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Dehydroxylated Amination Accompanied by 1,2-Sulfur Immigration

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Supporting Information

1. General Information

Unless otherwise noted, all reactions were carried out in reaction tube (5 mL from Synware) equipped with a Teflon-coated magnetic stir bar. All commercially available reagents (anilines and thiols) were used without further purification. *β*-sulfur substituted aryl alcohols were prepared according to literature.[1,2] *R*-2-((4-chlorophenyl)thio)-2-phenylethan-1-ol was prepared according to literature using (R)-Styrene oxide (98% *ee*).[1] Analytical thin layer chromatography (TLC) was performed using Silica Gel 60 F25 plates (Qingdao, 0.25 mm thick). GC-MS data were recorded on an Agilent Technologies 7890A GC system coupled with Agilent Technologies 5975C mass spectrometer using HP-5MS column (30 m x 0.250 mm, 0.25 μ) purchased from Agilent Technologies. Enantioselectivity was determined by Agilent LC 1260 with chiral column. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ or DMSO using 300 MHz, 400 MHz Varian NMR spectrometer. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual $CDCl_3$ (7.27 ppm) or the central peak of DMSO-d_6 (2.50 ppm).

2. General Experimental details

2.1 General procedure for dehydroxylated *N*-alkyl amination

A 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with *β*-sulfur substituted aryl alcohols (0.2 mmol). With the rubber septum fitted to the vial, the vessel was degassed using a vent needle for ca. 30 sec and charged with a nitrogen balloon. PBr_3 (0.3 mmol)(pre-dissolved in 1 mL DCM) was added via syringe. Next, anilines (0.3 mmol) (pre-dissolved in another 1 mL DCM) was added slowly via syringe. The top of the vial was wrapped in Parafilm® and the mixture was stirred at room temperature for 4-16 h. After completion, stirring was stopped and septum was opened. NaOH aqueous solution (1M, 1 mL) was slowly added in portion and further stirred for extra 30 seconds. The mixture was then diluted with DCM and washed with water and brine respectively. The collected organic solution was concentrated in vacuo and the crude material was further purified via column chromatography (EA/PE from 1/10 to 1/4).

2.2 General procedure for synthesis of *N*-(1-(4-bromophenyl)-2-((4-chlorophenyl)thio)ethyl) -4-methylaniline **4r**

A 100 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with 2-(4-bromophenyl)-2-((4-chlorophenyl)thio)ethan-1-ol (1.71g, 5 mmol).

With the rubber septum fitted to the vial, the vessel was degassed using a vent needle for ca. 30 sec and charged with a nitrogen balloon. PBr_3 (2g, 7.5 mmol)(pre-dissolved in 25 mL DCM) was added via syringe. Next, p-toluidine (0.8g, 7.5 mmol) (pre-dissolved in another 25 mL DCM) was added slowly via syringe. The top of the vial was wrapped in Parafilm® and the mixture was stirred at room temperature for 4-16 h. After completion, stirring was stopped and septum was opened. NaOH aqueous solution (1M, 20 mL) was slowly added in portion and further stirred for extra 5 min. The mixture was then diluted with DCM and washed with water and brine respectively. The collected organic solution was concentrated in vacuo and the crude material was further purified via column chromatography (EA/PE =1/5), yield product *N*-(1-(4-bromophenyl)-2 -((4-chlorophenyl)thio)ethyl)-4-methylaniline **4s** as a brown oil (1.83g, 85%).^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.53 – 7.42 (m, 2H), 7.36 – 7.22 (m, 6H), 6. 95 (d, *J*=8.3 Hz, 2H), 6.44 (d, *J*=8. 4Hz, 2H), 4.64 – 4.10 (m, 2H), 3.34 (dd, *J*=13.5 Hz,, 4.5 Hz,, 1H), 3.14 (dd, *J*=13.5 Hz,, 9.0 Hz,, 1H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.4, 141.4, 133.3, 133.2, 132.2, 132.0, 129.7, 129.4, 128.2, 127.6, 121.4, 114.1, 56.8, 42.8, 20. 5. GC-MS(EI):431/433m/z, HRMS (CI-TOF) m/z $M+H^+$ calcd for $C_{21}H_{20}BrClNS^+$ 432.0183, found 431.0185

2.3 controlled experiments

2.3.1 Procedure for controlled experiment a

A 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with 2-((4-chlorophenyl)thio)-2-phenylethan-1-ol (52.8 mg, 0.2 mmol). PBr_3 (81.0 mg, 0.3 mmol)(pre-dissolved in 2 mL DCM) was added via syringe. The mixture was stirred at room temperature for 4 h. (note: the reaction was conducted in air, without solvent seasoning). After completion, stirring was stopped. The mixture was then diluted with DCM and washed with water and brine respectively. The collected organic solution was concentrated in vacuo and the crude material was further purified via column chromatography (EA/PE = 1/20) to give 2-((4-chlorophenyl)thio)-1-phenylethan-1-ol (42 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (m, 9H), 4.65 (dd, *J* = 9.1, 3.5 Hz, 1H), 3.20 (dd, *J* = 13.8, 3.7 Hz, 1H), 3.03 (dd, *J* = 13.7, 9.2 Hz, 1H), 2.73 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 133.6, 132.9, 131.5, 129.3, 128.6, 128.1, 125.9, 71.9, 44.1; GC-MS(EI):264m/z. The analytic data is in accordance with literature[2].

Procedure for controlled experiment b

A 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with 2-((4-chlorophenyl)thio)-1-phenylethan-1-ol (0.2 mmol). With the rubber septum fitted to the vial, the vessel was degassed using a vent needle for ca. 30 sec and charged with a nitrogen balloon. PBr_3 or NBS (0.3 mmol)(pre-dissolved in 1 mL DCM) was added via syringe. The reaction mixture was stirred at room temperature for 2 hours. Next, p-toluidine (0.3 mmol) (pre-dissolved in another 1 mL DCM) was added slowly via syringe and further stirred at room temperature for 4 h. After completion, stirring was stopped and septum was opened. For reactions using PBr_3, NaOH aqueous solution (1M, 1 mL) was slowly added in portion and further stirred for extra 30 seconds. The mixture was then diluted with DCM and washed with water and brine respectively. The collected organic solution was detected by GC-Ms using naphthaline as a standard and crude ^{1}H NMR. For reactions using NBS, the reaction mixture was passed through a short column and detected by GC-Ms using naphthaline as a standard.

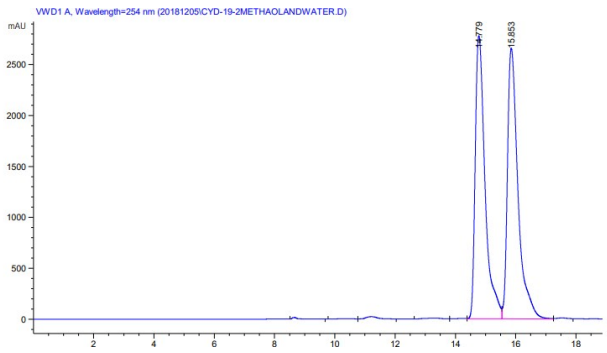
Procedure for controlled experiment c

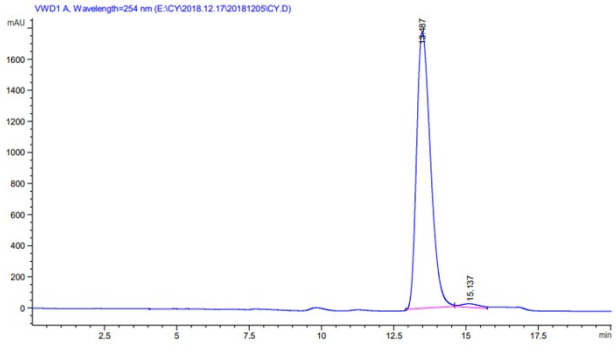
A 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with 2-((4-chlorophenyl)thio)-1-phenylethan-1-ol (52.8 mg, 0.2 mmol). With the rubber septum fitted to the vial, the vessel was degassed using a vent needle for ca. 30 sec and charged with

a nitrogen balloon. DCM (2 mL) was added via syringe. The reaction was cooled in iced bath. Next, (0.3 mmol)(pre-dissolved in 1 mL DCM) was added slowly via syringe to get a light brown solution. Then p-toluidine (0.3 mmol) (pre-dissolved in another 1 mL DCM) was added slowly via syringe. was added and the mixture was stirred at room temperature for 16 h. After completion, stirring was stopped and septum was opened. NaOH aqueous solution (1M, 1 mL) was slowly added in portion and further stirred for extra 30 seconds. The mixture was then diluted with DCM and washed with water and brine respectively. The collected organic solution was purified via column chromatography (EA/PE from 1/10 to 1/4) to give product (50.8 mg, 72%). ^{1}H NMR identified the isolated product as a mixture of *N*-(2-((4-chlorophenyl)thio)-1-phenylethyl)-4-methylaniline **3a** and *N*-(2-((4-chlorophenyl)thio)- 2-phenylethyl)-4-methylaniline **3a'** (**3a/3a'**=12/1).

Procedure for controlled experiment d

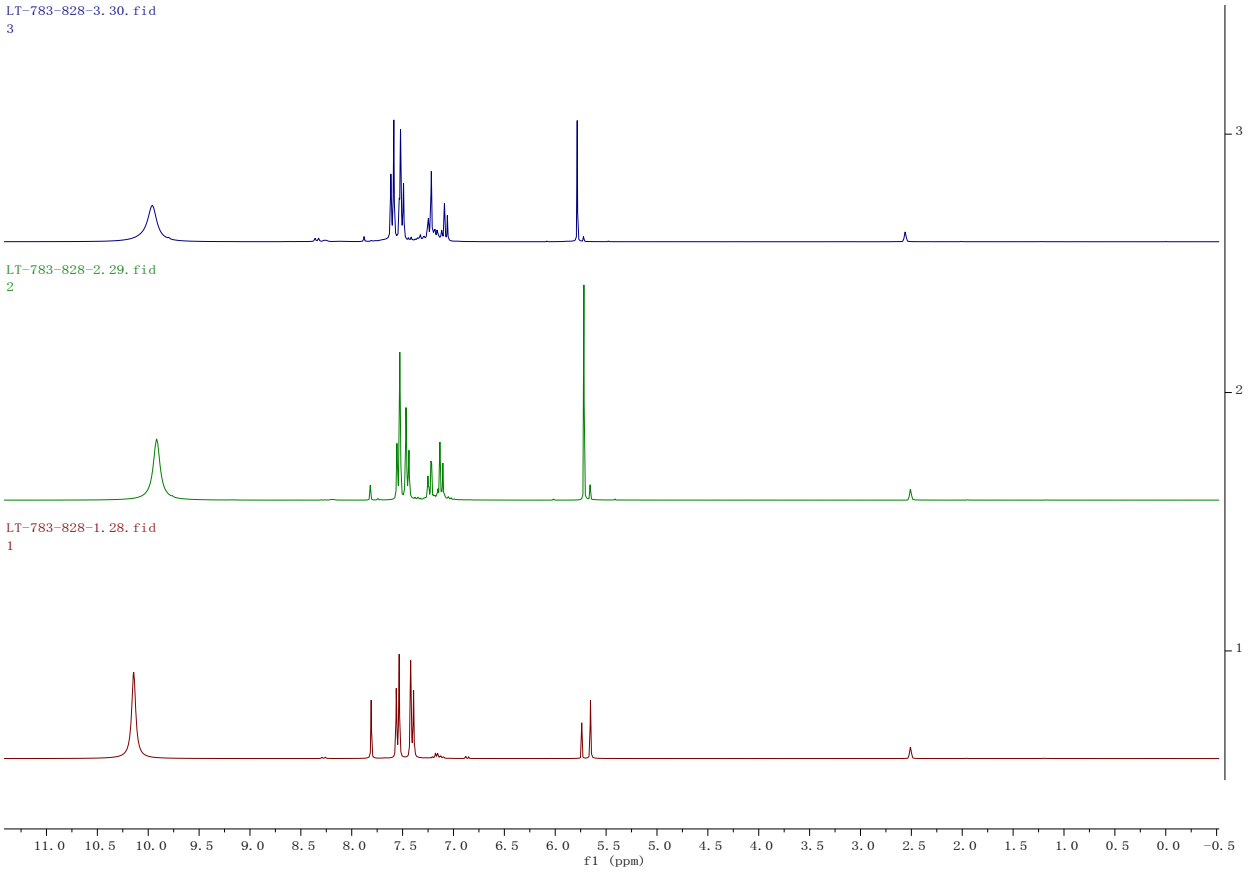
A 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with *R*-2-((4-chlorophenyl)thio)-2-phenylethan-1-ol (52.8 mg, 0.2 mmol). With the rubber septum fitted to the vial, the vessel was degassed using a vent needle for ca. 30 sec and charged with a nitrogen balloon. PBr_3 (81mg, 0.3 mmol)(pre-dissolved in 1 mL DCM) was added via syringe. Next, p-toluidine (42.8 mg, 0.3 mmol) (pre-dissolved in another 1 mL DCM) was added slowly via syringe. The top of the vial was wrapped in Parafilm® and the mixture was stirred at room temperature for 4 h. After completion, stirring was stopped and septum was opened. NaOH aqueous solution (1M, 1 mL) was slowly added in portion and further stirred for extra 30 seconds. The mixture was then diluted with DCM and washed with water and brine respectively. The collected organic solution was concentrated in vacuo and the crude material was further purified via column chromatography (EA/PE from 1/10 to 1/4) to give product R(or S)-**3a** in the yield of 85%, 96.7% *ee*.





Procedure for controlled experiment e

A 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with p-toluidine (42.8 mg, 0.3 mmol or 128.4 mg, 0.9 mmol) and DCM (1 mL). With the rubber septum fitted to the vial, the vessel was degassed using a vent needle for ca. 30 sec and charged with a nitrogen balloon. PBr_3 (81mg, 0.1-0.3 mmol)(pre-dissolved in 1 mL DCM) was added via syringe. The top of the vial was wrapped in Parafilm® and the mixture was stirred at room temperature for 5 min. After that, stirring was stopped and DCM was removed. The residue was introduced to d6-DMSO and tracked with ^1H NMR. The NMR spectra below showed the sequence formation of 4-MePhNHPBr$_2$, (4-MePhNH)$_2$PBr and (4-MePhNH)$_3$P and p-toluidine hydrobromide salt using . p-toluidine/PBr_3=3/1, 2/1, 1/1 respectively.



3. Analytical data

^1H, ^{13}C and HRMS for all unknown products **3a-3m, 4a-4q** were given. For compounds **3h**, **3k** and **3m,** abnormal HRMS was observed that in the case of [M-H_2]+H^+, which probably due to the loss of

H_2 during HRMS process.

N-(2-((4-chlorophenyl)thio)-1-phenylethyl)aniline. **3a***,* yellow oil, 57.6 mg, 85% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.52 – 7.31 (m, 9H), 7.21 (t, *J*=7.9 Hz, 2H), 6.81 (t, *J*=7.3Hz, 1H), 6.62 (d, *J*=8.3 Hz, 2H), 4.61 (s, 1H), 4.52 (dd, *J*=9.0, 4.5 Hz, 1H), 3.45 (dd, *J*=13.4, 4.5 Hz, 1H), 3.25 (dd, *J*=13.4, 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.1, 142.3, 133.7, 133.1, 132.0, 129.4, 129.3, 129.0, 127.8, 126.5, 118.2, 113.9, 57.2, 42.9. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{20}H_{19}ClNS^+$ 340.0921, found 340.0922

N-(2-((4-chlorophenyl)thio)-1-phenylethyl)-4-fluoroaniline. **3b,** yellow oil, 55.7 mg, 78% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40 – 7.24 (m, 9H), 6.89 – 6.76 (m, 2H), 6.52 – 6.40 (m, 2H), 4.51 (s, 1H), 4.35 (dd, *J*=9.0, 4.5 Hz, 1H), 3.39 (dd, *J*=13.5, 4.5 Hz, 1H), 3.17 (dd, *J*=13.5, 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.2(d, *^{1}JC-F=322Hz*), 143.3, 142.0, 133.4, 133.1, 132.1, 129.3, 128.9, 127.8, 126.4, 115.6(d, *^{2}JC-F* = 22Hz), 114.8(d, *^{3}JC-F* = 8Hz), 57.8, 42.9. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{20}H_{18}ClFNS^+$ 358.0827, found 358.0829.

N-(2-((4-chlorophenyl)thio)-1-phenylethyl)-4-methylaniline. **3c**, yellow oil, 56 mg, 80% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.45 – 7.20 (m, 11H), 6.94 (d, *J*=8.4 Hz, 2H), 6.46 (d, *J*=8.4 Hz, 2H), 4.65 –4.37 (m, 2H), 3.38 (dd, *J*=13.4, 4.7 Hz, 1H), 3.20 (dd, *J*=13.4, 8.8 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.7, 142.2, 133.7, 133.0, 132.0, 129.6, 129.2, 128.9, 127.6, 127.4, 126.5, 114.1, 57.6, 42.8, 20.4. HRMS (ESI) m/z M+H$^+$ calcd for $C_{21}H_{21}ClNS^+$ 354.1078, found 354.1074.

N-(2-((4-chlorophenyl)thio)-1-phenylethyl)-2-nitroaniline. **3d,** yellow oil, 63.7 mg, 83% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.74 (d, *J*=5.1 Hz, 1H), 8.20 (d, *J*=8.5 Hz, 1H), 7.47 – 7.19 (m, 10H), 6.66 (dd, *J*=8.3, 7.3 Hz, 1H), 6.57 (d, *J*=8.6 Hz, 1H), 4.70 (dt, *J*=10.8, 5.4 Hz, 1H), 3.46 (dd, *J*=13.6, 5.0Hz, 1H), 3.36 (dd, *J*=13.5, 8.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.1, 140.5, 136.0, 133.4, 133.3, 132.8, 132.3, 129.3, 129.2, 128.2, 126.8, 126.3, 116.1, 115.0, 56.8, 42.9. GC-MS(EI):384m/z, HRMS (CI-TOF) m/z M+Na$^+$ calcd for $C_{20}H_{17}ClN_2O_2SNa^+$ 407.0591, found 407.0596.

*N-(2-((4-chlorophenyl)thio)-1-phenylethyl)-2-methoxyaniline.***3e,** yellow oil, 41 mg, 56% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.48 – 7.23 (m, 9H), 6.88 – 6.78 (m, 1H), 6.77 – 6.64 (m, 2H), 6.35 – 6.24 (m, 1H), 5.13 (s, 1H), 4.48 (dd, *J*=8.6, 4.9 Hz, 1H), 3.93 (s, 3H), 3.41 (dd, *J*=13.4, 4.9 Hz, 1H), 3.30 (dd, *J*=13.4, 8.6, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.1, 142.3, 136.8, 134.0, 132.8, 131.8, 129.2, 128.9, 127.7, 126.5, 121.1, 117.2, 111.3, 109.4, 57.4, 55.6, 42.8. HRMS (CI-TOF) m/z M+H$^+$

calcd for $C_{21}H_{21}ClNOS^+$ 370.1027, found 370.1032

N-(2-((4-chlorophenyl)thio)-1-phenylethyl)-3-methoxyaniline. **3f,** yellow oil, 54.6 mg, 74% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42 – 7.23 (m, 9H), 7.02 (t, *J*=8.1 Hz, 1H), 6.34 – 6.25 (m, 1H), 6.20 – 6.13 (m, 1H), 6.07 (t, *J*=2.3 Hz, 1H), 4.59 (s, 1H), 4.43 (dd, *J*=8.7, 4.8 Hz, 1H), 3.70 (s, 3H), 3.38 (dd, *J*=13.5, 4.8 Hz, 1H), 3.20 (dd, *J*=13.5, 8.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.6, 148.3, 142.0, 133.5, 133.1, 132.0, 129.9, 129.3, 128.9, 127.8, 126.4, 107.0, 103.3, 100.0, 57.2, 55.0, 42.7. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{21}H_{21}ClNOS^+$ 370.1027, found 370.1028

*N-(2-((4-chlorophenyl)thio)-1-phenylethyl)-4-methoxyaniline.***3g** yellow oil, 44.3 mg, 60% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42 – 7.23 (m, 9H), 6.76 – 6.68 (m, 2H), 6.54 – 6.44 (m, 2H), 4.35 (dd, *J*=8.8, 4.6 Hz, 1H), 3.72 (s, 3H), 3.37 (dd, *J*=13.4, 4.6 Hz, 1H), 3.18 (dd, *J*=13.4, 8.9 Hz, 1H), 1.31 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.6, 142.3, 141.2, 133.7, 133.0, 132.0, 129.2, 128.9, 127.7, 126.5, 115.4, 114.8, 58.1, 55.7, 42.9. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{21}H_{21}ClNOS^+$ 370.1027, found 370.1028

3,4-dichloro-N-(2-((4-chlorophenyl)thio)-1-phenylethyl)aniline. **3h,** yellow oil, 65 mg, 80% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.46 – 7.24 (m, 9H), 7.12 (d, *J*=8.7 Hz, 1H), 6.60 (d, *J*=2.7, 1H), 6.33 (dd, *J*=8.7, 2.7 Hz, 1H), 4.63 (s, 1H), 4.35 (dd, *J*=9.1, 4.4 Hz, 1H), 3.38 (dd, *J*=13.6, 4.4 Hz, 1H), 3.14 (dd, *J*=13.6, 9.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 146.5, 141.1, 133.4, 132.9, 132.7, 132.2, 130.6, 129.4, 129.1, 128.1, 126.3, 120.7, 115.1, 113.4, 57.0, 42.7. HRMS (CI-TOF) m/z [M-H_2]+H$^+$ calcd for $C_{20}H_{15}Cl_3NS^+$ 405.9985, found 405.9981.

*N-(2-((4-chlorophenyl)thio)-1-phenylethyl)-2-methyl-4-nitroaniline.***3i** yellow semi-solid, 67.7 mg, 85% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.81 (dd, *J*=9.0, 2.3Hz, 1H), 7.43 – 7.16 (m, 9H), 6.16 (d, *J*=9.0 Hz, 1H), 5.10 (s, 1H), 4.64 – 4.42 (m, 1H), 3.46 (dd, *J*=13.8, 4.2 Hz, 1H), 3.23 (dd, *J*=13.8, 9.1 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.3, 140.4, 138.3, 133.6, 132.6, 132.2, 129.5, 129.2, 128.3, 126.1, 125.9, 124.3, 122.0, 109.8, 56.7, 42.7, 17.4. HRMS (CI-TOF) m/z M+Na$^+$ calcd for $C_{21}H_{19}ClN_2O_2SNa^+$ 421.0748, found 421.0747

*N-(2-((4-chlorophenyl)thio)-1-phenylethyl)-4-methoxy-2-nitroaniline.***3j** brown oil, 62 mg, 75% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.66 (d, *J*=5.6 Hz, 1H), 7.65 (d, *J*=3.0 Hz, 1H), 7.45 – 7.21 (m, 9H), 6.95 (dd, *J*=9.3, 3.0 Hz, 1H), 6.52 (d, *J*=9.4 Hz, 1H), 4.66 (dt, *J*=8.4, 5.3 Hz, 1H), 3.77 (s, 3H), 3.44 (dd, *J*=13.6, 4.9 Hz, 1H), 3.33 (dd, *J*=13.6, 8.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.1, 140.8, 139.8, 133.3, 133.2, 132.2, 131.9, 129.3, 129.2, 128.2, 126.7, 126.2, 116.4, 107.4, 56.9, 55.8, 42.8. HRMS (CI-TOF) m/z M+Na$^+$ calcd for $C_{21}H_{19}ClN_2O_3SNa^+$ 437.0697, found 437.0698.

*2-bromo-N-(2-((4-chlorophenyl)thio)-1-phenylethyl)-5-fluoroaniline.***3k** yellow oil, 69 mg, 80% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.45 – 7.21 (m, 10H), 6.37 – 6.25 (m, 1H), 6.01 (dd, *J*=11.3, 2.8Hz, 1H), 5.36 (s, 1H), 4.38 (dt, *J*=8.8, 4.4 Hz, 1H), 3.43 (dd, *J*=13.7, 4.5 Hz, 1H), 3.24 (dd, *J*=13.7, 8.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.9(d, *^{1}JC-F=242* Hz), 145.1*(d,^{3}JC-F=11* Hz*)*, 140.8, 133.4, 133.0, 132.8(d,*^{3}JC-F*=11Hz),132.3, 129.4, 129.1, 128.1, 126.2, 105.1(*d,^{2}JC-F=23* Hz*)*, 104.3(*d,^{4}JC-F*=2 Hz), 100.3 *(d,^{2}JC-F=28* Hz*)*, 57.1, 42.9, HRMS (CI-TOF) m/z [M-H_2]+H^+ calcd for $C_{20}H_{15}BrClFNS^+$ 433.9776, found 433.9770

*4-bromo-N-(2-((4-chlorophenyl)thio)-1-phenylethyl)-N-methylaniline.***3l** yellow oil, 71.5 mg, 83% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.46 – 7.11 (m, 11H), 6.69 – 6.58 (m, 2H), 5.07 (dd, *J*=9.0, 6.2 Hz, 1H), 3.61 (dd, *J*=13.3, 6.1 Hz, 1H), 3.49 (dd, *J*=13.3, 9.1 Hz, 1H), 2.71 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.2, 139.1, 134.2, 132.7, 131.9, 131.7, 129.2, 128.8, 127.8, 127.1, 115.2, 109.4, 61.4, 37.0, 32.1. HRMS (CI-TOF) m/z M^+ calcd for $C_{21}H_{20}BrClNS^+$ 432.1083, found 432.1085

4-chloro-N-(2-((4-chlorophenyl)thio)-1-phenylethyl)aniline. **3m,** yellow oil, 64 mg, 86% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.47 – 7.26 (m, 9H), 7.15 – 7.03 (m, 2H), 6.51 – 6.41 (m, 2H), 4.61 (s, 1H), 4.38 (dd, *J*=9.1, 4.4 Hz, 1H), 3.40 (dd, *J*=13.5, 4.4 Hz,, 1H), 3.17 (dd, *J*=13.5, 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.6, 141.7, 133.3, 133.2, 132.2, 129.4, 129.1, 129.0, 127.9, 126.4, 122.7, 115.0, 57.2, 42.8. HRMS (CI-TOF) m/z [M-H_2]+H^+ calcd for $C_{20}H_{16}Cl_2NS^+$ 372.0375, found 372.0376.

*4-methyl-N-(1-phenyl-2-(p-tolylthio)ethyl)aniline.***4a** yellow oil, 51.2 mg, 77% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.51 – 7.29 (m, 7H), 7.20 (d, *J*=7.9 Hz, 2H), 7.00 (d, *J*=8.0 Hz, 2H), 6.57 – 6.48 (m, 2H), 4.72 – 4.37 (m, 2H), 3.44 (dd, *J*=13.5, 4.5 Hz,, 1H), 3.21 (dd, *J*=13.5, 9.1 Hz, 1H), 2.43 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.1, 142.9, 137.2, 131.5, 131.5, 130.0, 129.6, 128.9, 127.5, 127.1, 126.5, 114.2, 57.7, 43.5, 21.1, 20.5. HRMS (CI-TOF) m/z M+H^+ calcd for $C_{22}H_{24}NS^+$ 334.1624, found 334.1620

*4-methyl-N-(1-phenyl-2-(m-tolylthio)ethyl)aniline.***4b** yellow oil, 53.9 mg, 81% yield ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.52 – 7.20 (m, 8H), 7.15 – 7.09 (m, 1H), 6.99 (d, *J*=8.0 Hz, 2H), 6.51 (d, *J*=8.4 Hz,, 2H), 4.45 (m, 2H), 3.46 (dd, *J*=13.4, 4.5 Hz, 1H), 3.24 (dd, *J*=13.4, 9.1 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H).. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.0, 142.8, 139.0, 134.9, 131.4, 129.7, 129.0, 128.9, 127.8, 127.6, 127.6, 127.1, 126.5, 114.1, 57.7, 42.7, 21.4, 20.5. GC-MS(EI):333m/z, HRMS (CI-TOF) m/z M+H^+ calcd for $C_{22}H_{24}NS^+$ 334.1624, found 334.1627

*4-methyl-N-(2-(naphthalen-2-ylthio)-1-phenylethyl)aniline.***4c** yellow oil, 54.6 mg, 74% yield ^{1}H

NMR (300 MHz, $CDCl_3$) δ = 7.96 – 7.79 (m, 4H), 7.65 – 7.27 (m, 9H), 7.04 (d, *J*=8.4 Hz, 2H), 6.62 – 6.54 (m, 2H), 4.87 – 4.16 (m, 2H), 3.61 (dd, *J*=13.4, 4.6 Hz, 1H), 3.41 (dd, *J*=13.4, 8.8, 1H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.0, 142.7, 133.9, 132.9, 132.3, 129.8, 129.0, 128.9, 128.8, 128.3, 127.9, 127.7, 127.4, 127.3, 126.8, 126.6, 126.2, 114.2, 57.8, 42.6, 20.5. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{25}H_{24}NS^+$ 370.1624, found 370.1626

*N-(2-((4-(tert-butyl)phenyl)thio)-1-phenylethyl)-4-methylaniline.***4d** yellow oil, 53.2 mg, 71% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.30 (m, 9H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.55 – 6.48 (m, 2H), 4.92 – 4.10 (m, 2H), 3.46 (dd, *J* = 13.5, 4.5 Hz, 1H), 3.25 (dd, *J* = 13.5, 8.9 Hz, 1H), 2.30 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.3, 145.1, 142.8, 131.7, 130.9, 129.6, 128.9, 127.5, 127.1, 126.6, 126.3, 114.1, 57.9, 43.2, 34.6, 31.4, 20.5. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{25}H_{30}NS^+$ 376.2093, found 376.2094

*N-(2-((2,4-difluorophenyl)thio)-1-phenylethyl)-4-methylaniline.***4e** yellow oil, 59 mg, 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.27 (m, 6H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.95 – 6.81 (m, 2H), 6.55 – 6.44 (m, 2H), 4.50 (s, 1H), 4.37 (dd, *J* = 9.0, 4.6 Hz, 1H), 3.40 (dd, *J* = 13.5, 4.6 Hz, 1H), 3.15 (dd, *J* = 13.5, 9.0 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ164.4 (dq, *J*=250Hz, 12Hz), 144.8, 142.2, 135.9 (dd, *J* =9.0Hz, 2.0 Hz) , 129.7, 128.9, 127.7, 127.2, 126.5, 116.9, 114.0, 111.9(dd, *J* =21Hz, 3.8 Hz), 104.7(m), 57.5, 42.6, 20.5. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{21}H_{20}F_2NS^+$ 356.1279, found 356.1283.

*N-(2-((4-fluorophenyl)thio)-1-phenylethyl)-4-methylaniline.***4f** yellow oil, 52.6 mg, 78% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.53 – 7.30 (m, 7H), 7.14 – 6.94 (m, 4H), 6.52 (d, *J*=8.4, 2H), 4.77 – 3.93 (m, 2H), 3.41 (dd, *J*=13.5, 4.7, 1H), 3.21 (dd, *J*=13.5, 8.9, 1H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.8(d, *^{1}JC-F=225Hz*), 144.8, 142.5, 133.7(d, *^{3}JC-F=8Hz*), 130.1(d, *^{4}JC-F=4Hz*), 129.7, 128.9, 127.7, 127.3, 126.6, 116.3(d,*^{2}JC-F=22Hz*), 114.1, 57.6, 43.8, 20.4. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{21}H_{21}FNS^+$ 338.1373, found 338.1373.

*N-(2-((3-chlorophenyl)thio)-1-phenylethyl)-4-methylaniline.***4g** yellow oil, 54.5 mg, 80% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.23 (m, 9H), 7.01 (t, *J* = 7.3 Hz, 2H), 6.57 – 6.48 (m, 2H), 4.50 (m, *J* = 50.9, 25.4 Hz, 2H), 3.46 (dd, *J* = 13.3, 4.7 Hz, 1H), 3.29 (dd, *J* = 13.3, 8.7 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.7, 142.2, 137.7, 134.9, 130.1, 129.74, 129.5, 129.0, 127.9, 127.8, 127.3, 126.8, 126.5, 114.1, 57.5, 42.1, 20.5. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{21}H_{21}ClNS^+$ 354.1078, found 354.1077.

*N-(2-((2-methoxyphenyl)thio)-1-phenylethyl)-4-methylaniline.***4h** yellow oil, 52 mg, 75% yield ^{1}H

NMR (300 MHz, $CDCl_3$) δ = 7.56 – 7.25 (m, 7H), 7.04 – 6.90 (m, 4H), 6.57 – 6.46 (m, 2H), 4.81 – 4.38 (m, 2H), 3.91 (s, 3H), 3.46 (dd, *J*=13.3, 4.4 Hz, 1H), 3.20 (dd, *J*=13.3, 9.2 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.6, 145.3, 143.0, 132.6, 129.6, 128.8, 128.8, 127.5, 126.9, 126.5, 122.9, 121.2, 114.1, 111.0, 57.8, 55.8, 41.6, 20.4. HRMS (CI-TOF) m/z $M+H^+$ calcd for $C_{22}H_{24}NOS^+$ 350.1573, found 350.1577

*N-(1-(4-chlorophenyl)-2-((4-chlorophenyl)thio)ethyl)-4-methylaniline.***4i** yellow oil, 60 mg, 78% yield ^1H NMR (300 MHz, $CDCl_3$) δ = 7.24 – 7.13 (m, 8H), 6.85 – 6.72 (m, 2H), 6.37 – 6.20 (m, 2H), 4.48 – 3.96 (m, 2H), 3.20 (dd, *J*=13.5, 4.5 Hz, 1H), 3.00 (dd, *J*=13.5, 9.0 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.4, 140.9, 133.3, 133.2, 133.2, 132.2, 129.7, 129.4, 129.1, 127.9, 127.6, 114.1, 56.8, 42.9, 20.4. HRMS (CI-TOF) m/z $M+H^+$ calcd for $C_{21}H_{20}Cl_2NS^+$ 388.0688, found 388.0680.

*N-(1-(3-chlorophenyl)-2-((4-chlorophenyl)thio)ethyl)-4-methylaniline.***4j** yellow oil, 61 mg, 79% yield ^1H NMR (300 MHz, $CDCl_3$) δ = 7.44 – 7.23 (m, 8H), 6.97 (d, *J*=8.1 Hz, 2H), 6.54 – 6.41 (m, 2H), 4.73 – 3.89 (m, 2H), 3.36 (dd, *J*=13.6, 4.5 Hz, 1H), 3.15 (dd, *J*=13.6, 9.0 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.7, 144.4, 134.8, 133.3, 133.2, 132.3, 130.2, 129.8, 129.4, 127.9, 127.6, 126.6, 124.7, 114.0, 57.1, 42.8, 20.5. HRMS (CI-TOF) m/z $M+H^+$ calcd for $C_{21}H_{20}Cl_2NS^+$ 388.0688, found 388.0681

*N-(1-(2-chlorophenyl)-2-((4-chlorophenyl)thio)ethyl)-4-methylaniline.***4k** yellow oil, 42.6 mg, 55% yield ^1H NMR (300 MHz, $CDCl_3$) δ = 7.48 – 7.35 (m, 1H), 7.35 – 7.01 (m, 7H), 6.81 (d, *J*=8.1 Hz,, 2H), 6.27 (d, *J*=8.4 Hz, 2H), 4.69 (dd, *J*=9.3, 3.8 Hz, 1H), 4.48 (s, 1H), 3.38 (dd, *J*=13.7, 3.8 Hz,, 1H), 2.93 (dd, *J*=13.7, 9.3 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.2, 139.0, 133.1, 132.9, 132.6, 132.3, 129.9, 129.7, 129.2, 128.8, 127.9, 127.5, 113.9, 53.9, 40.3, 20.4. HRMS (CI-TOF) m/z $M+H^+$ calcd for$C_{21}H_{20}Cl_2NS^+$ 388.0688, found 388.0686.

*N-(2-((4-chlorophenyl)thio)-1-(4-fluorophenyl)ethyl)-4-methylaniline.***4l** yellow oil, 57 mg, 77% yield ^1H NMR (300 MHz, $CDCl_3$) δ = 7.48 – 7.27 (m, 6H), 7.16 – 6.96 (m, 4H), 6.52 (d, *J*=8.2 Hz, 2H), 4.43 (dt, *J*=38.7, 19.3 Hz, 2H), 3.40 (dd, *J*=13.4, 4.5 Hz, 1H), 3.21 (dd, *J*=13.4, 8.9 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.8(d, *^{1}JC-F=195Hz*), 144.6, 138.1(d, ^{4}JC-F=3Hz), 133.5, 133.2, 132.1, 129.8, 129.4, 128.1(d,^{3}JC-F=8Hz), 127.5, 115.8(d, *^{2}JC-F=21Hz*), 114.1, 56.8, 43.0, 20.5. HRMS (CI-TOF) m/z $M+H^+$ calcd for $C_{21}H_{20}ClFNS^+$ 372.0984, found 372.0977

*N-(2-((4-chlorophenyl)thio)-1-(p-tolyl)ethyl)-4-methylaniline.***4m** yellow oil, 58.7 mg, 80% yield Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ = 7.40 – 7.20 (m, 8H), 7.01 (d, *J*=8.2 Hz, 2H), 6.54 (d,

J=8.4 Hz, 2H), 4.63 – 4.32 (m, 2H), 3.42 (dd, *J*=13.4, 4.7 Hz, 1H), 3.24 (dd, *J*=13.3, 8.8 Hz, 1H), 2.43 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.9, 139.4, 137.4, 133.9, 132.9, 131.9, 129.7, 129.7, 129.7, 129.3, 127.2, 126.4, 114.1, 57.1, 42.8, 21.3, 20.5. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{22}H_{23}ClNS^+$ 368.1234, found 368.1228

*N-(2-((4-chlorophenyl)thio)-1-(4-methoxyphenyl)ethyl)-4-methylaniline.***4n** yellow oil, 57.5 mg, 75% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42 – 7.17 (m, 6H), 7.01 – 6.78 (m, 4H), 6.45 (d, *J*=8.4 Hz, 2H), 4.72 – 4.17 (m, 2H), 3.82 (s, 3H), 3.34 (dd, *J*=13.4, 4.8 Hz, 1H), 3.17 (dd, *J*=13.4, 8.7 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.1, 144.7, 134.2, 133.7, 132.9, 131.9, 129.6, 129.2, 127.5, 127.2, 114.2, 114.0, 56.8, 55.3, 42.8, 20.4. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{22}H_{23}ClNOS^+$ 384.1183, found 384.1185

*N-(1-(4-(tert-butyl)phenyl)-2-((4-chlorophenyl)thio)ethyl)-4-methylaniline.***4o** yellow oil, 67 mg, 82% yield ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.44 – 7.25 (m, 8H), 6.97 (d, *J*=8.2 Hz, 2H), 6.50 (d, *J*=8.4 Hz, 2H), 4.59 – 4.23 (m, 2H), 3.40 (dd, *J*=13.4, 4.8 Hz, 1H), 3.22 (dd, *J*=13.4, 8.7 Hz, 1H), 2.26 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.5, 144.8, 139.1, 133.9, 132.8, 131.8, 129.7, 129.2, 127.1, 126.1, 125.8, 114.0, 57.1, 42.7, 34.6, 31.4, 20.5. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{25}H_{29}ClNS^+$ 410.1704, found 410.1695

N-(2-(cyclohexylthio)-1-phenylethyl)-4-methylaniline. **4p** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.24 – 7.18 (m, 2H), 7.16 – 7.09 (m, 1H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.39 – 6.33 (m, 2H), 4.47 (s, 1H), 4.27 (dd, *J* = 9.0, 4.4 Hz, 1H), 2.94 (dd, *J* = 13.4, 4.4 Hz, 1H), 2.68 (dd, *J* = 13.4, 9.0 Hz, 1H), 2.51 – 2.39 (m, 1H), 2.08 (s, 3H), 1.83 (dd, *J* = 26.8, 11.2 Hz, 2H), 1.69 – 1.57 (m, 2H), 1.49 (m, 1H), 1.29 – 1.05 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.3, 143.3, 129.7, 128.9, 127.5, 127.0, 126.5, 114.2, 57.6, 43.5, 38.7, 33.8, 33.7, 26.2, 26.1, 25.9, 20.6. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{21}H_{28}NS^+$ 326.1937, found 326.1940

N-(2-(hexylthio)-1-phenylethyl)-4-methylaniline. **4q** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.12 (m, 5H), 6.79 (d, *J* = 8.2 Hz, 2H), 6.36 (d, *J* = 8.3 Hz, 2H), 4.46 (s, 1H), 4.26 (dd, *J* = 9.1, 4.4 Hz, 1H), 2.91 (dd, *J* = 13.5, 4.4 Hz, 1H), 2.66 (dd, *J* = 13.5, 9.1 Hz, 1H), 2.40 – 2.28 (m, 2H), 2.08 (s, 3H), 1.52 – 1.38 (m, 2H), 1.30 – 1.08 (m, 7H), 0.78 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 143.3, 129.7, 128.9, 127.5, 127.0, 126.5, 114.2, 57.1, 40.7, 32.0, 31.6, 29.6, 28.7, 22.1, 20.6, 14.2. HRMS (CI-TOF) m/z M+H$^+$ calcd for $C_{21}H_{30}NS^+$ 328.2093, found 328.2097

*N-(1-(4-bromophenyl)-2-((4-chlorophenyl)thio)ethyl)-4-methylaniline.***4r** as a brown oil (1.83g, 85%).^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.53 – 7.42 (m, 2H), 7.36 – 7.22 (m, 6H), 6.q95 (d, *J*=8.3 Hz,

2H), 6.44 (d, *J*=8.4 Hz, 2H), 4.64 – 4.10 (m, 2H), 3.34 (dd, *J*=13.5, 4.5 Hz, 1H), 3.14 (dd, *J*=13.5, 9.0 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.4, 141.4, 133.3, 133.2, 132.2, 132.0, 129.7, 129.4, 128.2, 127.6, 121.4, 114.1, 56.8, 42.8, 20. 5. HRMS (CI-TOF) m/z $M+H^+$ calcd for $C_{21}H_{20}BrClNS^+$ 432.0183, found 432.0185

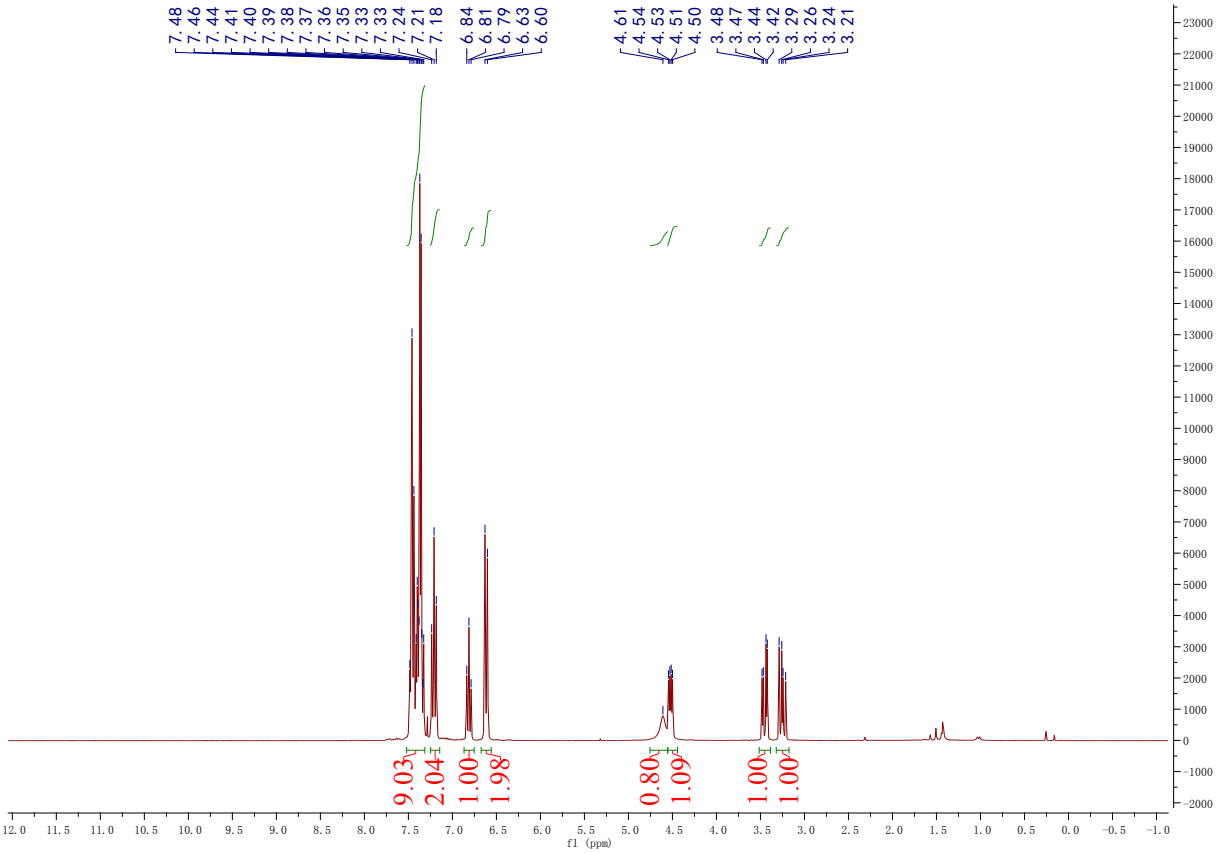
4. References

1 Wu, J.; Xia, H.-G. *Green Chem.* 2005, **7**(10), 708-710.

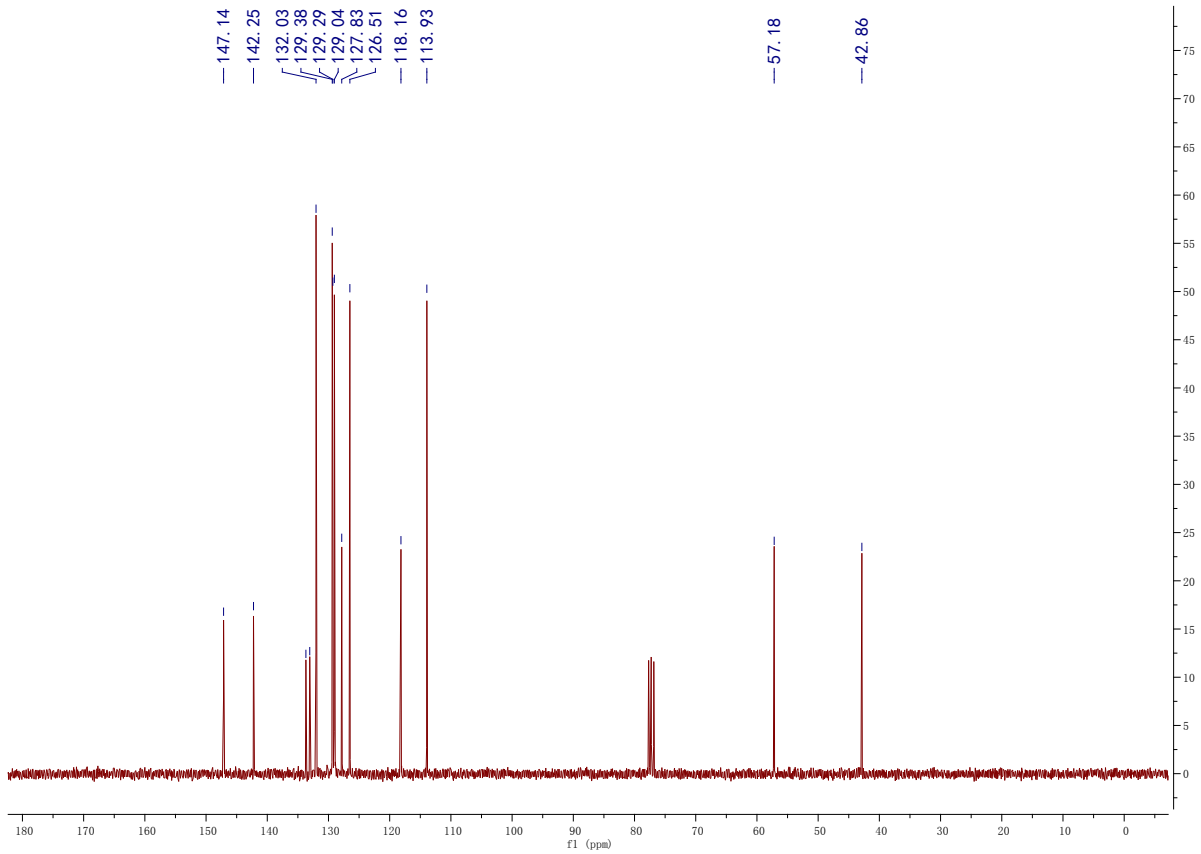
2 Abaee, S. M. Synth. Commun., 2008, **38**(2), 282-289

5. NMR Spectra

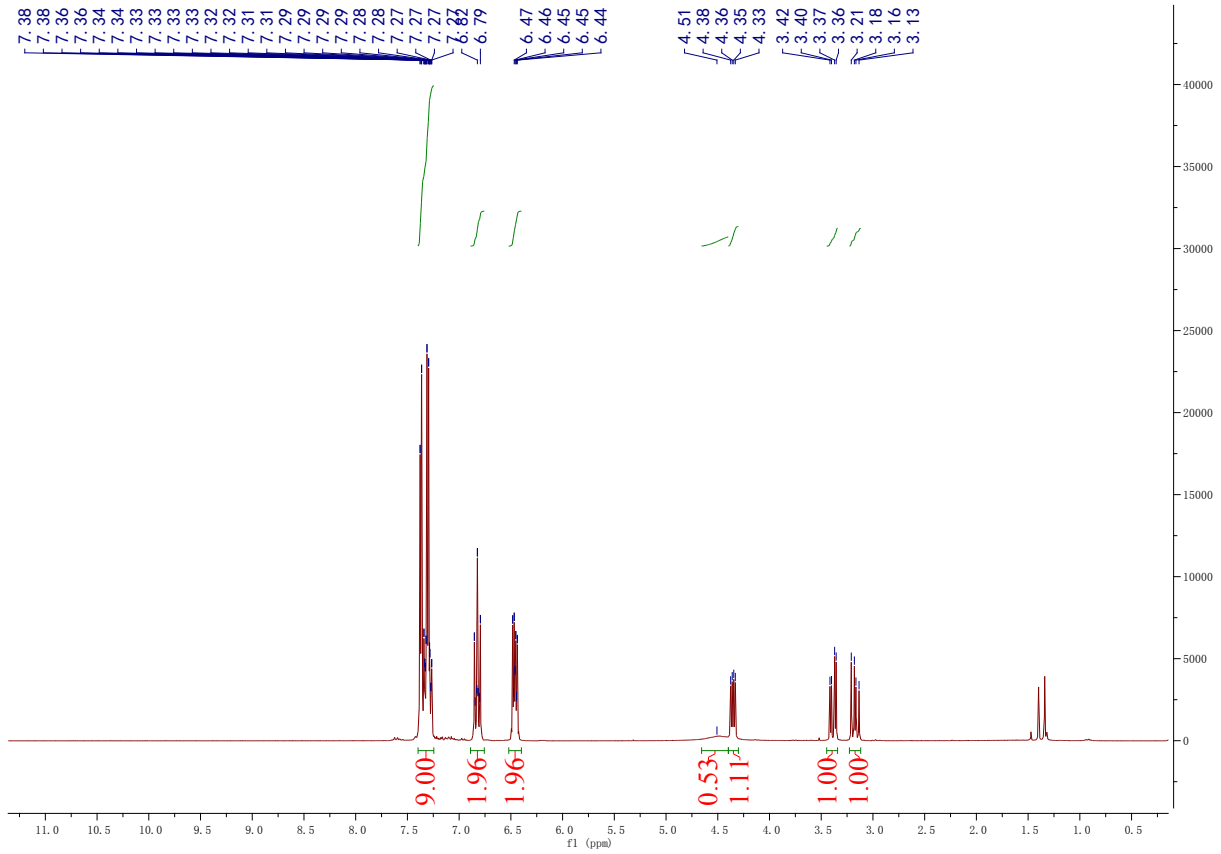
^{1}H NMR for **3a**



^{13}C NMR for **3a**



^{1}H NMR for **3b**



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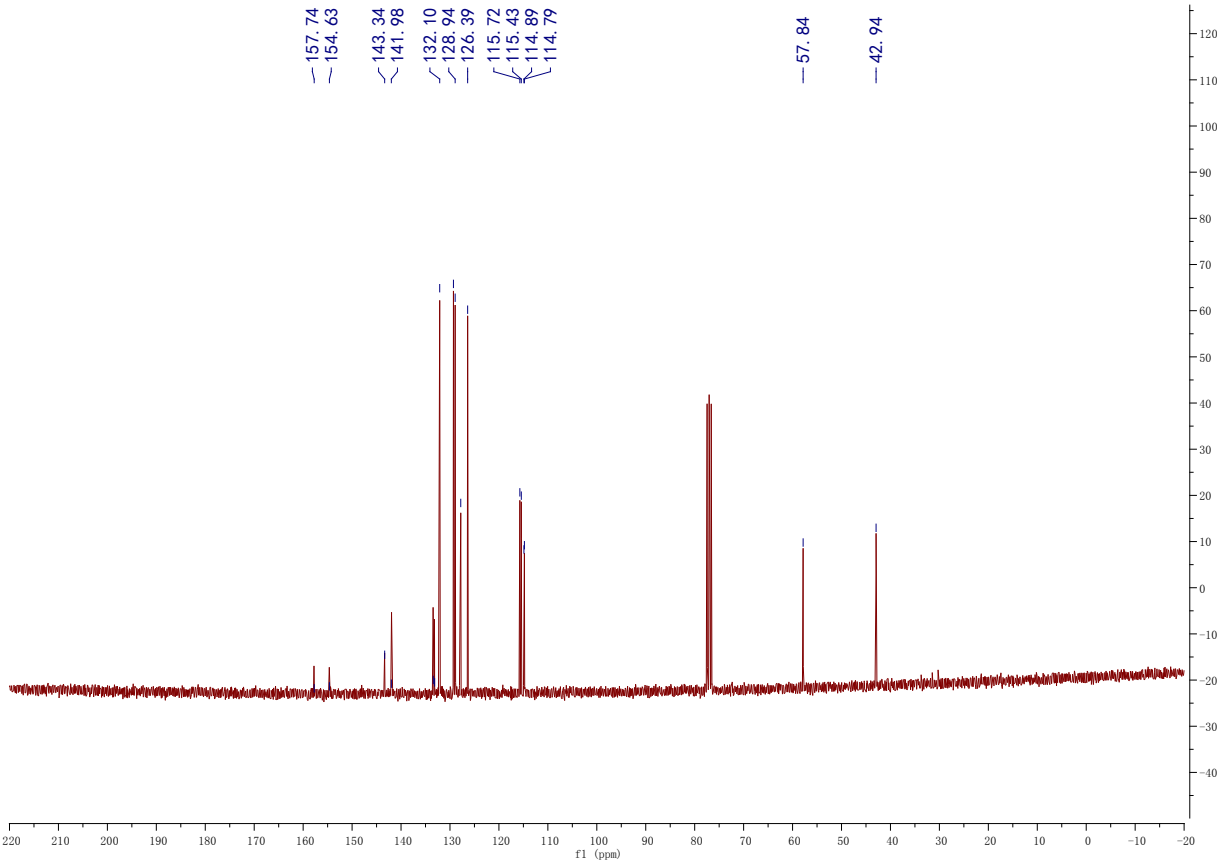
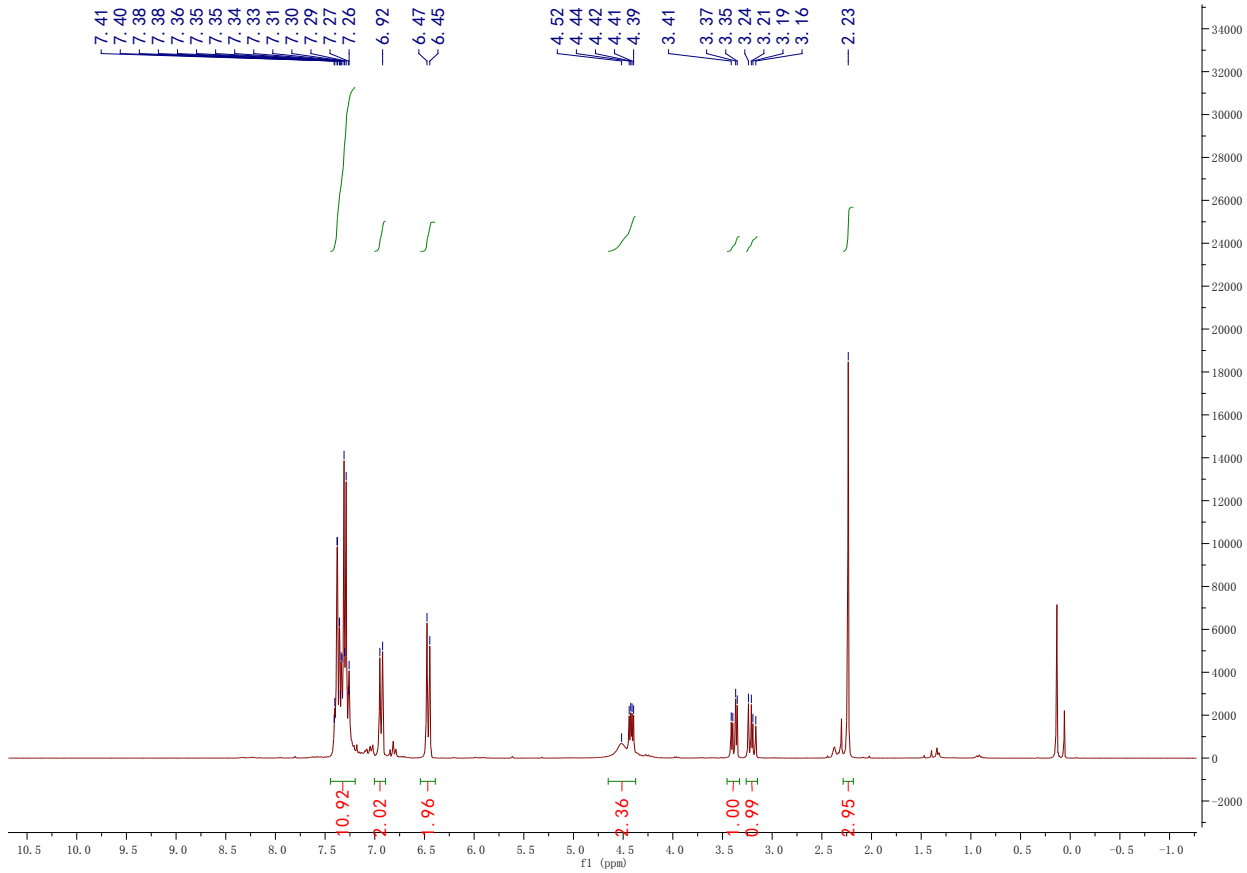
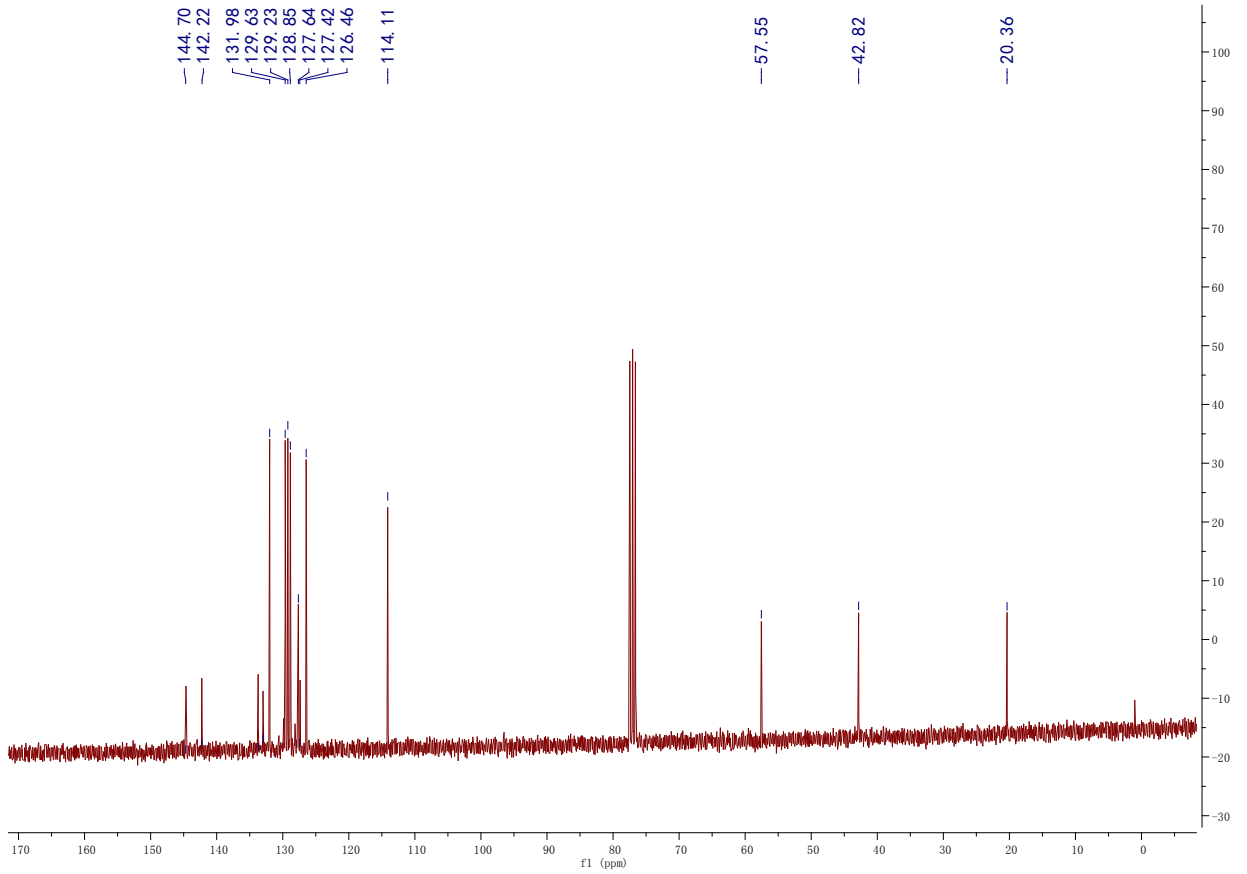


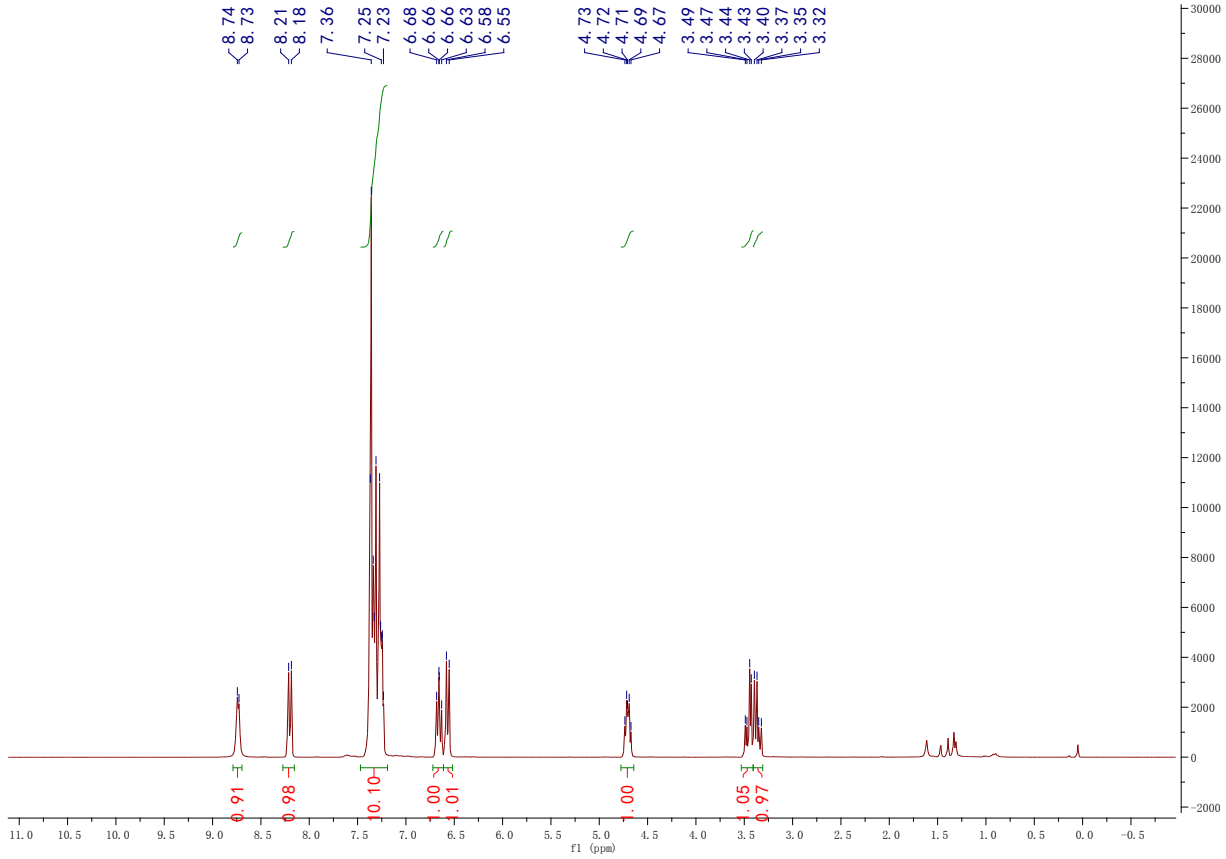
^{1}H NMR for **3c**



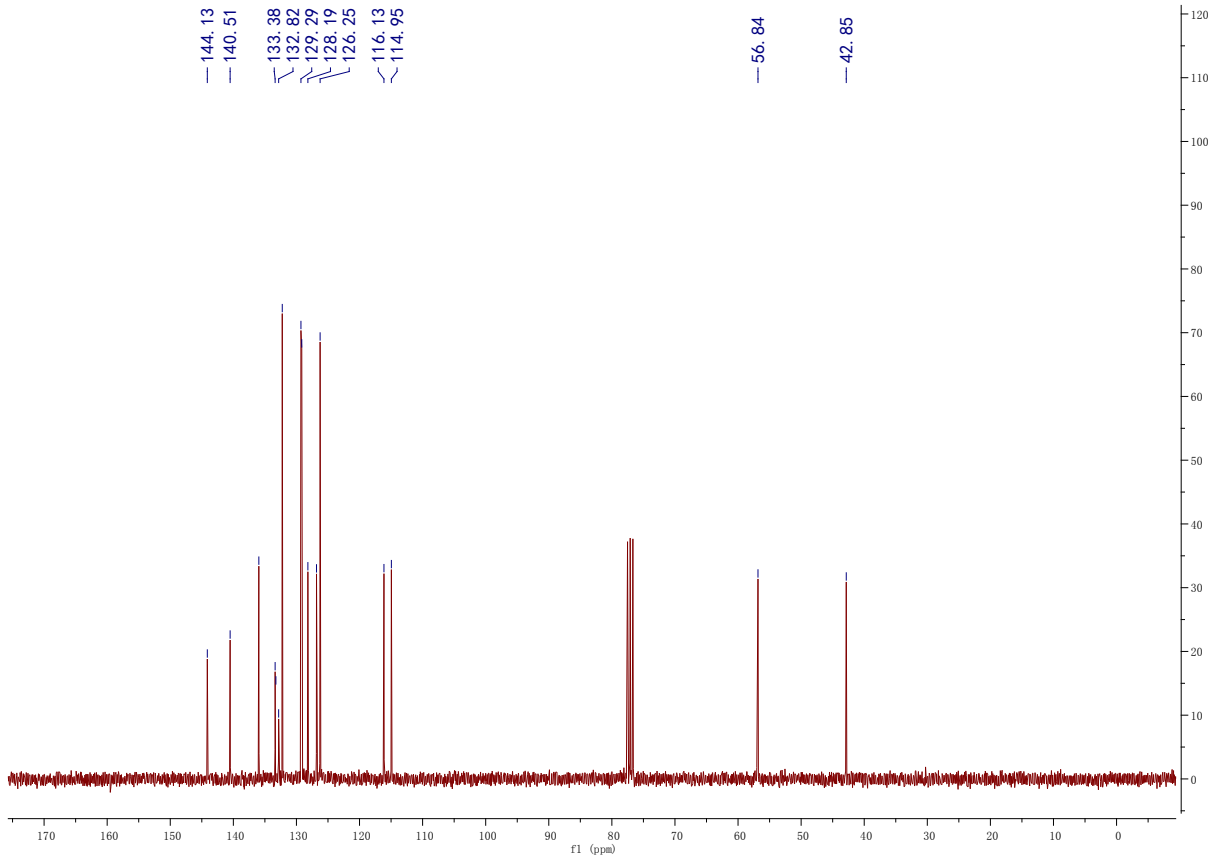
^{13}C NMR for **3c**



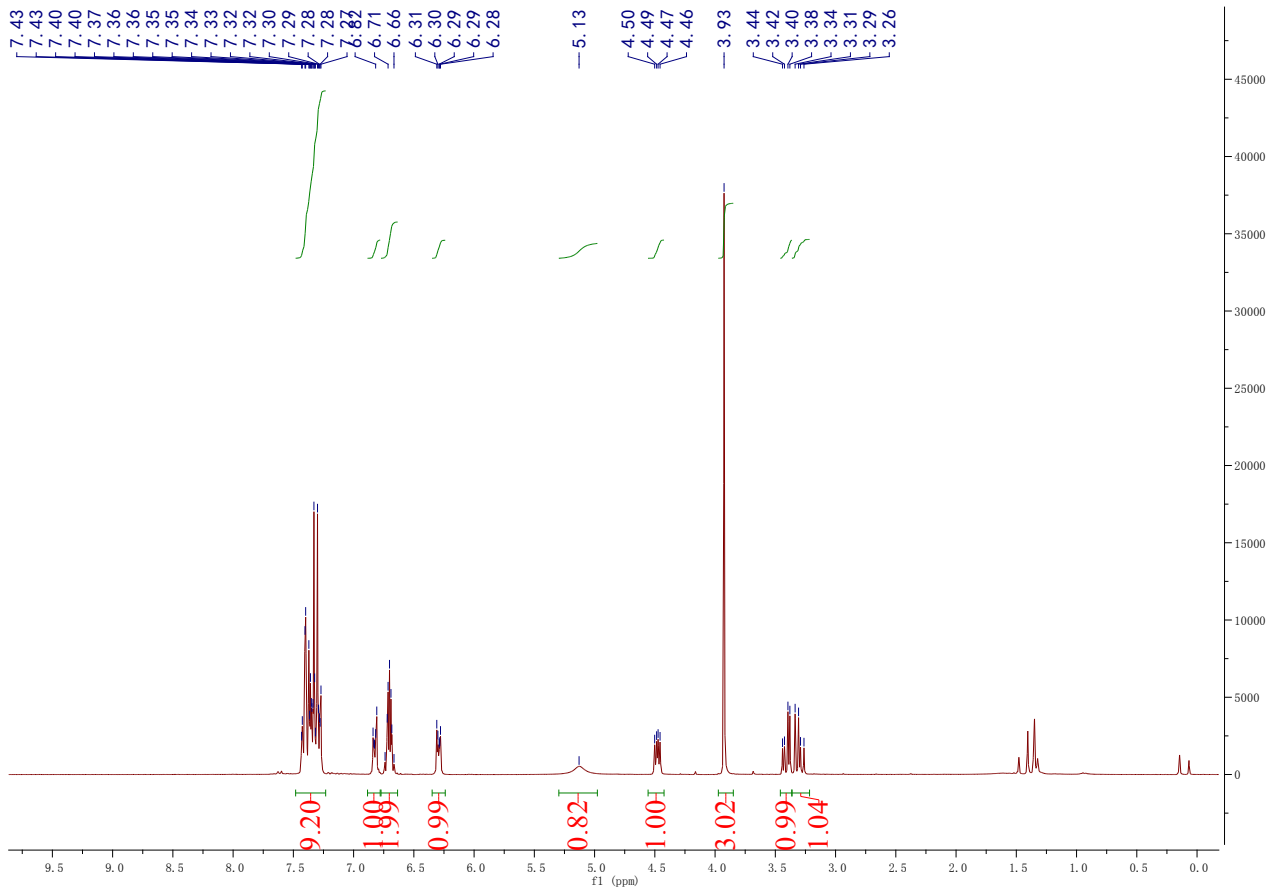
^{1}H NMR for **3d**



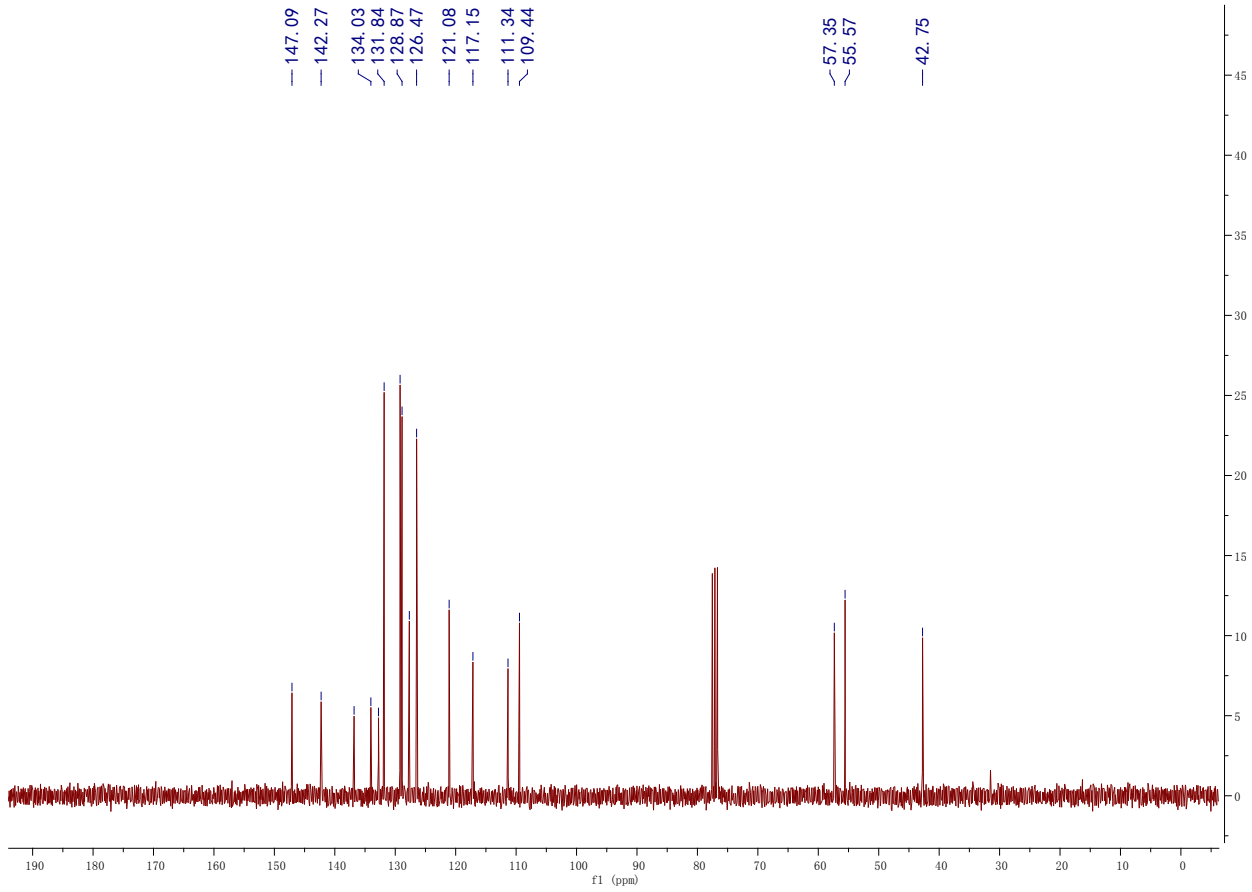
^{13}C NMR for **3d**



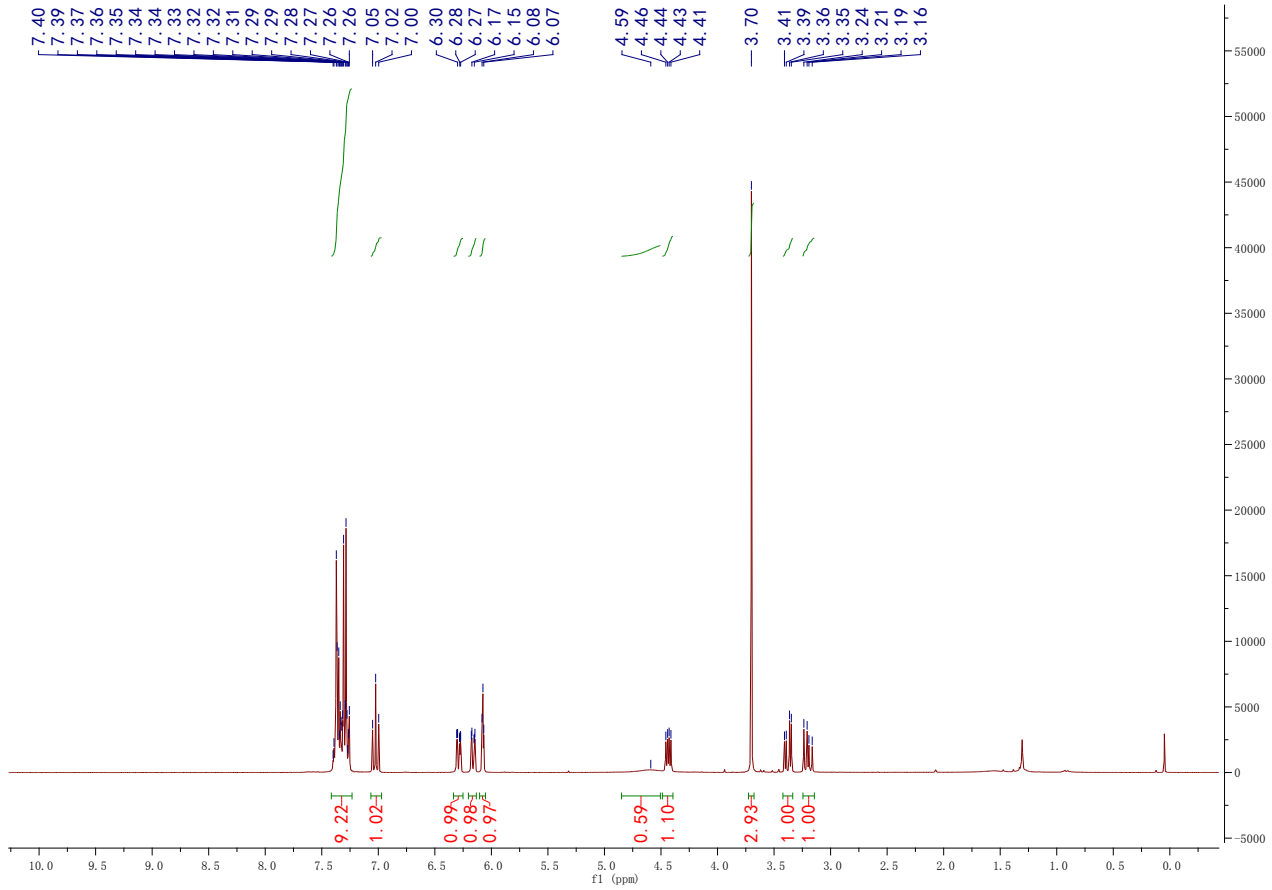
^{1}H NMR for **3e**



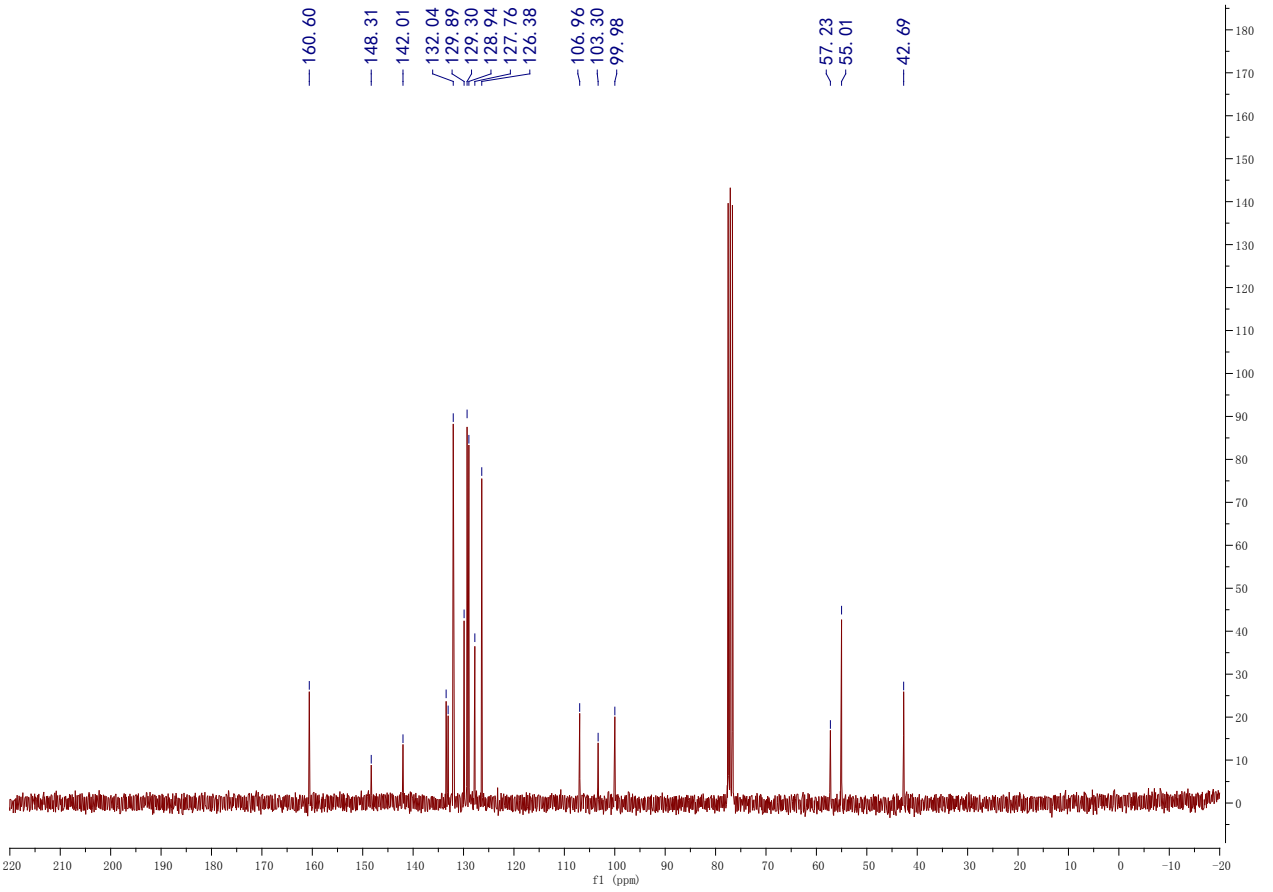
^{13}C NMR for **3e**



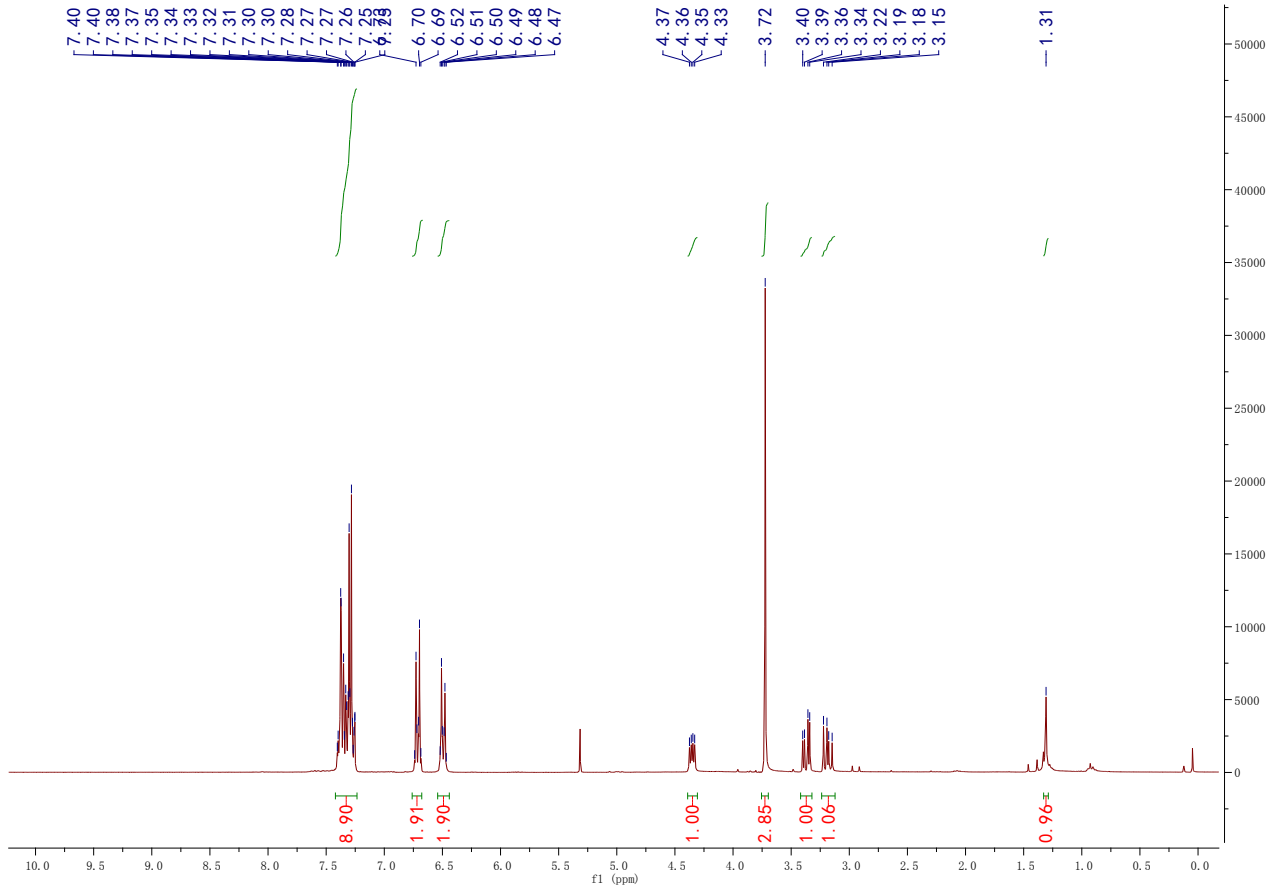
^{1}H NMR for **3f**



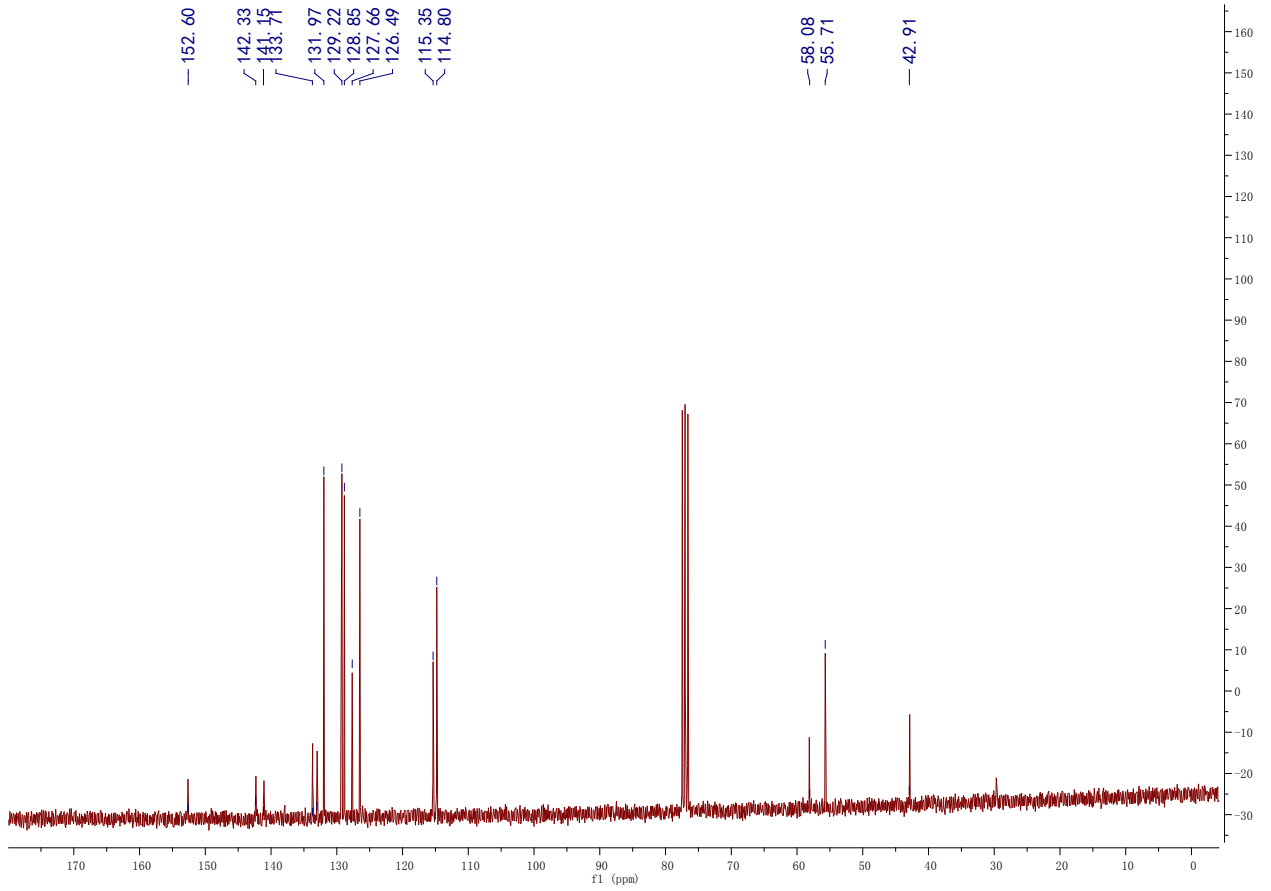
^{13}C NMR for **3f**



^{1}H NMR for **3g**



^{13}C NMR for **3g**



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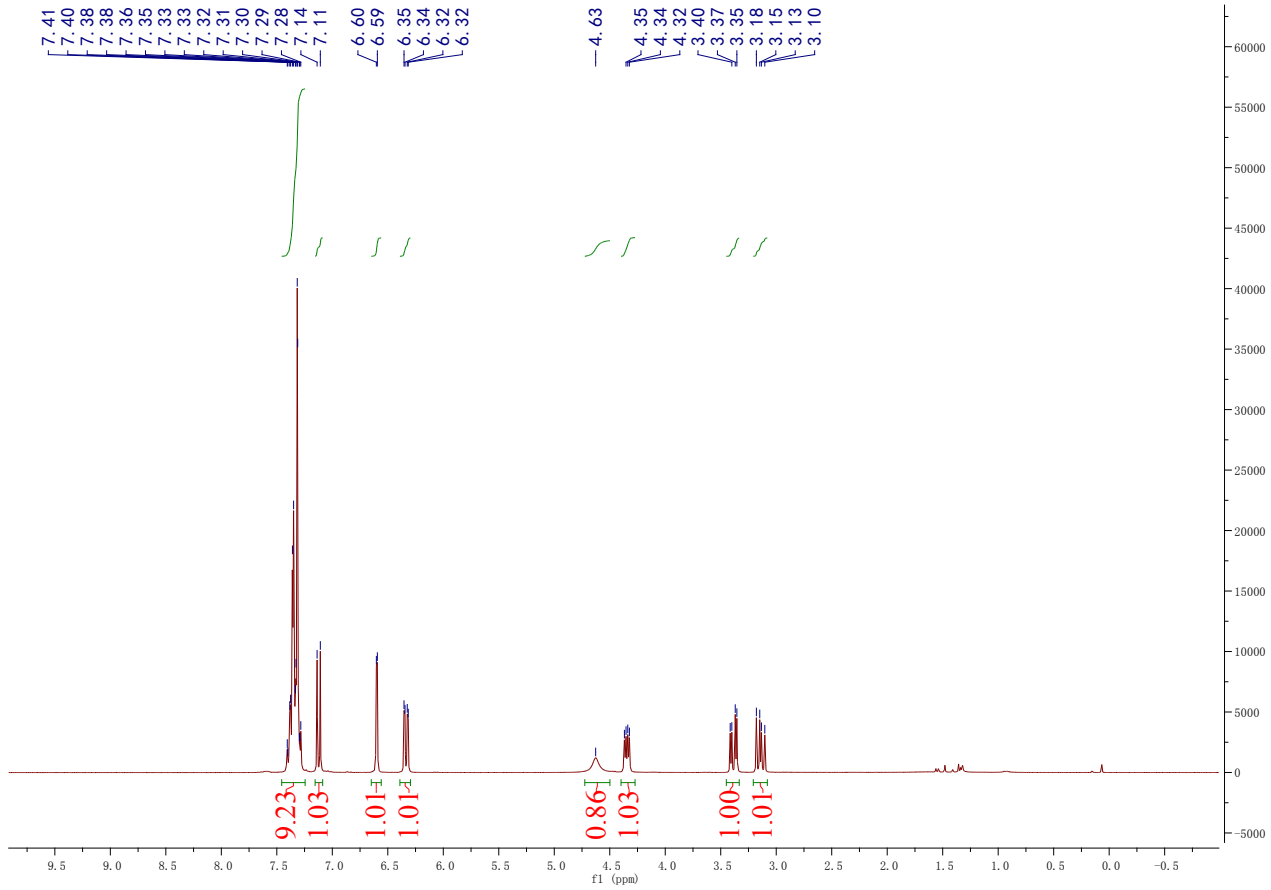

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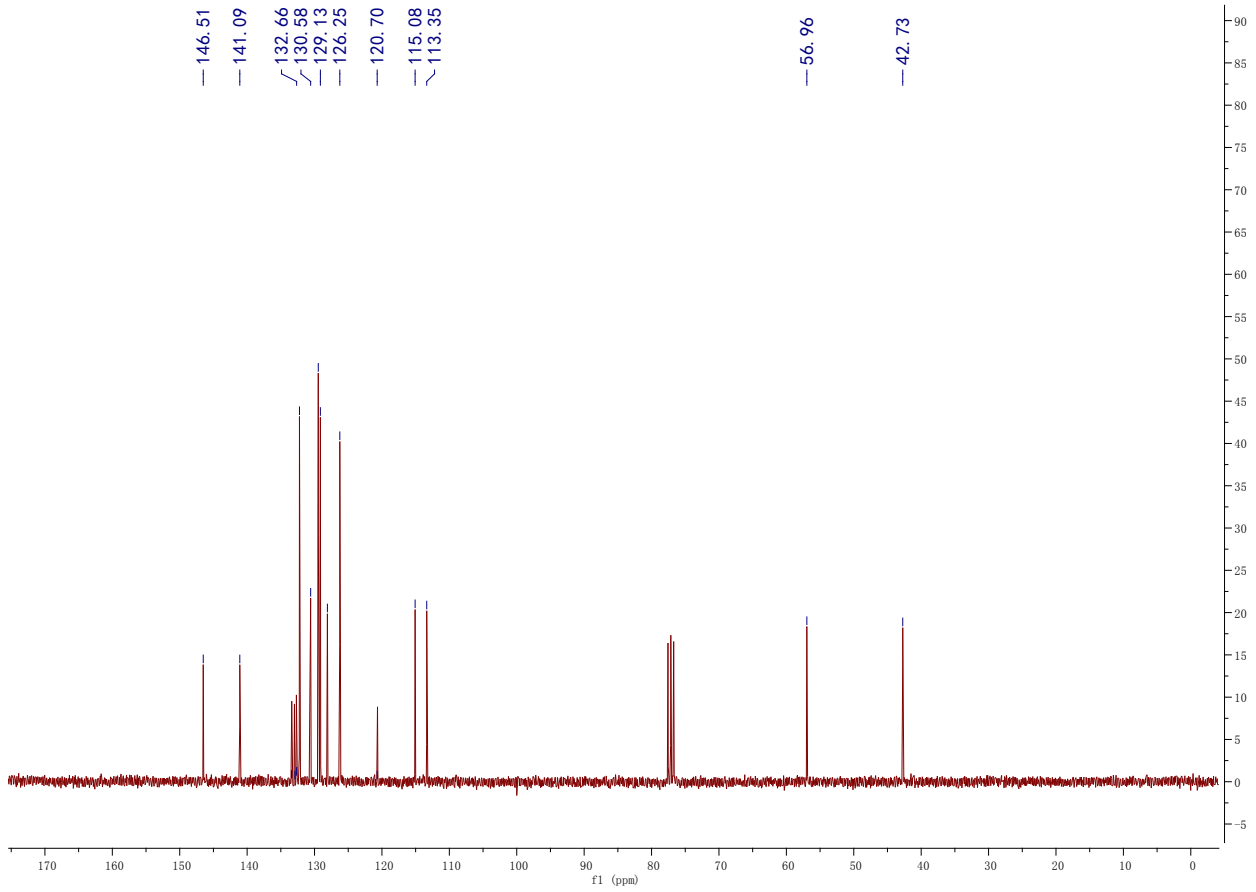
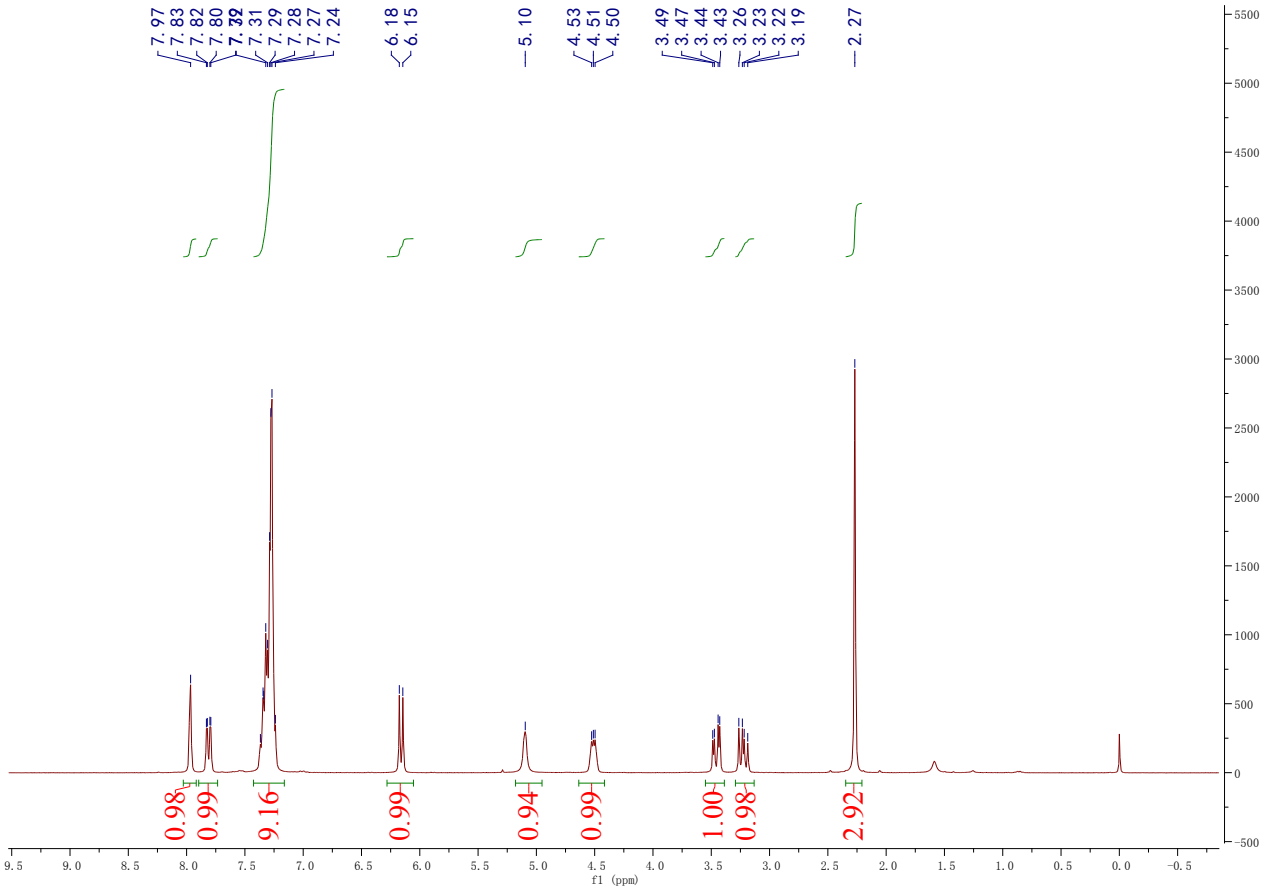


^{1}H NMR for **3i**



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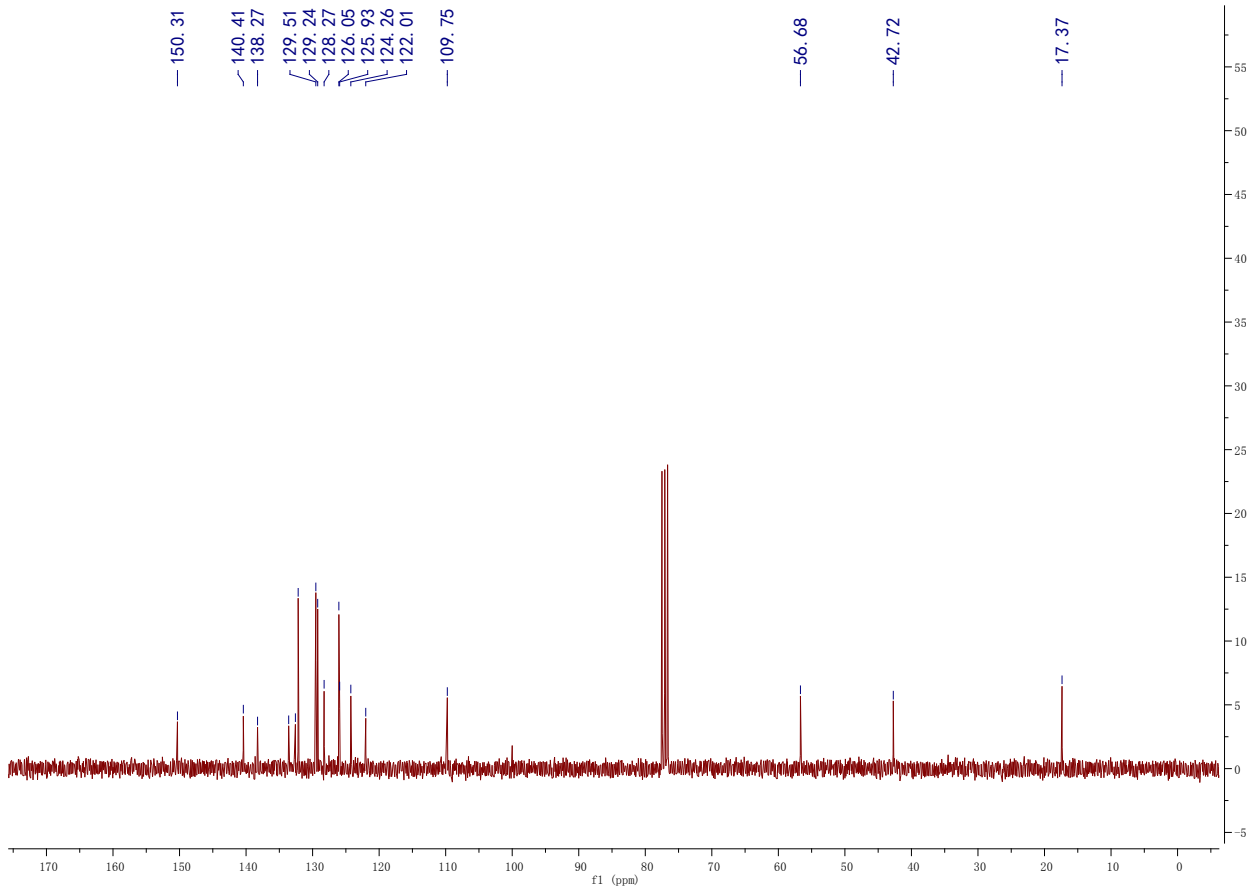
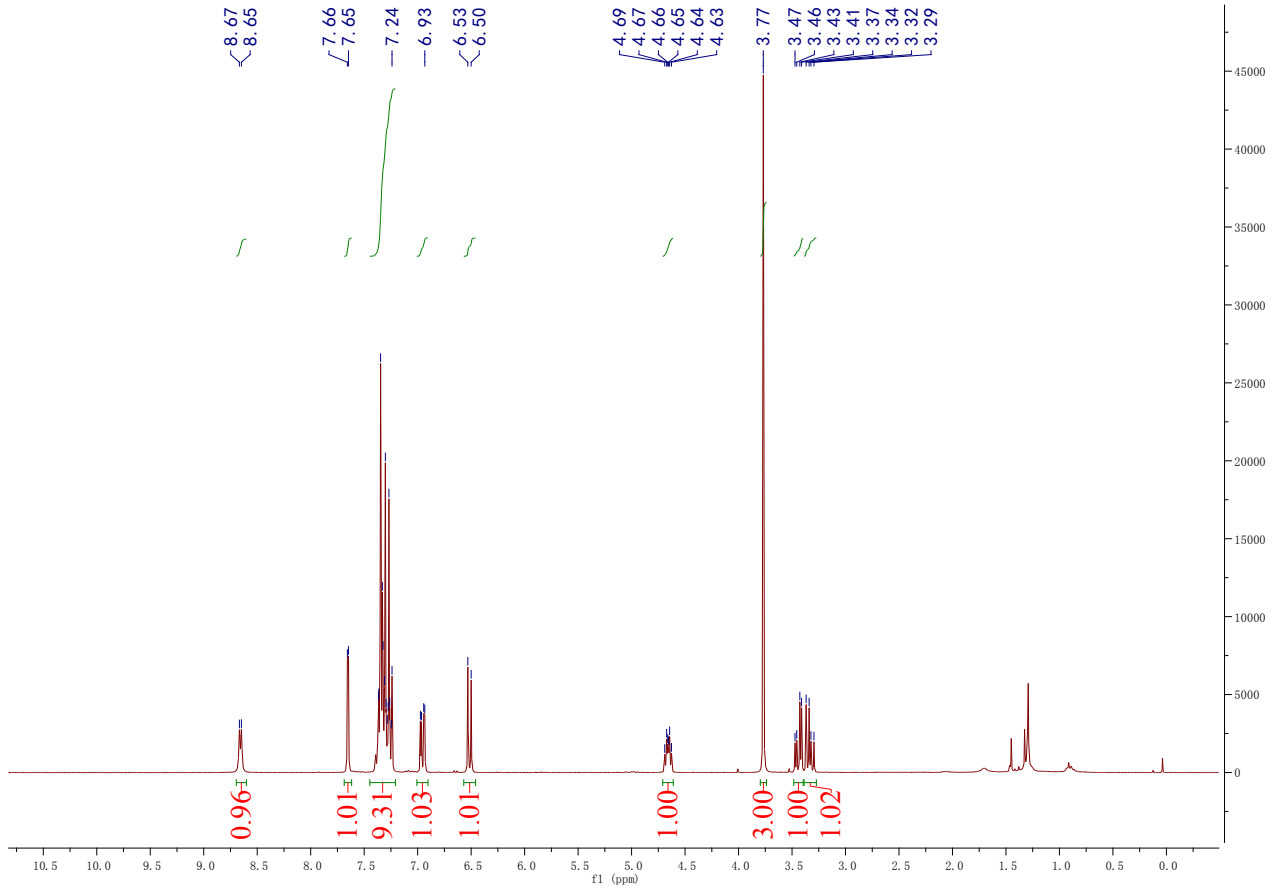


^{1}H NMR for **3j**



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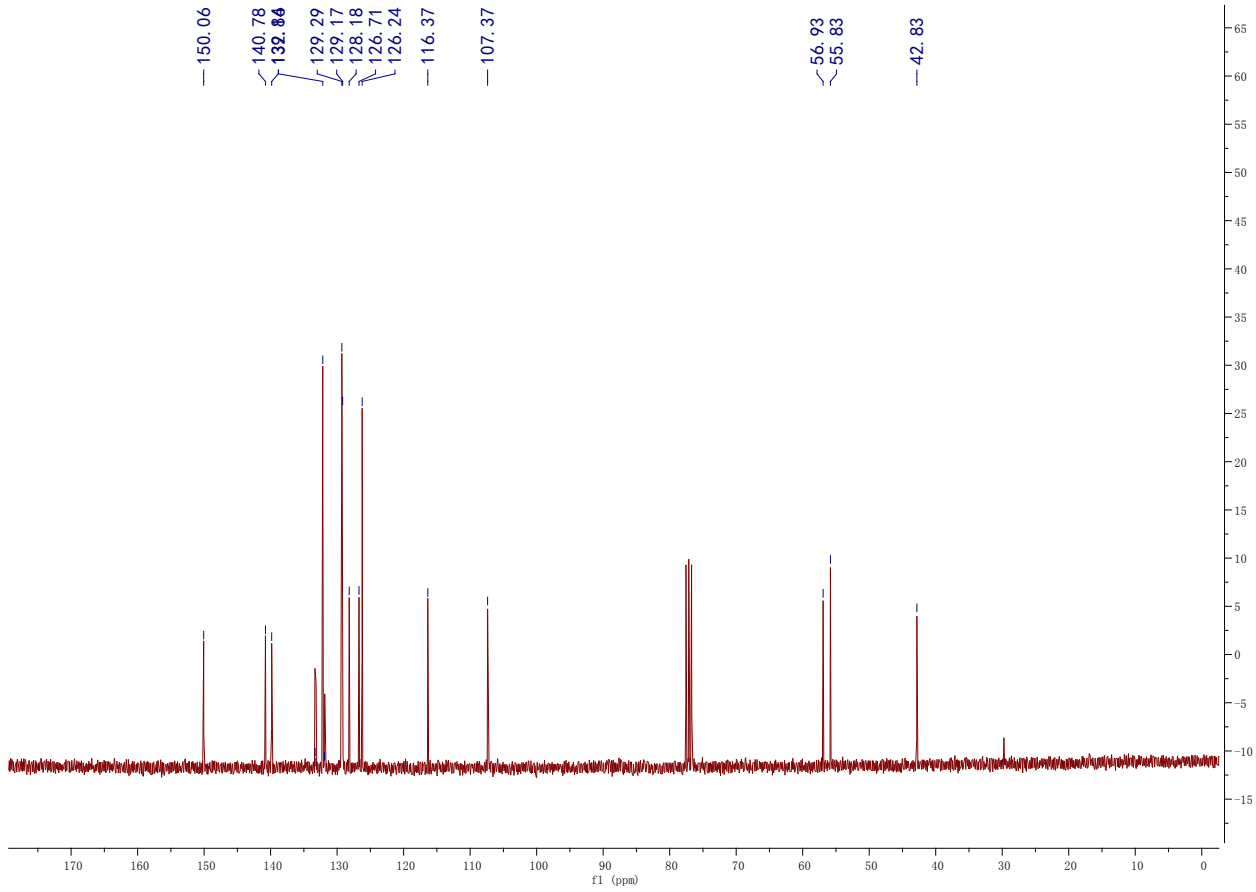
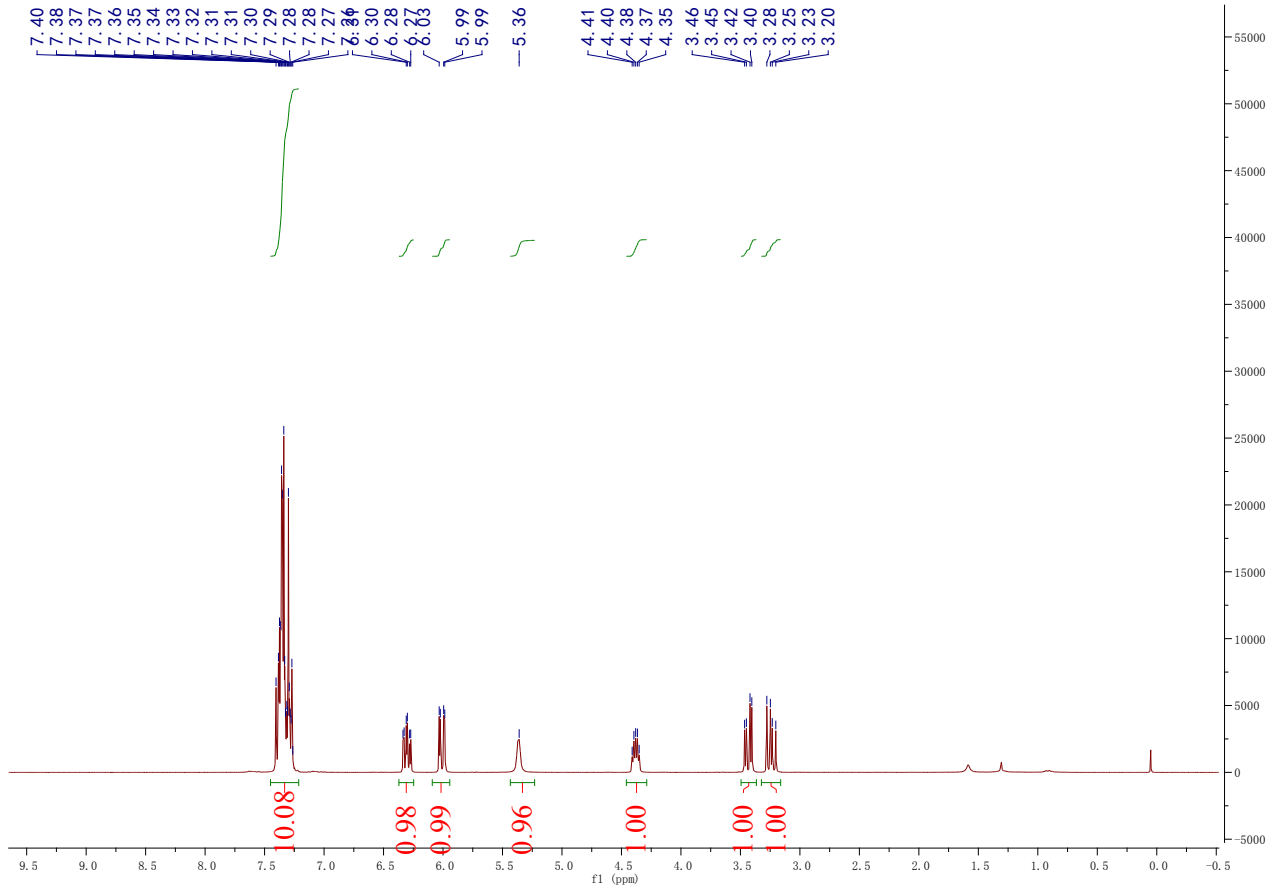
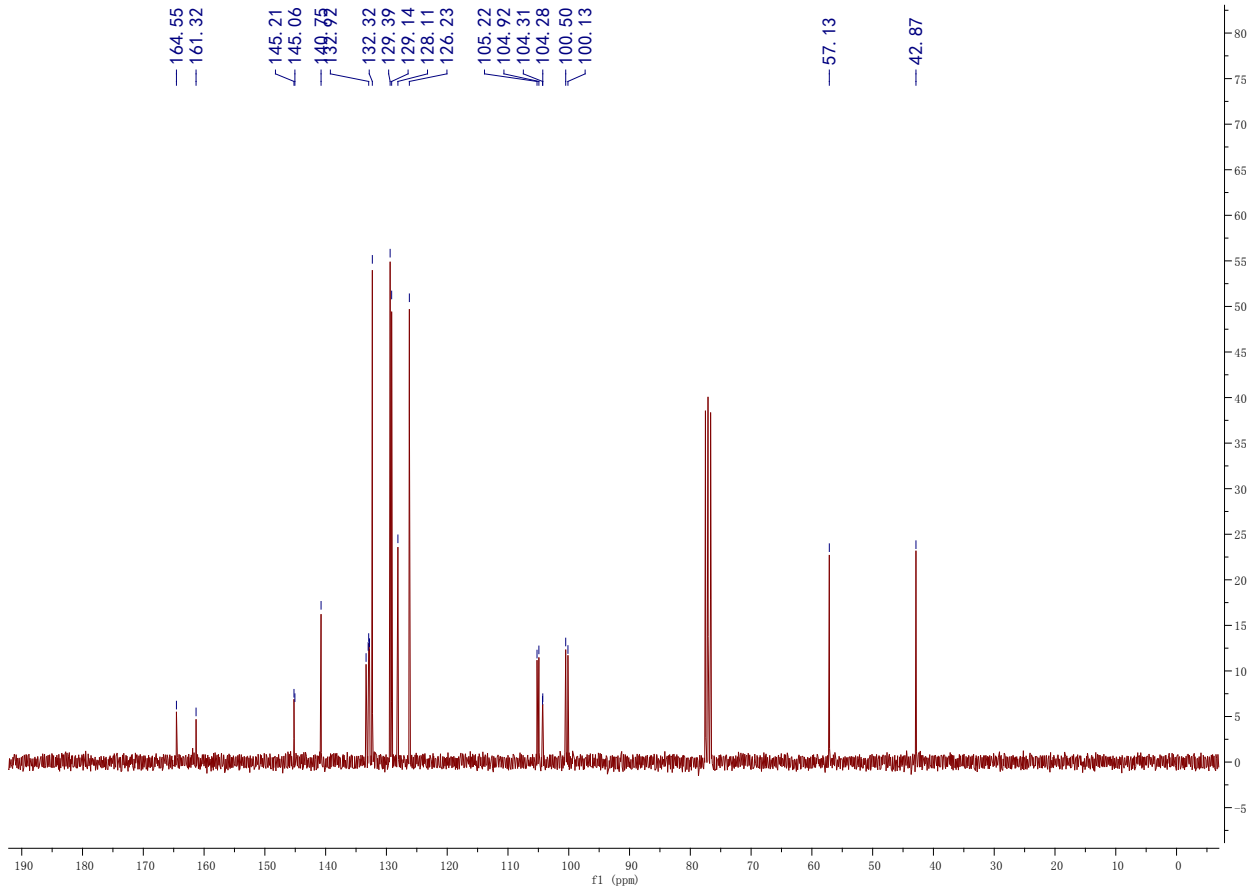


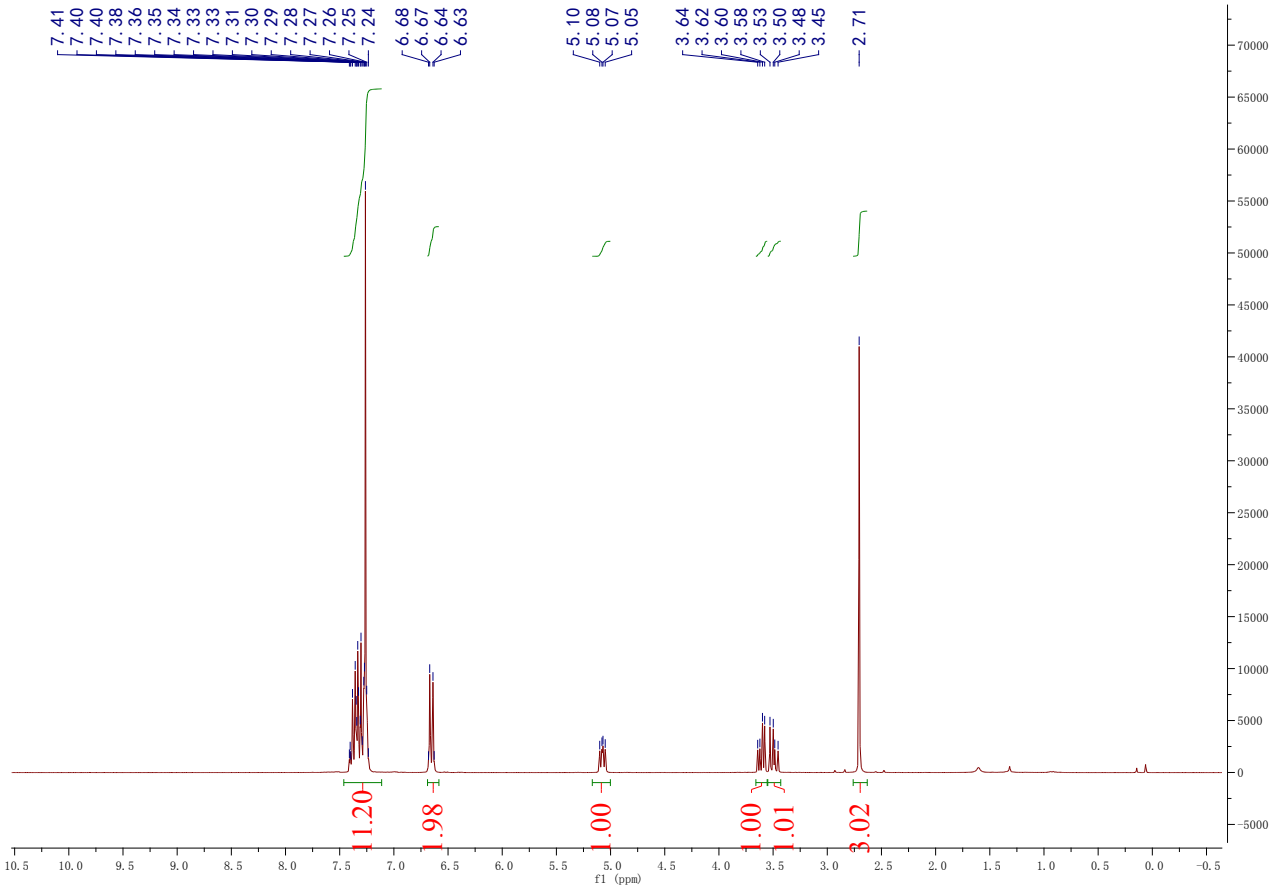
^{1}H NMR for **3k**



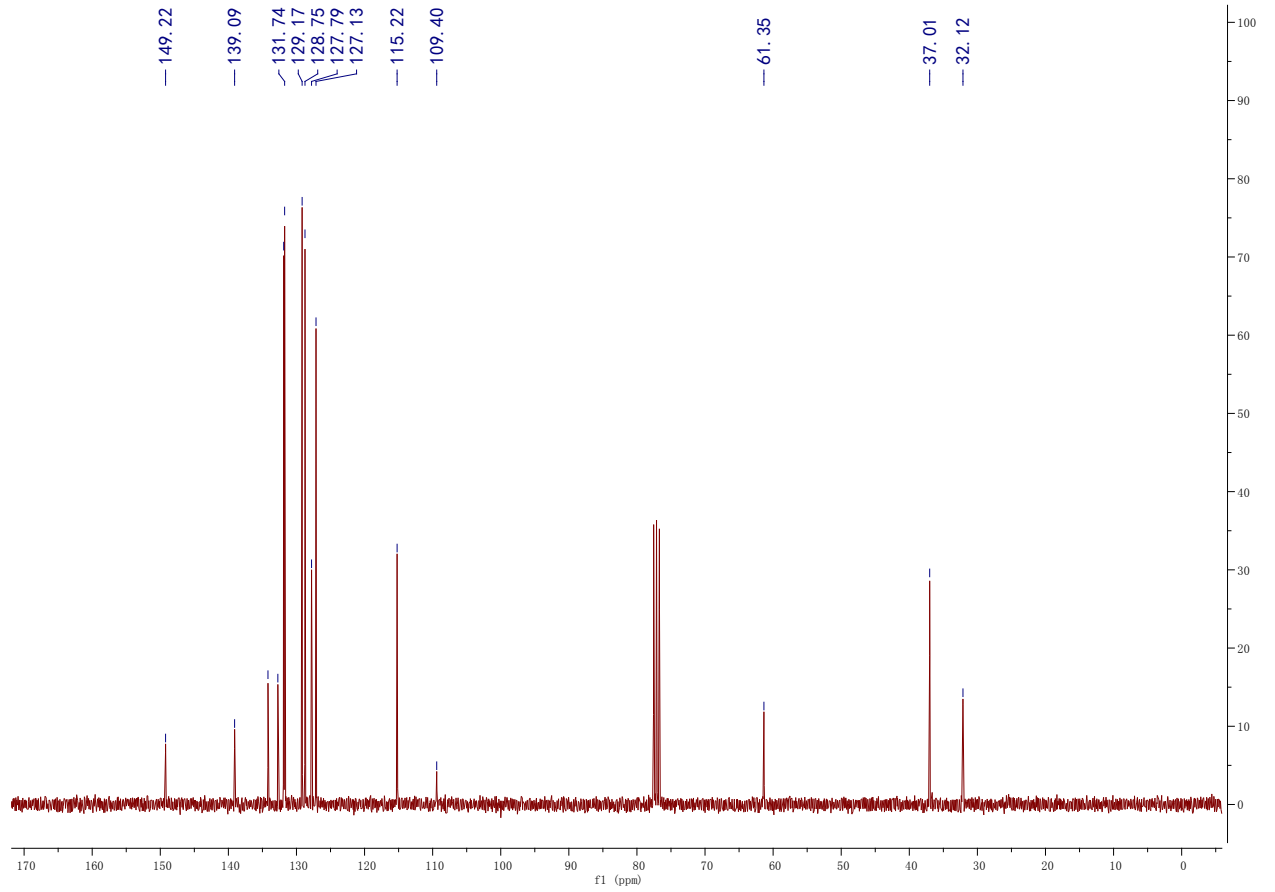
^{13}C NMR for **3k**



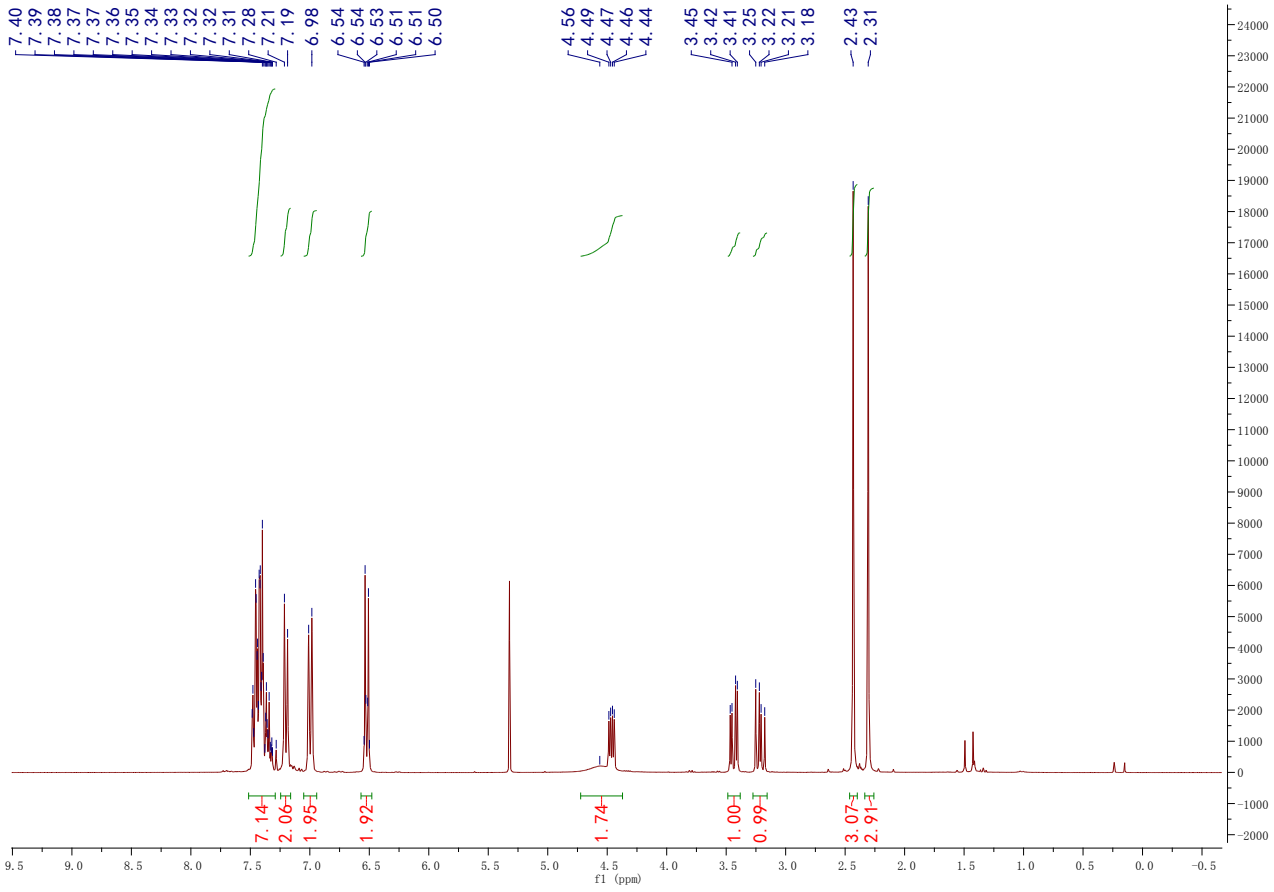
^{1}H NMR for **3l**



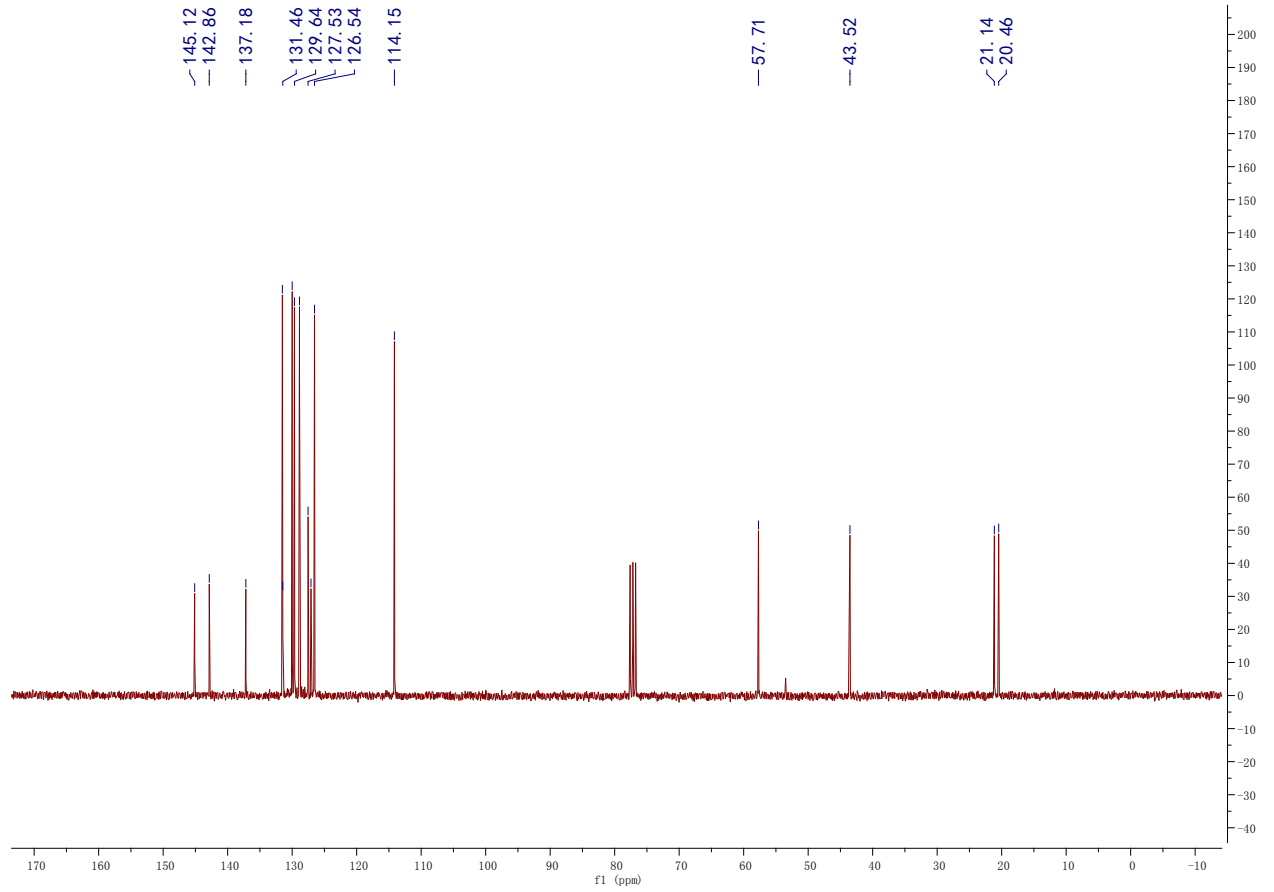
^{13}C NMR for **3l**



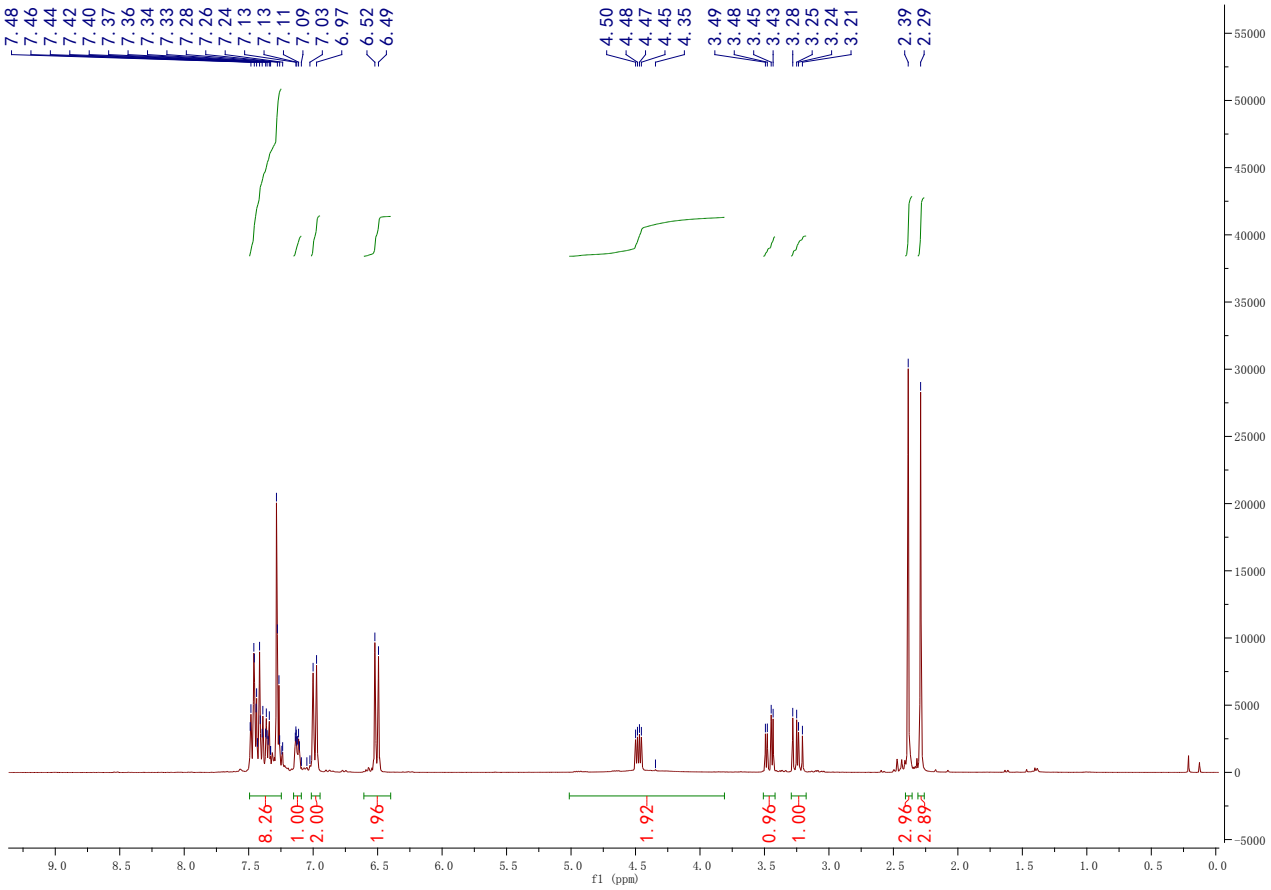
^{1}H NMR for **4a**



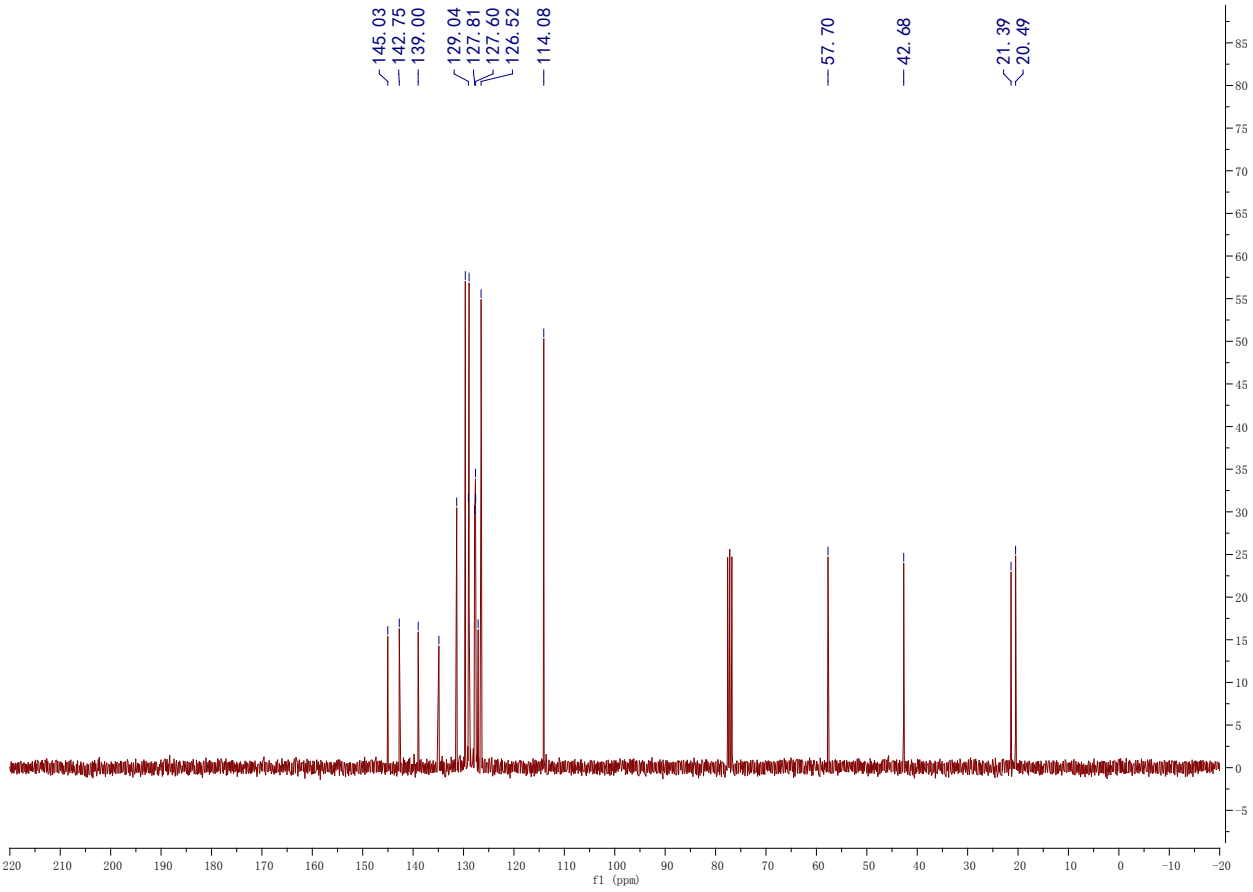
^{13}C NMR for **4a**



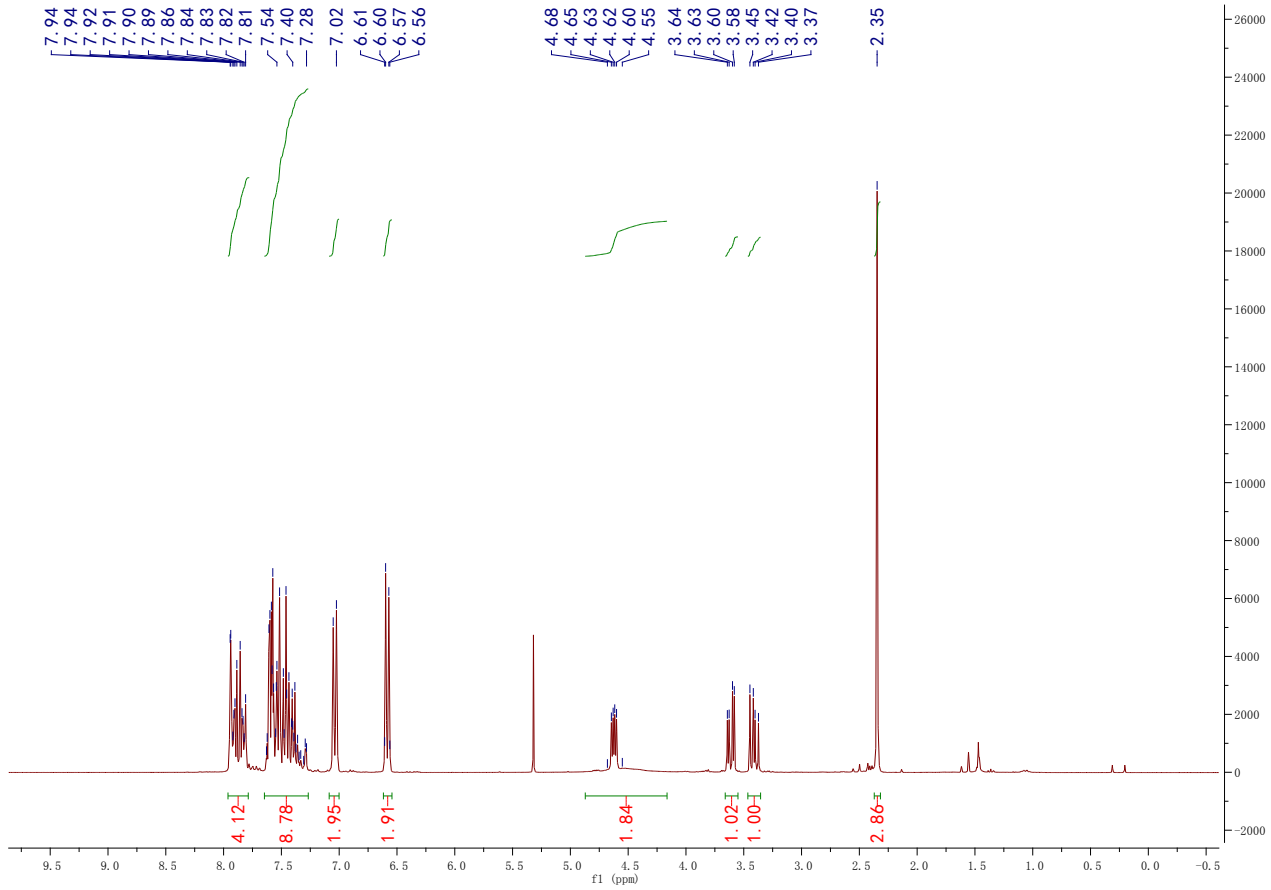
^{1}H NMR for **4b**



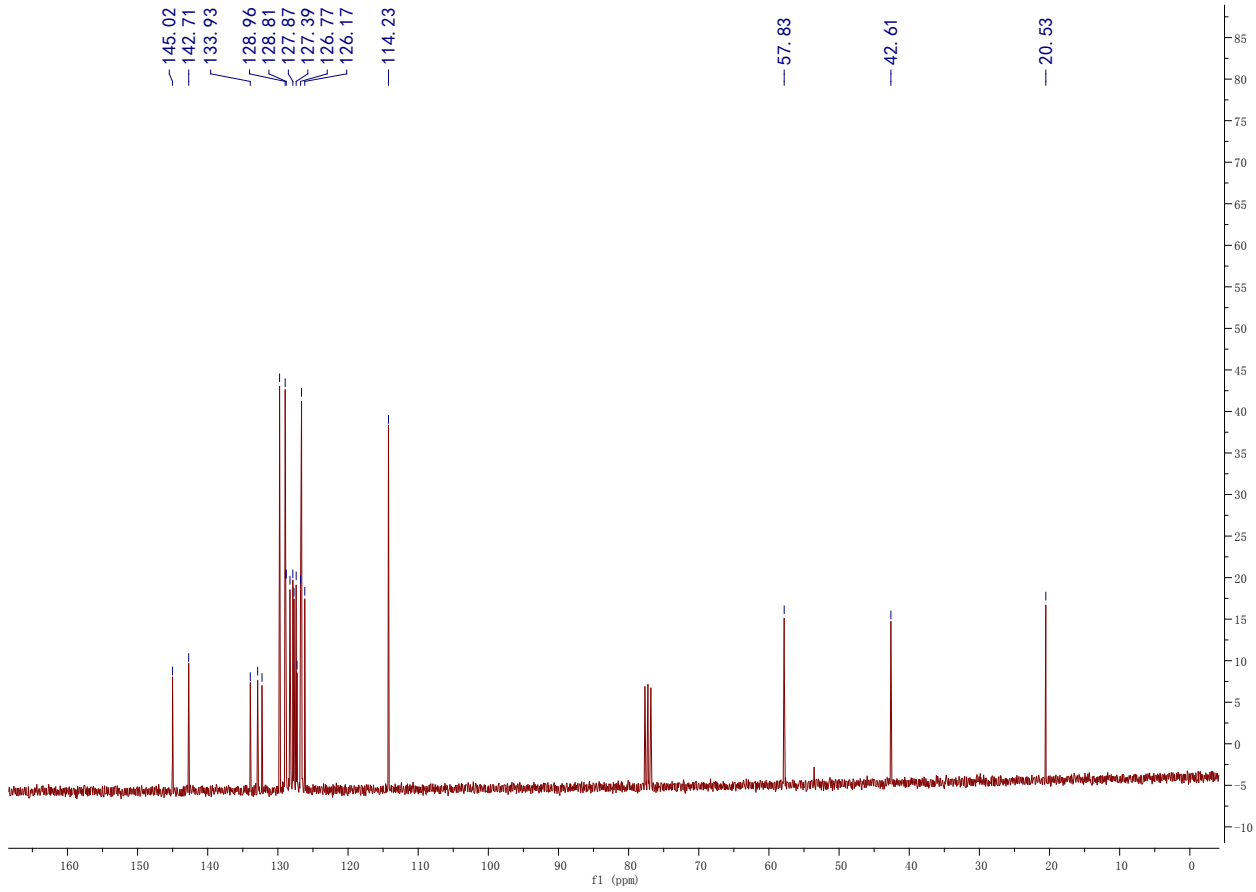
^{13}C NMR for **4b**



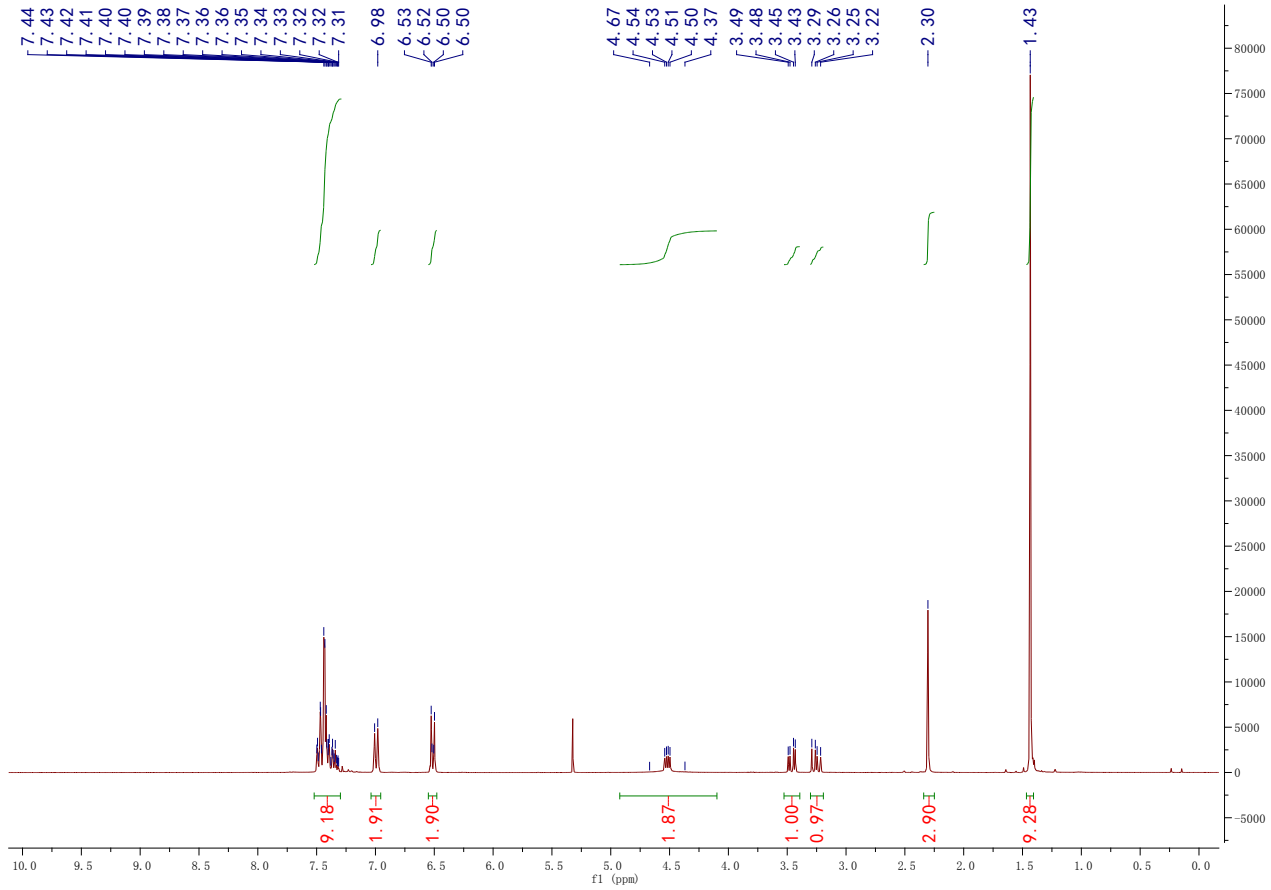
^{1}H NMR for **4c**



^{13}C NMR for **4c**



^{1}H NMR for **4d**



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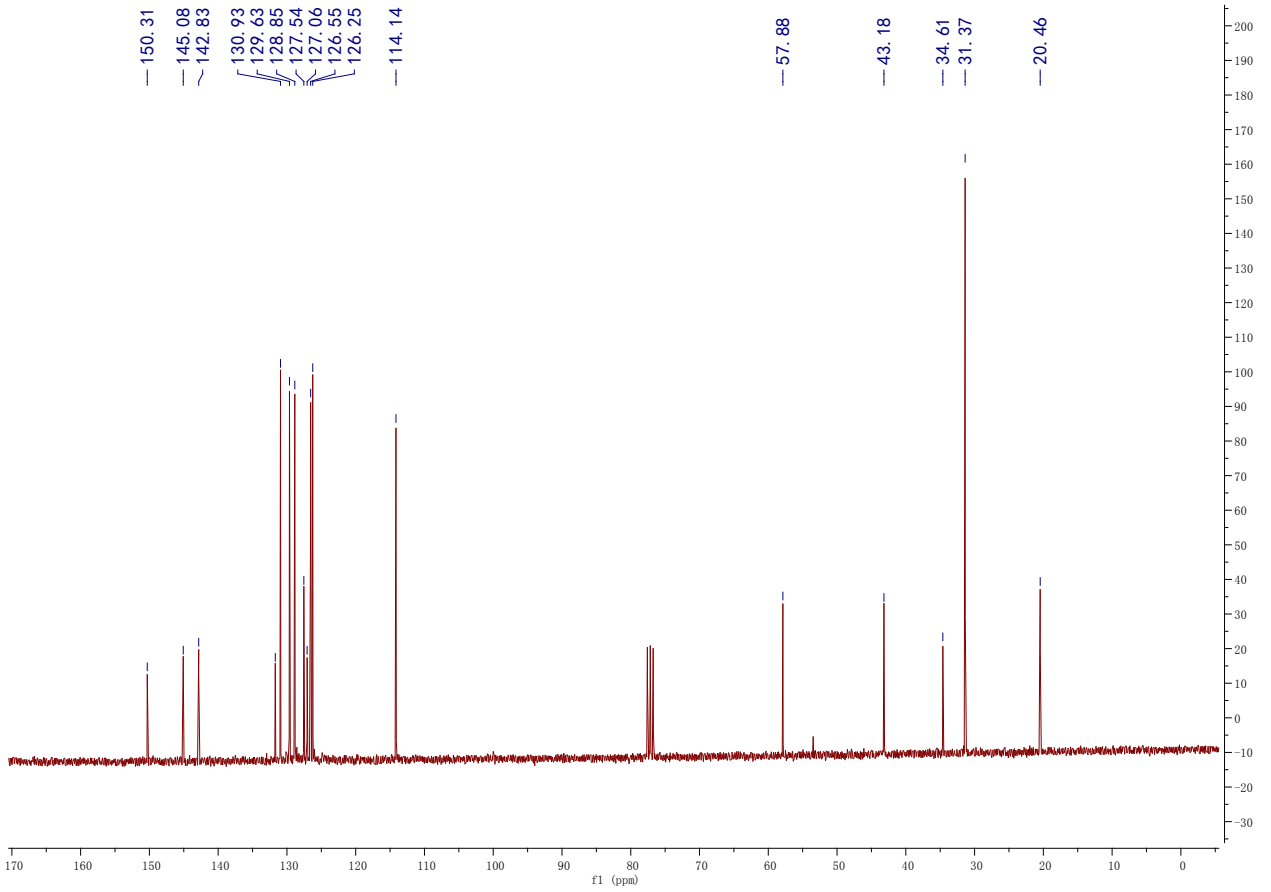
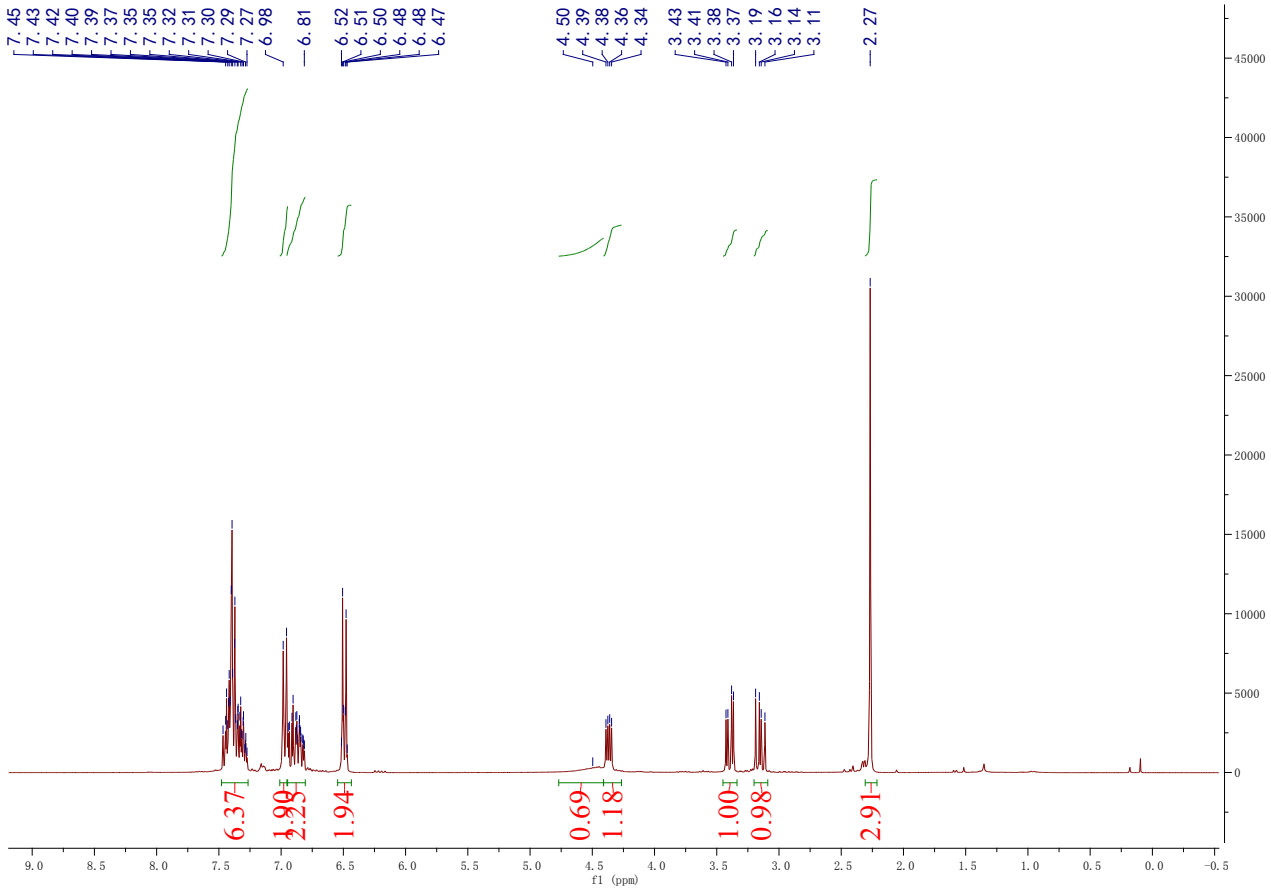


^{1}H NMR for **4e**



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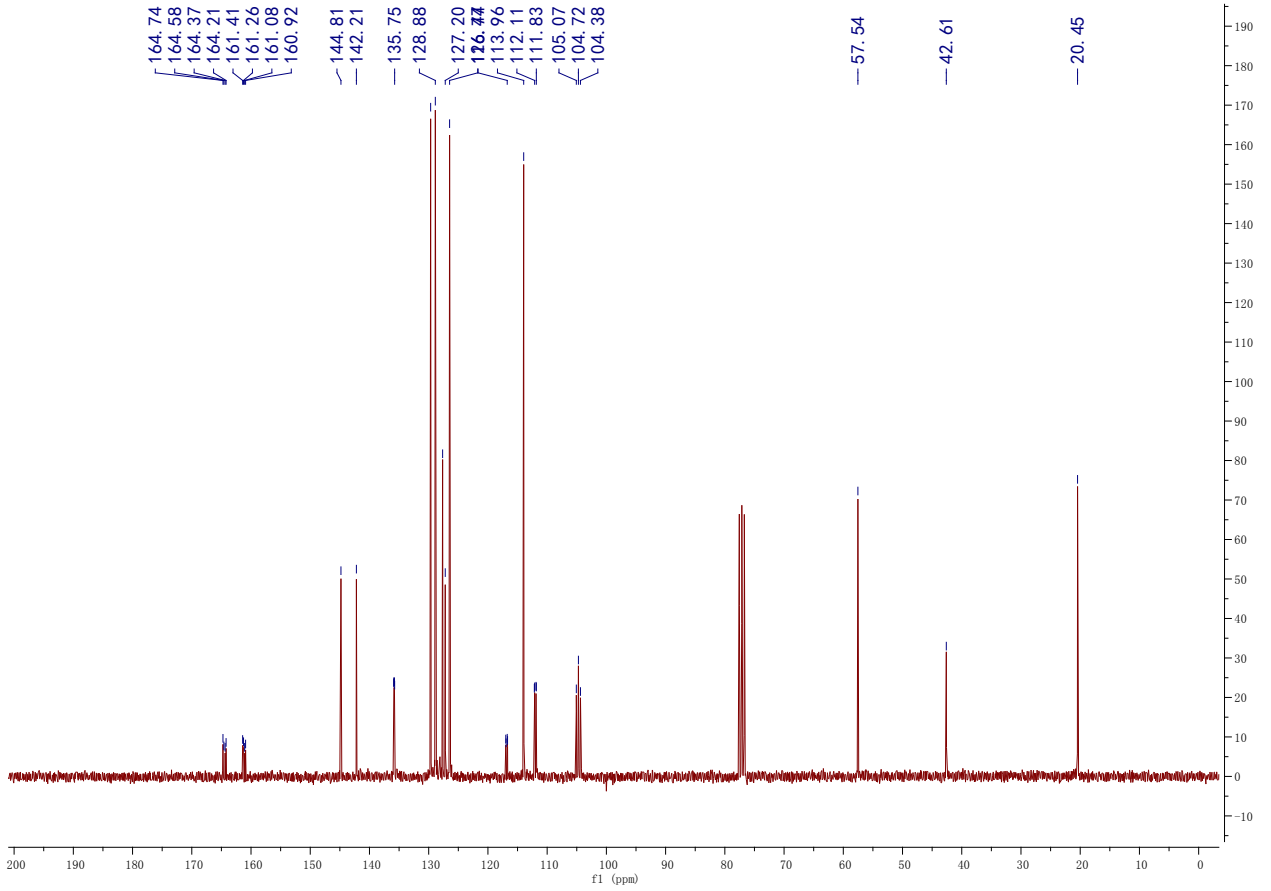

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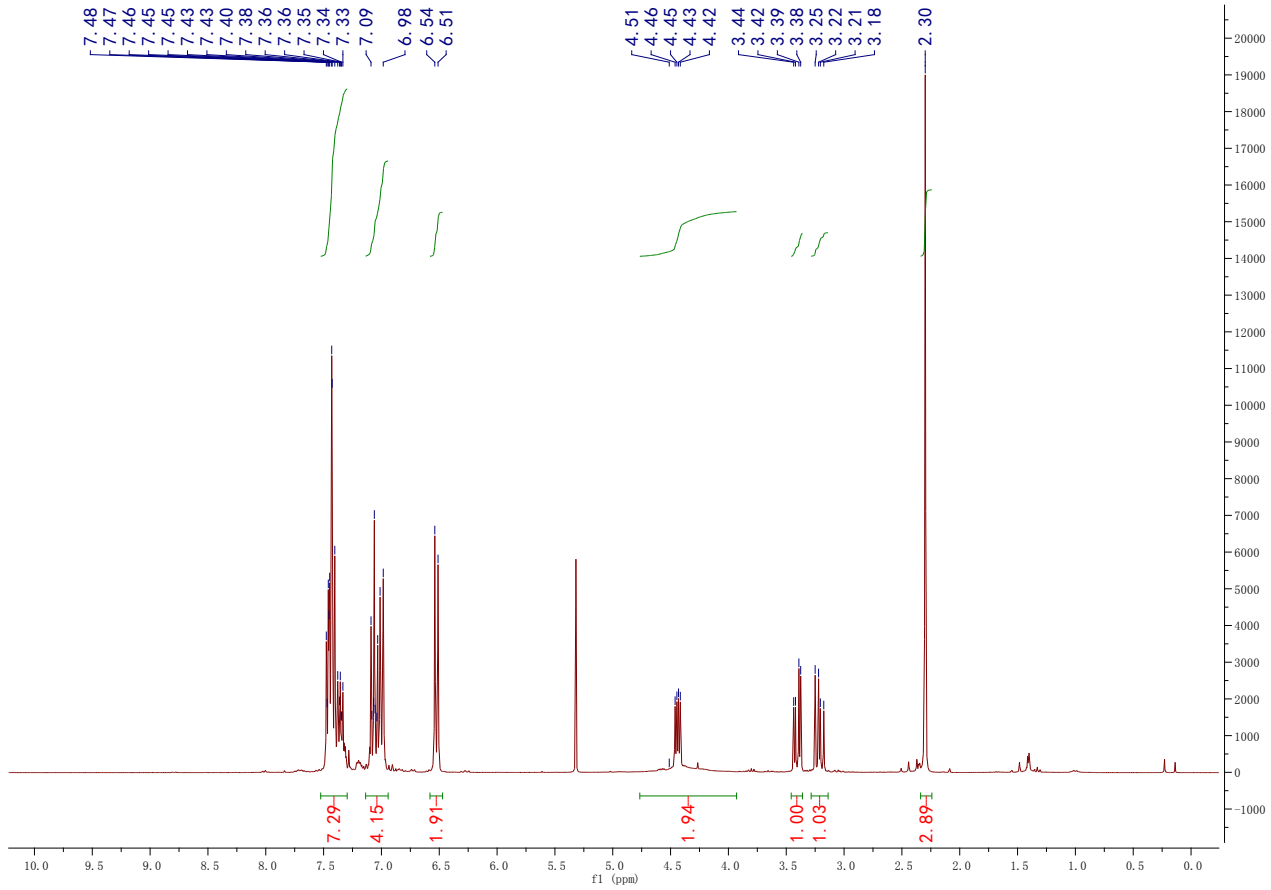
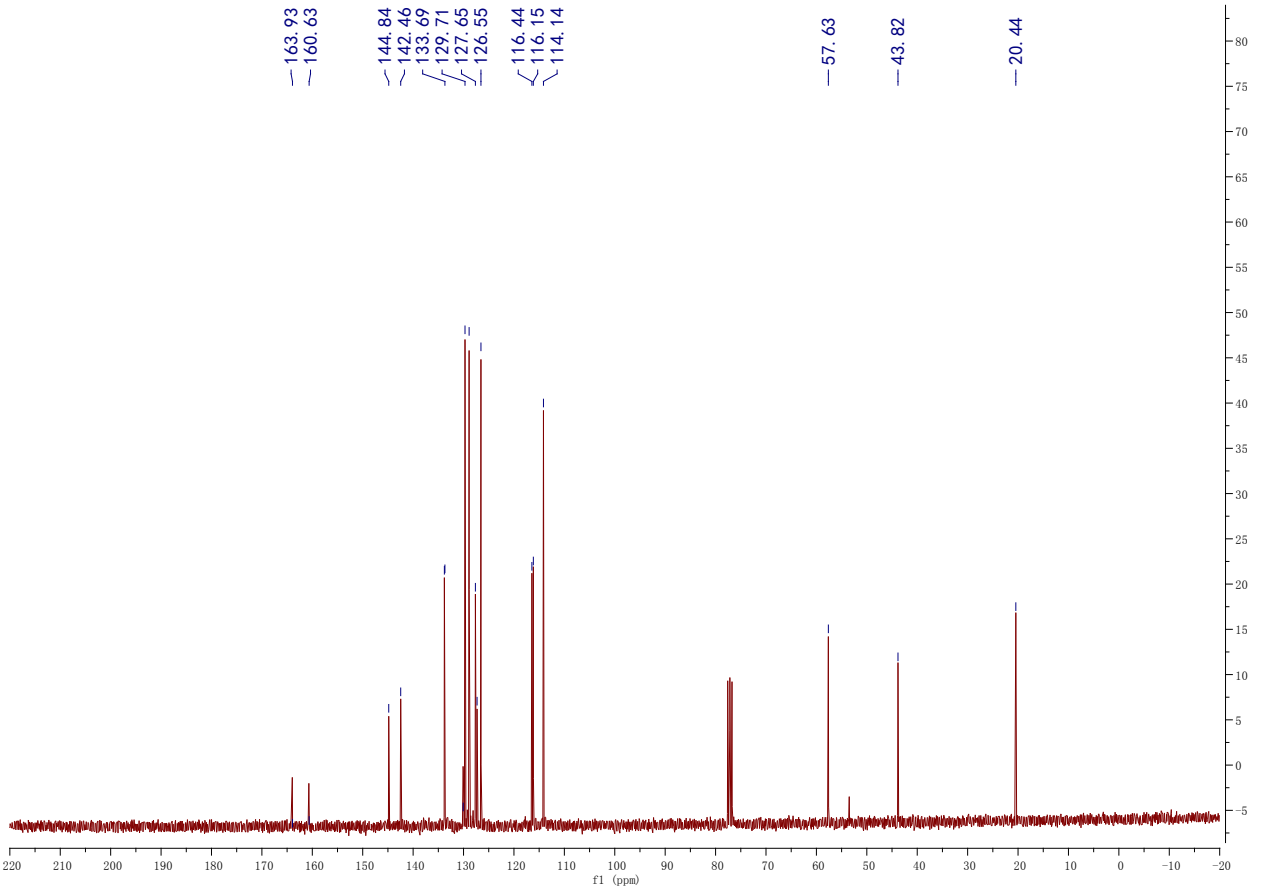
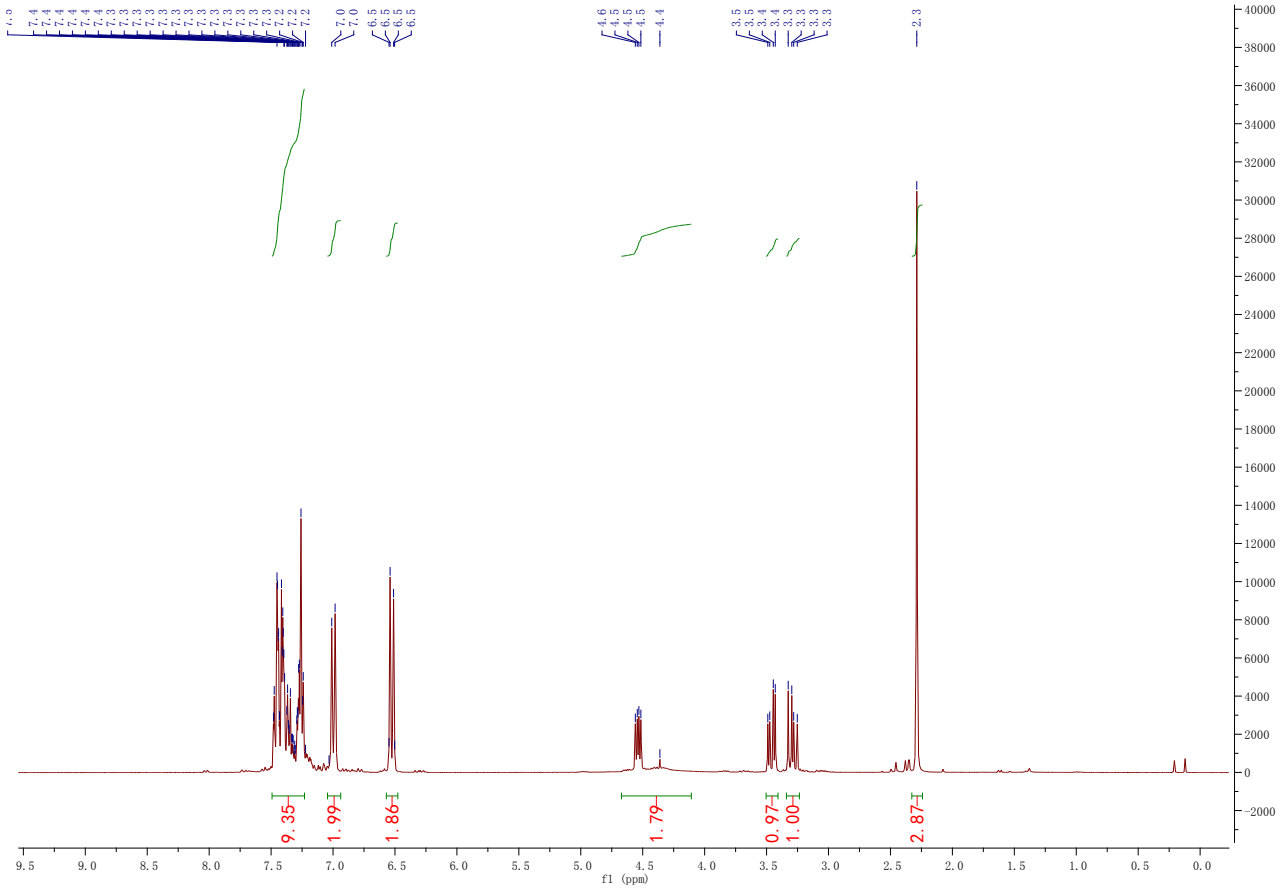


^{13}C NMR for **4f**



^{1}H NMR for **4g**



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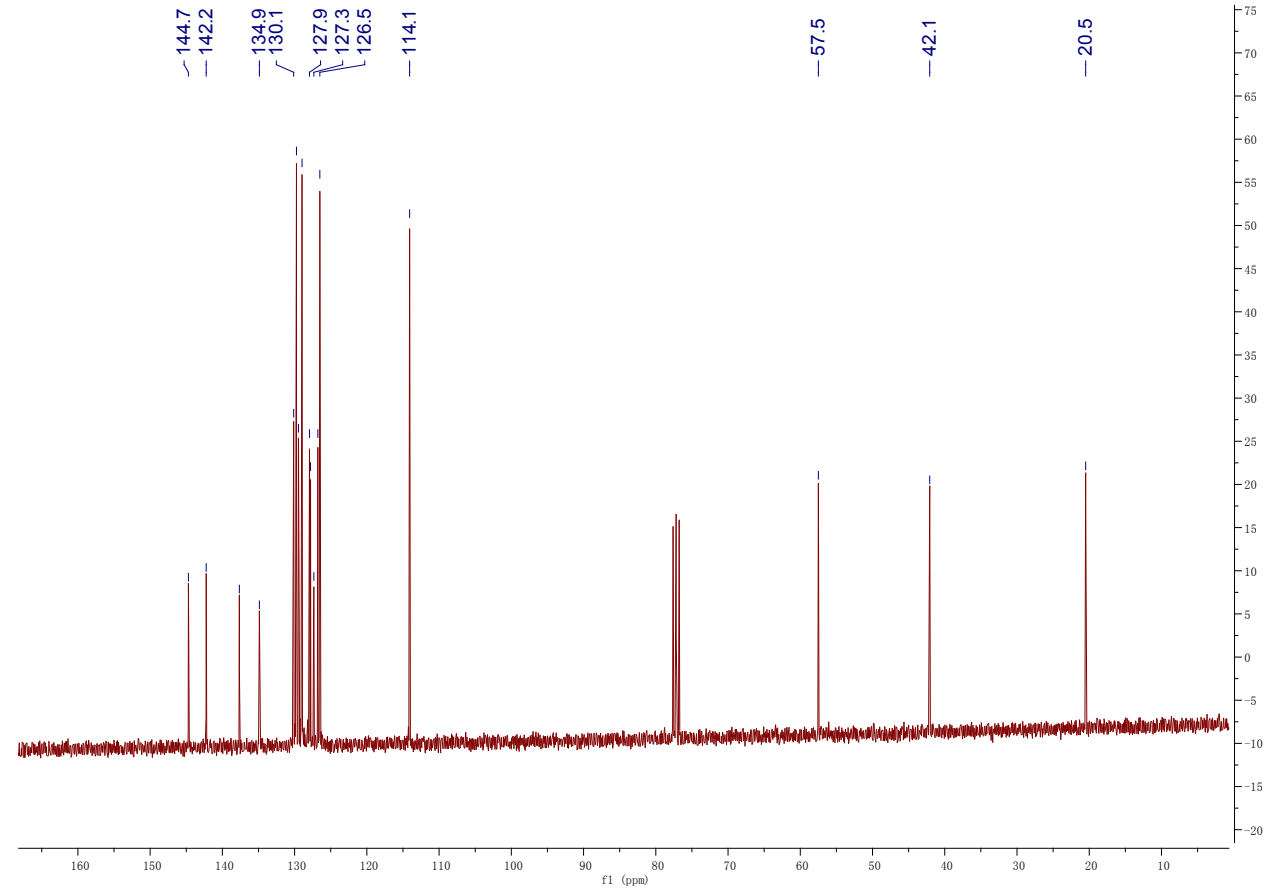
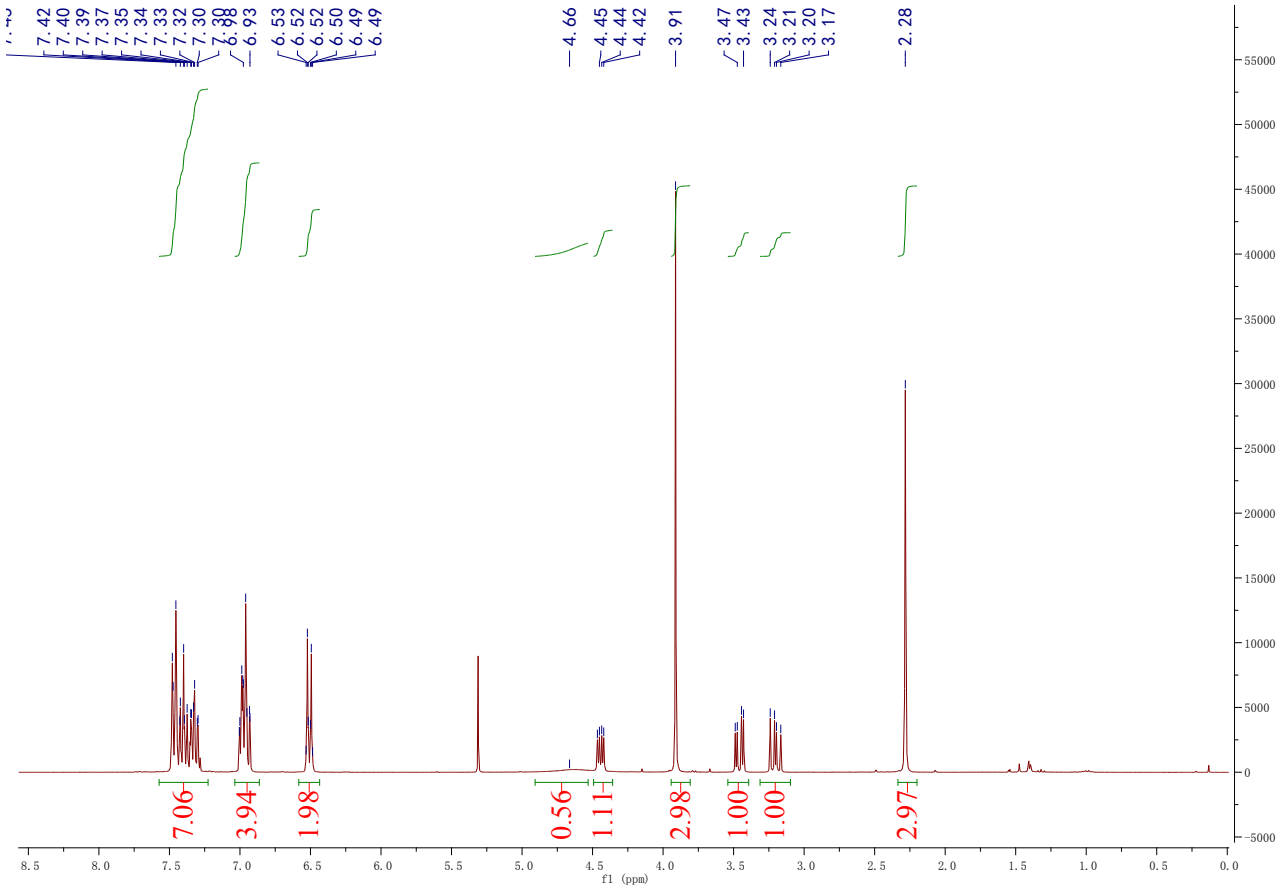


^{1}H NMR for **4h**



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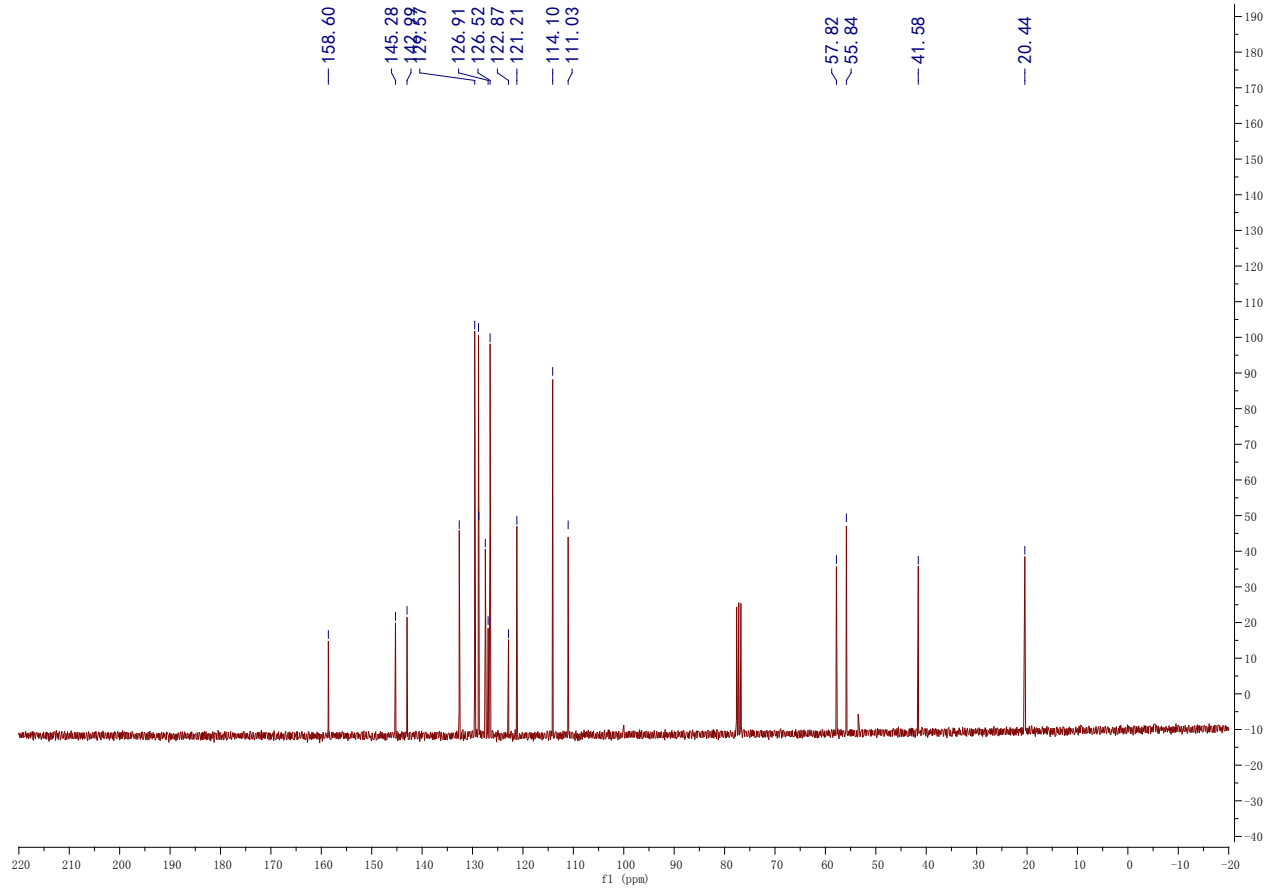
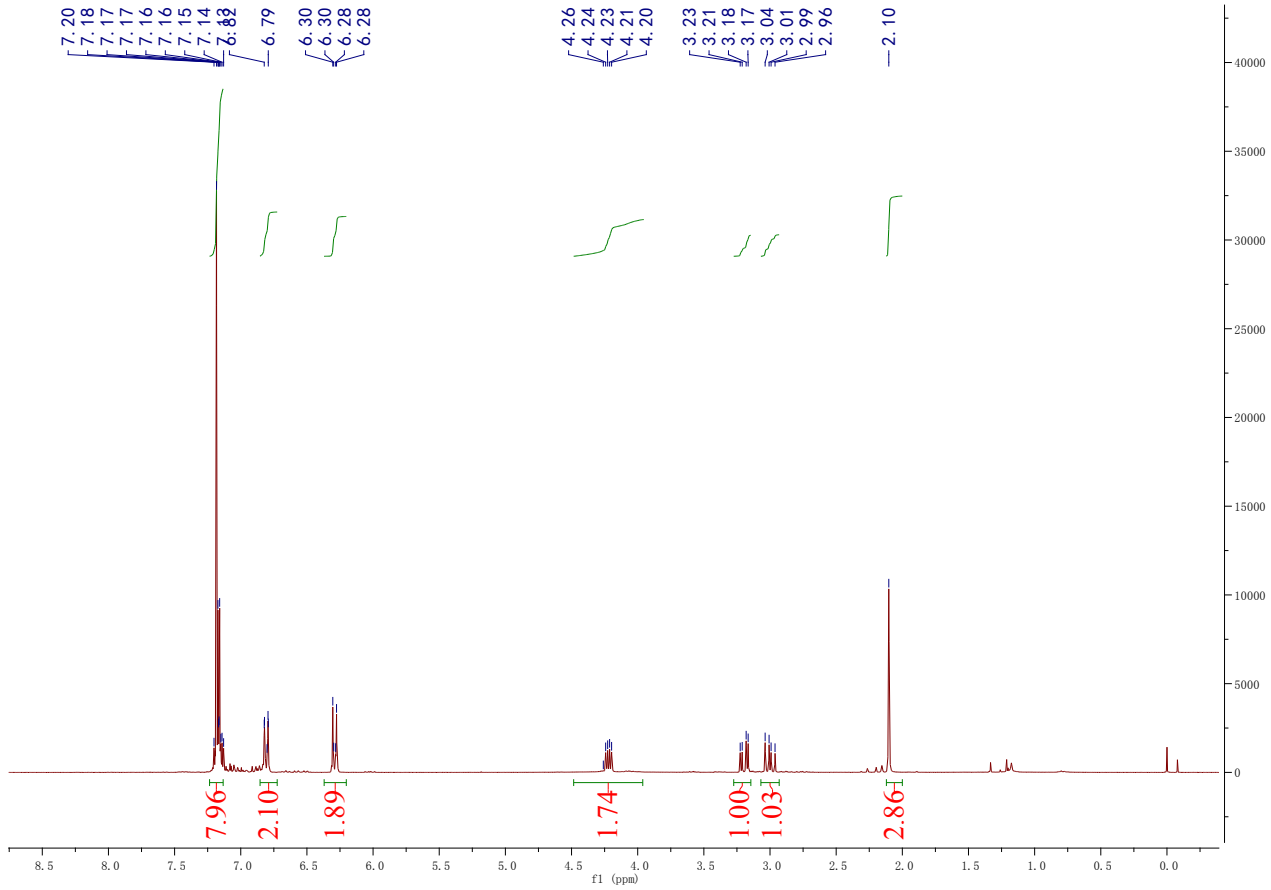


^{1}H NMR for **4i**



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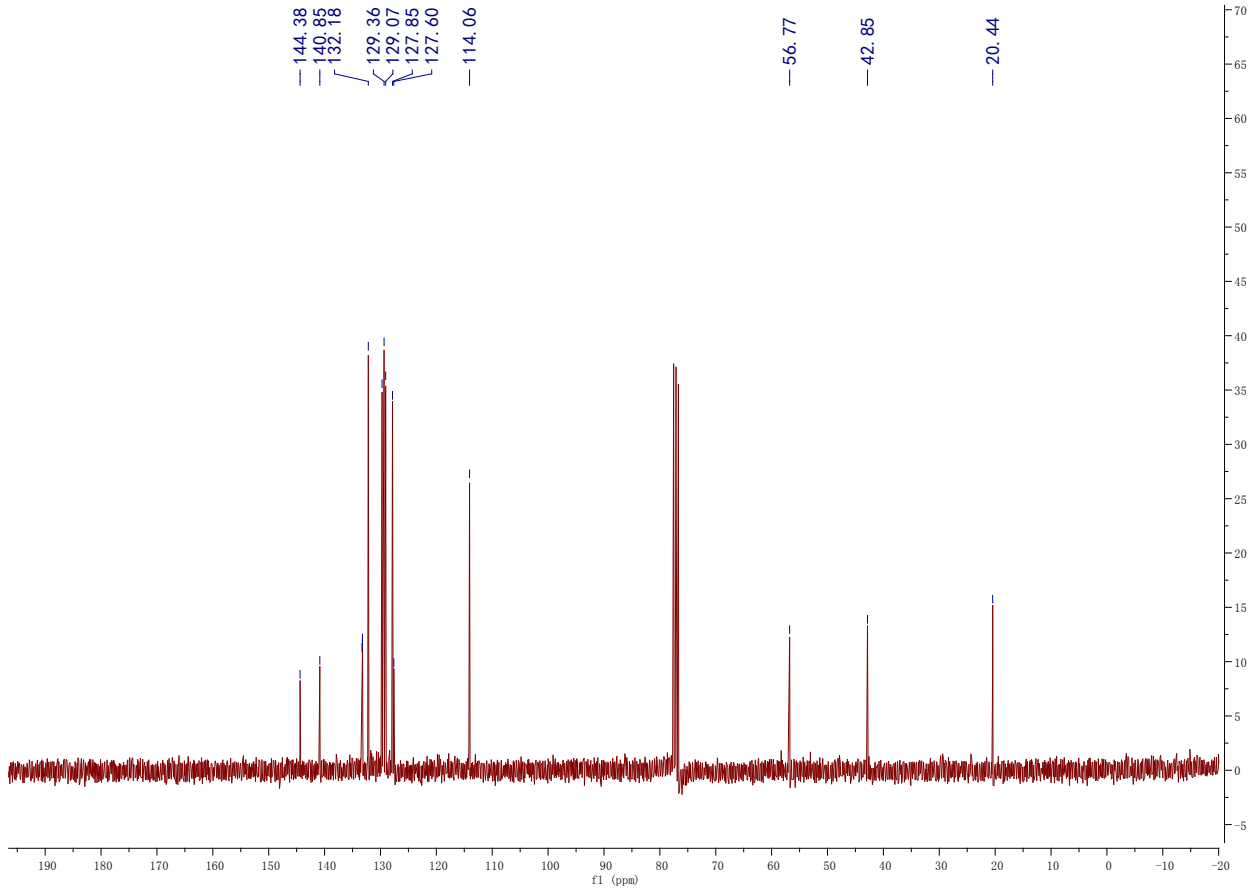
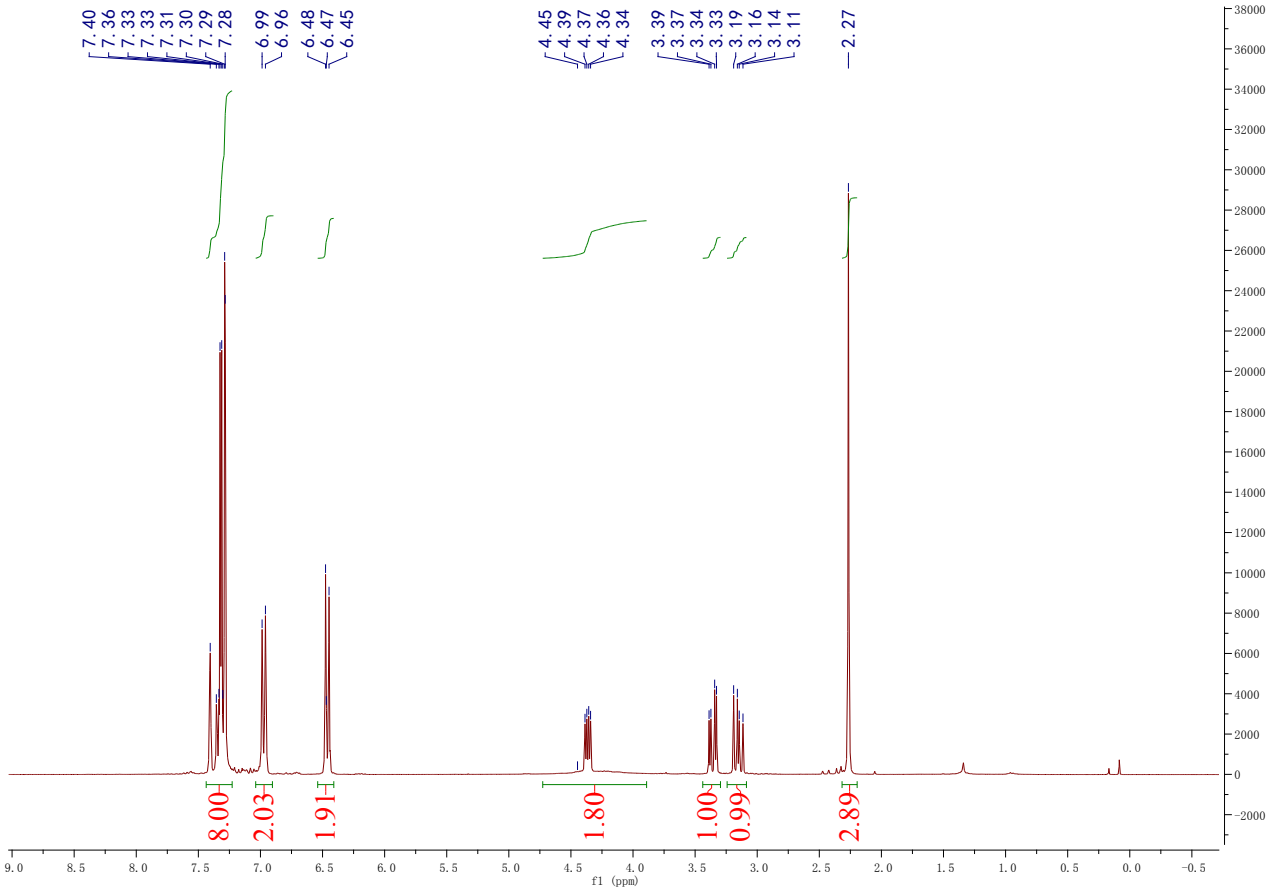
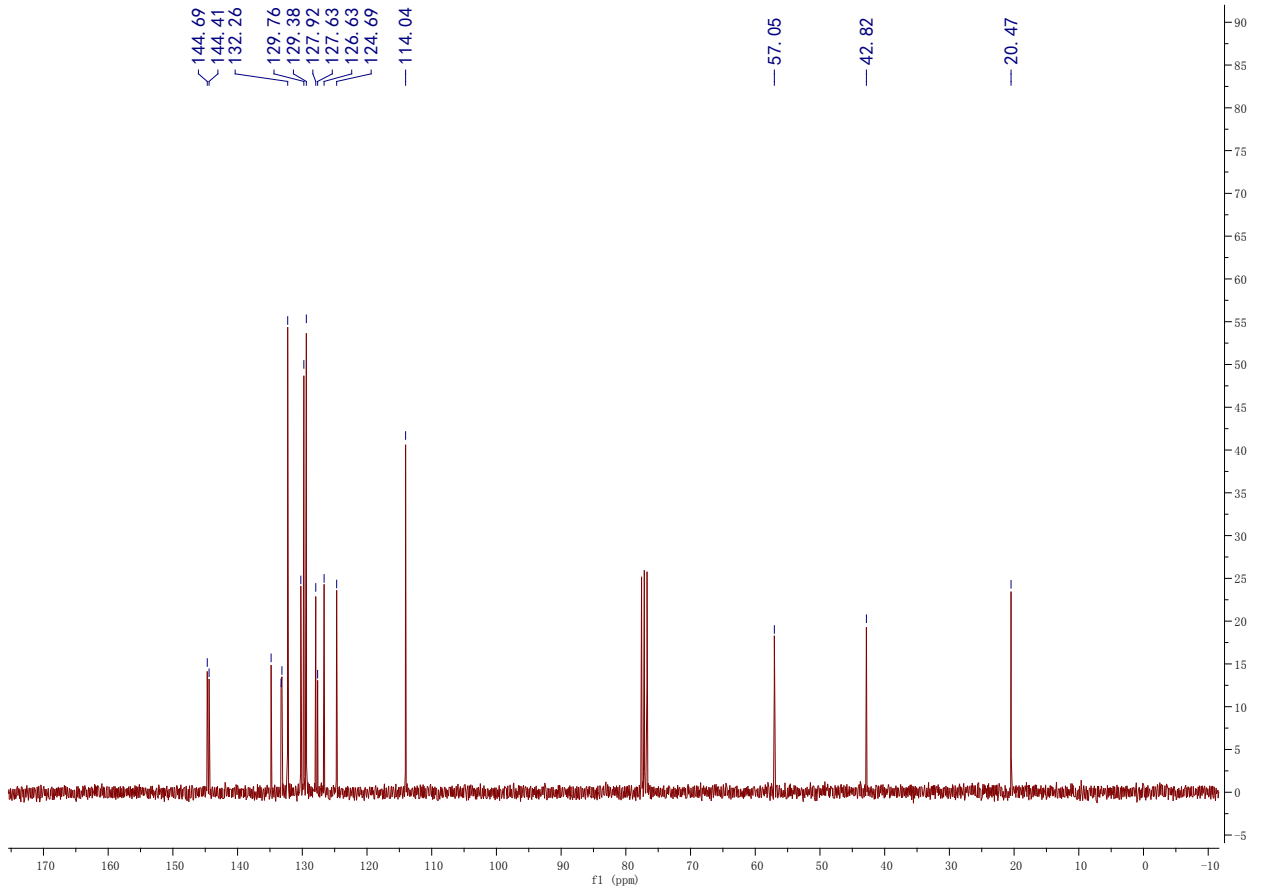


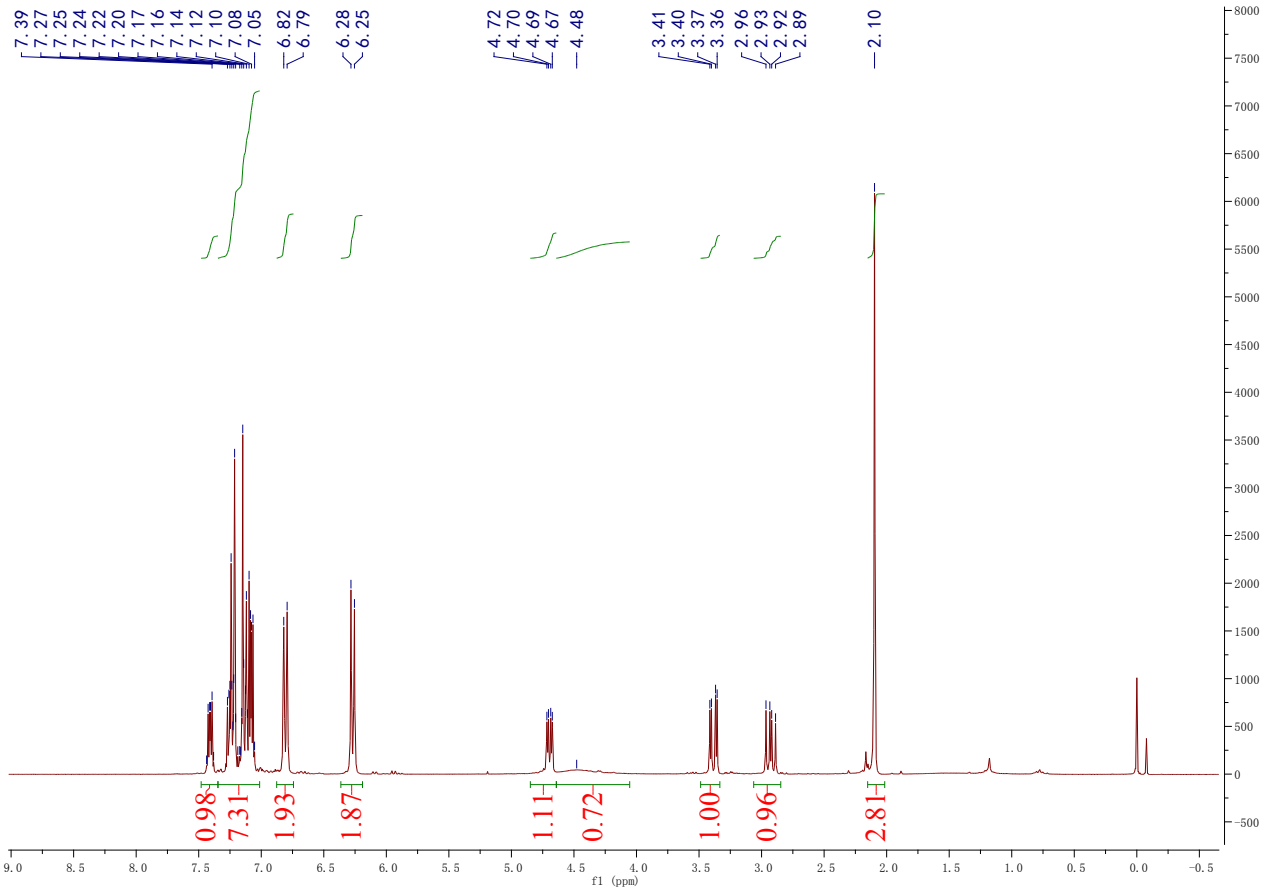
^{1}H NMR for **4j**



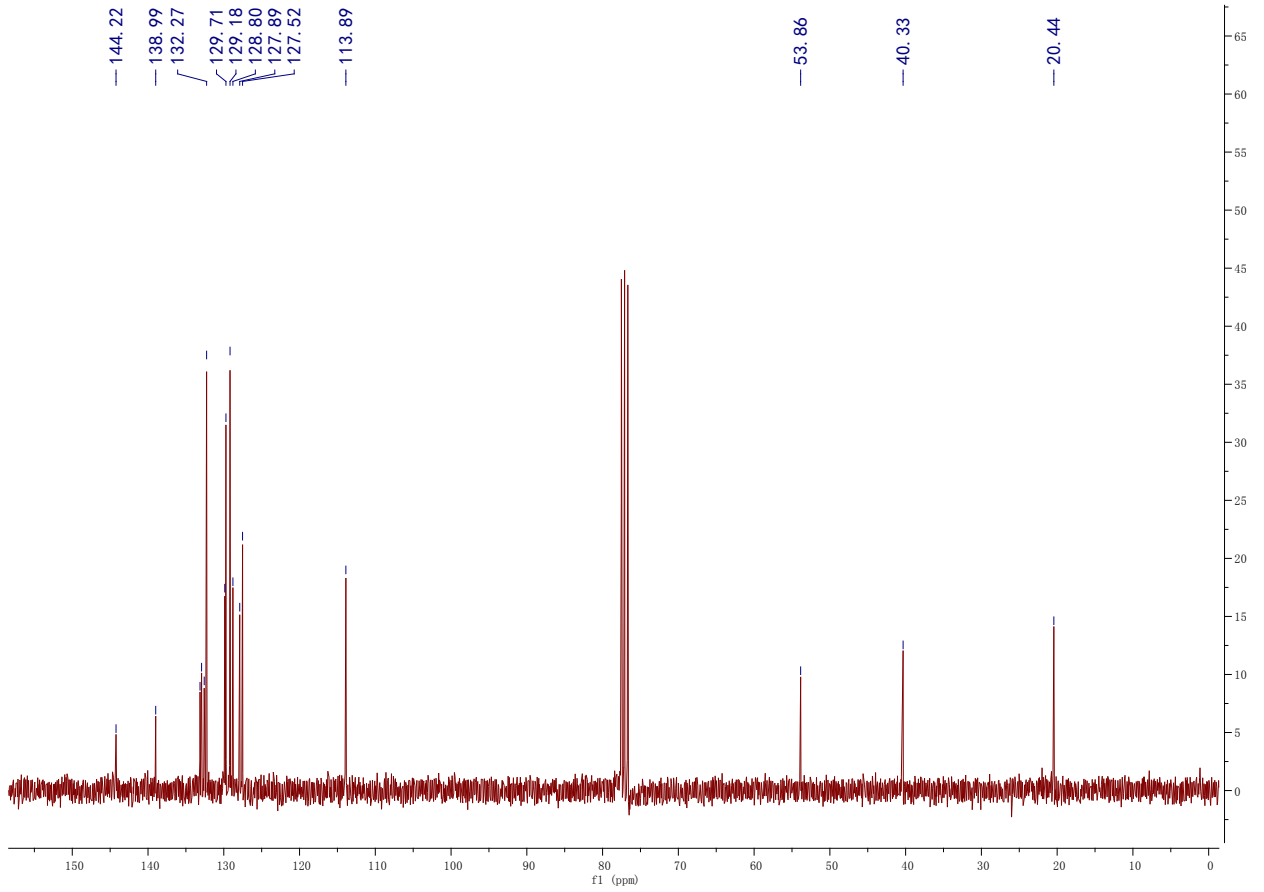
^{13}C NMR for **4j**



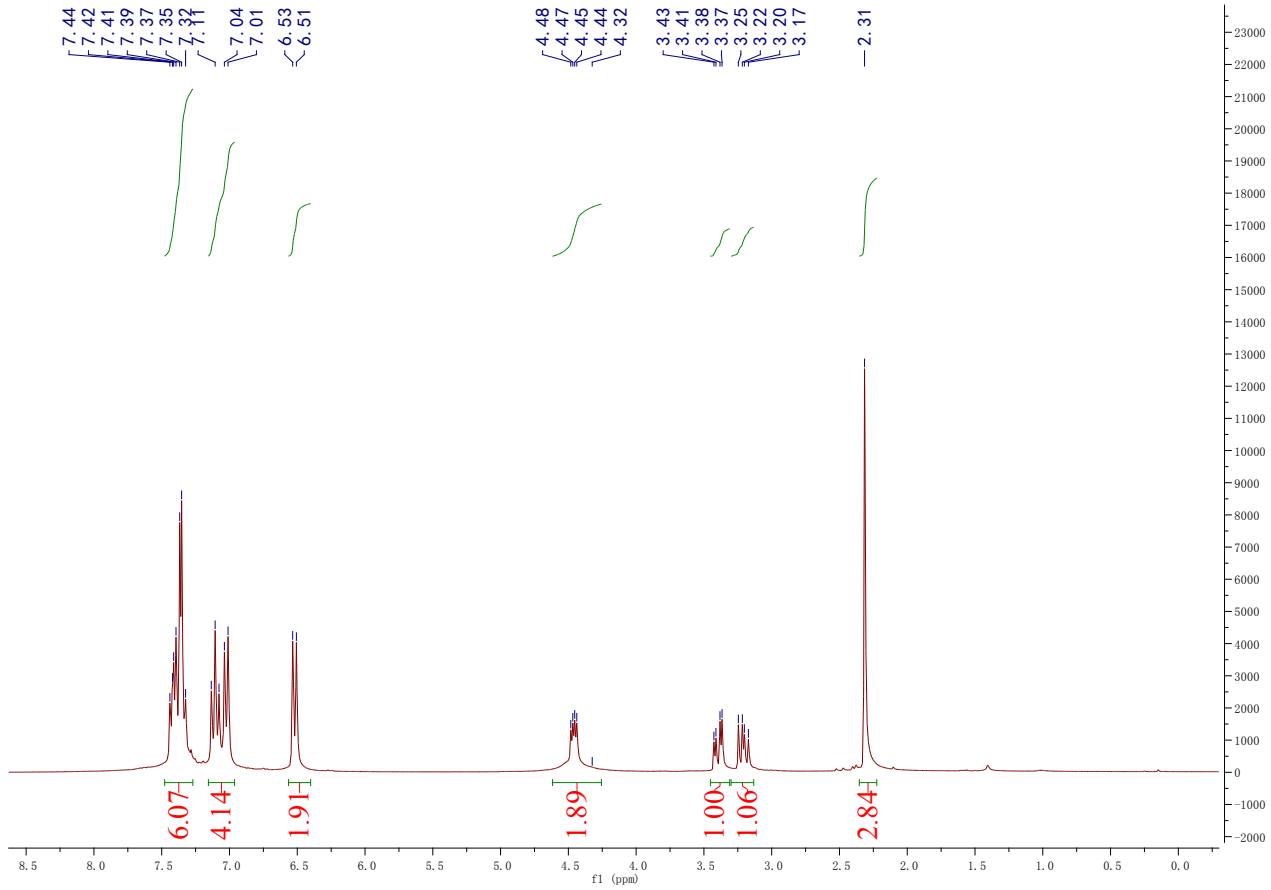
^{1}H NMR for **4k**



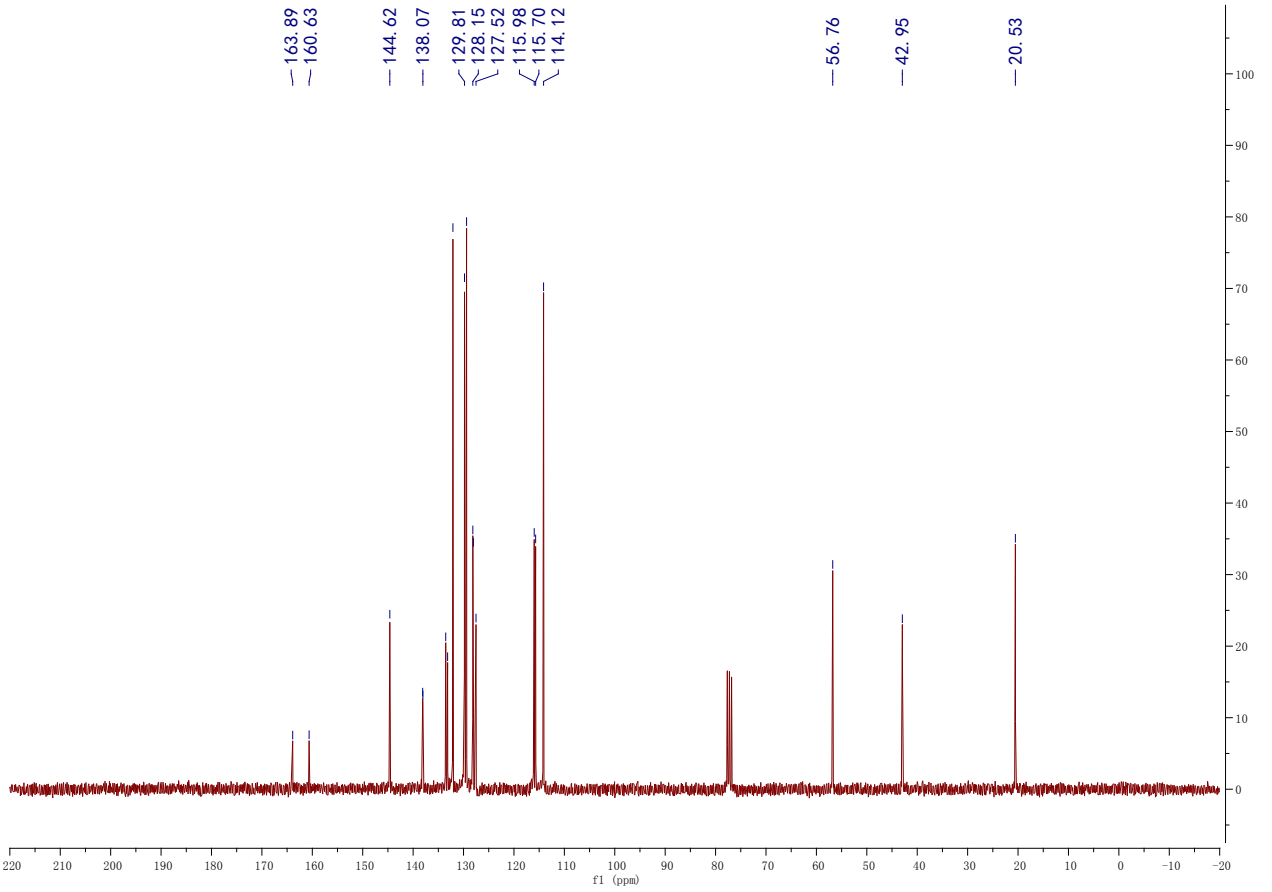
^{13}C NMR for **4k**



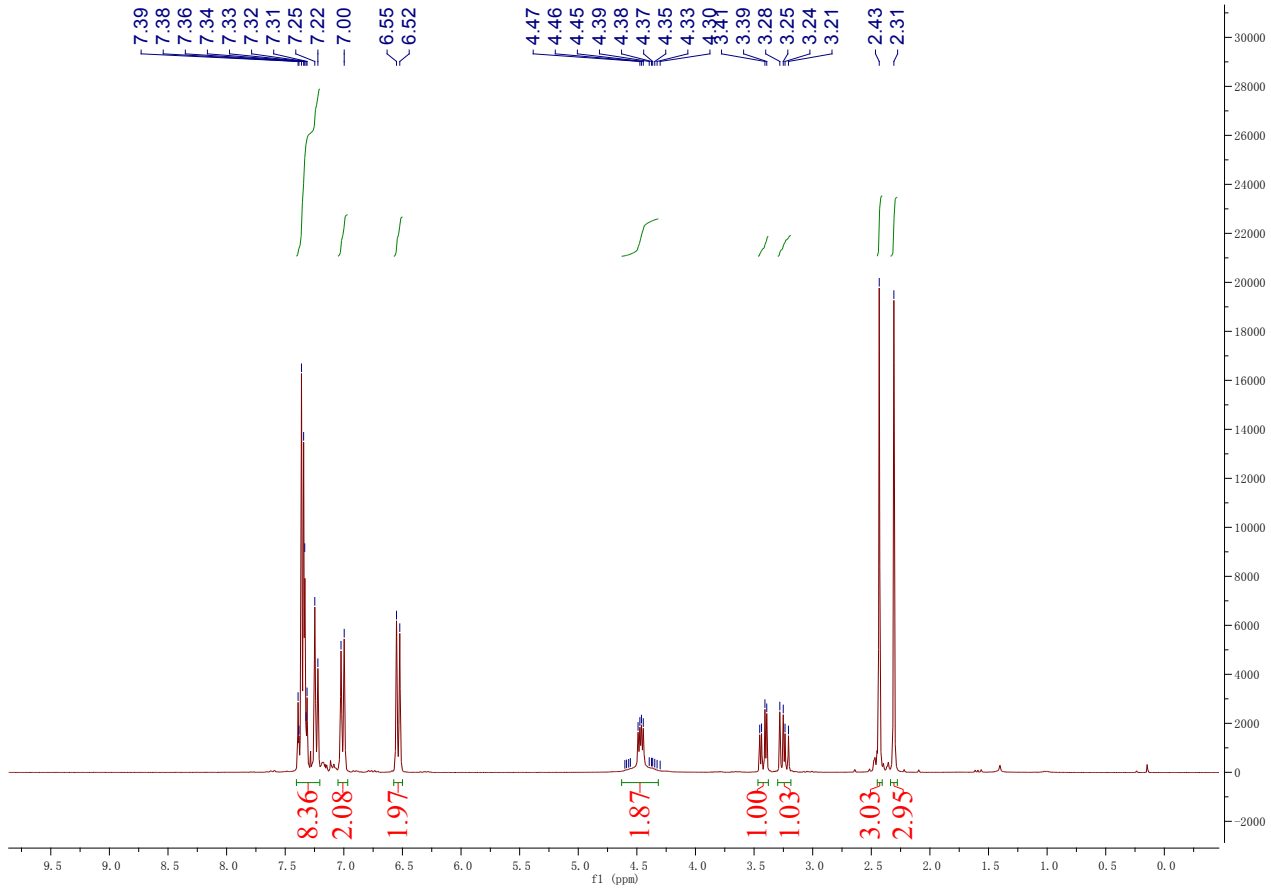
^{1}H NMR for **4l**



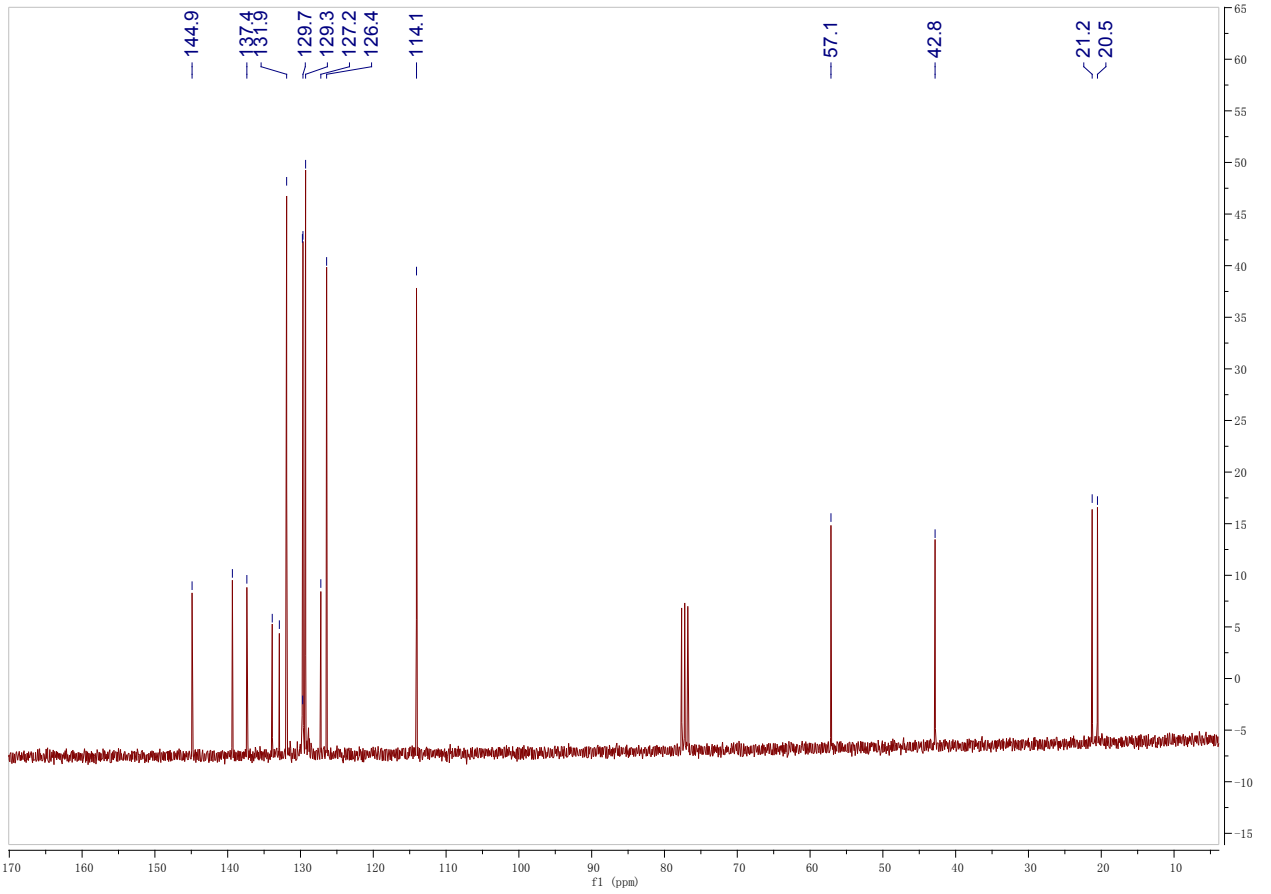
^{13}C NMR for **4l**



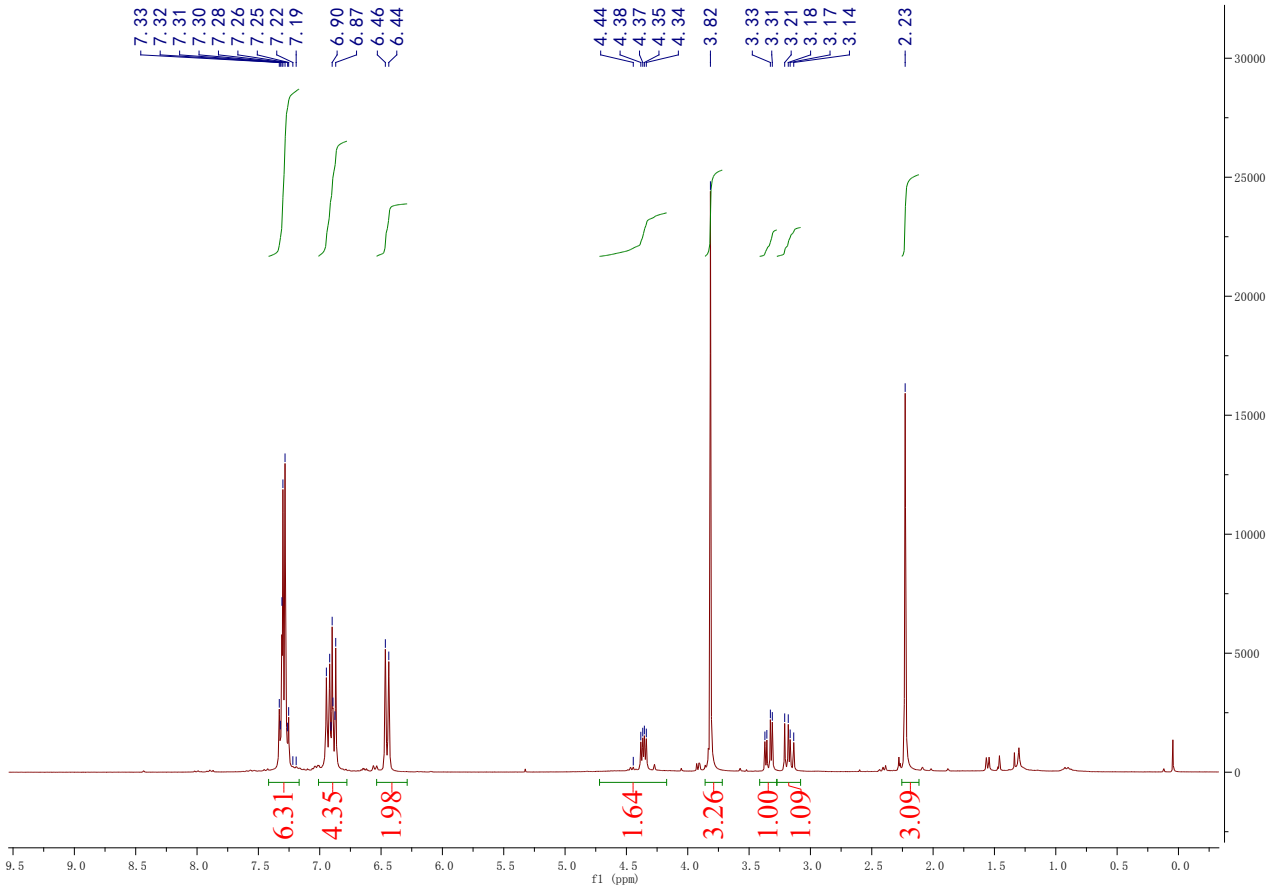
^{1}H NMR for **4m**



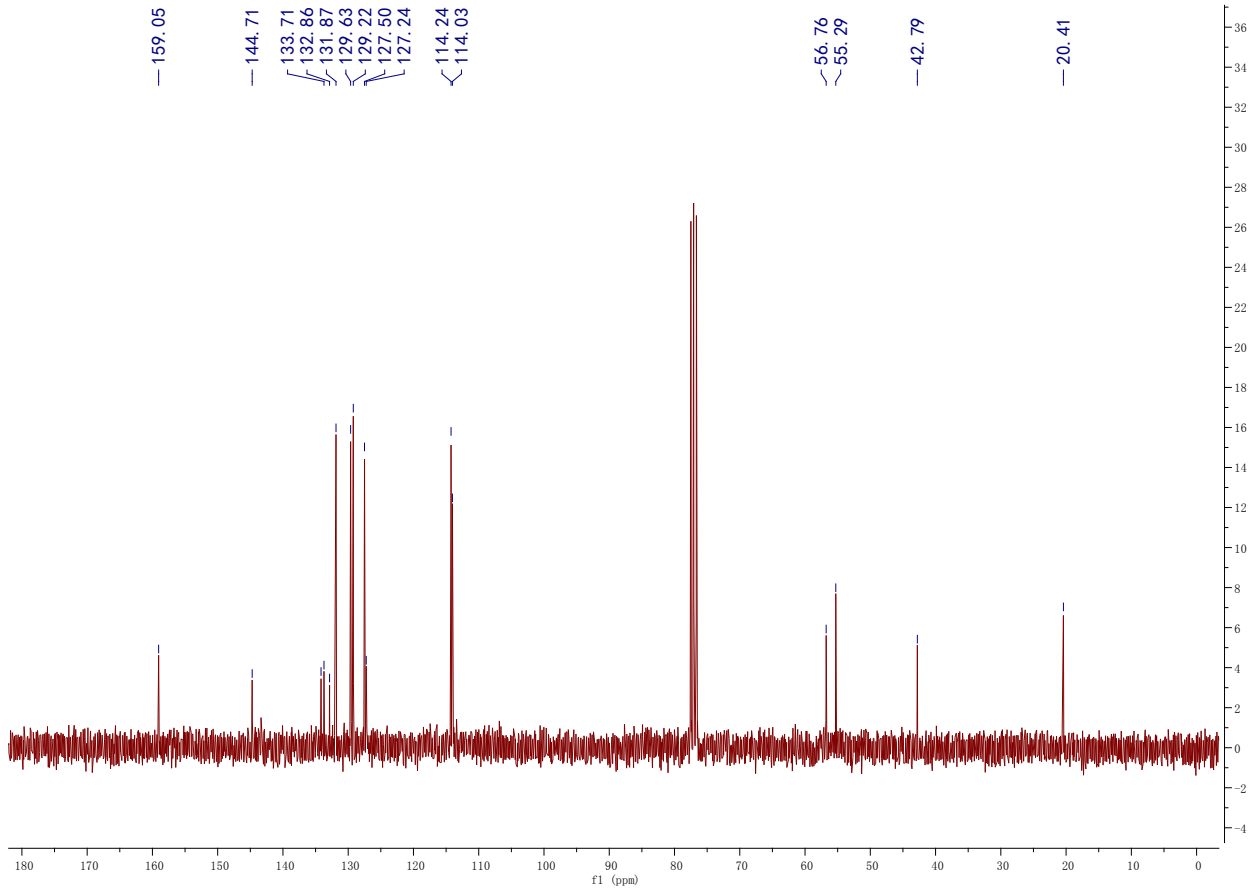
^{13}C NMR for **4m**



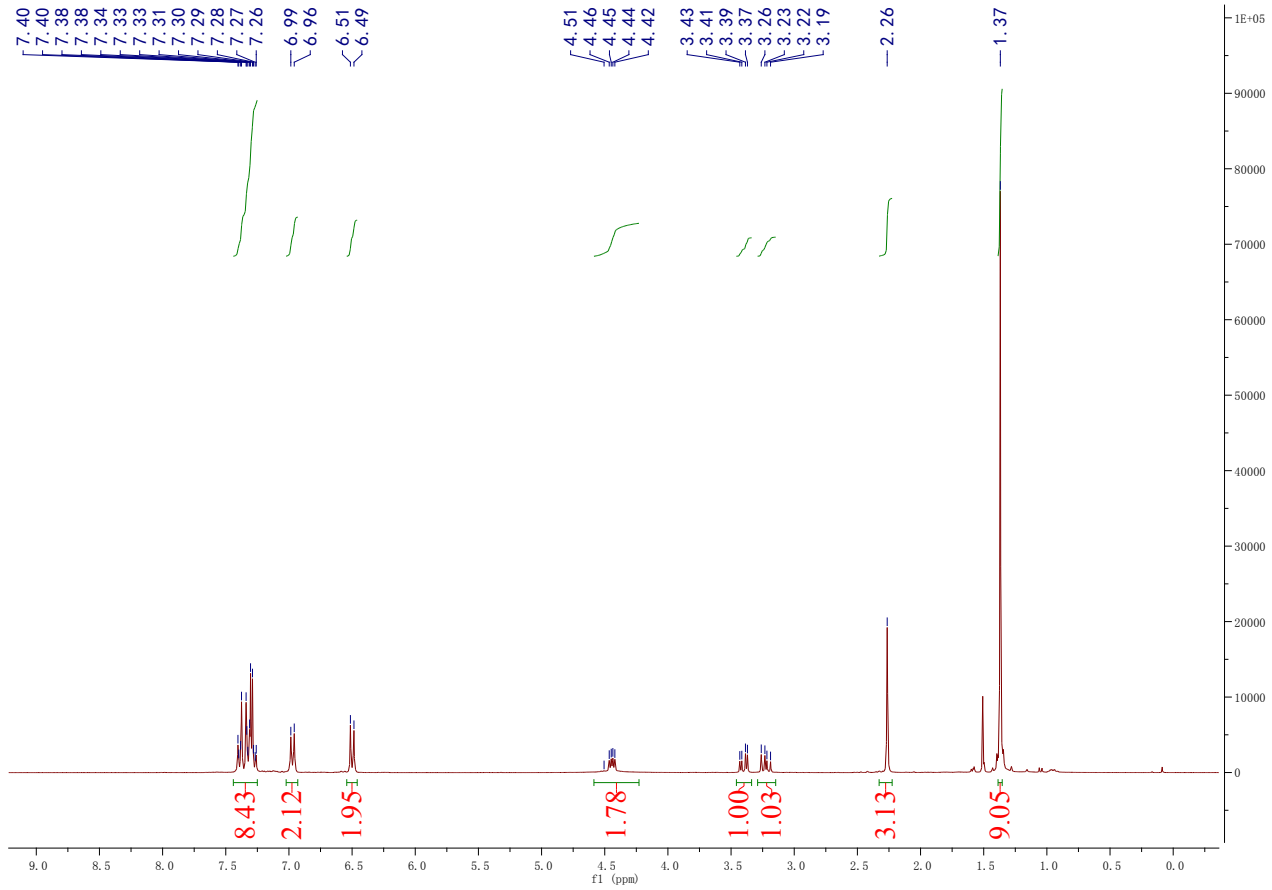
^{1}H NMR for **4n**



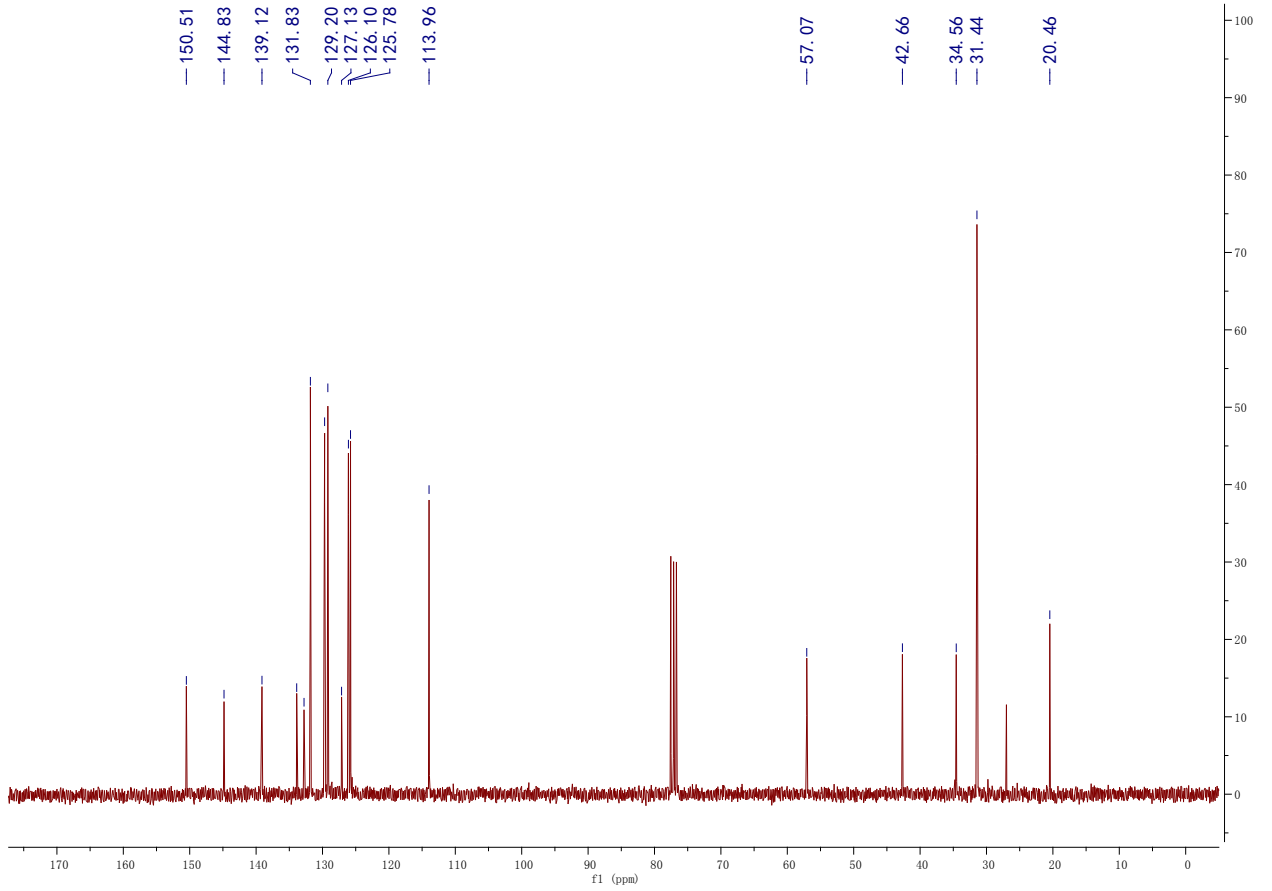
^{13}C NMR for **4n**



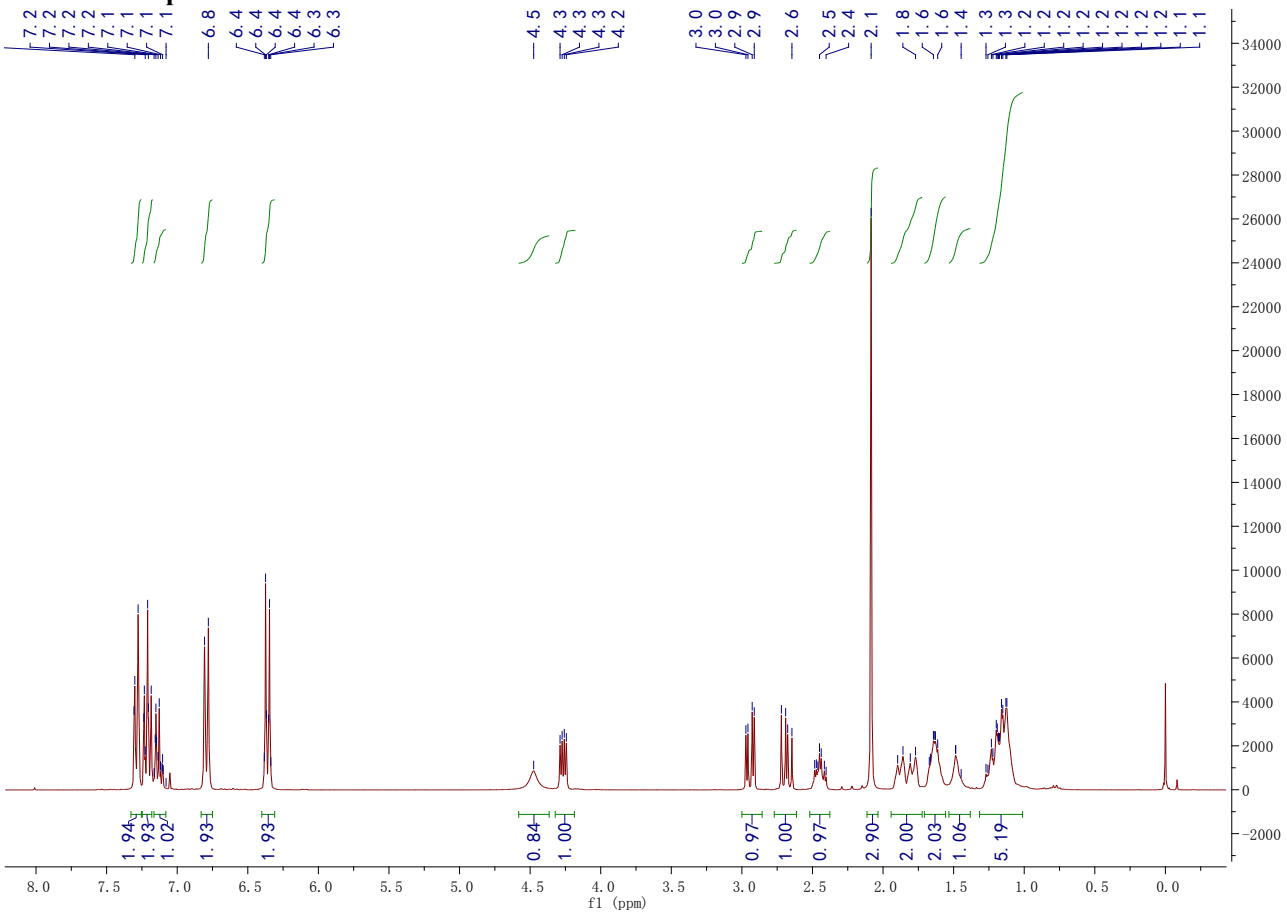
^{1}H NMR for **4o**



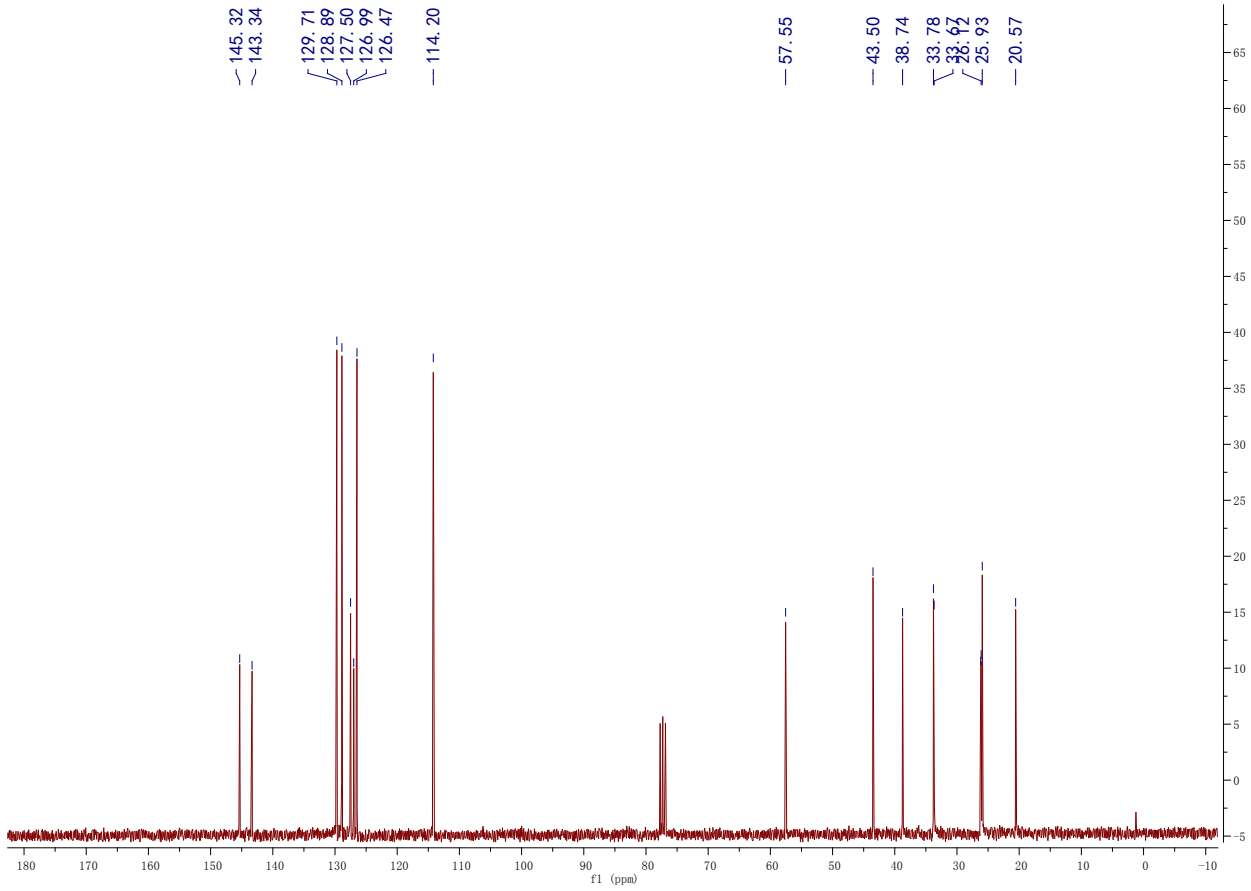
^{13}C NMR for **4o**



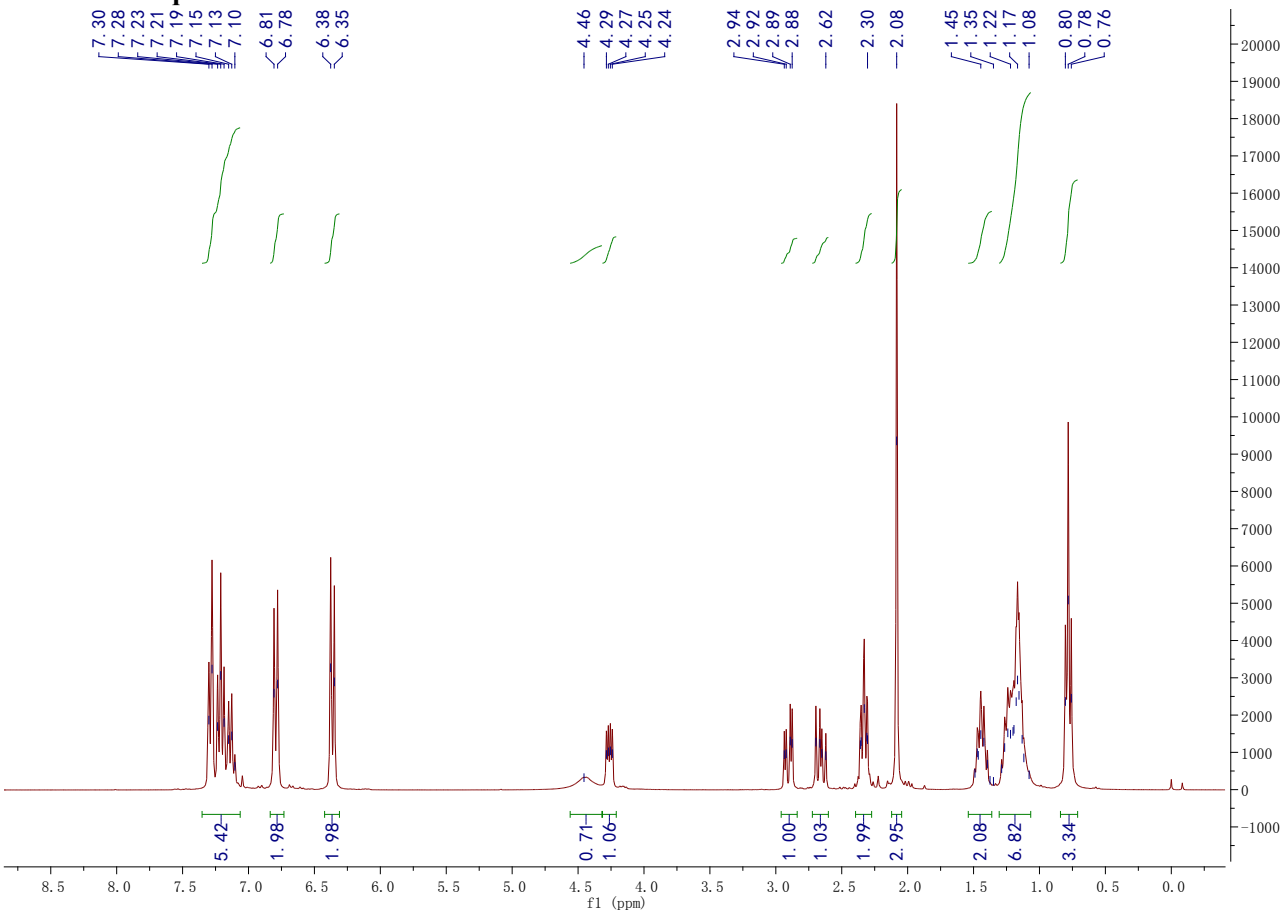
^{1}H NMR for **4p**



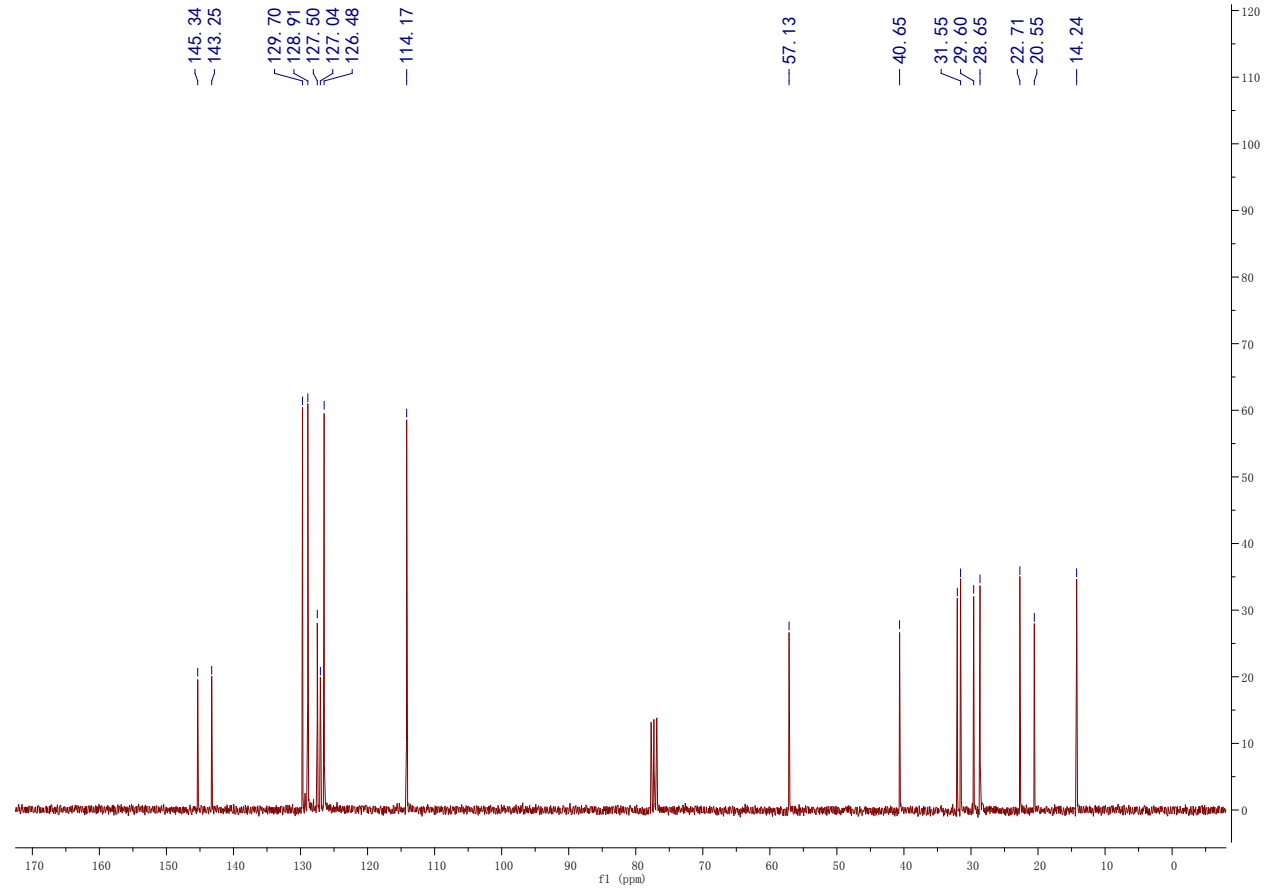
^{13}C NMR for **4p**



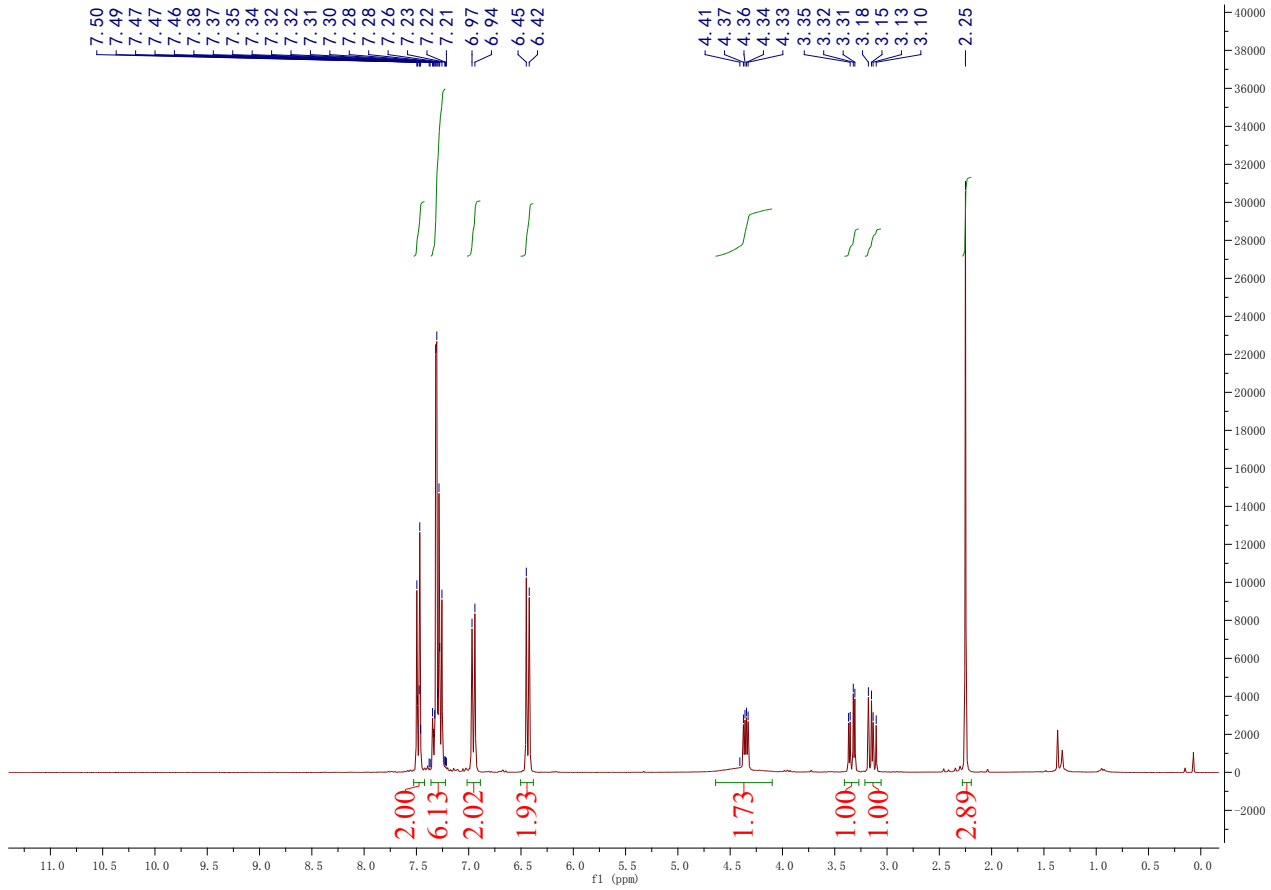
^{1}H NMR for **4q**



^{13}C NMR for **4q**



^{1}H NMR for **4r**



^{13}C NMR for **4r**