Electronic Supplementary Information

Palladium Salt and Functional Reduced Graphene Oxide Complex: An In Situ Preparation of a Generally Applicable Catalyst for C-C Coupling Reaction

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General Information

All reagents were purchased from commercial sources (Aldrich, TCI, Acros, Alfa Aesar, Aladdin, and Nanjing Chemical Reagent Co., Ltd.) Graphite powder was obtained from Alfa Aesar with 99.99995% purity, 100 mesh. All these reagents were used as received. Water was obtained from a Sartorius arium 611DI water purification system.

Transmission electron microscopy (TEM) was conducted on a JEM-1005 instrument (JEOL Co.) at 80 kV. High resolution transmission electron microscopy (HRTEM) was conducted on a JEM-2100 instrument (JEOL Co.) at 200 kV. Energy-dispersive X-ray (EDX) detector type: SUTW-Sapphire, KV: 200.00, Azimuth: 45.00, Elevation: 22.50, AMPT: 102.4. The width of sample cuvette was 10 mm. X-ray photoelectron spectroscopy (XPS) (VG Microtech 2000 ESCA) was performed using a monochromatized Al Kα X-ray source (1486.6 eV). Wide-angle X-ray diffraction (WAXD) patterns were recorded in transmission with a Bruker D8

Advance X-ray diffractometer. The wavelength used was Cu Kα (λ = 0.154 nm), and spectra were recorded in the 2θ range of 4–80 ° (step size 0.01 °). NMR Spectra were obtained with a Bruker AM 400 (^{1}H，400 MHz, ^{13}C 100.6 MHz) or a Bruker AM 300 (^{1}H 300 MHz, ^{13}C 75.5 MHz) and are reported in δ relative to $CHCl_3$ (^{1}H 7.26 ppm, ^{13}C 77.23 ppm) as an internal reference. MS Spectra was obtained with EI (Mircomass GC-TOF) or ESI (Thermo LCQ FLEET).

Preparation and Characterization of the FRGO catalysts

GO was firstly prepared by modified Hummers method. The synthesized GO was purified by washing with deionized water and centrifuged successively three times, and suspended in deionized water by ultrasonication. The GO suspension was frozen dried to obtain the GO powders. 0.1 g of GO powders was dispersed in 200 mL of DMF via ultrasonication for 0.5 h. 0.2 g of N-propylethane-1,2-diamine was then added to the GO dispersion and the mixture was stirred at 80 ℃ for 10 h. The resultant was filtrated and washed by DMF successively three times to remove the excess N-propylethane-1,2-diamine. N-propylethane-1,2-diamine-GO suspension was obtained after washing and dispersed in 200 mL of DMF by ultrasonication for another 30 min. 0.2 g of hydrazine hydrate was then added into the dispersion to reduce N-propylethane-1,2-diamine-GO at 90 ℃ for 24 h. Finally the mixture was filtrated and washed by DMF successively three times. The product was dispersed in DMF by ultrasonication with the concentration of 0.3 mg.mL^{-1}.

Characterization of the prepared FRGO

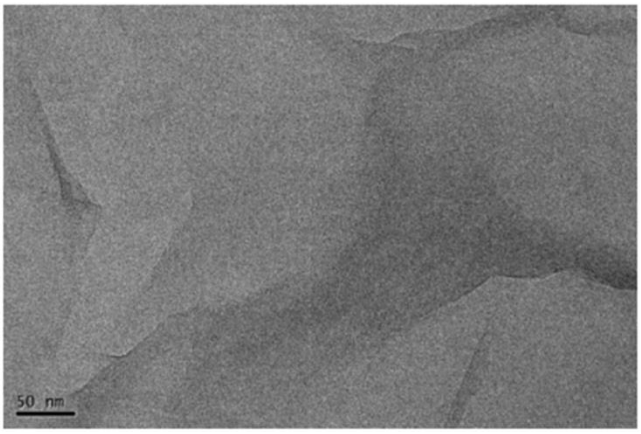


Figure S1. HRTEM image of FRGO

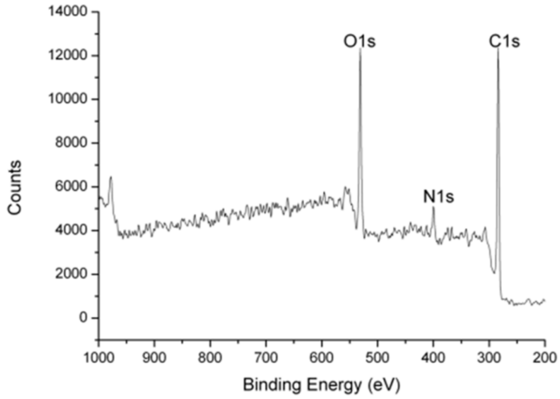


Figure S2. XPS analysis of FRGO

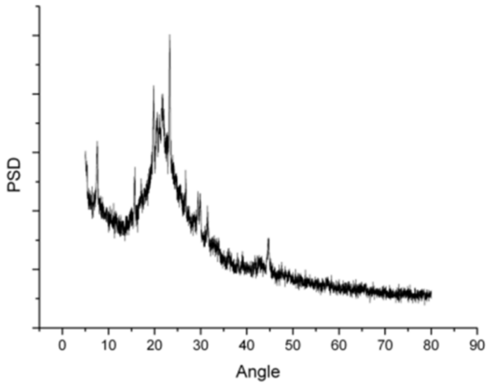


Figure S3. XRD pattern of FRGO

Preparation and characterization of the catalyst: Pd(II)-FRGO

The as-synthesized FRGO (2 mL, 0.3 mg/mL) and a DMF solution of $PdCl_2$ (0.125 ml 0.01 M) were mixed at room temperature to afford the Pd(II)-FRGO catalyst.

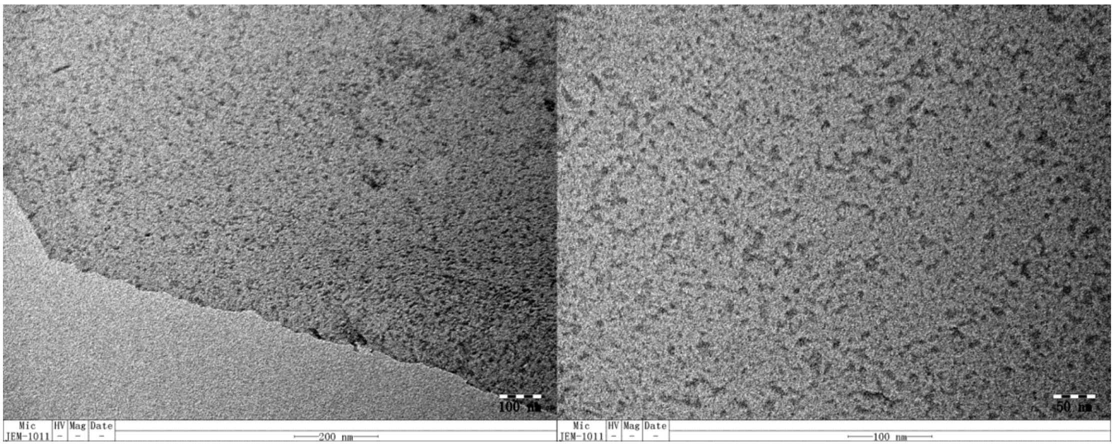


Figure S4. TEM images of the catalyst Pd(II)-FRGO complex

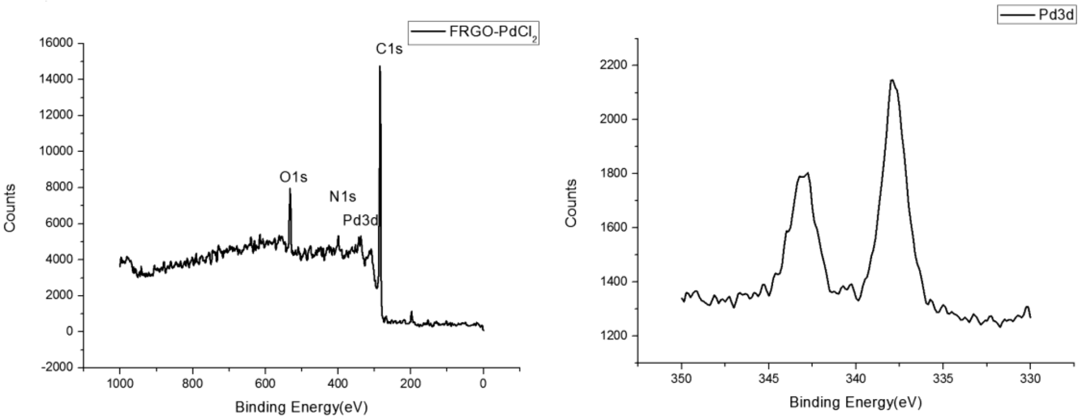


Figure S5. XPS result of the catalyst Pd(II)-FRGO complex

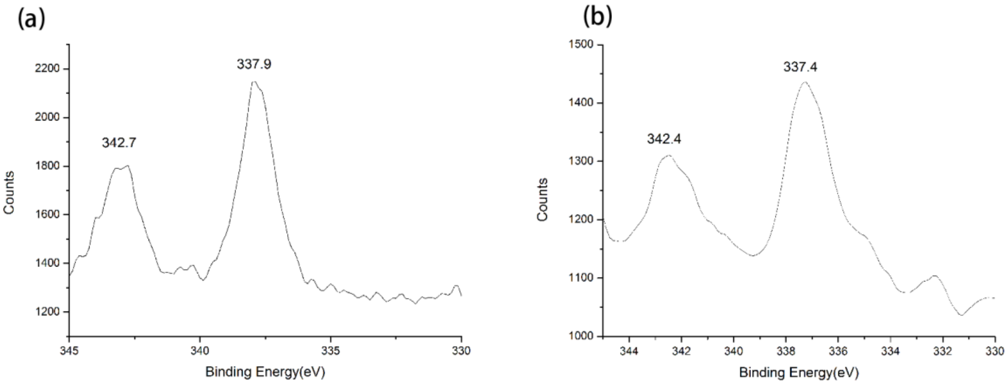
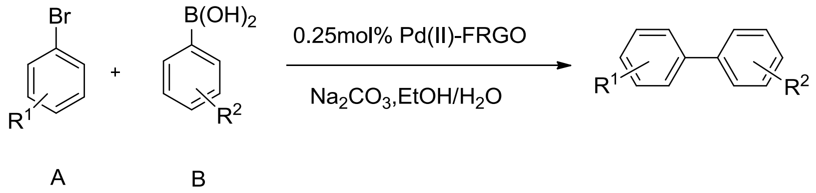


Figure S6. XPS result of the catalyst Pd(II)-FRGO complex before (a) or after (b) the reaction

XPS result of the catalyst before (a) and after (b) the reactions had been measured, and shown below, in which palladium remained in the divalent state through the reaction.

General procedure for the Suzuki reactions

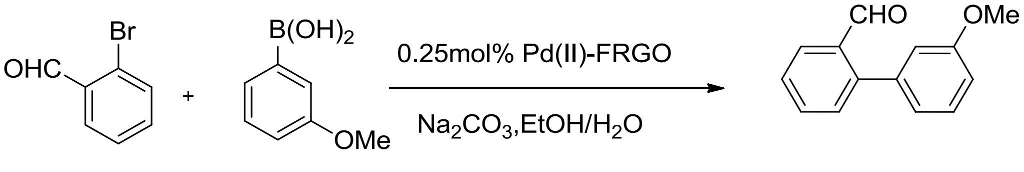


A 10 ml tube was charged with boronic acid (0.55 mmol, 1.1 eq.), sodium carbonate (106 mg, 1 mmol, 2 eq.), the bromoaryl (0.5 mmol, 1 eq.) and the Pd(II)-FRGO catalyst (0.25 mol %). Ethanol (2 mL) and water (2 mL) were added, the stirred at room temperature. The reaction was detected by TLC，after the reaction finished, the mixture was filtered over a small column of silica gel, the column washed with DCM (10 mL). The product was extracted into the organic phase (2x10 mL DCM), the united organic phases were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. In some cases purification of the crude product by column chromatography was needed.

Recycling Experiment

The results described below were obtained when centrifugation was applied to separate the catalysts from the reaction mixture and after washing with water and DMF (Table S1). This well cyclic performance anastomosed to the EDX result, as the palladium amount on the surface of the catalyst did not decreased during the reaction, although it might be poisoned slowly.

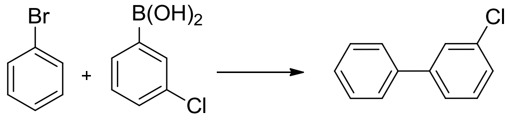
Table S1 Recycling Experiment with Pd(II)-FRGO



Run	Yield (%)
1	95
2	91
3	83
4	68

Spectroscopic data of the products of the Suzuki reactions

3-chloro-1,1'-biphenyl (9)[1]



1 **7a** **9**

^{1}H-NMR (400 MHz, $CDCl_3$):

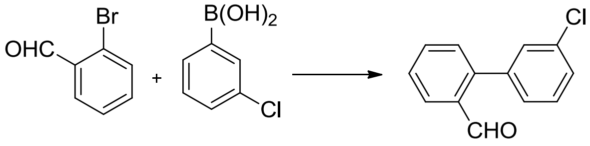
δ 7.57-7.61 (m, 3H), 7.46-7.50 (m, 3H), 7.33-7.42 (m, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 125.27, 127.09, 127.23, 127.27, 127.84, 128.86, 129.96, 134.62, 139.77, 143.04.

MS (GC/MS-EI, 70eV): *m/z* (%) = 188(100) [M$^+$], 190 (26).

3'-chloro-[1,1'-biphenyl]-2-carbaldehyde (10a)[2]



2 **7a** **10a**

^{1}H-NMR (400 MHz, $CDCl_3$):

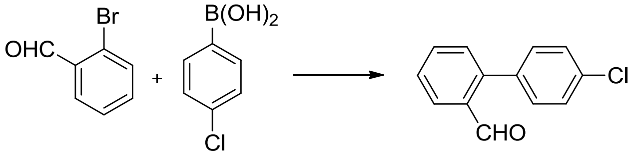
δ 9.98 (s, 1H), 8.04 (dd, *J* = 1.2 Hz, 7.6Hz, 1H), 7.65 (td, 1H), 7.53 (t, *J* = 7.6 Hz,1H), 7.43-7.38 (m, 4H), 7.25 (m, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 191.75, 144.22, 139.55, 134.44, 133.66, 133.57, 130.59, 129.80, 129.56, 128.31, 128.27, 128.22, 127.80.

MS (GC/MS-EI, 70eV): *m/z* (%) = 216 (23) [M$^+$], 215 (67) [(M-H)$^+$], 181 (46), 152 (100).

4'-chloro-[1,1'-biphenyl]-2-carbaldehyde (10b)[3]



10b

2 **7b**

^{1}H-NMR (400 MHz, $CDCl_3$):

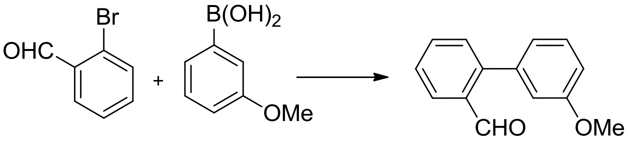
δ 9.96 (s, 1H), 8.02 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H), 7.64 (dt, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.39-7.45 (m, 3H), 7.30-7.32 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 191.77, 144.40, 136.14, 134.37, 133.60, 133.55, 131.18, 130.59, 128.56, 128.05, 127.83.

MS (GC/MS-EI, 70eV): *m/z* (%) = 216 (16) [M^+], 215 (76) [$(M-H)^+$], 181 (36), 152 (100).

3'-methoxy-[1,1'-biphenyl]-2-carbaldehyde (10c)[4]



2 **7c** **10c**

^{1}H-NMR (400 MHz, $CDCl_3$):

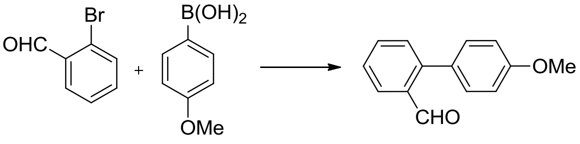
δ 10.0 (s, 1H), 8.02 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H), 7.62 (dt, 1H), 7.44-7. 50 (m,2H), 7.37 (t, *J* = 8.0 Hz, 1H), 6.91-6.99 (m, 3H), 3.84 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 192.32, 159.44, 145.73, 139.05, 133.65, 133.44, 130.53, 129.33, 127.74, 127.36, 122.62, 115.59, 113.53, 55.24.

MS (GC/MS-EI, 70eV): *m/z* (%) = 212 (89) [M^+], 184 (100).

4'-methoxy-[1,1'-biphenyl]-2-carbaldehyde (10d)[5]



2 **7d** **10d**

^{1}H-NMR (400 MHz, $CDCl_3$):

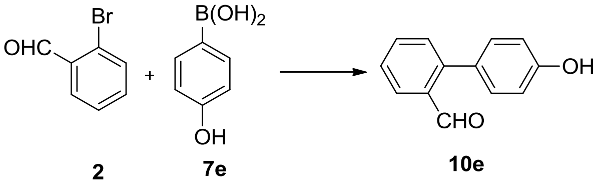
δ 10.0 (s, 1H), 7.99 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H), 7.60 (dt, 1H), 7.40-7.46 (m, 2H), 7.29 (m, 2H), 6.99 (m, 2H), 3.85 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 192.56, 159.61, 145.56, 133.65, 133.44, 131.21, 130.70, 129.91, 127.51, 127.28, 113.85, 55.29.

MS (GC/MS-EI, 70eV): *m/z* (%) = 212 (100) [M$^+$], 169 (28), 141 (43).

4'-hydroxy-[1,1'-biphenyl]-2-carbaldehyde (10e)



2 **7e** **10e**

^{1}H-NMR (400 MHz, CDCl$_3$):

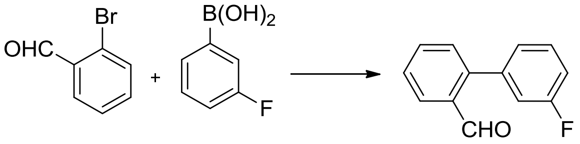
δ 9.88 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 5.2 Hz, 1H), 7.32-7.37 (m, 2H), 7.13 (d, *J* = 8 Hz, 2H), 7.05 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 2H).

^{13}C-NMR (100 MHz, CDCl$_3$):

δ 193.91, 156.37, 146.11, 133.95, 133.33, 131.43, 130.77, 129.51, 127.67, 127.33, 115.51.

MS (GC/MS-EI, 70eV): *m/z* (%) = 198 (100) [M$^+$], 197 (80) [(M-H)$^+$].

3'-fluoro-[1,1'-biphenyl]-2-carbaldehyde (10f)[6]



2 **7f** **10f**

^{1}H-NMR (400 MHz, CDCl$_3$):

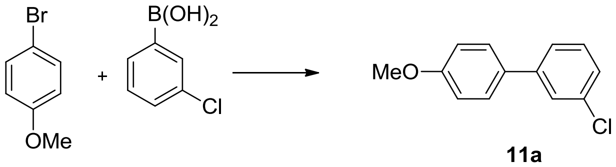
δ 9.98 (s, 1H), 8.03 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H), 7.65 (dt, 1H), 7.52 (m, 1H), 7.40-7.46 (m, 2H), 7.09-7.17 (m, 3H).

^{13}C-NMR (100 MHz, CDCl$_3$):

δ 191.83, 163.77, 161.30, 144.41, 144.39, 139.98, 139.90, 133.63, 133.62, 130.56, 129.96, 129.87, 128.22, 127.75, 125.98, 125.96, 116.99, 116.77, 115.16, 114.95.

MS (GC/MS-EI, 70eV): *m/z* (%) = 200 (22) [M$^+$], 199 (100) [(M-H)$^+$], 171 (22), 170 (37).

3-chloro-4'-methoxy-1,1'-biphenyl (11a)[7]



3 **7a** **11a**

^{1}H-NMR (400 MHz, CDCl$_3$):

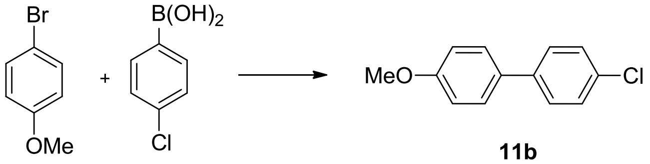
δ 7.6 (t, *J* = 2.0 Hz, 1H), 7.5 (m, 2H), 7.4 (m, 1H), 7.3 (t, *J* = 7.6 Hz, 1H), 7.2 (m, 1H), 7.0 (m, 2H), 3.9 (s, 3H).

^{13}C-NMR (100 MHz, CDCl$_3$):

δ 159.53, 142.60, 134.55, 132.18, 129.90, 128.09, 126.74, 126.57, 124.77, 114.27, 55.26.

MS (GC/MS-EI, 70eV): *m/z* (%) =218 (100) [M$^+$], 203 (77) [(M-CH$_3$)$^+$], 175 (75), 139 (32).

4-chloro-4'-methoxy-1,1'-biphenyl (11b)[8]



3 **7b** **11b**

^{1}H-NMR (400 MHz, CDCl$_3$):

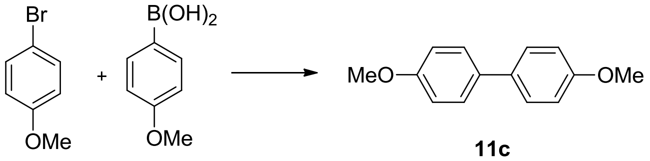
δ 7.52-7.50 (m, 4H), 7.41-7.36 (m,2H), 6.93 (m, 2H), 3.86 (s, 3H).

^{13}C-NMR (100 MHz, CDCl$_3$):

δ 159.30, 139.18, 132.58, 132.36, 128.78, 128.93, 127.84, 114.24, 55.25.

MS (GC/MS-EI, 70eV): *m/z* (%) =218 (100) [M$^+$], 203 (85) [(M-CH$_3$)$^+$], 175 (71), 139 (21).

4,4'-dimethoxy-1,1'-biphenyl (11c)[9]



3 **7d** **11c**

^{1}H-NMR (400 MHz, CDCl3):

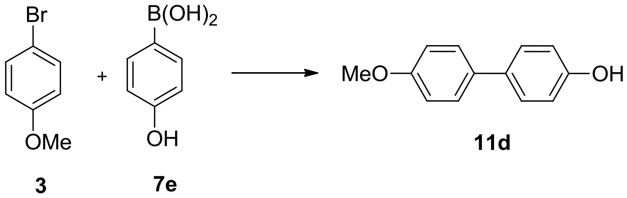
δ 7.48 (d, *J* = 8.4 Hz, 4H), 6.96 (d, *J* = 8.4 Hz, 4H),3.85 (s, 6H).

^{13}C-NMR (100 MHz, CDCl3):

δ 158.66, 133.46, 127.71, 114.14, 55.32.

MS (GC/MS-EI, 70eV): *m/z* (%) = 214 (95) [M^+], 199 (100) [$(M-CH_3)^+$], 171 (26).

4'-methoxy-[1,1'-biphenyl]-4-ol (11d)[10]



^{1}H-NMR (400 MHz, CD_3OD):

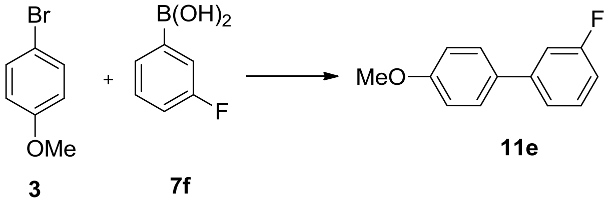
δ 7.43 (td, 2H), 7.37 (td, 2H) , 6.92 (td, 2H), 6.82 (td, 2H),3.79 (s, 3H).

^{13}C-NMR (100 MHz, CD_3OD):

δ 160.03, 157.56, 135.00, 133.64, 128.57, 128.40, 116.53, 115.11, 55.69.

MS (GC/MS-EI, 70eV): *m/z* (%) = 200 (100) [M^+], 185 (91) [$(M-CH_3)^+$], 157 (26).

3-fluoro-4'-methoxy-1,1'-biphenyl (11e)[11]



^{1}H-NMR (400 MHz, CDCl3):

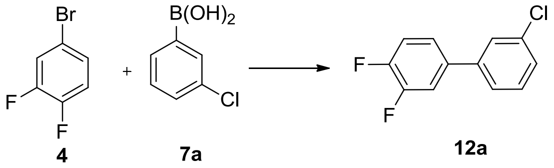
δ 7.39 (td, 2H), 7.11-7.27 (m, 3H), 6.84-6.90 (m, 3H), 3.72 (s, 3H).

^{13}C-NMR (100 MHz, CDCl3):

δ 164.41, 161.98, 159.52, 143.09, 143.02, 132.37, 132.35, 130.14, 130.06, 128.08, 122.24, 122.21, 114.25, 113.55, 113.44, 113.33, 113.22, 55.26.

MS (GC/MS-EI, 70eV): *m/z* (%) = 202 (100) [M^+], 187 (45) [$(M-CH_3)^+$], 159 (62).

3'-chloro-3,4-difluoro-1,1'-biphenyl (12a)



^{1}H-NMR (400 MHz, CDCl3):

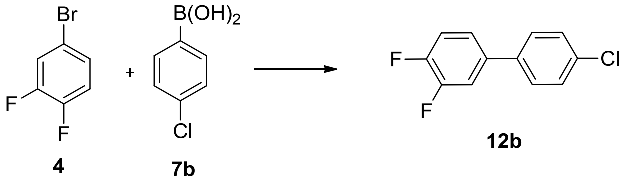
δ 7.18-7.52 (m, 7H).

^{13}C-NMR (100 MHz, CDCl3):

δ 151.82, 151.69, 151.53, 151.41, 149.35, 149.22, 149.05, 148.94, 141.55, 140.88, 136.88, 136.84, 136.82, 136.78, 134.85, 134.79, 130.15, 130.10, 127.85, 127.82, 127.20, 127.07, 125.22, 125.07, 123.08, 123.05, 123.02, 122.98, 117.77, 117.75, 117.59, 116.11, 115.93.

MS (GC/MS-EI, 70eV): *m/z* (%) = 224 (100) [M^{+}], 188 (89).

4'-chloro-3,4-difluoro-1,1'-biphenyl (12b)



^{1}H-NMR (400 MHz, CDCl3):

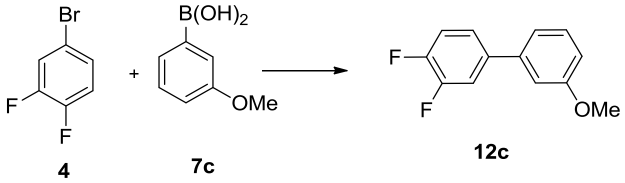
δ 7.17-7.47 (m, 7H).

^{13}C-NMR (100 MHz, CDCl3):

δ 151.82, 151.69, 151.36, 151.24, 149.35, 149.22, 148.88, 148.76, 138.39, 137.57, 137.54, 137.10, 137.07, 137.05, 137.01, 133.99, 133.72, 129.09, 129.01, 128.16, 122.92, 122.89, 122.86, 122.83, 117.74, 117.56, 115.96, 115.78.

MS (GC/MS-EI, 70eV): *m/z* (%) = 224 (100) [M^{+}], 188 (80).

3,4-difluoro-3'-methoxy-1,1'-biphenyl (12c)



^{1}H-NMR (400 MHz, CDCl3):

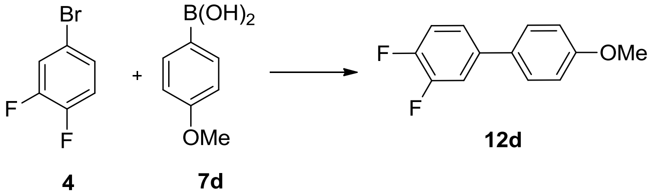
δ 7.32-7.36 (m, 2H), 7.25-7.30 (m, 1H), 7.17-7.22 (m, 1H), 7.09 (td, 1H), 7.03(t, *J* = 2.4 Hz, 1H), 6.92(m,1H),3.84(s,3H).

^{13}C-NMR (100 MHz, CDCl3):

δ 160.01, 151.71, 151.59, 151.24, 151.10, 149.24, 149.12, 148.76, 148.64, 140.58, 138.21, 138.16, 138.15, 138.10, 129.94, 123.04, 123.00, 122.97, 122.94, 119.36, 117.49, 117.33, 116.08, 115.90, 113.04, 112.78, 55.24.

MS (GC/MS-EI, 70eV): *m/z* (%) = 220 (100) [M$^+$], 190 (26), 177 (46).

3,4-difluoro-4'-methoxy-1,1'-biphenyl (12d) [12]



^{1}H-NMR (400 MHz, CDCl3):

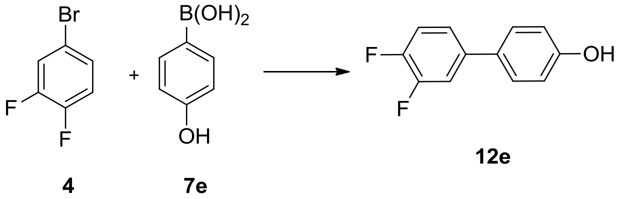
δ 7.40-7.44 (m, 2H), 7.27-7.33 (m, 1H), 7.12-7.23 (m, 2H), 6.93-9.96 (m, 2H), 3.82(s, 3H).

^{13}C-NMR (100 MHz, CDCl3):

δ 159.48, 151.73, 151.61, 150.75, 150.62, 149.27, 149.14, 148.29, 148.17, 138.00, 137.96, 137.94, 137.90, 131.59, 127.95, 122.46, 122.43, 122.40, 122.37, 117.45, 117.26, 115.50, 115.32, 114.31, 55.26.

MS (GC/MS-EI, 70eV): *m/z* (%) = 220 (100) [M$^+$], 187 (42) [(M-CH$_3$)$^+$],177 (67).

3',4'-difluoro-[1,1'-biphenyl]-4-ol (12e)



^{1}H-NMR (400 MHz, CDCl3):

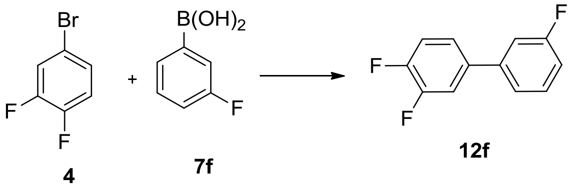
δ 7.38-7.41 (d, *J* = 8.4 Hz, 2H), 7.14-7.33 (m, 3H), 6.89-6.91(d, *J* = 8.8 Hz, 2H), 5.10 (s, 1H).

^{13}C-NMR (100 MHz, CDCl3):

δ 155.36, 151.72, 151.59, 150.79, 150.66, 149.26, 149.13, 148.33, 148.20, 137.90, 137.86, 137.83, 137.80, 131.95, 128.24, 122.48, 122.45, 122.42, 122.39, 117.47, 117.31, 117.29, 115.82, 115.53, 115.35.

MS (GC/MS-EI, 70eV): *m/z* (%) = 206 (100) [M$^+$], 177 (8).

3,3',4-trifluoro-1,1'-biphenyl (12f)



^{1}H-NMR (400 MHz, CDCl3):

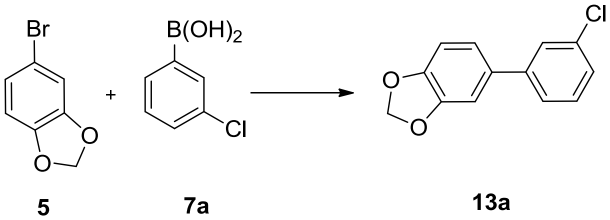
δ 7.34-7.43 (m, 2H), 7.19-7.30 (m, 4H), 7.4-7.09 (dt, 1H).

^{13}C-NMR (100 MHz, CDCl3):

δ 164.38, 161.93, 151.83, 151.70, 151.53, 151.41, 149.36, 149.23, 149.06, 148.93, 141.38, 141.36, 141.30, 137.04, 137.02, 137.00, 136.98, 136.96, 136.94, 130.51, 130.43, 123.08, 123.05, 123.02, 122.98, 122.73, 122.70, 122.59, 122.57, 117.77, 117.59, 116.15, 115.97, 114.75, 114.54, 114.03, 113.82.

MS (GC/MS-EI, 70eV): *m/z* (%) = 208 (3) [M$^+$], 206 (15), 149 (100).

5-(3-chlorophenyl)benzo[d][1,3]dioxole (13a)[13]



^{1}H-NMR (400 MHz, CDCl3):

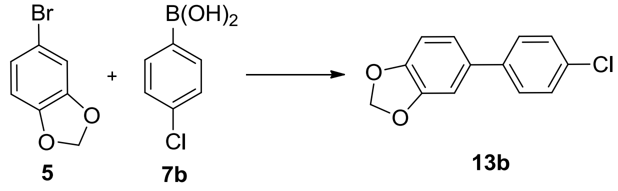
δ 7.48-7.49 (t, *J* = 2.0 Hz,1 H), 7.24-7.38 (m, 3H), 7.00-7.07 (m, 2H), 6.85-6.87 (m, 1H),5.99 (s, 2H).

^{13}C-NMR (100 MHz, CDCl3):

δ 148.20, 147.49, 142.69, 134.55, 134.03, 129.89, 126.95, 126.86, 124.95, 120.69, 108.61, 107.51, 101.24.

MS (GC/MS-EI, 70eV): *m/z* (%) = 232 (100) [M^+], 231 (90) [$(M-H)^+$],139 (85).

5-(4-chlorophenyl)benzo[d][1,3]dioxole (13b)[14]



^{1}H-NMR (400 MHz, CDCl3):

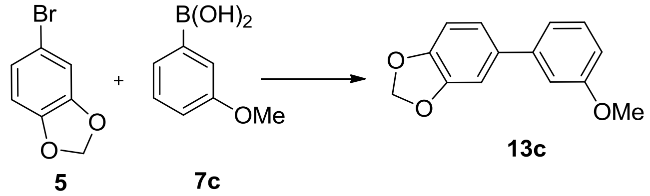
δ 7.33-7.43 (m, 4H) ,6.98-7.00 (m, 2H), 6.85-6.87 (m, 1H), 5.98(s, 2H).

^{13}C-NMR (100 MHz, CDCl3):

δ 148.18, 147.28, 139.32, 134.25, 132.90, 128.81, 128.03, 120.49, 108.60, 107.42, 101.20.

MS (GC/MS-EI, 70eV): *m/z* (%) = 232 (100) [M^+], 231 (41) [$(M-H)^+$], 139 (77).

5-(3-methoxyphenyl)benzo[d][1,3]dioxole (13c)[15]



^{1}H-NMR (400 MHz, CDCl3):

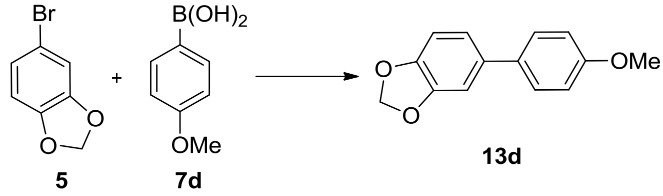
δ 7.29-7.36 (m, 1H), 7.03-7.18 (m, 4H), 6.84-6.90 (m, 2H), 5.97 (s, 2H), 3.83 (s, 3H).

^{13}C-NMR (100 MHz, CDCl3):

δ 159.86, 148.02, 147.12, 142.40,135.40, 129.67, 120.62,119.36, 112.62, 112.26, 108.48, 107.66, 101.11, 55.21.

MS (GC/MS-EI, 70eV): *m/z* (%) = 228 (100) [M^+], 227 (73) [$(M-H)^+$].

5-(4-methoxyphenyl)benzo[d][1,3]dioxole (13d)[16]



^{1}H-NMR (400 MHz, CDCl3):

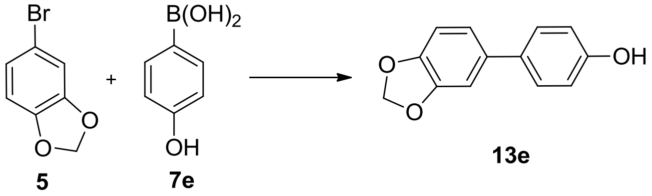
δ 7.45-7.47 (m, 2H), 6.96-7.06 (m, 4H), 6.87-6.89 (d, *J* = 8.0 Hz, 1H), 5.99 (s, 2H), 3.85 (s, 3H).

^{13}C-NMR (100 MHz, CDCl3):

δ 158.81, 148.00, 146.52, 135.23, 133.49, 127.81, 120.00, 114.10, 108.46, 107.30, 100.99, 55.25.

MS (GC/MS-EI, 70eV): *m/z* (%) = 228 (100) [M$^+$], 213 (66) [(M-CH$_3$)$^+$].

4-(benzo[d][1,3]dioxol-5-yl)phenol (13e)[17]



^{1}H-NMR (400 MHz, CDCl3):

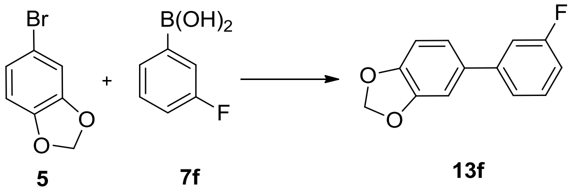
δ 7.38-7.40 (m, 2H), 7.00-7.01 (m, 2H), 6.85-6.88 (m, 3H), 5.98 (s, 2H), 4.95(s, 1H).

^{13}C-NMR (100 MHz, CDCl3):

δ 157.78, 148.02, 146.58, 135.23, 133.79, 128.11, 120.06, 115.58, 108.51, 107.36, 101.04.

MS (ESI) *m/z* calcd for $C_{13}H_9O_3$ [M-H$^+$] 213.06, found: 213.00.

5-(3-fluorophenyl)benzo-[1,3]dioxole(13f)



^{1}H-NMR (400 MHz, CDCl3):

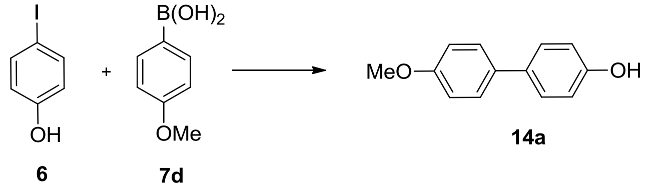
δ 7.18-7.37 (m, 3H), 6.98-7.03 (m, 3H), 6.86-6.88 (m, 1H), 5.99 (s, 2H).

^{13}C-NMR (100 MHz, CDCl3):

δ 164.34, 161.90, 148.19, 147.47, 143.18, 143.10, 134.22, 134.20, 130.16, 130.08, 122.43, 122.40, 120.67, 113.79, 113.74, 113.57, 113.52, 108.59, 107.52 ,101.23.

MS (GC/MS-EI, 70eV): *m/z* (%) = 216 (100) [M$^+$], 215 (64) [(M-H)$^+$],157 (31).

4'-methoxy-[1,1'-biphenyl]-4-ol (14a)[18]



^{1}H-NMR (400 MHz, CD_3OD):

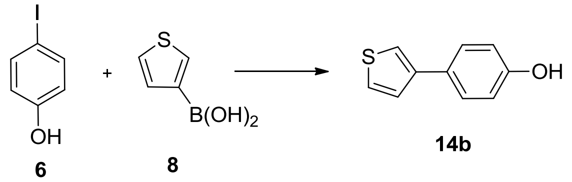
δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H),6.93(d, *J* = 8.8 Hz, 2H), 6.82(d, *J* = 8.4 Hz, 2H), 3.79(s, 3H).

^{13}C-NMR (100 MHz, CD_3OD):

δ 160.04, 157.58, 135.03, 133.65, 128.57, 128.40, 116.52, 116.11, 55.69.

MS (GC/MS-EI, 70eV): *m/z* (%) = 200 (99) [M^+], 185 (100) [$(M\text{-}CH_3)^+$], 157 (40).

4-(thiophen-3-yl)phenol (14b)[19]



^{1}H-NMR (300 MHz, CD_3OD):

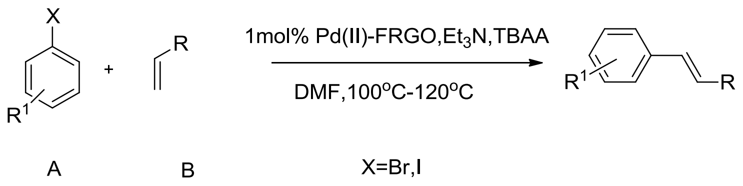
δ 7.46(d, *J* = 7.5 Hz，2H), 7.37 (m, 3H), 6.81 (d, *J*= 7.8 Hz, 2H).

^{13}C-NMR (100 MHz, CD_3OD):

δ 157.75, 143.53, 129.00, 128.46, 126.97, 126.84, 119.21, 116.52.

MS (GC/MS-EI, 70eV): *m/z* (%) = 176 (100) [M^+].

General procedure for the Heck reactions

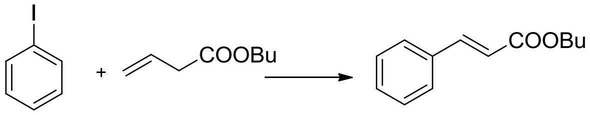


To a 15mL glass vessel was added tetrabutylammonium acetate (TBAA, 30.1 mg, 20 mol%), an aryl halide (0.5 mmol), an alkene (1.0 mmol), triethylamine (151.2 mg, 1.5 mmol), and DMF (5 mL). To the mixture was added Pd-FRGO (2 mol% Pd) in

2ml DMF, and the resulting suspension was heated at 120 ℃ for 20 h(100 ℃ for10 h when stilbenes as the alkene). After cooling to 25 ℃, the mixture was diluted with EtOAc (4 mL), washed with H_2O (2*10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated under the reduced pressure. The residue was purified by flash chromatography over silica gel eluting with hexane/EtOAc to afford the corresponding products.

Spectroscopic data of the products of the Heck reactions

butyl cinnamate (20e)[20]



15 **18** **20e**

^{1}H-NMR (400 MHz, CDCl3):

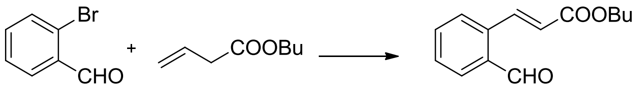
δ 7.67 (d, *J* = 16 Hz, 1H), 7.3-7.5 (m, 5H), 6.43 (d, *J* = 16 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 1.69 (tt, 2H), 1.43 (qt, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, CDCl3):

δ 167.02, 144.48, 134.41, 130.13, 128.80, 127.98, 118.23, 64.35, 30.71, 19.14, 13.68.

MS (GC/MS-EI, 70eV): *m/z* (%) = 204 (1) [M^+], 148 (42) [$(M\text{-}Bu+H)^+$], 147 (40) [$(M\text{-}Bu)^+$], 131 (100) [$(M\text{-}OBu)^+$],103 (42).

butyl 3-(2-formylphenyl)acrylate (20a)[21]



2 **18** **20a**

^{1}H-NMR (400 MHz, CDCl3):

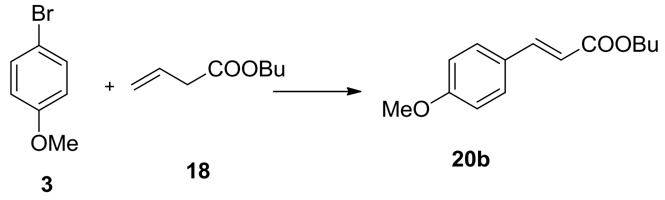
δ 10.31 (s, 1H), 8.52 (d, *J* = 16 Hz, 1H), 7.88-7.90 (m, 1H), 7.56-7.64 (m, 3H), 6.39 (d, *J* = 16 Hz,1H), 4.24 (t, *J*=6.8 Hz, 2H), 1.71 (tt, 2H), 1.45 (qt, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, CDCl3):

δ 191.73, 166.28, 140.84, 136.69, 133.87, 133.82, 132.14, 129.84, 127.96, 123.27, 64.69, 30.70, 19.17, 13.72.

MS (ESI) *m/z* calcd for $C_{14}H_{16}O_3Na$ [M+Na$^+$] 255.11, found: 255.33.

n-Butyl-4-methoxy cinnamate (20b)[22]



^{1}H-NMR (400 MHz, CDCl3):

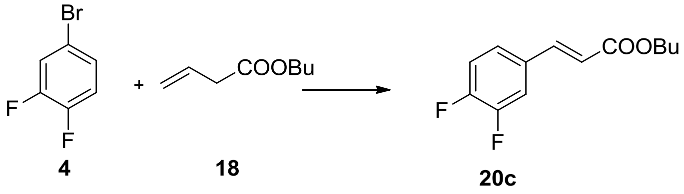
δ 7.64 (d, *J* = 16 Hz, 1H), 7.47-7.49 (m, 2H), 6.89-6.91 (m, 2H), 6.31 (d, *J* = 16 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 3H), 1.69 (tt, 2H),1.44 (qt, 2H), 0.96 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, CDCl3):

δ 167.44, 161.30, 144.18, 129.67, 127.20, 115.76, 114.28, 64.25, 55.34, 30.79, 19.19, 13.74.

MS (GC/MS-EI, 70eV): *m/z* (%) = 234 (8) [M$^+$], 178 (83) [(M-Bu+H)$^+$], 161 (100) [(M-OBu)$^+$], 133 (11).

n-butyl 3-(3,4-difluorophenyl)acrylate (20c) [23]



^{1}H-NMR (400 MHz, CDCl3):

δ 7.58 (d, *J* = 15.6 Hz, 2H) , 7.14-7.37 (m, 3H), 6.36 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 3H), 1.69 (tt, 2H), 1.43 (qt, 2H), 0.97 (t, *J*= 7.2 Hz, 3H).

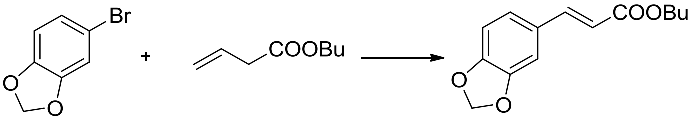
^{13}C-NMR (100 MHz, CDCl3):

δ 166.53, 152.72, 152.60, 151.86, 151.73, 150.21, 150.08, 149.38, 149.25, 142.13, 142.11, 142.08, 131.73, 131.67, 124.76, 124.72, 124.70, 124.66, 119.42, 119.40, 117.84, 117.67, 116.33, 116.32, 116.16, 116.14, 64.59, 30.69, 19.14, 13.67.

MS (GC/MS-EI, 70eV): *m/z* (%) = 240 (1) [M$^+$], 184 (73) [(M-Bu+H)$^+$],167 (100)

[(M-OBu)$^+$], 139 (24).

n-butyl 3-(benzo[d][1,3]dioxol-5-yl)acrylate (20d)[24]



5 **18** **20d**

^{1}H-NMR (400 MHz, CDCl$_3$):

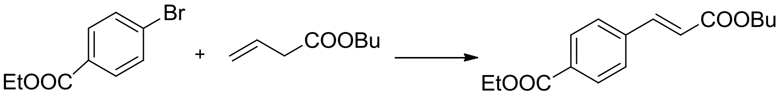
δ 7.58 (d, *J* = 11.6 Hz, 2H) ,6.99-7.03 (m, 2H), 6.81 (d, *J* = 8.4 Hz, 1H),6.26 (d, *J* = 12.0 Hz, 1H), 6.00 (s, 2H),4.19 (t, *J* = 6.8 Hz, 2H), 1.68 (tt, 2H), 1.43 (qt, 2H,), 0.96 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, CDCl$_3$):

δ 167.24, 149.29, 148.28, 144.19, 128.87, 124.32, 116.19, 108.48, 106.44, 101.49, 64.28, 30.75, 19.16, 13.71.

MS (GC/MS-EI, 70eV): *m/z* (%) = 248 (21) [M$^+$], 192 (100) [(M-Bu+H)$^+$], 175 (66) [(M-OBu)$^+$],145 (34).

ethyl 4-(3-butoxy-3-oxoprop-1-en-1-yl)benzoate (20f)[25]



16 **18** **20f**

^{1}H-NMR (400 MHz, CDCl3):

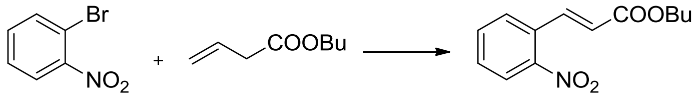
δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 16 Hz, 1H), 7.58 (d, *J* = 8 Hz, 2H), 6.52 (d, *J* = 16 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 4.22 (t, *J*= 6.4 Hz, 2H), 1.70 (tt, 2H), 1.30-1.57 (m, 5H), 0.97 (t, *J* = 7.2 Hz,3H).

^{13}C-NMR (100 MHz, CDCl3):

δ 166.42, 165.75, 142.99, 138.44, 131.53, 129.89, 127.69, 120.46, 64.44, 61.00, 30.60, 19.04, 14.14, 13.58.

MS (GC/MS-EI, 70eV): *m/z* (%) = 276 (2) [M$^+$], 220 (53) [(M-Bu+H)$^+$], 203 (30) [(M-OBu)$^+$], 192 (68) [(M-Bu+H-Et+H)$^+$], 175 (100) [(M-OBu-Et+H)$^+$],131 (52).

butyl 3-(2-nitrophenyl)acrylate(20g)[26]



17 **18** **20g**

^{1}H-NMR (400 MHz, CDCl3):

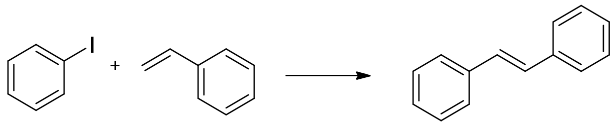
δ 8.11 (d, *J* = 11.6 Hz, 1H), 8.03–8.05 (m, 1H), 7.66–7.69 (m, 2H), 7.53–7.58 (m, 1H), 6.38 (d, *J* = 11.6 Hz, 1H), 4.23 (t, *J* = 6.8Hz, 2H), 1.66–1.74 (m, 2H), 1.40–1.49 (m, 2H), 0.97 (t, *J* = 7.6Hz, 3H).

^{13}C-NMR (100 MHz, CDCl3):

δ 165.76, 148.19, 139.71, 133.44, 130.49, 130.18, 129.02, 124.78, 123.22, 64.71, 30.56, 19.06,13.62.

MS (ESI) *m/z* calcd for $C_{13}H_{15}NO_4Na$ [M+Na$^+$] 272.10, found: 272.50.

1,2-diphenylethene (21d)[27]



15 **19** **21d**

^{1}H-NMR (400 MHz, CDCl3):

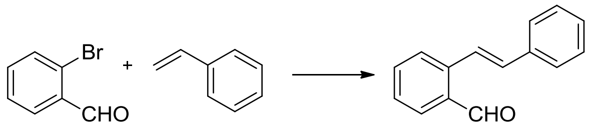
δ 7.51 (m, 4H), 7.36 (m, 4H), 7.21-7.27 (m, 2H), 7.10 (s, 2H).

^{13}C-NMR (100 MHz, CDCl3):

δ 137.30, 128.66, 127.60, 126.49.

MS (GC/MS-EI, 70eV): *m/z* (%) = 180 (84) [M$^+$], 179 (100) [(M-H)$^+$], 179 (84) [(M-2H)$^+$], 165 (58) [(M-CH$_3$)$^+$].

2-styrylbenzaldehyde (21a)[28]



2 **19** **21a**

^{1}H-NMR (400 MHz, $CDCl_3$):

δ 10.32 (s, 1H), 8.04 (d, *J* = 16.2 Hz, 1H), 7.83 (d, 8.0 Hz, 1H), 7.71 (d, *J* = 7.6Hz, 1H), 7.55-7.60 (m, 3H), 7.30-7.45 (m, 4H), 7 .04 (d, *J* = 16.4Hz, 1H).

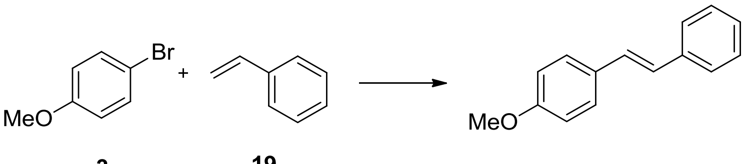
^{13}C-NMR (100 MHz, $CDCl_3$):

δ 192.62, 139.88, 136.83, 133.93, 133.67, 132.87, 132.29, 128.72, 128.26, 127.56, 127.11, 126.92, 124.71.

MS (ESI) *m/z* calcd for $C_{15}H_{14}O$ [M+H$^+$] 209.10, found: 209.50, $C_{15}H_{13}ONa$ [M+Na$^+$] 231.10, found: 231.50.

MS (GC/MS-EI, 70eV): *m/z* (%) = 208 (100) [M$^+$], 178 (65).

1-methoxy-4-styrylbenzene (21b)[27]



3 **19** **21b**

^{1}H-NMR (400 MHz, CDCl3):

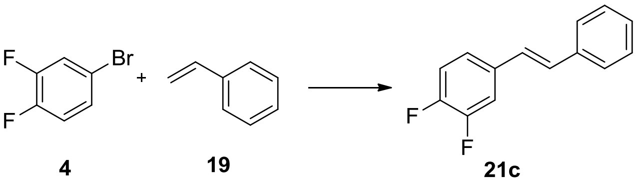
δ 7.44-7.50 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.24 (m,1H), 7.02 (*dd*, J=20.4 Hz, 22 Hz, 2H), 6.90 (m, 2H), 3.83 (s, 3H).

^{13}C-NMR (100 MHz, CDCl3):

δ 159.29, 137.63, 130.13, 128.62, 128.19, 127.70, 127.20, 126.60, 126.23, 114.11, 55.31.

MS (GC/MS-EI, 70eV): *m/z* (%) = 210 (100) [M$^+$], 195 (12) [(M-CH_3)$^+$], 167 (18) , 165 (29) , 152 (16).

1,2-difluoro-4-styrylbenzene (21c)[29]



4 **19** **21c**

^{1}H-NMR (400 MHz, $CDCl_3$):

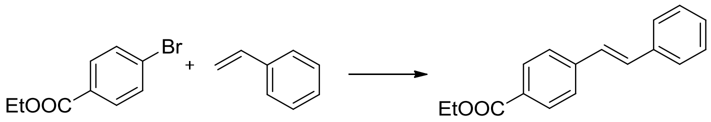
δ 7.47-7.51 (m, 2H), 7.25-7.39 (m, 4H), 7.11-7.19 (m, 2H), 7.00 (s, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 151.82, 151.69, 151.03, 150.90, 149.36, 149.23, 148.56, 148.43, 136.62, 134.64, 134.60, 134.58, 134.54, 129.73, 129.70, 128.72, 127.99, 126.54, 126.45, 126.43, 126.41, 122.73, 122.70, 122.67, 122.64, 117.43, 117.25, 114.65, 114.48.

MS (GC/MS-EI, 70eV): *m/z* (%) = 216 (100) [M^+], 215 (42) [$(M-H)^+$], 214 (19) [$(M-2H)^+$], 201 (21) [$(M-CH_3)^+$].

ethyl 4-styrylbenzoate (21e)[30]



16 **19** **21e**

^{1}H-NMR (400 MHz, $CDCl_3$):

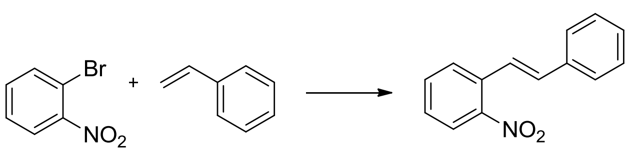
δ 8.03 (m, 2H), 7.58–7.52 (m, 4H), 7.41–7.36 (m, 2H), 7.32–7.27 (m, 1H), 7.13- 7.22 (m, 2H), 4.38 (q, *J* = 7.2Hz, 2H),1.40 (t, *J* = 7.6Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 166.36, 141.65, 136.72, 131.07, 129.94, 129.21, 128.73,128.17, 127.56, 126.74, 126.23, 60.87, 14.32.

MS (GC/MS-EI, 70eV): *m/z* (%) = 252 (71) [M^+], 207 (67) [$(M-OEt)^+$], 179 (70), 178 (100).

1-nitro-2-styrylbenzene (21f)[31]



17 **19** **21f**

^{1}H-NMR (400 MHz, $CDCl_3$):

δ 7.98 (dd, *J* = 1.2 Hz,8.1 Hz, 1H), 7.78 (d, *J* = 8.1Hz, 1H), 7.55–7.65(m, 4H), 7.31–7.45 (m , 4H), 7.11 (d, *J* = 16.2 Hz, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 147.92, 136.36, 133.72, 132.99, 132.86, 128.70, 128.50, 128.03, 127.85, 126.98

124.64, 123.35.

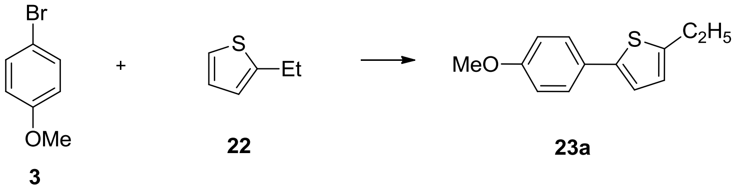
MS (GC/MS-EI, 70eV): *m/z* (%) = 225 (1) [M^+], 193 (100).

General procedure for the C-H activation reactions

To a 15mL glass vessel was added a 2-ethylthiophene (1 mmol), aryl bromides (0.5 mmol), cesium acetate (192 mg, 1 mmol), and DMF (5 mL) . To the mixture was added Pd(II)-FRGO (2mol % Pd) in 2ml DMF. The mixture was heated at 140 °C for 20 h. After cooling to 25 °C, the mixture was diluted with Et_2O (10 mL). The reaction mixture was washed with H_2O (2*10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel eluting with hexane to afford the corresponding products.

Spectroscopic data of the products of the C-H activation reactions

2-ethyl-5-(4-methoxyphenyl)thiophene (23a)[32]



^{1}H-NMR (400 MHz, $CDCl_3$):

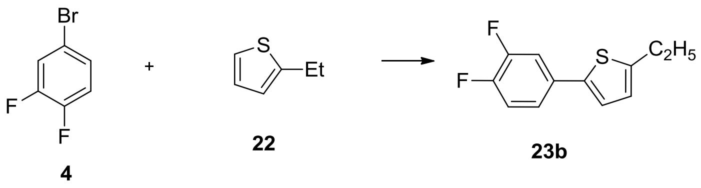
δ 7.48 (m, 2H), 7.00 (d, *J* = 3.6 Hz, 1H), 6.89 (m, 2H), 6.72 (d, *J* = 3.6 Hz, 1H),3.82 (s, 3H), 2.84(q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 158.83, 146.20, 141.50, 127.71, 126.78, 124.15, 121.62, 114.19, 55.33, 23.54, 15.92.

MS (GC/MS-EI, 70eV): *m/z* (%) = 218 (32) [M^+], 203 (100) [$(M-CH_3)^+$].

2-(3,4-difluorophenyl)-5-ethylthiophene (23b)



^{1}H-NMR (400 MHz, CDCl$_3$):

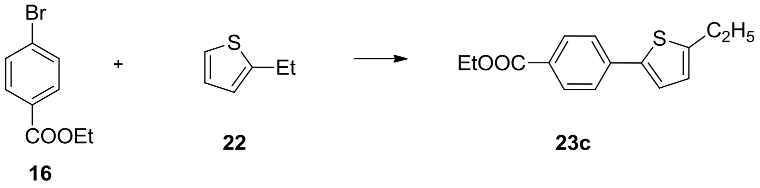
δ 7.31-7.36 (m, 1H), 7.22-7.26 (m, 1H), 7.09-7.16 (m, 1H), 7.05 (d, *J* = 3.6Hz, 1H), 6.74-6.76 (m, 1H), 2.85 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, CDCl$_3$):

δ 151.75, 150.75, 149.28, 148.28, 148.15, 148.03, 139.20, 132.03, 131.96, 124.47, 123.39, 123.37, 122.66, 121.45, 121.41, 121.39, 121.35, 117.65, 117.49, 117.48, 114.41, 114.22, 23.54, 15.85.

MS (GC/MS-EI, 70eV): *m/z* (%) = 224 (15) [M$^+$], 209 (100) [(M-CH$_3$)$^+$].

ethyl 4-(5-ethylthiophen-2-yl)benzoate (23c)[32]



^{1}H-NMR (400 MHz, CDCl$_3$):

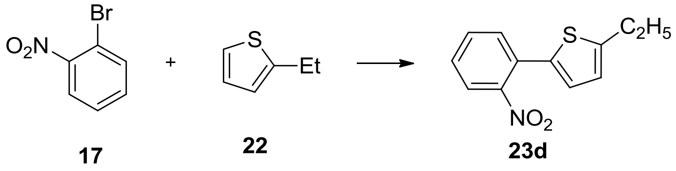
δ 8.01 (m, 2H), 7.60 (m, 2H), 7.23 (d, *J* = 3.6 Hz, 1H), 6.78 (m, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 2.86 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, CDCl$_3$):

δ 166.29, 148.88, 140.21, 138.85, 130.13, 128.55, 124.88, 124.68, 124.18, 60.85, 23.64, 15.80, 14.31.

MS (GC/MS-EI, 70eV): *m/z* (%) = 260 (39) [M$^+$], 245 (100) [(M-CH$_3$)$^+$], 217 (35).

2-ethyl-5-(2-nitrophenyl)thiophenes (23d)



^{1}H-NMR (400 MHz, CDCl$_3$):

δ 7.66-7.69 (m, 1H), 7.51-7.53 (m, 2H), 7.38-7.42 (m, 1H), 6.90(d, *J* = 4.0 Hz, 1H), 6.74-6.76 (m, 1H), 2.86 (q, *J* = 7.6 Hz, 2H),1.33 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, CDCl$_3$):

δ 149.68, 149.22, 134.12, 131.87, 131.69, 128.54, 128.03, 126.84, 124.17, 123.66, 23.37, 15.65.

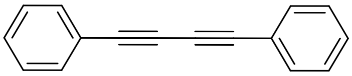
MS (GC/MS-EI, 70eV): *m/z* (%)=233 (12) [M^+],186 (52),171 (100),115 (79).

General procedure for the terminal alkyne C-H activation and Glaser reactions

A 10 ml tube was charged with alkyne (1 mmol, 1eq.), triethylamine (302 mg, 3 mmol), cuprous iodide (20 mg) and the Pd(II)-FRGO catalyst **(**0.5 mol %) and DMF (2 mL). The mixture was stirred at room temperature. The reaction was detected by TLC，after the reaction finished, the mixture was filtered over a small column of silica gel, the column washed with DCM (10 mL). The product was extracted into the organic phase (2x10 mL DCM), the united organic phases were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The purification of the crude product was manipulated by column chromatography.

Spectroscopic data of the products of the Glaser reactions

1,4-diphenylbuta-1,3-diyne(25)[33]



^{1}H-NMR (300 MHz, $CDCl_3$):

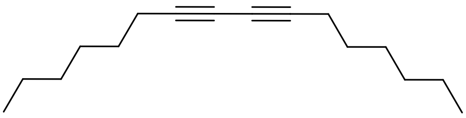
δ 7.44-7.47 (m,4H), 7.24-7.32 (m,6H).

^{13}C-NMR (75 MHz, $CDCl_3$):

δ 132.48, 129.19, 128.42, 121.78, 81.53, 73.89.

MS (GC/MS-EI, 70eV): *m/z* (%) = 202(100)[M^+].

hexadeca-7,9-diyne (27)[34]



^{1}H-NMR (300 MHz, $CDCl_3$):

δ 2.25 (t, *J* = 6.9 Hz, 4H),1.52 (m, 4H),1.24-1.43 (m, 12H), 0.89 (t, *J* = 6.9 Hz,6H).

^{13}C-NMR (75 MHz, $CDCl_3$):

δ 77.51, 65.22, 31.28, 28.51, 28.31, 22.50, 19.19, 14.01.

MS (GC/MS-EI, 70 eV): *m/z* (%) = 218 (2) [M^+], 203 (3) [$(M\text{-}CH_3)^+$], 119 (16), 105 (36), 91 (100), 79 (36).

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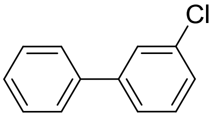
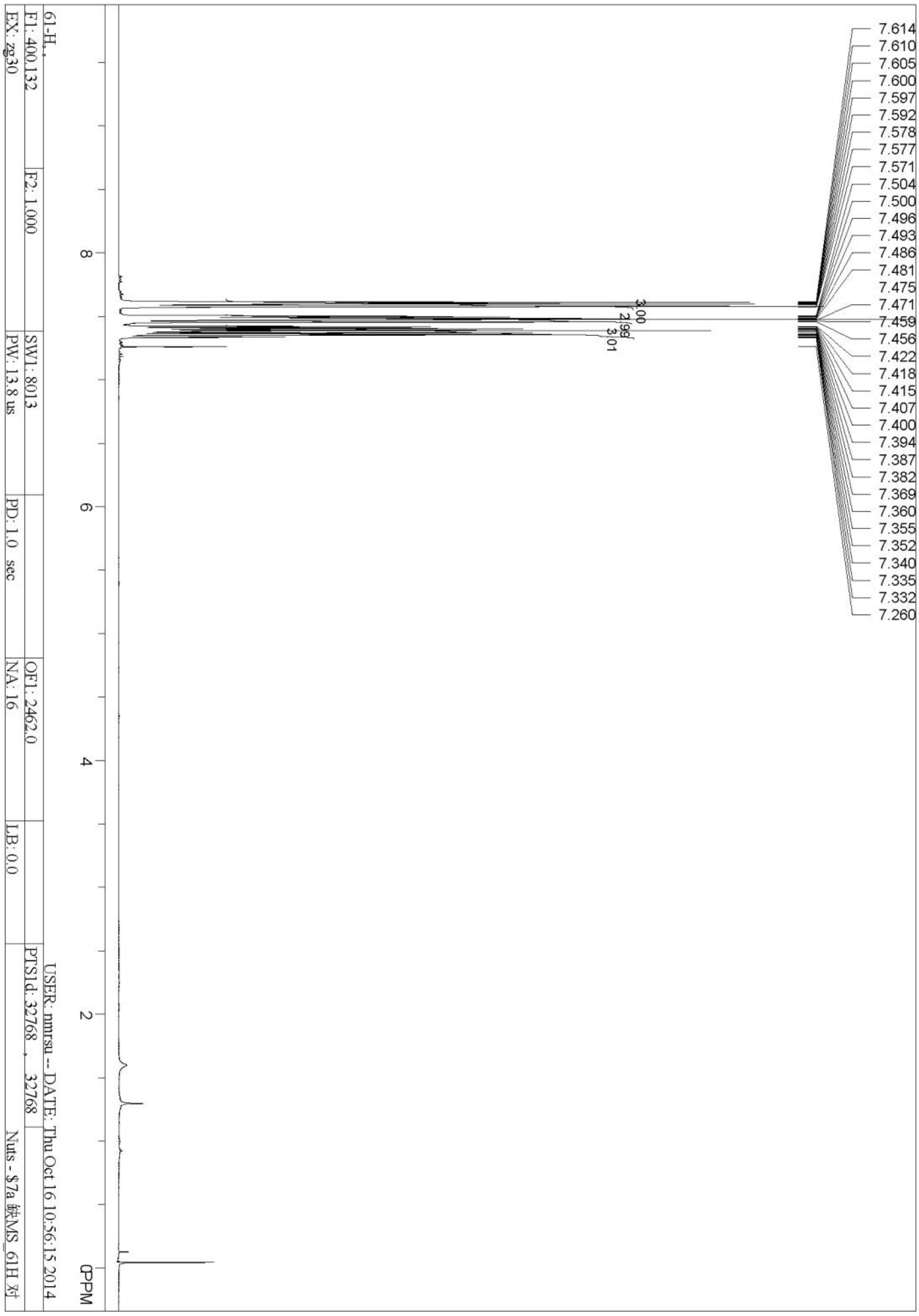
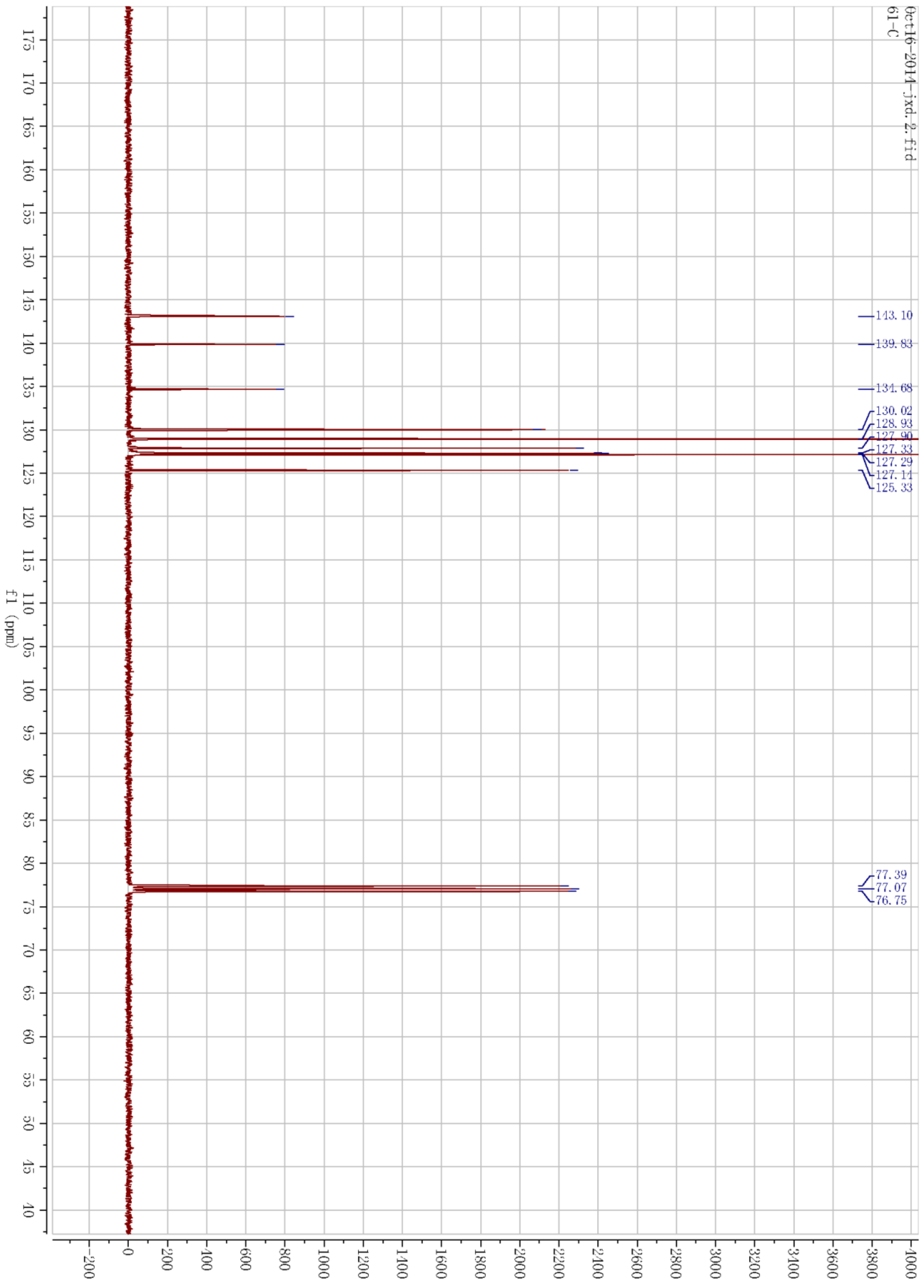
NMR spectra of compound **9**



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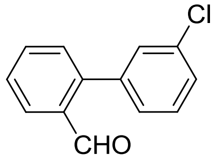
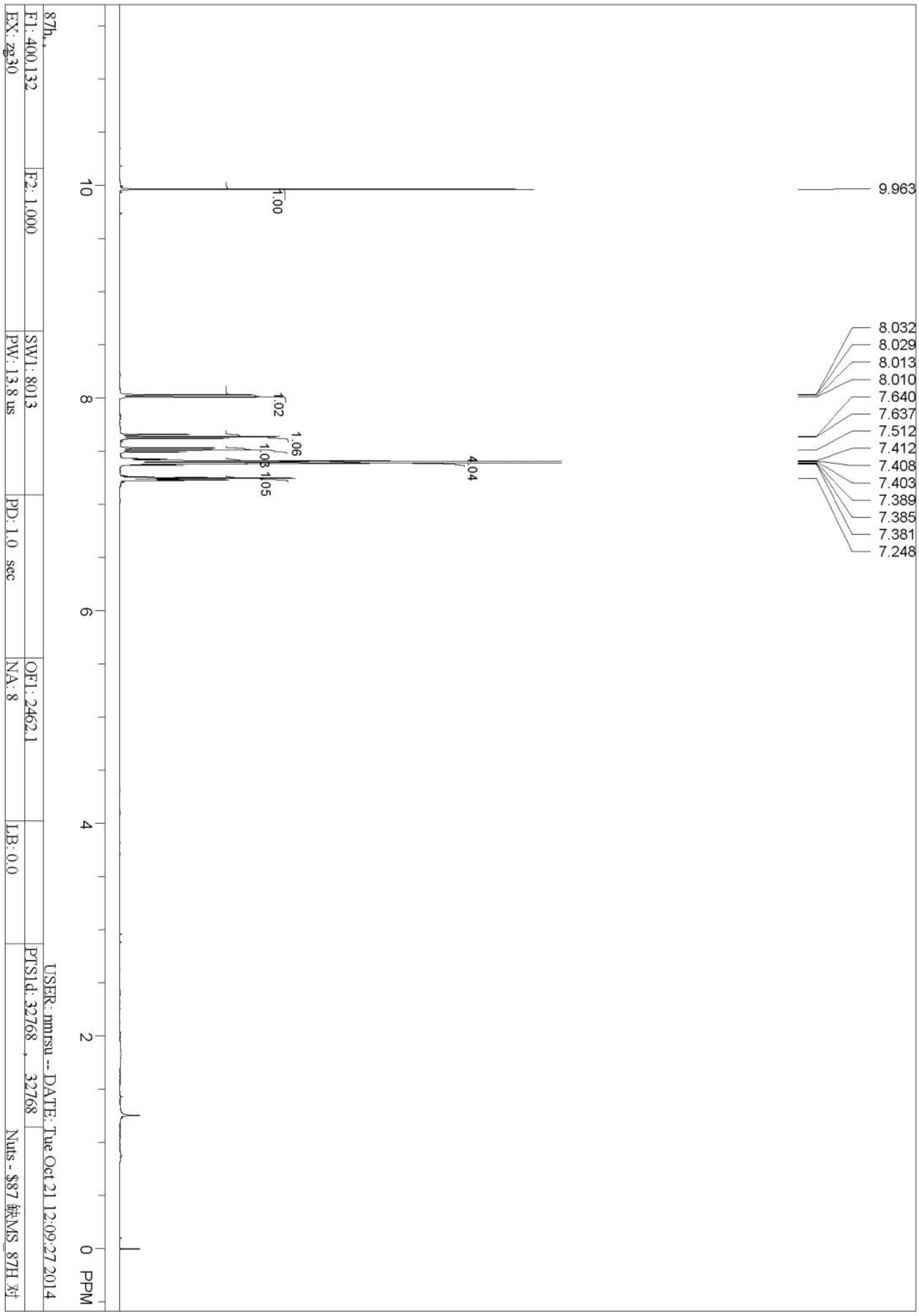
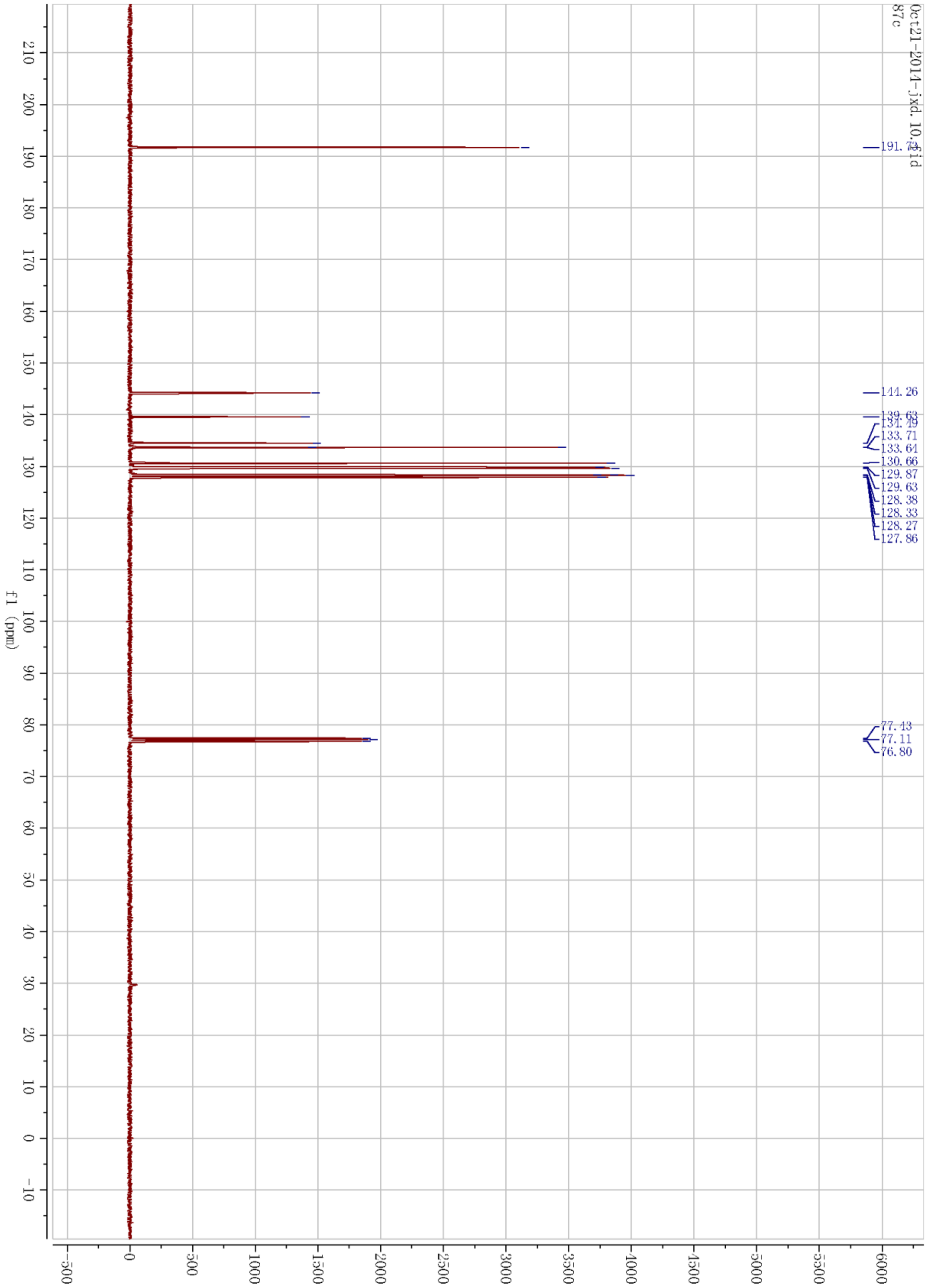
NMR spectra of compound **10a**



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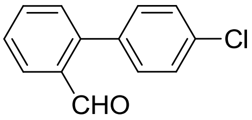
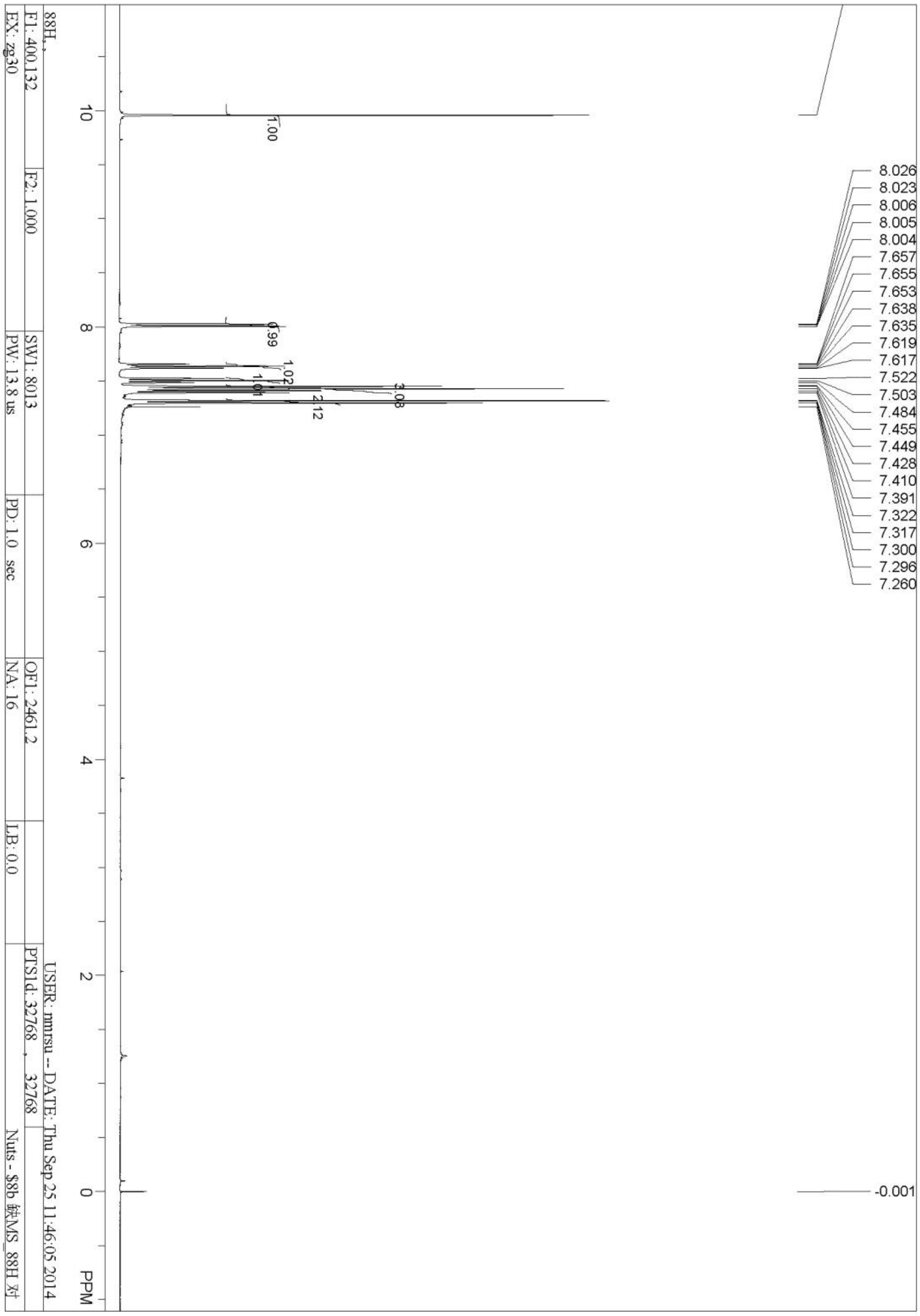
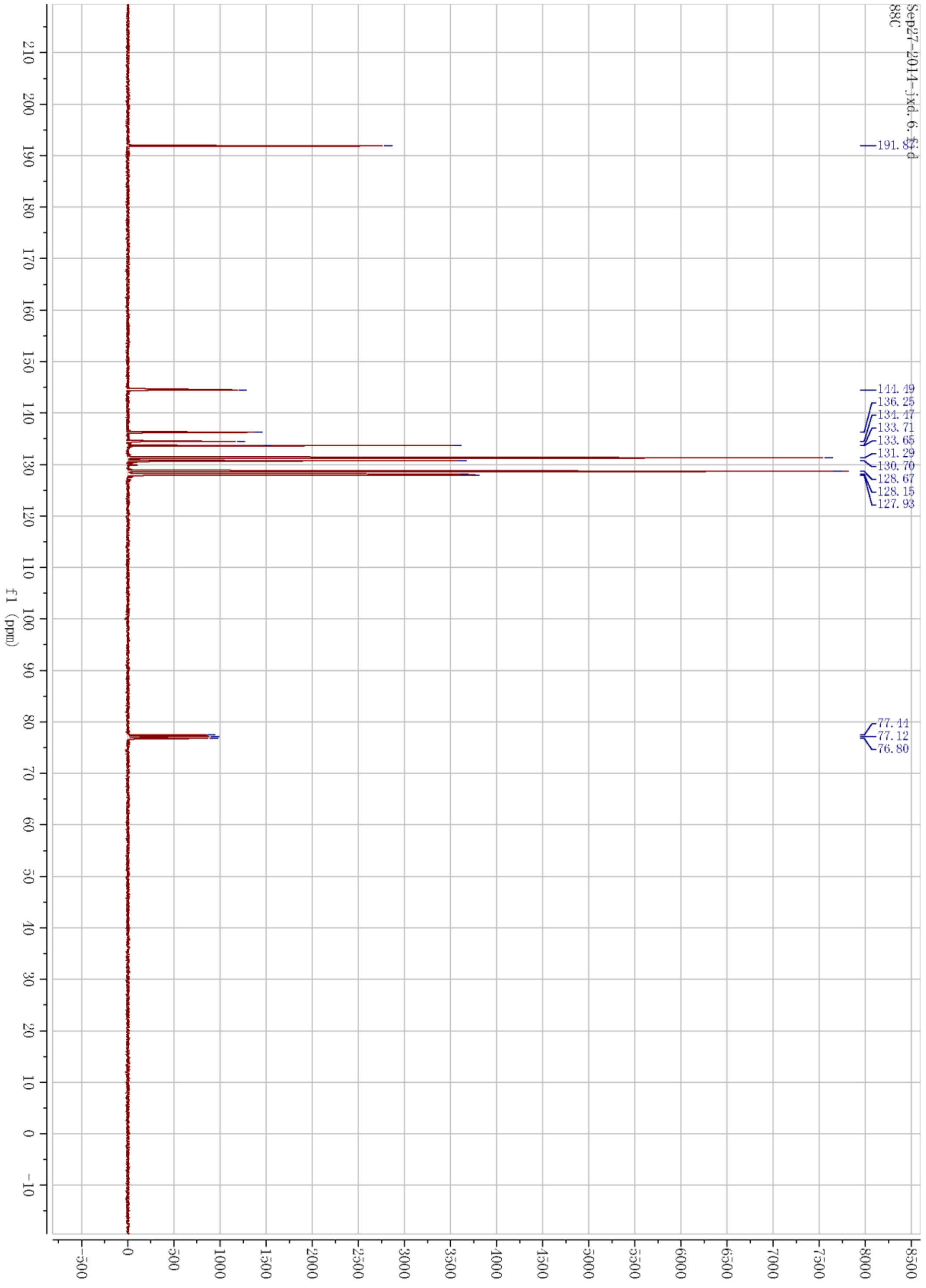
NMR spectra of compound **10b**



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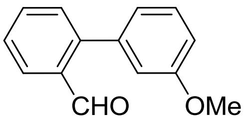
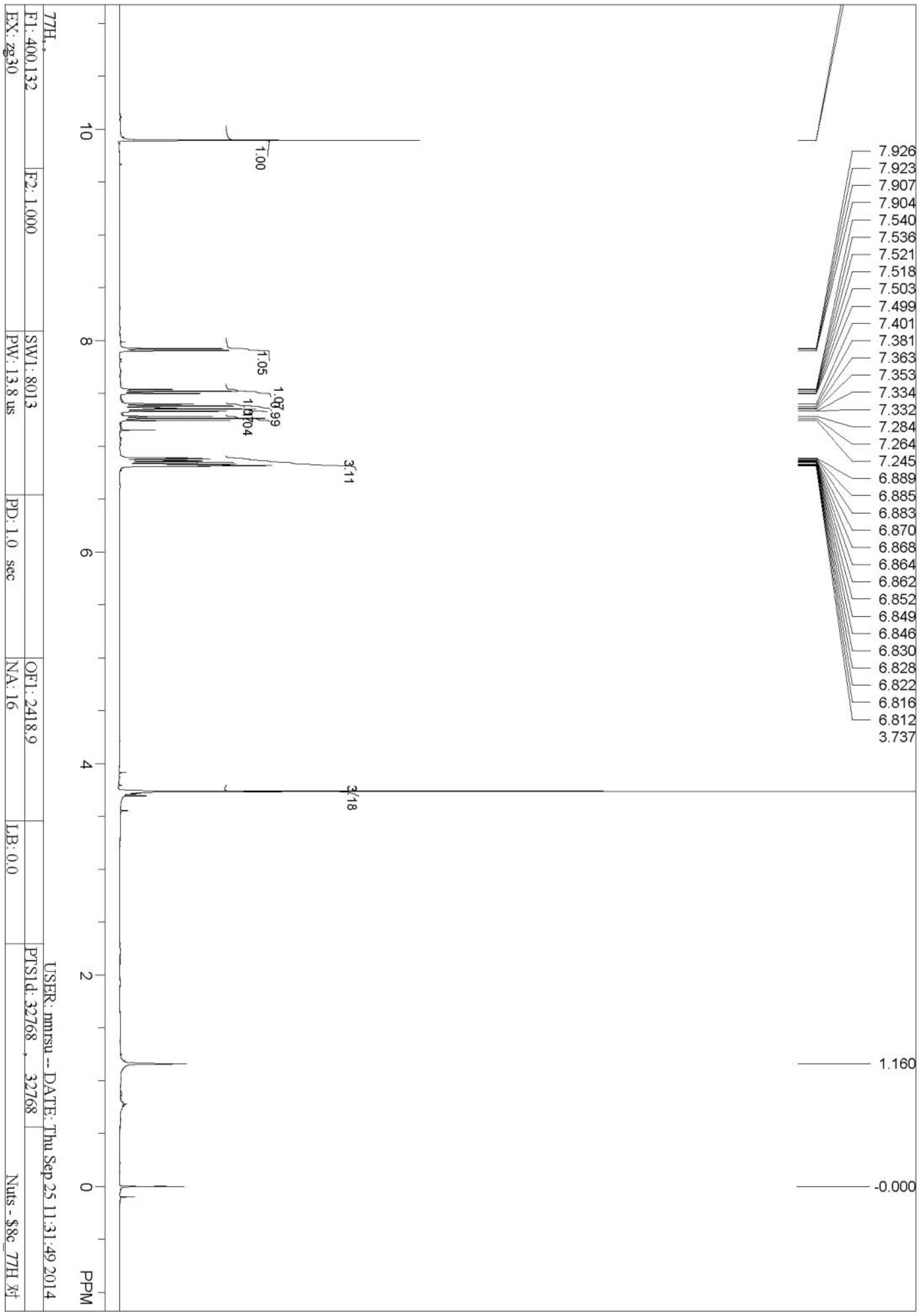
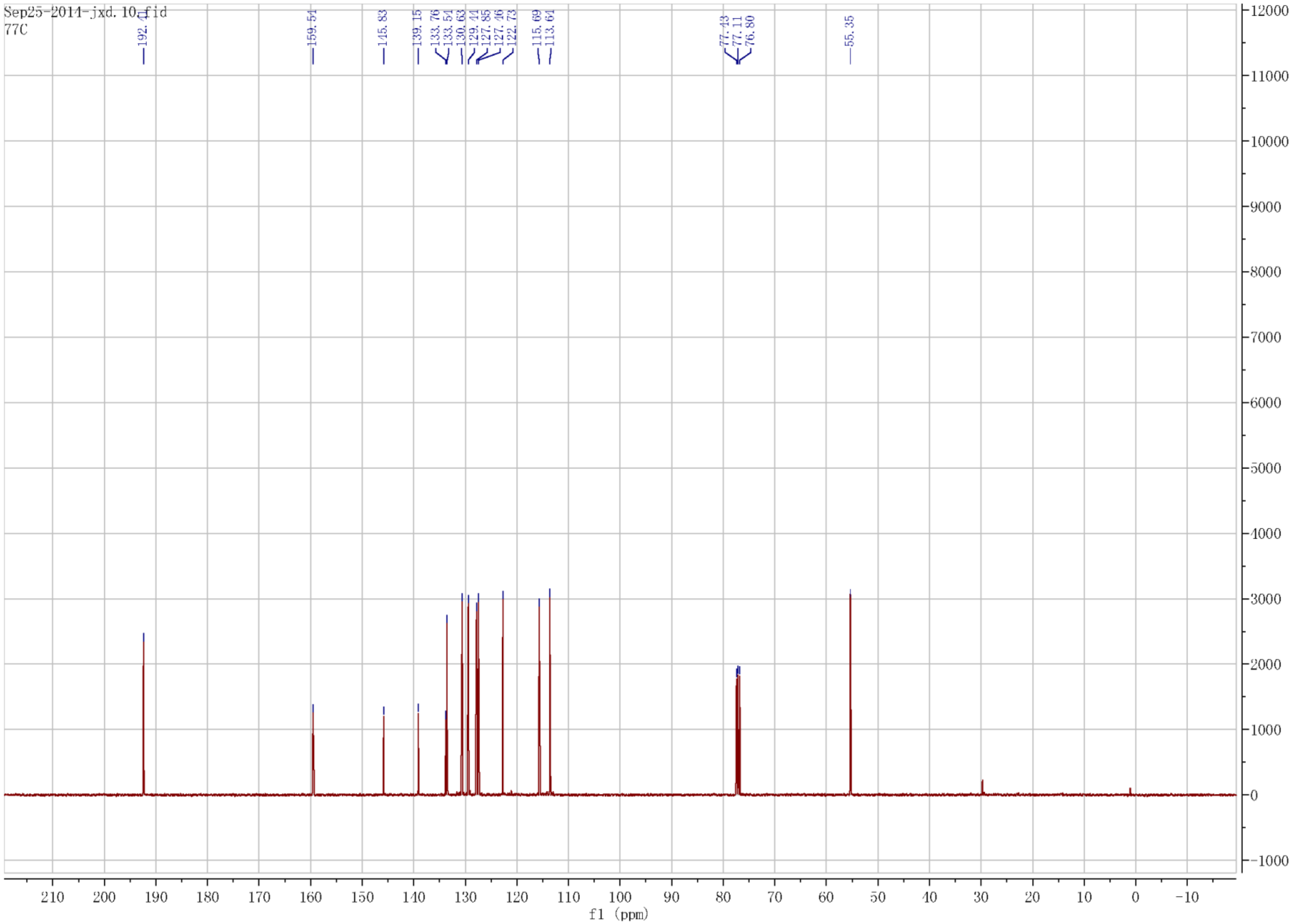
NMR spectra of compound **10c**



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1000
0
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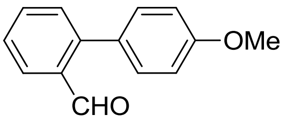
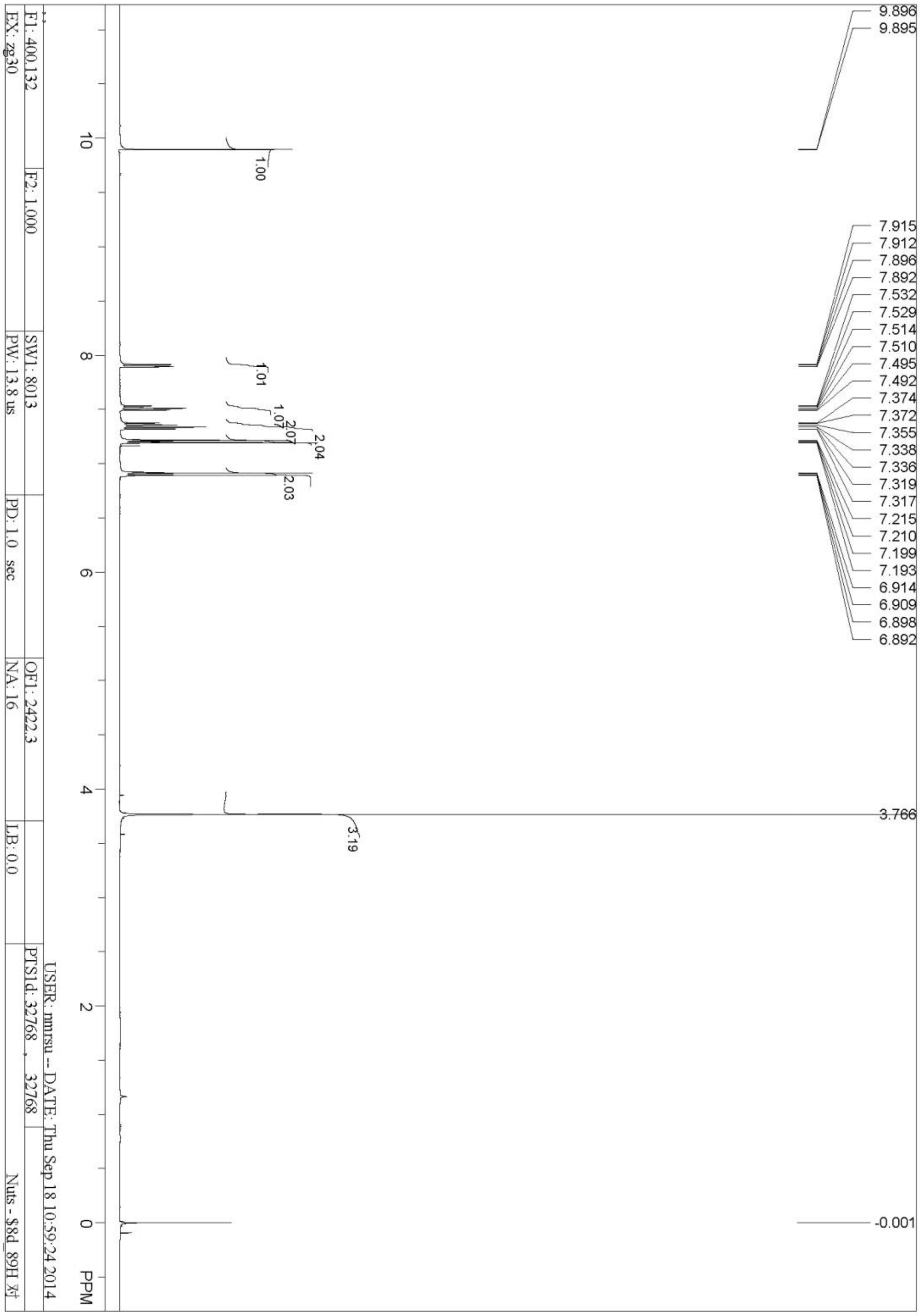
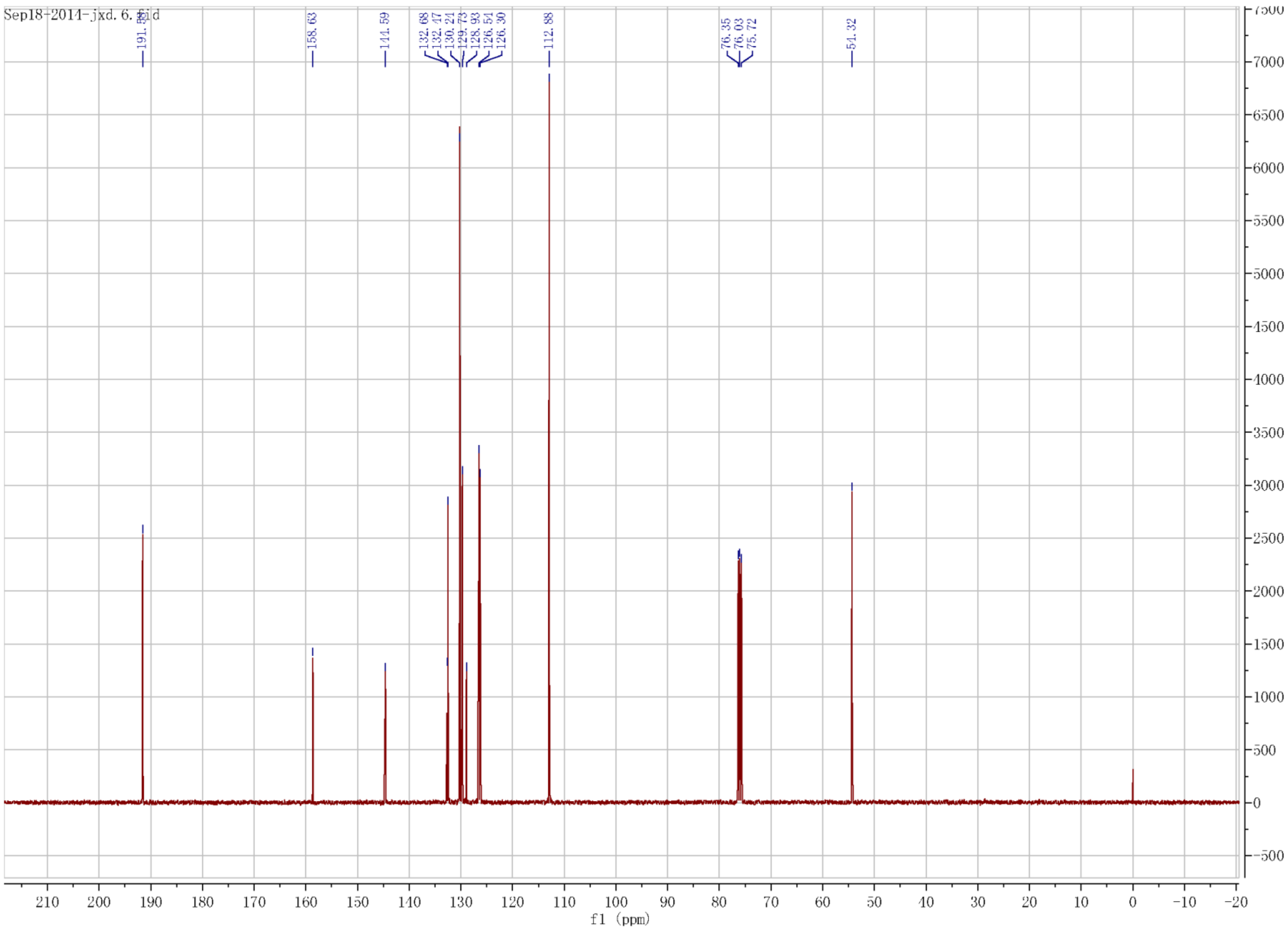
NMR spectra of compound **10d**



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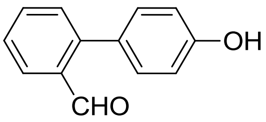
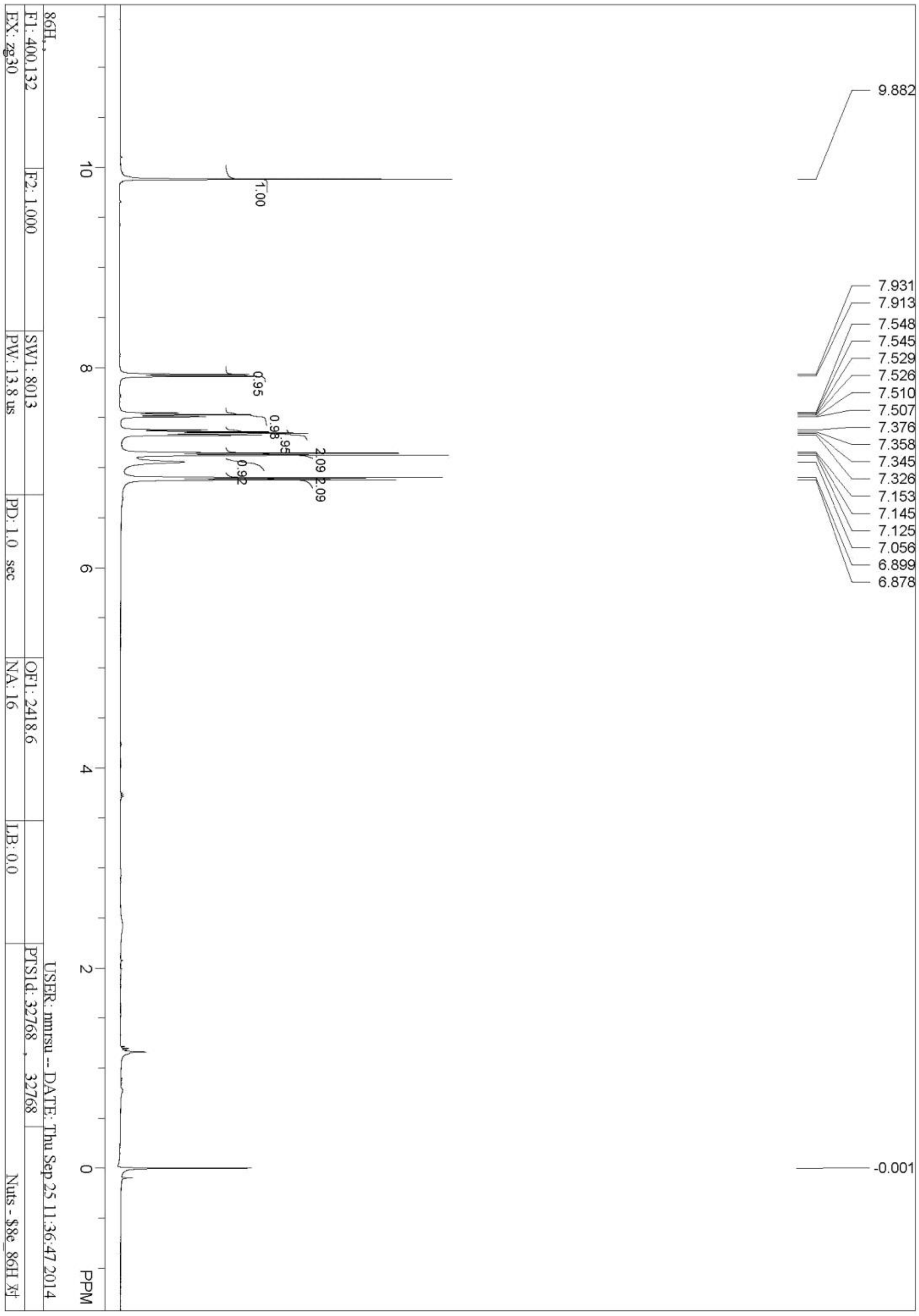
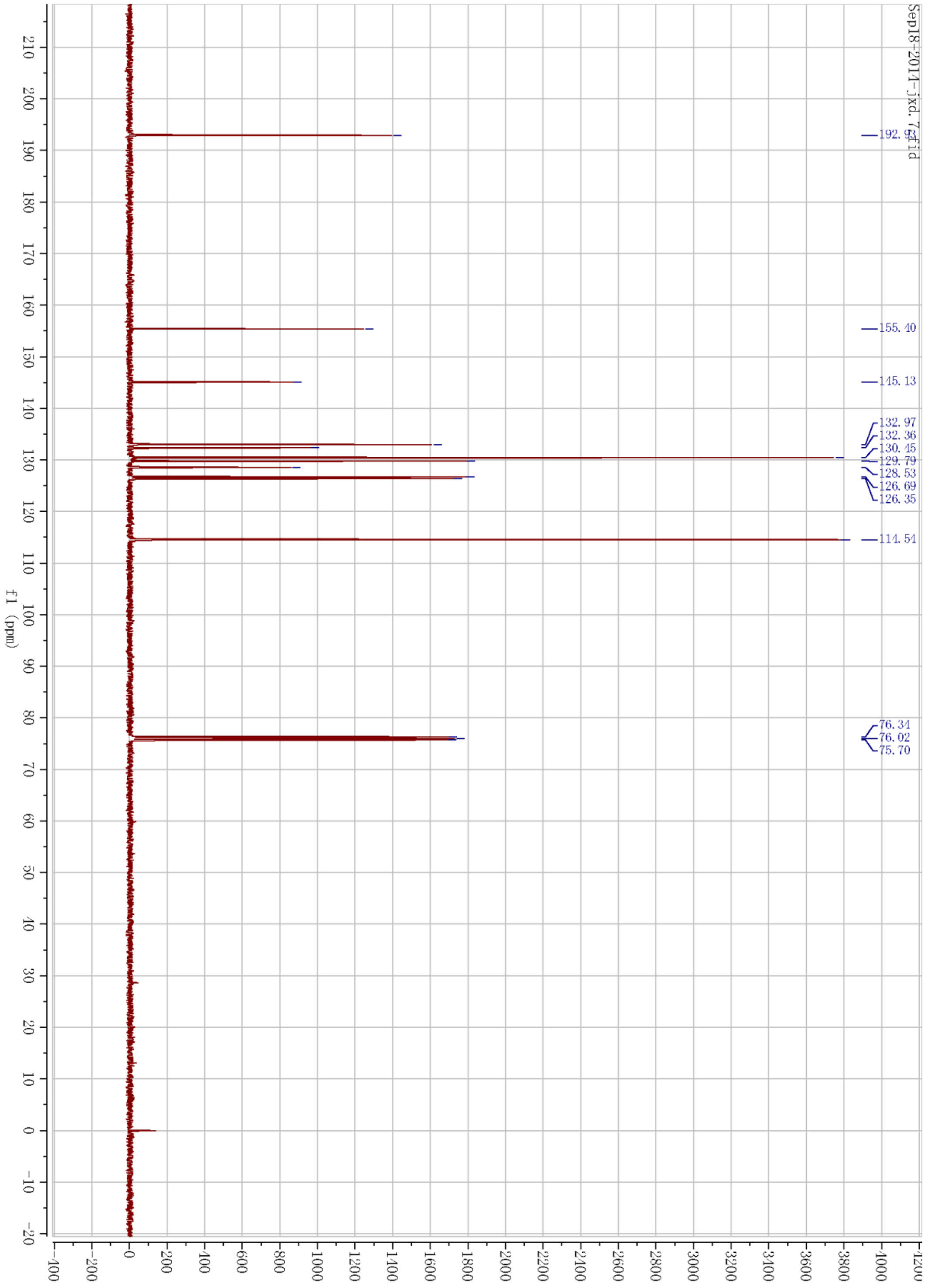
NMR spectra of compound **10e**



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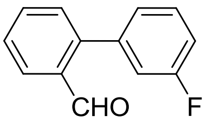
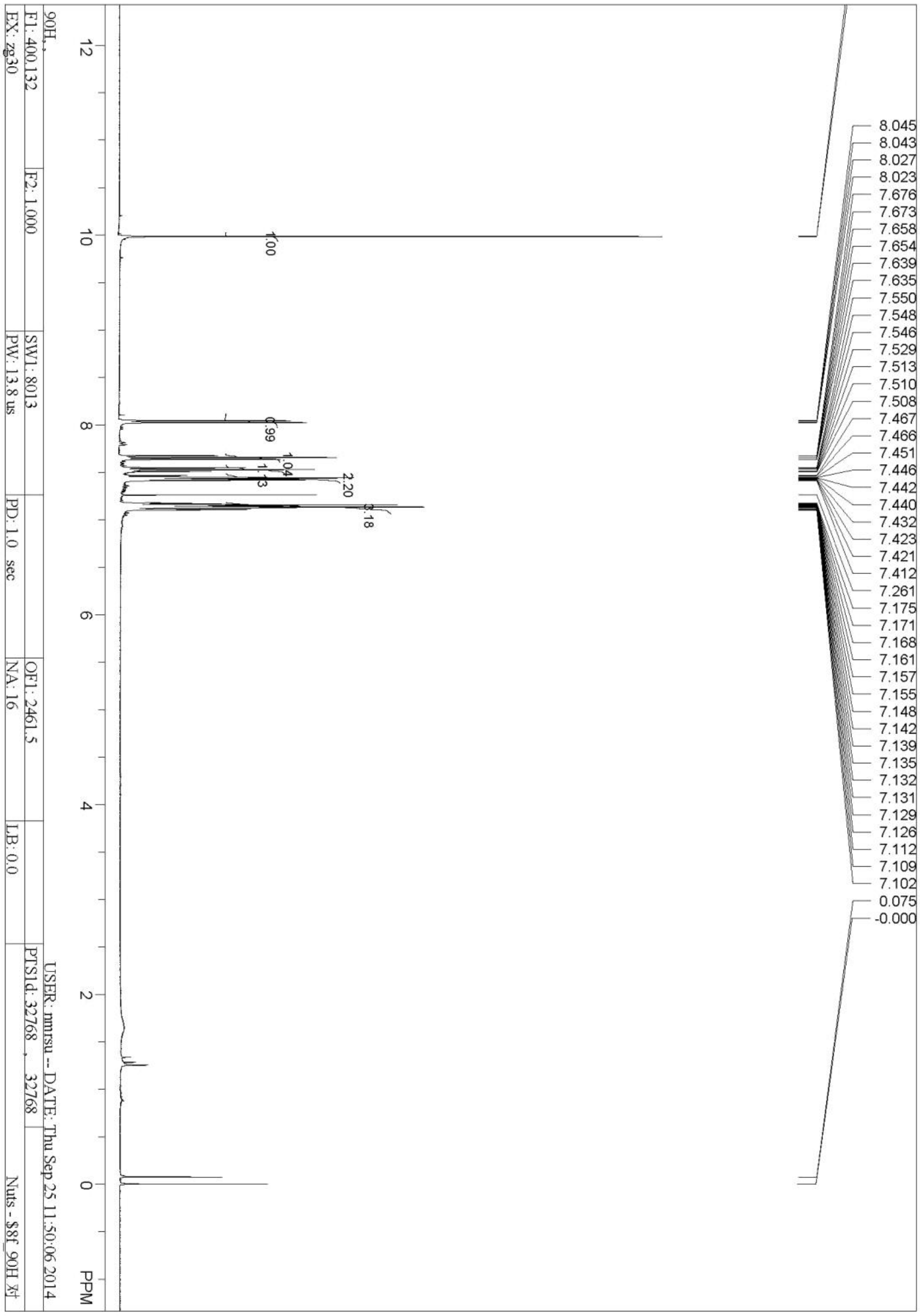
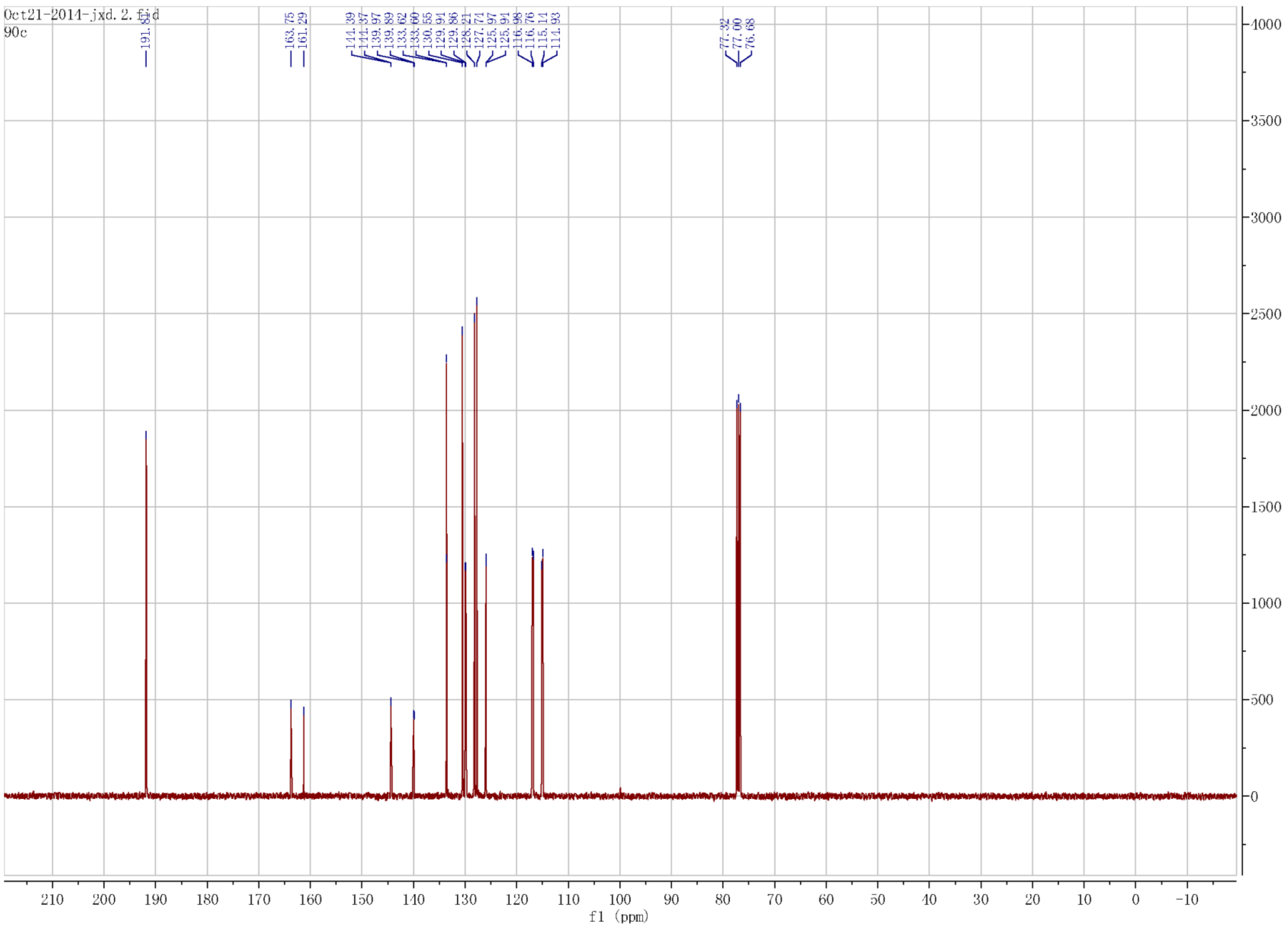
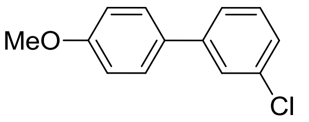
NMR spectra of compound **10f**

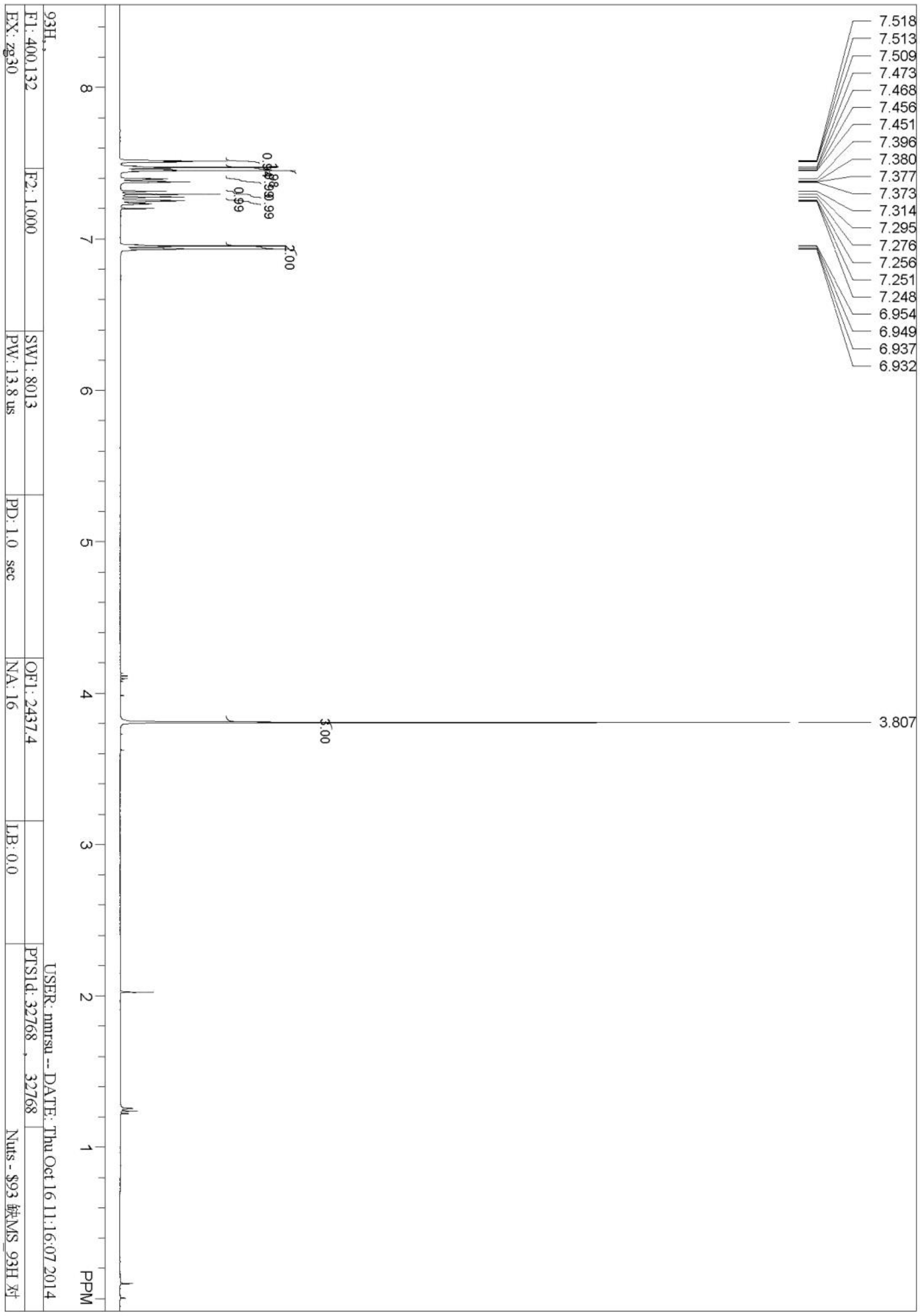


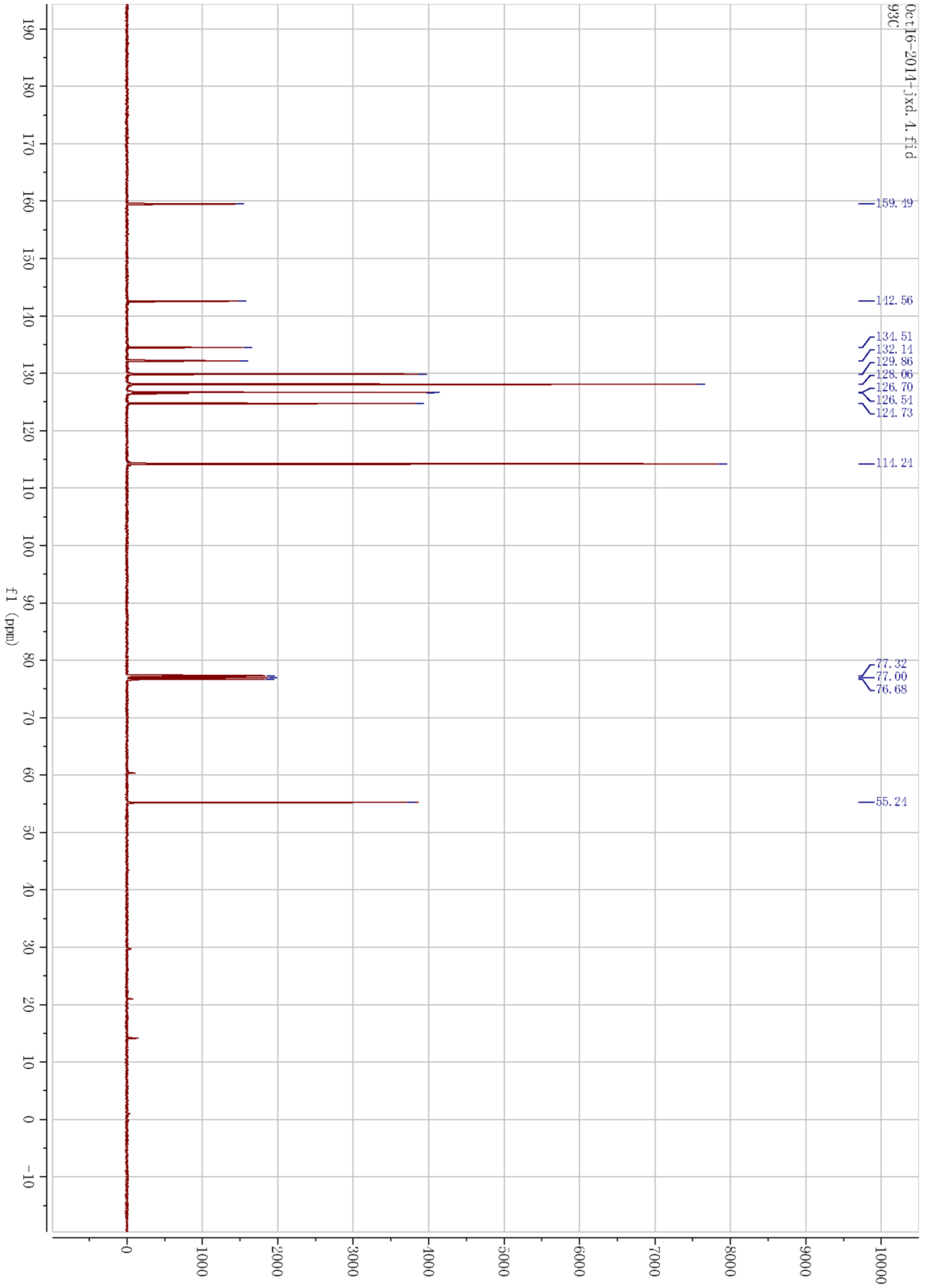



Oct21-2014-jxd.2.fid
90c
191.81
163.75
161.29
144.39
144.37
139.97
139.89
133.62
133.60
130.55
129.94
129.86
128.21
127.74
125.97
125.94
116.98
116.76
115.14
114.93
77.32
77.00
76.68
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

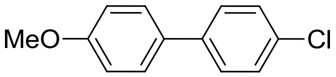
NMR spectra of compound **11a**

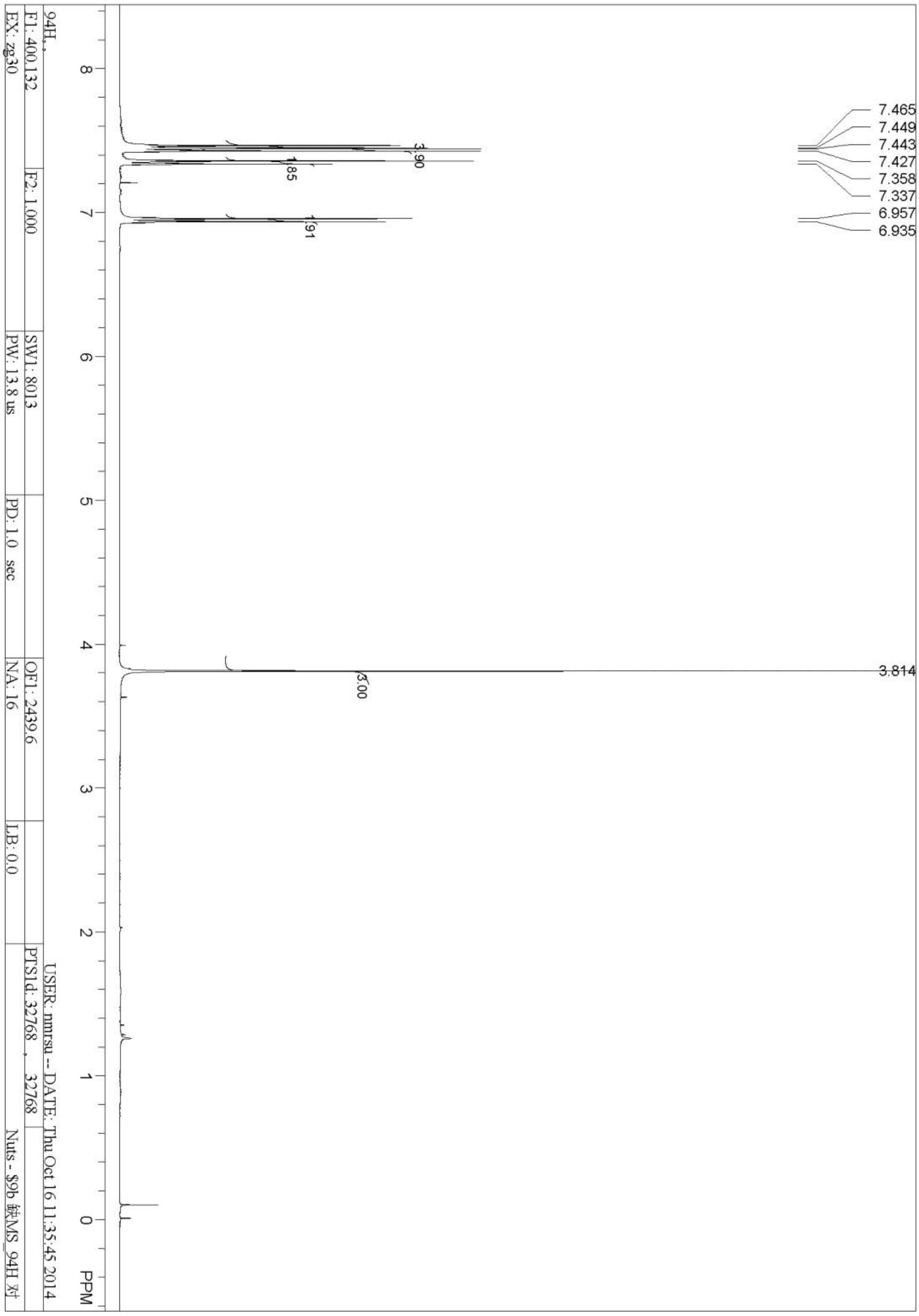


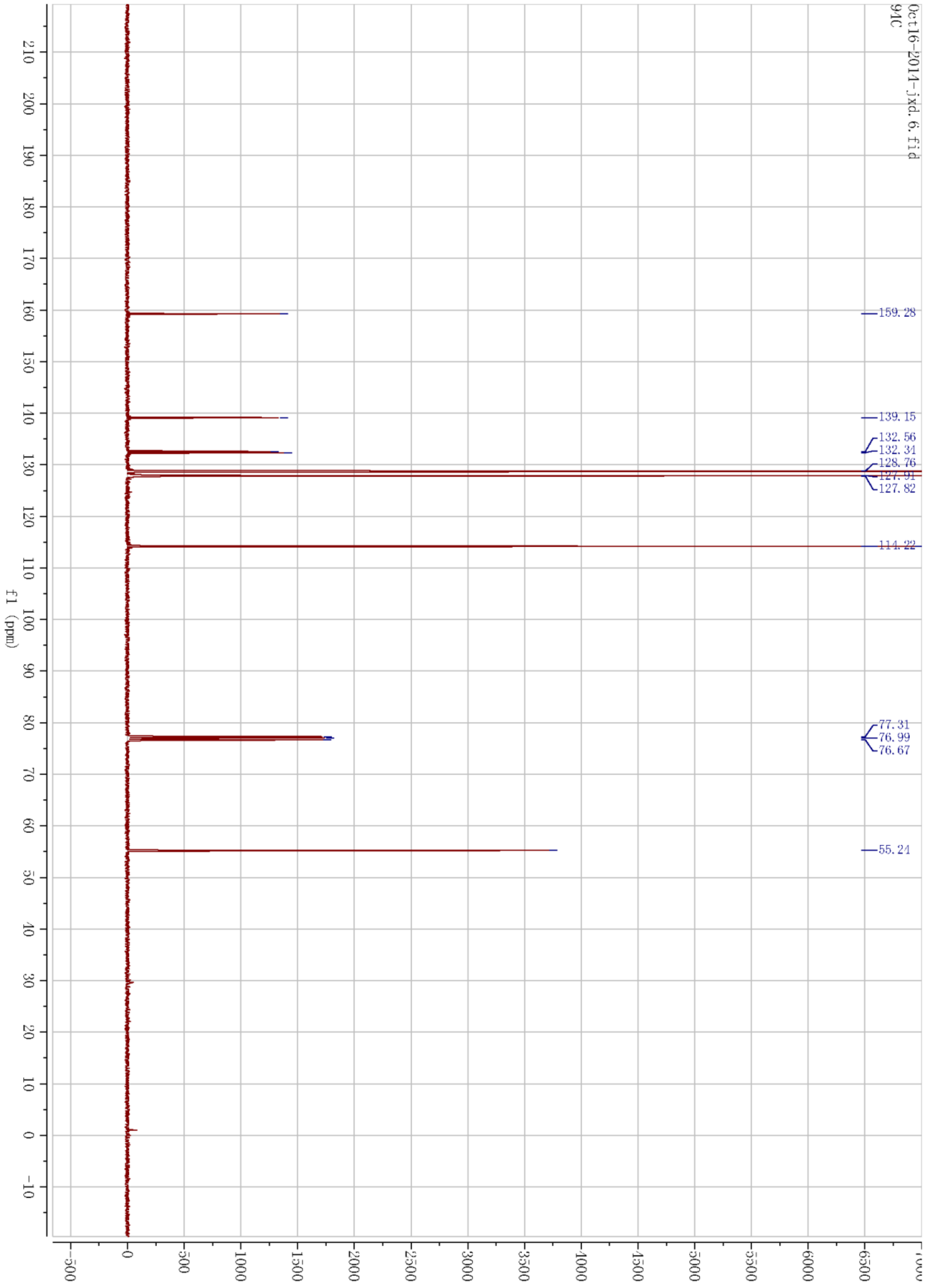



Oct16-2014-jxd.4.fid
93C
159.49
142.56
134.51
132.14
129.86
128.06
126.70
126.54
124.73
114.24
77.32
77.00
76.68
55.24
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000

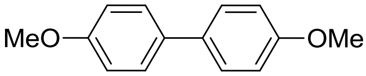
NMR spectra of compound **11b**

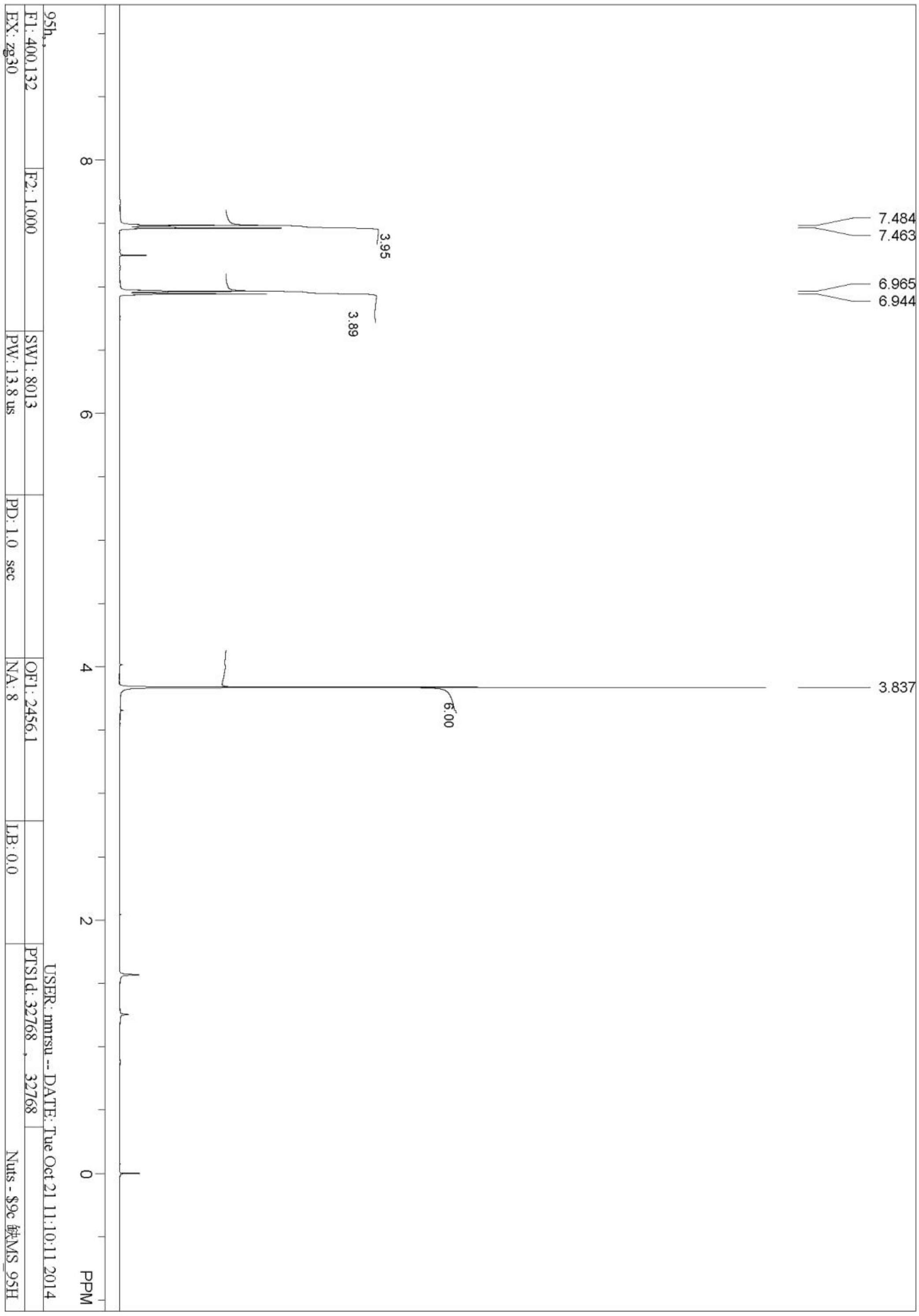


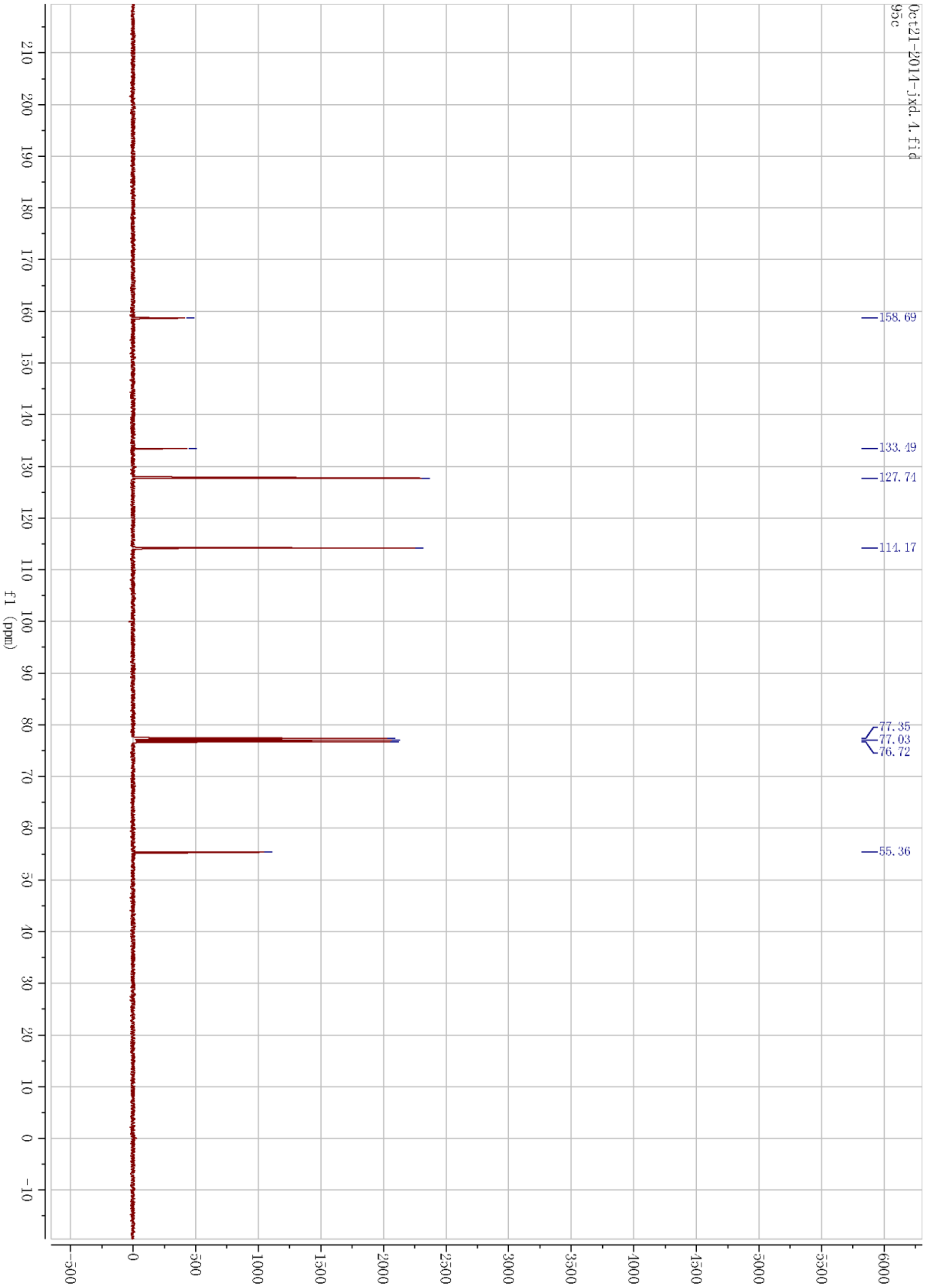



Oct16-2014-jxd.6.fid
91C
159.28
139.15
132.56
132.34
128.76
127.91
127.82
114.22
77.31
76.99
76.67
55.24
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500

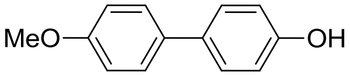
NMR spectra of compound **11c**

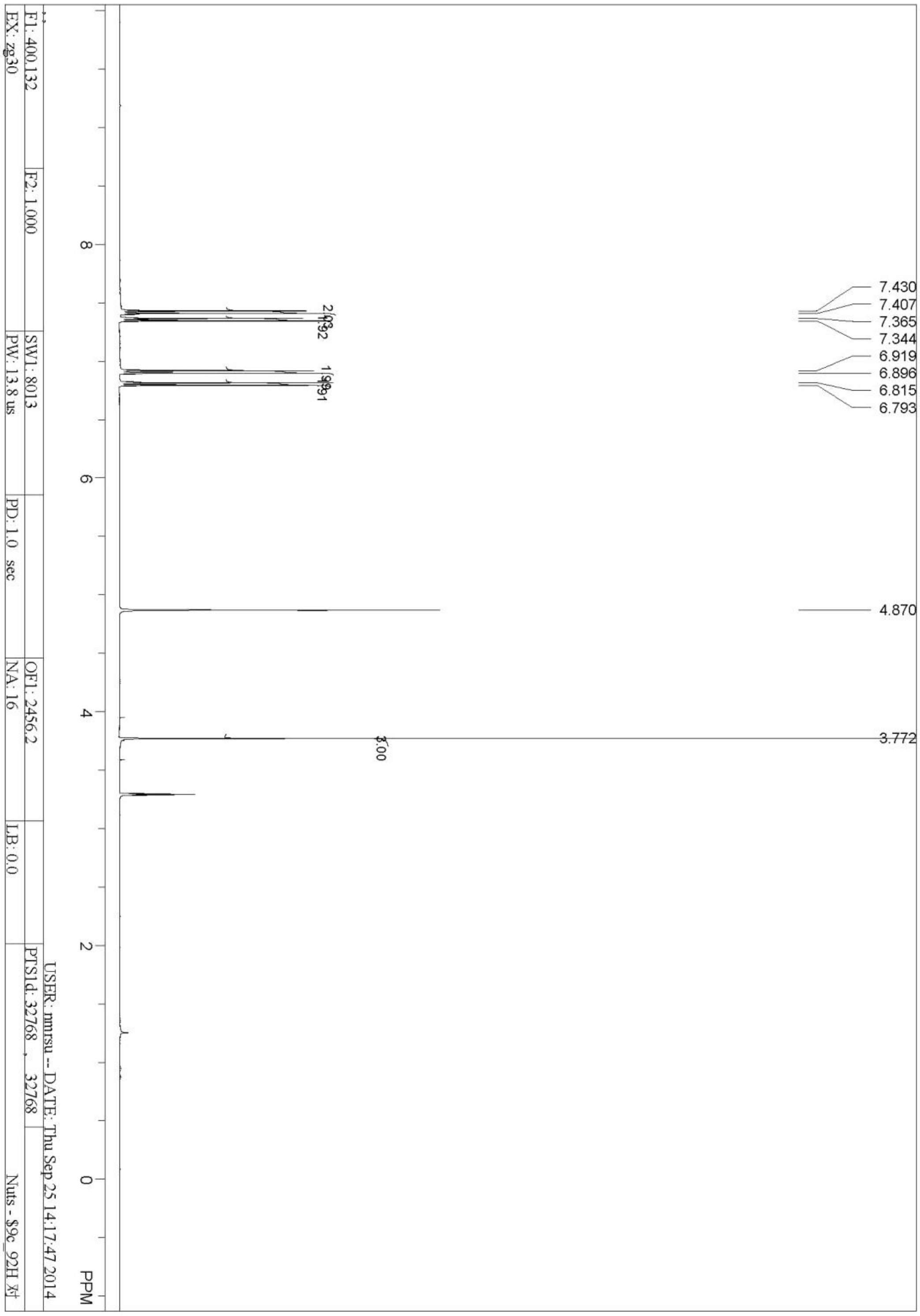


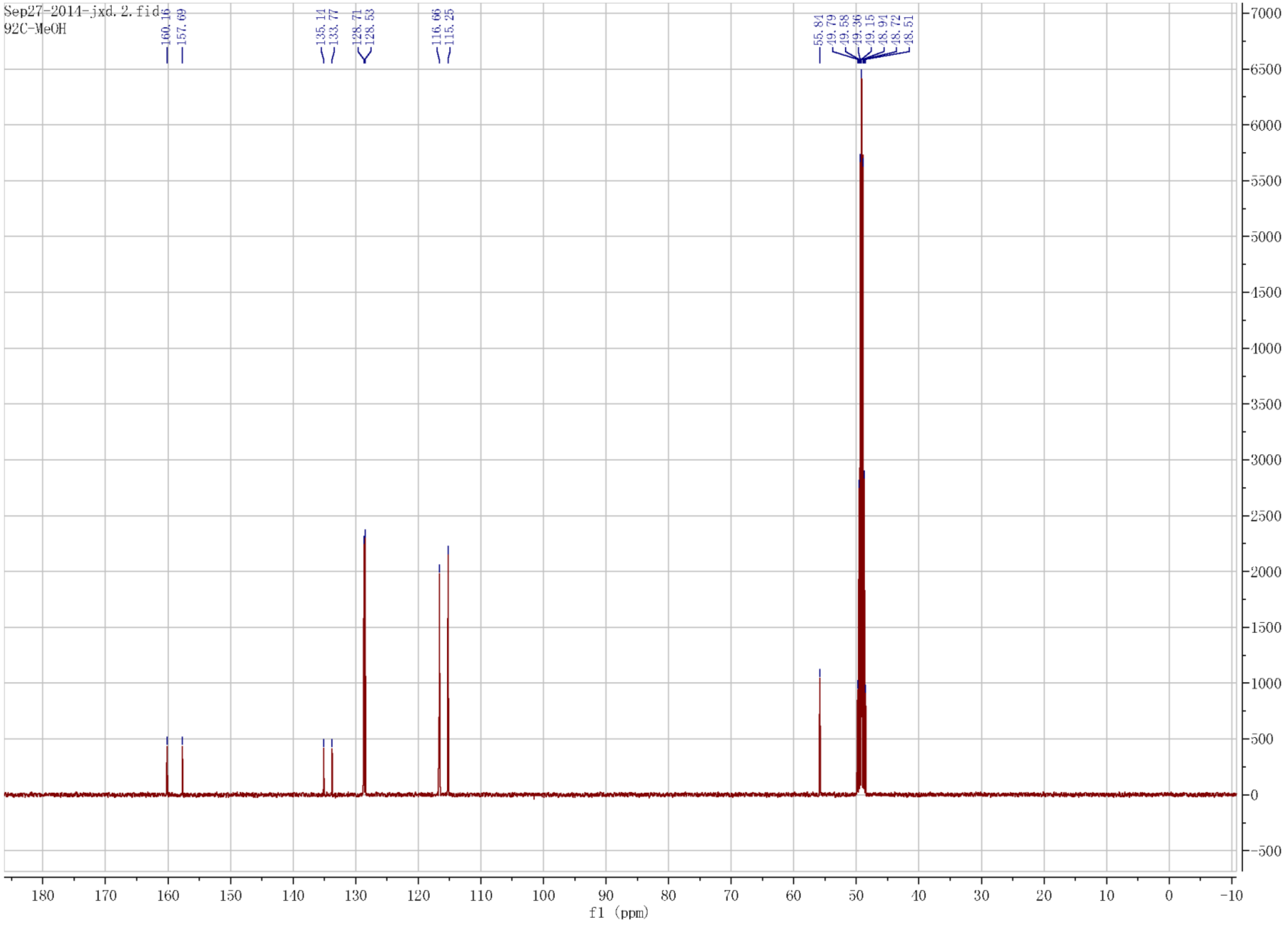



Oct21-2014-jxd.4.fid
95c
158.69
133.49
127.74
114.17
77.35
77.03
76.72
55.36
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000

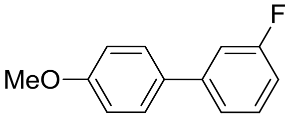
NMR spectra of compound **11d**

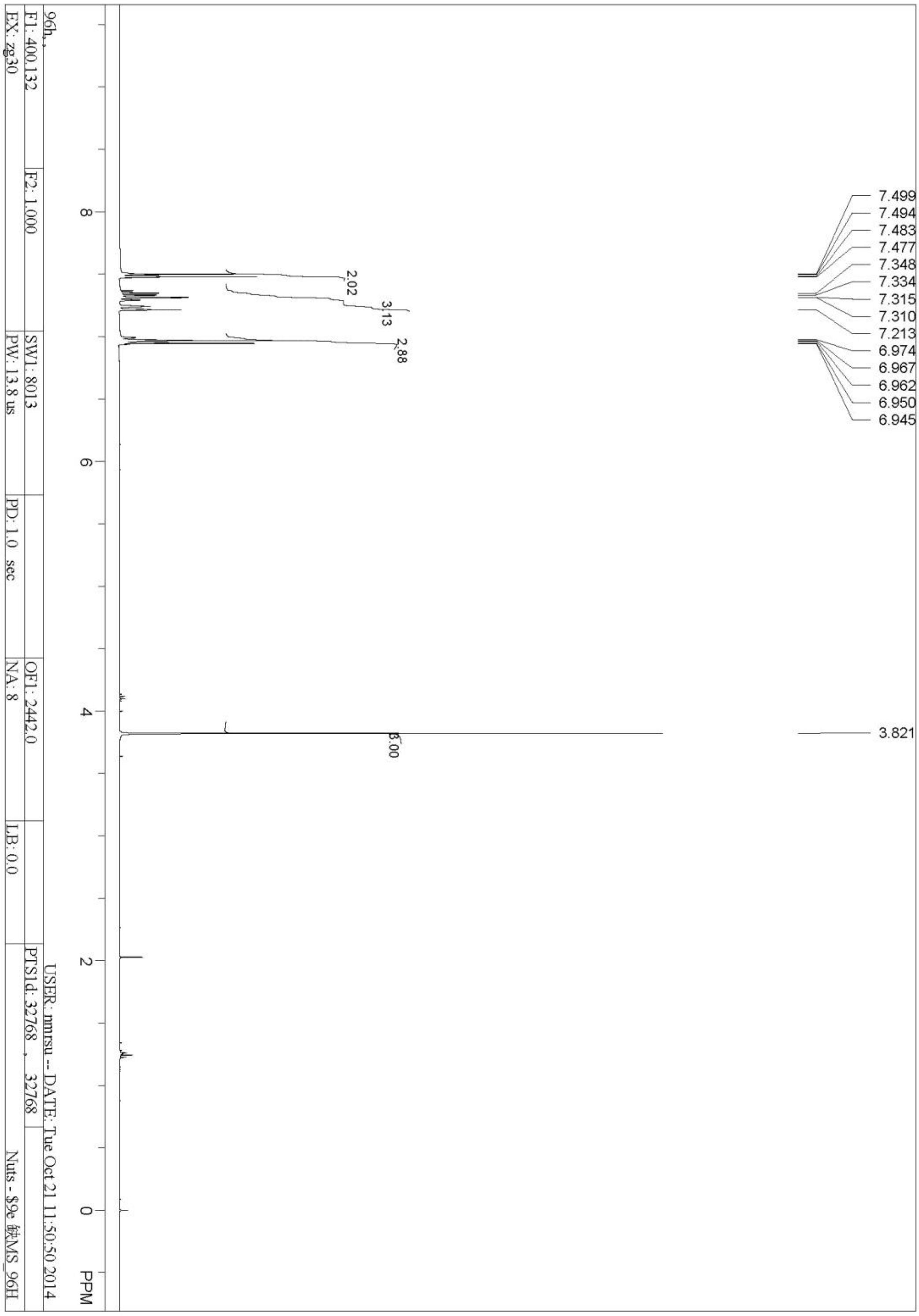


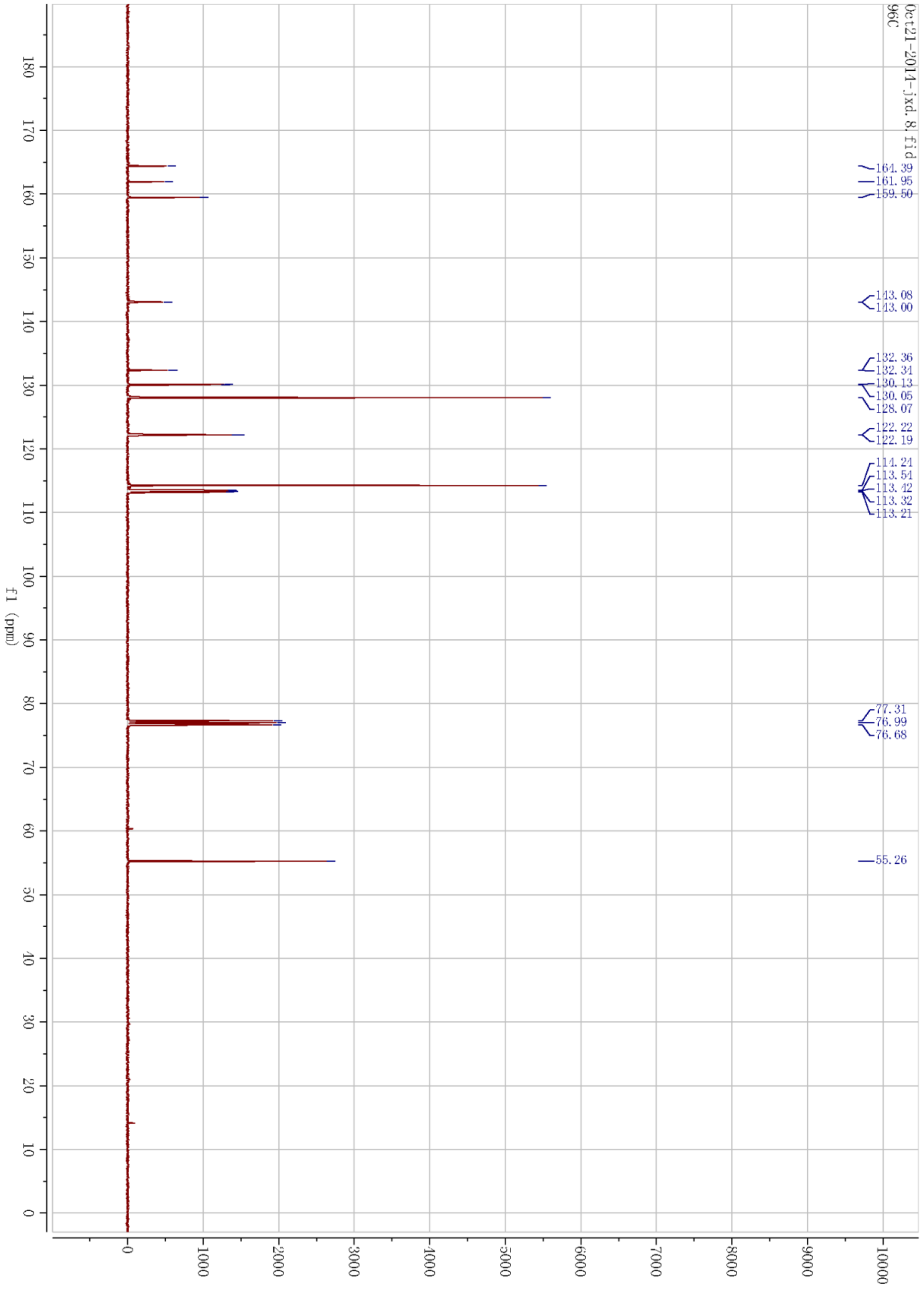



Sep27-2014-jxd.2.fid
92C-MeOH
160.16
157.69
135.14
133.77
128.71
128.53
116.66
115.25
55.84
49.79
49.58
49.36
49.15
48.94
48.72
48.51
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

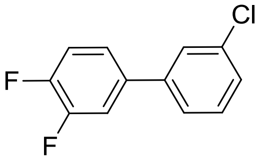
NMR spectra of compound **11e**

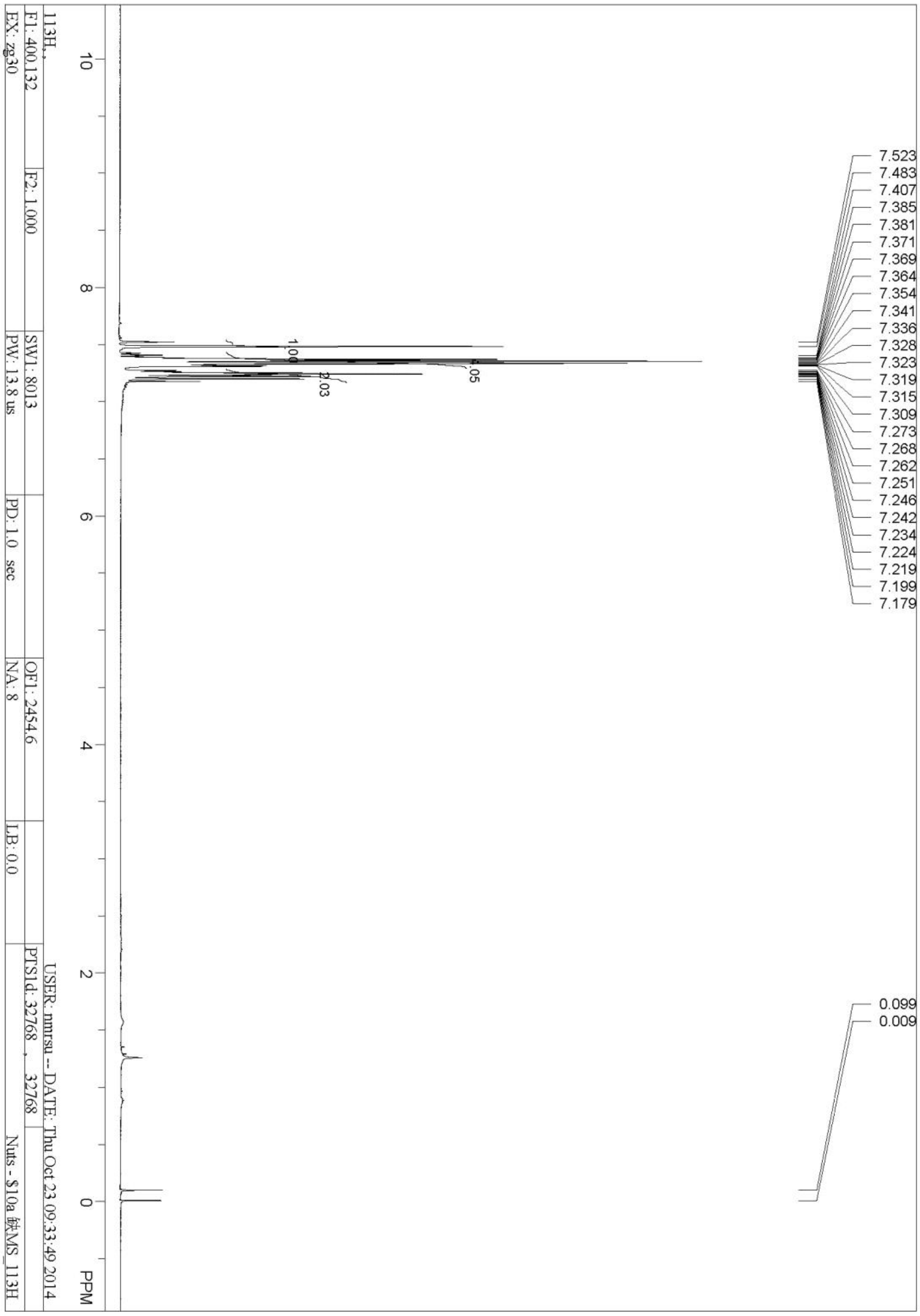


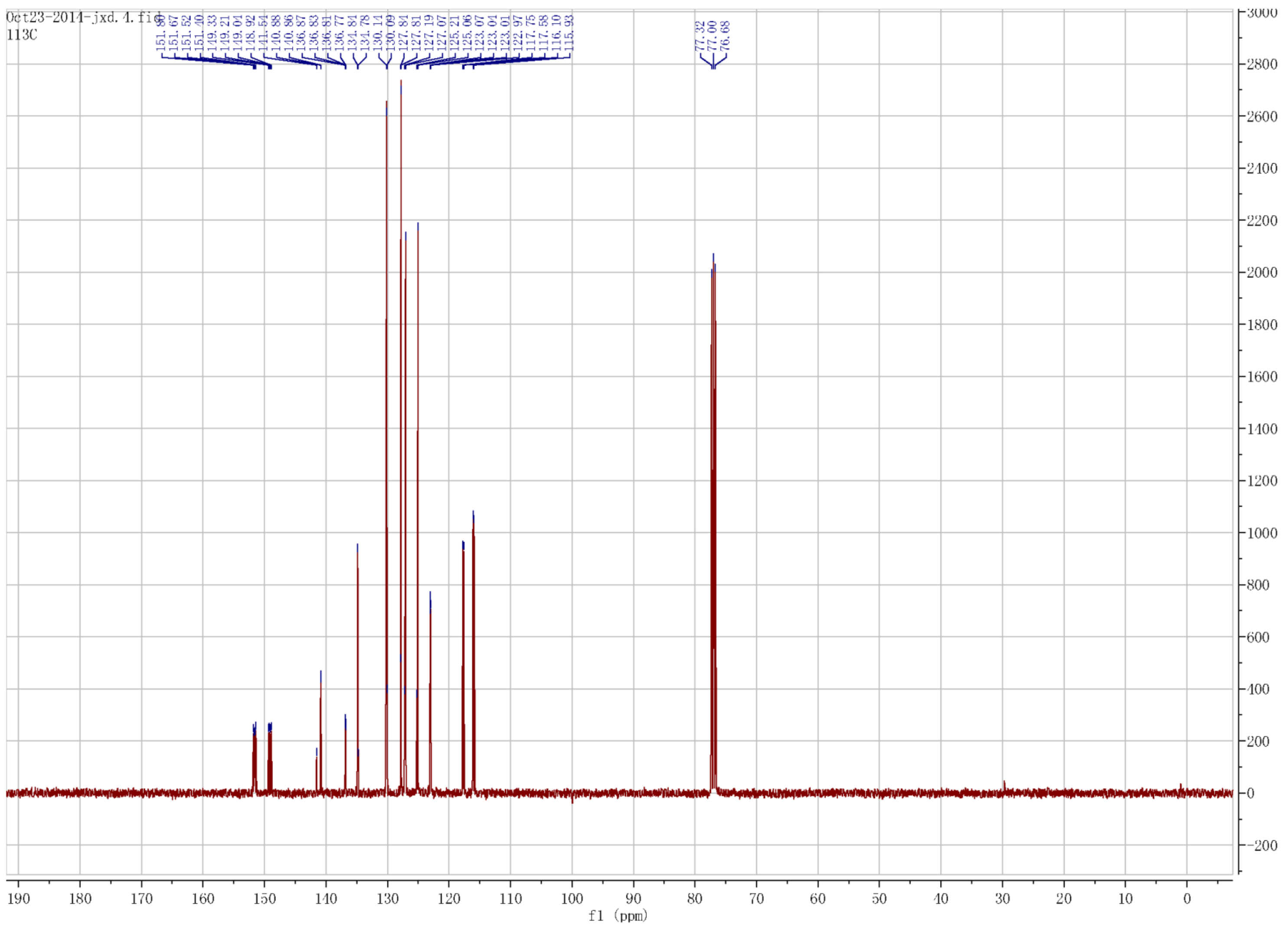



Oct21-2014-jxd.8.fid
96C
164.39
161.95
159.50
143.08
143.00
132.36
132.34
130.13
130.05
128.07
122.22
122.19
114.24
113.54
113.42
113.32
113.21
77.31
76.99
76.68
55.26
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000

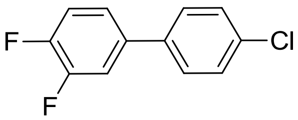
NMR spectra of compound **12a**

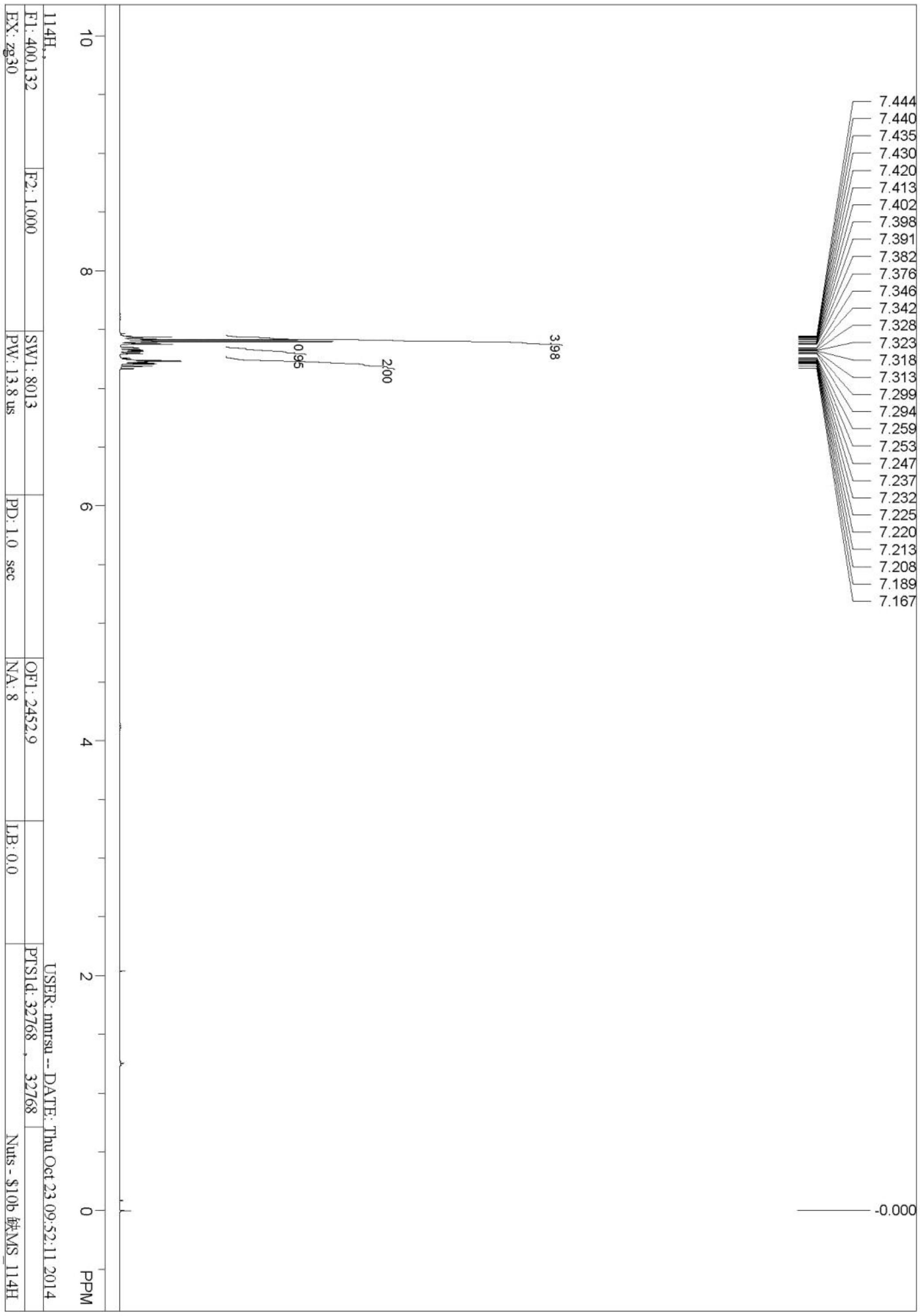


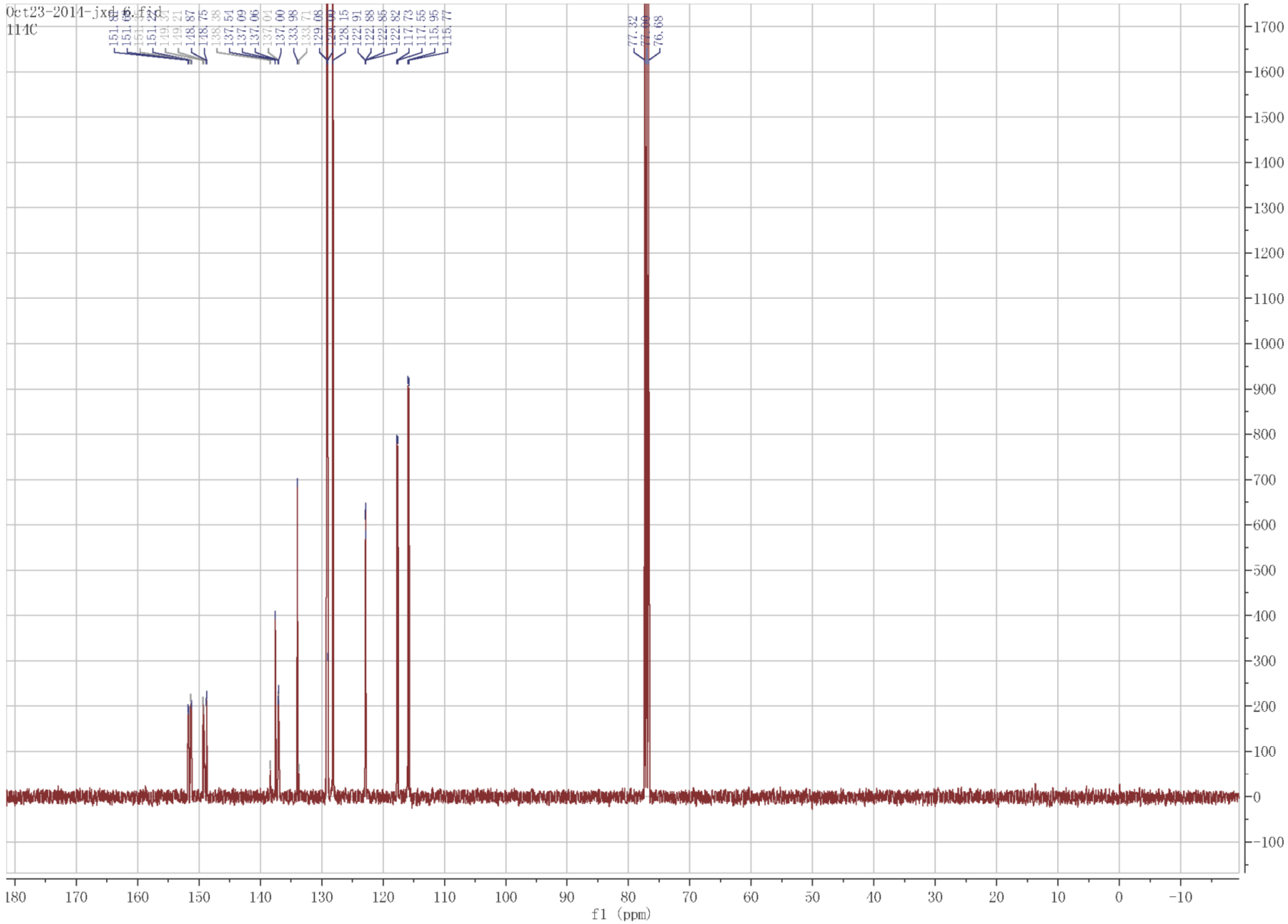



Oct23-2014-jxd.4.fid
113C
151.80
151.67
151.52
151.40
149.33
149.21
149.04
148.92
141.54
140.88
140.86
136.87
136.83
136.81
136.77
134.84
134.78
130.14
130.09
127.84
127.81
127.19
127.07
125.21
125.06
123.07
123.04
123.01
122.97
117.75
117.58
116.10
115.93
77.32
77.00
76.68
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

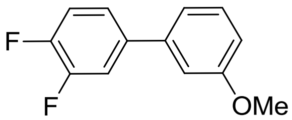
NMR spectra of compound **12b**

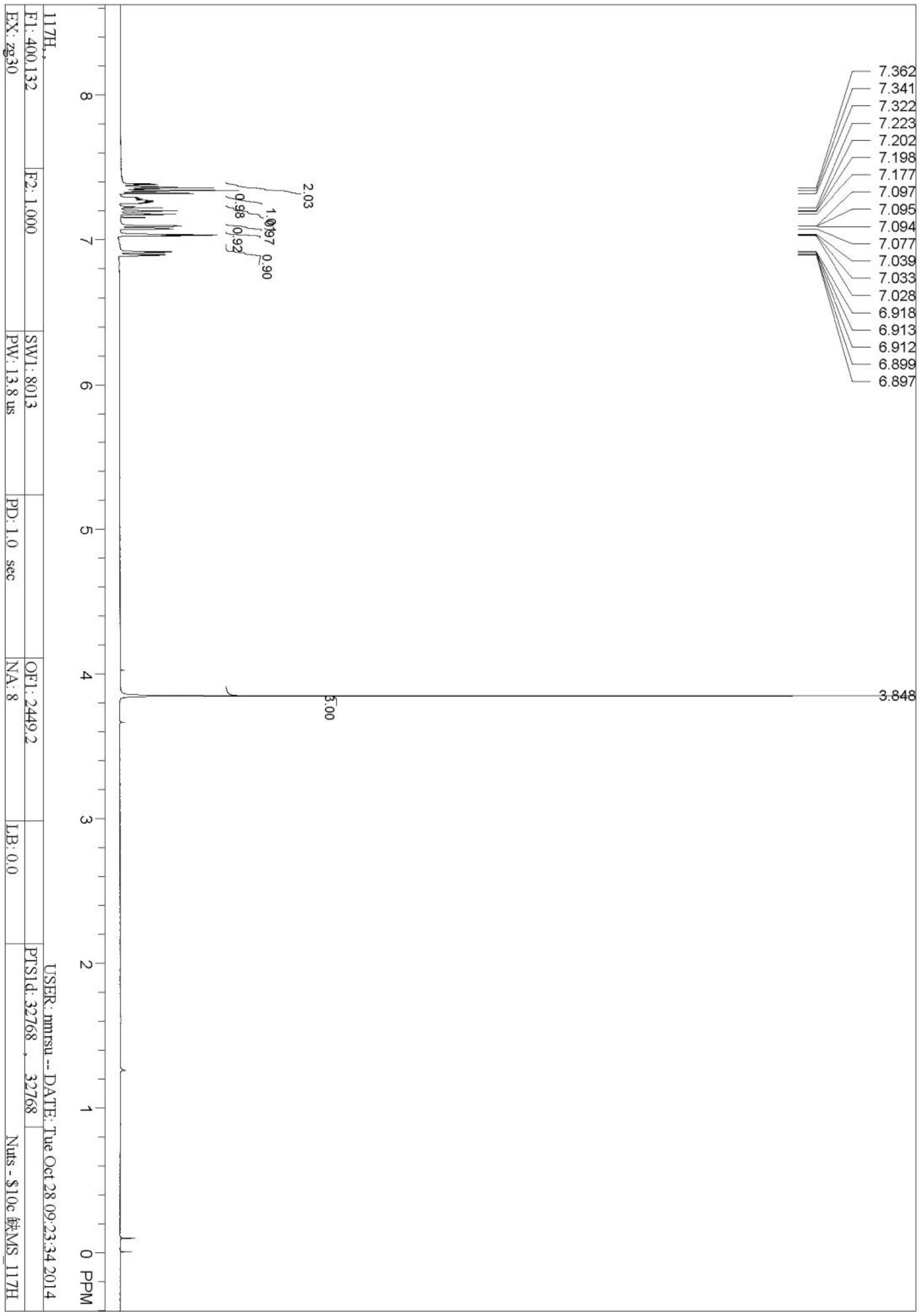


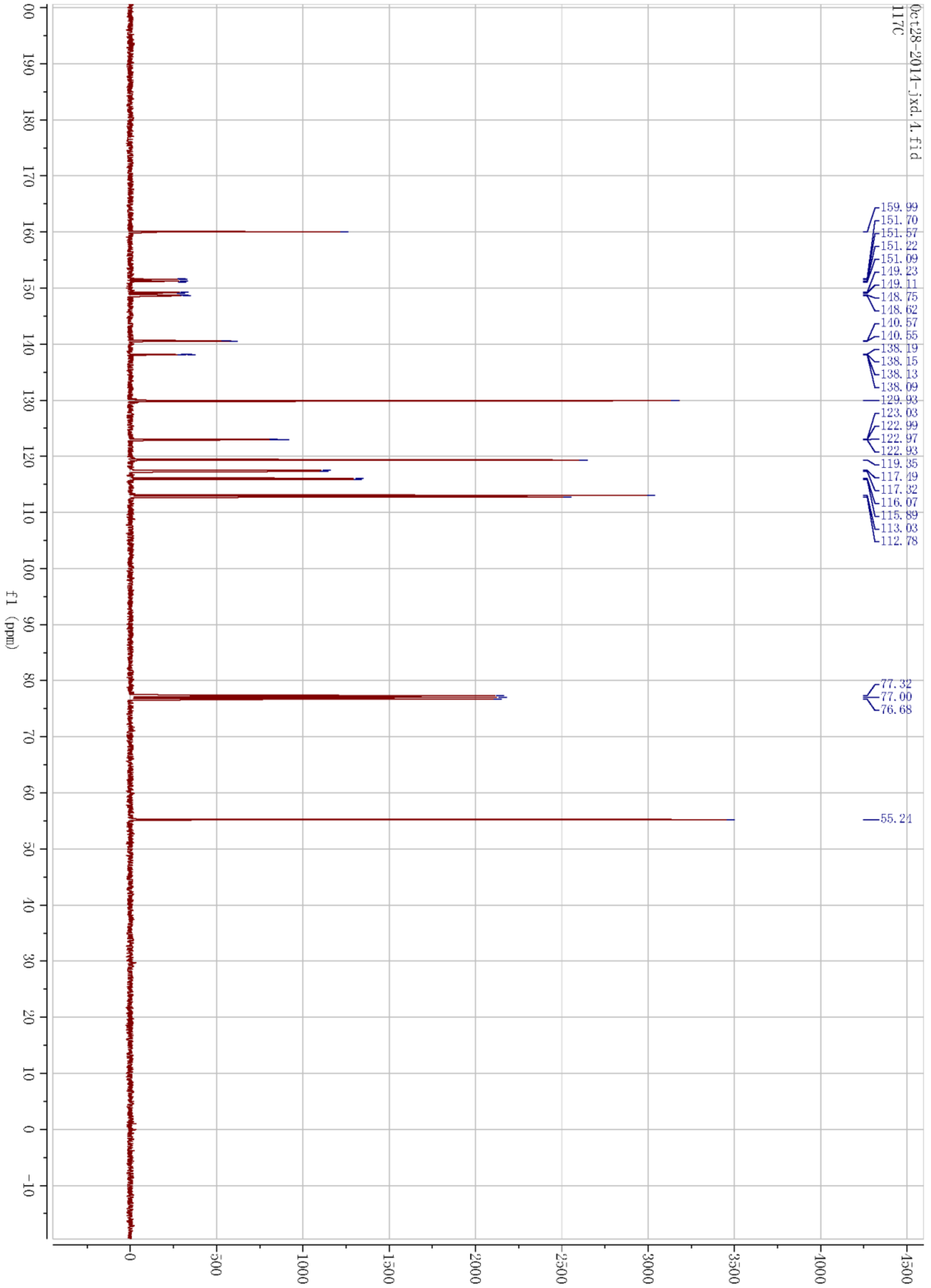



Oct23-2014-jxd.6.fid
114C
151.8
151.6
151.3
151.22
149.34
149.21
148.87
148.75
138.38
137.54
137.09
137.06
137.04
137.00
133.98
133.71
129.08
129.00
128.15
122.91
122.88
122.85
122.82
117.73
117.55
115.95
115.77
77.32
77.00
76.68
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

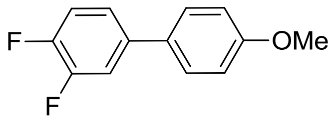
NMR spectra of compound **12c**

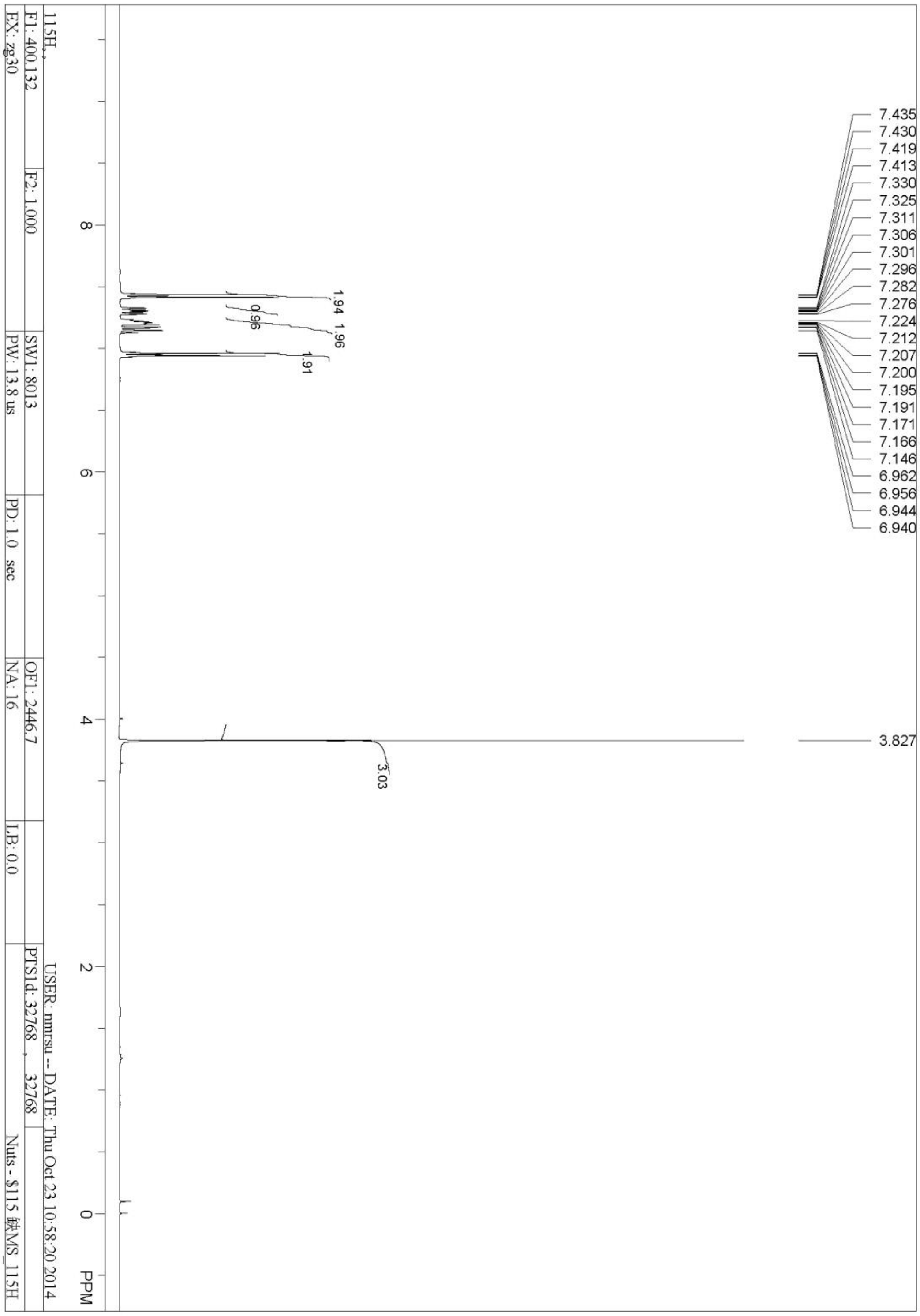


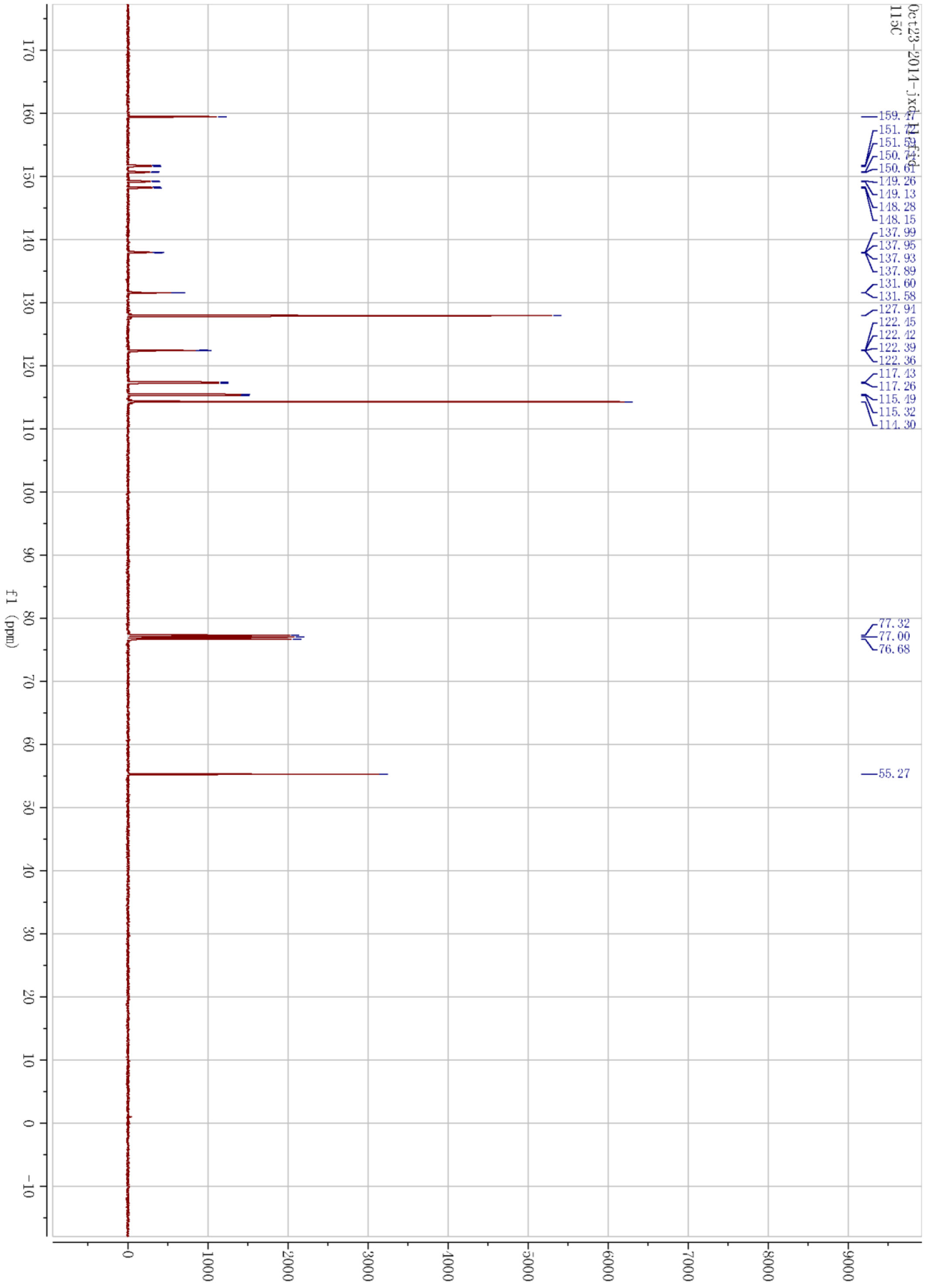



Oct28-2014-jxd.4.fid
117C
159.99
151.70
151.57
151.22
151.09
149.23
149.11
148.75
148.62
140.57
140.55
138.19
138.15
138.13
138.09
129.93
123.03
122.99
122.97
122.93
119.35
117.49
117.32
116.07
115.89
113.03
112.78
77.32
77.00
76.68
55.24
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
0
500
1000
1500
2000
2500
3000
3500
4000
4500

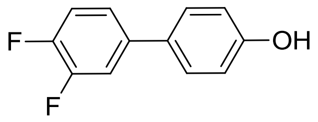
NMR spectra of compound **12d**

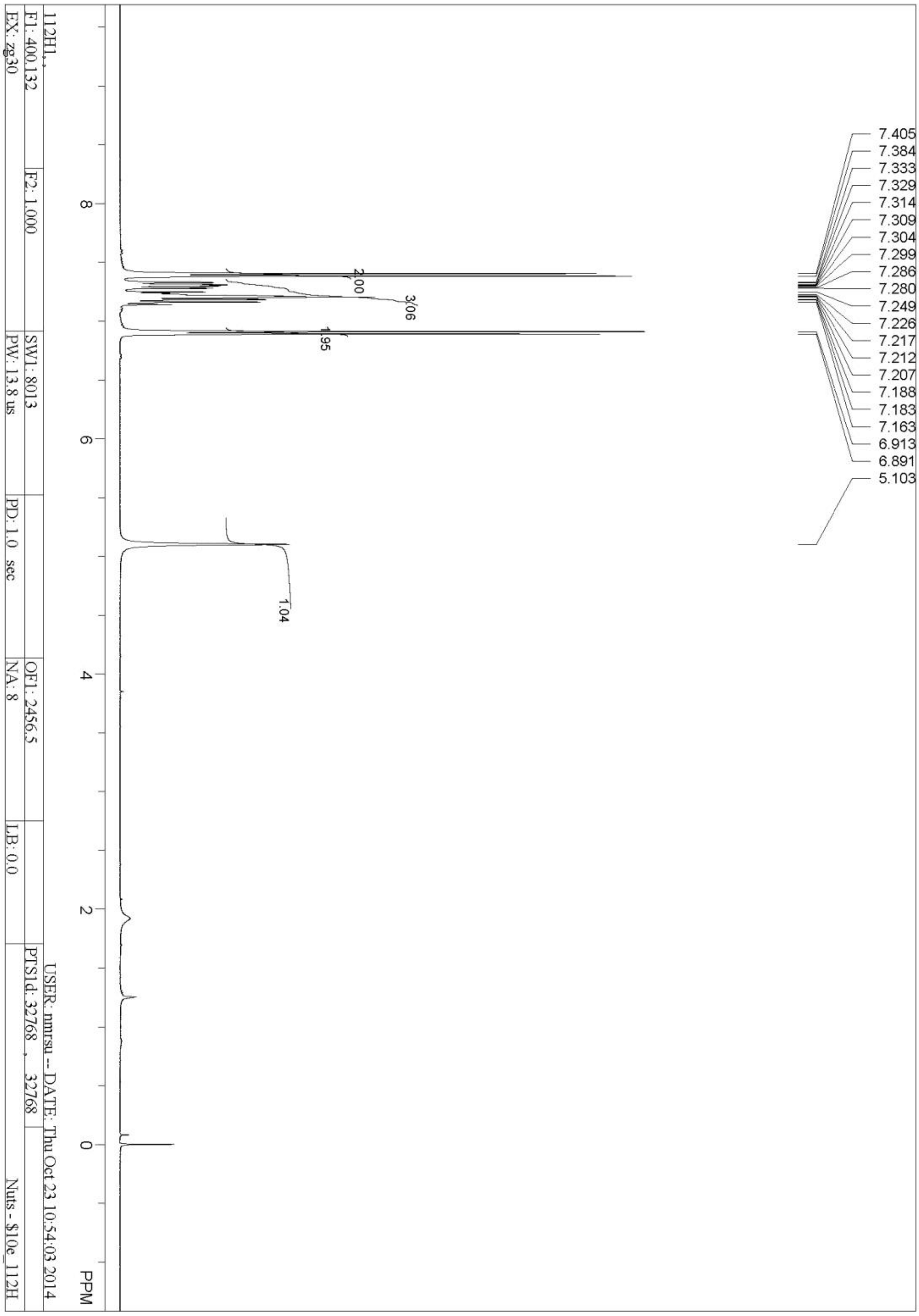


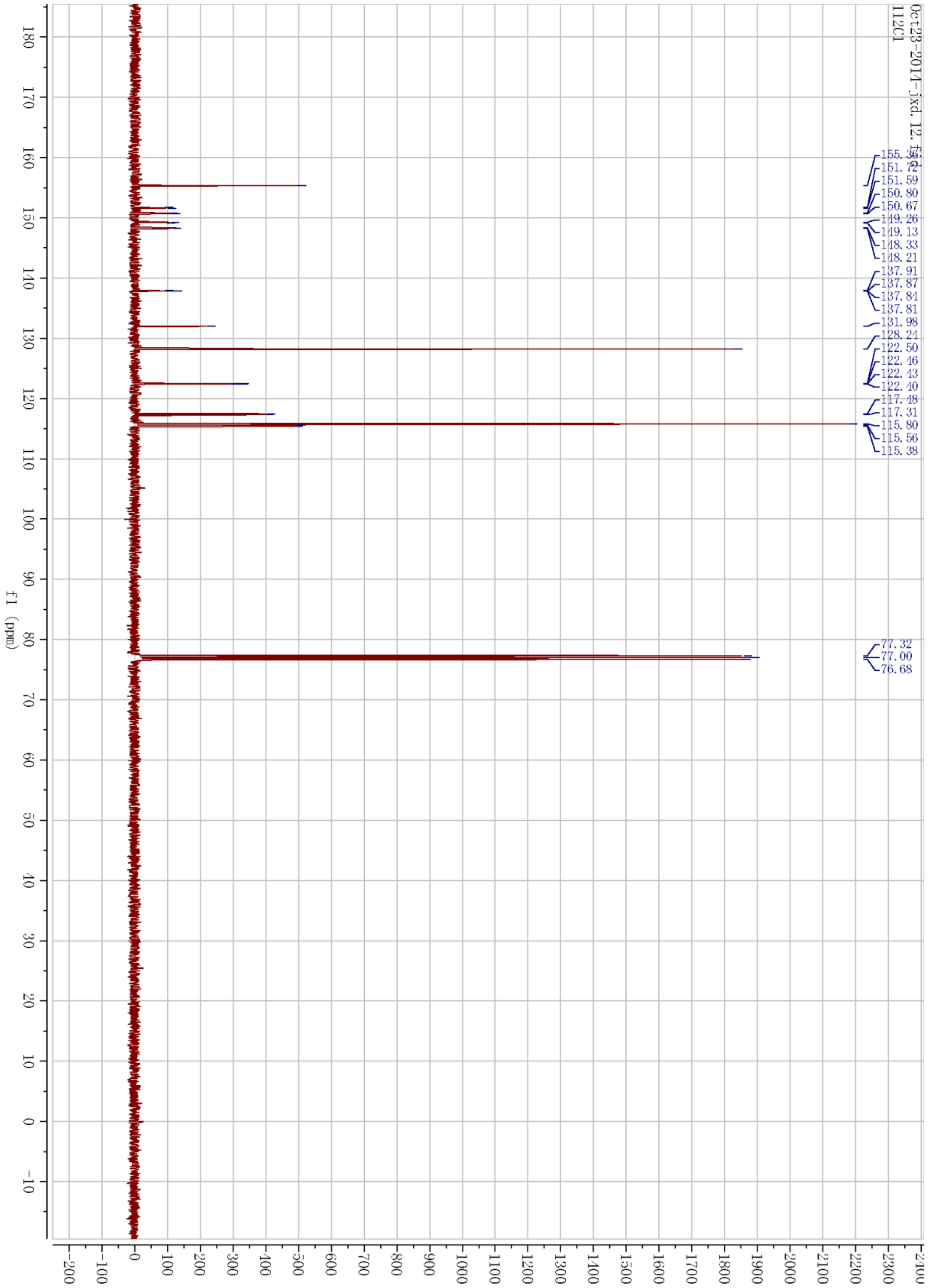



Oct23-2014-jxd-11[illegible].fid
115C
159.47
151.72
151.59
150.74
150.61
149.26
149.13
148.28
148.15
137.99
137.95
137.93
137.89
131.60
131.58
127.94
122.45
122.42
122.39
122.36
117.43
117.26
115.49
115.32
114.30
77.32
77.00
76.68
55.27
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
0
1000
2000
3000
4000
5000
6000
7000
8000
9000

NMR spectra of compound **12e**

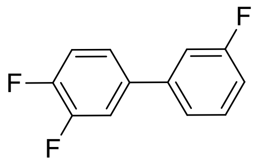


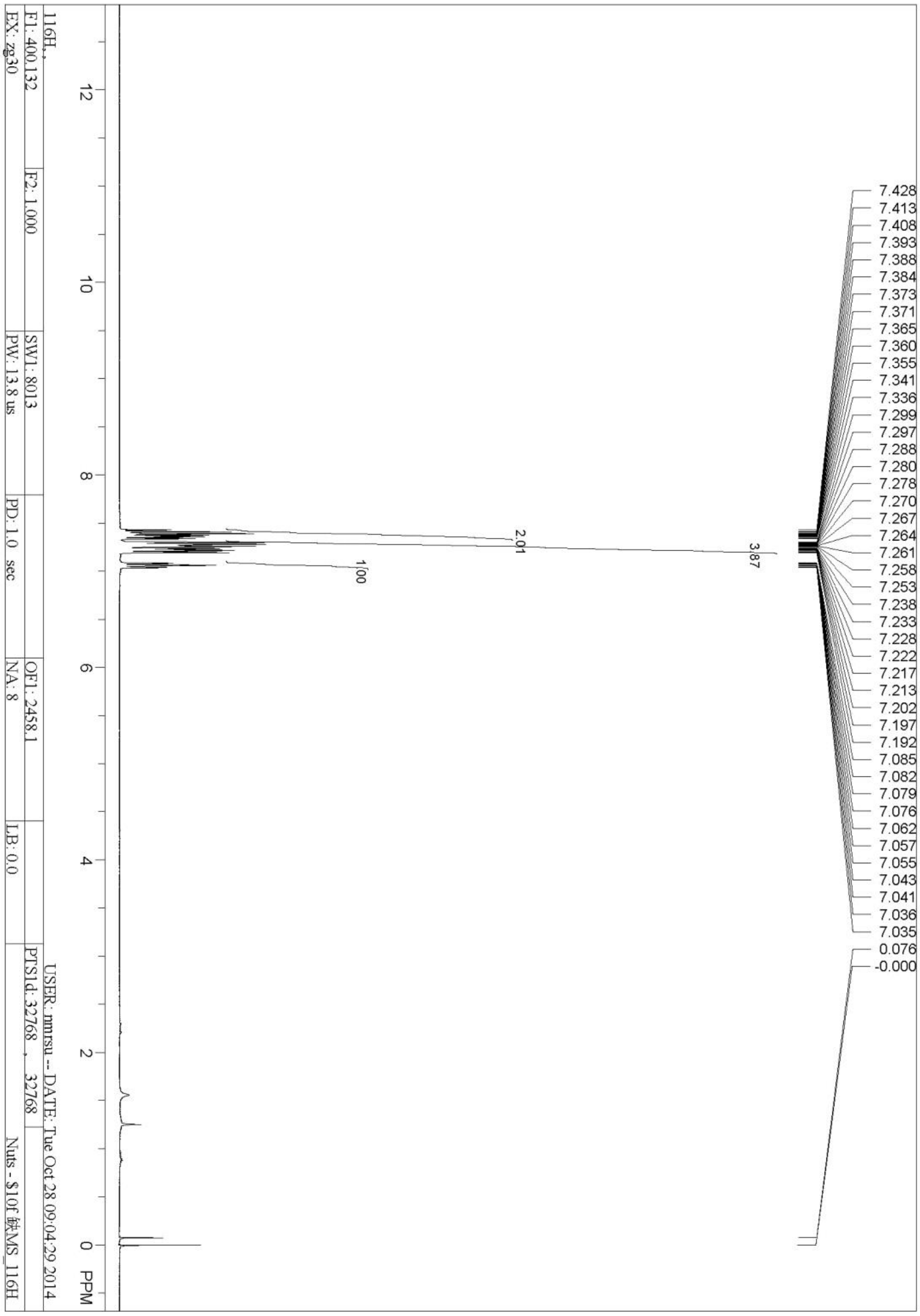


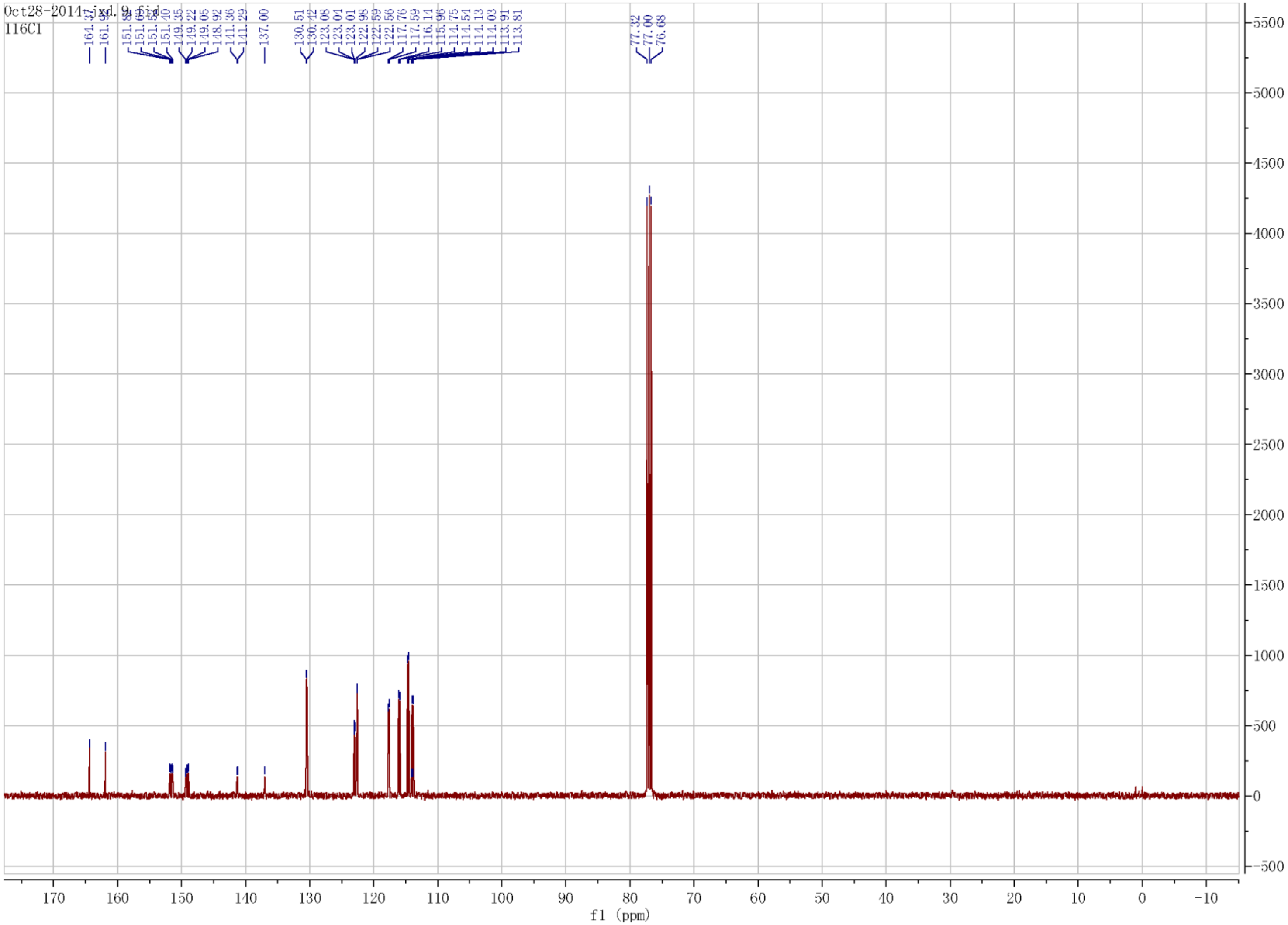


Oct23-2014-jxd.12.fid
112Cl
155.36
151.72
151.59
150.80
150.67
149.26
149.13
148.33
148.21
137.91
137.87
137.84
137.81
131.98
128.24
122.50
122.46
122.43
122.40
117.48
117.31
115.80
115.56
115.38
77.32
77.00
76.68
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-200
-100
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
2100
2200
2300
2400

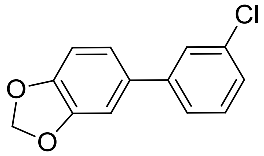
NMR spectra of compound **12f**

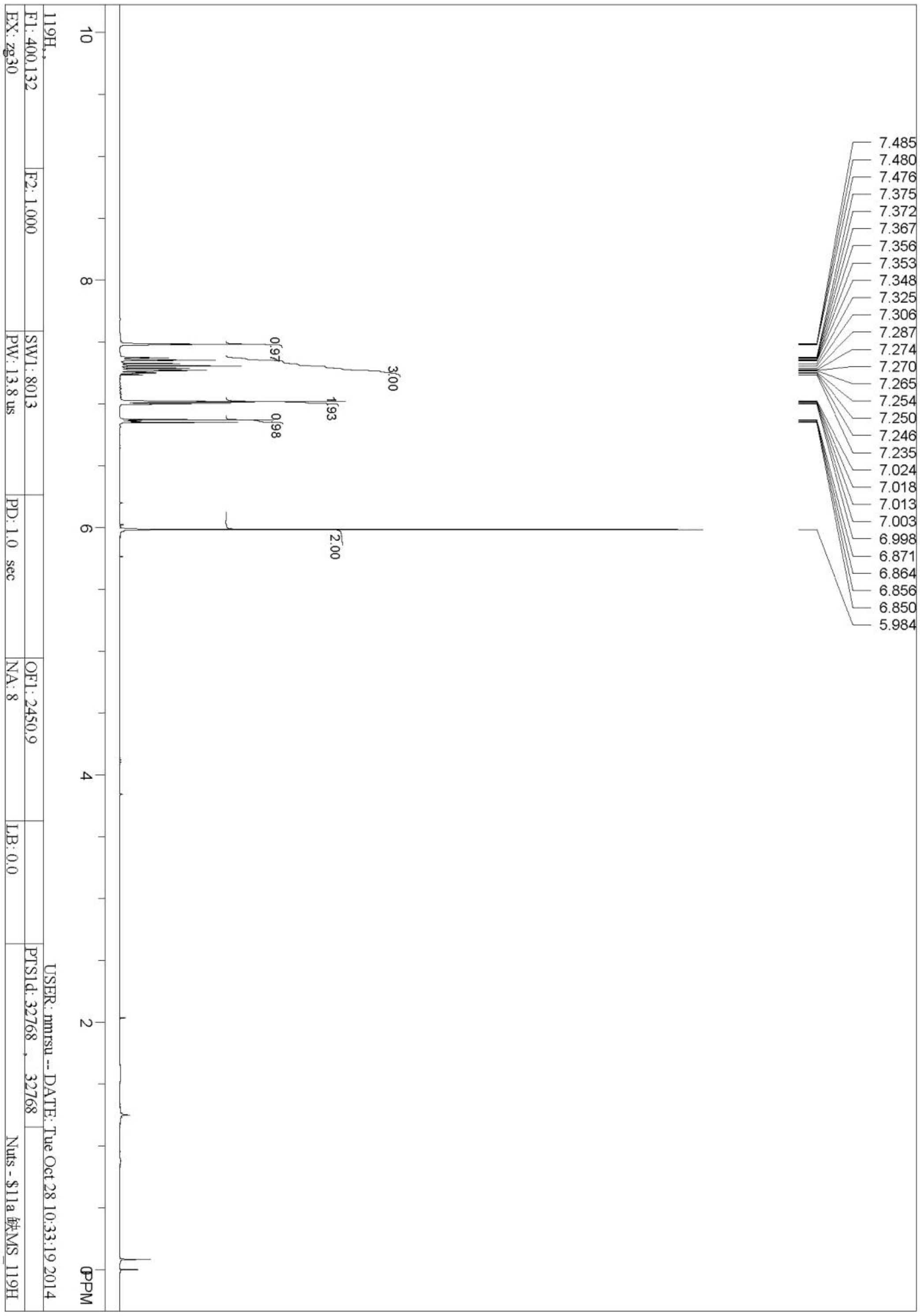


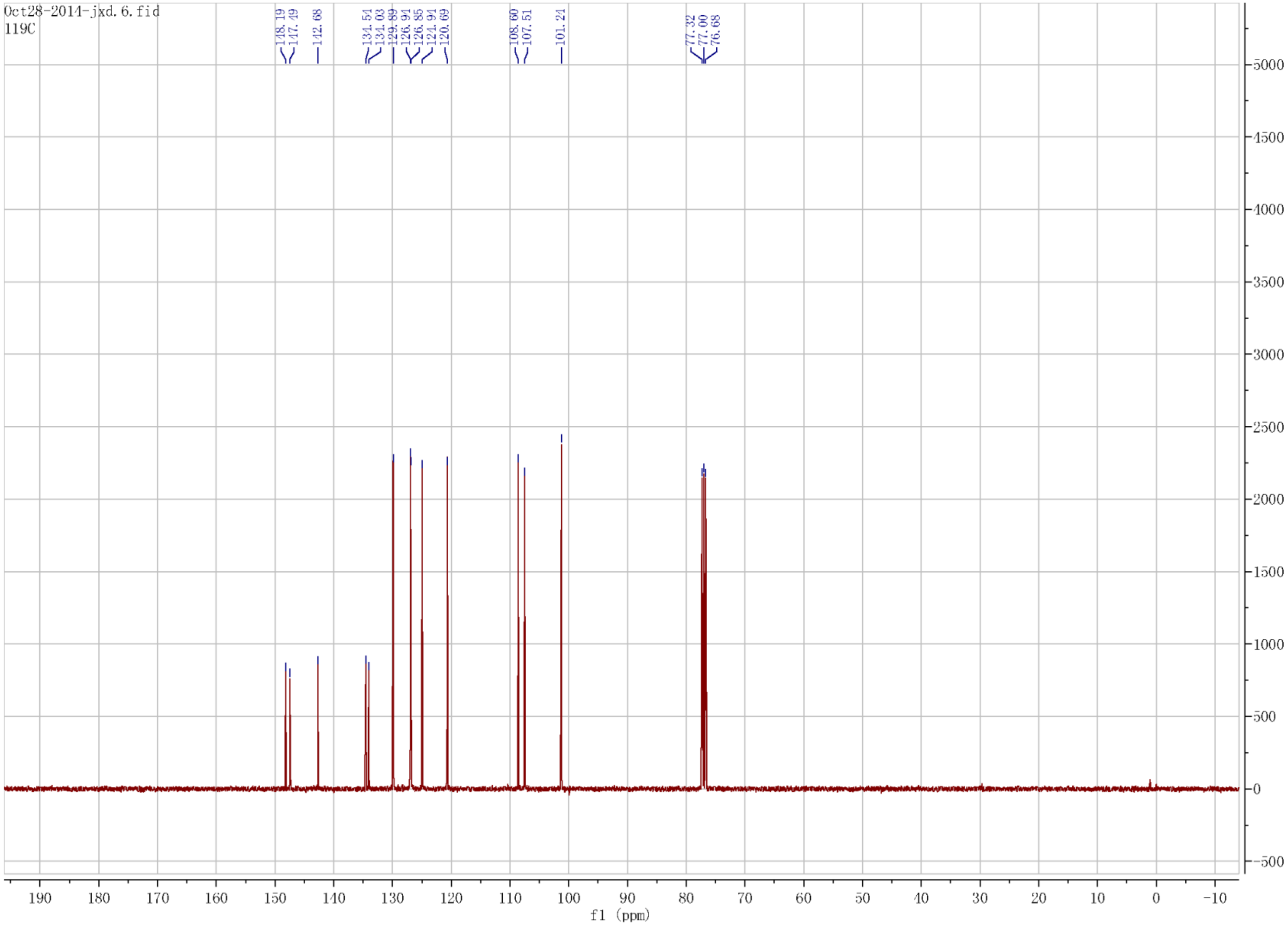



Oct28-2014-jxd.9.fid
116C1
164.37
161.9
151.8
151.69
151.5
151.40
149.35
149.22
149.05
148.92
141.36
141.29
137.00
130.51
130.42
123.08
123.04
123.01
122.98
122.59
122.56
117.76
117.59
116.14
115.96
114.75
114.54
114.13
114.03
113.91
113.81
77.32
77.00
76.68
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

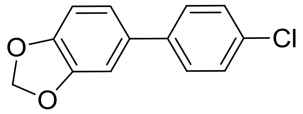
NMR spectra of compound **13a**

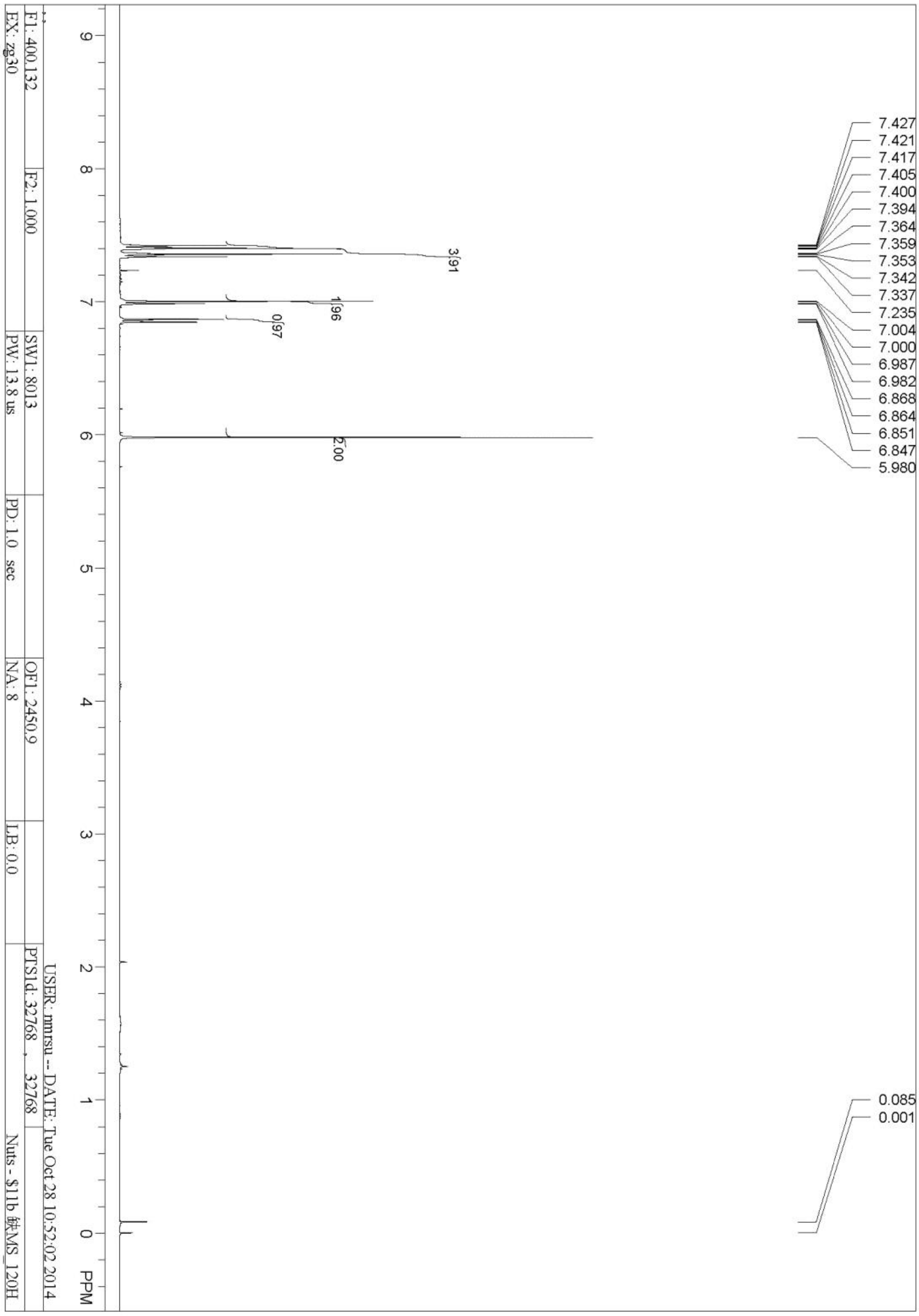


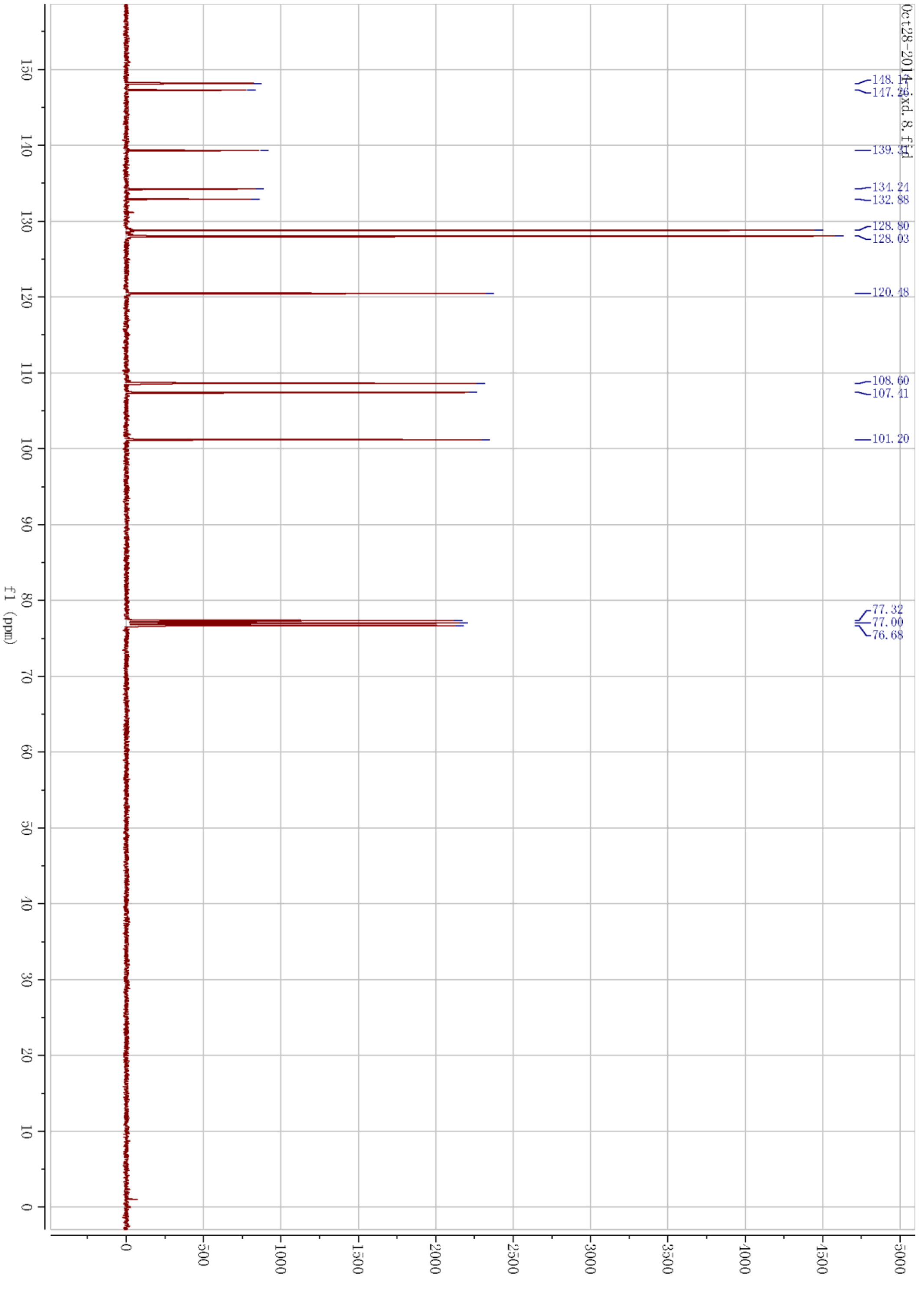



Oct28-2014-jxd.6.fid
119C
148.19
147.49
142.68
134.54
134.03
129.89
126.94
126.85
124.94
120.69
108.60
107.51
101.24
77.32
77.00
76.68
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

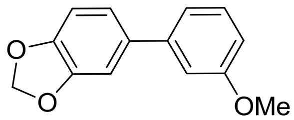
NMR spectra of compound **13b**

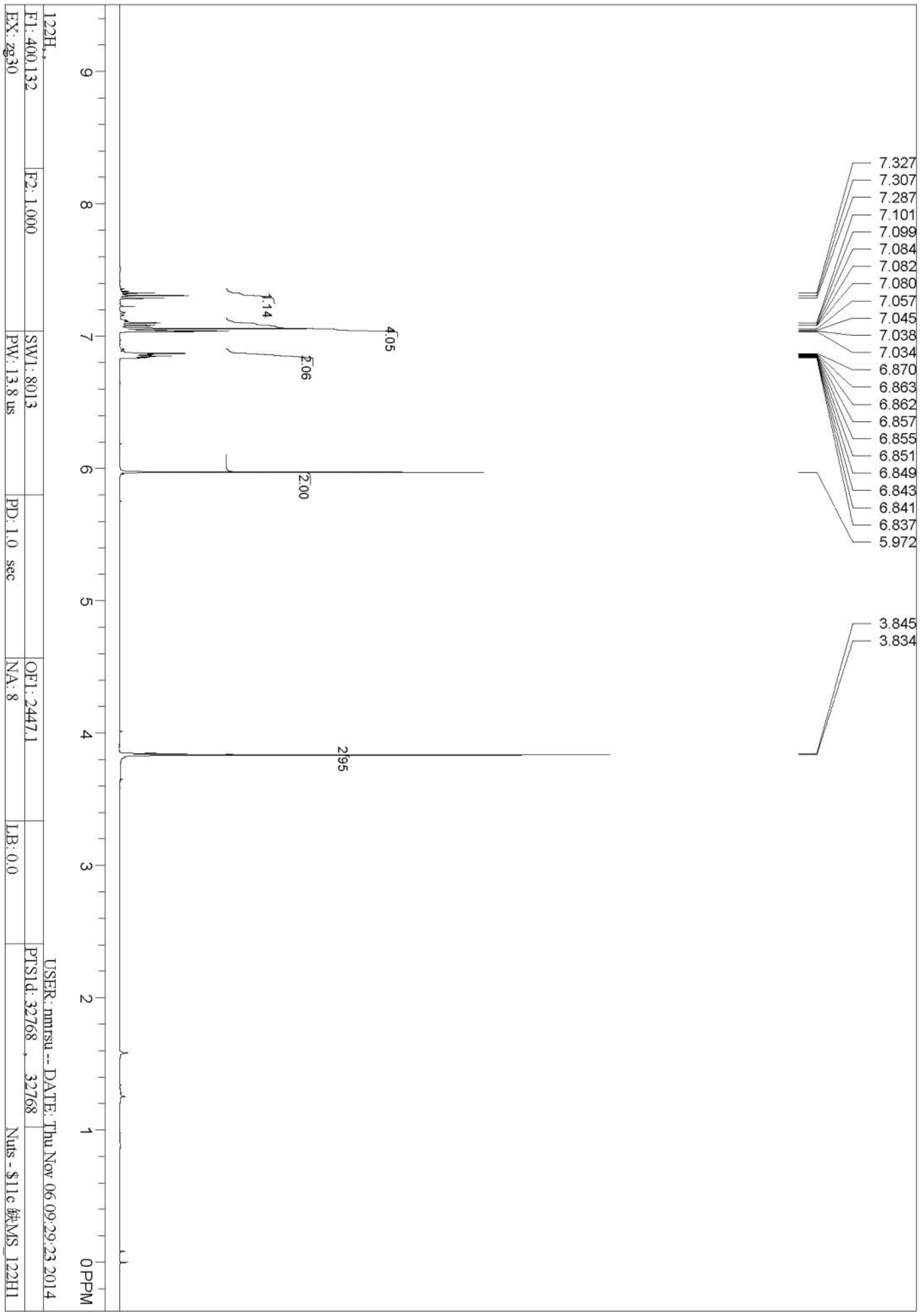


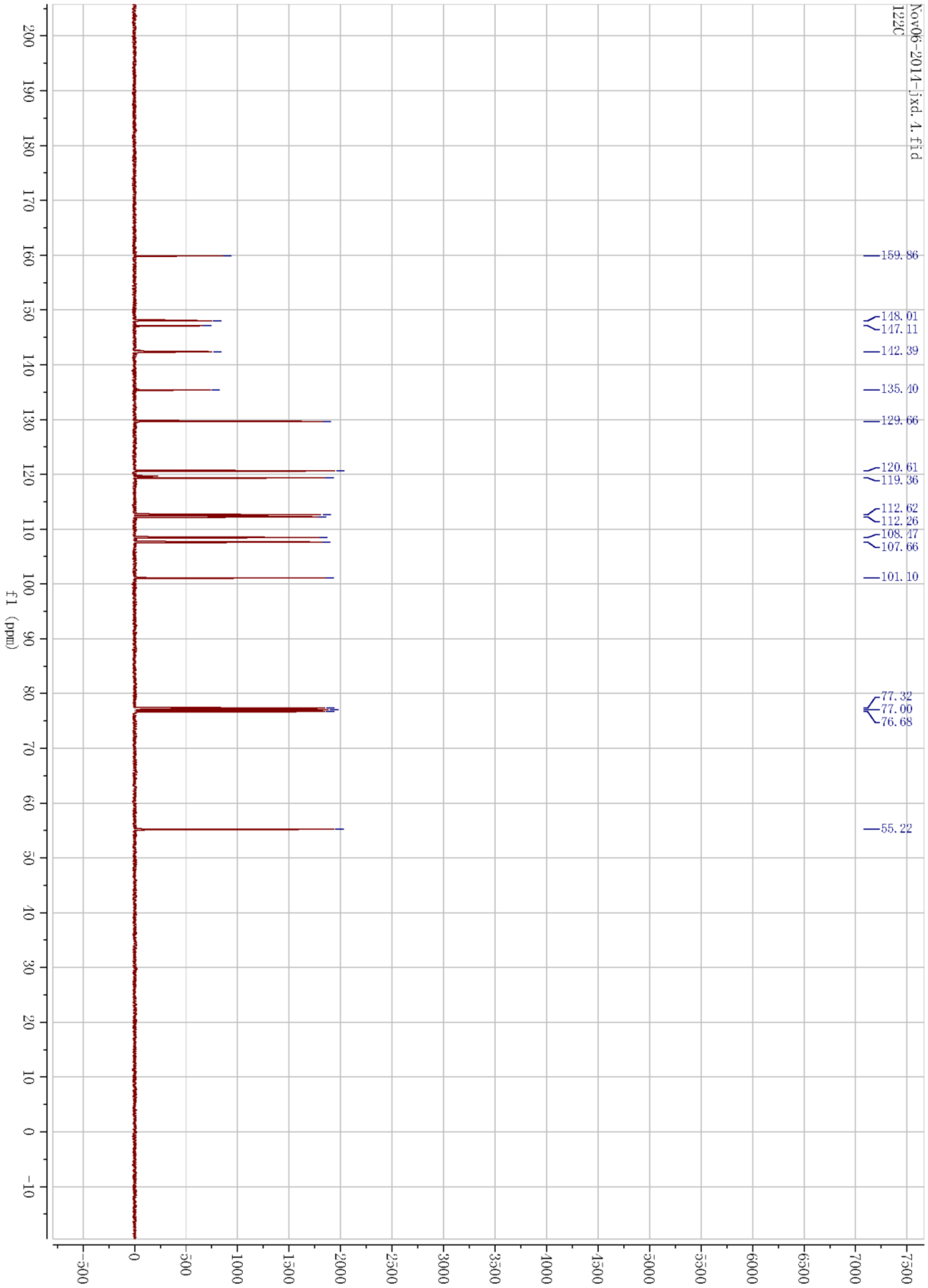


Oct28-2014-xxd.8.fid
148.11
147.26
139.31
134.24
132.88
128.80
128.03
120.48
108.60
107.41
101.20
77.32
77.00
76.68
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000

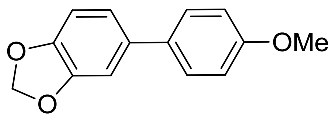
NMR spectra of compound **13c**

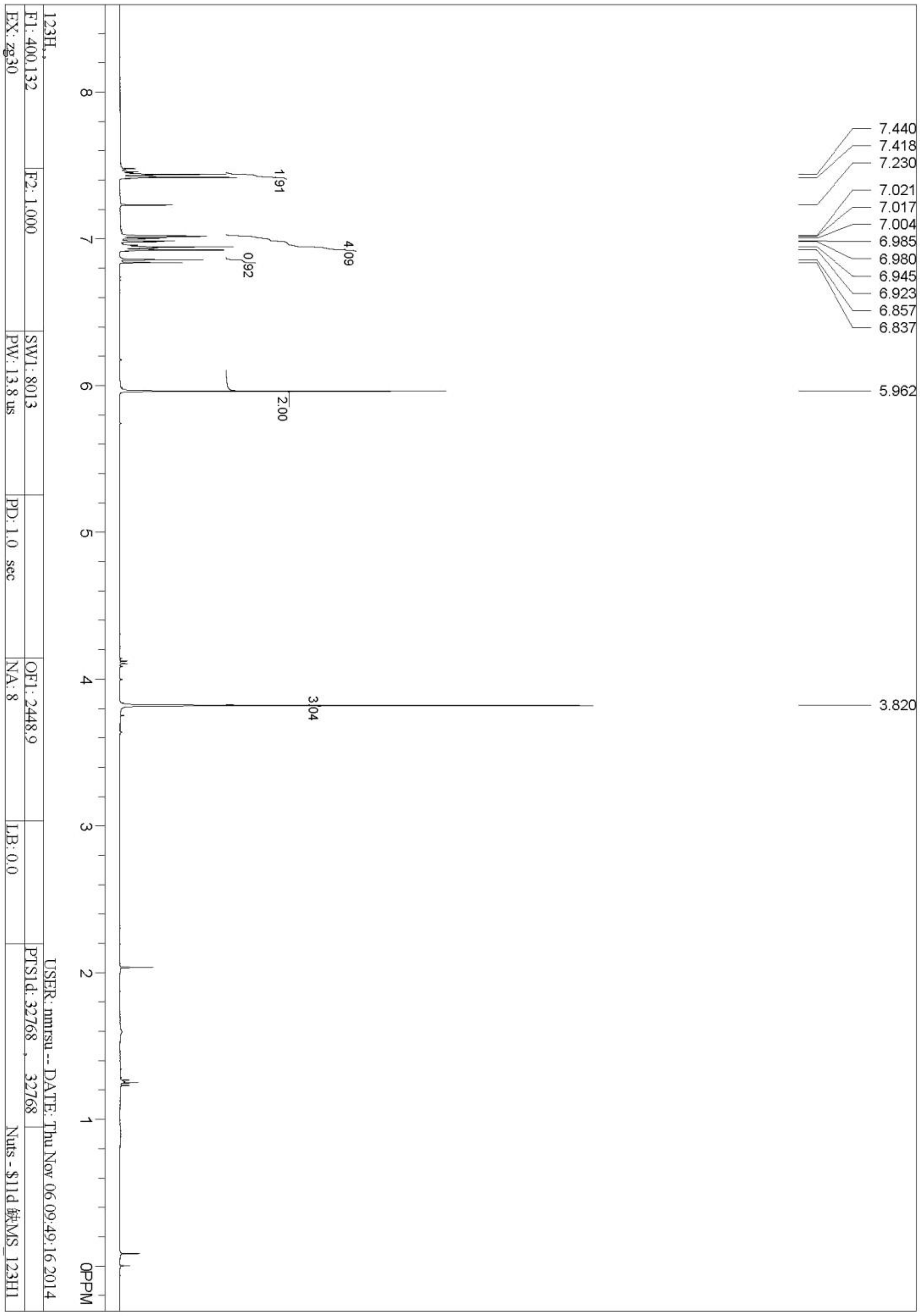


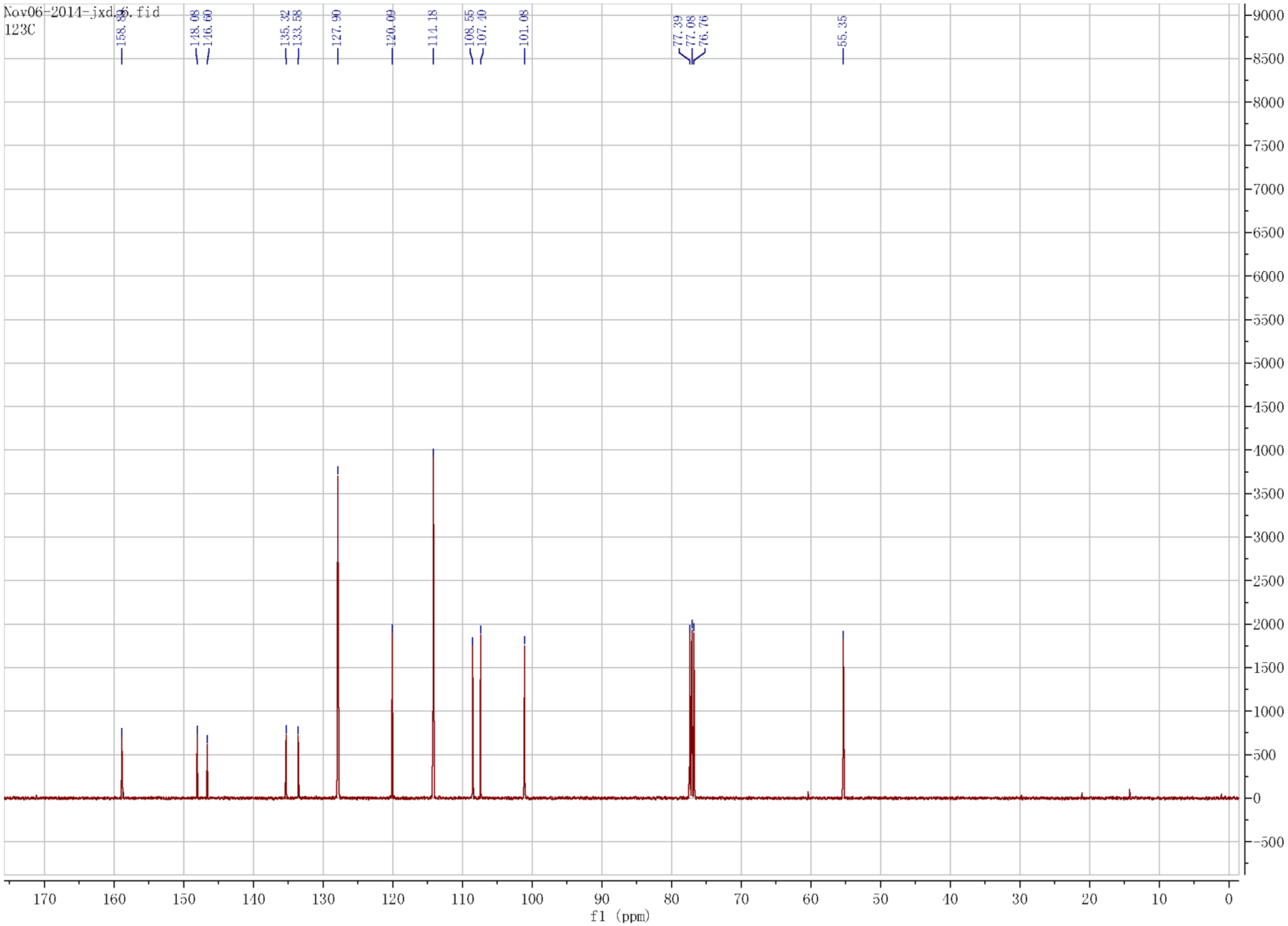



Nov06-2014-jxd.4.fid
122C
159.86
148.01
147.11
142.39
135.40
129.66
120.61
119.36
112.62
112.26
108.47
107.66
101.10
77.32
77.00
76.68
55.22
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
7500

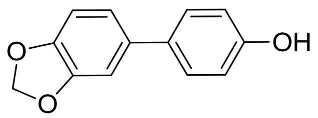
NMR spectra of compound **13d**

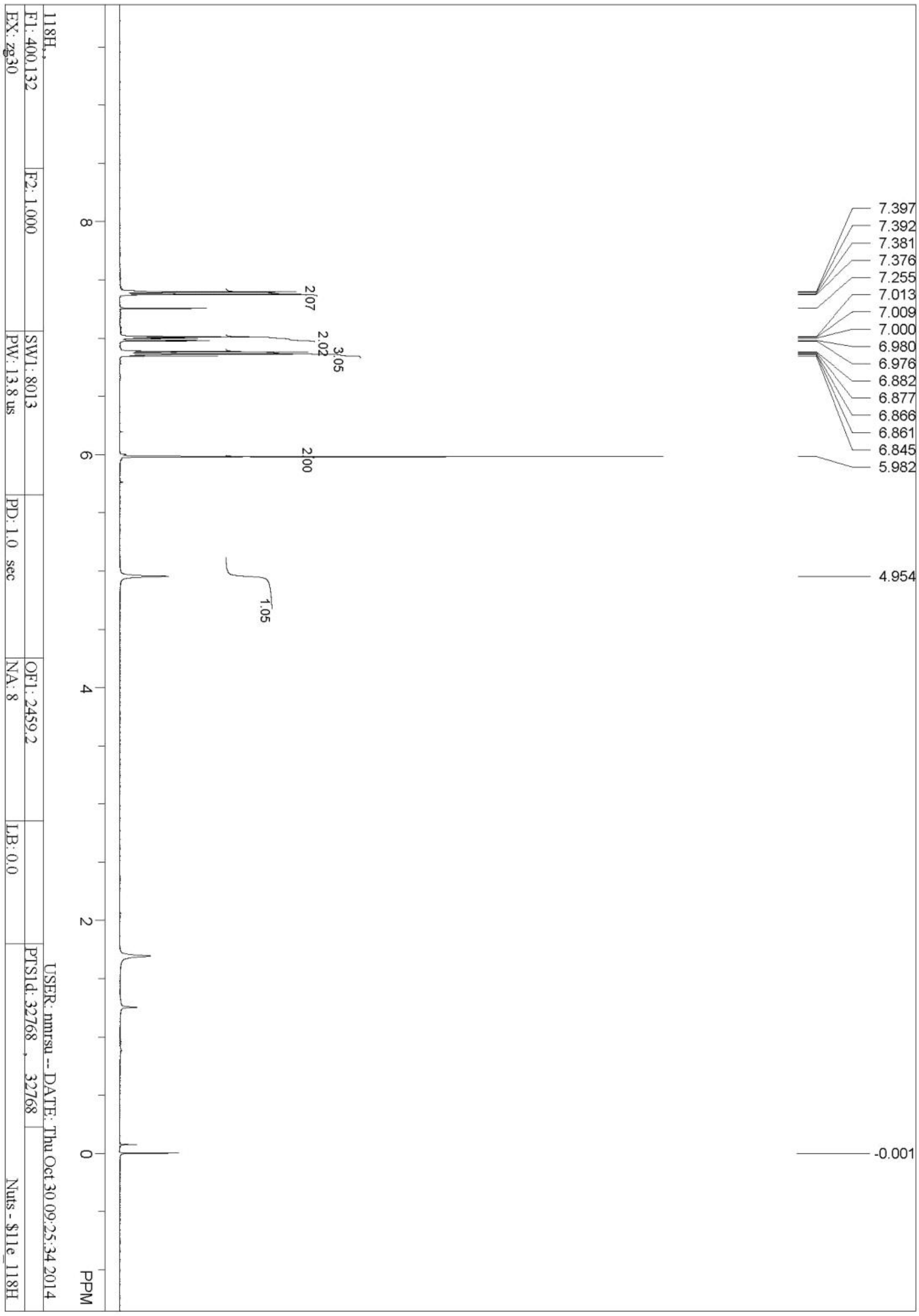


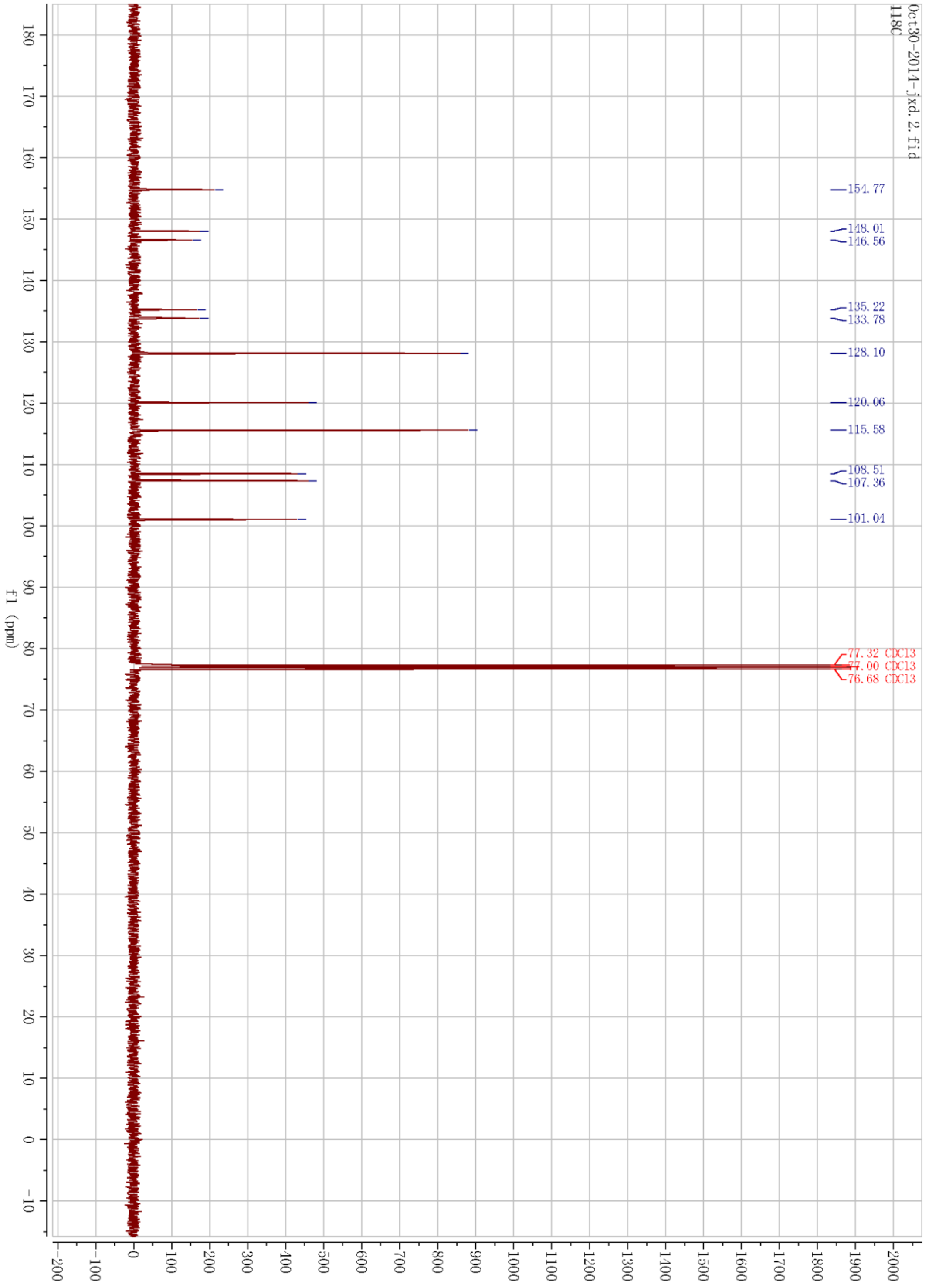



Nov06-2014-jxd-6.fid
123C
158.89
148.08
146.60
135.32
133.58
127.90
120.09
114.18
108.55
107.40
101.08
77.39
77.08
76.76
55.35
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

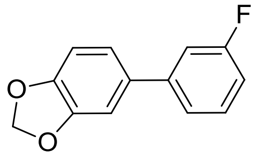
NMR spectra of compound **13e**

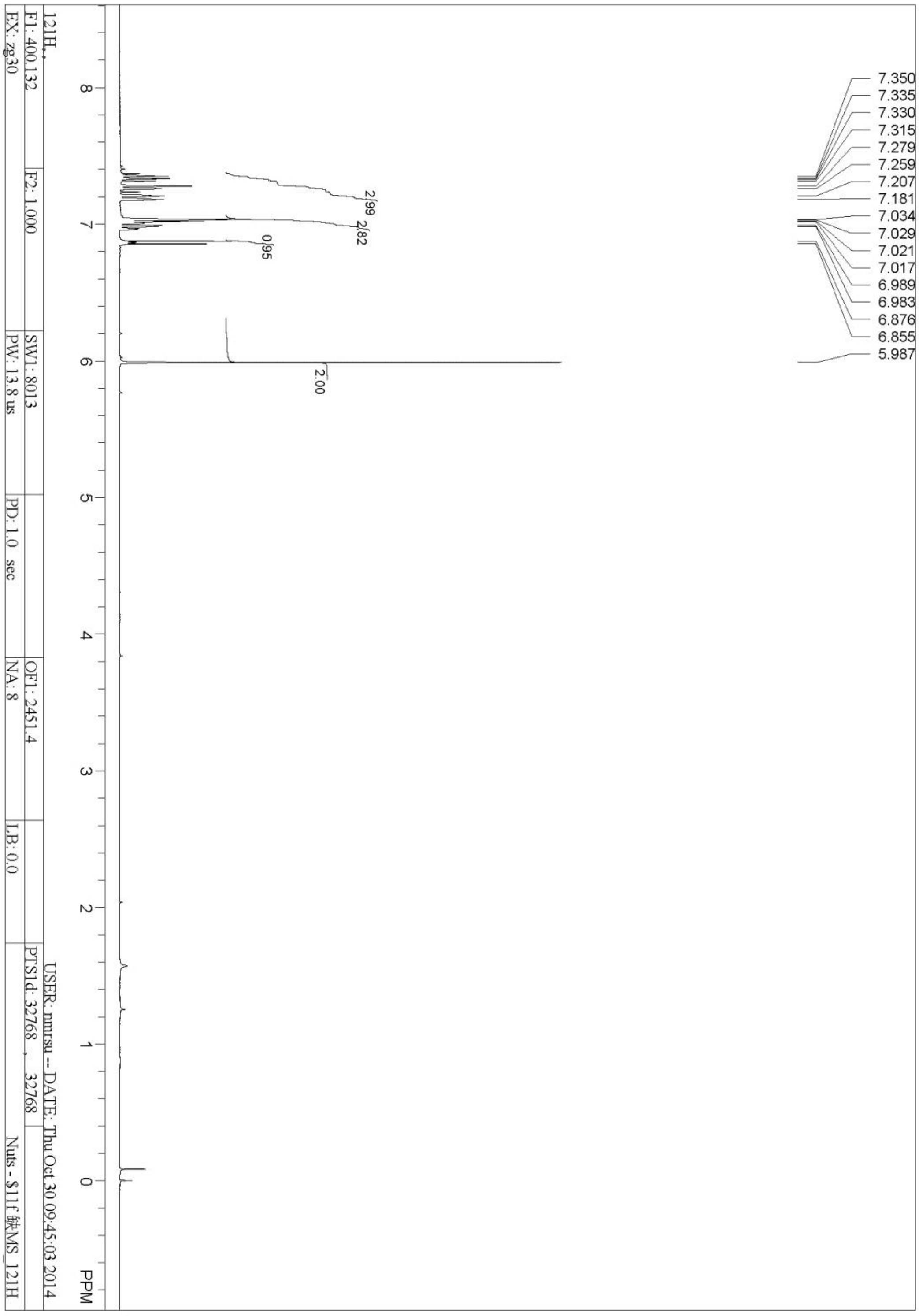


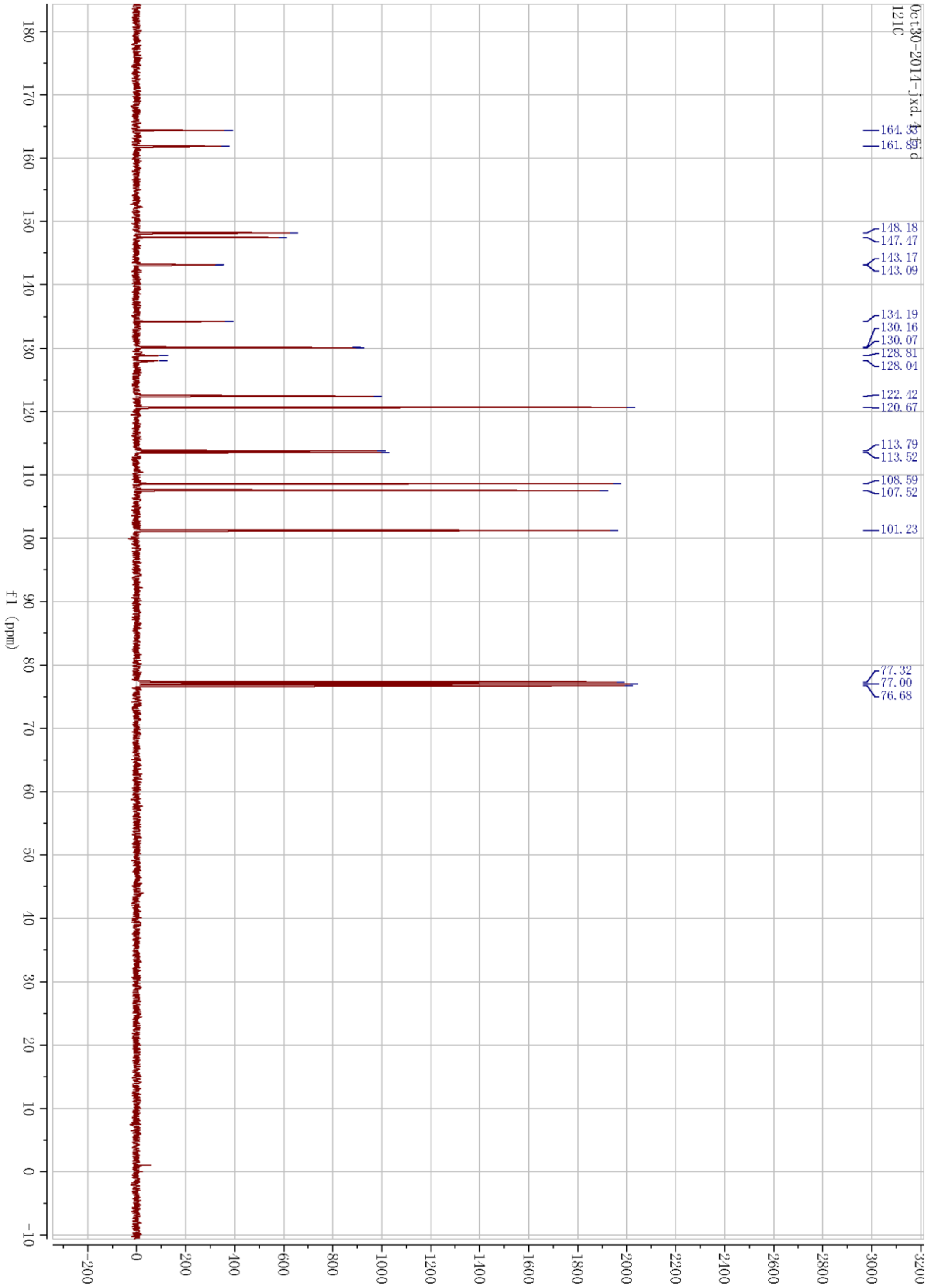



Oct30-2014-jxd.2.fid
118C
154.77
148.01
146.56
135.22
133.78
128.10
120.06
115.58
108.51
107.36
101.04
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-200
-100
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000

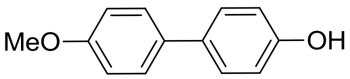
NMR spectra of compound **13f**

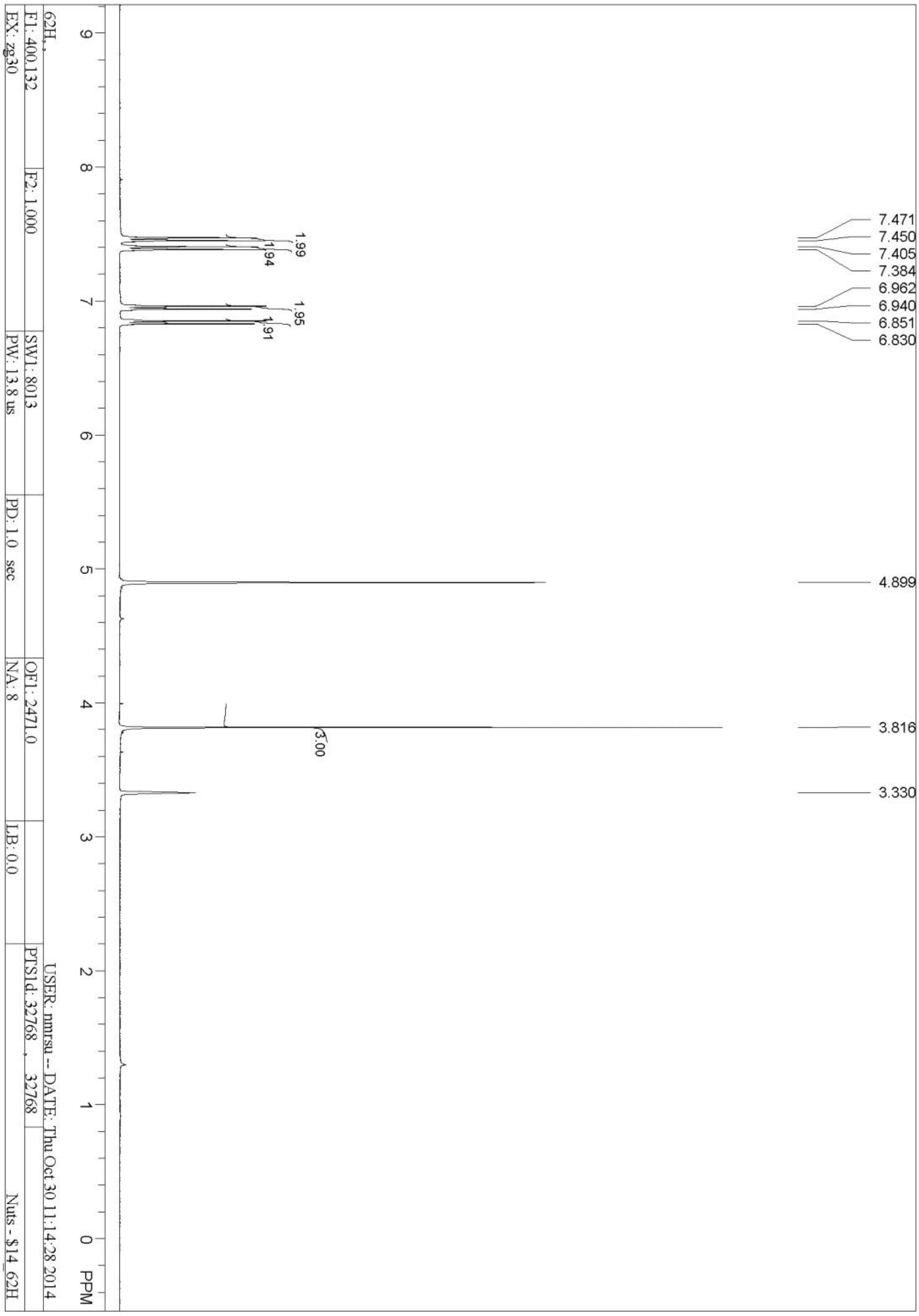


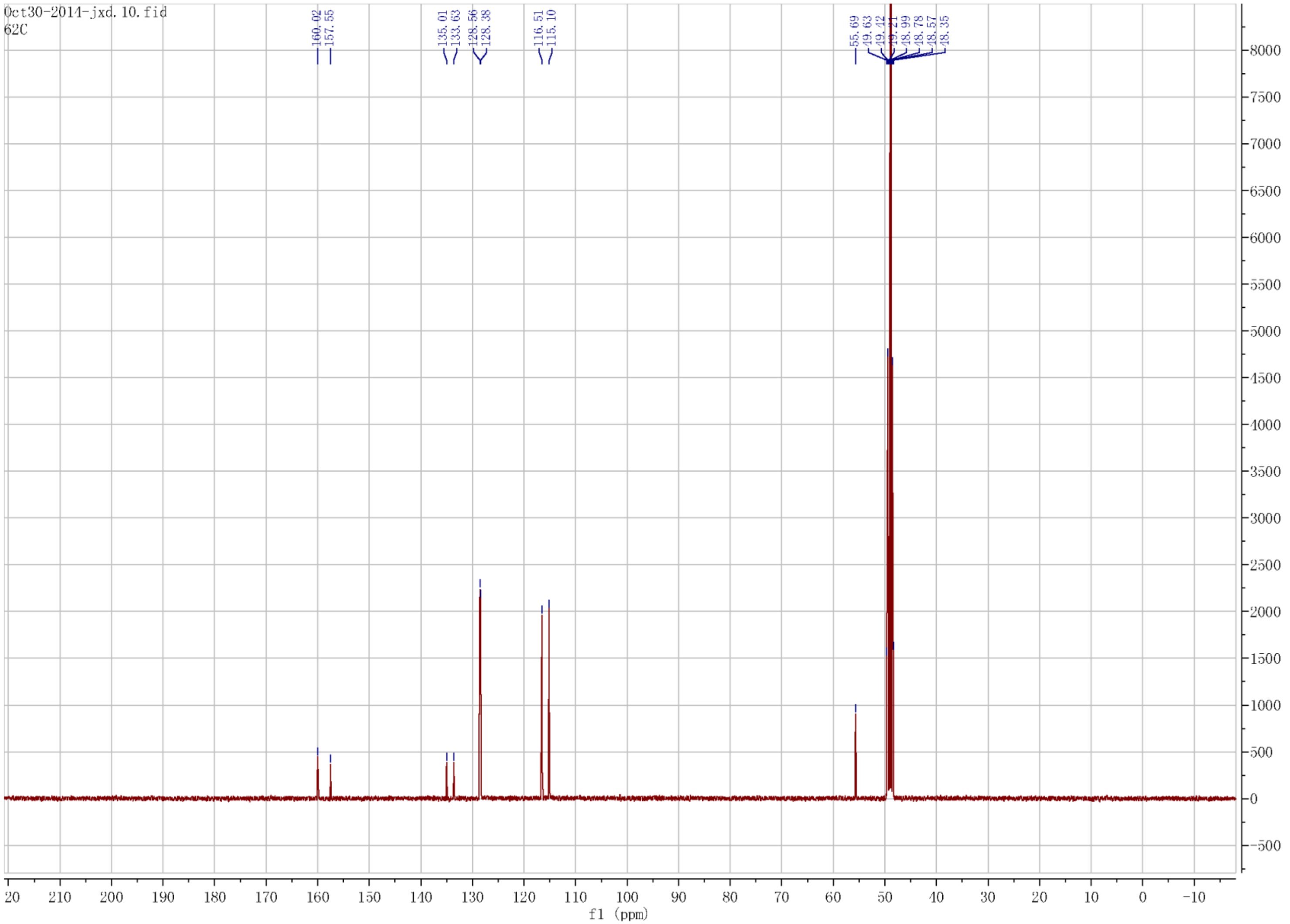



Oct30-2014-jxd.45.fid
121C
164.33
161.85
148.18
147.47
143.17
143.09
134.19
130.16
130.07
128.81
128.04
122.42
120.67
113.79
113.52
108.59
107.52
101.23
77.32
77.00
76.68
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-200
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200

NMR spectra of compound **14a**

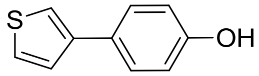


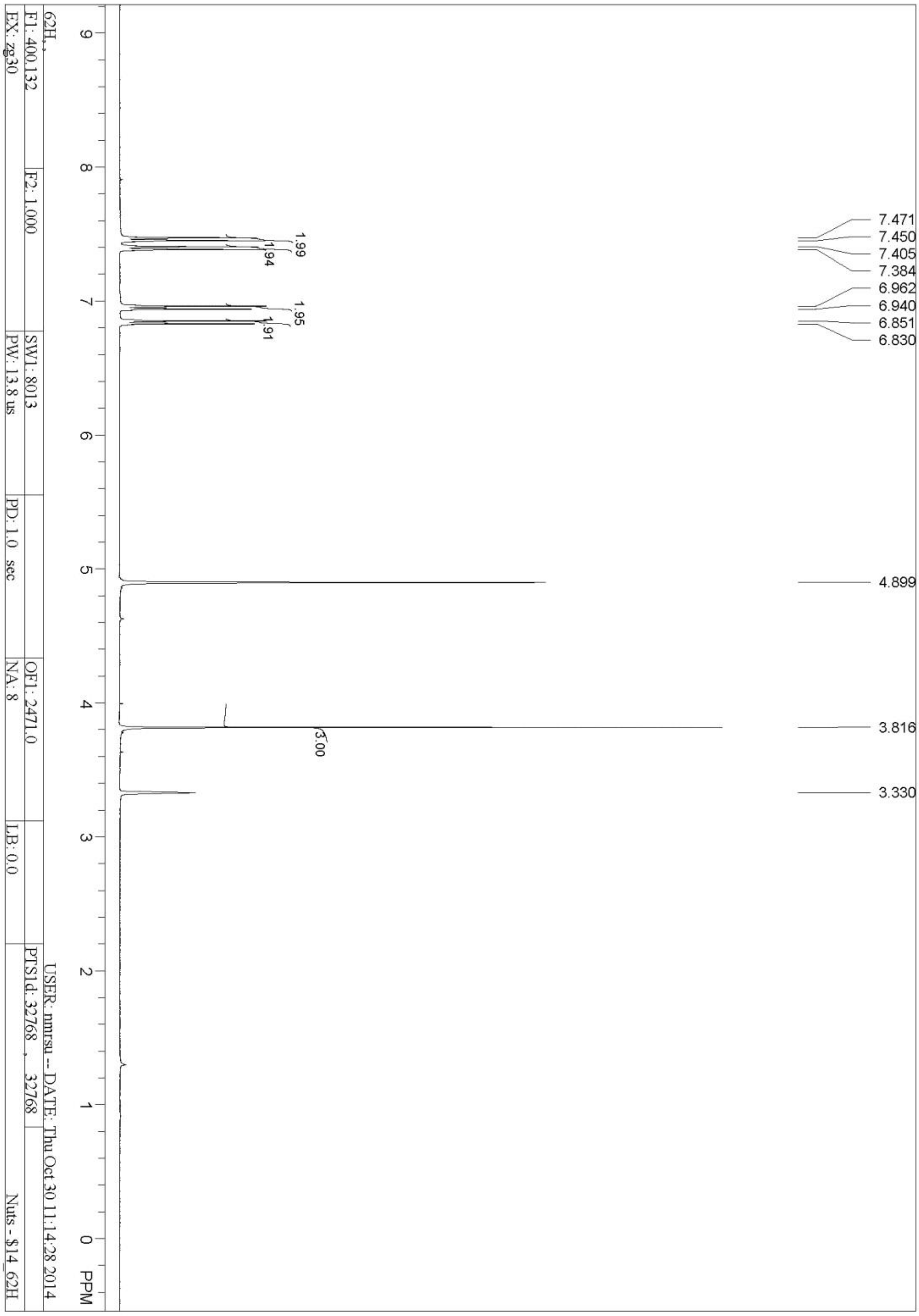


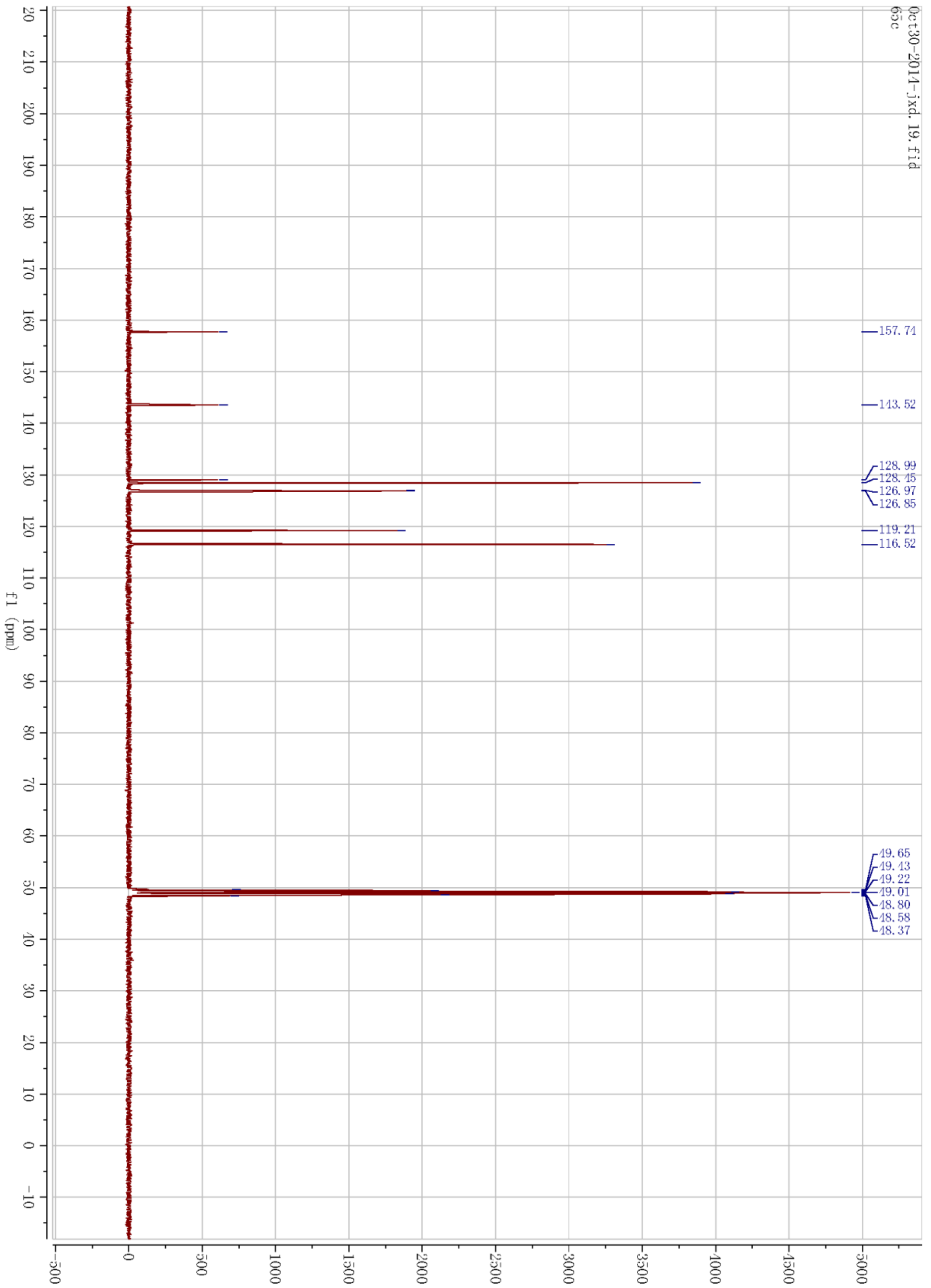


Oct30-2014-jxd.10.fid
62C
160.02
157.55
135.01
133.63
128.56
128.38
116.51
115.10
55.69
49.63
49.42
49.21
48.99
48.78
48.57
48.35
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

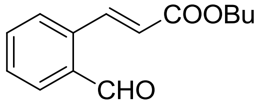
NMR spectra of compound **14b**

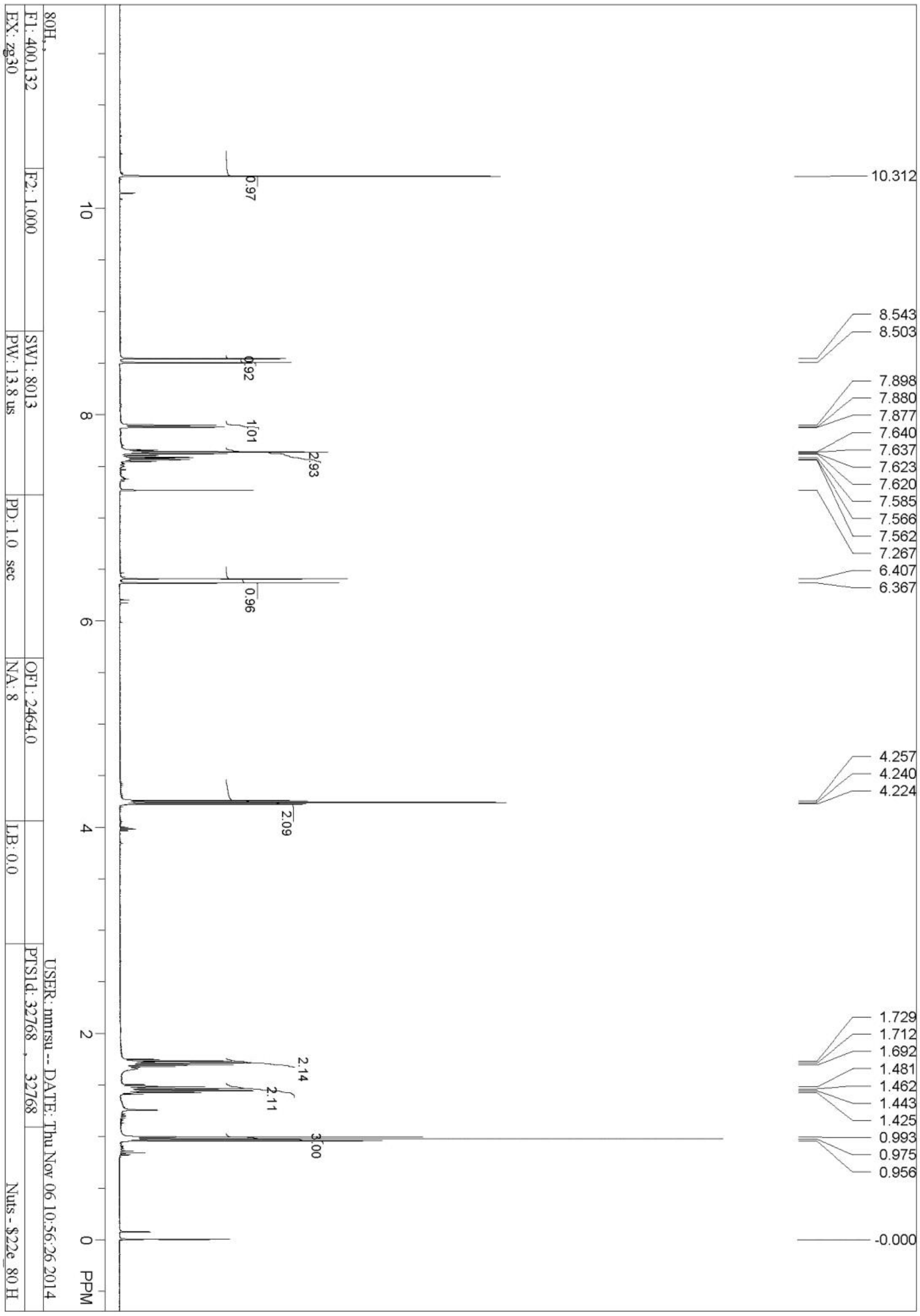


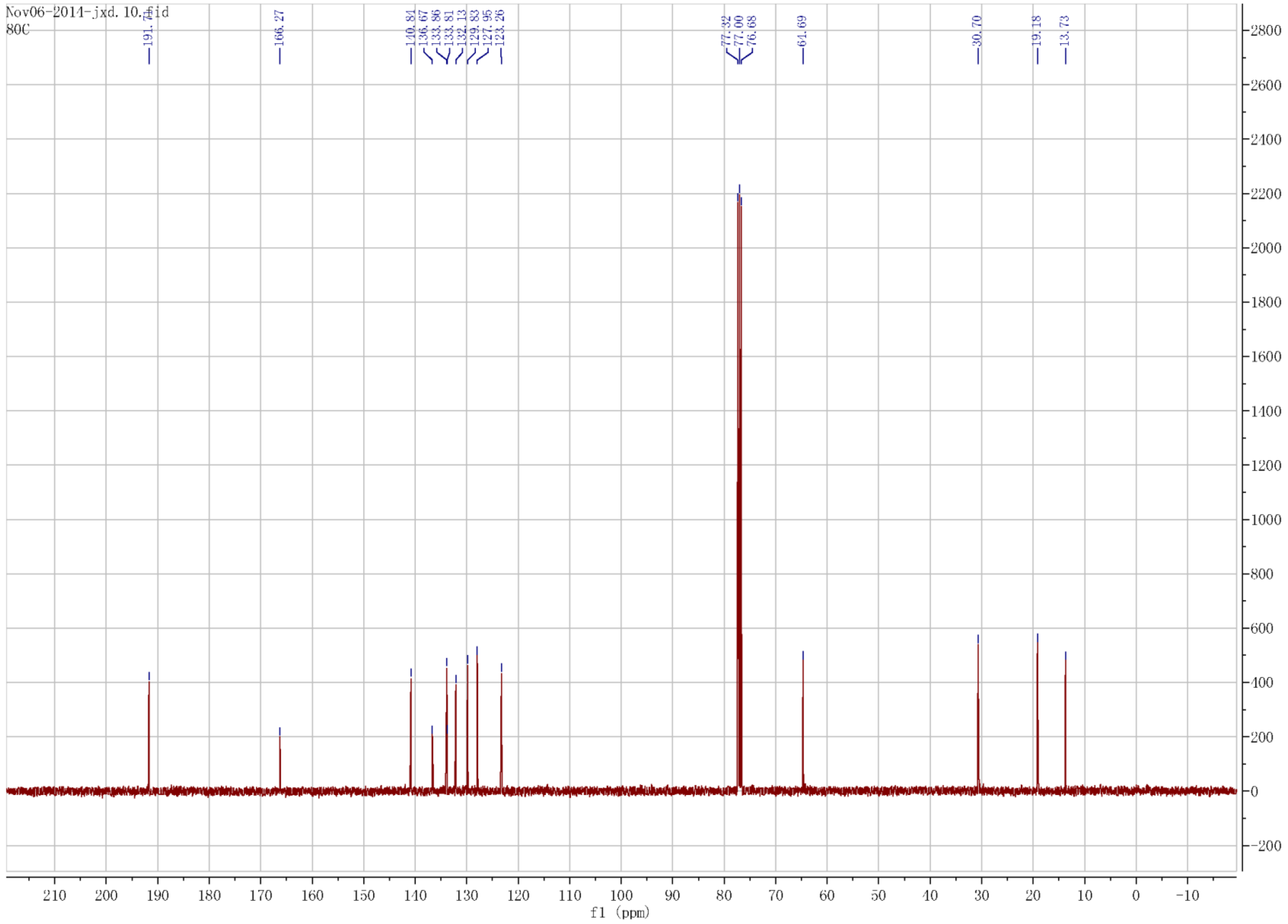



Oct30-2014-jxd.19.fid
65c
157.74
143.52
128.99
128.45
126.97
126.85
119.21
116.52
49.65
49.43
49.22
49.01
48.80
48.58
48.37
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000

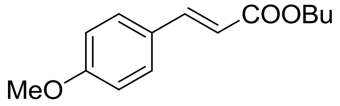
NMR spectra of compound **20a**

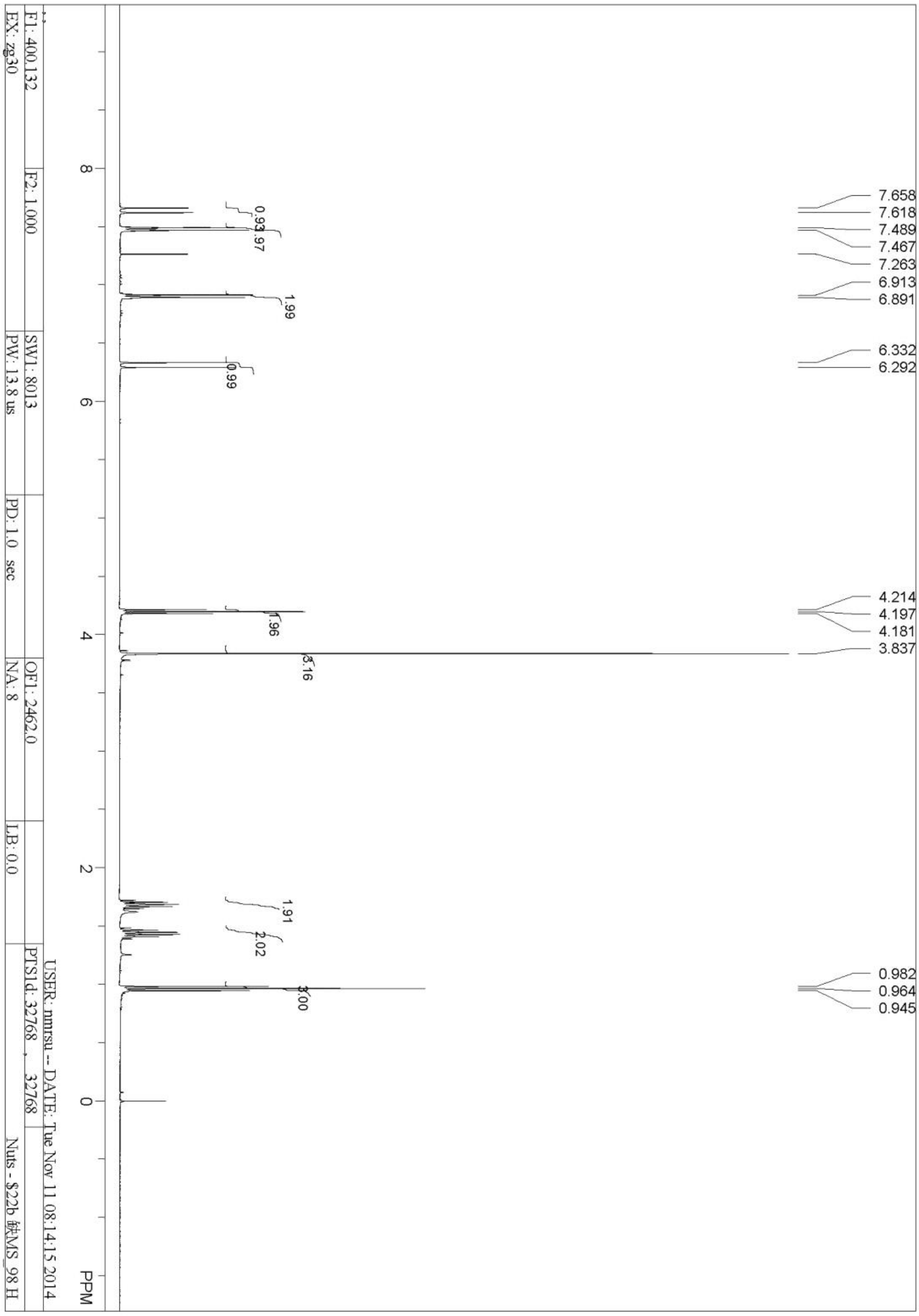


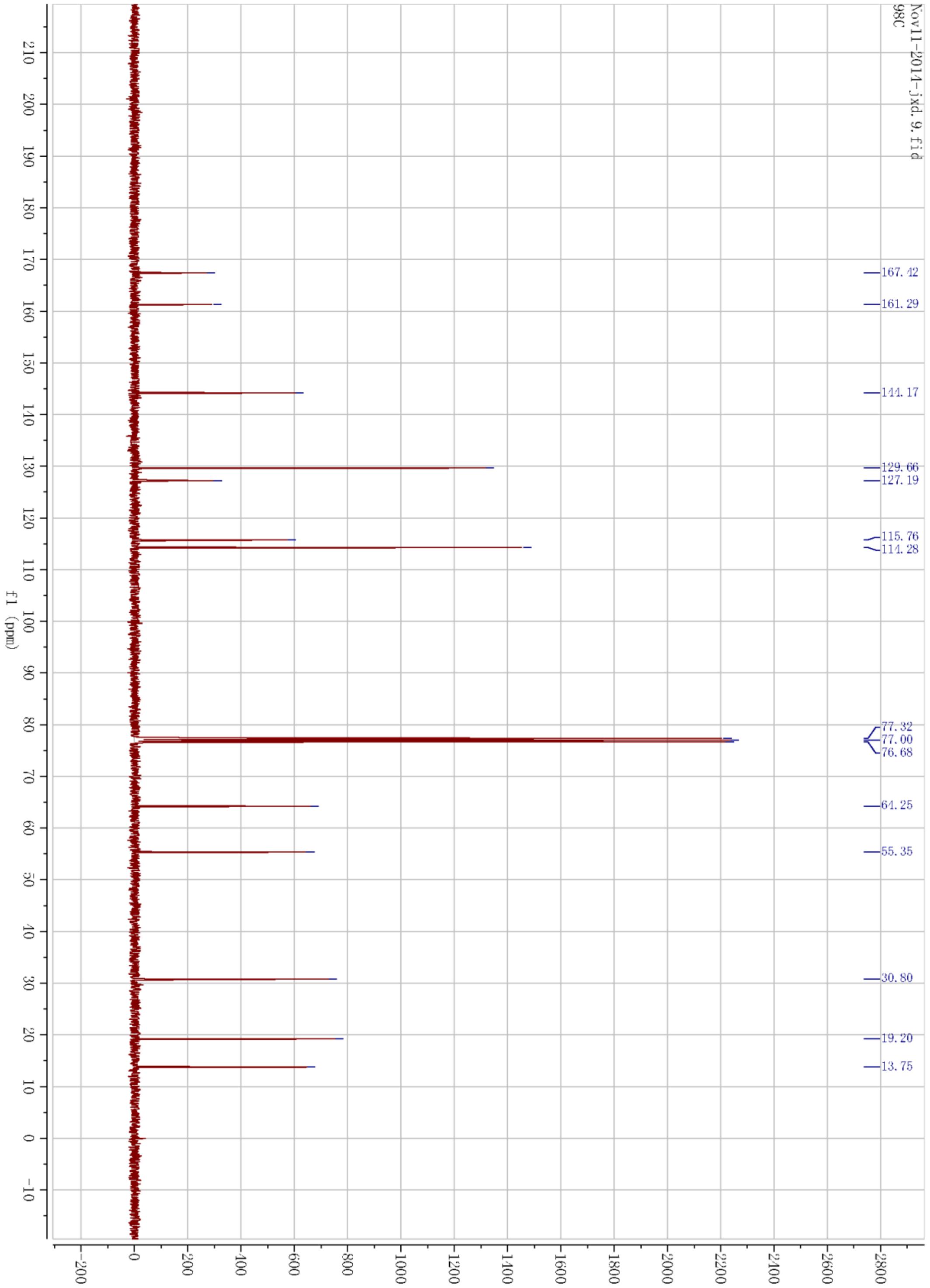



Nov06-2014-jxd.10.fid
80C
191.71
166.27
140.84
136.67
133.86
133.81
132.13
129.83
127.95
123.26
77.32
77.00
76.68
64.69
30.70
19.18
13.73
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

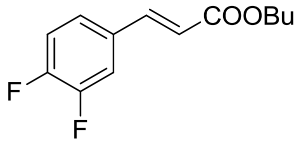
NMR spectra of compound **20b**

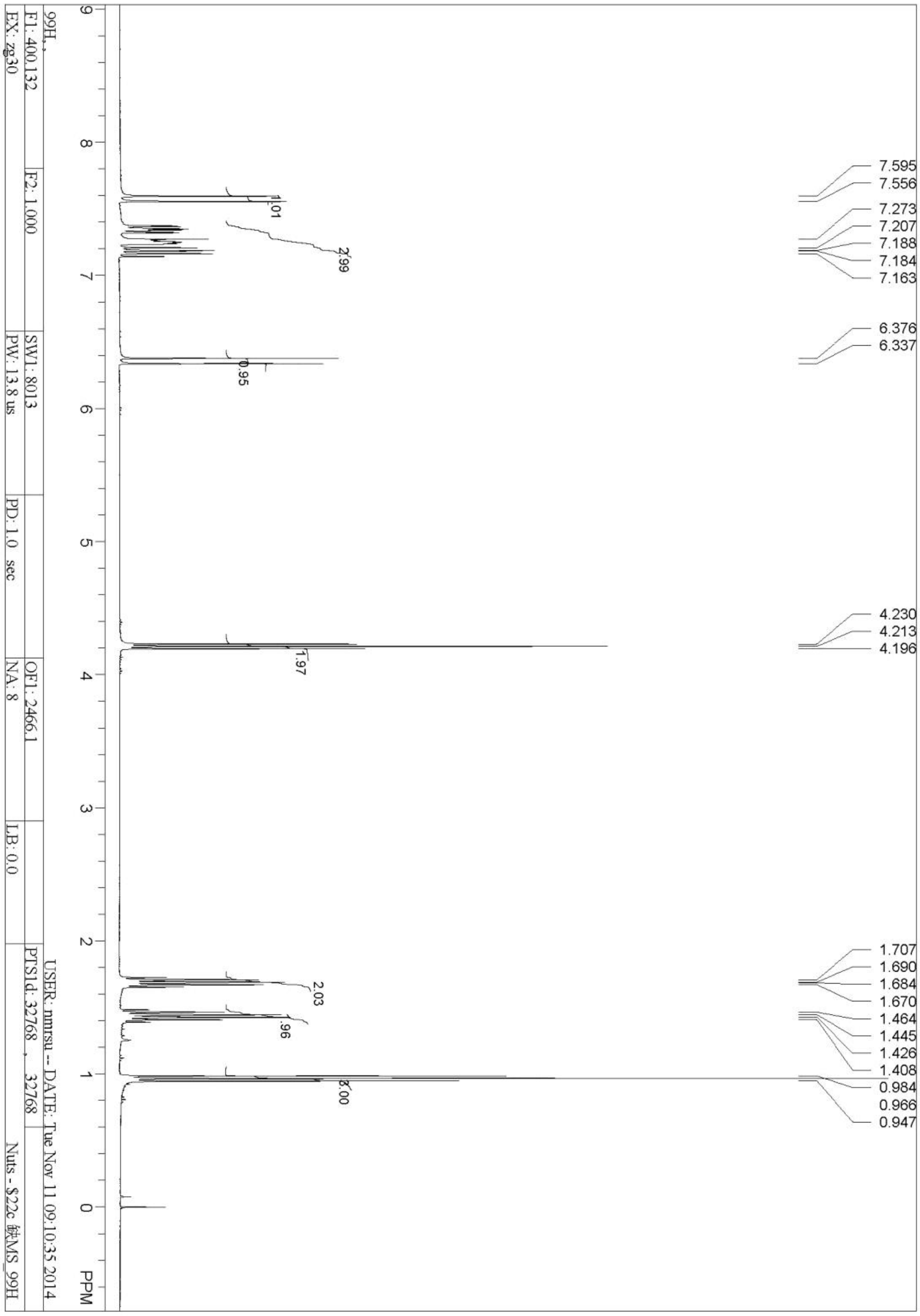


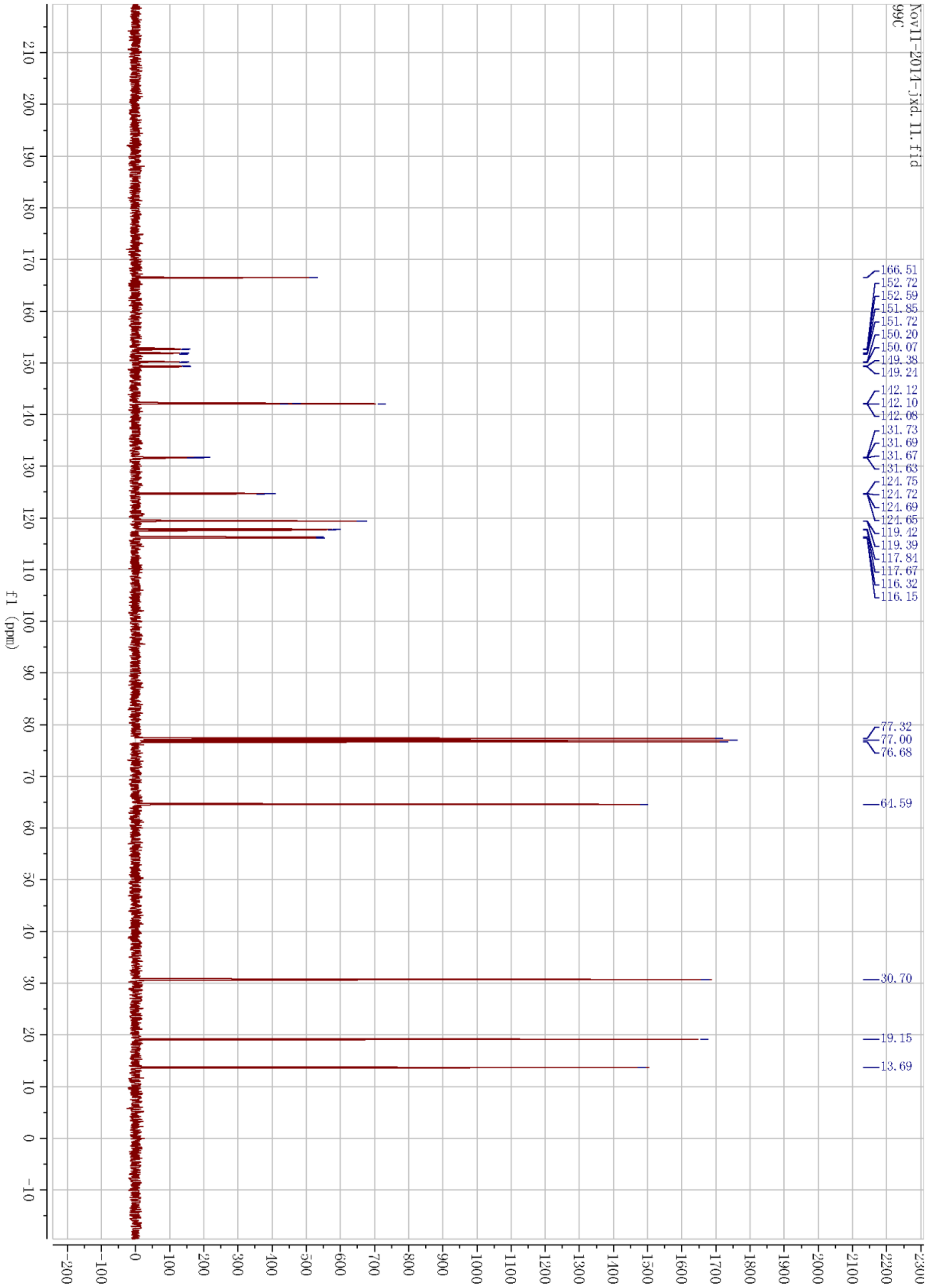



Nov11-2014-jxd.9.fid
98C
167.42
161.29
144.17
129.66
127.19
115.76
114.28
77.32
77.00
76.68
64.25
55.35
30.80
19.20
13.75
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-200
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800

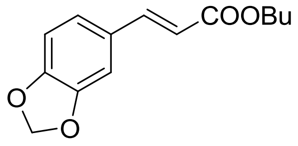
NMR spectra of compound **20c**

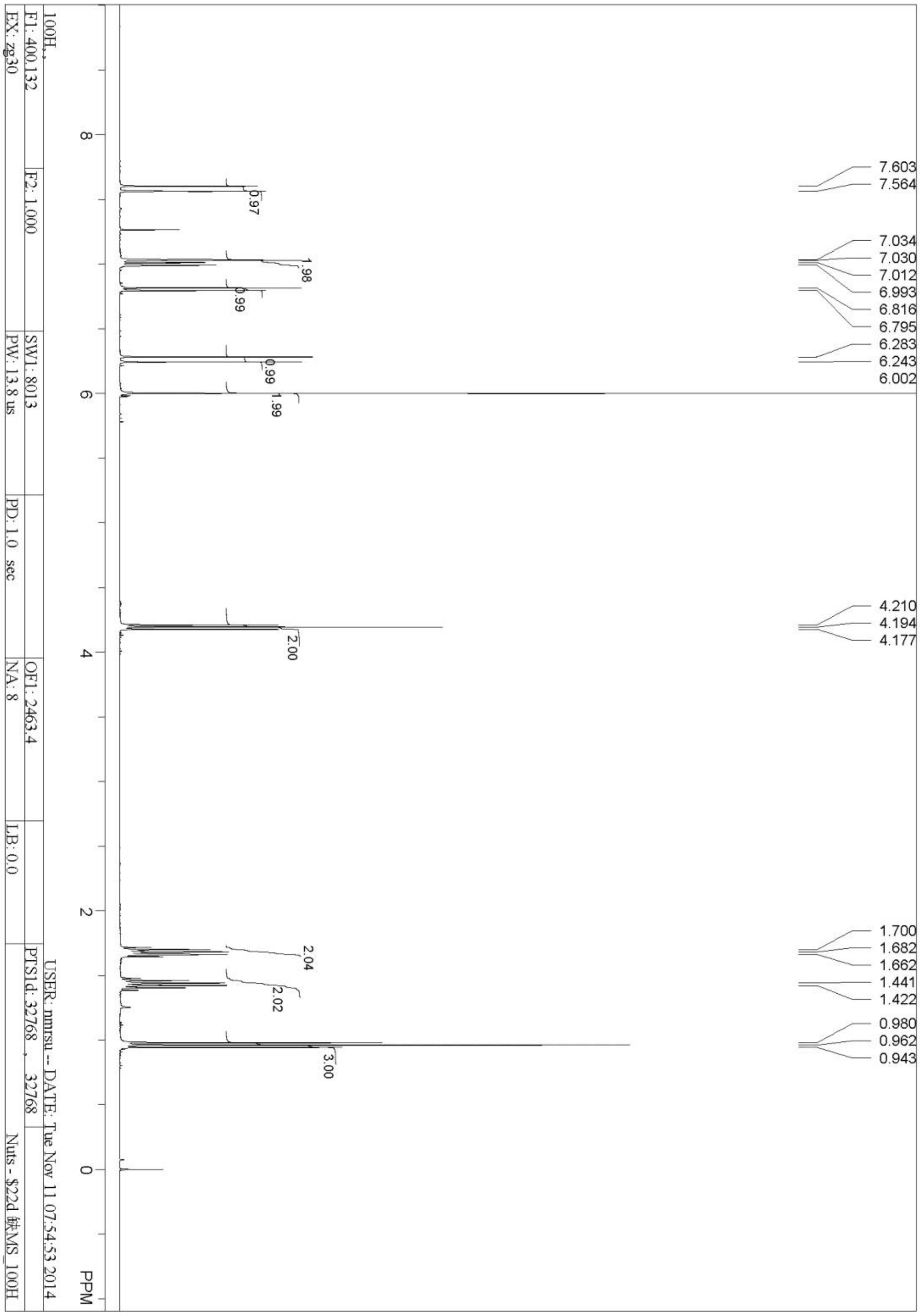


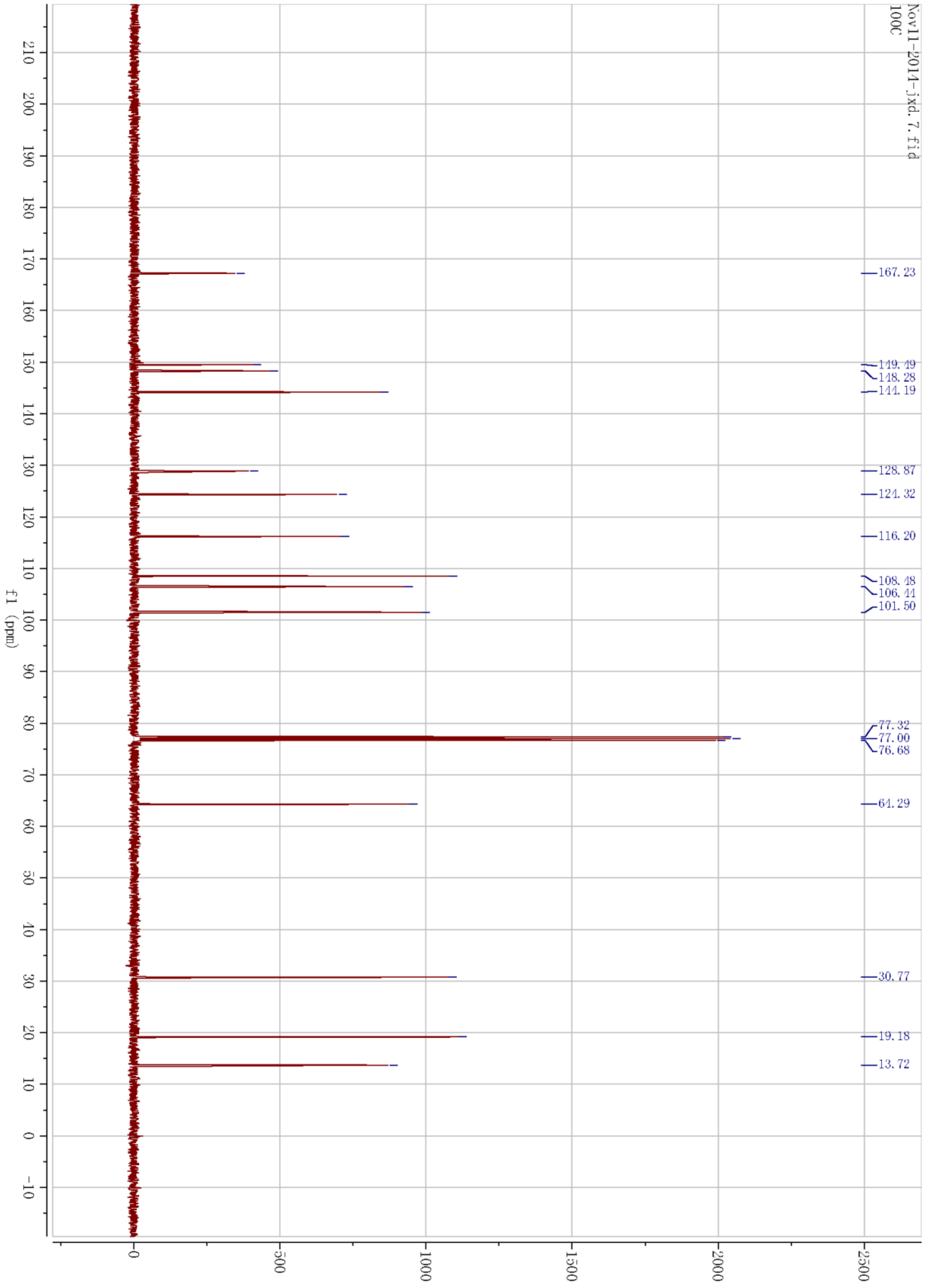



Nov11-2014-jxd.11.fid
99C
166.51
152.72
152.59
151.85
151.72
150.20
150.07
149.38
149.24
142.12
142.10
142.08
131.73
131.69
131.67
131.63
124.75
124.72
124.69
124.65
119.42
119.39
117.84
117.67
116.32
116.15
77.32
77.00
76.68
64.59
30.70
19.15
13.69
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-200
-100
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
2100
2200
2300

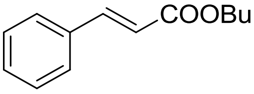
NMR spectra of compound **20d**

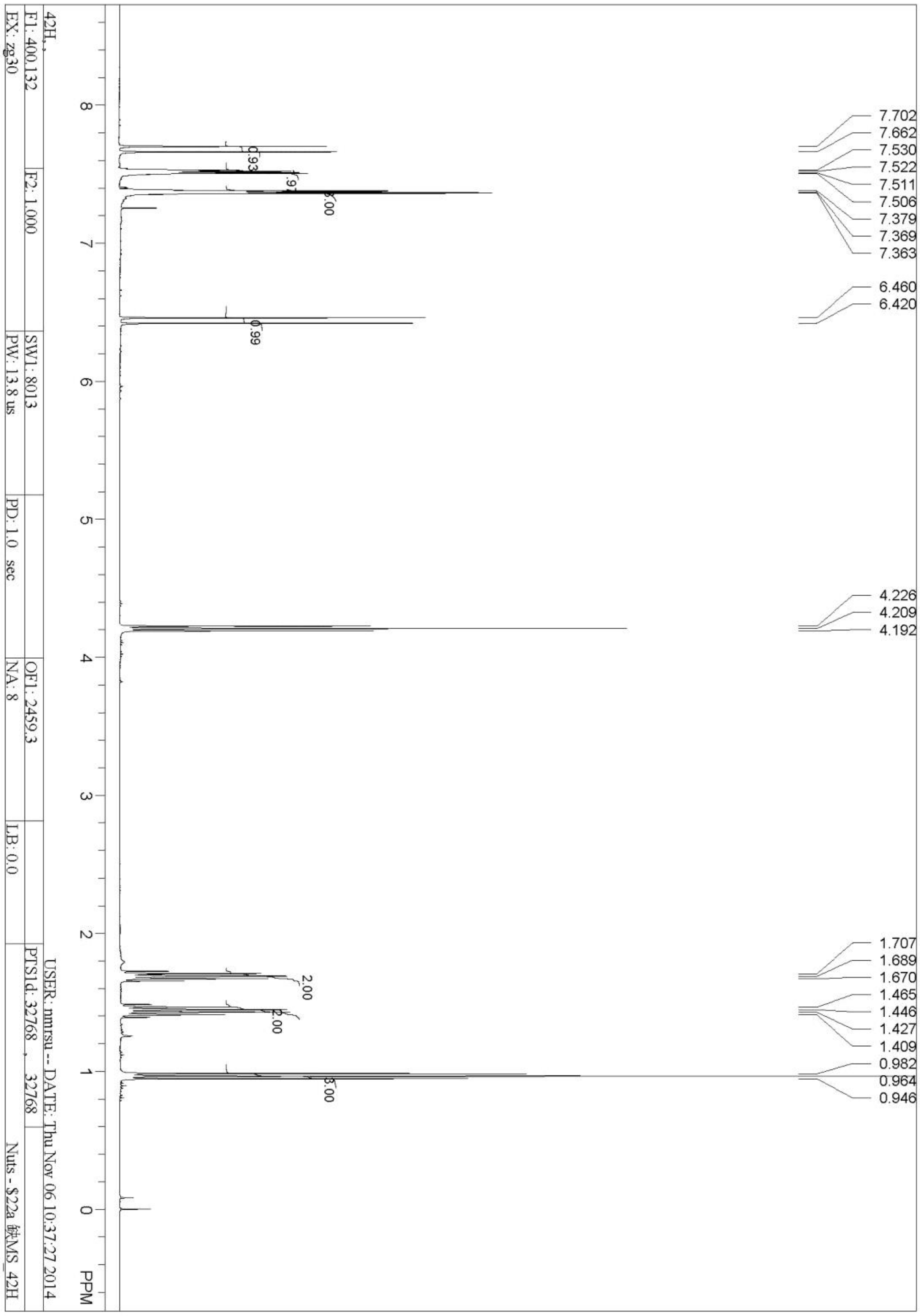


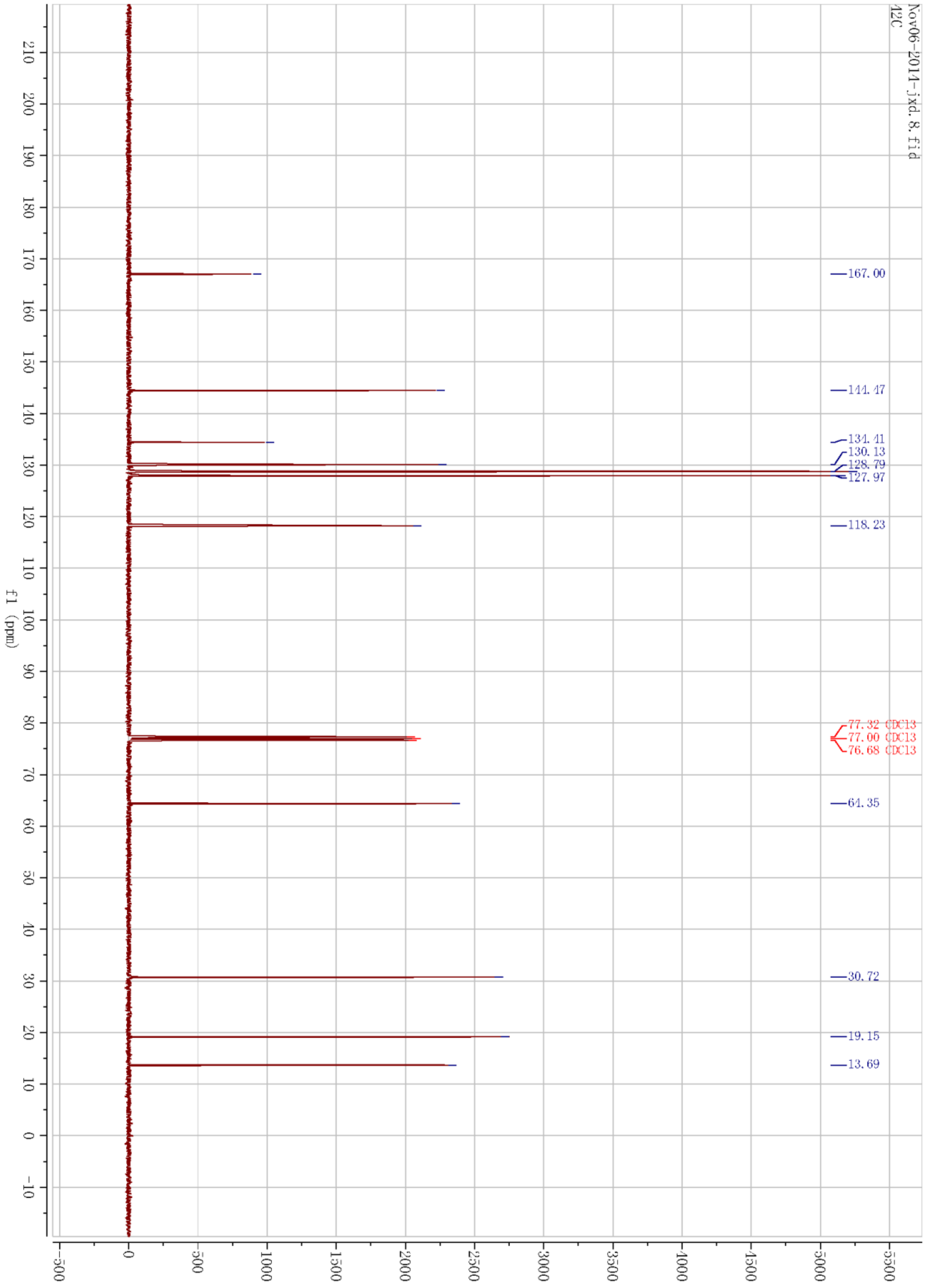



Nov11-2014-jxd.7.fid
100C
167.23
149.49
148.28
144.19
128.87
124.32
116.20
108.48
106.44
101.50
77.32
77.00
76.68
64.29
30.77
19.18
13.72
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
0
500
1000
1500
2000
2500

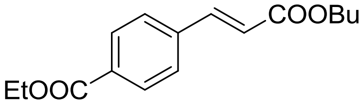
NMR spectra of compound **20e**

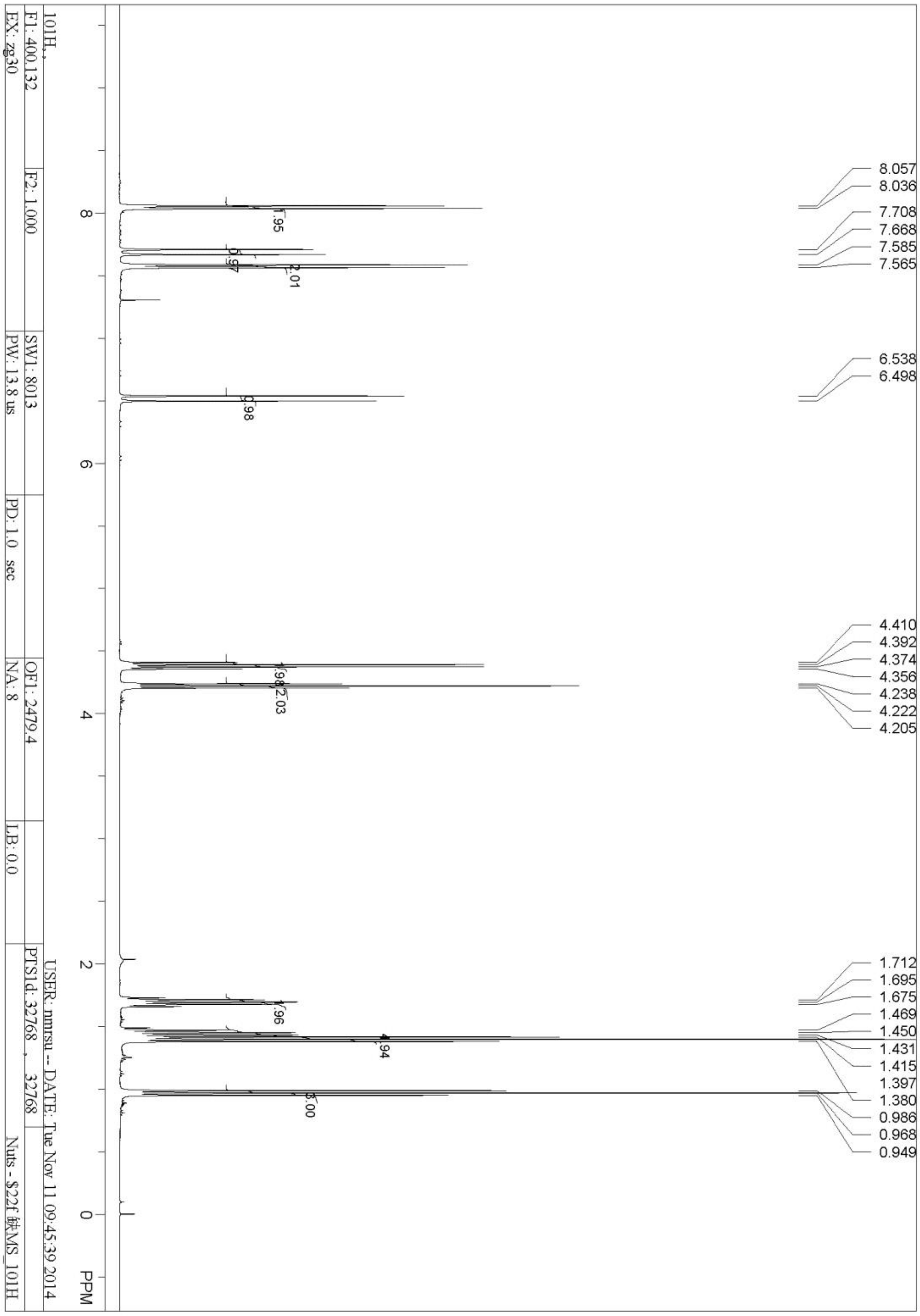


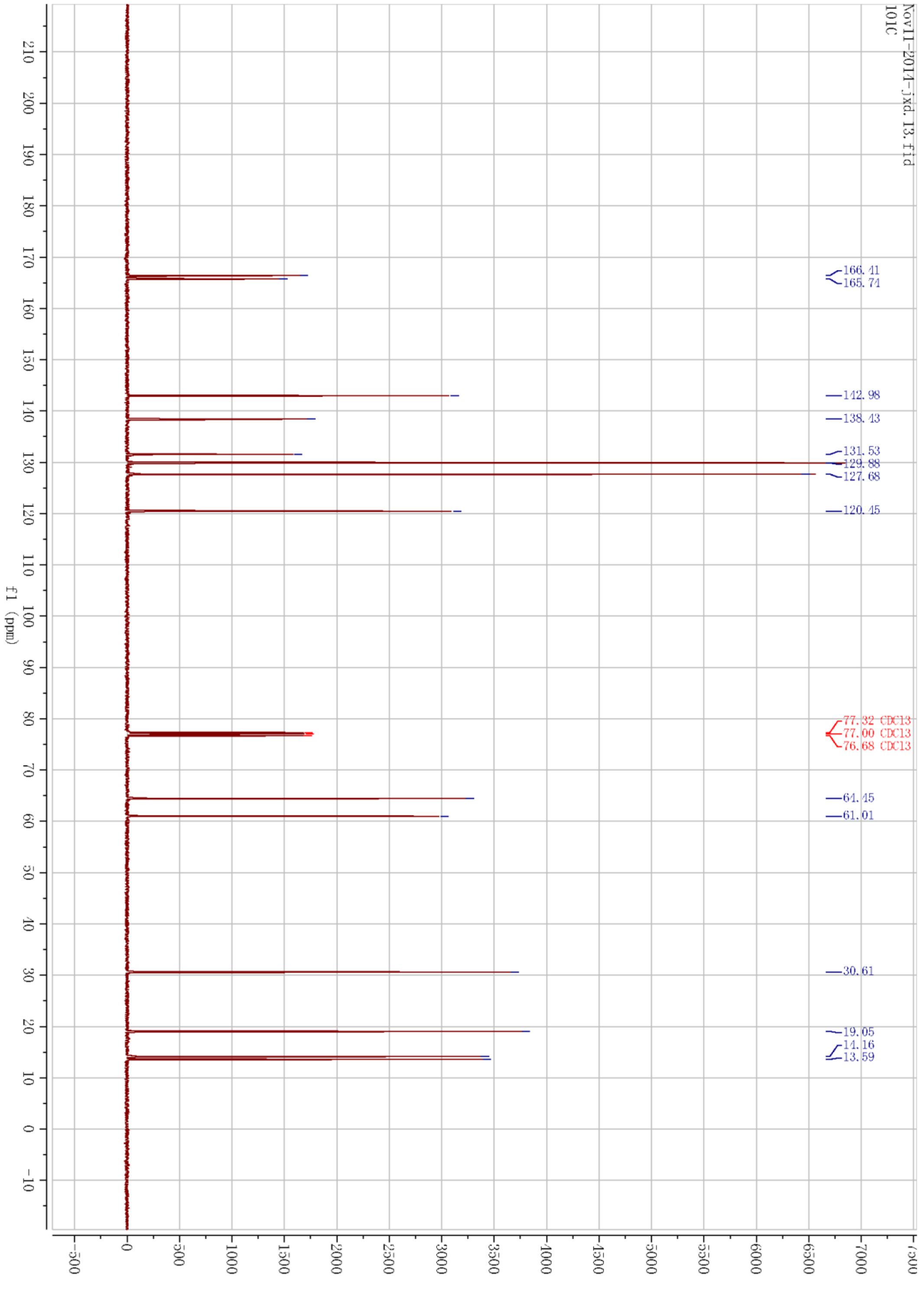



Nov06-2014-jxd.8.fid
12C
—167.00
—144.47
—134.41
—130.13
—128.79
—127.97
—118.23
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
—64.35
—30.72
—19.15
—13.69
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500

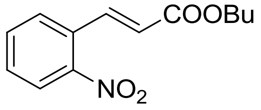
NMR spectra of compound **20f**

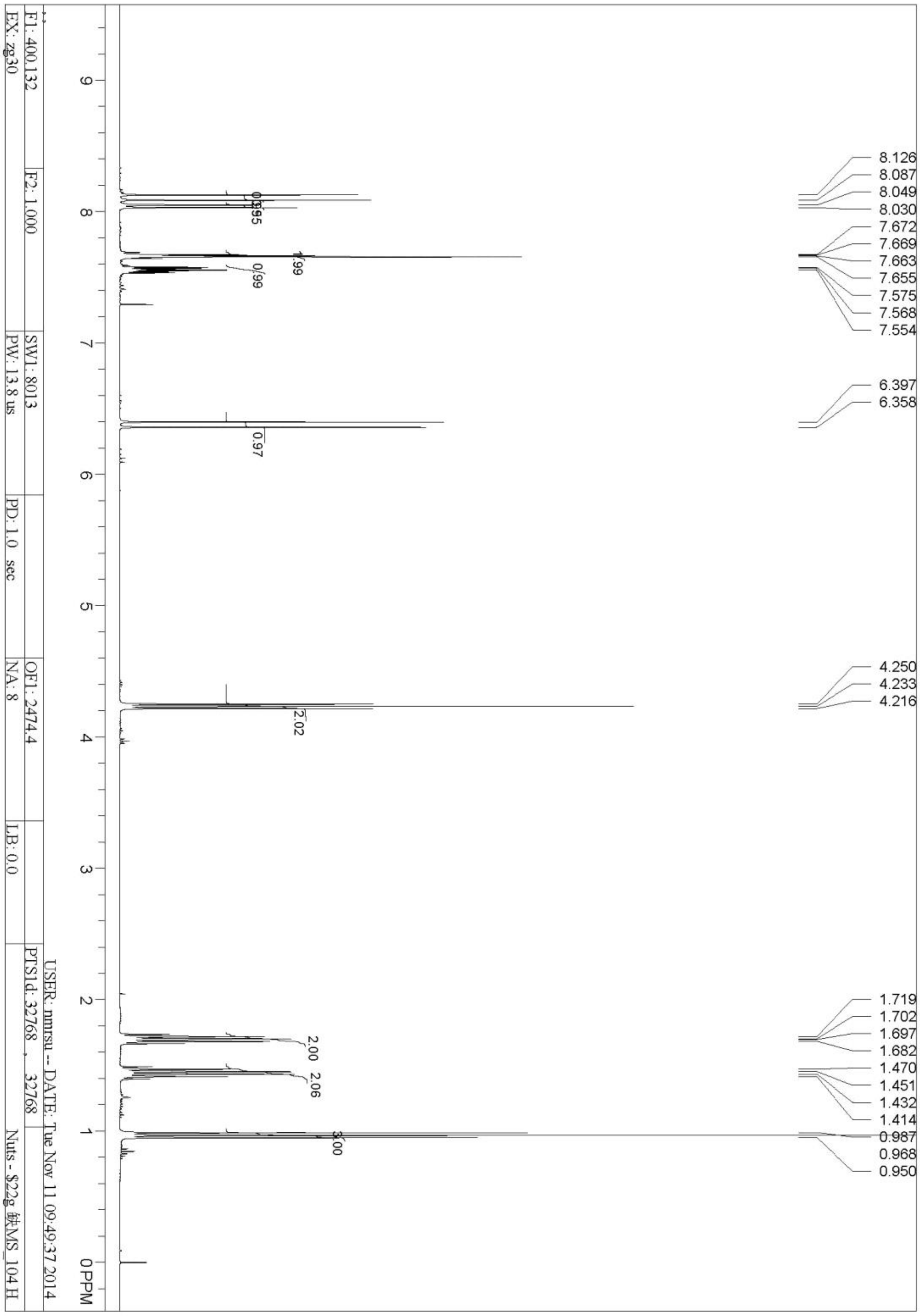


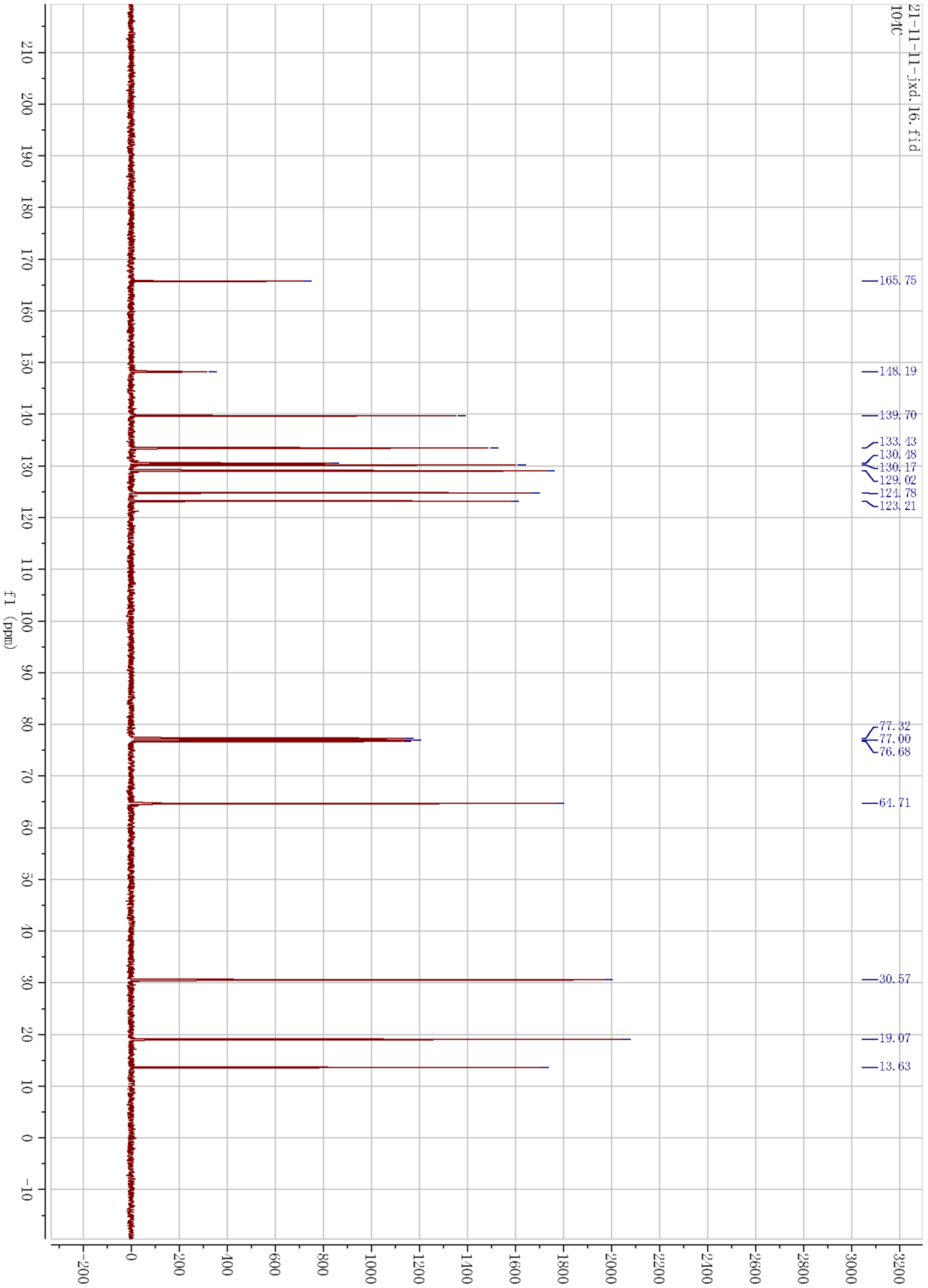



Nov11-2014-jxd.13.fid
101C
166.41
165.74
142.98
138.43
131.53
129.88
127.68
120.45
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
64.45
61.01
30.61
19.05
14.16
13.59
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
7500

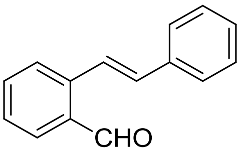
NMR spectra of compound **20g**

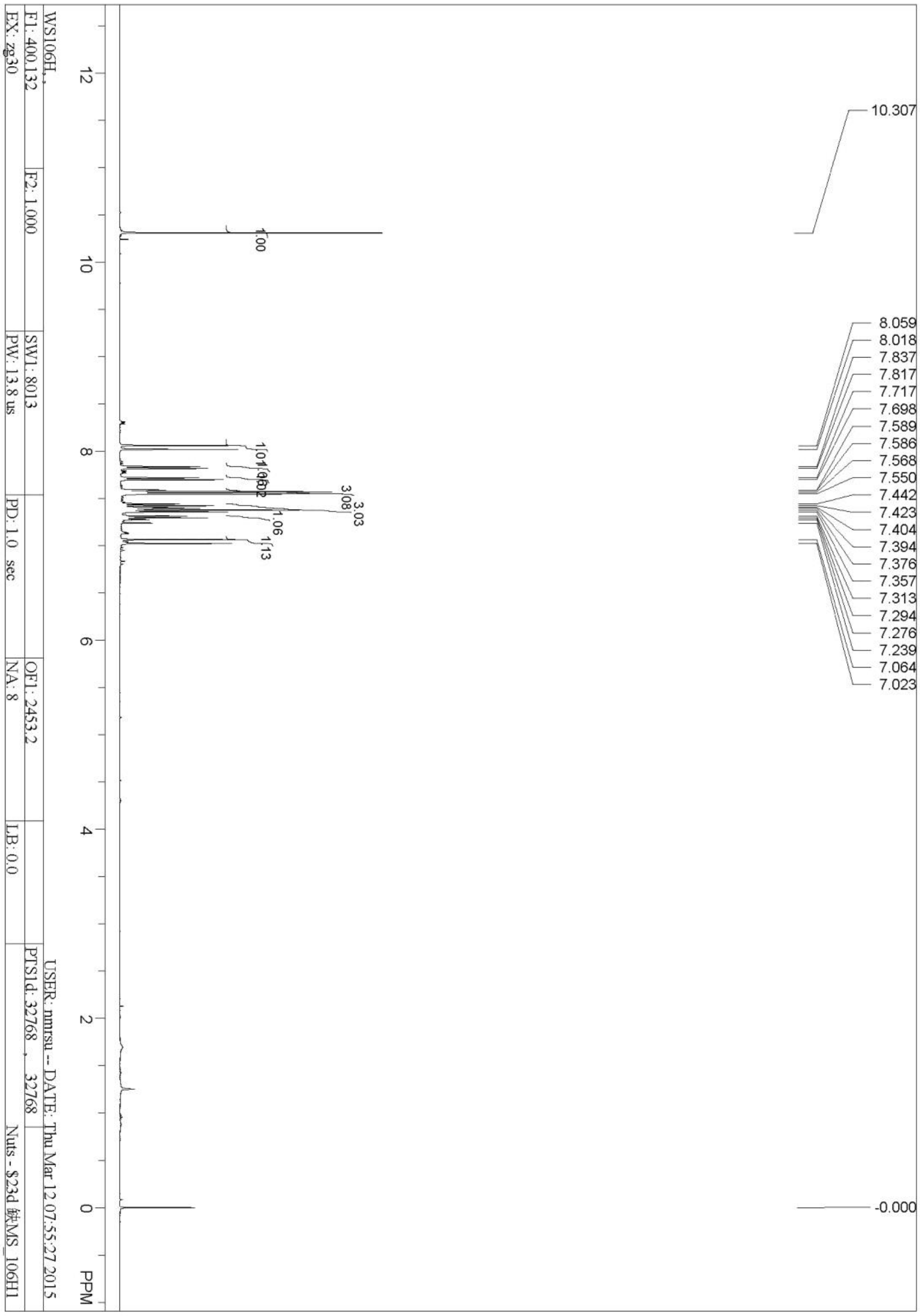


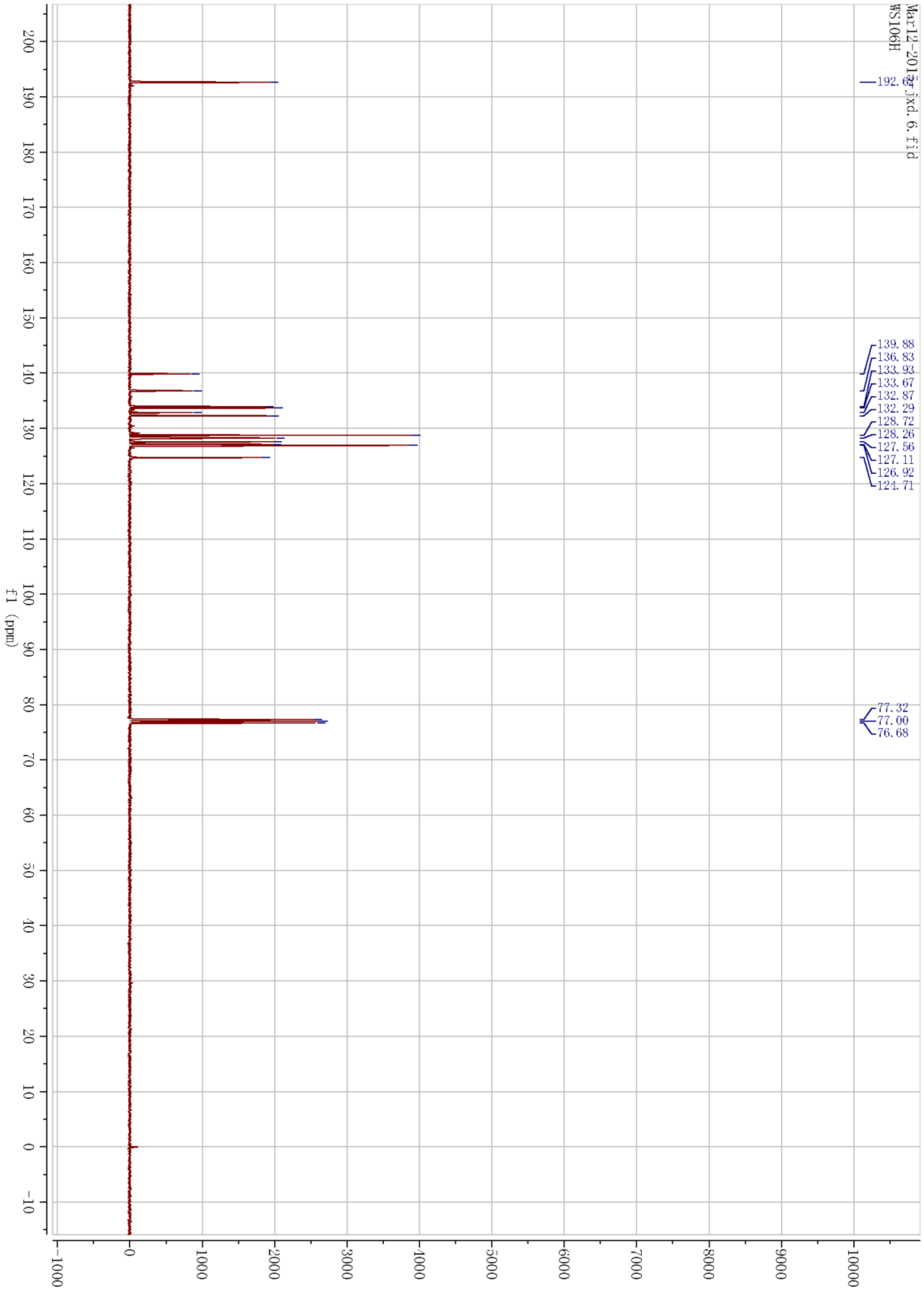



21-11-11-jxd.16.fid
104C
165.75
148.19
139.70
133.43
130.48
130.17
129.02
124.78
123.21
77.32
77.00
76.68
64.71
30.57
19.07
13.63
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-200
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200

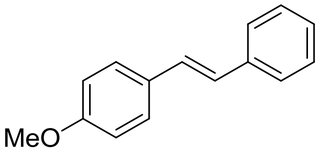
NMR spectra of compound **21a**

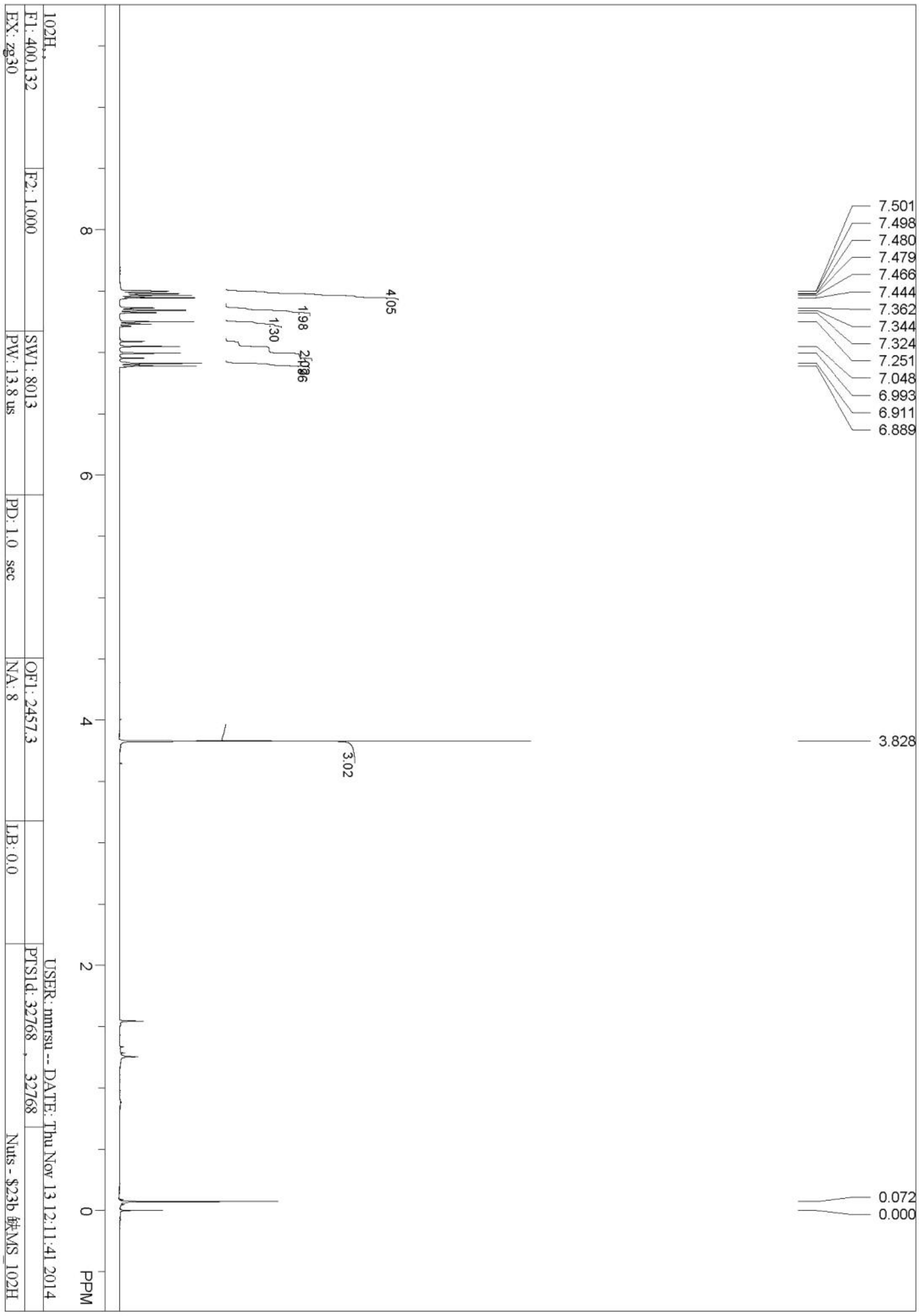


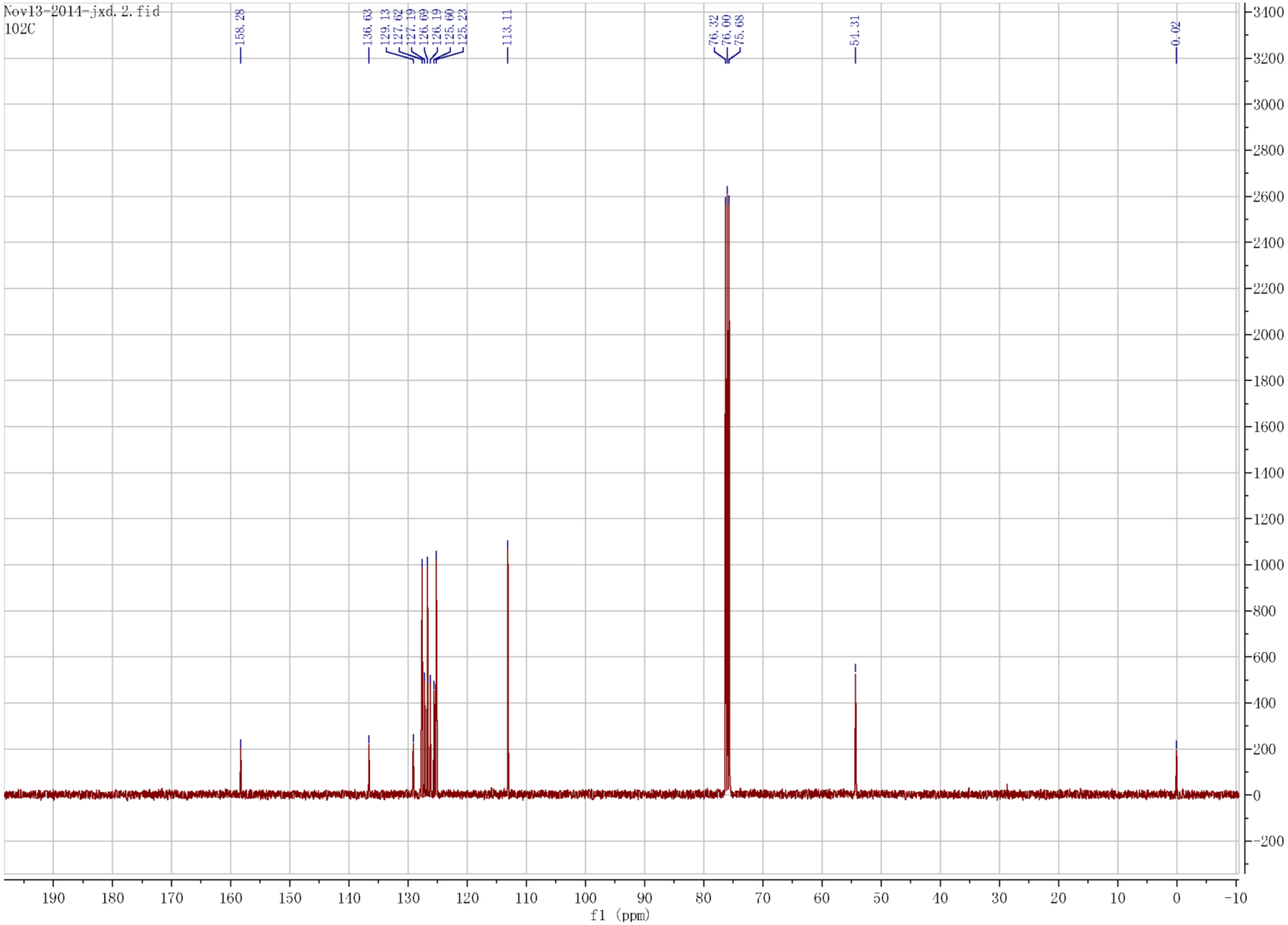



Mar12-2015-jxd.6.fid
WS106H
192.64
139.88
136.83
133.93
133.67
132.87
132.29
128.72
128.26
127.56
127.11
126.92
124.71
77.32
77.00
76.68
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000

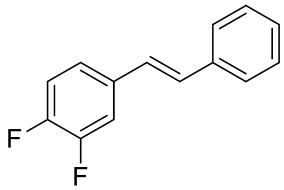
NMR spectra of compound **21b**

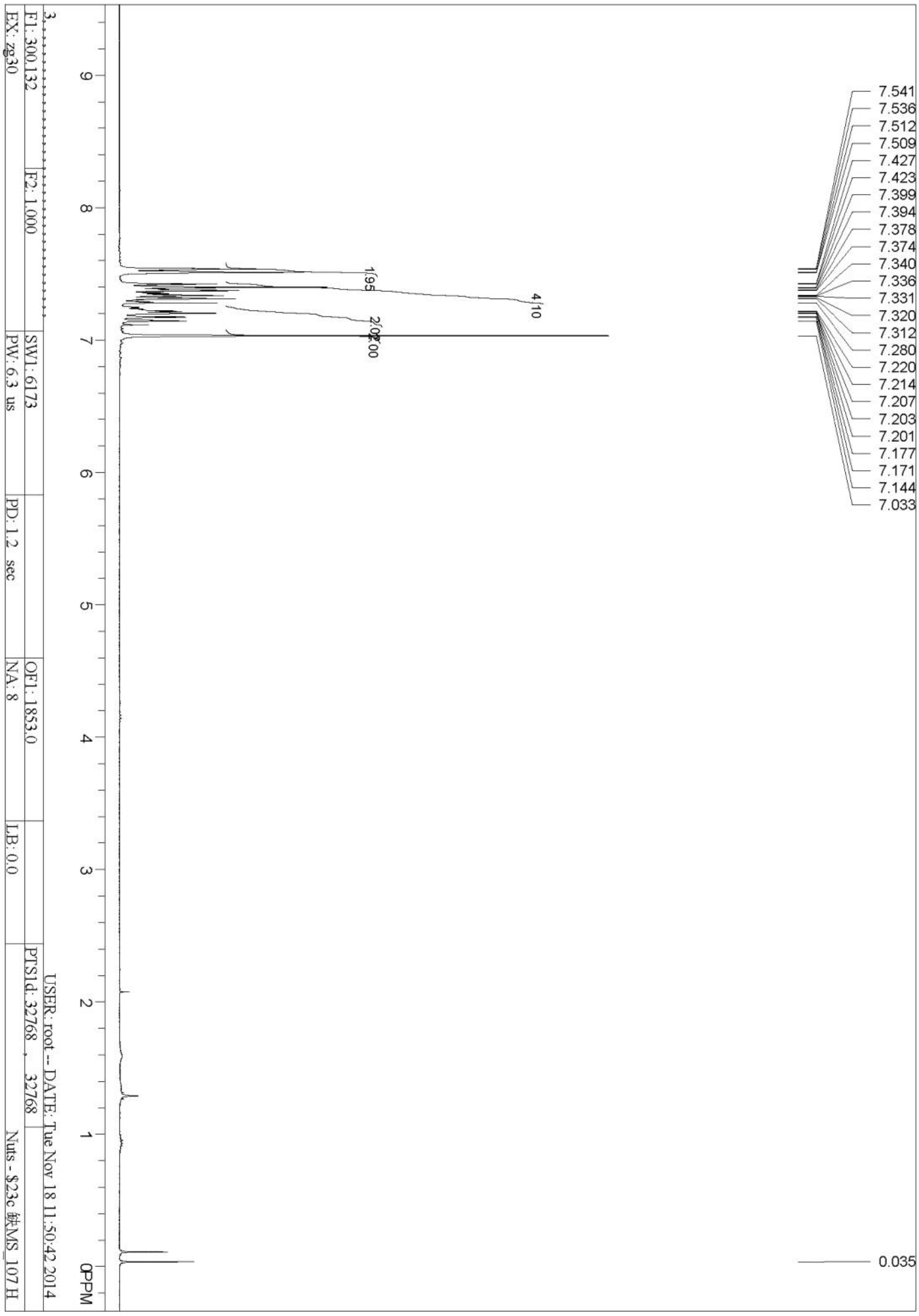


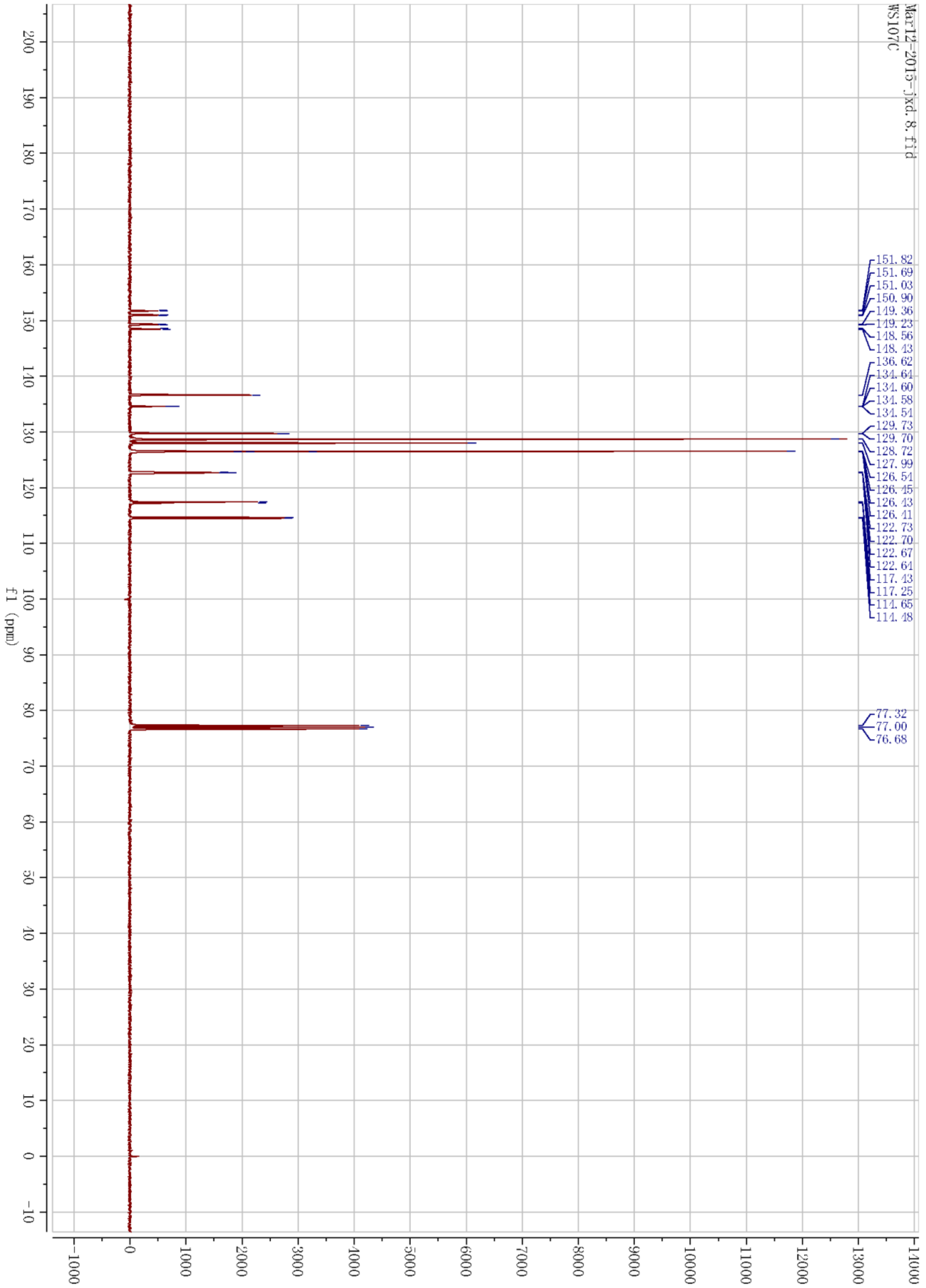



Nov13-2014-jxd.2.fid
102C
158.28
136.63
129.13
127.62
127.19
126.69
126.19
125.60
125.23
113.11
76.32
76.00
75.68
54.31
0.02
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

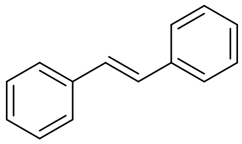
NMR spectra of compound **21c**

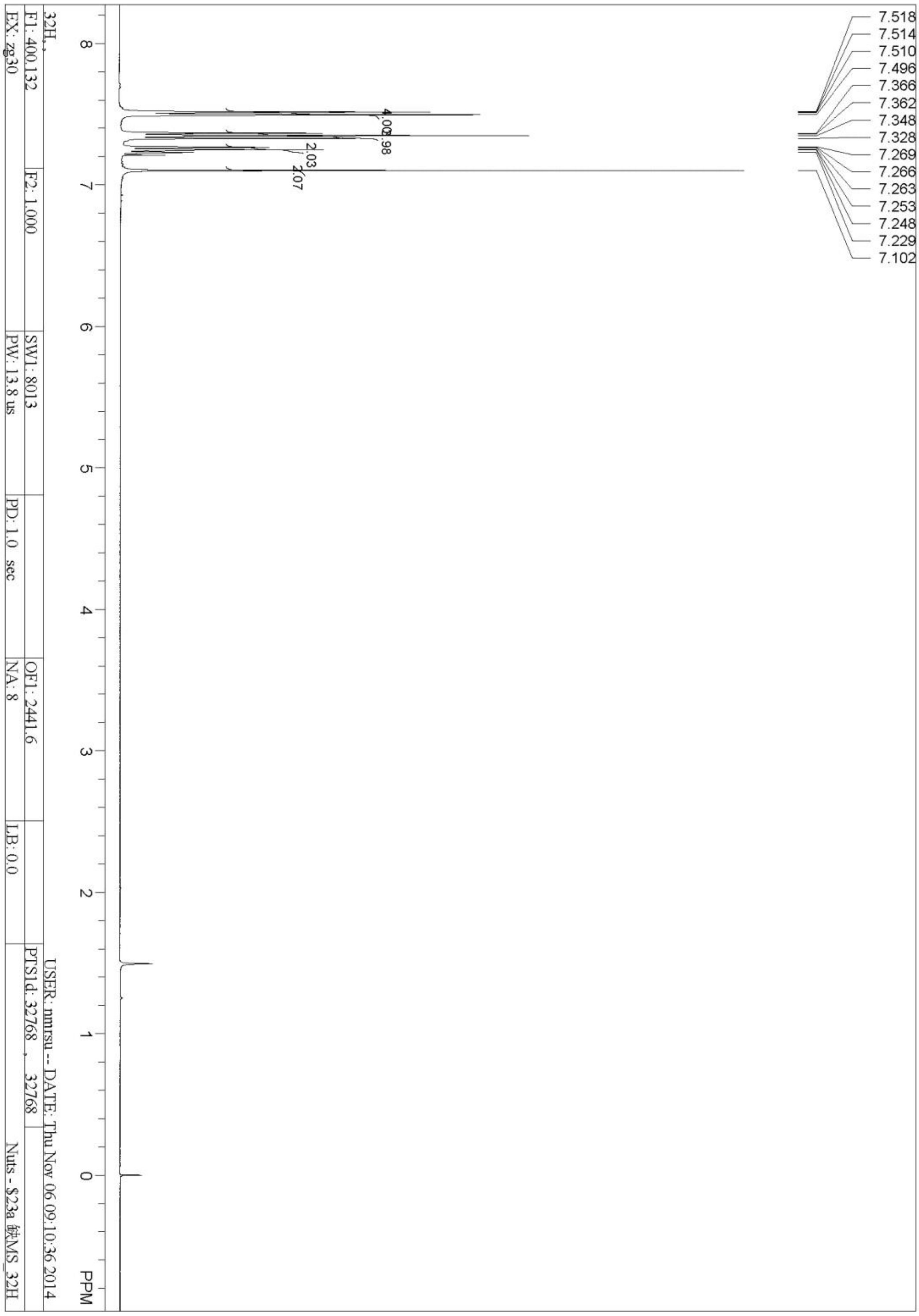


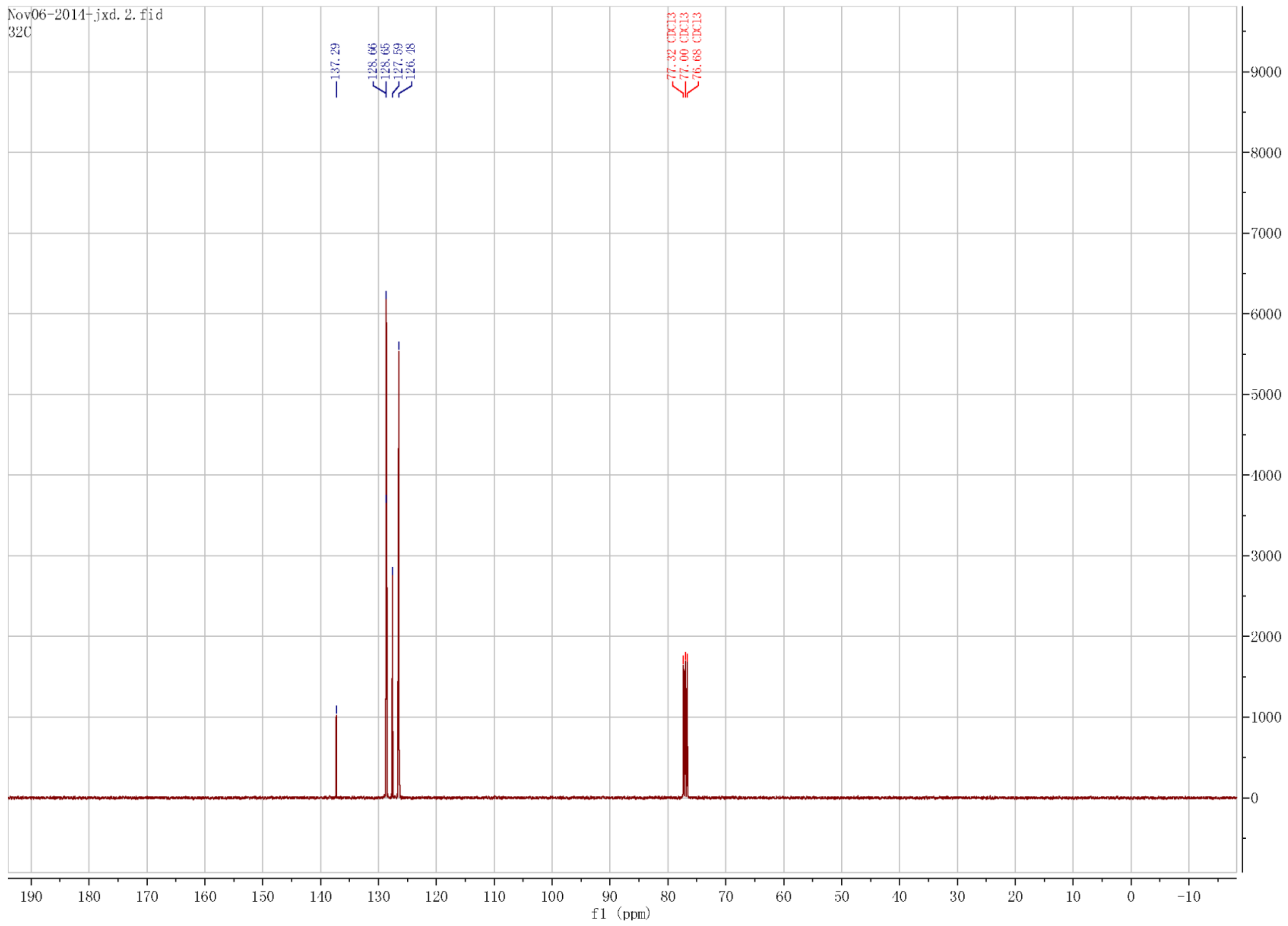



Mar12-2015-jxd.8.fid
WS107C
151.82
151.69
151.03
150.90
149.36
149.23
148.56
148.43
136.62
134.64
134.60
134.58
134.54
129.73
129.70
128.72
127.99
126.54
126.45
126.43
126.41
122.73
122.70
122.67
122.64
117.43
117.25
114.65
114.48
77.32
77.00
76.68
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000

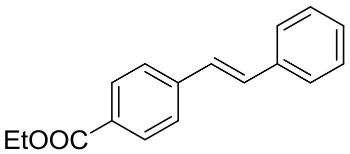
NMR spectra of compound **21d**

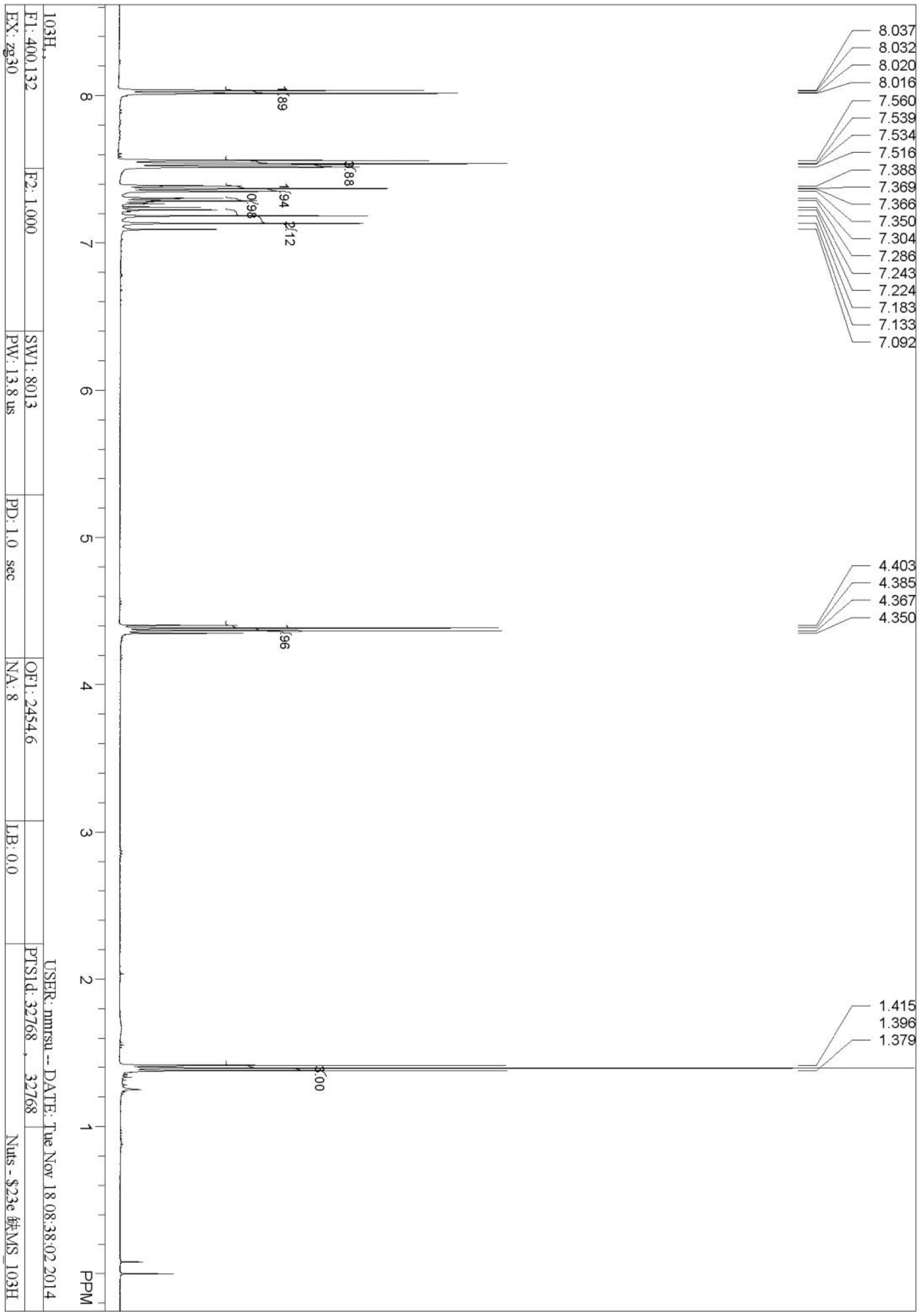


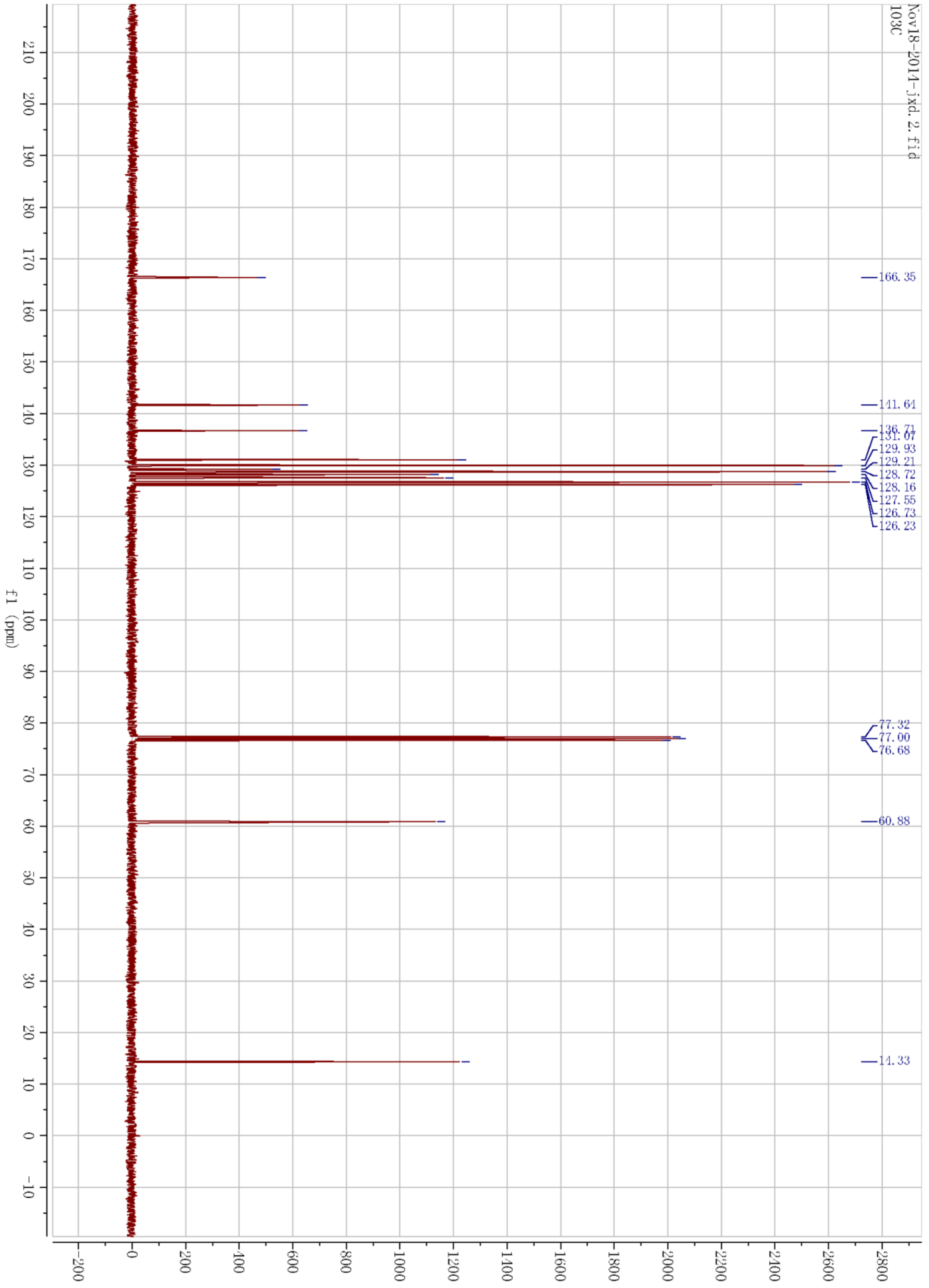



Nov06-2014-jxd.2.fid
32C
137.29
128.66
128.65
127.59
126.48
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

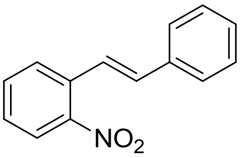
NMR spectra of compound **21e**

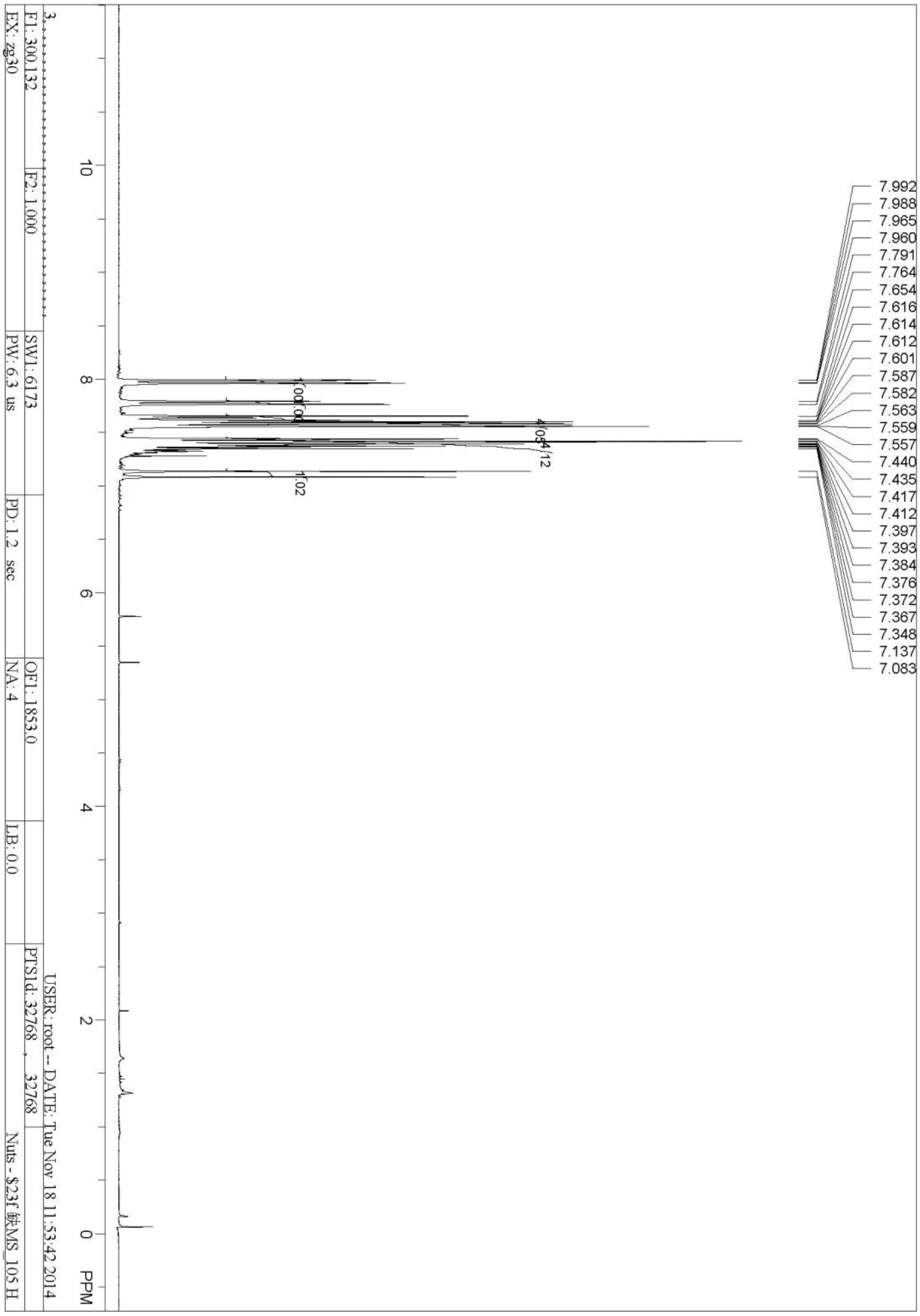


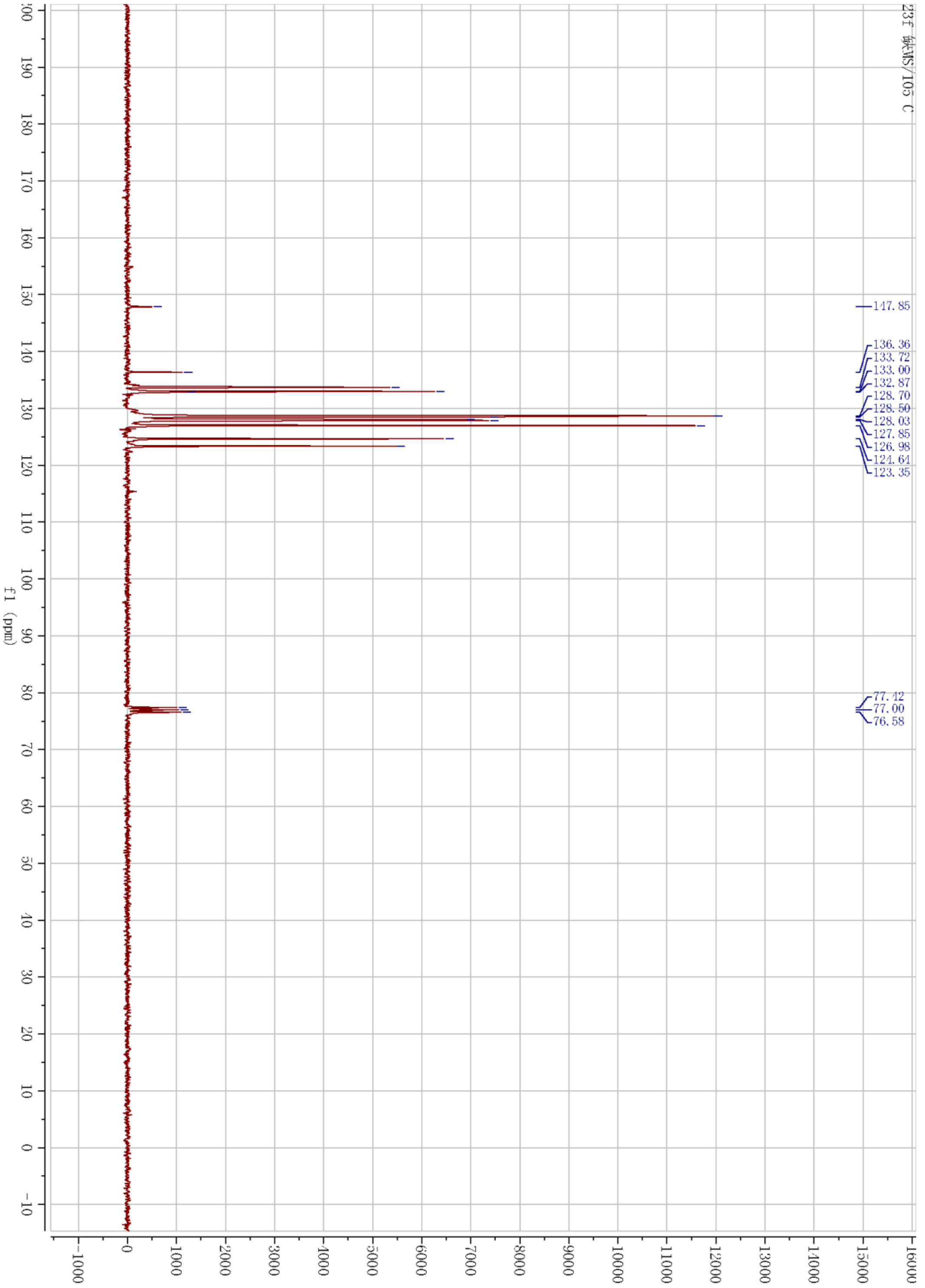



Nov18-2014-jxd.2.fid
103C
166.35
141.64
136.71
131.07
129.93
129.21
128.72
128.16
127.55
126.73
126.23
77.32
77.00
76.68
60.88
14.33
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-200
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800

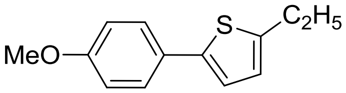
NMR spectra of compound **21f**

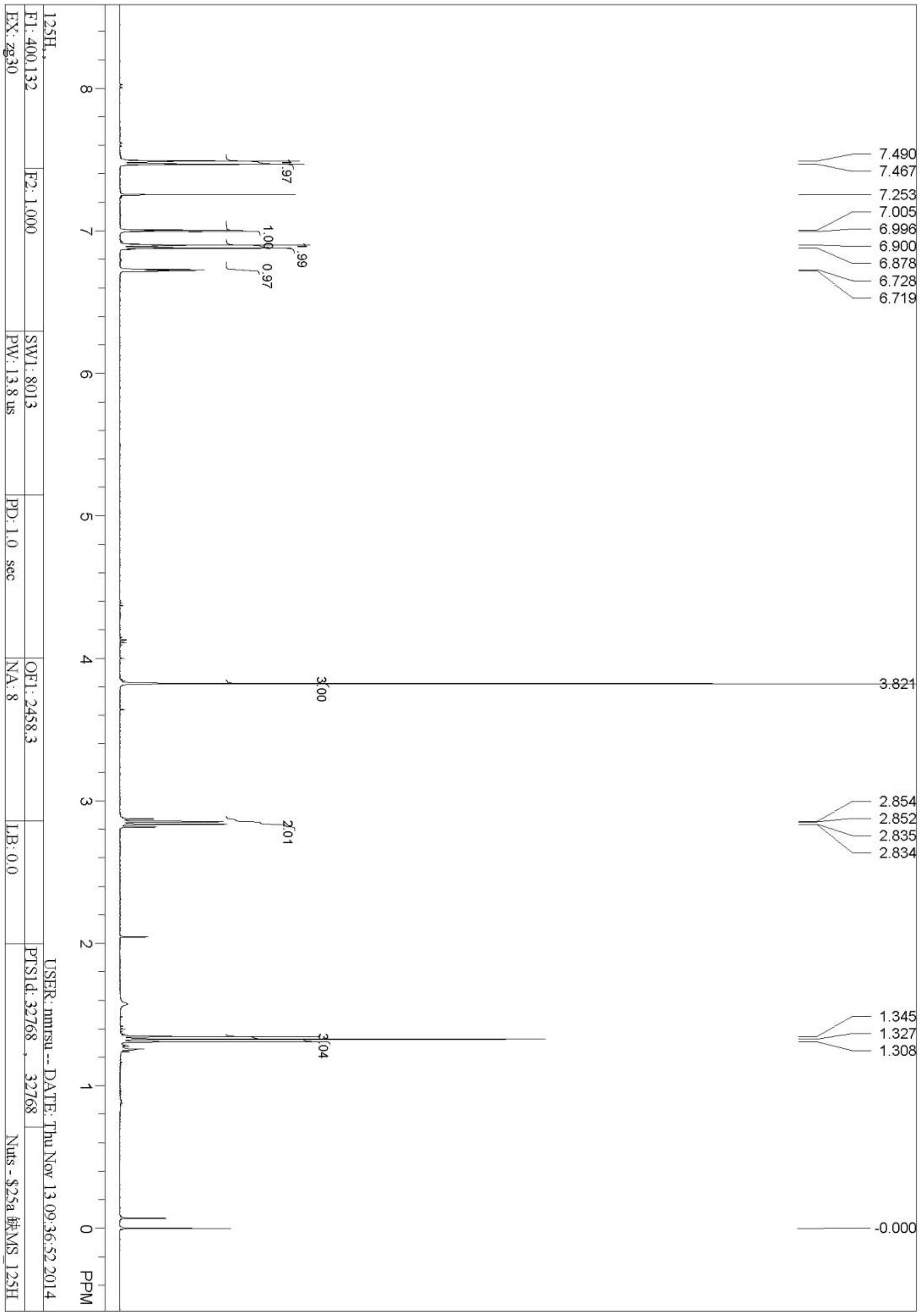


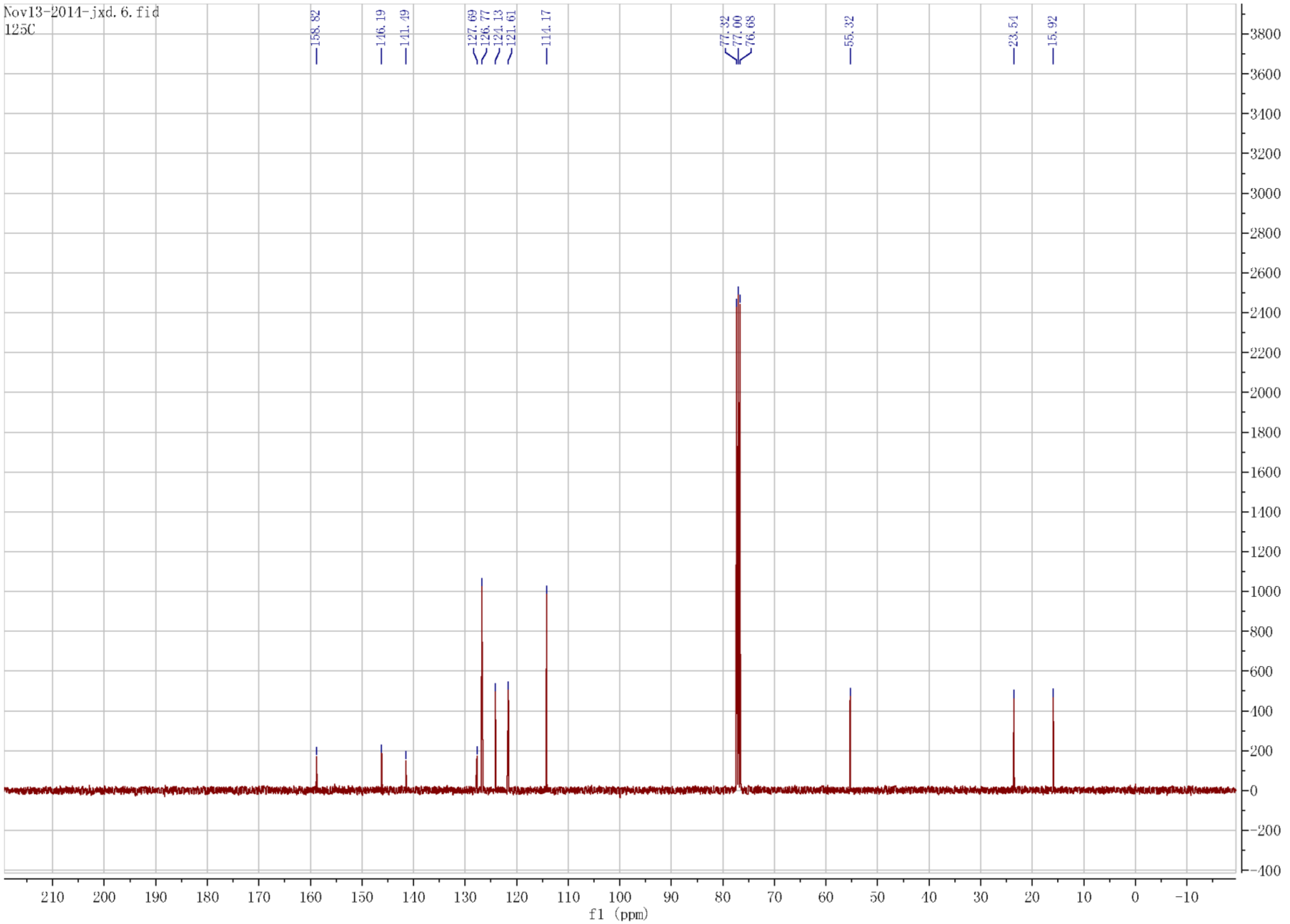



23f 缺MS/105 C
147.85
136.36
133.72
133.00
132.87
128.70
128.50
128.03
127.85
126.98
124.64
123.35
77.42
77.00
76.58
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000
16000

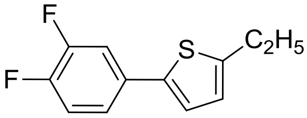
NMR spectra of compound **23a**

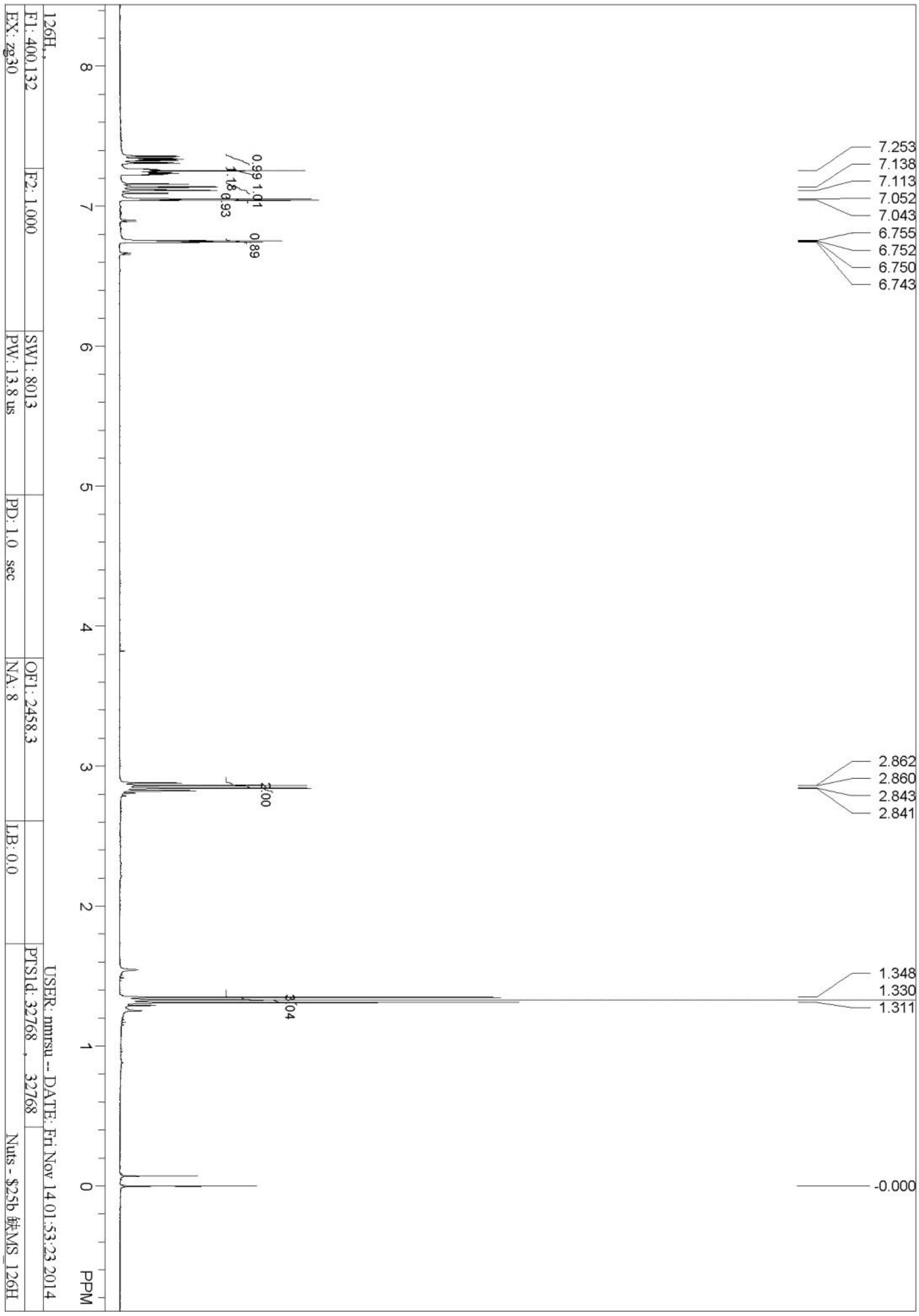


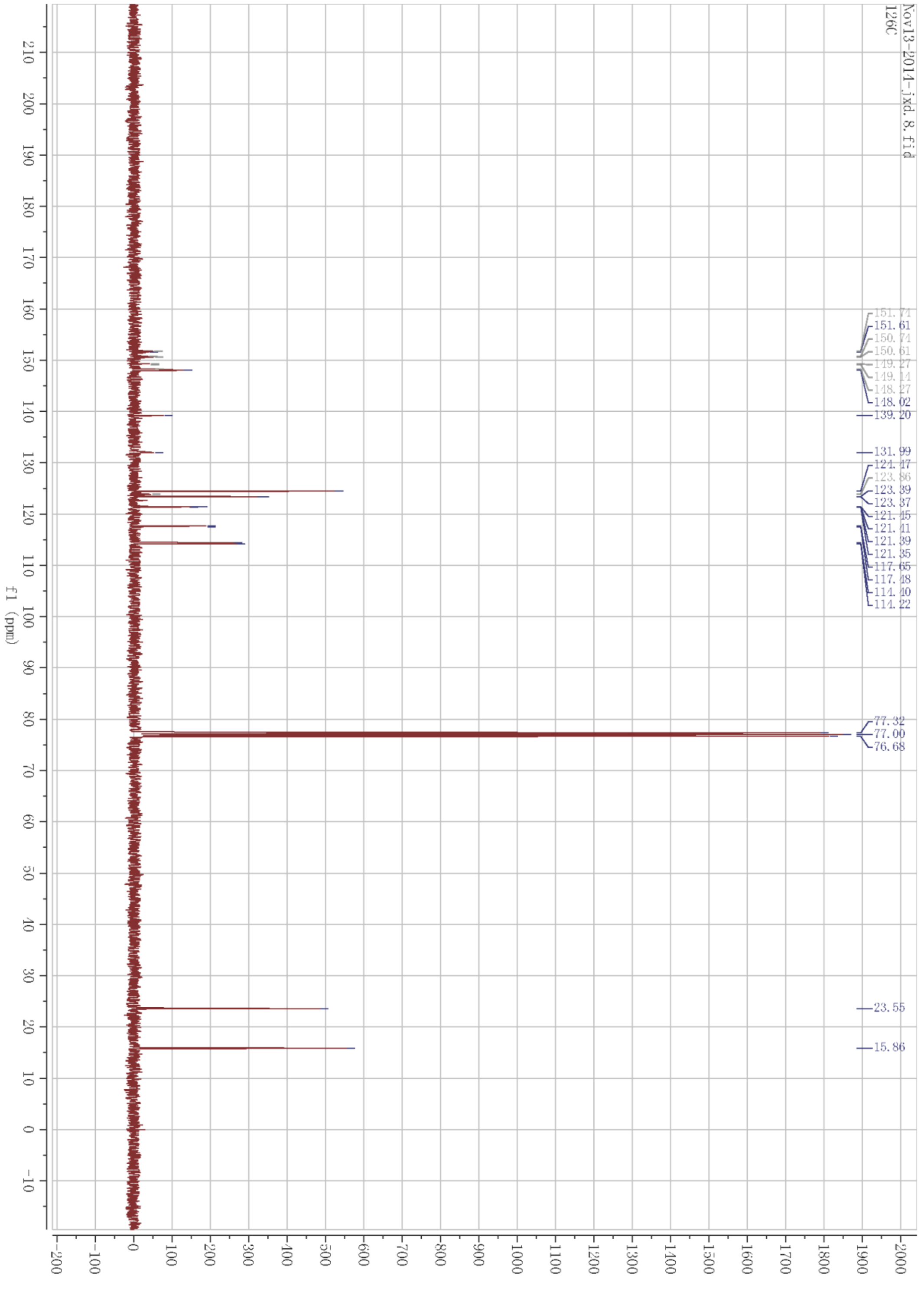



Nov13-2014-jxd.6.fid
125C
158.82
146.19
141.49
127.69
126.77
124.13
121.61
114.17
77.32
77.00
76.68
55.32
23.54
15.92
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400

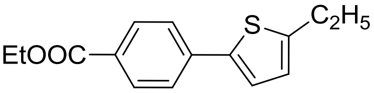
NMR spectra of compound **23b**

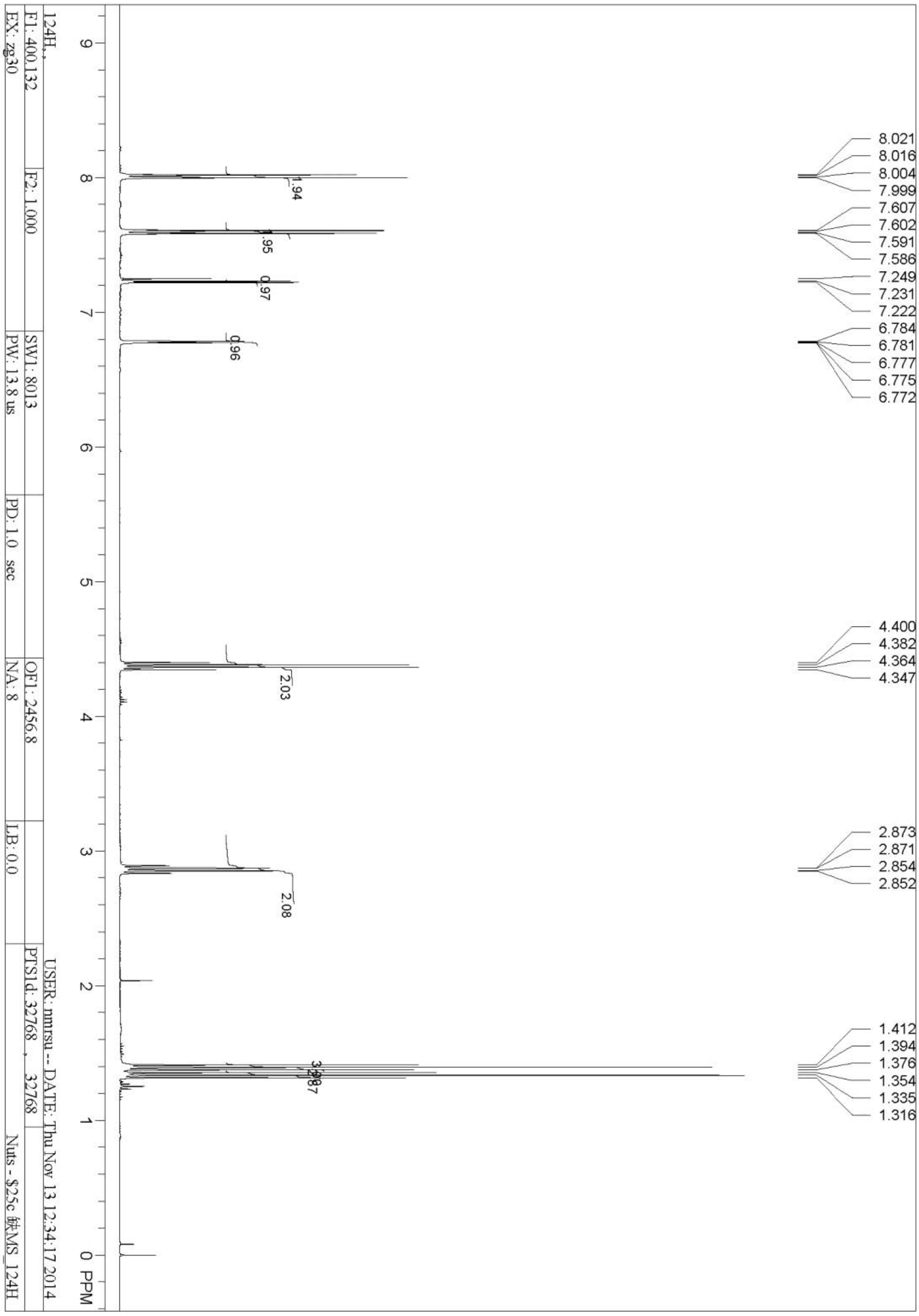


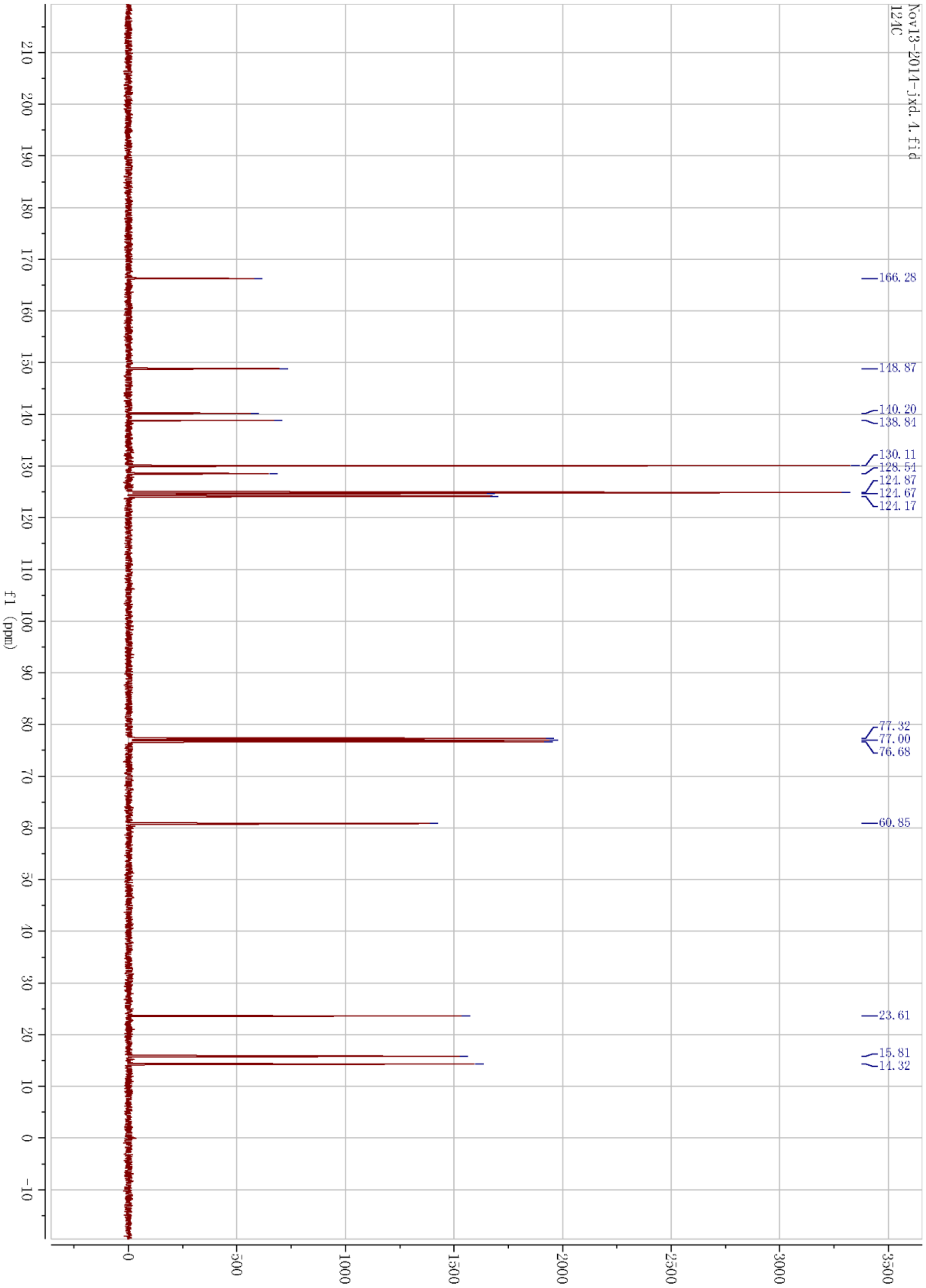



Nov13-2014-jxd.8.fid
I26C
151.74
151.61
150.74
150.61
149.27
149.14
148.27
148.02
139.20
131.99
124.47
123.86
123.39
123.37
121.45
121.41
121.39
121.35
117.65
117.48
114.40
114.22
77.32
77.00
76.68
23.55
15.86
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-200
-100
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000

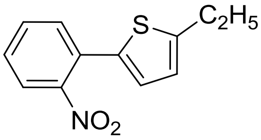
NMR spectra of compound **23c**

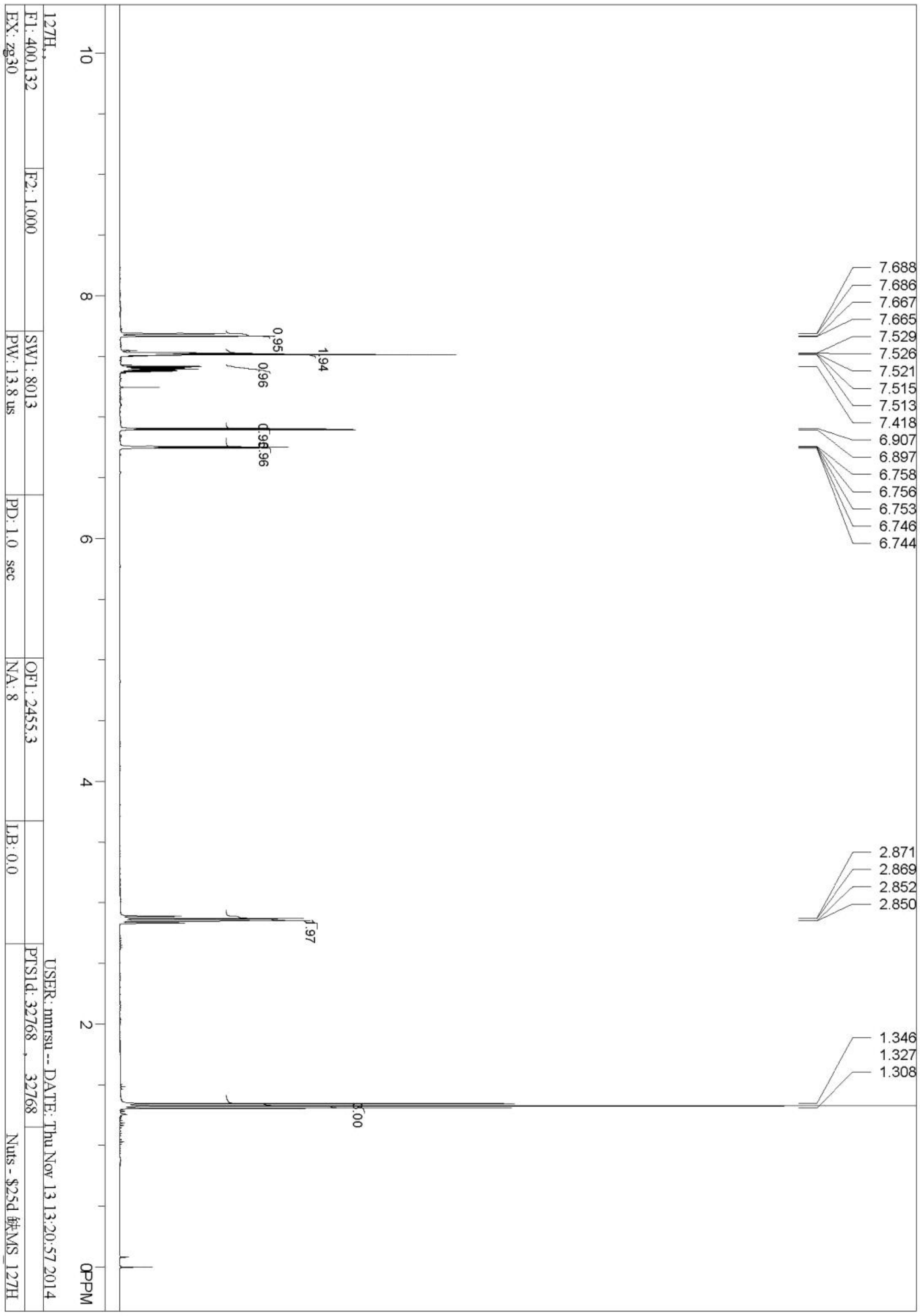


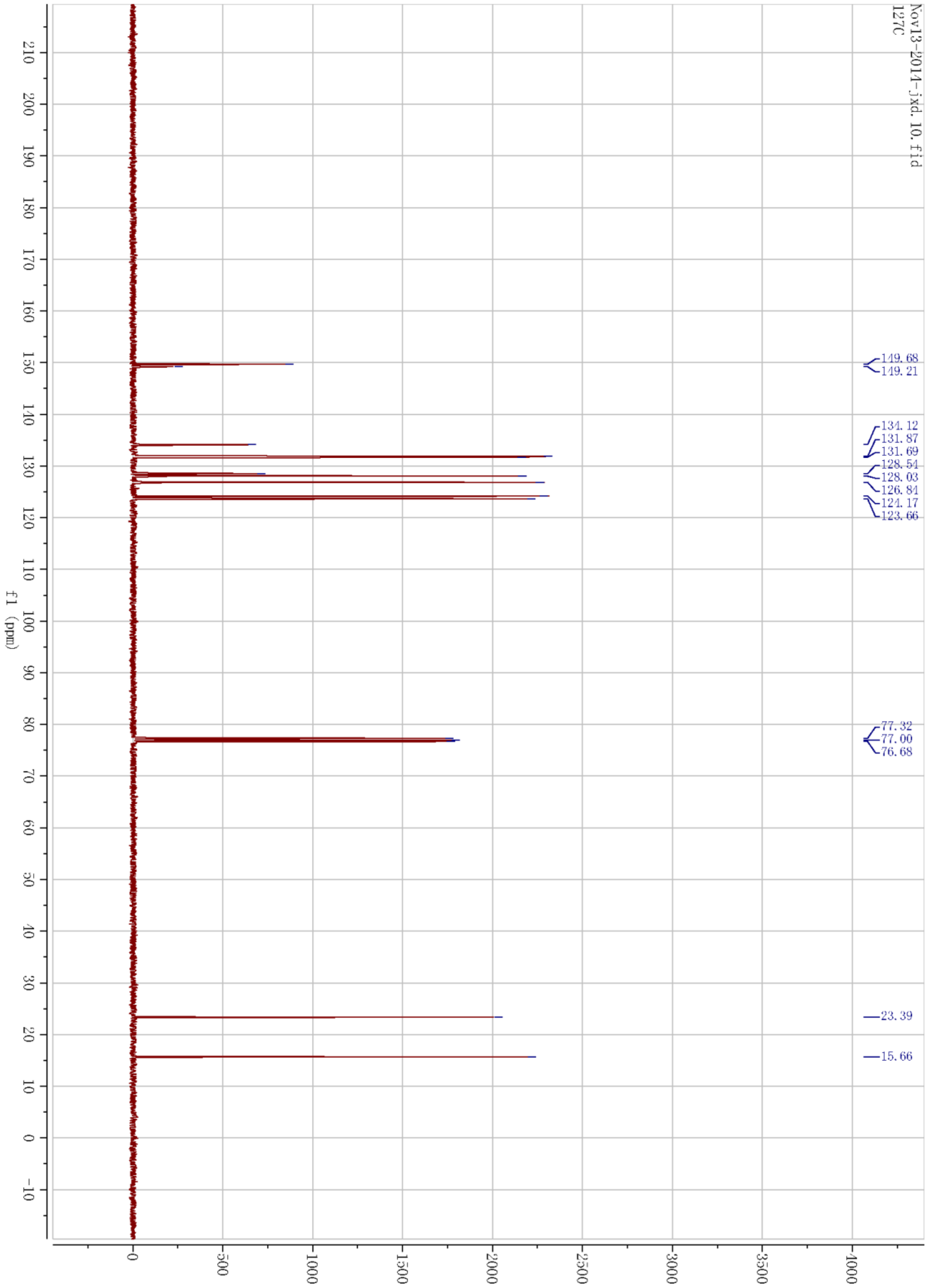



Nov13-2014-jxd.4.fid
124C
166.28
148.87
140.20
138.84
130.11
128.54
124.87
124.67
124.17
77.32
77.00
76.68
60.85
23.61
15.81
14.32
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
0
500
1000
1500
2000
2500
3000
3500

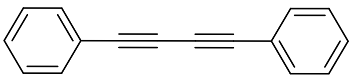
NMR spectra of compound **23d**

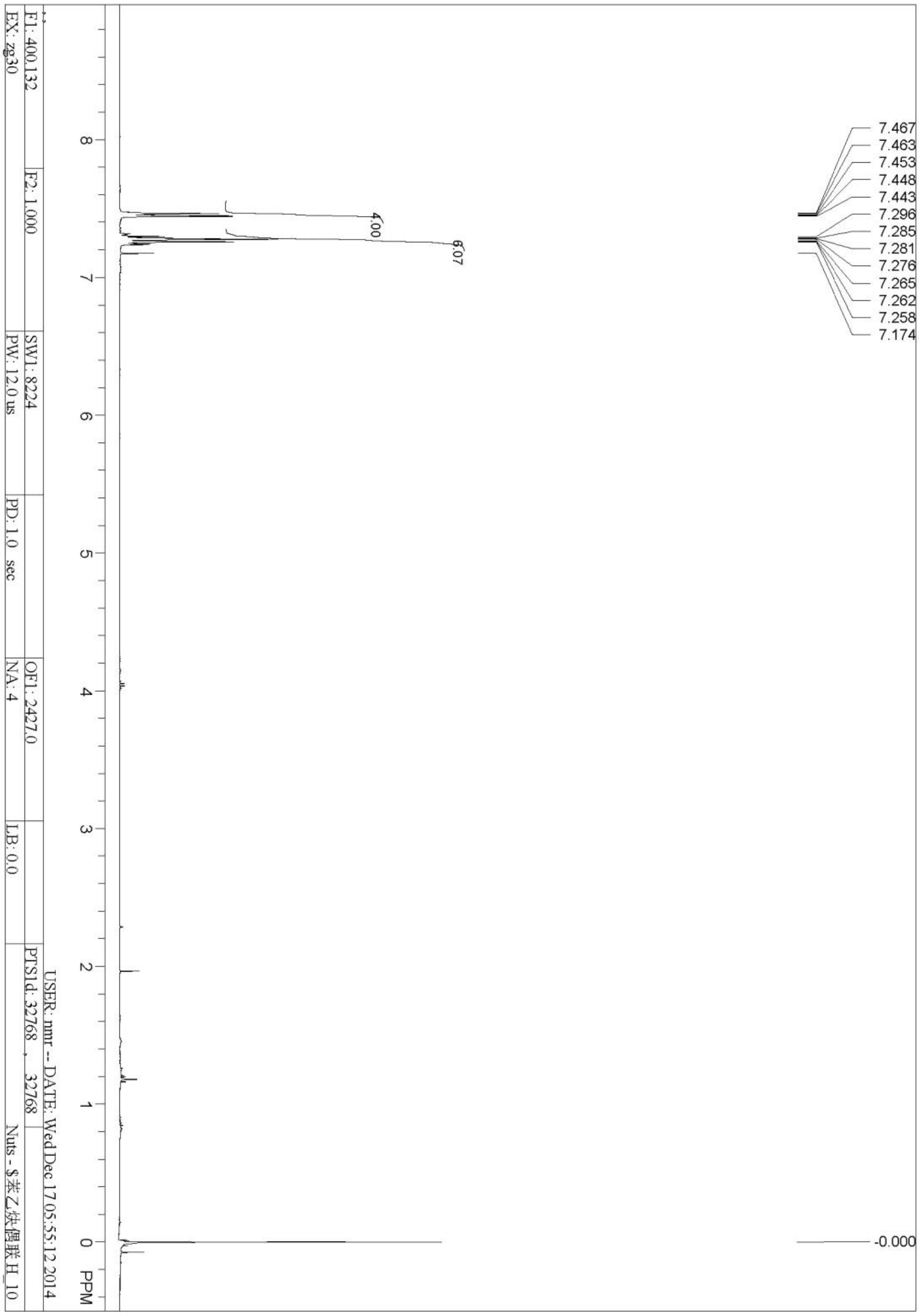


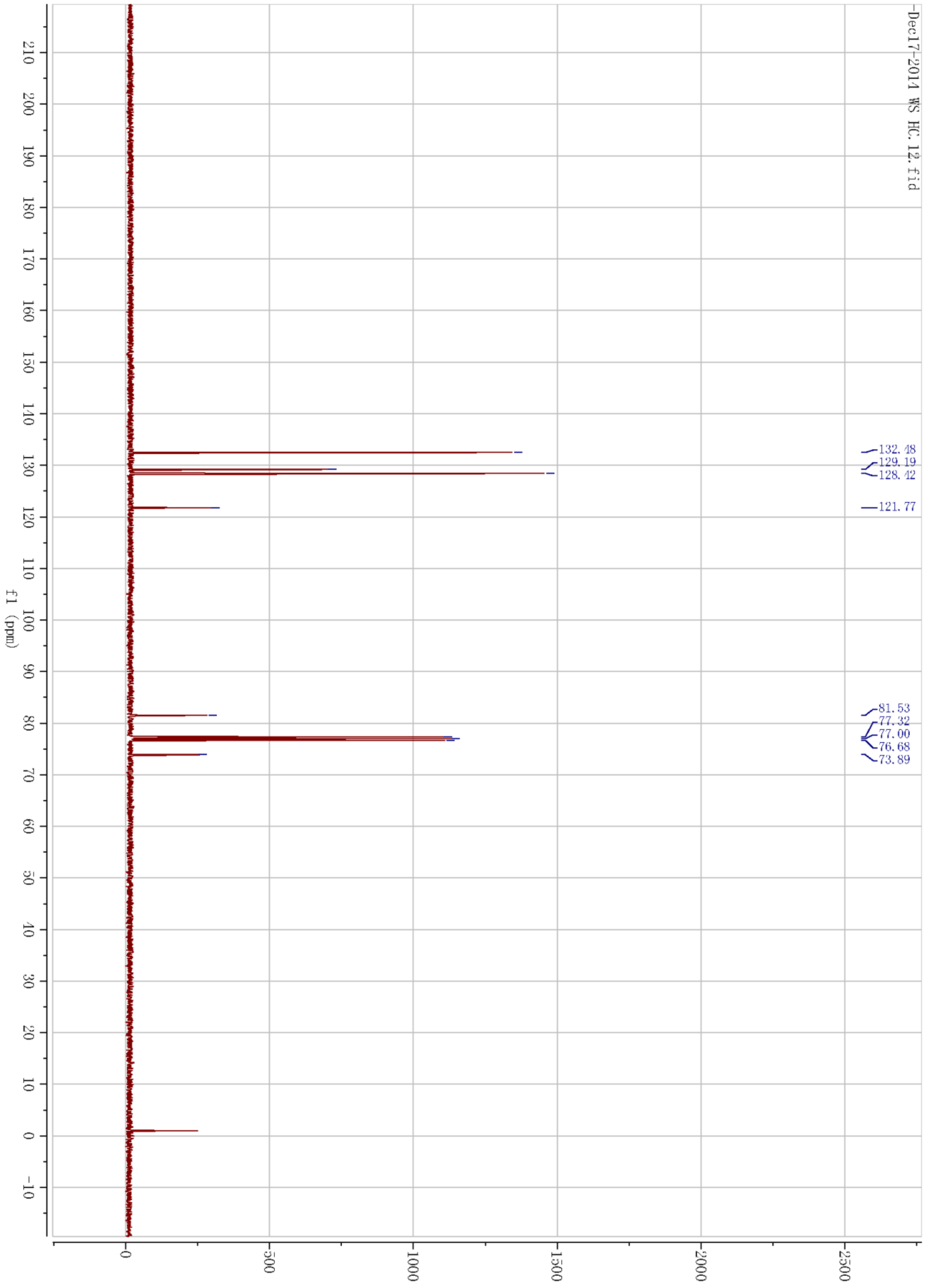



Nov13-2014-jxd.10.fid
127C
149.68
149.21
134.12
131.87
131.69
128.54
128.03
126.84
124.17
123.66
77.32
77.00
76.68
23.39
15.66
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
0
500
1000
1500
2000
2500
3000
3500
4000

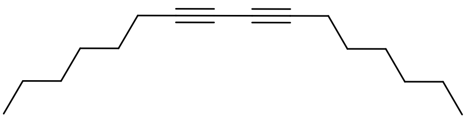
NMR spectra of compound **25**

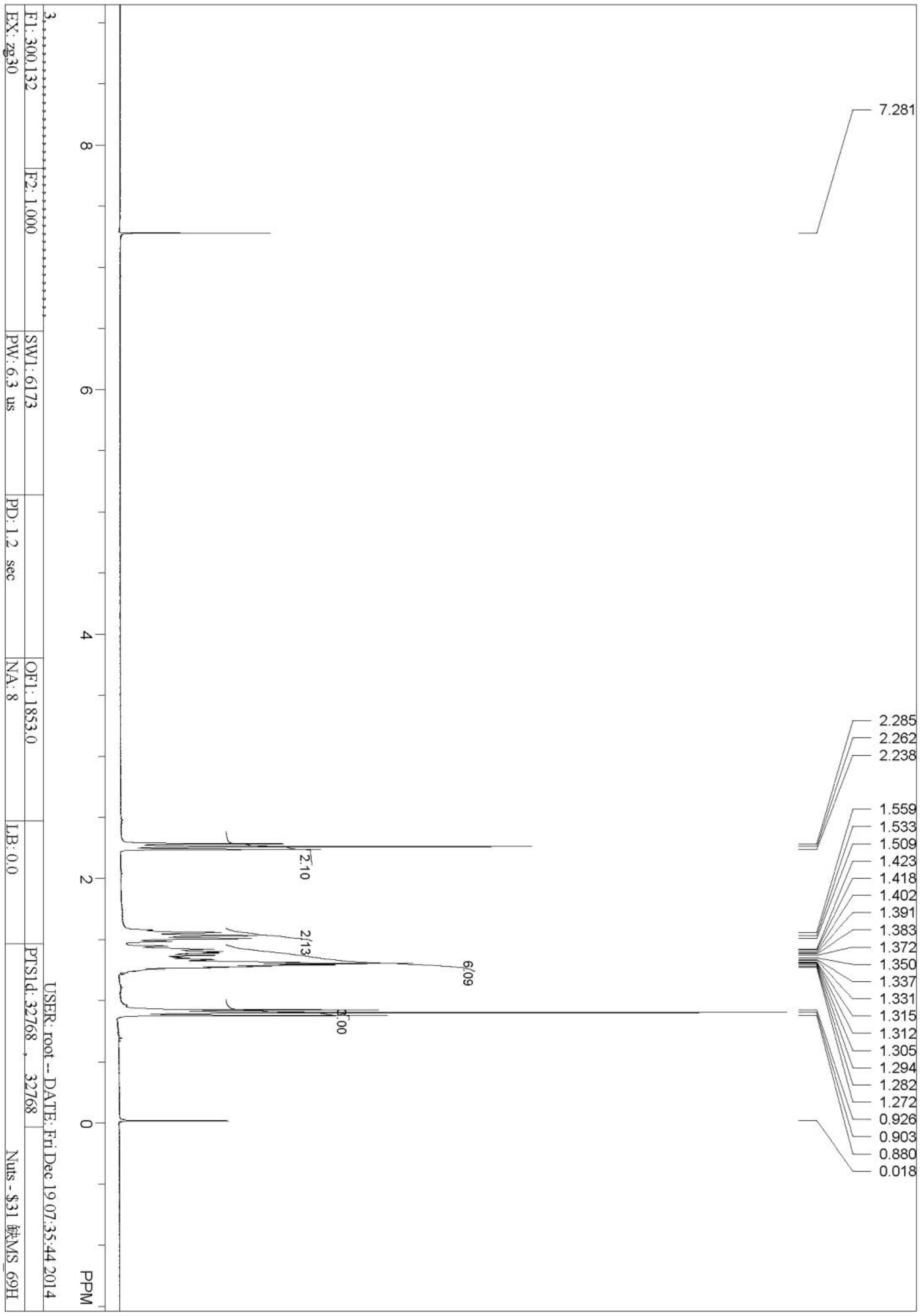


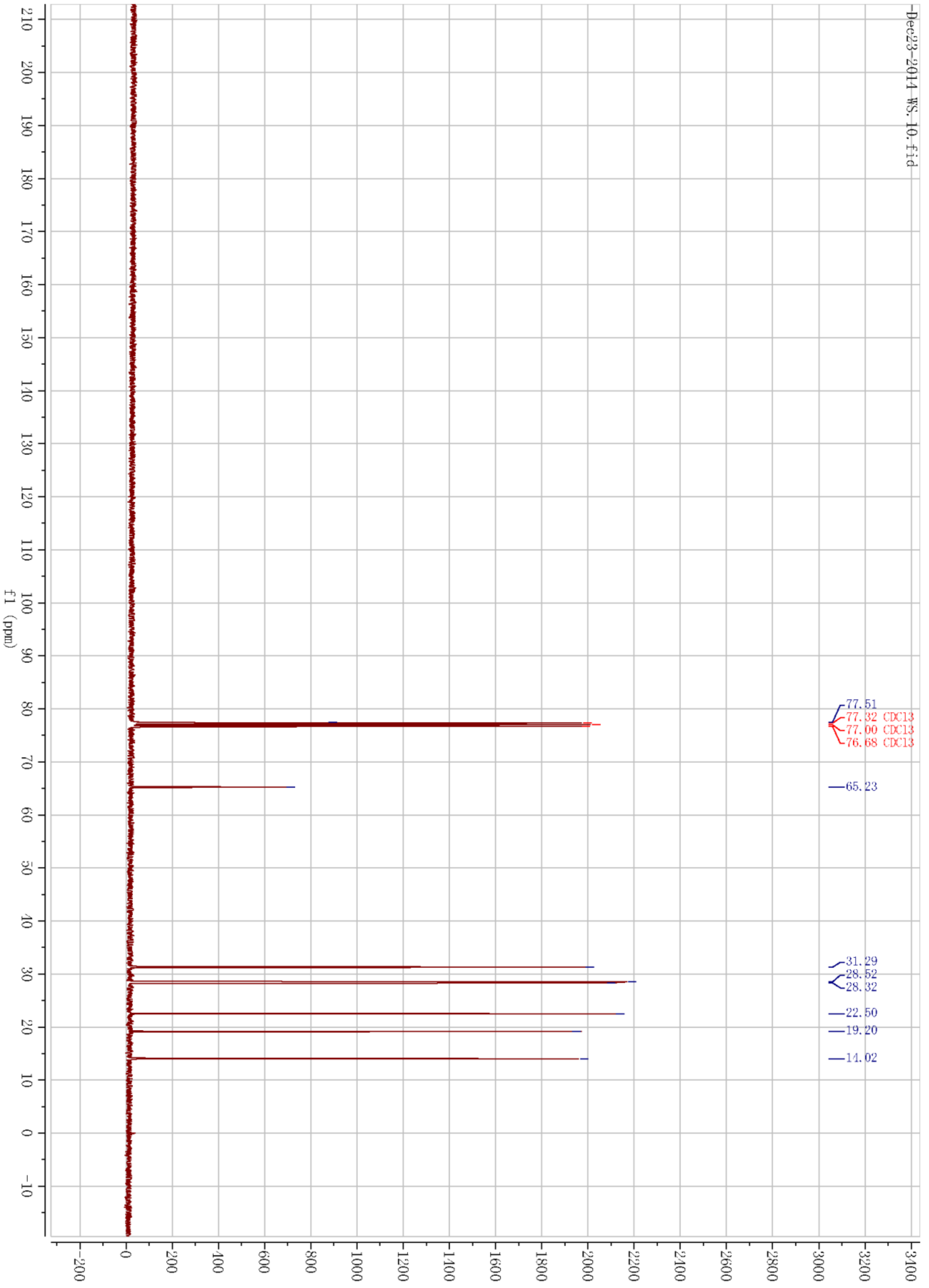



-Dec17-2014 WS HC.12.fid
132.48
129.19
128.42
121.77
81.53
77.32
77.00
76.68
73.89
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
0
500
1000
1500
2000
2500

NMR spectra of compound **27**






Dec23-2014 WS.10.fid
77.51
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
65.23
31.29
28.52
28.32
22.50
19.20
14.02
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-200
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
3400