Supplementary Materials

Rhodium(III)-catalyzed Redox-neutral [3+3] Annulation of *N*-Nitrosoanilines with Cyclopropenones: a Traceless Approach to Quinolin-4(1*H*)-one Scaffolds

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1. Control Experiments for the Mechanistic Studies

(a) H/D exchange of *N-nitrosoanilines* (1a) under CH_3OD/Rh(III) catalytical system.

To an oven-dried sealed tube charged with *N*-nitrosoaniline (**1a**) (27.3 mg, 0.20 mmol) and $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %), CH_3OD (0.1 mL) and $AgBF_4$ (39.0 mg, 0.20 mmol), DCE (10 mL) was added under argon atmosphere. The reaction mixture was then allowed to stir at 100 ℃ for 1 h. The corresponding reaction mixture was filtered through a pad of celite, washed with DCM and concentrated under reduced pressure. The deuterium incorporation *d*$_2$-**1a** was determined to be <5% by ^{1}H NMR method (**Figure S1**).

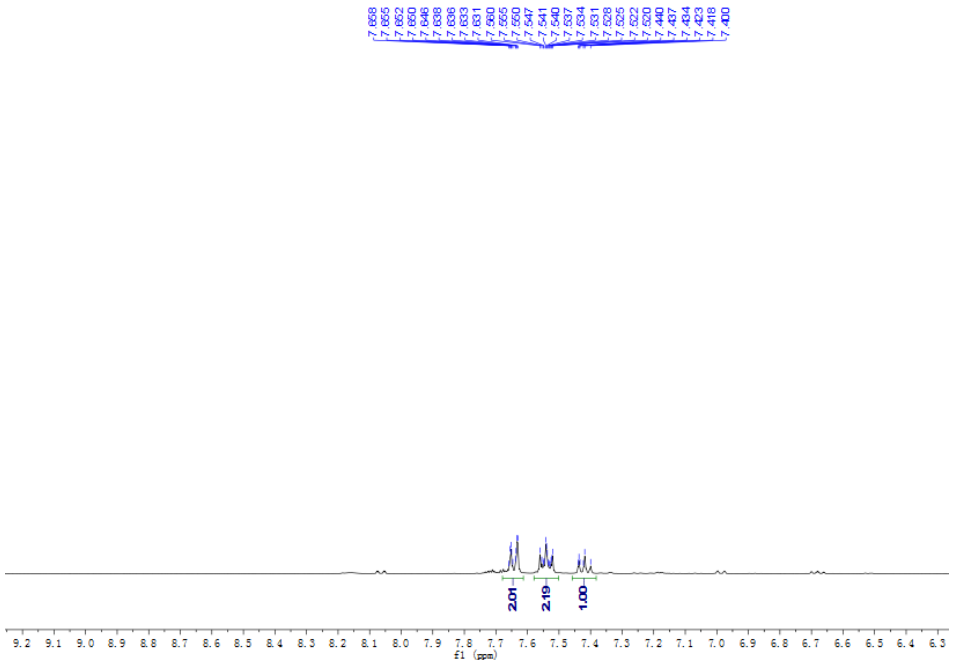


Figure S1. The ^{1}H NMR spectra of *d*$_2$-1a

(b) Kinetic isotope effect of the transformation

Compound *d*$_5$-**1a** (27.3 mg, 0.20 mmol), **1a** (27.3 mg, 0.20 mmol), 2a (43.6 mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %) and $AgBF_4$ (39.0 mg, 0.20 mmol) was combined in a 30 mL dried sealed tube under argon atmosphere. The reaction mixture was magnetically stirred and heated to 100 ℃ for 10 min, then the corresponding reaction mixture was filtered through a pad of celite, washed with DCM and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/dichloromethane/petroleum ether as eluent to afford the desired products **3a** and *d*$_4$-**3a** as yellow solid. The deuterium incorporation was determined to be $k_H/k_D = 1.7$ by ^{1}H NMR method (**Figure S2**).

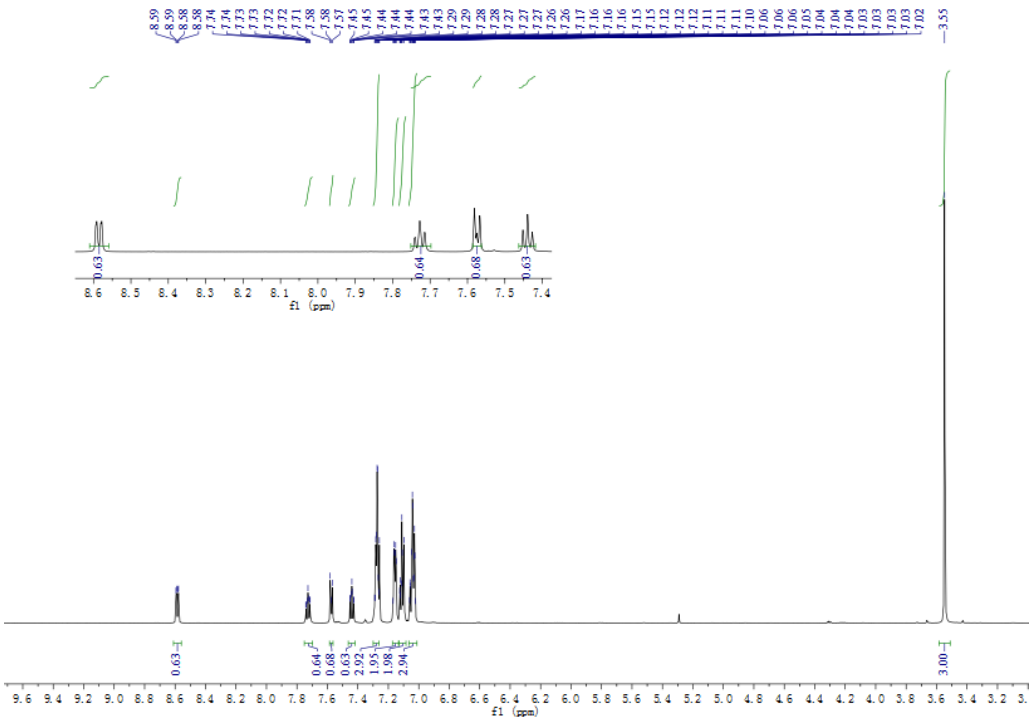


Figure S2. The conversion of 1a and d_5-1a was monitored by ^{1}H-NMR method

(c) Intermolecular competition experiments between 1d and 1k

N-methyl-*N*-(4-methylphenyl)nitrous amide (**1b**) (30.0 mg, 0.20 mmol), *N*-methyl-*N*-(4-(trifluoromethyl)phenyl)nitrous amide (**1e**) (40.8 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %), $AgBF_4$ (39.0 mg, 0.20 mmol), DCE (10 mL) and diphenylcyclopropenone (**2a**) (61.8 mg, 0.30 mmol) were added to a 35 mL Schlenk tube under Ar. The mixture was stirred at 100 ℃ for 30 min. After cooling to ambient temperature, the corresponding reaction mixture was washed with DCM and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the final products **3d** and **3k**.

2. X-ray Crystallographic Data

X-ray Single Crystal Structure Analysis of **3a**

X-ray crystallographic data of **3a** was solutions at T = 173 K：$C_{22}H_{17}NO$，*Mr* = 311.36, monoclinic. Space group *P-1*, a = 11.8987 (5) Å, b = 8.1773 (3) Å, c = 16.9235 (8) Å, α = 90°, β = 100.020(2)°, γ = 90 °, *V* = 1621.53 (12) $Å^3$, *Z* = 4.

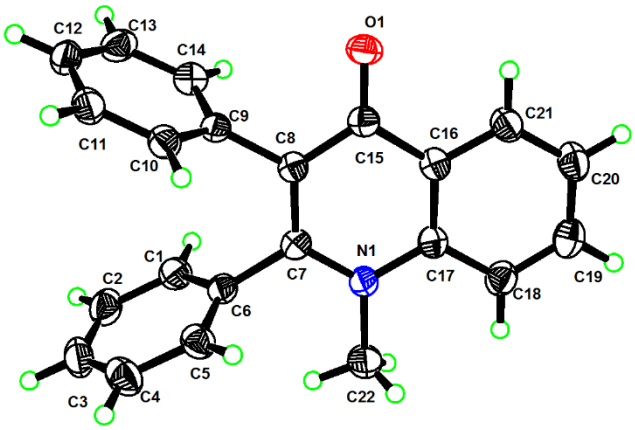
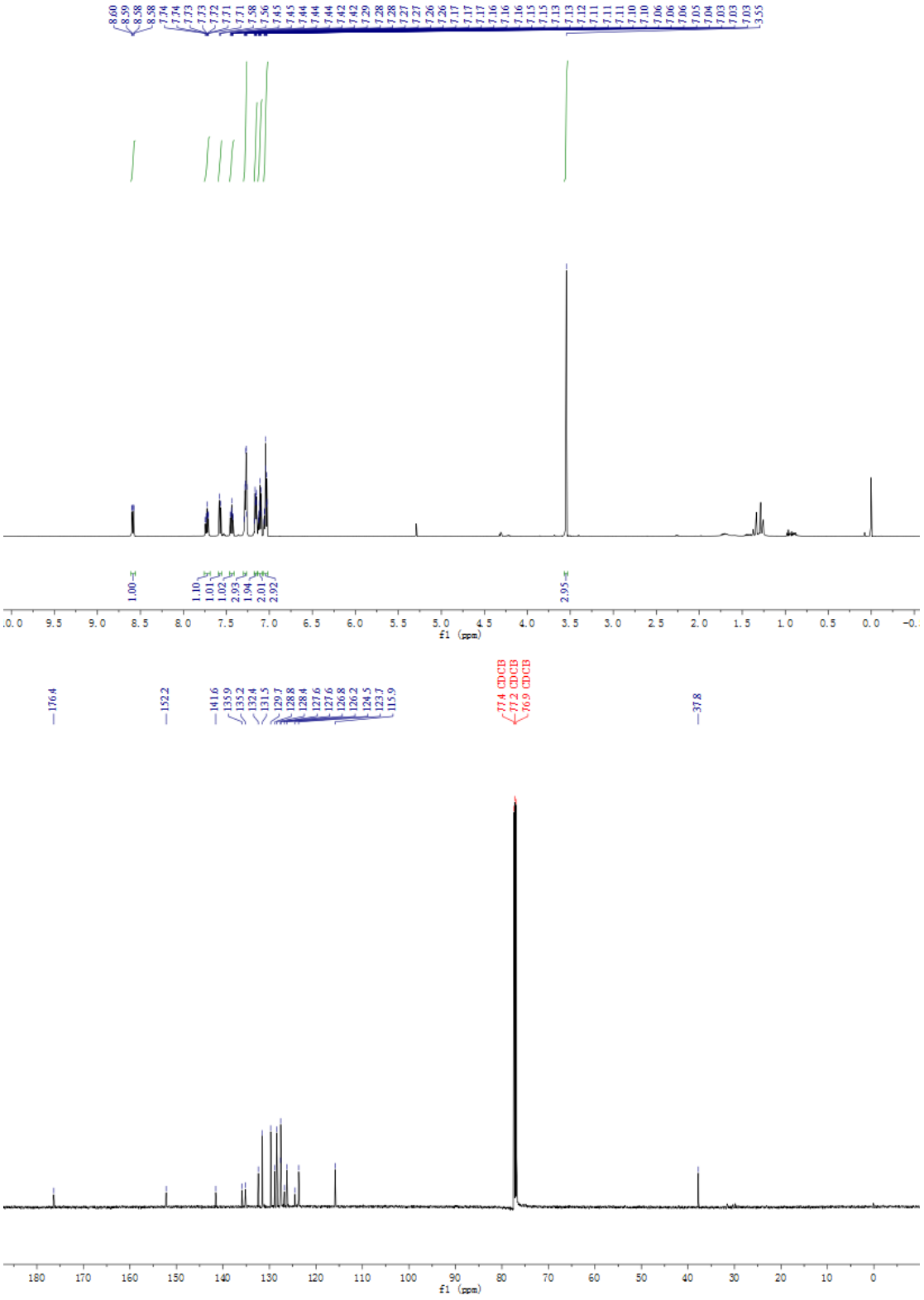


Figure S3: The crystal structure of **3a** by X-ray analysis.

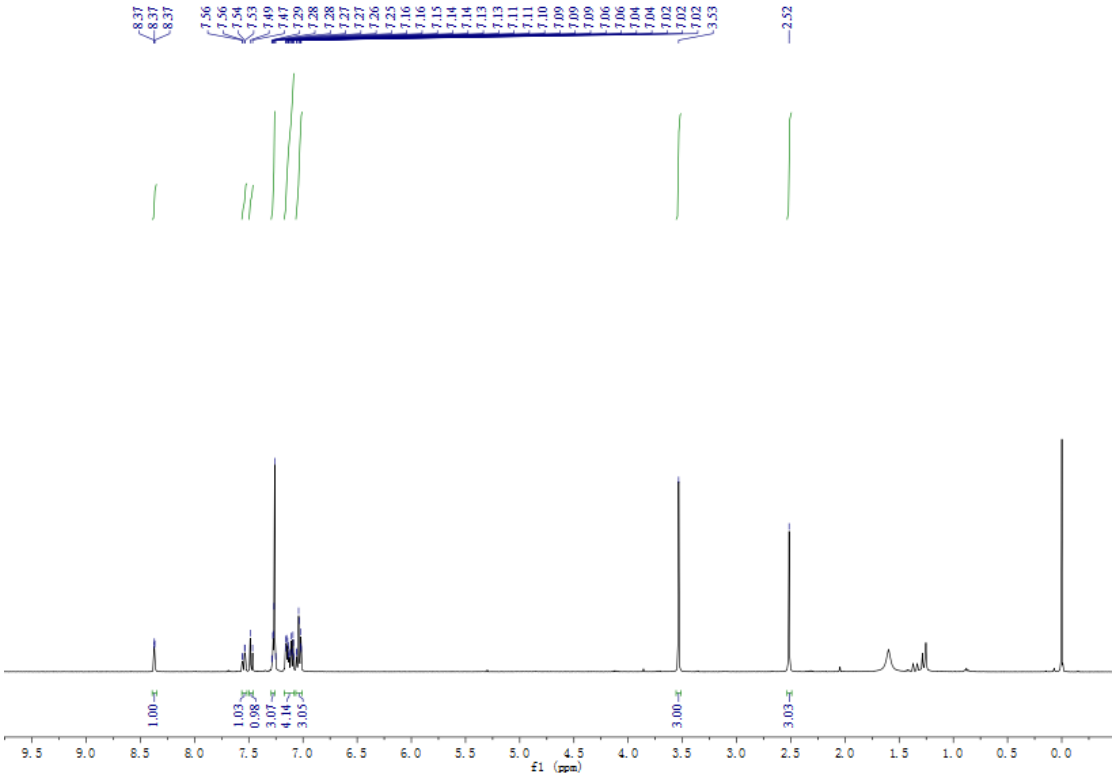
These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, the CCDC number is 1968674.

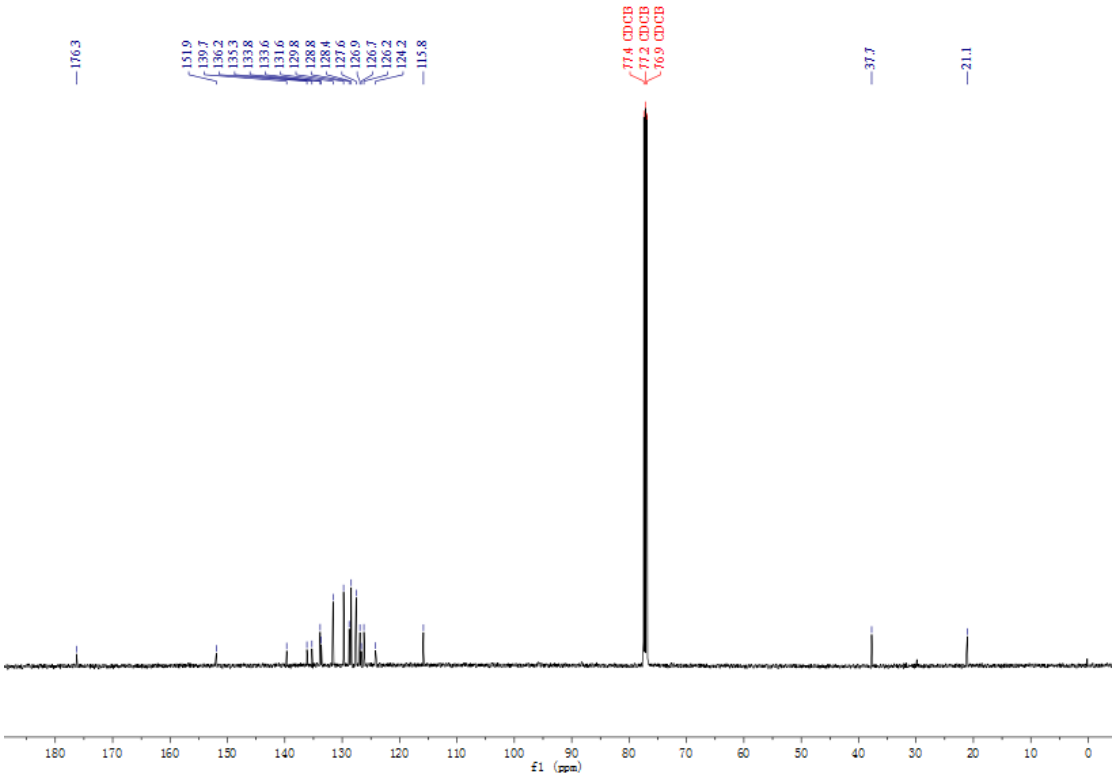
3. ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMRspectra

(1) The ^{1}H NMR and ^{13}C NMR spectrum for **3a**

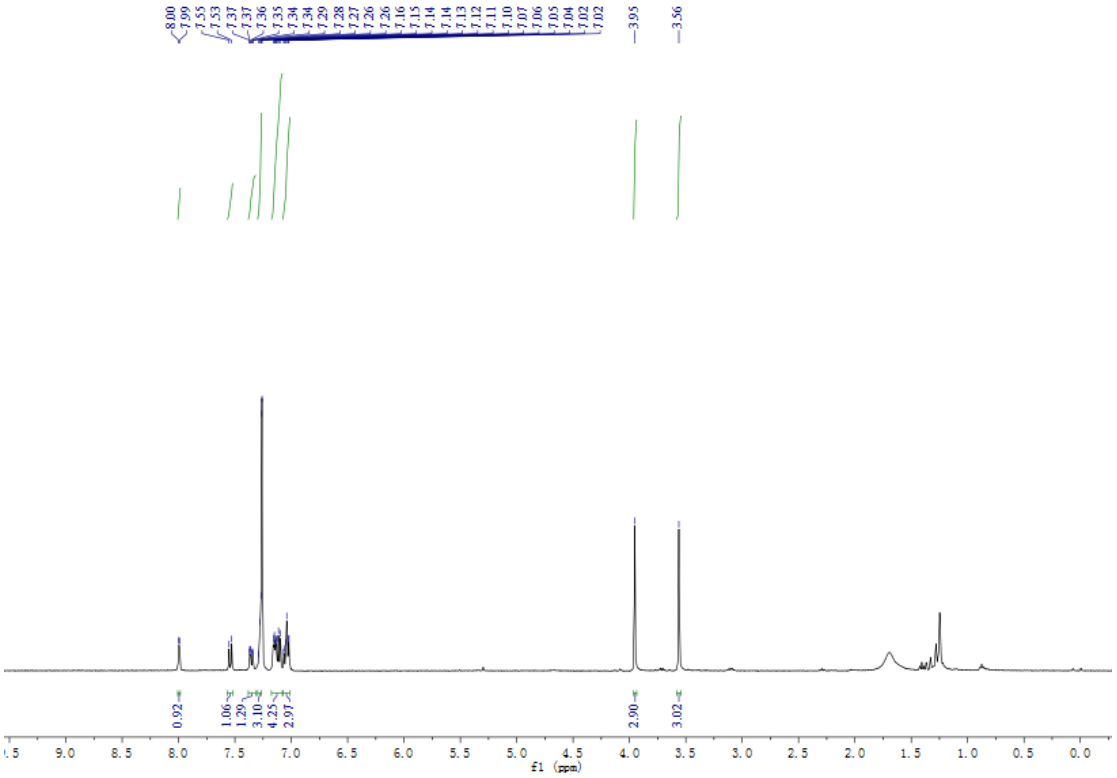


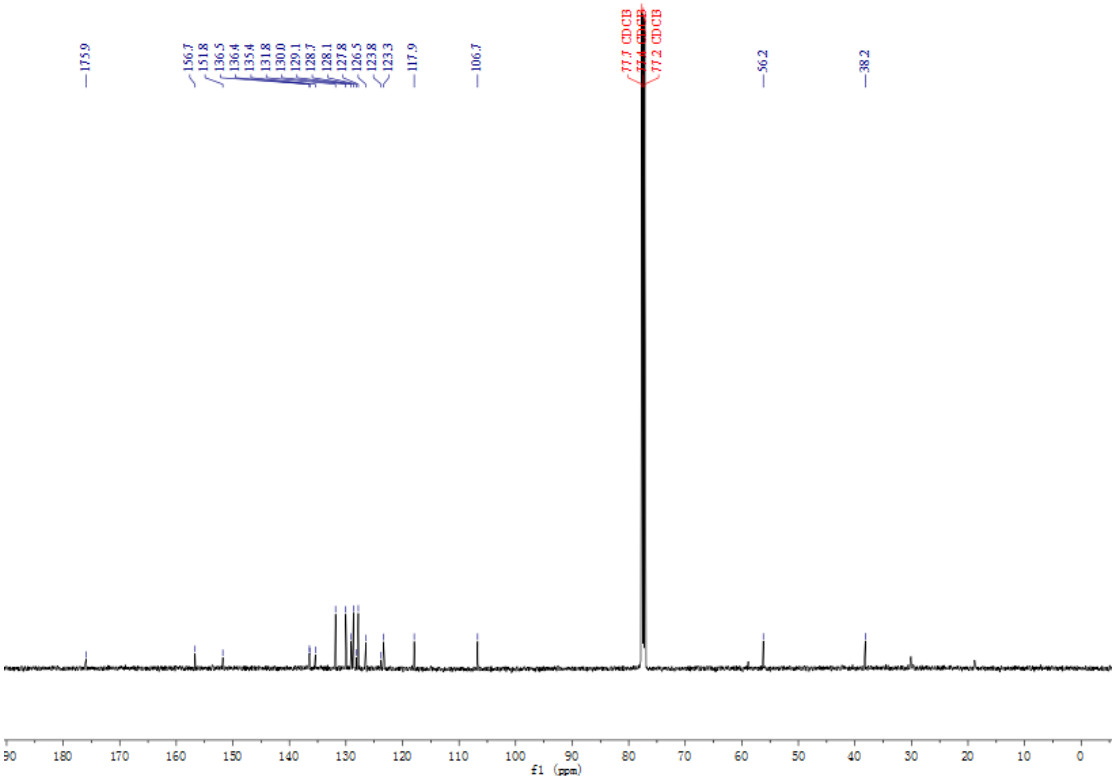
(2) The ^{1}H NMR and ^{13}C NMR spectrum for **3b**



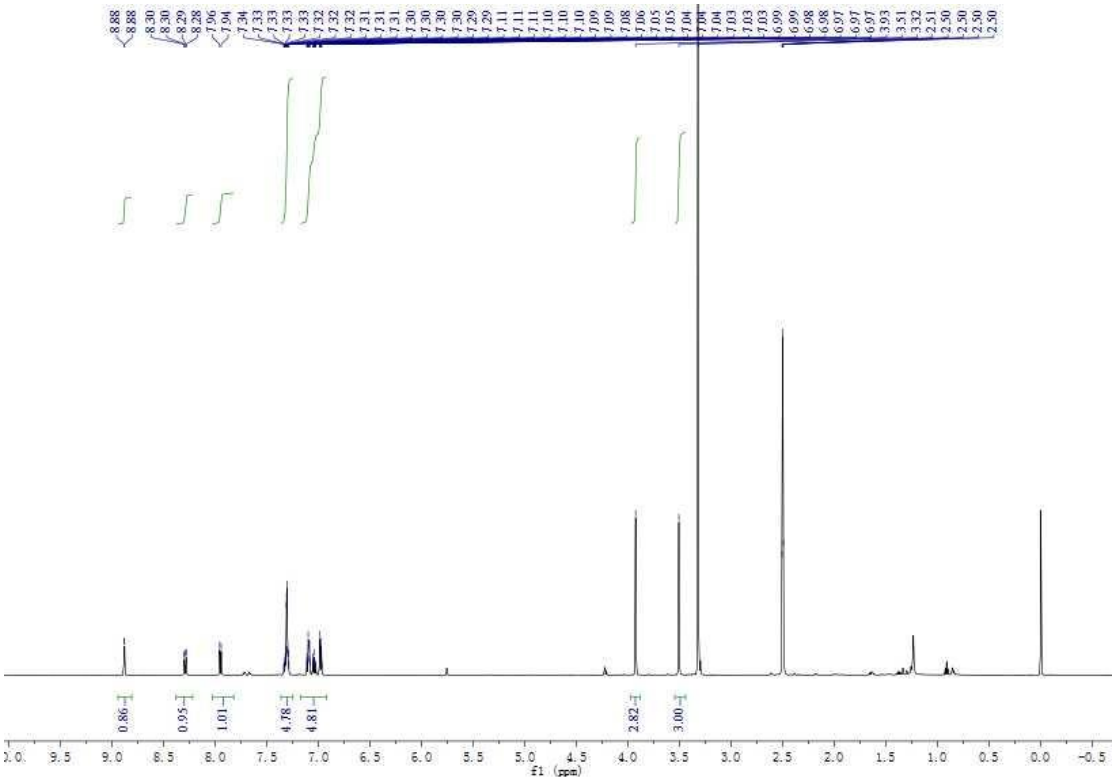


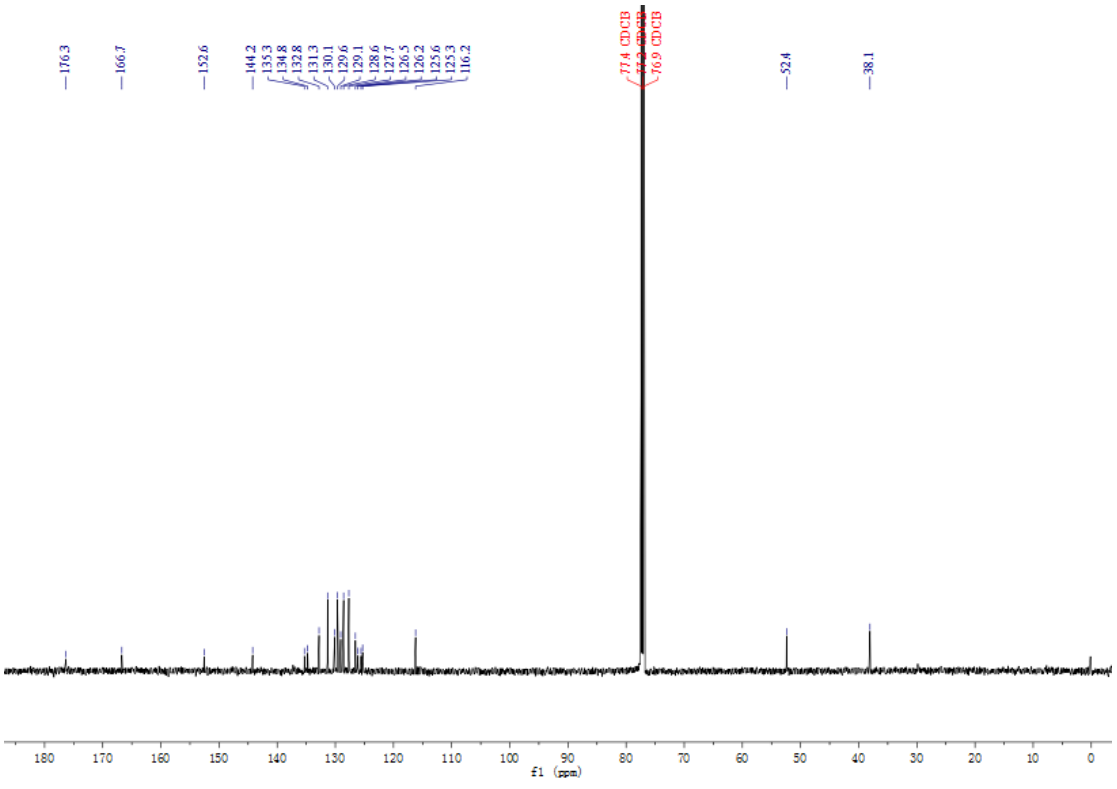
(3) The ^{1}H NMR and ^{13}C NMR spectrum for **3c**



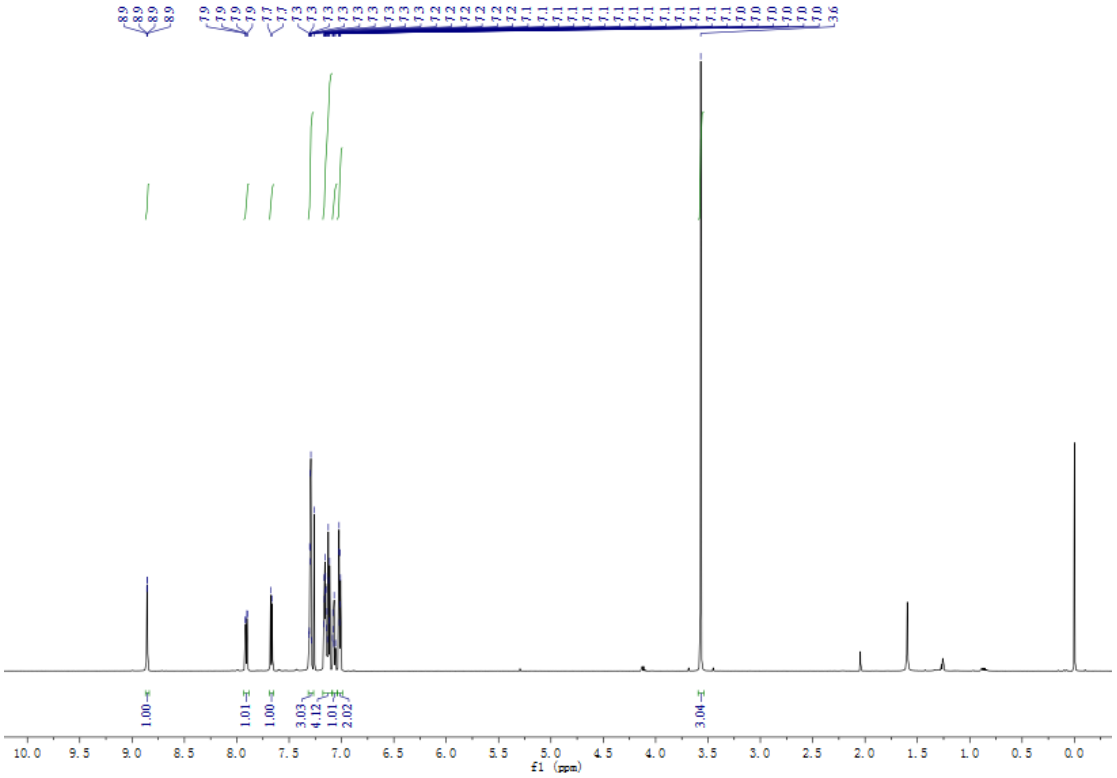


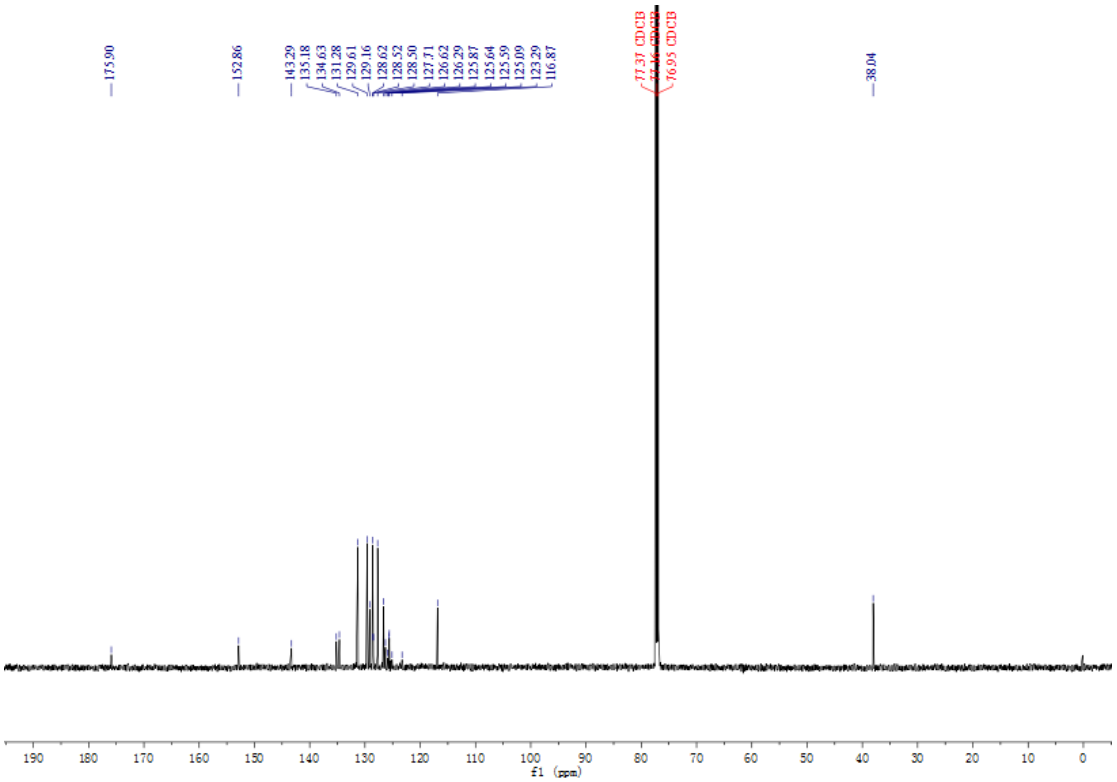
(4) The ^{1}H NMR and ^{13}C NMR spectrum for **3d**

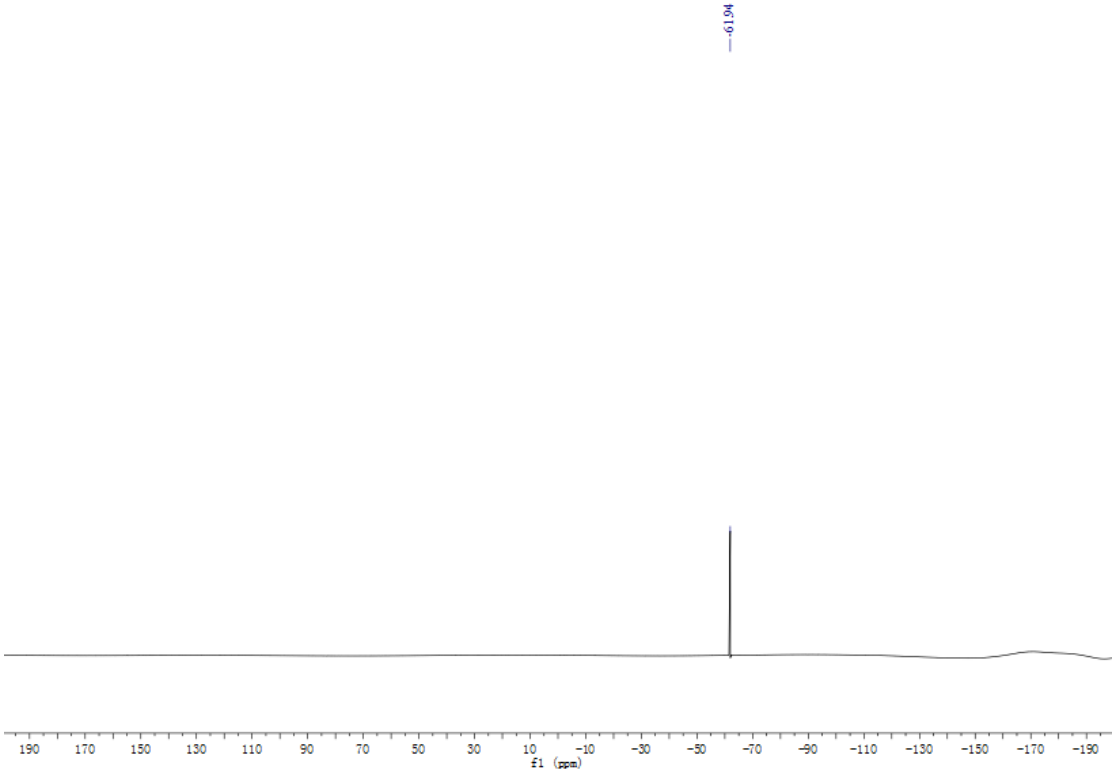




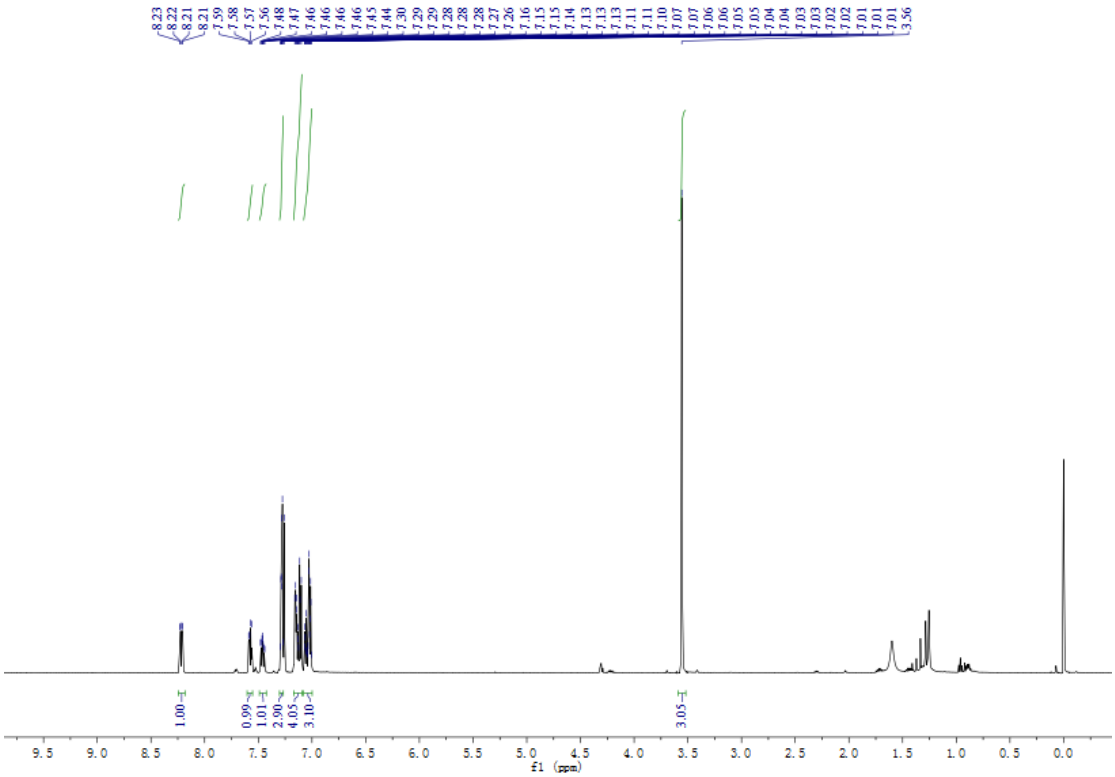
(5) The ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMRspectra for **3e**

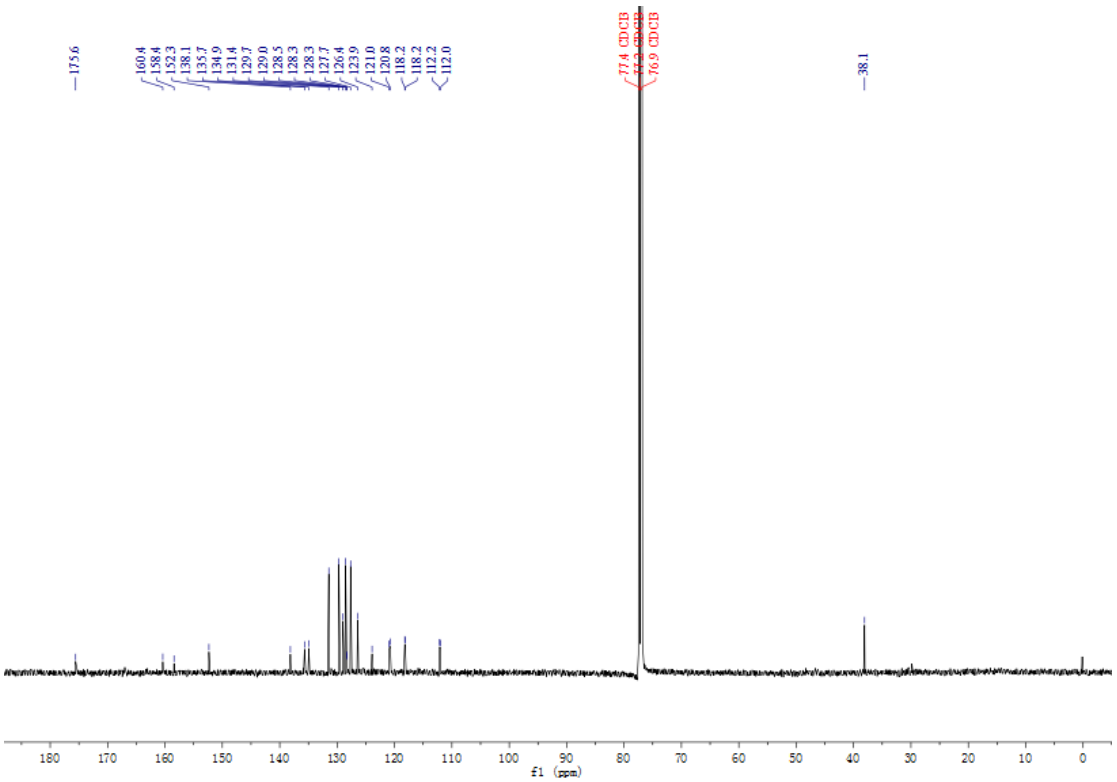






(6) The ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMRspectra for **3f**

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152.3
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135.7
134.9
131.4
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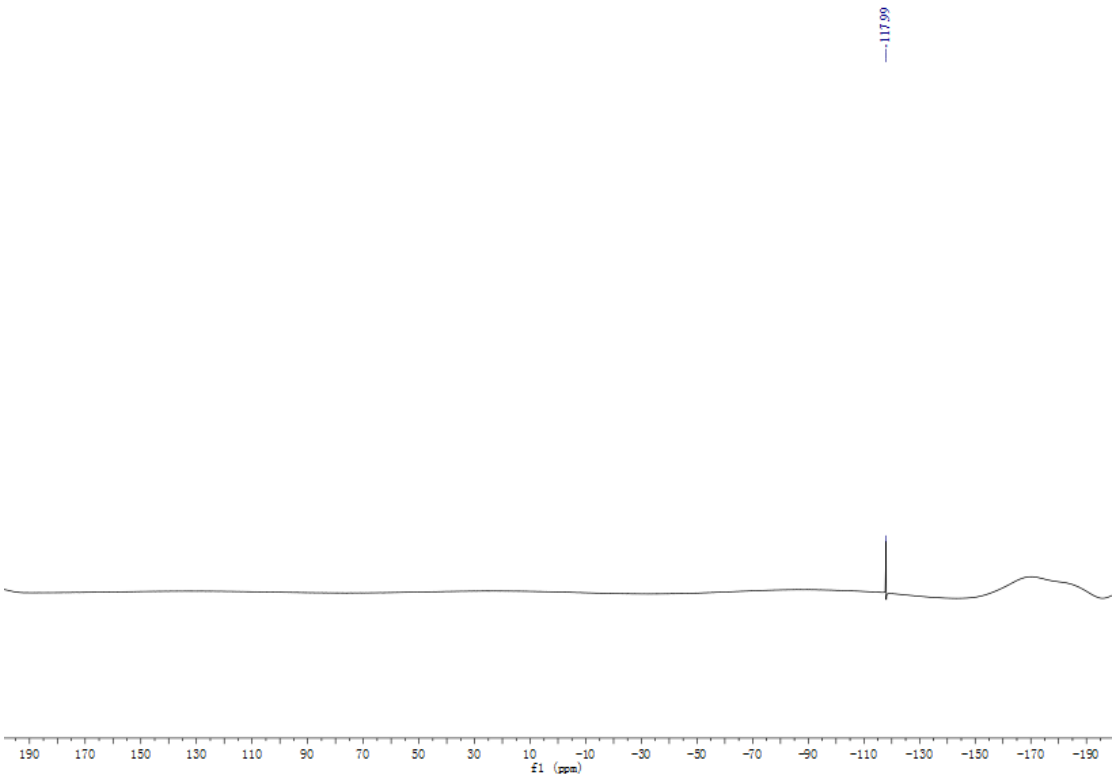
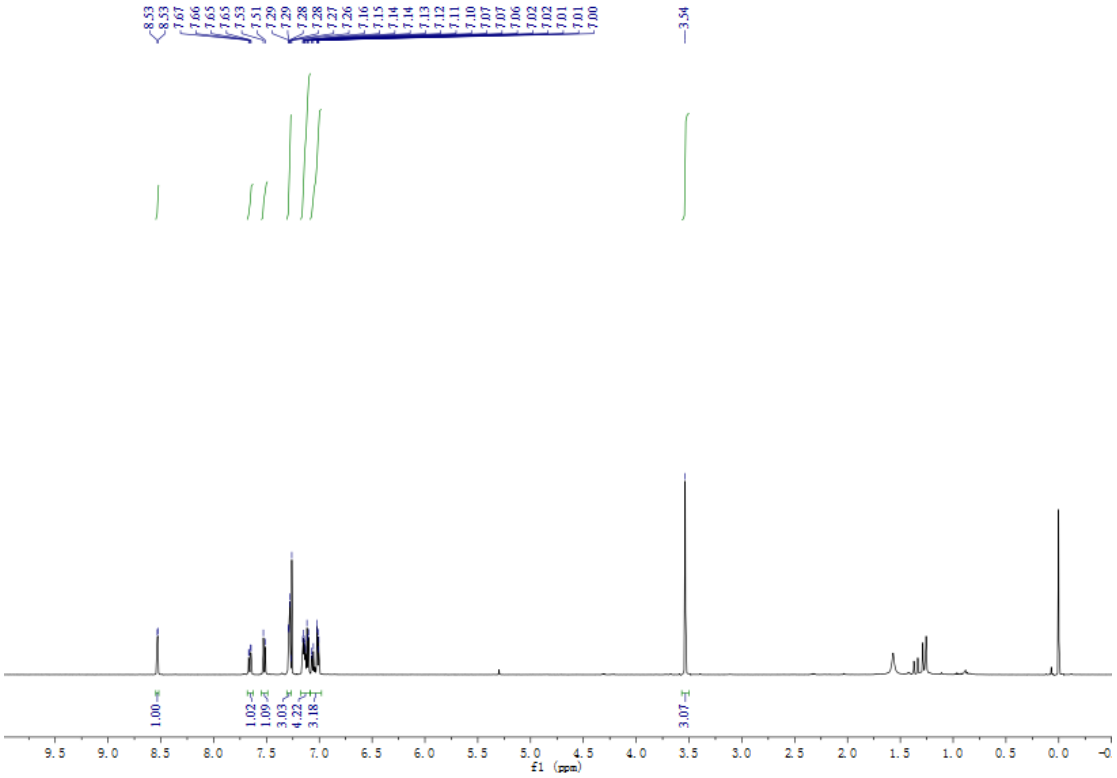
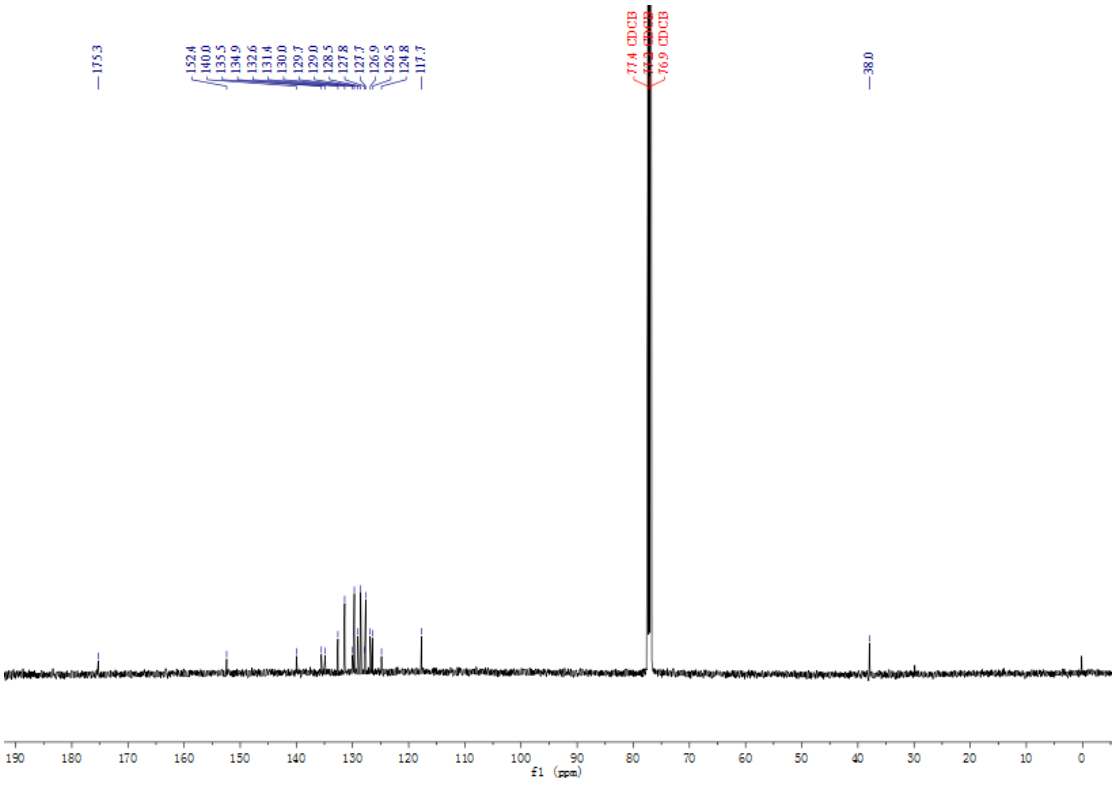
129.0
128.5
128.3
128.3
127.7
126.4
123.9
121.0
120.8
118.2
118.2
112.2
112.0
77.4 CDCl3
77.3 CDCl3
76.9 CDCl3
38.1
f1 (ppm)

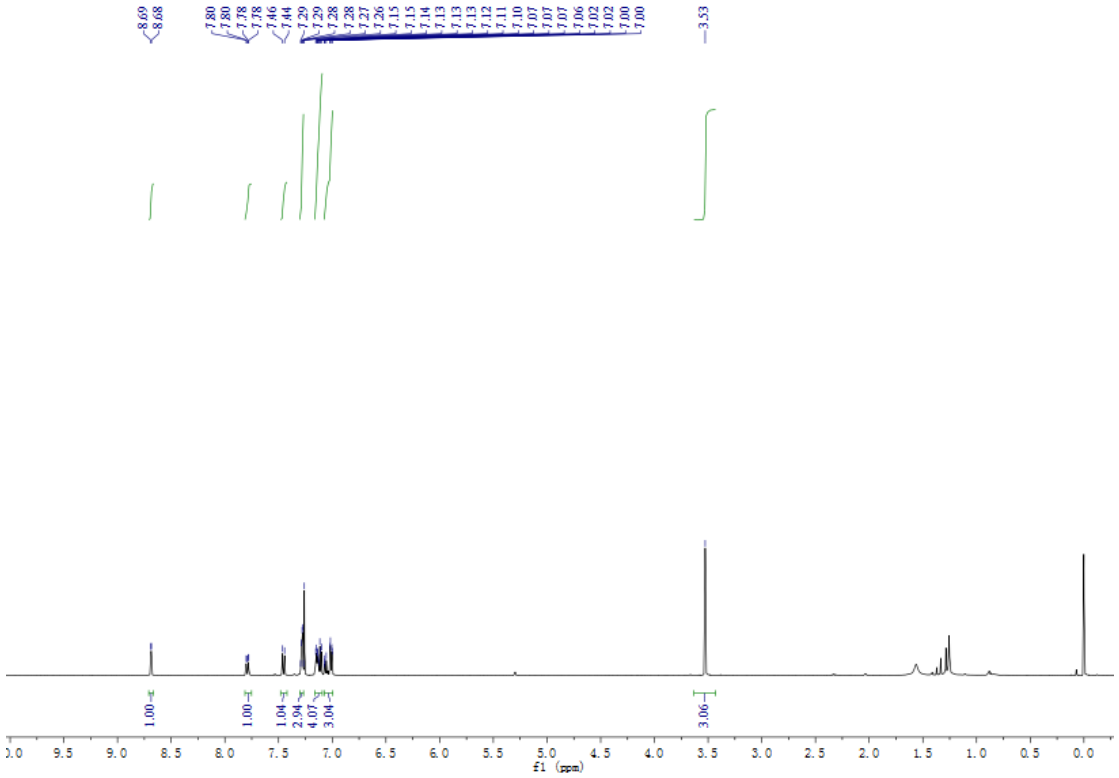

117.99
f1 (ppm)

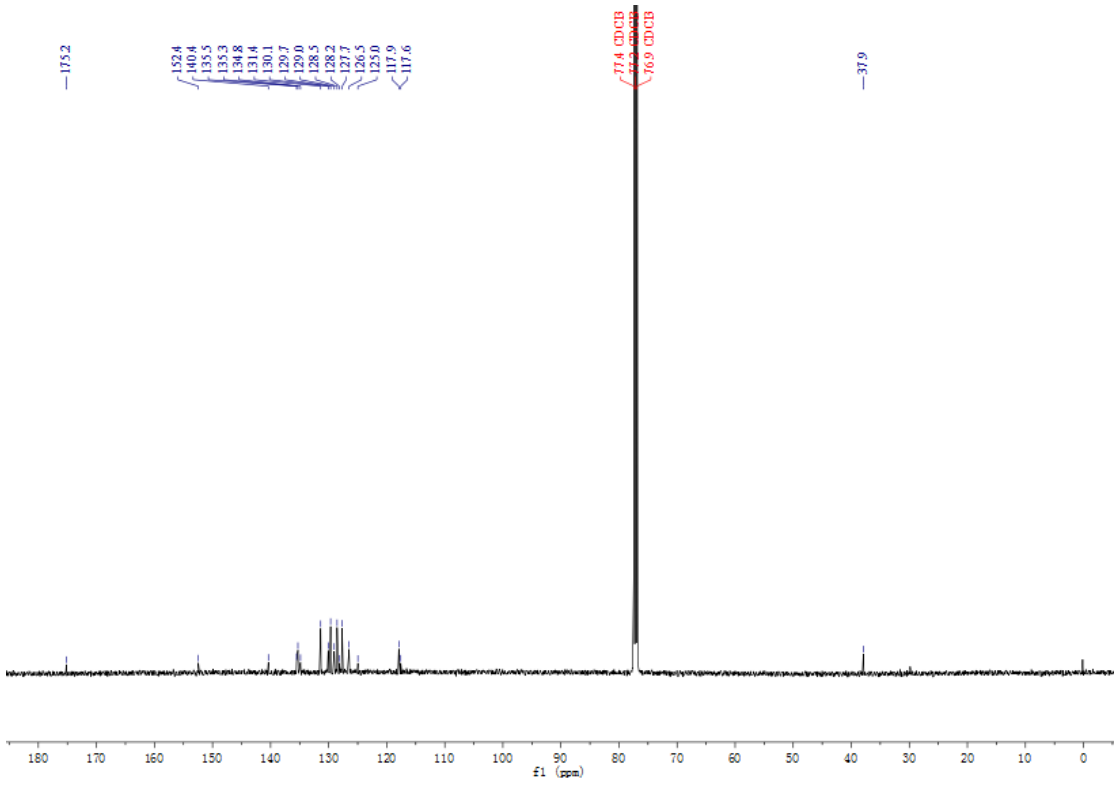
(7) The ^{1}H NMR and ^{13}C NMR spectrum for **3g**



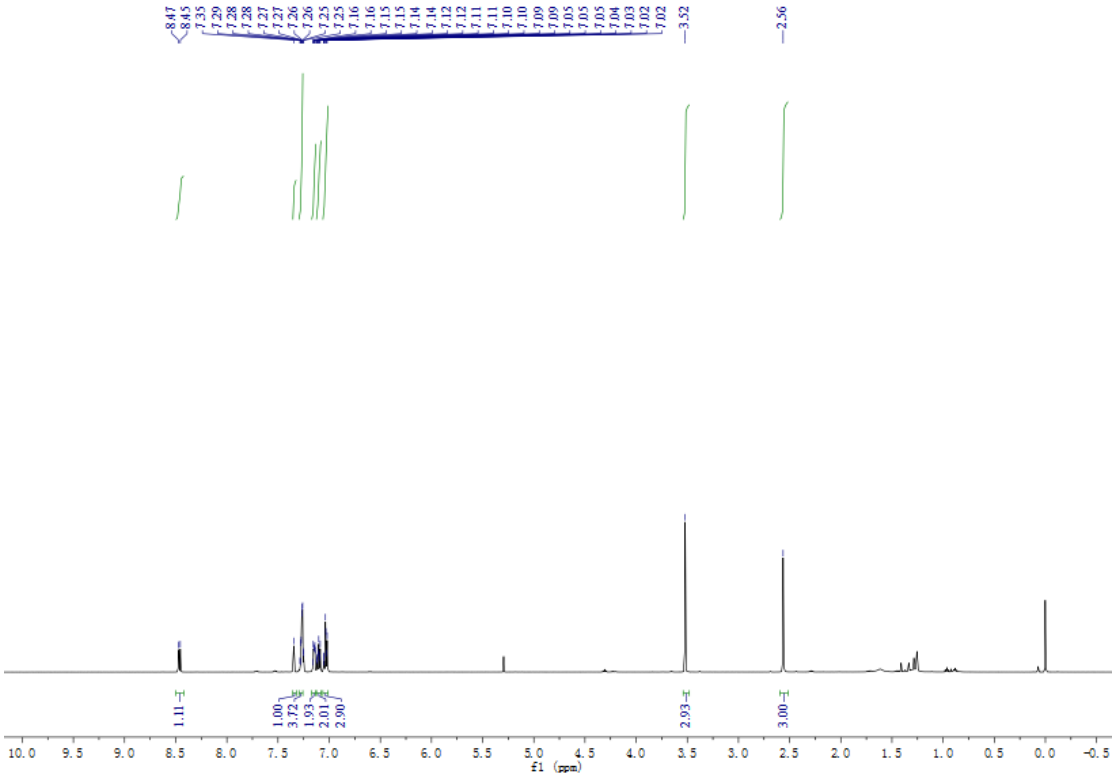


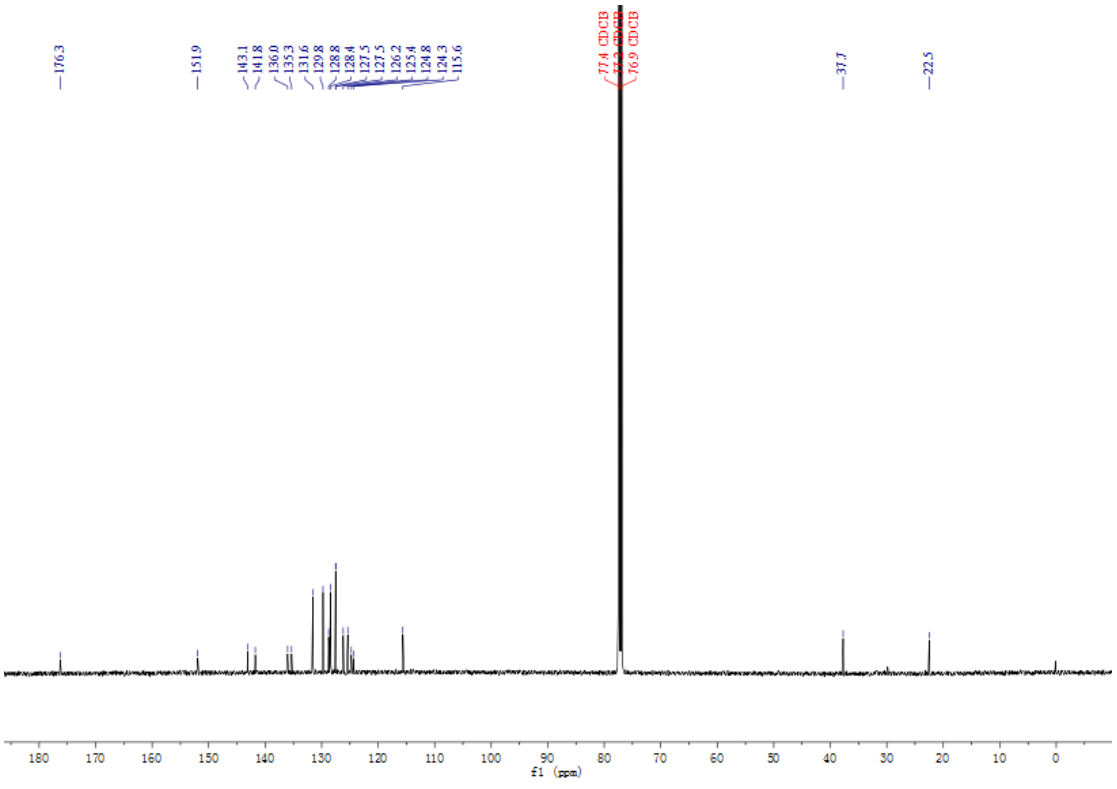
(8) The ^{1}H NMR and ^{13}C NMR spectrum for **3h**



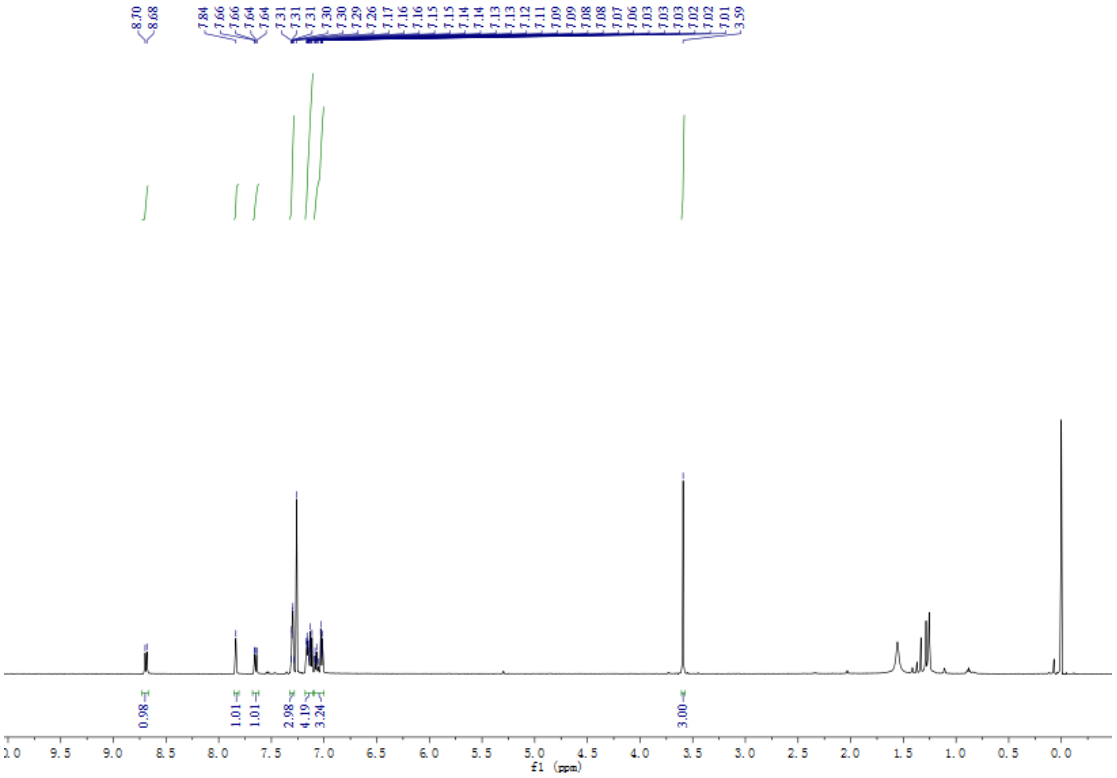


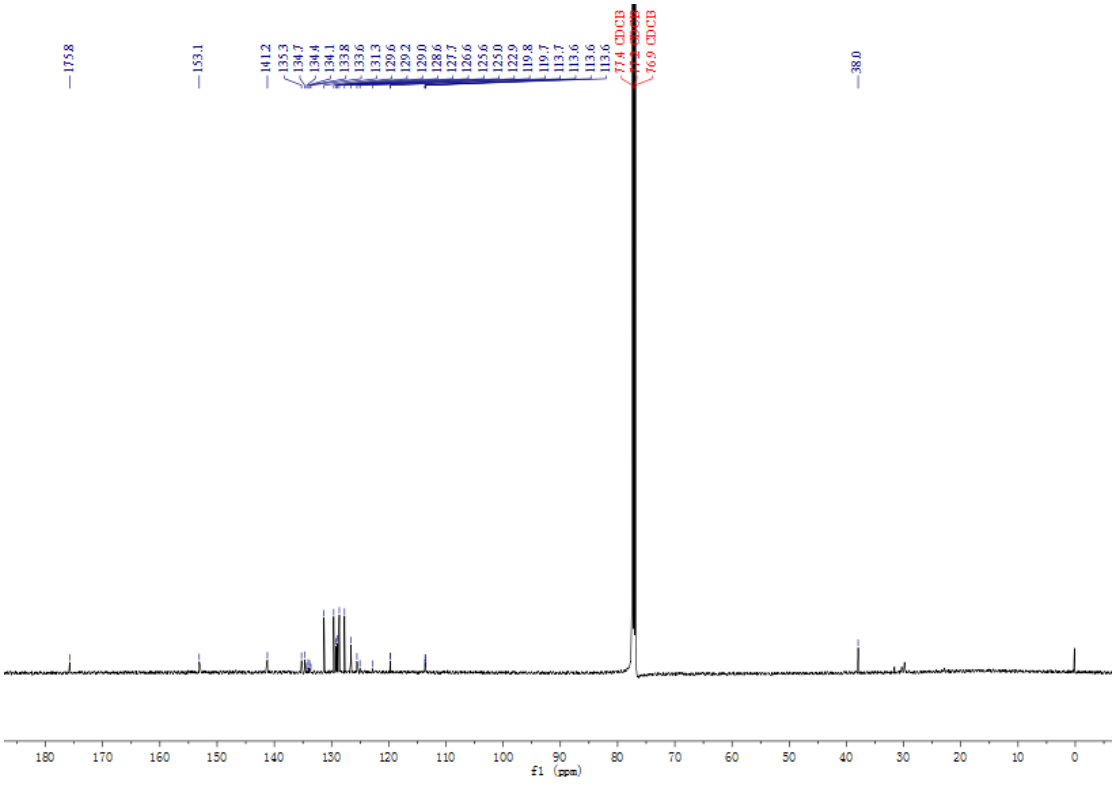
(9) The ^{1}H NMR and ^{13}C NMR spectrum for **3i**

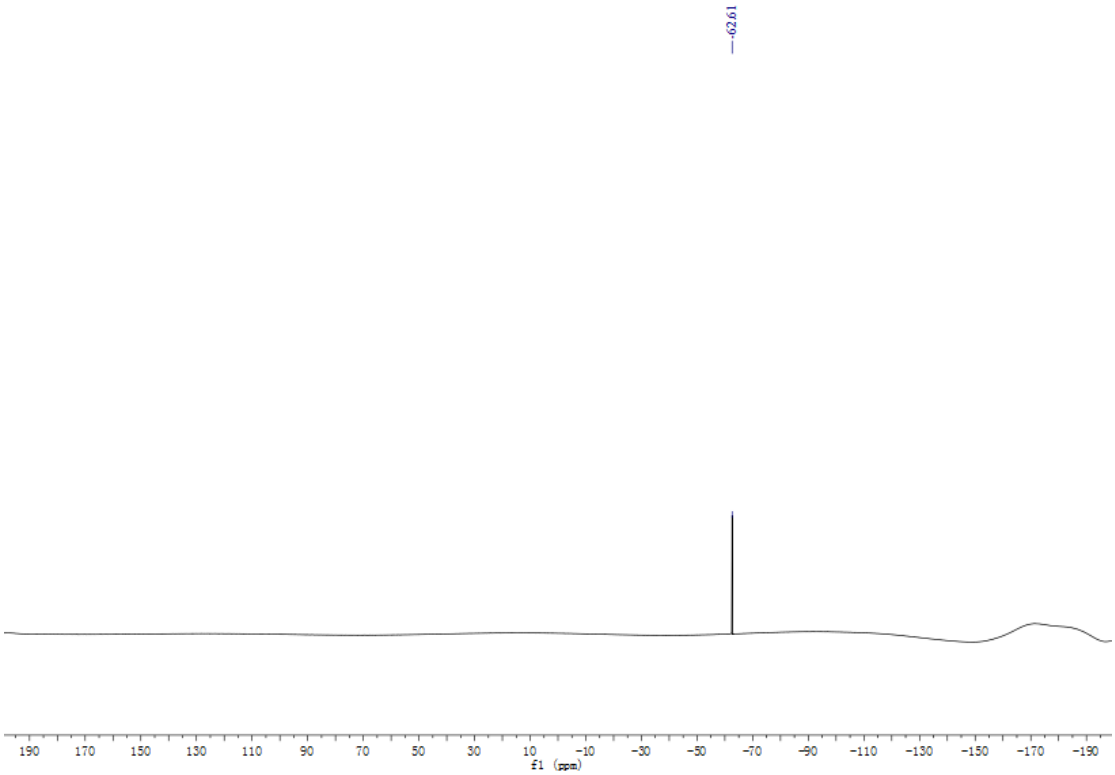




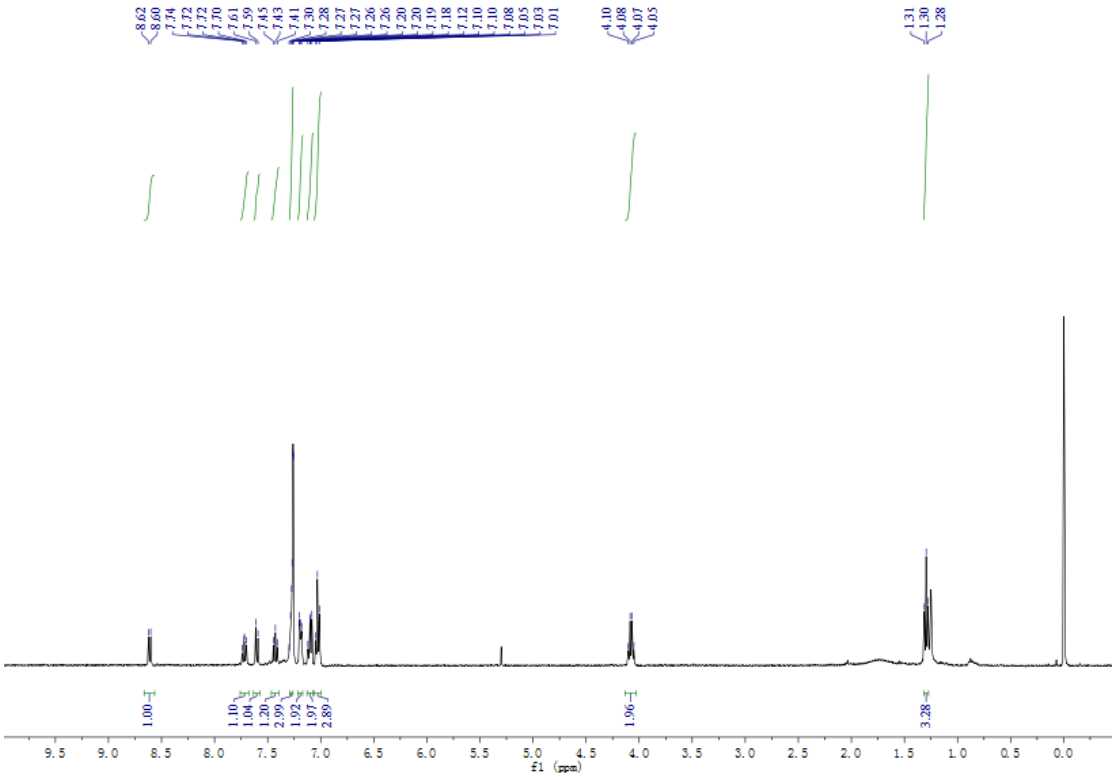
(10) The ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMRspectra for **3j**

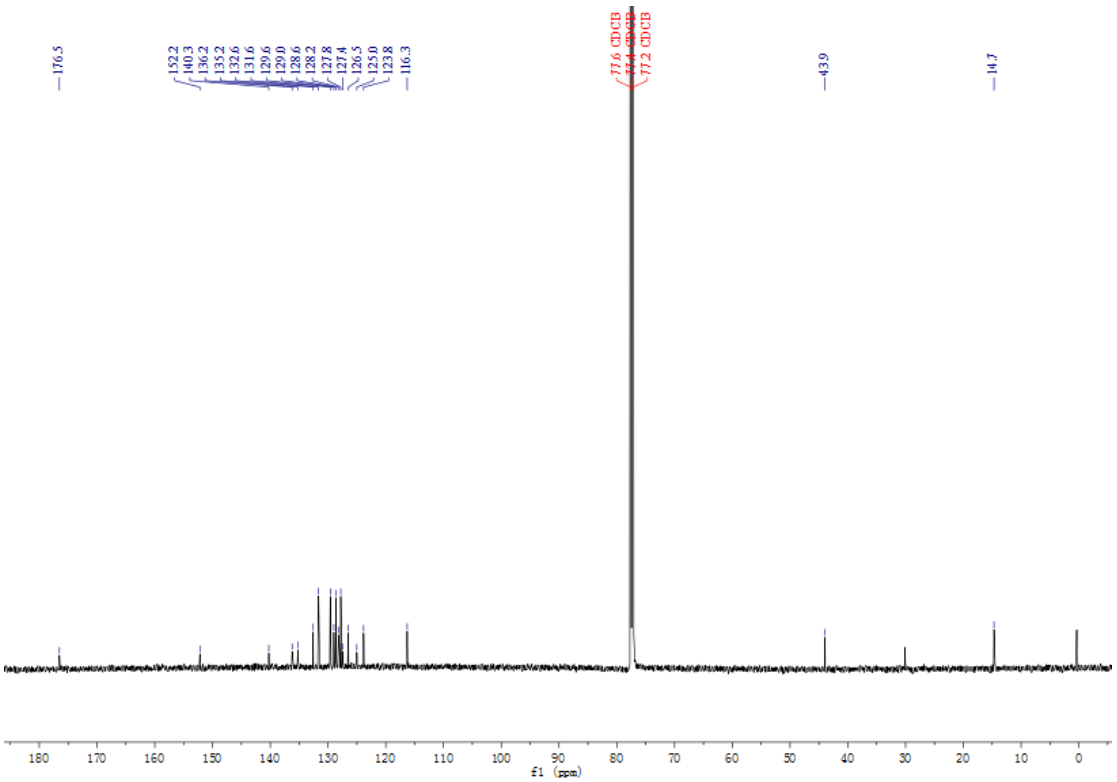




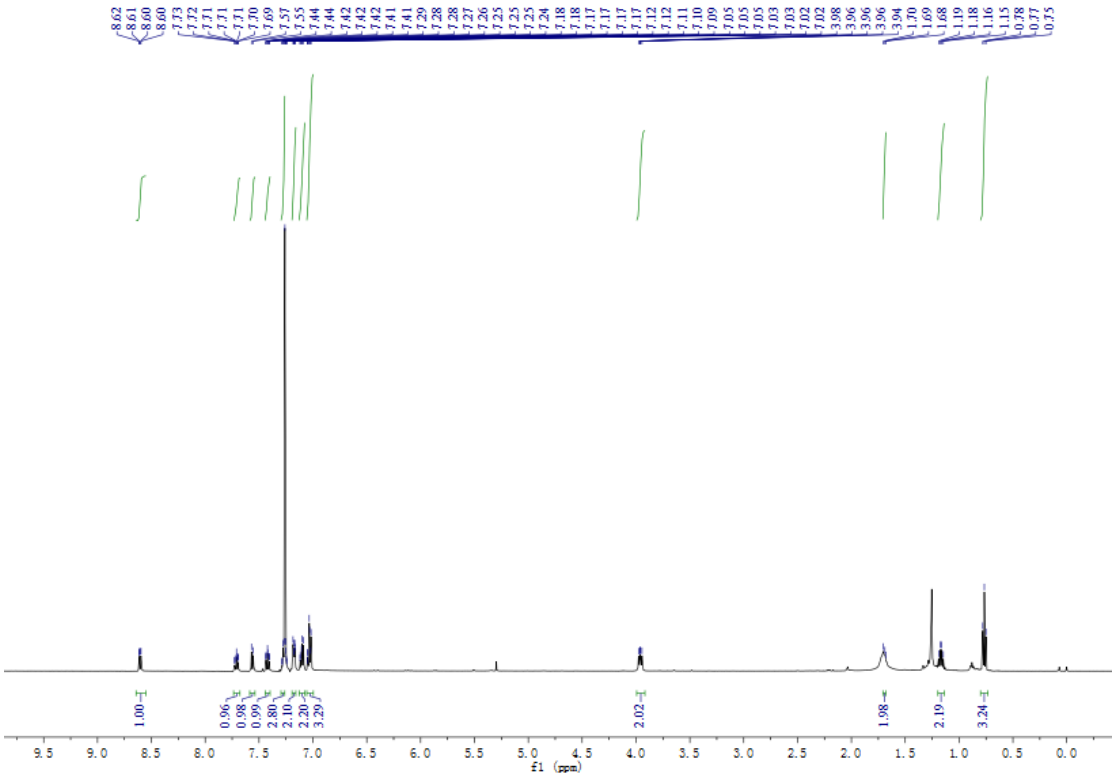


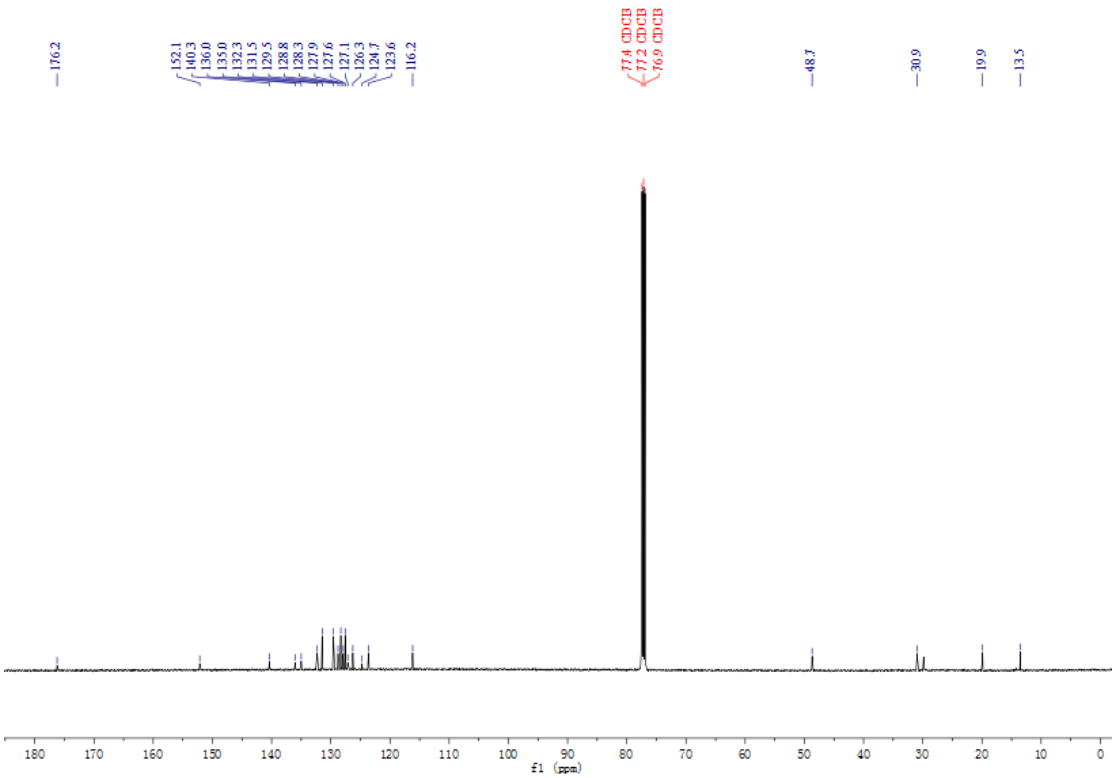
(11) The ^{1}H NMR and ^{13}C NMR spectrum for **3k**



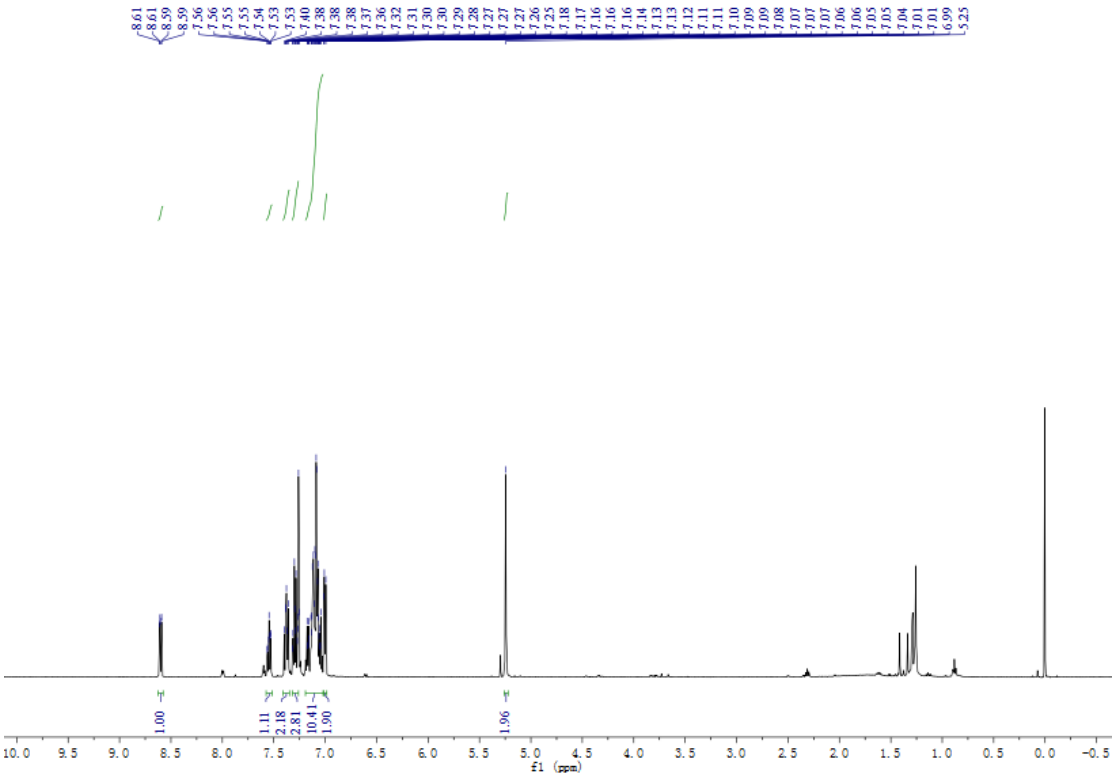


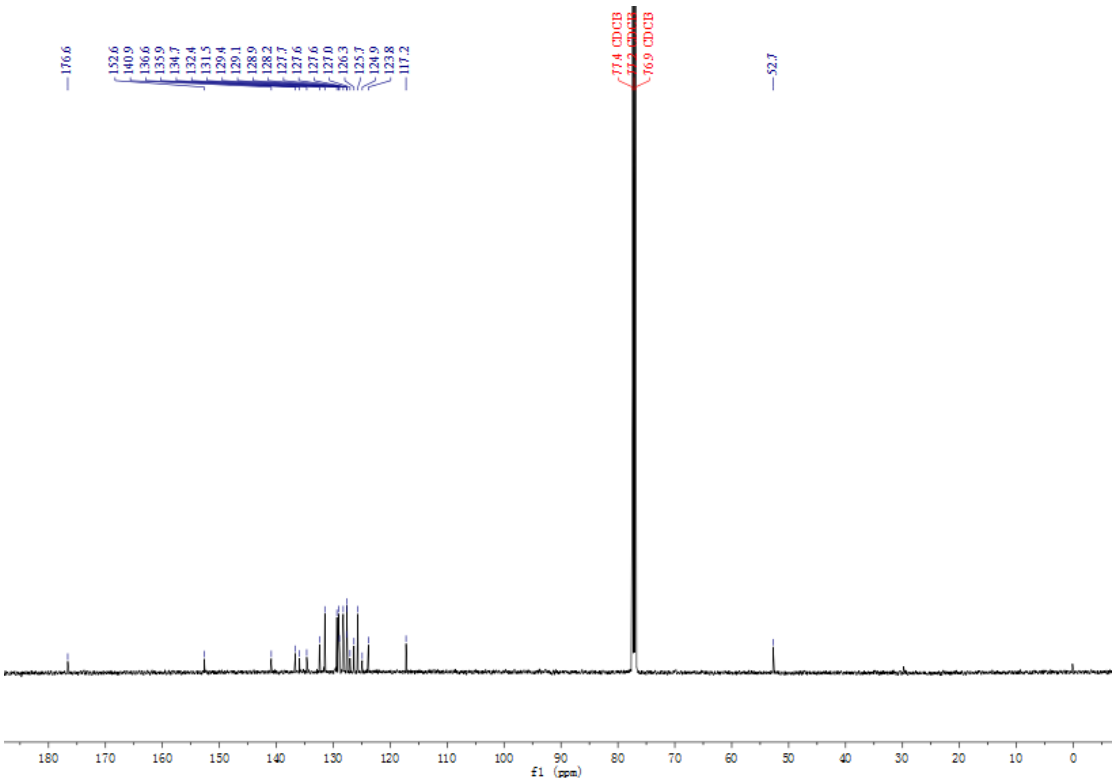
(12) The ^{1}H NMR and ^{13}C NMR spectrum for **3l**





(13) The ^{1}H NMR and ^{13}C NMR spectrum for **3m**





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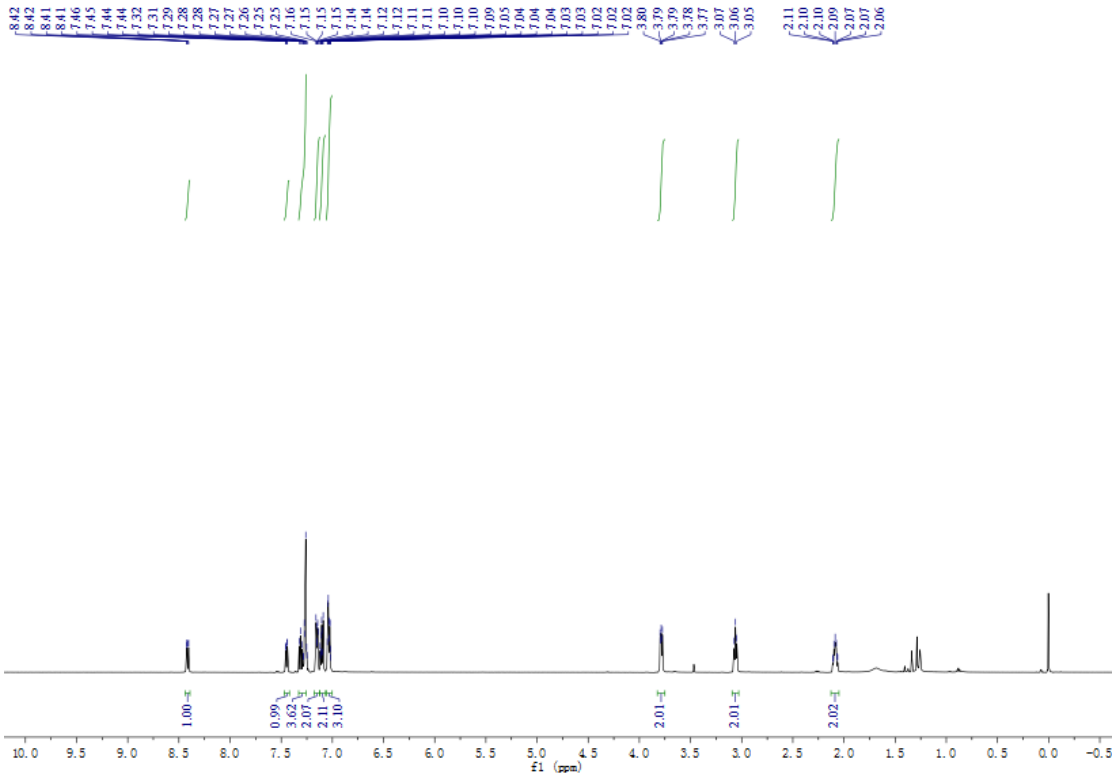

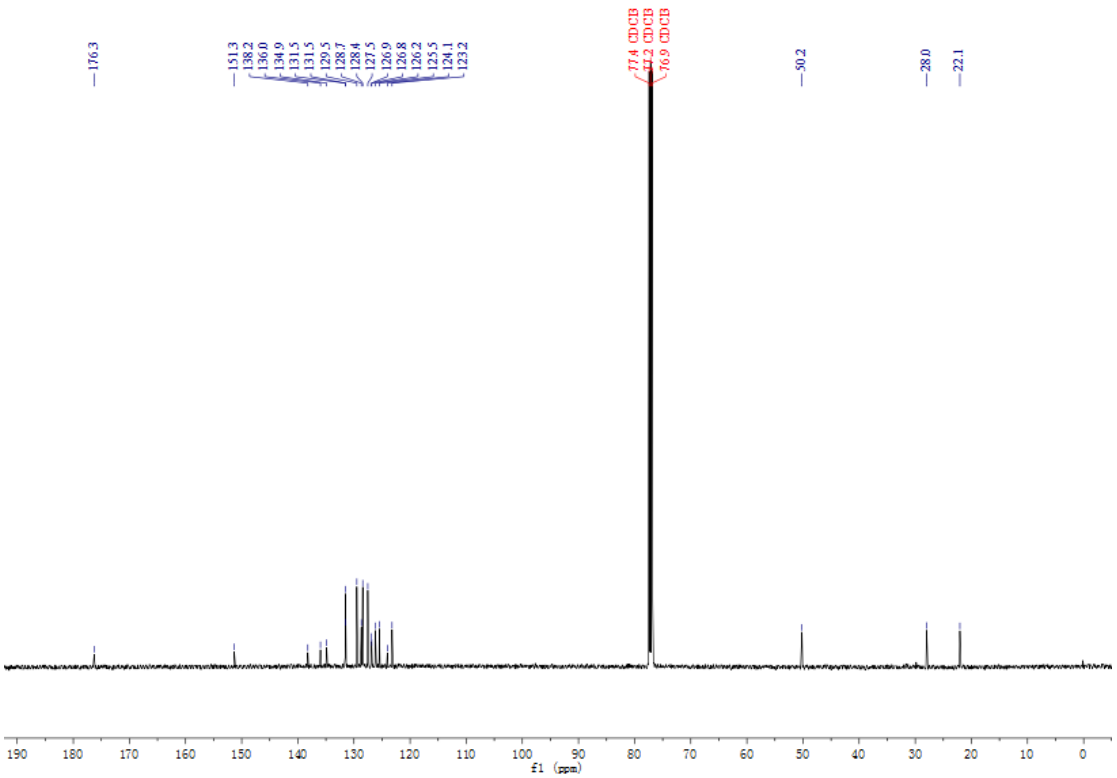

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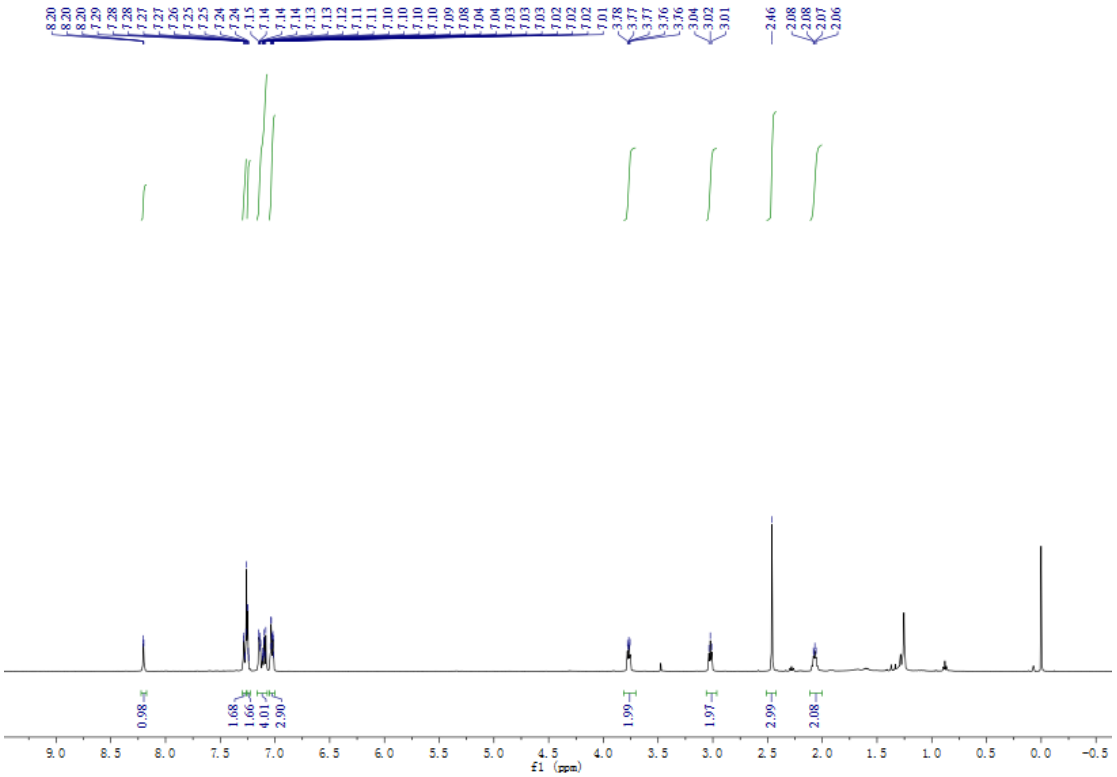
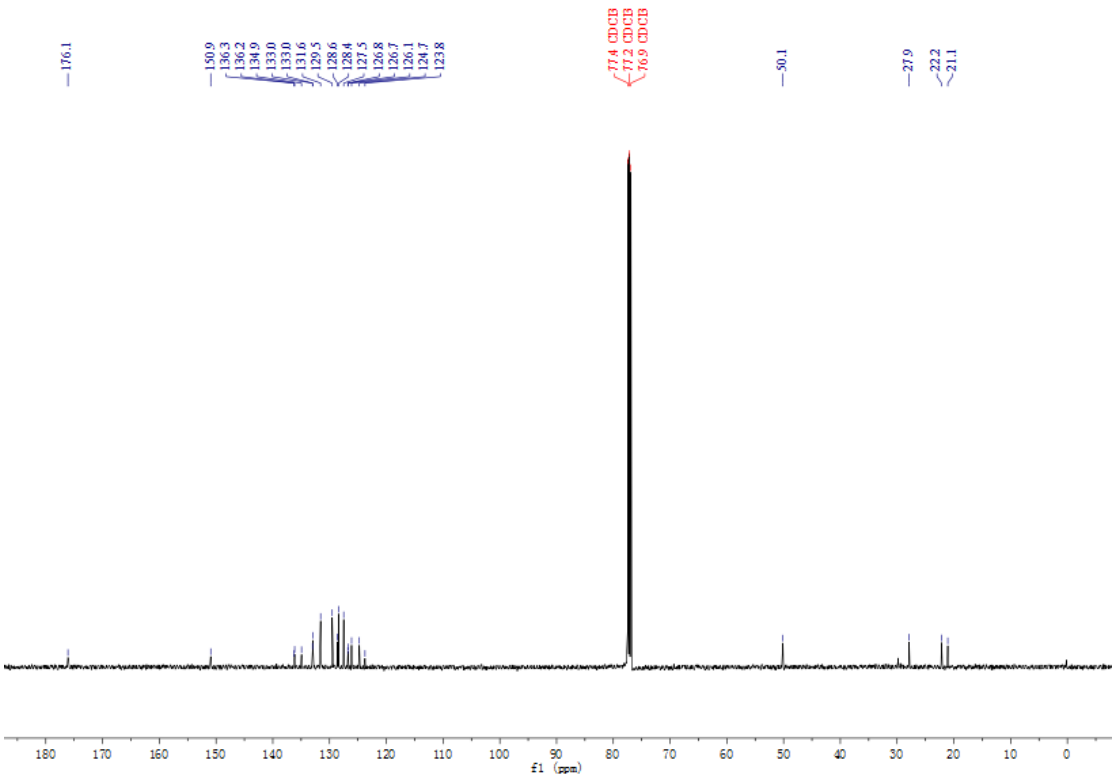
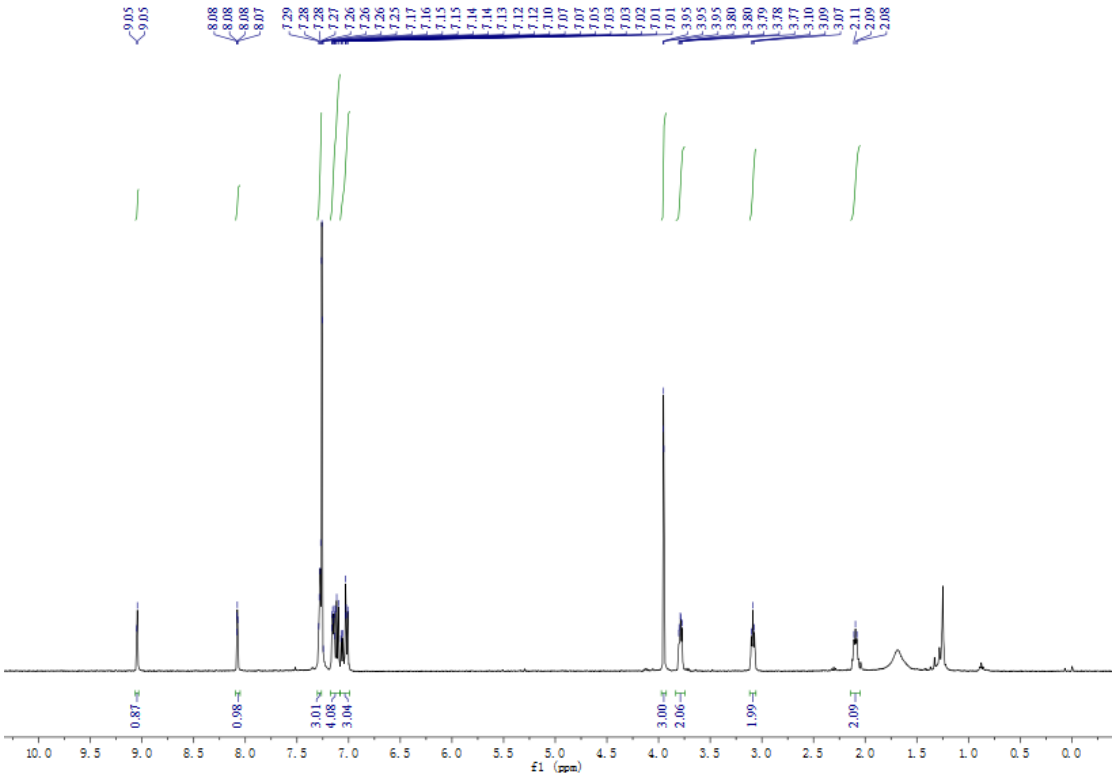
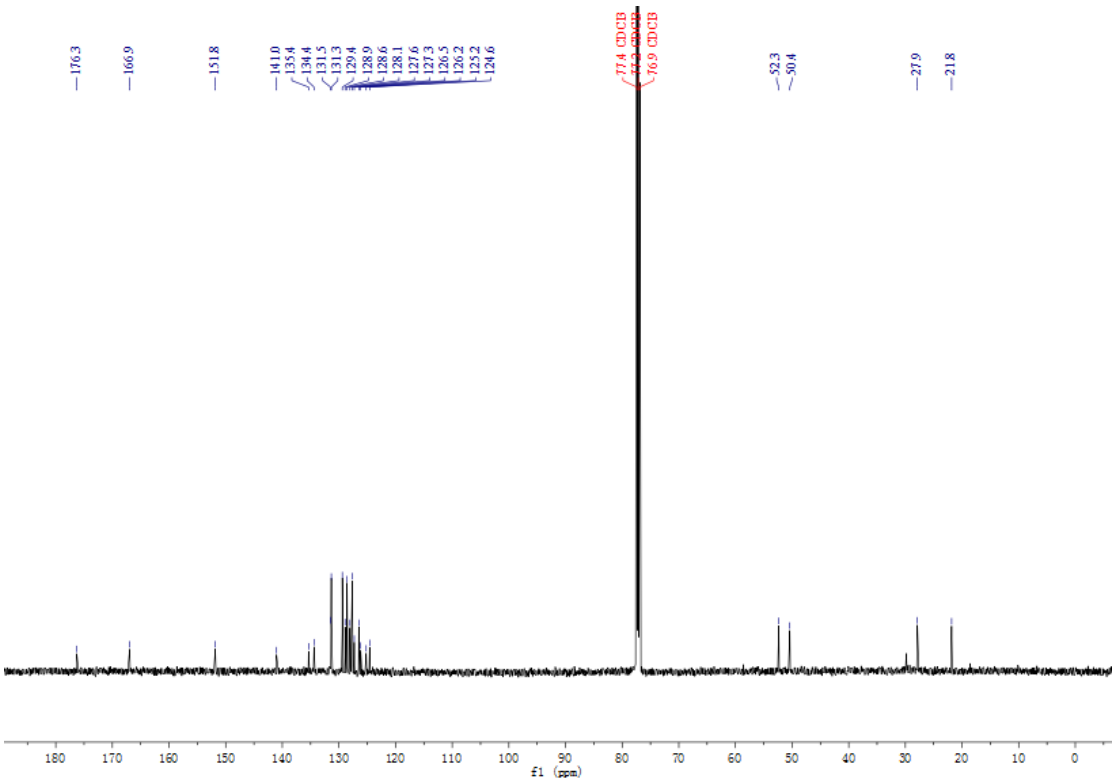


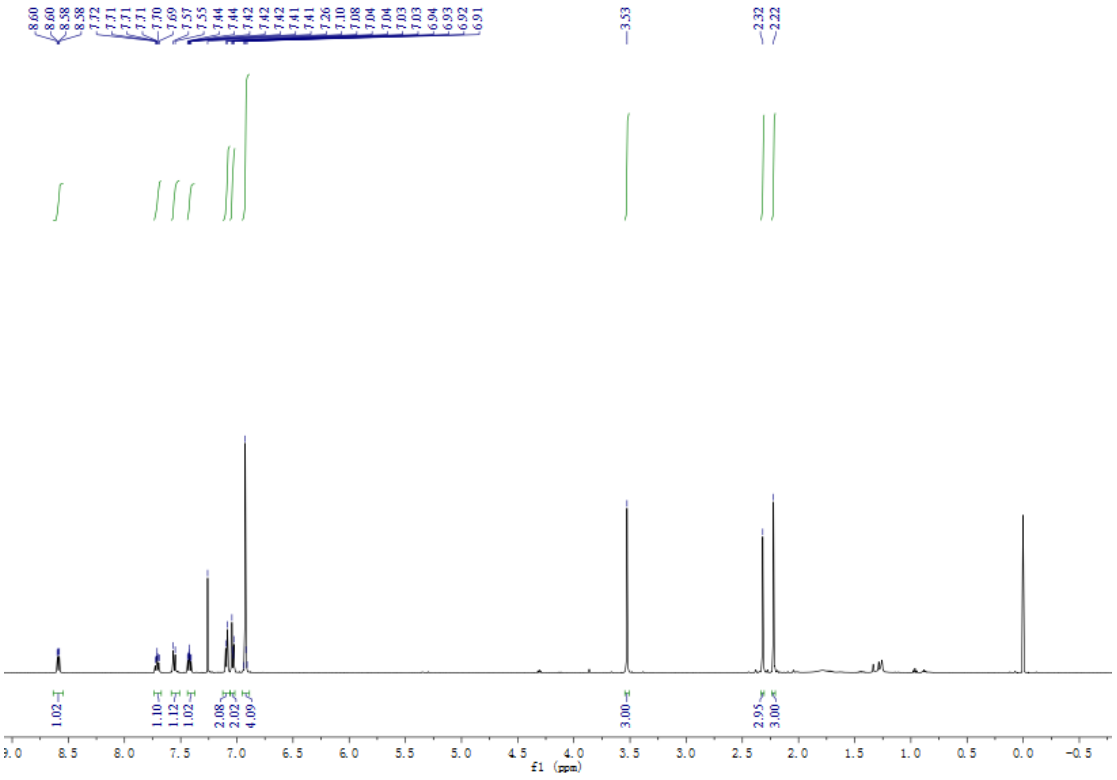


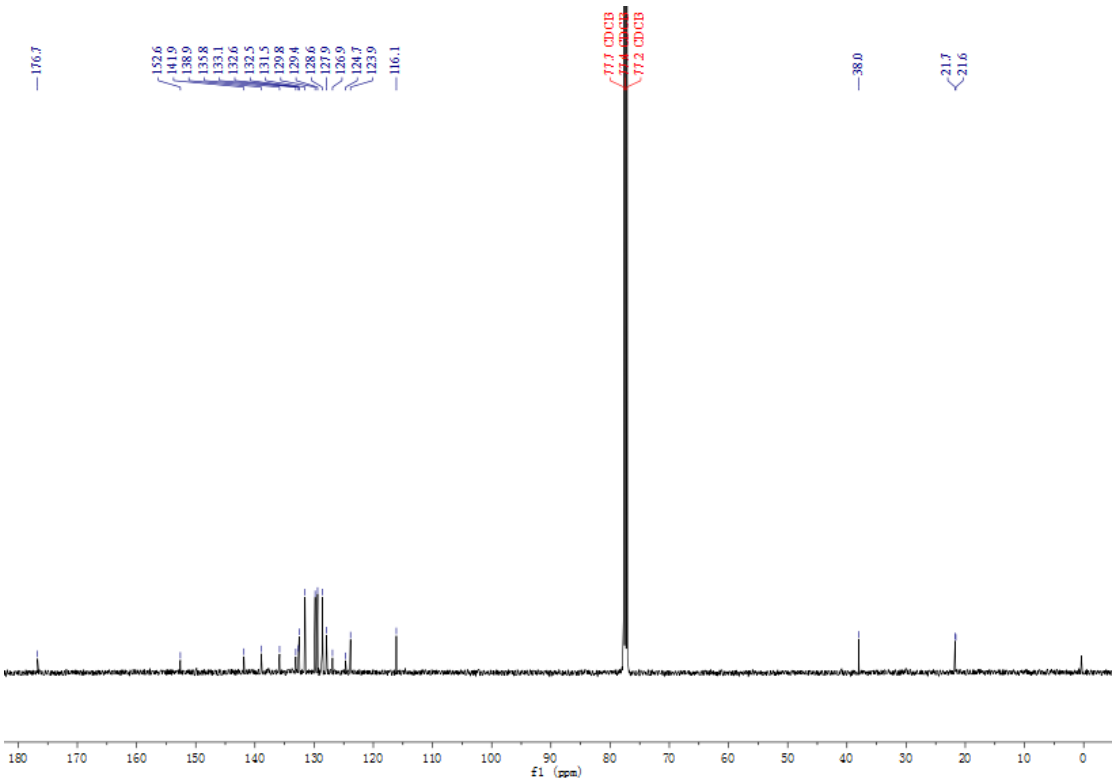
(16) The ^{1}H NMR and ^{13}C NMR spectrum for **3p**



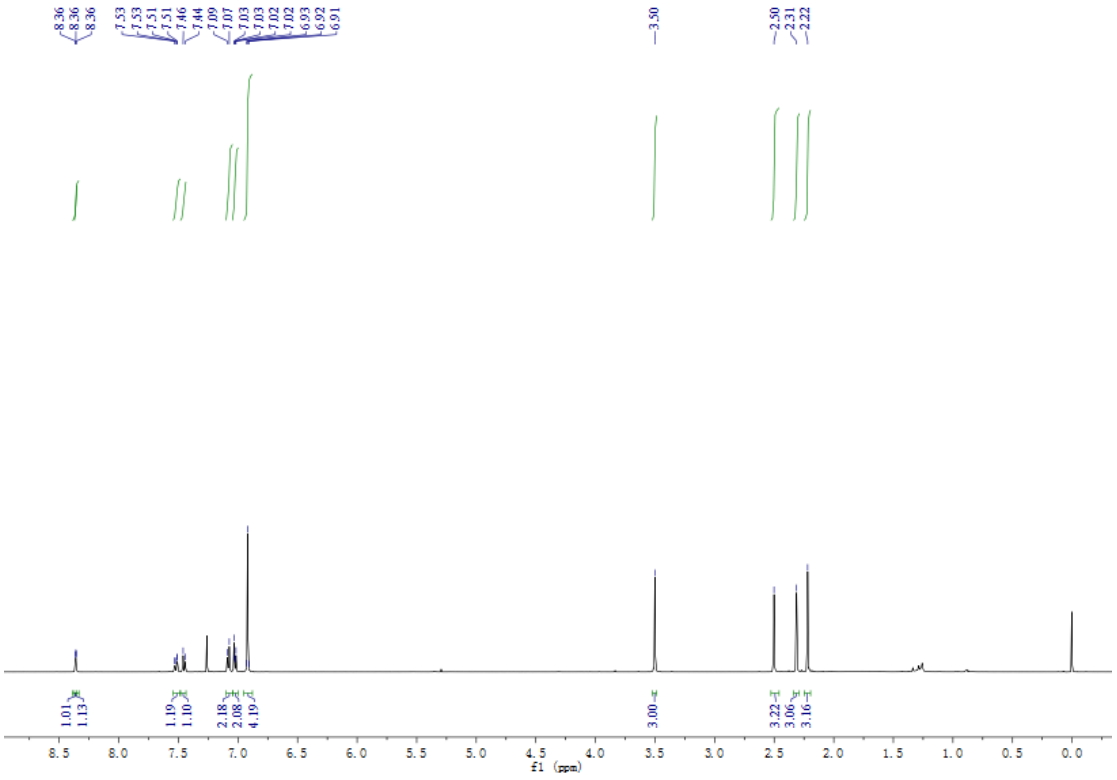


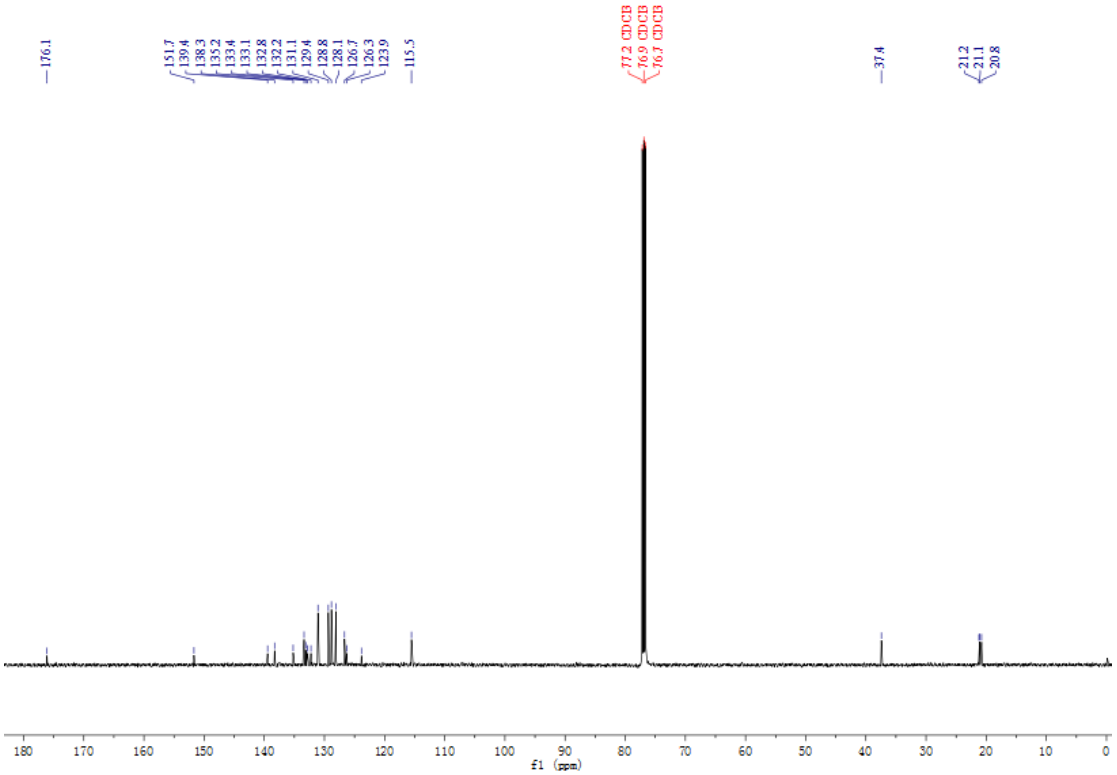
(17) The ^{1}H NMR and ^{13}C NMR spectrum for **4a**



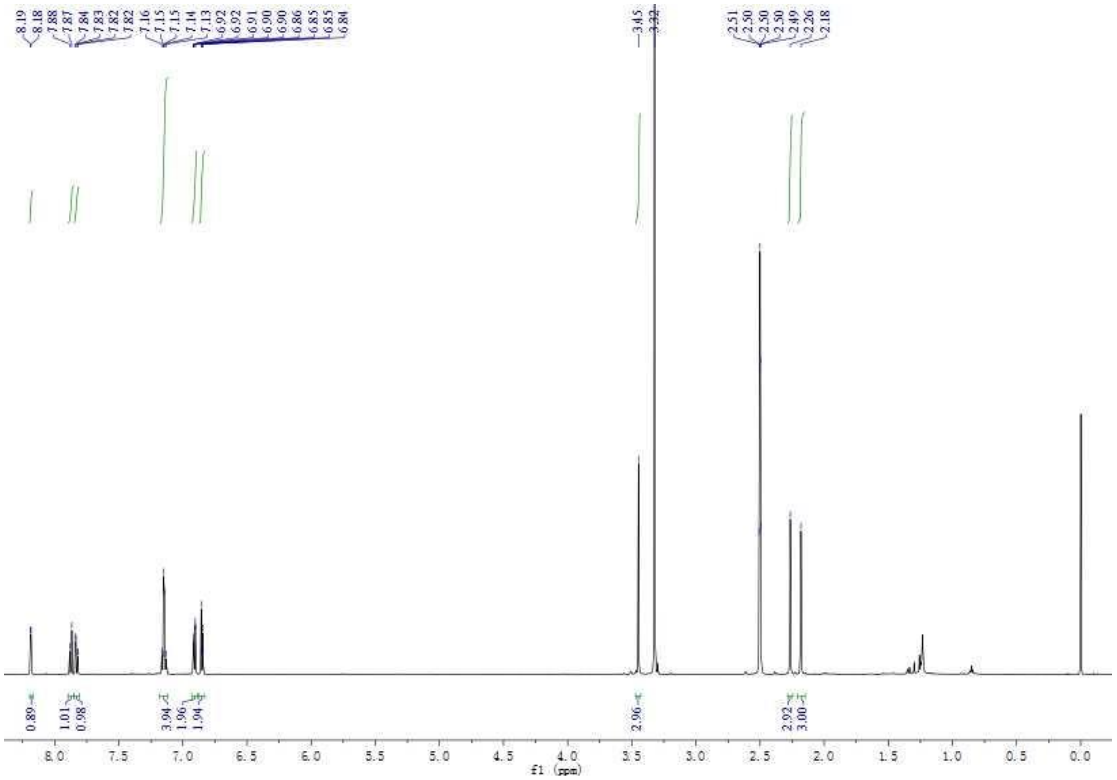


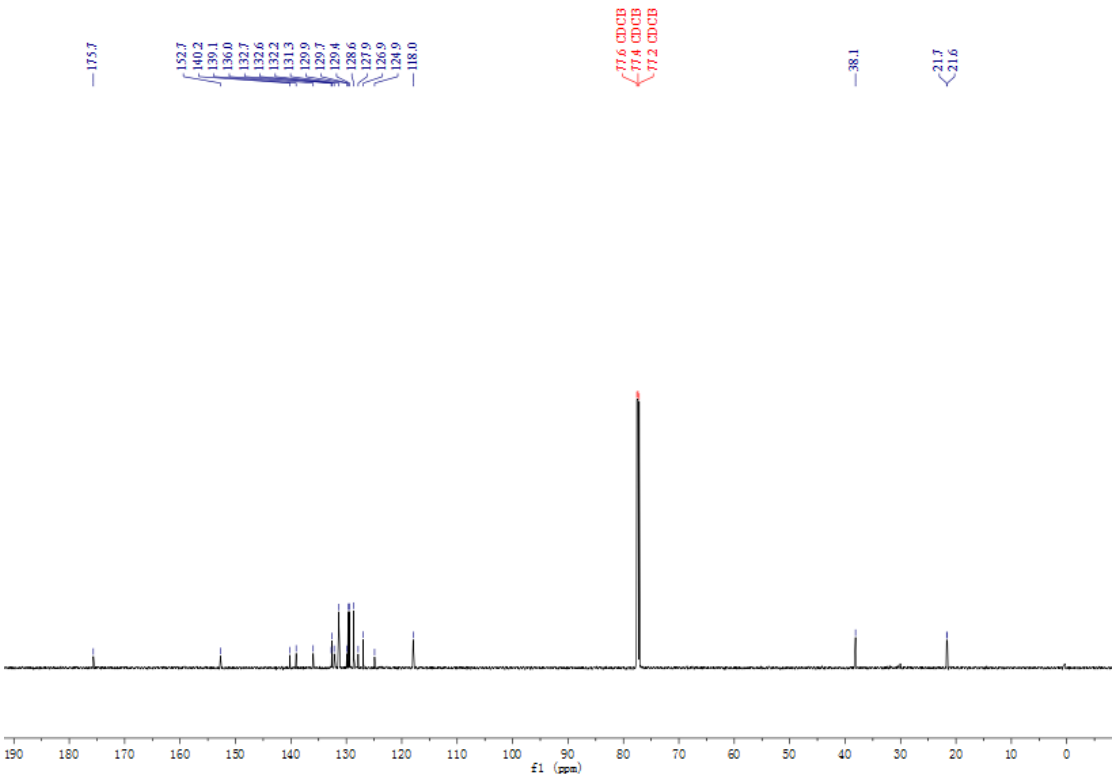
(18) The ^{1}H NMR and ^{13}C NMR spectrum for **4b**



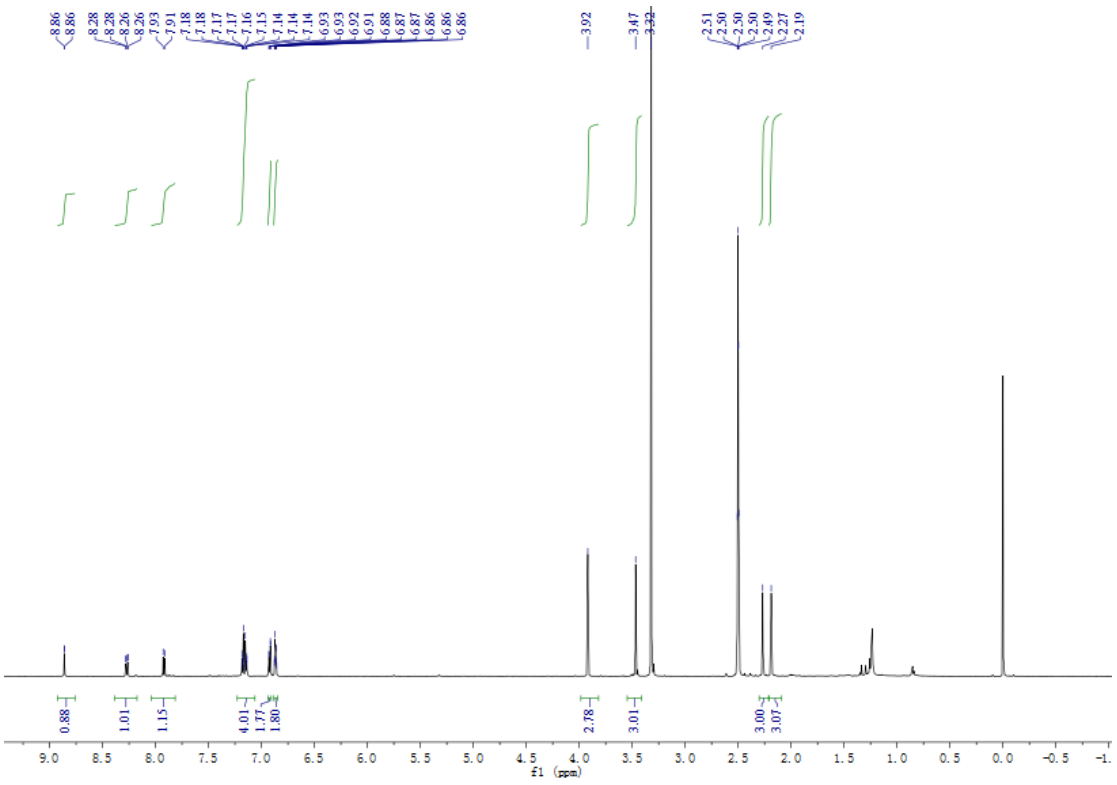


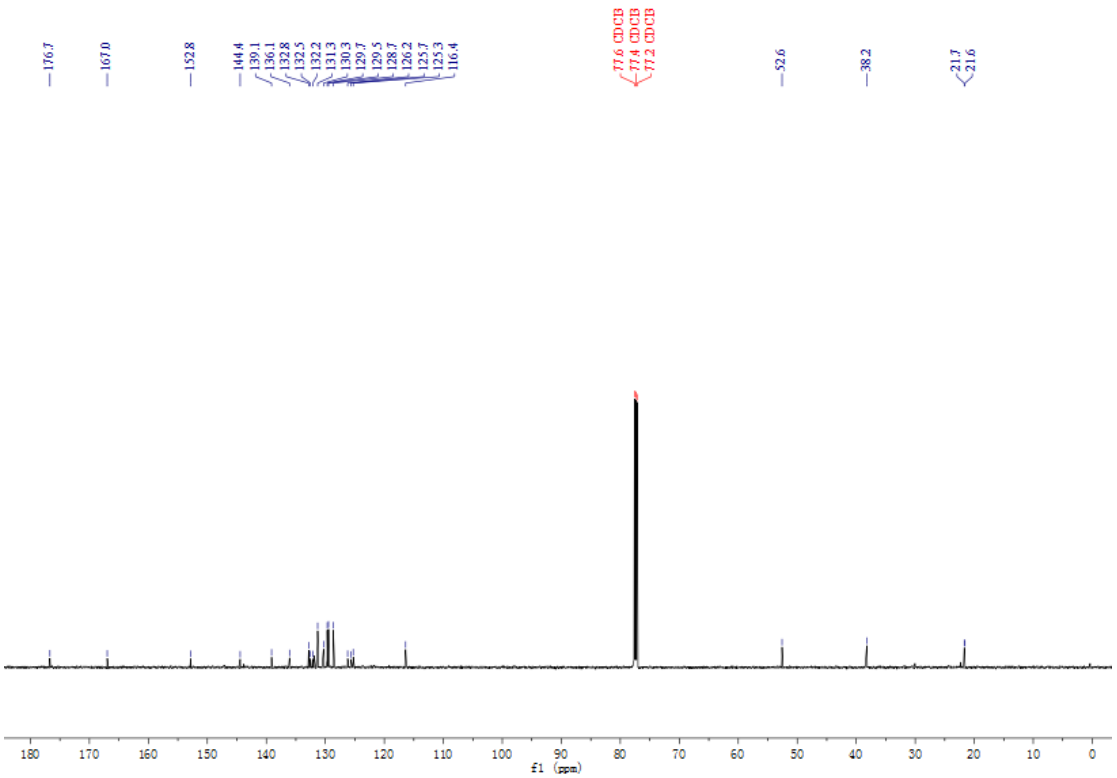
(19) The ^{1}H NMR and ^{13}C NMR spectrum for **4c**



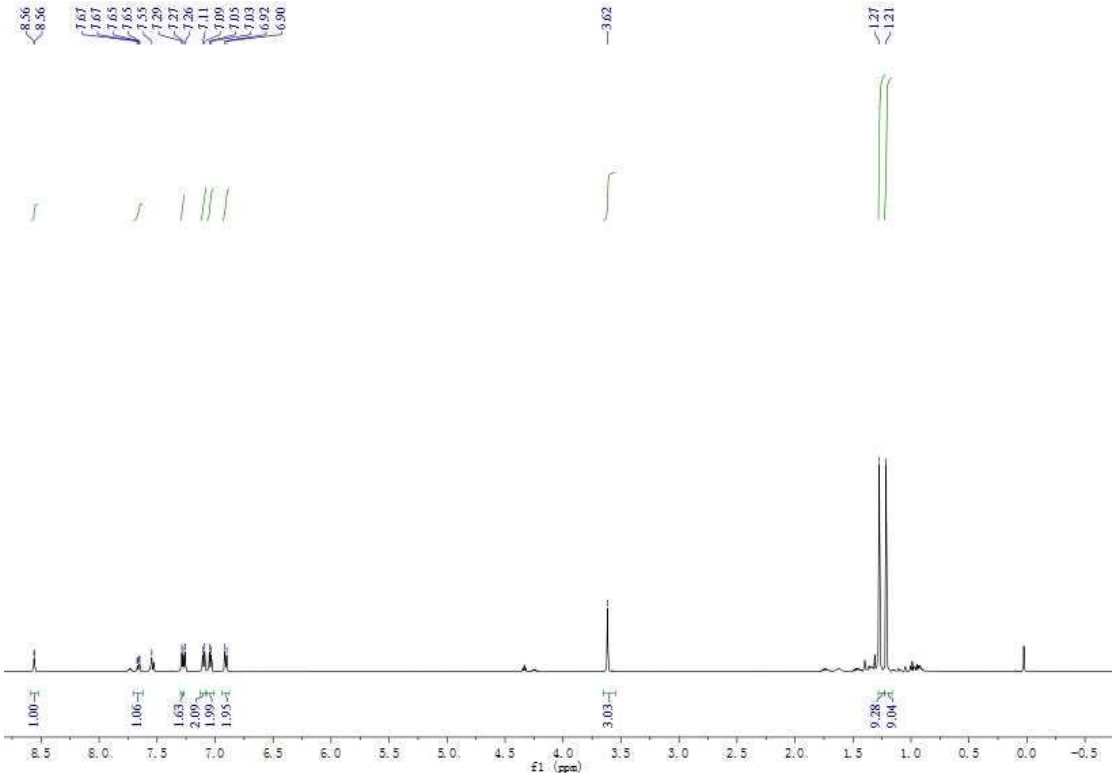


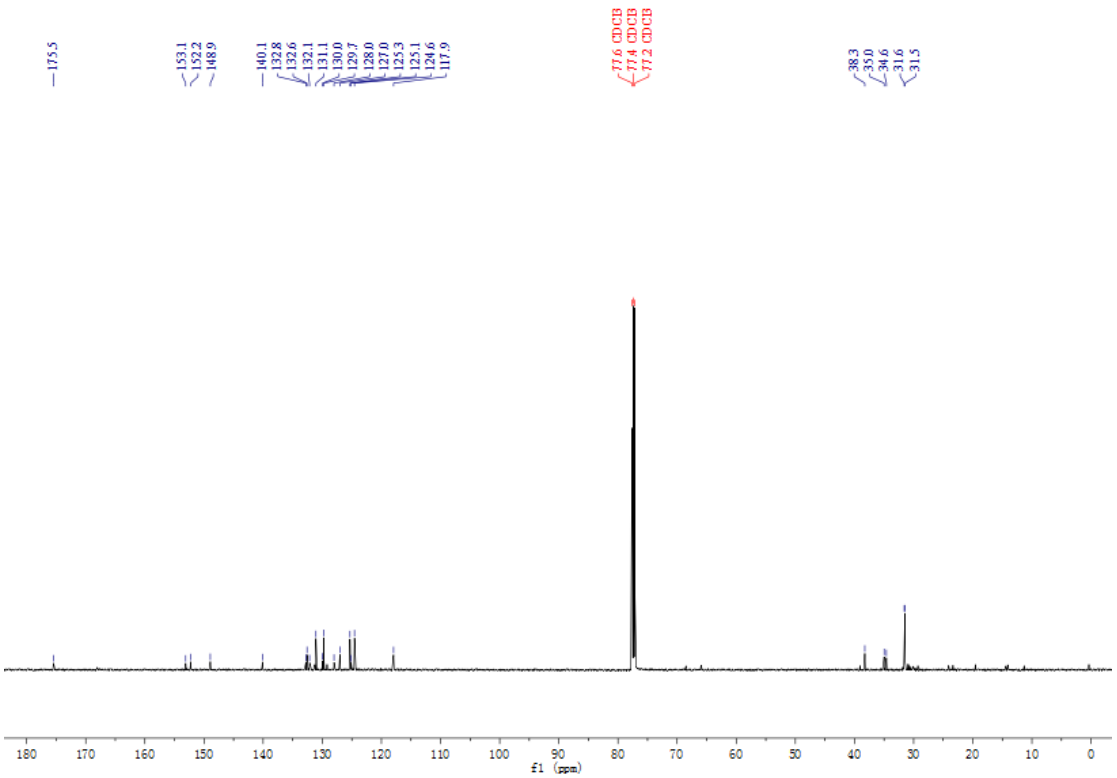
(20) The ^{1}H NMR and ^{13}C NMR spectrum for **4d**



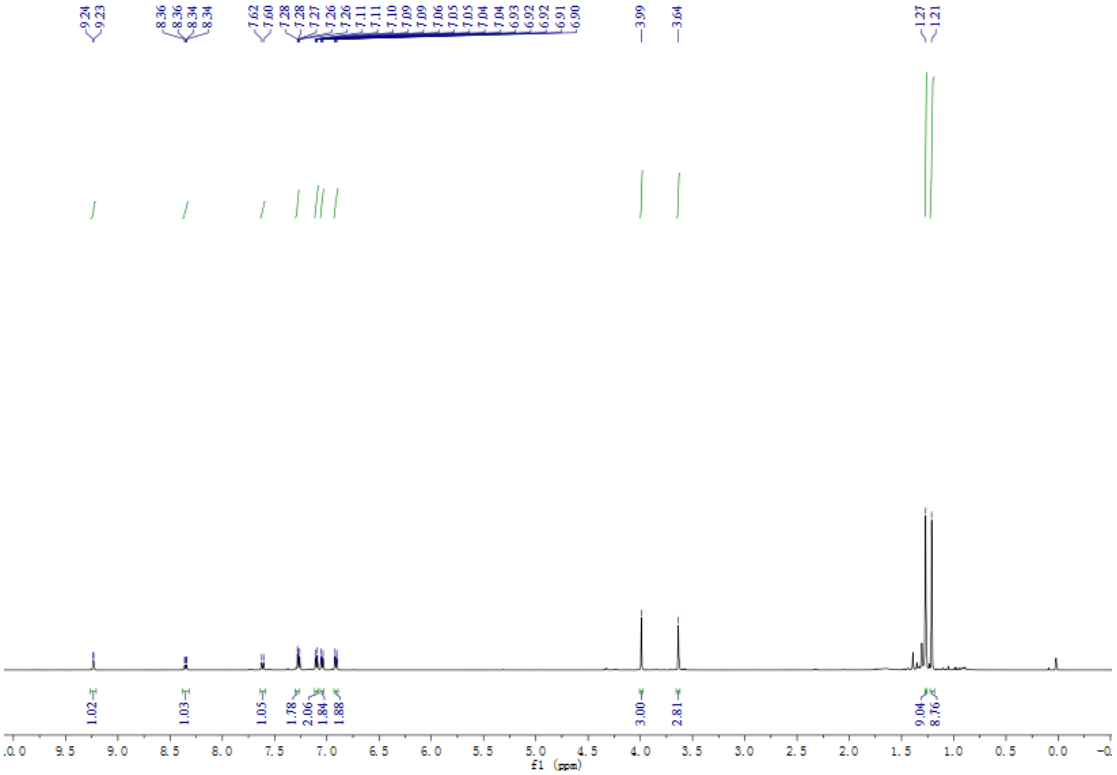


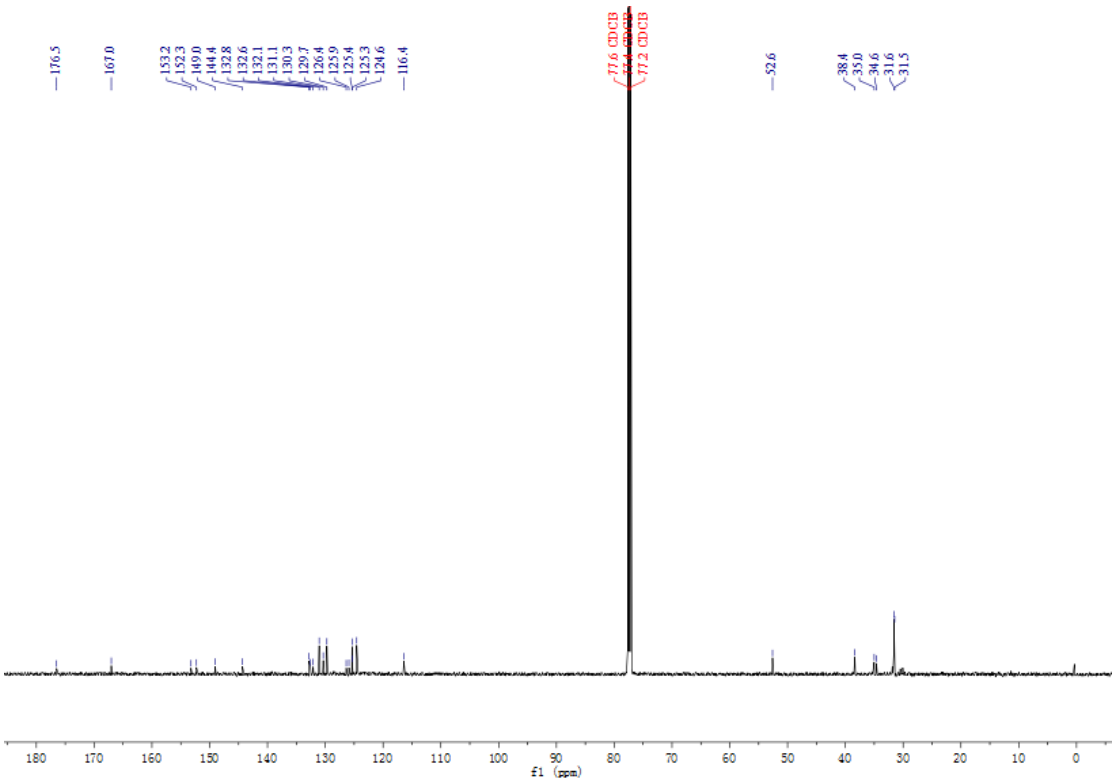
(21) The ^{1}H NMR and ^{13}C NMR spectrum for **4e**



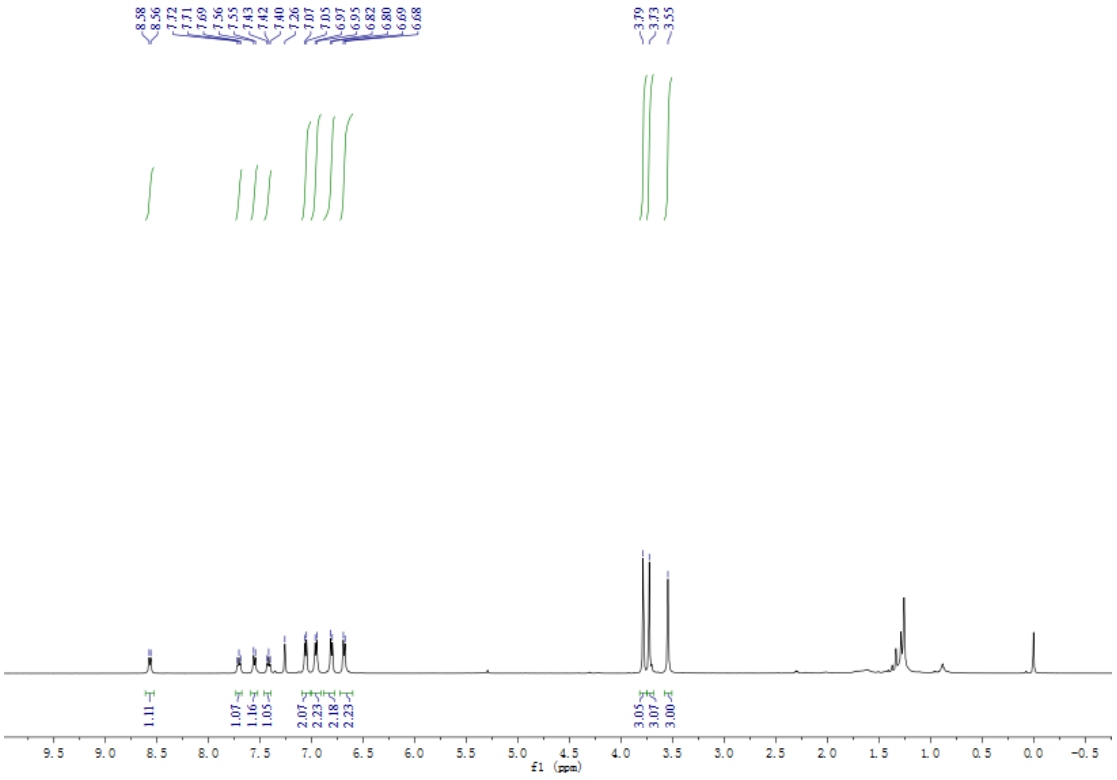


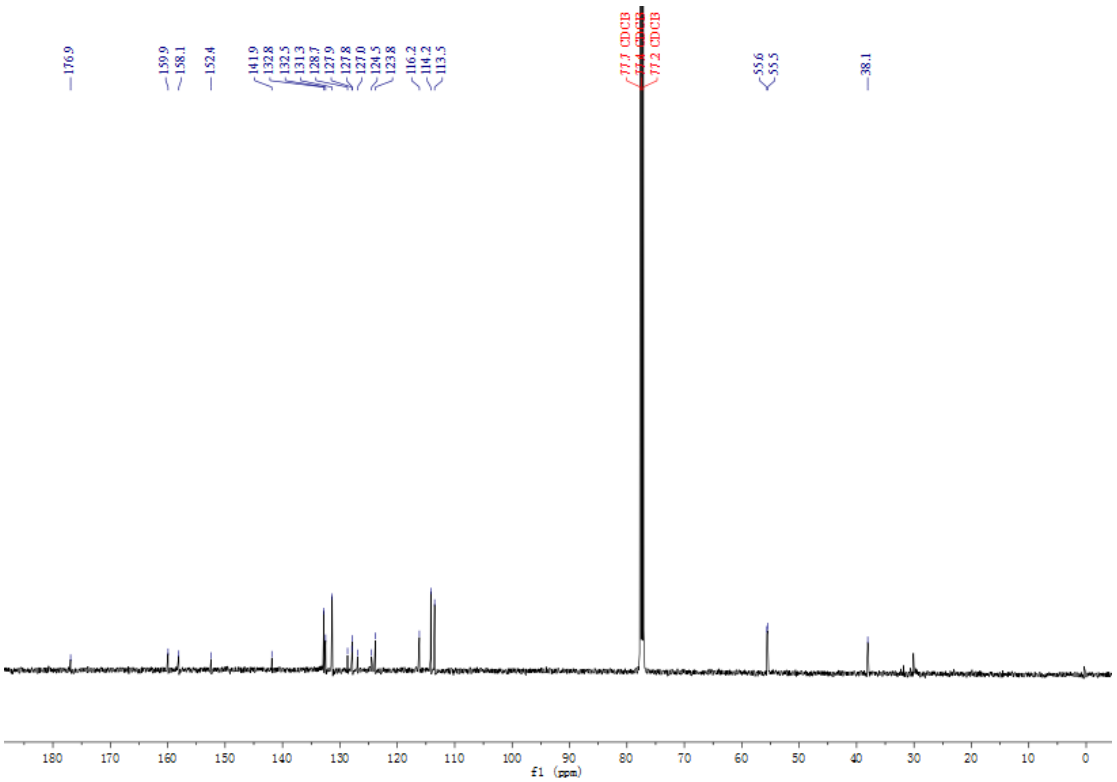
(22) The ^{1}H NMR and ^{13}C NMR spectrum for **4f**



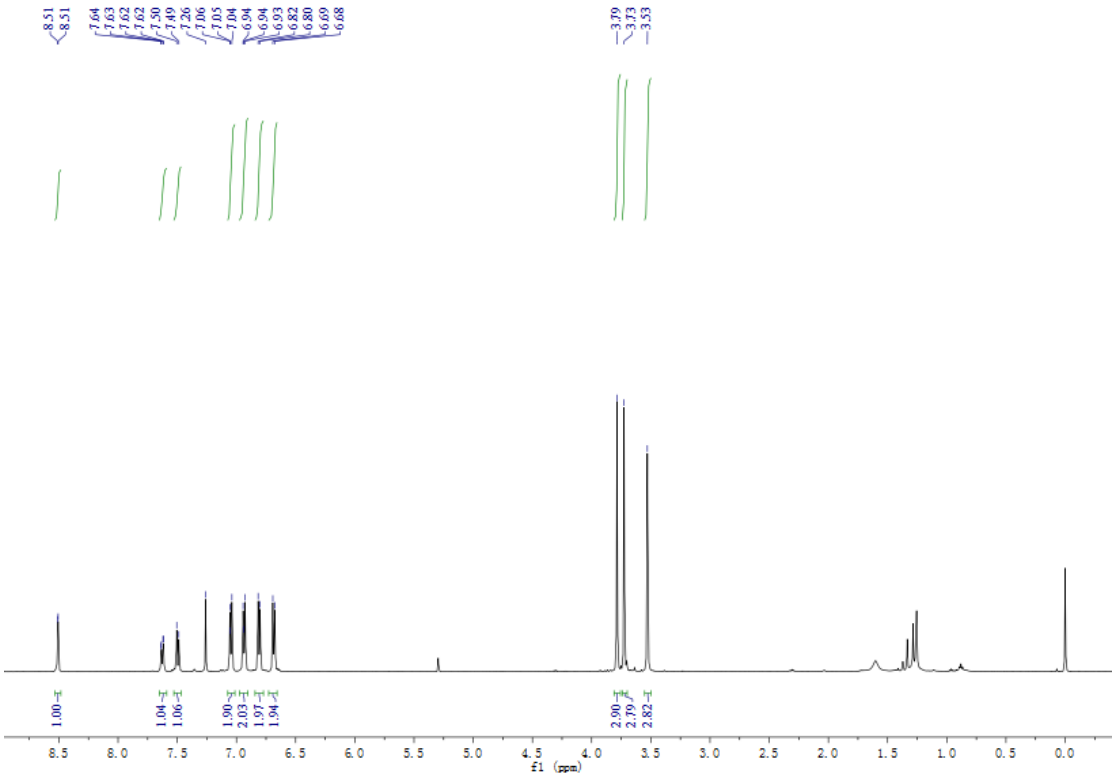


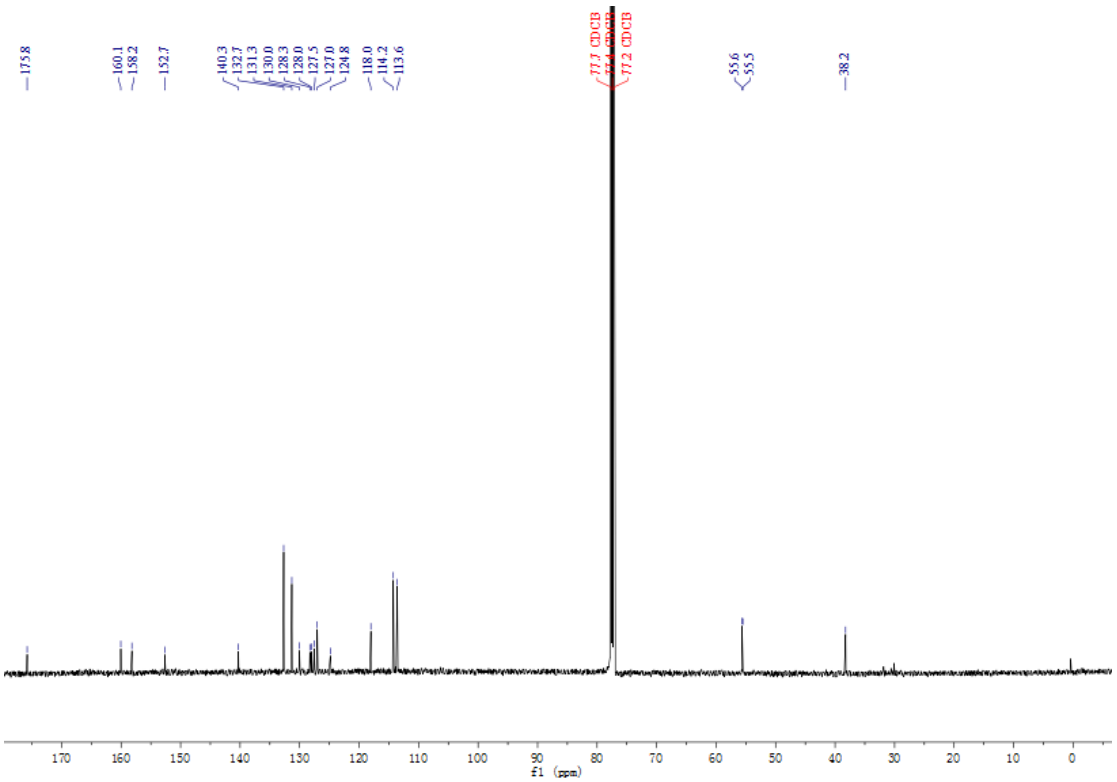
(23) The ^{1}H NMR and ^{13}C NMR spectrum for **4g**



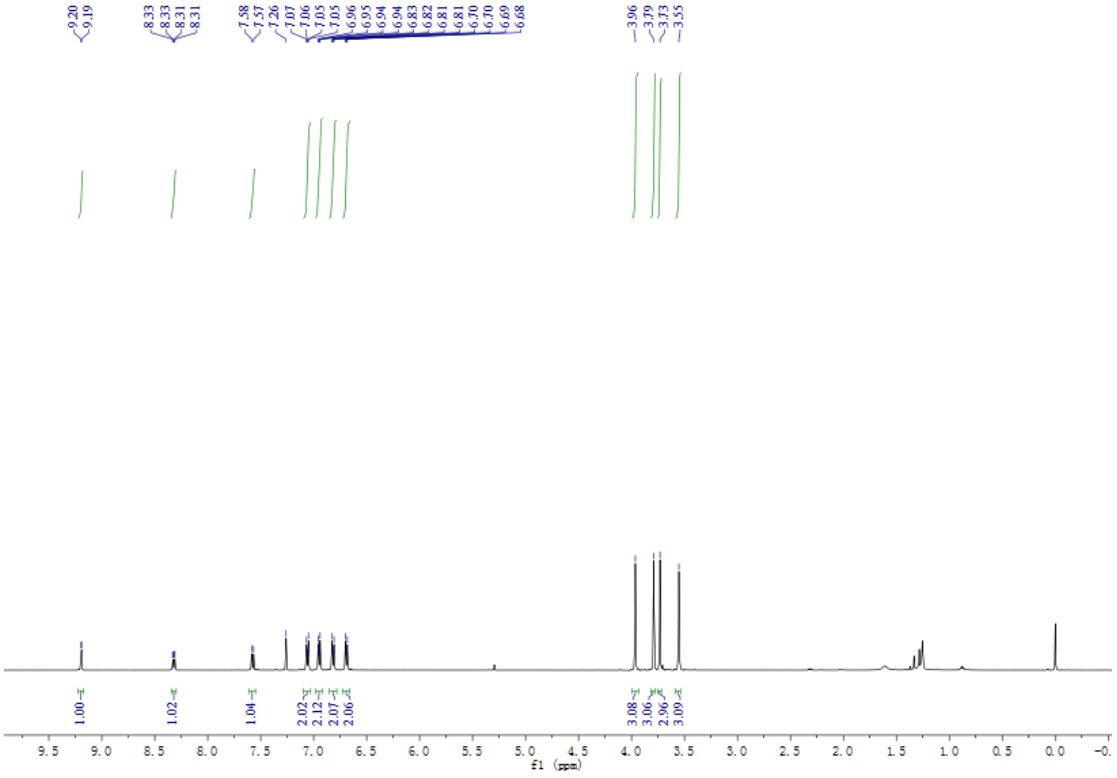


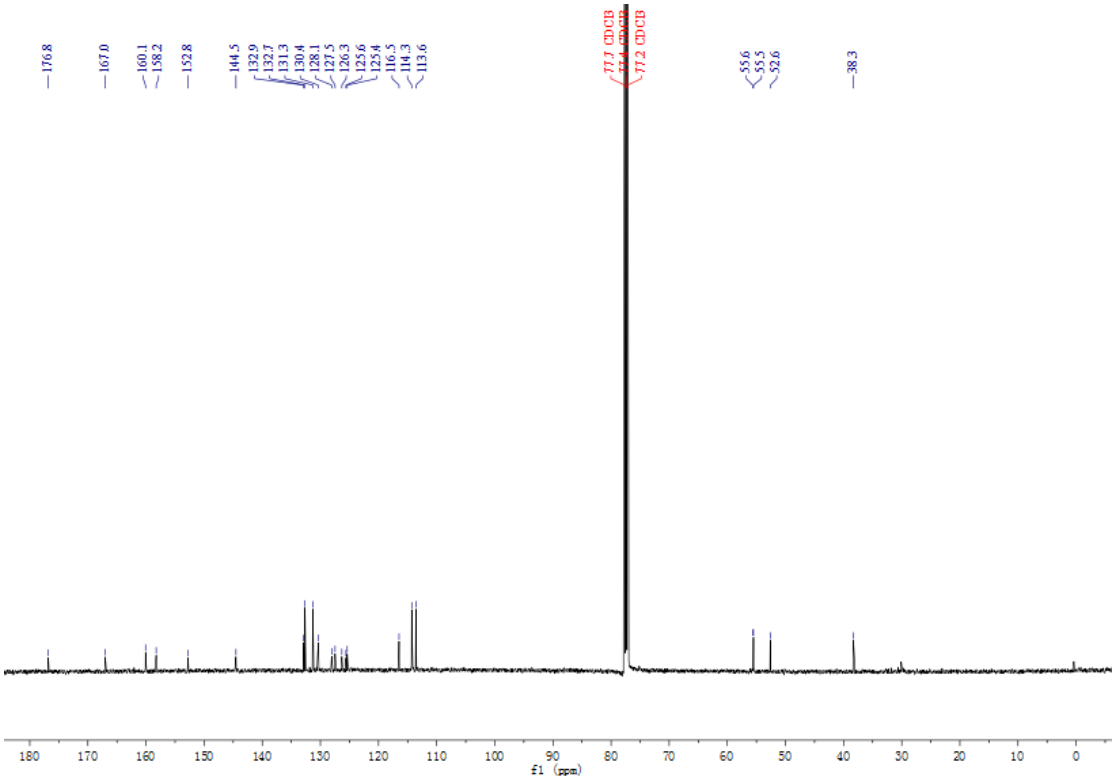
(24) The ^{1}H NMR and ^{13}C NMR spectrum for **4h**



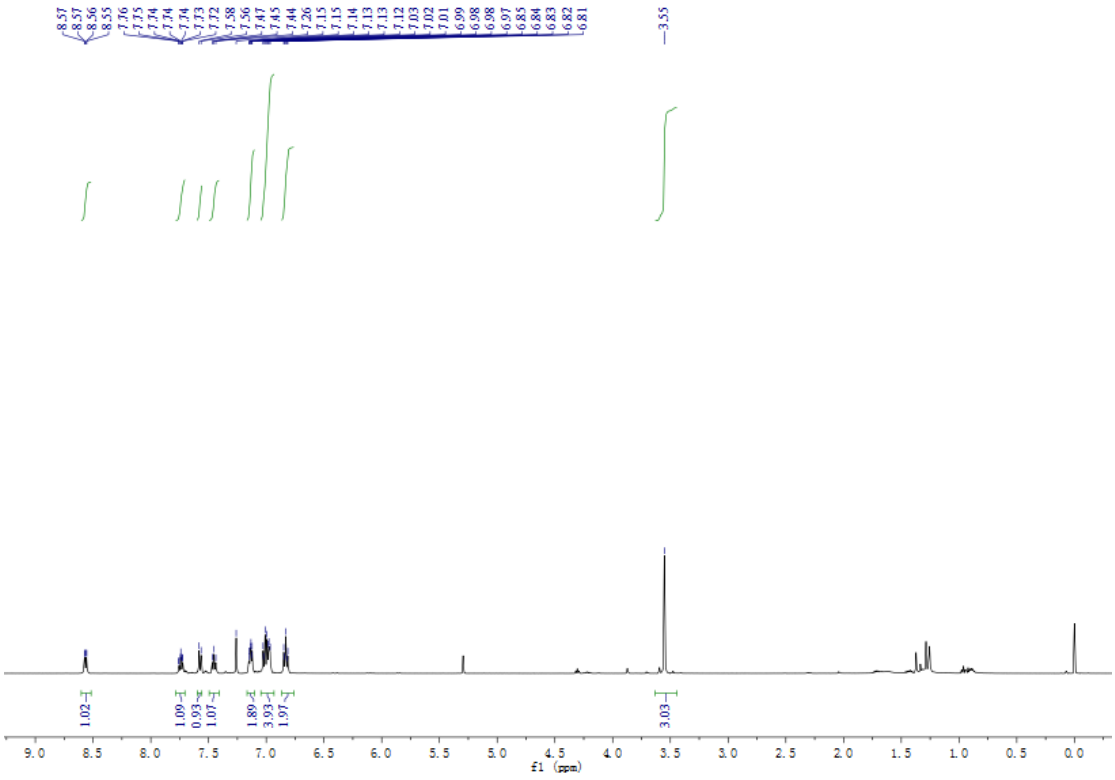


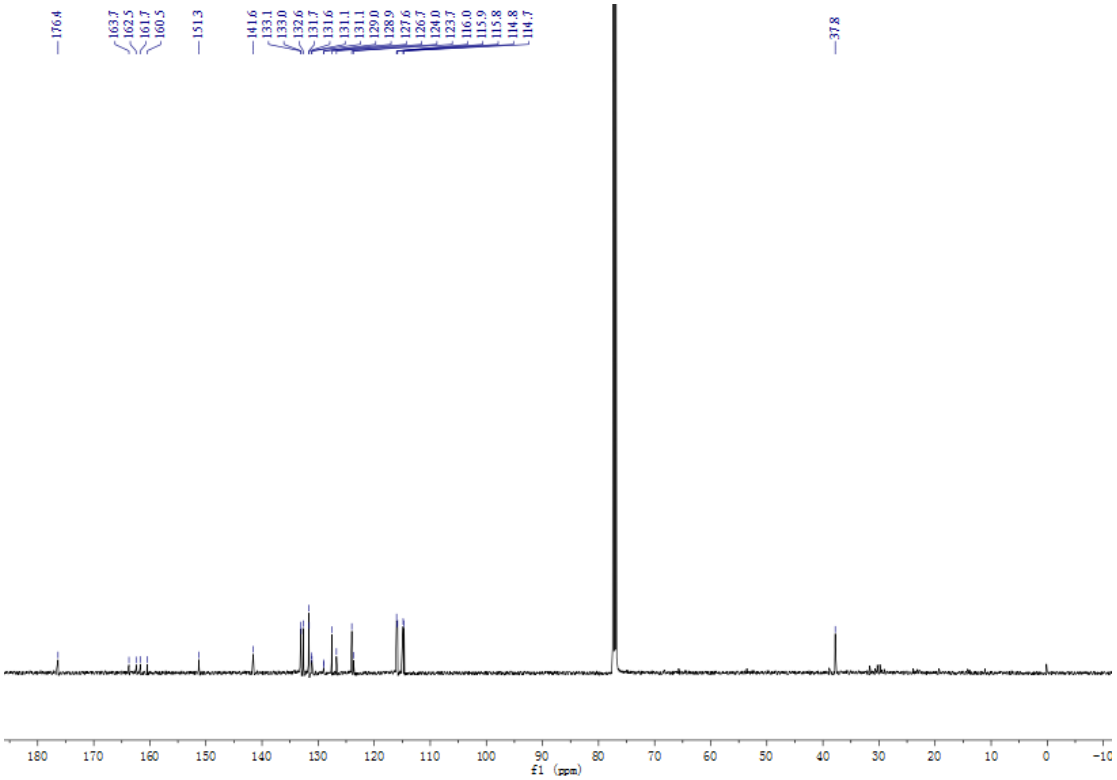
(25) The ^{1}H NMR and ^{13}C NMR spectrum for **4i**

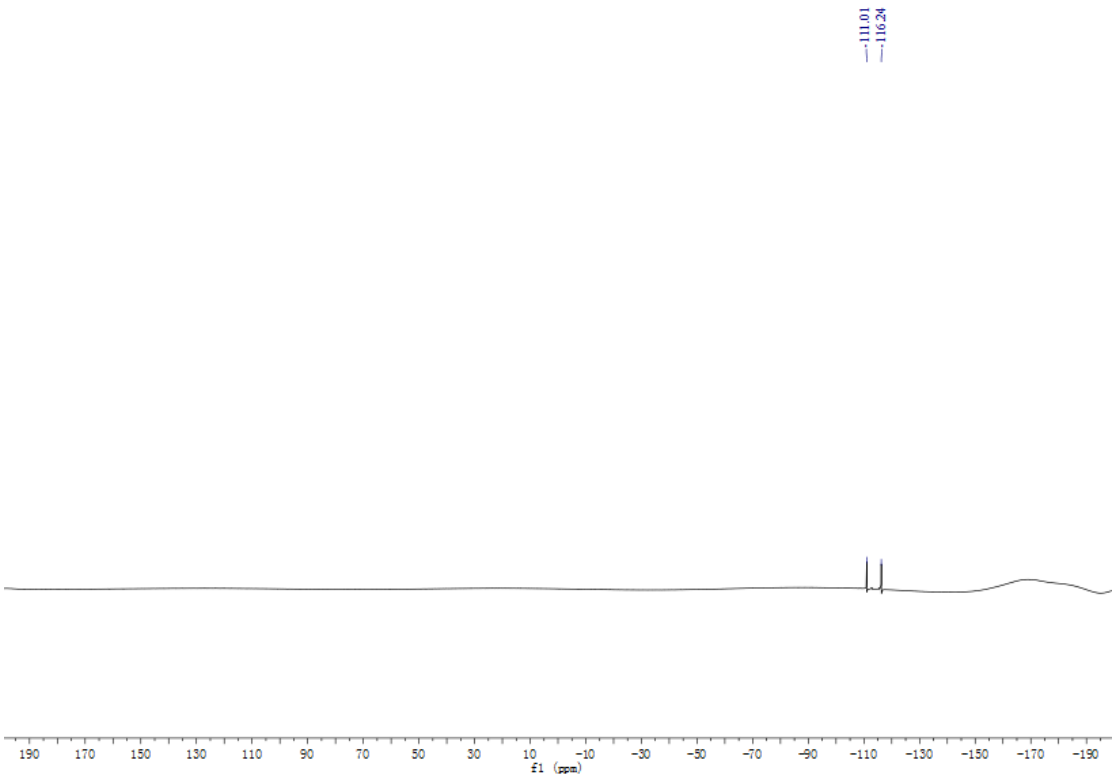




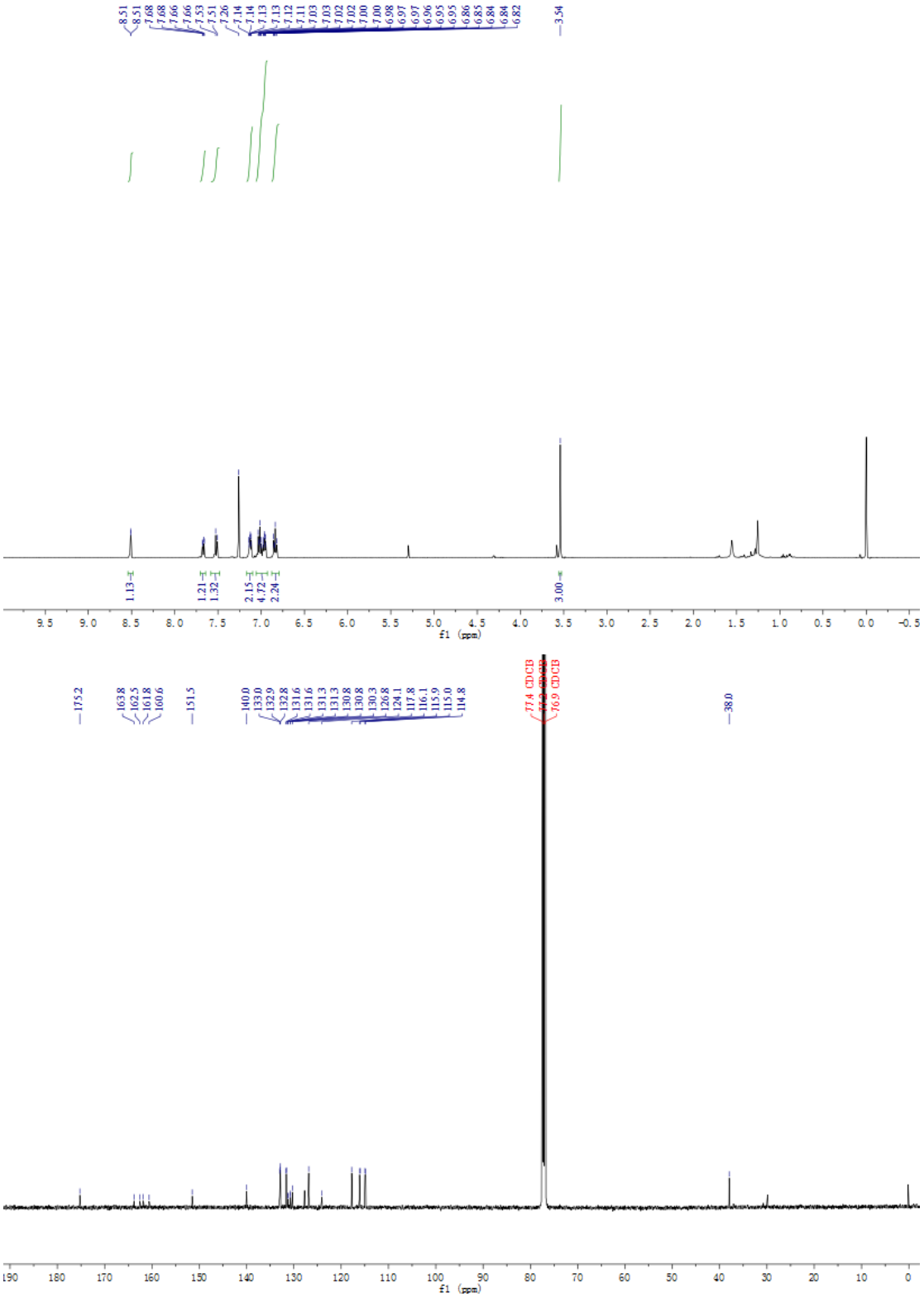
(26) The ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMRspectra for **4j**

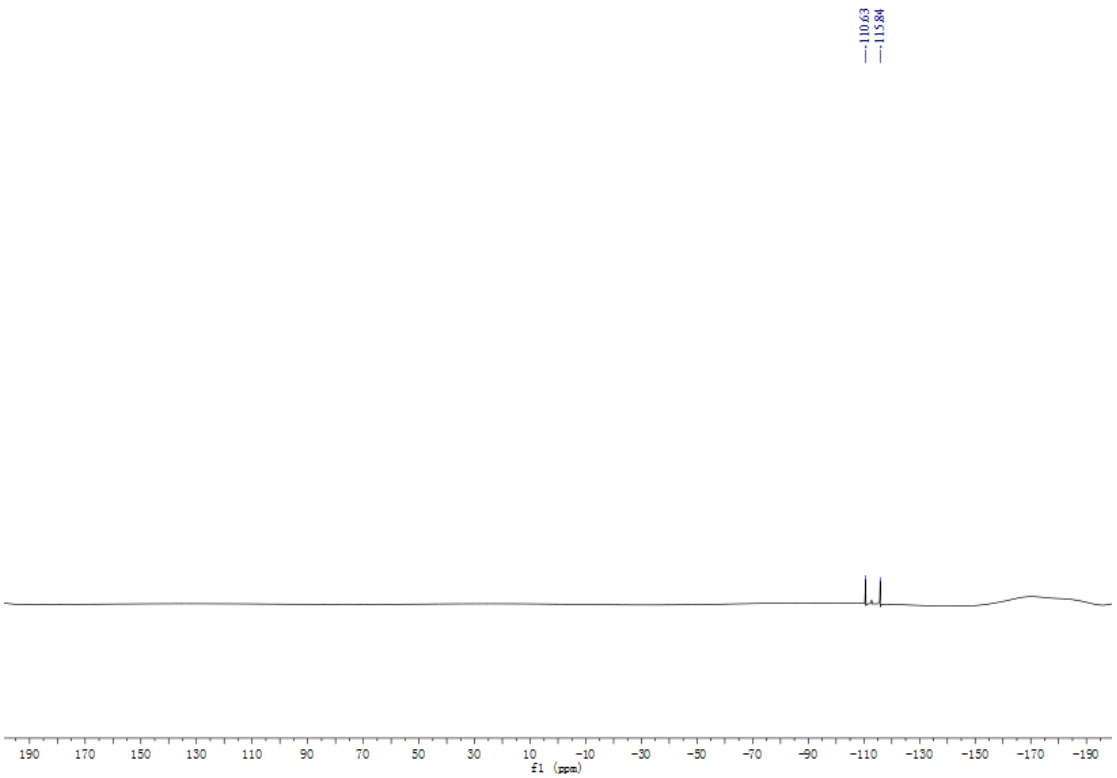



176.4
163.7
162.5
161.7
160.5
151.3
141.6
133.1
133.0
132.6
131.7
131.6
131.1
131.1
129.0
128.9
127.6
126.7
124.0
123.7
116.0
115.9
115.8
114.8
114.7
37.8
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

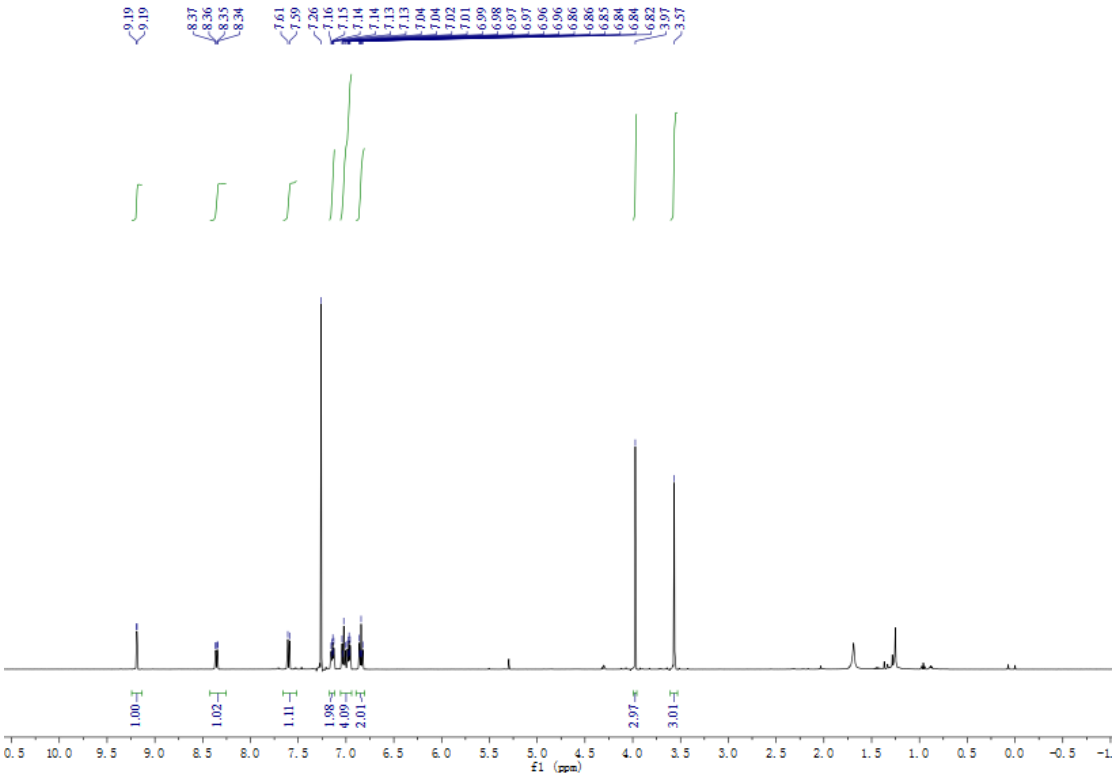

-111.01
-116.24
190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
f1 (ppm)

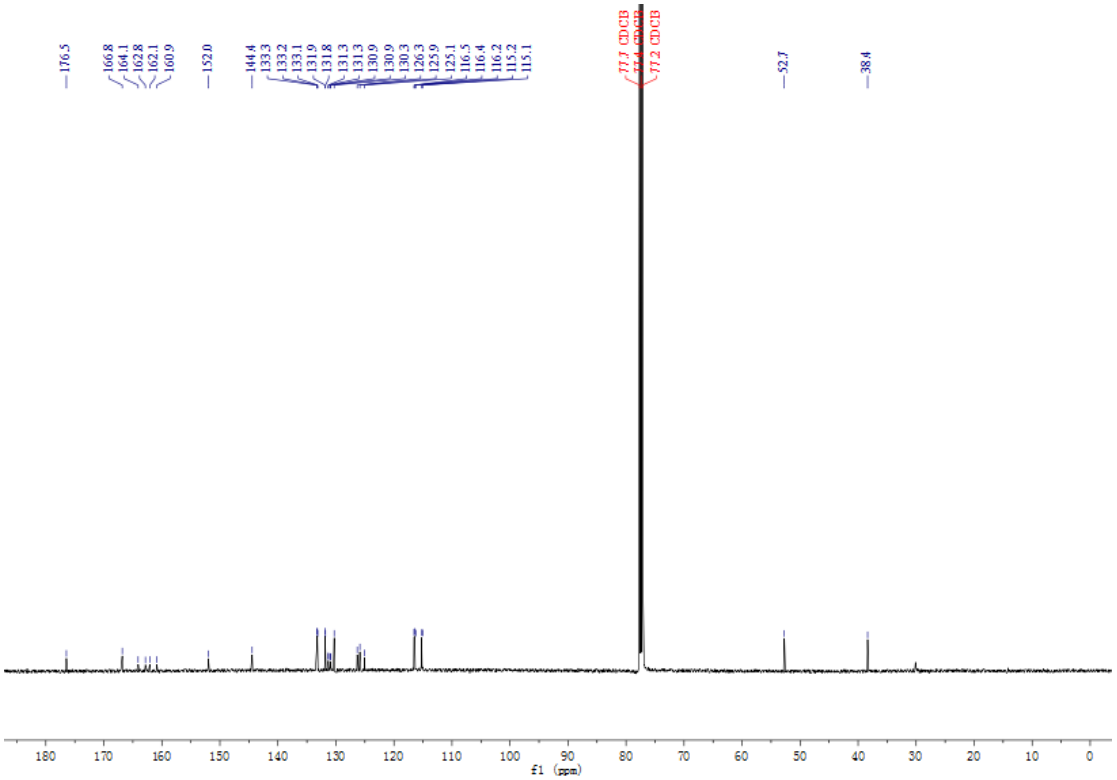
(27) The ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMRspectra for **4k**

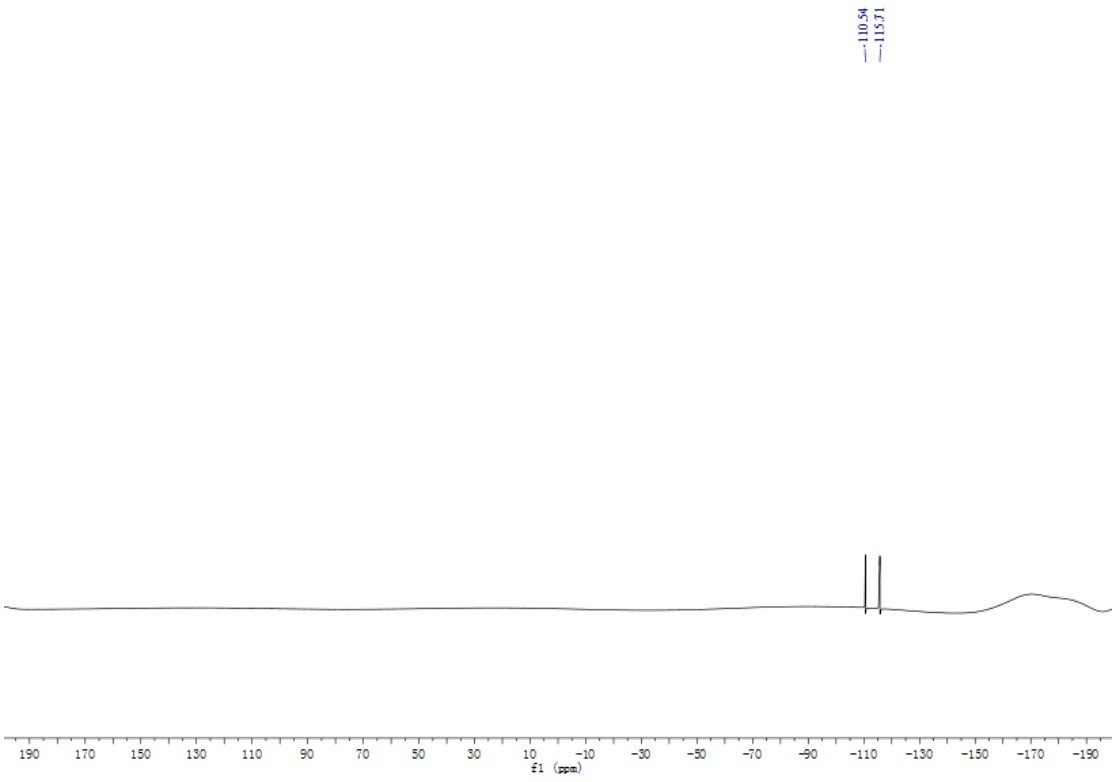




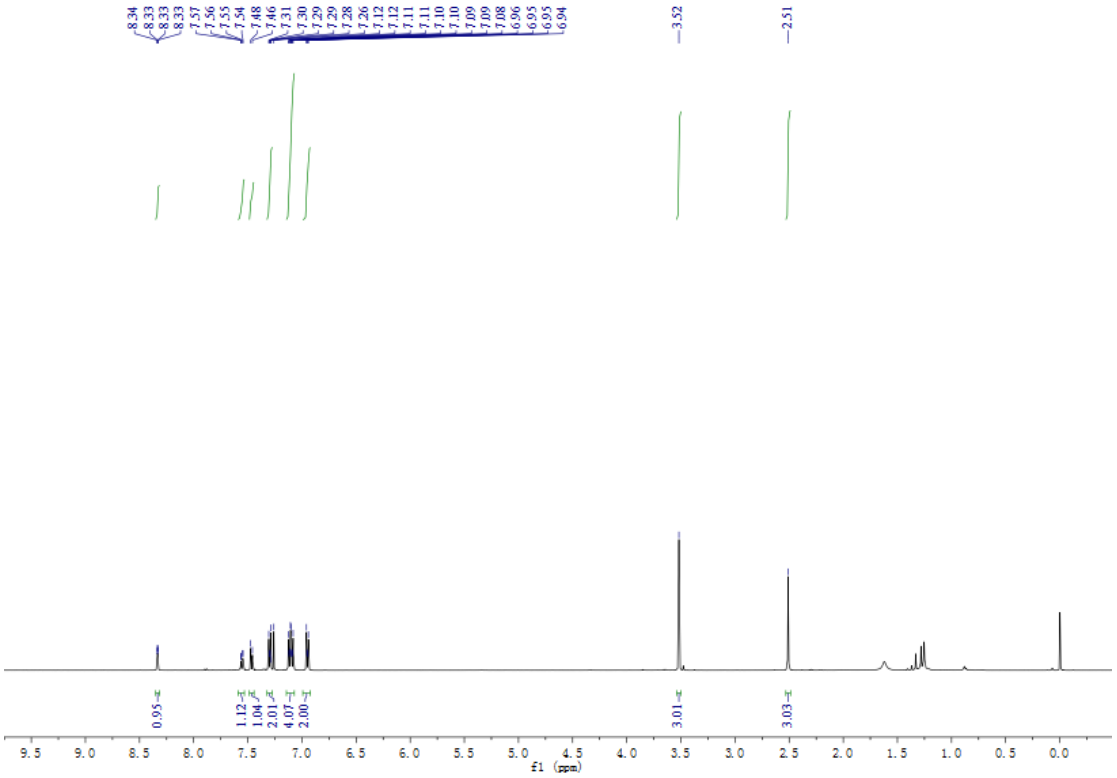
(28) The ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMRspectra for **4l**

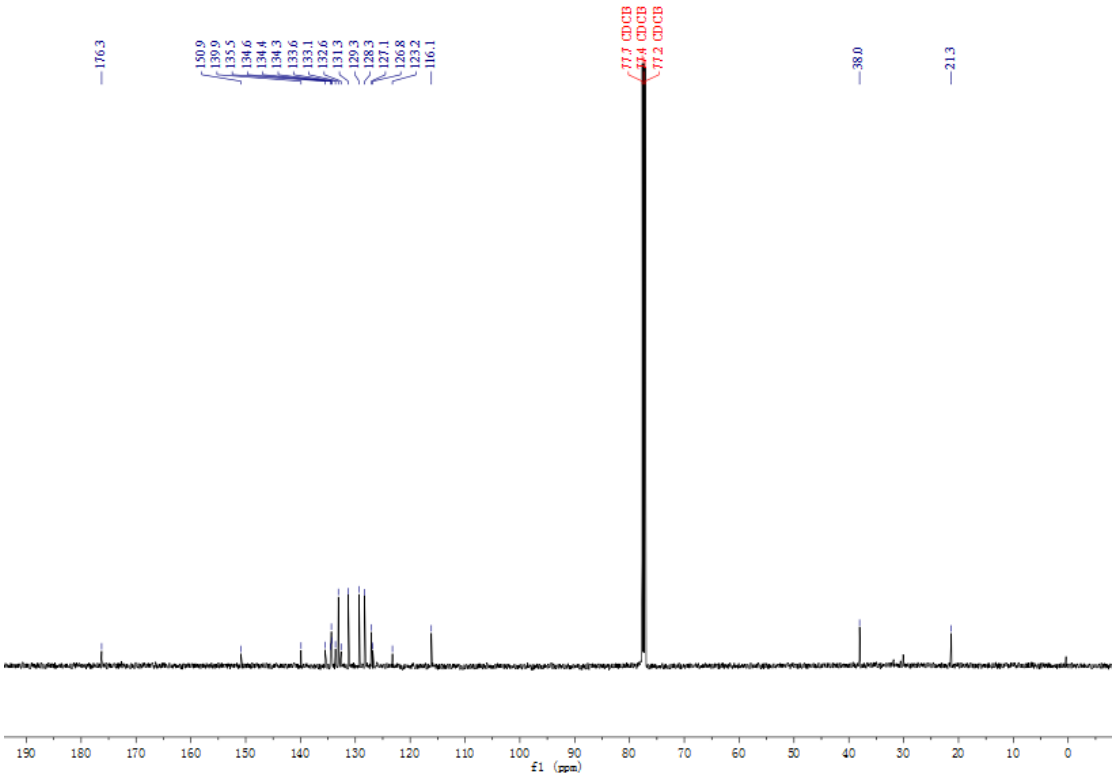



176.5
166.8
164.1
162.8
162.1
160.9
152.0
144.4
133.3
133.2
133.1
131.9
131.8
131.3
131.3
130.9
130.9
130.3
126.3
125.9
125.1
116.5
116.4
116.2
115.2
115.1
77.3 CDCl3
77.2 CDCl3
52.7
38.4
f1 (ppm)

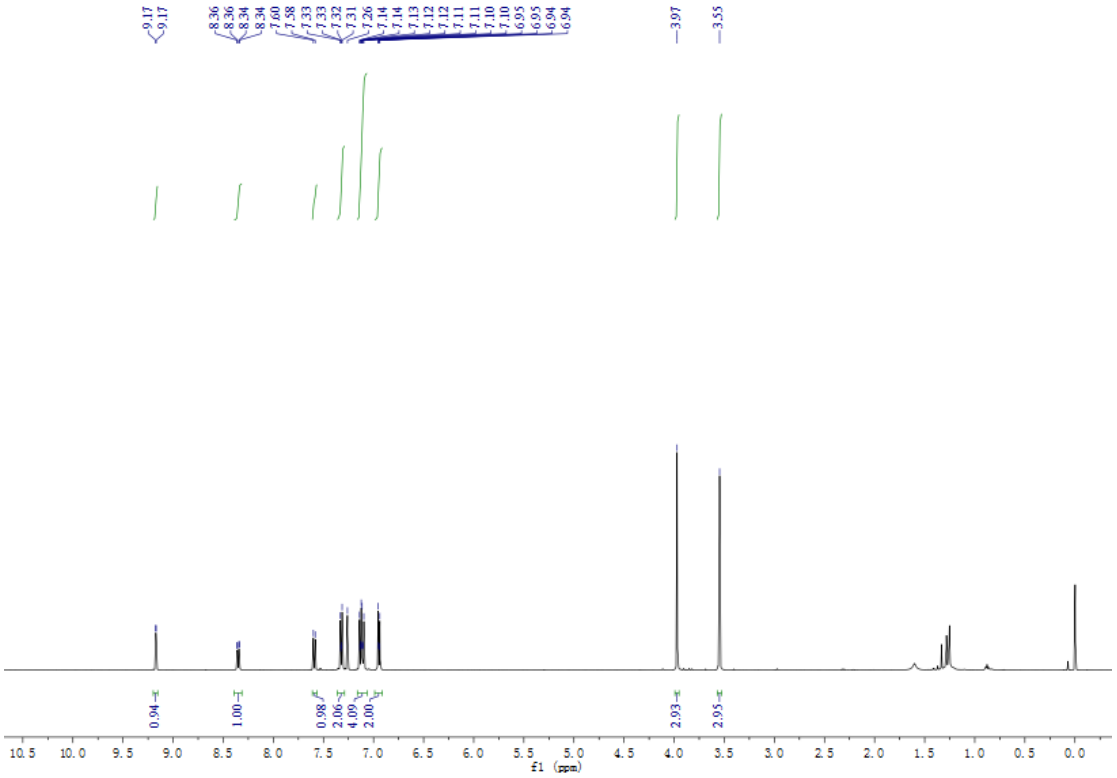

110.54
115.71
f1 (ppm)

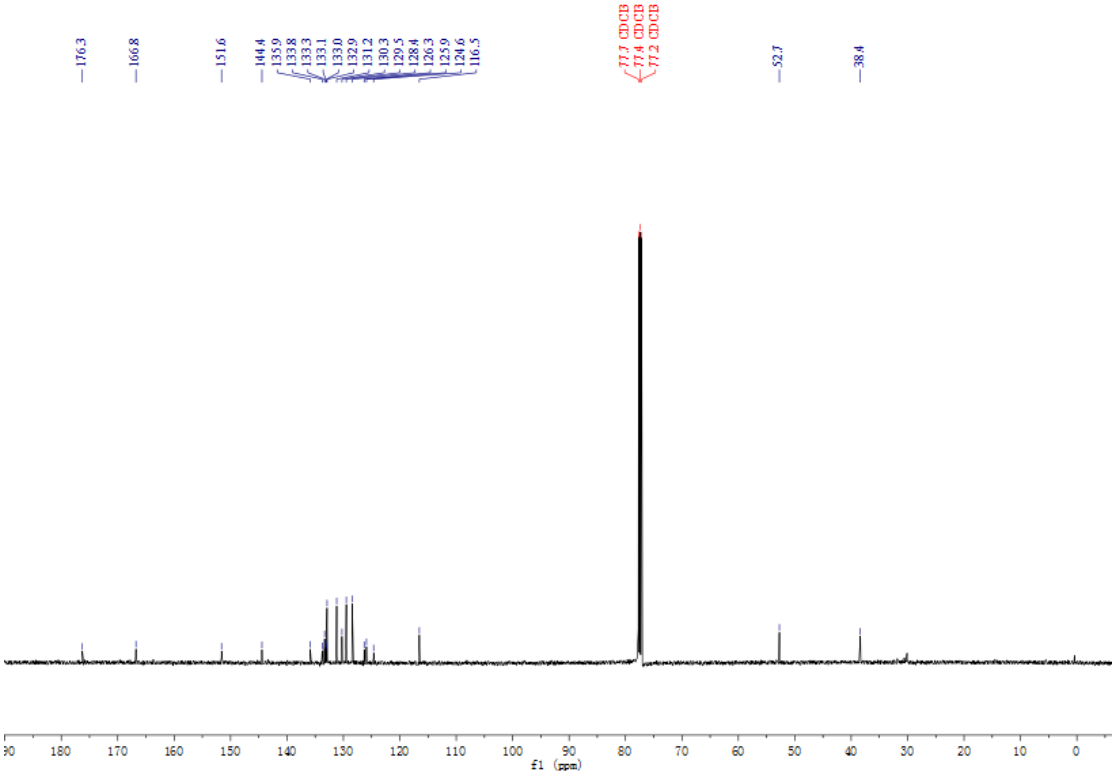
(29) The ^{1}H NMR and ^{13}C NMR spectrum for **4m**



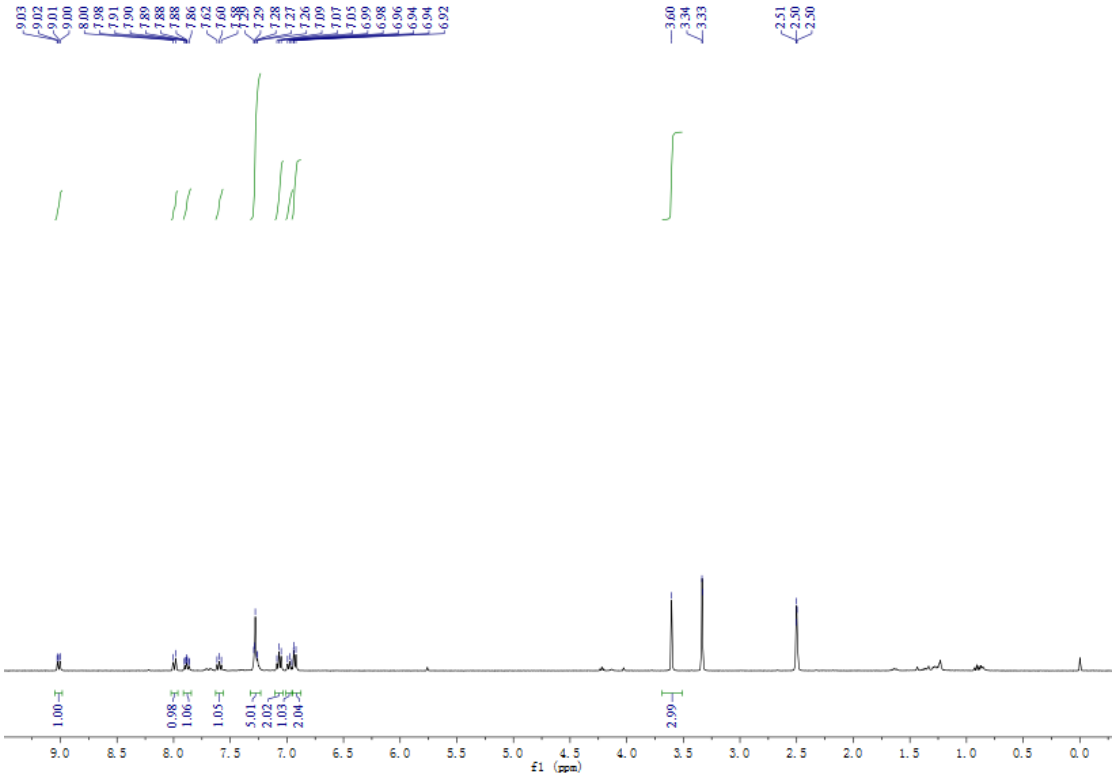


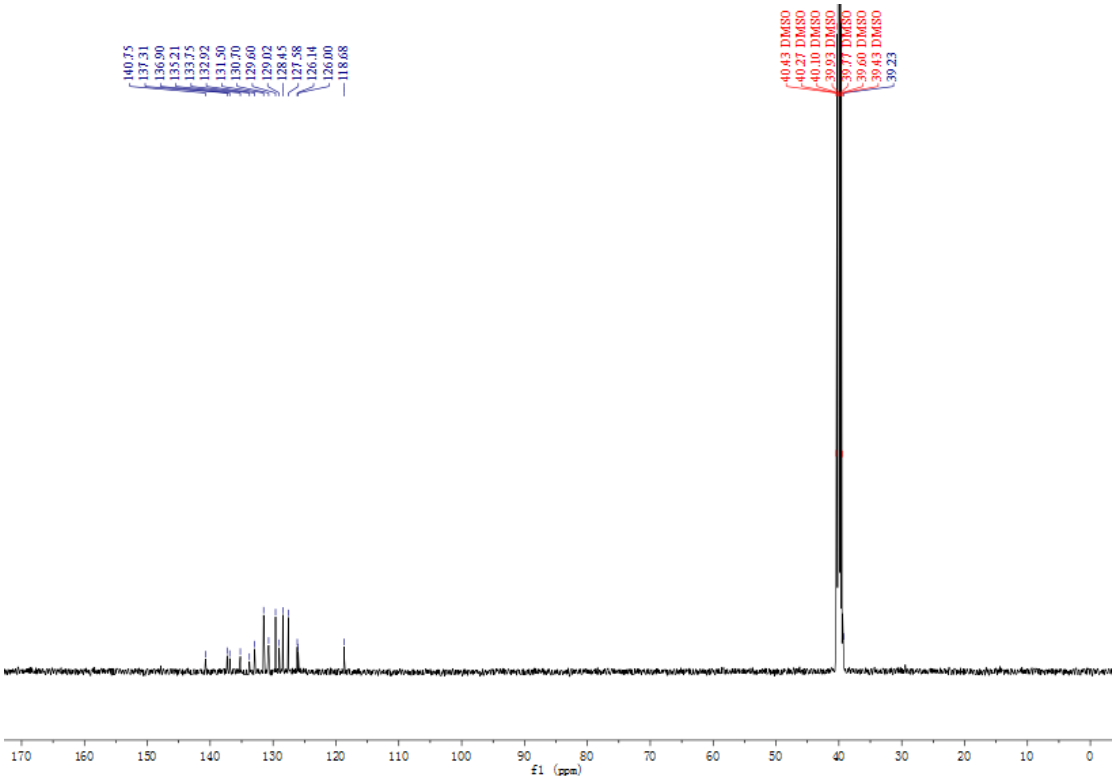
(30) The ^{1}H NMR and ^{13}C NMR spectrum for **4n**





(31) The ^{1}H NMR and ^{13}C NMR spectrum for **5**





(32) The ^{1}H NMR and ^{13}C NMR spectrum for **6**