Synthesis of Branched Ultra-High-Molecular-Weight Polyethylene Using Highly Active Neutral, Single-Component Ni(II) Catalysts

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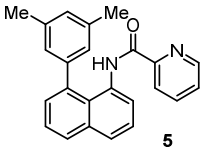
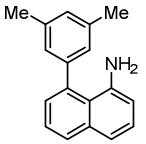
General Information

All manipulations of air- and water-sensitive compounds were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Argon was purified by passing through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Toluene was distilled under a nitrogen atmosphere from sodium/benzophenone prior to use and was degassed by freeze–pump–thaw methods (3 cycles). All deuterated solvents were dried under 4Å molecular seives. ^{1}H and ^{13}C NMR spectra were recorded at 400, 500, and 600 MHz. High-temperature NMR analysis of polyethylene was performed on a Bruker-DRX-500 at 120 °C[1]. ^{1}H and ^{13}C NMR spectra were referenced to solvent peaks. The branching structure was assigned according to literature protocols[1,2]. Elemental analyses were performed by Atlantic Microlabs Inc. (Norcross, GA, USA). High temperature gel permeation chromatography (GPC) was performed at Cornell University by Dr. Anne LaPointe on an Agilent PL-GPC 220 equipped with a refractive index (RI) detector and three PL-Gel Mixed B columns. GPC columns were eluted with 1,2,4-trichlorobenzene (TCB) containing 0.01 wt. % di-tert-butylhydroxytoluene (BHT) at 150 ° C with a run rate of 1.0 mL/min. The samples were prepared in TCB (with BHT) and heated at 150 ° C for at least 2 hours prior to injection. GPC data calibration was done with a combined set of monomodal polyethylene standards from Agilent (Mp = 5,310-701,000) and PSS (Mp = 338-126,000). Differential scanning calorimetry (DSC) was recorded on a TA Instruments DSC Q200. Samples were heated to 200 °C, cooled to -100 °C, and then scanned from −-100 to 200 °C with a scan rate of 10 °C/min. Py_2NiMe_2[3] and 2-hydroxy-3-(9-anthryl)benzaldehyde[4] were prepared according to literature procedures. Ethylene was purchased from Airgas and used without further purification.



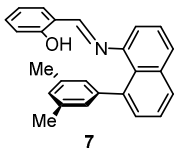
5

N-(8-(3,5-dimethylphenyl)naphthalen-1-yl)picolinamide, 5. N-(naphthalen-1-yl)picolinamide (5.1 g, 20.5 mmol), 1-iodo-3,5-dimethylbenzene (18.6 g, 80.3 mmol), AgOAc (5.1 g, 30.5 mmol), and $Pd(OAc)_2$ (0.1 g, 0.45 mmol) were placed in a Kontes flask. The resulting suspension was stirred at 140 °C for 24 h. After dilution with dichloromethane (ca. 40 mL) and column chromatography (hexanes/ethyl acetate, 90/10, then hexanes/ethyl acetate, 60/30), the solvent was evaporated to give yellow crystals of **5** (6.6 g, 91% yield). ^{1}H NMR (400 MHz,$CDCl_3$): δ 9.49 (s, 1H), 8.21-8.22 (m, 1H), 8.11 (t, *J* = 6.8 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.78-7.82 (m, 2H), 7.57 (t, J = 6.8 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.34-7.37 (m, 1H), 7.30 (dd, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H), 7.0 (s, 2H), 6.56 (s, 1H), 2.13 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.9, 149.8, 147.0, 142.6, 137.9, 137.4, 136.8, 135.4, 132.7, 130.0, 128.4, 128.3, 126.9, 126.5, 125.7, 125.7, 125.3, 124.8, 123.2, 121.7, 21.0. HRMS($C_{24}H_{20}N_2O$): (M+Na) Calcd: 375.1473, Found 375.1489.



6

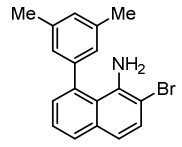
8-(3,5-Dimethylphenyl)naphthalen-1-amine 6. N-(8-(3,5-dimethylphenyl)naphthalen-1-yl)picolinamide **5** (4.2 g, 12 mmol) was refluxed for 6 h in ethanolic NaOH solution (4.8 g NaOH, 120 mmol in EtOH/H_2O, 10/1 v/v, 48 mL). The reaction mixture was cooled and diluted with an equal volume of water. The product was extracted with dichloromethane (3 × 20 mL). The organic layers were combined, dried with $MgSO_4$, and concentrated. After chromatography (hexane/ethyl acetate/triethylamine, 94/5/1), a thick yellow oil **6** was obtained (2.6 g, 88%). ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.76 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz , 1 H), 7.37 (t, *J* = 8.0 Hz, 1 H), 7.32 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.13 (dd, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H) 7.07 (s, 3H), 6.62 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz), 3.82 (br, 2H), 2.37 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.8, 143.4, 138.5, 137.4, 135.7, 128.9, 128.4, 127.8, 126.9, 126.4, 124.4, 120.6, 118.7, 110.9, 21.2. HRMS($C_{18}H_{17}N$): (M+H) Calcd: 248.1439, Found 248.1480.



7

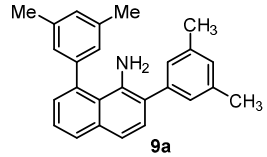
Salicylaldimine 7. To a methanol (15 mL) solution of 2-hydroxybenzaldehyde (0.95 g, 7.8 mmol) was added formic acid (5 drops) and 8-(3,5-dimethylphenyl)naphthalen-1-amine **6** (1.6 g, 6.5 mmol). The resulting mixture was heated to reflux for 2 hours. The mixture was cooled and a yellow solid precipitated from the reaction mixture. The solid was filtered, washed with cold methanol and dried to afford the salicylaldimine ligand **7** (1.8 g, 92%) as a yellow solid. ^{1}H NMR (400 MHz,$CDCl_3$): δ 11.48 (s, 1H), 8.13 (s, 1H), 7.89 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.27-7.31 (m, 1H), 7.17 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 6.91 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz,

1H), 6.77-6.84 (m, 4H), 6.56 (s, 1H), 2.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.6, 161.0, 148.3, 142.9, 139.8, 137.2, 135.2, 132.6, 131.8, 129.6, 127.9, 127.7, 127.6, 126.9, 125.8, 125.5, 125.2, 119.4, 118.2, 117.4, 116.6, 21.0. HRMS ($C_{25}H_{21}NO$): (M+Na) Calcd: 374.1521, Found 374.1532.



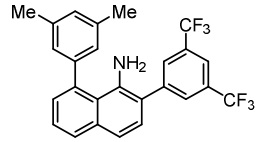
8

2-Bromo-8-(3,5-dimethylphenyl)naphthalen-1-amine 8. To a solution of NBS (0.79 g, 4.4 mmol) in dichloromethane (60 mL) cooled to −78 °C was added $ZrCl_4$ (0.01 g, 0.05 mmol), followed by 8-(3,5-dimethylphenyl)naphthalen-1-amine **6** (1.11 g, 4.4 mmol) in dichloromethane (20 mL) under argon atmosphere. The mixture was stirred for 1 h and then quenched by adding a saturated $NaHCO_3$ aqueous solution followed by extraction with CH_2Cl_2 (3 × 20 mL). The organic phase was washed with brine and dried over Na_2SO_4. After chromatography (hexane/ethyl acetate, 50/1), a yellow solid **8** was obtained (0.8 g, 56%), R_f = 0.3 (hexane/ ethyl acetate, 20/1). ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.14-7.18 (m, 2H), 7.08 (s, 1H), 7.05 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.9, 140.8, 138.4, 137.8, 134.7, 130.0, 129.3, 128.7, 128.5, 127.0, 124.8, 120.8, 118.7, 105.2, 21.3. HRMS ($C_{18}H_{16}BrN$): (M+Na) Calcd: 348.0364, Found 348.0357.



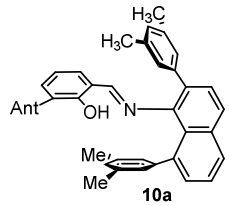
9a

2,8-Bis(3,5-dimethylphenyl)naphthalen-1-amine 9a. To a toluene solution (25 mL) of 1.0 g (3.1 mmol) 2-bromo-8-(3,5-dimethylphenyl)naphthalen-1-amine **8** was added an ethanol (5 mL) solution of 4.6 mmol 3,5-dimethylphenyl boronic acid. To the mixture was added Na_2CO_3 (12 mmol, 6.1 mL of a 2M solution in water). The biphasic mixture was flushed with argon and $Pd(PPh_3)_4$ (0. 21 g, 0.18 mmol) was added. The reaction mixture was stirred overnight at 90 °C. The organic layer was separated from the aqueous phase. The aqueous phase was extracted with diethyl ether (3 × 10 mL) and dried over Na_2SO_4. After chromatography (hexane/ethyl acetate, 50/1), a white solid **9a** was obtained (0.87 g, 81%), R_f = 0.3 (hexane/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 6.8 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 6.8 Hz, 1H), 7.08 (s, 2H), 7.04 (s, 2H), 7.01 (s, 1H), 6.94 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.8, 140.4, 138.9, 138.3, 137.5, 135.2, 128.9, 128.7, 128.6, 128.4, 128.4, 127.4, 127.0, 124.3, 122.6, 120.4, 117.8, 21.3. HRMS($C_{26}H_{25}N$): (M+Na) Calcd: 374.1885, Found 374.1883.



9b

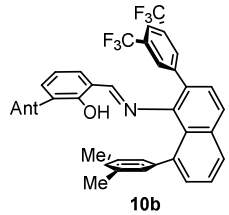
2-(3,5-Bis(trifluoromethyl)phenyl)-8-(3,5-dimethylphenyl)-naphthalen-1-amine 9b. The same procedure was used as that for the preparation of **9a**. Yield: **9b** (0.8 g, 72%). ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.93 (s, 2H), 7.81 (s, 1H), 7.79 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.44 (dd, *J* = 8.0 Hz, *J* = 6.8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1 H), 7.20 (dd, *J* = 6.8 Hz, *J* = 0.8 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.07 (s, 2H), 7.04 (s, 1H), 4.02 (s, 2H), 2.36 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.2, 142.9, 140.8, 139.1, 137.8, 135.8, 132.2 (q, *J* = 33.2 Hz), 130.2, 129.3, 129.1, 128.6, 127.8, 127.0, 125.3, 123.3 (q, *J* = 273.3 Hz), 120.8 (q, *J* = 4.5 Hz), 120.6, 118.8, 118.7, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.80. Anal. Calcd for $C_{16}H_{19}F_6N$: C, 67.97; H, 4.17; N, 3.05. Found: C, 68.00; H, 4.24: N, 3.01.



10a

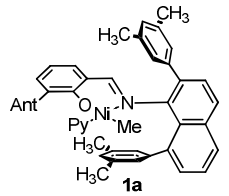
Salicylaldimine 10a. To a toluene (25 mL) solution of 2-hydroxy-3-(9-anthryl)benzaldehyde (0.32 g, 0.93 mmol) was added $TsOH{\cdot}H_2O$ (10 mg) and amine **9a** (0.33 g, 0.93 mmol). The resulting mixture was heated to reflux overnight. The solvent was

removed to afford a brown solid. The solid was recrystallized from methanol, affording **10a** (0.29 g, 50%). ^{1}H NMR (400 MHz,$CDCl_3$): δ 12.14 (s, 1H), 8.51 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.2 Hz, 1H), 7.88 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.52-7.47 (m, 3H), 7.44-7.40 (m, 2H), 7.35 (dd, *J* = 6.8 Hz, *J* = 0.8 Hz, 1H), 7.21 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.08 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 6.92 (t, *J* = 7.2 Hz, 1H) 6.90 (s, 2H), 6.79 (s, 1H), 6.71 (s, 2H), 6.65 (s, 1H), 2.16 (s, 6H), 1.90 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 167.3, 159.2, 144.3, 143.6, 139.7, 139.6, 137.7, 137.4, 135.6, 134.8, 132.8, 131.9, 131.6, 131.5, 130.6, 130.3, 128.5, 128.5, 128.2, 128.0, 127.9, 127.7, 127.0, 126.9, 126.8, 125.9, 125.9, 125.2, 125.2, 125.0, 124.5, 119.1, 117.8, 21.34, 21.1. HRMS($C_{47}H_{37}NO$): (M+Na) Calcd: 654.2773, Found 654.2772.



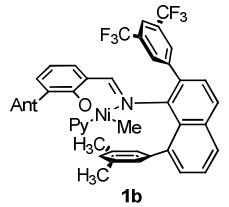
10b

Salicylaldimine 10b. The same procedure was used as that for the preparation of **10a**. Yield: **10b** (0.84 g, 66%). ^{1}H NMR (400 MHz,$CDCl_3$): δ 11.62 (s, 1H), 8.49(s, 1H), 8.04 (d, *J* = 8.0 Hz, 2H), 8.01 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.72 (s, 2H), 7.69 (s, 1H), 7.54-7.60 (m, 3H), 7.41-7.50 (m, 6H), 7.27 (d, *J* = 6.4 Hz, 1H), 7.12 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.69 (s, 2H), 6.60 (s, 1H), 1.87 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 168.94, 159.10, 144.81, 142.97, 142.27, 139.74, 138.02, 136.51, 135.68, 132.26, 132.23, 131.46, 131.40, 131.17 (q, *J* = 33.2 Hz), 130.36, 130.33, 130.30, 128.39, 128.11, 128.08, 128.05, 127.55, 126.91, 126.70, 126.64, 126.24, 126.20, 125.23, 125.00, 124.30, 123.21 (q, *J* = 273.3 Hz), 120.47 (q, *J* = 9.1 Hz), 118.51, 118.26, 21.06. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.75. HRMS($C_{47}H_{31}F_6NO$): (M+Na) Calcd: 762.2208, Found 762.2206.



1a

Complex 1a. To (pyridine)$_2$NiMe$_2$ (0.12 g, 0.5 mmol) and the ligand **10a** (0.16 g, 0.25 mmol) in a 50 mL septum-capped Schlenk tube was added toluene (15 mL) at 25 ^{o}C. The resulting red mixture was stirred for 3 h and filtered to remove nickel black. The solvent was removed to yield pure complex **1a** as a red powder (0.12 g, 62%). ^{1}H NMR (400 MHz,C_6D_6): δ 8.15-8.18 (m, 3H), 7.84-7.90 (m, 4H), 7.77-7.79 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.62-7.67 (m, 2H), 7.53 (d, J = 7.2, 1H), 7.43-7.46 (m, 3H), 7.30-7.34 (m, 3H), 7.19-7.21 (m, 2H), 7.01 (s, 2H), 6.84 (s, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.66 (s, 1H), 6.39 (t, *J* = 7.6 Hz, 1H), 6.22 (t, *J* = 7.6 Hz, 1H), 5.60 (t, *J* = 6.8 Hz, 2H), 2.29 (s, 6H), 2.16 (s, 3H), 2.05 (s, 3H), -1.03 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 167.9, 164.7, 150.7, 149.1, 143.8, 140.4, 140.2, 137.3, 137.0, 136.9, 135.5, 135.0, 134.2, 133.7, 132.7, 131.4, 131.3, 130.9, 130.4, 130.3, 129.4, 129.1, 128.7, 128.3, 18.1, 128.0, 127.9, 127.8, 127.7, 127.6, 126.3, 125.9, 124.9, 124.8, 124.7, 124.4, 124.2, 121.7, 120.0, 111.8, 21.2, 21.0, -9.84. Anal. Calcd for $C_{53}H_{44}N_2NiO$: C, 81.23; H, 5.66; N, 3.57. Found: C, 81.03; H, 5.86; N, 3.50.



1b

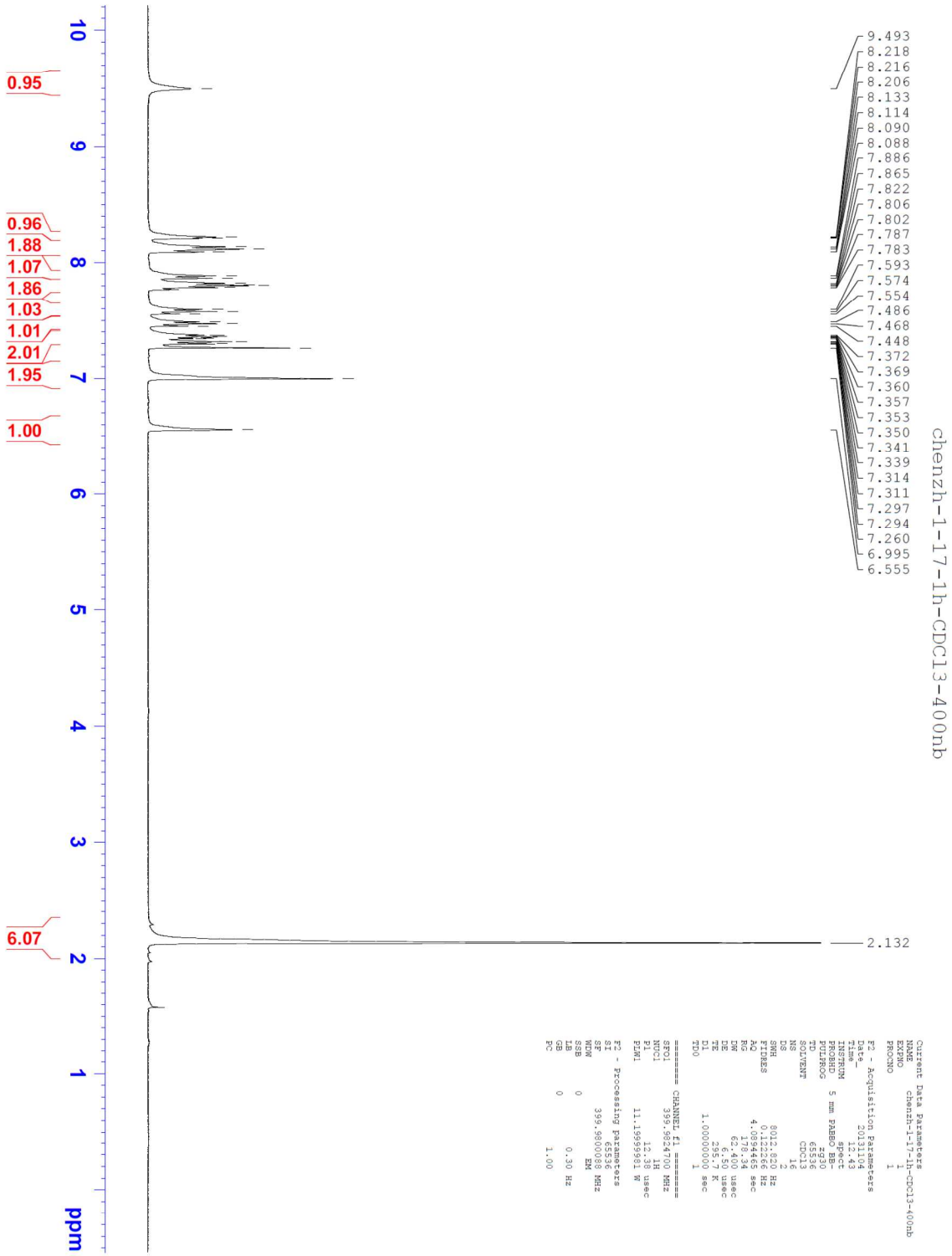
Complex 1b. The same procedure was used as that for the preparation of **1a**. Yield: **1b** (0.66, 98%). ^{1}H NMR (400 MHz,C_6D_6): δ 8.52 (s, 2H), 8.14 (d, *J* = 6.8 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.80-7.87 (m, 3H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.68 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.50 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.33-7.47 (m, 4H), 7.31 (t, *J* = 6.8 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.07-7.12 (m, 2H), 7.03 (s, 1H), 6.98 (s, 1H), 6.65 (dd, J = 8.0 Hz, *J* = 1.6 Hz, 1H), 6.61 (s, 1H), 6.35 (t, *J* = 7.6 Hz, 1H), 6.24 (t, *J* = 7.6 Hz, 1H), 5.63 (t, *J* = 7.2 Hz, 2H), 2.13 (s, 3H), 1.93 (s, 3H), -1.18 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 168.6, 165.6, 151.1, 150.3, 143.9, 143.7, 141.0, 137.6, 137.5, 136.9, 136.7, 135.7, 135.4, 134.2, 132.0, 131.8, 131.7, 131.6, 131.3, 130.9, 130.8, 130.2, 130.1, 129.5, 129.4, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.6, 127.5, 126.4, 126.2, 125.5, 125.3, 125.2, 125.1, 124.8, 124.7, 123.0, 122.4, 120.9, 120.1, 112.8, 21.6, 21.5, -9.13. ^{19}F NMR (376 MHz, C_6D_6): δ -62.25. Anal. Calcd for $C_{53}H_{38}F_6N_2NiO$: C, 71.40; H, 4.30; N, 3.14. Found: C, 71.45; H, 4.48; N, 3.15.

General Procedure for High-Pressure Ethylene Polymerizations.

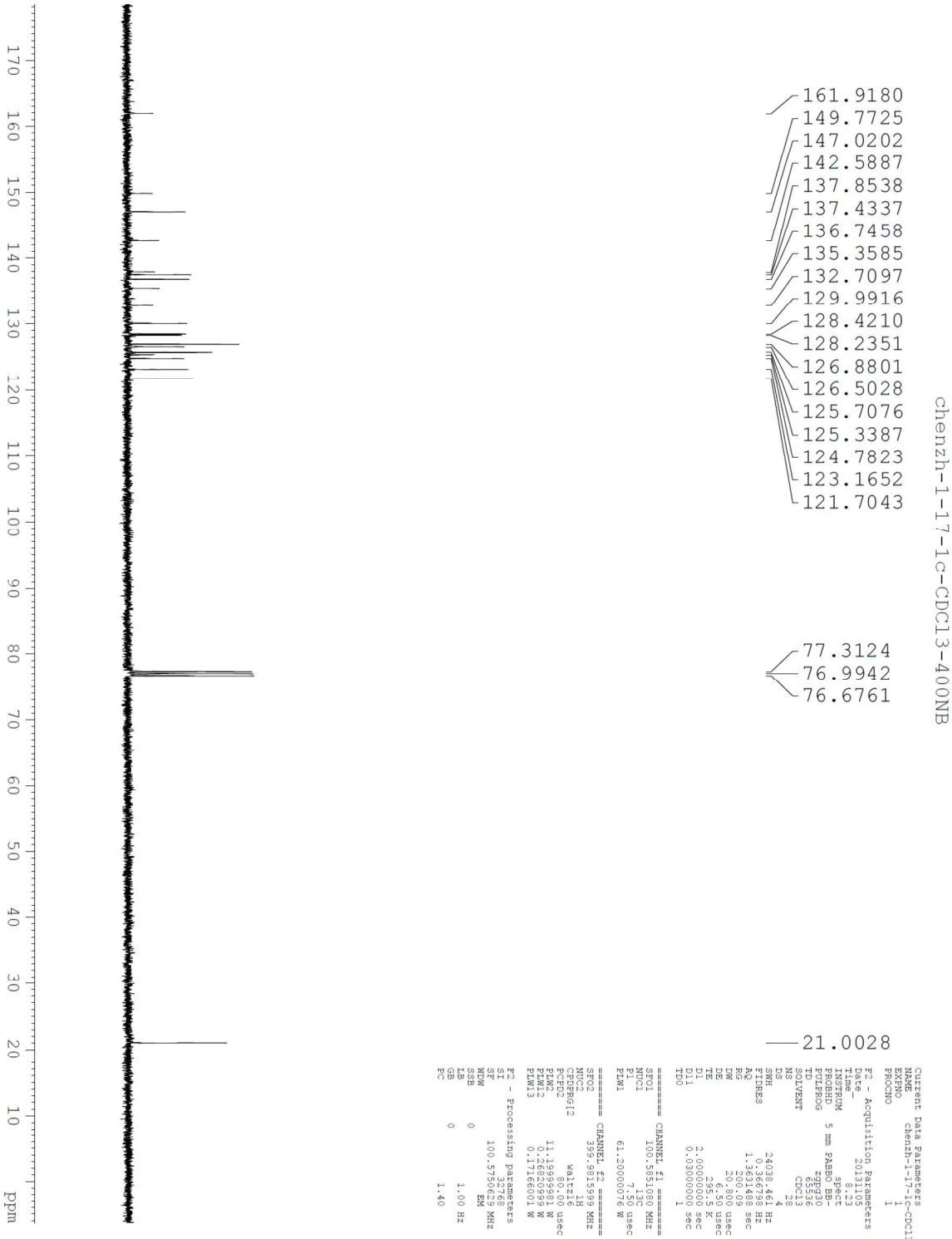
A 1000 mL Parr autoclave was heated under vacuum to 110 °C for two hours and then cooled to the desired reaction temperature and backfilled with ethylene. The autoclave was charged with toluene (180 mL), filled and evacuated twice with ethylene (200 psig), and pressurized with ethylene to 200 psig. The stirring motor was engaged, and the reactor was allowed to equilibrate at the desired temperature for 15 min. The catalyst was dissolved in 20 mL of toluene[5] and transferred via syringe into the vented autoclave with the stirring motor off. The autoclave was sealed and pressurized to the desired pressure, and the stirring motor was re-engaged. After the prescribed reaction time, the stirring motor was stopped, the reactor vented, and the polymer isolated via precipitation from methanol and dried in a vacuum oven.

General Procedure for Determination of Pyridine Exchange Kinetics. An NMR tube was charged with complex **1a** and CD_2Cl_2 (500 μL) under argon. The tube was sealed with a septum and cooled to - 90 °C. 4-Picoline in CD_2Cl_2 (200 μL) was injected slowly and the tube was warmed to -80.0 °C in the NMR probe. Conversion was observed via ^{1}H NMR spectroscopy as the resonance for the *para*-proton of the bound pyridine (6.13 ppm) diminished as the salicylaldiminato resonance at 6.41 ppm remained constant.

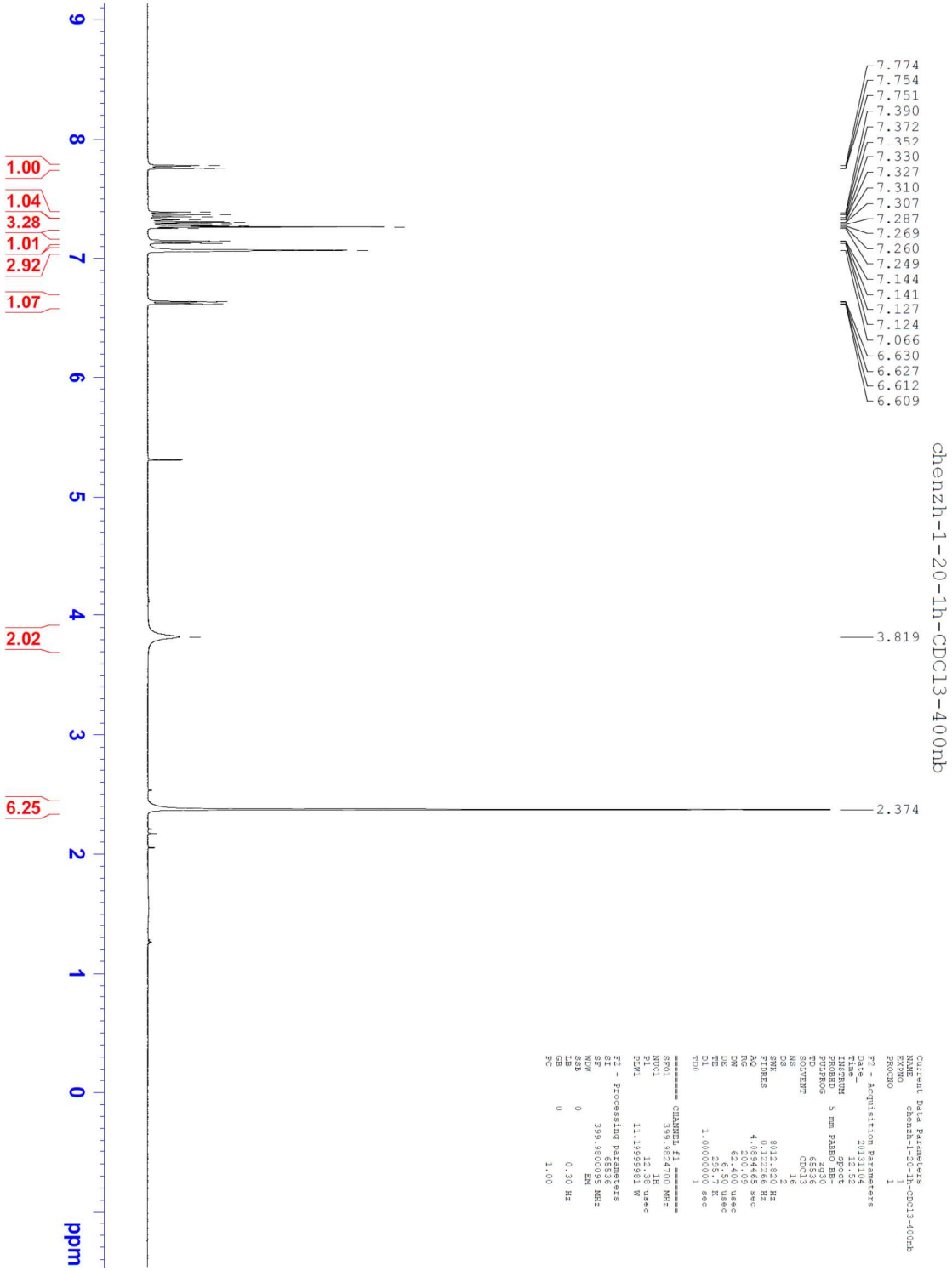
^{1}H NMR of **5** (400 MHz,$CDCl_3$):



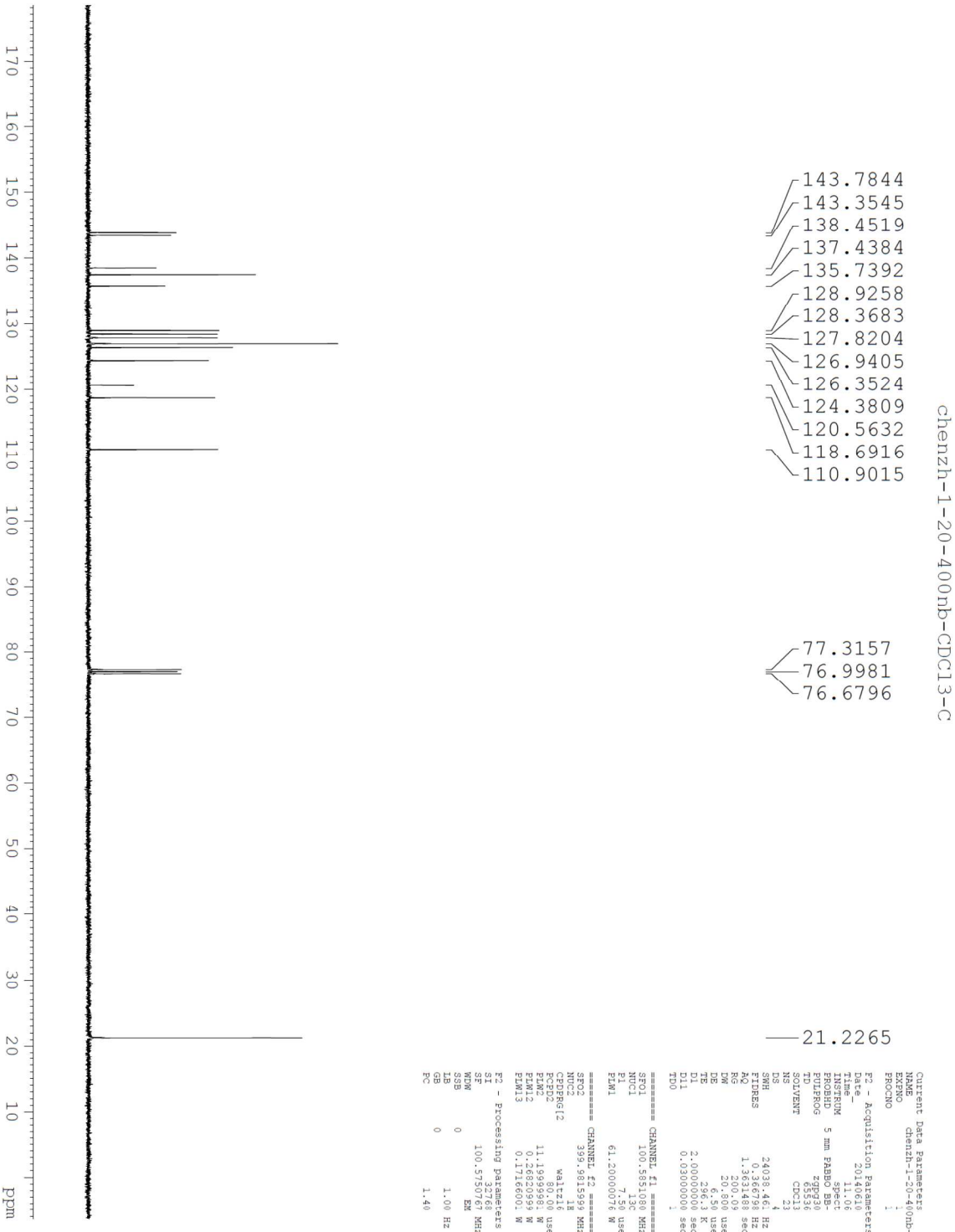
^{13}C NMR of **5** (101 MHz, $CDCl_3$):



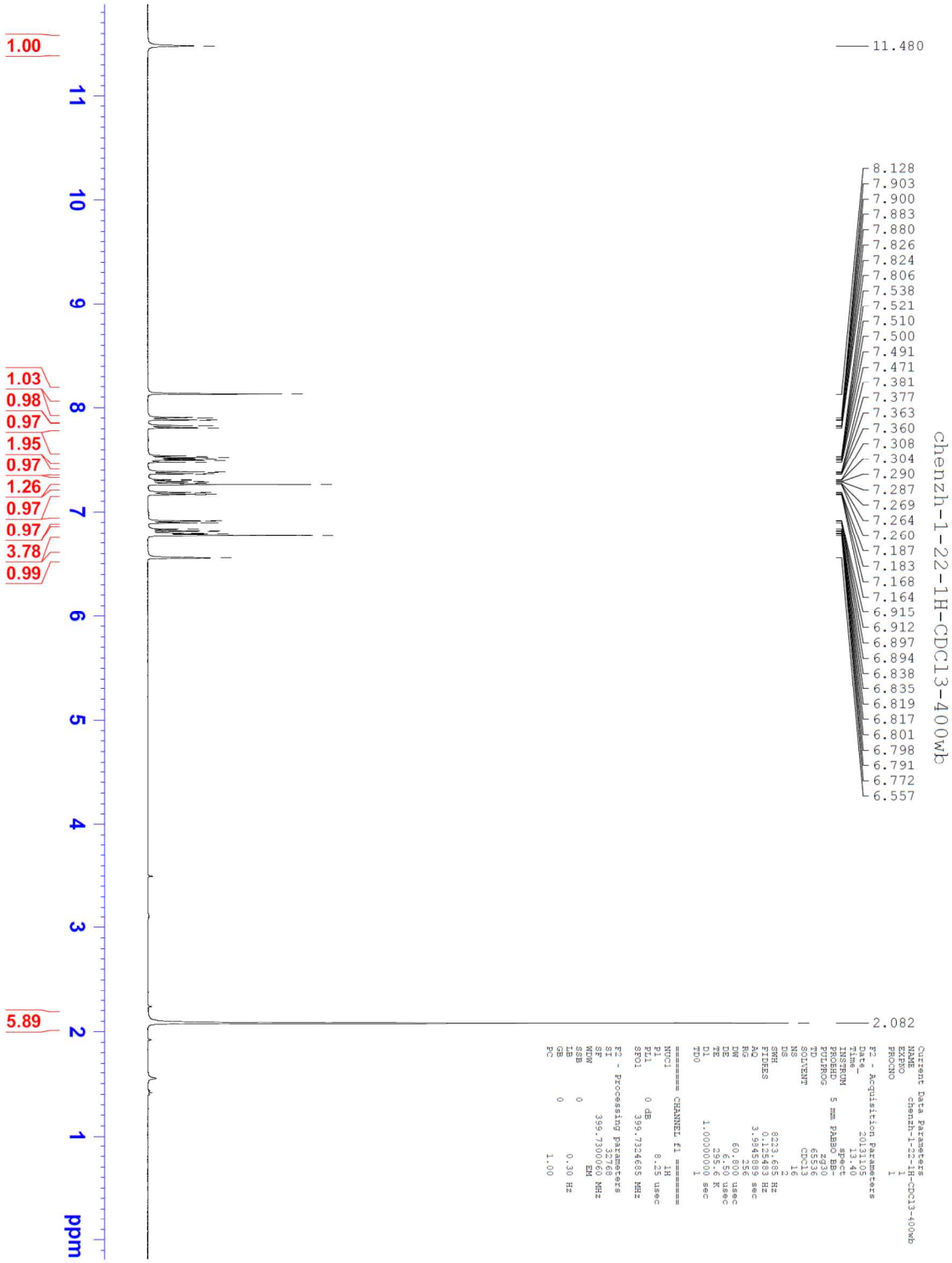
^{1}H NMR of **6** (400 MHz,$CDCl_3$):



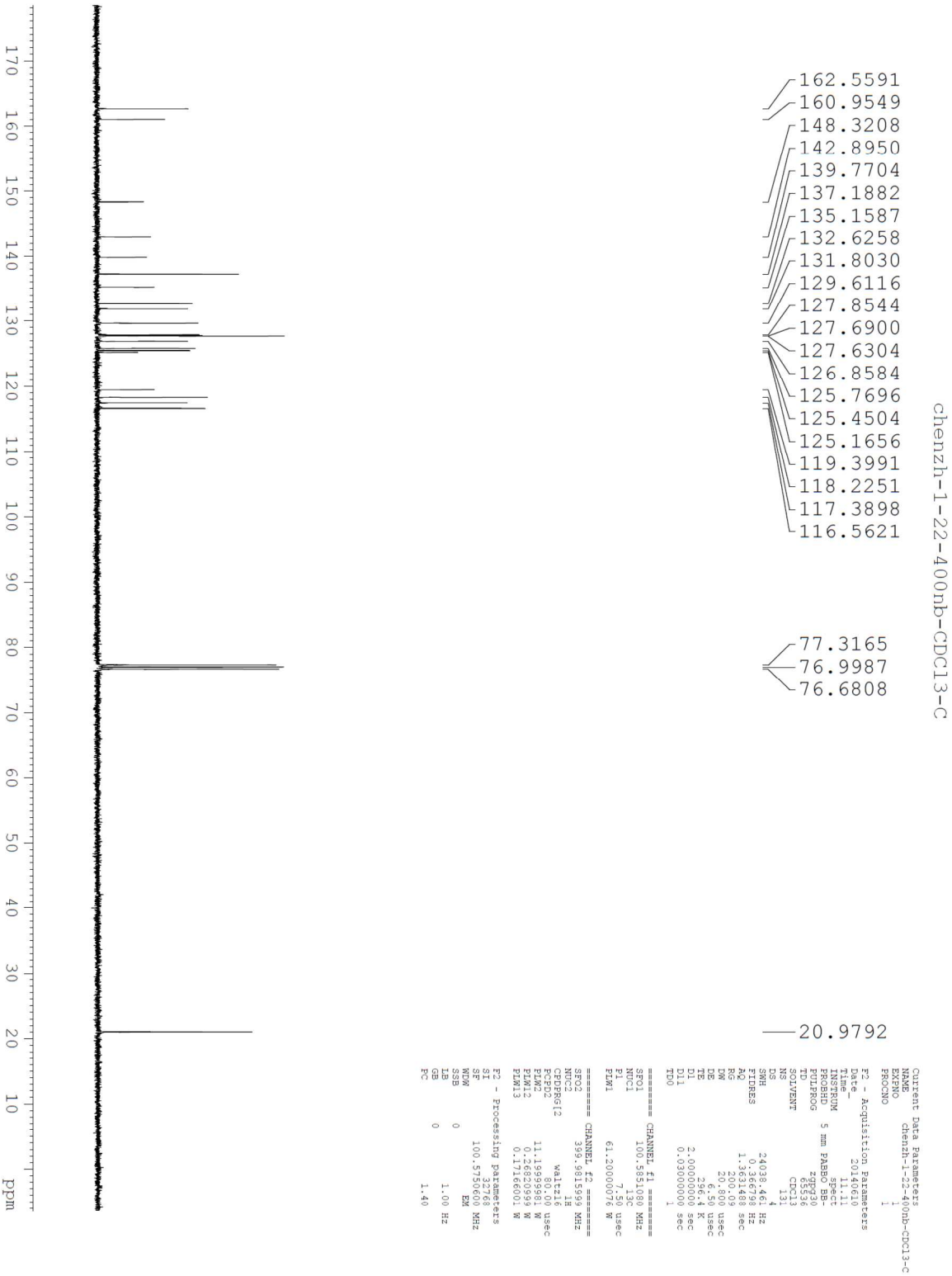
^{13}C NMR of **6** (101 MHz, $CDCl_3$):



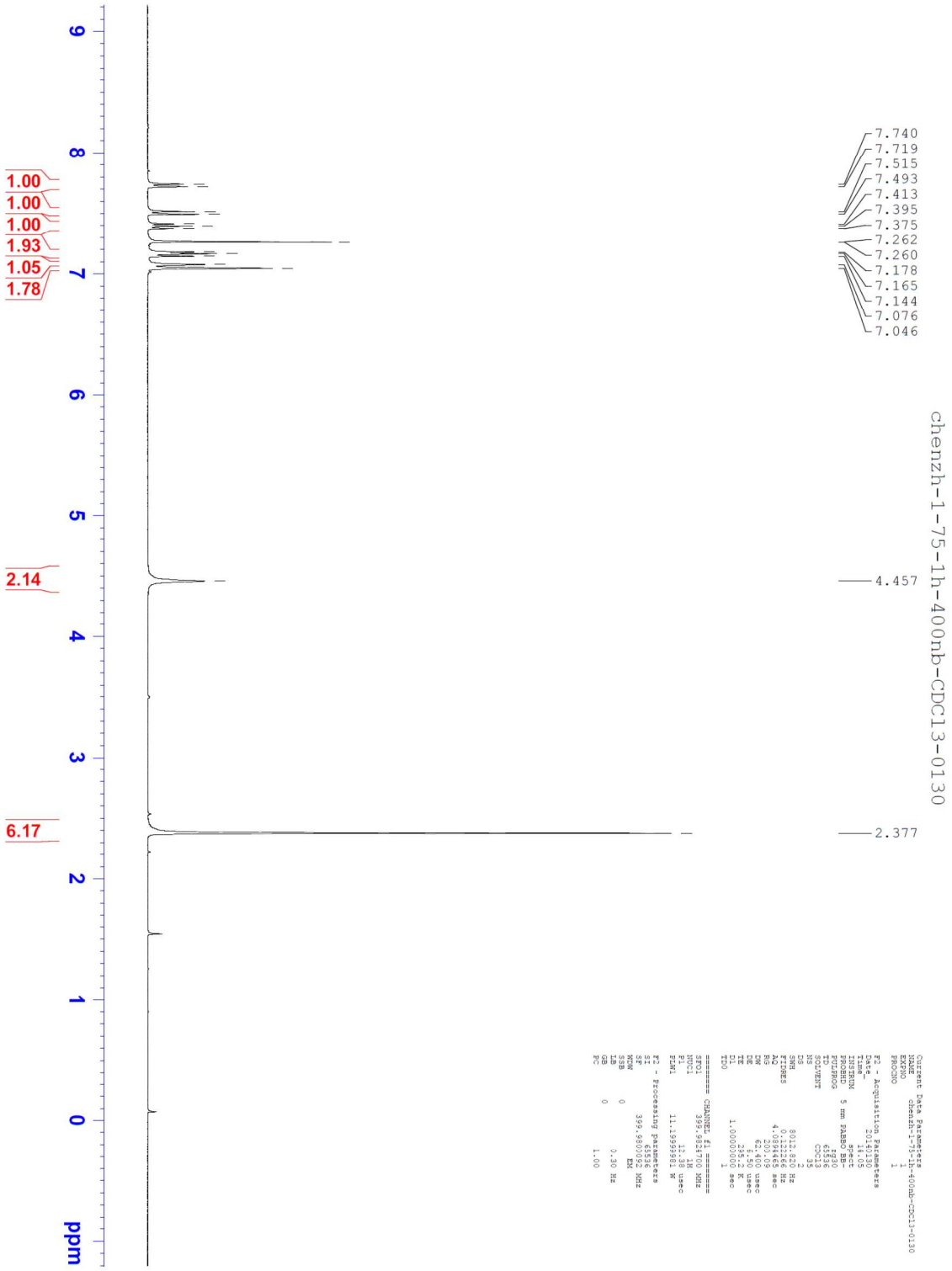
^{1}H NMR of **7** (400 MHz,$CDCl_3$):



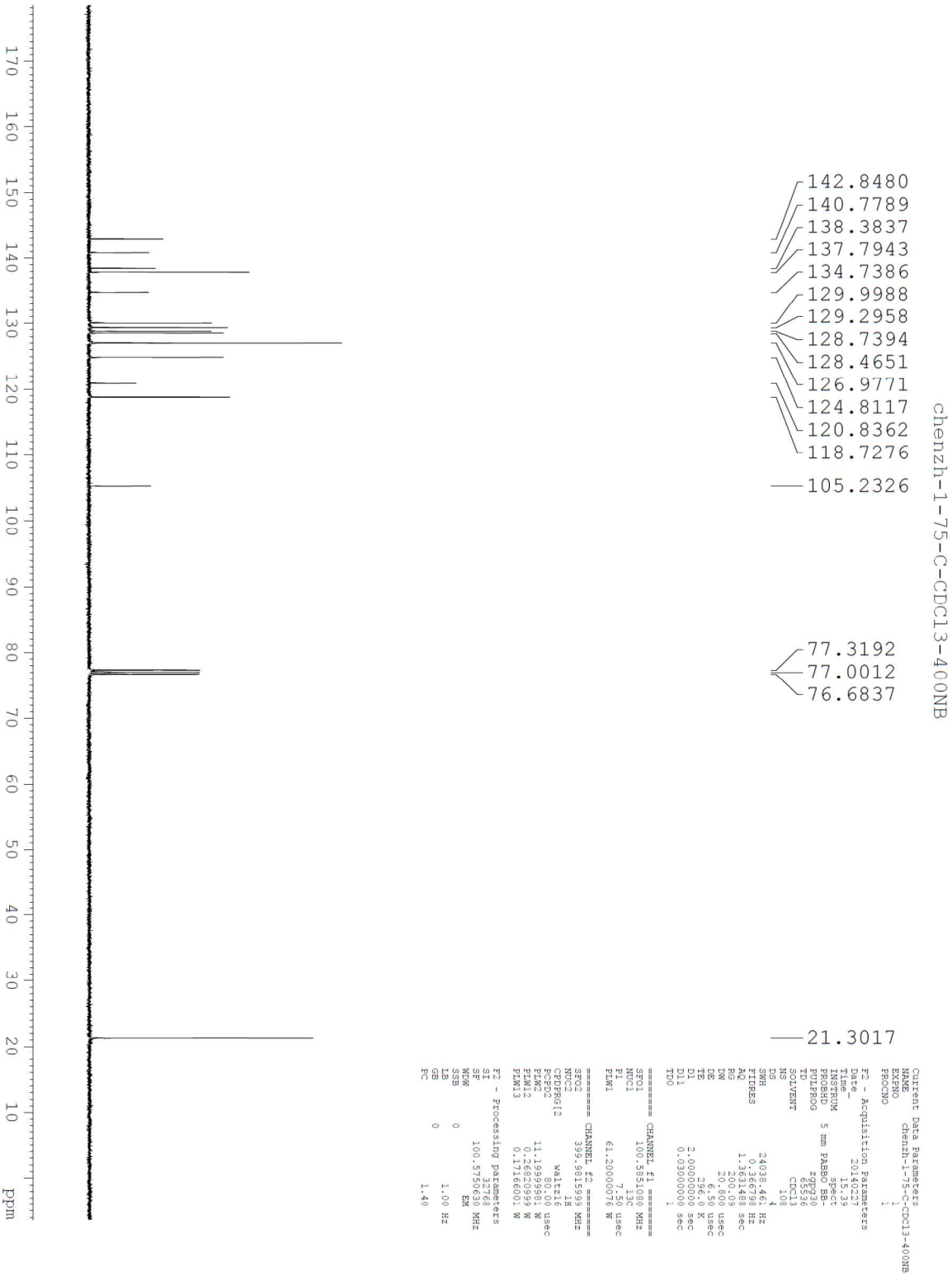
^{13}C NMR of **7** (101 MHz, $CDCl_3$):



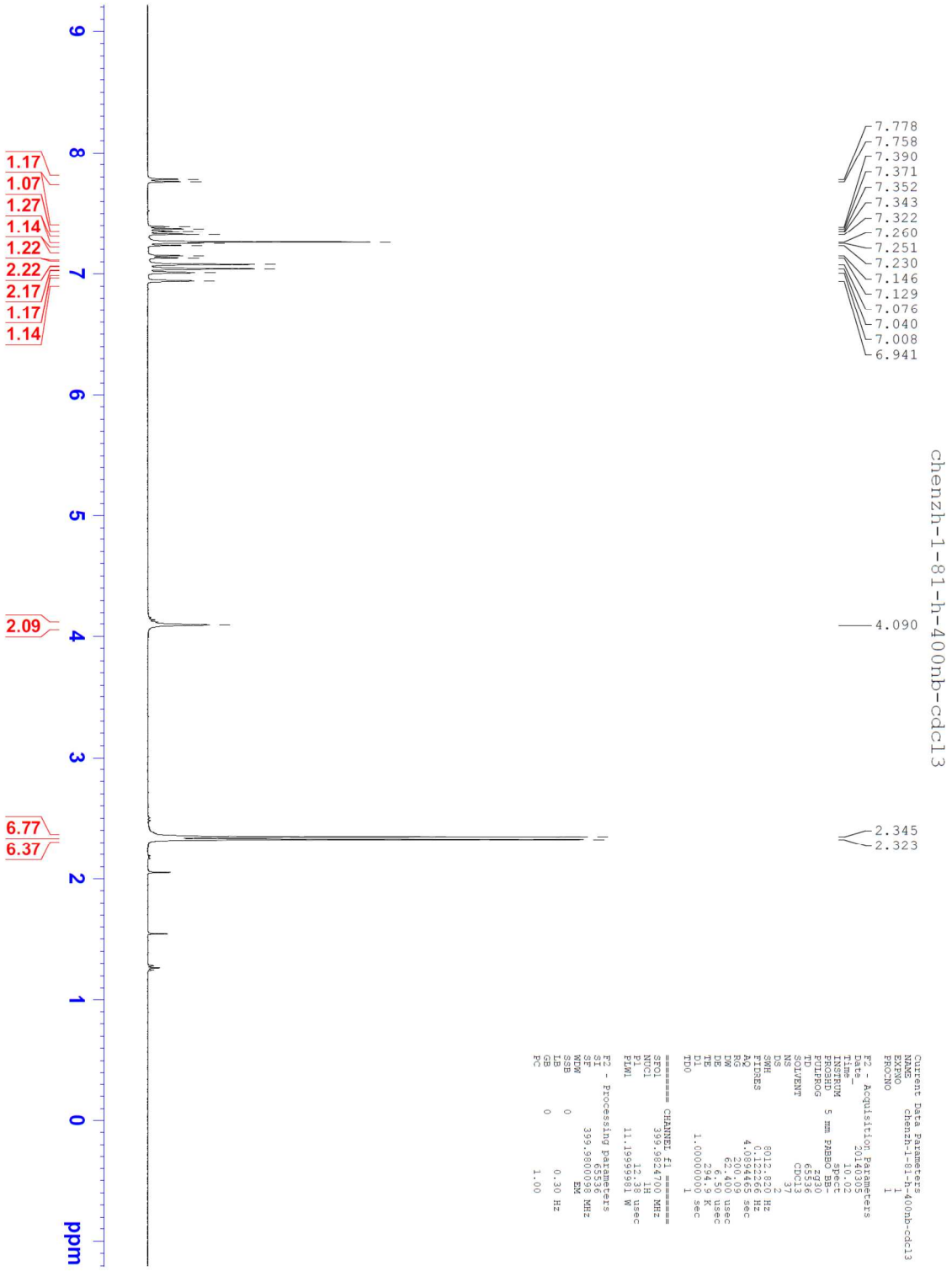
^{1}H NMR of **8** (400 MHz,$CDCl_3$):



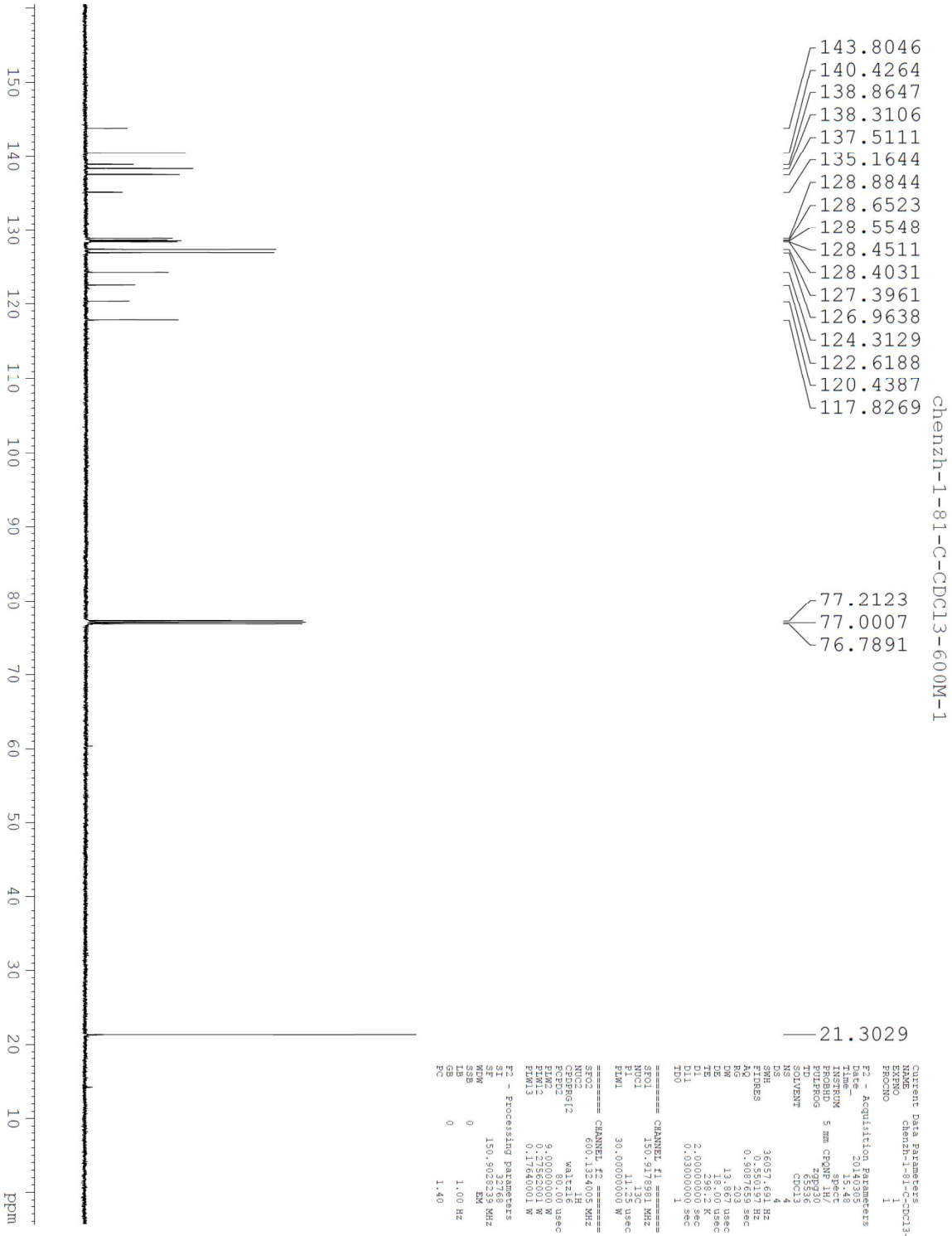
^{13}C NMR of **8** (101 MHz, $CDCl_3$):



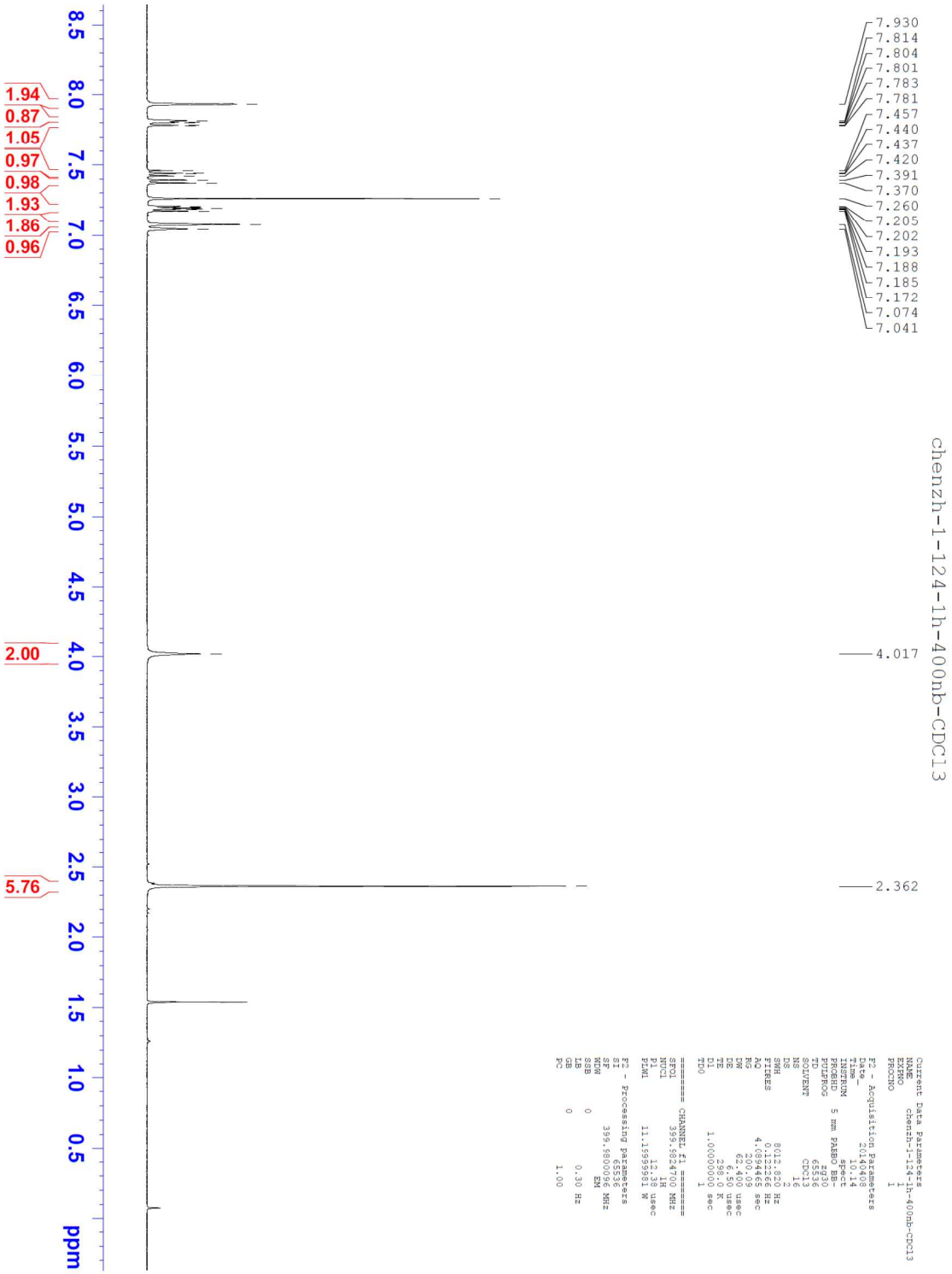
^{1}H NMR of **9a** (400 MHz, $CDCl_3$):



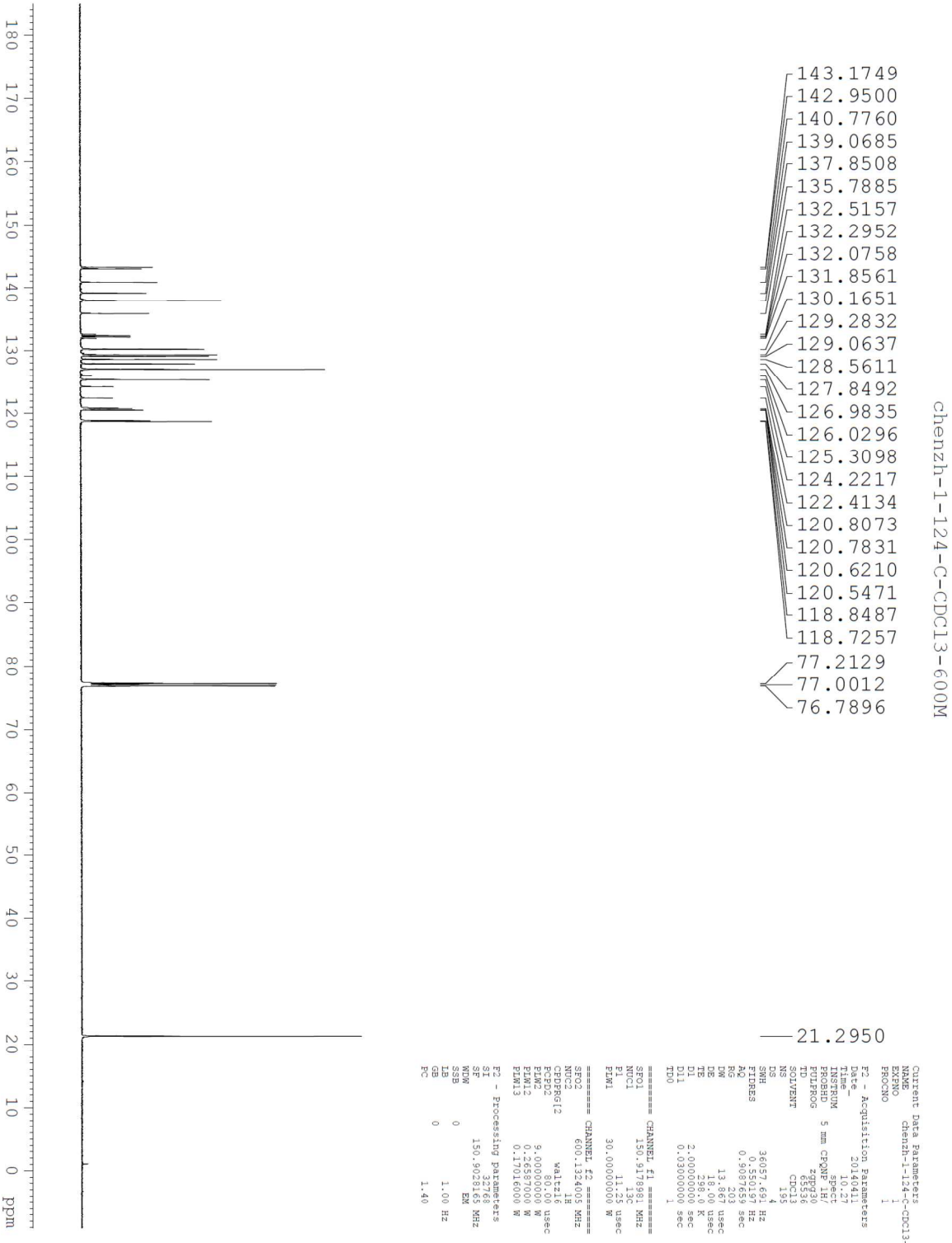
^{13}C NMR of **9a** (151 MHz, $CDCl_3$):



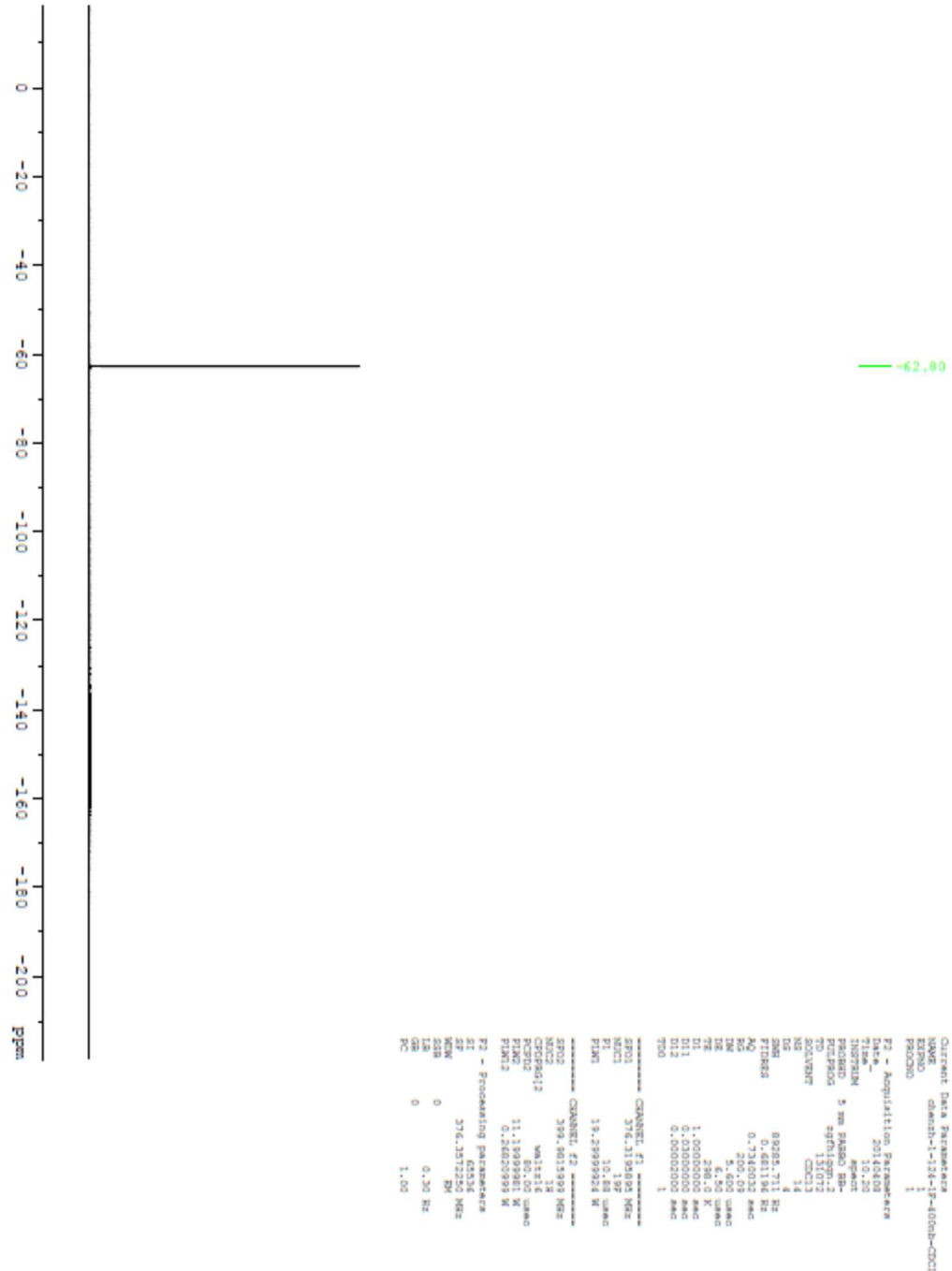
^{1}H NMR of **9b** (400 MHz,$CDCl_3$):



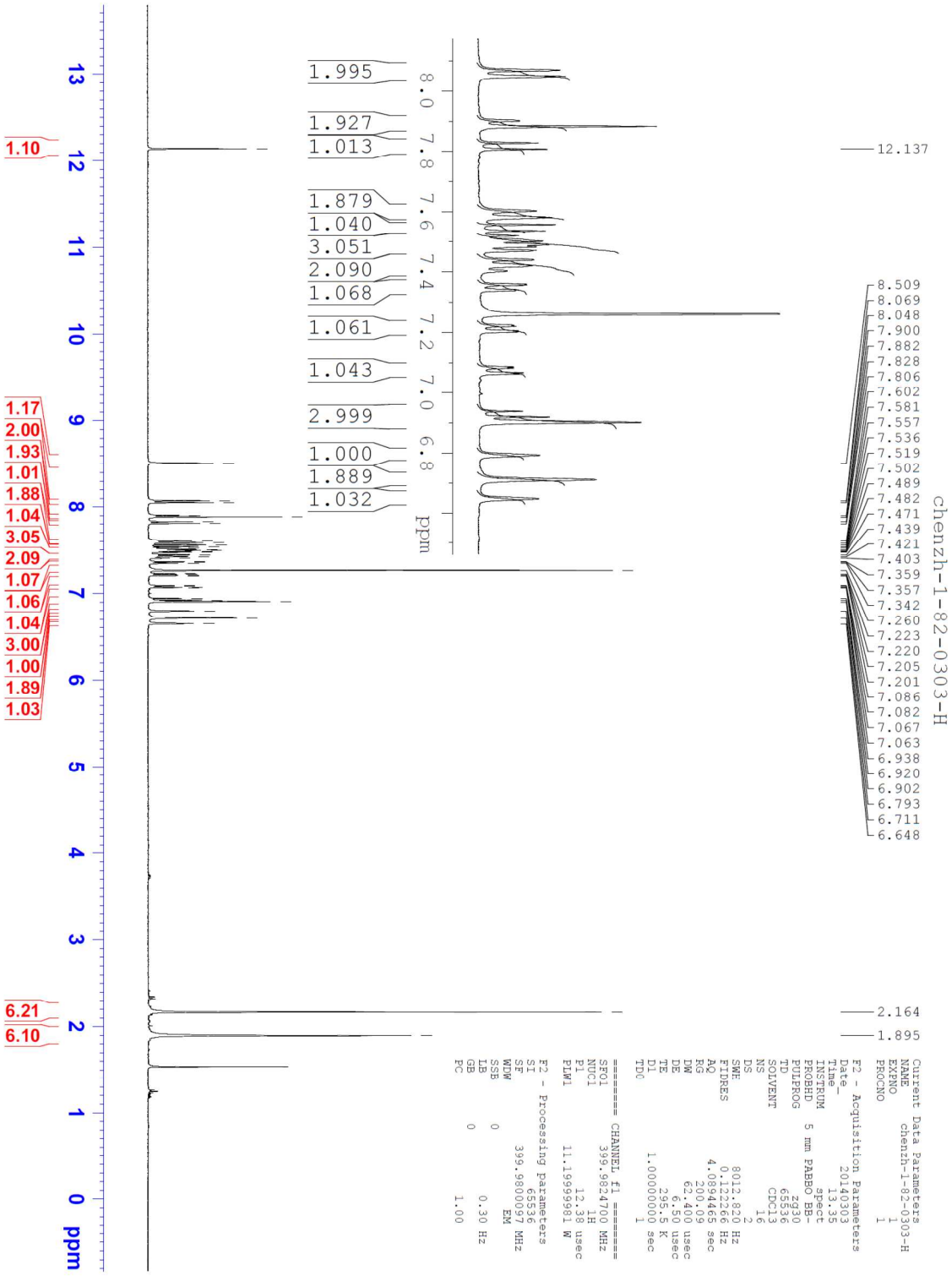
^{13}C NMR of **9b** (151 MHz, $CDCl_3$):



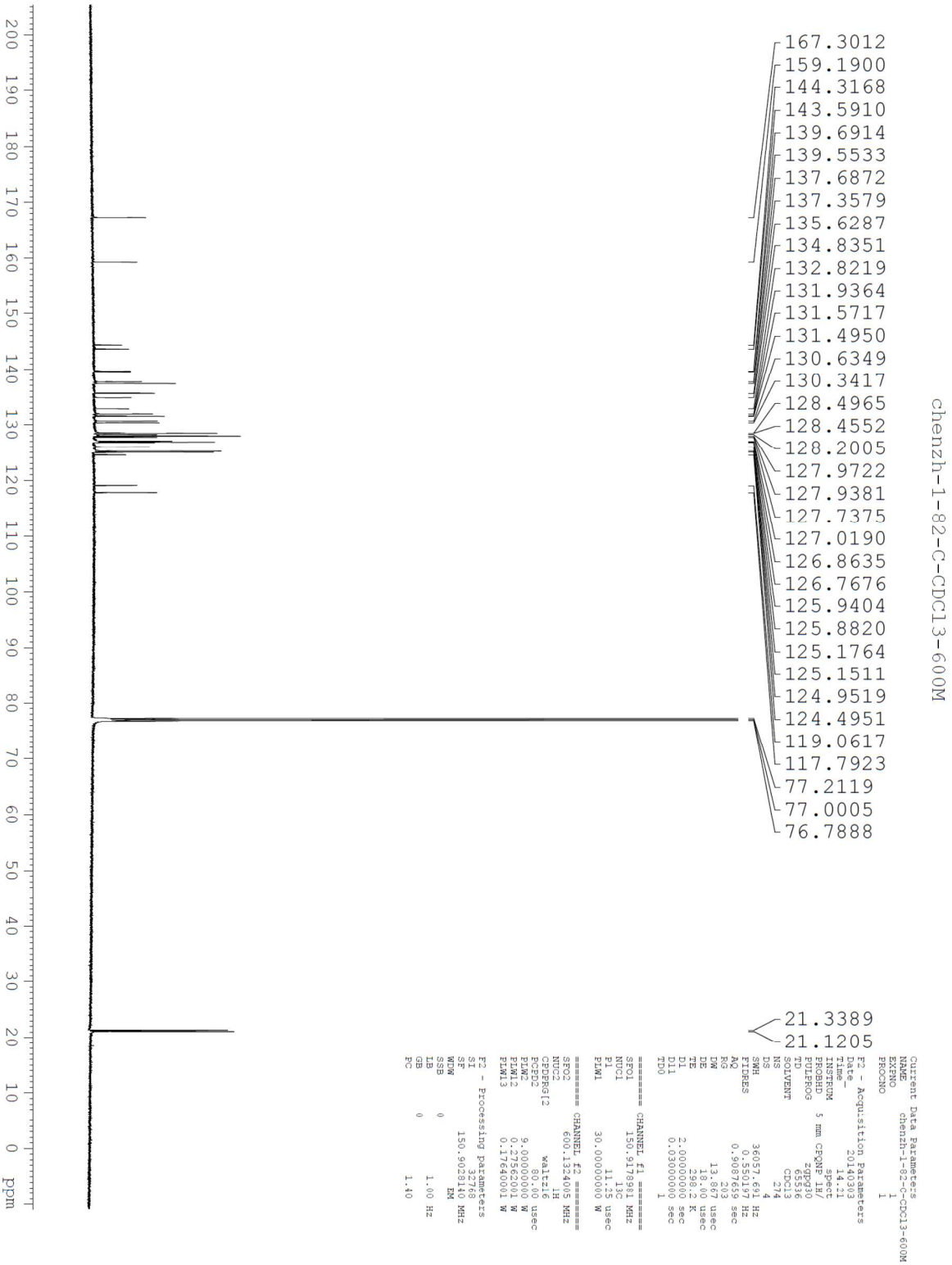
^{19}F NMR of **9b** (376 MHz, $CDCl_3$):



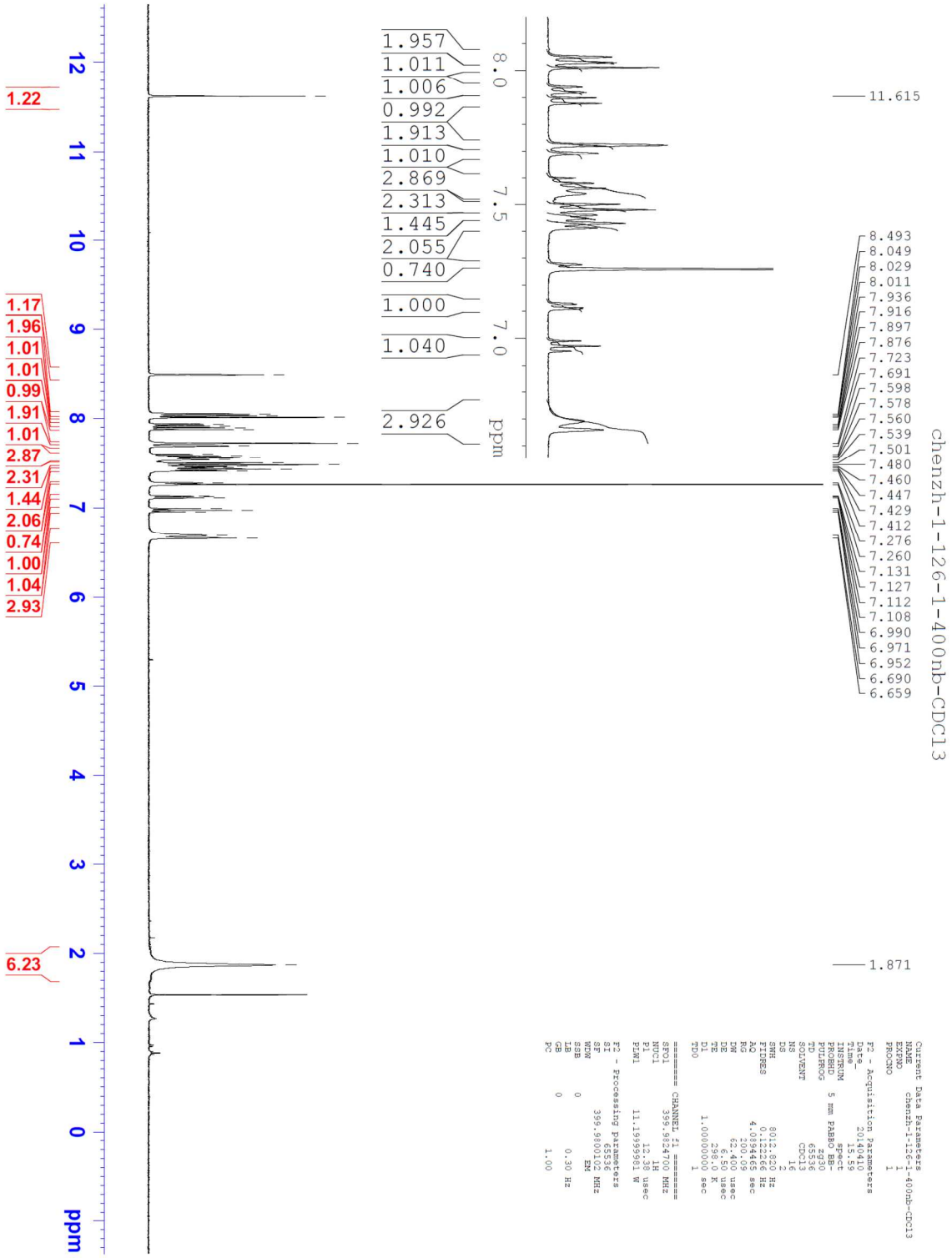
^{1}H NMR of **10a** (400 MHz,$CDCl_3$):



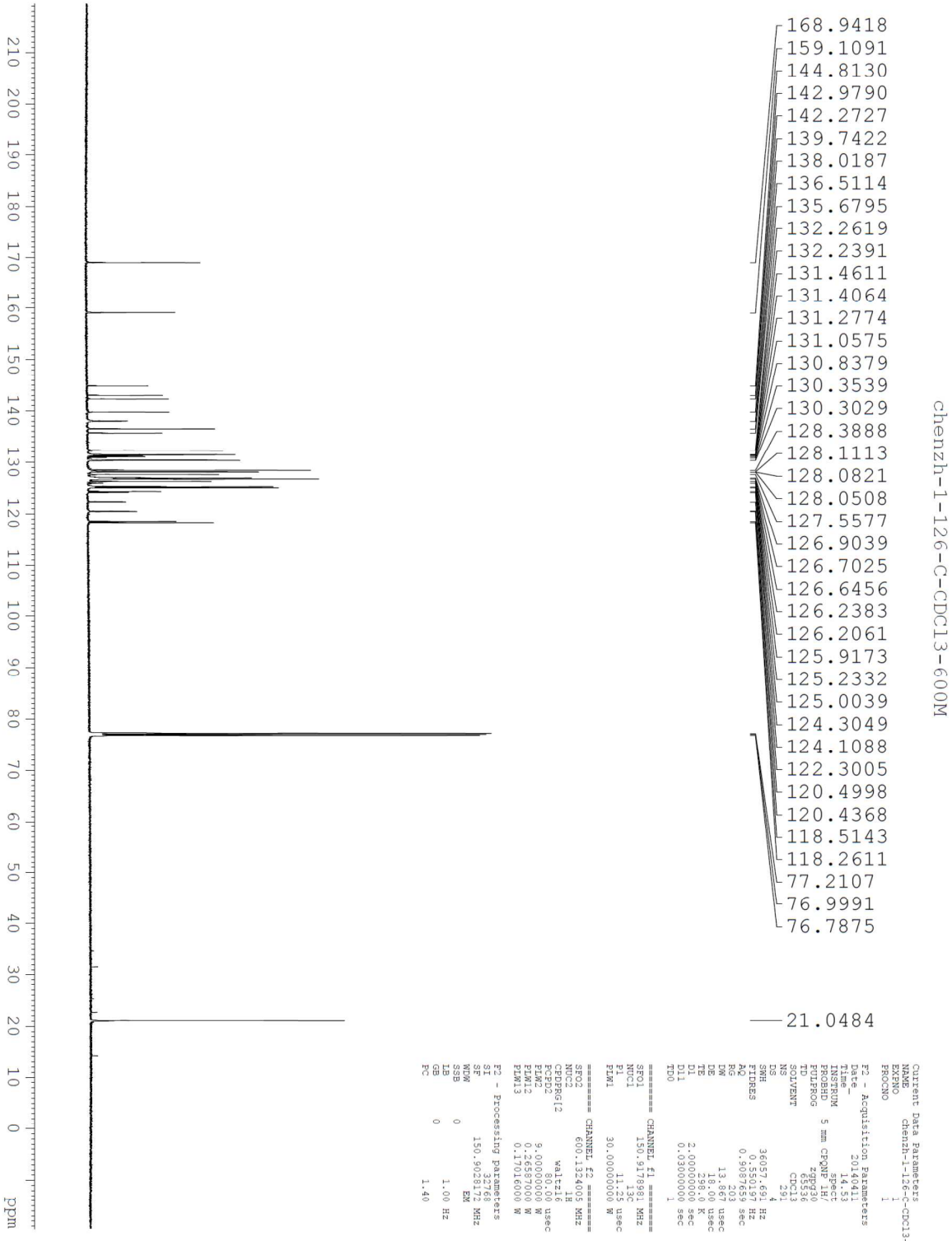
^{13}C NMR of **10a** (151 MHz, $CDCl_3$):



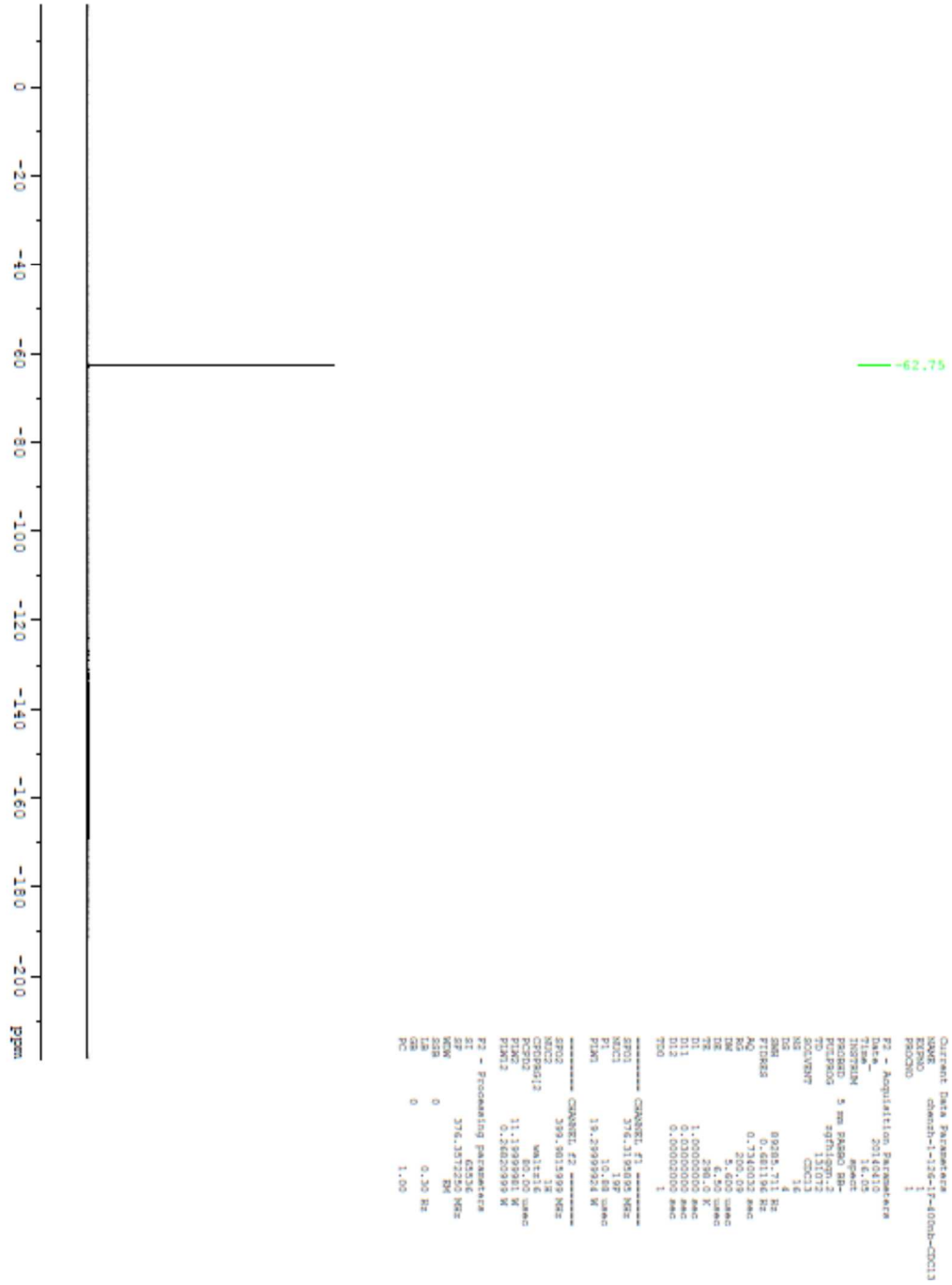
^{1}H NMR of **10b** (400 MHz, $CDCl_3$):



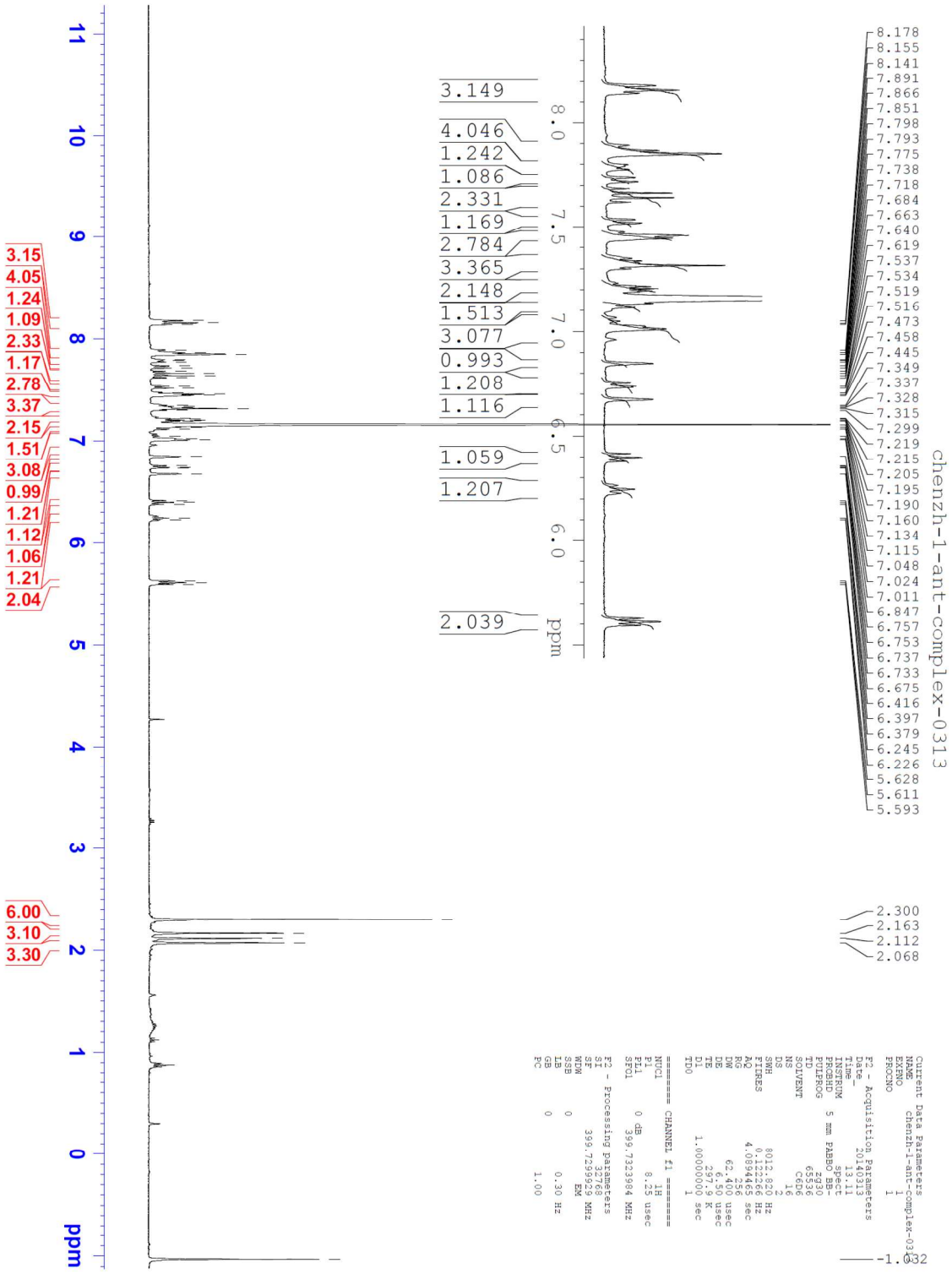
^{13}C NMR of **10b** (151 MHz, $CDCl_3$):



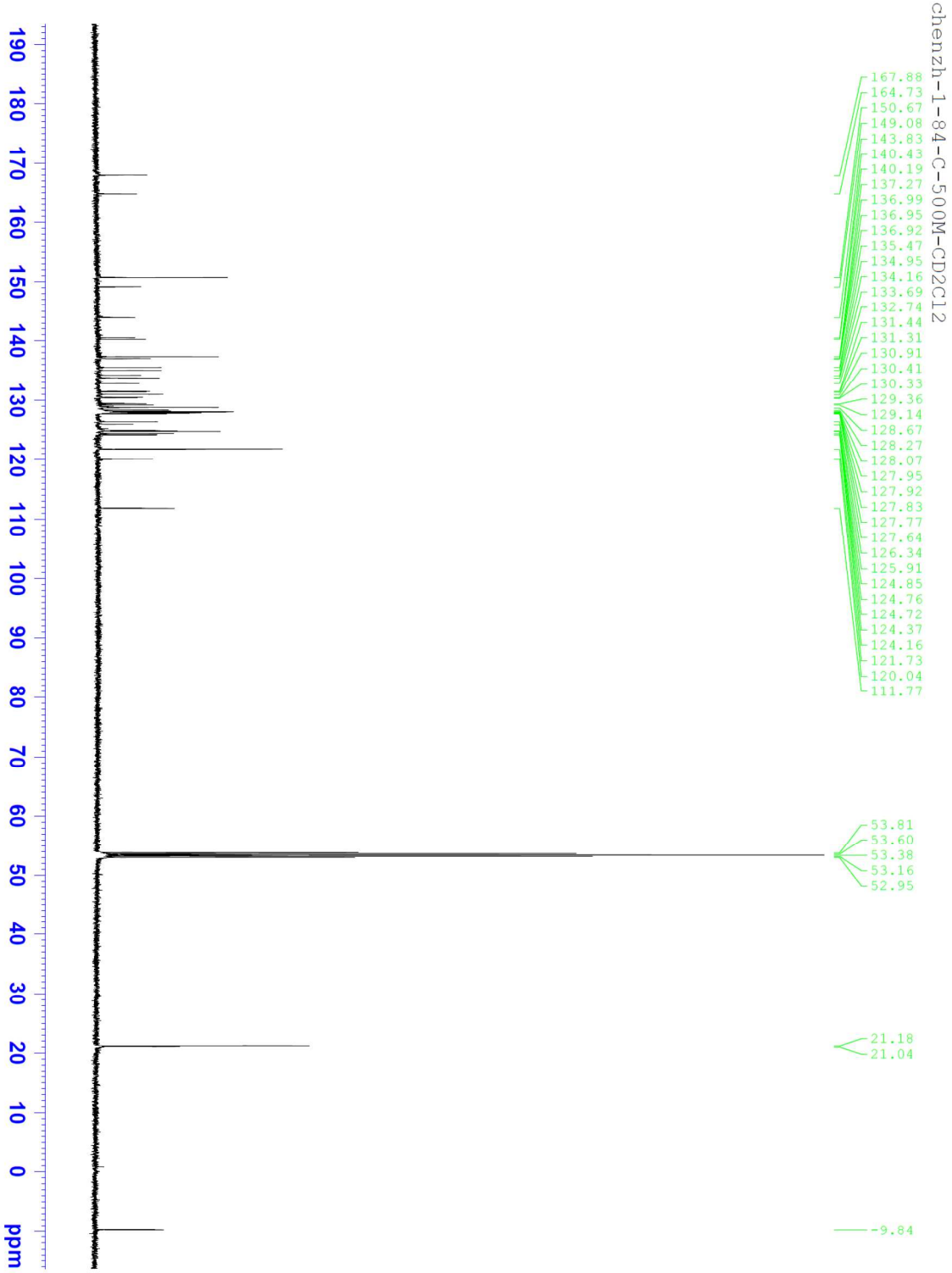
^{19}F NMR of **10b** (376 MHz, $CDCl_3$):



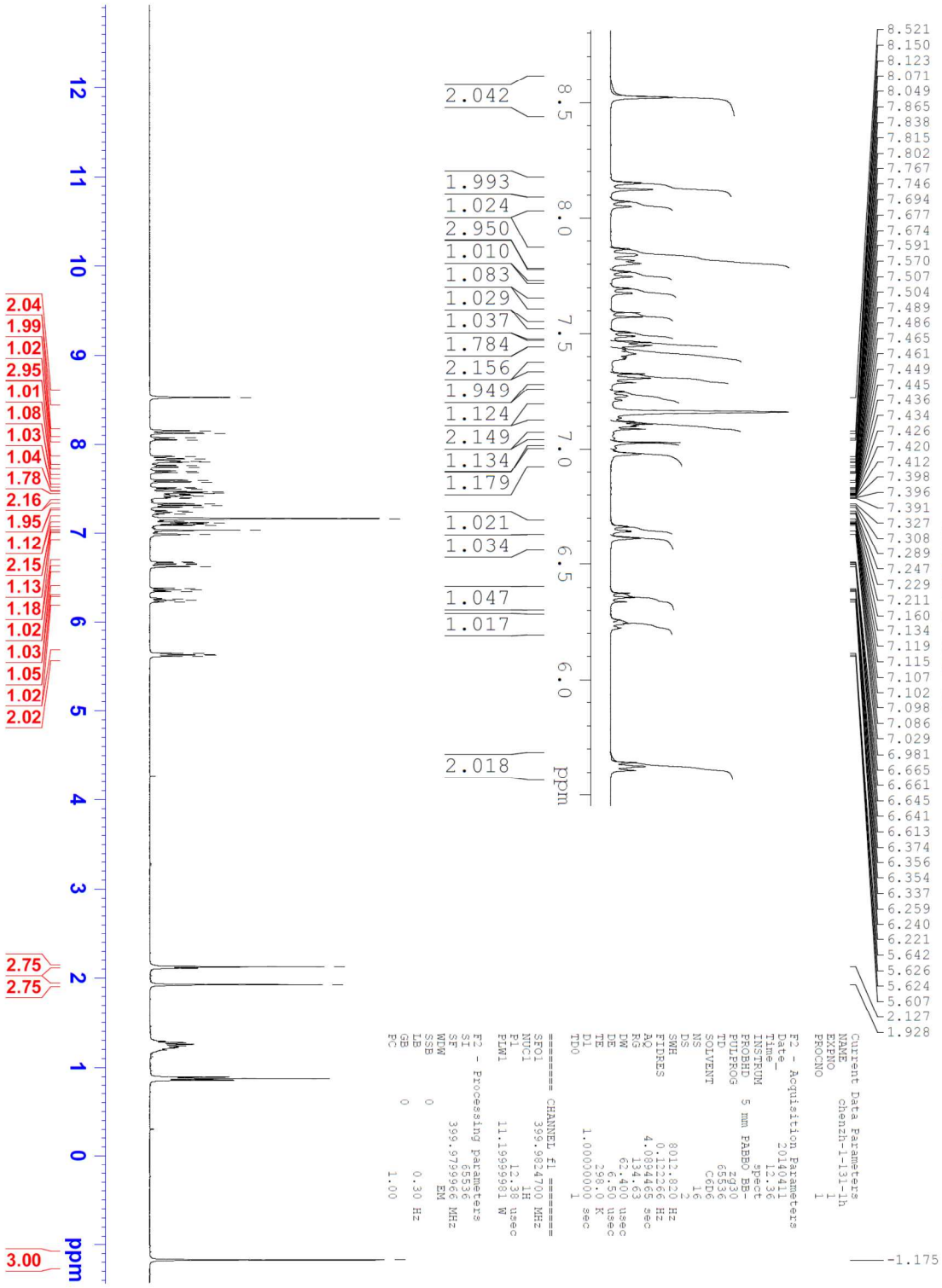
^{1}H NMR of **1a** (400 MHz,C_6D_6):



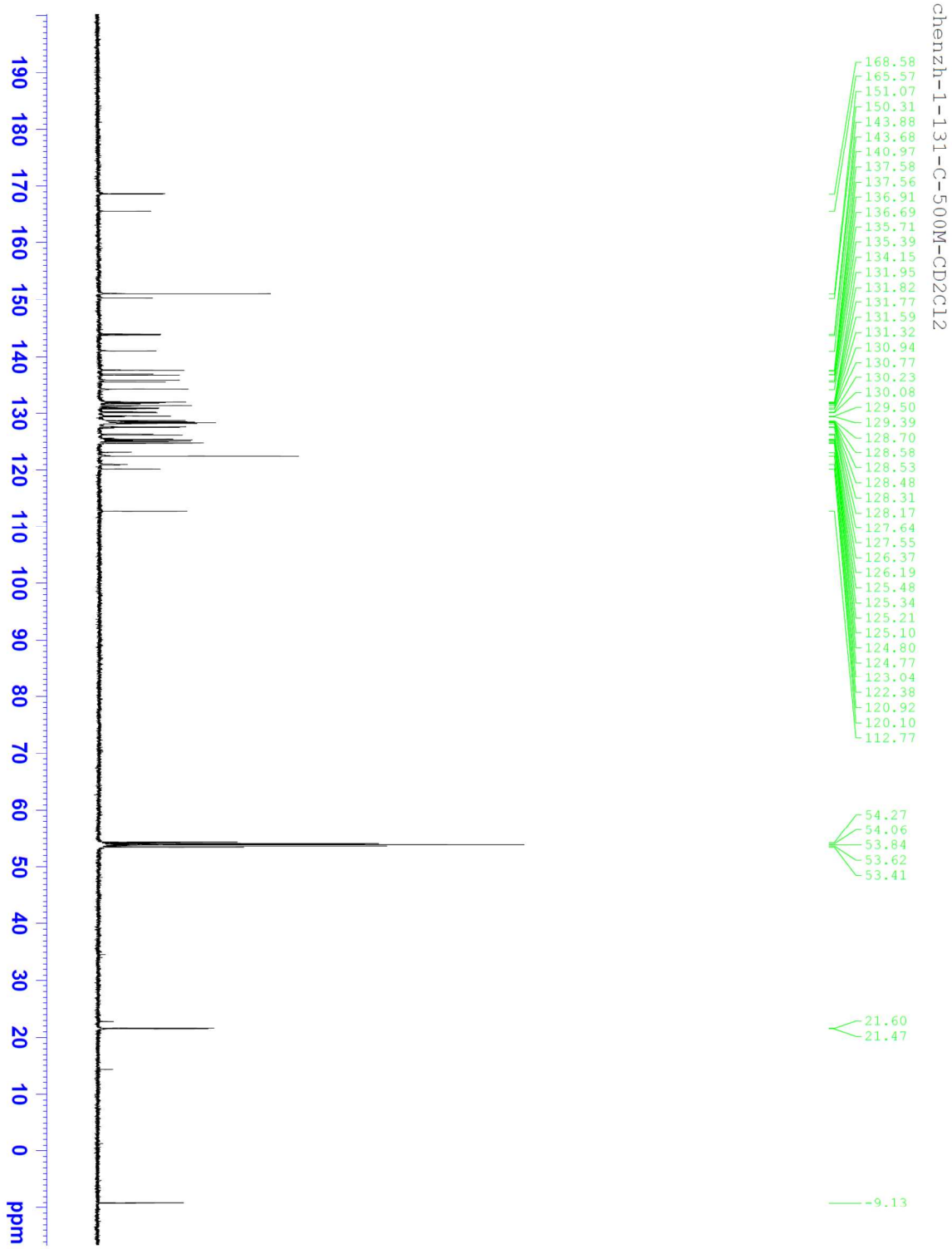
^{13}C NMR of **1a** (125 MHz, CD_2Cl_2):



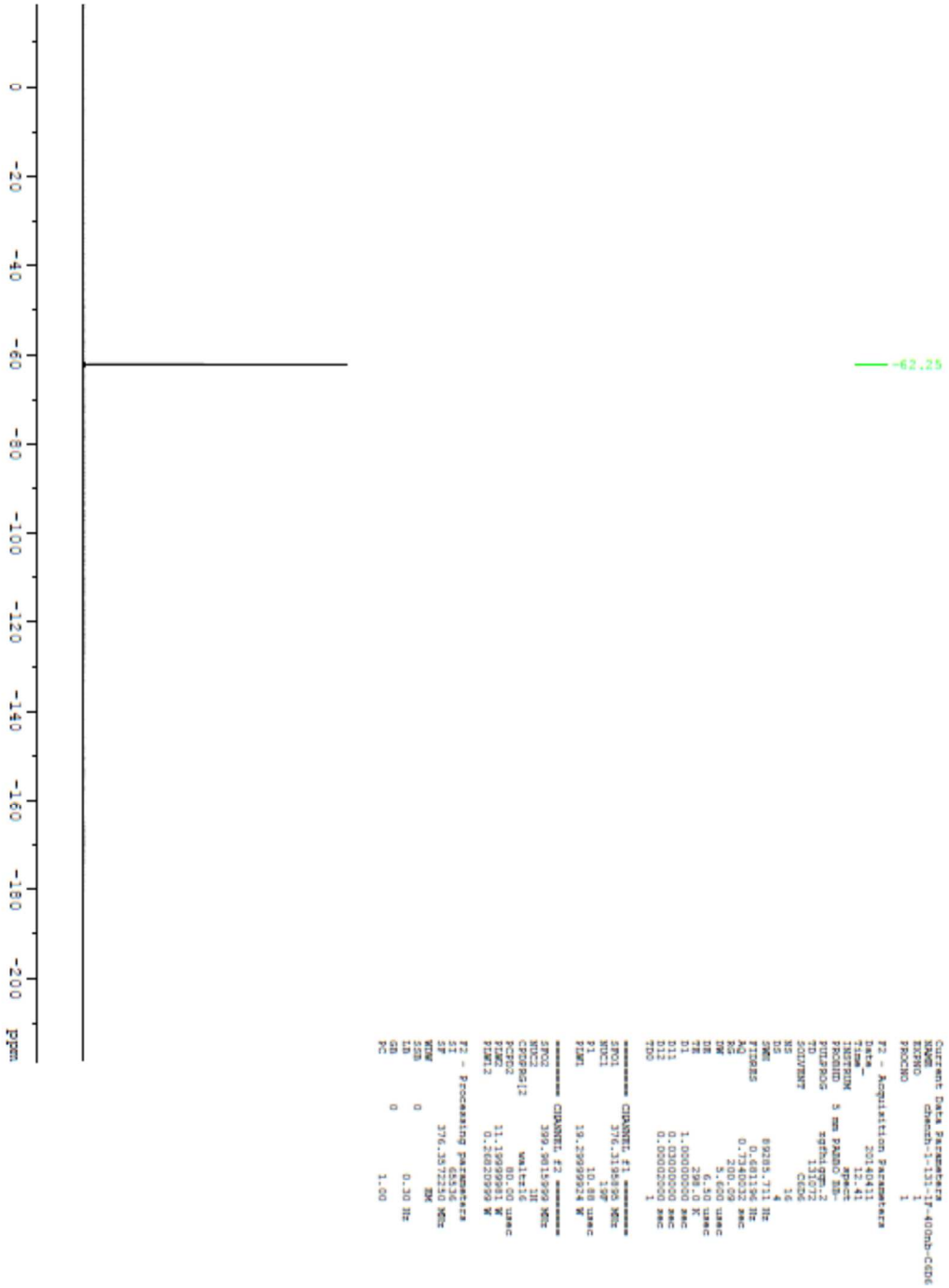
^{1}H NMR of **1b** (400 MHz,C_6D_6):



^{13}C NMR of **1b** (125 MHz, CD_2Cl_2):

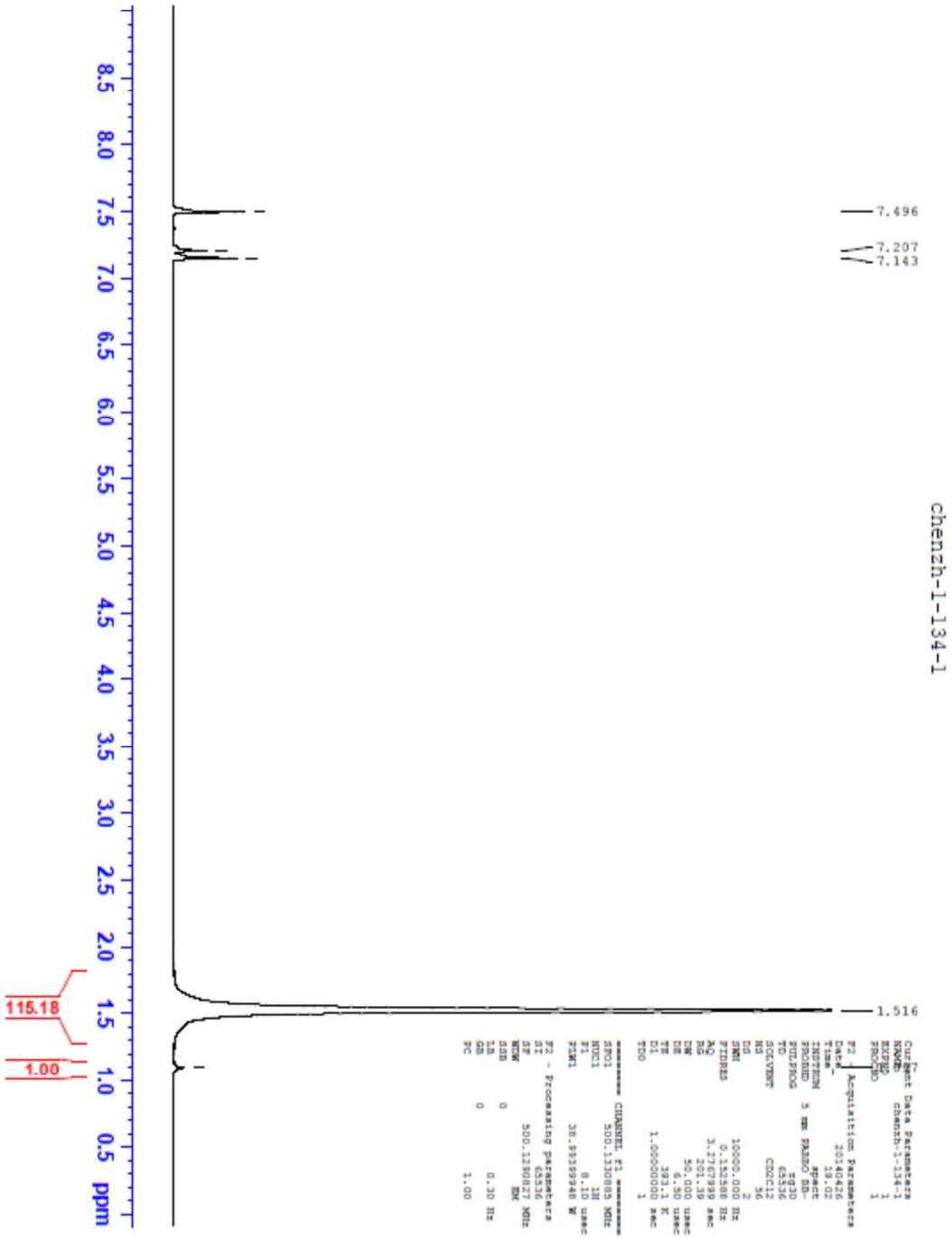


^{19}F NMR of **1b** (376 MHz, C_6D_6):



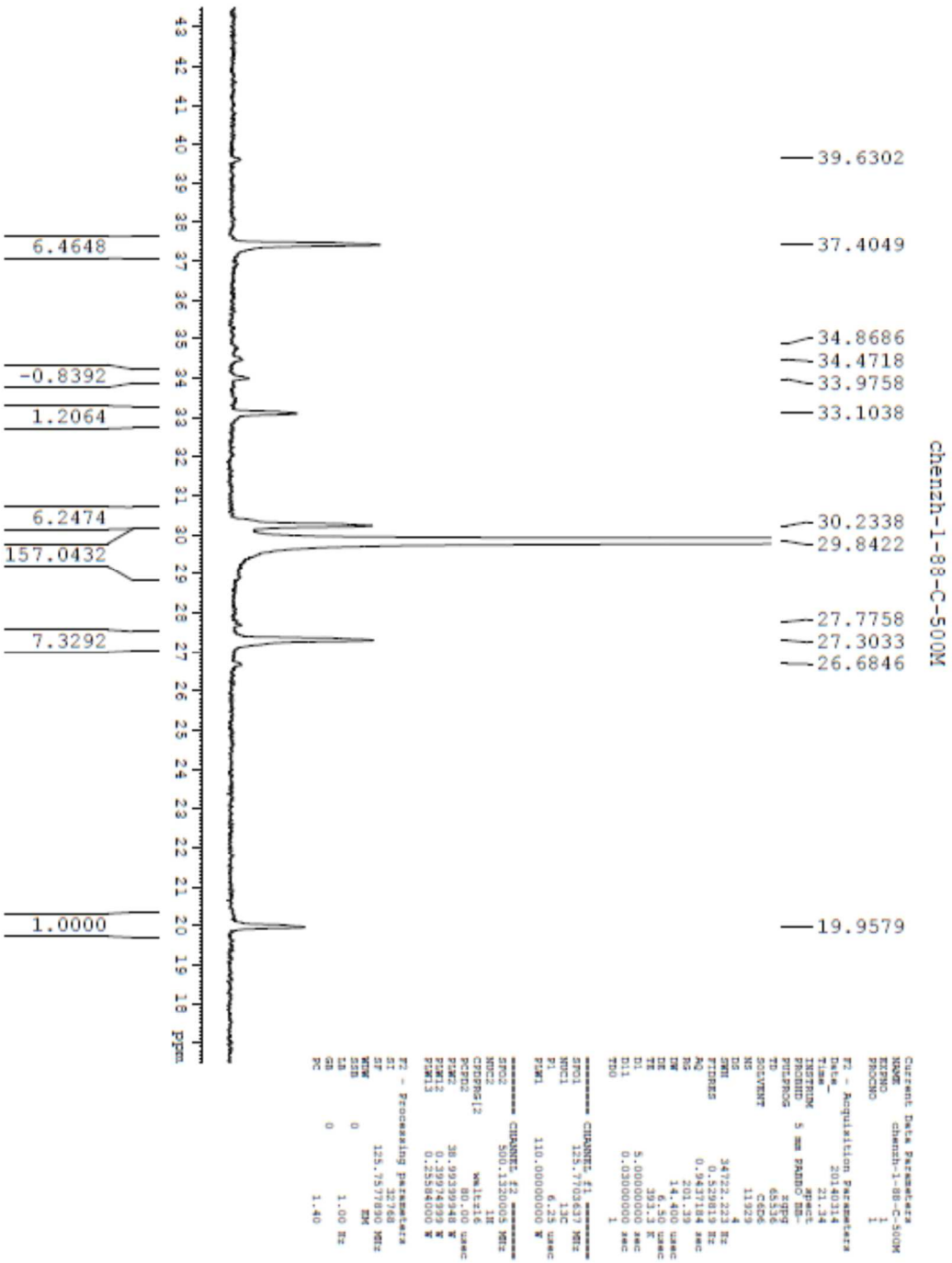
^{1}H NMR of polymer (500 MHz,C_6D_5Br):

Entry 4, Table 3



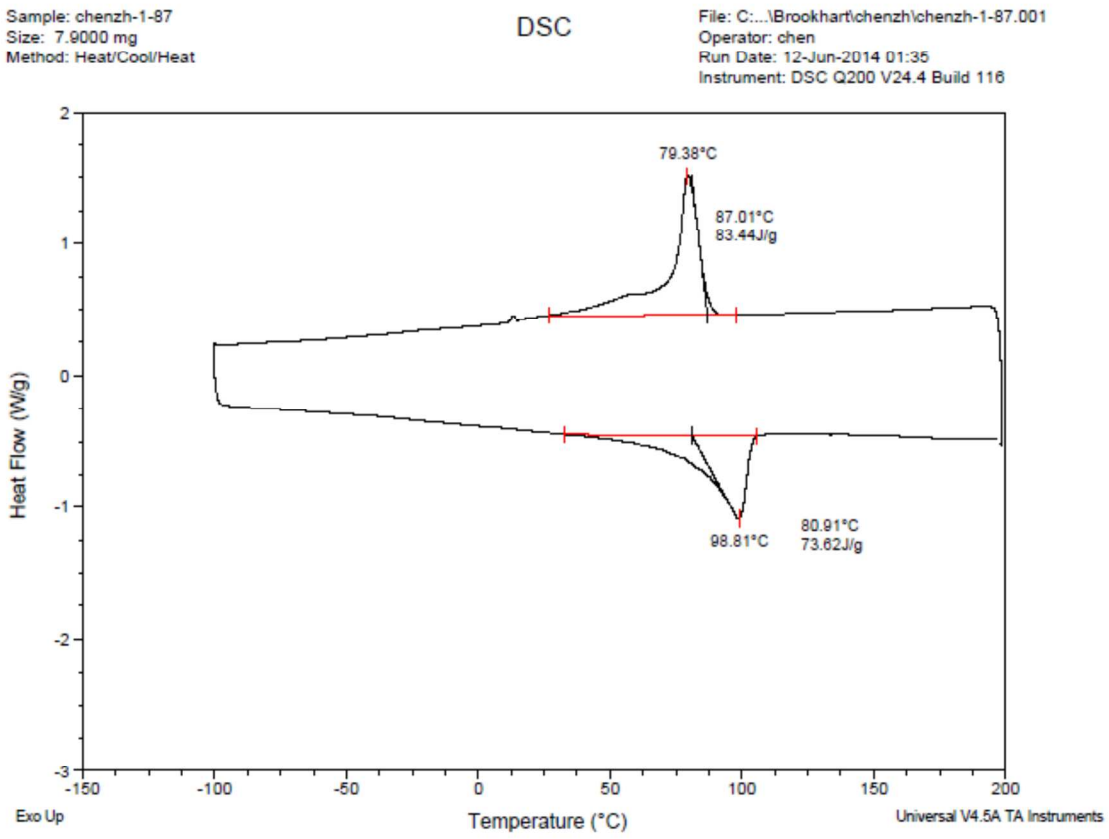
^{1}H NMR of polymer (125 MHz,C_6D_5Br):

Entry 2, Table 1

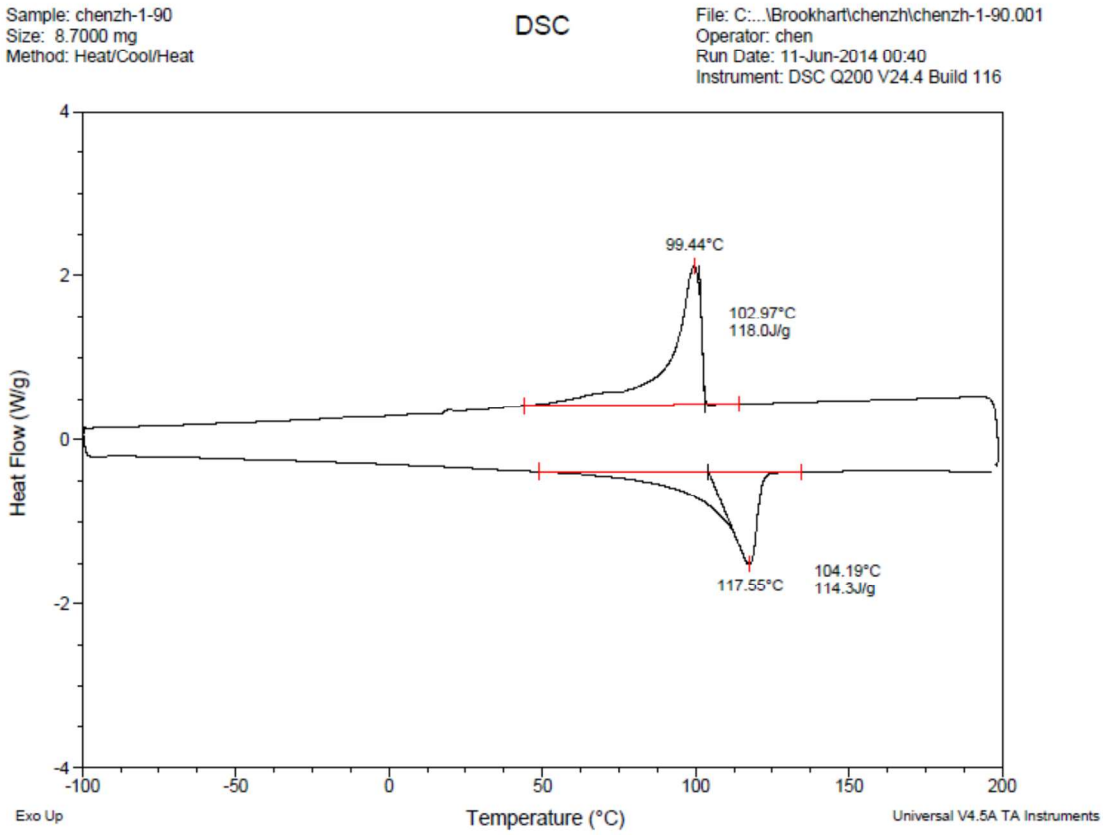


DSC

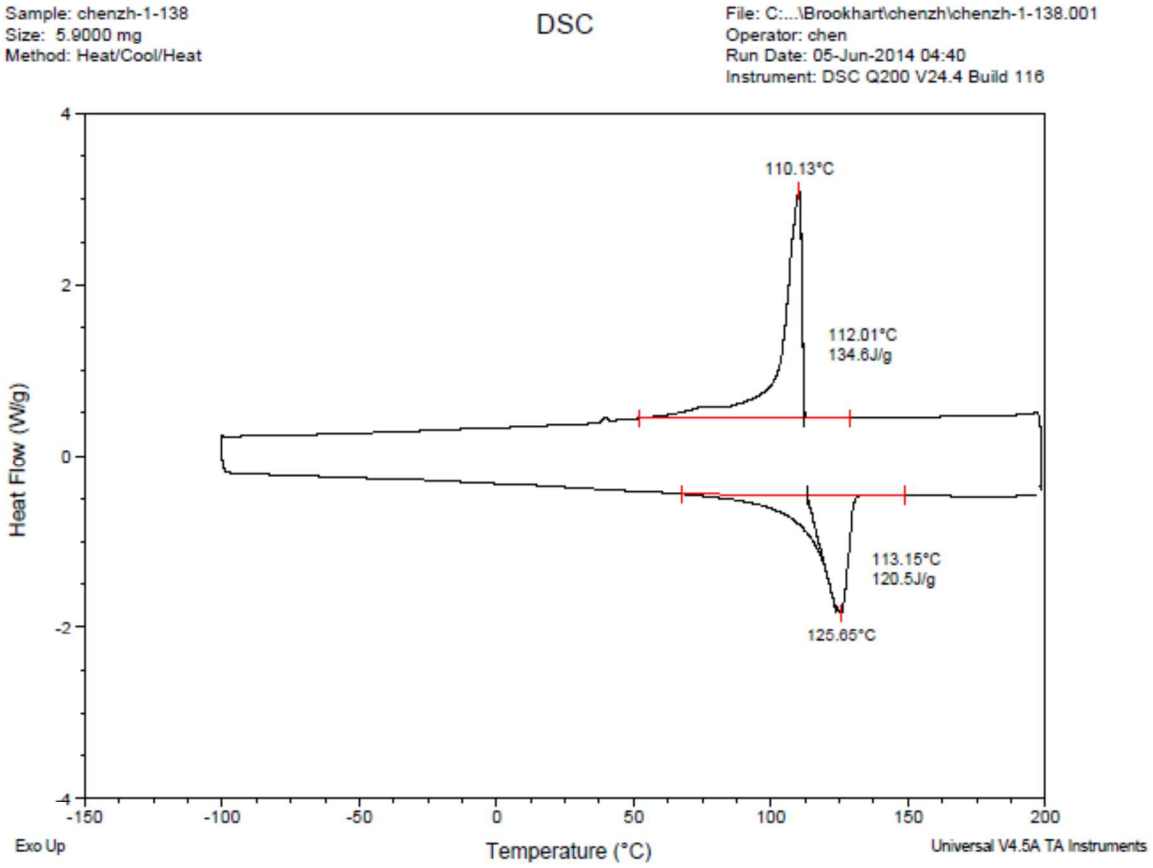
Entry 1, Table 1



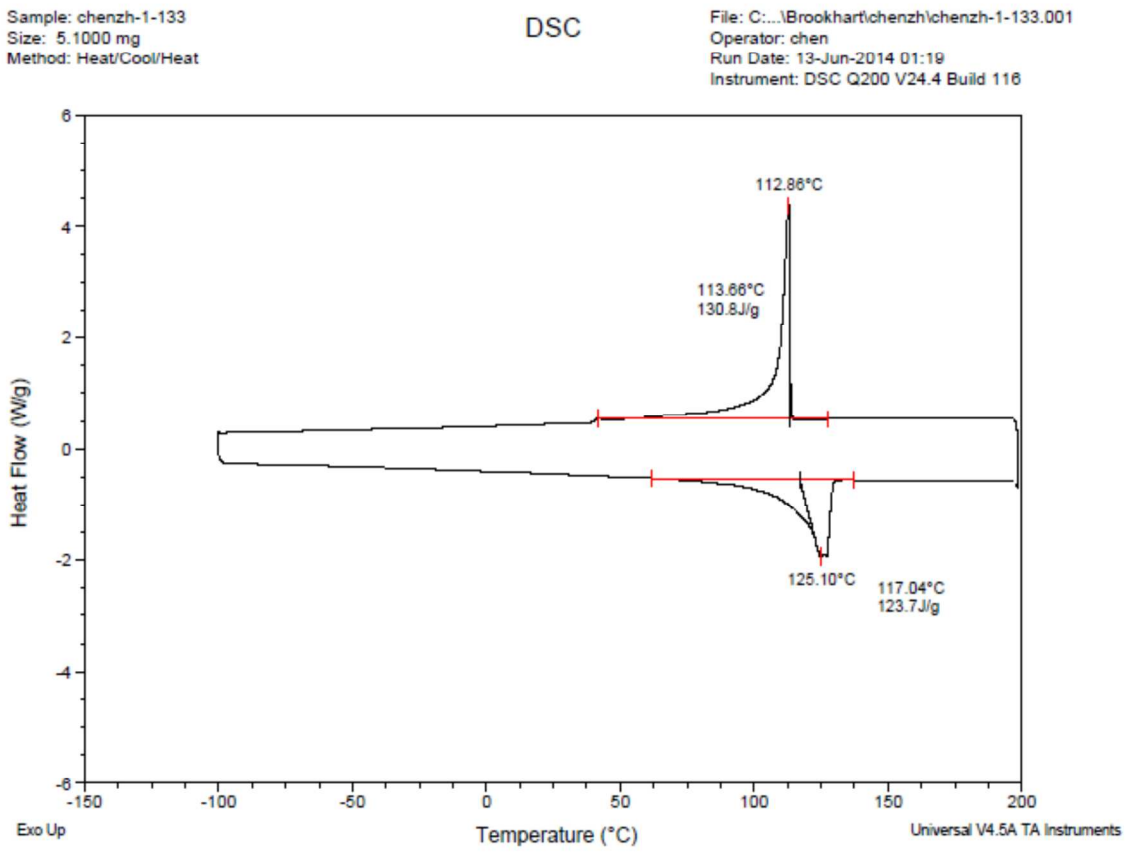
Entry 4, Table 1



Entry 1, Table 3

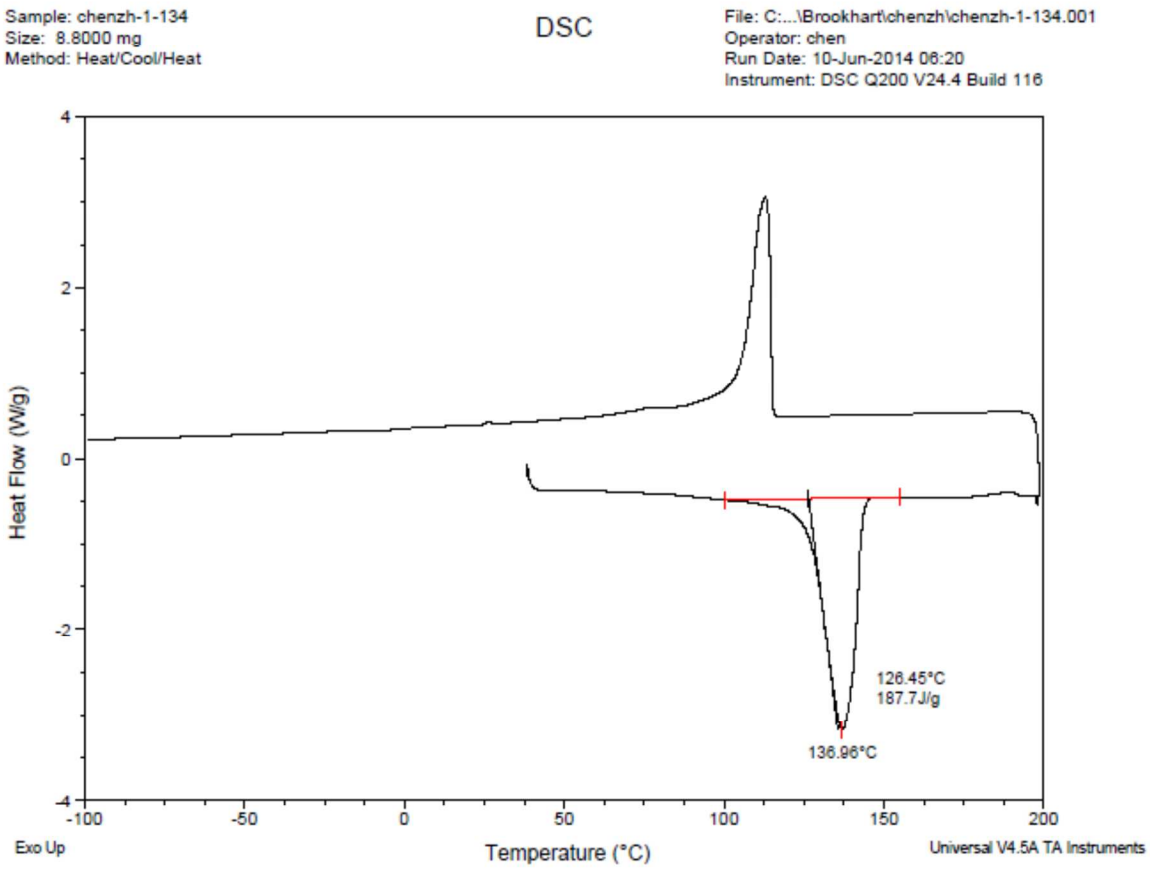


Entry 3, Table 3

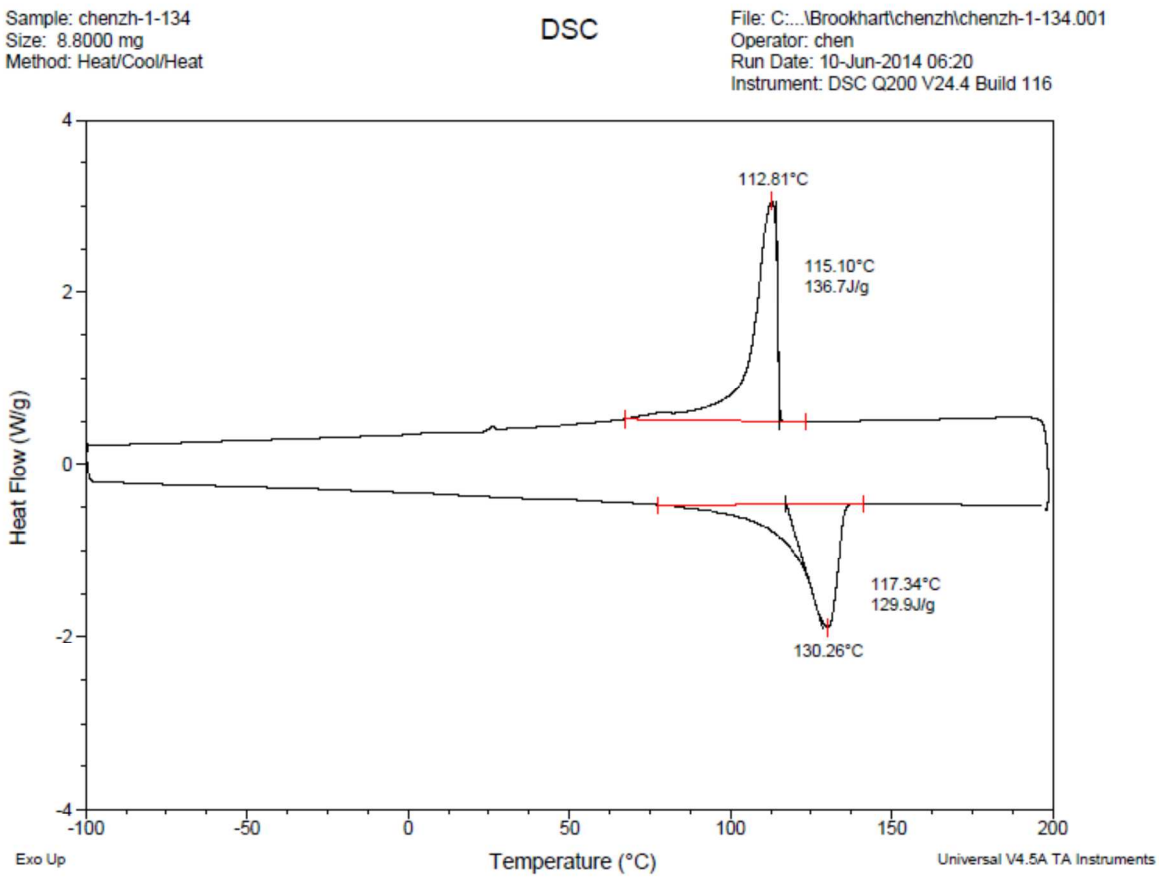


Entry 4, Table 3

First heating cycle



second heating cycle



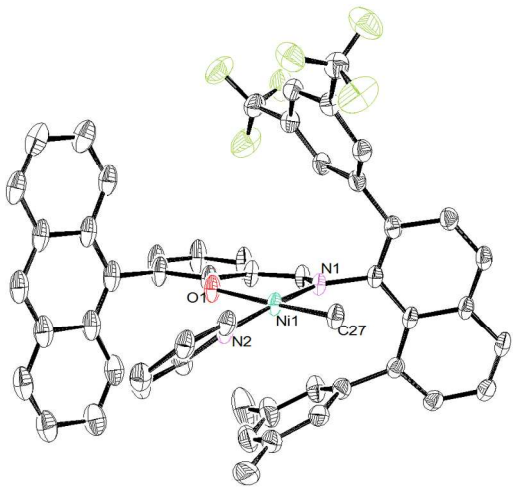


Figure S1. Solid state molecular structure of complex **1b** (ORTEP view, 30 % probability ellipsoids). Hydrogen atoms are omitted for clarity.

Table S1 Crystal data and structure refinement for **1b**.

Identification code	**1b**
Empirical formula	$C_{53}H_{38}F_6N_2NiO$
Formula weight	891.56
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	13.2308(2)
b/Å	19.6076(3)
c/Å	19.6682(3)
α/°	104.2310(12)
β/°	97.0730(12)
γ/°	107.1150(12)
Volume/Å^3	4620.37(13)
Z	4

ρ_{calc}g/cm^3	1.282
μ/mm^{-1}	1.142
F(000)	1840.0
Crystal size/mm^3	0.226 × 0.207 × 0.07
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.938 to 133.296
Index ranges	-15 ≤ h ≤ 15, -23 ≤ k ≤ 22, -23 ≤ l ≤ 23
Reflections collected	59860
Independent reflections	15838 [R_{int} = 0.0613, R_{sigma} = 0.0549]
Data/restraints/parameters	15838/1278/1195
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0635, wR_2 = 0.1723
Final R indexes [all data]	R_1 = 0.0918, wR_2 = 0.1880
Largest diff. peak/hole /e Å^{-3}	0.93/-0.49

Reference

(1) Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules*, **2000**, *33*, 6945-6952.
(2) Wiedemann, T.; Voit, G.; Tchernook, A.; Roesle, P.; Gottker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2014**, *136*, 2078-2085.
(3) Hidai, M.; Kashiwagi, T.; Ikeuchi, T.; Uchida, Y. *J. Organomet. Chem.* **1971**, *30*, 279-282.
(4) Göttker-Schnetmann, I.; Wehrmann, P.; Röhr, C.; Mecking, S. *Organometallics* **2007**, *26*, 2348-2362.
(5) We note that when this portion of toluene (20 mL) is thoroughly degassed a somewhat higher yield of PE can be obtained using **1b**.