Supporting Information

Selective Photochemical reduction of nitroarenes to *N*-arylhydroxylamines with γ-terpinene

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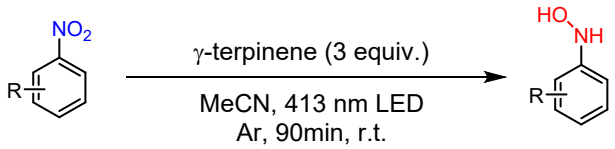
Content

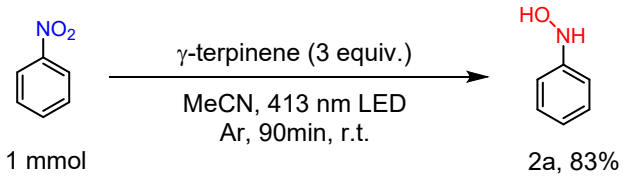
General Information

All chemical reagents were obtained from commercial suppliers and used without further purification. Photoreductive reaction was carried out in Schlenk tubes by a photochemical reactor (PR-6, Shanghai Titan Technology Co., Ltd). All reactions were carried out under Ar atmosphere at room temperature unless stated otherwise. Reactions were monitored by thin-layer chromatography on glass plates precoated with silica gel F254 and the plates were visualized by irradiation with ultraviolet light. Silica gel (100-200 mesh size) was used for column chromatography. High-performance liquid chromatography (Waters Alliance HPLC e2695, USA) and a reverse phase C18 column (250 x 4.6 mm) were used. All known compounds are identified by ^{1}H NMR and ^{13}C NMR and compared with previously reported data. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz, 126 MHz and 470 MHz in d_6-DMSO and chemical shifts were reported in ppm. and the solvent residual peak was used as an internal reference: proton (δ 2.50 ppm), carbon (δ 39.10 ppm). High resolution mass (HRMS) was collected from a TripleTOF 5600 system (SCIEX). GC-MS data was recorded on a ISQ LT Single Quadrupole Mass Spectrometer, coupled with a Trace 1300 Gas Chromatograph (Thermo Fisher Scientific).

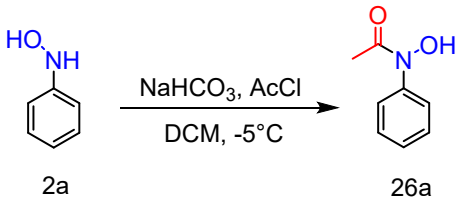
General Procedures



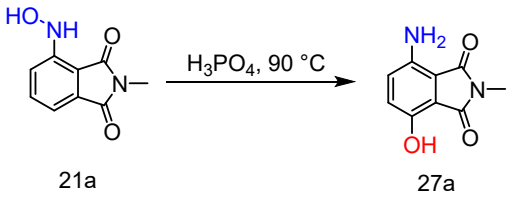
To the Schlenk tube containing the solution of nitroarenes (31 μL, 0.3 mmol) and MeCN, γ-terpinene (144 μL, 3 equiv.) was added. The tube was evacuated and refilled with Ar. The mixture was stirred at room temperature with the irradiation of 12W LED (413 nm). Upon completion, the solvent was removed under vacuum and the residue was purified by column chromatography with PE : EA (1:4 to 1:1) to give the corresponding products.



To the Schlenk tube containing the solution of nitroarenes (91 μL, 1 mmol) and MeCN, γ-terpinene (481 μL, 3 equiv.) was added. The tube was evacuated and refilled with Ar. The mixture was stirred at room temperature with the irradiation of 12W LED (413 nm). Upon completion, the solvent was removed under vacuum and the residue was purified by column chromatography with PE : EA (1:4) to give 2a in 83% yield (91 mg).

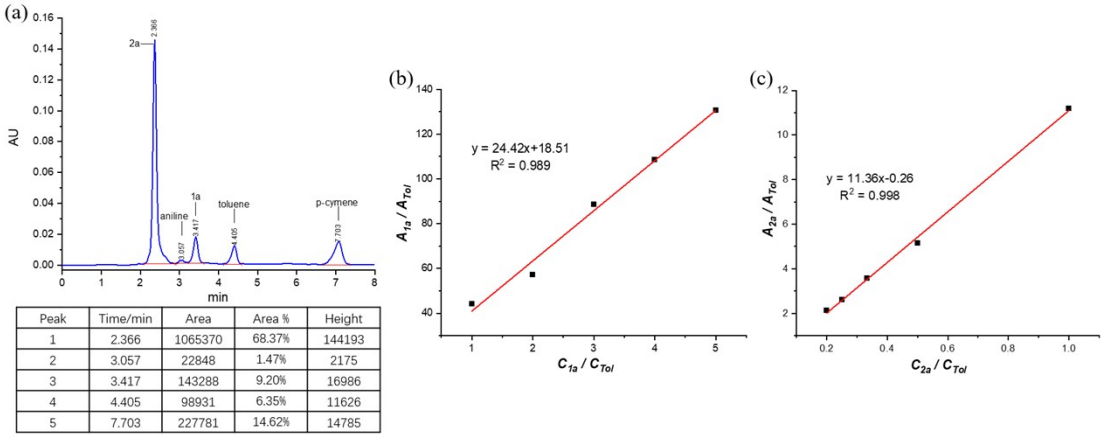


N-phenylhydroxylamine (2a, 22 mg, 0.2 mmol) was dissolved in DCM and the reaction mixture was cooled to 0 °C. $NaHCO_3$ (20 mg, 1.2 equiv.) and acetyl chloride (17 μL, 1.2 equiv.) were added. The reaction was monitored by TLC. Upon completion, the solvent was removed under vacuum and the residue was purified by column chromatography with PE : EA (1:3) to obtain *N*-hydroxy-*N*-phenylacetamide (26a) in 76% yield (23 mg).



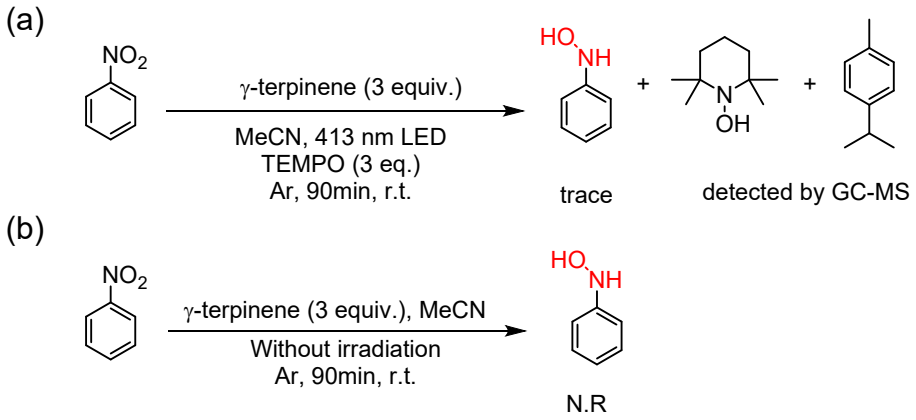
4-(hydroxyamino)-2-methylisoindoline-1,3-dione (21a, 38 mg, 0.2 mmol) was dissolved in phosphoric acid. The reaction was stirred at 90 °C and monitored by TLC. Upon completion, the pH of the solution was adjusted to be neutral with saturated Na_2CO_3 solution. The reaction mixture was extracted with DCM. The organic phase was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using with PE : EA (1:3) to yield 4-amino-7-hydroxy-2-methylisoindoline-1,3-dione (27a) in 73% yield (28 mg).

Supplementary data



Peak	Time/min	Area	Area %	Height
1	2.366	1065370	68.37%	144193
2	3.057	22848	1.47%	2175
3	3.417	143288	9.20%	16986
4	4.405	98931	6.35%	11626
5	7.703	227781	14.62%	14785

Scheme S1. (a) HPLC data of model reaction under standard conditions. Toluene was used as an internal standard. (b) The standard curve between 1a and toluene. (c) The standard curve between 2a and toluene.

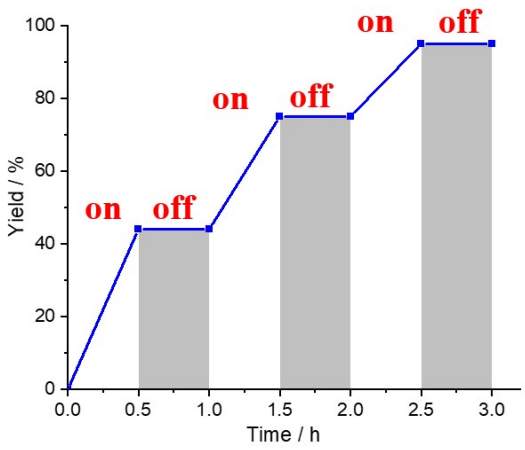


Scheme S2. The control experiment in the reduction of nitrobenzene with TEMPO (a) and without irradiation (b).

Reaction (a): To the Schlenk tube containing the solution of nitroarenes (20 μL, 0.2 mmol) and MeCN, γ-terpinene (96 μL, 3 equiv.) and TEMPO (94 mg, 3 equiv.) were added. The tube was evacuated and refilled with Ar. The mixture was stirred at room temperature with the irradiation of 12W LED (413 nm). The reaction was monitored by HPLC and GC-MS. 2a was not detected.

Reaction (b): To the Schlenk tube containing the solution of nitroarenes (20 μL, 0.2 mmol) and MeCN, γ-terpinene (96 μL, 3 equiv.) was added. The tube was evacuated and refilled with Ar. The

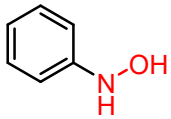
mixture was stirred at room temperature in dark environment. The reaction was monitored by HPLC. 2a was not detected.



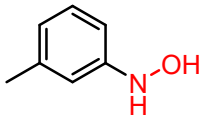
Scheme S3. The light on/off experiment.

Scheme S4. Pictures of Reaction set-up.

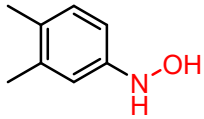
Characterization of compounds [1-7]



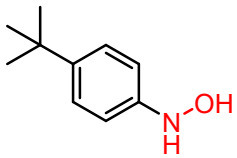
N-phenylhydroxylamine (2a): 30mg, 92% yield, pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.28 (s, 1H), 8.22 (s, 1H), 7.16 (t, J = 7.8 Hz, 2H), 6.84 (d, J = 8.3 Hz, 2H), 6.74 (t, J = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.54, 128.85, 119.66, 113.41.



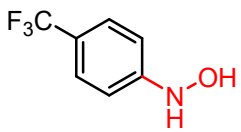
N-(m-tolyl)hydroxylamine (3a): 34mg, 92% yield, yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (s, 1H), 8.16 (s, 1H), 7.03 (t, J = 7.7 Hz, 1H), 6.70 - 6.60 (m, 2H), 6.56 (d, J = 7.4 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.54, 137.91, 128.74, 120.50, 113.96, 110.71, 21.75.



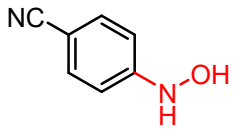
N-(3,4-dimethylphenyl)hydroxylamine (4a): 37 mg, 90% yield, pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.18 (s, 1H), 7.99 (s, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.64 (d, J = 2.3 Hz, 1H), 6.57 (m, 1H), 2.13 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 150.48, 136.26, 129.83, 127.09, 115.11, 111.18, 20.16, 19.03.



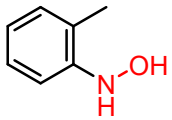
N-(4-(tert-butyl)phenyl)hydroxylamine (5a): 45mg, 91% yield, yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.21 (s, 1H), 8.07 (s, 1H), 7.18 (d, J = 8.2 Hz, 2H), 6.91 - 6.59 (m, 2H), 1.23 (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 150.05, 142.01, 125.41, 113.40, 34.13, 31.88.



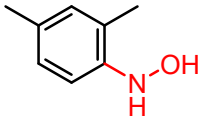
N-(4-(trifluoromethyl)phenyl)hydroxylamine (6a): 50 mg, 94% yield, pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.80 (s, 1H), 8.57 (s, 1H), 7.51 - 7.36 (m, 2H), 6.90 (d, J = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.60, 126.28, 126.25, 125.48 (q, J = 270.90 Hz, 1C), 119.17 (q, J = 31.88 Hz, 1C), 112.36. ^{19}F NMR (470 MHz, DMSO-d_6) δ -59.46.



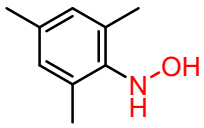
4-(hydroxyamino)benzonitrile (7a): 37 mg, 92% yield, yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.11 (s, 1H), 8.77 (s, 1H), 7.75 - 7.48 (m, 2H), 6.85 (m Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.82, 133.54, 120.59, 112.24, 99.57.



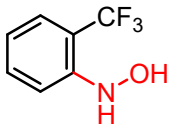
N-(o-tolyl)hydroxylamine (8a): 30 mg, 81% yield, yellow liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.18 (s, 1H), 7.88 (s, 1H), 7.07 (t, J = 3.1 Hz, 2H), 6.96 (d, J = 7.3 Hz, 1H), 6.68 (t, J = 4.1 Hz, 1H), 2.05 (s, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 150.05, 129.81, 126.67, 122.31, 119.45, 112.51, 17.28.



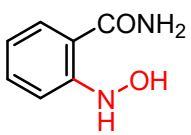
N-(2,4-dimethylphenyl)hydroxylamine (9a): 35 mg, 85% yield, orange solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.07 (s, 1H), 7.71 (s, 1H), 6.91 (d, J = 8.3 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 6.74 (d, J = 6.7 Hz, 1H), 2.12 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.65, 130.62, 127.98, 126.93, 122.53, 112.94, 20.64, 17.22.



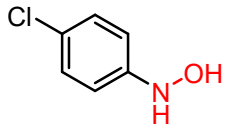
N-mesitylhydroxylamine (10a): 37 mg, 82% yield, pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.96 (s, 1H), 7.02 (s, 1H), 6.74 (s, 2H), 2.25 (s, 6H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 143.87, 133.22, 131.63, 129.19, 20.81, 18.39.



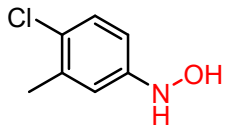
N-(2-(trifluoromethyl)phenyl)hydroxylamine (11a): 42 mg, 79% yield, brown liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.62 (s, 1H), 8.31 (s, 1H), 7.50 - 7.38 (m, 2H), 7.35 (d, J = 8.1 Hz, 1H), 6.85 (d, J = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.59, 133.70, 126.14 (q, J = 5.54 Hz, 1C), 123.81, 119.13, 114.50, 112.59 (q, J = 30.32 Hz, 1C). ^{19}F NMR (470 MHz, DMSO-d_6) δ -60.68.



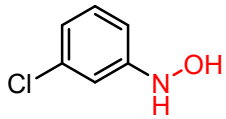
2-(hydroxyamino)benzamide (12a): 37 mg, 81% yield, yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.66 (s, 1H), 7.47 (s, 1H), 7.16 - 6.85 (m, 2H), 6.62 (s, 1H), 6.50 (s, 2H), 6.42 (d, J = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.74, 150.65, 132.33, 129.20, 116.85, 114.81, 114.15.



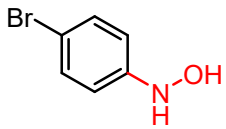
N-(4-chlorophenyl)hydroxylamine (13a): 39 mg, 91% yield, yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.45 (s, 1H), 8.41 (s, 1H), 7.19 (t, J = 8.2 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.46, 128.68, 122.94, 114.83.



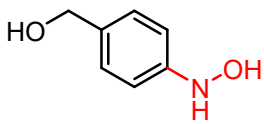
N-(4-chloro-3-methylphenyl)hydroxylamine (14a): 43 mg, 91% yield, pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.37 (s, 1H), 8.31 (s, 1H), 7.27 - 7.09 (m, 1H), 6.89 - 6.73 (m, 1H), 6.74 - 6.59 (m, 1H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.48, 135.53, 129.10, 123.35, 115.70, 112.57, 20.30.



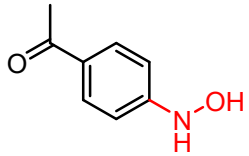
N-(3-chlorophenyl)hydroxylamine (15a): 40 mg, 93% yield, yellow liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.52 (s, 1H), 8.49 (s, 1H), 7.17 (t, J = 8.0 Hz, 1H), 6.85 (d, J = 2.2 Hz, 1H), 6.76 (d, J = 7.9 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.15, 133.72, 130.53, 118.98, 112.56, 111.78.



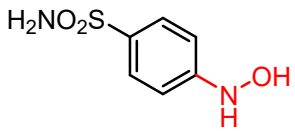
N-(4-bromophenyl)hydroxylamine (16a): 53mg, 94% yield, pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.43 (s, 1H), 8.40 (s, 1H), 7.30 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.86, 131.52, 115.30, 110.51.



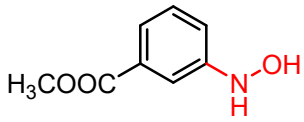
(4-(hydroxyamino)phenyl)methanol (17a): 37 mg, 89% yield, pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (s, 1H), 8.16 (s, 1H), 7.11 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.3 Hz, 2H), 4.92 (s, 1H), 4.36 (d, J = 5.5 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.40, 133.76, 127.62, 113.22, 63.40.



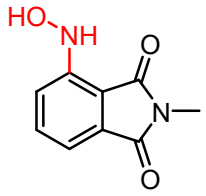
1-(4-(hydroxyamino)phenyl)ethan-1-one (18a): 42 mg, 93% yield, orange solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.95 (s, 1H), 8.62 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.2 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 196.10, 156.37, 130.28, 128.17, 111.38, 26.55.



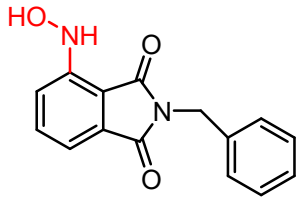
N-(4-((aminooxy)sulfonyl)phenyl)hydroxylamine (19a): 51mg, 90% yield, pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.79 (s, 1H), 8.58 (s, 1H), 7.58 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 6.1 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.14, 134.11, 127.30, 111.87.



Methyl 3-(hydroxyamino)benzoate (20a): 47 mg, 94% yield, yellow liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.52 (s, 1H), 8.50 (s, 1H), 7.45 (d, J = 1.9 Hz, 1H), 7.37 - 7.32 (m, 1H), 7.30 (m, 1H), 7.06 (m, 1H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.01, 152.84, 130.37, 129.28, 120.35, 117.89, 113.61, 52.46.

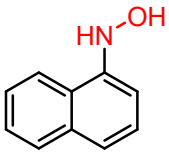


4-(hydroxyamino)-2-methylisoindoline-1,3-dione (21a): 52 mg, 90% yield, yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.07 (s, 1H), 8.89 (s, 1H), 7.62 (dd, J = 8.4, 7.1 Hz, 1H), 7.38 (d, J = 8.5 Hz, 1H), 7.16 (d, J = 7.4 Hz, 1H), 2.97 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.84, 168.63, 149.05, 135.94, 132.78, 118.52, 113.17, 111.07, 23.82. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_9H_8N_2O_3H^+$: 193.0608; Found 193.0607.

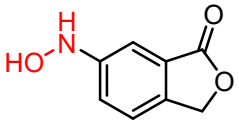


2-benzyl-4-(hydroxyamino)isoindoline-1,3-dione (22a): 71 mg, 88% yield, yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.00 (s, 1H), 8.91 (s, 1H), 7.56 (m, 7.1 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.25 - 7.18 (m, 5H), 7.10 (d, J = 7.1 Hz, 1H), 4.62 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.41, 168.30, 149.29, 137.39, 136.26, 132.51, 129.04, 128.00, 127.82, 118.70, 113.36, 110.58,

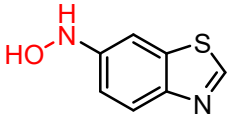
40.96.



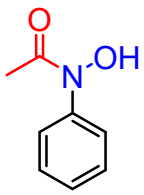
N-(naphthalen-1-yl)hydroxylamine (23a): 43 mg, 90% yield, brown liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.97 (s, 1H), 8.43 (s, 1H), 7.93 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.47 - 7.27 (m, 4H), 7.12 (d, J = 7.7 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.30, 133.83, 128.31, 126.81, 126.09, 124.84, 122.53, 122.06, 119.27, 106.95.



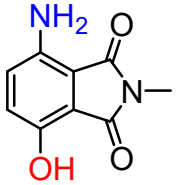
6-(hydroxyamino)isobenzofuran-1(3*H*)-one (24a): 44 mg, 89% yield, yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.67 (s, 1H), 8.61 (s, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.19 (d, J = 7.1 Hz, 2H), 5.29 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.54, 153.64, 138.49, 125.92, 123.24, 120.27, 107.18, 70.13.



N-(benzo[*d*]thiazol-6-yl)hydroxylamine (25a): 43 mg, 86% yield, yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.04 (s, 1H), 8.57 (d, J = 3.7 Hz, 2H), 7.85 (d, J = 8.8 Hz, 1H), 7.50 (d, J = 2.1 Hz, 1H), 6.99 (dd, J = 8.8, 2.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.93, 150.85, 147.50, 135.24, 123.14, 113.95, 104.31.



N-hydroxy-*N*-phenylacetamide (26a): 23 mg, 76% yield, brown liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.59 (s, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.39, 142.16, 128.82, 125.06, 120.76, 22.89.



4-amino-7-hydroxy-2-methylisoindoline-1,3-dione (27a): 28 mg, 73% yield, orange solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.87 (s, 1H), 6.96 (d, J = 9.0 Hz, 1H), 6.88 (d, J = 9.0 Hz, 1H), 5.94 (s, 2H), 2.91 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.49, 167.13, 146.47, 140.58,

126.71, 125.15, 113.20, 108.91, 23.43. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_9H_8N_2O_3H^+$: 193.0608; Found 193.0602.

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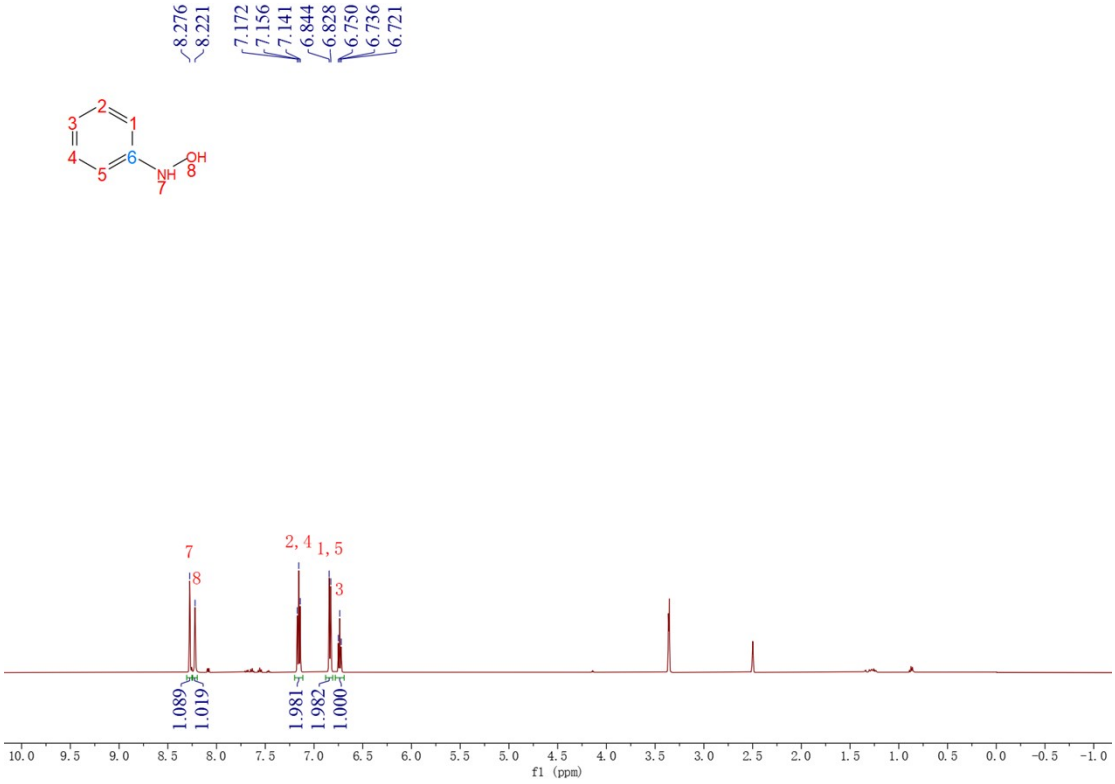
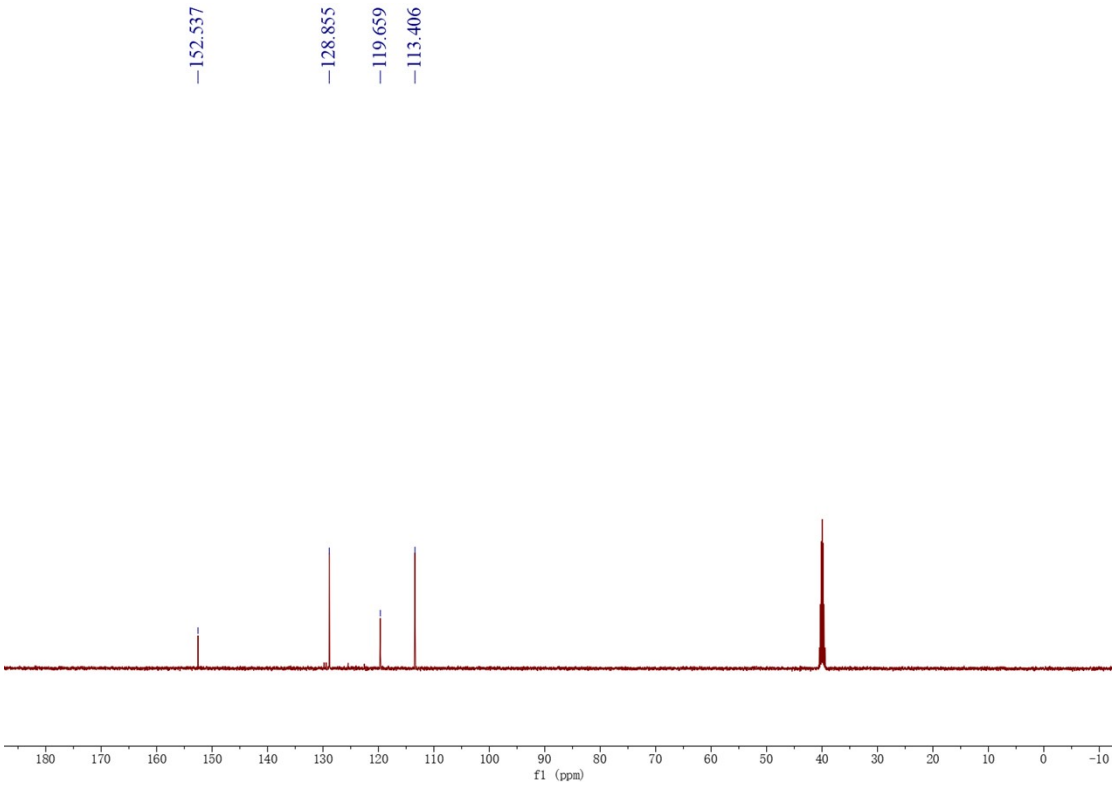
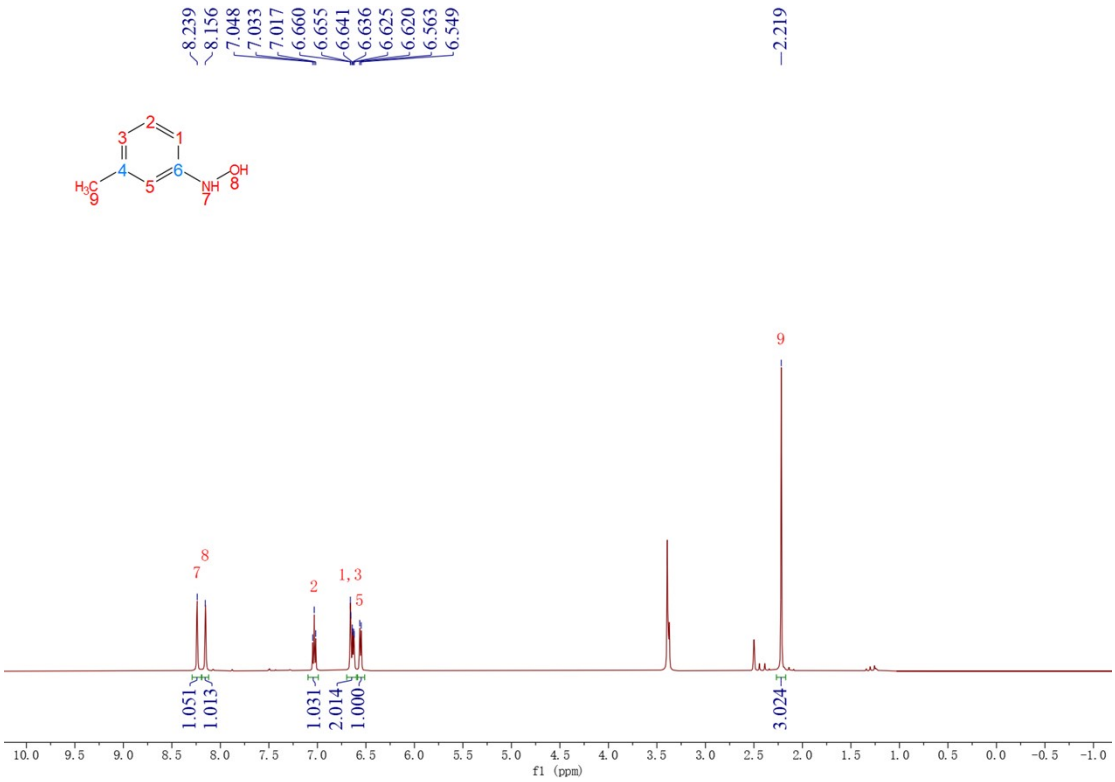
NMR spectra



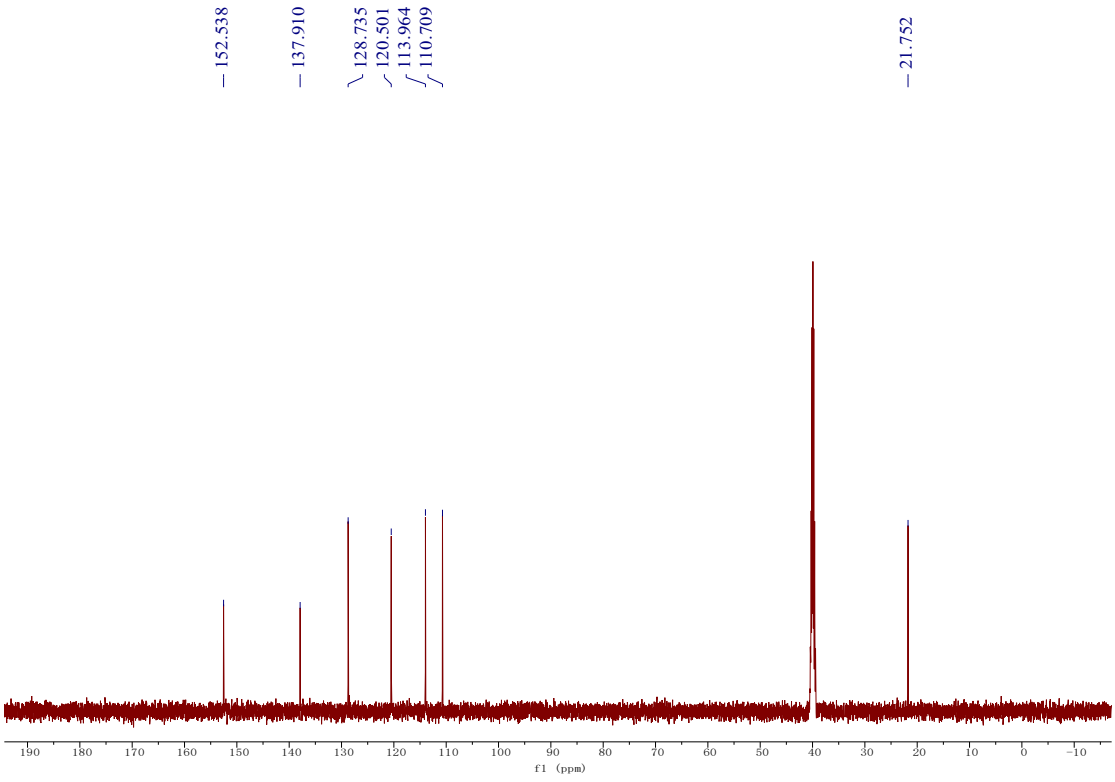
^{1}H NMR spectrum of compound 2a.



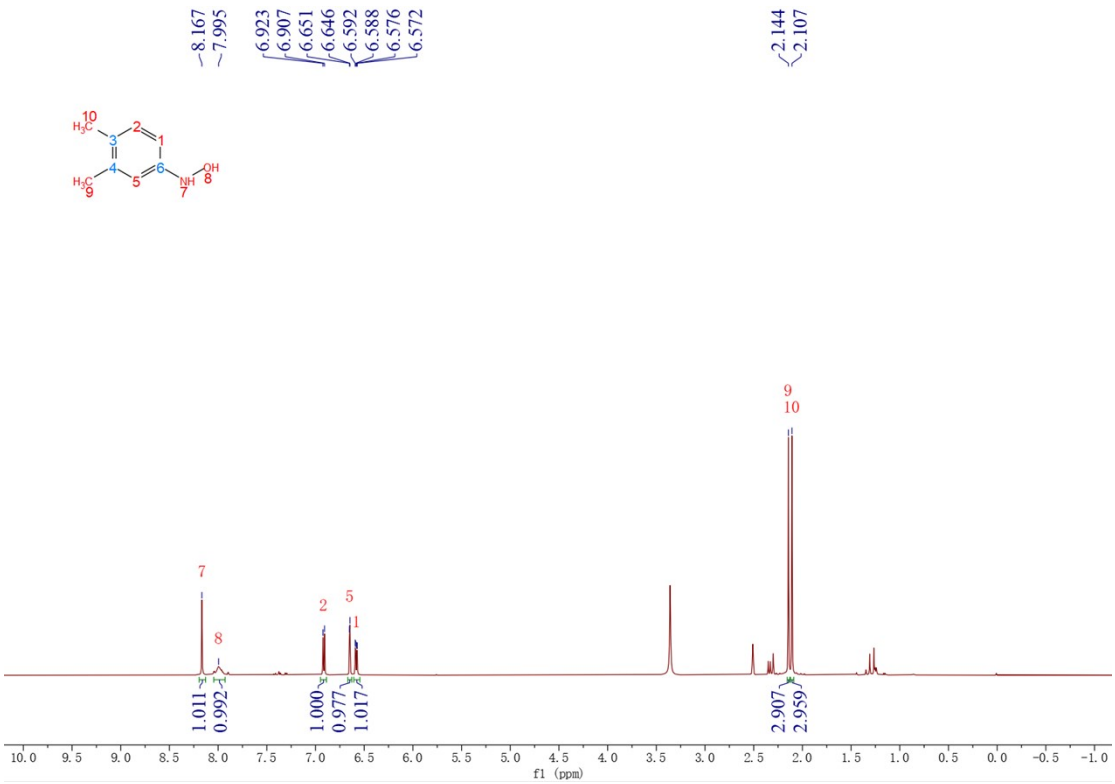
^{13}C NMR spectrum of compound 2a.



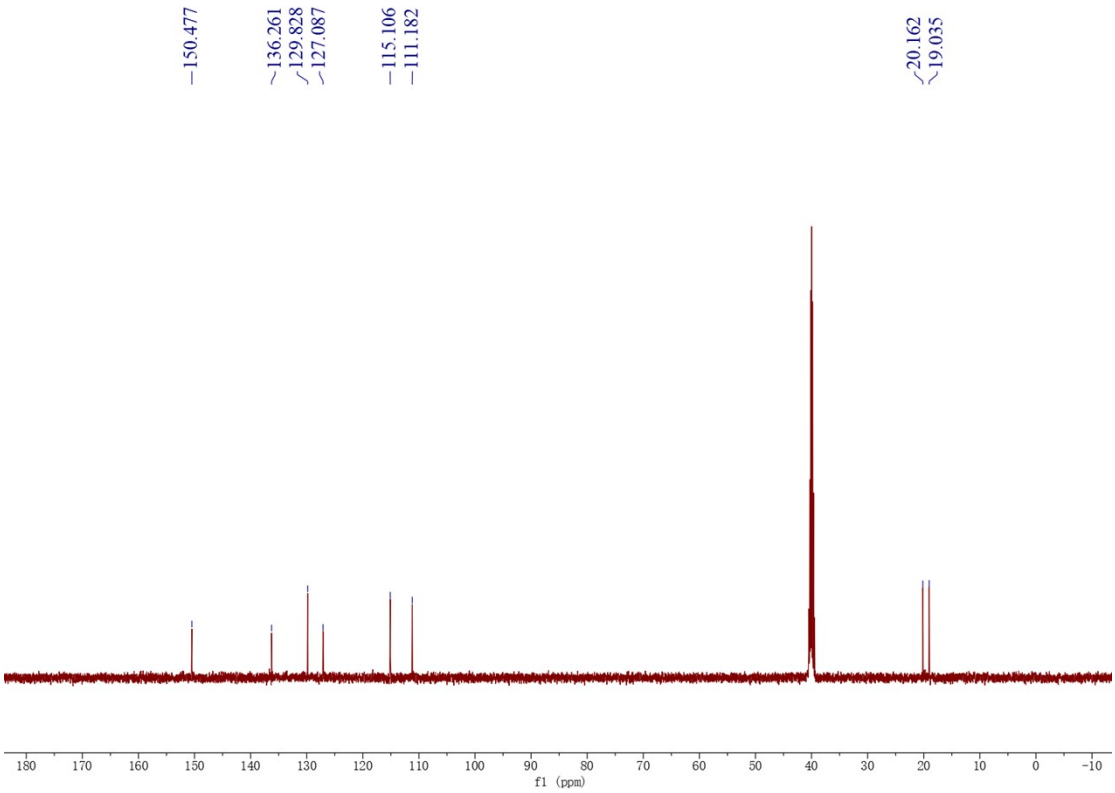
^{1}H NMR spectrum of compound 3a.



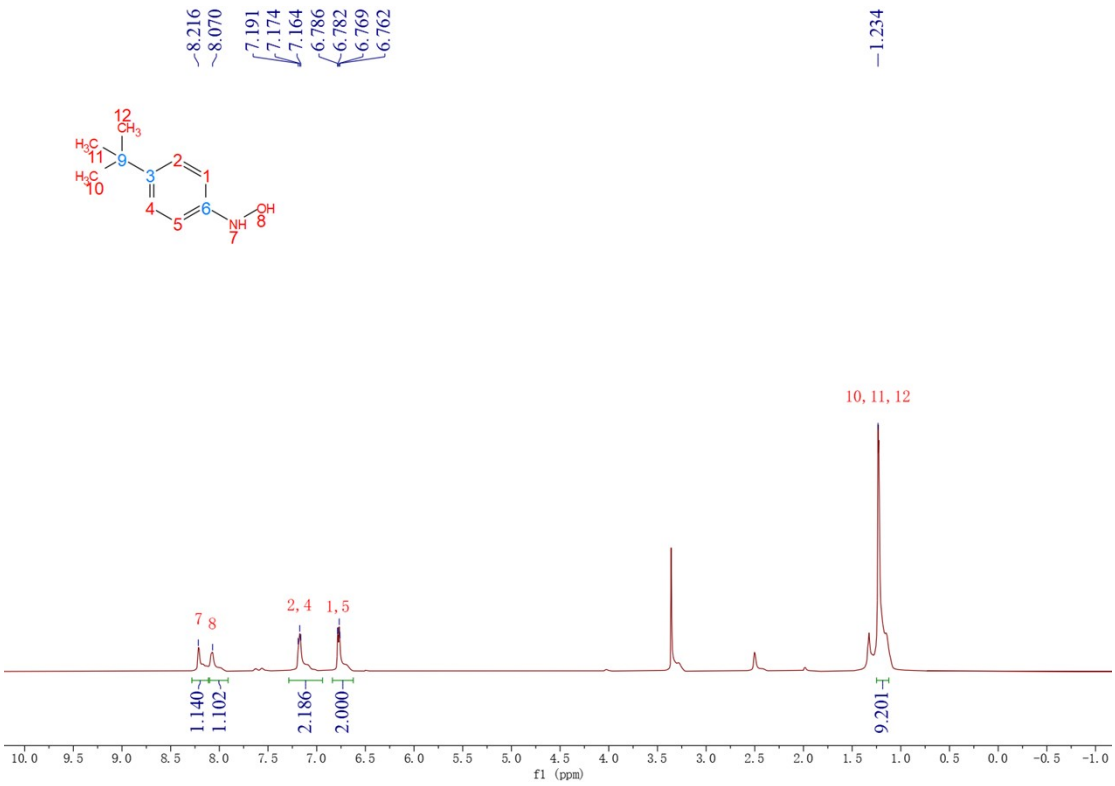
^{13}C NMR spectrum of compound 3a.



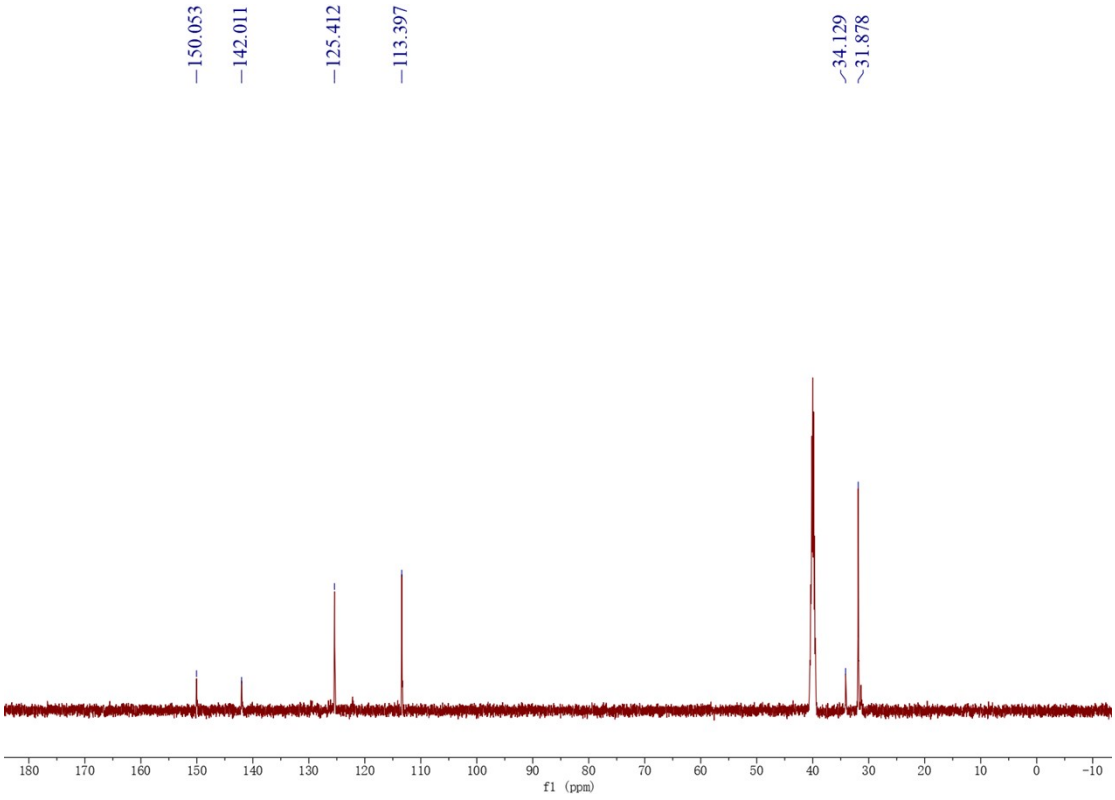
^{1}H NMR spectrum of compound 4a.



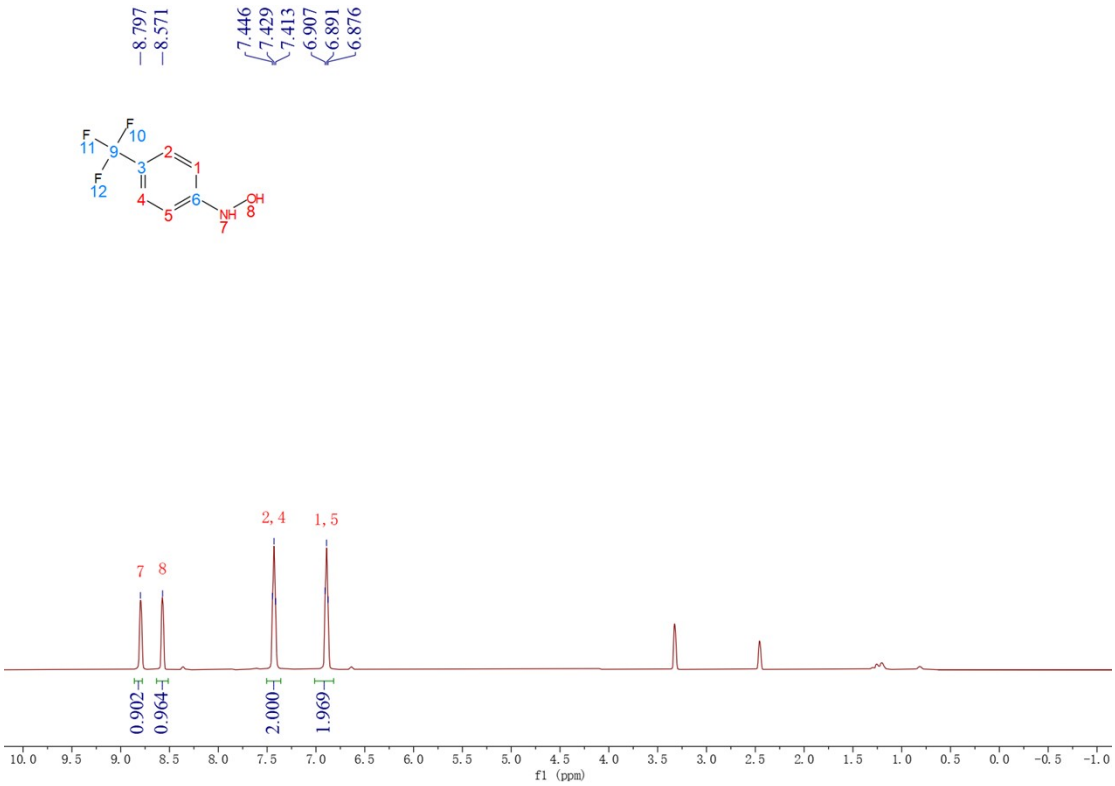
^{13}C NMR spectrum of compound 4a.



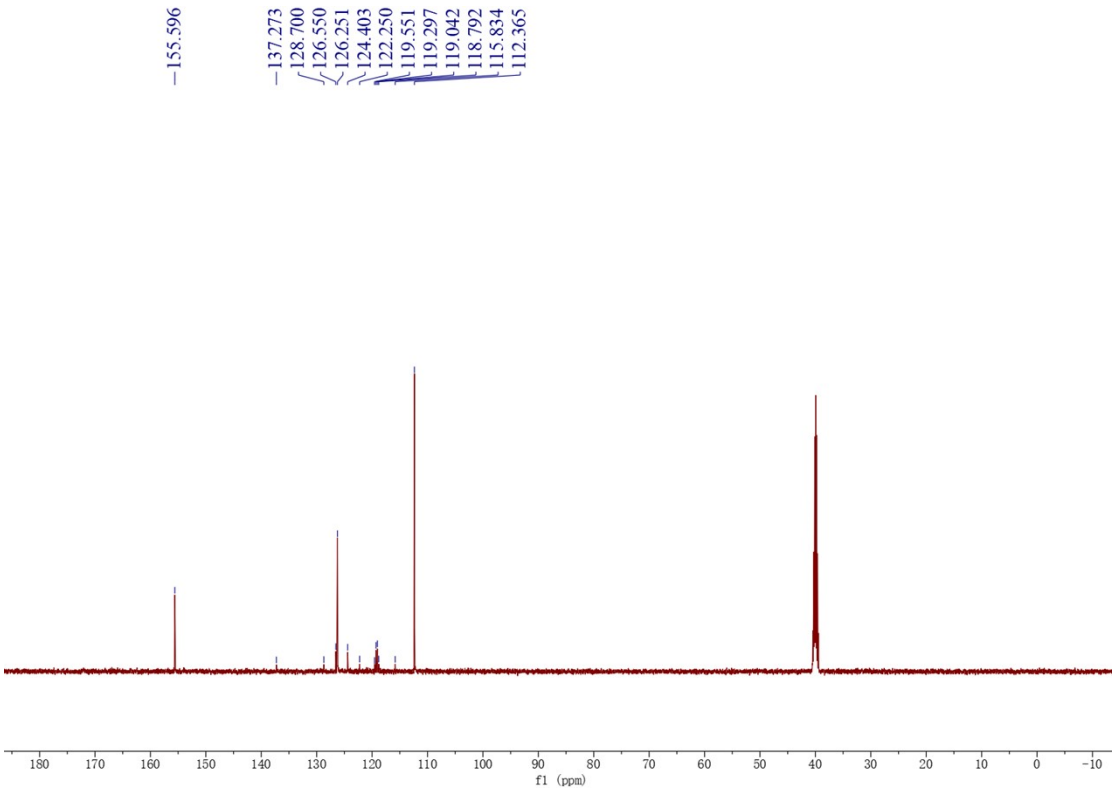
^{1}H NMR spectrum of compound 5a.



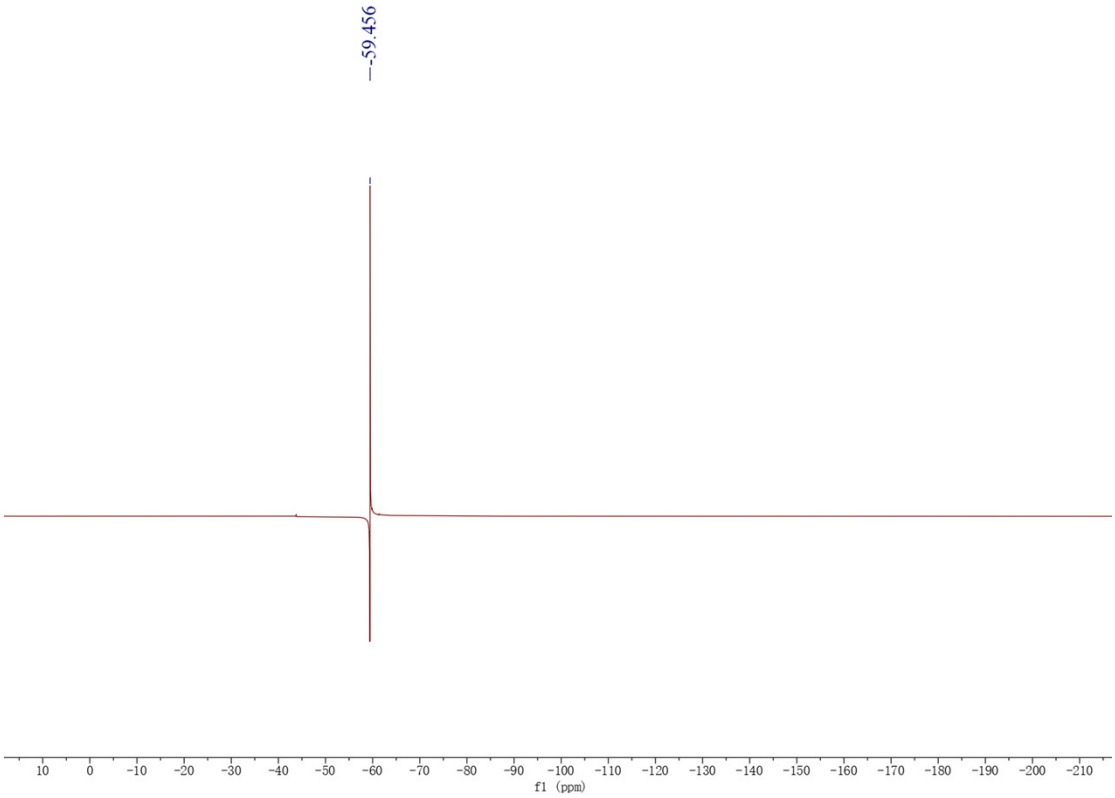
^{13}C NMR spectrum of compound 5a.



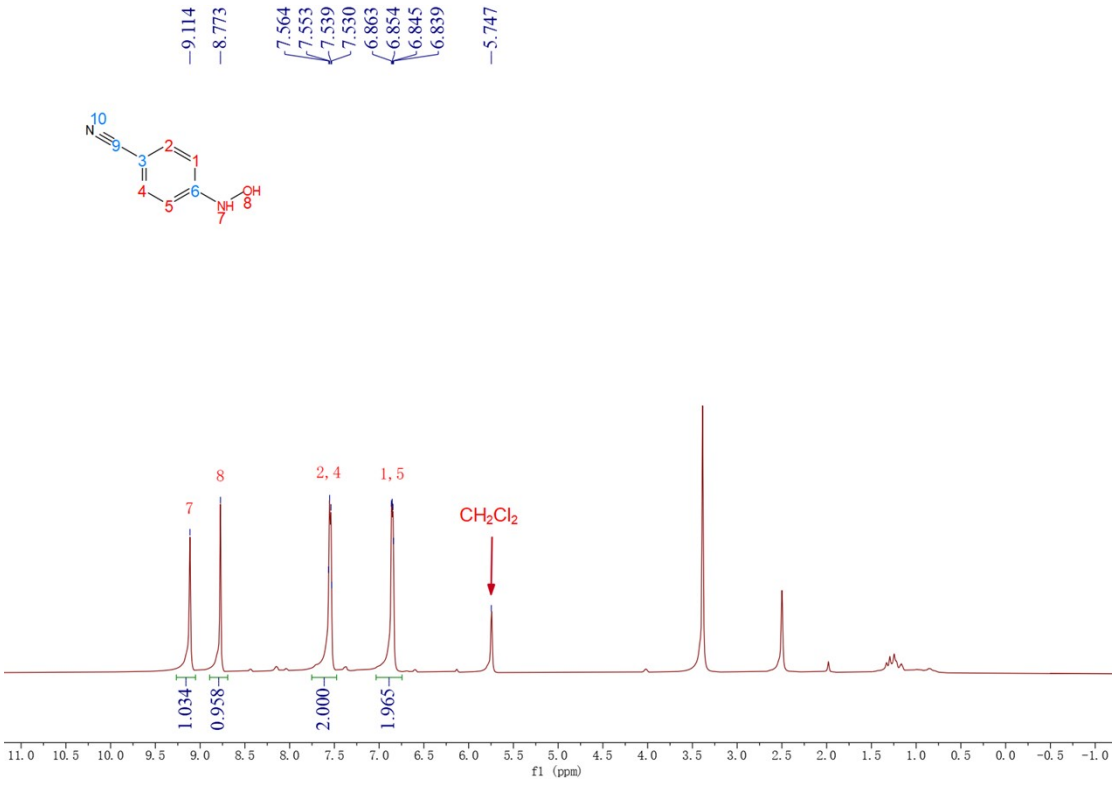
^{1}H NMR spectrum of compound 6a.



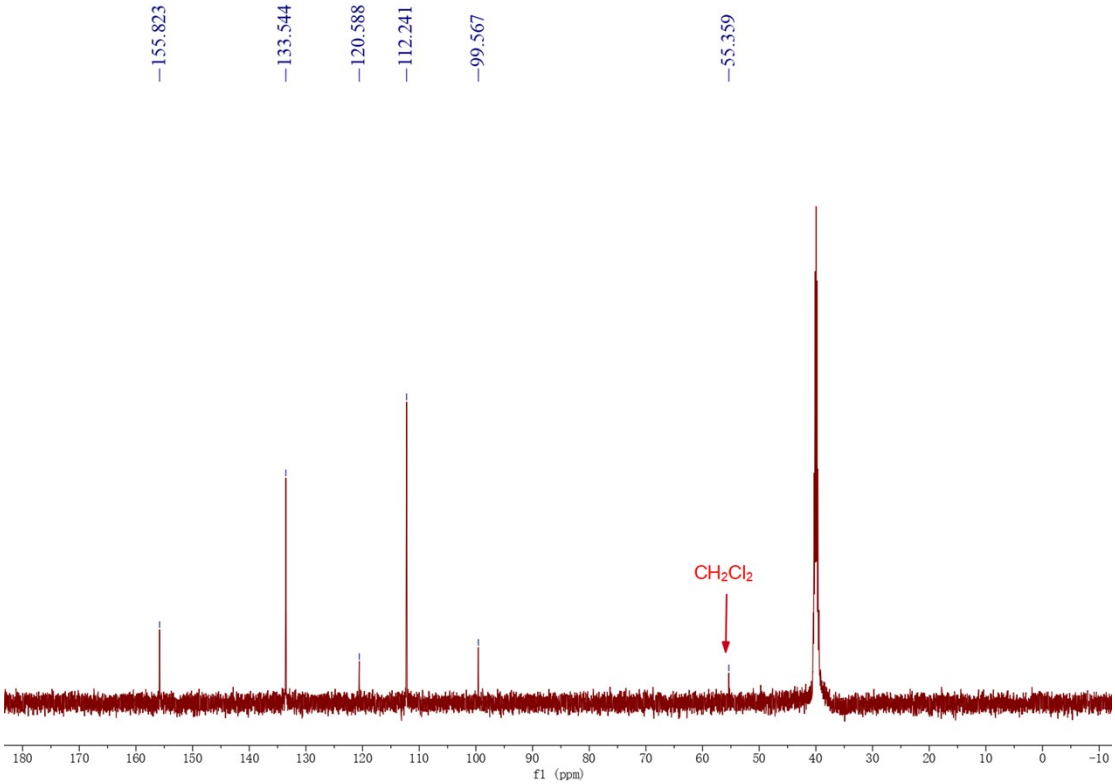
^{13}C NMR spectrum of compound 6a.



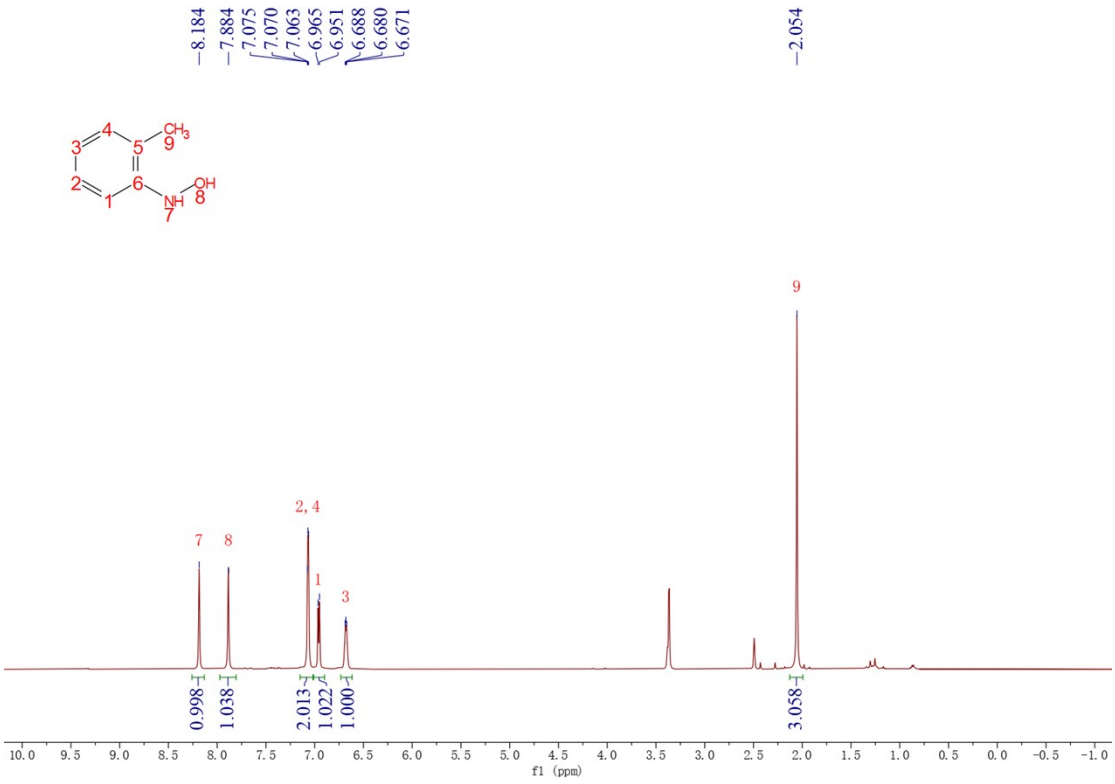
^{19}F NMR spectrum of compound 6a.



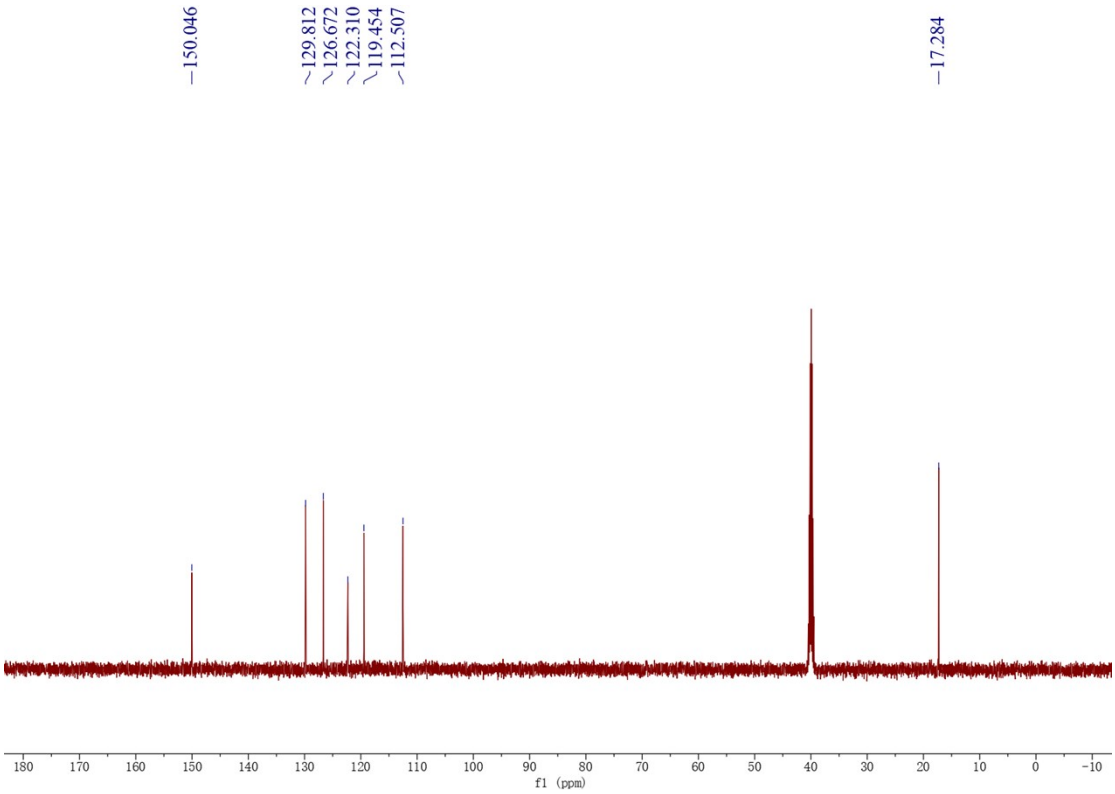
^{1}H NMR spectrum of compound 7a.



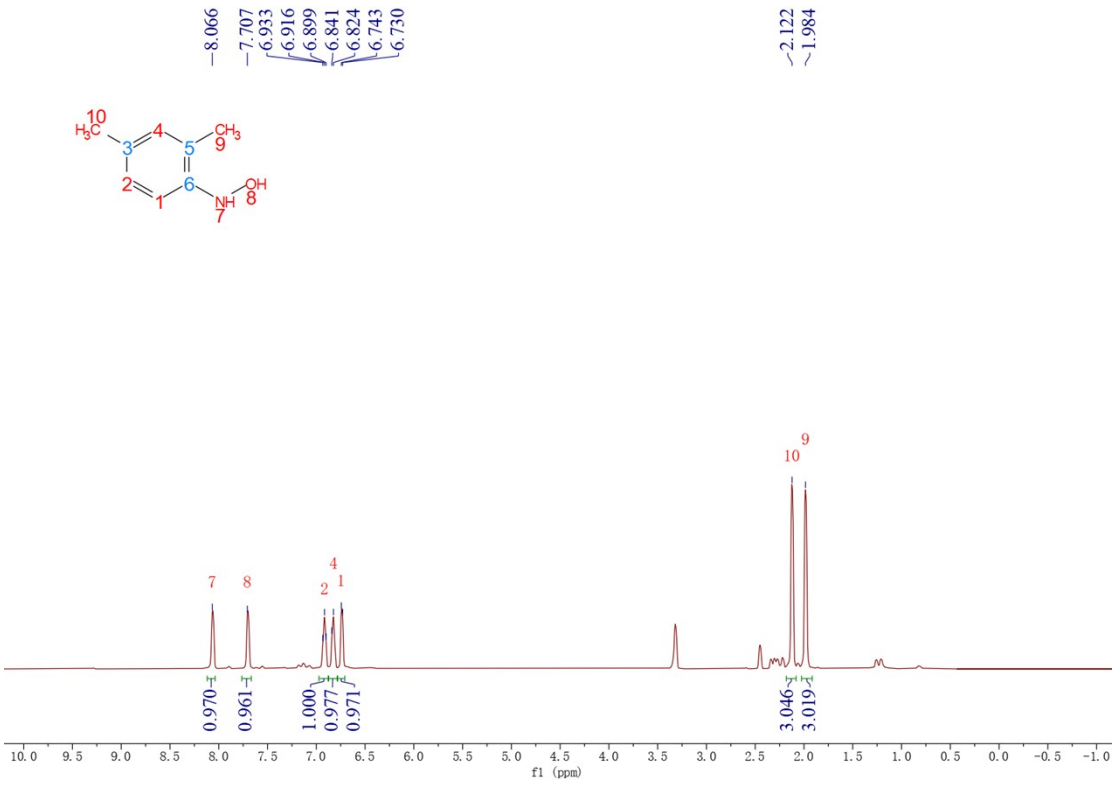
^{13}C NMR spectrum of compound 7a.



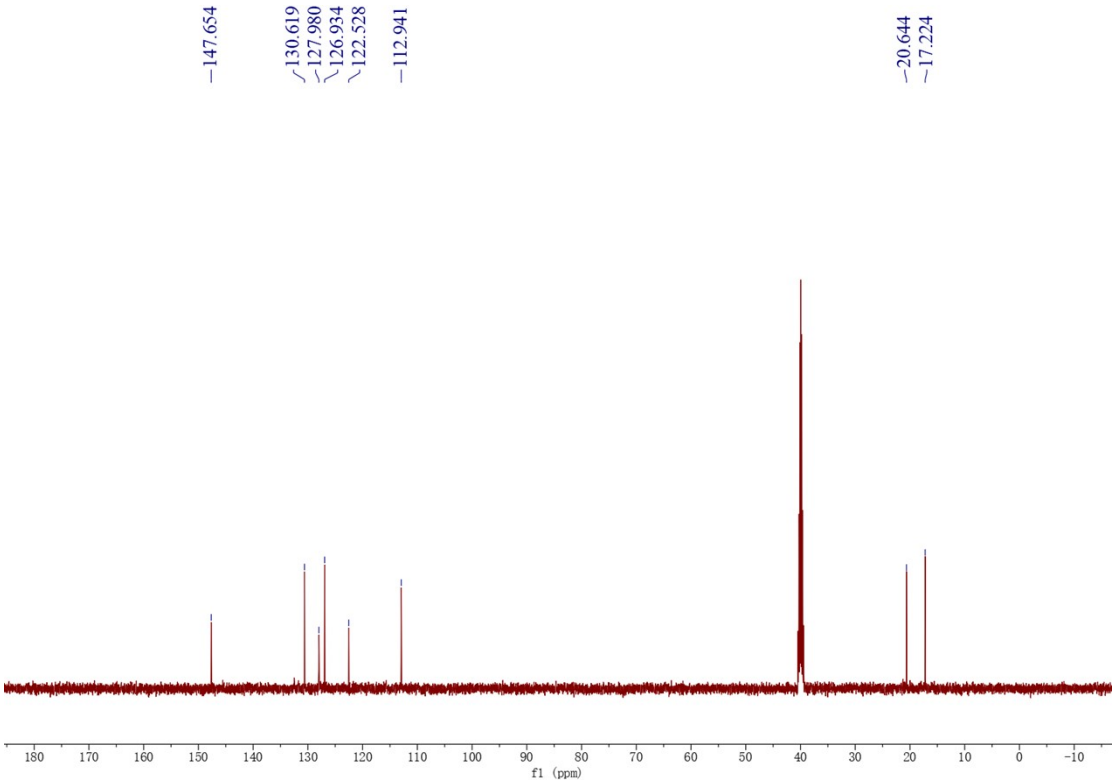
^{1}H NMR spectrum of compound 8a.



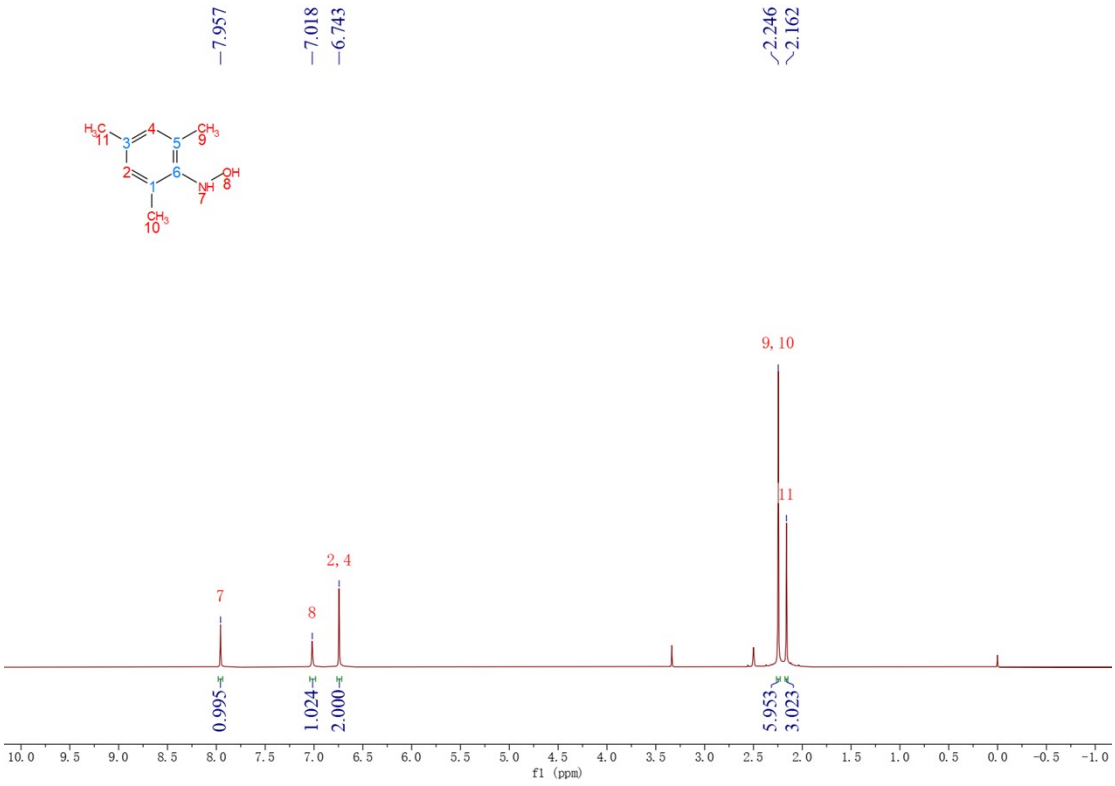
^{13}C NMR spectrum of compound 8a.



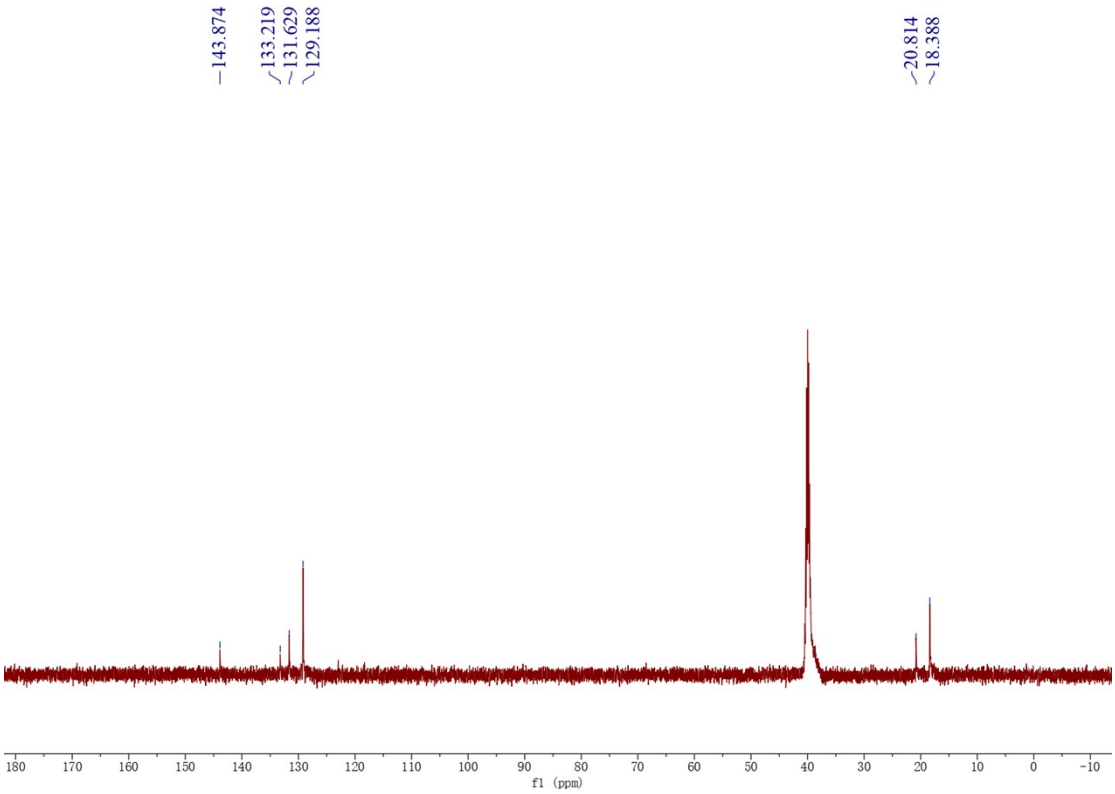
^{1}H NMR spectrum of compound 9a.



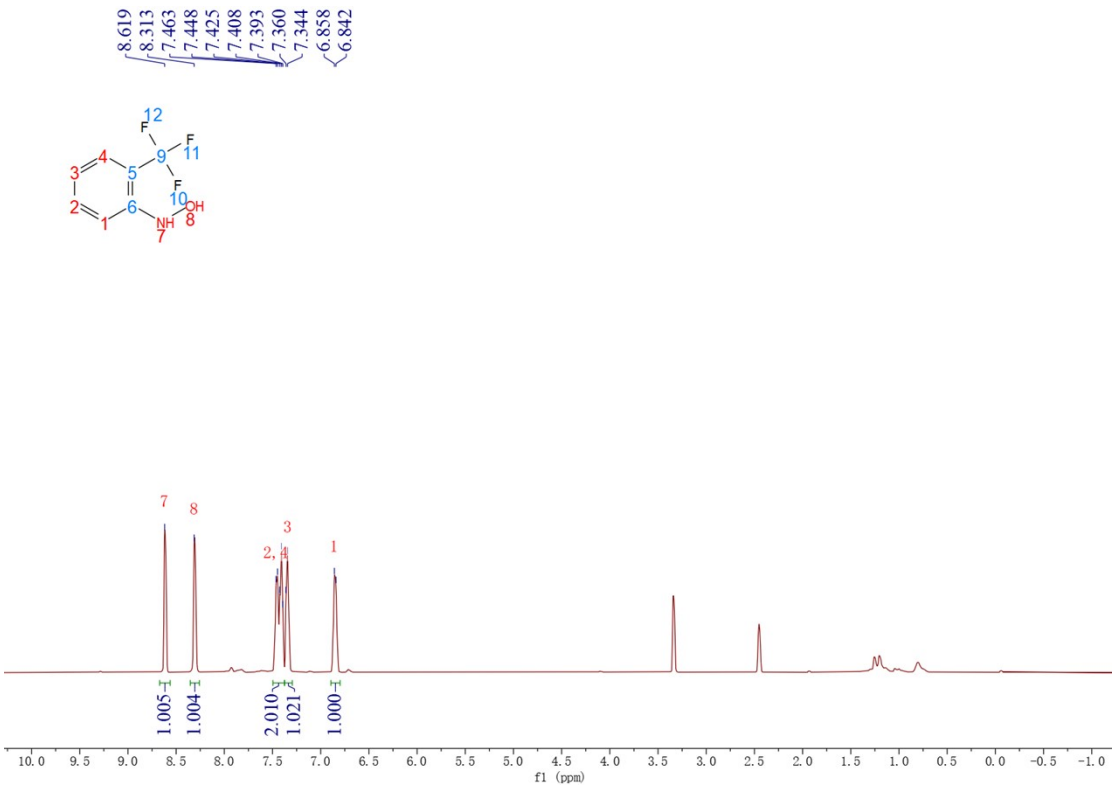
^{13}C NMR spectrum of compound 9a.



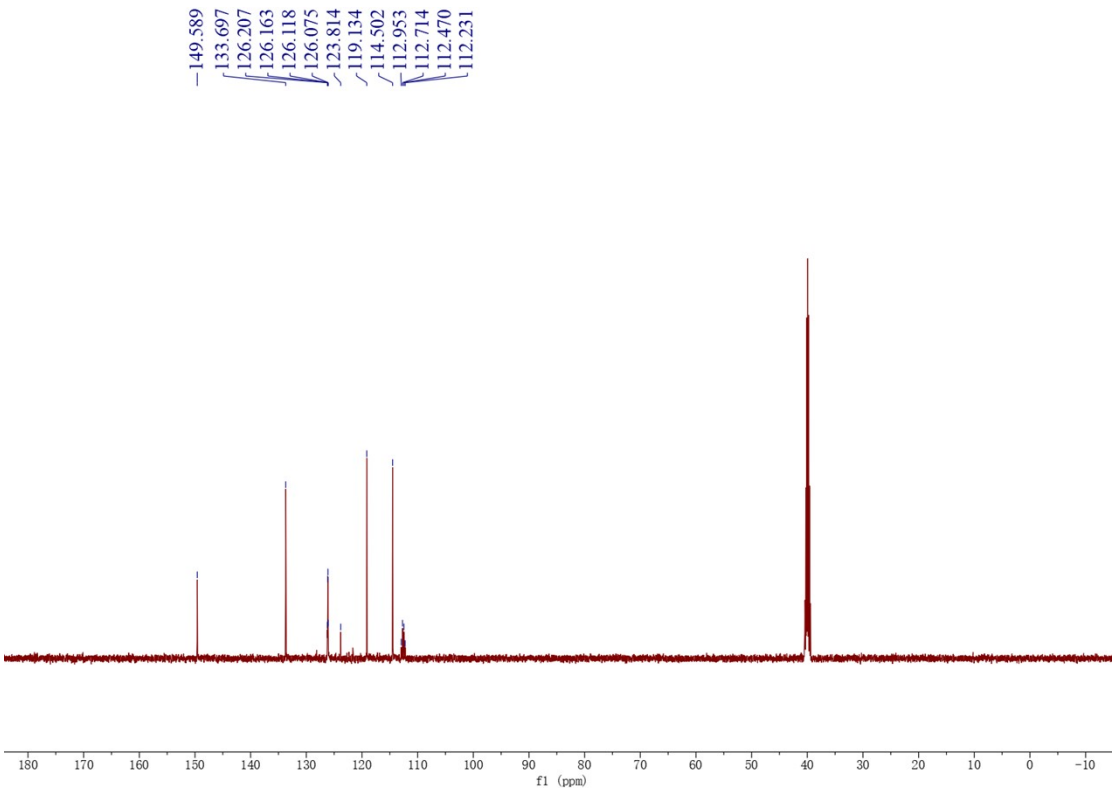
^{1}H NMR spectrum of compound 10a.



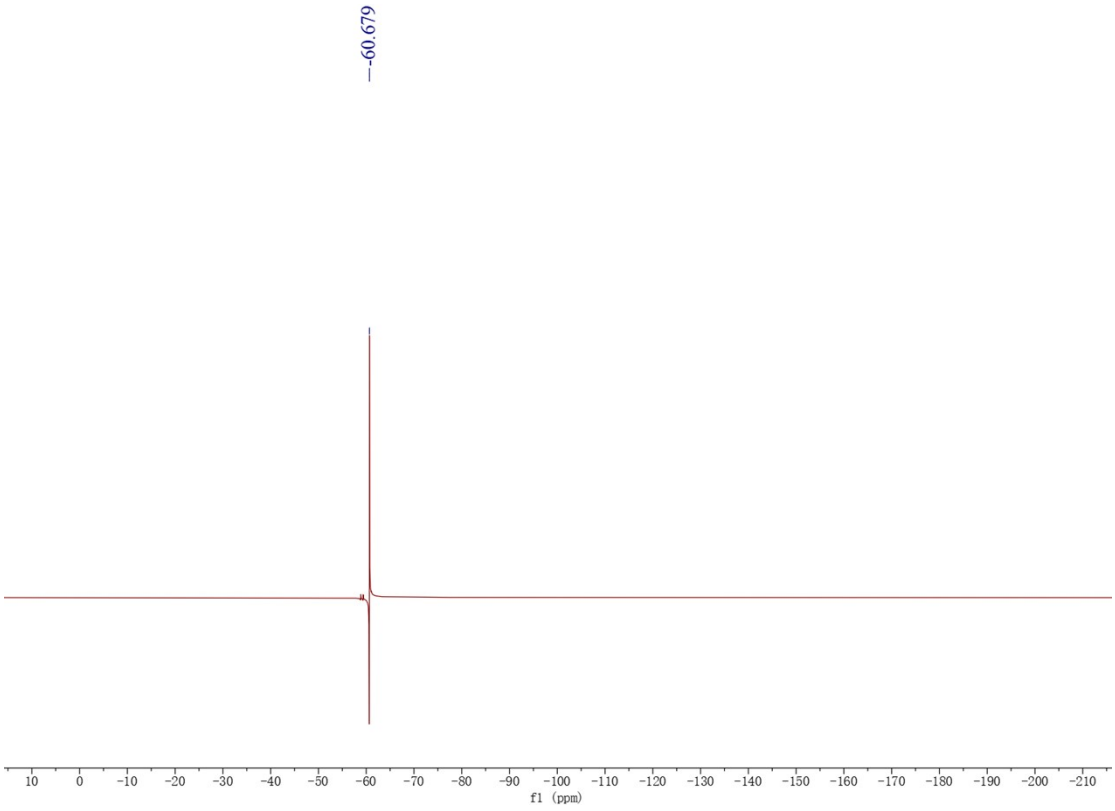
^{13}C NMR spectrum of compound 10a.



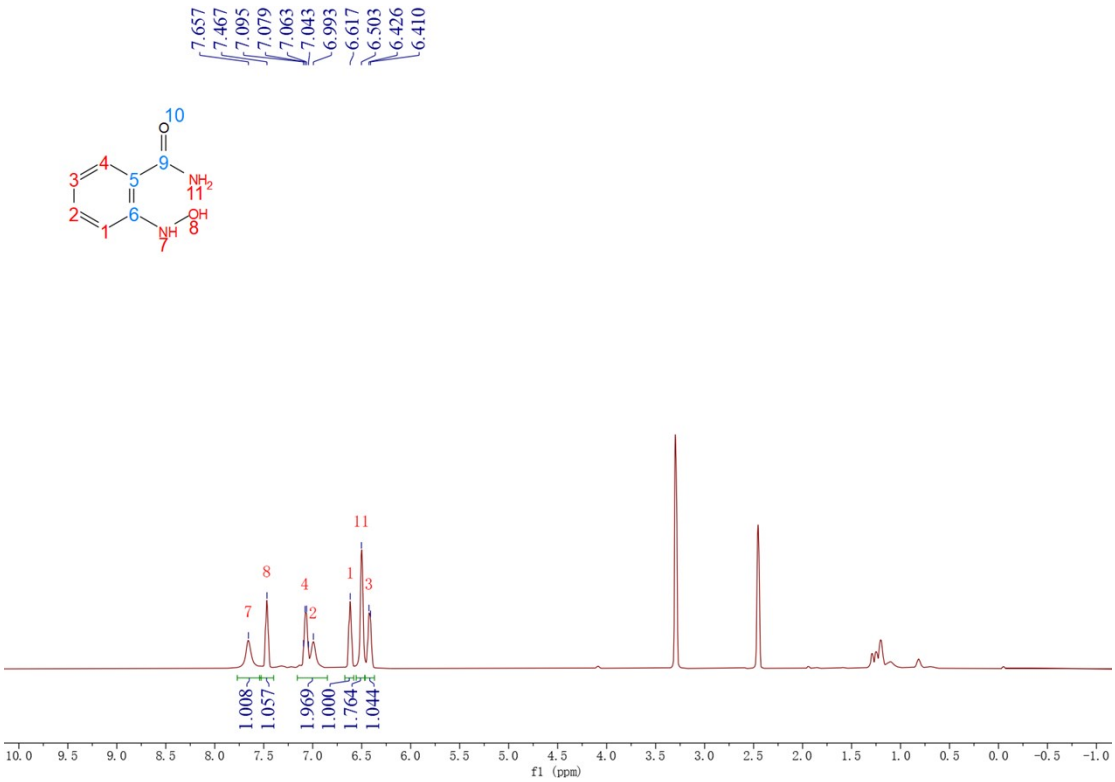
^{1}H NMR spectrum of compound 11a.



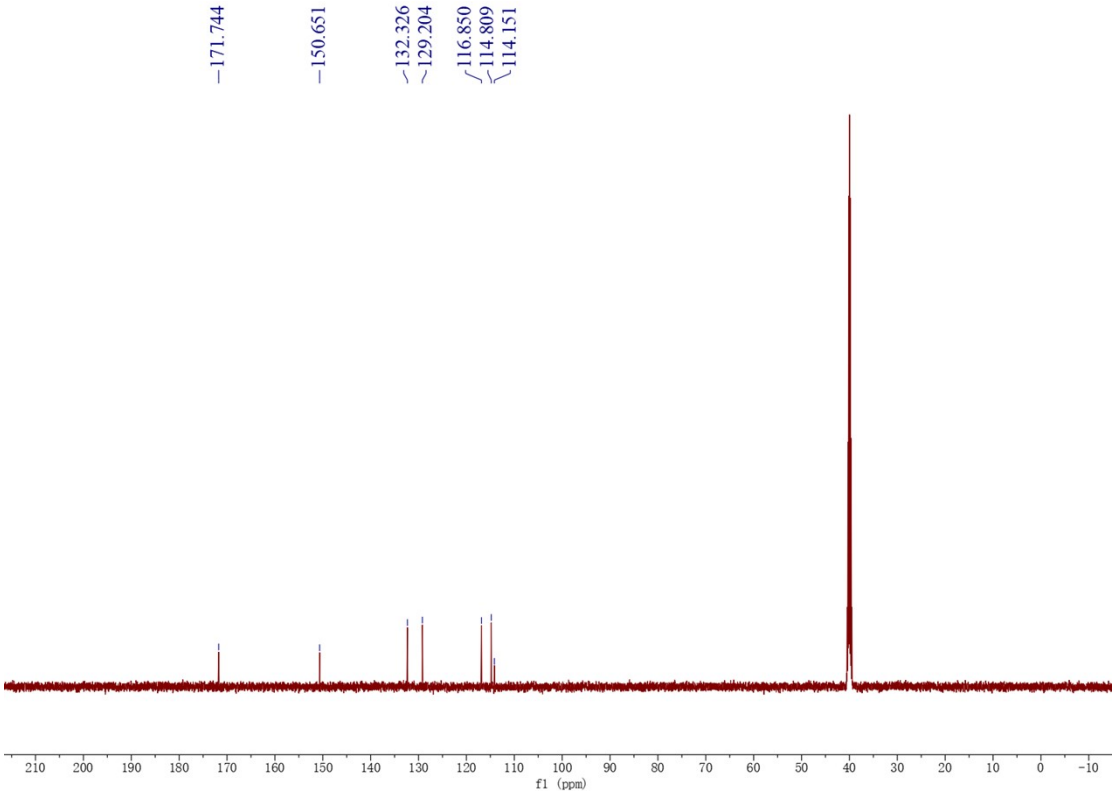
^{13}C NMR spectrum of compound 11a.



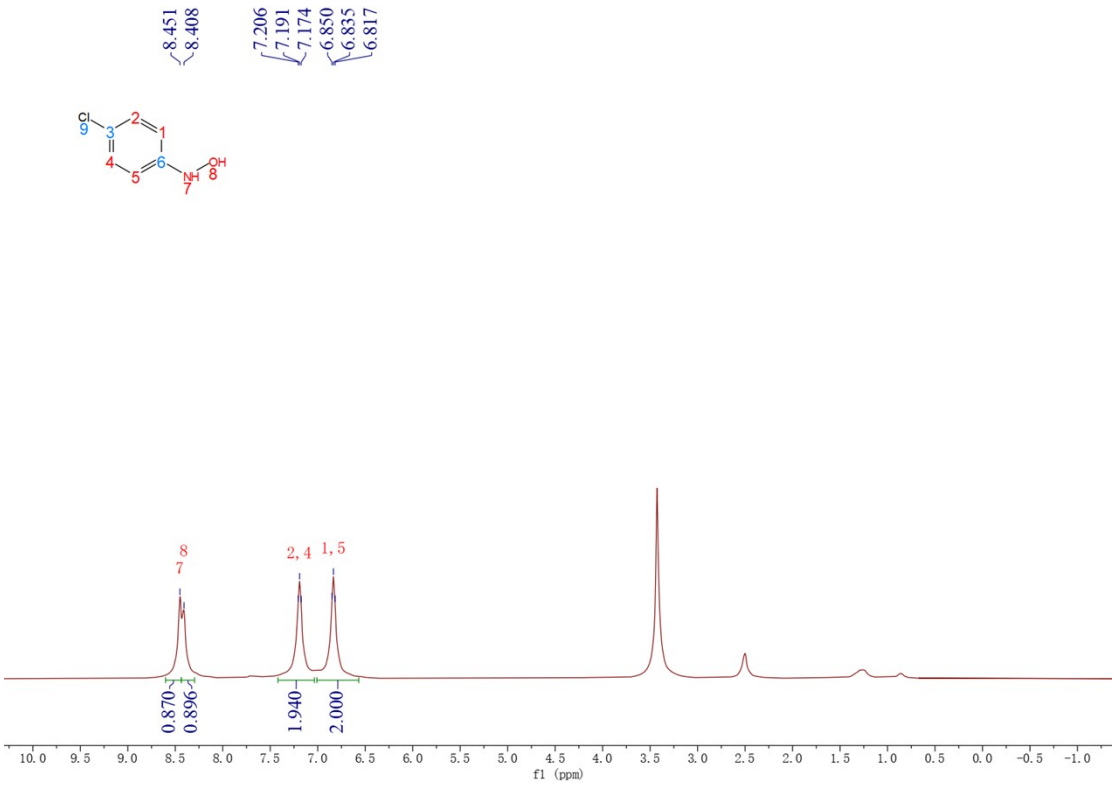
^{19}F NMR spectrum of compound 11a.



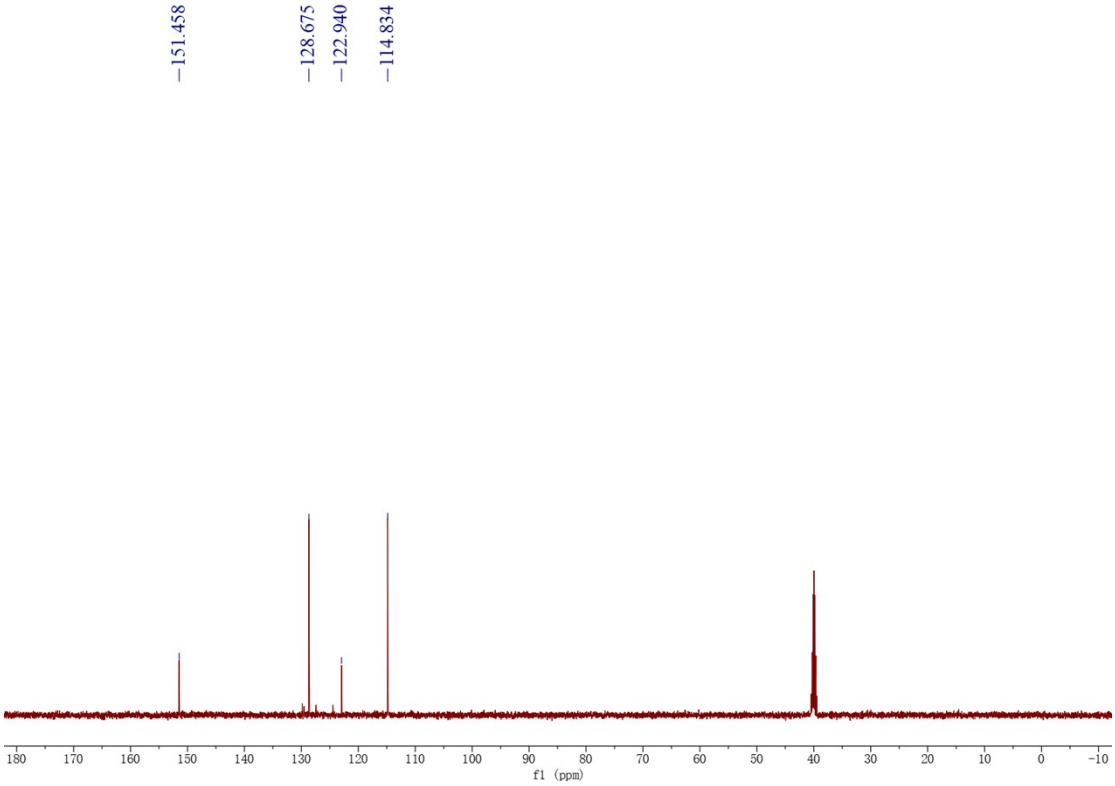
^{1}H NMR spectrum of compound 12a.



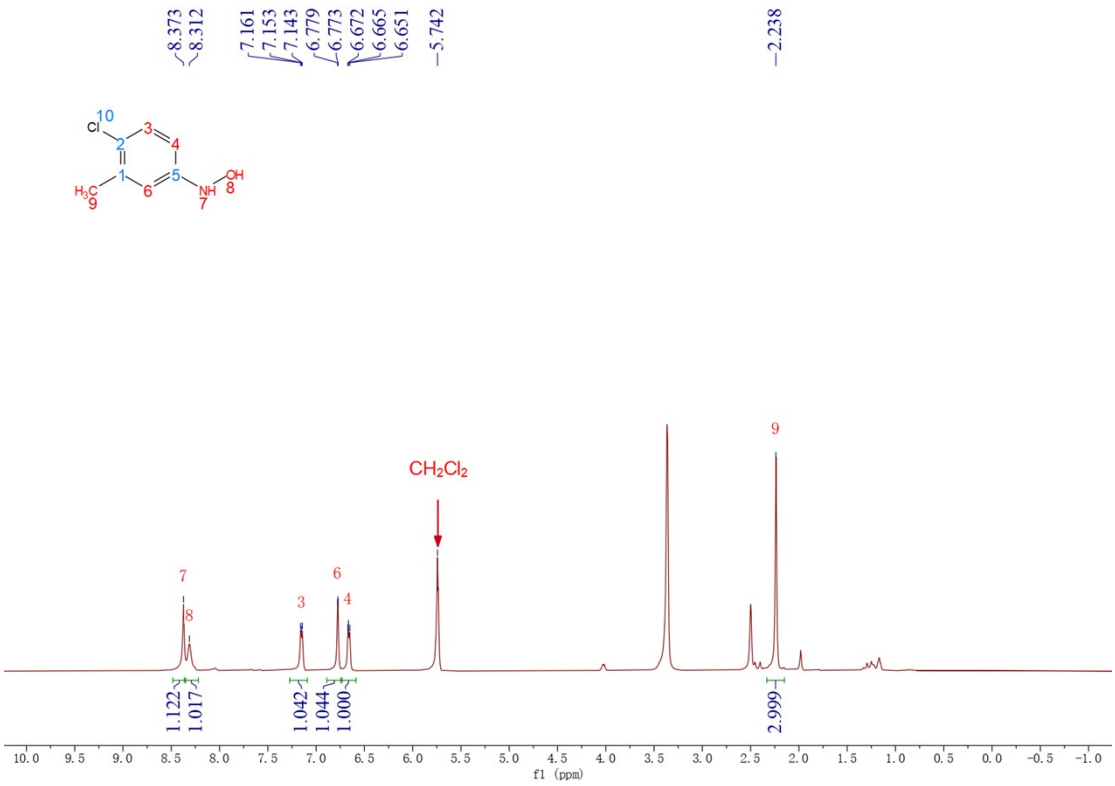
^{13}C NMR spectrum of compound 12a.



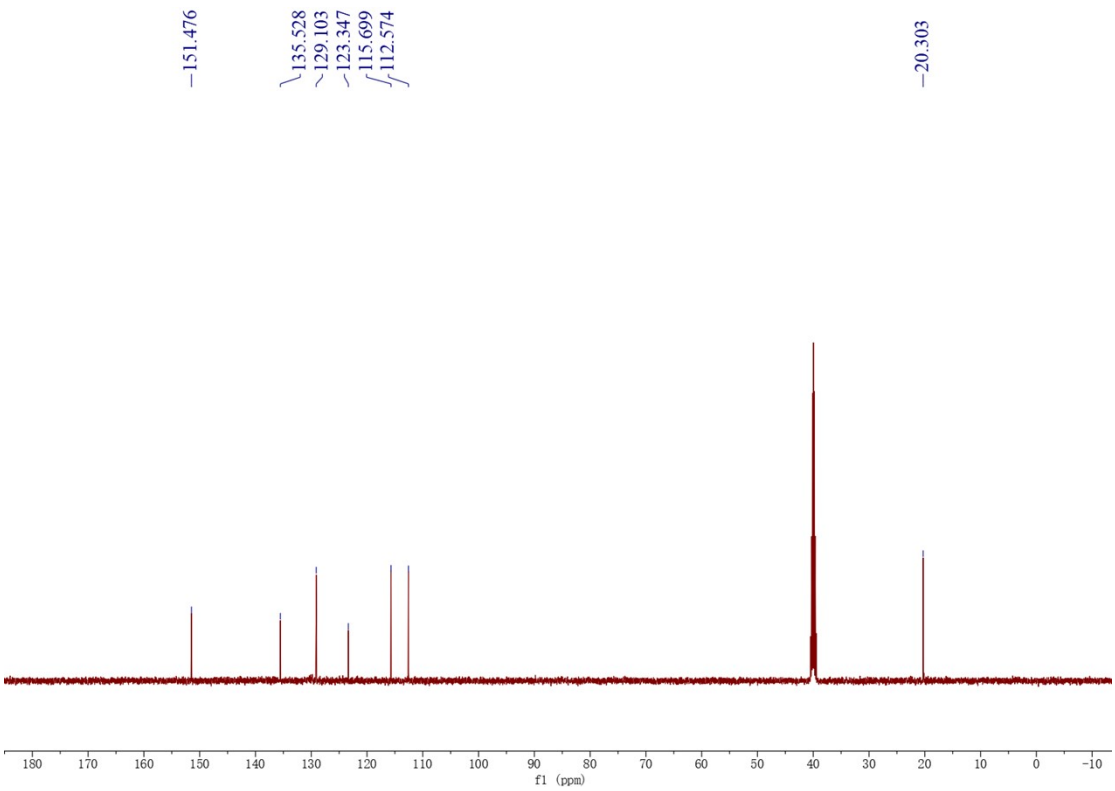
^{1}H NMR spectrum of compound 13a.



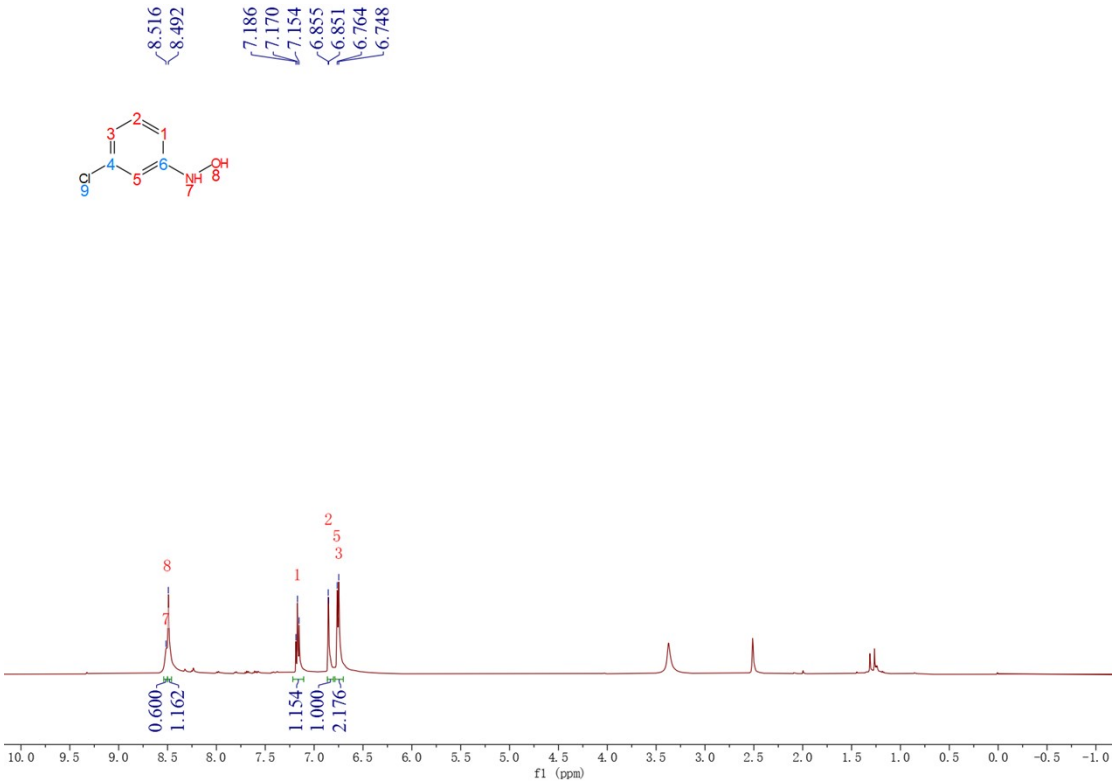
^{13}C NMR spectrum of compound 13a.



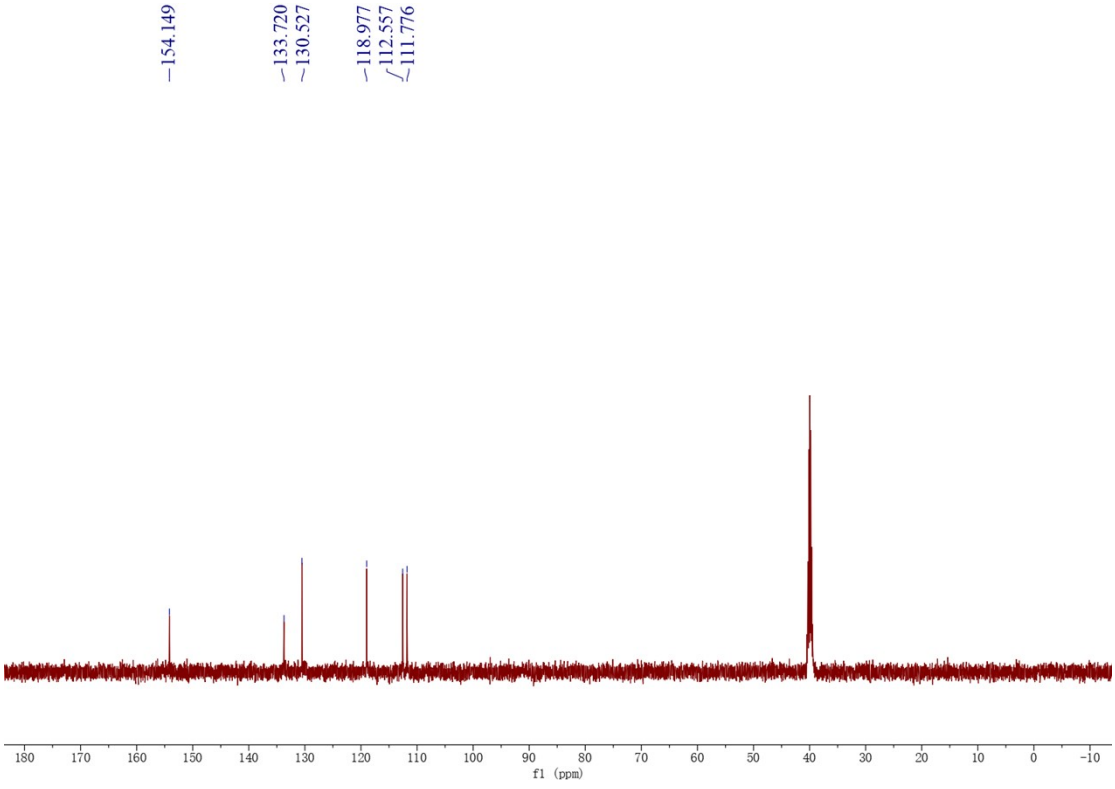
^{1}H NMR spectrum of compound 14a.



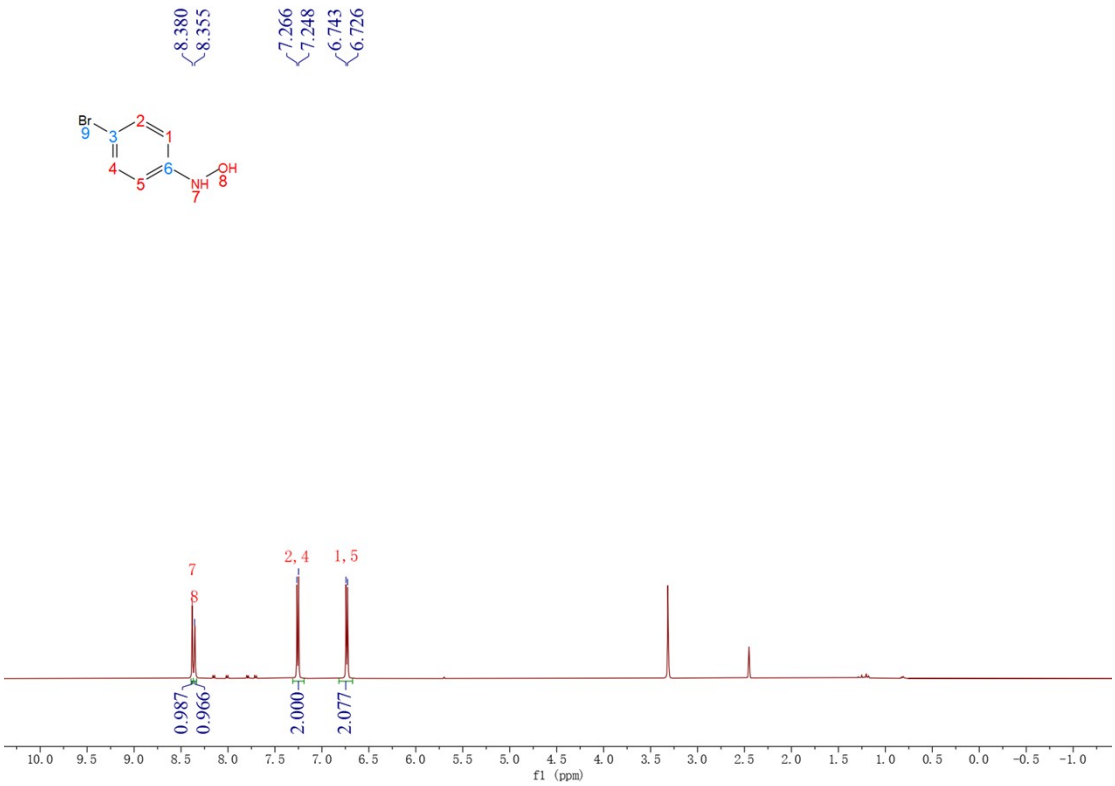
^{13}C NMR spectrum of compound 14a.



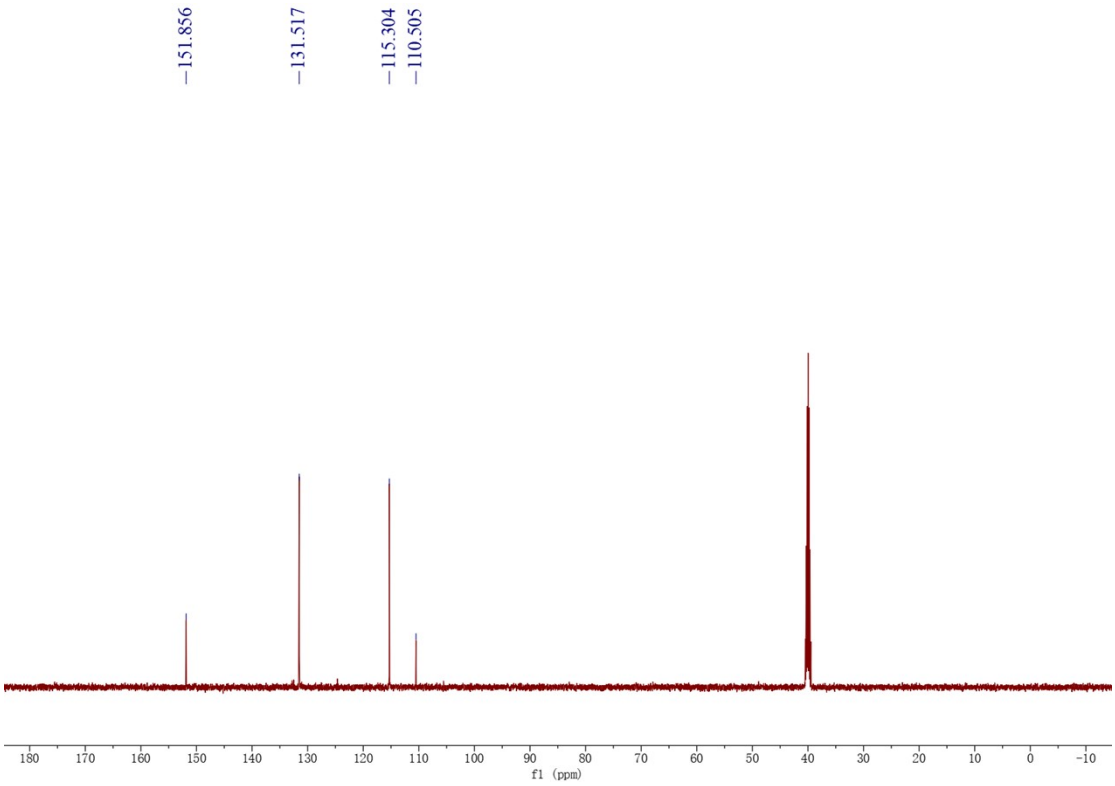
^{1}H NMR spectrum of compound 15a.



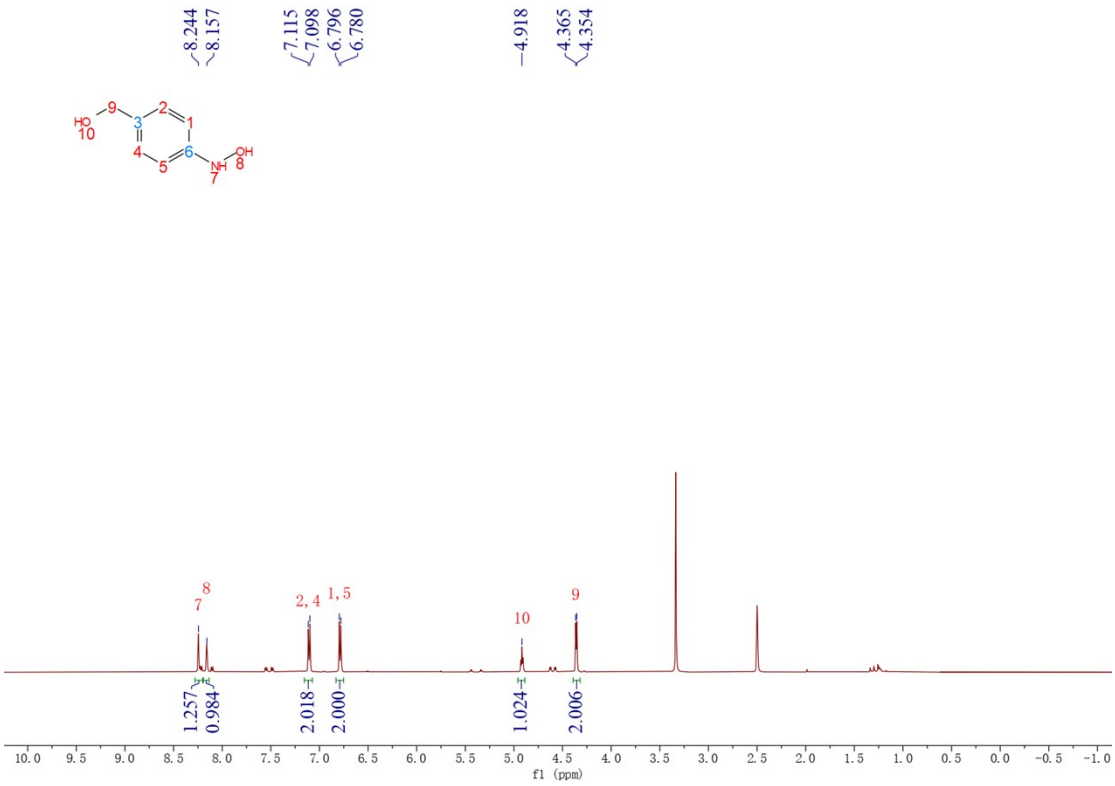
^{13}C NMR spectrum of compound 15a.



^{1}H NMR spectrum of compound 16a.



^{13}C NMR spectrum of compound 16a.



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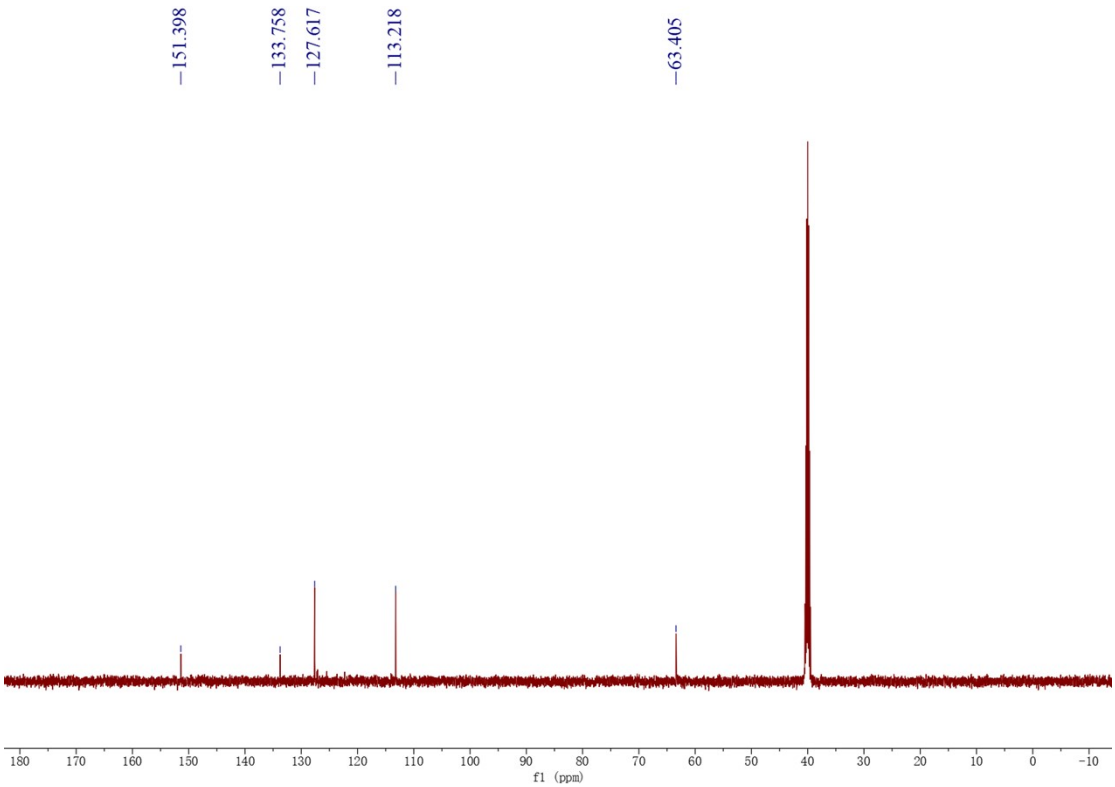
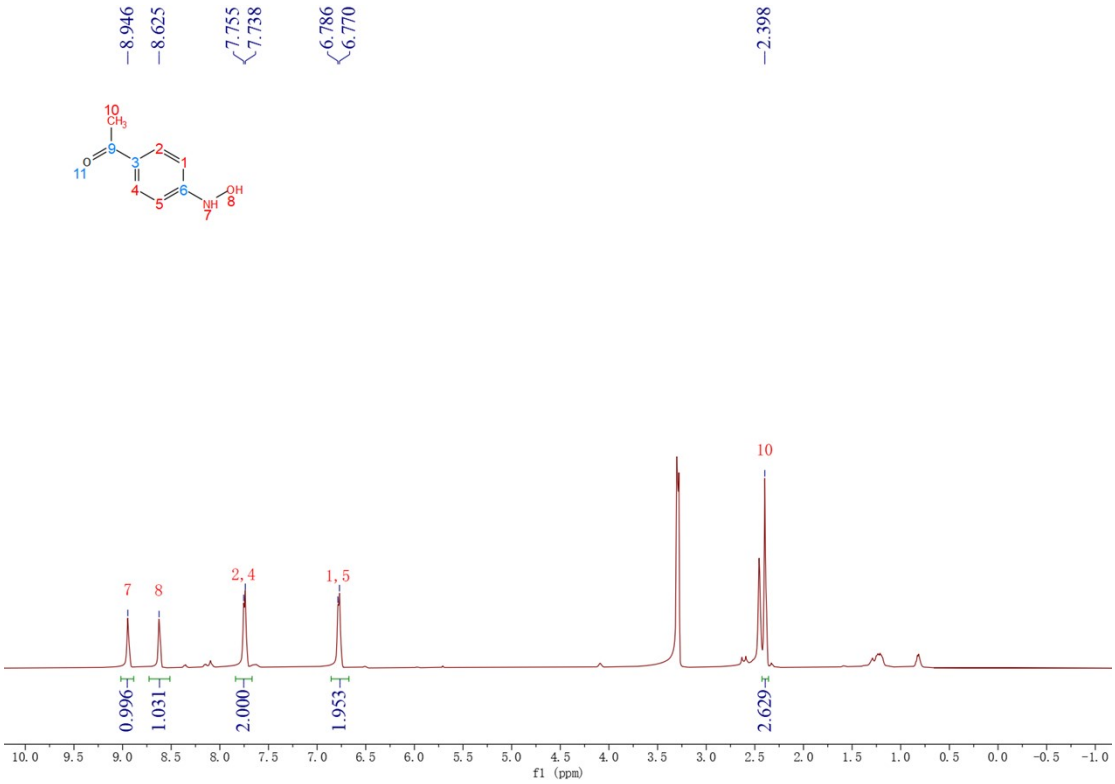


^{13}C NMR spectrum of compound 17a.



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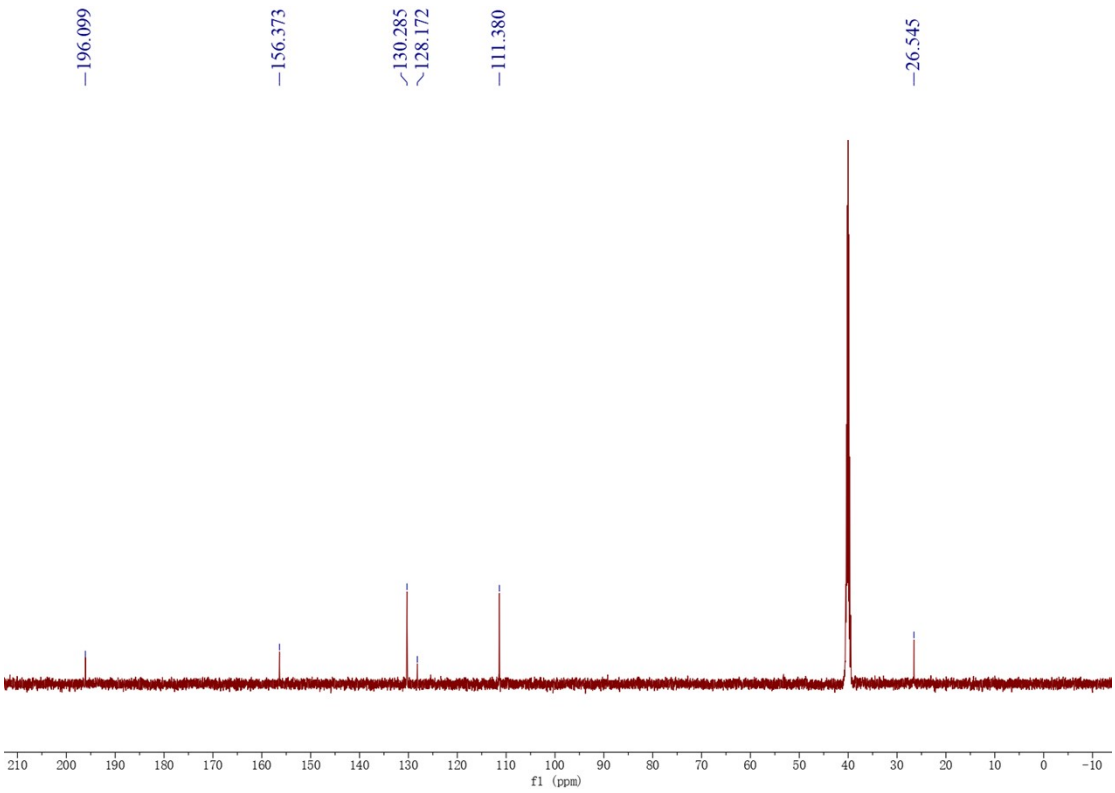

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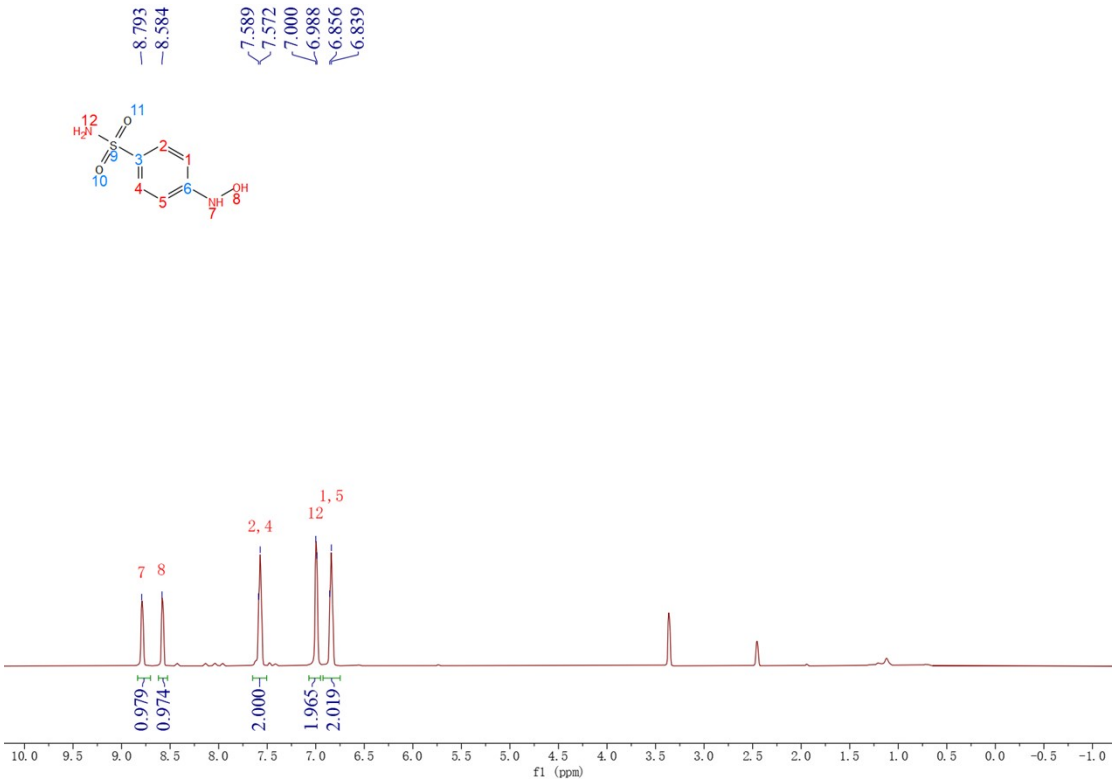
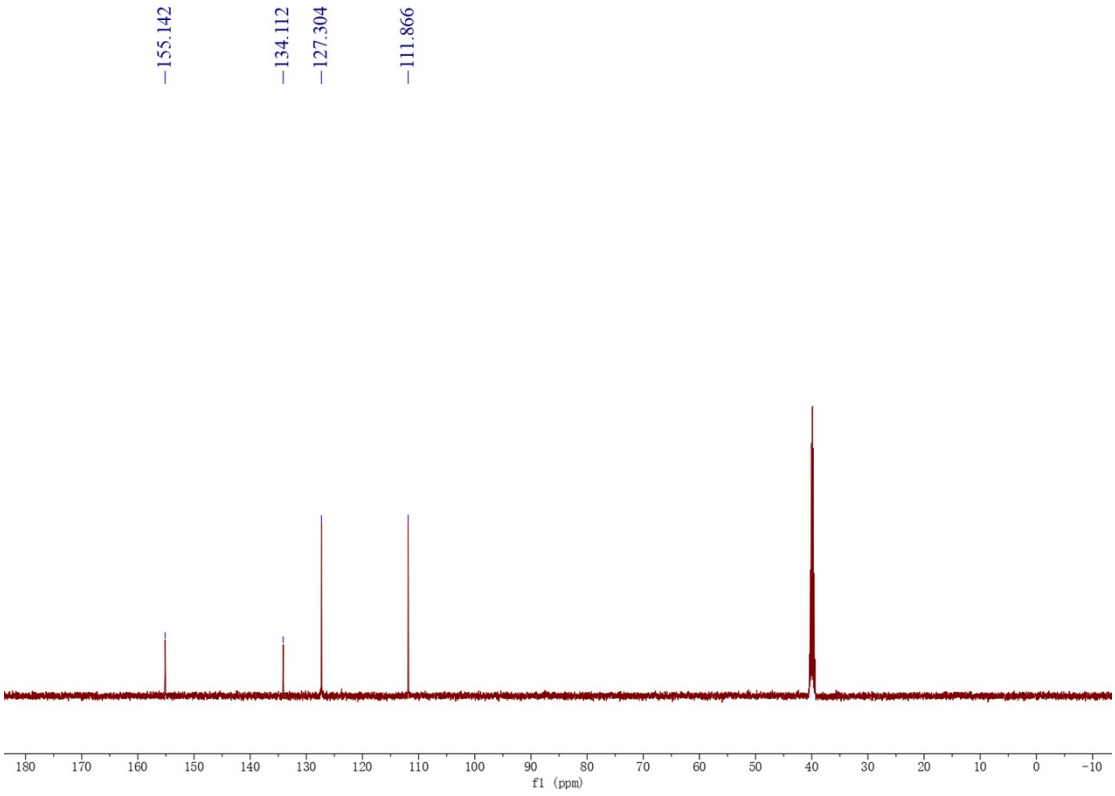
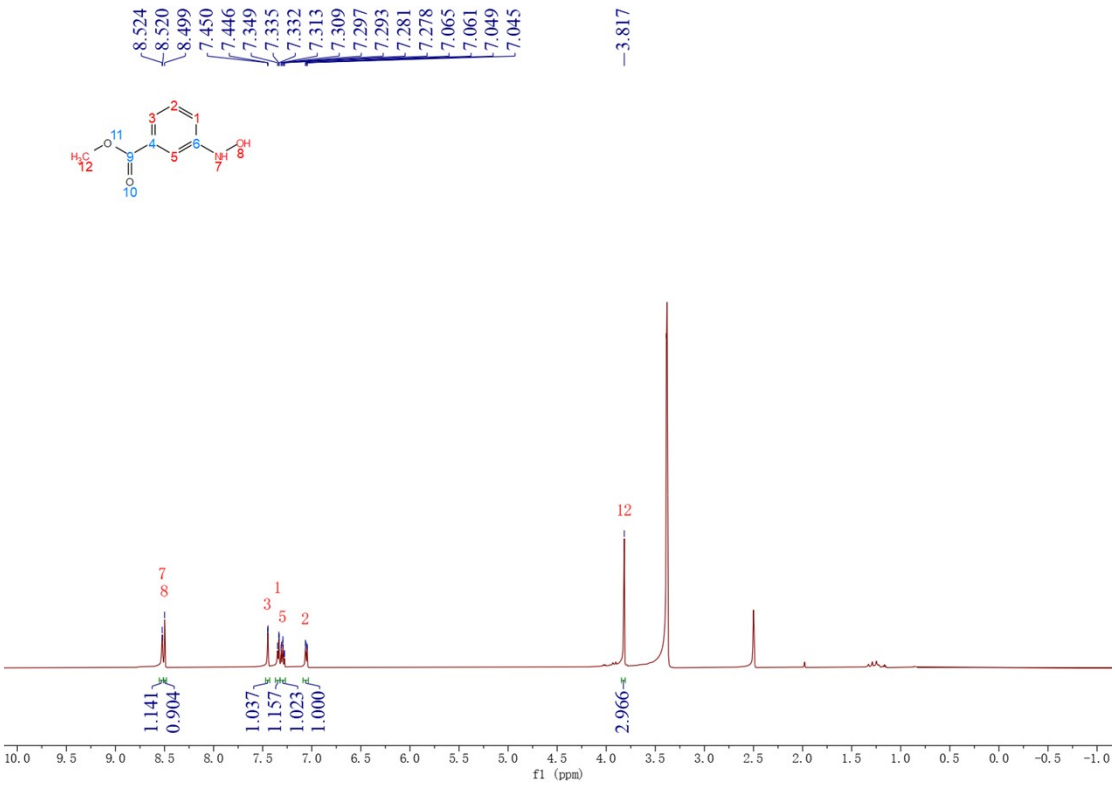


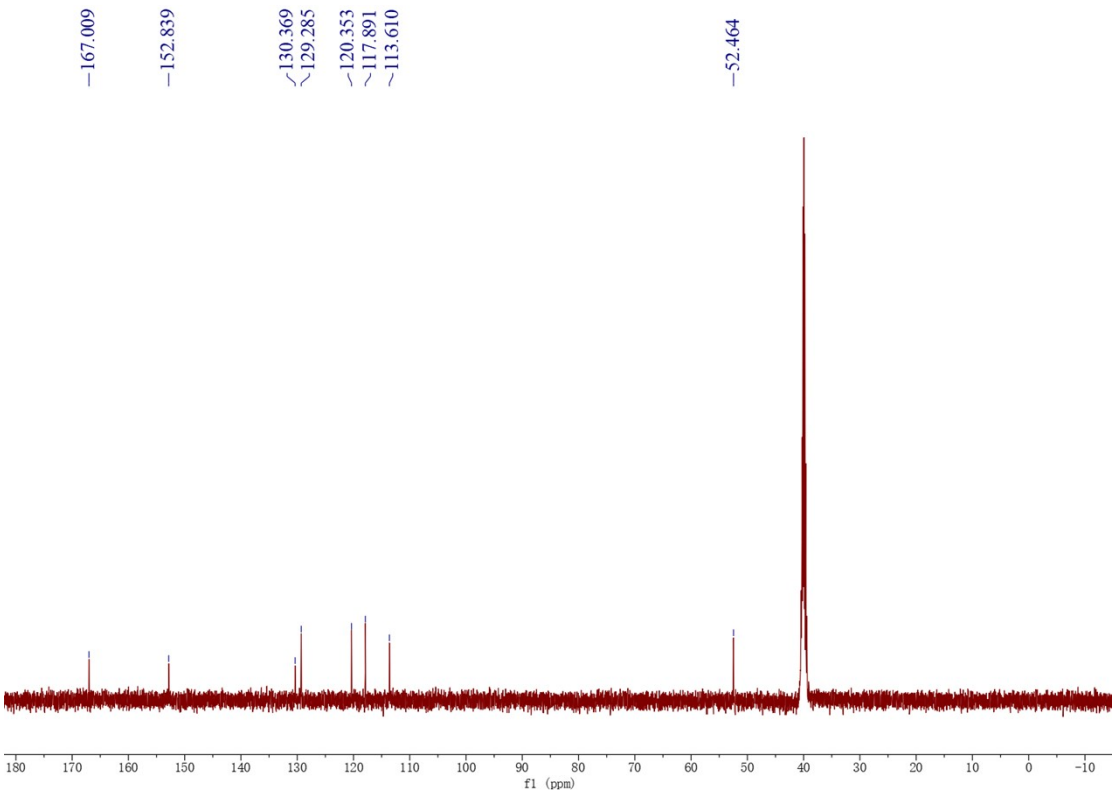
^{1}H NMR spectrum of compound 19a.



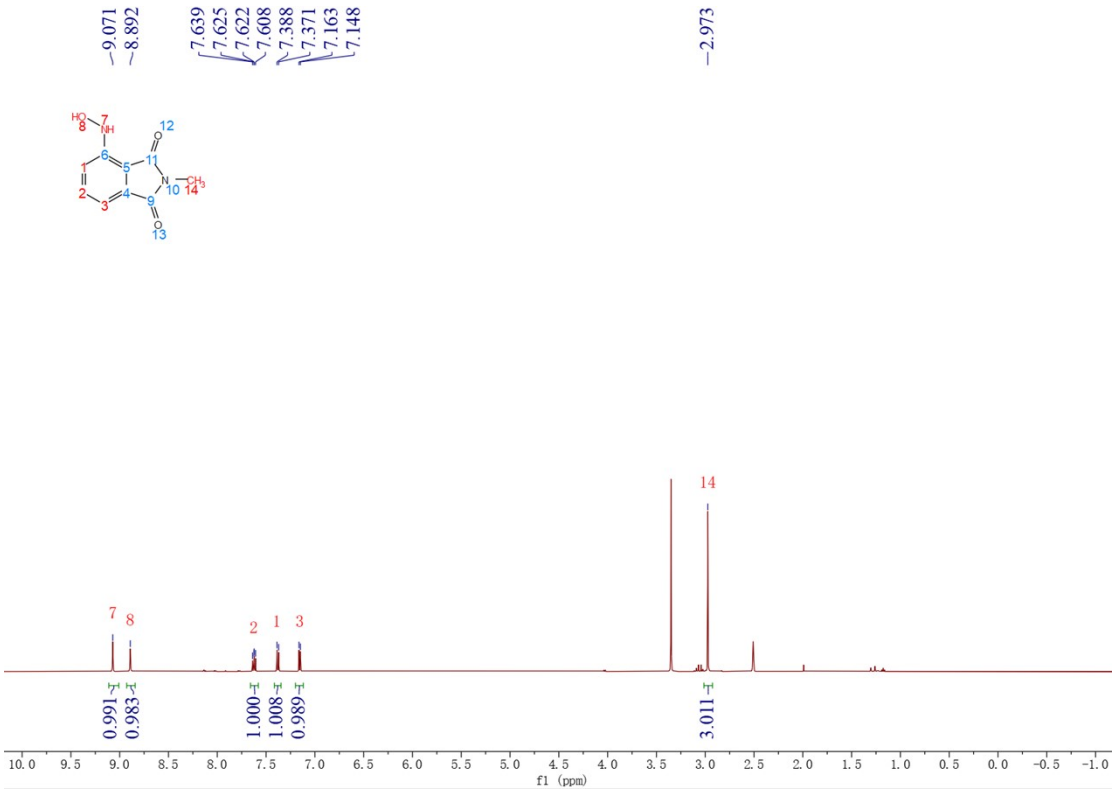
^{13}C NMR spectrum of compound 19a.



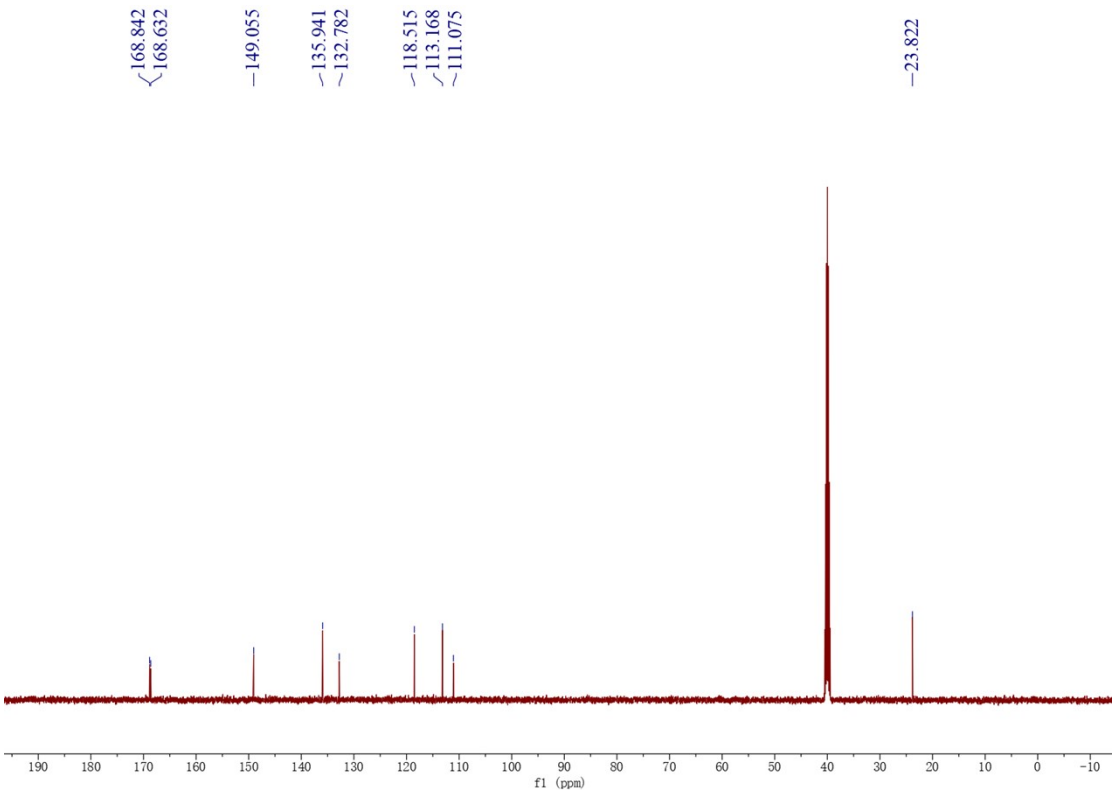
^{1}H NMR spectrum of compound 20a.



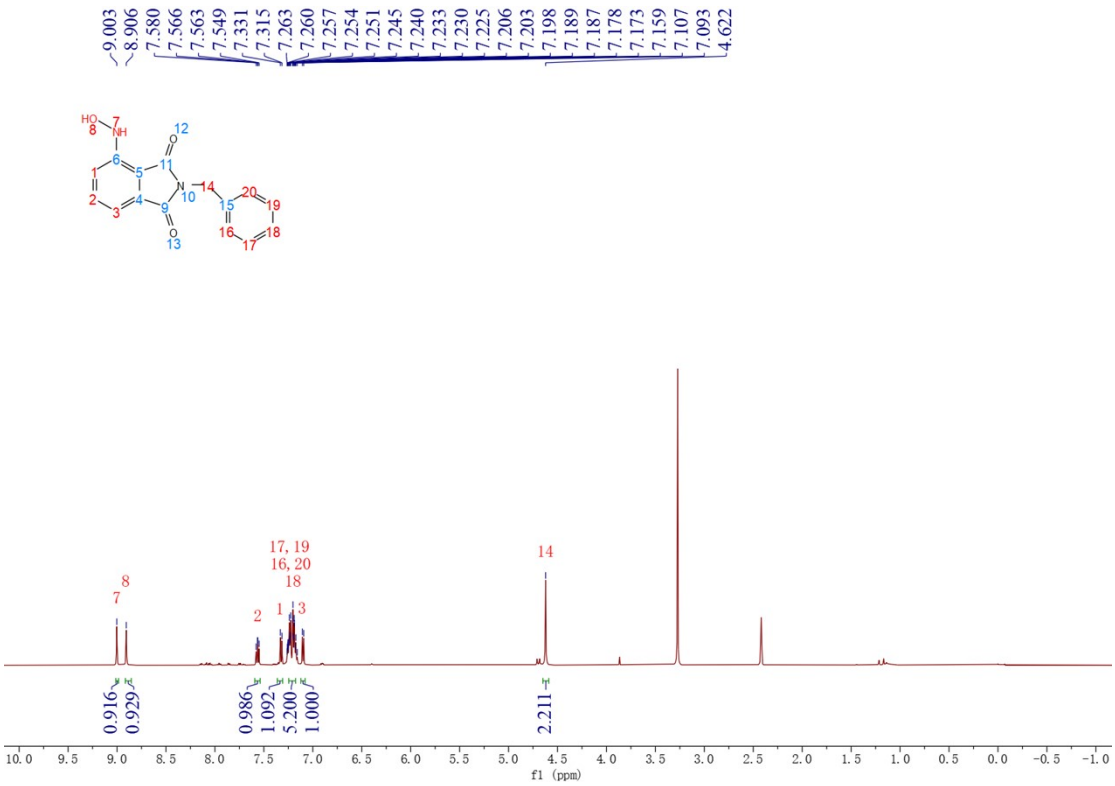
^{13}C NMR spectrum of compound 20a.



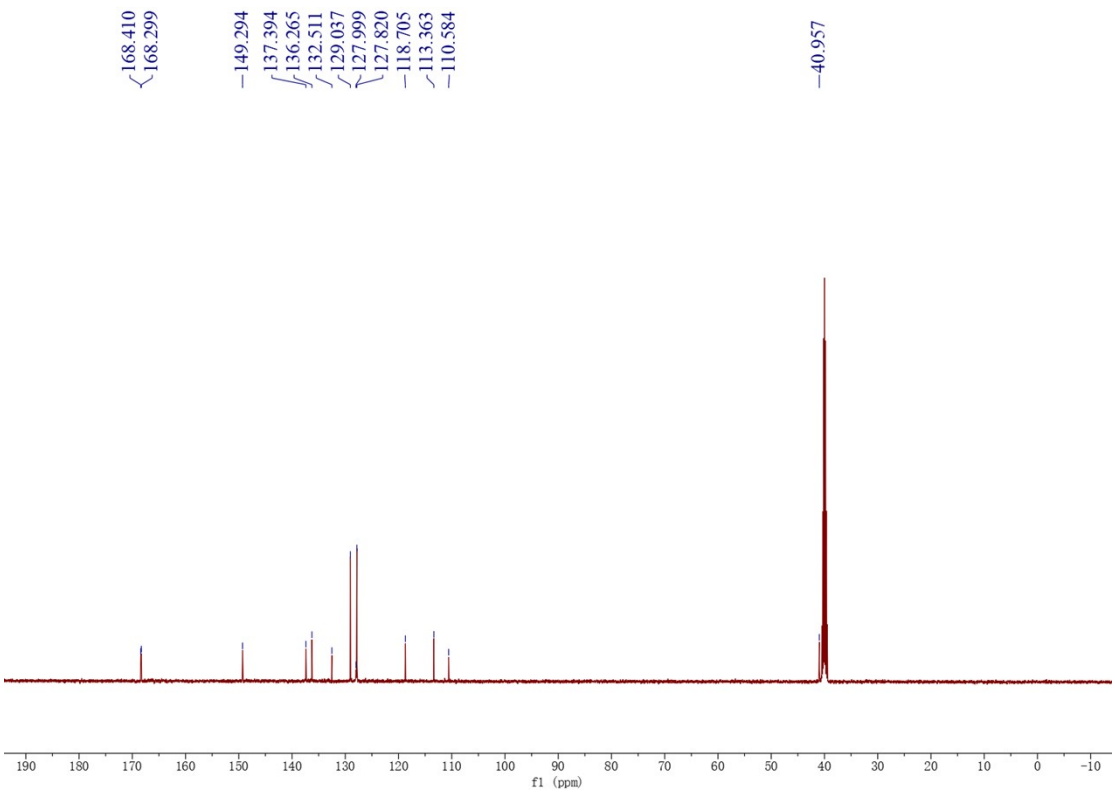
^{1}H NMR spectrum of compound 21a.



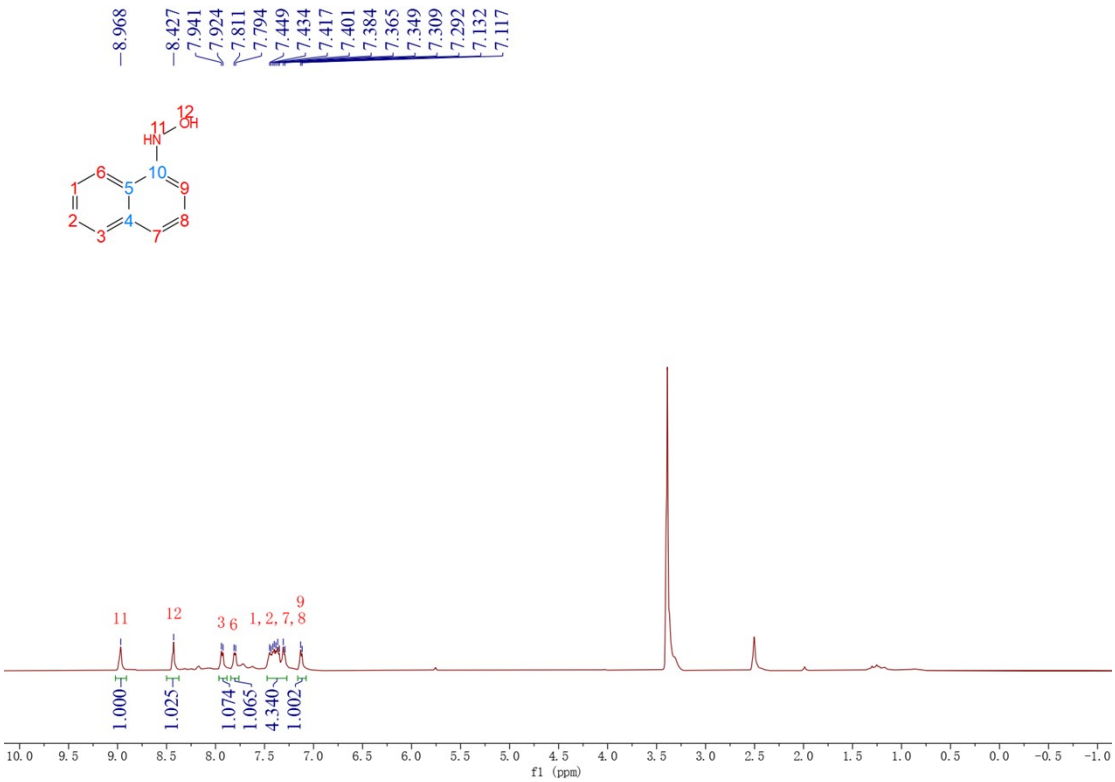
^{13}C NMR spectrum of compound 21a.



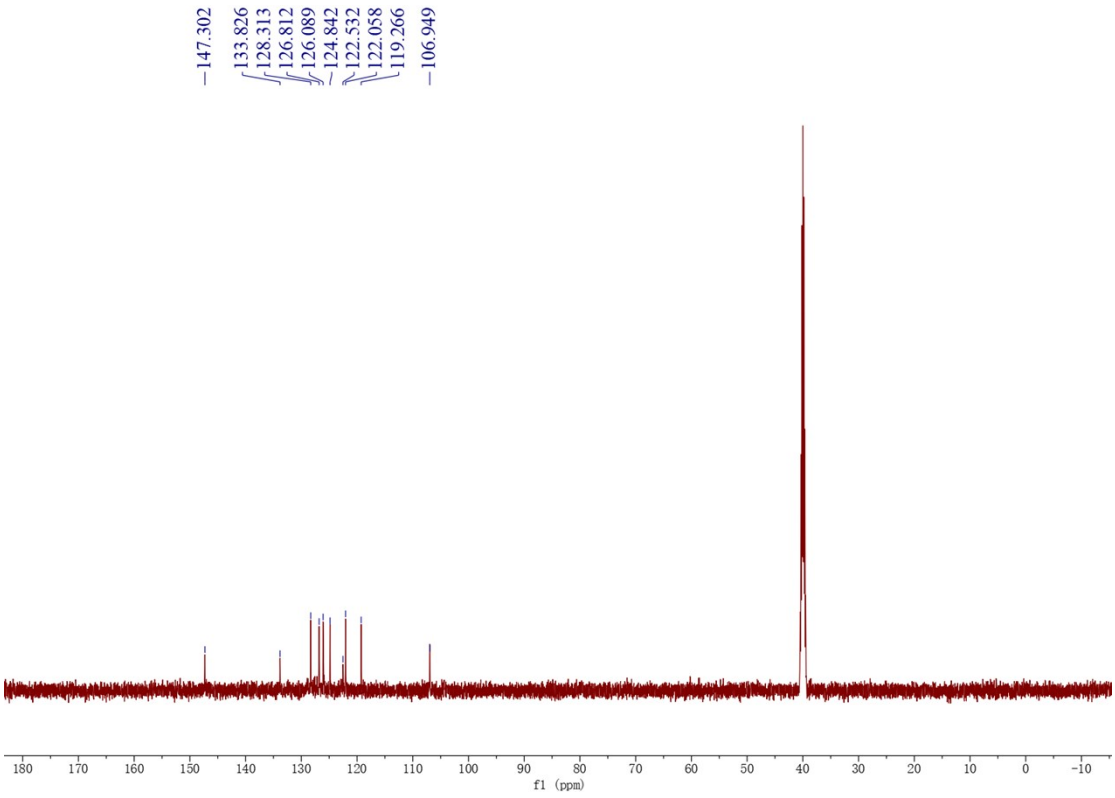
^{1}H NMR spectrum of compound 22a.



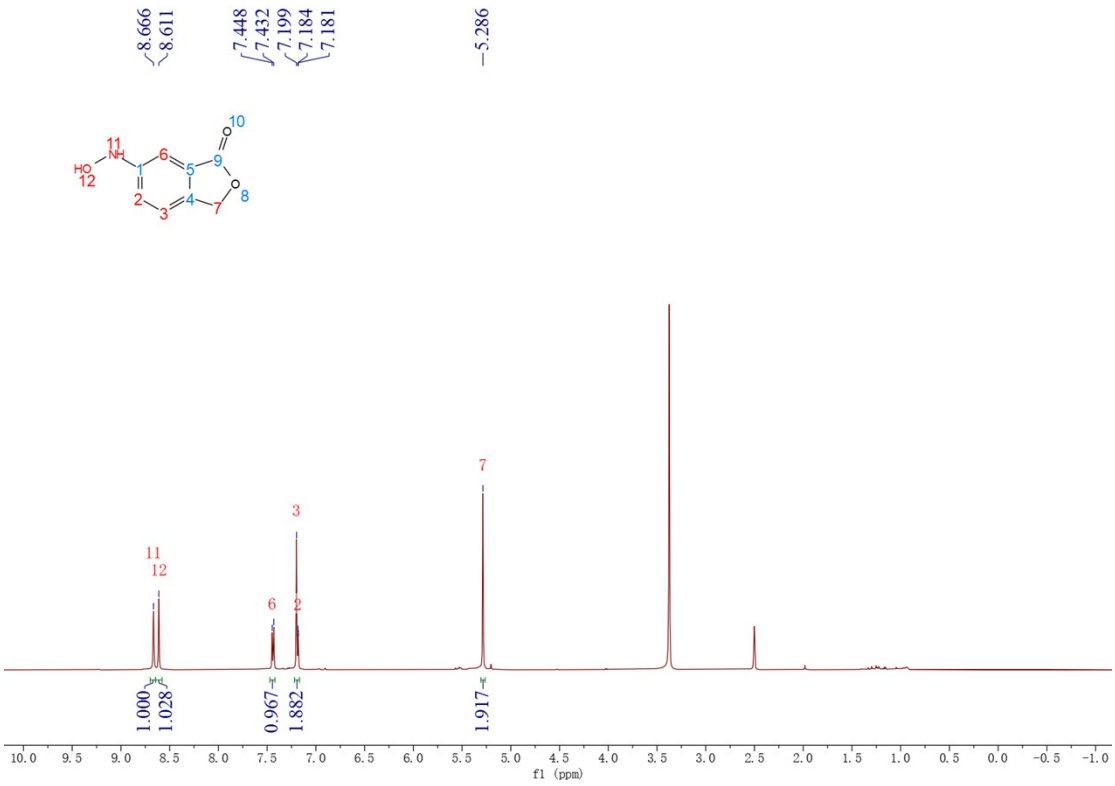
^{13}C NMR spectrum of compound 22a.



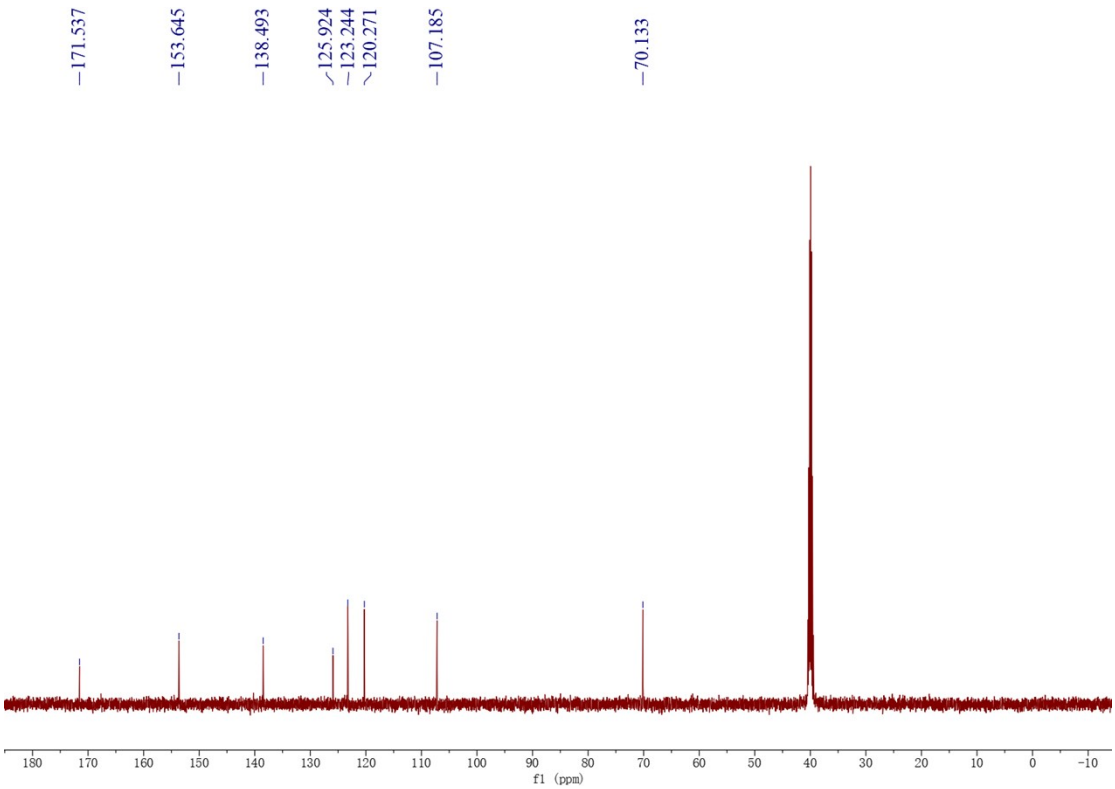
^{1}H NMR spectrum of compound 23a.



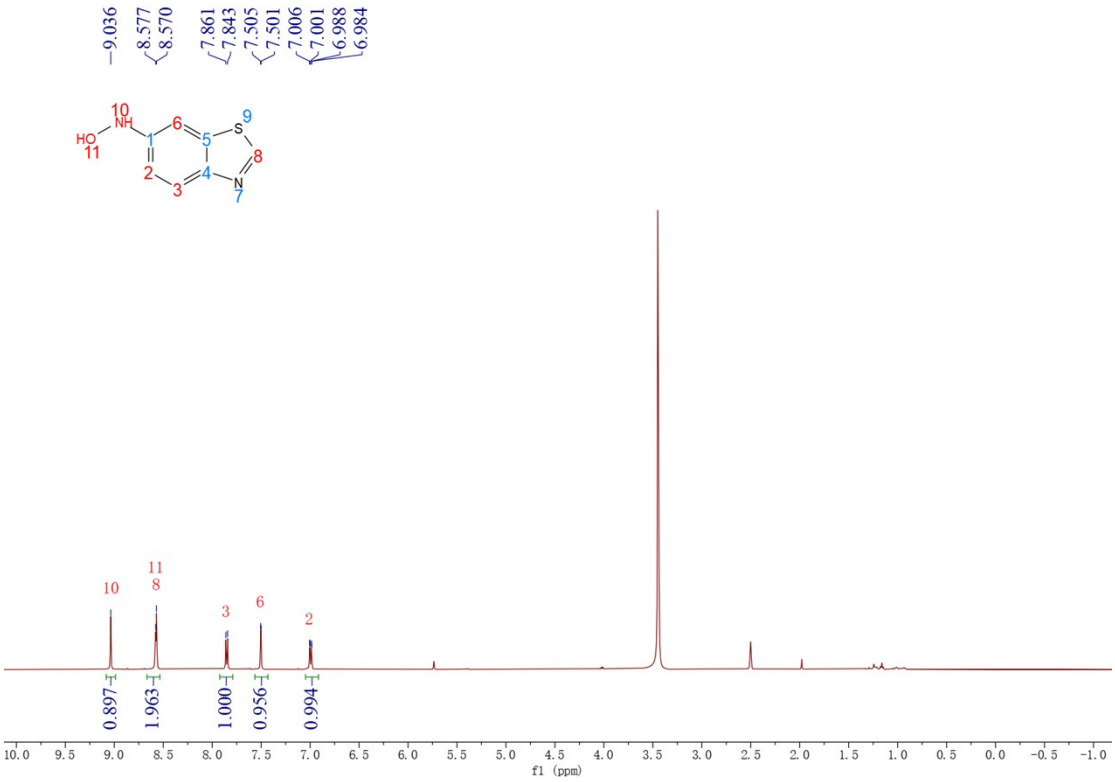
^{13}C NMR spectrum of compound 23a.



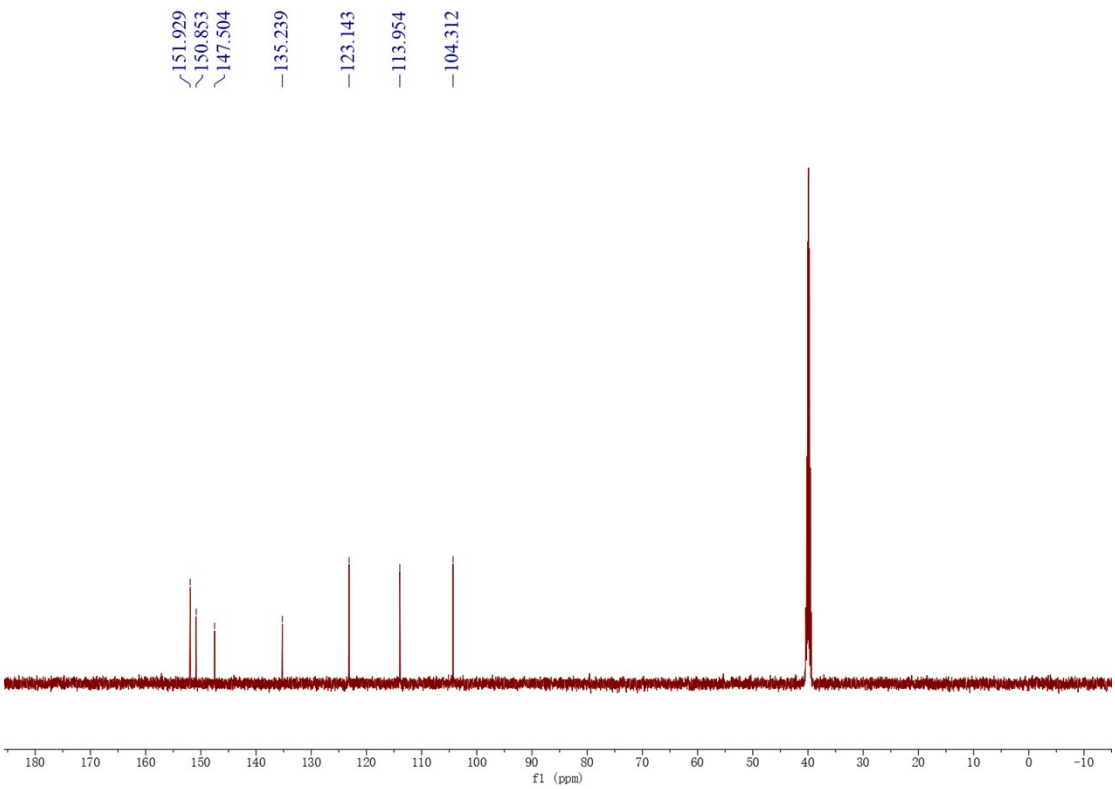
^{1}H NMR spectrum of compound 24a.



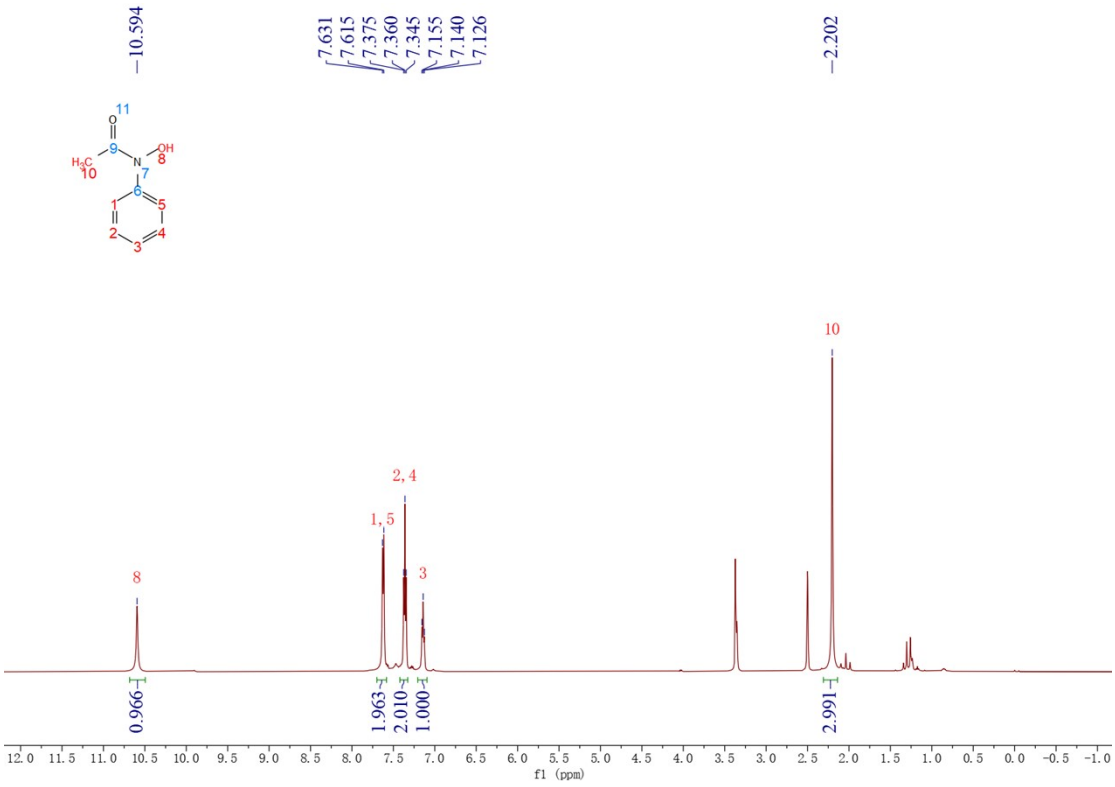
^{13}C NMR spectrum of compound 24a.



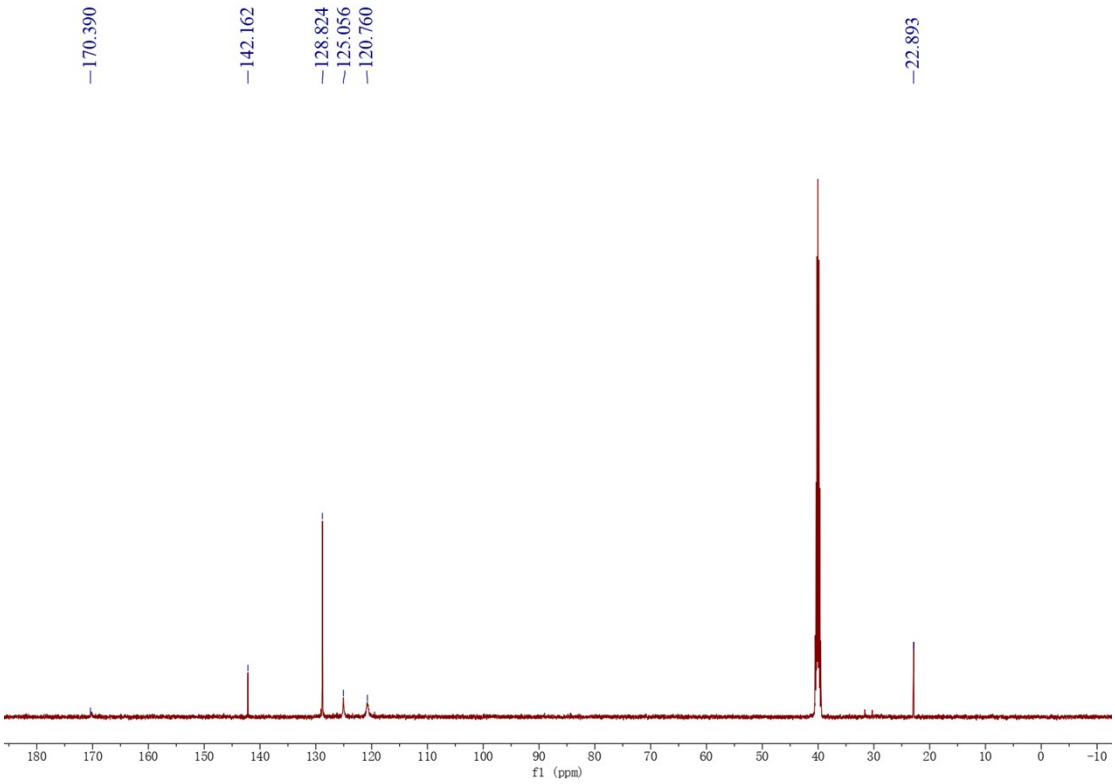
^{1}H NMR spectrum of compound 25a.



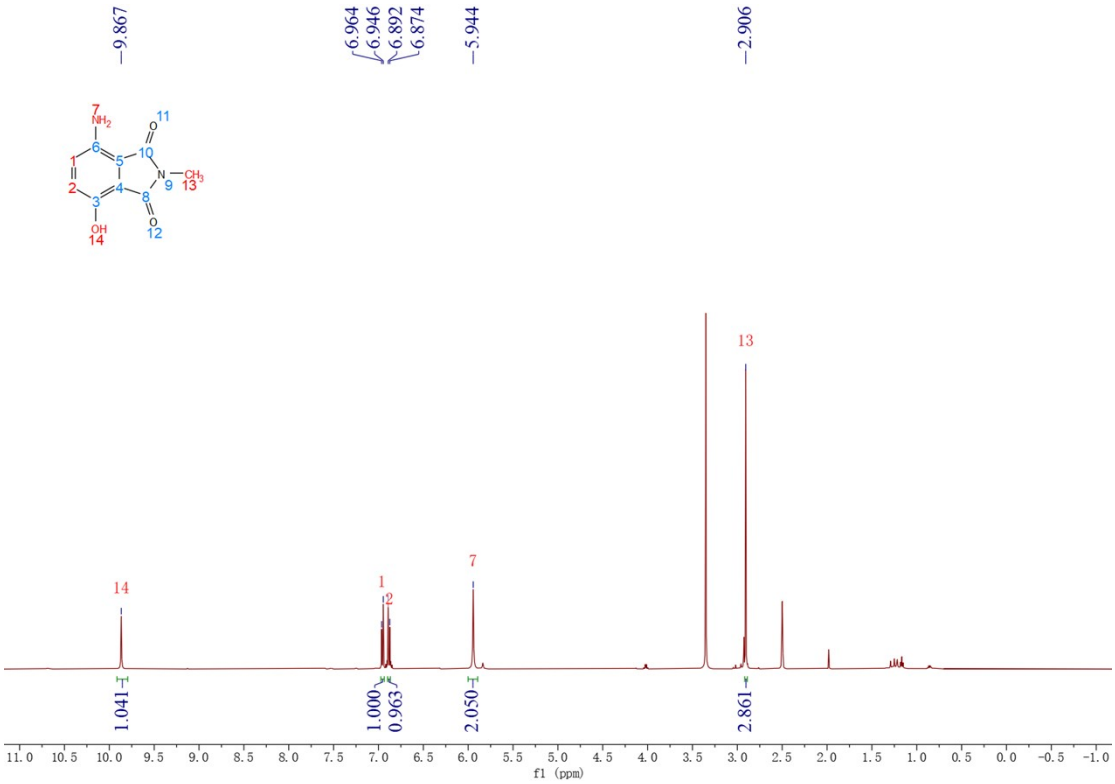
^{13}C NMR spectrum of compound 25a.



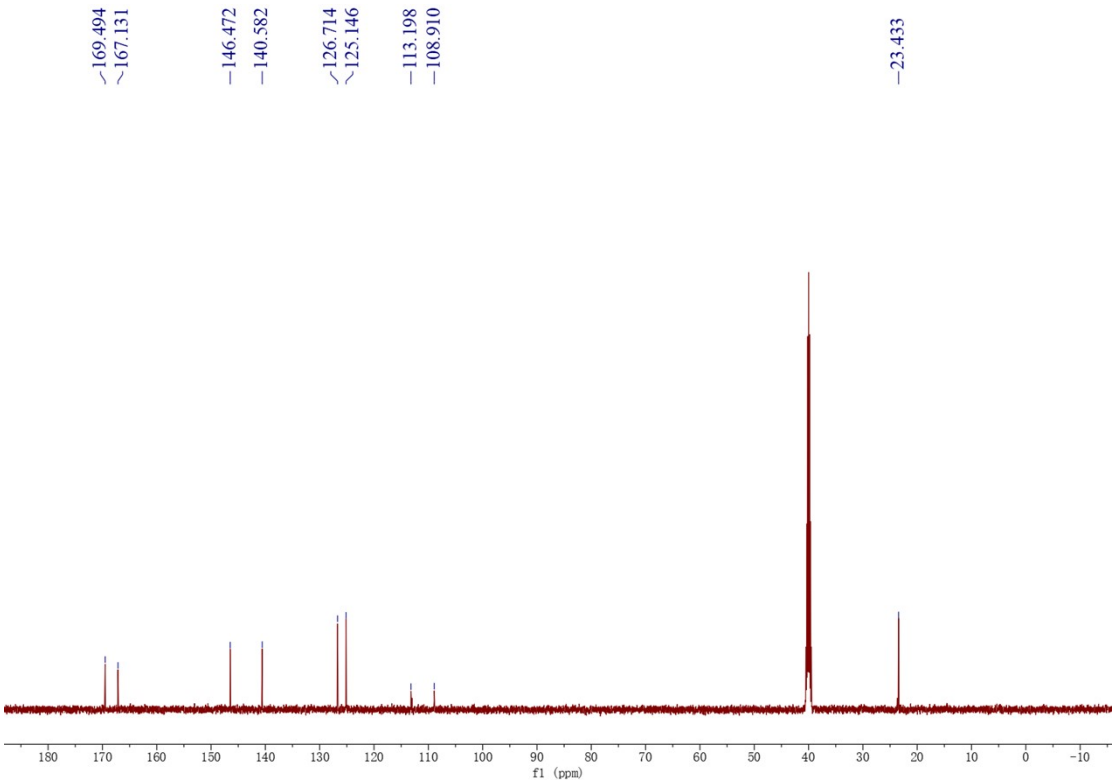
^{1}H NMR spectrum of compound 26a.



^{13}C NMR spectrum of compound 26a.



^{1}H NMR spectrum of compound 27a.



^{13}C NMR spectrum of compound 27a.