ESI for

Tungsten-doping promoted catalytic activity of polyaniline-supported palladium for suzuki-miyaura coupling reaction

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CONTENTS

1. Experimental details

General methods

Reagents and solvents were purchased from the reagent merchant and directly used after receiving without any special treatment. The reagents were analytical pure (AR). Melting-points of the products were determined by WRS-2A digital instrument. Fourier Transform infrared (FT-IR) spectra of the products were obtained by using an Antaris II spectrometer. NMR spectra were recorded on a Bruker Avance 400 instrument using $CDCl_3$ as the solvent and Me_4Si as the internal standard. Chemical shifts for ^1H NMR were referred to internal Me_4Si (0 ppm) and *J*-values were shown in Hz. XPS spectra were measured on the Thermo Fisher Scientific ESCALAB 250Xi X photoelectron spectrometer. Morphologies of the catalysts were analyzed by FE-SEM on Zeiss_Supra55 field emission scanning electron microscopy. ICP-MS analysis was performed on a PerkinElmer Optima 7300 DV inductively coupled plasma spectrometer.

Procedures for the preparation of Pd/W@PANI:

To a 250 mL beaker, 1.0 mL of aniline and 50 mL aqueous HCl (1 mol/L) were added. After stirring for 30 min, 25 mL of aqueous $PdCl_2$ (1 mg of $PdCl_2$ in 25 mL of 1 mol/L HCl) and 25 mL of aqueous Na_2WO_4 (25 mg of Na_2WO_4 in 25 mL of 1 mol/L HCl) were added into the beaker. 1 mL of H_2O_2 (30 w/w%) was then added and stirred to initiate the oxidative polymerization. The mixture was then stood at room temperature for 24 h, and neutrilized by 1 mol/L aqueous NaOH. The precipation was separated by centrifugation and washed by deionized water and EtOH for 3 times. After drying at 60 ^oC under vacuum for 24 h, the Pd/W@PANI material

was obtained.

General procedures for Pd/W@PANI-catalyzed Suzuki-Miyaura coupling reactions:

1 mmol of aryl boric acid **2**, 5 mg of Pd/W@PANI catalyst, 2 mmol of K_2CO_3 and a piece of magnetic bar were initially added into a 25 mL Schlenk tube, which was then charged with N_2. A solution of 1 mmol of aryl iodide **1** in 4 mL of EtOH was then injected into the reaction tube. The mixture was stirred at 100 ^oC for 48 h. The product was isolated by flash chromatography on silica using petroleum as eluent.

Details for the adsorption experiments of iodobenzene by Pd/W@PANI and Pd@PANI:

2.5 mmol of iodobenzene was dissolved in 250 mL of EtOAc in a volumetric flask to make a solution at 0.01 mol/L concentration. 20 mg of Pd/W@PANI was then added into this solution, which was shaken and then kept at room temperature. Six portions (5 mL for each time) of the solution were transferred into cuvettes at 0, 1, 3, 6, 12, 24 h (immersing time shown in Figure 2 in text) respectively to conduct the UV-vis analysis. The adsorption ratio of iodobenzene on catalyst was caltulated by the following equation:

Adsorption ratio = 100% - $(A_t/A_0) \times 100\%$,

where A_t = peak area of the λ_{max} (227 nm) at the immersion time (t); A_0 = peak area of the λ_{max} (227 nm) of the lodobenzene solution at 0.01 mol concentration.

Absorption of iodonbenze on Pd@PANI could be conducted similarly.

Characterization of the products

1,1′-Biphenyl (**3a**). 141.8 mg, yielding 92%; white solid, m. p. = 68.5–68.8 °C *(lit.* 68.5–70 °C); IR (KBr): 3047, 2982, 2873, 1947, 1874, 1693, 1646, 1484, 1427, 1373, 1345, 1304, 1173, 1144, 1113, 1087, 1073, 1020, 1006, 905, 726, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.65–7.63 (m, 4H), 7.48 (t, J = 7.5 Hz, 4H), 7.41–7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 141.2, 128.7, 127.3, 127.2; Known Compound.[1]

4-Methyl-1,1′-Biphenyl (**3b**). 151.3 mg, yielding 90%; white solid, m. p. = 45.0–46.4 °C (*lit*. 44–47 °C); IR (KBr): 3034, 2921,1904, 1586, 1475, 1273, 1071, 906, 754, 683, 470 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.61 (d, J = 6.7 Hz, 2H), 7.52 (d, J = 5.5 Hz, 2H), 7.44 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 6.7 Hz, 1H), 7.27 (d, J = 5.7 Hz, 2H), 2.42 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 141.1, 138.3, 137.0, 129.4, 128.7, 126.9, 21.1; Known Compound.[1]

4-Methoxy-1,1′-Biphenyl (**3c**). 130.7 mg, yielding 71%; white solid, m. p. = 85.2–86.1 °C (*lit*. 84.7–86.1 °C); IR (KBr): 2969, 1585, 1476, 1254, 1123,1037, 828, 753, 695, 564, 481 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.54 (t, J = 8.1 Hz, 4H), 7.42 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 6.8 Hz, 1H), 6.98 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 159.1, 140.8, 133.7, 128.7, 128.1, 126.7(d), 114.1, 55.3; Known Compound.[1]

4-Fluoro-1,1′-Biphenyl (**3d**). 149.7 mg, yielding 87%; white solid, m. p. = 71.5–72.6 °C (*lit*. 71.1–73.1 °C); IR (KBr): 3087, 1892, 1667, 1592, 1480, 1409, 1335, 1238, 833, 757, 689, 483 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.57–7.54 (m, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.14 (t, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 163.7, 161.2, 140.2, 137.3, 128.8, 128.6, 127.2, 127.0, 115.7, 115.5; Known Compound.[1]

4-Methyl-1,1′-Biphenyl (**3e**). 153.0 mg, yielding 91%; white solid, m. p. = 45.3–46.4 °C (*lit*. 44–47 °C); IR (KBr): 3035, 2922, 1904, 1585, 1471, 1274, 1071, 905, 753, 684, 472 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.58 (d, J = 6.4 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.34–7.30 (m, 1H), 7.25 (d, J = 6.8 Hz, 2H), 2.40 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 141.1, 138.3, 137.0, 129.4, 128.6, 126.9, 21.0; Known Compound.[1]

3-Methyl-1,1′-Biphenyl (**3f**). 131.1 mg, yielding 78%; colorless liquid; IR (film): 3031, 2917, 1605, 1483, 1077, 1024, 883, 791, 754, 697, 616, 576, 443 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.40 (t, J = 7.1 Hz, 2H), 7.34–7.30 (m, 3H), 7.25–7.22 (m, 4H), 2.26 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 142.0, 141.9, 135.3, 130.3, 129.8, 129.2, 128.1, 127.3, 126.8, 125.8, 20.5; Known Compound.[1]

4-Methoxy-1,1′-Biphenyl (**3g**). 156.5 mg, yielding 85%; white solid, m. p. = 85.1–86.1 °C (*lit*. 84.7–86.1 °C); IR (film): 2970, 1586, 1475, 1253, 1125, 1038, 829, 752, 694, 562, 483 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.64–7.59 (m, 4H), 7.48 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.04 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 159.1, 140.9, 133.7, 128.7, 128.1, 126.7, 126.6, 114.1, 55.3; Known Compound.[1]

4-Ethoxy-1,1′-Biphenyl (**3h**). 160.5 mg, yielding 81%; white solid, m. p. = 71.0–72.2 °C (*lit*. 72–73 °C); IR (film): 2978, 1605, 1487, 1116, 1052, 835, 762, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.56–7.51 (m, 4H), 7.41 (t, J = 7.7 Hz, 2H), 7.31–7.24 (m, 1H), 6.97 (d, J = 8.7 Hz, 2H), 4.07 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 158.5, 140.8, 133.5, 128.6, 128.1, 126.7, 126.5, 114.7, 63.4, 14.8; Known Compound.[1]

4-Fluoro-1,1′-Biphenyl (**3i**). 148.0 mg, yielding 86%; white solid, m. p. = 71.2–72.7 °C (*lit*. 71.1–73.1 °C); IR (film): 3086, 1893, 1665, 1593, 1482, 1407, 1336, 1235, 835, 756, 687, 482 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.53 (d, J = 7.8 Hz, 4H), 7.42 (t, J = 7.7 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.11 (t, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 163.7, 161.2, 140.2, 137.3, 128.8, 128.6, 127.2, 127.0, 115.7, 115.5; *Known Compound.*[1]

4-Nitro-1,1′-Biphenyl (**3j**). 119.4 mg, yielding 60%; colorless solid, m. p. = 113.5–114.5 °C (*lit*. 113–114 °C); IR (film): 3376, 3214, 3028, 2927, 1886, 1617, 1520, 1488, 1423, 1286, 1187, 1078, 913, 832, 765, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 8.29 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 6.9 Hz, 2H), 7.51–7.44 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 147.6, 138.7, 129.1, 128.9, 127.7, 127.3, 124.1; Known Compound.[1]

1-Phenylnaphthalene (**3k**). 126.5 mg, yielding 62%; green solid, m. p. = 45.7–46.8 °C (*lit*. 46–47 °C); IR (film): 3060, 2928, 1592, 1496, 1450, 1395, 1028, 967, 778, 705, 613, 562, 437 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 8.13–8.00 (m, 3H), 7.69–7.56 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 140.7, 140.2, 133.7, 131.6, 130.0, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.3; Known Compound.[1]

2-Phenylthiophene (**3l**). 94.4 mg, yielding 59%; colorless solid, m. p. = 40.7–41.1 °C (*lit*. 40.5–41.6 °C); IR (film): 3070, 1601, 1490, 1451, 1209, 1080, 954, 907, 847,756, 697, 457 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.62 (d, J = 8.2 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.32 – 7.25 (m, 3H), 7.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 144.4, 134.4, 128.8, 127.9, 127.4, 125.9, 124.7, 123.0; Known Compound.[1]

Reference

1. Z. Han and L. Yu, *Mater. Lett*., 2016, **84**, 312.

2. Analysis of the materials

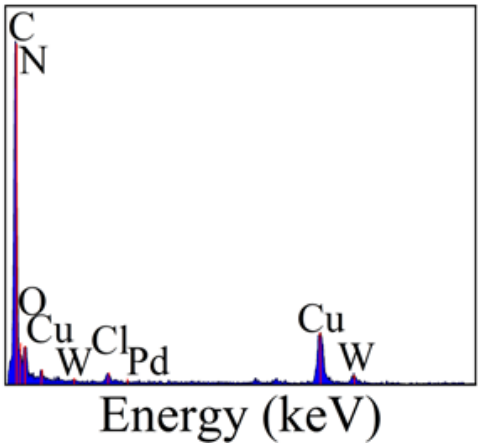

Figure S1. Characterization Pd/W@PANI: EDX spectral image.

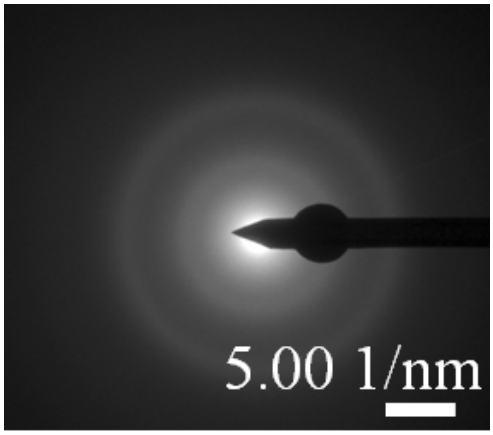

Figure S2. Characterization Pd/W@PANI: Electron diffraction pattern.

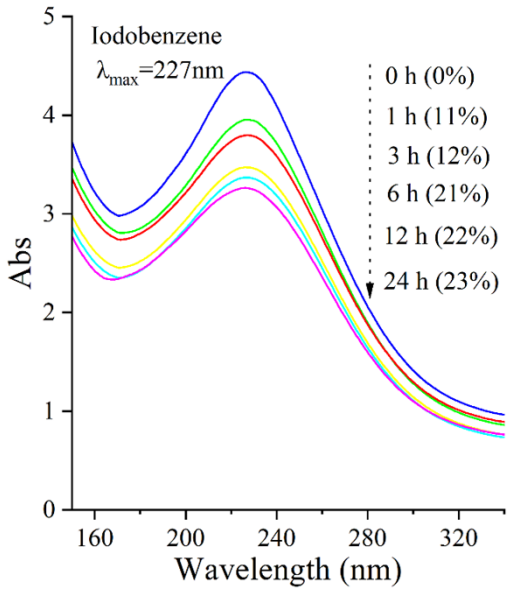

Figure S3. Absorption of iodobenzene onto W/PANI

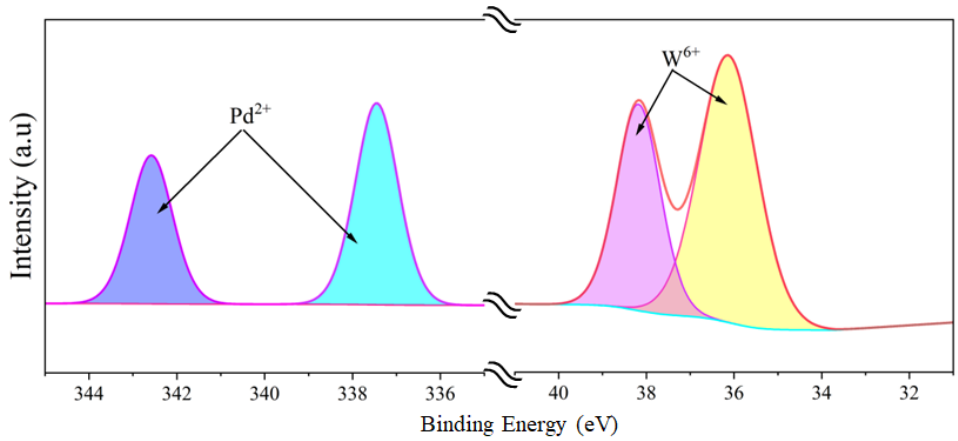

Figure S4. XPS spectrum of Pd/W@PANI before reaction

Table S1. Data of the used Pd/W@PANI XPS data analysis

Name	Peak BE	Area (P) CPS.eV	Atomic %
Pd $3d_{3/2}$	343.1	518.17	42.72
Pd $3d_{5/2}$	342.1	217.72	17.95
Pd $3d_{3/2}$	338.0	207.17	17.08
Pd $3d_{5/2}$	335.7	269.88	22.25

Table S2. Data of the used Pd @PANI XPS data analysis

Name	Peak BE	Area (P) CPS.eV	Atomic %
Pd $3d_{3/2}$	342.5	732.29	49.87
Pd $3d_{5/2}$	340.3	332.15	22.62
Pd $3d_{3/2}$	337.6	307.33	20.93
Pd $3d_{5/2}$	334.5	96.62	6.58

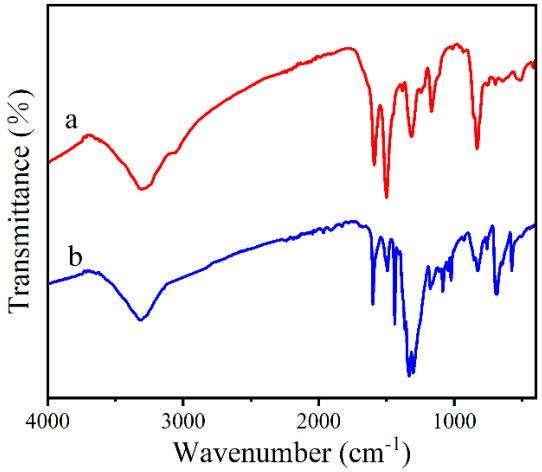

Figure S5. FT-IR spectra of W/PANI before (a) and after (b) treatment: 1 mmol $PhB(OH)_2$ and 50 mg W/PANI were heated in 4 mL of EtOH at 100 °C for 48 h.

3. NMR of compound 3

3a , ^{1}H NMR, $CDCl_3$, 400 MHz

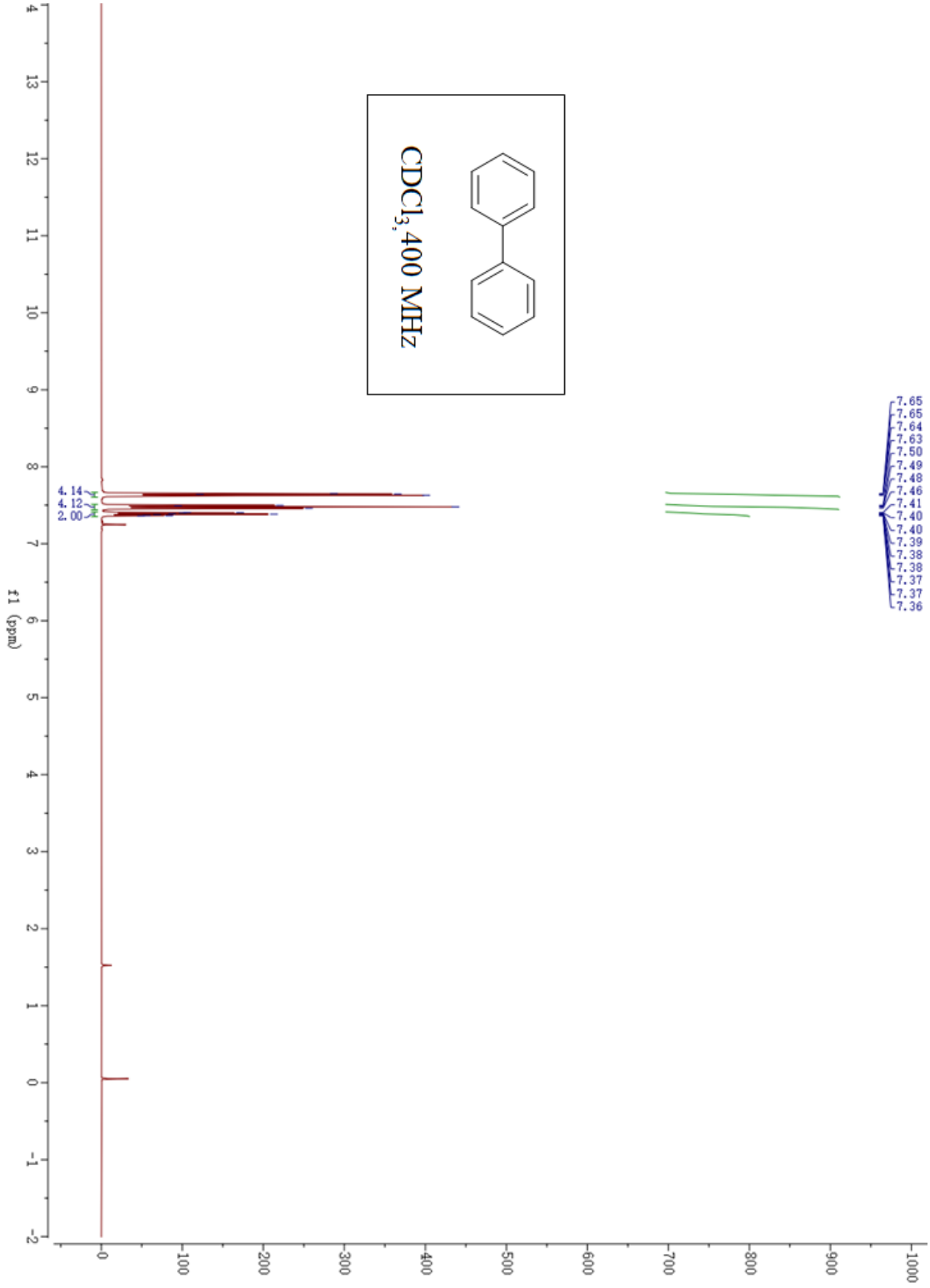

Figure S5. ^{1}H NMR spectrum of **3a**

3a, ^{13}C NMR, $CDCl_3$, 100 MHz

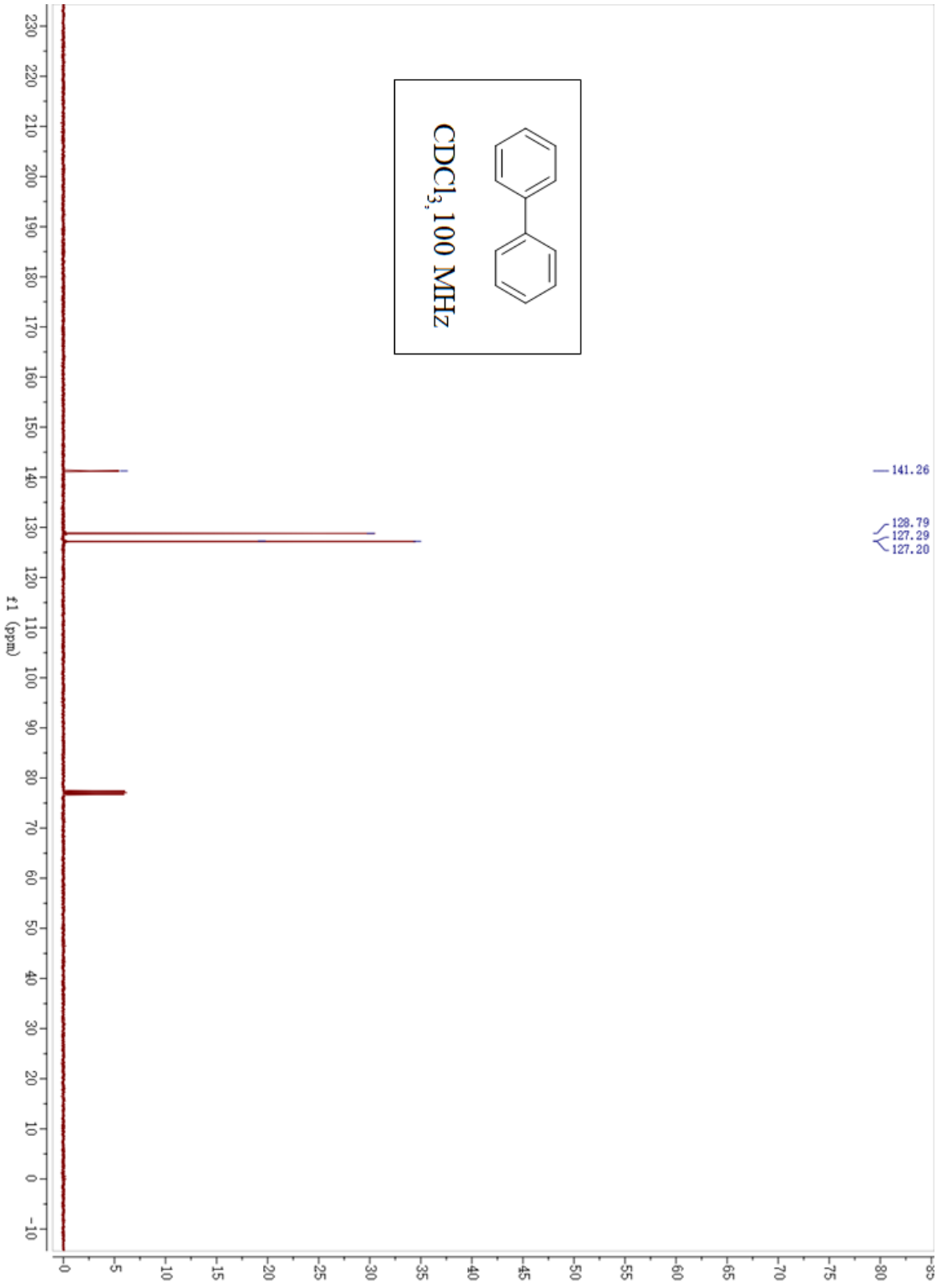

Figure S6. ^{13}C NMR spectrum of **3a**

3b , ^{1}H NMR, $CDCl_3$, 400 MHz

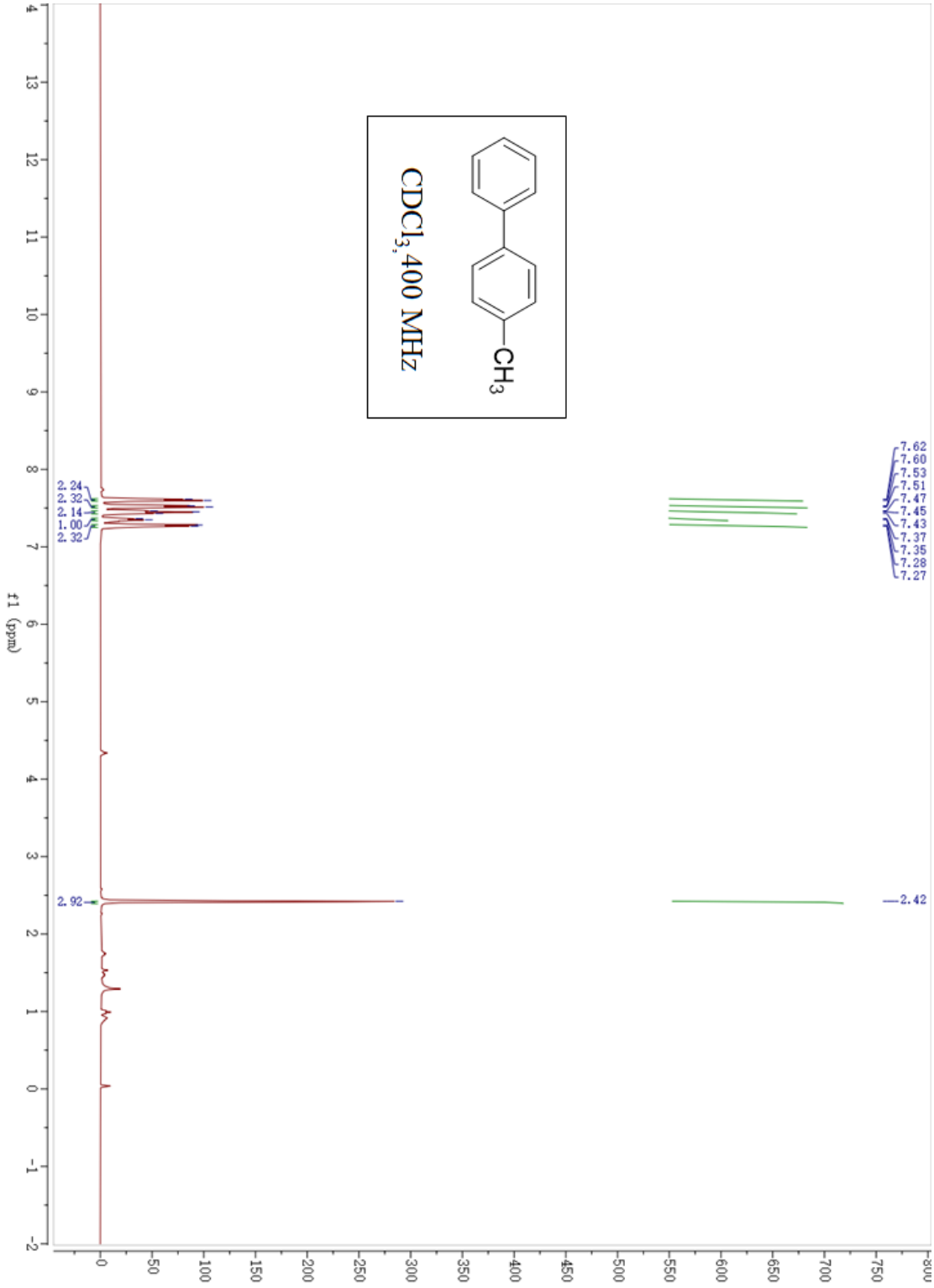

Figure S7. ^{1}H NMR spectrum of **3b**

3b, ^{13}C NMR, $CDCl_3$, 100 MHz

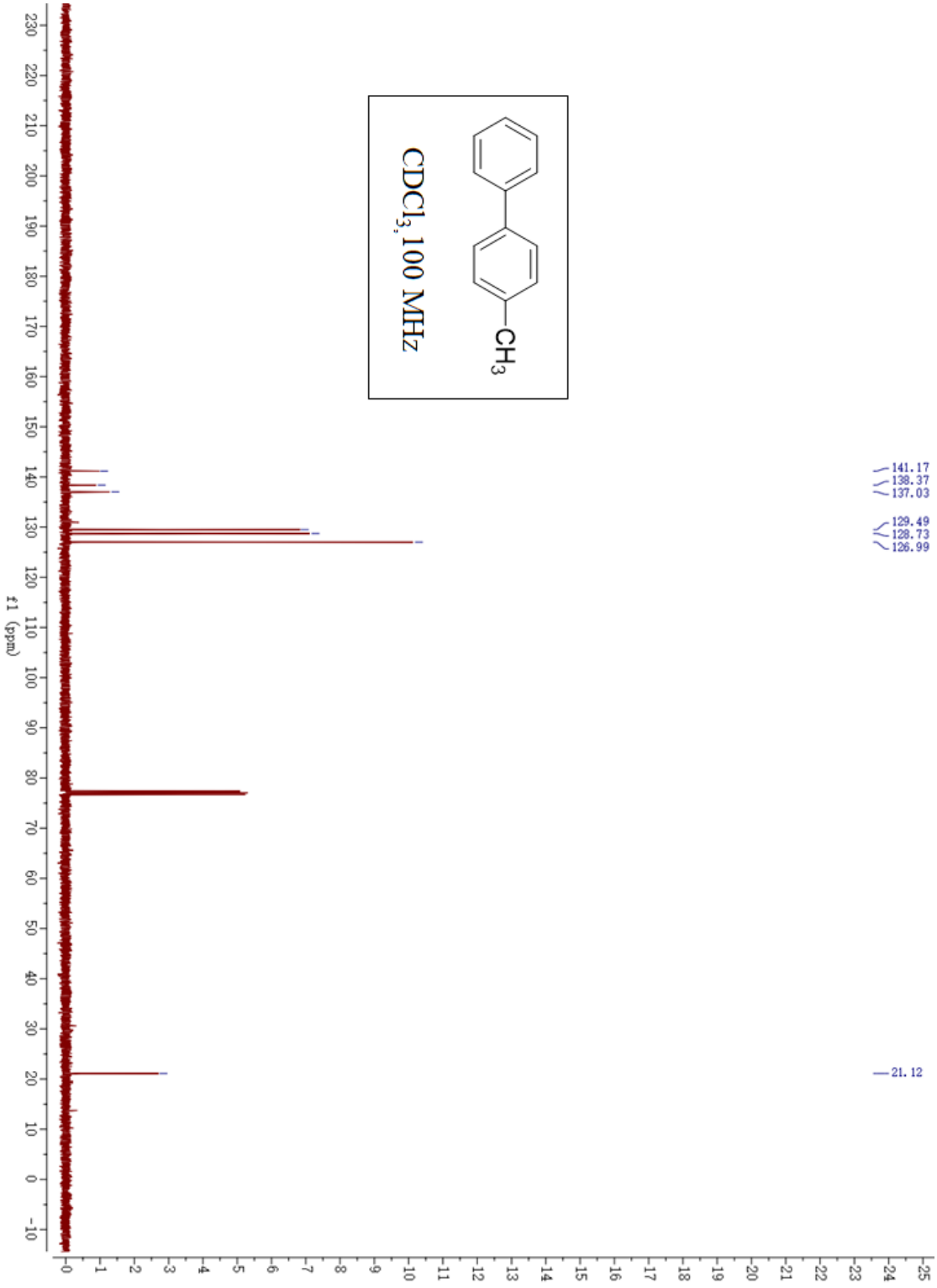

Figure S8. ^{13}C NMR spectrum of **3b**

3c , ^{1}H NMR, $CDCl_3$, 400 MHz

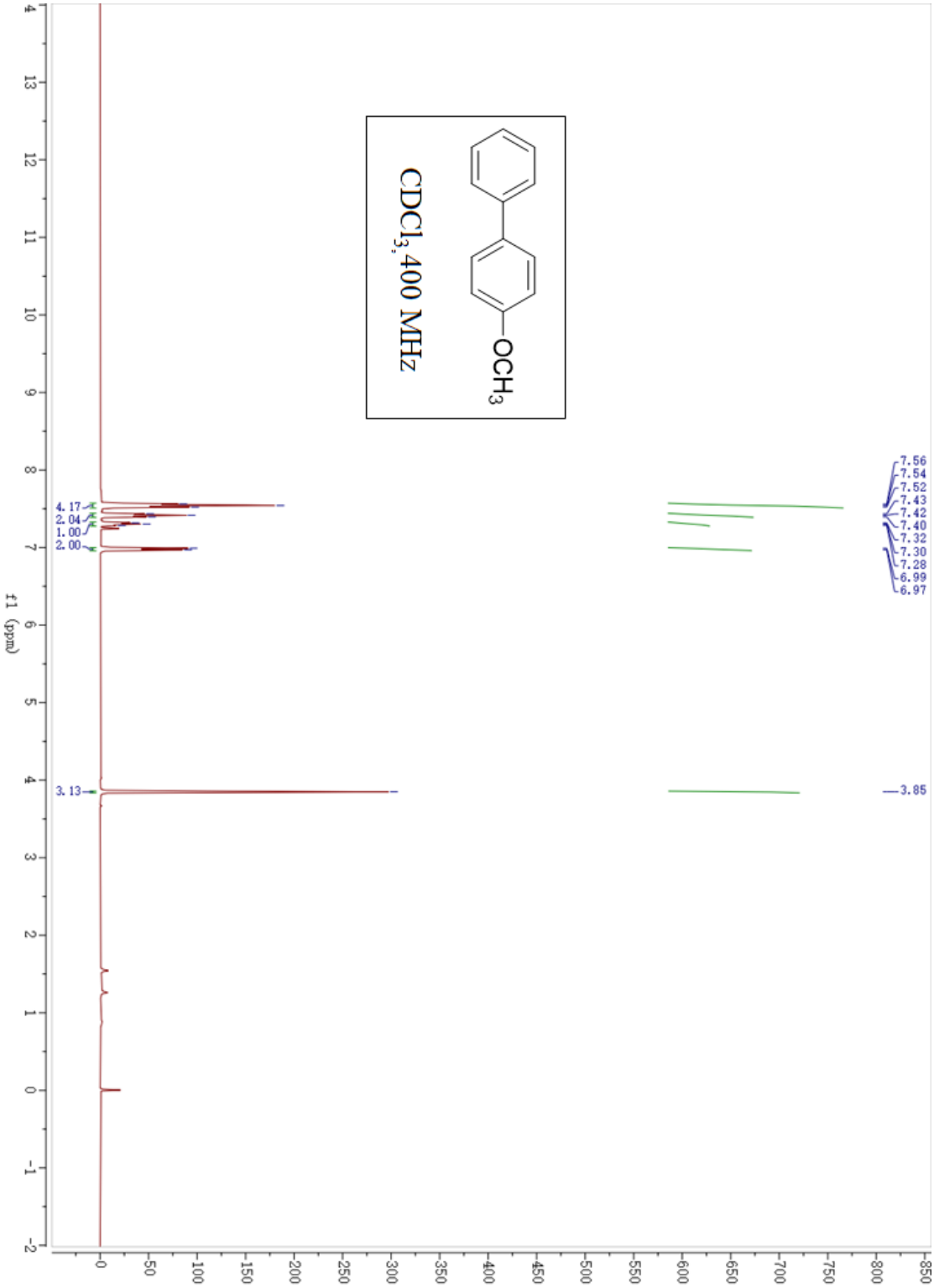

Figure S9. ^{1}H NMR spectrum of **3c**

3c, ^{13}C NMR, $CDCl_3$, 100 MHz

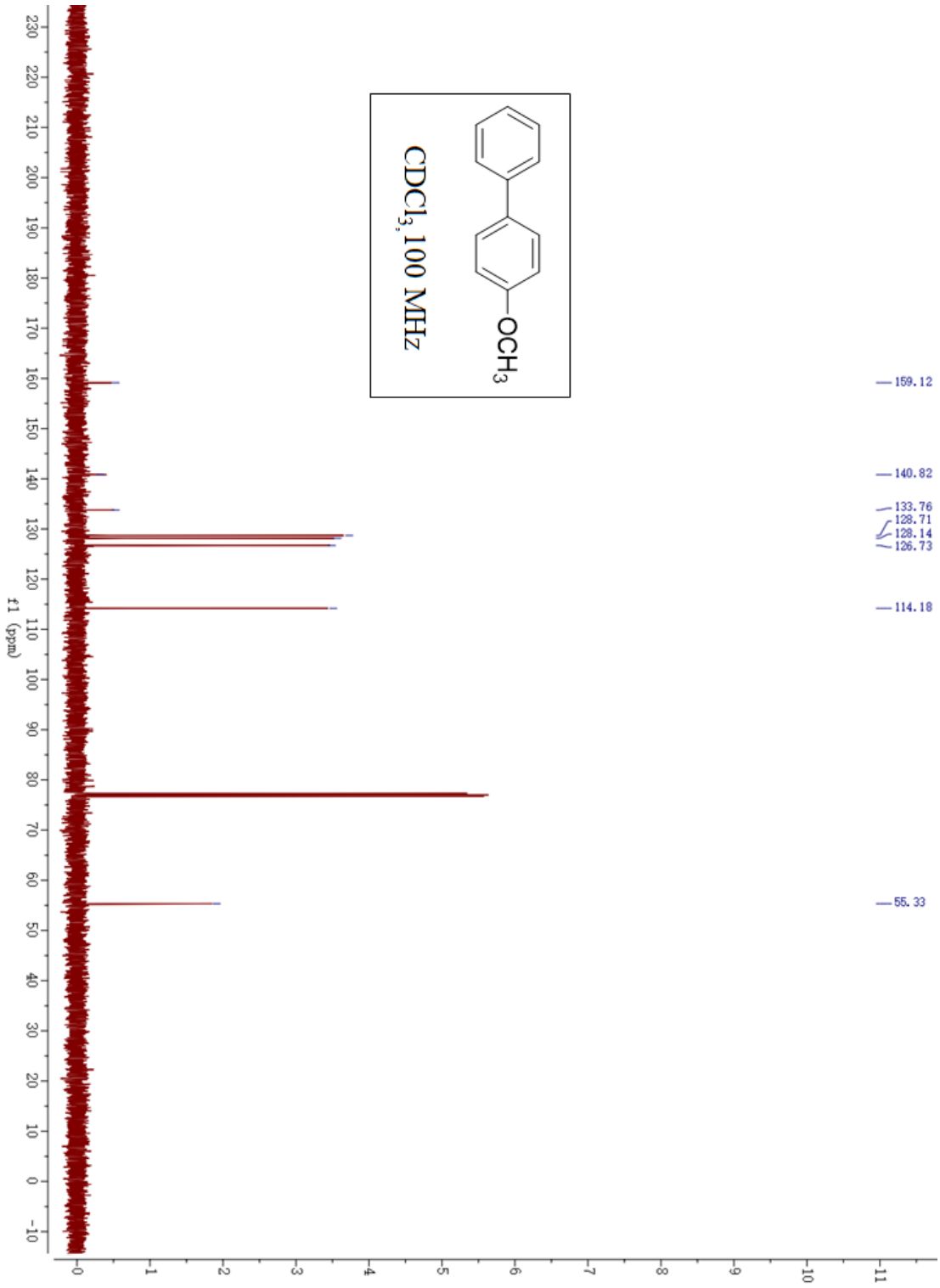

Figure S10. ^{13}C NMR spectrum of **3c**

3d , ^{1}H NMR, $CDCl_3$, 400 MHz

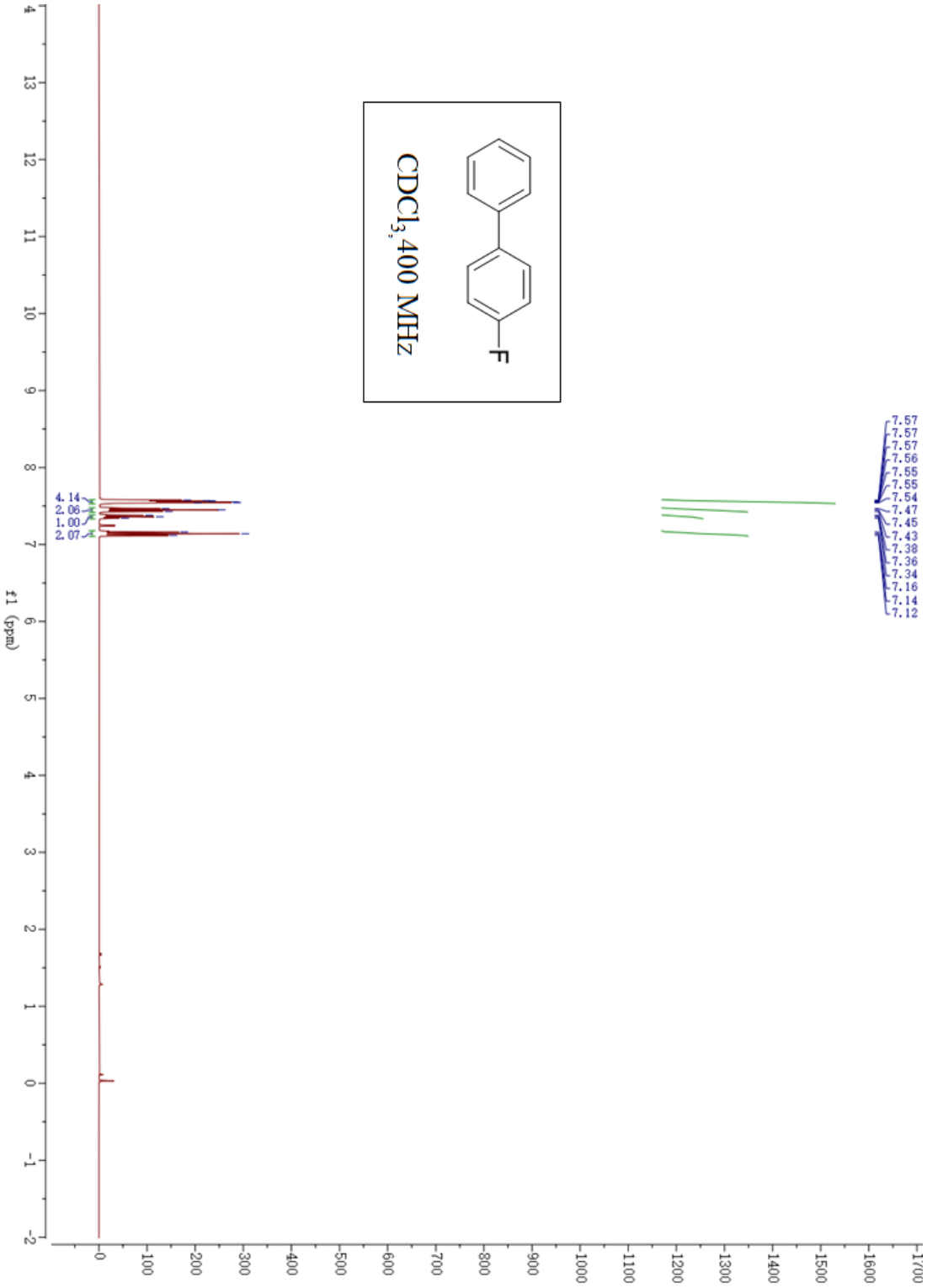

Figure S11. ^{1}H NMR spectrum of **3d**

3d, ^{13}C NMR, $CDCl_3$, 100 MHz

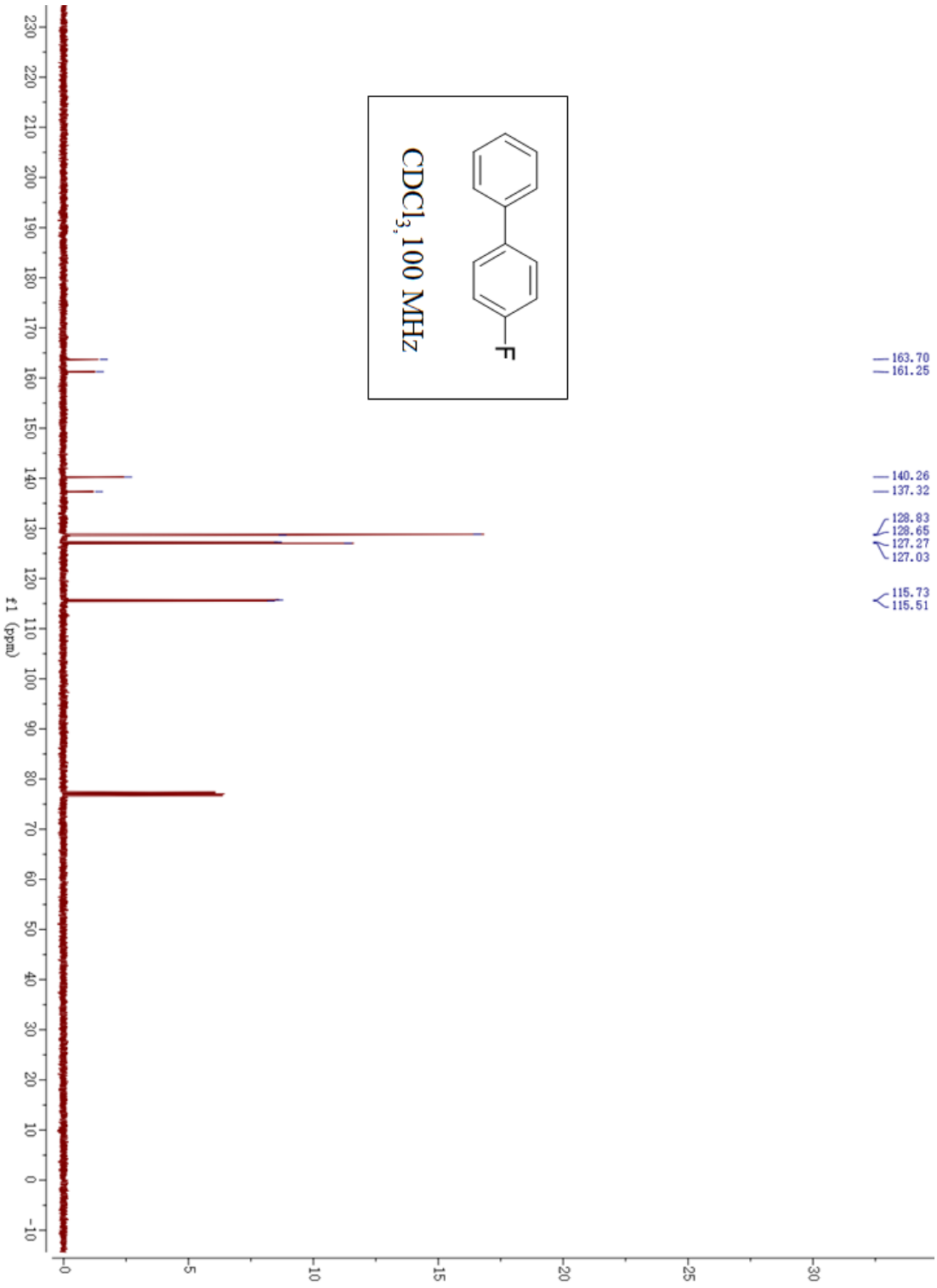

Figure S12. ^{13}C NMR spectrum of **3d**

3e , ^{1}H NMR, $CDCl_3$, 400 MHz

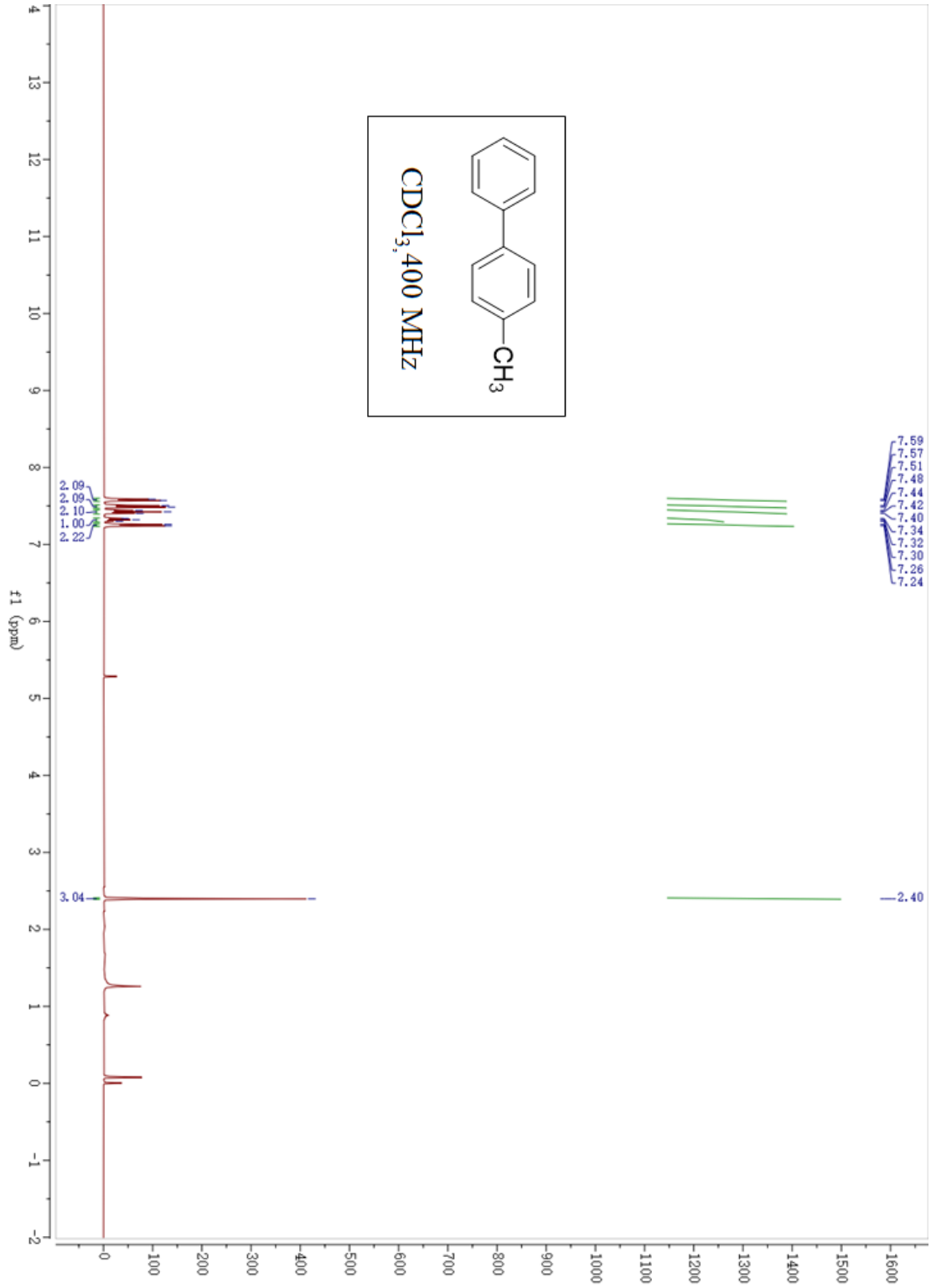

Figure S13. ^{1}H NMR spectrum of **3e**

3e, ^{13}C NMR, $CDCl_3$, 100 MHz

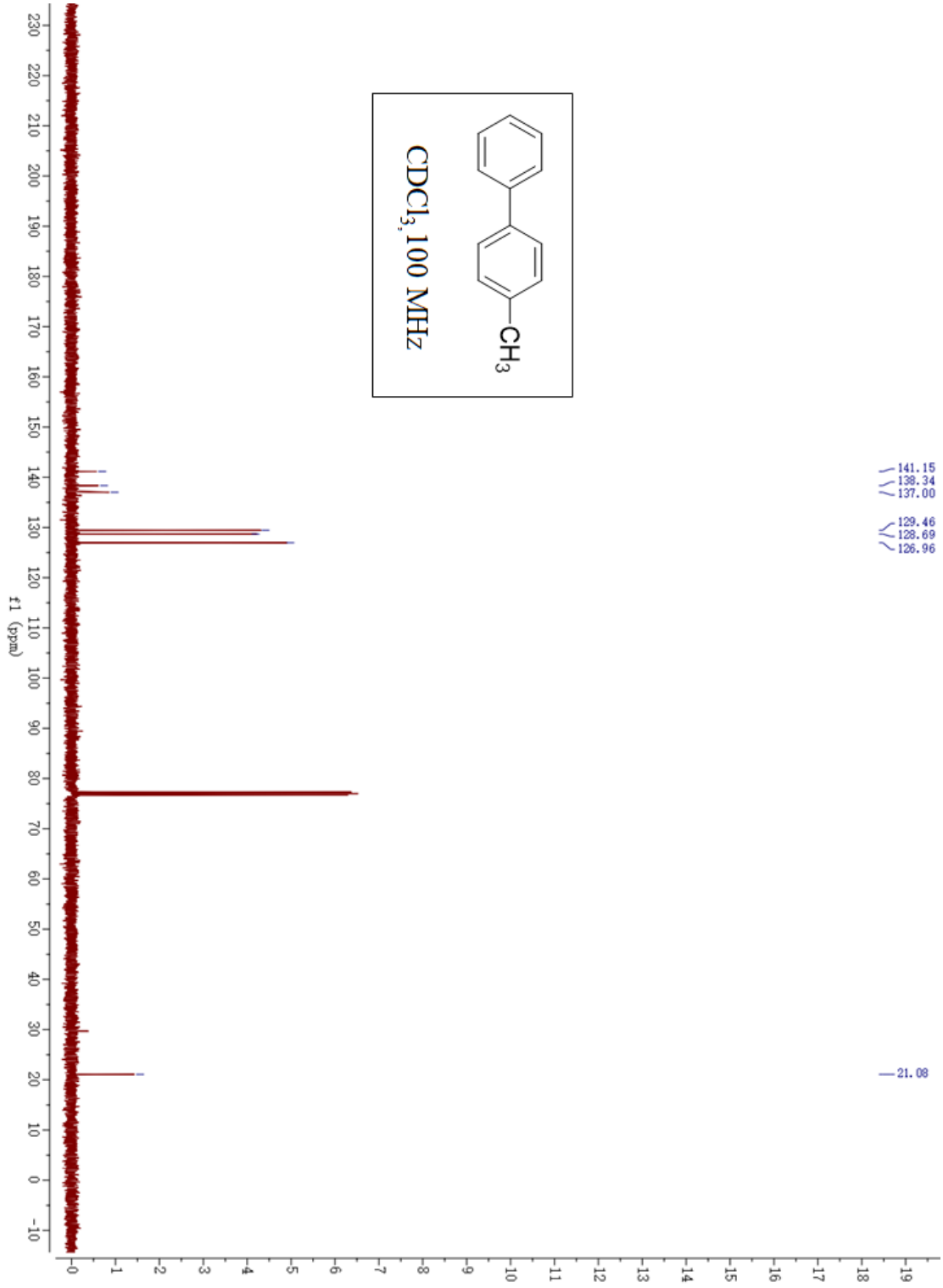

Figure S14. ^{13}C NMR spectrum of **3e**

3f, ^{1}H NMR, $CDCl_3$, 400 MHz

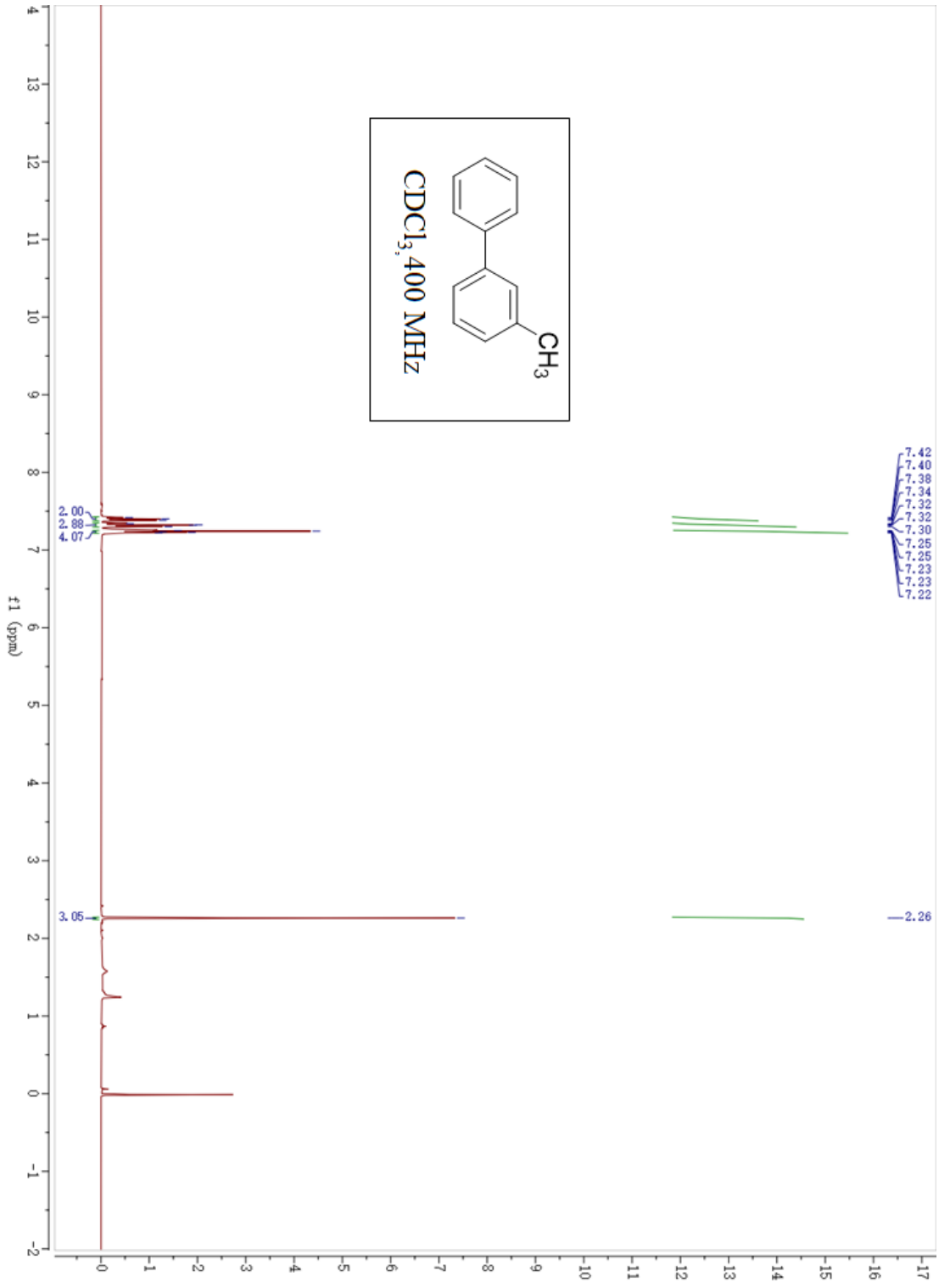

Figure S15. ^{1}H NMR spectrum of **3f**

3f, ^{13}C NMR, $CDCl_3$, 100 MHz

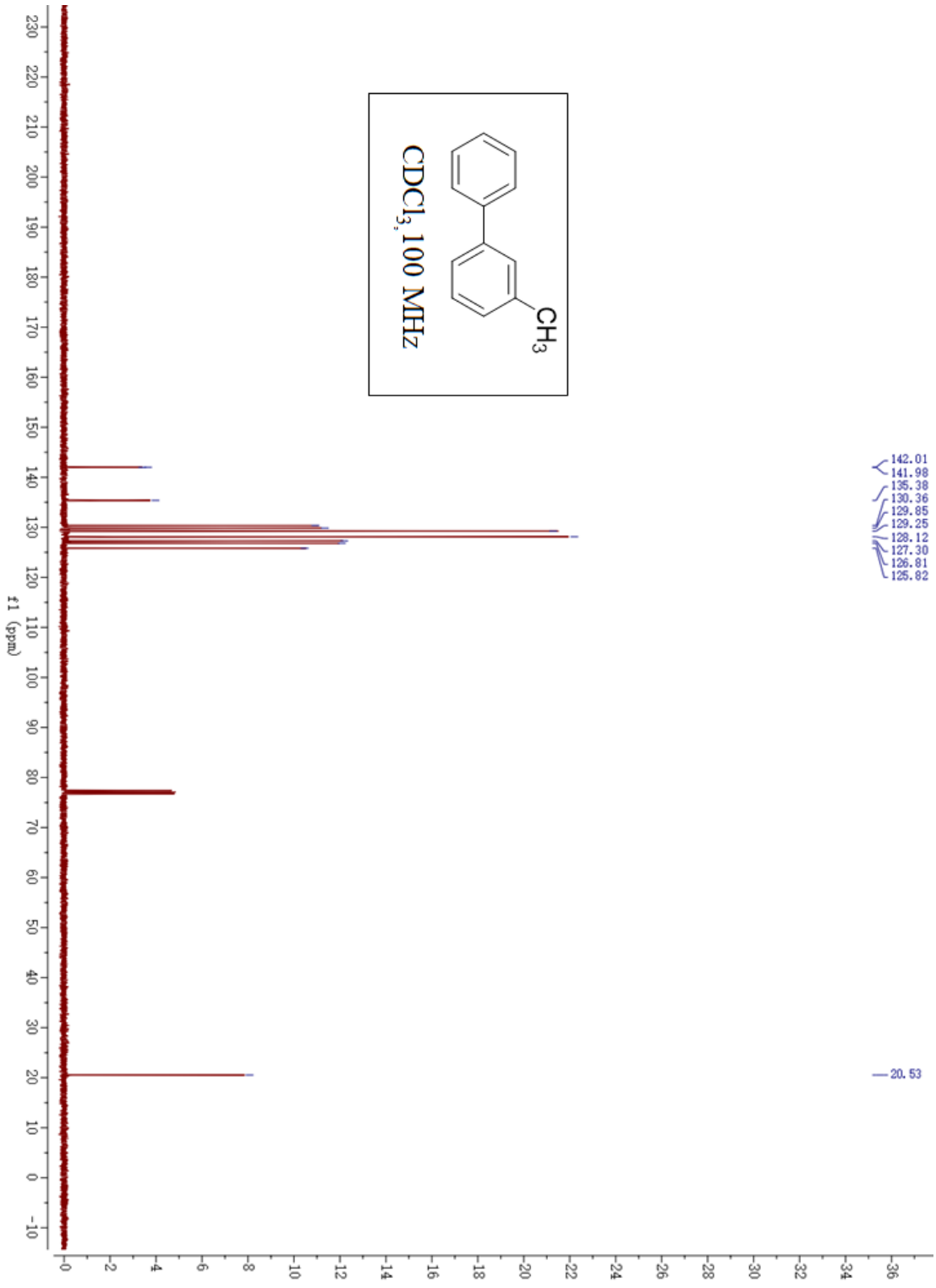

Figure S16. ^{13}C NMR spectrum of **3f**

3g , ^{1}H NMR, $CDCl_3$, 400 MHz

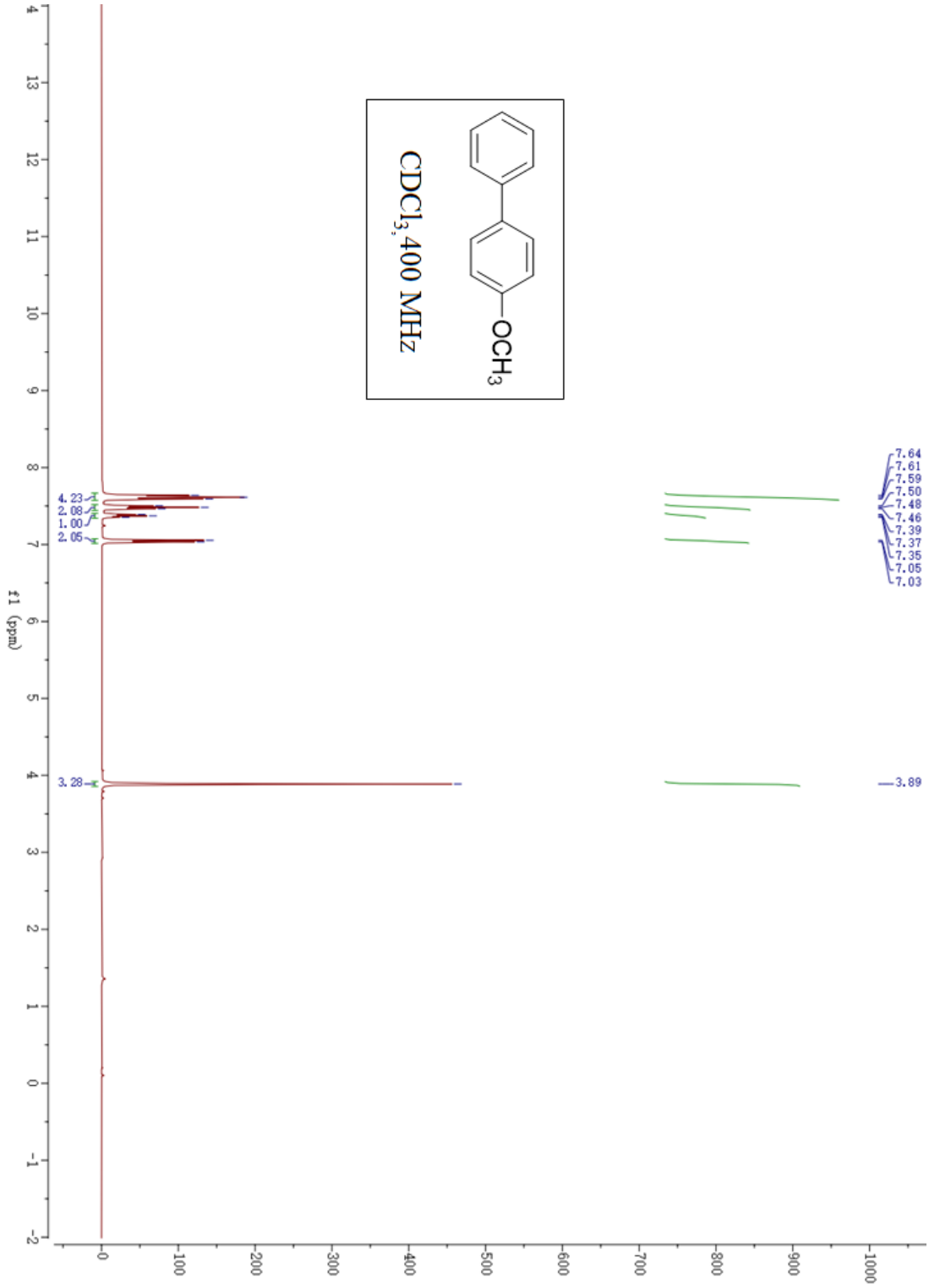

Figure S17. ^{1}H NMR spectrum of **3g**

3g, ^{13}C NMR, $CDCl_3$, 100 MHz

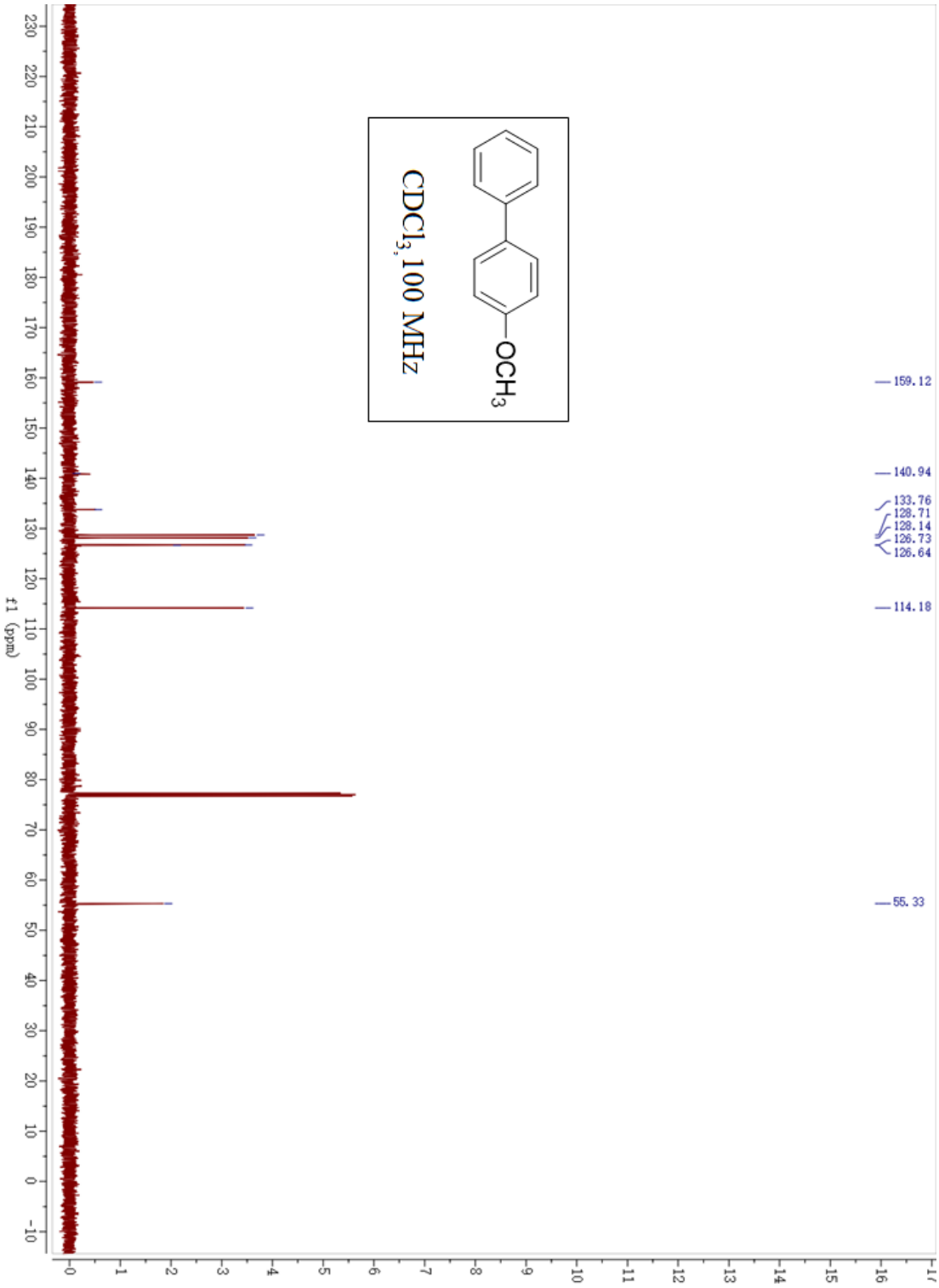

Figure S18. ^{13}C NMR spectrum of **3g**

3h , ^{1}H NMR, $CDCl_3$, 400 MHz

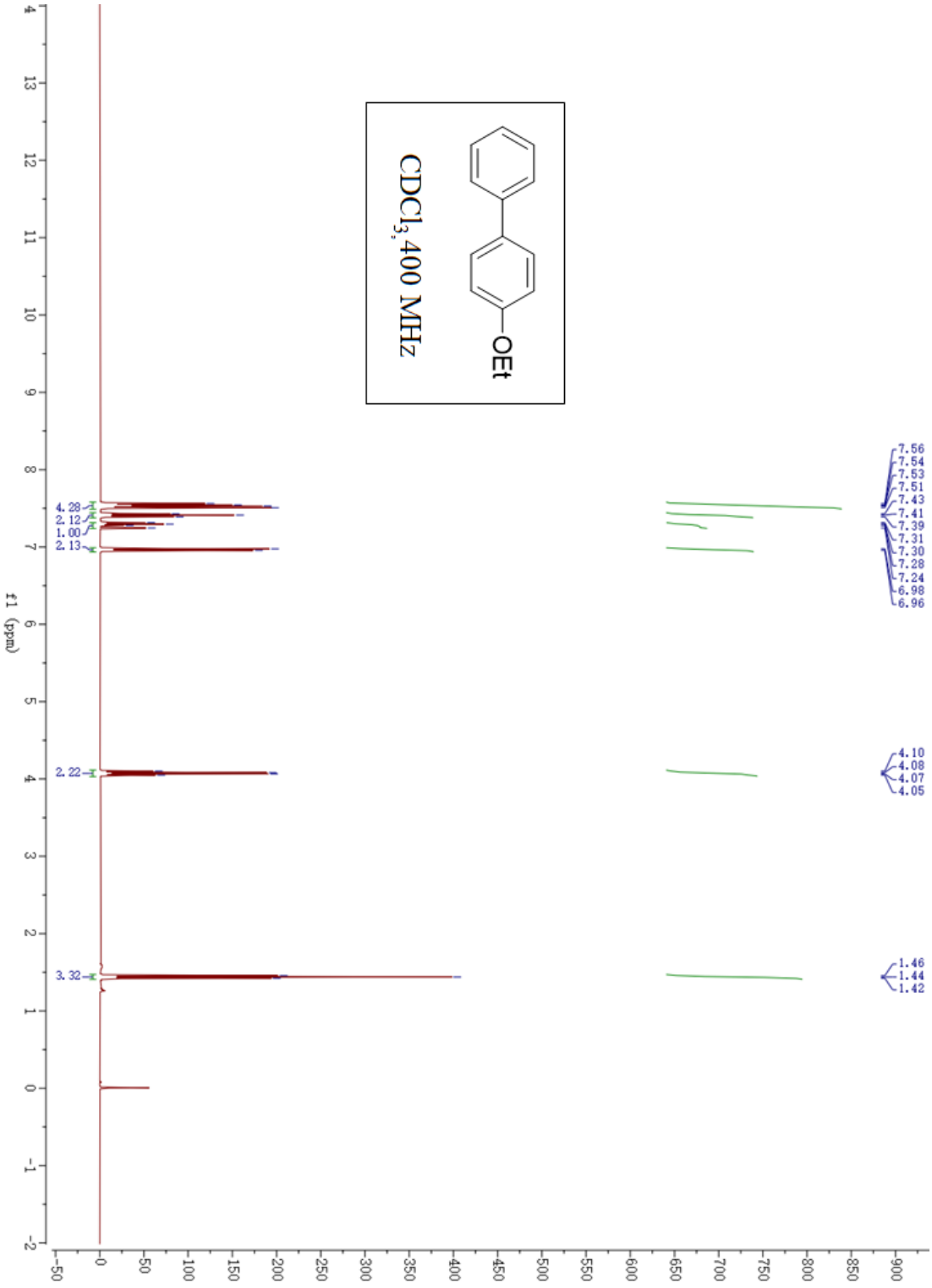

Figure S19. ^{1}H NMR spectrum of **3h**

3h, ^{13}C NMR, $CDCl_3$, 100 MHz

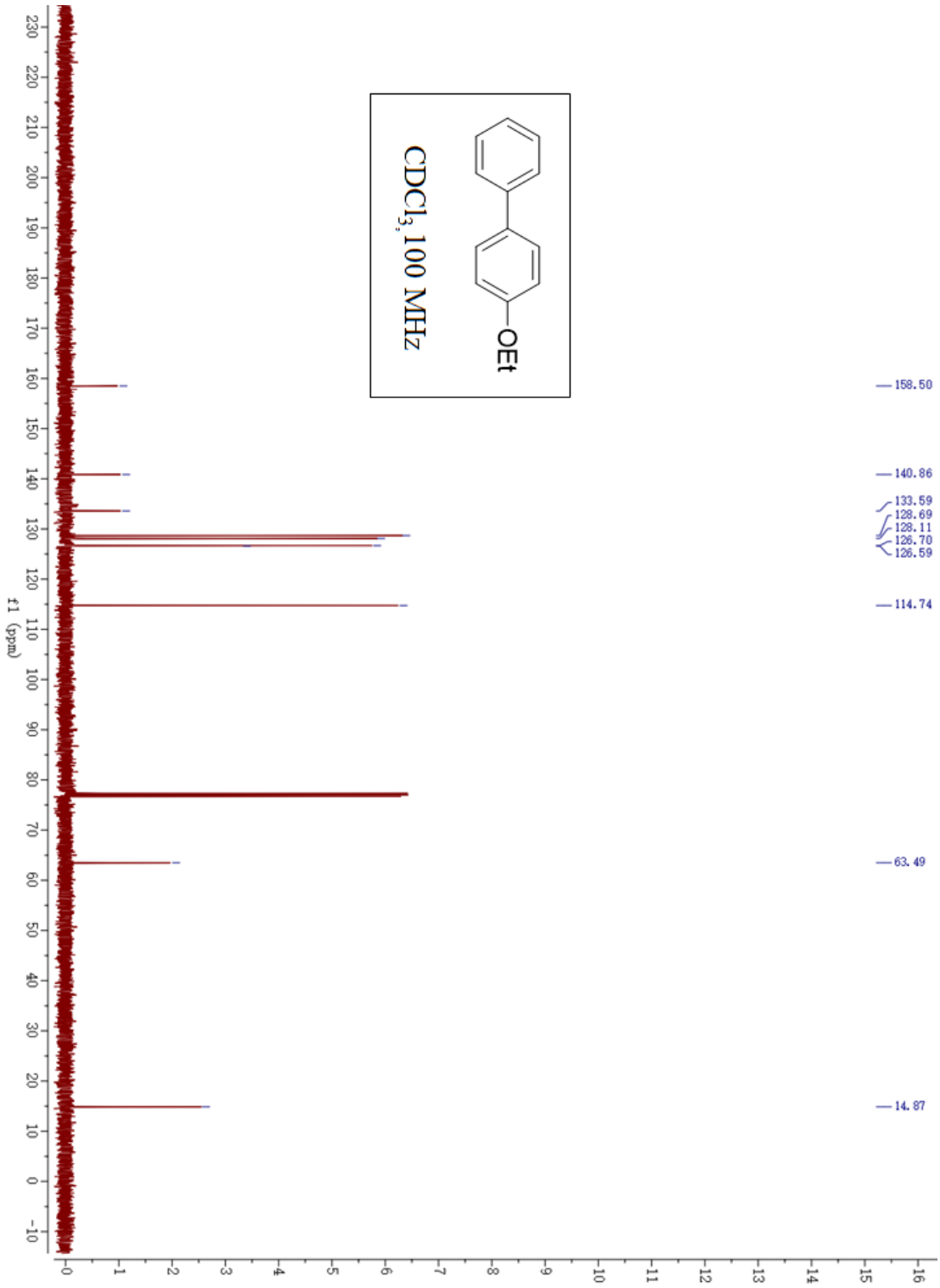

Figure S20. ^{13}C NMR spectrum of **3h**

3i , ^{1}H NMR, $CDCl_3$, 400 MHz

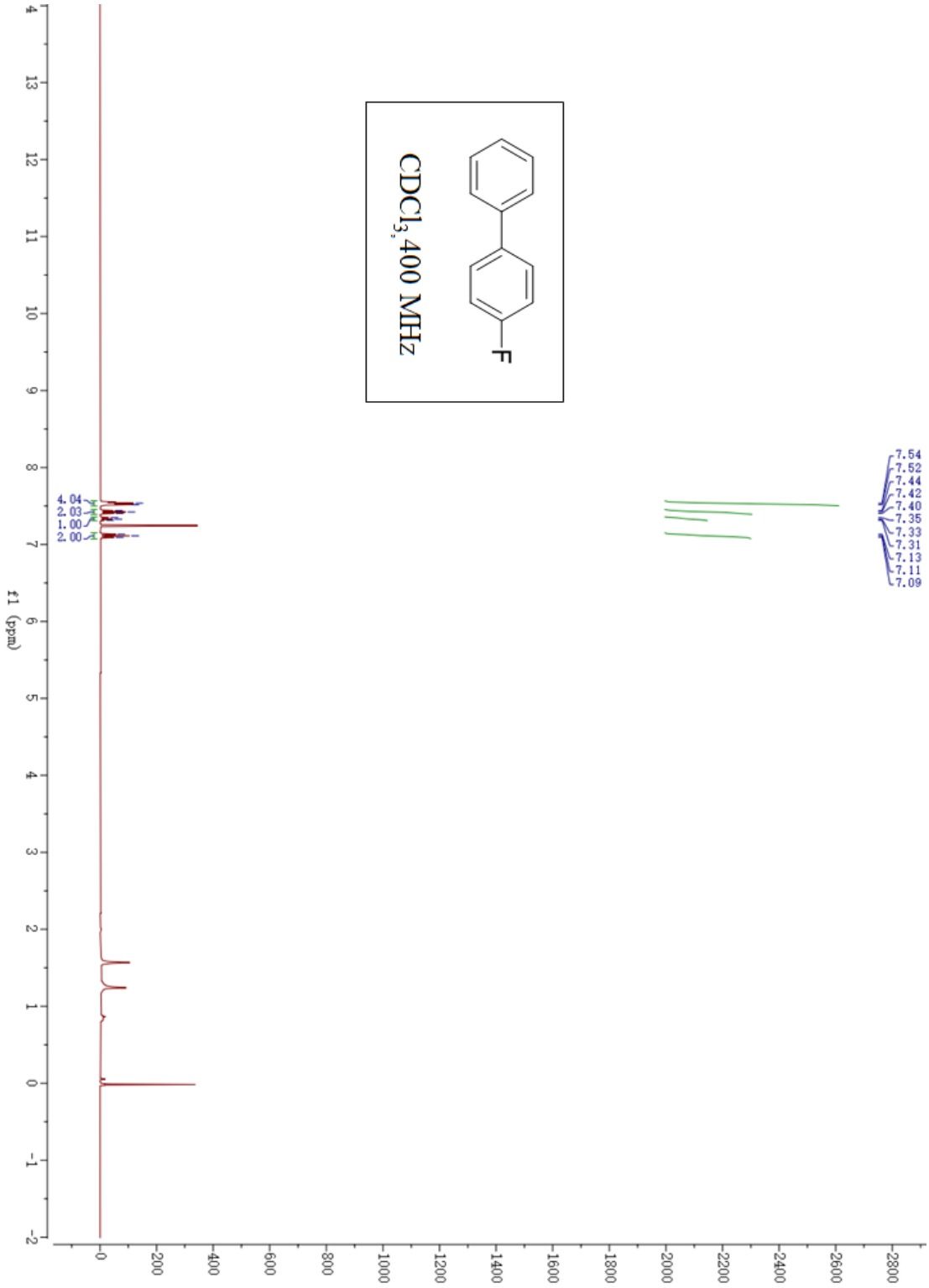

Figure S21. ^{1}H NMR spectrum of **3i**

3i, ^{13}C NMR, $CDCl_3$, 100 MHz

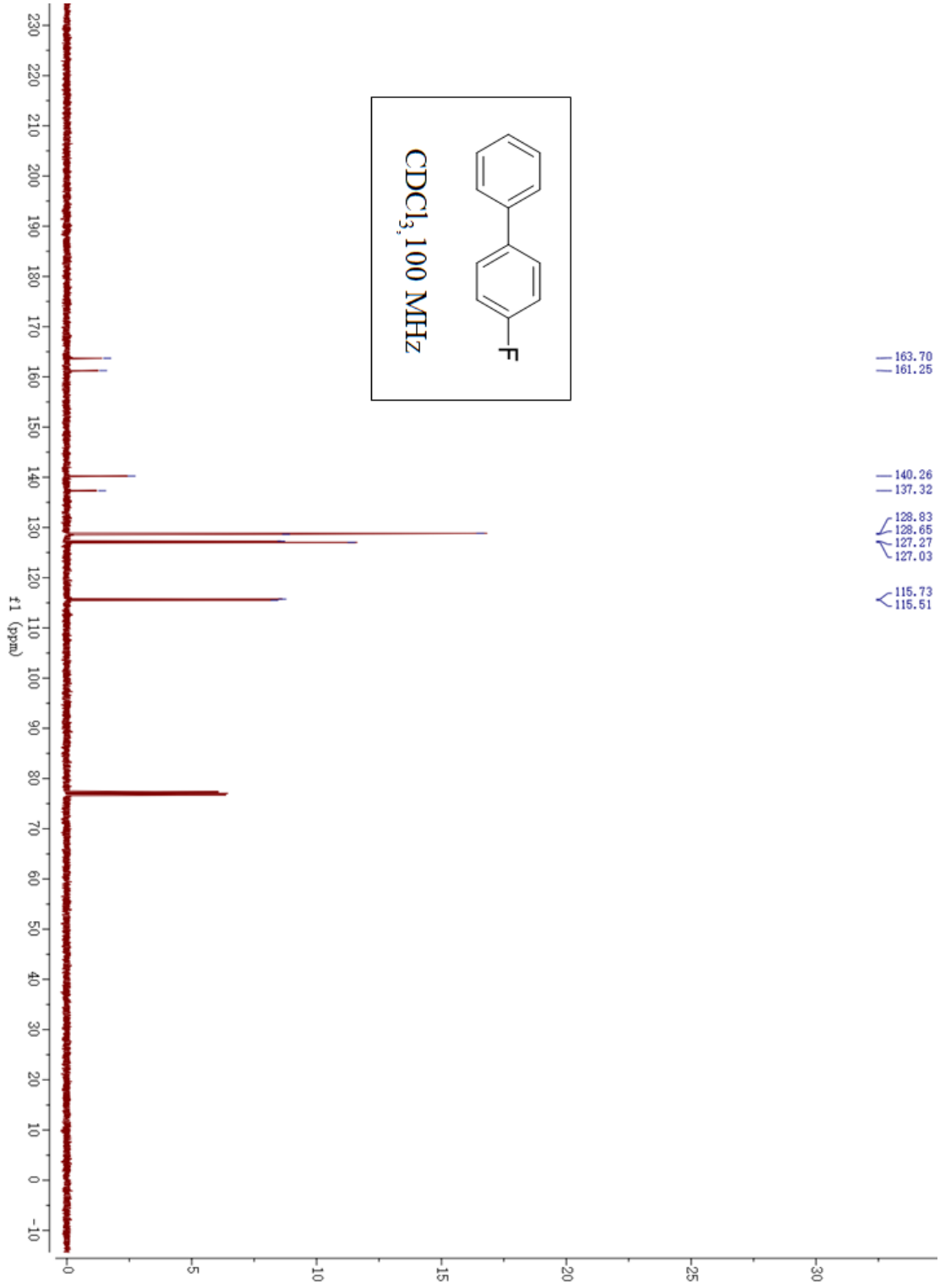

Figure S22. ^{13}C NMR spectrum of **3i**

3j , ^{1}H NMR, $CDCl_3$, 400 MHz

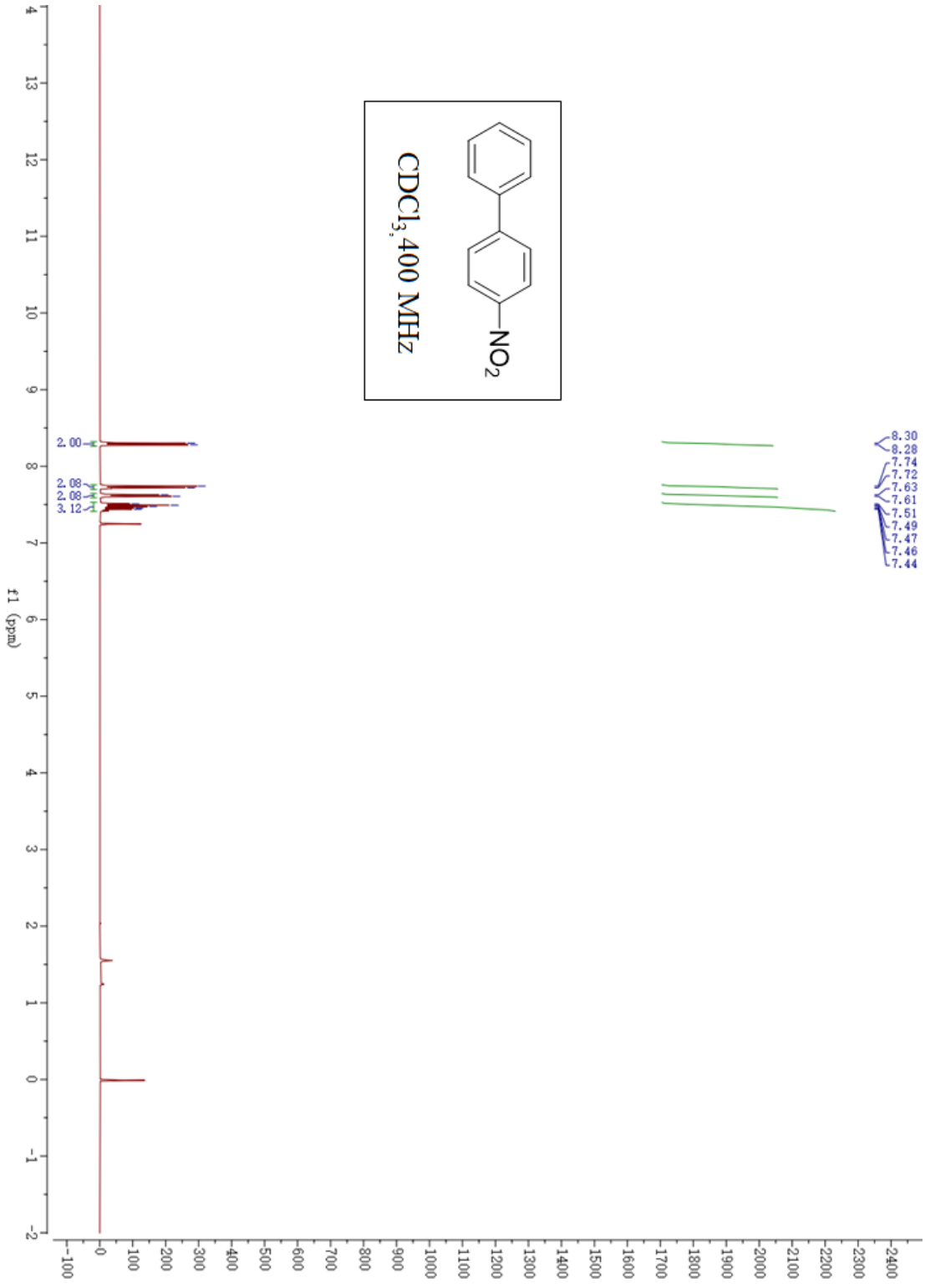

Figure S23. ^{1}H NMR spectrum of **3j**

3j, ^{13}C NMR, $CDCl_3$, 100 MHz

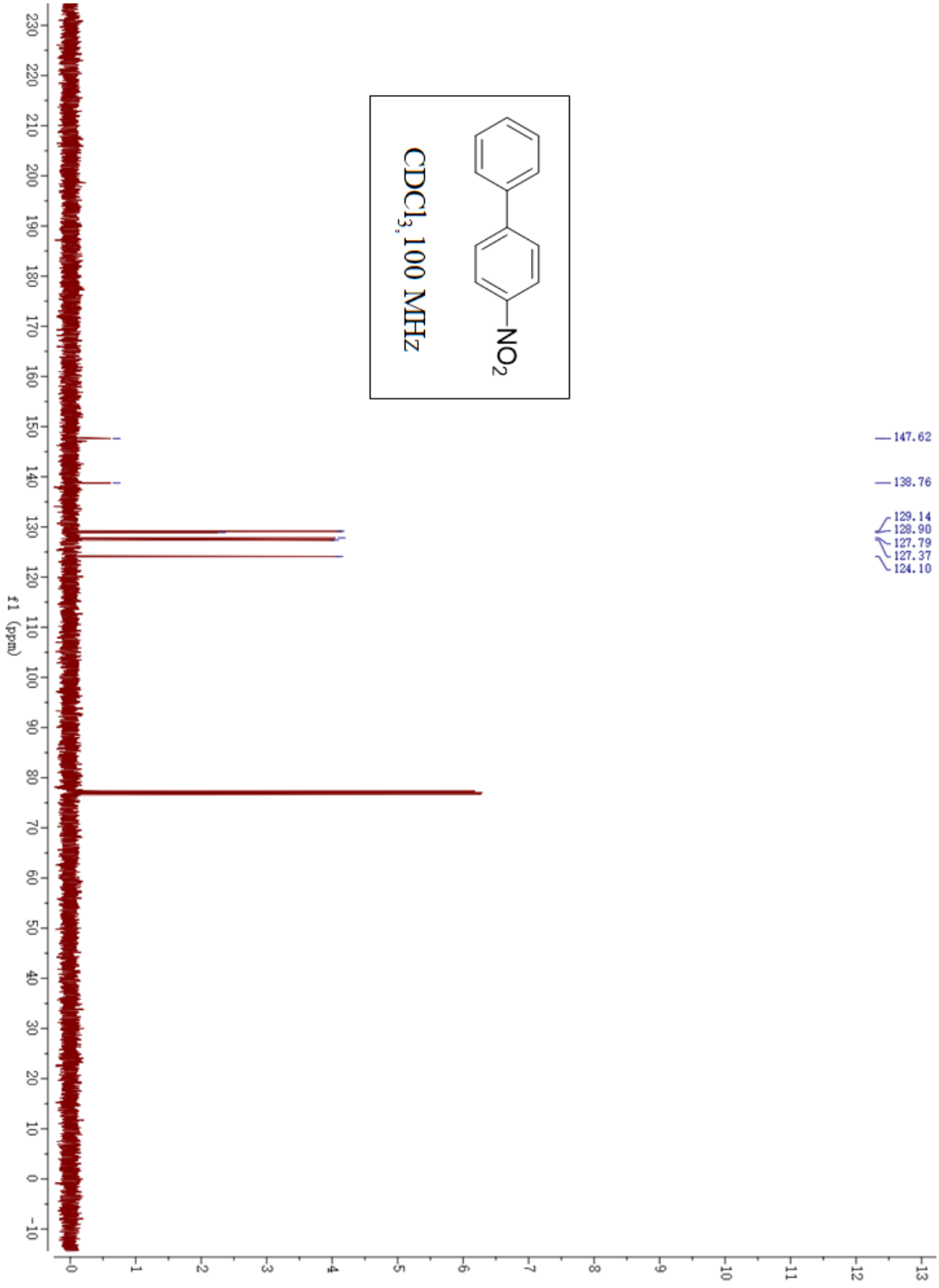

Figure S24. ^{13}C NMR spectrum of **3j**

3k , ^{1}H NMR, $CDCl_3$, 400 MHz

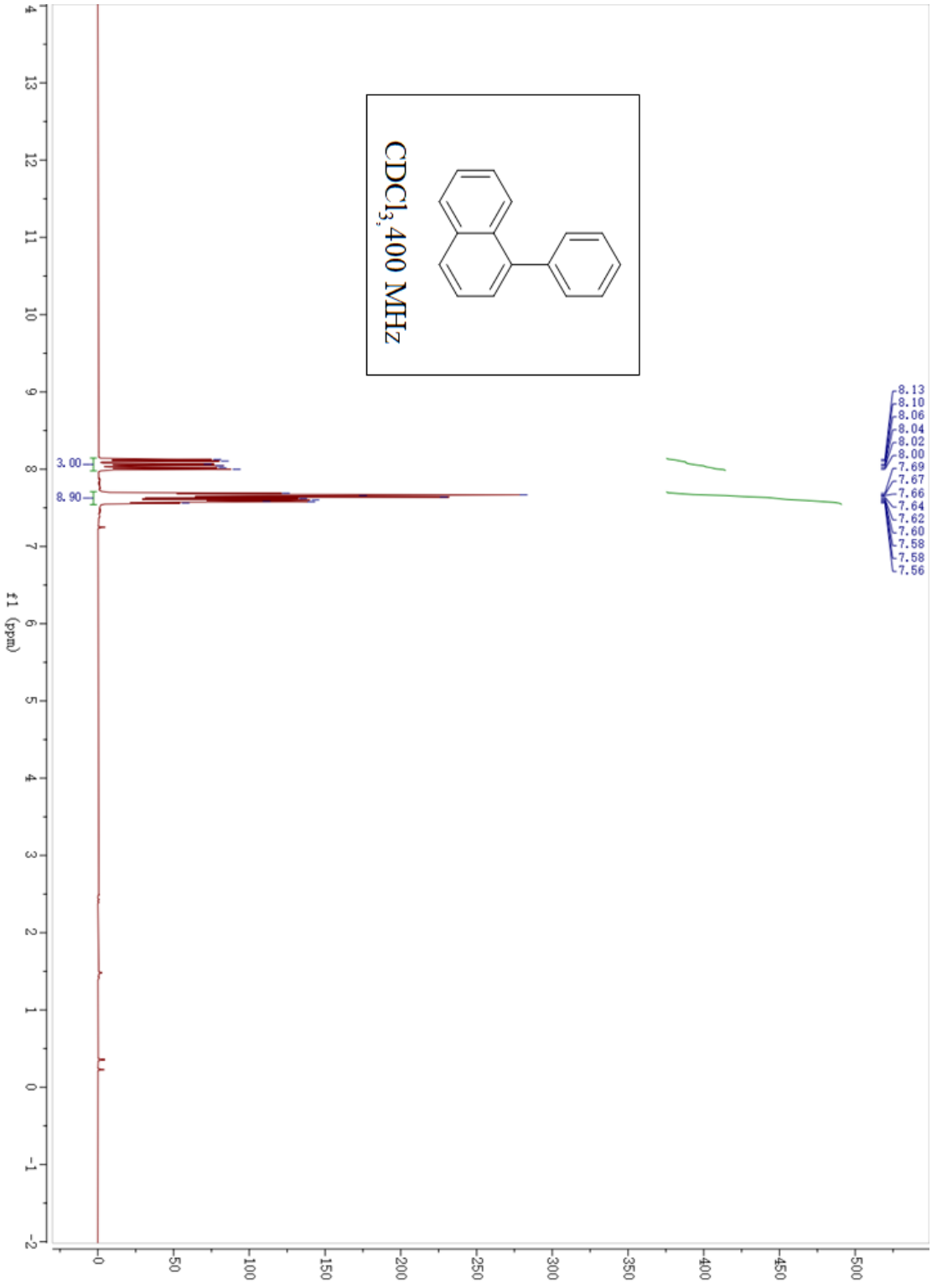

Figure S25. ^{1}H NMR spectrum of **3k**

3k, ^{13}C NMR, $CDCl_3$, 100 MHz

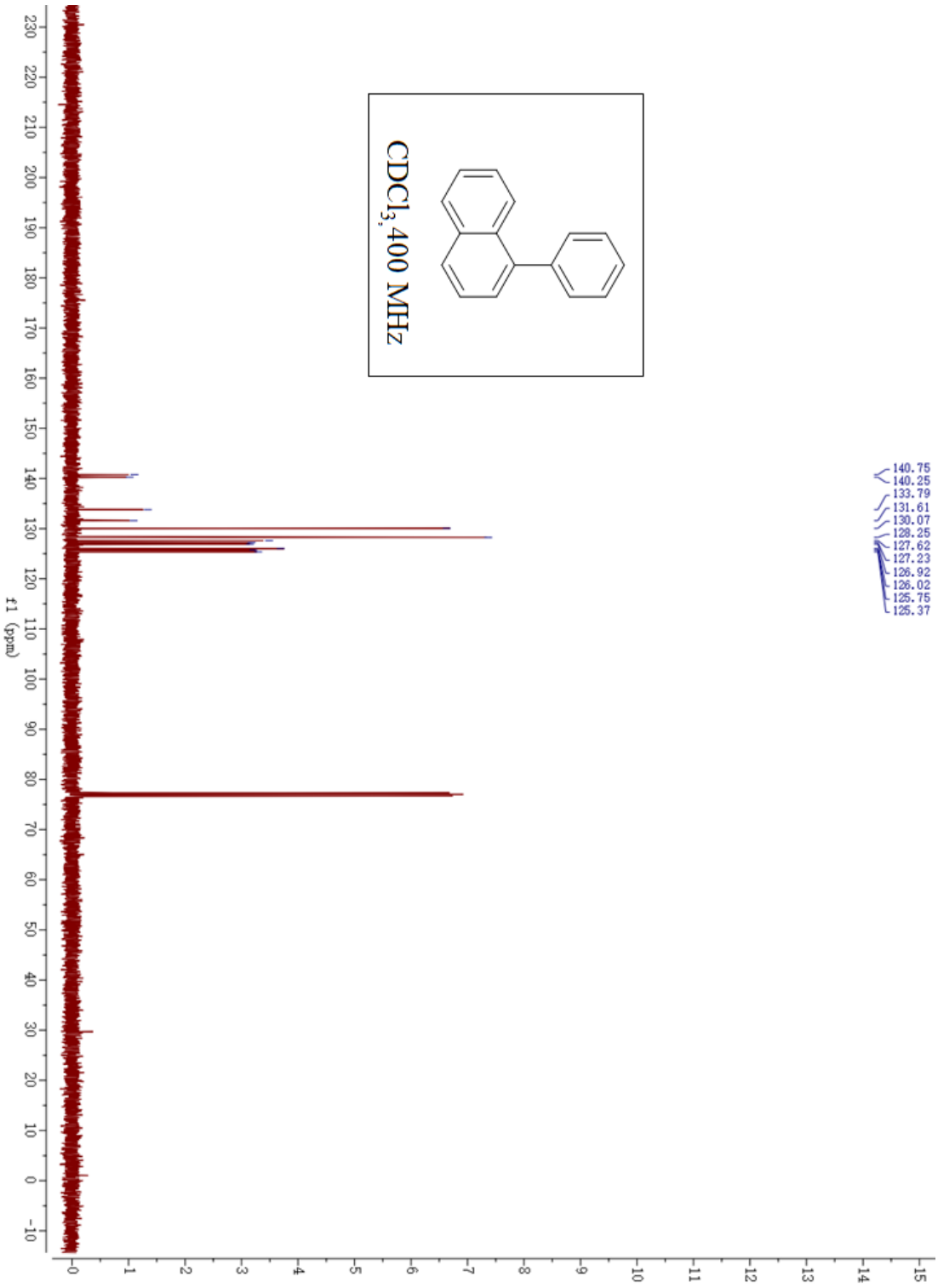

Figure S26. ^{13}C NMR spectrum of **3k**

3l, ^{1}H NMR, $CDCl_3$, 400 MHz

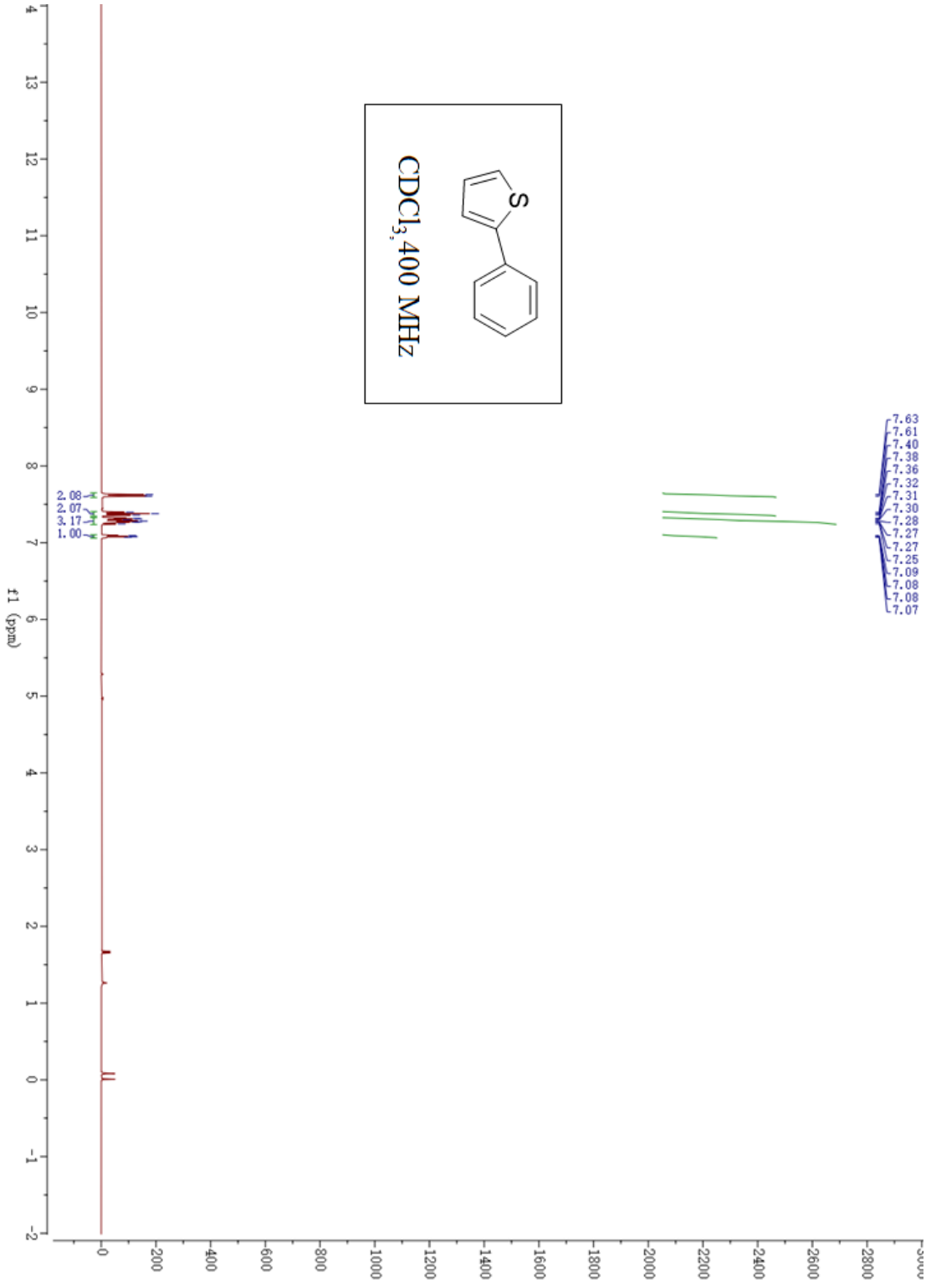

Figure S27. ^{1}H NMR spectrum of **3l**

3l, ^{13}C NMR, $CDCl_3$, 100 MHz

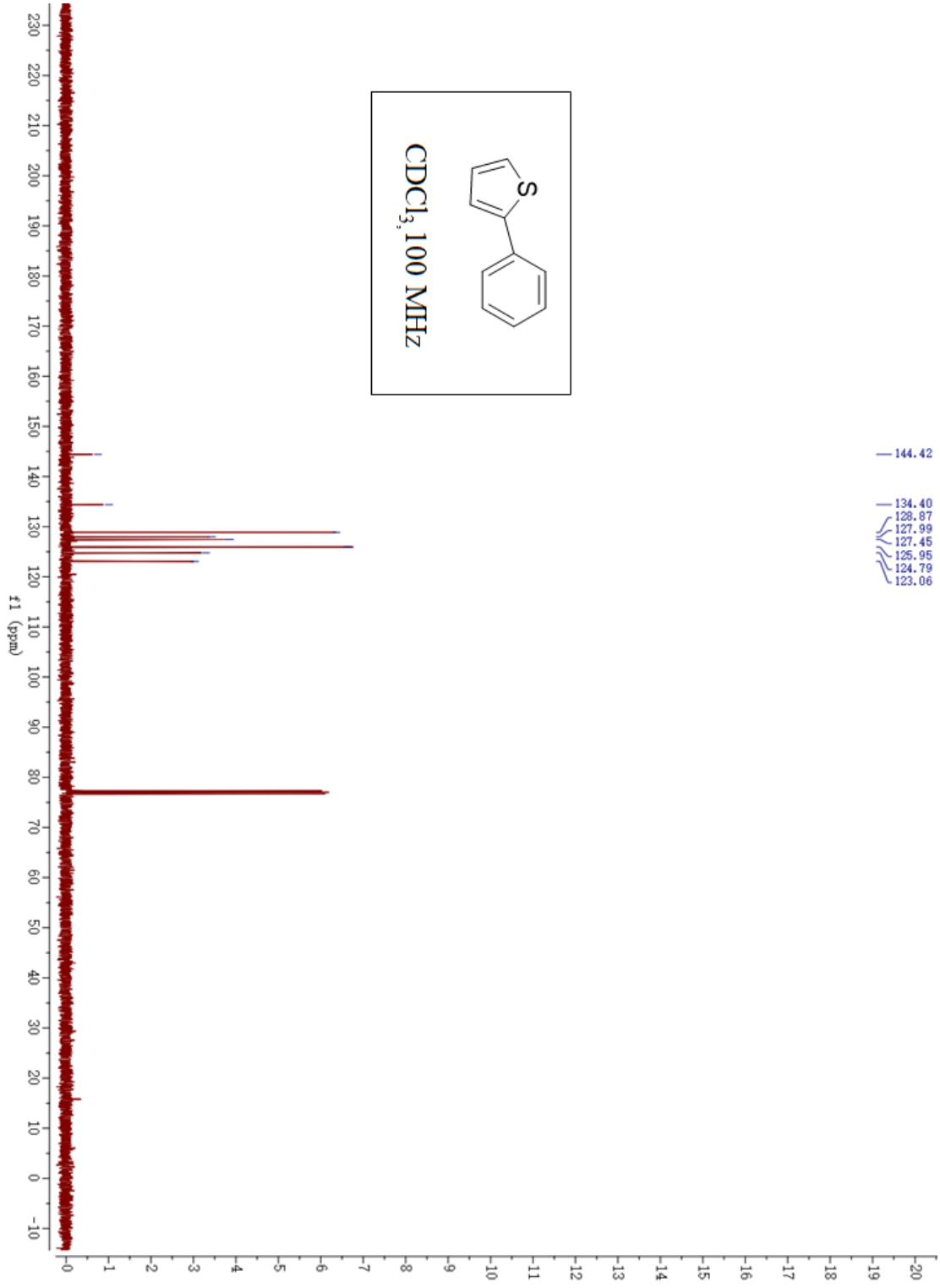

Figure S28. ^{13}C NMR spectrum of **3l**