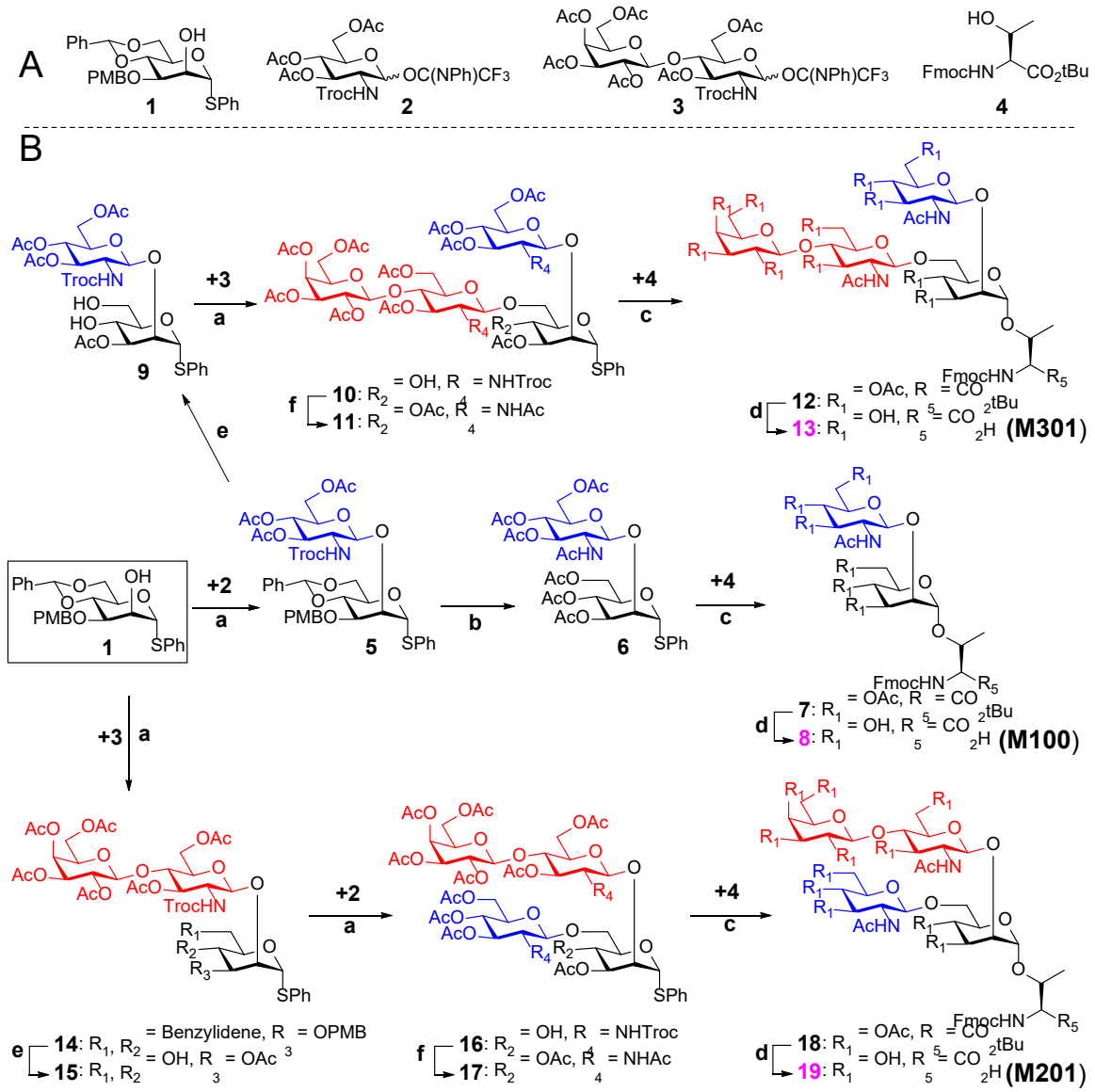


Figure 1. The building blocks (A) for the assembly of the 3 O-mannosyl scaffold structures, and the synthetic scheme (B). Reagents and conditions: (a) TMSOTf, DCM, -60 °C, **5**: 85%; **10**: 79%; **14**: 75%; **16**: 82%; (b) (i) TFA, DCM; (ii) Zn, AcOH; (iii) Ac_2O, Py, 80% over three steps; (c) NIS, AgOTf, DCM/Et_2O=1:1, 0 °C, **7**: 93%; **12**: 89%; **18**: 83%; (d) (i) TFA, DCM; (ii) NaOMe, MeOH; (iii) FmocOSu, $NaHCO_3$, Acetone/H_2O=3:1, **8**: 90%; **13**: 85%; **19**: 87%; (e) (i) DDQ, DCM/PBS Buffer=9:1; (ii) Ac_2O, Py; (iii) EtSH, TsOH, DCM, **9**: 77%; **15**: 81%; (f) (i) Zn, AcOH; (ii) Ac2O, Py, **11**: 87%; **17**: 82%.

Additional Materials:

All chemicals were purchased as reagent grade and used without further purification. Anhydrous dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), tetrahydrofuran (THF), *N,N*-dimethyl formamide (DMF), diethyl ether (Et_2O), toluene, and methanol (MeOH) were purchased from a commercial source without further distillation. Pulverized Molecular Sieves MS-4 Å (Aldrich) for glycosylation was activated by heating at 350 °C for 3 h. Reactions were monitored by analytical thin-layer chromatography (TLC) in EM silica gel 60 F254 plates and visualized under UV (254 nm) and/or by staining with acidic ceric ammonium molybdate or *p*-anisadehyde. Flash chromatography was performed on silica gel (Merck) of 40-63µm particle size and P2 gel (Biorad). ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz), and Bruker AVANCE 600 (600 MHz) spectrometer at 25 °C. All ^1H Chemical shifts (in ppm) were assigned according to $CDCl_3$ (δ= 7.24 ppm) and D_2O (δ = 4.79 ppm) and all ^{13}C NMR was calibrated with $CDCl_3$ (δ = 77.00 ppm). Coupling constants (*J*) are reported in hertz (Hz). Splitting patterns are described using the following abbreviations: s, singlet; brs, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; m, multiplet. 1H NMR spectra are reported in the following order: chemical shift, multiplicity, coupling constant(s), and number(s) of protons. All NMR signals were assigned on the basis of ^1H NMR, COSY, HSQC, HMQC, and ^{13}C NMR experiments. HPLC-MS experiments were performed on an LTQ-Orbitrap Elite mass spectrometer (Thermo Fisher) equipped with EASY-spray source and nano-LC UltiMate 3000 high-performance liquid chromatography system (Thermo Fisher). Samples were transmitted into MS with a silica column. LTQ-Orbitrap Elite mass spectrometer was operated in the data-dependent mode. A full-scan survey MS experiment (m/z range was set according to the molecular weight of O-mannose glycan; automatic gain control target, 1,000,000 ions; resolution at 400 m/z, 240,000; maximum ion accumulation time, 200 ms) was acquired by the Orbitrap mass spectrometer. MALDI-TOF MS analyses were performed on UltrafleXtreme MALDI TOF/TOF Mass Spectrometer (Bruker). Scan range of MS was set according to the molecular weight of O-mannose glycans, and reflector mode was used for O-mannose glycan analysis. Mass spectra were obtained in both positive and negative extraction mode with the following voltage settings: ion source 1 (19.0 kV), ion source 2 (15.9 kV), and lens (9.3 kV). The reflector voltage was set to 20 kV. The laser was pulsed at 7 Hz and the pulsed ion extraction time was set at 400 ns. The laser power was kept in the range of 40–90%.

General Procedures in the Synthesis

A) Glycosylation using *N*-phenyltrifluoroacetimidate donor

a) A mixture of glycosyl donor (1.2 mmol), glycosyl acceptor (1 mmol) and 4 Å molecular sieves (equivalent to the weight of glycosyl donor) in 5 mL of anhydrous CH_2Cl_2 was stirred at room temperature under argon atmosphere for 1 h.

b) The reaction mixture from step a was cooled to -60 °C using dry ice and ethyl acetate.

! CAUTION Proper clothing and gloves are must to get protected from cold burns.

c) TMSOTf (0.2 mmol) was slowly added to the reaction mixture from step b at -60 °C and stirred for 1 h.

d) The reaction mixture from step c was quenched with triethylamine (0.2 mmol).

Δ Critical Step The reaction should be quenched only after checking for the completion of the reaction by TLC.

e) The reaction mixture from step d was filtered and concentrated *in vacuo.* The crude was purified by flash column chromatography over 60 Å silica gel using hexanes and ethyl acetate.

B) Glycosylation using a thio donor

a) A mixture of thioether donor (1 mmol), amino acid acceptor **4** (1.5-2 mmol) and 4 Å molecular sieves (equivalent to the weight of glycosyl donor) in 10 mL of anhydrous Et_2O/CH_2Cl_2 (1:1, v/v) were stirred at room temperature under argon atmosphere for 1 h.

b) The reaction mixture from step a was cooled to 0 °C. NIS (1.5 mmol) and AgOTf (0.2 mmol) were added to the reaction mixture at the same temperature. The reaction mixture was stirred for 10 h before it was quenched with triethylamine (0.2 mmol).

Δ Critical Step The reaction should be quenched only after checking for the completion of the reaction by TLC.

c) The reaction mixture from step b was filtered. The filtrate was diluted with 50 mL of CH_2Cl_2 and washed with 5% aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude was purified by flash column chromatography over 60 Å silica gel using hexanes and ethyl acetate.

C) Global deprotection of Ac and ^{t}Bu and reintroduction of Fmoc

a) Glycosyl amino acid derivative (1 mmol) was dissolved in 5 mL of TFA/CH_2Cl_2 (1:1, v/v) and stirred at room temperature under argon atmosphere for 4 h.

! CAUTION TFA is a highly corrosive liquid.

b) The mixture from step a was concentrated *in vacuo* and the crude residue was dissolved in MeOH. NaOMe in MeOH was added to the solution until pH reaches 10. After stirring at room temperature for 2 h, the solution was neutralized with ion-exchange resin (H+), then filtered and concentrated *in vacuo*.

c) To the crude product from step b, $NaHCO_3$ (4 mmol) and 9-fluorenylmethyl-Nsuccimidylcarbonate (3 mmol) were dissolved in 10 mL of H_2O/acetone (1:1, v/v) and this mixture was stirred at room temperature. After 2 h, the mixture was concentrated *in vacuo* and the crude was purified by flash column chromatography over 60 Å silica gel using hexanes and ethyl acetate.

D) Transformation of PMB to Ac and cleavage of benzylidene

a) A solution of oligosaccharide (1 mmol) was dissolved in a 10 mL mixture of CH_2Cl_2/H_2O (30:1, v/v).

b) The reaction mixture from step a was cooled to 0 °C and DDQ (1.2 mmol) was added and stirred at room temperature for 3 h.

c) To the reaction mixture from step b, triethyl amine (0.2 mmol) was added and the solvent was removed *in vacuo*.

d) The crude from step c was dissolved in 10 mL of CH_2Cl_2 and cooled to 0 °C. Acetic anhydride (3 mmol) and triethyl amine (5 mmol) were added and stirred at room temperature for 12 h and concentrated *in vacuo.*

e) The crude product from step d was dissolved in 10 mL of anhydrous MeOH. TsOH (0.1 mmol) and EtSH (6 mmol) were added and stirred at room temperature for 6 h. The reaction

mixture was quenched with triethyl amine (0.1 mmol) and concentrated *in vacuo.* The crude was purified by flash column chromatography over 60 Å silica gel using hexanes and ethyl acetate.

E) Transformation of NHTroc to NHAc

a) N-Troc protected oligosaccharide (1 mmol) was dissolved in 5 mL of AcOH at room temperature, followed by addition of Zn dust (<10 micron, 10 mmol) and stirred at room temperature at 40 °C for 24 h.

Δ Critical Step 10 g of Zn dust was washed with 50 ml of 1 M HCl and successively with 50 mL of H_20, acetone and diethyl ether before using it for the reaction.

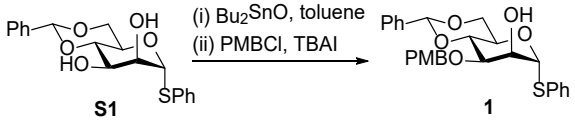
b) The reaction mixture from step a was concentrated *in vacuo* to obtain crude amine.

c) The reaction mixture from step b was dissolved in 5 mL of pyridine and 4 mL of acetic anhydride was slowly added at 0 °C. The reaction was slowly allowed to room temperature and stirred for 12 h.

d) The solvent was evaporated from the reaction mixture from step c and dissolved in 50 mL of ethyl acetate. The organic layer was and washed with aqueous HCl (1 M), saturated aqueous $NaHCO_3$, and brine solution. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo.* The crude was purified by flash column chromatography over 60 Å silica gel using hexanes and ethyl acetate.

Procedures:

Synthesis of Compound 1:



1) In a 500 mL round bottom flask, 13.40 g (37.2 mmol) of compound **S1**[1] was dissolved in 250 mL of anhydrous toluene and 10.23 g (40.9 mmol) of dibutyltin oxide was added under nitrogen atmosphere.

2) The reaction mixture from step 1 was refluxed for 3 h and concentrated *in vacuo.*

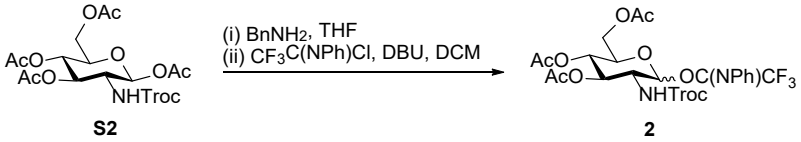
Δ Critical Step The reaction must be checked for the complete formation of the acetal before removing the solvent.

3) The crude from step 2 was dissolved in 250 mL of anhydrous toluene. 15.09 g (40.9 mmol) of tetrabutylammonium iodide and 6.39 mL (40.9 mmol) of 4-Methoxybenzyl chloride were added successively and stirred at 70 °C for 12 h.

4) The solvent in the step 3 was evaporated and dissolved in 300 mL of ethyl acetate. The organic layer was washed with 200 mL of saturated aq. $NaHCO_3$ and water. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*.

5) The crude from step 4 was purified by flash column chromatography over 60 Å silica gel using hexanes and ethyl acetate (4:1, v/v) to obtain 16.26 g (91%) of compound **1** as a white foam.

Synthesis of Compound 2:



S2 **2**

6) In a 250 mL round bottom flask, 5.70 g (10.9 mmol) of compound **S2** was dissolved in 100 mL of anhydrous THF and 2.10 mL (19.6 mmol) of benzylamine was added at room temperature under nitrogen atmosphere.

7) The reaction mixture from step 6 was stirred at room temperature for 8 h and the solvent was evaporated to dryness and dissolved in 300 mL of ethyl acetate.

Δ Critical Step The reaction must be checked for the completion and prolonged stirring results in the deprotection of other acetyl groups.

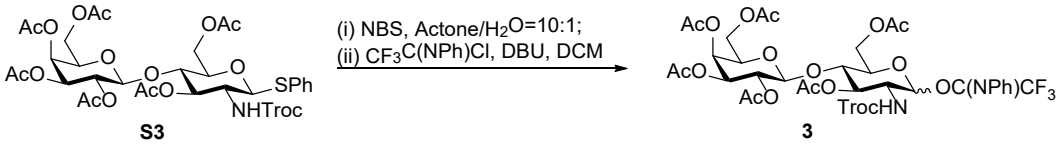
8) The organic layer from step 7 was washed with 150 mL of saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtrated, concentrated and dried under high vacuum for 2 h.

9) The crude from step 8 was dissolved in 200 mL of anhydrous CH_2Cl_2. 3.42 mL (21.8 mmol) of 2,2,2-Trifluoro-N-phenylacetimidoyl Chloride and 2.44 mL (16.4 mmol) of 1,8-diazabicyclo-[5,4,0]-7-undecene were added successively at 0 °C under nitrogen atmosphere.

10) The reaction mixture from step 9 was allowed to stir at room temperature for 2 h and concentrated to dryness below 30 °C. The crude residue was purified by flash column chromatography over 60 Å silica gel using hexanes and ethyl acetate (4:1, v/v) to obtain 5.5 g (77%) of compound **2** as a white foam.

! CAUTION Compound **2** is unstable and must be consumed immediately. The compound can be stored at -20 °C for a couple of days.

Synthesis of Compound 3:



S3 **3**

11) In a 250 mL round bottom flask, 5.10 g (5.9 mmol) of **S3**[2] was dissolved in 60 mL of acetone/H_2O (10:1, v/v) mixture.

12) The solution from step 11 was cooled to -30 °C and 5.25 g (29.5 mmol) of N-Bromosuccinimide was added and stirred at the same temperature for 2 h.

13) The reaction mixture from step 12 was quenched with 10 mL of 5% aqueous $Na_2S_2O_3$ and 10 mL of aqueous $NaHCO_3$. The mixture was diluted with 300 mL of ethyl acetate and washed with 200 mL of 5% aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$ and brine. The organic layer was dried over anhydrous sodium sulphate, filtered and concentrated.

14) The crude residue from step 13 was dissolved in 100 mL of anhydrous CH_2Cl_2. 1.85 mL (11.8 mmol) of 2,2,2-Trifluoro-N-phenylacetimidoyl Chloride and 1.32 mL (8.9 mmol) of 1,8-diazabicyclo-[5,4,0]-7-undecene were added successively at 0 °C under nitrogen atmosphere.

15) The reaction mixture from step 14 was allowed to stir at room temperature for 2 h and concentrated to dryness below 30 °C. The crude residue was purified by flash column chromatography over 60 Å silica gel using hexanes and acetone (4:1, v/v) to obtain 4.29 g (75%) of compound **3** as a white foam.

! CAUTION Compound **3** is unstable and must be consumed immediately. The compound can be stored at -20 °C for a couple of days.

Synthesis of Compound 5:

16) In a 250 mL round bottom flask, 3.37 g (7.0 mmol) of compound **1** was glycosylated with the freshly prepared 5.50 g (8.43 mmol) of compound **2** using the general procedure **A** to obtain 5.63 g (85%) of compound **5** as a white foam.

Synthesis of Compound 6:

17) In a 100 mL round bottom flask, 2.83 g (3.0 mmol) of compound **5** was dissolved in 50 mL of TFA/ CH_2Cl_2 (10:1, v/v) mixture and stirred at room temperature for 1 h under argon atmosphere.

18) The reaction mixture from step 17 was diluted with 100 mL of CH_2Cl_2 and neutralized by slow addition of saturated aqueous $NaHCO_3$.

! CAUTION The reaction has to be cooled if heat generation is observed.

19) The organic layer was separated and washed with 50 mL of brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated.

20) The crude residue from step 19 was used in obtaining 1.74 g (80%) of compound **6** as a white foam by following the general procedure **E**.

Synthesis of Compound 7:

21) In a 100 mL round bottom flask, 1.74 g (2.4 mmol) of compound **6** obtained from step 20 was glycosylated with 1.43 g (3.6 mmol) of compound **4** to obtain 2.27 g (93%) of compound **7** as a white foam by following the general procedure **B**.

Synthesis of Compound 8:

22) In a 100 mL round bottom flask, 2.13 g (2.1 mmol) of compound **7** obtained from step 21 was converted to 1.34 g (90%) of compound **8** as a white foam by following the general procedure **C**.

Synthesis of Compound 9:

23) In 250 mL round bottom flask, 3.58 g (3.8 mmol) of compound **5** obtained from step 16 was converted to 2.27 g (77%) of compound **9** as a white foam using general procedure **C**.

Synthesis of Compound 10:

24) In a 250 mL round bottom flask, 2.10 g (2.7 mmol) of compound **9** obtained from step 23 was glycosylated with 3.05 g (3.2 mmol) of freshly made glycosyl donor **3** to obtain 3.26 g (79%) of **10** as a white foam by following the general procedure **A**.

Synthesis of Compound 11:

25) In a 100 mL round bottom flask, 3.10 g (2.0 mmol) of compound **10** obtained from step 24 was converted to 2.30 g (87%) of compound **11** as a white foam by following the general procedure **C**.

Synthesis of Compound 12:

26) In a 250 mL round bottom flask, 2.0 g (1.5 mmol) of compound **11** from step 25 was glycosylated with 1.19 g (3.0 mmol) of compound **4** to obtain 2.12 g (89%) of compound **12** as a white foam by following the general procedure **B**.

Synthesis of Compound 13:

27) In a 100 mL round bottom flask, 1.90 g (1.2 mmol) of compound **12** from step 26 was converted to 1.11 g (85%) of compound **13** as a white foam by following the general procedure **C**.

Synthesis of Compound 14:

28) In a 250 mL round bottom flask, 1.8 g (3.8 mmol) of compound **1** obtained from step 5 was glycosylated with 4.23 g (4.5 mmol) of freshly synthesized donor **3** to obtain 3.46 g (75%) of compound **14** by following the general procedure **A**.

Synthesis of Compound 15:

29) In a 250 mL round bottom flask, 3.3 g (2.7 mmol) of compound **14** obtained from step 28 was converted to 2.31 g (81%) of compound **15** as a white foam by following the general procedure **C**.

Synthesis of Compound 16:

30) In a 250 mL round bottom flask, 2.10 g (2.0 mmol) of compound **15** obtained from step 29 was glycosylated with 1.54 g (2.4 mmol) of freshly synthesized donor **2** to obtain 2.75 g (82%) of compound **16** as a white foam by following the general procedure **A**.

Synthesis of Compound 17:

31) In a 250 mL round bottom flask, 2.50 g (1.6 mmol) of compound **16** from step 30 converted to 1.75 g (82%) of compound **17** as white foam by following the general procedure **C**.

Synthesis of Compound 18:

32) In a 250 mL round bottom flask, 1.57 g (1.2 mmol) of compound **17** obtained from step 31 was glycosylated with 0.98 g (2.4 mmol) of compound **4** to obtain 1.56 g (83%) of compound **18** as a white foam by following the general procedure **B**.

Synthesis of Compound 19:

32) In a 100 mL round bottom flask, 1.90 g (1.2 mmol) of compound **18** obtained from step 31 was converted to 1.09 g (87%) of compound **19** as a white foam by following the general procedure **C**.

Analytical Data:

Compound 1: R_f = 0.28 (hexane/ethyl acetate, 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.46 – 7.34 (m, 5H), 7.35 – 7.25 (m, 5H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.61 (s, 1H), 5.57 (s, 1H), 4.81 (d, *J* = 11.4 Hz, 1H), 4.66 (d, *J* = 11.4 Hz, 1H), 4.33 (td, *J* = 9.8, 4.9 Hz, 1H), 4.25 – 4.11 (m, 3H), 3.93 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.84 (t, *J* = 10.3 Hz, 1H), 3.80 (s, 3H), 2.95 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.47, 137.42, 133.27, 131.65, 129.74, 129.61, 129.10, 128.94, 128.20, 127.63, 126.05, 113.90, 101.57, 87.76, 78.92, 75.35, 72.87, 71.32, 68.48, 64.57, 55.23; MALDI-MS: $[M+Na]^+$ $C_{27}H_{28}O_6SNa$ calculated for 503.1504, found 503.1515.

Compound 5: R_f = 0.30 (hexane/ethyl acetate, 3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 2H), 7.49 – 7.37 (m, 5H), 7.37 – 7.30 (m, 5H), 6.94 – 6.84 (m, 2H), 5.64 (s, 1H), 5.54 (dd, *J* = 10.7, 9.3 Hz, 1H), 5.48 (d, *J* = 1.4 Hz, 1H), 5.37 – 5.30 (m, 1H), 5.14 – 5.01 (m, 2H), 4.78 (d, *J* = 11.2 Hz, 1H), 4.74 – 4.63 (m, 2H), 4.52 (d, *J* = 12.5 Hz, 1H), 4.40 (dd, *J* = 3.3, 1.6 Hz, 1H), 4.35 – 4.11 (m, 5H), 3.96 (dd, *J* = 9.8, 3.2 Hz, 1H), 3.88 – 3.78 (m, 4H), 3.77 – 3.70 (m, 1H), 3.44 (dt, *J* = 10.9, 8.1 Hz, 1H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.63, 170.27, 169.58, 159.40, 137.50, 133.42, 131.72, 129.87, 129.66, 129.23, 128.94, 128.25, 127.91, 126.06, 113.87, 101.55, 87.40, 78.75, 76.40, 74.40, 72.49, 72.09, 68.80, 68.49, 65.32, 62.16, 60.42, 55.26, 21.06, 20.71, 20.65, 20.58; MALDI-MS: $[M+Na]^+$ $C_{42}H_{46}Cl_3NO_{15}SNa$ calculated for 964.1552, found 964.1538.

Compound 6: R_f = 0.30 (hexane/acetone, 3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.42 (m, 2H), 7.41 – 7.24 (m, 3H), 5.73 (d, *J* = 7.9 Hz, 1H), 5.51 (t, *J* = 9.9 Hz, 1H), 5.45 (s, 1H), 5.30 (t, *J* = 10.0 Hz, 1H), 5.12 – 4.95 (m, 2H), 4.53 – 4.41 (m, 2H), 4.33 – 4.20 (m, 2H), 4.11 – 3.97 (m, 2H), 3.72 (dd, *J* = 10.2, 5.1 Hz, 1H), 3.59 (dt, *J* = 11.5, 8.1 Hz, 1H), 2.11 – 2.07 (m, 6H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 – 1.99 (m, 6H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.78, 170.67, 170.62, 170.50, 170.35, 169.56, 169.51, 133.14, 131.55, 129.18, 127.87, 98.40, 85.07, 75.47, 71.84, 71.47, 70.46, 69.53, 68.83, 66.20, 62.71, 62.05, 55.63, 23.19, 20.75, 20.72, 20.70, 20.67, 20.63; $[M+Na]^+$ $C_{32}H_{41}NO_{16}SNa$ calculated for 750.2044, found 750.2032.

Compound 7: R_f = 0.29 (hexane/acetone, 3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.4 Hz, 2H), 7.72 – 7.54 (m, 2H), 7.47 – 7.29 (m, 4H), 5.76 (d, *J* = 7.9 Hz, 1H), 5.56 (d, *J* = 9.0 Hz, 1H), 5.43 (t, *J* = 9.8 Hz, 1H), 5.23 (t, *J* = 9.7 Hz, 1H), 5.10 – 4.94 (m, 2H), 4.91 – 4.80 (m, 2H), 4.58 – 4.14 (m, 8H), 4.14 – 4.05 (m, 2H), 4.05 – 3.88 (m, 2H), 3.72 – 3.51 (m, 2H), 2.08 (s, 6H), 2.07 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.95 (s, 3H), 1.53 (s, 9H), 1.32 (d, *J* = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.65, 170.60, 170.56, 169.47, 169.32, 156.52, 143.84, 143.74, 141.31, 127.78, 127.11, 125.18, 120.04, 99.00, 98.89, 82.67, 74.15, 71.86, 71.65, 69.95, 69.21, 68.79, 67.36, 66.09, 62.89, 62.10, 58.92, 55.31, 47.17, 28.03, 23.24, 20.75, 20.71, 20.64, 17.88; $[M+Na]^+$ $C_{49}H_{62}N_2O_{21}Na$ calculated for 1037.3743, found 1037.3752.

Compound 8: R_f = 0.40 (ethyl acetate/methanol/H_2O, 4:2:0.5, v/v); ^{1}H NMR (400 MHz, D_2O) δ 7.74 – 7.60 (m, 2H), 7.60 – 7.40 (m, 2H), 7.40 – 7.18 (m, 4H), 4.60 (dd, *J* = 10.7, 4.9 Hz, 1H), 4.42 – 4.27 (m, 2H), 4.23 (d, *J* = 6.3 Hz, 1H), 4.12 – 3.96 (m, 1H), 3.83 – 3.71 (m,

4H), 3.71 – 3.42 (m, 7H), 3.42 – 3.30 (m, 3H), 3.27 (s, 1H), 1.96 (s, 3H), 0.94 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, D_2O) δ 174.87, 158.05, 143.91, 143.49, 140.96, 140.91, 127.96, 127.41, 124.90, 124.78, 120.09, 100.01, 98.04, 77.19, 75.59, 73.28, 73.05, 69.84, 69.26, 67.22, 65.92, 61.60, 60.52, 55.26, 47.10, 22.35, 18.33; $[M-H]^-$ $C_{33}H_{41}N_2O_{15}$ calculated for 705.2585, found 705.2470.

Compound 9: R_f = 0.33 (hexane/acetone, 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.5 Hz, 2H), 7.36 – 7.19 (m, 3H), 6.00 (d, *J* = 8.2 Hz, 1H), 5.35 (s, 1H), 5.25 (t, *J* = 9.9 Hz, 1H), 4.99 (t, *J* = 9.5 Hz, 1H), 4.88 (d, *J* = 9.6 Hz, 1H), 4.71 – 4.56 (m, 2H), 4.52 – 4.37 (m, 2H), 4.33 – 4.15 (m, 2H), 4.15 – 3.97 (m, 2H), 3.87 (t, *J* = 10.5 Hz, 1H), 3.80 – 3.45 (m, 4H), 2.93 (d, *J* = 8.7 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.99, 170.89, 170.77, 169.52, 154.57, 133.42, 131.69, 129.27, 127.94, 100.41, 95.00, 85.81, 76.94, 74.56, 73.42, 73.20, 71.77, 71.35, 68.58, 64.12, 62.12, 61.50, 56.05, 20.91, 20.68, 20.59; $[M+Na]^+$ $C_{29}H_{36}Cl_3NO_{15}SNa$ calculated for 798.0769, found 798.0778.

Compound 10: R_f = 0.35 (hexane/acetone, 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.7 Hz, 2H), 7.39 – 7.24 (m, 3H), 6.32 (d, *J* = 8.4 Hz, 1H), 6.05 (d, *J* = 8.4 Hz, 1H), 5.45 (s, 1H), 5.43 – 5.31 (m, 3H), 5.09 (dd, *J* = 10.3, 7.9 Hz, 1H), 5.05 – 4.91 (m, 3H), 4.86 (dd, *J* = 9.8, 2.6 Hz, 1H), 4.78 (d, *J* = 8.2 Hz, 1H), 4.76 – 4.62 (m, 3H), 4.59 – 4.44 (m, 3H), 4.41 (s, 1H), 4.26 (dd, *J* = 12.3, 5.4 Hz, 1H), 4.20 – 4.00 (m, 6H), 3.96 (d, *J* = 10.9 Hz, 1H), 3.92 – 3.81 (m, 2H), 3.79 – 3.65 (m, 2H), 3.61 (dd, *J* = 8.7, 3.8 Hz, 1H), 3.49 (dq, *J* = 17.4, 8.7 Hz, 2H), 3.00 (s, 1H), 2.15 (s, 3H), 2.13 (s, 6H), 2.09 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.77, 170.68, 170.50, 170.40, 170.19, 170.12, 169.52, 169.11, 155.08, 154.61, 133.76, 130.97, 129.19, 127.63, 101.24, 100.97, 99.16, 95.48, 95.35, 85.16, 76.47, 74.73, 74.52, 73.30, 72.72, 72.47, 71.97, 71.14, 70.99, 70.74, 69.15, 68.88, 67.77, 66.67, 63.87, 62.07, 60.93, 56.75, 56.14, 21.03, 20.94, 20.88, 20.72, 20.69, 20.63, 20.60, 20.50; $[M+Na]^+$ $C_{56}H_{70}Cl_6N_2O_{32}SNa$ calculated for 1547.1661, found 1547.1603.

Compound 11: R_f = 0.22 (hexane/acetone, 3:2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 2H), 7.35 – 7.26 (m, 3H), 7.26 – 7.20 (m, 1H), 6.46 (d, *J* = 10.0 Hz, 1H), 5.89 (dd, *J* = 10.7, 9.2 Hz, 1H), 5.68 (d, *J* = 1.1 Hz, 1H), 5.50 – 5.37 (m, 2H), 5.34 (d, *J* = 2.8 Hz, 1H), 5.14 – 4.99 (m, 3H), 4.99 – 4.82 (m, 2H), 4.54 – 4.36 (m, 3H), 4.26 (dd, *J* = 12.2, 5.9 Hz, 1H), 4.22 – 4.11 (m, 3H), 4.11 – 4.00 (m, 4H), 3.95 (dd, *J* = 12.1, 2.2 Hz, 1H), 3.85 (t, *J* = 7.1 Hz, 1H), 3.80 – 3.66 (m, 2H), 3.53 (ddd, *J* = 9.7, 5.0, 1.8 Hz, 1H), 3.15 (d, *J* = 10.8 Hz, 1H), 3.02 – 2.89 (m, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 2.08 (s, 6H), 2.07 (s, 3H), 2.05 (s, 3H), 2.04 (d, *J* = 3.8 Hz, 3H), 2.02 (d, *J* = 4.8 Hz, 6H), 1.99 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.69, 172.18, 170.86, 170.60, 170.31, 170.29, 170.08, 170.00, 169.93, 169.78, 169.08, 133.09, 130.04, 129.24, 127.24, 102.96, 101.07, 96.29, 83.45, 77.41, 77.09, 76.78, 76.15, 74.31, 72.83, 72.75, 71.88, 70.88, 70.62, 70.55, 70.43, 69.98, 69.53, 69.15, 68.44, 66.51, 65.77, 62.35, 62.07, 60.57, 56.92, 53.49, 23.28, 23.25, 21.02, 20.89, 20.80, 20.67, 20.64, 20.61, 20.58, 20.52, 20.48; $[M+Na]^+$ $C_{56}H_{74}N_2O_{31}SNa$ calculated for 1325.3894, found 1325.3935.

Compound 12: R_f = 0.24 (hexane/acetone, 3:2, v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.69 – 7.52 (m, 2H), 7.44 – 7.37 (m, 2H), 7.37 – 7.30 (m, 3H), 6.44 (d, *J* = 10.0 Hz, 1H), 5.95 – 5.85 (m, 1H), 5.60 (d, *J* = 9.3 Hz, 1H), 5.43 – 5.31 (m, 3H), 5.17 – 5.01 (m, 3H), 4.96 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.94 – 4.83 (m, 2H), 4.54 – 4.42 (m, 3H), 4.42 – 4.23 (m, 5H), 4.23 – 4.02 (m, 7H), 3.97 – 3.83 (m, 2H), 3.83 – 3.70 (m, 2H), 3.70 – 3.60 (m, 1H), 3.60 – 3.52 (m, 1H), 3.14 (d, *J* = 11.3 Hz, 1H), 2.91 (dd, *J* = 17.8, 7.9 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.09 (s, 3H), 2.07 (t, *J* = 2.7 Hz, 6H), 2.05 (s, 3H),

2.04 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 1.52 (s, 9H), 1.31 – 1.24 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.57, 172.20, 170.87, 170.63, 170.32, 170.11, 170.04, 169.97, 169.93, 169.89, 169.10, 169.03, 156.59, 143.95, 143.79, 141.29, 127.71, 127.11, 127.08, 125.25, 119.98, 119.95, 102.90, 101.11, 98.35, 96.47, 82.46, 78.01, 76.15, 72.90, 72.80, 72.71, 71.80, 70.91, 70.64, 70.62, 70.07, 69.85, 69.17, 69.09, 68.32, 67.25, 66.52, 65.79, 62.39, 61.97, 60.57, 59.03, 56.99, 53.51, 47.20, 28.11, 23.30, 23.28, 21.04, 20.93, 20.85, 20.81, 20.69, 20.63, 20.61, 20.58, 20.50, 18.06; $[M+Na]^+$ $C_{73}H_{95}N_3O_{36}Na$ calculated for 1612.5593, found 1612.5678.

Compound 13: R_f = 0.30 (ethyl acetate/methanol/H_2O, 4:2:0.5, v/v); ^{1}H NMR (400 MHz, MeOD) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.74 – 7.58 (m, 2H), 7.44 – 7.27 (m, 4H), 4.55 (d, *J* = 7.7 Hz, 1H), 4.50 – 4.31 (m, 5H), 4.23 (t, *J* = 6.7 Hz, 1H), 4.18 – 4.02 (m, 2H), 4.01 – 3.84 (m, 5H), 3.84 – 3.51 (m, 14H), 3.51 – 3.30 (m, 6H), 2.08 (s, 3H), 2.06 (s, 3H), 1.22 (d, *J* = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, MeOD) δ 173.40, 172.73, 157.41, 144.06, 143.80, 141.18, 127.42, 126.85, 124.88, 119.55, 103.81, 101.78, 98.66, 79.69, 79.33, 76.38, 75.74, 75.04, 73.89, 73.41, 72.46, 71.20, 70.54, 69.85, 68.93, 68.64, 67.77, 66.59, 61.16, 60.88, 60.39, 55.28, 47.08, 22.35, 22.12, 18.44; $[M-H]^-$ $C_{47}H_{64}N_3O_{25}$ calculated for 1071.3907, found 1071.3741.

Compound 14: R_f = 0.33 (hexane/acetone, 3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.46 – 7.25 (m, 10H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.62 (s, 1H), 5.48 (s, 1H), 5.43 – 5.23 (m, 3H), 5.12 (dd, *J* = 10.4, 7.9 Hz, 1H), 4.97 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.81 (d, *J* = 8.2 Hz, 1H), 4.75 – 4.62 (m, 3H), 4.59 – 4.45 (m, 3H), 4.34 (d, *J* = 1.7 Hz, 1H), 4.30 – 4.03 (m, 6H), 3.94 – 3.86 (m, 2H), 3.85 – 3.72 (m, 5H), 3.65 – 3.51 (m, 2H), 2.15 (s, 3H), 2.06 (s, 3H), 2.06 (s, 6H), 2.04 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.40, 170.33, 170.15, 170.08, 169.09, 159.30, 153.99, 137.55, 133.40, 131.49, 130.00, 129.44, 129.24, 128.90, 128.23, 127.84, 126.10, 113.80, 101.53, 100.98, 99.17, 95.32, 86.79, 78.47, 76.24, 74.48, 74.23, 73.00, 71.90, 71.38, 70.97, 70.75, 69.13, 68.46, 66.69, 65.30, 62.24, 60.94, 55.98, 55.26, 20.82, 20.79, 20.66, 20.63, 20.61, 20.52; $[M+Na]^+$ $C_{54}H_{62}Cl_3NO_{23}SNa$ calculated for 1252.2397, found 1252.2444.

Compound 15: R_f = 0.22 (hexane/acetone, 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.6 Hz, 2H), 7.34 – 7.21 (m, 3H), 6.07 (d, *J* = 9.1 Hz, 1H), 5.35 (s, 1H), 5.32 (d, *J* = 3.1 Hz, 1H), 5.10 – 4.99 (m, 2H), 4.94 (dd, *J* = 10.4, 3.3 Hz, 1H), 4.87 (dd, *J* = 9.9, 2.6 Hz, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.52 – 4.42 (m, 2H), 4.38 (d, *J* = 11.7 Hz, 3H), 4.31 – 4.19 (m, 1H), 4.15 – 3.98 (m, 4H), 3.94 – 3.78 (m, 2H), 3.78 – 3.63 (m, 3H), 3.63 – 3.53 (m, 1H), 3.43 (d, *J* = 3.9 Hz, 1H), 2.97 (d, *J* = 8.7 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.12, 170.46, 170.42, 170.15, 170.13, 169.44, 154.88, 133.34, 131.56, 129.27, 127.88, 101.17, 100.94, 95.06, 85.69, 76.09, 74.58, 73.61, 73.28, 72.73, 71.63, 70.83, 70.69, 69.19, 66.66, 63.99, 62.23, 61.48, 60.91, 55.97, 20.87, 20.78, 20.75, 20.64, 20.58, 20.47; $[M+Na]^+$ $C_{41}H_{52}Cl_3NO_{23}SNa$ calculated for 1086.1614, found 1086.1658.

Compound 16: R_f = 0.25 (hexane/acetone, 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.34 – 7.21 (m, 3H), 6.96 (d, *J* = 7.0 Hz, 1H), 5.93 (d, *J* = 9.7 Hz, 1H), 5.73 (t, *J* = 10.0 Hz, 1H), 5.43 (s, 1H), 5.33 (d, *J* = 3.2 Hz, 1H), 5.18 – 4.89 (m, 6H), 4.81 (dd, *J* = 10.0, 2.7 Hz, 1H), 4.72 – 4.53 (m, 3H), 4.50 – 4.38 (m, 3H), 4.36 (s, 1H), 4.24 (dd, *J* = 12.3, 4.4 Hz, 1H), 4.16 – 4.03 (m, 4H), 4.03 – 3.89 (m, 4H), 3.85 (t, *J* = 6.6 Hz, 1H), 3.83 – 3.65 (m, 3H), 3.65 – 3.56 (m, 1H), 3.17 (dd, *J* = 18.1, 8.0 Hz, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H), 2.01 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.80, 170.59, 170.51, 170.42, 170.14, 170.10, 169.76, 169.29, 154.95, 133.57, 130.98, 129.18, 127.65, 101.23, 100.94, 100.49, 96.05, 94.96, 85.58,

77.60, 76.27, 75.19, 74.19, 73.55, 72.93, 72.63, 71.62, 71.44, 70.96, 70.87, 70.45, 69.34, 69.09, 67.65, 66.80, 63.26, 62.51, 62.13, 61.26, 57.10, 55.69, 21.02, 20.88, 20.81, 20.75, 20.64, 20.60, 20.57, 20.55, 20.48; $[M+Na]^+$ $C_{56}H_{70}Cl_6N_2O_{32}SNa$ calculated for 1547.1661, found 1547.1738.

Compound 17: R_f = 0.22 (hexane/acetone, 3:2, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 2H), 7.36 – 7.26 (m, 2H), 7.26 – 7.19 (m, 1H), 7.10 (d, *J* = 6.9 Hz, 1H), 6.55 (d, *J* = 9.9 Hz, 1H), 5.84 (dd, *J* = 10.6, 8.9 Hz, 1H), 5.74 (s, 1H), 5.50 – 5.38 (m, 2H), 5.33 (d, *J* = 2.8 Hz, 1H), 5.15 – 4.98 (m, 4H), 4.94 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.48 (d, *J* = 7.9 Hz, 1H), 4.37 – 3.97 (m, 11H), 3.85 (t, *J* = 7.0 Hz, 1H), 3.77 – 3.55 (m, 3H), 3.19 (d, *J* = 10.9 Hz, 1H), 2.90 (dt, *J* = 10.5, 8.1 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.03 (s, 6H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.73, 172.09, 171.03, 170.70, 170.63, 170.53, 170.35, 170.26, 170.10, 169.92, 169.37, 169.32, 168.87, 133.13, 129.74, 129.24, 127.13, 103.01, 100.62, 96.29, 83.11, 77.85, 74.47, 72.98, 72.86, 71.86, 70.99, 70.57, 70.47, 70.36, 69.49, 69.07, 68.55, 68.49, 66.62, 65.93, 62.44, 61.96, 60.78, 57.07, 53.41, 23.32, 23.16, 21.08, 21.05, 20.70, 20.69, 20.67, 20.61, 20.57, 20.55, 20.52, 20.48; $[M+Na]^+$ $C_{56}H_{74}N_2O_{31}SNa$ calculated for 1325.3894, found 1325.3946.

Compound 18: R_f = 0.23 (hexane/acetone, 3:2, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.71 – 7.51 (m, 2H), 7.49 – 7.25 (m, 5H), 7.05 (d, *J* = 7.0 Hz, 1H), 6.51 (d, *J* = 9.6 Hz, 1H), 5.87 – 5.72 (m, 1H), 5.57 (d, *J* = 9.3 Hz, 1H), 5.41 – 5.28 (m, 3H), 5.19 – 5.01 (m, 4H), 5.01 – 4.87 (m, 2H), 4.59 – 4.41 (m, 3H), 4.41 – 3.96 (m, 16H), 3.90 – 3.81 (m, 1H), 3.81 – 3.70 (m, 1H), 3.70 – 3.55 (m, 3H), 3.17 (d, *J* = 11.2 Hz, 1H), 2.88 (dd, *J* = 17.5, 8.1 Hz, 1H), 2.18 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 2.04 (s, 6H), 2.02 (s, 3H), 1.97 (s, 3H), 1.94 (s, 3H), 1.52 (s, 9H), 1.27 (d, *J* = 8.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.45, 172.04, 171.00, 170.70, 170.62, 170.57, 170.35, 170.22, 170.12, 169.82, 169.38, 169.01, 156.57, 143.95, 143.78, 141.28, 127.70, 127.10, 125.25, 119.98, 102.88, 101.06, 98.03, 96.56, 82.47, 78.21, 77.93, 72.88, 72.79, 71.91, 71.03, 70.88, 70.52, 69.85, 69.50, 69.22, 69.11, 68.61, 68.38, 67.25, 66.53, 65.93, 62.51, 62.00, 60.61, 58.98, 57.02, 53.84, 53.48, 47.19, 29.28, 28.13, 23.28, 23.18, 21.09, 20.72, 20.68, 20.63, 20.59, 20.53, 17.95; $[M+Na]^+$ $C_{73}H_{95}N_3O_{36}Na$ calculated for 1612.5593, found 1612.5663.

Compound 19: R_f = 0.30 (ethyl acetate/methanol/H_2O, 4:2:0.5, v/v); ^1H NMR (400 MHz, D_2O) δ 7.68 – 7.56 (m, 2H), 7.56 – 7.36 (m, 2H), 7.36 – 7.16 (m, 5H), 4.59 – 4.51 (m, 1H), 4.47 (d, *J* = 8.4 Hz, 1H), 4.43 – 4.23 (m, 4H), 4.18 (d, *J* = 6.4 Hz, 1H), 4.09 (d, *J* = 10.3 Hz, 1H), 3.98 (d, *J* = 4.8 Hz, 1H), 3.90 – 3.80 (m, 4H), 3.80 – 3.55 (m, 16H), 3.55 – 3.42 (m, 5H), 3.41 – 3.24 (m, 5H), 1.97 (s, 3H), 1.95 (s, 4H), 0.95 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, D_2O) δ 174.59, 174.15, 158.00, 143.88, 143.45, 140.96, 140.90, 127.97, 127.43, 124.80, 120.11, 102.90, 101.16, 99.84, 98.22, 78.31, 77.18, 76.85, 75.90, 75.31, 74.56, 73.93, 72.48, 71.95, 70.94, 70.06, 69.21, 68.56, 67.59, 65.98, 61.02, 60.87, 59.88, 55.57, 54.82, 48.89, 47.09, 22.50, 22.33, 18.49; $[M+Na]^+$ $C_{47}H_{65}N_3O_{25}Na$ calculated for 1094.3805, found 1094.3876.

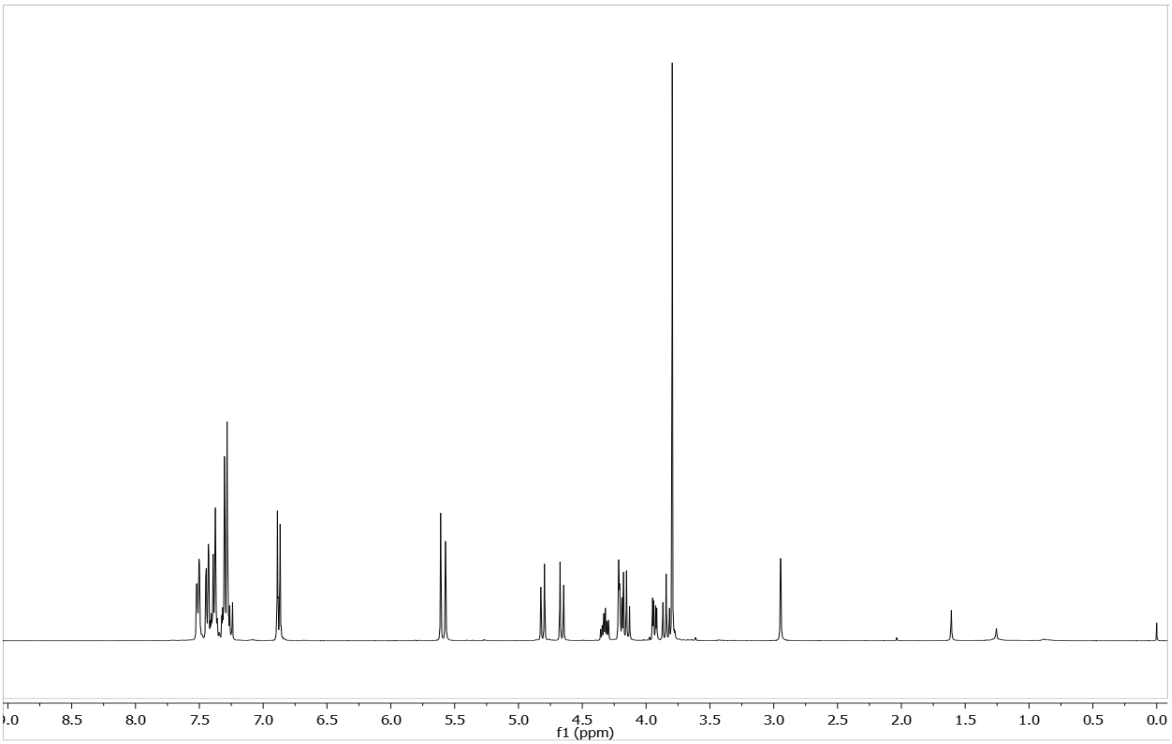
Reference:

1) Wang, Z.; Chinoy, Z. S.; Ambre, S. G.; Peng, W.; McBride, R.; de Vries, R. P.; Glushka, J.; Paulson, J. C.; Boons, G. J., A general strategy for the chemoenzymatic synthesis of asymmetrically branched N-glycans. *Science* **2013,** *341* (6144), 379-83.

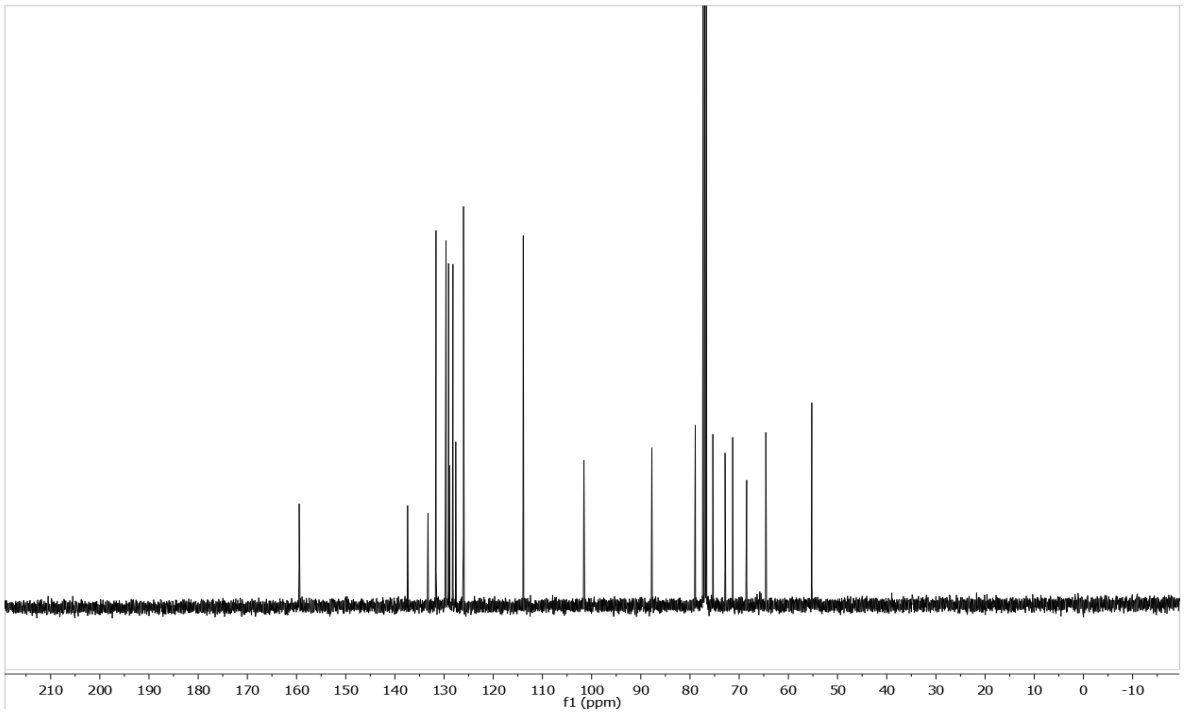
2) Yan, F.; Mehta, S.; Eichler, E.; Wakarchuk, W. W.; Gilbert, M.; Schur, M. J.; Whitfield, D. M., Simplifying oligosaccharide synthesis: efficient synthesis of lactosamine and siaylated lactosamine oligosaccharide donors. *The Journal of organic chemistry* **2003,** *68* (6), 2426-31.

NMR spectra

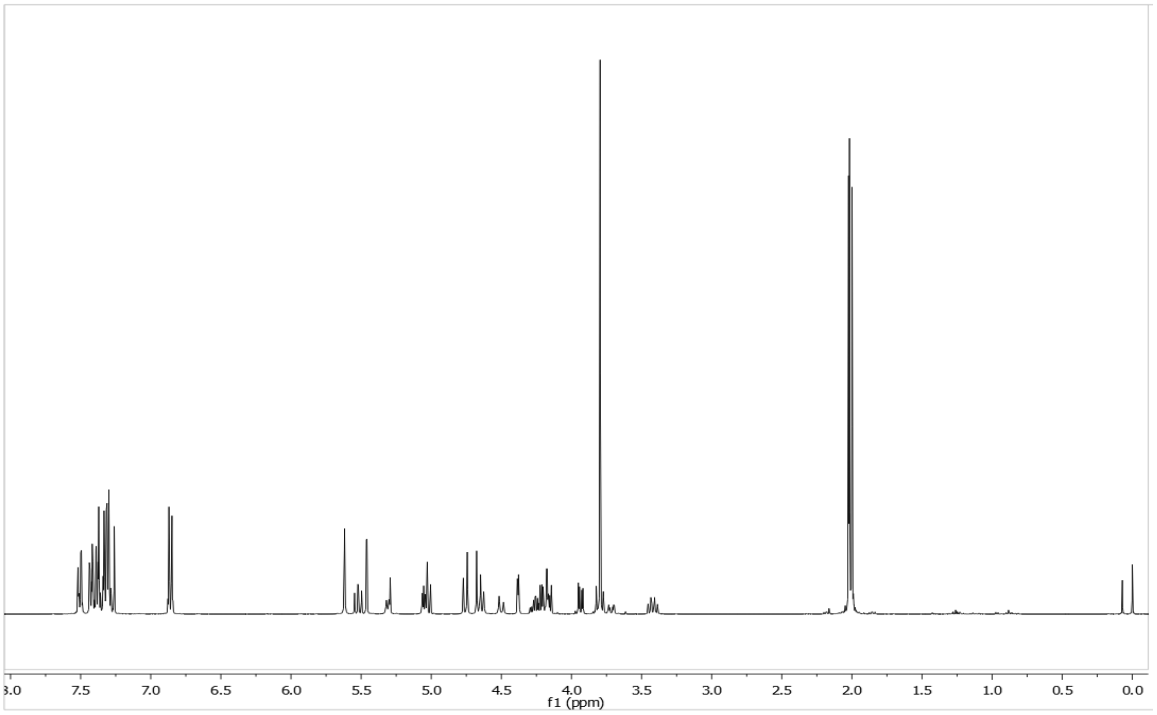
^{1}H NMR of Compound 1



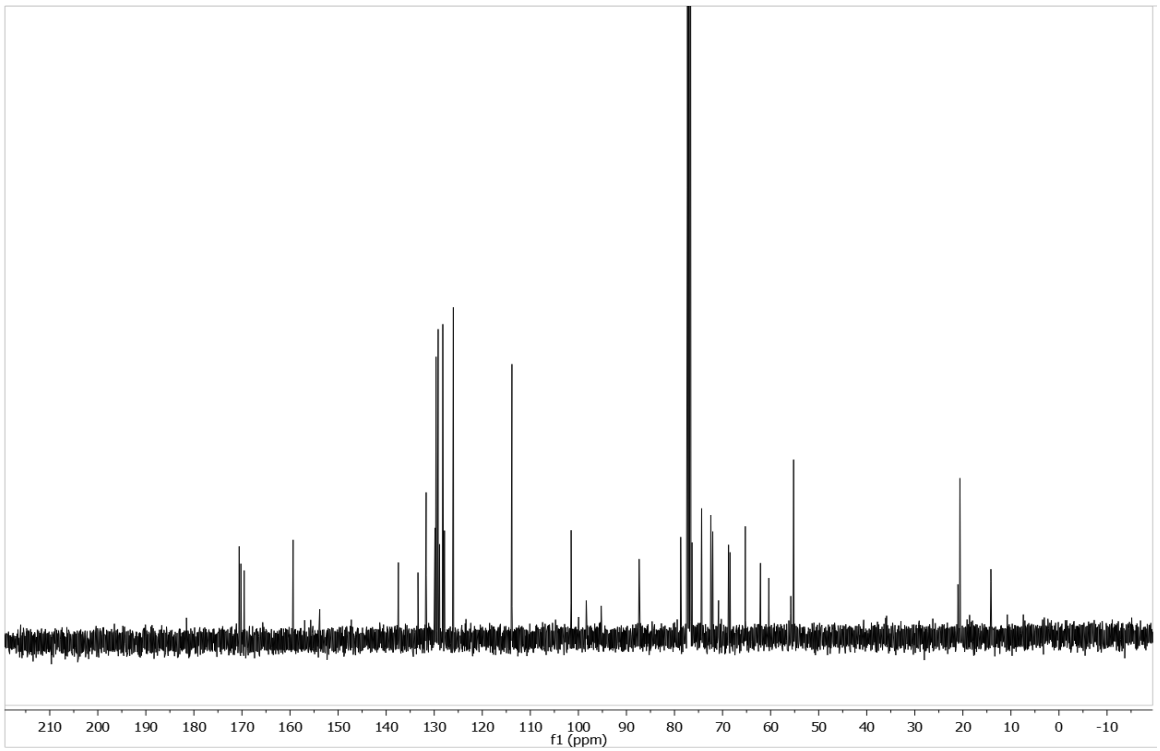
^{13}C NMR of Compound 1



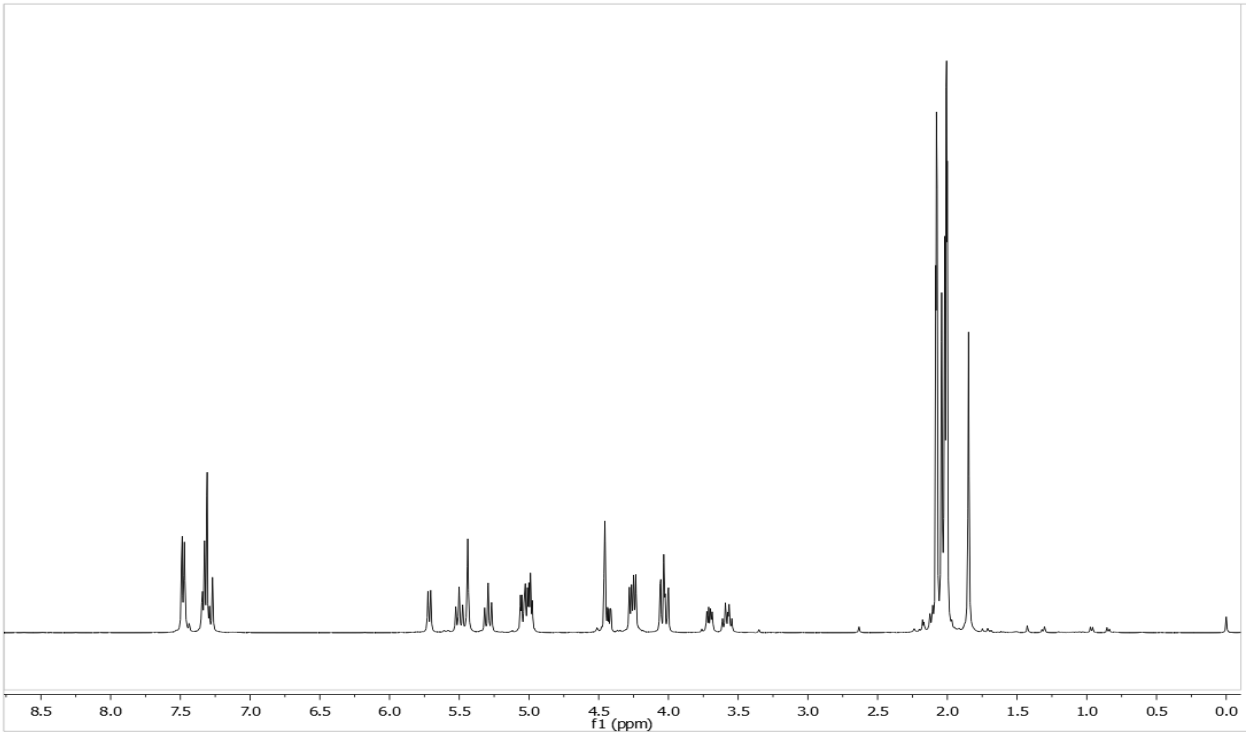
^{1}H NMR of Compound 5



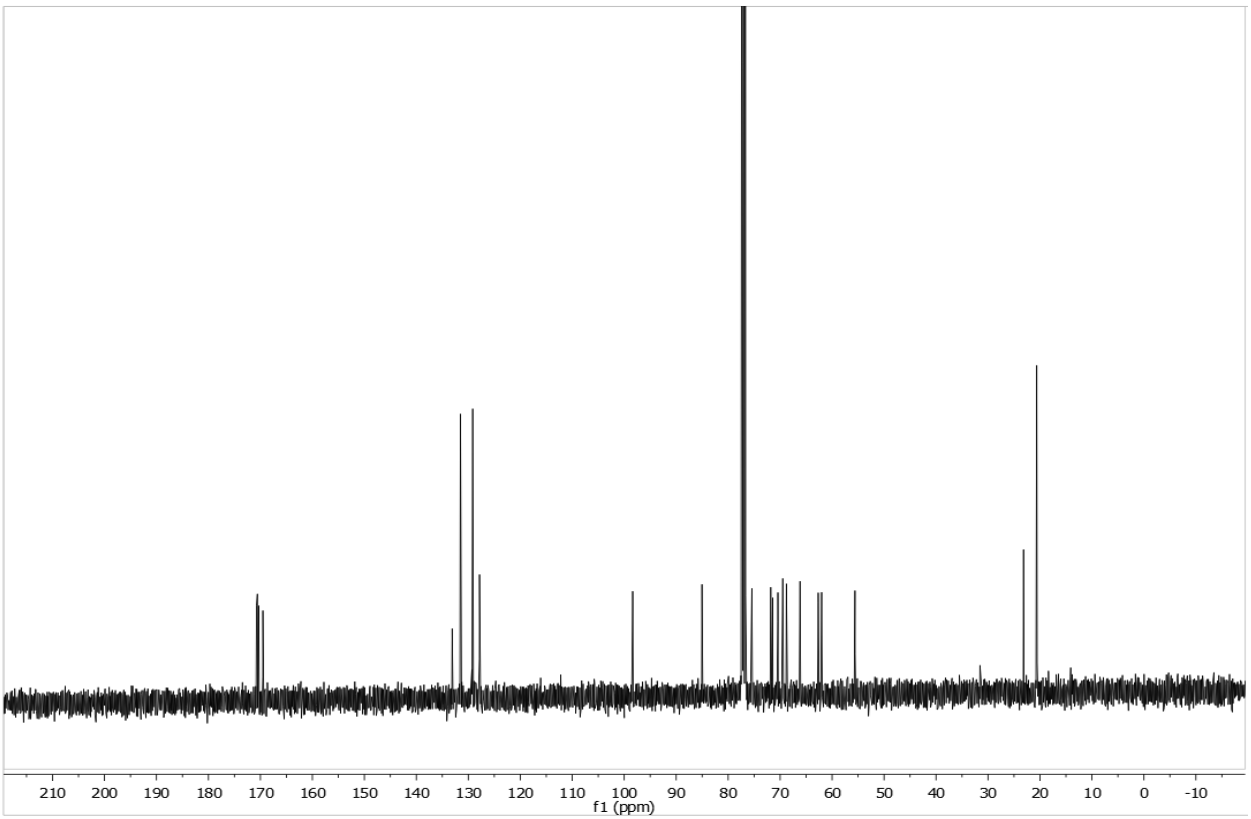
^{13}C NMR of Compound 5



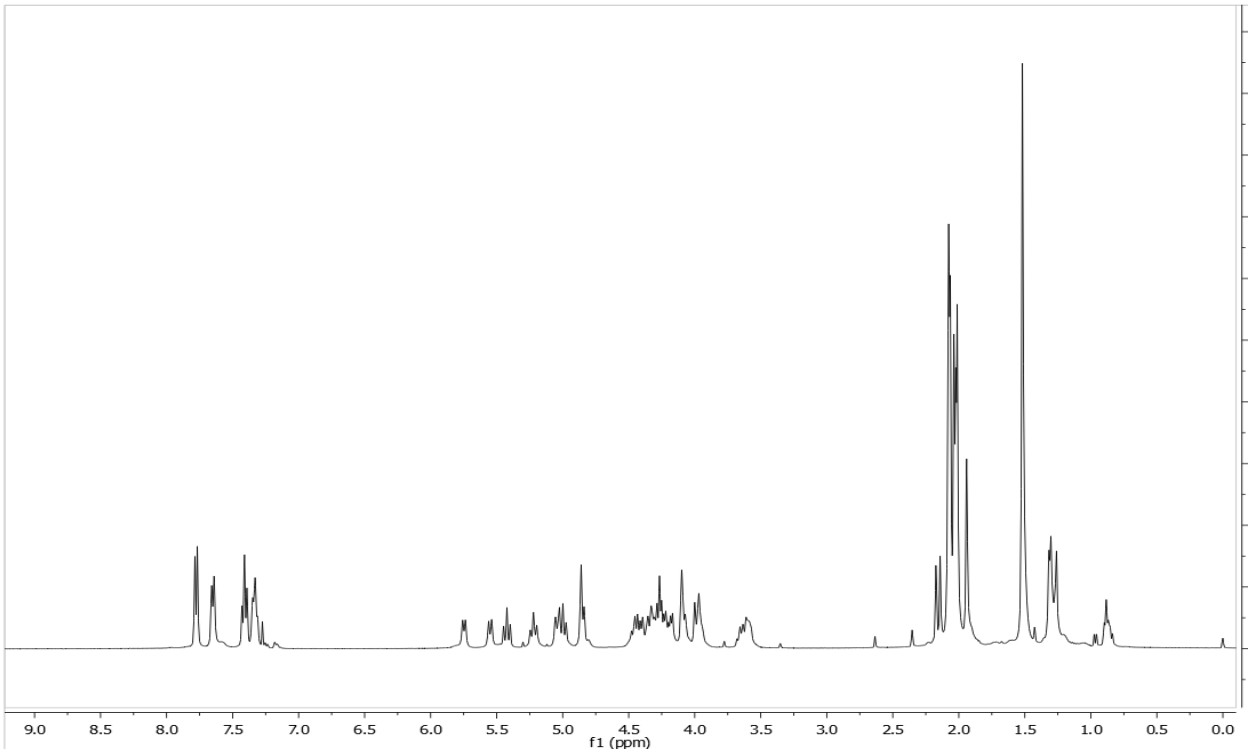
^{1}H NMR of Compound 6



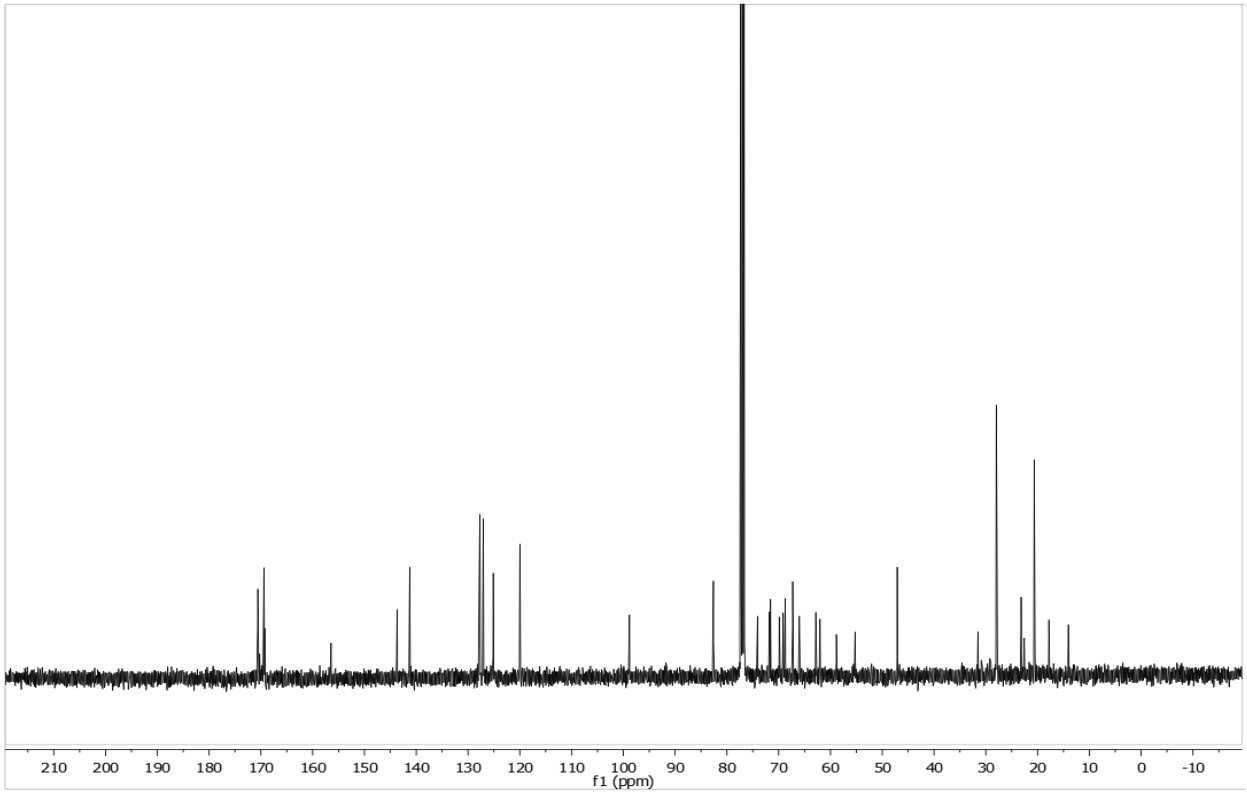
^{13}C NMR of Compound 6



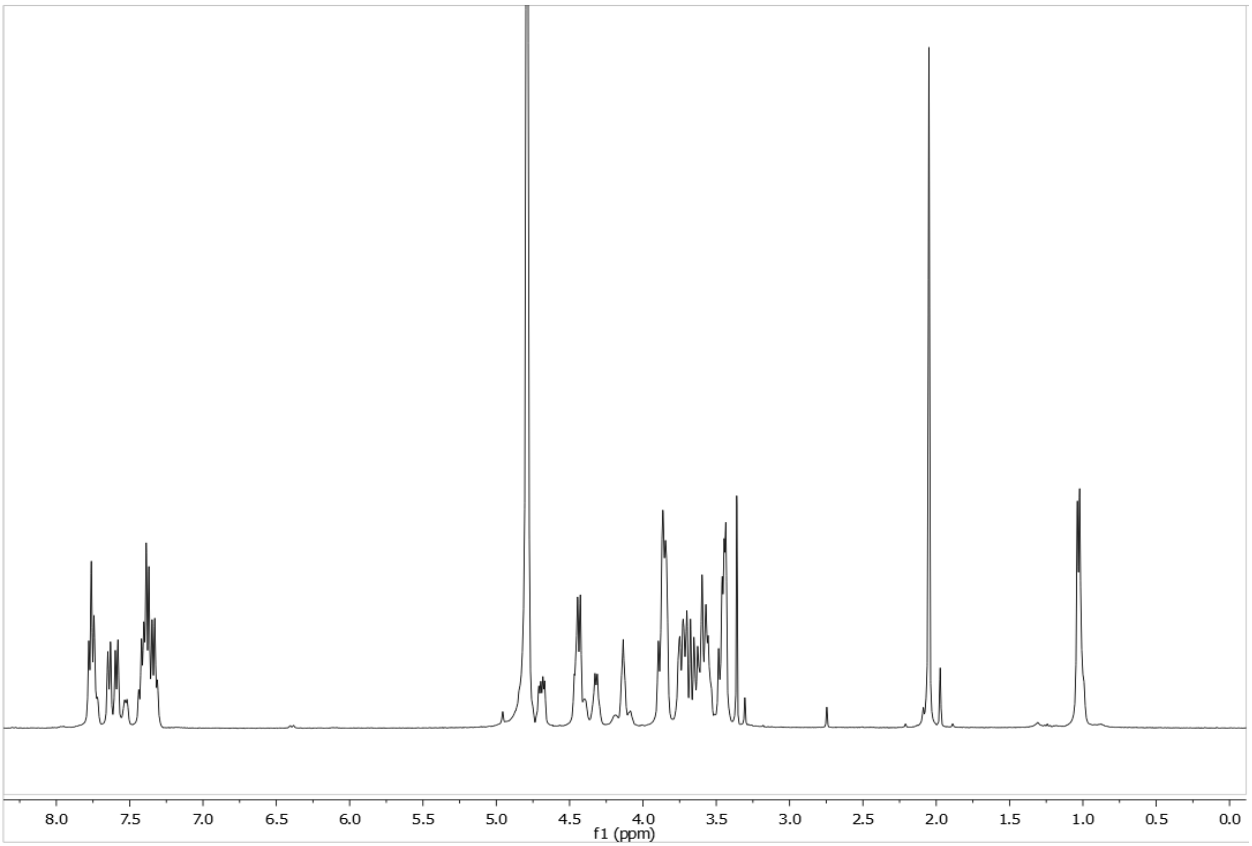
^{1}H NMR of Compound 7



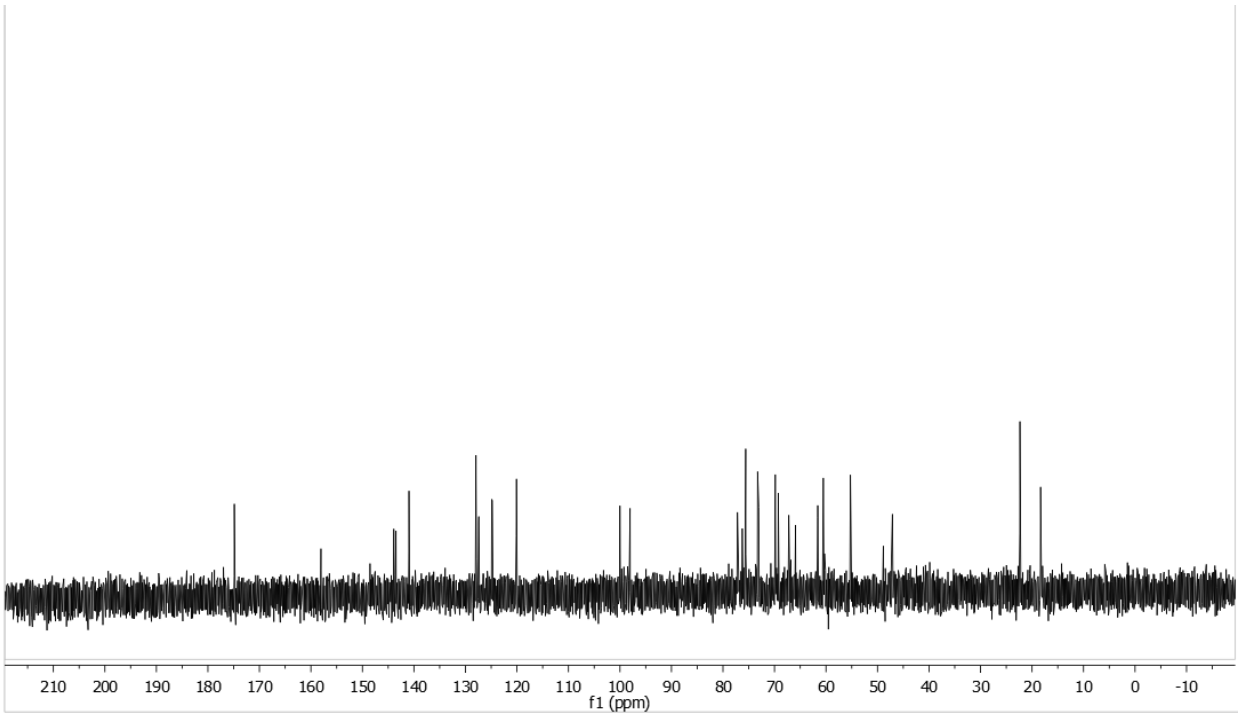
^{13}C NMR of Compound 7



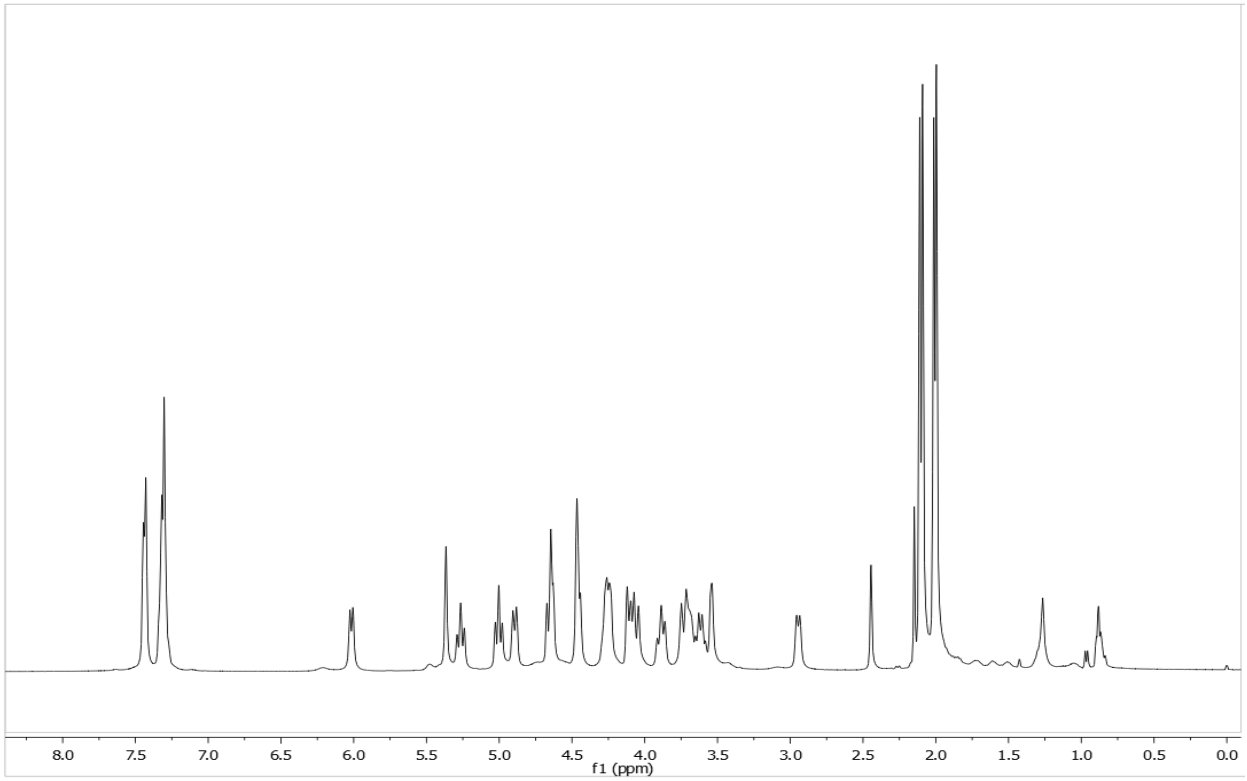
^{1}H NMR of Compound 8 (M100)



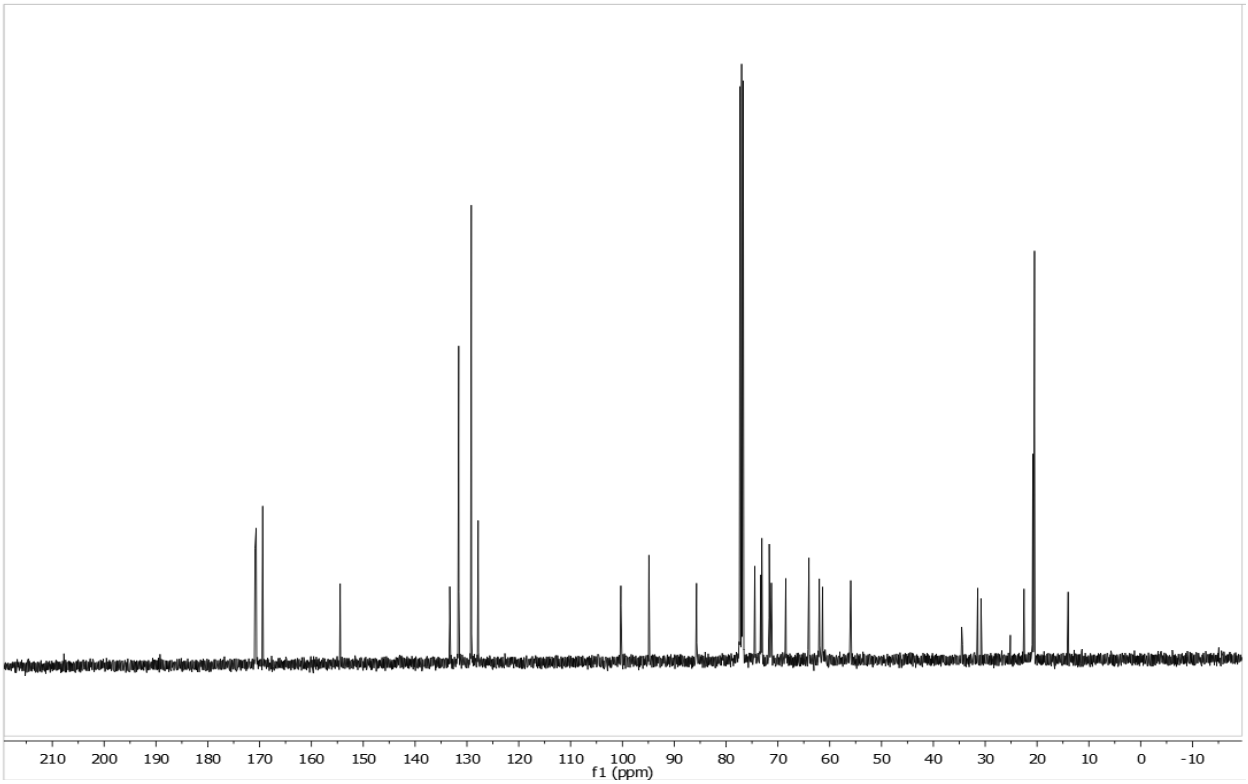
^{13}C NMR of Compound 8 (M100)



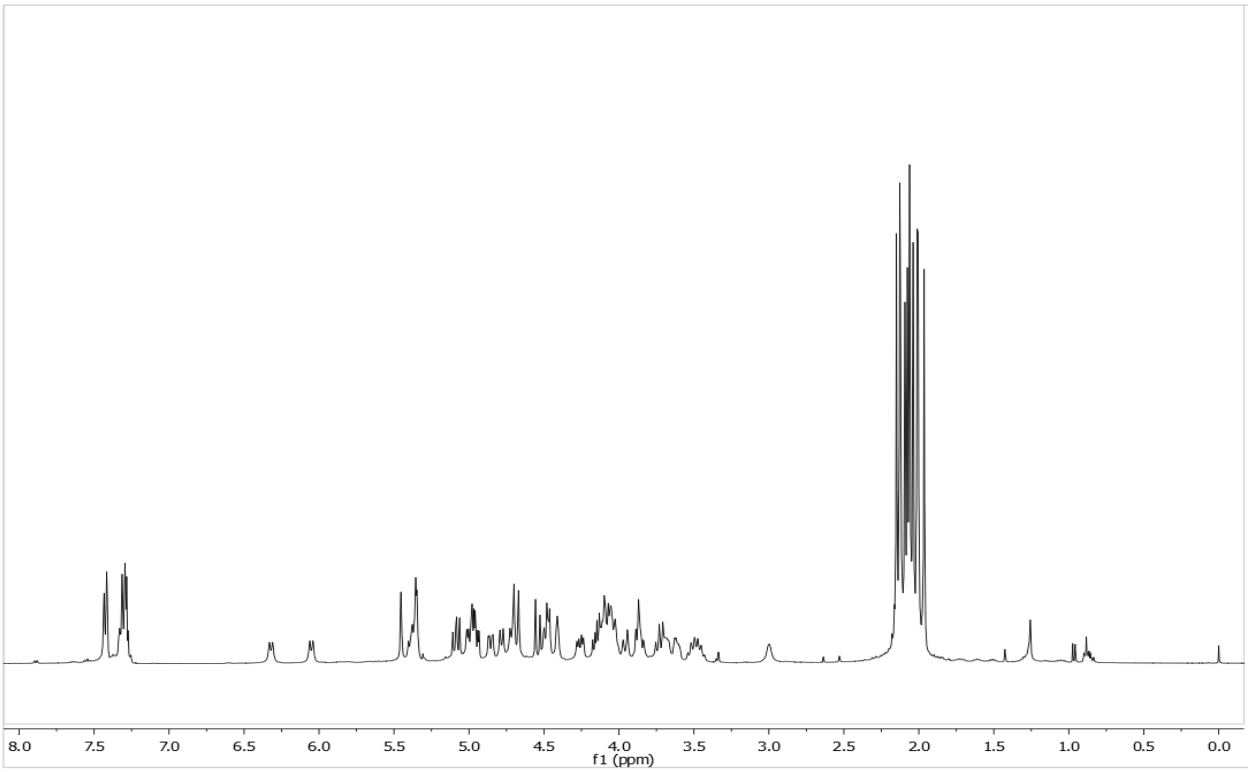
^{1}H NMR of Compound 9



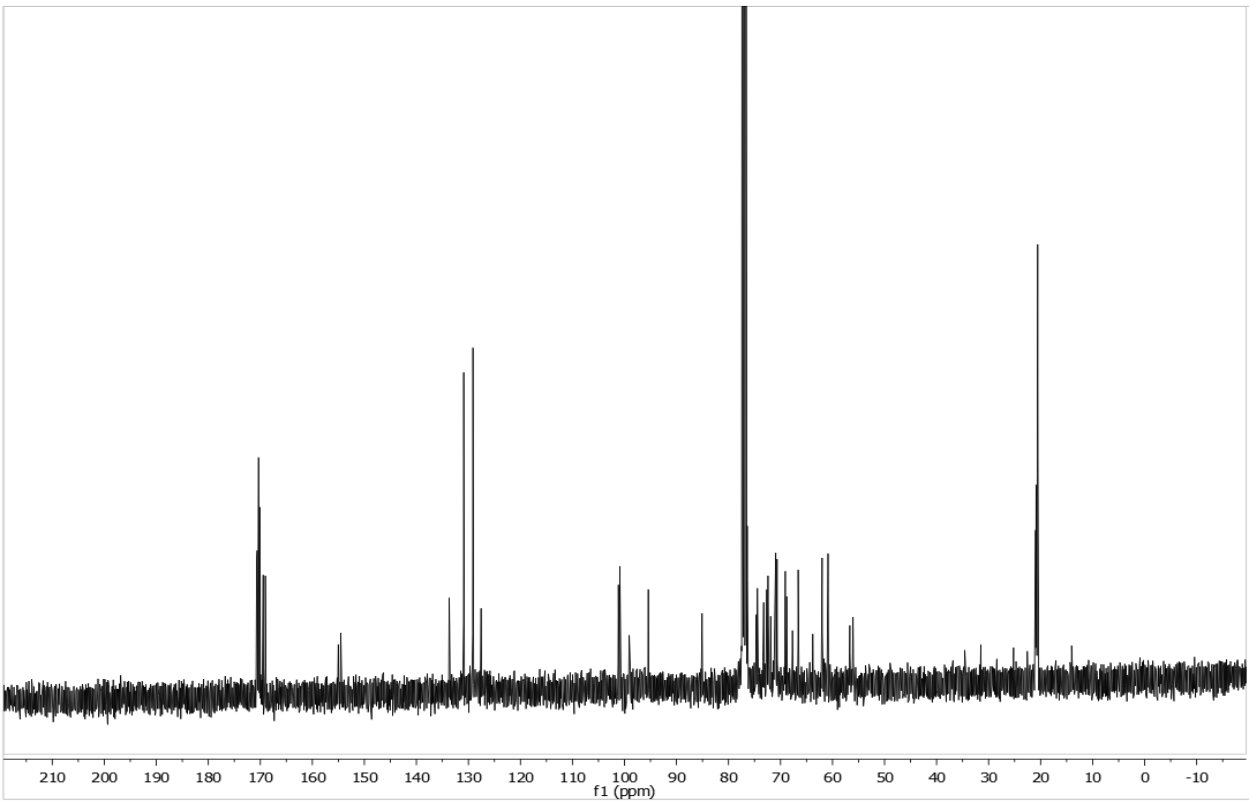
^{13}C NMR of Compound 9



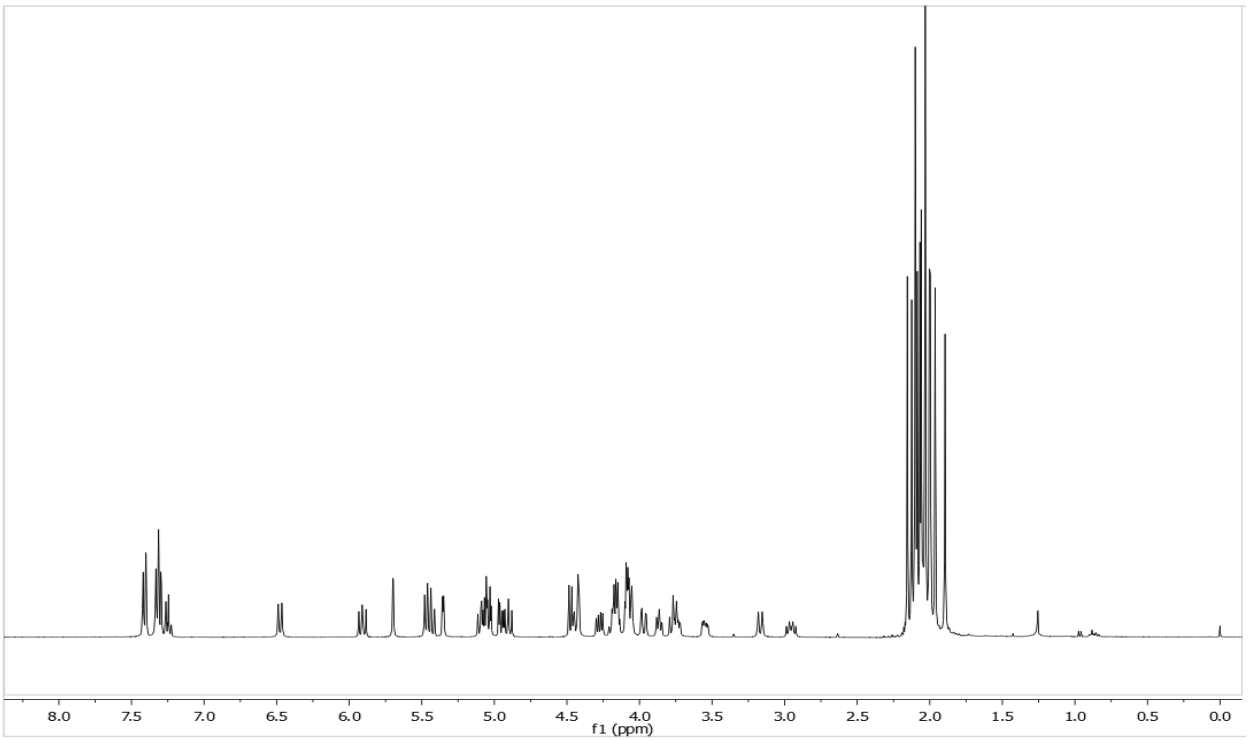
^{1}H NMR of Compound 10



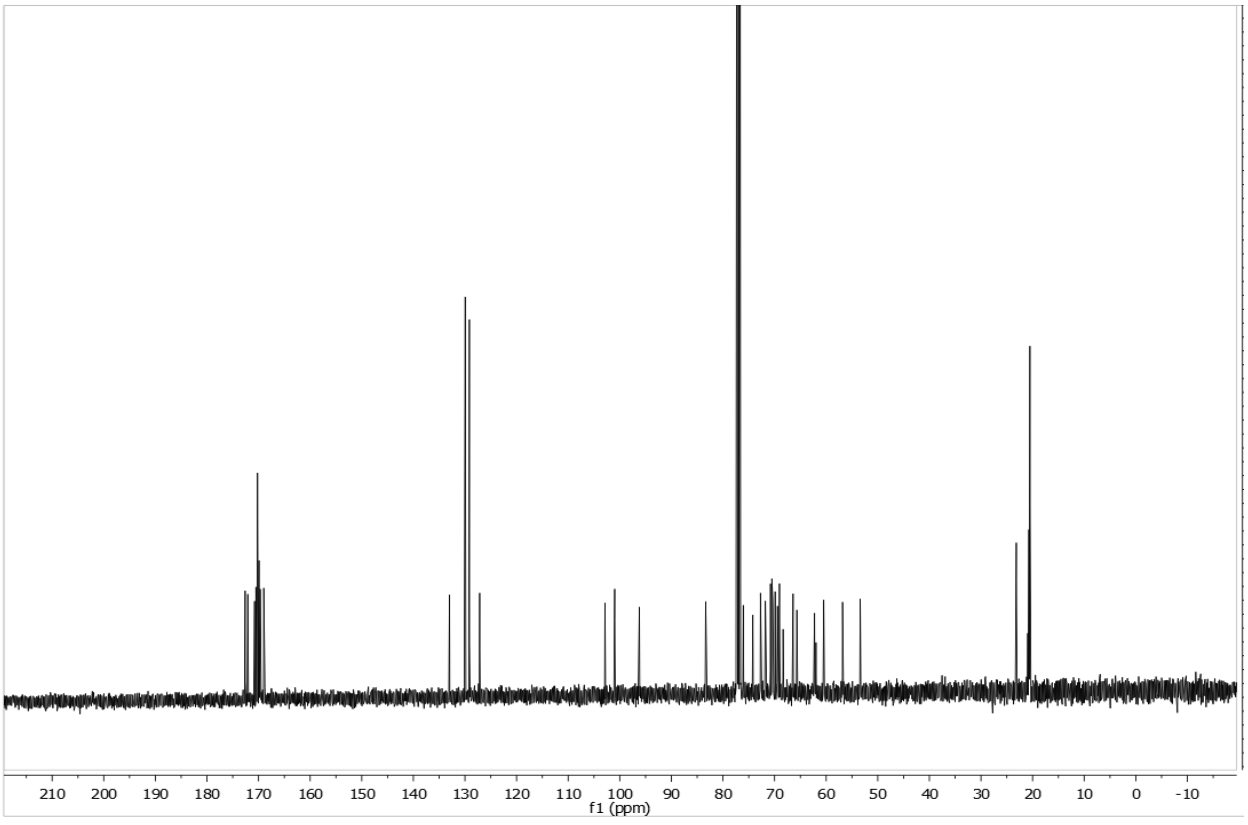
^{13}C NMR of Compound 10



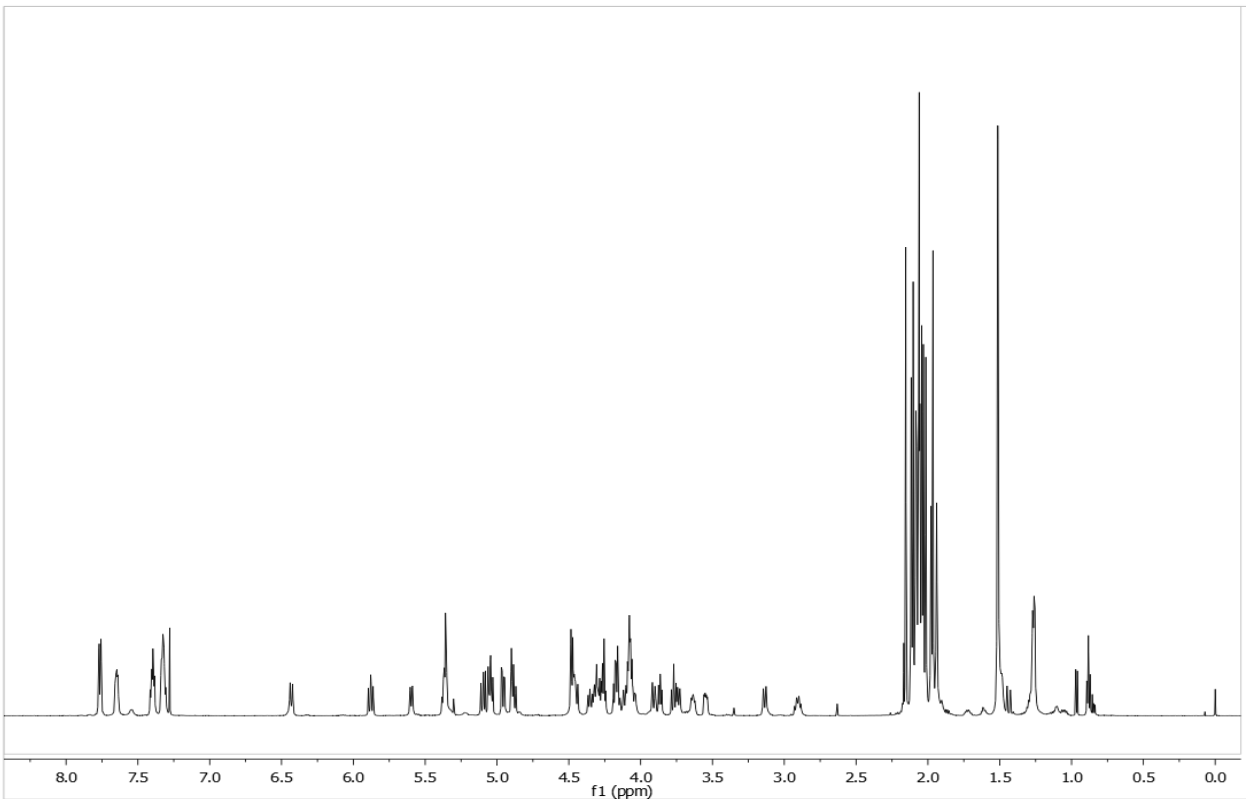
^{1}H NMR of Compound 11



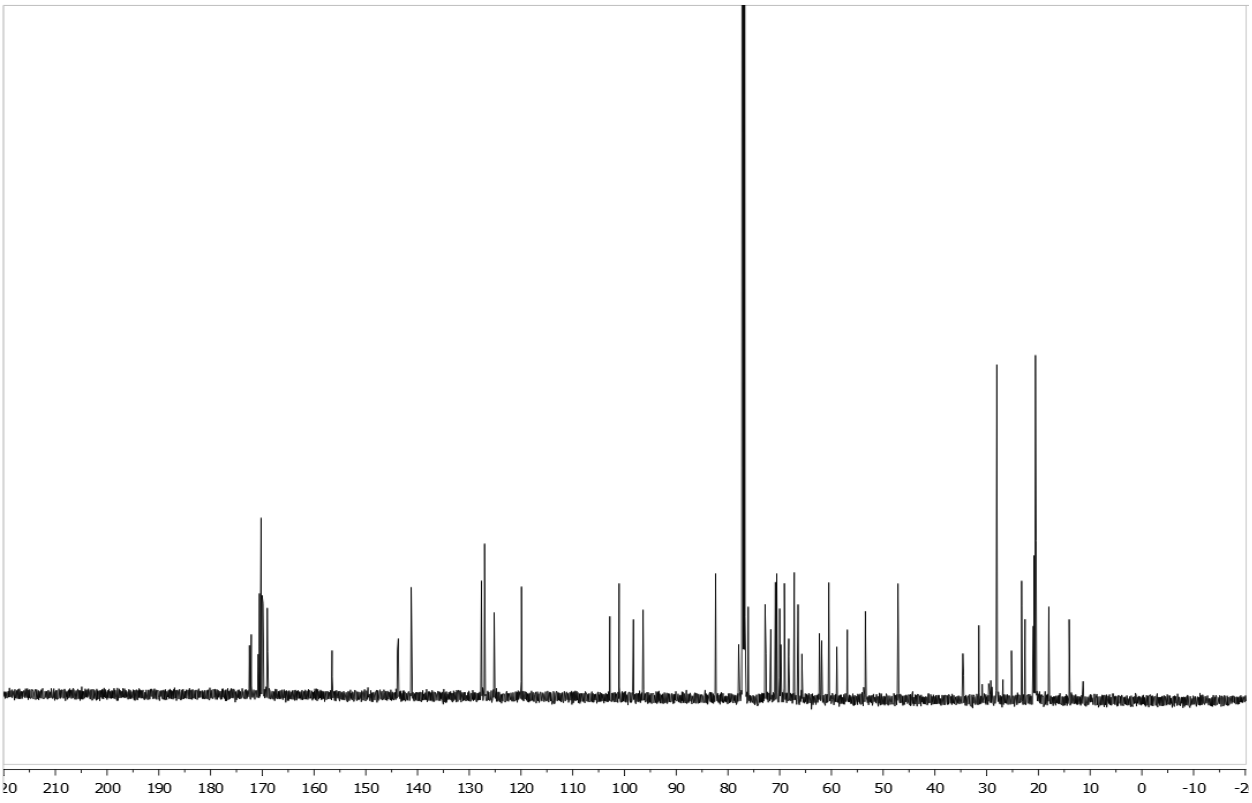
^{13}C NMR of Compound 11



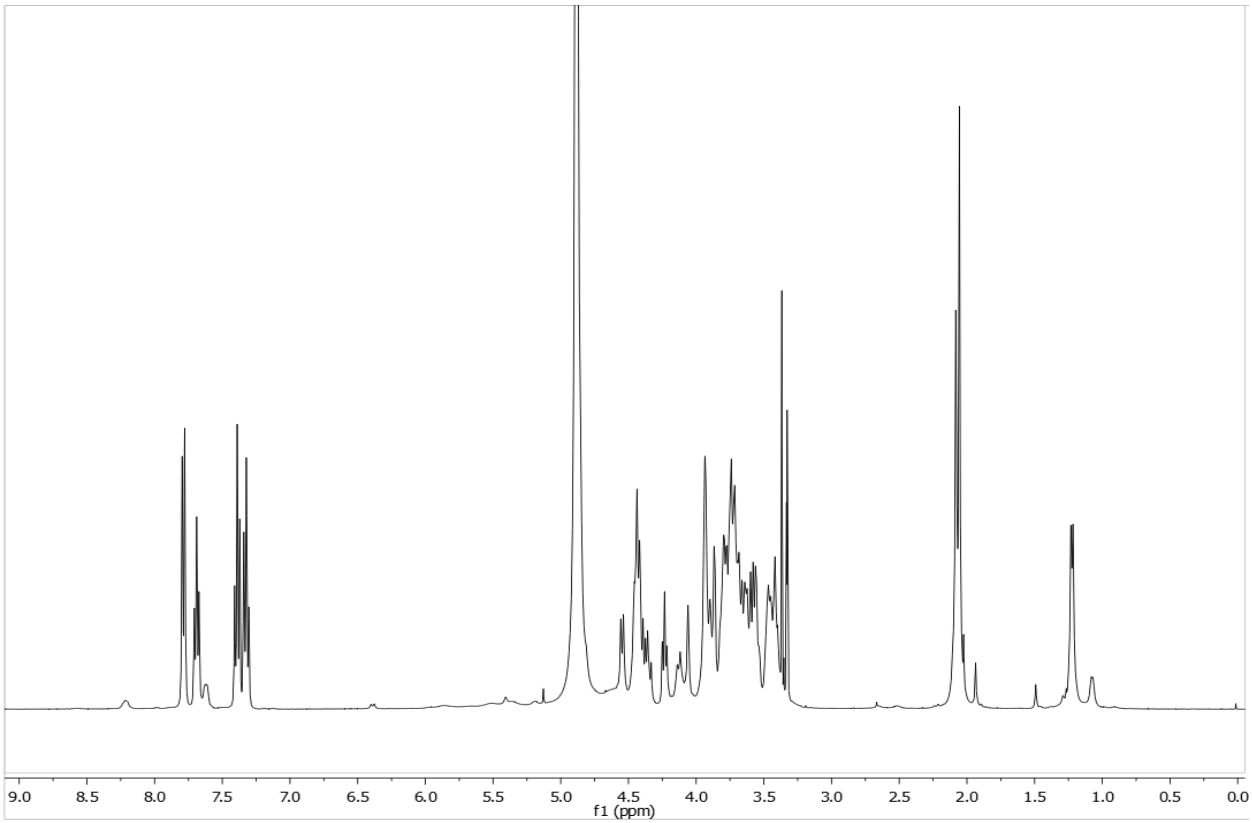
^{1}H NMR of Compound 12



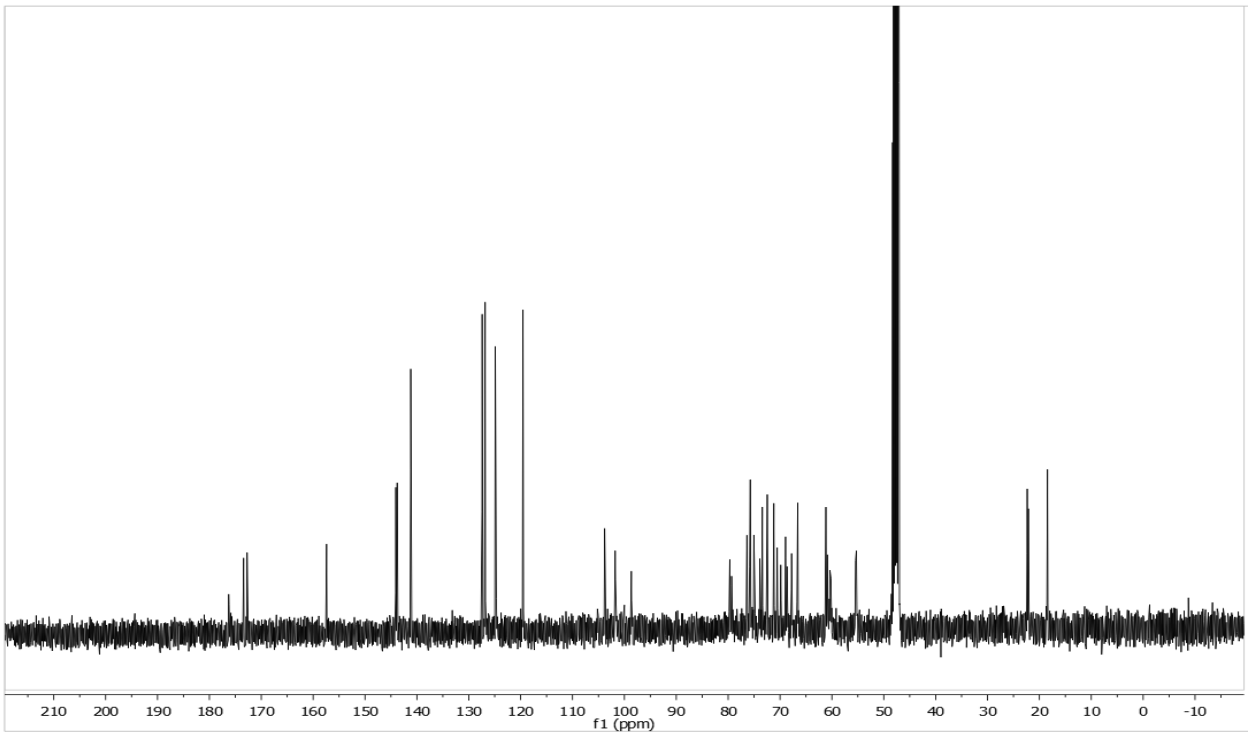
^{13}C NMR of Compound 12



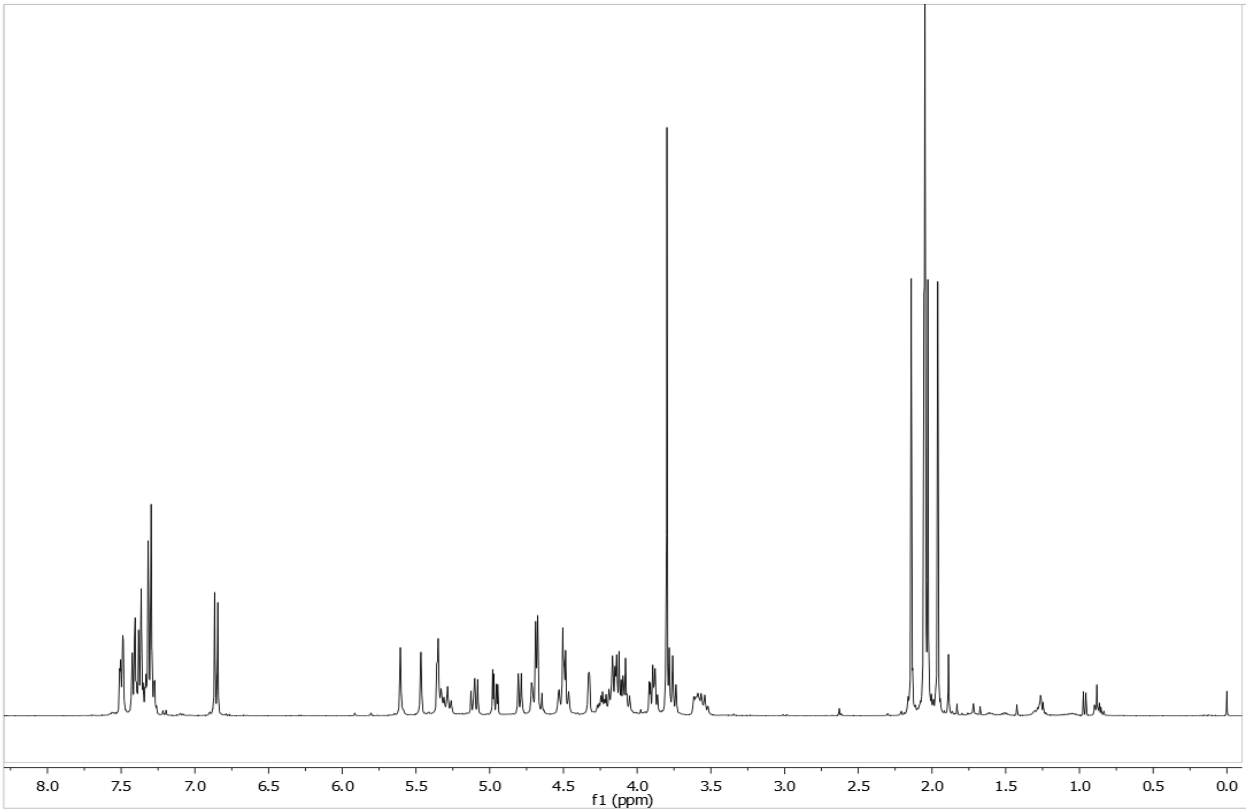
^{1}H NMR of Compound 13 (M301)



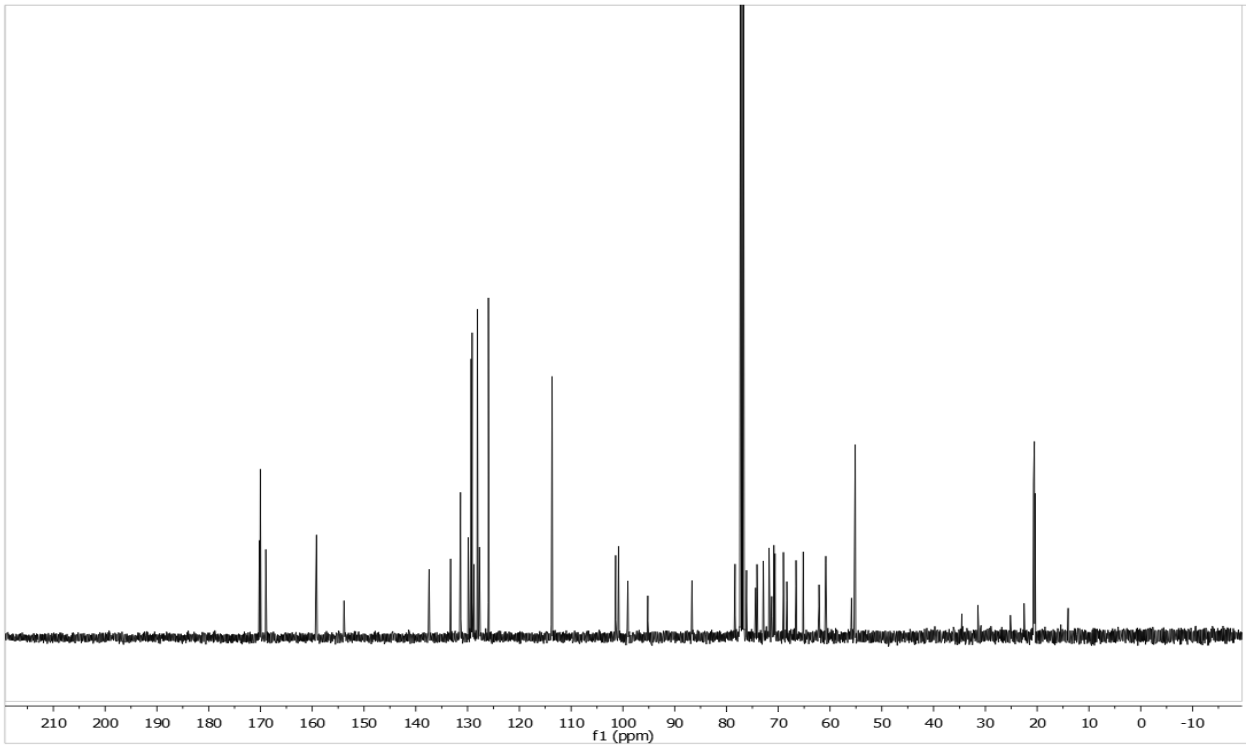
^{13}C NMR of Compound 13 (M301)



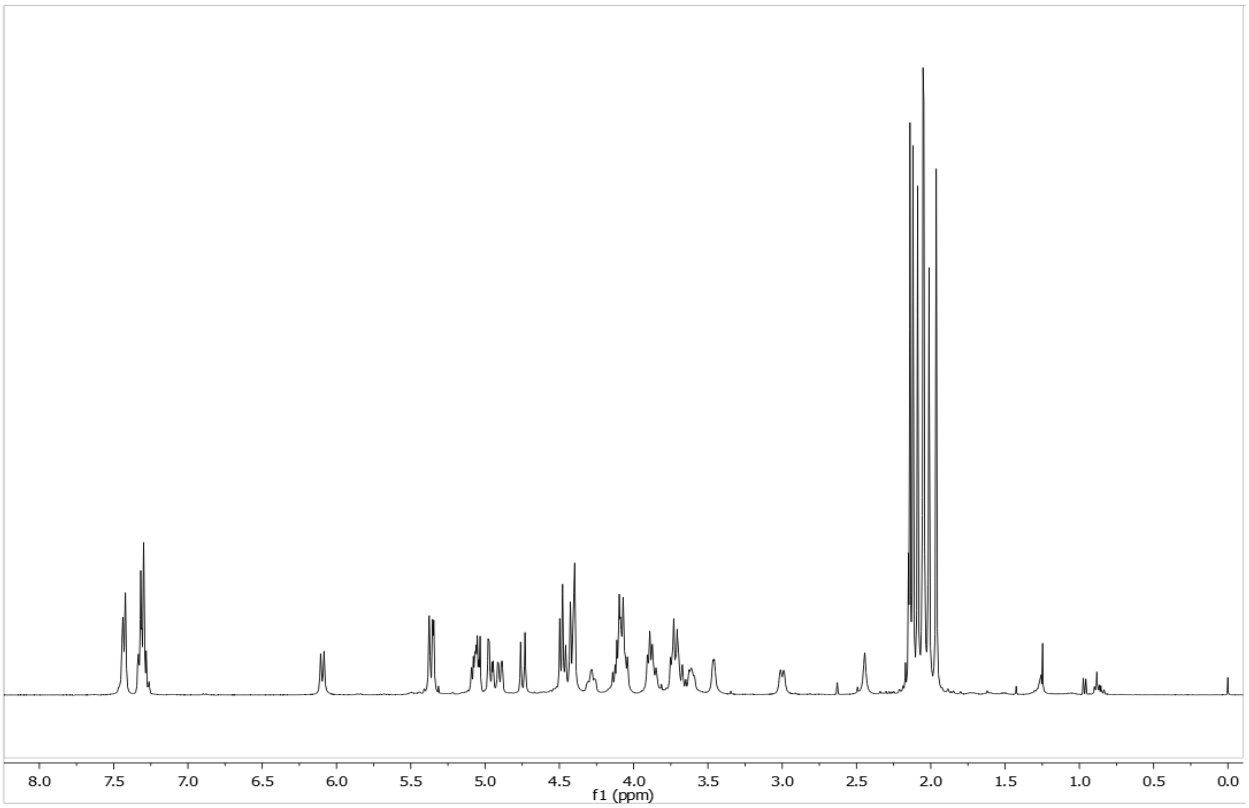
^{1}H NMR of Compound 14



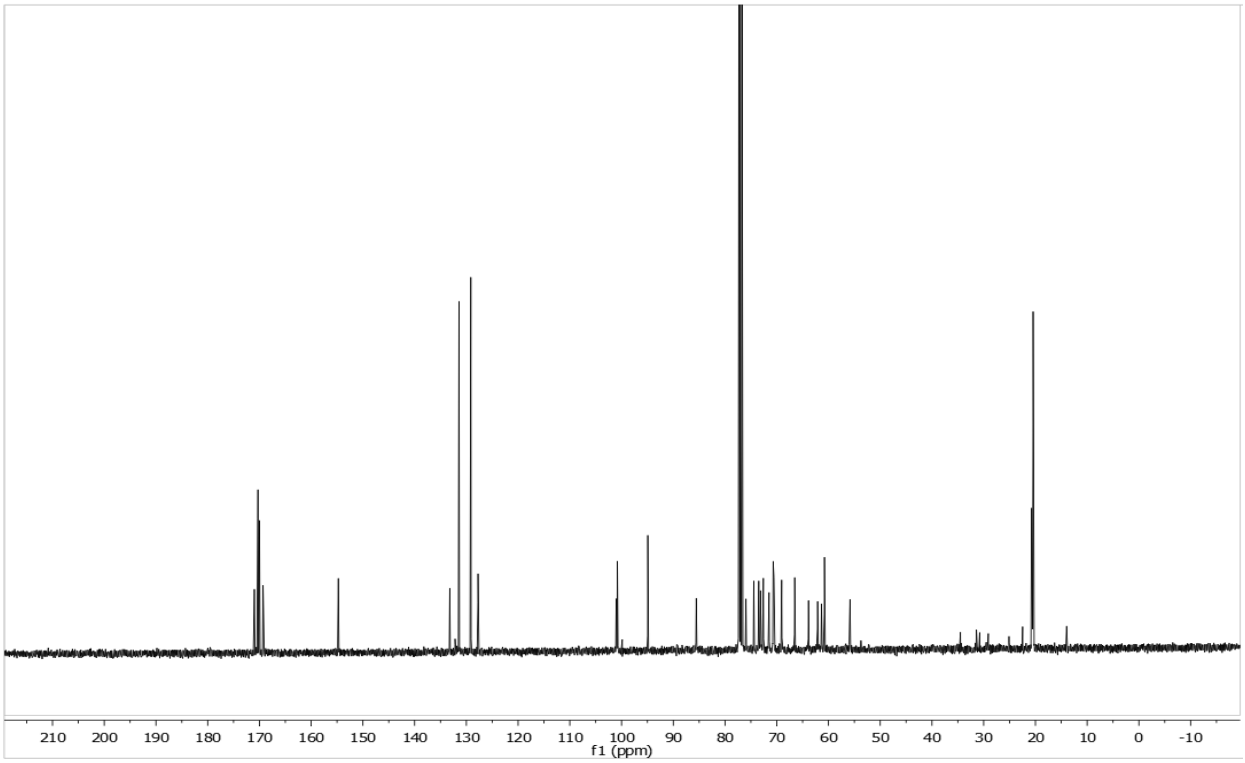
^{13}C NMR of Compound 14



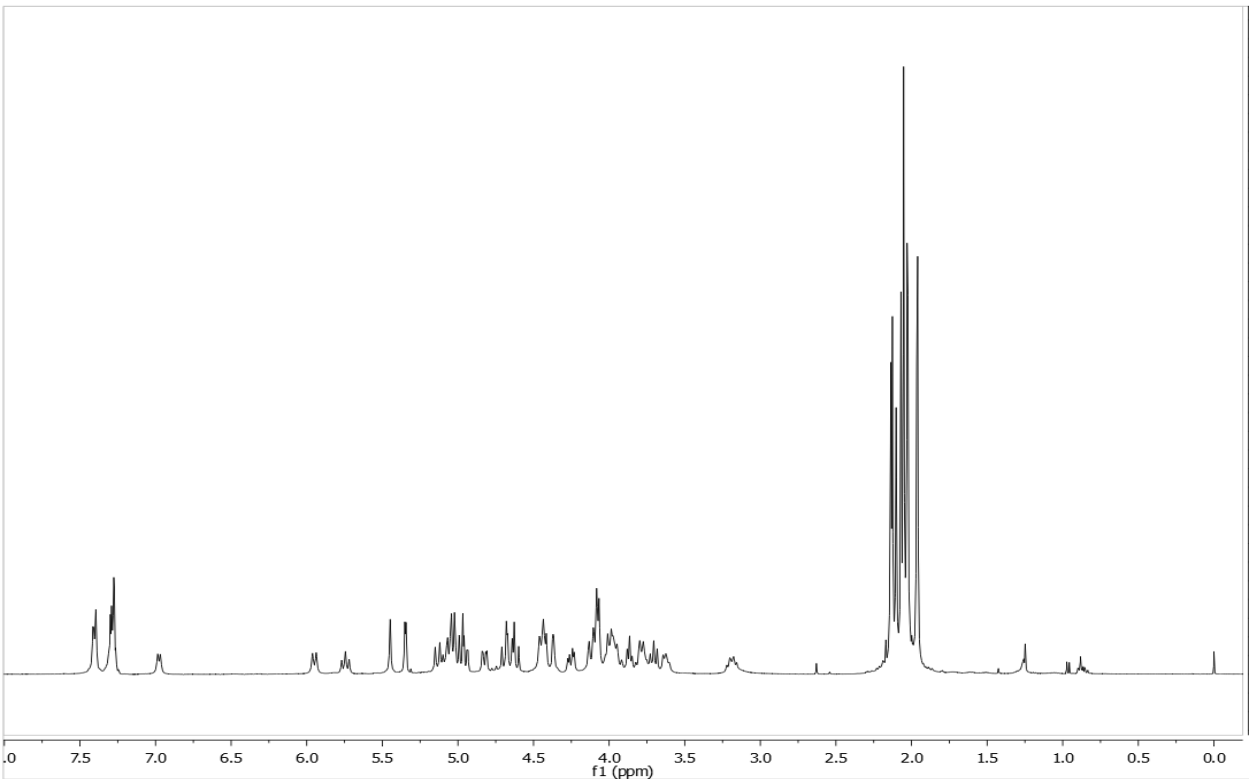
^{1}H NMR of Compound 15



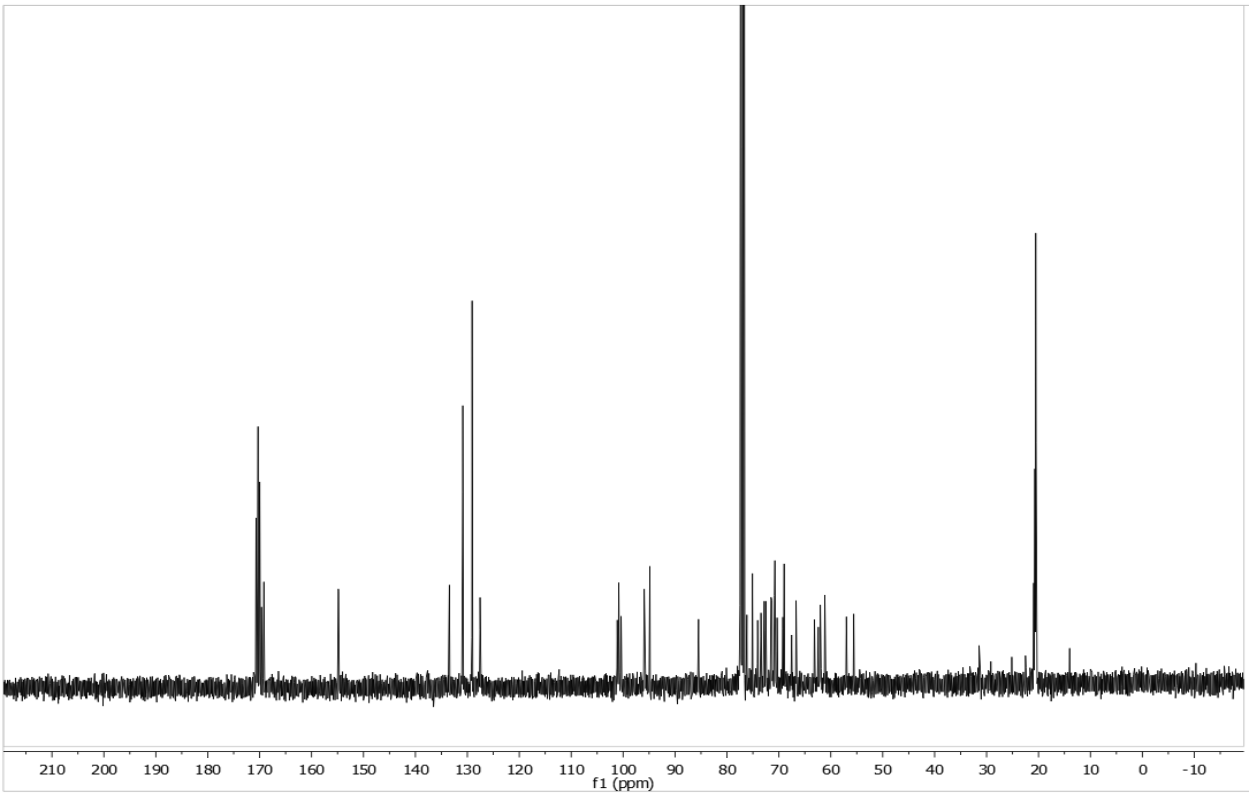
^{13}C NMR of Compound 15



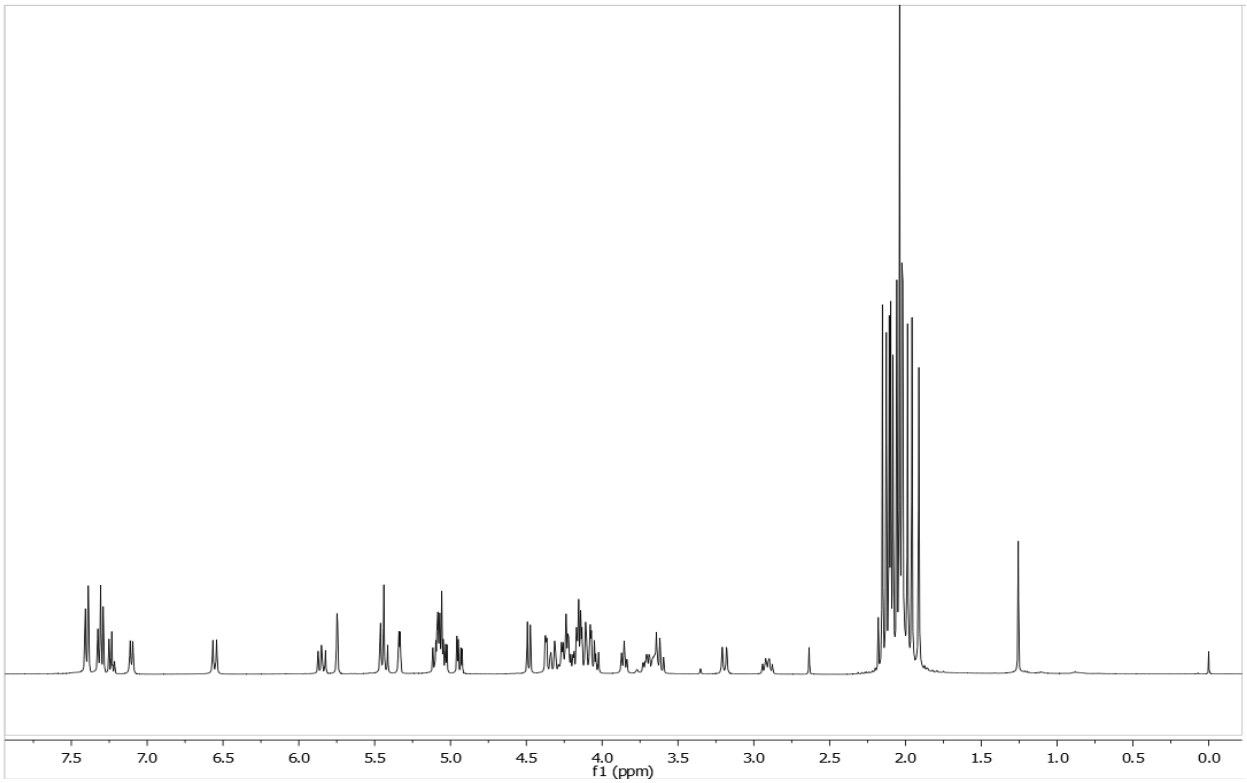
^{1}H NMR of Compound 16



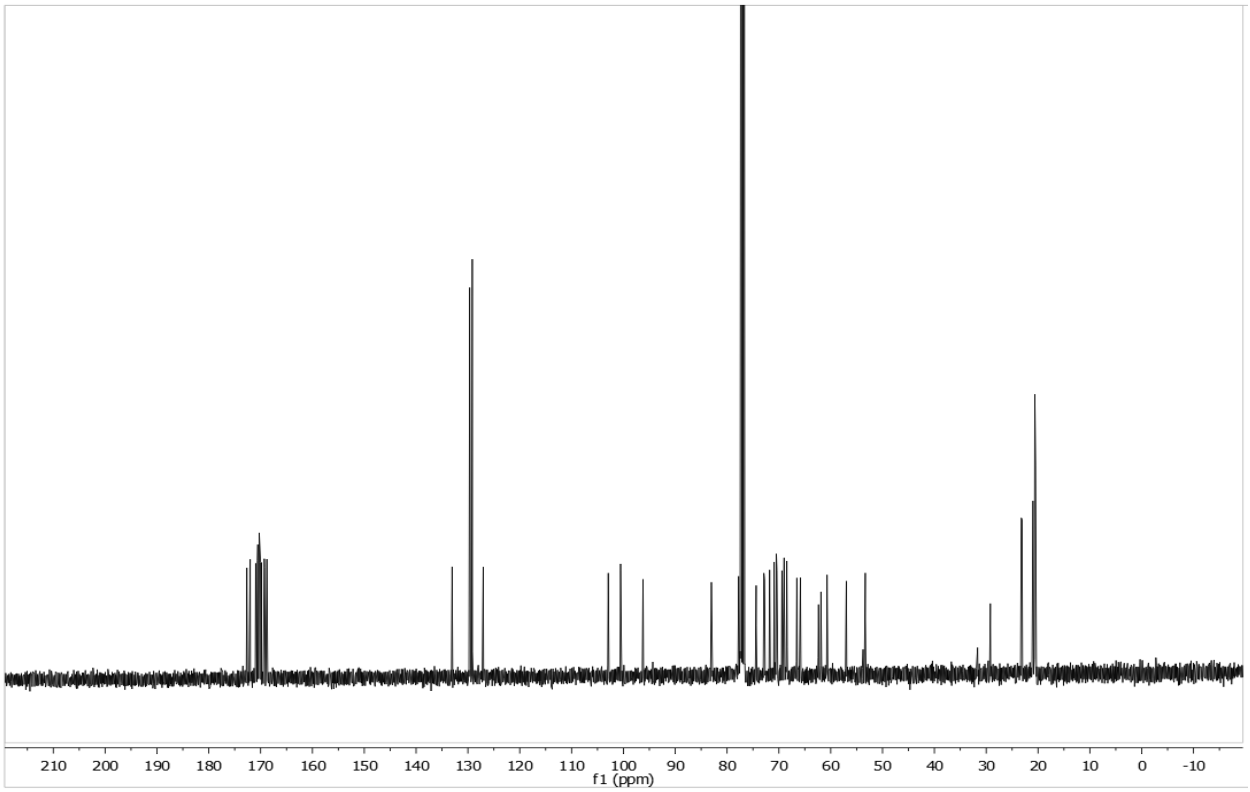
^{13}C NMR of Compound 16



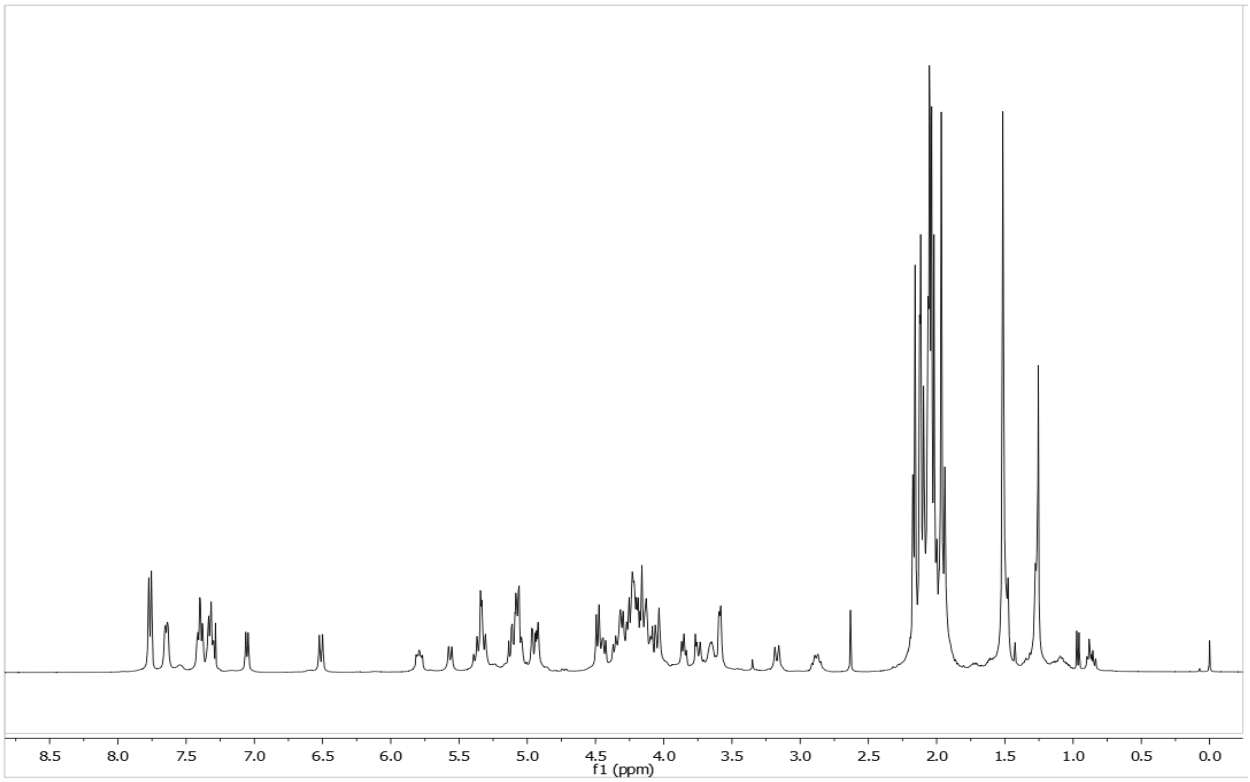
^{1}H NMR of Compound 17



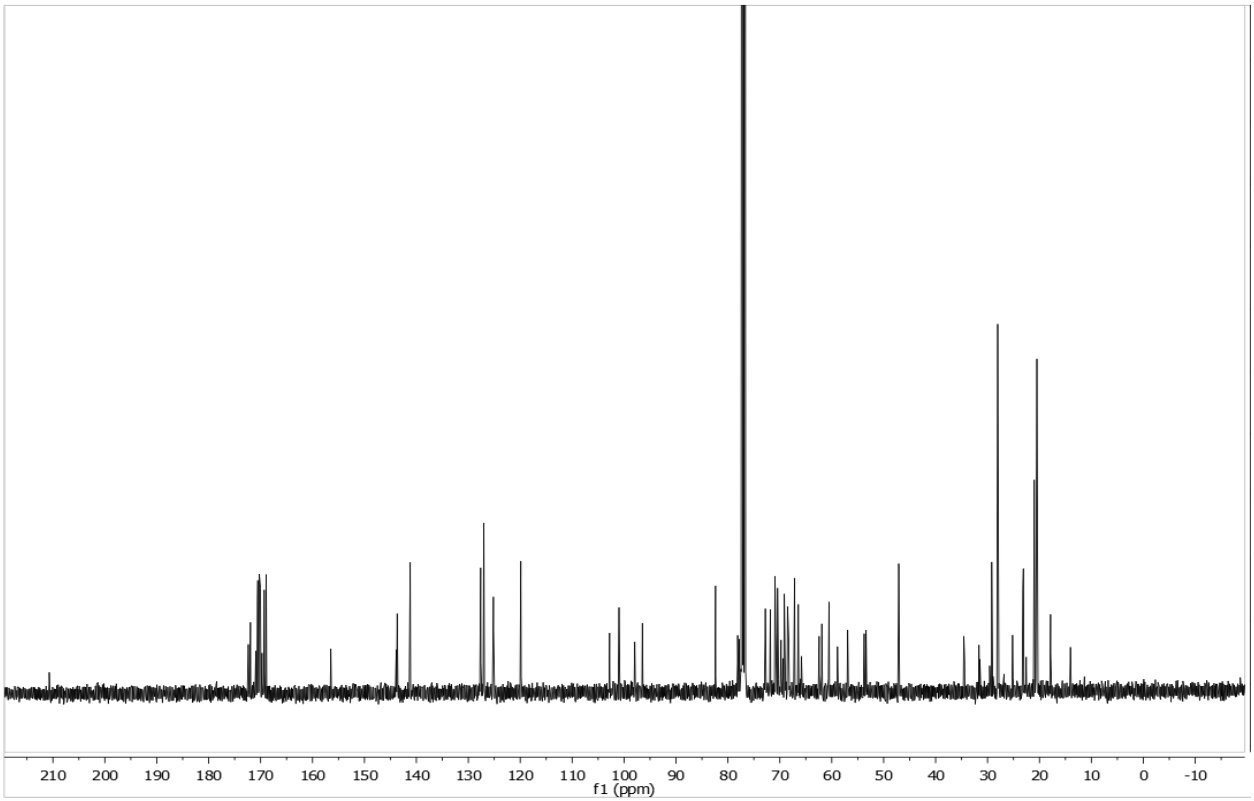
^{13}C NMR of Compound 17



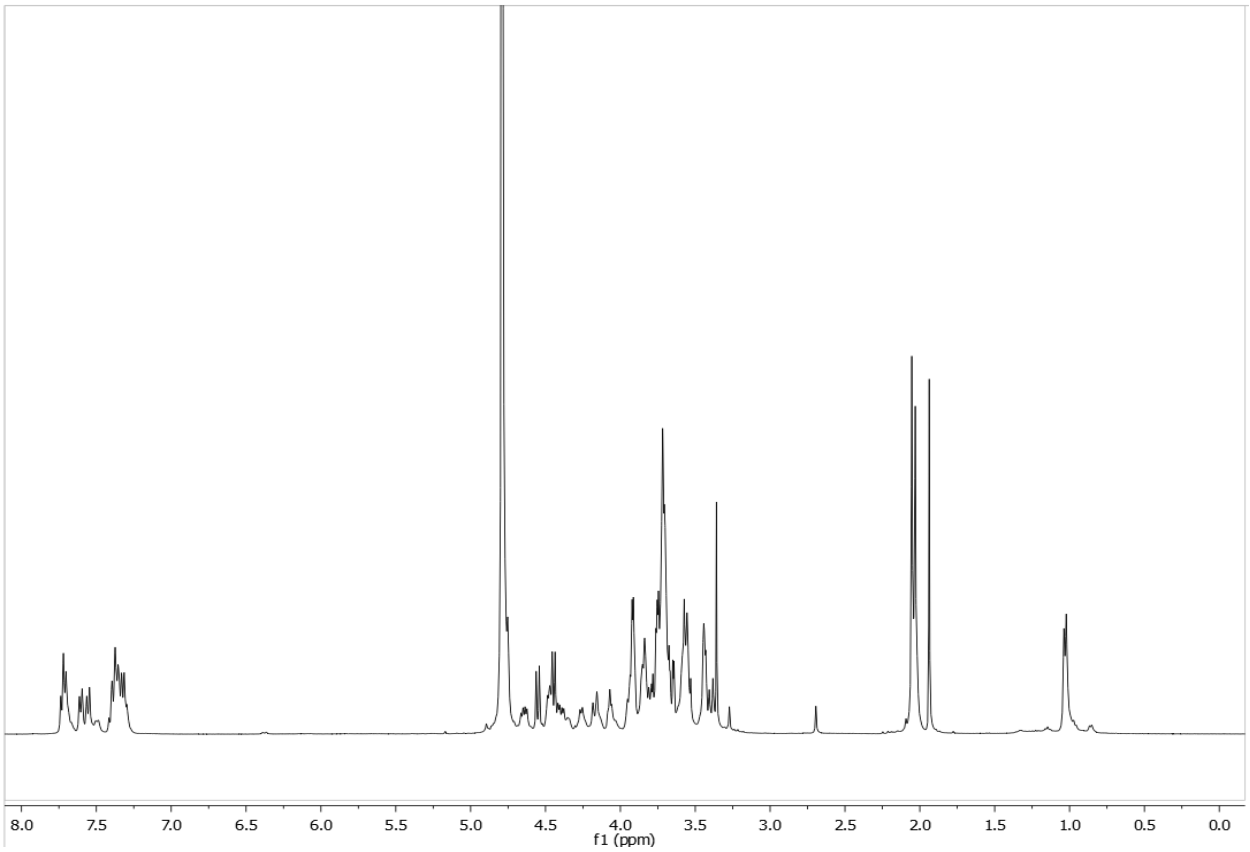
^{1}H NMR of Compound 18



^{13}C NMR of Compound 18



^{1}H NMR of Compound 19 (M201)



^{13}C NMR of Compound 19 (M201)