Supporting Information

Palladium-Catalyzed, Ligand-Free Suzuki Reaction in Water Using Aryl Fluorosulfates

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General Remarks

All reagents were purchased and used as received except when indicated. Solvents were purified by standard procedures. Unless otherwise noted, all the reactions were carried out under air. Analytical thin-layer chromatography (TLC) was performed on Silicycle silica gel plates with F-254 as an indicator and compounds were visualized by irradiating with UV light or spraying. Column chromatography was performed with silica gel (300-400 mesh). NMR data were recorded on either a Varian Mercury-vx300 spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C, 282 MHz for ^{19}F) or Varian Mercury-400 spectrometer (400 MHz for ^{1}H, 101.5 MHz for ^{13}C, 376 MHz for ^{19}F). ^{1}H NMR spectra were referenced to a TMS as an internal standard or to a solvent signal ($CDCl_3$: δ 7.26 ppm), ^{13}C NMR spectra were referenced to a TMS as an internal standard or to a solvent signal ($CDCl_3$: δ 77.0 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet) and coupling constants (Hz).

1. General Procedure for the Preparation of Aryl Fluorosulfates

In a 100 mL three-necked flask equipped with a stirring bar, phenol (20.0 mmol, 1.0 equiv) and Et_3N (24.0 mmol, 1.2 equiv) were dissolved in 40 mL CH_2Cl_2. SO_2F_2 was introduced by bubbling through the solution. The reaction was monitored by TLC. After 2 to 6 h at room temperature, CH_2Cl_2 was removed *in vacuo.* The residue was dissolved in ethyl acetate, and washed successively with 1 M HCl, sat. $NaHCO_3$, and brine. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to give the target product with no future purification (4-cyanophenyl fluorosulfate and 2-cyanophenyl fluorosulfate were purified by flash silica gel column chromatography).

2. General Procedure for the Suzuki Coupling Reaction

Aryl-OSO_2F (1.0 mmol, 1.0 equiv), arylboronic acid (1.5 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.2 mg, 1 mol%), Et_3N (3.0 mmol, 3.0 equiv) and H_2O (3.0 mL) were successively added to a 25 mL flask equipped with a stirring bar. The reaction mixture was stirred at room temperature in air. After the reaction was stopped, the solution was diluted with ethyl acetate, washed with water and brine,

dried (Na_2SO_4), filtered and concentrated under vacuum. Flash chromatography (PE:EA=50:1~100:1) of the residue afforded the target products.

3. Procedures for Heck, Sonogashira and Homocoupling Reactions

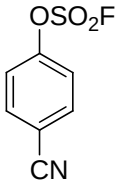
To a solution of 4-nitrophenyl fluorosulfate (0.442 g, 2.0 mmol) in DMF (5.0 mL) were added Et_3N (0.34 mL, 2.4 mmol), methyl acrylate (0.36 mL, 4.0 mmol), dppp (25 mg, 0.06 mmol), and $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), and the mixture was stirred at 80 °C under Argon for 24 h. After cooling, the mixture was diluted with CH_2Cl_2, washed with 5% HCl, water and brine, dried (Na_2SO_4), filtered and concentrated under vacuum. Flash chromatography (PE:EA=50:1) of the residue afforded the target product as a light yellow solid; yield: 0.261 g, 63 %.

A mixture of $PdCl_2(PPh_3)_2$ (28 mg, 0.04 mmol), 2-formylphenyl fluorosulfate (0.408 g, 2.0 mmol), phenylacetylene (0.31 mL, 2.8 mmol), Et_3N (0.70 mL, 5.0 mmol) and DMF (0.70 mL), was stirred at 80 °C under Argon for 4 h. After cooling, the mixture was diluted with ether, washed with water and brine, dried (Na_2SO_4), filtered and concentrated under vacuum. Flash chromatography (PE:EA=50:1) of the residue afforded the target product as a brown oil; yield: 0.300 g, 73 %.

In a 10 mL Schlenk tube was charged with $NiCl_2(PPh_3)_2$ (131 mg, 0.20 mmol), Zn (0.221 g, 3.4 mmol), Bu_4NI (1.107 g, 3.0 mmol) and a stirring bar. THF (1.0 mL) was added via s syringe. The mixture was stirred at room temperature for 5 min. Ethyl 4-[(fluorosulphonyl)oxy]benzoate (0.496 g, 2.0 mmol) was dissolved in THF (1.0 mL) and added to the tube via a syringe. The reaction mixture was heated to the reflux temperature under Argon for 20 h. The reaction mixture was then cooled, filtered, diluted with CH_2Cl_2, washed with water and brine, dried (Na_2SO_4), filtered and concentrated under vacuum. Flash chromatography (PE:EA=50:1) of the residue afforded the target product as a white solid; yield: 0.207 g, 69 %.

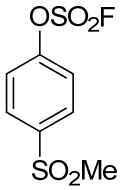
4. Characterization Data for Aryl Fluorosulfates and Coupling Products

4-cyanophenyl fluorosulfate (ALD00404)



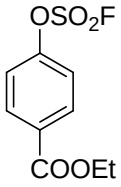
Yield: 3.7 g, 92% (purified by flash silica gel column chromatography, PE:EA=10:1), white solid; mp: 35-37 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.82 (d, *J* = 8.9 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 152.2, 134.6, 122.1 (d, *J* = 1.1 Hz), 117.0, 113.1. **^{19}F NMR (282 MHz, $CDCl_3$) δ:** 38.9; **IR (cm^{-1}):** 3112, 1498, 1448, 1238, 1153, 918, 598, 544. **MS (EI) m/z (relative intensity):** 201 ($[M]^+$, 52), 90 (100). **HRMS (EI) Calcd. for** $C_7H_4FNO_3S$: 200.9896. **Found:** 200.9900.

4-(methylsulphonyl)phenyl fluorosulfate (ALD00410)



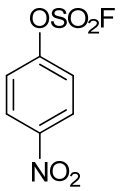
Yield: 5.0 g, 98%, white solid; mp: 79-81 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.10 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 3.09 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 152.9, 141.0, 130.2, 122.1 (d, *J* = 1.0 Hz), 44.3 (s). **^{19}F NMR (282 MHz, $CDCl_3$) δ:** 38.9. **IR (cm^{-1}):** 1442, 1298, 1240, 1151, 924, 782, 590, 527. **MS (EI) m/z (relative intensity):** 254 ($[M]^+$, 65), 175 (100). **HRMS (EI) Calcd. for** $C_7H_7FO_5S_2$: 253.9719. **Found:** 253.9716.

Ethyl 4-[(fluorosulphonyl)oxy]benzoate (ALD 00412)



Yield: 4.9 g, 99%, colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.17 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 164.8, 152.7, 131.9, 130.9, 120.8 (d, *J* = 1.1 Hz), 61.6, 14.2. **^{19}F NMR (282 MHz, $CDCl_3$) δ:** 38.2. **IR (cm^{-1}):** 1724, 1456, 1281, 1236, 1109, 919, 816, 586. **MS (EI) m/z (relative intensity):** 248 ($[M]^+$, 9), 203 (100). **HRMS (EI) Calcd. for** $C_9H_9FO_5S$: 248.0155. **Found:** 248.0151.

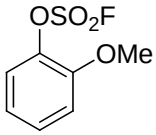
4-nitrophenyl fluorosulfate (ALD00414)



Yield: 3.7 g, 84%, yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.38 (d, *J* = 9.1 Hz, 2H), 7.56 (d, *J* = 9.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 153.3, 147.3, 126.1, 122.1 (d, *J* = 1.1 Hz). **^{19}F**

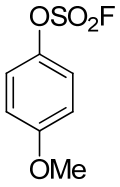
NMR (282 MHz, $CDCl_3$) δ: 42.8. **IR (cm^{-1}):** 1533, 1457, 1354, 1238, 1151, 915, 823, 586. **MS (EI) m/z (relative intensity):** 221 ($[M]^+$, 100). **HRMS (EI) Calcd. for** $C_6H_4FNO_5S$: 220.9794. **Found:** 220.9792.

2-methoxyphenyl fluorosulfate (ALD00416)



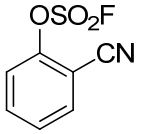
Yield: 4.1 g, 99%, colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.39 – 7.28 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 151.1, 138.9, 129.6, 122.3, 120.8, 113.4, 56.1. **^{19}F NMR (282 MHz, $CDCl_3$) δ:** 39.2. **IR (cm^{-1}):** 1502, 1449, 1262, 1234, 1190, 1105, 917, 819. **MS (EI) m/z (relative intensity):** 206 ($[M]^+$, 100). **HRMS (EI) Calcd. for** $C_7H_7FO_4S$: 206.0049. **Found:** 206.0044.

4-methoxyphenyl fluorosulfate (ALD00418)



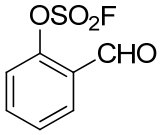
Yield: 4.1 g, 99%, light yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.25 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 9.2 Hz, 2H), 3.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 159.3, 143.5, 121.9 (d, *J* = 1.0 Hz), 115.1, 55.6. **^{19}F NMR (282 MHz, $CDCl_3$) δ:** 35.9. **IR (cm^{-1}):** 1504, 1448, 1258, 1235, 1144, 934, 838, 553. **MS (EI) m/z (relative intensity):** 206 ($[M]^+$, 59), 123 (100). **HRMS (EI) Calcd. for** $C_7H_7FO_4S$: 206.0049. **Found:** 206.0050.

2-cyanophenyl fluorosulfate (ALD00420)



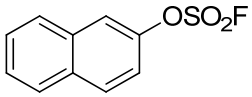
Yield: 3.0 g, 75% (purified by flash silica gel column chromatography, PE:EA=10:1), light yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.79 (dd, *J* = 12.6, 7.7 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 149.7, 135.1 (d, *J* = 1.9 Hz), 134.4, 129.3, 122.2, 113.2, 107.0. **^{19}F NMR (282 MHz, $CDCl_3$) δ:** 40.3. **IR (cm^{-1}):** 1489, 1458, 1238, 1165, 1092, 912, 827, 767. **MS (EI) m/z (relative intensity):** 201 ($[M]^+$, 48), 117 (100). **HRMS (EI) Calcd. for** $C_7H_4FNO_3S$: 200.9896. **Found:** 200.9898.

2-formylphenyl fluorosulfate (ALD00422)



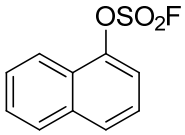
Yield: 3.5 g, 86%, light yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 10.30 (s, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 186.2, 150.5, 135.9, 130.8, 129.3, 128.1, 122.0. **^{19}F NMR (282 MHz, $CDCl_3$) δ:** 38.9. **IR (cm^{-1}):** 1709, 1609, 1456, 1235, 1161, 923, 837, 572. **MS (EI) m/z (relative intensity):** 204 ($[M]^+$, 26), 120 (100). **HRMS (EI) Calcd. for** $C_7H_5FO_4S$: 203.9893. **Found:** 203.9894.

Naphthalen-2-yl fluorosulfate (ALD00424)



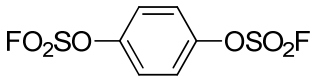
Yield: 4.5 g, 99%, brown solid; mp: 33-34 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.97 – 7.79 (m, 4H), 7.63 – 7.54 (m, 2H), 7.43 (d, *J* = 9.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 147.6, 133.3, 132.5, 130.8, 128.1, 128.0, 127.6, 127.3, 119.0, 118.8. **^{19}F NMR (282 MHz, $CDCl_3$) δ:** 37.3 .**IR (cm^{-1}):** 1447.6, 1242.7, 1229.0, 1112.4, 960.6, 886.9, 800.1, 756.5. **MS (EI) m/z (relative intensity):** 226 ($[M]^+$, 25), 115 (100). **HRMS (EI) Calcd. for** $C_{10}H_7FO_3S$: 226.0100. **Found:** 226.0101.

Naphthalen-1-yl fluorosulfate (ALD00430)



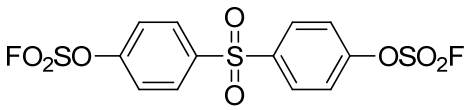
Yield: 4.5 g, 99%, colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.12 (d, *J* = 8.1 Hz, 1H), 7.95 – 7.84 (m, 2H), 7.70 – 7.44 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 146.1, 134.9, 128.7, 128.0, 127.8, 127.4, 125.6, 125.0, 120.5, 117.5 (d, *J* = 1.1 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ:** 38.6. **IR (cm^{-1}):** 1452, 1235, 1210, 1010, 919, 841, 798, 768. **MS (EI) m/z (relative intensity):** 226 ($[M]^+$, 89), 115 (100). **HRMS (EI) Calcd. for** $C_{10}H_7FO_3S$: 226.0100. **Found:** 226.0098.

1,4-phenylene difluorosulfate (ALD00384)



Yield: 5.3 g, 97%, white solid; mp: 75-77 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.50 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 148.9, 123.3 (d, *J* = 1.1 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ:** 35.8. **IR (cm^{-1}):** 1492, 1456, 1235, 1135, 919, 807, 784, 598. **MS (EI) m/z (relative intensity):** 274 ($[M]^+$, 24), 191 (100). **HRMS (EI) Calcd. for** $C_6H_4F_2O_6S_2$: 273.9417. **Found:** 273.9419.

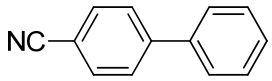
Bis-4-[(fluorosulphonyl)oxy]phenyl sulphone (ALD00428)



Yield: 8.0 g, 97%, white solid; mp: 112-114 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.09 (d, *J* = 7.7 Hz, 4H), 7.53 (d, *J* = 8.3 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 152.9, 141.2, 130.6, 122.4 (d, *J* = 0.9 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ:** 39.1. **IR (cm^{-1}):** 1488, 1456, 1235, 1143, 914, 814,

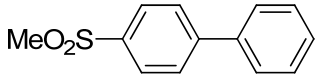
691, 594. **MS (EI) m/z (relative intensity):** 414 ([M]$^+$, 24), 223 (100). **HRMS (EI) Calcd. for** $C_{12}H_8F_2O_8S_3$: 413.9349. **Found:** 413.9353.

4-phenylbenzonitrile (Table 2, entry 5)



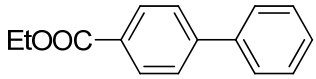
Yield: 0.173 g, 97%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.70 (q, *J* = 8.3 Hz, 4H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.53 – 7.40 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 145.6, 139.1, 132.5, 129.0, 128.6, 127.6, 127.1, 118.9, 110.8. **MS (EI) m/z (relative intensity):** 179 ([M]$^+$, 100). (*Org. Lett.* **2001**, *3*, 3049)

4-(methylsulfonyl)biphenyl (Table 3, entry 1)



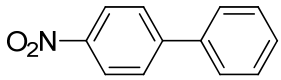
Yield: 0.216 g, 93%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.01 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.53 – 7.39 (m, 3H), 3.10 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 146.6, 139.0, 139.0, 129.0, 128.6, 127.9, 127.8, 127.3, 44.6. **MS (EI) m/z (relative intensity):** 232 ([M]$^+$, 84), 153 (100). (*J. Org. Chem.* **2005**, *70*, 2696)

Ethyl 4-phenylbenzoate (Table 3, entry 2)



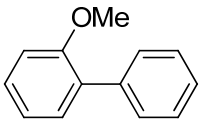
Yield: 0.224 g, 99%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.12 (d, *J* = 8.1 Hz, 2H), 7.72 – 7.57 (m, 4H), 7.44 (dt, *J* = 22.6, 7.1 Hz, 3H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 166.4, 145.4, 139.9, 130.0, 129.2, 128.8, 128.0, 127.2, 126.9, 60.9, 14.3. **MS (EI) m/z (relative intensity):** 226 ([M]$^+$, 44), 181 (100).(*J. Org. Chem.* **2007**, *72*, 9346)

4-nitrobiphenyl (Table 3, entry 3)



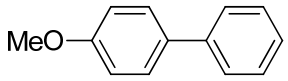
Yield: 0.192 g, 96%, light yellow solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.28 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 6.9 Hz, 2H), 7.54 – 7.42 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 147.5, 147.0, 138.6, 129.1, 128.8, 127.7, 127.3, 124.0. **MS (EI) m/z (relative intensity):** 199 ([M]$^+$, 90), 152 (100). (*J. Org. Chem.* **2005**, *70*, 2696)

2-methoxybiphenyl (Table 3, entry 4)



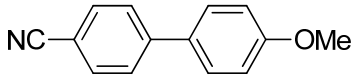
Yield: 0.174 g, 94%, colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.62 (d, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 3H), 7.14 – 7.02 (m, 2H), 3.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 156.4, 138.5, 130.8, 130.7, 129.5, 128.6, 127.9, 126.9, 120.8, 111.2, 55.5. **MS (EI) m/z (relative intensity):** 184 ([M]$^+$, 100). (*J. Org. Chem.* **2011**, *76*, 1467)

4-methoxybiphenyl (Table 3, entry 5)



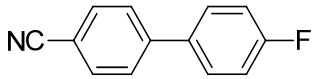
Yield: 0.166 g, 90%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.57 (t, *J* = 6.9 Hz, 4H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 6.8 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3. **MS (EI) m/z (relative intensity):** 184 ([M]$^+$, 100). (*Org. Lett.* **2001**, *3*, 3049)

4-cyano-4'-methoxybiphenyl (Table 3, entry 6)



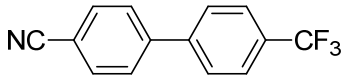
Yield: 0.194 g, 93%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.66 (dd, *J* = 15.9, 8.1 Hz, 4H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 160.1, 145.1, 132.5, 131.4, 128.3, 127.0, 119.0, 114.5, 110.0, 55.3. **MS (EI) m/z (relative intensity):** 209 ([M]$^+$, 100). (*Green Chem.* **2013**, *15*, 3150)

4-cyano-4'-fluorobiphenyl (Table 3, entry 7)



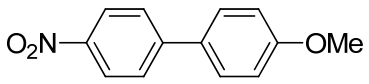
Yield: 0.185 g, 94%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.66 (dd, *J* = 22.5, 8.2 Hz, 4H), 7.55 (dd, *J* = 7.9, 5.8 Hz, 2H), 7.15 (t, *J* = 8.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 163.0 (d, *J* = 248.8 Hz), 144.4, 135.1 (d, *J* = 3.4 Hz), 132.5, 128.8 (d, *J* = 8.3 Hz), 127.4, 118.7, 116.0 (d, *J* = 21.7 Hz), 110.8. **^{19}F NMR (282 MHz, $CDCl_3$) δ:** -113.5 (m). **MS (EI) m/z (relative intensity):** 197 ([M]$^+$, 100). (*J. Org. Chem.* **2007**, *72*, 9346)

4-cyano-4'-trifluoromethylbiphenyl (Table 3, entry 8)



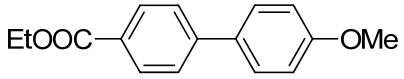
Yield: 0.225 g, 91%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.80 – 7.65 (m, 8H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 144.0, 142.6, 132.7, 130.6 (q, *J* = 32.6 Hz), 127.9, 127.6, 126.0 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.1 Hz), 118.5, 111.9. **^{19}F NMR (282 MHz, $CDCl_3$) δ:** -63.0. **MS (EI) m/z (relative intensity):** 247 ([M]$^+$, 100). (*J. Org. Chem.* **2007**, *72*, 9346)

4-nitro-4'-methoxybiphenyl (Table 3, entry 9)



Yield: 0.214 g, 93%, light yellow solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.23 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 160.4, 147.1, 146.4, 130.9, 128.5, 127.0, 124.0, 114.5, 55.3. **MS (EI) m/z (relative intensity):** 229 ([M]$^+$, 100). (*J. Org. Chem.* **2009**, *74*, 6283)

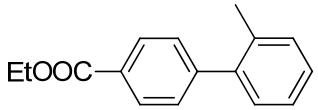
Ethyl 4'-methoxybiphenyl-4-carboxylate (Table 3, entry 10)



Yield: 0.238 g, 93%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.09 (d, *J* = 8.3 Hz, 2H), 7.59

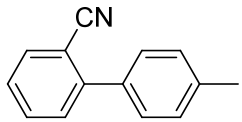
(dd, *J* = 14.0, 8.6 Hz, 4H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 166.5, 159.7, 145.0, 132.3, 130.0, 128.5, 128.3, 126.3, 114.3, 60.8, 55.3, 14.3. **MS (EI) m/z (relative intensity):** 256 ($[M]^+$, 100). (*DaltonTran.* **2012**, *41,* 10453)

Ethyl 2'-methylbiphenyl-4-carboxylate (Table 3, entry 11)



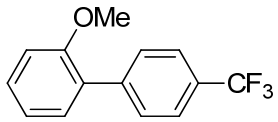
Yield: 0.239 g, 99%, colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.09 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.19 (m, 4H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 166.5, 146.6, 140.9, 135.1, 130.4, 129.5, 129.3, 129.2, 128.9, 127.8, 125.9, 60.9, 20.4, 14.3. **MS (EI) m/z (relative intensity):** 240 ($[M]^+$, 58), 185 (100). (*DaltonTran.* **2012**, *41,* 10453)

2-cyano-4'-methylbiphenyl (Table 3, entry 12)



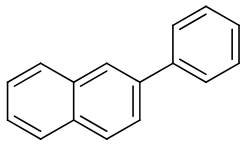
Yield: 0.138 g, 71%, light yellow solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.76 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.46 (dt, *J* = 15.2, 8.4 Hz, 4H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 145.4, 138.6, 135.2, 133.6, 132.7, 129.9, 129.4, 128.5, 127.2, 118.8, 111.1, 21.2. **MS (EI) m/z (relative intensity):** 193 ($[M]^+$, 100). (*Green Chem.* **2012**, *14*, 2999)

2-methoxy-4'-trifluoromethylbiphenyl (Table 3, entry 13)



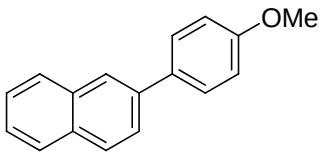
Yield: 0.219 g, 87%, colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.72 – 7.62 (m, 4H), 7.43 – 7.31 (m, 2H), 7.06 (dd, *J* = 17.2, 8.0 Hz, 2H), 3.85 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 156.4, 142.2, 130.7, 129.8, 129.5, 129.2, 128.9 (q, *J* = 32.2 Hz) 124.9 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.9 Hz), 121.0, 111.3, 55.5. **^{19}F NMR (282 MHz, $CDCl_3$) δ:** -62.8. **MS (EI) m/z (relative intensity):** 252 ($[M]^+$, 100).(*Adv. Synth, Catal.* **2004**, *346*, 1669)

2-phenylnaphthalene (Table 3, entry 14)



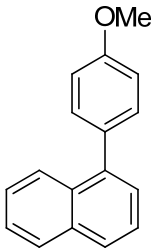
Yield: 0.193 g, 94%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.13 (s, 1H), 7.96 (t, *J* = 9.7 Hz, 3H), 7.87 – 7.74 (m, 3H), 7.57 (d, *J* = 4.9 Hz, 4H), 7.47 (d, *J* = 7.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 141.1, 138.5, 133.6, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.2, 125.9, 125.8, 125.5. **MS (EI) m/z (relative intensity):** 204 ($[M]^+$, 100). (*Org. Lett.* **2001**, *3*, 3049)

2-(4'-methoxyphenyl)naphthalene (Table 3, entry 15)



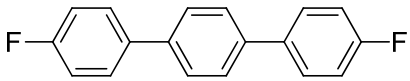
Yield: 0.233 g, 99%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.04 (s, 1H), 7.92 (dd, *J* = 11.5, 7.5 Hz, 3H), 7.73 (dd, *J* = 16.3, 8.6 Hz, 3H), 7.58 – 7.45 (m, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 159.2, 138.1, 133.7, 133.6, 132.3, 128.4, 128.3, 128.0, 127.6, 126.2, 125.6, 125.4, 125.0, 114.3, 55.3. **MS (EI) m/z (relative intensity):** 234 ($[M]^+$, 100). (*Green Chem.* **2013**, *15*, 3150)

1-(4'-methoxyphenyl)naphthalene (Table 3, entry 16)



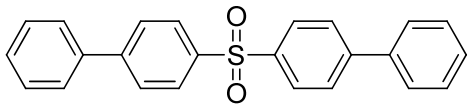
Yield: 0.220 g, 94%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.97 (dd, *J* = 13.5, 8.1 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.51 (dt, *J* = 14.0, 6.7 Hz, 6H), 7.08 (d, *J* = 8.1 Hz, 2H), 3.93 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 158.9, 139.9, 133.8, 133.1, 131.8, 131.1, 128.2, 127.3, 126.9, 126.0, 125.9, 125.7, 125.4, 113.7, 55.3. **MS (EI) m/z (relative intensity):** 234 ($[M]^+$, 100). (*J. Org. Chem.* **2013**, *78*, 118243)

4, 4''-difluoro-[1,1';4',1'']terphenyl (Table 3, entry 17)



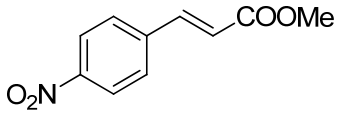
Yield: 0.248 g, 93%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.64 – 7.54 (m, 8H), 7.15 (t, *J* = 8.6 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 162.5 (d, *J* = 246.5 Hz), 139.1, 136.7, 128.6 (d, *J* = 8.0 Hz), 127.4, 115.7 (d, *J* = 21.5 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ:** -116.0 (m). **MS (EI) m/z (relative intensity):** 266 ($[M]^+$, 100). (*J. Org. Chem.* **2012**, *77*, 6608)

Bis-biphenyl-4-yl sulphone (Table 3, entry 18)



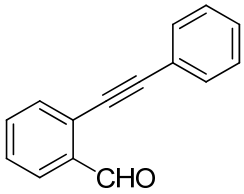
Yield: 0.354 g, 95%, white solid; mp: 230-231 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.06 (d, *J* = 8.2 Hz, 4H), 7.72 (d, *J* = 8.1 Hz, 4H), 7.58 (d, *J* = 8.0 Hz, 4H), 7.51 – 7.38 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 146.1, 140.2, 139.1, 129.0, 128.5, 128.1, 127.9, 127.3. **MS (EI) m/z (relative intensity):** 370 ($[M]^+$, 60), 201 (100). **HRMS (EI) Calcd. for** $C_{24}H_{18}O_2S$: 370.1028. **Found:** 370.1027.

(*E*)-methyl 4-nitrocinnamate (Table 4, entry 1)



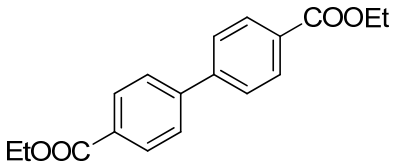
Yield: 0.261 g, 63%, light yellow solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.23 (d, *J* = 8.7 Hz, 2H), 7.73 (s, 1H), 7.66 (d, *J* = 8.9 Hz, 3H), 6.55 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 166.4, 148.5, 141.8, 140.4, 128.6, 124.1, 122.0, 52.0. **MS (EI) m/z (relative intensity):** 207 ($[M]^+$, 49), 176 (100). (*Org. Lett.* **2011**, 1*3*, 2646)

2-(2'-phenylethynyl)benzaldehyde (Table 4, entry 2)



Yield: 0.300 g, 73%, brown oil. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 10.66 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.54 (m, 4H), 7.47 – 7.36 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 191.5, 135.7, 133.7, 133.1, 131.6, 129.0, 128.5, 128.4, 127.1, 126.7, 122.2, 96.3, 84.8. **MS (ESI) m/z:** 207.2 $[M+H]^+$. (*J. Org. Chem.* **2013**, *78*, 6657)

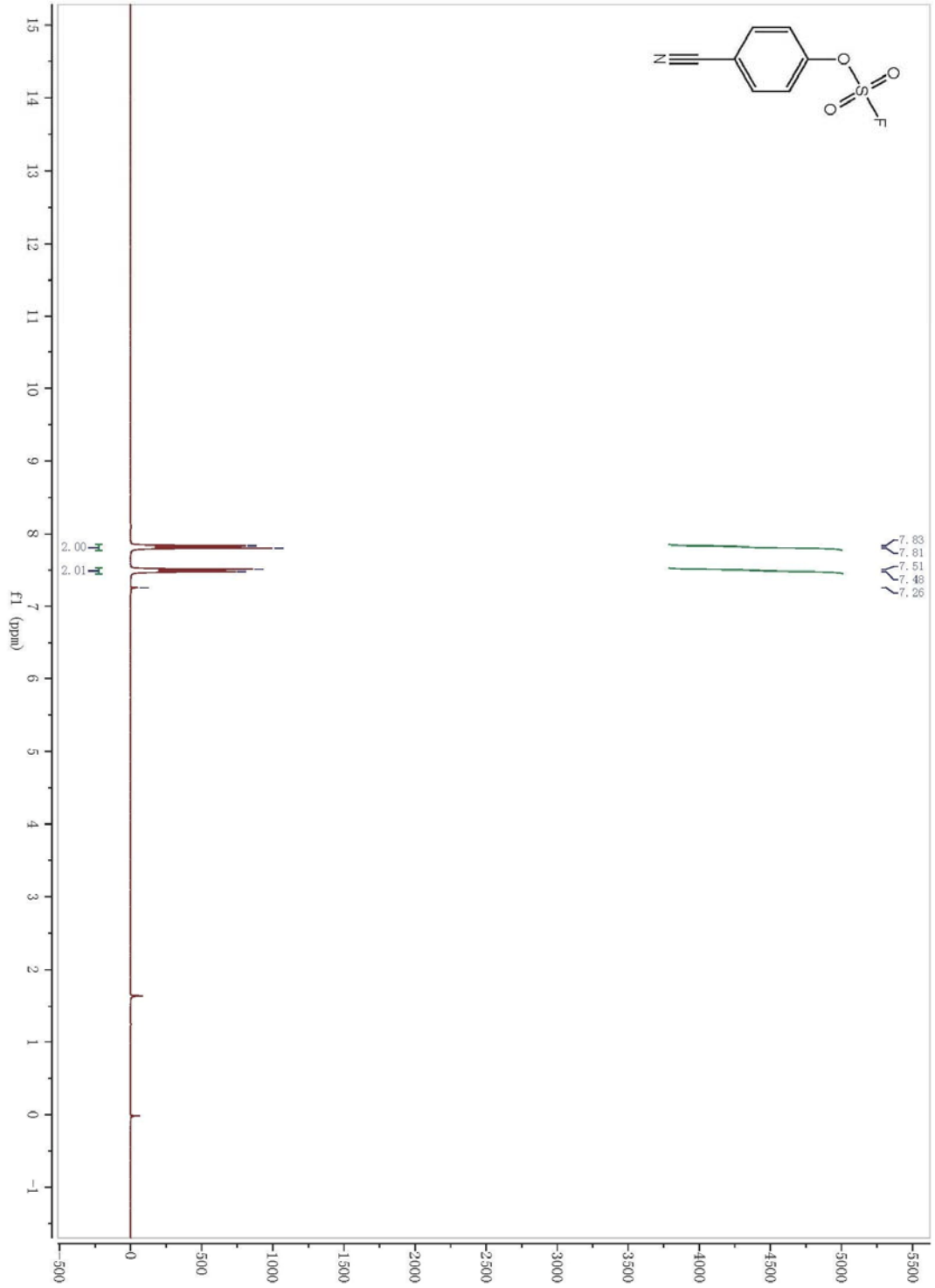
4,4'-dicarbethoxybiphenyl (Table 4, entry 3)



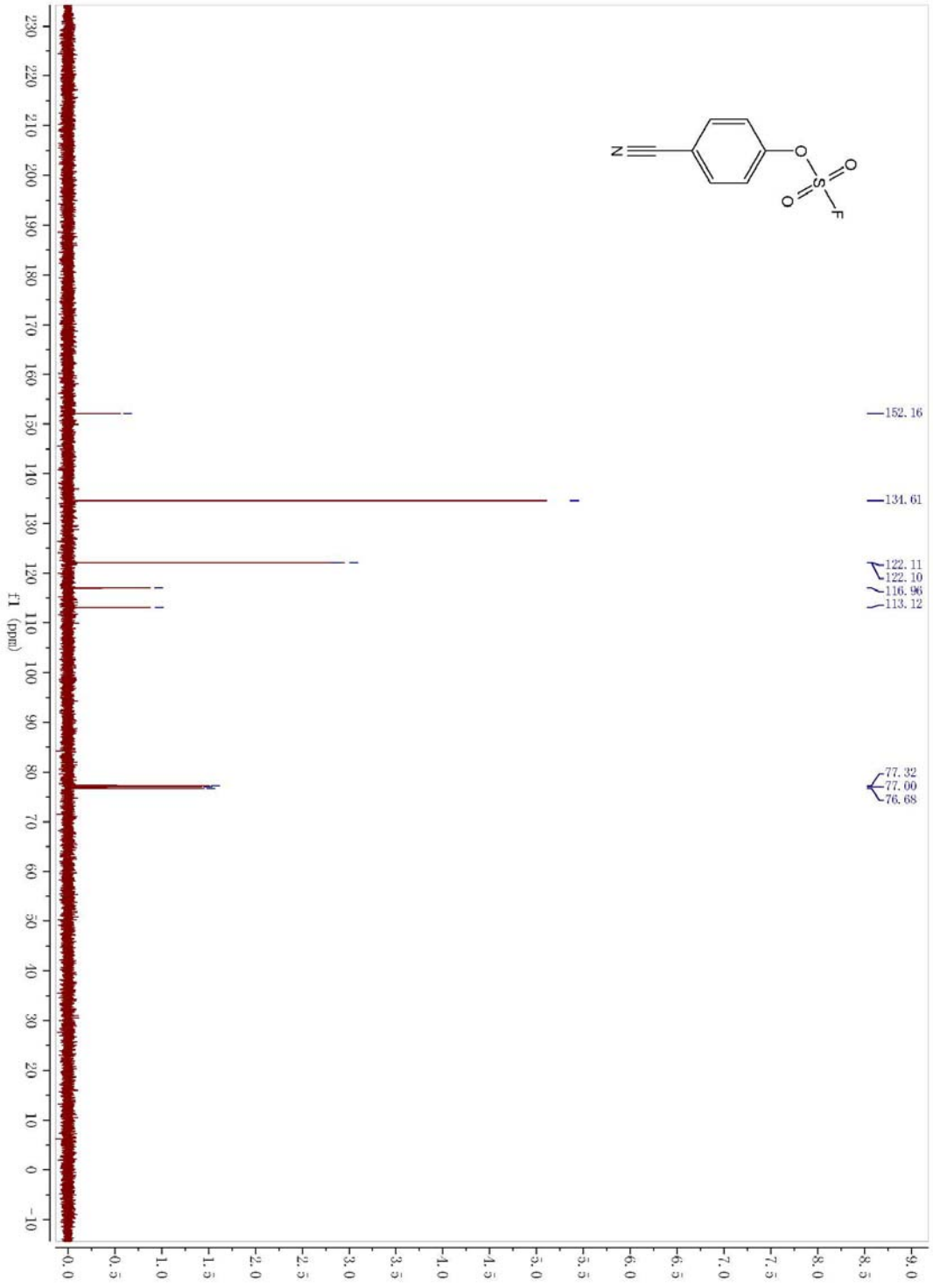
Yield: 0.207 g, 69%, white solid. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 8.13 (d, *J* = 7.9 Hz, 4H), 7.67 (d, *J* = 8.0 Hz, 4H), 4.40 (q, *J* = 7.0 Hz, 4H), 1.41 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 166.2, 144.14, 130.0, 130.0, 127.1, 61.0, 14.3. **MS (EI) m/z (relative intensity):** 298 ($[M]^+$, 44), 253 (100). (*J. Org. Chem.* **2006**, *71*, 1284)

5. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectras

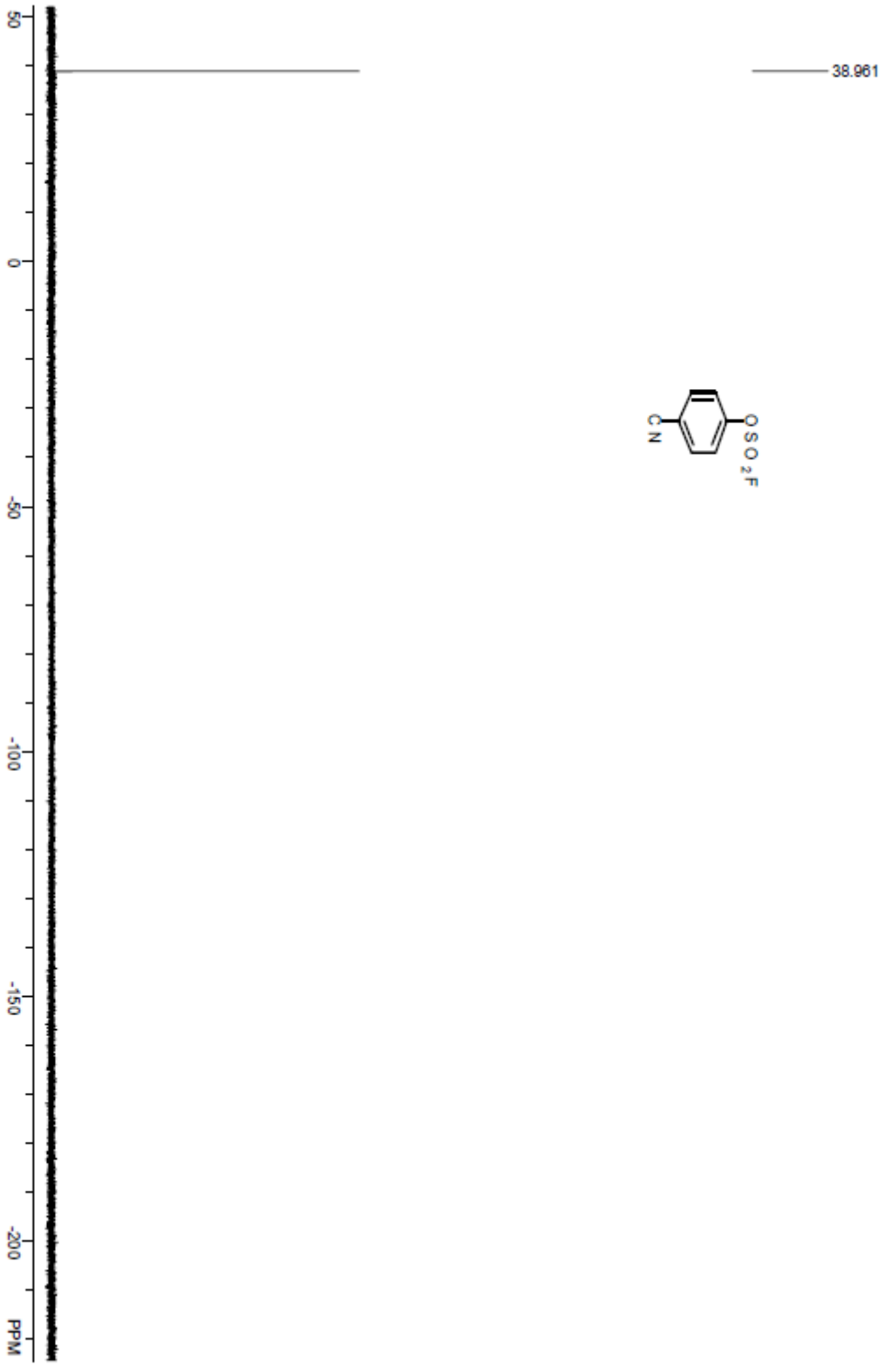
^{1}H NMR for ALD00404



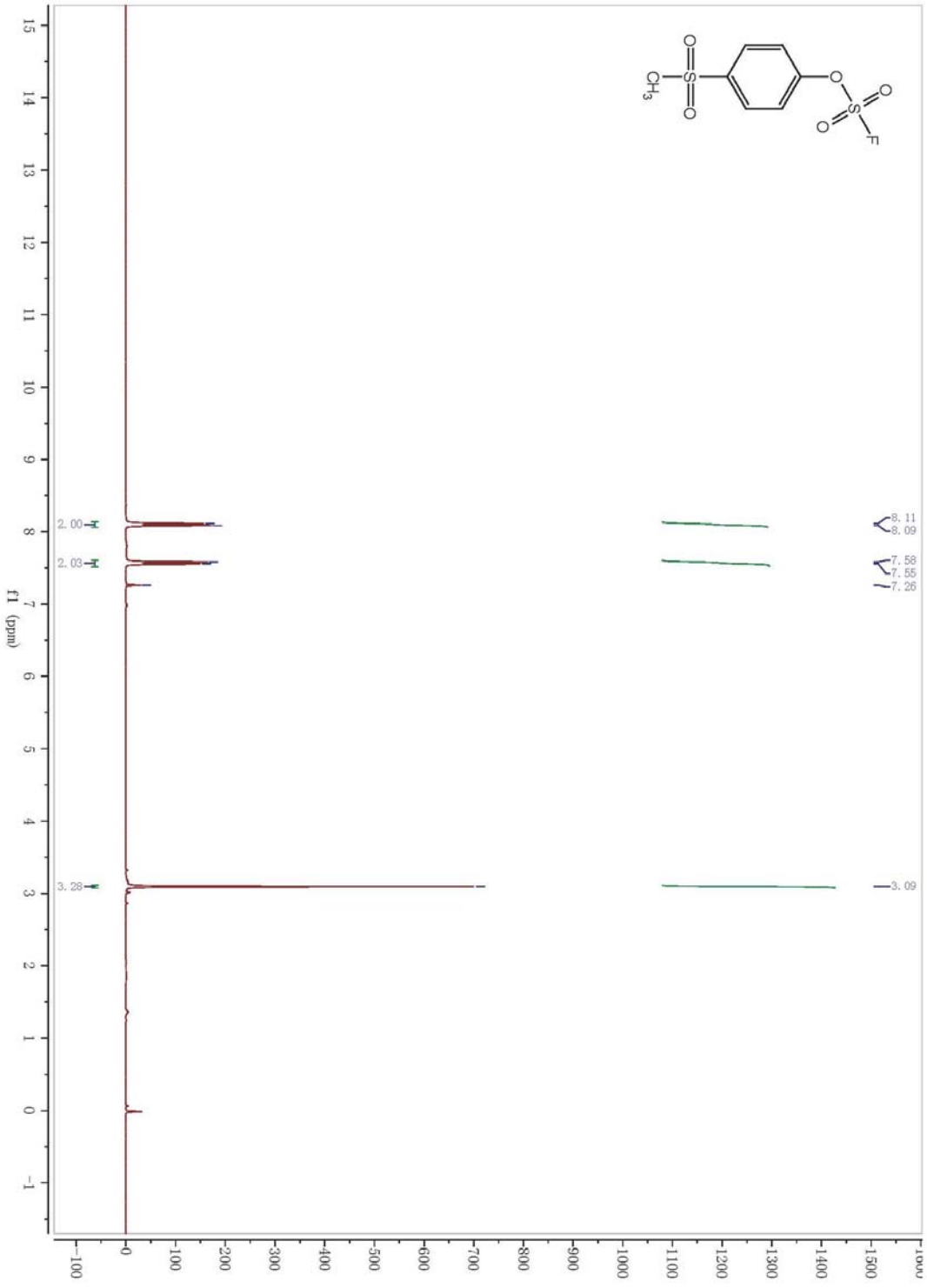
^{13}C NMR for ALD 00404



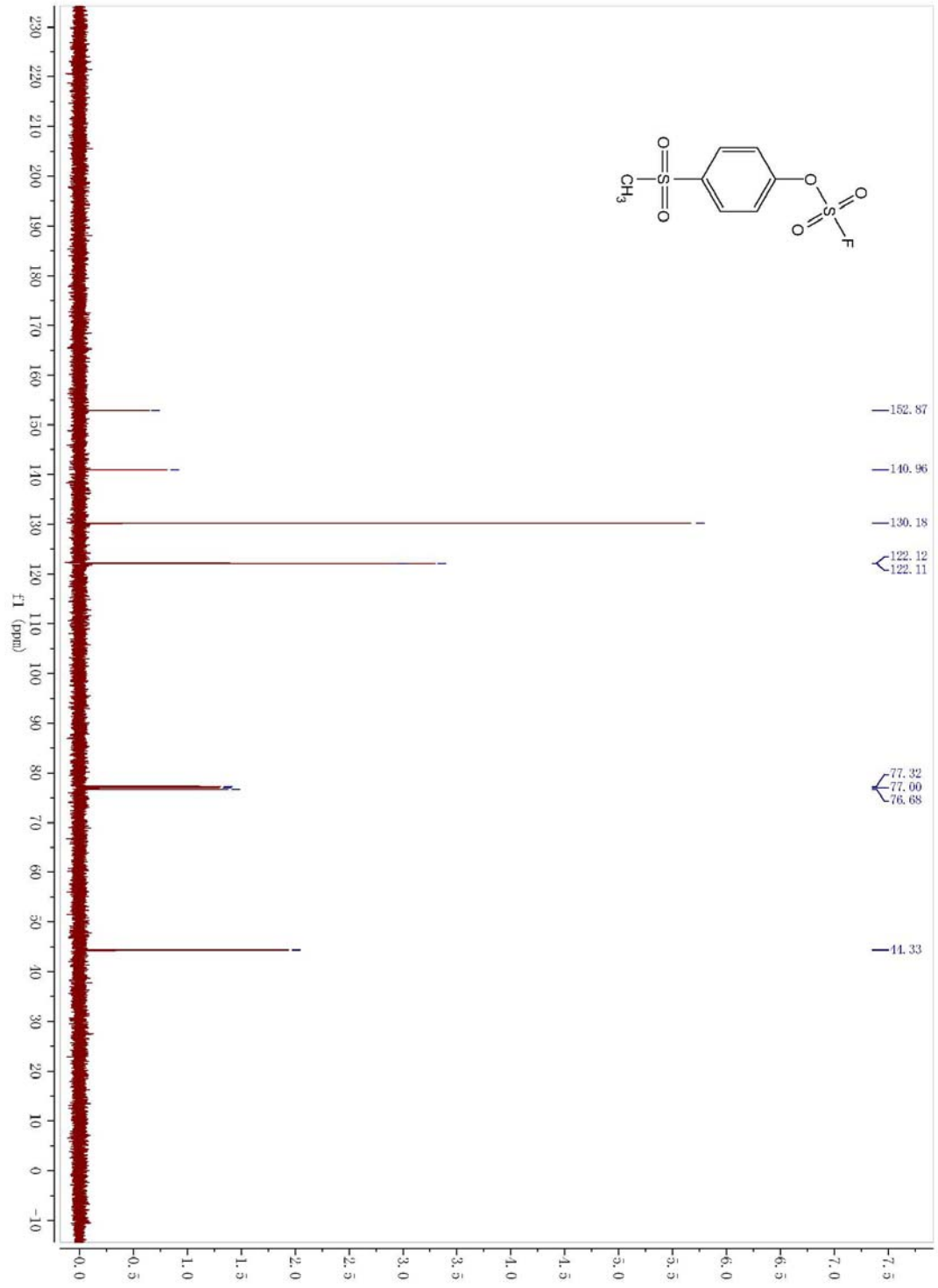
^{19}F NMR for ALD 00404



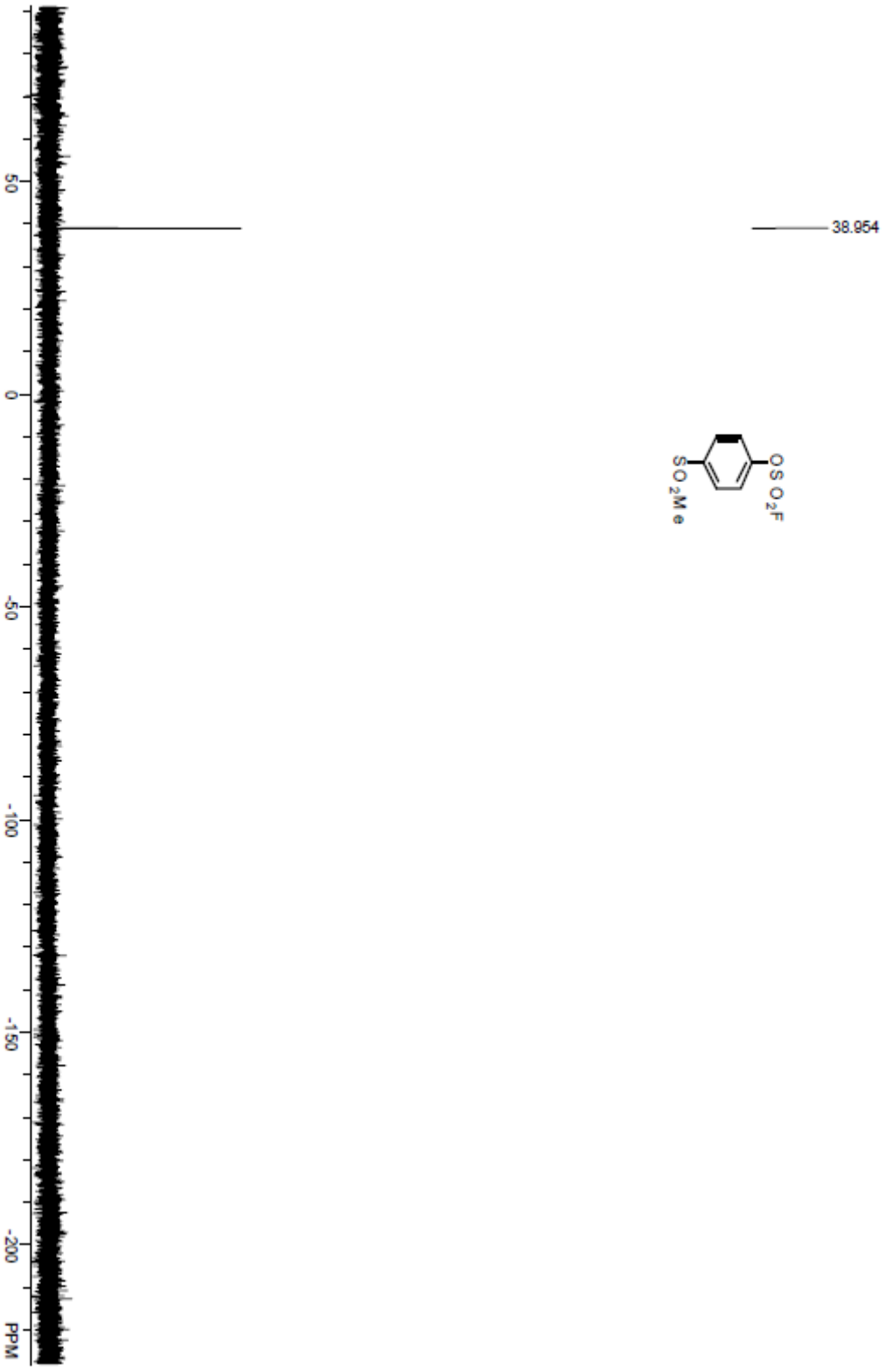
^{1}H NMR for ALD 00410



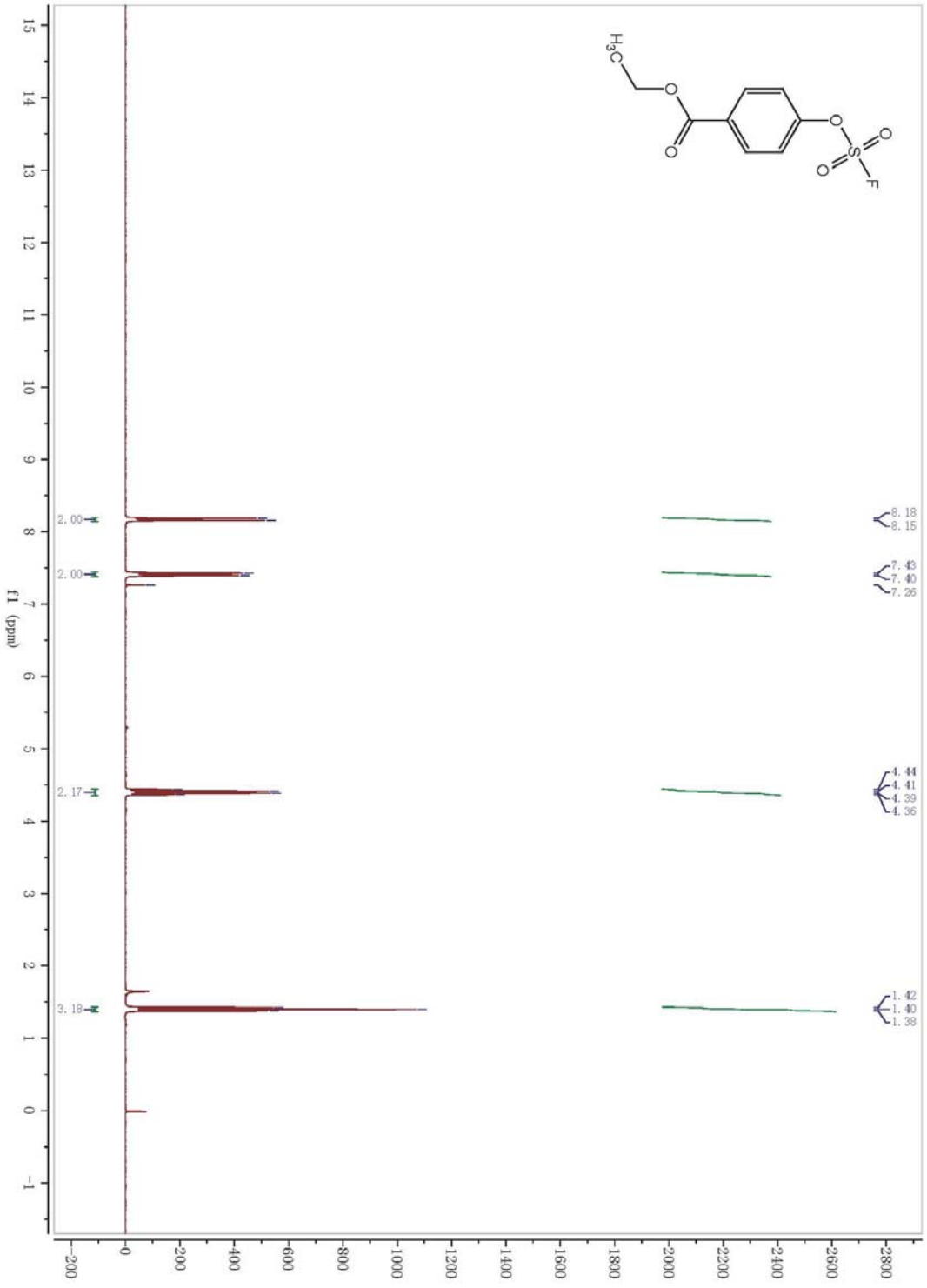
^{13}C NMR for ALD 00410



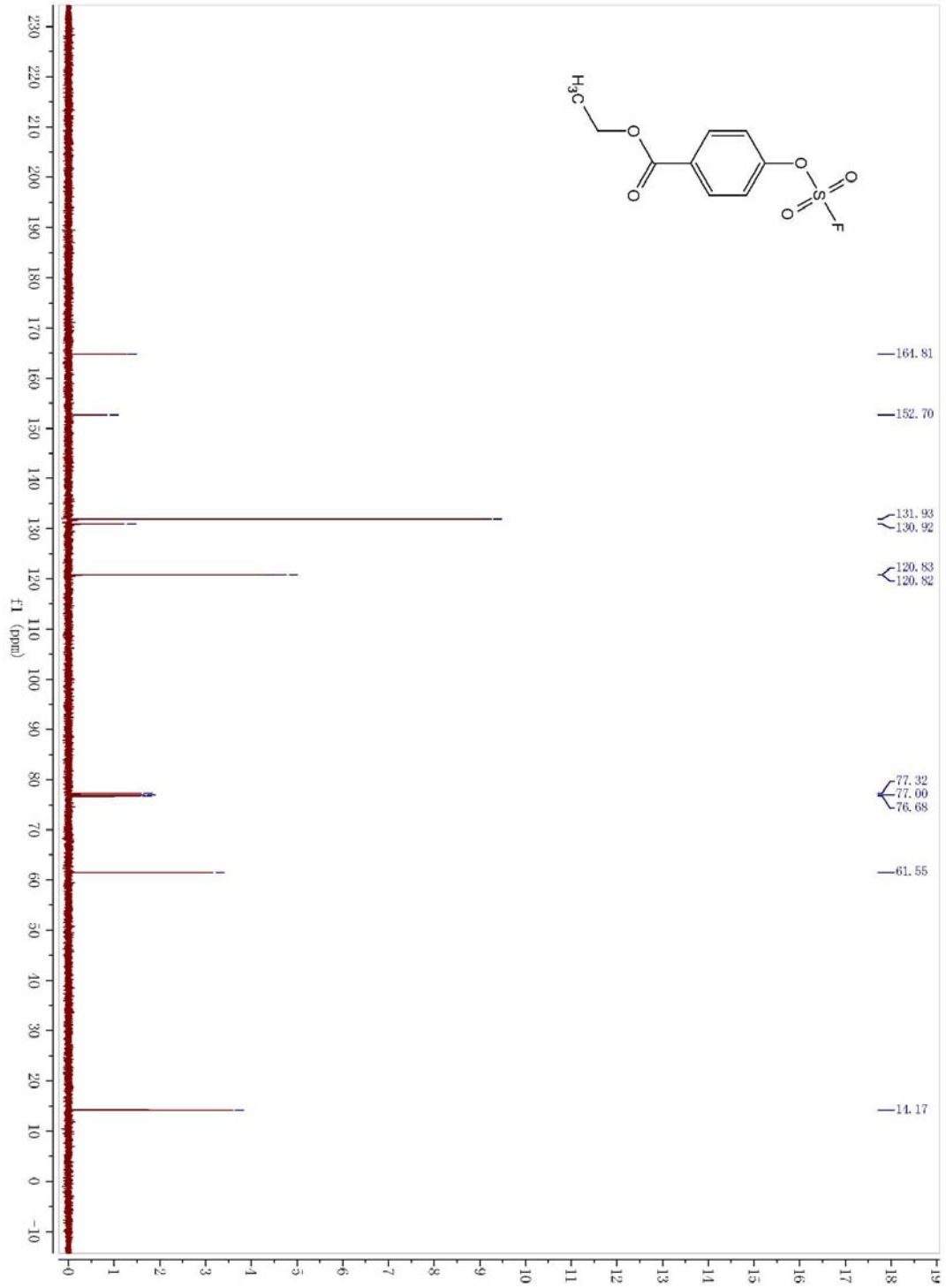
^{19}F NMR for ALD 00410



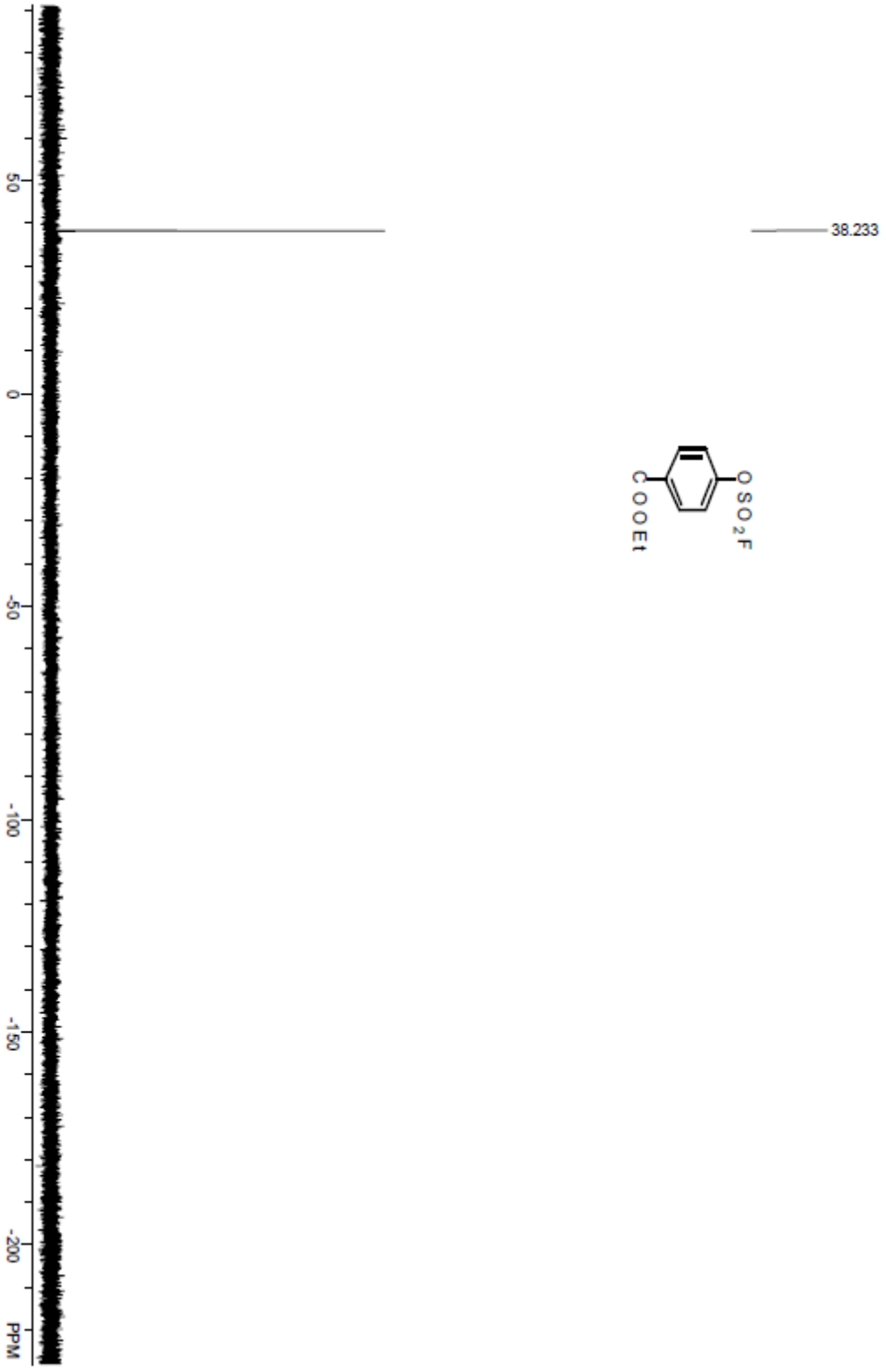
^{1}H NMR for ALD 00412



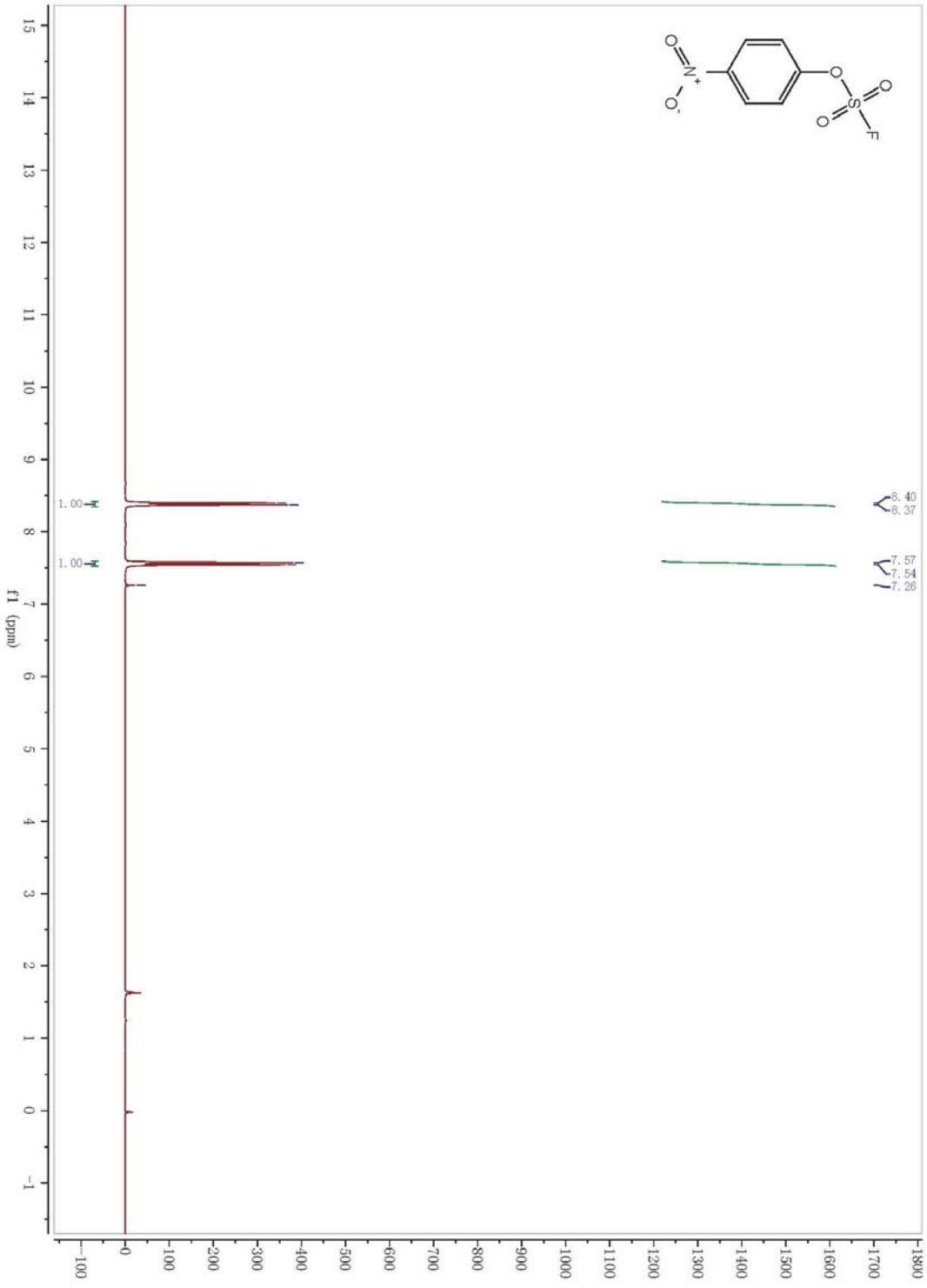
^{13}C NMR for ALD 00412



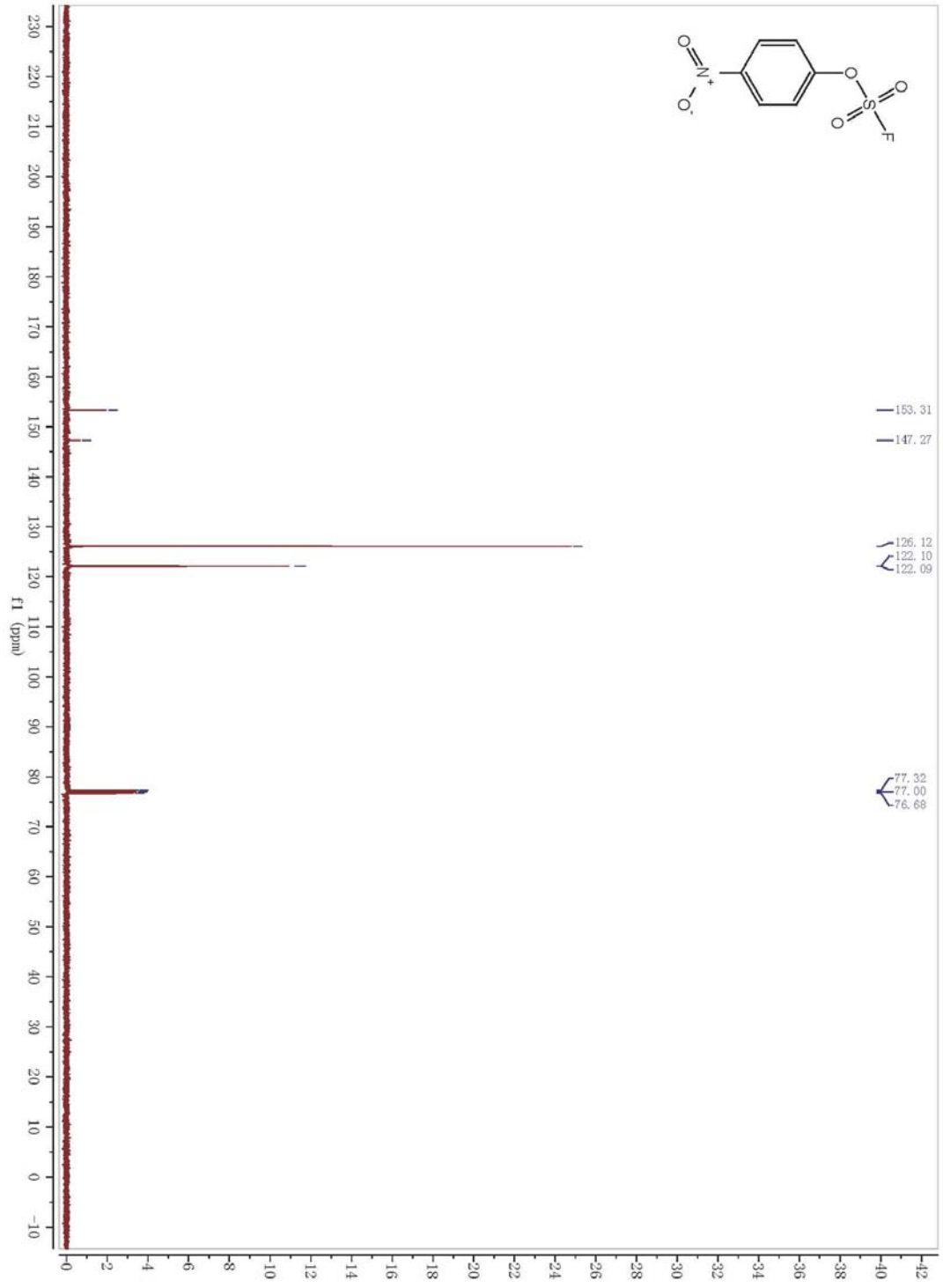
^{19}F NMR for ALD 00412



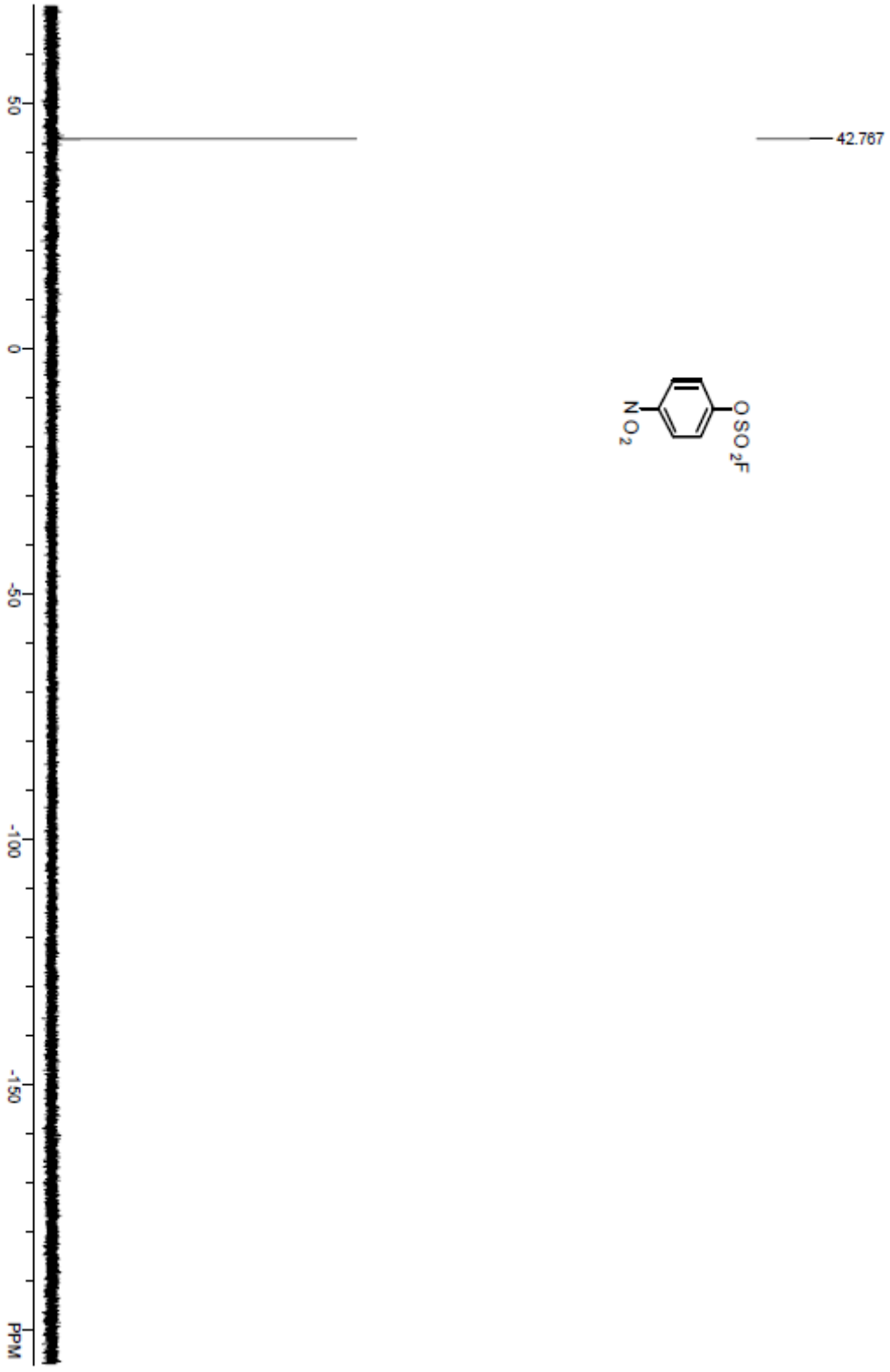
^{1}H NMR for ALD 00414



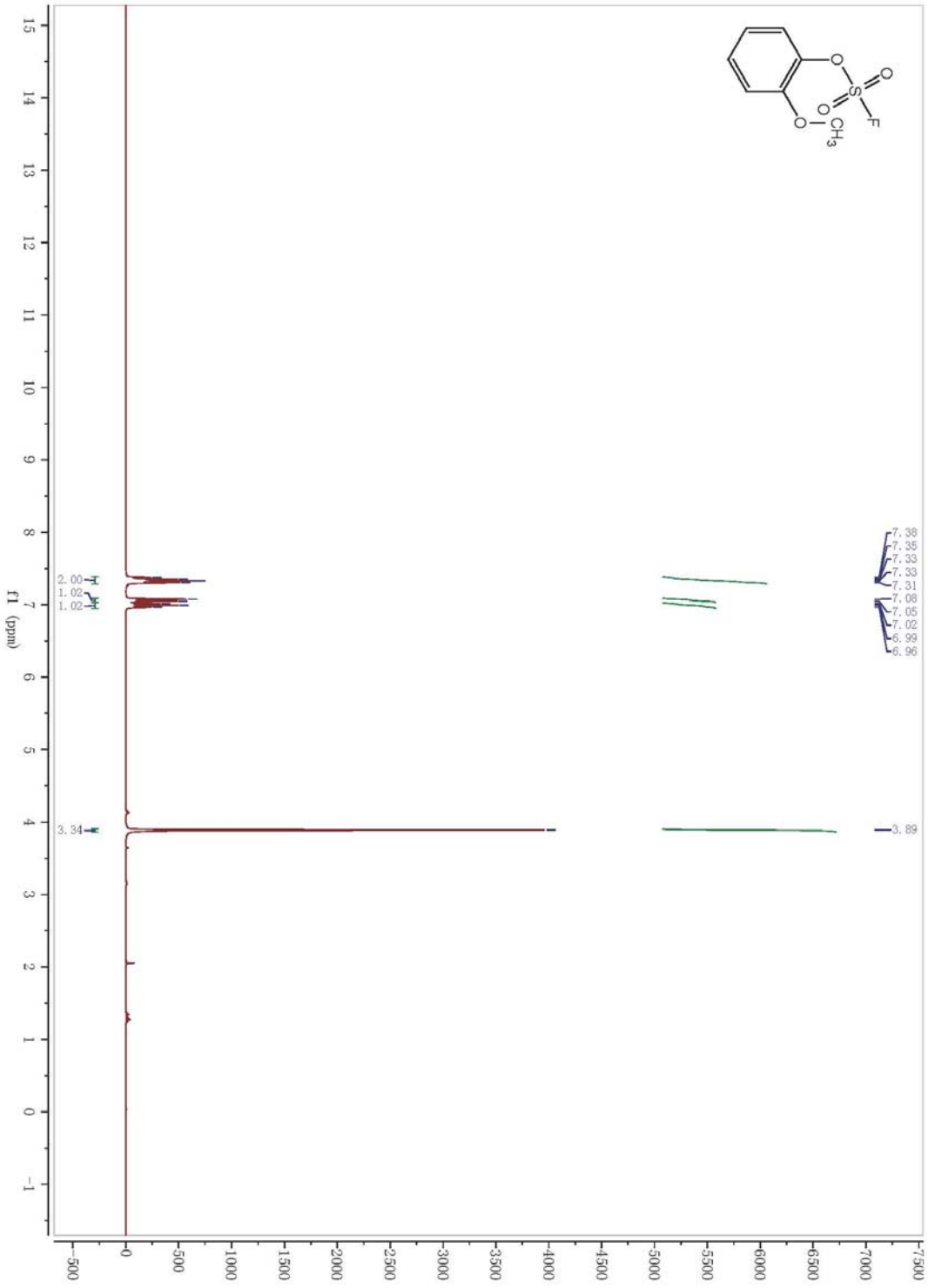
^{13}C NMR for ALD 00414



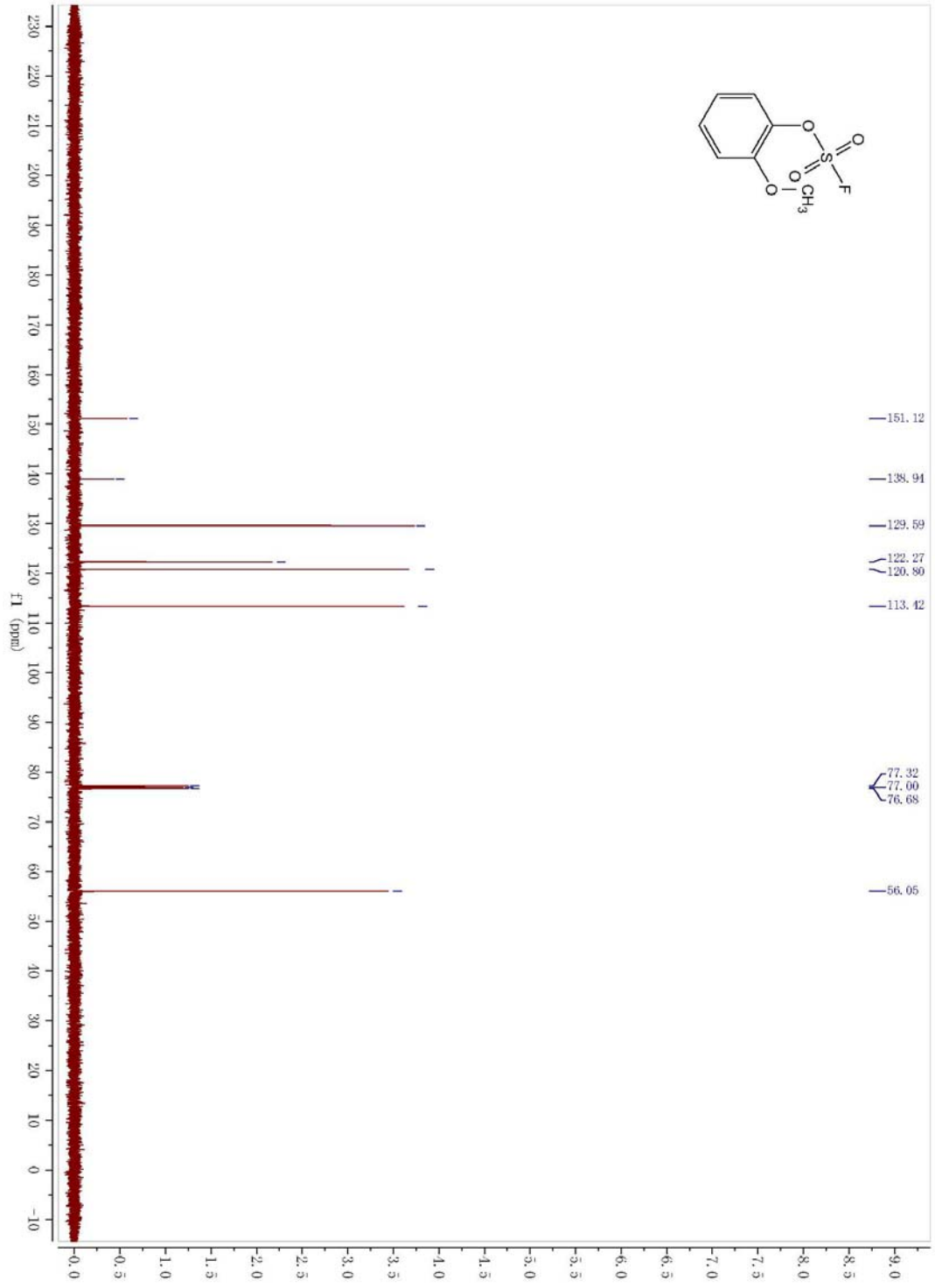
^{19}F NMR for ALD 00414



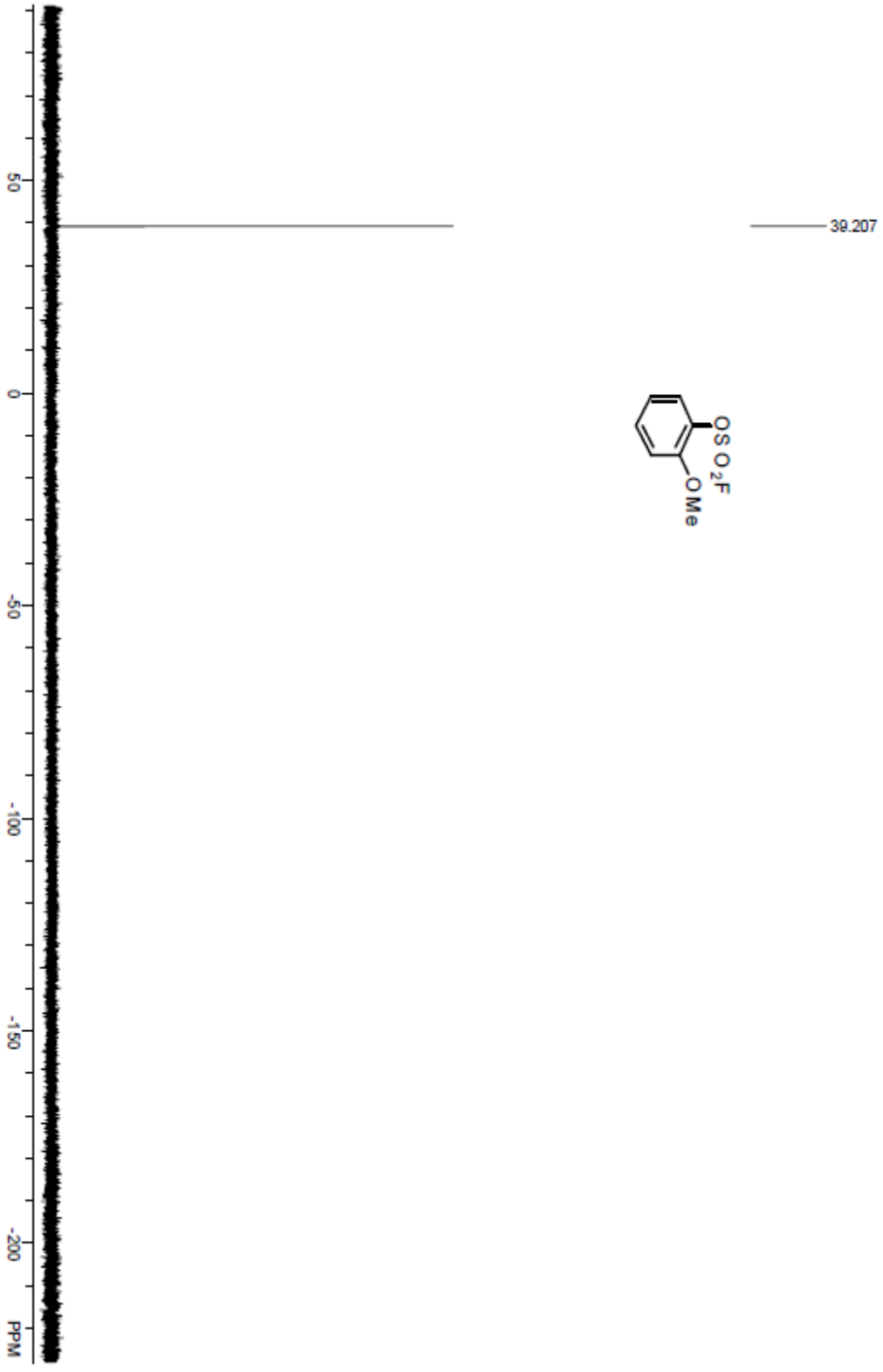
^{1}H NMR for ALD 00416



^{13}C NMR for ALD 00416



^{19}F NMR for ALD 00416



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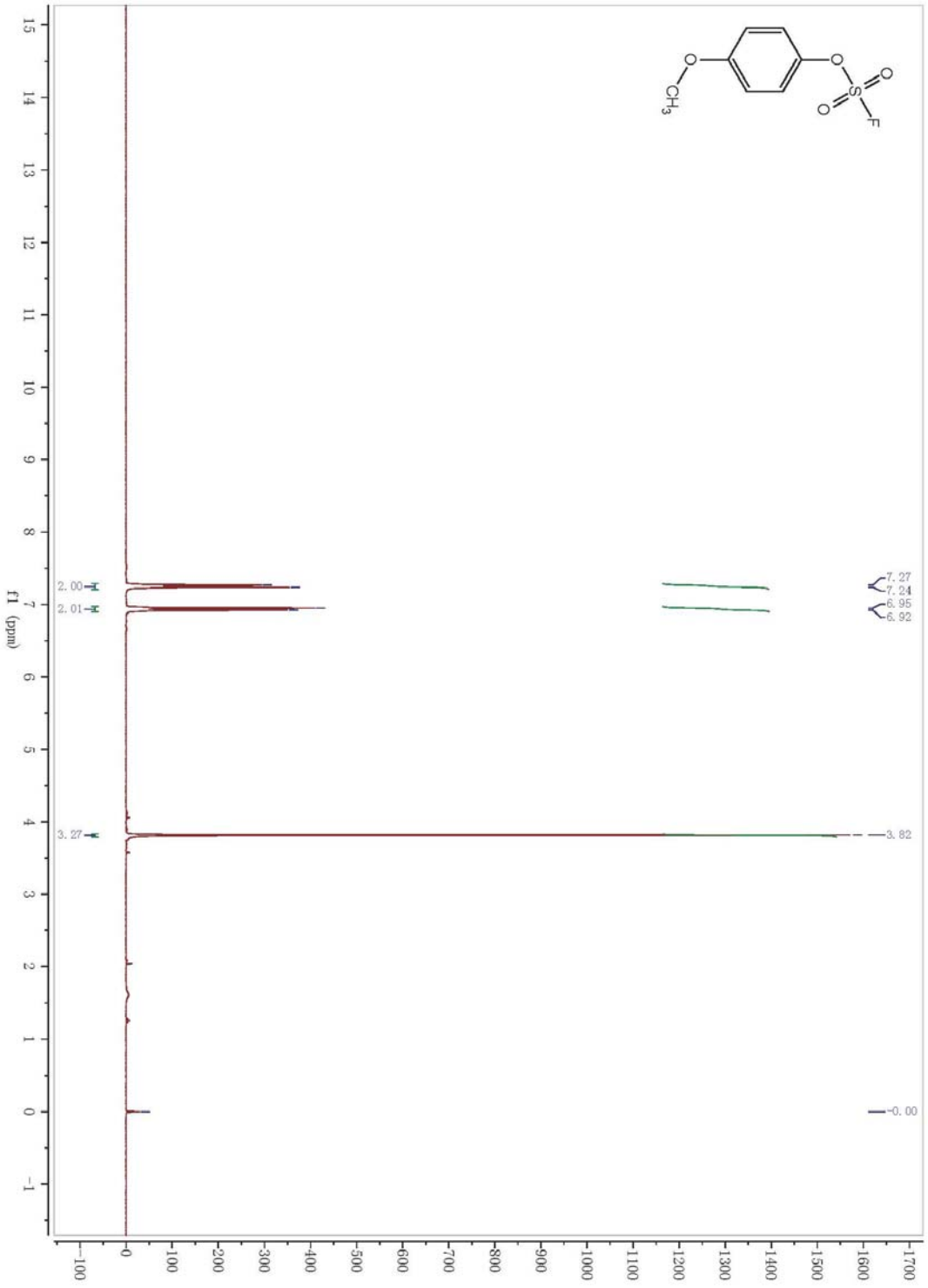
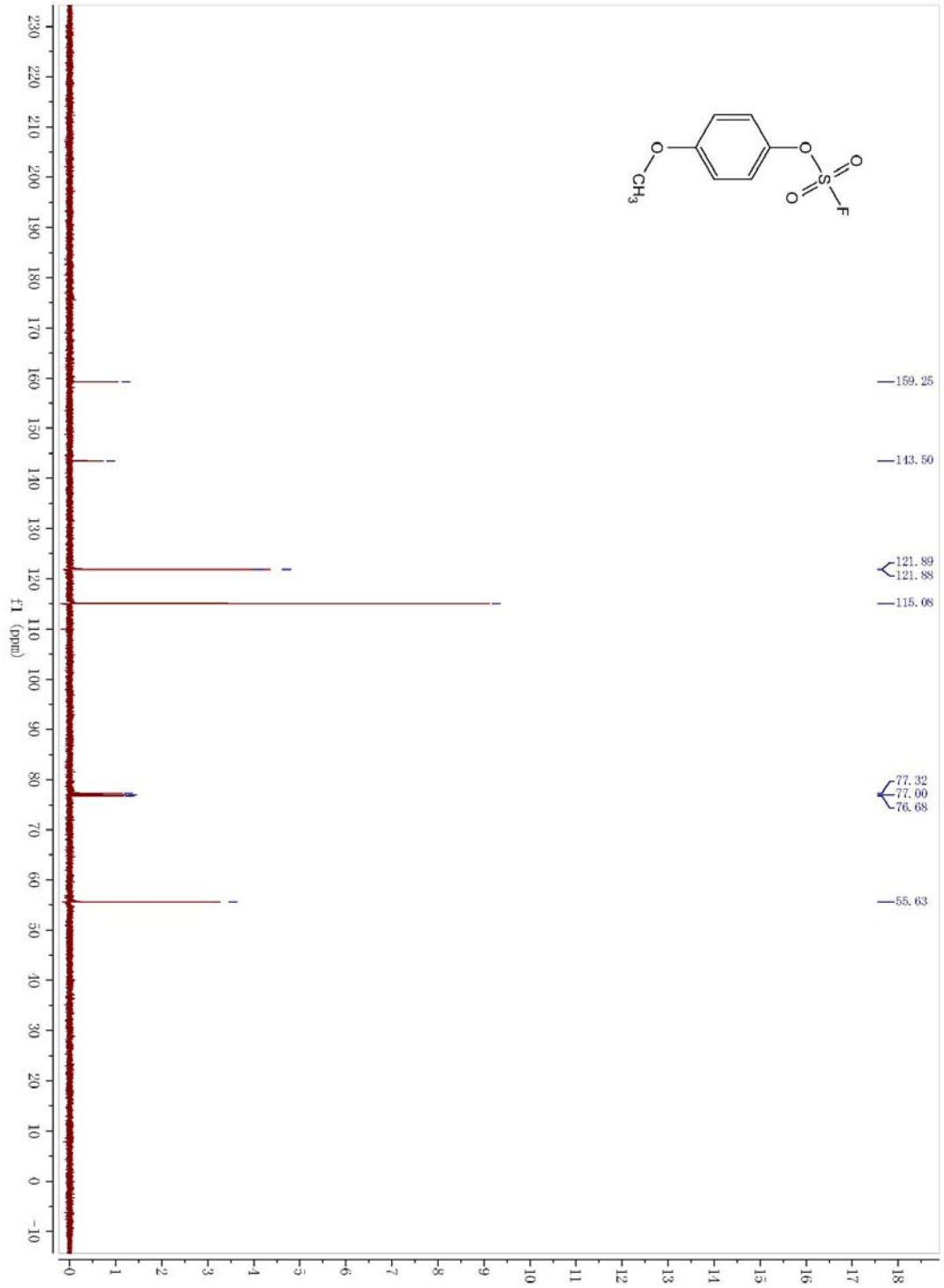
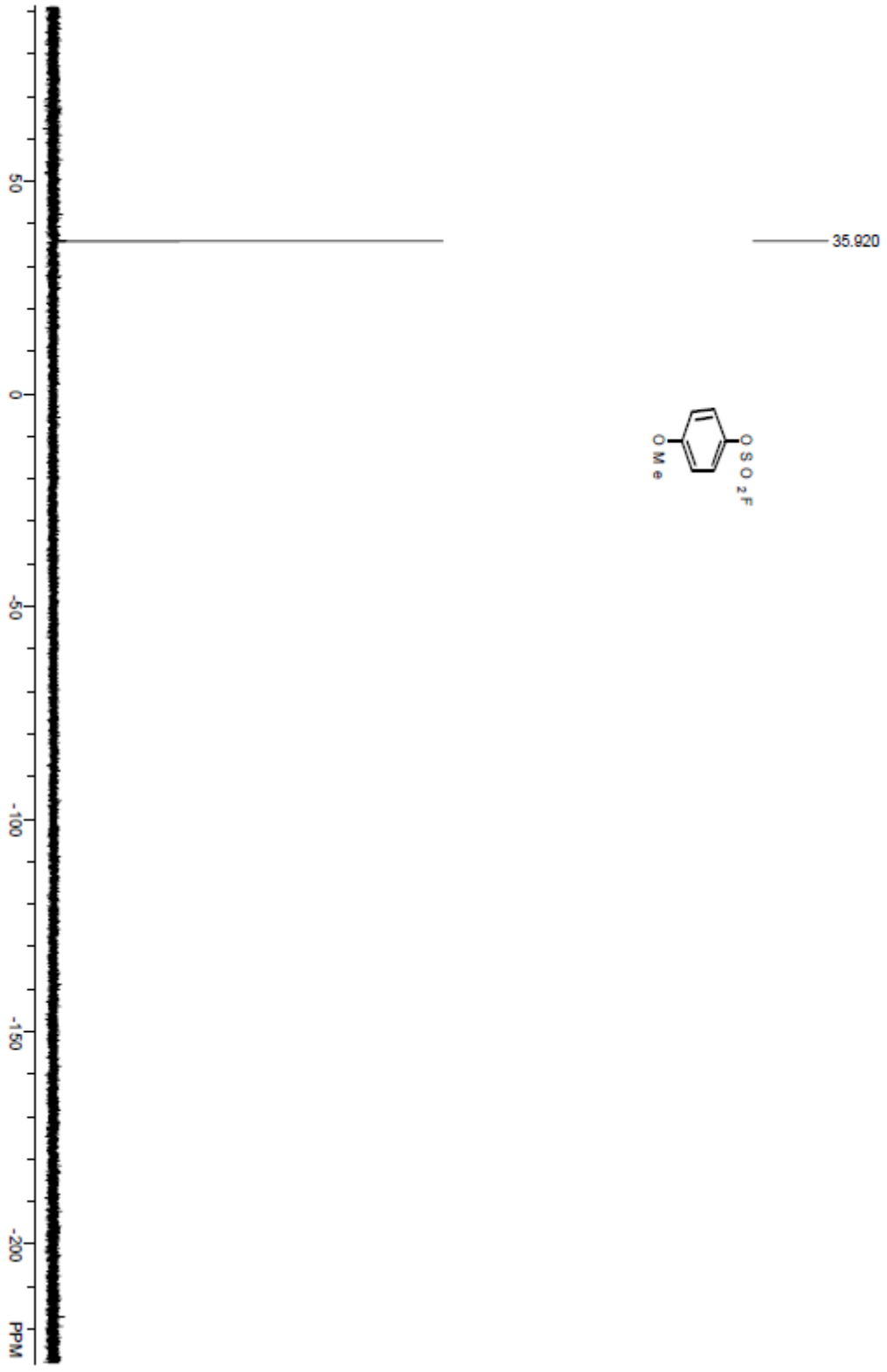


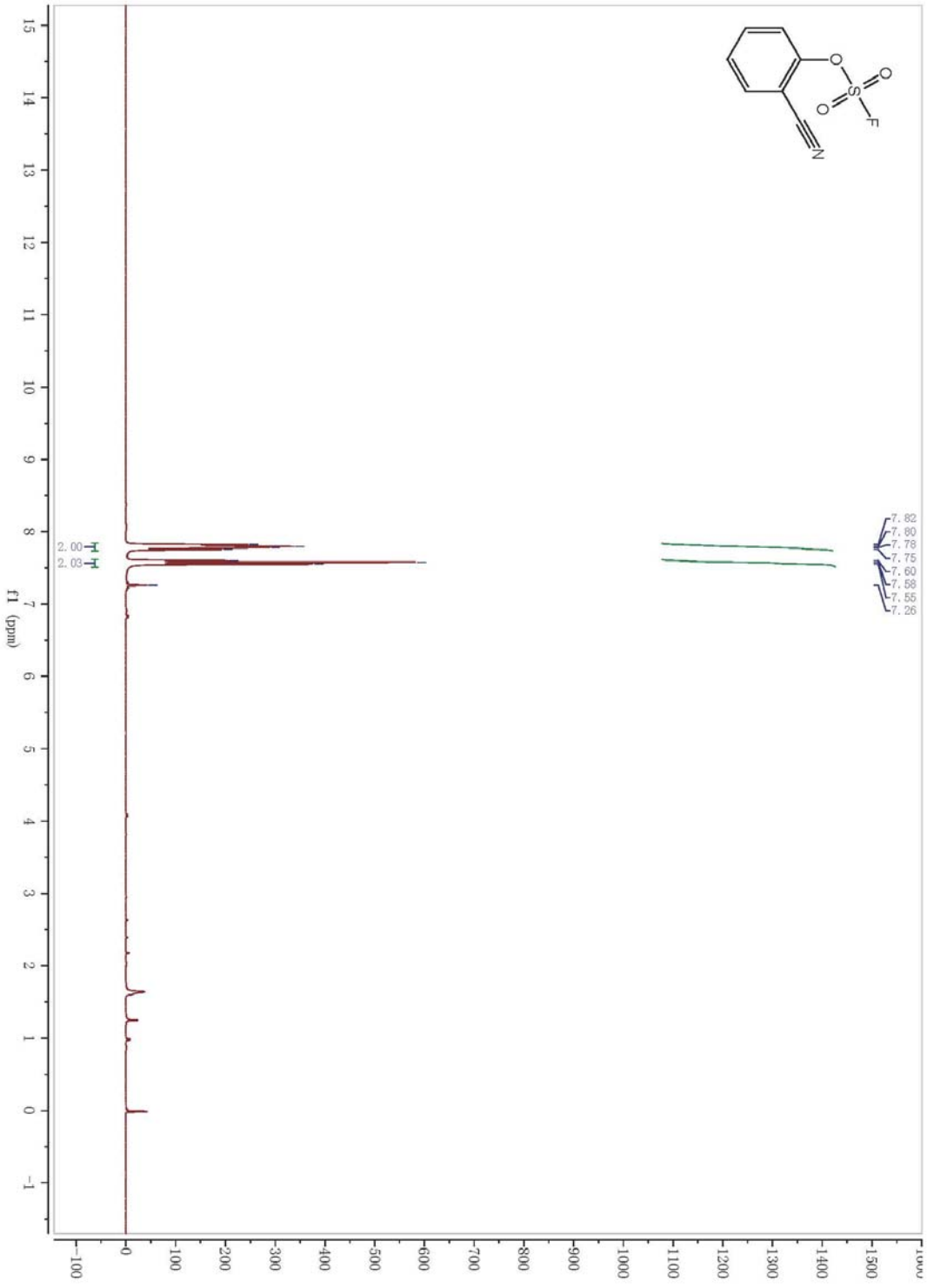
^{13}C NMR for ALD 00418



^{19}F NMR for ALD 00418



^{1}H NMR for ALD 00420



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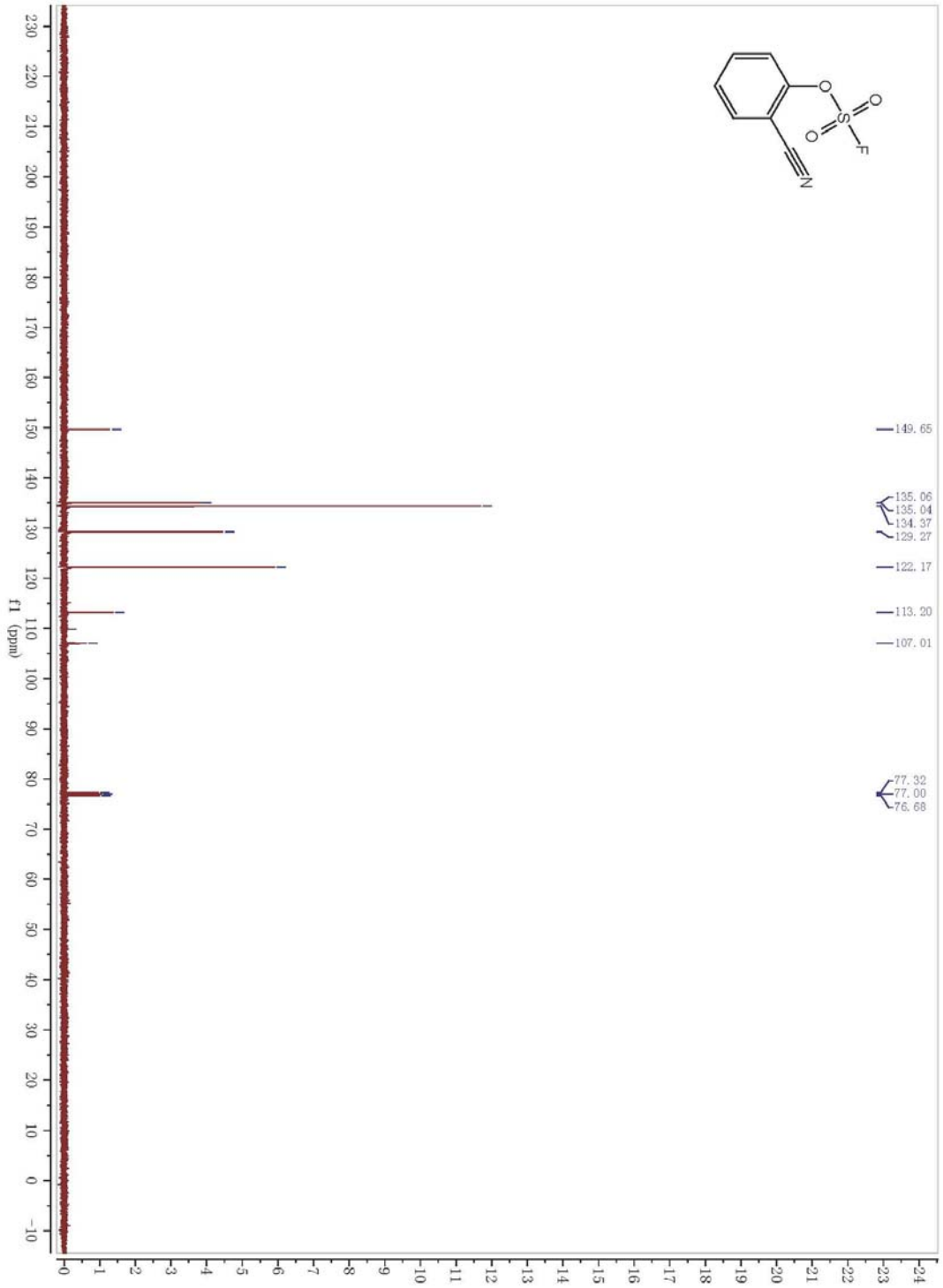

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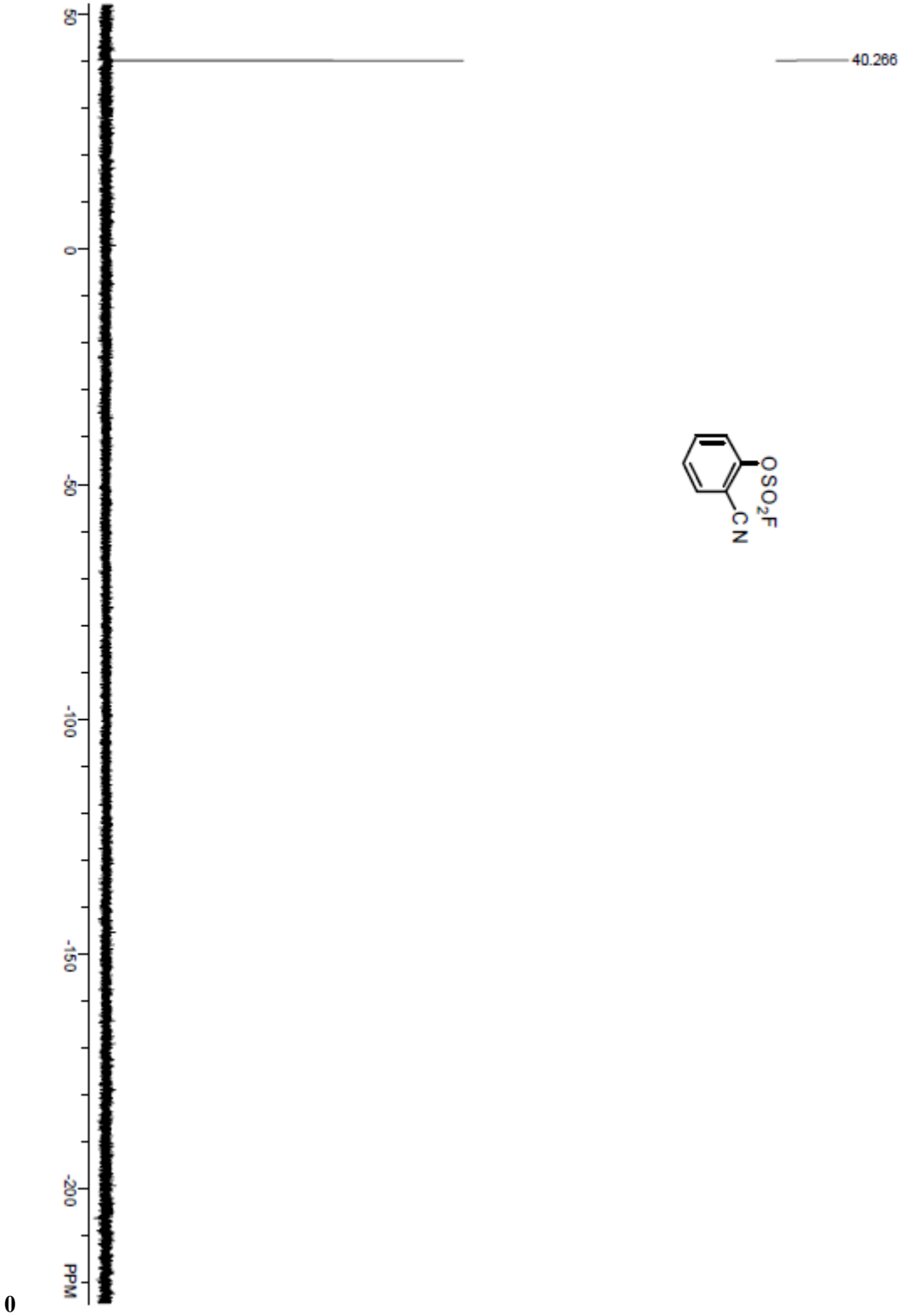

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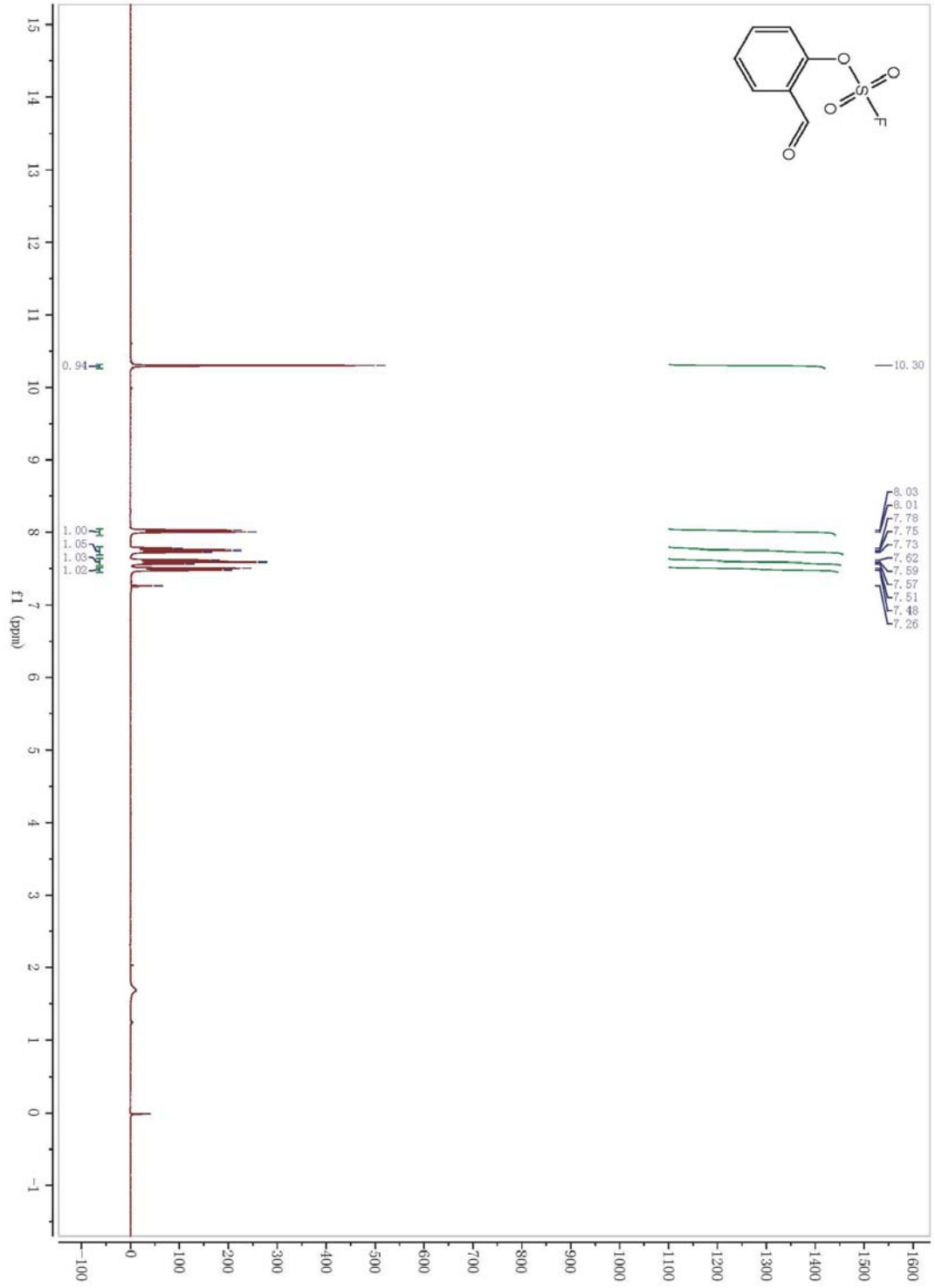
^{1}H NMR for ALD 00422



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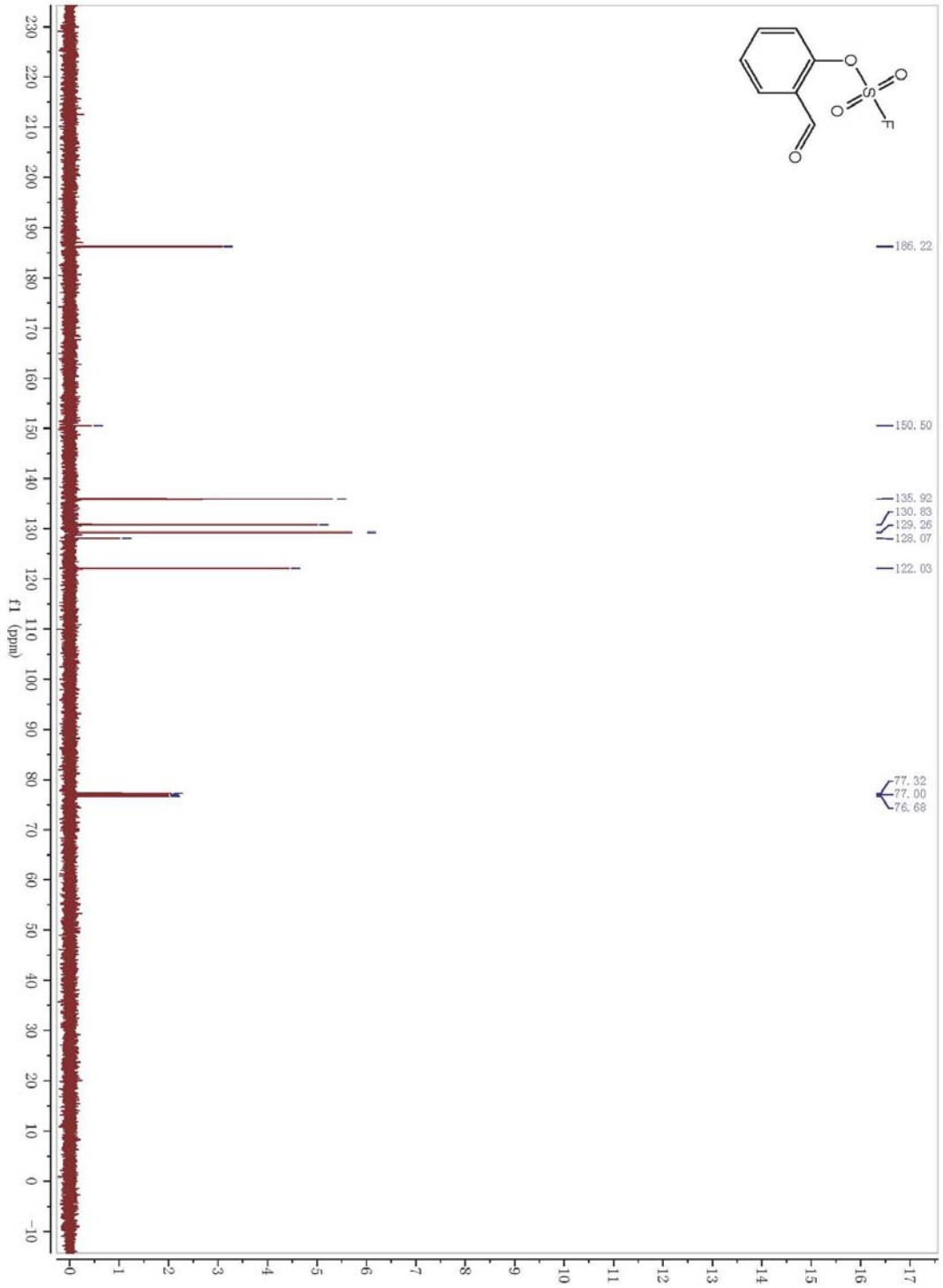

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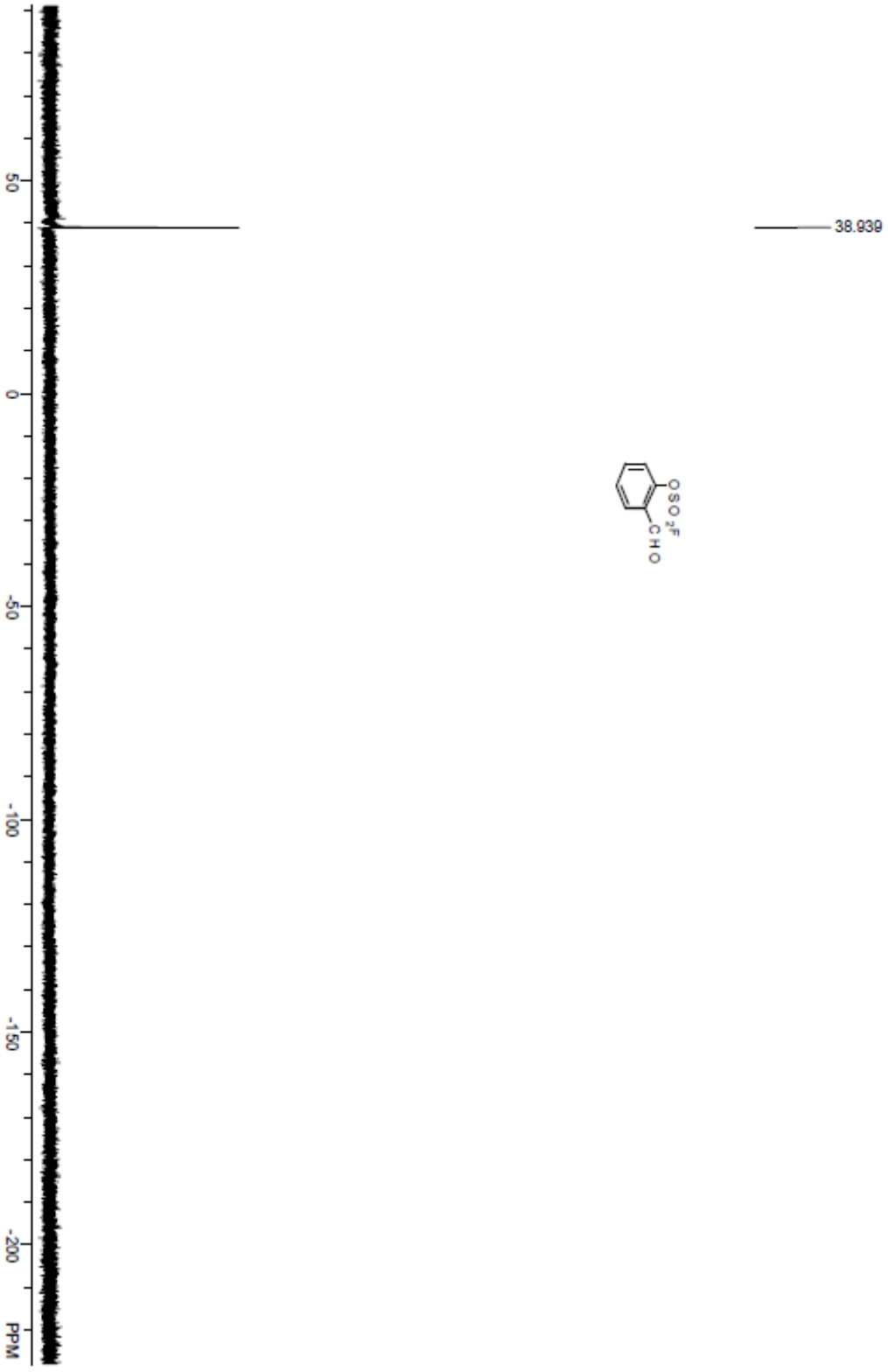
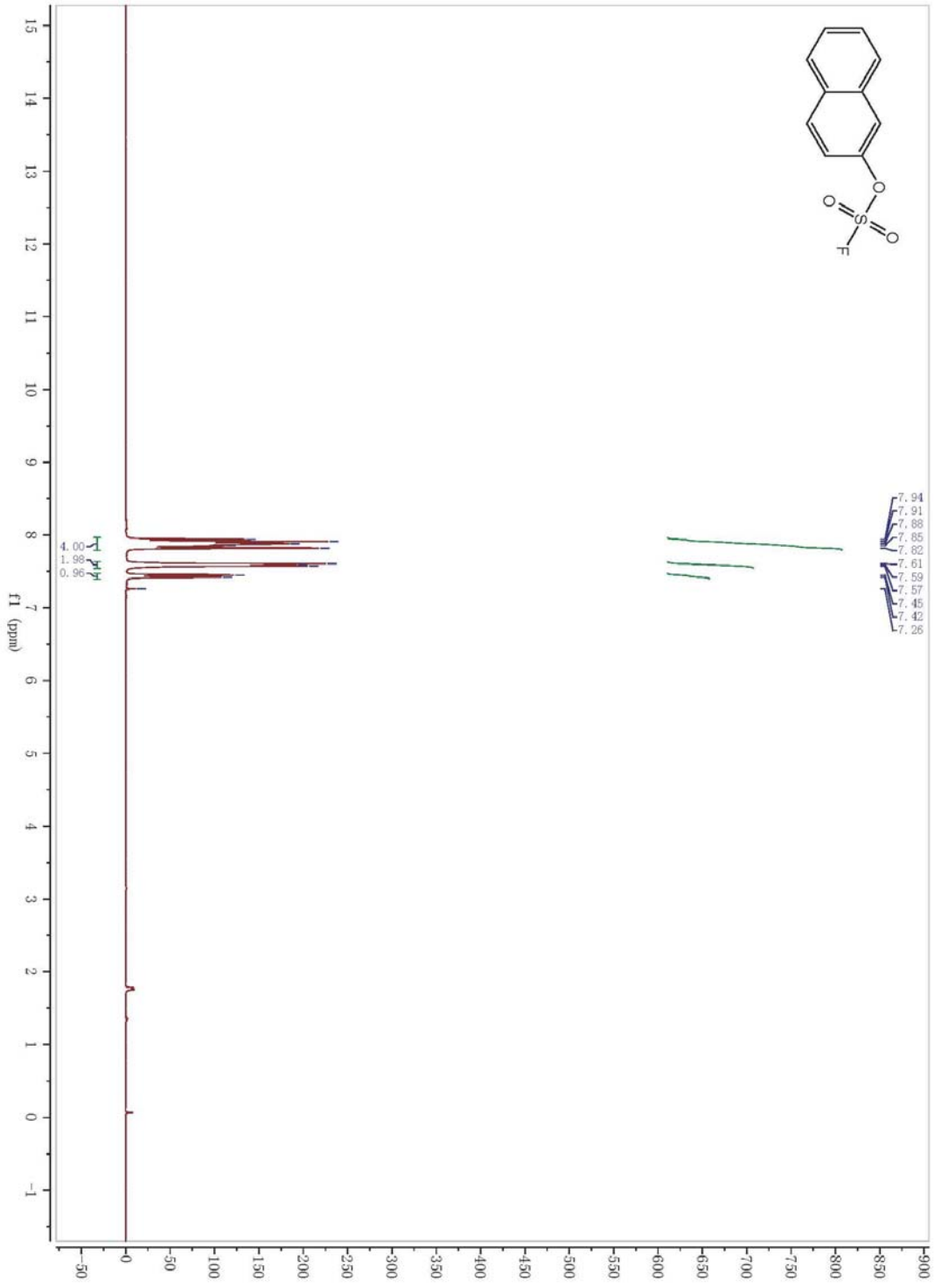


^{1}H NMR for ALD 00424



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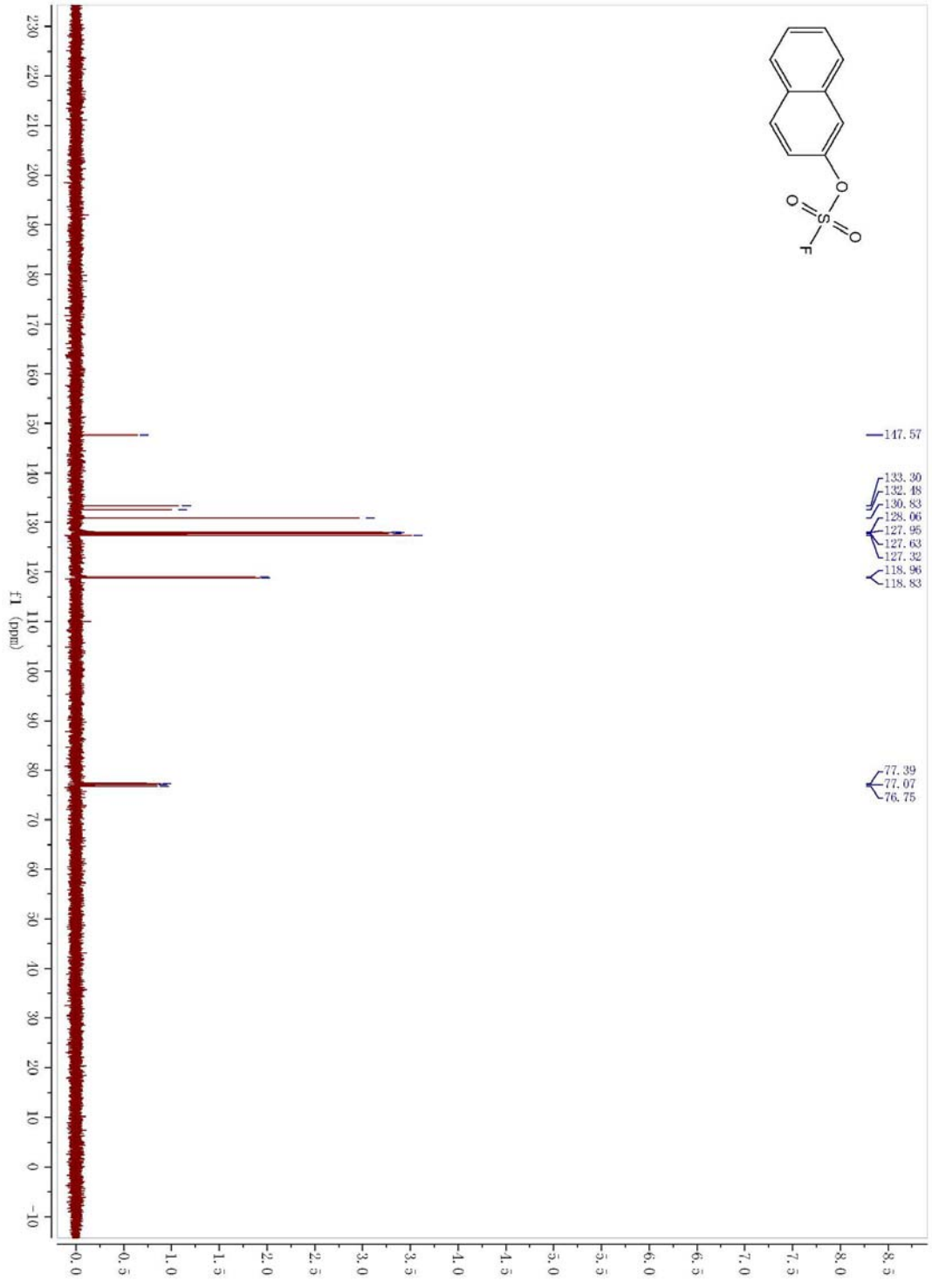

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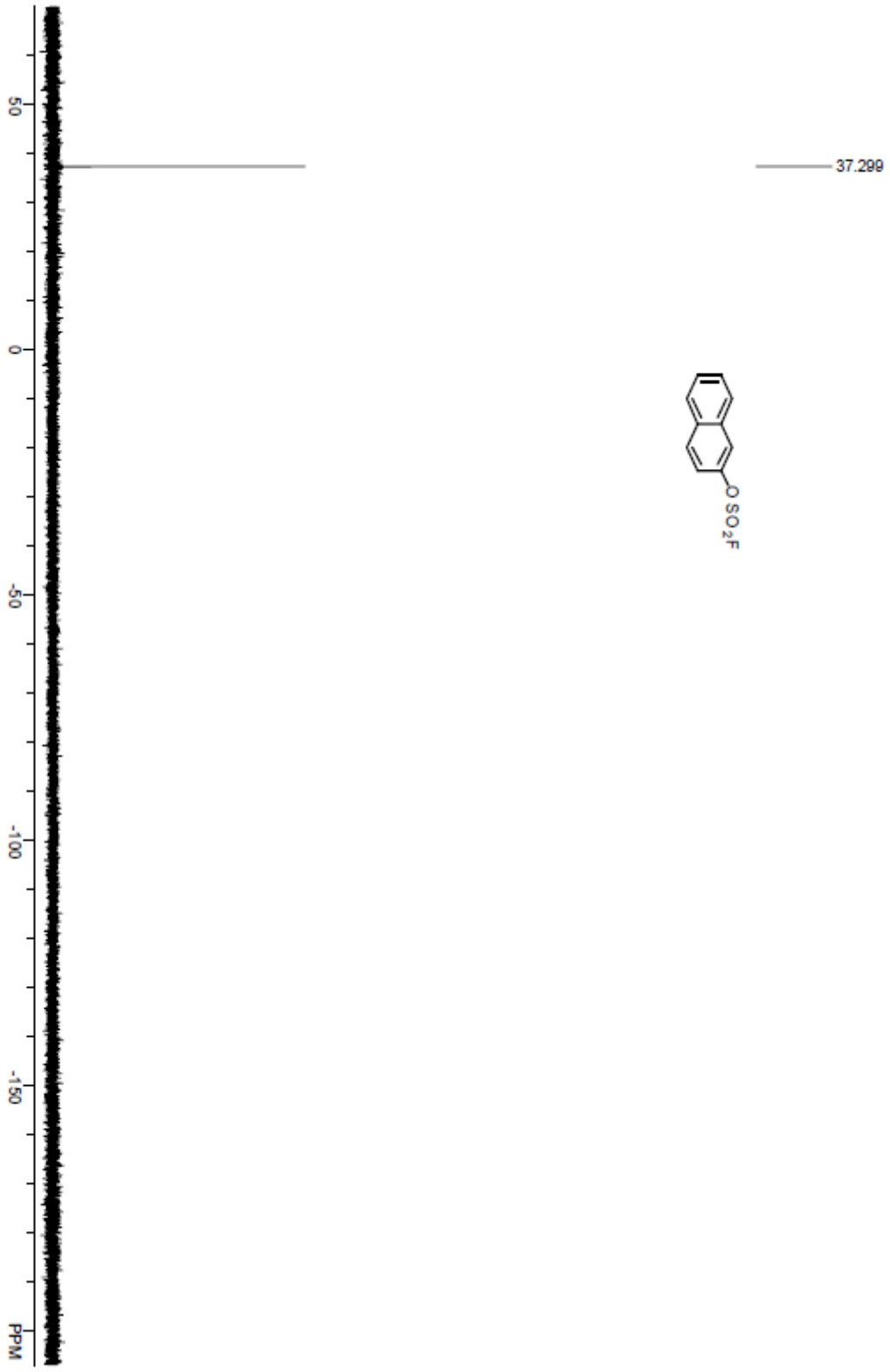
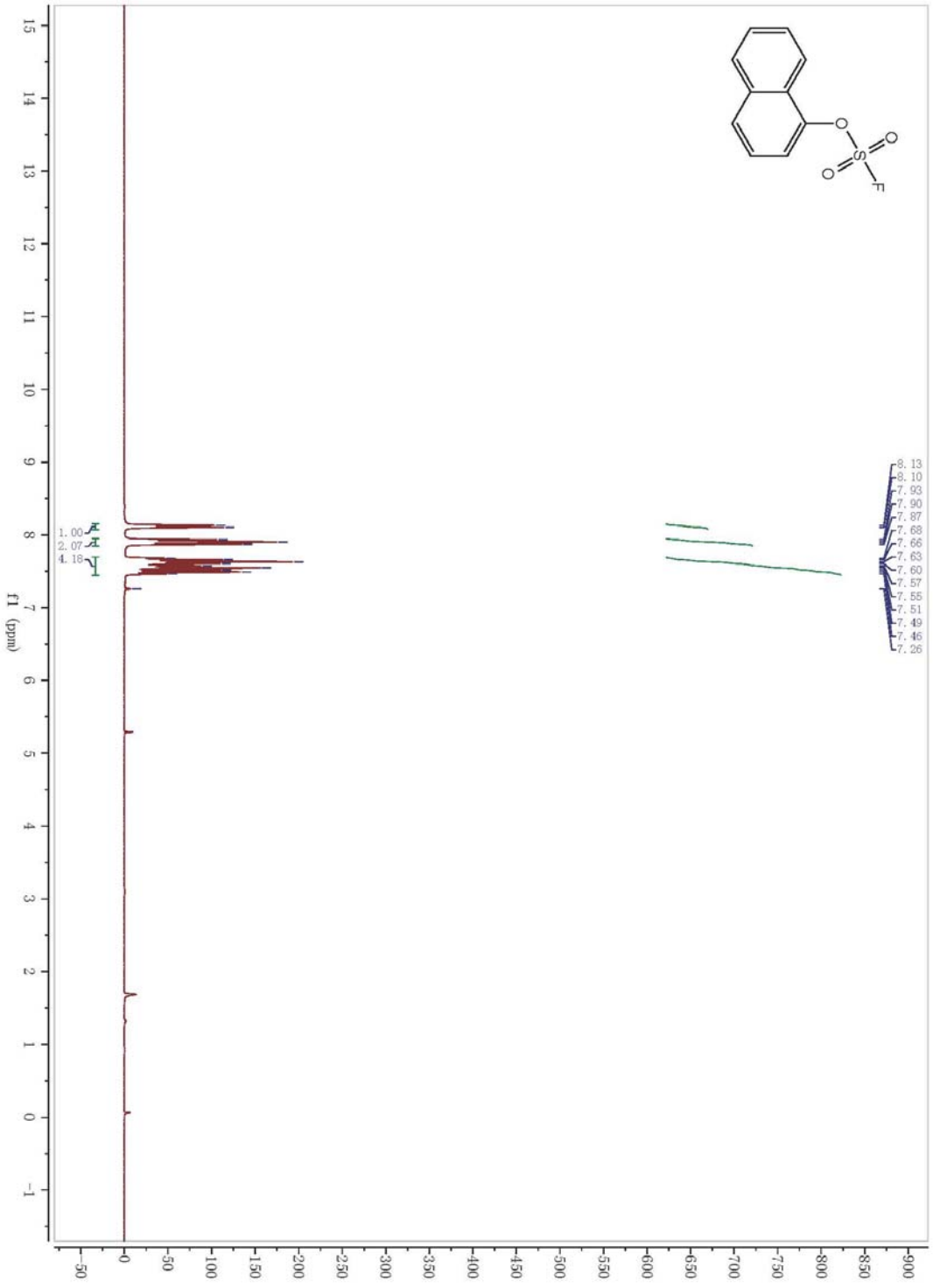


^{1}H NMR for ALD 00430



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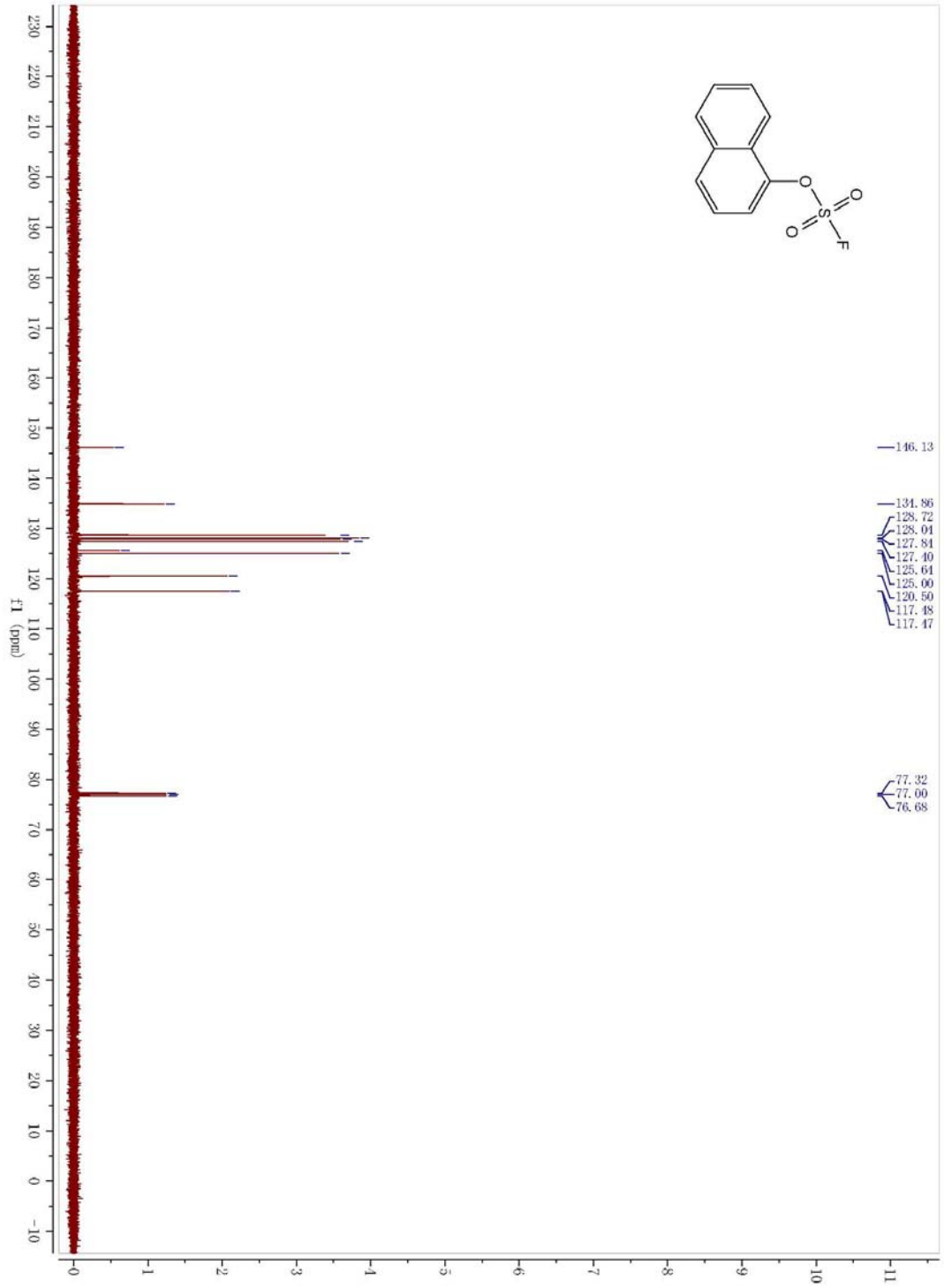

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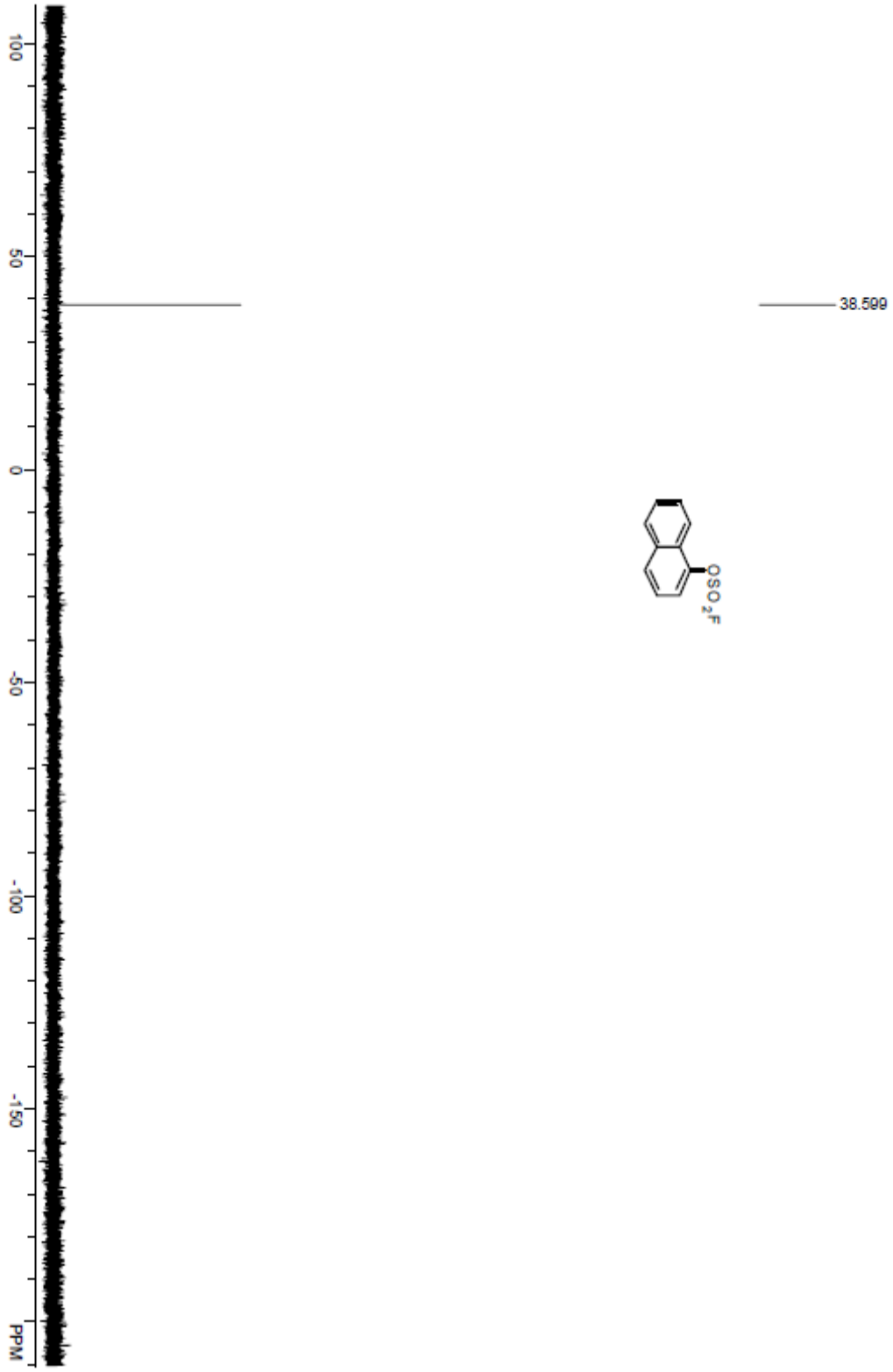
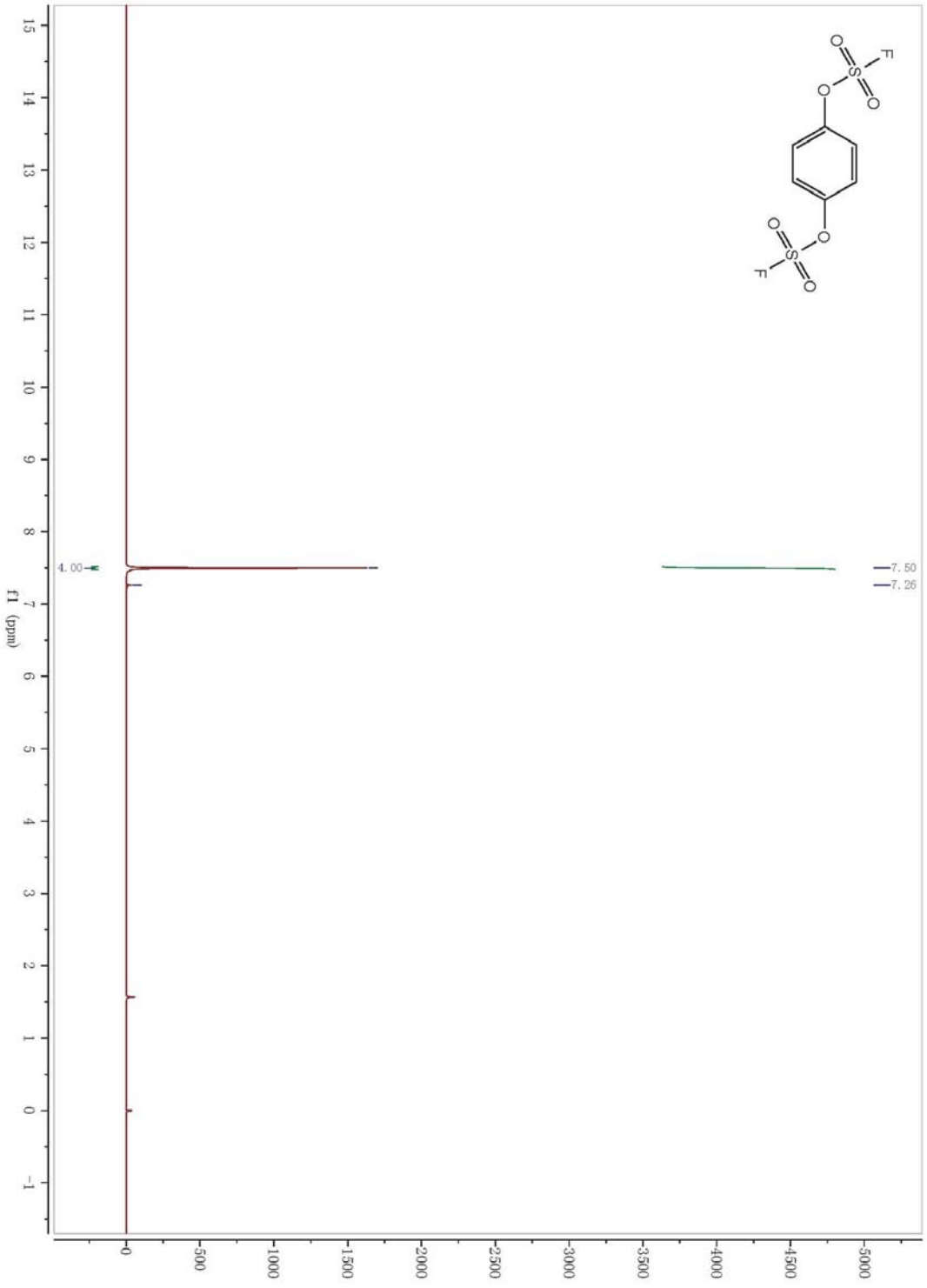


^{19}H NMR for ALD 00384



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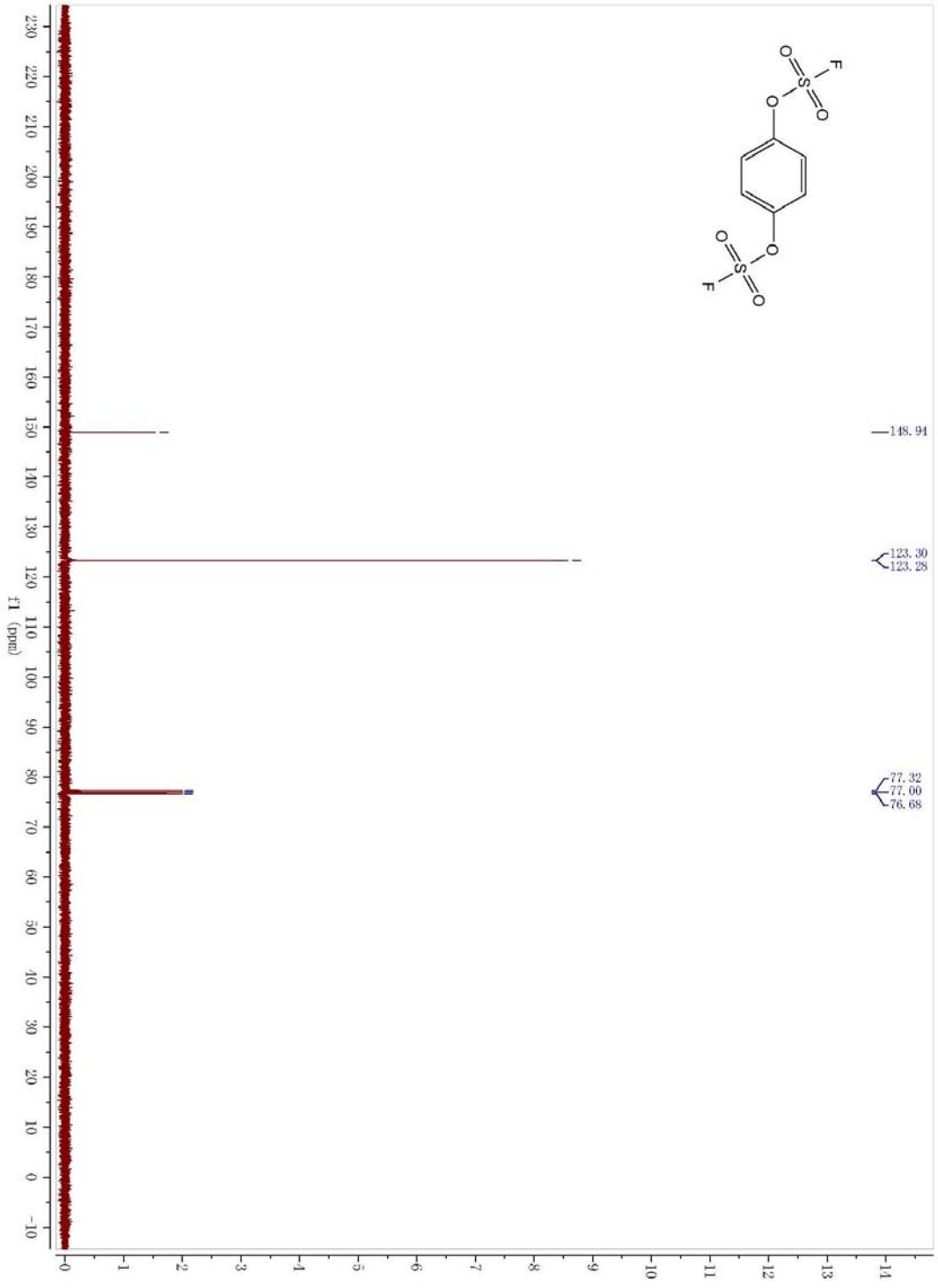

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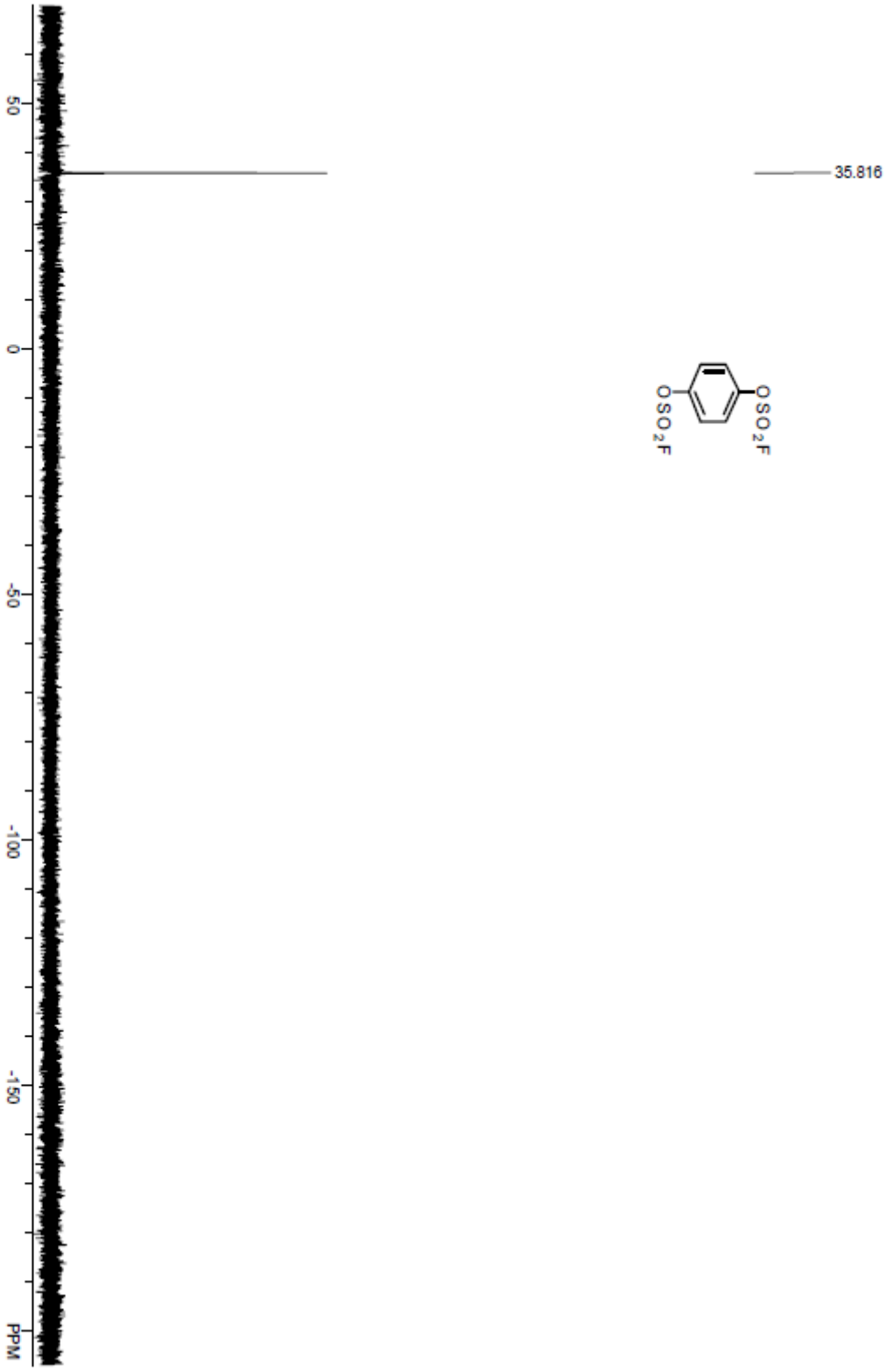
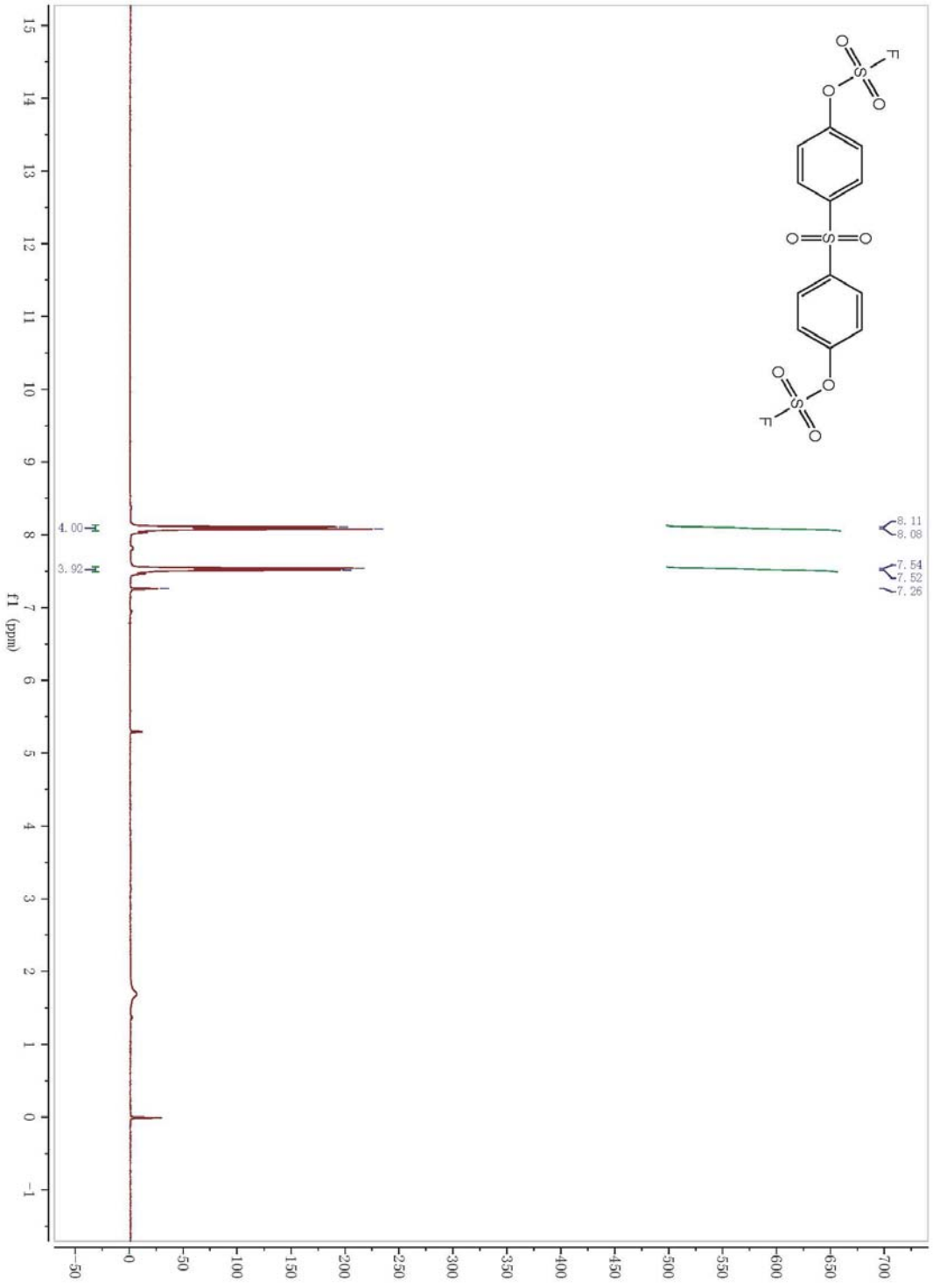


[1]HNMR for ALD 00428



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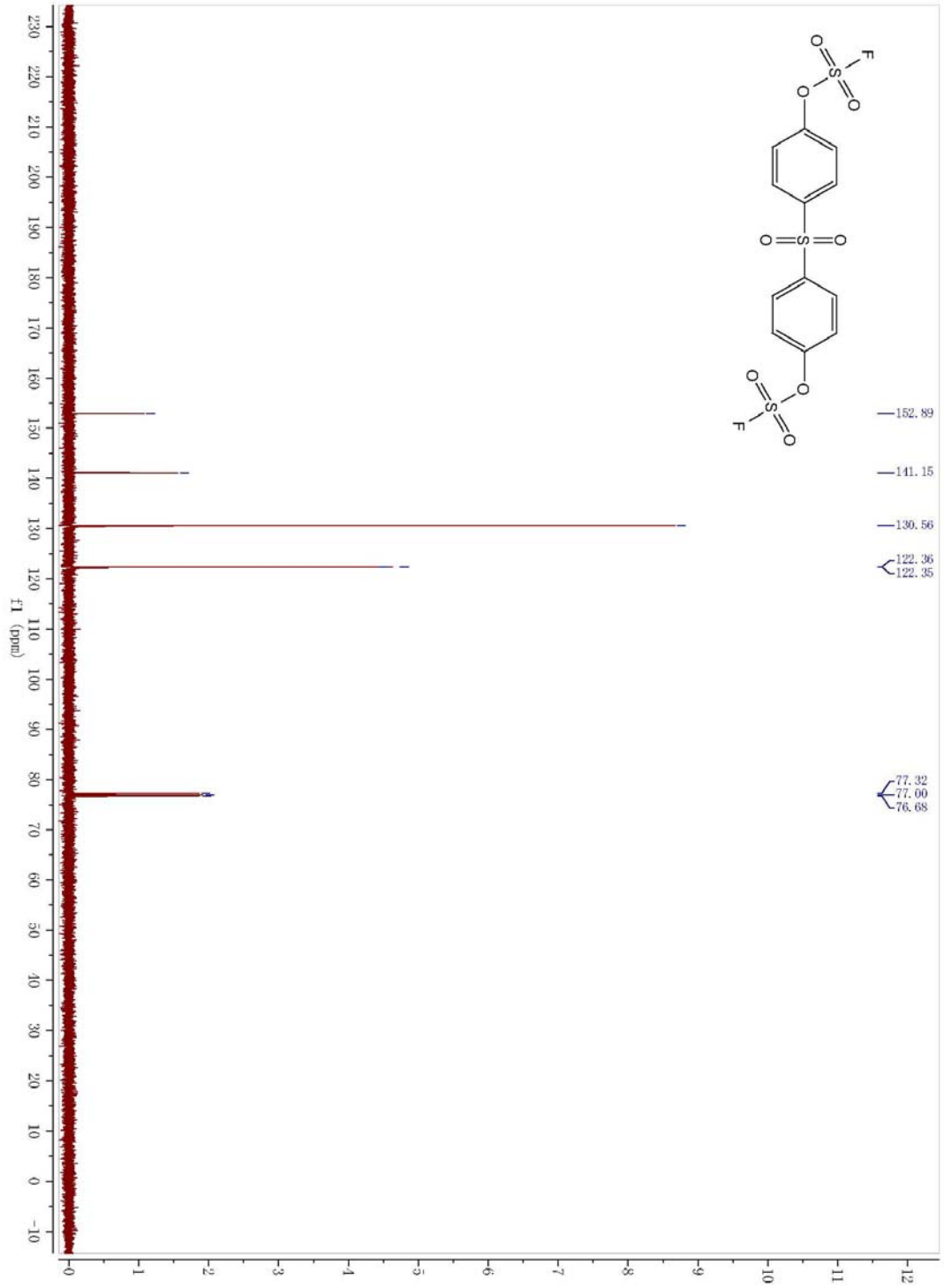

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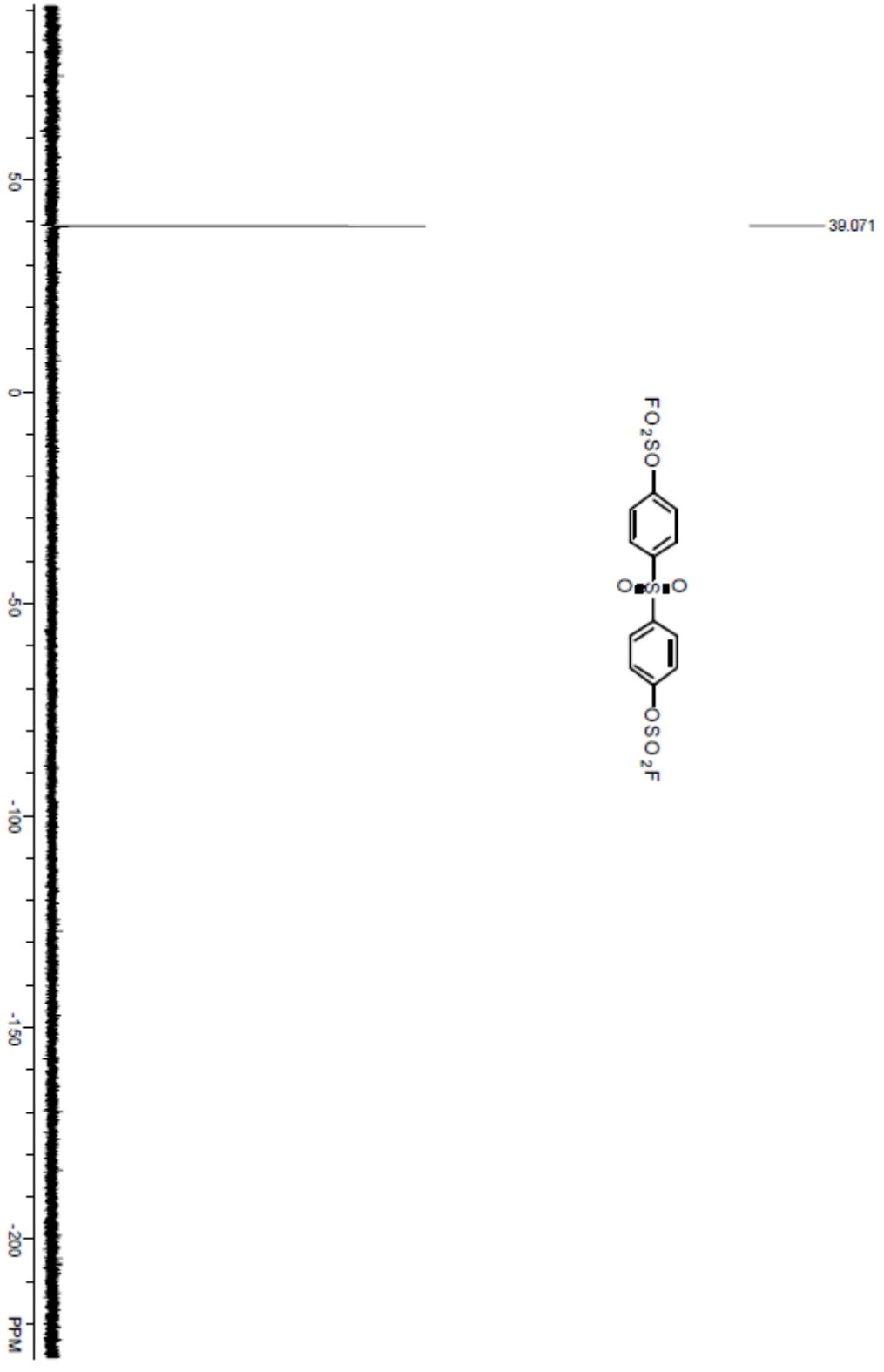
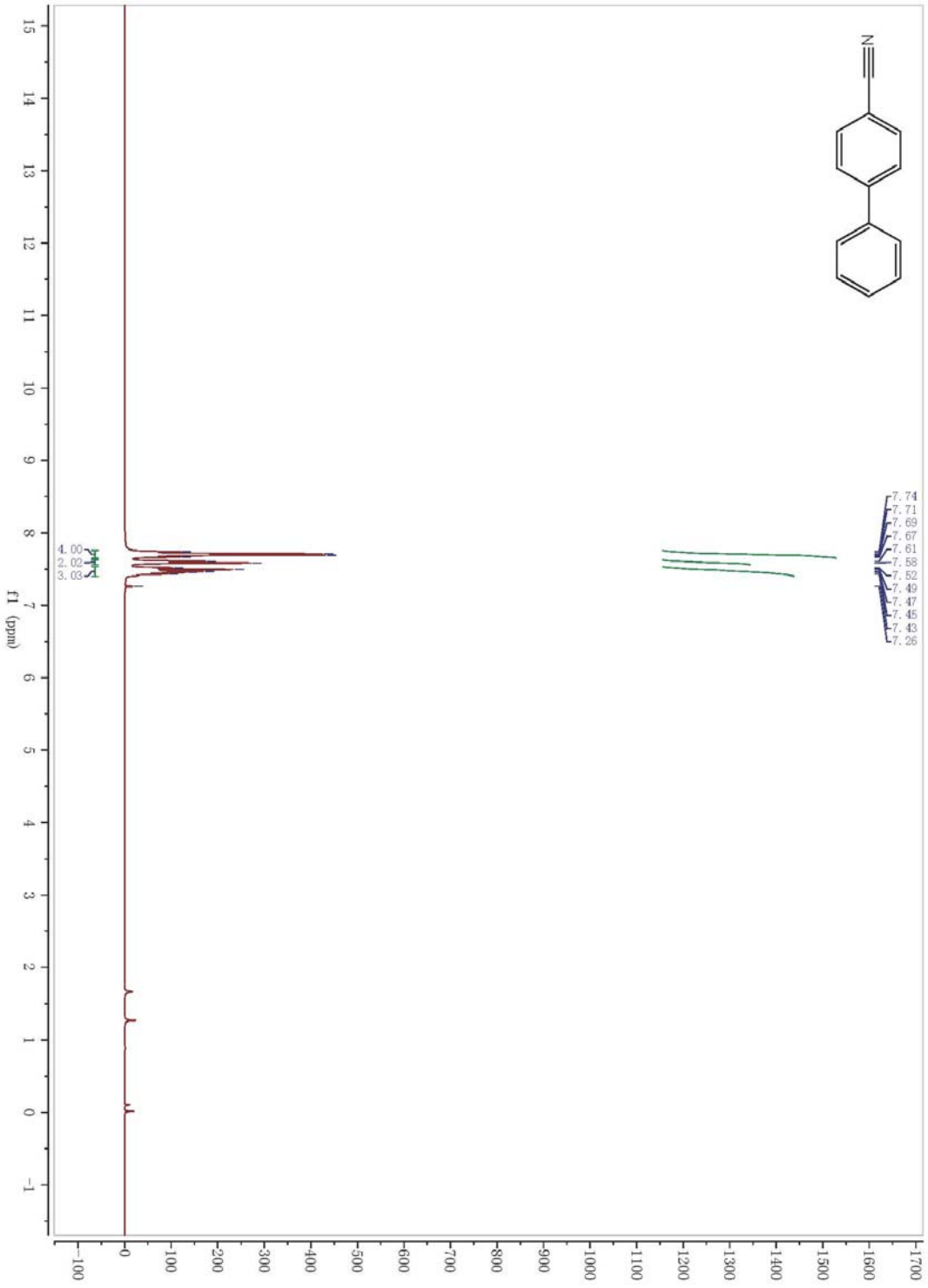
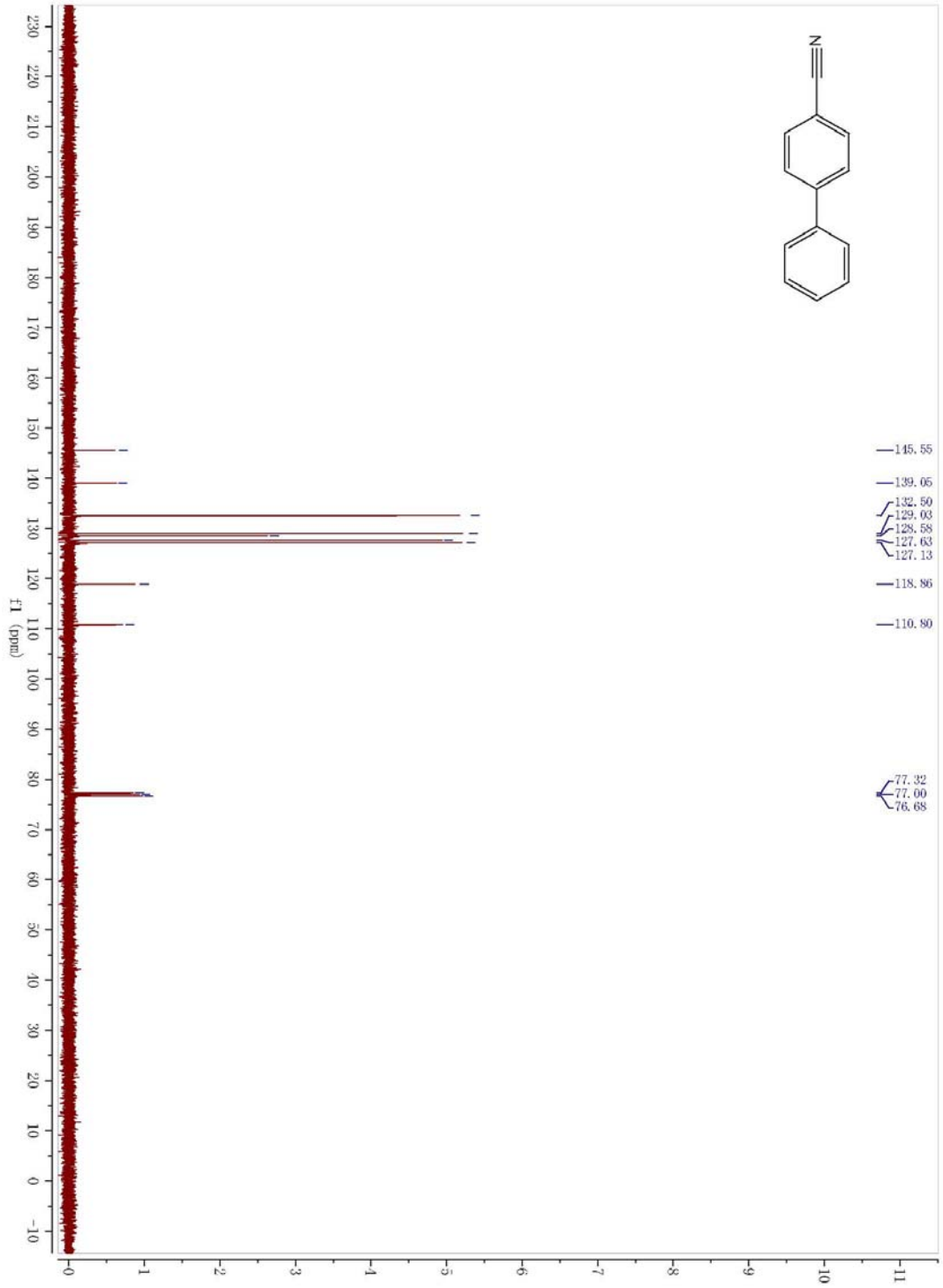


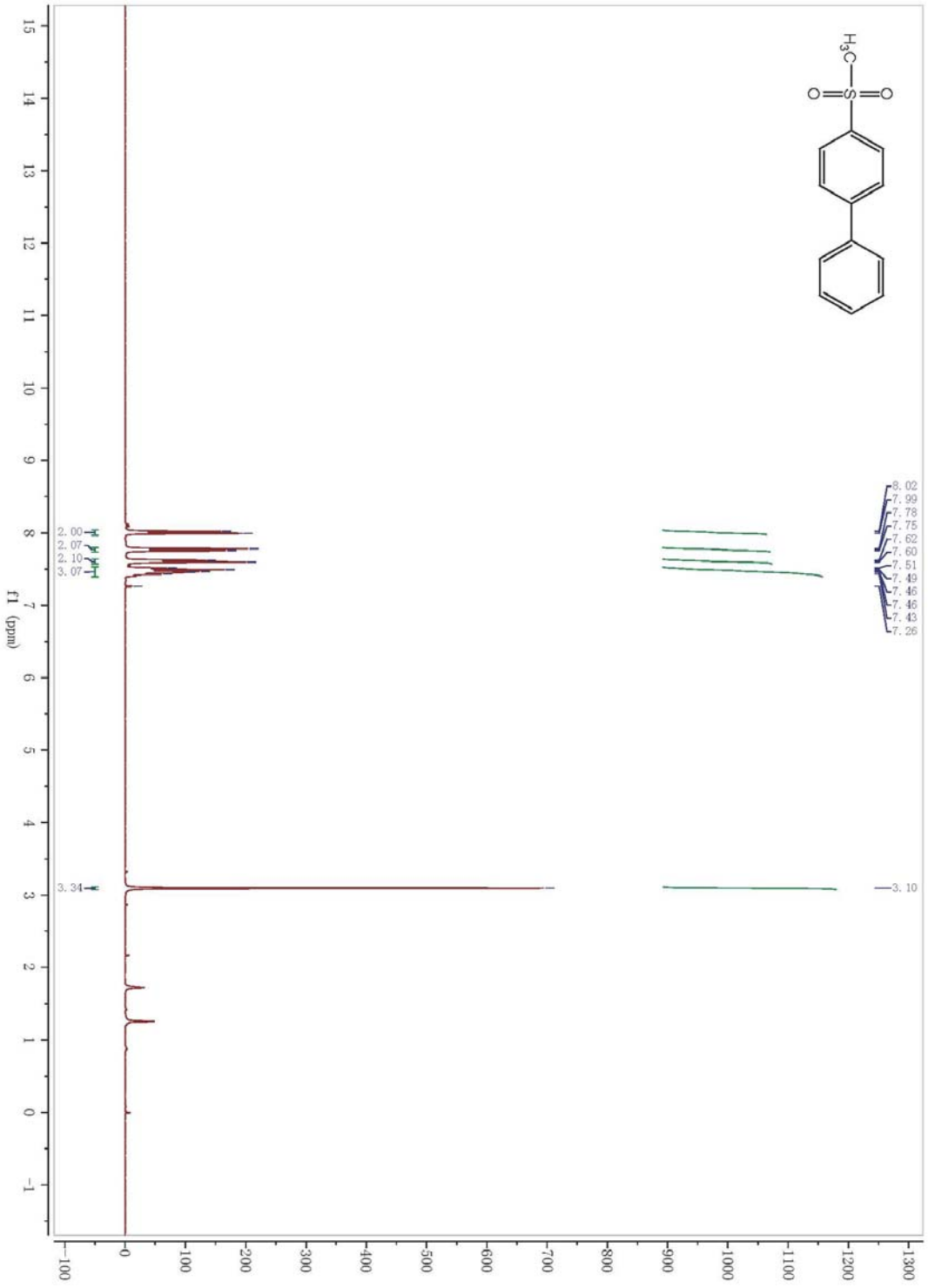
^{1}H NMR for the product of Table 2 entry 5



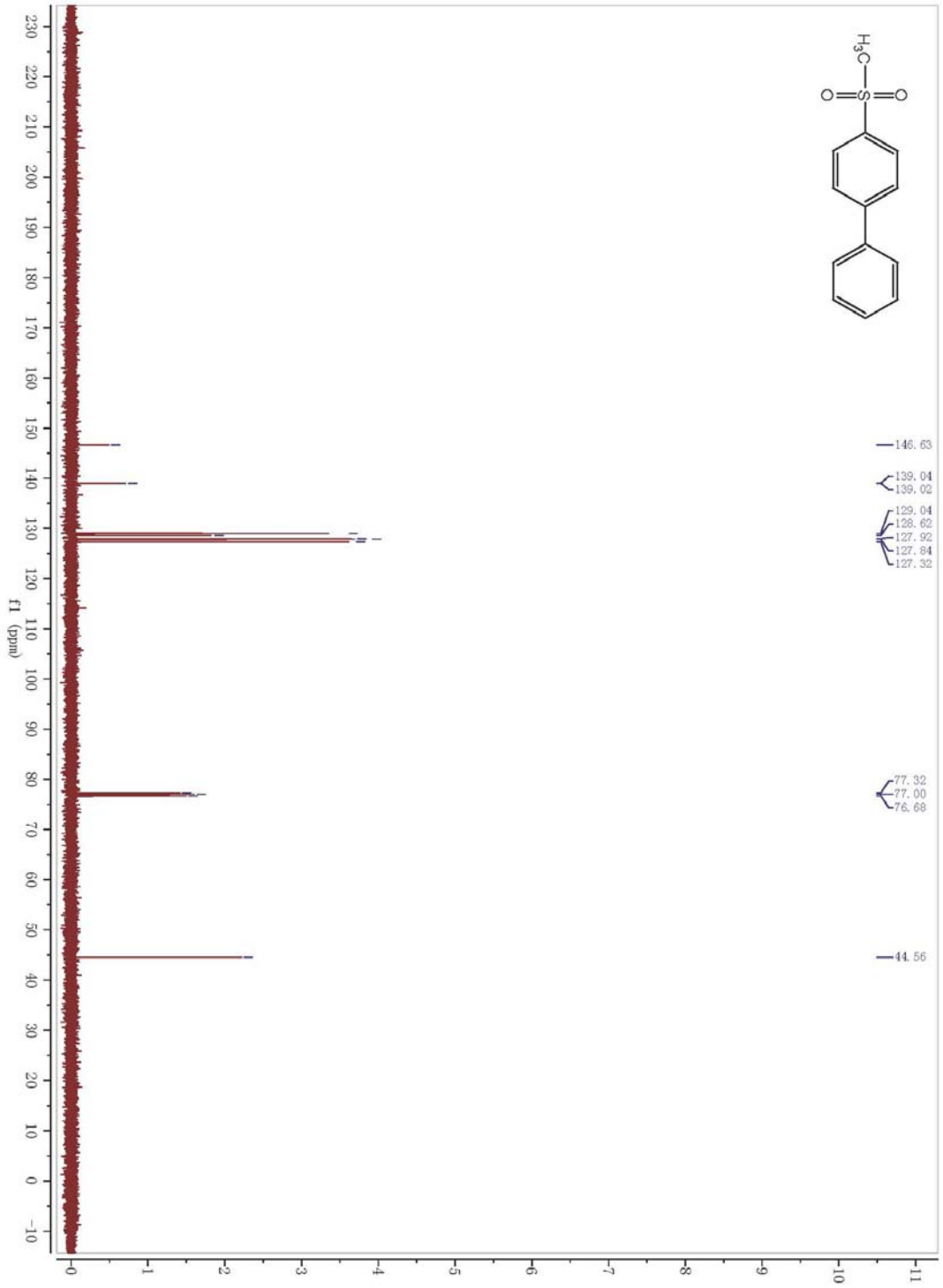
^{13}C NMR for the product of Table 2 entry 5



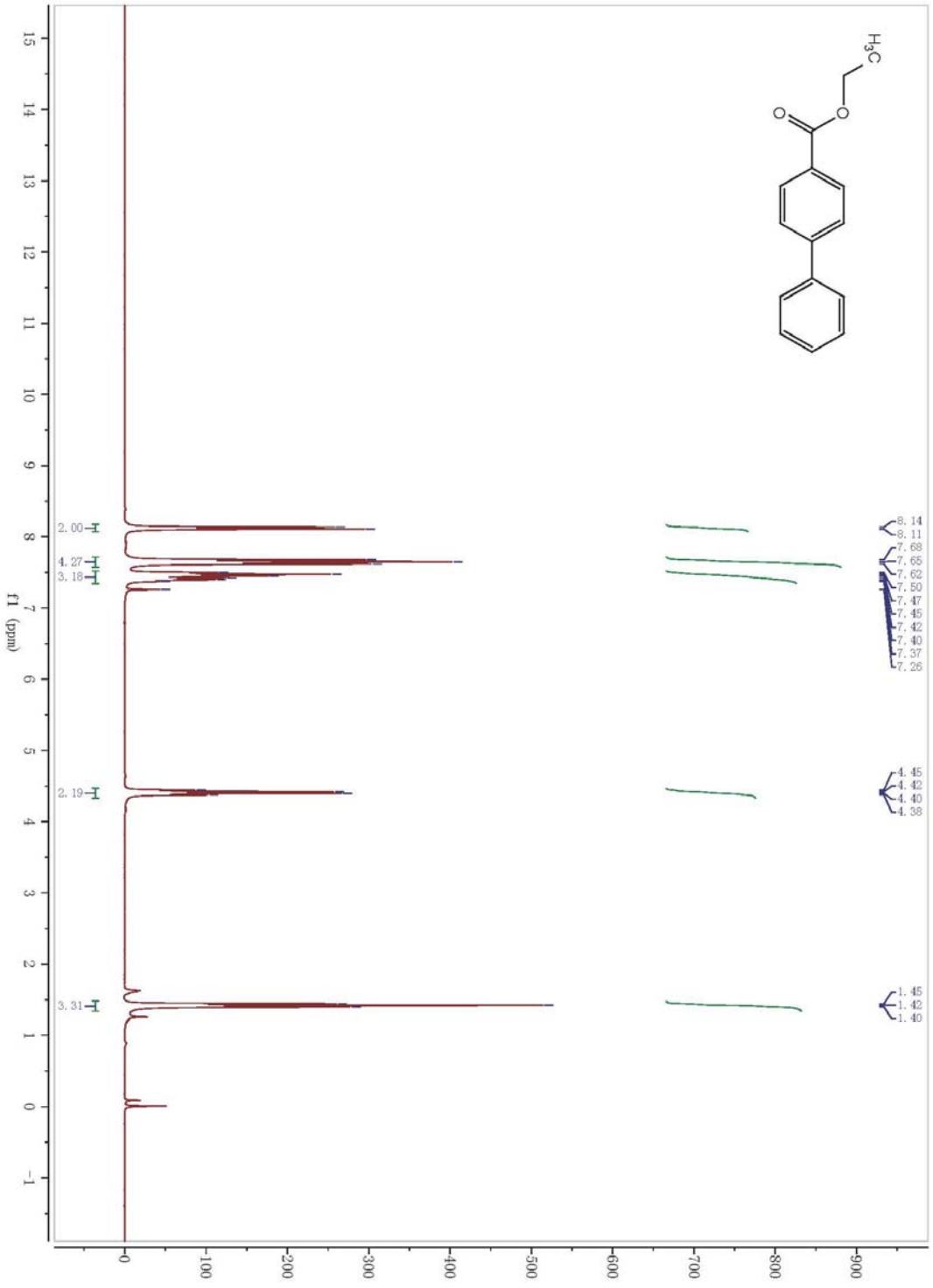
^{1}H NMR for the product of Table 3 entry 1



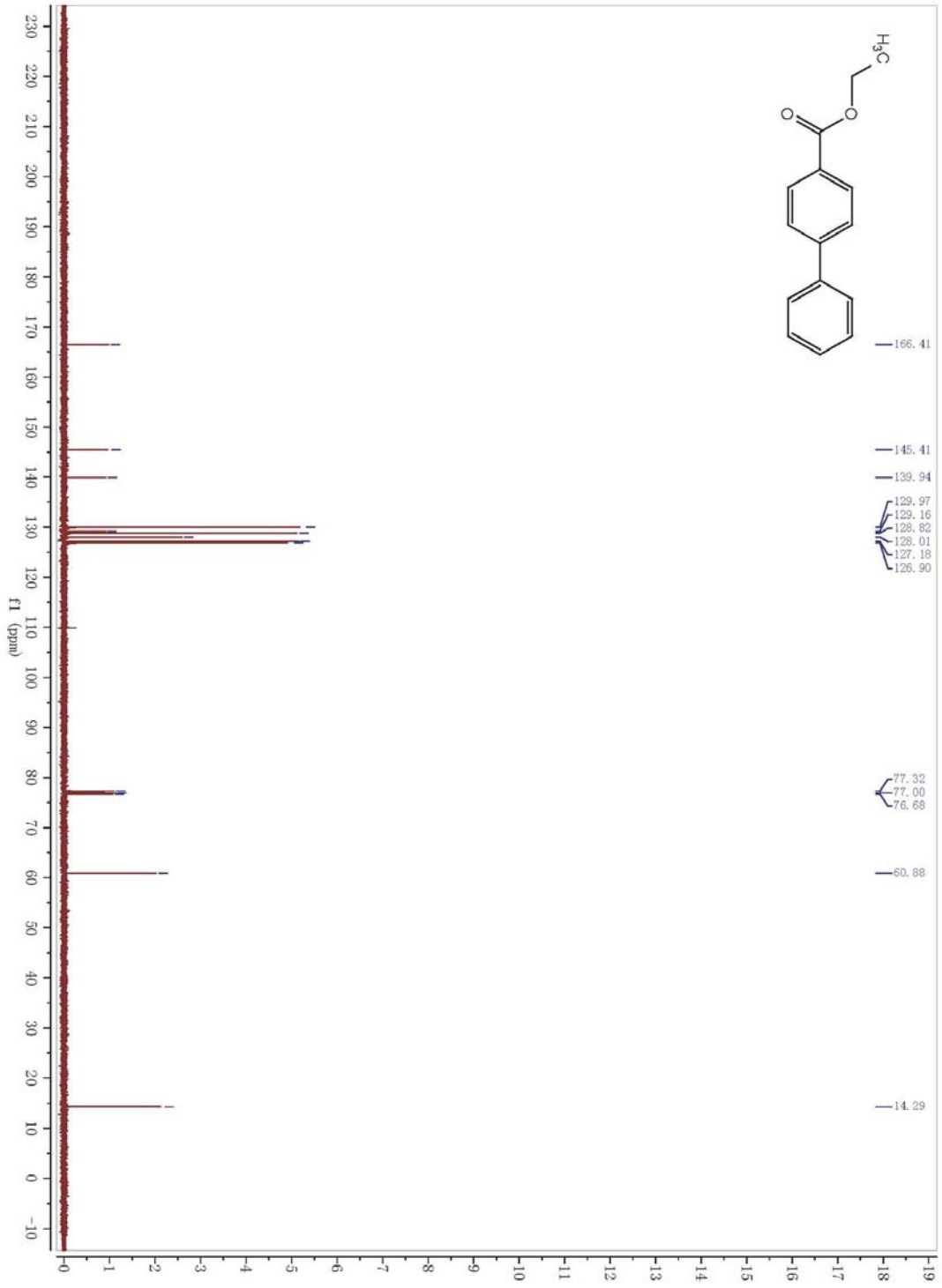
^{13}C NMR for the product of Table 3 entry 1



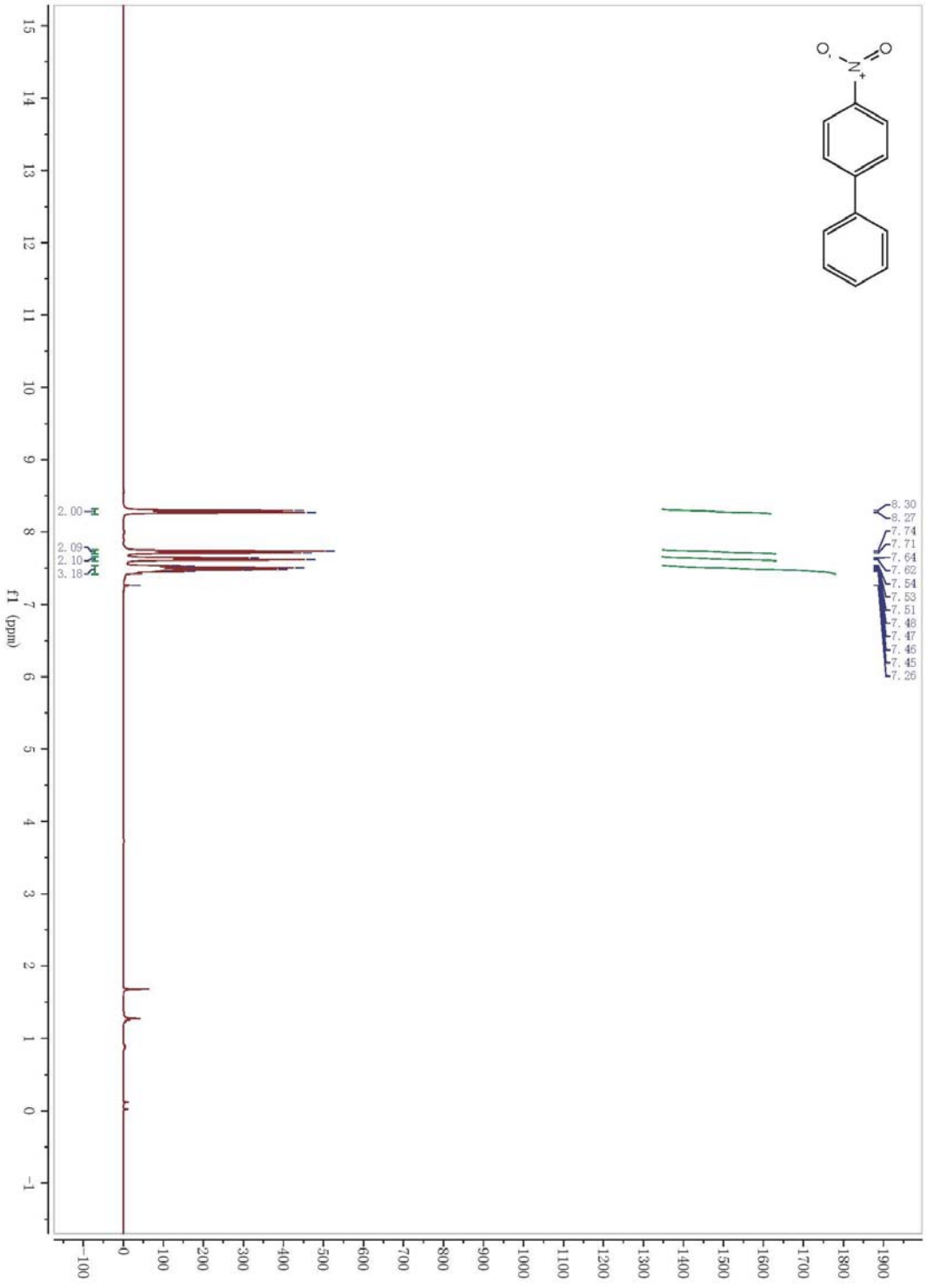
^{1}H NMR for the product of Table 3 entry 2



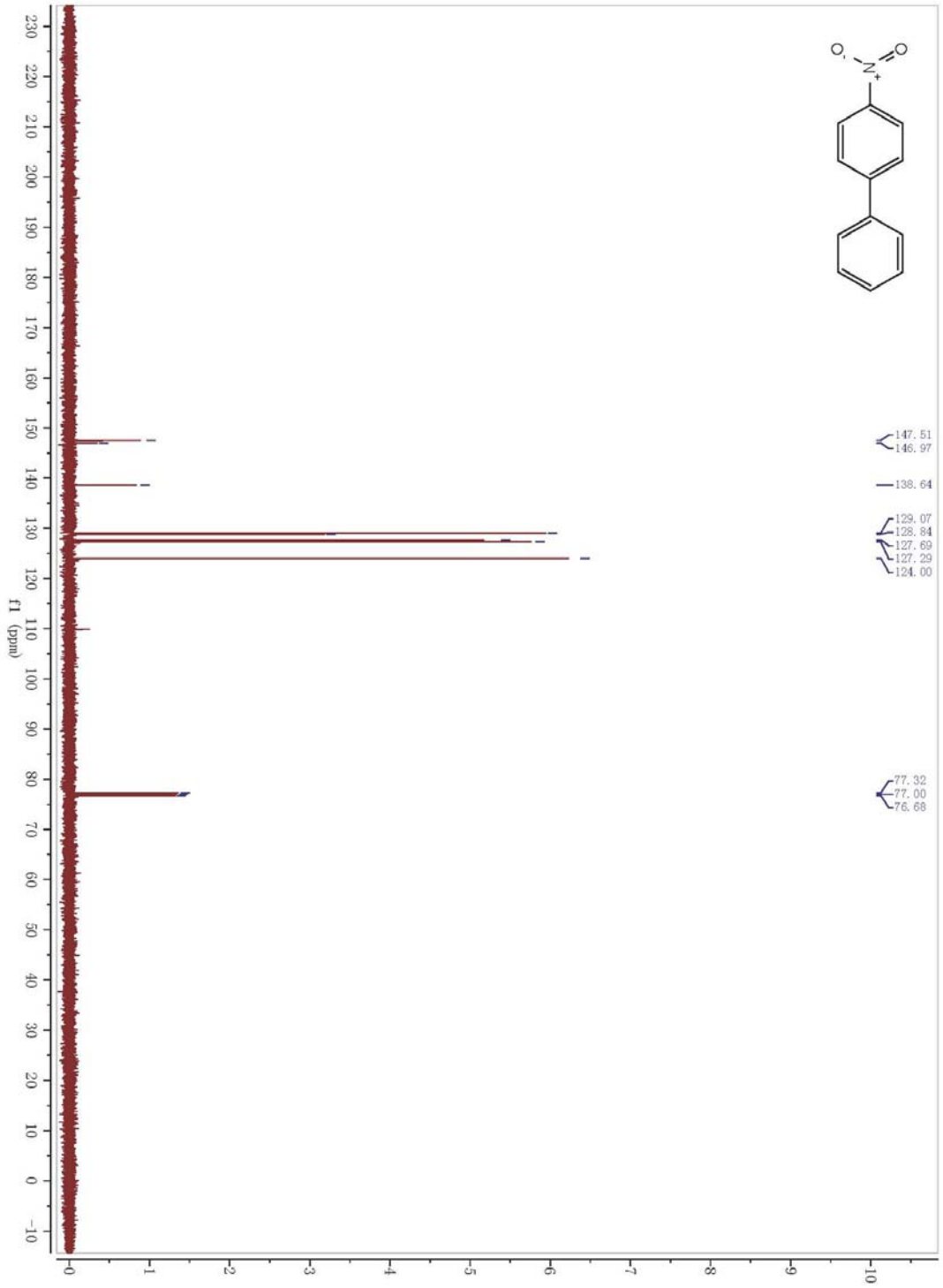
^{13}C NMR for the product of Table 3 entry 2



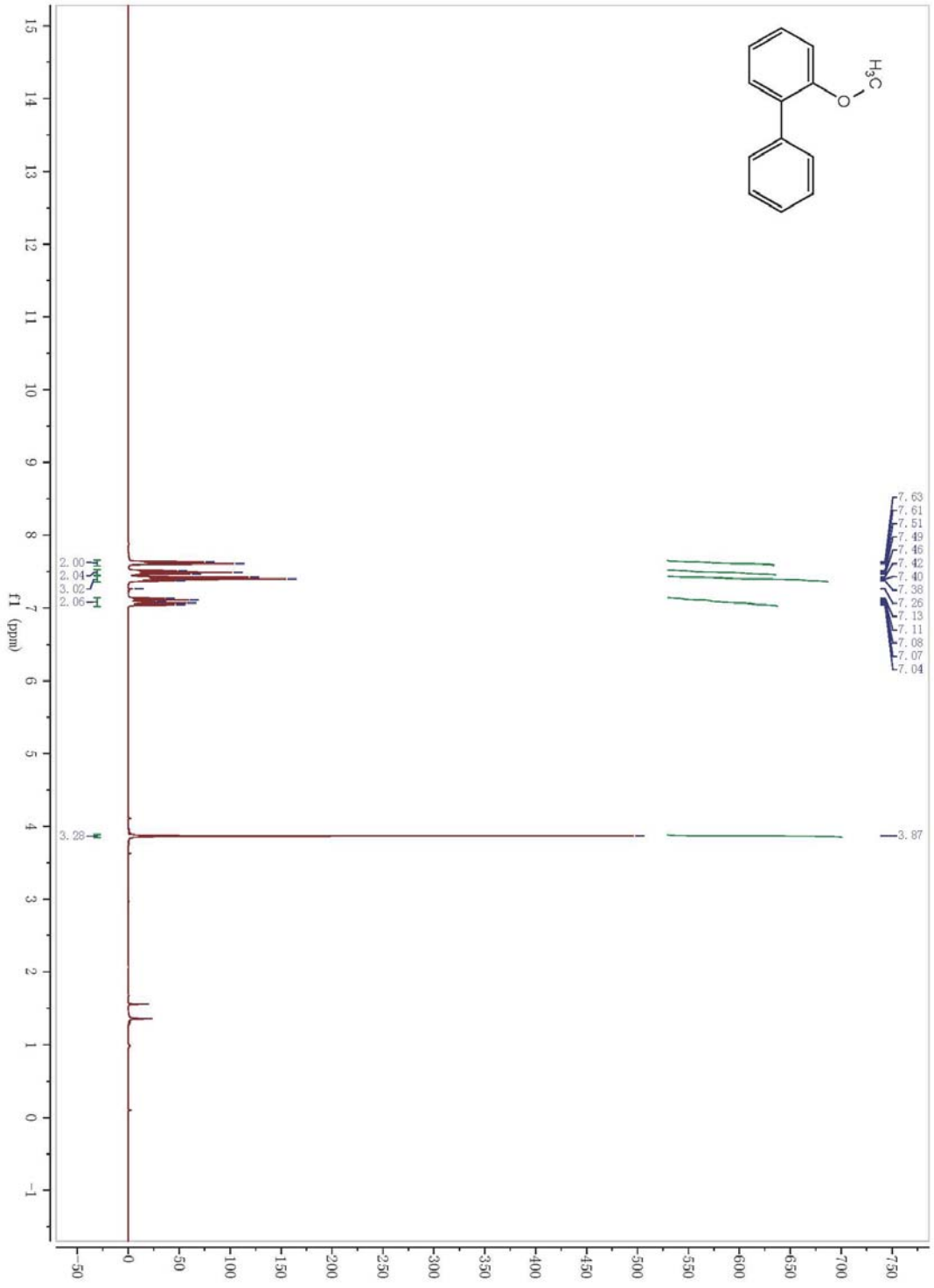
^{1}H NMR for the product of Table 3 entry 3



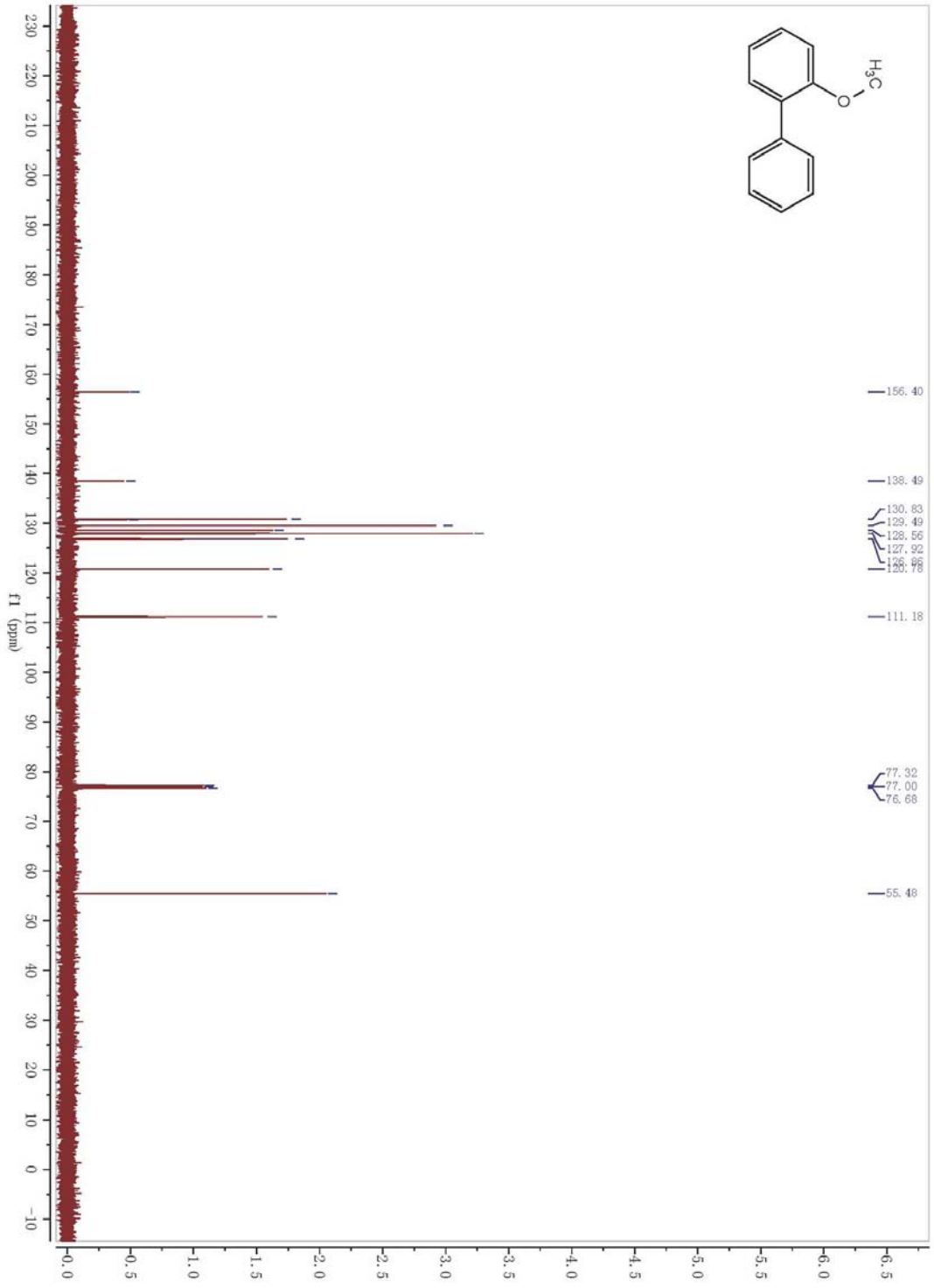
^{13}C NMR for the product of Table 3 entry 3



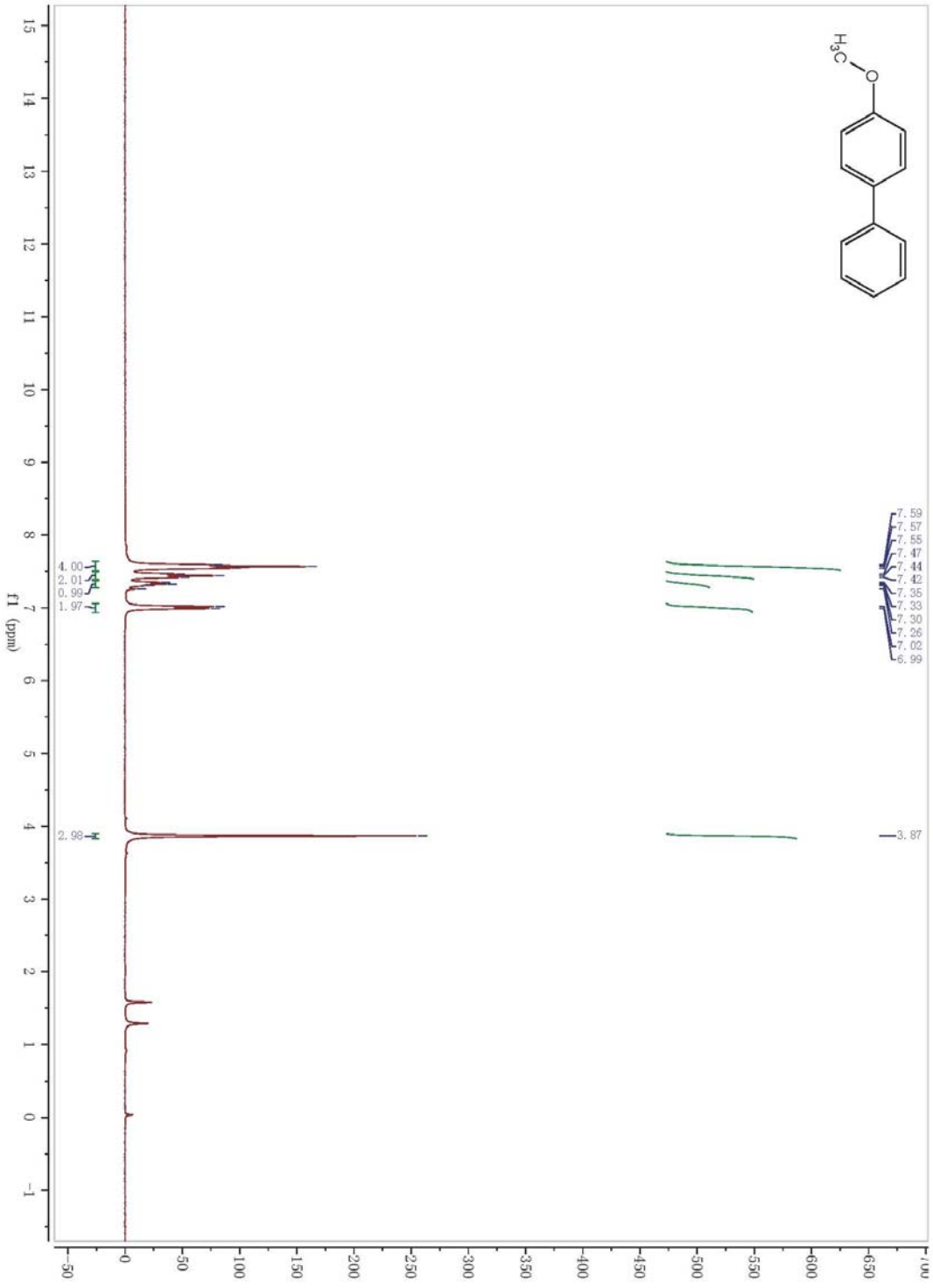
^{1}H NMR for the product of Table 3 entry 4



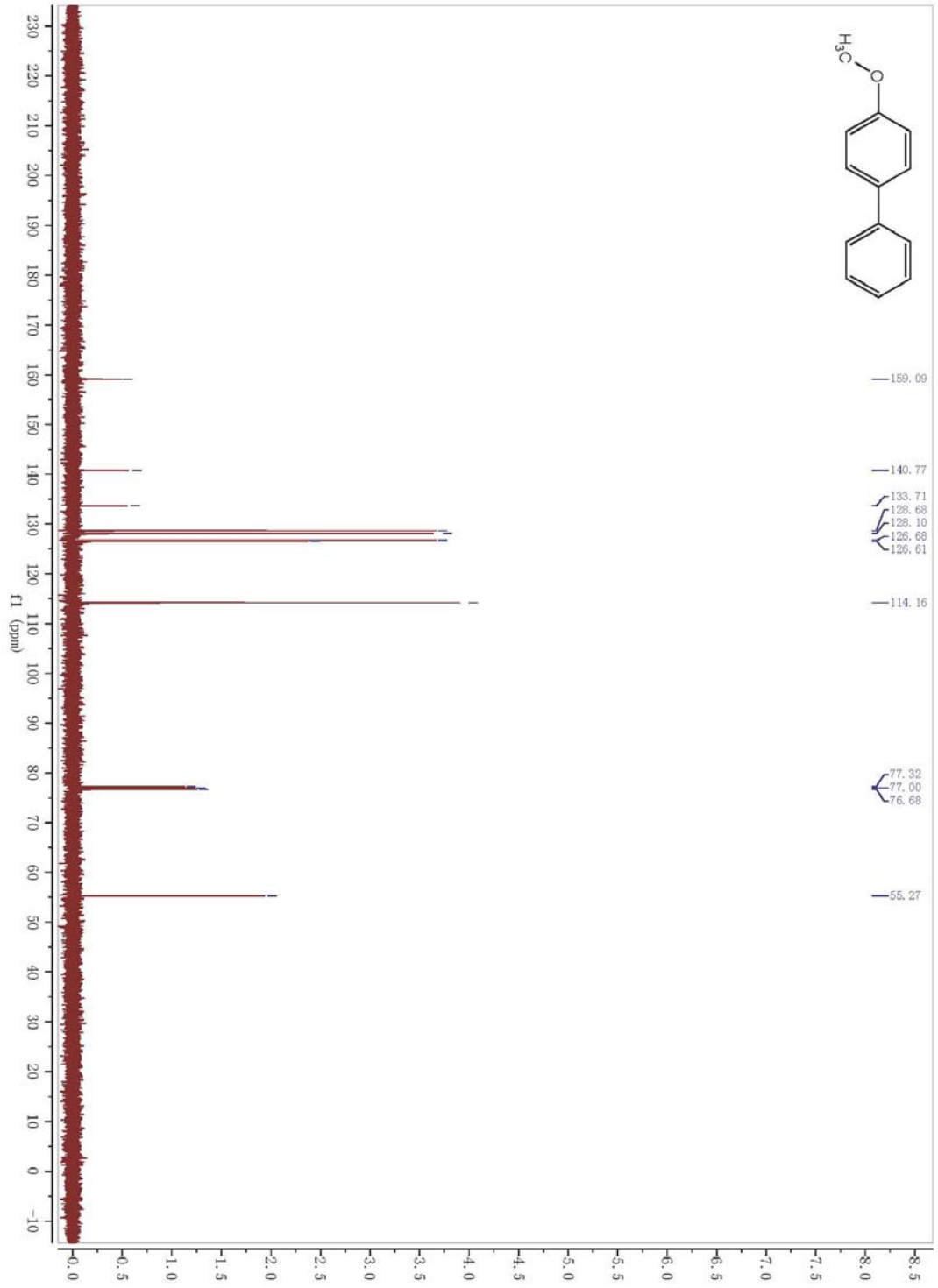
^{13}C NMR for the product of Table 3 entry 4



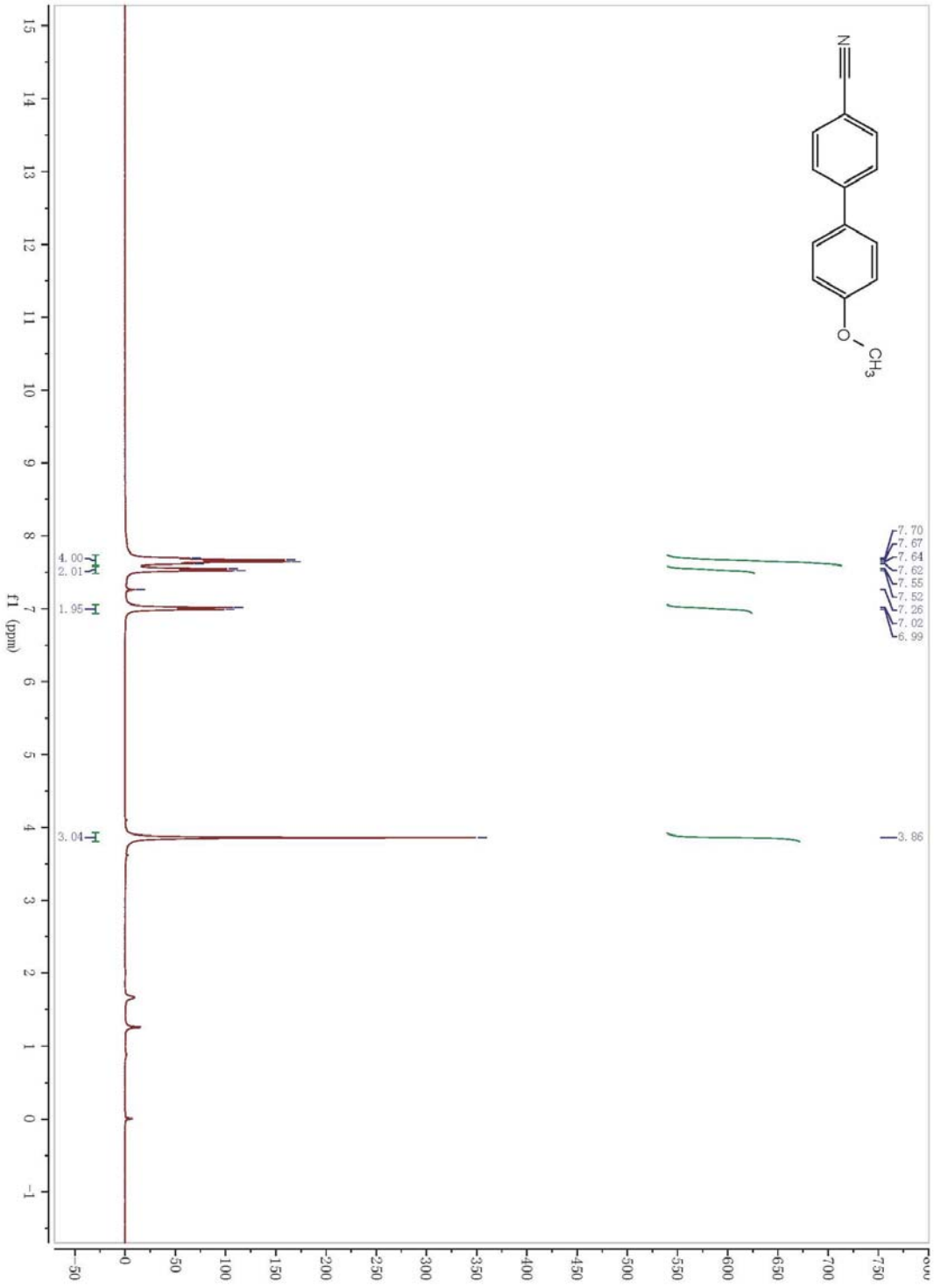
^{1}H NMR for the product of Table 3 entry 5



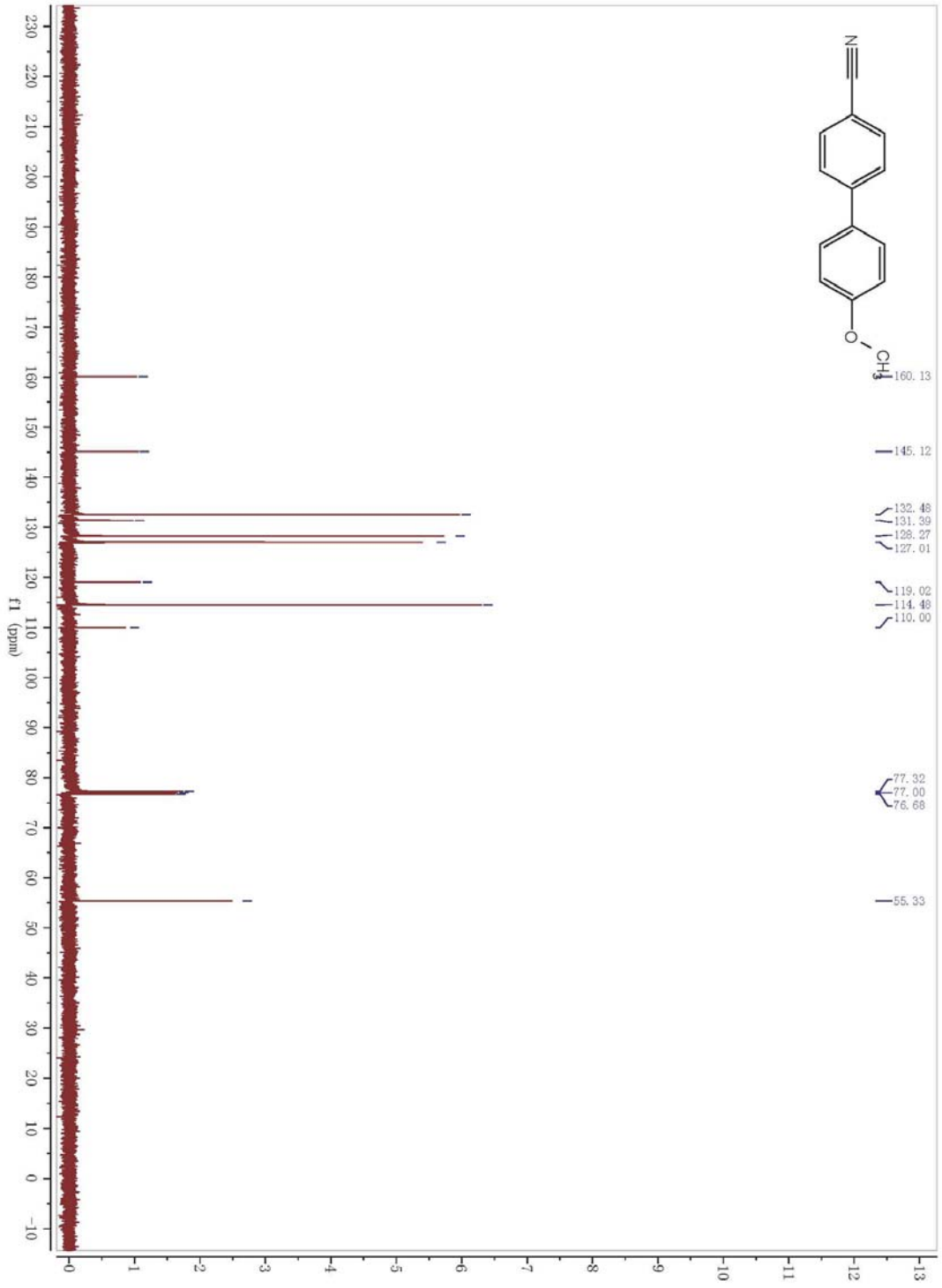
^{13}C NMR for the product of Table 3 entry5



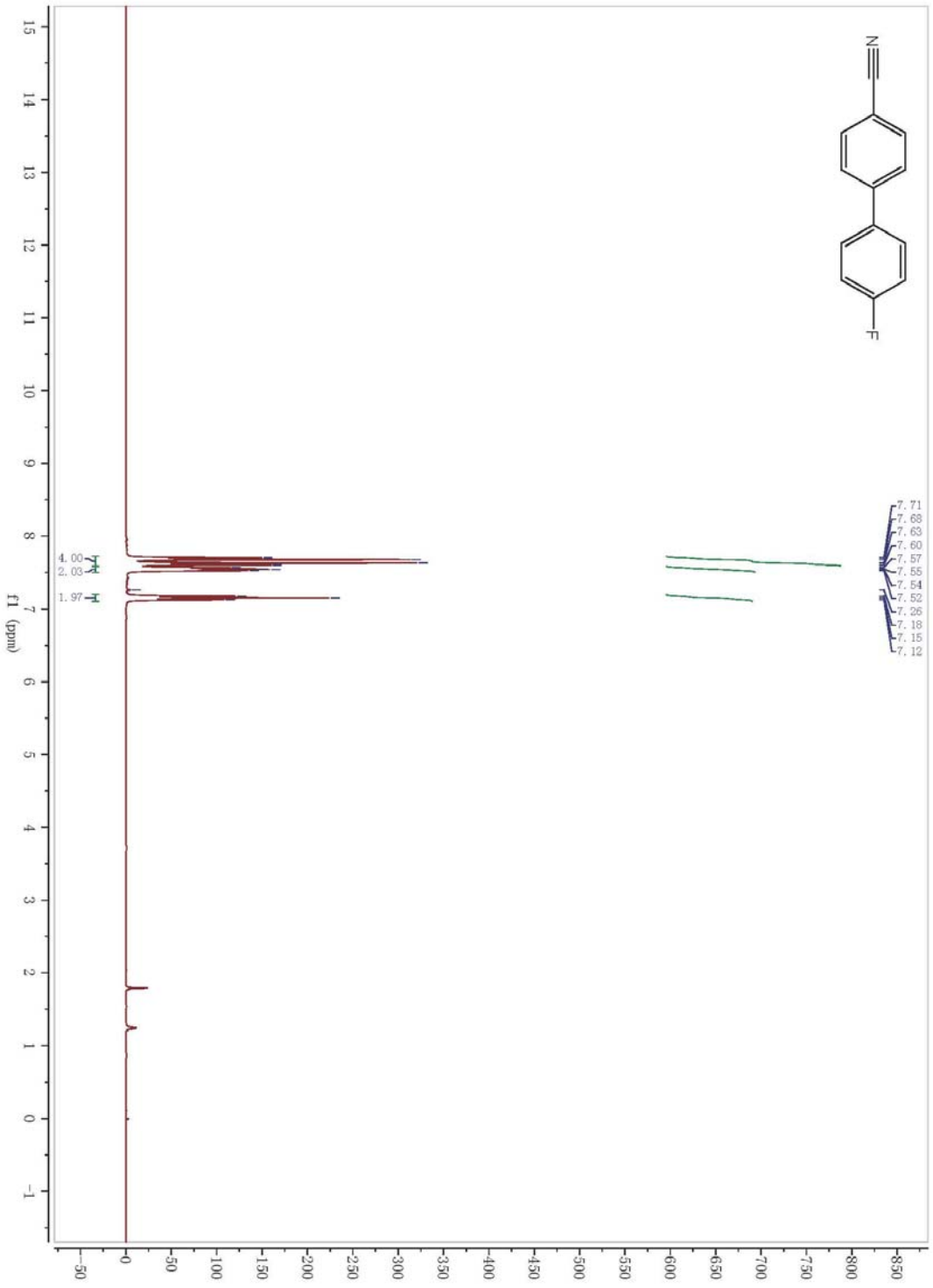
^{1}H NMR for the product of Table 3 entry 6



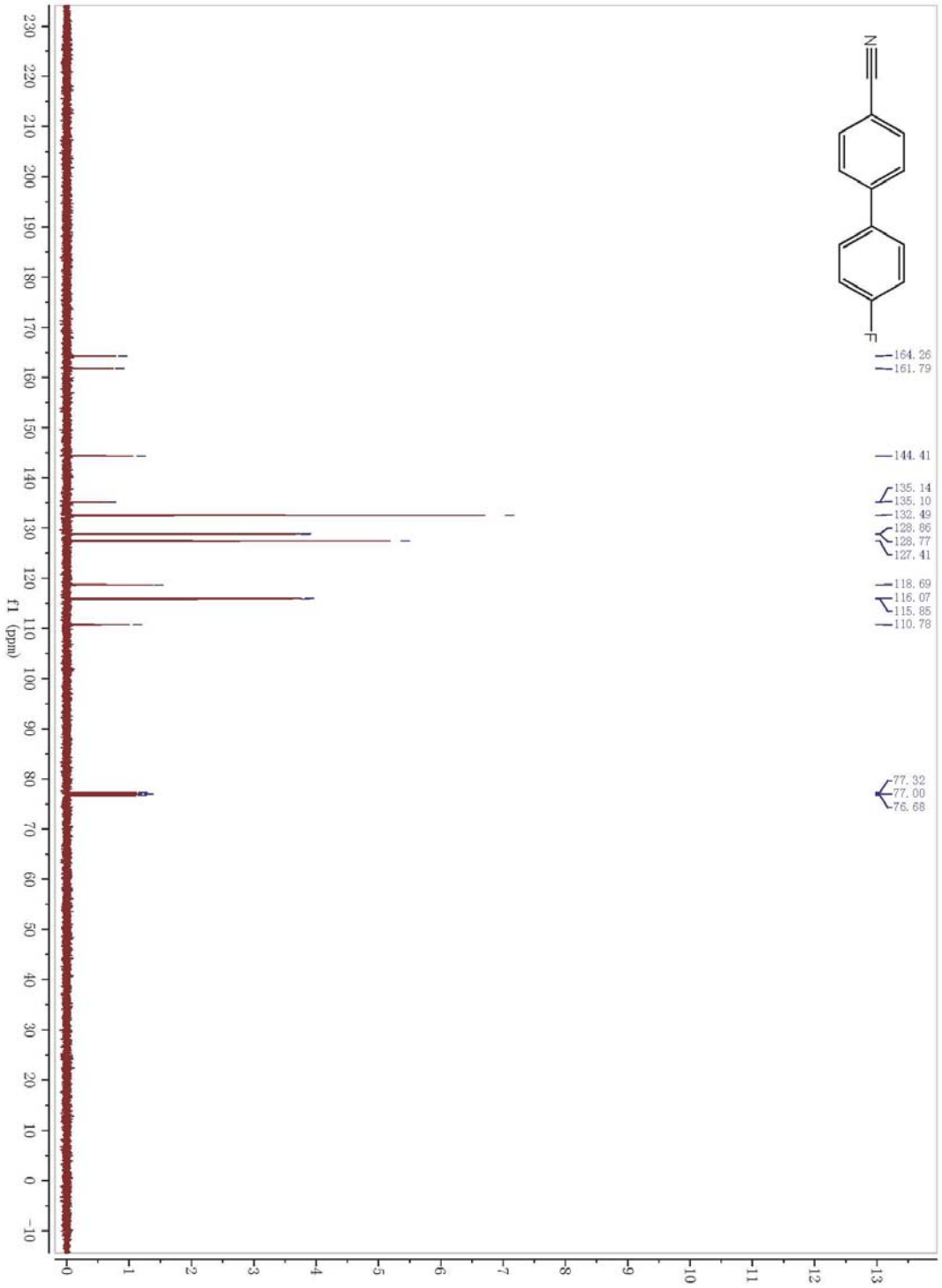
^{13}C NMR for the product of Table 3 entry 6



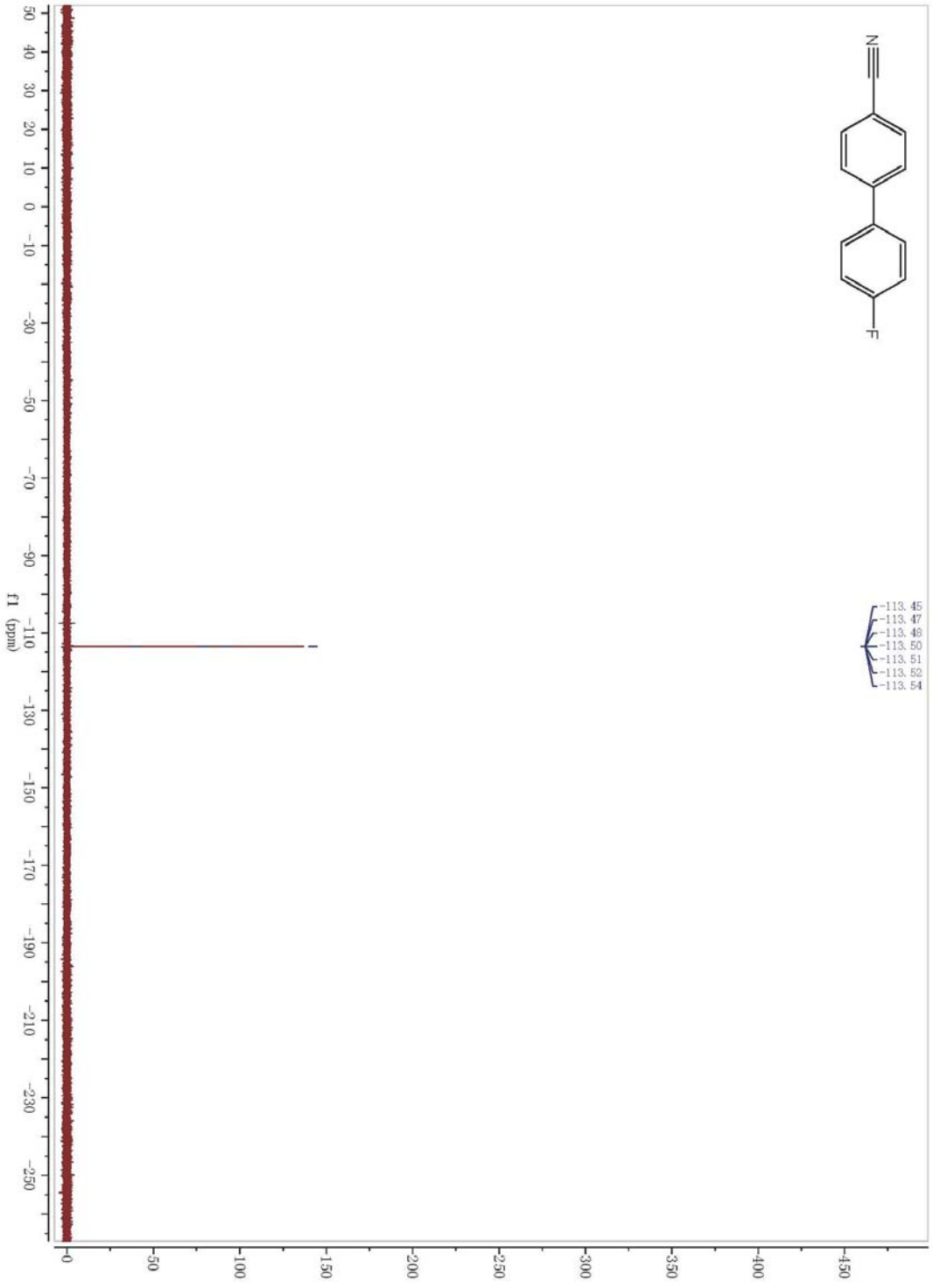
^{1}H NMR for the product of Table 3 entry 7



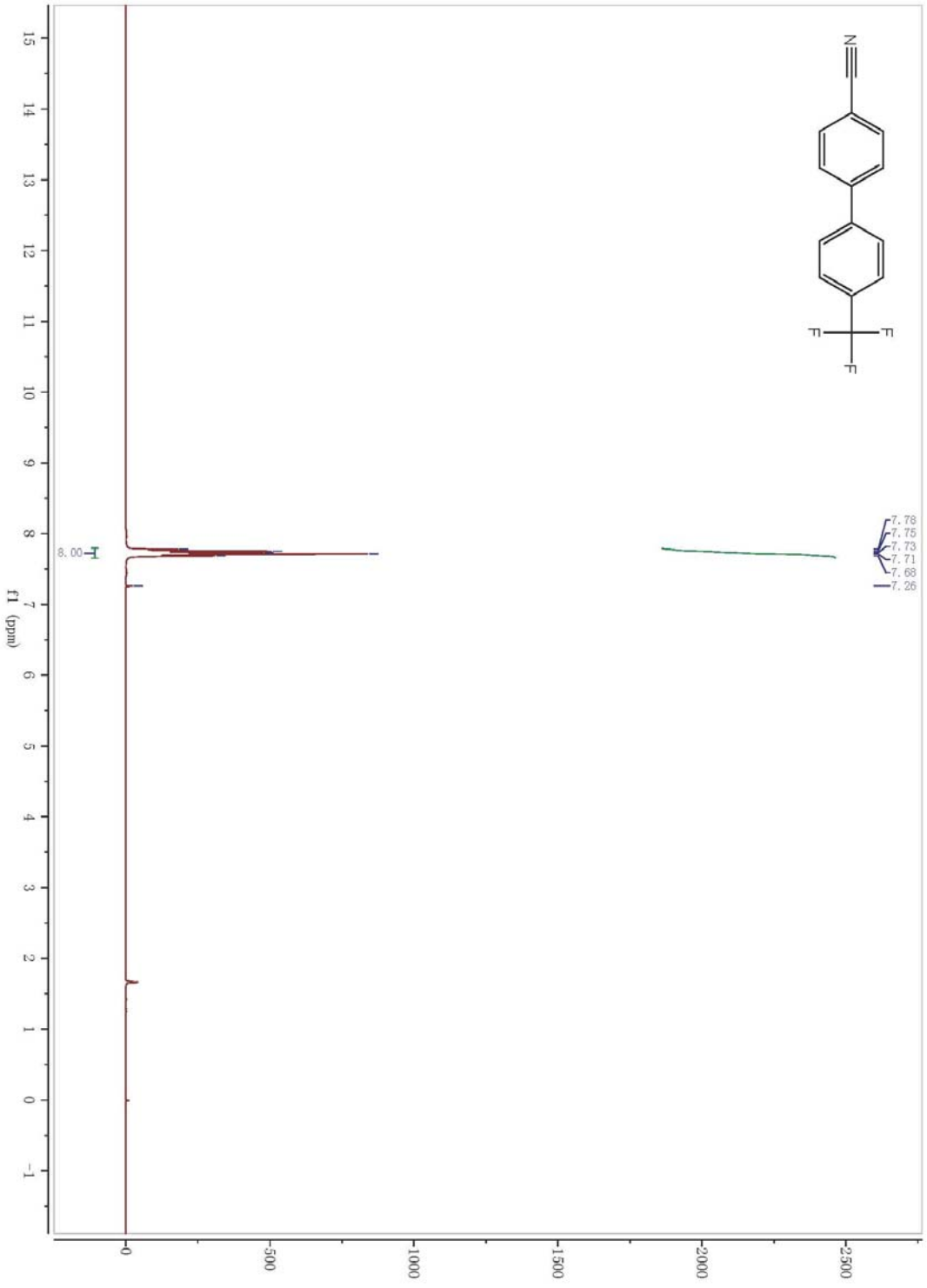
^{13}C NMR for the product of Table 3 entry 7



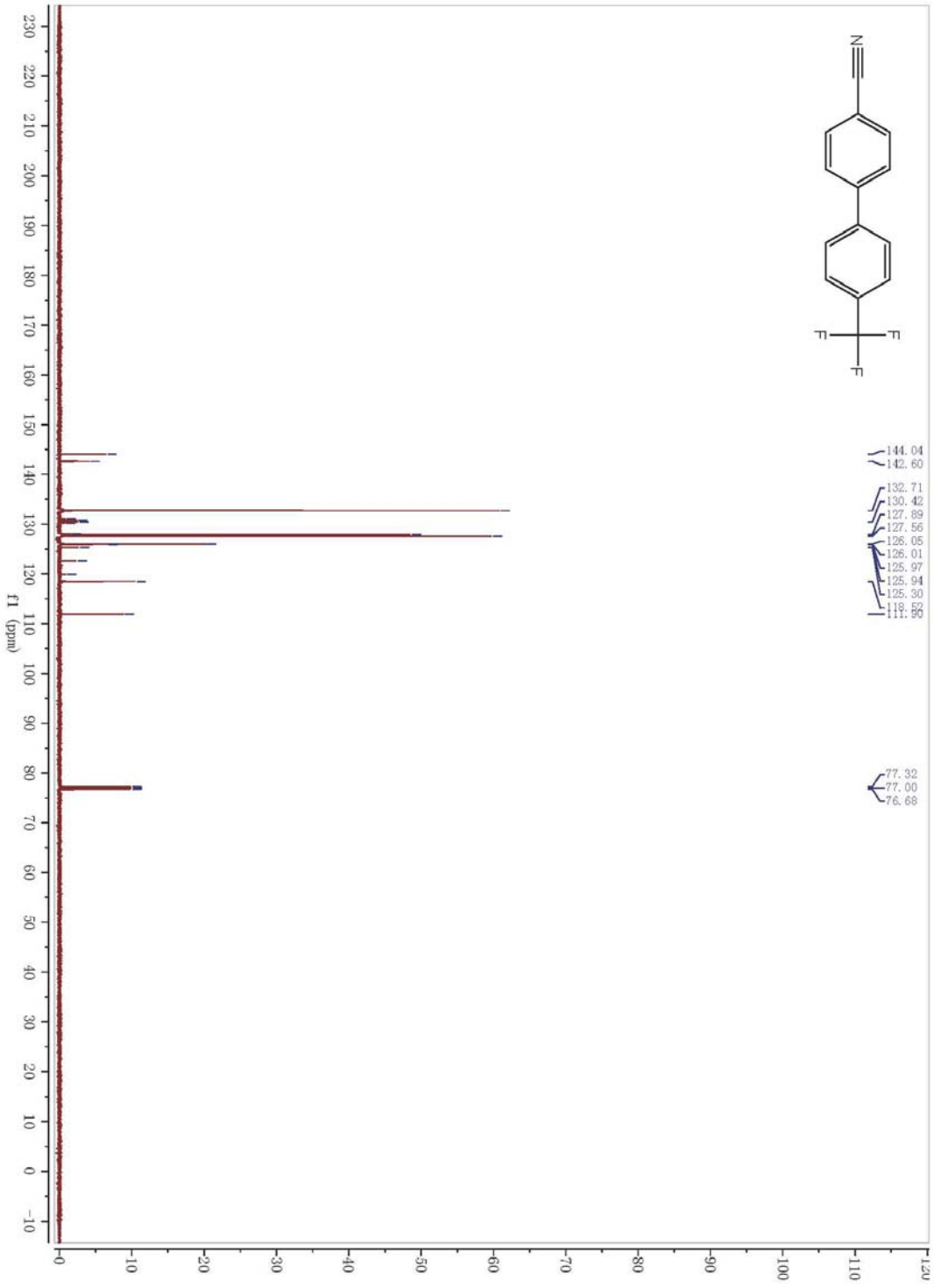
^{19}F NMR for the product of Table 3 entry 7



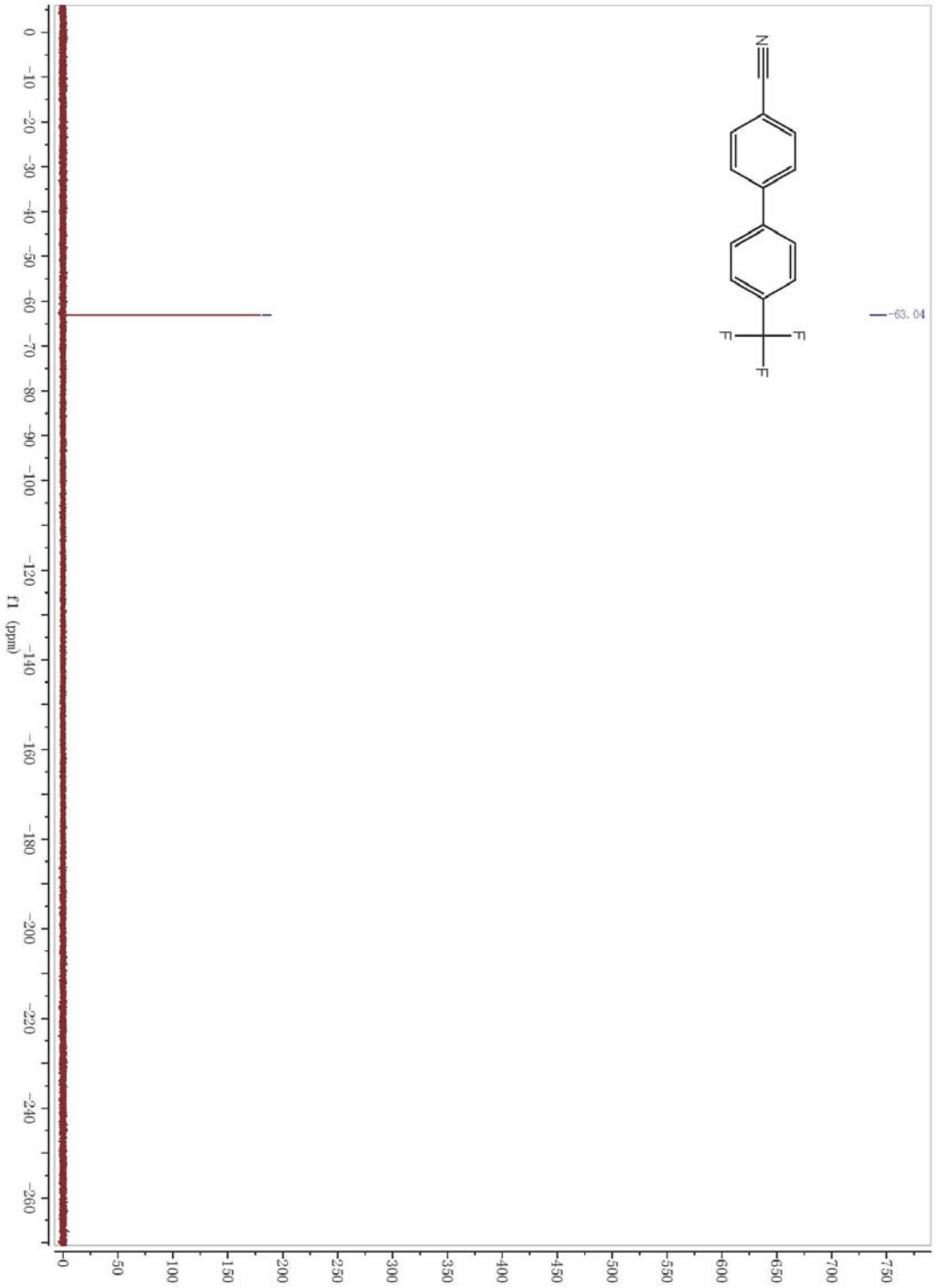
^{1}H NMR for the product of Table 3 entry 8



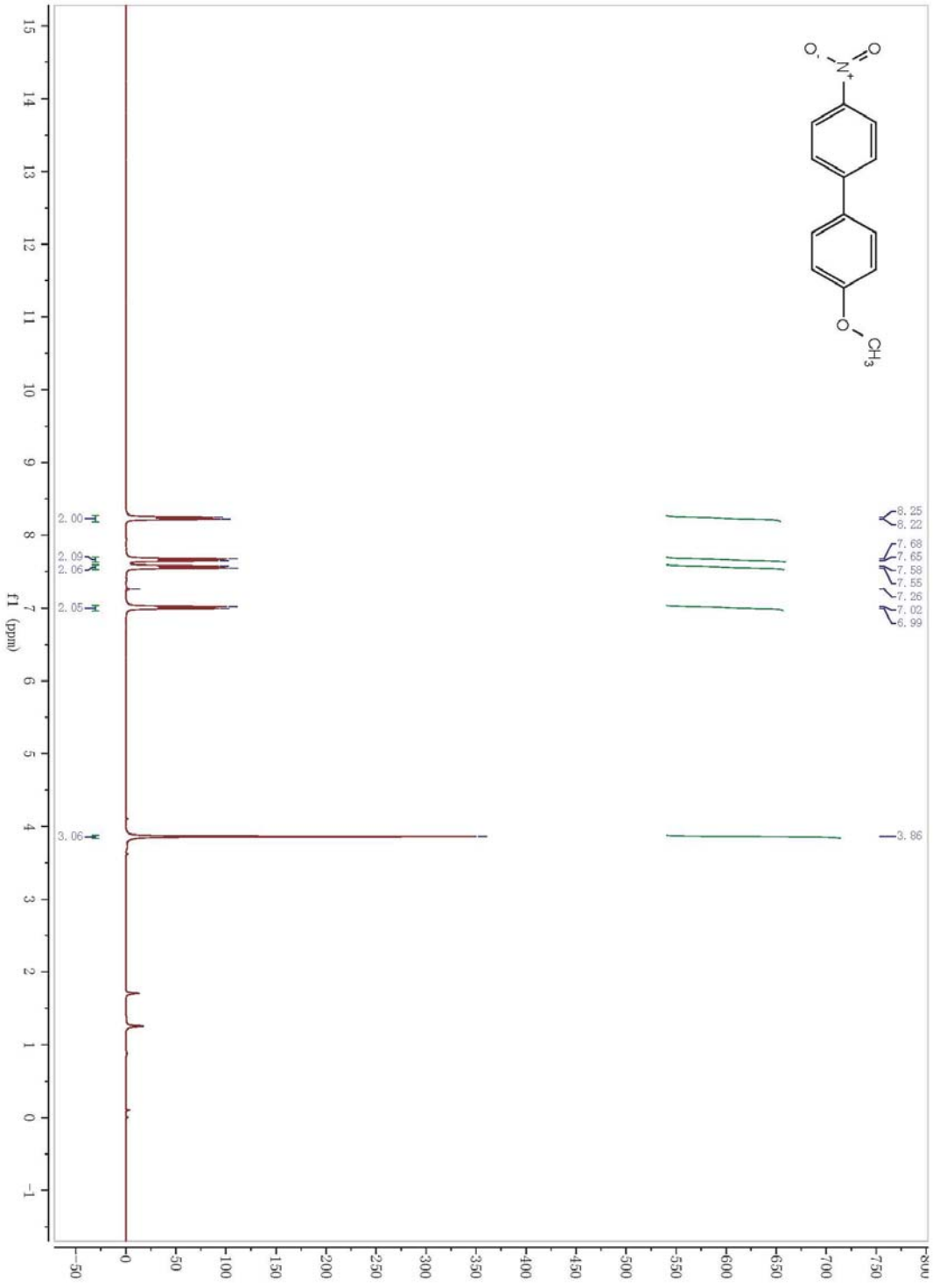
^{13}CNMR for the product of Table 3 entry 8



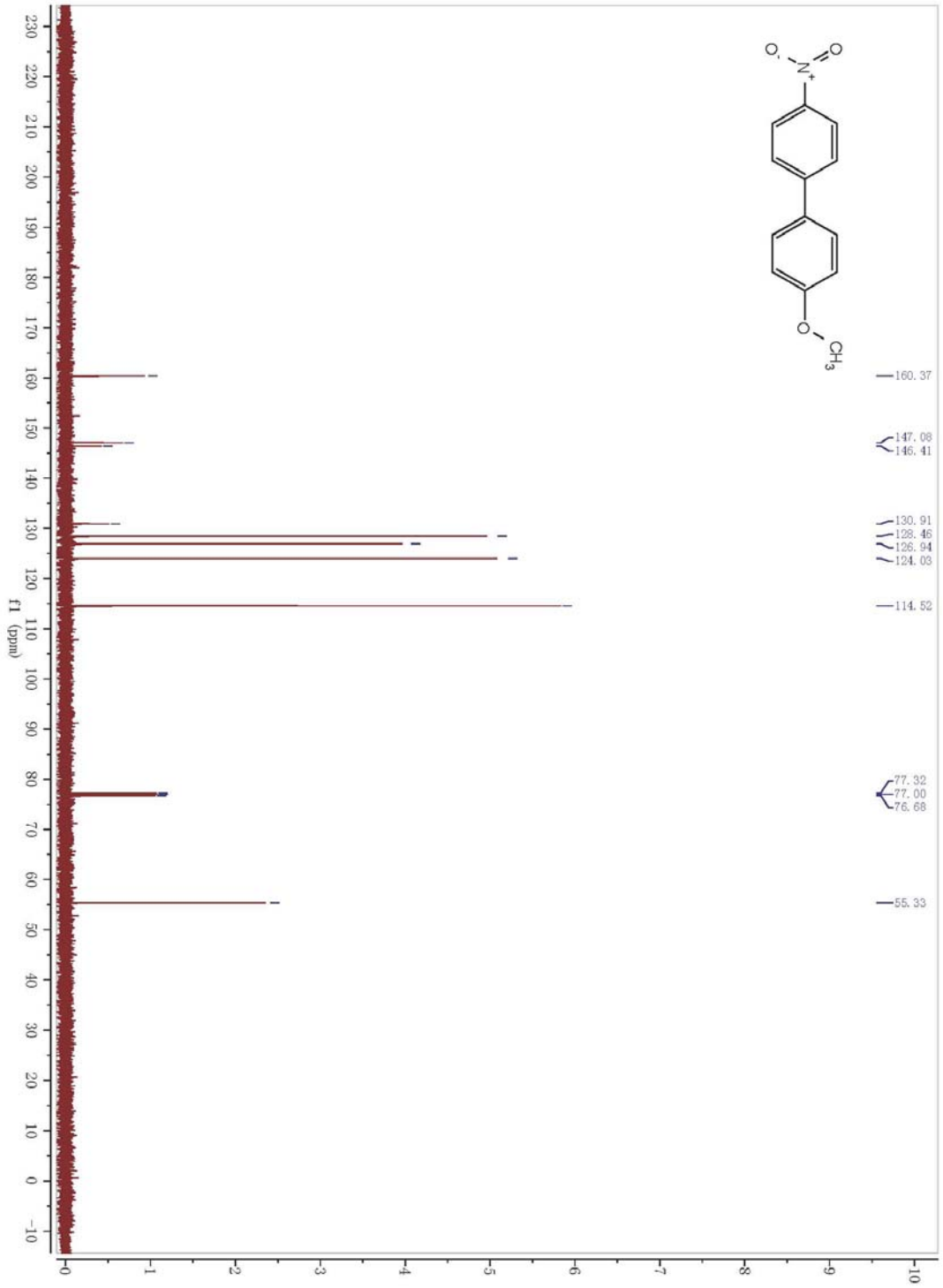
^{19}F NMR for the product of Table 3 entry 8



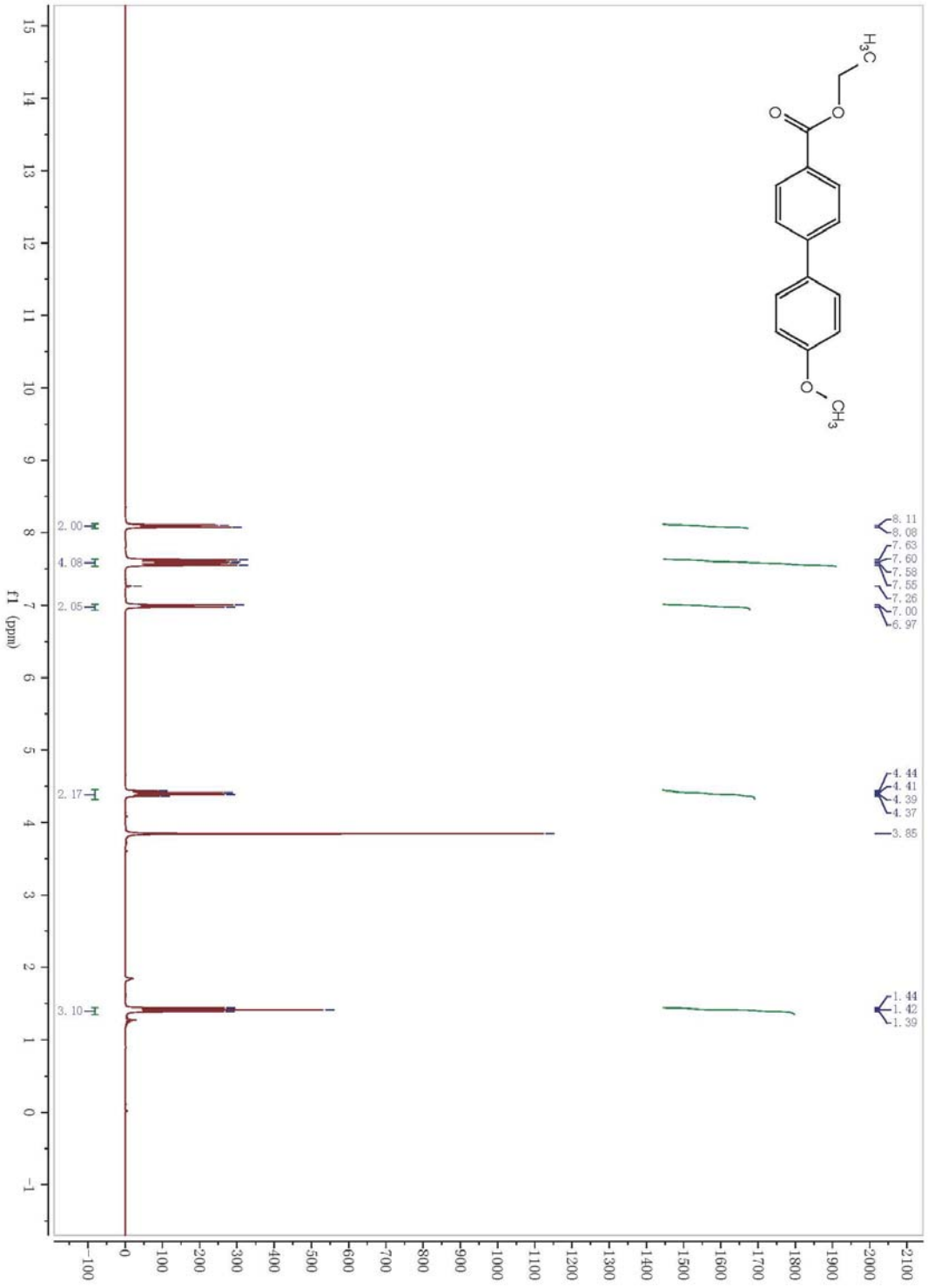
^{1}H NMR for the product of Table 3 entry 9



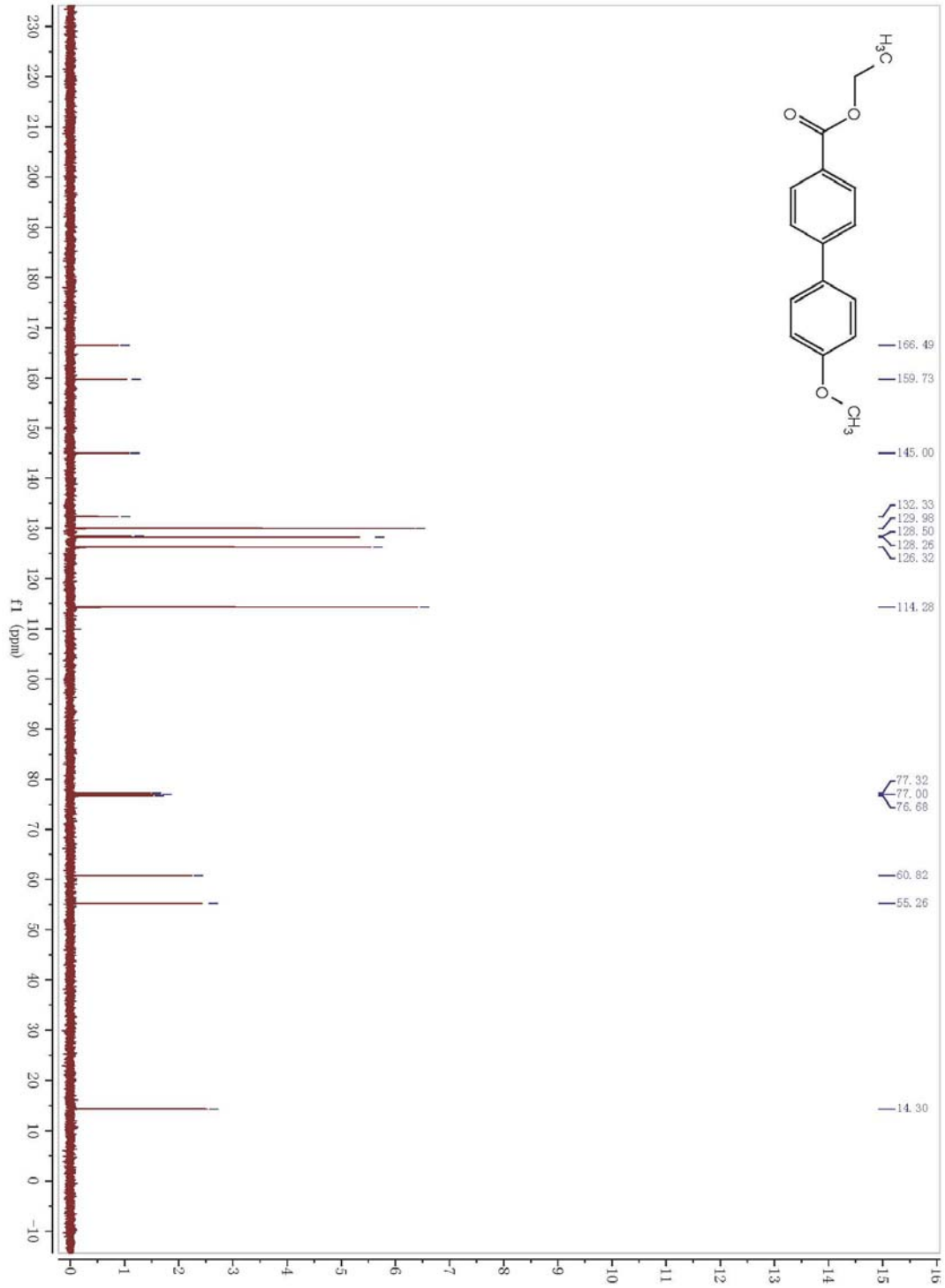
^{13}C NMR for the product of Table 3 entry 9



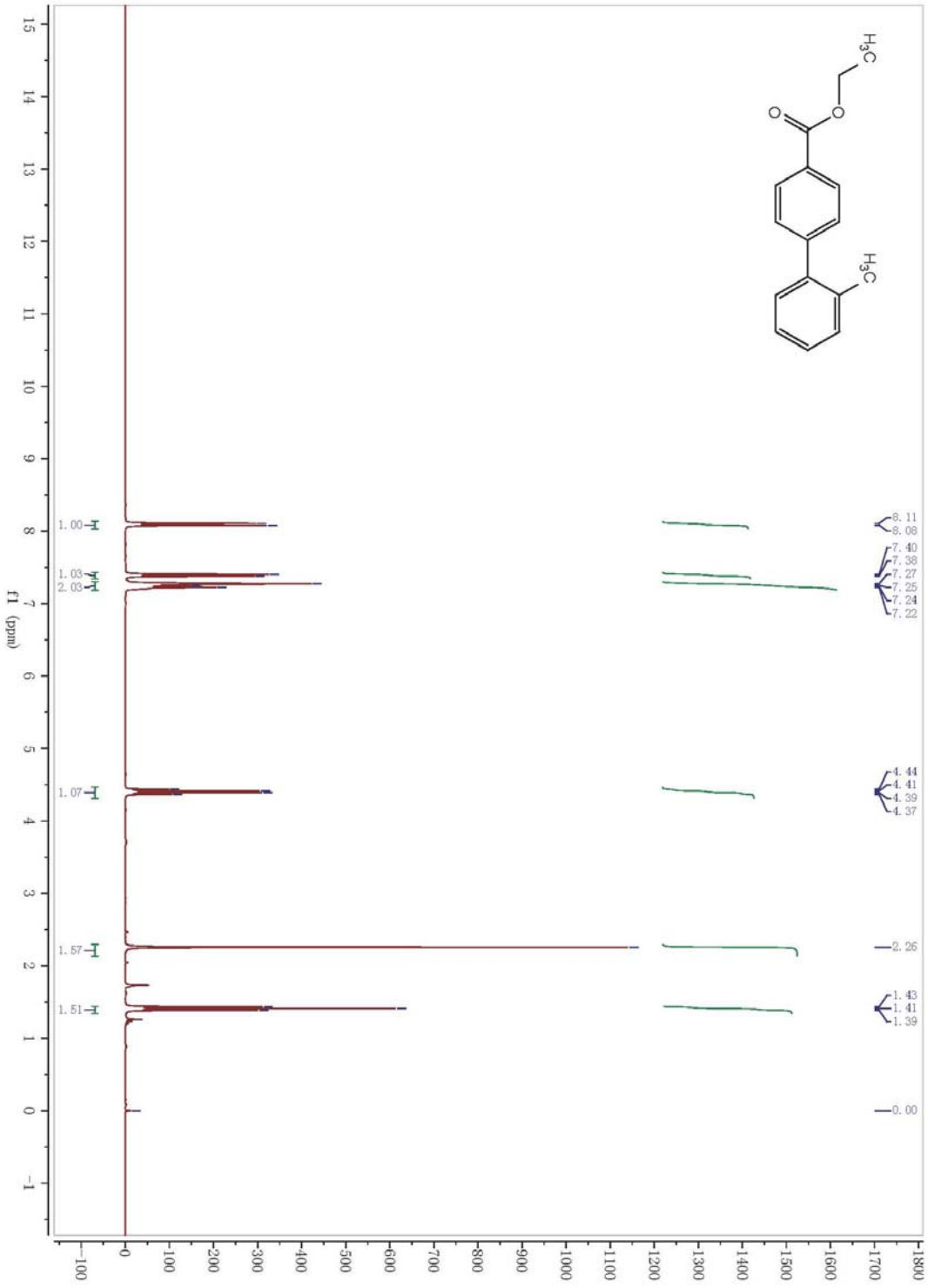
^{1}H NMR for the product of Table 3 entry 10



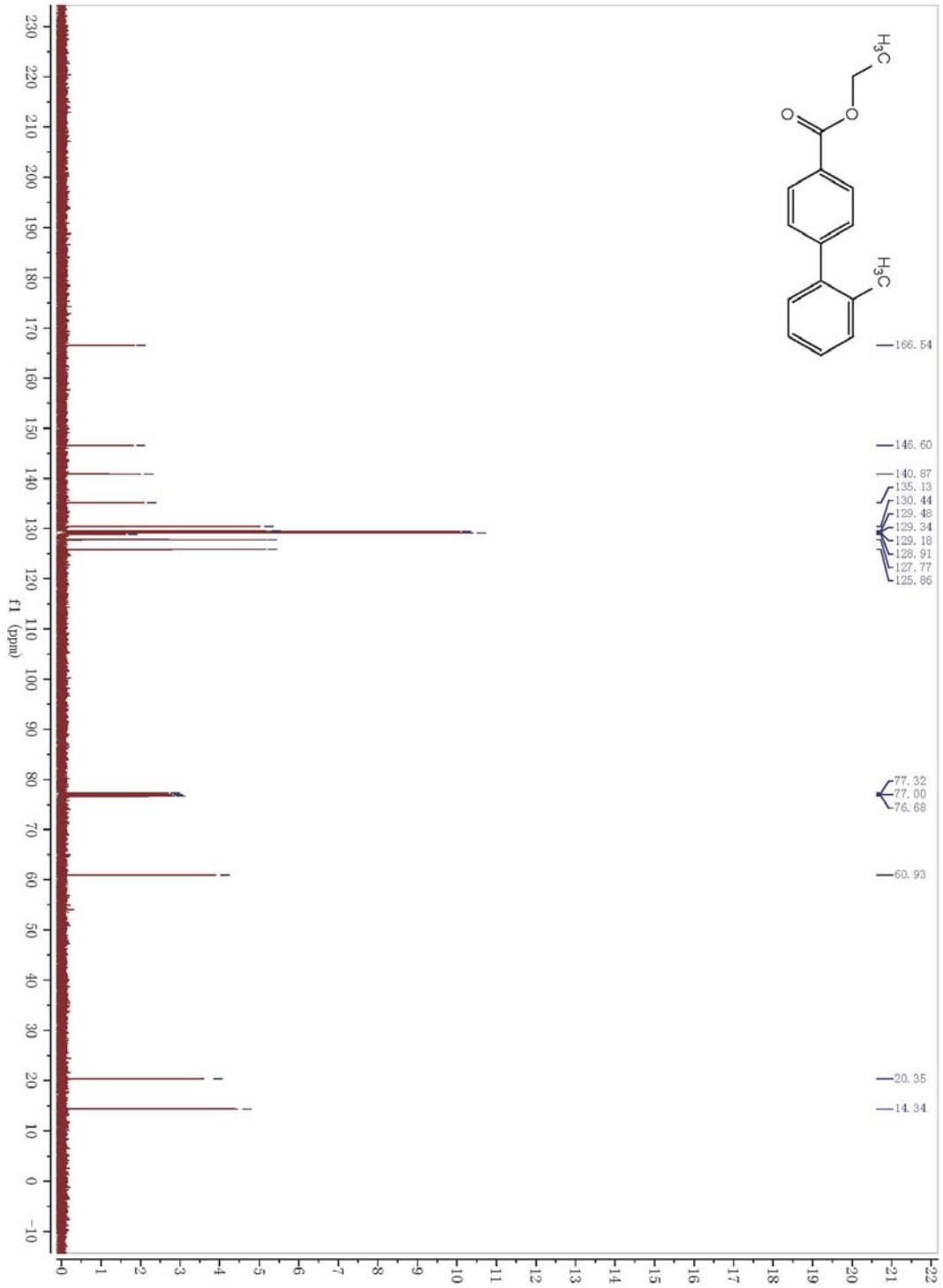
^{13}C NMR for the product of Table 3 entry 10



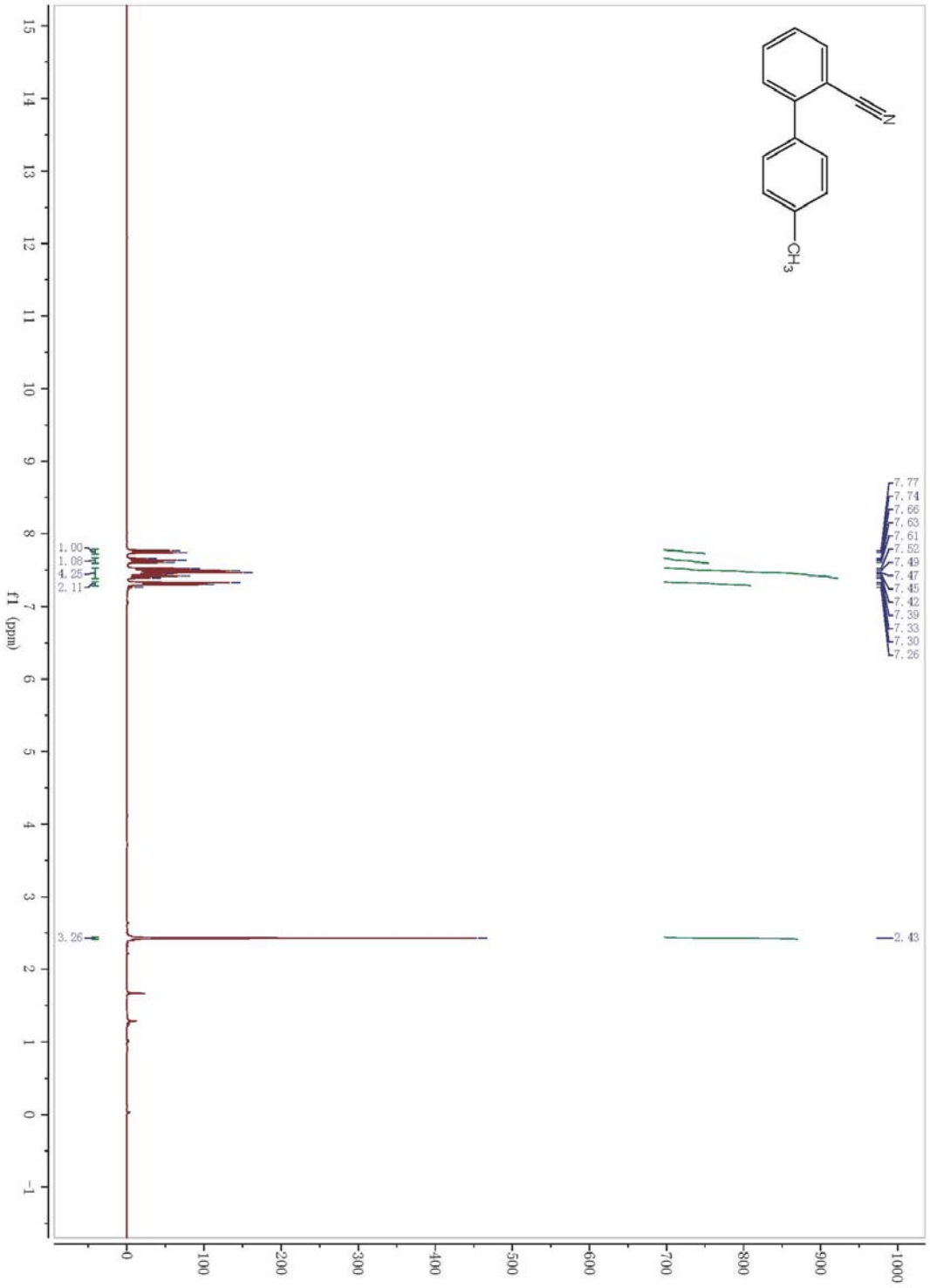
^{1}H NMR for the product of Table 3 entry 11



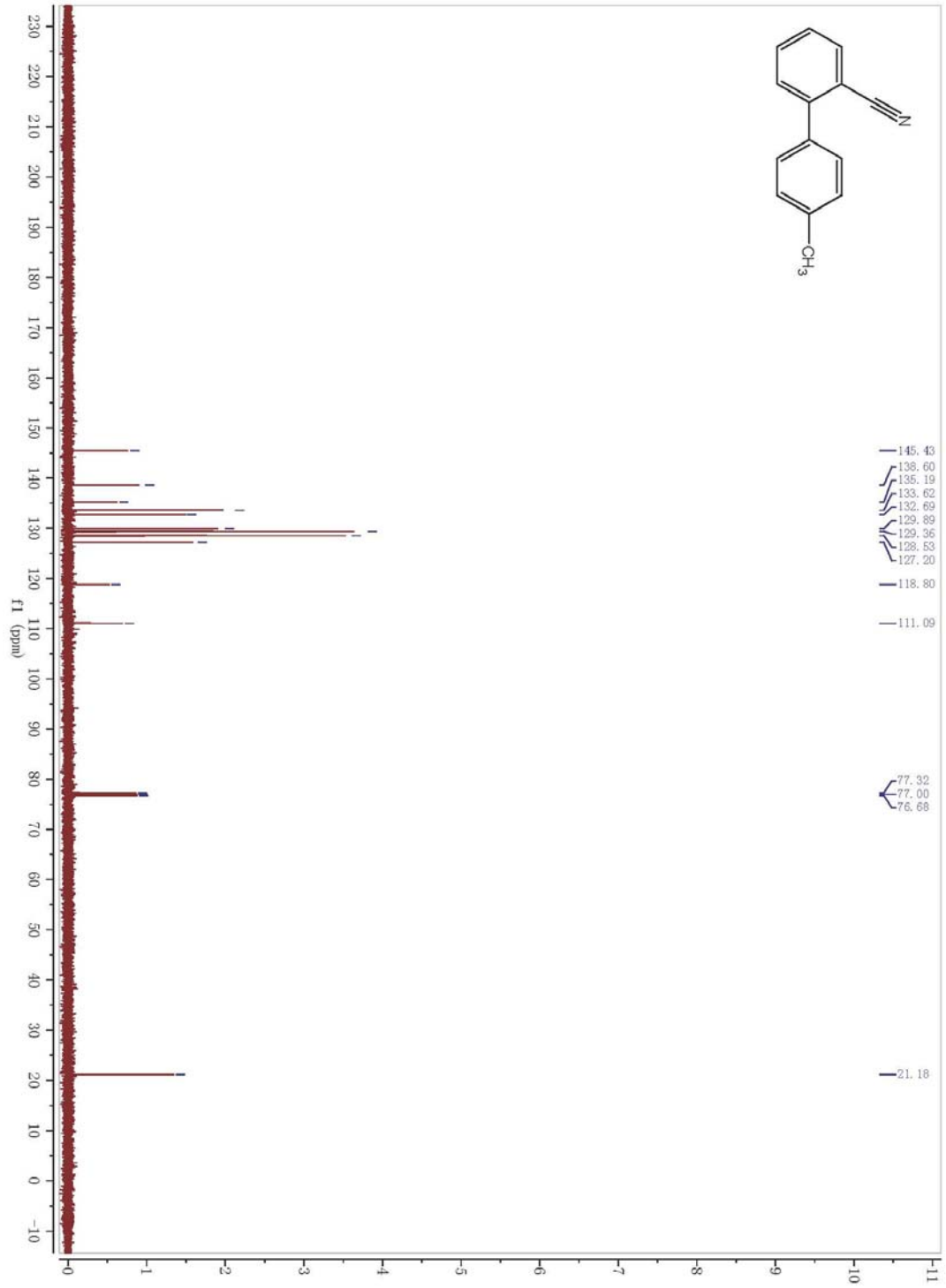
^{13}C NMR for the product of Table 3 entry 11



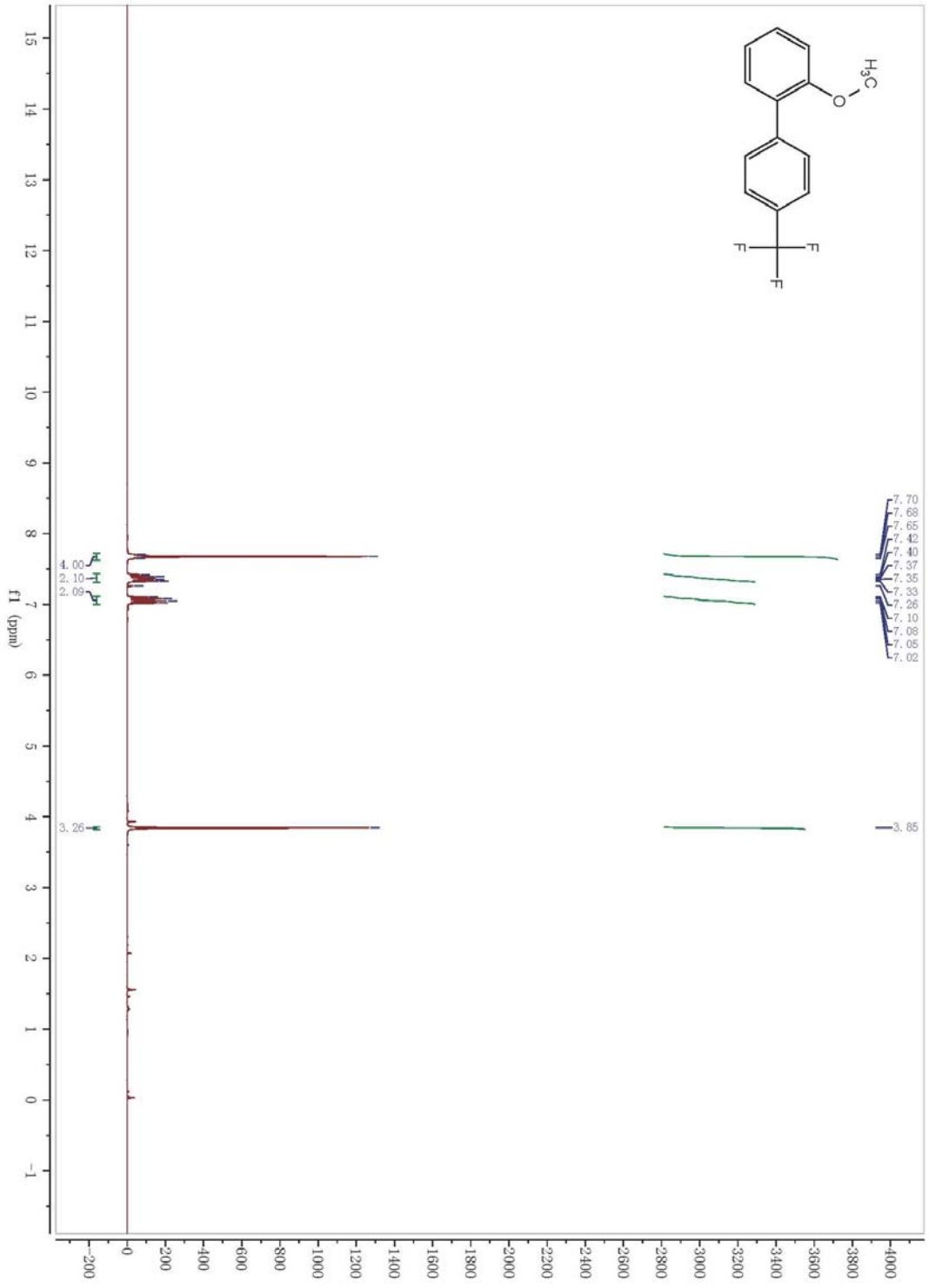
^{1}H NMR for the product of Table 3 entry 12



^{13}C NMR for the product of Table 3 entry 12



^{1}H NMR for the product of Table 3 entry 13



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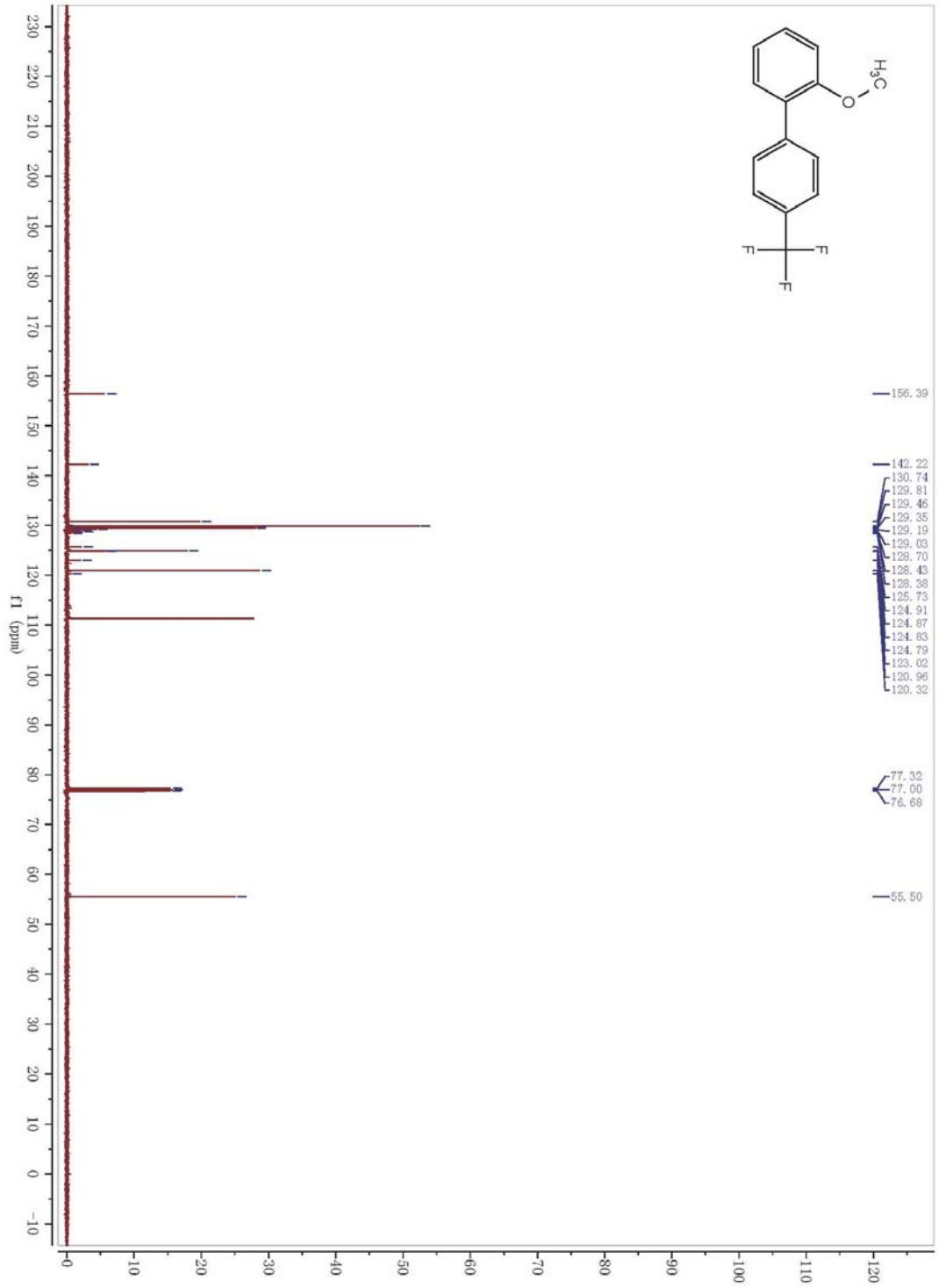
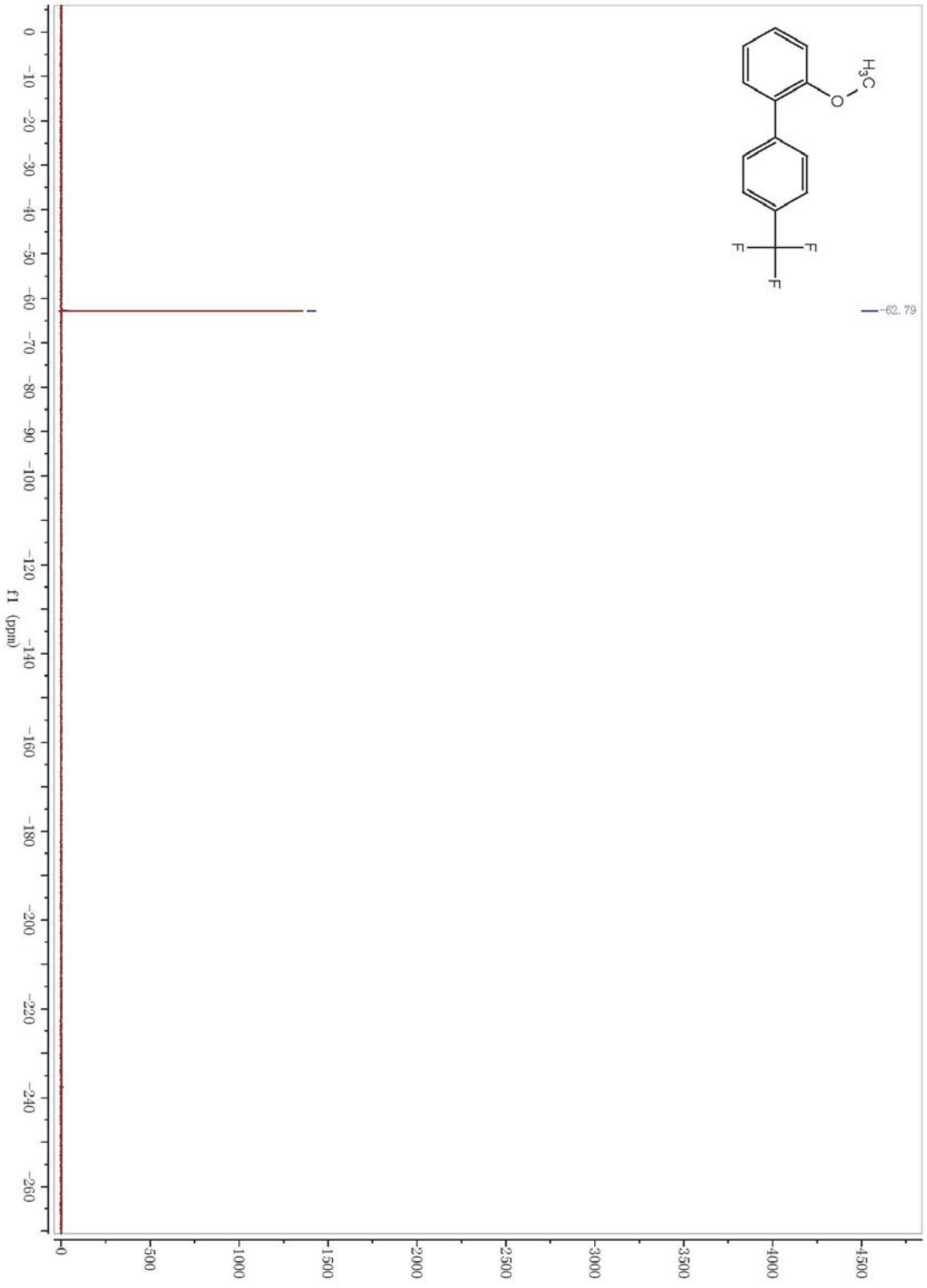
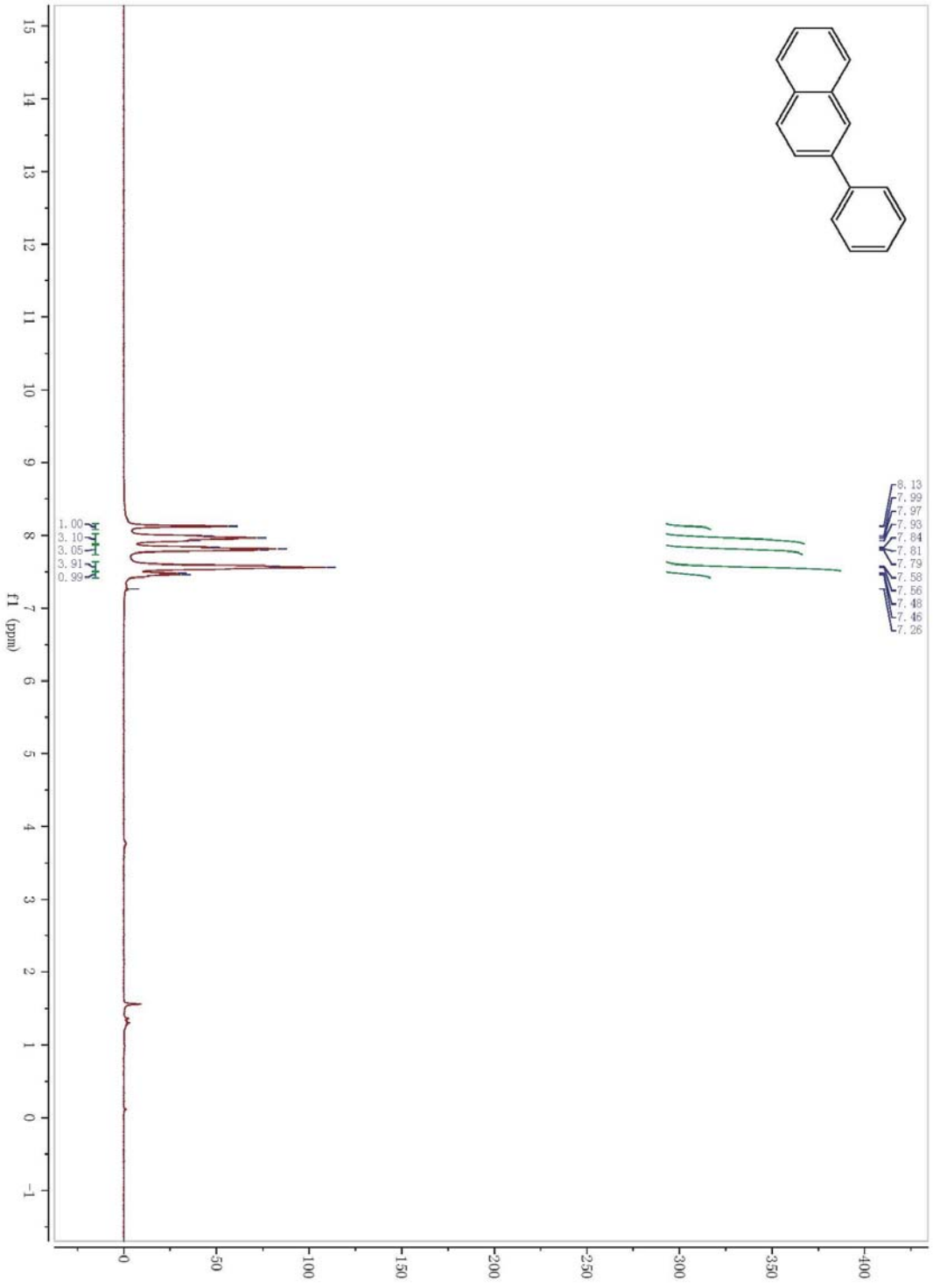


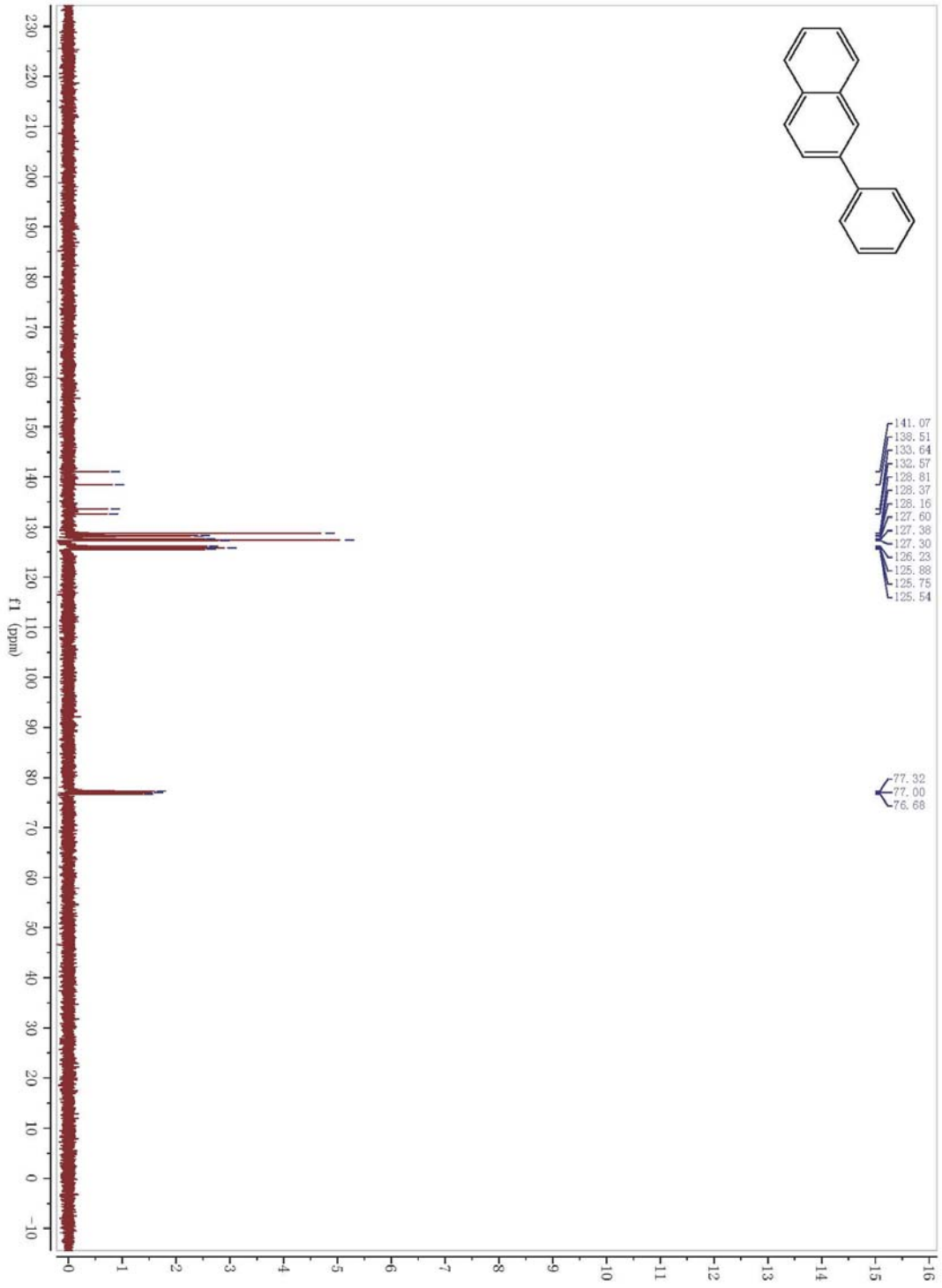
^{19}F NMR for the product of Table 3 entry 13



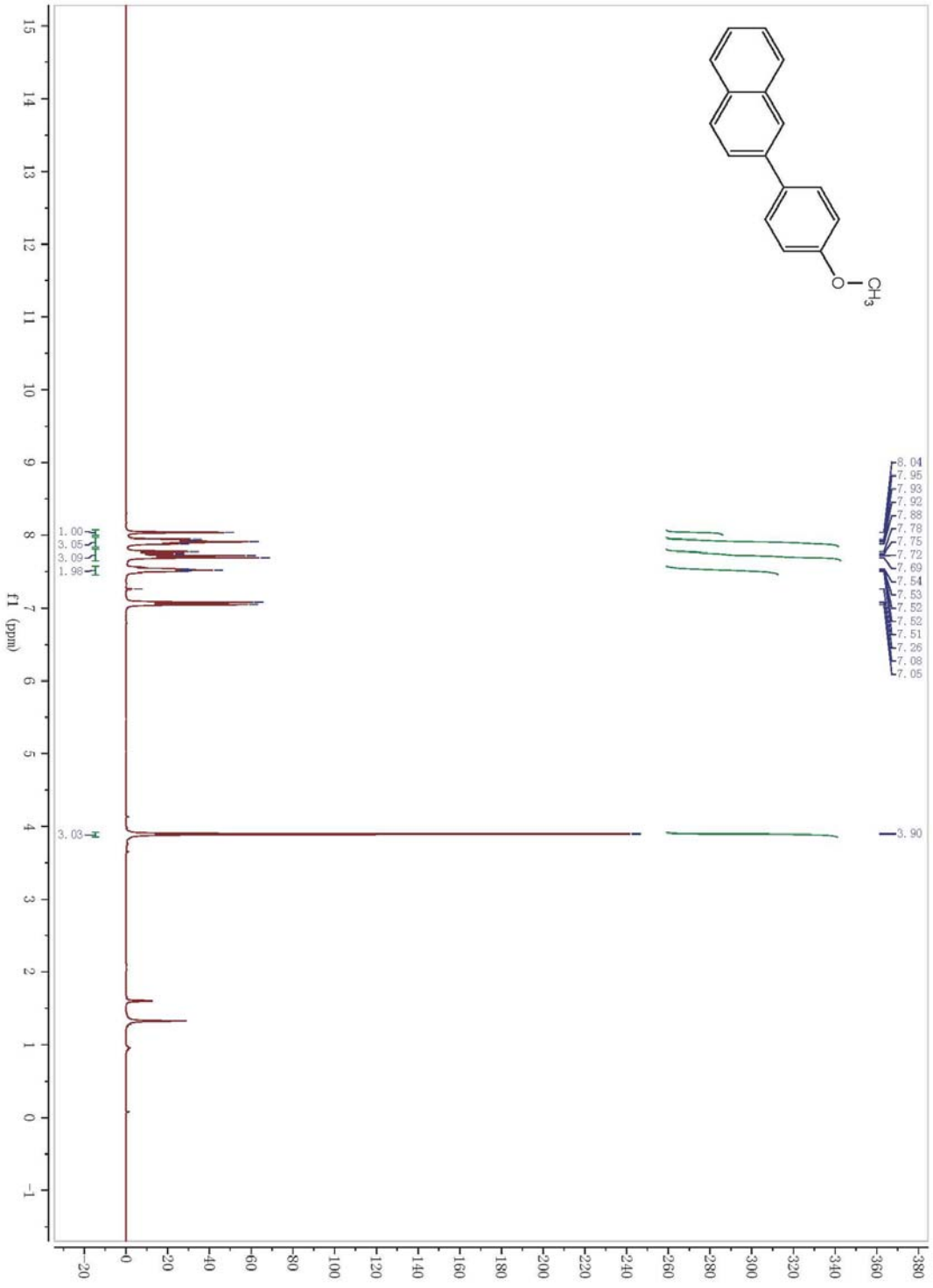
^{1}H NMR for the product of Table 3 entry 14



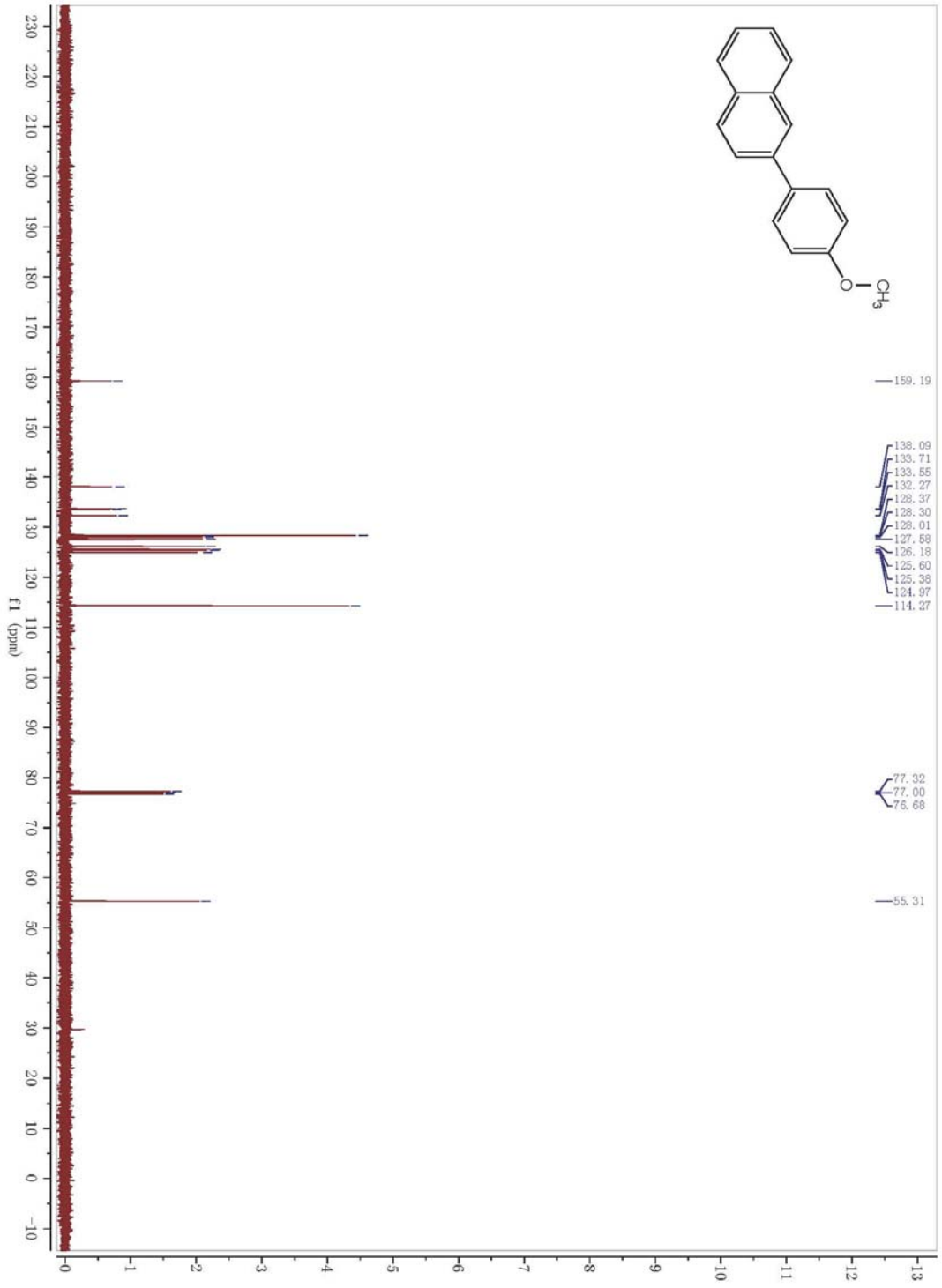
^{13}C NMR for the product of Table 3 entry 14



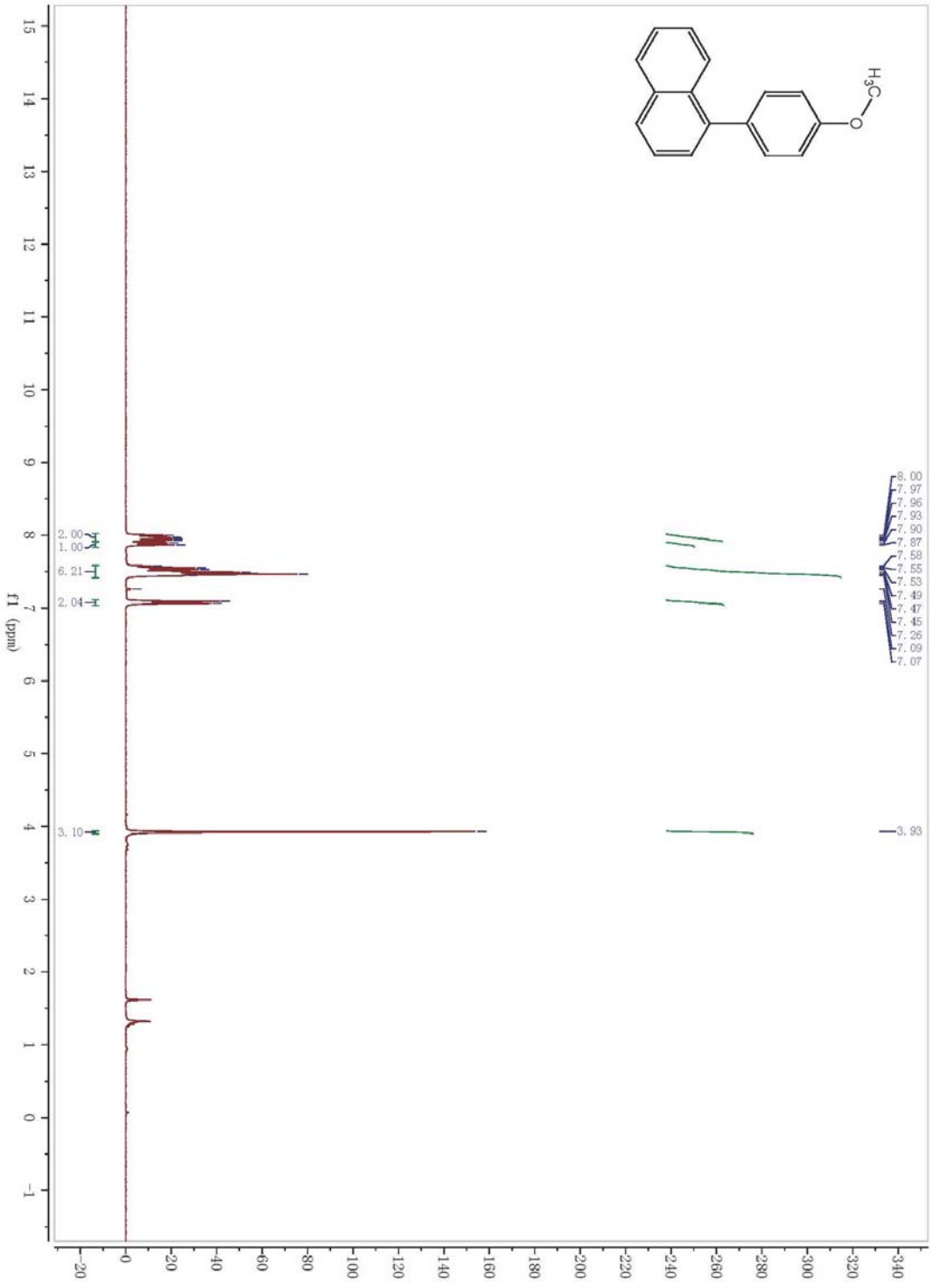
^{1}H NMR for the product of Table 3 entry 15



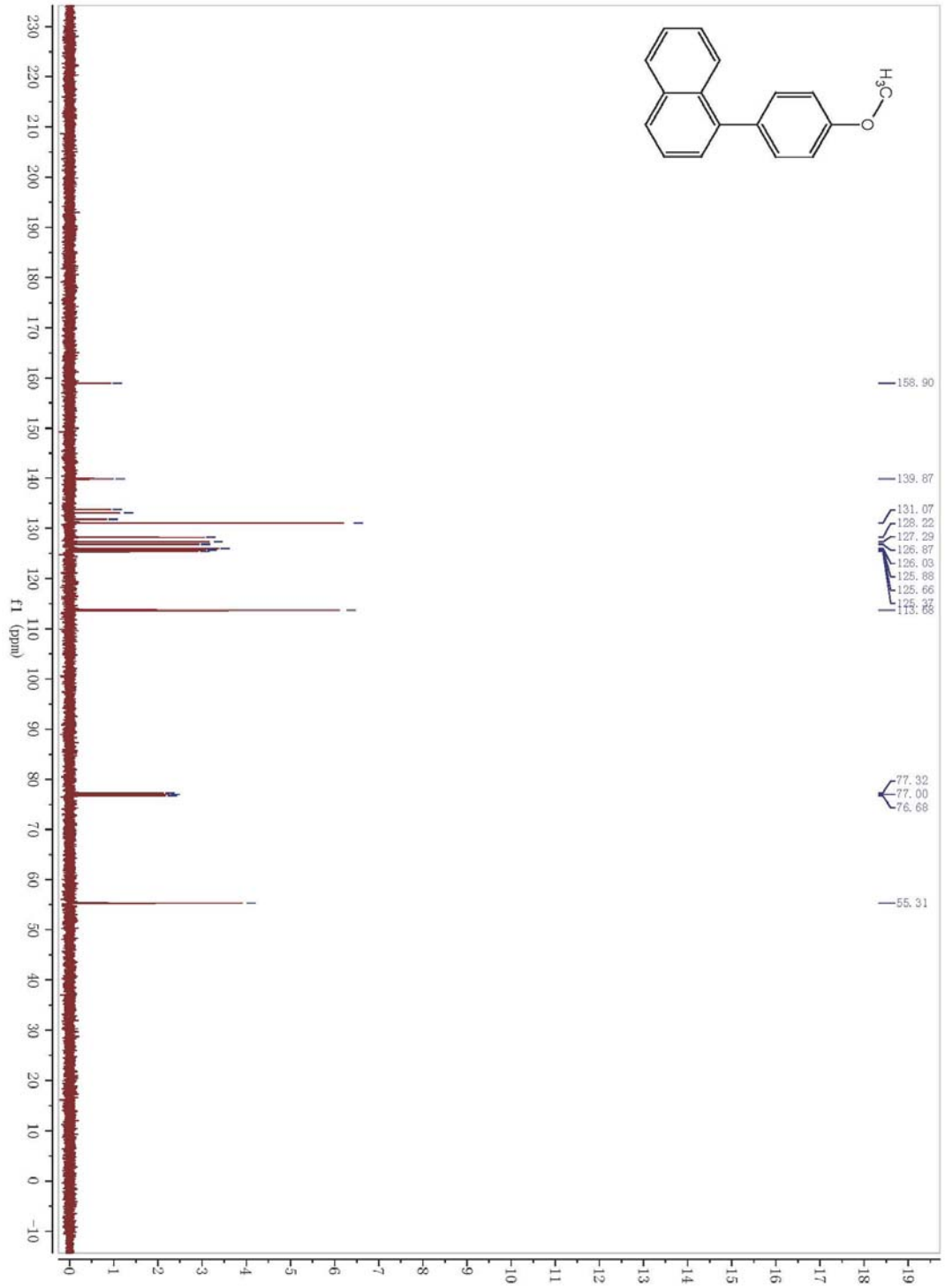
^{13}C NMR for the product of Table 3 entry 15



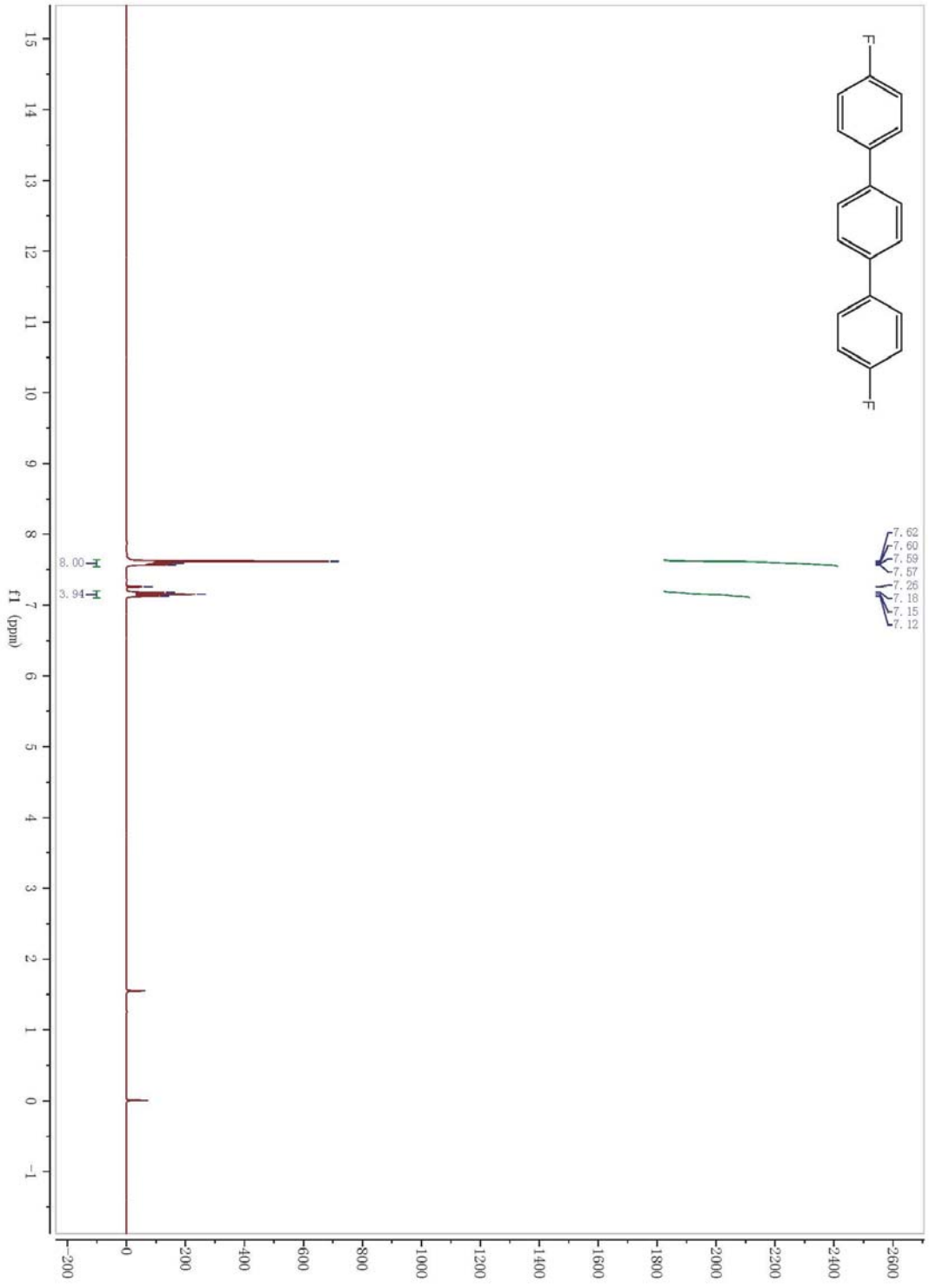
^{1}H NMR for the product of Table 3 entry 16



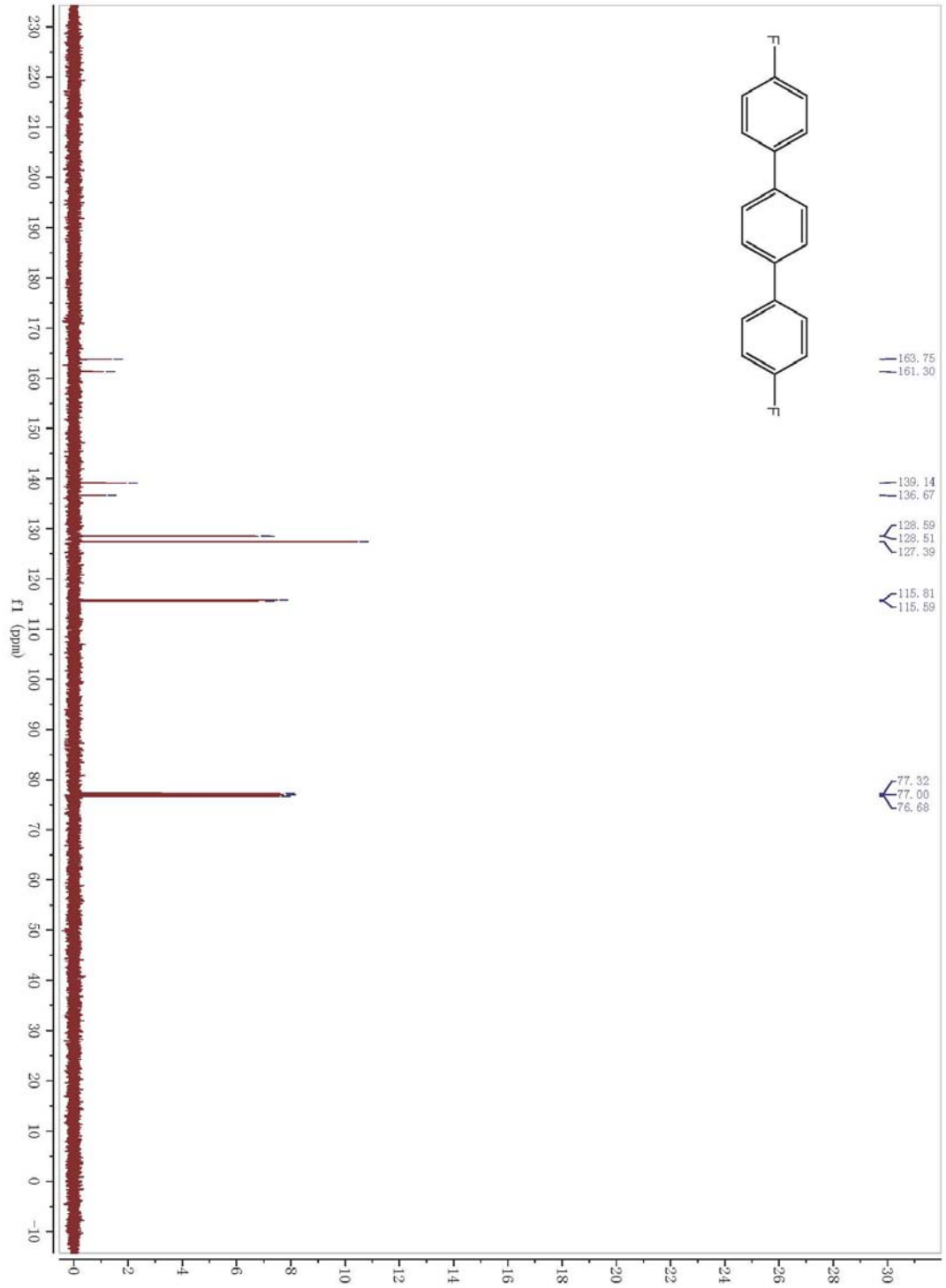
^{13}C NMR for the product of Table 3 entry 16



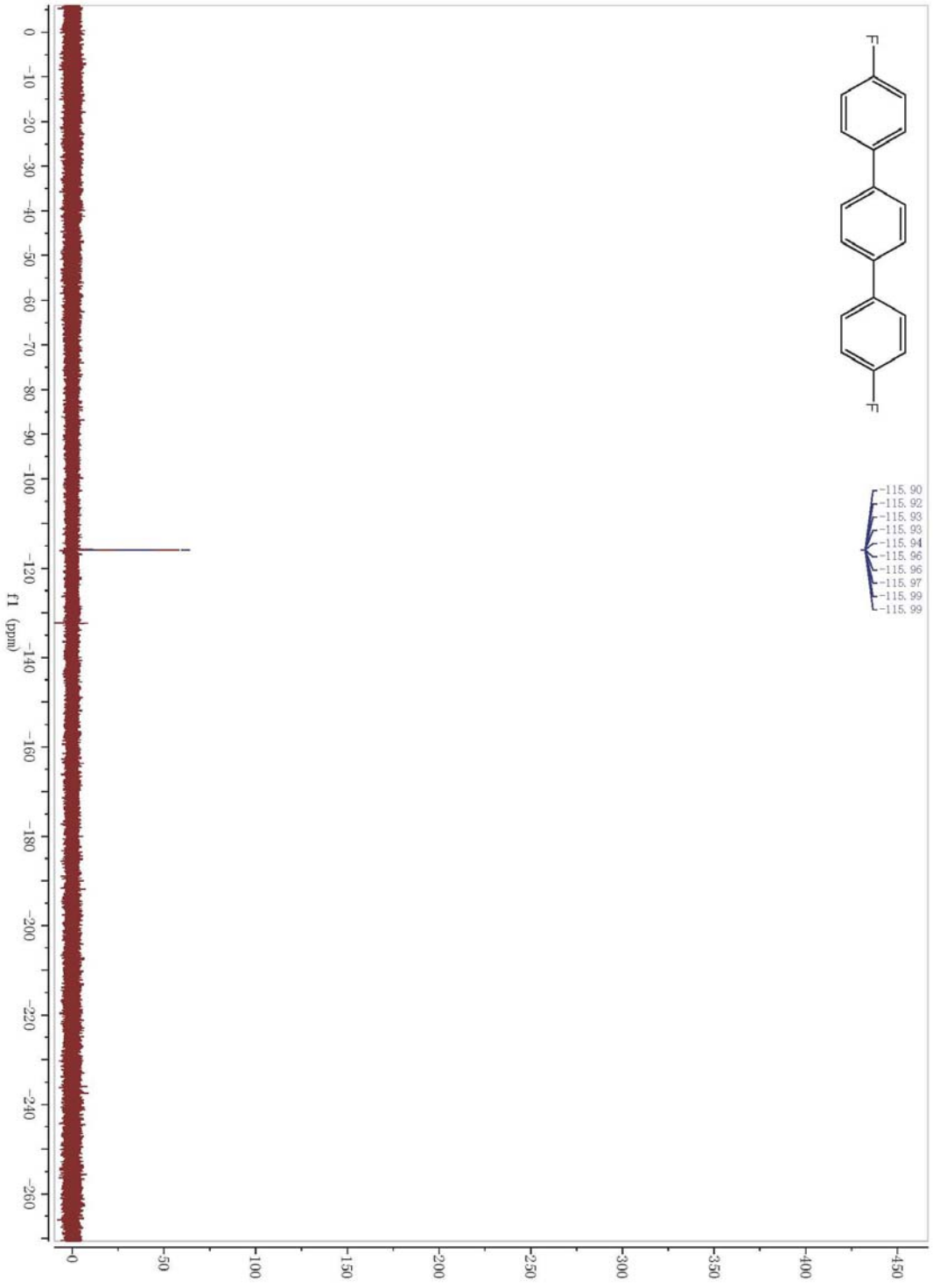
^{1}H NMR for the product of Table 3 entry 17



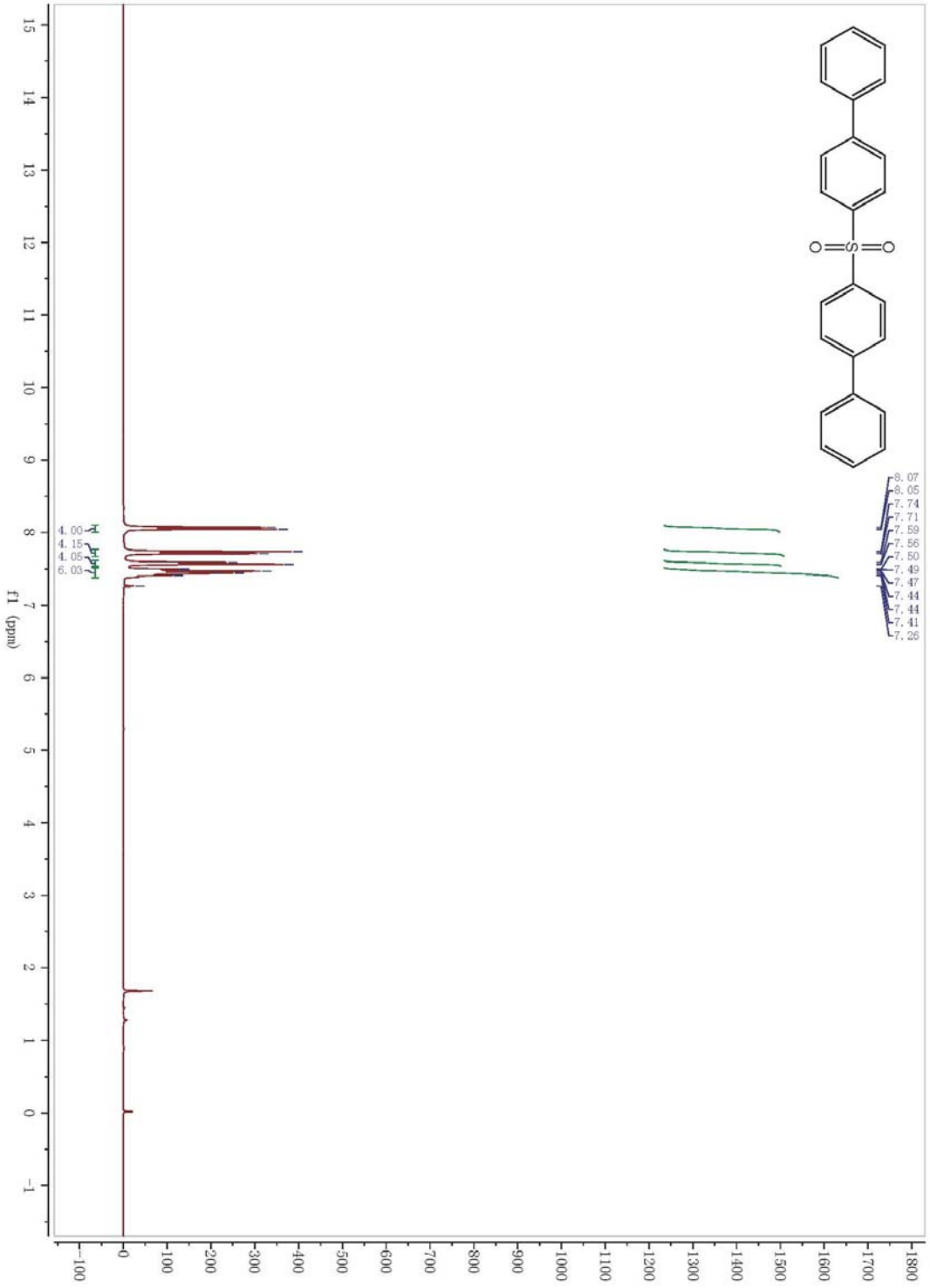
^{13}C NMR for the product of Table 3 entry 17



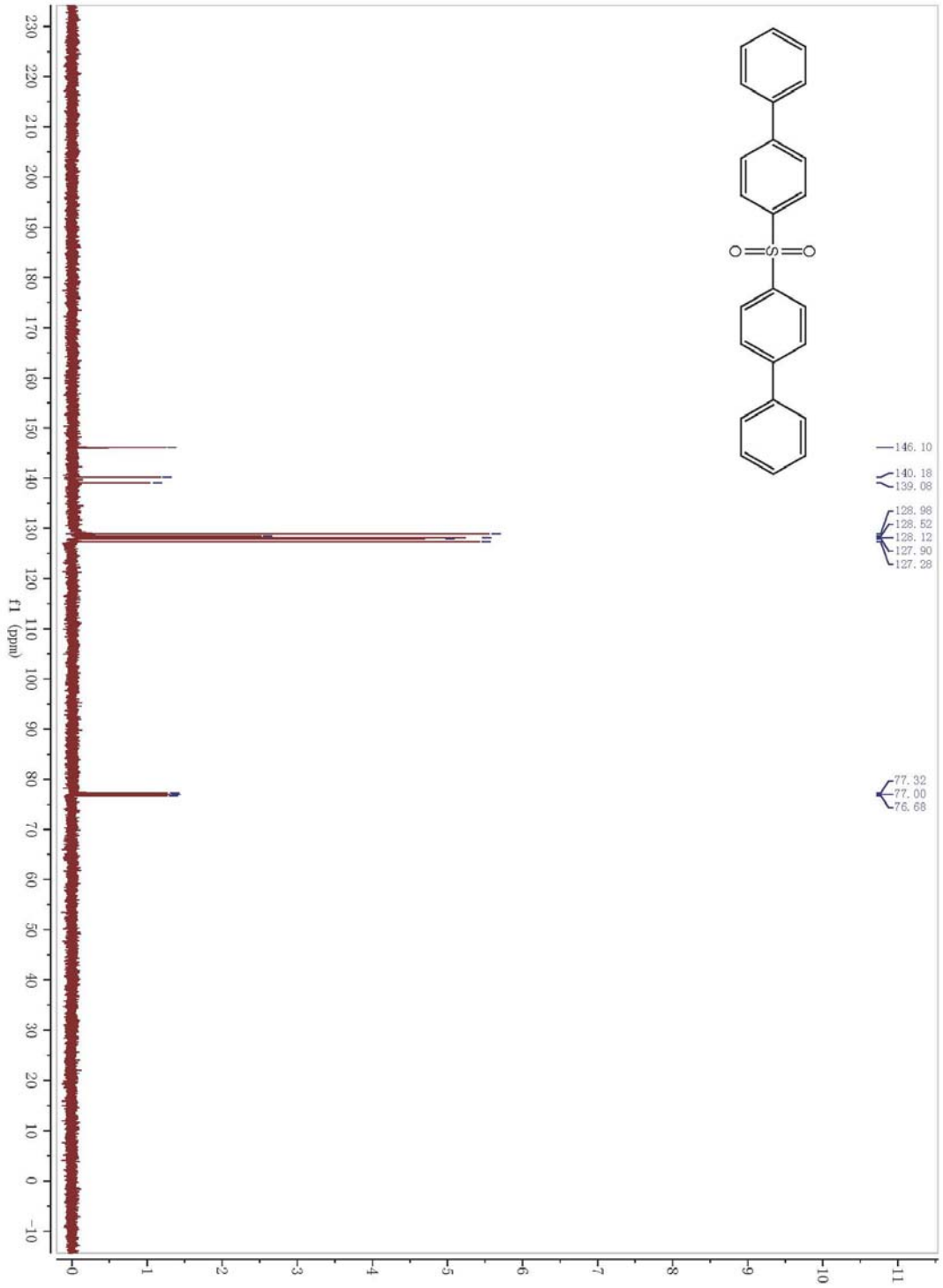
^{19}F NMR for the product of Table 3 entry 17



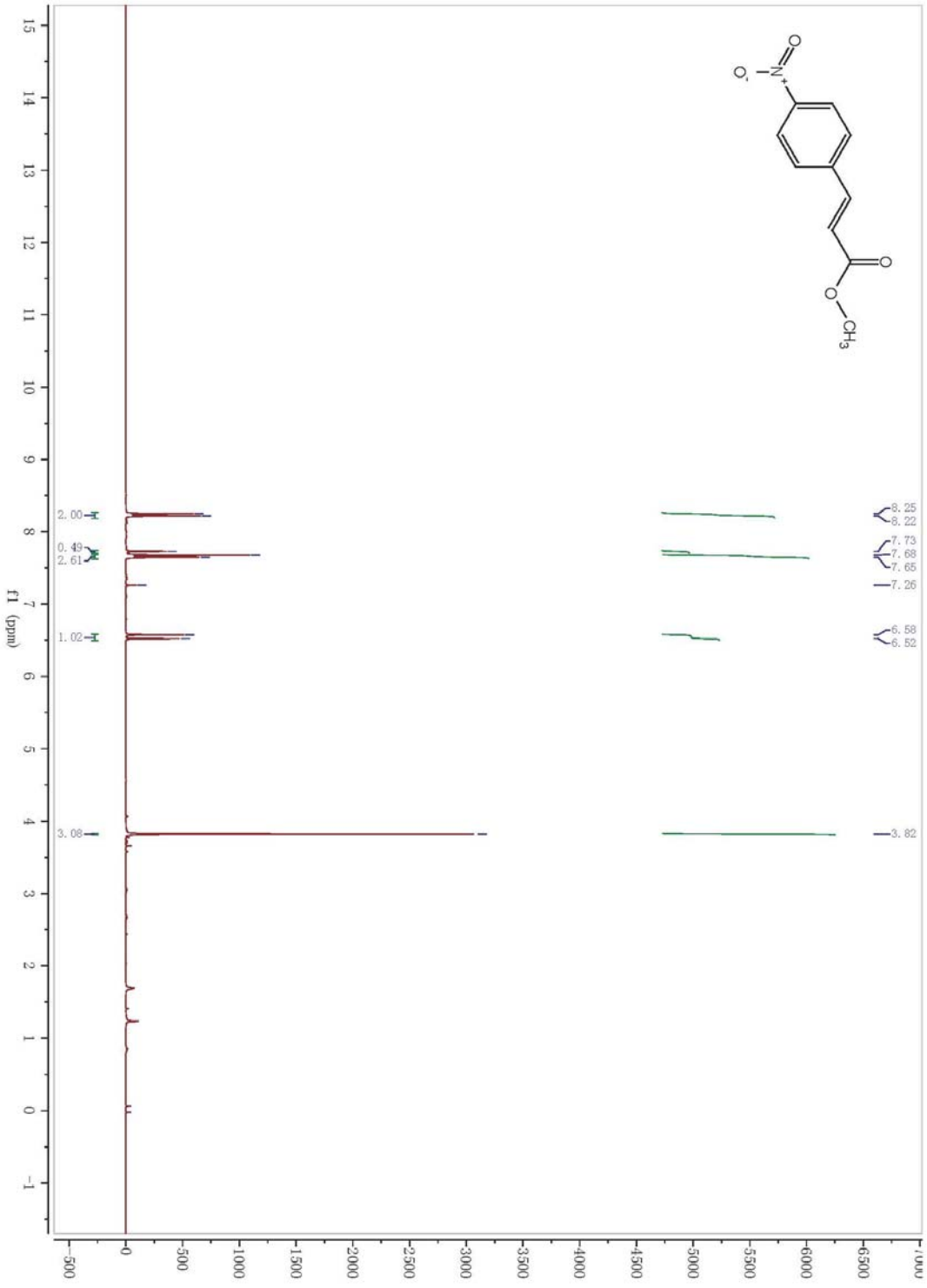
^{1}H NMR for the product of Table 3 entry 18



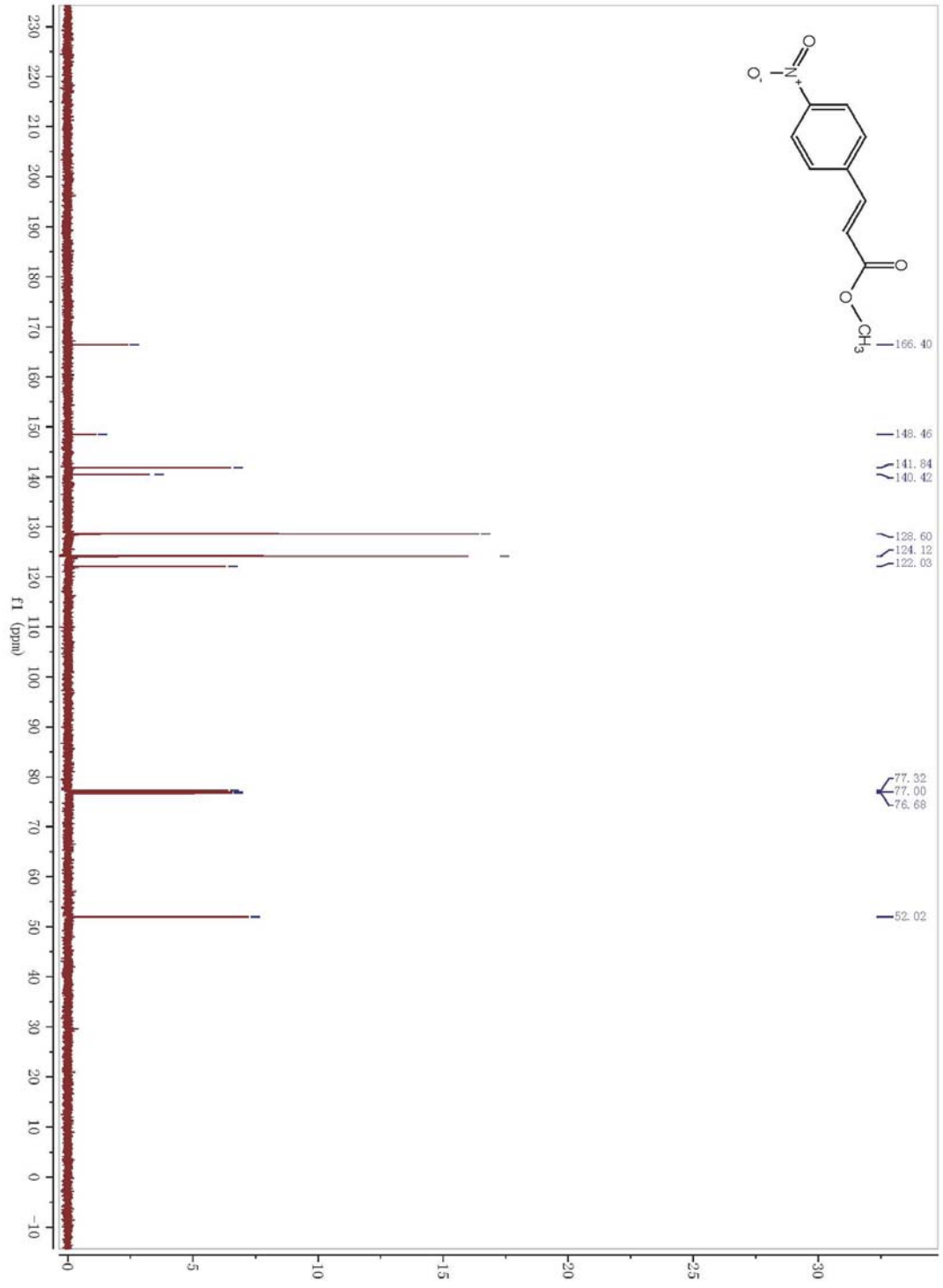
^{13}C NMR for the product of Table 3 entry 18



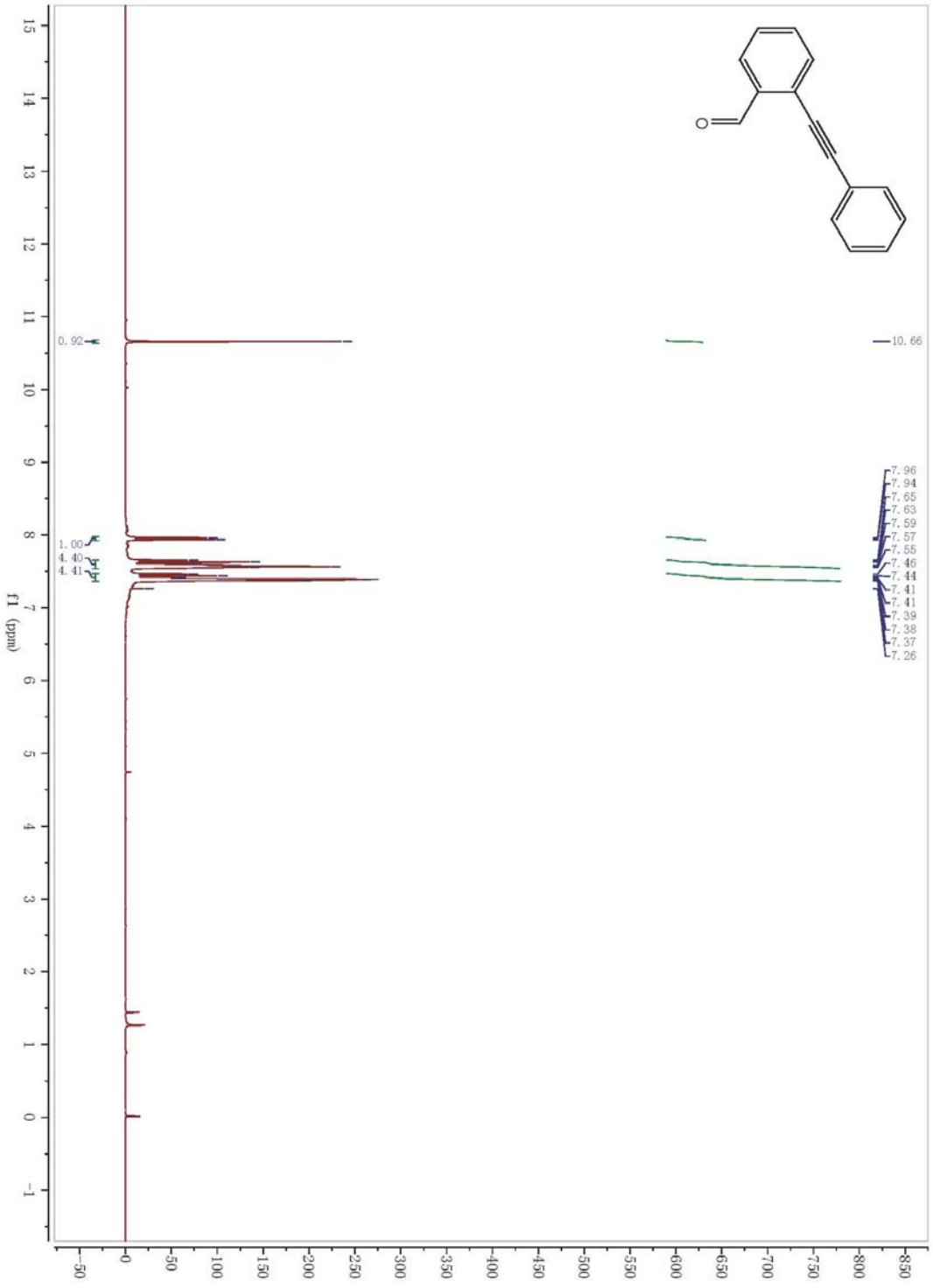
[1] H NMR for the product of Table 4 entry 1



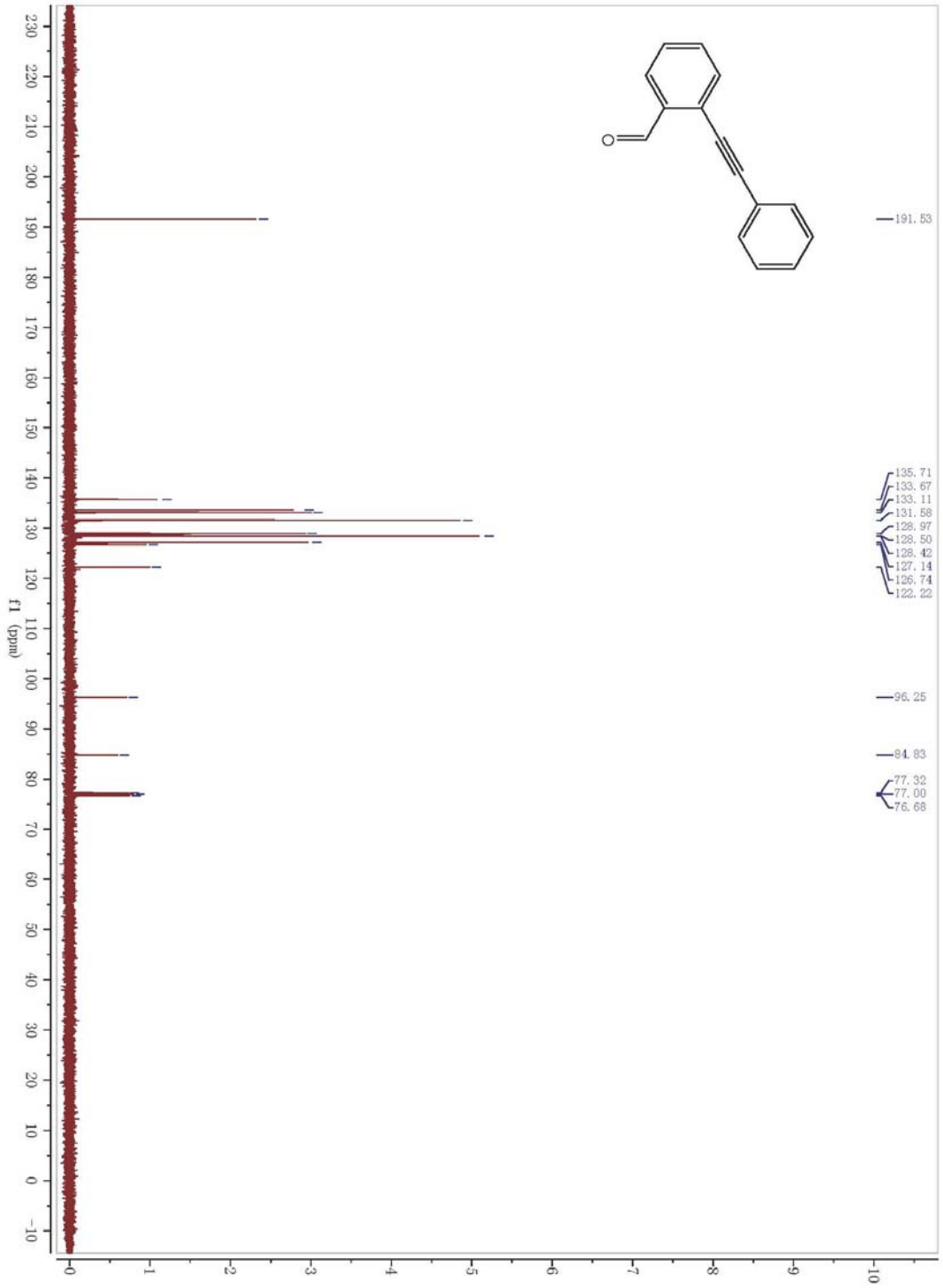
^{13}C NMR for the product of Table 4 entry1



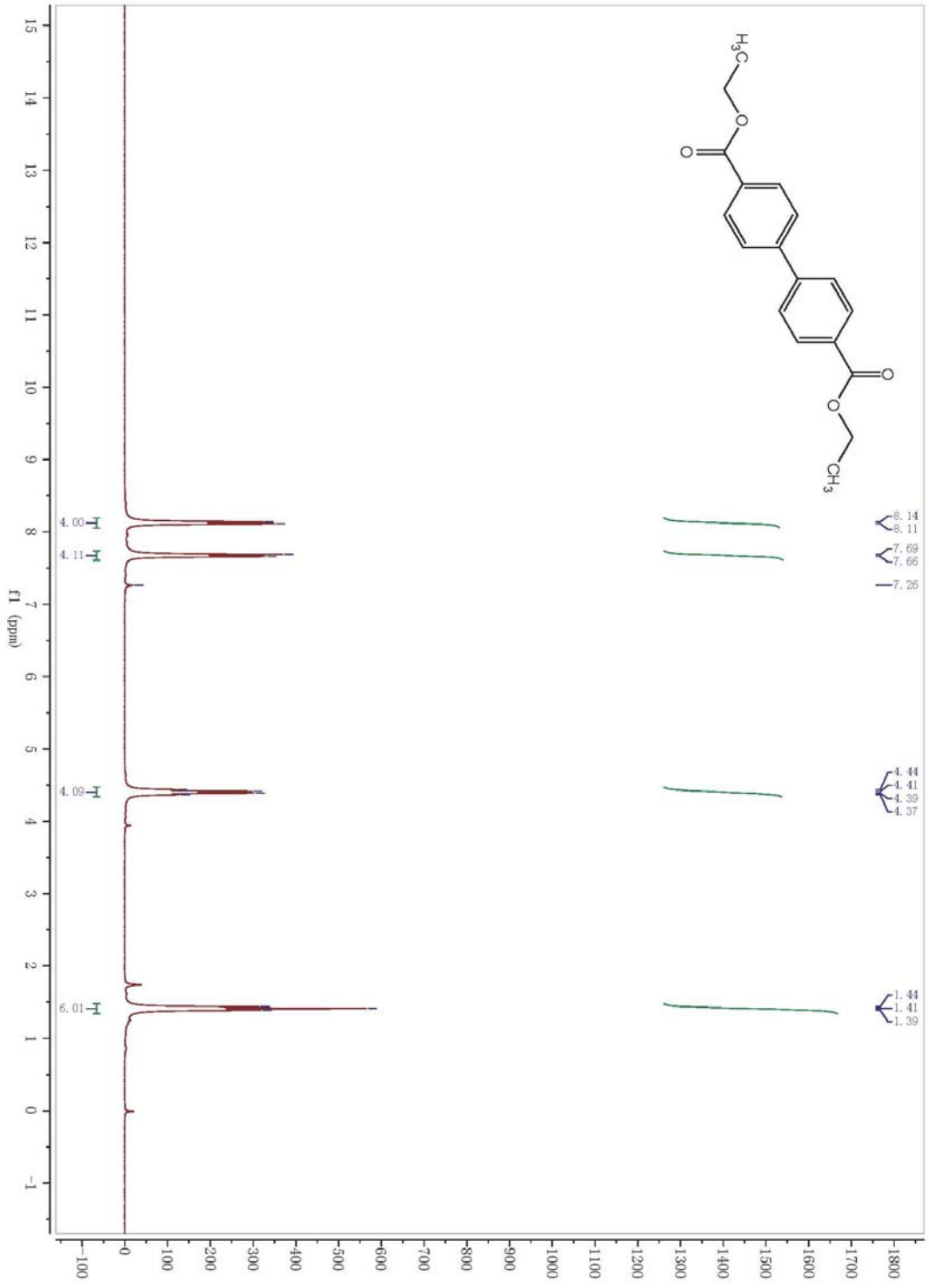
^{1}H NMR for the product of Table 4 entry 2



^{13}C NMR for the product of Table 4 entry 2



^{1}H NMR for the product of Table 4 entry 3



^{13}C NMR for the product of Table 4 entry 3