Facile Synthesis of Size Dependent Ru(II)- Carbohydrate Dendrimers via Click Chemistry

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1. General Information

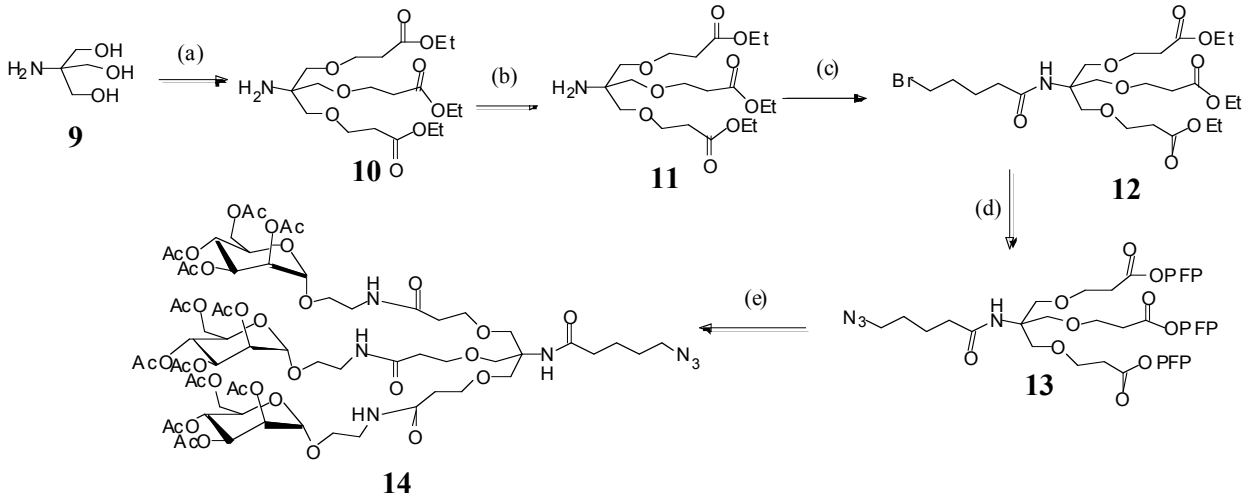
All chemicals used were reagent grade and used as supplied except where noted. Dichloromethane (CH_2Cl_2) was purified by a Cycle-Tainer Solvent Delivery System. Triethylamine was distilled over CaH_2 prior to use. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates (0.25 mm). Compounds were visualized by UV irradiation or dipping the plate in CAN solution followed by heating. Flash column chromatography was carried out using force flow of the indicated solvent on Fluka Kieselgel 60 (230-400 mesh).

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 (300 MHz) or Bruker DRX500 (500 MHz) spectrometer. High-resolution mass spectra (HR MALDI MS) were performed by the Mass Spectrometry-service at the Laboratory for Organic Chemistry at ETH Zurich and MPI Berlin. ESI-MS were run on an Agilent 1100 Series LC/MSD instrument. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer. Optical rotation measurements were conducted using a Perkin-Elmer 241 polarimeter.

$RuCl_3 \cdot xH_2O$ and 2,3,4,5,6-pentafluorophenol were purchased from Fluka. Acrylonitrile was purchased from Alfa Aesar and used directly in the reaction. ConcanavalinA and GNA were purchased from Appli Chem (Axon Lab AG). Synthesis of 2,2'-bipyridine-4,4'-dicarboxylic acid, *cis*-$Ru(bipy)_2Cl_2$ was carried out as described previously.[1] Absorption spectra were recorded using a Varian CARY 50 spectrophotometer fitted with Hellma optical fibers (Hellma, 041.002-UV) and an immersion probe made of quartz suprazil (Hellma, 661.500-QX). Fluorescence emission spectra were recorded on a Perkin-Elmer LS-50B spectrofluorometer.

Synthesis of 1 and 2.

Compound **10**, **11, 15, 16, 23** and **mannose-tripod** were synthesized according to published procedures.[2,3]



Scheme 1. Reagents and Conditions: (a) Acrylonitrile /NaOH (40%); (b) Conc HCl/EtOH, 51%; (c) bromo-pentanoic acid/DIC/HOBT/DCM, 69%; (d) NaN_3/DMF, NaOH/MeOH; pentafluorophenol (PFP)/DIC/HOBT/DCM, 86%; (e) 2-(*t*-butoxycarbonylamino)ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannoside. /DCM/TEA, 47%.

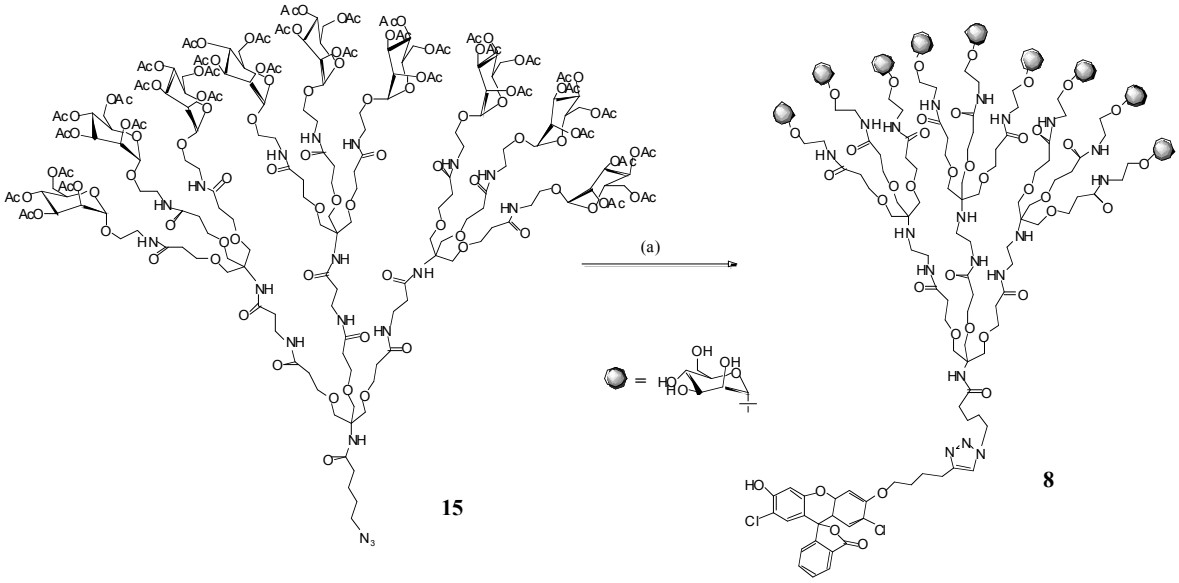
***N*-{Tris[3-[ethylcarboxyl-ethoxy)methyl]}methylamide}-5-bromo pentamide 12**. To a solution of *N*-{tris[(3-[ethylcarboxyl-ethoxy)methyl]}methylamine (5 g, 11.8 mmol) and 5-bromo valeric acid (2.1 g, 11.8 mmol) in dichloromethane (20 mL) at 0 °C, were added diisopropyl carbadiazime (2.25 ml, 12.2 mmol) and 1-hydroxybenzotriazole (0.15 g, 1.18 mmol) The reaction mixture was stirred at room temperature for 12 h and concentrated *in vacuo*. The crude residue was purified by flash silica column chromatography to yield *N*-{tris[3-[ethylcarboxyl-ethoxy)methyl]}methylamide}-3-bromo pentamide (4.8 g, 69%). R_f = 0.5 (CH_2Cl_2/MeOH, 98:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.14 (q, J = 7.2 Hz, 6H), 3.67 (br. s, 11H), 3.41 (t, J = 6.6 Hz, 2H), 2.52 (t, J = 6.0 Hz, 6H), 2.17 (t, J = 6.6 Hz, 2H), 1.9-1.7 (m, 4H), 1.6-1.4 (m, 2H), 1.24 (t, J = 6.9 Hz, 9H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.4, 171.4, 69.5, 66.5, 60.7, 60.3, 35.2, 33.4, 33.3, 24.5, 14.1, FTIR($CHCl_3$): 3390, 2982, 2873, 1734, 1726, 1643, 1521 cm^{-1}. HRMS (MALDI-ToF) (*m/z*) calcd. for $C_{24}H_{42}BrNO_{10}Na$ 606.1884, found: 606.1878.

***N*-{Tris[3-[ethylcarboxyl-ethoxy)methyl]}methylamide}-5-azido pentamide**. *N*-{tris[(3-[ethylcarboxyl-ethoxy)methyl]}methylamine}-5-bromo pentamide (3.0 g, 5.14 mmol) and sodium azide (1.34 g, 20.58 mmol) in anhydrous DMF (20 mL) were mixed and stirred at 70 °C for 24 h. The crude residue was dissolved in 20 mL water and extracted with 40 mL ethyl acetate. The organic layer was washed five times with 20 mL water and concentrated *in vacuo*. The crude product was purified by flash silica column chromatography to yield *N*-{tris[3-[ethylcarboxyl-ethoxy)methyl]}methylamide}-5-azido pentamide (2.35 g, 72%). R_f = 0.5 (CH_2Cl_2/MeOH, 98:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.14 (q, J = 7.2 Hz, 6H), 3.69 (br. s, 11H), 3.31 (t, J = 6.6 Hz, 2H), 2.52 (t, J = 6.0 Hz, 6H), 2.18 (t, J = 6.6 Hz, 2H), 1.71-1.62 (m, 6H), 1.27 (t, J = 6.9 Hz, 9H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.4, 171.5, 69.1, 66.6, 60.3, 51.1, 36.2, 35.3, 28.2, 32.6, 20.8, 14.1, FTIR($CHCl_3$): 3390, 2982, 2873, 1734, 1726, 1643, 1521 cm^{-1}. HRMS (MALDI-ToF) (*m/z*) calcd. for $C_{24}H_{42}N_4O_{10}Na$ 569.2793, found: 569.2802.

***N*-{Tris[3-[pentafluoro phenyl carboxyl-ethoxy)methyl]}methyl amide}-5-azido pentamide 13.** *N*-{Tris[3-[ethylcarboxyl-ethoxy)methyl]} methylamine}-5-azido pentamide (2.5 g, 3.57 mmol) was dissolved in ethanol (20 mL) and sodium hydroxide solution (aqueous, 1 N, 2 mL) was added and the mixture was stirred at room temperature for 2 h, concentrated in *vacuo*, adjusted to pH 5 with hydrochloric acid (aqueous 1 N, 3 mL) and extracted with ethyl acetate.

The organic layer was dried with sodium sulfate and concentrated to dryness under reduced pressure. The residue was dissolved in dichloromethane (10 mL) and 2,3,4,5,6-pentafluorophenol (4.2 g, 17.8 mmol) was added. After cooling to 0 °C, diisopropyl carbadiazine (3.95 mL, 19.9 mmol) was added and the reaction mixture was stirred for 12 h at room temperature. The reaction mixture was concentrated in *vacuo* and purified by silica column flash chromatography to afford *tert*-butoxycarbonyl-3-{*N*-{tris[3-[pentafluorophenylcarboxyl-ethoxy)methyl]}methylamide}-5-azido pentamide (3.7 g, 86%). R_f = 0.6 (CH_2Cl_2/EtOH, 88:12); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (br. s, 12H), 3.24 (t, J = 6.6 Hz, 2H), 2.92 (t, J = 6.0 Hz, 7H), 2.17 (t, J = 6.6 Hz, 2H), 1.71-1.62 (m, 6H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 69.9, 65.9, 59.6, 36.6, 34.1, 28.2, 24.2. FTIR($CHCl_3$): 3688, 3385, 1749, 1658, 1522, 1359 cm^{-1}. HRMS (MALDI-ToF) (*m/z*) calcd. for $C_{36}H_{27}F_{15}N_4O_{10}Na$ 983.1385, found: 983.1388.

***Tris*[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy]methyl]methylamide }-5-azido pentamide 14.** 2-(*tert*-Butoxycarbonylamino)ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside **8** (0.97 g, 1.96 mmol) was dissolved in 10 mL dichloromethane/trifluoroacetic acid (3:1) and stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure and the resulting oil was dissolved in anhydrous dichloromethane (20 mL). To this mixture was added *tert*-butoxycarbonyl-3-{*N*-{tris[3-[pentafluoro-phenyl-carboxyl-ethoxy)methyl]}methyl amine}-3-*β*-alanine **4** (0.5 g, 0.49 mmol) adjusted to pH 8 with triethylamine (TEA) and the mixture was stirred at room temperature for 12 h. The solvent was evaporated *in vacuo* and purified by flash silica column chromatography (0.37 g, 47%). R_f = 0.45 (CH_2Cl_2/MeOH, 93:7); $[\alpha]_D^{r.t}$ = +21.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.79 (br.s, 2H), 6.43 (br.s, 1H), 5.30 (br.s, 1H), 5.27-5.20 (m, 9H), 4.80 (s, 3H), 4.25 (dd, J = 9.0, 5.1 Hz, 3H), 4.10 (dd, J = 2.1, 9.9 Hz, 3H), 3.90 (br.s, 3H), 3.76 (dd, J = 4.5, 5.4 Hz, 3H), 3.68 (dd, J = 5.4, 6.0 Hz, 6H), 3.64 (s, 6H), 3.54-3.52 (m, 6H), 3.37 (br.s, 8H), 2.42 (t, J = 5.4 Hz, 6H), 2.12 (s, 9H), 2.07 (s, 9H), 2.02 (s, 9H), 1.96 (s, 9H), 1.71-1.62 (m, 6H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.4, 170.5, 170.0, 169.5, 155.8, 97.6, 69.3, 69.2, 68.6, 67.3, 67.1, 66.0, 62.4, 59.8, 39.0, 37.9, 36.5, 23.5, 20.3; FTIR($CHCl_3$): 3376, 2918, 1751, 1663, 1515, 1457, 1250 cm^{-1}; HRMS (MALDI-ToF) (*m/z*) calcd. for $C_{69}H_{105}N_5O_{39}Na$ 1580.6080; found: 1580.6076.



Scheme 2. Reagents and Conditions: (a) $CuSO_4$/ascorbic acid/THF:H_2O(1:1); NaOMe, MeOH.

General Procedure A: Click Reaction.

The azide-tripodal sugar (2.0 eq per alkyl group) and acetylene-fluorescent probe (1 eq) were dissolved in 10 mL tetrahydrofuran/water (2:1). To this mixture, copper sulfate (2 eq per alkyl group) and ascorbic acid (2 eq per alkyl group) were added and stirred at room temperature for 12 h. The solvent was evaporated *in vacuo* and purified by flash silica column chromatography.

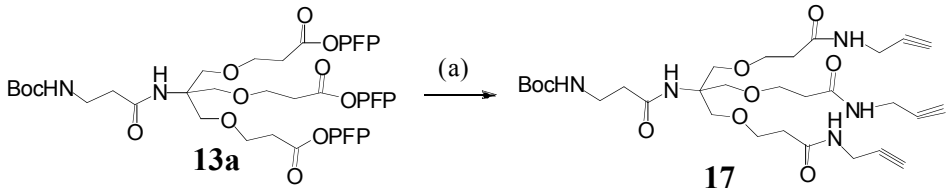
General Procedure B: Synthesis of Fluorescent-Sugar Complex.

Ruthenium(II) complex or fluorescein-dendrimer (1.0 eq) and sodium methoxide (10 eq) were dissolved in methanol (10 ml) and stirred at room temperature for 2 h. The solvent was then evaporated *in vacuo*, the residue was redissolved in water and dialyzed against water using 500 molecular weight cut-off resin. After two days of dialysis the sample was lyophilized.

(ii) 2,7-Dichlorofluorescein 3'-butyl-triazole-3'-{tris[2'-ethoxy-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside-ethoxy]methyl]methylamide}-5-pentamide 15. General procedure A with 2,7-dichlorofluorescein-propylene (5 mg, 0.012 mmol), 3-{tris[3-carboxyl ethoxy]methyl] 3'-{tris[2'-ethoxy-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside-ethoxy]methyl]methylamide}-5-azido pentamide (30 mg, 6.01 μmol), copper sulfate (1.8 mg, 0.012 mmol), ascorbic acid (2.1 mg, 0.012 mmol) and flash silica column chromatography by using CH_2Cl_2/CH_3OH (17-20%) as eluent yielded 27 mg (84%) of 2,7-dichlorofluorescein-3'-propyl-triazole-3'-{tris[2'-ethoxy-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside-ethoxy]methyl]methylamide}-5-pentamide R_f 0.5 (CH_2Cl_2: MeOH = 87:13); $[\alpha]_D^{r.t}$ = +11.2 (c =1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21-

8.07 (m, 1H), 7.78-7.69 (m, 2H); 7.58 (br, 1H); 7.39 (br, 1H); 7.31 (br, 1H); 7.28-7.18 (m, 1H); 6.75 (m, 1H); 5.27-5.22 (m, 27H); 4.29 (dd, J = 9.0, 5.1 Hz, 9H); 4.21 (s, 4H); 4.18-4.04 (m, 9H); 3.82-3.74 (m,12H); 3.77-3.54 (br.s, 64H); 3.59-3.55 (m, 16H); 3.56-3.37 (m, 38H); 2.57 (br, 2H); 2.47 (br, 32H); 2.13 (s, 27H); 2.06 (s, 27H); 2.04 (s, 27H); 1.96 (s, 27H); 1.72 (br, 2H); 1.47 (br, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 173.5; 171.1, 170.3, 170.2, 162.3, 156.3, 154.1, 151.8, 138.3, 135.5, 131.2, 130.6, 128.7, 127.1, 124.2, 123.1, 98.5, 68.9, 98.1, 66.7, 66.1, 63.1, 60.2, 39.3, 37.5, 24.8, 18.4. HRMS-MALDI (m/z): $[M+ Na]^+$ Calcd for $C_{236}H_{335}N_{19}O_{123}Cl_2$ 5495.9818; Found : 5495.9821.

(ii) 2,7-Dichlorofluorescein 3'-butyl-triazole-3'-{tris[2'-ethoxy-α-D-mannopyranoside -ethoxy]methyl]methylamide}-5-pentamide. General procedure C with 2,7-dichlorofluorescein 3'-propyl-triazole-3'-{tris[2'-ethoxy-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside-ethoxy] methyl]methylamide}-5-pentamide (25 mg, 4.6 μmol) and sodium methoxide (1 mg) gave 12 mg (61%) of 2,7-dichlorofluorescein 3'-propyl-triazole-3'-{tris[2'-ethoxy-α-D- mannopyranoside ethoxy] methyl]methylamide}-5-pentamide $[\alpha]_D^{r.t}$ = +22.4 (c =1.0, H_2O); ^{1}H-NMR (300MHz, CD_3OD): δ 8.21 (d, J = 2.7 Hz, 1H), 7.77-7.69 (m, 2H); 7.58 (d, J = 3.0 Hz, 1H); 7.37 (br, 1H); 7.31 (d, J = 2.7 Hz, 1H); 7.18 (d, J = 3.0 Hz, 1H); 6.87-6.75 (m, 2H); 4.78 (s, 9H); 3.74-3.62 (m, 110H); 3.54 (m, 26H); 3.51-3.41 (m, 24H); 2.57 (br, 2H); 2.47 (br, 32H); 1.47 (br, 2H); 1.07 (br, 2H); ^{13}C-NMR (125MHz, MeOD/D_2O): δ 167.3, 156.3, 153.7, 151.2, 144.2, 138.3, 135.6, 134.2, 133.5, 131.2, 130.6, 100.6, 73.7, 70.8, 70.3, 68.8, 67.2, 66.1, 61.7, 58.9, 37.6, 35.7, 24.3, 18.7. MALDI-HRMS (m/z): $[M+1]^+$ Calcd for Calcd for $C_{166}H_{266}N_{19}O_{88}Cl_2$ 4003.6222; Found : 4003.624.

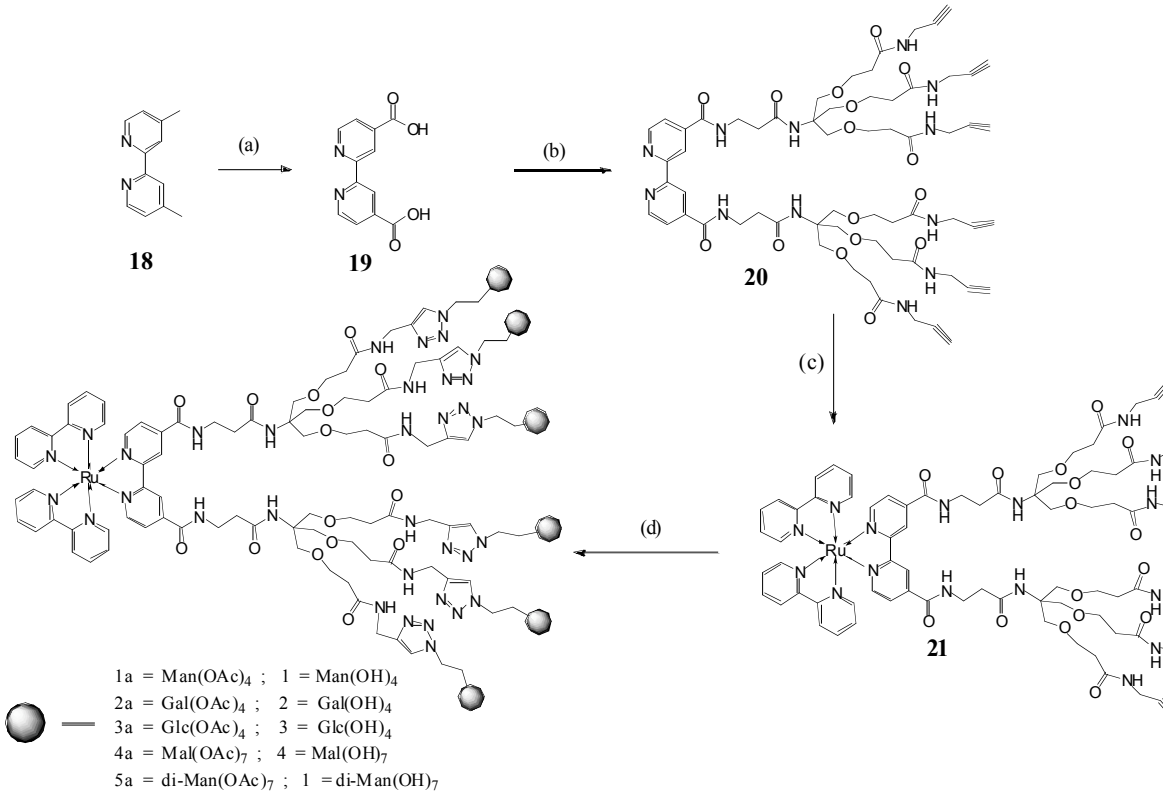


13a **17**

Scheme 3. Reagents and Conditions: (a) propargyl amine/TEA/DCM,

***tert*-Butoxycarbonyl-3-{*N*-{tris[3-[propargyl-methyl]}methylamide}-3-*β*-alanine 17.** Propargylamine (0.11 g, 1.98 mmol), *tert*-butoxycarbonyl-3-{*N*-{tris[3-[pentafluoro phenyl carboxyl-ethoxy)methyl]}methyl amide}-3-β-alaine (0.5 g, 0.49 mmol) were dissolved in 10 mL

of DCM, adjusted to pH 8 with triethylamine (TEA) and the mixture stirred at room temperature for 12 h. The solvent was evaporated *in vacuo* and purified by flash silica column chromatography using CH_2Cl_2/CH_3OH (6-7%) as eluent yield *tert*-butoxycarbonyl-3-{*N*-{tris[3-[propagyl-methyl]}methyl amide}-3-*β*-alanine (0.23 g, 77%). R_f = 0.45 (CH_2Cl_2/MeOH, 93:7); ^{1}H NMR (300MHz, $CDCl_3$): *δ* 7.58 (br, 1H); 7.29 (br, 2H); 6.45 (br, 1H); 5.43 (br, 1H), 3.89 (dd, *J* = 3.6 Hz, 6H); 3.59-3.51 (m, 12H); 3.26 (q, *J* = 4.2 Hz, 2H); 2.39 (t, *J* = 3.6 Hz, 6H); 2.23 (s, 3H); 1.43 (br, 9H). ^{13}C NMR (75MHz, $CDCl_3$): *δ* 172.1, 69.5, 68.4, 66.3, 60.5, 60.3, 54.3, 35.1, 25.2, 15.6. HRMS (MALDI-ToF) (*m/z*) calcd. for $C_{30}H_{45}N_5O9Na$ 642.3117, found: 642.3122.



Scheme 4. Reagents and Conditions: (a) CrO_3/Conc H_2SO_4, 98%, (b) Comp **16**/TEA/DCM, 12 h, 63%, (c) *cis*-Ru(bipy)$_2Cl_2$/EtOH, 12 h, 52%, (d) $CuSO_4$/ascorbic acid/THF:H_2O (1:1) 12 h. 86-91%; NaOMe, MeOH.

General Procedure C: Synthesis of Bipyridine Derivatives.

2,2'Bipyridine-4,4'-dicarboxylic acid (1.0 eq) was dissolved in $SOCl_2$ (1 mL) and refluxed under nitrogen for 12 h. Excess $SOCl_2$ was removed in *vacuo* and the crude 2,2'bipyridine-4,4'-dicarboxylic acyl chloride was used directly in the next step. Boc-protected amino-tripod (3.0 eq)

was dissolved dichloromethane/trifluoroacetic acid (10 mL, 3:1 resp) and stirred at room temperature for 1 h. The mixture was concentrated *in vacuo* and then redissolved in dichloromethane (20 mL). To this mixture was added 2,2'bipyridine-4,4'-dicarboxylic acyl chloride (1 eq) and the pH adjusted using TEA to pH 8. The reaction mixture was stirred for 12 h, the solvent removed *in vacuo* and the mixture purified by silica column flash chromatography.

General Procedure D: Synthesis of Ruthenium(II)-complexes.

The bipyridine-sugar derivative (1.0 eq) and *cis*-ruthenium(II)bis(bipyridine)dichloride (1.1 eq) were dissolved in de-oxygenated ethanol (30 mL) and the mixture was refluxed for 6-8 h. The compound was then purified by silica column flash chromatography.

(i) 1,1'-(2,2'-Bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[propargyl-methyl]methyl amide 20. General procedure C with *tert*-butoxycarbonyl-3-{*N*-{tris[3-[propagyl-methyl]}methyl amide}-3-*β*-alanine (0.2 g, 0.32 mmol), 2,2'bipyridine-4,4'-dicarboxylic acid (26 mg, 0.11 mmol) and flash silica column chromatography by using CH_2Cl_2/CH_3OH (7-8%) as eluent yielded 1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[propargyl-methyl]methyl amide **20** (0.29 g, 69%). R_f = 0.5 (CH_2Cl_2/MeOH, 92:8); ^{1}H NMR (300 MHz, MeOD): δ 8.85 (dd, J = 4.5 Hz, 4H); 7.75 (d, J = 5.4 Hz, 2H); 3.87 (br, 12H); 3.59-3.51 (m, 24H); 3.24 (br, 4H); 2.59 (t, J = 5.4 Hz, 12H); 2.24 (t, J = 5.4 Hz, 12H); ^{13}C NMR (75MHz, $CDCl_3$): δ 173.7, 163.1, 162.6, 121.2, 115.3, 80.1, 72.3, 67.3, 60.3, 54.3, 37.1, 27.2, HRMS-MALDI (m/z): $[M+ Na]^+$ Calcd for $C_{63}H_{82}N_{12}O_{16}Na$ 1285.5869; Found: 1285.5876.

(ii) *Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-Bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[propargyl-methyl]methyl amide 21. General procedure D with *cis*-ruthenium(II) bis (bipyridine)dichloride (46 mg, 0.095 mmol) and 1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[propargyl-methyl]methyl amide (0.1 g, 0.079 mmol) and purification by flash silica column chromatography by using acetronitrile/water/saturated KNO_3 (8:1.5:0.5) as eluent yielded *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[propargyl-methyl]methyl amide **21** (68 mg, 51%). R_f = 0.5 (acetonitrile/sat aq. KNO_3, 85:15); ^{1}H NMR (300 MHz, CD_3OD): δ 9.18 (br.s, 2H); 8.72 (d, J = 7.1 Hz, 4H), 8.18 (t, J = 5.4 Hz, 4H), 8.14 (d, J = 4.8 Hz, 4H), 7.85 (dd, J = 5.7, 4.8 Hz, 6H), 7.52 (t, J = 4.5 Hz, 4H), 7.36 (br.s, 1H), 3.87 (br, 12H); 3.59-3.51 (m, 24H); 3.24 (br, 4H); 2.59 (t, J = 5.4 Hz, 12H); 2.24 (t, J = 5.4 Hz, 12H); ^{13}C NMR (75MHz, CD_3OD): δ 173.7, 165.2, 158.5, 157.8, 153.1, 152.5, 152.1, 143.3,

139.1, 128.7, 126.2, 125.3, 123.2, 80.1, 72.3, 69.3, 67.8, 60.3, 37.1, 27.2, HRMS-MALDI (*m/z*): Calcd for $C_{160}H_{215}N_{16}O_{76}Ru$ 1660.6077; Found: 1660.6085.

***Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy-propane-triazole}methyl] methyl amide 1a.** General procedure A with *Cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[propargyl-methyl]methyl amide (10 mg, 0.6 μmol), 2-azido-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside (30 mg, 0.007 mmol), copper sulfate (12 mg, 0.007 mmol) and ascorbic acid (13 mg, 0.007 mmol) and purification by flash silica column chromatography by using acetronitrile/water/saturated KNO_3 (7.5:1:1.5) as eluent yielded *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy}methyl] methylamide (21 mg, 84%). R_f = 0.5 (acetonitrile/sat aq. KNO_3, 80:20); $[\alpha]_D^{r.t}$ = +12.9 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): *δ* 9.18 (br.s, 2H), 8.72 (d, *J* = 7.1 Hz, 4H), 8.18 (d, *J* = 5.4 Hz, 6H), 8.04 (s, 6H), 7.85 (dd, *J* = 5.7, 4.8 Hz, 6H), 7.45 (t, *J* = 4.5 Hz, 4H), 7.36 (br.s, 2H), 5.27-5.2 (m, 36H), 4.67 (br.s, 12H), 4.51 (br.s, 6H), 4.22-4.10 (m, 12H), 4.01 (m, 6H), 3.75-3.25 (m, 42H), 2.62 (br.s, 4H), 2.44 (t, *J* = 5.7 Hz, 12H), 2.13 (s, 18H), 2.04 (s, 18H), 2.03 (s, 18H), 1.95 (s, 18H), ^{13}C NMR (75MHz, CD_3OD): *δ* 173.7, 171.9, 171.0, 165.2, 158.5, 157.4, 152.1, 151.5, 143.3, 139.1, 128.7, 126.2, 125.3, 123.2, 117.4, 98.6, 70.4, 70.3, 69.5, 68.3, 67.4, 66.9, 63.3, 61.3, 39.9, 37.9, 20.5; HRMS-MALDI (*m/z*): Calcd for $C_{178}H_{232}N_{34}O_{76}Ru$ 4163.4378; Found: 4163.4377.

***Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-*α*-D-mannopyranoside-ethoxy-propane-triazole}methyl] methyl amide 1.** General procedure B with *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy-propane-triazole}methyl] methyl amide (20 mg, 0.48 μmol) and sodium methoxide (5 mg, 0.009 mmol) gave 11 mg (73%) of *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-*α*-D-mannopyranoside-ethoxy-propane-triazole}methyl] methyl amide $[\alpha]_D^{r.t}$ = +7.1 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): *δ* 9.12 (br.s, 2H), 8.74 (d, *J* = 7.1 Hz, 4H), 8.18 (d, *J* = 5.4 Hz, 6H), 8.04 (s, 6H), 7.84 (dd, *J* = 5.7, 4.8 Hz, 6H), 7.46 (t, *J* = 4.5 Hz, 4H), 7.36 (br.s, 2H), 4.79 (br.s, 6H), 3.79-3.55 (m, 56H), 3.54-3.35 (m, 16H), 3.33-3.23 (m,

12H), 2.55 (t, *J* = 6.3 Hz, 4H), 2.34 (t, *J* = 6.6 Hz, 12H) ^{13}C NMR (75MHz, CD_3OD): δ 173.7, 167.2, 160.5, 160.4, 156.1, 155.5, 147.3, 139.1, 128.7, 126.2, 125.3, 120.2, 98.6, 73.4, 70.7, 70.1, 68.3, 67.4, 66.9, 63.3, 61.3, 39.9, 37.9, 22.5, 17.3; HRMS-MALDI (*m/z*): Calcd for $C_{130}H_{184}N_{34}O_{52}Ru$ 3155.1842; Found: 3155.1822.

***Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside-propane-triazole}methyl]methyl amide 2a.** General procedure A with *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[propargyl-methyl]methyl amide (10 mg, 0.6 μmol), 2-azido-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside (30 mg, 0.007 mmol), copper sulfate (12 mg, 0.007 mmol) and ascorbic acid (13 mg, 0.007 mmol) and purification by flash silica column chromatography by using acetronitrile/water/saturated KNO_3 (7.5:1:1.5) as eluent yielded *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy}methyl] methylamide (22 mg, 86%). R_f = 0.5 (acetonitrile/sat aq. KNO_3, 80:20); $[\alpha]_D^{r.t}$ = +1.9 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): δ 9.12 (s, 2H), 8.75 (d, *J* = 7.1 Hz, 4H), 8.14 (t, *J* = 4.8 Hz, 6H), 8.01 (d, *J* = 5.7 Hz, 4H), 7.92 (s, 2H), 7.85 (br.s, 8H), 7.53 (q, *J* = 4.5 Hz, 4H), 5.37 (d, *J* = 3.0 Hz, 6H), 5.13-5.08 (m, 22H), 4.71 (d, *J* = 4.5 Hz, 6H), 4.61 (s, 6H), 4.47 (s, 6H), 4.21-3.91 (m, 28H), 3.78-3.55 (m, 42H), 2.62 (t, *J* = 6.3 Hz, 4H), 2.41 (t, *J* = 5.1 Hz, 12H), 2.12 (s, 18H), 2.05 (s, 18H), 2.00 (s, 18H), 1.95 (s, 18H), ^{13}C NMR (75 MHz, CD_3OD): δ 173.2, 171.6, 171.2, 170.6, 165.2, 158.5, 157.7, 153.0, 151.7, 149.4, 139.1, 135.8, 125.3, 102.8, 72.0. 71.5, 70.0, 69.6, 69.0, 68.5, 68.3, 61.3, 54.5, 40.3, 38.2, 20.4; HRMS-MALDI (*m/z*): Calcd for $C_{178}H_{232}N_{34}O_{76}Ru$ 4163.4378; Found: 4163.4375.

***Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-*β*-D-galactopyranoside-ethoxy-propane-triazole}methyl] methyl amide 2.** General procedure B with *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside-ethoxy-propane-triazole }methyl] methyl amide (15 mg, 0.48 μmol), sodium methoxide (4 mg, 0.009 mmol) gave 9 mg (71%) of *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-*β*-D-galactopyranoside-ethoxy-propane-triazole}methyl] methyl amide $[\alpha]_D^{r.t}$ = - 3.5

(c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): δ 9.12 (s, 2H), 8.75 (d, J = 7.1 Hz, 4H), 8.14 (t, J = 4.8 Hz, 6H), 8.01 (d, J = 5.7 Hz, 4H), 7.92 (s, 2H), 7.85 (br.s, 8H), 7.53 (q, J = 4.5 Hz, 4H), 4.79 (br.s, 6H), 3.52 (d, J = 5.7 Hz, 6H), 3.95-3.35 (m, 94H), 2.55 (t, J = 6.3 Hz, 4H), 2.34 (t, J = 6.6 Hz, 12H) ^{13}C NMR (75MHz, CD_3OD): δ 173.7, 167.2, 160.5, 160.4, 156.1, 155.5, 147.3, 139.1, 138.9, 128.7, 125.2, 125.3, 103.6, 76.4, 75.2, 72.1, 70.8, 70.3, 69.4, 63.8, 61.3, 55.9, 40.9, 37.5, 17.3; HRMS-MALDI (*m/z*): Calcd for $C_{130}H_{184}N_{34}O_{52}Ru$ 3155.1842; Found: 3155.1821.

***Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-glucosepyranoside-propane-triazole}methyl]methyl amide 3a.** General procedure A with *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[propargyl-methyl]methyl amide (7mg, 0.4 μmol), 2-azido-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-glucosepyranoside (30 mg, 0.007 mmol), copper sulfate (12 mg, 0.007 mmol) and ascorbic acid (13 mg, 0.007 mmol) and purification by flash silica column chromatography by using acetronitrile/water/saturated KNO_3 (7.5:1:1.5) as eluent yielded *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy}methyl] methylamide (17 mg, 79%). R_f = 0.5 (acetonitrile/sat aq. KNO_3, 80:20); $[\alpha]_D^{r.t}$ = +2.6 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): δ 9.14 (s, 2H), 8.72 (d, J = 7.1 Hz, 4H), 8.14 (t, J = 4.8 Hz, 6H), 8.01 (m, J = 5.7 Hz, 4H), 7.85 (dd, J = 5.7, 4.8 Hz, 8H), 7.53 (t, J = 4.5 Hz, 4H), 7.30 (br.s, 1H), 5.26 (t, J = 3.0 Hz, 6H), 5.07 (t, J = 3.0 Hz, 6H), 4.71 (d, J = 4.5 Hz, 6H), 4.61 (s, 6H), 4.48 (s, 6H), 4.31-3.79 (m, 28H), 3.78-3.55 (m, 42H), 2.62 (t, J = 6.3 Hz, 4H), 2.41 (t, J = 5.1 Hz, 12H), 2.12 (s, 18H), 2.05 (s, 18H), 2.00 (s, 18H), 1.95 (s, 18H),^{13}C NMR (75 MHz, CD_3OD): δ 173.4, 173.1, 171.6, 171.4, 170.8, 165.2, 162.8, 158.5, 157.7, 153.0, 151.7, 143.4, 139.1, 132.8, 128.7, 128.4, 125.3, 101.7, 72.0. 71.5, 70.4, 69.6, 69.0, 68.5, 68.3, 62.3, 61.3, 38.2, 36.7, 20.4; HRMS-MALDI (*m/z*): Calcd for $C_{178}H_{232}N_{34}O_{76}Ru$ 4163.4378; Found: 4163.4375.

***Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-*β*-D-glucosepyranoside-ethoxy-propane-triazole}methyl] methyl amide 3.** General procedure B with *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-glucosepyranoside-ethoxy-propane-triazole }methyl] methyl amide (15 mg, 0.48 μmol), sodium methoxide (4 mg, 0.009 mmol) gave 9 mg (71%) of *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-*β*-D-glucosepyranoside-ethoxy-propane-triazole}methyl] methyl amide $[\alpha]_D^{r.t}$ = -

7.9 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): δ 9.12 (s, 2H), 8.75 (d, J = 7.1 Hz, 4H), 8.14 (t, J = 4.8 Hz, 6H), 8.01 (d, J = 5.7 Hz, 4H), 7.85 (m, 10H), 7.53 (t, J = 4.5 Hz, 4H), 4.29 (d, J = 4.8 Hz, 6H), 3.95-3.79 (m, 16H), 3.75-3.63 (m, 36H), 3.51-3.23 (m, 44H), 2.55 (t, J = 6.3 Hz, 4H), 2.34 (t, J = 6.6 Hz, 12H) ^{13}C NMR (75MHz, CD_3OD): δ 173.7, 167.2, 160.5, 160.4, 156.1, 155.5, 147.3, 139.1, 138.9, 128.7, 125.2, 125.3, 103.6, 76.4, 75.2, 72.1, 70.8, 70.3, 69.4, 63.8, 61.3, 55.9, 40.9, 37.5, 17.3; HRMS-MALDI (*m/z*): Calcd for $C_{130}H_{184}N_{34}O_{52}Ru$ 3155.1842; Found: 3155.1821.

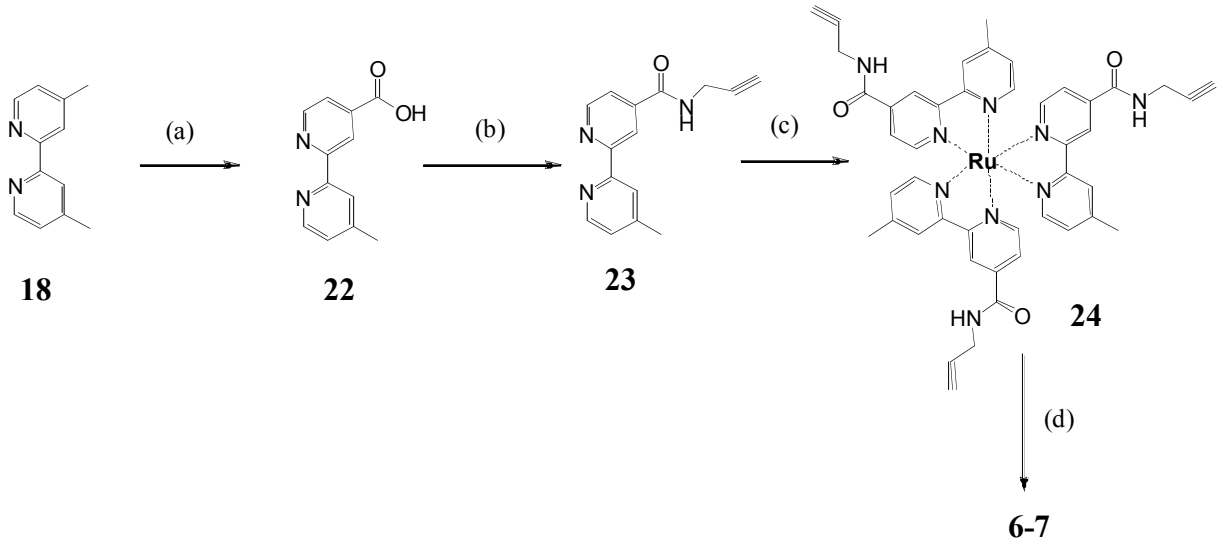
***Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6,2',3',4',6'-octa-*O*-acetyl-*α*(1-4)-D-diglucosepyranoside-ethoxy-propane-triazole}methyl] methyl amide 4a.** General procedure A with *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[propargyl-methyl]methyl amide (7 mg, 0.4 μmol), 2-azido-ethoxy-2,3,4,6,2',3',4',6'-octa-*O*-acetyl-*α(1-4)*-D-diglucosepyranoside (50 mg, 0.007 mmol), copper sulfate (12 mg, 0.007 mmol) and ascorbic acid (13 mg, 0.007 mmol) and purification by flash silica column chromatography by using acetronitrile/water/saturated KNO_3 (7.5:1:1.5) as eluent yielded *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6,2',3',4',6'-octa-*O*-acetyl-*α*(1-4)-D-diglucopyranoside-ethoxy-propane-triazole}methyl] methyl amide (28 mg, 85%). R_f = 0.5 (acetonitrile/sat aq. KNO_3, 80:20); $[\alpha]_D^{r.t}$ = +22.9 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): δ 9.16 (br.s, 2H), 8.72 (d, J = 7.1 Hz, 4H), 8.18-8.14 (m, 4H), 8.0 (d, J = 6.0 Hz, 2H), 7.85-7.72 (m, 12H), 7.52 (t, J = 4.5 Hz, 4H), 5.47-5.23 (m, 18H), 5.12 (t, J = 4.5 Hz, 14H), 4.72 (br.s, 6H), 4.57 (m, 16H), 4.27-3.84 (m, 56H), 3.79-3.36 (m, 48H), 2.62 (t, J = 6.9 Hz, 4H), 2.44 (t, J = 5.7 Hz, 12H), 2.13-1.79 (m, 126H), ^{13}C NMR (75MHz, CD_3OD): δ 173.7, 173.2, 171.9, 171.0, 165.2, 158.5, 157.8, 153.1, 152.5, 152.1, 143.3, 139.1, 128.7, 126.2, 125.3, 123.2, 117.8, 98.5, 97.3, 76.8, 73.2, 71.8, 69.7, 69.5, 68.3, 67.4, 66.9, 63.3, 61.3, 39.9, 37.9, 37.1,20.5; HRMS-MALDI (*m/z*): Calcd for $C_{250}H_{328}N_{34}O_{124}Ru$ 5891.9449; Found: 5891.9458.

***Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-*α*(1-4)-D-diglucosepyranoside-ethoxy-propane-triazole}methyl] methyl amide 4.** General procedure B with *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-*α*(1-4)-D-diglucosepyranoside-ethoxy-propane-triazole }methyl]

methyl amide (15 mg, 0.48 μmol), sodium methoxide (4 mg, 0.009 mmol) gave 9 mg (71%) of *Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy- *α*(1-4)-D-diglucosepyranoside -ethoxy-propane-triazole}methyl] methyl amide R_f = 0.5 (acetonitrile/sat aq. KNO_3, 80:20); $[\alpha]_D^{r.t}$ = - 7.2 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): *δ* 9.16 (br.s, 2H), 8.72 (d, *J* = 7.1 Hz, 4H), 8.18-8.14 (m, 4H), 8.0 (d, *J* = 6.0 Hz, 2H), 7.85-7.72 (m, 12H), 7.52 (t, *J* = 4.5 Hz, 4H), 5.47 (s, 12H), 4.52 (d, *J* = 5.7 Hz, 12H), 3.92 (d, *J* = 5.7 Hz, 18H), 3.75-3.55 (m, 54H), 3.48-3.21 (m, 52H), 2.55 (t, *J* = 6.3 Hz, 4H), 2.34 (t, *J* = 6.6 Hz, 12H); ^{13}C NMR (75MHz, CD_3OD): *δ* 173.7, 167.2, 160.5, 160.4, 156.1, 155.5, 147.3, 139.1, 138.9, 128.7, 125.2, 125.3, 103.5, 97.8, 76.4, 75.2, 73.8, 73.6, 72.1, 71.7, 70.9, 70.8, 70.3, 69.4, 63.8, 62.3, 61.3, 57.8, 55.2, 17.3; HRMS-MALDI (*m/z*): Calcd for $C_{166}H_{244}N_{34}O_{82}Ru$ 4127.5612; Found 4127.5632.

***Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6,2',3',4',6'-octa-*O*-acetyl-*α*(1-4)-D-dimannopyranoside-ethoxy-propane-triazole}methyl] methyl amide 5a.** General procedure A with *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[propargyl-methyl]methyl amide (5 mg, 0.3 μmol), 2-azido-ethoxy-2,3,4,6,2',3',4',6'-octa-*O*-acetyl-*α(1-4)*-D-dimannopyranoside (25 mg, 0.003 mmol), copper sulfate (6 mg, 0.003 mmol) and ascorbic acid (6 mg, 0.007 mmol) and purification by flash silica column chromatography by using acetronitrile/water/saturated KNO_3 (7.5:1:1.5) as eluent yielded *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6,2',3',4',6'-octa-*O*-acetyl-*α*(1-4)-D-dimannopyranoside-ethoxy-propane-triazole}methyl] methyl amide (15 mg, 86%). R_f = 0.5 (acetonitrile/sat aq. KNO_3, 85:15); $[\alpha]_D^{r.t}$ = +38.9 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): *δ* 9.18 (br.s, 2H), 8.72 (d, *J* = 7.1 Hz, 4H), 8.18 (t, *J* = 5.4 Hz, 4H), 8.04 (br.s, 6H), 7.81 (br.s, 6H), 7.45 (br.s, 6H), 7.36 (br.s, 1H), 5.37-5.27 (m, 18H), 5.27-5.14 (m, 18H), 4.72-4.56 (m, 12H), 4.52-4.39 (m, 12H), 4.22-3.71 (m, 56H), 3.71-3.36 (m, 68H), 2.62 (t, *J* = 6.9 Hz, 4H), 2.44 (t, *J* = 5.7 Hz, 12H), 2.13-1.87 (m, 126H); ^{13}C NMR (75MHz, CD_3OD): *δ* 173.7, 173.2, 171.9, 171.1, 171.0, 165.2, 163.2, 158.5, 157.8, 153.1, 152.5, 152.1, 143.3, 139.1, 128.7, 126.2, 125.3, 123.2, 117.8, 98.5, 70.4, 70.3, 69.7, 69.5, 68.3, 67.4, 66.9, 63.3, 61.3, 39.9, 37.9, 37.1,20.5; HRMS-MALDI (*m/z*): Calcd for $C_{250}H_{328}N_{34}O_{124}Ru$ 5891.9449; Found: 5891.9458.

***Cis*-Ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-*α*(1-4)-D-dimannosepyranoside-ethoxy-propane-triazole}methyl] methyl amide 5.** General procedure B with *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy-*α*(1-4)-D-dimannosepyranoside-ethoxy-propane-triazole }methyl] methyl amide (15 mg, 0.48 μmol), sodium methoxide (4 mg, 0.009 mmol) gave 9 mg (71%) of *cis*-ruthenium(II)bis(bipyridine){1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-*β*-propane-{tris-[3-4-ethoxy- *α*(1-4)-D-diglucosepyranoside -ethoxy-propane-triazole}methyl] methyl amide R_f = 0.5 (acetonitrile/sat aq. KNO_3, 80:20); $[\alpha]_D^{r.t}$ = + 2.1 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): *δ* 9.16 (br.s, 2H), 8.71 (d, *J* = 7.1 Hz, 4H), 8.17-8.14 (m, 4H), 8.01 (d, *J* = 6.0 Hz, 2H), 7.85-7.72 (m, 12H), 7.52 (t, *J* = 4.5 Hz, 4H), 5.44 (s, 12H), 3.87-3.81 (m, 32H), 3.73-3.51 (m, 54H), 3.46-3.24 (m, 52H), 2.55 (t, *J* = 6.3 Hz, 4H), 2.34 (t, *J* = 6.6 Hz, 12H); ^{13}C NMR (75MHz, CD_3OD): *δ* 173.7, 167.2, 160.5, 160.4, 156.1, 155.5, 147.3, 139.1, 138.9, 128.7, 125.2, 125.3, 103.1, 101.3, 75.1, 74.2, 74.1, 73.9, 73.1, 71.5, 70.3, 70.1, 69.2, 63.4, 62.1, 61.2, 58.6, 54.1, 18.7; HRMS-MALDI (*m/z*): Calcd for $C_{166}H_{244}N_{34}O_{82}Ru$ 4127.5612; Found 4127.5632:



Scheme 4. Reagents and Conditions: (a) SeO_2/Conc H_2SO_4, 98%, (b) propargyl amine/DCM/TEA, 77%, (c) $RuCl_3$/EtOH/AcOH, 12 h, 39%, (d) $CuSO_4$/ascorbic acid/ **14** or **15**/THF:H_2O(1:1) 12 h, 76-87%, NaOMe/ MeOH, 76%.

4'-Methyl-2,2'-bipyridine-4-carbonyl Propargyl Amine 23. 4'-Methyl-2,2'-bipyridine-4-carboxylic acid (0.22 g, 1.0 mmol), propargylamine hydrochloride (0.092 g, 1 mmol), HOBt (0.15 g, 1 mmol) and DIPEA (0.21 mL) were dissolved in anhydrous DMF (15 mL) and cooled to 0^{O}C. DCC (0.25 g, 1.2 mmol) was dissolved in DMF (3 mL) and added dropwise to the reaction mixture. The mixture was stirred at room temperature overnight. DCU was filtered off and the solvent was removed by vacuum distillation. The remaining solid compound was dissolved in ethyl acetate and washed with sodium bicarbohydrate (5%), 0.5 N HCl, brine and dried over sodium sulfate. The solvent was removed by rotary evaporator and the compound was purified by column chromatography using 4% methanol in chloroform as eluent afforded 0. 19 g (76%). R_f = 0.5 (CH_2Cl_2/MeOH, 96:4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 (d, J = 4.5 Hz, 1H), 8.81 (br.s, 1H), 8.43 (d, J = 5.4 Hz, 1H), 8.23 (br.s, 1H), 7.78 (d, J = 4.5 Hz, 1H), 7.26 (br.s, 1H), 7.09 (d, J = 4.5 Hz, 1H), 4.23 (d, J = 5.4 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$): δ 172.6, 166.2, 157.3, 153.1, 150.2, 143.7, 122.3, 117.8, 113.7, 70.1, 68.9, 52.4, 37.5; HRMS-MALDI (m/z): $[M]^+$ Calcd for $C_{15}H_{13}N_3O$: 251.1059; Found: 251.1054.

Ruthenium(II) Tris (4'-Methyl-2,2'-bipyridine-4-carbonyl propargyl amine) 24. 4'-Methyl-2,2'-bipyridine-4-carbonyl propargyl amine (0.3 g, 0.093 mmol) and ruthenium trichloride (60 mg, 0.023 mmol) were dissolved in ethanol : chloroform : acetic acid (30 mL, 1:1:0.2) and the mixture was refluxed for 12 h. The product was purified by flash silica column chromatography by chloroform/methanol (8:2- 7.5:2.5) as eluent to give 0.17 g (39%) of ruthenium(II)tris)[{1,1'-(2,2'-bipyridine-4,4'-diyl)bis-3-β-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside-ethoxy}methyl]methyl amide] R_f 0.3 (chloroform/ methanol = 8:2); $[\alpha]_D^{r.t}$ = +2.9 (c =1.0, H_2O); ^{1}H NMR (300MHz, CD_3OD): δ 9.12 (br.s, 3H); 8.5 (br.s, 3H), 7.9 (dd, J = 5.7 Hz, 3H), 7.79 (br.s, 3H), 7.59 (br.s, 3H), 7.32 (br.s, 3H), 4.32 (s, 9H), 2.01 (s, 12H); ^{13}C NMR (125MHz, CD_3OD): δ 174.2, 173.2, 165.8, 158.4, 153.2, 149.4, 142.6, 123.5, 117.5, 113.6, 71.2, 68.7, 53.1, 36.2; HRMS-MALDI (m/z): $[M+ 1]^+$ Calcd for $C_{45}H_{39}N_9O_3Ru$: 856.2219 Found: 856.2217.

***Cis*-Ruthenium(II) Tris { 4'-Methyl-2,2'-bipyridine-3-β-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside-ethoxy-propane-triazole}methyl] methyl amide 6a.** General procedure A with ruthenium(II) tris (4'-methyl-2,2'-bipyridine-4-carbonyl propargyl amine) (5 mg, 0.6 µmol), *N*-{tris[3-[4-ethoxy-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside -ethoxy)methyl]}methyl amide}-5-azido pentamide (54 mg, 0.0035 mmol), copper sulfate (6 mg,

0.0035 mmol) and ascorbic acid (7 mg, 0.0035 mmol) and purification by flash silica column chromatography by using acetronitrile/water/saturated KNO_3 (7.5:1:1.5) as eluent yielded *cis*-Ruthenium(II) tris { 4'-methyl-2,2'-bipyridine-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy-propane-triazole}methyl] methyl amide (28 mg, 87%). R_f = 0.5 (acetonitrile/sat aq. KNO_3, 80:20); $[\alpha]_D^{r.t}$ = +18.3 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): *δ* 9.18 (br.s, 3H), 8.71 (br.s, 3H), 7.91 (dd, *J* = 5.4 Hz, 3H), 7.82 (s, 3H), 7.61 (br.s, 6H), 7.32 (br.s, 3H), 5.27-5.2 (m, 54H), 4.21 (dd, *J* = 5.4 Hz, 18H), 4.22-4.10 (m, 24H), 3.85-3.51 (m, 65H), 3.51-3.26 (m, 28H), 2.62 (br.s, 6H), 2.44 (t, *J* = 5.7 Hz, 18H), 2.13 (s, 27H), 2.04 (s, 27H), 2.03 (s, 27H), 1.95 (s, 27H), ^{13}C NMR (75MHz, CD_3OD): *δ* 173.7, 171.9, 171.0, 165.1, 156.4, 149.3, 145.1, 135.7, 98.4, 71.2, 70.4, 70.3, 69.5, 68.3, 67.4, 66.9, 63.3, 61.3, 39.9, 37.9, 20.5; HRMS-MALDI (*m/z*): Calcd for $C_{243}H_{342}N_{30}O_{114}Ru$ 5606.093; Found: 5606.098.

***Cis*-Ruthenium(II) tris { 4'-Methyl-2,2'-bipyridine-3-*β*-propane-{tris-[3-4-ethoxy-*α*-D-mannopyranoside-ethoxy-propane-triazole}methyl] methyl amide 6.** General procedure B with *Cis*-ruthenium(II) tris {4'-methyl-2,2'-bipyridine-3-*β*-propane-{tris-[3-4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy-propane-triazole}methyl] methyl amide (20 mg, 0.36 μmol), sodium methoxide (5 mg, 0.009 mmol) gave 13 mg (76%) of *Cis*-Ruthenium(II) tris {4'-Methyl-2,2'-bipyridine-3-*β*-propane-{tris-[3-4-ethoxy-*α*-D-mannopyranoside-ethoxy-propane -triazole}methyl] methyl amide $[\alpha]_D^{r.t}$ = +3.3 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): *δ* 9.18 (s, 3H), 8.71 (s, 3H), 7.91 (dd, *J* = 5.4 Hz, 3H), 7.82 (s, 3H), 7.64 (br.s, 6H), 7.32 (br.s, 3H), 4.77 (br.s, 9H), 3.79-3.55 (m, 78H), 3.54-3.35 (m, 48H), 3.33-3.23 (m, 38H), 2.51-2.41 (m, 24H), ^{13}C NMR (75MHz, CD_3OD): *δ* 173.7, 165.1, 156.4, 149.3, 145.1, 135.7, 98.6, 73.4, 70.7, 70.1, 68.3, 67.4, 66.9, 63.3, 61.3, 39.9, 37.9, 22.5, 17.3; HRMS-MALDI (*m/z*): Calcd for $C_{171}H_{1270}N_{30}O_{78}Ru$ 4093.7127; Found: 4093.7125.

***Cis*-Ruthenium(II) tris { 4'-Methyl-2,2'-bipyridine-3-*β*-propane-{3-{tris[3-carboxyl ethoxy] methyl]3'-{tris-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-manno pyranoside -ethoxy]methyl] methylamide}-5-triazole pentamide 7a.** General procedure A with ruthenium(II) tris (4'-methyl-2,2'-bipyridine-4-carbonyl propargyl amine) (2 mg, 0.26 μmol), *N*-{tris[3-[4-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside -ethoxy)methyl]}methyl amide}-5-azido pentamide (69 mg, 0.0012 mmol), copper sulfate (2 mg, 0.0012 mmol) and ascorbic acid (2 mg, 0.0012 mmol) and purification by flash silica column chromatography by using acetronitrile/water/saturated KNO_3 (7.5:1:1.5) as eluent yielded *cis*-ruthenium(II) tris {4'-Methyl-

2,2'-bipyridine-3-*β*-propane-{3-{tris[3-carboxylethoxy]methyl]3'-{tris-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-manno pyranoside -ethoxy]methyl] methylamide}-5-triazole pentamide (28 mg, 77%). R_f = 0.5 (acetonitrile/sat aq. KNO_3, 80:20); $[\alpha]_D^{r.t}$ = +0.3 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): *δ* 9.18 (br.s, 3H), 8.71 (br.s, 3H), 7.91 (br.s, 3H), 7.82 (s, 3H), 7.61 (br.s, 6H), 7.32 (br.s, 3H), 5.27-5.2 (m, 162H), 4.21 (dd, *J* = 5.4 Hz, 54H), 4.22-4.10 (m, 72H), 3.85-3.51 (m, 195H), 3.51-3.26 (m, 84H), 2.44 (br.s, 54H), 2.13 (s, 81H), 2.04 (s, 81H), 2.03 (s, 81H), 1.95 (s, 81H), ^{13}C NMR (75MHz, CD_3OD): *δ* 173.7, 171.9, 171.0, 165.1, 156.4, 149.3, 145.1, 135.7, 98.4, 71.2, 70.4, 70.3, 69.5, 68.3, 67.4, 66.9, 63.3, 61.3, 39.9, 37.9, 20.5; HRMS-MALDI (*m/z*): Calcd for $C_{666}H_{984}N_{66}O_{348}Ru$ 15576.0374; Found: 7789.0185 $(M+2H/2)^+$.

***Cis*-Ruthenium(II) tris { 4'-Methyl-2,2'-bipyridine-3-*β*-propane-{ tris[3-carboxyl ethoxy] methyl]3'-{tris-[2-ethoxy-*α*-D-manno pyranoside -ethoxy]methyl] methylamide}-5-triazole pentamide 7.** General procedure B with *cis*-ruthenium(II) tris { 4'-methyl-2,2'-bipyridine-3-*β*-propane-{3-{tris[3-carboxyl ethoxy]methyl]3'-{tris-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-manno pyranoside -ethoxy]methyl] methylamide}-5-triazole pentamide (20 mg, 0.36 μmol), sodium methoxide (5 mg, 0.009 mmol) gave 13 mg (76%) of *cis*-ruthenium(II) tris {4'-methyl-2,2'-bipyridine-3-*β*-propane-{tris[3-carboxylethoxy]methyl]3'-{tris-[2-ethoxy-*α*-D-manno pyranoside -ethoxy]methyl] methylamide}-5-triazole pentamide $[\alpha]_D^{r.t}$ = -5.4 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, CD_3OD): *δ* 9.18 (s, 3H), 8.71 (s, 3H), 7.91 (dd, *J* = 5.4 Hz, 3H), 7.82 (s, 3H), 7.64 (br.s, 6H), 7.32 (br.s, 3H), 4.77 (br.s, 9H), 3.79-3.55 (m, 78H), 3.54-3.35 (m, 48H), 3.33-3.23 (m, 38H), 2.51-2.41 (m, 24H), HRMS-MALDI (*m/z*): Calcd for $C_{450}H_{768}N_{66}O_{240}Ru$ 11038.8964; Found: 5520.4482 $(M+2H/2)^+$.

3. Photophysical Properties.

The emission spectra of complexes **1-8** are shown in Figure 1. Upon excitation at the corresponding MLCT band, a maximum emission at 645-648 nm were observed for complexes **1-7**. This fluorescent emission originated from an excited-state intramolecular energy transfer (ESIET). Quantum yields have been calculated using the equation,

$$\mathbf{\Phi_{comp}/\Phi_{ref} = A_{comp} * [C]_{ref} / A_{ref} * [C]_{comp}}$$

Where **[C]** refers to the concentration of the samples and **A** to the area of the emission spectra. Here, $Ru(bipy)_3(Cl)_2$ was used as a reference compound of quantum yield Φ_{ref} = 0.062.[4]

4. Turbidity Assay.

To a solution of the lectin ConA (1.0 mg/ml, 0.1mL) in HEPES buffer (10 mM Hepes, pH 6.5, 1mM $MgCl_2$, 1mM $CaCl_2$, 1% BSA) were added to complexes **1-7** (1.0 mM, H2O). The time dependent turbidity kinetics were recorded by measuring the absorption coefficient at 500 nm at intervals of 1 min. After 25 min, the solution was restored to its clear state by addition of mannose (100 mM, 0.01 mL) to the solution.

To a solution of lectin (1.0 mg/ml, 0.1ml) in HEPES buffer (10 mM Hepes pH 6.5, 1mM MgCl2, 1mM CaCl2, 1% BSA) and was added complex **1-7** (1.0 mM, H_2O). The fluorescence spectra was recorded after 20 min.

5. Imaging Experiment

The snapshot experiment was performed with 0.5 mM of **1, 6,** and **7** complex and 1 mg/mL (0.1 ml) of ConA lectin in HEPES buffer solution (10 mM Hepes pH 6.5, 1mM $MgCl_2$, 1mM $CaCl_2$, 1%BSA). Complex **7** showed turbidity with ConA after 10 min.

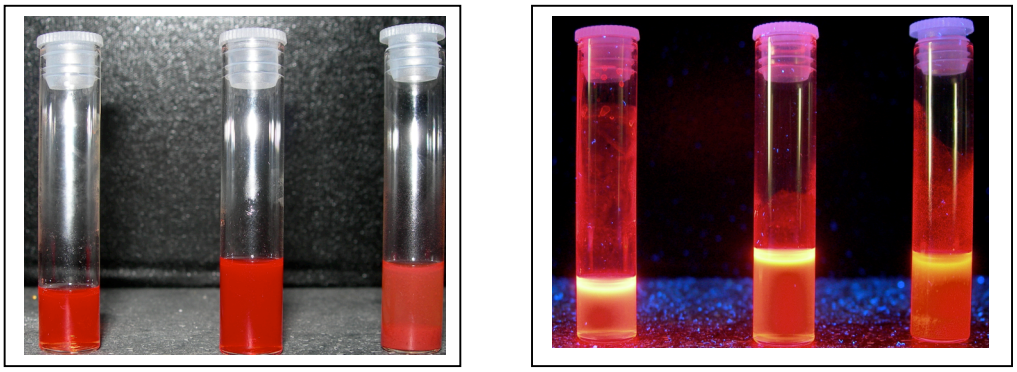


Fig 1. Visible and fluorescent image of complex **1, 6** and **7** in presence of ConA excited by UV lamp at 365 nm.

7. Computational Studies.

The size of the dendrimer was determined by minimizing the 3D structure of complexes **1, 6, 7** and **8** using MM2 structure of 2D and setting the steric energy (26- 47 kcal mol^{-1}).

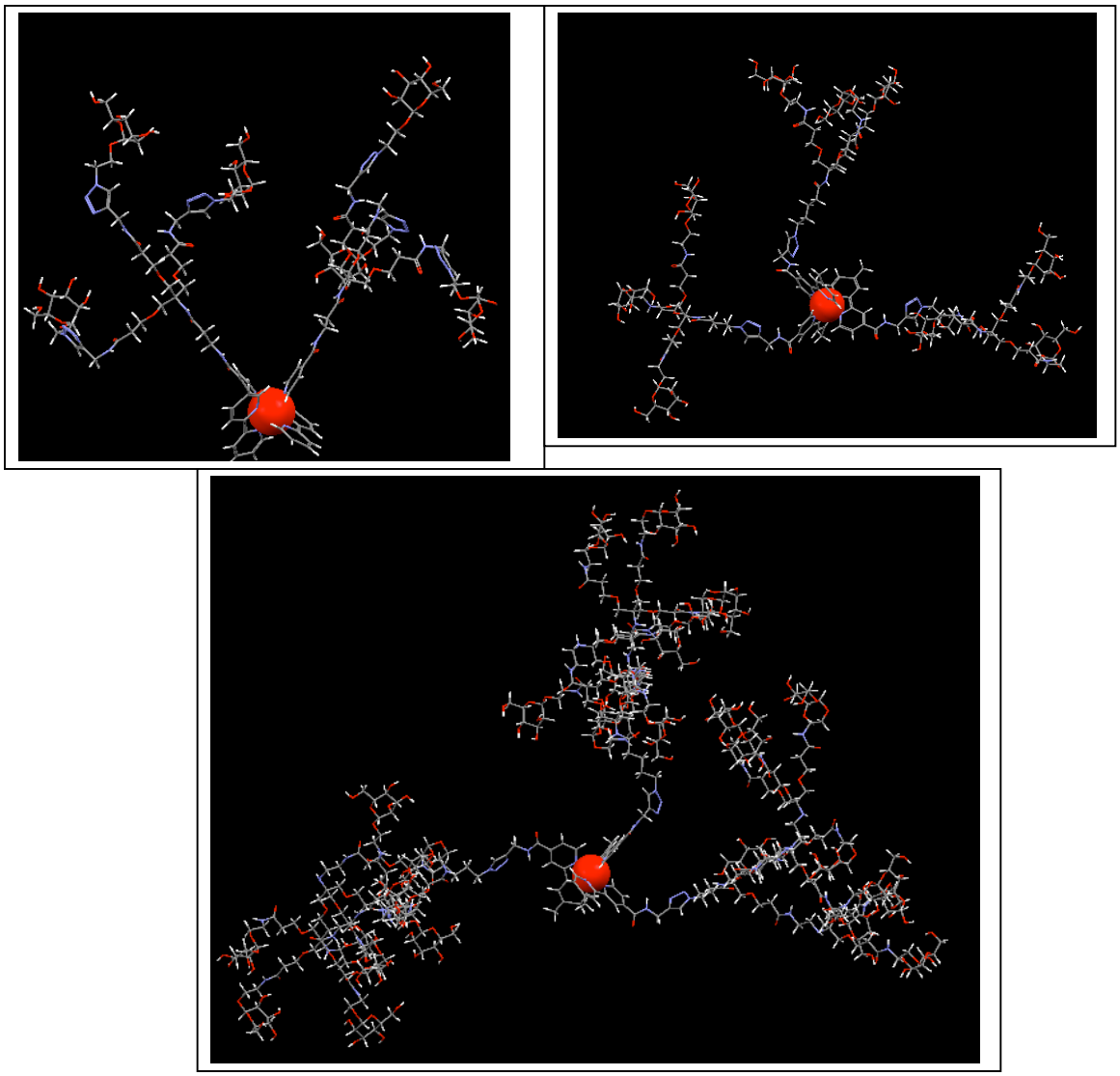


Fig 2. 3D structures of complex **1**, **6** and **7**.

6. References

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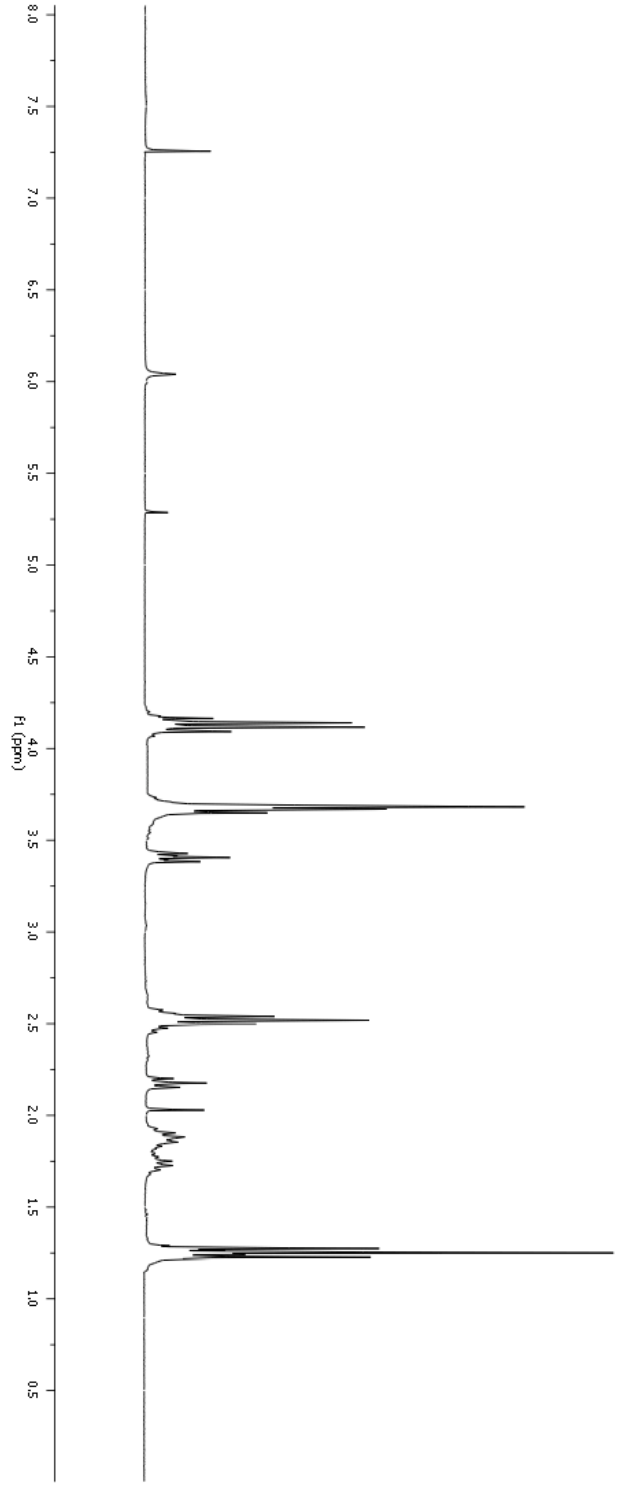

Fig 3. ^{1}H-NMR of Comp 12

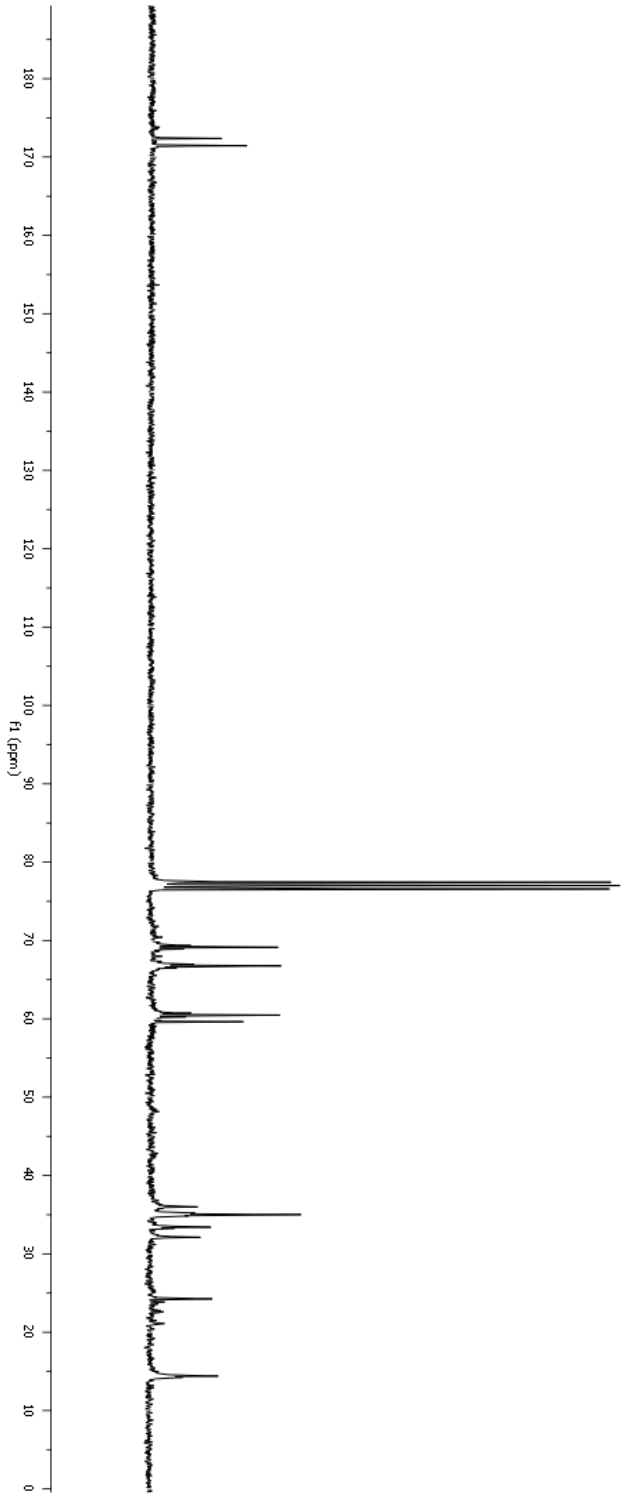

Fig 4. ^{13}C-NMR of Comp 12

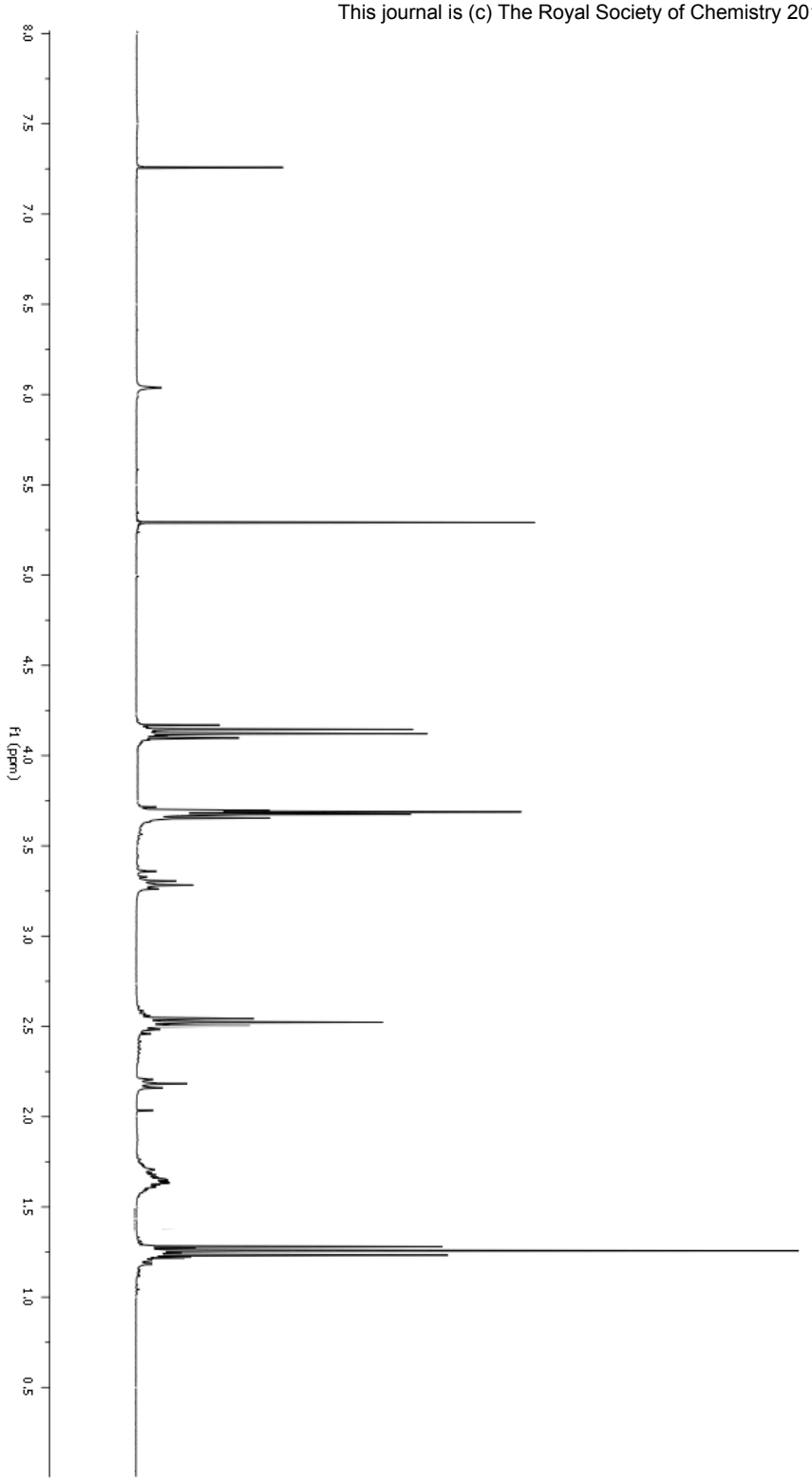

Fig 5. ^{1}H-NMR of Comp 12a

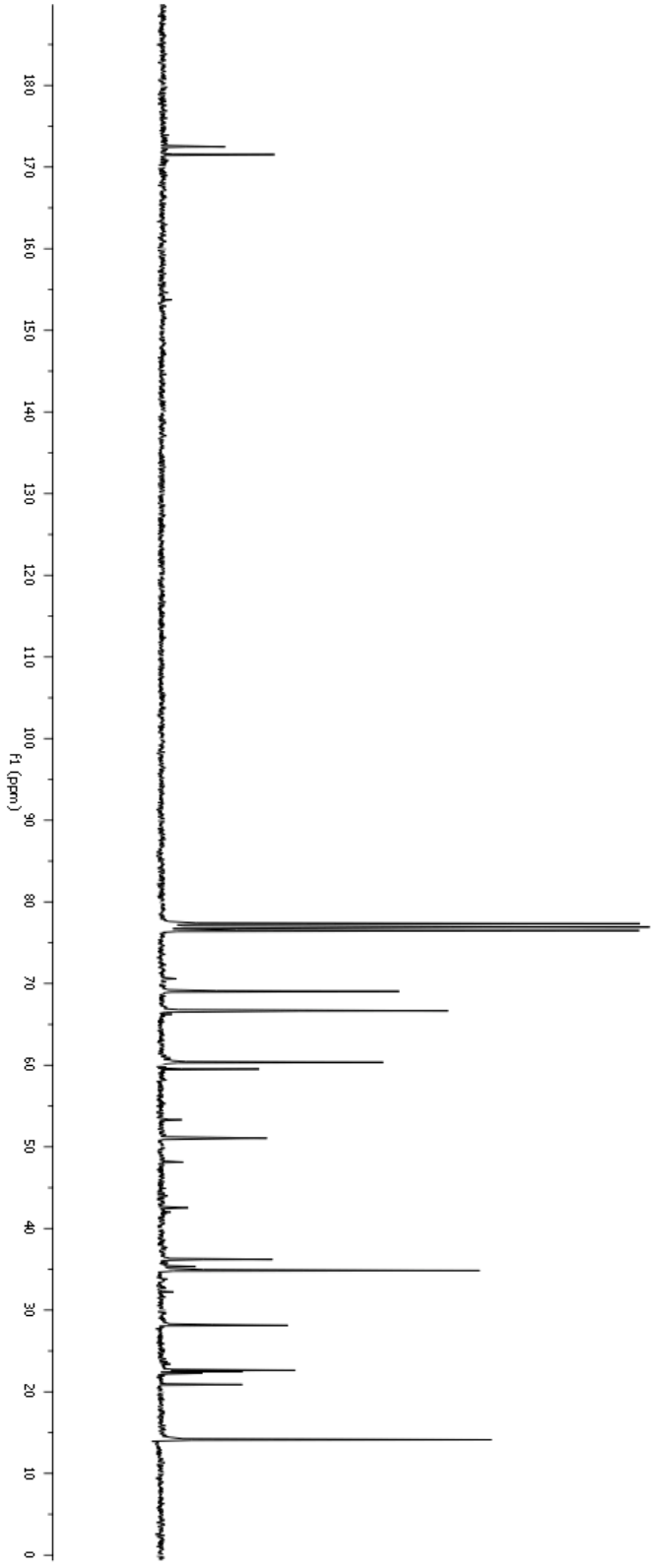

Fig 4. ^{13}C-NMR of Comp 12a

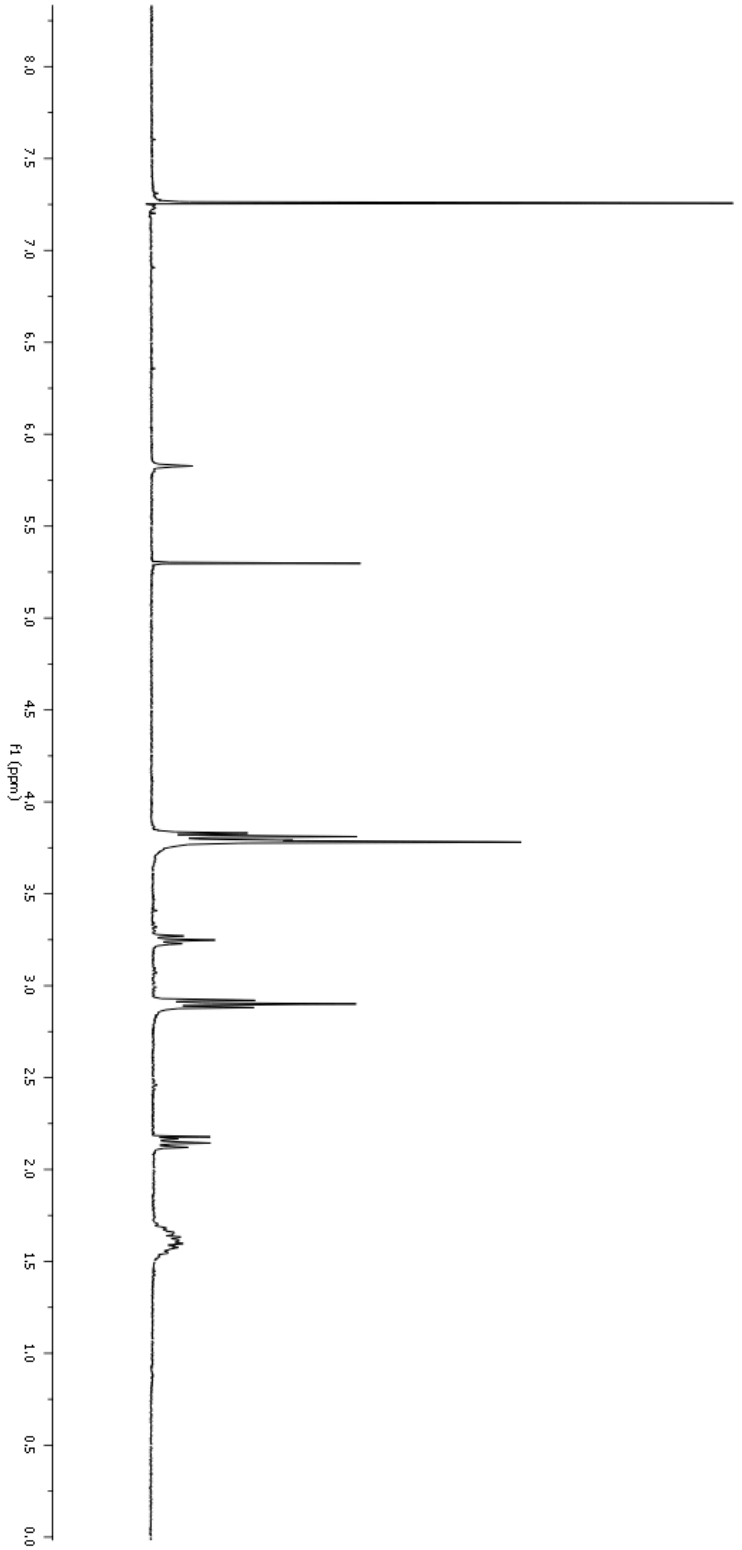

Fig 7. ^{1}H-NMR of Comp 13

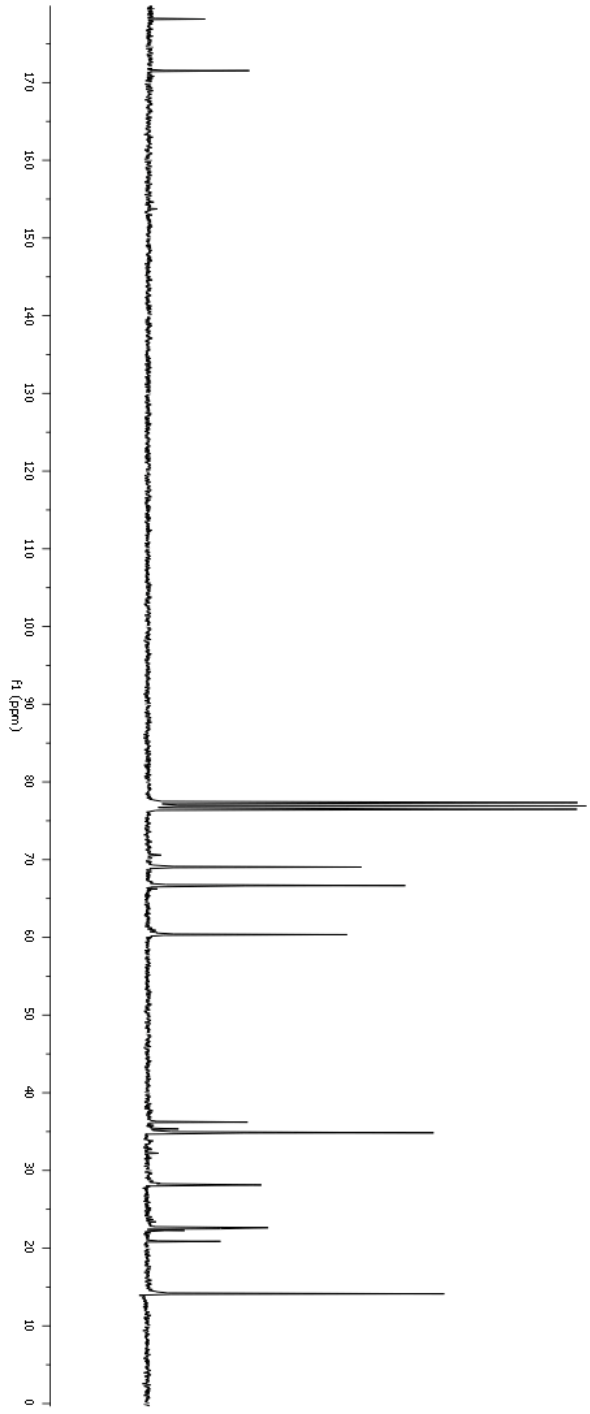

Fig 8. ^{13}C-NMR of Comp 13

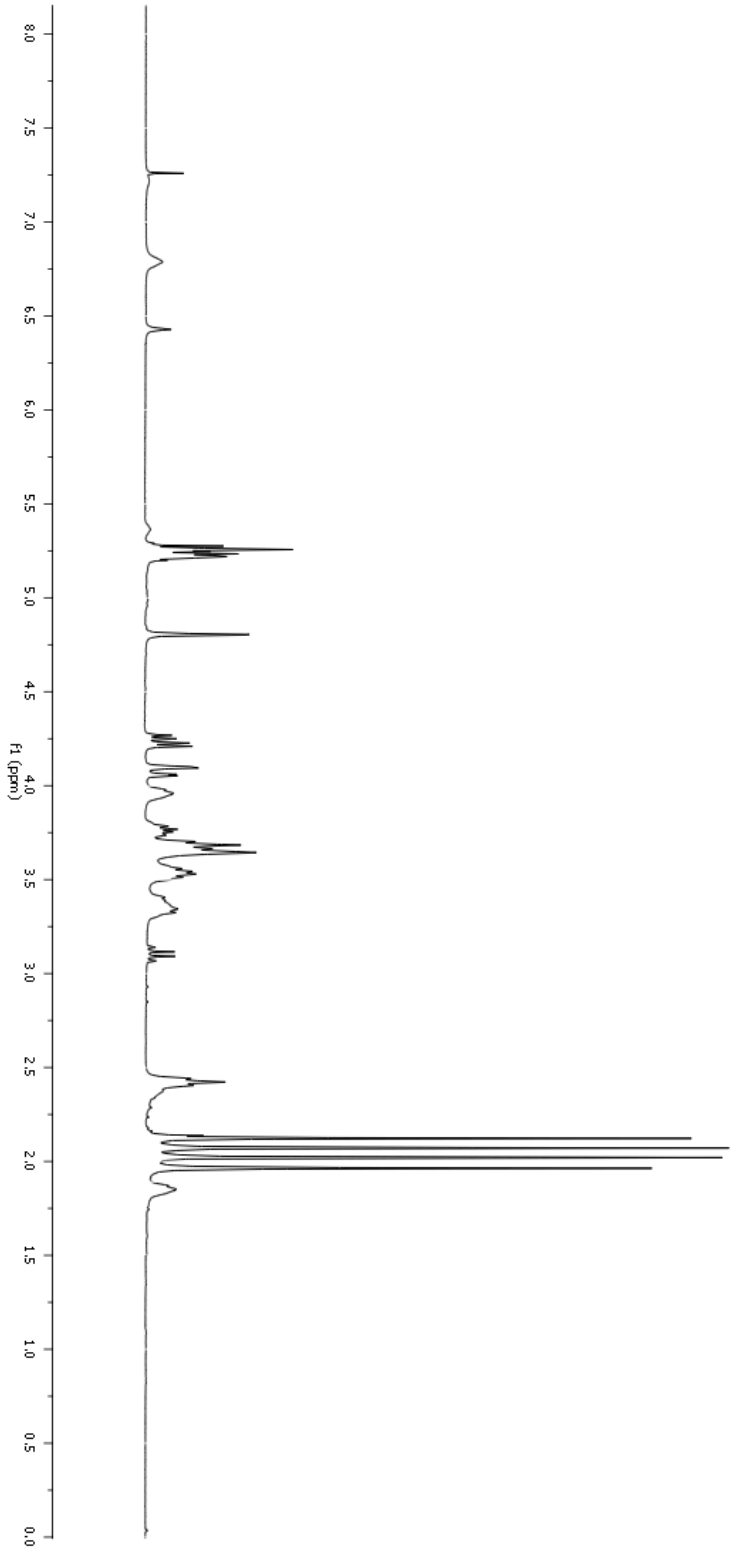

Fig 9. ^{1}H-NMR of Comp 14

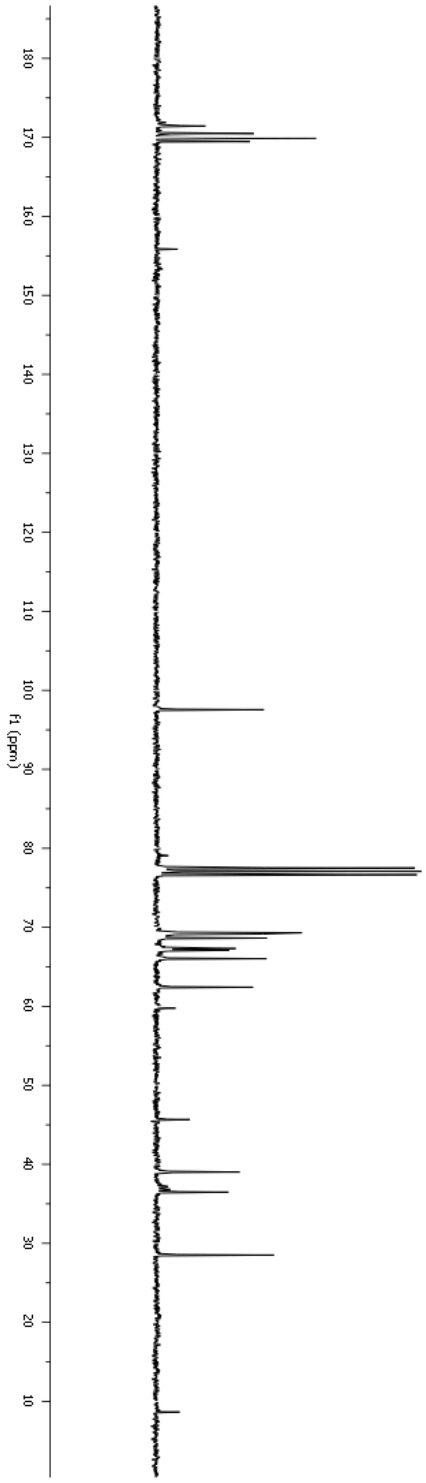

Fig 10. ^{13}C-NMR of Comp 14

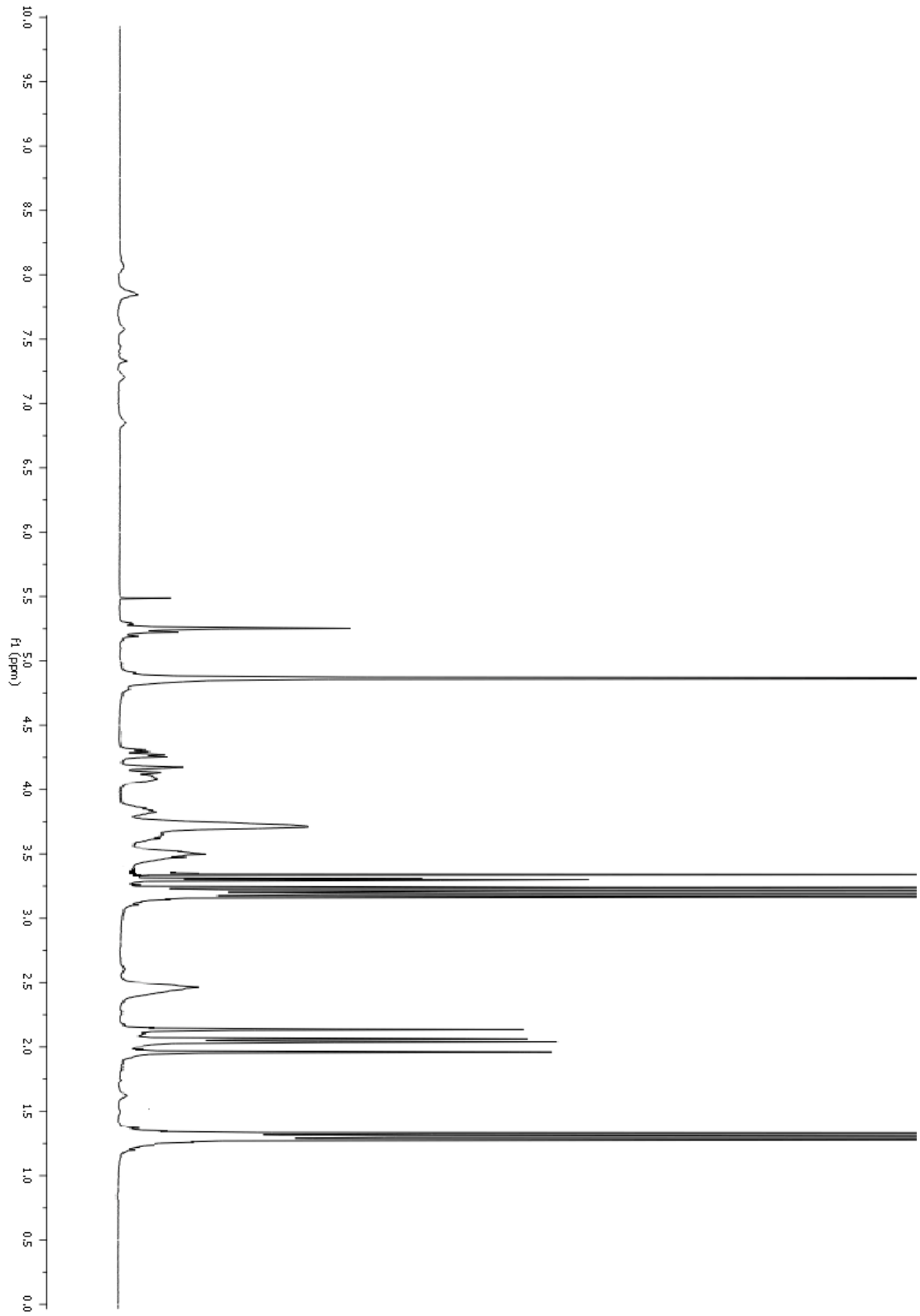

Fig 11. ^{1}H-NMR of Comp 8a

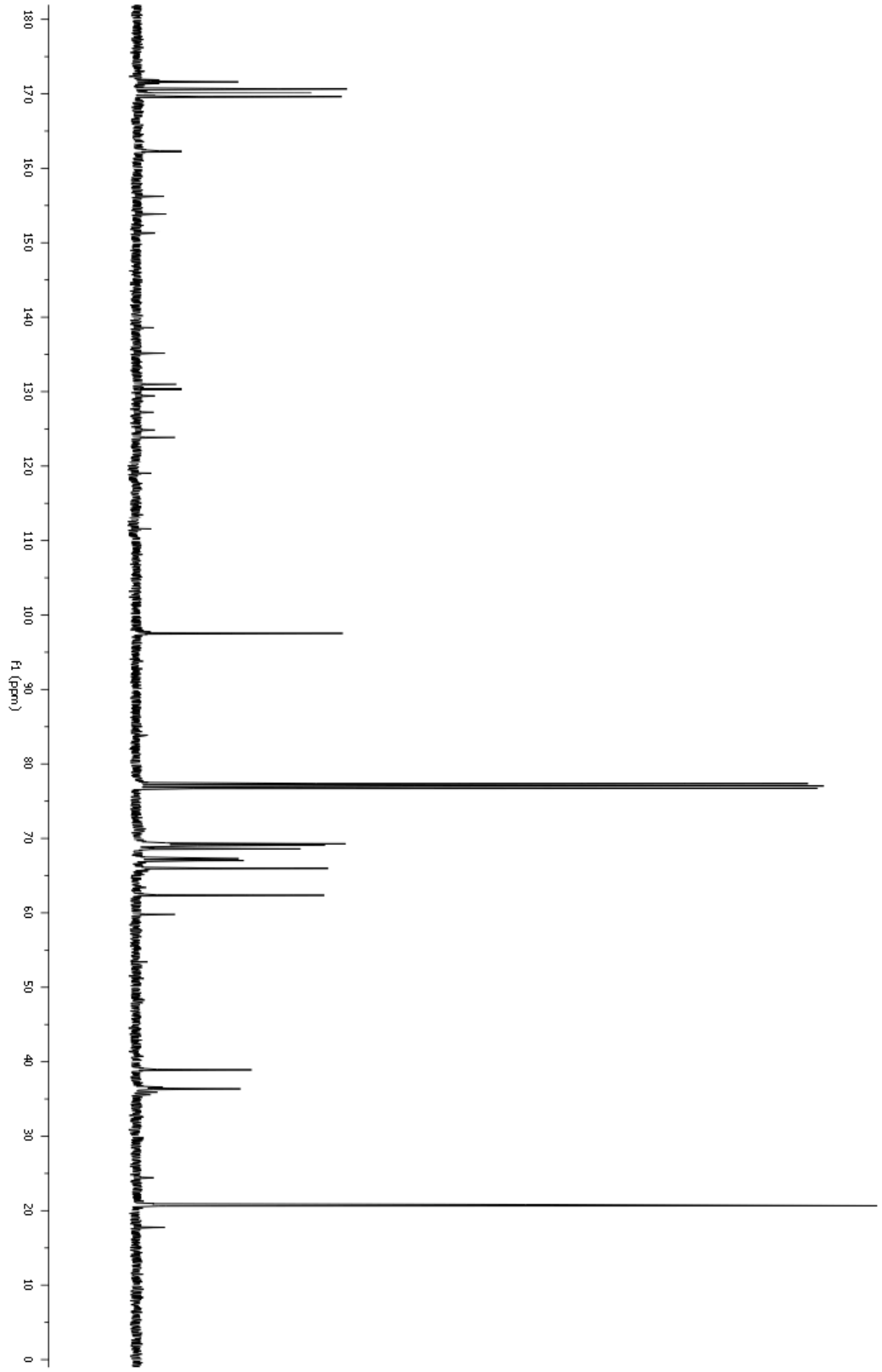

Fig 12. ^{13}C-NMR of Comp 8a

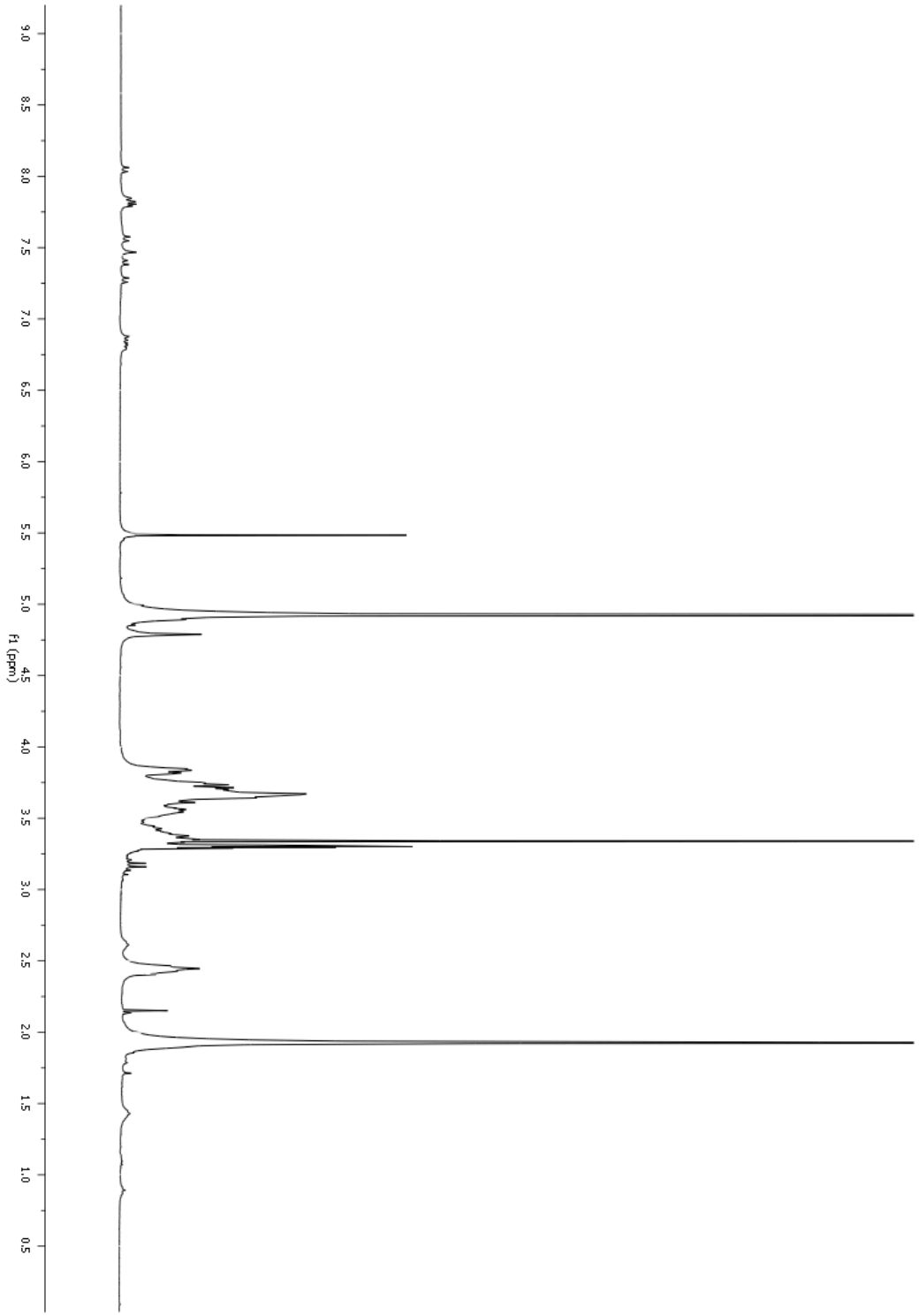

Fig 14. ^{1}H-NMR of Comp 8

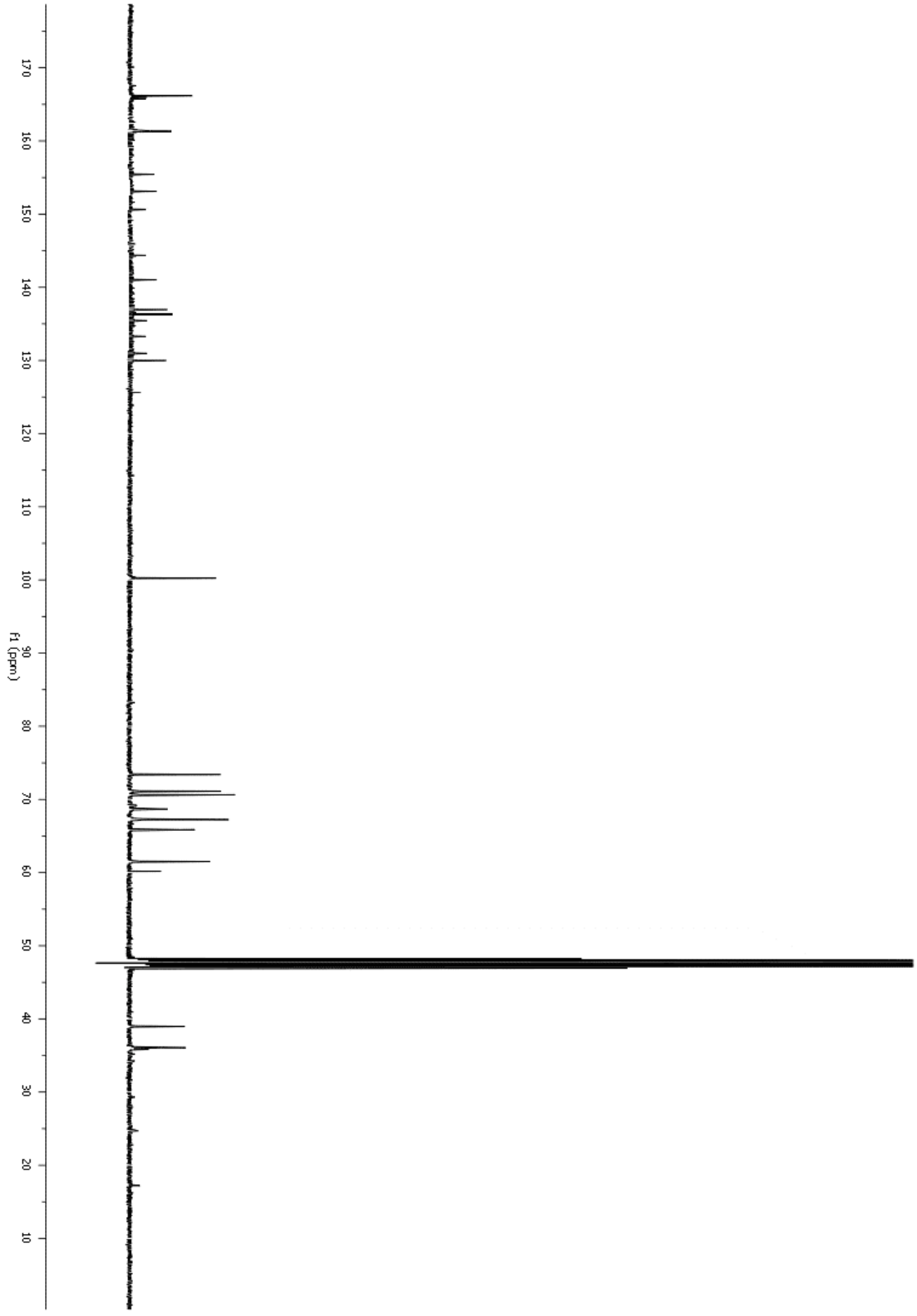

Fig 14. ^{13}C-NMR of Comp 8

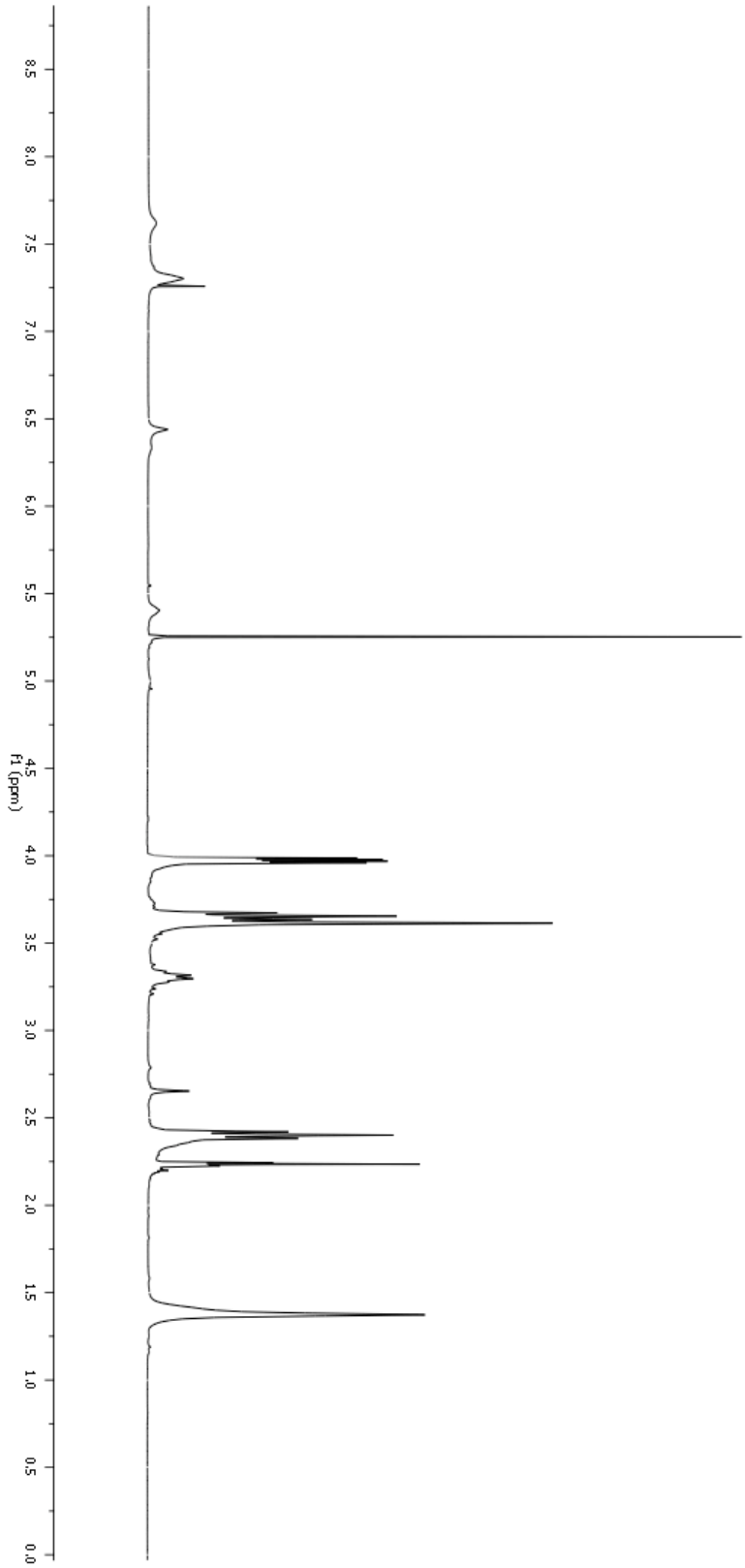

Fig 15. ^{1}H-NMR of Comp 17

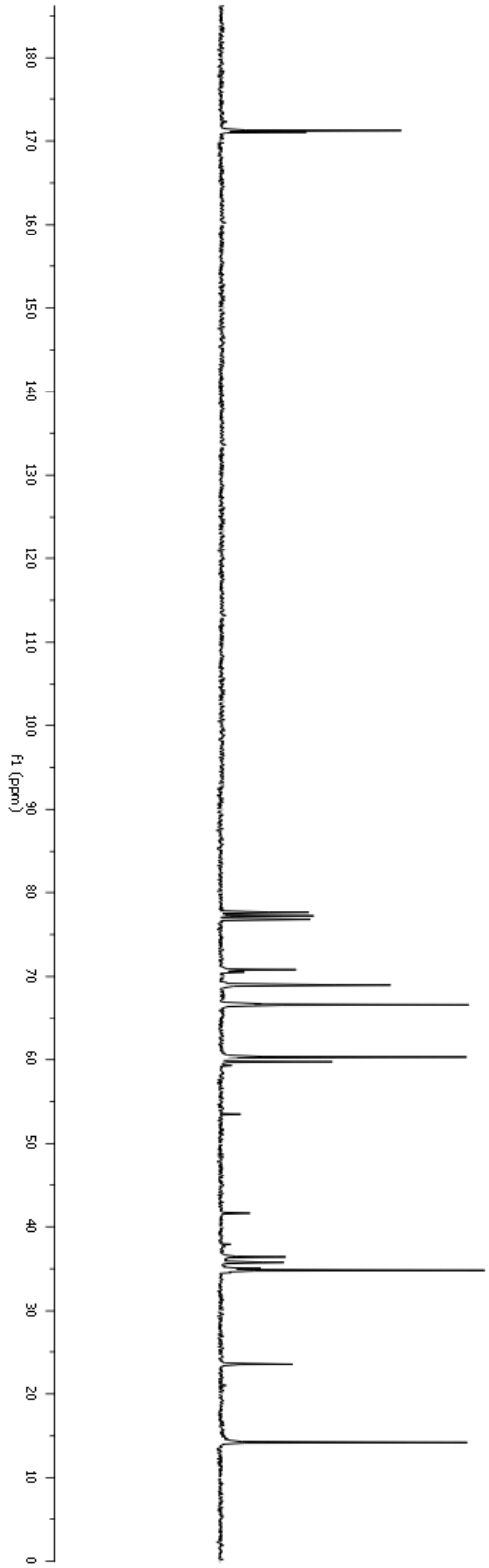

Fig 16. ^{13}C-NMR of Comp 17

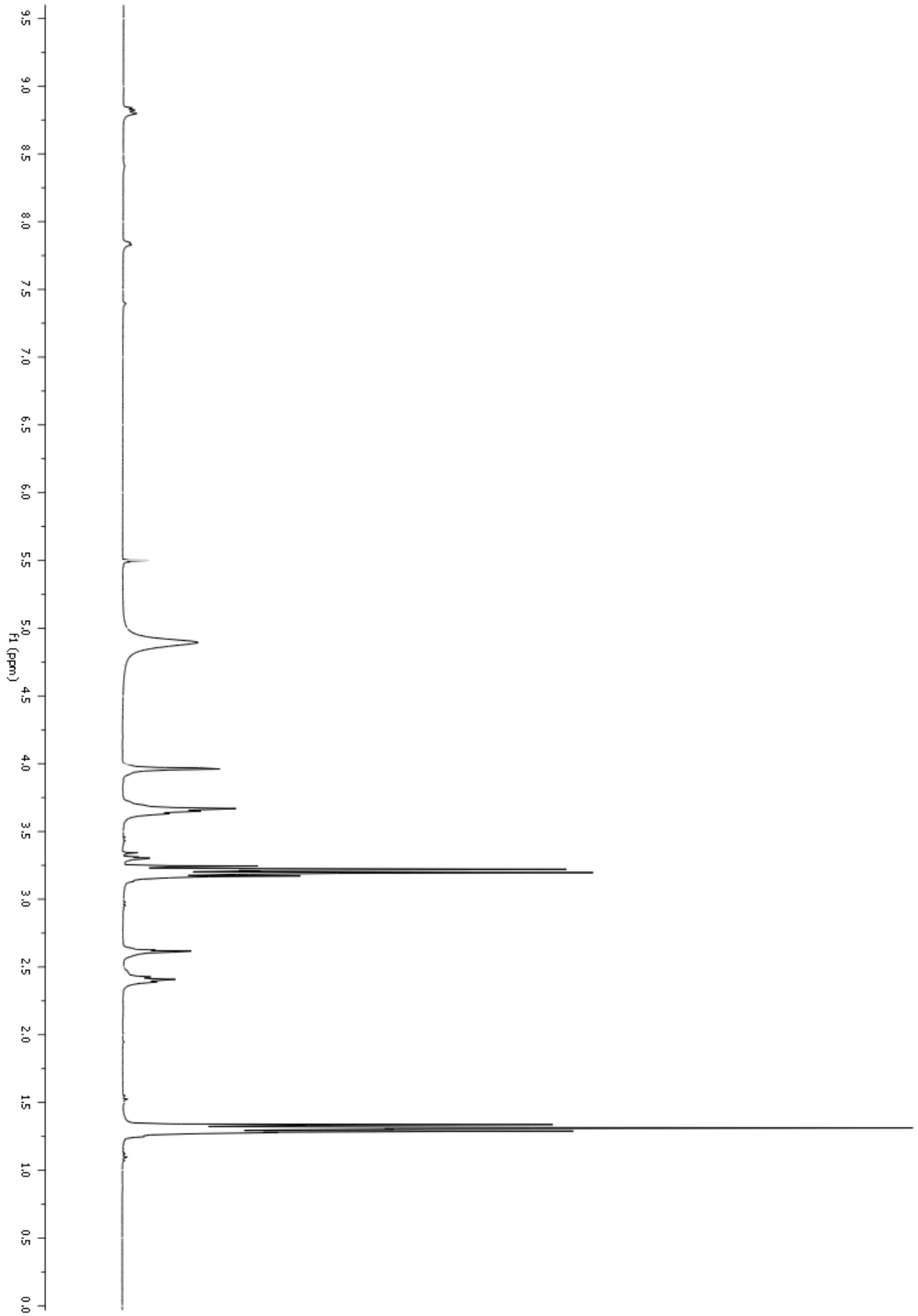

Fig 17. ^{1}H-NMR of Comp 20

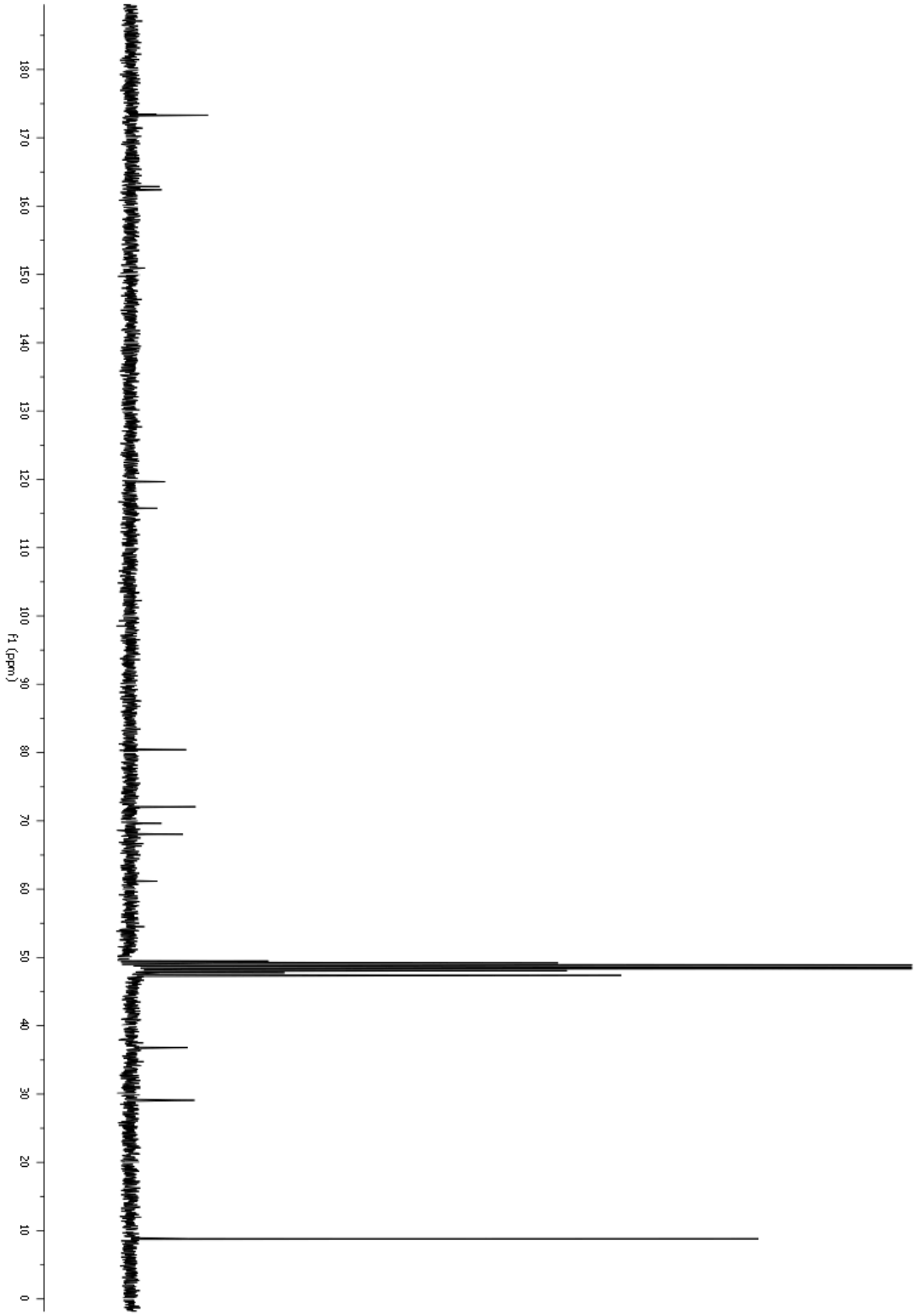

Fig 18. ^{13}C-NMR of Comp 20

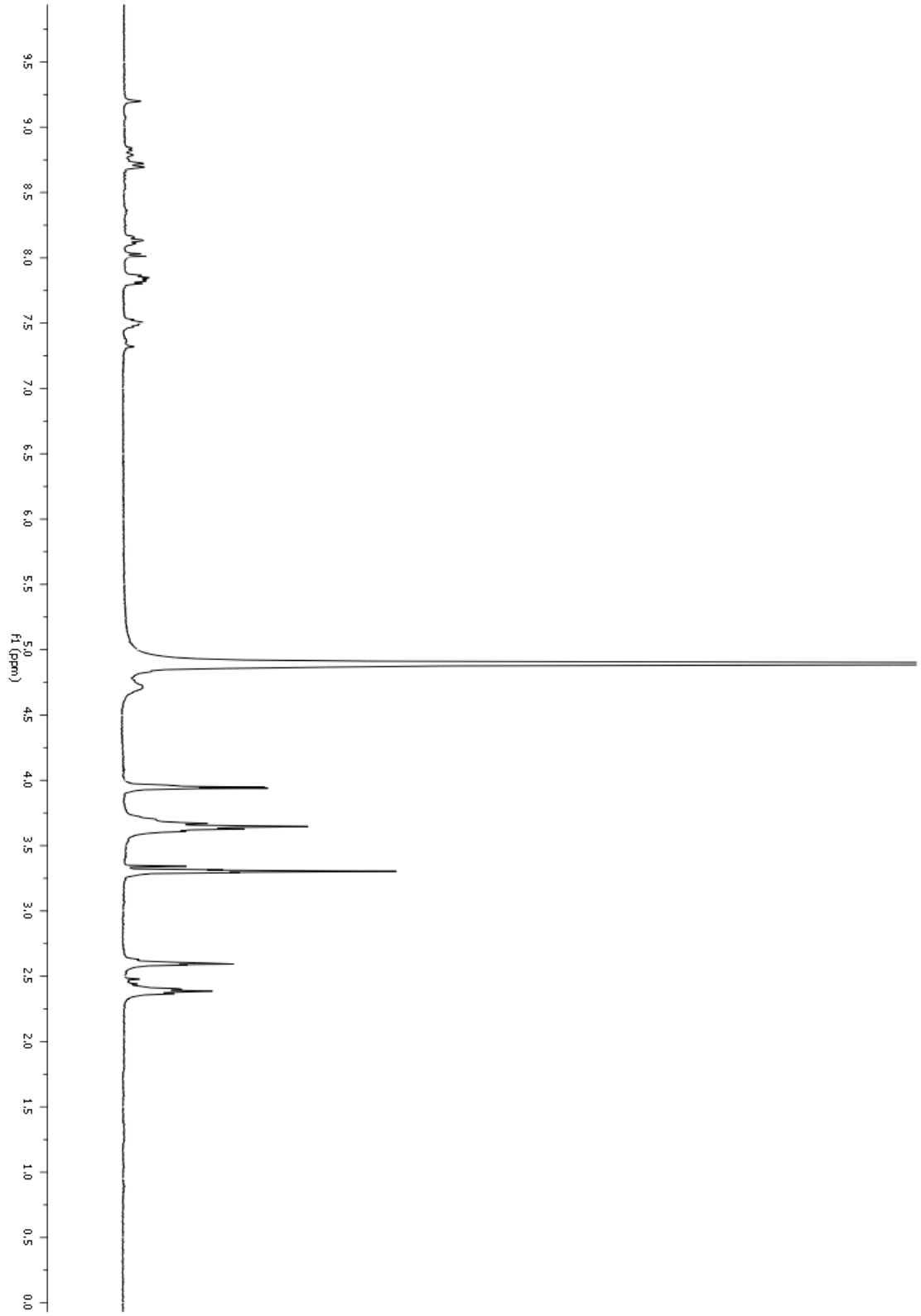

Fig 19. ^{1}H-NMR of Comp 21

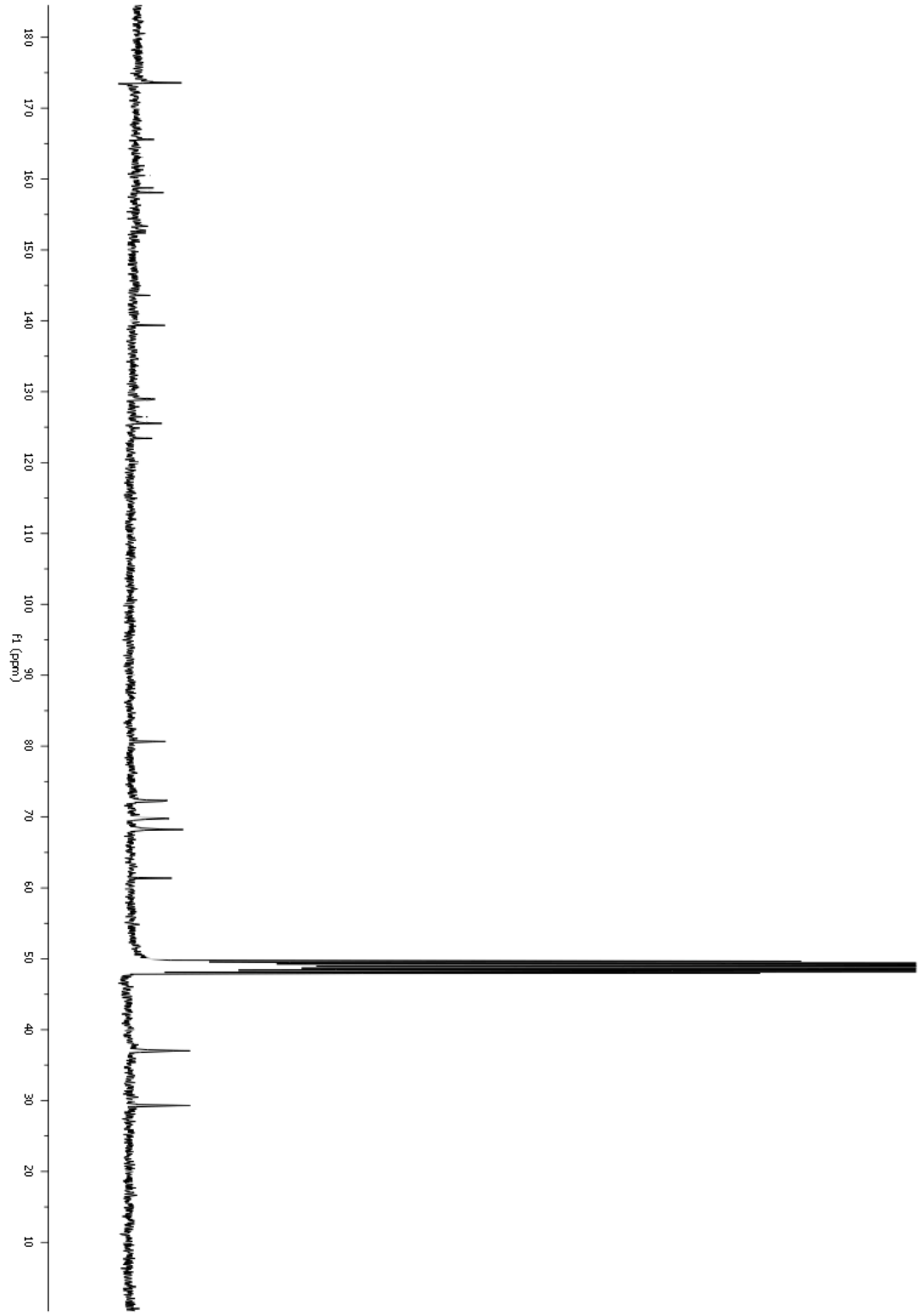

Fig 20. ^{13}C-NMR of Comp 21

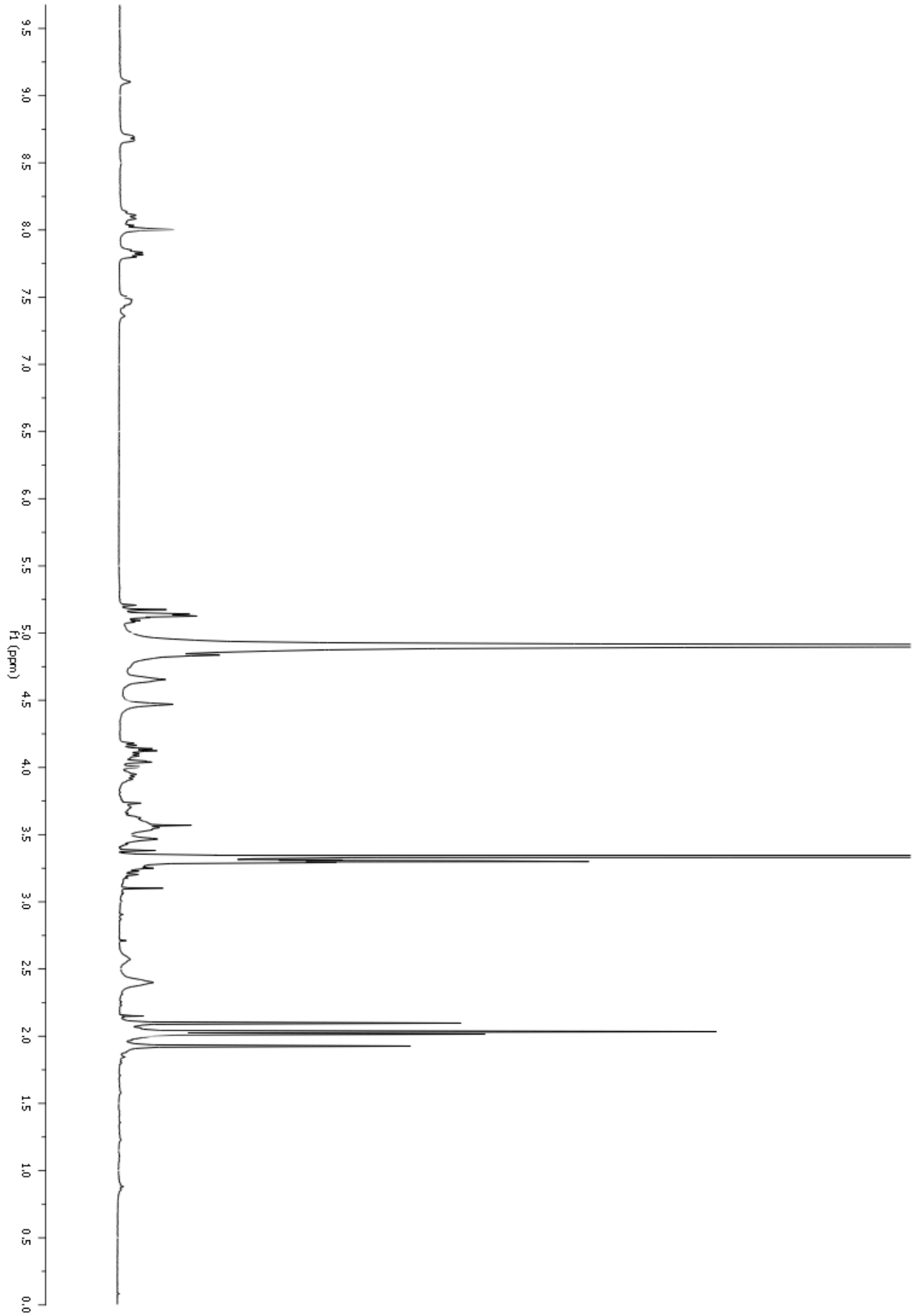

Fig 21. ^{1}H-NMR of Comp 1a

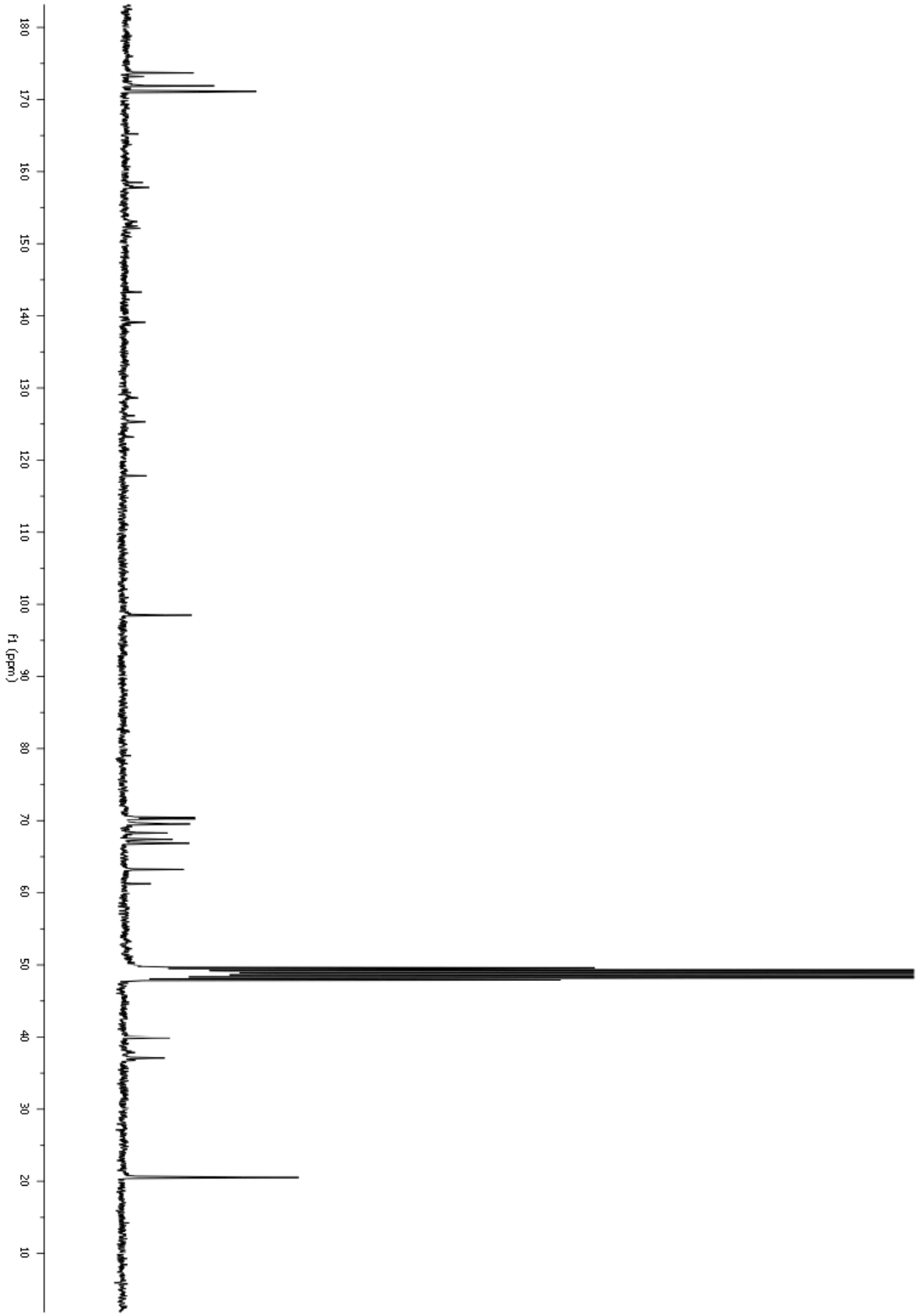

Fig 22. ^{13}C-NMR of Comp 1a

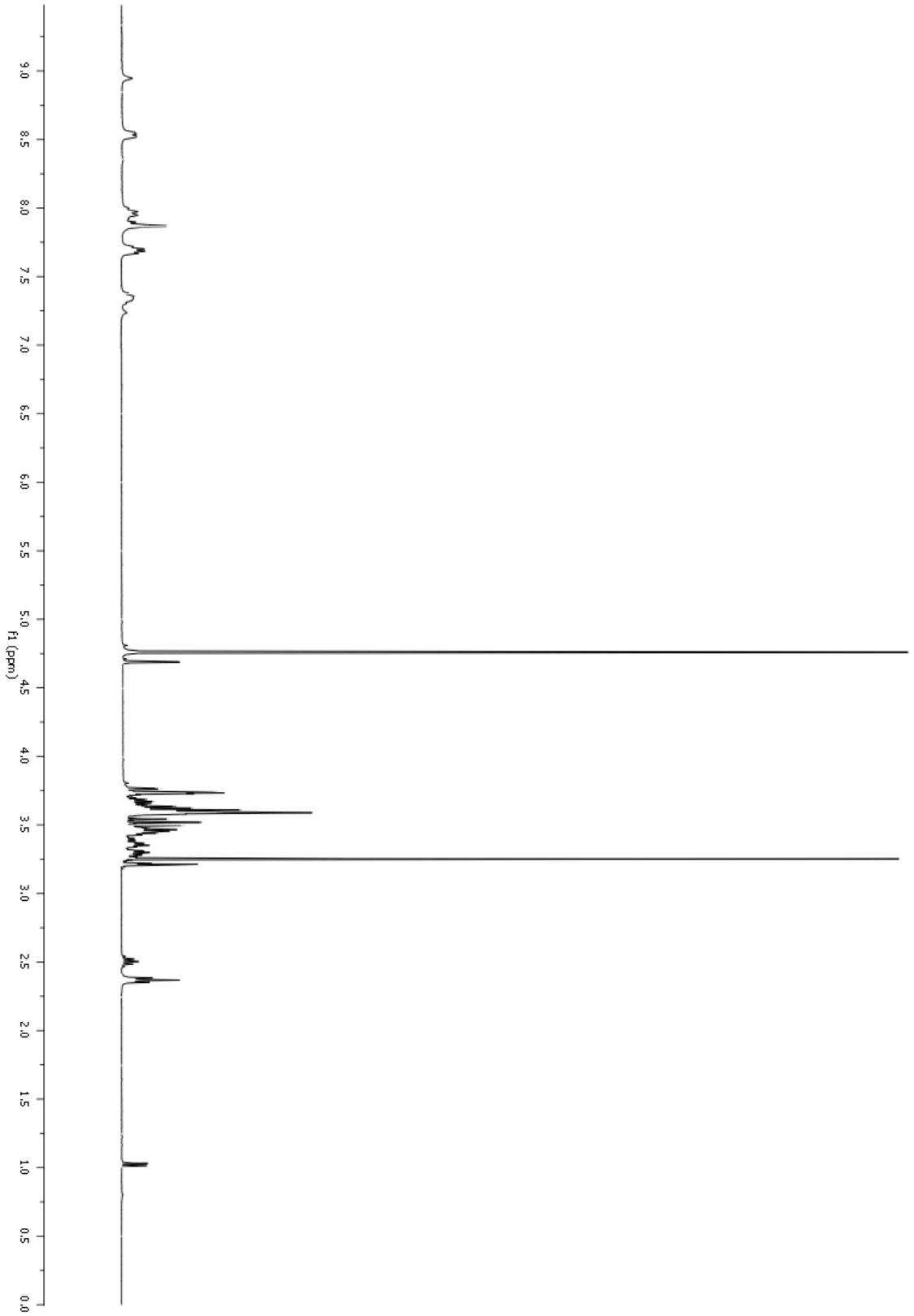

Fig 23. ^{1}H-NMR of Comp 1

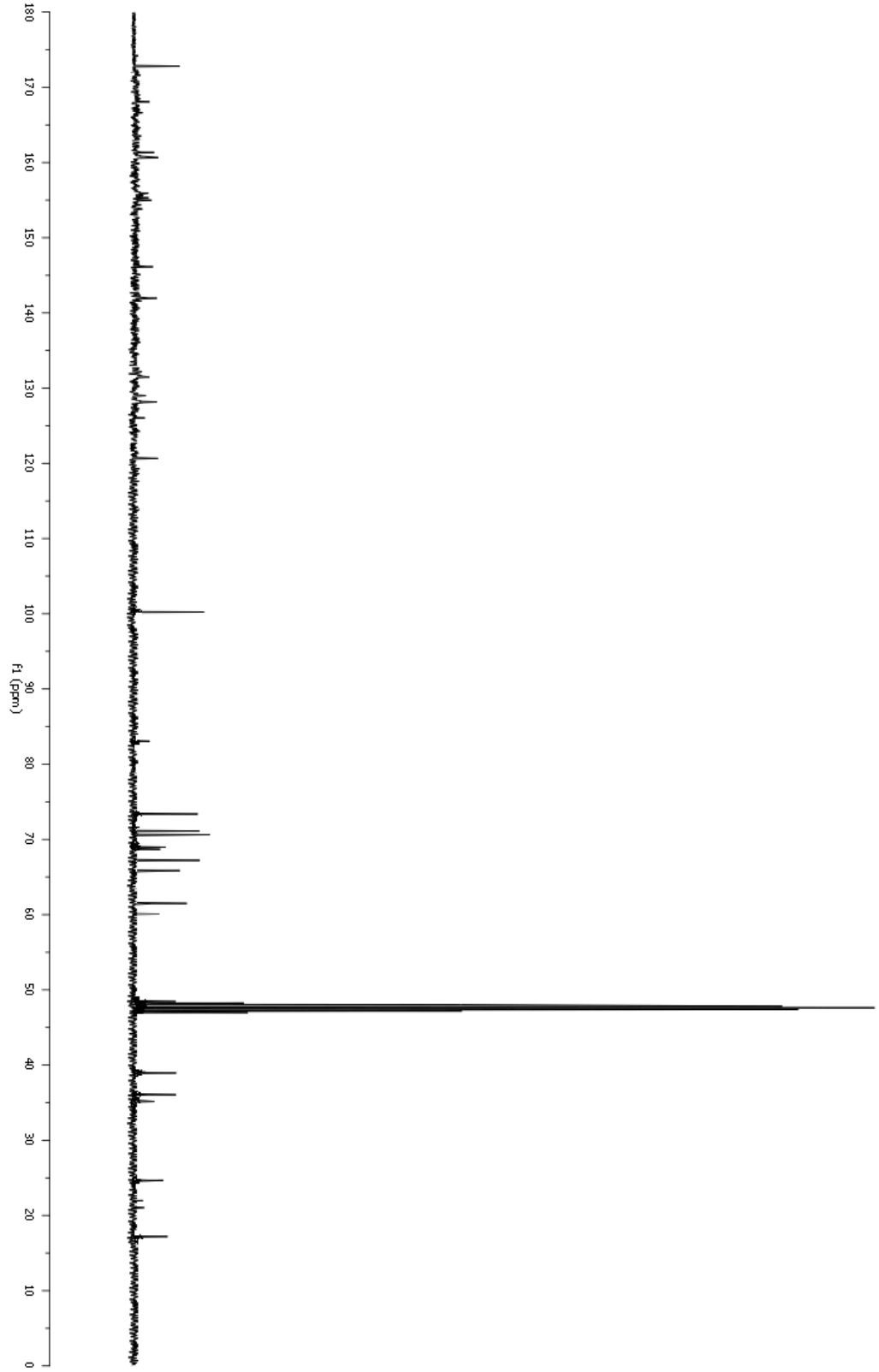

Fig 24. ^{13}C-NMR of Comp 1

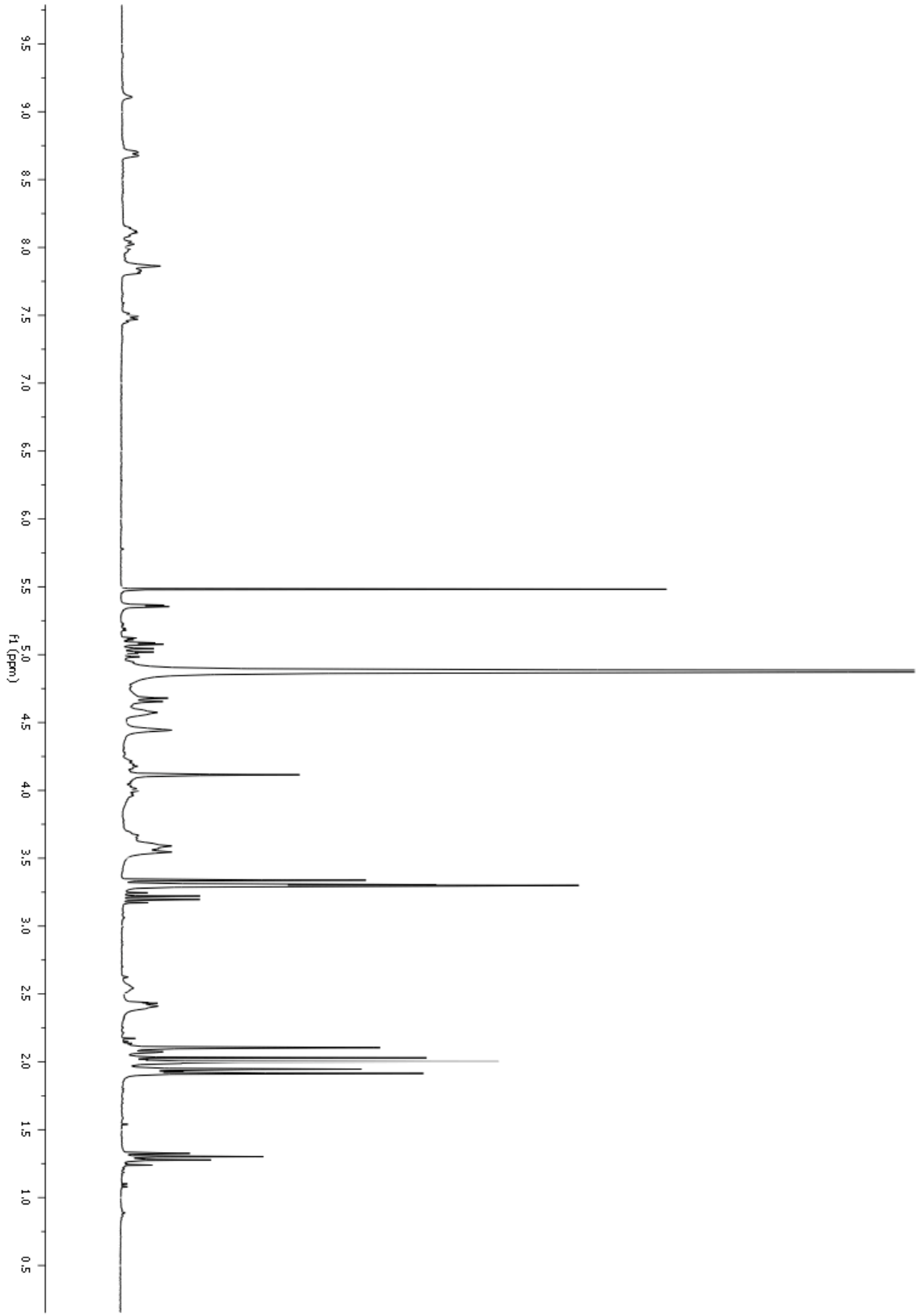

Fig 25. ^{1}H-NMR of Comp 2a

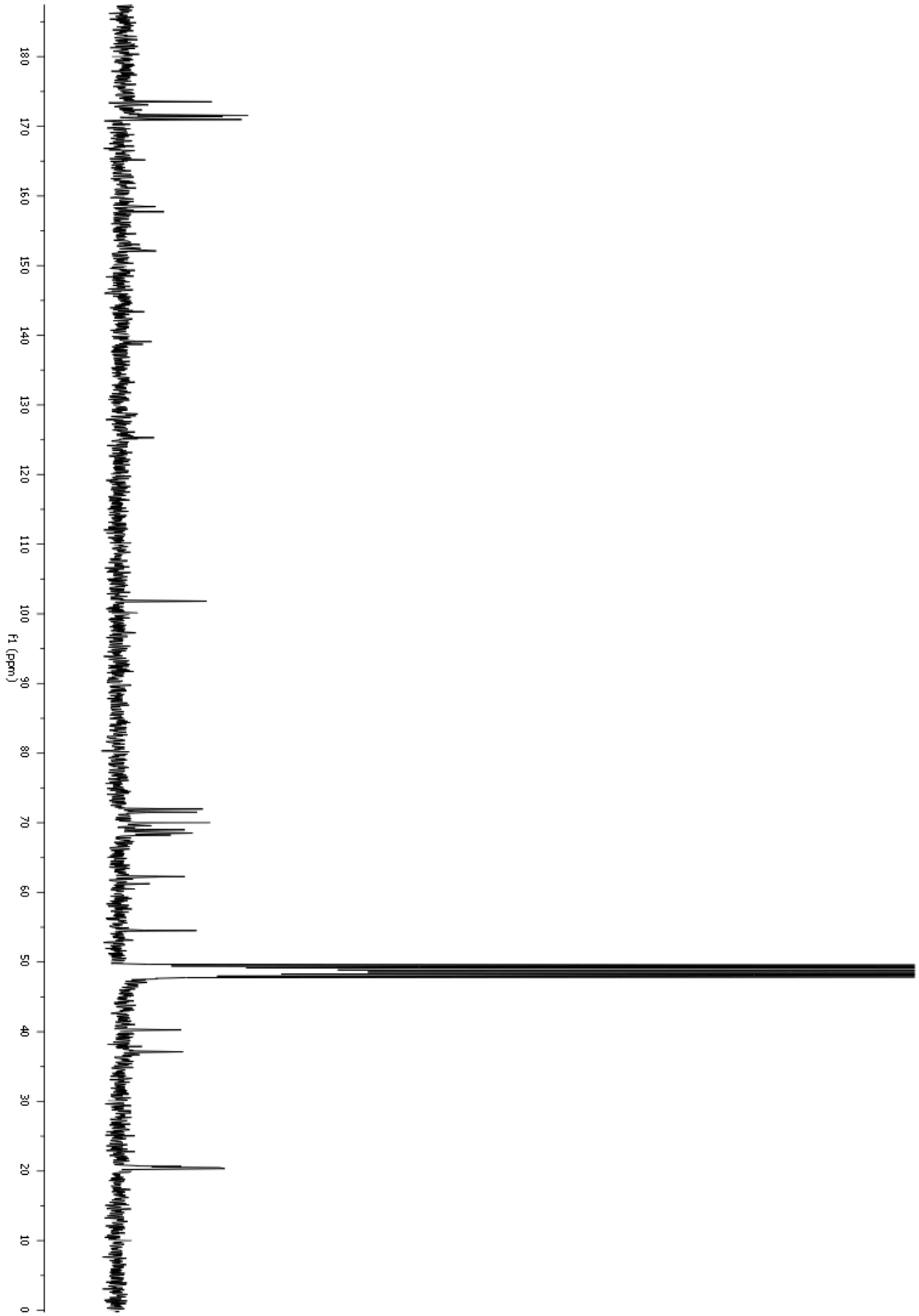

Fig 26. ^{13}C-NMR of Comp 2a

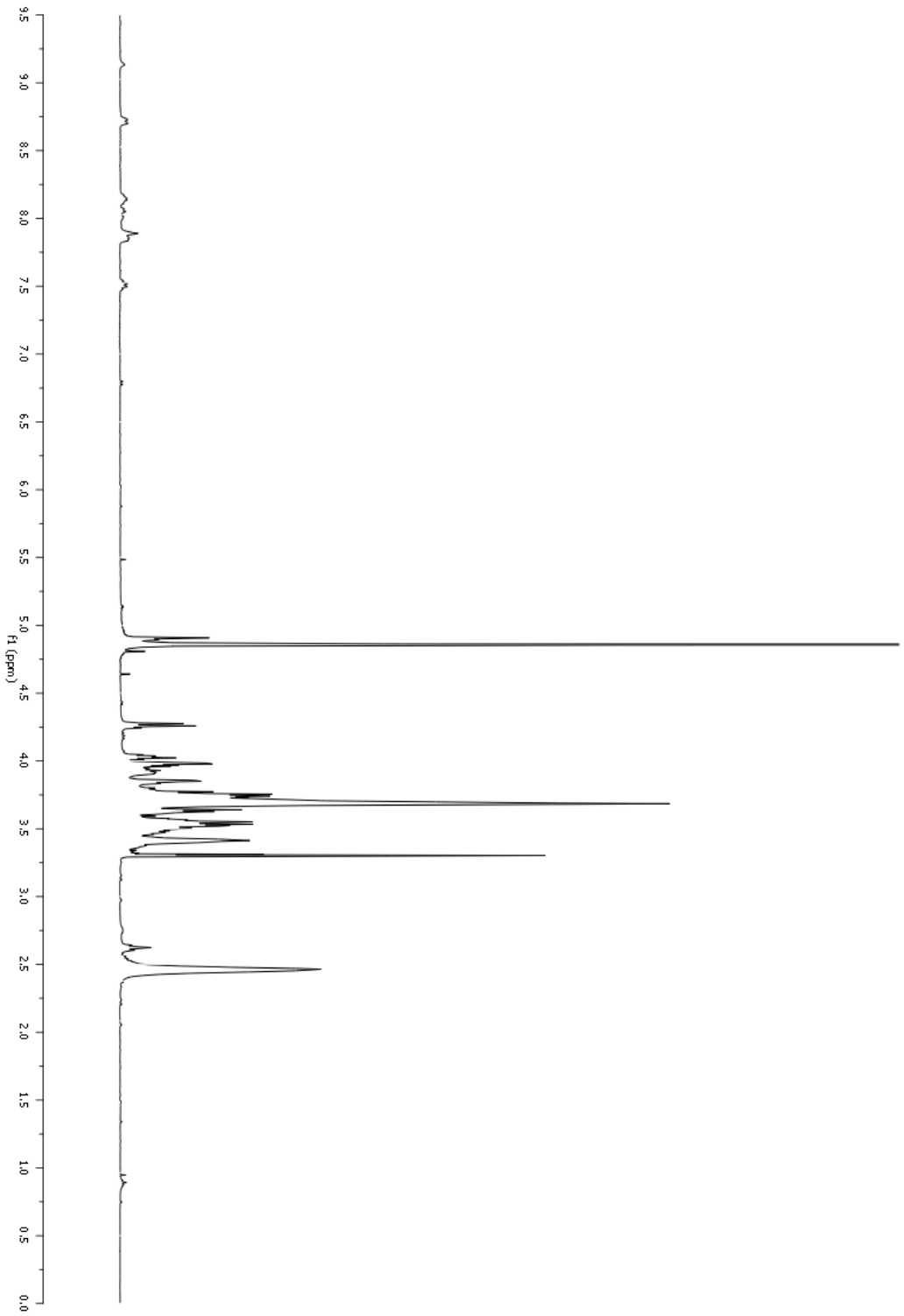

Fig 27. ^{1}H-NMR of Comp 2

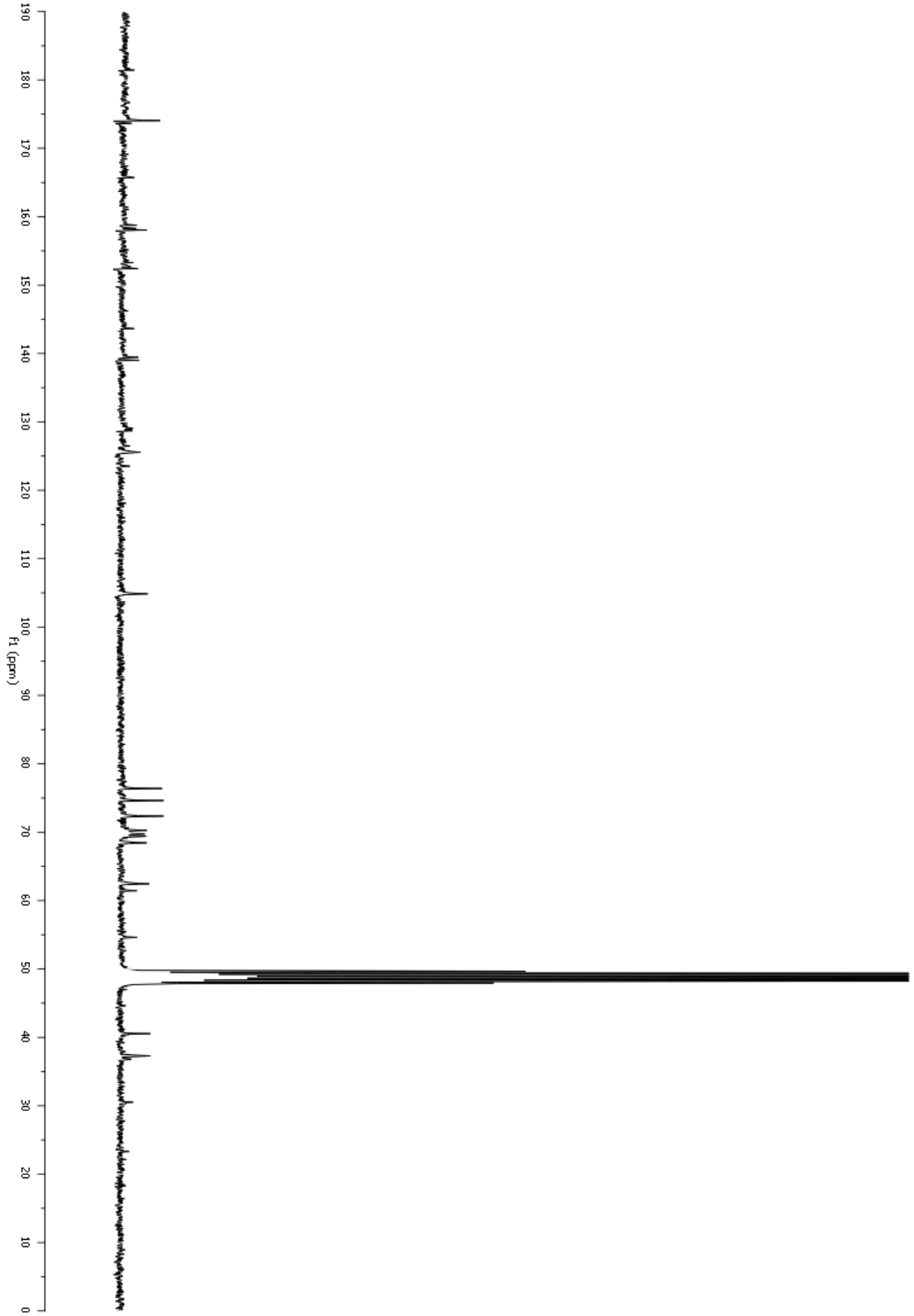

Fig 28. ^{1}H-NMR of Comp 2

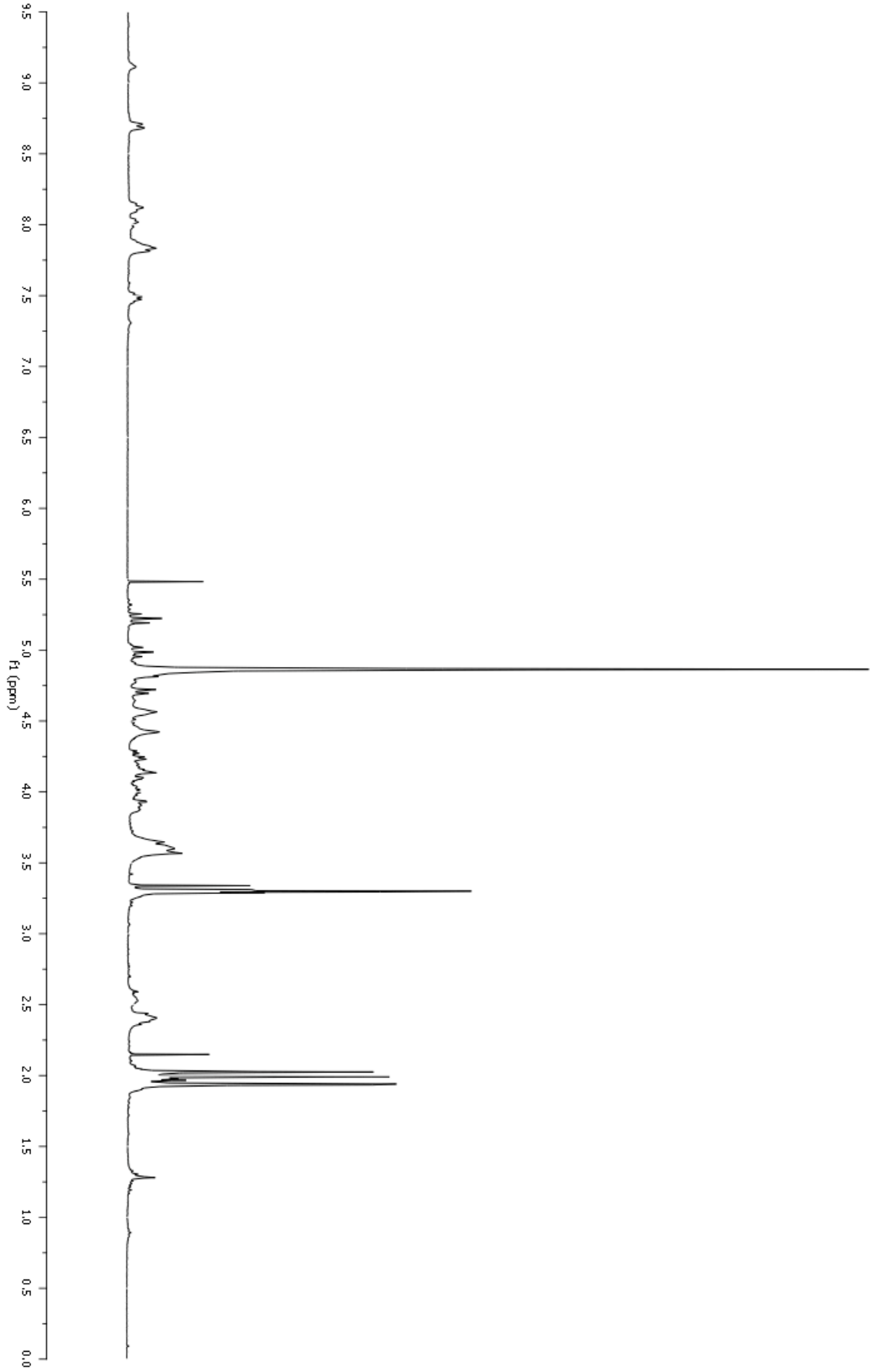

Fig 29. ^{1}H-NMR of Comp 3a

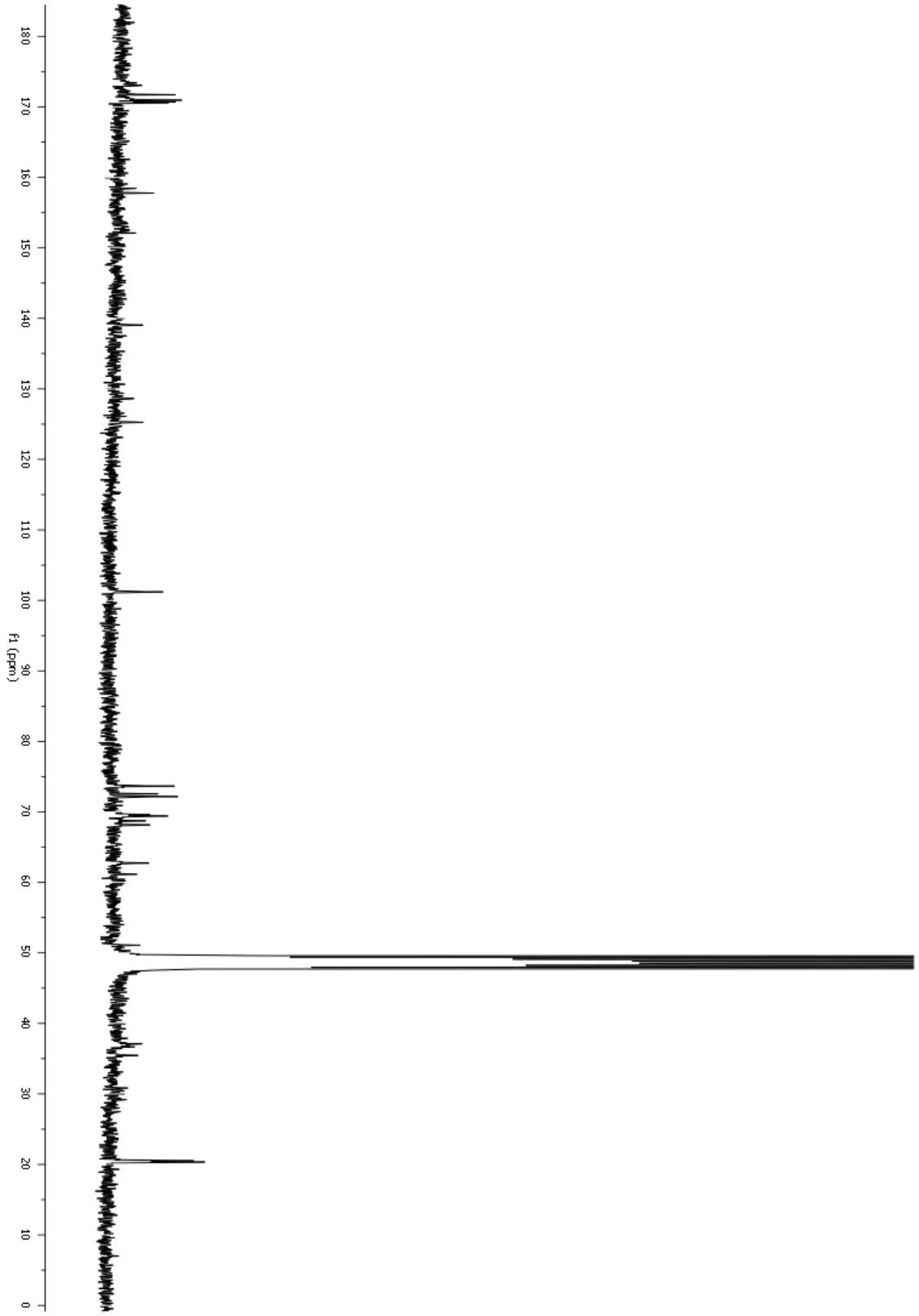

Fig 30. ^{13}C-NMR of Comp 3a

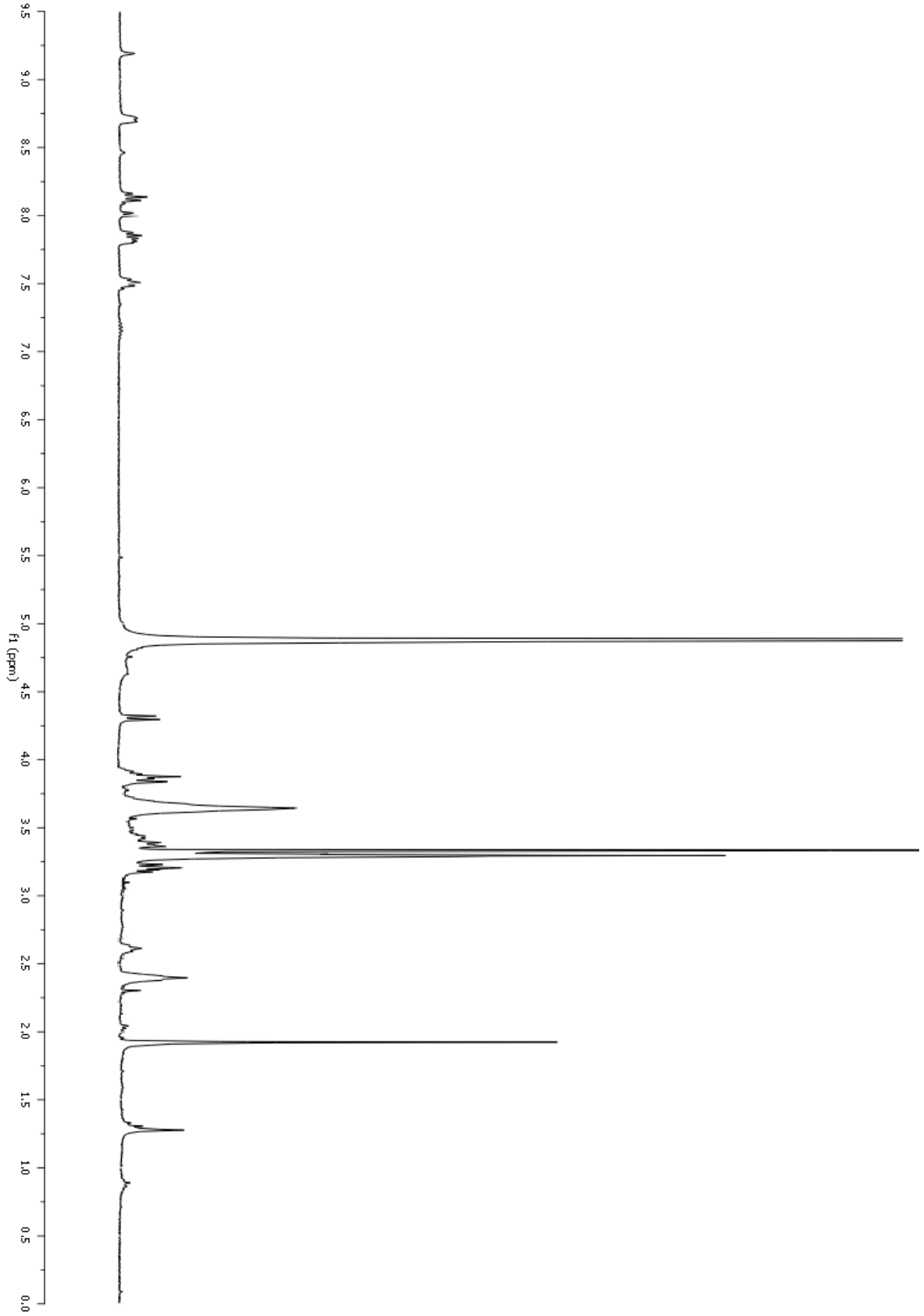

Fig 31. ^{1}H-NMR of Comp 3

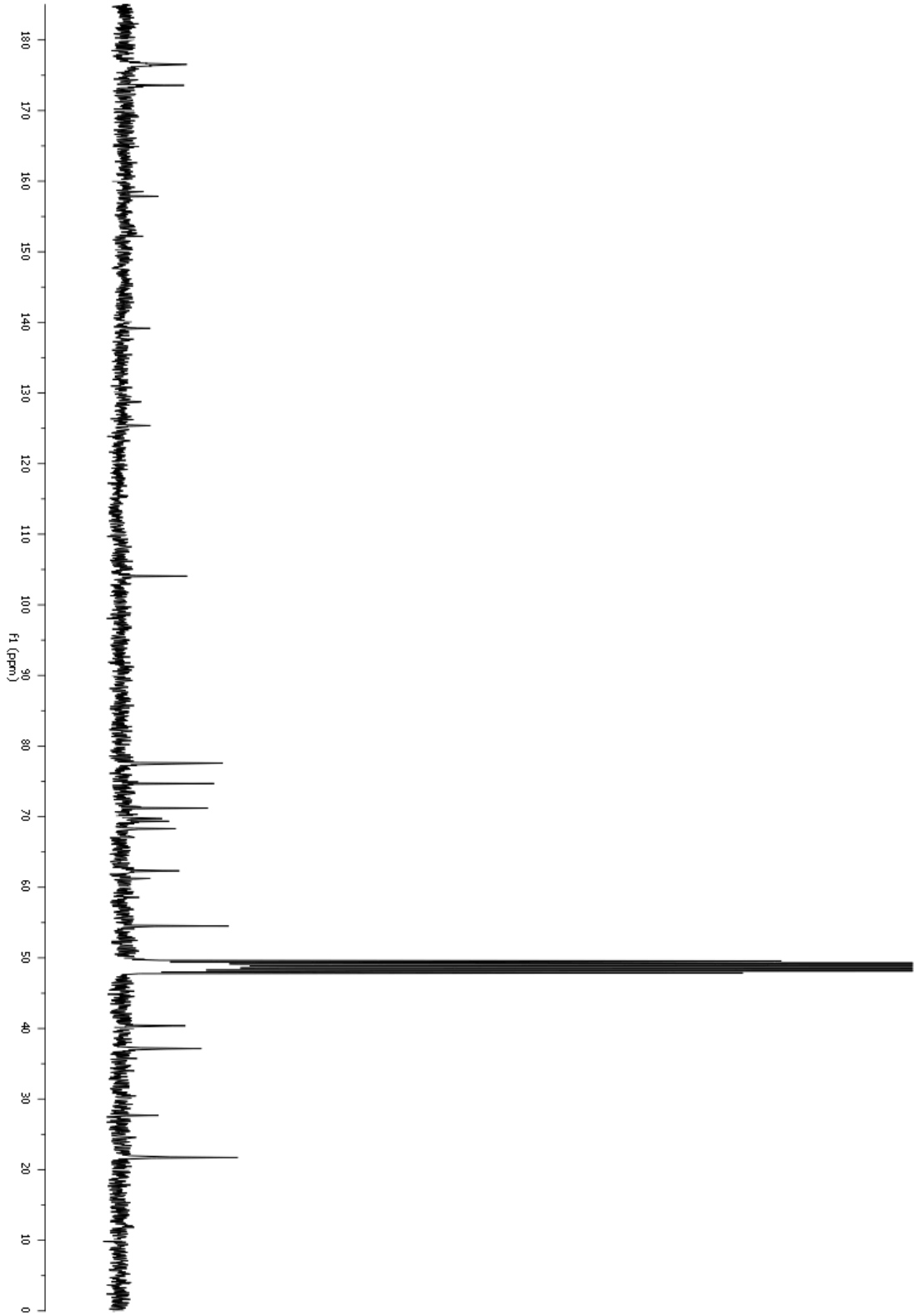

Fig 32. ^{1}H-NMR of Comp 3

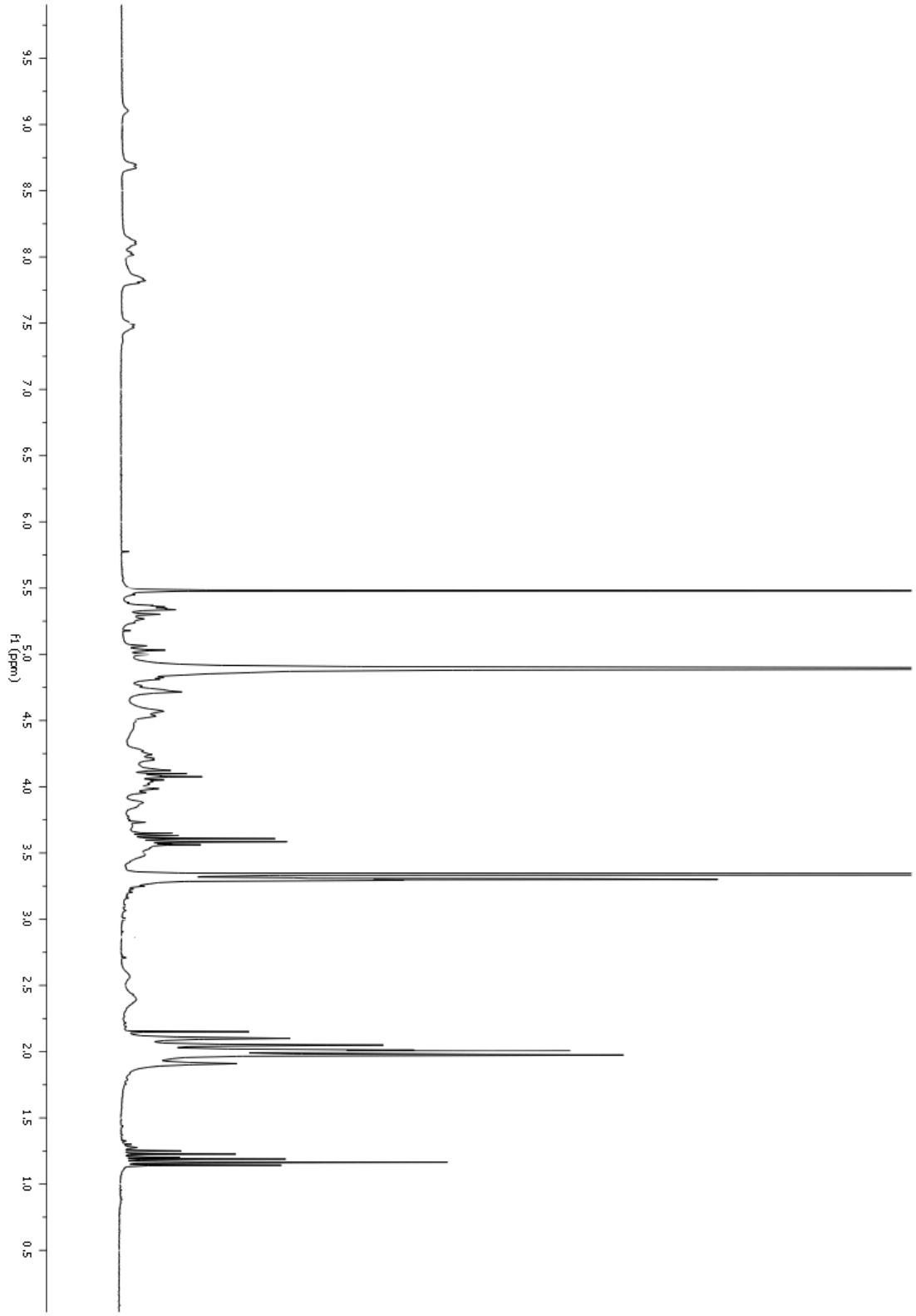

Fig 33. ^{1}H-NMR of Comp 4a

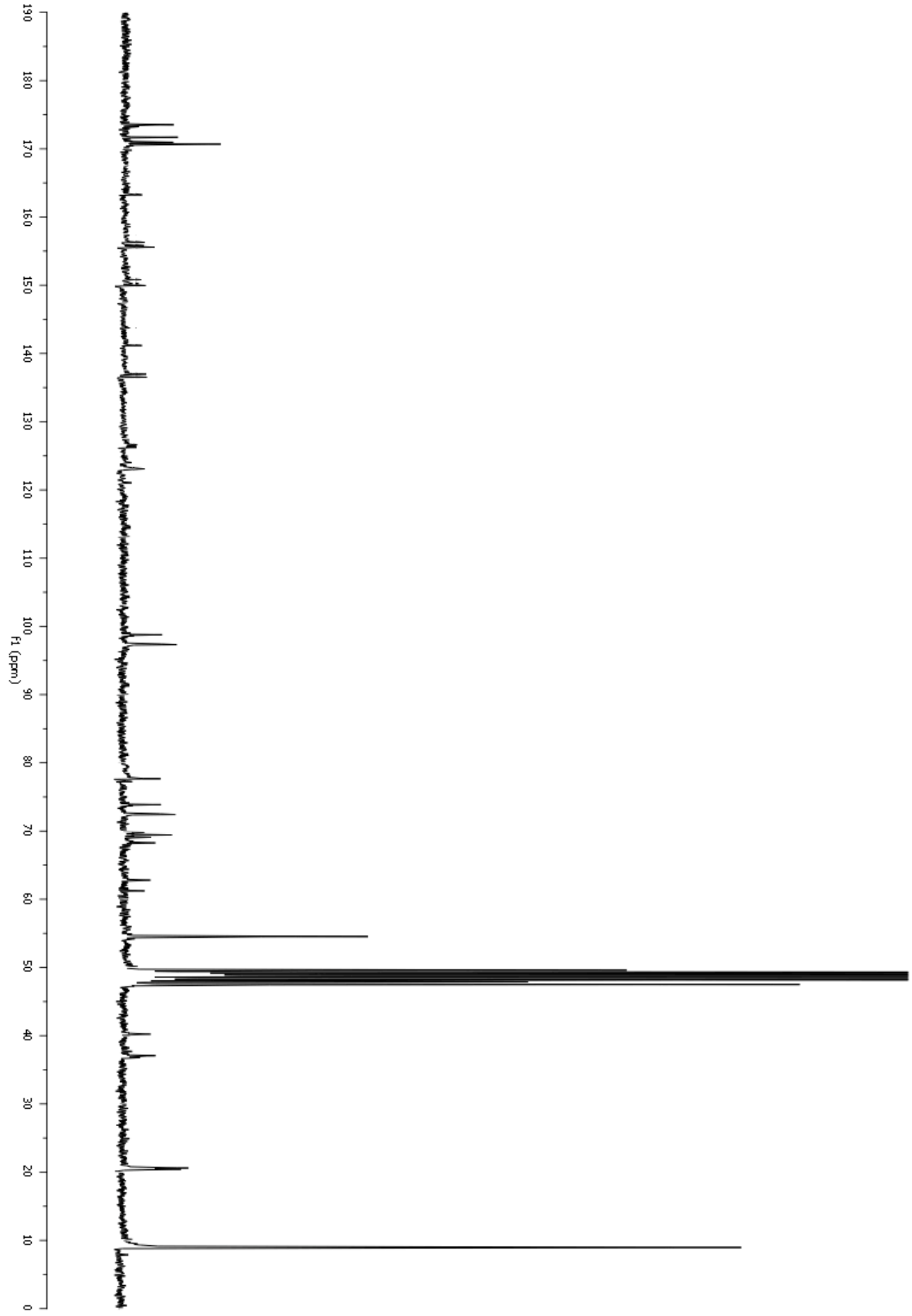

Fig 34. ^{13}C-NMR of Comp 4a

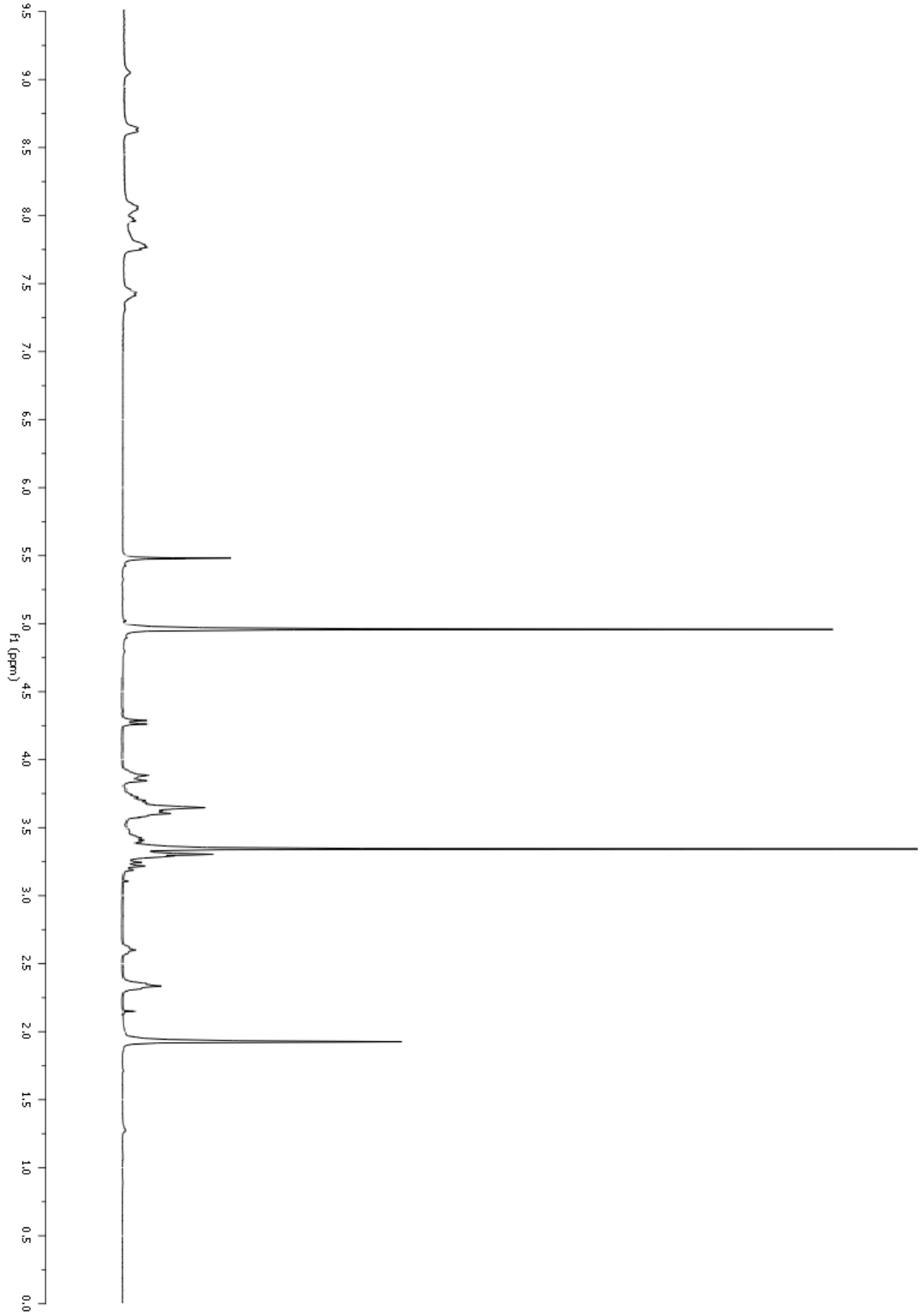

Fig 35. ^{1}H-NMR of Comp 4

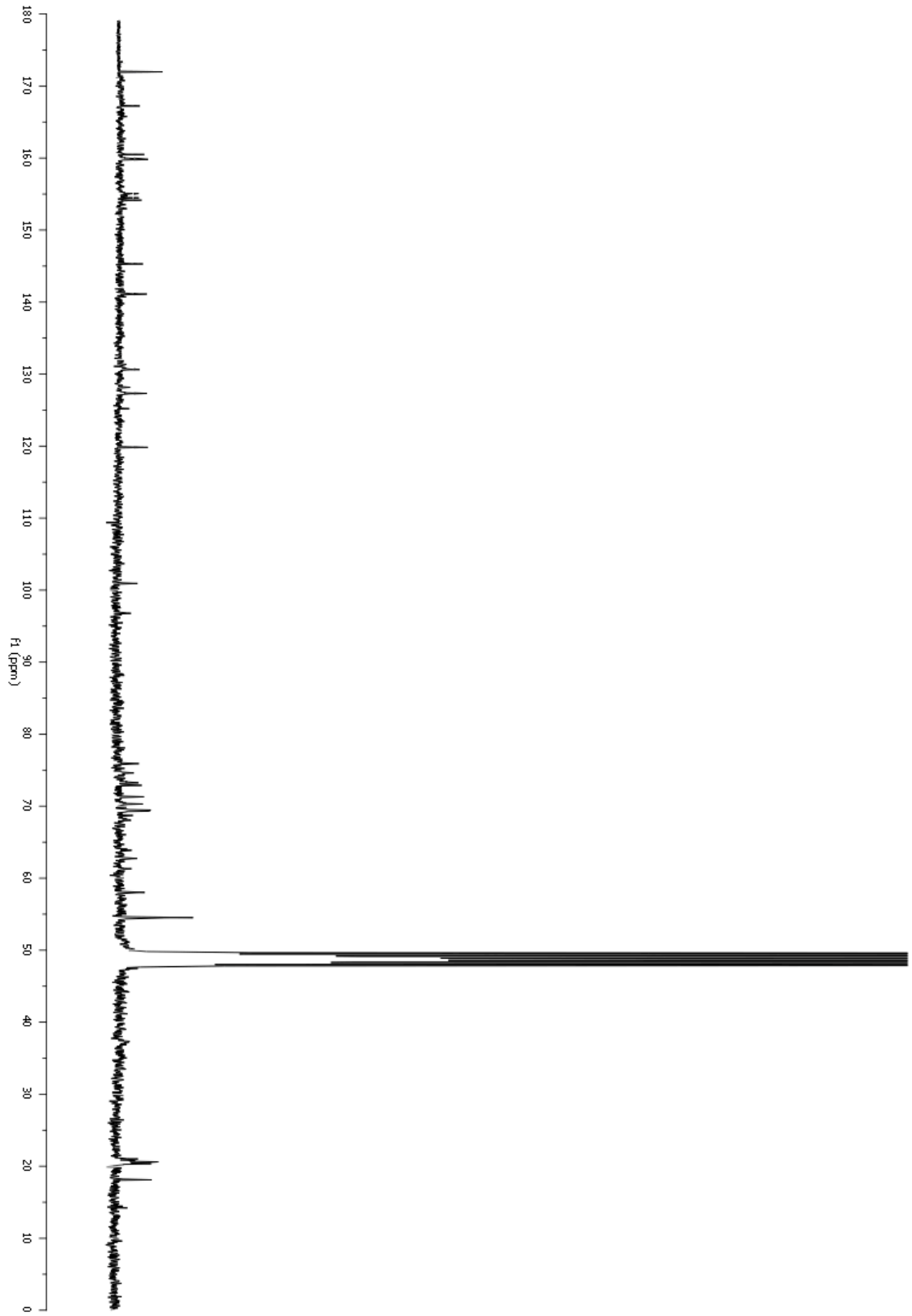

Fig 36. ^{13}C-NMR of Comp 4

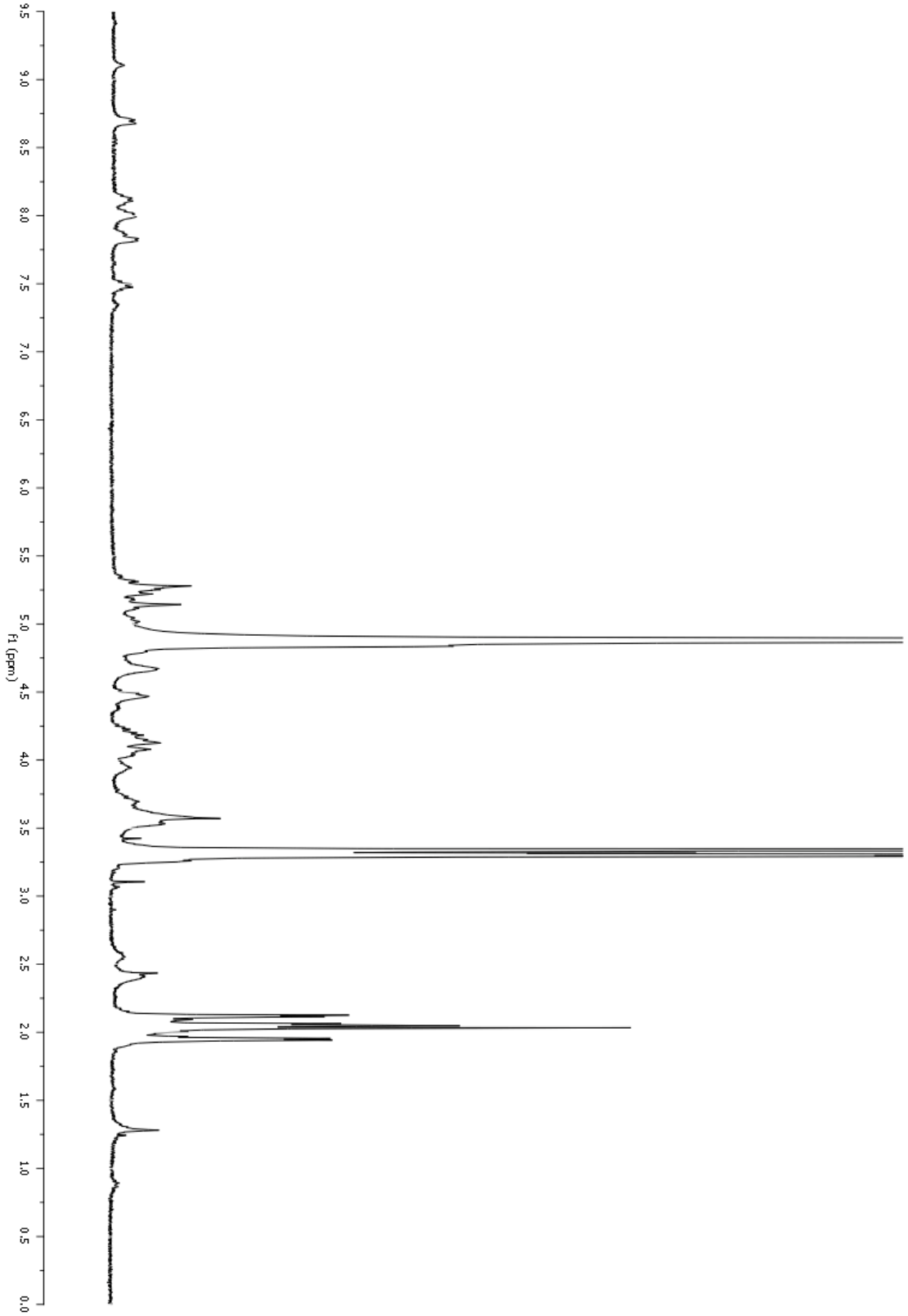

Fig 37. ^{1}H-NMR of Comp 5a

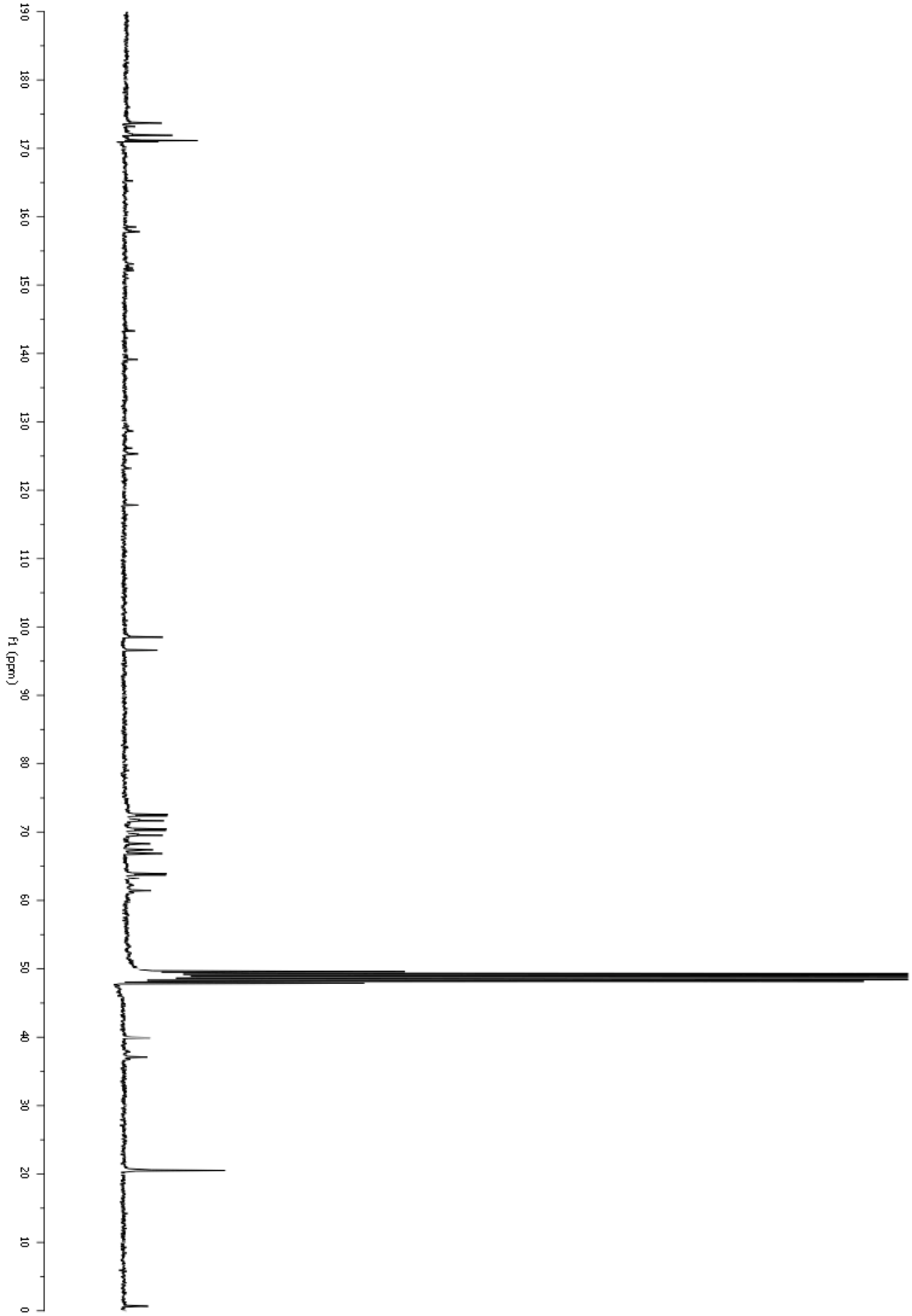

Fig 38. ^{13}C-NMR of Comp 5a

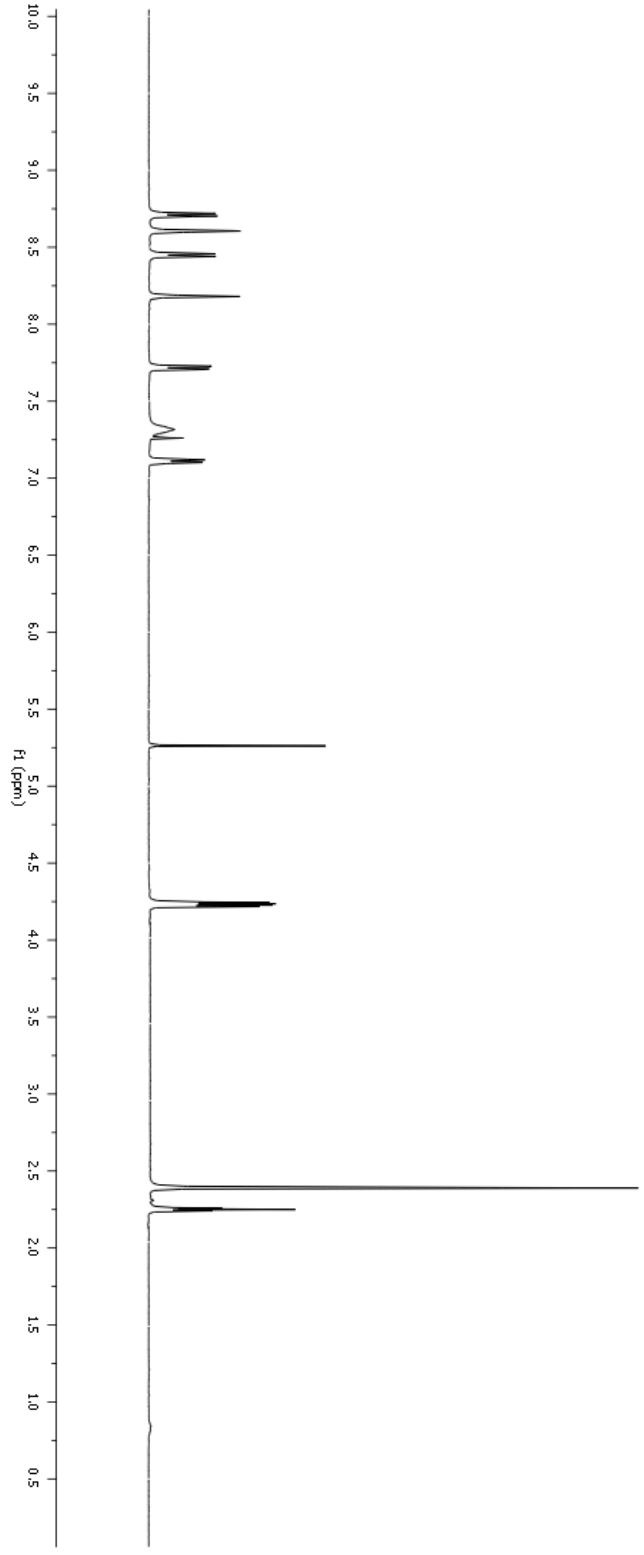

Fig 39. ^{1}H-NMR of Comp 23

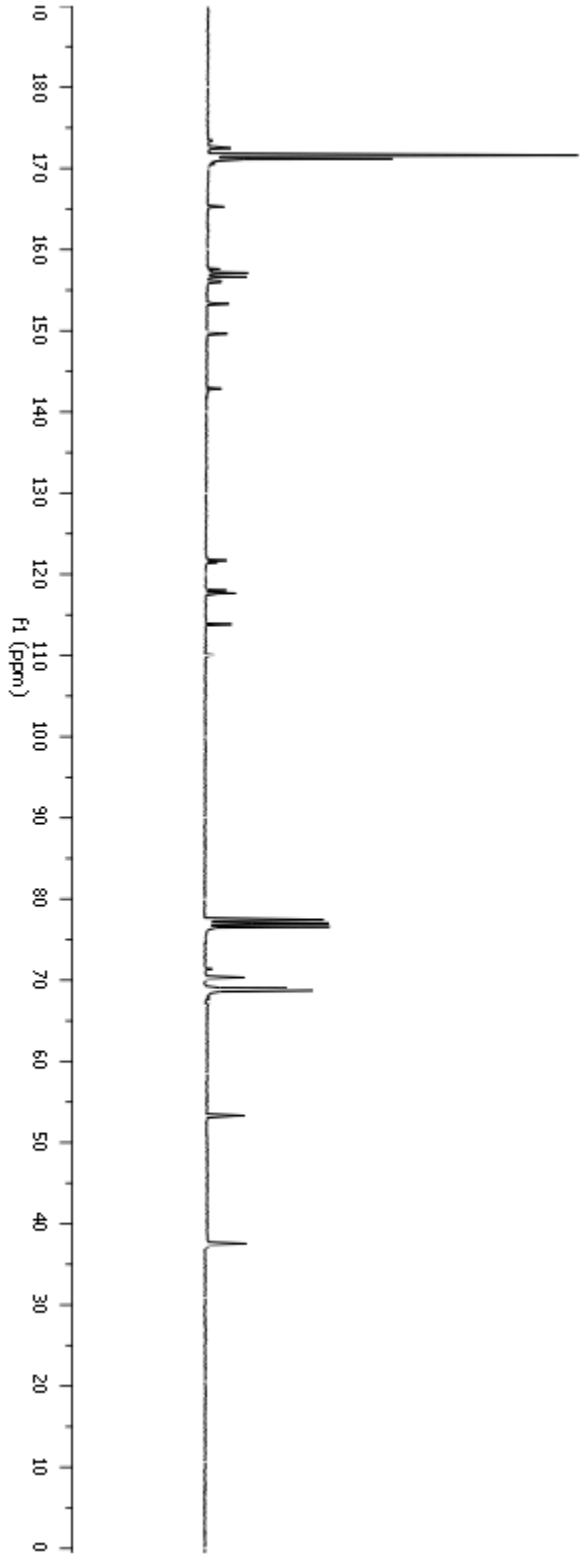

Fig 40. ^{13}C-NMR of Comp 23

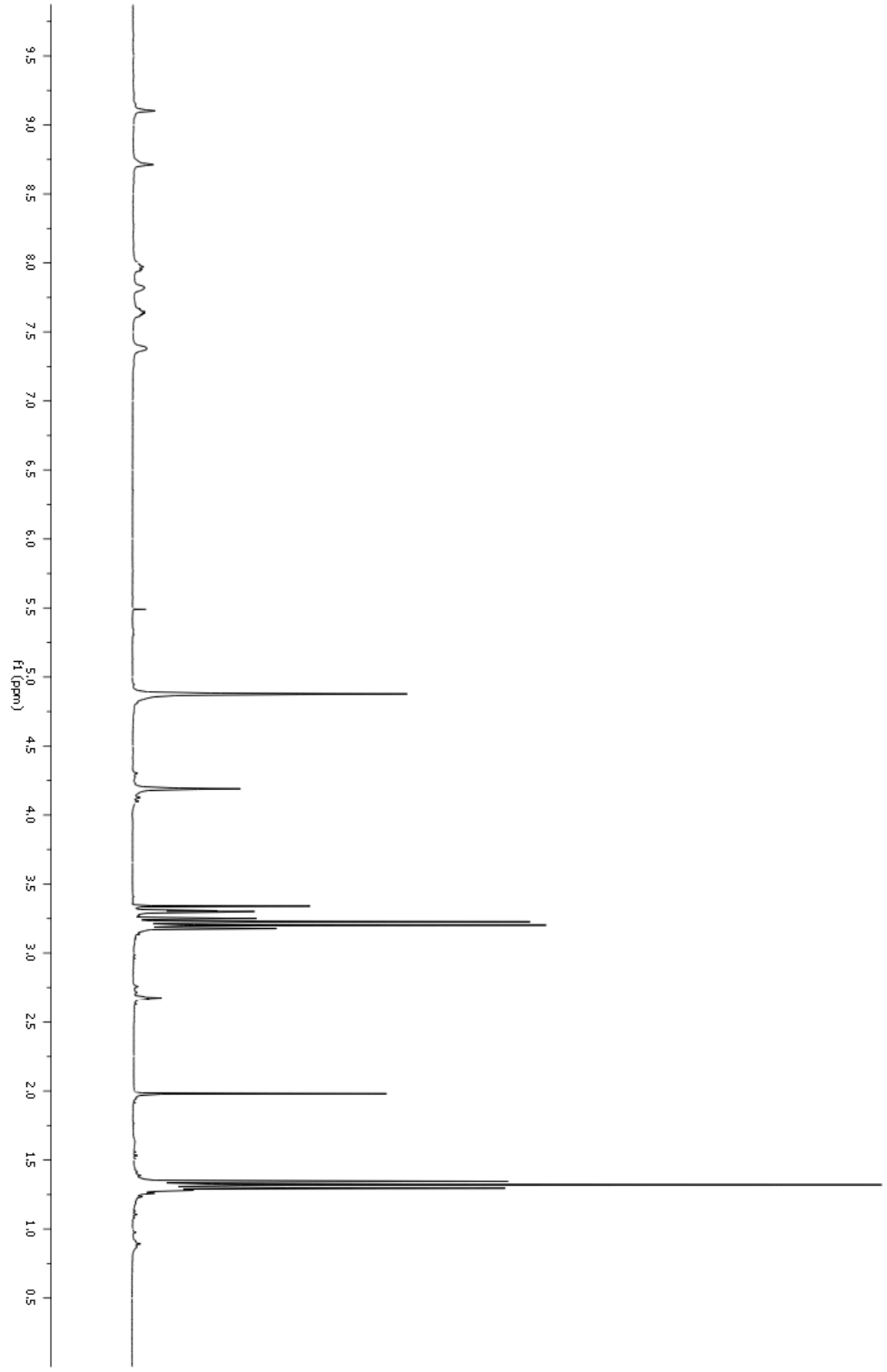

Fig 41. ^{1}H-NMR of Comp 24

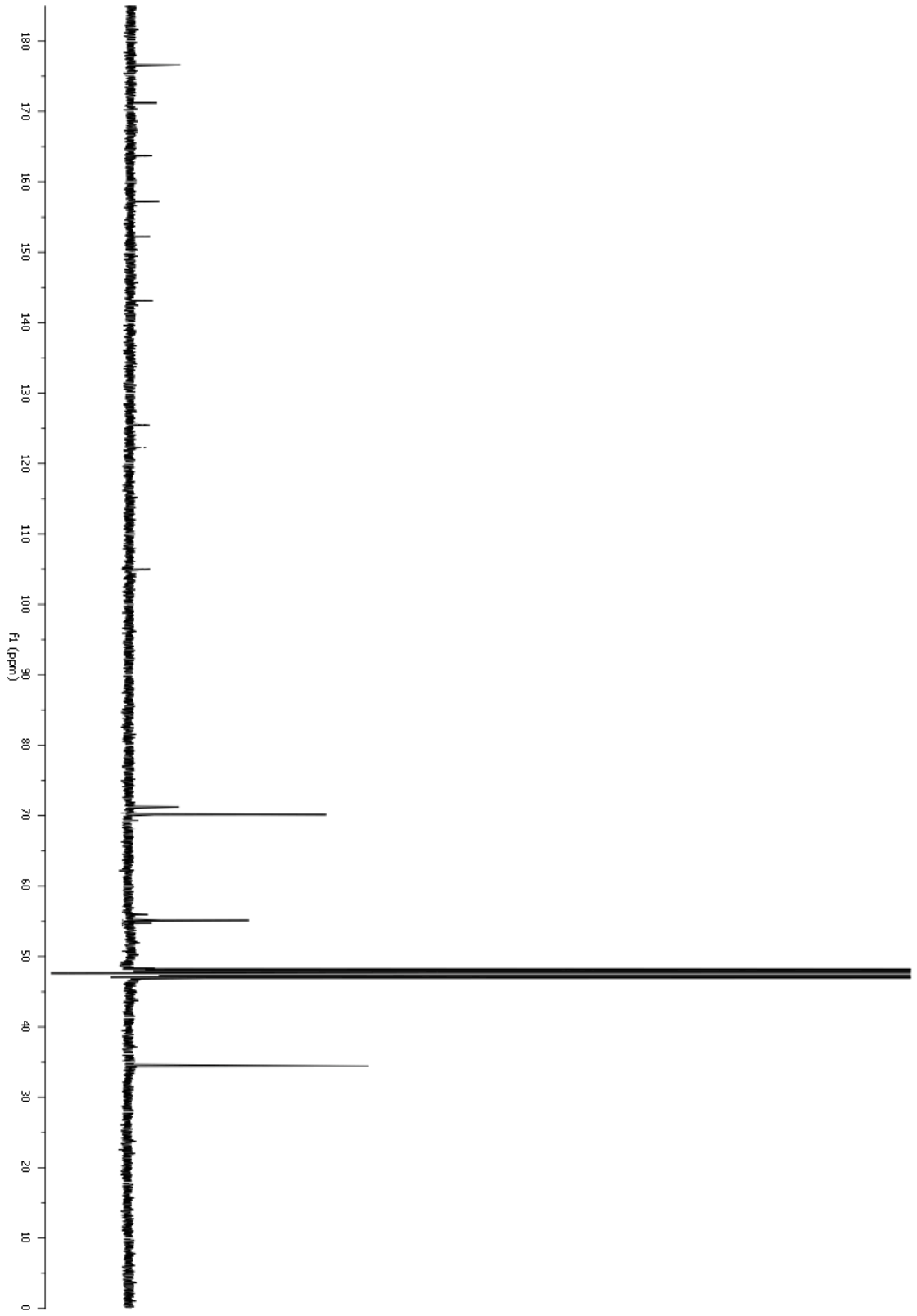

Fig 42. ^{13}C-NMR of Comp 24

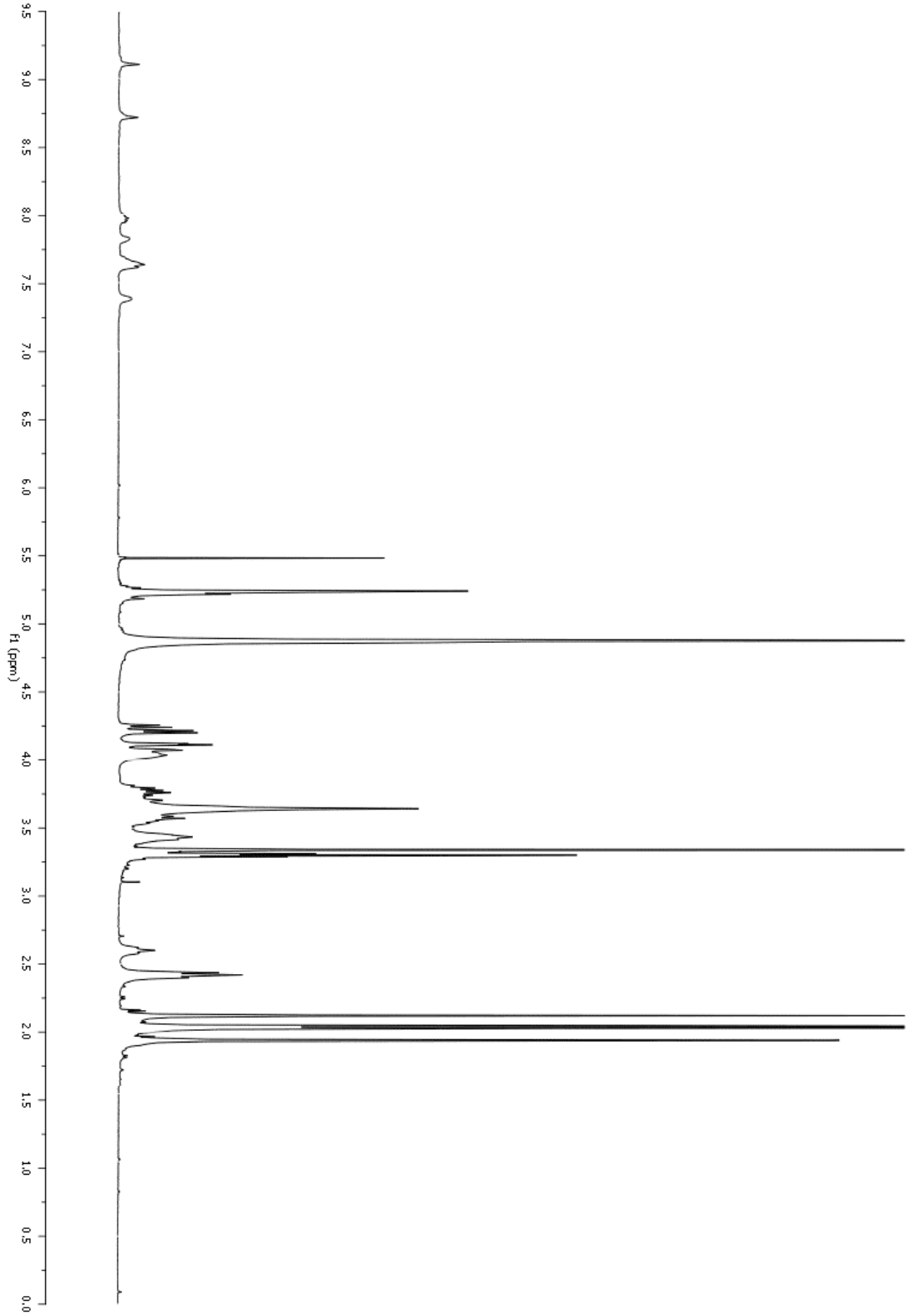

Fig 43. ^{1}H-NMR of Comp 6a

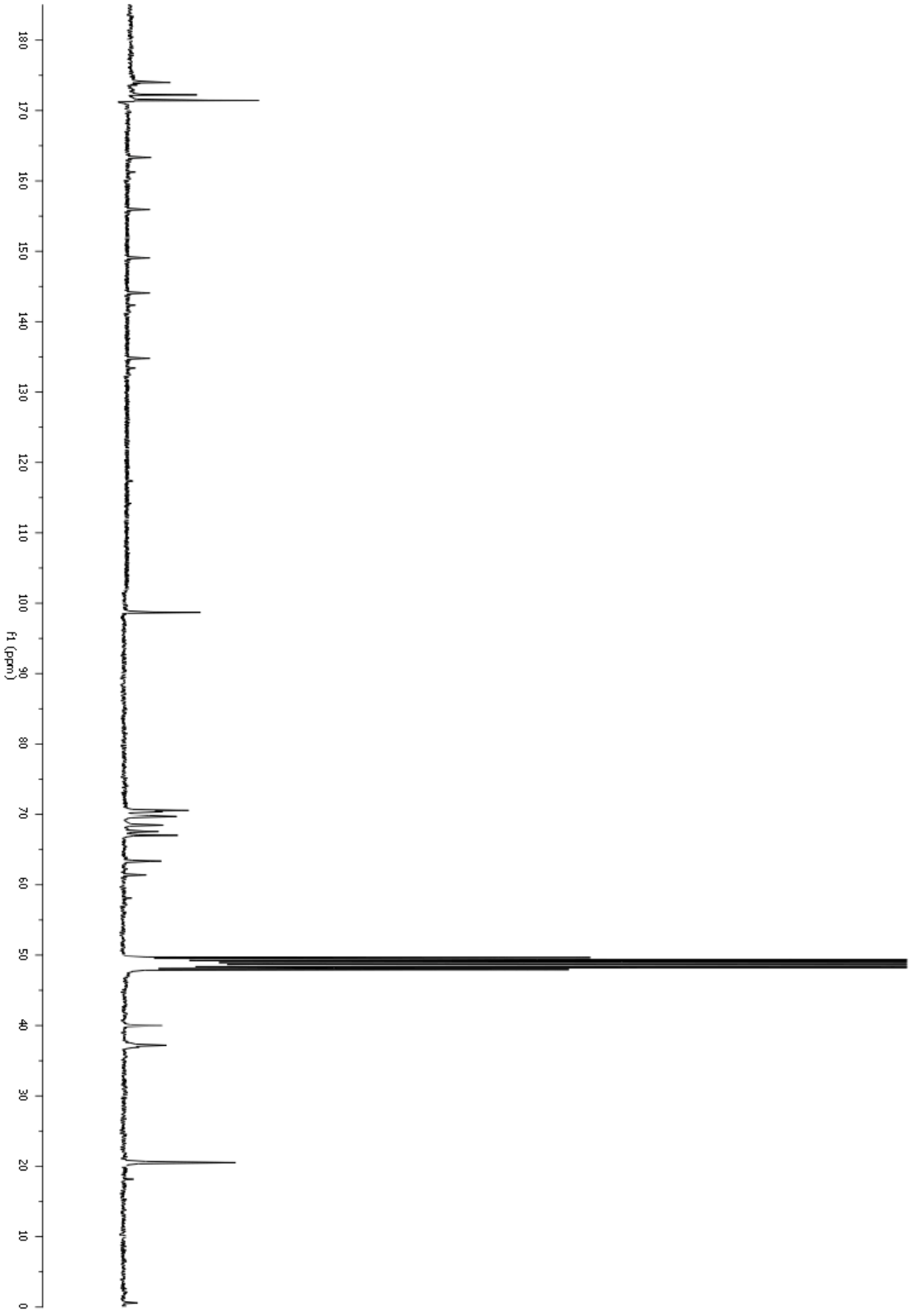

Fig 44. ^{13}C-NMR of Comp 6a

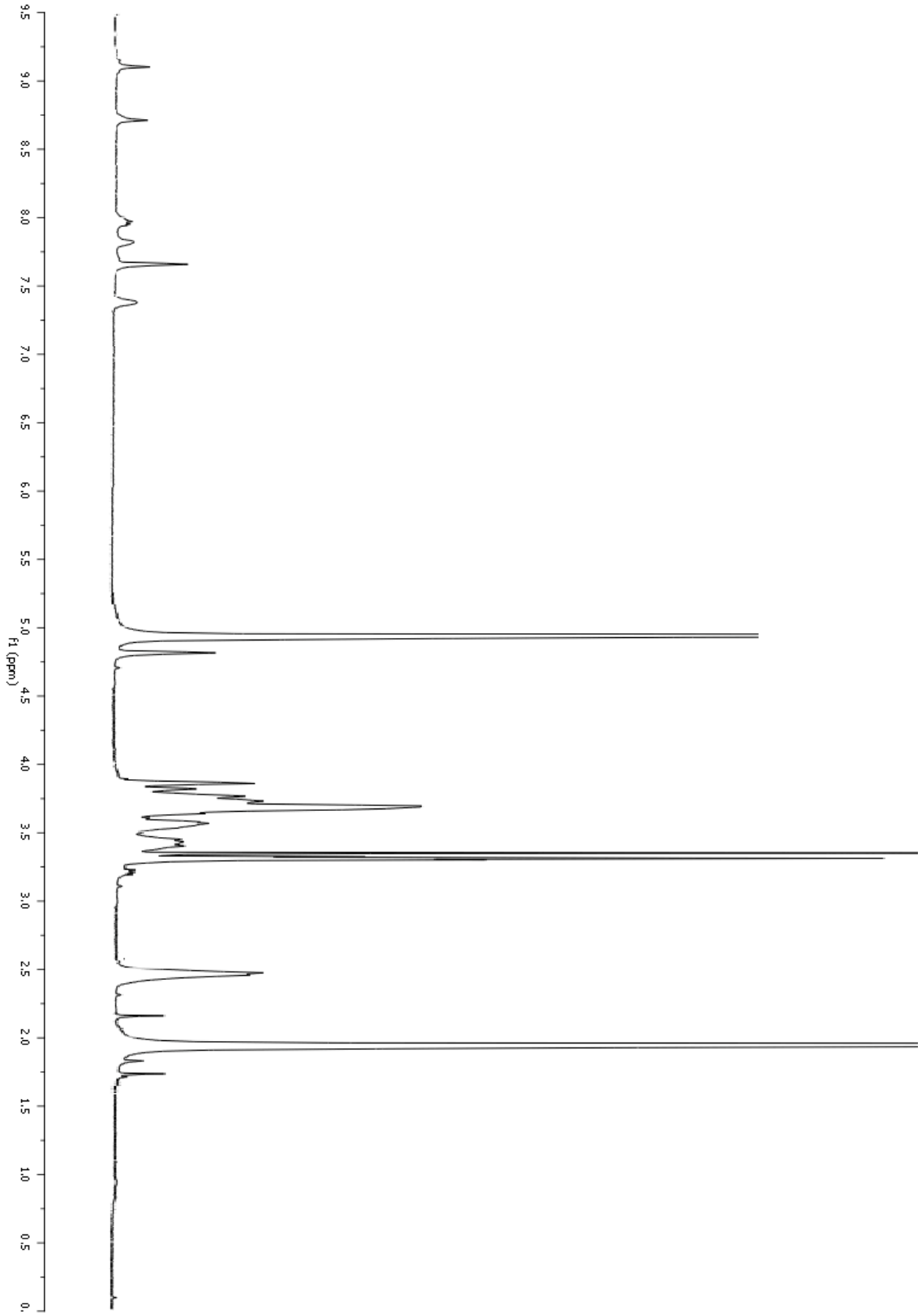

Fig 45. ^{1}H-NMR of Comp 6

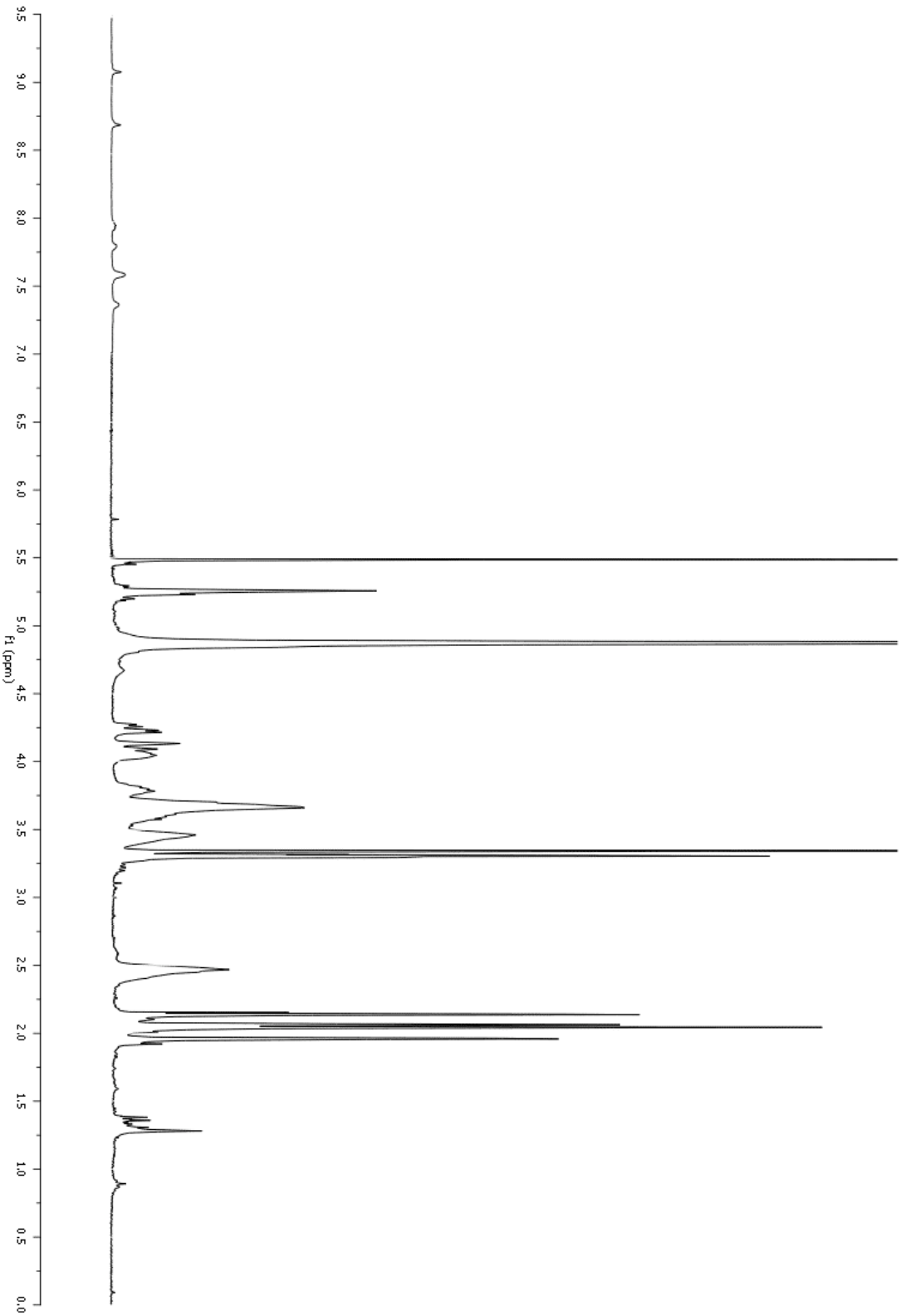

Fig 44. ^{1}H-NMR of Comp 7a

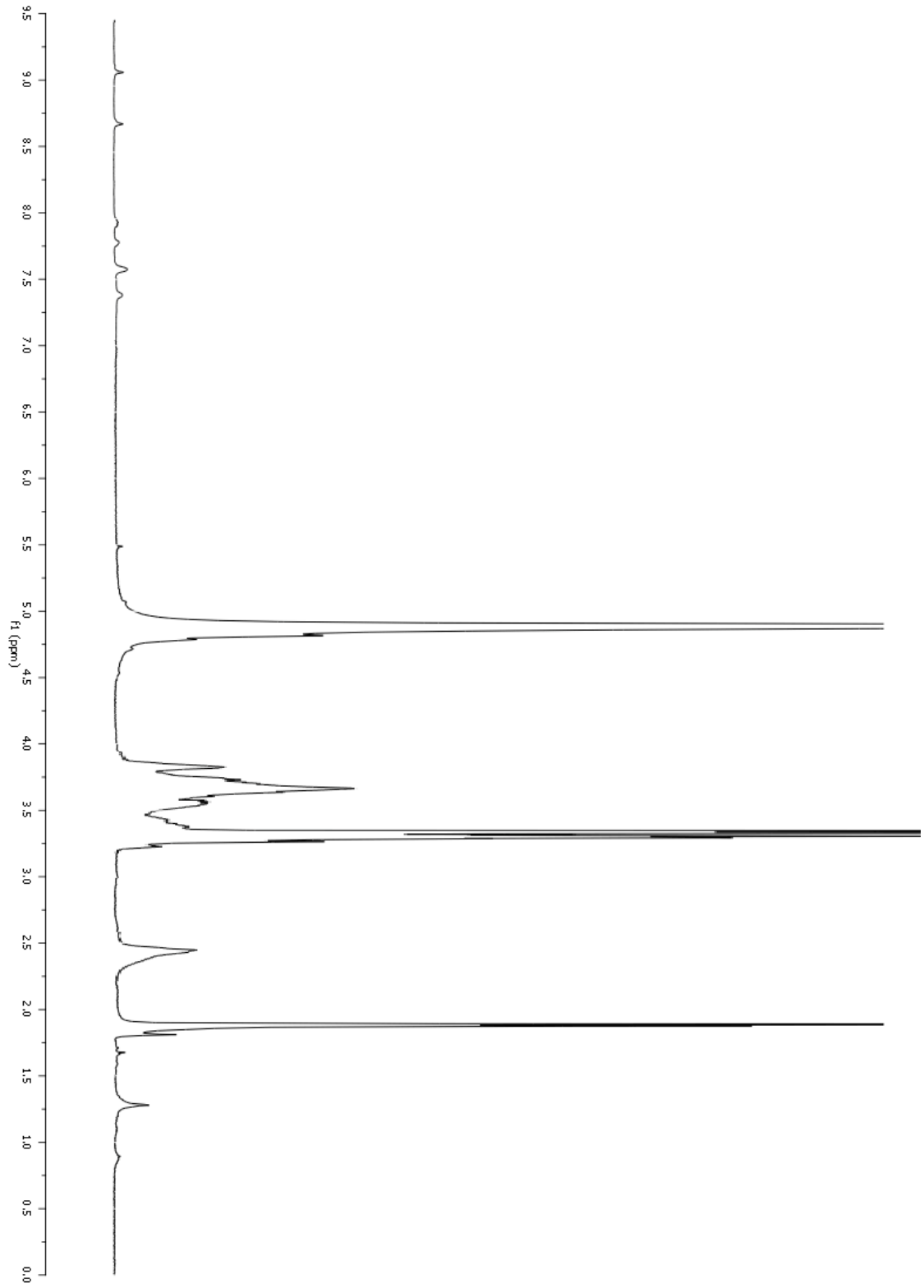

Fig 44. ^{1}H-NMR of Comp 7.