

Supporting Information

Pd(II)-Catalyzed Sequential C-C/C-O Bond Formations: A New Strategy to Construct Trisubstituted Furans

Meifang Zheng, Liangbin Huang, Wanqing Wu, and Huanfeng Jiang*

School of Chemistry and Chemical Engineering, South China University of Technology,
Guangzhou 510640, China

E-mail: jianghf@scut.edu.cn; Fax and Tel.: (+86) 20-87112906

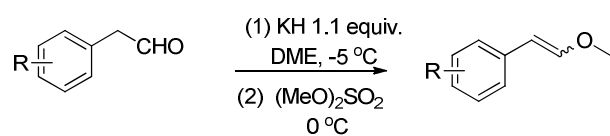
Table of Contents

General methods.....	SI 2
General procedure for the synthesis of vinyl ethers.....	SI 2
Procedure for Synthesis of buta-1,3-dienylbenzene.....	SI 2
Procedure for the synthesis of styryl acetate.....	SI 3
General procedure for the synthesis of trisubstituted furans.....	SI 3
Analysis data for compounds 3aa-3na and 3nf	SI 4
¹ H and ¹³ C spectra of selected compounds.....	SI 10

General methods

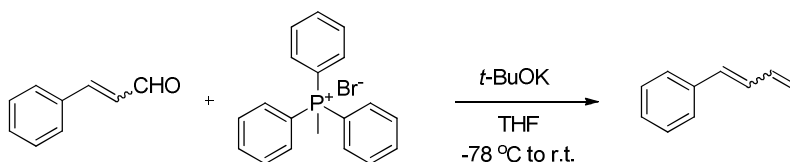
^1H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using CDCl_3 as solvent and TMS as an internal standard. Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich, Acros and Alfa Aesar Chemicals.

General procedure for the synthesis of vinyl ethers



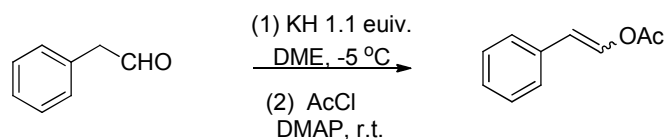
Methyl 2-arylvinyl ethers were prepared by the reaction of phenylethanal enolate with dimethylsulfate according to the known procedure.¹ To a solution of phenylacetaldehyde derivatives (0.601 g, 5 mmol) in dry 1,2-dimethoxyethane (1 mL) was added a stirred suspension of potassium hydride (0.22 g, 5.5 mmol) in dry 1,2-dimethoxyethane (3 mL) under nitrogen at -5 °C. Hydrogen evolution was quantitative within 10-12 min. To the enolate solution thus obtained was added, with stirring under nitrogen at 0 °C, a solution of dimethyl sulfate (10 mmol). After the addition was complete, stirring was continued for 15 min at room temperature. The mixture was then extracted with hexane (10 mL). The organic layer was dried with MgSO_4 and evaporated in vacuum. Then the concentrated crude product was subjected to isolation by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (50:1) to afford a Z/E mixture.¹

Synthesis of buta-1,3-dienylbenzene



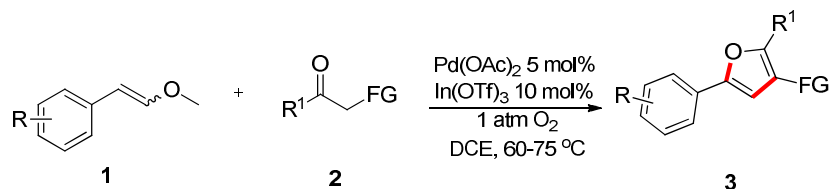
To an oven dried 100 mL round bottom flask equipped with a stir bar, was added 1.45 g (3.90 mmol, 1.30 equiv.) methyltriphenylphosphonium bromide and 13 mL of THF under a N_2 atmosphere. To the cloudy mixture 1.05 mL of a 4.0 mol/L THF solution of *t*-BuOK was added. The reaction mixture was stirred at room temperature for 10 min, to give an orange color. The reaction was cooled to -78 °C and 0.55 mL of cinnamaldehyde (3 mmol, 1.0 equiv.) was added dropwise. The mixture was allowed to slowly warm to room temperature, and stirred for 15 h. To the red mixture was added 20 mL of hexane. The cloudy mixture was filtered and concentrated in vacuum and subjected to isolation by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (20:1) to afford buta-1,3-dien-1-ylbenzene.²

Procedure for the synthesis of styryl acetate



To a solution of phenylacetaldehyde (0.601 g, 5 mmol) in dry 1,2-dimethoxyethane (1 mL) was added a stirred suspension of potassium hydride (0.22 g, 5.5 mmol) in dry 1,2-dimethoxyethane (3 mL) under nitrogen at -5 °C. Hydrogen evolution was quantitative within 10-12 min. The enolate solution thus obtained was added by syringe to a solution of excess acetyl chloride (0.785 g, 10 mmol) in 1,2-dimethoxyethane (2 mL) containing 4-dimethylaminopyridine (0.03 g, 0.25 mmol). Stirring was continued for 15 min at room temperature. Then the reaction mixture was slurried into a two-phase ice-water/hexane system. After separation, the organic phase was washed twice with saturated aqueous NaHCO₃, then with water, and dried over MgSO₄. The solvent was evaporated in vacuum and the crude product was subjected to isolation by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (15:1) to afford a Z/E mixture.¹

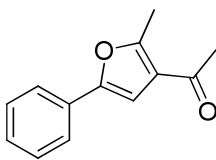
General procedure for the synthesis of trisubstituted furans



To a Schlenk tube β -methoxystyrene (**1a**, 0.3 mmol), Pd(OAc)₂ catalyst (0.02 mmol), In(OTf)₃ (0.06 mmol), acetatylacetone (**2a**, 0.36 mmol) and 1,2-dichloroethane (1 mL) were added. Then the tube was charged with O₂ (1 atm), and was stirred at 75 °C (oil bath temperature) for 18 h. After cooling, the solvent was diluted with water and extracted with diethyl ether. The ether layer was washed with aqueous NaCl, and dried with anhydrous MgSO₄. Volatiles were removed under reduced pressure and the crude product was subjected to isolation by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (10:1 to 50:1) to afford furans.

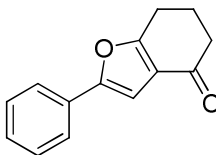
Analysis data for compound 3aa-3na and 3nf

1-(2-methyl-5-phenylfuran-3-yl)ethanone 3aa



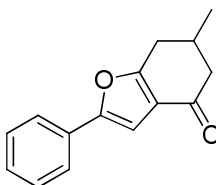
Yellow viscous oil. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, J = 8.0 Hz, 2H), 7.39 (t, 2H), 7.28 (t, 1H), 6.84 (s, 1H), 2.66 (s, 3H), 2.43 (s, J = 17.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.15, 157.94, 151.67, 129.92, 128.77, 127.78, 123.68, 123.24, 105.09, 29.19, 14.55; ν_{max} (film)/ cm^{-1} : 2921, 1764, 1603, 1243, 1180; ESI-HRMS calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2$ $[\text{M}+\text{H}]^+$ 201.0911, found 201.0909.

2-phenyl-6,7-dihydrobenzofuran-4(5H)-one 3ab



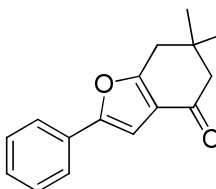
^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.34 – 7.24 (m, 1H), 6.88 (s, 1H), 2.94 (t, J = 6.2 Hz, 2H), 2.57 – 2.45 (m, 2H), 2.27 – 2.15 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.51, 166.70, 154.23, 129.81, 128.80, 128.49, 128.09, 123.97, 122.94, 100.88, 37.63, 23.45, 22.57; ν_{max} (film)/ cm^{-1} : 2986, 2943, 1742, 1672, 1373, 1241, 1046; ESI-HRMS calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2$ $[\text{M}+\text{H}]^+$ 213.0910, found 213.0903.

6-methyl-2-phenyl-6,7-dihydrobenzofuran-4(5H)-one 3ac



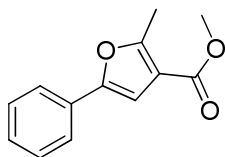
^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 7.4 Hz, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 6.86 (s, 1H), 2.98 (t, 1H), 2.65 – 2.38 (m, 3H), 2.25 (m, J = 27.3 Hz, 1H), 1.17 (d, J = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.07, 166.37, 154.39, 129.83, 128.79, 128.07, 123.94, 122.54, 100.82, 46.08, 31.49, 30.76, 21.07; ν_{max} (film)/ cm^{-1} : 3100, 2961, 1743, 1675, 1450, 1241; ESI-HRMS calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2$ $[\text{M}+\text{H}]^+$ 227.1067, found 227.1065.

6,6-dimethyl-2-phenyl-6,7-dihydrobenzofuran-4(5H)-one 3ad



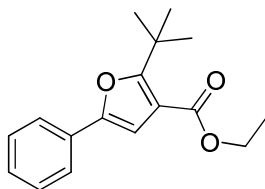
^1H NMR (400 MHz, CDCl_3) δ 7.26 (s, 1H), 7.16 (d, $J = 6.7$ Hz, 2H), 6.87 (d, $J = 6.5$ Hz, 1H), 2.28 (s, 2H), 2.16 (d, $J = 3.9$ Hz, 2H), 1.05 (d, $J = 4.2$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.14, 164.06, 138.89, 130.02, 129.02, 127.66, 126.09, 113.87, 51.09, 40.76, 38.20, 31.98, 29.69, 28.56, 28.54, 27.48; ν_{max} (film)/ cm^{-1} : 2958, 1746, 1666, 1378, 1242, 1049; ESI-HRMS calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$ $[\text{M}+\text{H}]^+$ 241.1218, found 241.1214.

methyl 2-methyl-5-phenylfuran-3-carboxylate 3ae



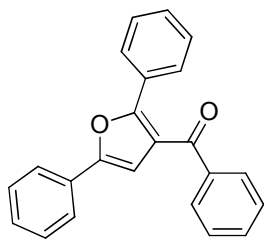
^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.2$ Hz, 2H), 7.59 – 7.34 (m, 3H), 6.84 (d, $J = 1.7$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 3H), 1.43 – 1.27 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.60, 157.50, 141.19, 129.80, 129.33, 128.40, 128.07, 113.91, 112.98, 60.54, 14.23; ν_{max} (film)/ cm^{-1} : 2991, 1764, 1376, 1242, 1055; ESI-HRMS calcd for $\text{C}_{13}\text{H}_{12}\text{O}_3$ $[\text{M}+\text{H}]^+$ 217.0859, found 217.0857.

ethyl 5-phenyl-2-(tert-butyl)furan-3-carboxylate 3af



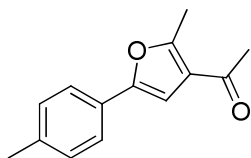
^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.59 (m, 2H), 7.38 (t, $J = 7.7$ Hz, 2H), 6.93 (s, 1H), 4.31 (q, $J = 7.1$ Hz, 2H), 1.50 (s, 9H), 1.38 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.64, 163.73, 149.63, 130.20, 128.70, 127.49, 123.60, 114.12, 107.53, 60.30, 34.80, 28.25, 14.33; ν_{max} (film)/ cm^{-1} : 2971, 1715, 1598, 1450, 1443; ESI-HRMS calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$ $[\text{M}+\text{H}]^+$ 273.3465, found 273.3461.

(2,5-diphenylfuran-3-yl)(phenyl)methanone 3ag



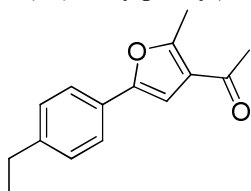
^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 7.3$ Hz, 2H), 7.77 (t, $J = 8.0$ Hz, 4H), 7.56 – 7.50 (d, 1H), 7.45 – 7.38 (m, 4H), 7.36 – 7.29 (m, 4H), 6.93 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.82, 155.01, 152.50, 138.03, 132.94, 129.78, 129.74, 129.04, 128.93, 128.87, 128.72, 128.40, 128.37, 128.18, 127.46, 124.10, 122.84, 108.69; ν_{max} (film)/ cm^{-1} : 3061, 1598, 1528, 1295, 1180, 2063; ESI-HRMS calcd for $\text{C}_{23}\text{H}_{16}\text{O}_2$ $[\text{M}+\text{H}]^+$ 325.1223, found 325.1219.

1-(2-methyl-5-(p-tolyl)furan-3-yl)ethanone 3ba



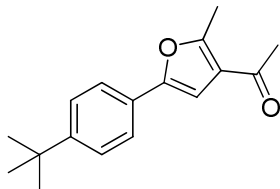
^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.7$ Hz, 1H), 7.70 (s, 1H), 7.45 (t, $J = 7.8$ Hz, 1H), 7.31 (m, $J = 17.8, 9.9$ Hz, 1H), 5.29 (d, $J = 43.5$ Hz, 1H), 2.82 – 2.53 (m, 3H), 2.14 (d, $J = 16.6$ Hz, 3H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.34, 196.74, 159.56, 139.38, 138.10, 129.43, 128.92, 125.22, 123.90, 98.43, 29.27, 26.68, 19.89; ν_{max} (film)/ cm^{-1} : 2992, 1764, 1376, 1242, 1056; ESI-HRMS calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$ $[\text{M}+\text{H}]^+$ 215.1067, found 215.1065.

1-(5-(4-ethylphenyl)-2-methylfuran-3-yl)ethanone 3ca



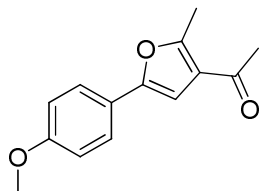
^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 6.71 (s, 1H), 2.68 – 2.53 (m, 5H), 2.37 (s, 3H), 1.18 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.22, 157.61, 151.96, 144.09, 128.26, 127.48, 123.77, 123.21, 104.36, 29.16, 28.65, 15.44, 14.52; ν_{max} (film)/ cm^{-1} : 2924, 1708, 1673, 1566, 1224; ESI-HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$ $[\text{M}+\text{H}]^+$ 229.2939, found 229.2935.

1-(5-(4-tert-butylphenyl)-2-methylfuran-3-yl)ethanone 3da



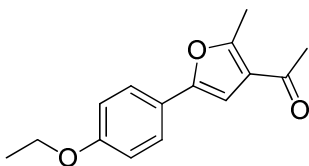
^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 6.83 (s, 1H), 2.69 (s, 2H), 2.48 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.22, 157.66, 151.90, 150.96, 127.23, 126.62, 125.69, 125.38, 123.52, 123.22, 104.44, 34.68, 31.35, 31.26, 29.19, 14.55; ν_{max} (film)/ cm^{-1} : 2957, 1501, 1463, 1363, 1228; ESI-HRMS calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{H}]^+$ 257.1536, found 257.1529.

1-(5-(4-ethoxyphenyl)-2-methylfuran-3-yl)ethanone 3ea



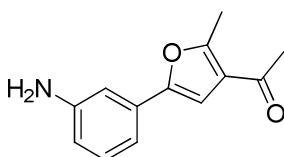
^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.70 (s, 1H), 3.87 (s, 3H), 2.65 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.20, 159.37, 157.28, 151.77, 125.18, 123.21, 122.96, 114.23, 103.46, 55.34, 29.16, 14.48; ν_{max} (film)/ cm^{-1} : 2926, 1672, 1594, 1502, 1248, 1174; ESI-HRMS calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3$ $[\text{M}+\text{H}]^+$ 231.1018, found 231.1013.

1-(5-(4-ethoxyphenyl)-2-methylfuran-3-yl)ethanone 3fa



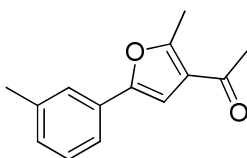
^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 6.69 (s, 1H), 4.06 (q, J = 7.0 Hz, 2H), 2.64 (s, 3H), 2.44 (s, 3H), 1.42 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.17, 158.76, 157.21, 151.84, 125.17, 123.21, 122.80, 114.77, 103.37, 63.55, 29.14, 14.79, 14.47; ν_{max} (film)/ cm^{-1} : 2982, 1763, 1672, 1501, 1244, 1173; ESI-HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$ $[\text{M}+\text{H}]^+$ 245.2931, found 245.2926.

1-(5-(3-aminophenyl)-2-methylfuran-3-yl)ethanone 3ga



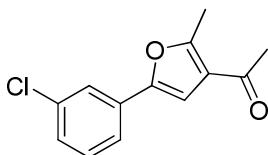
^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.8 Hz, 1H), 7.70 (s, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.30 (q, J = 7.9, 1.2 Hz, 2H), 5.25 (s, N-H), 2.60 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.34, 159.53, 139.39, 138.11, 129.43, 128.93, 125.22, 123.92, 29.29, 26.69, 19.90; ν_{max} (film)/ cm^{-1} : 3361, 2993, 1763, 1601, 1242, 1187; ESI-HRMS calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 216.1031, found 216.1025.

1-(5-(3-methylphenyl)-2-methylfuran-3-yl)ethanone 3ha



^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.40 (t, 2H), 7.29 (d, J = 7.6 Hz, 1H), 7.10 (d, J = 7.5 Hz, 1H), 6.83 (s, 1H), 2.66 (s, 3H), 2.45 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.17, 157.83, 151.86, 138.43, 129.85, 128.68, 128.60, 124.32, 123.20, 120.88, 104.96, 29.15, 21.46, 14.51; ν_{max} (film)/ cm^{-1} : 2922, 1764, 1673, 1555, 1239; ESI-HRMS calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$ $[\text{M}+\text{H}]^+$ 215.1067, found 215.1062.

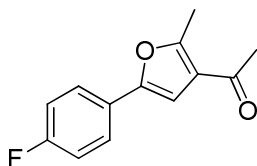
1-(5-(3-chlorophenyl)-2-methylfuran-3-yl)ethanone 3ia



^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.7 Hz, 1H), 7.70 (s, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.31 (d, J = 7.9 Hz, 1H), 5.24 (s, 1H), 2.60 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.34, 159.56, 139.38, 138.10, 129.43, 128.92, 125.22, 123.90, 98.43, 29.27, 19.89; ν_{max} (film)/ cm^{-1} : 2925, 1711, 1660,

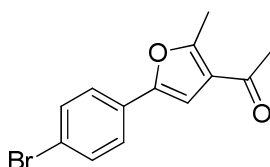
1598, 1427, 1268; ESI-HRMS calcd for C₁₃H₁₁ClO₂ [M+H]⁺ 235.0531, found 235.0533.

1-(5-(4-fluorophenyl)-2-methylfuran-3-yl)ethanone 3ja



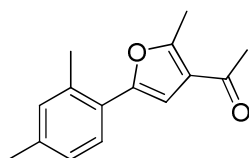
¹H NMR (400 MHz, CDCl₃) δ 7.50 (s, 4H), 6.85 (s, 1H), 2.65 (s, 3H), 2.45 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 193.90, 158.22, 150.64, 131.92, 128.84, 125.16, 123.36, 121.58, 105.67, 29.14, 14.53; ν_{max} (film)/cm⁻¹: ESI-HRMS calcd for C₁₃H₁₁FO₂ [M+H]⁺ 219.0826, found 219.0819.

1-(5-(4-bromophenyl)-2-methylfuran-3-yl)ethanone 3ka



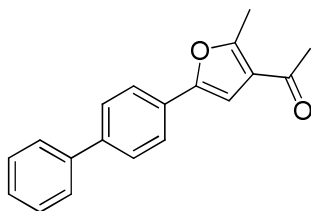
¹H NMR (400 MHz, CDCl₃) δ 7.50 (s, 4H), 6.84 (s, 1H), 2.65 (s, 3H), 2.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 193.90, 158.22, 150.64, 131.92, 128.84, 125.16, 123.36, 121.58, 105.67, 77.34, 77.03, 76.71, 29.14, 14.53; ν_{max} (film)/cm⁻¹: 2992, 1764, 1682, 1377, 1243; ESI-HRMS calcd for C₁₃H₁₁BrO₂ [M+H]⁺ 279.0027, found 279.0031.

1-(5-(2,4-dimethylphenyl)-2-methylfuran-3-yl)ethanone 3la



¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.4 Hz, 1H), 7.06 (s, 2H), 6.66 (s, 1H), 2.66 (s, 3H), 2.46 (s, 6H), 2.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 194.24, 157.26, 151.48, 137.79, 134.53, 131.94, 126.96, 126.79, 126.52, 123.11, 108.05, 29.17, 21.68, 21.10, 14.51; ν_{max} (film)/cm⁻¹: 2943, 1764, 1608, 1382, 1257, 1052; ESI-HRMS calcd for C₁₅H₁₆O₂ [M+H]⁺ 229.2937, found 229.2933.

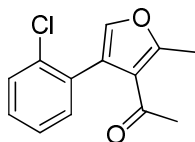
1-(5-([1,1'-biphenyl]-4-yl)-2-methylfuran-3-yl)ethanone 3ma



¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 2.2 Hz, 2H), 7.74 (d, *J* = 2.1 Hz, 2H), 7.49 (m, *J* = 13.7, 6.5 Hz, 4H), 6.91 (s, 1H), 2.71 (s, 3H), 2.50 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 194.07, 158.04, 151.49, 140.49, 140.44, 129.16, 129.07, 128.85, 127.68, 127.50, 127.43,

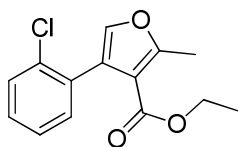
127.34, 126.92, 124.11, 105.23, 29.17, 14.56; ν_{\max} (film)/ cm^{-1} : 2924, 2362, 1711, 1659, 1571, 1475, 1427, 1381; ESI-HRMS calcd for $\text{C}_{19}\text{H}_{16}\text{O}_2$ 277.1224, $[\text{M}+\text{H}]^+$ found 277.1217.

1-(4-(2-chlorophenyl)-2-methylfuran-3-yl)ethanone 3na



^1H NMR (400 MHz, CDCl_3) δ 7.83 (q, $J = 7.9, 1.6$ Hz, 1H), 7.44 (q, $J = 8.0, 1.1$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.25 – 7.18 (m, 1H), 2.67 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.24, 157.99, 147.89, 130.77, 130.05, 128.43, 128.29, 127.68, 126.93, 123.18, 111.17, 29.15, 14.44; ν_{\max} (film)/ cm^{-1} : 2991, 1764, 1676, 1377, 1241, 1055; ESI-HRMS calcd for $\text{C}_{13}\text{H}_{11}\text{ClO}_2$ $[\text{M}+\text{H}]^+$ 235.0531, found 235.0534.

ethyl 4-(2-chlorophenyl)-2-methylfuran-3-carboxylate 3nf



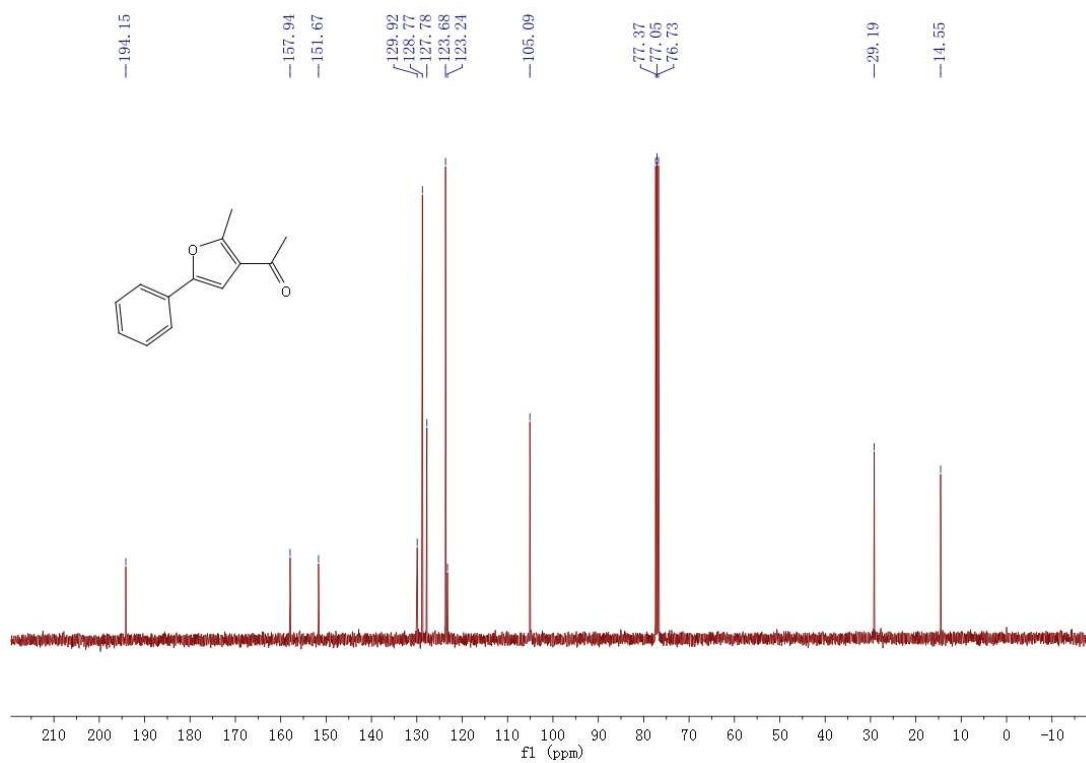
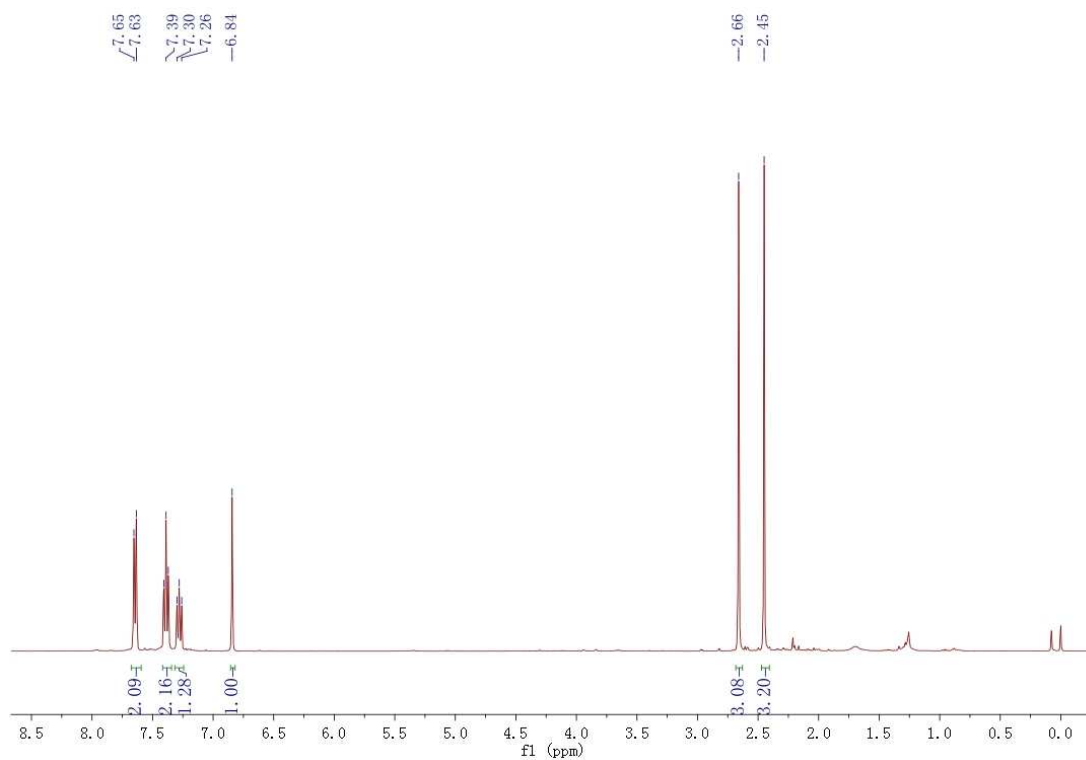
^1H NMR (400 MHz, CDCl_3) δ 7.82 (q, $J = 7.9, 1.5$ Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.34 (s, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.20 (t, $J = 6.9$ Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 2.66 (s, 3H), 1.37 (t, $J = 5.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.98, 158.67, 147.94, 130.75, 130.13, 128.45, 128.28, 127.59, 126.84, 115.51, 111.48, 60.26, 14.41, 13.86; ν_{\max} (film)/ cm^{-1} : 2983, 1708, 1430, 1225, 1100, 1031; ESI-HRMS calcd for $\text{C}_{14}\text{H}_{13}\text{ClO}_3$ $[\text{M}+\text{H}]^+$ 265.0627, found 265.0623.

References:

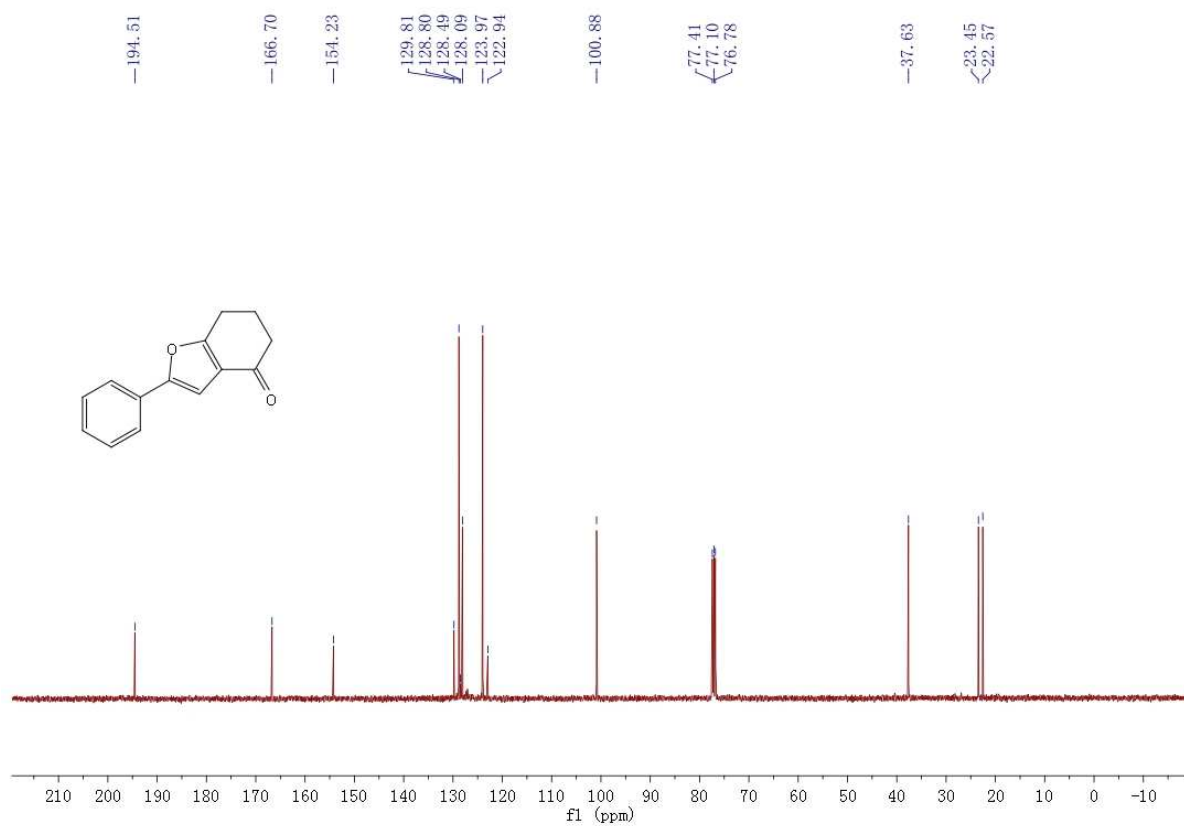
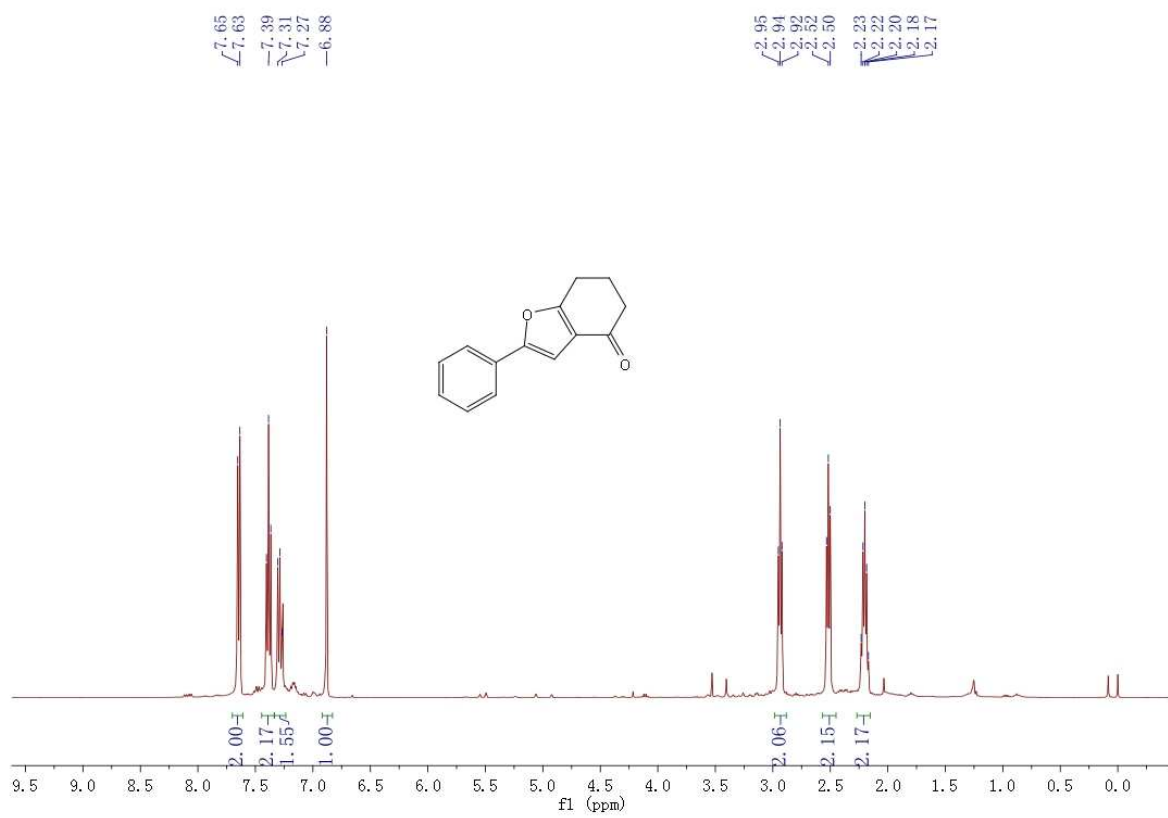
- [1] Ladjama, D.; Riehl, J. J. *Synthesis* **1979**, 11, 504-507.
- [2] Liao, L.; Sigman, M. S. *J. Am. Chem. Soc.* **2010**, 132, 10209-10211.

¹H and ¹³C spectra of selected compounds

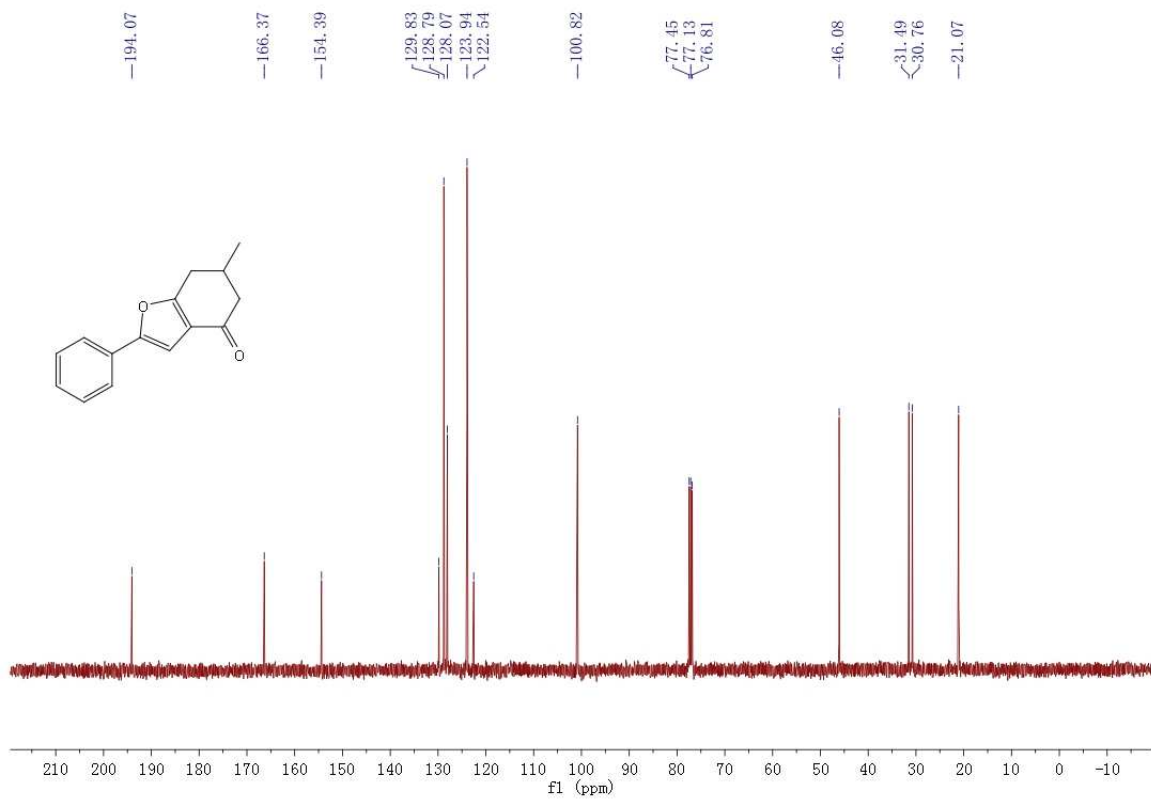
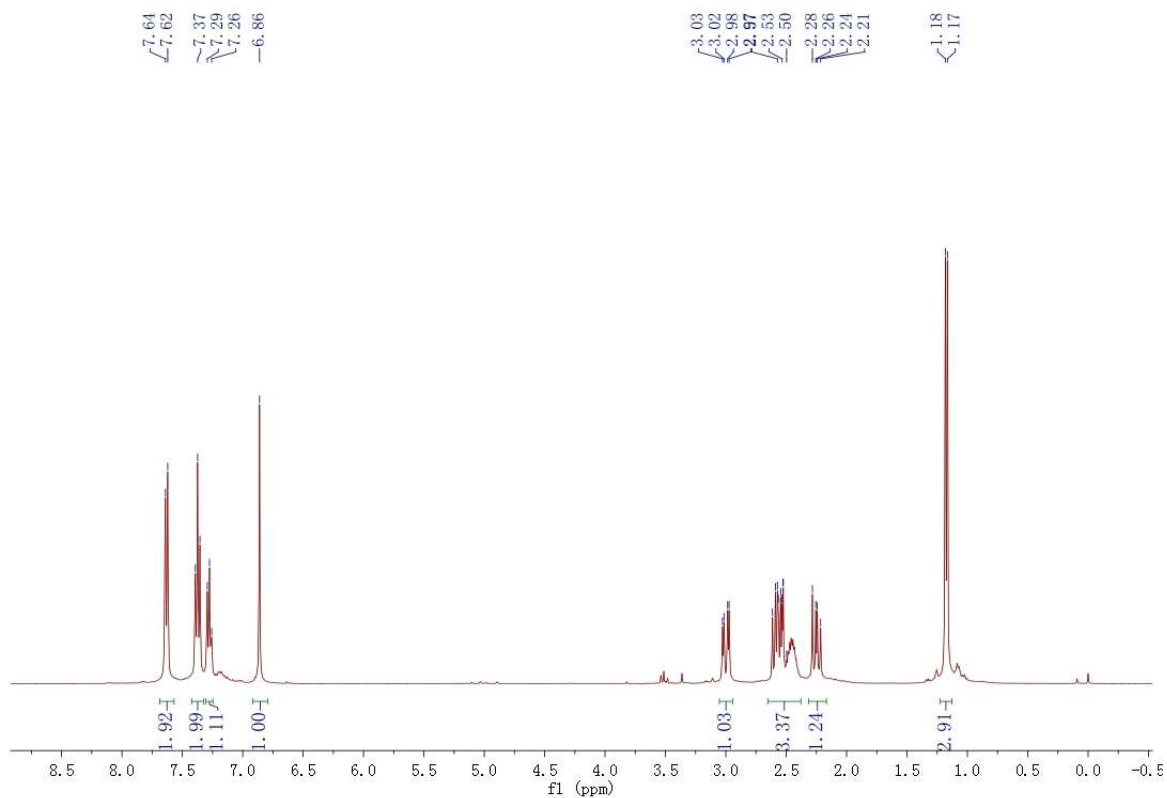
3aa

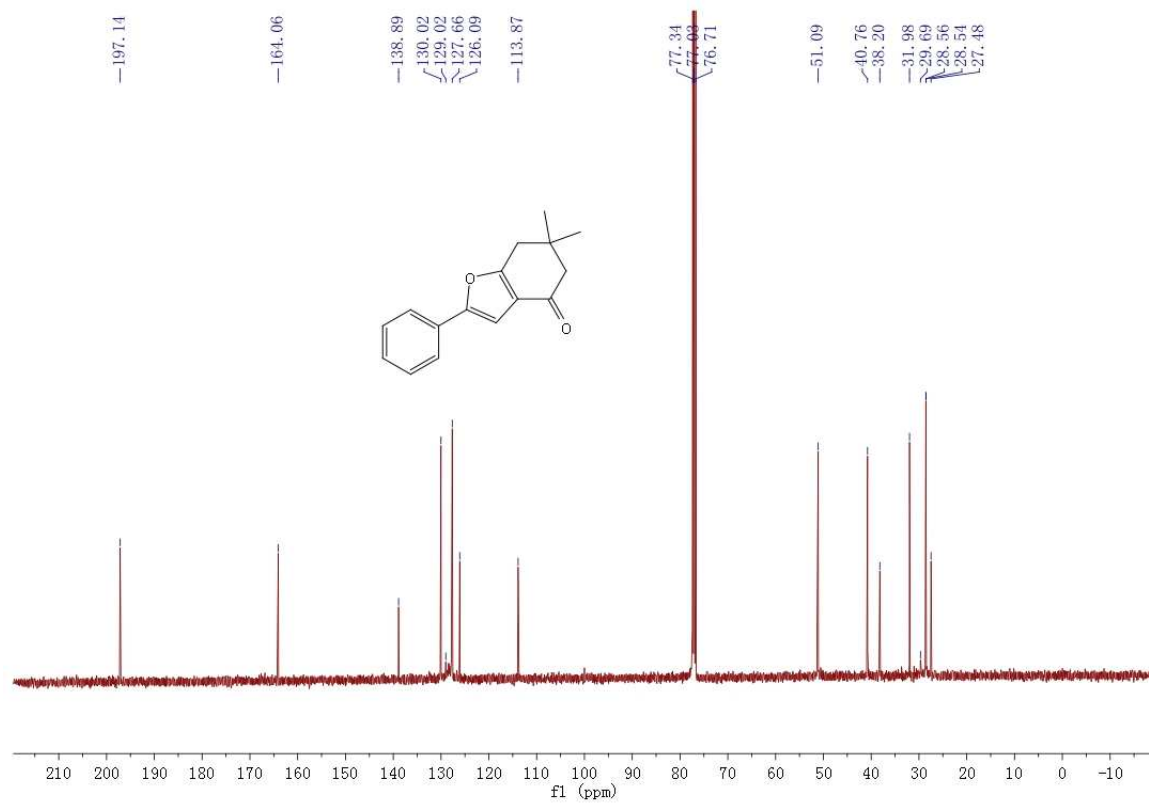


3ab

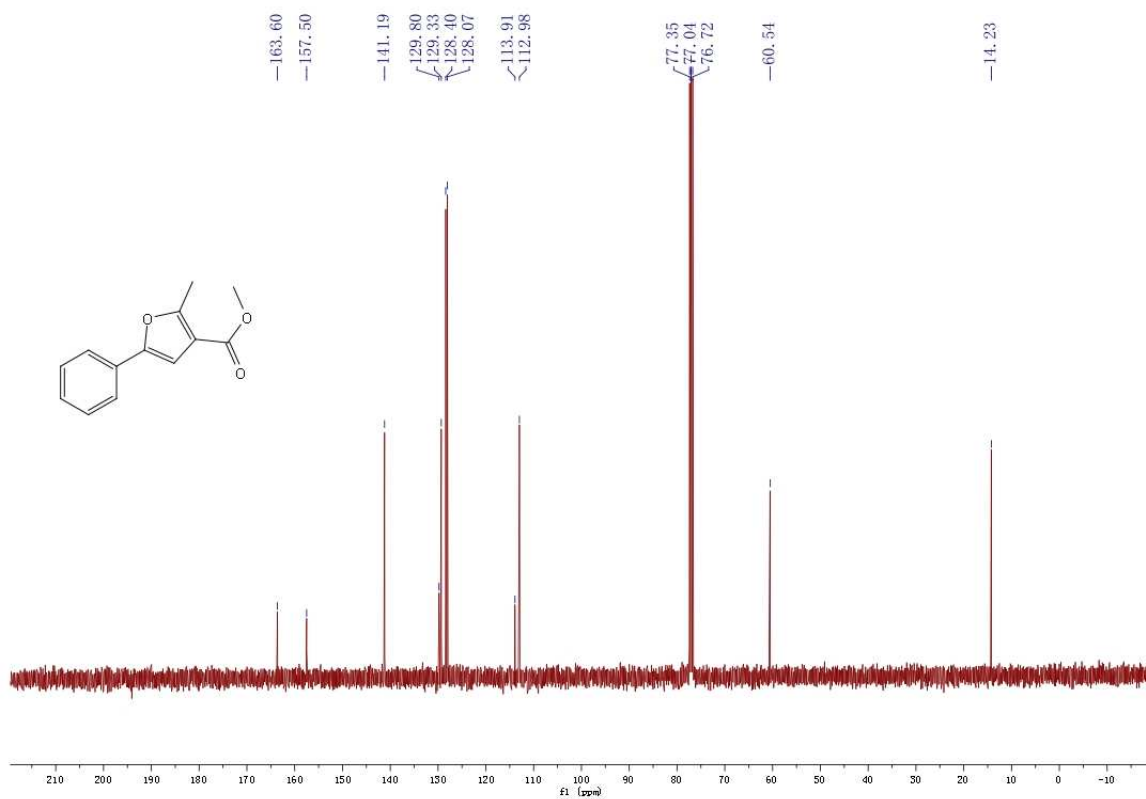
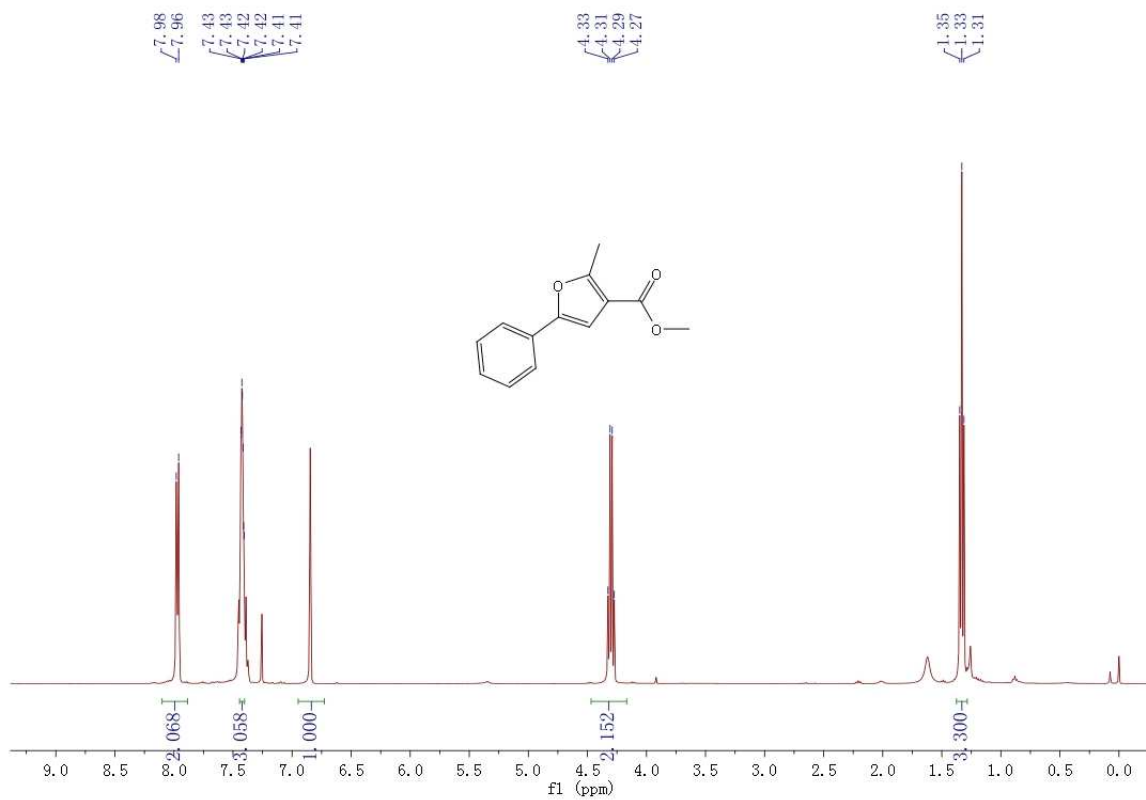


3ac

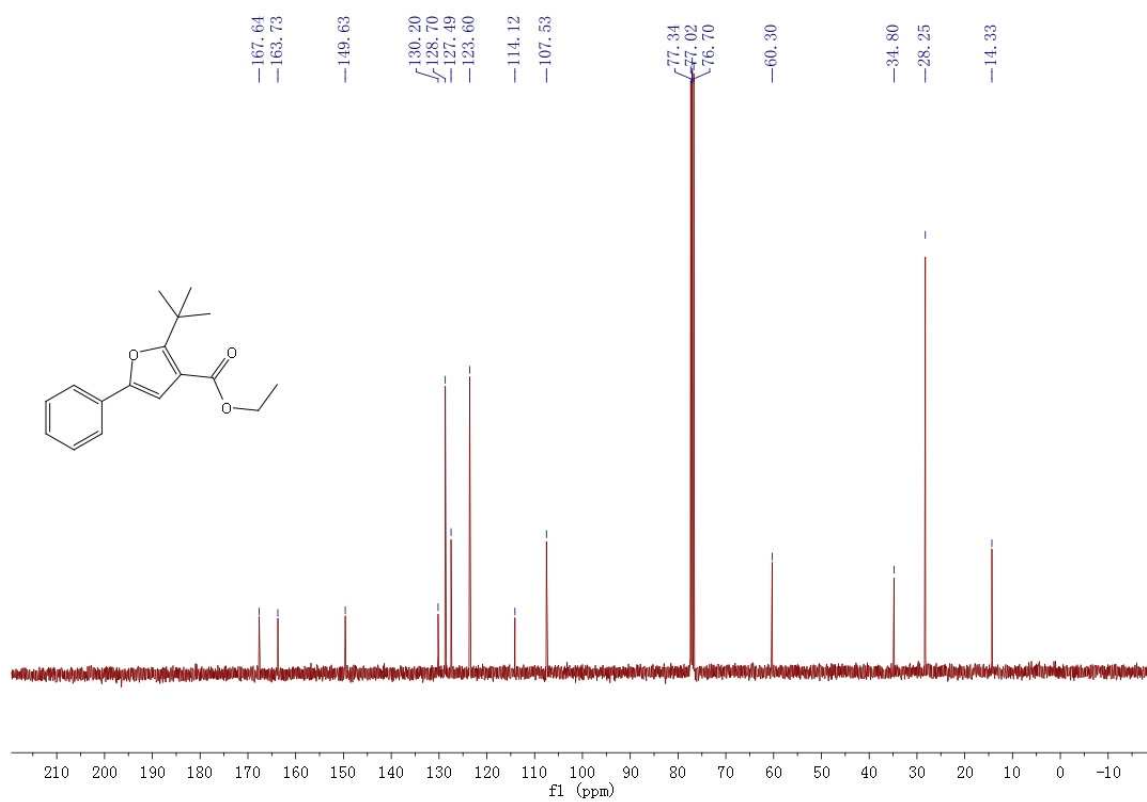
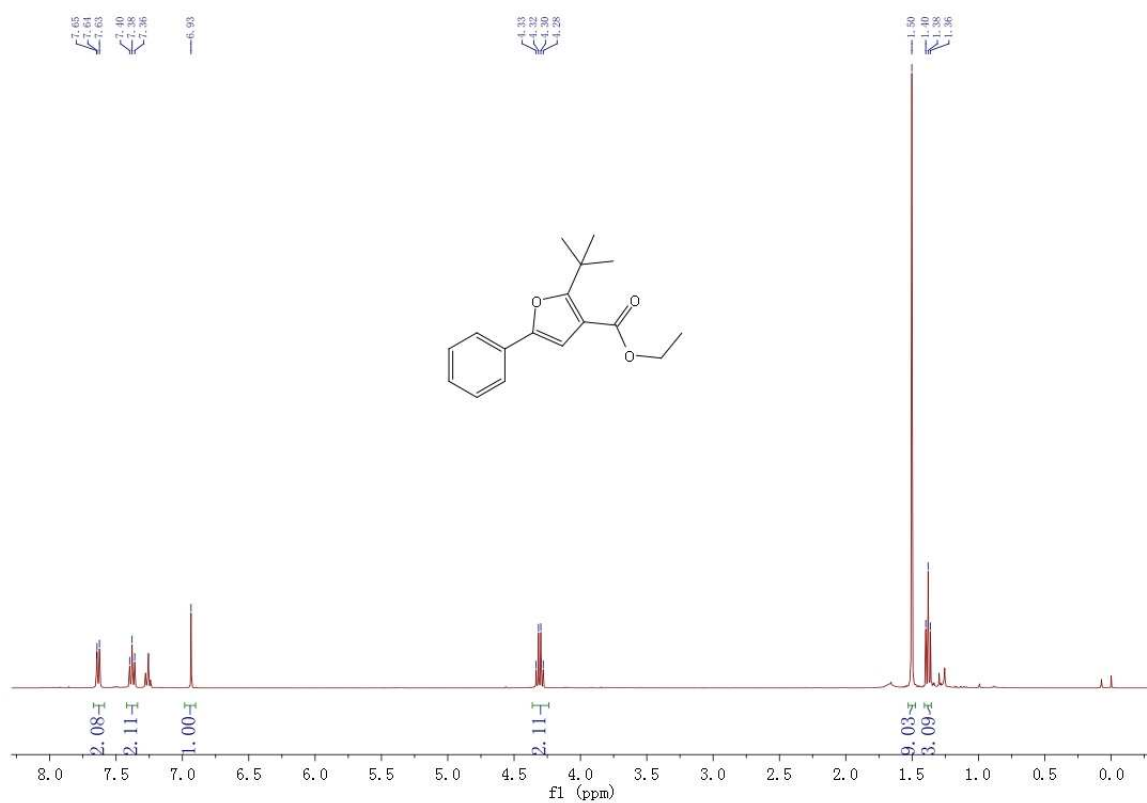


$$\begin{array}{r} -7.26 \\ -7.17 \\ \hline -14.43 \end{array}$$


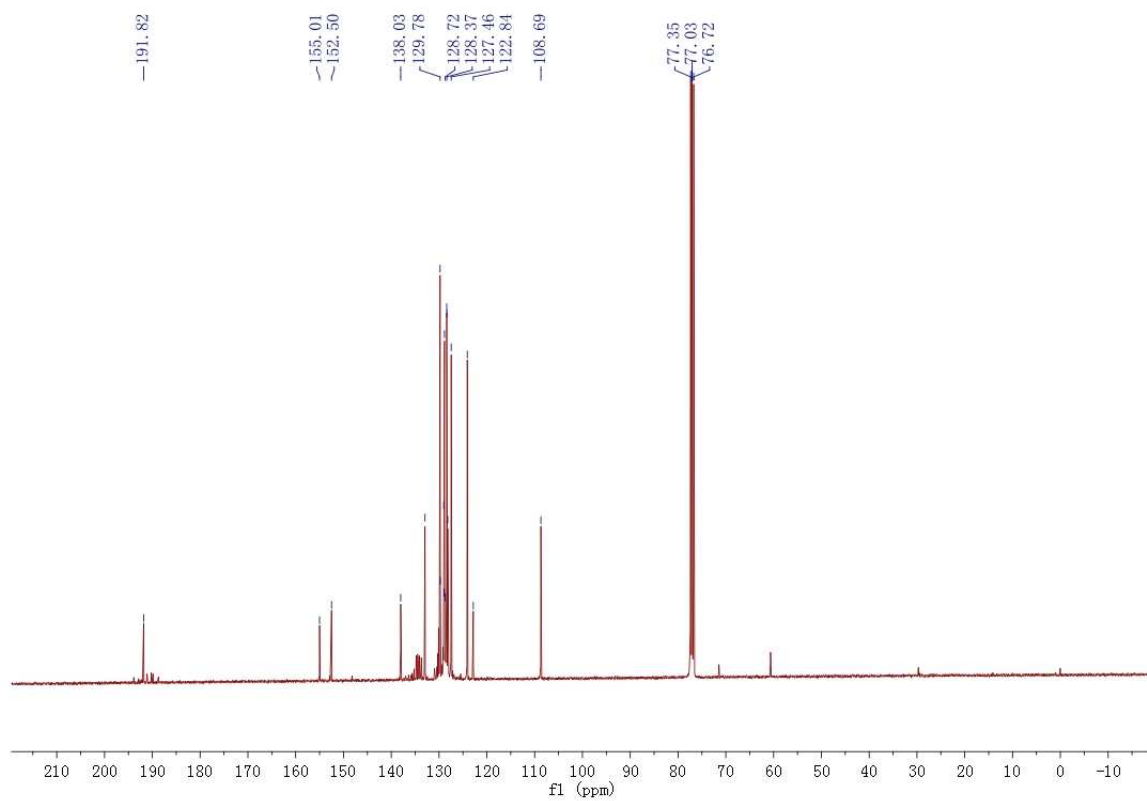
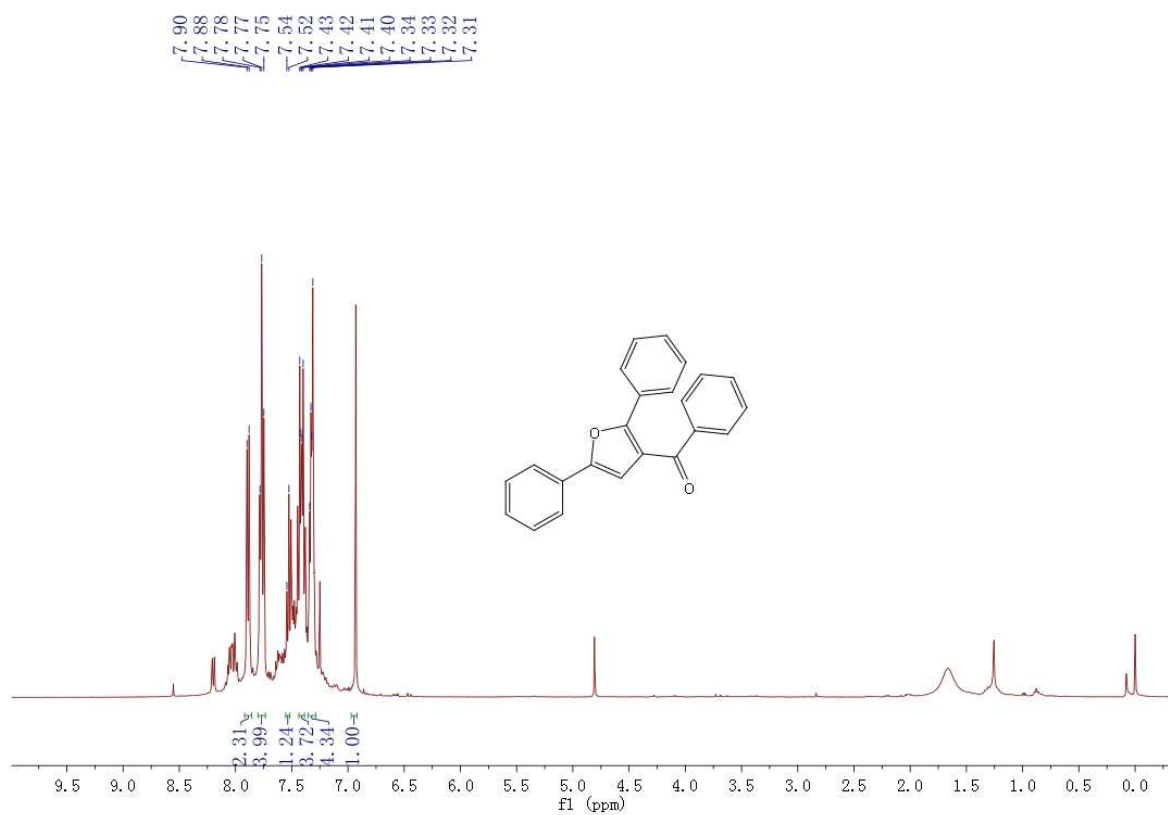
3ac



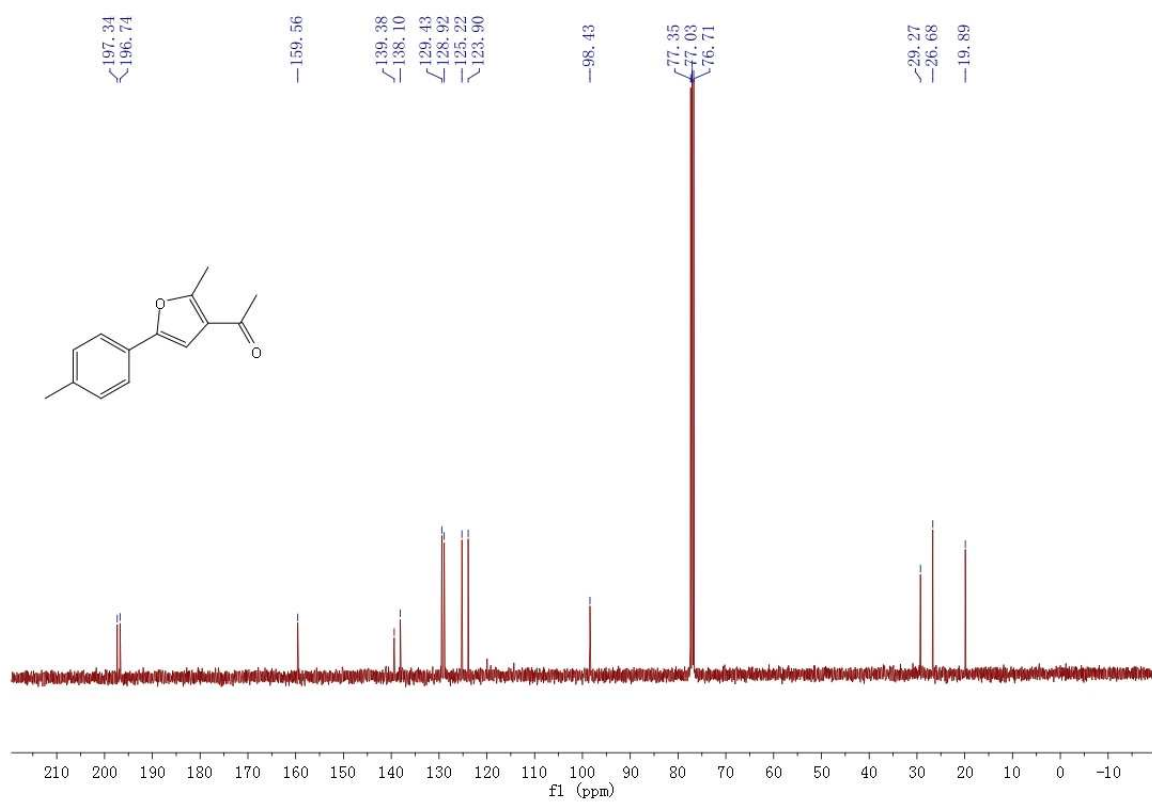
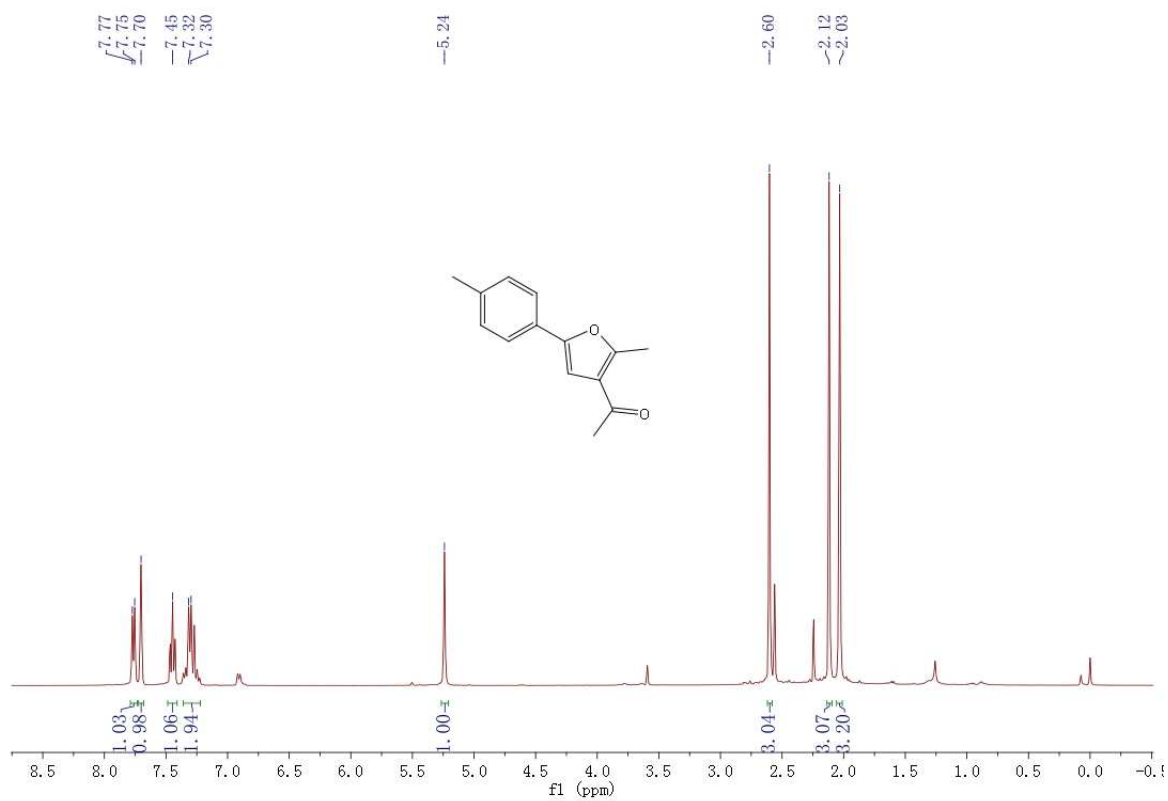
3af



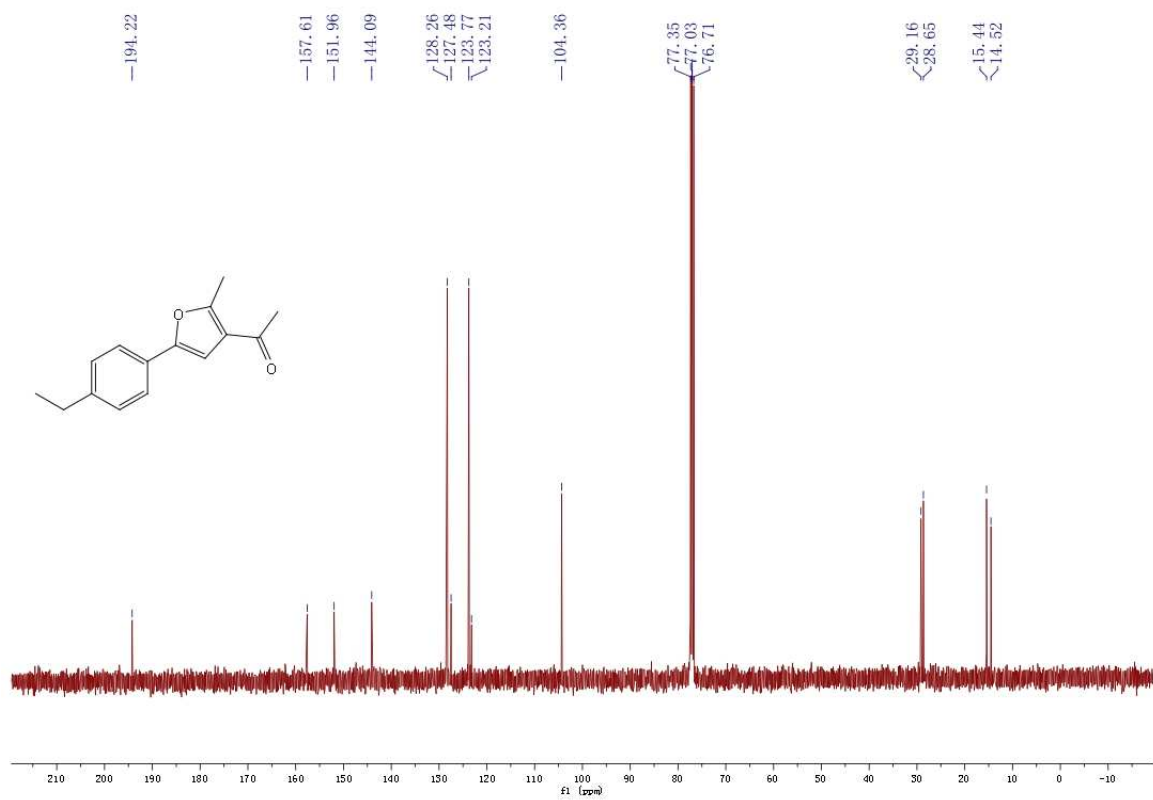
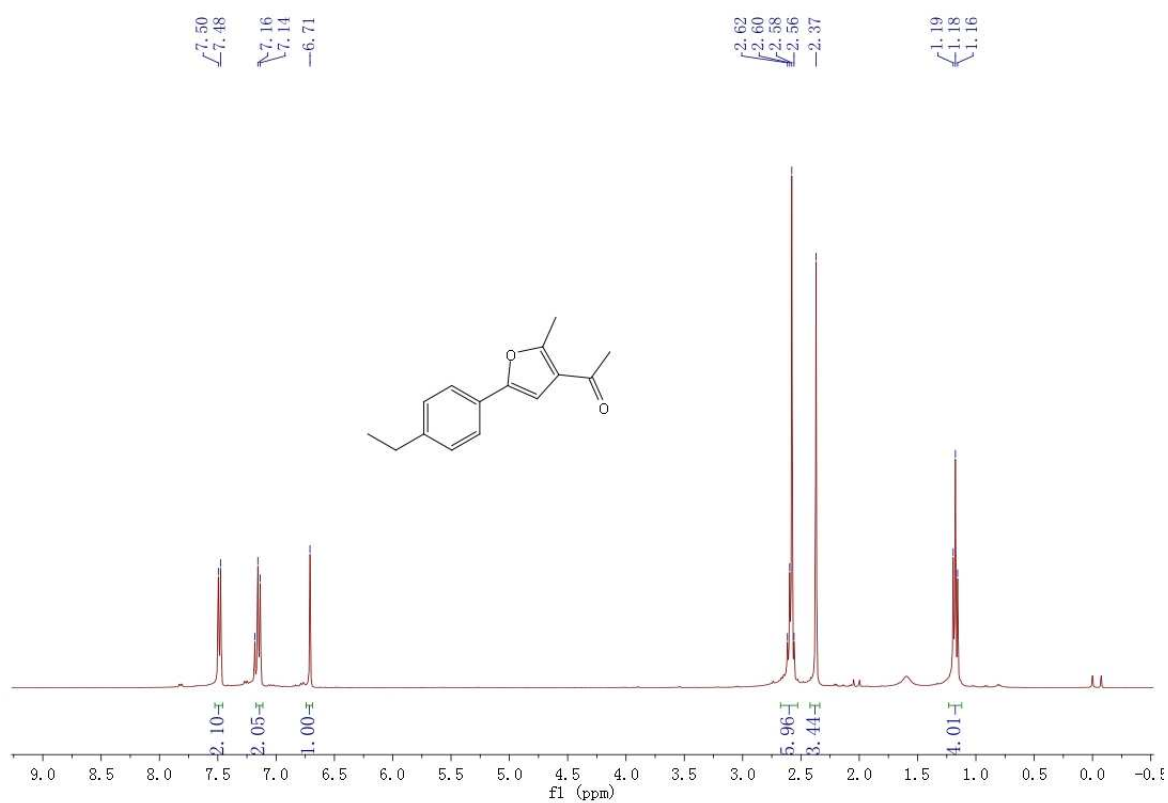
3ag



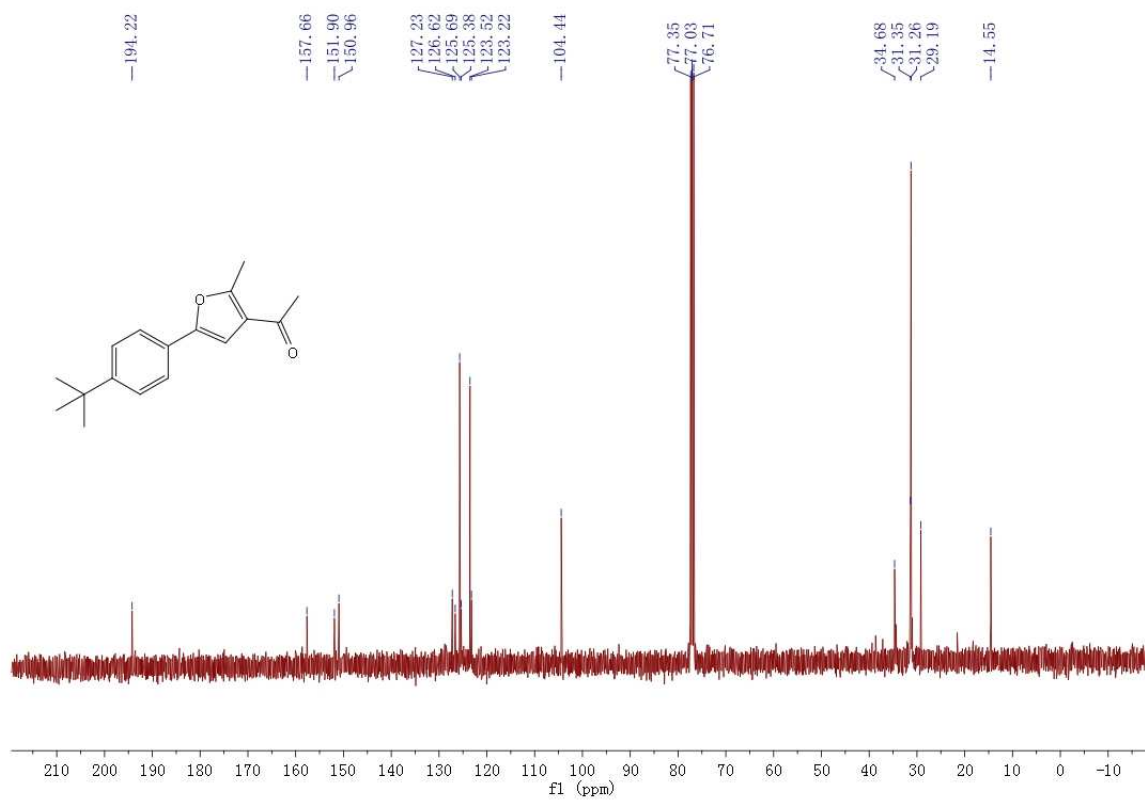
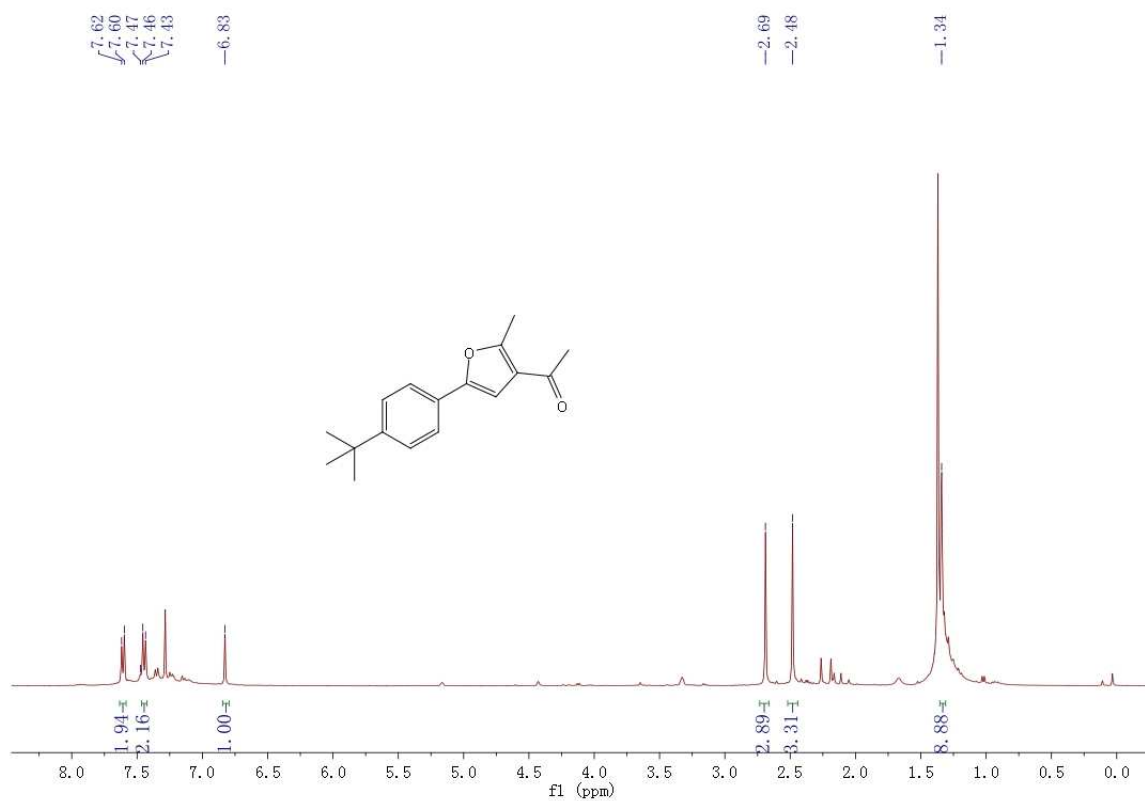
3ba



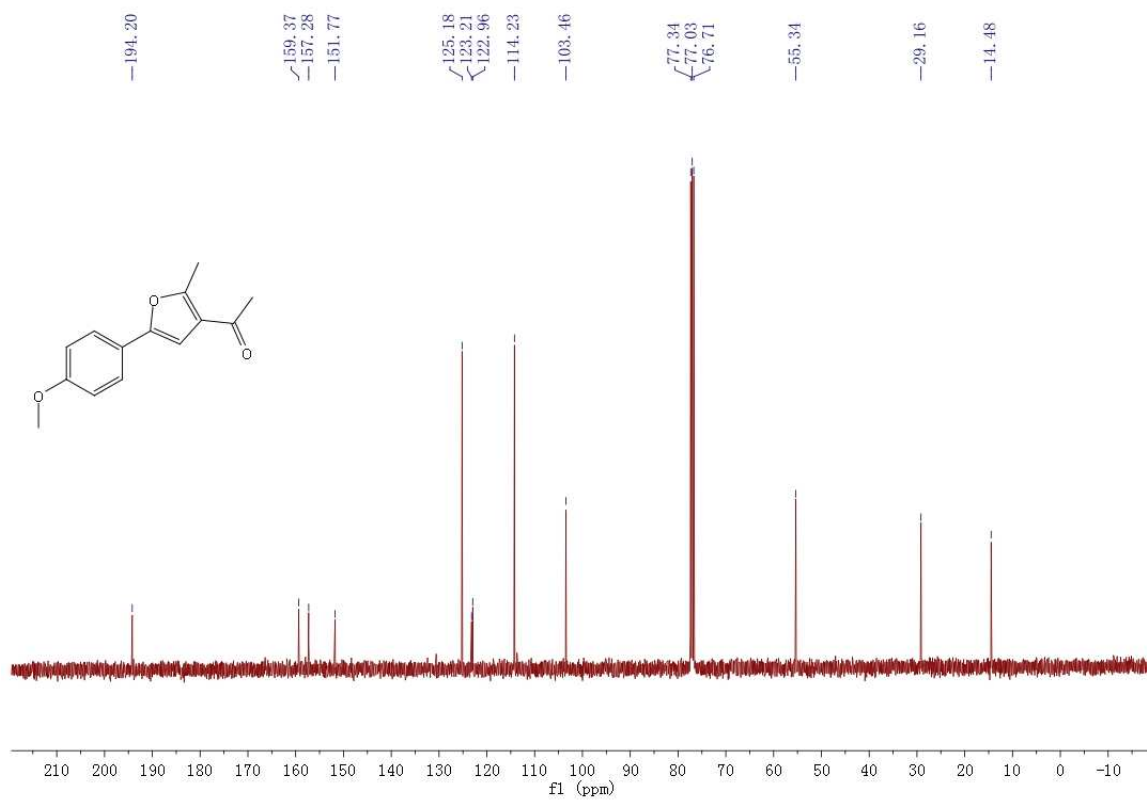
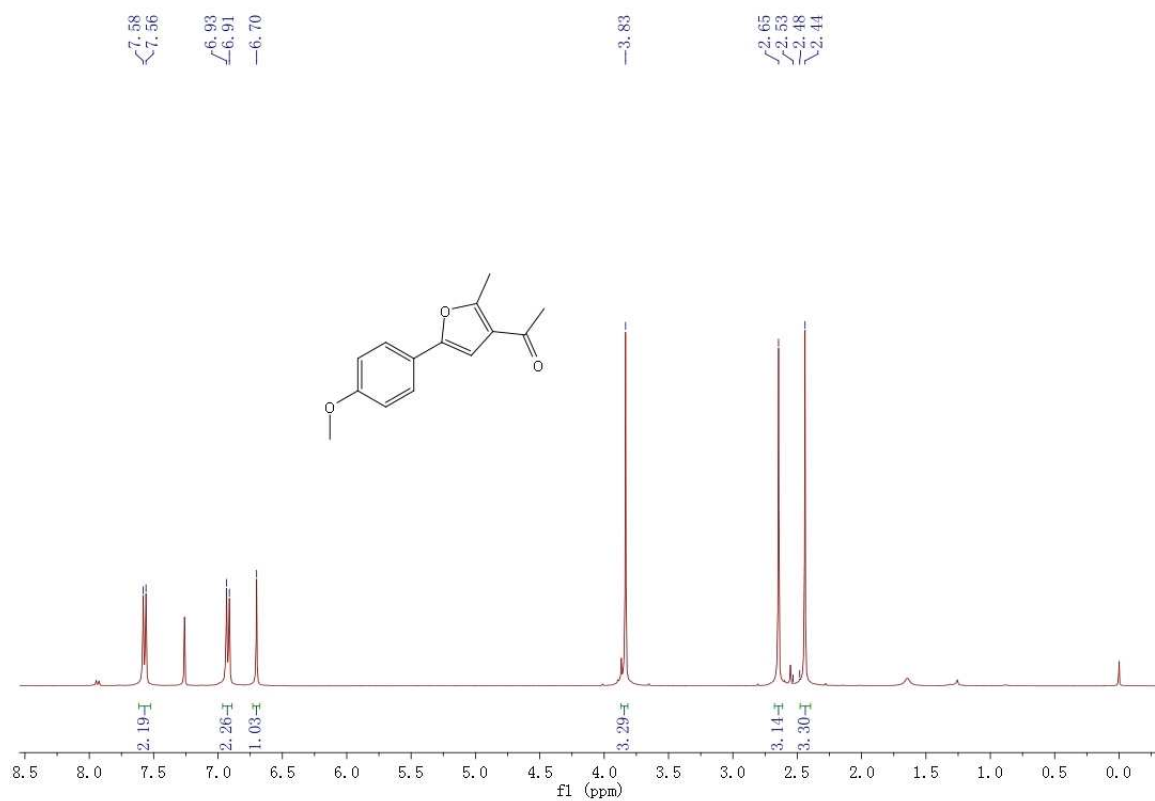
3ca



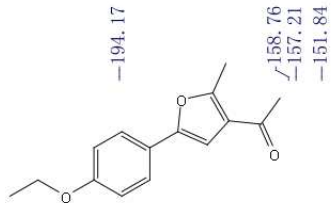
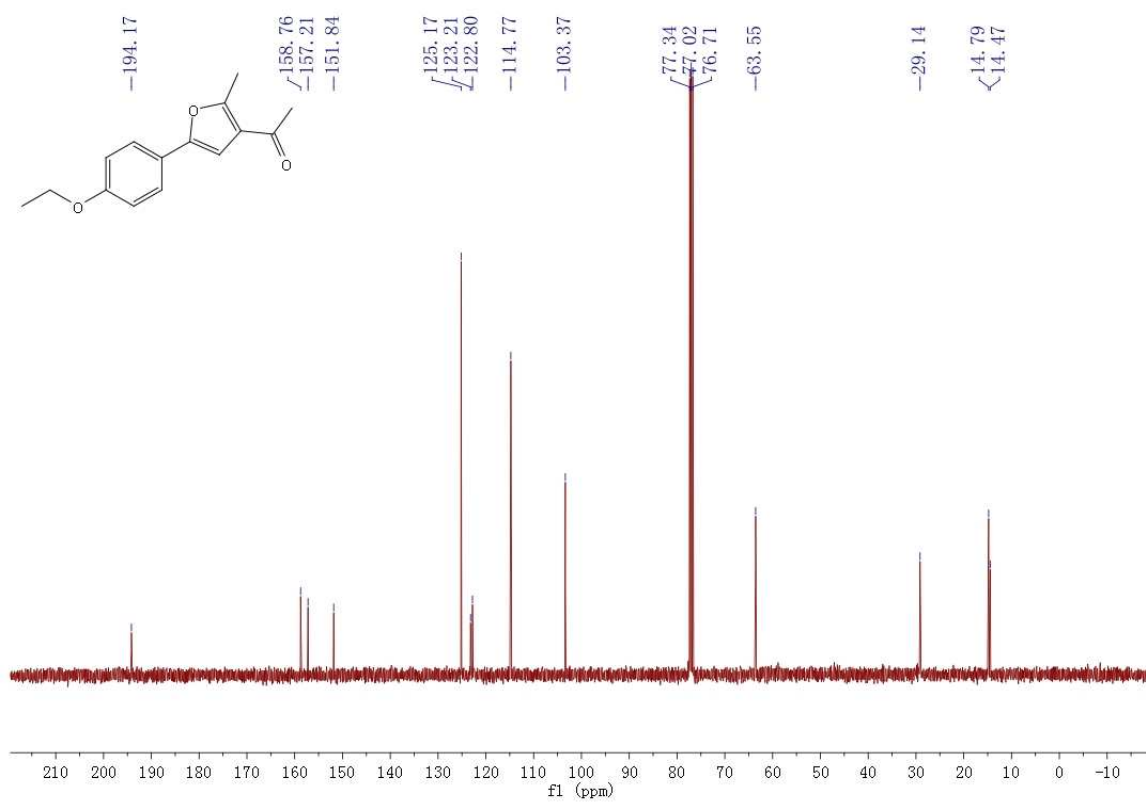
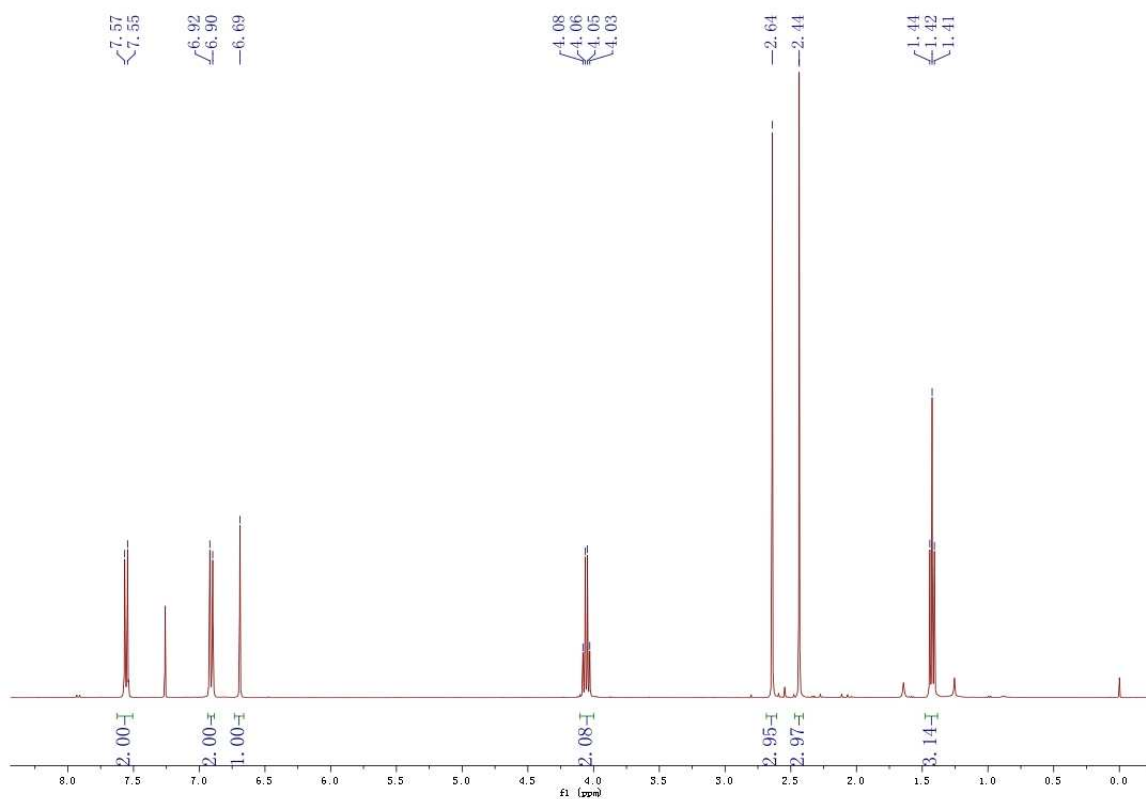
3da



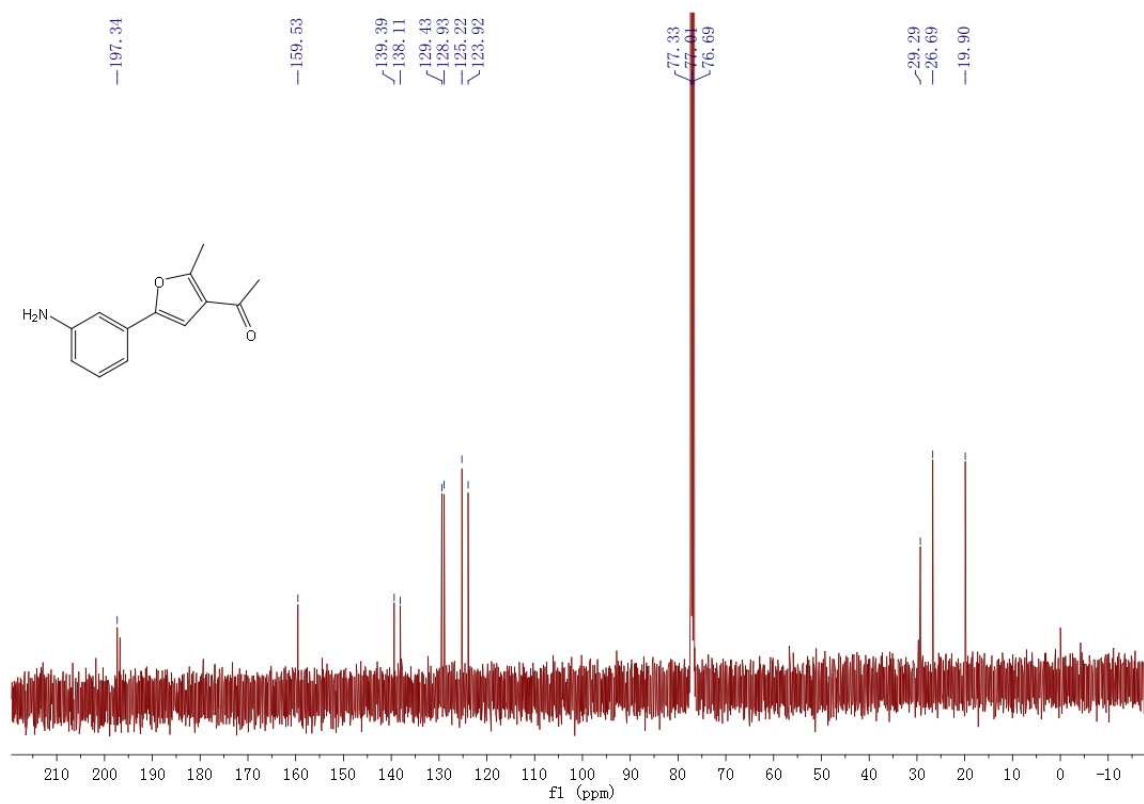
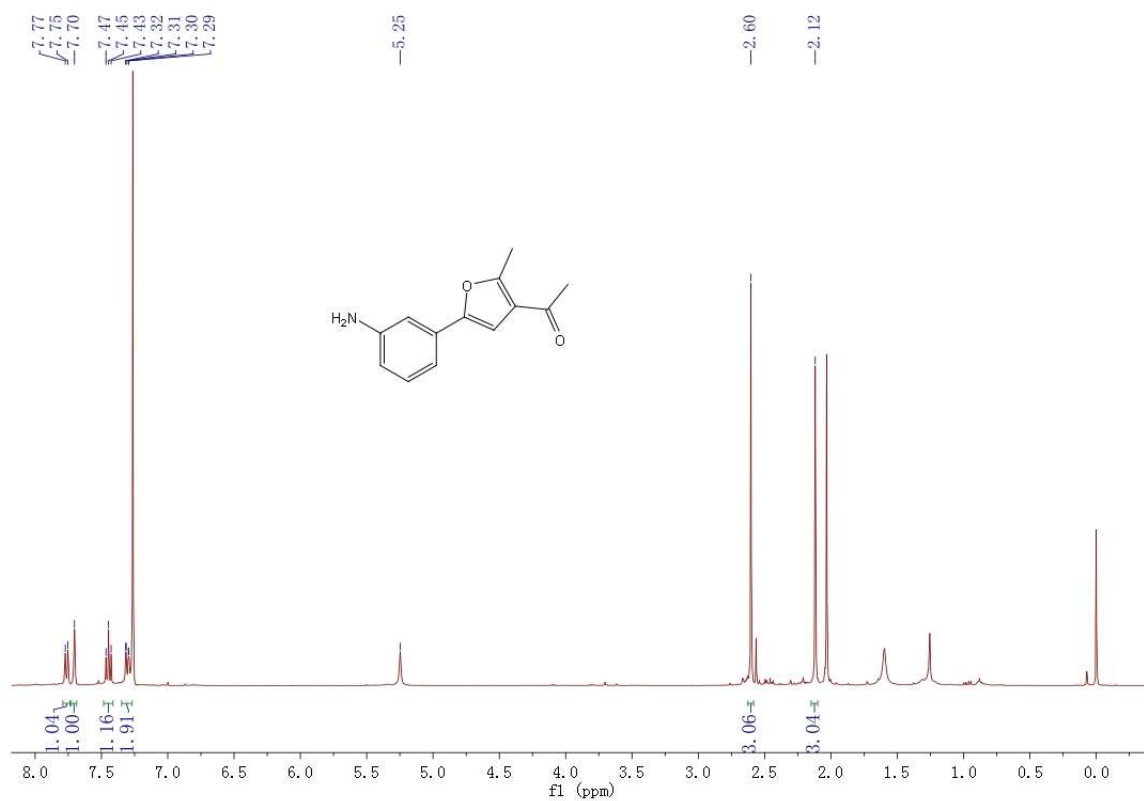
3ea



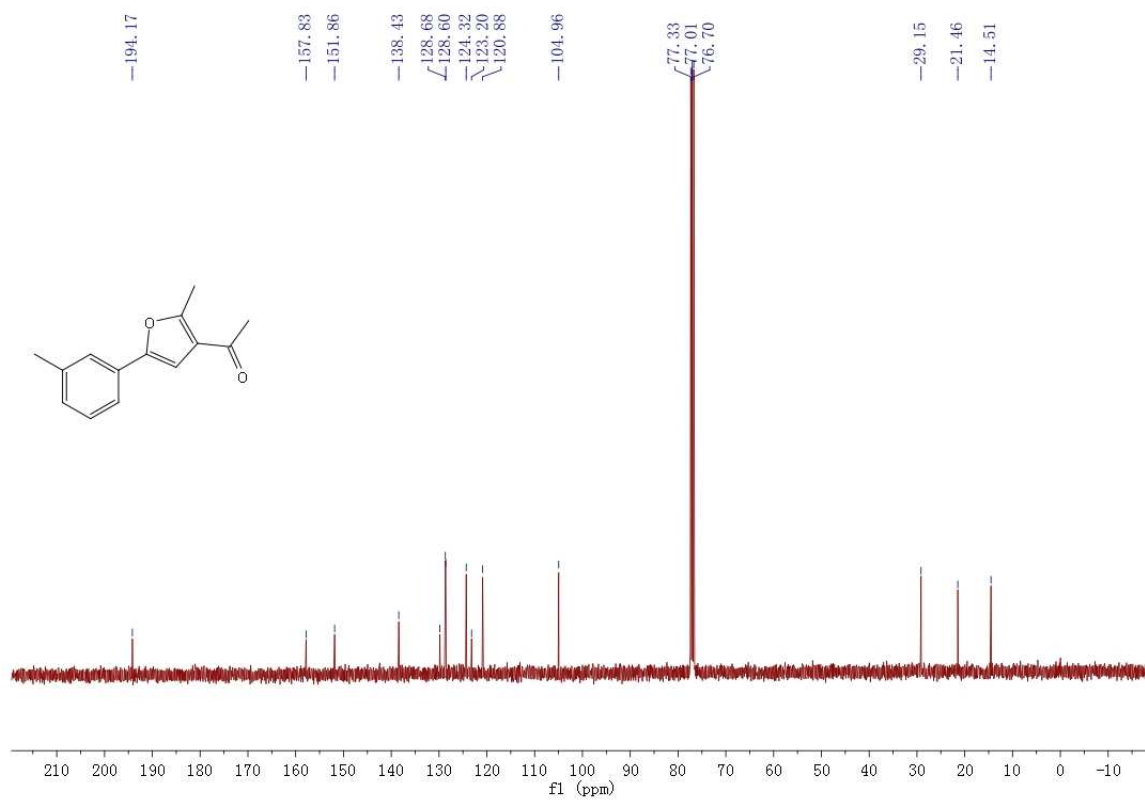
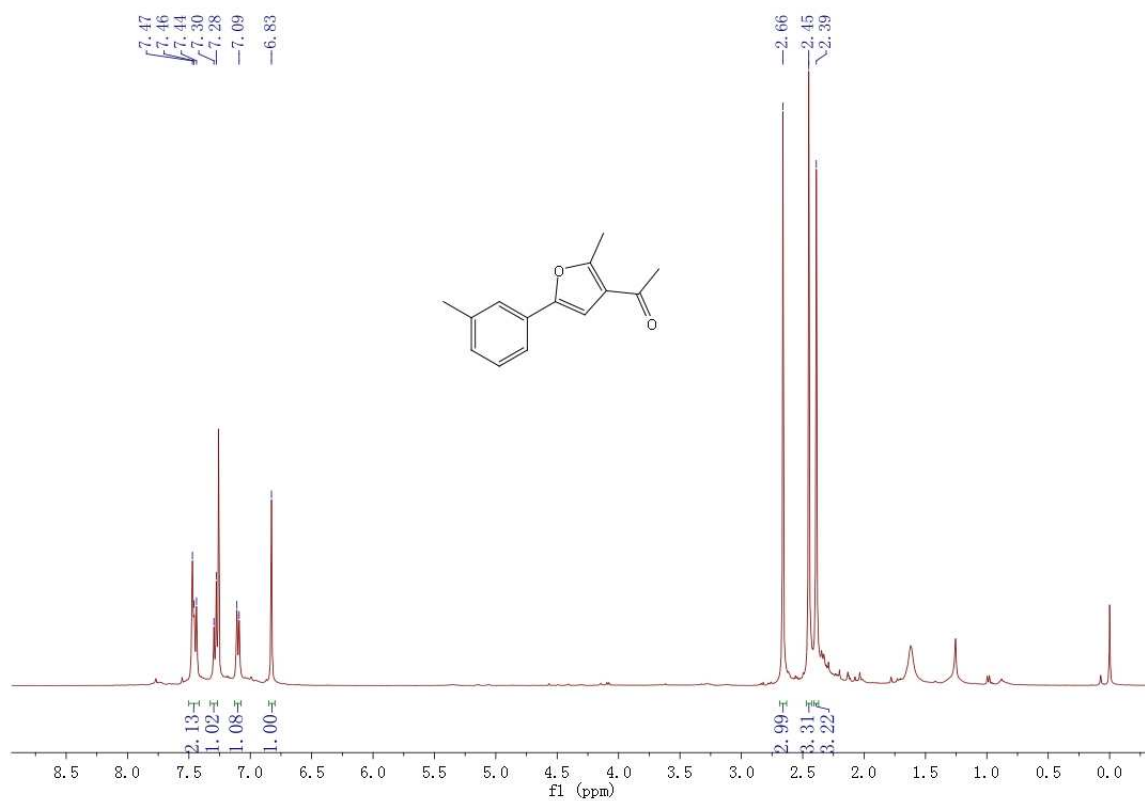
3fa



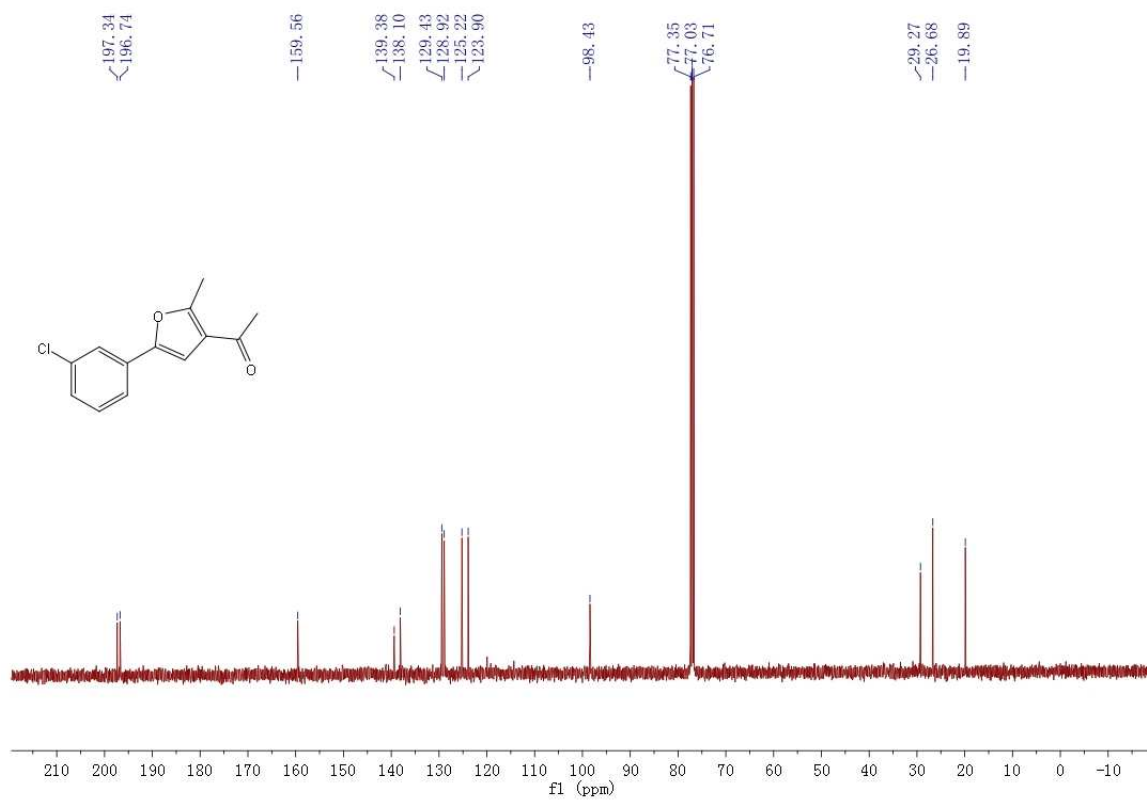
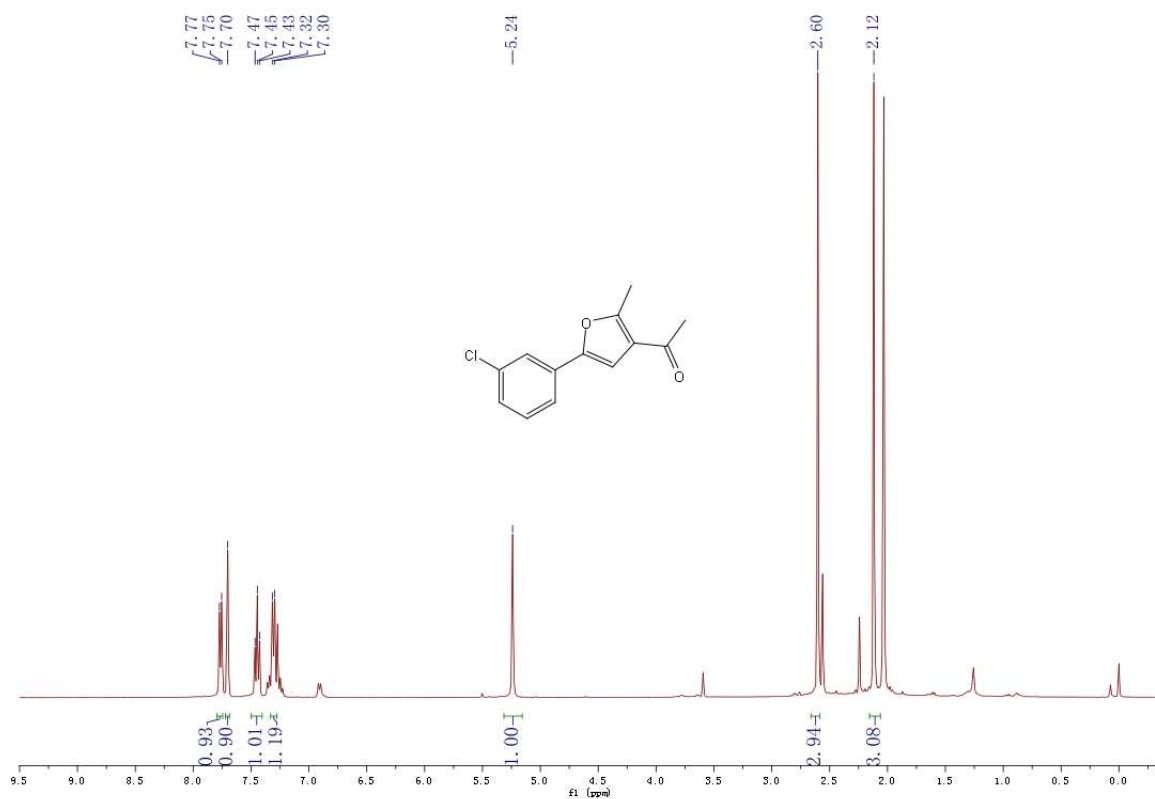
3ga



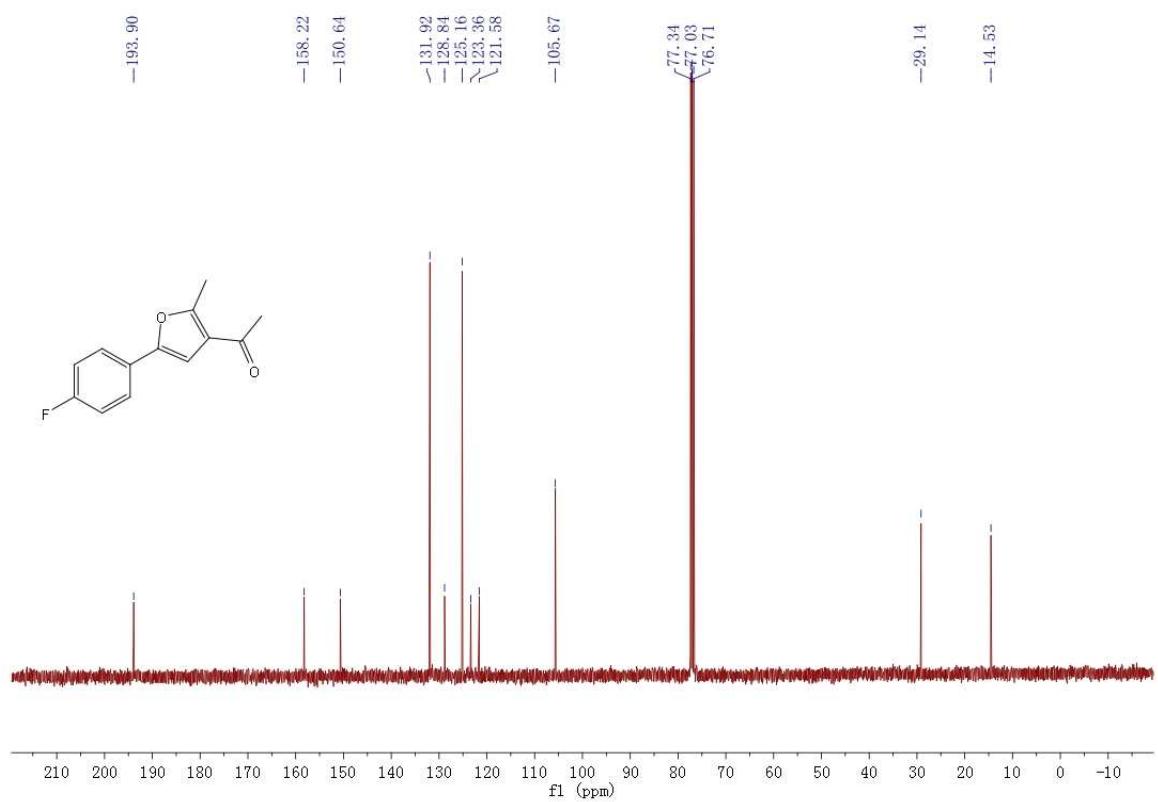
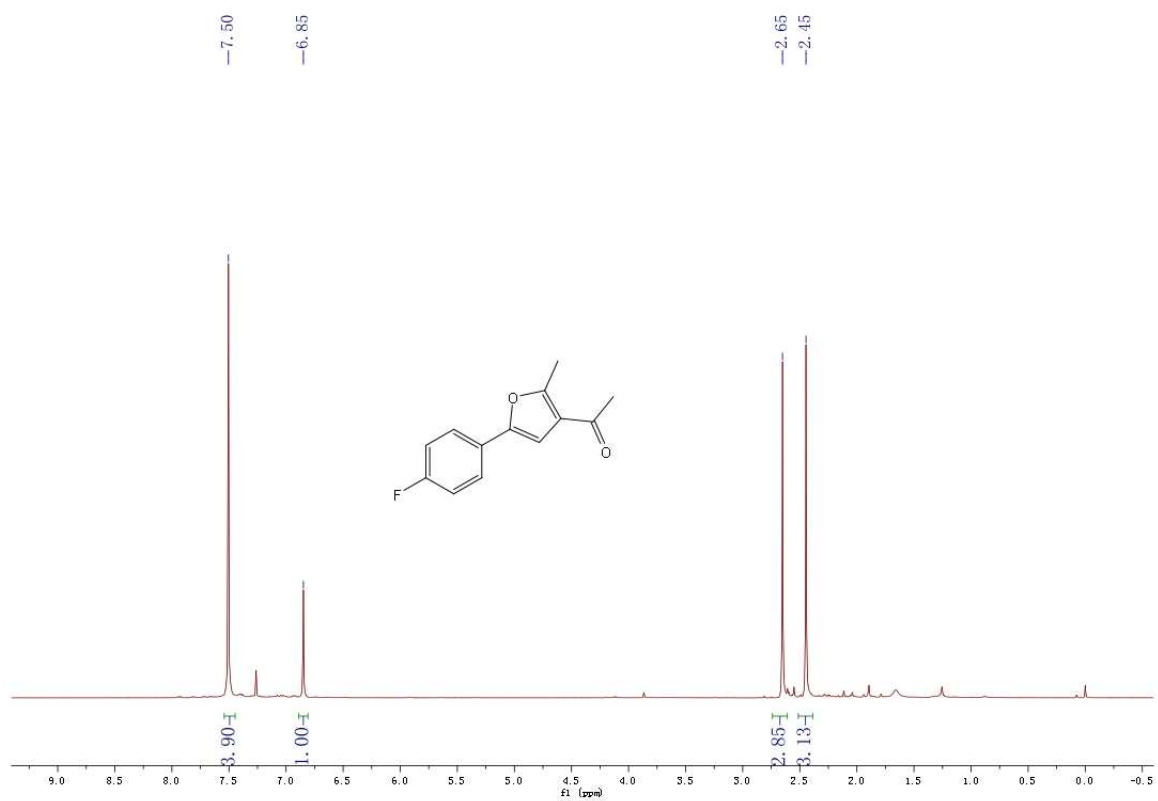
3ha



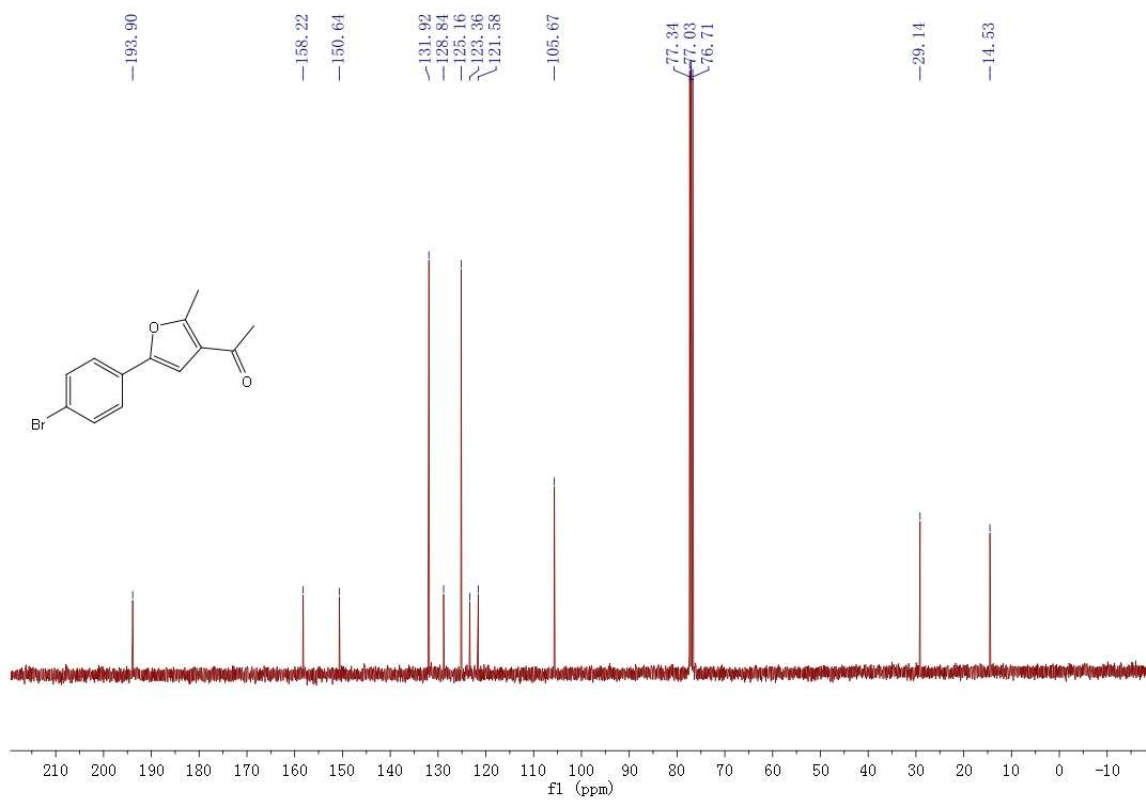
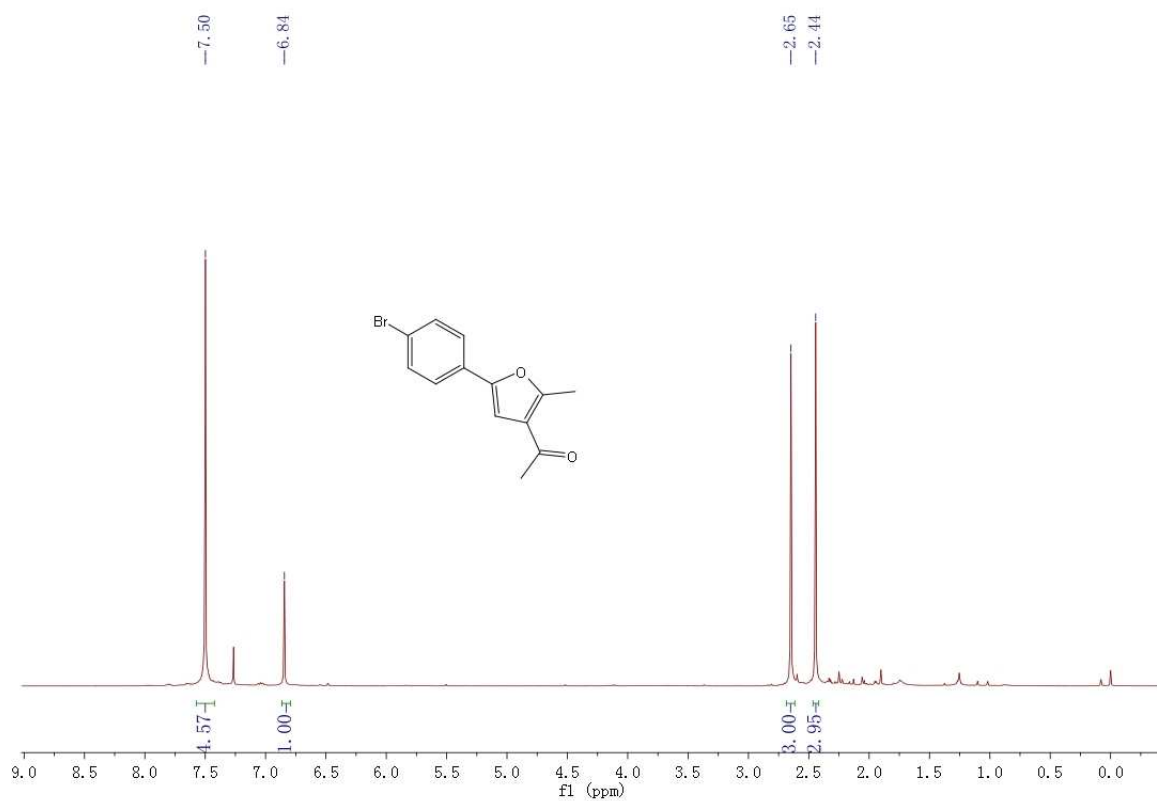
3ia



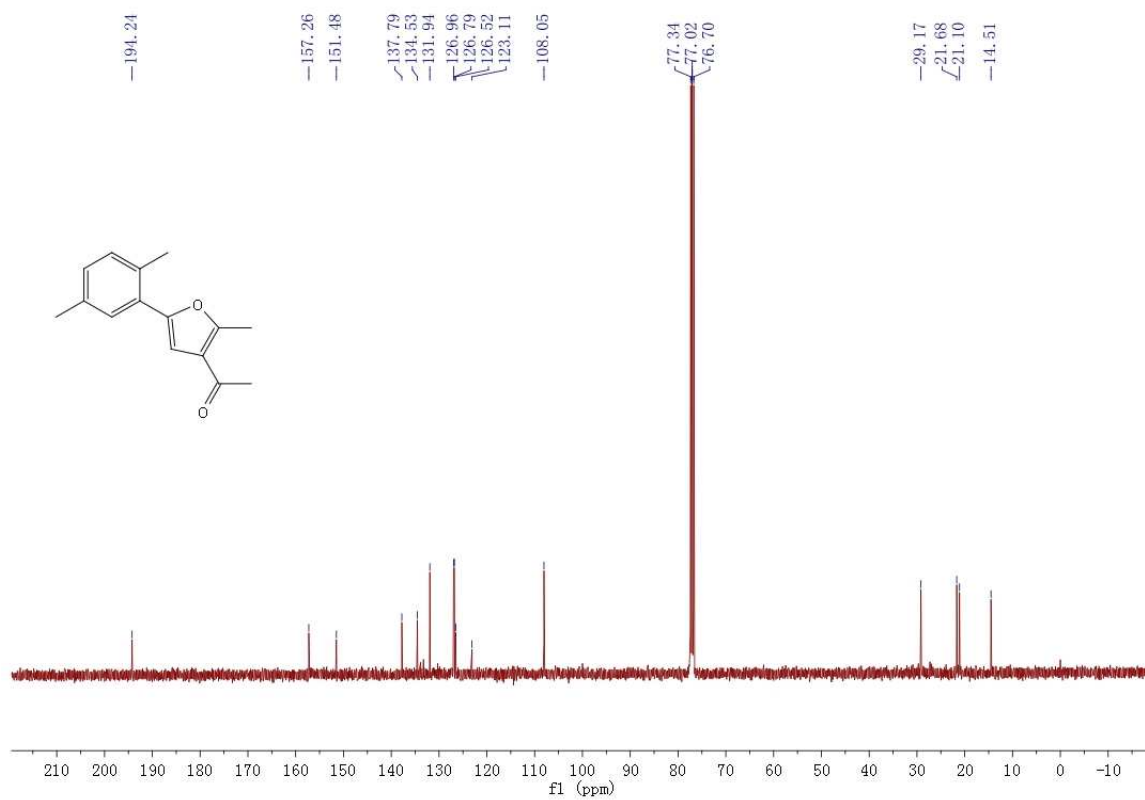
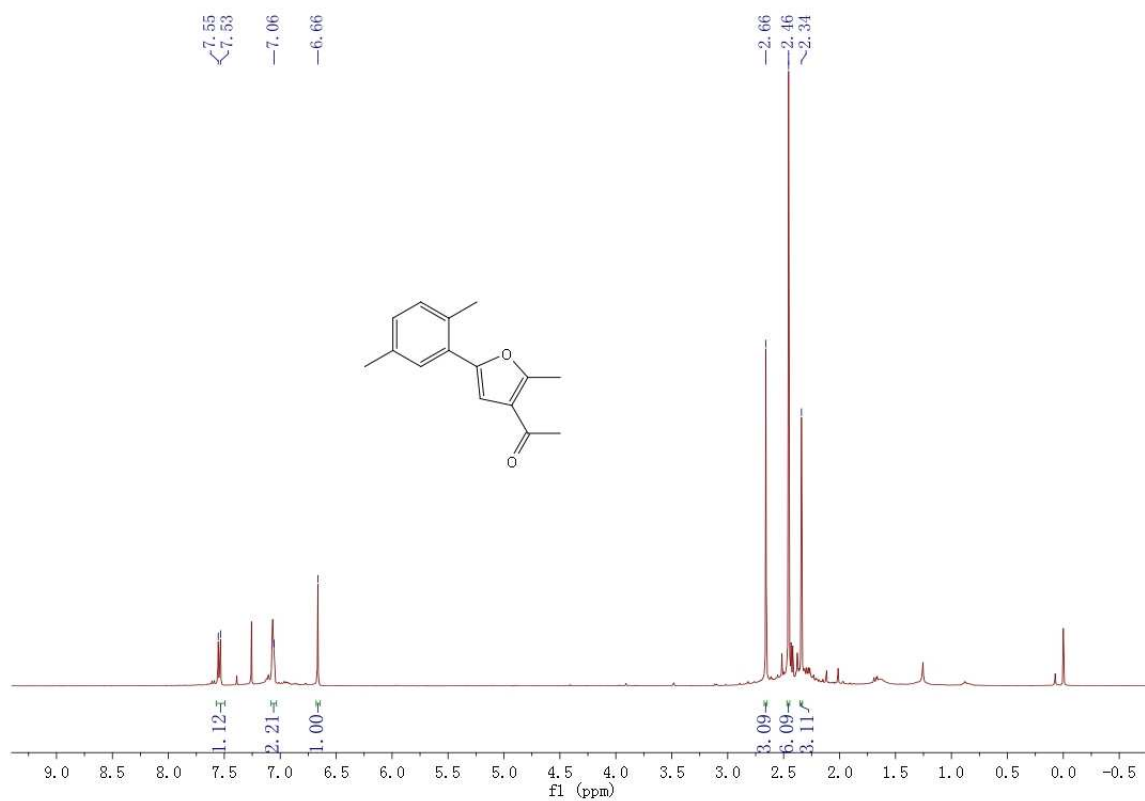
3ja



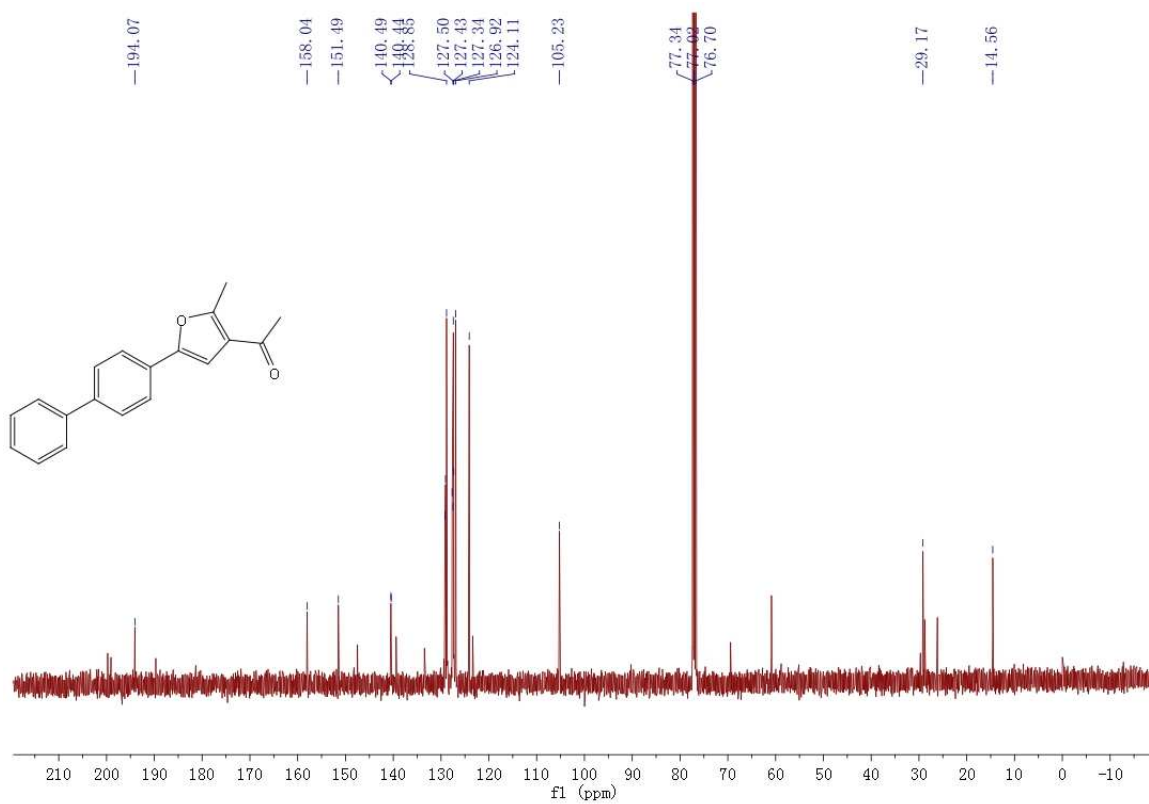
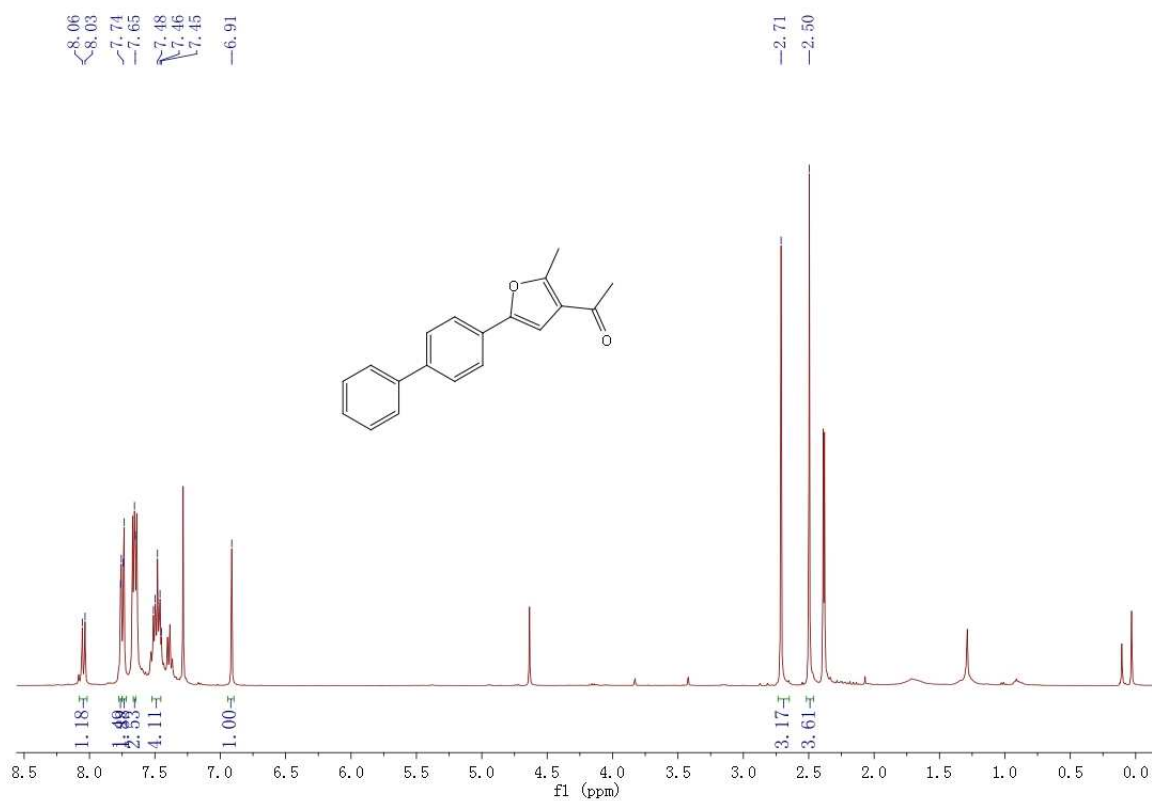
3ka



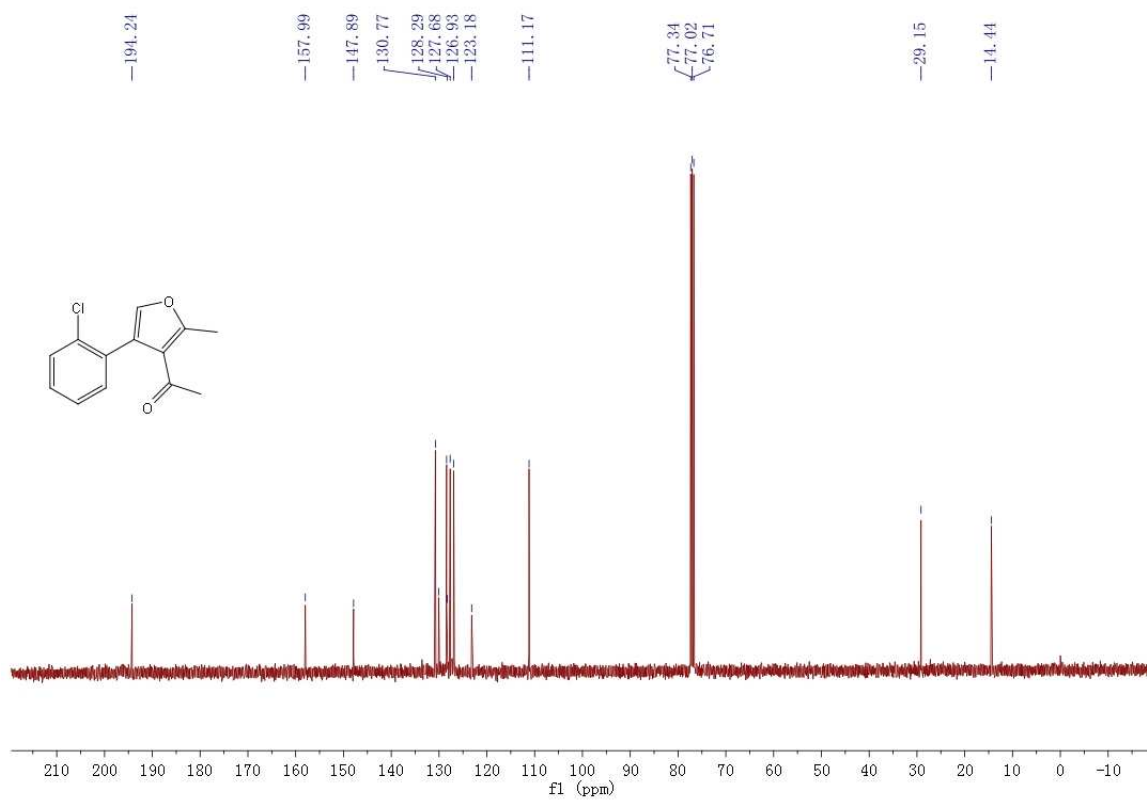
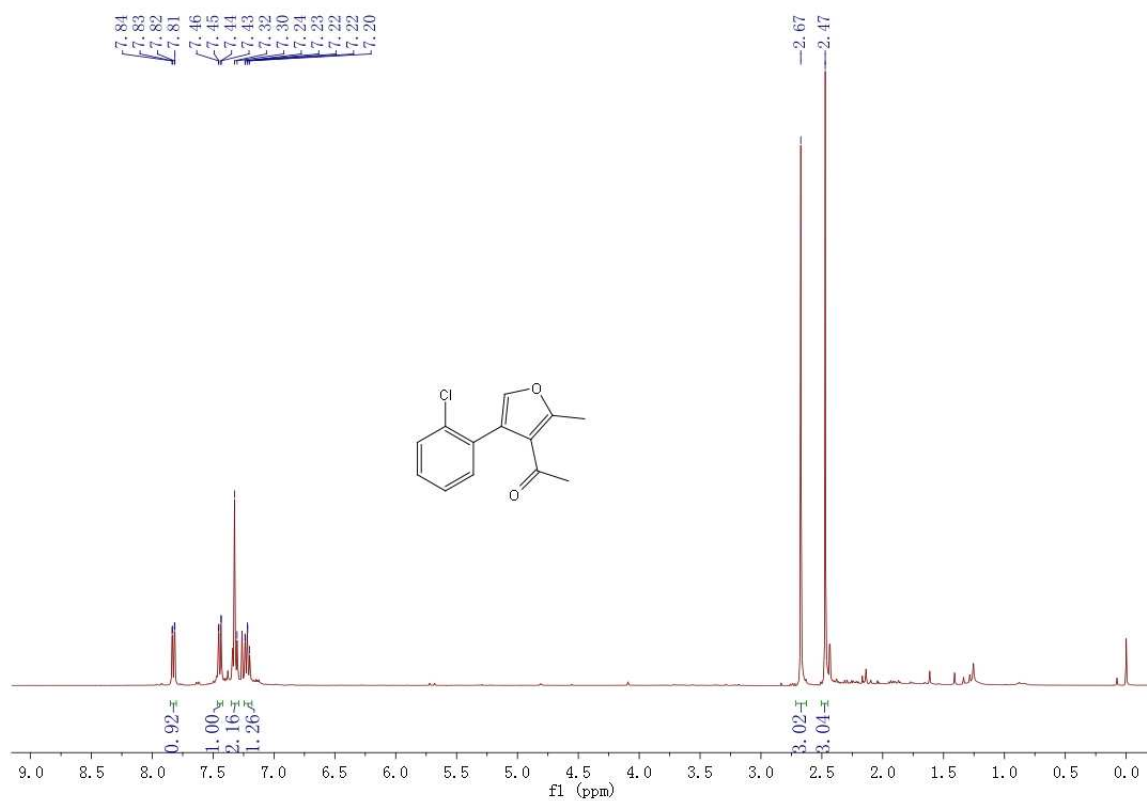
3la



3ma



3na



3nf

