Supporting Information

Electrochemical selenium-catalyzed *para*-amination of *N*-aryloxyamides: access to polysubstituted aminophenols

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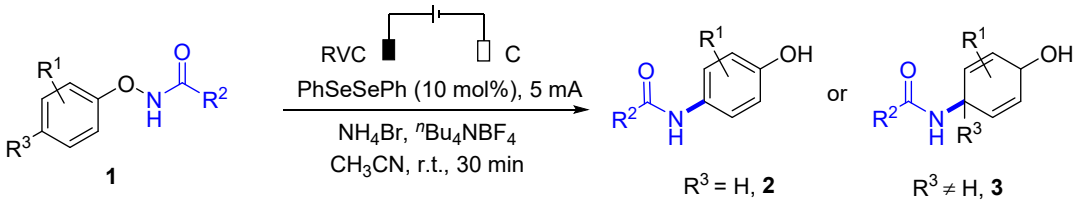
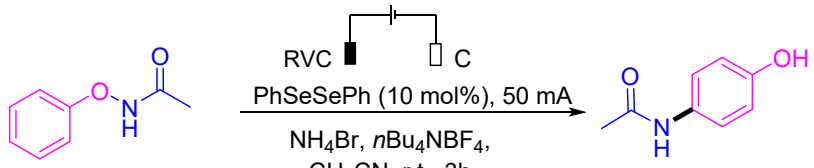
1. General information

Without special instructions, all reagents and solvents were commercially available and were not further purified. Column chromatography was carried out using silica gel (300-400 mesh). NMR spectroscopy was performed on Bruker AV-400 instruments. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00) and relative to the signal of DMSO (2.5 ppm). The abbreviations used to explain the multiplicities were as follows: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00) and relative to the signal of DMSO (39.5 ppm). HRMS spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization. Cyclic voltammograms were recorded on a CHI 660E potentiostat.

2. Procedures for the electrolysis

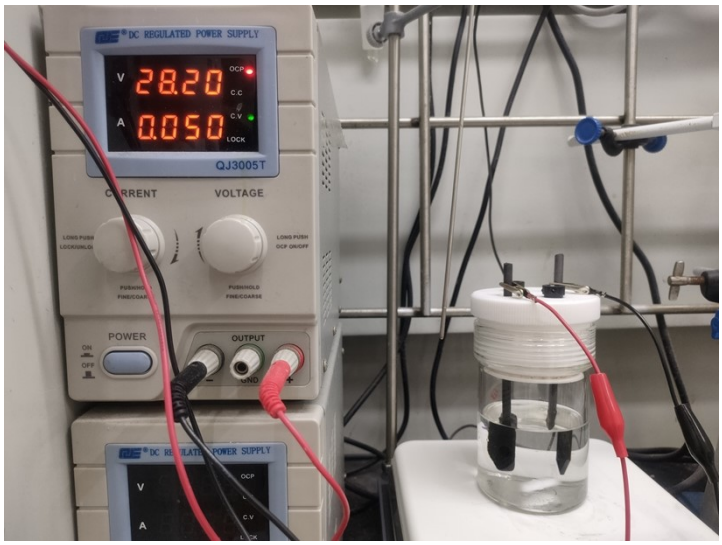


The *N*-aryloxyamide **1** (0.3 mmol, 1.0 equiv.), diphenyl diselenide (0.03 mmol, 0.1 equiv.), NH_4Br (0.03 mmol, 0.1 equiv.), nBu_4NBF_4 (0.3 mmol, 1.0 equiv.) were placed in a 10 mL three-necked round-bottomed flask. The flask was equipped a reticulated vitreous carbon (RVC) (100 PPI, 1 cm × 1 cm × 1.2 cm) anode and a graphite rod (*Φ* 6 mm) cathode and CH_3CN (8 mL) was added. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA until complete consumption of *N*-aryloxamide, which reaction progress was monitored by TLC. When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3×5 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure products **2** and **3** were obtained by flash column chromatography on silica gel (silica gel 300-400 mesh; gradient elution with hexane and ethyl acetate, 50:1 to 20:1). After using the electrode, immerse it in ethanol and clean it with ultrasound for 10 minutes.

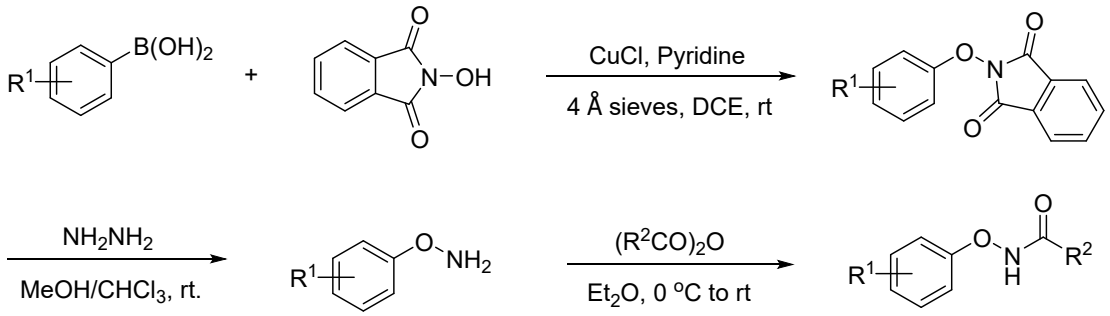


1a [10 mmol, 1.51 g] **2a**, 79%, 1.19 g

The *N*-aryloxyamide **1a** (10 mmol, 1.0 equiv.), diphenyl diselenide (1 mmol, 0.1 equiv.), NH_4Br (1 mmol, 0.1 equiv.), nBu$_4$NBF$_4$ (10 mmol, 1.0 equiv.) were placed in a 350 mL flask. The flask was equipped a reticulated vitreous carbon (RVC) (100 PPI, 3 cm × 3 cm × 1.5 cm) anode and a graphite rod (Φ 8 mm) cathode and CH_3CN (160 mL) was added. The reaction mixture was stirred and electrolyzed at a constant current of 50 mA until complete consumption of *N*-aryloxamide **1a**, which reaction progress was monitored by TLC. When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate. The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure products **2a** were obtained by flash column chromatography on silica gel (silica gel 300-400 mesh; gradient elution with hexane and ethyl acetate, 50:1 to 20:1).



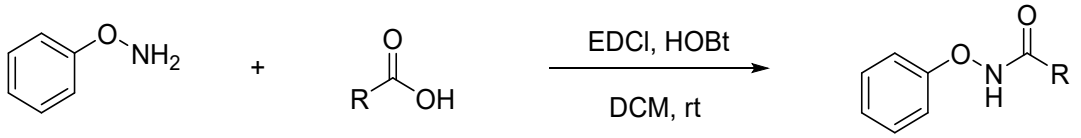
3. Procedure for the synthesis *N*-aryloxyamides



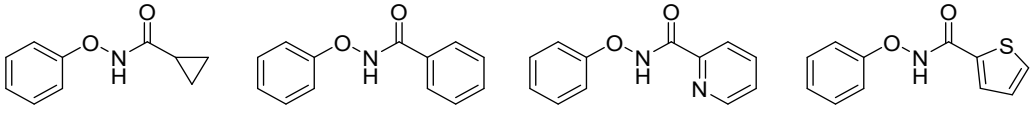
Following a literature report[1], in a 250mL round-bottom flask, *N*-hydroxyphthalimide (1.63 g, 10 mmol), cooper (I) chloride (0.99 g, 10 mmol), freshly activated 4 Å molecular sieves (2.5 g), and phenylboronic acid (2.44 g, 20 mmol) were combined in 1,2-dichloroethane (0.2 M). The pyridine (0.8 mL, 11 mmol) was then added to the suspension. The reaction mixture was open to the atmosphere and stirred at room temperature over 24-48 h. Upon completion, silica gel was added to the flask and the solvent was removed under vacuum. The desired *N*-aryloxyphthalimide were obtained by flash column chromatography on silica gel.

Hydrazine monohydrate (2 mL, 40 mmol) was added to the solution of Naryloxyphthalimide (2.40 g, 10 mmol) in 10% MeOH in $CHCl_3$ (0.1 M). The reaction was allowed to stir at room temperature over 12 h. Upon completion, the reaction mixture was filtered off and washed with CH_2Cl_2.The filtrate was concentrated under reduced pressure, and purified by flash silica gel column chromatography to give the corresponding *N*-aryloxyamine.

In a 20 mL round-bottom flask, *N*-aryloxyamine (1 g, 10 mmol) was dissolved in ether (0.2 M). The flask was cooled in an ice bath, to which corresponding anhydride (2.2 mL, 20 mmol) was slowly added. The ice bath was allowed to warm to room temperature and the mixture was stirred for 3 h at room temperature. The reaction mixture was concentrated under reduced pressure and purified by flash silica gel column chromatography to give *N*-aryloxyamides.



To a solution of *N*-aryloxyamine (3.0 mmol) and acid (3.0 mmol) in CH_2Cl_2 (12.0 ml) at 0℃ were added HOBt (3.3 mmol) and EDCI (3.3 mmol). The reaction mixture was stirred at room temperature for 10 h, then washed with 5% aqueous HCl (3×15 ml), 5% aqueous $NaHCO_3$ (20.0 ml), H_2O (20.0 ml), and brine (20.0 ml), and dried (Na_2SO_4).[2] Purification by flash chromatography afforded the corresponding *N*-aryloxyamides:

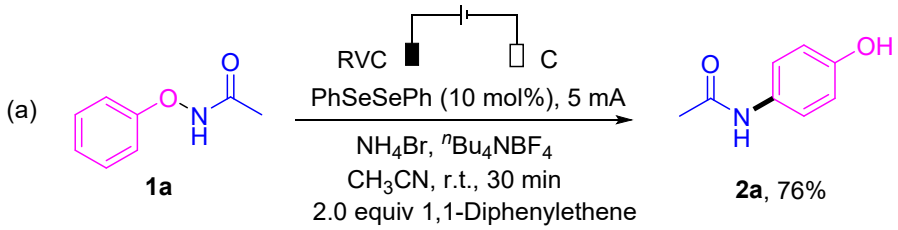


References

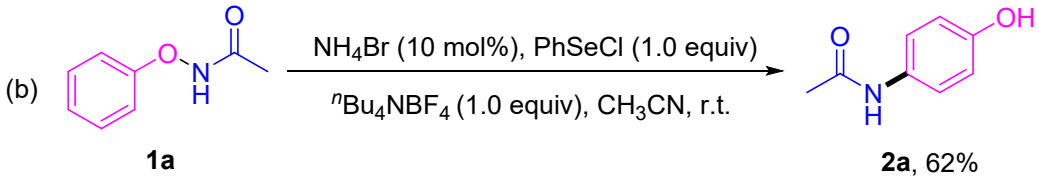
1 H. M. Petrassi, K. B. Sharpless and J. W. Kelly, *Org. Lett.*, 2001, **3**, 139-142.

2 D. Yan, G. Wang, F. Xiong, W.-Y. Sun, Z. Shi, Y. Lu, S. Li and J. Zhao, *Nature Commun.*, 2018, **9**, 4293-4301.

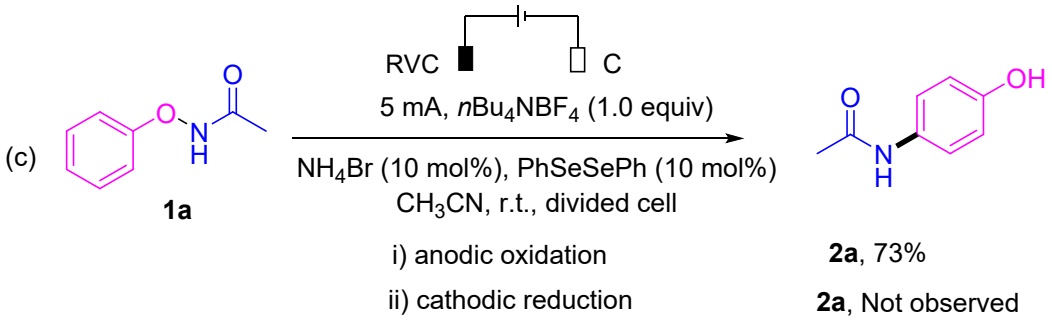
4. Procedure for control experiments



The *N*-aryloxyamide **1a** (0.3 mmol, 1.0 equiv.), diphenyl diselenide (0.03 mmol, 0.1 equiv.), NH_4Br (0.03 mmol, 0.1 equiv.), nBu$_4$NBF$_4$ (0.3 mmol, 1.0 equiv.), 1,1-Diphenylethene (0.6 mmol, 2.0 equiv.) were placed in a 10 mL three-necked round-bottomed flask. The flask was equipped a reticulated vitreous carbon (RVC) (100 PPI, 1 cm × 1 cm × 1.2 cm) anode and a graphite rod (Φ 6 mm) cathode and CH_3CN (8 mL) was added. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA until complete consumption of *N*-aryloxamide **1a**, which reaction progress was monitored by TLC. When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3×5 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product **2a** were obtained by flash column chromatography on silica gel (silica gel 300-400 mesh; gradient elution with hexane and ethyl acetate, 50:1 to 20:1).



The *N*-aryloxyamide **1a** (0.3 mmol, 1.0 equiv.), PhSeCl (0.3 mmol, 1.0 equiv.), NH_4Br (0.03 mmol, 0.1 equiv.), nBu$_4$NBF$_4$ (0.3 mmol, 1.0 equiv.) were placed in a 10 mL three-necked round-bottomed flask. The reaction mixture was stirred until complete consumption of *N*-aryloxamide **1a**, which reaction progress was monitored by TLC. When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3×5 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product **2a** were obtained by flash column chromatography on silica gel (silica gel 300-400 mesh; gradient elution with hexane and ethyl acetate, 50:1 to 20:1).



The *N*-aryloxyamide **1a** (0.3 mmol, 1.0 equiv.), diphenyl diselenide (0.03 mmol, 0.1 equiv.), NH_4Br (0.03 mmol, 0.1 equiv.), $n Bu_4NBF_4$ (0.3 mmol, 1.0 equiv.) were placed in a 10 mL flask. The flask was equipped a reticulated vitreous carbon (RVC) (100 PPI, 1 cm × 1 cm × 1.2 cm) anode and a graphite rod (Φ 6 mm) cathode and CH_3CN (8 mL) was added. Electrolysis was carried out in the divided cell at room temperature, which using a constant current of 5 mA until the substrate was completely consumed (monitored by TLC). When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3×5 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product **2a** were obtained at the anode by flash column chromatography on silica gel (silica gel 300-400 mesh; gradient elution with hexane and ethyl acetate, 50:1 to 20:1).

5. Procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three electrodes cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. 10.0 mL CH_3CN containing 0.1 M $^nBu_4NBF_4$ were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to 3.0 V. The results of cyclic voltammetry were showed in Figure S1.

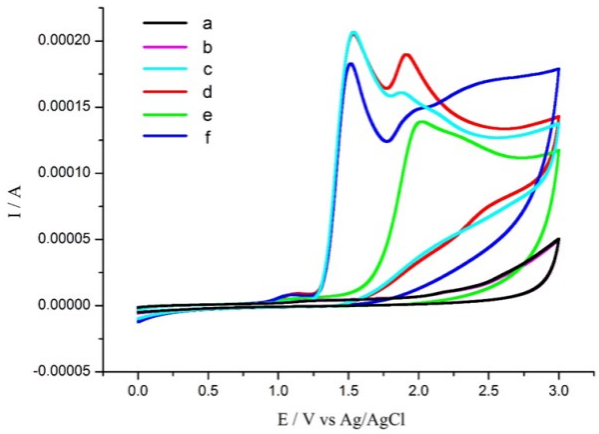
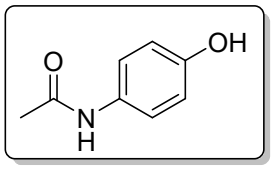
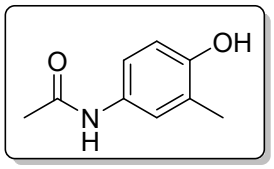


Figure S1. Cyclic voltammograms of reactants and their mixtures in 0.1 M $LiClO_4/CH_3CN$ using a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.1 M in CH_3CN) as counter and reference electrode at 100 mV/s scan rate: (a) $^nBu_4NBF_4$ (0.1 M)；(b) NH_4Br (3 mM)；(c) PhSeSePh (3 mM)；(d) NH_4Br (3 mM) + PhSeSePh (3 mM)；(e) **1a** (5 mM)；(f) NH_4Br (3 mM) + PhSeSePh (3 mM) + **1a** (5 mM).

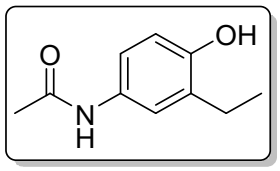
6. Characterization data for all products



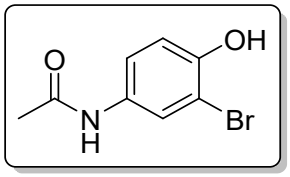
***N*-(4-hydroxyphenyl)acetamide (2a)**[2]. white solid (yield = 87%, 39.4 mg) mp: 166-167 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.65 (s, 1H), 9.15 (s, 1H), 7.35 – 7.32 (m, 2H), 6.69 – 6.65 (m, 2H), 1.97 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 167.53, 153.13, 131.05, 120.82, 115.00, 23.76; **HRMS** (m/z) (ESI): calcd for $C_8H_{10}NO_2$ $[M+H]^+$: 152.0706, found: 152.0707.



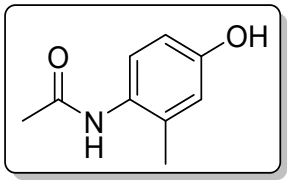
***N*-(4-hydroxy-3-methylphenyl)acetamide (2b)**[2]. white solid (yield = 72%, 35.8 mg); mp: 178-179 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.58 (s, 1H), 9.02 (s, 1H), 7.25 – 7.23 (m, 1H), 7.18 – 7.14 (m, 1H), 7.68 – 7.65 (m, 1H), 2.08 (s, 3H), 1.97 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 167.52, 151.27, 130.90, 123.65, 122.17, 118.11, 114.37, 23.81, 16.23; **HRMS** (m/z) (ESI): calcd for $C_9H_{12}NO_2$ $[M+H]^+$: 166.0863, found: 166.0863.



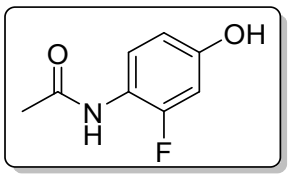
***N*-(3-ethyl-4-hydroxyphenyl)acetamide (2c)**[2]. White solid (yield = 78%, 42.0 mg); mp: 140 – 141 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.60 (s, 1H), 9.02 (s, 1H), 7.23 (d, J = 2.5 Hz, 1H), 7.20 (dd, J = 8.5, 2.6 Hz, 1H), 6.68 (d, J = 8.5 Hz, 1H), 2.49 (q, J = 7.2 Hz, 2H), 1.98 (s, 3H), 1.11 (t, J = 7.5 Hz, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 167.49, 150.79, 131.08, 129.73, 120.49, 118.05, 114.54, 23.80, 22.87, 14.20; **HRMS** (m/z) (ESI): calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$: 180.1019, found: 180.1019.



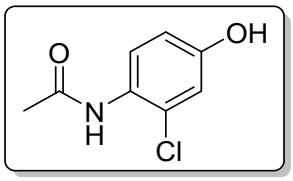
***N*-(3-bromo-4-hydroxyphenyl)acetamide (2d)**[2]. White solid (yield = 68%, 47.0 mg); mp: 155 – 156 ℃; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.94 (s, 1H), 9.81 (s, 1H), 7.82 (d, J = 2.5 Hz, 1H), 7.26 (dd, J = 8.7, 2.5 Hz, 1H), 6.87 (d, J = 8.7 Hz, 1H), 1.99 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ167.86, 149.79, 132.12, 123.45, 119.74, 116.09, 108.56, 23.81; **HRMS** (m/z) (ESI): calcd for $C_8H_9BrNO_2$ $[M+H]^+$: 229.9811, found: 229.9810.



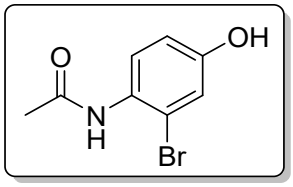
***N*-(4-hydroxy-2-methylphenyl)acetamide (2e)**[2]. White solid (yield = 79%, 39.3 mg); mp: 128 – 129 ℃; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.19 (s, 1H), 9.09 (s, 1H), 7.02 (d, J = 8.5 Hz, 1H), 6.58 (d, J = 2.8 Hz, 1H), 6.53 (dd, J = 8.5, 2.8 Hz, 1H), 2.07 (s, 3H), 1.98 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 168.15, 154.88, 133.95, 127.90, 127.07, 116.52, 112.52, 23.02, 18.01; **HRMS** (m/z) (ESI): calcd for $C_9H_{12}NO_2$ $[M+H]^+$: 166.0863, found: 166.0862.



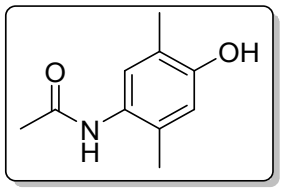
***N*-(2-fluoro-4-hydroxyphenyl)acetamide (2f)**[2]. White solid (yield = 77%, 39.2 mg); mp: 123 – 124 ℃; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.72 (s, 1H), 9.40 (s, 1H), 7.39 (t, J = 9.0 Hz, 1H), 6.59 (dd, J = 12.3, 2.6 Hz, 1H), 6.56 – 6.30 (m, 1H), 2.00 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 168.33, 155.24 (d, J= 244.8 Hz), 155.46 (d, J= 10.9 Hz), 126.56(d, J= 3.5 Hz), 117.14(d, J= 12.5 Hz), 110.83(d, J= 2.7 Hz), 102.67(d, J= 22.2 Hz), 23.08; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -121.96; **HRMS** (m/z) (ESI): calcd for $C_8H_9FNO_2$ $[M+H]^+$: 170.0612, found: 170.0611.



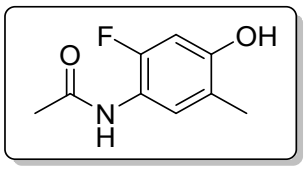
***N*-(2-chloro-4-hydroxyphenyl)acetamide (2g)**. White solid (yield = 75%, 41.7 mg); mp: 123 – 124 ℃; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.79 (s, 1H), 9.32 (s, 1H), 7.29 (d, J = 8.7 Hz, 1H), 6.84 (d, J = 2.7 Hz, 1H), 6.70 (dd, J = 8.7, 2.7 Hz, 1H), 2.01 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 168.49, 155.64, 128.57, 126.40, 115.53, 114.34, 22.98; **HRMS** (m/z) (ESI): calcd for $C_8H_9ClNO_2$ $[M+H]^+$: 186.0316, found: 186.0316.



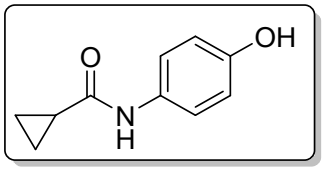
***N*-(2-bromo-4-hydroxyphenyl)acetamide (2h)**[2]. White solid (yield = 62%, 41.7 mg); mp: 112 – 113 ℃; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.80 (s, 1H), 9.30 (s, 1H), 7.22 (d, J = 8.7 Hz, 1H), 7.00 (d, J = 2.7 Hz, 1H), 6.74 (dd, J = 8.7, 2.7 Hz, 1H), 2.00 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 168.47, 155.96, 129.13, 127.81, 119.78, 118.54, 114.89, 22.94; **HRMS** (m/z) (ESI): calcd for $C_8H_9BrNO_2$ $[M+H]^+$: 229.9811, found: 229.9812.



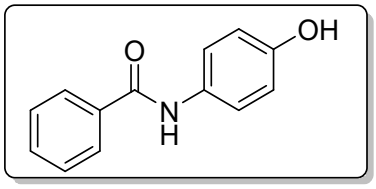
***N*-(4-hydroxy-2,5-dimethylphenyl)acetamide (2i)**. White solid (yield = 73%, 41.7 mg); mp: 174 – 175 ℃; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.05 (s, 1H), 9.04 (s, 1H), 6.91 (s, 1H), 6.58 (s, 1H), 2.04 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 168.10, 152.89, 130.83, 128.28, 127.54, 120.96, 115.89, 23.02, 17.60, 15.61; **HRMS** (m/z) (ESI): calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$: 180.1019, found: 180.1018.



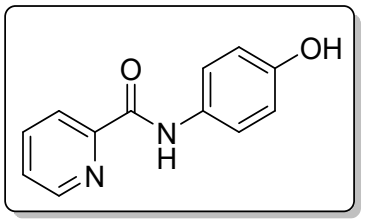
***N*-(2-fluoro-4-hydroxy-5-methylphenyl)acetamide (2j)**[2]. White solid (yield = 69%, 37.7 mg); mp: 146 – 147 ℃; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.61 (s, 1H), 9.35 (s, 1H), 7.27 (d, J = 9.0 Hz, 1H), 6.59 (d, J = 11.9 Hz, 1H), 2.05 (s, 3H), 1.99 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.32, 153.25 (d, J = 243.2 Hz), 153.02 (d, J = 10.0 Hz), 127.49 (d, J = 3.3 Hz), 119.45 (d, J = 3.1 Hz), 116.50 (d, J = 12.4 Hz), 101.90 (d, J = 22.3 Hz), 23.09, 15.42; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -125.98; **HRMS** (m/z) (ESI): calcd for $C_9H_{11}FNO_2$ $[M+H]^+$: 184.0768, found: 184.0768.



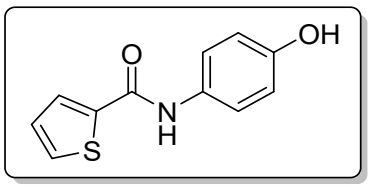
***N*-(4-hydroxyphenyl)cyclopropanecarboxamide (2k)**[2]. White solid (yield = 77%, 41.0 mg); mp: 208 – 209 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.90 (s, 1H), 9.13 (s, 1H), 7.36 – 7.32 (m, 2H), 6.68 – 6.64 (m, 2H), 1.70 (m, 1H), 0.76 – 0.71 (m, 4H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 170.82, 153.05, 131.15, 120.75, 115.01, 14.34, 6.77; **HRMS** (m/z) (ESI): calcd for $C_{10}H_{12}NO_2$ $[M+H]^+$: 178.0863, found: 178.0862.



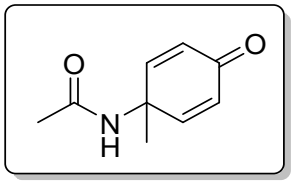
***N*-(4-hydroxyphenyl)benzamide (2l)**[2]. White solid (yield = 84%, 53.7 mg); mp: 213 – 214 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.04 (s, 1H), 9.27 (s, 1H), 7.96 – 7.91 (m, 2H), 7.57 – 7.49 (m, 5H), 6.78 – 6.73 (m, 2H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ m; **HRMS** (m/z) (ESI): calcd for $C_{13}H_{12}NO_2$ $[M+H]^+$: 214.0863, found: 214.0862.



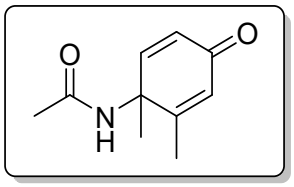
***N*-(4-hydroxyphenyl)picolinamide (2m)**[2]. White solid (yield = 84%, 53.7 mg); mp: 162 – 163 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.41 (s, 1H), 9.30 (s, 1H), 8.73 – 8.69 (m, 1H), 8.15 – 8.11 (m, 1.1 Hz, 1H), 8.07 – 8.02 (m, 1H), 7.69 – 7.63 (m, 3H), 6.77 – 6.73 (m, 2H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 161.85, 153.90, 150.20, 148.39, 138.09, 130.02, 126.69, 122.19, 121.93, 115.07; **HRMS** (m/z) (ESI): calcd for $C_{12}H_{11}N_2O_2$ $[M+H]^+$: 215.0815, found: 215.0816.



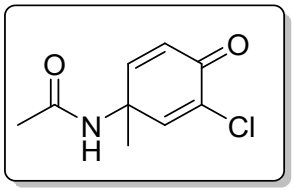
***N*-(4-hydroxyphenyl)thiophene-2-carboxamide (2n)**[2]. White solid (yield = 72%, 47.3 mg); mp: 157 – 158 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.02 (s, 1H), 9.30 (s, 1H), 7.96 (dd, J = 3.8, 1.2 Hz, 1H), 7.80 (dd, J = 5.0, 1.1 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.20 (dd, J = 5.0, 3.7 Hz, 1H), 6.76 – 6.73 (m, 2H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 159.47, 153.87, 140.47, 131.34, 130.15, 128.57, 128.03, 122.44, 115.09; **HRMS** (m/z) (ESI): calcd for $C_{11}H_{10}NO_2S$ $[M+H]^+$: 220.0427, found: 220.0425.



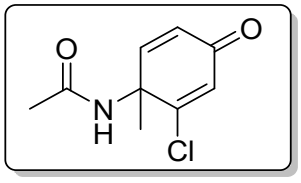
***N*-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (3a)**[2]. White solid (yield = 73%, 36.3 mg); mp: > 300 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.31 (s, 1H), 6.93 – 6.90 (m, 2H), 6.08 – 6.04 (m, 2H), 1.80 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 184.95, 169.08, 154.21, 126.54, 51.91, 25.80, 22.72; **HRMS** (m/z) (ESI): calcd for $C_9H_{12}NO_2$ $[M+H]^+$: 166.0863, found: 166.0862.



***N*-(1,2-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (3b)**[2]. White solid (yield = 67%, 36.2 mg); mp: > 300 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.38 (s, 1H), 6.83 (d, J = 9.9 Hz, 1H), 6.01 (dd, J = 9.9, 2.0 Hz, 1H), 5.98 – 5.96 (m, 1H), 1.83 (d, J = 1.4 Hz, 3H), 1.82 (s, 3H), 1.29 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 185.21, 168.80, 163.33, 155.54, 126.02, 125.73, 54.20, 25.98, 22.39, 18.30; **HRMS** (m/z) (ESI): calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$: 180.1019, found: 180.1017.

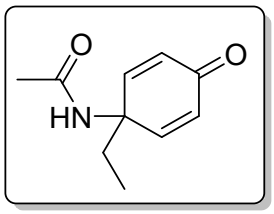


***N*-(3-chloro-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (3c)**[2]. White solid (yield = 81%, 48.4 mg); mp: > 300 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.47 (s, 1H), 7.24 (d, J = 2.8 Hz, 1H), 6.96 (dd, J = 9.9, 2.8 Hz, 1H), 6.22 (d, J = 9.9 Hz, 1H), 1.81 (s, 3H), 1.40 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 178.11, 169.30, 154.99, 150.68, 129.65, 125.32, 53.99, 25.24, 22.59; **HRMS** (m/z) (ESI): calcd for $C_9H_{11}ClNO_2$ $[M+H]^+$: 200.0473, found: 200.0473.

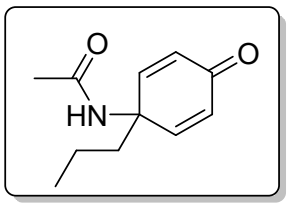


***N*-(2-chloro-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (3d)**. White solid (yield = 72%, 43.0 mg); mp: > 300 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.62 (s, 1H), 6.96 (d, J =

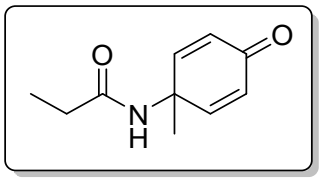
10.0 Hz, 1H), 6.44 (d, *J* = 1.8 Hz, 1H), 6.14 (dd, *J* = 9.9, 1.8 Hz, 1H), 1.83 (s, 3H), 1.42 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 184.02, 168.98, 159.40, 154.11, 127.55, 125.71, 55.27, 25.43, 22.29; **HRMS** (m/z) (ESI): calcd for $C_9H_{11}ClNO_2$ $[M+H]^+$: 200.0473, found: 200.0473.



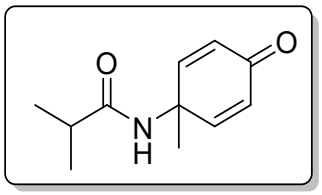
***N*-(1-ethyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (3e)**[2]. White solid (yield = 72%, 38.8 mg); mp: > 300 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.20 (s, 1H), 6.83 – 6.80 (m, 2H), 6.17 – 6.13 (m, 2H), 1.82 (s, 3H), 1.76 (q, *J* = 7.5 Hz, 2H), 0.71 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 185.32, 169.11, 152.52, 128.02, 55.79, 30.26, 22.81, 7.46; **HRMS** (m/z) (ESI): calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$: 180.1019, found: 180.1016.



***N*-(4-oxo-1-propylcyclohexa-2,5-dien-1-yl)acetamide (3f)**[2]. White solid (yield = 69%, 40.2 mg); mp: > 300 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.20 (s, 1H), 6.87 – 6.84 (m, 2H), 6.14 – 6.11 (m, 2H), 1.81 (s, 3H), 1.71 – 1.67 (m, 2H), 1.17 – 1.12 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 185.29, 169.09, 152.83, 127.69, 55.41, 22.80, 16.20, 13.94; **HRMS** (m/z) (ESI): calcd for $C_{11}H_{16}NO_2$ $[M+H]^+$: 194.1176, found: 194.1175.



***N*-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)propionamide (3g)**[2]. White solid (yield = 63%, 34.0 mg); mp: > 300 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.21 (s, 1H), 6.92 – 6.89 (m, 2H), 6.08 – 6.05 (m, 2H), 2.08 (q, *J* = 7.6 Hz, 2H), 1.35 (s, 3H), 0.94 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 184.96, 172.77, 154.32, 126.54, 51.83, 28.25, 25.81, 9.68; **HRMS** (m/z) (ESI): calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$: 180.1019, found: 180.1020.



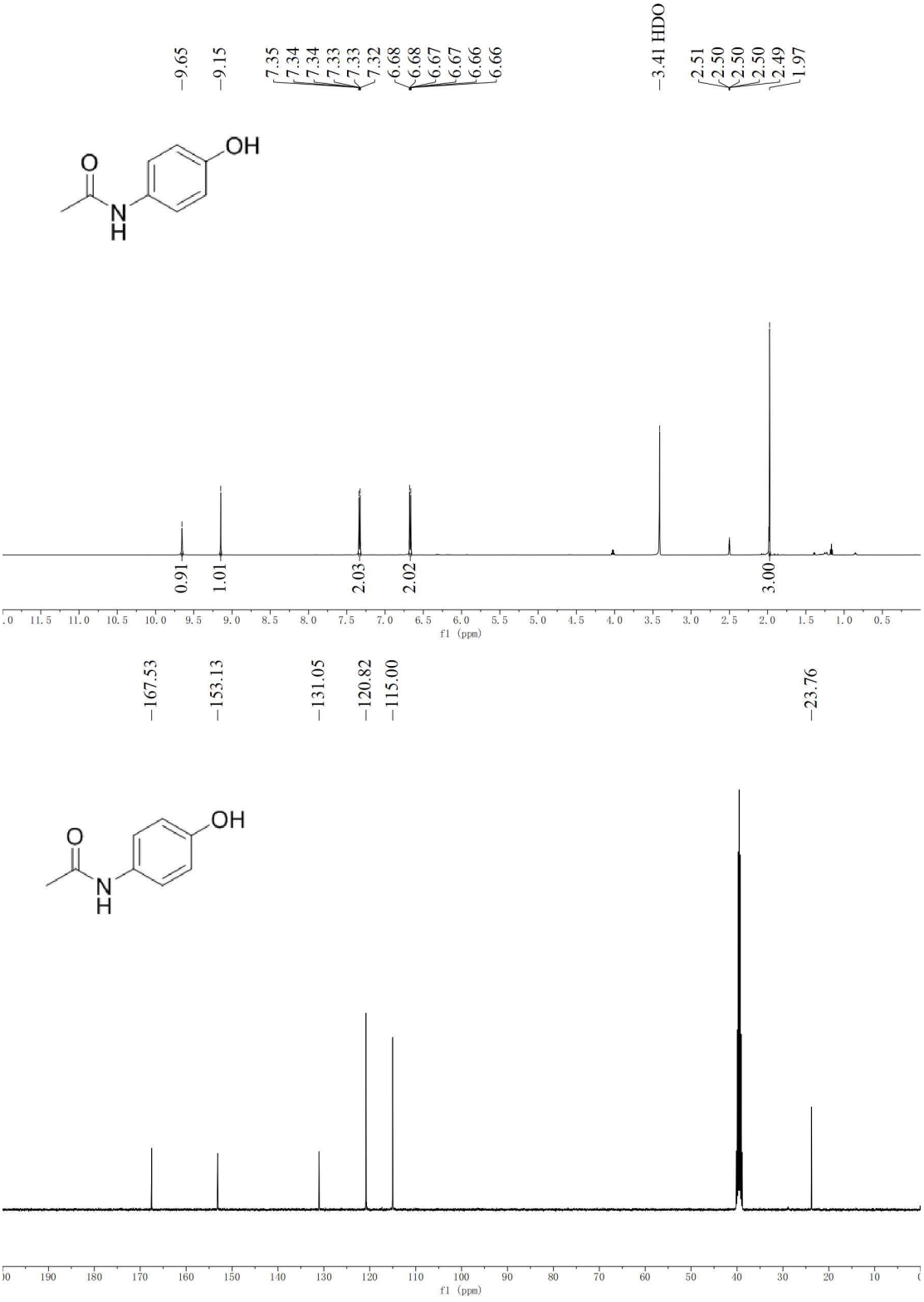
***N*-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)isobutyramide (3h)**[2]. White solid (yield = 43%, 24.6 mg); mp: > 300 ℃; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.18 (s, 1H), 6.91 – 6.87 (m, 2H), 6.09 – 6.04 (m, 2H), 2.44 – 2.36 (m, 1H), 1.36 (s, 3H), 0.96 (d, J = 6.8 Hz, 6H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 184.92, 176.07, 154.33, 126.55, 51.76, 33.66, 25.81, 19.50; **HRMS** (m/z) (ESI): calcd for $C_{11}H_{16}NO_2$ $[M+H]^+$: 194.1176, found: 194.1176.

References

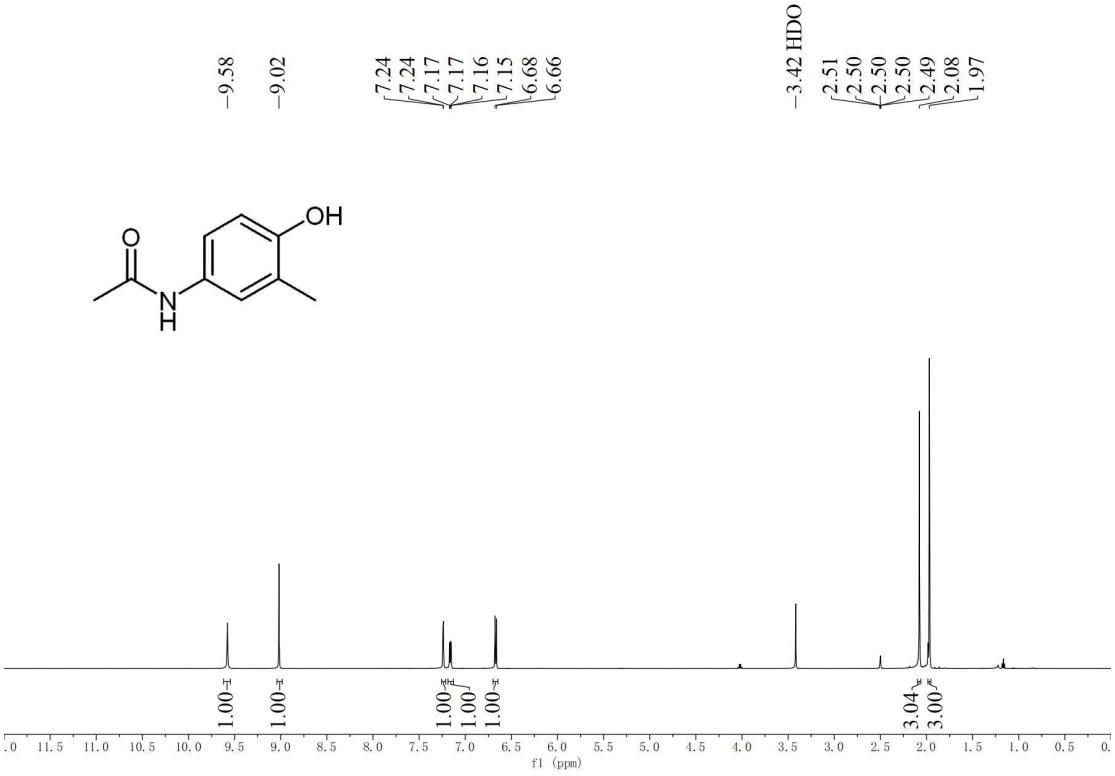
2 D. Yan, G. Wang, F. Xiong, W.-Y. Sun, Z. Shi, Y. Lu, S. Li and J. Zhao, *Nature Commun.*, 2018, **9**, 4293-4301.

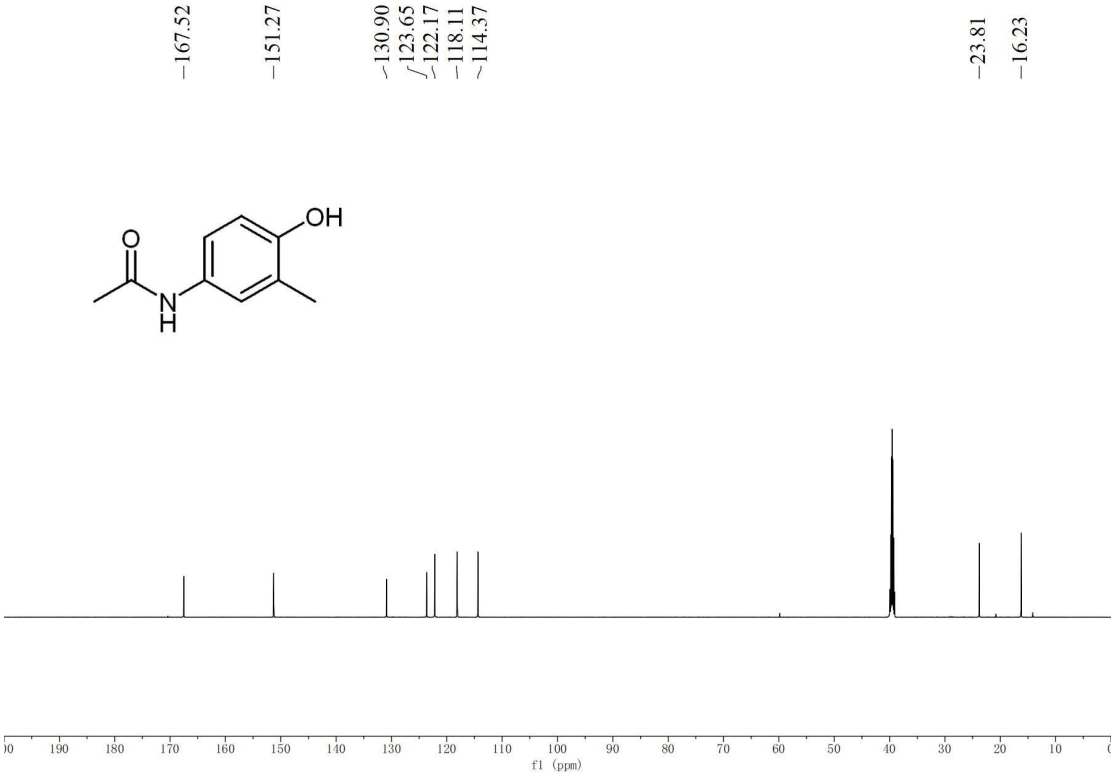
7. Copies of ^{1}H and ^{13}C NMR spectra for all products

N-(4-hydroxyphenyl)acetamide (2a)

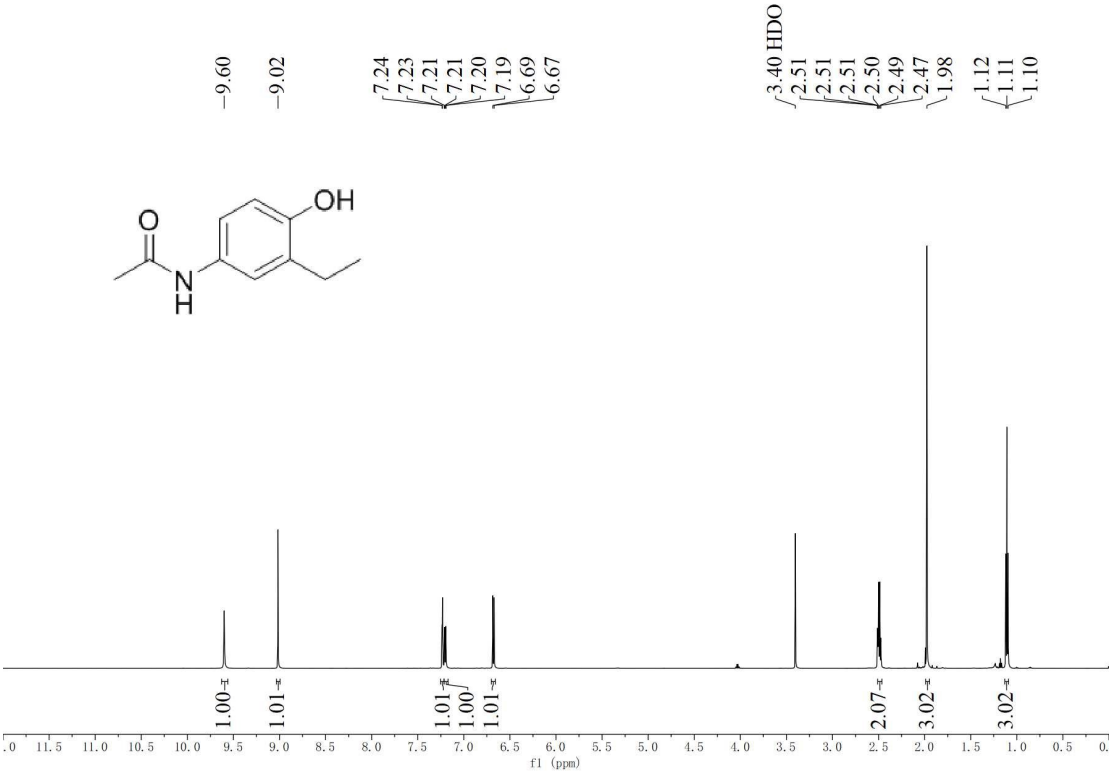


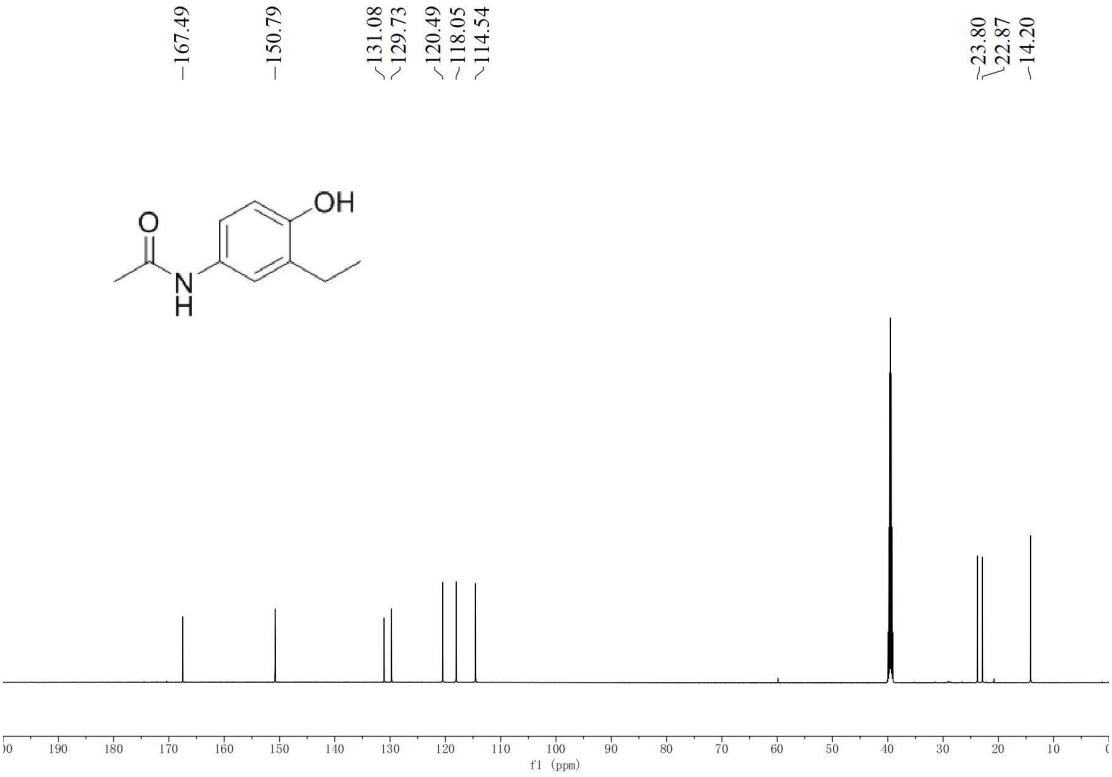
N-(4-hydroxy-3-methylphenyl)acetamide (2b)



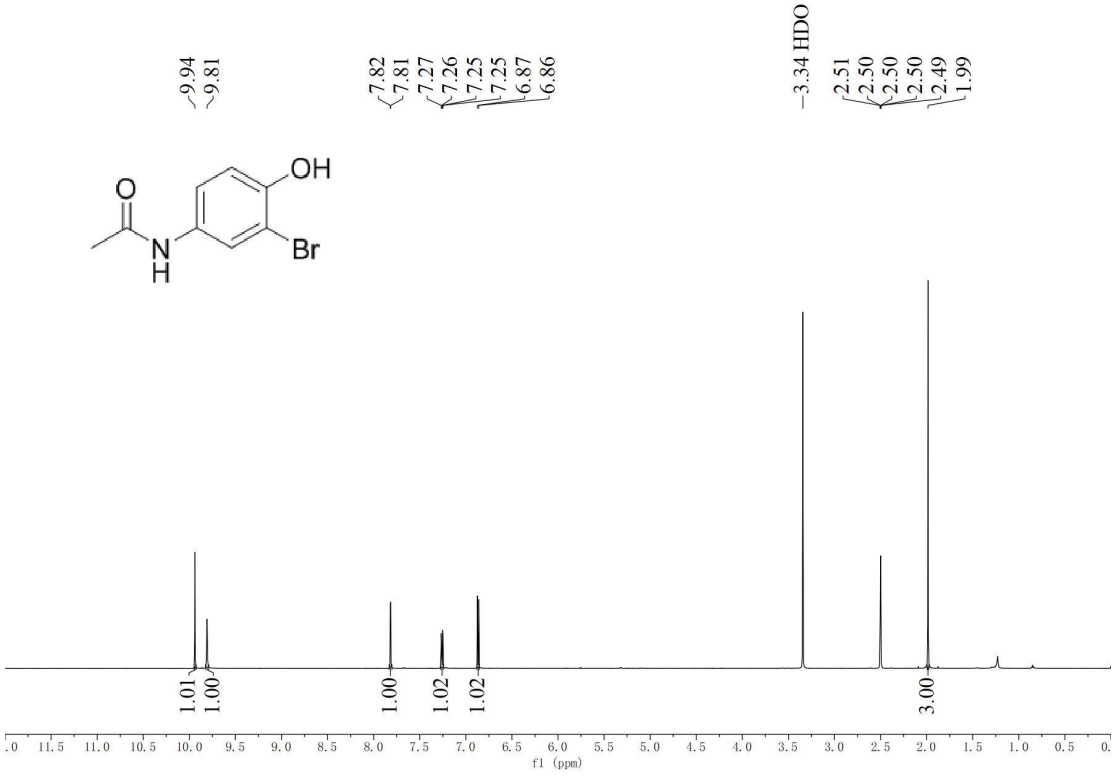


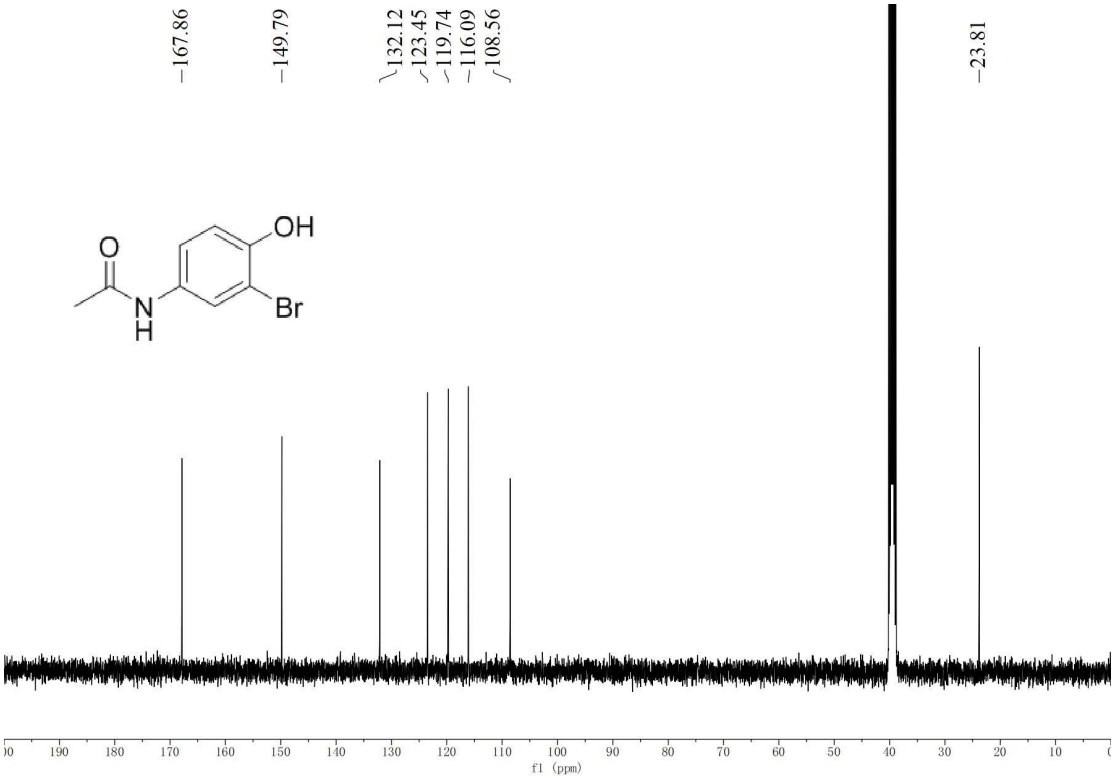
N-(3-ethyl-4-hydroxyphenyl)acetamide (2c)



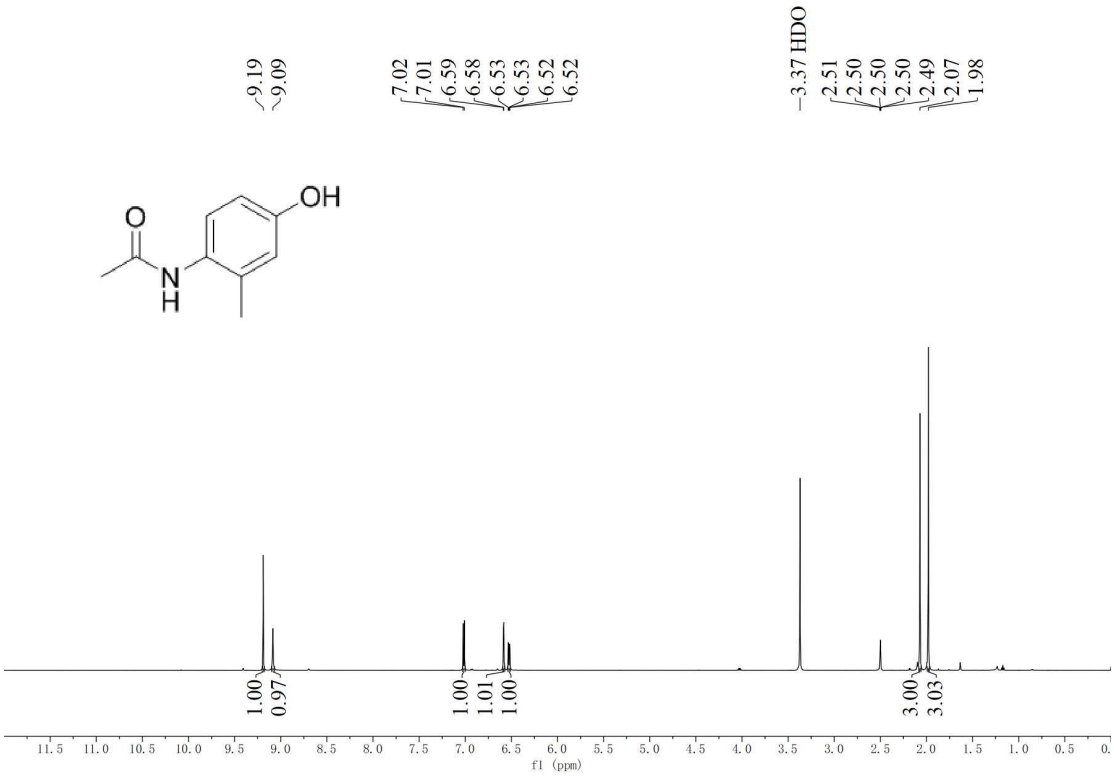


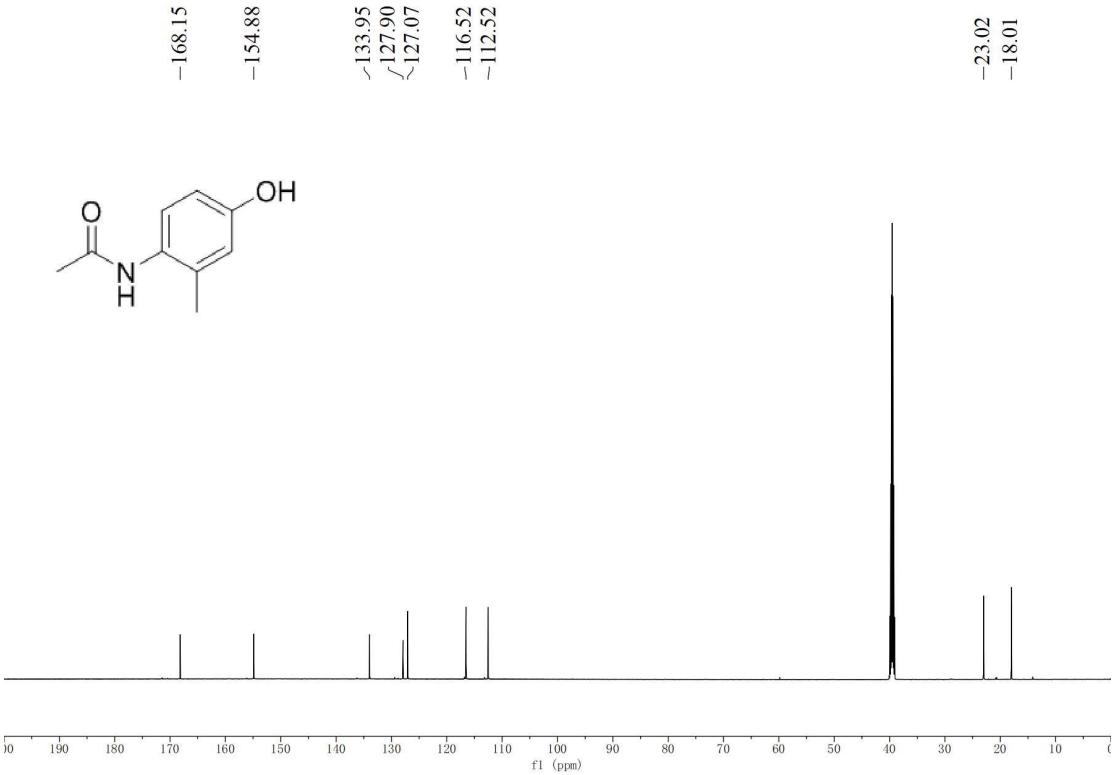
N-(3-bromo-4-hydroxyphenyl)acetamide (2d)



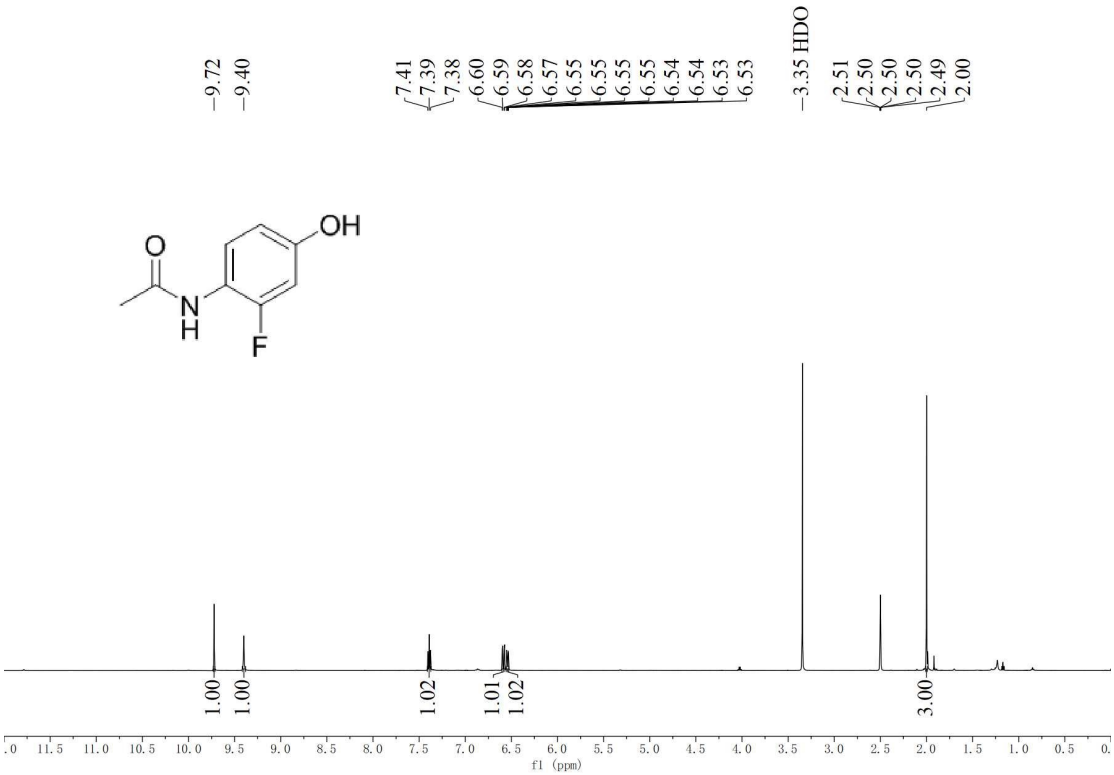


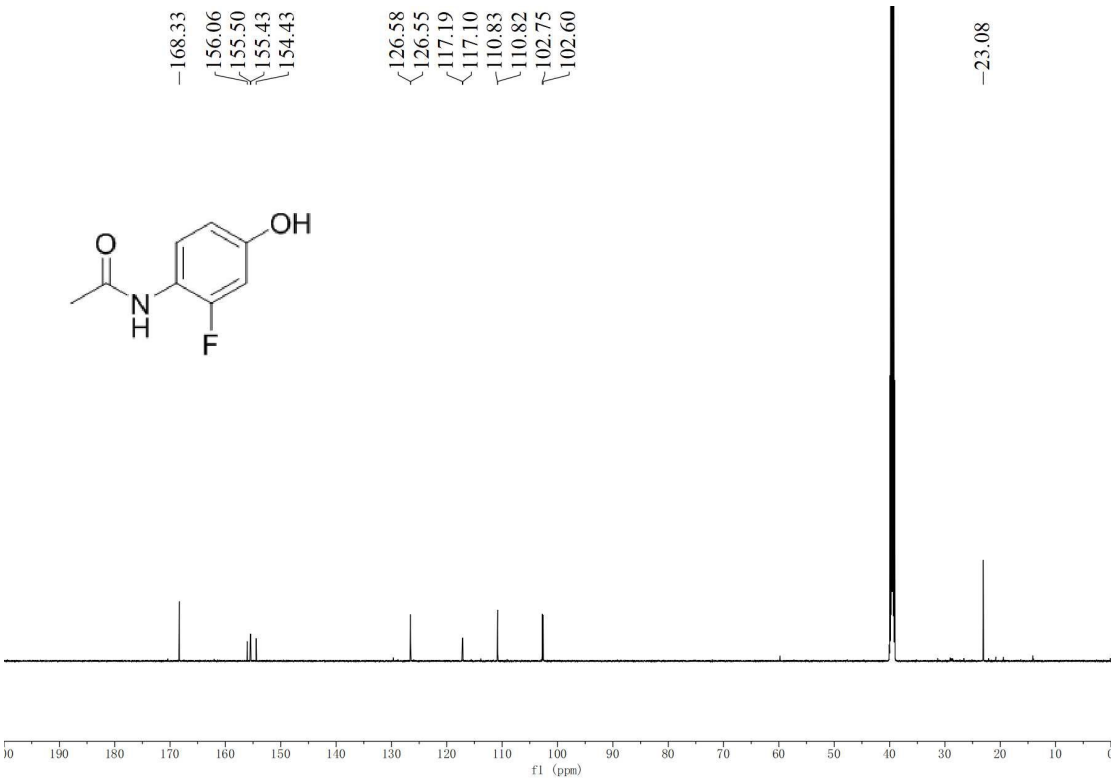
N-(4-hydroxy-2-methylphenyl)acetamide (2e)

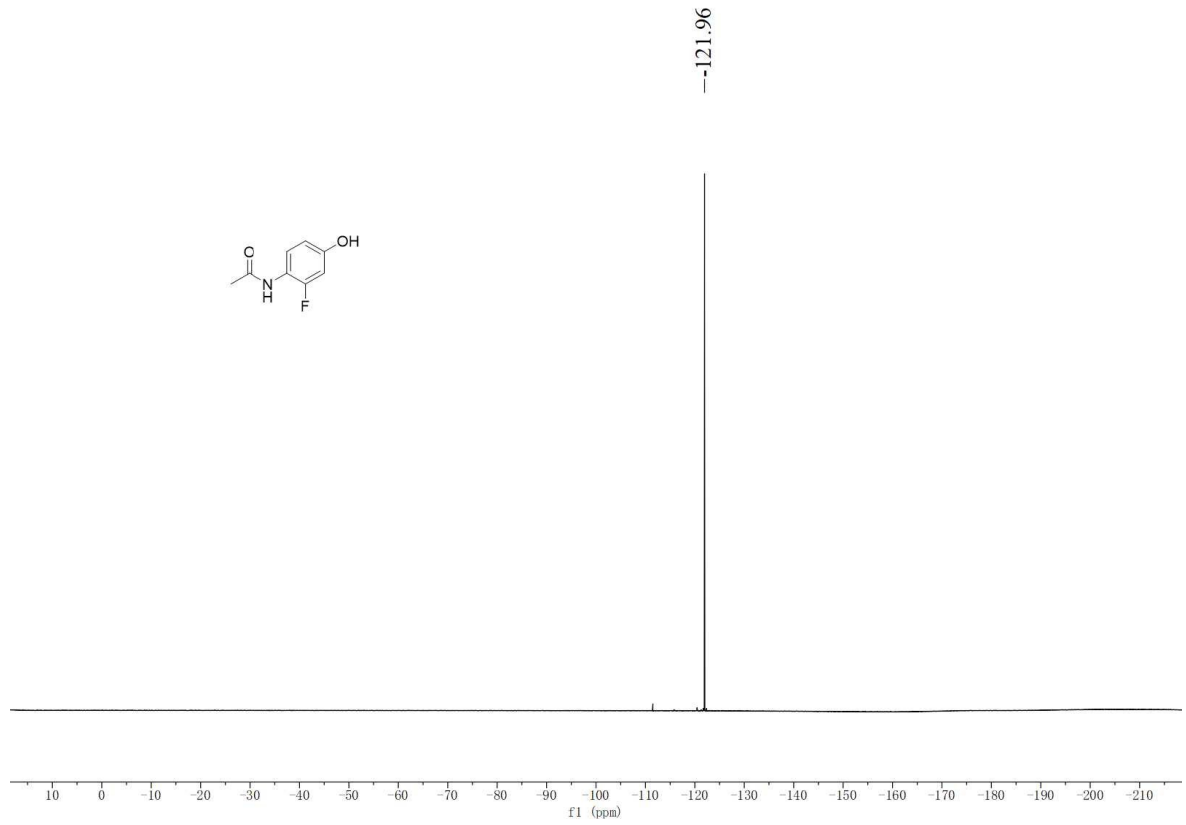




N-(2-fluoro-4-hydroxyphenyl)acetamide (2f)



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H
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-190
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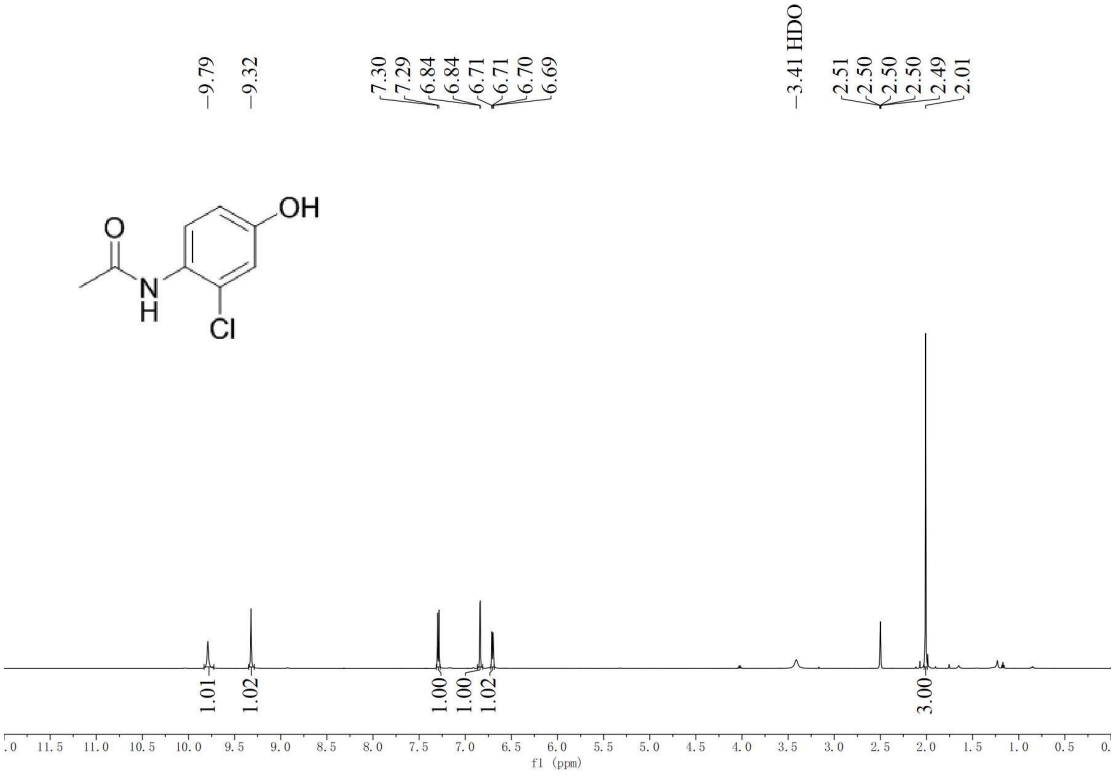
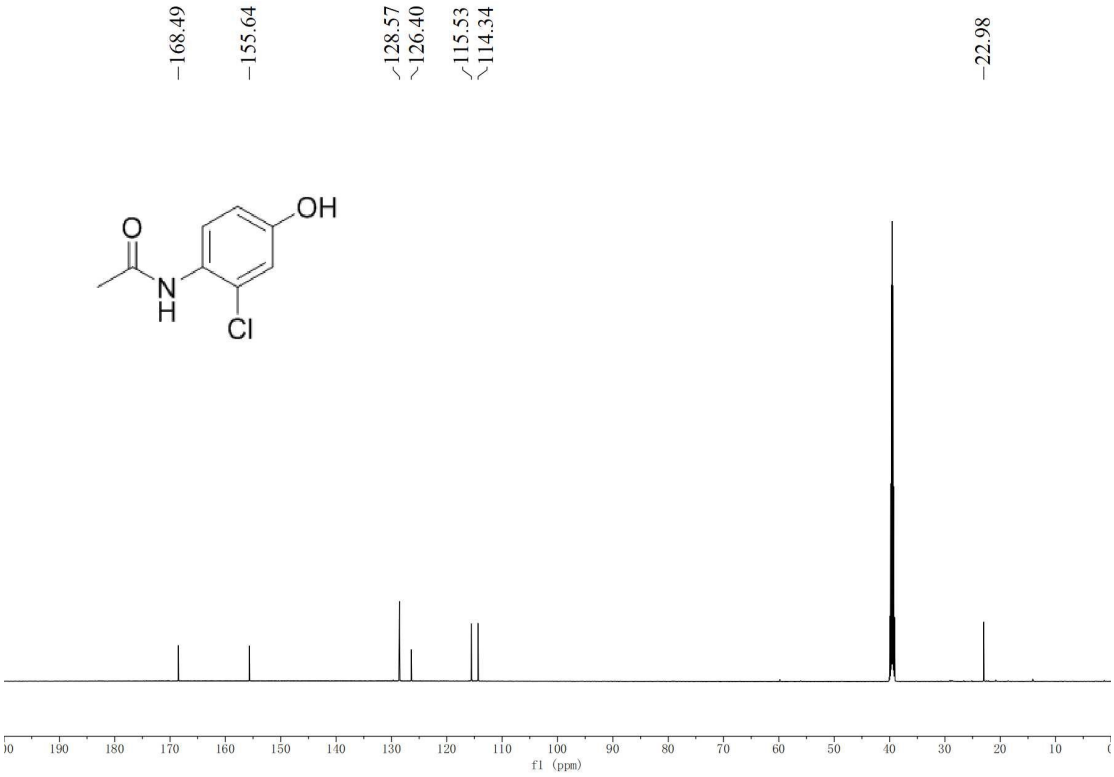
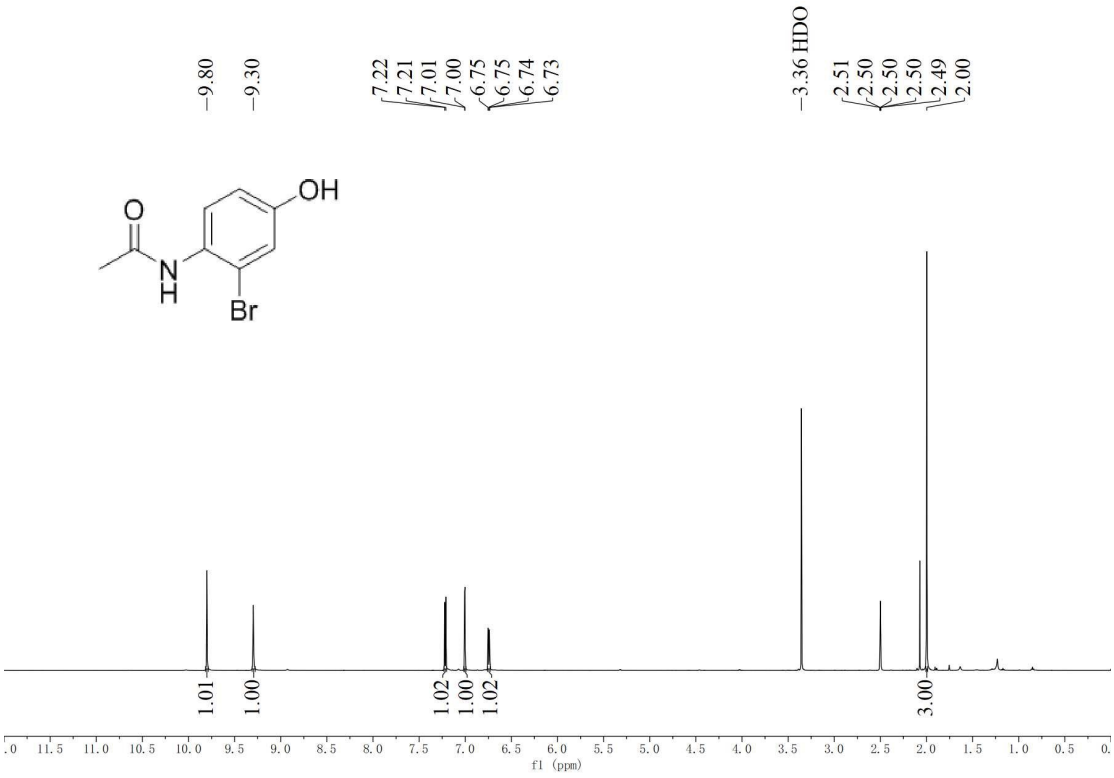
f1 (ppm)

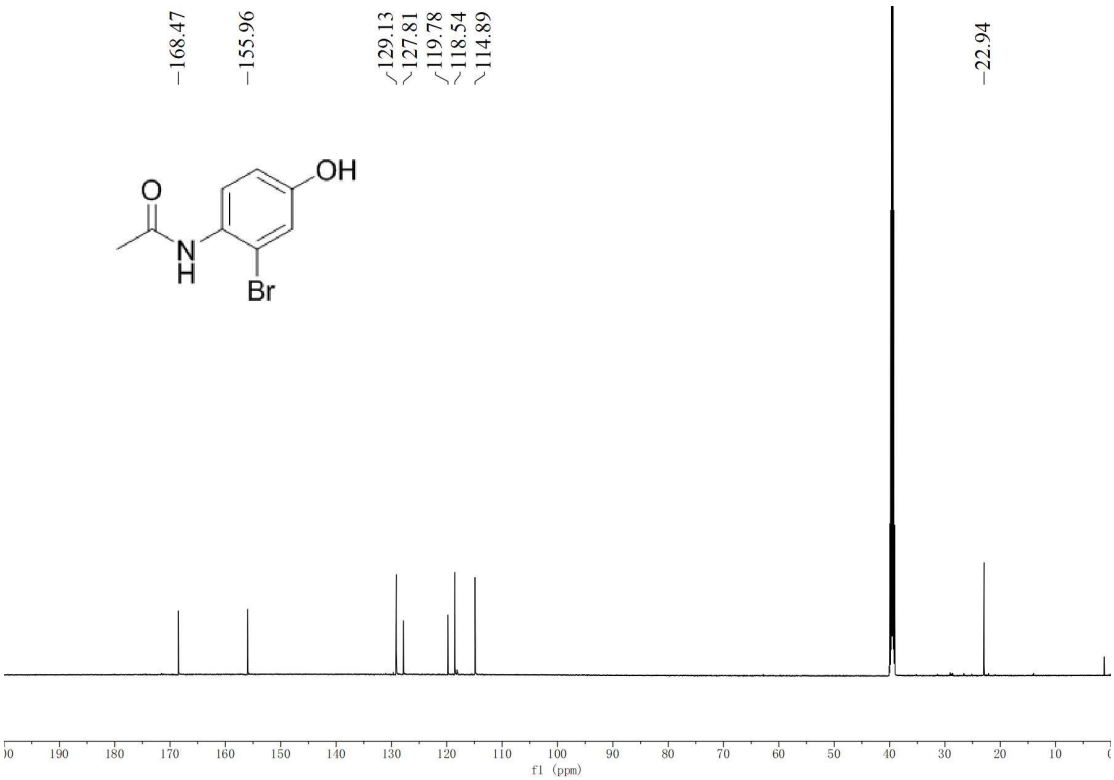
N-(2-chloro-4-hydroxyphenyl)acetamide (2g)



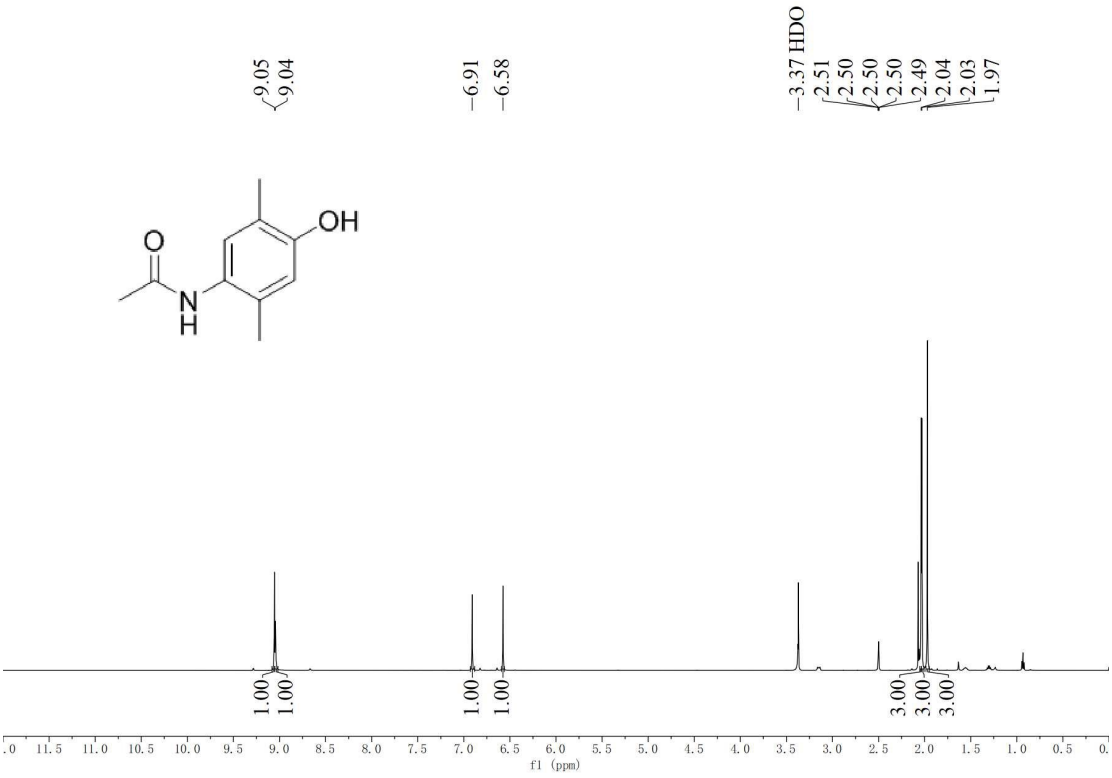


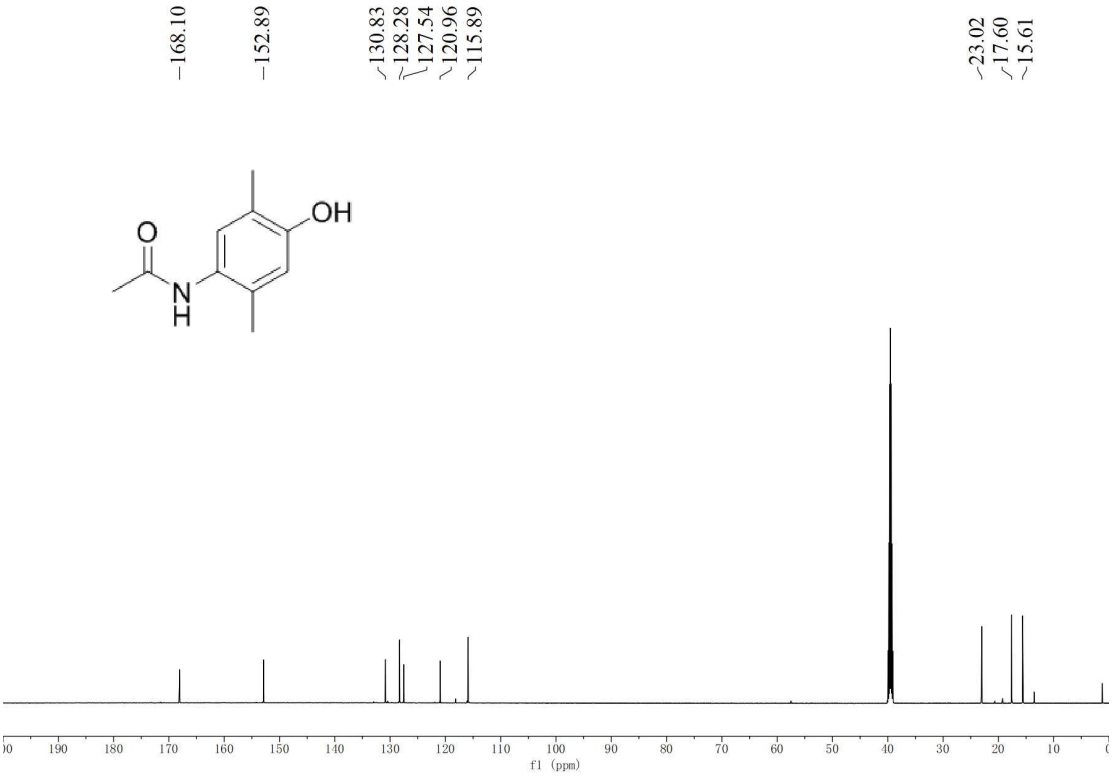
N-(2-bromo-4-hydroxyphenyl)acetamide (2h)



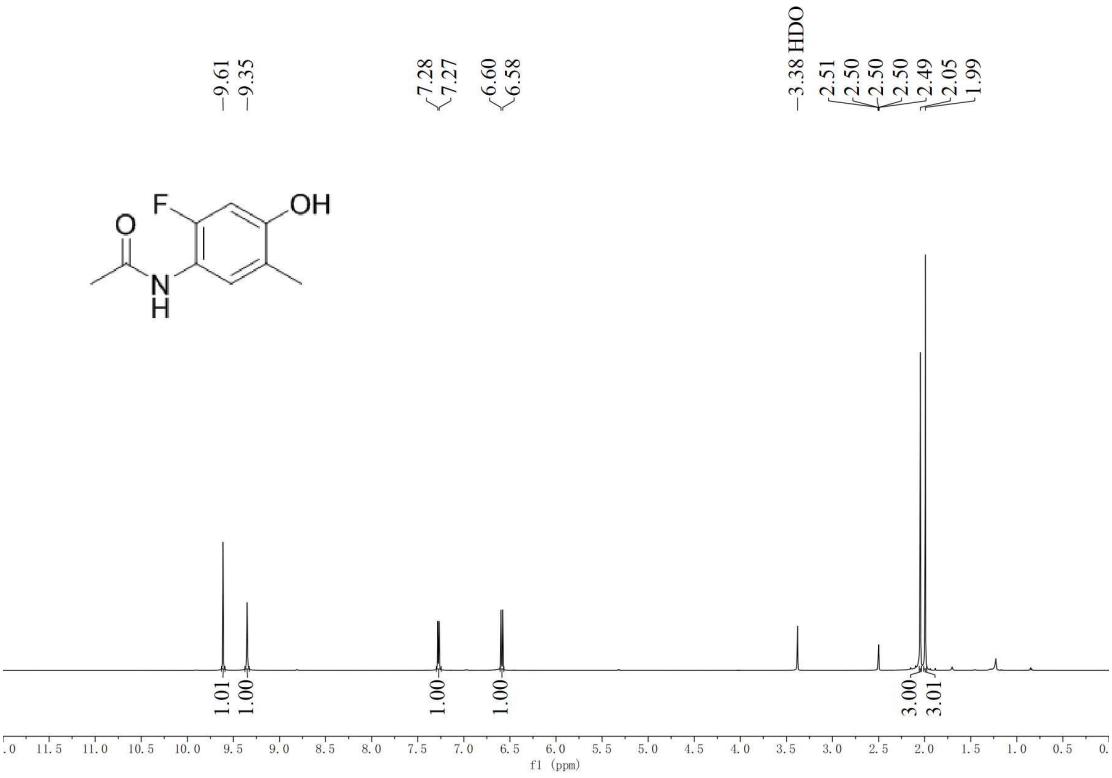


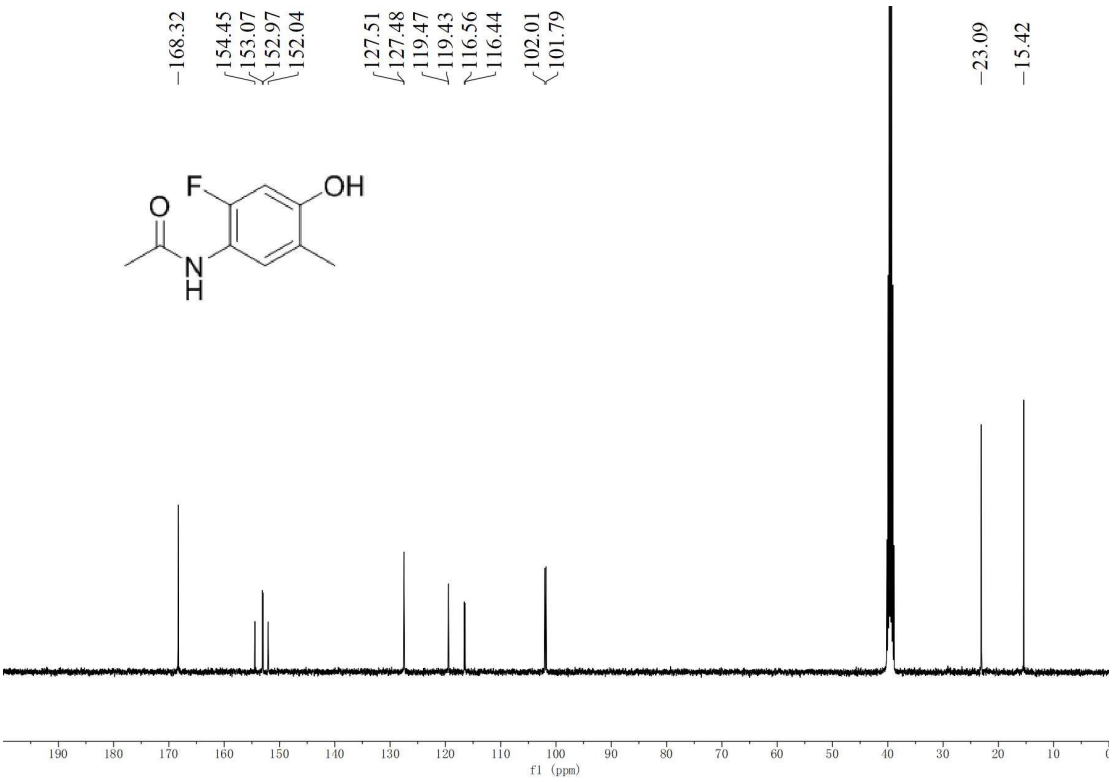
N-(4-hydroxy-2,5-dimethylphenyl)acetamide (2i)

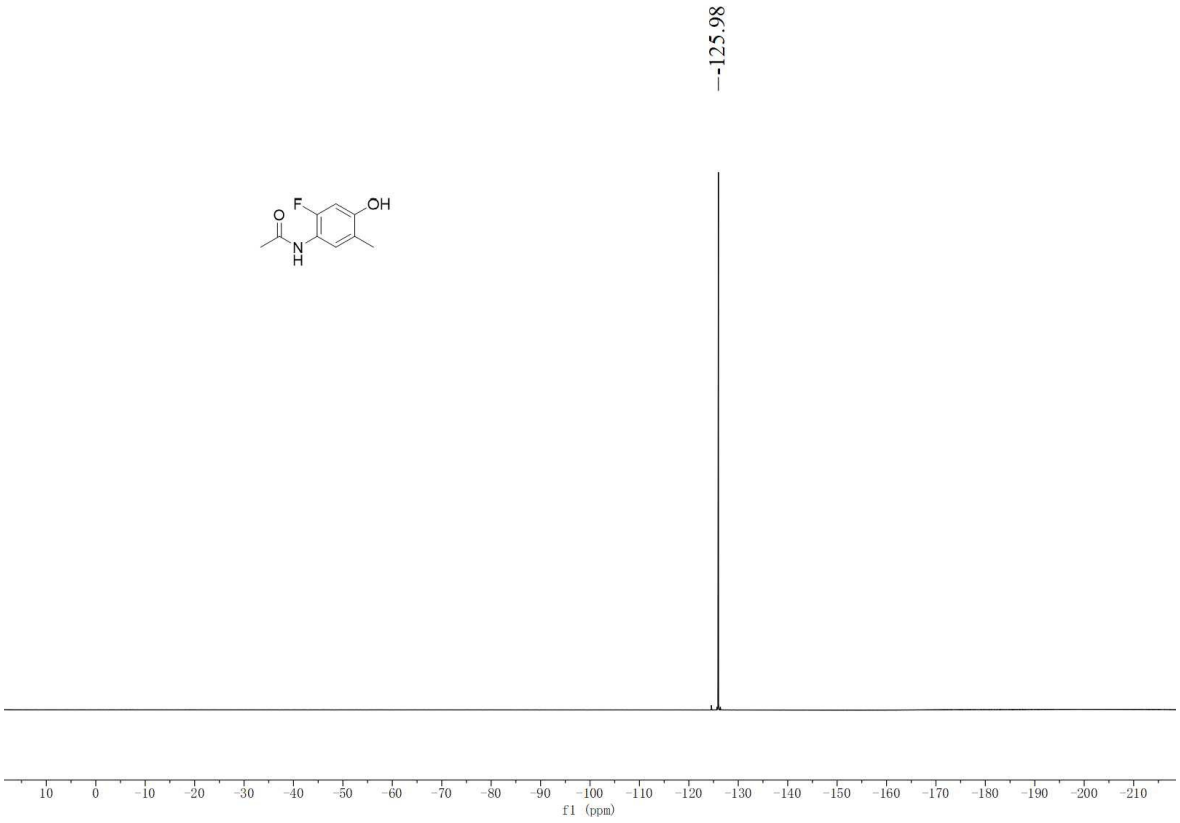




N-(2-fluoro-4-hydroxy-5-methylphenyl)acetamide (2j)



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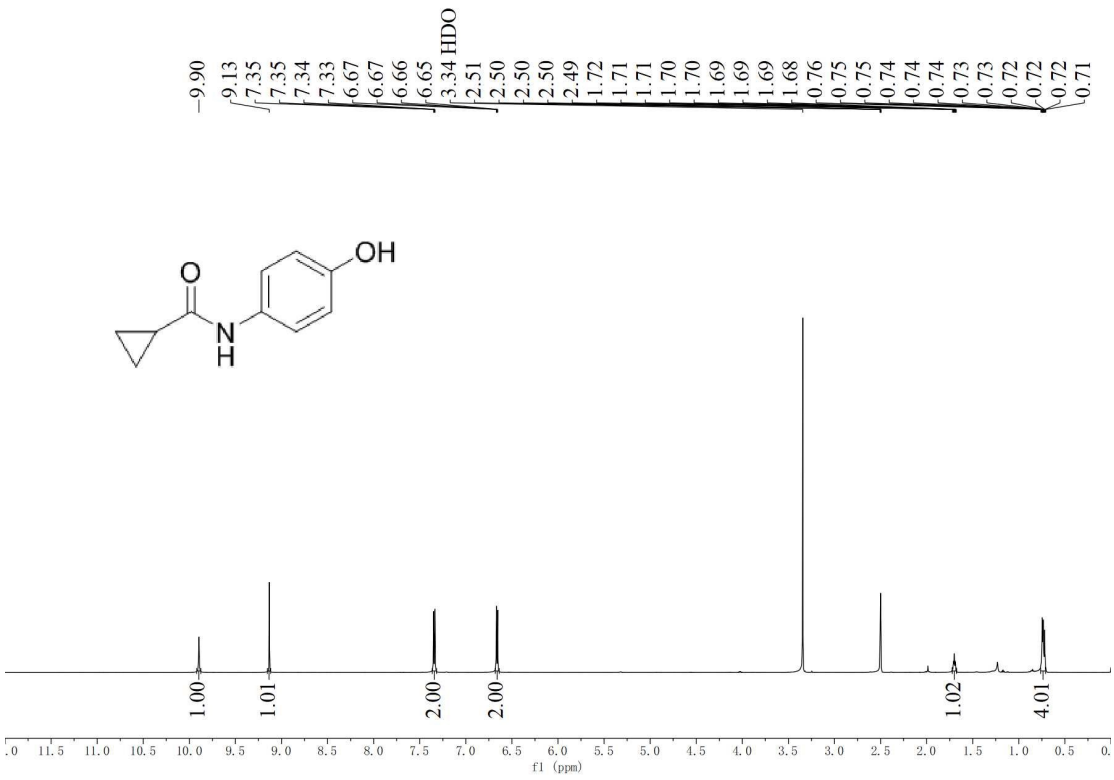
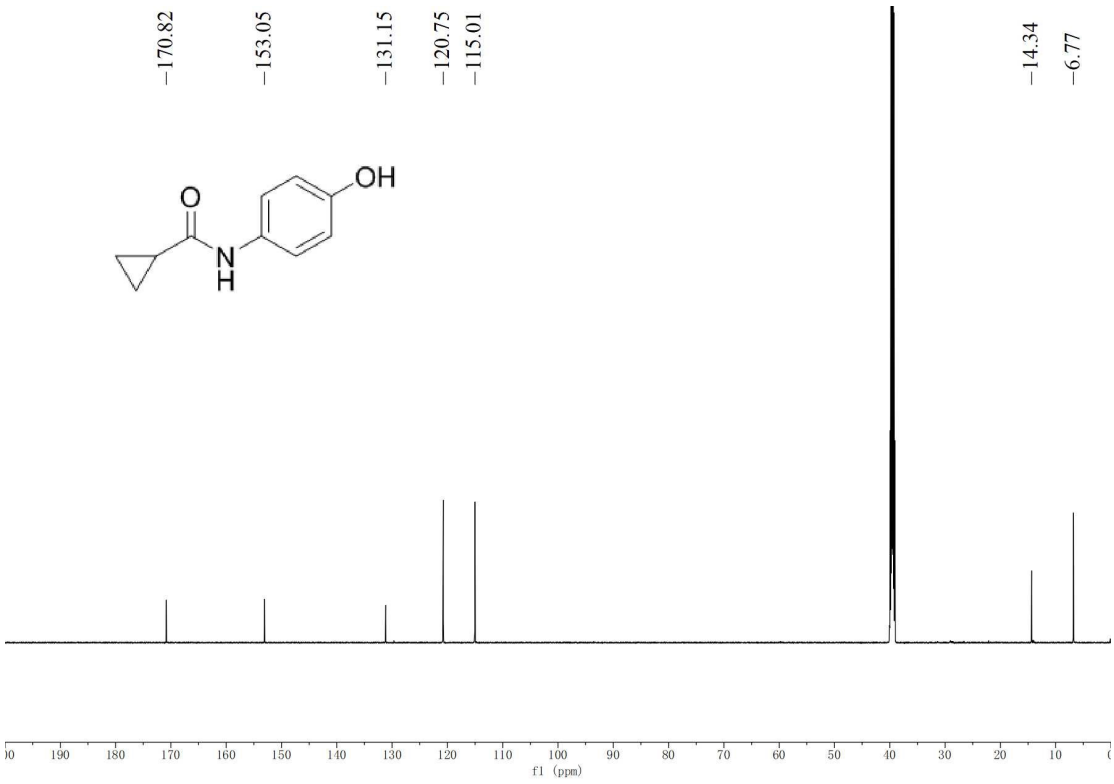
-210
f1 (ppm)

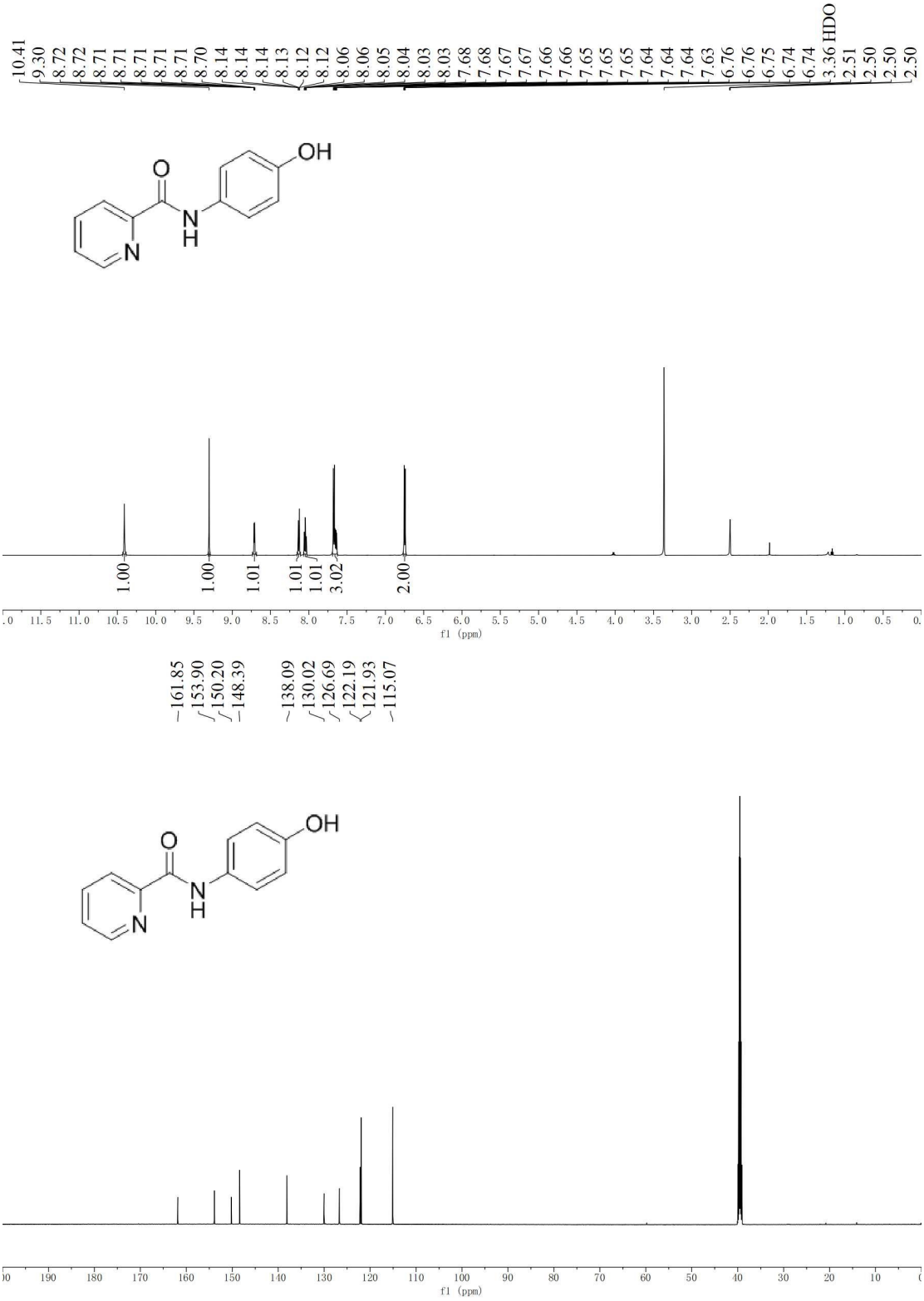
N-(4-hydroxyphenyl)cyclopropanecarboxamide (2k)



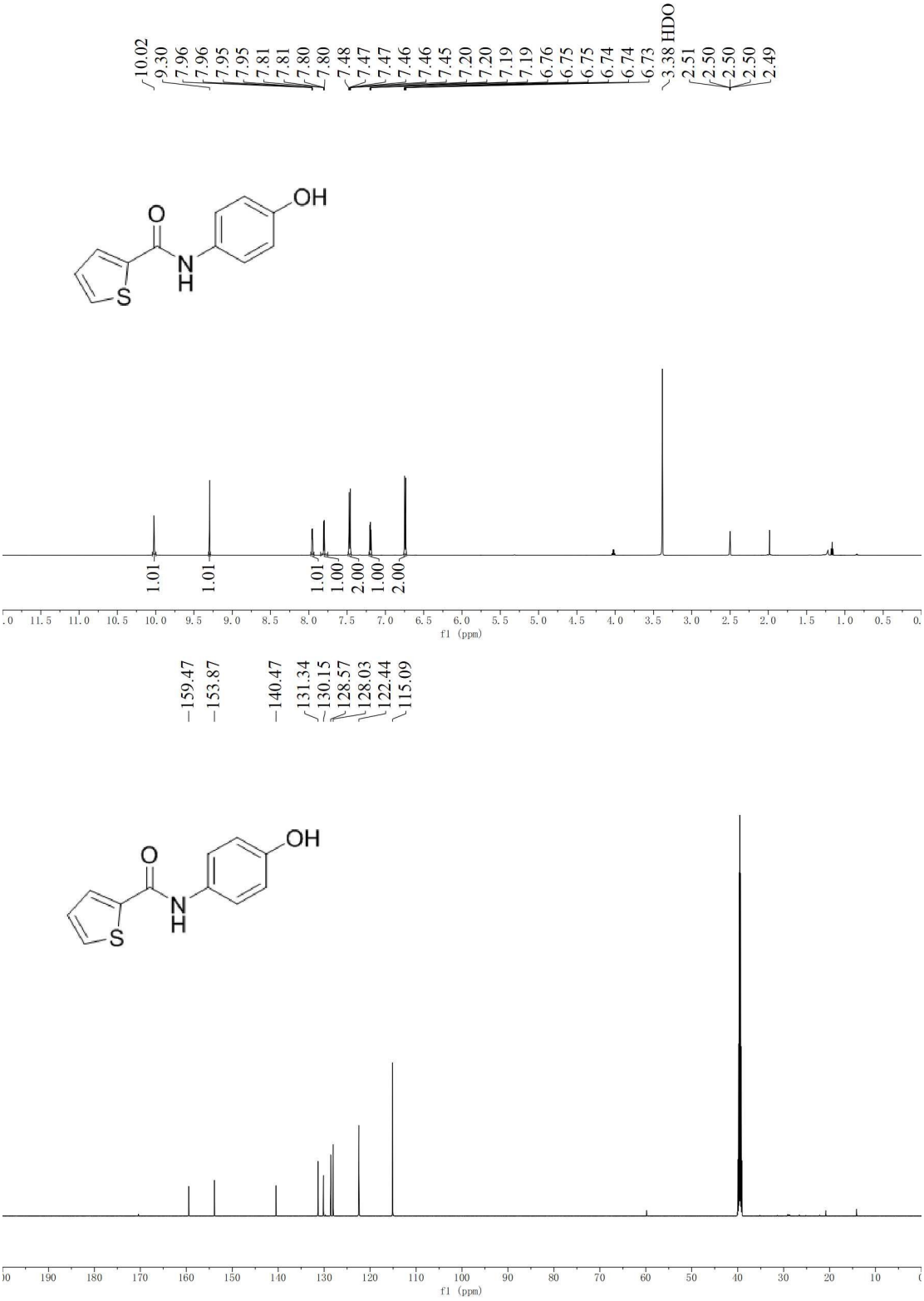


N-(4-hydroxyphenyl)benzamide (2l)

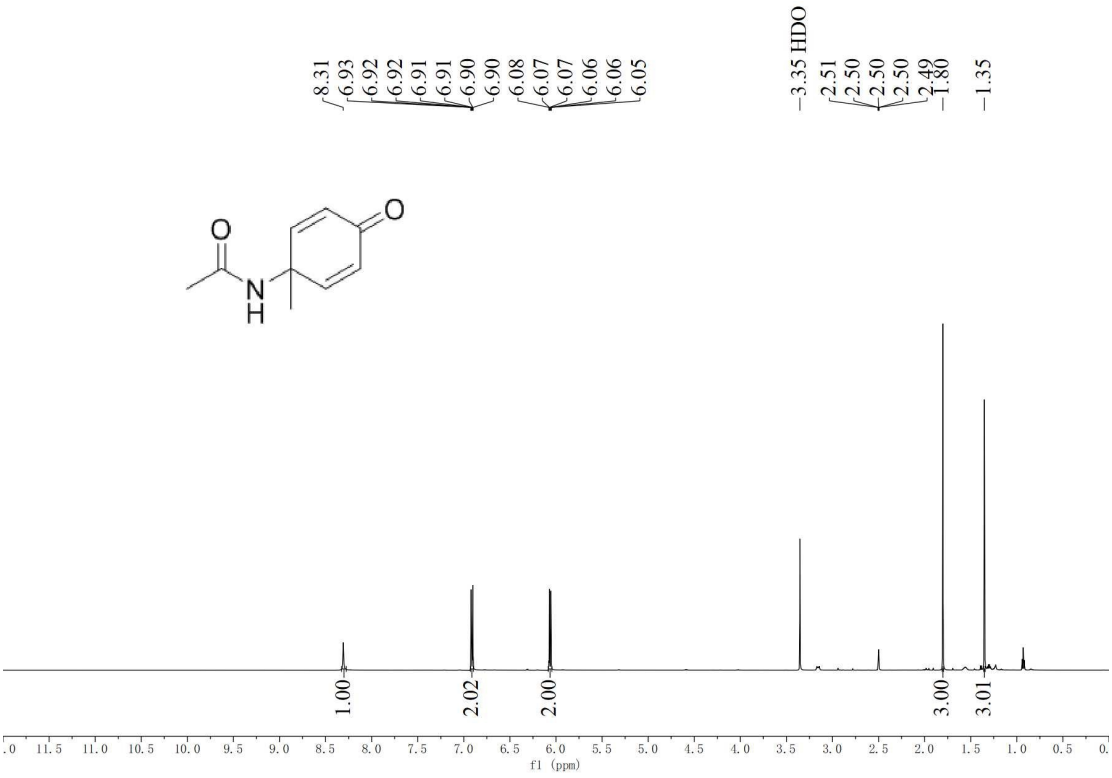
N-(4-hydroxyphenyl)picolinamide (2m)

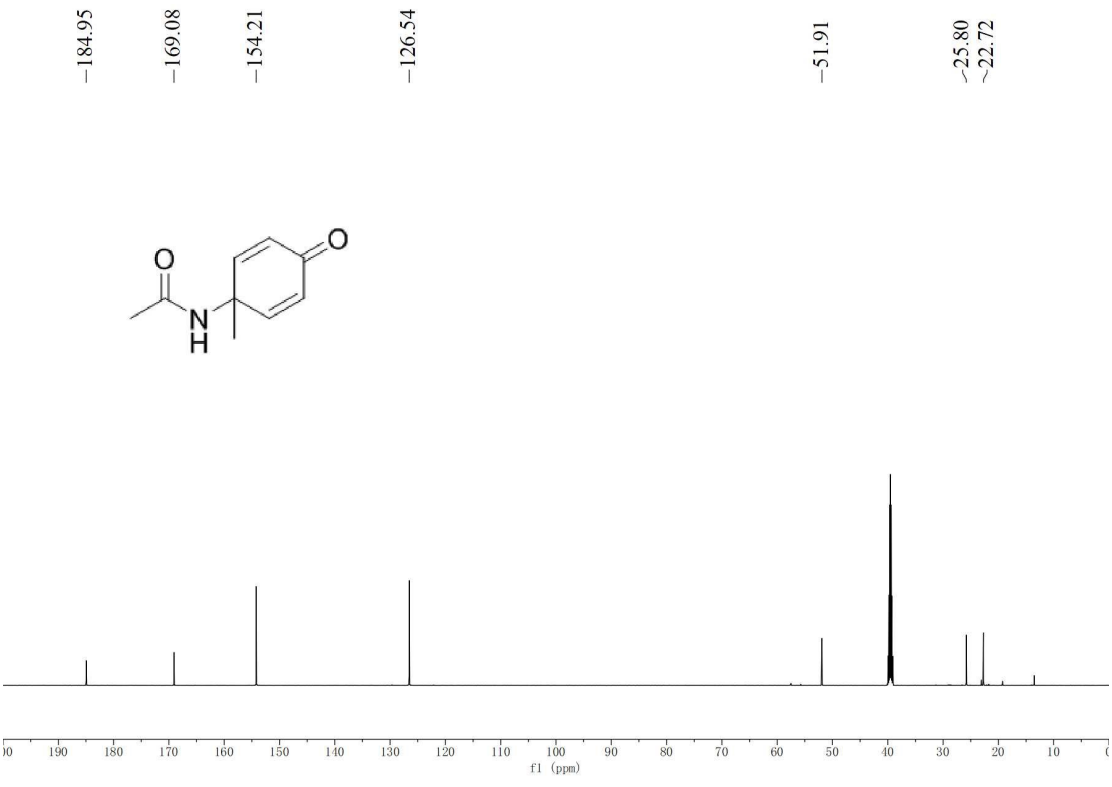


N-(4-hydroxyphenyl)thiophene-2-carboxamide (2n)

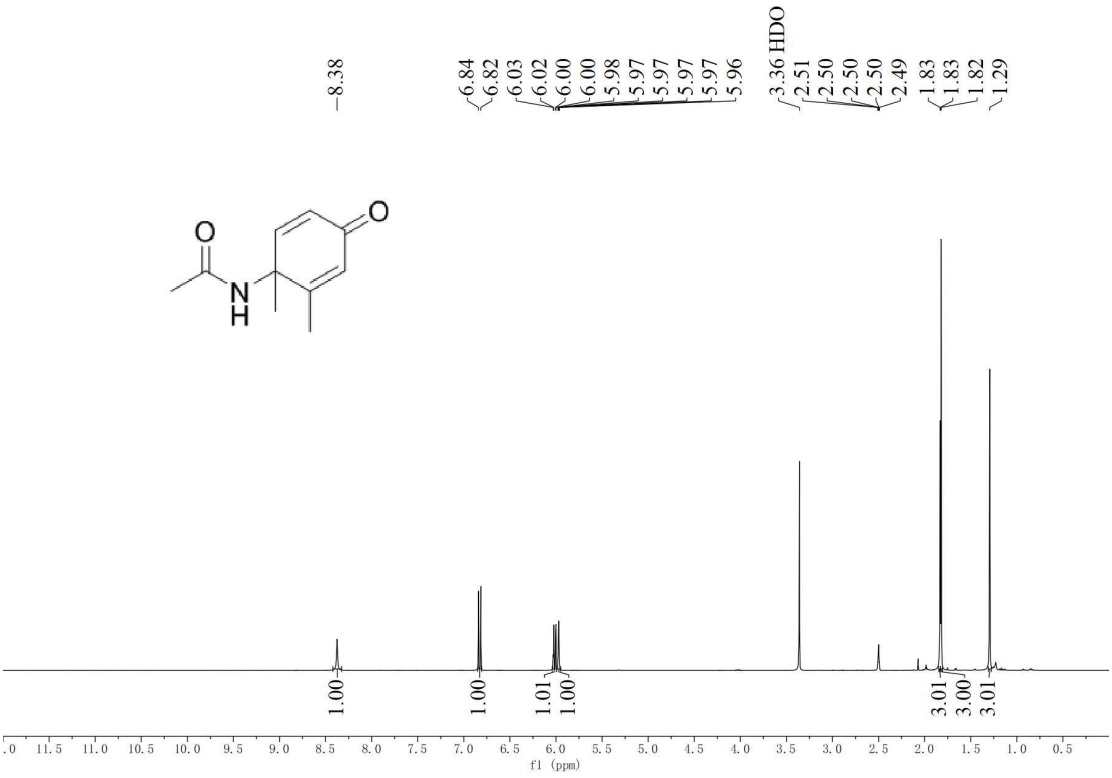


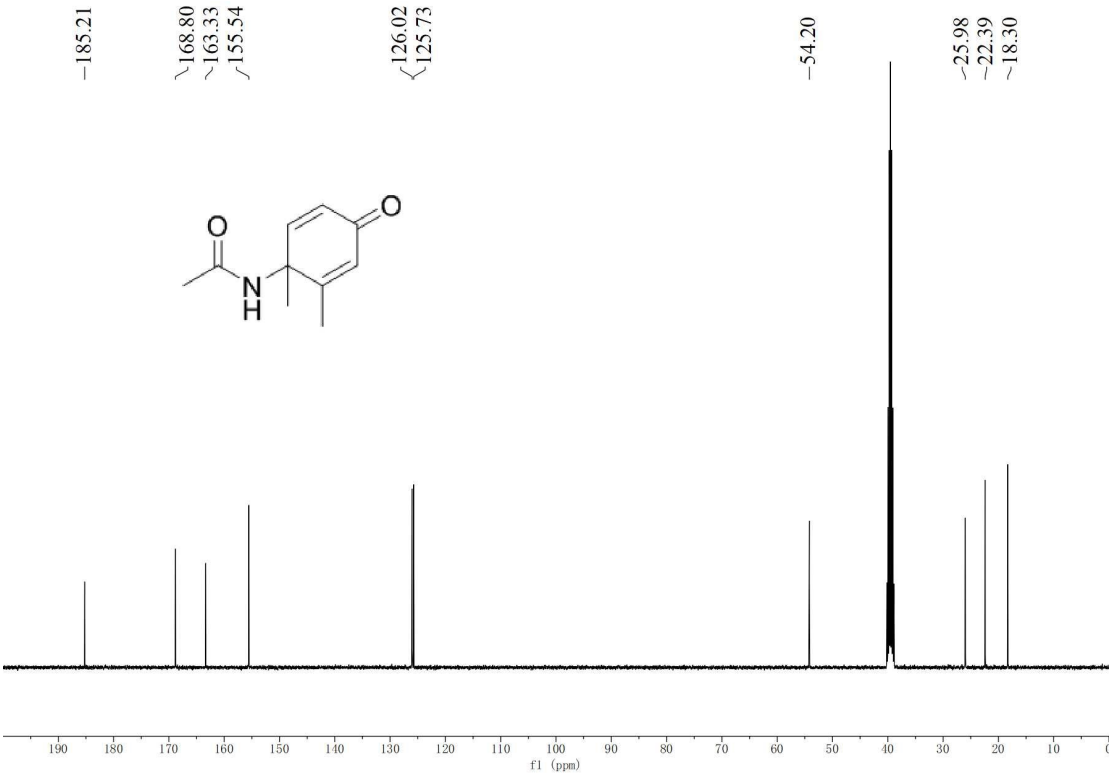
N-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (3a)



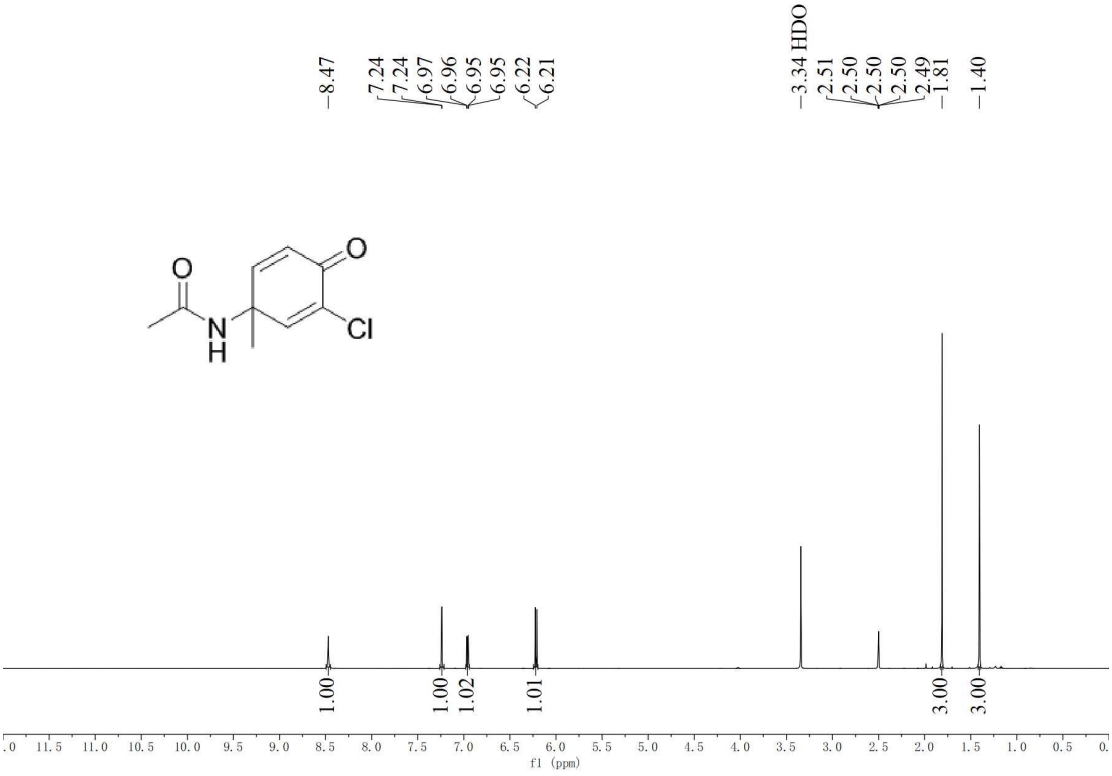


N-(1,2-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (3b)

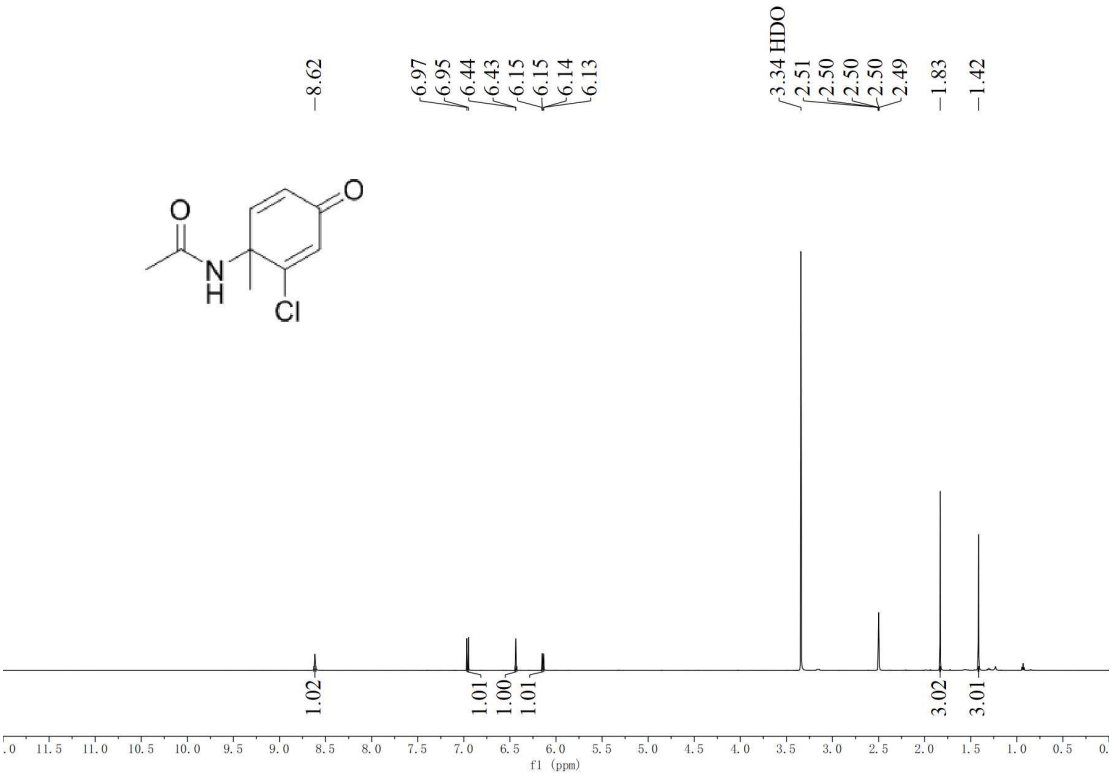


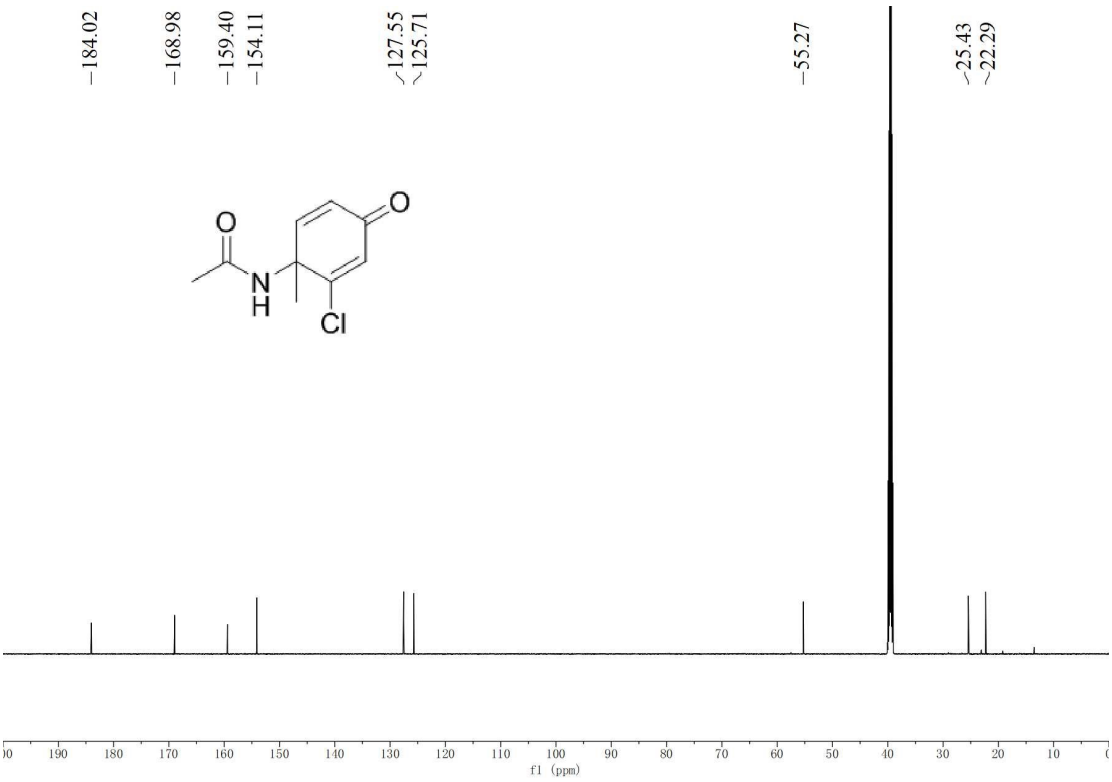


N-(3-chloro-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (3c)

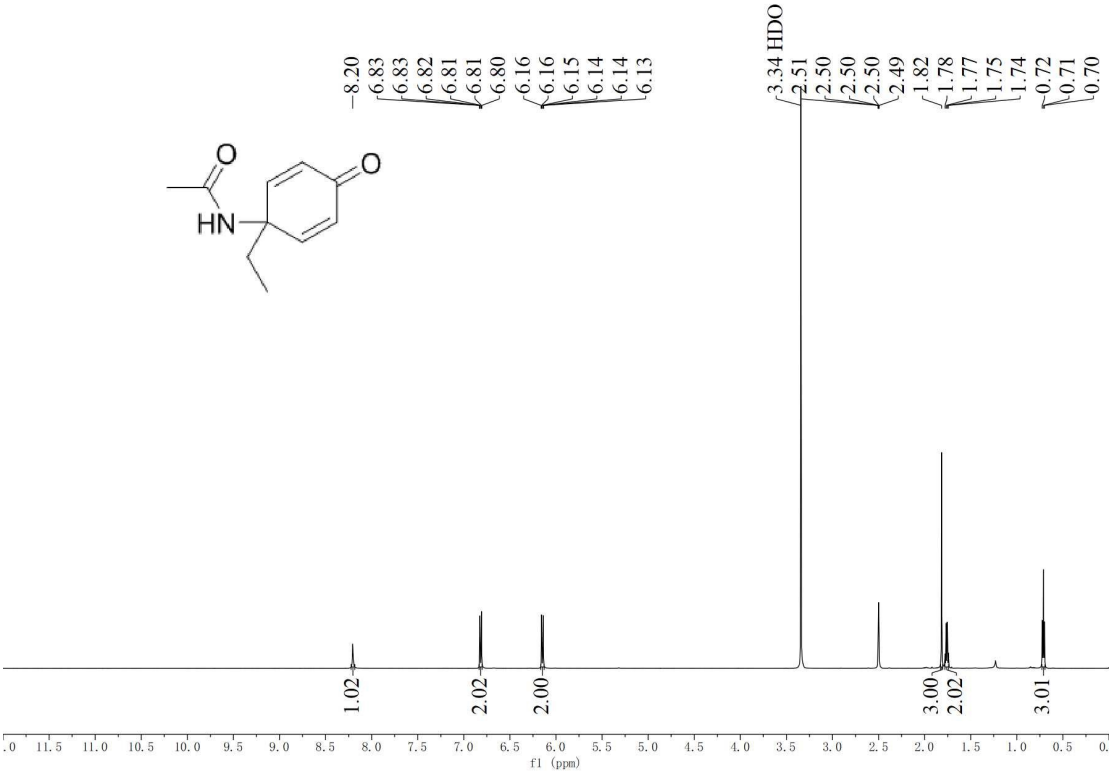


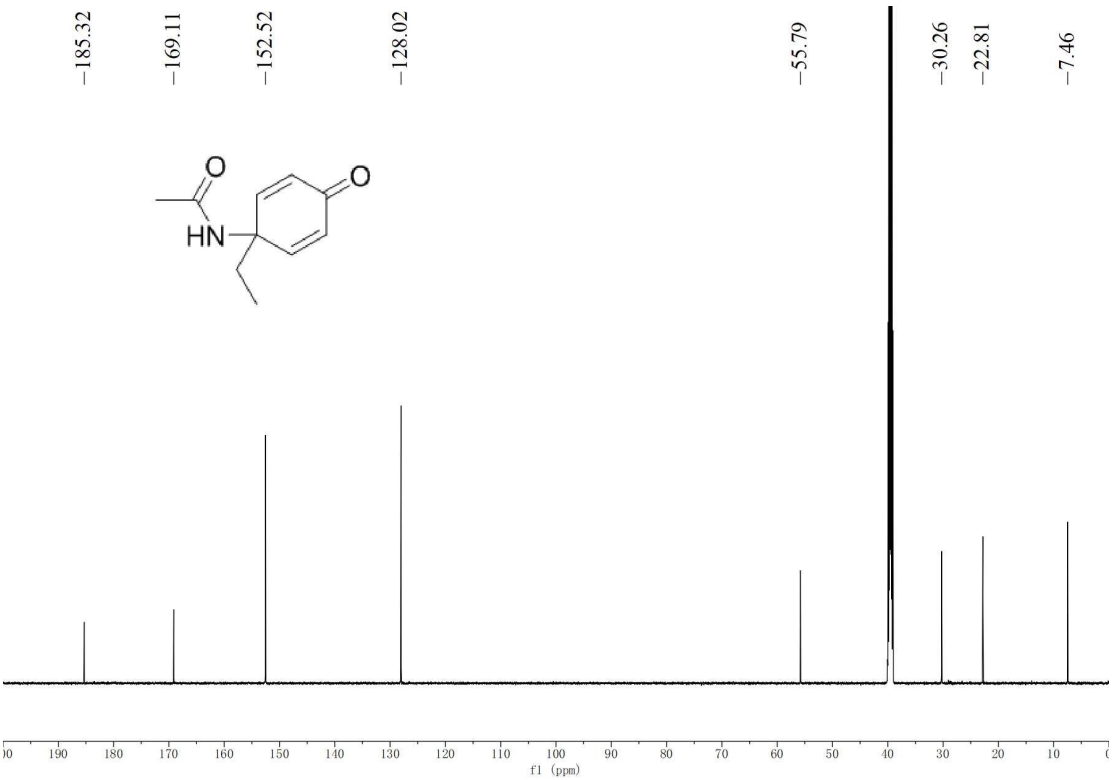
N-(2-chloro-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (3d)



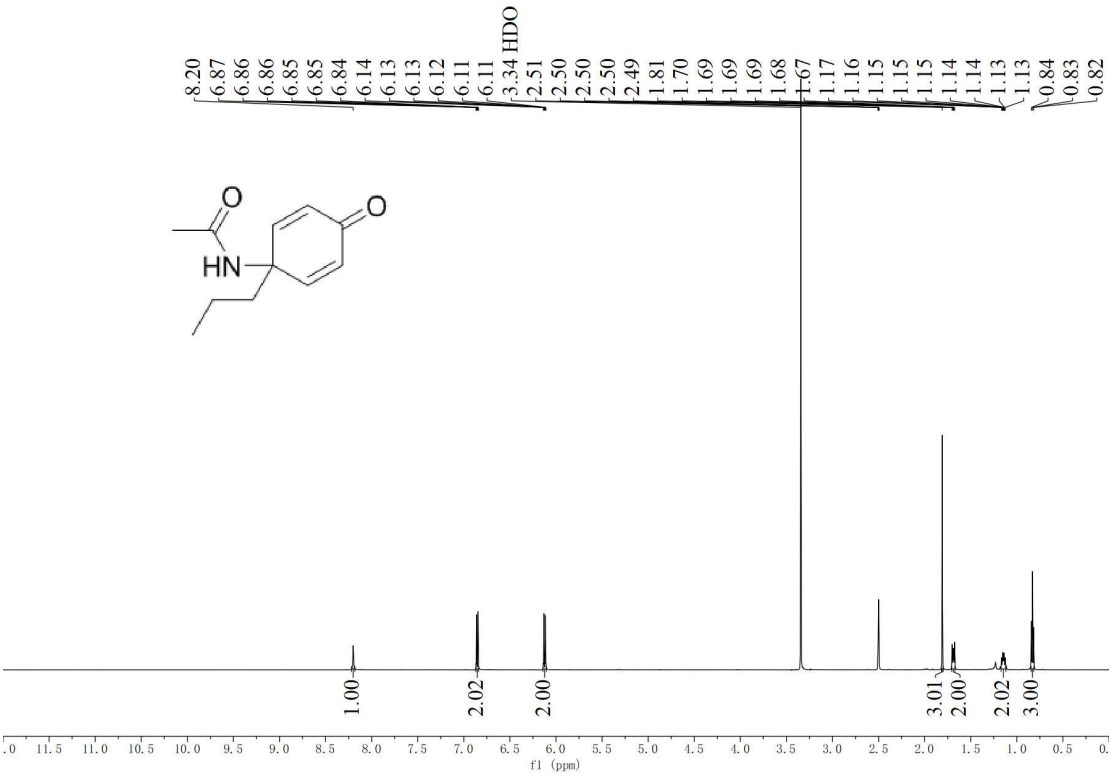


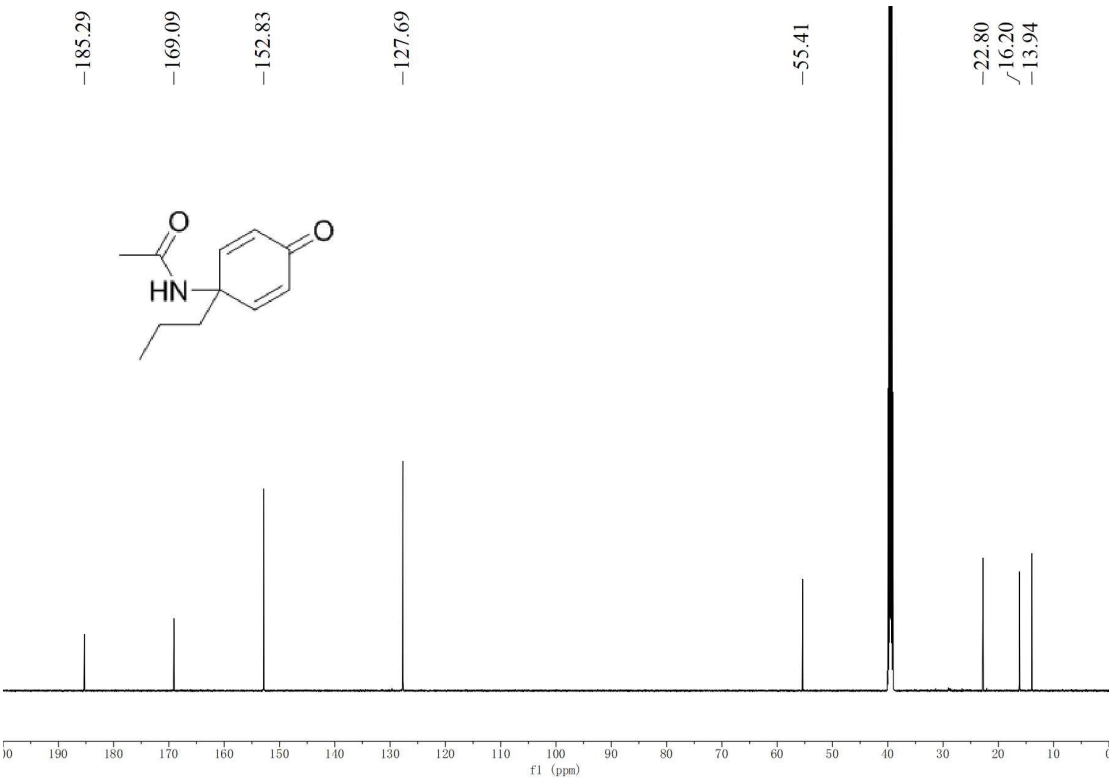
N-(1-ethyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (3e)



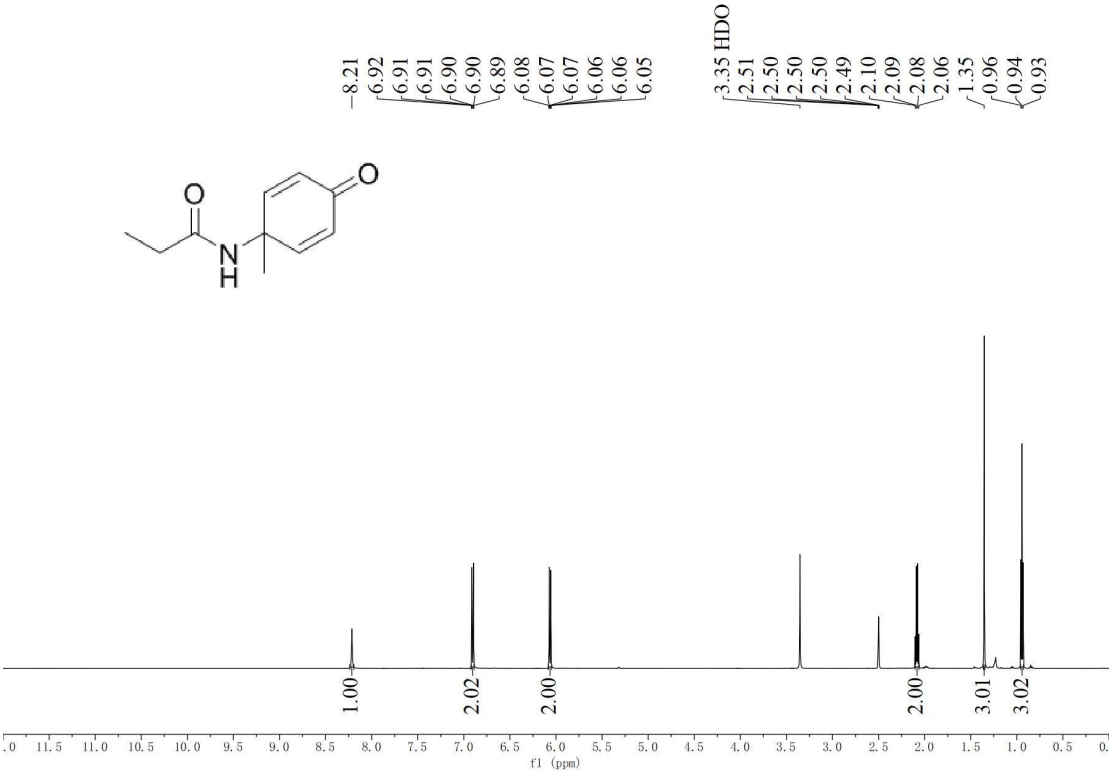


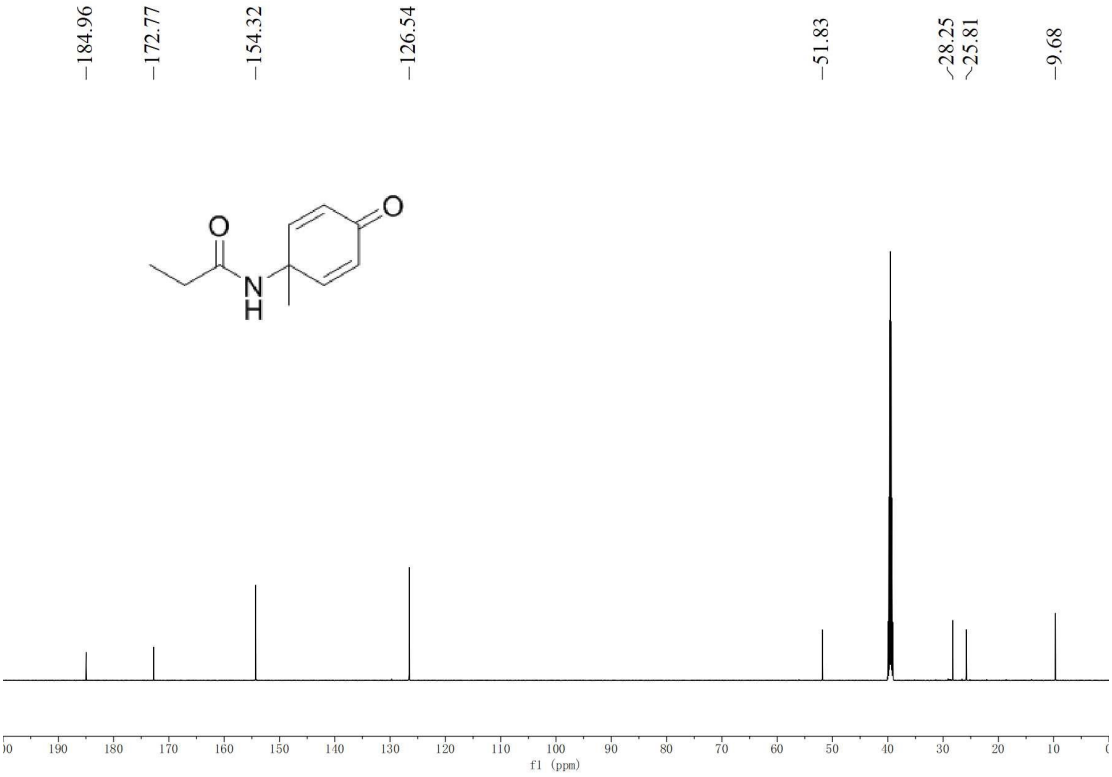
N-(4-oxo-1-propylcyclohexa-2,5-dien-1-yl)acetamide (3f)





N-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)propionamide (3g)





N-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)isobutyramide (3h)