Electronic Supplementary Material

Highly efficient air oxidation of aryl and alkyl boronic acids by microwave-assisted under transition metal-free conditions

Weiyan Yin[a*], Xizhi Pan[a], Wenxi Leng[a], Jian Chen[b*] and Haifeng He[c*]

[a] Hubei Key Laboratory of Biomass Fibers and Eco-dyeing & Finishing, School of Chemistry and Chemical Engineering, Wuhan Textile University, Wuhan 430073, P. R. China. Email: hpywy2006@163.com

[b] School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Wuhan 430070, P. R. China. Email: chenjian0501@163.com

[c] School of Chemistry and Chemical Engineering, Jiangxi Science and Technology Normal University, Nanchang 330013, P. R. China. Email: hehf0427@jxstnu.com.cn

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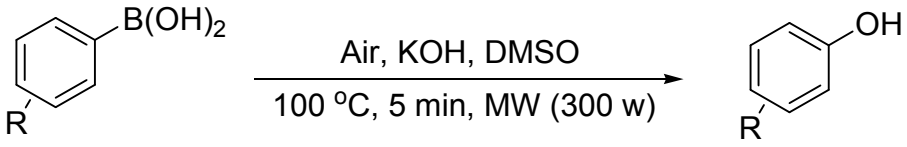
1. General Information

All the boronic acids were bought from Sigma Aldrich and Alfa-Aesar and used as received. All solvents and the other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. China, which were of analytical reagent grade and used without further purification.

^{1}H NMR spectra and **^{13}C NMR** spectra were recorded on a Bruker AV-400 spectrometer at 400 MHz for **^{1}H NMR** and 100 MHz for **^{13}C NMR** with $CDCl_3$ or DMSO-d_6 as the solvent. For **^{1}H NMR** spectra, chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. For **^{13}C NMR** spectra, chemical shifts are reported in ppm with the internal chloroform signal at 77.3 ppm and DMSO-d_6 signal at 39.6 ppm as the standard. The melting points of the products were determined by an X-4 micro-melting point apparatus (Beijing, China). Microwave irradiation experiments were performed in a MAS-IIPlus microwave reactor (Shanghai, China).

2. General procedure for the air oxidation of boronic acids



1 **2**

Boronic acids (1 mmol), KOH (3 mmol), and DMSO (3 mL) were added to a microwave reaction vessel and the reaction mixture was heated to 100 °C by microwave irradiation using a MAS-IIPlus microwave reactor under air, and then irradiated a further 5 minutes. After completion of the reaction and cooling to room temperature, it was quenched by adding HCl (2.0 M, 5.0 mL), followed by the

addition of two portions of 10 mL of EtOAc to extract the product. The combined organic phase was then washed twice with water (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue after evaporation was purified by column chromatography on silica gel to get the desired product. The products were confirmed by **^{1}H NMR** and **^{13}C NMR** spectroscopy.

3. Spectroscopic Data of Products

Phenol (2a)[1]. Colorless solid, yield 92.2 mg (98%), melting point: 43 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm): 9.37 (s, 1 H), 7.16-7.21 (m, 2 H), 6.76-6.87 (m, 3 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ (ppm): 157.36, 129.35, 118.82, 115.26.

o-Cresol (2b)[1]. Colorless solid, yield 102.7 mg (95%), melting point: 30 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.09-7.16 (m, 2 H), 6.88 (t, J =7.4 Hz, 1 H), 6.79 (d, J = 8.0 Hz, 1 H), 4.89 (s, 1 H), 2.28 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 153.75, 131.07, 127.15, 123.80, 120.80, 114.94, 15.74.

m-Cresol (2c)[1]. White solid, yield 103.8 mg (96%), melting point: 11 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.21 (t, J =7.6 Hz, 1 H), 6.86 (d, J = 7.6 Hz, 1 H), 6.77 (d, J = 7.9 Hz, 2 H), 6.50 (s, 1 H), 2.38 (s, 3 H). **^{13}C NMR** (100MHz, $CDCl_3$) δ(ppm): 155.28, 140.01, 129.59, 121.86, 116.31, 112.56, 21.39.

p-Cresol (2d)[1]. Colorless solid, yield 106.0 mg (98%), melting point: 35 °C. **^{1}H NMR** (400MHz, $CDCl_3$) δ (ppm): 7.07 (d, J = 8.3 Hz, 2 H), 6.78 (d, J = 8.4 Hz, 2 H), 5.70 (s, 1 H), 2.31 (s, 3 H). **^{13}C NMR** (100MHz, $CDCl_3$) δ(ppm): 153.09, 130.16, 130.11, 115.24, 20.50.

4-Methoxyphenol (2e)[1]. White solid, yield 122.8 mg (99%), melting point: 56 °C. **^{1}H NMR** (400MHz, $CDCl_3$) δ (ppm): 6.77-6.81 (m, 4 H), 5.08 (s, 1 H), 3.77 (s, 3 H). **^{13}C NMR** (100MHz, $CDCl_3$) δ (ppm): 153.59, 149.58, 116.17, 115.01, 55.94.

2-Fluorophenol (2f)[2]. Colorless solid, yield 104.3 mg (93%), melting point: 16 °C. **^{1}H NMR** (400MHz, $CDCl_3$) δ (ppm): 7.02-7.11 (m, 3 H), 6.85-6.89 (m, 1 H), 5.88 (s, 1 H). **^{13}C NMR** (100MHz, $CDCl_3$) δ (ppm): 152.19, 150.30, 143.55, 143.44, 124.89, 124.86, 120.94, 120.88, 117.47, 117.45, 115.70, 115.55.

4-Fluorophenol (2g)[1]. Yellow solid, yield 106.4 mg (95%), melting point: 45 ℃. **^{1}H NMR** (400MHz, $CDCl_3$) δ (ppm): 6.91-6.95 (m, 2 H), 6.78-6.81 (m, 2 H). **^{13}C NMR** (100MHz, $CDCl_3$) δ (ppm): 158.39, 156.50, 151.13, 151.12, 116.44, 116.38, 116.21, 116.03.

4-chlorophenol (2h)[3]. White solid, yield 118.7 mg (92%), melting point: 43 °C. **^{1}H NMR** (400MHz, $CDCl_3$) δ (ppm): 7.16-7.13 (m, 2 H), 6.72-6.75 (m, 2 H), 5.08 (s, 1 H). **^{13}C NMR** (100MHz, $CDCl_3$) δ (ppm): 153.94, 129.62, 125.75, 116.80.

2,4-Dichlorophenol (2i)[3]. White solid, yield 148.3 mg (91%), melting point: 42 °C. **^{1}H NMR** (400MHz, DMSO-d_6) δ(ppm): 10.42 (s, 1 H), 7.38 (d, J = 1.9 Hz, 1 H), 7.15-7.17 (m, 1 H), 6.96 (d, J = 8.7 Hz, 1 H). **^{13}C NMR** (100MHz, DMSO-d_6) δ (ppm): 152.27, 129.03, 127.80, 122.62, 120.60, 117.64.

2-Chloro-5-methylphenol (2j)[4]. Gray solid, yield 133.0 mg (93%), melting point: 46 °C. **^{1}H NMR** (400MHz, DMSO-d_6) δ (ppm): 9.94 (s, 1 H), 7.13-7.16 (m, 1 H), 6.80 (s, 1 H), 6.57 (d, J = 8.0 Hz, 1 H), 2.34 (s, 3 H). **^{13}C NMR** (100MHz, DMSO-d_6) δ (ppm): 152.71, 137.49, 129.33, 120.65, 117.18, 116.68, 20.49.

2,6-Di-tert-butyl-4-methylphenol (2k)[5]. White solid, yield 206.8 mg (94%), melting point: 69 °C. **^{1}H NMR** (400MHz, DMSO-d_6) δ (ppm): 6.88 (s, 2 H), 6.62 (s, 1 H), 2.35 (s, 3 H), 1.38(s, 18 H). **^{13}C NMR** (100MHz, DMSO-d_6) δ (ppm): 151.48, 139.10, 127.94, 124.84, 21.01.

α-Naphthol (2l) [1]. Yellow solid, yield 132.5 mg (92%), melting point: 96 °C. **^{1}H NMR** (400MHz, $CDCl_3$) δ(ppm): 8.19-822 (m, 1 H), 7.82-7.85 (m, 1 H), 7.46-7.52 (m, 3 H), 7.31-7.34 (m, 1 H), 6.82 (dd, *J* = 7.4, 0.5Hz, 1 H), 4.58 (s, 1 H). **^{13}C NMR** (100MHz, $CDCl_3$) δ (ppm): 151.38, 134.80, 127.71, 126.47, 125.86, 125.29, 124.39, 121.55, 120.73, 108.68.

β-Naphthol (2m)[1]. Red solid, yield 135.4 mg (94%), melting point: 120 °C. **^{1}H NMR** (400MHz, $CDCl_3$) δ (ppm): 7.75-7.79 (m, 2 H), 7.68 (d, *J* = 8.2 Hz, 1 H), 7.42-7.46 (m, 1 H), 7.34-7.36 (m, 1 H), 7.16 (d, *J* = 2.4 Hz, 1 H), 7.12 (dd, *J* = 8.8, 2.5 Hz, 1 H). **^{13}C NMR** (100MHz, $CDCl_3$) δ (ppm): 153.35, 134.61, 129.87, 128.96, 127.78, 126.54, 126.39, 123.64, 117.77, 109.54.

p-Hydroxybenzaldehyde (2n)[3]. Yellow solid, yield 109.8 mg (90%), melting point: 113 °C. **^{1}H NMR** (400MHz, DMSO-d_6) δ (ppm): 10.57 (s, 1 H), 9.77 (s, 1 H), 7.74 (d, *J* = 8.1 Hz, 2 H), 6.93 (d, *J*= 8.2 Hz, 2 H). **^{13}C NMR** (100MHz, DMSO-d_6) δ (ppm): 190.75, 163.29, 132.02, 128.40, 115.80.

salicylamide (2o)[6]. White solid, yield 121.9 mg (89%), melting point:142 °C. **^{1}H NMR** (400MHz, DMSO-d_6) δ (ppm): 13.03 (s, 1 H), 8.40 (s, 1 H), 7.86 (d, *J* = 8.0 Hz, 2 H), 7.38 (t, *J* = 7.7 Hz, 1 H), 6.82-6.89 (m, 2 H). **^{13}C NMR** (100MHz, DMSO-d_6) δ (ppm): 172.14, 161.10, 134.02, 128.08, 118.31, 117.39, 114.36.

Benzyl 4-hydroxybenzoate (2p)[7]. Colorless solid, yield 198.4 mg (87%), melting point: 110 °C. **^{1}H NMR** (400MHz, DMSO-d_6) δ (ppm): 10.49 (s, 1 H), 7.87 (d, J = 7.2 Hz, 2H), 7.33-7.45 (m, 5 H), 6.88 (d, J = 7.2 Hz, 2 H), 5.29 (s, 2 H). **^{13}C NMR** (100MHz, DMSO-d_6) δ (ppm): 165.39, 162.17, 136.47, 131.51, 128.44, 127.93, 127.81, 120.15, 115.39, 65.55.

m-Trifluoromethylphenol (2q)[8]. Yellow liquid, yield 132.8 mg (82%). **^{1}H NMR** (400MHz, $CDCl_3$) δ (ppm): 7.35 (t, J = 8.0 Hz, 1 H), 7.22 (t, J = 7.8 Hz, 1 H), 7.02-7.04 (m, 1 H), 6.14 (s, 1 H). **^{13}C NMR** (100MHz, $CDCl_3$) δ (ppm): 155.4, 132.5, 132.25, 131.99, 131.73, 130.35, 118.87, 118.86, 117.85, 117.82, 112.36, 112.33.

p-nitrophenol (2r)[1]. Yellow solid, yield 107.0 mg (77%), melting point: 112 °C. **^{1}H NMR** (400MHz, DMSO-d_6) δ (ppm): 10.96 (s, 1 H), 8.03 (s, 2 H), 6.87 (s, 2 H). **^{13}C NMR** (100MHz, DMSO-d_6) δ (ppm): 163.82, 139.55, 125.93, 115.57.

4-Methyl-3-nitrophenol (2s)[9]. Withe solid, yield 122.4 mg (80%), melting point:75 °C. **^{1}H NMR** (400MHz, DMSO-d_6) δ (ppm): 10.11 (s, 1 H), 7.33 (s, 1 H), 7.22 (d, J = 8.2 Hz, 1 H), 7.01 (d, J = 8.3 Hz, 1 H), 2,36 (s, 3 H). **^{13}C NMR** (100MHz, DMSO-d_6) δ (ppm): 156.02, 148.98, 133.44, 122.58, 120.81, 110.44, 18.71.

1-pentanol (2t)[10]. Colorless liquid, yield 83.5 mg (95%). **^{1}H NMR** (400MHz, DMSO-d_6) δ (ppm): 4.33 (t, J = 5.7 Hz, 1 H), 3.35-3.40 (m, 2 H), 1.40 (dd, J = 13.4, 6.7 Hz, 2 H), 1.27 (dd, J = 11.9, 8.4 Hz, 4 H), 0.86 (t, J = 6.8 Hz, 3 H). **^{13}C NMR** (100MHz, DMSO-d_6) δ (ppm): 60.68, 32.19, 27.71, 22.00, 13.90.

4. References

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5. Copies of ^{1}H NMR and ^{13}C NMR spectra of 2a-2t.

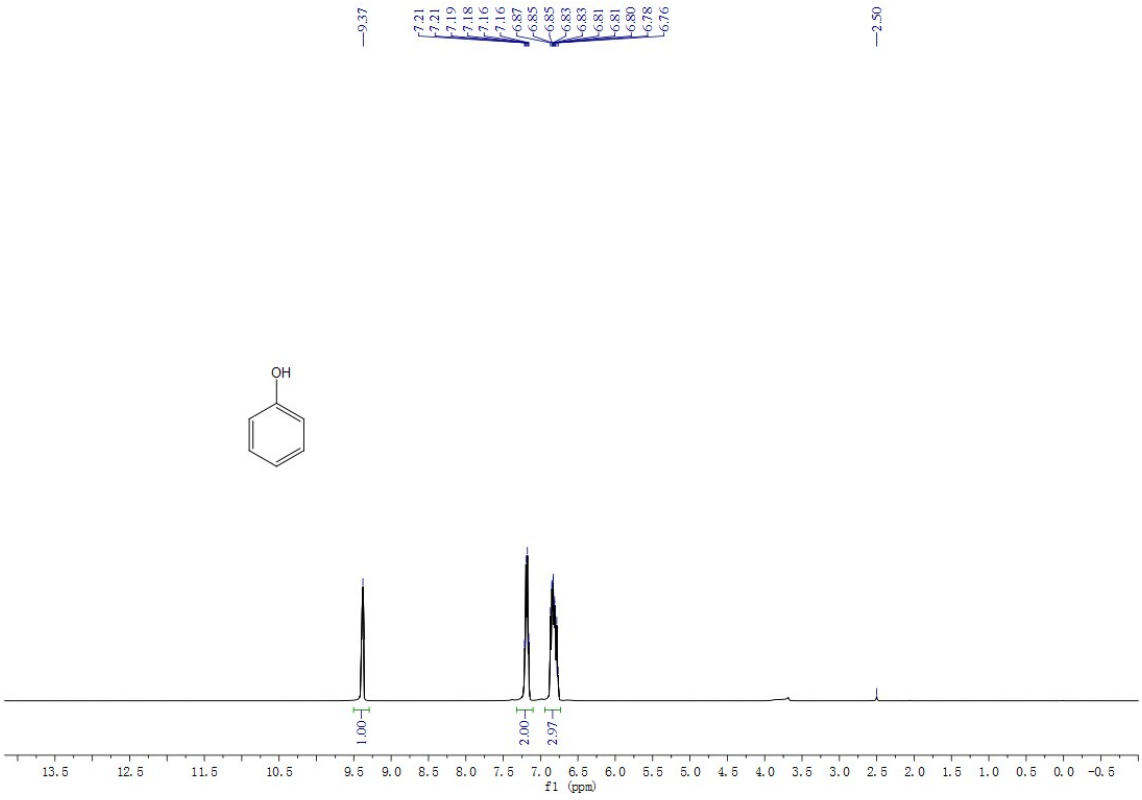

Fig. 1 The **^{1}H NMR** spectra of **2a**

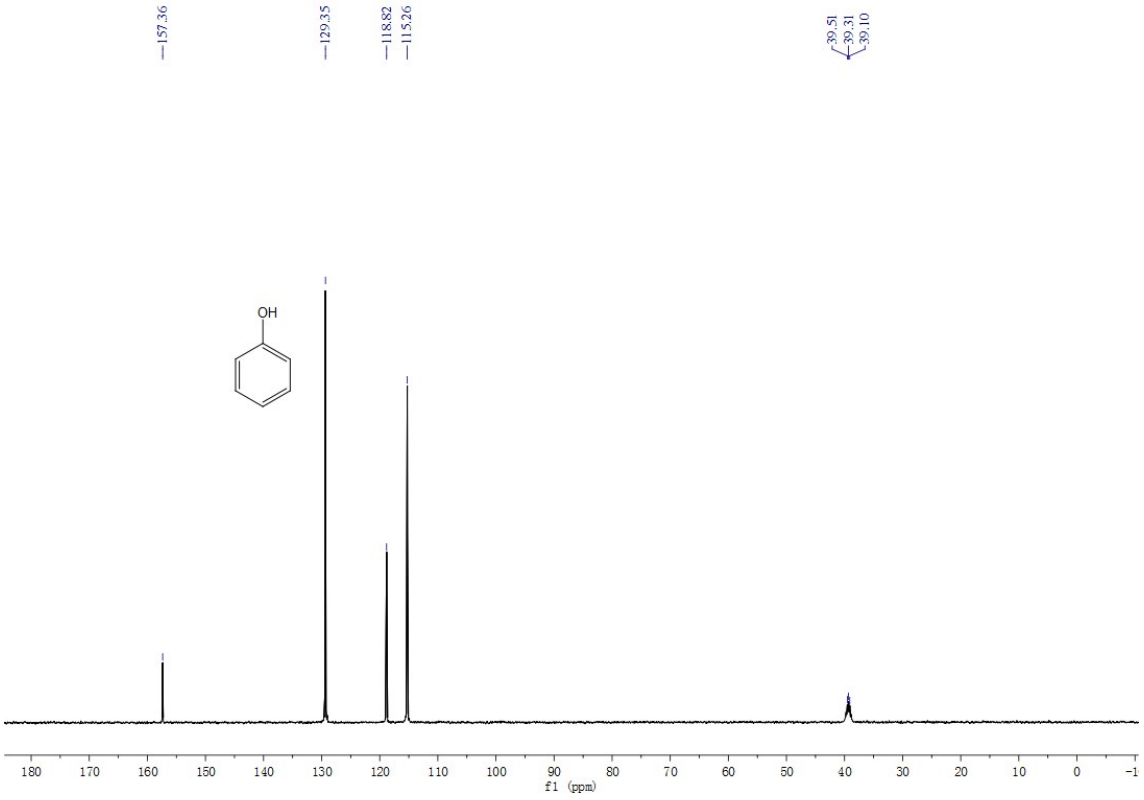

Fig. 2 The ^{13}C **NMR** spectra of **2a**

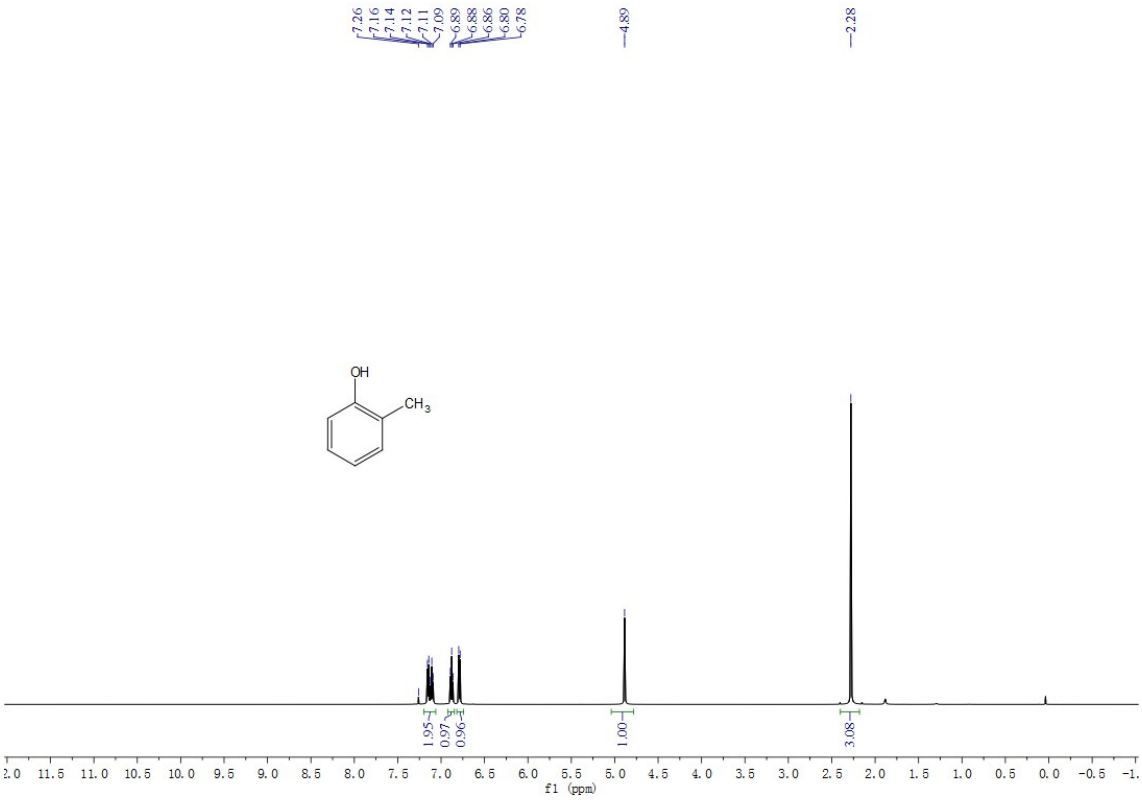

Fig. 3 The **^{1}H NMR** spectra of **2b**

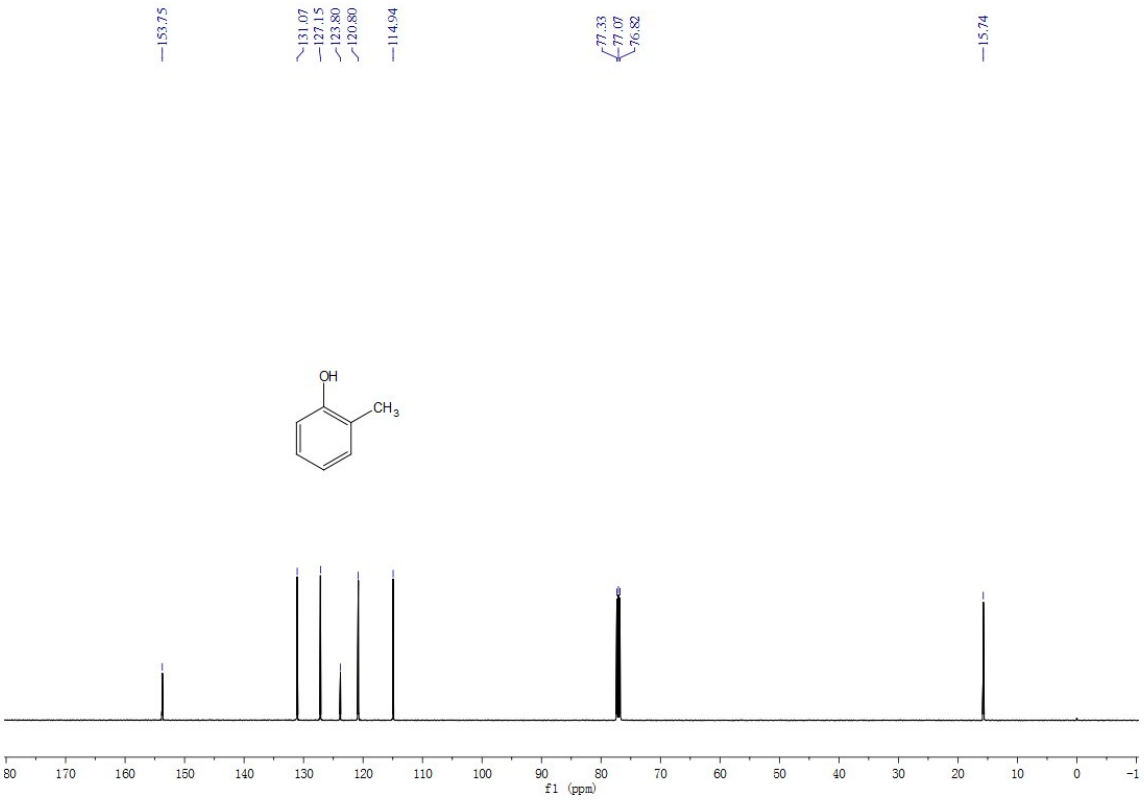

Fig. 4 The ^{13}C **NMR** spectra of **2b**

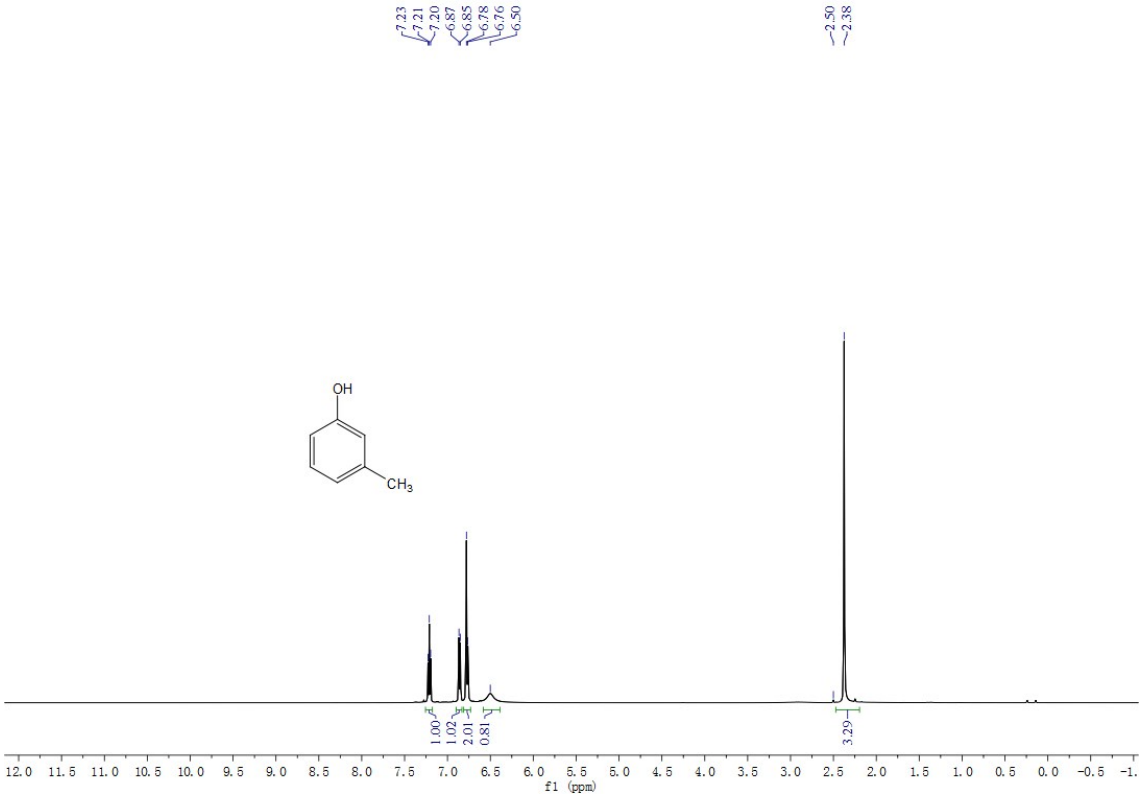

Fig. 5 The **^{1}H NMR** spectra of **2c**

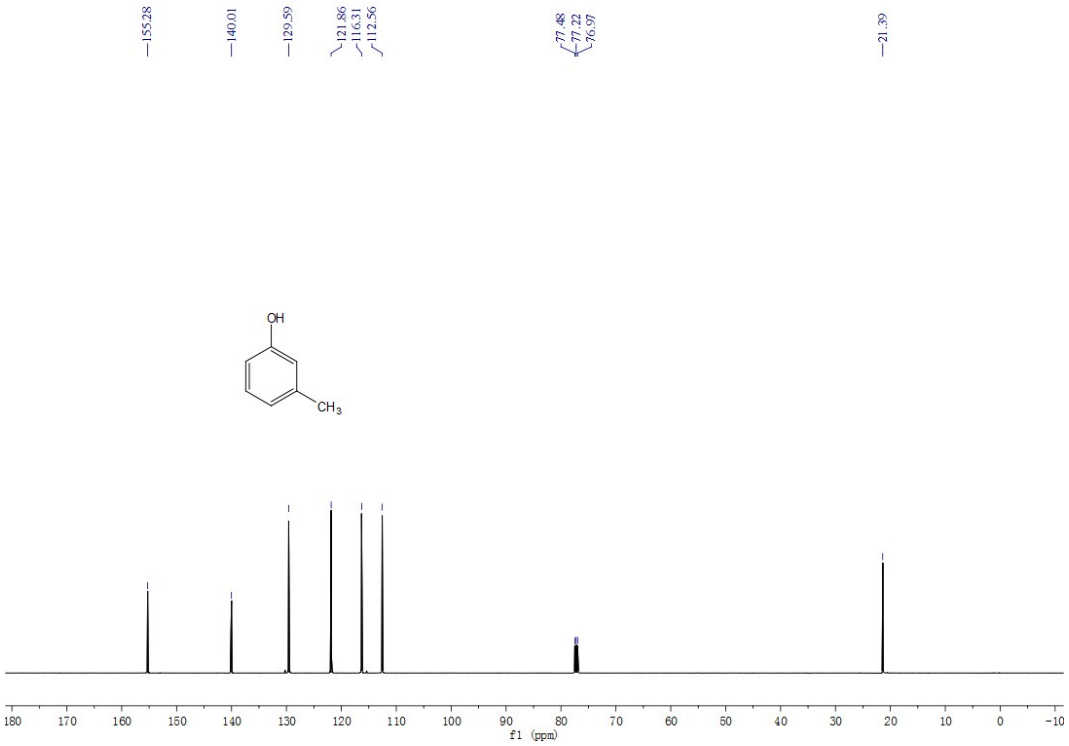

Fig. 6 The ^{13}C **NMR** spectra of **2c**

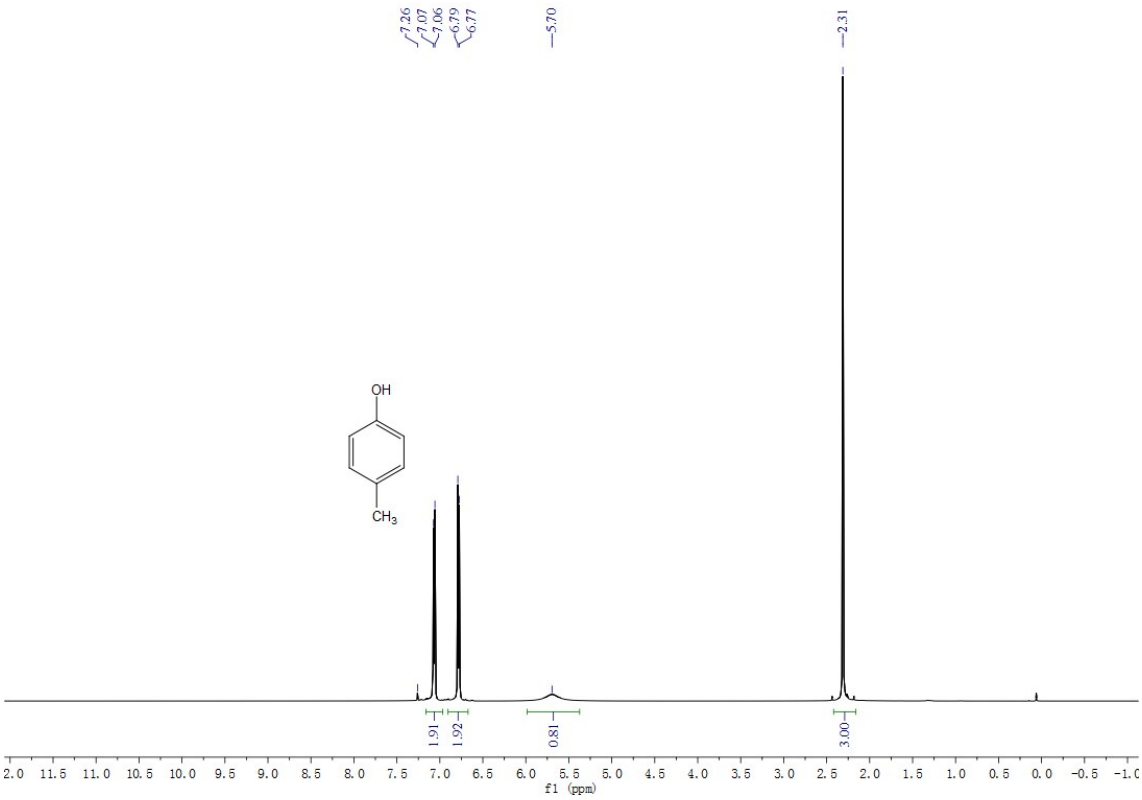

Fig. 7 The **^{1}H NMR** spectra of **2d**

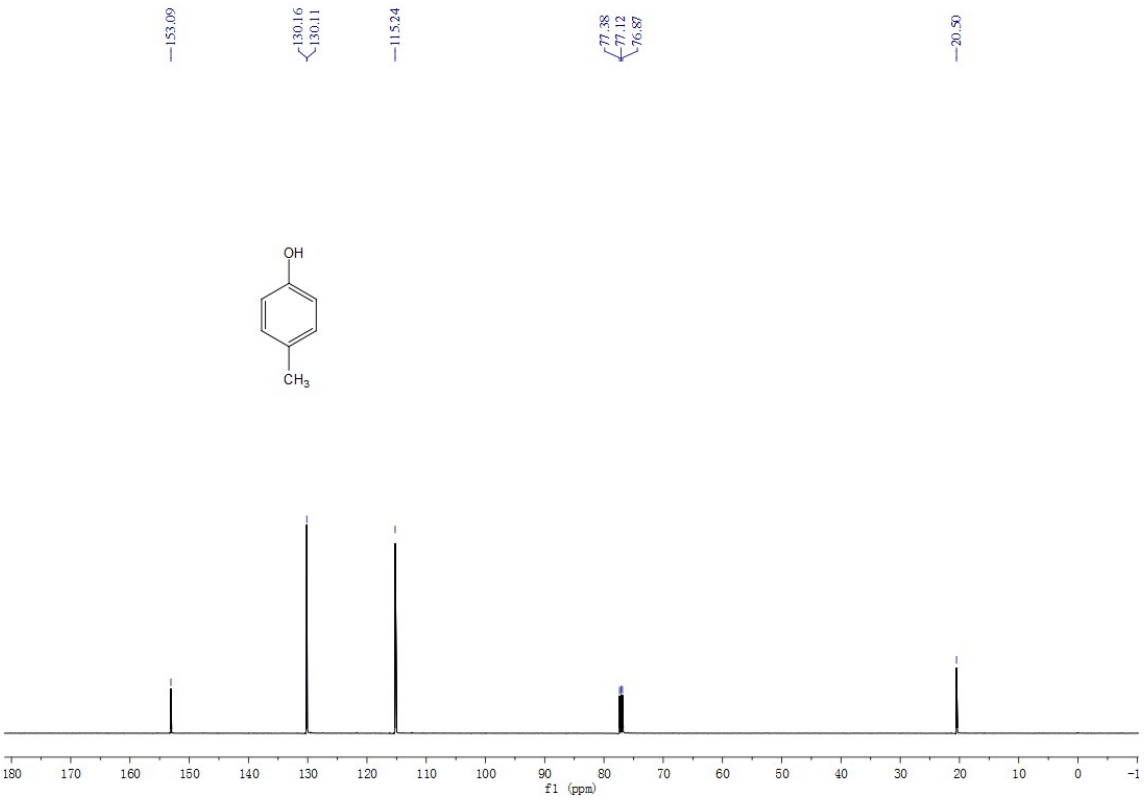

Fig. 8 The ^{13}C **NMR** spectra of **2d**

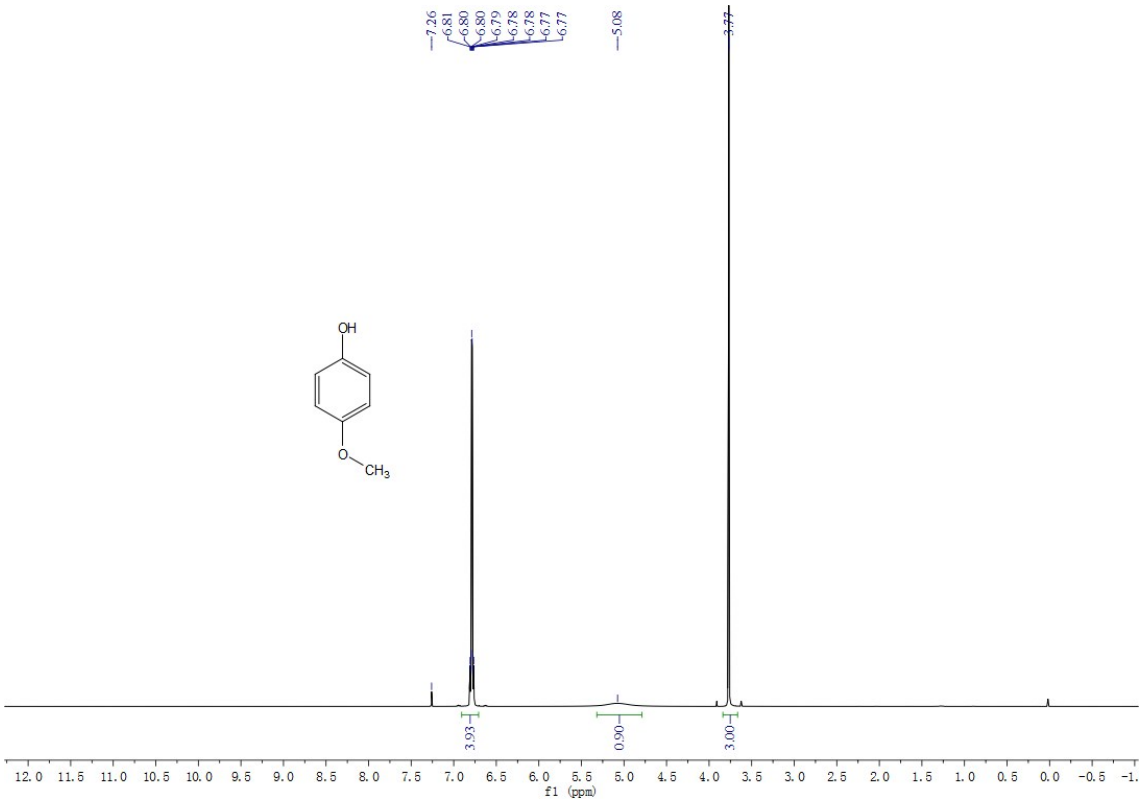

Fig. 9 The **^{1}H NMR** spectra of **2e**

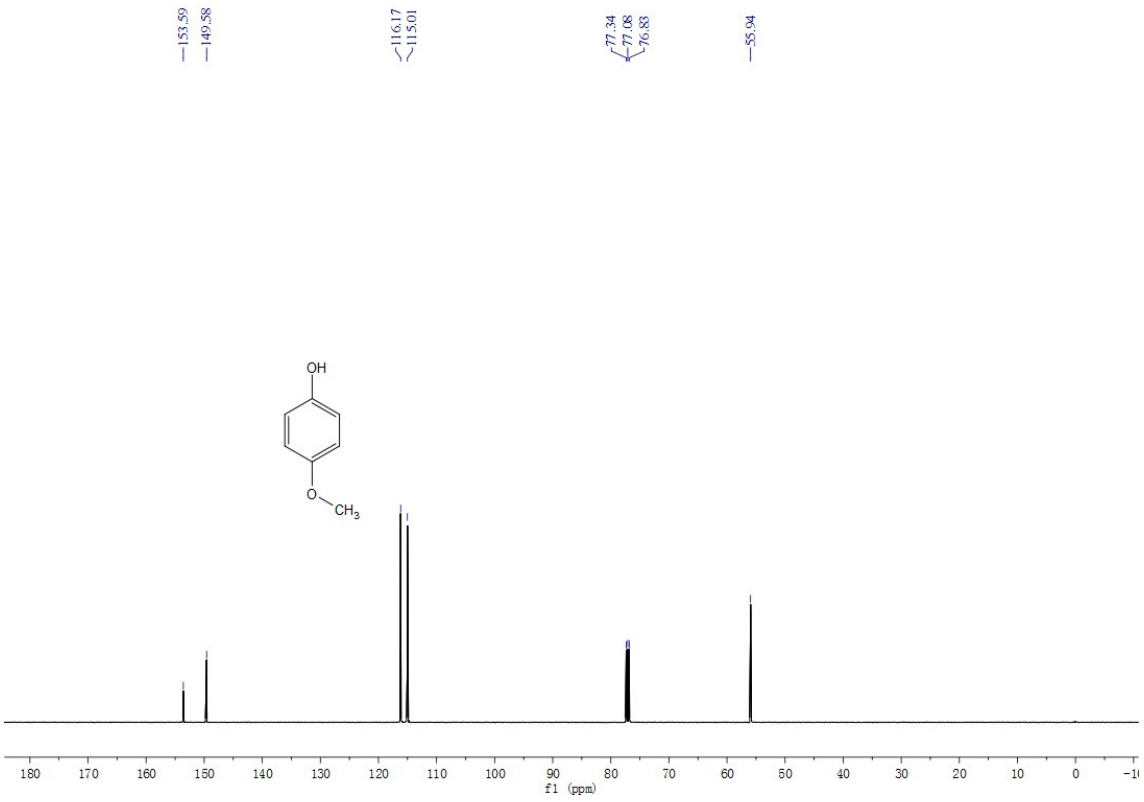

Fig. 10 The **^{13}C NMR** spectra of **2e**

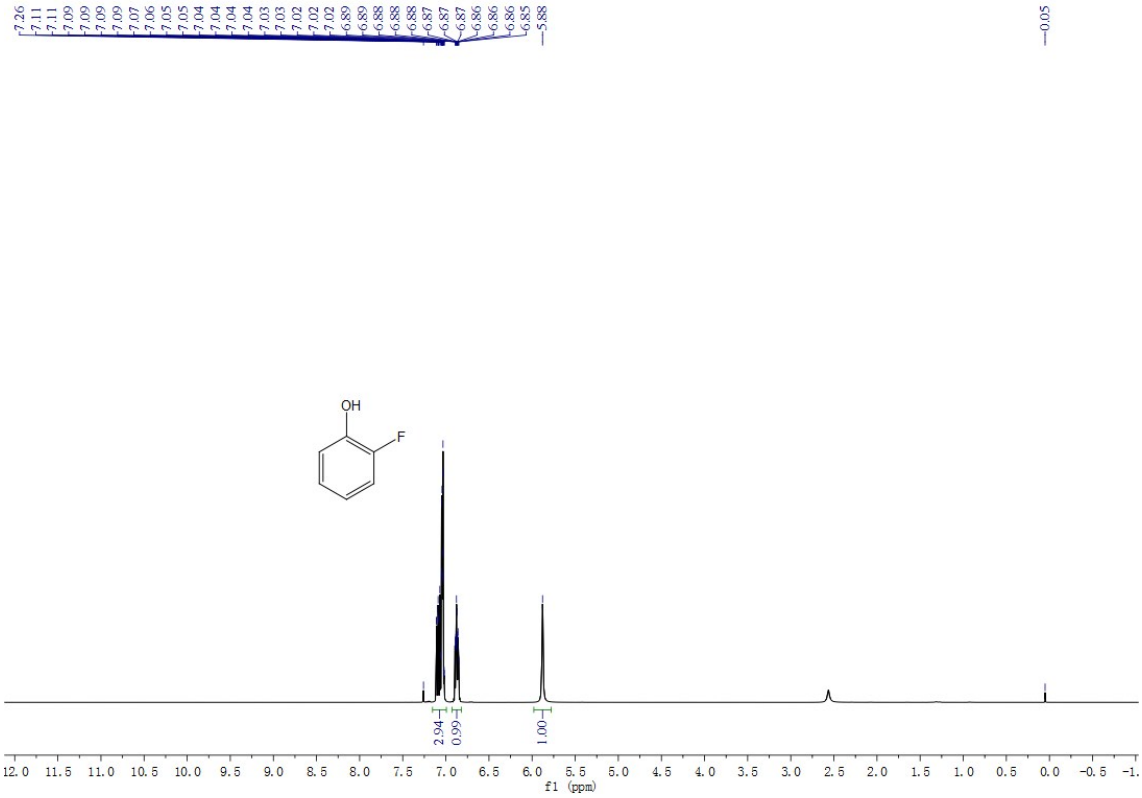

Fig. 11 The **^{1}H NMR** spectra of **2f**

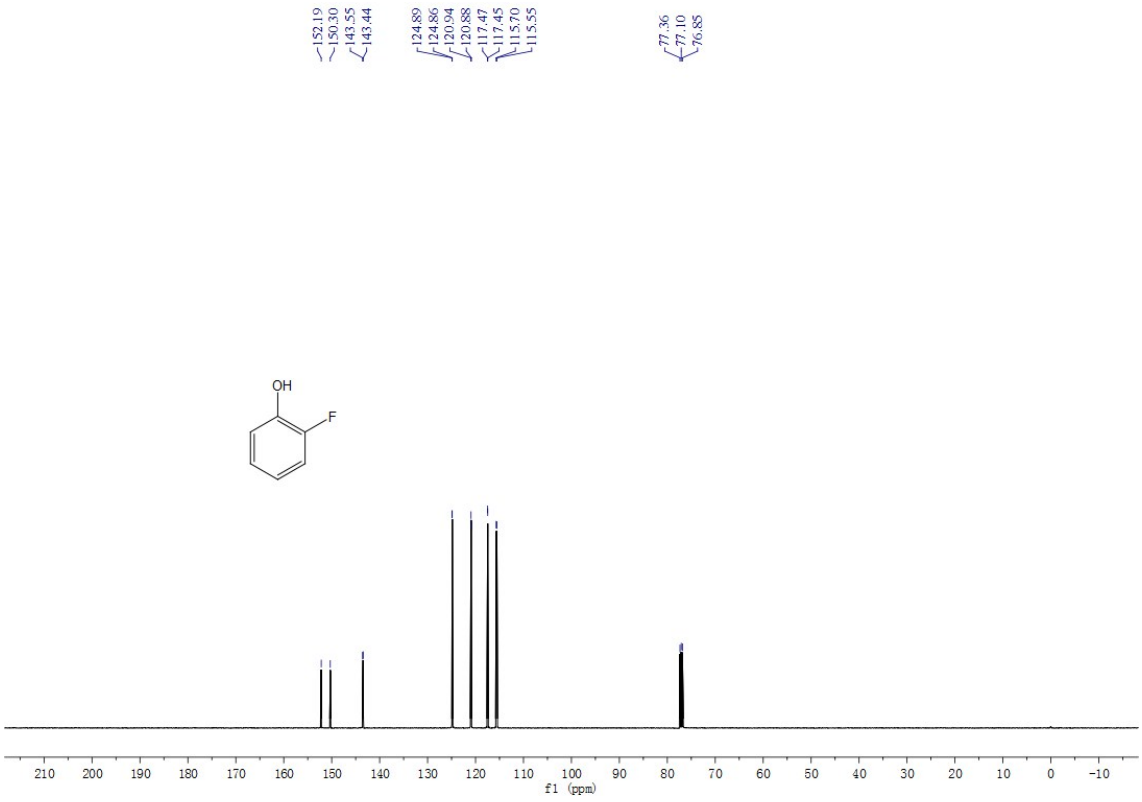

Fig. 12 The ^{13}C **NMR** spectra of **2f**

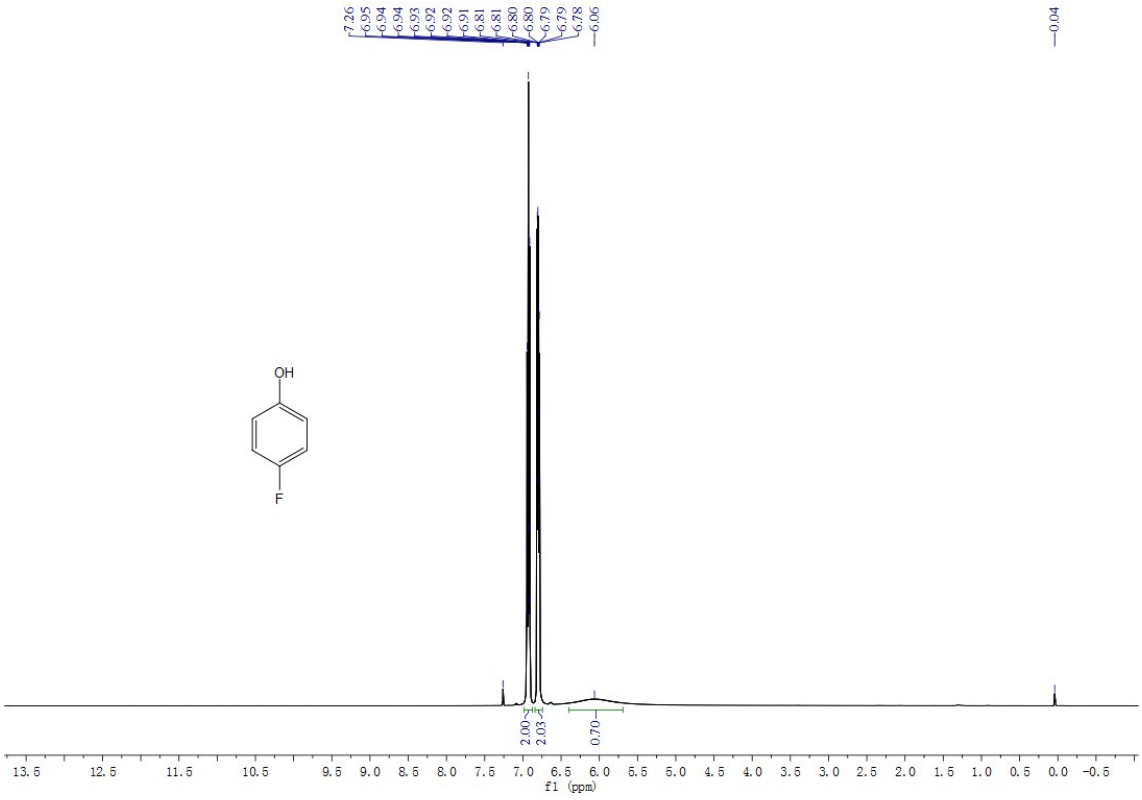

Fig. 13 The **^{1}H NMR** spectra of **2g**

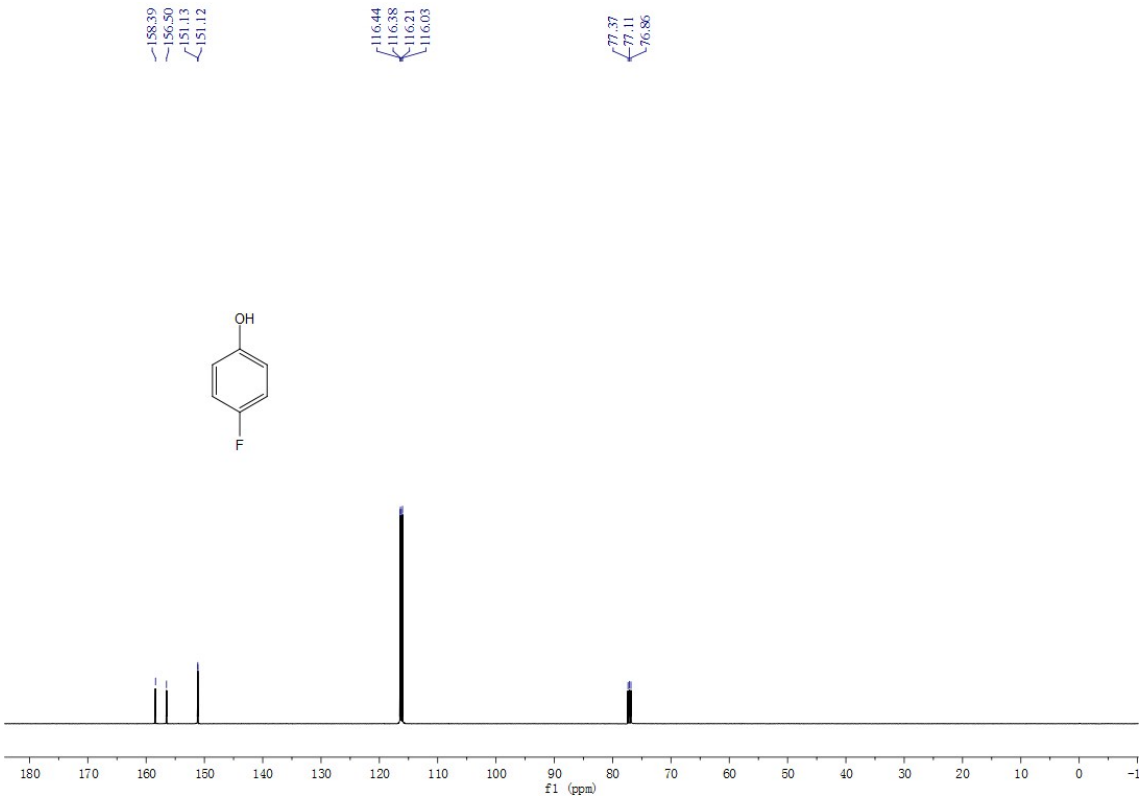

Fig. 14 The **^{13}C NMR** spectra of **2g**

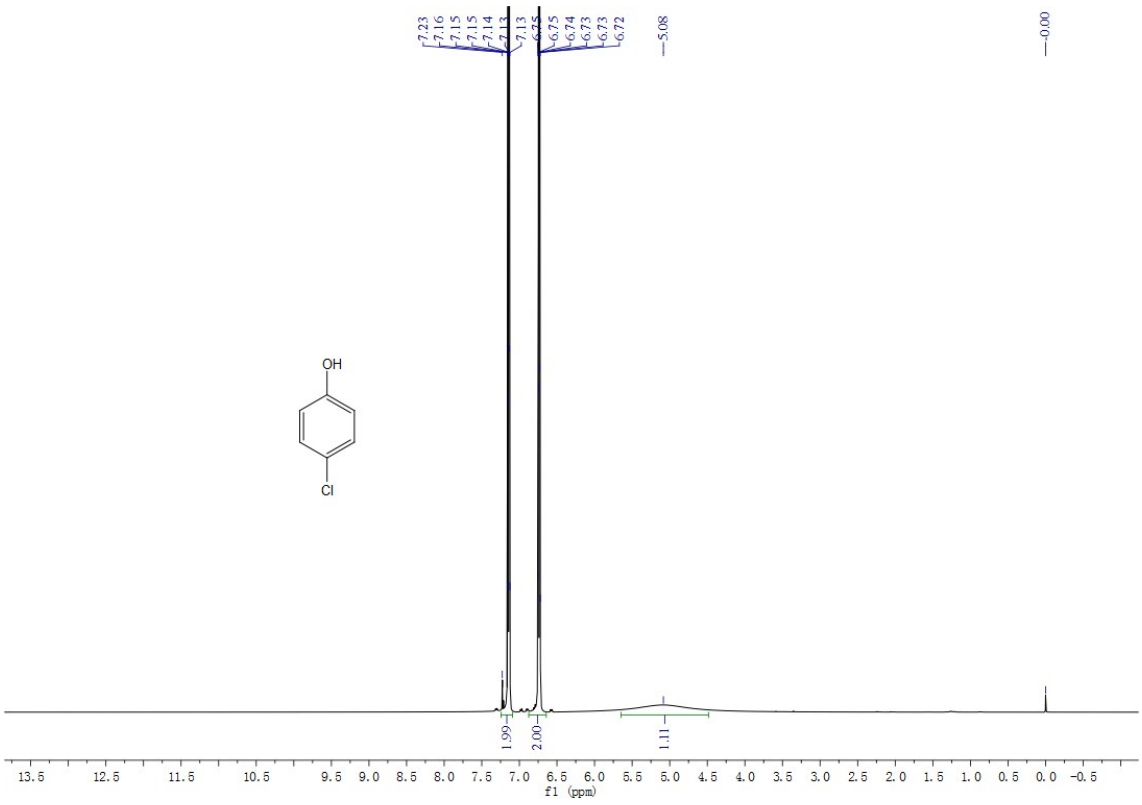

Fig. 15 The **^{1}H NMR** spectra of **2h**

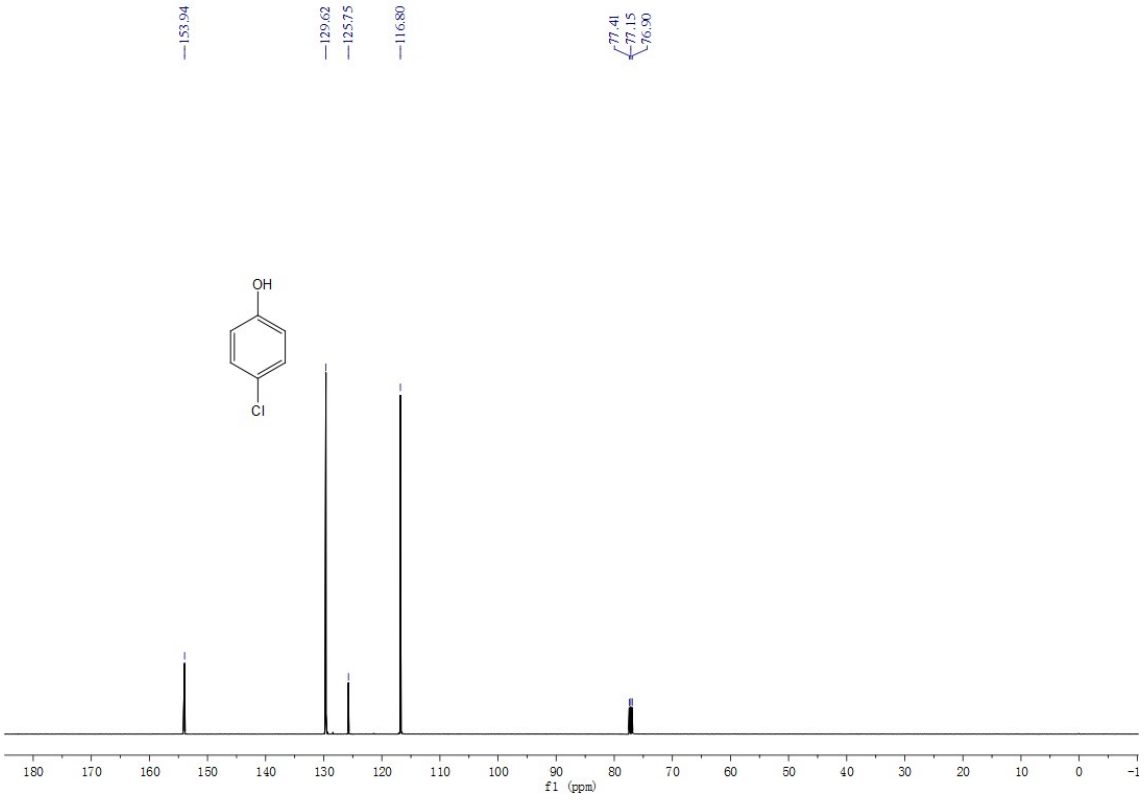

Fig. 16 The **^{13}C NMR** spectra of **2h**

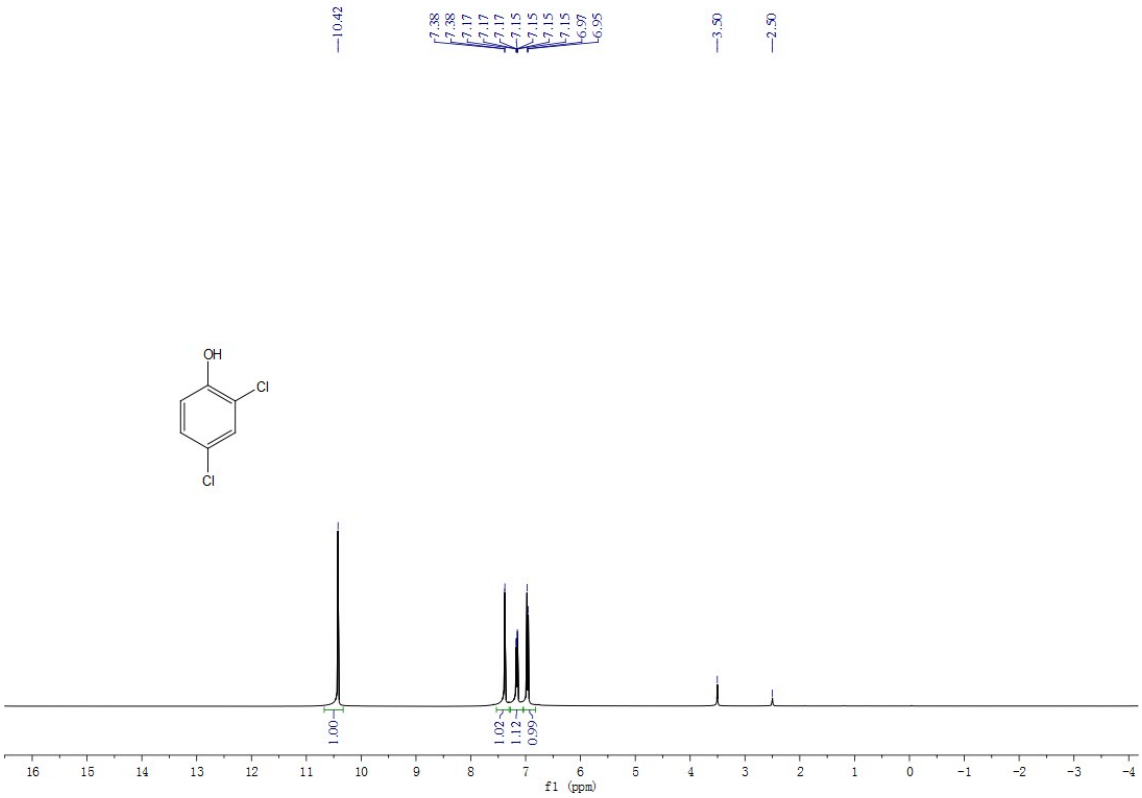

Fig. 17 The **^{1}H NMR** spectra of **2i**

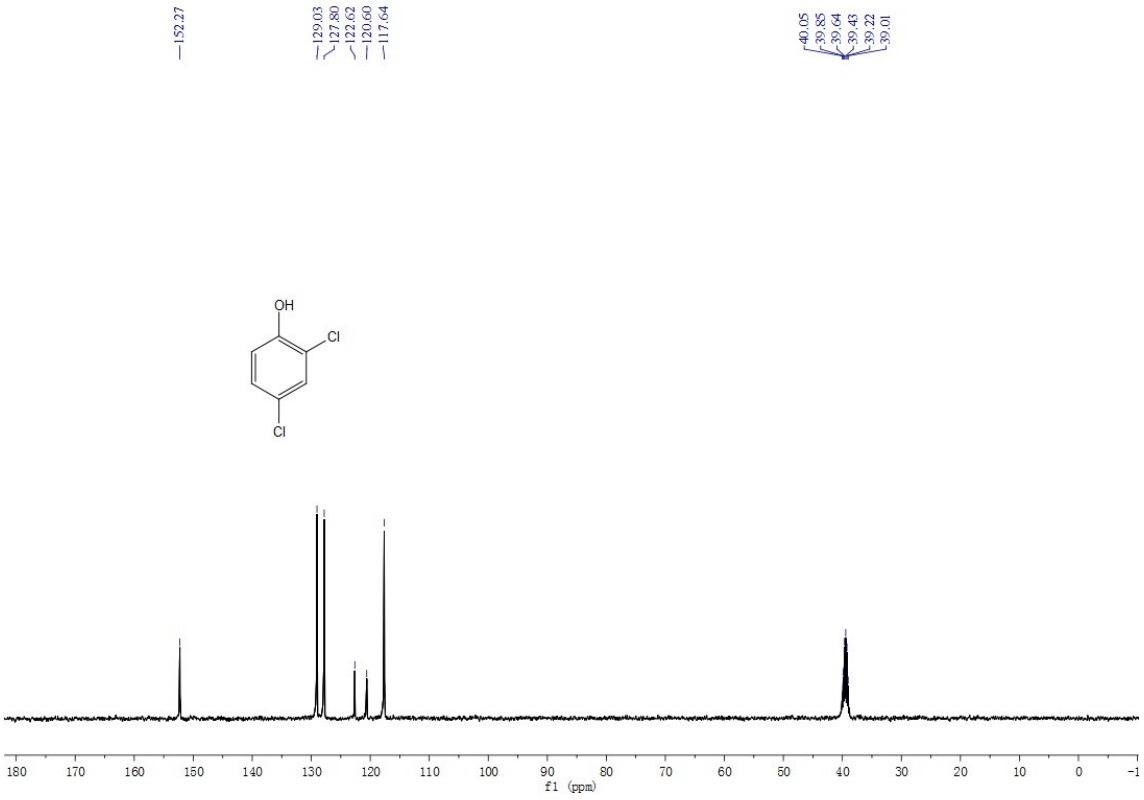

Fig. 18 The ^{13}C **NMR** spectra of **2i**

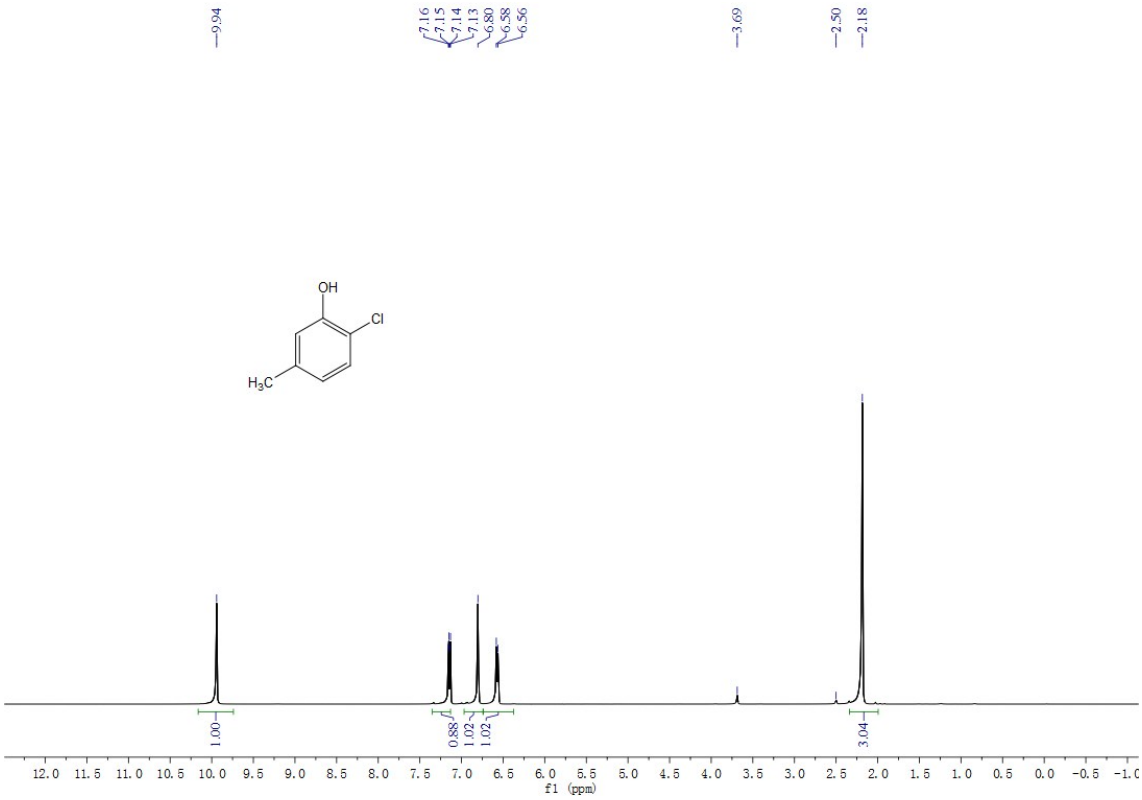

Fig. 19 The **^{1}H NMR** spectra of **2j**

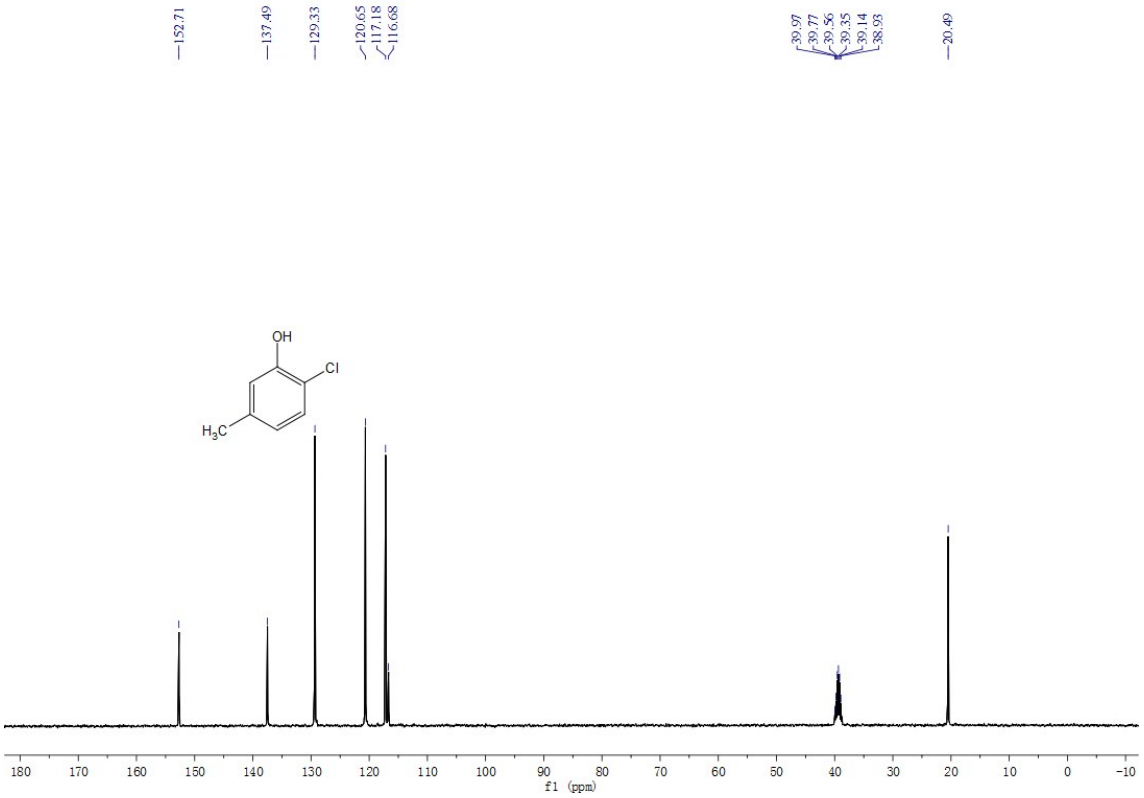

Fig. 20 The **^{13}C NMR** spectra of **2j**

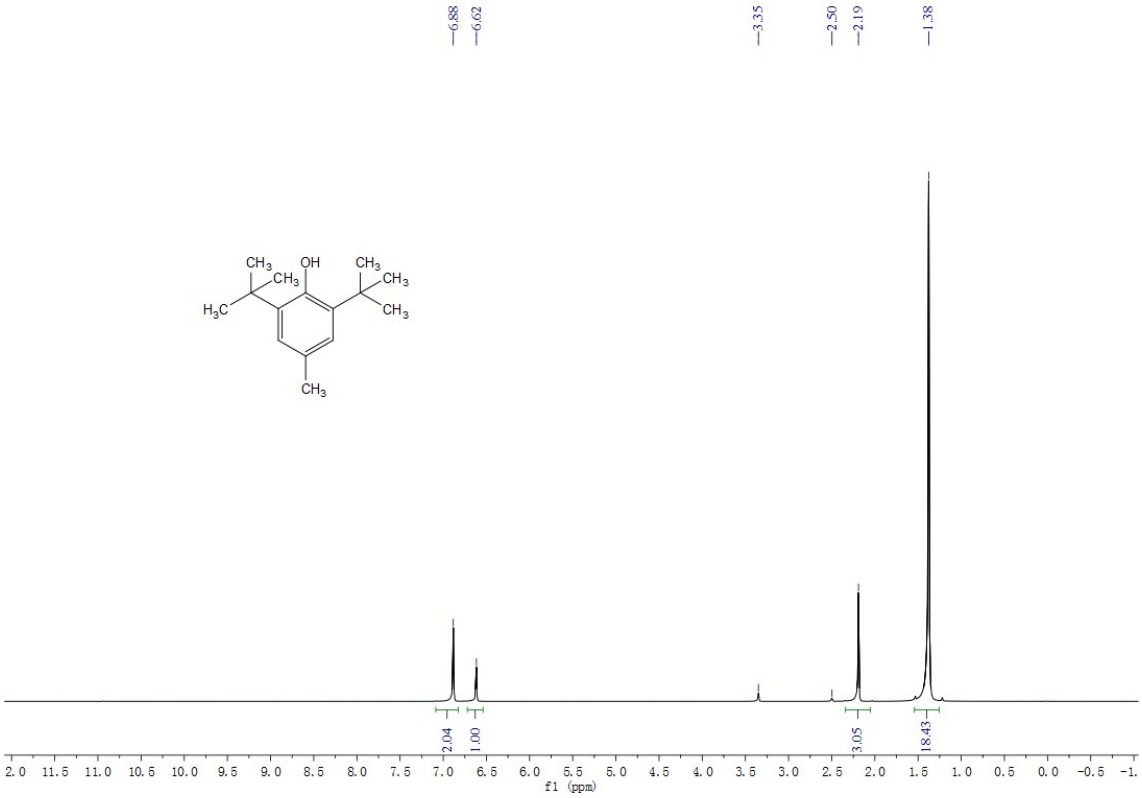

Fig. 21 The **^{1}H NMR** spectra of **2k**

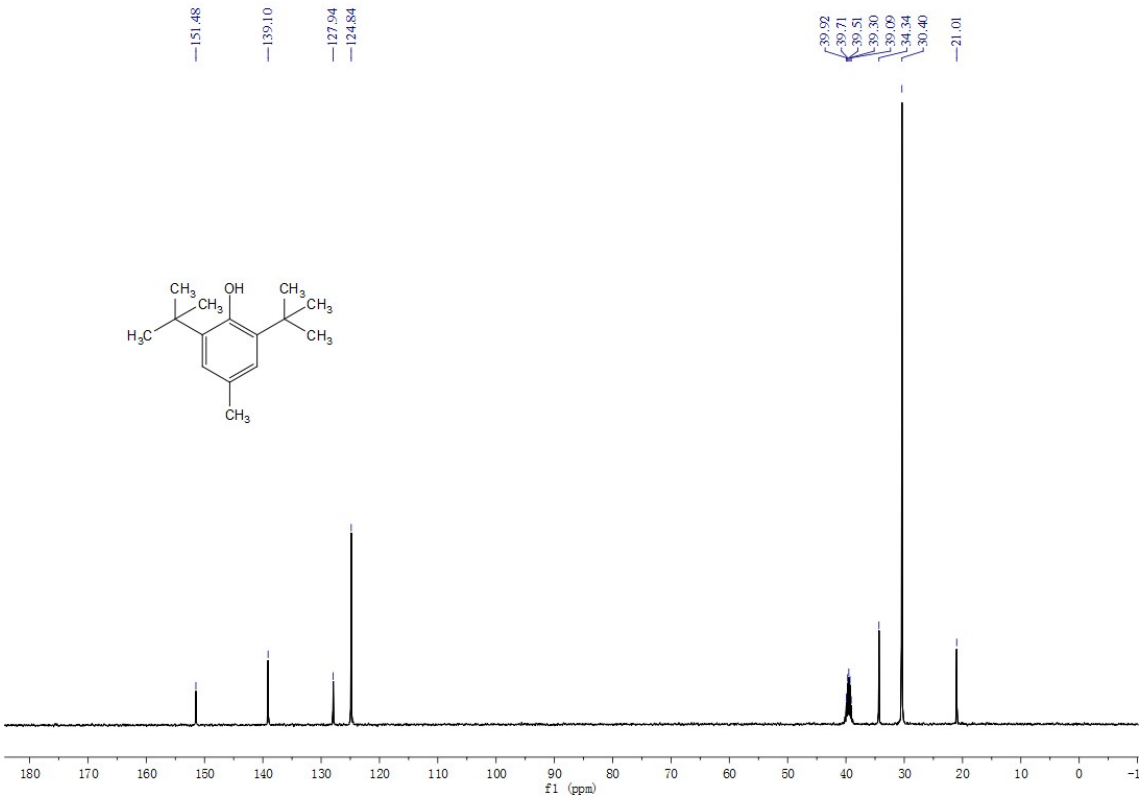

Fig. 22 The **^{13}C NMR** spectra of **2k**

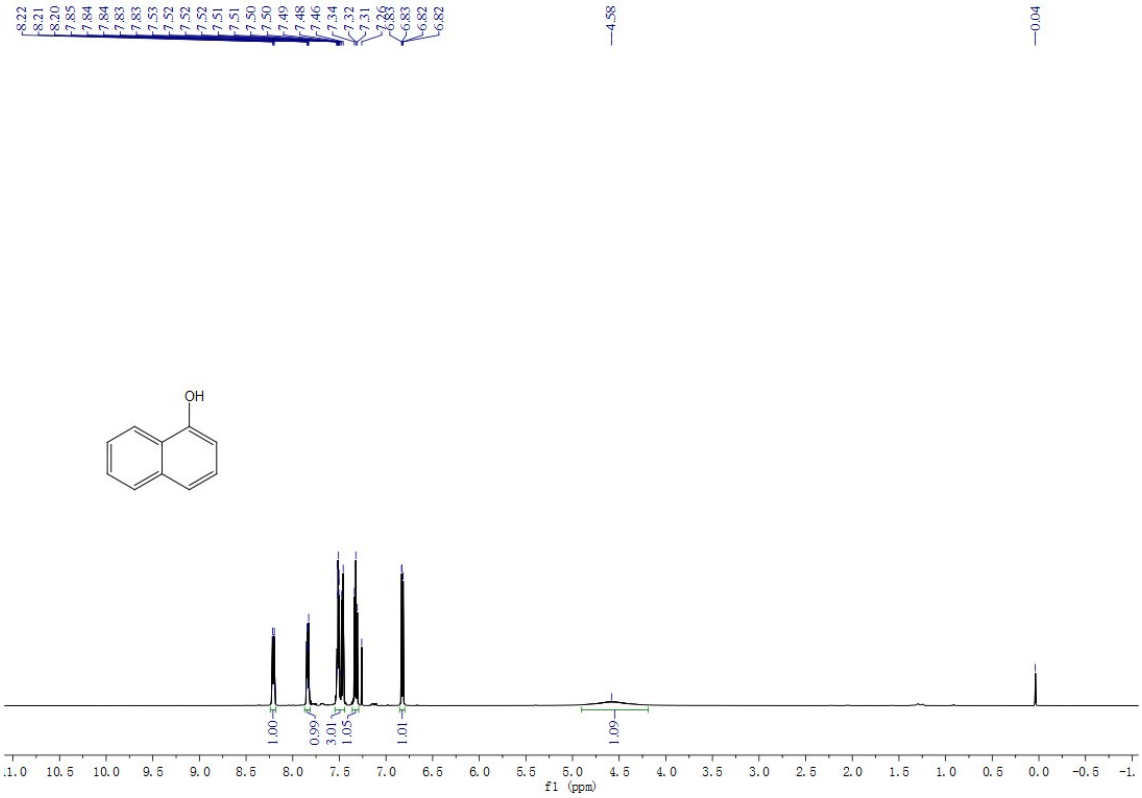

Fig. 23 The **^{1}H NMR** spectra of **2l**

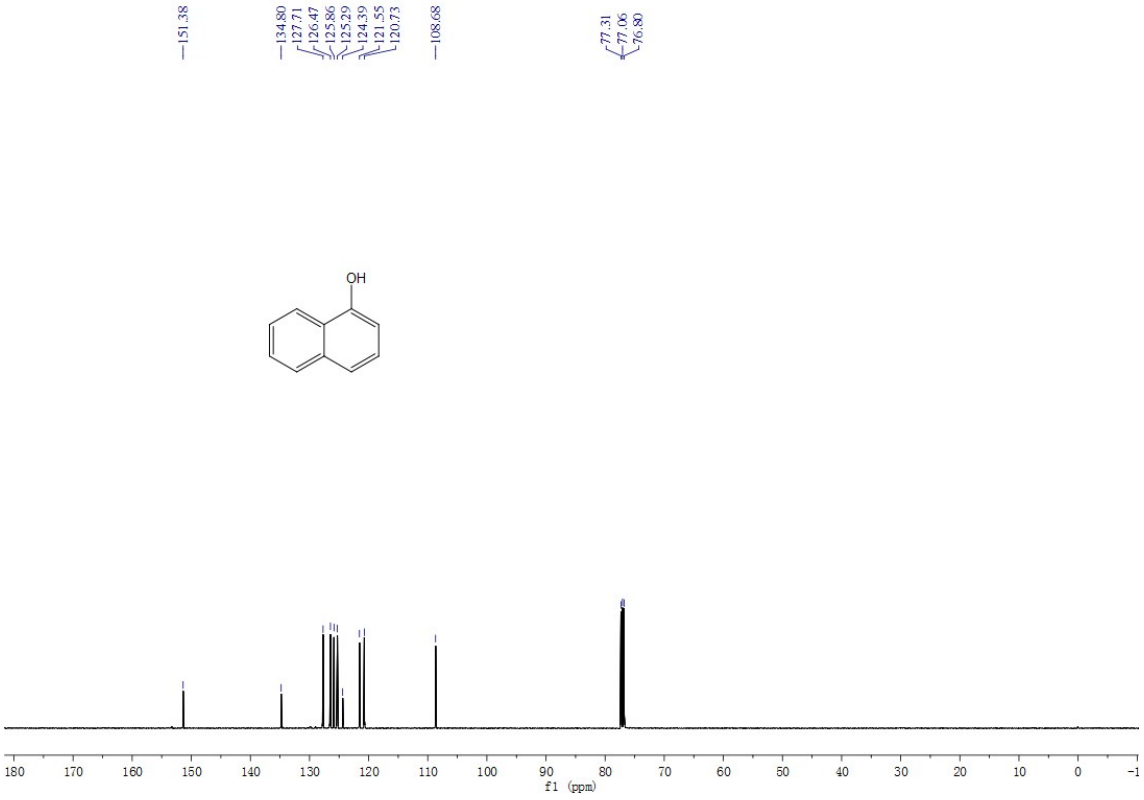

Fig. 24 The ^{13}C **NMR** spectra of **2l**

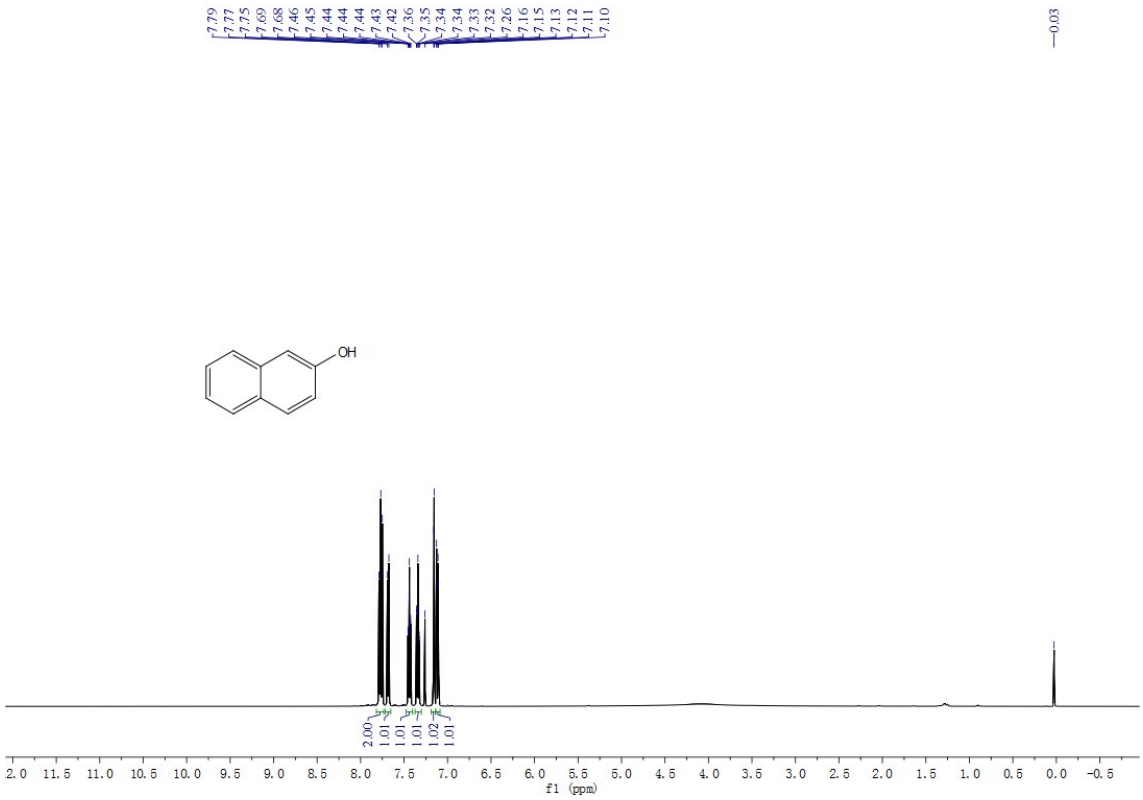

Fig. 25 The **^{1}H NMR** spectra of **2m**

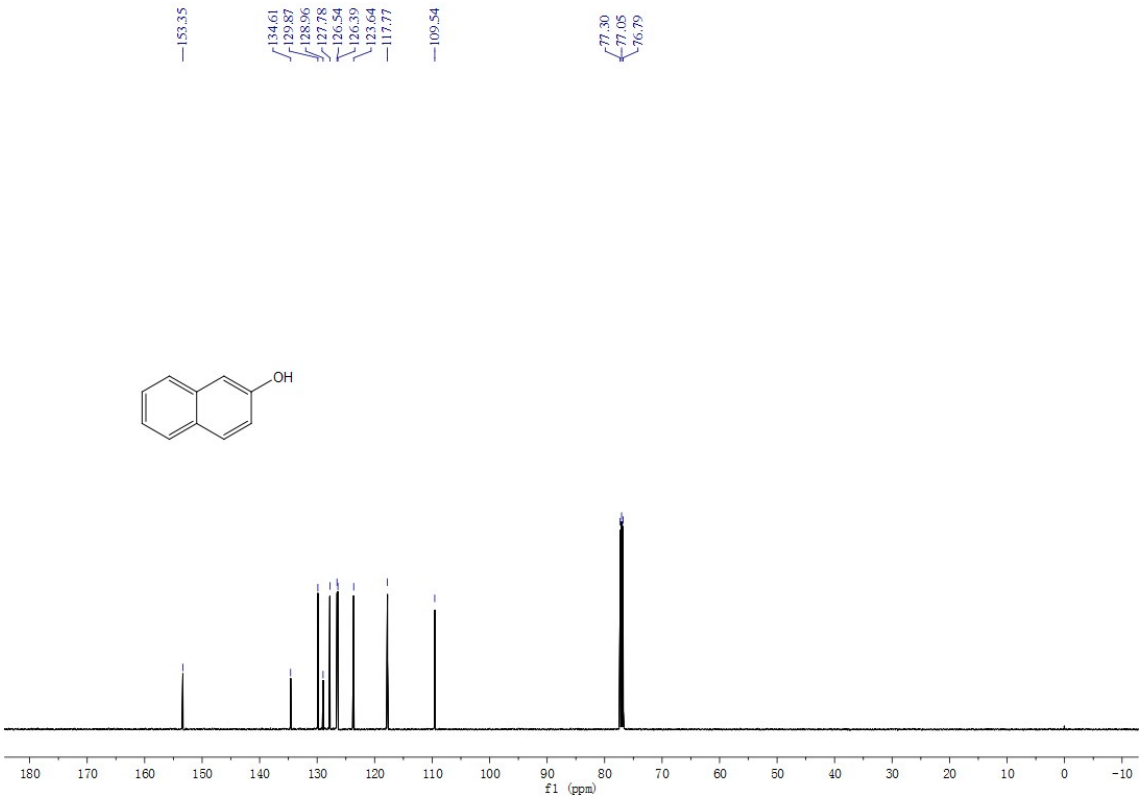

Fig. 26 The **^{13}C NMR** spectra of **2m**

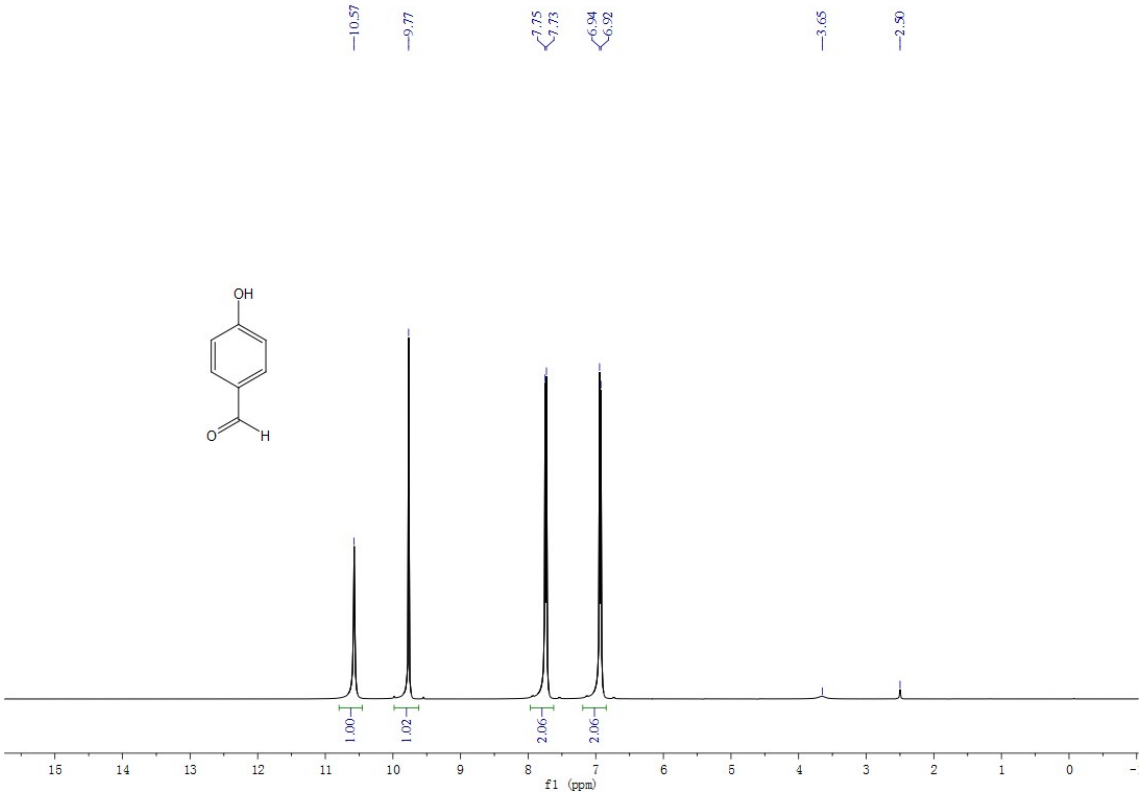

Fig. 27 The **^{1}H NMR** spectra of **2n**

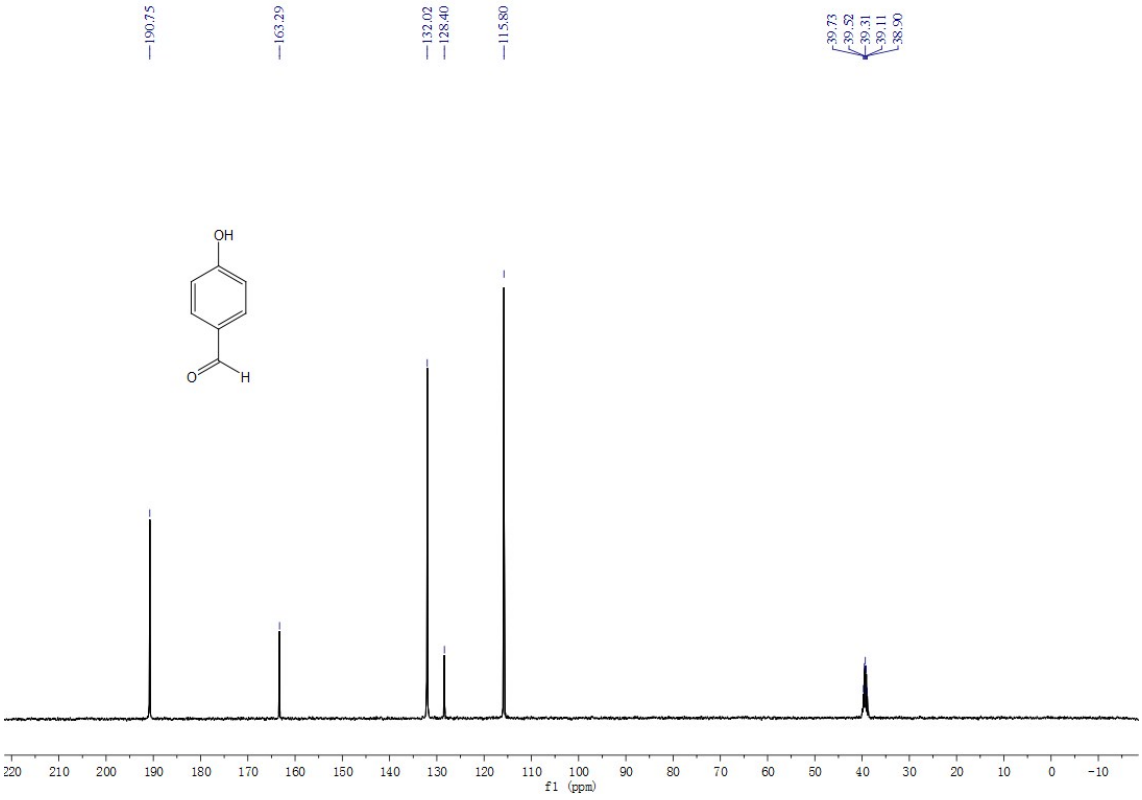

Fig. 28 The **^{13}C NMR** spectra of **2n**

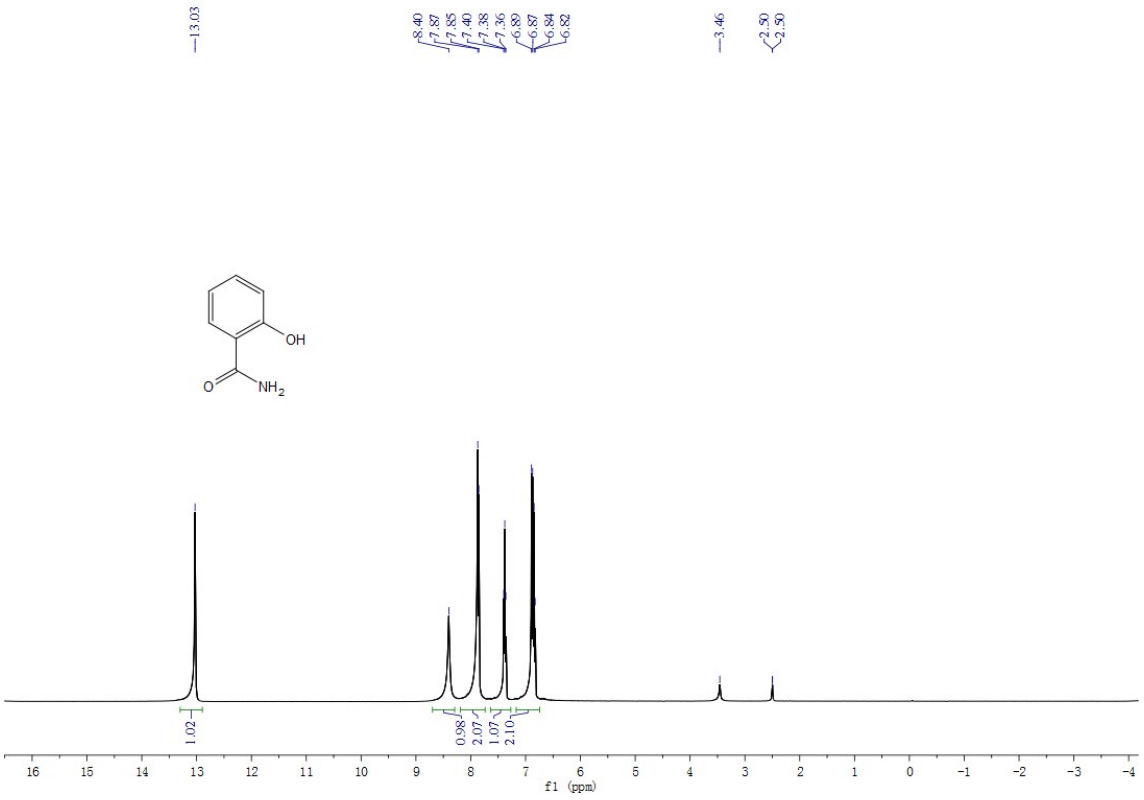

Fig. 29 The **^{1}H NMR** spectra of **2o**

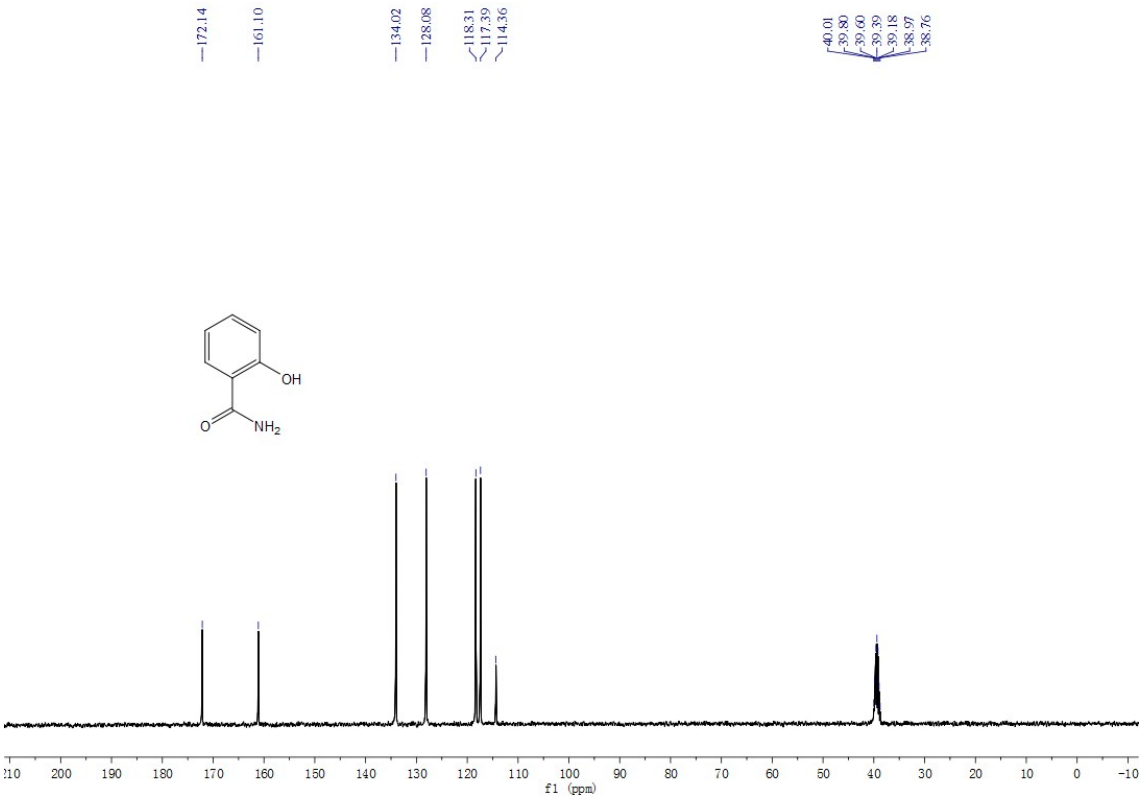

Fig. 30 The **^{13}C NMR** spectra of **2o**

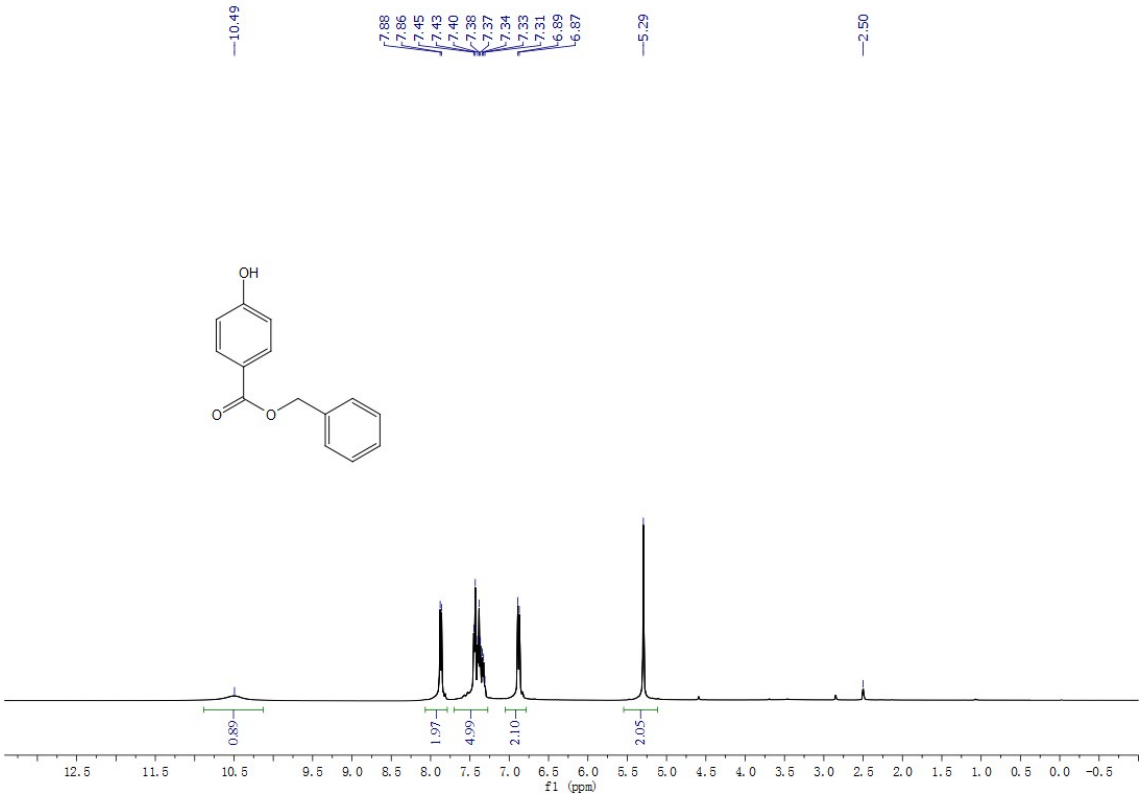

Fig. 31 The **^{1}H NMR** spectra of **2p**

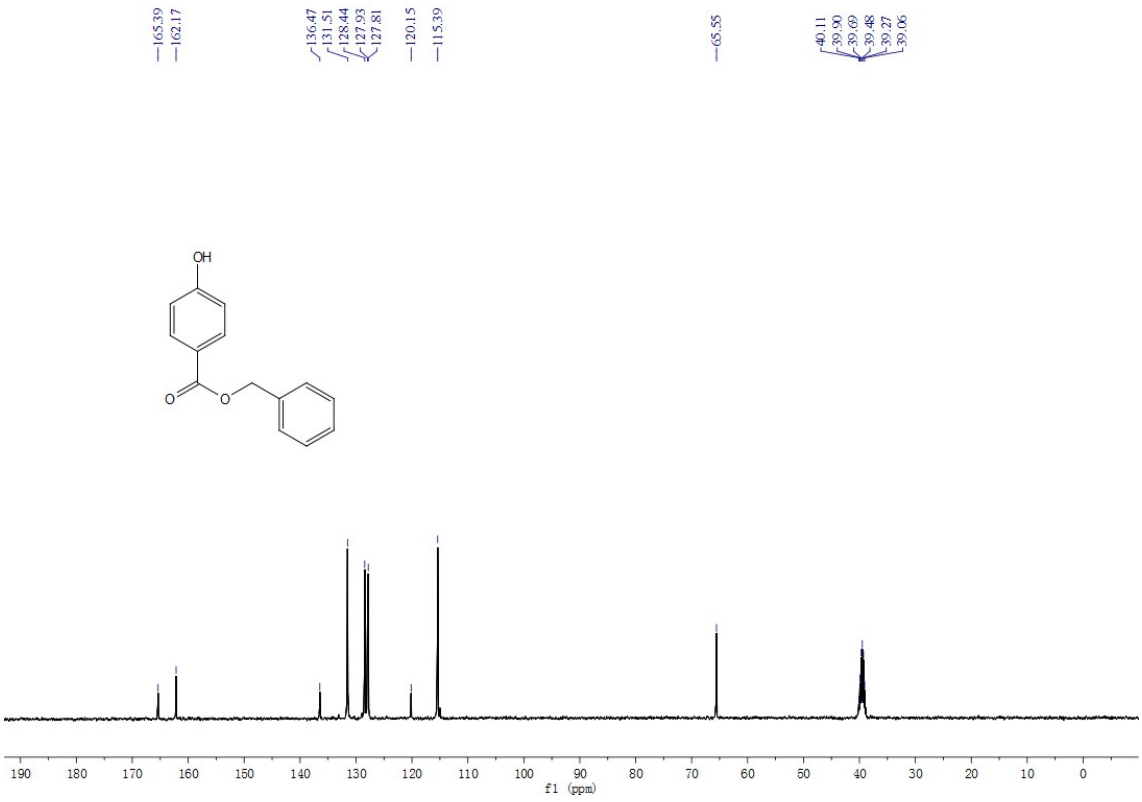

Fig. 32 The **^{13}C NMR** spectra of **2p**

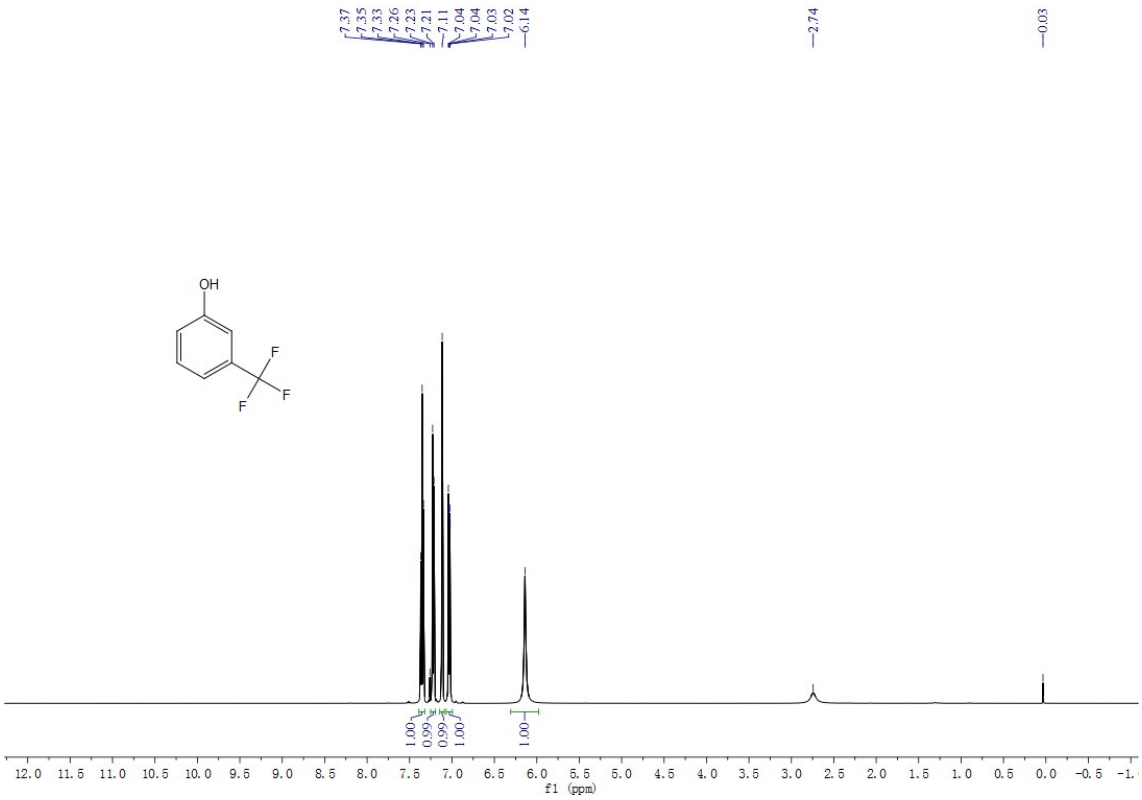

Fig. 33 The **^{1}H NMR** spectra of **2q**

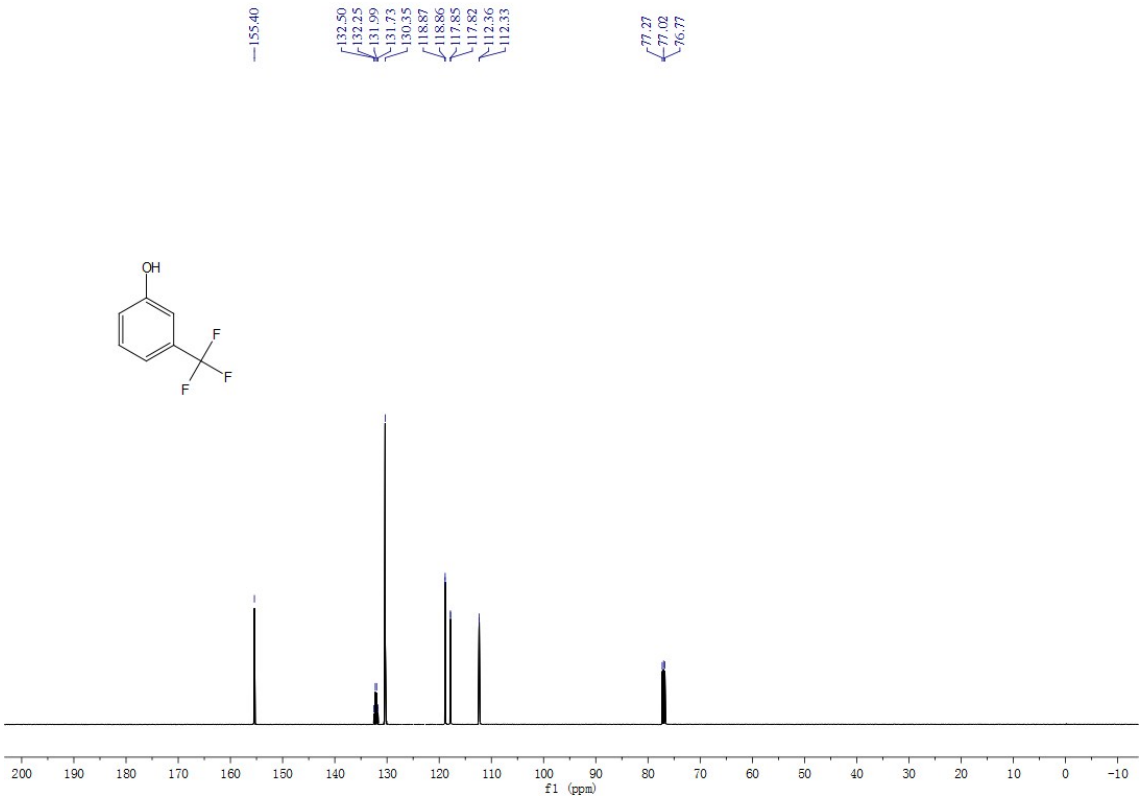

Fig. 34 The **^{13}C NMR** spectra of **2q**

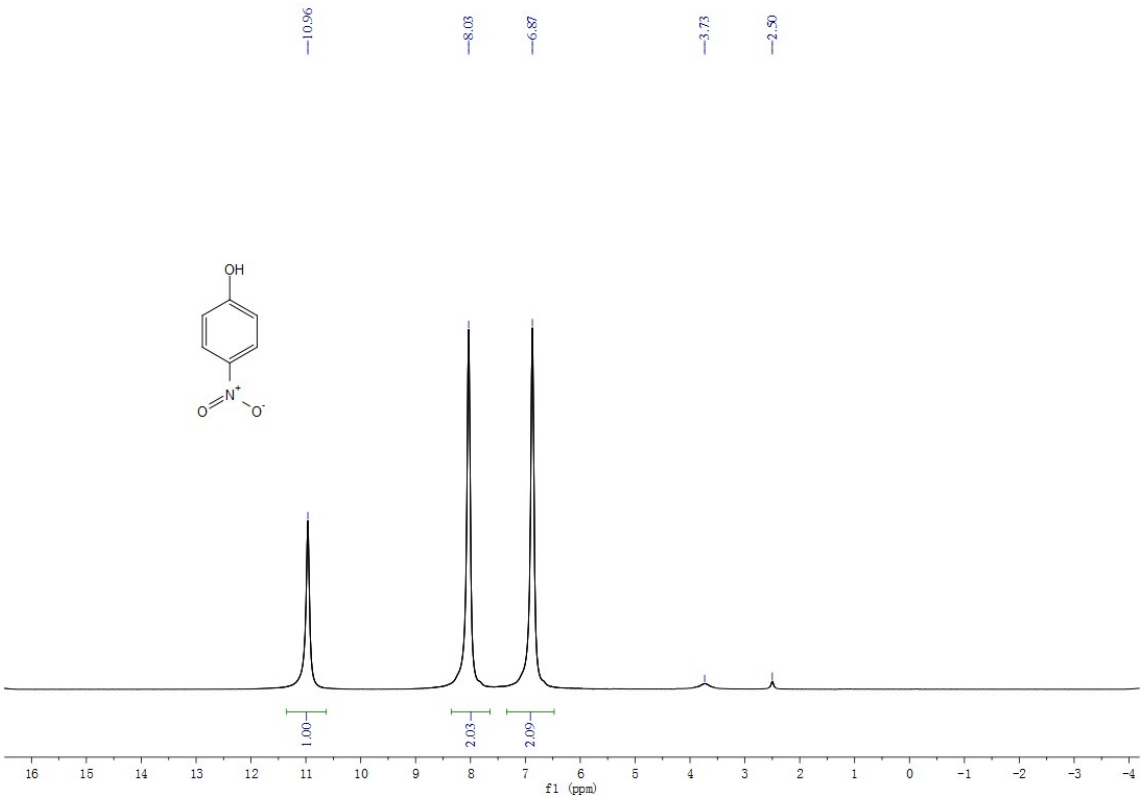

Fig. 35 The **^{1}H NMR** spectra of **2r**

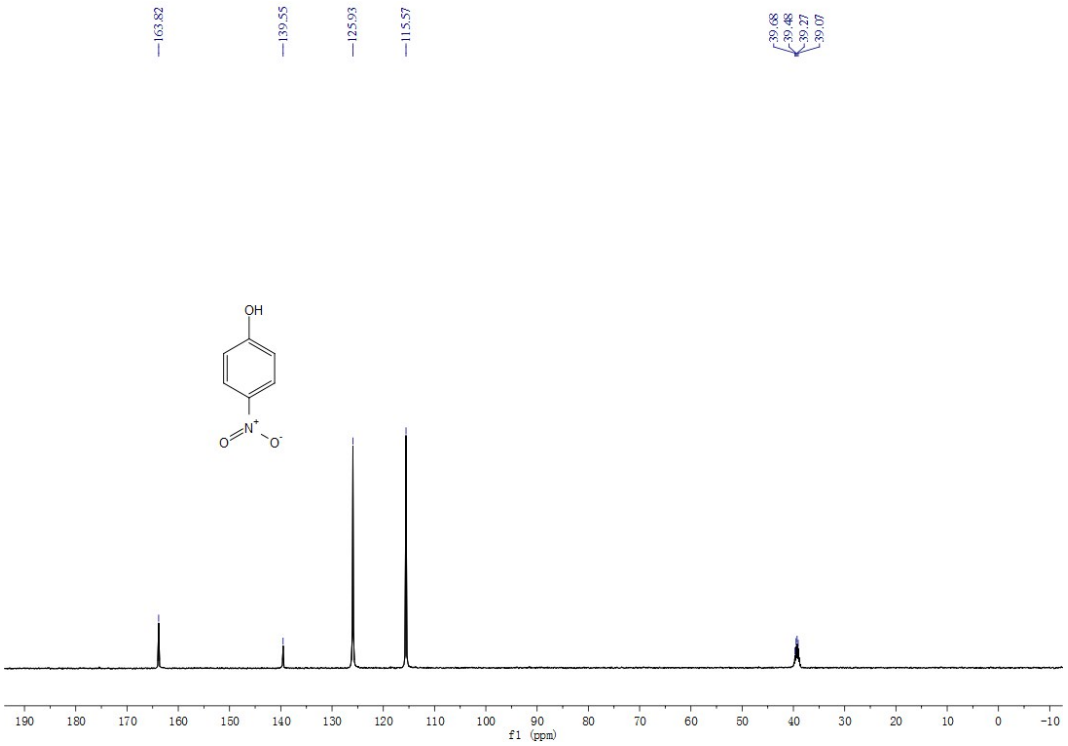

Fig. 36 The **^{13}C NMR** spectra of **2r**

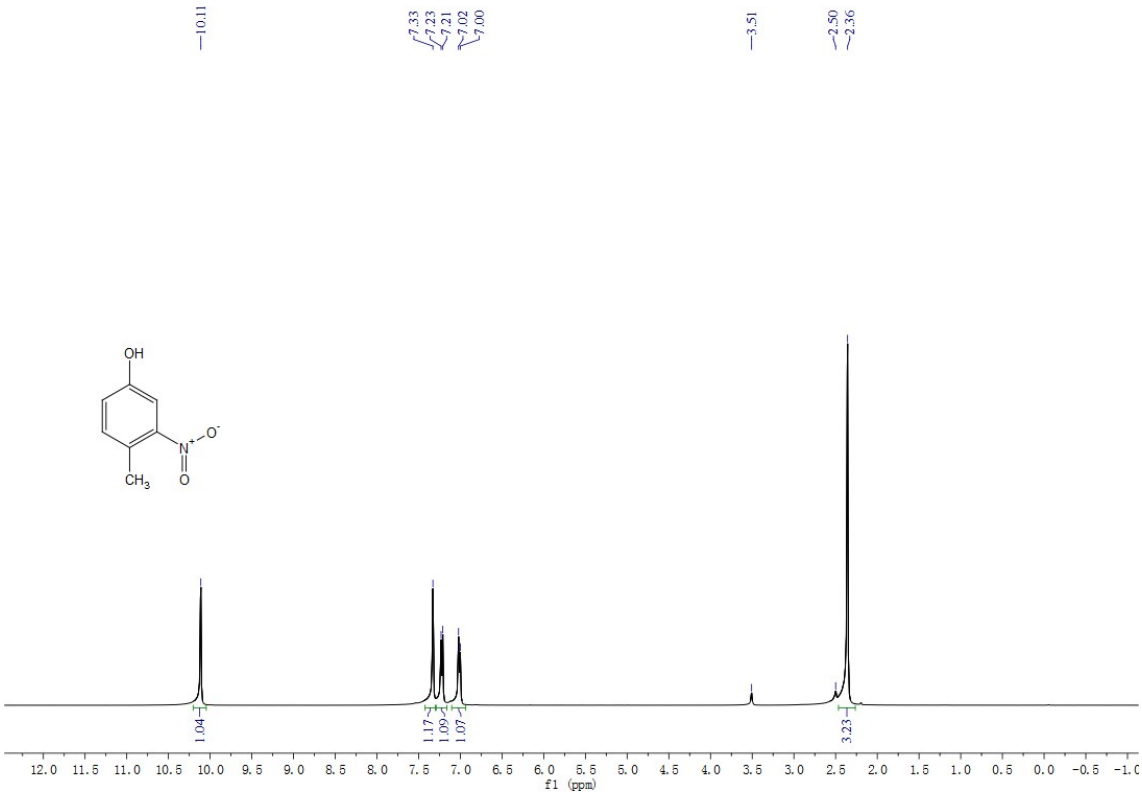

Fig. 37 The **^{1}H NMR** spectra of **2s**

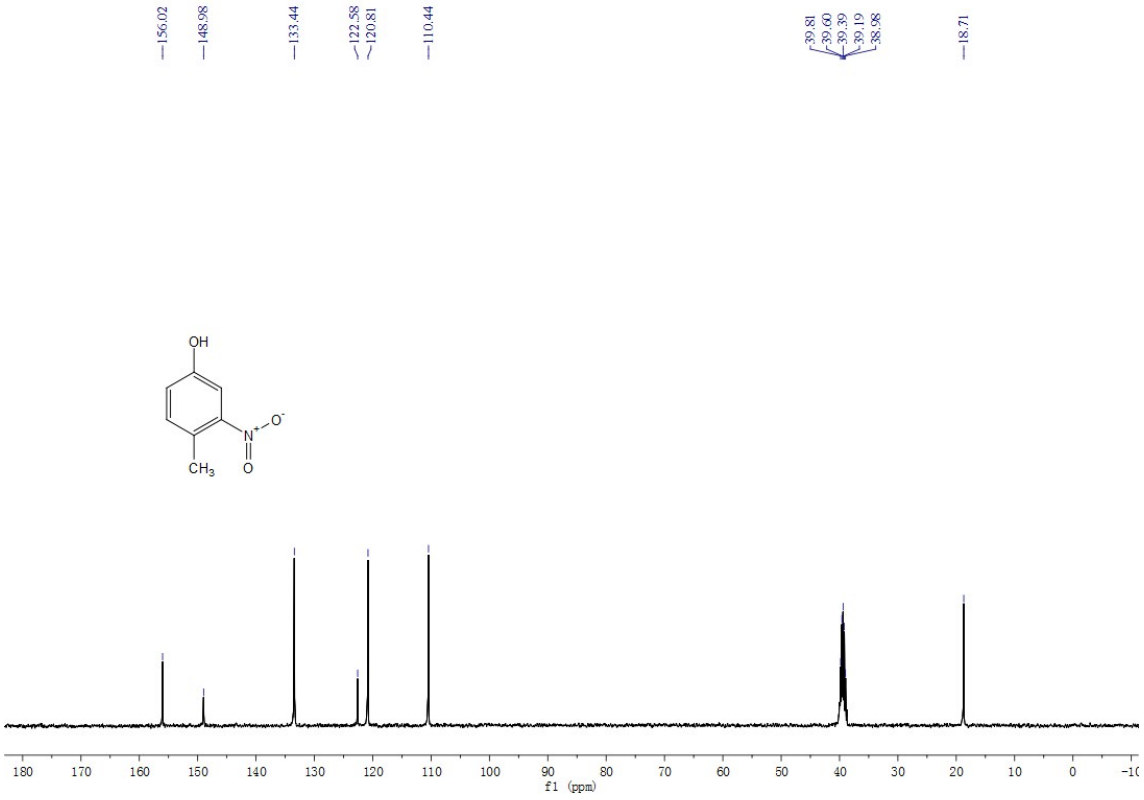

Fig. 38 The **^{13}C NMR** spectra of **2s**

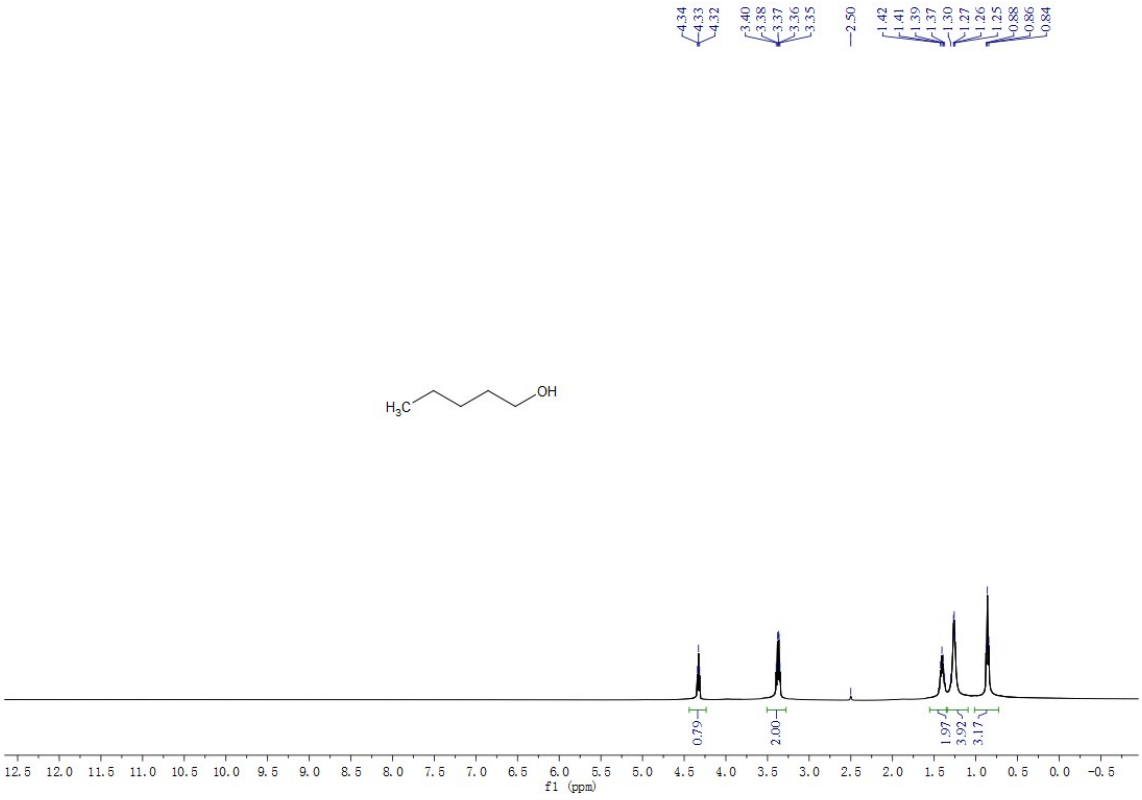

Fig. 39 The **^{1}H NMR** spectra of **2t**

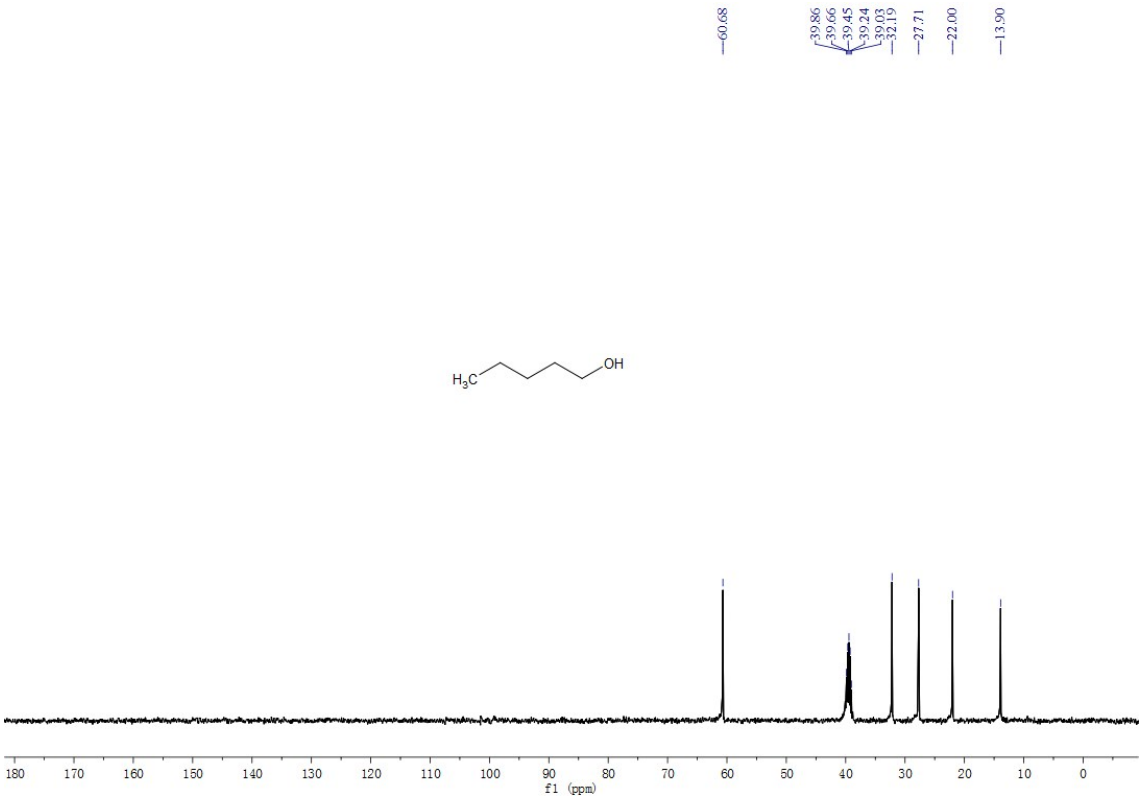

Fig. 40 The **^{13}C NMR** spectra of **2t**