SUPPORTING INFORMATION

Title: Iodine-catalyzed sulfonylation of sulfonyl hydrazides with *tert*-amines: a green and efficient protocol for the synthesis of sulfonamides

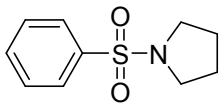
Author(s): Jinyang Chen,[a]Xiaoran Han,[a] Lan Mei, [a] Jinchuan Liu,[a],* Kui Du,[a] Tuanwu Cao,[a],* Qiang Li[b]

1. General Information

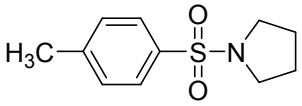
All reactions were carried out in anhydrous solvent using commercially available reagents that were purchased and used as received. Analytical thin layer chromatography (TLC) was performed on pre-coated 0.25 mm thick silica gel 60-F_{254} plates (Merck or Whatman PE SIL G/UV); visualized using UV light and by treatment with a $KMnO_4$, followed by heating. All compounds were purified by flash chromatography using silica gel 100-200 (Greagent G72651J) and gave spectroscopic data consistent with being ⩾95% the assigned structure. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer in CDCl3 at ambient temperature; chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference (δ_H = 7.26 ppm and δ_C = 77.16 ppm). IR spectra were recorded on an Agilent Technologies Cary 630 FT-IR (ATR) or Perkin-Elmer FT-IR Spectrum 100 (ATR) spectrometer; wavenumbers (ν) are given in cm^{-1}.

2. Experimental Procedure and characterization data of 3a-3w

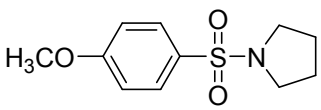
General procedure for the synthesis of compounds 3a: A mixture of 4-methoxybenzenesulfonohydrazide **1a** (0.3 mmol), 1-ethyl-pyrrolidine **2a** (0.3 mmol), I_2 (20 mol%), tert-butyl hydroperoxide (0.6 mmol) and H_2O (3.0 mL) was sealed in a 25 mL tube with a Teflon lined cap. The tube was then placed in an oil bath, stirred and heated at 80 °C for 8 h. After cooling to room temperature, the reaction was quenched with water (20 mL) and the reaction mixture was extracted with ethyl acetate (25 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified over a column of silica gel (eluent: hexane/ethyl acetate = 8:1) to afford the desired product **3a**.



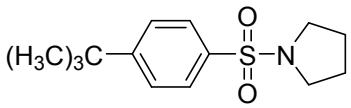
1-(phenylsulfonyl)pyrrolidine 3a **(3a)**[1]: (Yellow oil, 50.7 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.61-7.52 (m, 3H), 3.26-3.22 (m, 4H), 1.76-1.72 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.70, 132.67, 129.06, 127.41, 47.96, 25.18.



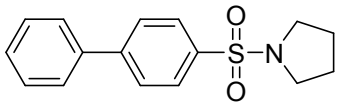
1-tosylpyrrolidine **(3b)** [1]**:** (White solid, 55.4 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 4.0 Hz, 4H), 2.34 (s, 3H), 1.66 (d, *J* = 8.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.30, 133.76, 129.58, 127.46, 47.88, 25.11, 21.43.



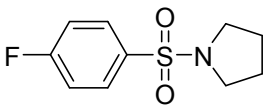
***1-((4-methoxyphenyl)sulfonyl)pyrrolidine* (3c)** [1]**:** (White solid, 61.5 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 3H), 3.12 (s, 4H), 1.65 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.77, 129.43, 128.19, 114.08, 55.52, 47.82, 25.01.



1-((4-(tert-butyl)phenyl)sulfonyl)pyrrolidine (3d) [2] **:** (White solid, 65.8 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 4.0 Hz, 2H), 7.53 (d, *J* = 4.0 Hz, 2H), 3.25 (s, 4H), 1.76 (s, 4H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$)δ 156.12, 133.74, 127.32, 125.88, 47.83, 35.03, 31.02, 25.12.

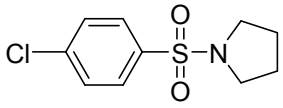


***N-(4-(trifluoromethyl)benzyl)benzothioamide* (3e)** [3]: (White solid, 67.2 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 4.0 Hz, 2H), 7.30 (t, *J* = 4.0 Hz, 1H), 3.18 (t, *J* = 4.0 Hz, 4H), 1.66 (t, *J* = 4.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.27, 139.13, 135.40, 128.97, 128.37, 127.94, 127.49, 127.18, 47.91, 25.14.

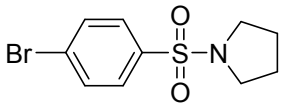


***1-((4-fluorophenyl)sulfonyl)pyrrolidine* (3f)**[3]**:** (White solid, 49.5 mg, 72%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d,d, J_1= 4.0 Hz, J_2= 8.0 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 2H), 3.25 (t, *J* =

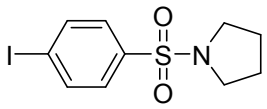
4.0 Hz, 4H), 1.79-1.76 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.28, 163.75, 133.07, 133.04, 130.09, 130.00, 116.31, 116.09, 47.91, 25.16.



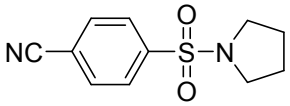
1-((4-chlorophenyl)sulfonyl)pyrrolidine **(3g)**[4]**:** (Brown solid, 55.3 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 4.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 3.25-3.22 (m, 4H), 1.78 (d, *J* = 4.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.94, 135.42, 129.27, 128.82, 47.92, 25.18.



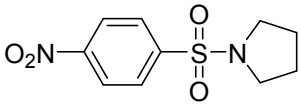
1-((4-bromophenyl)sulfonyl)pyrrolidine **(3h)** [4]**:** (White solid, 65.3 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.69-7.64 (m, 4H), 3.23-3.19 (m, 4H), 1.76-1.74 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.95, 132.25, 128.92, 127.45, 47.92, 25.18.



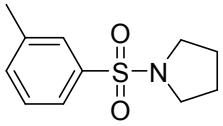
1-((4-iodophenyl)sulfonyl)pyrrolidine **(3i)**[3]**:** (Yellow solid, 78.9 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 12.0 Hz, 4H), 1.78 (d, *J* = 4.0 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.23, 136.59, 128.82, 99.97, 47.94, 25.21.



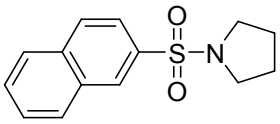
4-(pyrrolidin-1-ylsulfonyl)benzonitrile **(3j)** [3]**:** (White solid, 49.6 mg, 70%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 3.20 (t, *J* = 8.0 Hz, 4H), 3.22-3.19 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.13, 132.78, 127.76, 117.25, 115.99, 47.85, 25.11.



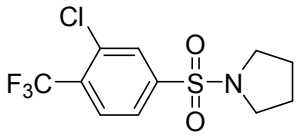
1-((4-nitrophenyl)sulfonyl)pyrrolidine **(3k)** [3] (White solid, 50.0 mg, 65%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 12.0 Hz, 2H), 8.04(d, *J* = 8.0 Hz, 2H), 3.31 (d, *J* = 4.0 Hz, 4H), 1.83 (t, *J* = 4.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.06, 143.07, 128.55, 124.36, 48.09, 25.38.



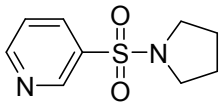
1-(m-tolylsulfonyl)pyrrolidine **(3l)** [3]**:** (White solid, 52.7 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.32 (s, 2H), 3.15 (s, 4H), 2.34 (s, 3H), 2.35(s, 3H), 1.66 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.15, 136.56, 133.42, 128.88, 127.80, 124.59, 47.92, 25.18, 21.37.



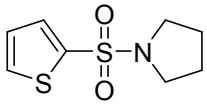
1-(naphthalen-2-ylsulfonyl)pyrrolidine **(3m)** [3]**:** (White solid, 65.1 mg, 83%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.52-7.45 (m, 2H), 3.18 (s, 4H), 1.59 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.66, 133.82, 132.04, 129.16, 129.06, 128.56, 128.54, 127.79, 127.40, 122.80, 47.93, 25.12.



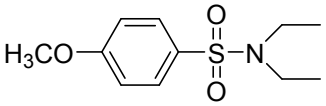
1-((3-chloro-4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (3n) [3]***:*** (Yellow solid, 74.4 mg, 79%). **NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 3.19 (t, *J* = 6.0 Hz, 4H), 1.76 (t, *J* = 6.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.10, 136.74, 132.53, 131.60, 129.59, 129.27, 126.73, 126.68, 126.63, 126.57, 123.49, 120.77, 77.47, 77.15, 76.83, 48.10, 25.38.



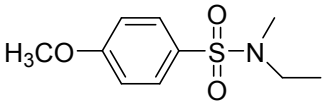
3-(pyrrolidin-1-ylsulfonyl)pyridine **(3o)** [3]: (Yellow solid, 47.8 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.75 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.8 Hz, 1H), 3.20 (t, *J* = 4.0 Hz, 4H), 1.72 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.03, 147.83, 134.89, 133.57, 123.75, 47.81, 25.11.



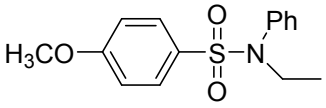
1-(thiophen-2-ylsulfonyl)pyrrolidine (3p): [3] (Yellow solid, 47.6 mg, 73%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 4.0 Hz, 1H), 7.49 (d, *J* = 4.0 Hz, 1H), 7.07 (t, *J* = 4.0 Hz, 1H), 3.20 (t, *J* = 4.0 Hz, 4H), 1.68 (t, *J* = 8.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.58, 131.97, 131.66, 127.45, 48.14, 25.19.



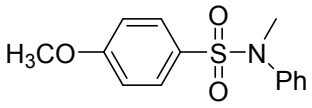
N,N-diethyl-4-methoxybenzenesulfonamide (3q) [5]***:*** (Yellow oil, 61.3 mg, 84%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 3H), 3.21 (d,d, J_1= 8.0 Hz, J_2= 8.0 Hz, 4H), 1.12 (t, *J* = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.54, 132.03, 129.04, 114.10, 55.55, 41.92, 14.10.



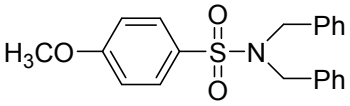
4-methoxy-N-methyl-N-propylbenzenesulfonamide (3r) [3]**:** (Yellow oil, 55.7 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 2.88 (t, *J* = 4.0 Hz, 2H), 2.63(s, 3H), 1.49 (d, d, J_1= 8.0 Hz, J_2= 16.0 Hz 2H), 0.86 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.71, 129.33, 129.09, 114.12, 55.55, 51.69, 34.49, 20.80, 11.00.



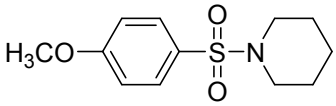
N-ethyl-4-methoxy-N-phenylbenzenesulfonamide (3s): [5] (Yellow oil, 65.6 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 3H), 3.59 (d, d, J_1= 8.0 Hz, J_2= 16.0 Hz, 2H), 1.06 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.90, 139.08, 130.27, 129.88, 129.09, 129.05, 127.92, 113.98, 55.68, 45.54, 14.12.



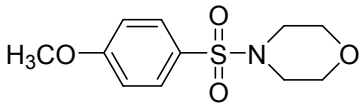
4-methoxy-N-methyl-N-phenylbenzenesulfonamide (3t) [5]**:** (Yellow oil, 68.2 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.31-7.23 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 3H), 3.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.09, 141.83, 130.09, 128.93, 128.29, 127.34, 126.76, 113.97, 55.68, 38.15.



N,N-dibenzyl-4-methoxybenzenesulfonamide (3u)[3]: (Yellow solid, 86.0 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.38-7.30 (m, 3H), 7.21 (s, 3H), 7.06 (s, 4H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.03 (s, 4H), 3.87 (S, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.86, 135.82, 132.44, 129.41, 128.65, 128.49, 127.69, 114.30, 55.72, 50.54.

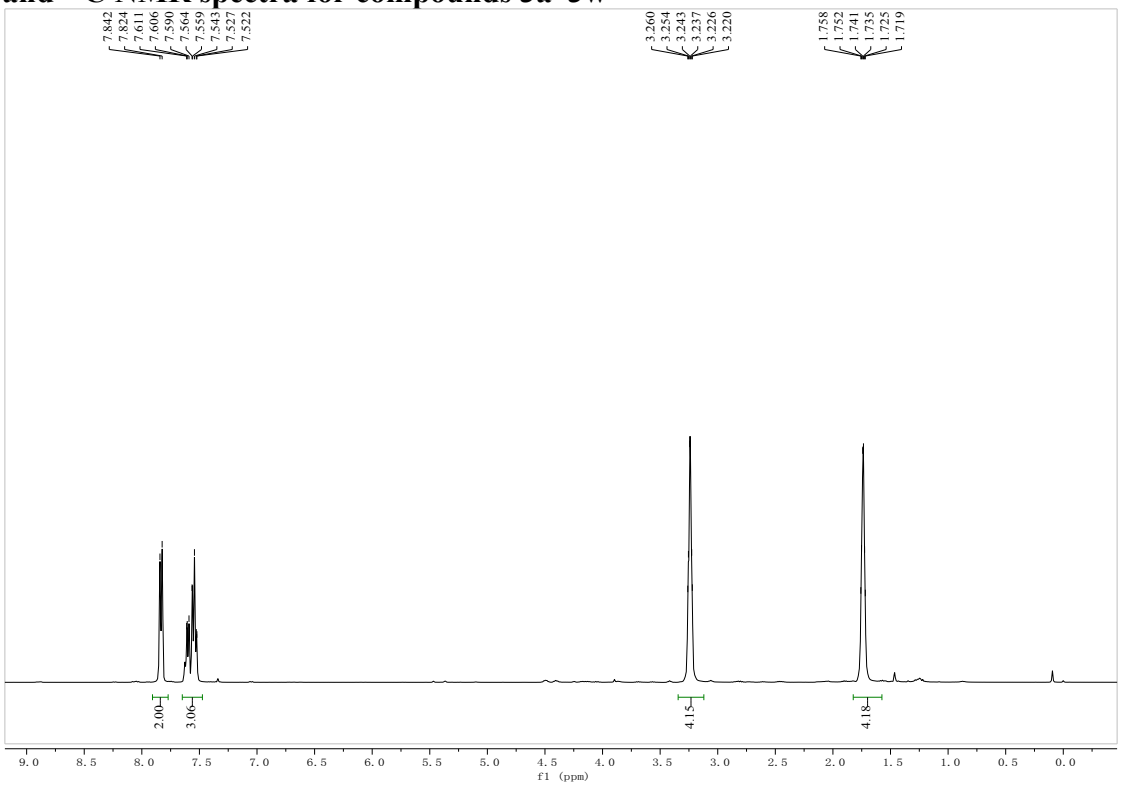


1-((4-methoxyphenyl)sulfonyl)piperidine (3v)[3]: (Yellow oil, 64.3 mg, 84%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.77 (s, 3H), 2.85 (t, *J* = 4.0 Hz, 4H), 1.53 (t, *J* = 4.0 Hz, 4H), 1.31 (d, *J* = 4.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.79, 129.63, 127.63, 114.05, 55.56, 46.87, 25.05, 23.40.

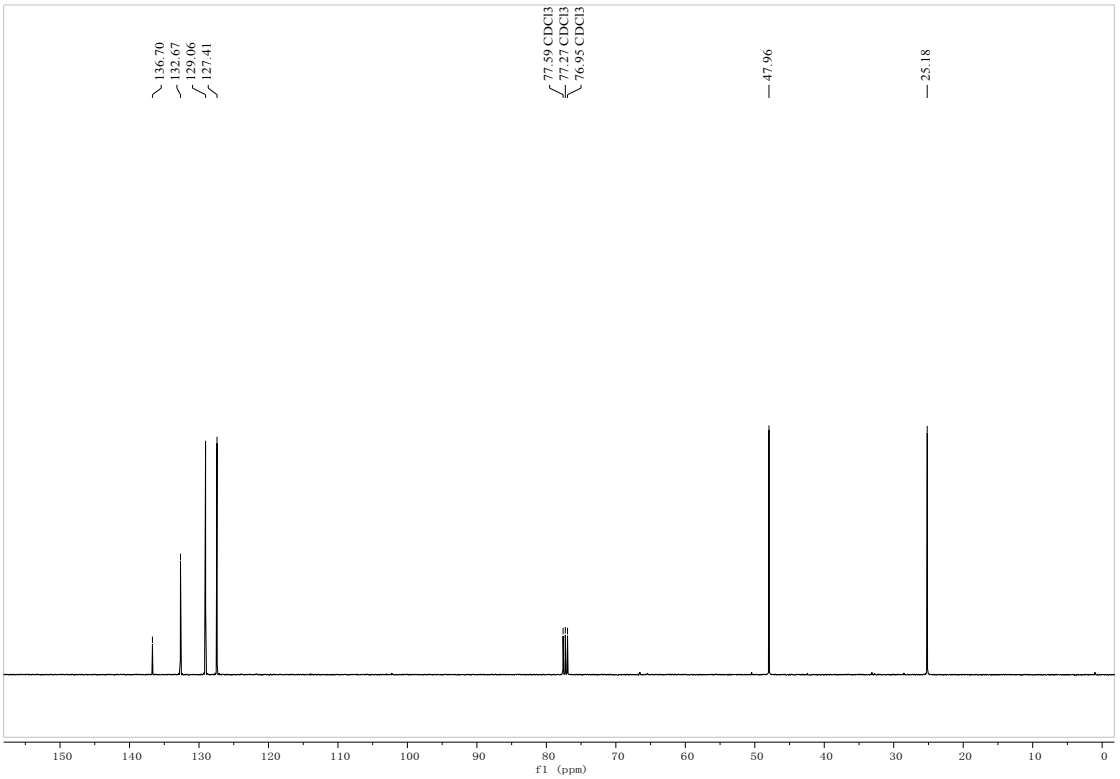


4-((4-methoxyphenyl)sulfonyl)morpholine (3w)[3]: (Yellow oil, 64.8 mg, 84%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 3H), 3.64 (s, 4H), 2.87 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.16, 129.90, 126.35, 114.25, 65.95, 55.61, 45.94.

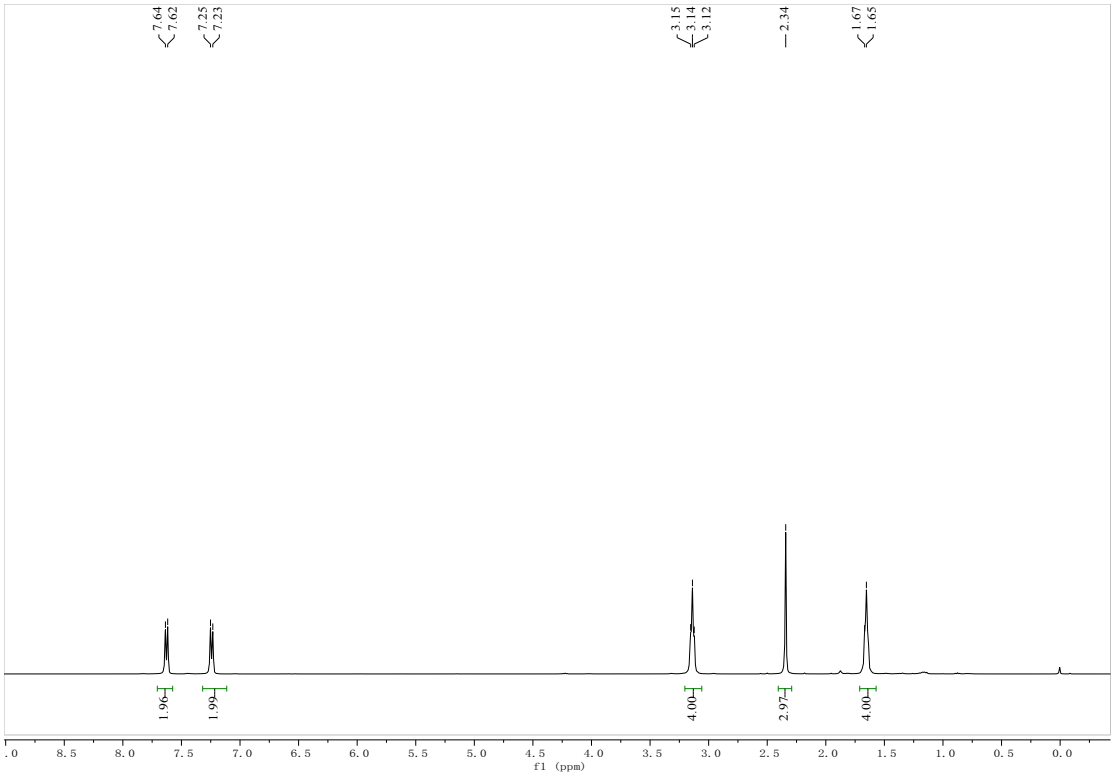
^{1}H and ^{13}C NMR spectra for compounds 3a–3w



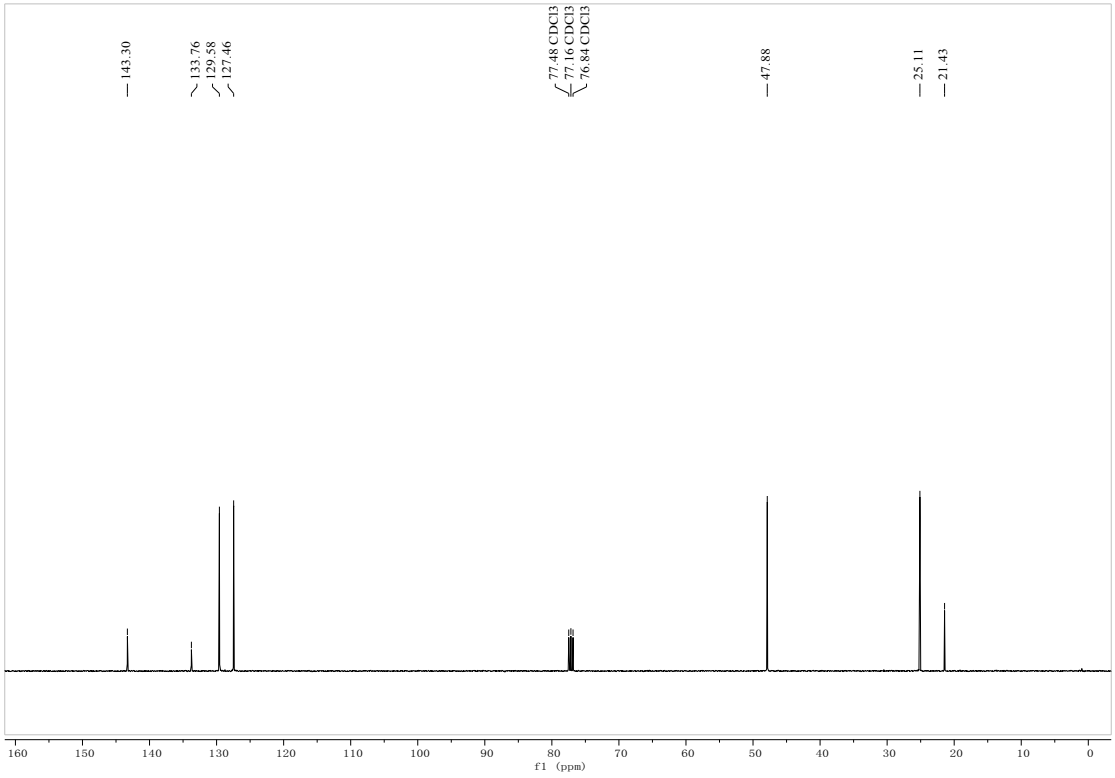
^{1} H NMR of compound **3a** in $CDCl_3$



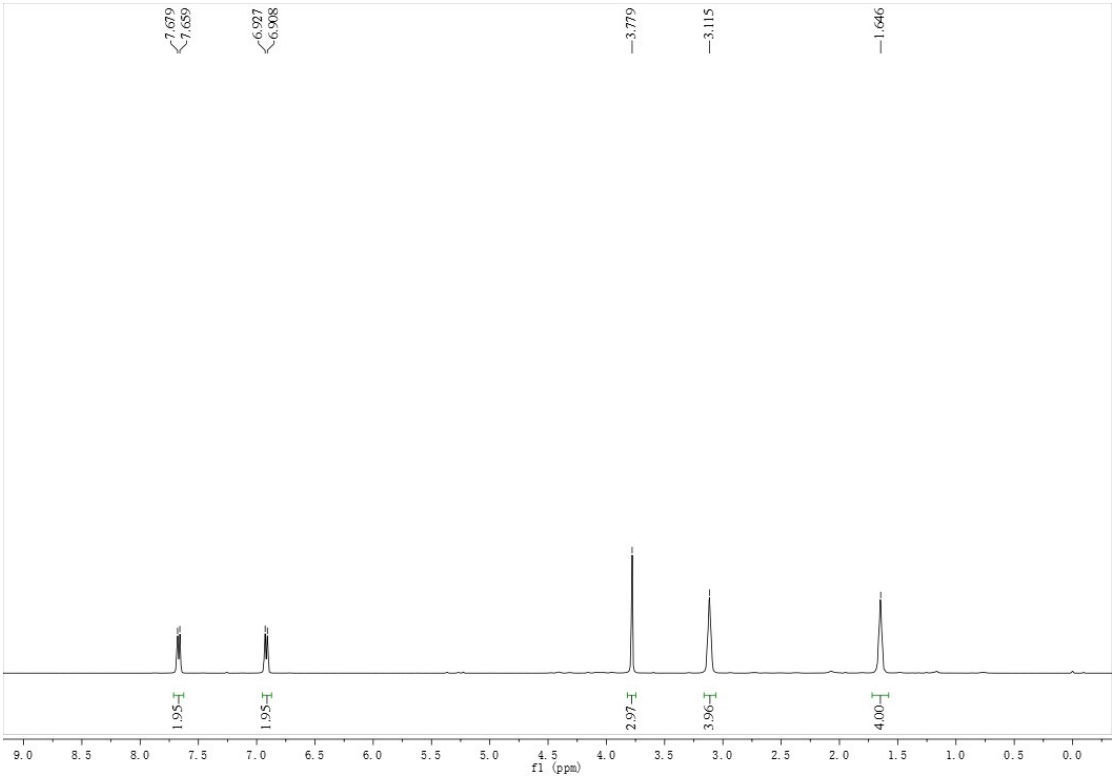
^{13} C NMR of compound **3a** in $CDCl_3$



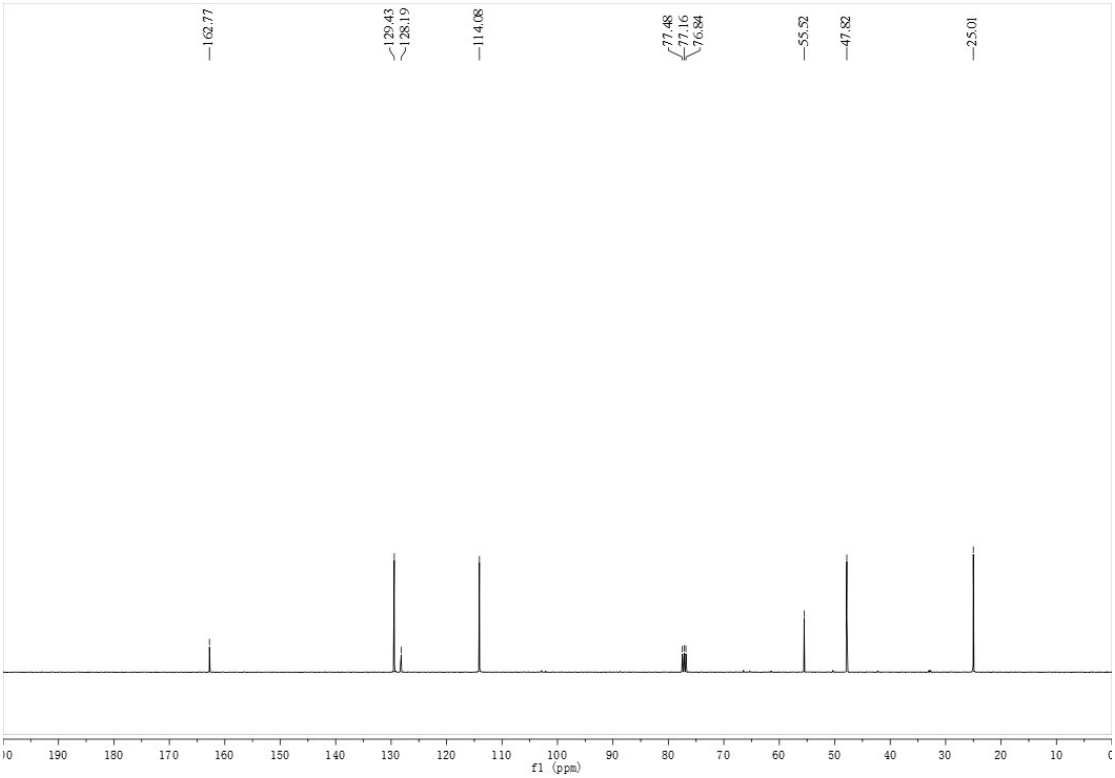
^{1} H NMR of compound **3b** in $CDCl_3$



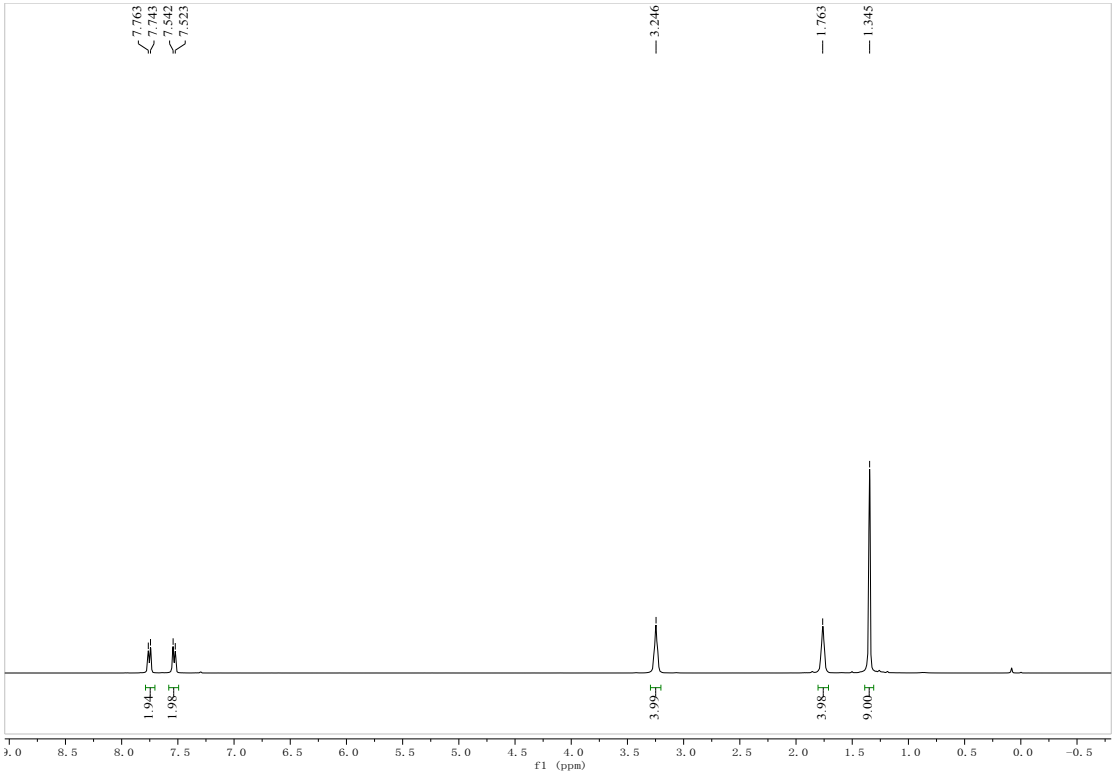
^{13} C NMR of compound **3b** in $CDCl_3$



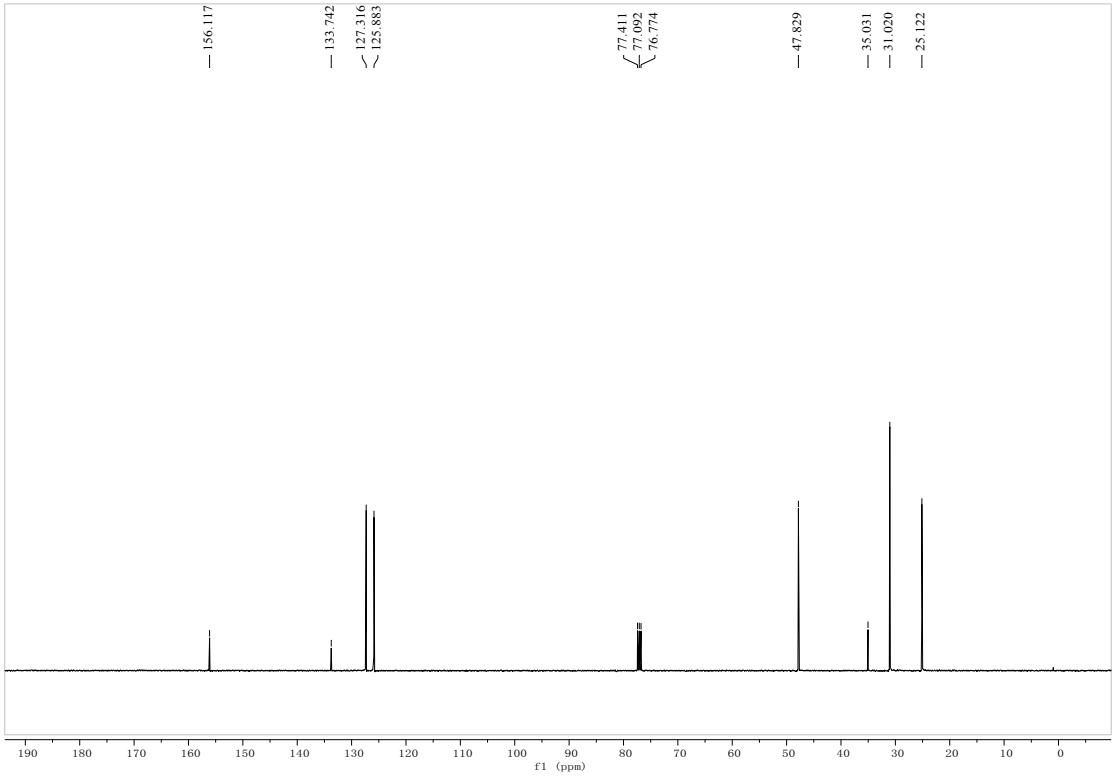
^{1} H NMR of compound **3c** in $CDCl_3$



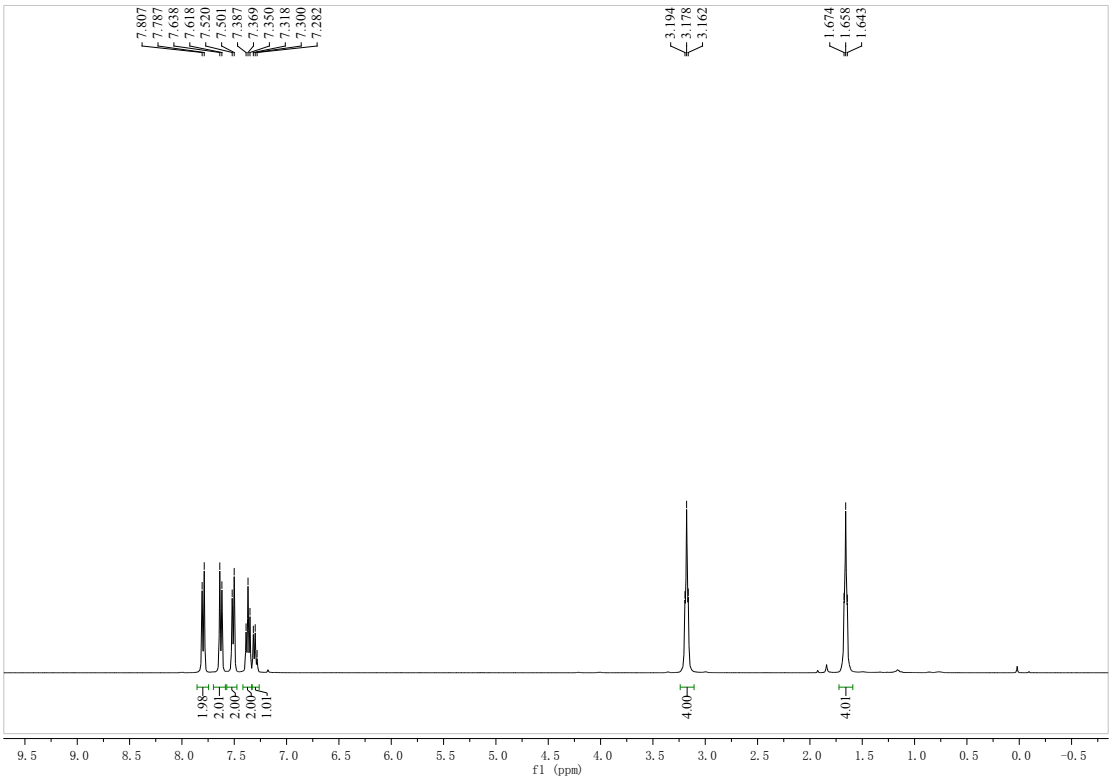
^{13} C NMR of compound **3c** in $CDCl_3$



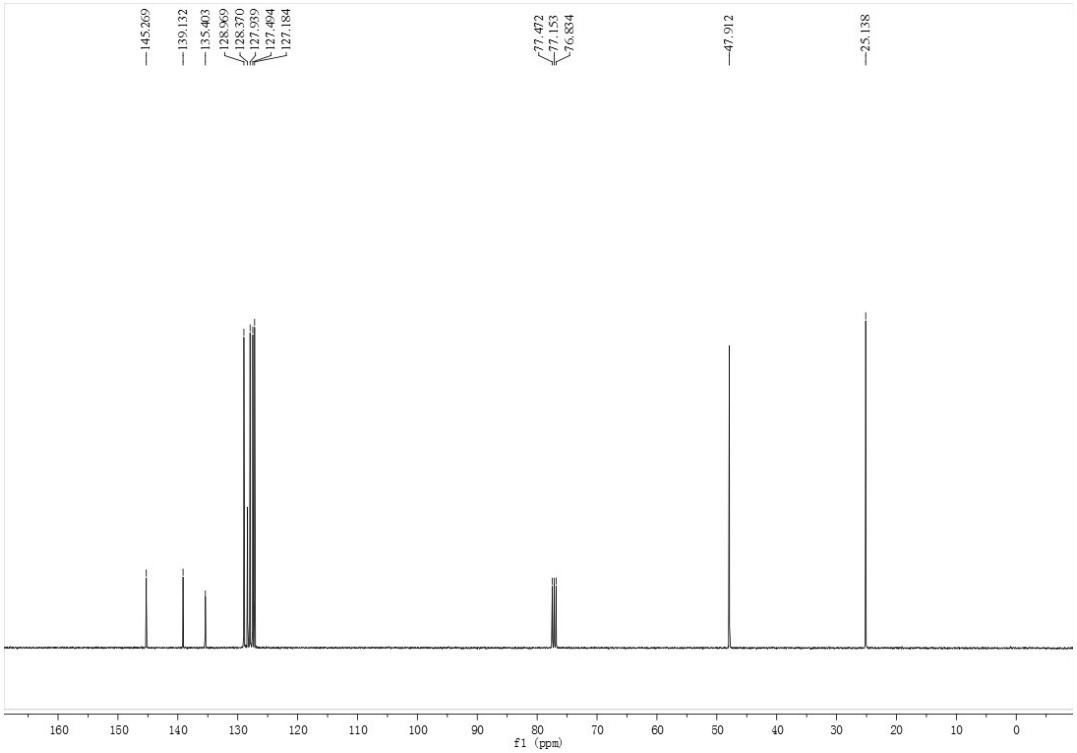
^{1} H NMR of compound **3d** in $CDCl_3$



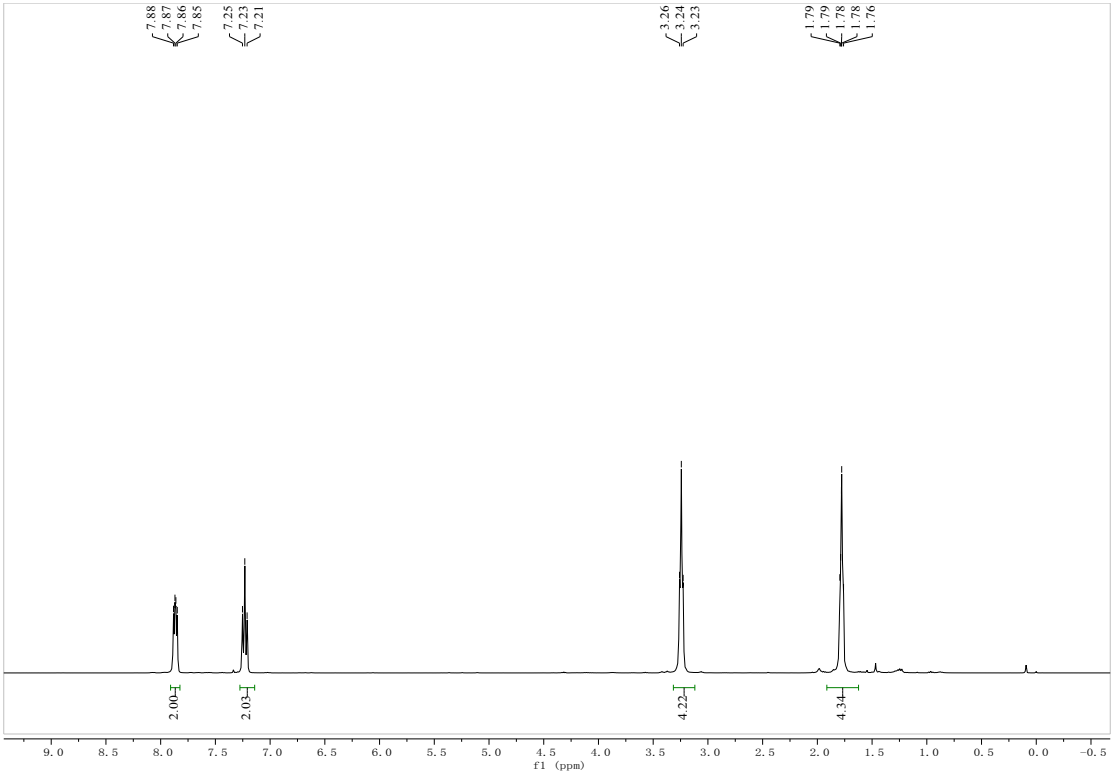
^{13} C NMR of compound **3d** in $CDCl_3$



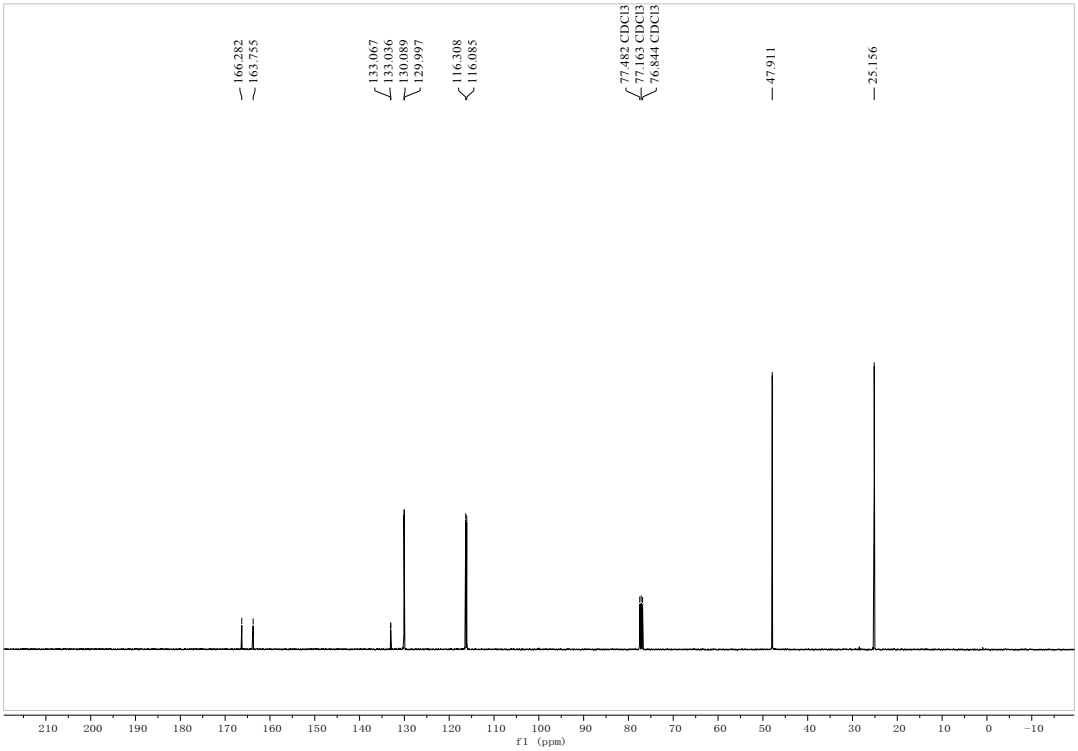
^{1} H NMR of compound **3e** in $CDCl_3$



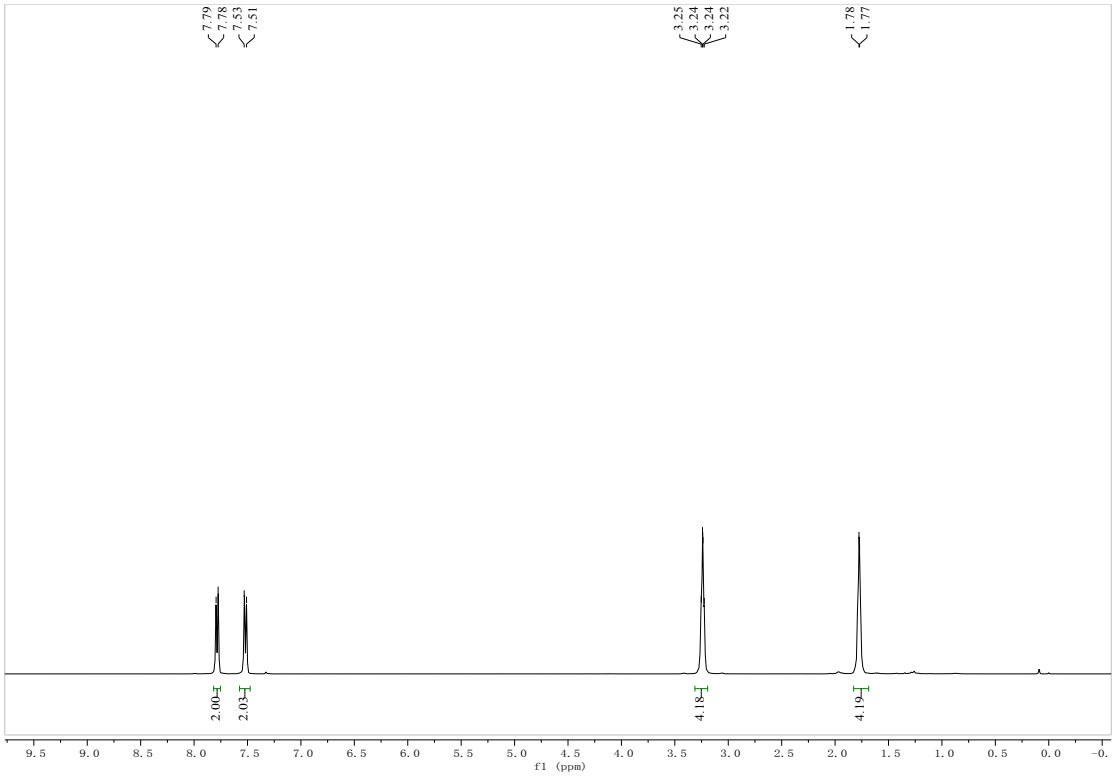
^{13} C NMR of compound **3e** in $CDCl_3$



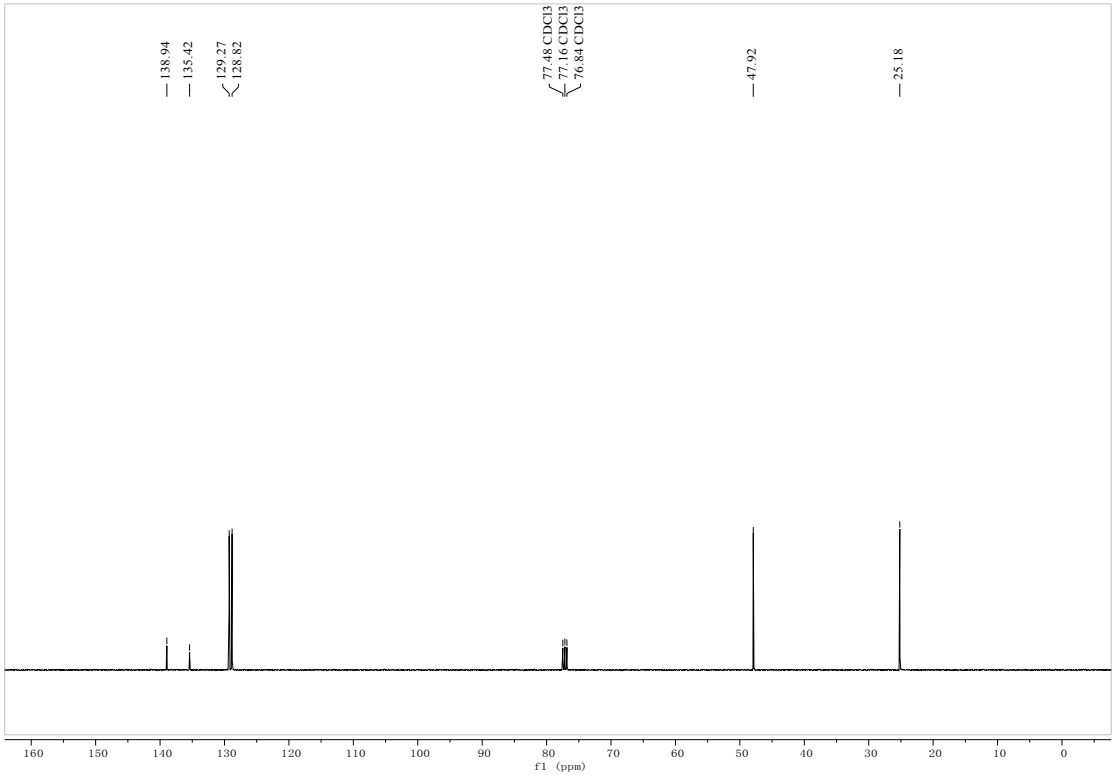
[1] H NMR of compound **3f** in $CDCl_3$



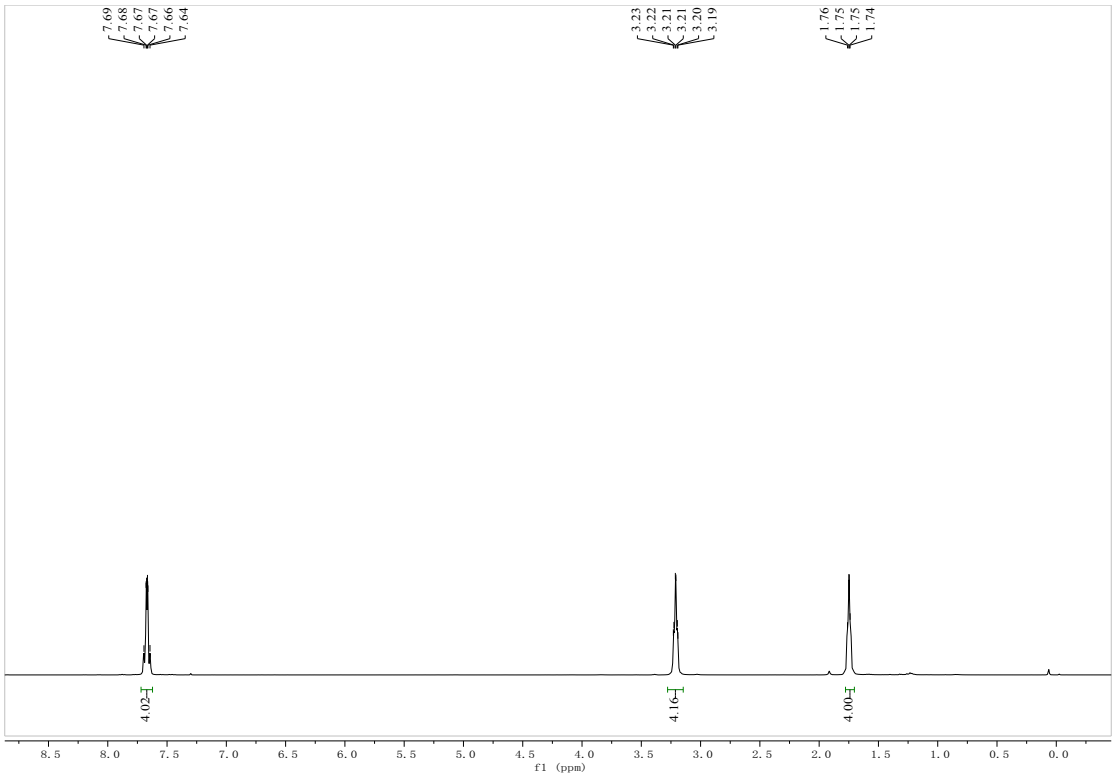
[13] C NMR of compound **3f** in $CDCl_3$



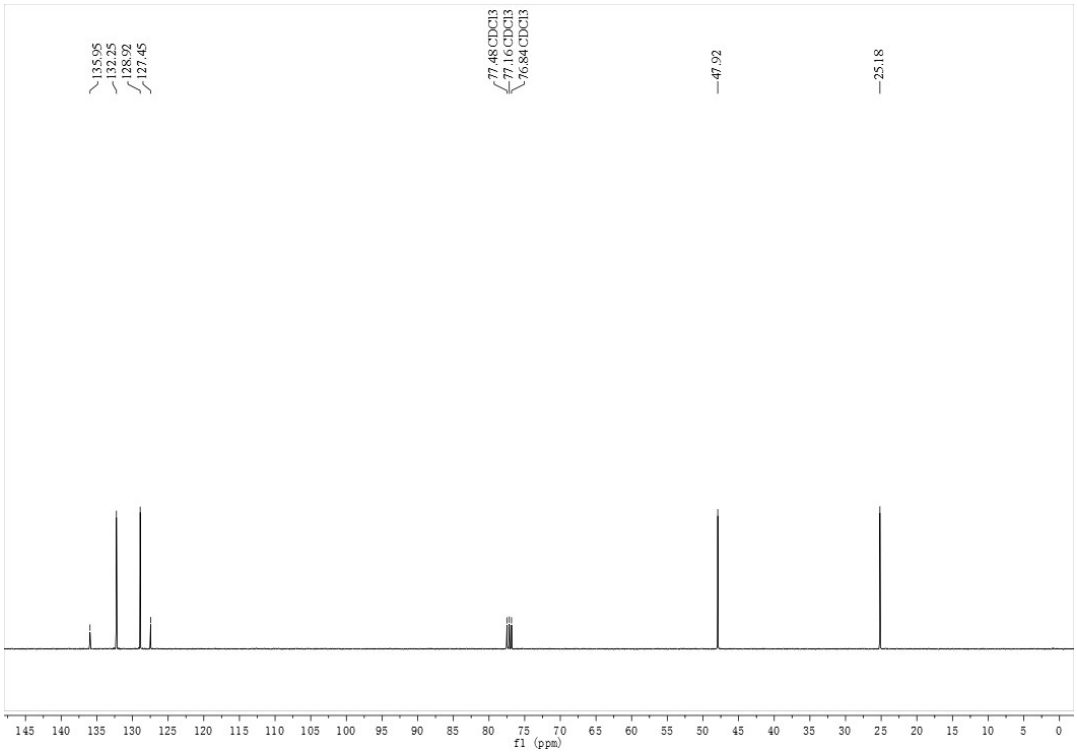
^{1} H NMR of compound **3g** in $CDCl_3$



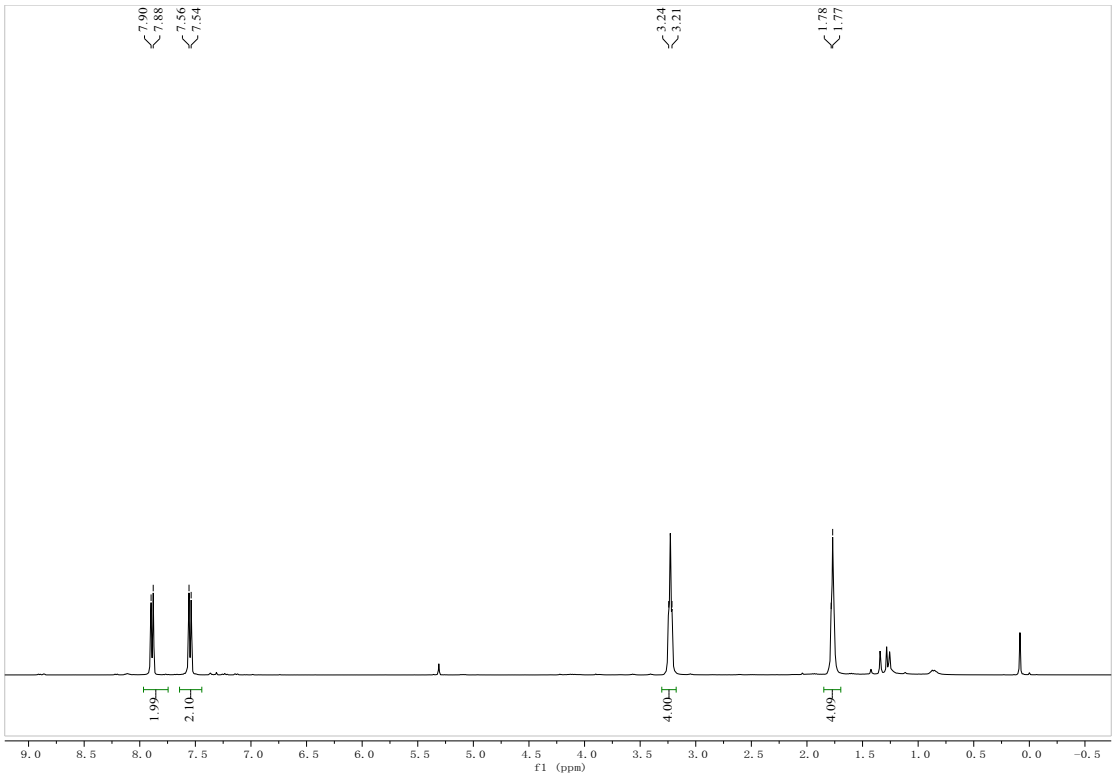
^{13} C NMR of compound **3g** in $CDCl_3$



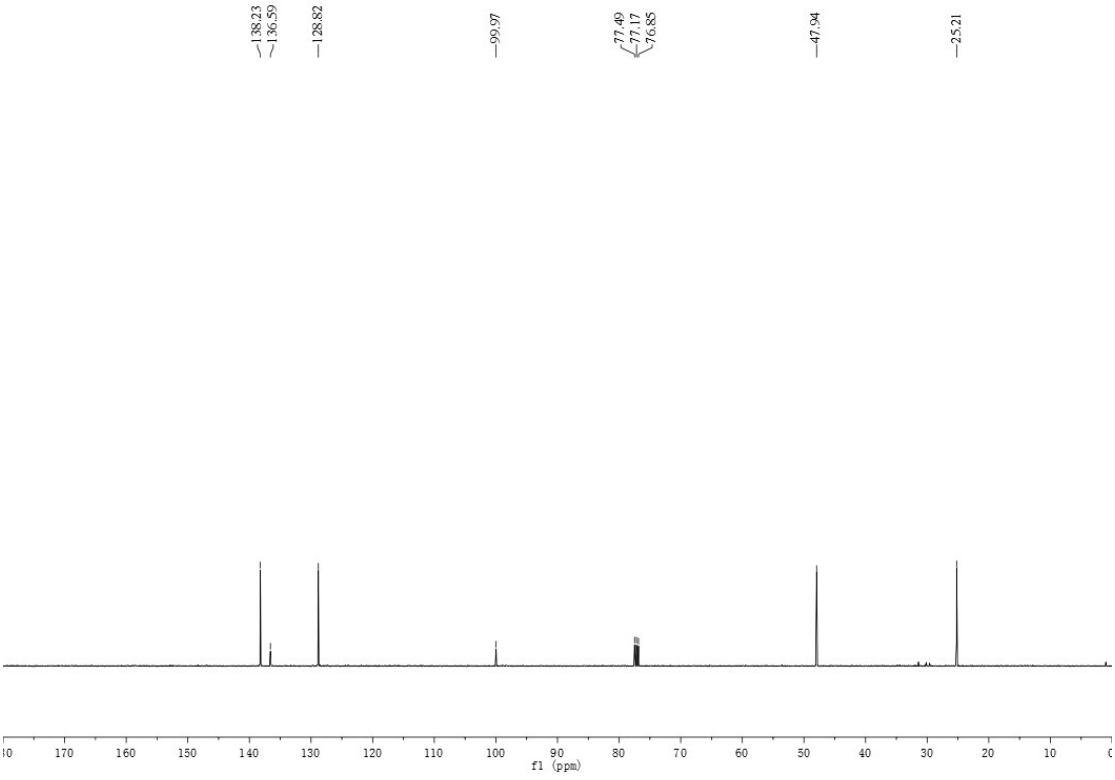
^{1} H NMR of compound **3h** in $CDCl_3$



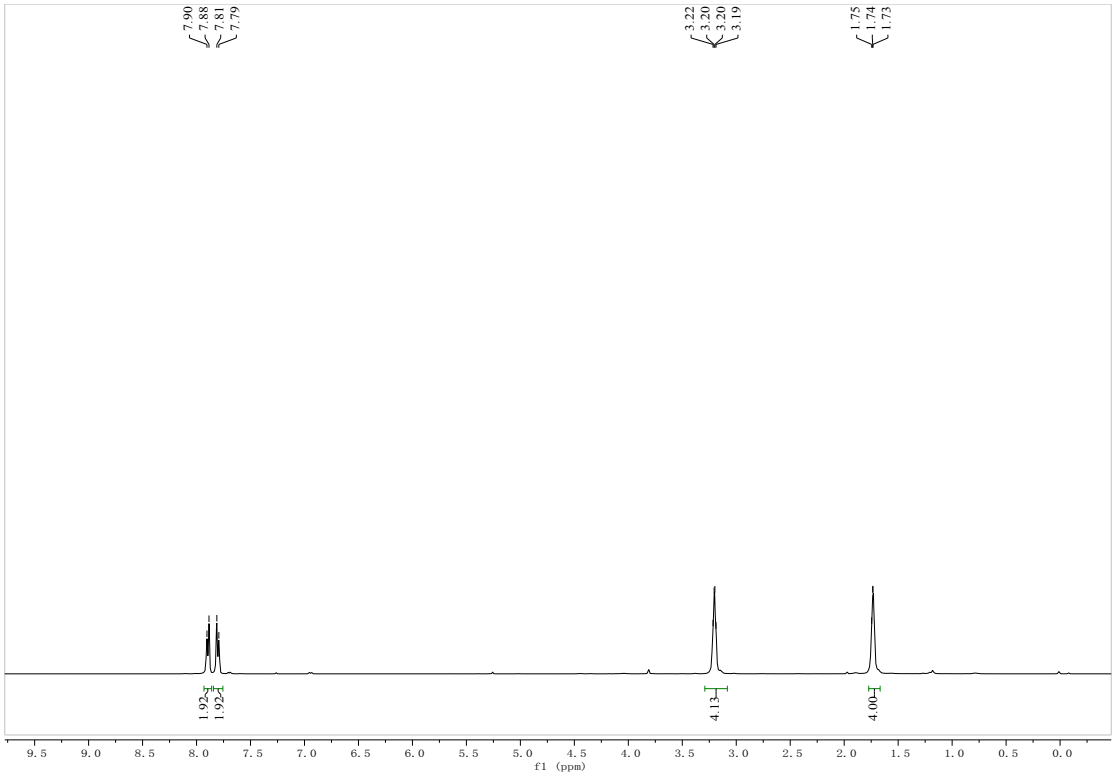
^{13} C NMR of compound **3h** in $CDCl_3$



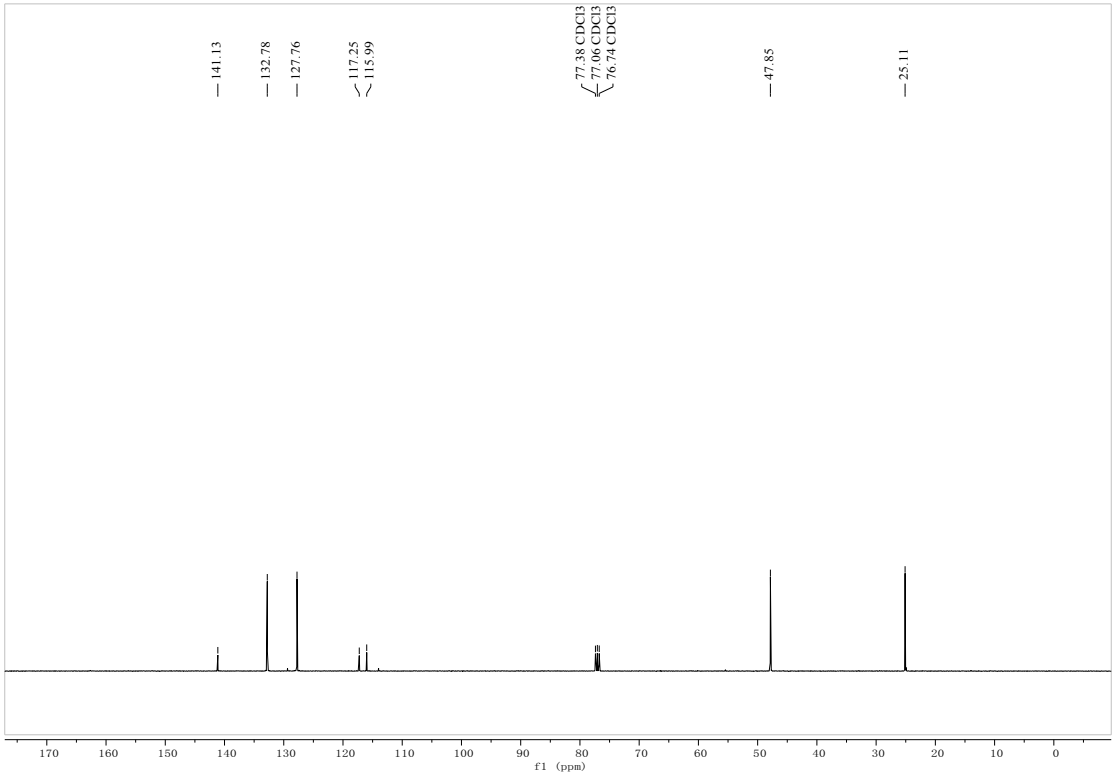
^{1} H NMR of compound **3i** in $CDCl_3$



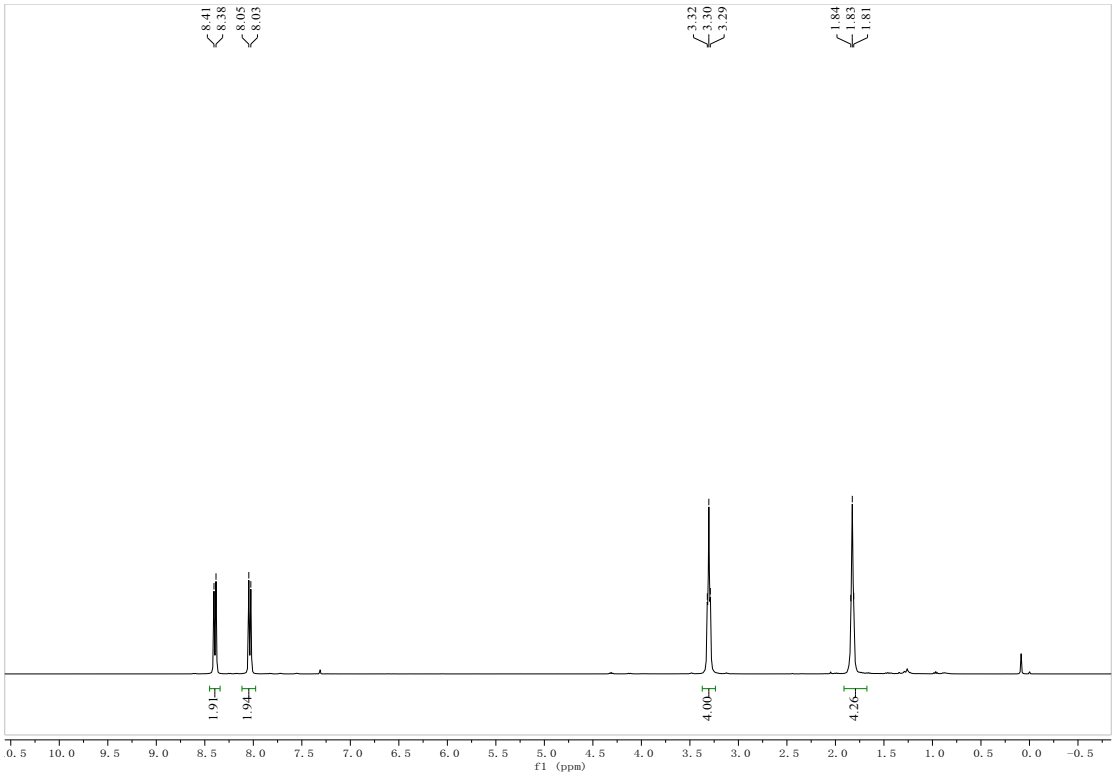
^{13} C NMR of compound **3i** in $CDCl_3$



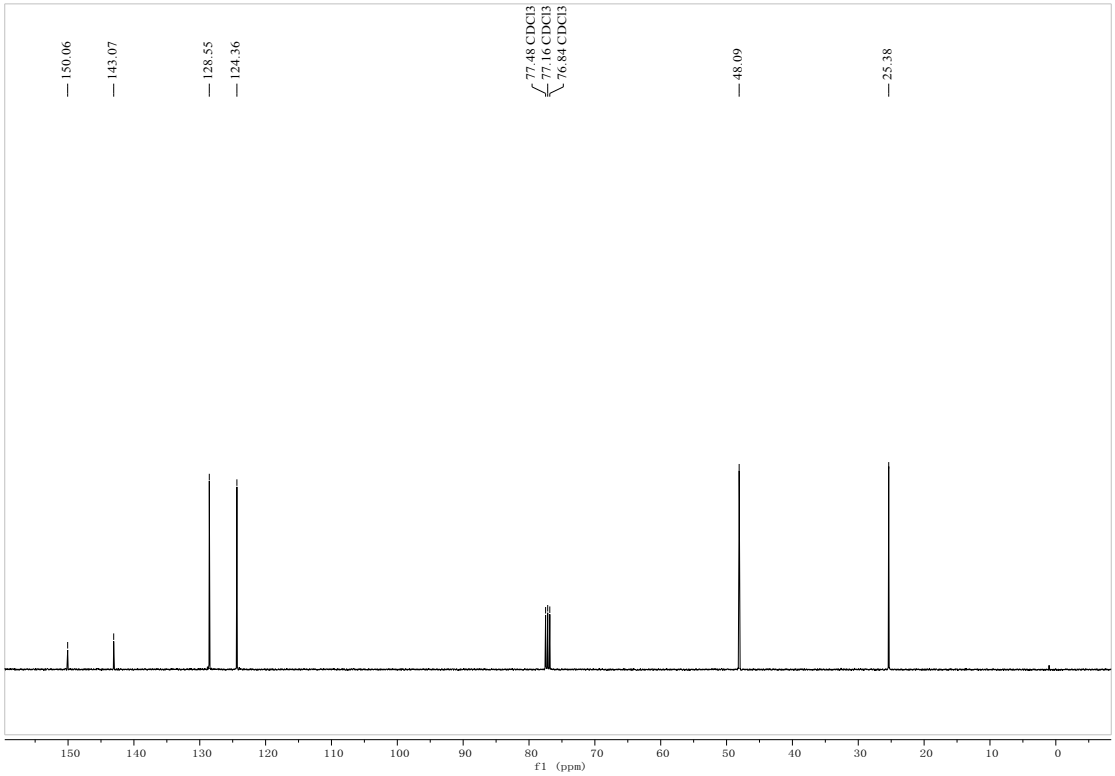
^{1} H NMR of compound **3j** in $CDCl_3$



^{13} C NMR of compound **3j** in $CDCl_3$



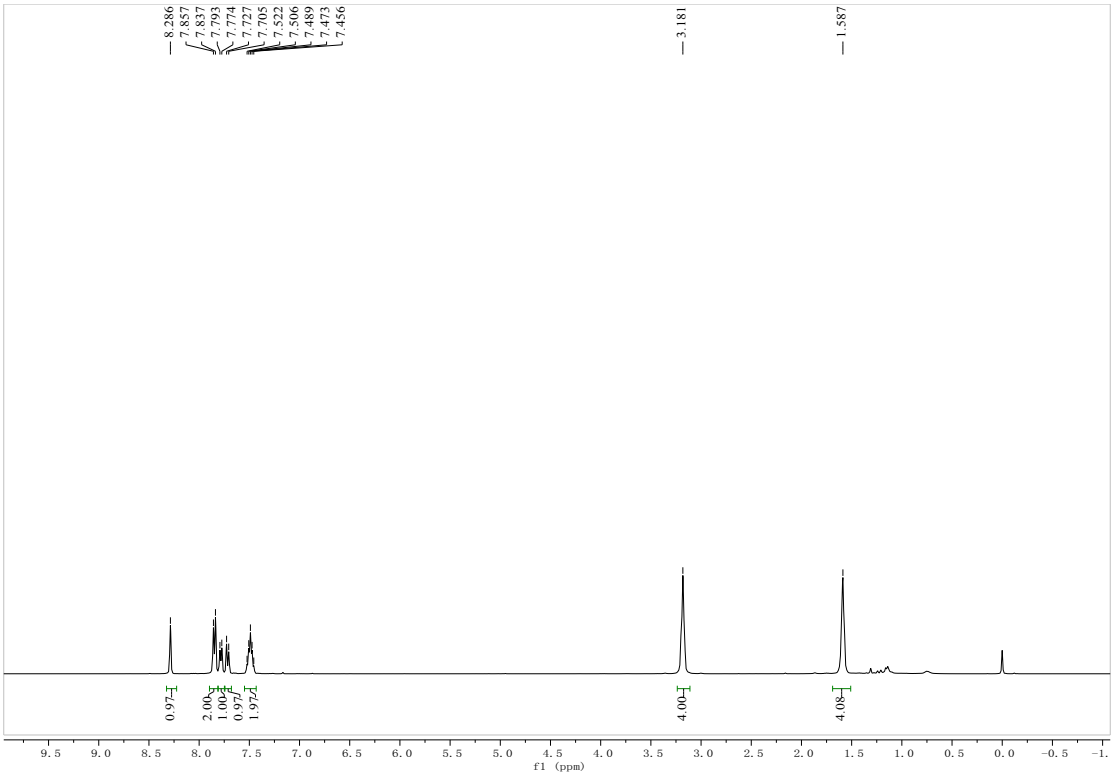
^{1} H NMR of compound **3k** in $CDCl_3$



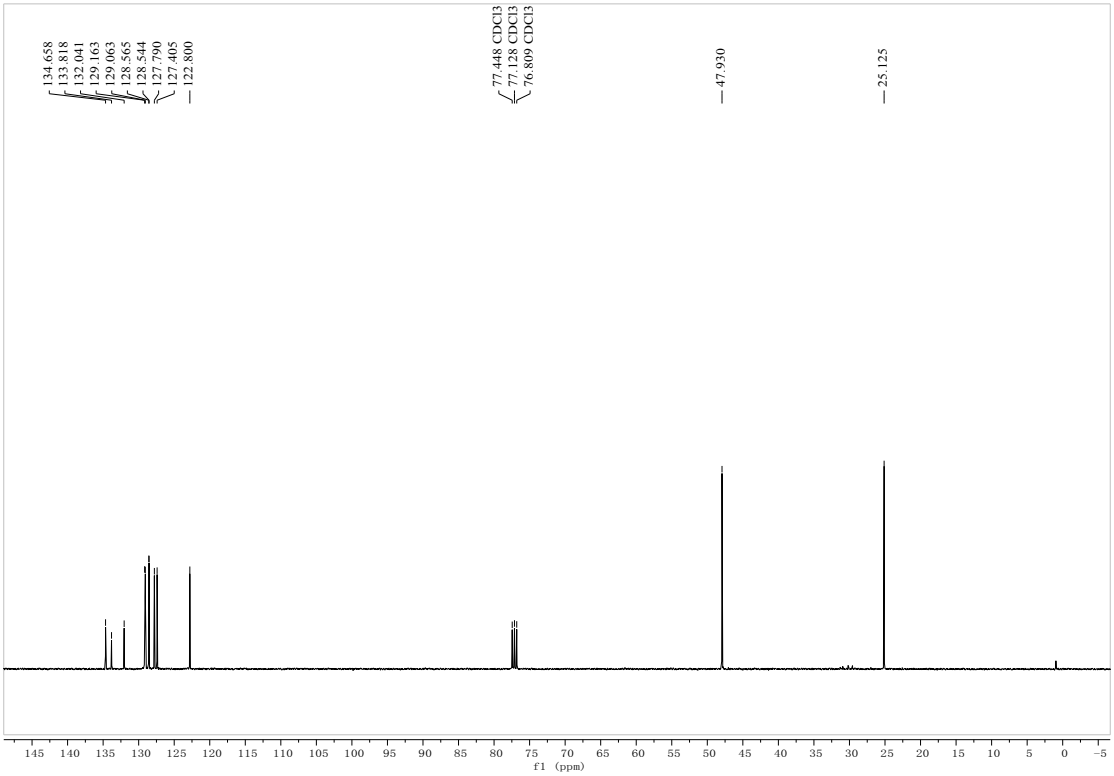
^{13} C NMR of compound **3k** in $CDCl_3$

^{1} H NMR of compound **3l** in $CDCl_3$

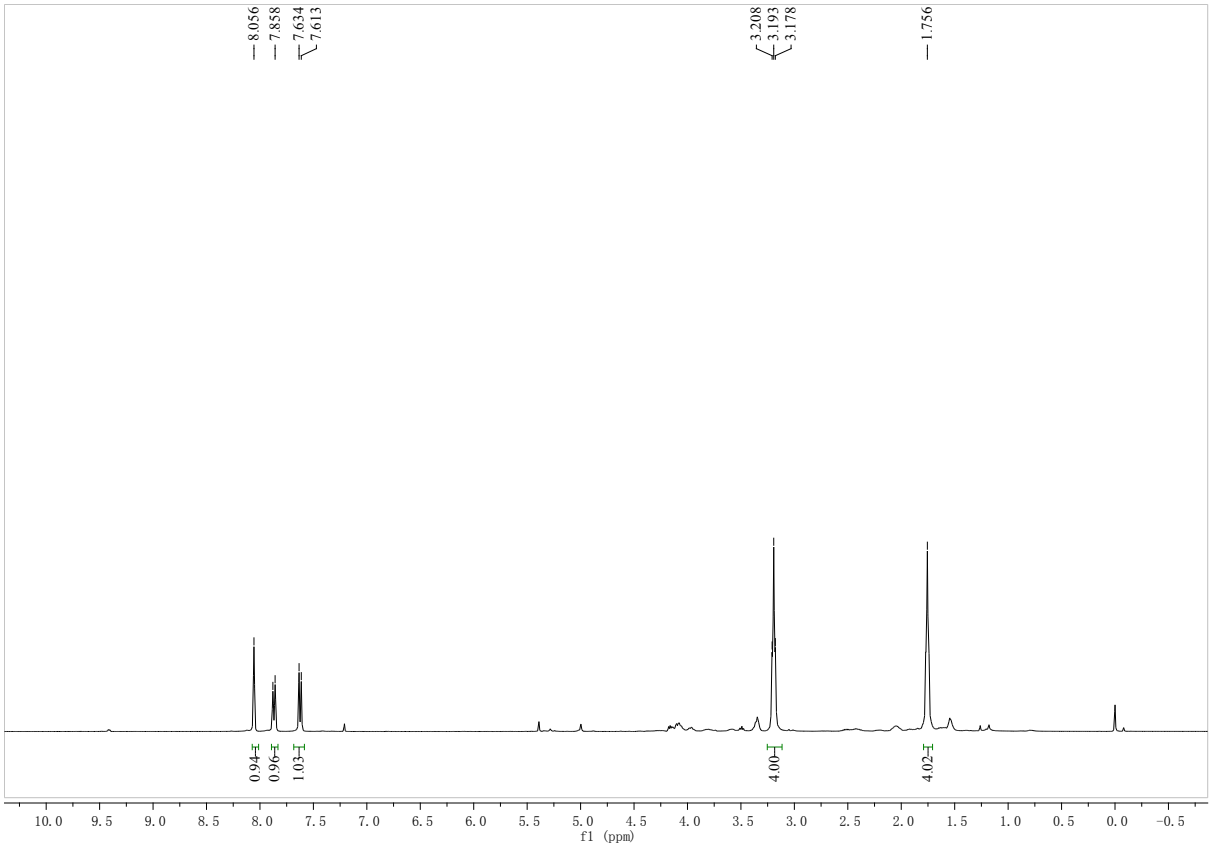
^{13} C NMR of compound **3l** in $CDCl_3$



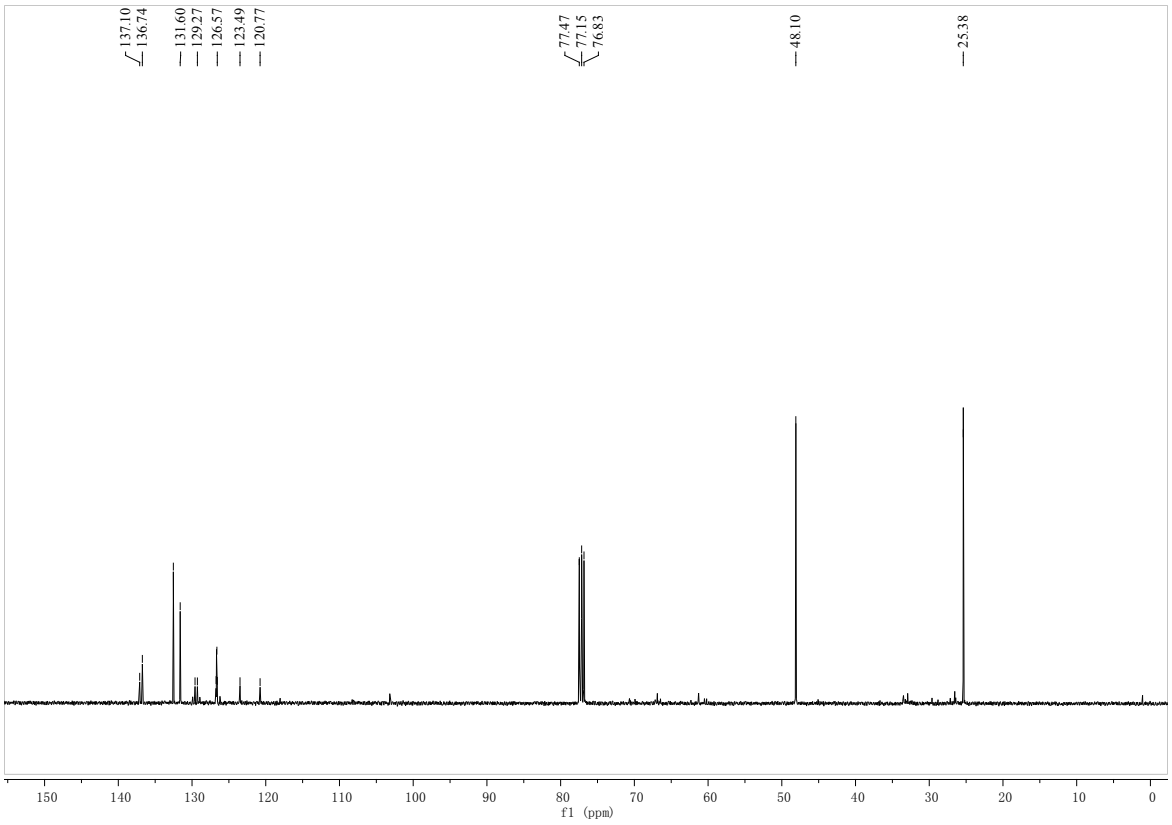
^{1} H NMR of compound **3m** in $CDCl_3$



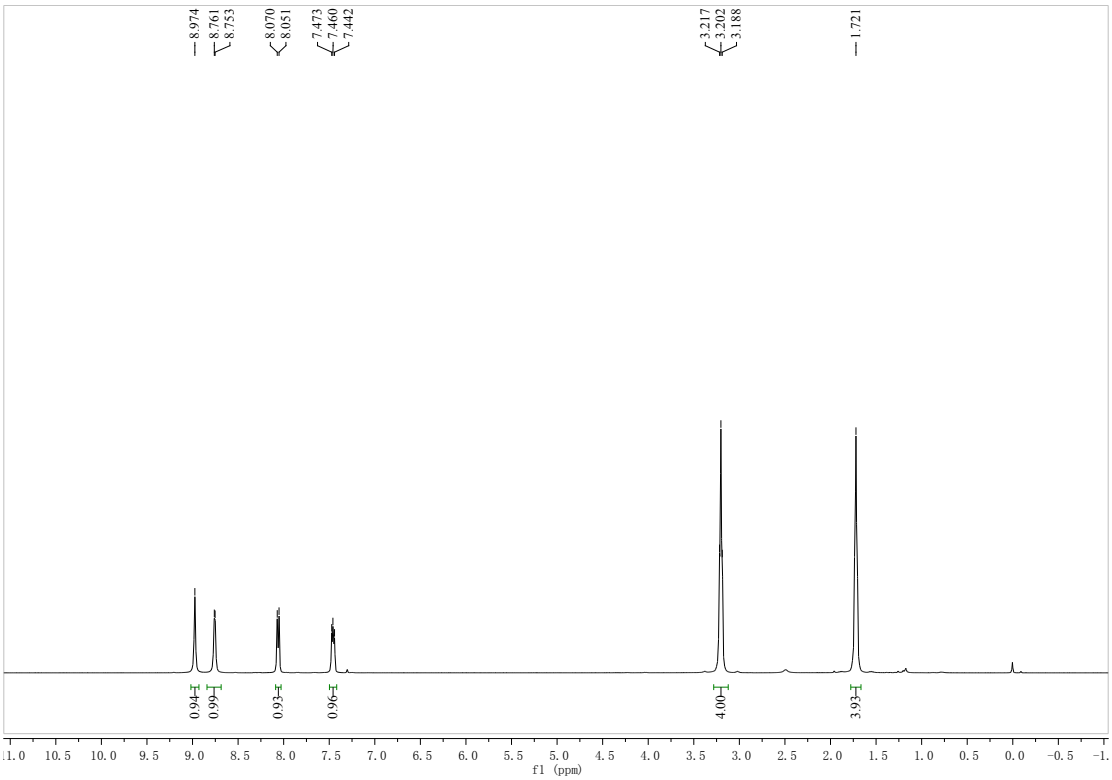
^{13} C NMR of compound **3m** in $CDCl_3$



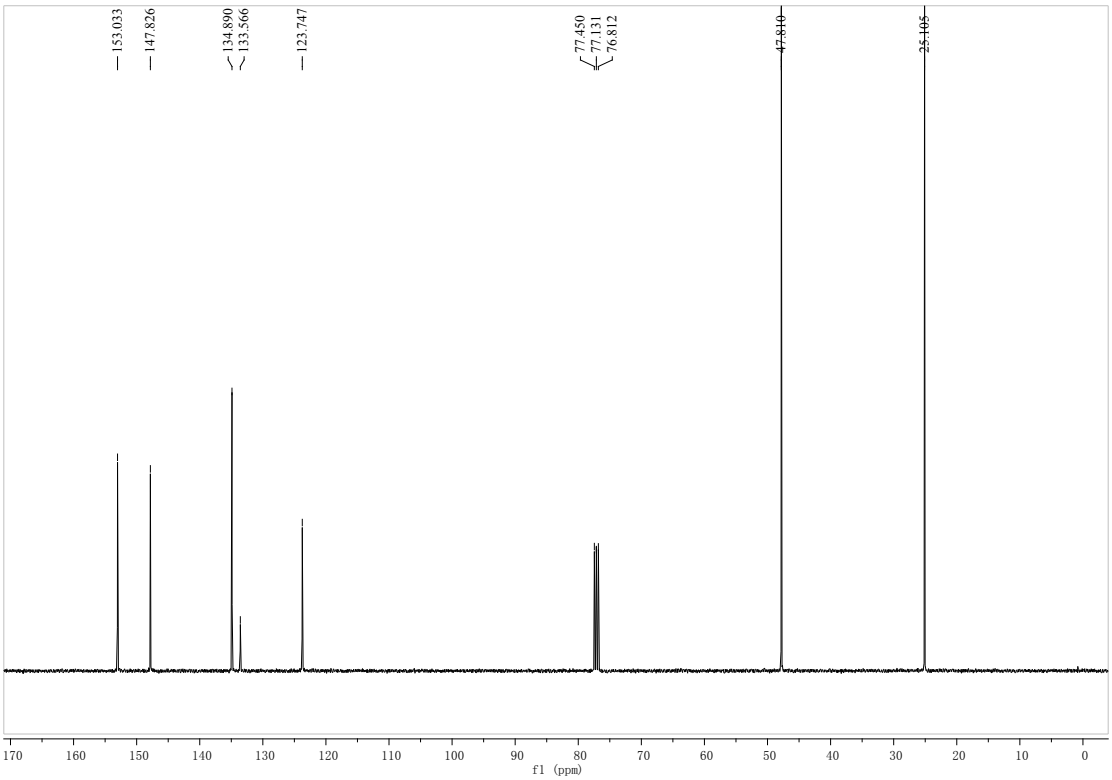
^{1} H NMR of compound **3n** in $CDCl_3$



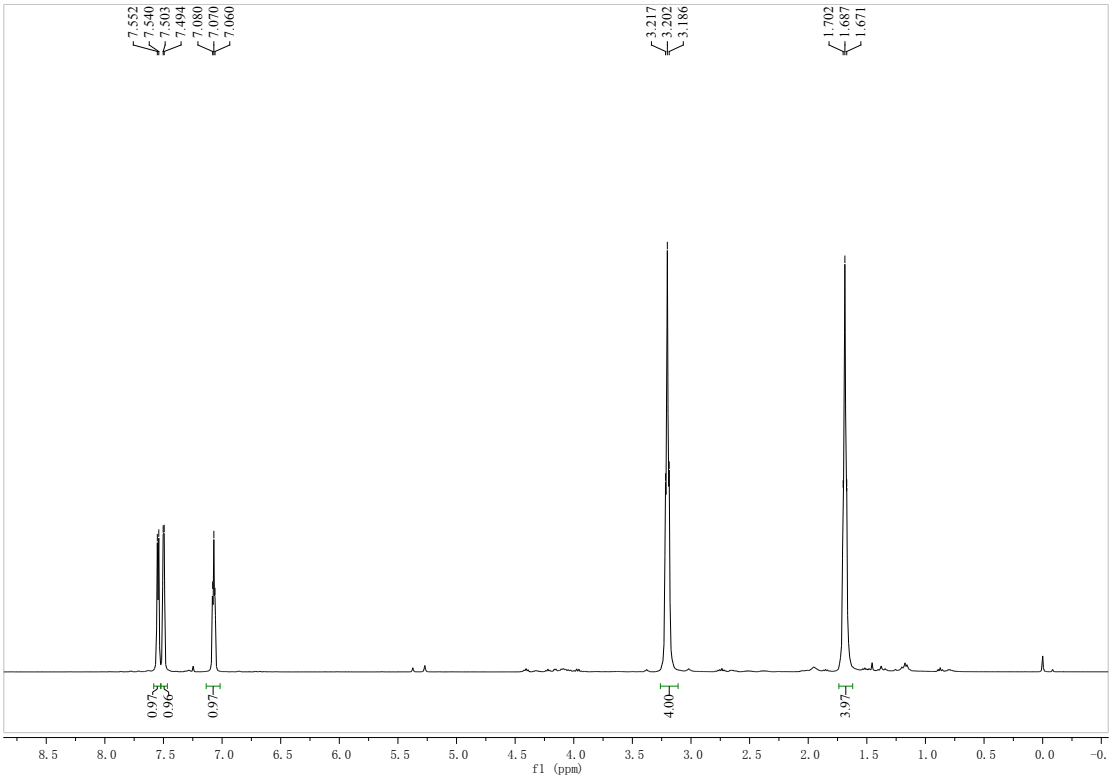
^{13} C NMR of compound **3n** in $CDCl_3$



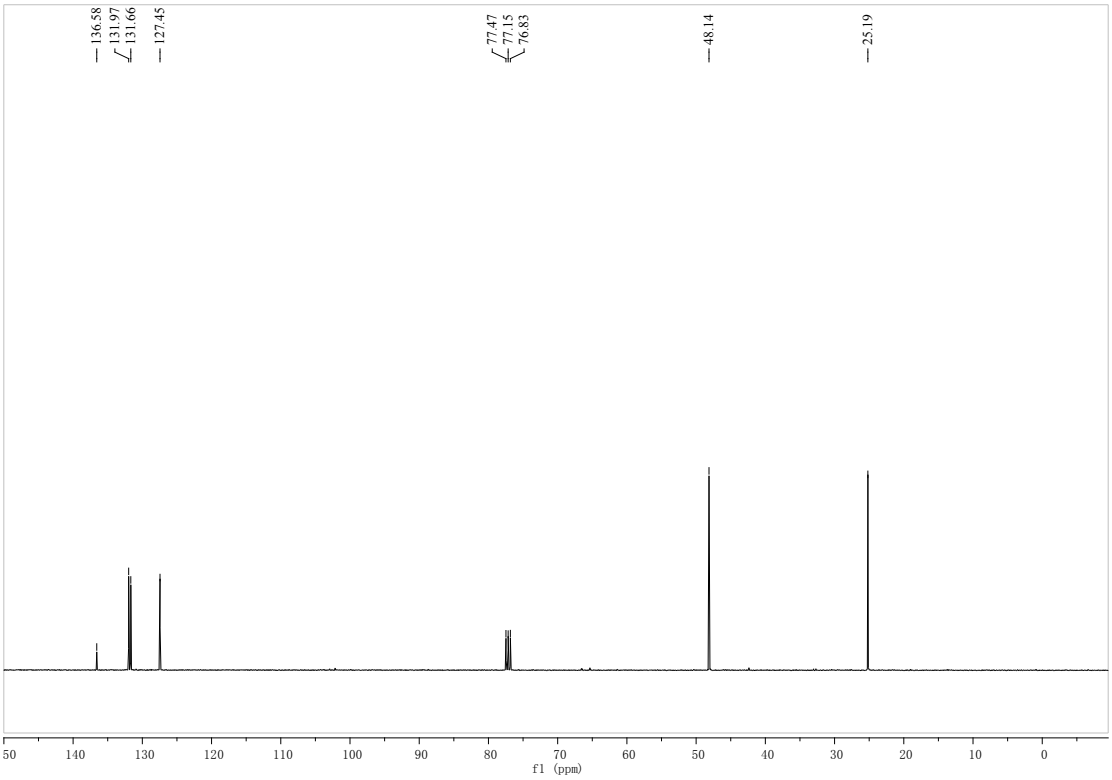
^{1} H NMR of compound **3o** in $CDCl_3$



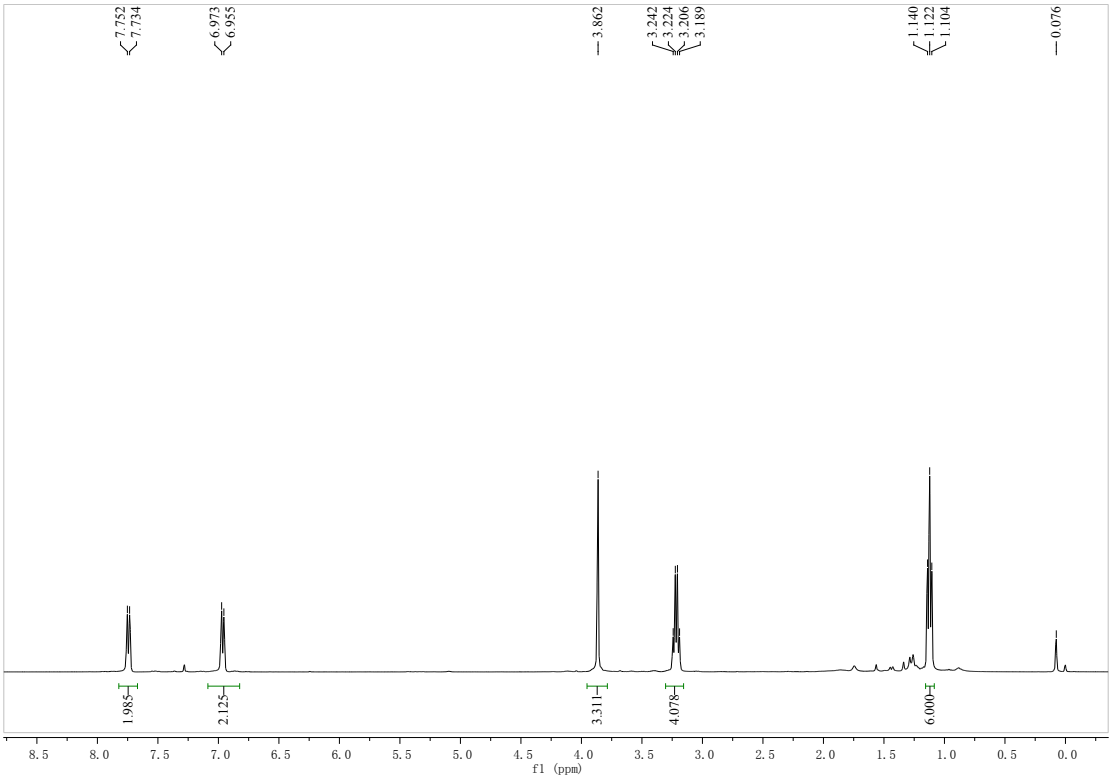
^{13} C NMR of compound **3o** in $CDCl_3$



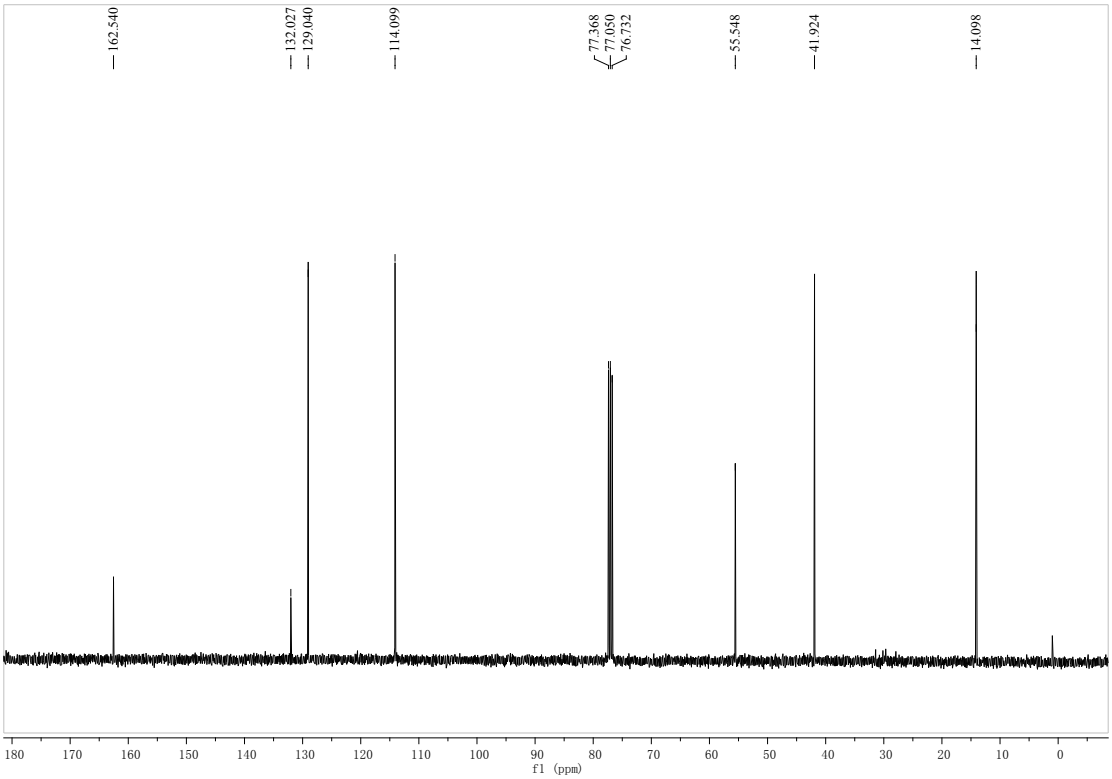
^{1} H NMR of compound **3p** in $CDCl_3$



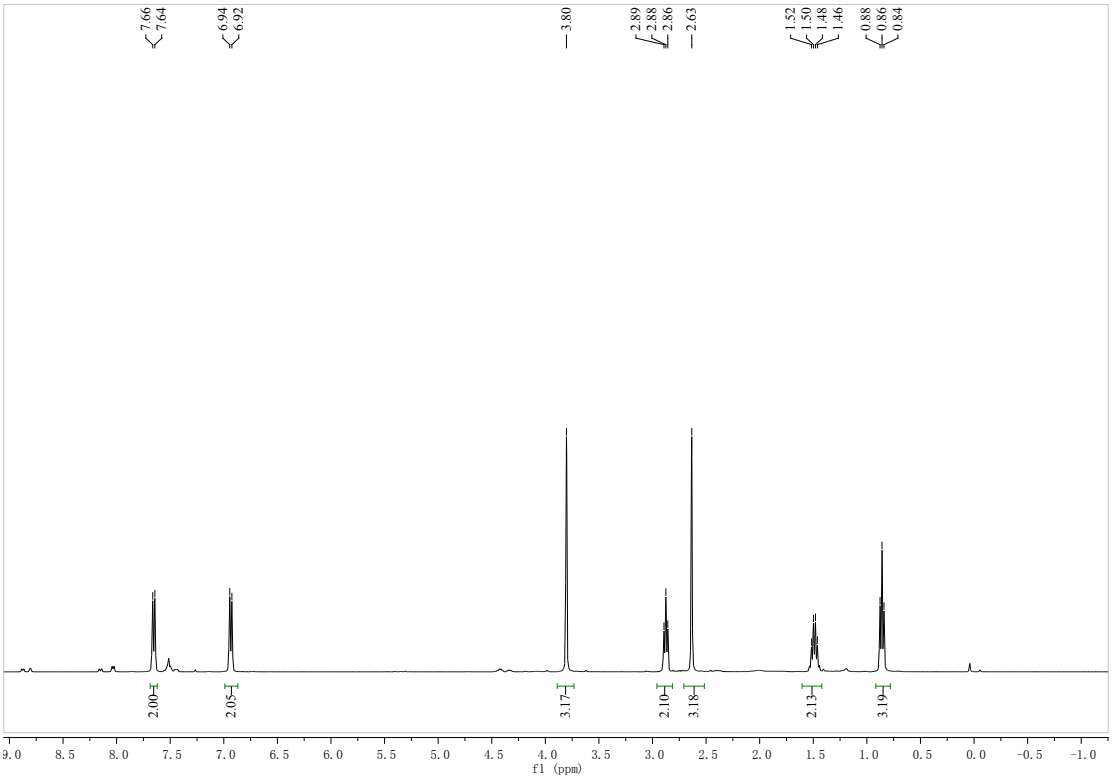
^{13} C NMR of compound **3p** in $CDCl_3$



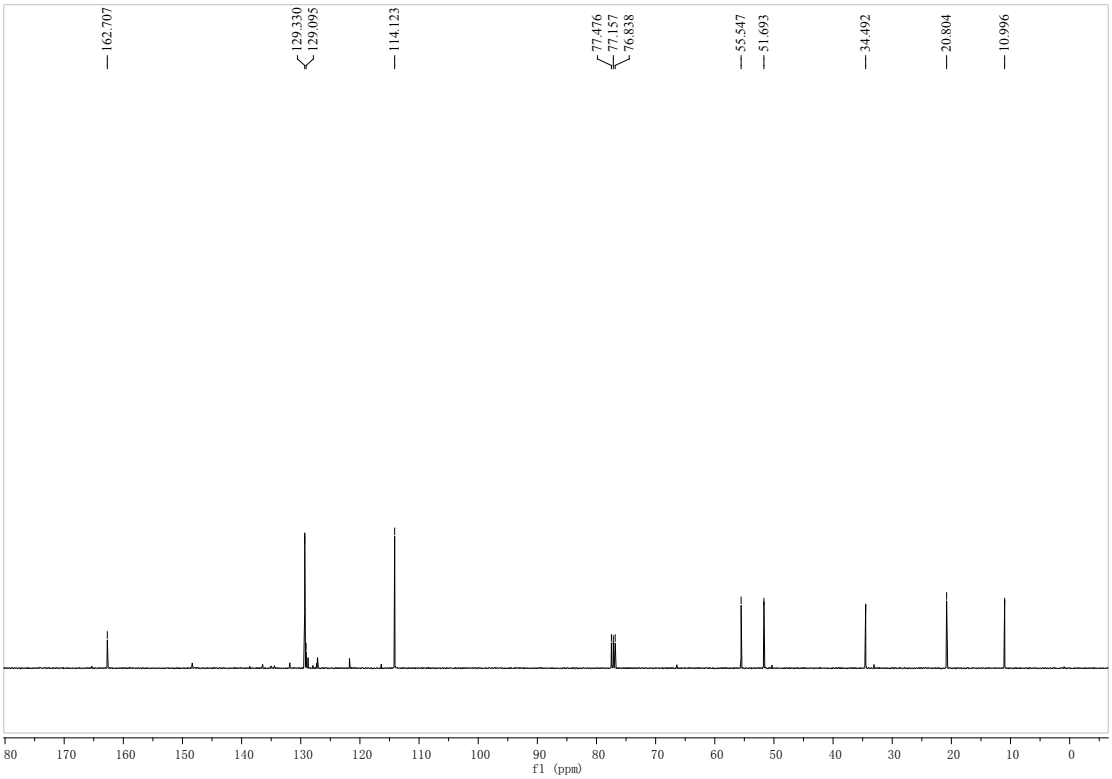
^{1} H NMR of compound **3q** in $CDCl_3$



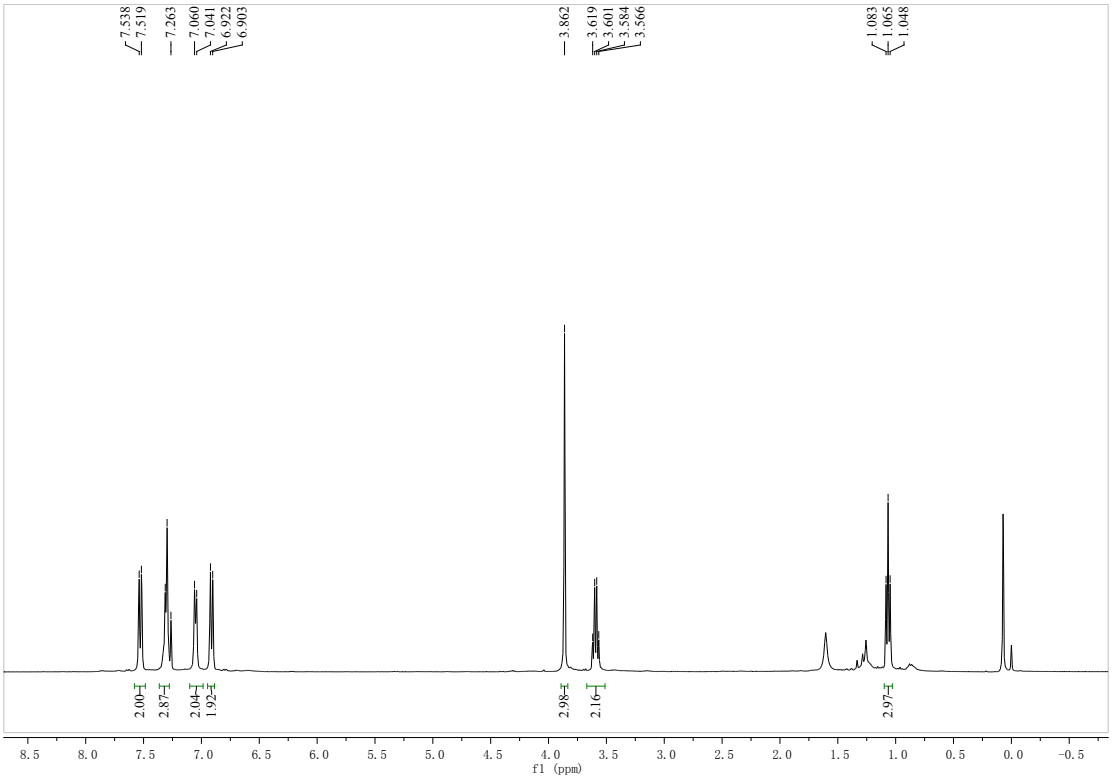
^{13} C NMR of compound **3q** in $CDCl_3$



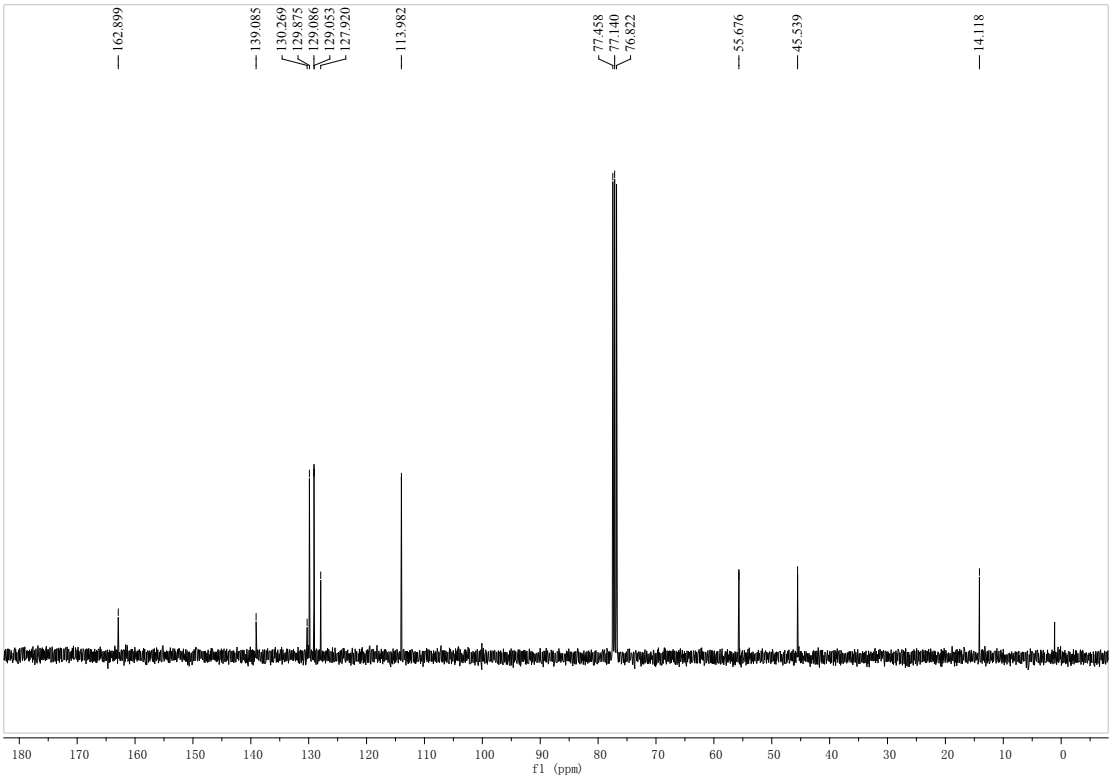
^{1} H NMR of compound **3r** in $CDCl_3$



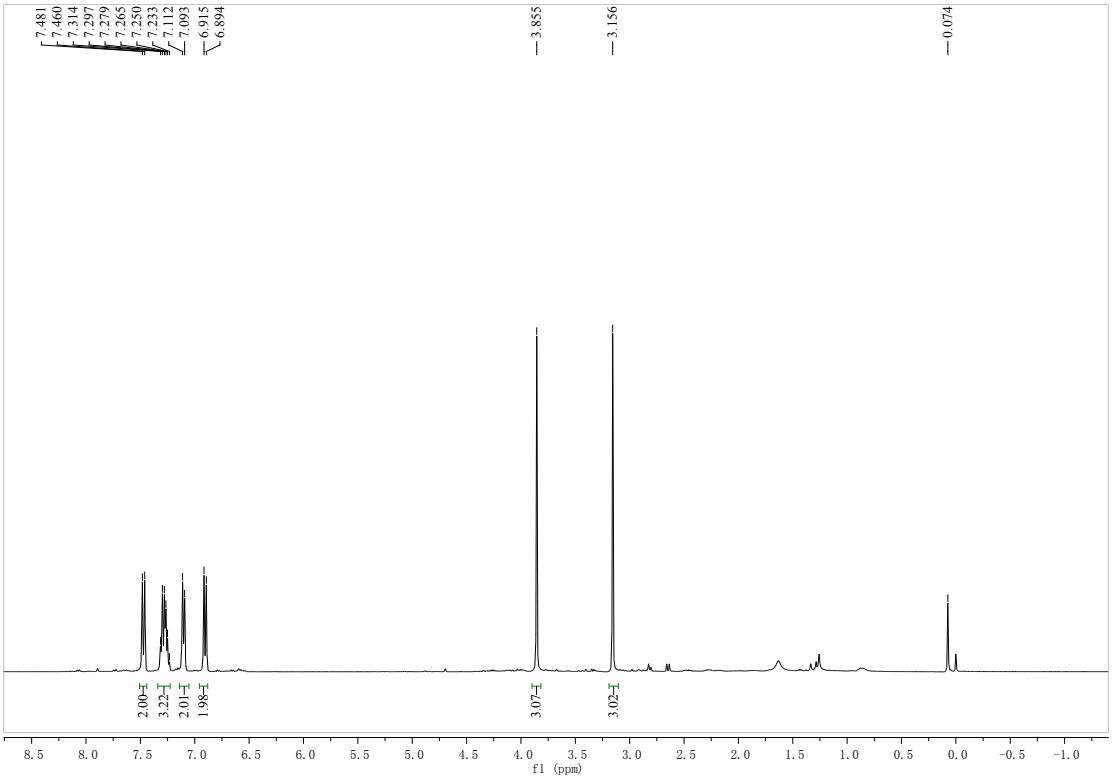
^{13} C NMR of compound **3r** in $CDCl_3$



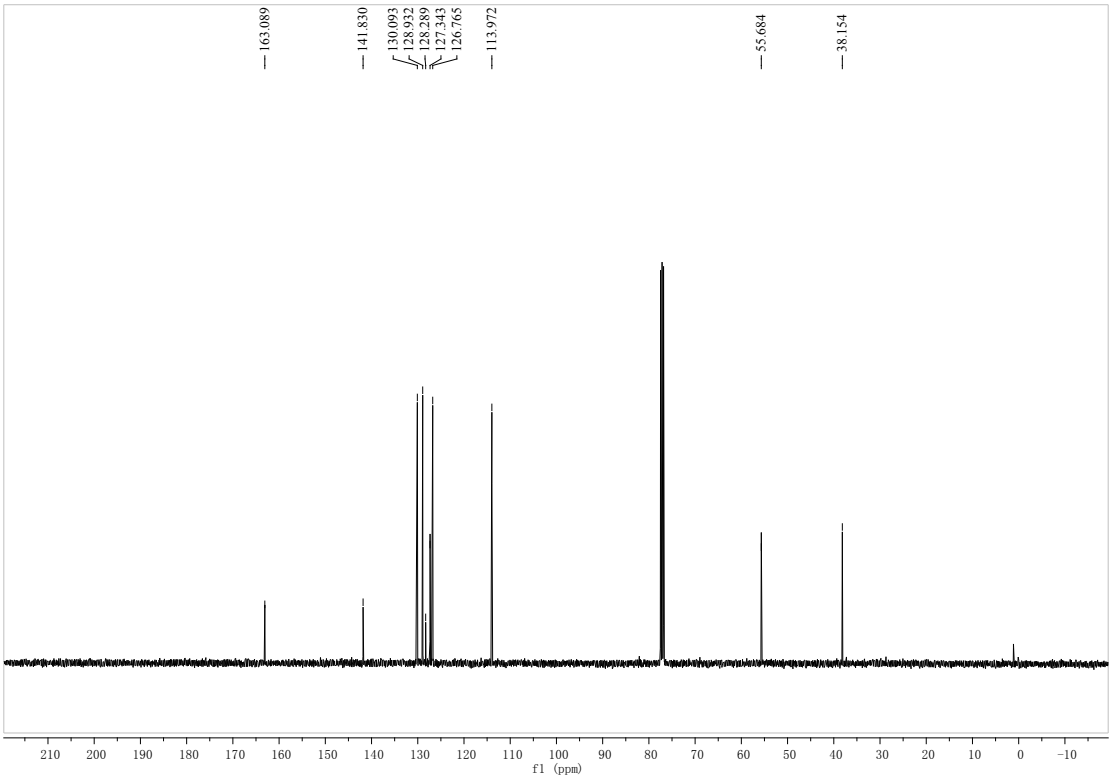
^{1} H NMR of compound **3s** in $CDCl_3$



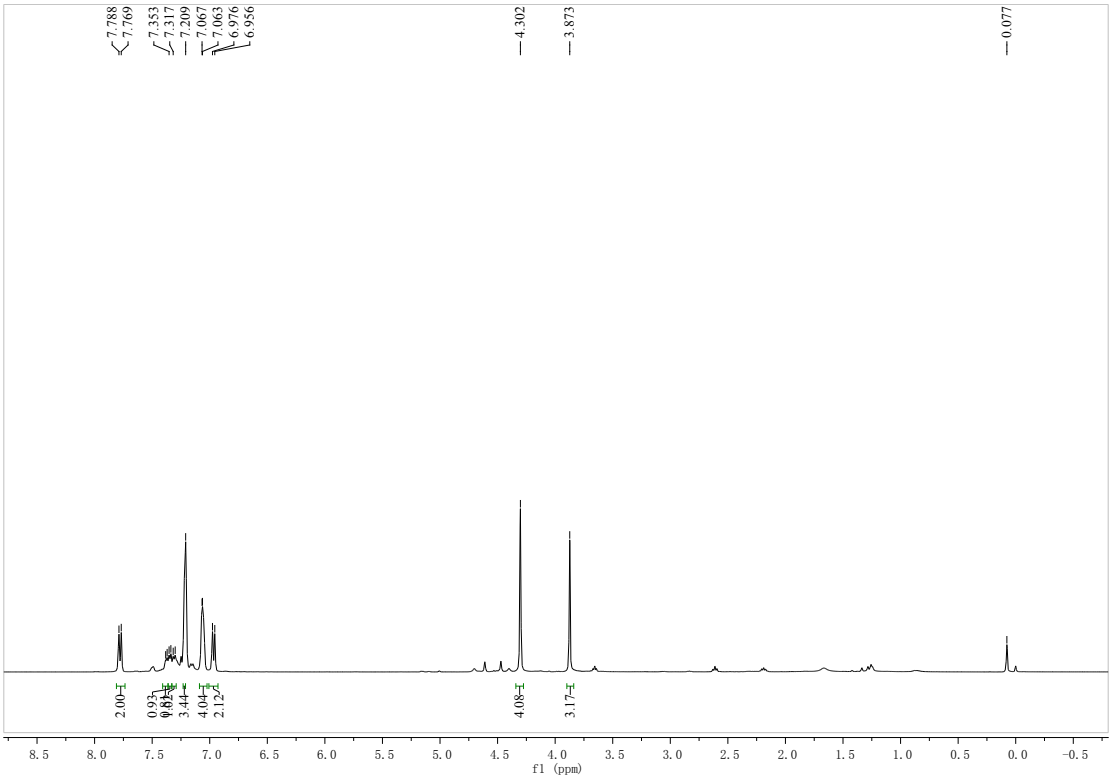
^{13} C NMR of compound **3s** in $CDCl_3$



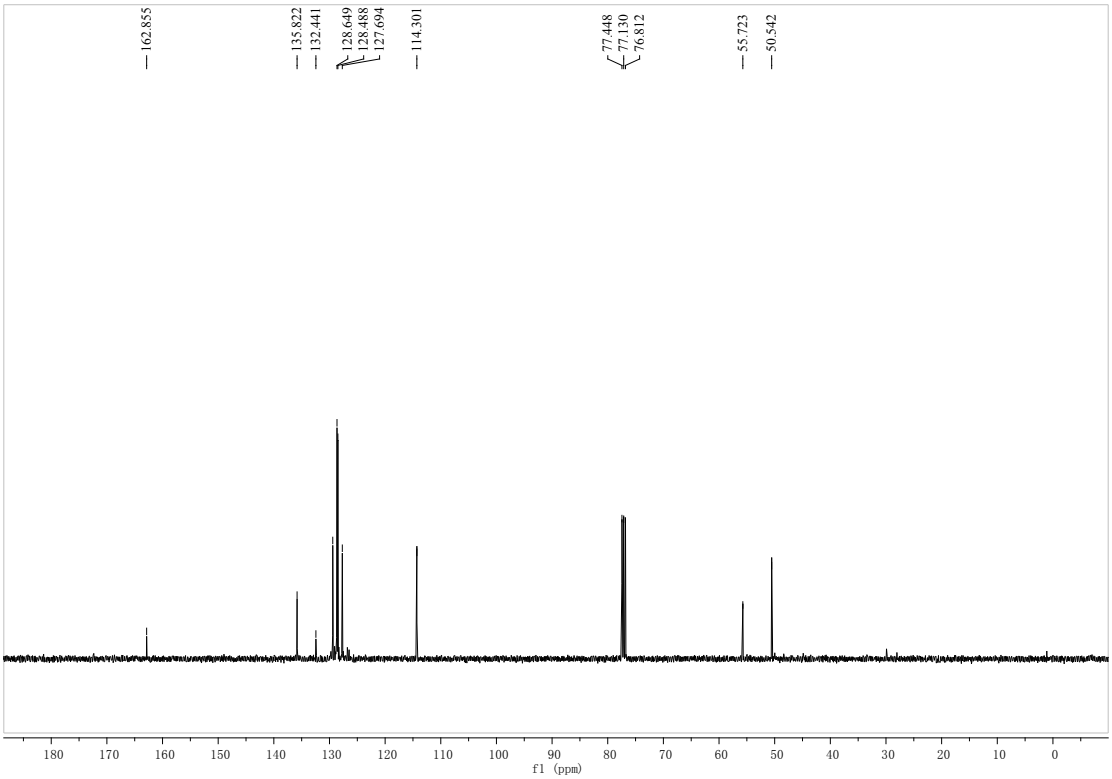
[1] H NMR of compound **3t** in $CDCl_3$



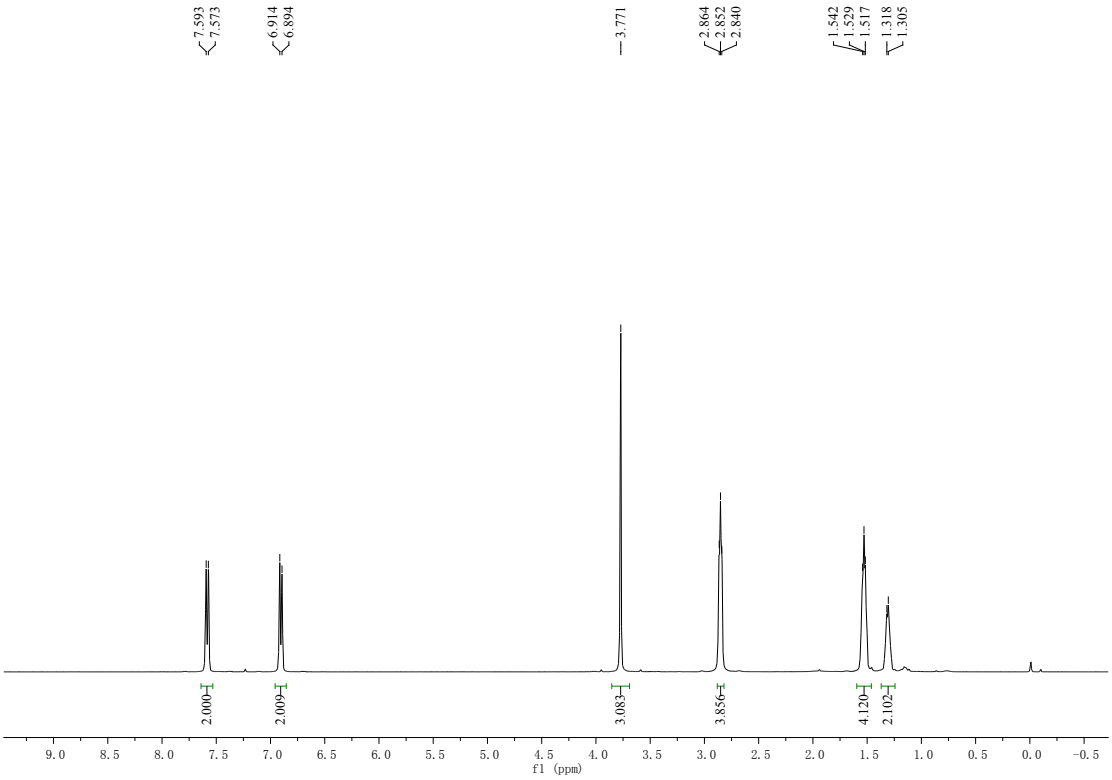
[13] C NMR of compound **3t** in $CDCl_3$



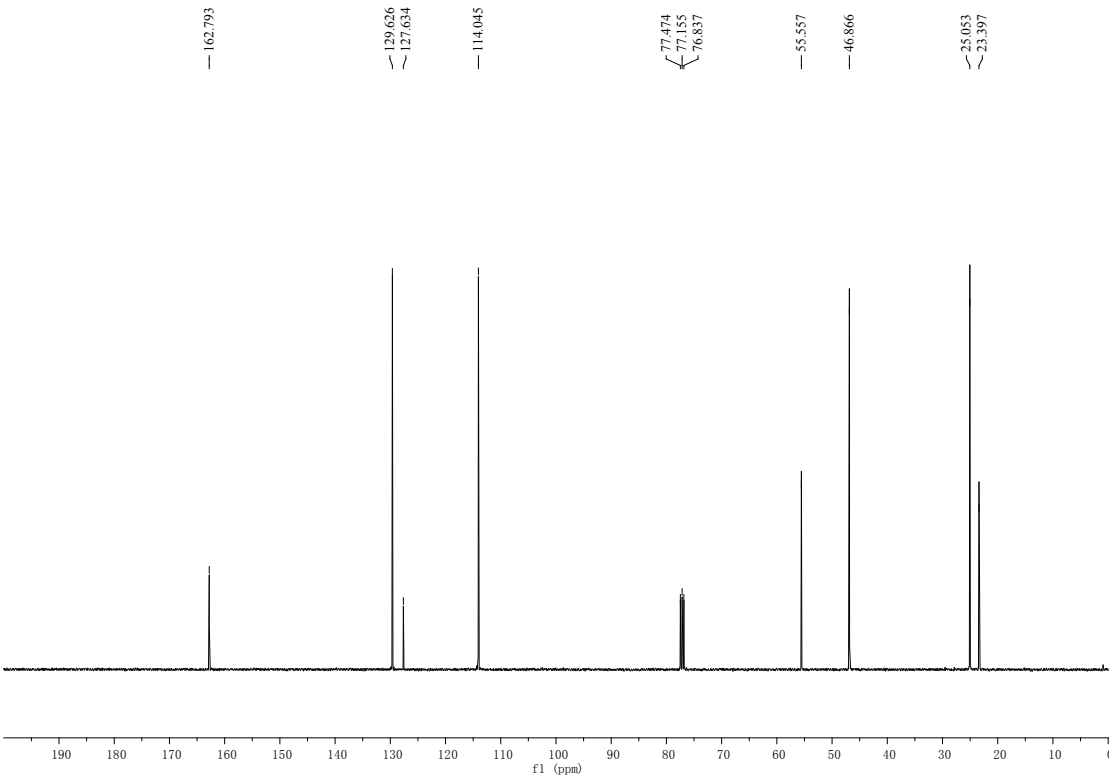
^{1} H NMR of compound **3u** in $CDCl_3$



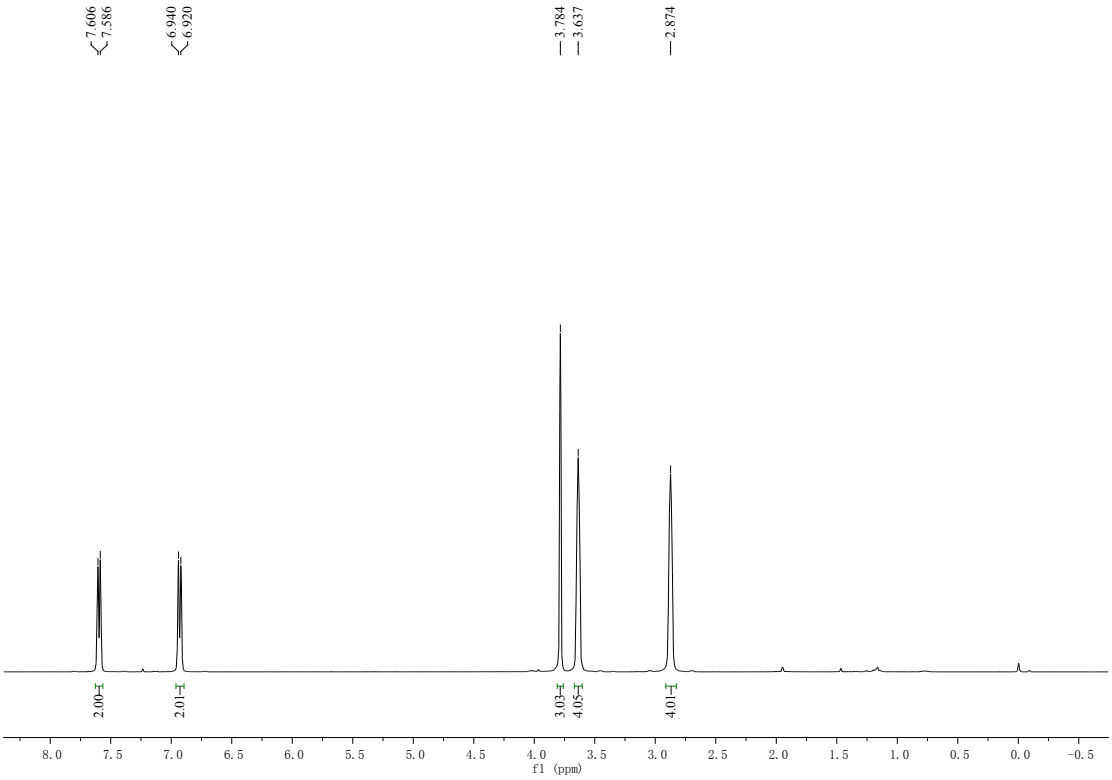
^{13} C NMR of compound **3u** in $CDCl_3$



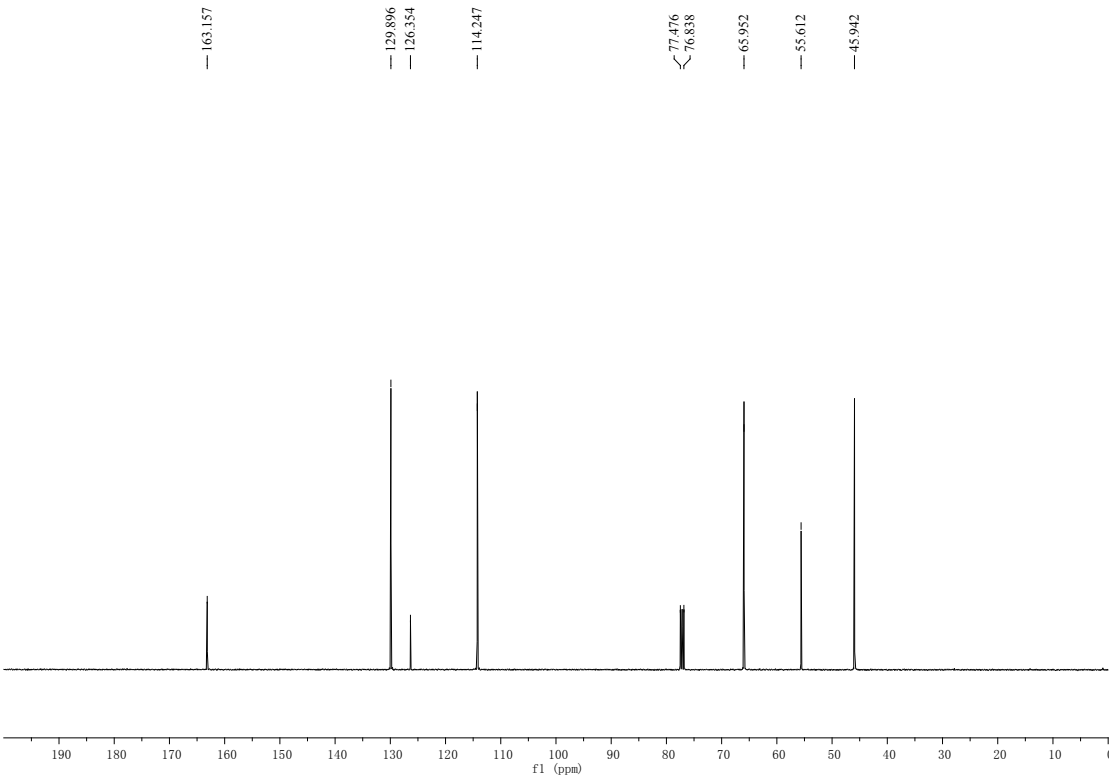
^{1} H NMR of compound **3v** in $CDCl_3$



^{13} C NMR of compound **3v** in $CDCl_3$



^{1}H NMR of compound **3w** in $CDCl_3$



^{13}C NMR of compound **3w** in $CDCl_3$

3. References

[1] S. K. R. Parumala, R. K. Peddinti, *Tetrahedron Lett.,* 2016, **57**, 1232;

[2] H. Zhu, Y. Shen, Q. Deng, T. Tu, *Chem. Commun*., 2015, **51**, 16573

[3] H. Jiang, X. Tang, Z. Xu, H. Wang, K. Han, X. Yang, Y. Zhou, Y.-L. Feng, X.-Y. Yu, Q. Gui, *Org. Biomol. Chem*., 2019, **17**, 2715.

[4] X. Tang, L. Huang, C. Qi, X. Wu, W. Wu, H. Jiang, *Chem. Commun*., 2013, **49**, 6102;

[5] J. Ji, Z. Liu, P. Liu, Sun, P. *Org. Biomol. Chem.,* 2016, **14**, 7018