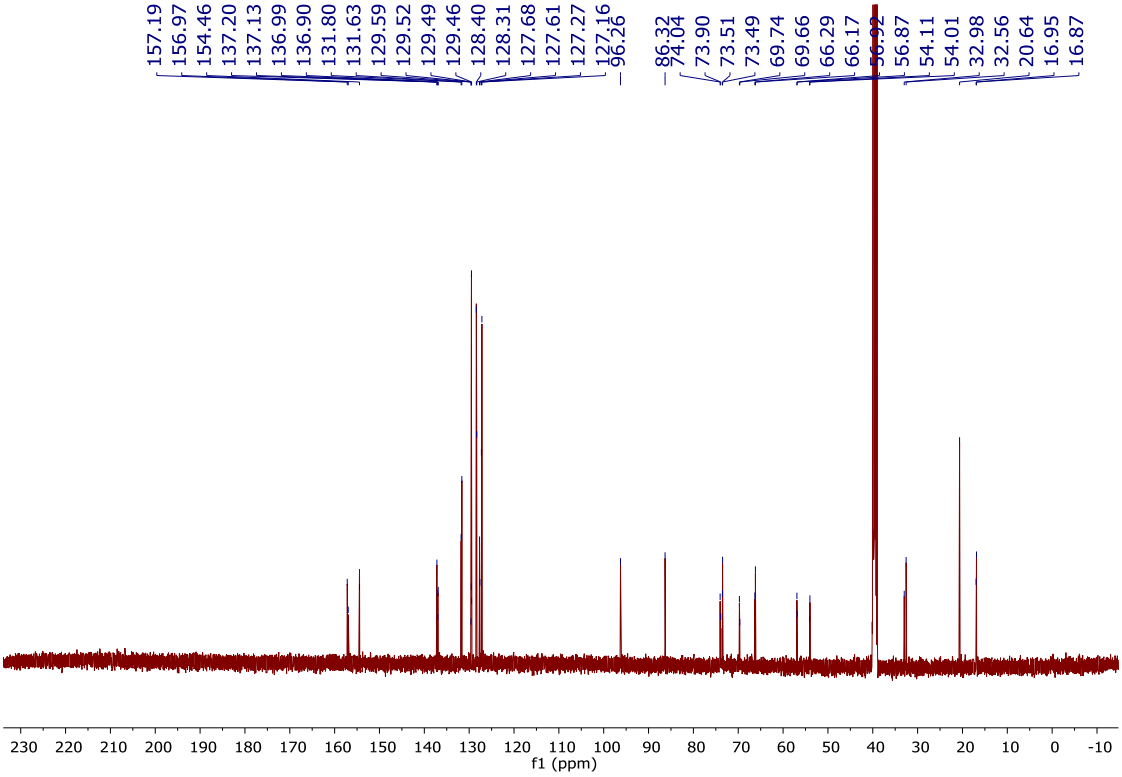
^{1}H-NMR of **4** (500 MHz d^{6}-DMSO)



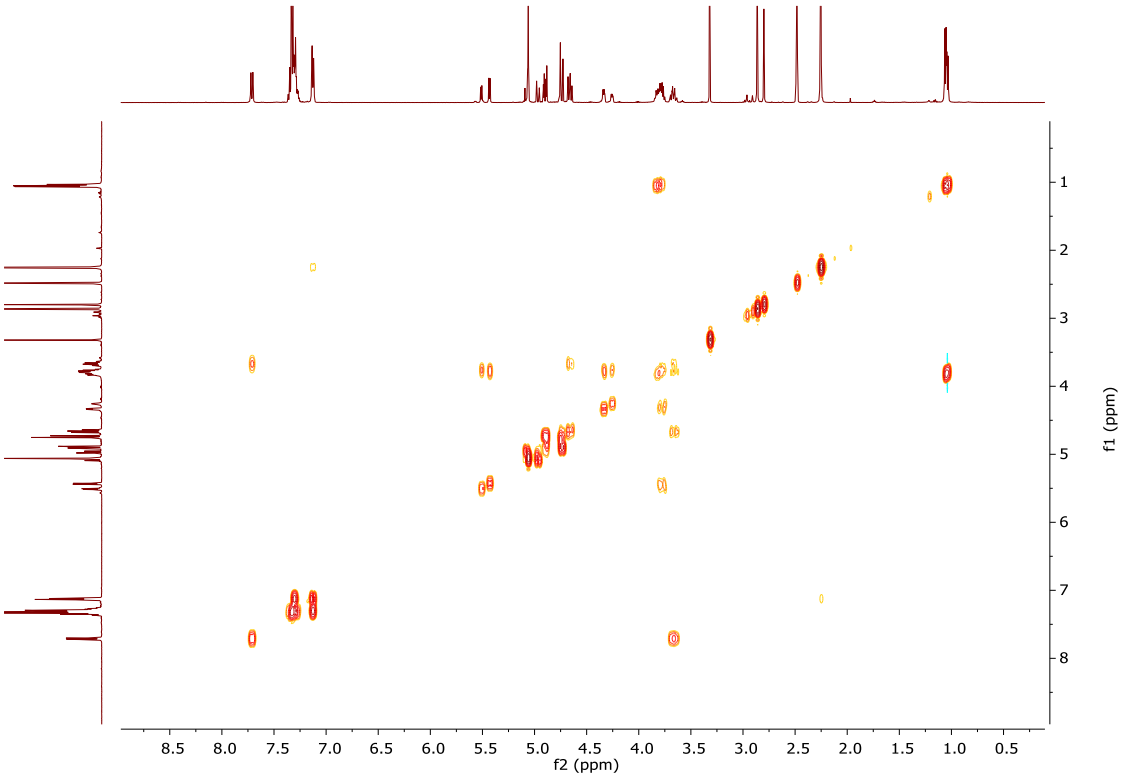
^{1}H-NMR of **4** (500 MHz d^{6}-DMSO, VT at 90 °C)



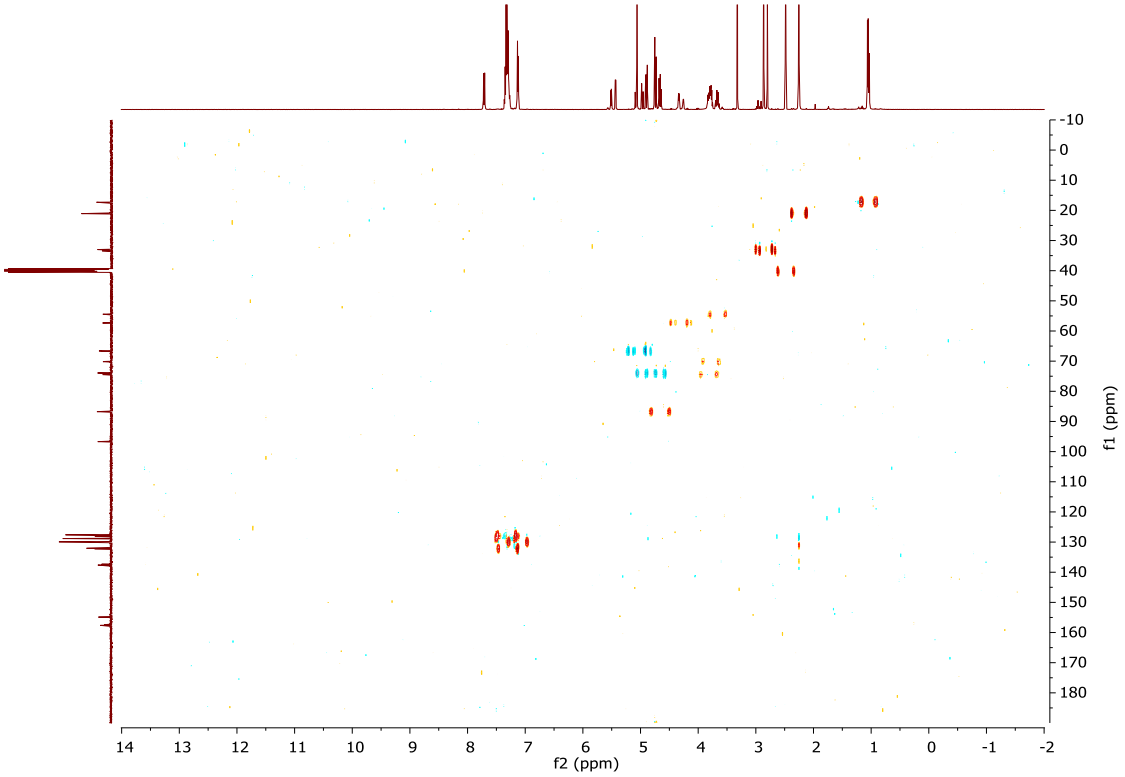
^{13}C-NMR of **4** (125 MHz d^6-DMSO)



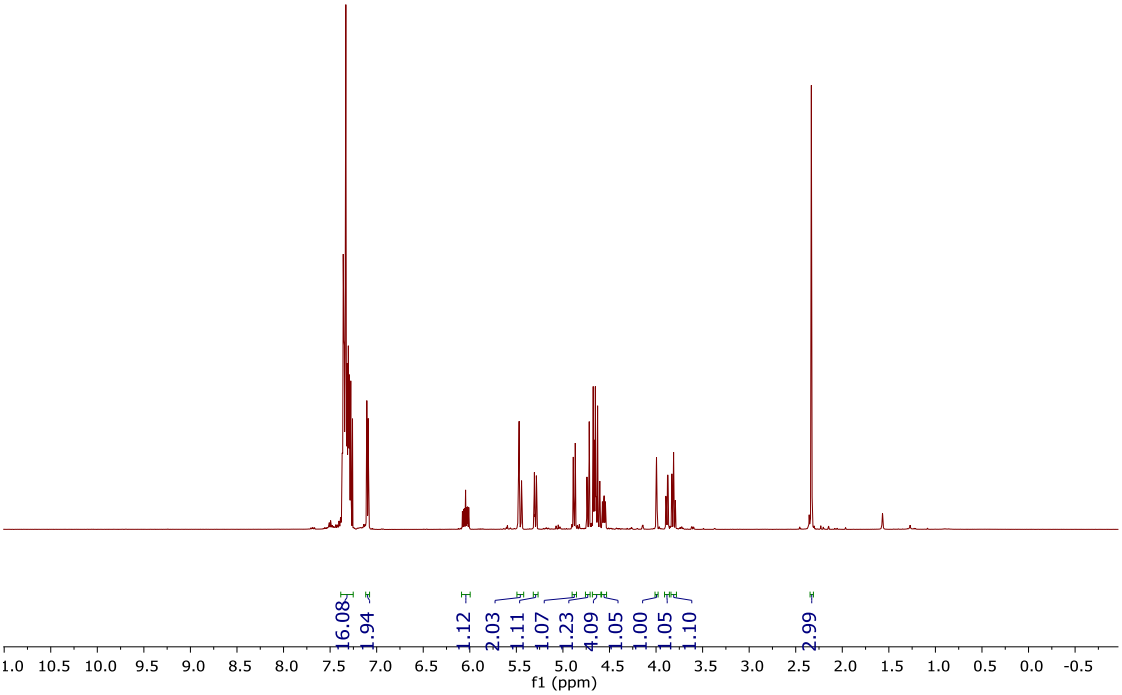
^{1}H-^{1}H gCOSY of **4** (500 MHz d^6-DMSO)



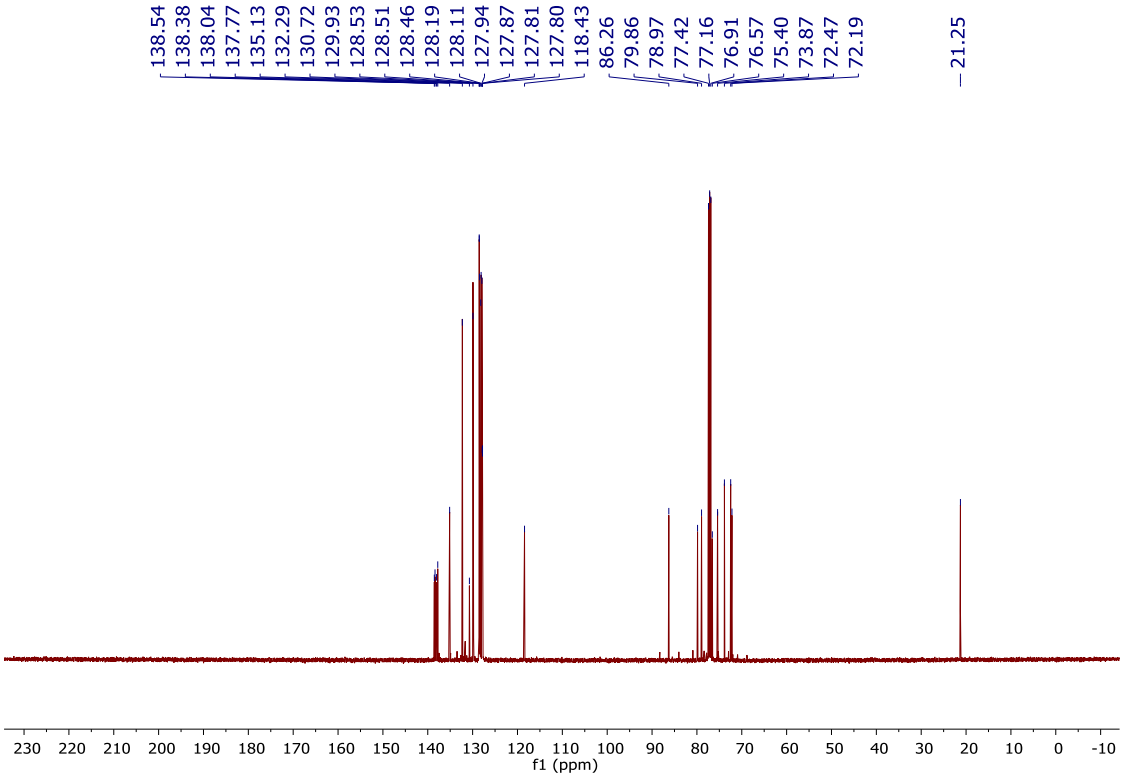
^{1}H-^{13}C gHSQCAD of **4** (500 MHz d^{6}-DMSO)



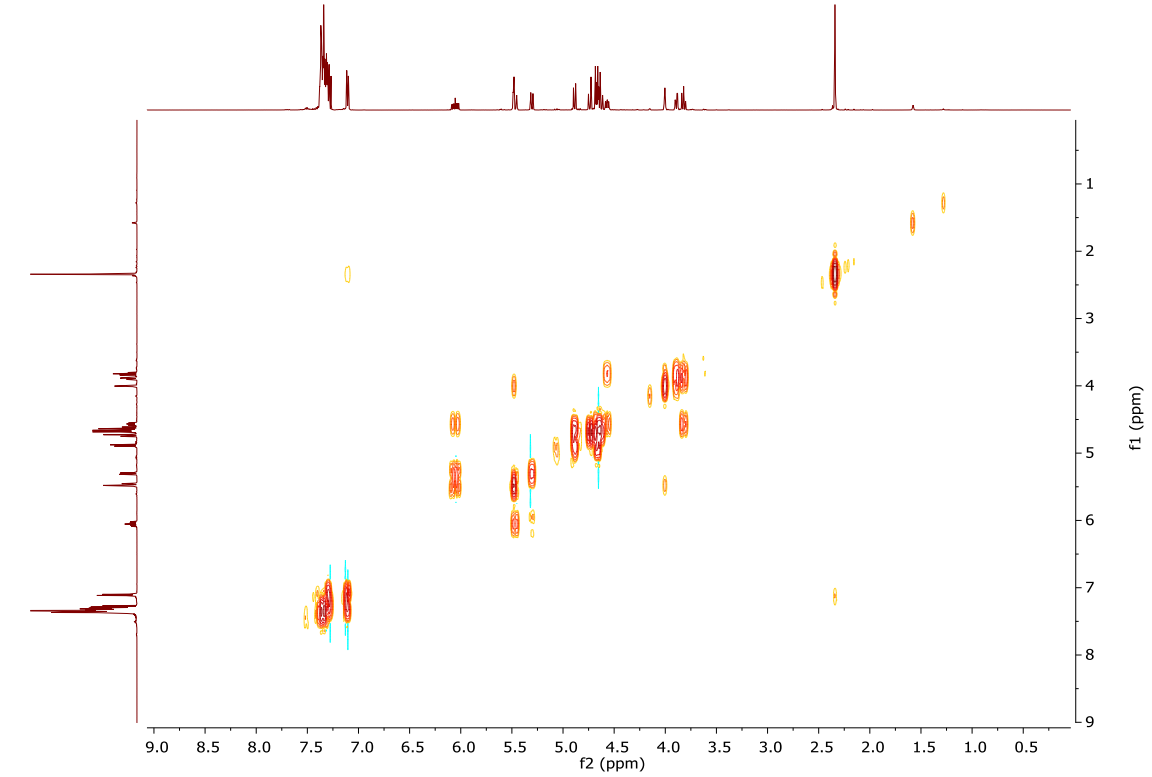
^{1}H-NMR of **20** (500 MHz $CDCl_3$)



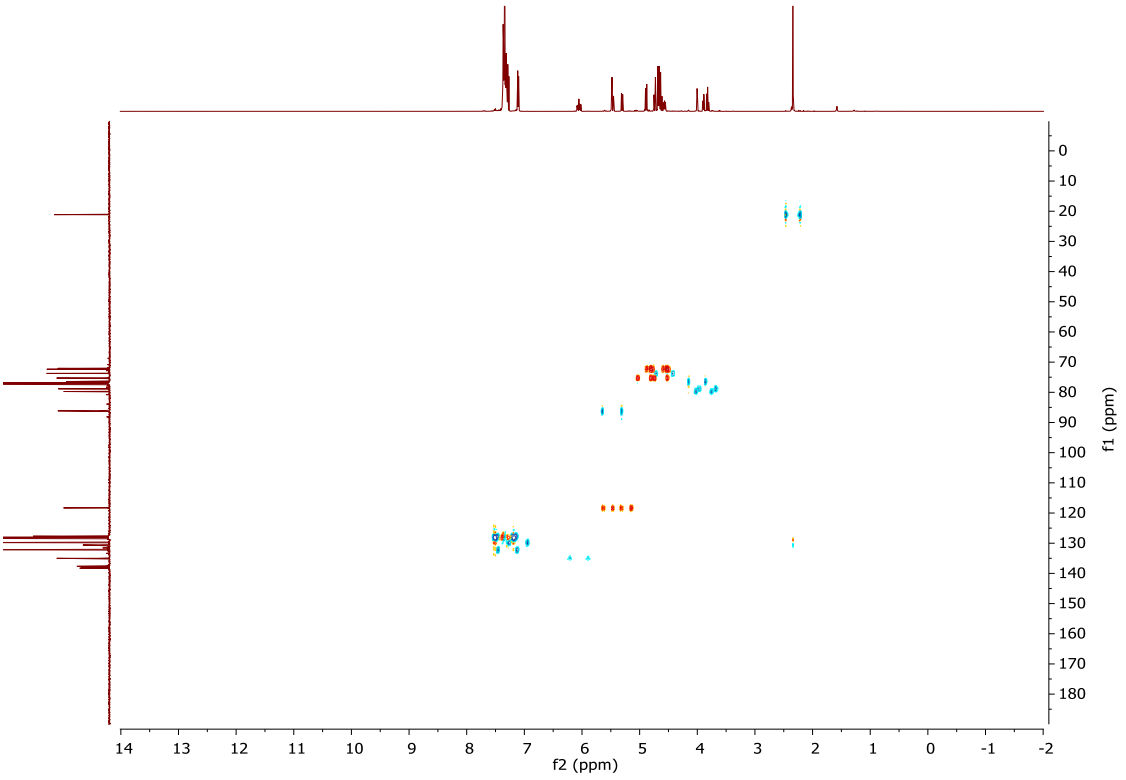
^{13}C-NMR of **20** (125 MHz $CDCl_3$)



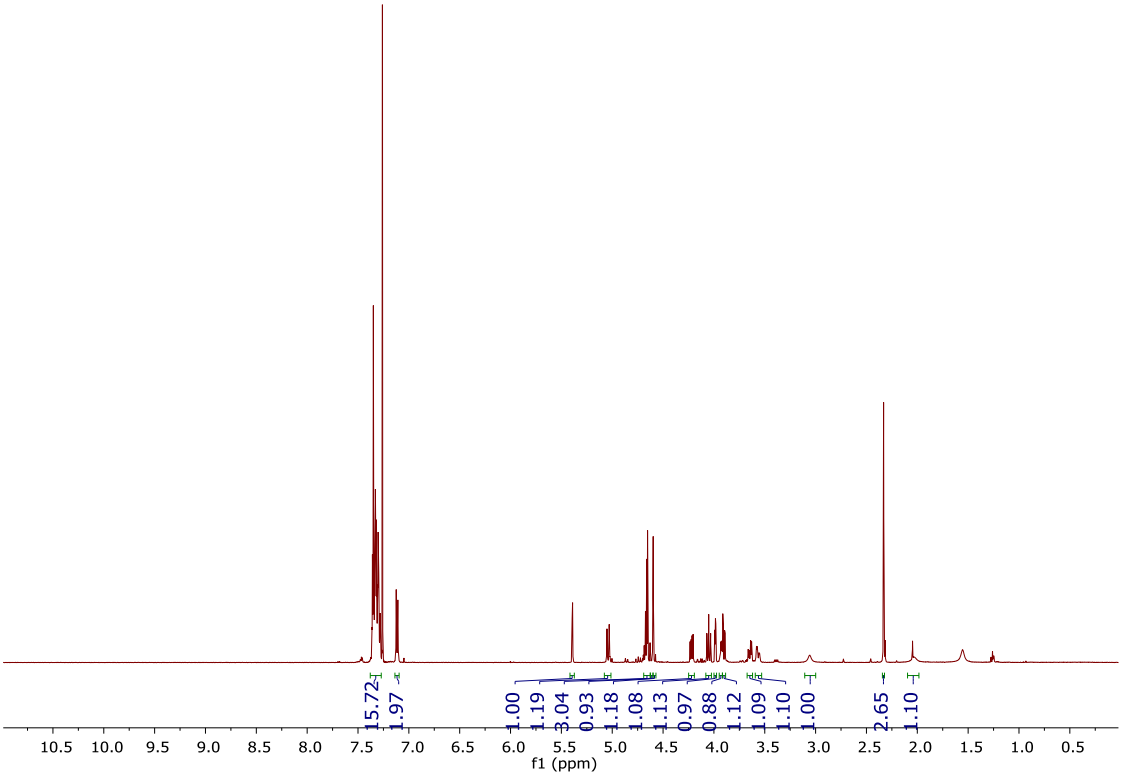
^{1}H-^{1}H gCOSY of **20** (500 MHz $CDCl_3$)



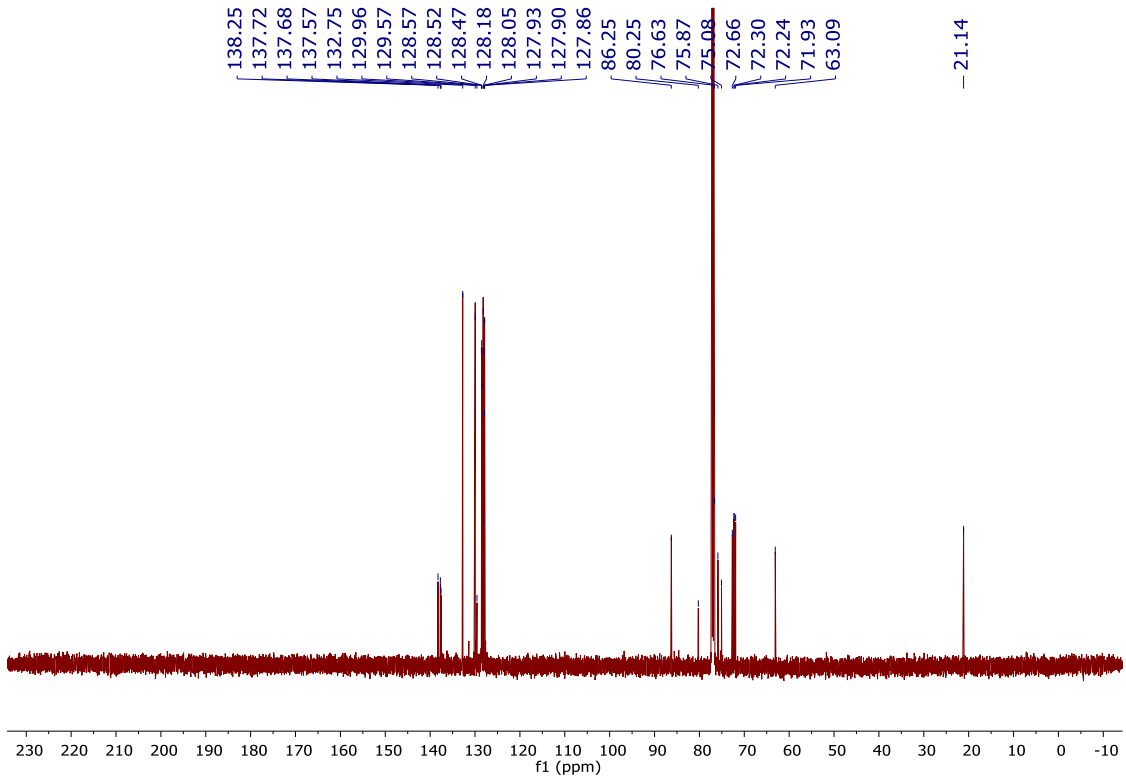
^{1}H-^{13}C gHSQCAD of **20** (500 MHz $CDCl_3$)



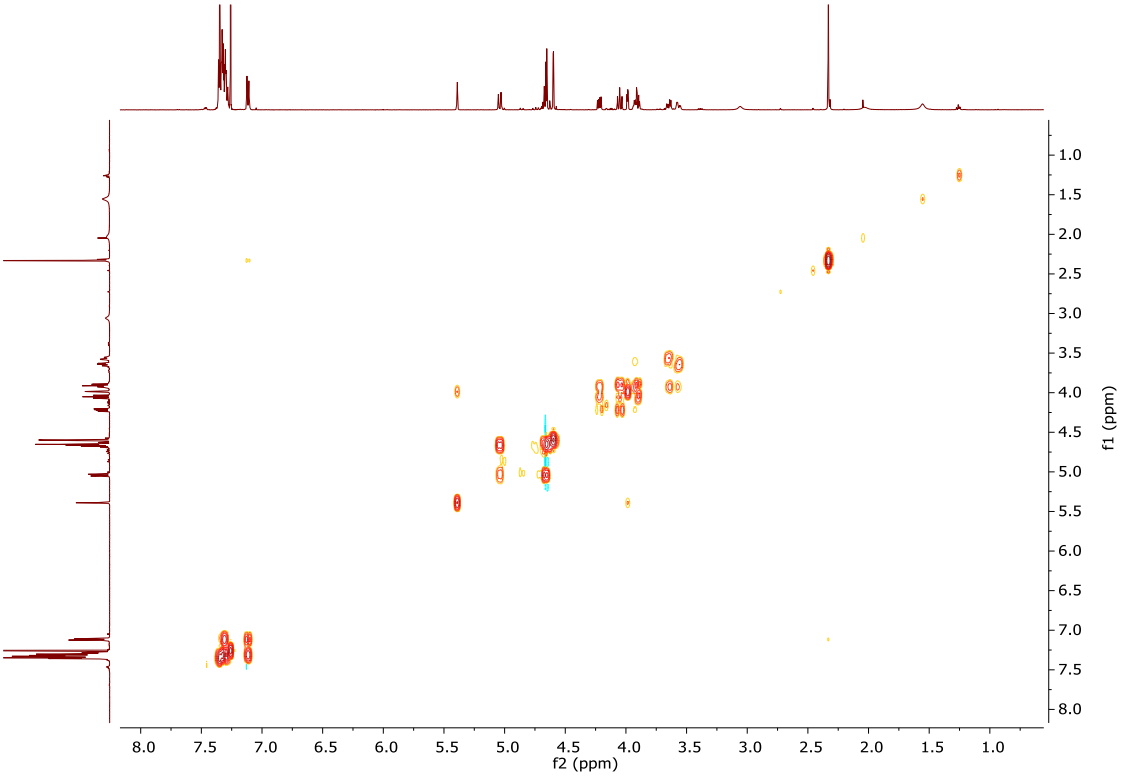
^{1}H-NMR of **21** (500 MHz $CDCl_3$)



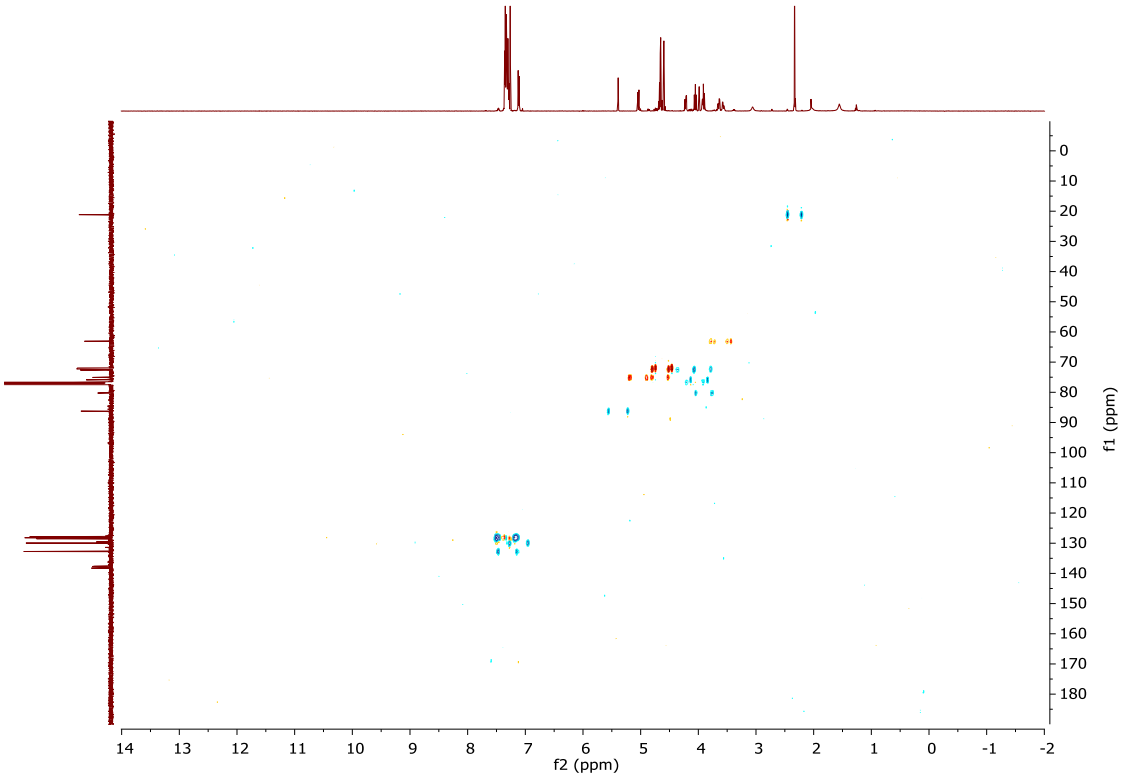
^{13}C-NMR of **21** (125 MHz $CDCl_3$)



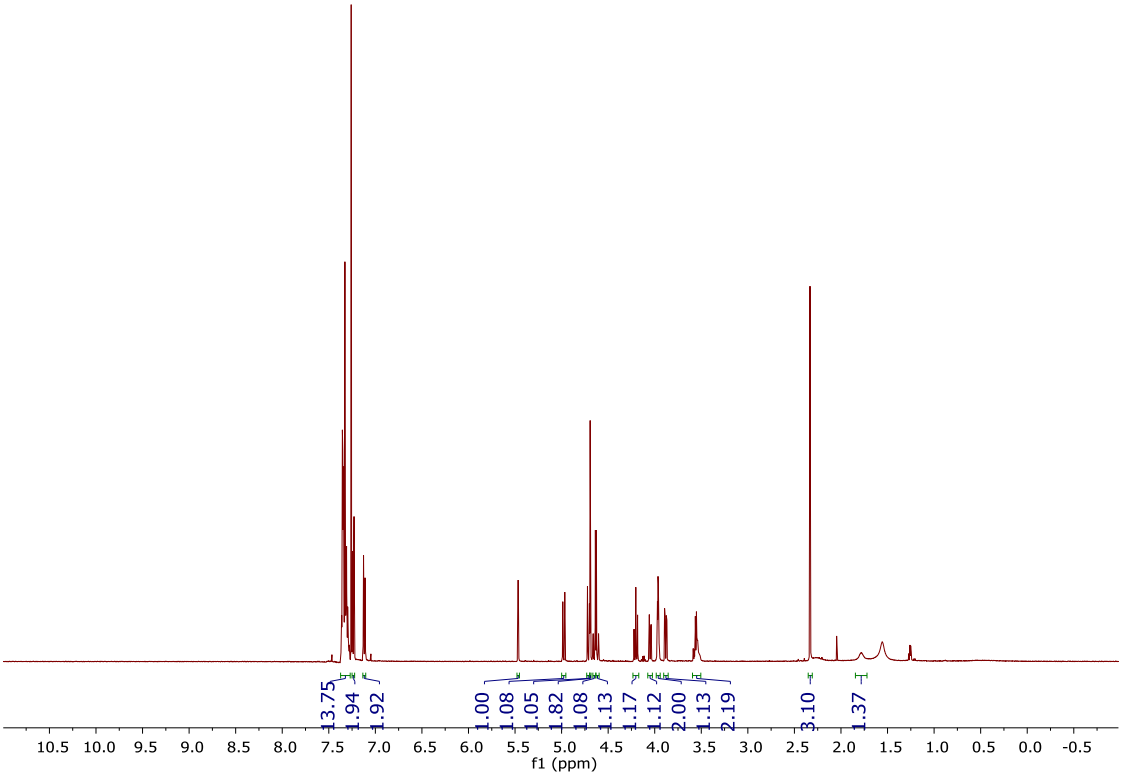
^{1}H-^{1}H gCOSY of **21** (500 MHz $CDCl_3$)



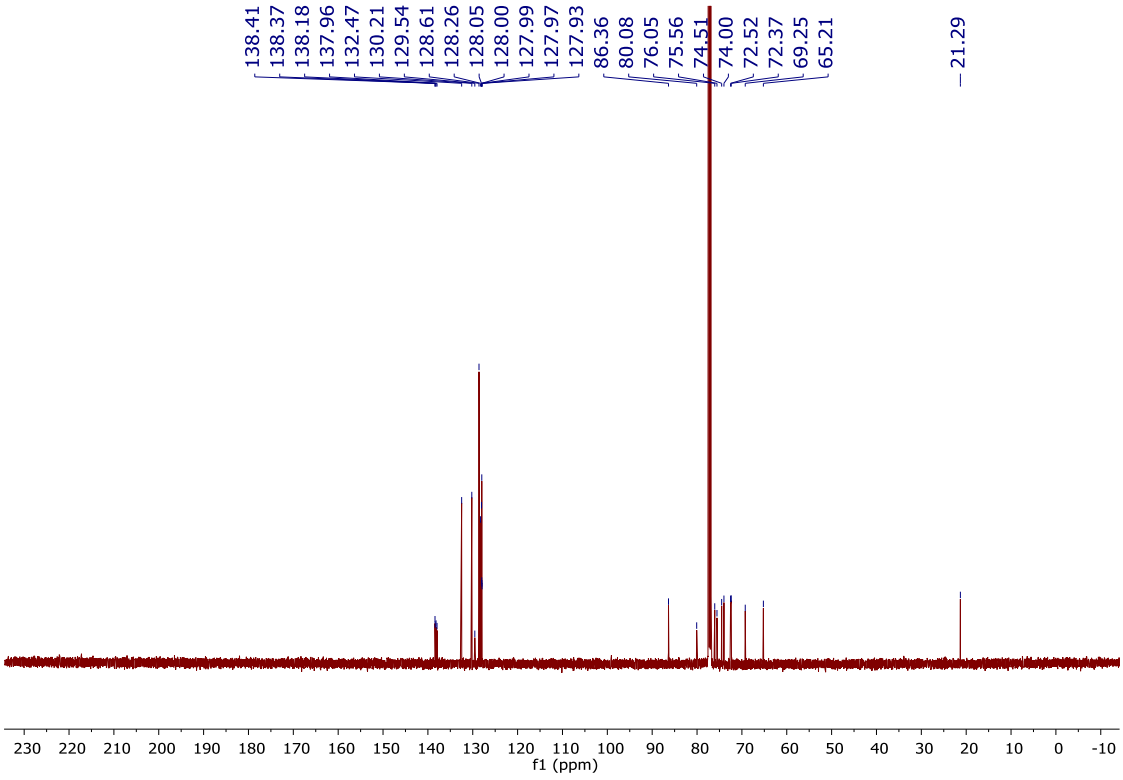
^{1}H-^{13}C gHSQCAD of **21** (500 MHz $CDCl_3$)



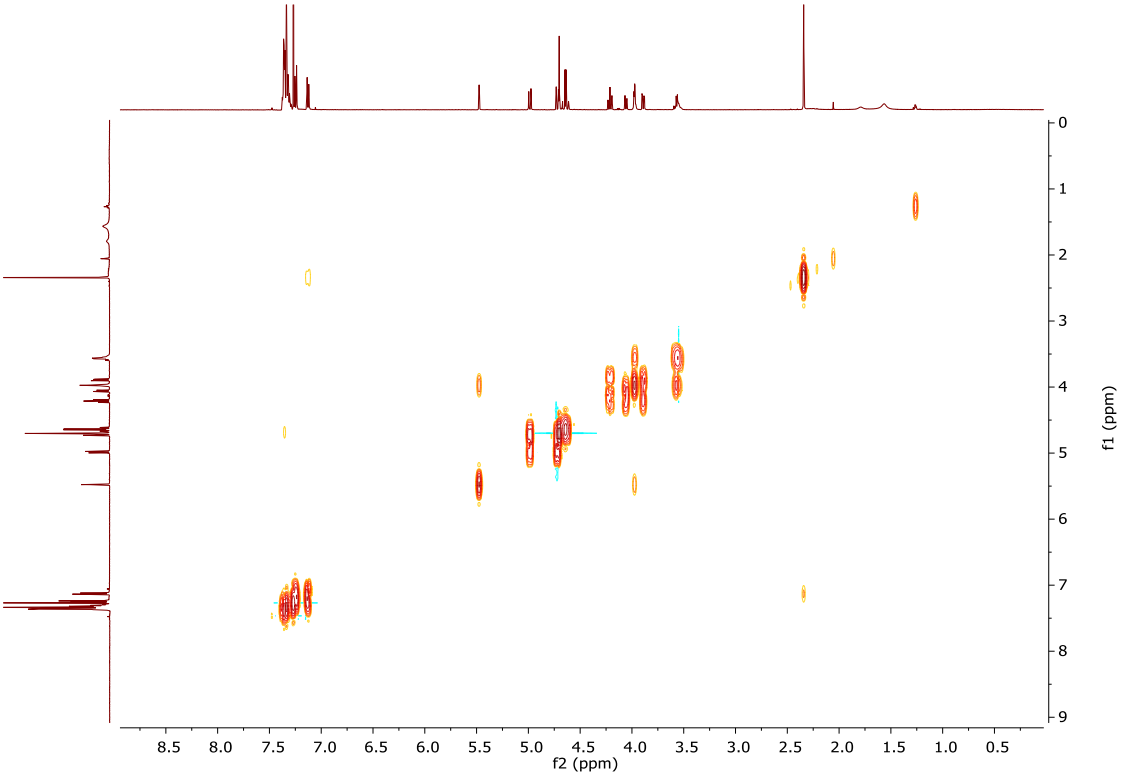
^{1}H-NMR of **22** (500 MHz $CDCl_3$)



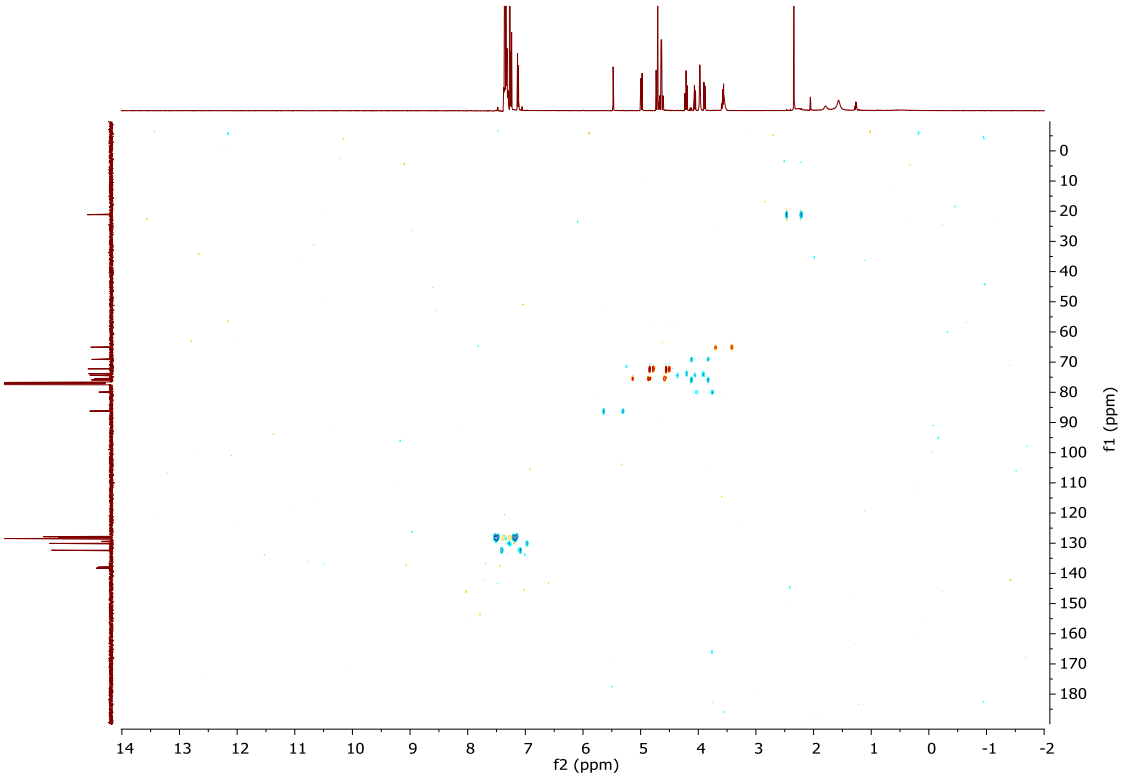
^{13}C-NMR of **22** (125 MHz $CDCl_3$)



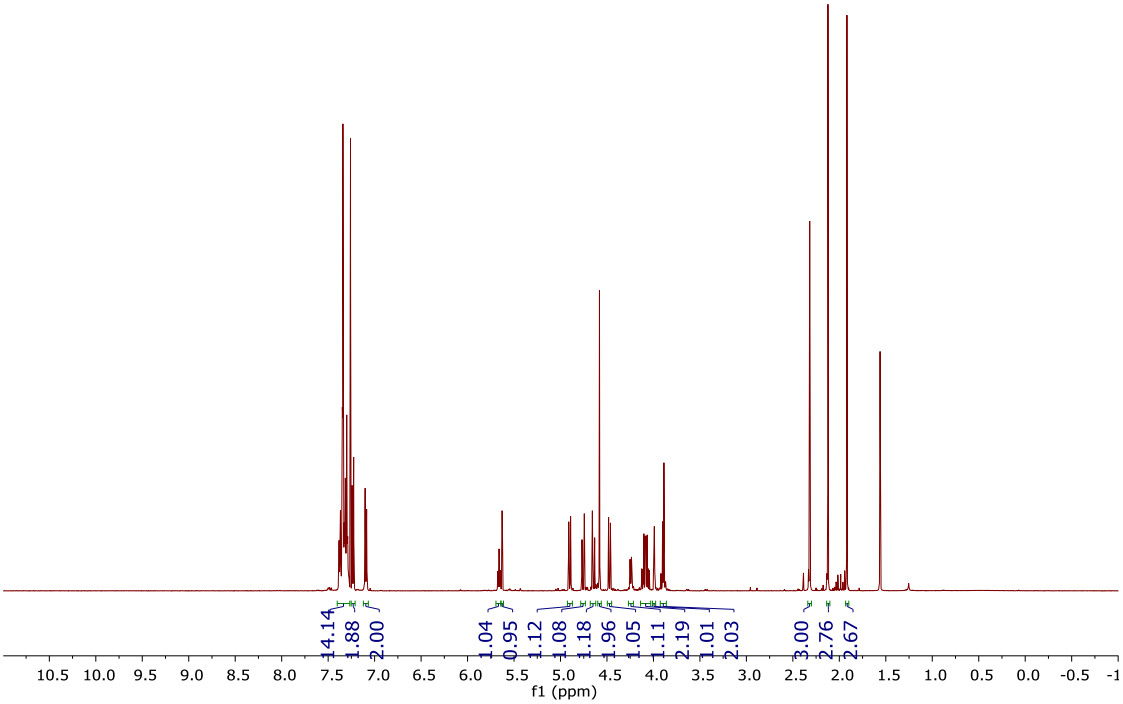
^{1}H-^{1}H gCOSY of **22** (500 MHz $CDCl_3$)



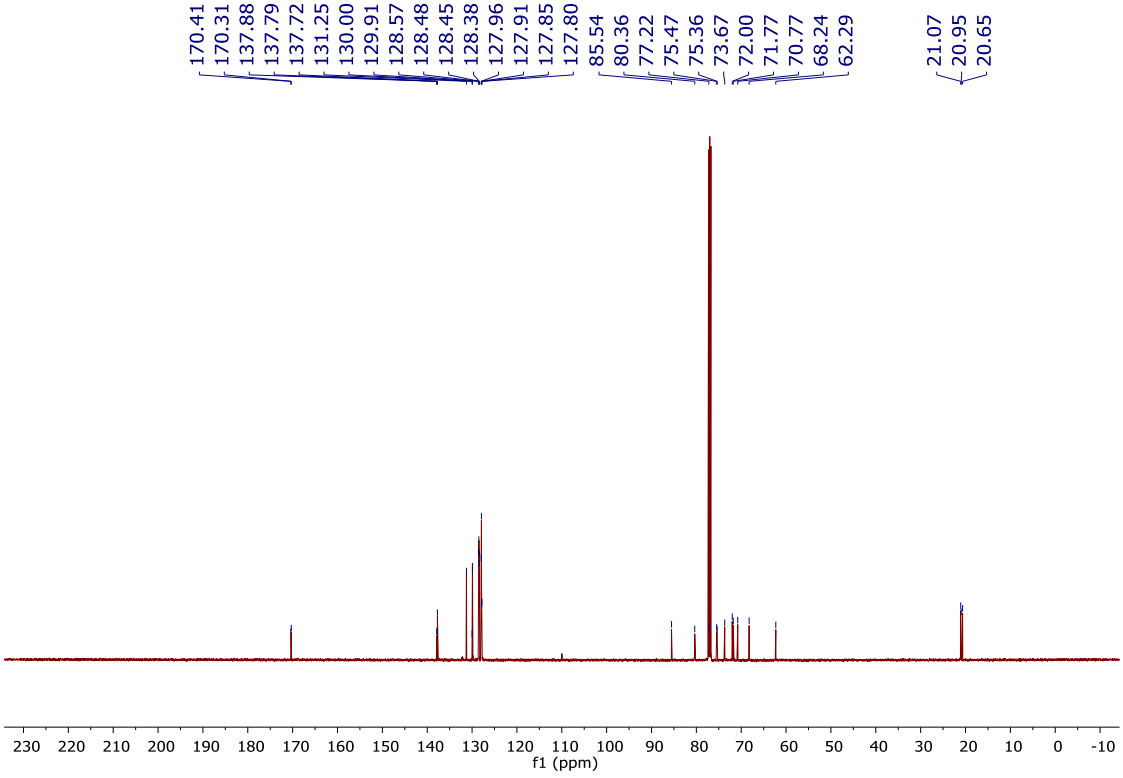
^{1}H-^{13}C gHSQCAD of **22** (500 MHz $CDCl_3$)



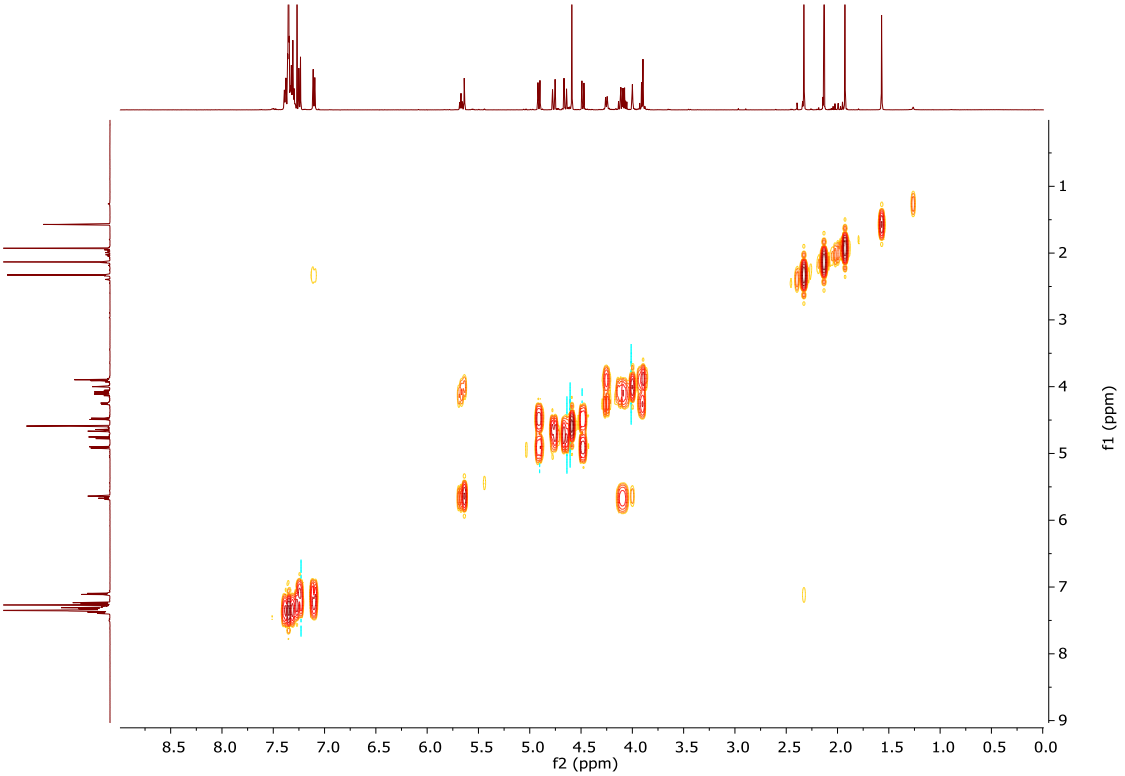
^{1}H-NMR of **2** (500 MHz $CDCl_3$)



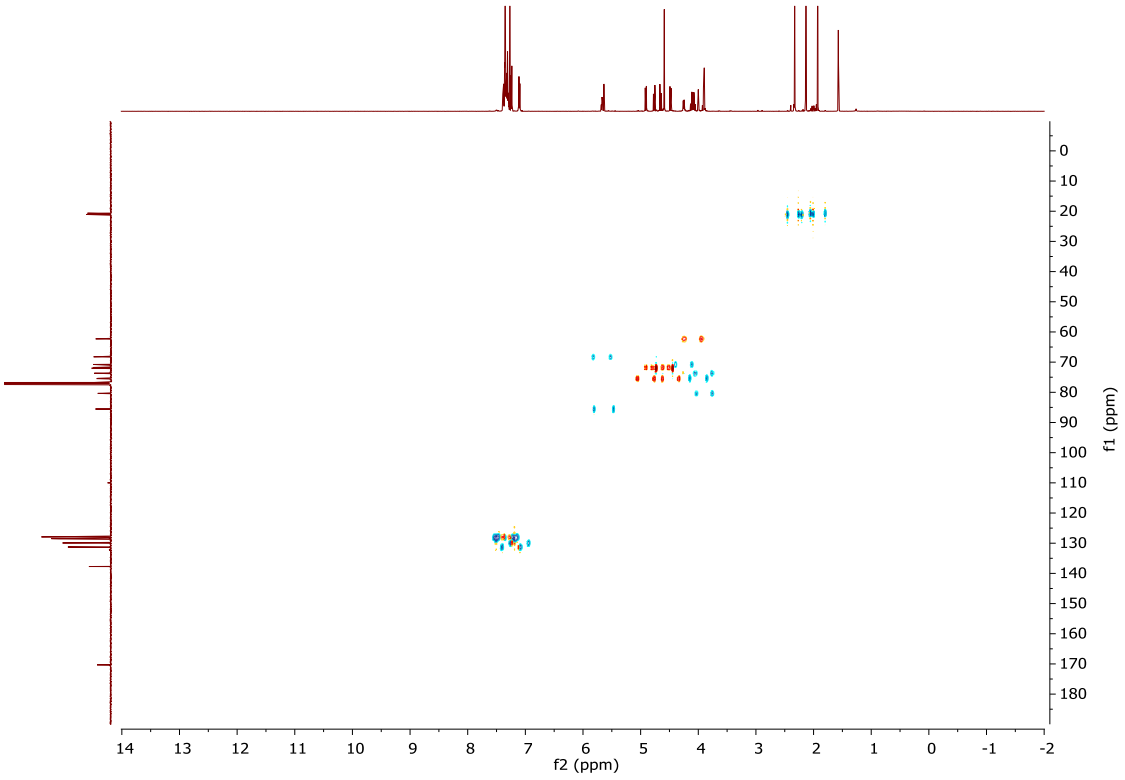
^{13}C-NMR of **2** (125 MHz $CDCl_3$)



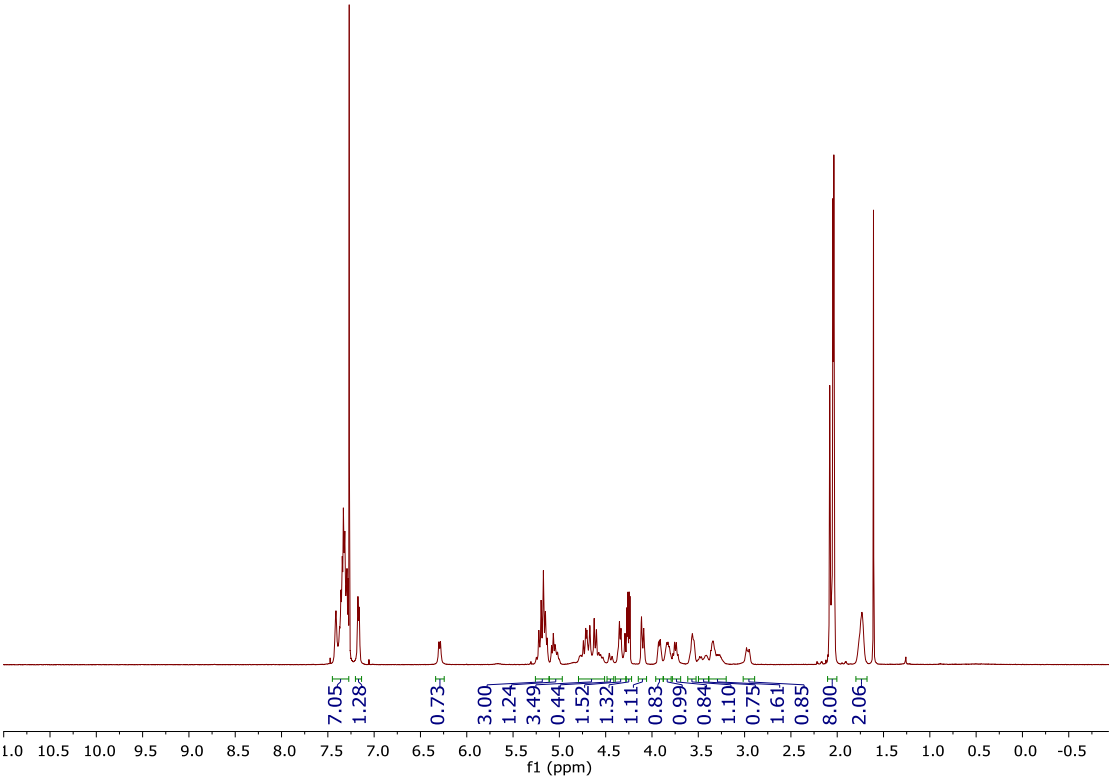
^{1}H-^{1}H gCOSY of **2** (500 MHz $CDCl_3$)



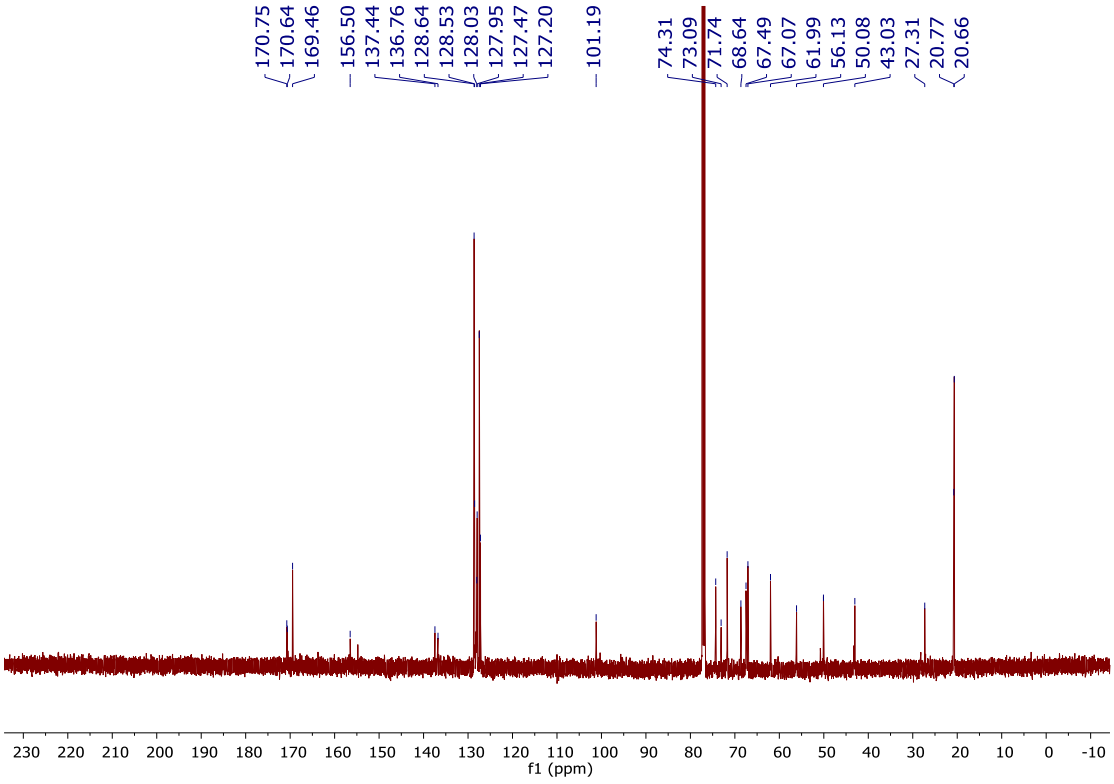
^{1}H-^{13}C gHSQCAD of **2** (500 MHz $CDCl_3$)



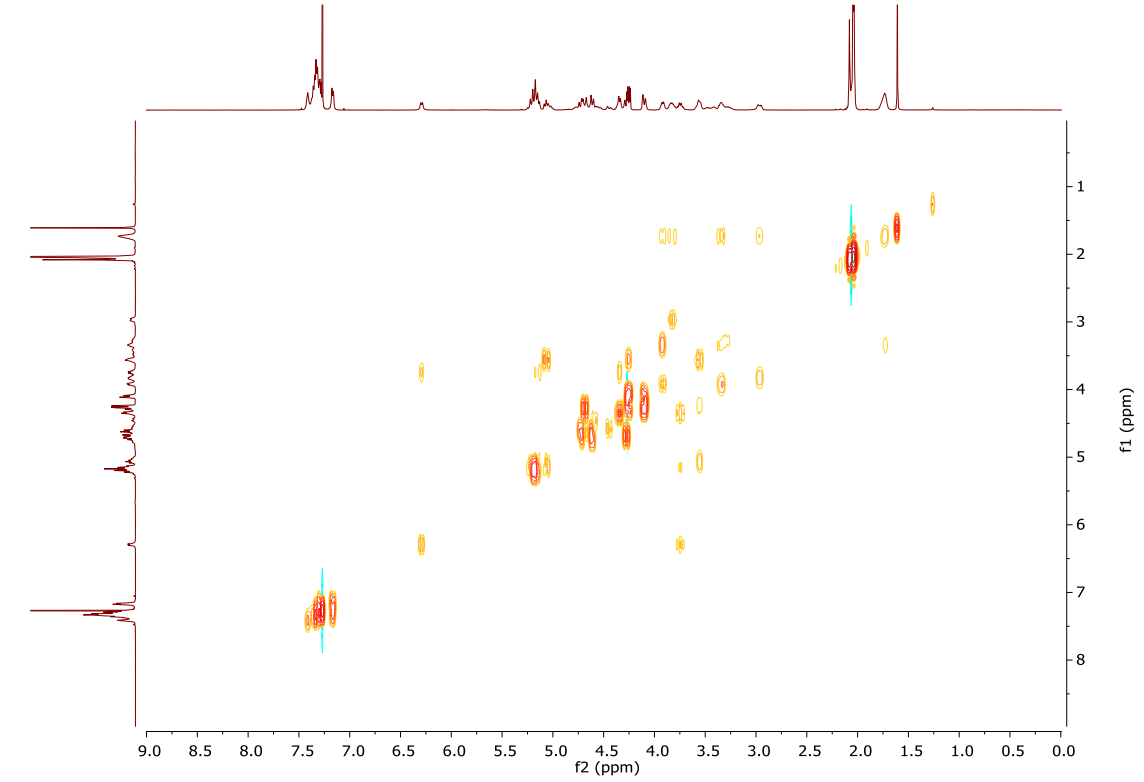
^{1}H-NMR of **S3** (500 MHz $CDCl_3$)



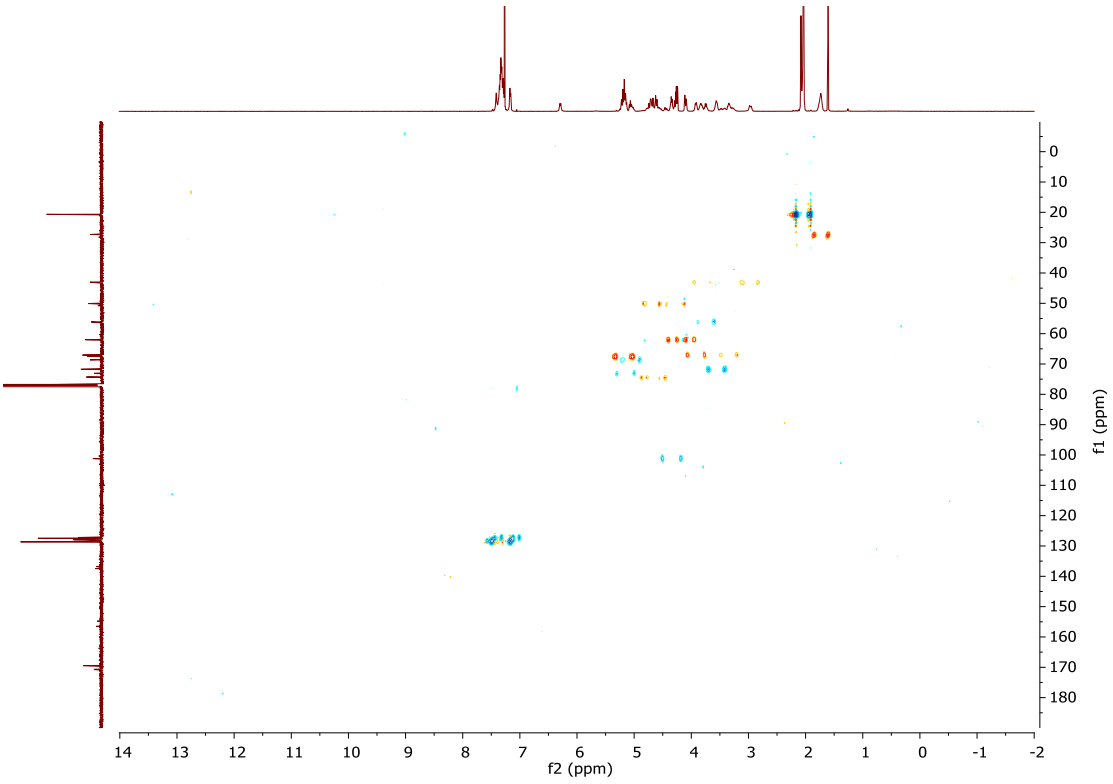
^{13}C-NMR of **S3** (125 MHz $CDCl_3$)



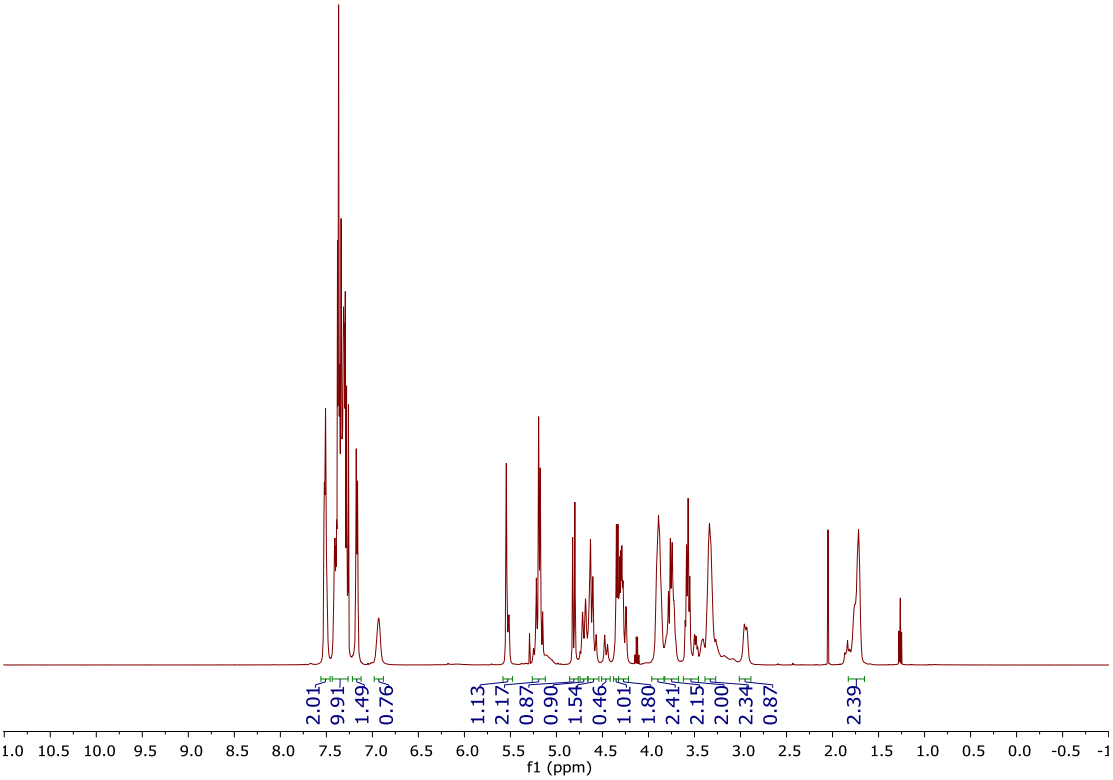
^{1}H-^{1}H gCOSY of **S3** (500 MHz $CDCl_3$)



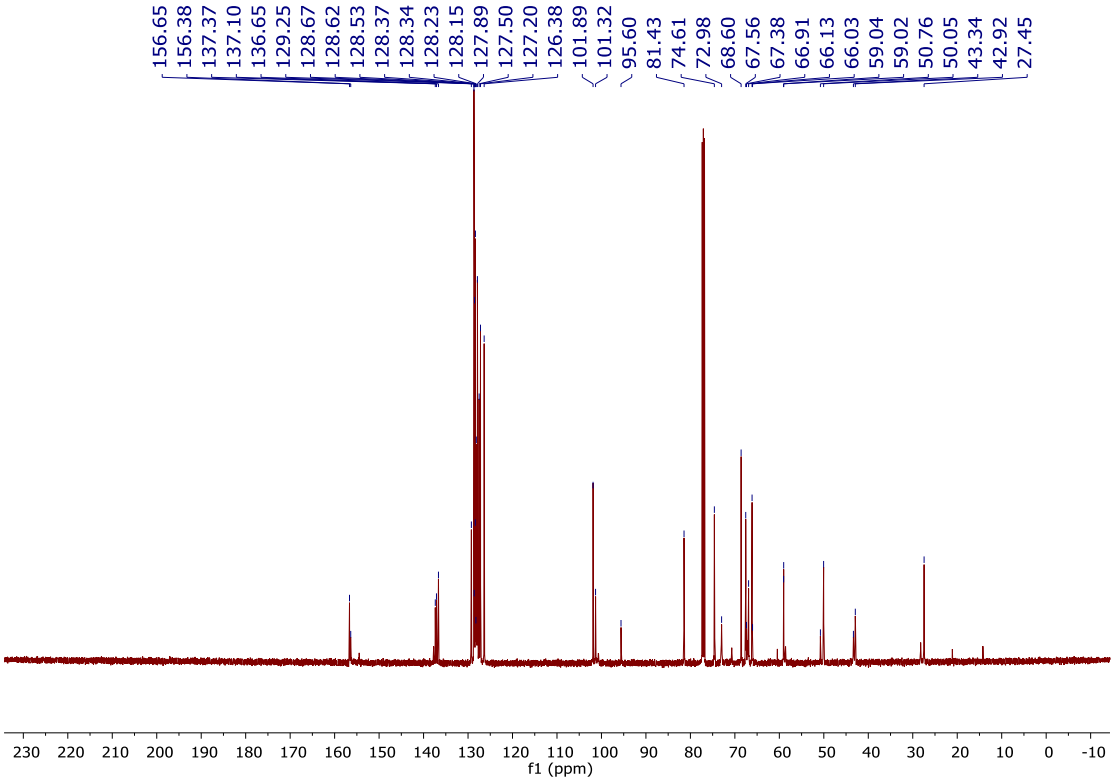
^{1}H-^{13}C gHSQCAD of **S3** (500 MHz $CDCl_3$)



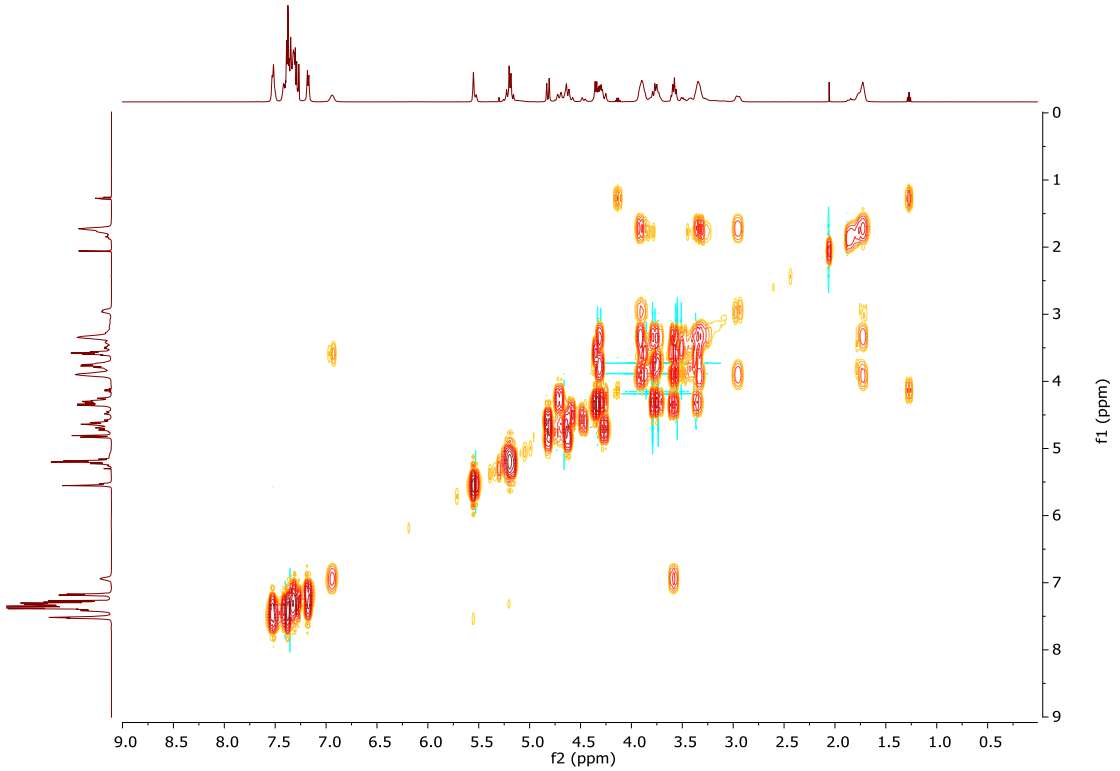
^{1}H-NMR of **S4** (500 MHz $CDCl_3$)



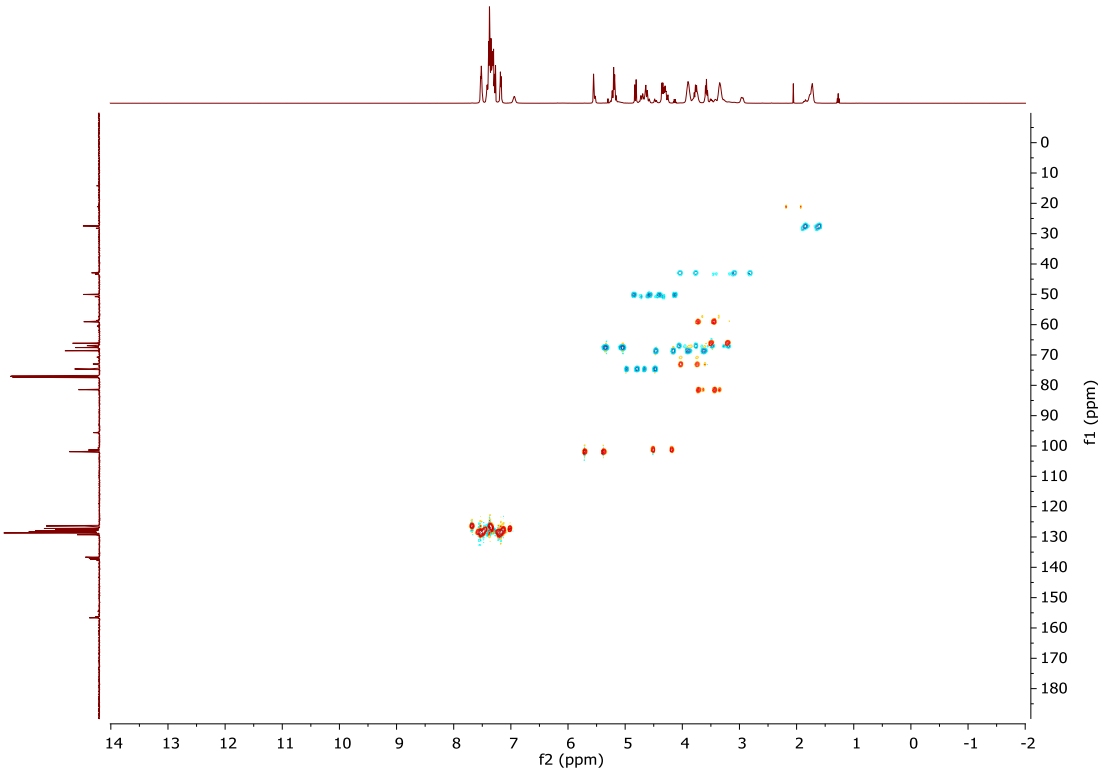
^{13}C-NMR of **S4** (125 MHz $CDCl_3$)



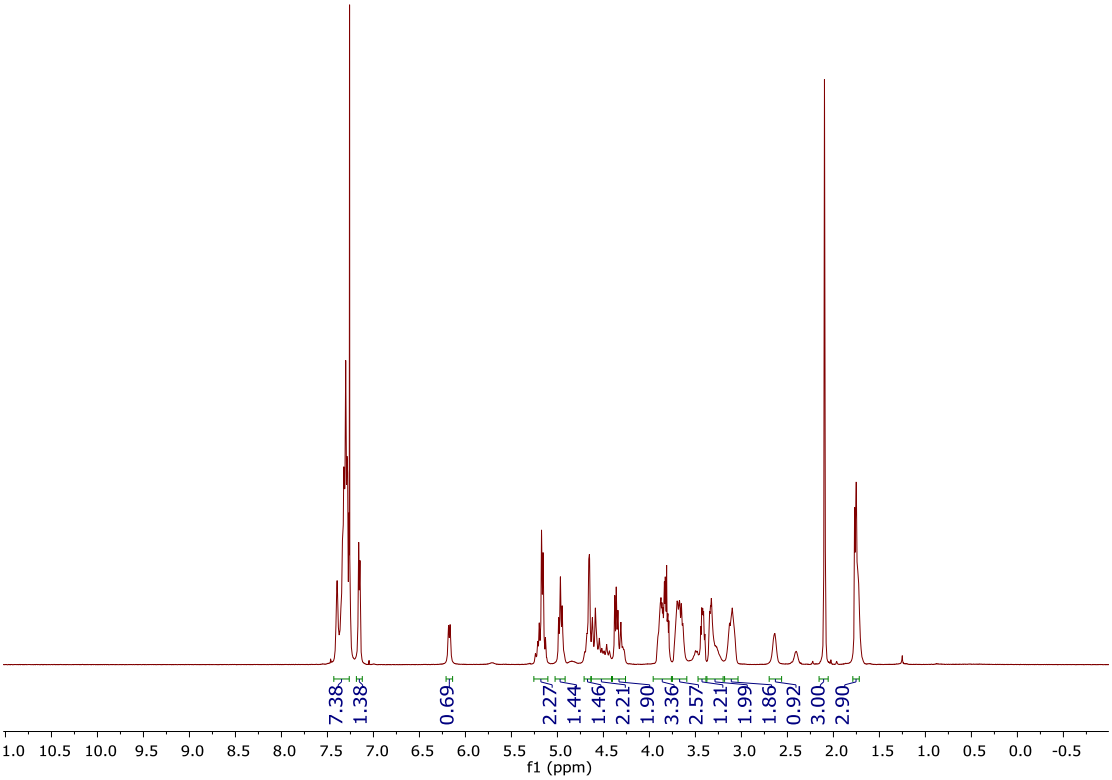
^{1}H-^{1}H gCOSY of **S4** (500 MHz $CDCl_3$)



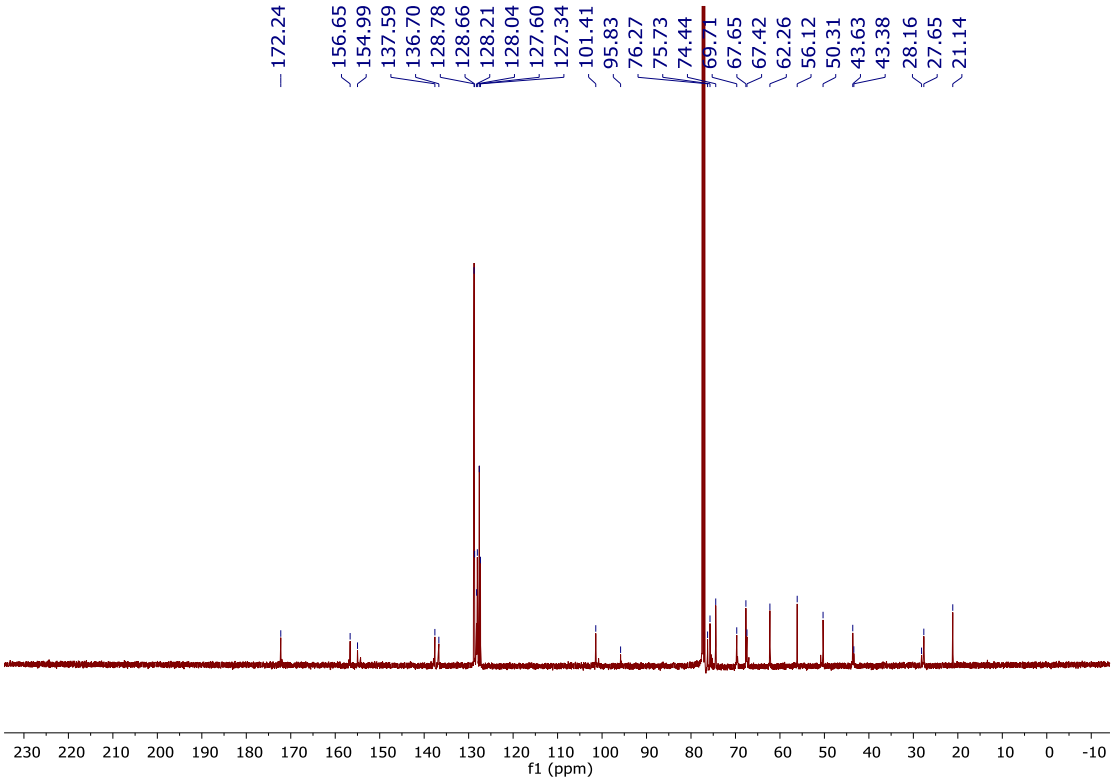
^{1}H-^{13}C gHSQCAD of **S4** (500 MHz $CDCl_3$)



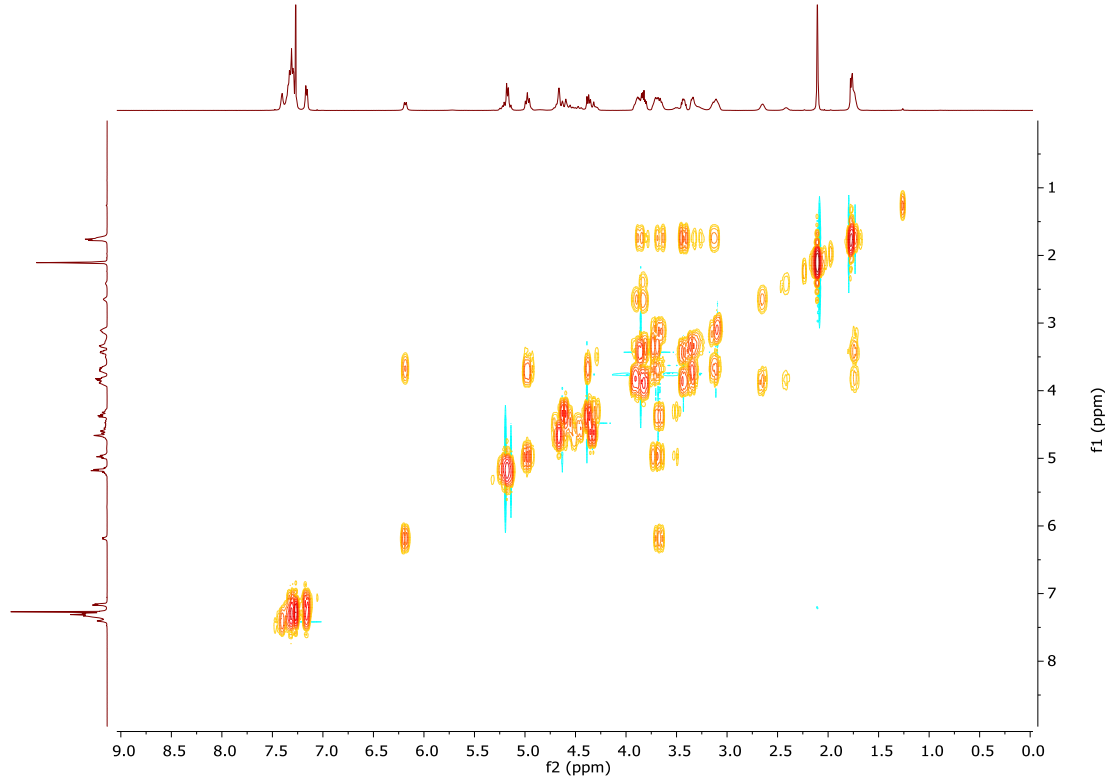
^{1}H-NMR of **S5** (500 MHz $CDCl_3$)



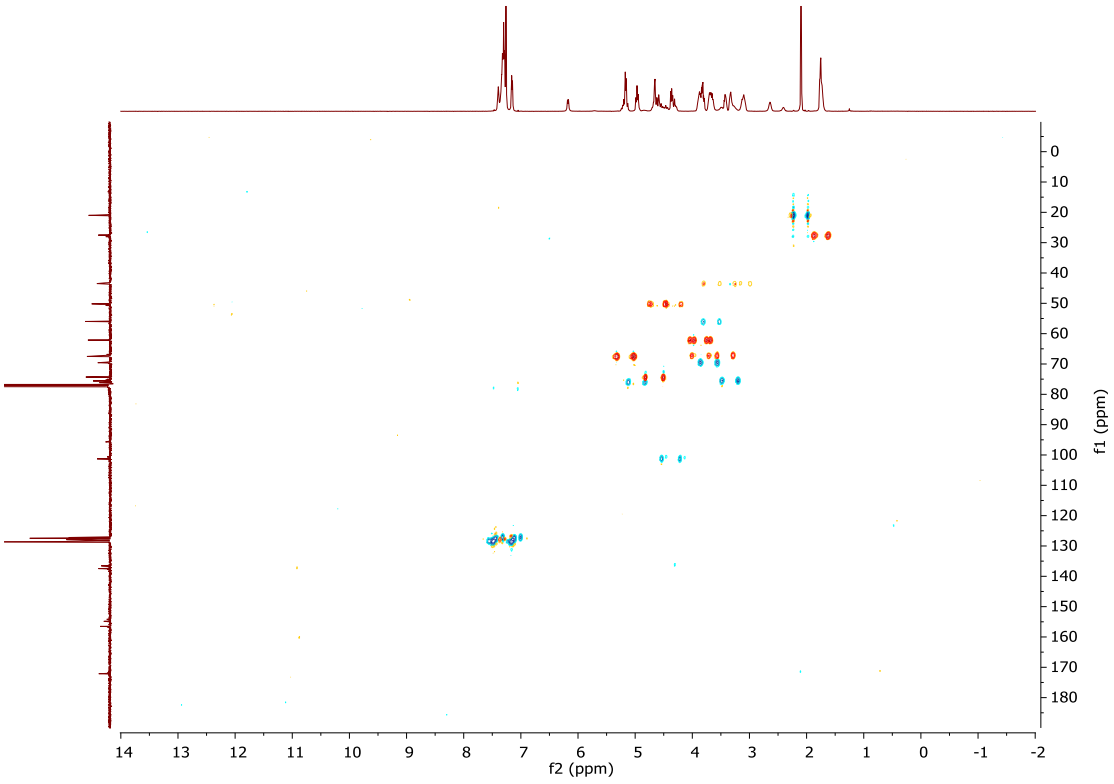
^{13}C-NMR of **S5** (125 MHz $CDCl_3$)



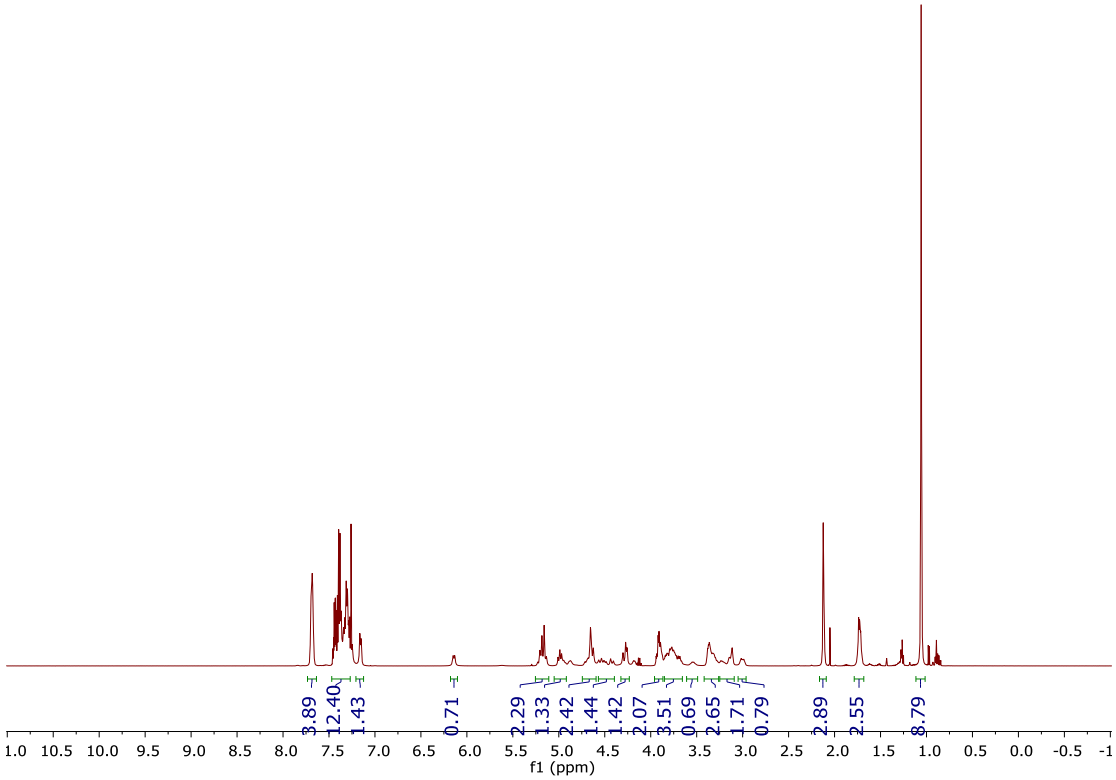
^{1}H-^{1}H gCOSY of **S5** (500 MHz $CDCl_3$)



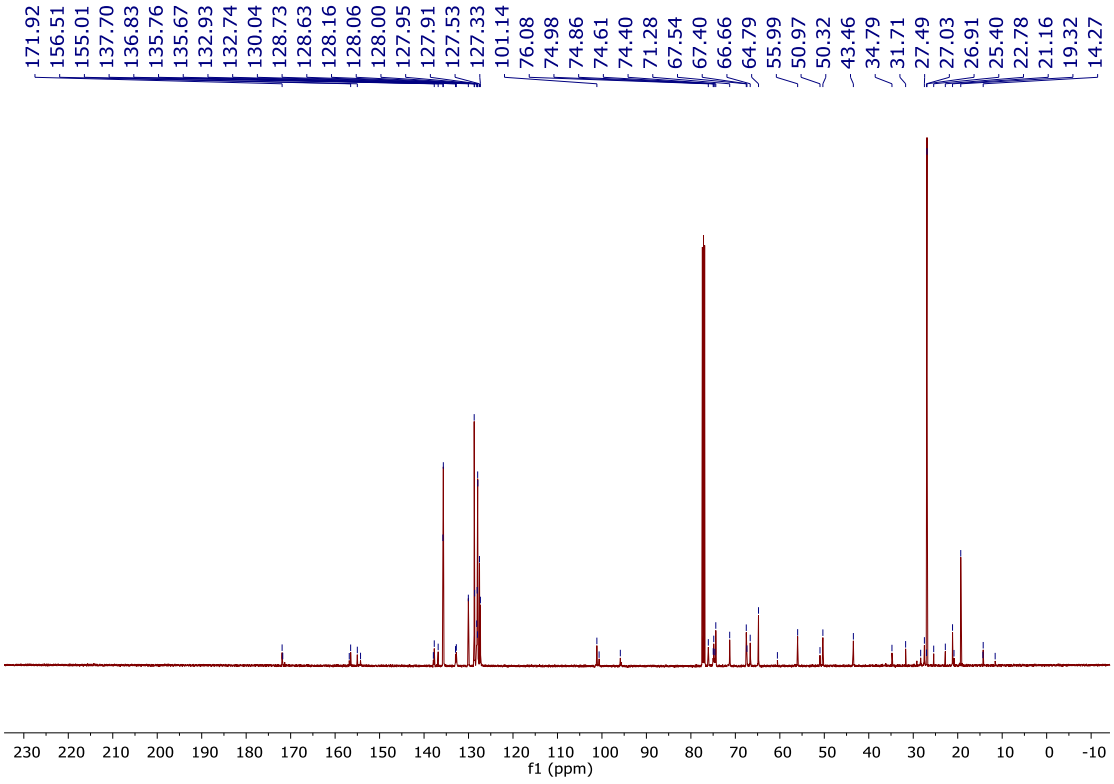
^{1}H-^{13}C gHSQCAD of **S5** (500 MHz $CDCl_3$)



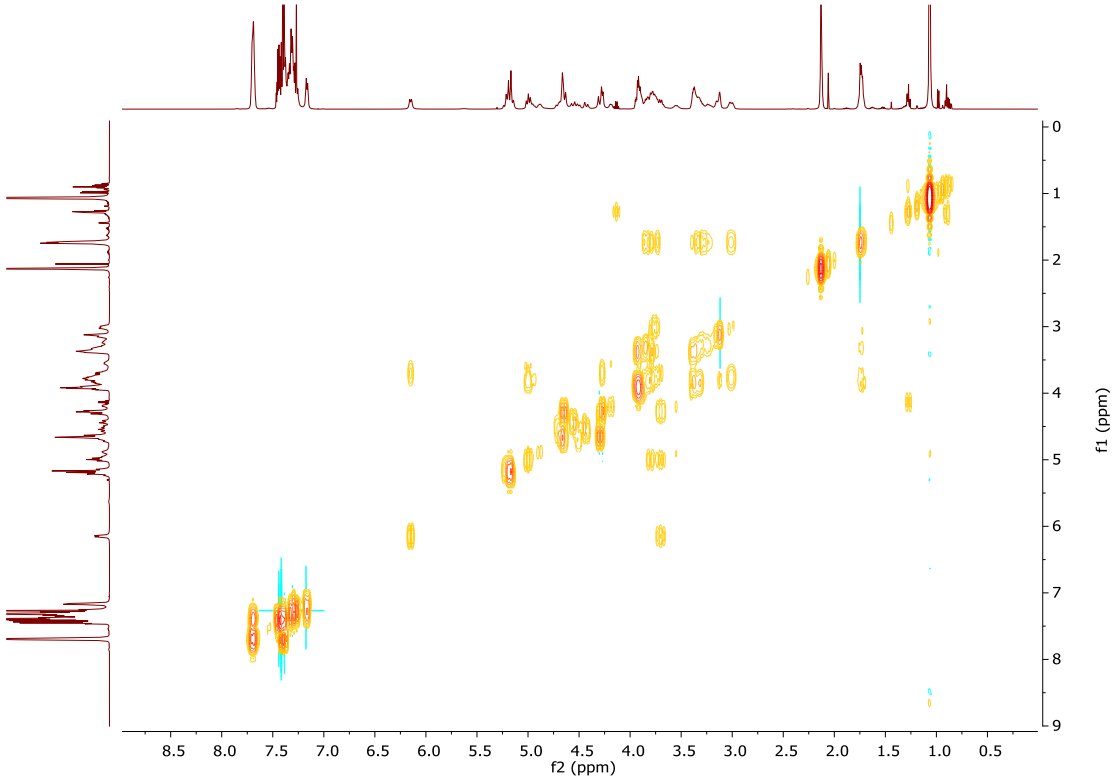
^{1}H-NMR of **3** (500 MHz $CDCl_3$)



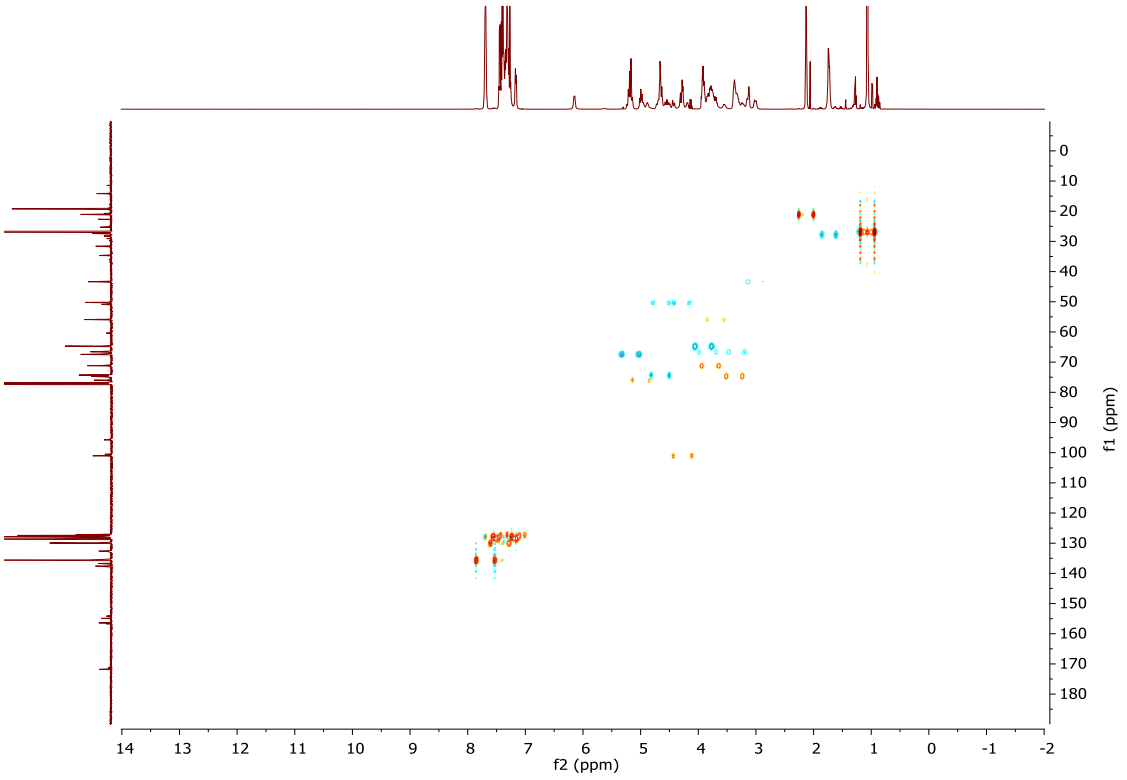
^{13}C-NMR of **3** (125 MHz $CDCl_3$)



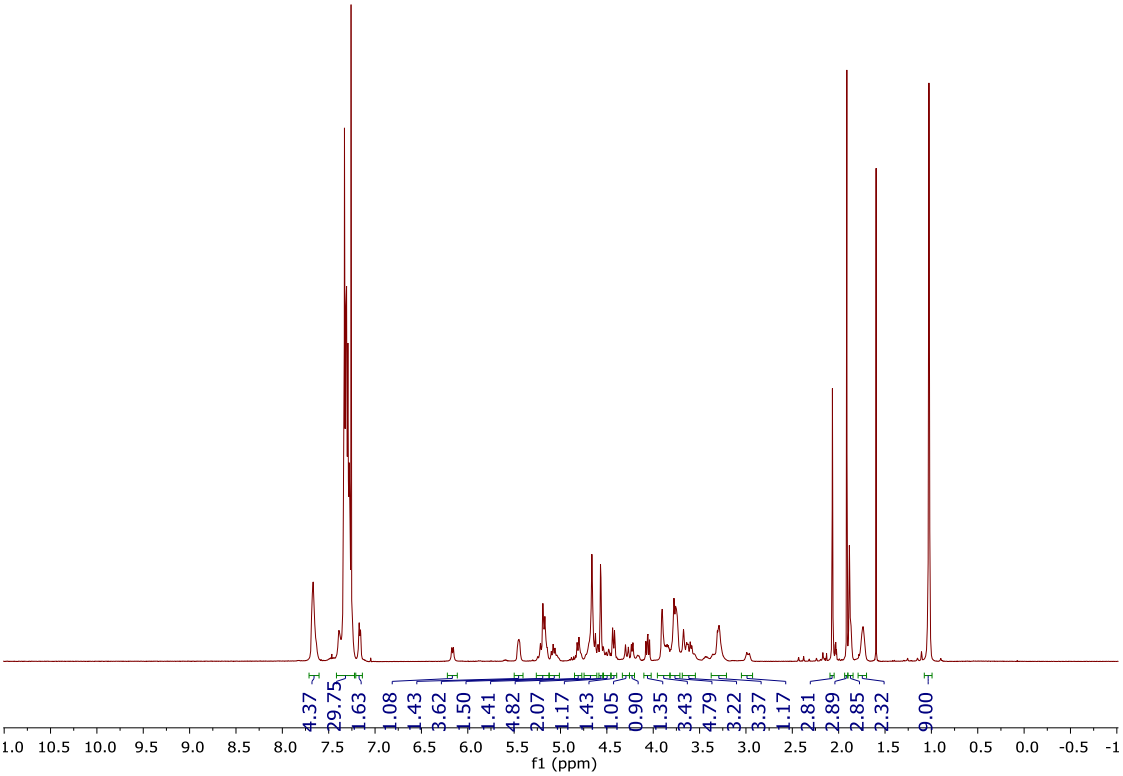
^{1}H-^{1}H gCOSY of **3** (500 MHz $CDCl_3$)



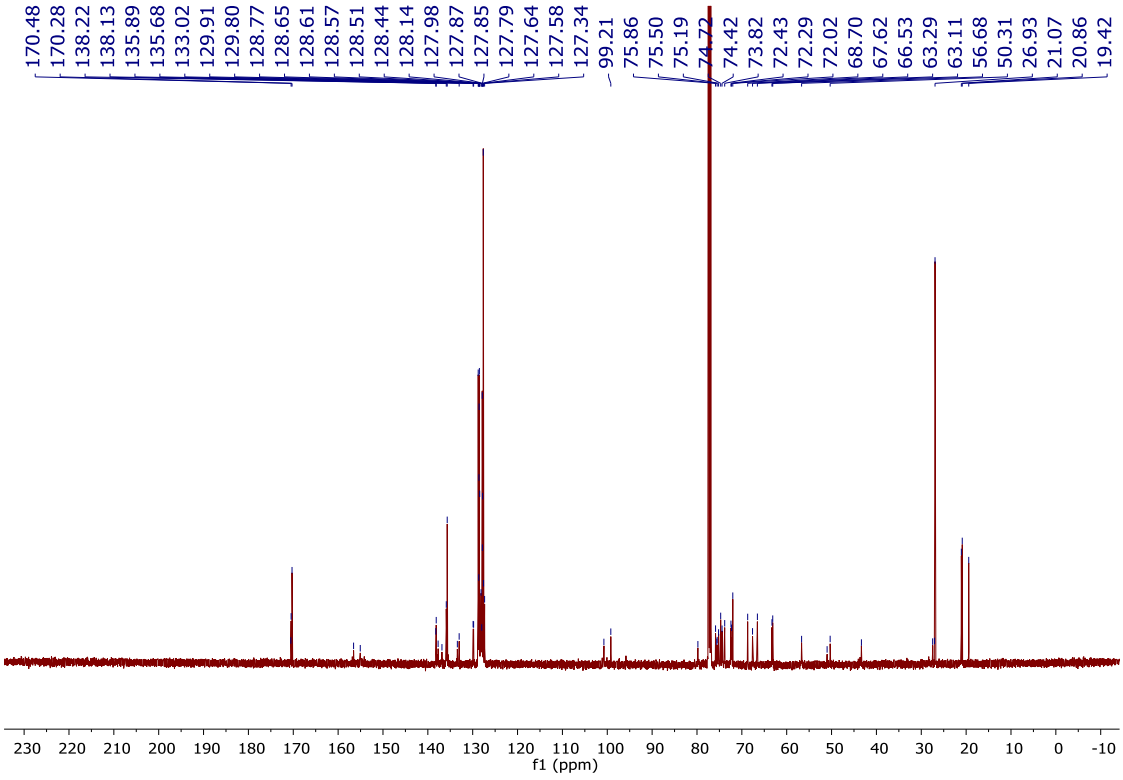
^{1}H-^{13}C gHSQCAD of **3** (500 MHz $CDCl_3$)



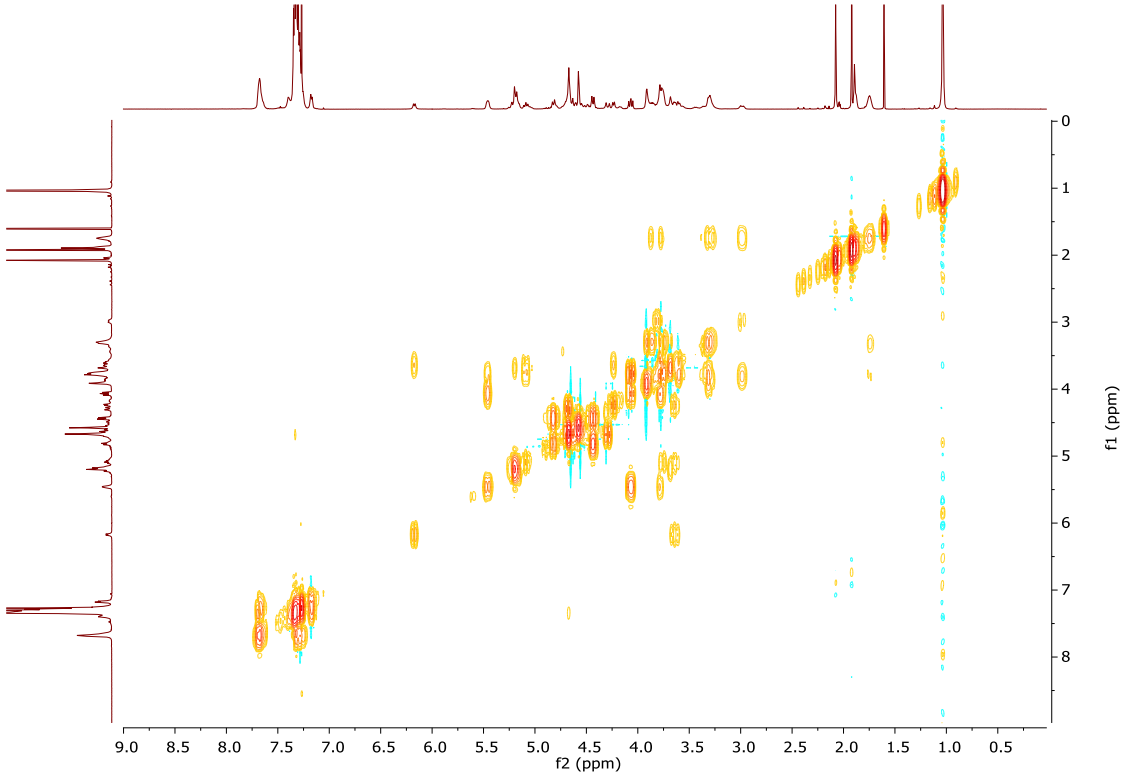
^{1}H-NMR of **23** (500 MHz $CDCl_3$)



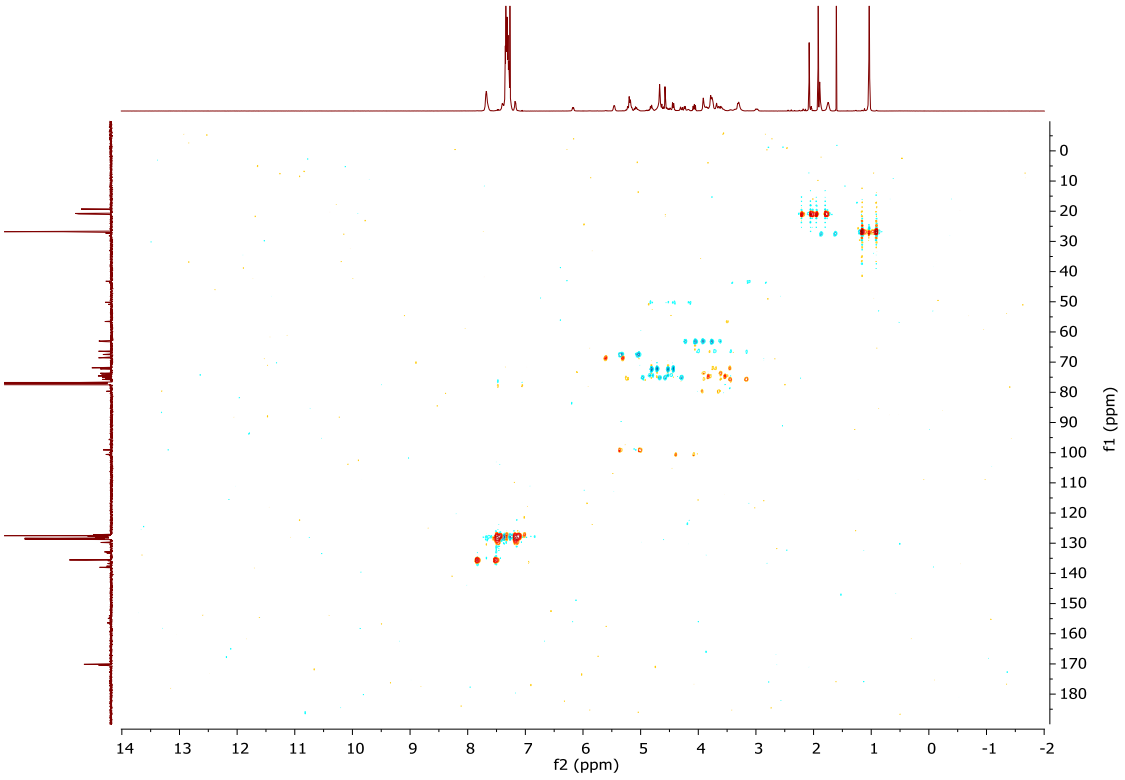
^{13}C-NMR of **23** (125 MHz $CDCl_3$)



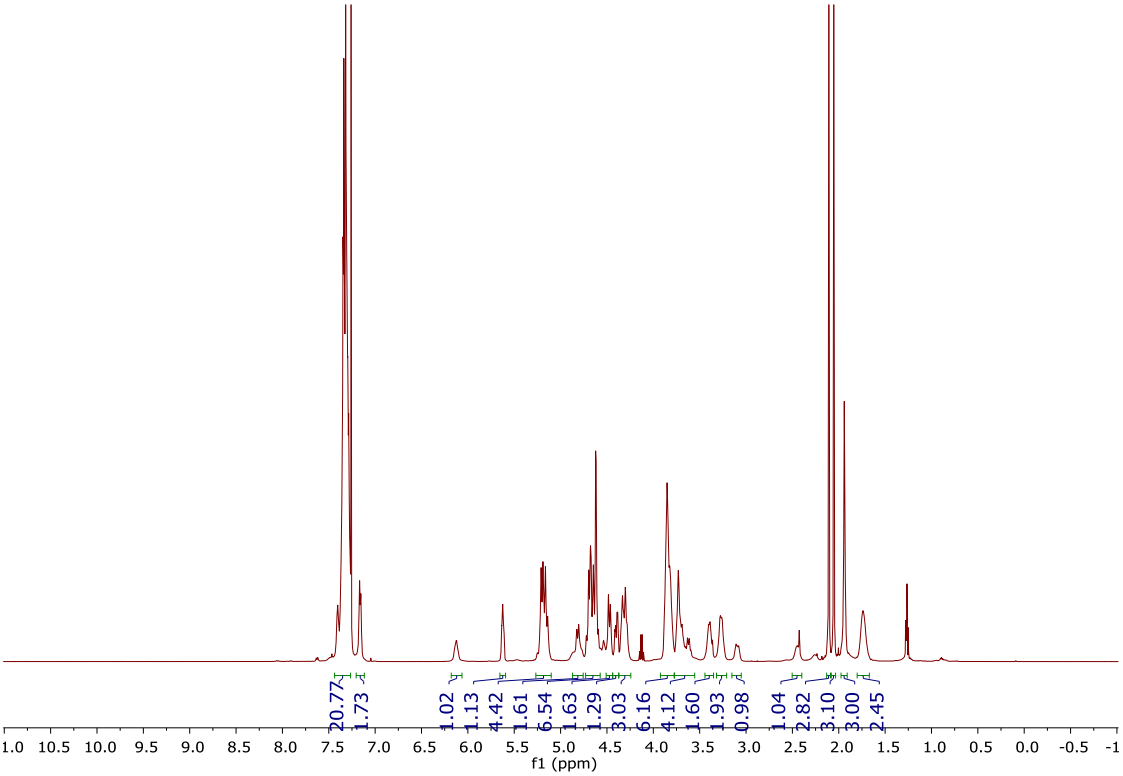
^{1}H-^{1}H gCOSY of **23** (500 MHz $CDCl_3$)



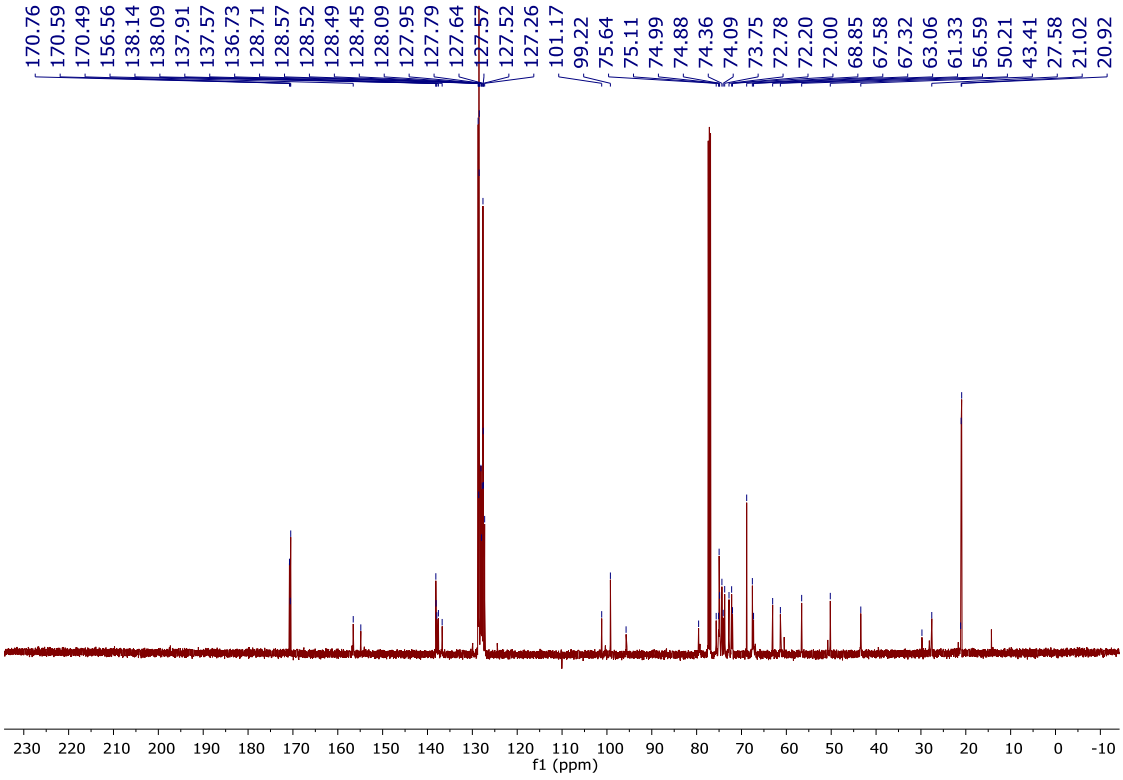
^{1}H-^{13}C gHSQCAD of **23** (500 MHz $CDCl_3$)



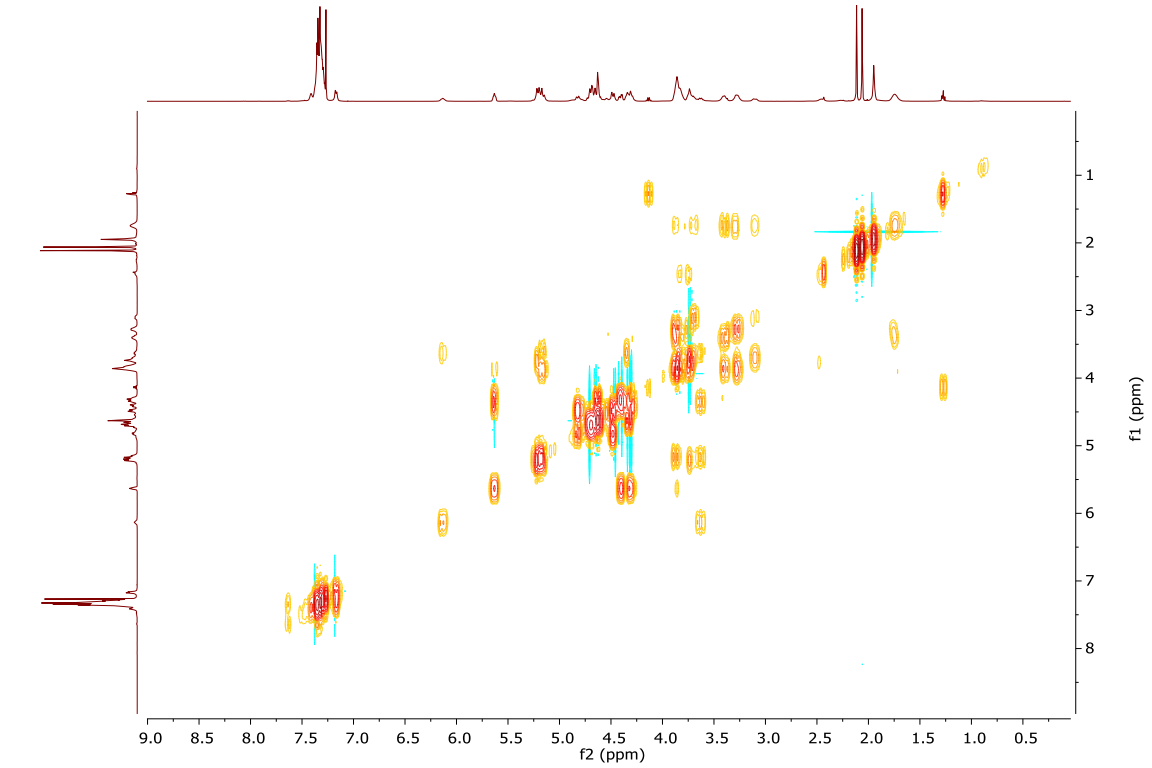
^{1}H-NMR of **24** (500 MHz $CDCl_3$)



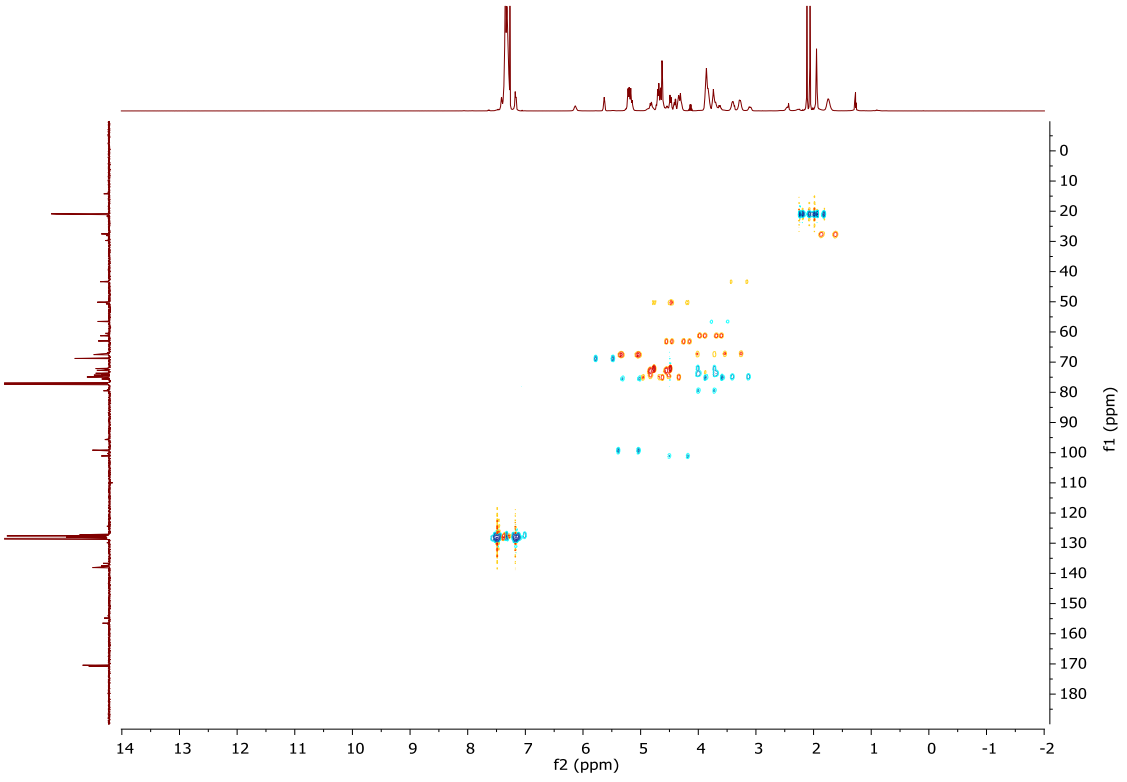
^{13}C-NMR of **24** (125 MHz $CDCl_3$)



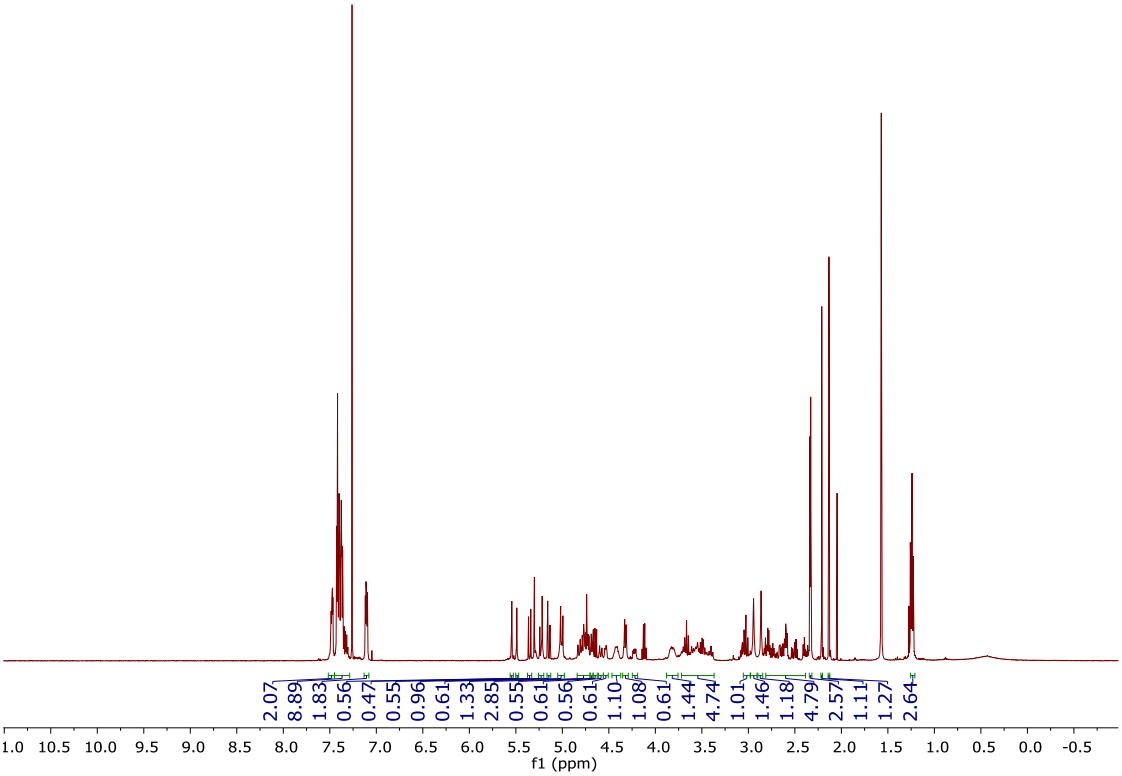
^{1}H-^{1}H gCOSY of **24** (500 MHz $CDCl_3$)



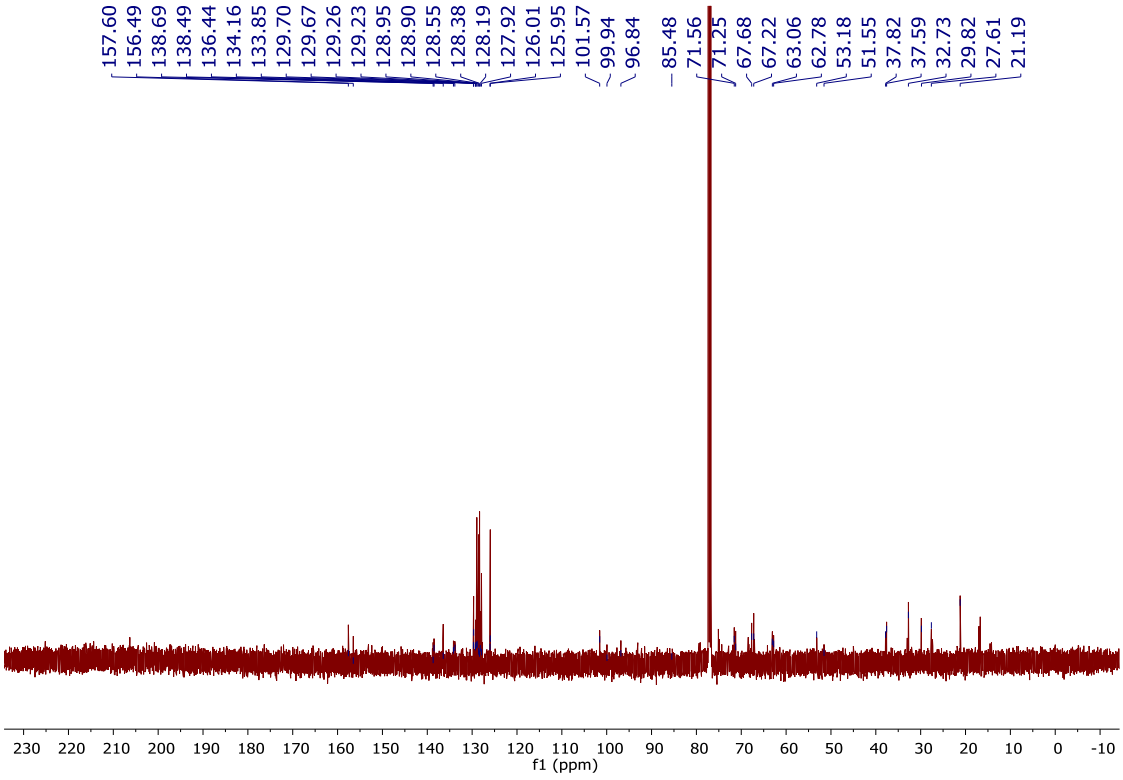
^{1}H-^{13}C gHSQCAD of **24** (500 MHz $CDCl_3$)



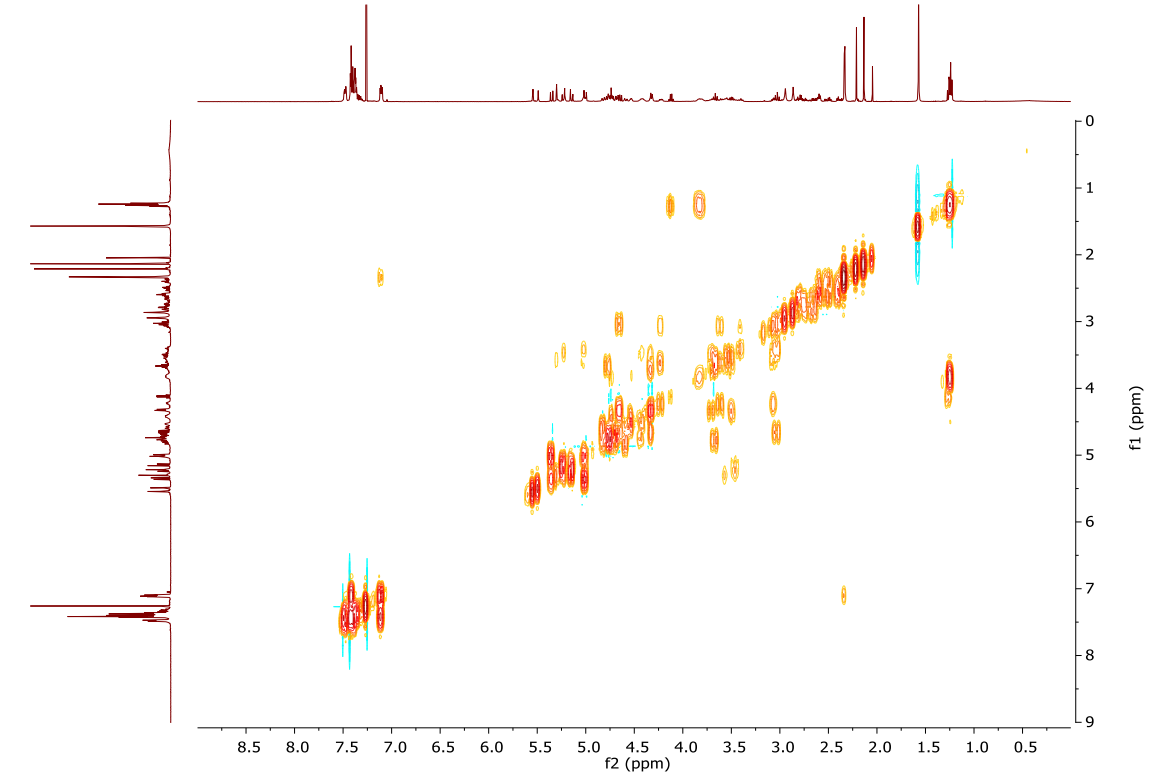
^{1}H-NMR of **25** (500 MHz $CDCl_3$)



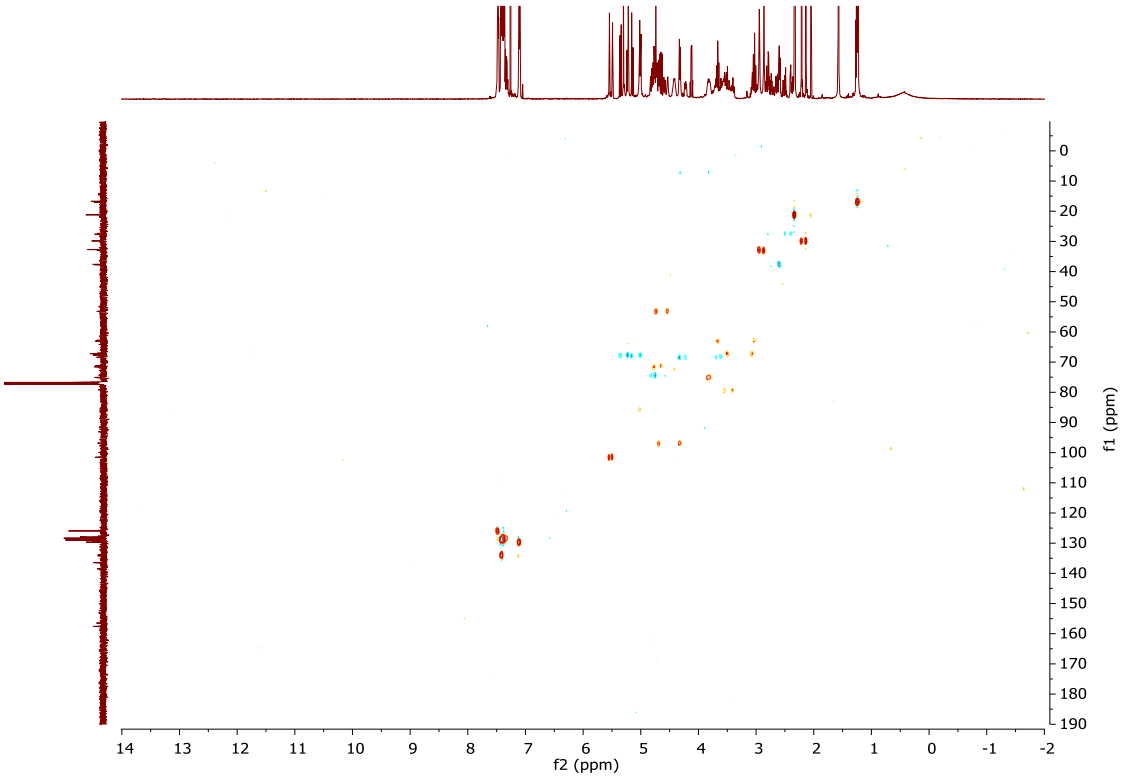
^{13}C-NMR of **25** (125 MHz $CDCl_3$)



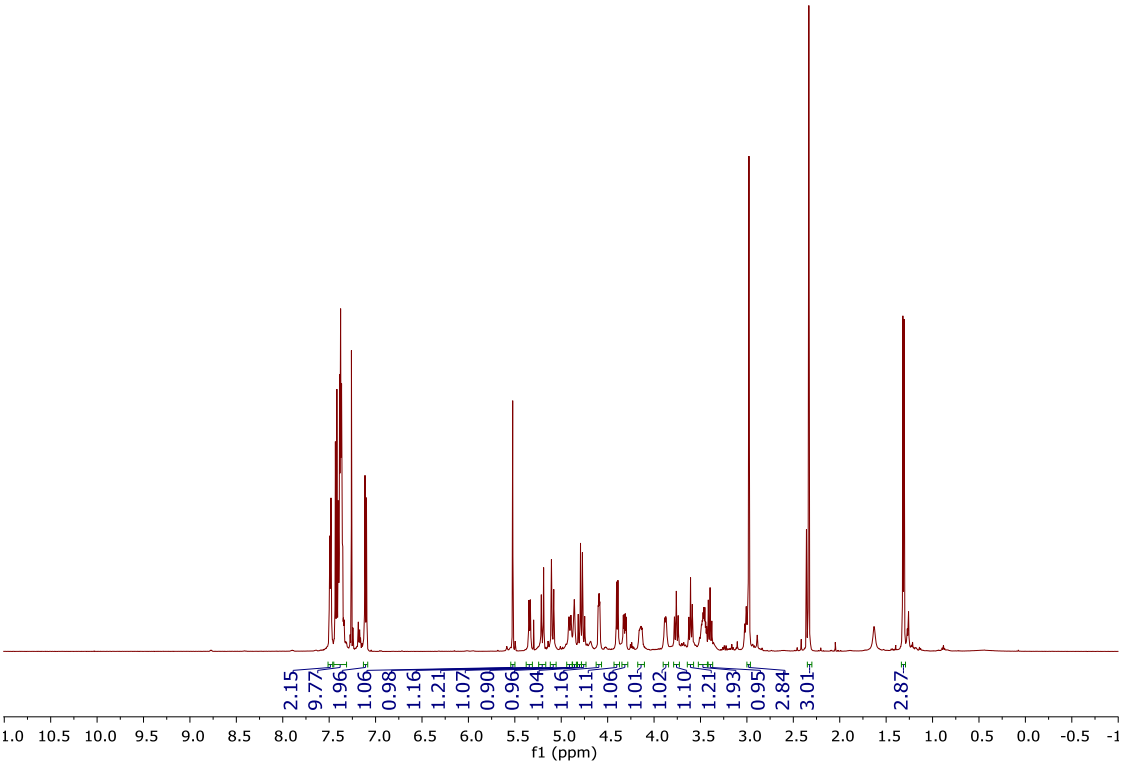
^{1}H-^{1}H gCOSY of **25** (500 MHz $CDCl_3$)



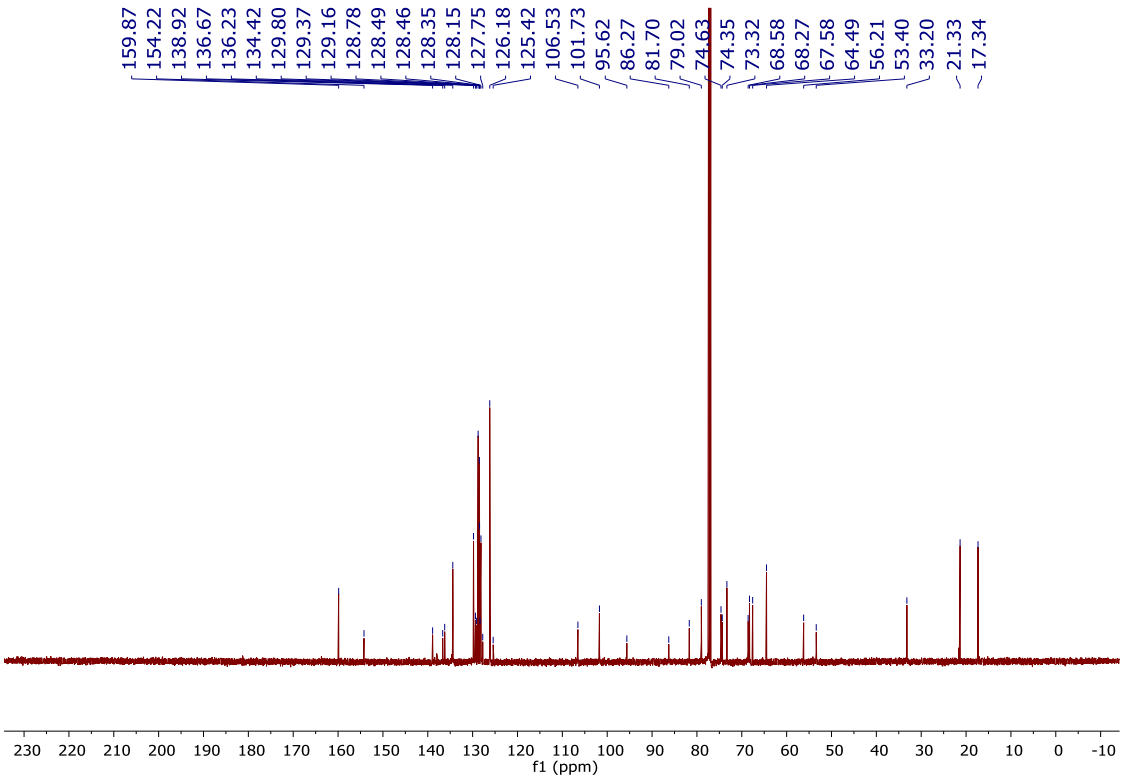
^{1}H-^{13}C gHSQCAD of **25** (500 MHz $CDCl_3$)



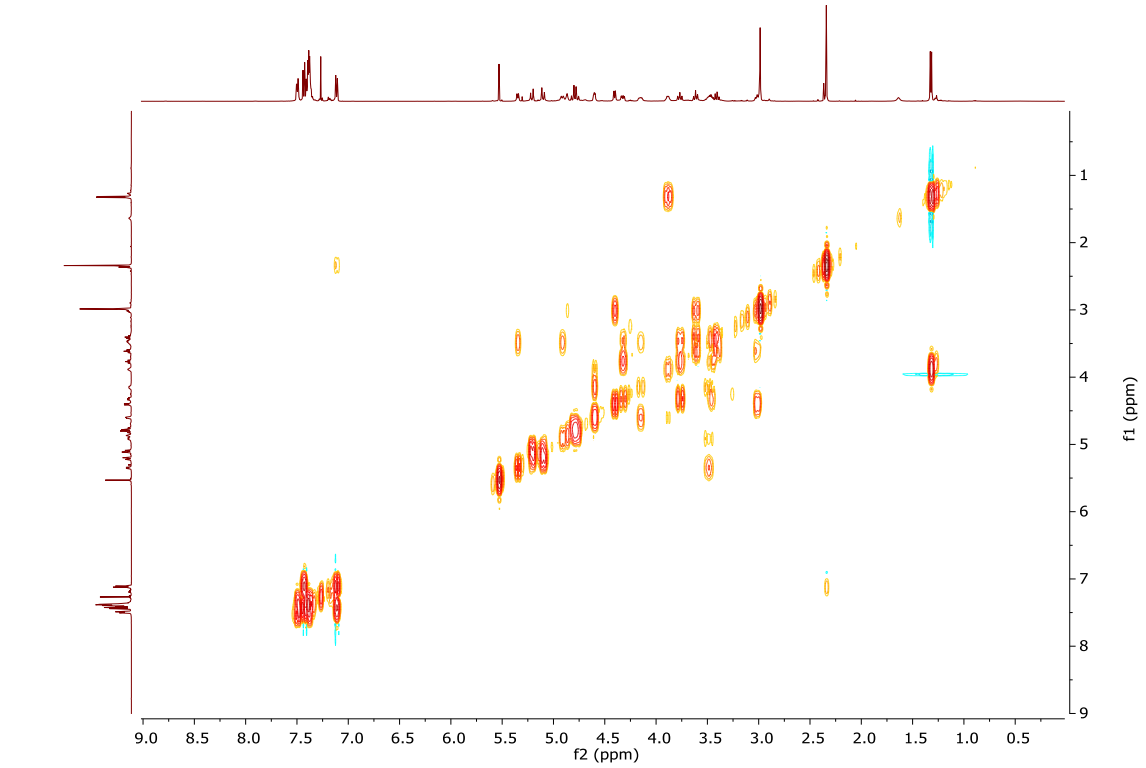
^{1}H-NMR of **26** (500 MHz $CDCl_3$)



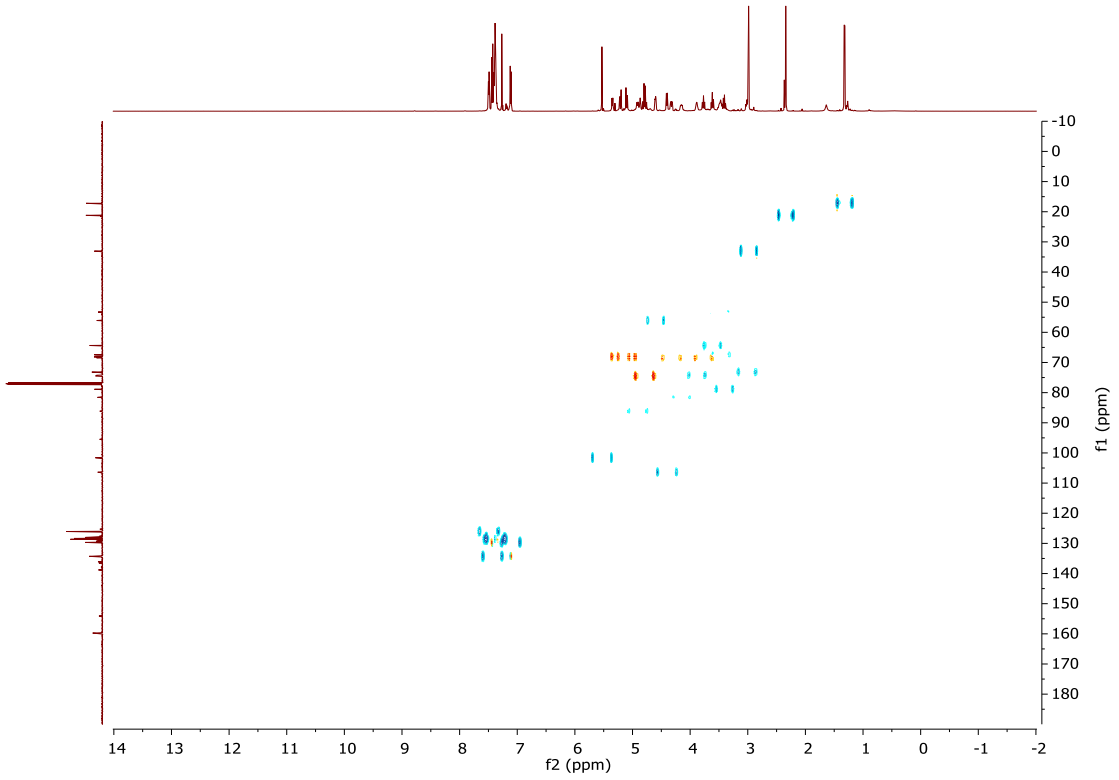
^{13}C-NMR of **26** (125 MHz $CDCl_3$)



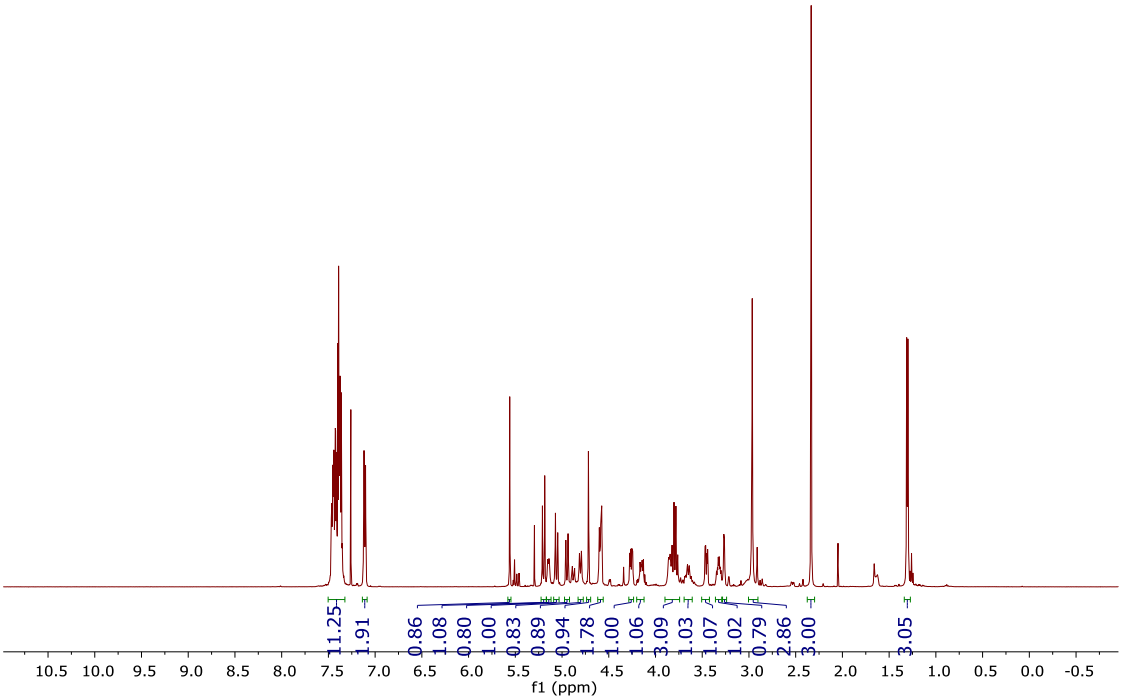
^{1}H-^{1}H gCOSY of **26** (500 MHz $CDCl_3$)



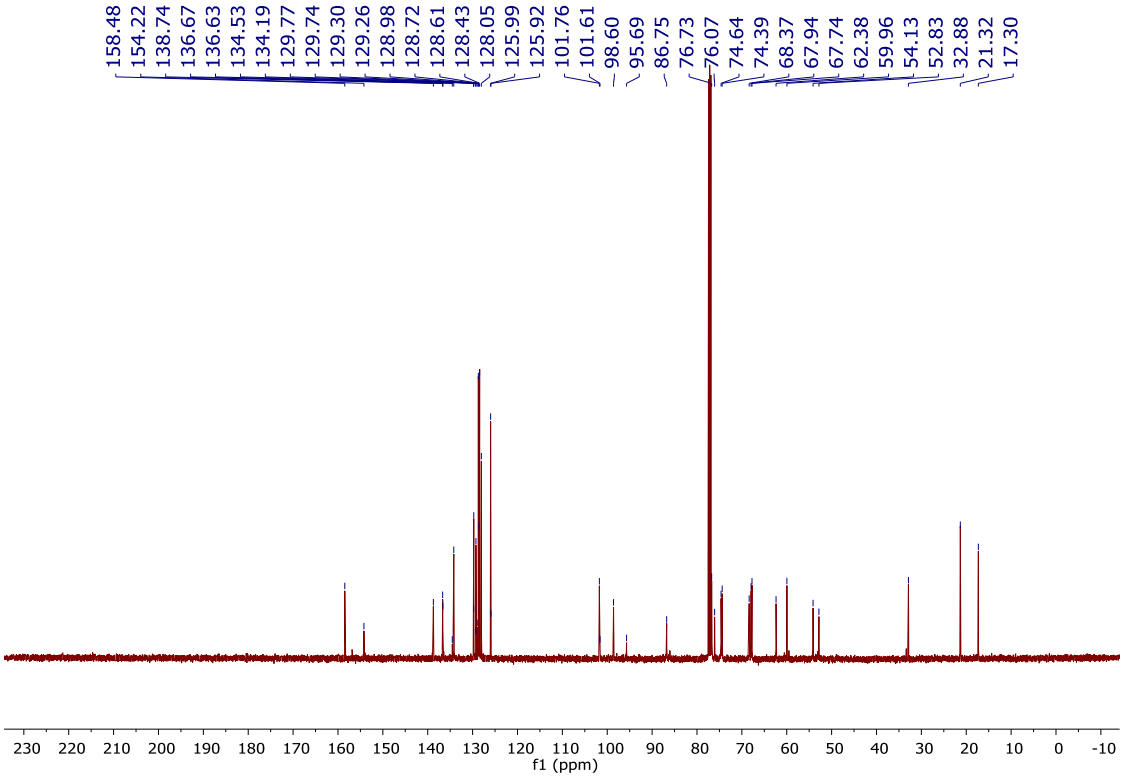
^{1}H-^{13}C gHSQCAD of **26** (500 MHz $CDCl_3$)



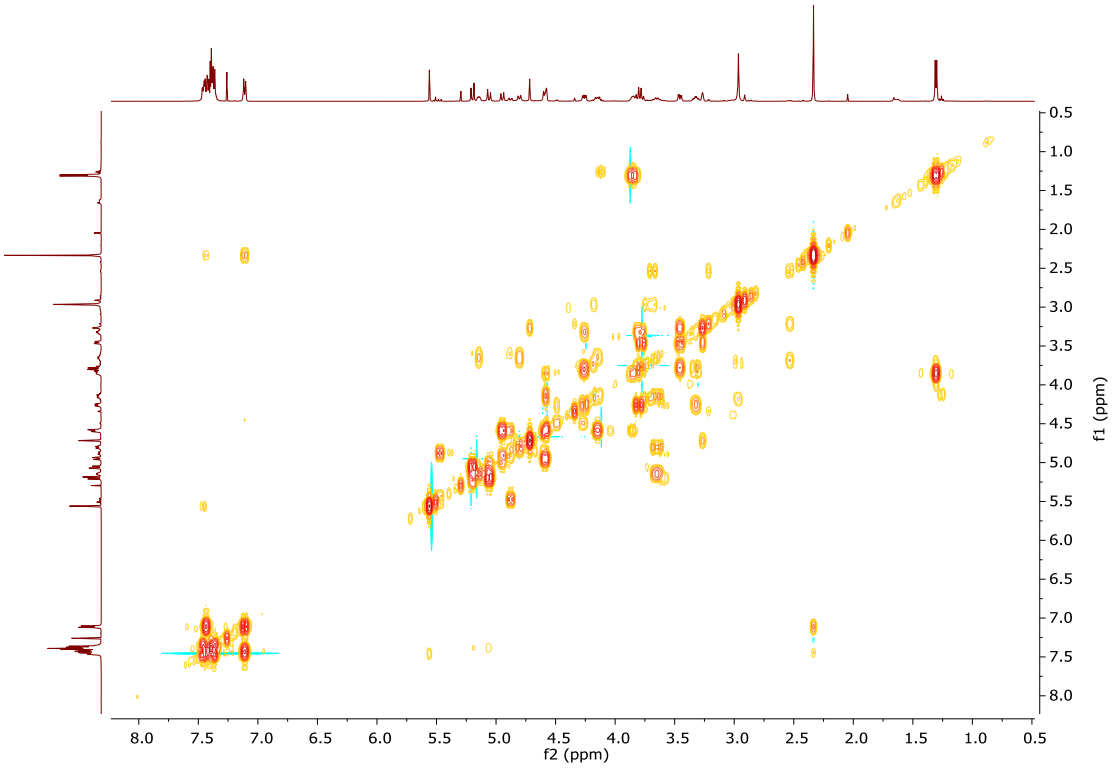
^{1}H-NMR of **27** (500 MHz $CDCl_3$)



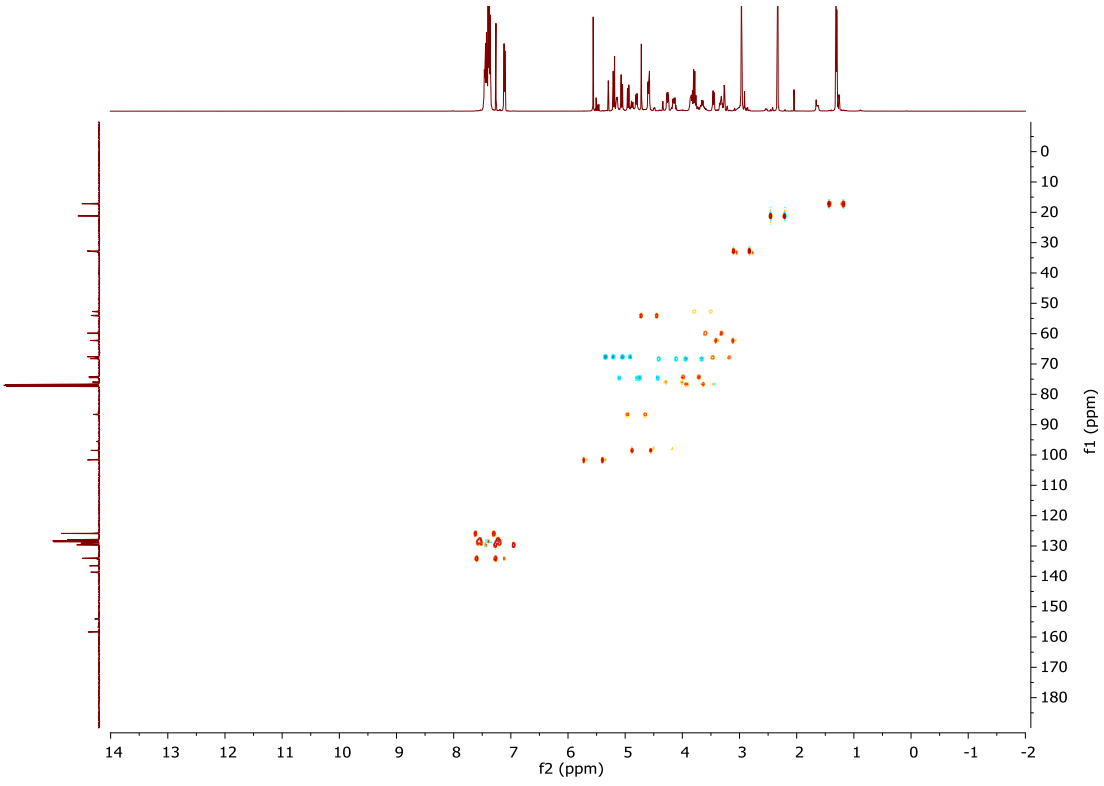
^{13}C-NMR of **27** (125 MHz $CDCl_3$)



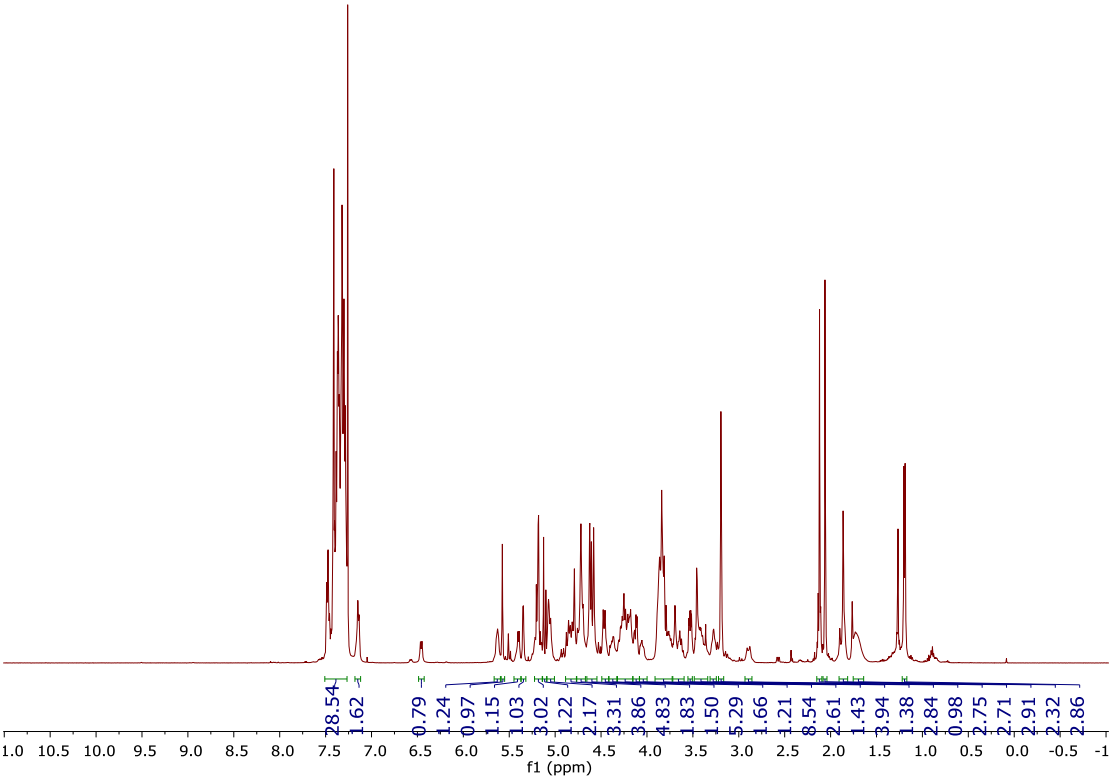
^{1}H-^{1}H gCOSY of **27** (500 MHz $CDCl_3$)



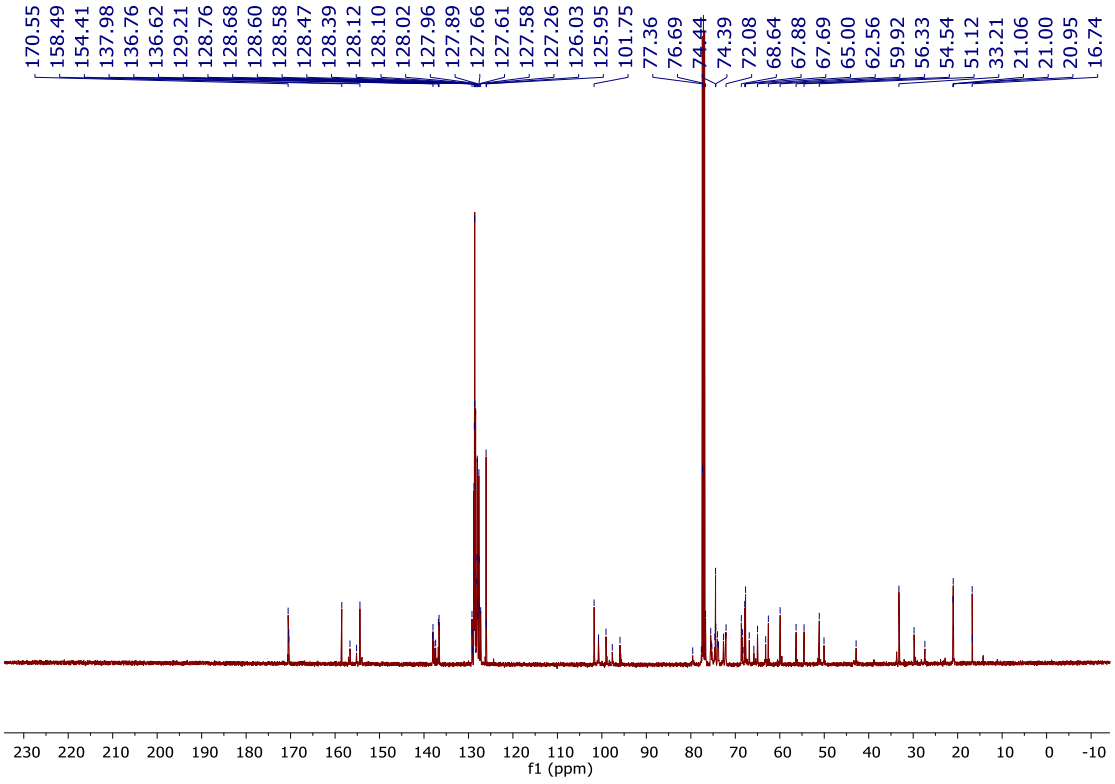
^{1}H-^{13}C gHSQCAD of **27** (500 MHz $CDCl_3$)



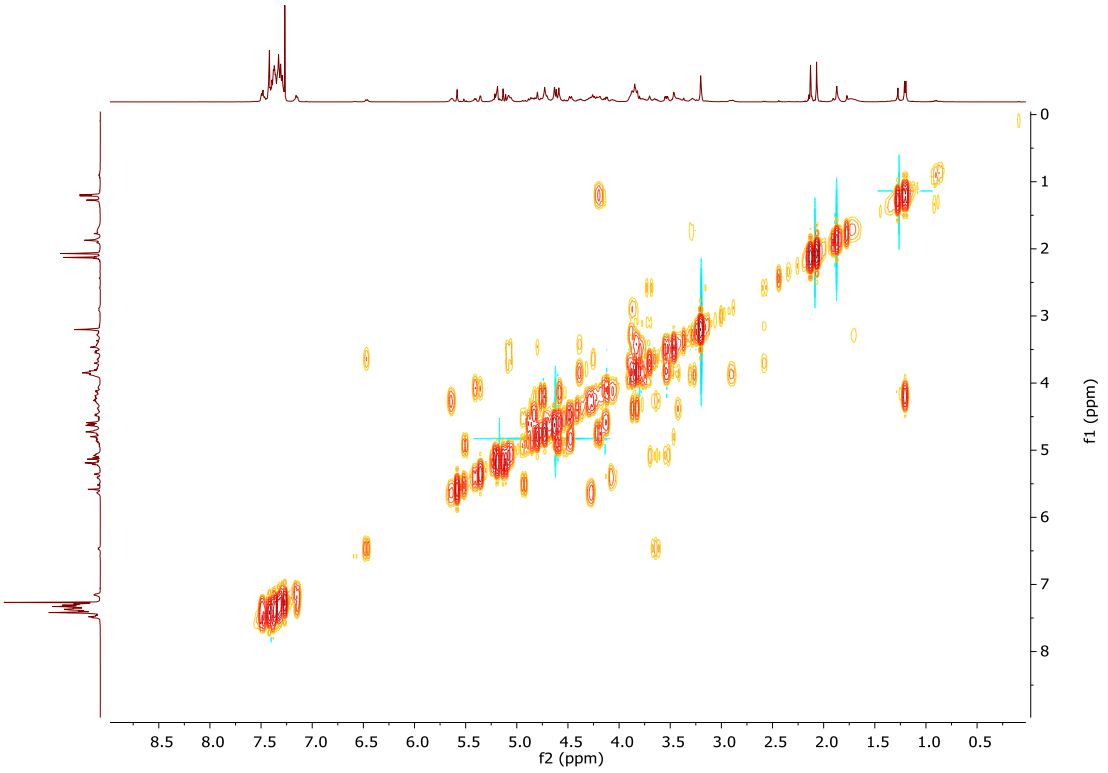
^{1}H-NMR of **28** (500 MHz $CDCl_3$)



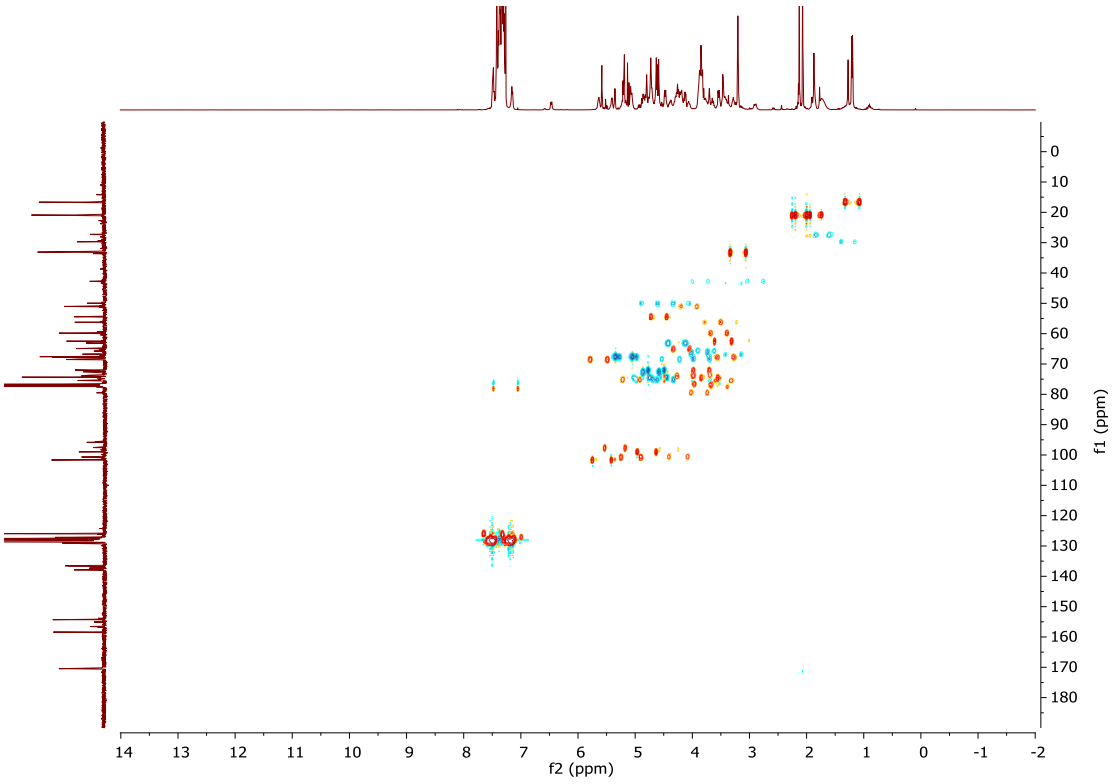
^{13}C-NMR of **28** (125 MHz $CDCl_3$)



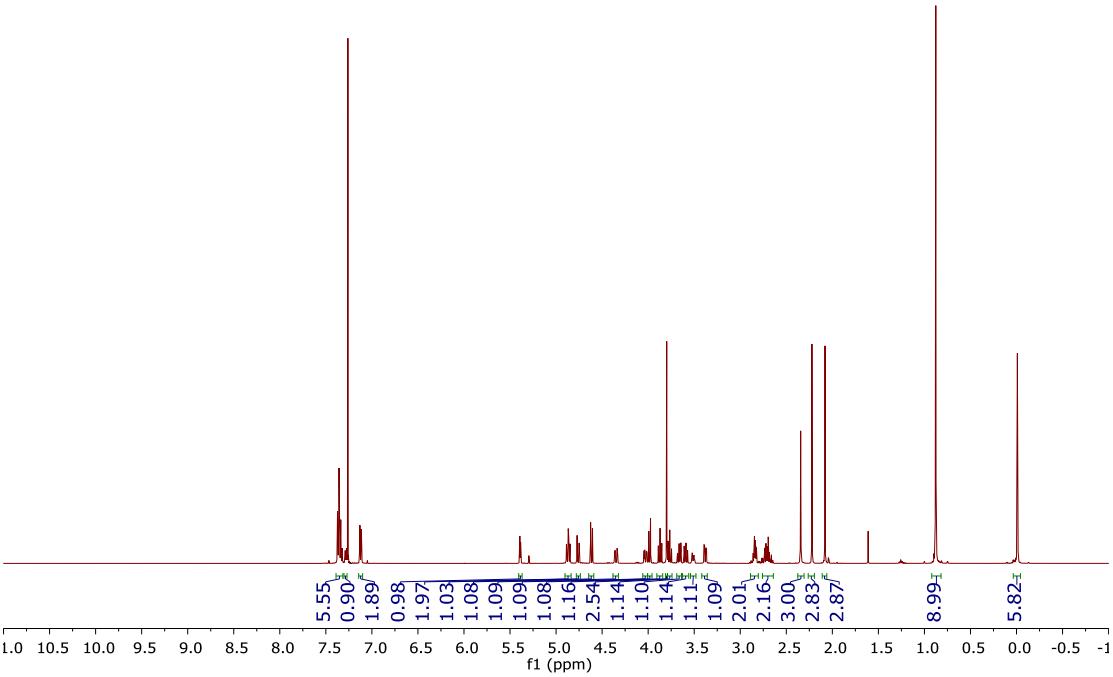
^{1}H-^{1}H gCOSY of **28** (500 MHz $CDCl_3$)



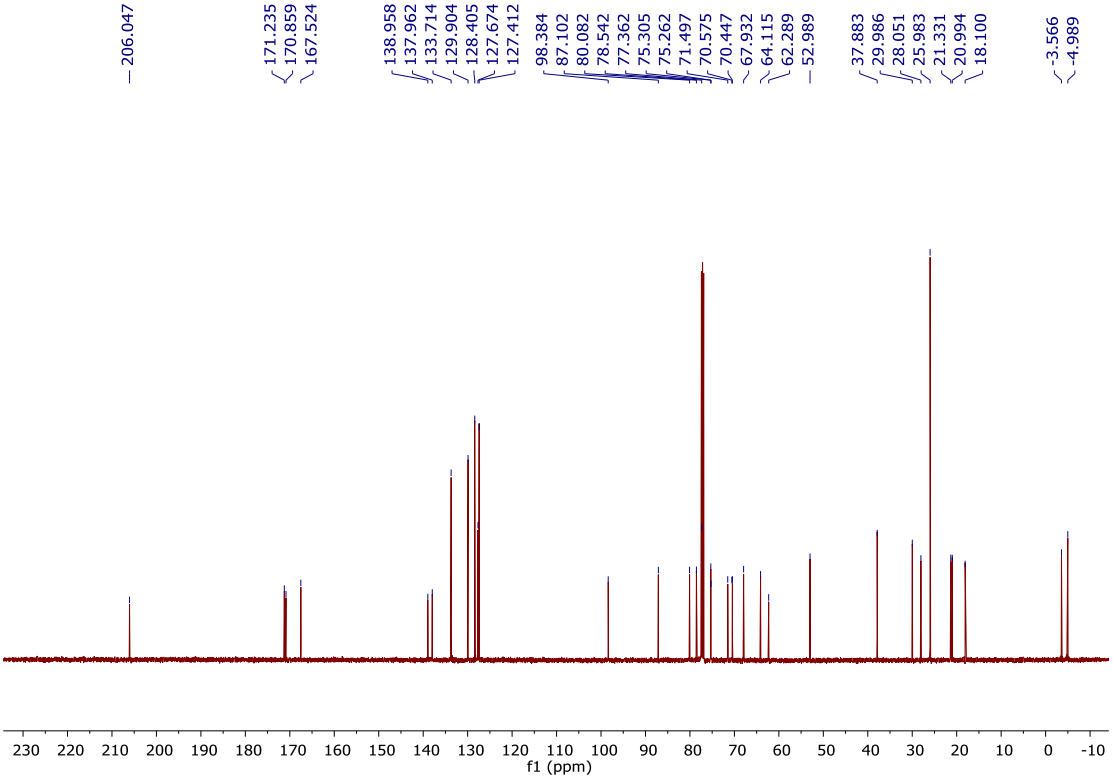
^{1}H-^{13}C gHSQCAD of **28** (500 MHz $CDCl_3$)



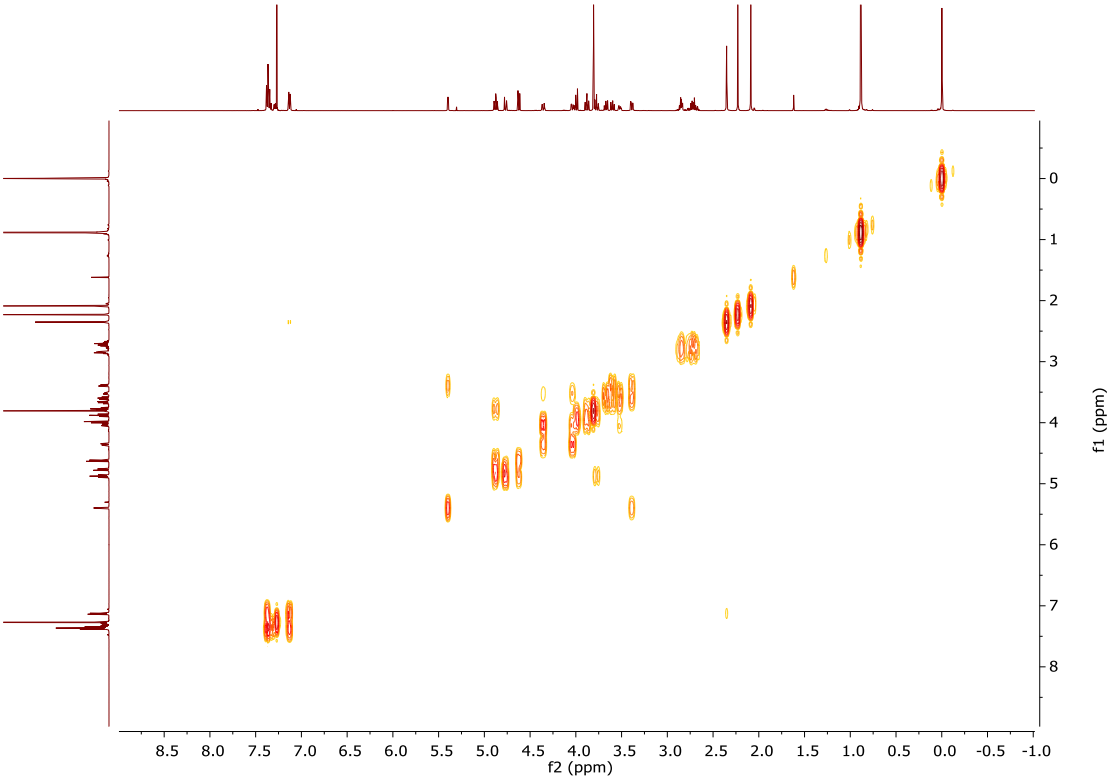
^{1}H-NMR of **29** (500 MHz $CDCl_3$)



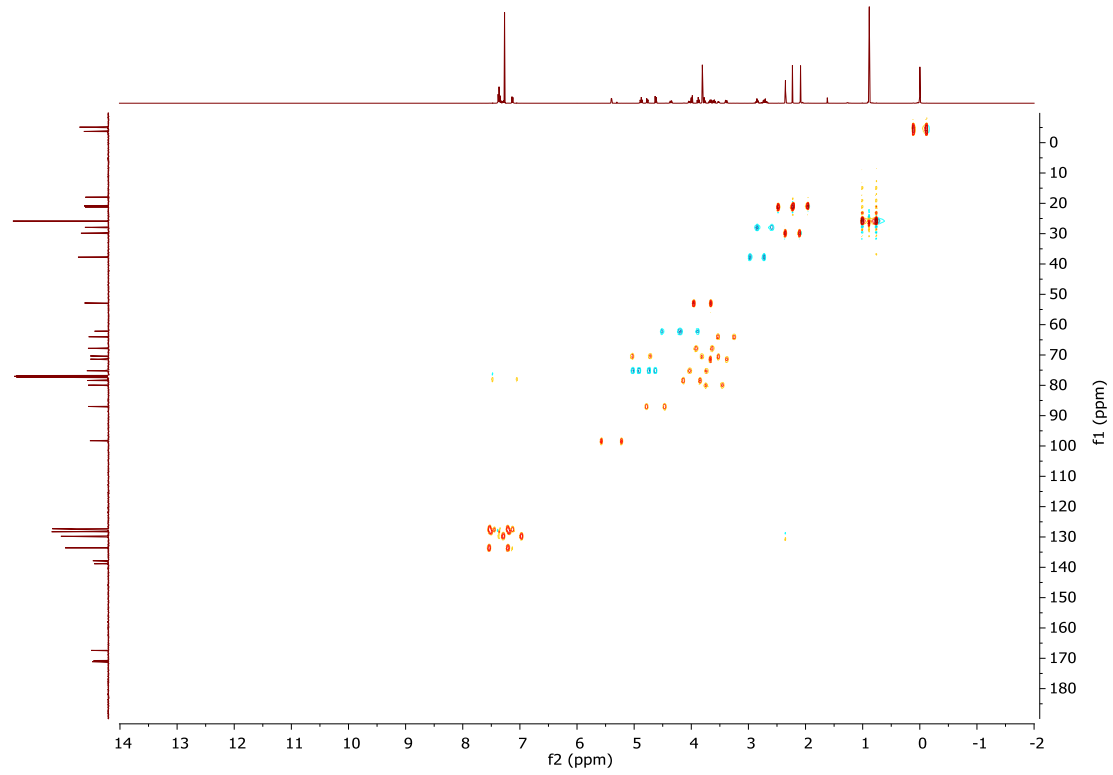
^{13}C-NMR of **29** (125 MHz $CDCl_3$)



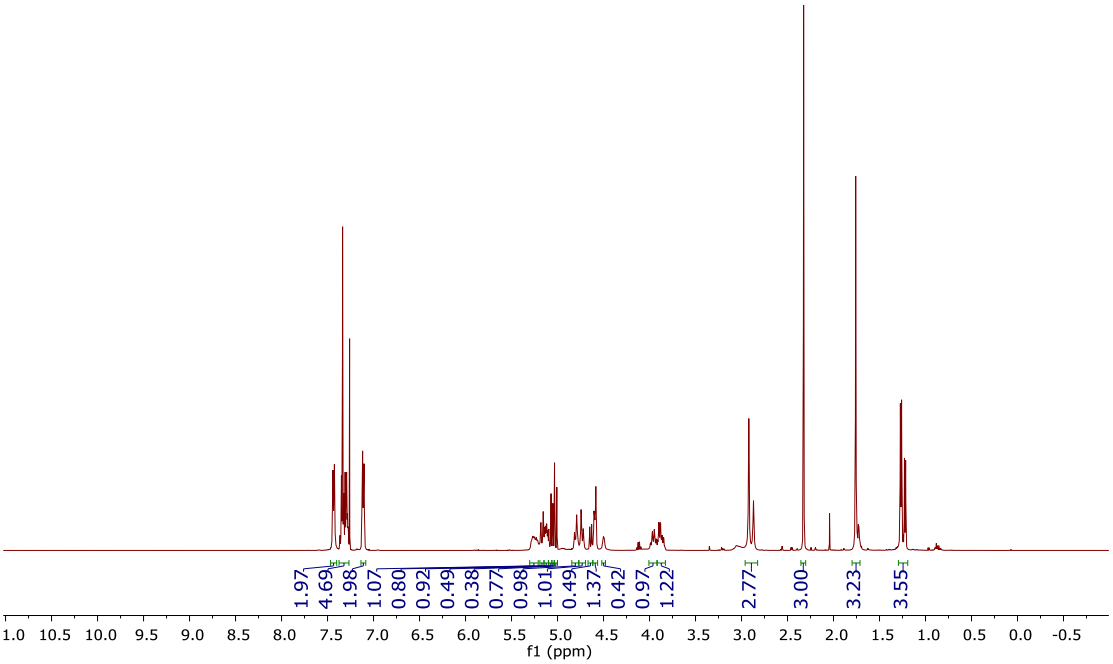
^{1}H-^{1}H gCOSY of **29** (500 MHz $CDCl_3$)



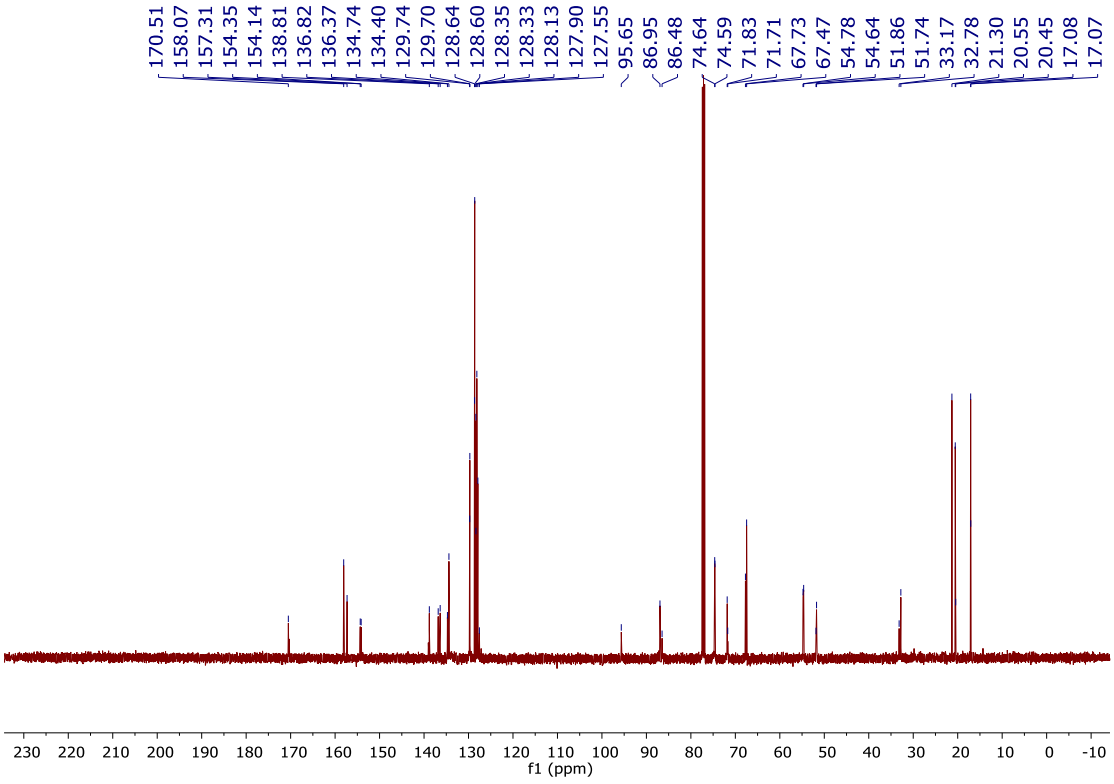
^{1}H-^{13}C gHSQCAD of **29** (500 MHz $CDCl_3$)



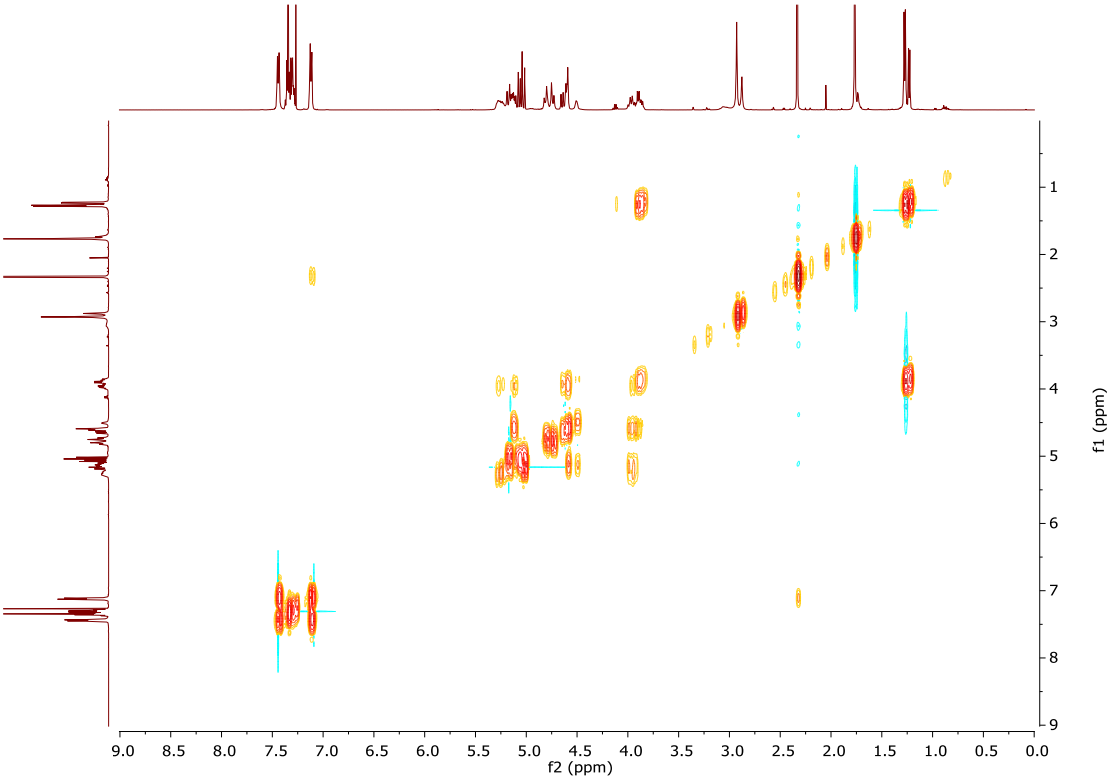
^{1}H-NMR of **31** (500 MHz $CDCl_3$)



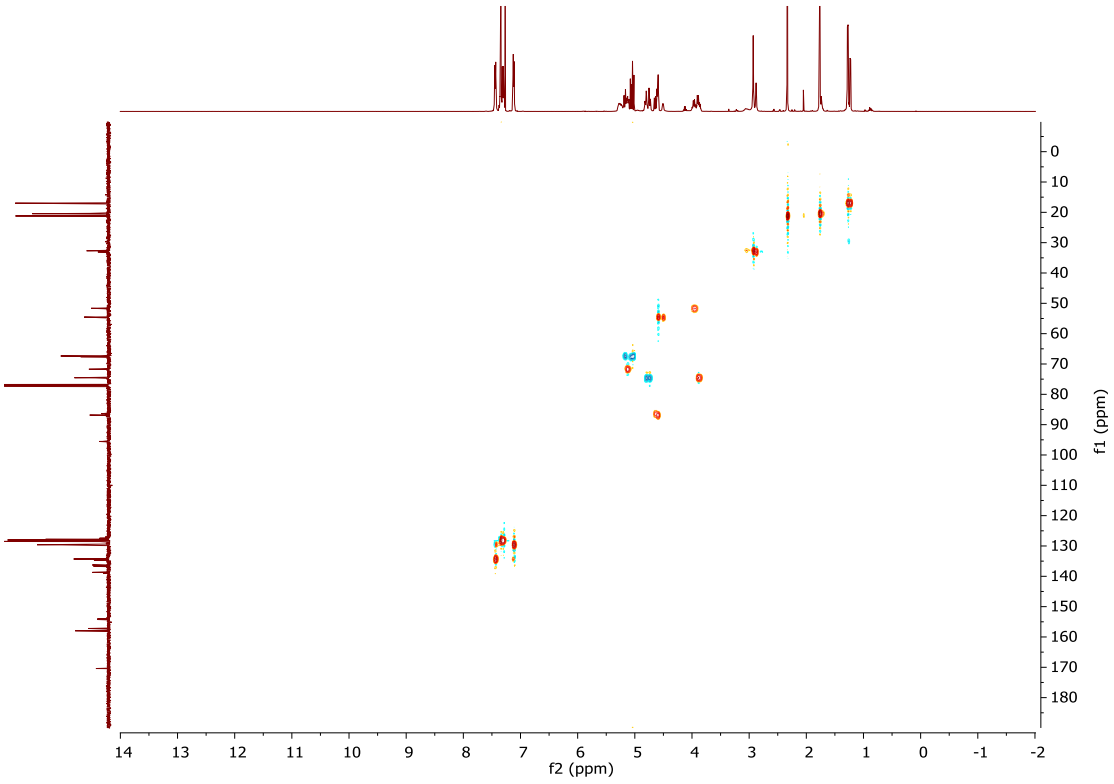
^{13}C-NMR of **31** (125 MHz $CDCl_3$)



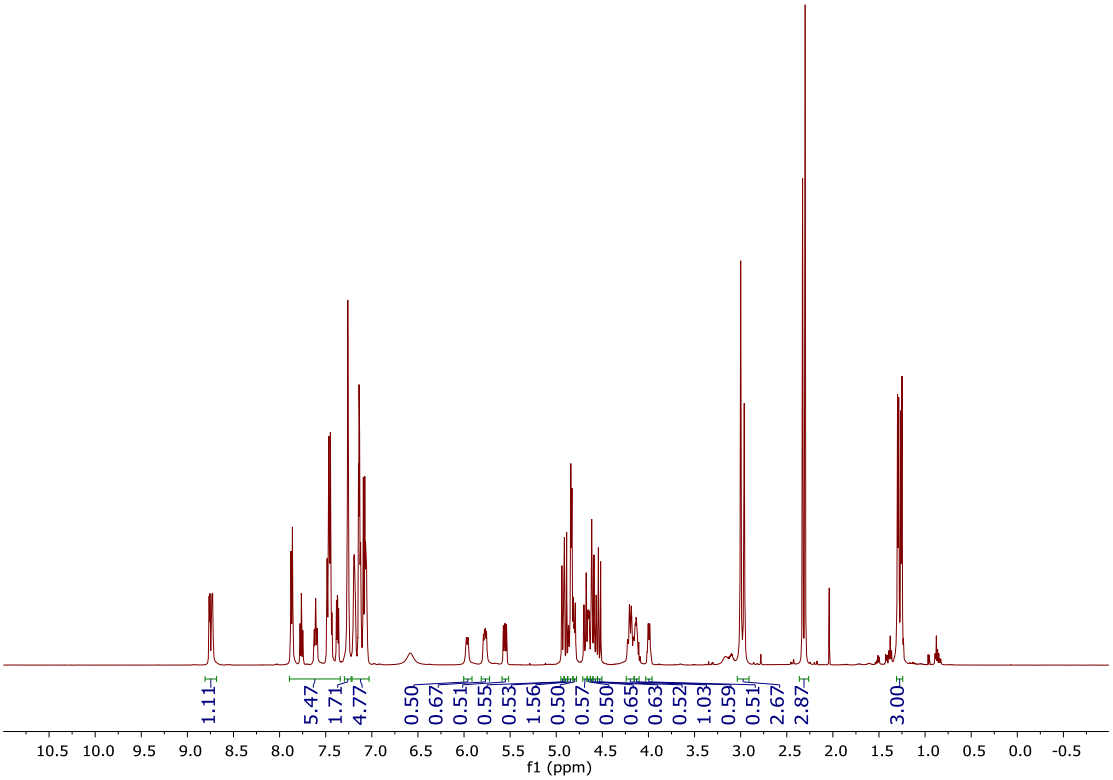
^{1}H-^{1}H gCOSY of **31** (500 MHz $CDCl_3$)



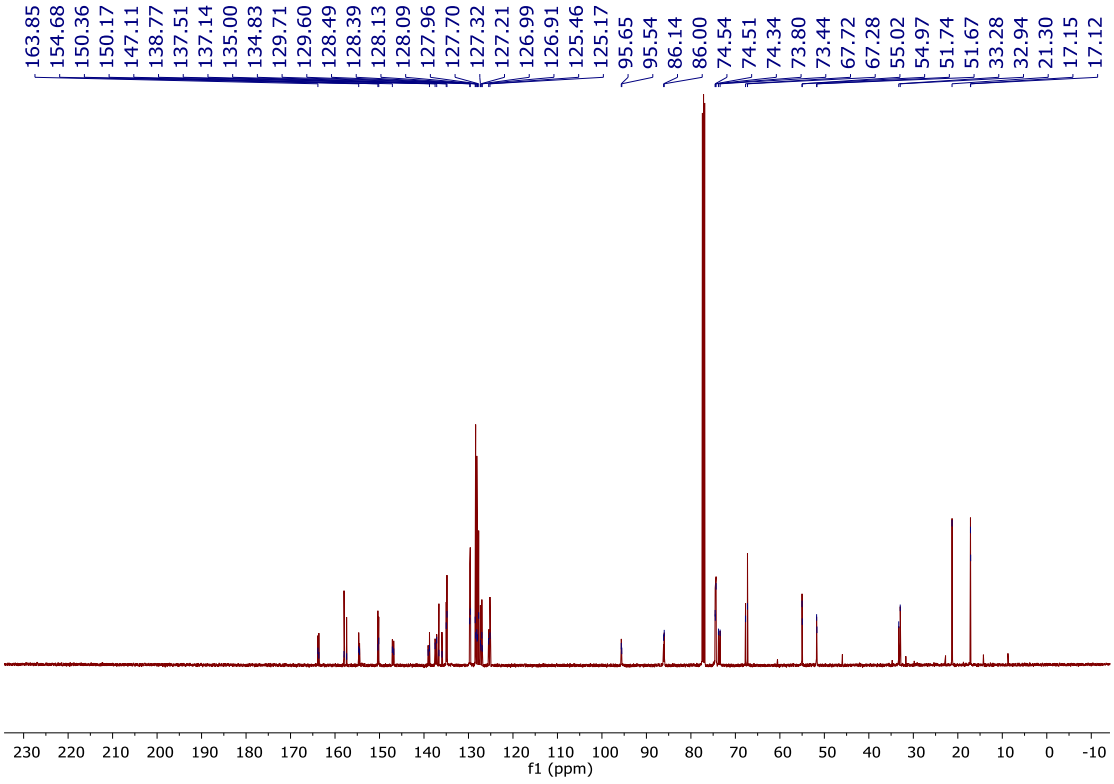
^{1}H-^{13}C gHSQCAD of **31** (500 MHz $CDCl_3$)



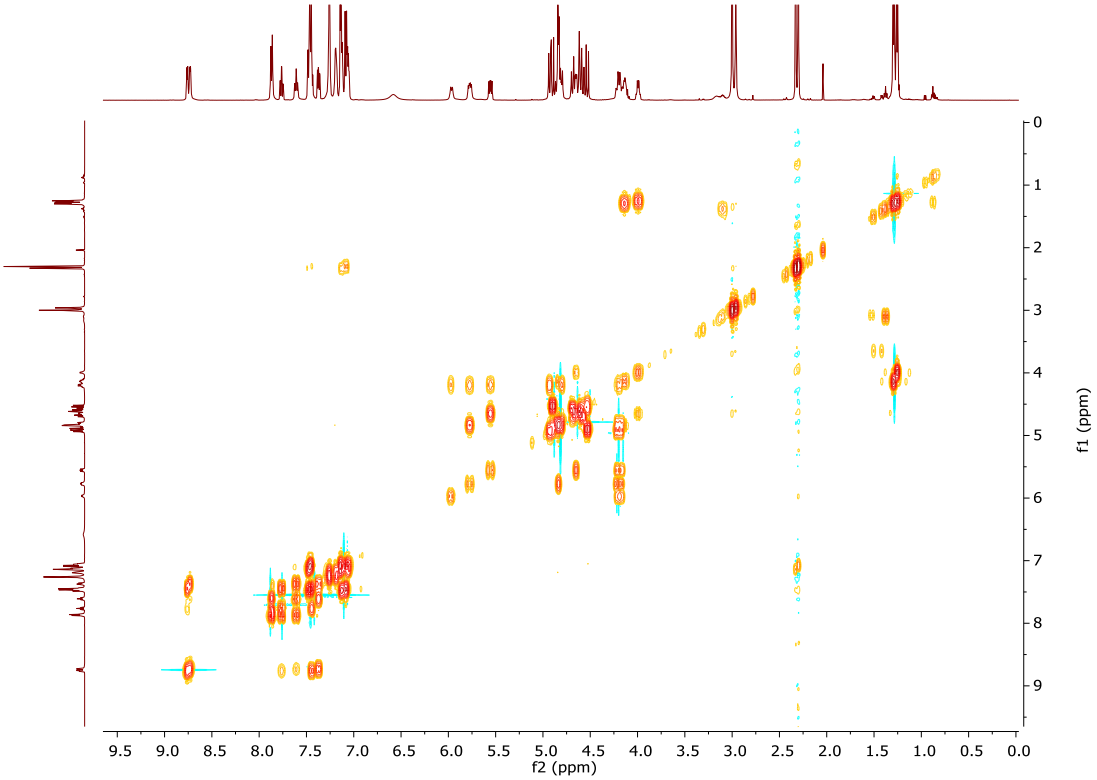
^{1}H-NMR of **32** (500 MHz $CDCl_3$)



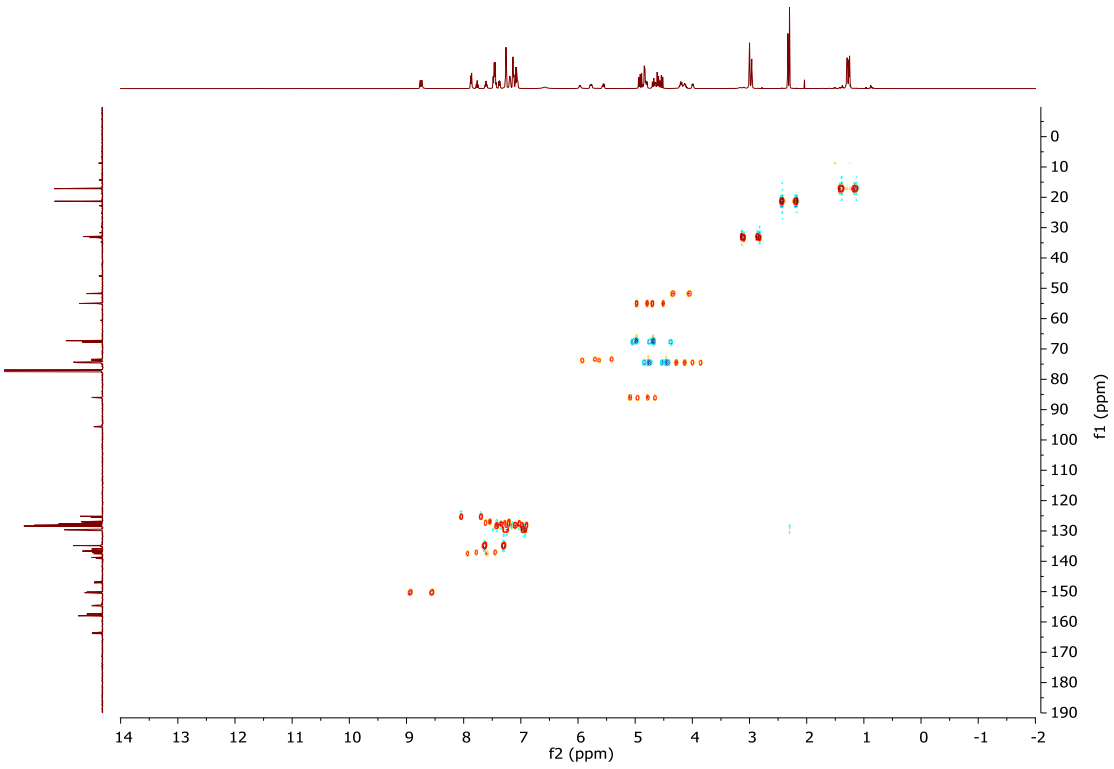
^{13}C-NMR of **32** (125 MHz $CDCl_3$)



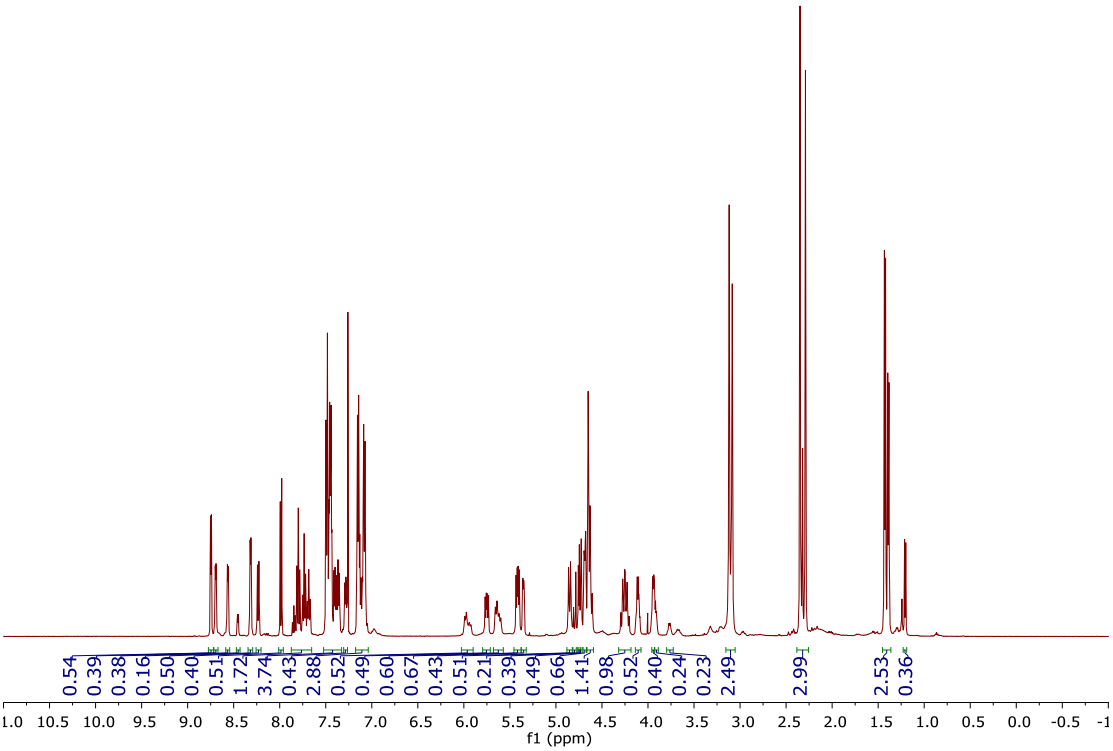
^{1}H-^{1}H gCOSY of **32** (500 MHz $CDCl_3$)



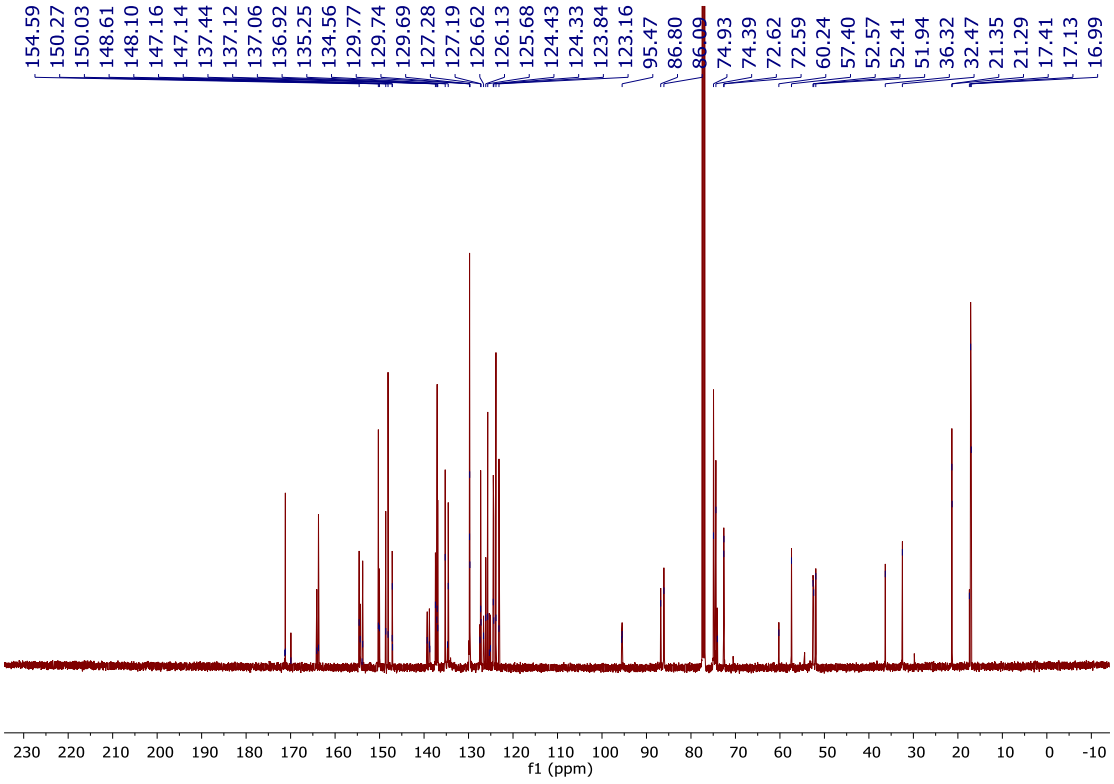
^{1}H-^{13}C gHSQCAD of **32** (500 MHz $CDCl_3$)



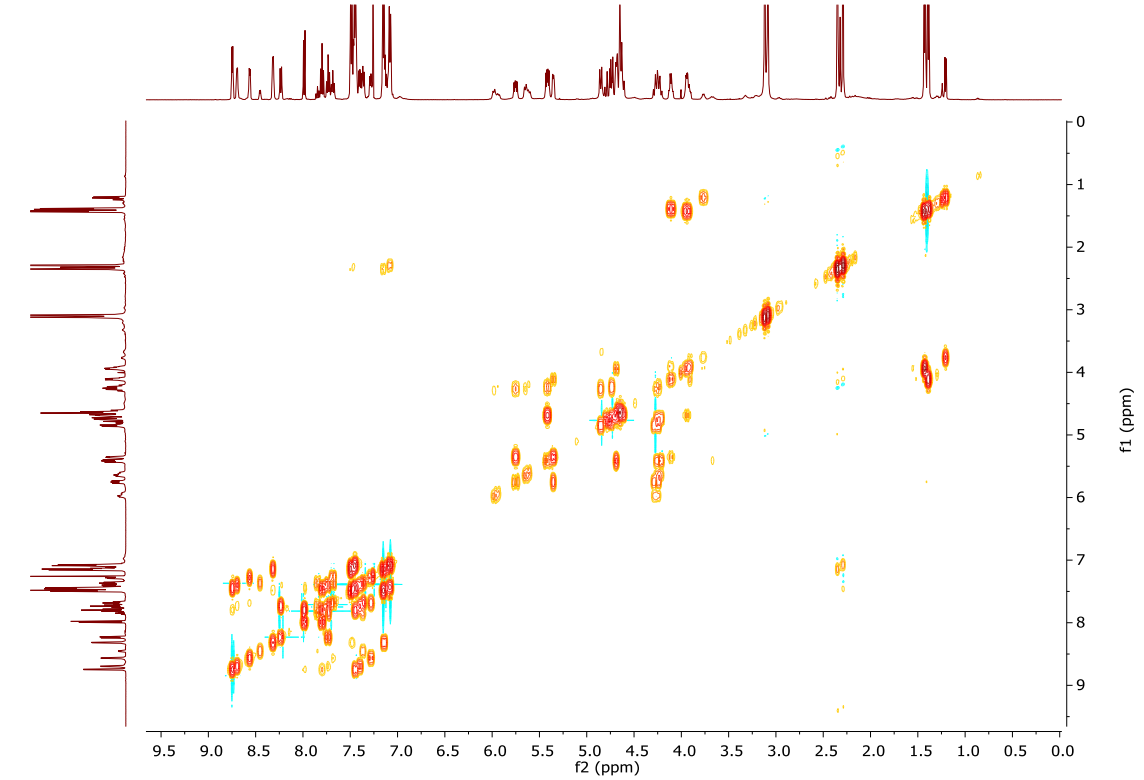
^{1}H-NMR of **33** (500 MHz $CDCl_3$)



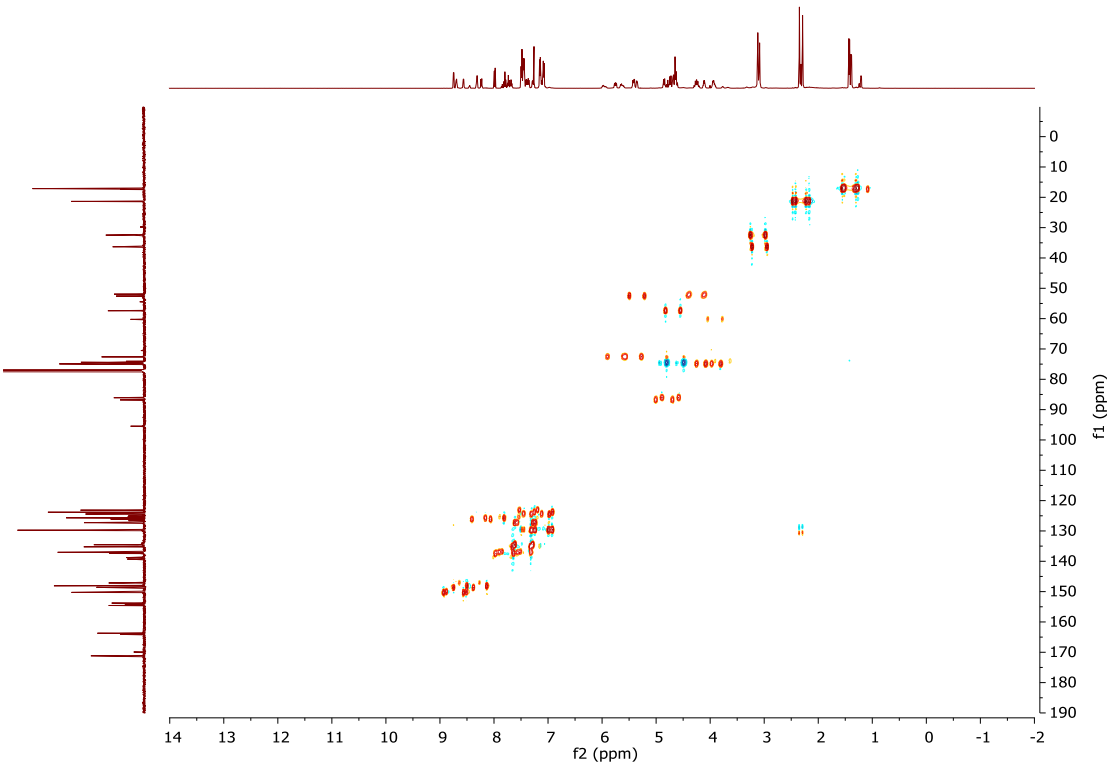
^{13}C-NMR of **33** (125 MHz $CDCl_3$)



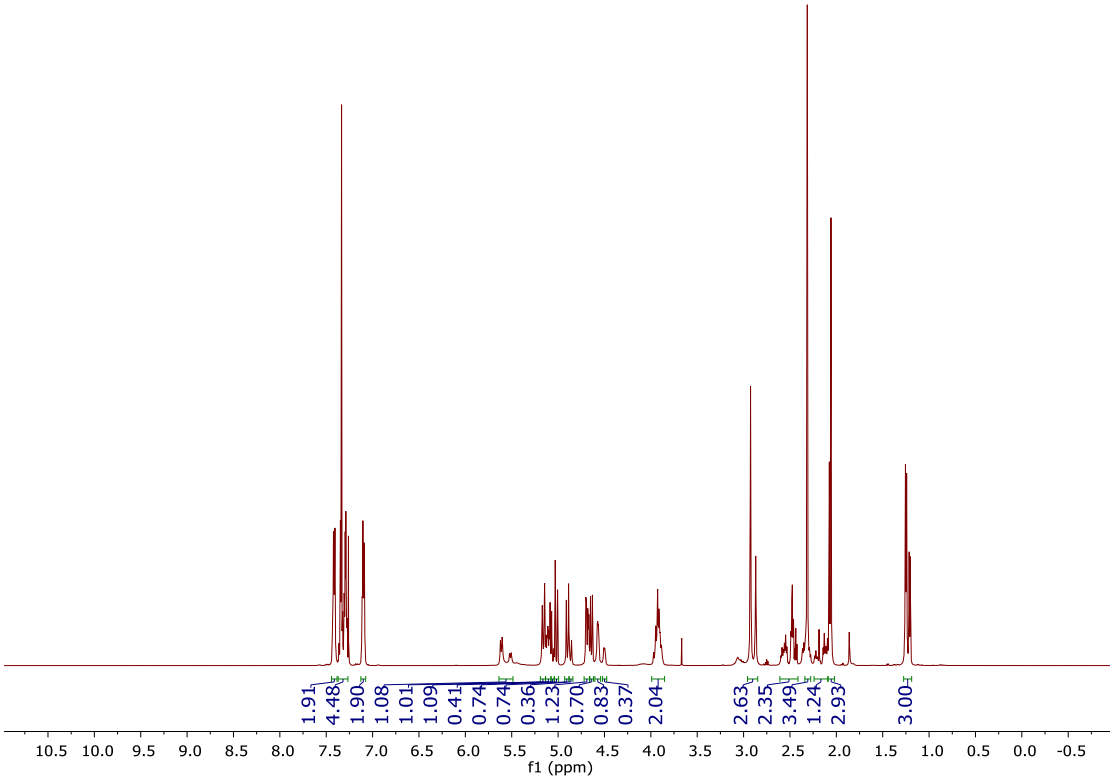
^{1}H-^{1}H gCOSY of **33** (500 MHz $CDCl_3$)



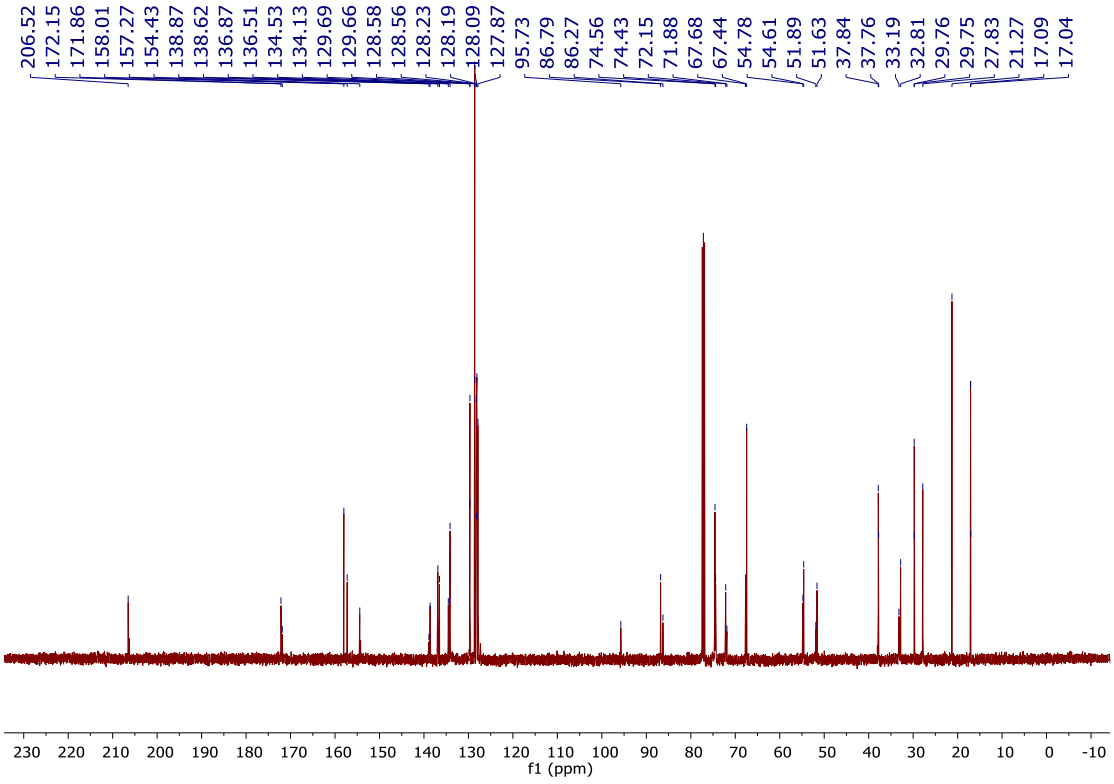
^{1}H-^{13}C gHSQCAD of **33** (500 MHz $CDCl_3$)



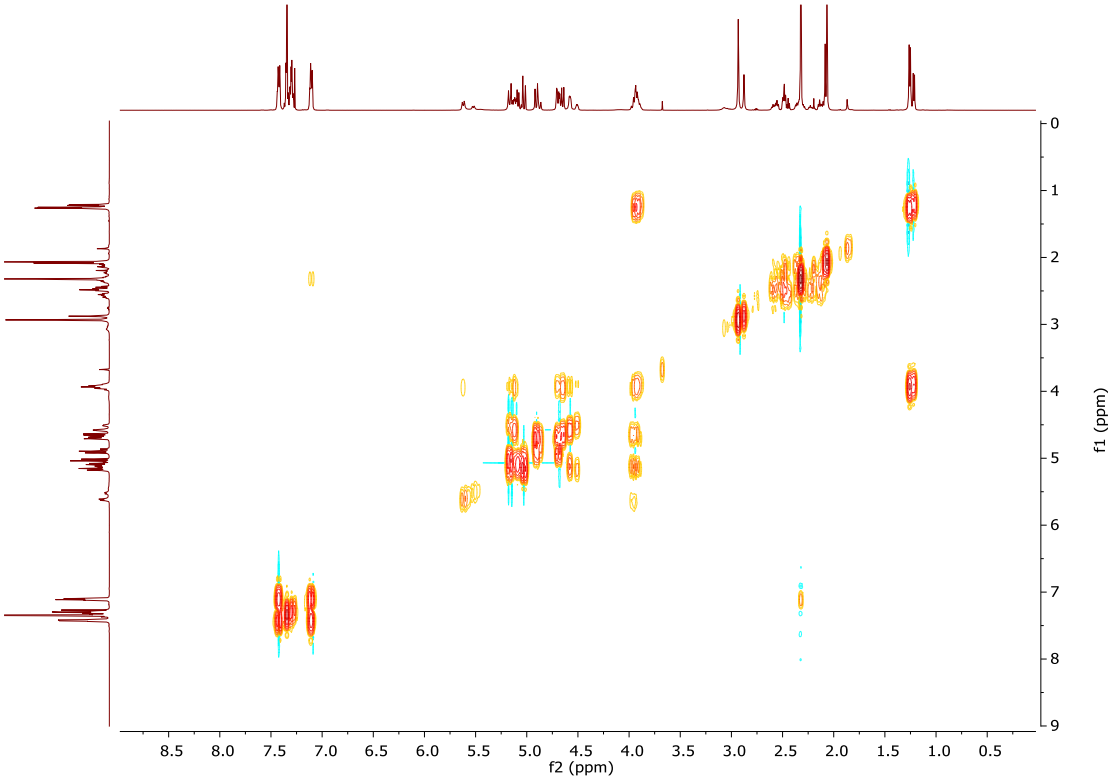
^{1}H-NMR of **34** (500 MHz $CDCl_3$)



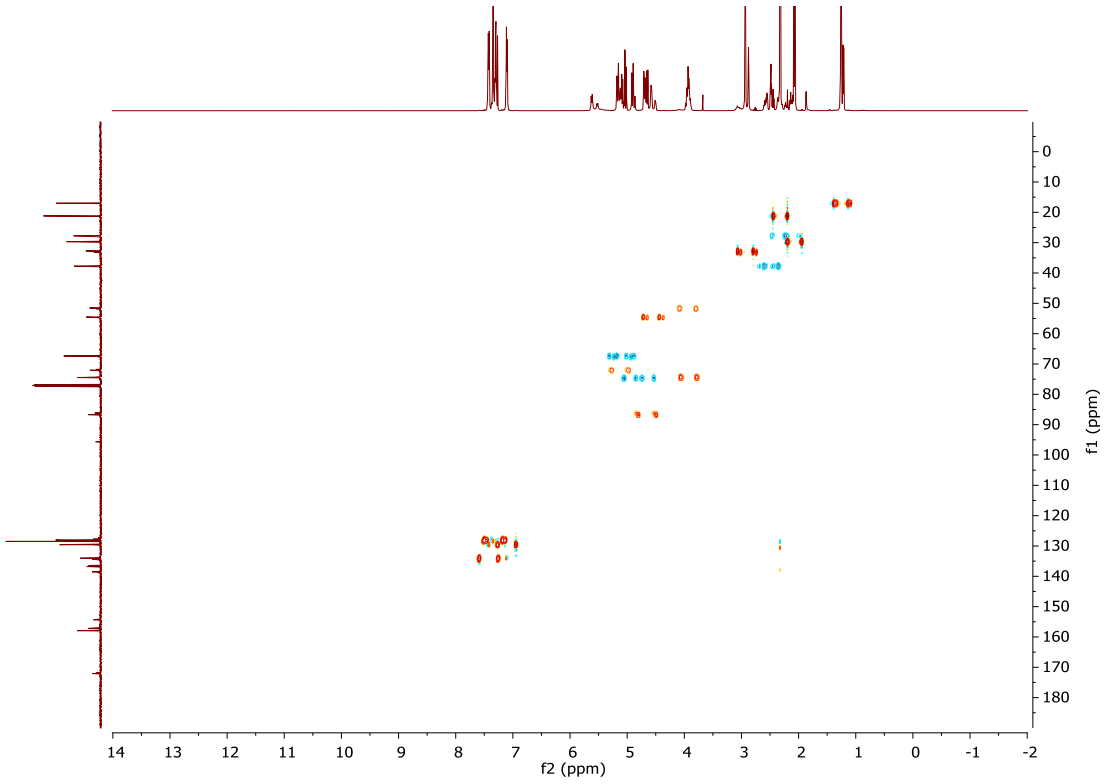
^{13}C-NMR of **34** (125 MHz $CDCl_3$)



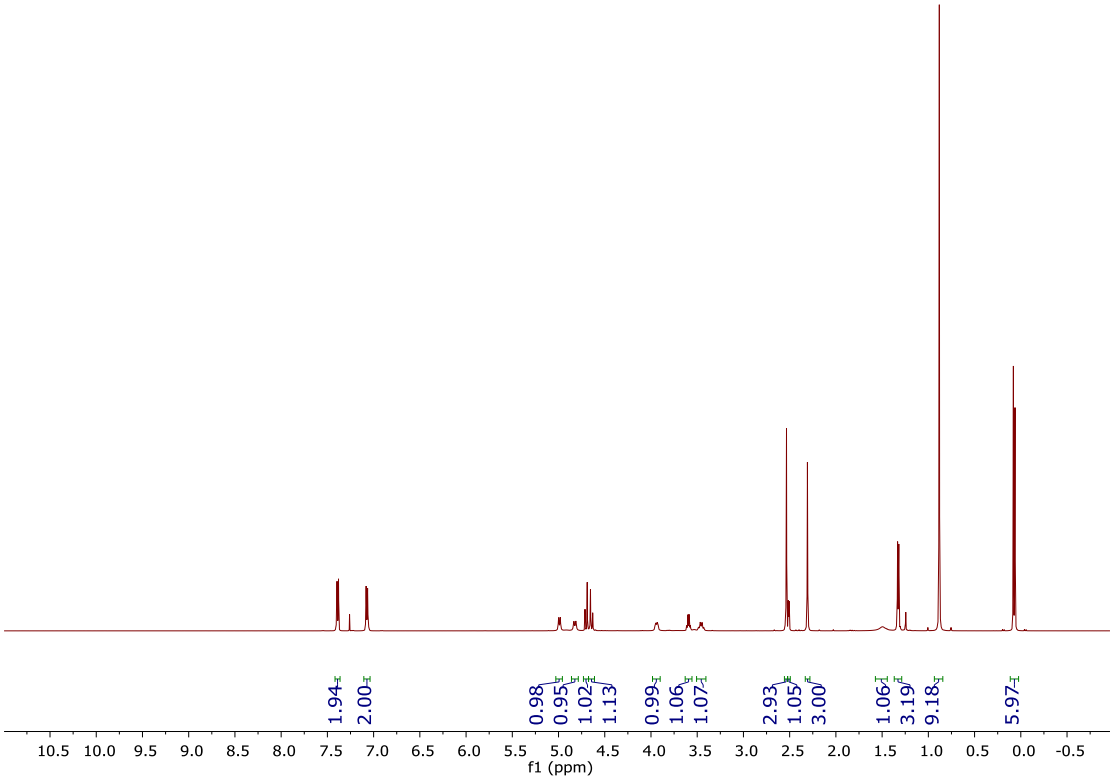
^{1}H-^{1}H gCOSY of **34** (500 MHz $CDCl_3$)



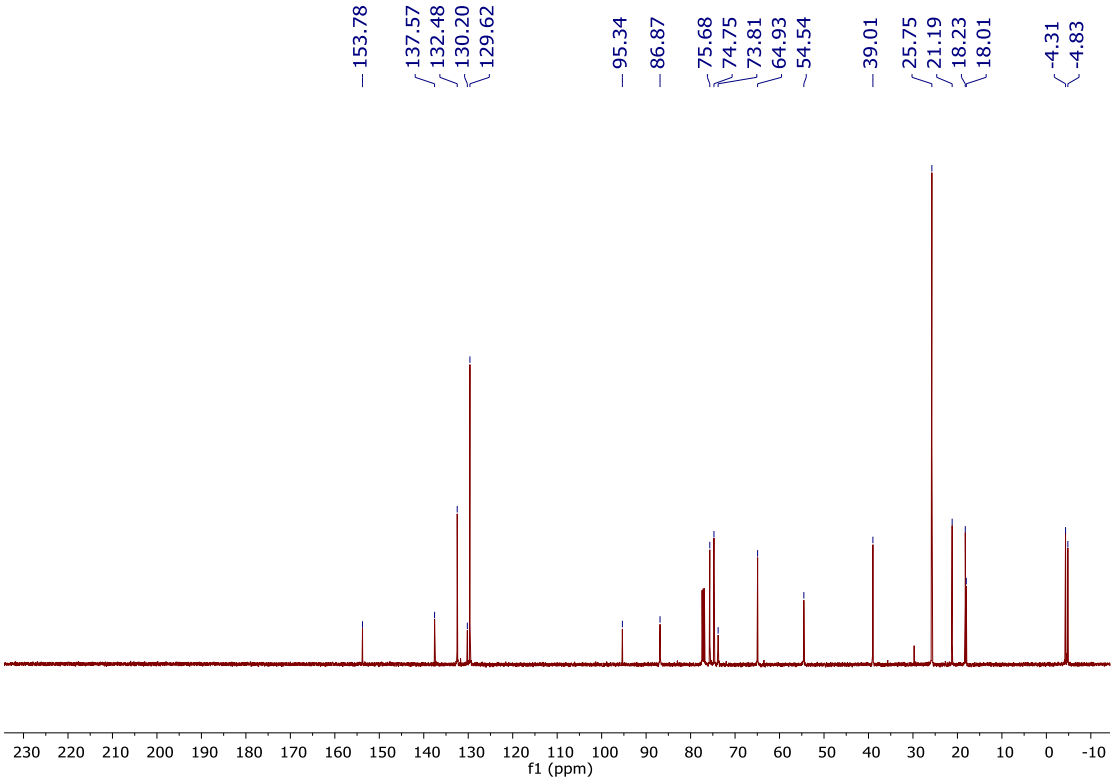
^{1}H-^{13}C gHSQCAD of **34** (500 MHz $CDCl_3$)



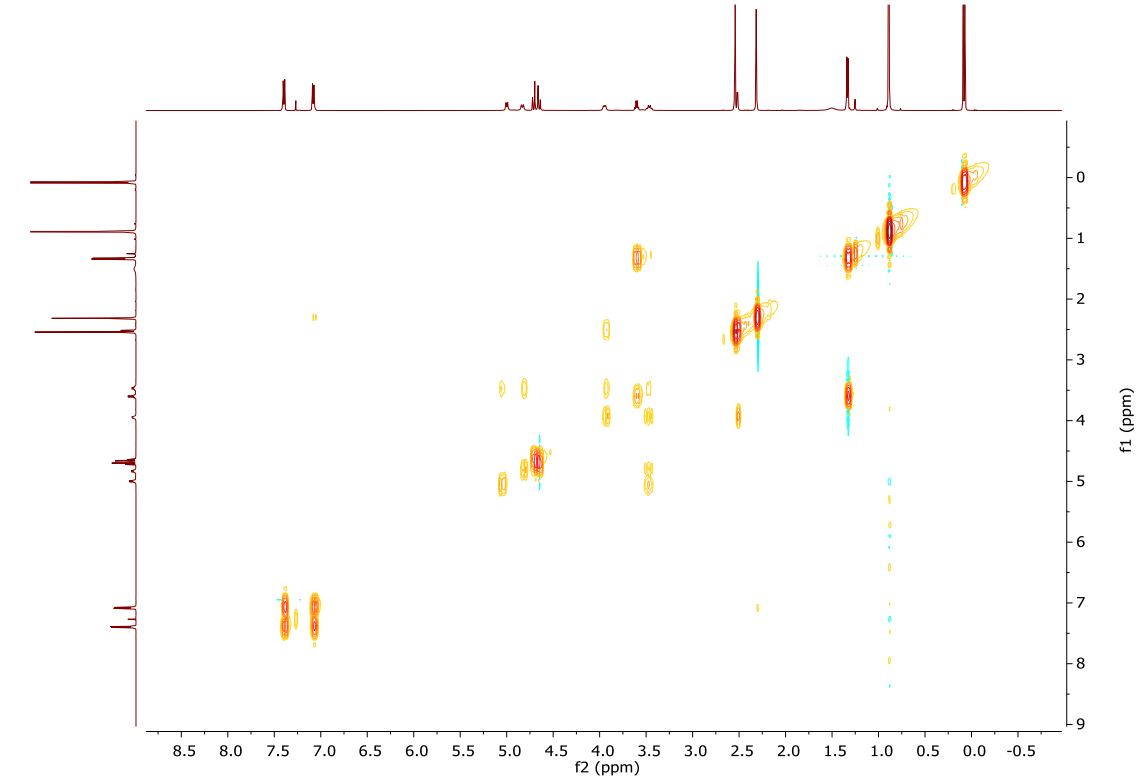
^{1}H-NMR of **35** (500 MHz $CDCl_3$)



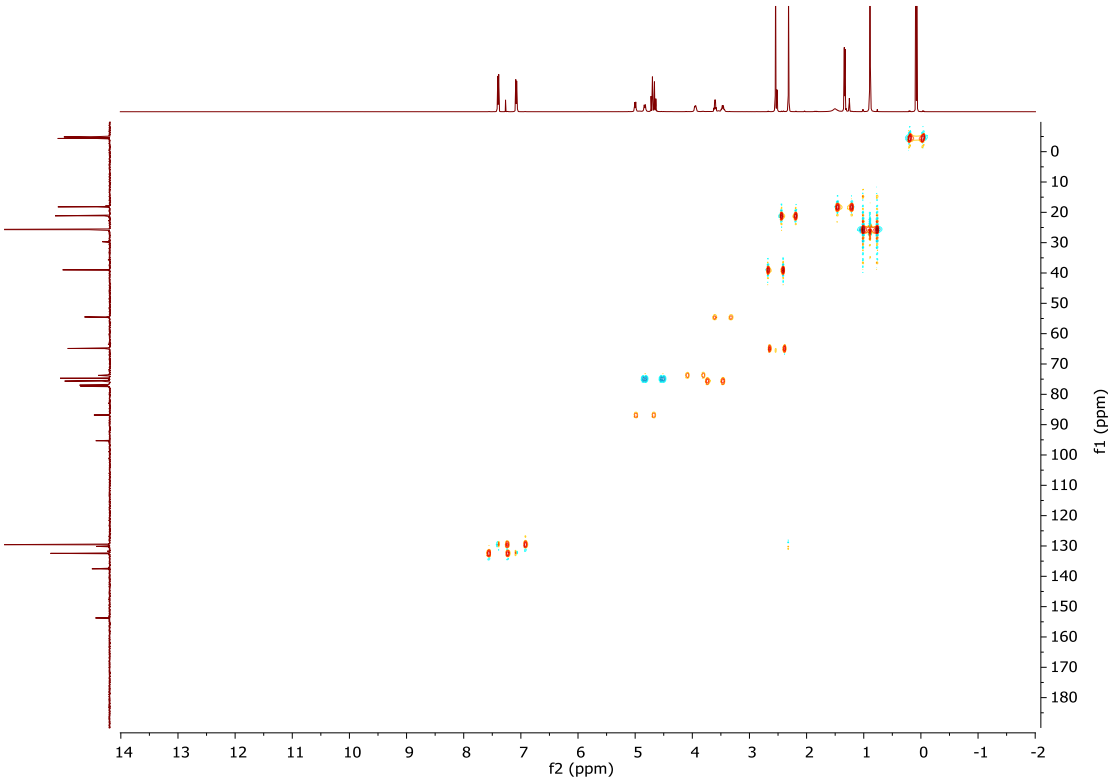
^{13}C-NMR of **35** (125 MHz $CDCl_3$)



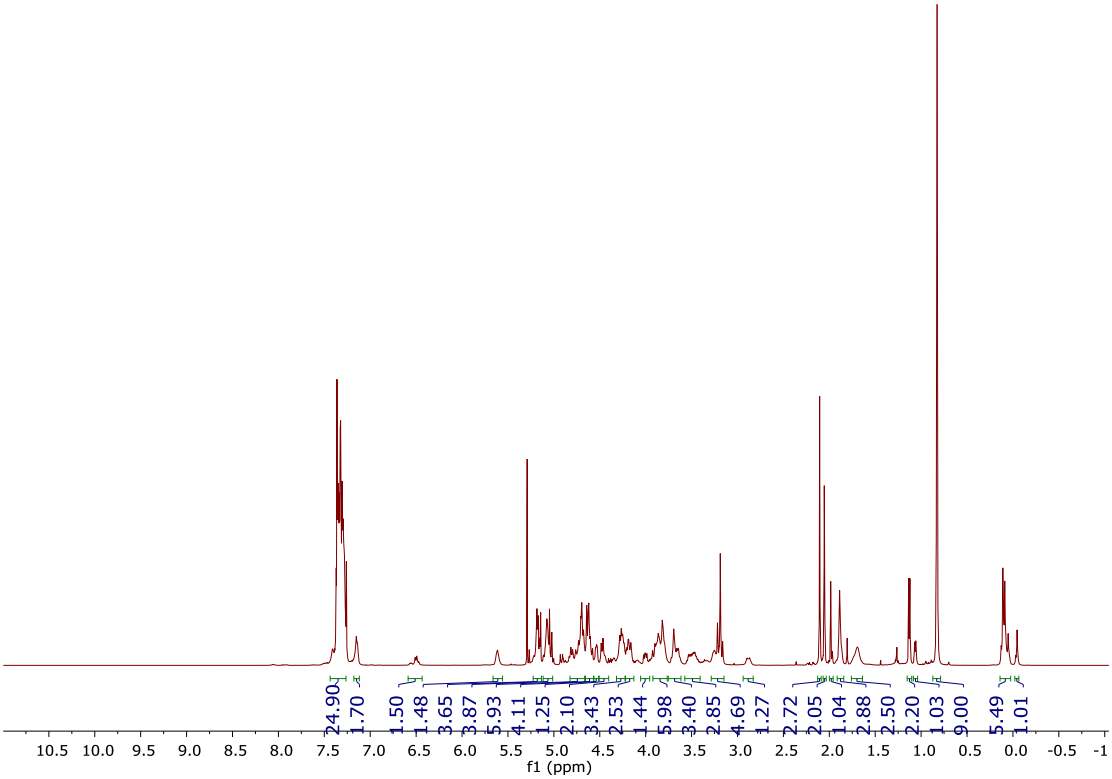
^{1}H-^{1}H gCOSY of **35** (500 MHz $CDCl_3$)



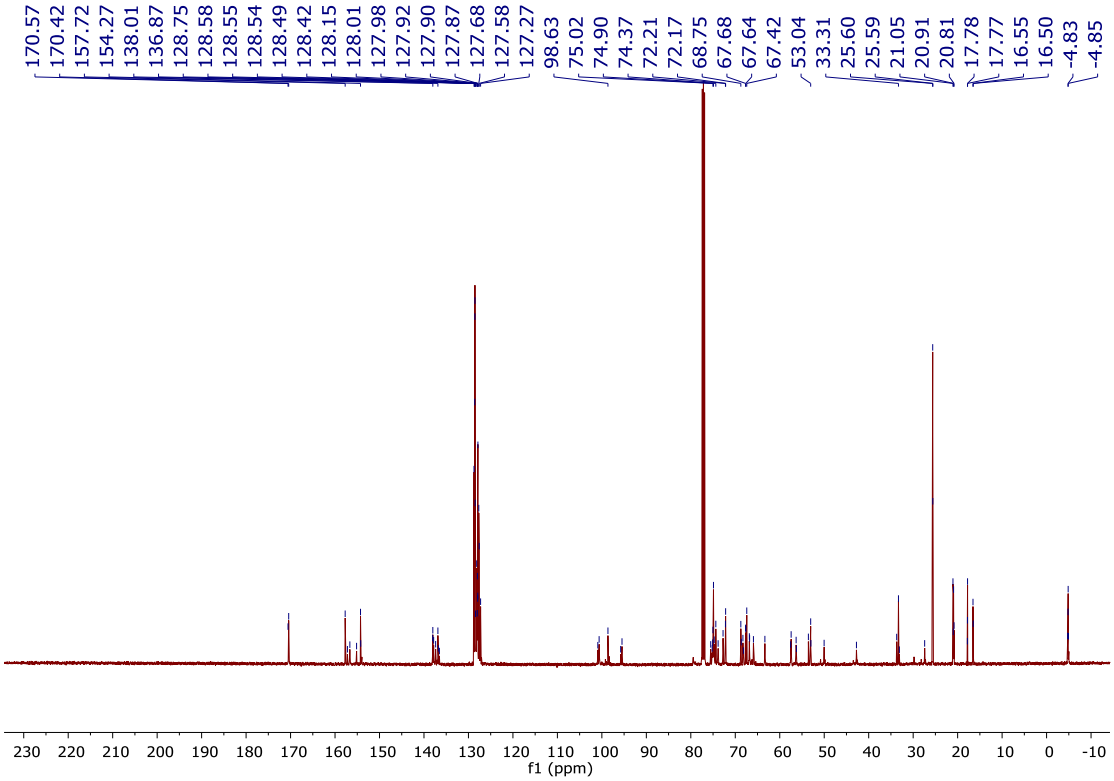
^{1}H-^{13}C gHSQCAD of **35** (500 MHz $CDCl_3$)



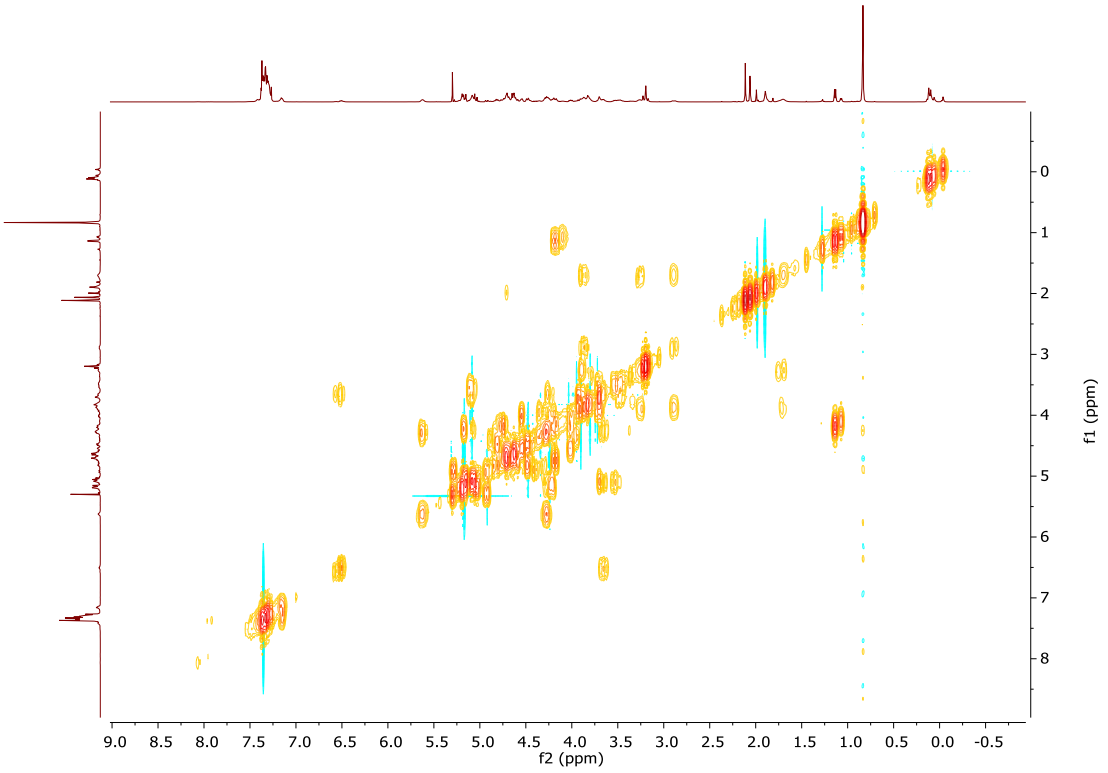
^{1}H-NMR of **36α** (500 MHz $CDCl_3$)



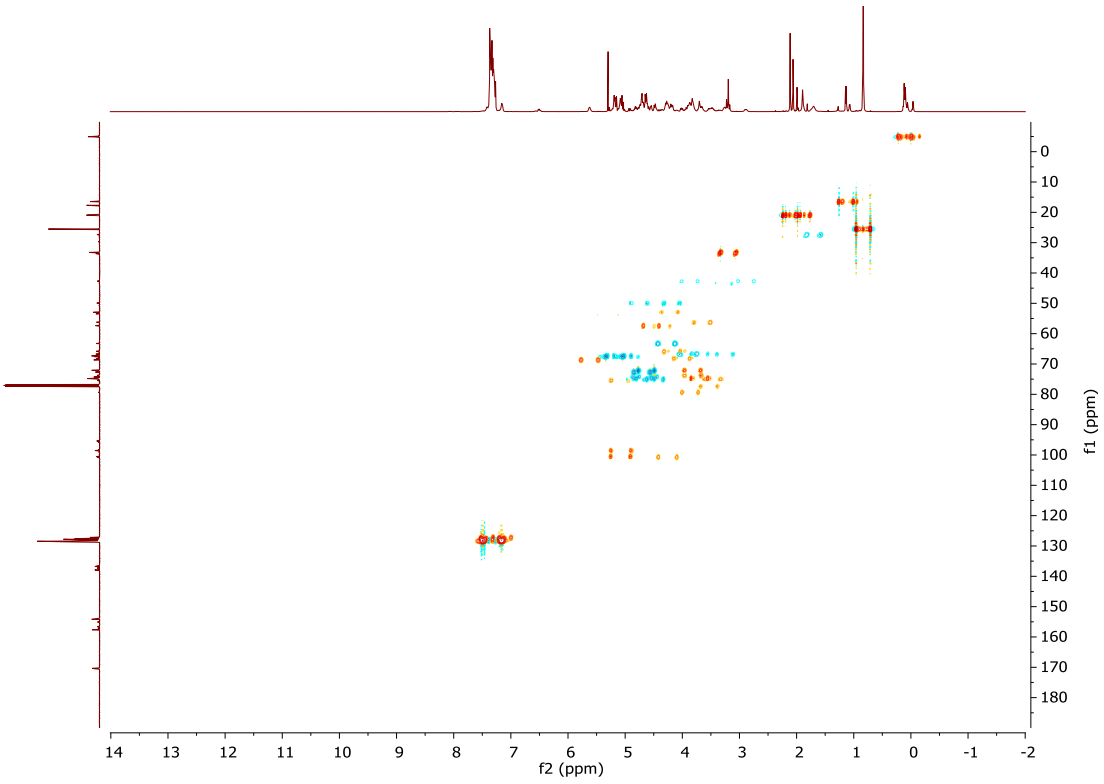
^{13}C-NMR of **36α** (125 MHz $CDCl_3$)



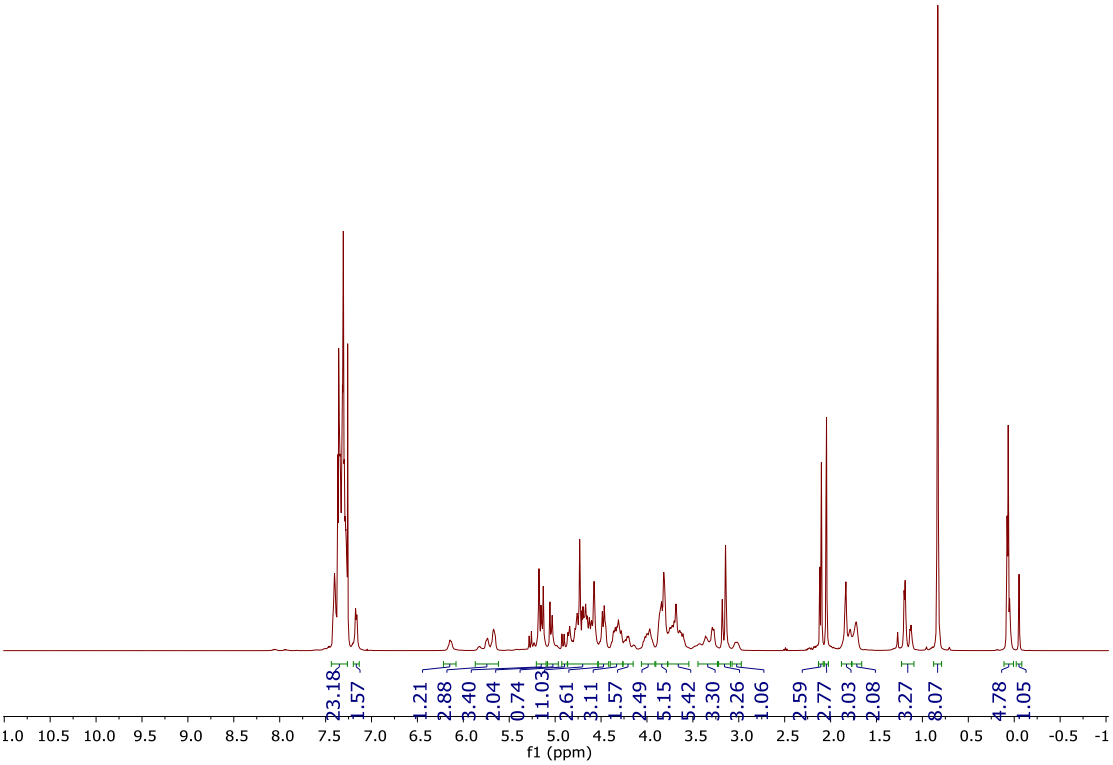
^{1}H-^{1}H gCOSY of **36α** (500 MHz $CDCl_3$)



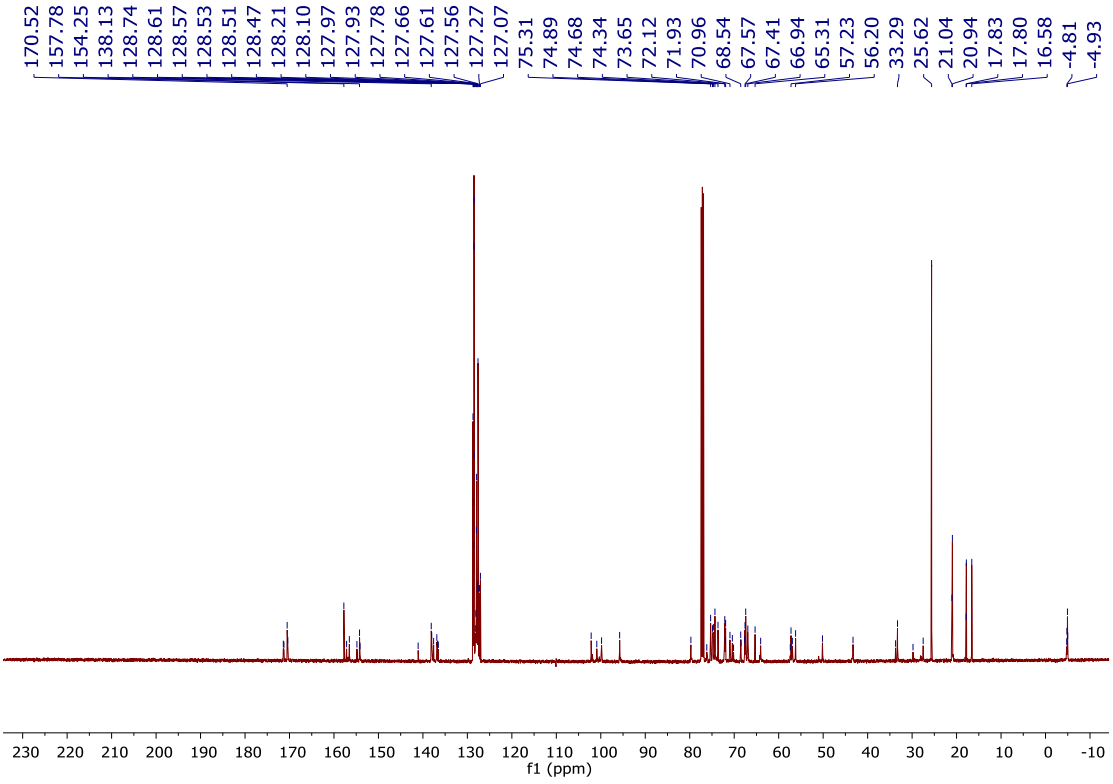
^{1}H-^{13}C gHSQCAD of **36α** (500 MHz $CDCl_3$)



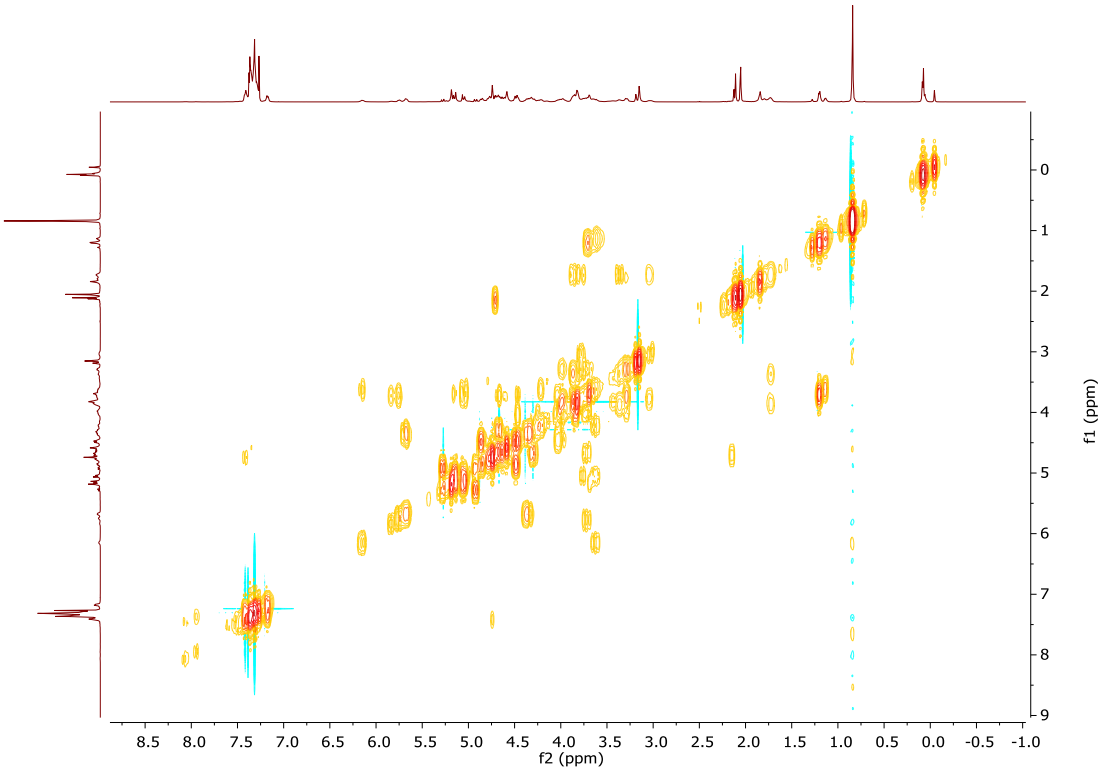
^{1}H-NMR of **36β** (500 MHz $CDCl_3$)



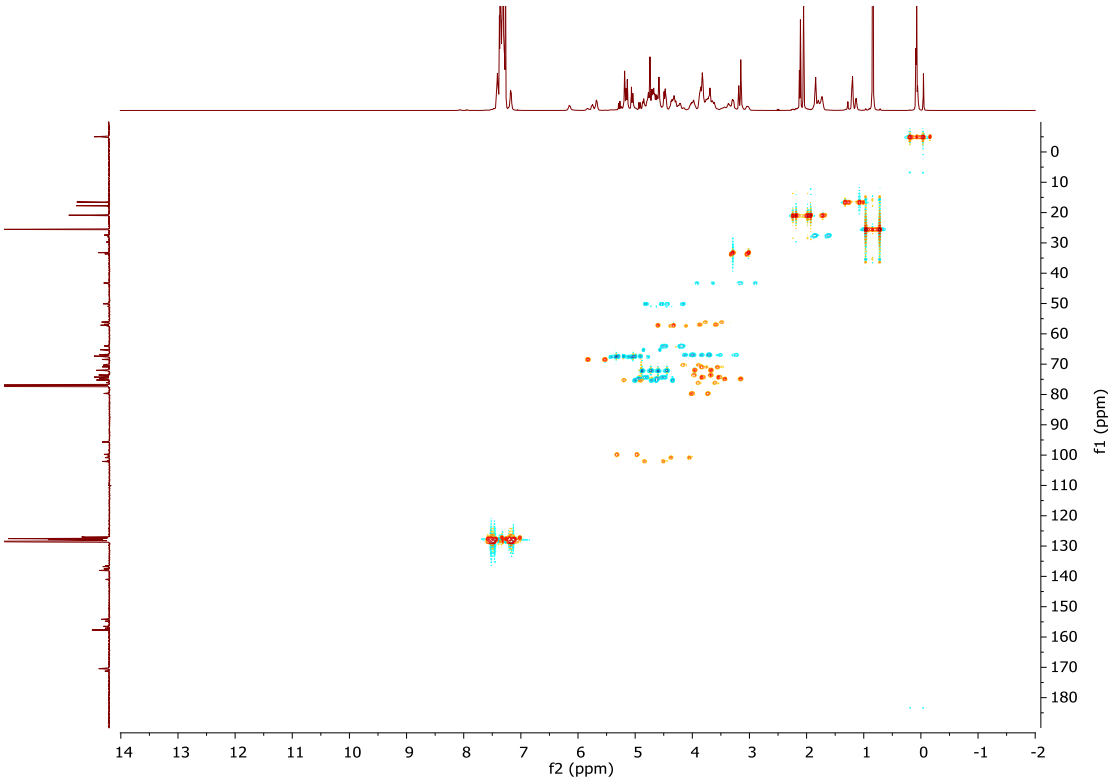
^{13}C-NMR of **36β** (125 MHz $CDCl_3$)



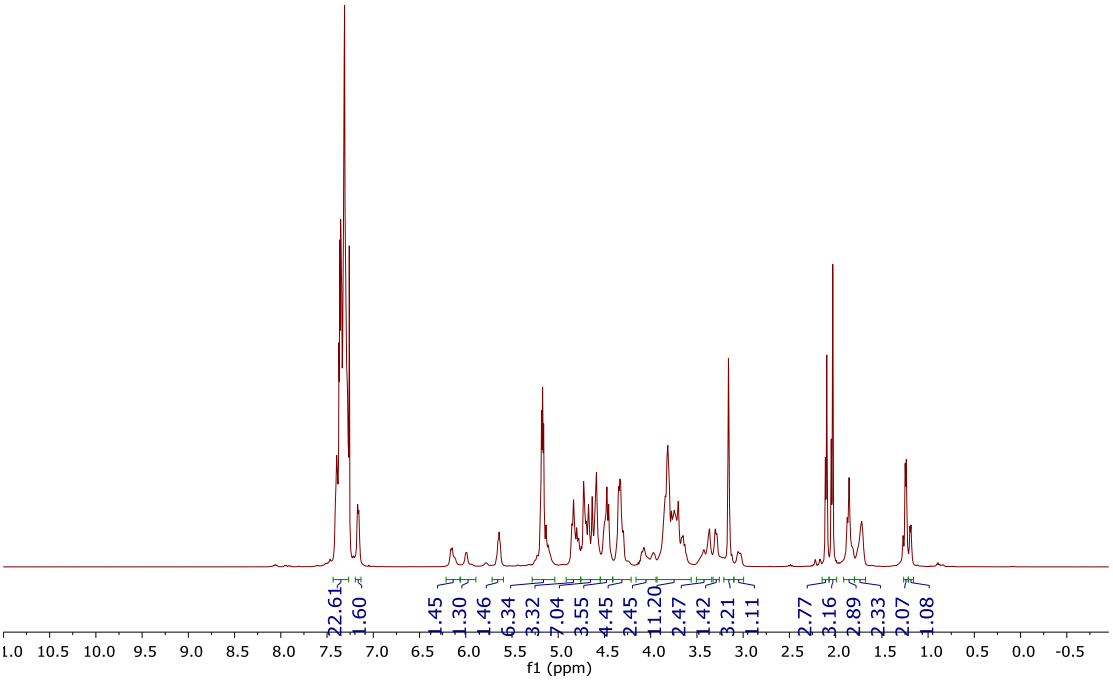
^{1}H-^{1}H gCOSY of **36β** (500 MHz $CDCl_3$)



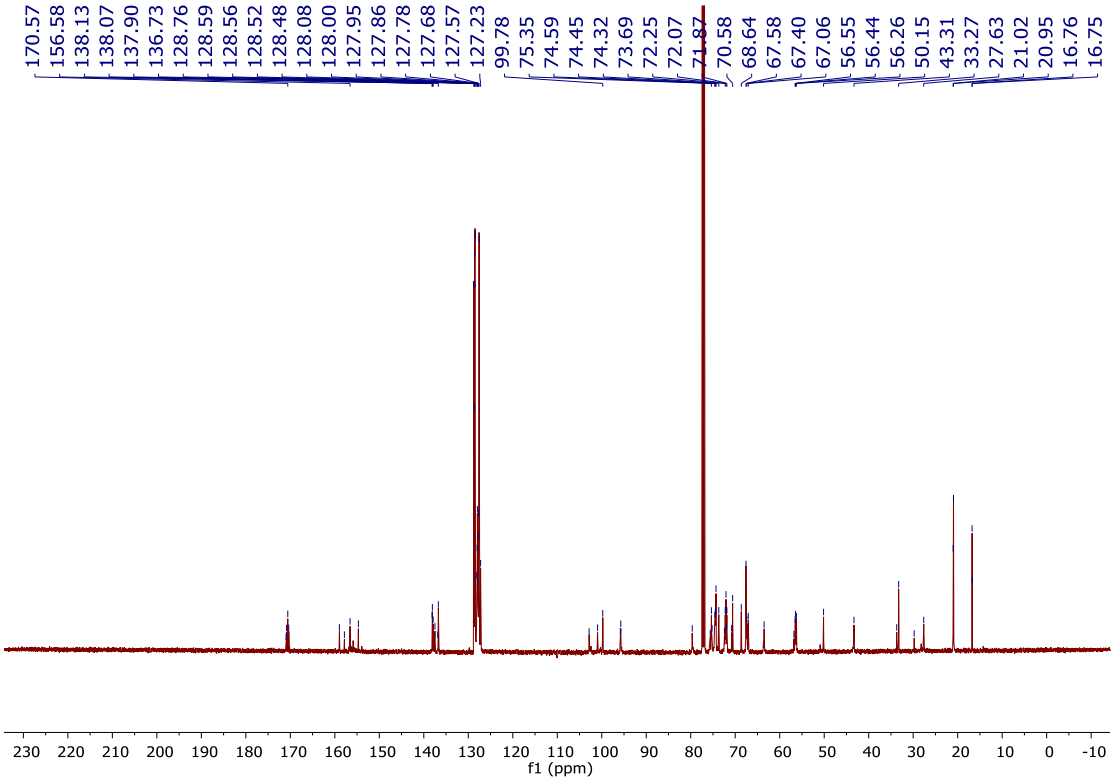
^{1}H-^{13}C gHSQCAD of **36β** (500 MHz $CDCl_3$)



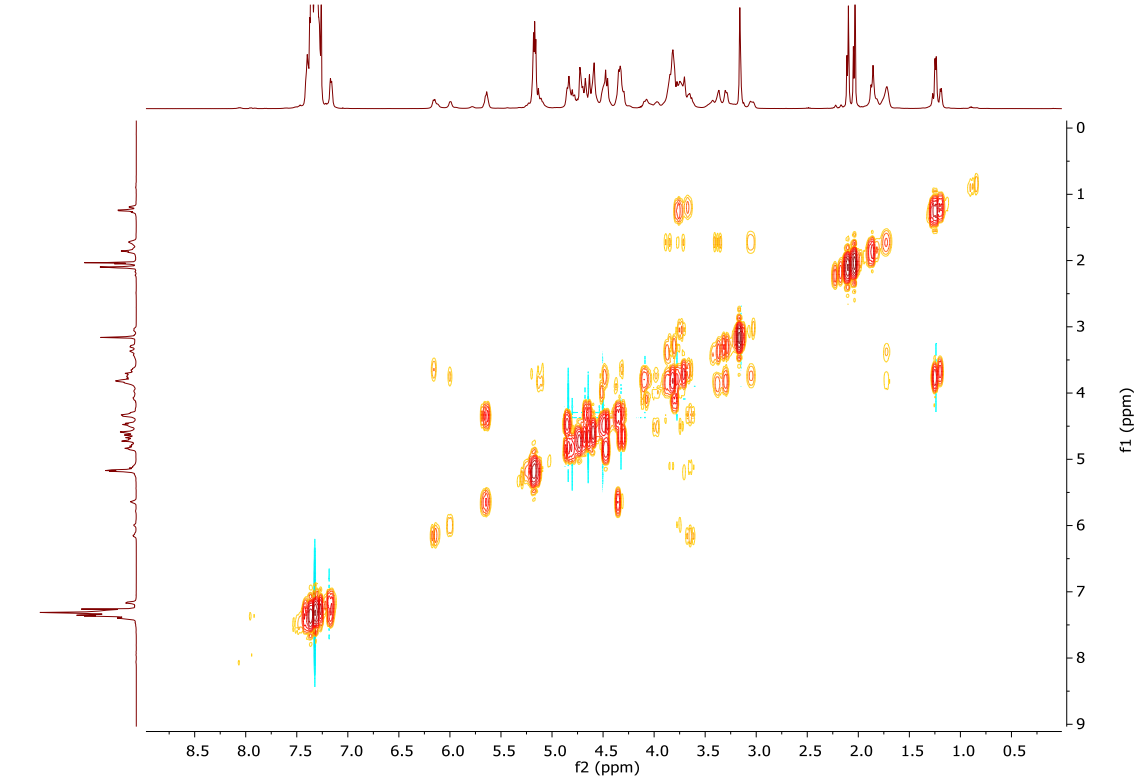
^{1}H-NMR of **37** (500 MHz $CDCl_3$)



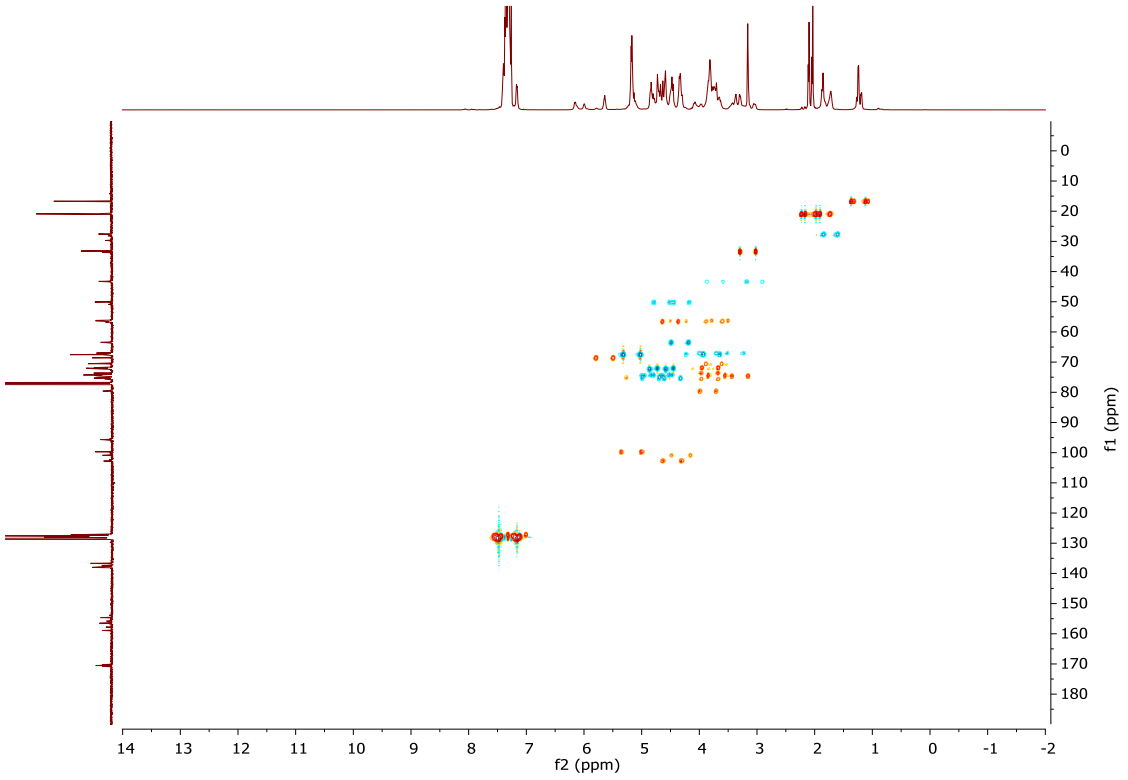
^{13}C-NMR of **37** (125 MHz $CDCl_3$)



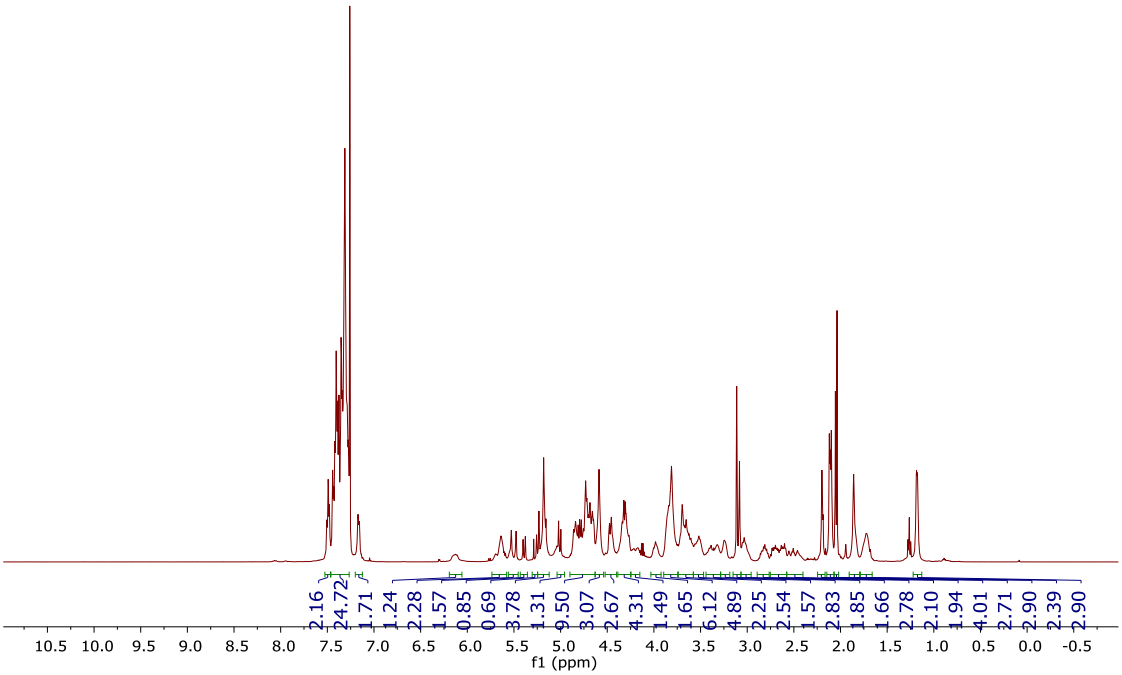
^{1}H-^{1}H gCOSY of **37** (500 MHz $CDCl_3$)



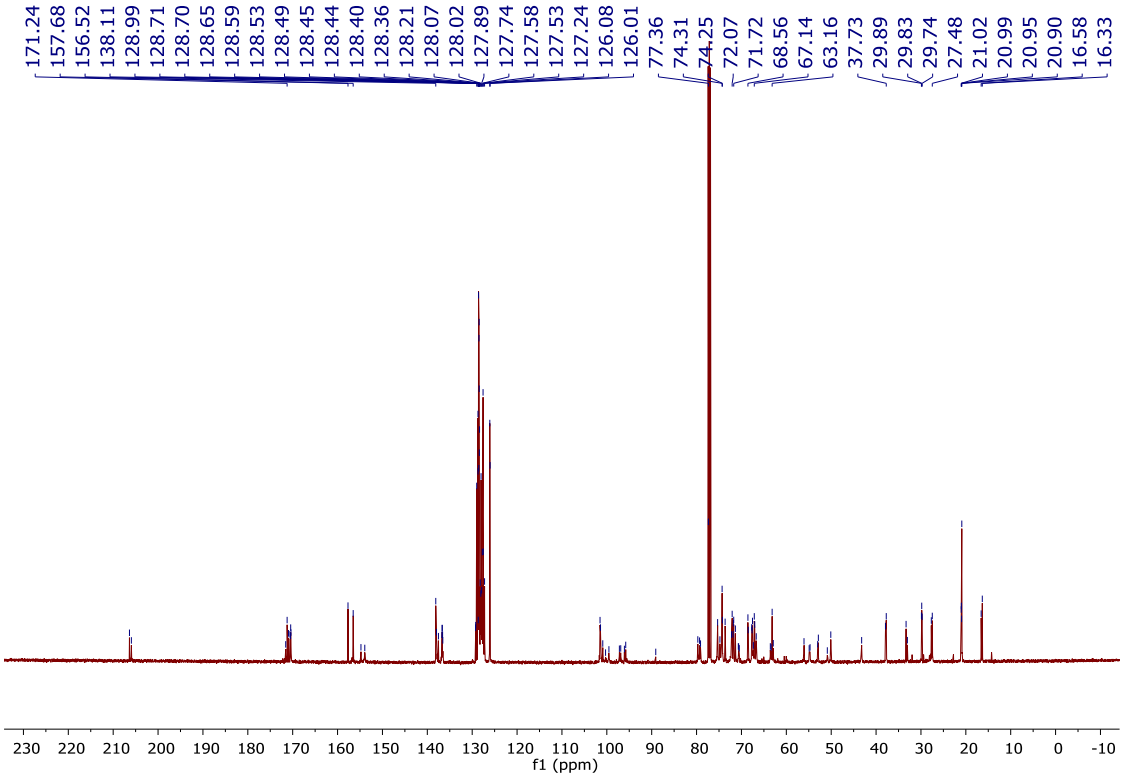
^{1}H-^{13}C gHSQCAD of **37** (500 MHz $CDCl_3$)



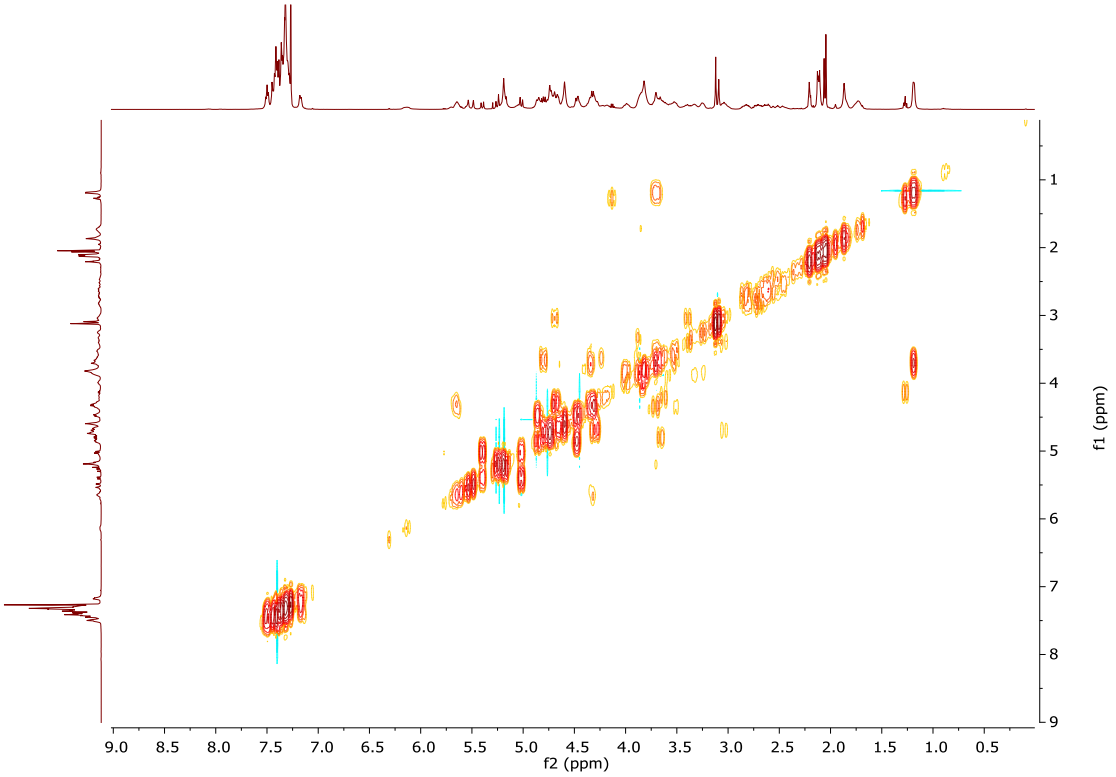
^{1}H-NMR of **38** (500 MHz $CDCl_3$)



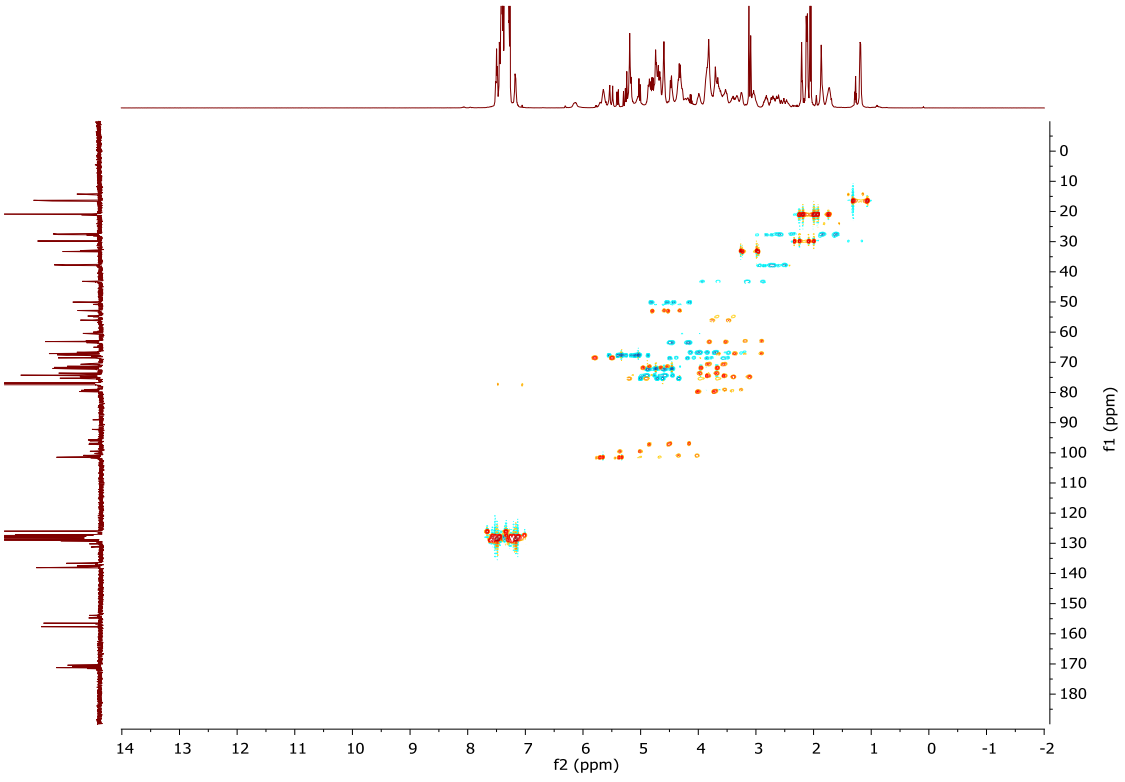
^{13}C-NMR of **38** (125 MHz $CDCl_3$)



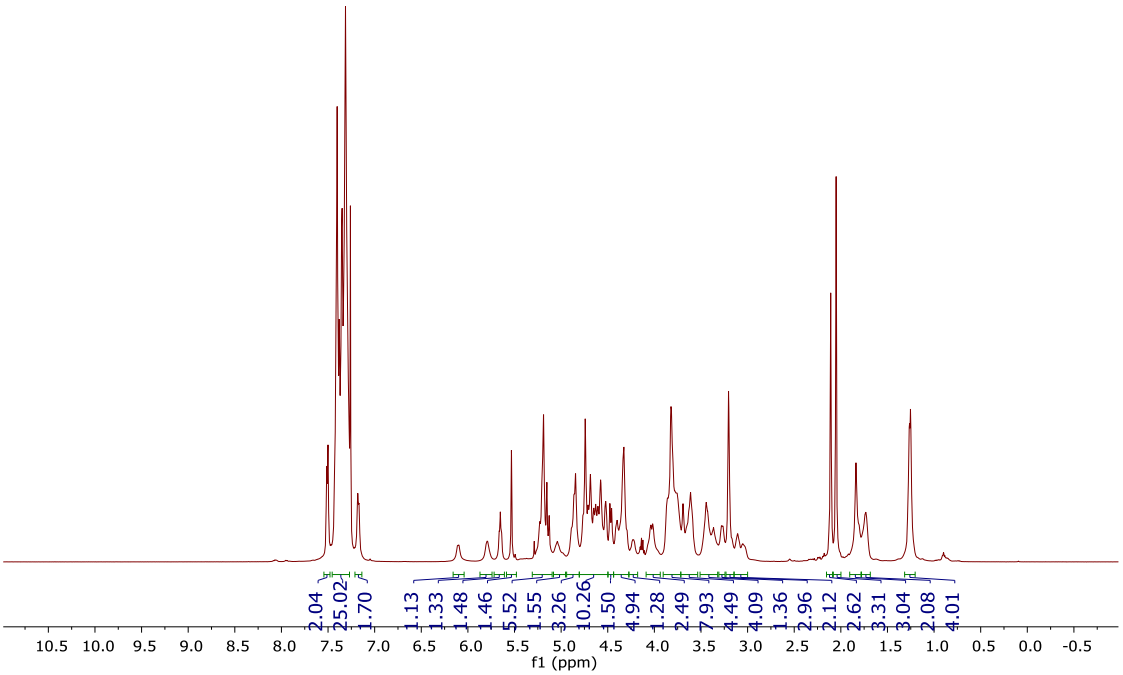
^{1}H-^{1}H gCOSY of **38** (500 MHz $CDCl_3$)



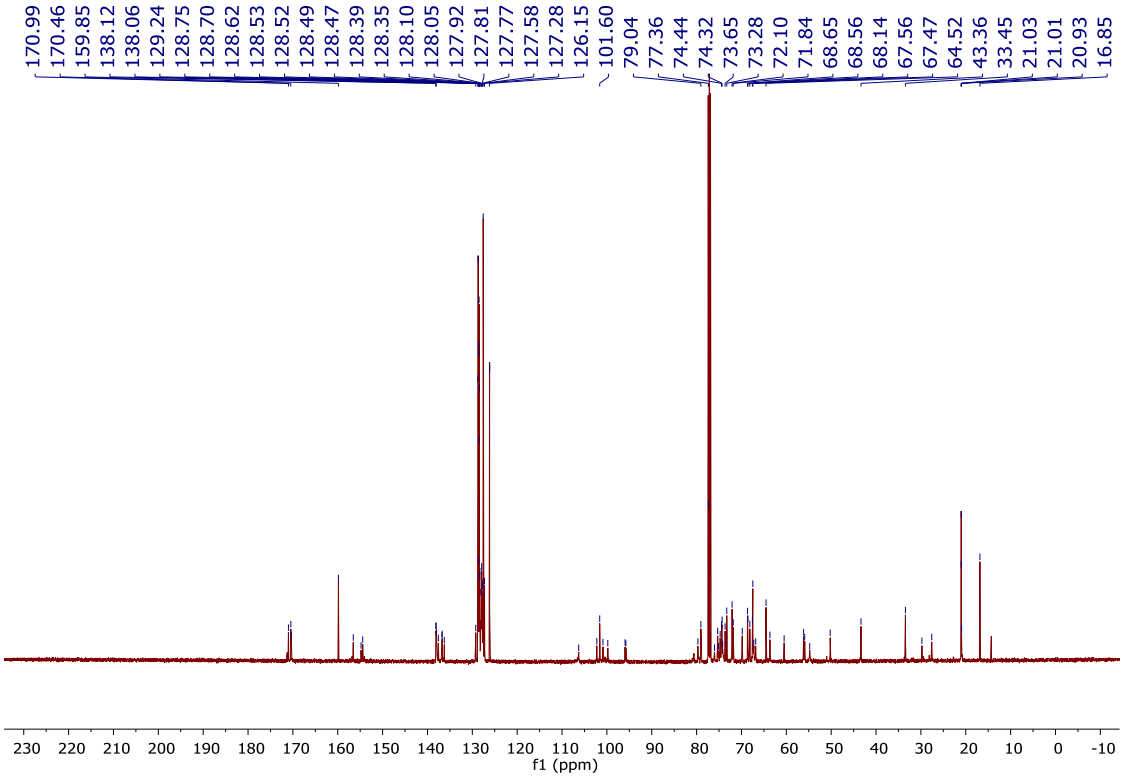
^{1}H-^{13}C gHSQCAD of **38** (500 MHz $CDCl_3$)



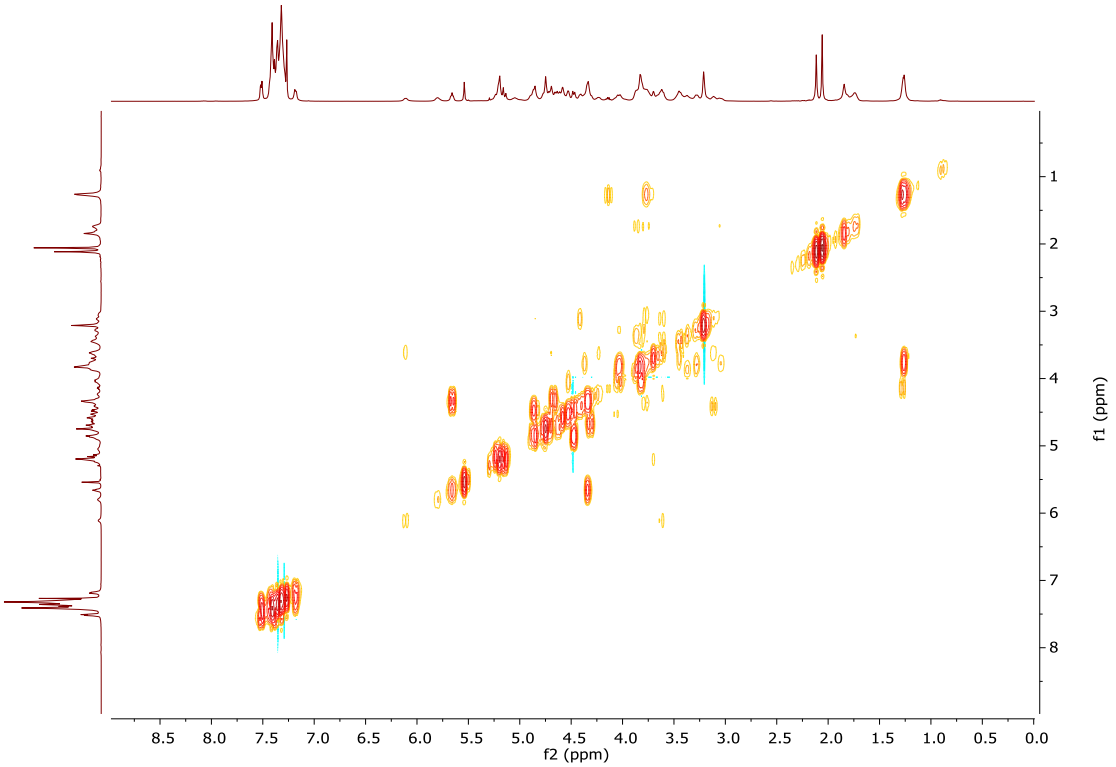
^{1}H-NMR of **39** (500 MHz $CDCl_3$)



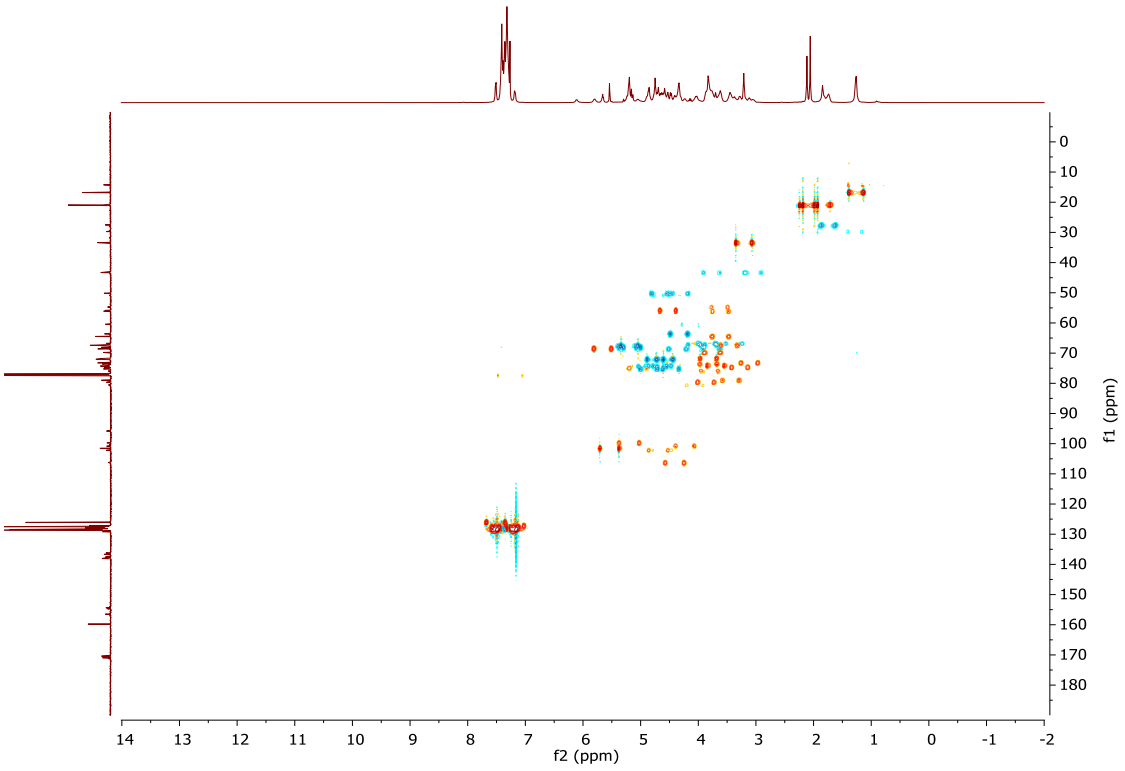
^{13}C-NMR of **39** (125 MHz $CDCl_3$)



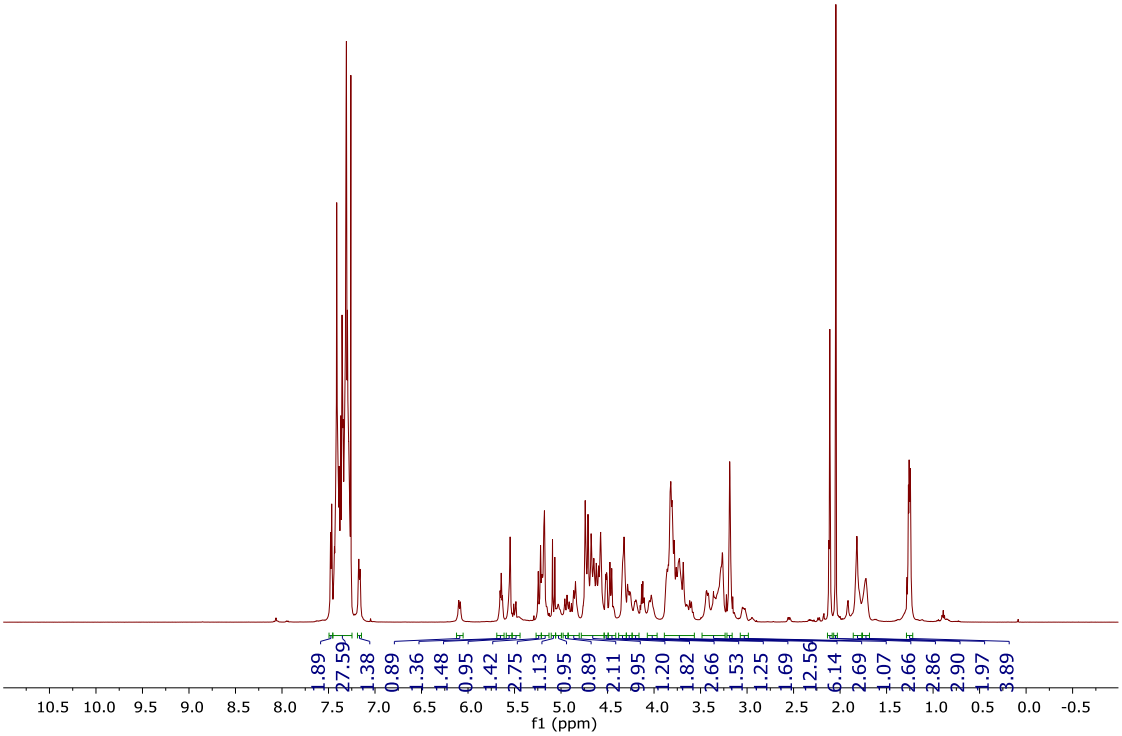
^{1}H-^{1}H gCOSY of **39** (500 MHz $CDCl_3$)



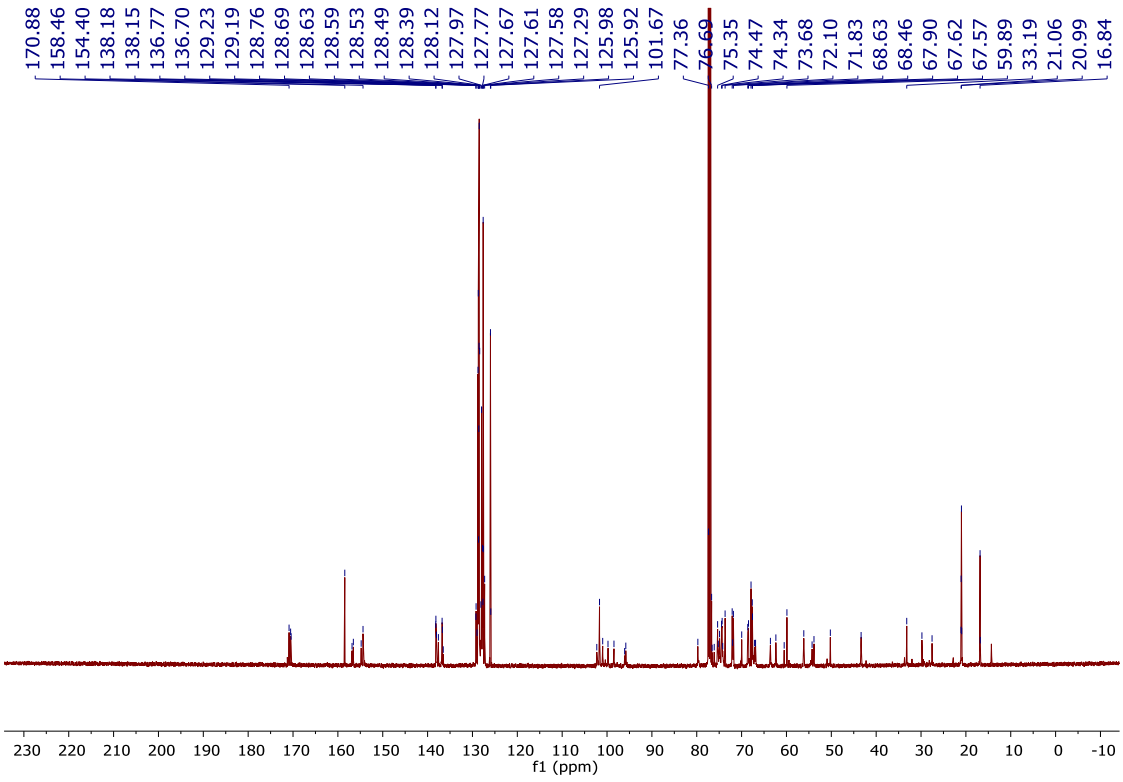
^{1}H-^{13}C gHSQCAD of **39** (500 MHz $CDCl_3$)



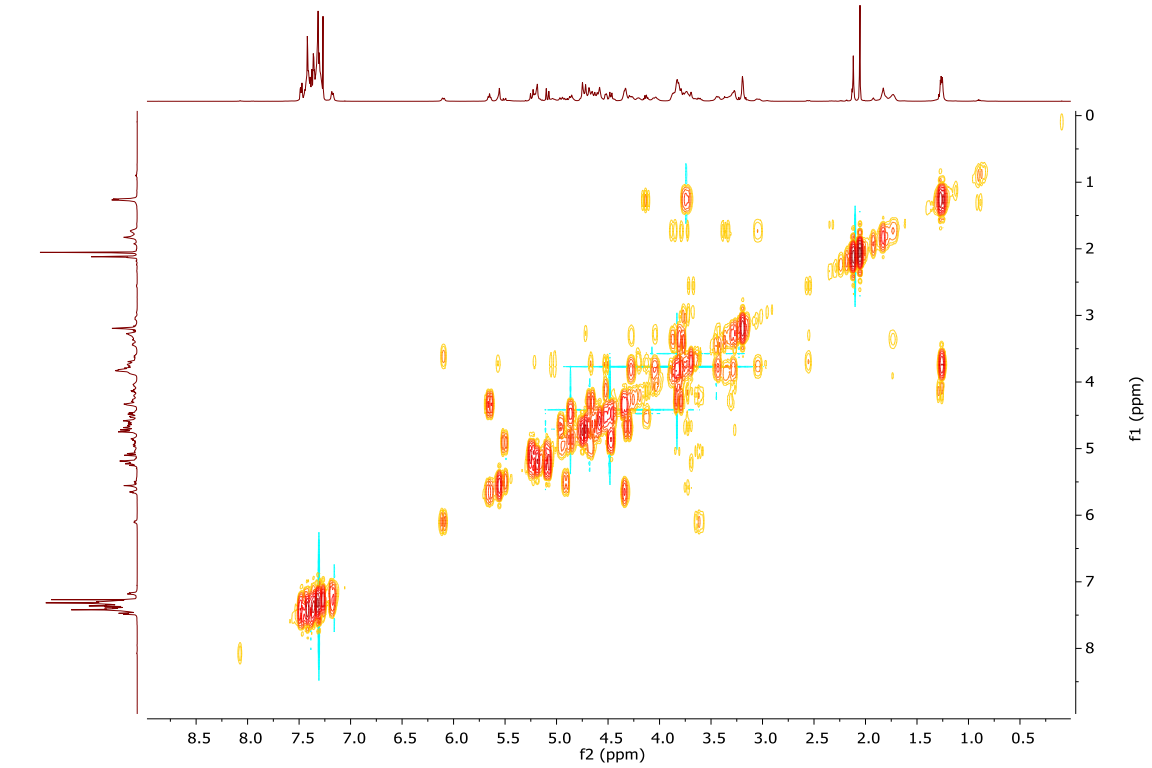
^{1}H-NMR of **40** (500 MHz $CDCl_3$)



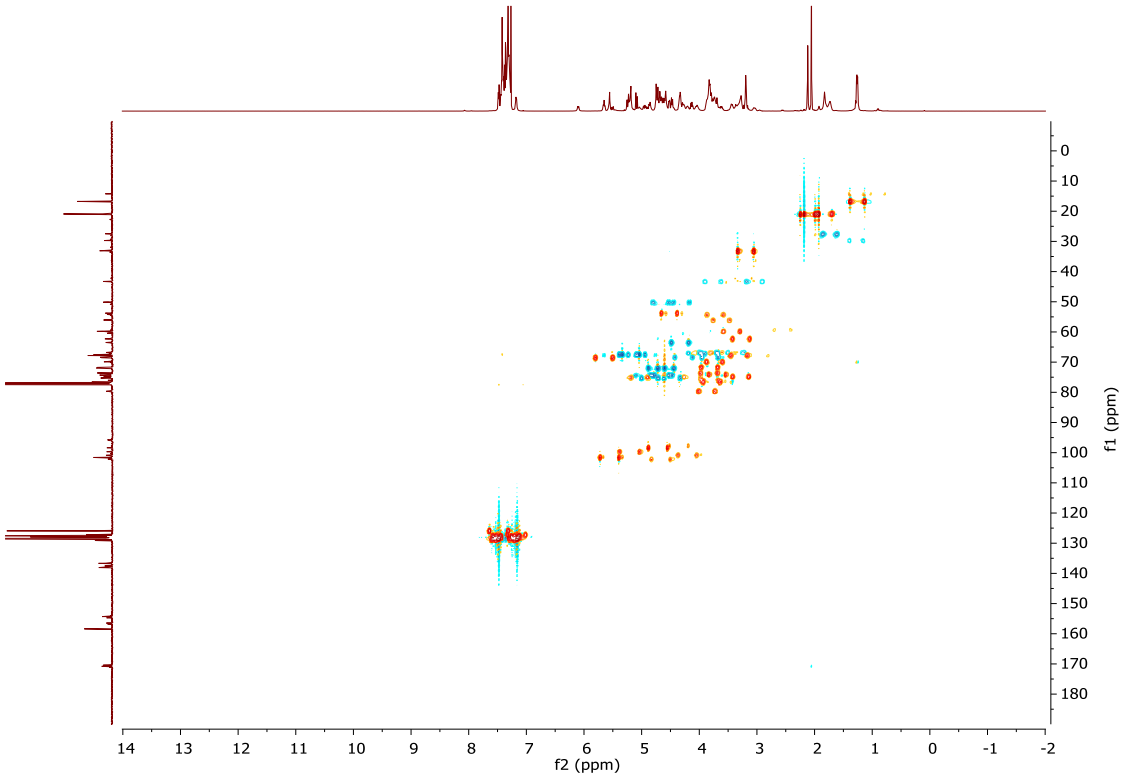
^{13}C-NMR of **40** (125 MHz $CDCl_3$)



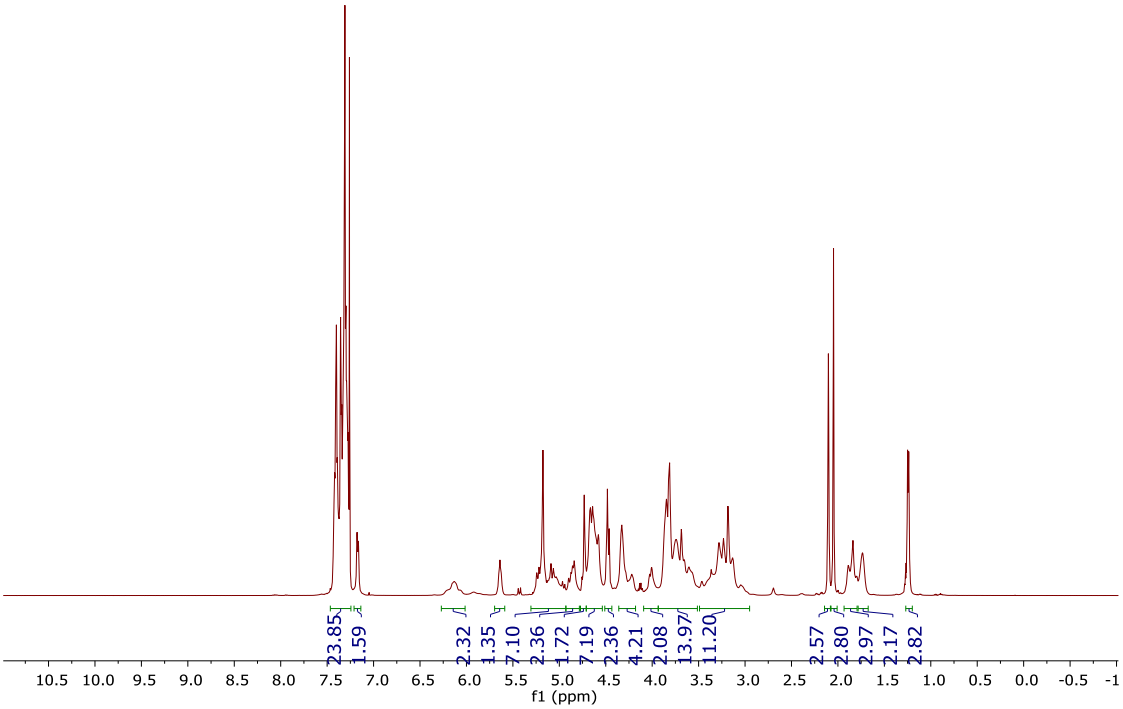
^{1}H-^{1}H gCOSY of **40** (500 MHz $CDCl_3$)



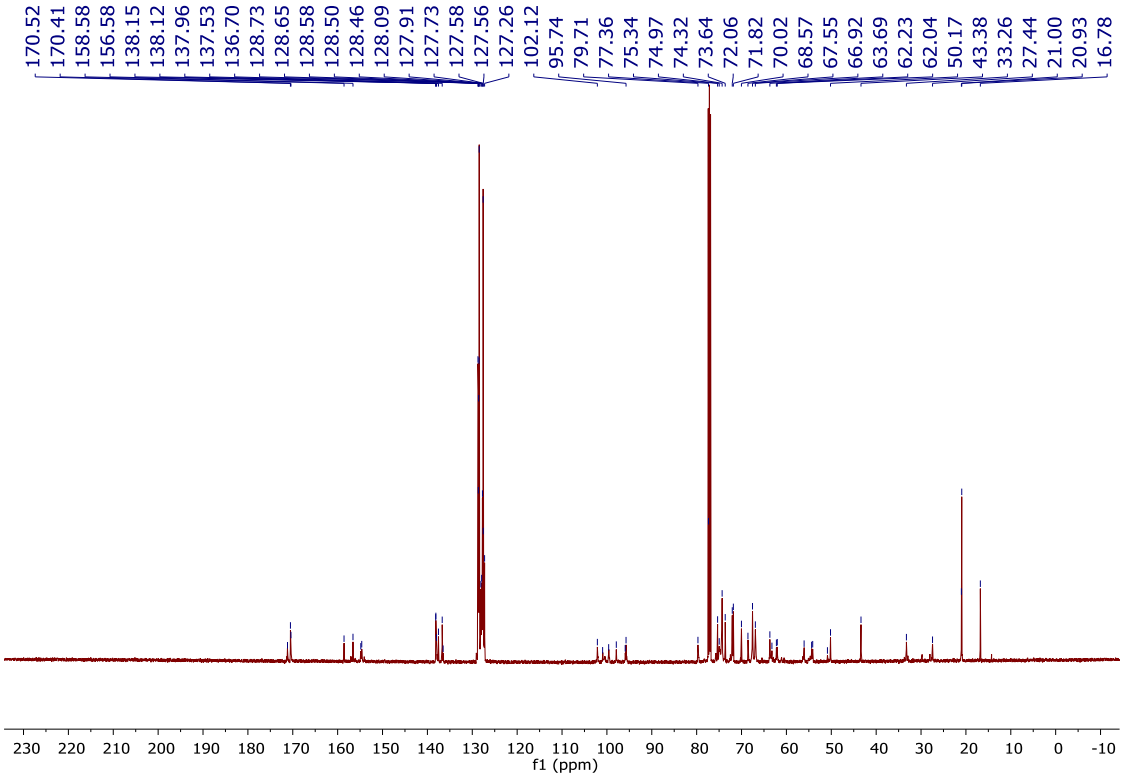
^{1}H-^{13}C gHSQCAD of **40** (500 MHz $CDCl_3$)



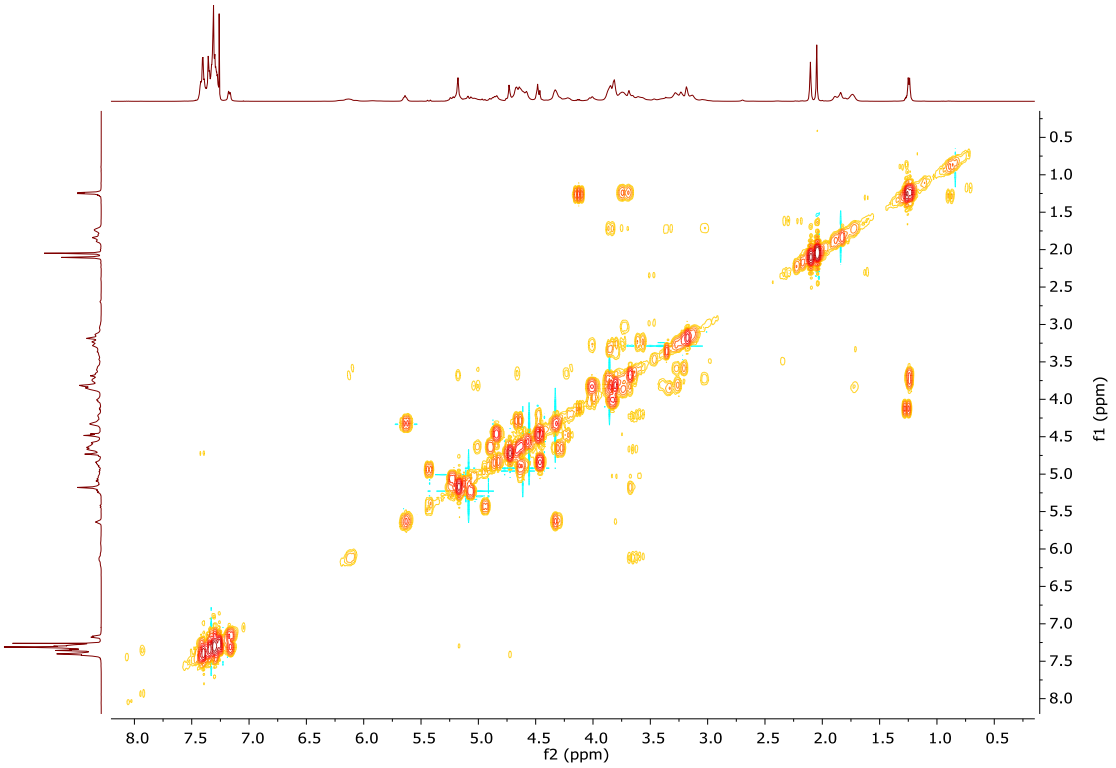
^{1}H-NMR of **41** (500 MHz $CDCl_3$)



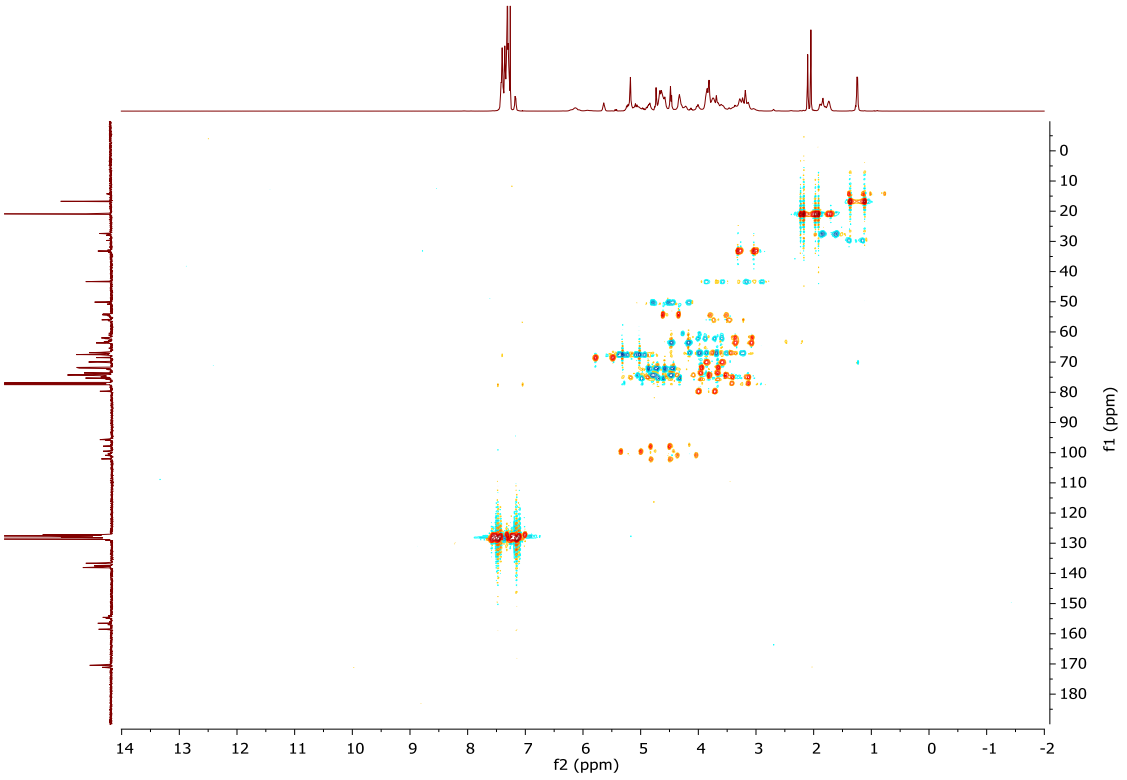
^{13}C-NMR of **41** (125 MHz $CDCl_3$)



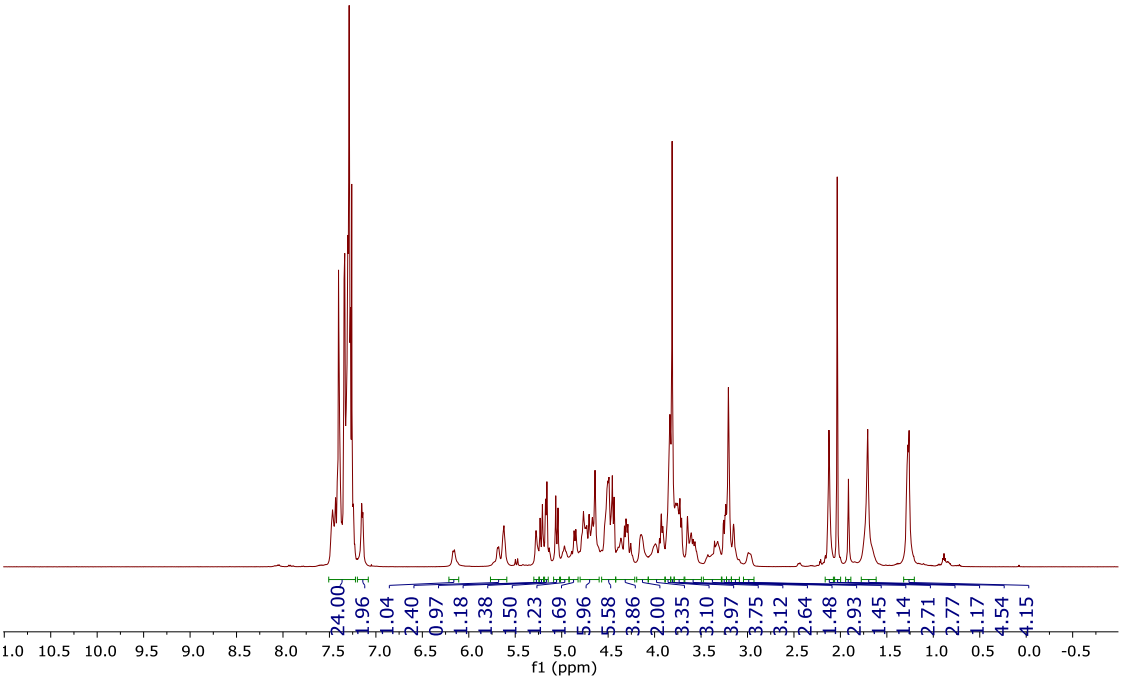
^{1}H-^{1}H gCOSY of **41** (500 MHz $CDCl_3$)



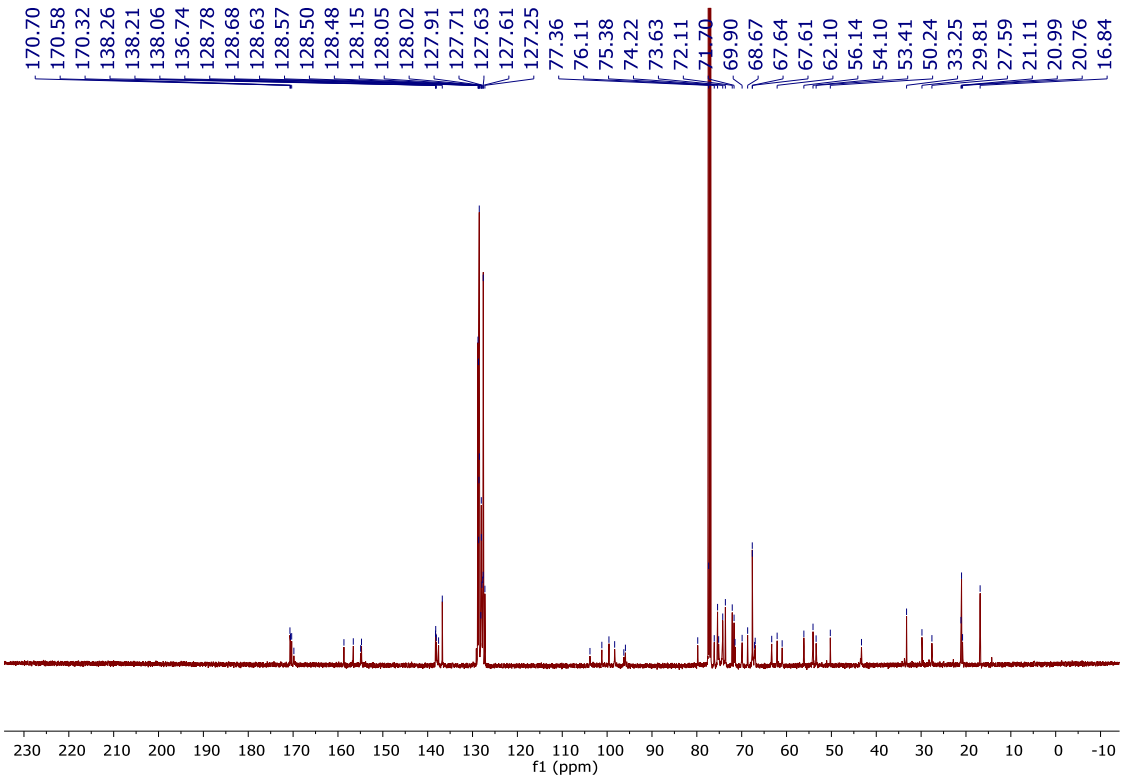
^{1}H-^{13}C gHSQCAD of **41** (500 MHz $CDCl_3$)



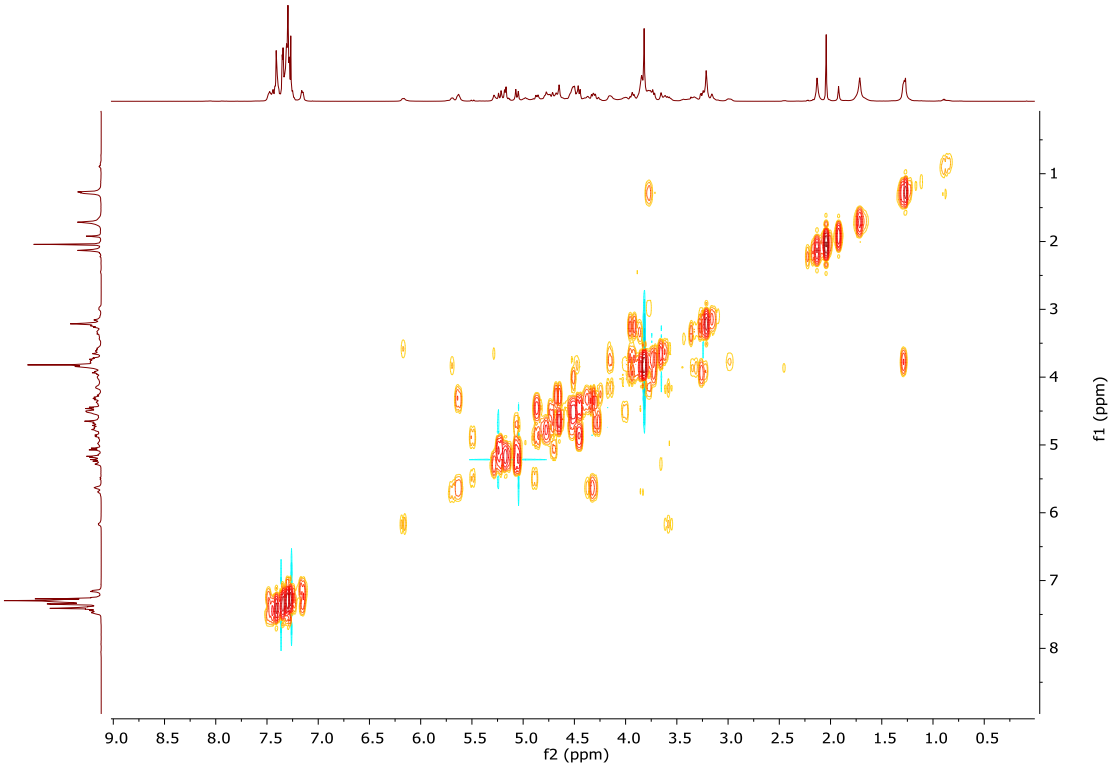
^{1}H-NMR of **42** (500 MHz $CDCl_3$)



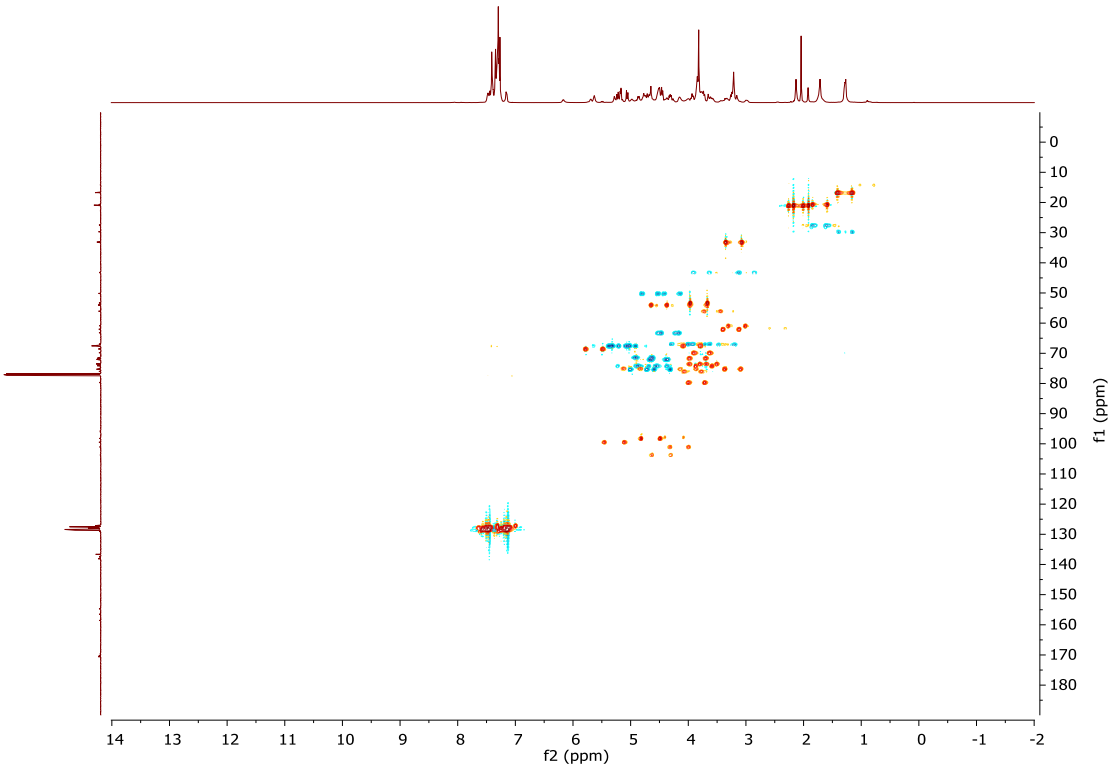
^{13}C-NMR of **42** (125 MHz $CDCl_3$)



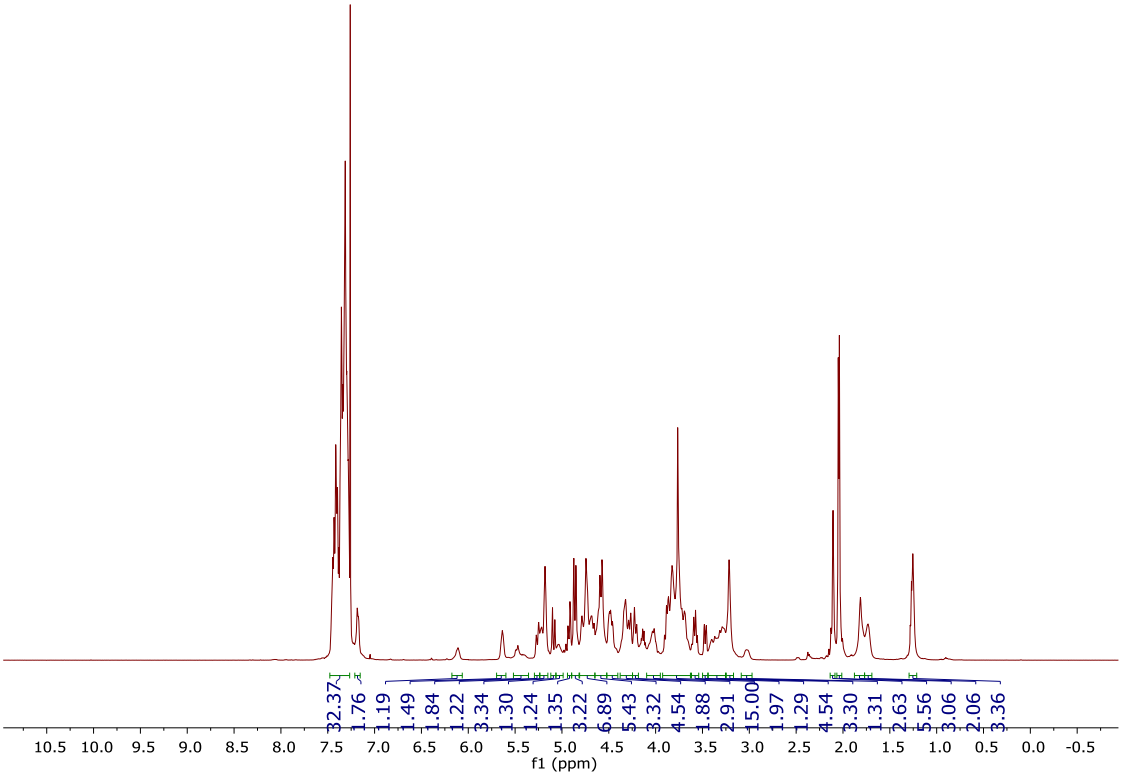
^{1}H-^{1}H gCOSY of **42** (500 MHz $CDCl_3$)



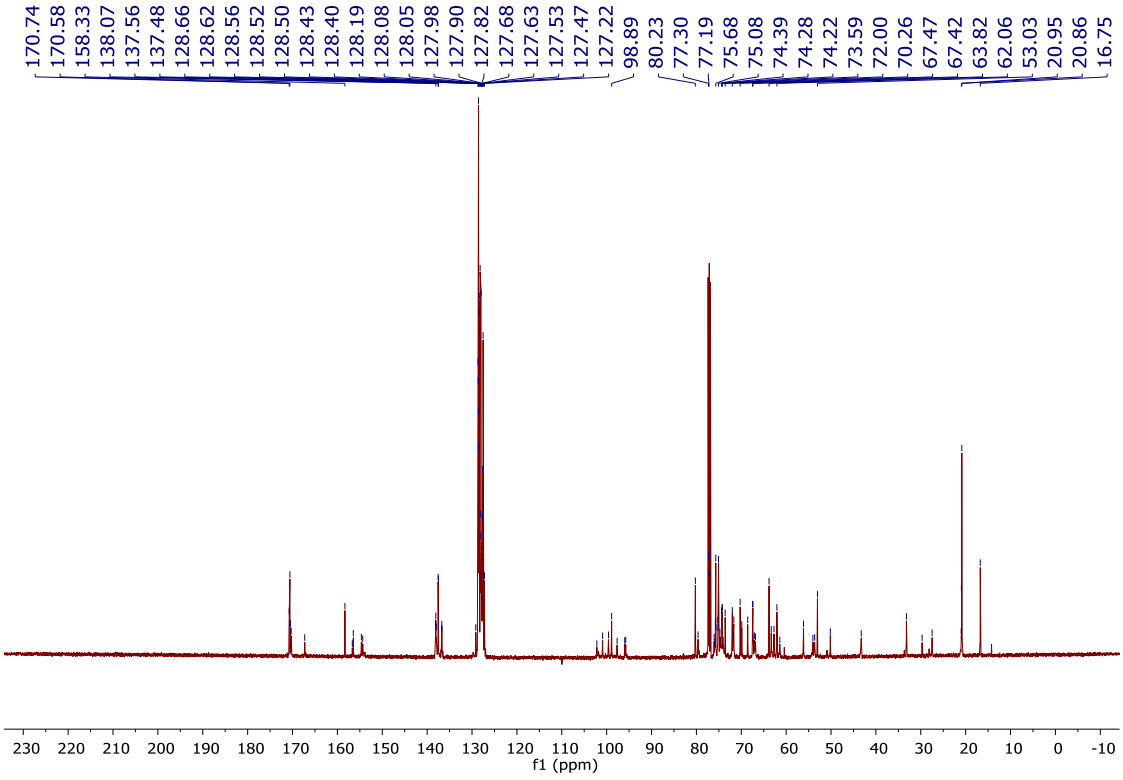
^{1}H-^{13}C gHSQCAD of **42** (500 MHz $CDCl_3$)



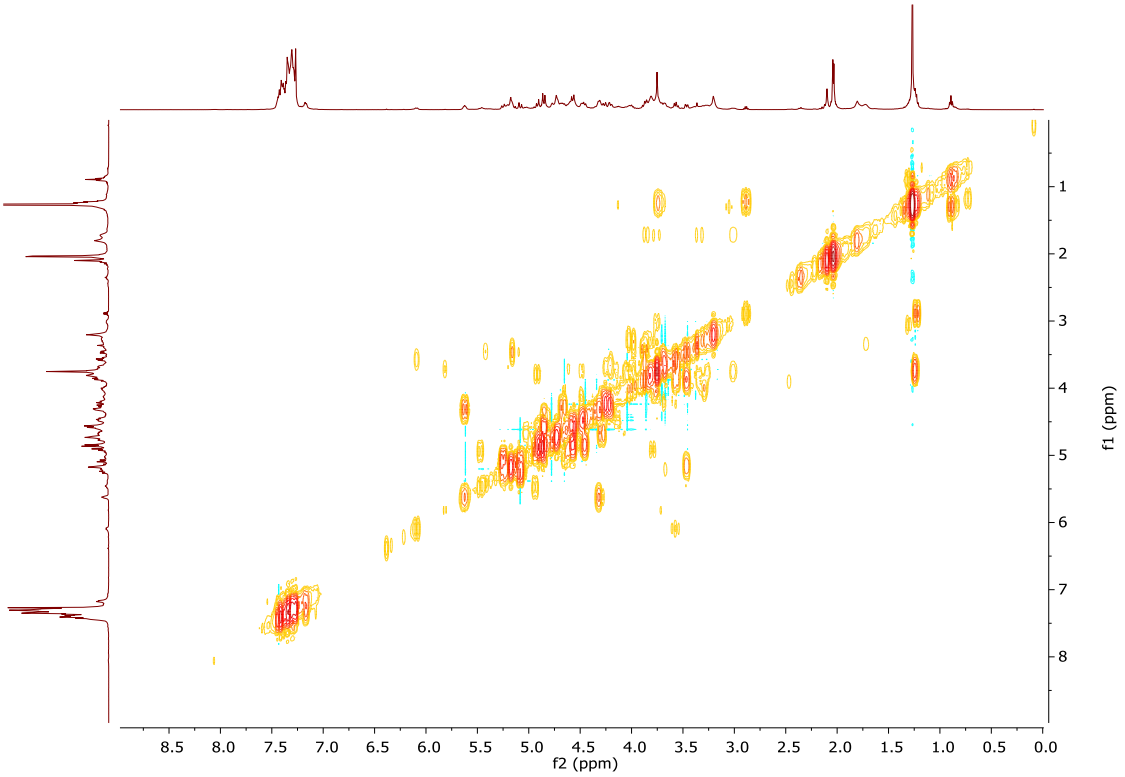
^{1}H-NMR of **43** (500 MHz $CDCl_3$)



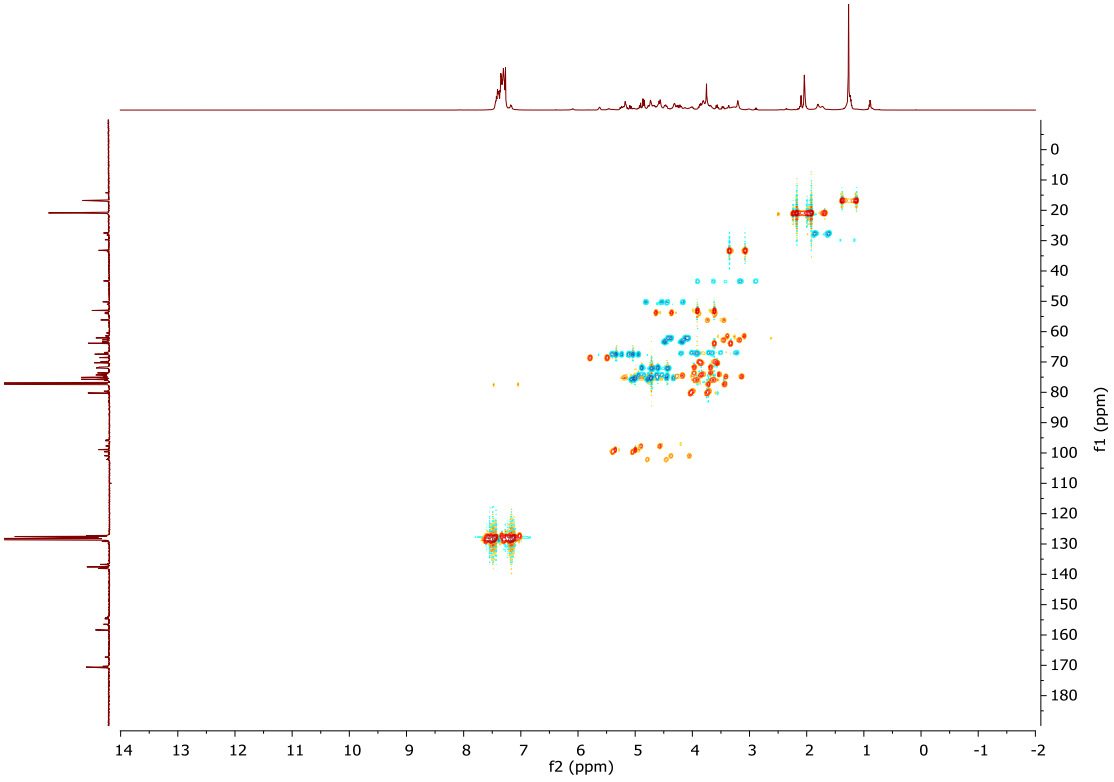
^{13}C-NMR of **43** (125 MHz $CDCl_3$)



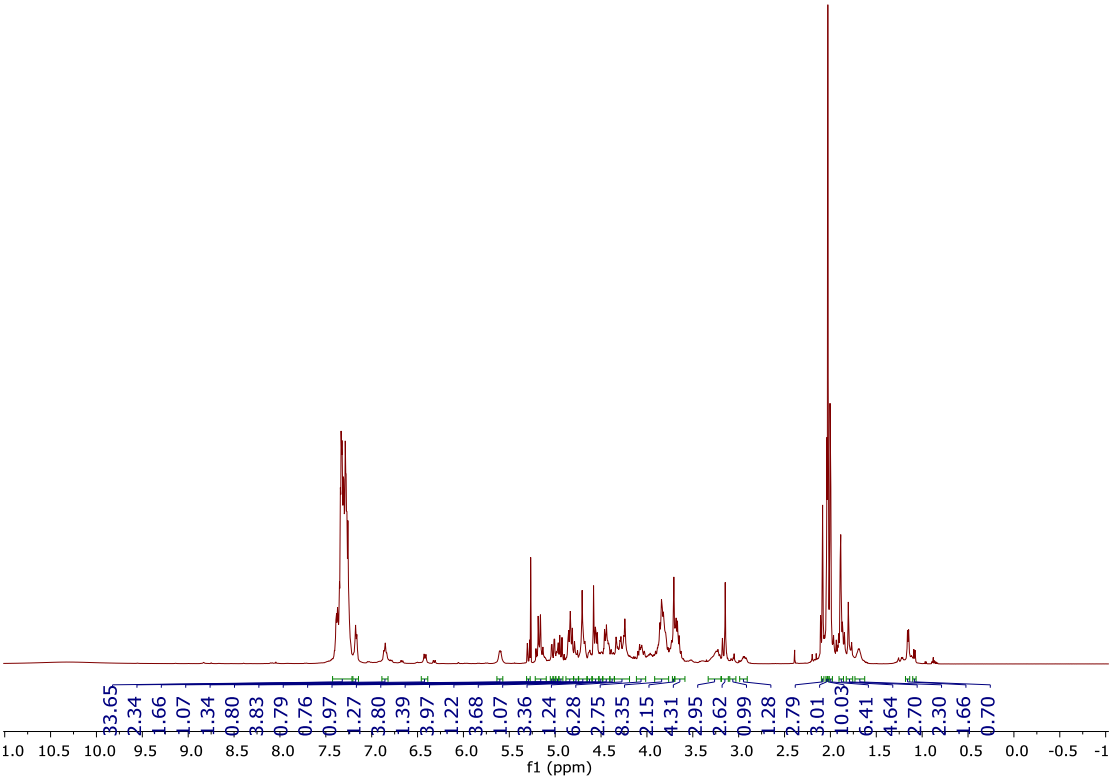
^{1}H-^{1}H gCOSY of **43** (500 MHz $CDCl_3$)



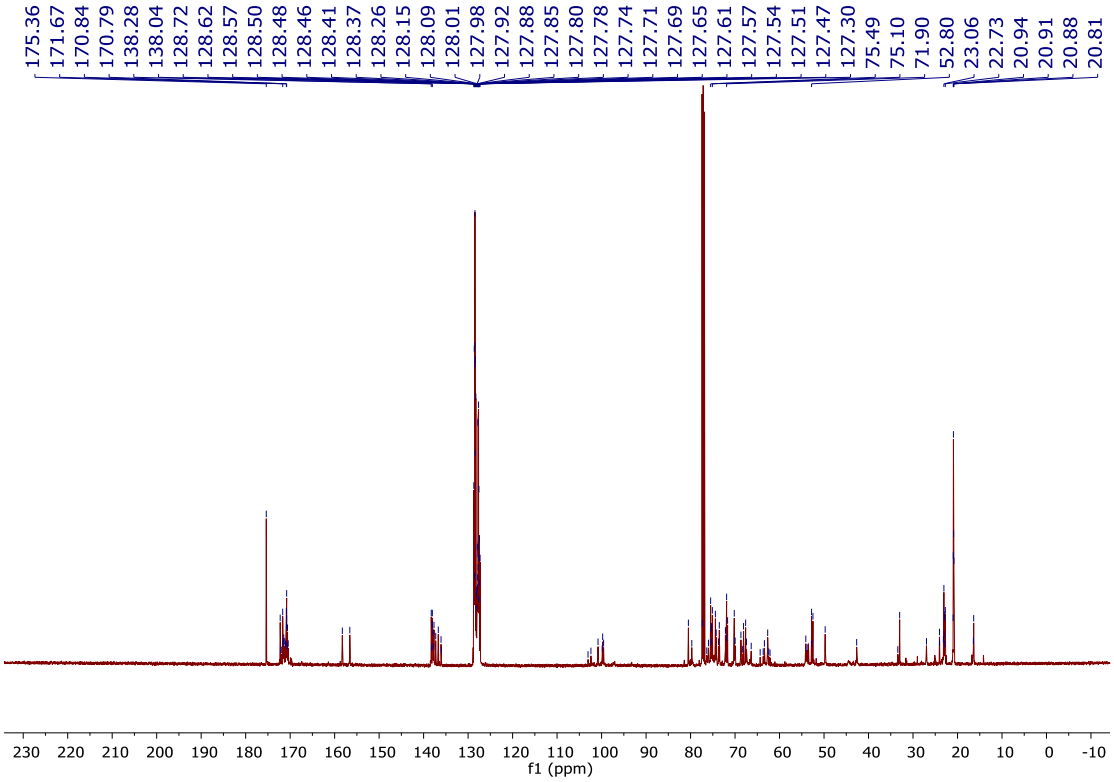
^{1}H-^{13}C gHSQCAD of **43** (500 MHz $CDCl_3$)



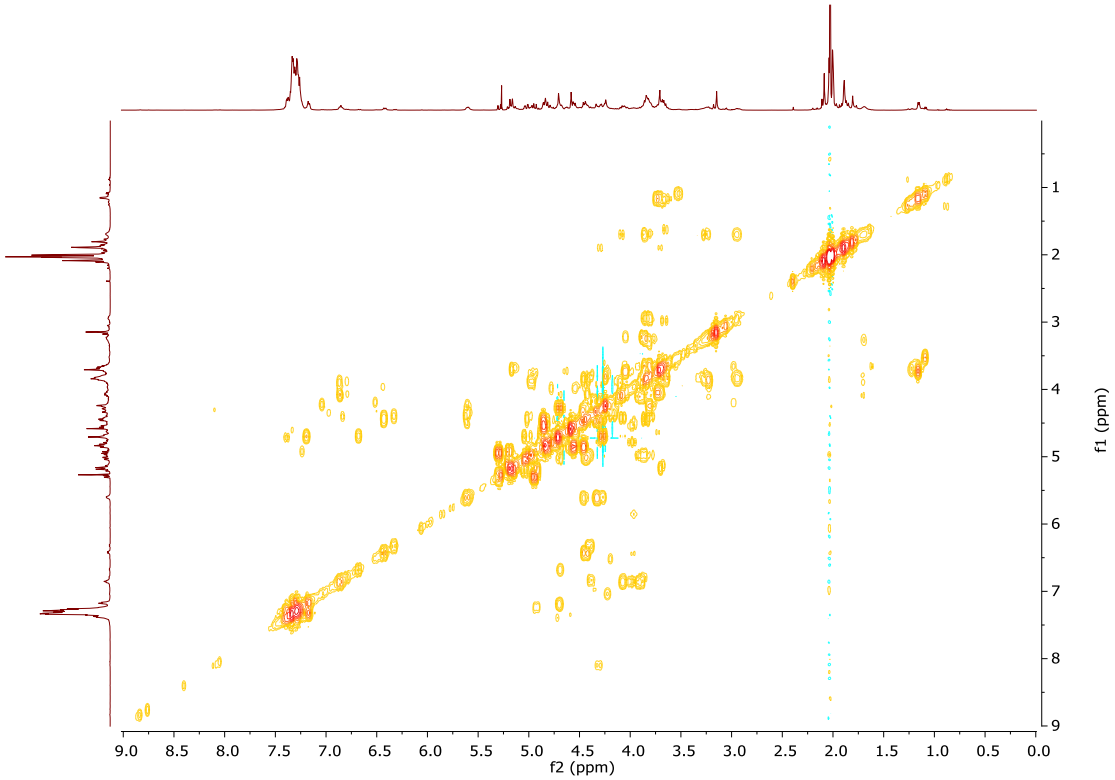
^{1}H-NMR of **44** (500 MHz $CDCl_3$)



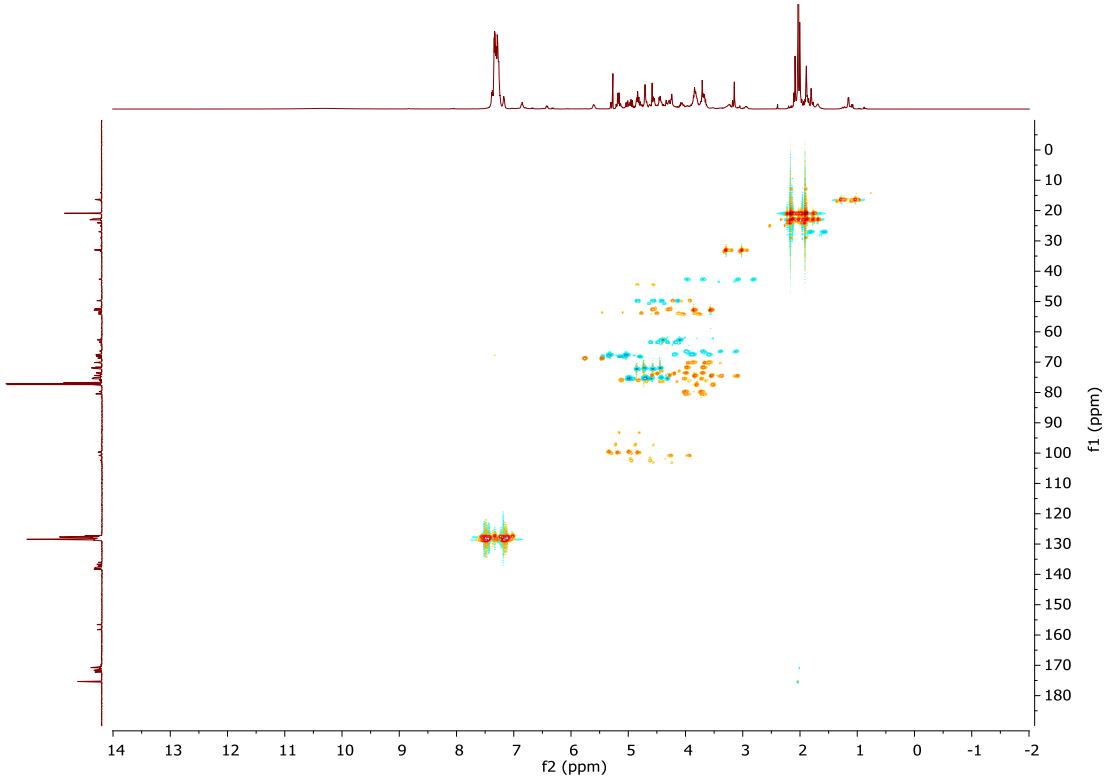
^{13}C-NMR of **44** (125 MHz $CDCl_3$)



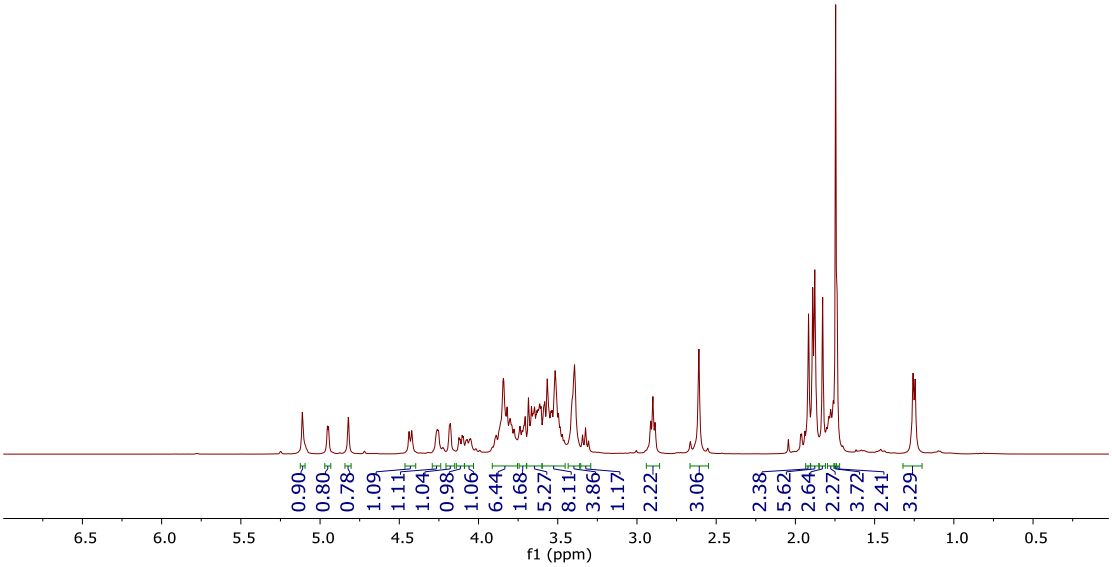
^{1}H-^{1}H gCOSY of **44** (500 MHz $CDCl_3$)



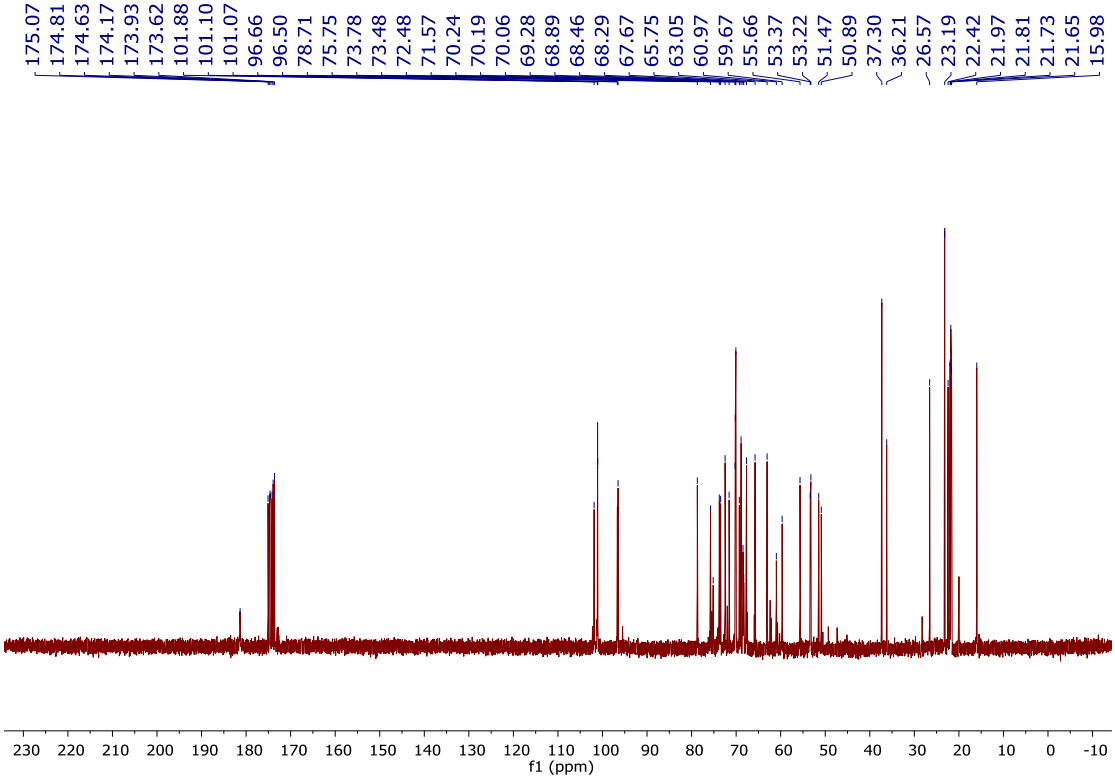
^{1}H-^{13}C gHSQCAD of **44** (500 MHz $CDCl_3$)



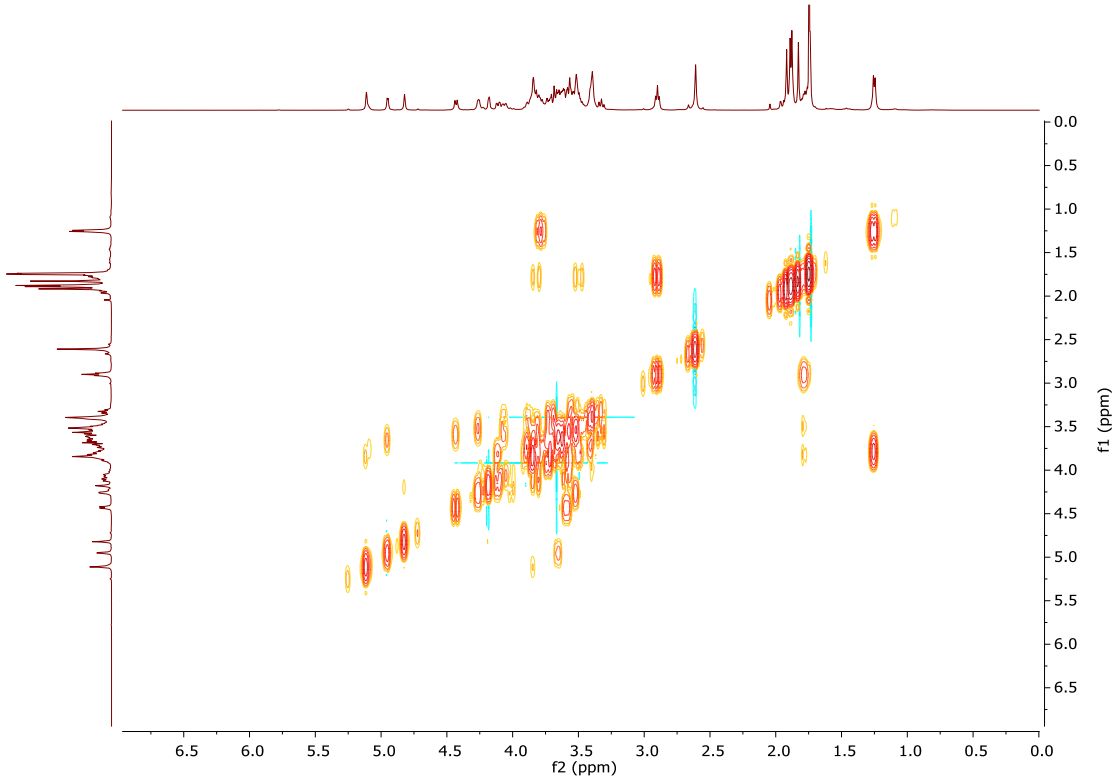
^{1}H-NMR of **1** (500 MHz D_2O, PRESAT)



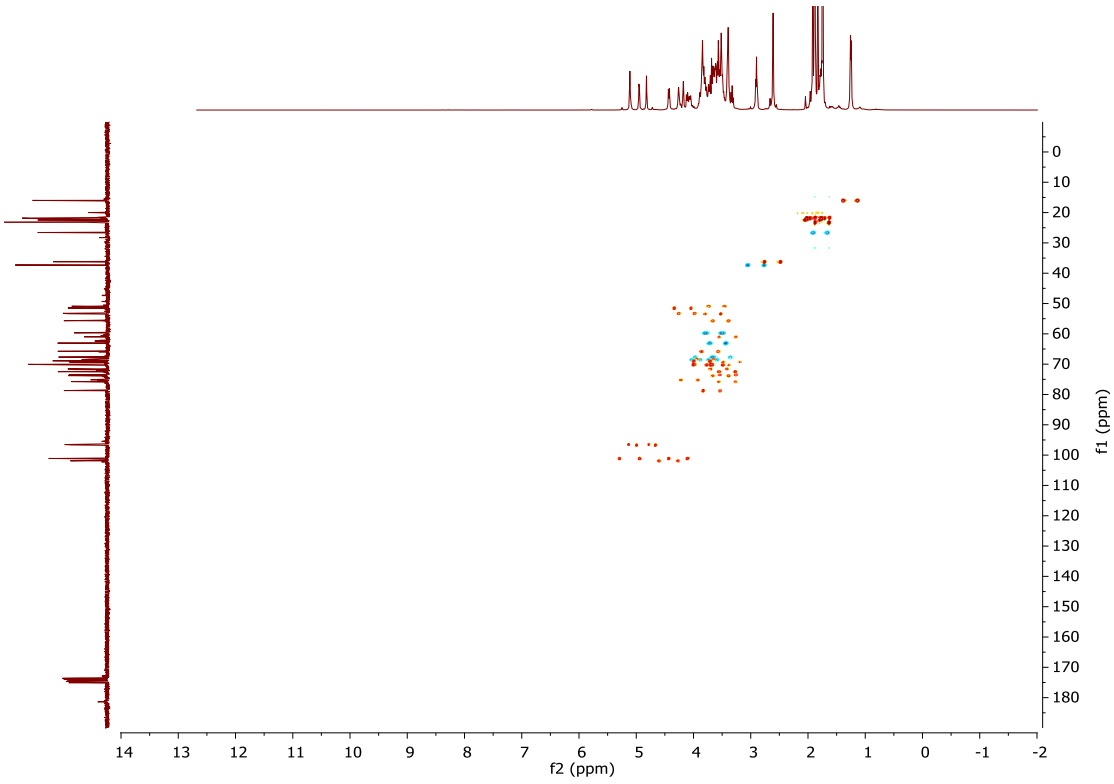
^{13}C-NMR of **1** (125 MHz D_2O)



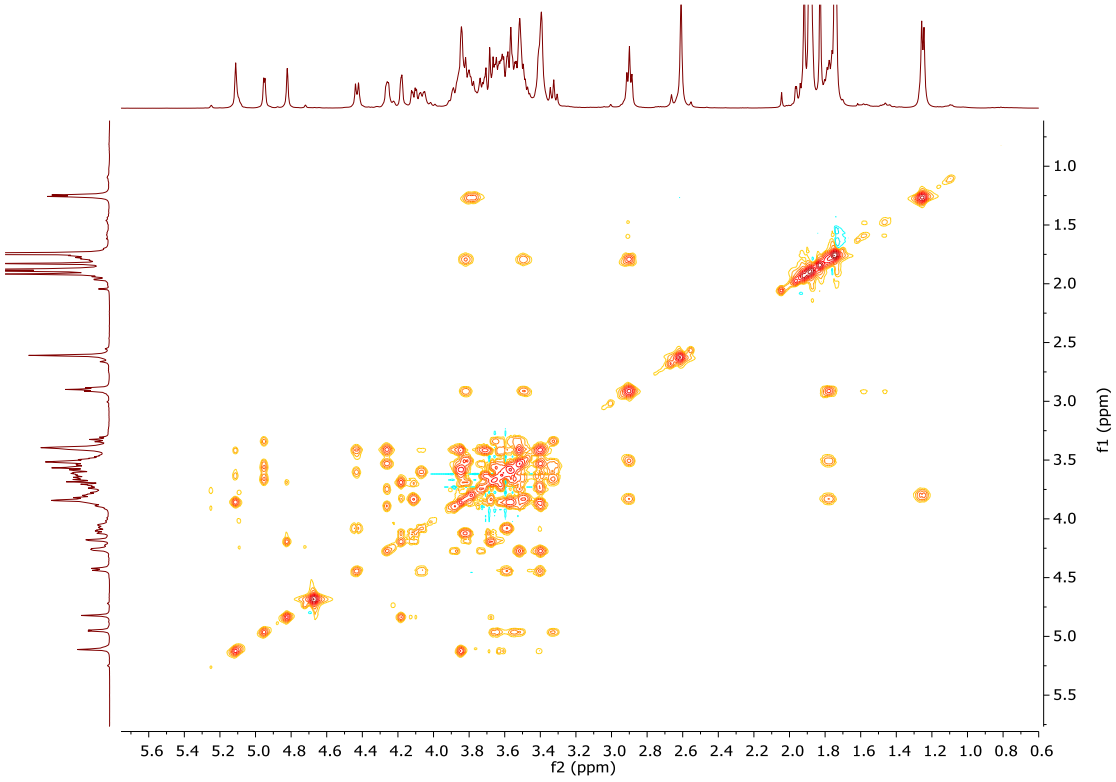
^{1}H-^{1}H gCOSY of **1** (500 MHz D_2O)



^{1}H-^{13}C gHSQCAD of **1** (500 MHz D_2O)



^{1}H-^{1}H TOCSY of **1** (500 MHz D_2O)



^{1}H-NMR of **46** (500 MHz CD_3OD)