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Regioselective S_N2 reactions for rapid synthesis of azidoinositols by one-pot sequence-specific nucleophilyses

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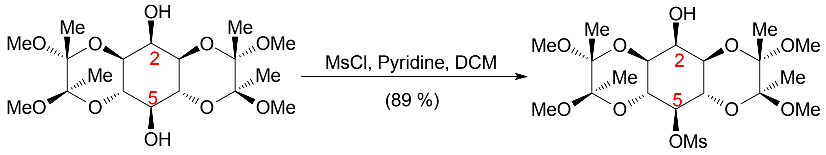
1. Materials and methods

All the required chemicals were purchased from Spectrochem and Sigma Aldrich. The solvents were purchased from Merck (LR grade). Thin layer chromatography was carried out using pre-coated silica gel 60 F254 (Merck) plates. The chromatograms were visualized under UV light and by dipping the plates into a solution of cerium ammonium molybdate stain, followed by heating with a hot air gun. Flash column chromatography was performed using silica gel (200–400 mesh). The ^{1}H, ^{13}C and ^{19}F NMR, COSY, DEPT, Heteronuclear Multiple Quantum Coherence (HMQC), Heteronuclear Multiple Bond Correlation spectra were recorded with an Avance III-500 (Bruker) NMR spectrometer. The ^{1}H NMR spectra were recorded at 500 MHz and are reported as chemical shifts (singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and integration. The ^{13}C NMR spectra were completely proton decoupled and recorded at 125 MHz. All NMR signals were assigned based on ^{1}H and ^{13}C NMR, DEPT, COSY and HMQC experiments. The chemical shifts of the proton (δ) and carbon signals are reported in ppm with reference to the internal standard tetramethylsilane (TMS, δ = 0.0 ppm) or with the solvent reference relative to TMS. IR data were recorded on a IR Prestige-21 instrument using the KBr pellet method. Molecular mass of the compounds was determined using a GCMSQP2010Plus Gas Chromatography Mass Spectrometer. CHNS analysis were carried out in a Vario MICRO

Cube Elementar CHNS Analyzer. Melting points were recorded on a Stuart, SMP 30 melting point apparatus. Single crystal X-ray intensity data were collected on a Bruker KAPPA APEX-II diffractometer in omega and phi scan mode, MoKα = 0.71073 Å at 298 K.

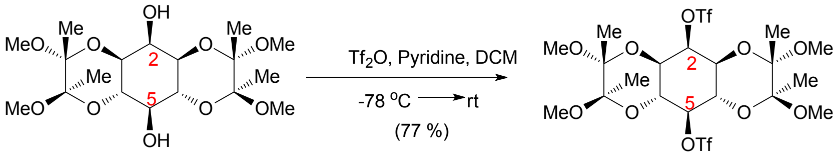
2. Synthesis procedures and nucleophilyses studies

a) Synthesis of mesylate 7:



To a stirred suspension of diol **1** (300 mg, 0.735 mmol), in a mixture of dry DCM (10 mL) and dry pyridine (0.5 mL, 3.675 mmol) mesyl chloride (1.5 mL, 0.882 mmol) was added in drops at 0 °C. The reaction mixture was allowed to stir for 12 hours, and then quenched with triethylamine. The reaction mixture was concentrated and then purified by column chromatography using a mixture of petroleum ether and ethylacetate (7:3, v/v) as eluent. A white solid was obtained (316 mg, 89 %). The melting point could not be obtained as the compound charred on heating to 235 °C. ^{1}H NMR ($CDCl_3$) δ 4.55 (t, J = 9.8 Hz, 1H, H-5), 4.11 (t, J = 9.95 Hz, 2H, H-4 & H-6), 3.97 (s, 1H, H-2), 3.54 (dd, J = 1.4 Hz, J = 10.05 Hz, 2H, H-1 & H-3), 3.20 (s, 6H, OCH_3), 3.18 (s, 6H, OCH_3), 3.06 (s, 3H, Ms-H), 2.34 (s, 1H, -O*H*), 1.27 (s ,6H, CH_3), 1.23 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 100.18, 99.60, 79.68 (C-5), 68.58 (C-2), 68.26 (C-4 & C-6), 66.74 (C-1 & C-3), 48.10 (OCH_3), 47.95 (OCH_3), 38.75 (-SO_2-CH_3), 17.57 (CH_3), 17.54 (CH_3). IR (KBr): 1364 cm^{-1}, 1125 cm^{-1} (S=O); 3489 cm^{-1} (OH). Elemental analysis, Calculated for $C_{19}H_{34}O_{12}S$, C= 46.90, H = 7.04, S = 6.59; Found C = 46.70, H = 7.37, S = 6.89. Calculated m/z = 486.17; Found m/z = 487.17 (M+H). The compound was crystallized from a mixture of ethylacetate and petroleum ether.

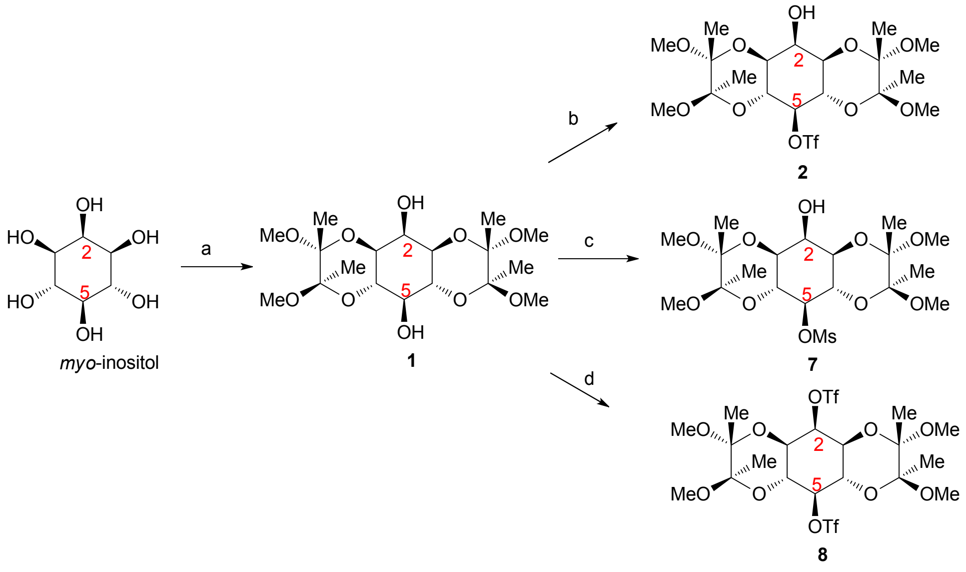
b) Synthesis of ditriflate 8:



1

8

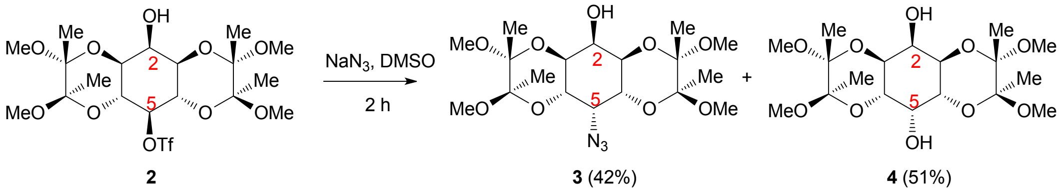
To the diol **1**[1] (2 g, 4.90 mmol) in a mixture of dry DCM (40 mL) and dry pyridine (5 mL), a solution of trifluoromethanesulfonic anhydride (2.5 mL, 14.7 mmol) in dry DCM (10 mL), was added drop wise through an addition funnel at -78 °C under nitrogen atmosphere. The cooling bath was removed and stirring continued for 12 hours. The reaction mixture was then washed with saturated sodium bicarbonate solution and brine. The organic layer was concentrated and the product purified by column chromatography (1:10, EtOAc : petroleum ether, v/v) to get an off-white solid (2.54 g, 77 %). The melting point could not be obtained as the compound charred on heating to 200 °C. ^{1}H NMR ($CDCl_3$) δ 4.97 (t, J = 2.45 Hz, 1H, H-2), 4.74 (t, J = 9.9 Hz, 1H, H-5) 4.08 (t, J = 10.1 Hz, 2H, H-4 & H-6), 3.72 (dd J = 2.45 Hz, J = 10.1 Hz, 2H, H-1 & H-3), 3.19 (s, 12H, $OC\mathit{H}_3$), 1.22 (s, 6H, $C\mathit{H}_3$),1.22 (s, 6H, $C\mathit{H}_3$); ^{13}C NMR ($CDCl_3$) δ 100.64 (C-8), 99.89 (C-7), 83.13 (C-5), 82.67 (C-2), 66.10 (C-1 & C-3), 65.55 (C-4 & C-6), 48.42 ($O\mathit{C}H_3$), 48.15 ($O\mathit{C}H_3$), 17.22 ($\mathit{C}H_3$), 17.04 ($\mathit{C}H_3$). Elemental analysis, calculated for $C_{20}H_{30}O_{14}S_2F_6$, C = 35.72, H = 4.50, S = 9.54; Found C = 35.80, H = 4.49, S = 9.55; Calculated m/z = 672.09; Found m/z = 672.10. The compound was crystallized from benzene/chloroform (1:1) mixture.



Scheme S1. Synthesis of compounds **2**, **7** and **8**. a)[1] Butanedione, MeOH, $CH(OMe)_3$, CSA, reflux, 24 h, 28 %; b)[1]Tf_2O, pyridine, CH_2Cl_2, -78 °C to rt, 12 h, 77%; c) MsCl, pyridine, CH_2Cl_2, 0 °C to rt, 12 h, 89 %; d) Tf_2O (excess), pyridine, CH_2Cl_2, -78 ° C to rt, 12 h, 77 %.

c) Synthesis of azide 3:

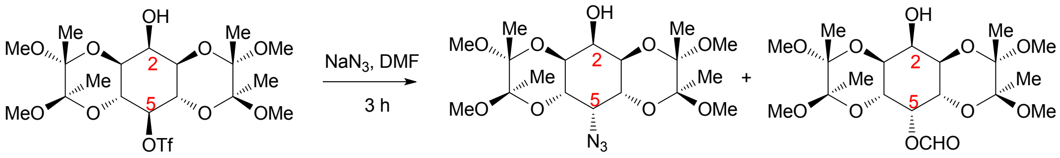
(i) In DMSO



To a mixture of triflate[1] **2** (1 g, 1.85 mmol) and NaN_3 (1.20 g, 18.5 mmol), dry DMSO (2 mL) was added (DMSO is added after azide in an attempt to slow down the solvolysis of triflate) and the reaction mixture was stirred for 2 hours. Then reaction mixture was taken in ethyl acetate, washed with water and brine. The organic layer was extracted, concentrated and the products were purified using column chromatography. (3:7, EtOAc : petroleum ether, v/v). The azide **3** was obtained as an off-white solid (338 mg, 42 %) along with the diol **4** (1:1, EtOAc : petroleum ether, v/v) (400 mg, 51 %). Azide **3:** ^{1}H NMR (DMSO-d_6) δ 5.00 (d, J = 4.8 Hz, 1H, -O*H*), 4.11 (t, J = 3 Hz, 1H, H-5), 3.96 (dd, J = 10 Hz, J = 3 Hz, 2H, H-4 & H-6), 3.82 (s, 1H, H-2), 3.61 (dd, J = 10 Hz, J = 1.5 Hz, 2H, H-1 & H-3), 3.16 (s, 6H, OCH_3), 3.14 (s, 6H, OCH_3), 1.18 (s, 12H, CH_3); **^{13}C** NMR (DMSO-d_6) δ 99.46 (C-8), 99.43 (C-7), 67.68 (C-2), 67.30 (C-1 & C-3), 65.97 (C-4 & C-6), 61.30 (C-5), 48.09 (O*C*H_3), 48.00 (O*C*H_3), 18.08 (*C*H_3), 17.96 (*C*H_3). IR (KBr): 3437 cm^{-1} (-OH), 2100 cm^{-1} (azide); Elemental analysis, calculated for $C_{18}H_{31}N_3O_9$, C= 49.88, H = 7.21, N = 9.69; Found C = 49.82, H = 7.05, N = 9.37; Calculated m/z = 433.21; Found m/z = 434.20 (M+H). The melting point could not be obtained as the compound charred on heating to 210 °C.

The **^{1}H** NMR of the compound **4** in DMSO-d_6 matched with those previously reported.[1]

(ii) In DMF

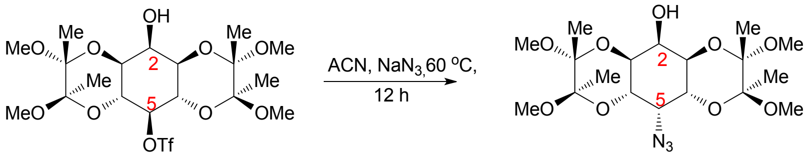


2 **3** (58%) **6** (15%)

To a solution of triflate[1] **2** (50 mg, 0.092 mmol) in dry DMF (0.5 mL), NaN_3 (59.8 mg, 0.92 mmol), was added and the reaction mixture was stirred for 3 hours. Then reaction mixture was taken in ethyl acetate, washed with water and brine. The organic layer was extracted, concentrated and the products were purified using column chromatography (3:7, EtOAc : petroleum ether, v/v). The azide **3** was obtained as an off-white solid (23 mg, 58 %), along with the monoformate **6** (6 mg, 15 %). A small amount of the diol **4** (3 mg, 8 %) formed from the formate **6** during elution in the column. Monoformate **6**: ^{1}H (DMSO-d_6) δ 8.30 (s, 1H, -OC*H*O), 5.23 (s, 1H, H-5), 5.07 (d, J = 4.5 Hz, -O*H*), 4.00 (dd, J = 10.5 Hz, J = 3 Hz, 2H, H-4 & H-6), 3.89 (m, 1H, H-2), 3.67 (dd, J = 10.5 Hz, J = 2.5 Hz, 2H, H-1 & H-3), 3.15 (s, 6H, OCH_3), 3.14 (s, 6H, OCH_3), 1.18 (s, 6H, CH_3), 1.13 (s, 6H, CH_3); **^{13}C** NMR (DMSO-d_6) δ 162.73 (*C*HO), 99.44 (C-7 & C-8), 70.97 (C-5), 67.65 (C-2), 67.37 (C-1 & C-3), 65.04 (C-4 & C-6), 48.08 (O*C*H_3), 47.98 (O*C*H_3), 18.12 (*C*H_3), 17.98 (*C*H_3). IR (KBr): 3468 cm^{-1}(OH),1728 cm^{-1}

(C=O, OCHO). Elemental analysis, Calculated for $C_{19}H_{32}O_{11}$, C= 52.29, H = 7.39; Found C = 52.17, H = 7.56. Calculated m/z = 436.19; Found m/z = 438.80 (M+2H). Crystals of monoformate **6** were obtained from ethylacetate by slow evaporation. The formate **6** melted at 285 °C.

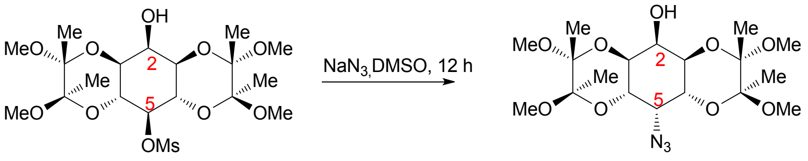
(iii) In Acetonitrile



2 **3** (73%)

To a solution of triflate[1] **2** (50 mg, 0.092 mmol) in dry acetonitrile (0.5 mL), NaN_3 (59.8 mg, 0.92 mmol), was added and the reaction mixture was heated at 60 °C for 12 hours. Then the reaction mixture was taken in ethyl acetate, washed with water and brine. The organic layer was extracted, concentrated and the products were purified using column chromatography (3:7, EtOAc : petroleum ether, v/v) to obtain the azide **3** (30 mg, 73%).

(iv) From mesylate 7



7 **3** (90%)

To a solution of mesylate **7** (50 mg, 0.092 mmol) in dry DMSO (0.5 mL), NaN_3 (59.8 mg, 0.92 mmol), was added and the reaction mixture was stirred at rt for 12 hours. Then reaction mixture was taken in ethyl acetate, washed with water and brine. The organic layer was extracted, concentrated and the products were purified using column chromatography (3:7, EtOAc : petroleum ether, v/v) to obtain the azide **3** (36 mg, 90%).

d) Solvolysis: NMR studies

General Procedure: 2 mg of the sample (**2**, **7** or **8**) was dissolved in 0.5 mL of DMSO-d_6 or DMF-d_7 and the sample was sealed in an NMR tube. The reaction was periodically monitored by ^{1}H NMR and ^{19}F NMR.

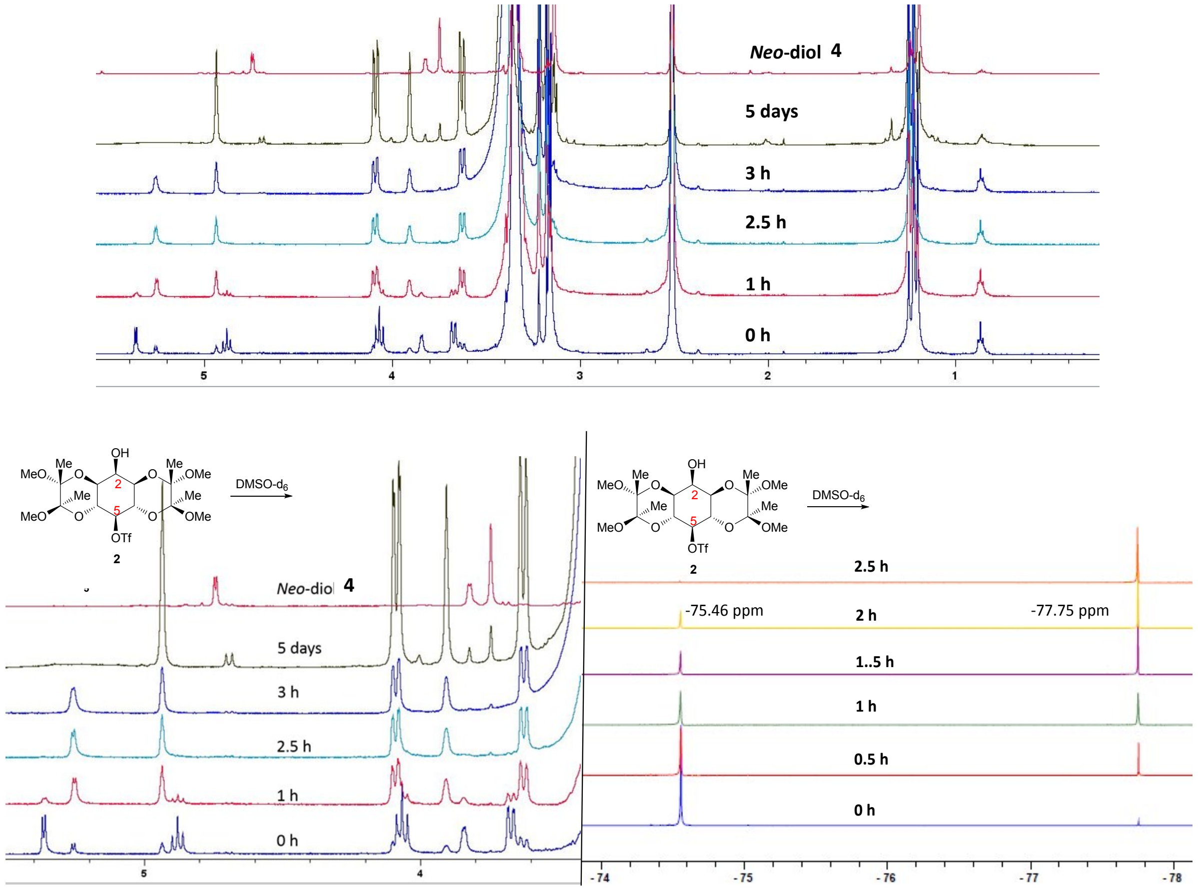


Figure S1. A time dependent ^{1}H NMR spectra analysis and ^{19}F NMR study of triflate **2** in DMSO-d$_6$.

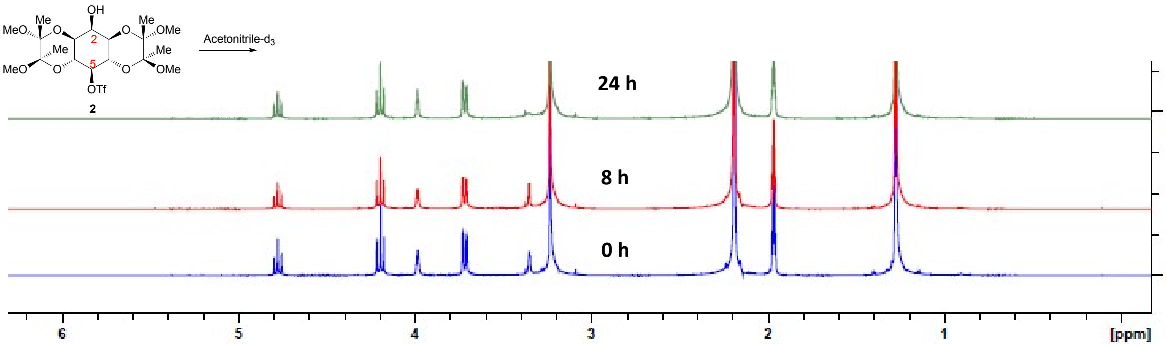


Figure S2. A time dependent study of ^{1}H NMR of triflate **2** in acetonitrile-d$_3$. The triflate group does not undergo solvolysis with time.

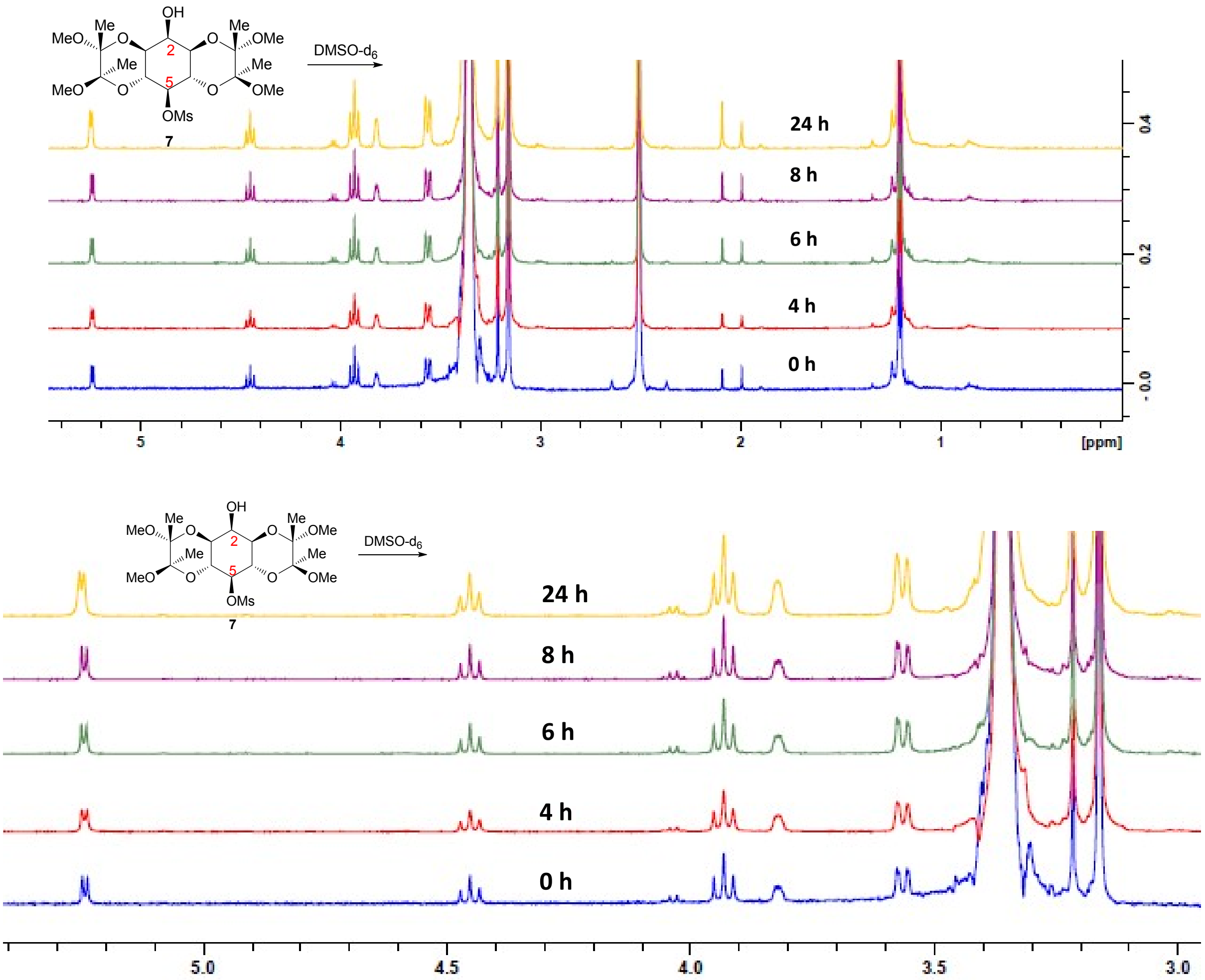


Figure S3. A time dependent study of ^{1}H NMR of mesylate **7** in DMSO-d$_6$. The mesyl group does not undergo solvolysis in DMSO-d$_6$.

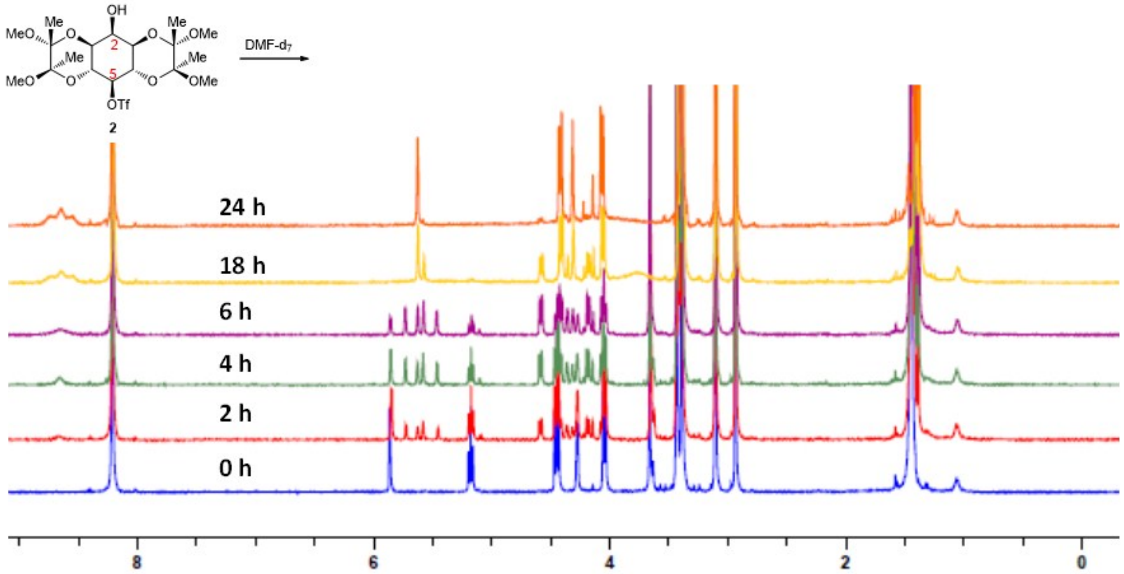


Figure S4. A time dependent study of ^{1}H NMR of triflate **2** in DMF-d$_7$.

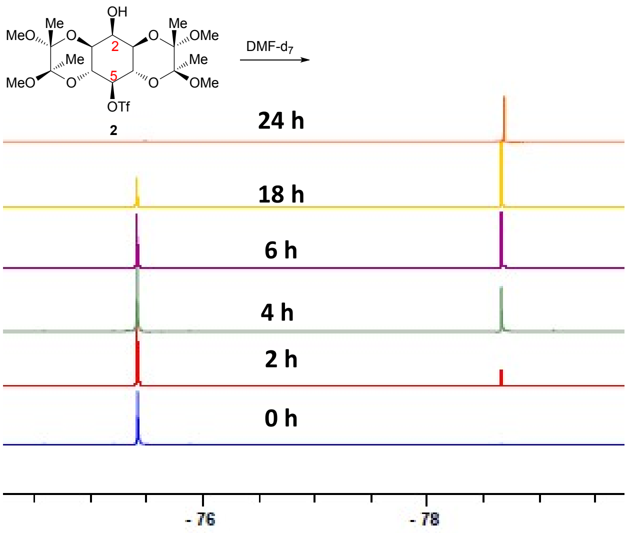


Figure S5. A time dependent study of ^{19}F NMR of triflate **2** in DMF-d$_7$.

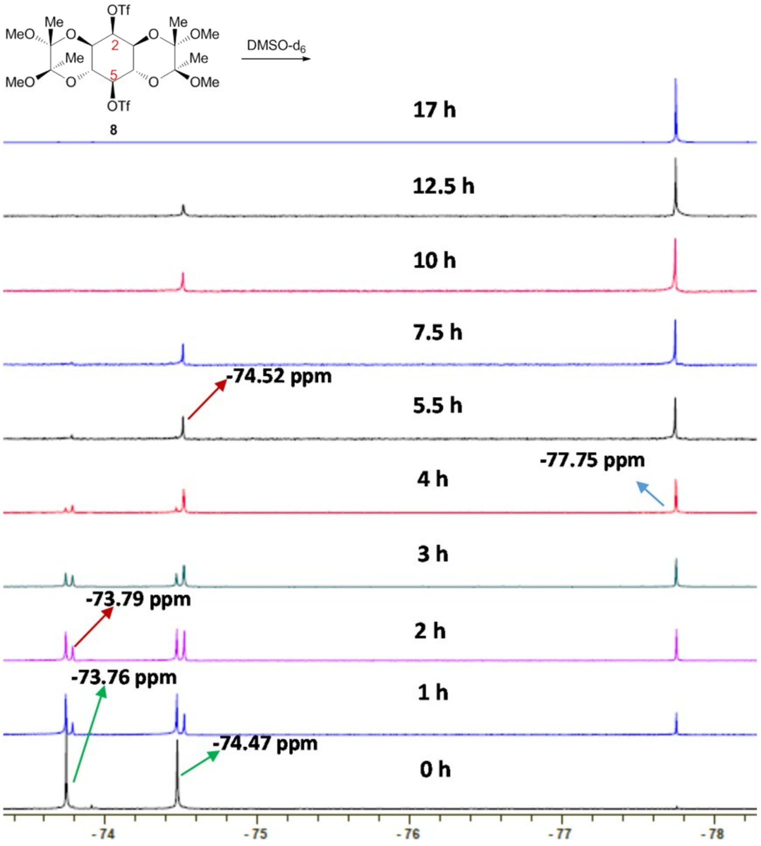


Figure S6. A time dependent study of ^{19}F NMR of ditriflate **8** in DMSO-d$_6$.

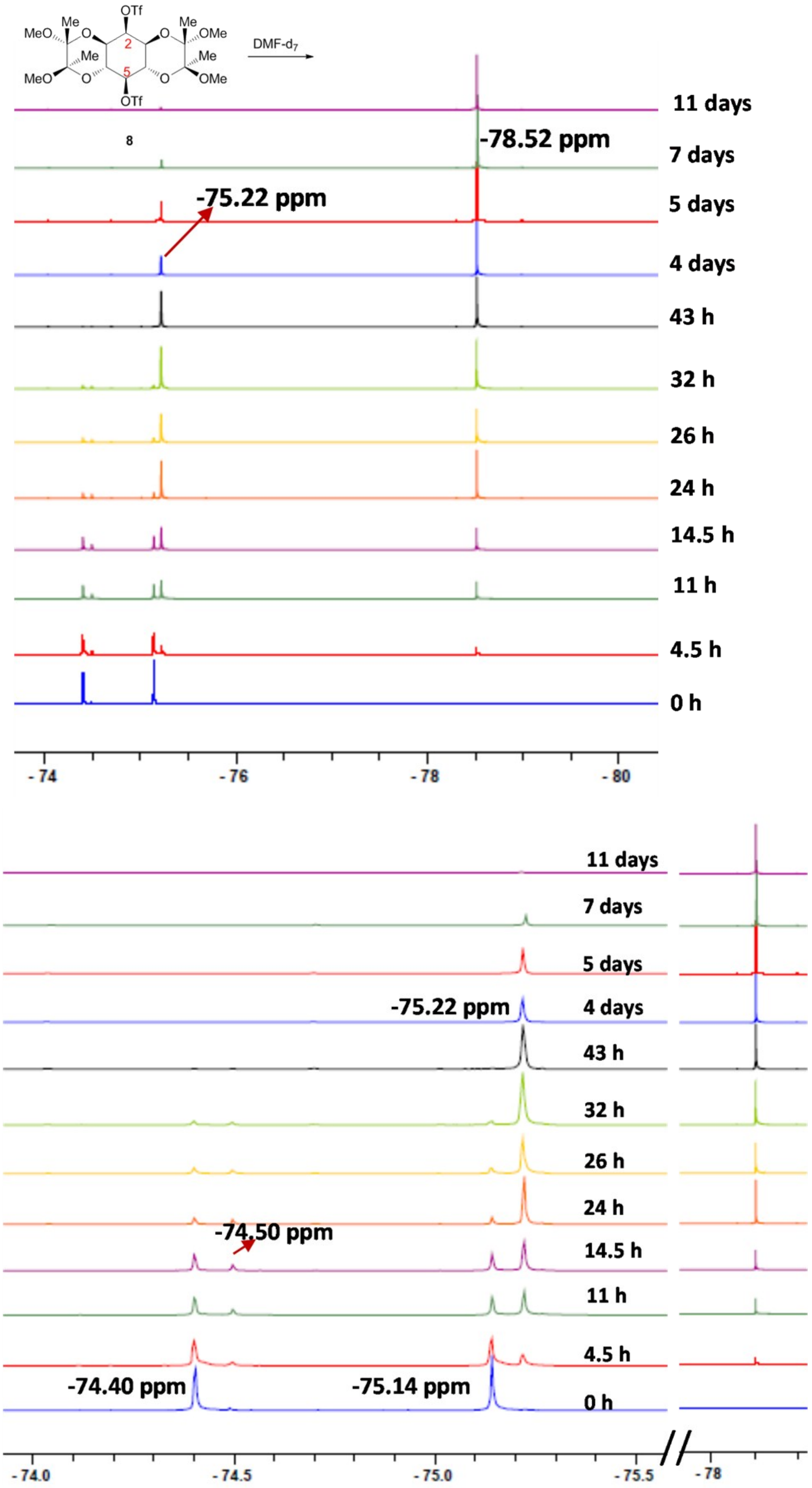


Figure S7. A time dependent study of ^{19}F NMR of ditriflate **8** in DMF-d_7.

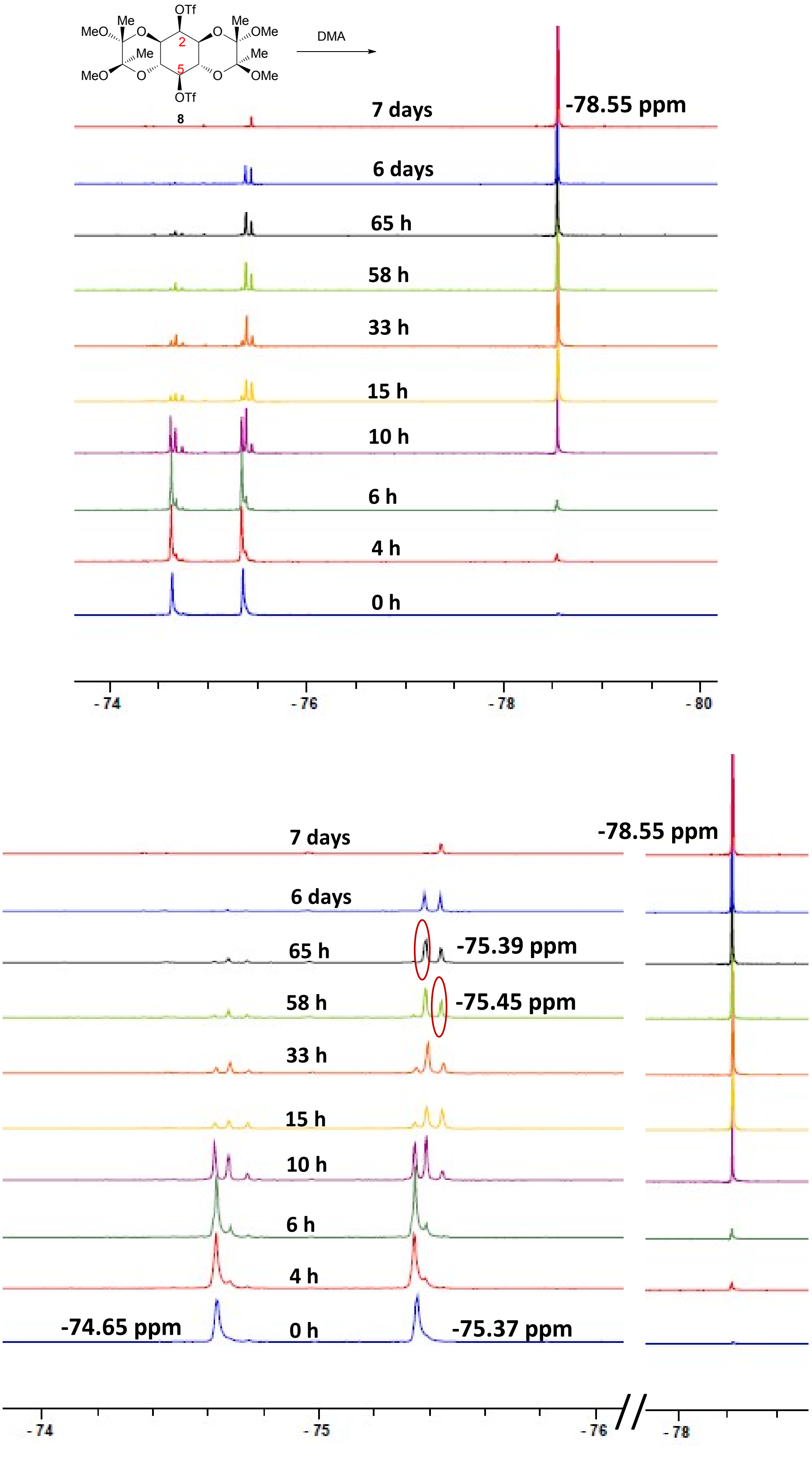
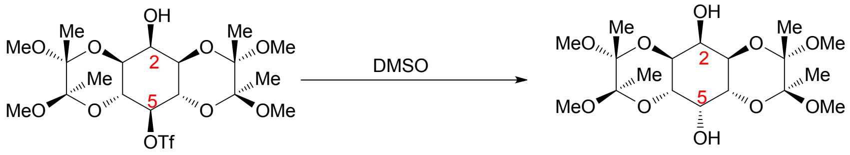


Figure S8. A time dependent study of ^{19}F NMR of ditriflate **8** in DMA (The sample was taken in DMA and externally locked with DMSO-d_6 as the solvent)

e). Nucleophilyses studies

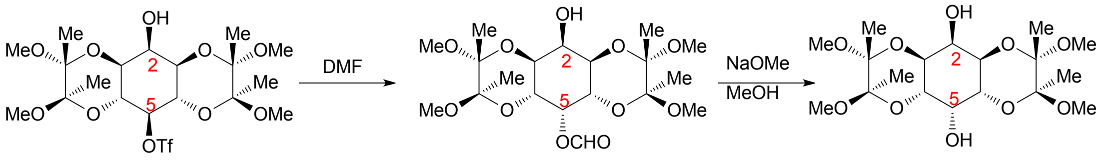
(a) Solvolysis of triflate 2 in DMSO:



2 **4**

20 mg of triflate **2** was dissolved in 0.5 mL of DMSO at room temperature. After the reaction is complete (2.5 h), added 0.5 mL water to precipitate out a white solid **6** (12.6 mg, 83 %). The ^{1}H and ^{13}C NMR of the compound in CDCl$_3$ matched with those previously reported.[1]

(b) Solvolysis of triflate 2 in DMF:

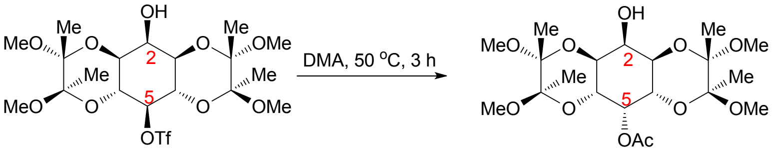


2 **6** **4**

100 mg of triflate **2** was dissolved in 5 mL of DMF, at room temperature. After the reaction is complete (17 h), water was added and the formate **6** was precipitated out as a white solid (73 mg, 91 %).

To **6** (10 mg) added 3 mg of NaOMe and MeOH (2 mL) and stirred for 5 min, concentrated the reaction mixture to get the diol **4** as a white solid in quantitative yield (9 mg, 97 %).

(b) Solvolysis of triflate 2 in DMA:

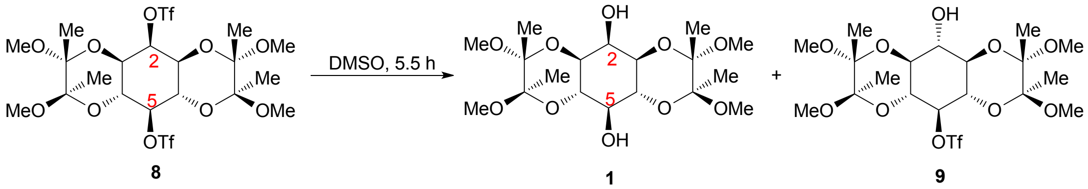


2 **5**

Triflate **2** underwent solvolysis in DMA to yield acetate **5**. The reaction was carried out as per reported procedures.[1] 100 mg of the triflate was dissolved in DMA and heated to 50 °C for 3h. Then the reaction mixture was concentrated under vacuum, then dissolved in dichloromethane, washed with water. The organic layer was concentrated to give a white solid **5**[1] (71 mg, 86 %).

(c) Solvolysis and azidolysis of ditriflate 8 in DMSO:

(i) 50 mg (0.074 mmol) of compound **8** was dissolved in 2 mL of DMSO at room temperature. After 5.5 h, the above mixture was taken in ethyl acetate, washed with water and brine. The organic layer was extracted, concentrated and the products purified by column chromatography (3:7, EtOAc : petroleum ether, v/v). Diol **1** (12 mg, 40 %), triflate **9,** (15 mg, 38 %).



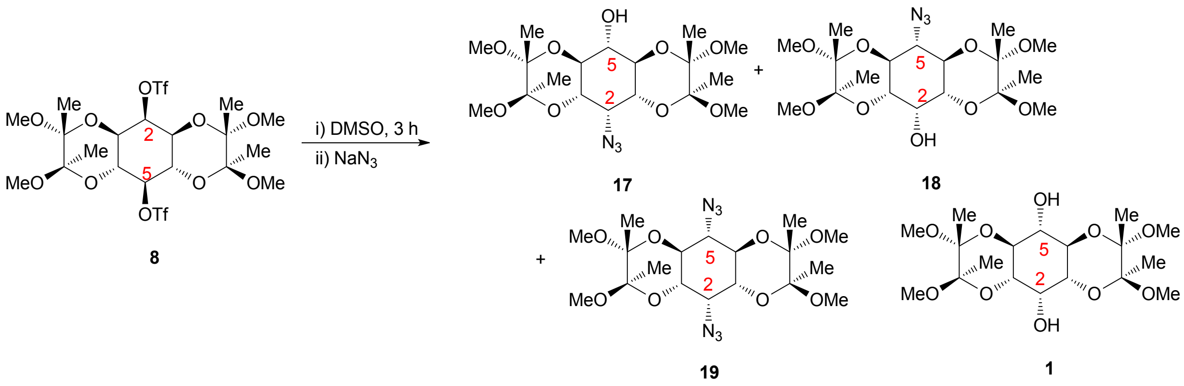
Compound **1**: The ^{1}H NMR of the diol **1** matched with previous reports. [1]

Compound **9**: A white solid was obtained. ^{1}H NMR ($CDCl_3$) δ 4.76 (t, *J* = 9.75 Hz, 1H, H-5), 3.70 (m, 3H, H-4, H-6 & H-2), 3.53 (t, *J* = 9.8 Hz, 2H, H-1 & H-3), 3.21 (s, 6H, OCH_3), 3.19 (s, 6H, OCH_3), 2.36 (s, 1H, O*H*), 1.26 (s, 6H, CH_3), 1.24 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 99.84, 99.75 (C-7 & C-8), 83.49 (C-;17.26 (CH_3). ^{19}F NMR ($CDCl_3$) δ -74.35 ppm. IR (KBr): 3589 cm^{-1} (-OH), 1379 cm^{-1}, 1139 cm^{-1} (S=O); Elemental analysis, calculated for $C_{19}H_{31}F_3O_{12}S$, C= 42.22, H = 5.78, S = 5.93; Found C = 42.48, H = 5.81, S = 5.89; The compound was crystallized from chloroform. The melting point could not be obtained as the compound charred on heating to 143 °C.

(ii) 50 mg (0.074mmol) of ditriflate **8** was dissolved in 2 mL of DMSO at room temperature.

Precipitation by addition of water (0.5 mL) after 17 h gave the diol **1** (25 mg, 85 %) as a white solid.

(iii) 100 mg (0.148 mmol) of the ditriflate **8** was taken in 2 mL of DMSO and left undisturbed for 3 h. Then NaN_3, (96.2 mg, 1.48 mmol) was added to the mixture and allowed to stir for an hour. The reaction mixture was then dissolved in ethyl acetate, washed with water and brine. The organic layer was extracted, concentrated and the products purified by column chromatography **17**, **18**, **19** (1:4, EtOAc : petroleum ether, v/v); **1** (1:1, EtOAc : petroleum ether, v/v). The products obtained were **17** (17 mg, 26 %), **18** (12 mg, 18 %), **1** (26 mg, 44 %) **19** (7 mg, 10 %). The compounds **18**, **19** and **1** were crystallized from chloroform.



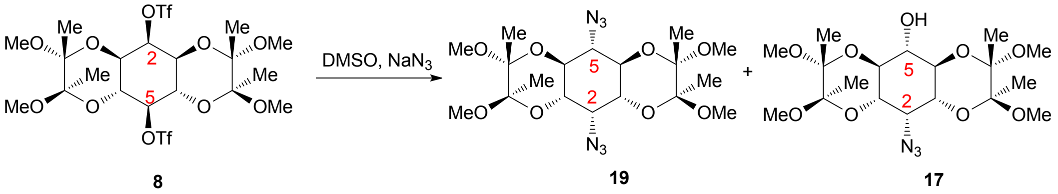
Compound **17**: ^{1}H NMR (DMSO-d$_6$) δ 5.19 (d, J = 5.9 Hz, 1H, -OH), 4.07 (t, J = 3 Hz, 1H, H-2), 3.66 (dd, J = 3 Hz, J = 10 Hz, 2H, H-1 & H-3), 3.55 (t, J = 10 Hz, 2H, H-4 & H-6), 3.52 (1H, H-5), 3.18 (s, 12H, OCH_3), 1.20 (s, 6H, CH_3), 1.19 (s, 6H, CH_3); ^{13}C NMR (CDCl$_3$) δ 99.71, 99.13, 69.95 (C-4 & C-6), 68.87 (C-5), 67.51 (C-1 & C-3), 61.10 (C-2) 48.18 (OCH_3), 47.74 (OCH_3), 17.95 (CH_3), 17.84 (CH_3). IR (KBr): 3483 cm^{-1} (-OH), 2108 cm^{-1} (azide); Elemental analysis, calculated for $C_{18}H_{31}N_3O_9$, C= 49.88, H = 7.21, N = 9.69; Found C = 49.54, H = 6.93, N = 9.73; Calculated m/z = 433.20; Found m/z = 433.24. The melting point of the compound is 220 °C.

Compound **18**: ^{1}H NMR (CDCl$_3$) δ 3.97 (t, J = 2.5 Hz, 1H, H-2), 3.90 (t, 2H, J = 10 Hz, H-4 & H-6), 3.52 (dd, 2H, J = 2.5 Hz, J = 10 Hz, H-1 & H-3), 3.44 (t, J = 10 Hz, 1H, H-5 & H-3), 3.24 (s, 6H, OCH_3), 3.19 (s, 6H, OCH_3), 2.33 (s, 1H, -OH), 1.27 (s, 6H, CH_3), 1.26 (s, 6H, CH_3); ^{13}C NMR (CDCl$_3$) δ 99.14, 98.66 (C-7 & C-8), 67.99 (C-1 & C-3), 67.76 (C-5), 66.91 (C-4 &C-6), 59.96 (C-2) 47.13 (OCH_3), 46.96 (OCH_3), 16.64 (CH_3), 16.55 (CH_3). IR (KBr): 3442 cm^{-1} (-OH), 2108 cm^{-1} (azide); Elemental analysis, calculated for $C_{18}H_{31}N_3O_9$, C= 49.88, H = 7.21, N = 9.69; Found C = 49.83, H = 7.53, N = 9.63; The compound melts at 228 °C. Calculated m/z = 433.20; Found m/z = 434.35 (M+H). The compound was crystallized from chloroform.

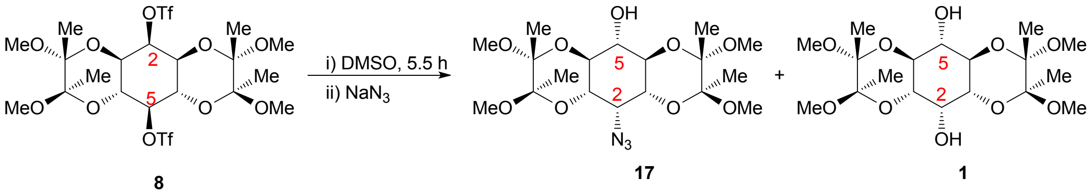
Compound **19**: A pale yellow solid was obtained. ^{1}H NMR (CDCl$_3$) δ 3.83 (t, J = 3.05 Hz, 1H, H-2), 3.79 (t, J = 10.1 Hz, 2H, H-4 & H-6), 3.61 (dd, J = 10.1 Hz, J = 3.05 Hz, 2H, H-1 & H-3), 3.39 (t, J = 10.1 Hz, 1H, H-5), 3.24 (s, 6H, OCH_3), 3.20 (s, 6H, OCH_3), 1.26 (s, 6H, CH_3), 1.25 (s, 6H, CH_3); ^{13}C NMR (CDCl$_3$) δ 100.19, 99.70 (C-7 & C-8), 68.38

(C-1 & C-3), 68.22 (C-4 & C-6), 60.87 (C-5), 60.17 (C-2), 48.26 (O*C*H_3), 48.07 (O*C*H_3), 17.59 (*C*H_3), 17.43 (*C*H_3). IR (KBr): 2104 cm^{-1} (azide); Elemental analysis, calculated for $C_{18}H_{30}N_6O_8$, C= 47.16, H = 6.60, N = 18.33; Found C = 47.19, H = 6.53, N = 18.41; Calculated m/z = 458.21, Found m/z = 457.89; The compound melts at 202 ^{o}C. The compound was crystallized from chloroform.

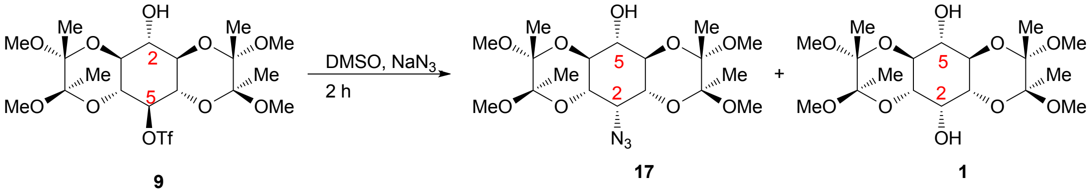
(iv) 100 mg (0.148 mmol) of the ditriflate **8** along with NaN_3 (96.2 mg, 1.48 mmol) was dissolved in DMSO (0.5 mL) and the reaction mixture was stirred at room temperature for an hour (Since DMSO and N_3^- compete as nucleophiles in this case, a mixture of the triflate **8** and NaN_3 is taken and then DMSO is added to it). The above mixture was then taken in ethyl acetate, washed with water and brine and the organic layer was extracted, concentrated and the products purified by column chromatography (1:4, EtOAc: petroleum ether, v/v). Diazide **19** (44 mg, 65 %), Mono azide **17** (7 mg, 11 %).



(v) 100 mg (0.148 mmol) of the ditriflate **8** was taken in 2 mL of DMSO and left undisturbed for 5.5 h. NaN_3, (96.2 mg, 1.48 mmol) was added to the mixture and allowed to stir for an hour. The reaction mixture was dissolved in ethylacetate washed with water and brine. The organic layer was concentrated and the products **17** (19 mg, 30 %) and **1** (29 mg, 49 %) were separated by column chromatography **17**, **1** (1:1, EtOAc : petroleum ether, v/v).



(**vi**) To 100 mg (0.185 mmol) of triflate **9** in DMSO, added NaN_3 (120 mg, 1.85 mmol) and stirred for 2 h. Then ethyl acetate was added to the reaction mixture washed with water and brine. The organic layer was extracted, concentrated and the products **17** (43 mg, 54%), **1** (27 mg, 36%) were purified by column chromatography (1:1, EtOAc : petroleum ether, v/v).



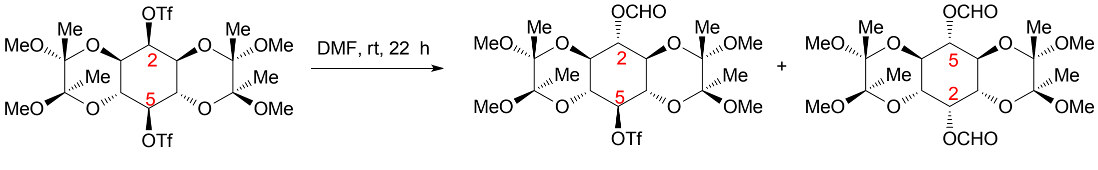
9

17

1

d) Solvolysis and azidolysis of ditriflate 8 in DMF:

(i) 100 mg of compound **8** (0.148 mmol) was dissolved in 2 mL of DMF at room temperature. After 22 h, the above mixture was taken in ethyl acetate, washed with water and brine. The organic layer was extracted, concentrated and the products **10** (49 mg, 58 %) (1:9, EtOAc: petroleum ether v/v) and **11** (25 mg, 36 %) (1:4, EtOAc : petroleum ether) were purified by column chromatography.



8

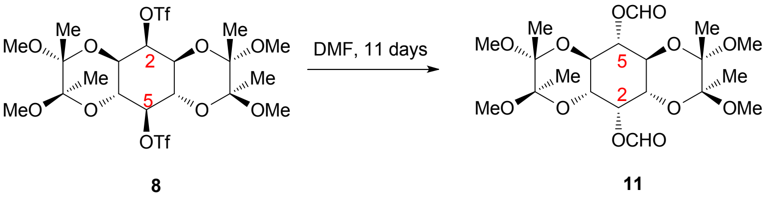
10

11

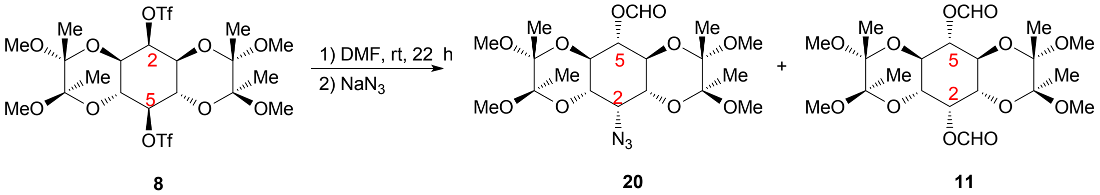
11 : ^{1}H NMR (CDCl$_3$) δ 8.22 (s, 1H, -OC*H*O), 8.19 (s, 1H, -OC*H*O), 5.49 (s, 1H, H-2), 4.86(t, *J* = 10 Hz, 1H, H-5), 4.04 (t, *J* = 10 Hz, 2H, H-4 & H-6), 3.76 (dd, *J* = 2.5 Hz, *J* = 10 Hz, 2H, H-1 & H-3), 3.25 (s, 6H, OMe), 3.22 (s, 6H, OMe), 1.24 (s, 12H, Me); ^{13}C NMR δ 159.88 (-O*C*HO), 159.12 (-O*C*HO), 99.11, 98.53, 71.06 (C-5), 67.31 (C-2), 66.21 (C-4 & C-6), 65.70 (C-1 & C-3), 47.19 (-O*C*H$_3$), 46.88 (-O*C*H$_3$), 16.54 (-*C*H$_3$), 16.38 (-*C*H$_3$); Elemental analysis, Calculated for $C_{20}H_{32}O_{12}$, C= 51.72, H = 6.94; Found C= 51.52, H = 6.88; The melting point of the compound could not be obtained as the compound charred on heating to 175 °C. Calculated m/z = 464.19, Found m/z = 463.45 (M-H).

10 : ^{1}H NMR (CDCl$_3$) δ 8.09 (s, 1H, -OC*H*O), 4.92 (t, *J* = 9.7 Hz, 1H, H-2), 4.75 (t, *J* = 9.7 Hz, 1H, H-5), 3.78 (t, *J* = 9.95 Hz, 2H, H-4 & H-6), 3.68 (t, *J* = 9.95 Hz, 2H, H-1 & H-3), 3.18 (s, 6H, OMe), 3.14 (s, 6H, OMe), 1.23 (s, 6H, Me), 1.20 (s, 6H, Me); ^{13}C NMR δ 160.17 (-O*C*HO), 99.93, 99.89, 82.82 (C-5), 69.90 (C-2), 67.70 (C-4 & C-6), 67.59 (C-1 & C-3), 48.08 (-O*C*H$_3$), 47.99 (-O*C*H$_3$), 17.37 (-*C*H$_3$), 17.19 (-*C*H$_3$); ^{19}F NMR -74.31 ppm; Elemental analysis, Calculated for $C_{20}H_{31}F_3O_{13}S$, C= 42.25, H = 5.50, S = 5.64; Found , C= 42.55, H = 5.52, S = 5.63; The melting point of the compound could not be obtained as the compound charred on heating to 155 °C. Calculated m/z = 568.14, Found m/z = 569.34 (M+H). IR (KBr): 1728 cm^{-1} (C=O, OCHO).

(ii) 50 mg (0.074 mmol) of ditriflate **8** was dissolved in 2 mL of DMF at room temperature. Precipitation by addition of water (1 mL) after 11 days gave the di-formate **11** as a white solid (29 mg, 86 %).

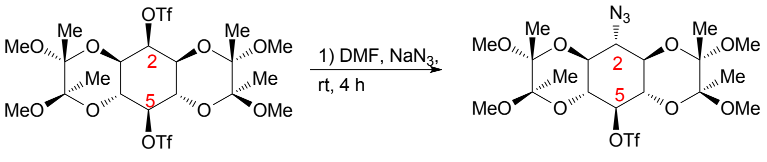


(iii) 100 mg (0.148 mmol) of the ditriflate **8** was taken in 2 mL of DMF and left undisturbed for 22 h. $NaN_{3,}$ (48.1 mg, 0.74 mmol) was added to the mixture and allowed to stir for an hour. The above mixture was taken in ethyl acetate, washed with water and brine. The organic layer was extracted, concentrated and the products **20** (40 mg, 58 %) and **11** (25 mg, 36 %) were purified by column chromatography **20 (**1:4, EtOAc: petroleum ether), **11** (1:4, EtOAc : petroleum ether).



Azide **20**: ^{1}H NMR ($CDCl_3$) δ 8.10 (s, 1H, -OC*H*O), 4.72 (t, *J* = 10 Hz, 1H, H-5), 3.98 (t, *J* = 10 Hz, 2H, H-4 & H-6), 3.87 (s, 1H, H-2), 3.66 (d, *J* = 10 Hz*, J* = 3.5 Hz, 2H, H-1 & H-3), 3.20 (s, 6H, OMe), 3.16 (s, 6H, OMe), 1.25 (s, 6H, Me), 1.18 (s, 6H, Me); ^{13}C NMR δ 159.85 (-O*C*HO), 99.22, 98.47, 70.99 (C-5), 66.81 (C-1 & C-3), 65.99 (C-4 & C-6), 59.13 (C-2), 47.21 (-OCH_3), 46.92 (-OCH_3), 16.51 (-CH_3), 16.41 (-CH_3); IR (KBr): 2110 cm^{-1} (azide), 1728 cm^{-1} (C=O, OCHO). Calculated m/z = 461.46; Found m/z = 461.45. Elemental analysis, Calculated for $C_{19}H_{31}N_3O_{10}$, C = 49.45, H = 6.77, N = 9.11; Found, C = 49.55, H = 6.87, N = 9.10; The melting point of the compound could not be obtained as it charred on heating to 145 ^{o}C.

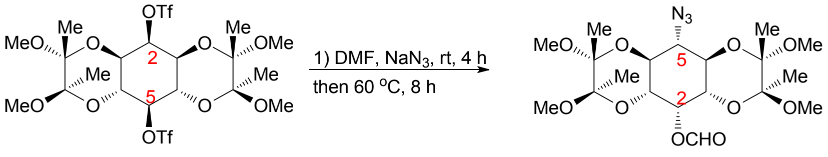
(iv) 100 mg (0.148 mmol) of ditriflate **8** was dissolved in dry DMF and to it NaN_3 (9.67 mg, 0.148 mmol) was added and the reaction mixture was allowed to stir at room temperature for 4 h. The starting material was completely consumed. The reaction mixture was taken in ethylacetate, washed with water and brine, and the organic layer was extracted. The organic layer was concentrated and the product **14** (70 mg, 83 %) purified by column chromatography **(**1:19, EtOAc: petroleum ether).



8 **14**

14 ^{1}H NMR (CDCl$_3$) δ 4.69 (t, J = 9.8 Hz, 1H, H-5), 3.74 (t, J = 9.8 Hz, 2H, H-4 & H-6), 3.50 (m, 3H, H-1, H-3 & H-2), 3.22 (s, 6H, OMe), 3.19 (s, 6H, OMe), 1.27 (s, 6H, Me), 1.23 (s, 6H, Me); ^{13}C NMR δ 100.12, 99.90, 82.87 (C-5), 68.93 (C-1 & C-3), 68.17 (C4 & C-6), 59.60 (C-2), 48.11 (2 x-OCH$_3$), 17.40 (-CH$_3$), 17.17 (-CH$_3$); ^{19}F NMR: -74.33 ppm; IR (KBr): 2112 cm^{-1} (azide), 1138 cm^{-1} (S=O). Elemental analysis, Calculated for $C_{19}H_{30}F_3N_3O_{11}S$, C = 40.35, H = 5.35, N = 7.43, S = 5.67; Found, C = 40.64, H = 5.33, N = 7.20, S = 5.61; The melting point of the compound is 192 ^{o}C. Calculated m/z = 565.15; Found m/z = 566.23 (M+H).

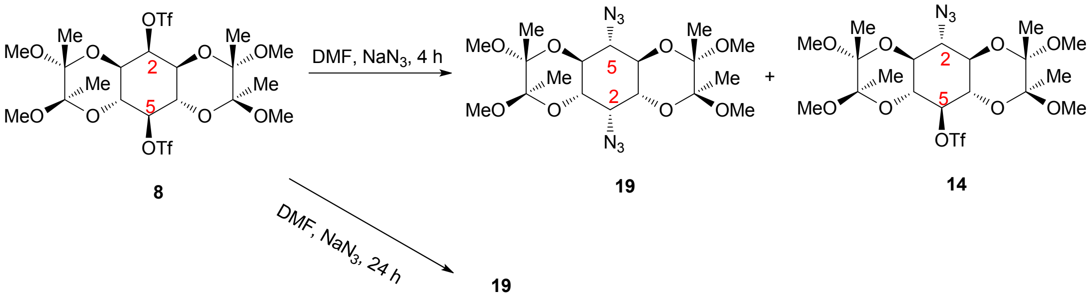
(v) 100 mg (0.148 mmol) of ditriflate **8** was dissolved in dry DMF and to it NaN$_3$ (9.67 mg, 0.148 mmol) was added and the reaction mixture was allowed to stir at room temperature for 4 h. The starting material was completely consumed. Then the reaction mixture was heated to 60 ^{o}C for 8 h. The above reaction mixture was then taken in ethylacetate, washed with water and brine, and the organic layer was extracted. The organic layer was concentrated and the product **15** (58 mg, 85%) purified by column chromatography **(**1:4, EtOAc: petroleum ether). ^{1}H NMR (CDCl$_3$) δ 8.20 (s, 1H, OCHO), 5.46 (s, 1H, H-2), 3.85 (t, J = 10 Hz, 2H, H-4 & H-6), 3.72 (d, J = 10 Hz, 2H, H-1 & H-3), 3.54 (t, J = 10 Hz, 1H, H-5), 3.30 (s, 6H, OMe), 3.25 (s, 6H, OMe), 1.31 (s, 6H, Me), 1.25 (s, 6H, Me); ^{13}C NMR δ 159.15 (CHO), 99.06, 98.74, 67.42 (C-4 & C-6), 66.23 (C-1 & C-3), 59.84 (C-5), 47.22, 47.00 (-OCH$_3$), 16.59 (-CH$_3$), 16.37 (-CH$_3$); IR (KBr): 2106 cm^{-1} (azide), 1374 cm^{-1} (C=O). Elemental analysis, Calculated for $C_{19}H_{31}N_3O_{10}$, C = 49.45, H = 6.77, N = 9.11; Found, C = 49.44, H = 6.63, N = 9.10 The melting point of the compound is 193 ^{o}C. Calculated m/z = 461.46; Found m/z = 461.46.



8 **15**

(vi) 100 mg (0.148 mmol) of ditriflate **8** was dissolved in dry DMF and to it NaN$_3$ (96 mg, 1.48 mmol) was added and the reaction mixture was allowed to stir at room temperature.

The reaction mixture was quenched with water after 4 h as starting material was completely consumed. The above mixture was taken in ethylacetate, washed with water and brine and the organic layer was extracted. The organic layer was concentrated and the products **14** (35 mg, 42 %) and **19** (33 mg, 48 %) were purified by column chromatography.

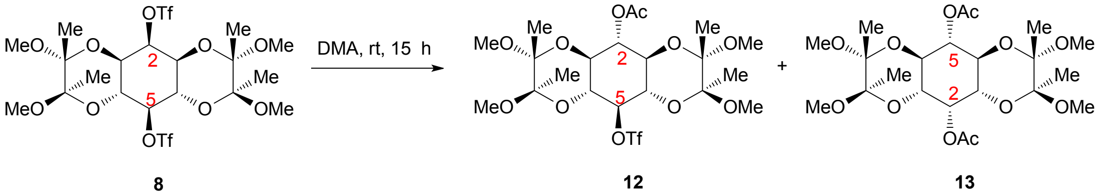


The reaction when continued for 24 h yielded only the azide **19** (51 mg, 75 %).

e) Solvolysis and azidolysis of ditriflate 8 in DMA:

i) 100 mg (0.148 mmol) of ditriflate **8** was dissolved in 2 mL of DMA at room temperature and left undisturbed for 15 h. To the above mixture water was added and the reaction mixture was concentrated (evaporated off DMA & water). The products **12** (37 mg, 43 %) and **13** (40 mg, 55 %) were purified by column chromatography; **12** (1:5, EtOAc: petroleum ether), **13** (1:4, EtOAc : petroleum ether).

12; ^{1}H NMR (CDCl$_3$) δ 5.09 (t, J = 10 Hz, 1H, H-2), 4.74 (t, J = 10 Hz, 1H, H-5), 3.78 (t, J = 10 Hz, 2H, H-4 & H-6), 3.61 (t, J = 10 Hz, 2H, H-1 & H-3), 3.17 (s, 6H, OMe), 3.14 (s, 6H, OMe), 2.02 (s, 3H, OAc), 1.22 (s, 6H, Me), 1.18 (s, 6H, Me); ^{13}C NMR δ 168.36 (OAc), 98.78, 98.67, 82.16 (C-5), 67.65(C-2), 67.00 (C-1 & C-3), 66.63 (C-4 & C-6), 46.95 (-O*C*H$_3$), 46.69 (-O*C*H$_3$), 19.66 (OAc), 16.39 (-*C*H$_3$), 16.18 (-*C*H$_3$); ^{19}F NMR -74.35 ppm. IR (KBr): 1751 cm^{-1} (C=O), 1142 cm^{-1} (S=O). Calculated m/z = 582.15; Found m/z = 583.05. Elemental analysis, Calculated for $C_{21}H_{33}F_3O_{13}S$, C = 43.30, H = 5.71, S = 5.50; Found, C = 43.60, H = 5.73, S = 5.71; The melting point of the compound could not be obtained as the compound charred on heating to 150 °C.

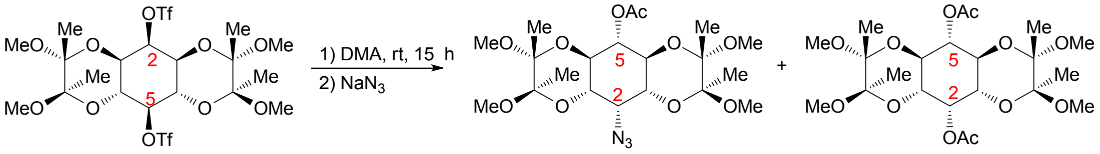


13 ; ^{1}H NMR (CDCl$_3$) δ 5.35 (s, 1H, H-2), 5.04 (t, J = 10 Hz, 1H, H-5), 3.90 (t, J = 10 Hz, 2H, H-4 & H-6), 3.66 (dd, J = 10 Hz, J = 1.5 Hz, 2H, H-1 & H-3), 3.17 (s, 12H, OMe), 2.08 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.15 (s, 12H, Me); ^{13}C NMR δ 169.47 (OAc), 168.88 (OAc), 98.84, 98.28, 69.35 (C-5), 68.09 (C-2), 66.58 (C-4 & C-6), 65.97 (C-1 & C-3), 47.02 (-OCH$_3$), 46.59 (-OCH$_3$), 20.13 (OAc), 19.77 (OAc), 16.58 (-CH$_3$), 16.38 (-CH$_3$); The melting point of the compound was found to be 178 ^{o}C. IR (KBr): 1751 cm^{-1} (C=O). Calculated m/z = 492.22; Found m/z = 493.51 (M+H). Elemental analysis, Calculated for $C_{22}H_{36}O_{12}$, C = 53.65, H = 7.37; Found, C = 53.76, H = 7.47.

ii) 100 mg (0.148 mmol) of ditriflate **8** was dissolved in 2 mL of DMA at room temperature. Precipitation by addition of water after 7 days gave the diacetate **13** as a pale-yellow solid (66 mg, 90 %).

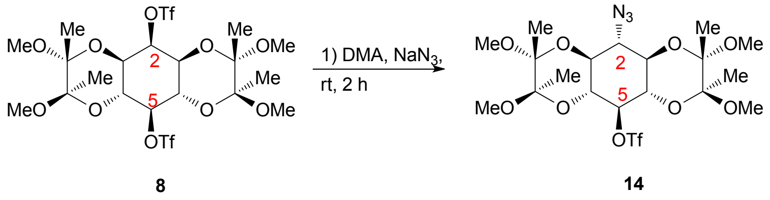
8 **13**

iv) 100 mg (0.148 mmol) of the ditriflate **8** was taken in 2 mL of DMA and left undisturbed for 15 h. NaN$_{3,}$ (48.1 mg, 0.74 mmol) was then added to the mixture and allowed to stir for 2 hours. The above mixture was taken in ethyl acetate, washed with water and brine. The organic layer was extracted, concentrated and the products **21** (34 mg, 49 %) and **13** (29 mg, 40 %) were purified by column chromatography. **21 (**1:4, EtOAc: petroleum ether), **13** (1:4, EtOAc : petroleum ether). **21** ^{1}H NMR (CDCl$_3$) δ 5.34 (s, 1H, H-2), 3.76 (t, J = 10 Hz, 2H, H-4 & H-6), 3.59 (dd, J = 10 Hz, J = 1.5 Hz, 2H, H-1 & H-3), 3.59 (t, J = 10 Hz, 1H, H-5), 3.23 (s, 6H, OMe), 3.17 (s, 6H, OMe), 2.08 (s, 3H, OAc), 1.19 (s, 12H, Me); ^{13}C NMR δ 169.47 (OAc), 98.90, 98.68, 67.91 (C-2), 67.46 (C-4 & C-6), 66.47 (C-1 & C-3), 59.94 (C-2), 47.16 (-OCH$_3$), 47.00 (-OCH$_3$), 20.13 (OAc), 16.59 (-CH$_3$), 16.37 (-CH$_3$).

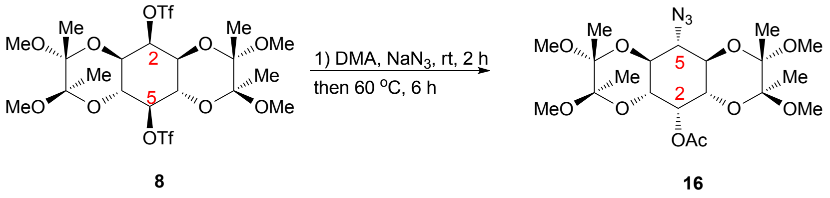


8 **21** **13**

(v) 100 mg (0.148 mmol) of ditriflate **8** was dissolved in dry DMA and to it NaN$_3$ (9.67 mg, 0.148 mmol) was added and the reaction mixture was allowed to stir at room temperature for 2 h. The starting material was completely consumed. The reaction mixture was taken in ethylacetate, washed with water and brine, and the organic layer was extracted. The organic layer was concentrated and the product **14** (67 mg, 80 %) purified by column chromatography **(**1:19, EtOAc: petroleum ether).



(vi) 100 mg (0.148 mmol) of ditriflate **8** was dissolved in dry DMA and to it NaN_3 (9.67 mg, 0.148 mmol) was added and the reaction mixture was allowed to stir at room temperature for 2 h. The starting material was completely consumed. Then the reaction mixture was heated to 60 °C for 6 h. The above reaction mixture was then taken in ethylacetate, washed with water and brine, and the organic layer was extracted. The organic layer was concentrated and the product **16** (51 mg, 73 %) purified by column chromatography **(**1:4, EtOAc: petroleum ether).

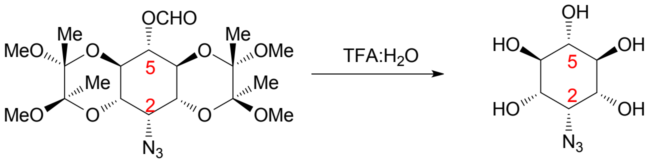


16 ^{1}H NMR ($CDCl_3$) δ 5.40 (s, 1H, H-2), 3.85 (t, J = 10 Hz, 2H, H-4 & H-6), 3.66 (dd, J = 2.5 Hz, J = 10 Hz, 2H, H-1 & H-3), 3.55 (t, J = 10 Hz, 1H, H-5), 3.30 (s, 6H, OMe), 3.24 (s, 6H, OMe), 2.12 (s, 3H, OAc), 1.31 (s, 6H, Me), 1.23 (s, 6H, Me); ^{13}C NMR δ 169.29 (C=O, OAc), 98.90, 98.68, 67.90 (C-2), 67.46 (C-4 & C-6), 66.47 (C-1 & C-3), 59.95 (C-5), 47.16 ($-OCH_3$), 46.99 ($-OCH_3$), 20.10 (OAc), 16.59 ($-CH_3$), 16.38 ($-CH_3$); The melting point of the compound was found to be 176 °C. IR (KBr): 2113 cm^{-1},1751 cm^{-1} (C=O). Calculated m/z = 475.21; Found m/z = 475.10; Elemental analysis, Calculated for $C_{20}H_{33}N_3O_{10}$, C = 50.52, H = 7.00, N = 8.84; Found, C = 50.54, H = 7.17, N = 8.86.

4. Synthesis of azido-inositols

a) Synthesis of 2-azido *myo*-inositol

To 50 mg of azide **20** added 0.5 mL of trifluoroacetic acid (TFA) and 0.1 mL of water and stirred for 25 min. The solution turned yellow and a polar spot formed. The above mixture was concentrated and dried under vacuum. Then washed with n-hexane three times and dried, to yield 2-azido *myo*-inositol (20 mg, 90 %).

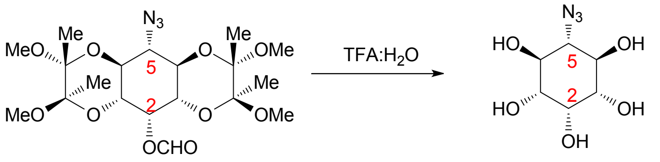


20 **2-azido *myo*-inositol**

^{1}H NMR (DMSO-d$_6$) δ 3.82 (s,1H, H-2), 3.36 (dd, J = 3 Hz, J = 9.5 Hz, 2H, H-1 & H-3), 3.21 (t, J = 9.5 Hz, 2H, H-4 & H-6), 2.89 (t, J = 9.5 Hz, 1H, H-5); ^{13}C NMR δ 75.09 (C-5), 73.12 (C-4 & C-6), 70.67 (C-1 & C-3), 68.28 (C-2); IR (KBr): 3308 cm^{-1} (broad, -OH), 2114 cm^{-1} (azide); Elemental analysis, calculated for $C_6H_{11}N_3O_5$, C = 35.12, H = 5.40, N = 20.48; Found C = 35.11, H = 5.46, N = 20.50.

b) Synthesis of 5-azido *myo*-inositol

To 50 mg of azide **15** added 0.5 mL of trifluoroacetic acid (TFA) and 0.1 mL of water and stirred for 25 min. The solution turned yellow and a polar spot formed. The above mixture was concentrated and dried under vacuum. Then washed with n-hexane three times and dried, to yield 5-azido *myo*-inositol (20 mg, 90 %).

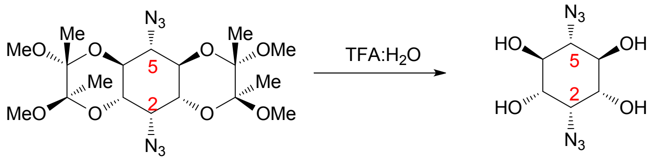


15 **5-azido *myo*-inositol**

^{1}H NMR (DMSO-d$_6$) δ 3.71 (s,1H, H-2), 3.37 (t, J = 9.5 Hz, 2H, H-4 & H-6), 3.20 (dd, J = 1.5 Hz, J = 9.5 Hz, 2H, H-1 & H-3), 2.99 (t, J = 9.5 Hz, 1H, H-5); ^{13}C NMR δ 72.74, 72.40, 71.50, 69.51; IR (KBr): 3358 cm^{-1}and 3180 cm^{-1} (broad, -OH), 2127 cm^{-1} (azide); Elemental analysis, calculated for $C_6H_{11}N_3O_5$, C= 35.12, H = 5.40, N = 20.48; Found C = 35.19, H = 5.42, N = 20.51.

c) Synthesis of 2,5-diazido *myo*-inositol

To 50 mg of diazide **19** added 0.5 mL of trifluoroacetic acid (TFA) and 0.1 mL of water and stirred for 10 min. The solution turned yellow and a polar spot formed. The above mixture was concentrated and dried under vacuum. Then washed with n-hexane three times and dried, to yield 2,5-diazido *myo*-inositol (23.9 mg, 95 %).



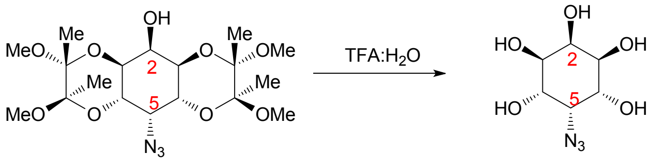
19

2,5-diazido *myo*-inositol

^{1}H NMR (DMSO-d_6) δ 5.36 (m, 4H, -OH, exchange with D_2O), 3.83 (t, J = 3 Hz, 1H, H-2), 3.47 (dd, J = 3 Hz, J = 9.5 Hz, 2H, H-1 & H-3), 3.24 (t, J = 9.5 Hz, 2H, H-4 & H-6), 3.02 (t, J = 9.5 Hz, 1H, H-5); ^{13}C NMR δ 71.78 (C-4 & C-6), 71.06 (C-1 & C-3), 69.17 (C-5) 68.15 (C-2); IR (KBr): 3358 cm^{-1}and 3180 cm^{-1} (broad, -OH), 2127 cm^{-1} (azide); Elemental analysis, calculated for $C_6H_{10}N_6O_4$, C= 31.31, H = 4.38, N = 36.51; Found C = 31.40, H = 4.39, N = 36.63. IR (KBr): 3354 cm^{-1} (broad, -OH), 2127 cm^{-1} and 2212 cm^{-1} (azide).

d) Synthesis of 5-azido *neo*-inositol

To 50 mg of azide **3** added 0.5 mL of trifluoroacetic acid (TFA) and 0.1 mL of water and stirred for 10 min. The solution turned yellow and a polar spot formed. The above mixture was concentrated and dried under vacuum. Then washed with n-hexane three times and dried, to yield 5-azido *neo*-inositol (22.3 mg, 94 %).



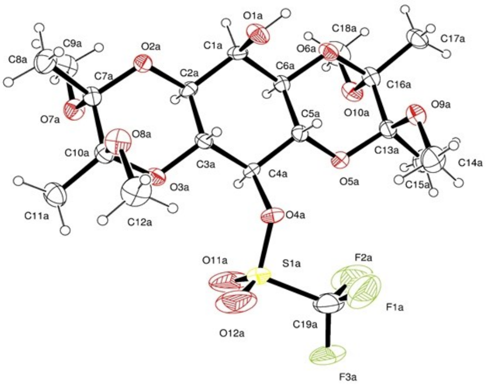
3

5-azido *neo*-inositol

^{1}H NMR (DMSO-d_6) δ 4.96 (d, 2H, J = 4.5 Hz -OH, exchange with D_2O), 4.53 (d, 1H, J = 3.5 Hz, -OH, exchange with D_2O), 4.47 (d, 2H, J = 6 Hz, -OH, exchange with D_2O), 3.82 (m, 1H, H-2), 3.70 (m, 3H), 3.34 (d, 2H); ^{13}C NMR δ 74.10, 70.65, 69.22, 63.12. IR (KBr): 3360 cm^{-1} (broad, -OH), 2135 cm^{-1} (azide); Elemental analysis, calculated for $C_6H_{11}N_3O_5$, C= 35.12, H = 5.40, N = 20.48; Found C = 35.15, H = 5.39, N = 20.44.

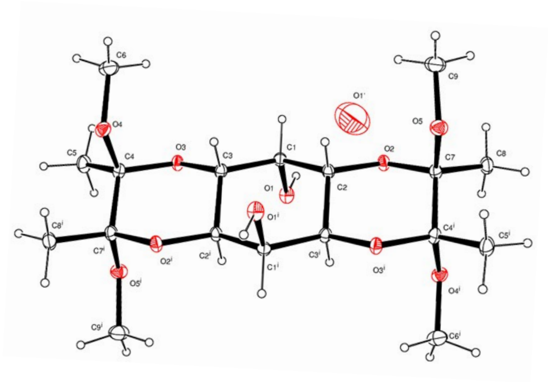
4. Crystal structures

(i) Crystal structure of monotriflate **2** (Data CCDC 1532609)



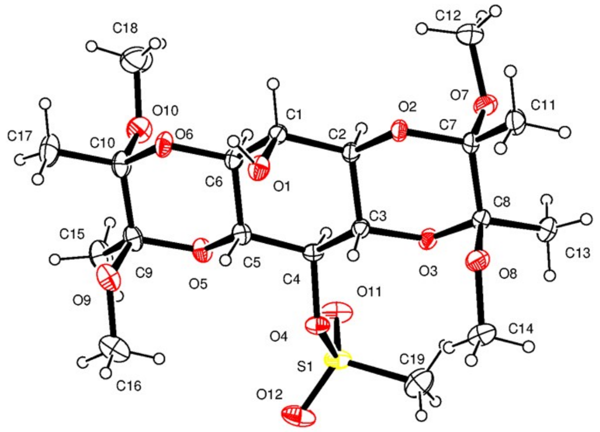
Empirical formula	C19 H31 F3 O12 S
Formula weight	540.50
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 19.882(2) A α = 90 deg.
	b = 11.2489(12) A β = 111.666(5) deg.
	c = 24.609(3) A γ = 90 deg.
Volume	5115.0(10) A^3
Z, Calculated density	8, 1.404 Mg/m^3
Absorption coefficient	0.206 mm^-1
F(000)	2272
Crystal size	0.20 x 0.15 x 0.10 mm
Theta range for data collection	1.13 to 25.00 deg.
Limiting indices	-23<=h<=21, 0<=k<=13, 0<=l<=29
Reflections collected / unique	8862 / 8862 [R(int) = 0.0000]
Completeness to theta = 25.00	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9797 and 0.9600
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8862 / 6 / 696
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.1278, wR2 = 0.3429
R indices (all data)	R1 = 0.2001, wR2 = 0.3741
Extinction coefficient	0.0051(7)
Largest diff. peak and hole	0.599 and -0.677 e.A^-3

(ii) Crystal structure of neo-diol **4** (Data CCDC 1532607)



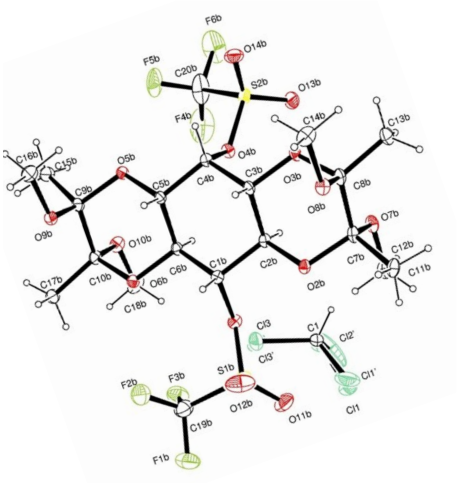
Empirical formula	C18 H32 O12	
Formula weight	440.43	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 25.8732(15) Å	a= 90°.
	b = 7.1173(4) Å	b= 116.770(2)°.
	c = 12.9798(7) Å	g = 90°.
Volume	2134.0(2) Å^{3}	
Z	4	
Density (calculated)	1.371 Mg/m^{3}	
Absorption coefficient	0.116 mm^{-1}	
F(000)	944	
Crystal size	0.200 x 0.130 x 0.100 mm^{3}	
Theta range for data collection	2.995 to 25.999°.	
Index ranges	-31<=h<=31, -7<=k<=8, -15<=l<=16	
Reflections collected	8642	
Independent reflections	2099 [R(int) = 0.0827]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9898 and 0.9796	
Refinement method	Full-matrix least-squares on F^{2}	
Data / restraints / parameters	2099 / 0 / 141	
Goodness-of-fit on F^{2}	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1258	
R indices (all data)	R1 = 0.0718, wR2 = 0.1393	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.540 and -0.222 e.Å^{-3}	

(iii) Crystal structure of mesylate **7** (Data CCDC 1532606)



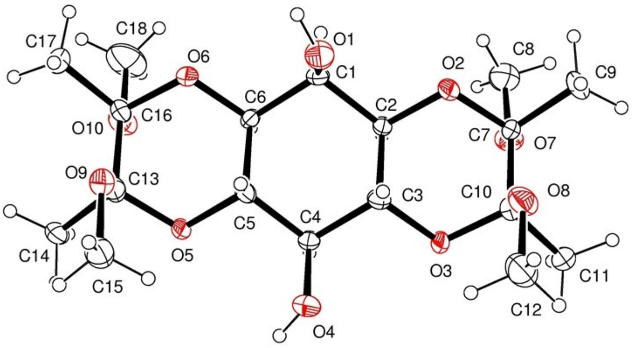
Empirical formula	C19 H34 O12 S	
Formula weight	486.52	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.0560(4) Å	a= 90°.
	b = 12.5770(4) Å	b= 91.265(2)°.
	c = 17.1284(5) Å	g = 90°.
Volume	2381.15(13) Å^3	
Z	4	
Density (calculated)	1.357 Mg/m^3	
Absorption coefficient	0.195 mm^{-1}	
F(000)	1040	
Crystal size	0.150 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.009 to 25.998°.	
Index ranges	-13<=h<=13, -15<=k<=14, -20<=l<=21	
Reflections collected	19788	
Independent reflections	4682 [R(int) = 0.0827]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9807 and 0.9713	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4682 / 0 / 298	
Goodness-of-fit on F^2	0.958	
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.0949	
R indices (all data)	R1 = 0.0609, wR2 = 0.1045	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.314 and -0.287 e.Å^{-3}	

(iv) Crystal structure of ditriflate **8** (Data CCDC 1532605)



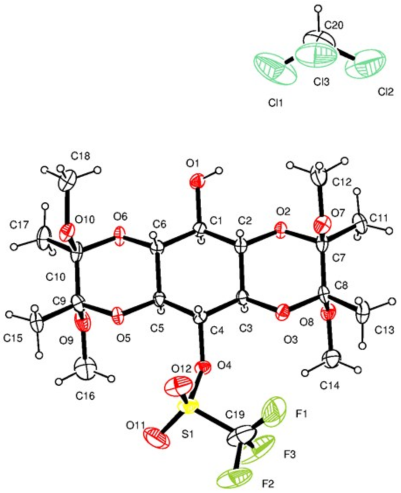
Empirical formula	C41 H61 Cl3 F12 O28 S4	
Formula weight	1464.48	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 17.375(2) Å	a= 90°.
	b = 16.966(2) Å	b= 97.576(6)°.
	c = 43.501(5) Å	g = 90°.
Volume	12711(3) Å^3	
Z	8	
Density (calculated)	1.530 Mg/m^3	
Absorption coefficient	0.390 mm^{-1}	
F(000)	6032	
Crystal size	0.200 x 0.150 x 0.150 mm^3	
Theta range for data collection	0.944 to 24.712°.	
Index ranges	-20<=h<=20, -19<=k<=19, -50<=l<=51	
Reflections collected	47771	
Independent reflections	10835 [R(int) = 0.0323]	
Completeness to theta = 25.242°	94.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9618 and 0.9495	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10835 / 0 / 821	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0719, wR2 = 0.1947	
R indices (all data)	R1 = 0.0850, wR2 = 0.2106	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.340 and -0.985 e.Å^{-3}	

(v) Crystal structure of diol **1** (Data CCDC 1532603)



Empirical formula	C18 H32 O12	
Formula weight	408.44	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P n	
Unit cell dimensions	a = 6.7657(3) Å	a= 90°.
	b = 13.1376(7) Å	b= 106.583(2)°.
	c = 11.8254(6) Å	g = 90°.
Volume	1007.38 Å^3	
Z	2	
R-factor (%)	5.51	

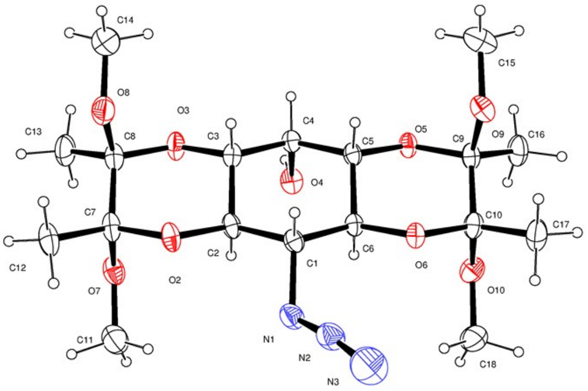
(vi) Crystal structure of *scyllo*-triflate **9** **(**Data CCDC 1532608)



Empirical formula	C20 H32 Cl3 F3 O12 S
Formula weight	659.86
Temperature	296(2) K
Wavelength	0.71073 Å

Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 11.401(2) Å	a= 90°.
	b = 22.024(5) Å	b= 90°.
	c = 11.813(3) Å	g = 90°.
Volume	2966.3(11) Å^3	
Z	4	
Density (calculated)	1.478 Mg/m^3	
Absorption coefficient	0.453 mm^{-1}	
F(000)	1368	
Crystal size	0.230 x 0.040 x 0.040 mm^3	
Theta range for data collection	2.571 to 25.997°.	
Index ranges	-9<=h<=13, -27<=k<=22, -14<=l<=12	
Reflections collected	12661	
Independent reflections	5066 [R(int) = 0.0686]	
Completeness to theta = 25.242°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9929 and 0.9603	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5066 / 37 / 353	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0773, wR2 = 0.1873	
R indices (all data)	R1 = 0.1575, wR2 = 0.2287	
Absolute structure parameter	0.58(8)	
Extinction coefficient	0.0079(19)	
Largest diff. peak and hole	0.300 and -0.333 e.Å^{-3}	

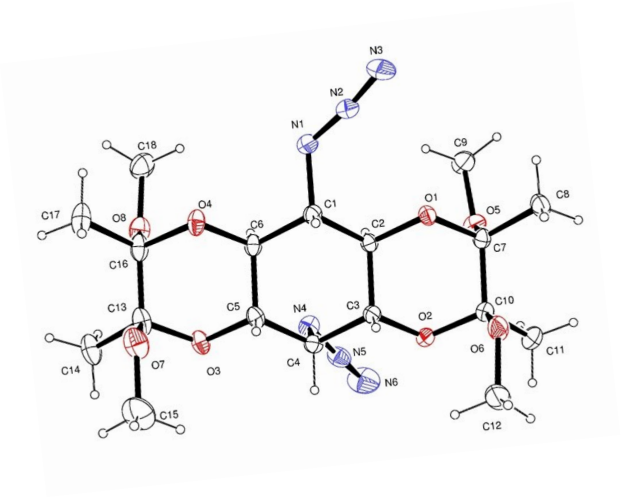
(vii) Crystal structure of 5-*myo* azide **18** (Data CCDC 1532602)



Empirical formula	C18 H31 N3 O9
Formula weight	433.46
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P b c n

Unit cell dimensions	a = 11.8946(3) Å	a= 90°.
	b = 17.0004(5) Å	b= 90°.
	c = 21.7463(8) Å	g = 90°.
Volume	4397.4(2) Å^3	
Z	8	
Density (calculated)	1.309 Mg/m^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	1856	
Crystal size	0.200 x 0.150 x 0.070 mm^3	
Theta range for data collection	2.538 to 26.000°.	
Index ranges	-14<=h<=14, -20<=k<=20, -26<=l<=18	
Reflections collected	20401	
Independent reflections	4323 [R(int) = 0.0436]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9927 and 0.9793	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4323 / 1 / 280	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0525, wR2 = 0.1234	
R indices (all data)	R1 = 0.1172, wR2 = 0.1495	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.415 and -0.160 e.Å^{-3}	

(viii) Crystal structure of diazide **19** (Data CCDC 1532604)



Empirical formula	C18 H30 N6 O8	
Formula weight	458.48	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.3487(4) Å	a= 90°.
	b = 22.2829(8) Å	b= 105.944(2)°.
	c = 17.8108(6) Å	g = 90°.
Volume	4712.4(3) Å^3	
Z	8	
Density (calculated)	1.292 Mg/m^3	
Absorption coefficient	0.102 mm^{-1}	
F(000)	1952	
Crystal size	0.200 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.181 to 26.372°.	
Index ranges	-15<=h<=15, -27<=k<=26, -22<=l<=22	
Reflections collected	40102	
Independent reflections	9644 [R(int) = 0.0431]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9898 and 0.9797	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9644 / 0 / 577	
Goodness-of-fit on F^2	0.976	
Final R indices [I>2sigma(I)]	R1 = 0.0515, wR2 = 0.1354	
R indices (all data)	R1 = 0.1109, wR2 = 0.1681	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.174 and -0.193 e.Å^{-3}	

4. Spectral Data

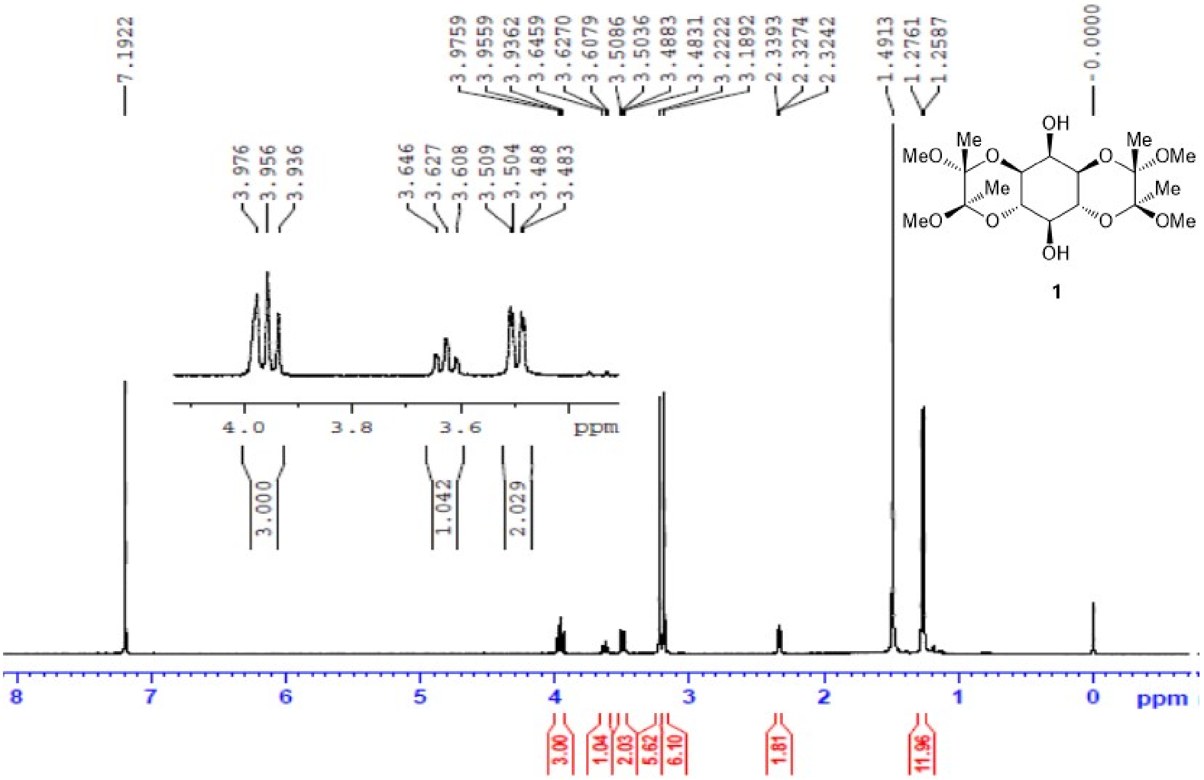


Figure S9. ^{1}H spectrum of diol **1** in $CDCl_3$.

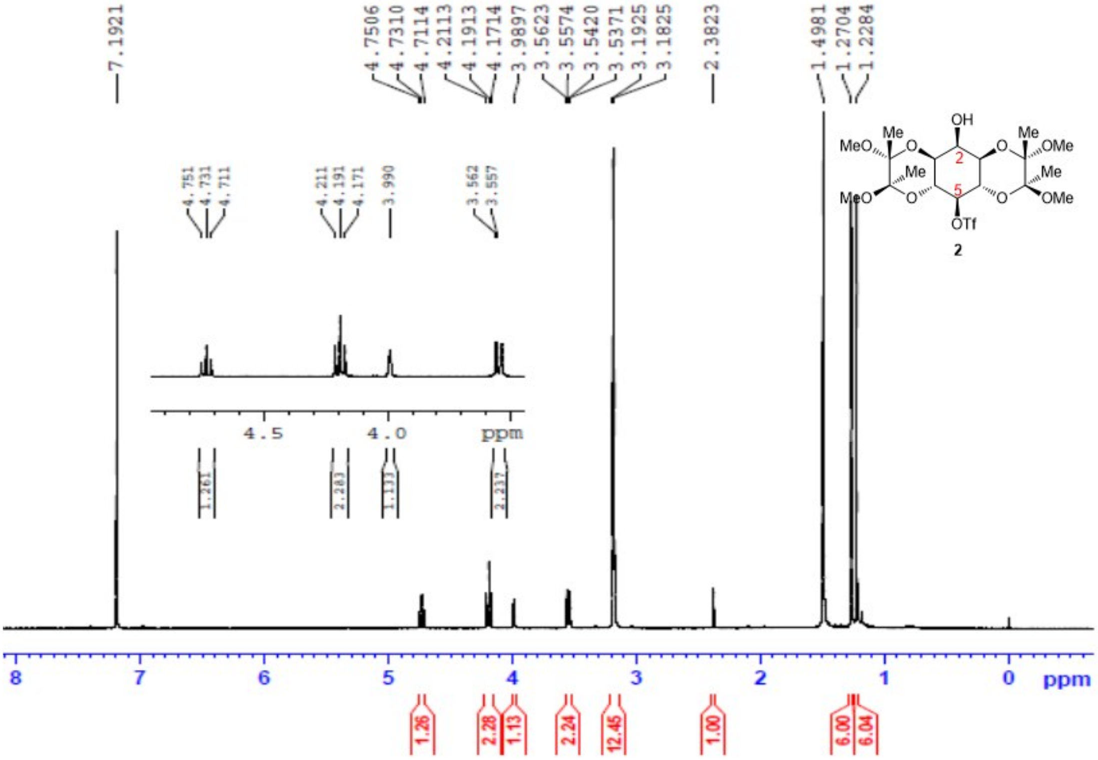


Figure S10. ^{1}H spectrum of monotriflate **2** in $CDCl_3$.

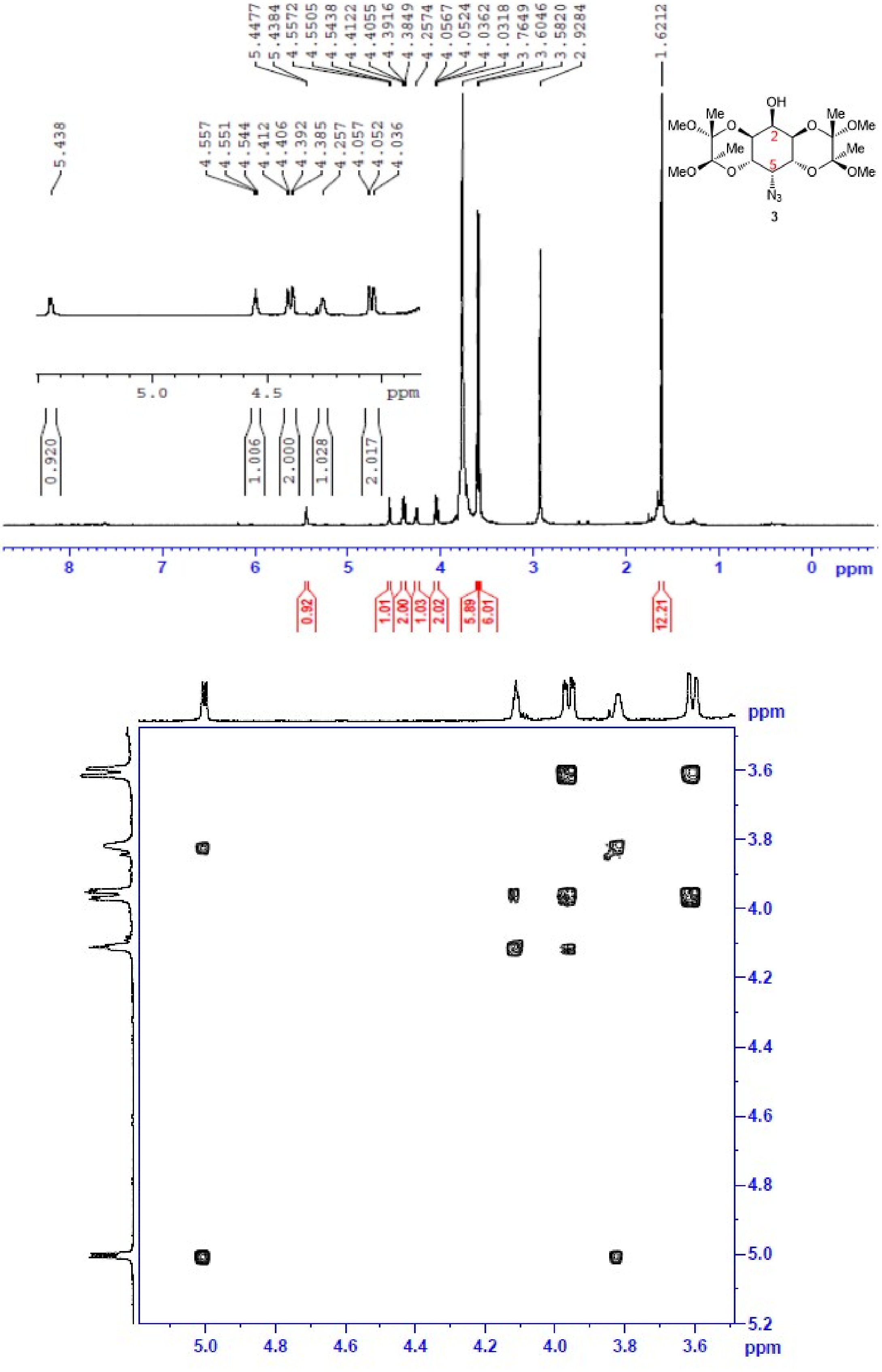


Figure S11. ^{1}H and COSY spectra of azide **3** in DMSO-d_6.

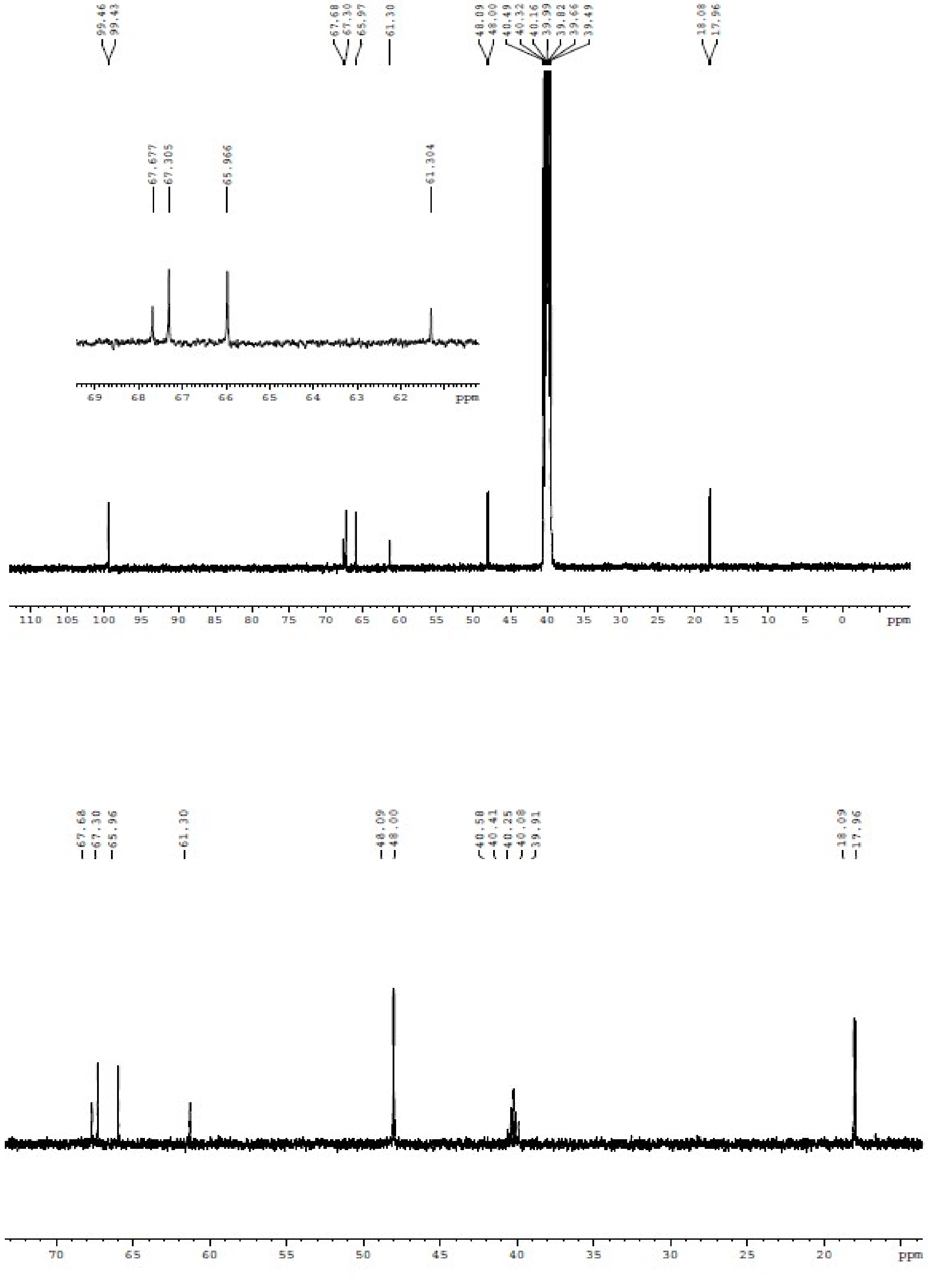


Figure S12. ^{13}C and DEPT spectra of azide **3** in DMSO-d$_6$.

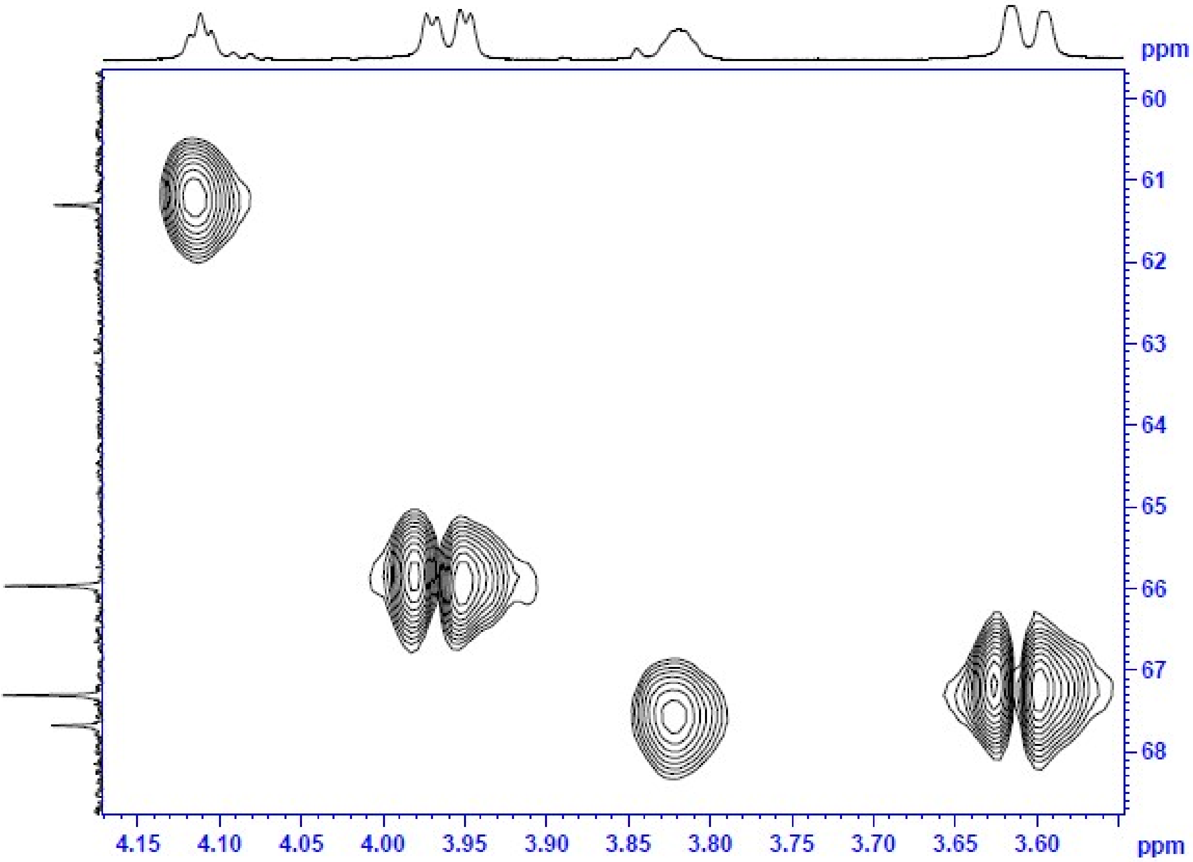


Figure S13. HMQC spectrum of azide **3** in DMSO-d$_6$.

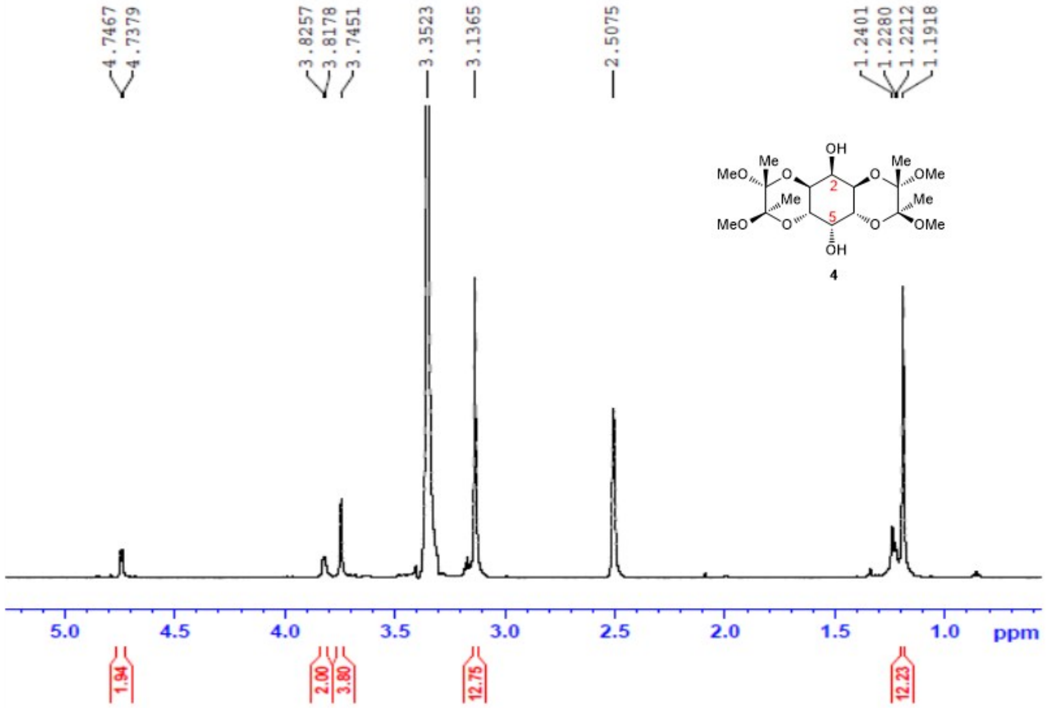


Figure S14. ^{1}H NMR spectrum of diol **4** in DMSO-d$_6$.

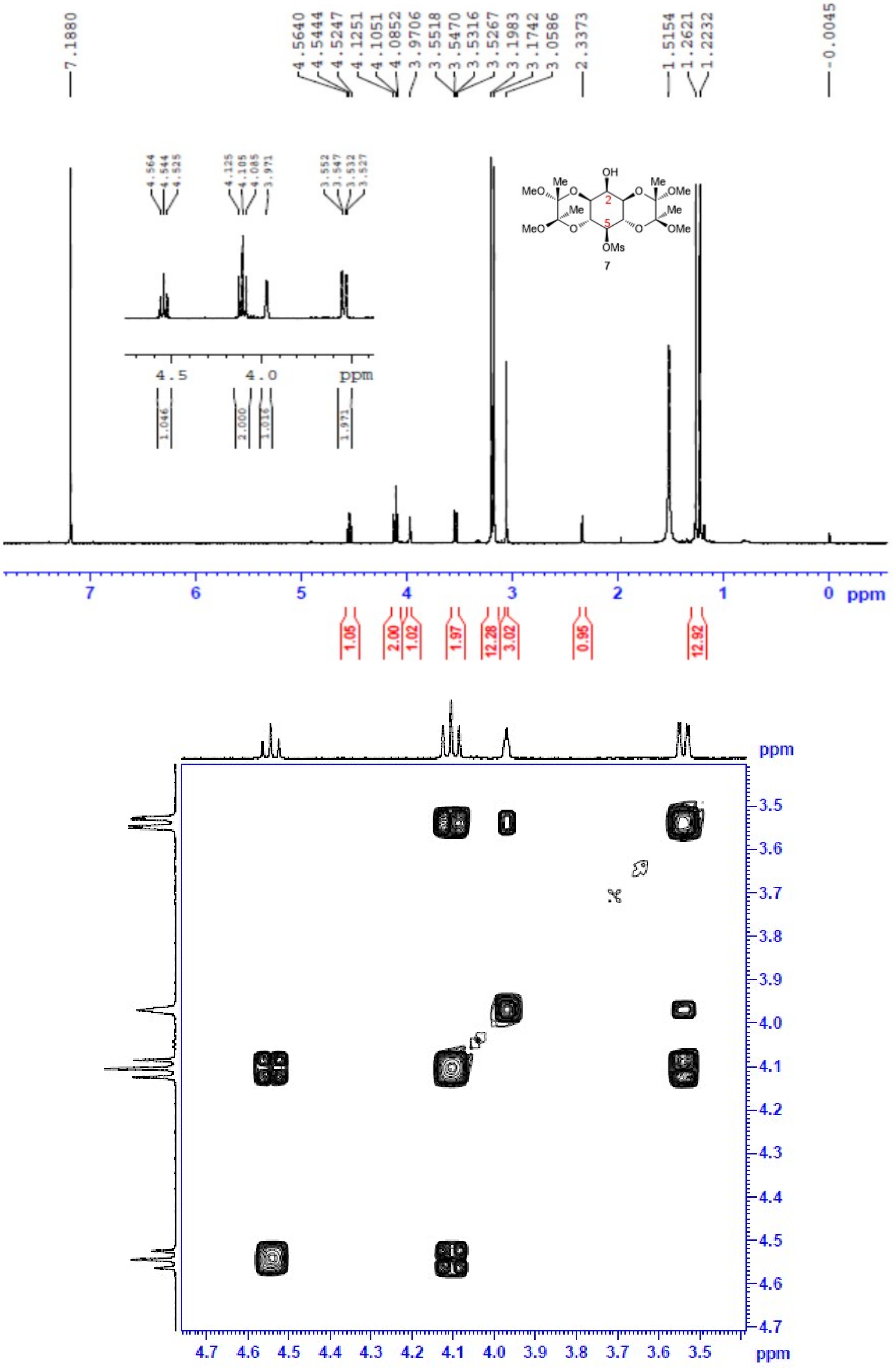


Figure S15. ^{1}H and COSY spectra of mesylate **7** in $CDCl_3$.

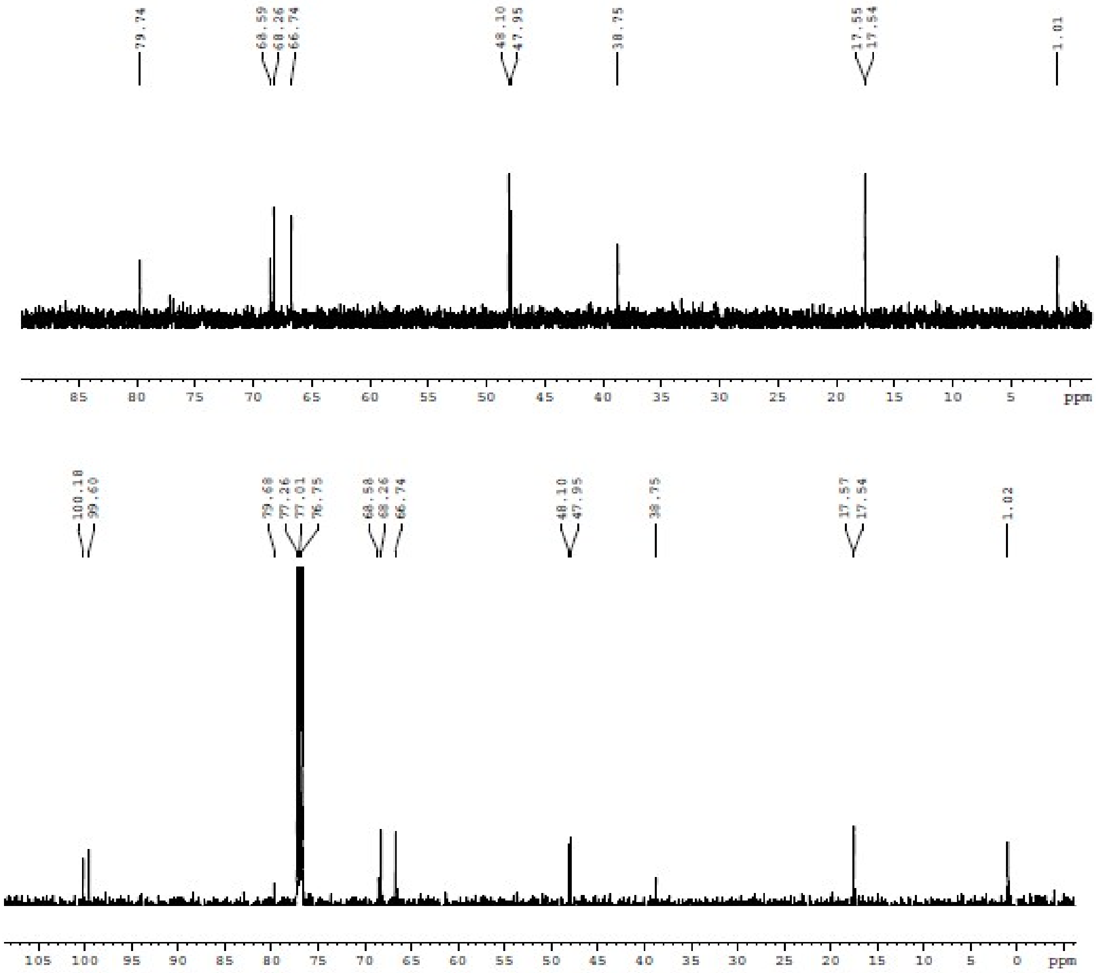


Figure S16. DEPT and ^{13}C spectra of mesylate **7** in CDCl$_3$.

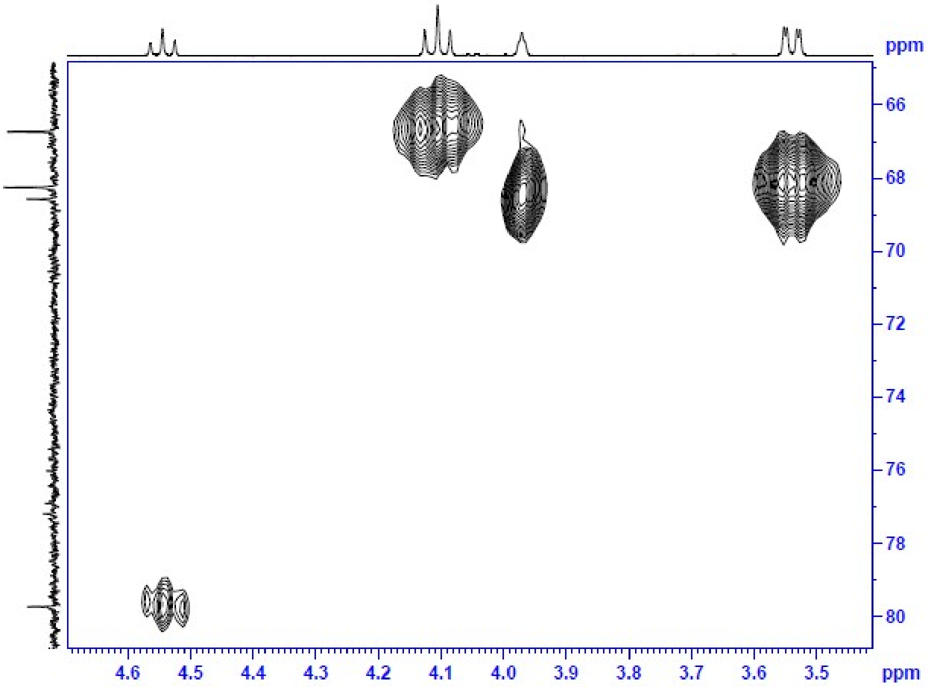


Figure S17. HMQC spectrum of mesylate **7** in CDCl$_3$.

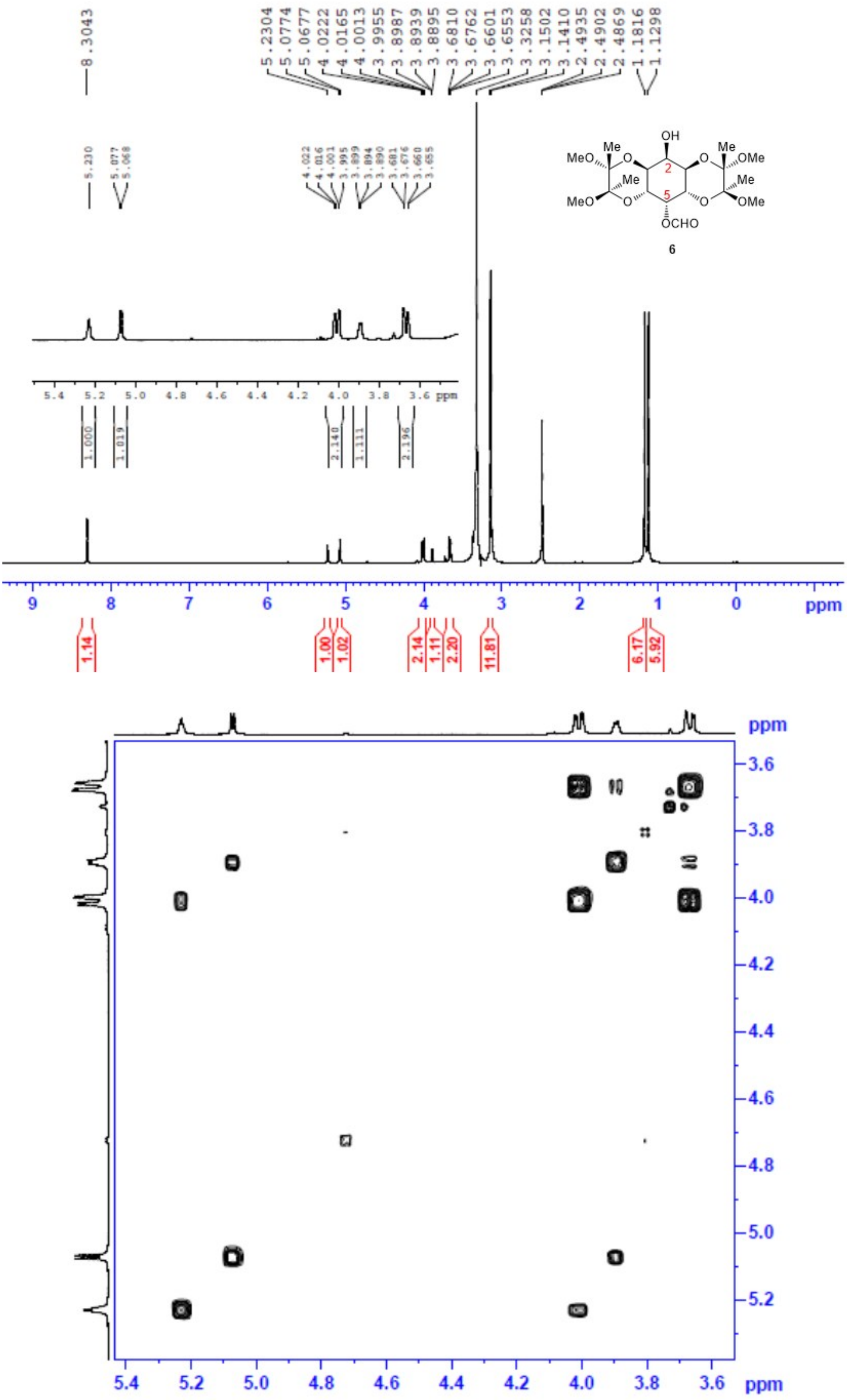


Figure S18. ^{1}H and COSY spectra of formate **6** in DMSO-d_6.

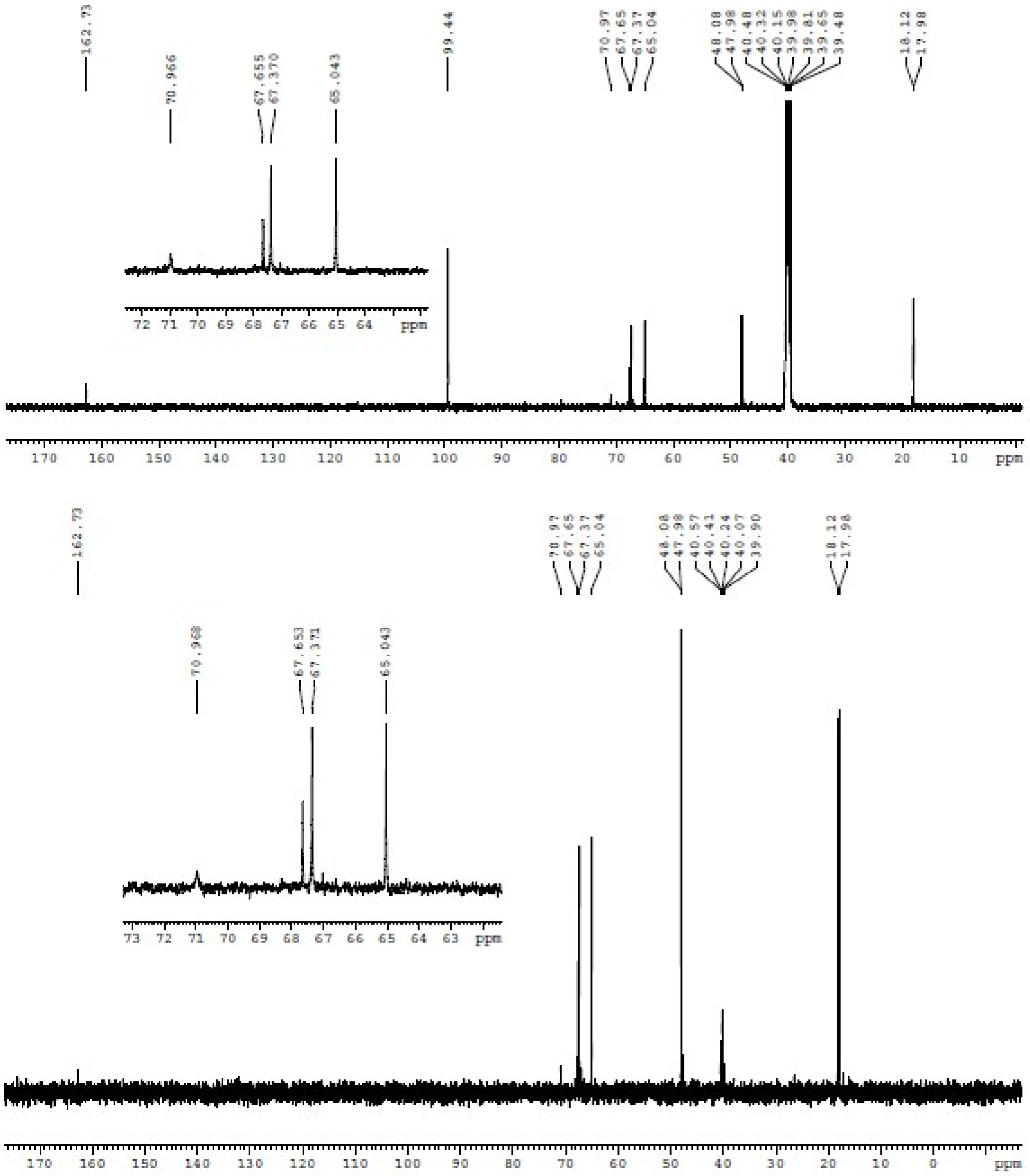


Figure S19. ^{13}C and DEPT spectra of formate **6** in DMSO-d$_6$.

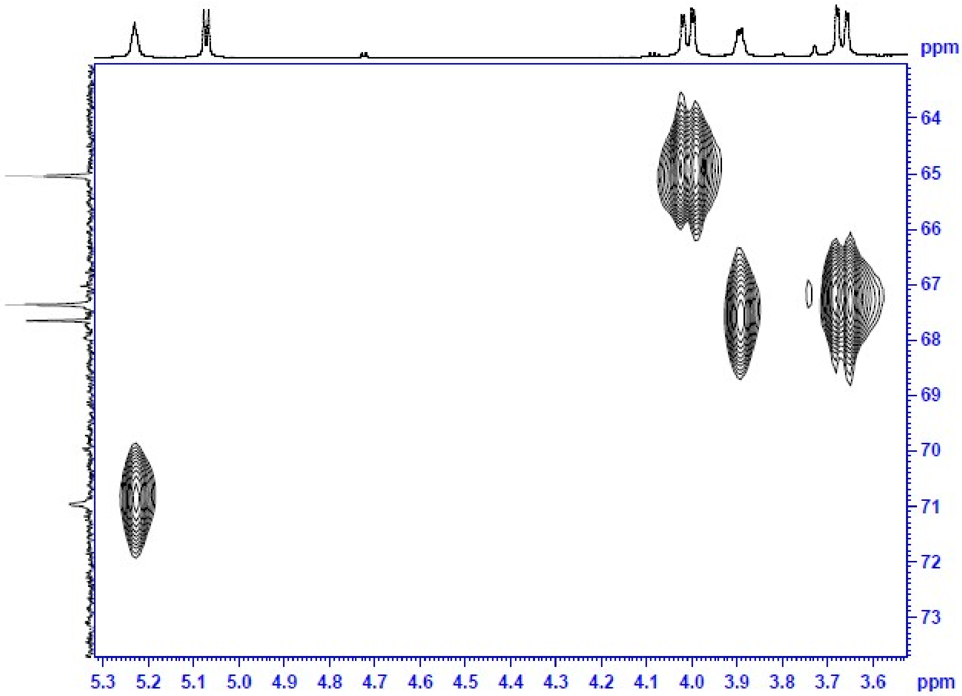


Figure S20. HMQC spectra of formate **6** in DMSO-d_6.

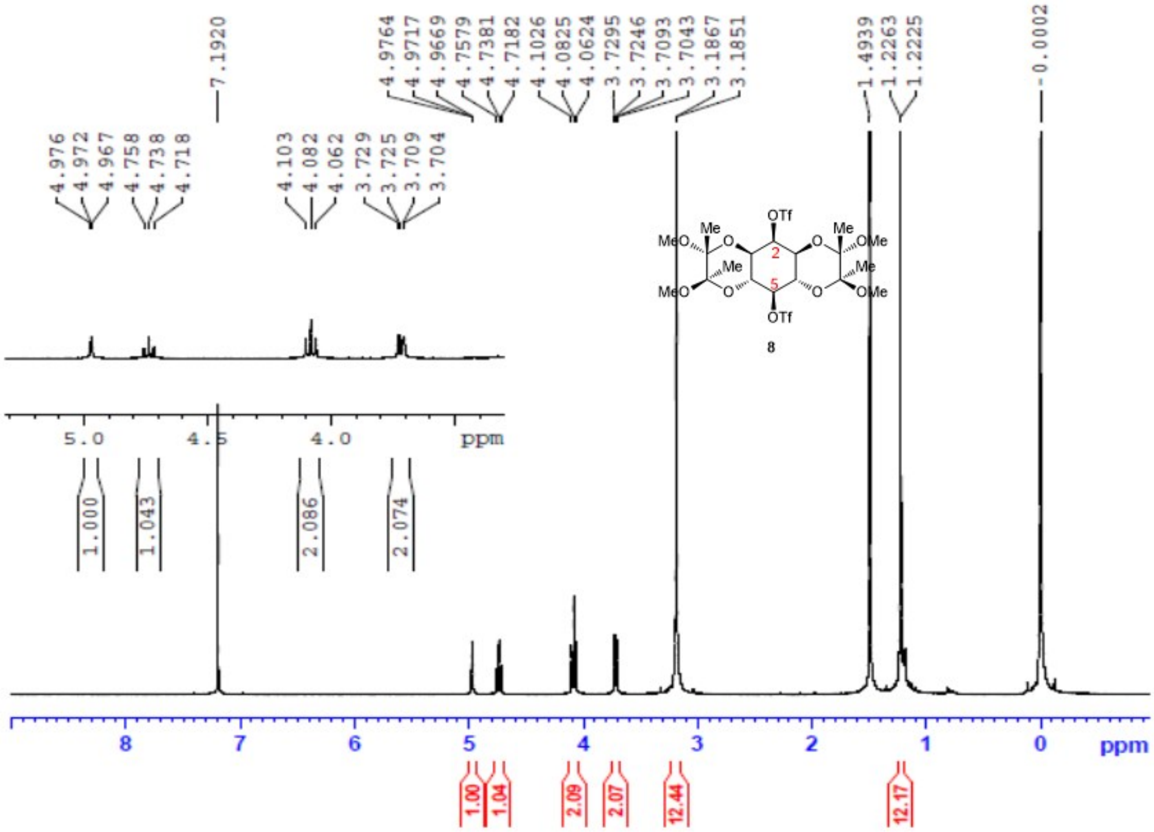


Figure S21. ^{1}H spectra of ditriflate **8** in $CDCl_3$

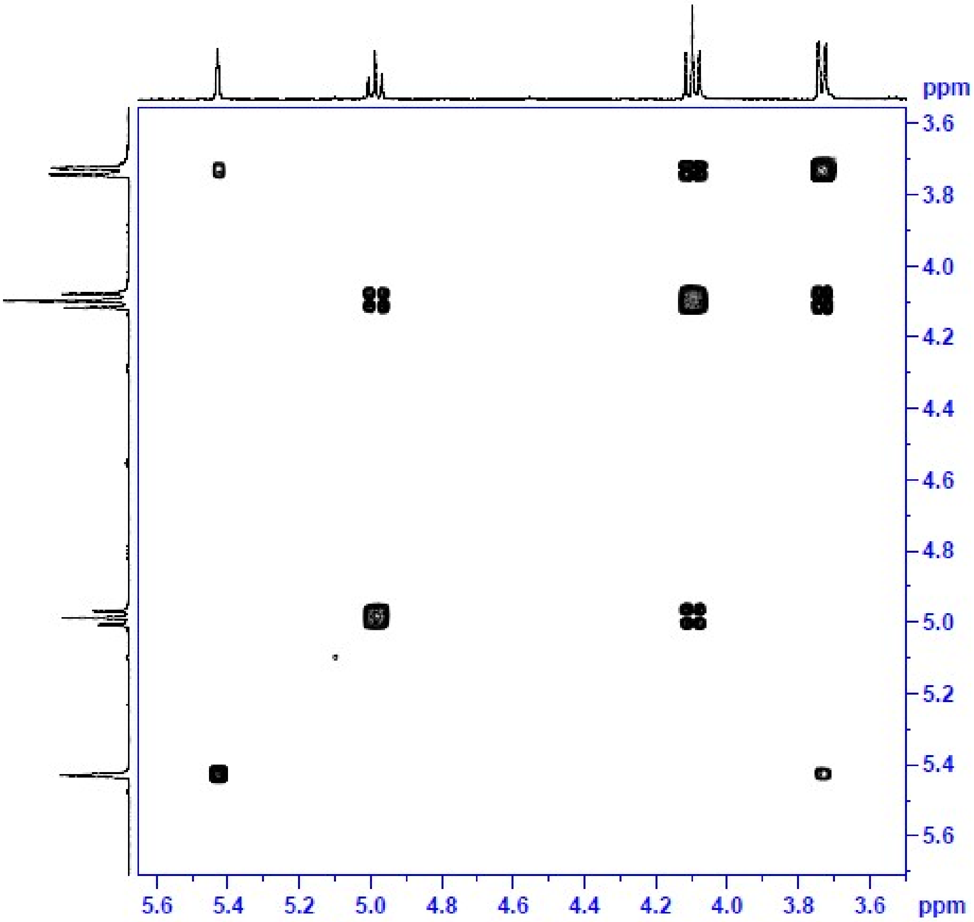


Figure S22. COSY spectra of ditriflate **8** in CDCl$_3$

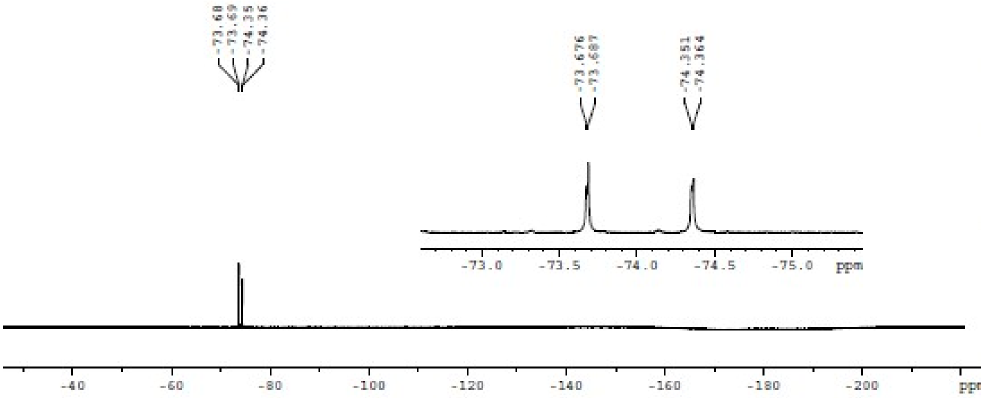


Figure S23. ^{19}F NMR spectra of ditriflate **8** in CDCl$_3$

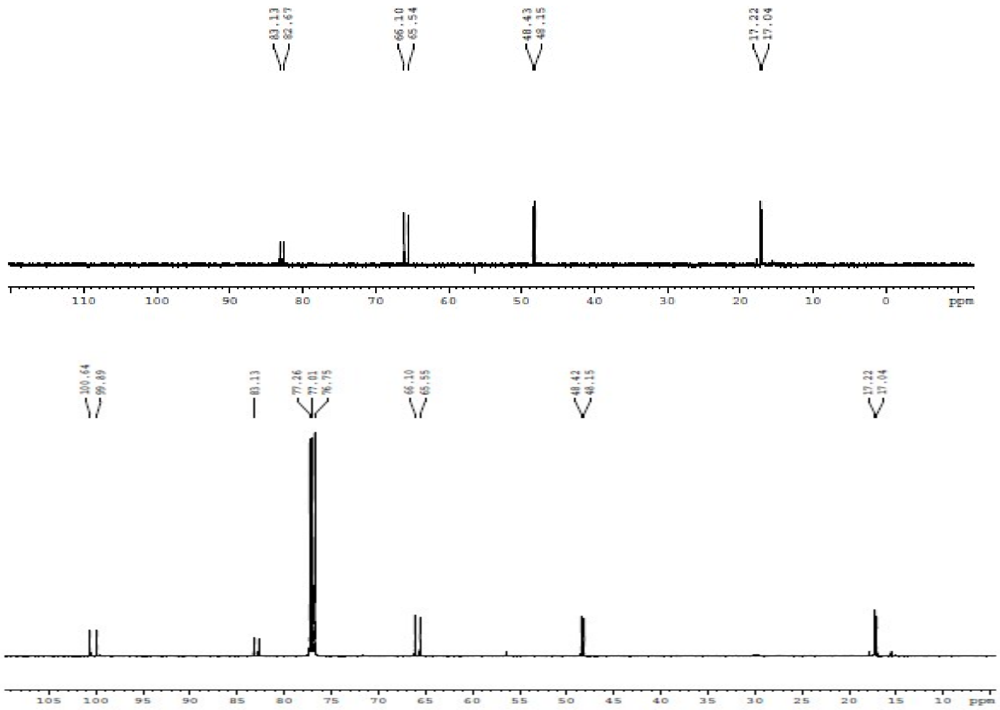


Figure S24. ^{13}C and DEPT spectra of ditriflate **8** in CDCl$_3$

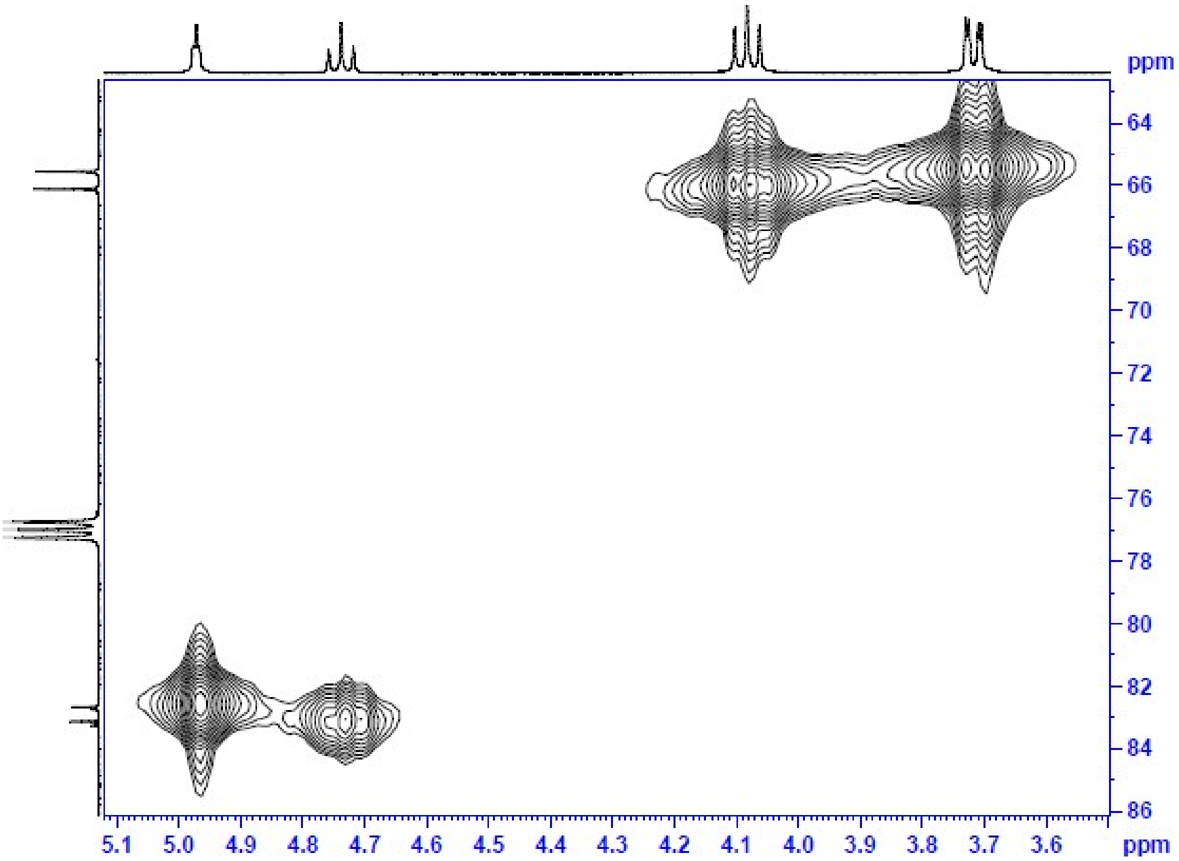


Figure S25. HMQC spectrum of ditriflate **8** in CDCl$_3$

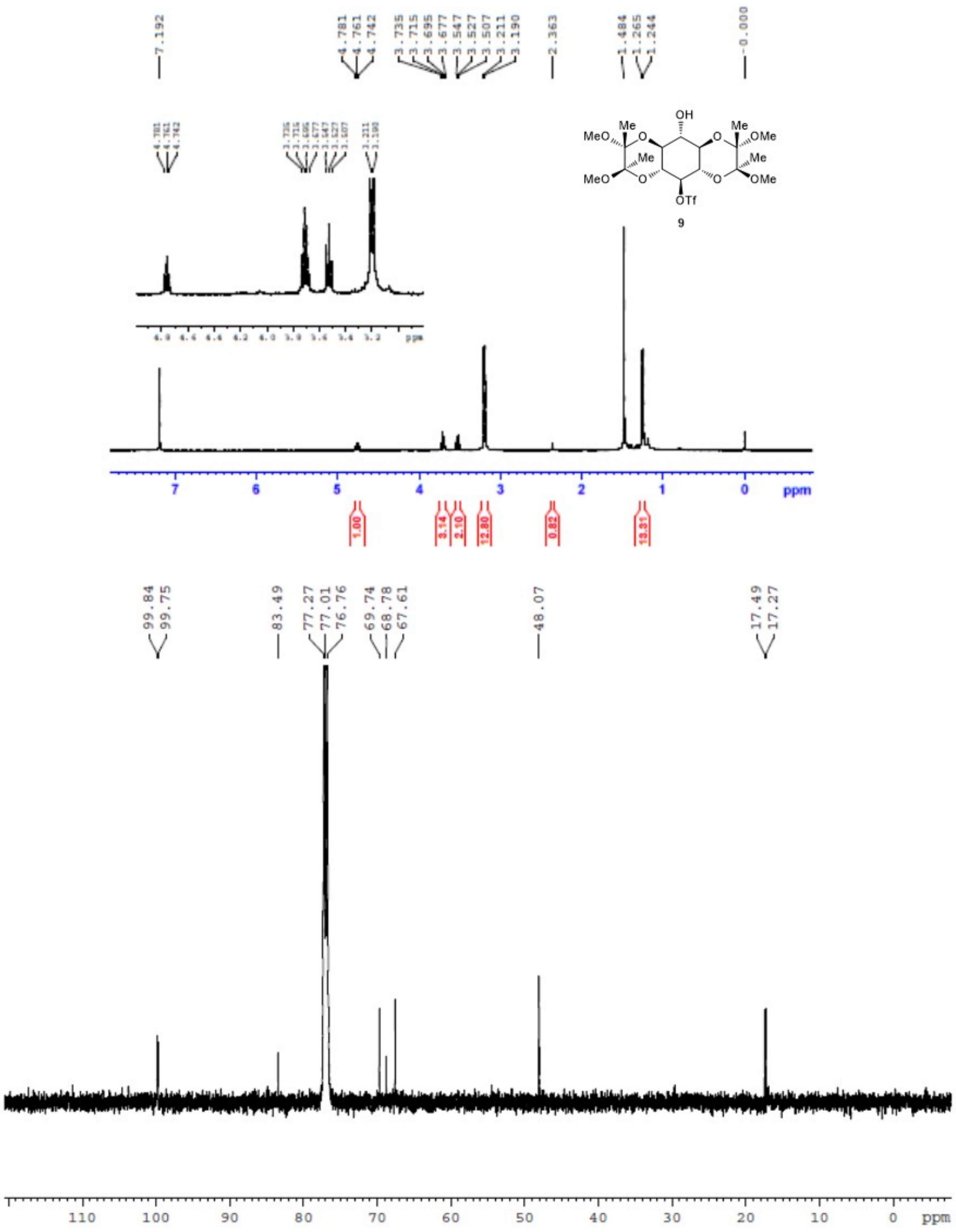


Figure S26. ^{1}H and ^{13}C spectra of triflate **9** in $CDCl_3$.

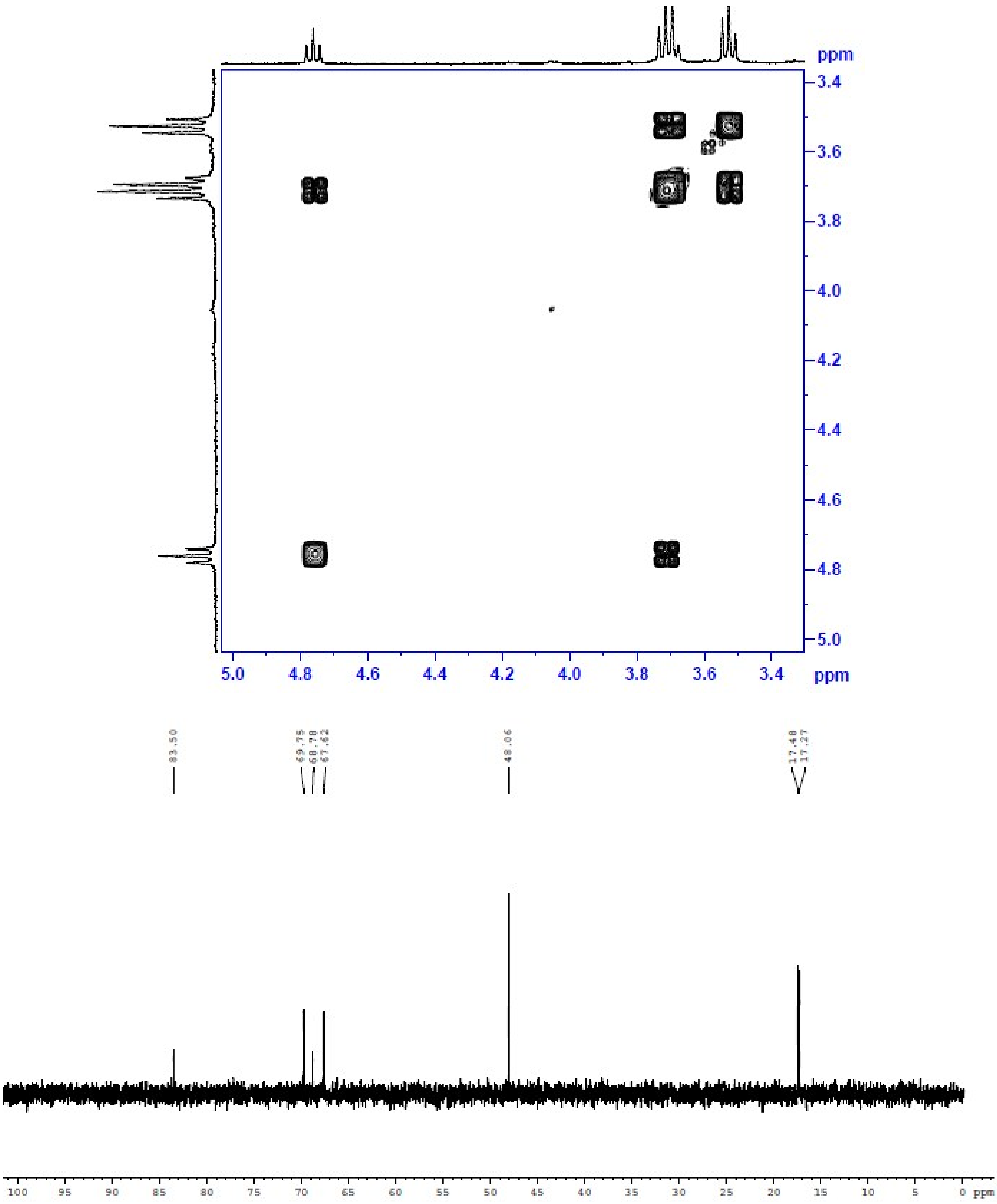


Figure S27. COSY and DEPT spectra of triflate **9** in $CDCl_3$.

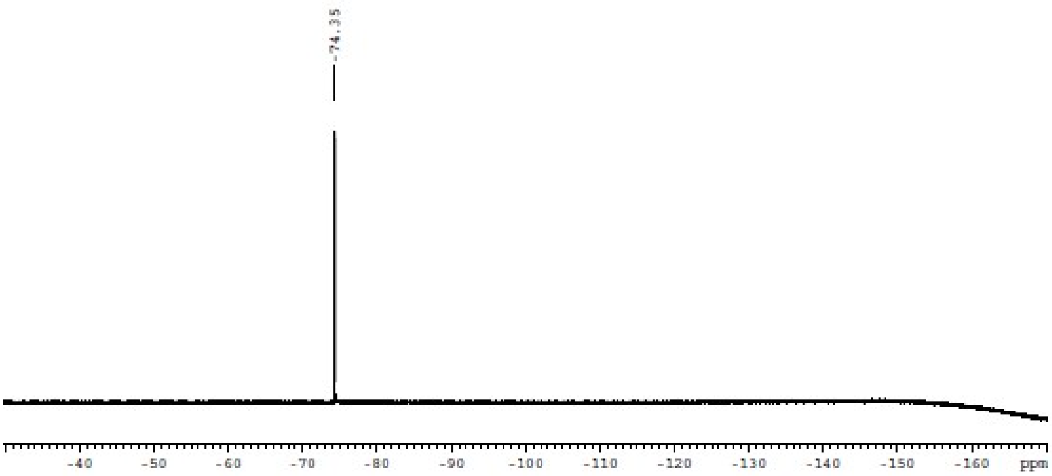


Figure S28. ^{19}F NMR spectra of triflate **9** in CDCl$_3$.

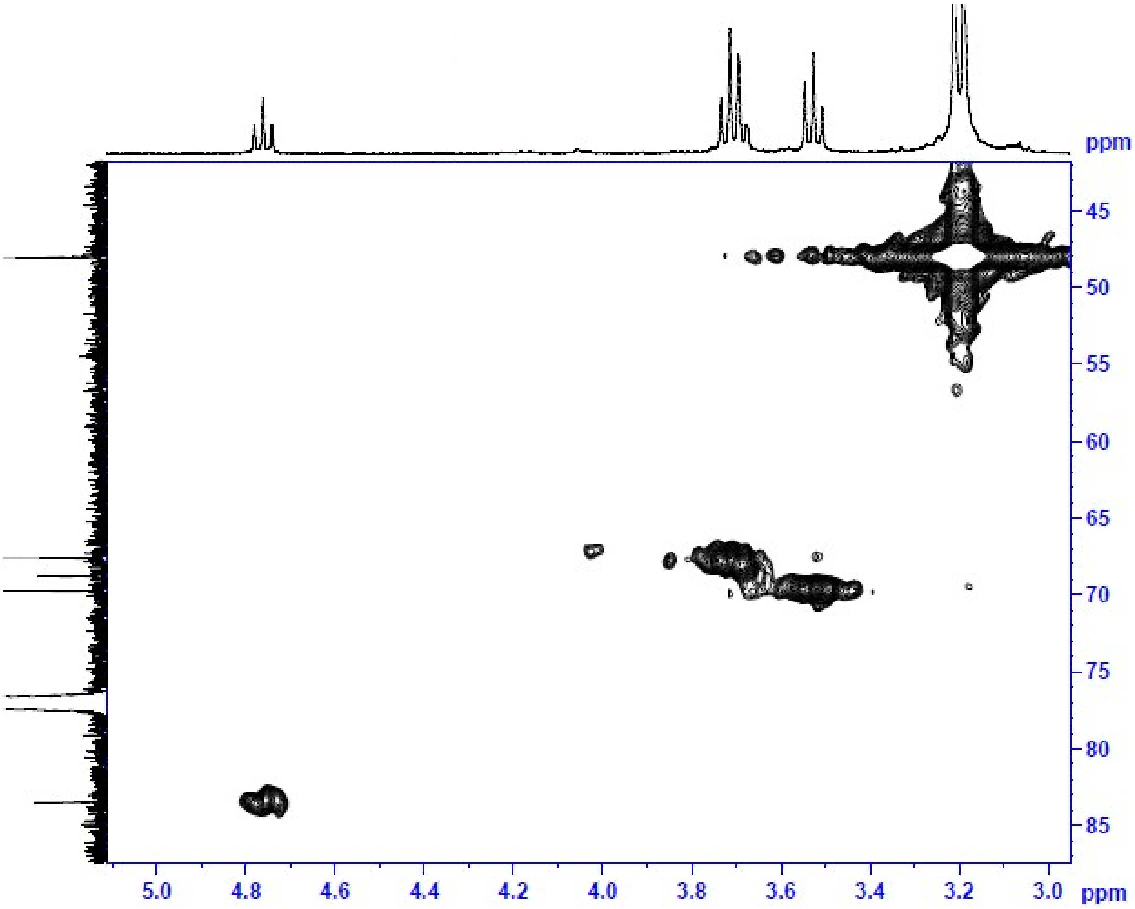


Figure S29. HMQC spectra of triflate **9** in CDCl$_3$.

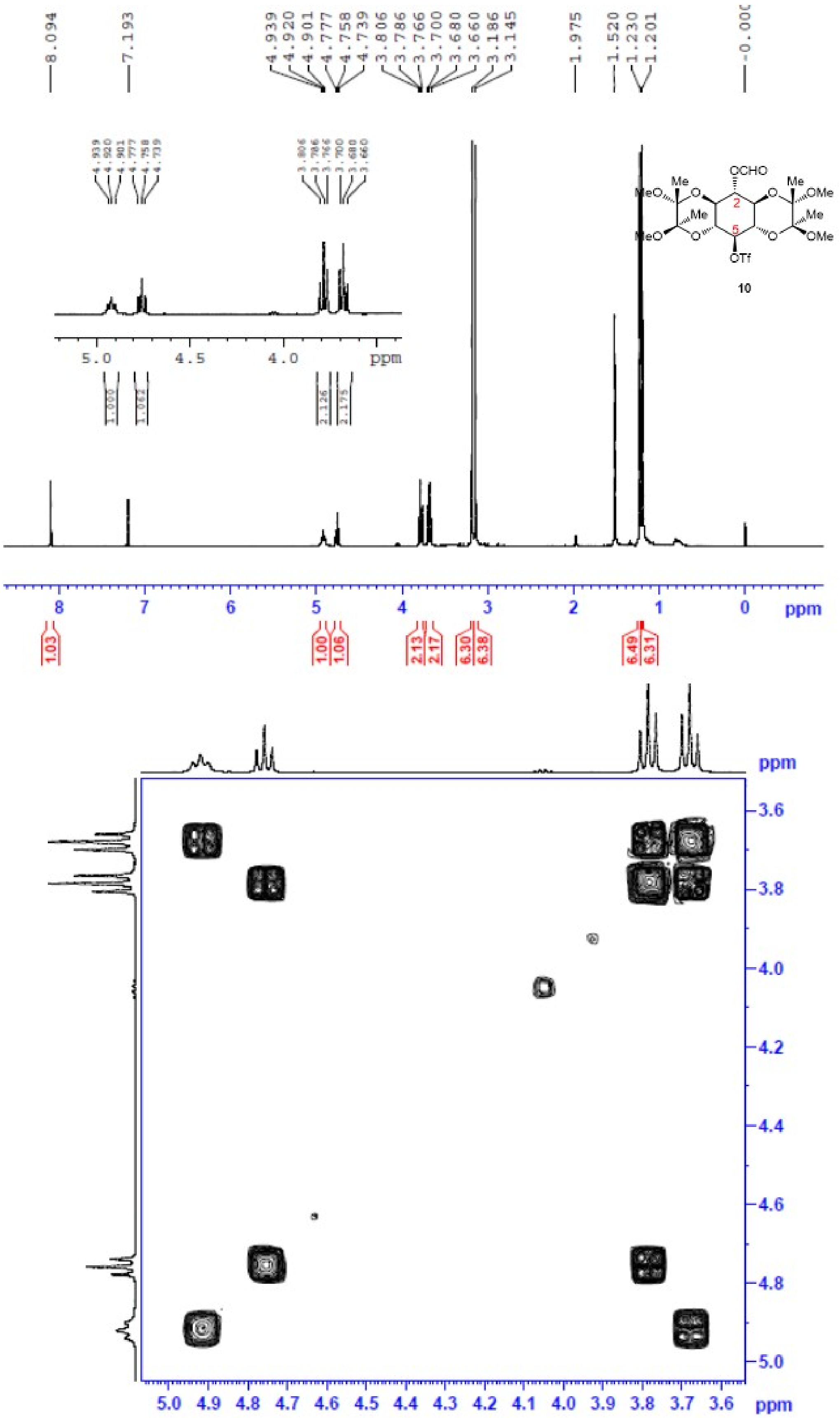


Figure S30. ^{1}H NMR and COSY spectra of compound **10** in CDCl$_3$.

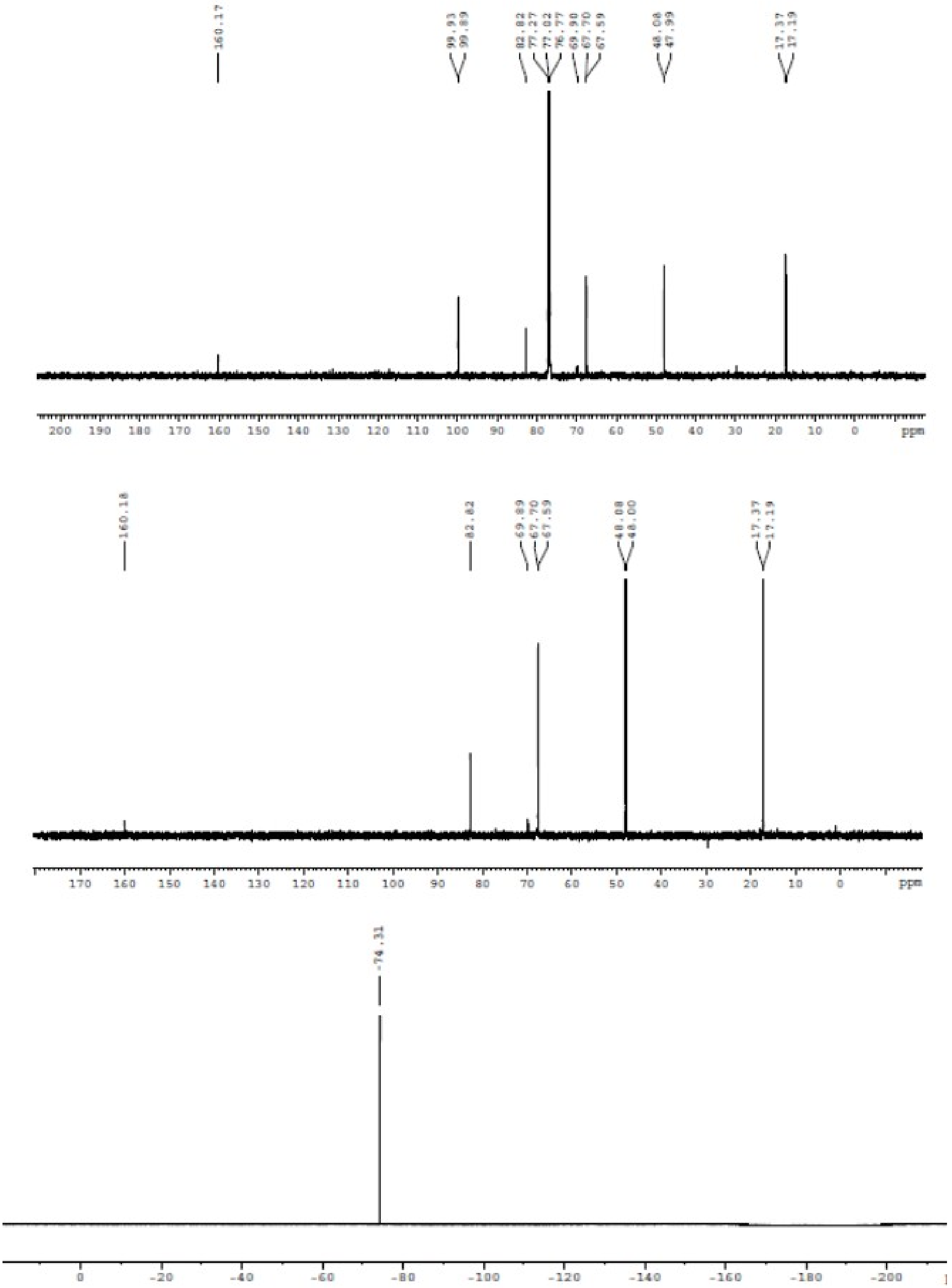


Figure S31. ^{13}C NMR, DEPT and ^{19}F NMR spectra of compound **10** in CDCl$_3$.

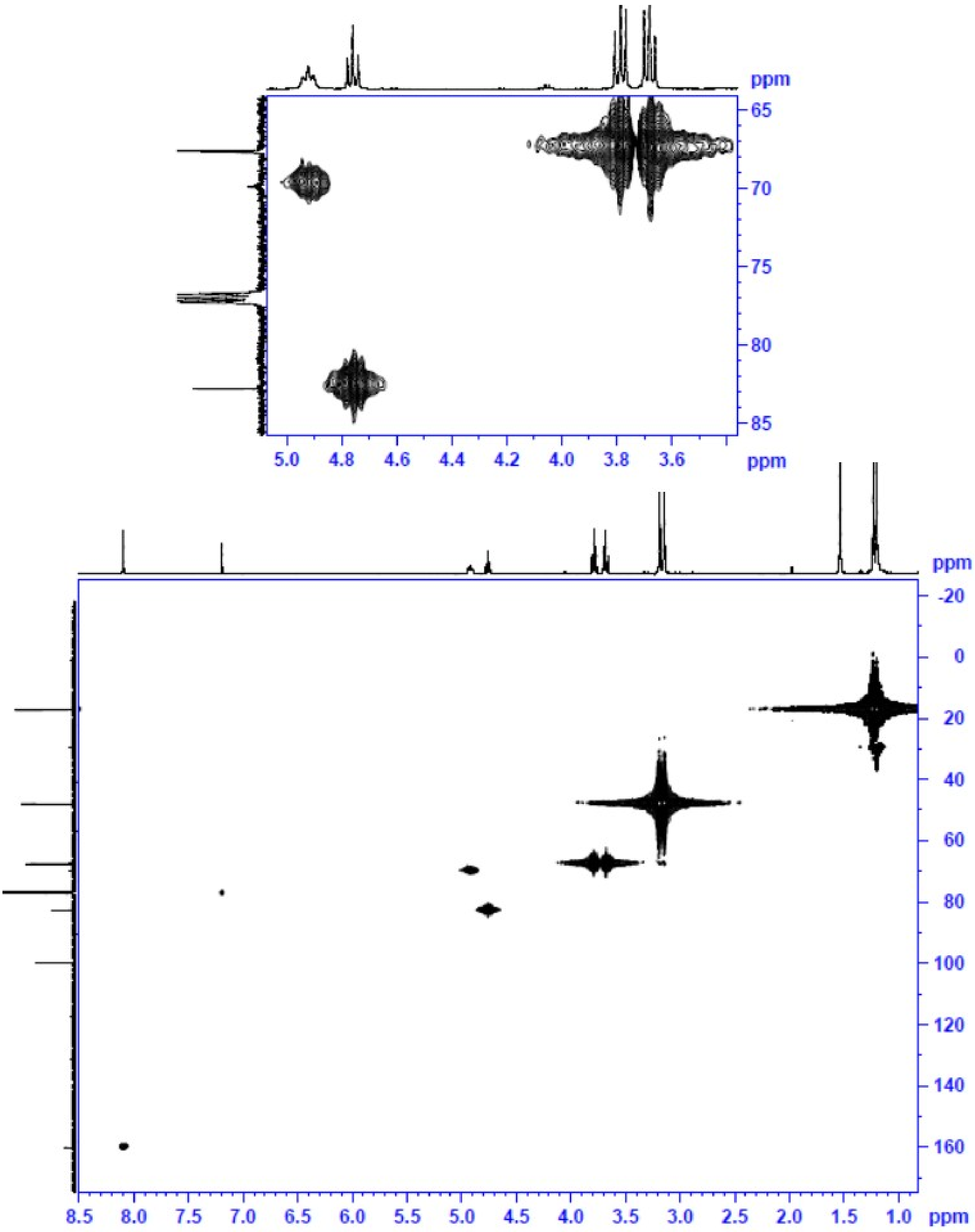


Figure S32. HMQC spectra of compound **10** in $CDCl_3$.

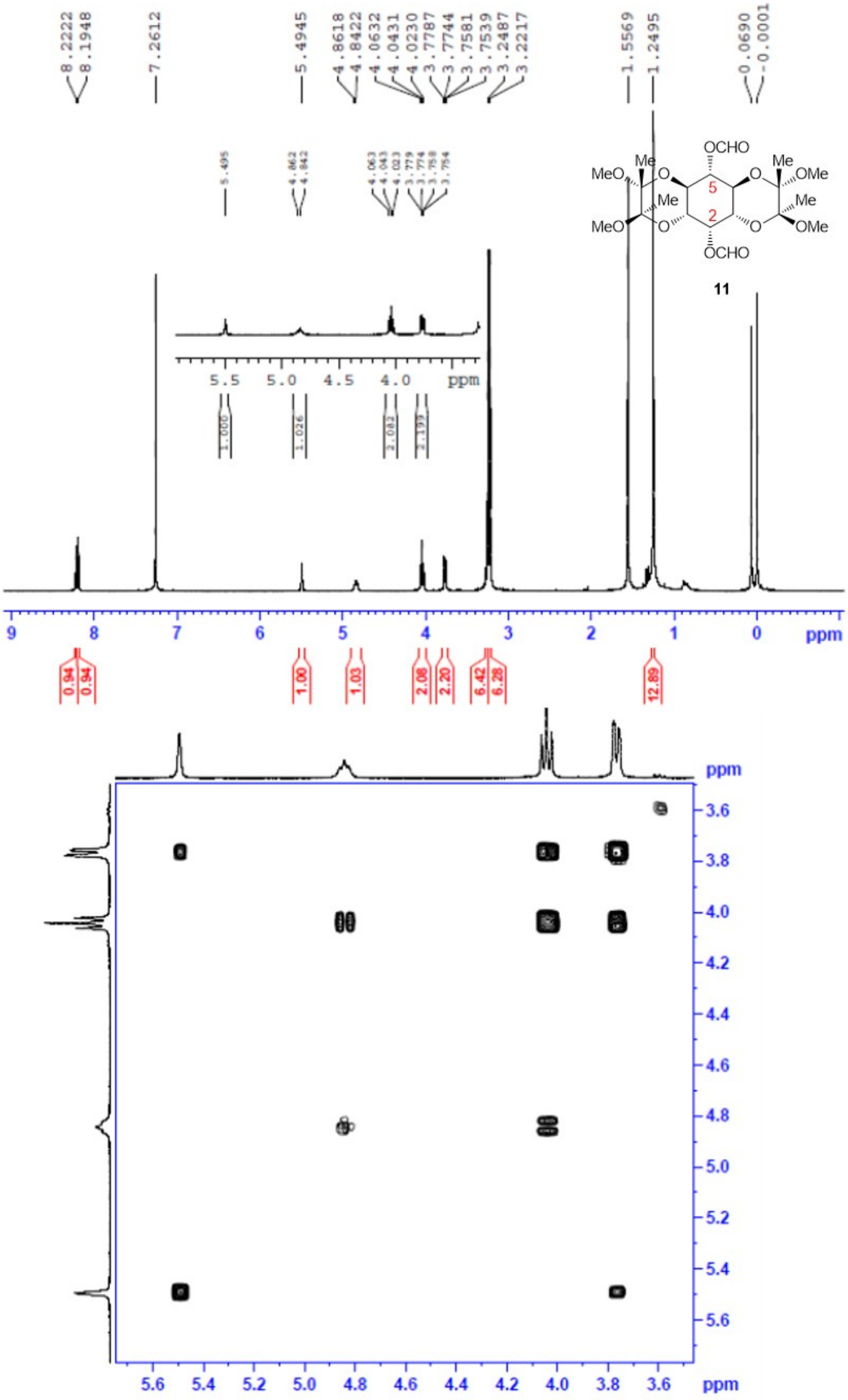


Figure S33. ^{1}H NMR and COSY spectra of compound **11** in $CDCl_3$.

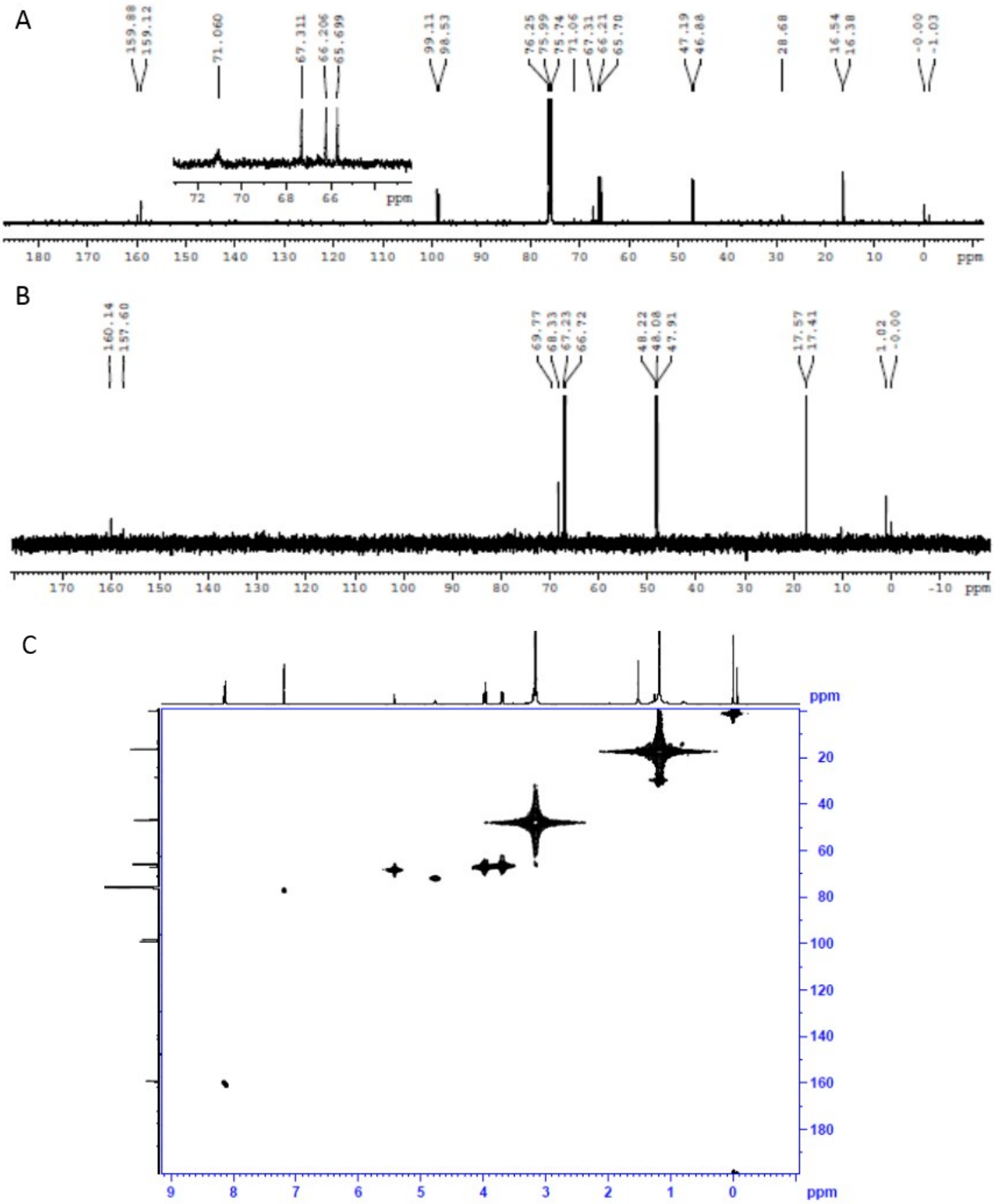


Figure S34. ^{13}C, DEPT and HMQC spectra of compound **11** in $CDCl_3$.

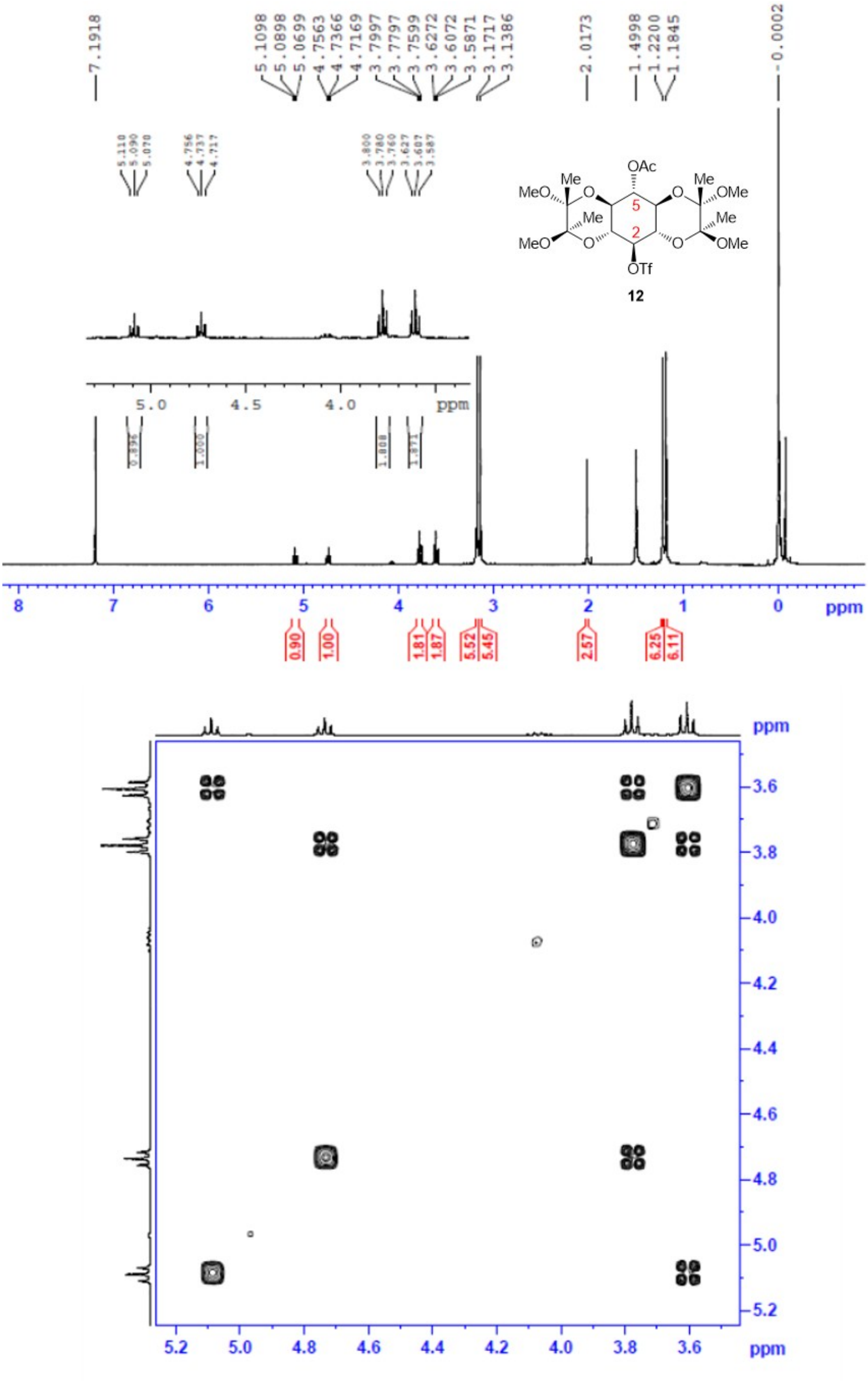


Figure S35. ^{1}H NMR and COSY spectra of compound **12** in $CDCl_3$.

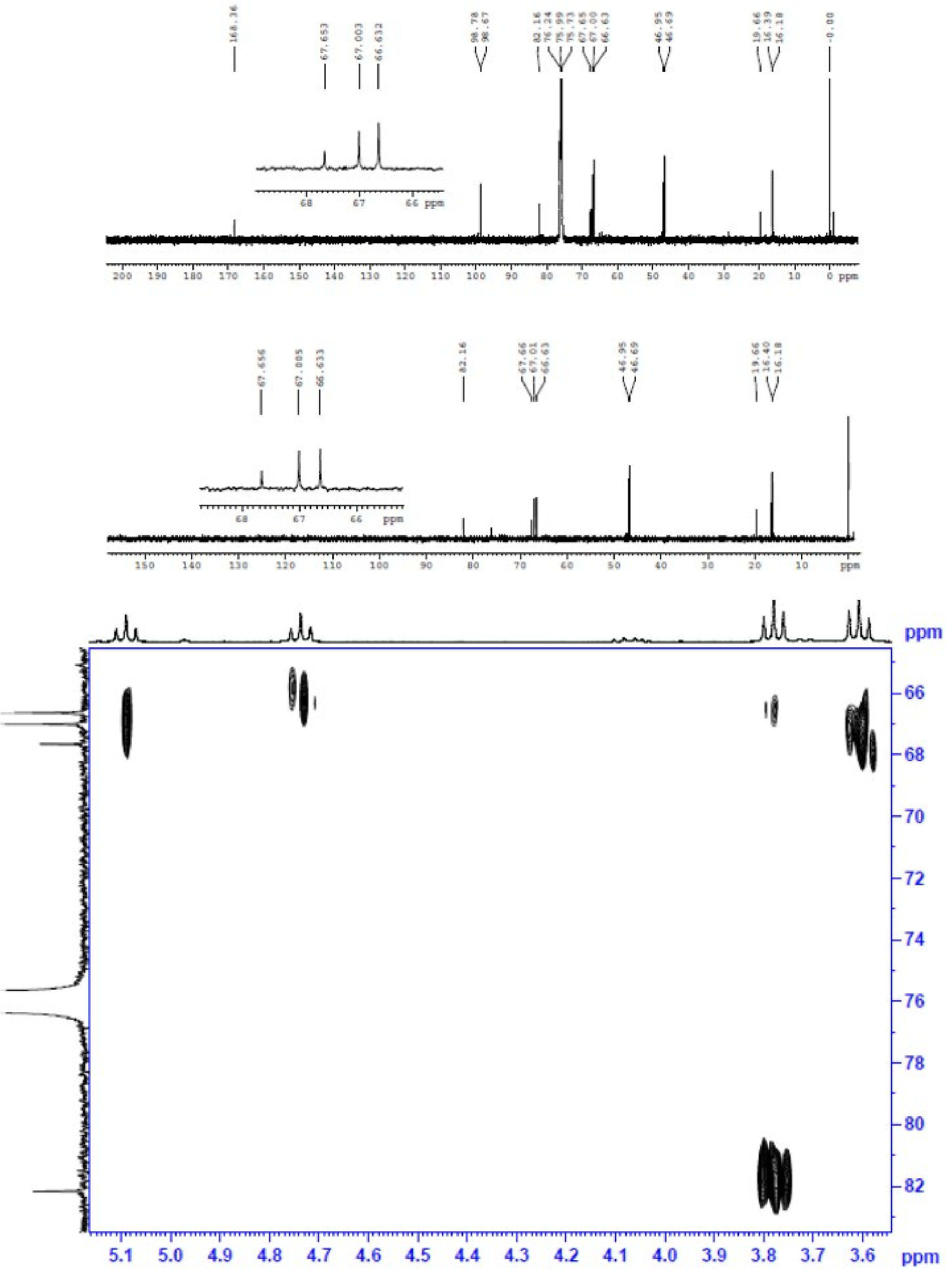


Figure S36. ^{13}C, DEPT and HMQC spectra of compound **12** in CDCl$_3$.

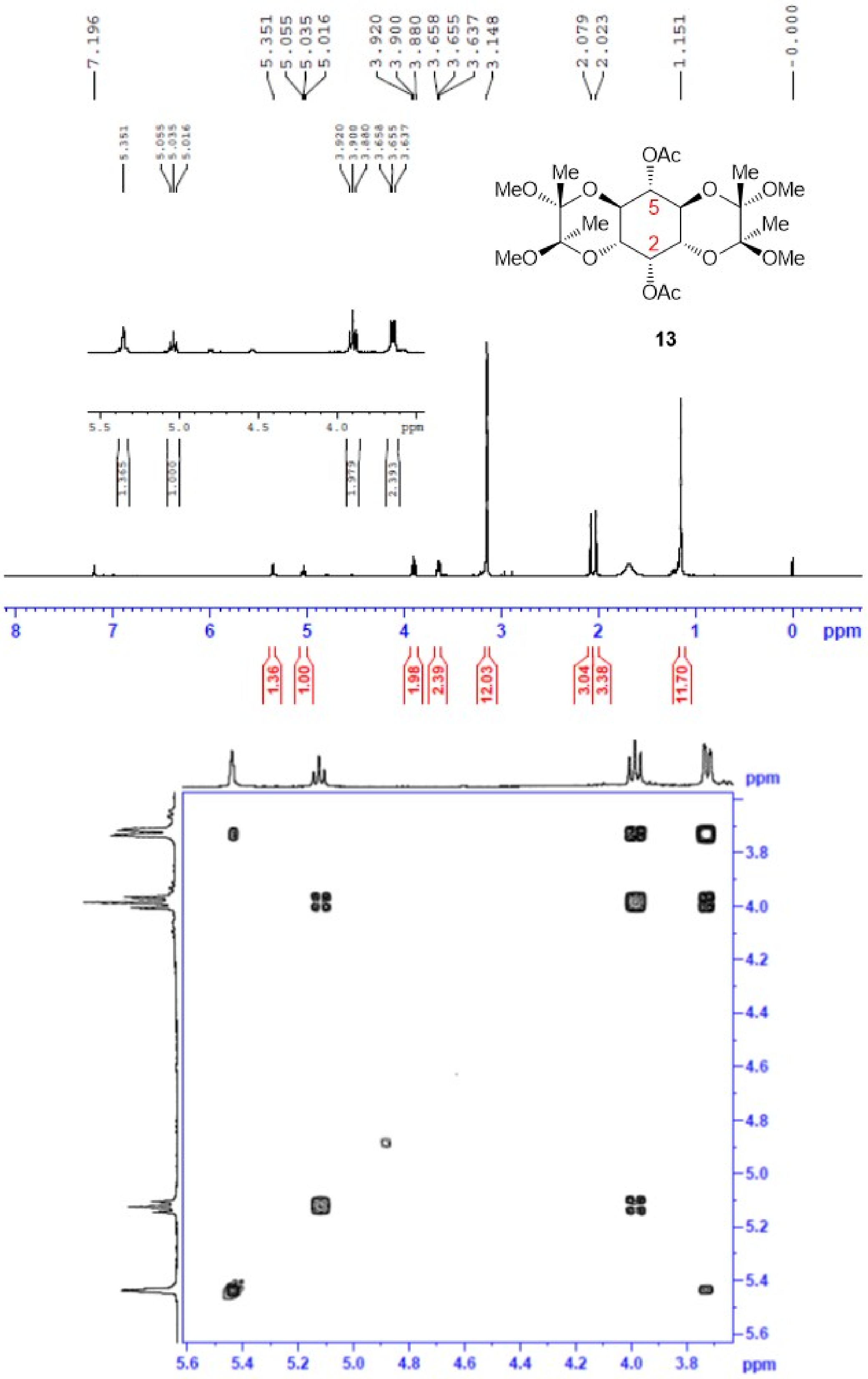


Figure S37. ^{1}H NMR and COSY spectra of compound **13** in $CDCl_3$

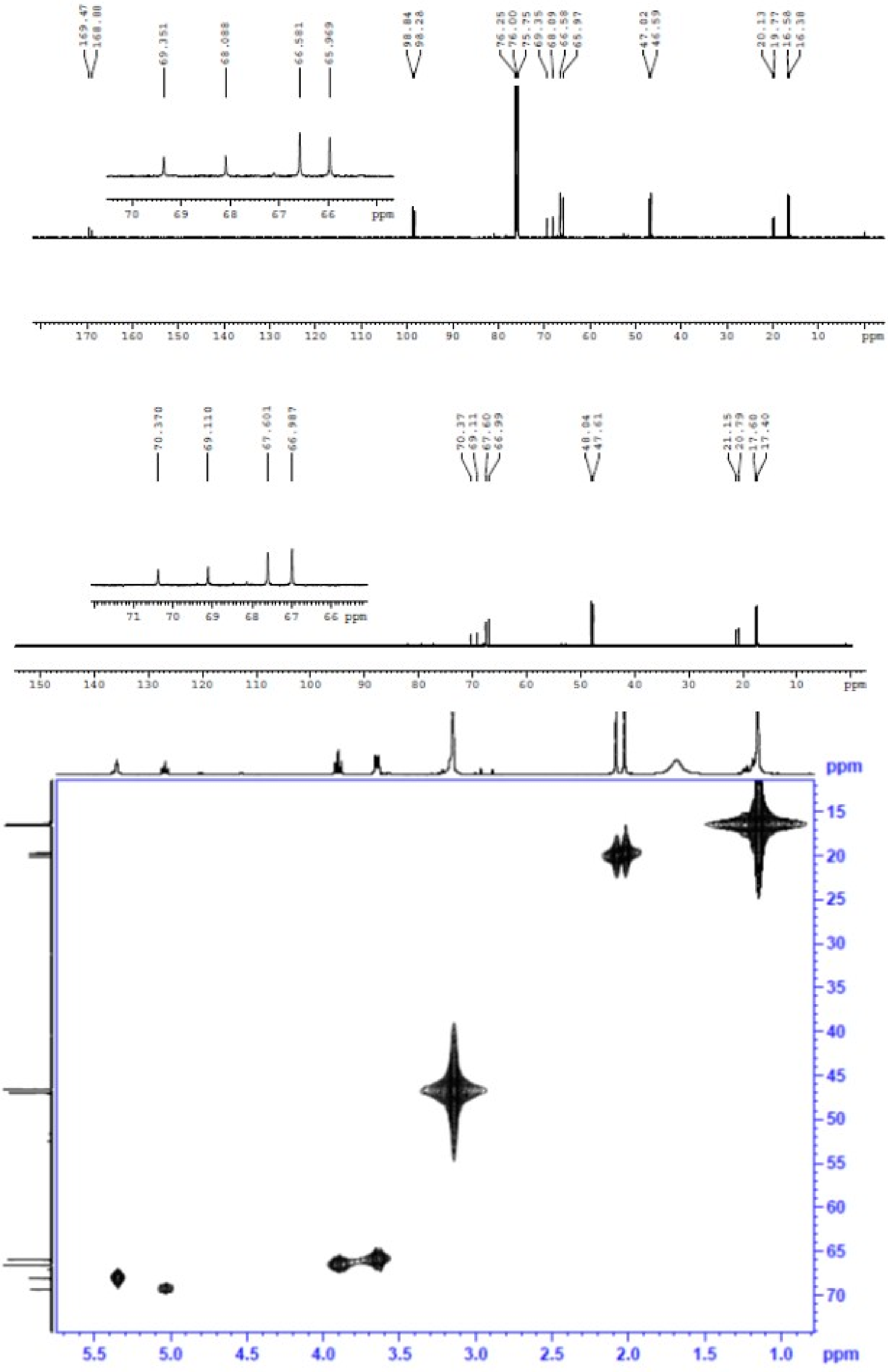


Figure S38. ^{13}C, DEPT and HMQC spectra of compound **13** in $CDCl_3$.

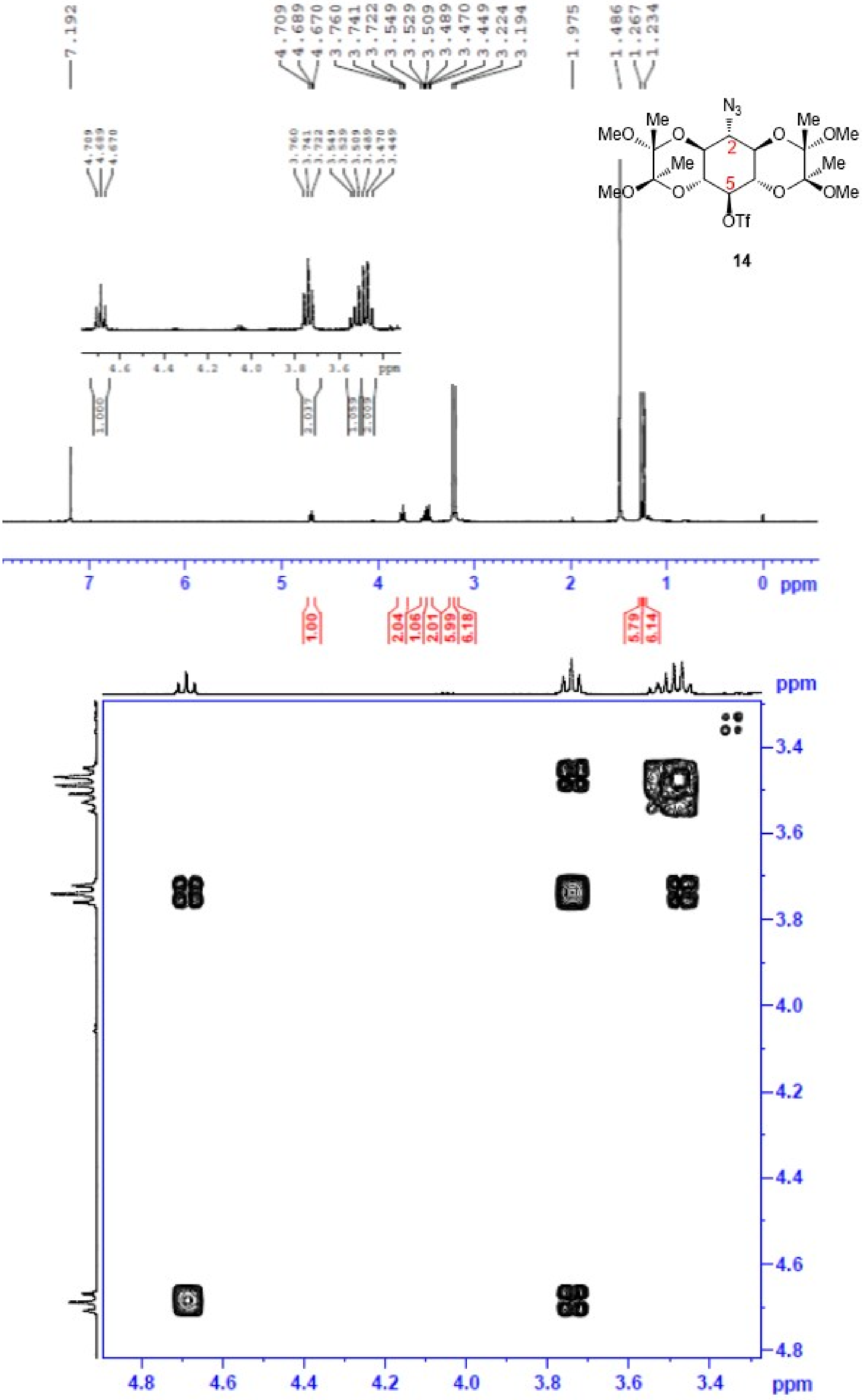


Figure S39. ^{1}H NMR and COSY spectra of compound **14** in $CDCl_3$

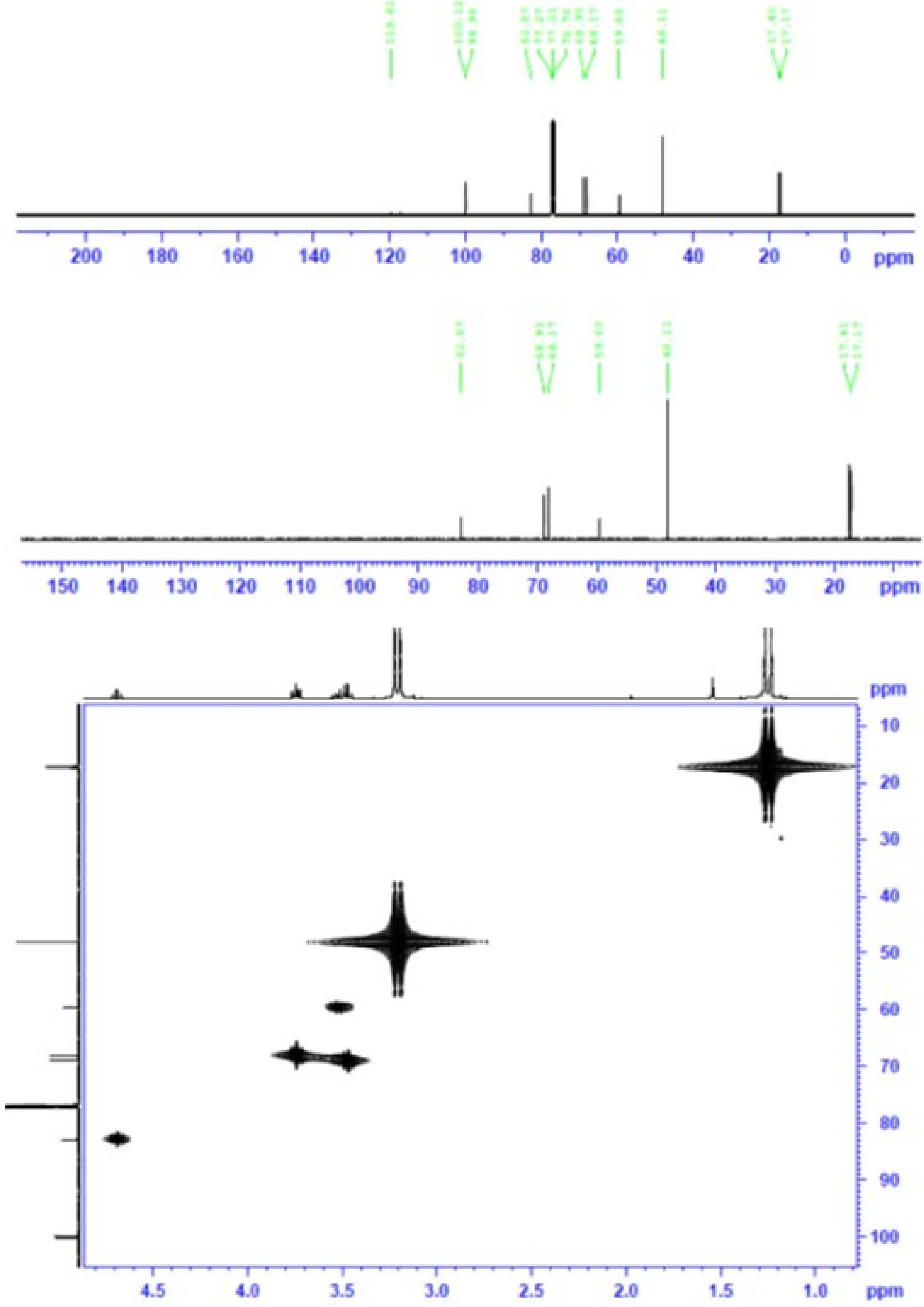


Figure S40. ^{13}C, DEPT and HMQC spectra of compound **14** in $CDCl_3$.

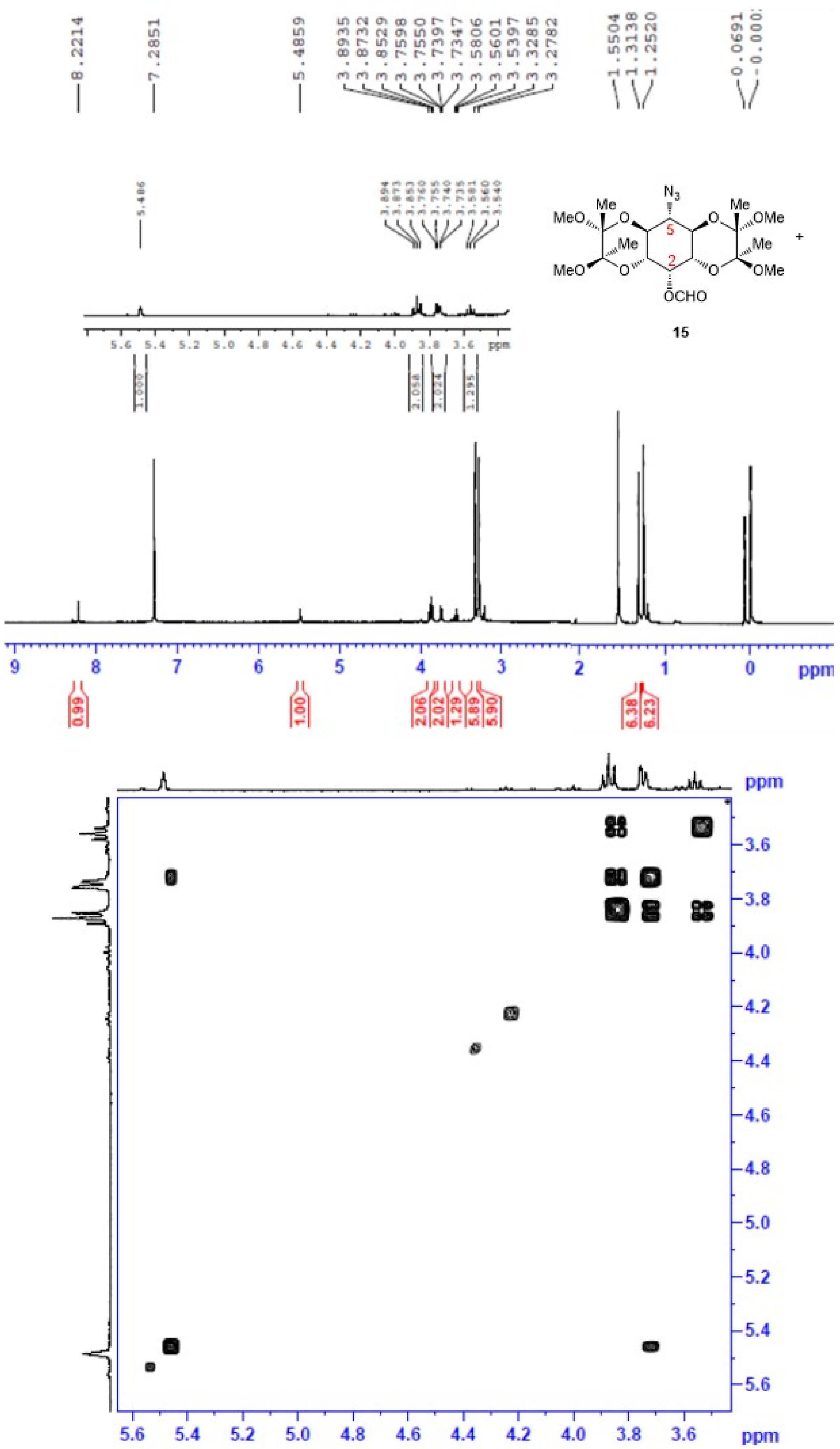


Figure S41. ^{1}H NMR and COSY spectra of compound **15** in $CDCl_3$

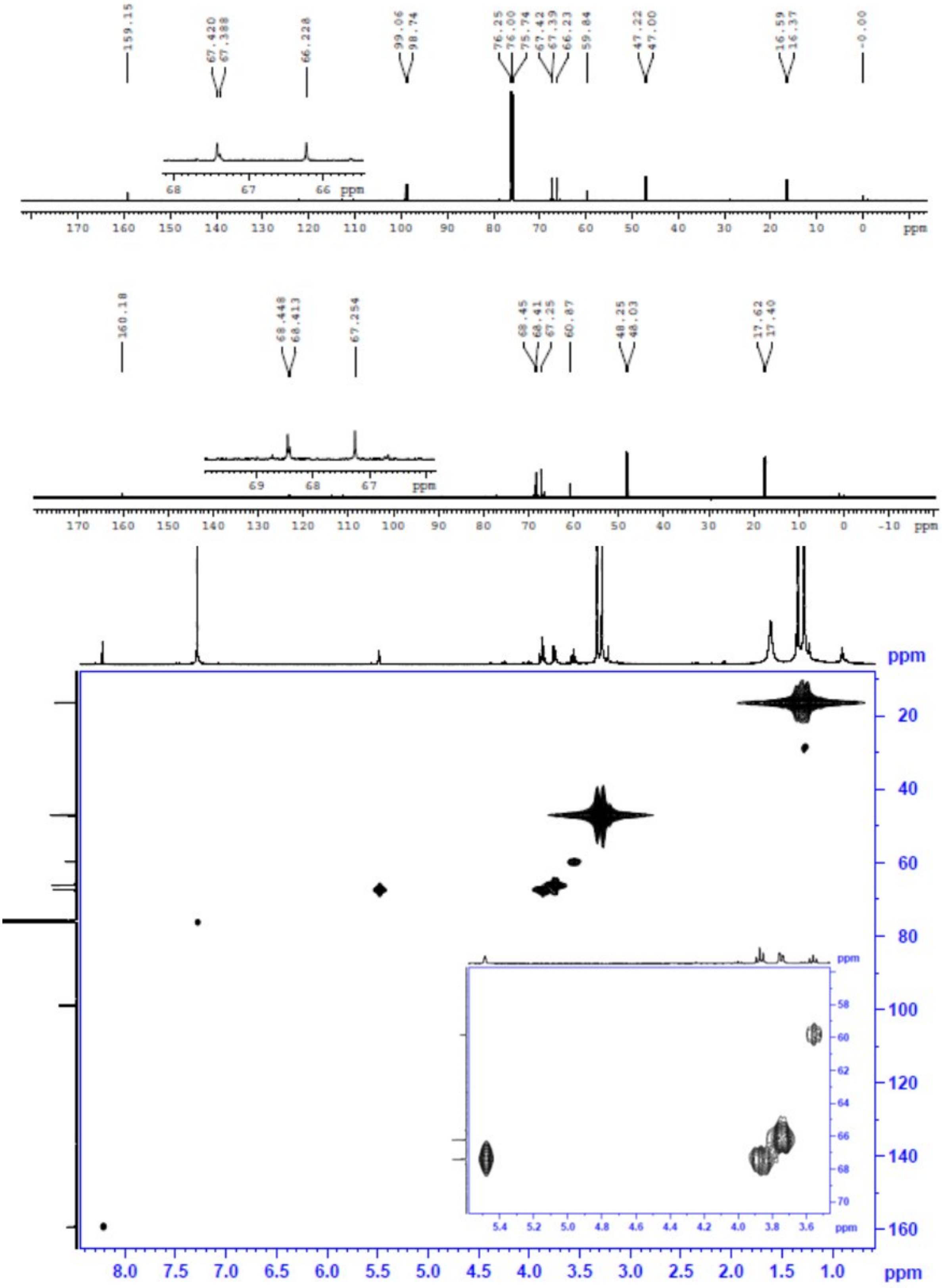
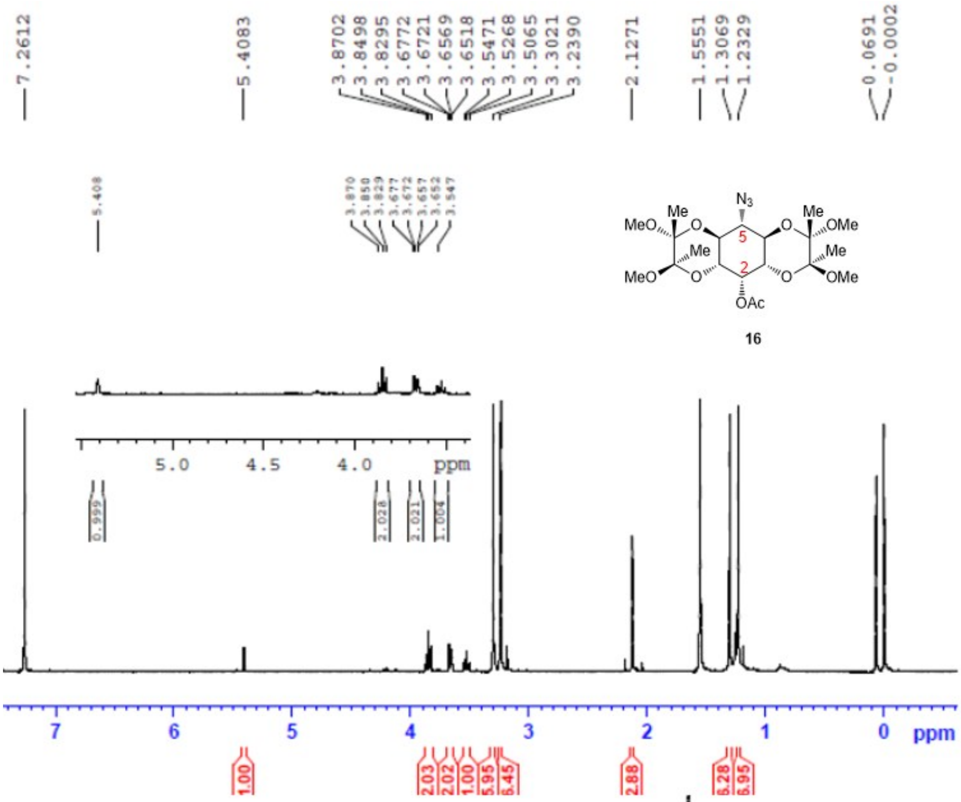


Figure S42. ^{13}C, DEPT and HMQC spectra of compound **15** in $CDCl_3$.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3.2390
2.1271
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1.3069
1.2329
0.0691
-0.0002
5.408
3.870
3.850
3.829
3.677
3.672
3.657
3.652
3.547
5.0
4.5
4.0
ppm
0.999
2.028
2.021
1.004
N3
MeO
Me
OMe
5
2
OAc
16
7
6
5
4
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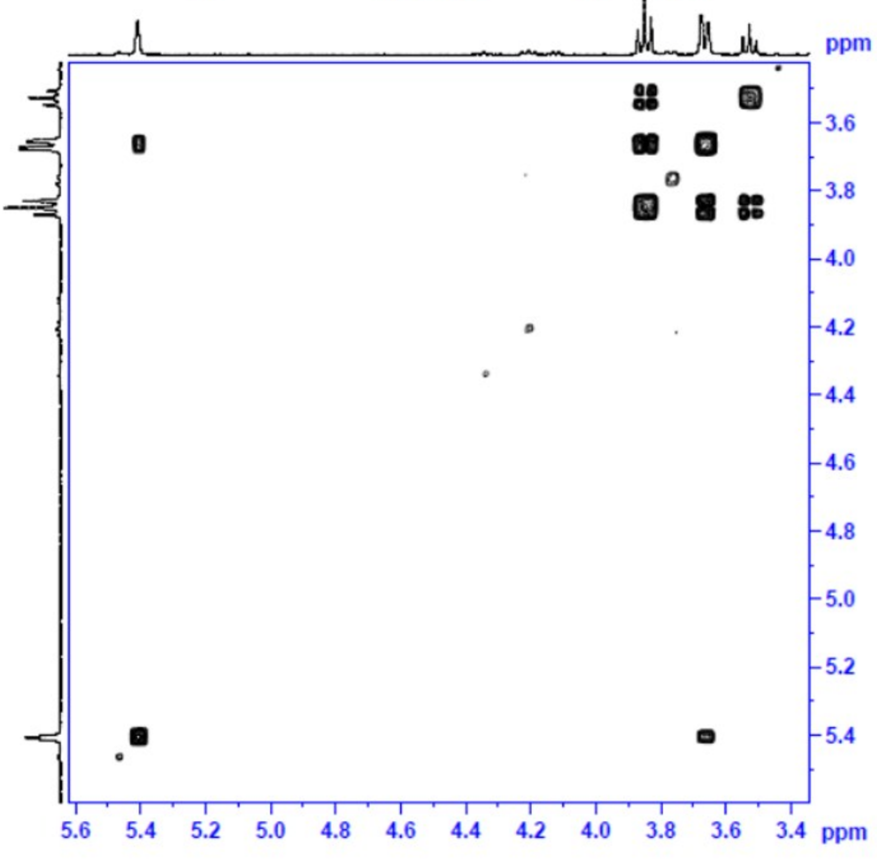
2.88
6.28
6.95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5.2
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5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm

Figure S43. ^{1}H NMR and COSY spectra of compound **16** in $CDCl_3$

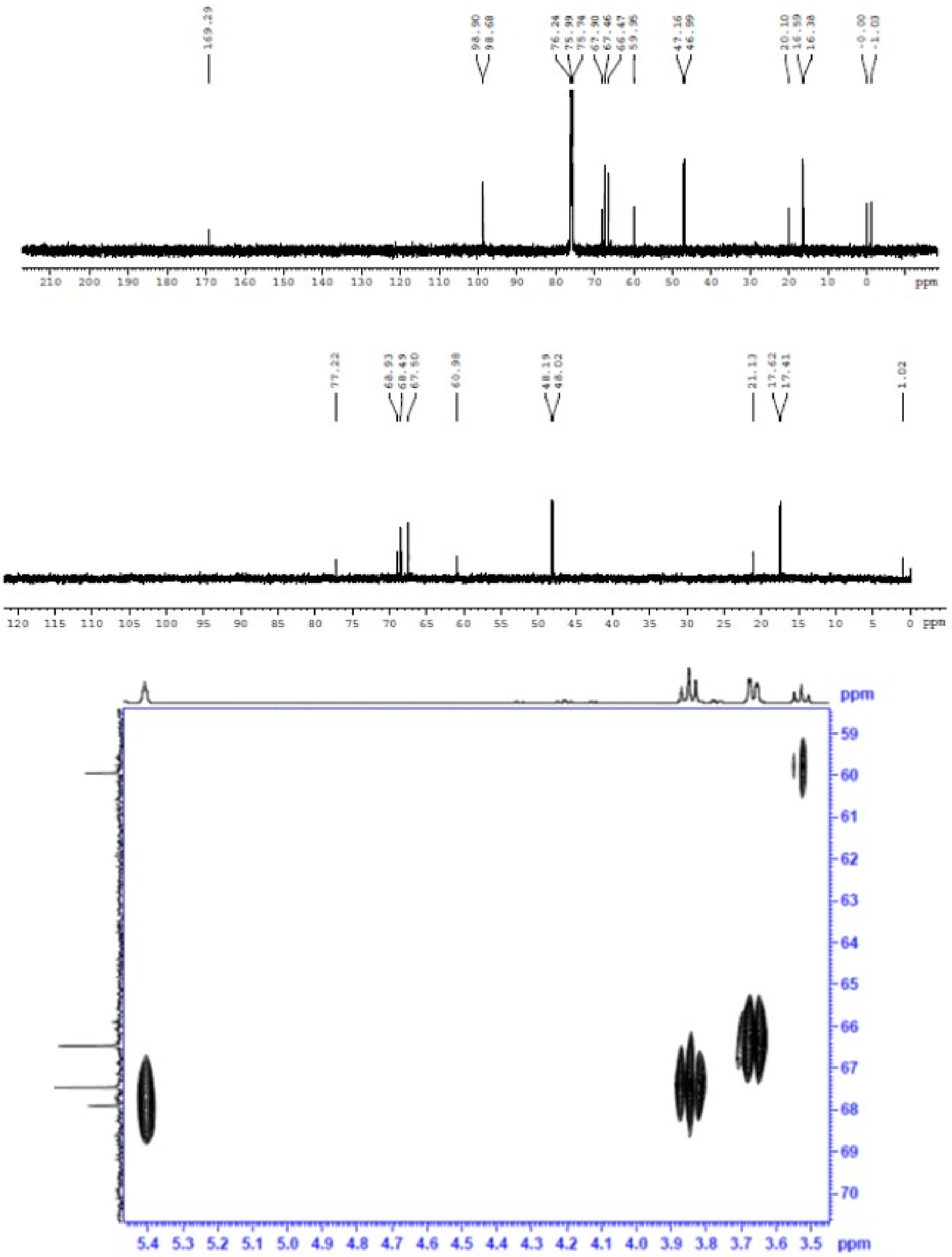

Figure S44. ^{13}C, DEPT and HMQC spectra of compound **16** in $CDCl_3$.

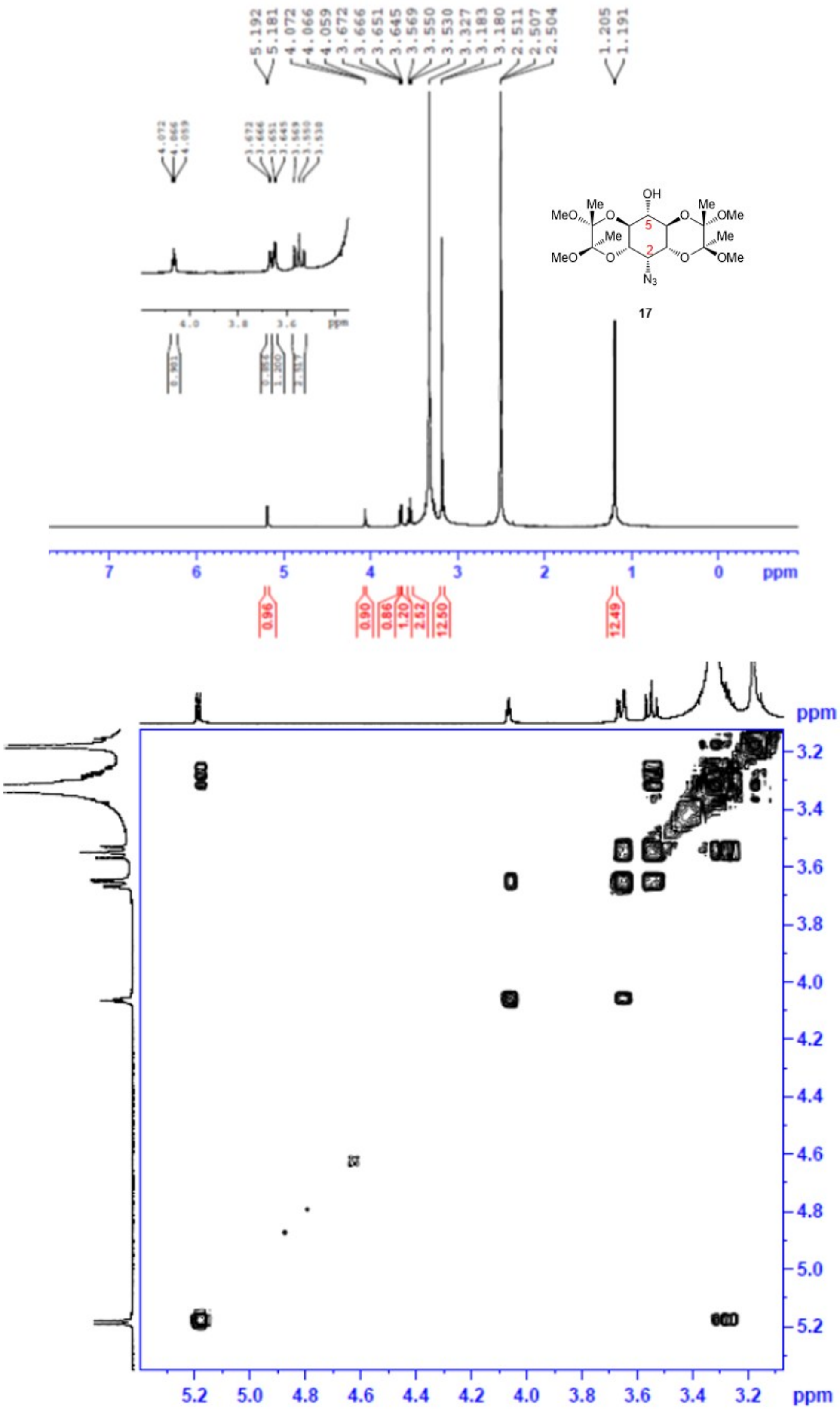

Figure S45. ^{1}H NMR and COSY spectra of compound **17** in DMSO-d_6

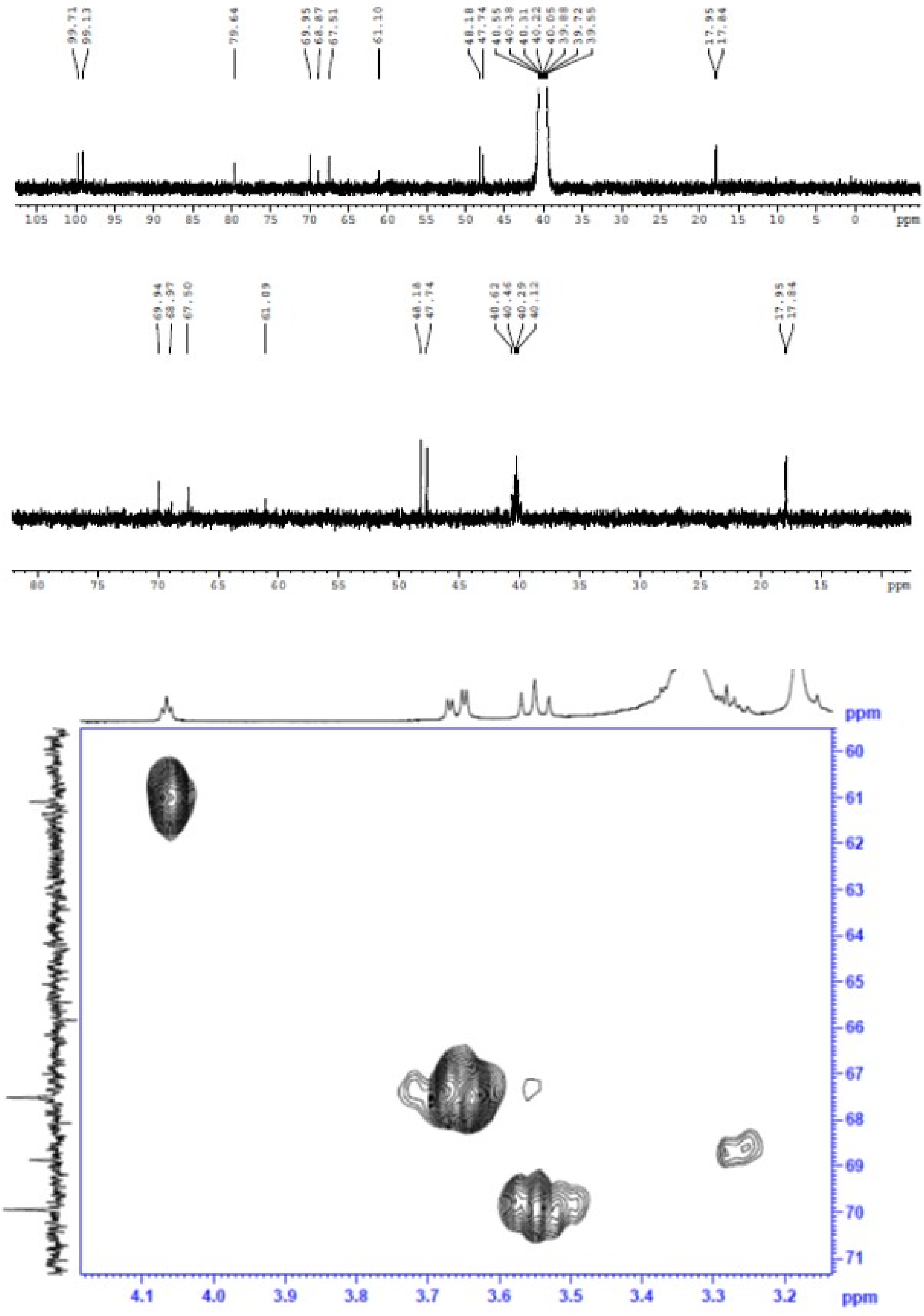

Figure S46. ^{13}C, DEPT and HMQC spectra of compound **17** in DMSO-d_6

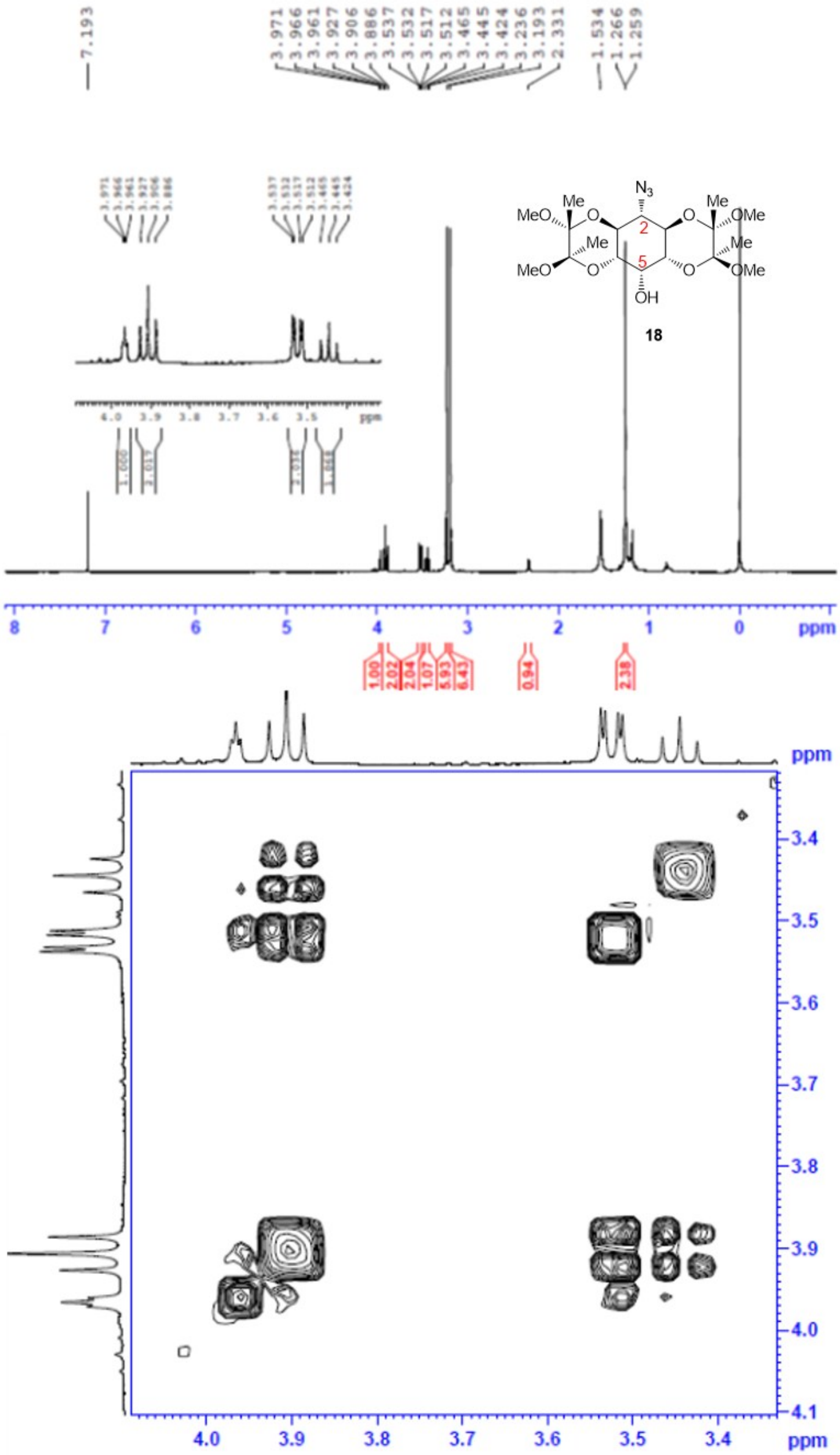

Figure S47. ^{1}H NMR and COSY spectra of compound **18** in $CDCl_3$

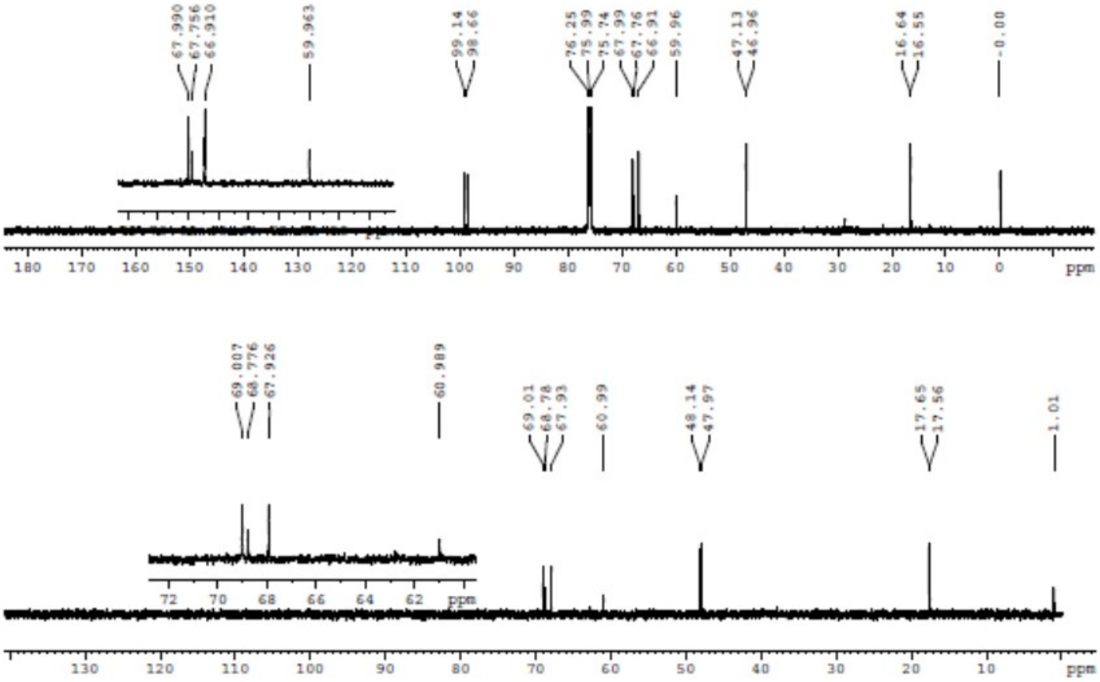

Figure S48. ^{13}C NMR and DEPT spectra of compound **18** in $CDCl_3$

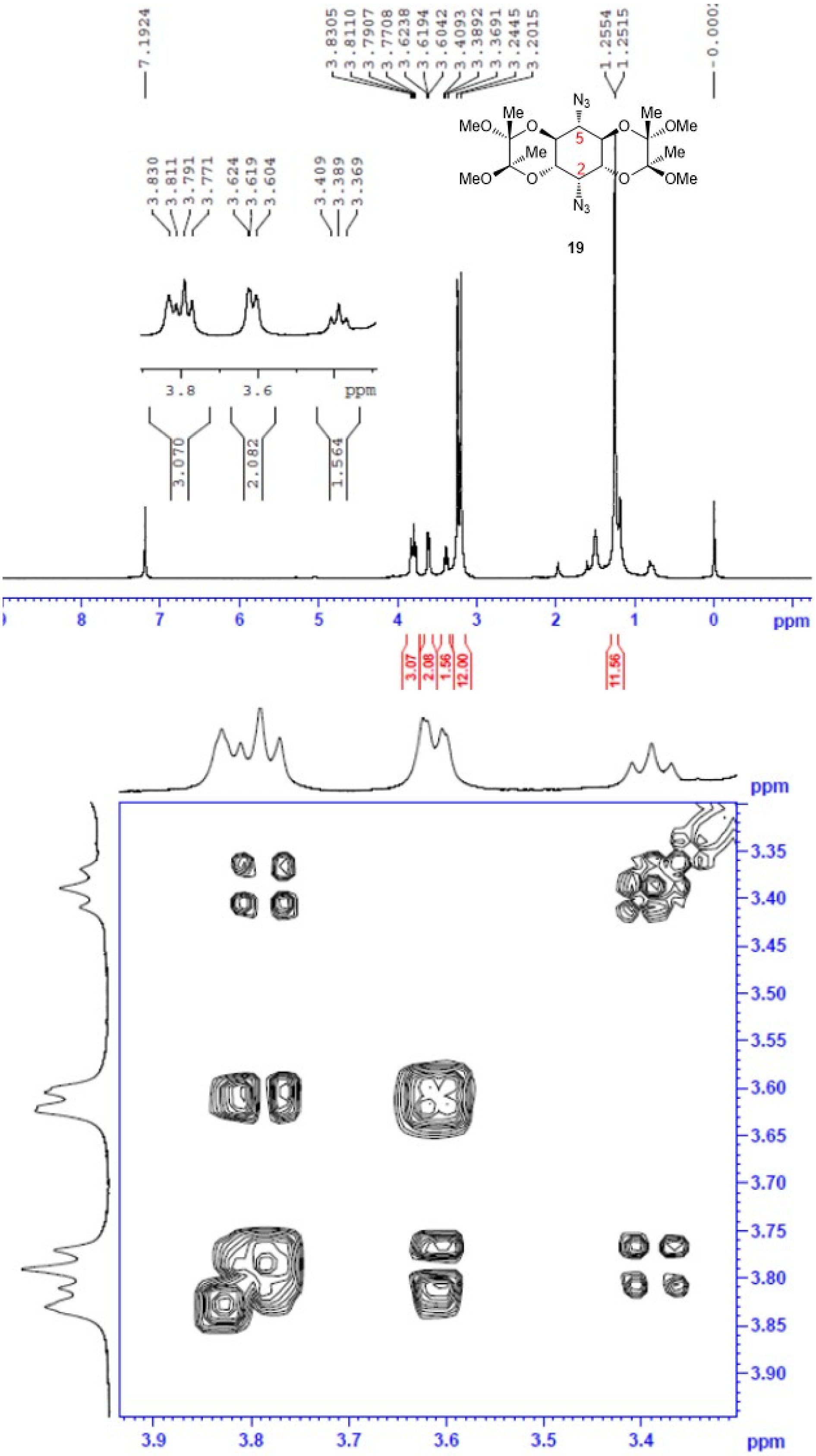

Figure S49. ^{1}H NMR and COSY spectra of compound **19** in $CDCl_3$

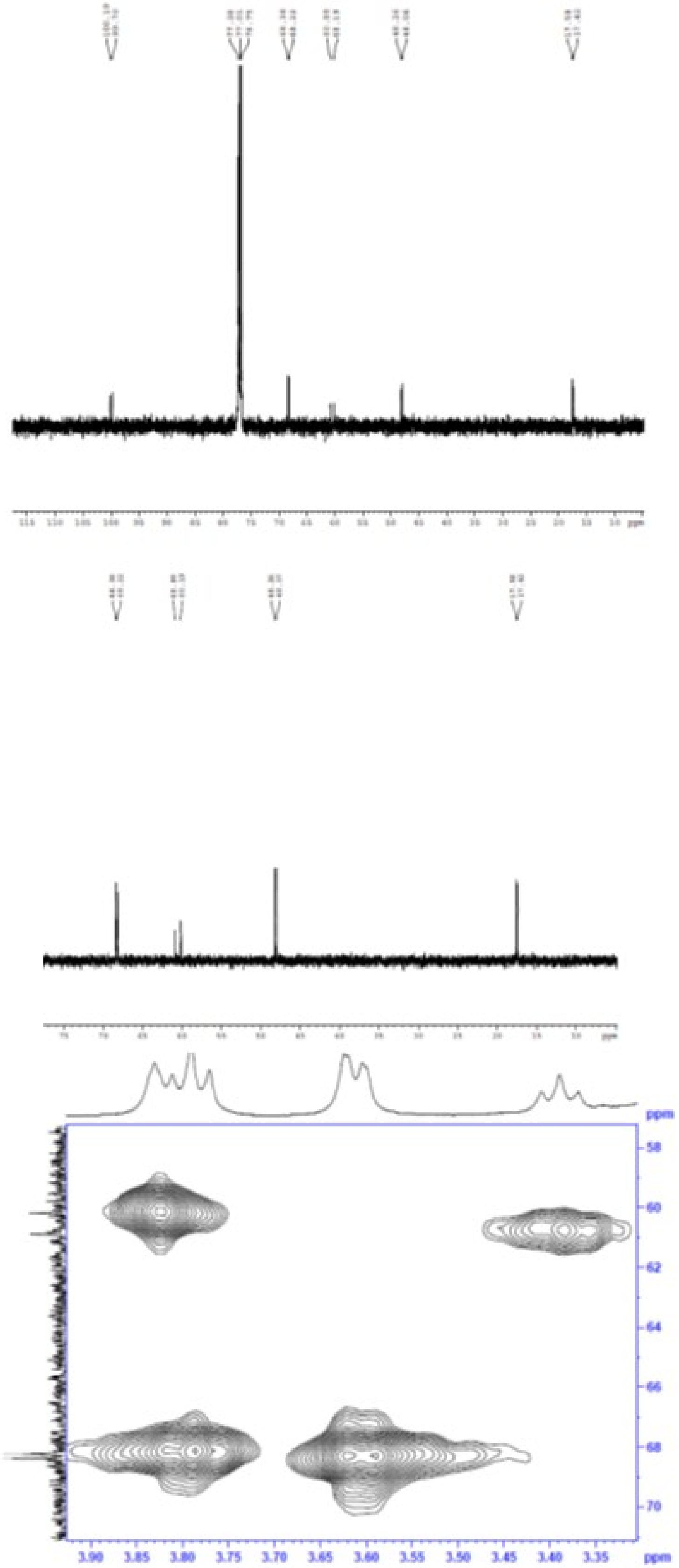

Figure S50. ^{13}C, DEPT, HMQC spectra of compound **19** in $CDCl_3$

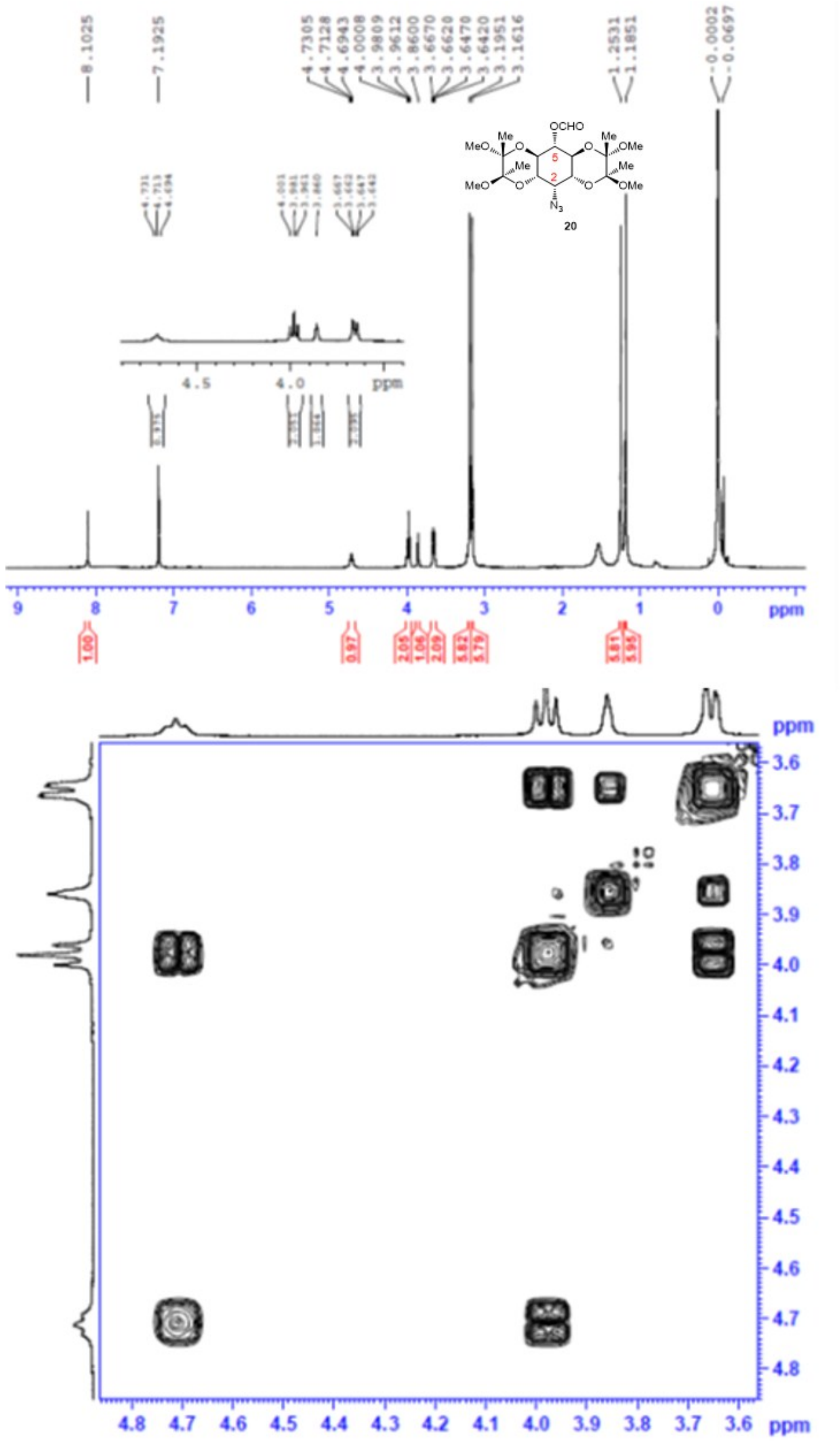

Figure S51. ^{1}H NMR and COSY spectra of compound **20** in $CDCl_3$

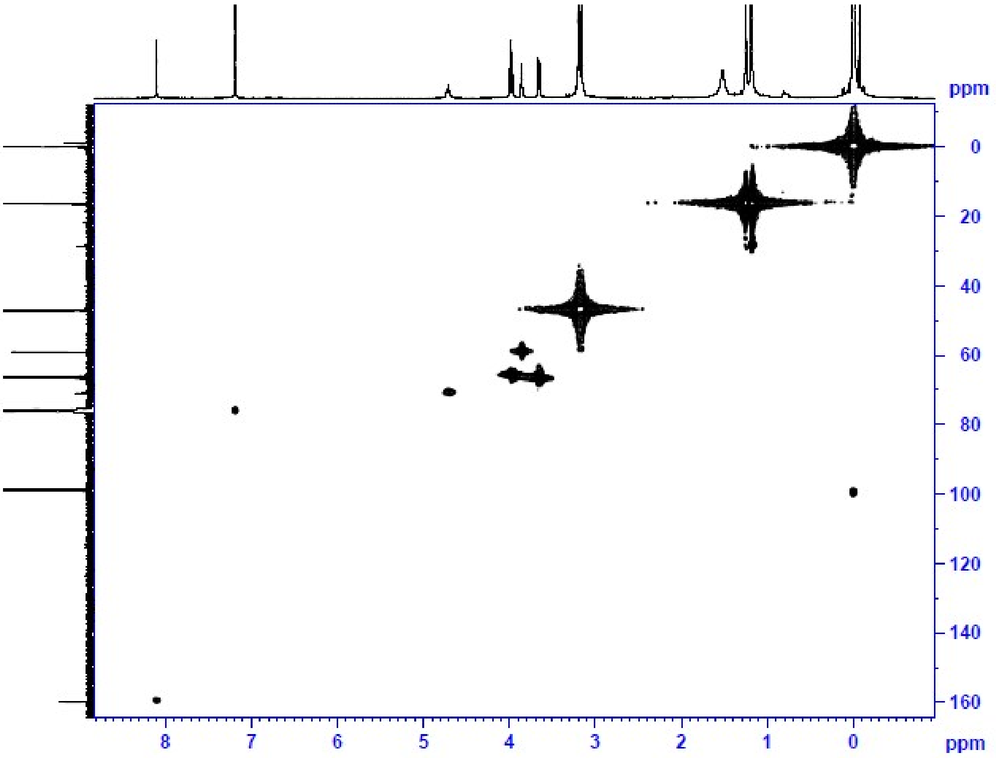

Figure S52. ^{13}C, DEPT, HMQC spectra of compound **20** in CDCl$_3$

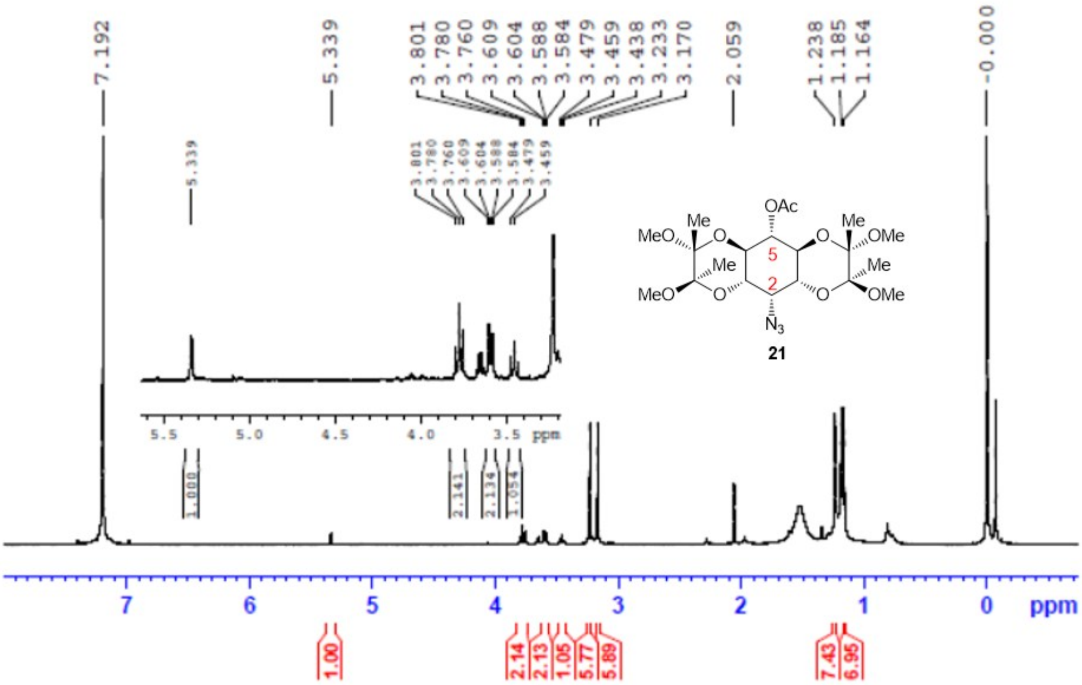

Figure S53. ^{1}H NMR spectra of compound **21** in CDCl$_3$

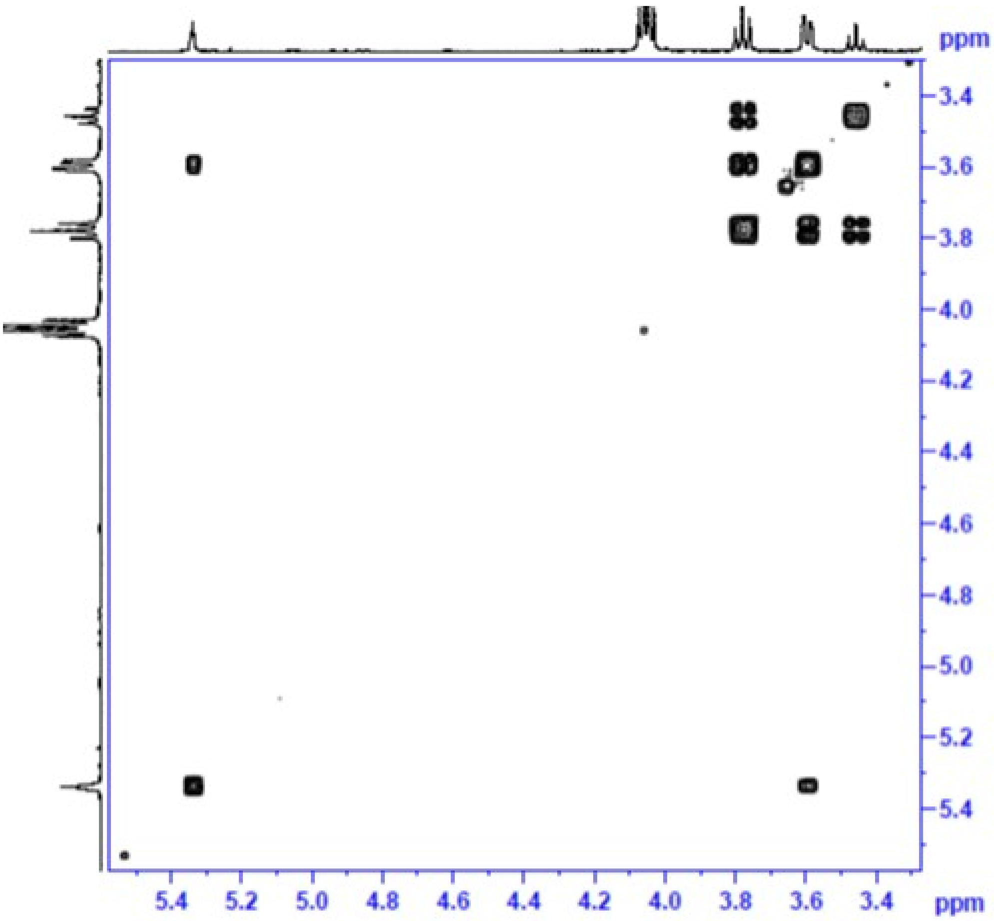

Figure S54. COSY spectra of compound **21** in $CDCl_3$

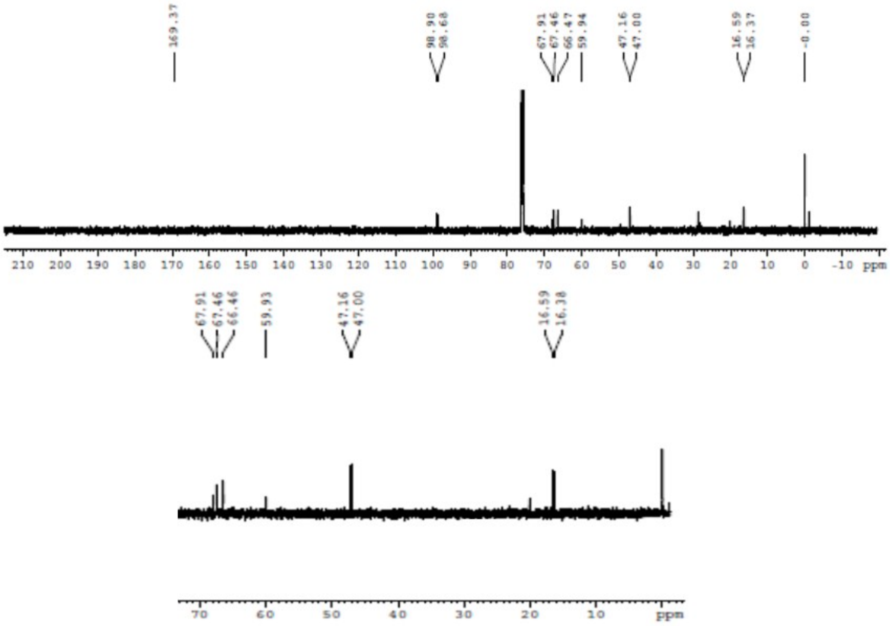

Figure S55. ^{13}C NMR spectra of compound **21** in $CDCl_3$

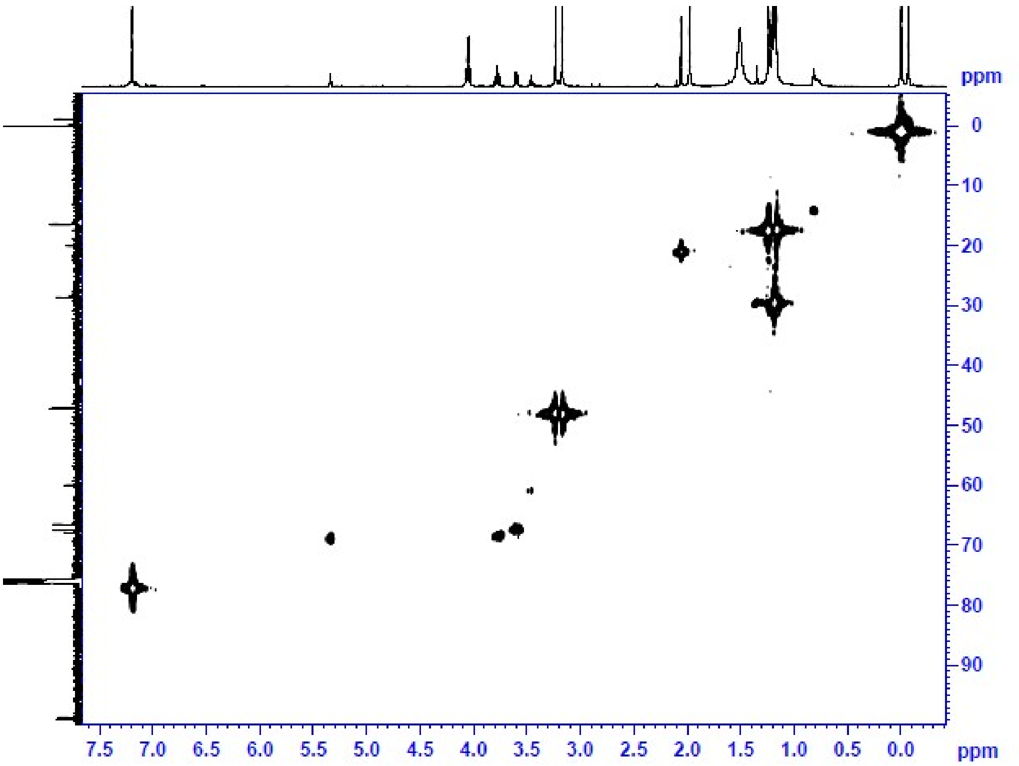

Figure S56. HMQC spectra of compound **21** in $CDCl_3$

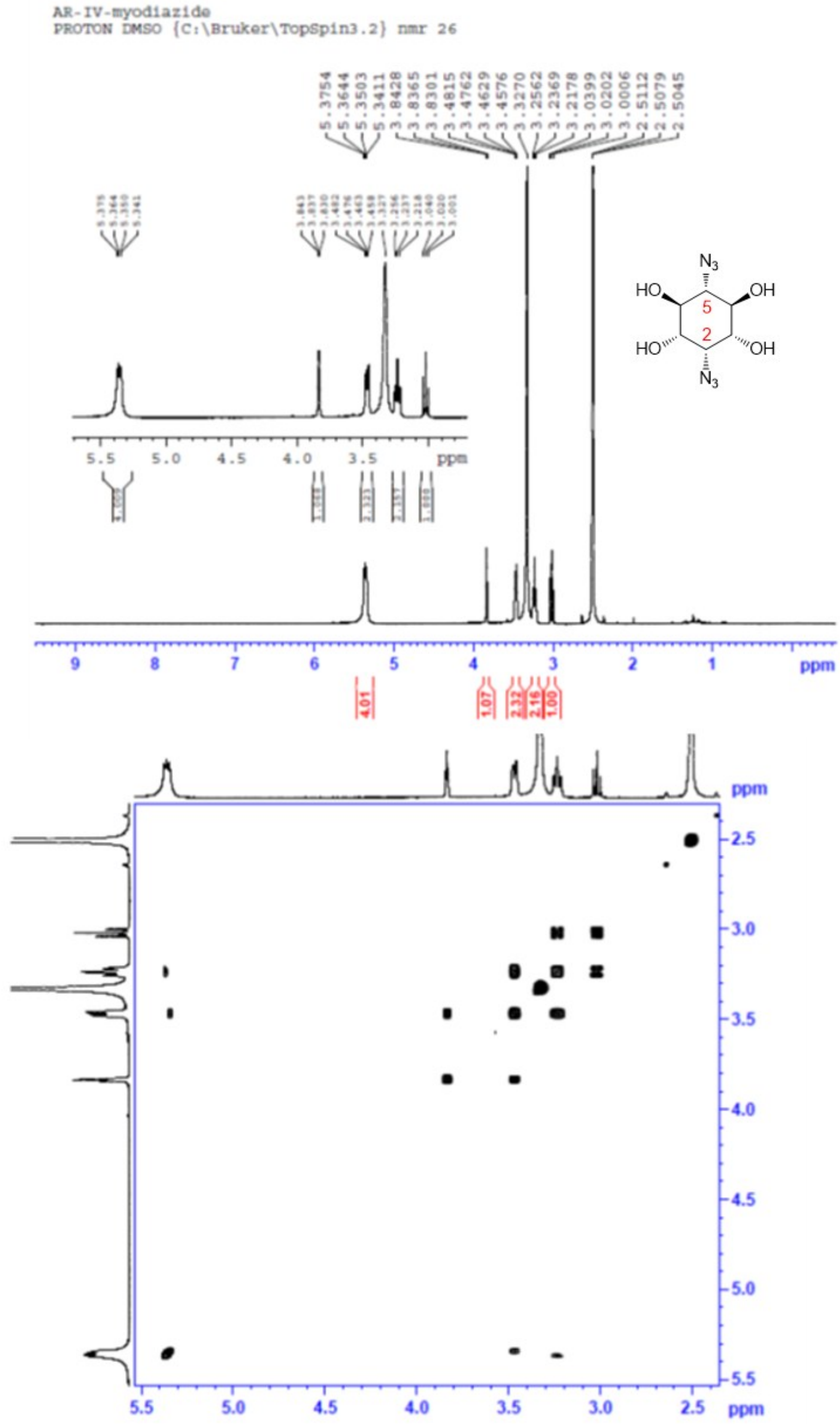

***Figure S57**.* ^{1}H NMR and COSY spectra of 2,5-diazido *myo*-inositol in DMSO-d$_6$

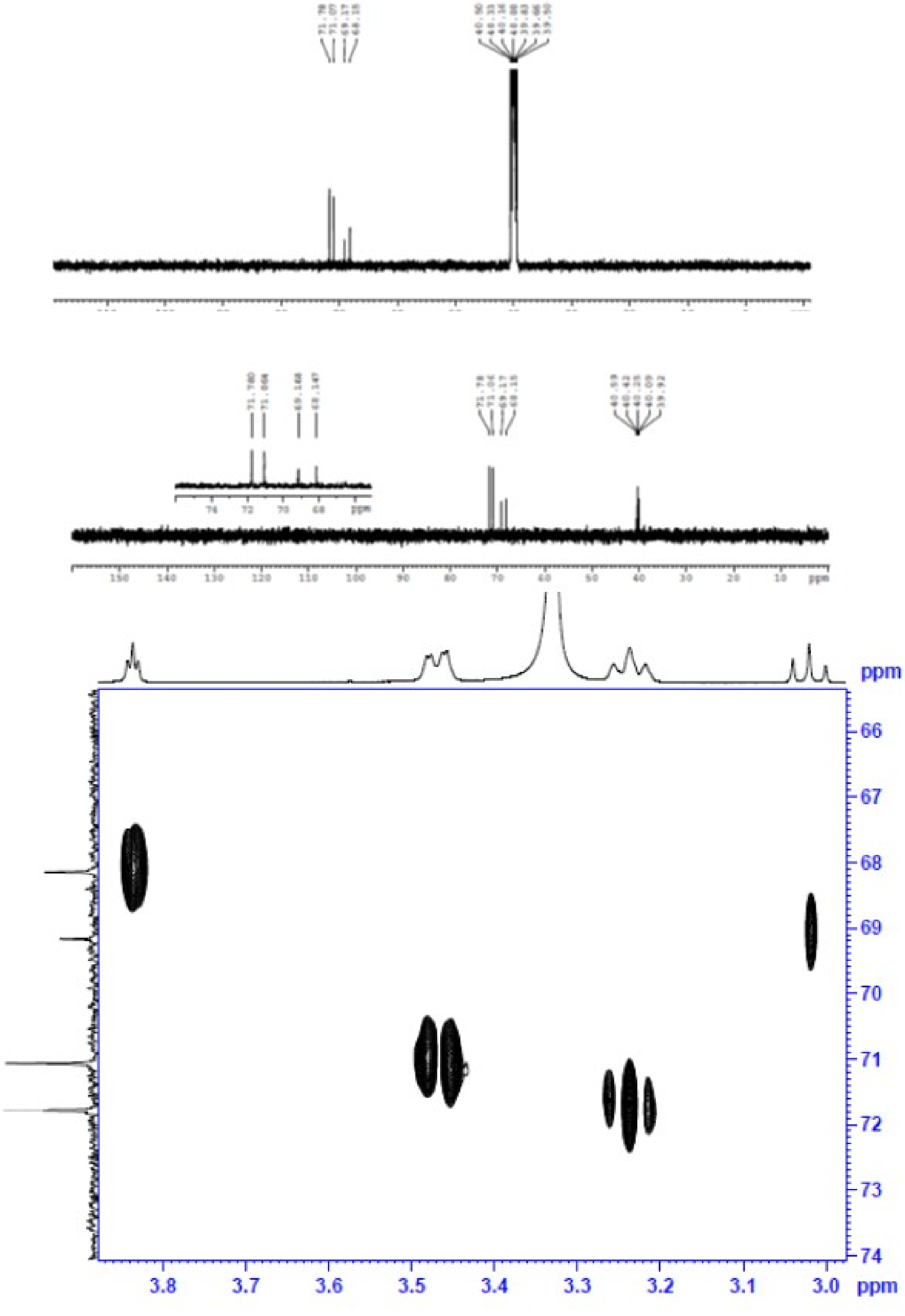

Figure S58. 13C, DEPT and HMQC spectra of 2,5-diazido *myo*-inositol in DMSO-d_6

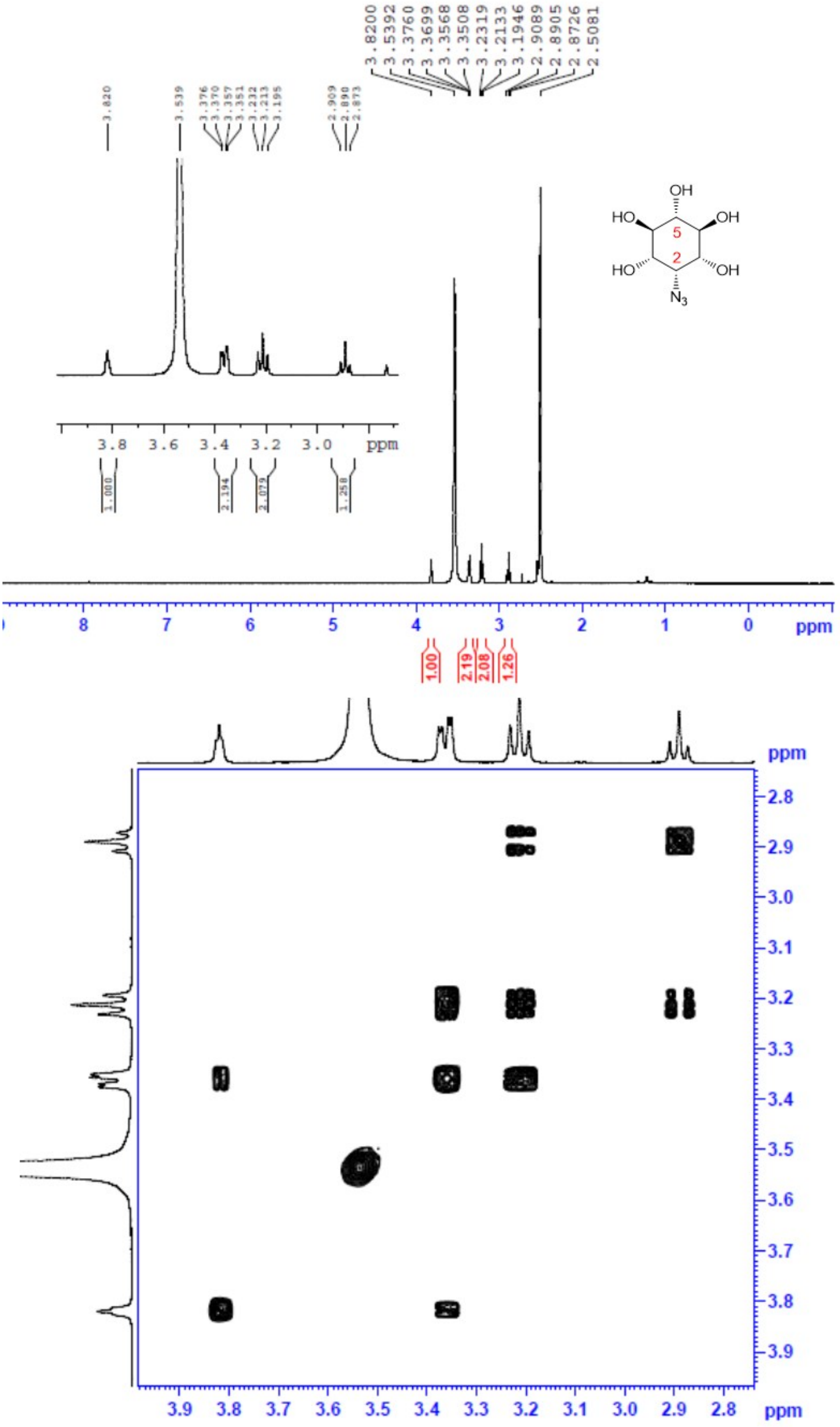

Figure S59. ^{1}H NMR and COSY of 2-azido *myo*-inositol in DMSO-d_6

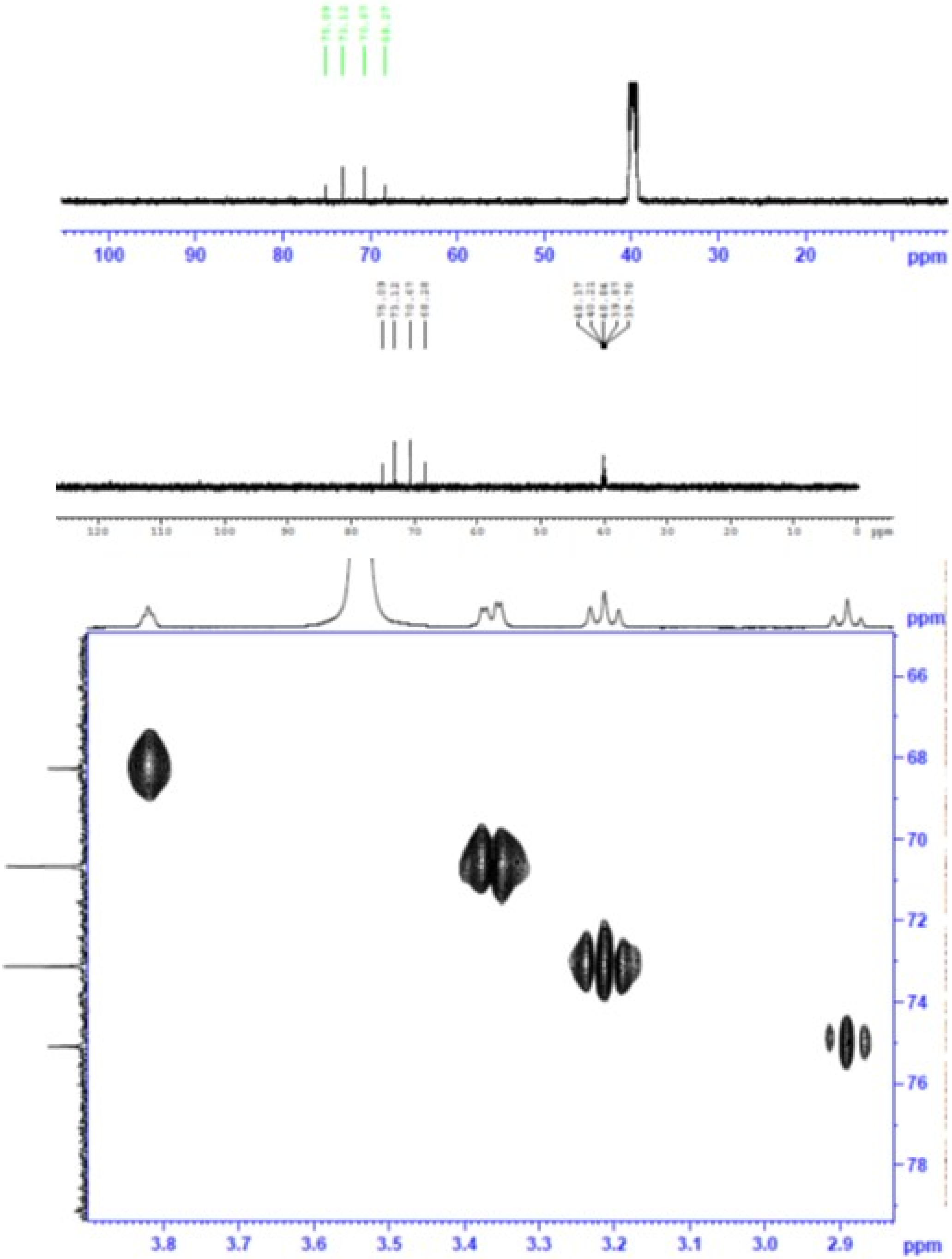

Figure S60. ^{13}C, DEPT and HMQC spectra of 2-azido *myo*-inositol in DMSO-d_6

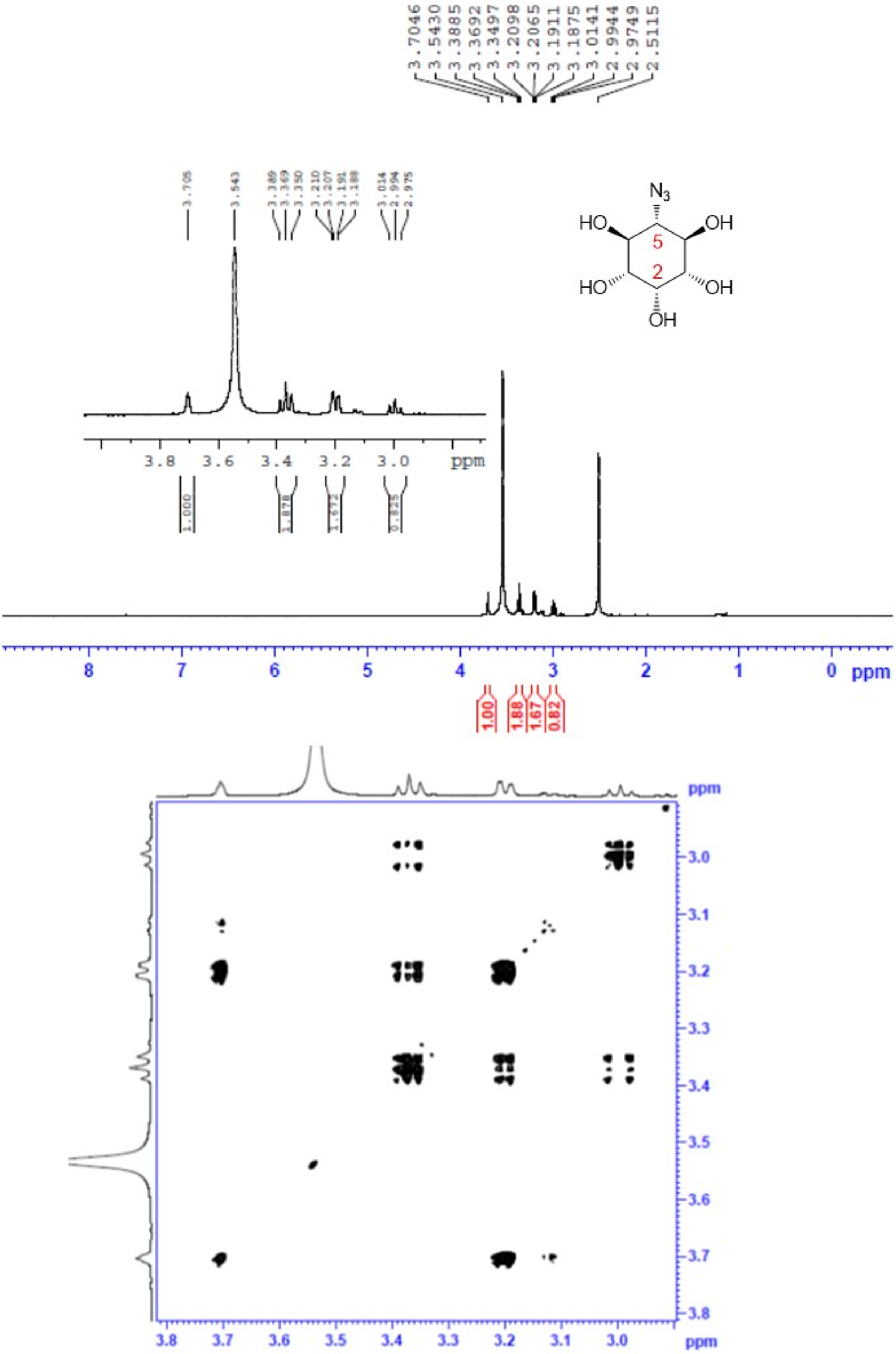

Figure S61. ^{1}H NMR and COSY of 5-azido *myo*-inositol in DMSO-d_6

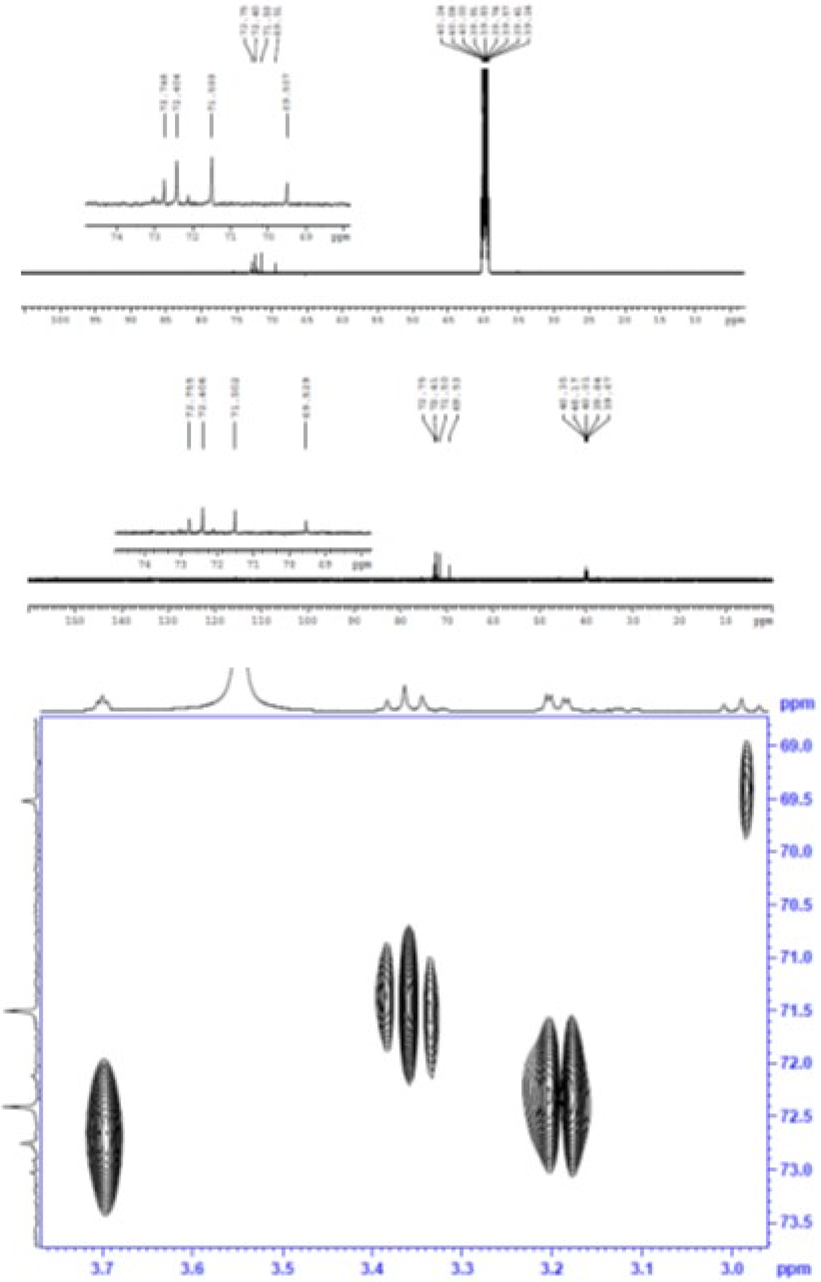

Figure S62. ^{13}C, DEPT and HMQC spectra of 5-azido *myo*-inositol in DMSO-d$_6$

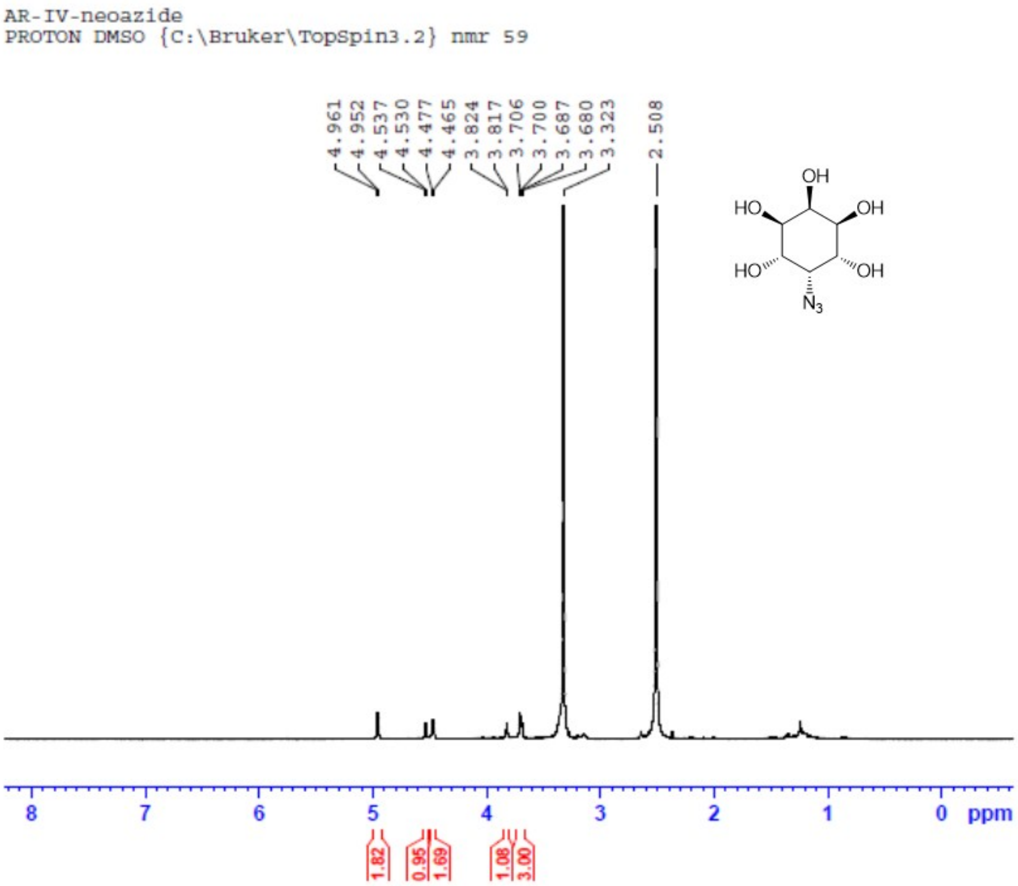

Figure S63. ^{1}H NMR spectra of 5-azido *neo*-inositol in DMSO-d$_6$

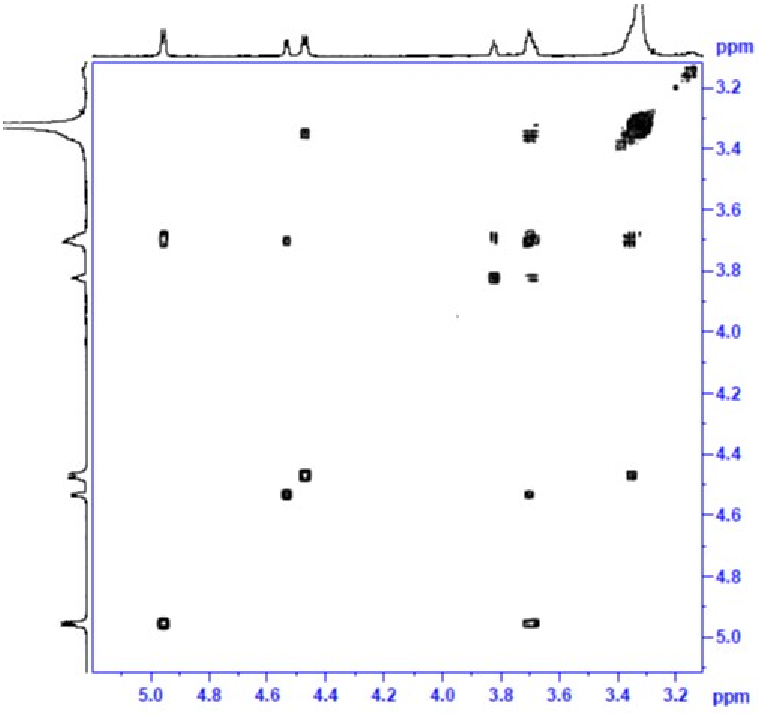

Figure S64. COSY spectra of 5-azido *neo*-inositol in DMSO-d$_6$

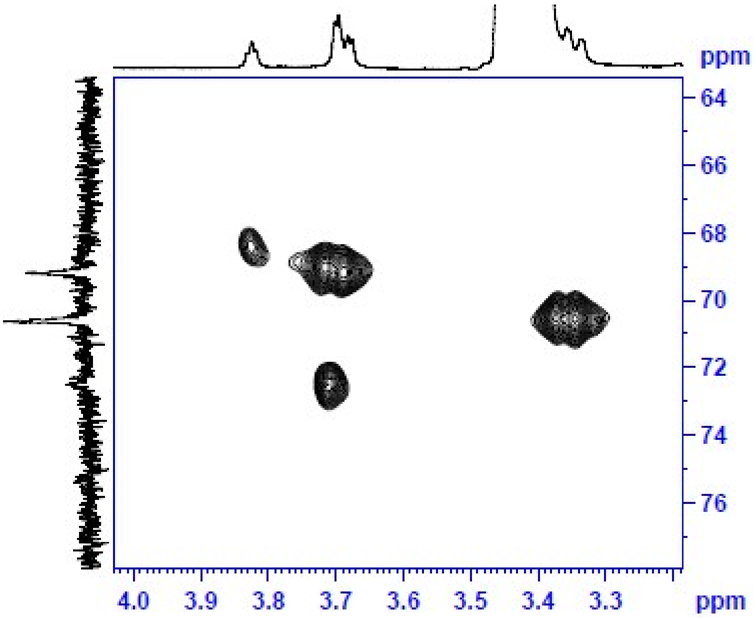

Figure S65. HMQC spectra of 5-azido *neo*-inositol in DMSO-d_6

6. Reference

1 A. M. Riley, D. J. Jenkins and B. V. L. Potter, *Carbohydr. Res.,* 1998, **314**, 277.