Supporting Information

Silver-Mediated Annulation between 5-H-1,2,3-Thiadiazoles and 1,3-Dicarbonyl Compounds to Construct Polysubstituted Furans

Mengxia Feng, Huanfeng Jiang and Liangbin Huang*

State Key Laboratory of Pulp and Paper Engineering, Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China

E-mail: huanglb@scut.edu.cn.

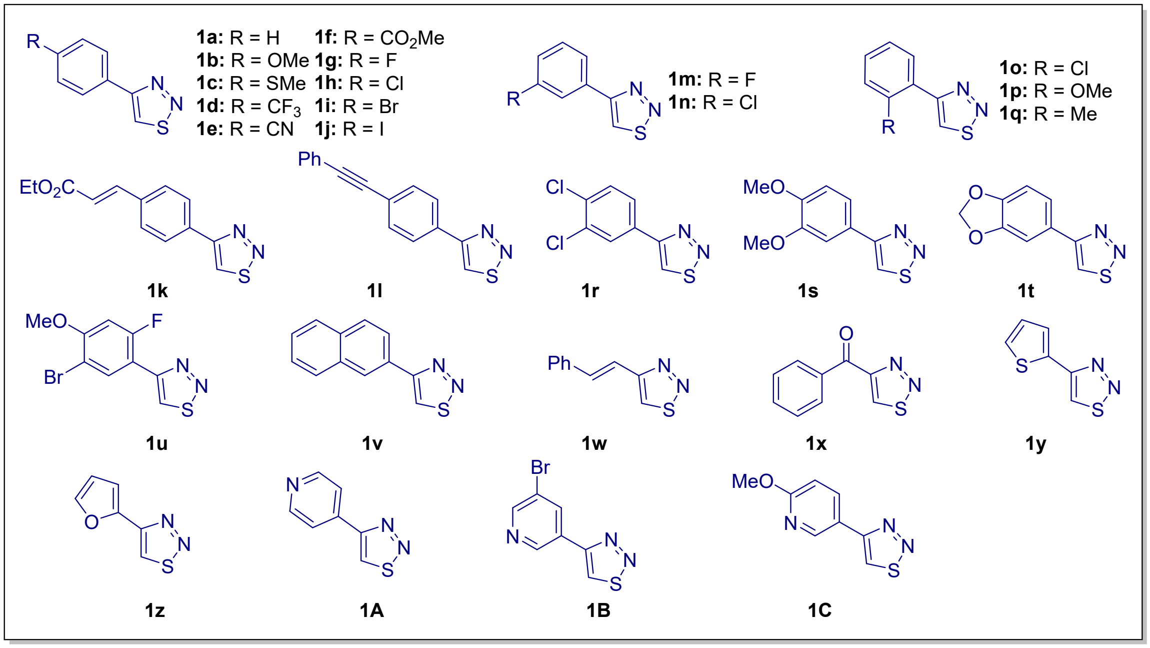
1. General Information

^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer or a Bruker DRX-500 spectrometer using Chloroform-d as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. Chemical shifts are reported in parts per million (ppm), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants (*J*) are reported in Hertz. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with an infrared Fourier spectrometer. GC analyses were performed on an Agilent 7890B GC equipped with HP-5 columns (30 m × 320 μm × 0.25 μm), FID detectors, and hydrogen as the carrier gas. GC/MS analyses were performed on a Shimadzu GCMS-QP2010SE equipped with an RTX-5MS column (30 m × 0.25 mm × 0.25 μm) with a quadrupole mass analyzer using helium as the carrier gas. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm.

Materials. All commercially available reagents were purchased and used without further purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF254) using UV light as a visualizing agent. Flash column chromatography was carried out using silica gel (200–300 mesh) with the indicated solvent system. All reactions were conducted in oven-dried Schlenk tubes. All the reaction temperatures reported are oil bath temperatures.

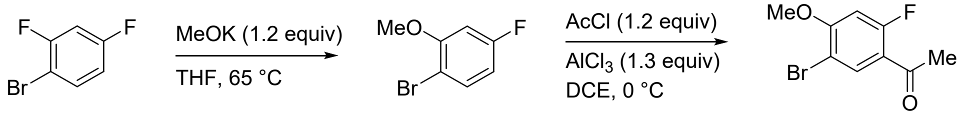
2. Experiment Section

1) Methods for the synthesis of 1,2,3-thiadiazole derivatives



Compound **1u** was a new compound and prepared by **method A** and **method B**. Other compounds were synthesized following the reported methods (**method B/C/D**). For the analysis data of 1,2,3-thiadiazoles, please refer to our previous article[1].

Method A[2]:



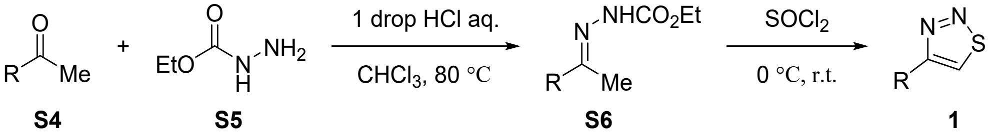
S1 **S2** **S3**

Following the slightly modified procedures, a mixture of 1-bromo-2,4-difluorobenzene **S1** (20.0 mmol, 1.00 equiv), MeOK (24.0 mmol, 1.20 equiv), and THF (10 mL) was stirred at 65 °C for 12 h. After cooling to room temperature, THF was removed under reduced pressure. The reaction mixture was diluted with brine, extracted with ethyl acetate, and dried over anhydrous $MgSO_4$. The solvent was removed and concentrated under reduced pressure to give 1-bromo-4-fluoro-2-methoxybenzene **S2**, not further purified.

Then a 50 mL reactor equipped with an overhead stirrer, a nitrogen inlet and a temperature probe was charged with anisole **S2** (3.80 g, 18.0 mmol) followed by 1,2-dichloroethane

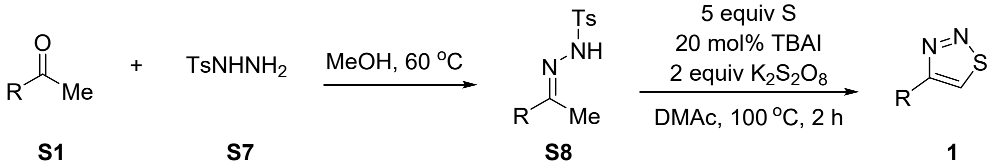
(17 mL). The solution was then cooled to 0 °C and $AlCl_3$ (3.22 g, 24.0 mmol) was added portion-wise such that the internal temperature did not rise above 6 °C. Acetyl chloride (1.75 g, 22.0 mmol) was then added dropwise over the course of 40 minutes with cooling to maintain the internal temperature below 10 °C. The reaction mixture was aged for 0.5 hour at 0 °C (at this point, HPLC assay showed no more starting material). The batch was transferred into a 100 mL extractor containing H_2O (25 mL) and EtOAc (40 mL) at 0 °C at a rate such that the internal temperature remained below 20 °C. The batch was stirred for 10 min and the bottom aqueous layer was cut away. The organic layer was washed with 1N HCl (20 mL), half saturated $NaHCO_3$ (20 mL) and half saturated brine (10 mL). The organic layer was then concentrated under vacuum and the crude residue was purified by column chromatography using silica gel with petroleum ether /ethyl acetate = 20:1 as the eluent to afford acetophenone **S3** as white needles.

Method B[3]:



A mixture of methyl ketone **S4** (10 mmol) and ethyl hydrazine carboxylate **S5** (1.2 equiv) was dissolved in dry, hot chloroform. When the reaction mixture started refluxing, one drop of concentrated hydrochloric acid were added and the mixture was then refluxed overnight with continuous removal of the water generated. The solvent was removed under vacuum and the residue was washed several times with diethyl ether or chloroform to remove excess reactants. Next, an excess amount of thionyl chloride was stirred at 0 °C and the hydrazones **S6** were added in several portions. The mixtures were stirred at room temperature overnight until no more hydrogen chloride was produced. The remaining thionyl chloride was evaporated under vacuum and the residue was washed with diethyl ether to give good yields of the corresponding 1,2,3-thiadiazoles as fine powders. A recrystallization from chloroform or dimethylsulfoxide was carried out when necessary.

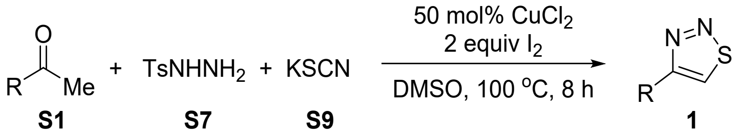
Method C[4]:



p-Toluenesulfonylhydrazide **S7** (1.86 g, 10 mmol) was placed in a round-bottom boiling flask equipped with a reflux condenser in 10 mL of dry methanol; the methyl ketone **S1** (10 mmol) was added slowly, and the mixture was heated in an oil bath at 60 °C. Within 5−60 min, *N*-tosylhydrazone began to precipitate. The mixture was cooled to 0 °C, and the product was collected on a Büchner funnel, washed with petroleum ether, and then dried in vacuum to afford the pure product quantatively.

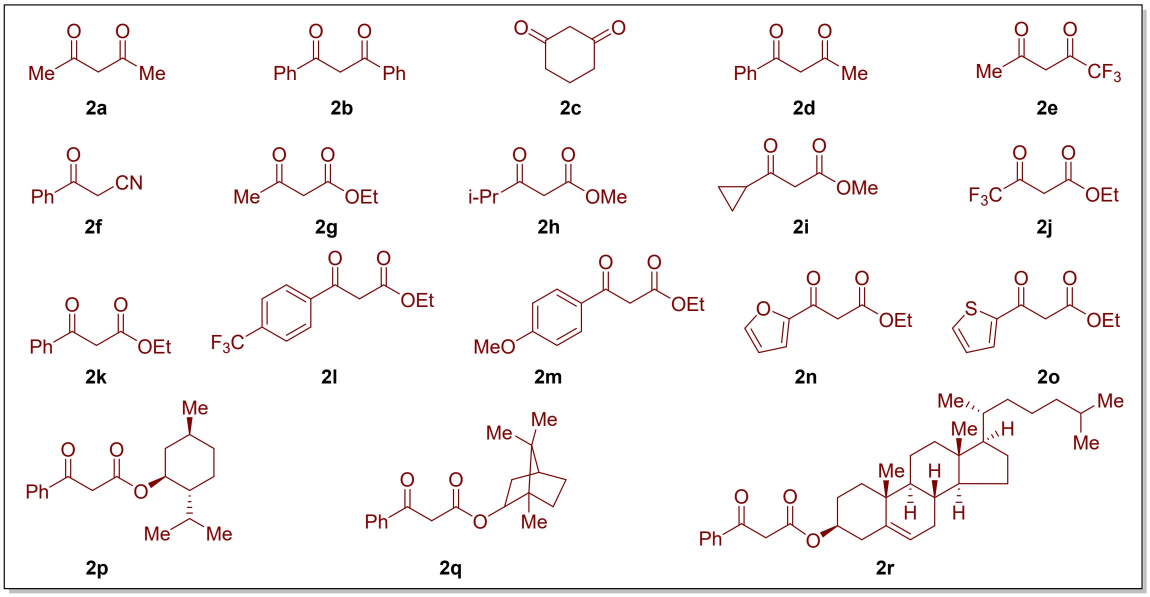
A sealed tube was charged with *N*-tosylhydrazone **S8** (8 mmol), sulfur (5.0 equiv), TBAI (0.2 equiv), $K_2S_2O_8$ (2.0 equiv), and DMAc (30 mL). The mixture was stirring under air at 100 °C for 2 h. The mixture was washed with water and extracted by ethyl acetate and then concentrated in vacuum, and the residue was purified by preparative TLC (petroleum ether /ethyl acetate) to afford the desired product.

Method D[5]:



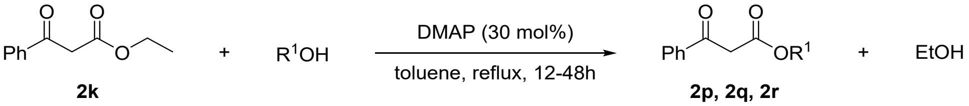
A sealed tube was charged with methyl ketone **S1** (5.0 mmol), *p*-toluenesulfonylhydrazide **S7** (1.0 equiv), and potassiumthiocyanate **S9** (1.0 equiv), iodine (2.0 equiv) at room temperature, and DMSO (15 mL) was added. The resulting mixture was stirred at 100 °C for 8h. After the reaction completed, the mixture was quenched with saturation $Na_2S_2O_3$ solution (50mL), extracted with EtOAc (3×50 mL). The combined organiclayers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatographyonsilicagel (petroleum ether /ethyl acetate = 20:1) to give the product.

2) Methods for the synthesis of 1,3-dicarbonyl compounds



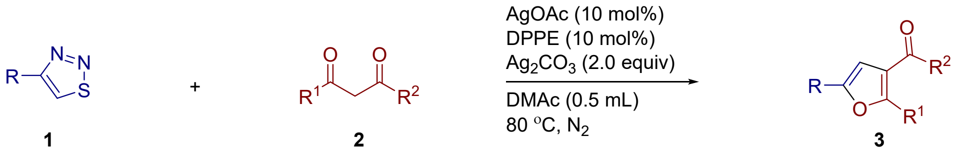
Compound **2p、2q、2r** were known compounds and were synthesized following the reported **method E**. Other compounds were commercially available (purchased from Energy Chemical, Bidepharm and Innochem) and used without further purification.

Method E[6]:



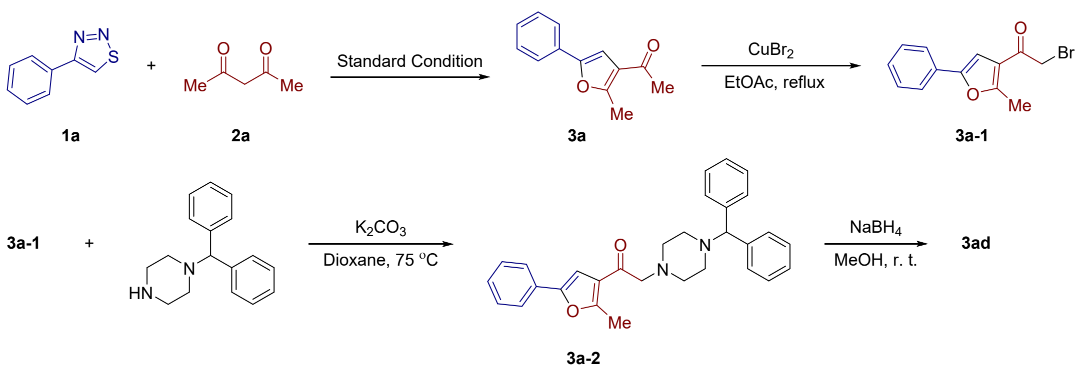
Aromatic β-ketoesters **2p**, **2q**, **2r** were prepared from the corresponding β-keto esters **2k** according to a slightly modified literature procedure. To a flask equipped with a Dean-Stark trap and reflux condenser was added ethyl 3-oxo-3-phenylpropanoate **2k** (2 mmol), corresponding alcohol (4 mmol), DMAP (73.3 mg, 0.6 mmol) in toluene (40 mL). The mixture was heated to reflux, distilling the ethanol formed during the reaction. After completion, monitored by ^{1}H NMR spectroscopy, the reaction mixture was directly loaded onto silica gel and purified by flash chromatography (eluting in gradient from petroleum ether/ethyl acetate 98:2 to 95:5) to give the aromatic β-ketoesters **2p, 2q, 2r.**

3) General procedure for preparation of polysubstituted furans



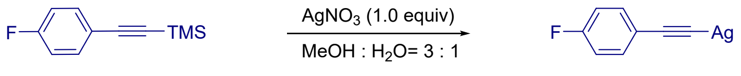
To a 5 mL oven-dried sealed reaction vial equipped with a magnetic stirring particle, AgOAc (10 mol%, 3.34 mg), DPPE (1,2-Bis(diphenylphosphino)ethane) (10 mol%, 7.97 mg), Ag_2CO_3 (2.0 equiv., 110.30 mg), 5-H-1,2,3-thiadiazole **1** (0.2 mmol) and 1,3-dicarbonyl compound **2** (0.4 mmol, 2.0 equiv.) were added sequentially, then 0.5 mL solvent of DMAc (99.8%, Extra Dry) were added finally and the resulting mixture was stirred at 80 °C in a heating mantle for 24 h. After the reaction completed, the mixture was quenched with 1 N HCl solution (10 mL), extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding products.

4) Route for preparation of postfunctionalization of trisubstituted 2-acetyl furan of 3ad[7-9]



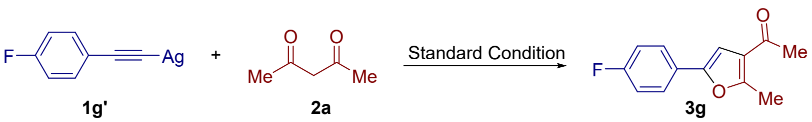
Under the operation of our standard conditions, 1.5 g of target product **3a** was obtained from substrates **1a** and **2a** in 10mmol scale. Subsequent modification step 1): Bromination of **3a**, a solution of **3a** (5 mmol) in ethyl acetate (30 mL) was added to a reaction flask equipped with a magnetic stir bar, followed by the addition of $CuBr_2$ (1.7 equiv.). The reaction mixture was then stirred vigorously and heated to reflux. When the reaction reached completion, as judged by TLC, the reaction mixture was allowed to cool to room temperature, filtered, and evaporated under reduced pressure. The crude product was purified using silica gel column chromatography to afford **3a-1** (88% yield). step 2): To a solution of compound **3a-1** (3 mmol) and benzhydrylpiperazine (0.9 equiv.) in 1,4-dioxane (20 mL) was added K_2CO_3 (1.0 equiv.) and the mixture was stirred at 75 °C for 3-4 h under nitrogen. After completion of the reaction (indicated by TLC) the mixture was concentrated under reduced pressure and diluted with cold water (25 mL). The mixture was extracted with EtOAc (3 × 20 mL). The combined organic layer was collected, washed with water (2 · 10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under low vacuum. The product **3a-2** (90% yield) obtained was used for the next step. Step 3): To a solution of **3a-2** (3 mmol) in MeOH (15 mL) was added $NaBH_4$ (3.0 equiv.) at rt, and the resulting mixture was stirred at this temperature for 30 min. Upon completion, the mixture was quenched with saturated NH_4Cl solution 5 mL, extracted with EtOAc (3 × 15 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4, filtered, and concentrated to get the crude product. The residue was purified chromatography (petroleum ether/ethyl acetate 20 : 1) to get the desired compound **3ad** as a sticky yellowish gel (88% yield).

5) Details for control experiments[10]



1g'

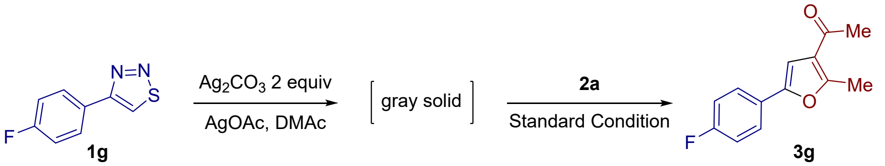
To a solution of (4-fluorophenylethynyl)trimethylsilane (5 mmol) in 20 mL aqueous methanol (H_2O:MeOH = 1:3), was added silver nitrate (5 mmol) at room temperature. The starting materials rapidly disappeared and a yellowish gray precipitate formed within 15-20 min. This solid was recovered by filtration and washed with cold methanol (stored at 0 °C). Subsequent drying led to the 4-fluoro-phenylacetylene silver **1g'** as a yellowish gray precipitate powder.



1g' **2a** **3g**

w/wo Ag$_2$CO$_3$, **3g** < 5% yield

To a 5 mL oven-dried sealed reaction vial equipped with a magnetic stirring particle, AgOAc (10 mol%, 3.34 mg), DPPE (10 mol%, 7.97 mg), with or without Ag$_2$CO$_3$ (2.0 equiv, 110.30 mg), **1g’** (0.2 mmol) and acetylacetone **2a** (0.4 mmol, 2.0 equiv) were added sequentially, then 0.5 mL solvent of DMAc (99.8%, Extra Dry) were added finally and the resulting mixture was stirred at 80 °C in a heating mantle for 24 h. The mixture was quenched with 1 N HCl solution (10 mL), extracted with EtOAc (3 × 10 mL). After filtration from a small column filled with cotton, silica gel and anhydrous sodium sulfate, the GC yield was given with n-dodecane as the internal standard.



1g **3g**

w/wo Ag$_2$CO$_3$, **3g:** n.d.

To a 5 mL oven-dried sealed reaction vial equipped with a magnetic stirring particle, AgOAc (10 mol%, 3.34 mg), DPPE (10 mol%, 7.97 mg), Ag$_2$CO$_3$ (2.0 equiv, 110.30 mg), **1g** (0.2 mmol) were added sequentially, then 0.5 mL solvent of DMAc (99.8%, Extra Dry) were added finally and the resulting mixture was stirred at 80 °C in a heating mantle. After 2.5 hours of reaction, the mixture was filtered and washed with DCM (3 × 10 mL). The residue was further analyzed by infrared spectroscopy.

To a 5 mL oven-dried sealed reaction vial equipped with a magnetic stirring particle, AgOAc (10 mol%, 3.34 mg), DPPE (10 mol%, 7.97 mg), with or without Ag$_2$CO$_3$ (2.0 equiv, 110.30 mg), gray solid (the residue) (0.2 mmol) and acetylacetone **2a** (0.4 mmol, 2.0 equiv) were added sequentially, then 0.5 mL solvent of DMAc (99.8%, Extra Dry) were added finally and the resulting mixture was stirred at 80 °C in a heating mantle for 24 h. The mixture was quenched with 1 N HCl solution (10 mL), extracted with EtOAc (3 × 10 mL). After filtration from a small column filled with cotton, silica gel and anhydrous sodium sulfate, the GC yield was given with n-dodecane as the internal standard.

The Results of Infrared Spectra Analysis:

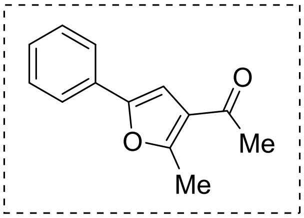
IR: ν(C≡C) = 2050 cm^{-1}, (4-F-PhC≡C-Ag, reported)[11]

IR: ν (C≡C) = 2024 cm^{-1} (4-F-PhC≡C-Ag, prepared according to the above method)

IR: ν (C≡C) = 2238 cm^{-1} (The gray solid collected from the above operation)

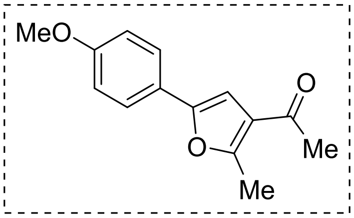
3. Analysis Data for the Products

1-(2-methyl-5-phenylfuran-3-yl)ethan-1-one (3a)[10]



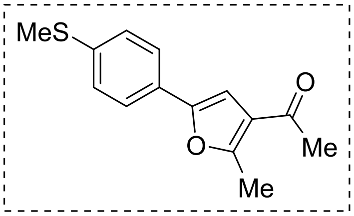
According to the general procedure, the reaction gave **3a** in 75% yield (30 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.71 – 7.59 (m, 2H), 7.39 (t, *J* = 10.0 Hz, 2H), 7.32 – 7.22 (m, 1H), 6.84 (s, 1H), 2.66 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.1, 157.9, 151.6, 129.8, 128.7, 127.7, 123.6, 123.2, 105.0, 29.1, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{13}H_{12}O_2+H^+$ 201.0916; found: 201.0908.

1-(5-(4-methoxyphenyl)-2-methylfuran-3-yl)ethan-1-one (3b)[12]



According to the general procedure, the reaction gave **3b** in 48% yield (22 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.64 – 7.52 (m, 2H), 6.93 – 6.89 (m, 2H), 6.70 (s, 1H), 3.83 (s, 3H), 2.64 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.2, 159.3, 157.3, 151.7, 125.2, 123.2, 122.9, 114.2, 103.4, 55.3, 29.1, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{14}H_{14}O_3+H^+$ 231. 1021; found: 231.1014.

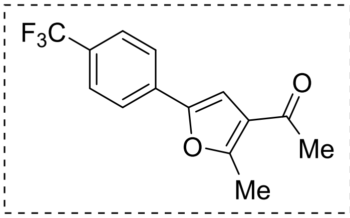
1-(2-methyl-5-(4-(methylthio)phenyl)furan-3-yl)ethan-1-one (3c)[13]



According to the general procedure, the reaction gave **3c** in 60% yield (30 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ethyl acetate = 10/1). ^{1}H

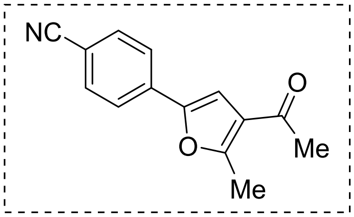
NMR (500 MHz, Chloroform-d) δ 7.55 (d, *J* = 10.0 Hz, 2H), 7.26 (d, *J* = 10.0 Hz, 2H), 6.79 (s, 1H), 2.65 (s, 3H), 2.50 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.0, 157.7, 151.3, 138.2, 126.7, 126.6, 124.0, 123.2, 104.6, 29.1, 15.6, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{14}H_{14}O_2S+H^+$ 247.0793; found: 247.0786.

1-(2-methyl-5-(4-(trifluoromethyl)phenyl)furan-3-yl)ethan-1-one (3d)



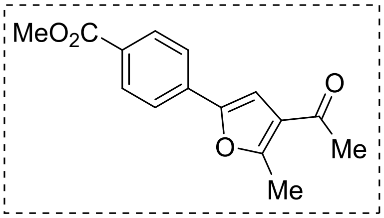
According to the general procedure, the reaction gave **3d** in 76% yield (41 mg) as a pale yellow solid (flash column chromatography eluent, petrol ether/ethyl acetate = 10/1). IR (KBr) ν_{max}: 2925, 1670, 1615, 1324, 1241, 1113, 1069, 834 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.72 (d, J = 5.0 Hz, 2H), 7.62 (d, *J* = 5.0 Hz, 2H), 6.96 (s, 1H), 2.67 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.7, 158.8, 150.1, 133.2 – 132.5 (m), 129.4 (q, *J* = 32.8 Hz), 125.8 (q, *J* = 3.8 Hz), 124.0 (d, *J* = 271.9 Hz), 123.6, 123.4, 107.1, 29.1, 14.5. ^{19}F NMR (471 MHz, Chloroform-d) δ -62.61. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{14}H_{11}F_3O_2+H^+$ 269.0789; found: 269.0781.

4-(4-acetyl-5-methylfuran-2-yl)benzonitrile (3e)[13]



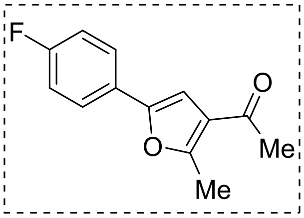
According to the general procedure, the reaction gave **3e** in 74% yield (33 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.71 (d, *J* = 5.0 Hz, 2H), 7.65 (d, *J* = 10.0 Hz, 2H), 7.01 (s, 1H), 2.67 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.6, 159.4, 149.6, 133.7, 132.6, 123.8, 123.6, 118.7, 110.7, 108.2, 29.1, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{14}H_{11}NO_2+H^+$ 226.0868; found: 226.0860.

methyl 4-(4-acetyl-5-methylfuran-2-yl)benzoate (3f)[14]



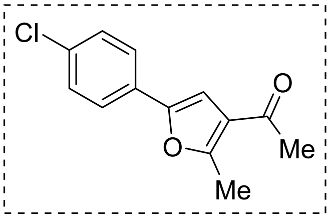
According to the general procedure, the reaction gave **3f** in 75% yield (39 mg) as a white solid (flash column chromatography eluent, petrol ether/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.03 (d, *J* = 10.0 Hz, 2H), 7.67 (d, *J* = 10.0 Hz, 2H), 6.96 (s, 1H), 3.91 (s, 3H), 2.66 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.8, 166.6, 158.9, 150.5, 133.8, 130.1, 128.9, 123.4, 123.2, 107.3, 52.1, 29.1, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{15}H_{14}O_4+H^+$ 259.0970; found: 259.0963.

1-(5-(4-fluorophenyl)-2-methylfuran-3-yl)ethan-1-one (3g)[15]



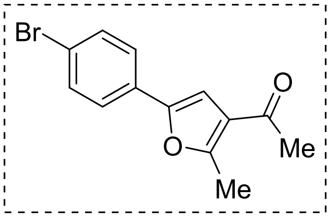
According to the general procedure, the reaction gave **3g** in 66% yield (29 mg) as a pale yellow solid (flash column chromatography eluent, petrol ether/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.65 – 7.54 (m, 2H), 7.07 (t, *J* = 10.0 Hz, 2H), 6.77 (s, 1H), 2.64 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.0, 162.3 (d, *J* = 247.7 Hz), 157.8, 150.8, 126.2 (d, *J* = 3.3 Hz), 125.4 (d, *J* = 8.1 Hz), 123.2, 115.8 (d, *J* = 22.0 Hz), 104.7 (d, *J* = 1.3 Hz), 29.1, 14.4. ^{19}F NMR (471 MHz, Chloroform-d) δ -113.50. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{13}H_{11}FO_2+H^+$ 219.0821; found: 219.0814.

1-(5-(4-chlorophenyl)-2-methylfuran-3-yl)ethan-1-one (3h)[13]



According to the general procedure, the reaction gave **3h** in 67% yield (31 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.55 (d, *J* = 10.0 Hz, 2H), 7.34 (d, *J* = 10.0 Hz, 2H), 6.82 (s, 1H), 2.65 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.9, 158.1, 150.6, 133.4, 128.9, 128.3, 124.8, 123.3, 105.5, 29.1, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{13}H_{11}ClO_2+H^+$ 235.0526; found: 235.0518.

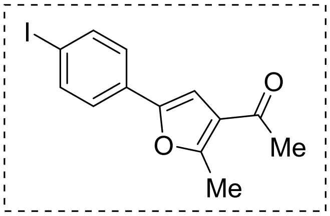
1-(5-(4-bromophenyl)-2-methylfuran-3-yl)ethan-1-one (3i)[12]



According to the general procedure, the reaction gave **3i** in 74% yield (41 mg) as a gray solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.48 (s, 4H), 6.83 (s, 1H), 2.64 (s, 3H), 2.43

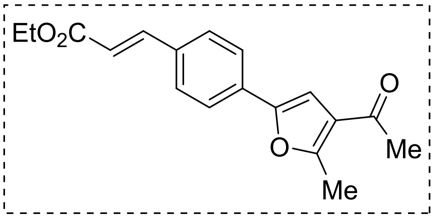
(s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.8, 158.1, 150.5, 131.8, 128.7, 125.1, 123.3, 121.5, 105.6, 29.1, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{13}H_{11}BrO_2+H^+$ 279.0021; found: 279.0013.

1-(5-(4-iodophenyl)-2-methylfuran-3-yl)ethan-1-one (3j)



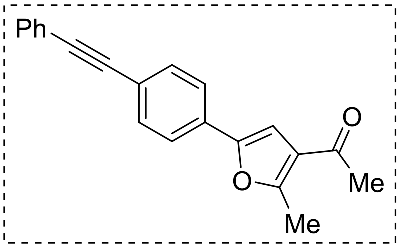
According to the general procedure, the reaction gave **3j** in 65% yield (42 mg) as a pale yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2920, 1658, 1567, 1401, 1234, 944, 816, 628 cm^{-1}. ^1H NMR (500 MHz, Chloroform-d) δ 7.69 (d, *J* = 5.0 Hz, 2H), 7.35 (d, *J* = 5.0 Hz, 2H), 6.85 (s, 1H), 2.64 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.8, 158.2, 150.6, 137.8, 129.3, 125.2, 123.3, 105.7, 92.9, 29.1, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{13}H_{11}IO_2+H^+$ 326.9882; found: 326.9874.

ethyl (E)-3-(4-(4-acetyl-5-methylfuran-2-yl)phenyl)acrylate (3k)



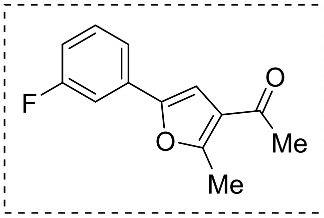
According to the general procedure, the reaction gave **3k** in 64% yield (38 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2921, 1685, 1596, 1308, 1171, 955, 819, 630 cm^{-1}. ^1H NMR (500 MHz, Chloroform-d) δ 7.72 – 7.60 (m, 3H), 7.53 (d, *J* = 5.0 Hz, 2H), 6.90 (s, 1H), 6.43 (d, *J* = 15.0 Hz, 1H), 4.26 (q, *J* = 5.0 Hz, 2H), 2.65 (s, 3H), 2.44 (s, 3H), 1.33 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.8, 166.9, 158.5, 150.8, 143.7, 133.6, 131.3, 128.5, 123.9, 123.4, 118.1, 106.3, 60.5, 29.1, 14.5, 14.3. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{18}H_{18}O_4+H^+$ 299.1283; found: 299.1277.

1-(2-methyl-5-(4-(phenylethynyl)phenyl)furan-3-yl)ethan-1-one (3l)



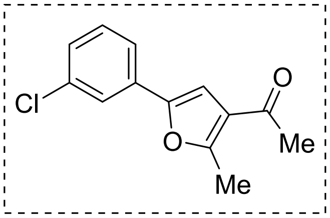
According to the general procedure, the reaction gave **3l** in 65% yield (39 mg) as a pale yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2922, 1671, 1565, 1412, 1237, 947, 838, 757 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.62 (d, *J* = 10.0 Hz, 2H), 7.58 – 7.50 (m, 4H), 7.39 – 7.31 (m, 3H), 6.88 (s, 1H), 2.67 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.9, 158.3, 151.0, 132.0, 131.5, 129.4, 128.3, 123.4, 123.3, 123.1, 122.4, 105.9, 90.5, 89.2, 29.1, 14.5. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. For $C_{21}H_{16}O_2$+H$^+$ 301.1229; found: 301.1221.

1-(5-(3-fluorophenyl)-2-methylfuran-3-yl)ethan-1-one (3m)



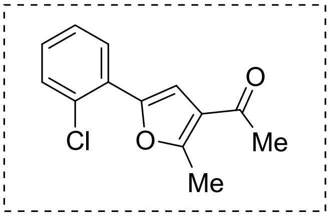
According to the general procedure, the reaction gave **3m** in 55% yield (24 mg) as a pale yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2921, 1670, 1610, 1561, 1437, 1236, 945, 783 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 – 7.42 (m, 1H), 7.36 – 7.31 (m, 2H), 6.94 – 6.98 (m, 1H), 6.87 (s, 1H), 2.66 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.9, 163.1 (d, *J* = 245.6 Hz), 158.3, 150.4 (d, *J* = 3.0 Hz), 131.9 (d, *J* = 8.5 Hz), 130.4 (d, *J* = 8.4 Hz), 123.3, 119.3 (d, *J* = 2.9 Hz), 114.5 (d, *J* = 21.3 Hz), 110.6 (d, *J* = 23.7 Hz), 106.1, 29.1, 14.5. ^{19}F NMR (471 MHz, Chloroform-d) δ -112.57. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{13}H_{11}FO_2$+H$^+$ 219.0821; found: 219.0814.

1-(5-(3-chlorophenyl)-2-methylfuran-3-yl)ethan-1-one (3n)[15]



According to the general procedure, the reaction gave **3n** in 74% yield (35 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.62 (s, 1H), 7.50 (d, *J* = 10.0 Hz, 1H), 7.30 (t, *J* = 10.0 Hz, 1H), 7.23 (d, *J* = 5.0 Hz, 1H), 6.86 (s, 1H), 2.65 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.8, 158.4, 150.1, 134.8, 131.5, 130.0, 127.6, 123.6, 123.2, 121.6, 106.1, 29.1, 14.5. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{13}H_{11}ClO_2$+H$^+$ 235.0526; found: 235.0519.

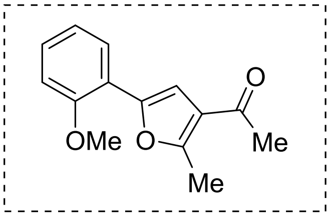
1-(5-(2-chlorophenyl)-2-methylfuran-3-yl)ethan-1-one (3o)[16]



According to the general procedure, the reaction gave **3o** in

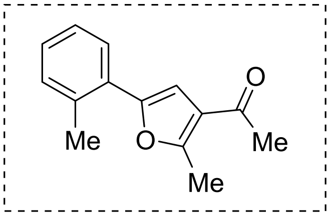
72% yield (34 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.82 (d, *J* = 10.0 Hz, 1H), 7.43 (d, *J* = 5.0 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.21 (t, *J* = 10.0 Hz, 1H), 2.67 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.2, 157.9, 147.8, 130.7, 130.0, 128.4, 128.2, 127.6, 126.9, 123.1, 111.1, 29.1, 14.4. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{13}H_{11}ClO_2+H^+$ 235.0526; found: 235.0517.

1-(5-(2-methoxyphenyl)-2-methylfuran-3-yl)ethan-1-one (3p)[17]



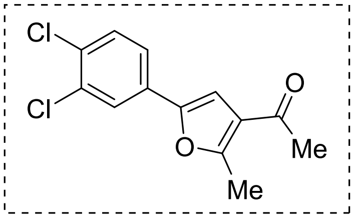
According to the general procedure, the reaction gave **3p** in 68% yield (31 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.81 (dd, *J* = 10.0, 5.0 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.12 (s, 1H), 7.00 – 7.04 (m, 1H), 6.97 (d, *J* = 10.0 Hz, 1H), 3.97 (s, 3H), 2.66 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.6, 157.0, 155.3, 147.9, 128.4, 125.7, 123.2, 120.7, 118.8, 110.9, 110.0, 55.4, 29.2, 14.4. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{14}H_{14}O_3+H^+$ 231.1021; found: 231.1014.

1-(2-methyl-5-(o-tolyl)furan-3-yl)ethan-1-one (3q)



According to the general procedure, the reaction gave **3q** in 68% yield (29 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2924, 1674, 1563, 1401, 1231, 949, 758, 631 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.65 (t, *J* = 10.0 Hz, 1H), 7.23 (t, *J* = 10.0 Hz, 3H), 6.71 (d, *J* = 10.0 Hz, 1H), 2.65 (d, *J* = 10.0 Hz, 3H), 2.46 (dd, *J* = 10.0, 5.0 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.1, 157.4, 151.1, 134.5, 131.1, 129.1, 127.8, 126.8, 126.0, 123.1, 108.6, 29.1, 21.8, 14.4. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{14}H_{14}O_2+H^+$ 215.1072; found: 215.1066.

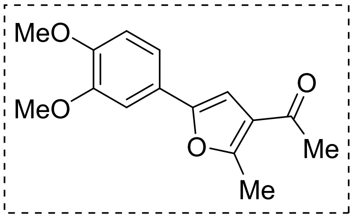
1-(5-(3,4-dichlorophenyl)-2-methylfuran-3-yl)ethan-1-one (3r)



According to the general procedure, the reaction gave **3r** in

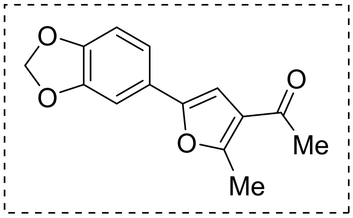
70% yield (38 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2922, 1673, 1598, 1463, 1405, 1236, 948, 811 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.68 (s, 1H), 7.41 (s, 2H), 6.84 (s, 1H), 2.64 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.6, 158.5, 149.2, 133.0, 131.3, 130.7, 129.7, 125.2, 123.3, 122.7, 106.5, 29.1, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{13}H_{10}Cl_2O_2+H^+$ 269.0136; found: 269.0127.

1-(5-(3,4-dimethoxyphenyl)-2-methylfuran-3-yl)ethan-1-one (3s)[12]



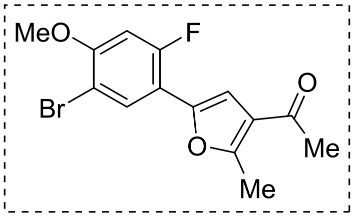
According to the general procedure, the reaction gave **3s** in 71% yield (37 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.19 (dd, J = 10.0, 5.0 Hz, 1H), 7.13 (d, J = 5.0 Hz, 1H), 6.87 (d, J = 10.0 Hz, 1H), 6.71 (s, 1H), 3.93 (s, 3H), 3.89 (s, 3H), 2.64 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.1, 157.3, 151.6, 149.1, 148.9, 123.2, 123.1, 116.5, 111.4, 107.0, 103.7, 55.9, 29.1, 14.4. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{15}H_{16}O_4+H^+$ 261.1127; found: 261.1119.

1-(5-(benzo[d][1,3]dioxol-5-yl)-2-methylfuran-3-yl)ethan-1-one (3t)[13]



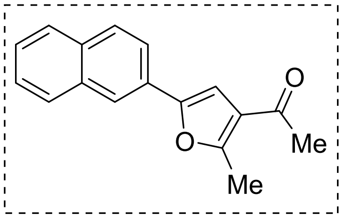
According to the general procedure, the reaction gave **3t** in 50% yield (25 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.19 – 7.12 (m, 1H), 7.08 (s, 1H), 6.81 (d, J = 10.0 Hz, 1H), 6.68 (d, J = 5.0 Hz, 1H), 5.97 (s, 2H), 2.62 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.0, 157.3, 151.4, 148.0, 147.3, 124.3, 123.1, 117.6, 108.6, 104.4, 103.9, 101.2, 29.1, 14.4. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{14}H_{12}O_4+H^+$ 245.0814; found: 245.0806.

1-(5-(5-bromo-2-fluoro-4-methoxyphenyl)-2-methylfuran-3-yl)ethan-1-one (3u)



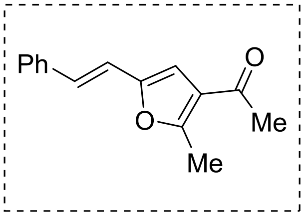
According to the general procedure, the reaction gave **3u** in 81% yield (53 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2926, 1673, 1597, 1483, 1373, 1221, 1052, 953 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.88 (d, *J* = 5.0 Hz, 1H), 6.85 (s, 1H), 6.68 (d, *J* = 15.0 Hz, 1H), 3.88 (s, 3H), 2.62 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.0, 158.1 (d, *J* = 251.4 Hz), 157.5, 155.7 (d, *J* = 10.1 Hz), 144.4 (d, *J* = 3.3 Hz), 129.3 (d, *J* = 4.6 Hz), 123.2 (d, *J* = 1.1 Hz), 112.0 (d, *J* = 13.7 Hz), 109.0 (d, *J* = 11.2 Hz), 106.4 (d, *J* = 3.3 Hz), 100.7 (d, *J* = 26.9 Hz), 56.5, 29.1, 14.3. ^{19}F NMR (471 MHz, Chloroform-d) δ -111.86. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{14}H_{12}BrFO_3+H^+$ 327.0032; found: 327.0024.

1-(2-methyl-5-(naphthalen-2-yl)furan-3-yl)ethan-1-one(3v)[12]



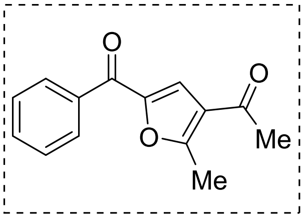
According to the general procedure, the reaction gave **3v** in 80% yield (40 mg) as a brown solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.11 (s, 1H), 7.89 – 7.78 (m, 3H), 7.72 – 7.70 (m, 1H), 7.51 – 7.45 (m, 2H), 6.94 (s, 1H), 2.70 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.0, 158.1, 151.6, 133.3, 132.7, 128.5, 128.1, 127.7, 127.1, 126.6, 126.1, 123.3, 122.1, 121.8, 105.6, 29.1, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{17}H_{14}O_2+H^+$ 251.1072; found: 251.1064.

(E)-1-(2-methyl-5-styrylfuran-3-yl)ethan-1-one (3w)



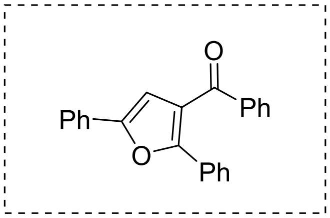
According to the general procedure, the reaction gave **3w** in 56% yield (25 mg) as a gray solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2923, 1671, 1581, 1406, 1214, 953, 749, 691 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.46 (d, *J* = 5.0 Hz, 2H), 7.35 (t, *J* = 10.0 Hz, 2H), 7.26 (t, *J* = 10.0 Hz, 1H), 7.03 (d, *J* = 20.0 Hz, 1H), 6.80 (d, *J* = 15.0 Hz, 1H), 6.53 (s, 1H), 2.64 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.0, 158.2, 150.9, 136.6, 128.7, 127.8, 127.8, 126.3, 123.1, 115.5, 108.5, 29.1, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{15}H_{14}O_2+H^+$ 227.1072; found: 227.1064.

1-(5-benzoyl-2-methylfuran-3-yl)ethan-1-one (3x)[18]



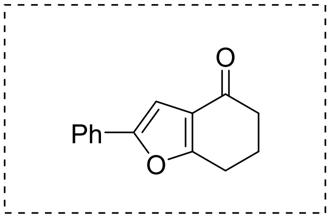
According to the general procedure, the reaction gave **3x** in 63% yield (29 mg) as a Orange oily (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.93 (d, *J* = 5.0 Hz, 2H), 7.59 – 7.63 (m, 1H), 7.51 (t, *J* = 10.0 Hz, 2H), 7.39 (s, 1H), 2.73 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.2, 182.1, 163.1, 149.5, 136.9, 132.8, 129.1, 128.5, 123.2, 120.7, 29.0, 14.9. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{14}H_{12}O_3$+H$^+$ 229.0865; found: 229.0857.

(2,5-diphenylfuran-3-yl)(phenyl)methanone (4a)[19]



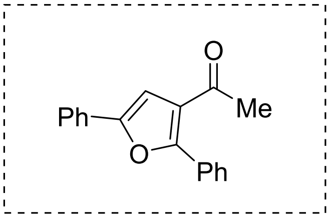
According to the general procedure, the reaction gave **4a** in 71% yield (46 mg) as a yellow oily liquid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 – 7.88 (m, 2H), 7.83 – 7.74 (m, 4H), 7.58 – 7.51 (m, 1H), 7.48 – 7.38 (m, 4H), 7.37 – 7.30 (m, 4H), 6.94 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 191.7, 154.9, 152.4, 138.0, 132.9, 129.7, 129.7, 129.0, 128.8, 128.4, 128.3, 128.1, 127.4, 124.0, 122.8, 108.7. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{23}H_{16}O_2$+H$^+$ 325.1229; found: 325.1221.

2-phenyl-6,7-dihydrobenzofuran-4(5H)-one (4b)[19]



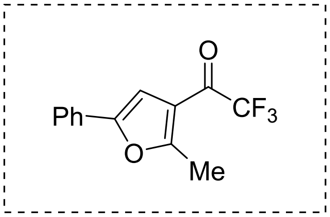
According to the general procedure, the reaction gave **4b** in 40% yield (17 mg) as a yellow oily liquid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.69 – 7.62 (m, 2H), 7.39 (t, *J* = 5.0 Hz, 2H), 7.30 (t, *J* = 10.0 Hz, 1H), 6.89 (s, 1H), 2.96 (t, *J* = 5.0 Hz, 2H), 2.53 (t, *J* = 10.0 Hz, 2H), 2.25 – 2.20 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.5, 166.7, 154.2, 129.8, 128.8, 128.1, 123.9, 122.9, 100.8, 37.6, 23.4, 22.5. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{14}H_{12}O_2$+H$^+$ 213.0916; found: 213.0907.

1-(2,5-diphenylfuran-3-yl)ethan-1-one (4c)



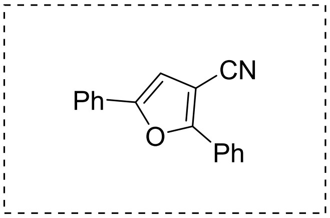
According to the general procedure, the reaction gave **4c** in 39% yield (20 mg) as a pale yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2923, 1678, 1537, 1484, 1259, 1219, 939, 699 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.98 (d, *J* = 5.0 Hz, 2H), 7.74 (d, *J* = 5.0 Hz, 2H), 7.50 – 7.41 (m, 5H), 7.37 – 7.29 (m, 1H), 7.04 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.0, 155.7, 152.6, 130.0, 129.7, 129.6, 128.8, 128.6, 128.3, 128.2, 124.2, 124.0, 107.1, 29.8. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{18}H_{14}O_2+H^+$ 263.1072; found: 263.1063.

2,2,2-trifluoro-1-(2-methyl-5-phenylfuran-3-yl)ethan-1-one (4d)



According to the general procedure, the reaction gave **4d** in 46% yield (23 mg) as a yellow oily liquid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2922, 1702, 1564, 1189, 1147, 903, 757, 693 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.70 – 7.65 (m, 2H), 7.42 (t, *J* = 10.0 Hz, 2H), 7.36 – 7.31 (m, 1H), 6.93 – 6.91 (m, 1H), 2.75 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 176.3 (d, *J* = 36.2 Hz), 164.2, 153.0, 129.0, 128.9, 128.4, 124.0, 119.8, 117.5 – 115.2 (m), 103.6 (q, *J* = 3.3 Hz), 14.9. ^{19}F NMR (471 MHz, Chloroform-d) δ -75.42. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{13}H_9F_3O_2+H^+$ 255.0633; found: 255.0544.

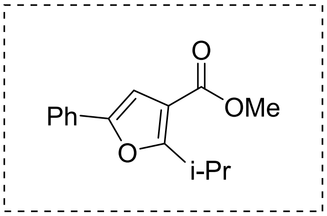
2,5-diphenylfuran-3-carbonitrile (4e)[19]



According to the general procedure, the reaction gave **4e** in 42% yield (21 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.08 – 8.05 (m, 2H), 7.72 (d, *J* = 5.0 Hz, 2H), 7.53 – 7.50 (m, 2H), 7.47 – 7.44 (m, 3H), 7.39 – 7.36 (m, 1H), 6.87 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 158.7, 153.6, 130.1, 129.1, 129.0, 128.9, 128.7, 128.1, 125.3, 124.2, 114.9, 107.7, 93.4. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for

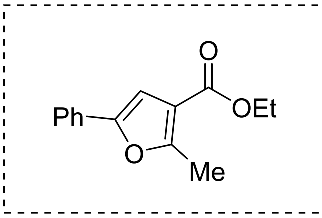
$C_{17}H_{11}NO+H^+$ 246.0919; found: 245.9866.

methyl 2-isopropyl-5-phenylfuran-3-carboxylate (4f)[20]



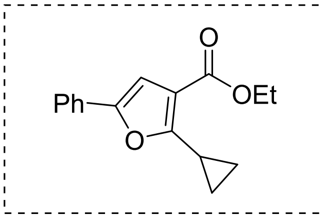
According to the general procedure, the reaction gave **4f** in 50% yield (24 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.64 (d, *J* = 10.0 Hz, 2H), 7.38 (t, *J* = 10.0 Hz, 2H), 7.28 – 7.25 (m, 1H), 6.87 (s, 1H), 3.86 (s, 3H), 3.83 – 3.76 (m, 1H), 1.34 (d, *J* = 5.0 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-d) δ 166.7, 164.3, 151.4, 130.2, 128.7, 127.6, 123.6, 113.1, 105.3, 51.3, 27.4, 20.8. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{15}H_{16}O_3+H^+$ 245.1172; found: 245.1178.

ethyl 2-methyl-5-phenylfuran-3-carboxylate (4g)[20]



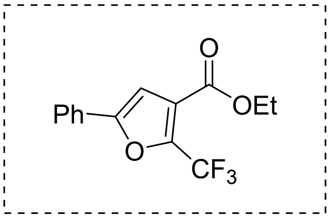
According to the general procedure, the reaction gave **4g** in 72% yield (33 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.63 – 7.60 (m, 2H), 7.36 (t, *J* = 10.0 Hz, 2H), 7.25 – 7.22 (m, 1H), 6.87 (s, 1H), 4.30 (q, *J* = 5.0 Hz, 2H), 2.63 (s, 3H), 1.35 (t, *J* = 5.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 164.0, 158.6, 151.7, 130.1, 128.7, 127.6, 123.6, 115.4, 105.5, 60.2, 14.3, 13.9. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{14}H_{14}O_3+H^+$ 231.1021; found: 231.1014.

ethyl 2-cyclopropyl-5-phenylfuran-3-carboxylate (4h)



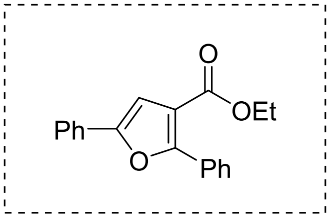
According to the general procedure, the reaction gave **4h** in 52% yield (26 mg) as a yellow oily liquid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2925, 1711, 1604, 1421, 1231, 1066, 757, 692 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 – 7.51 (m, 2H), 7.43 – 7.32 (m, 2H), 7.28 – 7.21 (m, 1H), 6.87 (s, 1H), 4.34 (q, *J* = 10.0 Hz, 2H), 2.87 – 2.80 (m, 1H), 1.39 (t, *J* = 10.0 Hz, 3H), 1.19 – 1.16 (m, 2H), 1.14 – 1.07 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 164.3, 162.6, 150.3, 130.0, 128.6, 127.4, 123.4, 114.9, 105.8, 60.1, 14.4, 9.4, 8.9. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{16}H_{16}O_3+H^+$ 257.1178; found: 257.1172.

ethyl 5-phenyl-2-(trifluoromethyl)furan-3-carboxylate (4i)[21]



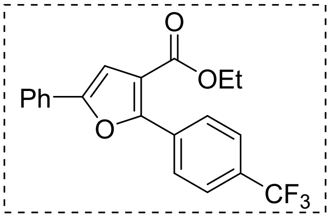
According to the general procedure, the reaction gave **4i** in 48% yield (27 mg) as a yellow oily liquid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^1H NMR (500 MHz, Chloroform-d) δ 7.71 (d, *J* = 10.0, 2H), 7.46 – 7.43 (m, 2H), 7.40 – 7.37 (m, 1H), 7.05 (s, 1H), 4.38 (q, *J* = 5.0 Hz, 2H), 1.39 (t, *J* = 5.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 160.9, 154.8, 142.0, 129.3, 129.0, 128.4, 124.6, 121.4 – 121.2 (m), 118.7 (d, *J* = 269.4 Hz), 106.9, 61.6, 14.0. ^{19}F NMR (471 MHz, Chloroform-d) δ -61.39. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{14}H_{11}F_3O_3+H^+$ 285.0739; found: 285.0730.

ethyl 2,5-diphenylfuran-3-carboxylate (4j)[19]



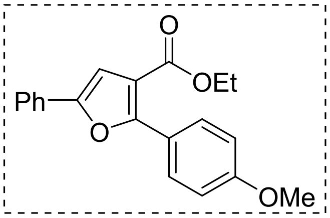
According to the general procedure, the reaction gave **4j** in 77% yield (45 mg) as a yellow liquid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^1H NMR (500 MHz, Chloroform-d) δ 8.12 – 8.07 (m, 2H), 7.79 – 7.73 (m, 2H), 7.50 – 7.46 (m, 2H), 7.45 – 7.41 (m, 3H), 7.35 – 7.30 (m, 1H), 7.11 (s, 1H), 4.35 (q, *J* = 5.0 Hz, 2H), 1.38 (t, *J* = 5.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 163.5, 156.4, 152.3, 129.7, 129.3, 128.8, 128.3, 128.1, 128.0, 123.9, 115.7, 107.9, 60.6, 14.2. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{19}H_{16}O_3+H^+$ 293.1178; found: 293.1168.

ethyl 5-phenyl-2-(4-(trifluoromethyl)phenyl)furan-3-carboxylate (4k)



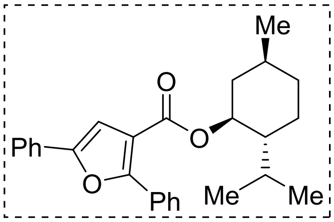
According to the general procedure, the reaction gave **4k** in 64% yield (46 mg) as a yellow liquid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2927, 1719, 1323, 1232, 1116, 845, 765, 687 cm^{-1}. ^1H NMR (400 MHz, Chloroform-d) δ 8.23 (d, *J* = 10.0 Hz, 2H), 7.80 – 7.66 (m, 4H), 7.52 – 7.41 (m, 2H), 7.38 – 7.31 (m, 1H), 7.11 (s, 1H), 4.36 (q, *J* = 10.0 Hz, 2H), 1.39 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 163.2, 154.4, 153.1, 132.9, 130.9, 130.5, 129.4, 128.9, 128.4, 125.0, 124.1, 122.6, 117.3, 108.1, 60.9, 14.2. ^{19}F NMR (376 MHz, Chloroform-d) δ -62.77. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{20}H_{15}F_3O_3+H^+$ 361.1052; found: 361.1046.

ethyl 2-(4-methoxyphenyl)-5-phenylfuran-3-carboxylate (4l)[22]



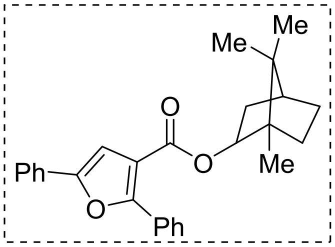
According to the general procedure, the reaction gave **4l** in 66% yield (43 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.11 – 8.04 (m, 2H), 7.76 – 7.70 (m, 2H), 7.44 – 7.39 (m, 2H), 7.35 – 7.27 (m, 1H), 7.07 (s, 1H), 7.02 – 6.93 (m, 2H), 4.34 (q, J = 10.0 Hz, 2H), 3.87 (s, 3H), 1.38 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 163.7, 160.4, 156.8, 151.6, 129.9, 129.9, 128.7, 127.8, 123.9, 122.5, 114.5, 113.5, 107.8, 60.5, 55.3, 14.3.

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 2,5-diphenylfuran-3-carboxylate (4m)



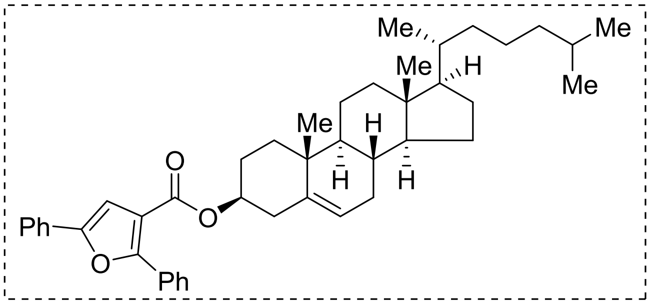
According to the general procedure, the reaction gave **4m** in 65% yield (51 mg) as a pale yellow liquid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). $[\alpha]_D^{25}$ = -120.0 (*c* = 0.1, CH_2Cl_2). IR (KBr) ν_{max}: 2947, 2866, 1711, 1483, 1230, 1096, 759, 689 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.15 – 8.08 (m, 2H), 7.82 – 7.73 (m, 2H), 7.50 – 7.47 (m, 2H), 7.45 – 7.41 (m, 3H), 7.35 – 7.30 (m, 1H), 7.10 (s, 1H), 4.92 (td, *J* = 10.0, 5.0 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.99 – 1.93 (m, 1H), 1.78 – 1.69 (m, 2H), 1.62 – 1.45 (m, 2H), 1.29 – 1.26 (m, 1H), 1.19 – 1.05 (m, 2H), 0.94 (dd, *J* = 15.0, 5.0 Hz, 6H), 0.82 (d, *J* = 5.0, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 163.0, 156.4, 152.2, 129.8, 129.8, 129.2, 128.7, 128.4, 128.0, 128.0, 124.0, 116.1, 107.8, 74.5, 47.1, 41.0, 34.3, 31.4, 26.4, 23.5, 22.0, 16.4. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{27}H_{30}O_3+H^+$ 403.2273; found: 403.2262.

(2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2,5-diphenylfuran-3-carboxylate (4n)



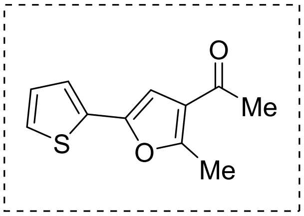
According to the general procedure, the reaction gave **4n** in 64% yield (50 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). $[\alpha]_D^{25}$ = -30.6 (c = 0.2, CH_2Cl_2). IR (KBr) ν_{max}: 2950, 1711, 1481, 1231, 1097, 1014, 759, 688 cm^{-1}. ^1H NMR (500 MHz, Chloroform-d) δ 8.12 – 8.04 (m, 2H), 7.82 – 7.73 (m, 2H), 7.50 – 7.41 (m, 5H), 7.36 – 7.29 (m, 1H), 7.11 (s, 1H), 5.14 – 5.11 (m, 1H), 1.96 – 1.90 (m, 1H), 1.84 – 1.70 (m, 2H), 1.40 – 1.24 (m, 3H), 1.14 (dd, J = 10.0, 5.0 Hz, 1H), 0.97 (s, 3H), 0.92 (d, J = 5.0 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-d) δ 163.8, 156.4, 152.3, 129.8, 129.8, 129.3, 128.7, 128.4, 128.1, 128.0, 124.0, 107.8, 80.4, 48.9, 47.8, 44.9, 36.8, 28.0, 27.3, 19.7, 18.8, 13.6. HRMS-ESI (m/z): $[M+H]^+$ Calcd. for $C_{27}H_{28}O_3+H^+$ 401.2117; found: 401.2127.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2,5-diphenylfuran-3-carboxylate (4o)



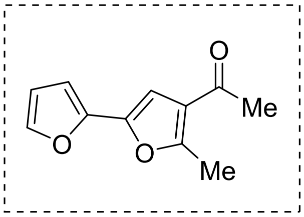
According to the general procedure, the reaction gave **4o** in 60% yield (75 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). $[\alpha]_D^{25}$ = -13.2 (c = 0.2, CH_2Cl_2). IR (KBr) ν_{max}: 2945, 1713, 1480, 1229, 1097, 1005, 758, 690 cm^{-1}. ^1H NMR (500 MHz, Chloroform-d) δ 8.13 – 8.04 (m, 2H), 7.77 – 7.70 (m, 2H), 7.49 – 7.36 (m, 5H), 7.32 – 7.26 (m, 1H), 7.08 (s, 1H), 5.40 (d, J = 10.0 Hz, 1H), 4.85 – 4.78 (m, 1H), 2.49 – 2.36 (m, 2H), 2.05 – 1.93 (m, 3H), 1.91 – 1.86 (m, 1H), 1.76 – 1.62 (m, 1H), 1.61 – 1.05 (m, 18H), 1.04 (s, 3H), 1.02 – 0.96 (m, 3H), 0.91 (d, J = 5.0 Hz, 3H), 0.87 (dd, J = 10.0, 5.0 Hz, 6H), 0.67 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 162.9, 156.3, 152.2, 139.5, 129.8, 129.8, 129.2, 128.7, 128.4, 128.0, 128.0, 123.9, 122.8, 116.1, 108.0, 74.4, 56.6, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 31.8, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{44}H_{56}O_3+H^+$ 633.4308; found: 633.4294.

1-(2-methyl-5-(thiophen-2-yl)furan-3-yl)ethan-1-one (5a)[12]



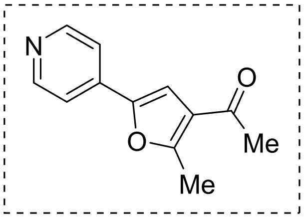
According to the general procedure, the reaction gave **5a** in 41% yield (17 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.29 – 7.18 (m, 2H), 7.04 (dd, *J* = 10.0, 5.0 Hz, 1H), 6.68 (s, 1H), 2.64 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.9, 157.6, 147.2, 132.6, 127.7, 124.6, 123.1, 105.0, 29.1, 14.4. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{11}H_{10}O_2S+H^+$ 207.0480; found: 207.0472.

1-(5-methyl-[2,2'-bifuran]-4-yl)ethan-1-one (5b)[23]



According to the general procedure, the reaction gave **5b** in 55% yield (21 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.41 (s, 1H), 6.73 (s, 1H), 6.55 (s, 1H), 6.45 (s, 1H), 2.63 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 194.0, 157.7, 145.5, 144.3, 142.1, 122.6, 111.4, 105.7, 105.0, 29.1, 14.3. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{11}H_{10}O_3+H^+$ 191.0708; found: 191.0700.

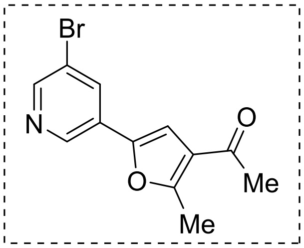
1-(2-methyl-5-(pyridin-4-yl)furan-3-yl)ethan-1-one (5c)



According to the general procedure, the reaction gave **5c** in 72% yield (29 mg) as a pale yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2921, 1672, 1603, 1413, 1243, 950, 823, 655 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.58 (d, J = 5.0 Hz, 2H), 7.46 (d, *J* = 5.0 Hz, 2H), 7.06 (s, 1H), 2.66 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.5, 159.5, 150.2, 148.9, 136.5, 123.4, 117.5, 108.8, 29.1, 14.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for

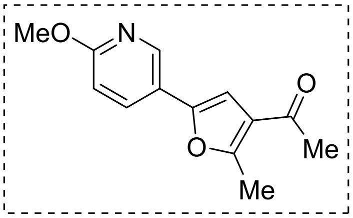
$C_{12}H_{11}NO_2$+H$^+$ 202.0868; found: 202.0860.

1-(5-(5-bromopyridin-3-yl)-2-methylfuran-3-yl)ethan-1-one (5d)



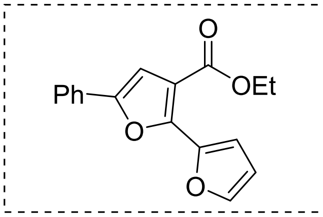
According to the general procedure, the reaction gave **5d** in 72% yield (40 mg) as a pale yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2921, 1674, 1599, 1559, 1425, 1252, 953, 757 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.77 (s, 1H), 8.53 (s, 1H), 8.03 (s, 1H), 6.97 (s, 1H), 2.66 (d, *J* = 5.0 Hz, 3H), 2.44 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.4, 159.3, 149.2, 147.0, 143.0, 133.0, 127.3, 123.3, 120.9, 107.8, 29.1, 14.5. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{12}H_{10}BrNO_2$+H$^+$ 279.9973; found: 279.9965.

1-(5-(6-methoxypyridin-3-yl)-2-methylfuran-3-yl)ethan-1-one (5e)



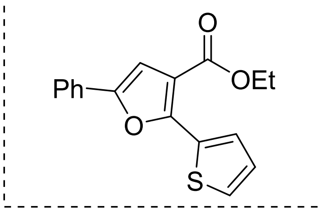
According to the general procedure, the reaction gave **5e** in 72% yield (33 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2926, 1673, 1577, 1485, 1371, 1281, 1022, 757 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.44 (d, *J* = 5.0 Hz, 1H), 7.80 – 7.77 (m, 1H), 6.76 (d, *J* = 10.0 Hz, 1H), 6.74 (s, 1H), 3.95 (s, 3H), 2.64 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.9, 163.6, 157.8, 149.2, 142.5, 134.3, 123.1, 119.8, 110.9, 104.4, 53.6, 29.1, 14.4. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{13}H_{13}NO_3$+H$^+$ 232.0974; found: 232.0965.

ethyl 5-phenyl-[2,2'-bifuran]-3-carboxylate (5f)[12]



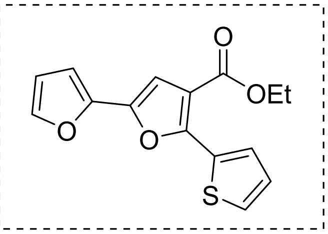
According to the general procedure, the reaction gave **5f** in 60% yield (34 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 – 7.73 (m, 2H), 7.59 – 7.57 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.35 – 7.27 (m, 1H), 7.05 (s, 1H), 6.58 – 6.56 (m, 1H), 4.37 (q, *J* = 8.0 Hz, 2H), 1.41 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 162.8, 152.2, 147.9, 144.5, 143.4, 129.5, 128.7, 128.1, 124.0, 114.4, 113.3, 111.9, 107.1, 60.6, 14.3.

ethyl 5-phenyl-2-(thiophen-2-yl)furan-3-carboxylate (5g)



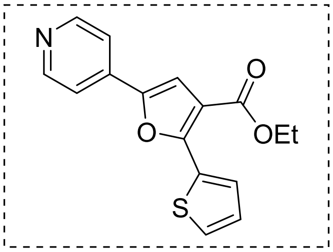
According to the general procedure, the reaction gave **5g** in 74% yield (44 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2925, 1711, 1595, 1489, 1244, 1093, 761, 699 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.14 (d, *J* = 5.0 Hz, 1H), 7.78 – 7.69 (m, 2H), 7.48 – 7.39 (m, 3H), 7.32 (t, *J* = 10.0 Hz, 1H), 7.15 – 7.14 (m, 1H), 7.05 (s, 1H), 4.39 (q, *J* = 10.0 Hz, 2H), 1.43 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 163.3, 152.0, 151.6, 131.6, 129.4, 128.7, 128.7, 128.0, 127.9, 127.4, 123.9, 114.1, 107.4, 60.6, 14.3. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{17}H_{14}O_3S+H^+$ 299.0742; found: 299.0664.

ethyl 5-(thiophen-2-yl)-[2,2'-bifuran]-4-carboxylate (5h)[13]



According to the general procedure, the reaction gave **5h** in 46% yield (26 mg) as a brown solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 20/1). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.10 – 8.09 (m, 1H), 7.49 – 7.38 (m, 2H), 7.13 (dd, *J* = 5.1, 4.0 Hz, 1H), 6.93 (s, 1H), 6.67 (d, *J* = 4.0 Hz, 1H), 6.49 – 6.48 (m, 1H), 4.37 (q, *J* = 8.0 Hz, 2H), 1.40 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 163.1, 151.7, 145.2, 144.2, 142.5, 131.3, 128.9, 128.0, 127.4, 113.8, 111.5, 107.4, 106.5, 60.7, 14.3. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{15}H_{12}O_4S+H^+$ 289.0535; found: 289.0529.

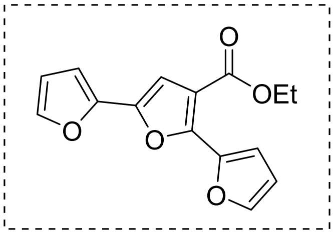
ethyl 5-(pyridin-4-yl)-2-(thiophen-2-yl)furan-3-carboxylate (5i)



According to the general procedure, the reaction gave **5i** in 63% yield (38 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 5/1). IR (KBr) ν_{max}: 2926, 1713, 1604, 1251, 1096, 822, 771, 707 cm^{-}

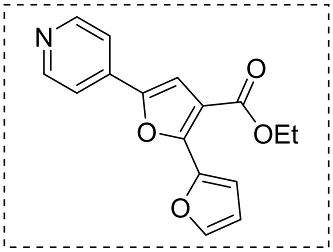
^{1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.64 – 8.59 (m, 2H), 8.16 – 8.15 (m, 1H), 7.54 – 7.50 (m, 2H), 7.48 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.23 (s, 1H), 7.14 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.37 (q, *J* = 8.0 Hz, 2H), 1.40 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 162.7, 153.4, 150.3, 148.6, 136.1, 130.9, 129.6, 128.8, 127.6, 117.7, 114.2, 111.2, 60.8, 14.3. HRMS-ESI (*m/z*): [M+H]$^{+}$ Calcd. for $C_{16}H_{13}NO_3S+H^+$ 300.0694; found: 300.0689.

ethyl [2,2':5',2''-terfuran]-3'-carboxylate (5j)



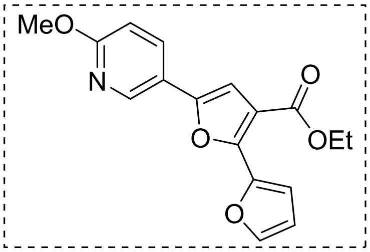
According to the general procedure, the reaction gave **5j** in 41% yield (22 mg) as a white solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 20/1). IR (KBr) ν_{max}: 2924, 1713, 1543, 1459, 1243, 1105, 1008, 741 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.64 – 7.53 (m, 2H), 7.46 – 7.45 (m, 1H), 6.93 (s, 1H), 6.70 (d, *J* = 4.0 Hz, 1H), 6.56 – 6.55 (m, 1H), 6.49 – 6.48 (m, 1H), 4.35 (q, *J* = 8.0 Hz, 2H), 1.39 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 162.7, 147.7, 145.2, 144.8, 144.3, 143.5, 142.6, 114.2, 113.6, 112.0, 111.5, 107.1, 106.7, 60.6, 14.3. HRMS-ESI (*m/z*): [M+H]$^{+}$ Calcd. for $C_{15}H_{12}O_5+H^+$ 273.0763; found: 273.0758.

ethyl 5-(pyridin-4-yl)-2-(thiophen-2-yl)furan-3-carboxylate (5k)



According to the general procedure, the reaction gave **5k** in 54% yield (30 mg) as a brown solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 5/1). IR (KBr) ν_{max}: 2926, 1713, 1602, 1382, 1245, 1111, 821, 761 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.66 – 8.54 (m, 2H), 7.62 – 7.61 (m, 1H), 7.58 – 7.57 (m, 1H), 7.56 – 7.54 (m, 2H), 7.22 (s, 1H), 6.57 – 6.55 (m, 1H), 4.34 (q, *J* = 8.0 Hz, 2H), 1.38 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 162.3, 150.2, 149.2, 149.2, 144.0, 143.9, 136.2, 117.7, 114.6, 114.5, 112.1, 110.8, 60.8, 14.3. HRMS-ESI (*m/z*): [M+H]$^{+}$ Calcd. for $C_{16}H_{13}NO_4+H^+$ 284.0923; found: 284.0917.

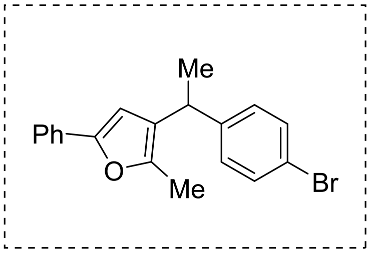
ethyl 5-(6-methoxypyridin-3-yl)-[2,2'-bifuran]-3-carboxylate (5l)



According to the general procedure, the reaction gave **5l** in

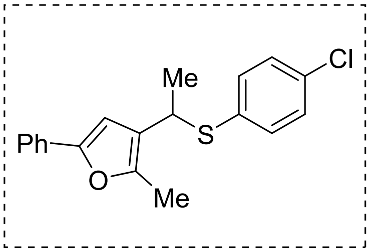
45% yield (29 mg) as a brown solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 5/1). IR (KBr) ν_{max}: 2934, 1714, 1486, 1282, 1247, 1110, 1025, 746 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.54 (d, *J* = 4.0 Hz, 1H), 7.91 – 7.88 (m, 1H), 7.60 – 7.46 (m, 2H), 6.93 (s, 1H), 6.78 (d, *J* = 8.0, 1H), 6.56 – 6.54 (m, 1H), 4.35 (q, *J* = 8.0 Hz, 2H), 3.96 (s, 3H), 1.39 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 163.8, 162.7, 149.9, 147.9, 144.4, 143.4, 143.0, 134.5, 119.5, 114.4, 113.3, 112.0, 111.0, 106.4, 60.6, 53.6, 14.3. HRMS-ESI (*m/z*): [M+H]$^+$ Calcd. for $C_{17}H_{15}NO_5+H^+$ 314.1028; found: 314.1023.

3-(1-(4-bromophenyl)ethyl)-2-methyl-5-phenylfuran (3ab)



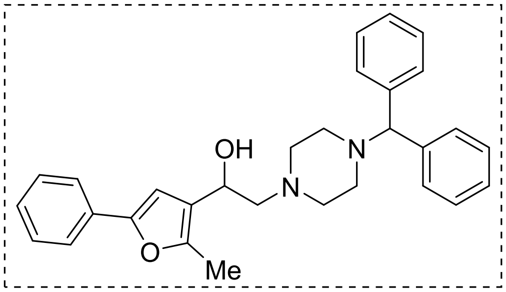
According to the article **scheme 5**, the reaction gave **3ab** in 80% yield (41 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 10/1). IR (KBr) ν_{max}: 2968, 2923, 1483, 1266, 1070, 1011, 823, 755, 693 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.66 – 7.59 (m, 2H), 7.44 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 7.25 – 7.19 (m, 1H), 7.17 – 7.11 (m, 2H), 6.52 (s, 1H), 3.95 (q, *J* = 10.0 Hz, 1H), 2.25 (s, 3H), 1.56 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 151.3, 146.9, 145.1, 131.4, 130.9, 128.9, 128.5, 126.7, 125.1, 123.2, 119.7, 105.4, 35.0, 22.0, 11.9. HRMS-ESI (m/z): [M+H]$^+$ Calcd. for $C_{19}H_{17}BrO+H^+$ 341.0541; found: 341.0536.

3-(1-((4-chlorophenyl)thio)ethyl)-2-methyl-5-phenylfuran (3ac)



According to the article **scheme 5**, the reaction gave **3ac** in 40% yield (26 mg) as a yellow solid (flash column chromatography eluent, petrol ether/ ethyl acetate = 30/1). IR (KBr) ν_{max}: 2924, 1712, 1474, 1243, 1093, 1020, 818, 756, 695 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 – 7.59 (m, 2H), 7.38 – 7.34 (m, 2H), 7.29 – 7.19 (m, 5H), 6.63 (s, 1H), 4.17 (q, *J* = 8.0 Hz, 1H), 2.02 (s, 3H), 1.59 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 151.7, 147.8, 135.1, 133.9, 133.3, 130.8, 128.8, 128.6, 126.9, 123.3, 123.1, 104.5, 40.1, 21.4, 11.5. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{19}H_{17}ClOS+H^+$ 329.0767; found: 329.0761.

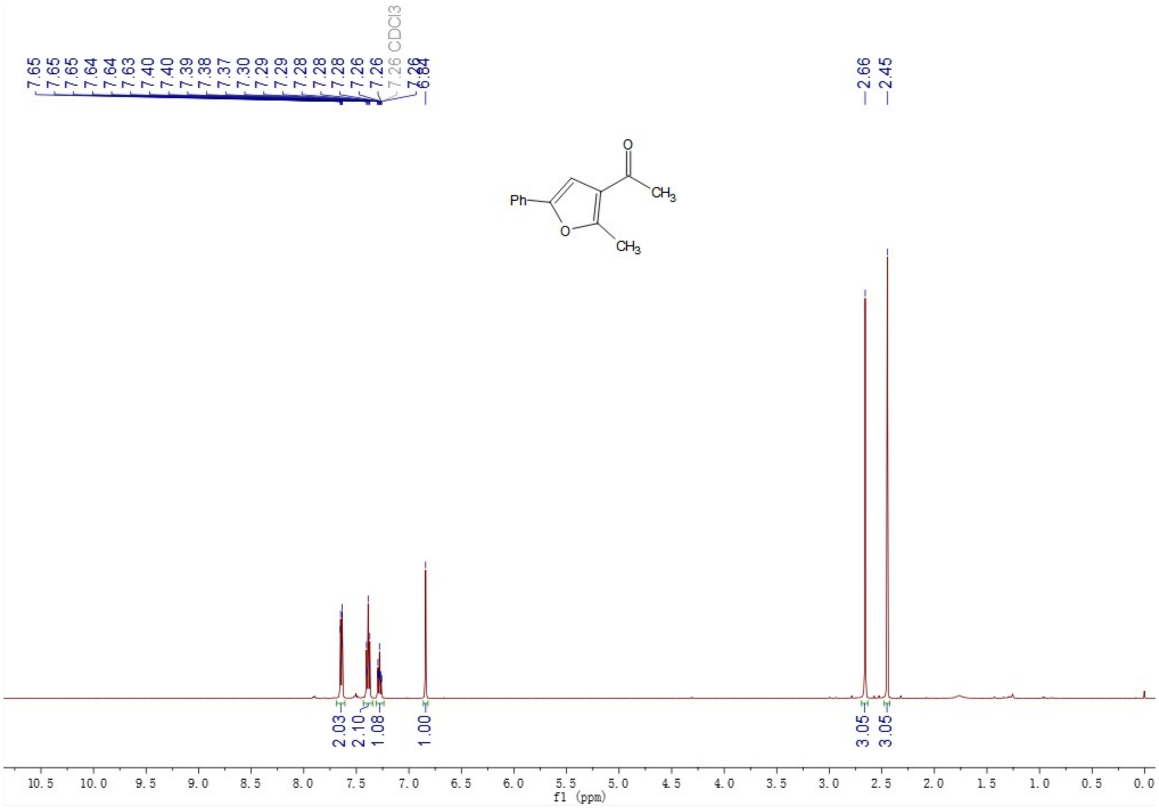
2-(4-benzhydrylpiperazin-1-yl)-1-(2-methyl-5-phenylfuran-3-yl)ethan-1-ol (3ad)



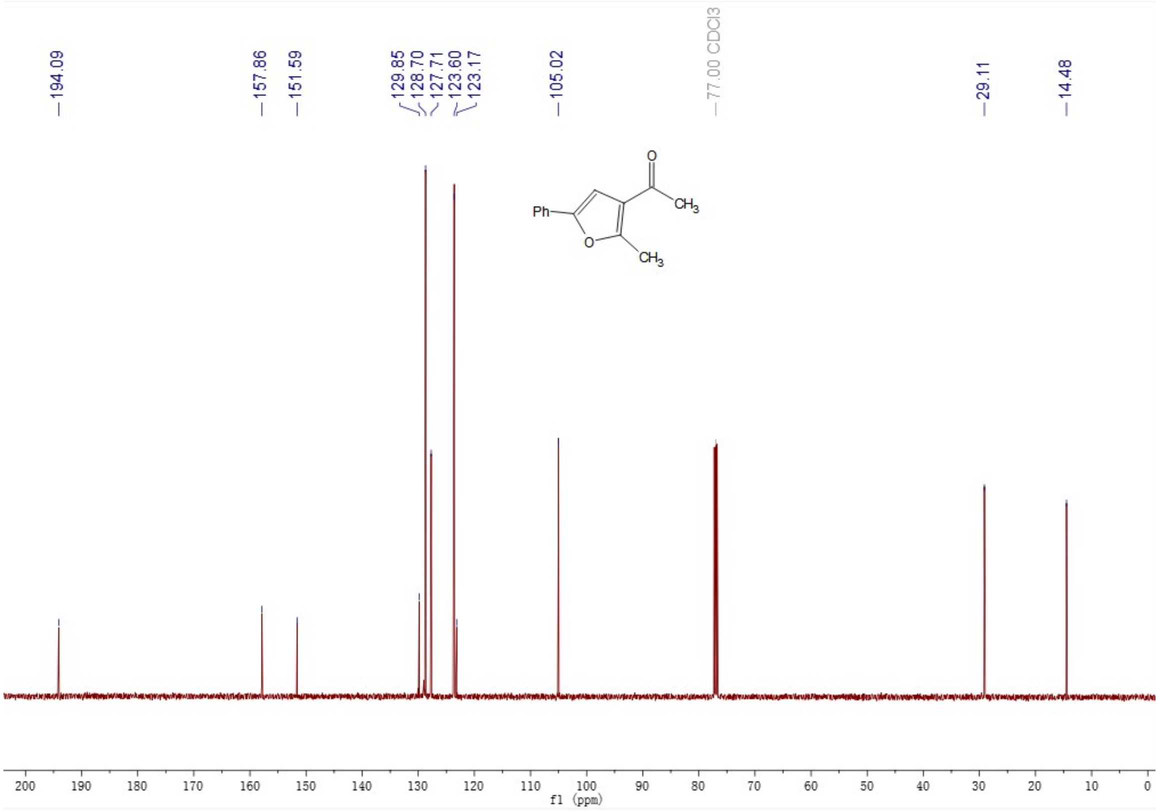
According to 4) route for preparation of **3ad**, a sticky yellowish gel of product was obtained. IR (KBr) ν_{max}: 3071, 2932, 2815, 1449, 1294, 1145, 751, 701 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.68 – 7.63 (m, 2H), 7.51 – 7.44 (m, 4H), 7.38 (t, *J* = 8.0 Hz, 3H), 7.32 (t, *J* = 8.0 Hz, 3H), 7.23 (q, *J* = 8.0 Hz, 3H), 6.66 (s, 1H), 4.72 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.29 (s, 1H), 3.96 (s, 1H), 2.83 (s, 2H), 2.76 – 2.43 (m, 8H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 151.8, 148.3, 142.6, 130.9, 128.5, 128.4, 127.8, 127.8, 126.9, 126.8, 123.3, 121.7, 104.4, 76.1, 64.2, 61.5, 51.8, 12.0. HRMS-ESI (*m/z*): $[M+H]^+$ Calcd. for $C_{30}H_{32}N_2O_2+H^+$ 453.2542; found: 453.2548.

4. NMR Spectra of the Products

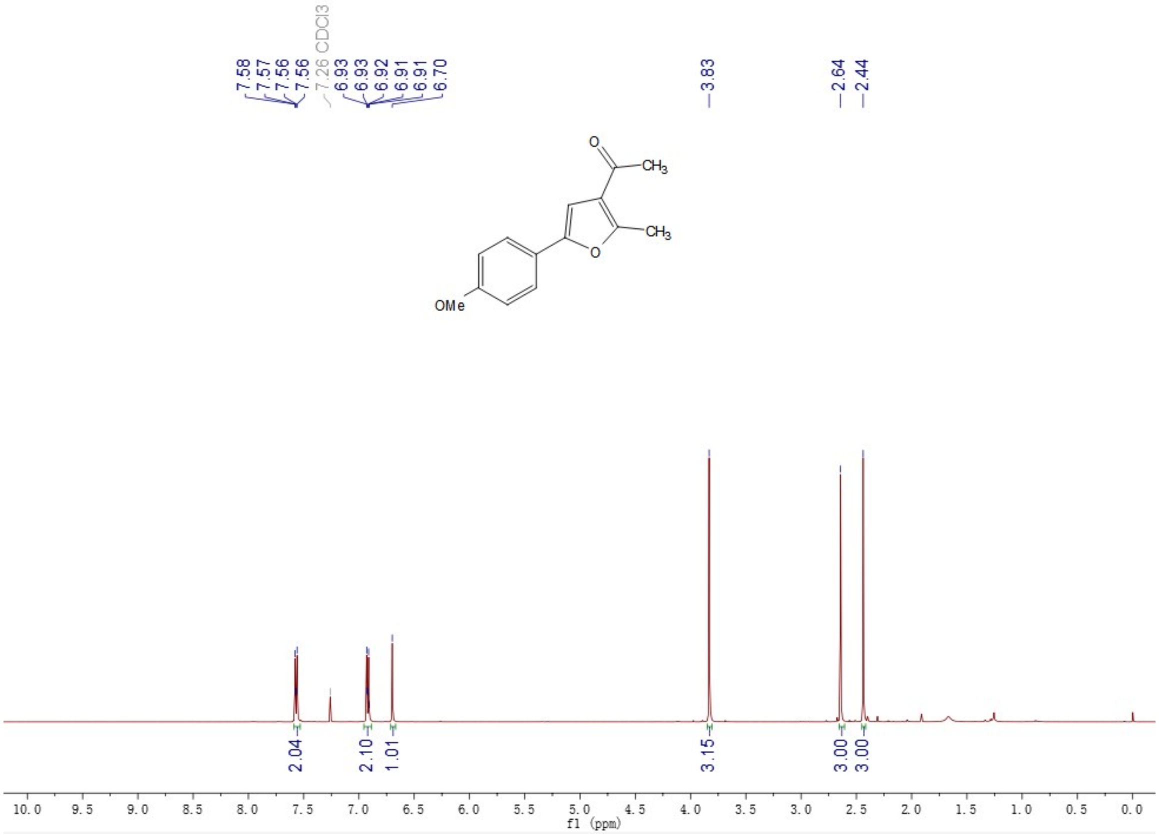
^{1}H NMR (500 MHz, Chloroform-d) of compound **3a.**



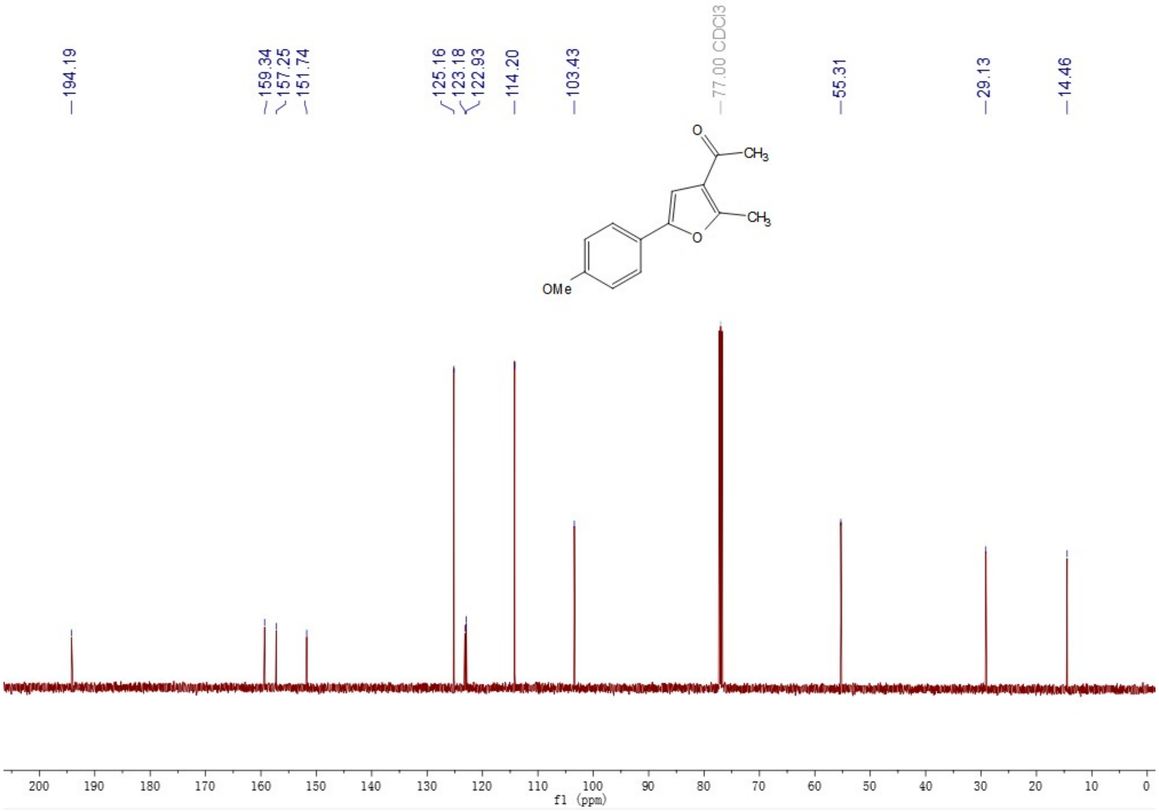
^{13}C NMR (126 MHz, Chloroform-d) of compound **3a.**



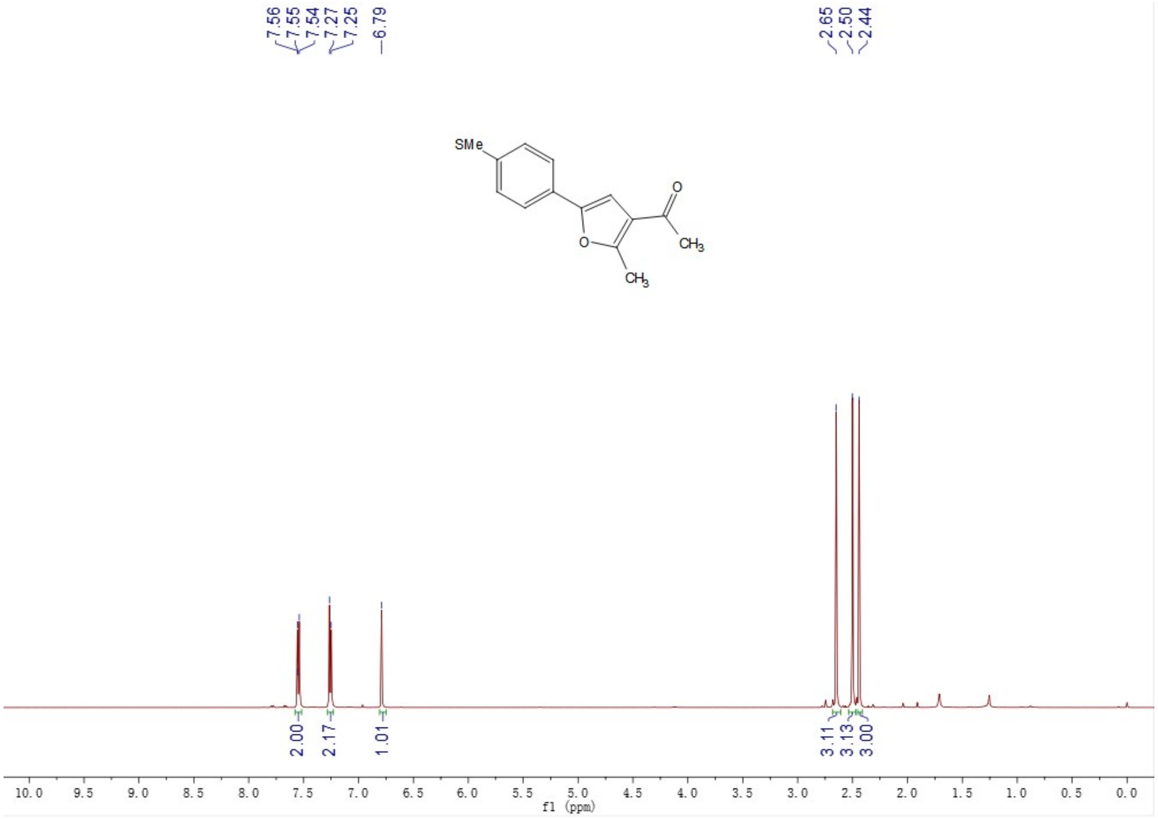
^{1}H NMR (500 MHz, Chloroform-d) of compound **3b.**



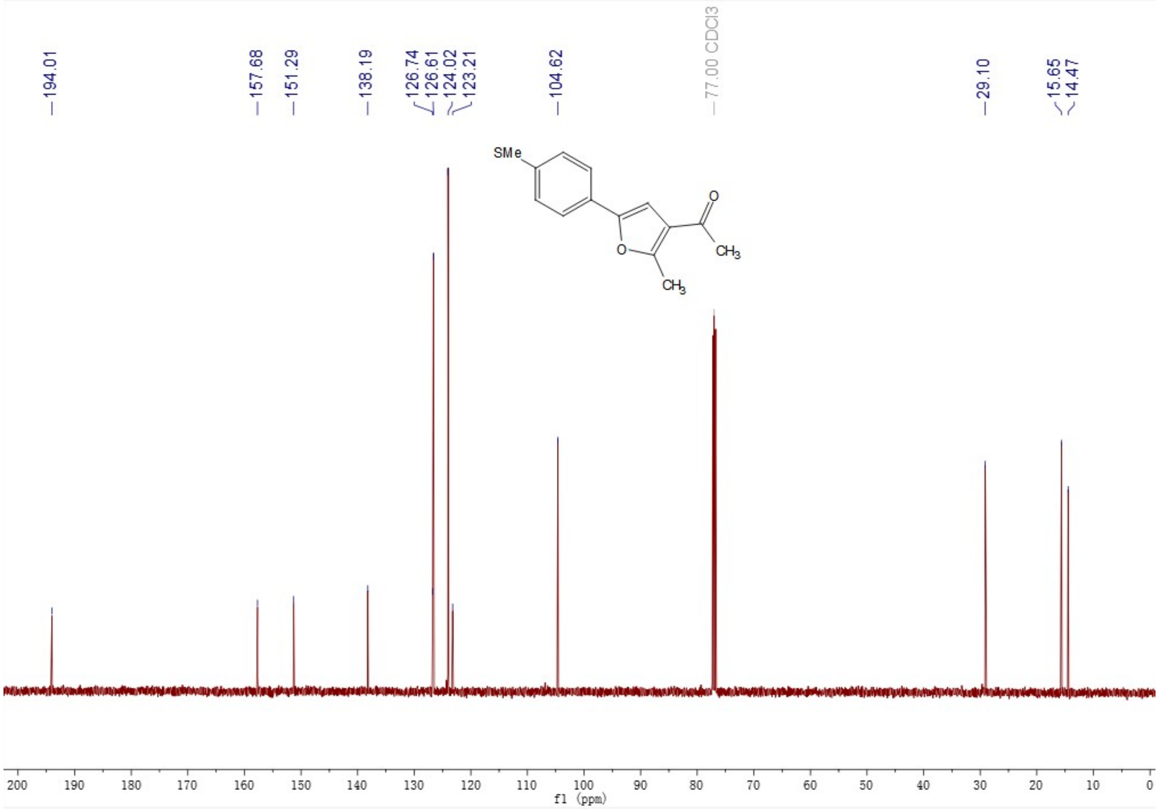
^{13}C NMR (126 MHz, Chloroform-d) of compound **3b.**



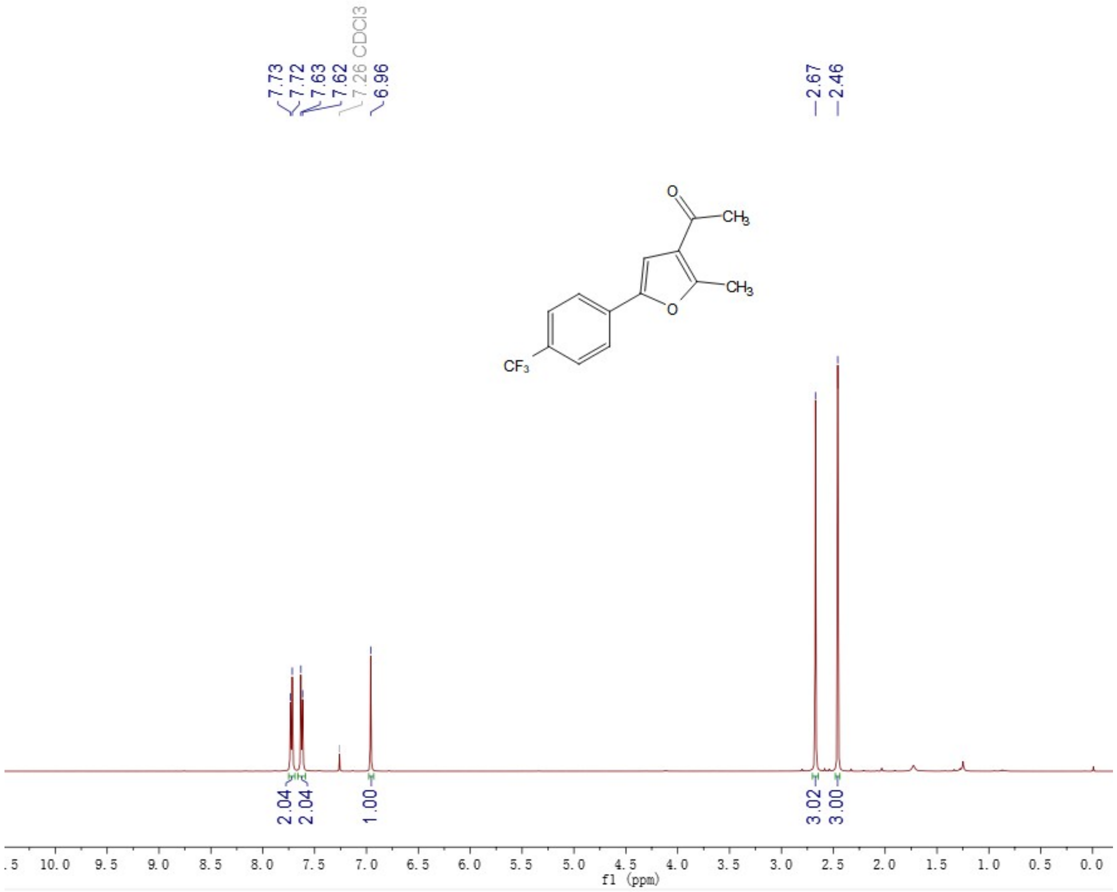
^{1}H NMR (500 MHz, Chloroform-d) of compound **3c.**



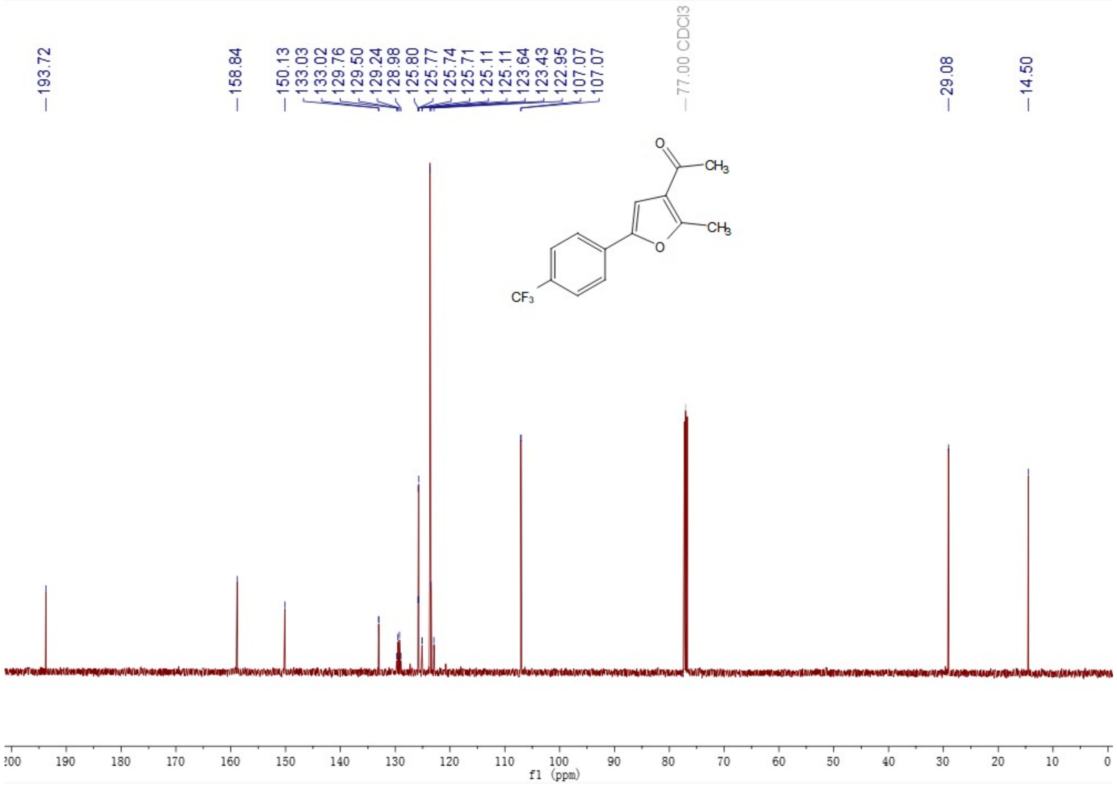
^{13}C NMR (126 MHz, Chloroform-d) of compound **3c.**



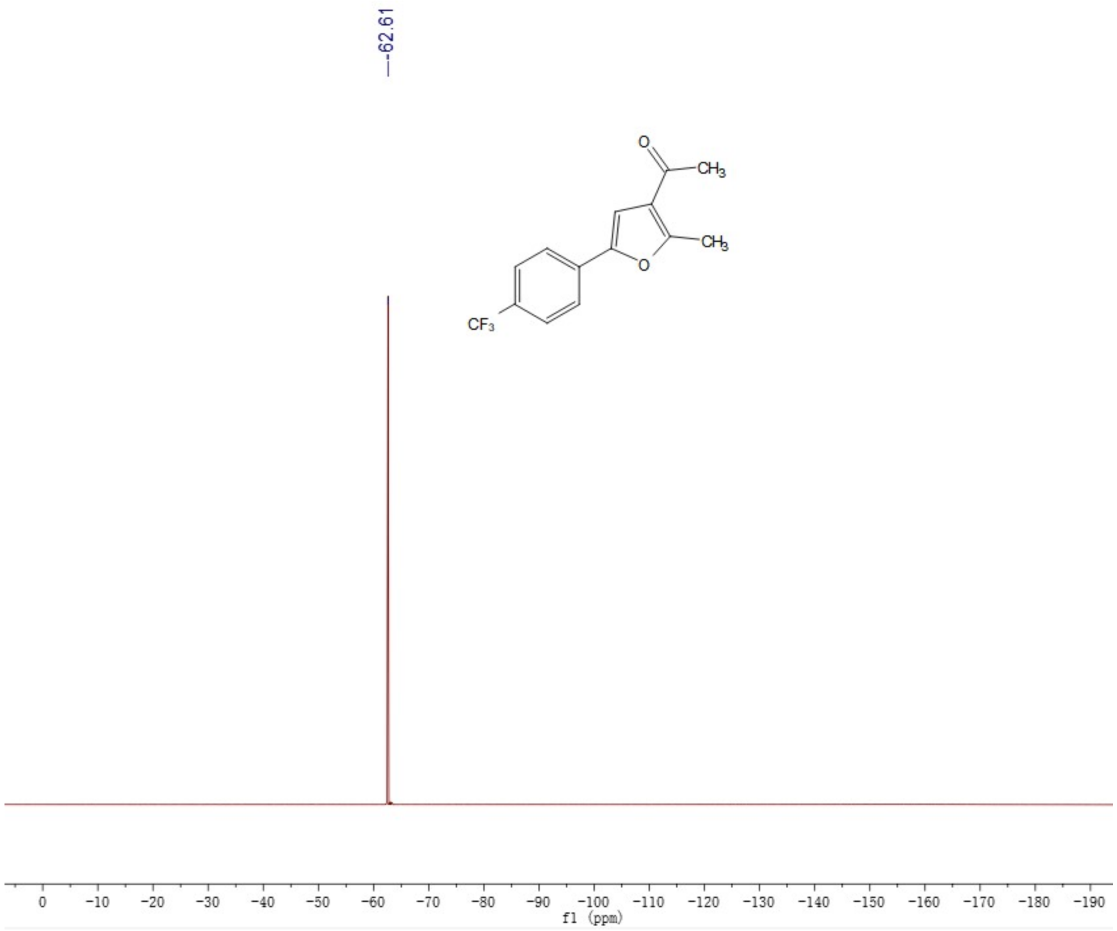
^{1}H NMR (500 MHz, Chloroform-d) of compound **3d.**



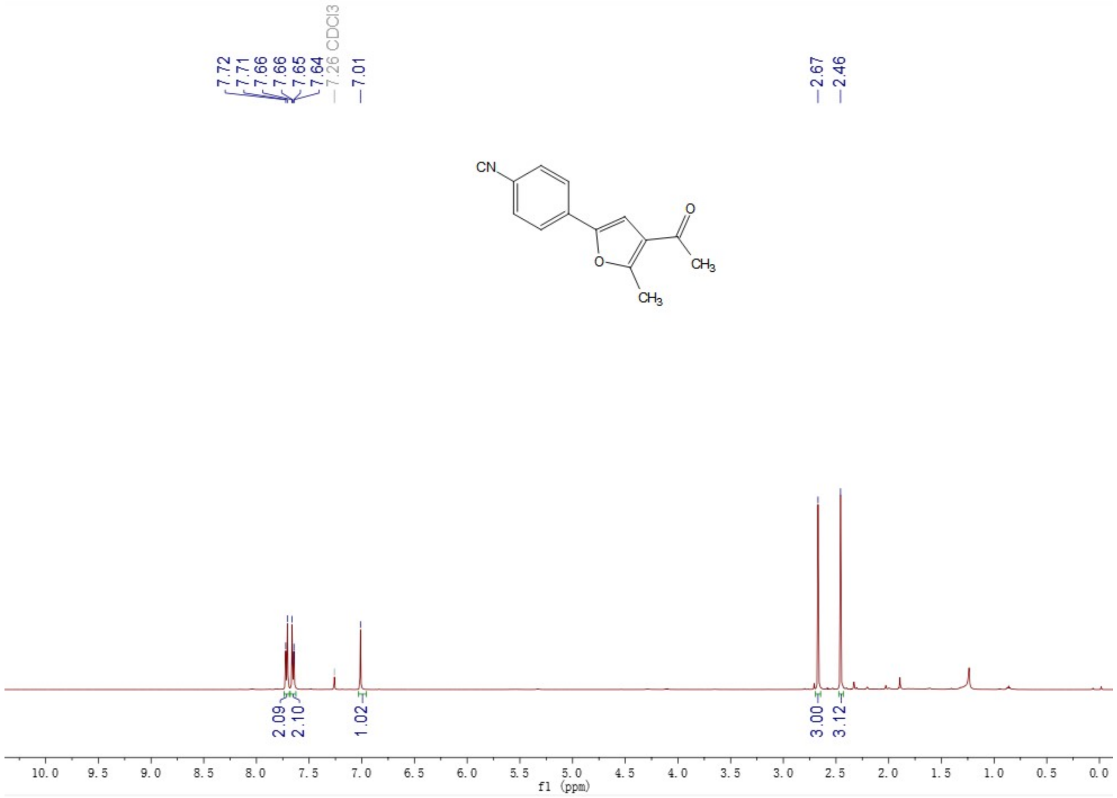
^{13}C NMR (126 MHz, Chloroform-d) of compound **3d.**



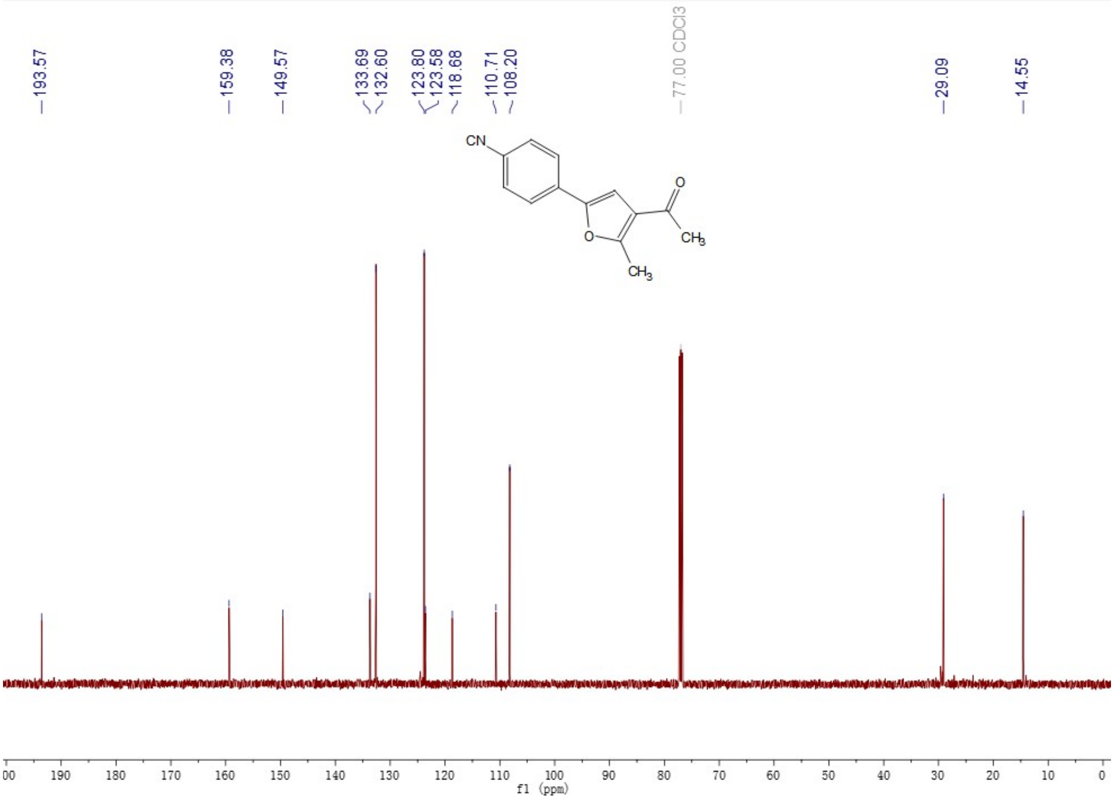
^{19}F NMR (471 MHz, Chloroform-d) of compound **3d.**



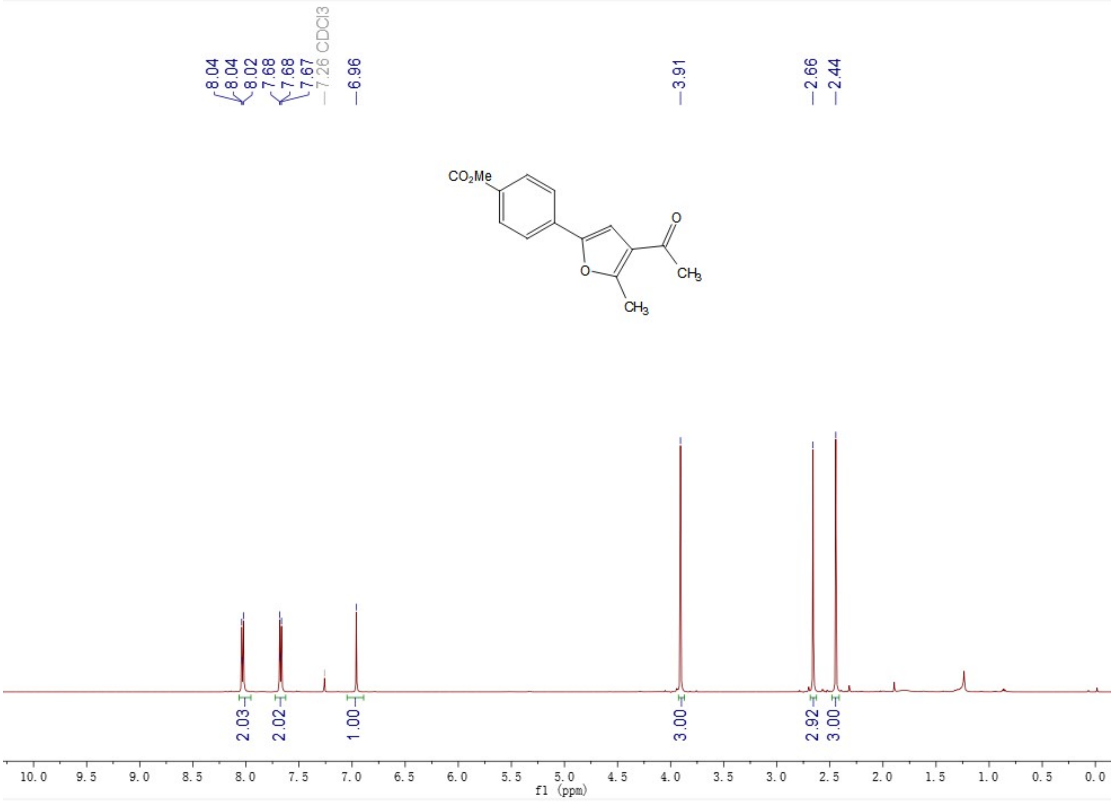
^{1}H NMR (500 MHz, Chloroform-d) of compound **3e.**



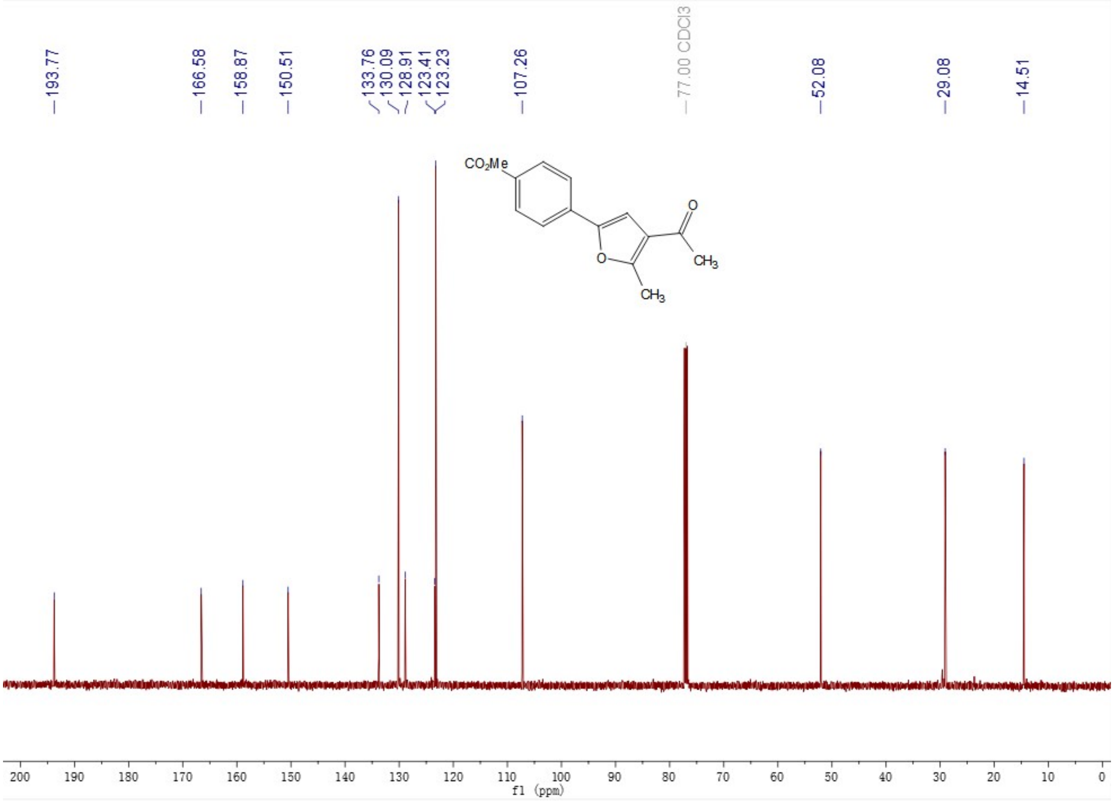
^{13}C NMR (126 MHz, Chloroform-d) of compound **3e.**



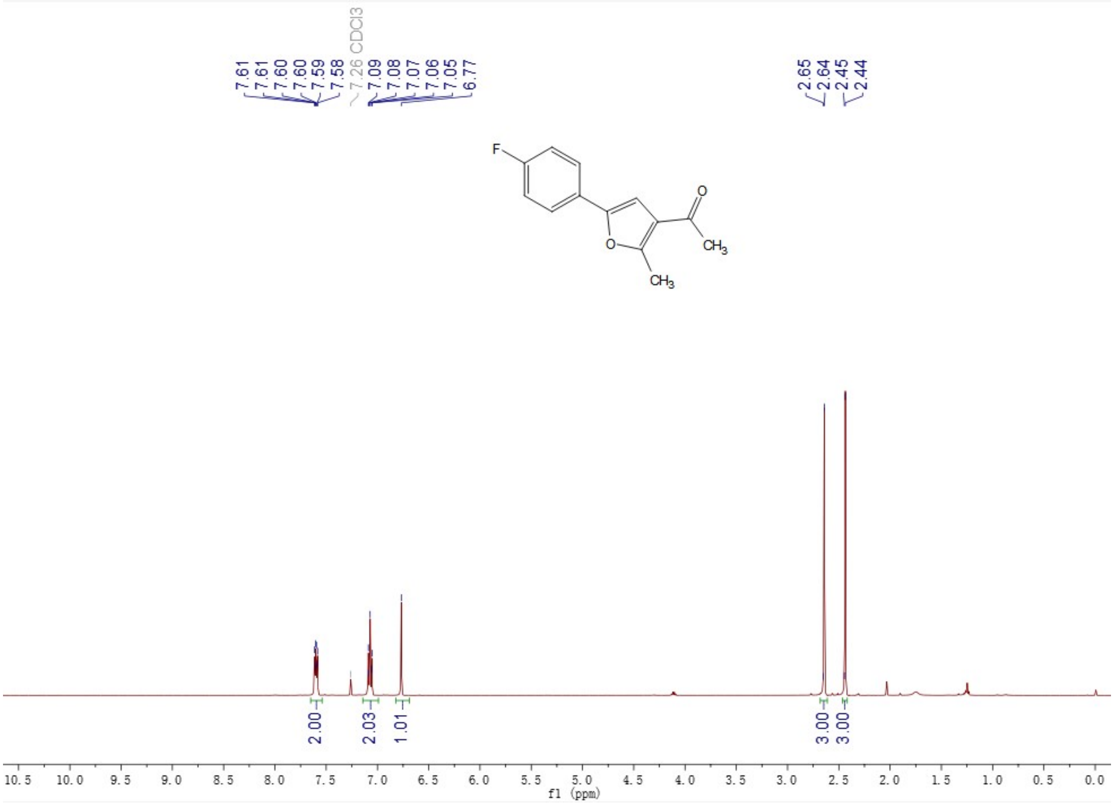
^{1}H NMR (500 MHz, Chloroform-d) of compound **3f.**



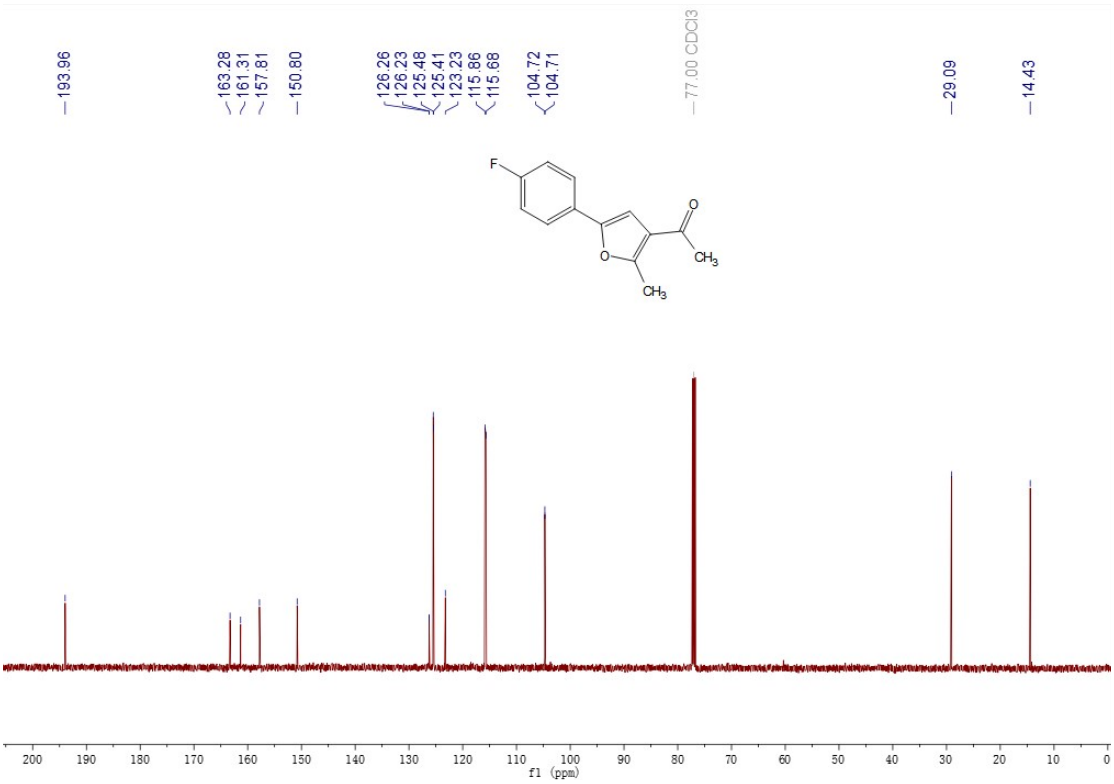
^{13}C NMR (126 MHz, Chloroform-d) of compound **3f.**



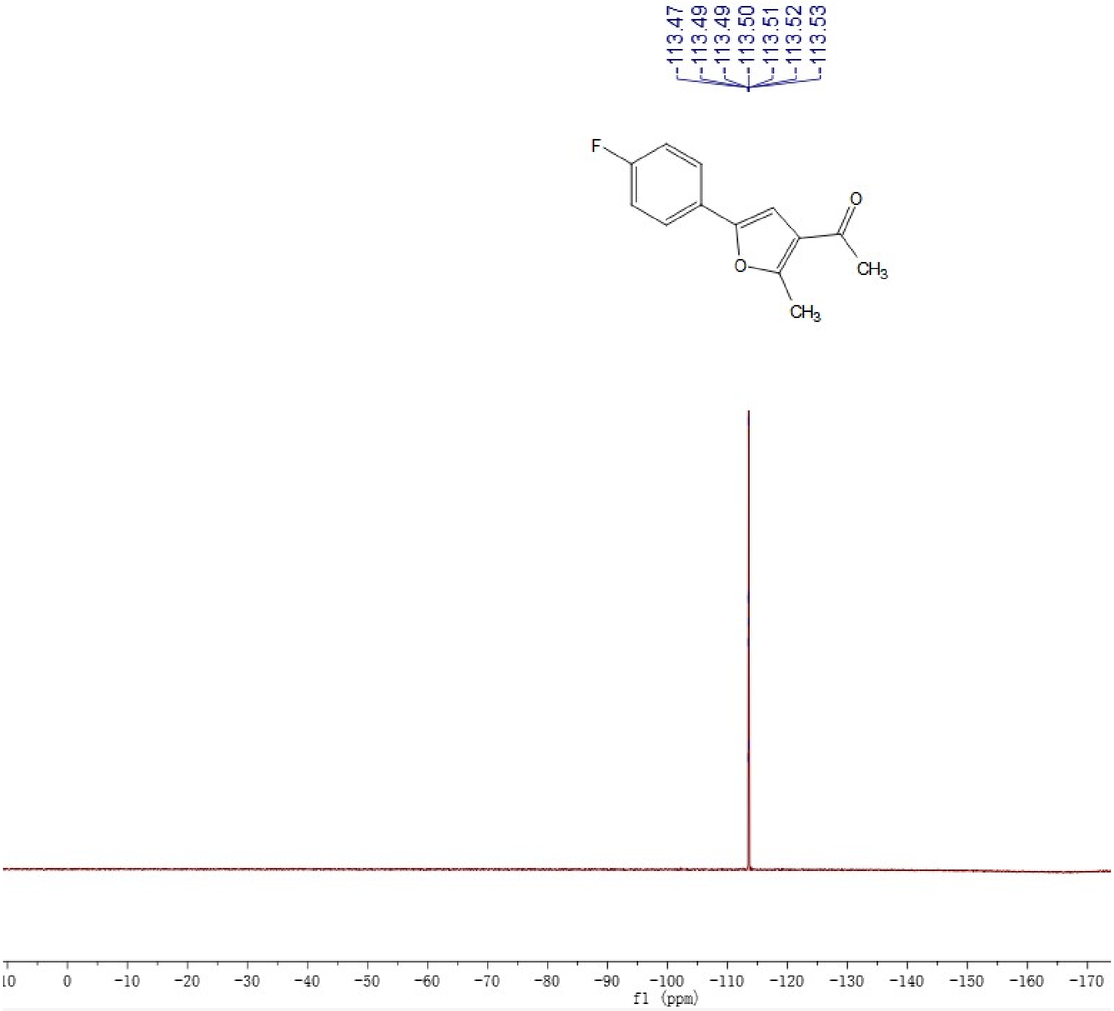
^{1}H NMR (500 MHz, Chloroform-d) of compound **3g.**



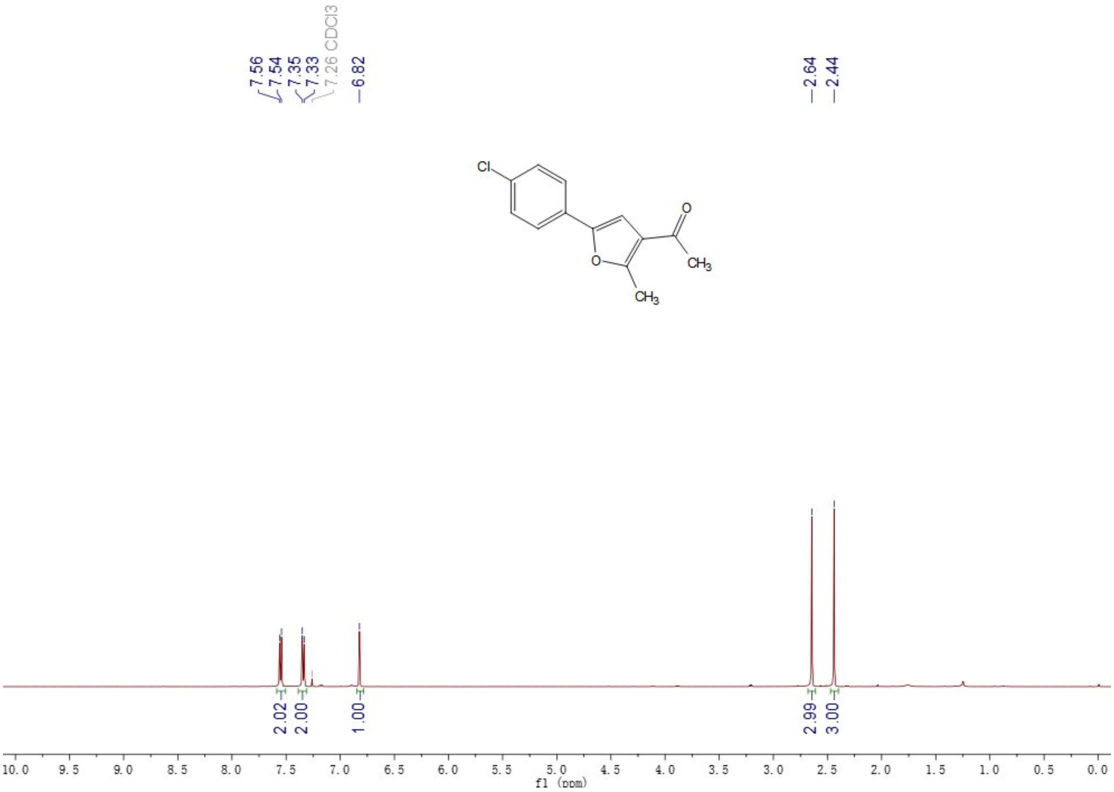
^{13}C NMR (126 MHz, Chloroform-d) of compound **3g.**



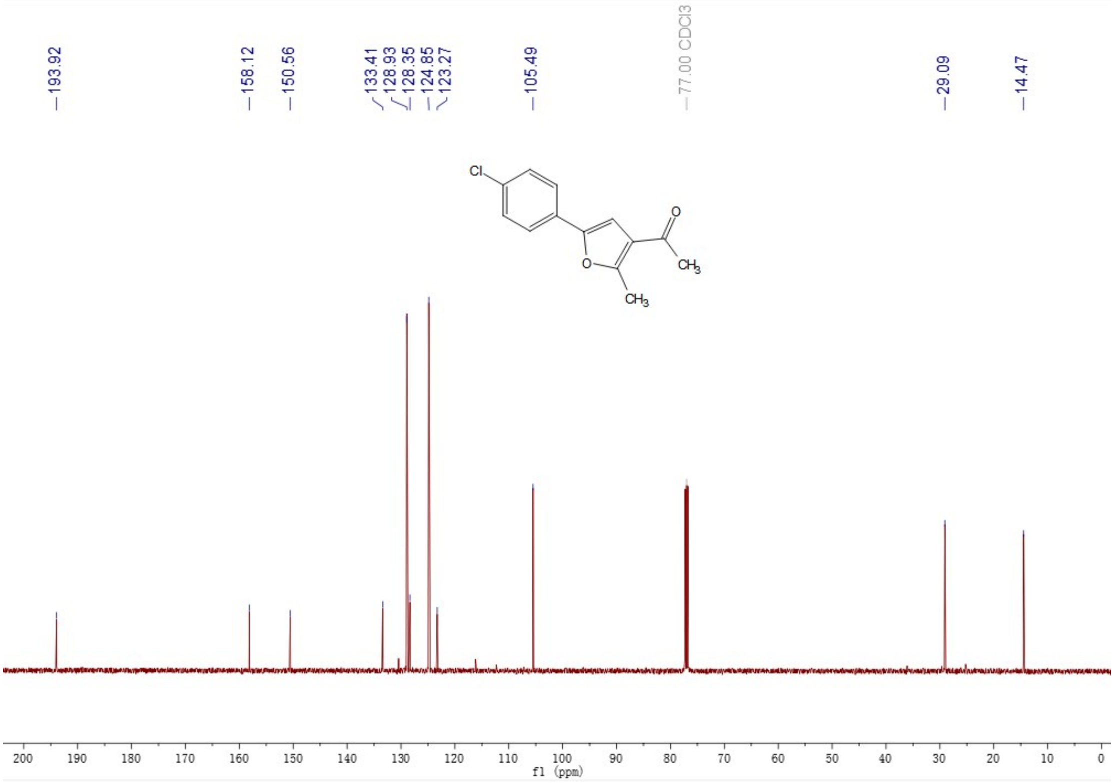
^{19}F NMR (471 MHz, Chloroform-d) of compound **3g.**



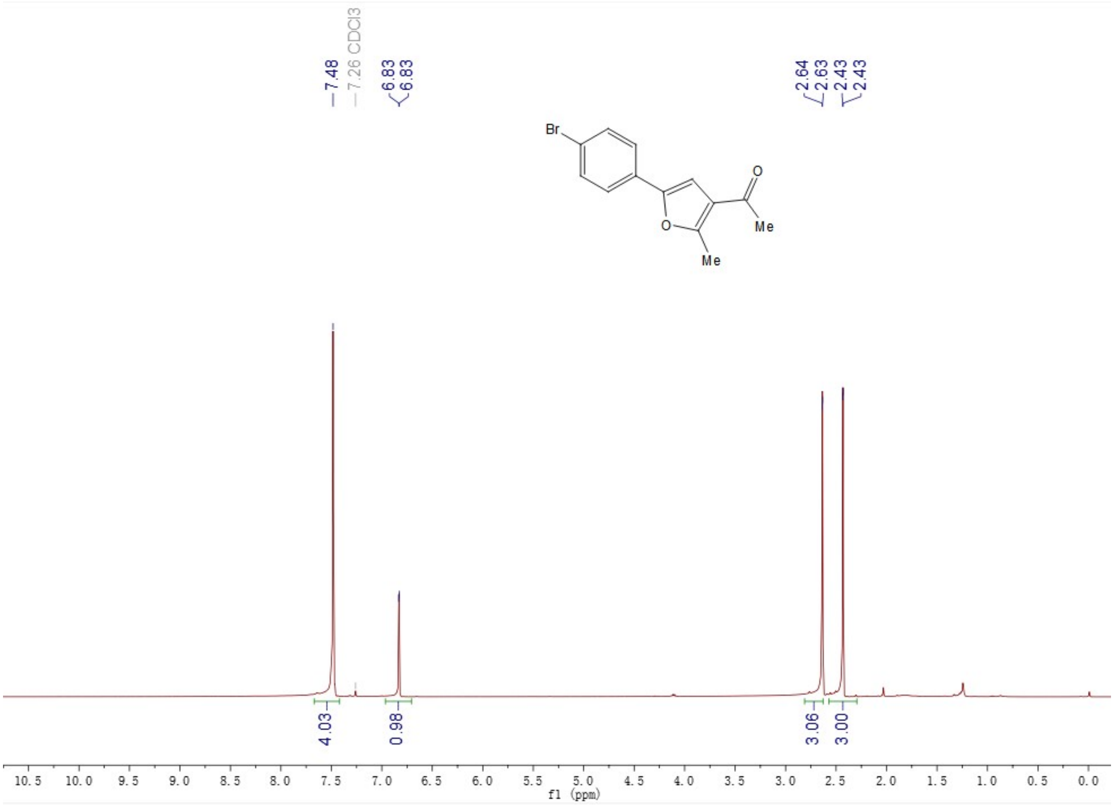
^{1}H NMR (500 MHz, Chloroform-d) of compound **3h.**



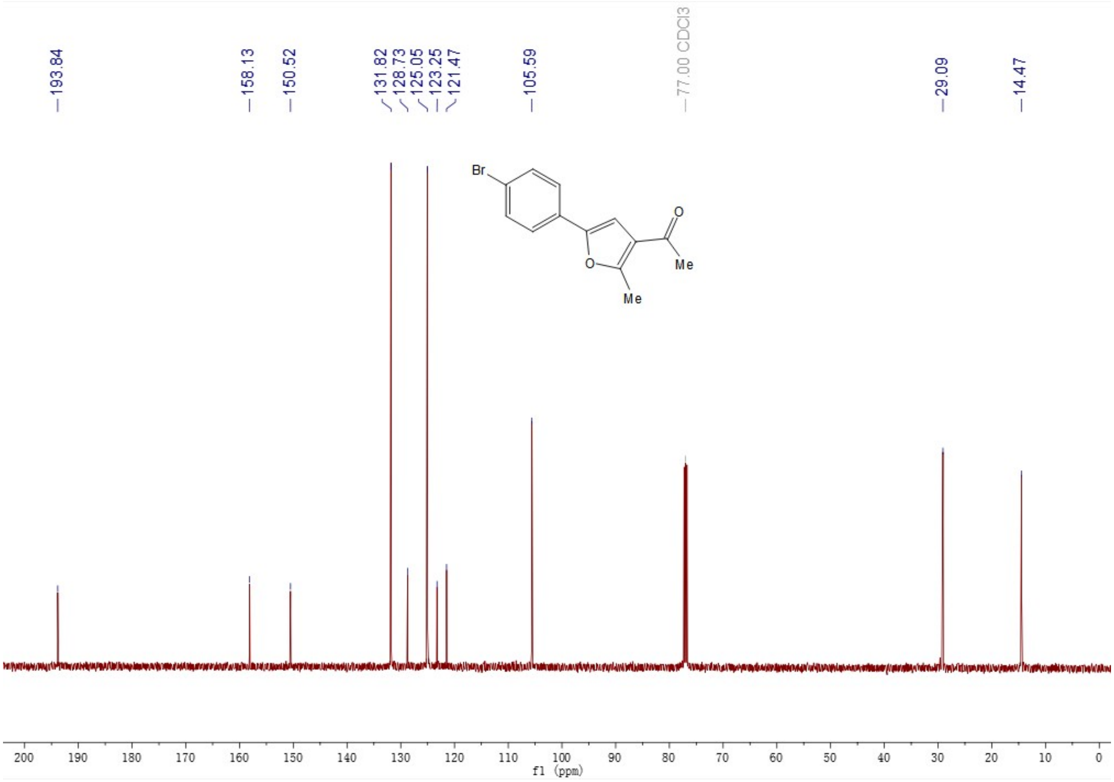
^{13}C NMR (126 MHz, Chloroform-d) of compound **3h.**



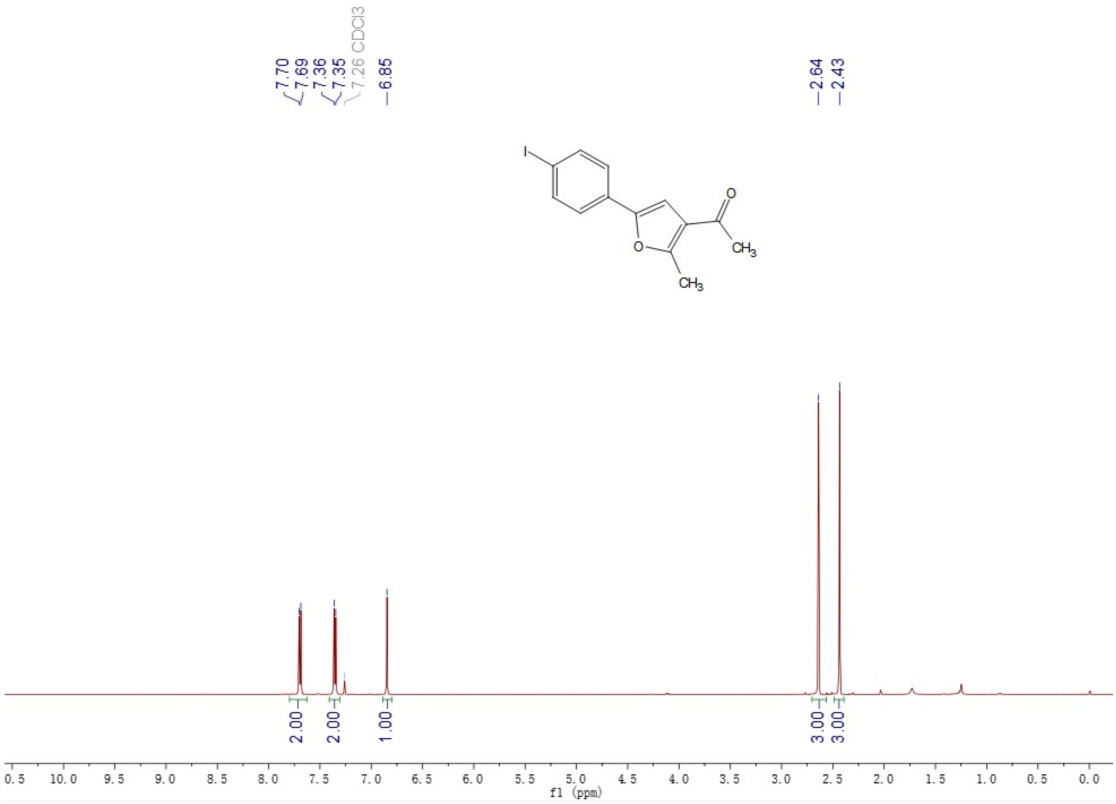
^{1}H NMR (500 MHz, Chloroform-d) of compound **3i.**



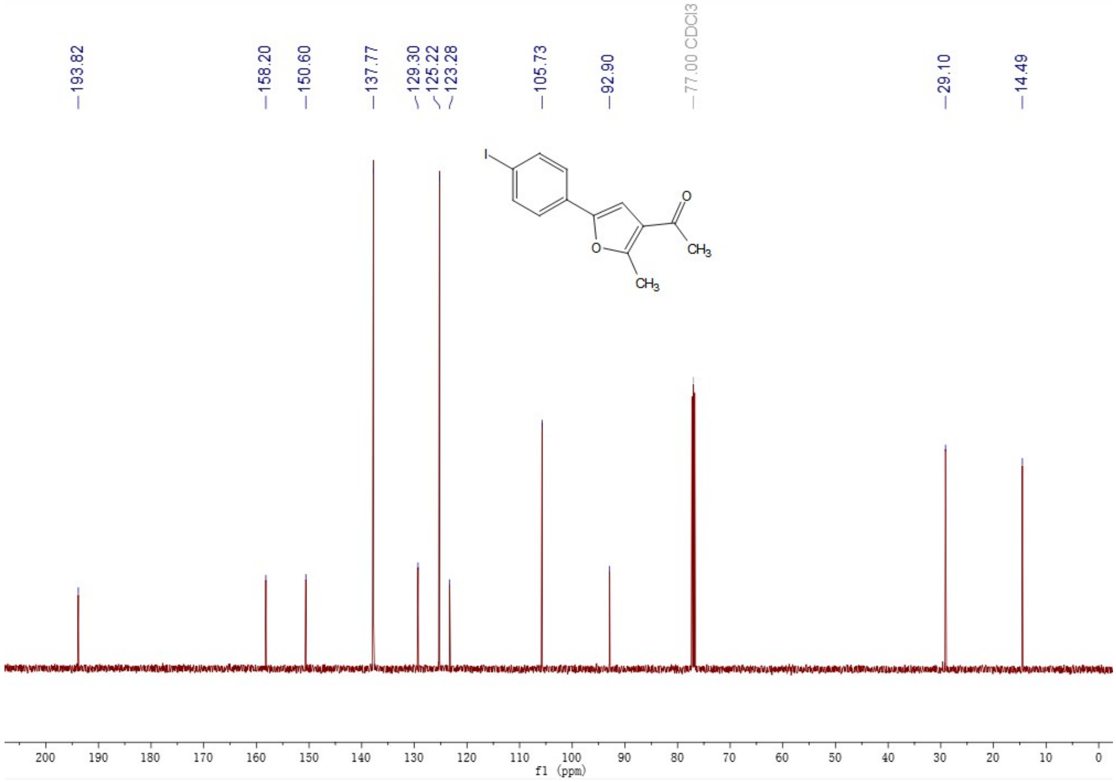
^{13}C NMR (126 MHz, Chloroform-d) of compound **3i.**



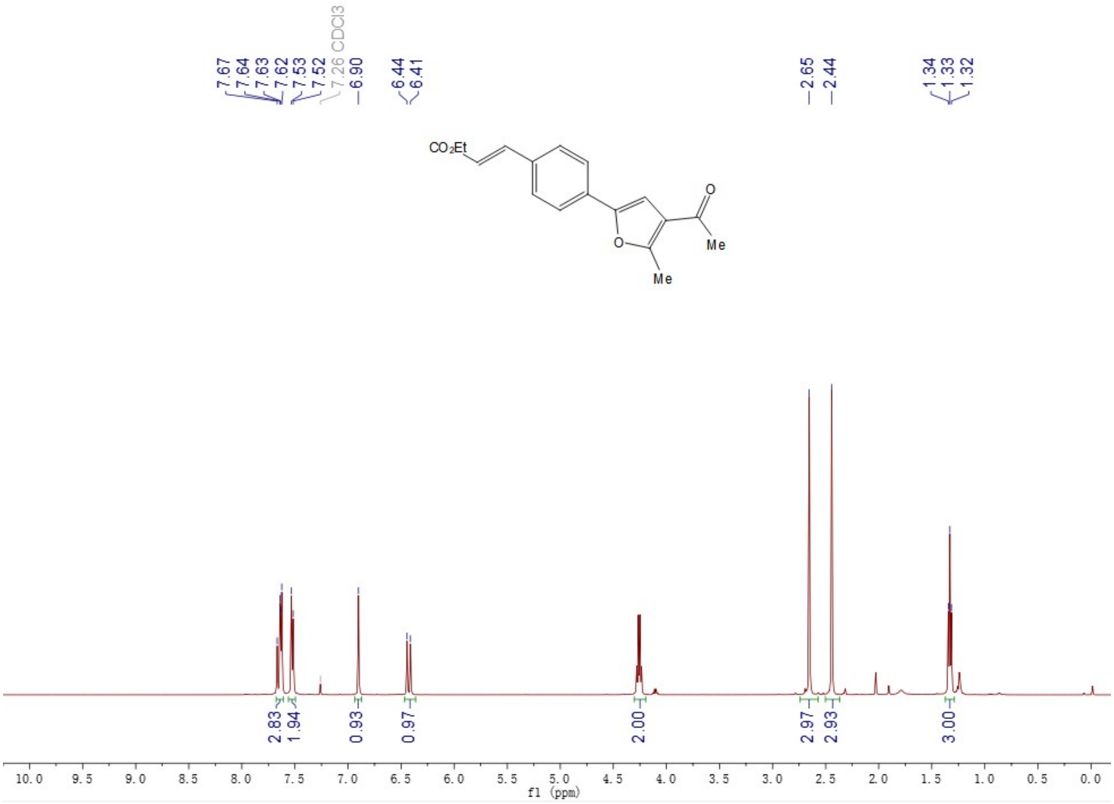
^{1}H NMR (500 MHz, Chloroform-d) of compound **3j.**



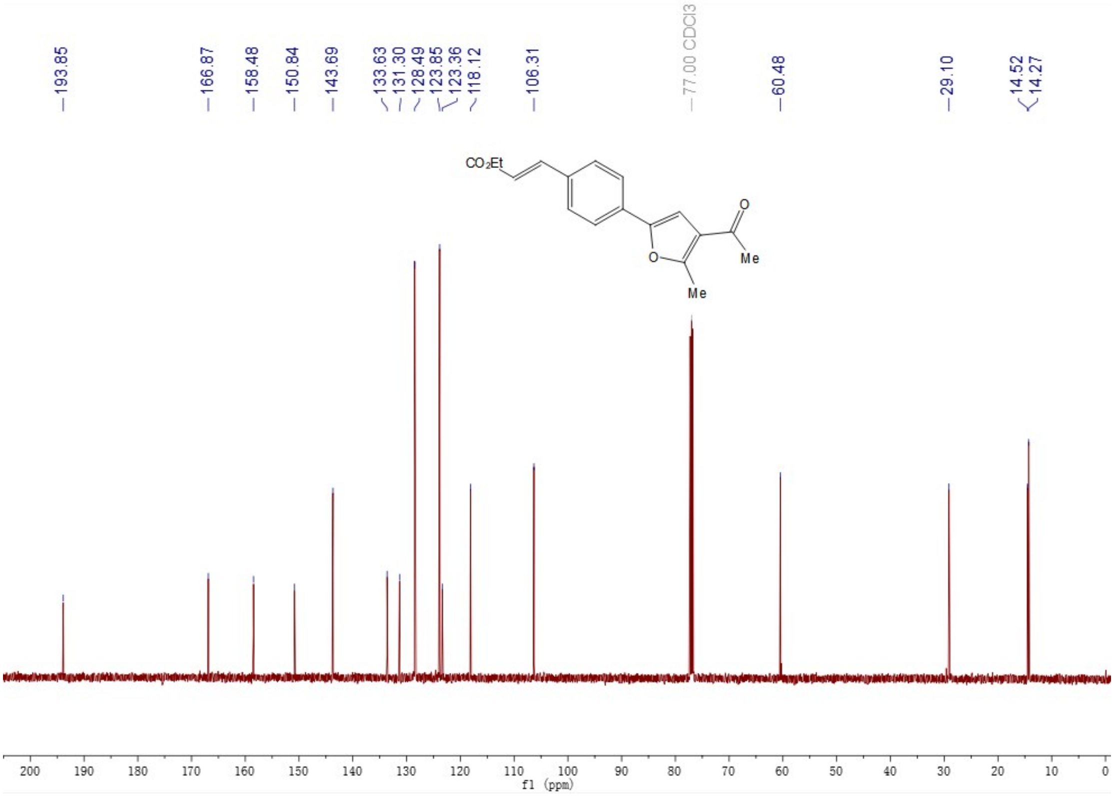
^{13}C NMR (126 MHz, Chloroform-d) of compound **3j.**



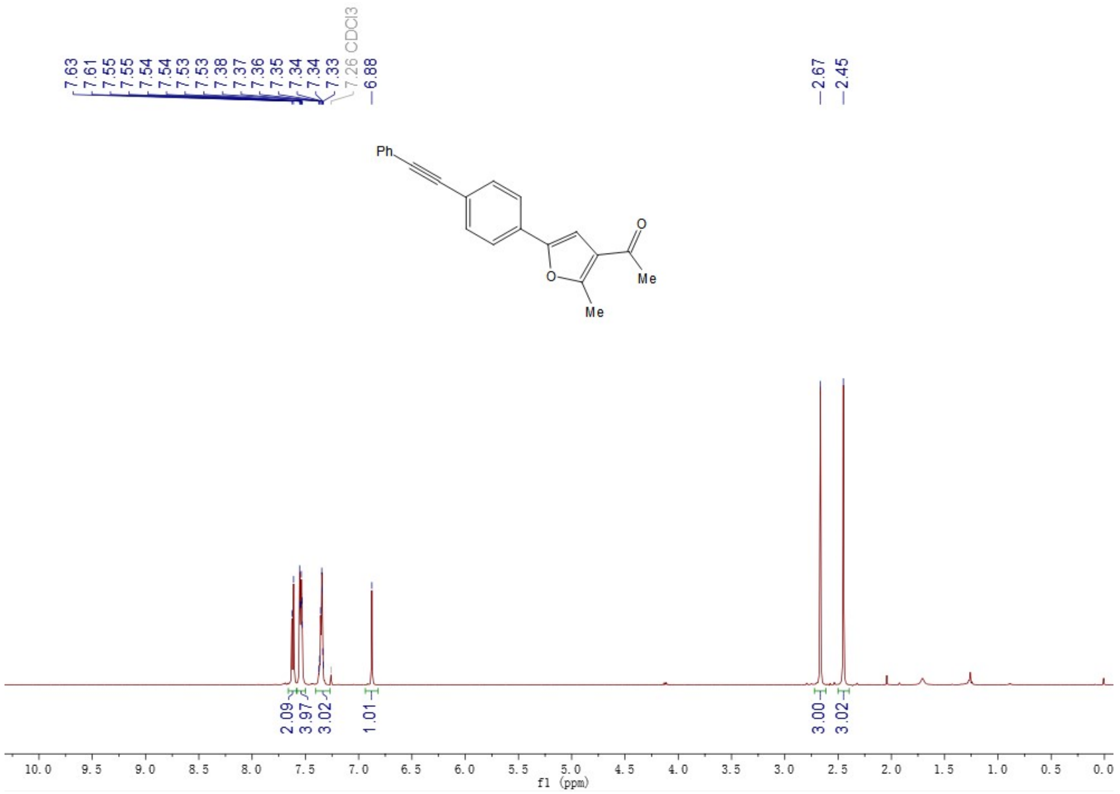
^{1}H NMR (500 MHz, Chloroform-d) of compound **3k.**



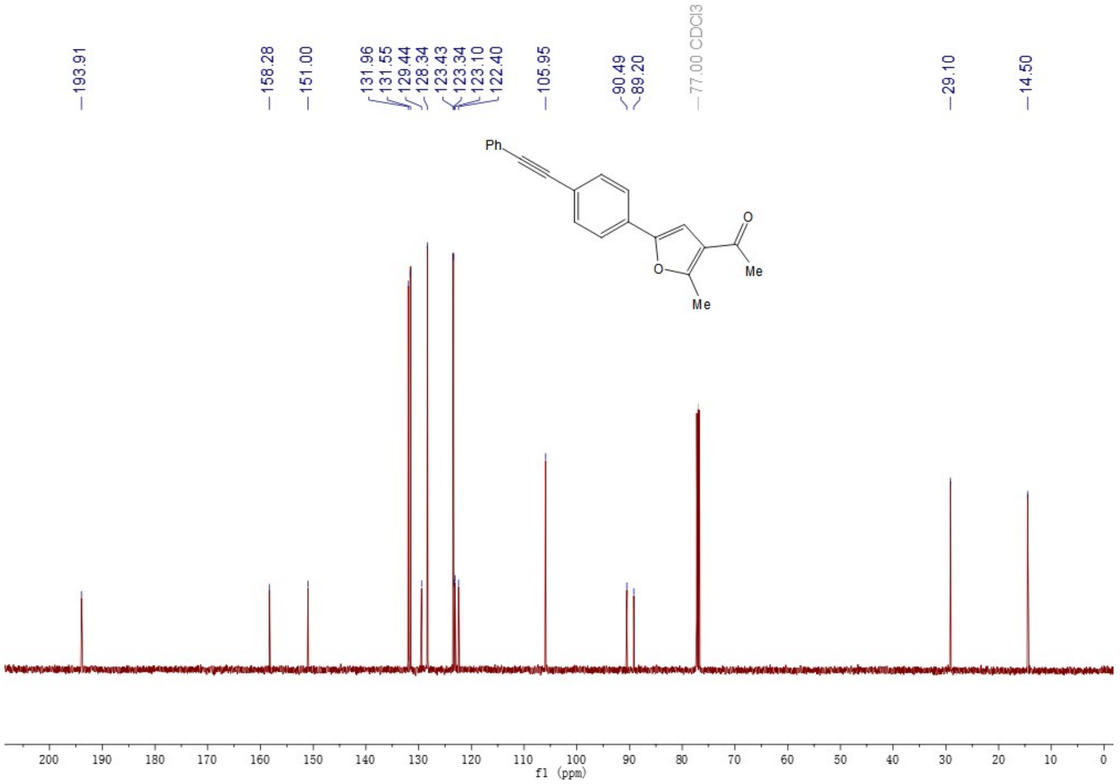
^{13}C NMR (126 MHz, Chloroform-d) of compound **3k.**



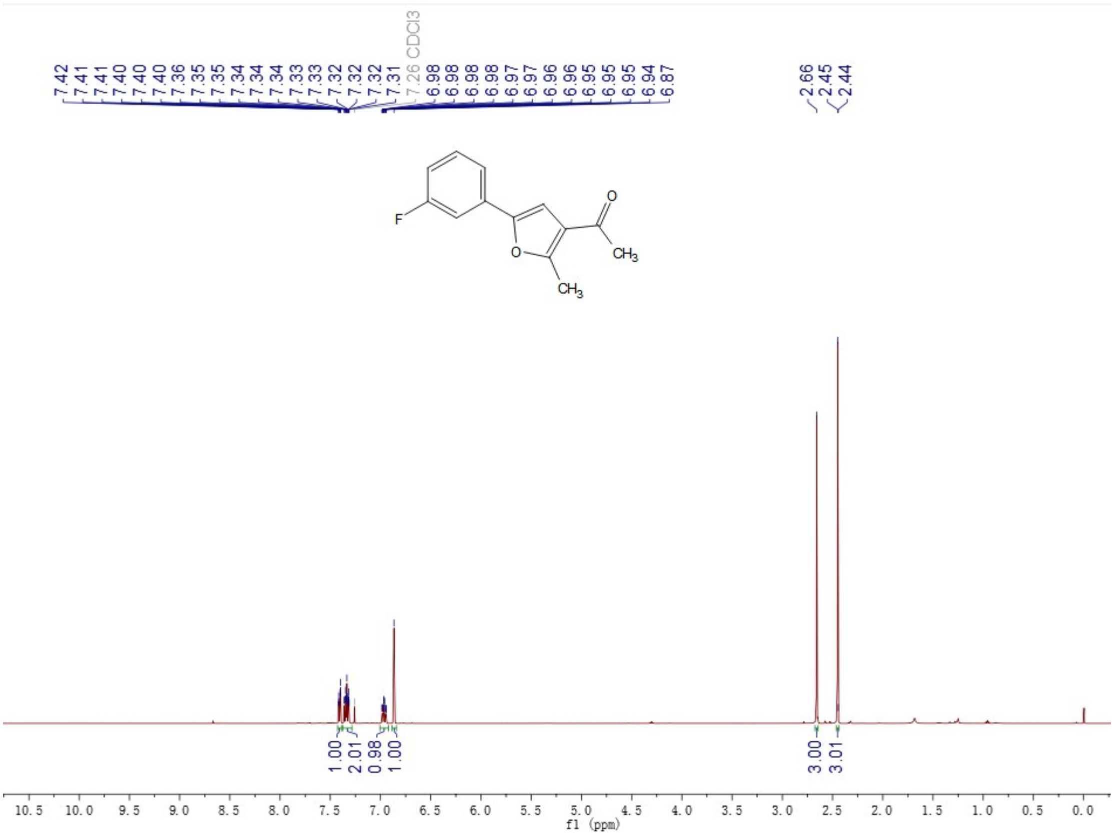
^{1}H NMR (500 MHz, Chloroform-d) of compound **3l.**



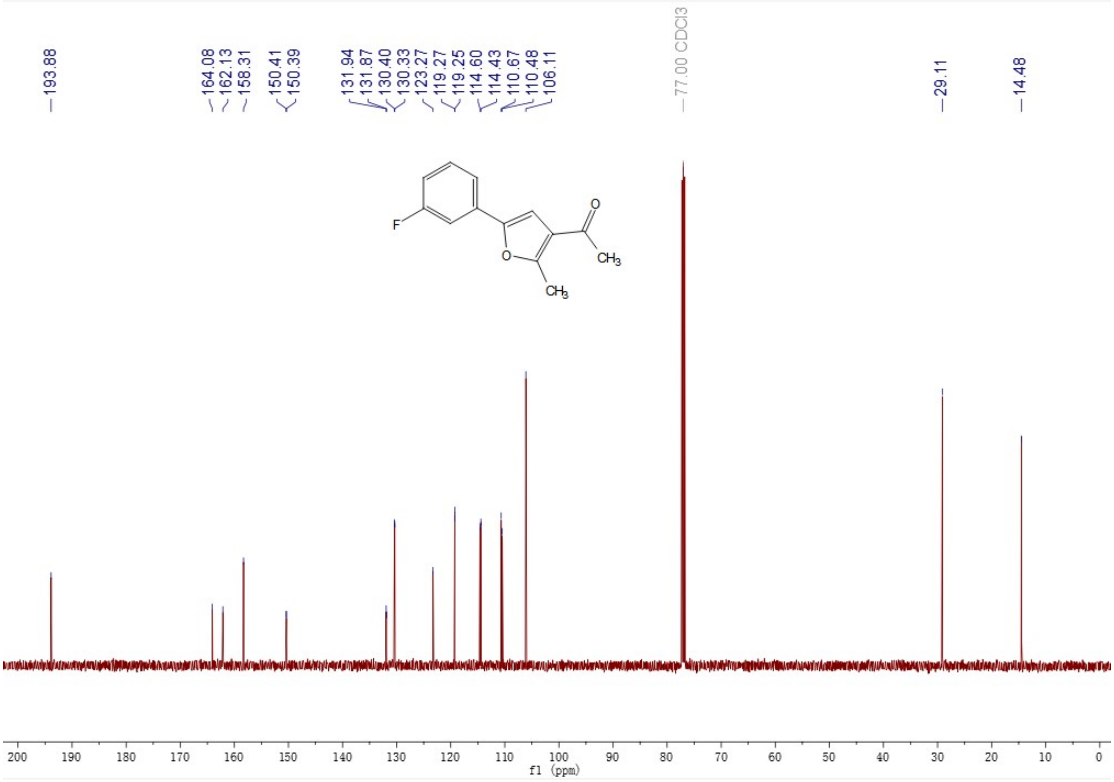
^{13}C NMR (126 MHz, Chloroform-d) of compound **3l.**



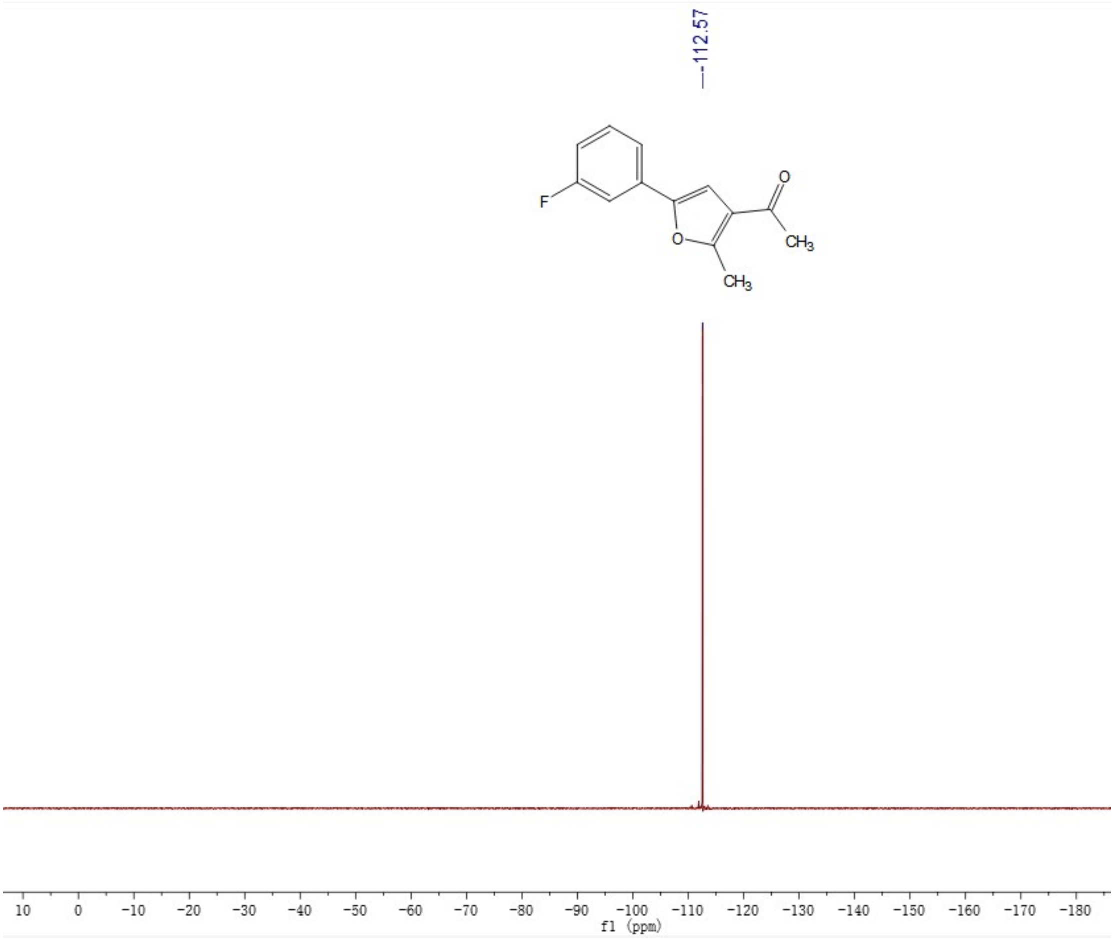
^{1}H NMR (500 MHz, Chloroform-d) of compound **3m.**



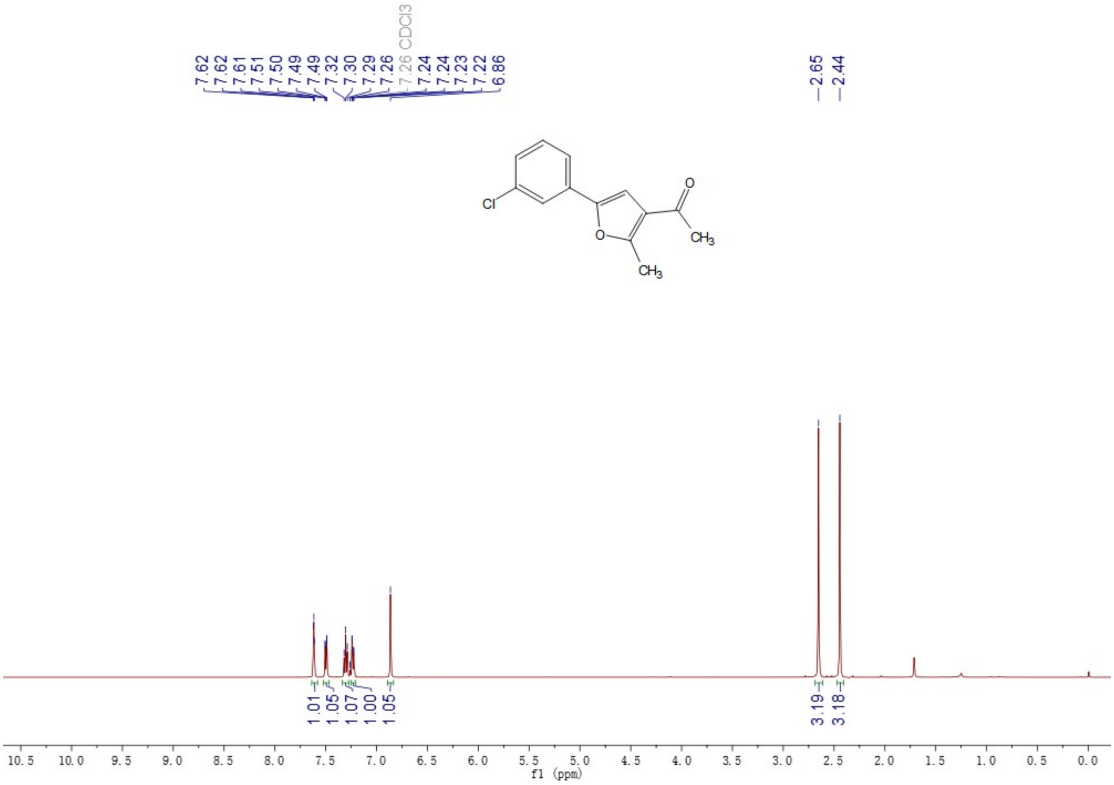
^{13}C NMR (126 MHz, Chloroform-d) of compound **3m.**



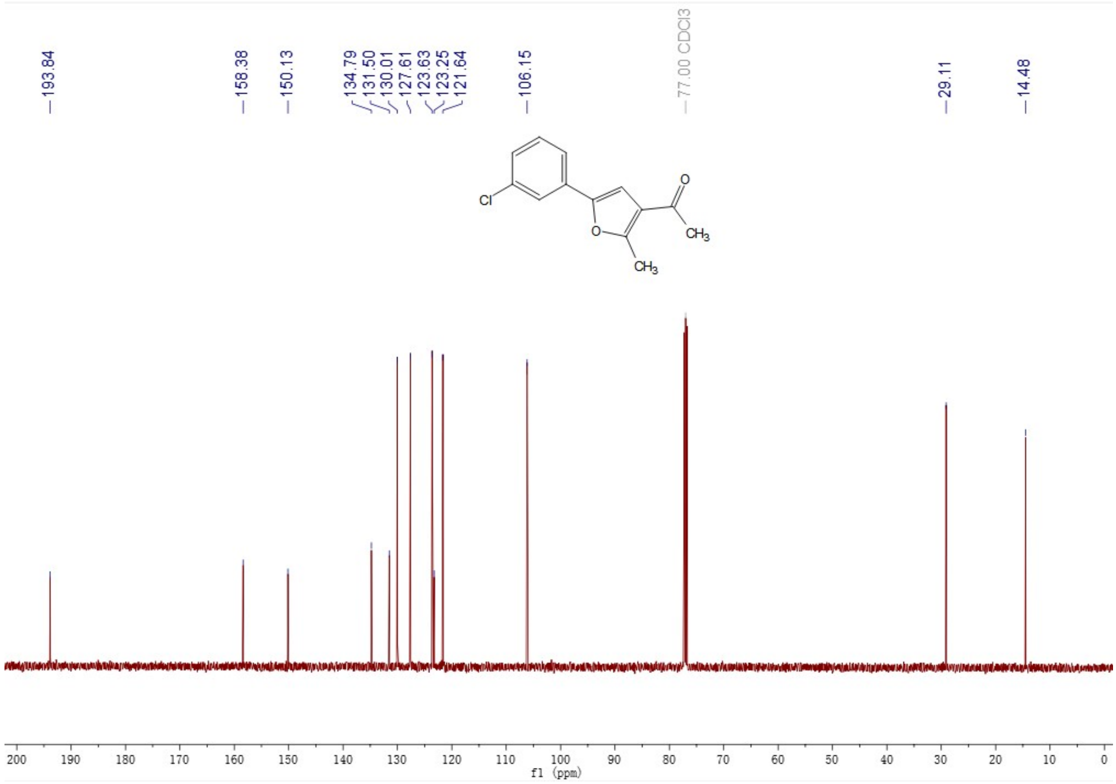
^{19}F NMR (471 MHz, Chloroform-d) of compound **3m.**



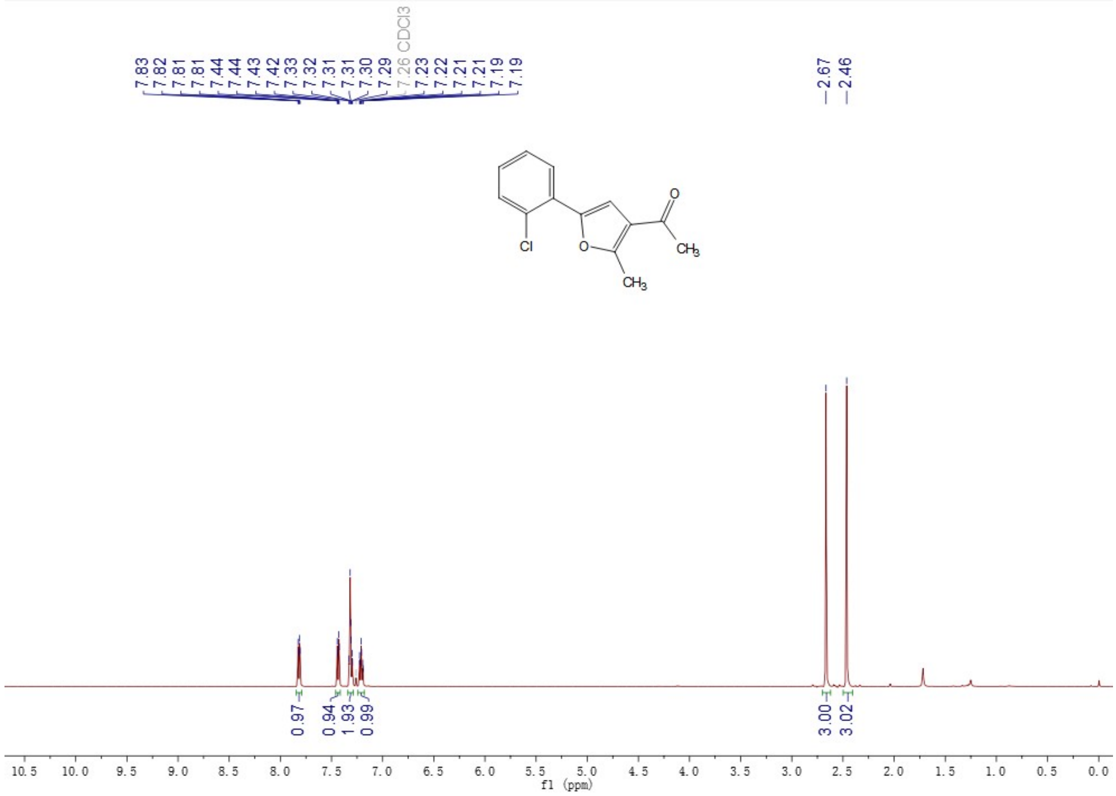
^{1}H NMR (500 MHz, Chloroform-d) of compound **3n.**



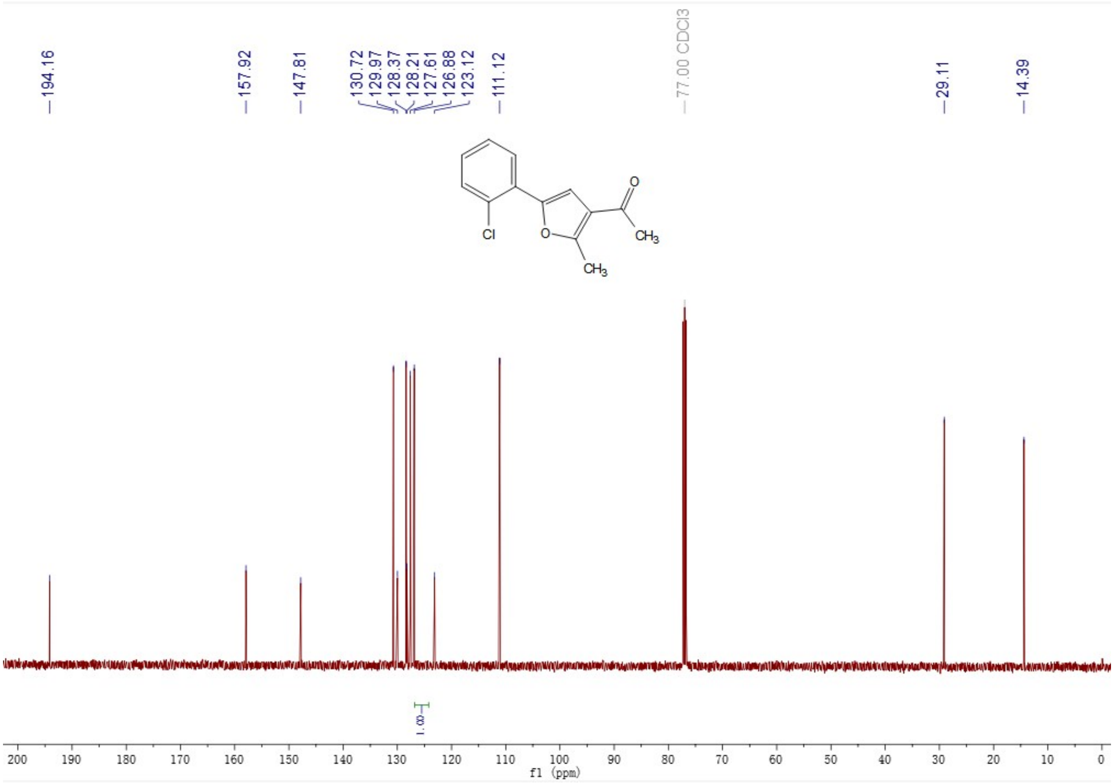
^{13}C NMR (126 MHz, Chloroform-d) of compound **3n.**



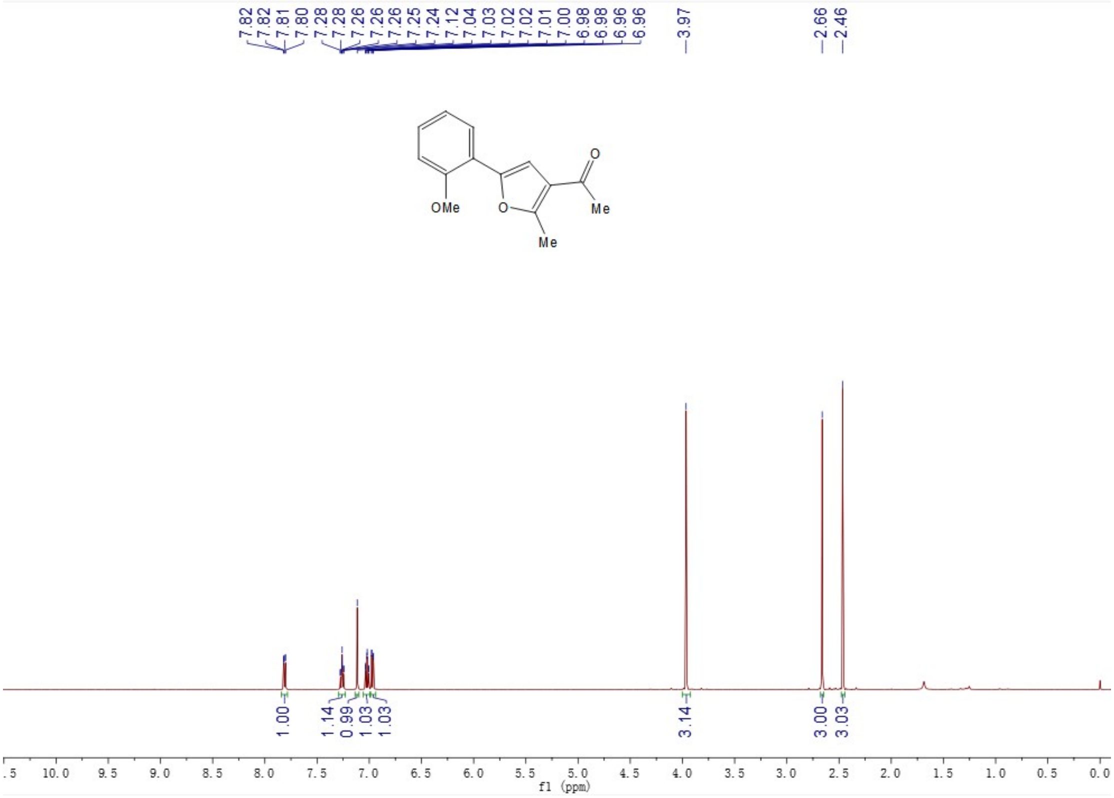
^{1}H NMR (500 MHz, Chloroform-d) of compound **3o.**



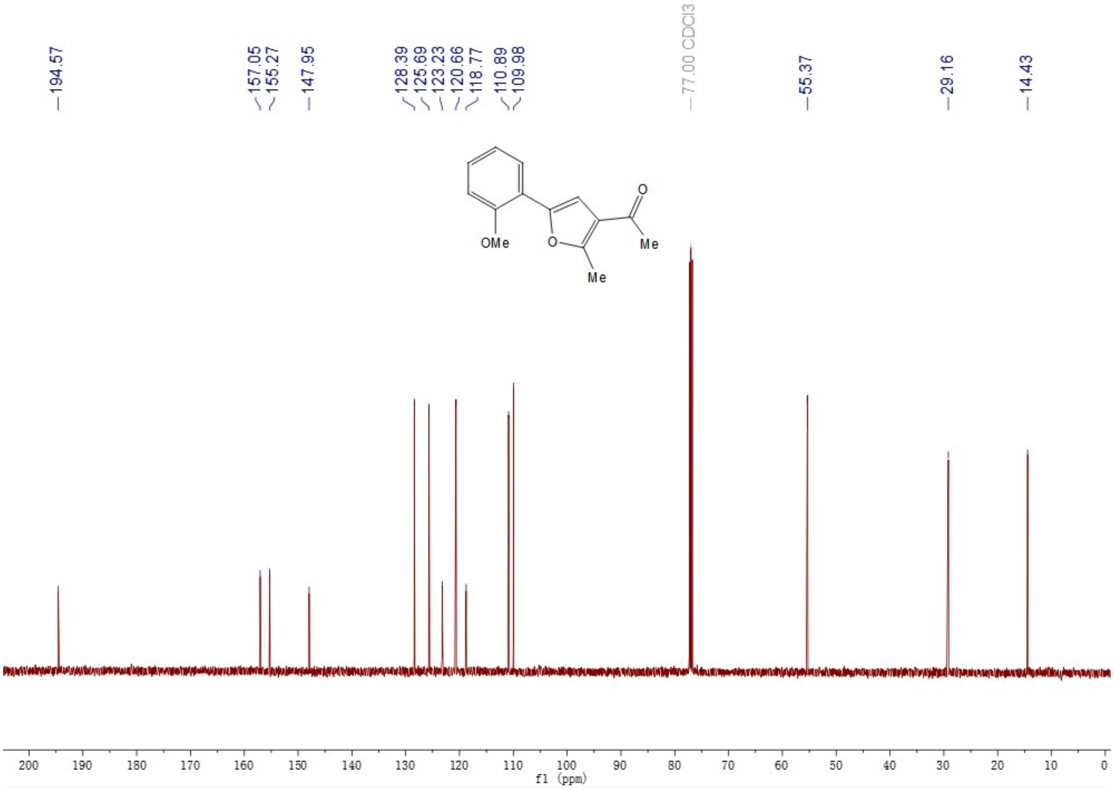
^{13}C NMR (126 MHz, Chloroform-d) of compound **3o.**



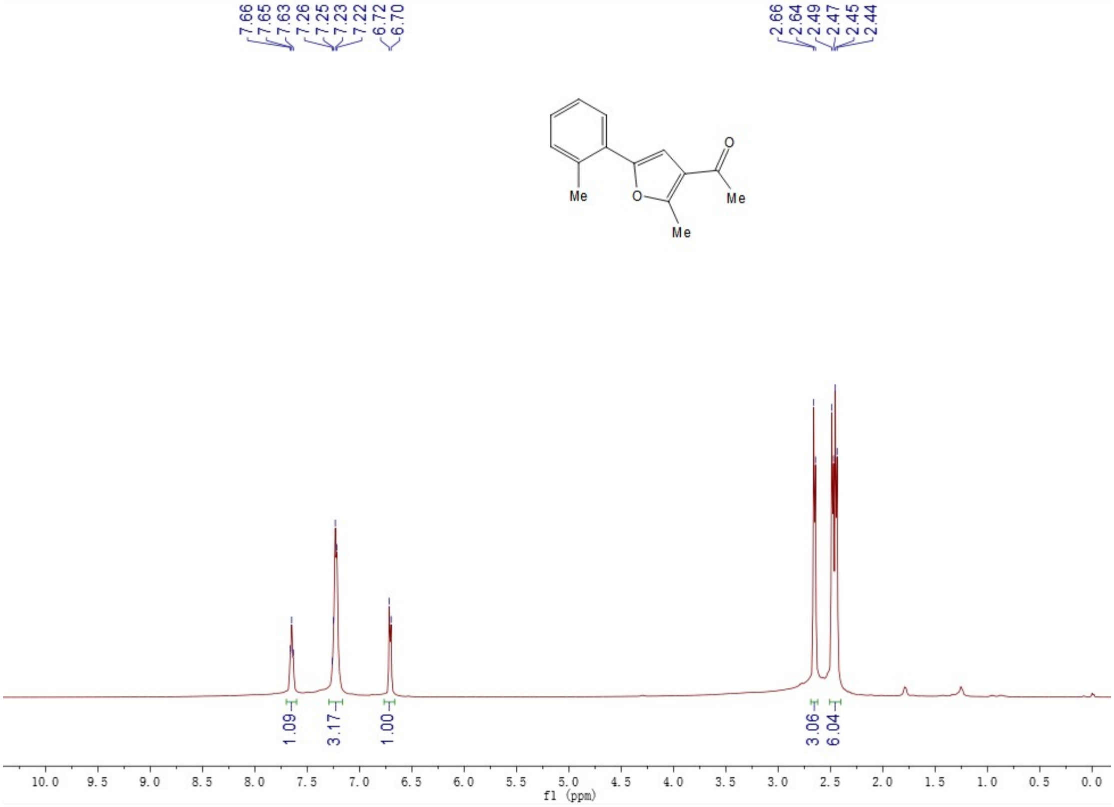
^{1}H NMR (500 MHz, Chloroform-d) of compound **3p.**



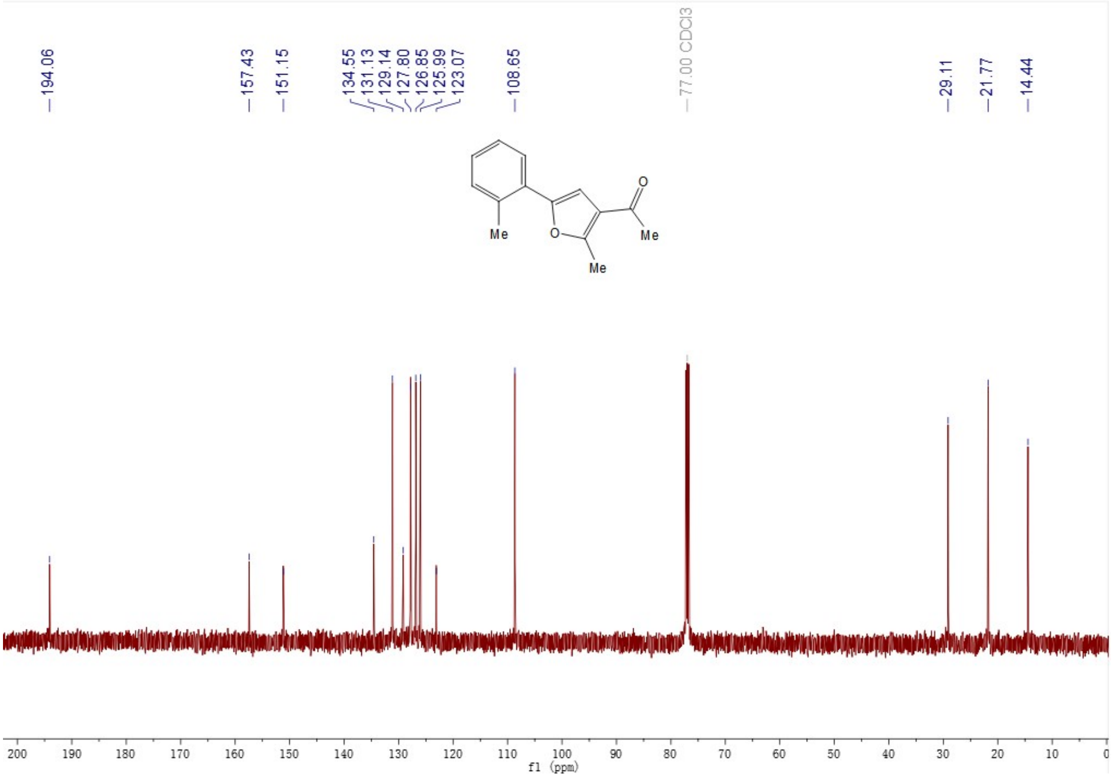
^{13}C NMR (126 MHz, Chloroform-d) of compound **3p.**



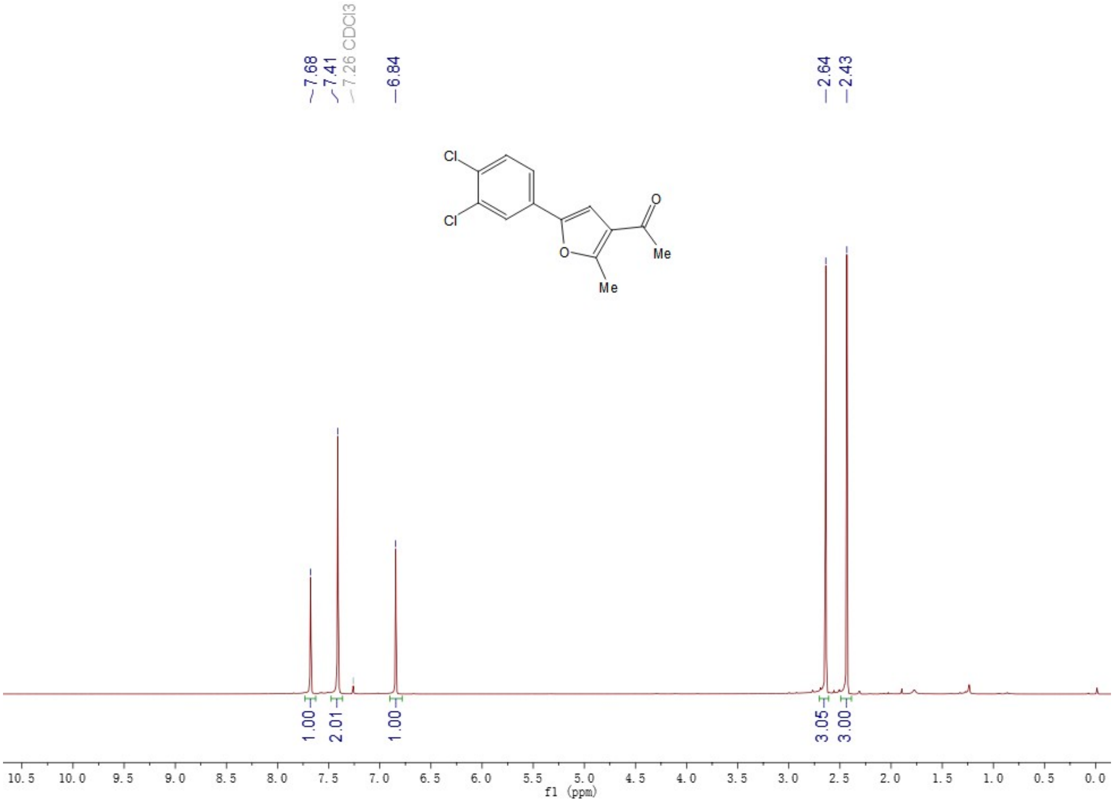
^{1}H NMR (500 MHz, Chloroform-d) of compound **3q.**



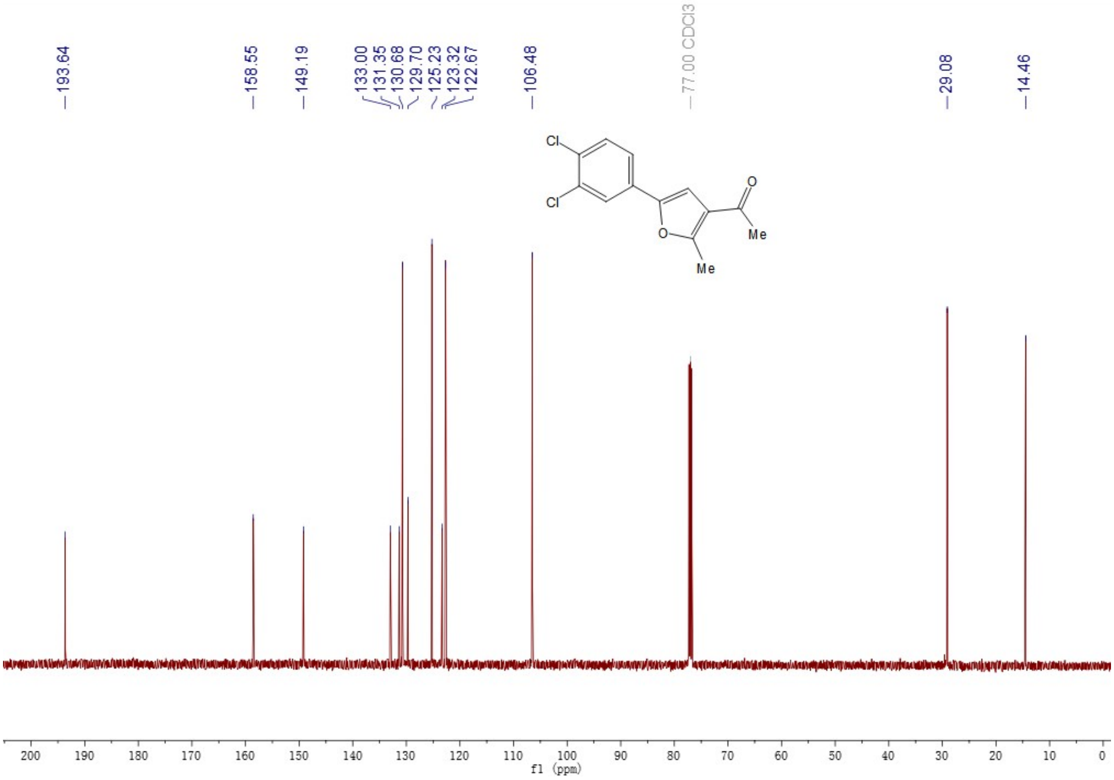
^{13}C NMR (126 MHz, Chloroform-d) of compound **3q.**



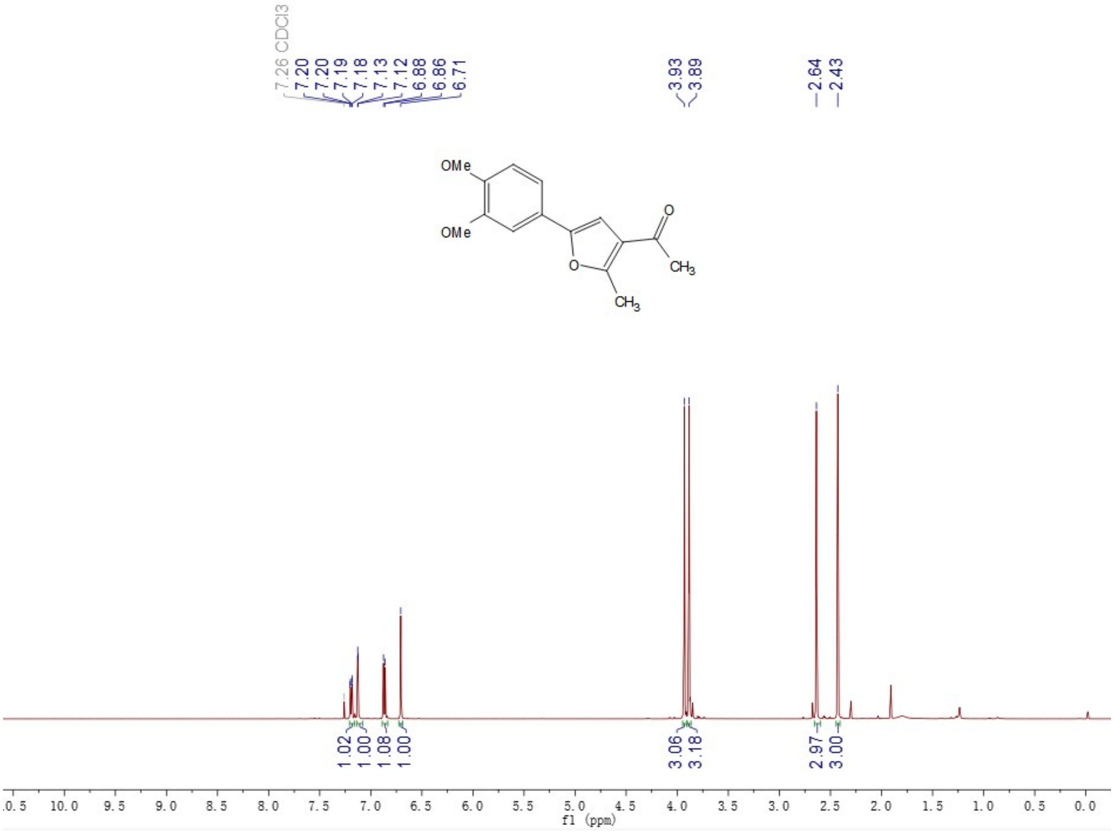
^{1}H NMR (400 MHz, Chloroform-d) of compound **3r.**



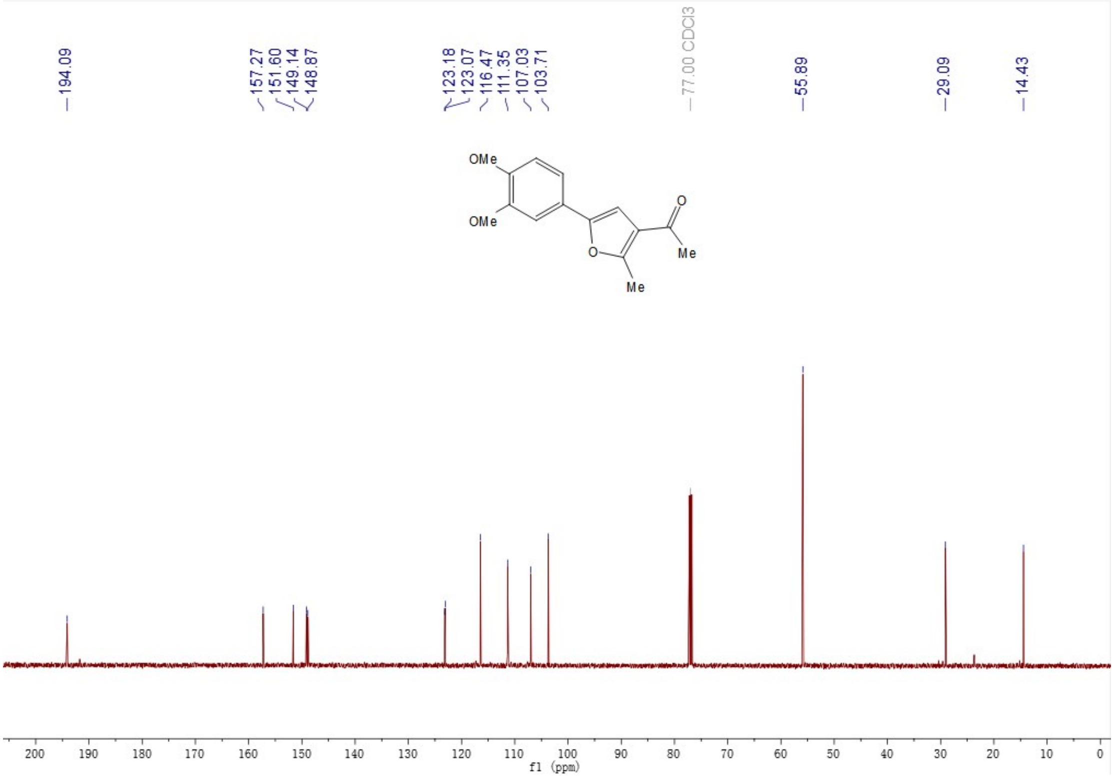
^{13}C NMR (126 MHz, Chloroform-d) of compound **3r.**



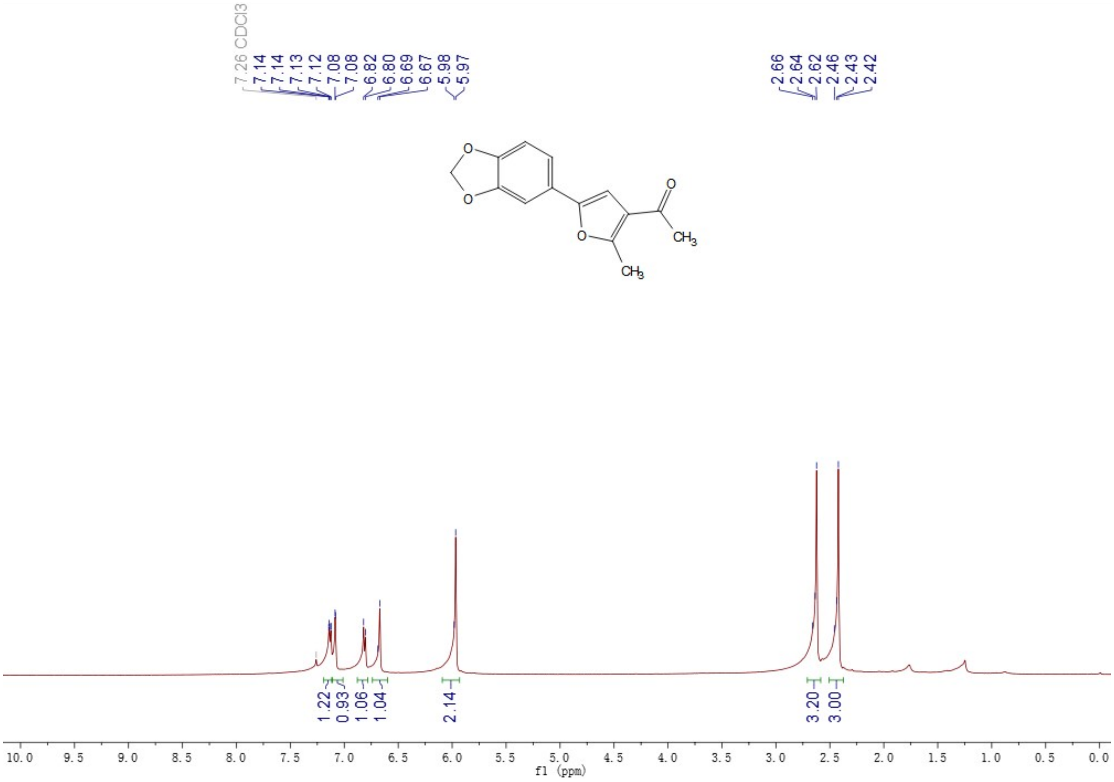
^{1}H NMR (500 MHz, Chloroform-d) of compound **3s.**



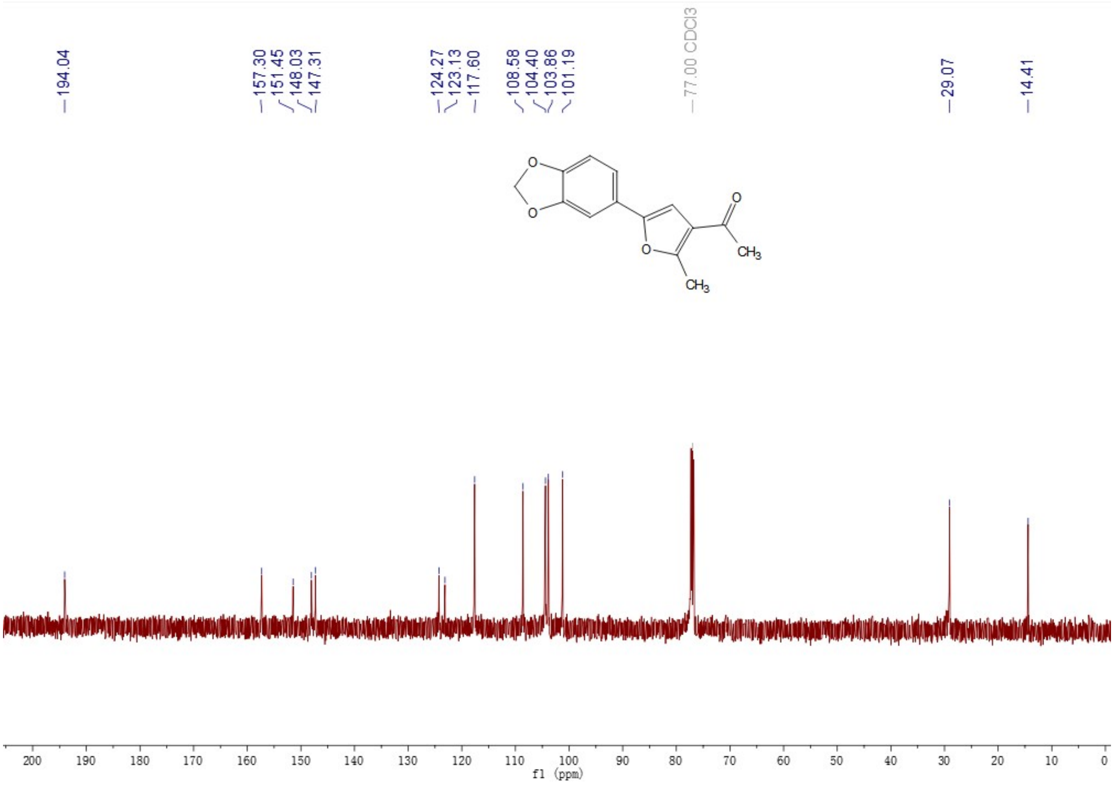
^{13}C NMR (126 MHz, Chloroform-d) of compound **3s.**



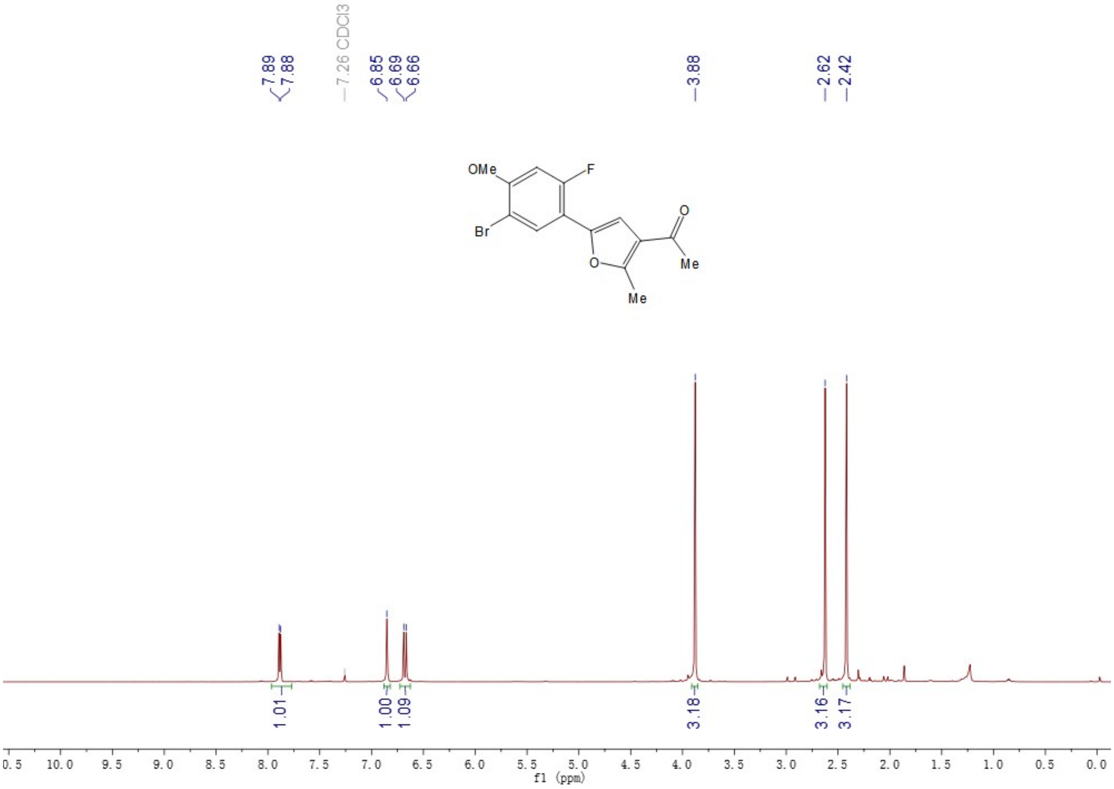
^{1}H NMR (500 MHz, Chloroform-d) of compound **3t.**



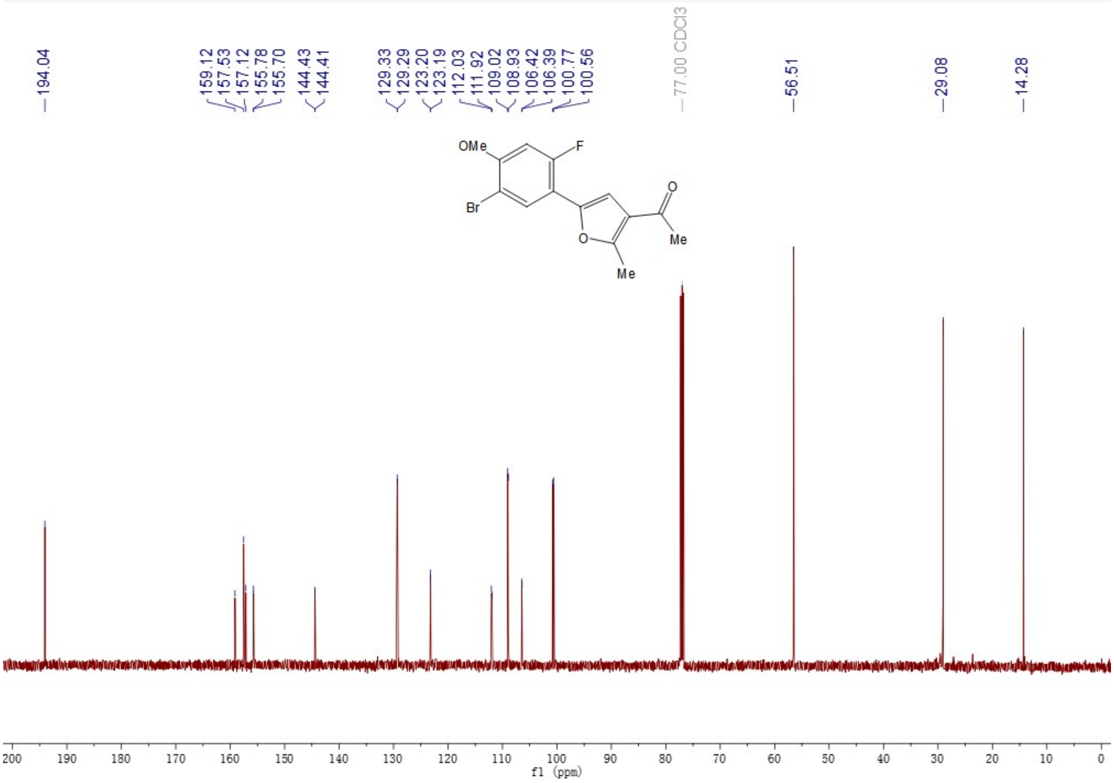
^{13}C NMR (126 MHz, Chloroform-d) of compound **3t.**



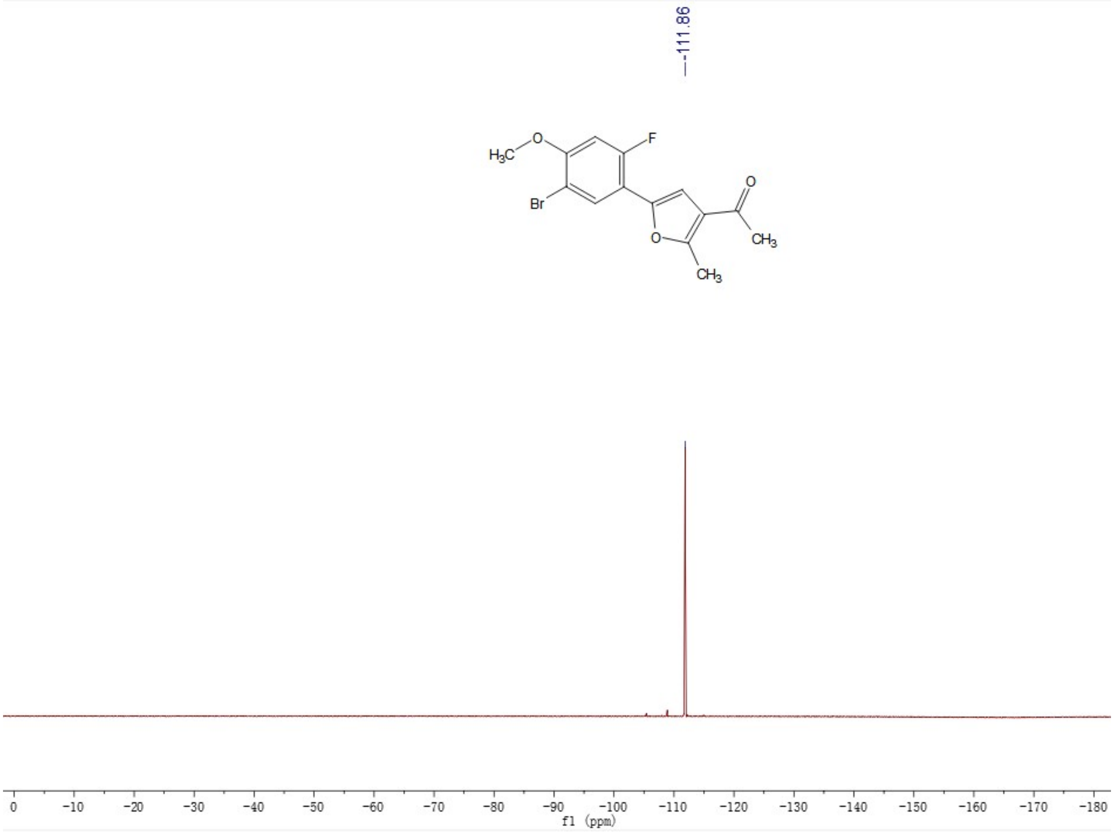
^{1}H NMR (500 MHz, Chloroform-d) of compound **3u.**



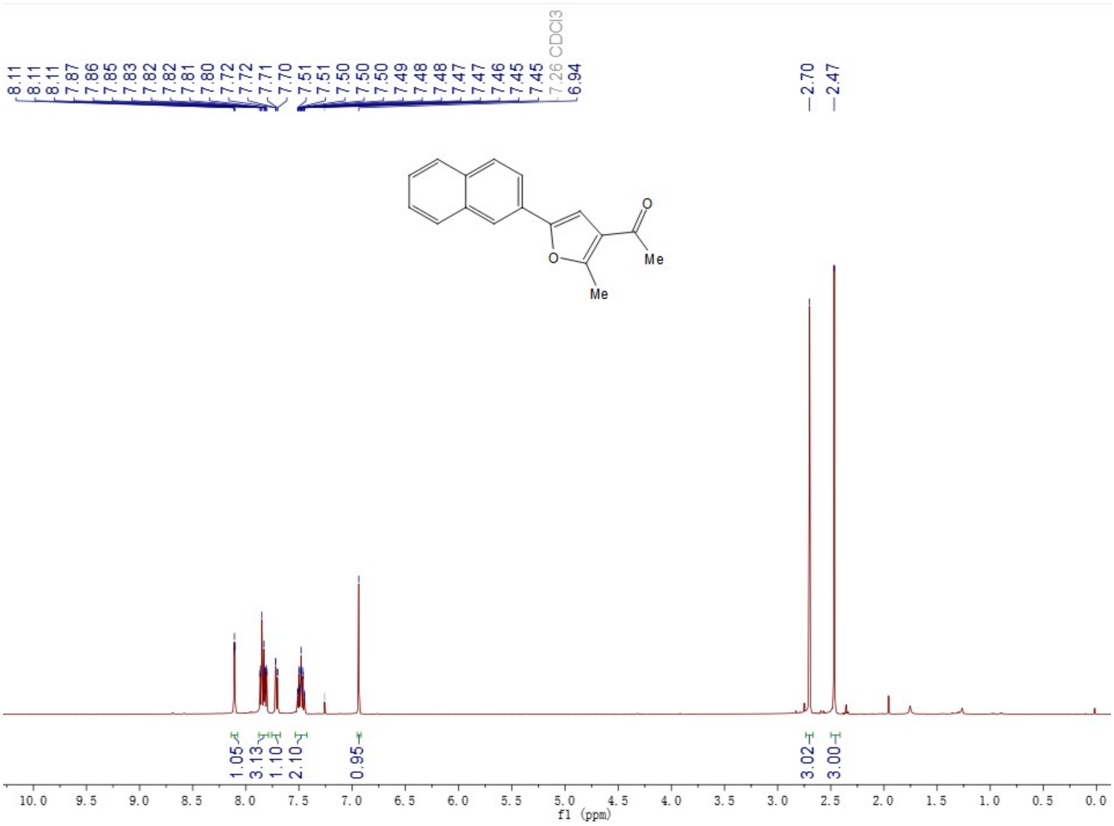
^{13}C NMR (126 MHz, Chloroform-d) of compound **3u.**



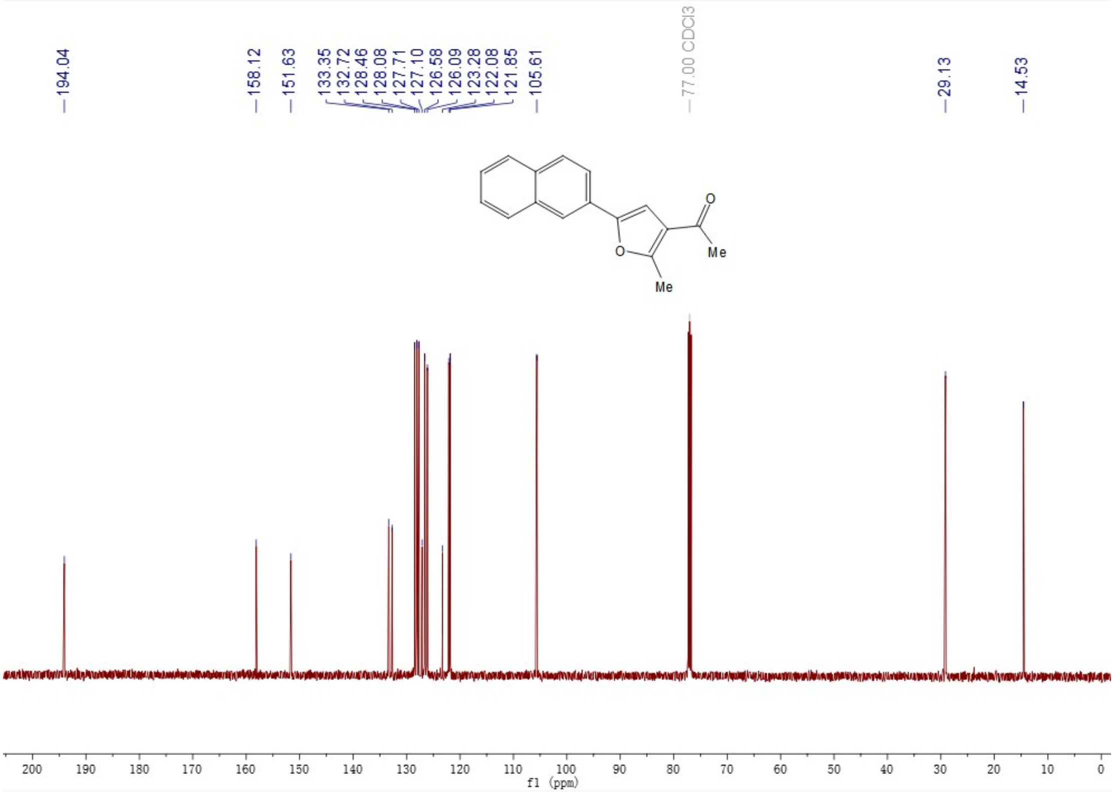
^{19}F NMR (471 MHz, Chloroform-d) of compound **3u.**



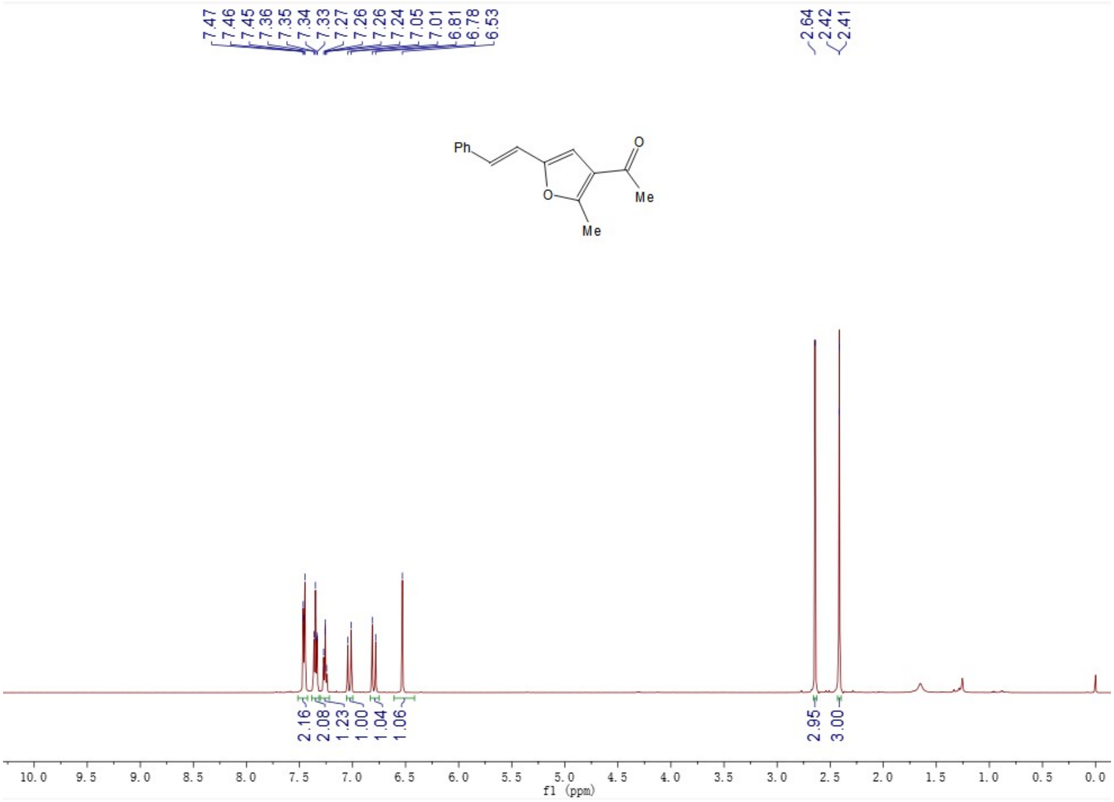
^{1}H NMR (500 MHz, Chloroform-d) of compound **3v.**



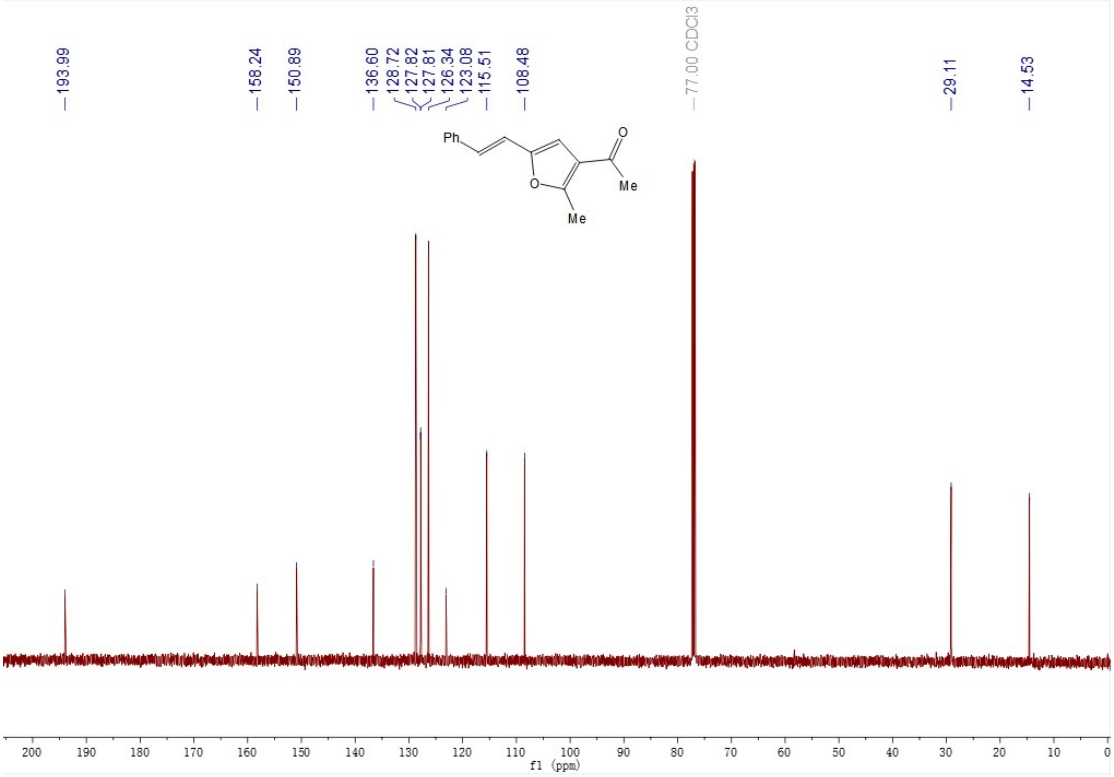
^{13}C NMR (126 MHz, Chloroform-d) of compound **3v.**



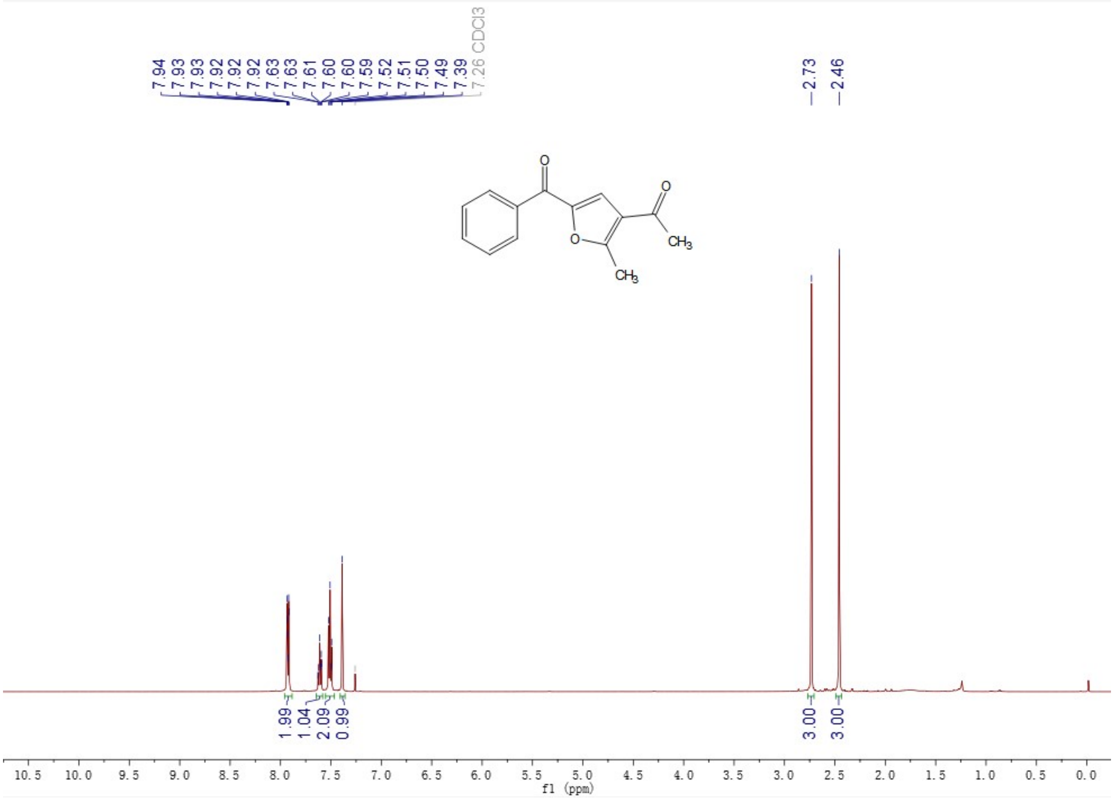
^{1}H NMR (500 MHz, Chloroform-d) of compound **3w.**



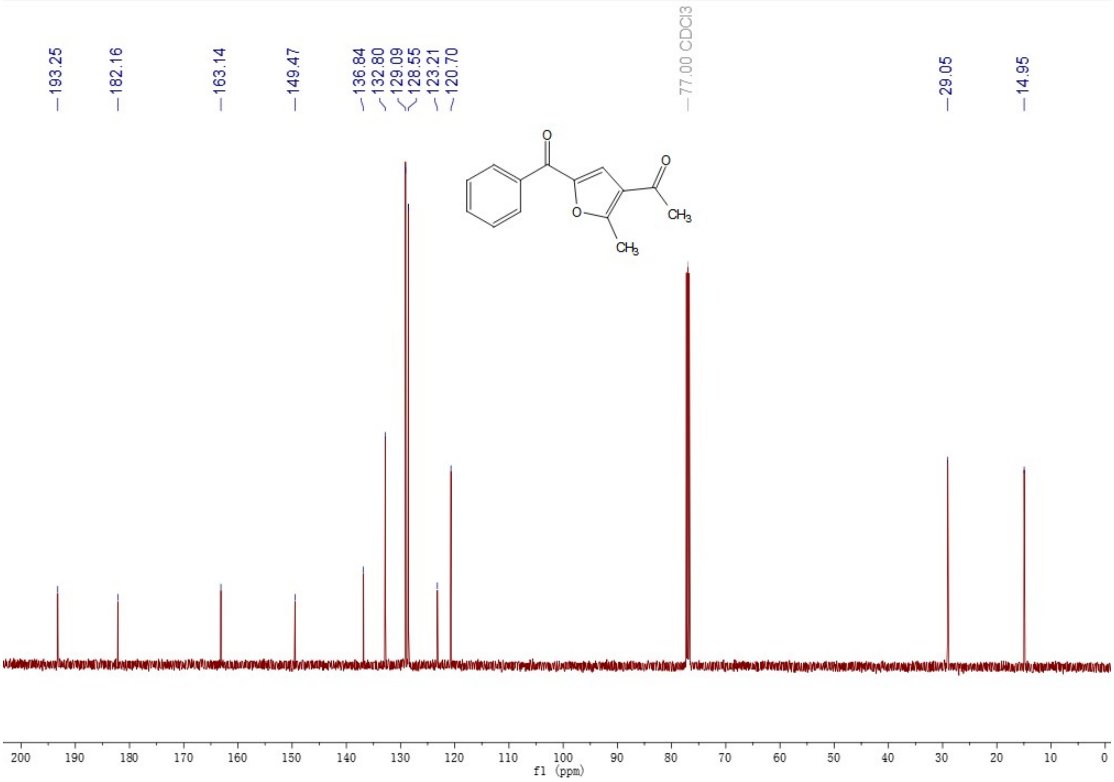
^{13}C NMR (126 MHz, Chloroform-d) of compound **3w.**



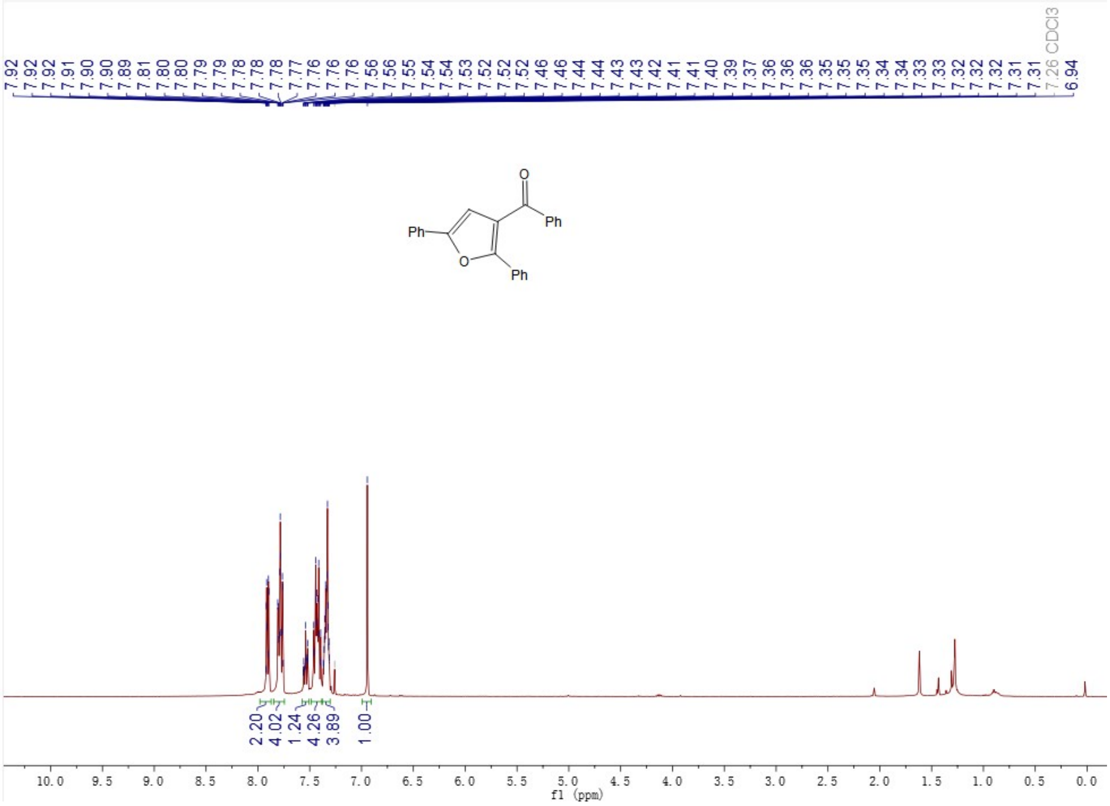
^{1}H NMR (400 MHz, Chloroform-d) of compound **3x.**



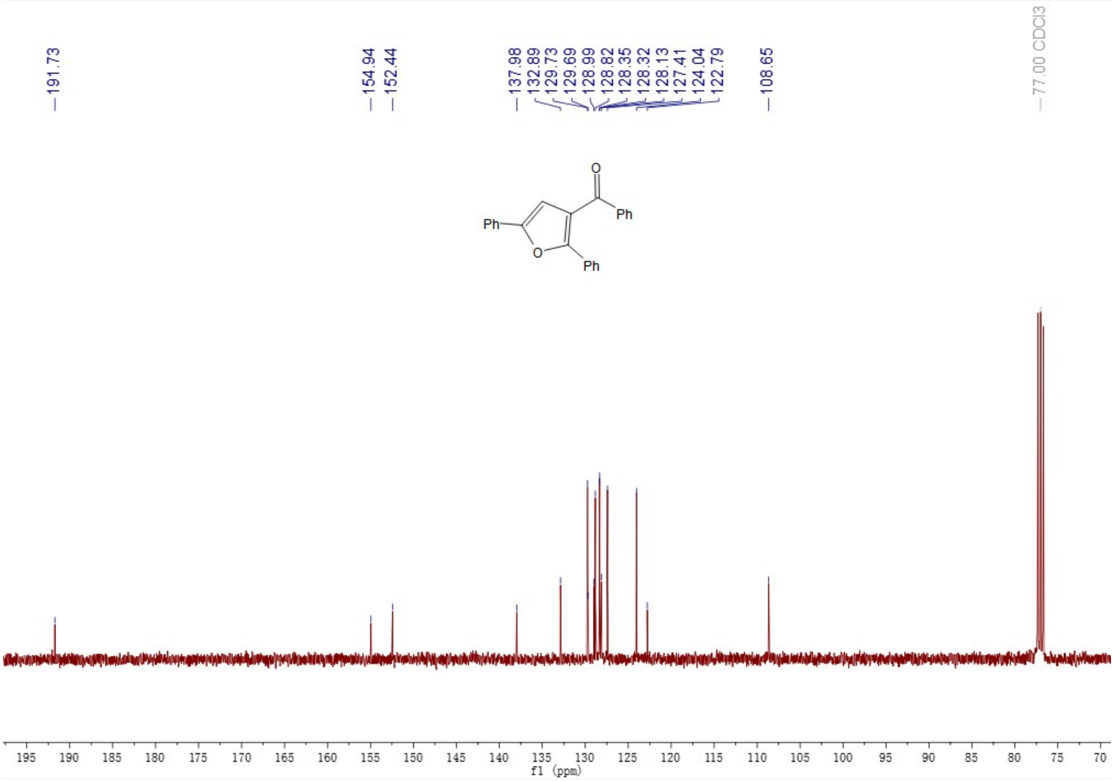
^{13}C NMR (101 MHz, Chloroform-d) of compound **3x.**



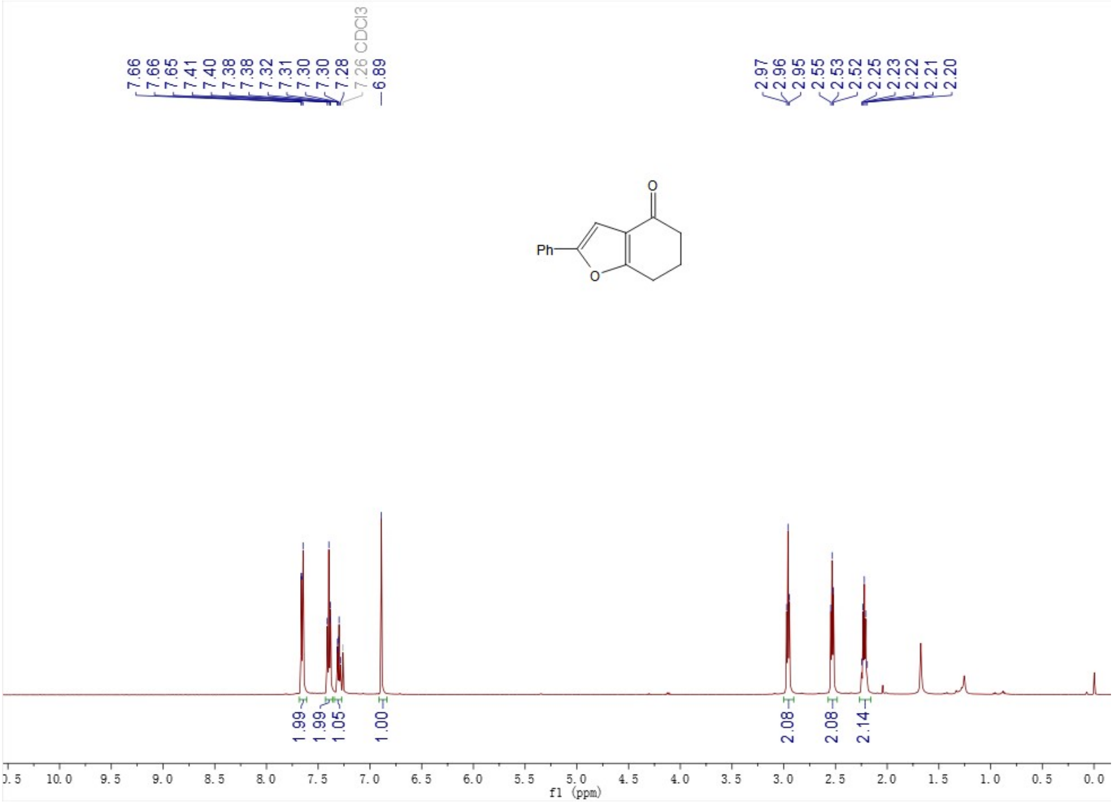
^{1}H NMR (400 MHz, Chloroform-d) of compound **4a.**



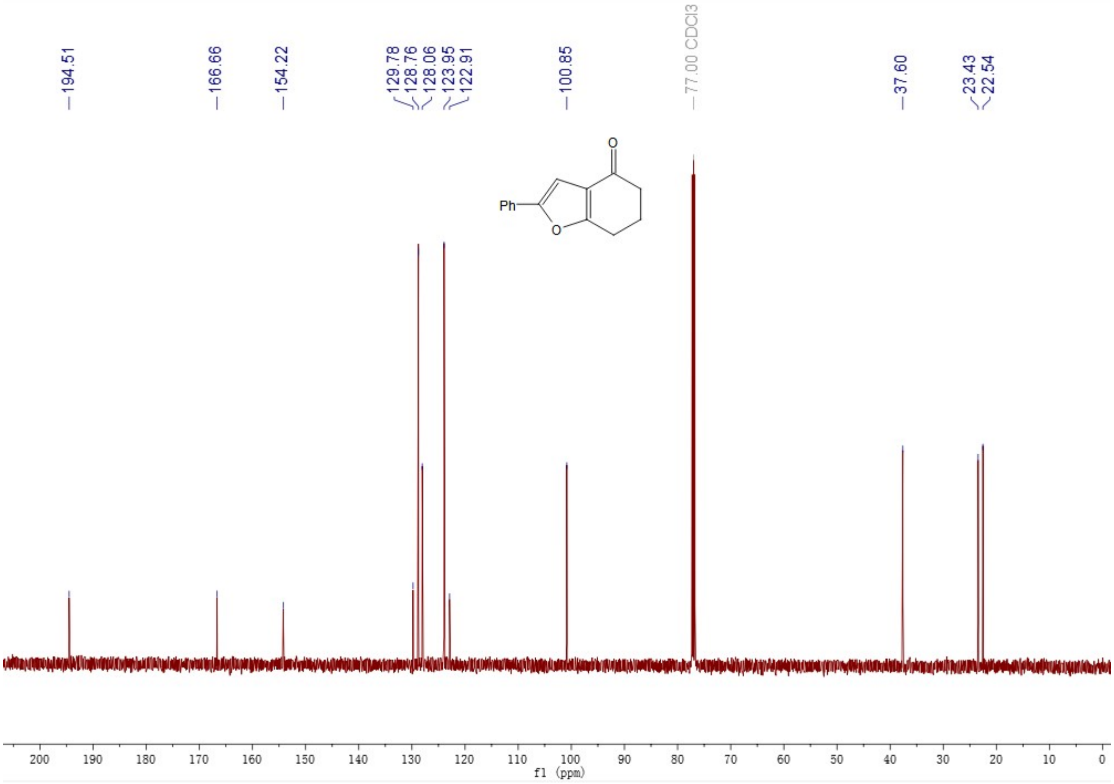
^{13}C NMR (101 MHz, Chloroform-d) of compound **4a.**



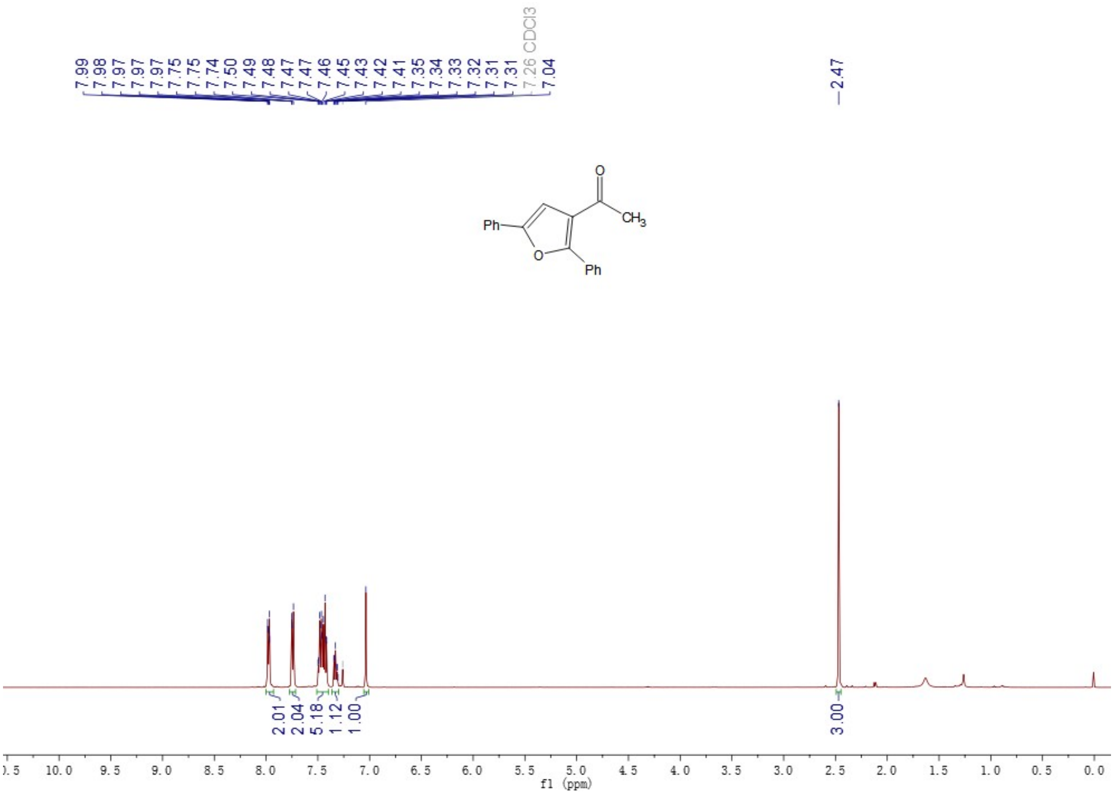
^{1}H NMR (500 MHz, Chloroform-d) of compound **4b.**



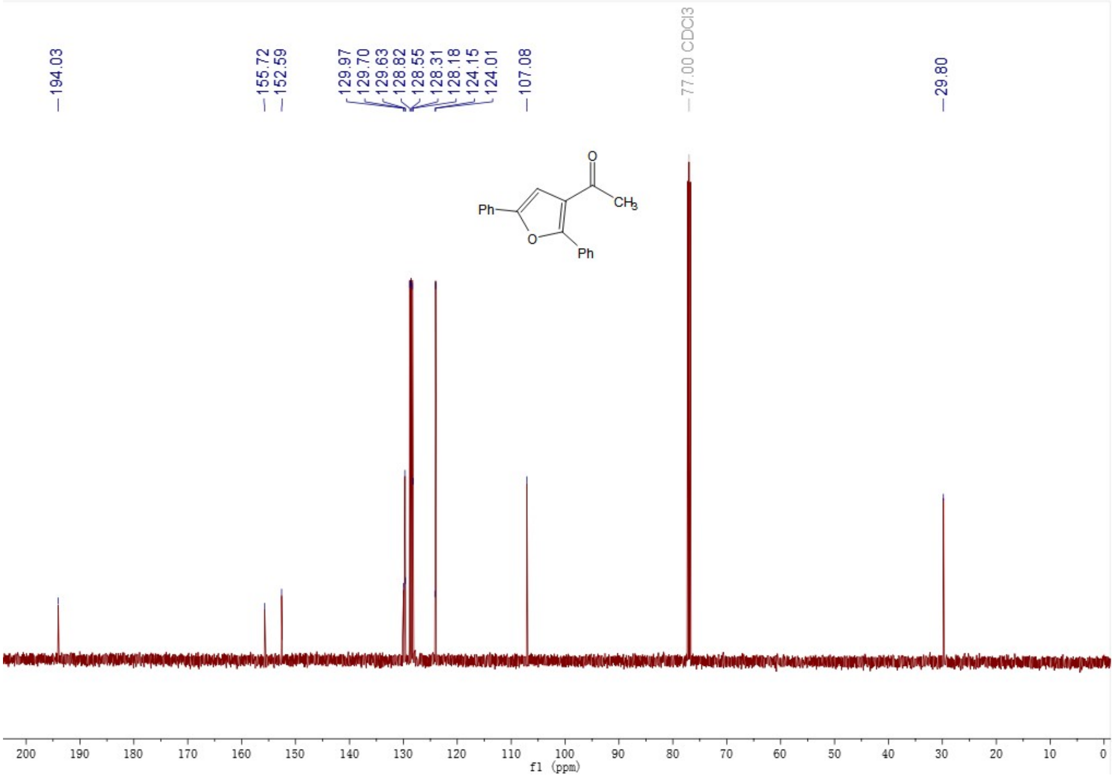
^{13}C NMR (126 MHz, Chloroform-d) of compound **4b.**



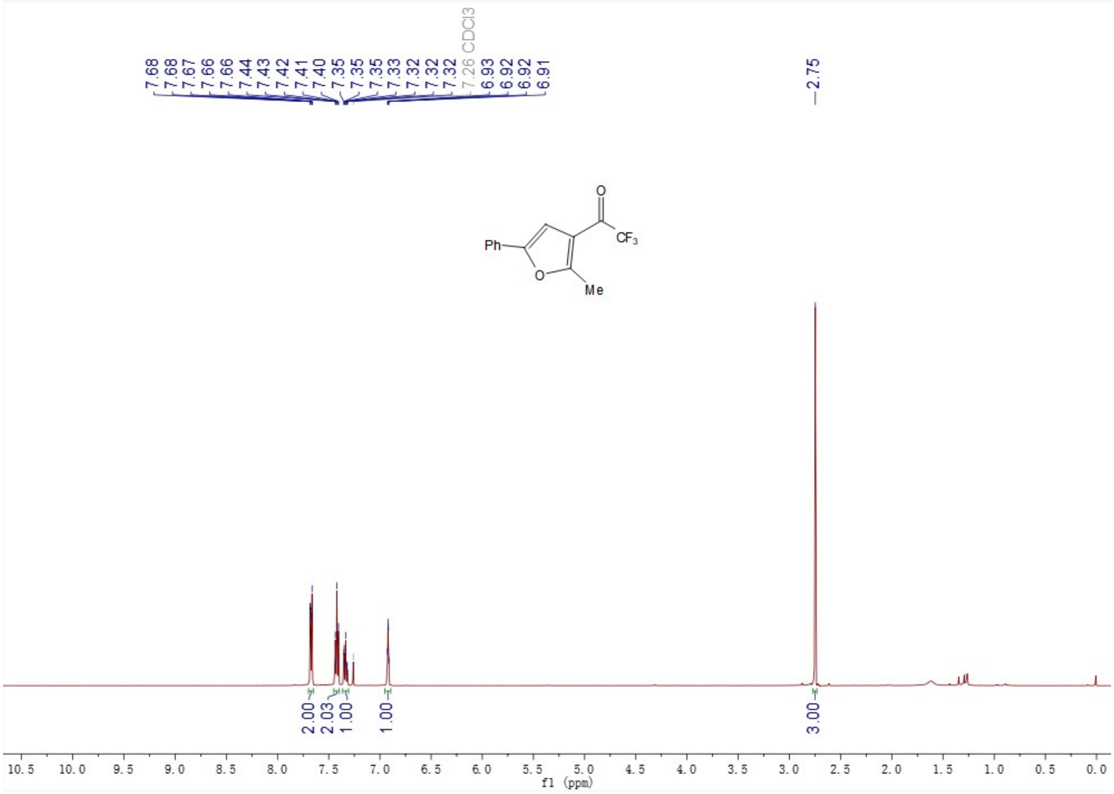
^{1}H NMR (500 MHz, Chloroform-d) of compound **4c.**



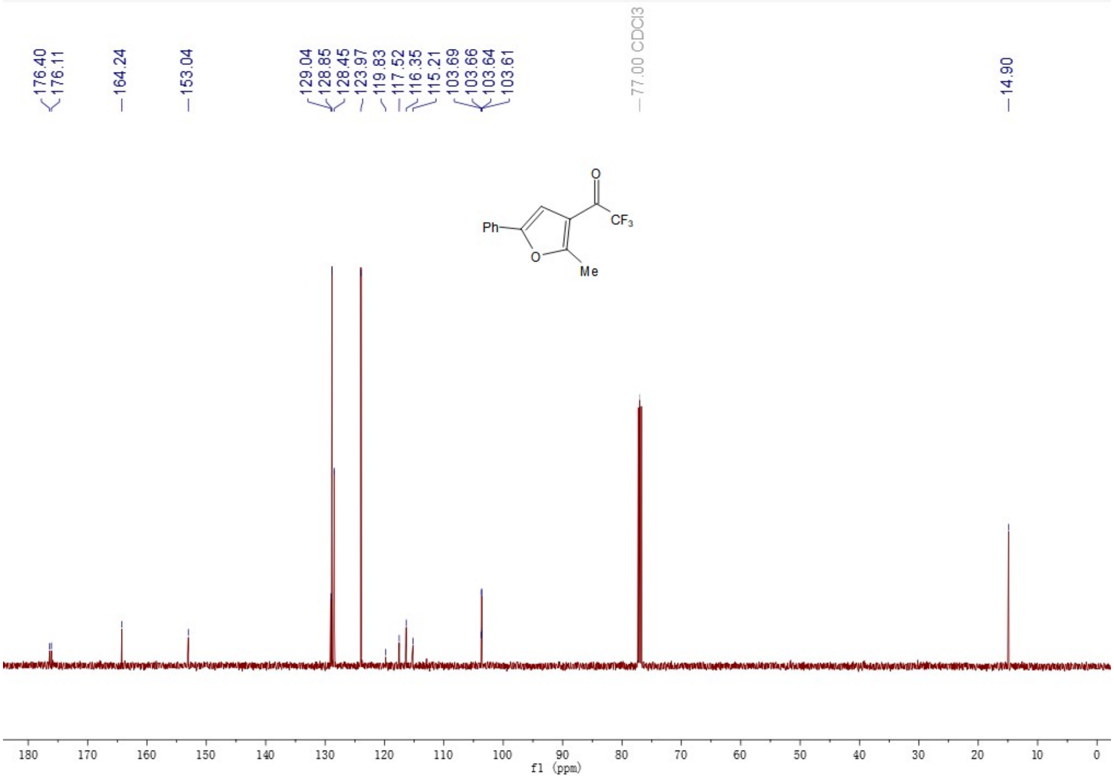
^{13}C NMR (126 MHz, Chloroform-d) of compound **4c.**



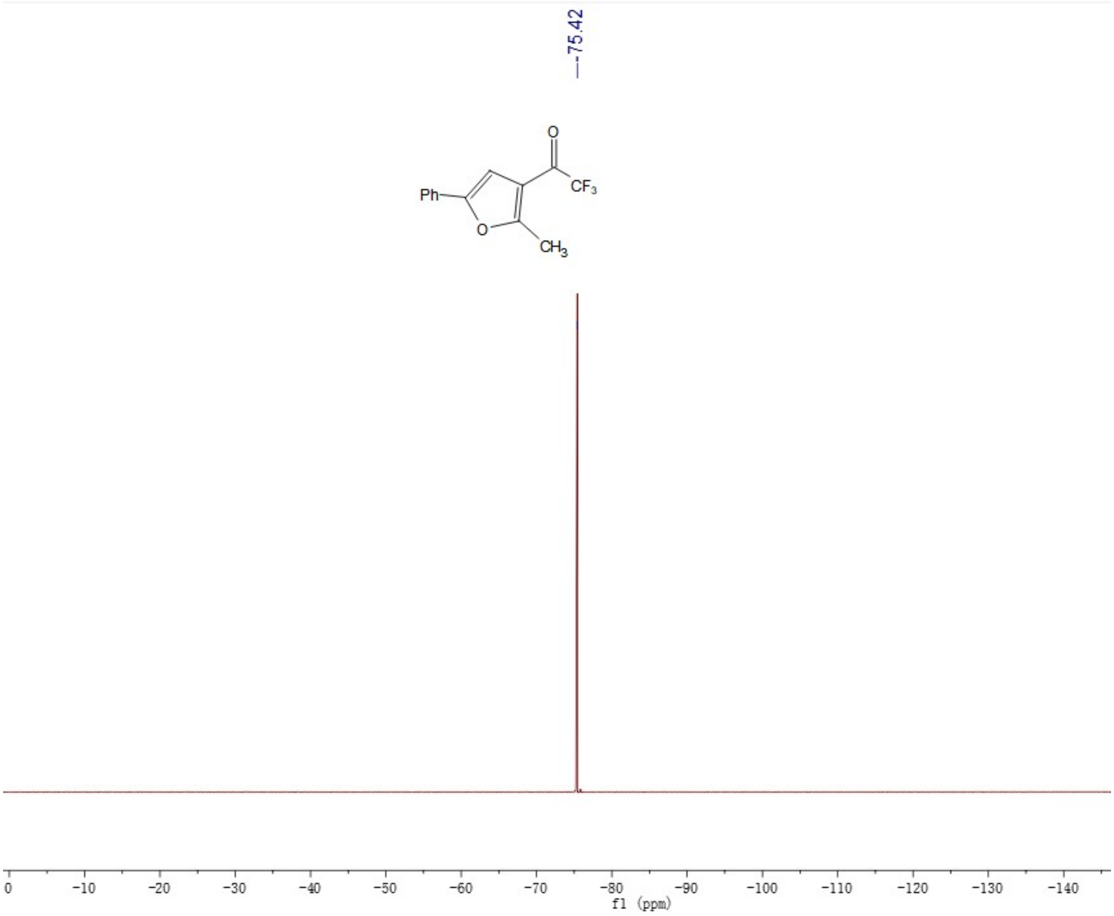
^{1}H NMR (500 MHz, Chloroform-d) of compound **4d.**



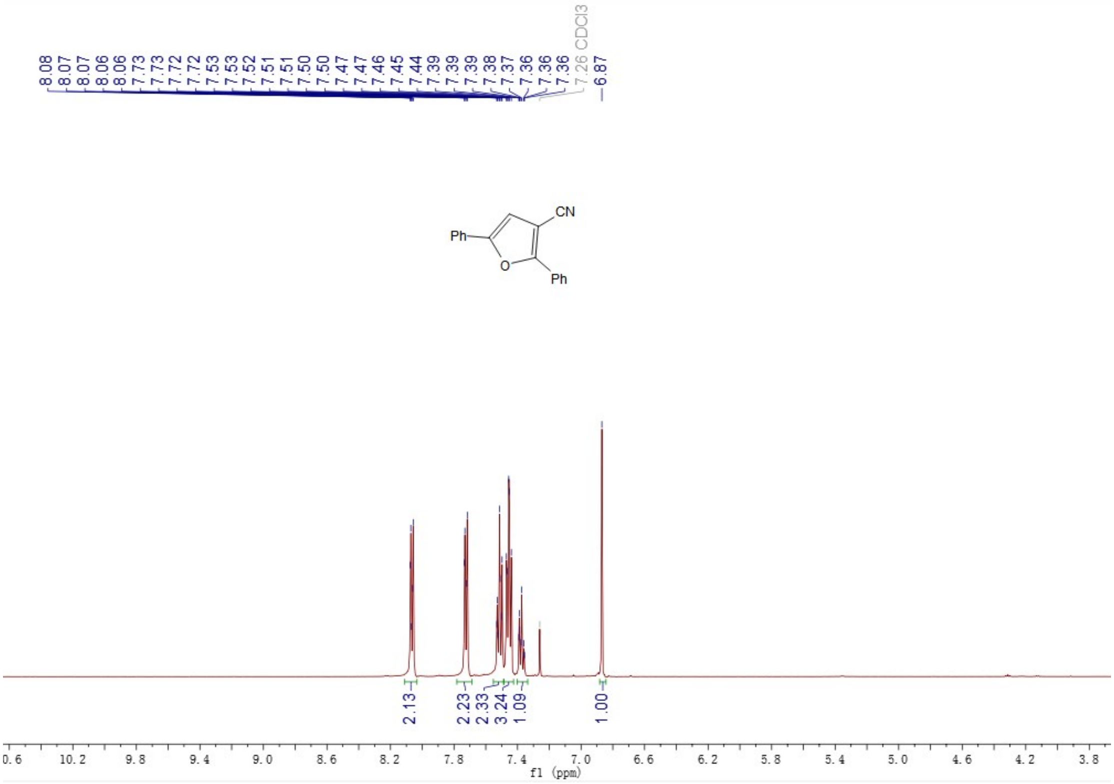
^{13}C NMR (126 MHz, Chloroform-d) of compound **4d.**



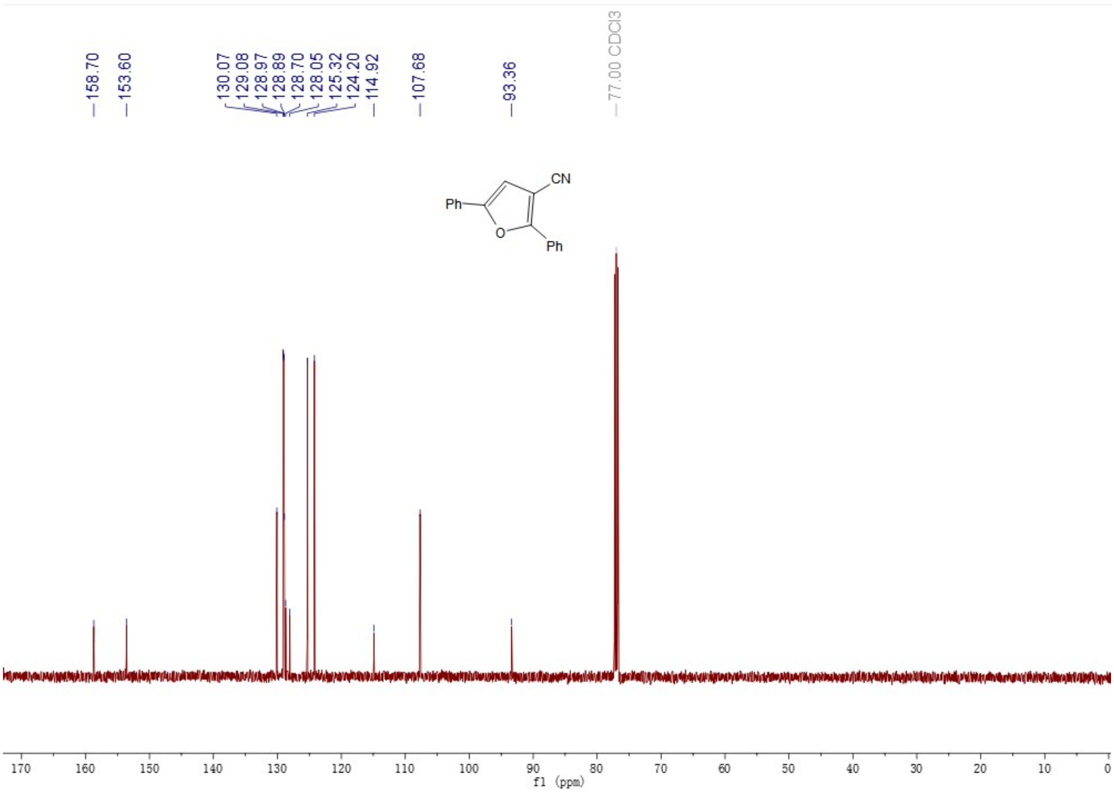
^{19}F NMR (471 MHz, Chloroform-d) of compound **4d.**



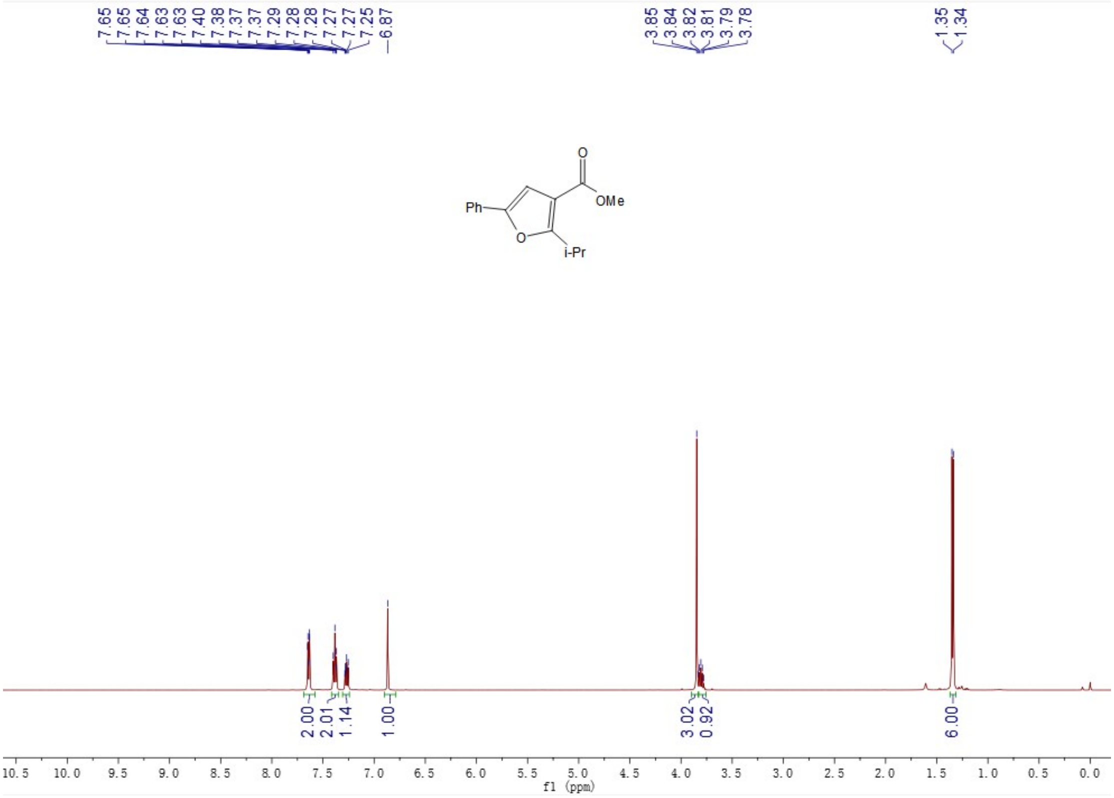
^{1}H NMR (500 MHz, Chloroform-d) of compound **4e.**



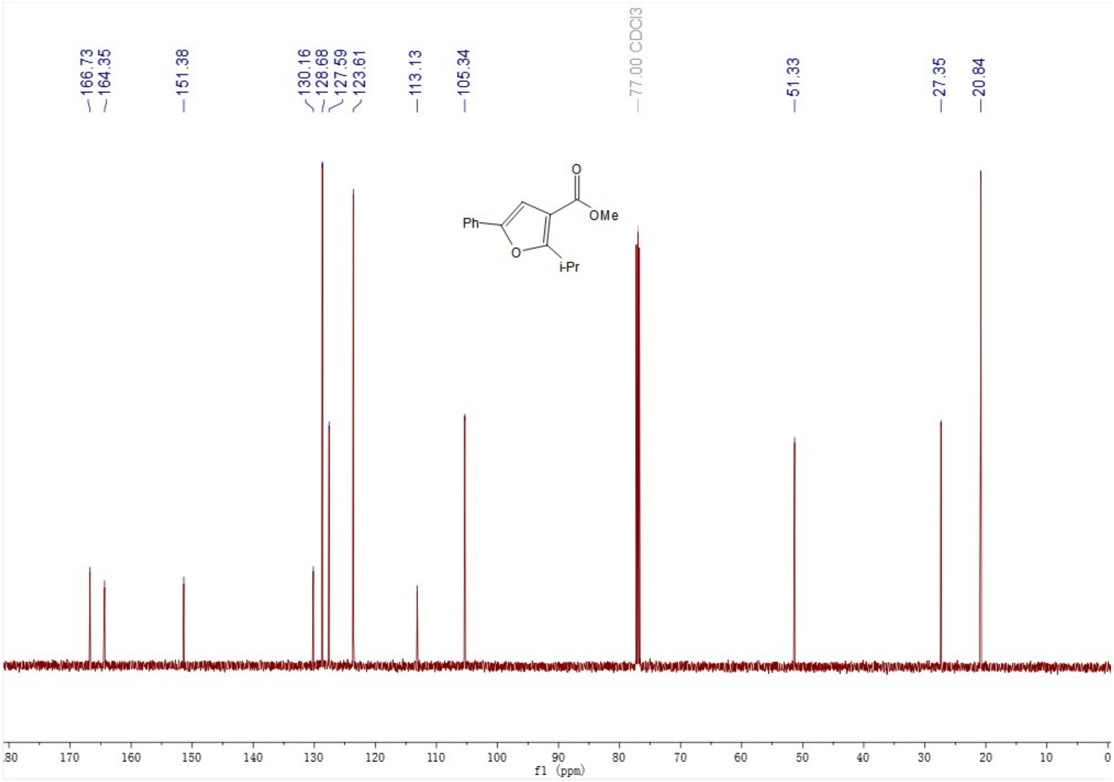
^{13}C NMR (126 MHz, Chloroform-d) of compound **4e.**



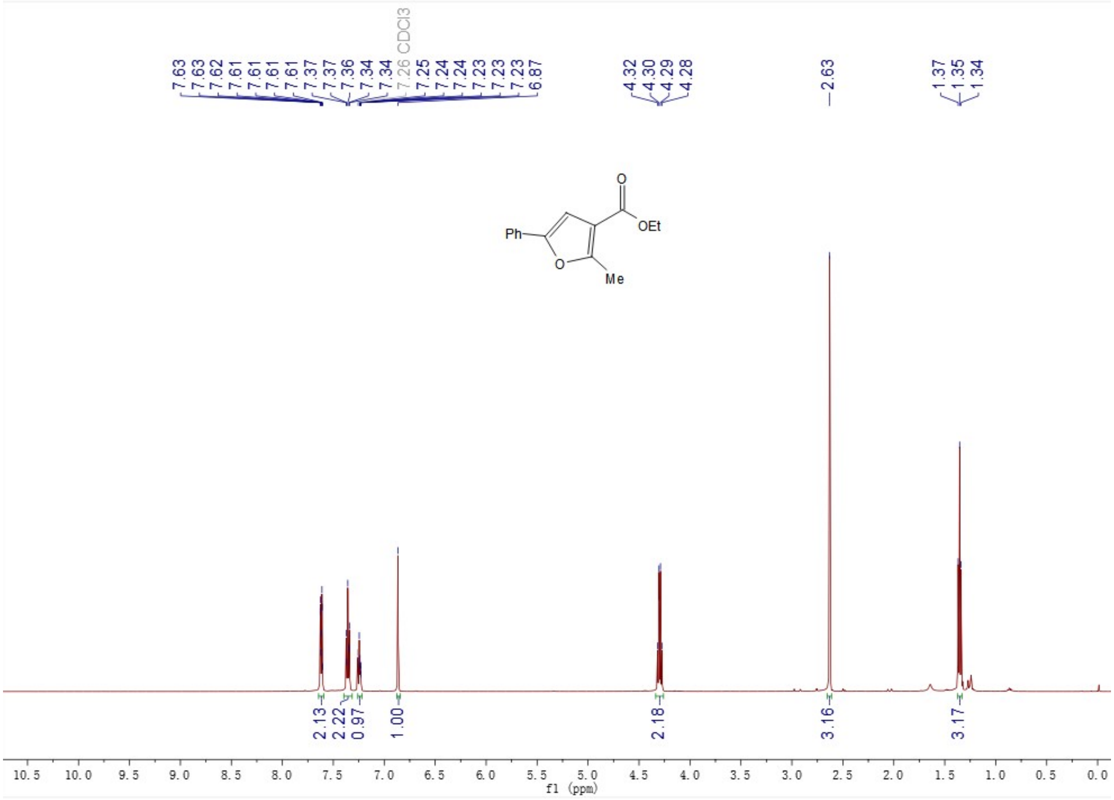
^{1}H NMR (500 MHz, Chloroform-d) of compound **4f.**



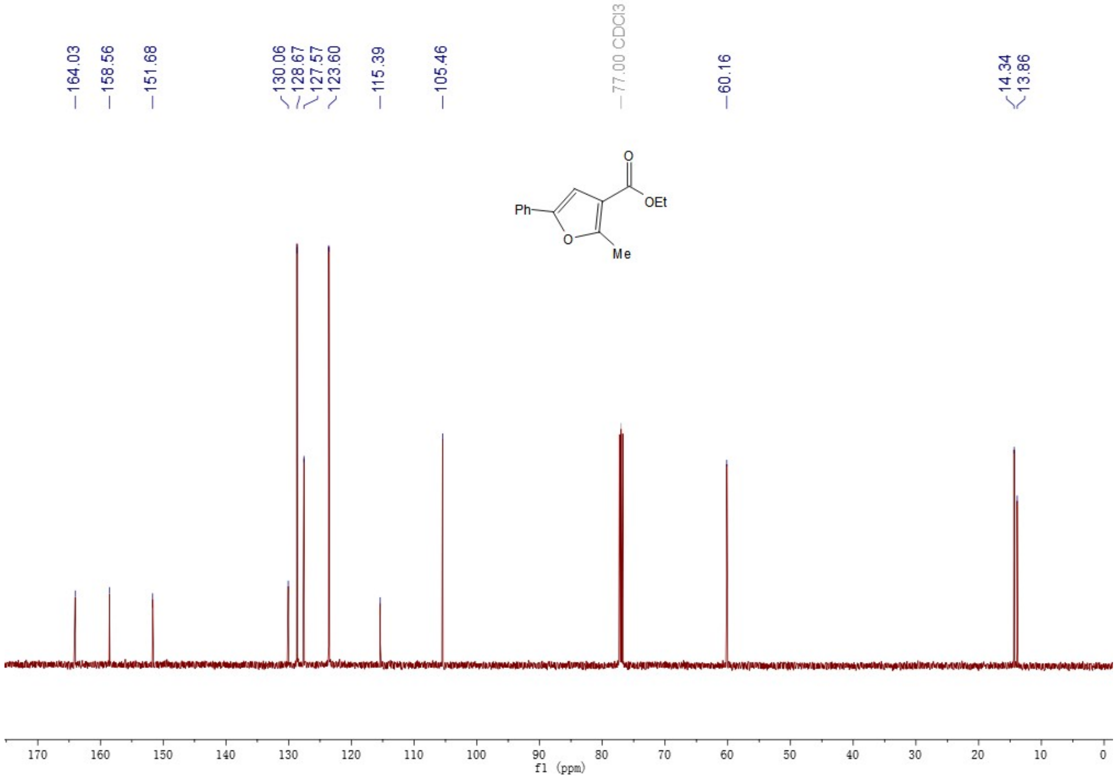
^{13}C NMR (126 MHz, Chloroform-d) of compound **4f.**



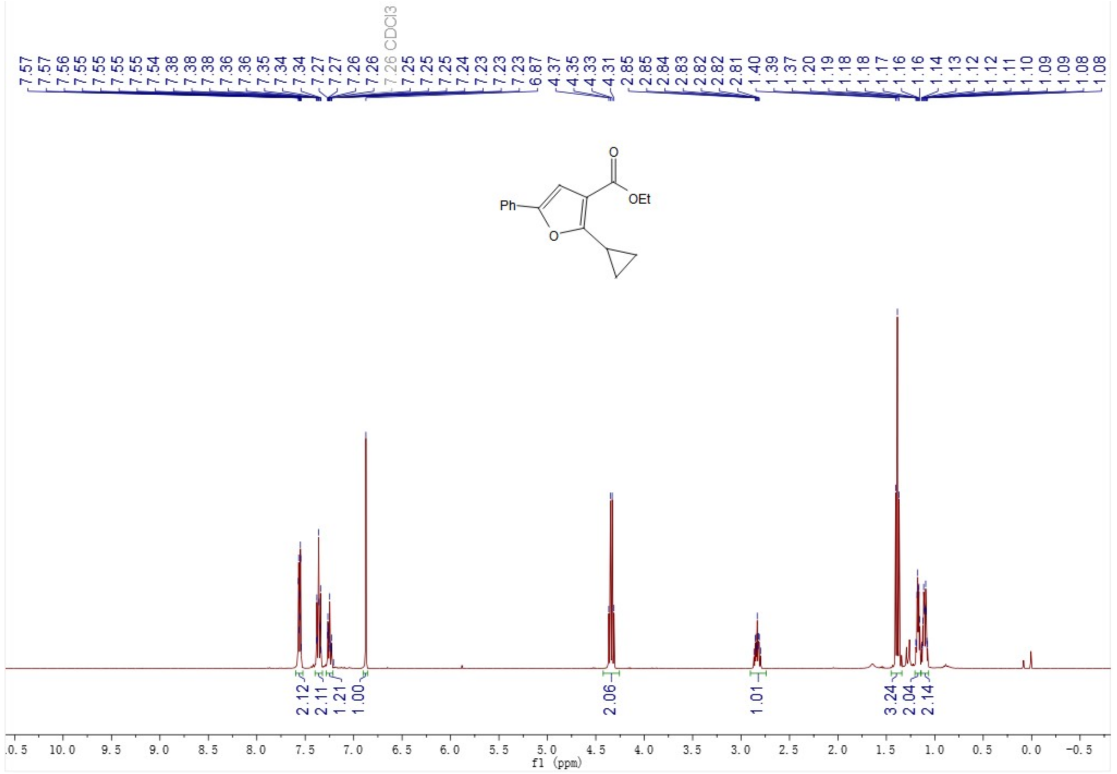
^{1}H NMR (500 MHz, Chloroform-d) of compound **4g.**



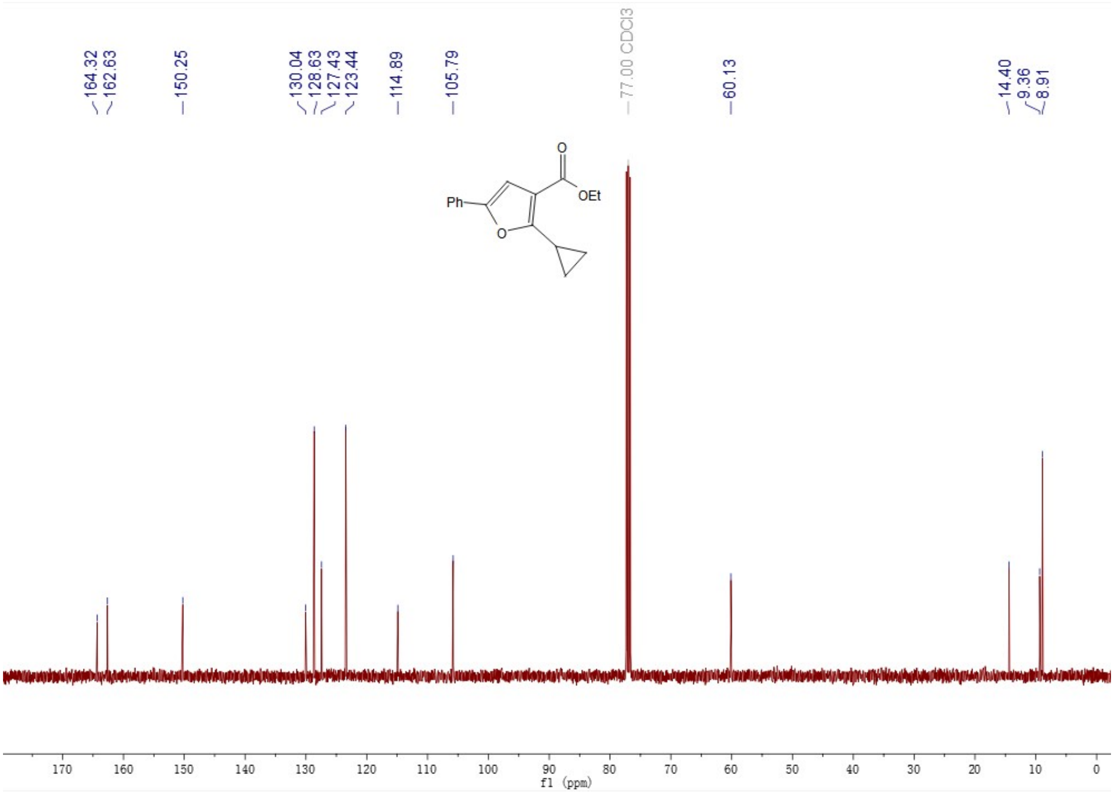
^{13}C NMR (126 MHz, Chloroform-d) of compound **4g.**



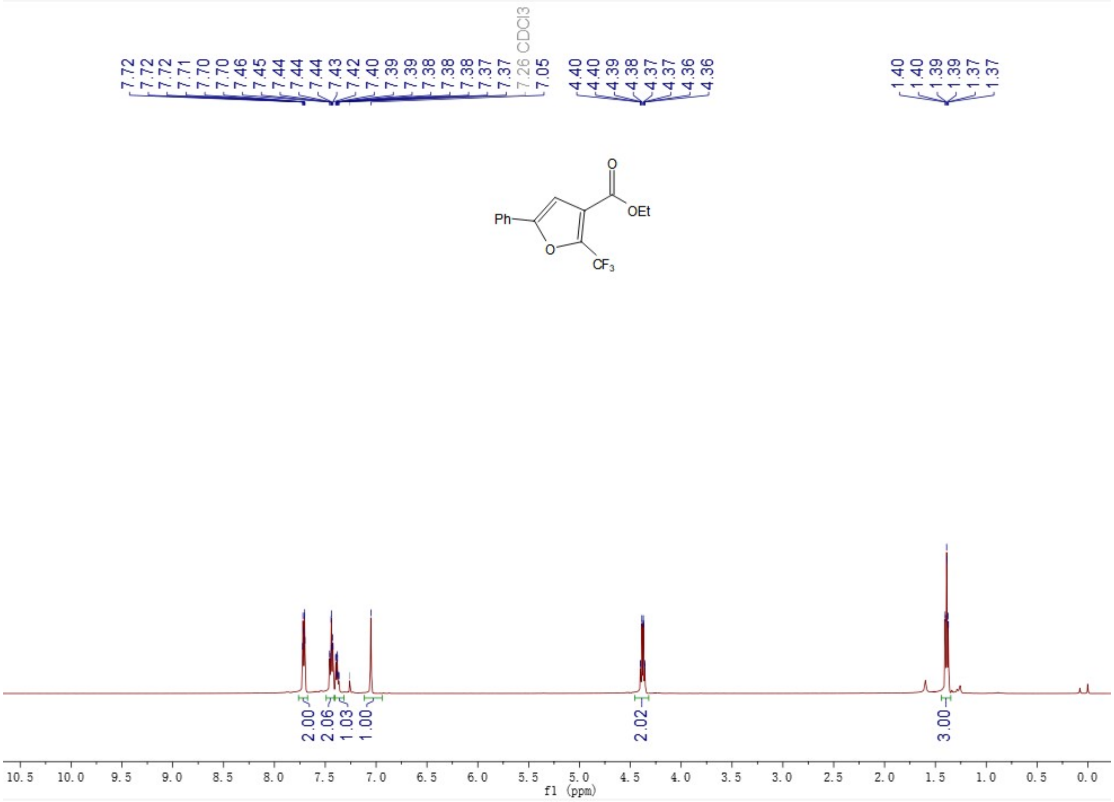
^{1}H NMR (500 MHz, Chloroform-d) of compound **4h.**



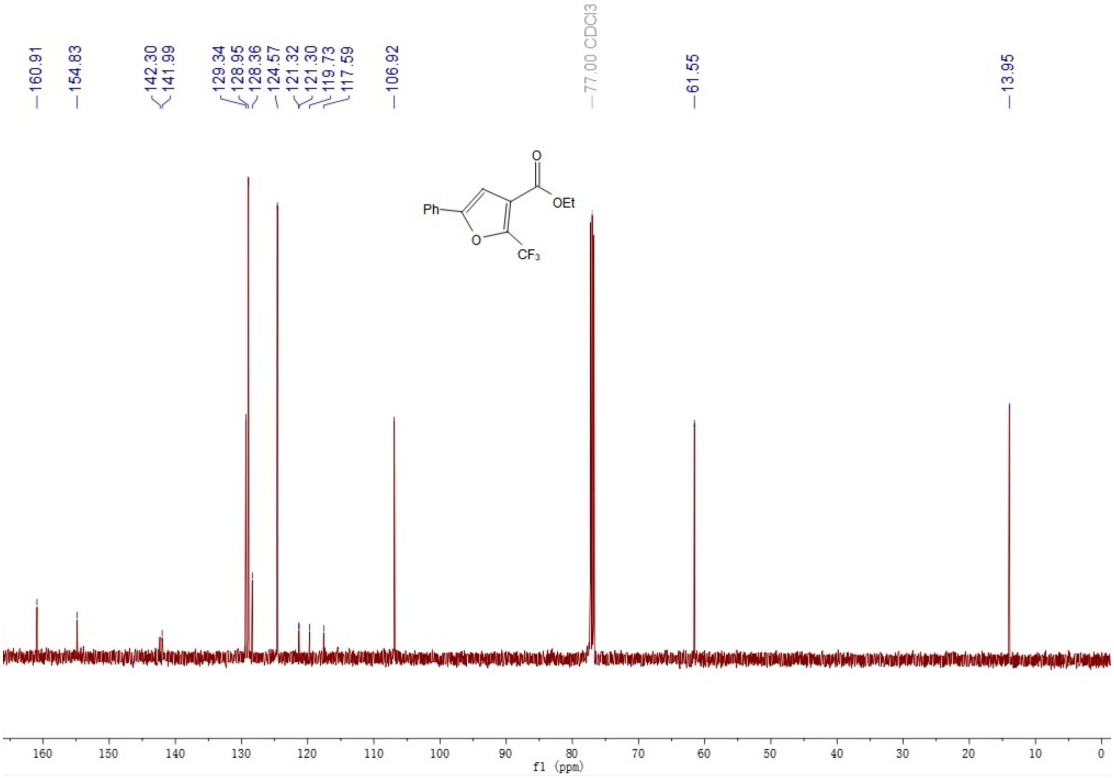
^{13}C NMR (101 MHz, Chloroform-d) of compound **4h.**



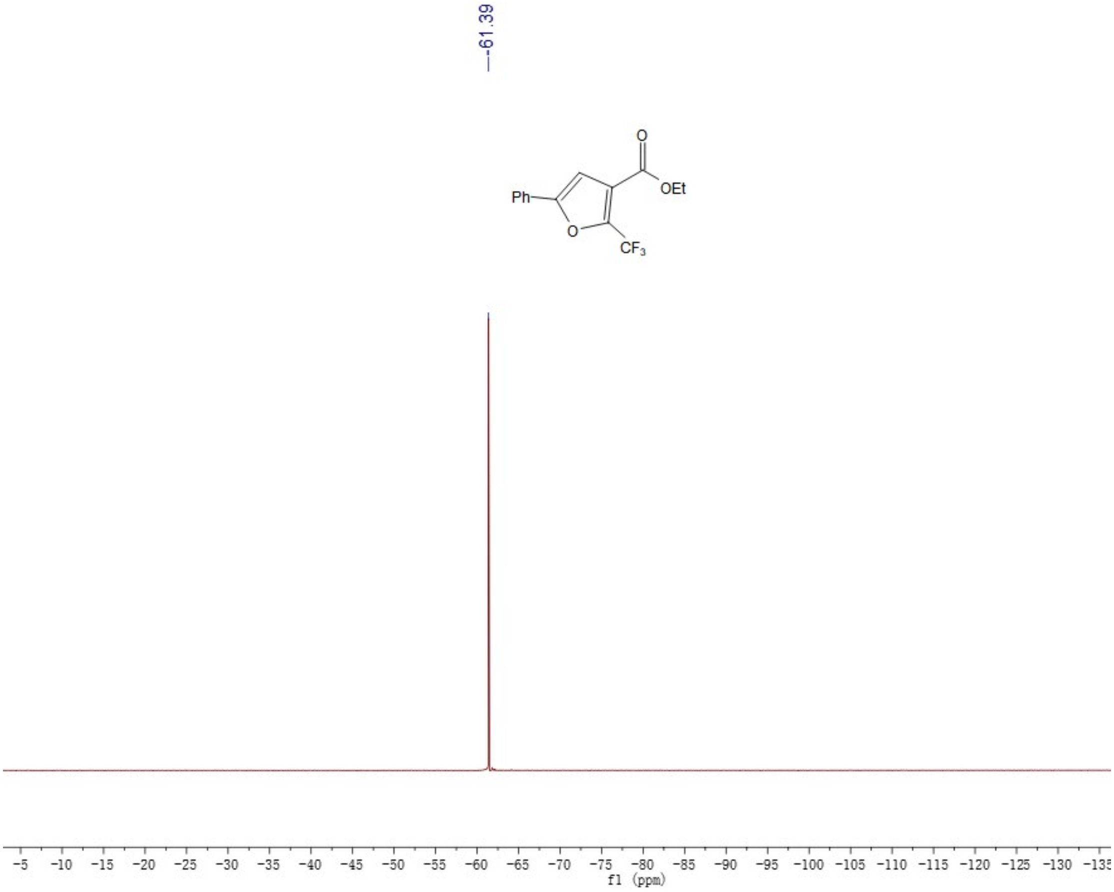
^{1}H NMR (500 MHz, Chloroform-d) of compound **4i.**



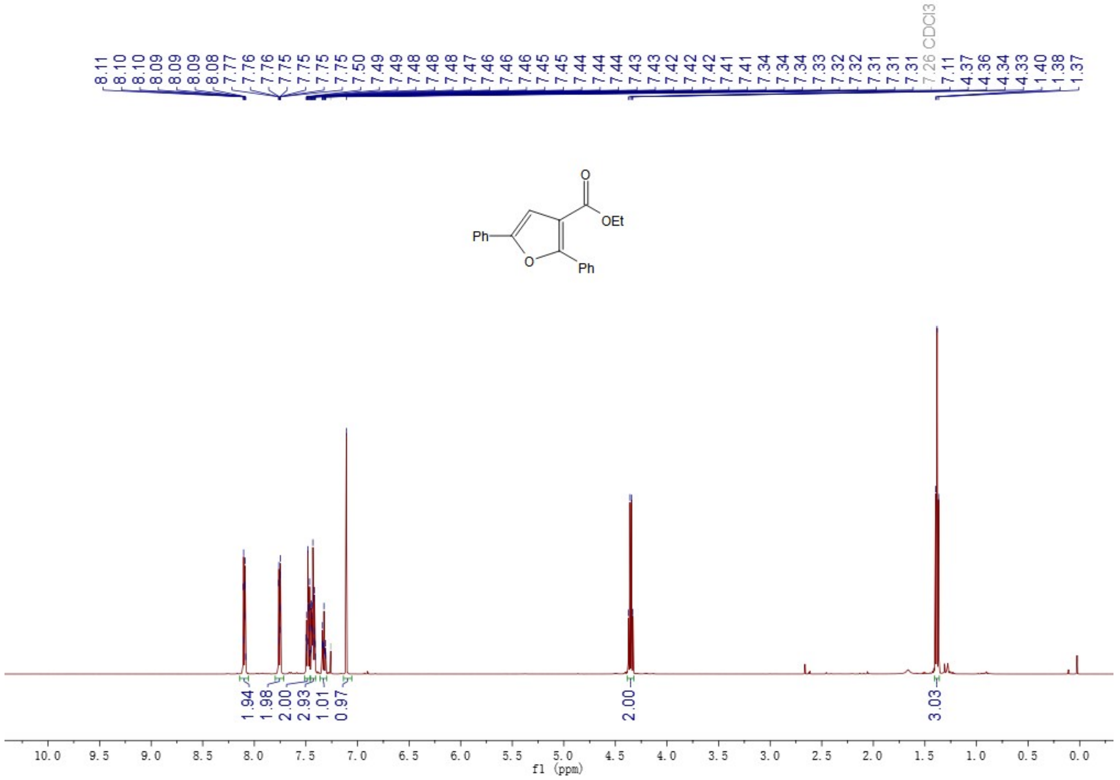
^{13}C NMR (126 MHz, Chloroform-d) of compound **4i.**



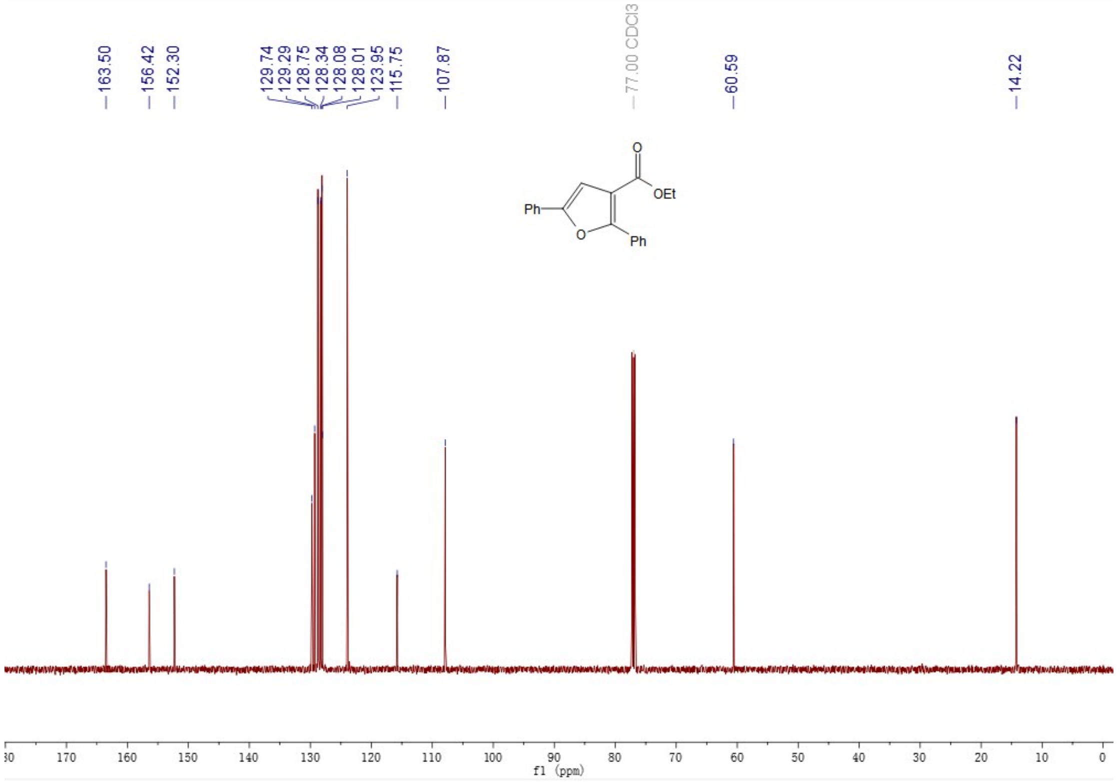
^{19}F NMR (471 MHz, Chloroform-d) of compound **4i.**



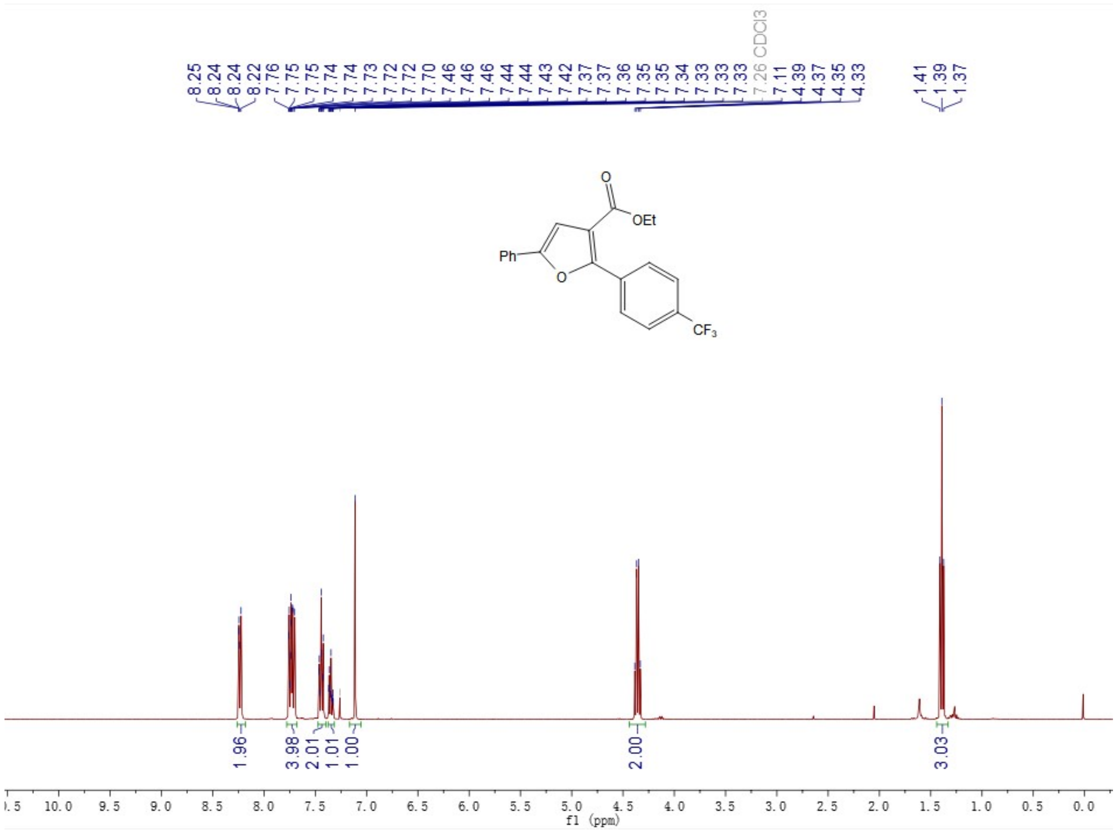
^{1}H NMR (500 MHz, Chloroform-d) of compound **4j.**



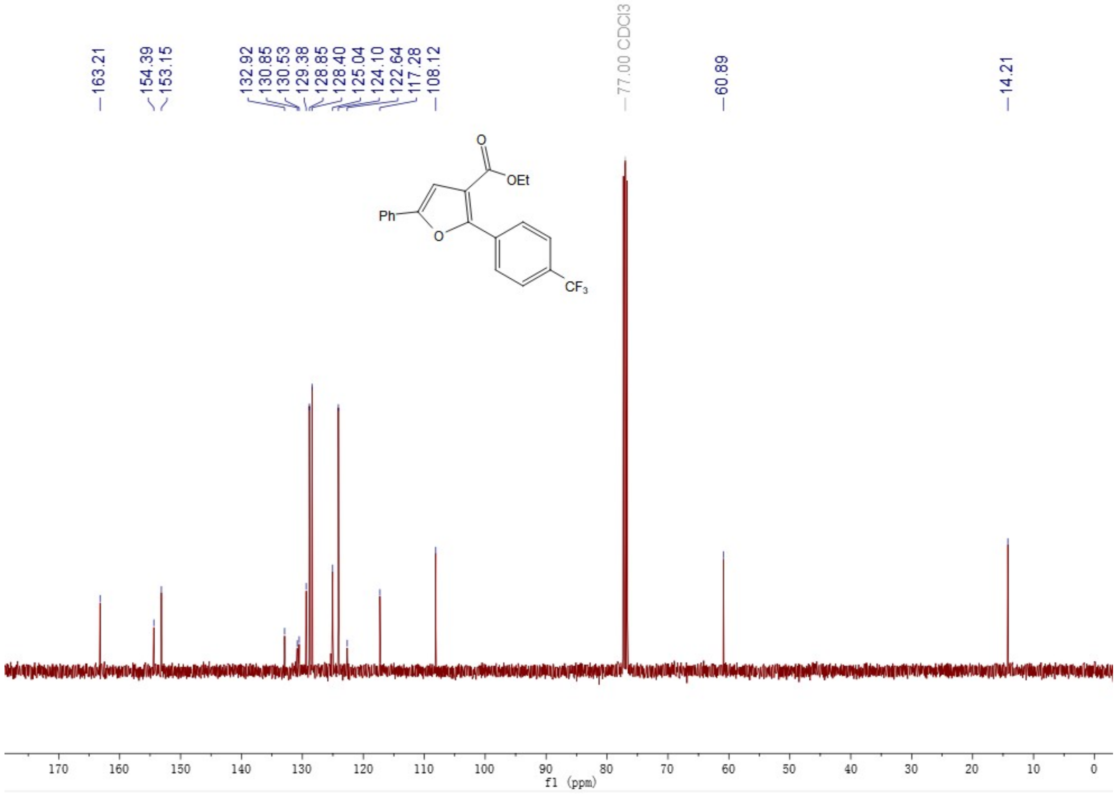
^{13}C NMR (126 MHz, Chloroform-d) of compound **4j.**



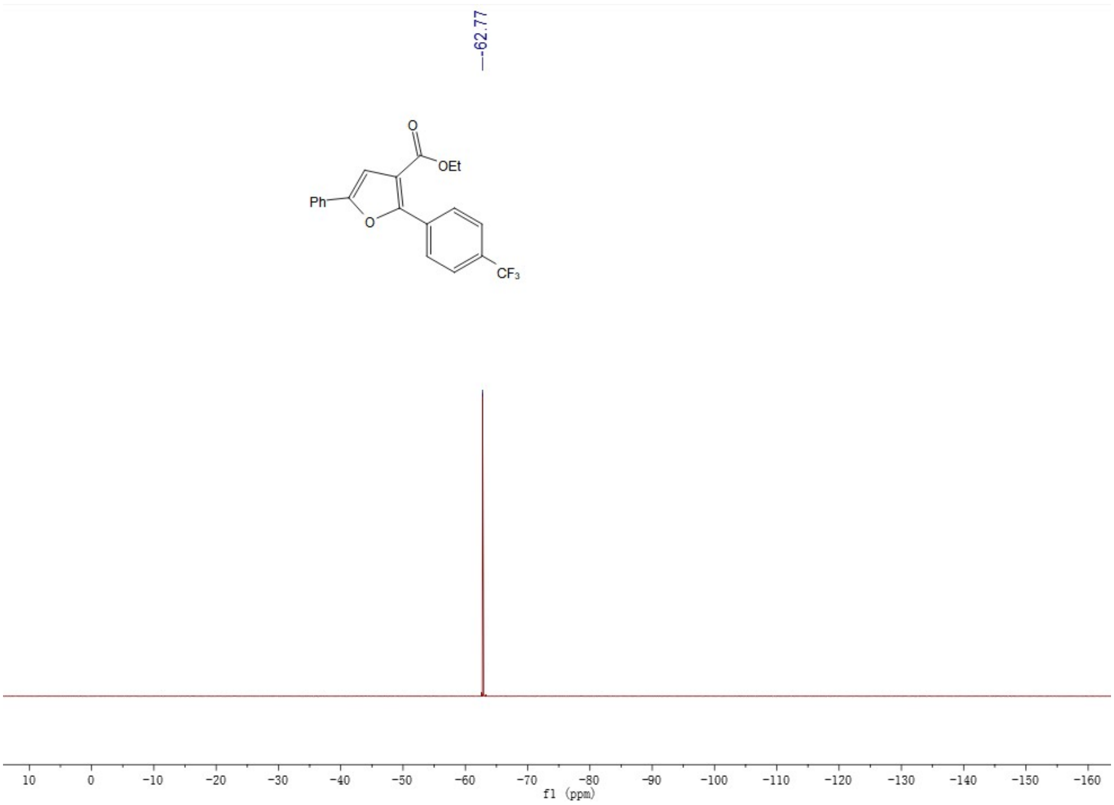
^{1}H NMR (400 MHz, Chloroform-d) of compound **4k.**



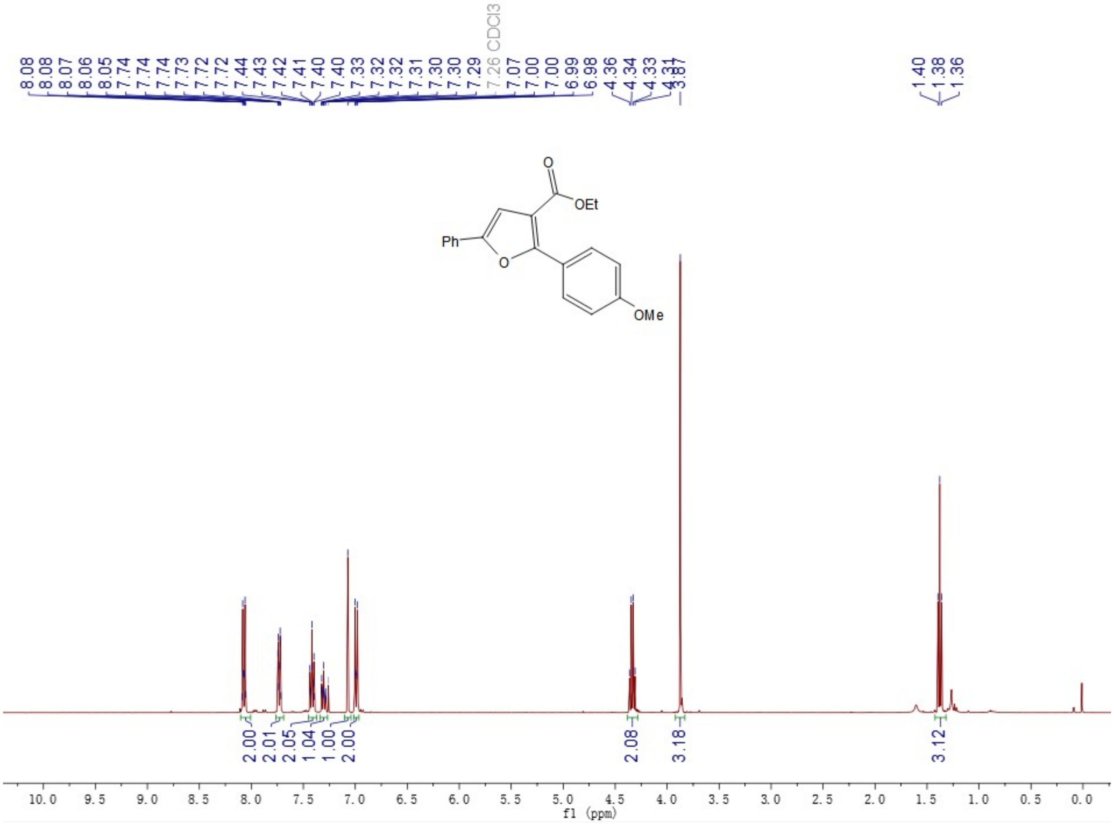
^{13}C NMR (101 MHz, Chloroform-d) of compound **4k.**



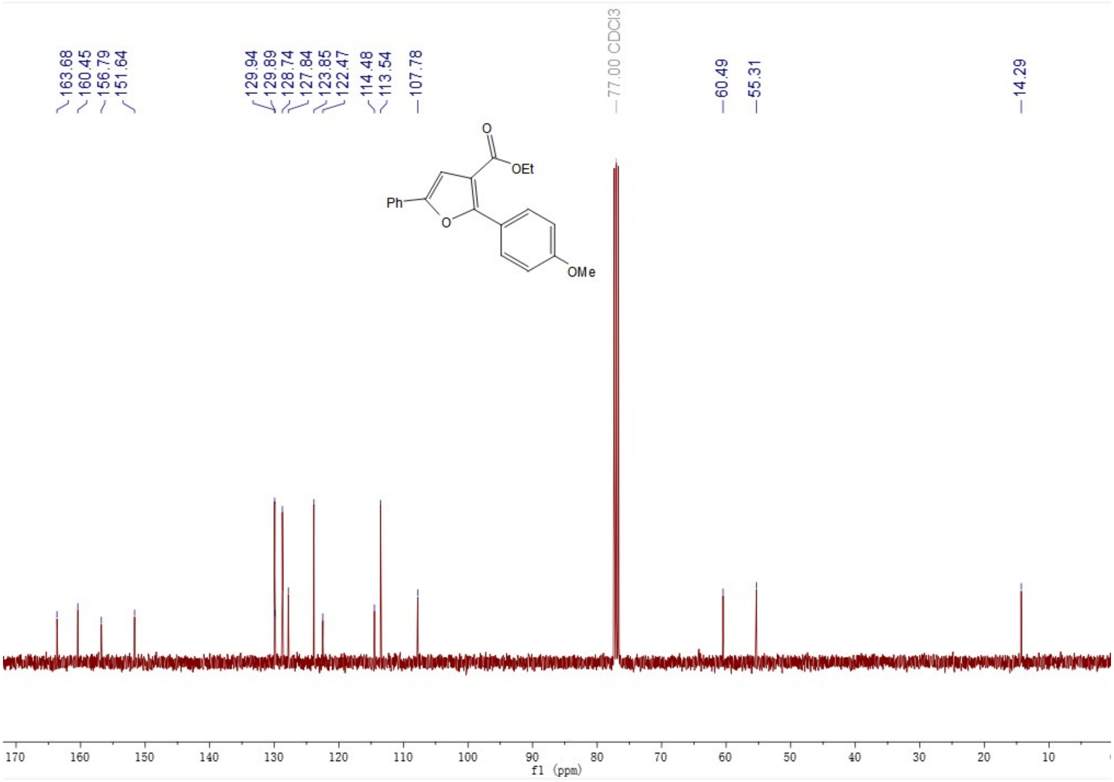
^{19}F NMR (376 MHz, Chloroform-d) of compound **4k.**



^{1}H NMR (400 MHz, Chloroform-d) of compound **4l.**

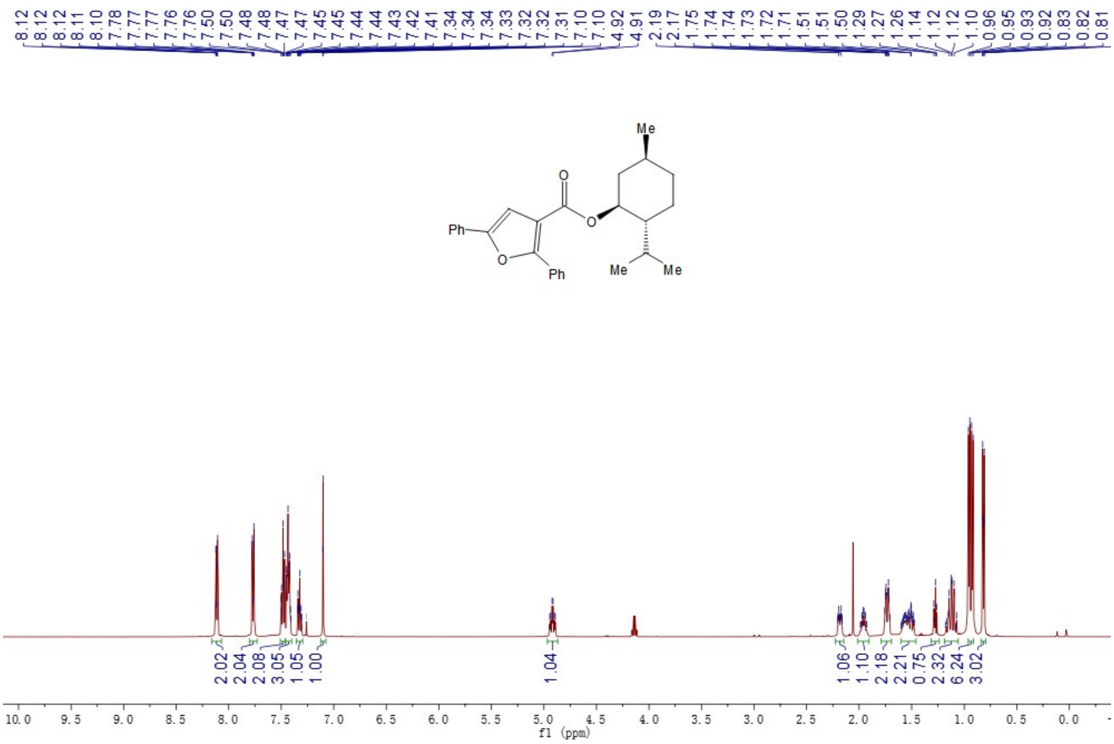


^{13}C NMR (101 MHz, Chloroform-d) of compound **4l.**

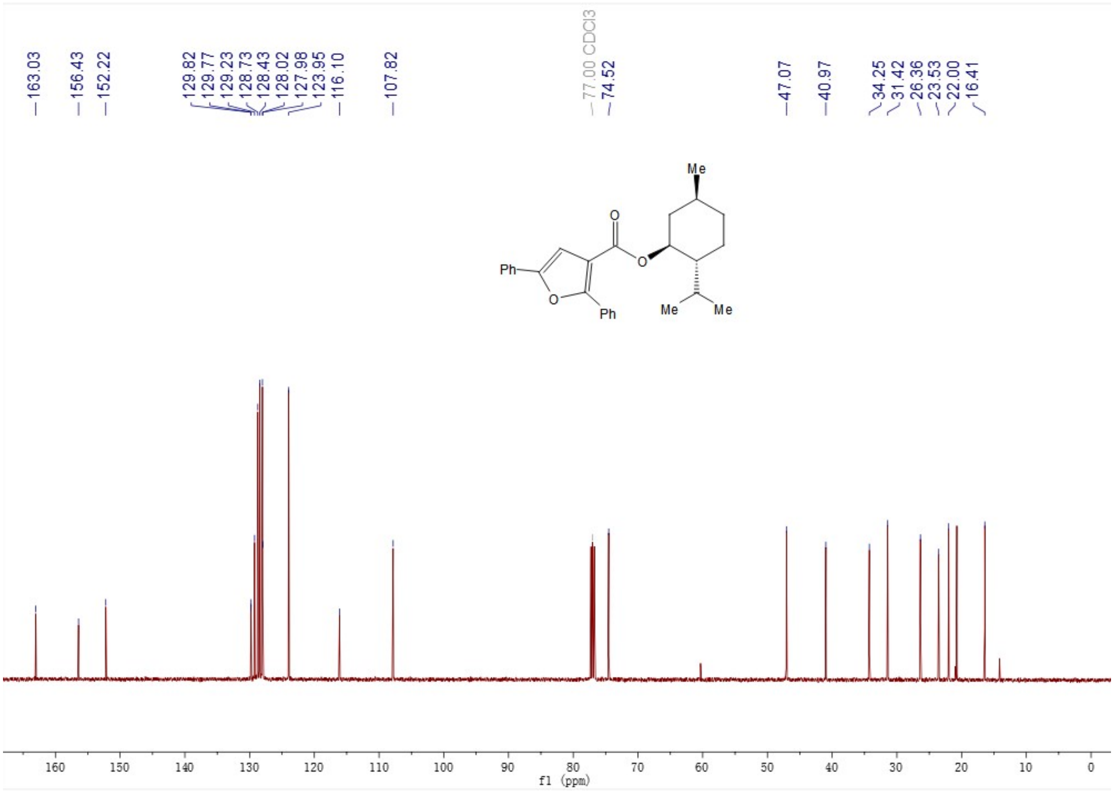


^{1}H NMR (500 MHz, Chloroform-d) of compound **4m.**

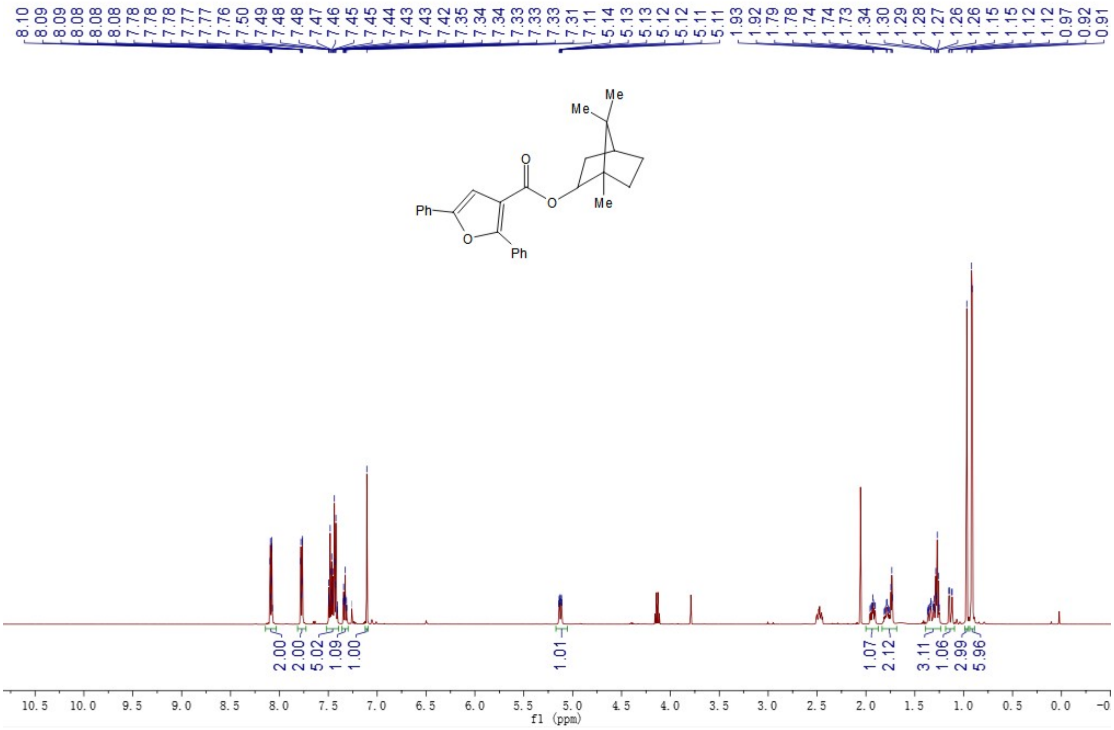
ff



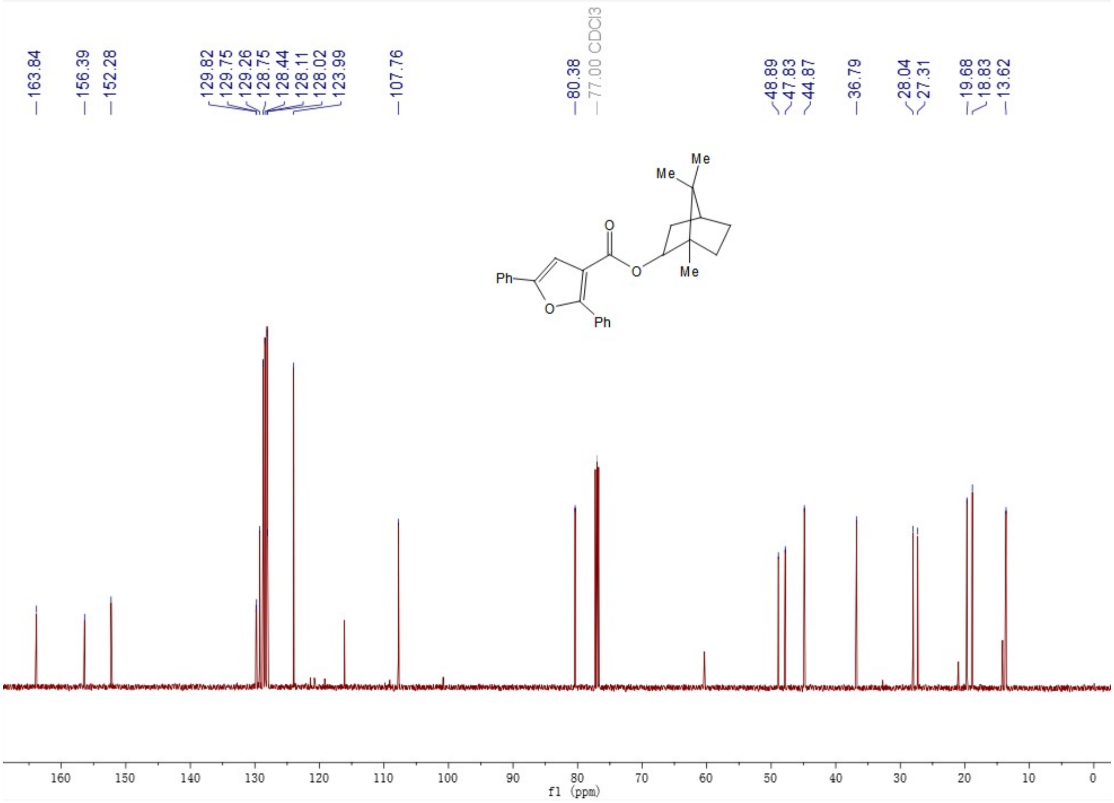
^{13}C NMR (126 MHz, Chloroform-d) of compound **4m.**



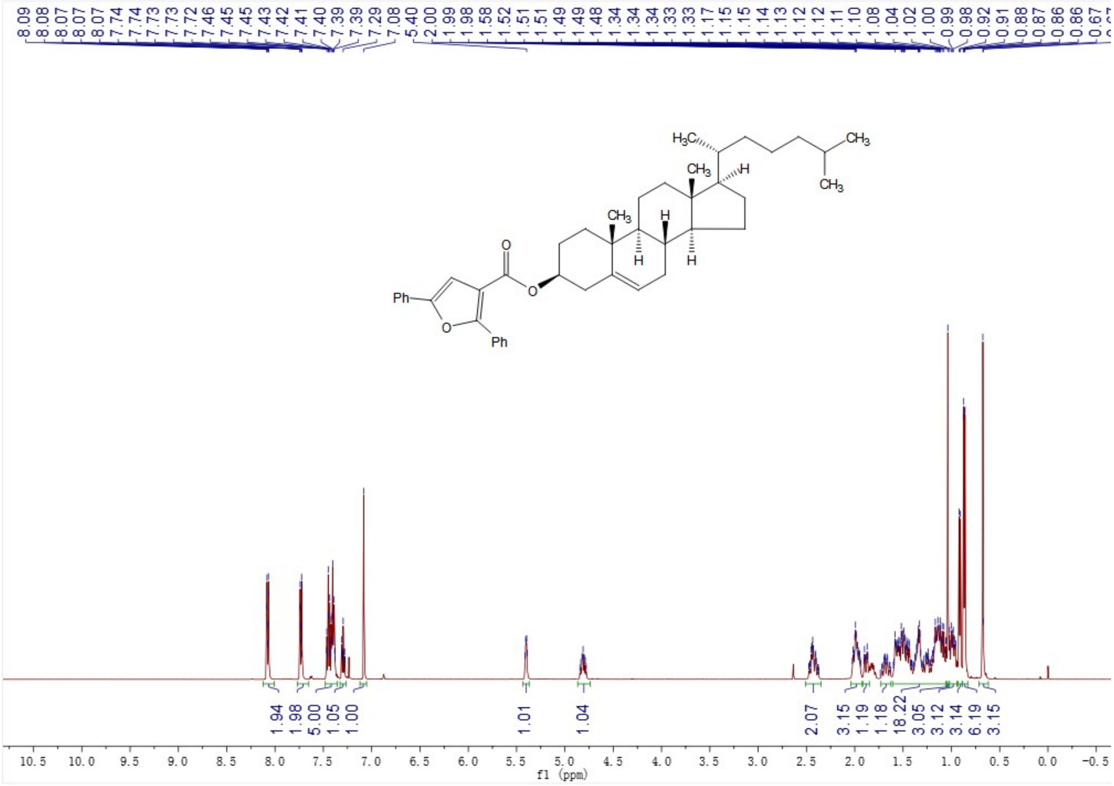
^{1}H NMR (500 MHz, Chloroform-d) of compound **4n.**



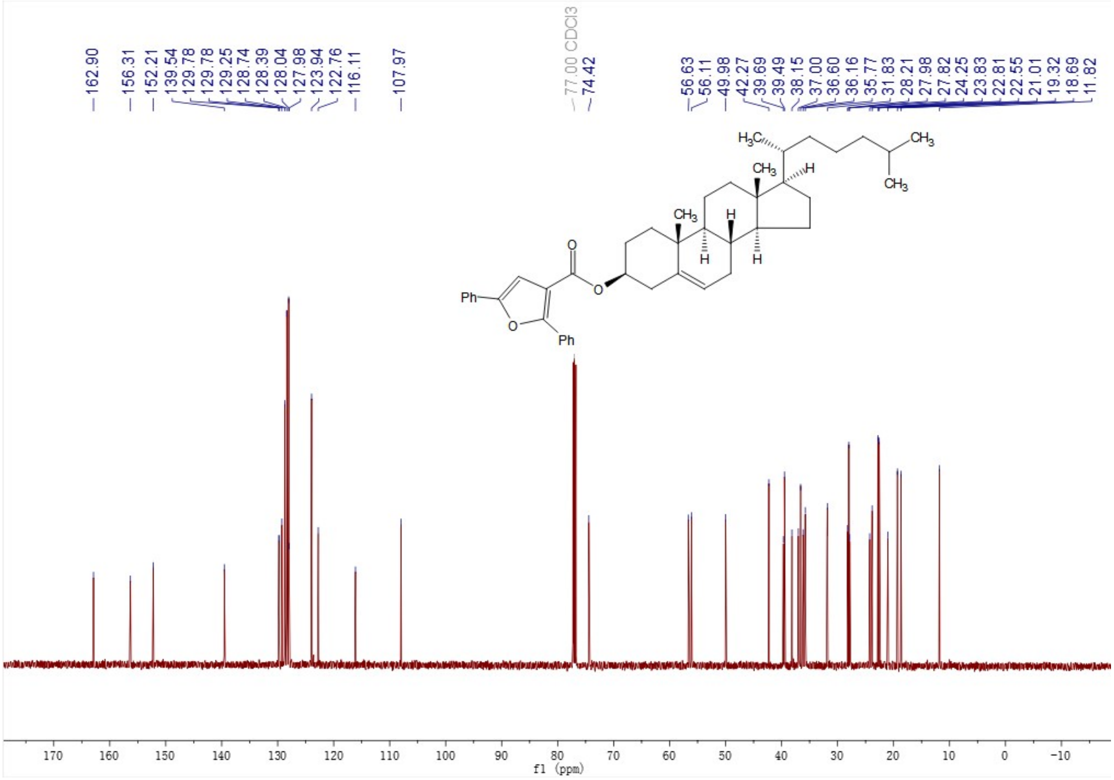
^{13}C NMR (126 MHz, Chloroform-d) of compound **4n.**



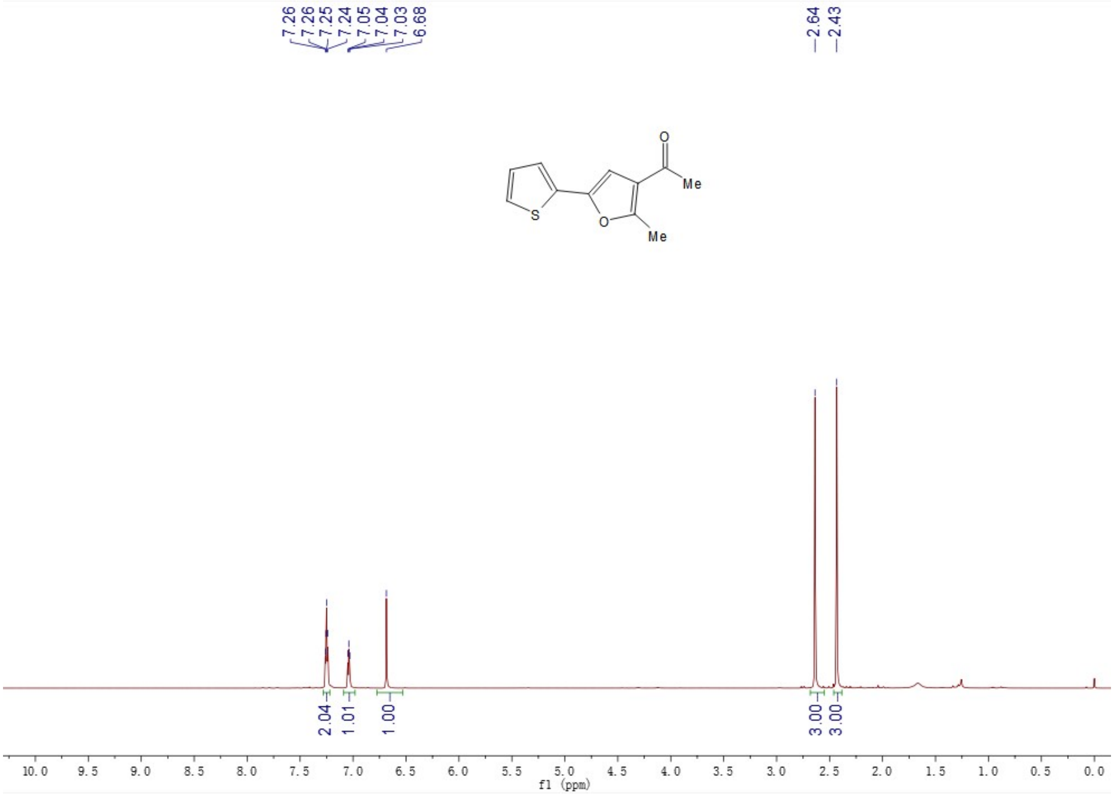
^{1}H NMR (500 MHz, Chloroform-d) of compound **4o.**



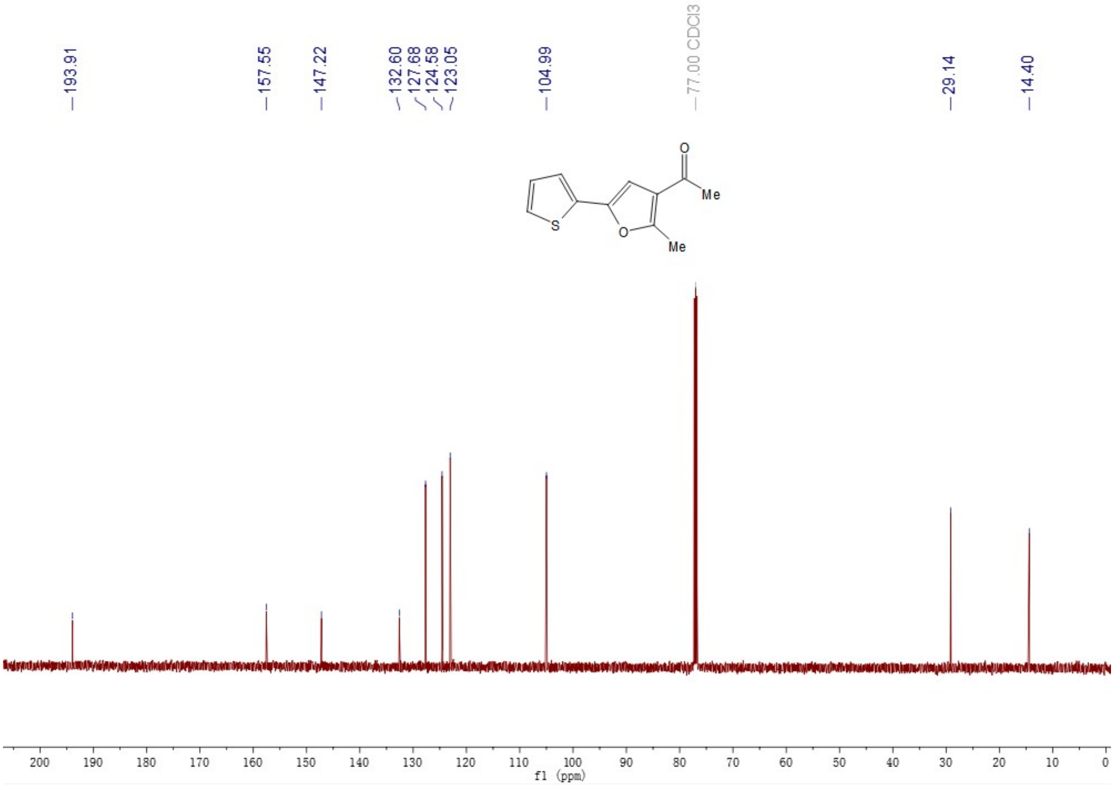
^{13}C NMR (126 MHz, Chloroform-d) of compound **4o.**



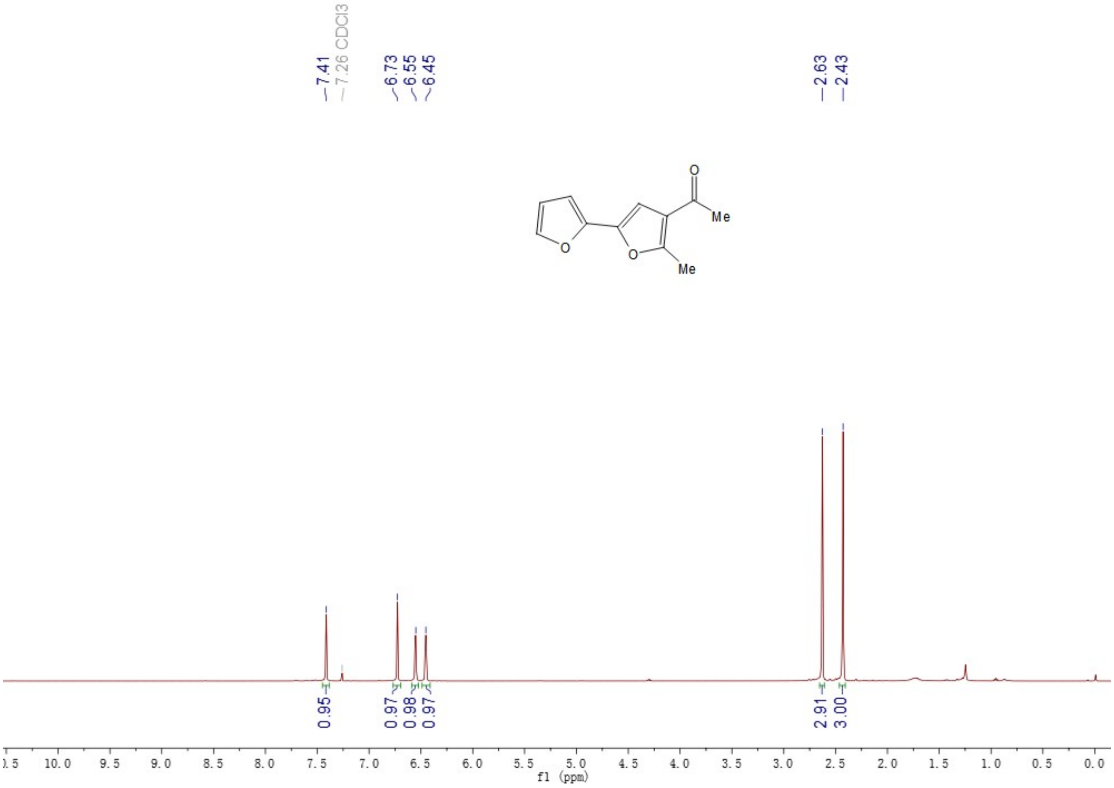
^{1}H NMR (500 MHz, Chloroform-d) of compound **5a.**



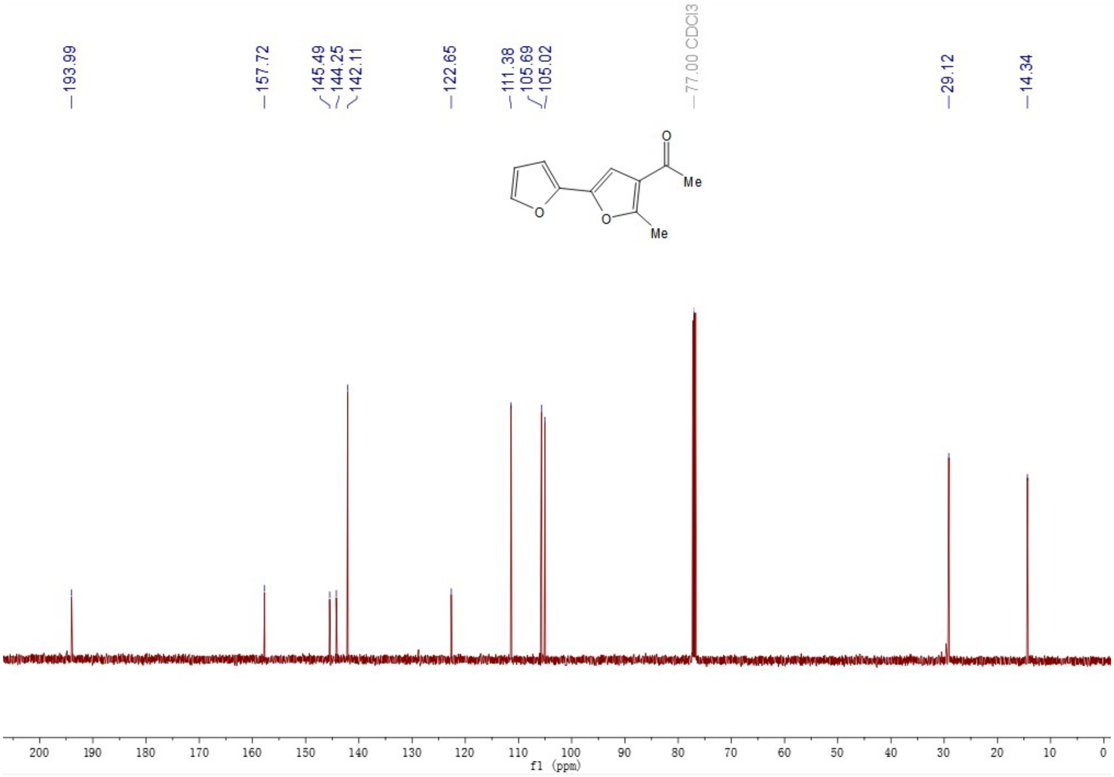
^{13}C NMR (126 MHz, Chloroform-d) of compound **5a.**



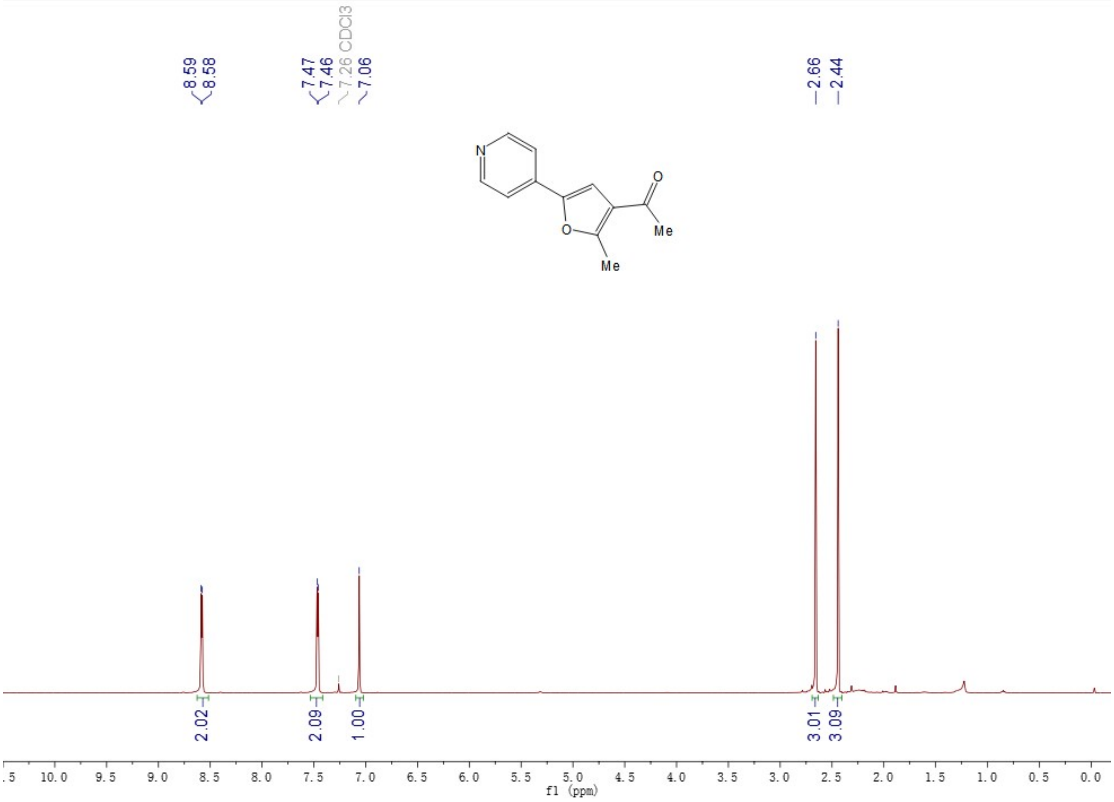
^{1}H NMR (400 MHz, Chloroform-d) of compound **5b.**



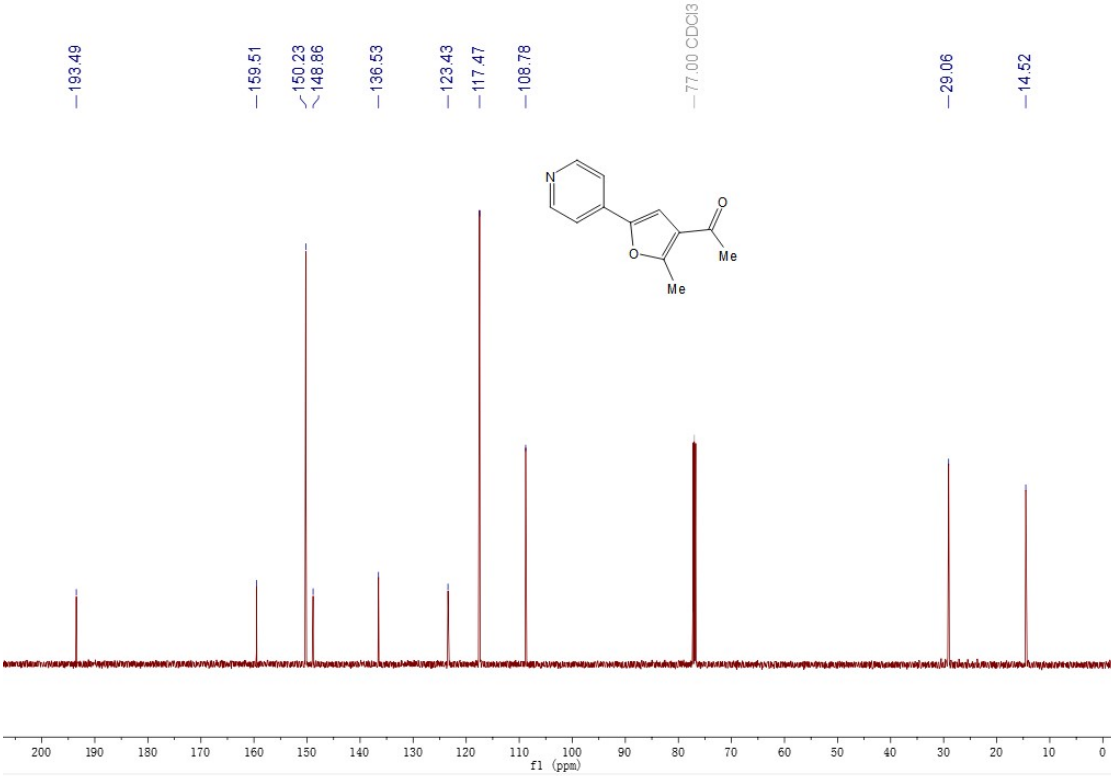
^{13}C NMR (101 MHz, Chloroform-d) of compound **5b.**



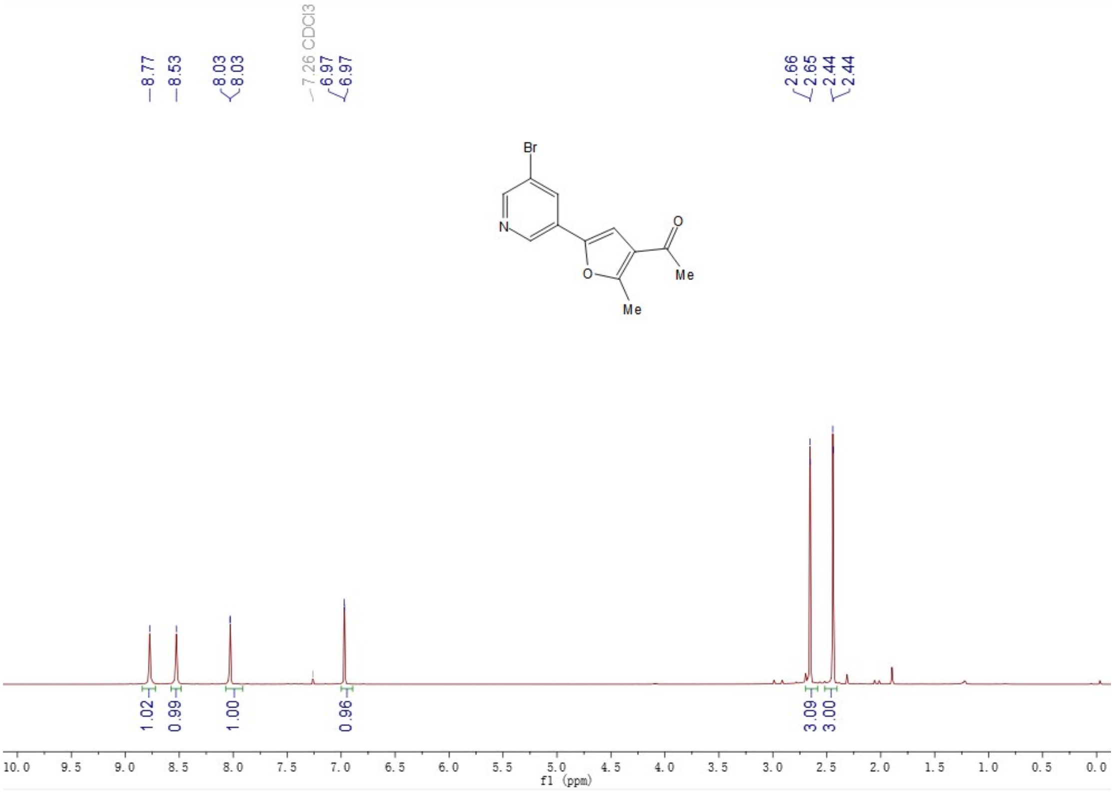
^{1}H NMR (500 MHz, Chloroform-d) of compound **5c.**



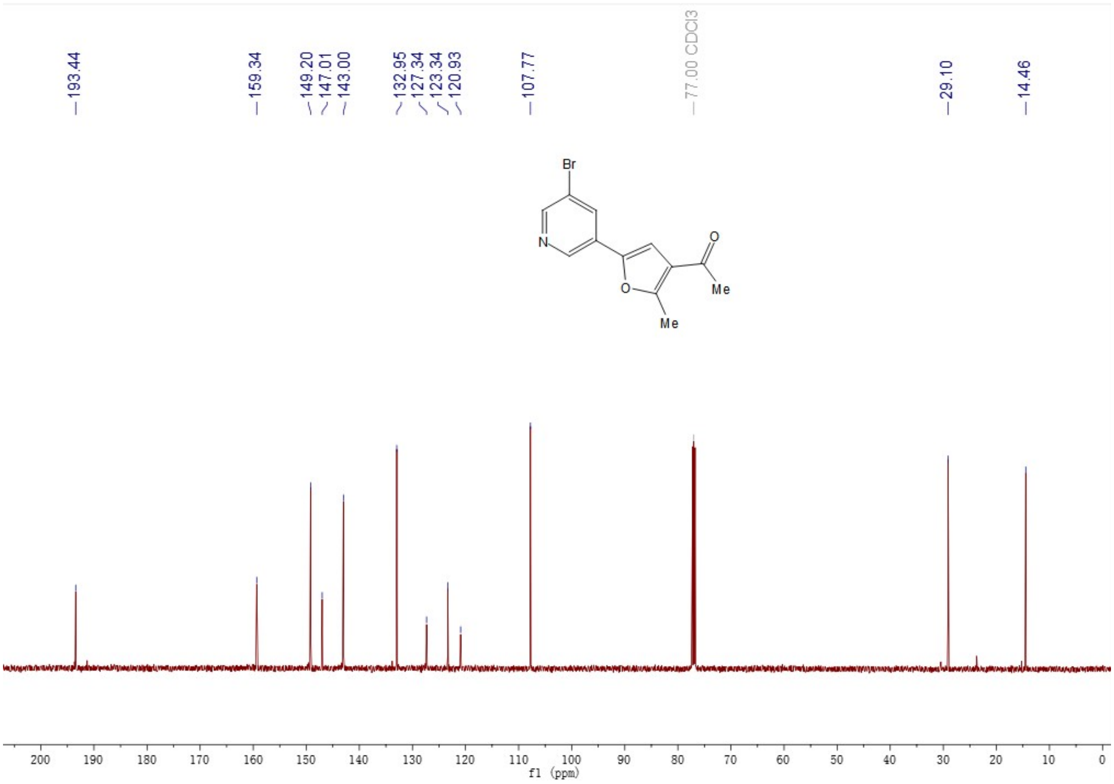
^{13}C NMR (126 MHz, Chloroform-d) of compound **5c.**



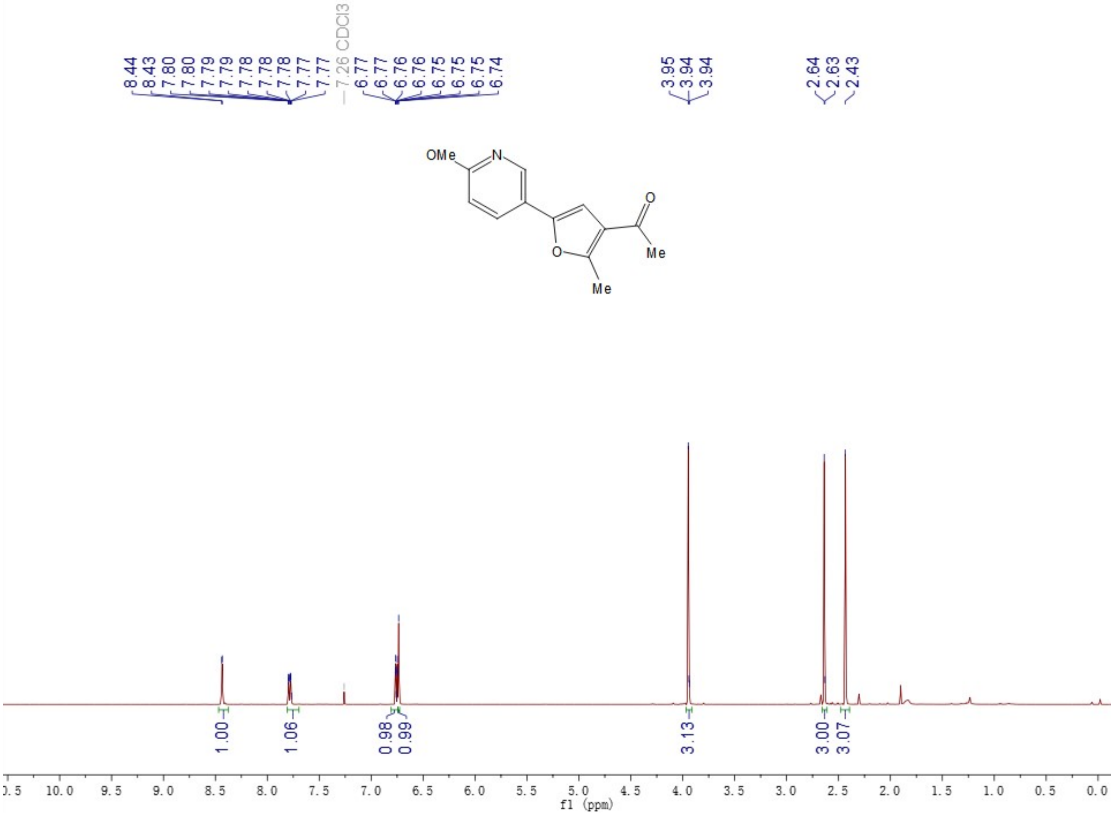
^{1}H NMR (500 MHz, Chloroform-d) of compound **5d.**



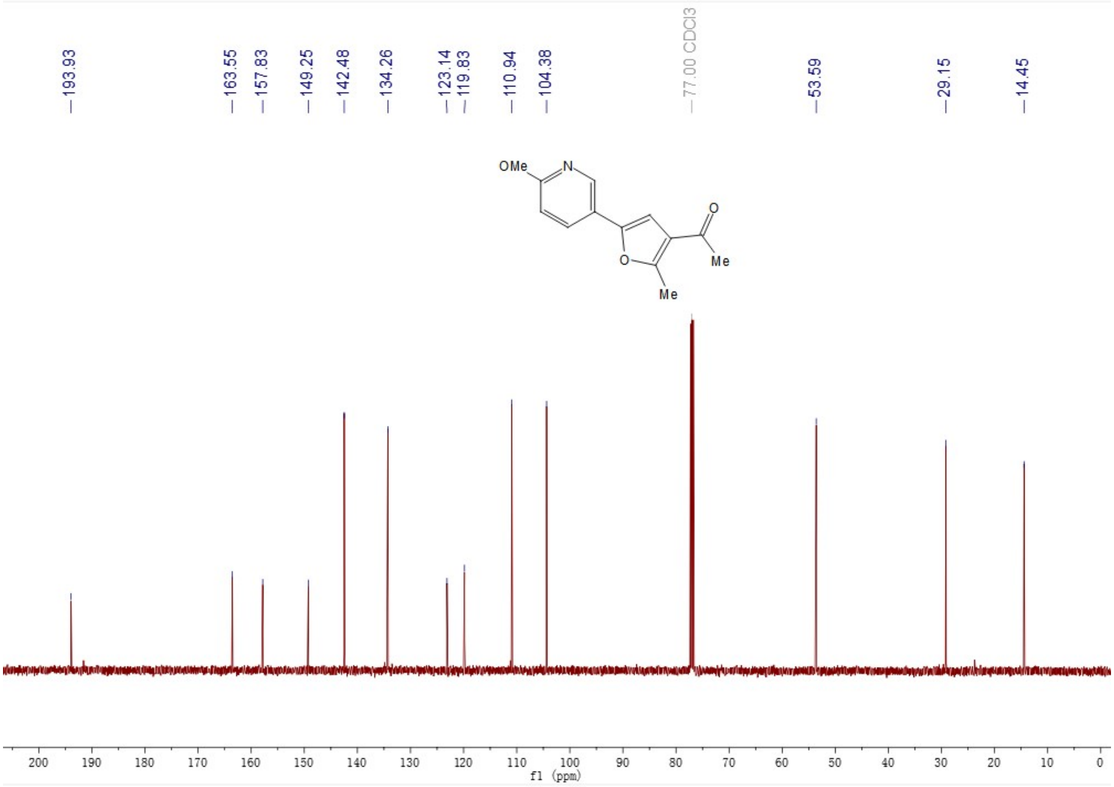
^{13}C NMR (126 MHz, Chloroform-d) of compound **5d.**



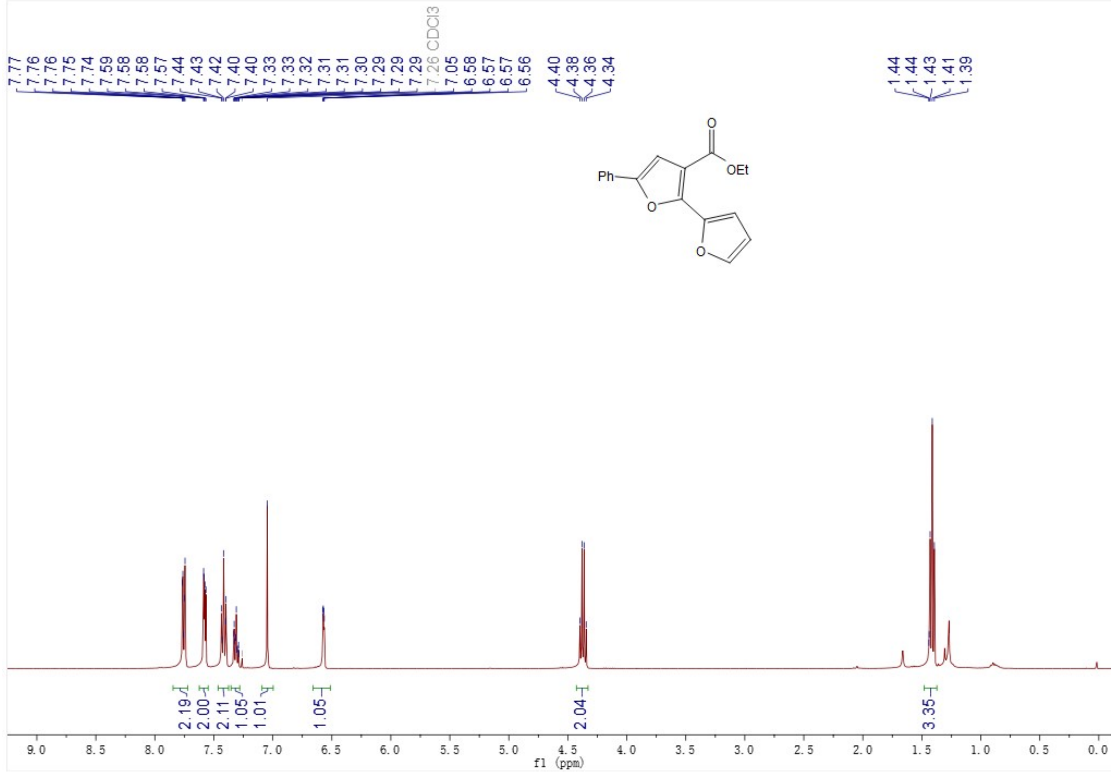
^{1}H NMR (500 MHz, Chloroform-d) of compound **5e.**



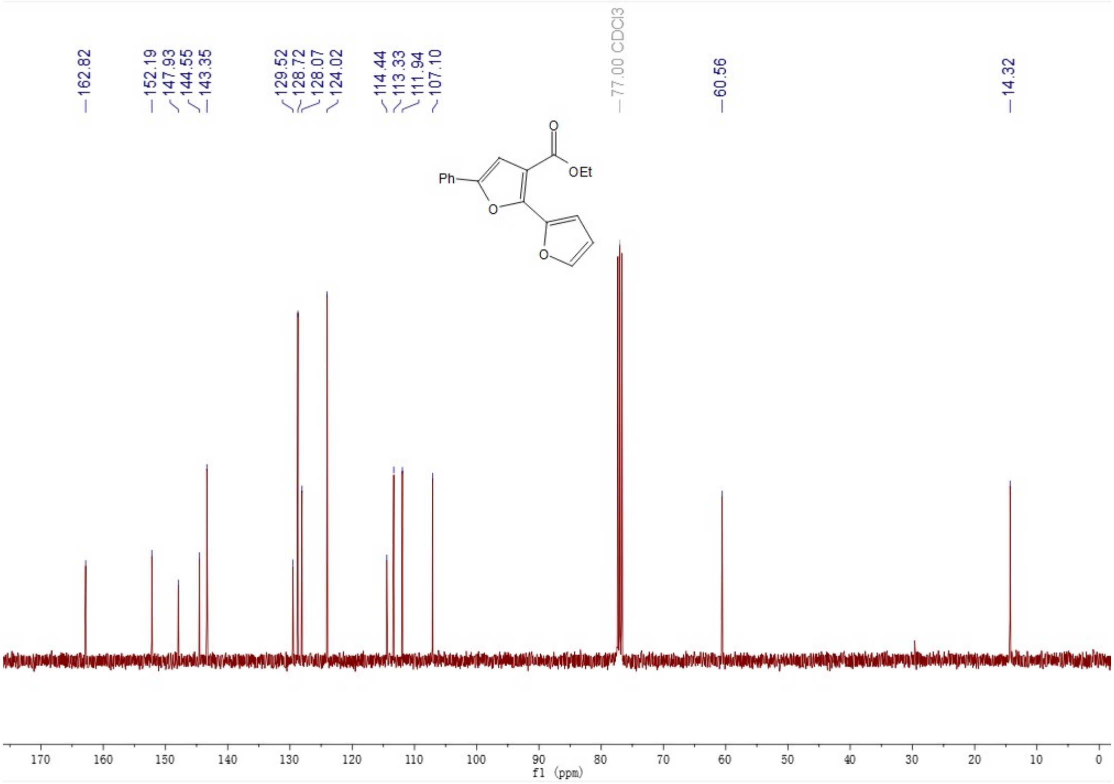
^{13}C NMR (126 MHz, Chloroform-d) of compound **5e.**



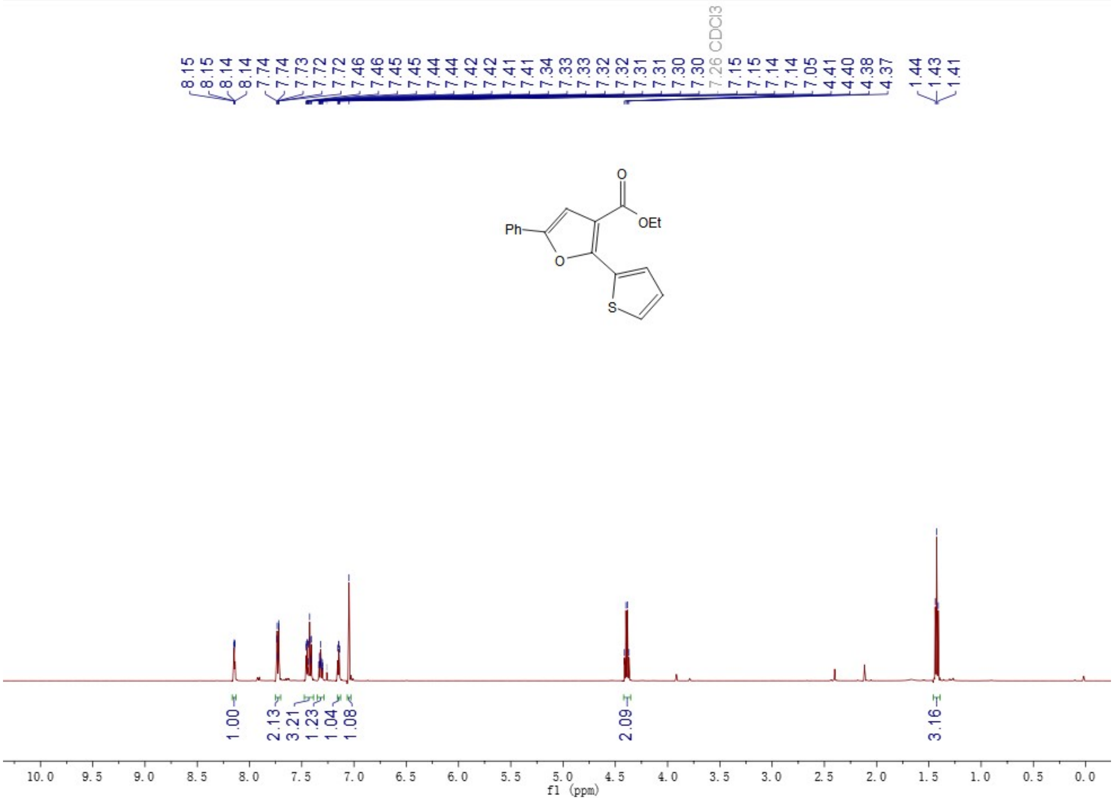
^{1}H NMR (400 MHz, Chloroform-d) of compound **5f.**



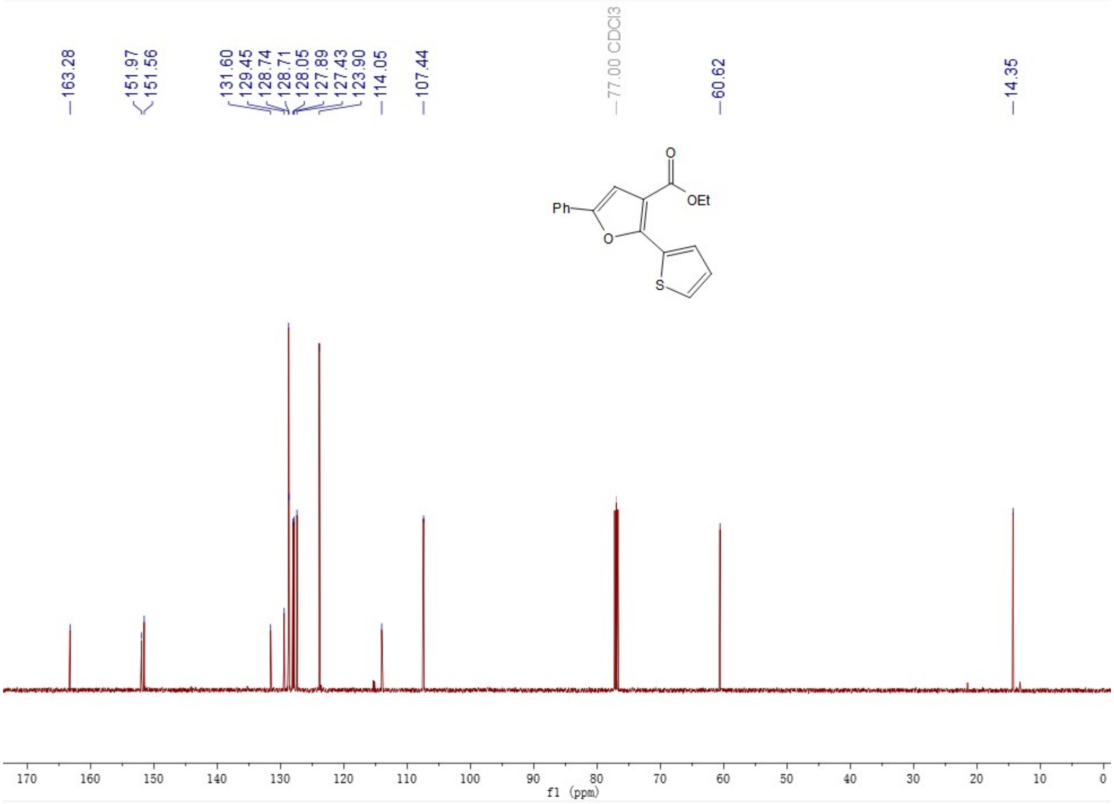
^{13}C NMR (101 MHz, Chloroform-d) of compound **5f.**



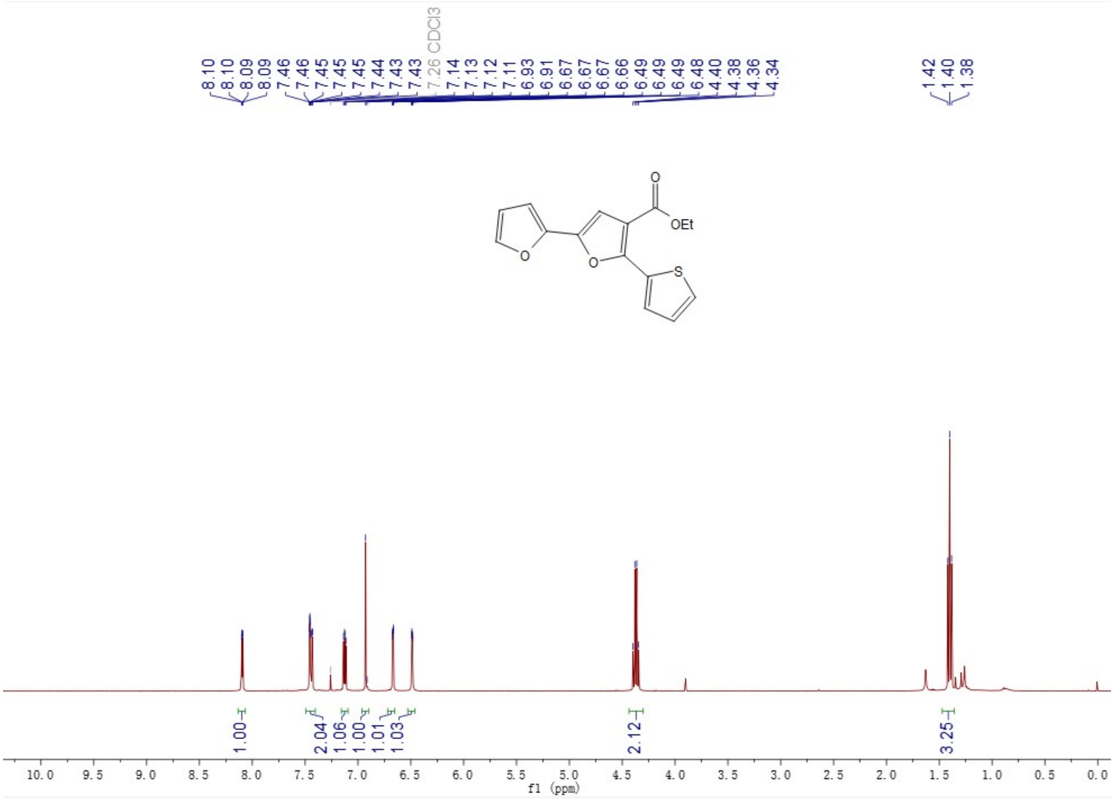
^{1}H NMR (500 MHz, Chloroform-d) of compound **5g.**



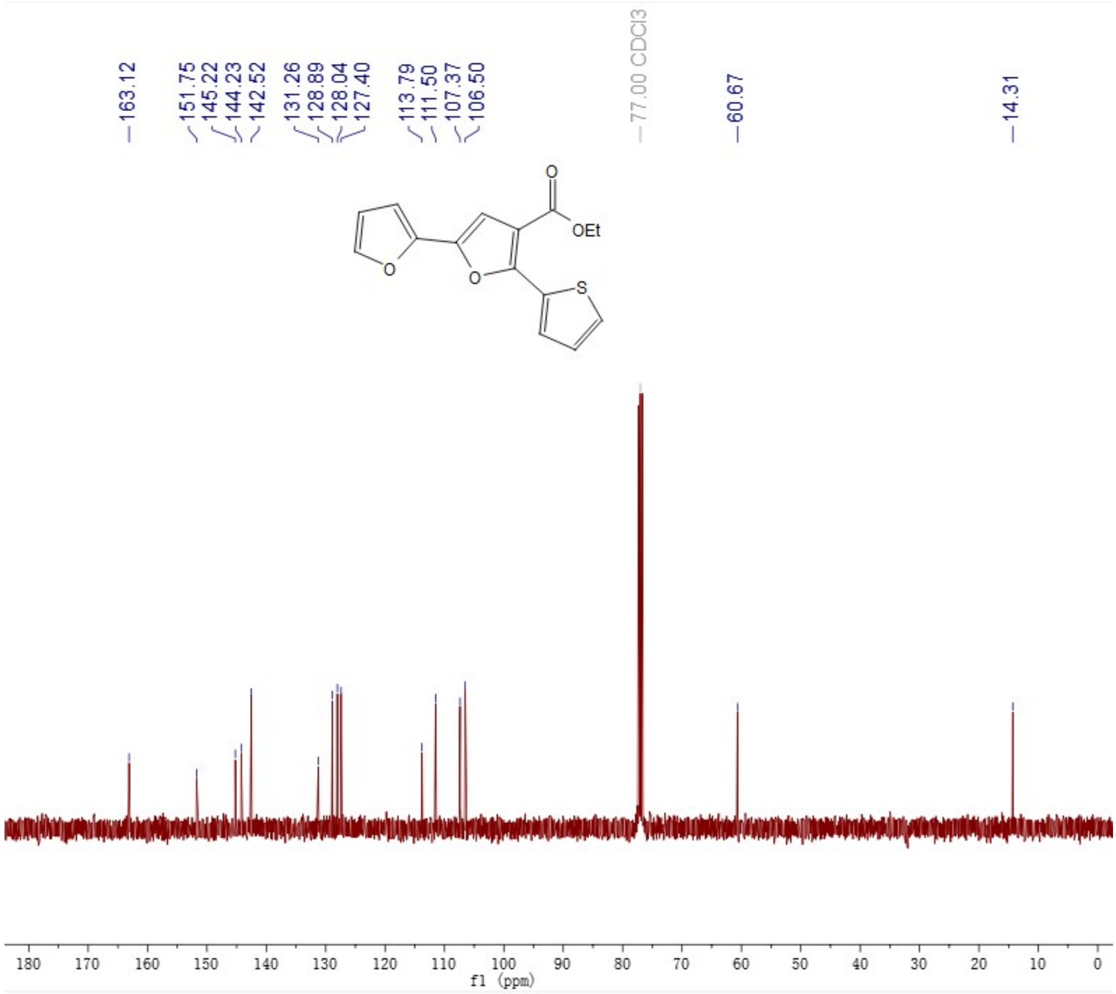
^{13}C NMR (126 MHz, Chloroform-d) of compound **5g.**



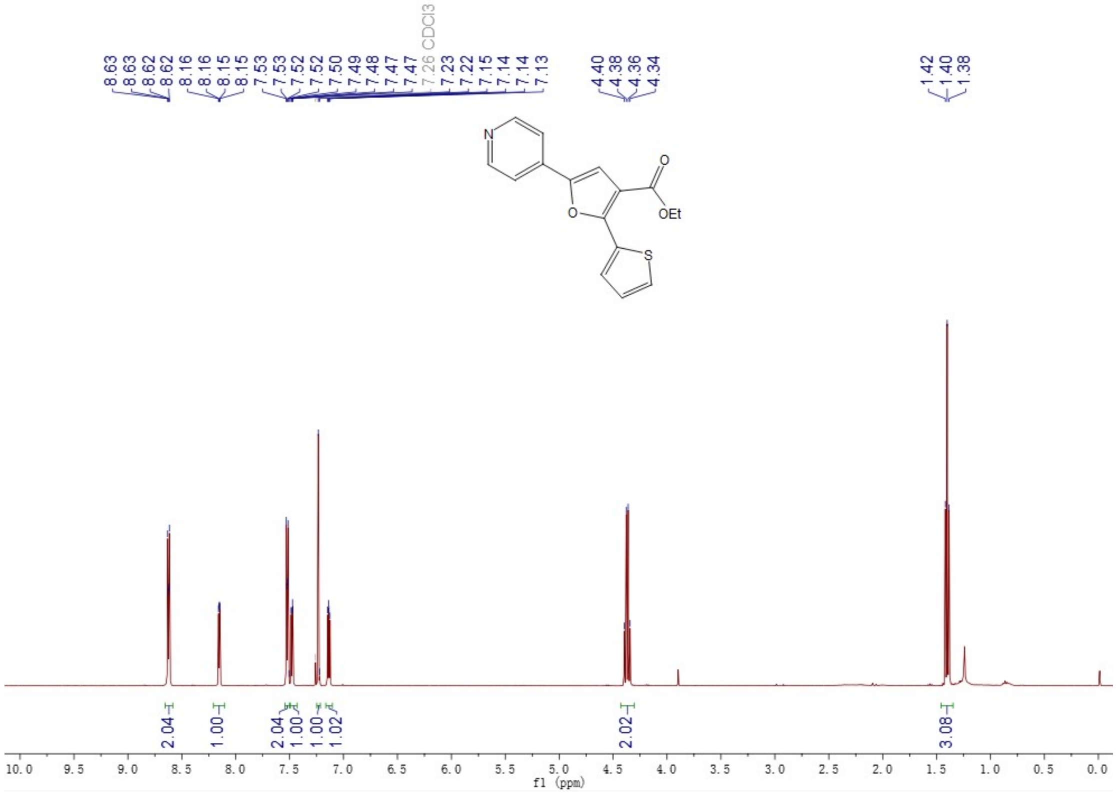
^{1}H NMR (400 MHz, Chloroform-d) of compound **5h.**



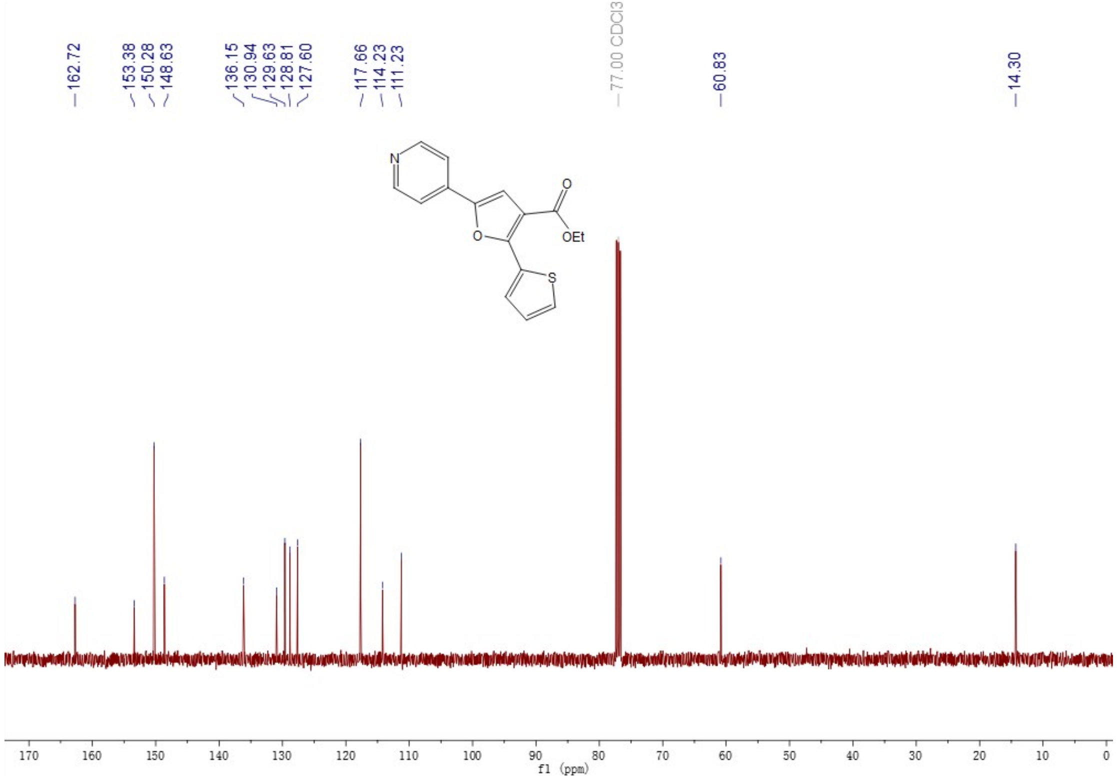
^{13}C NMR (101 MHz, Chloroform-d) of compound **5h.**



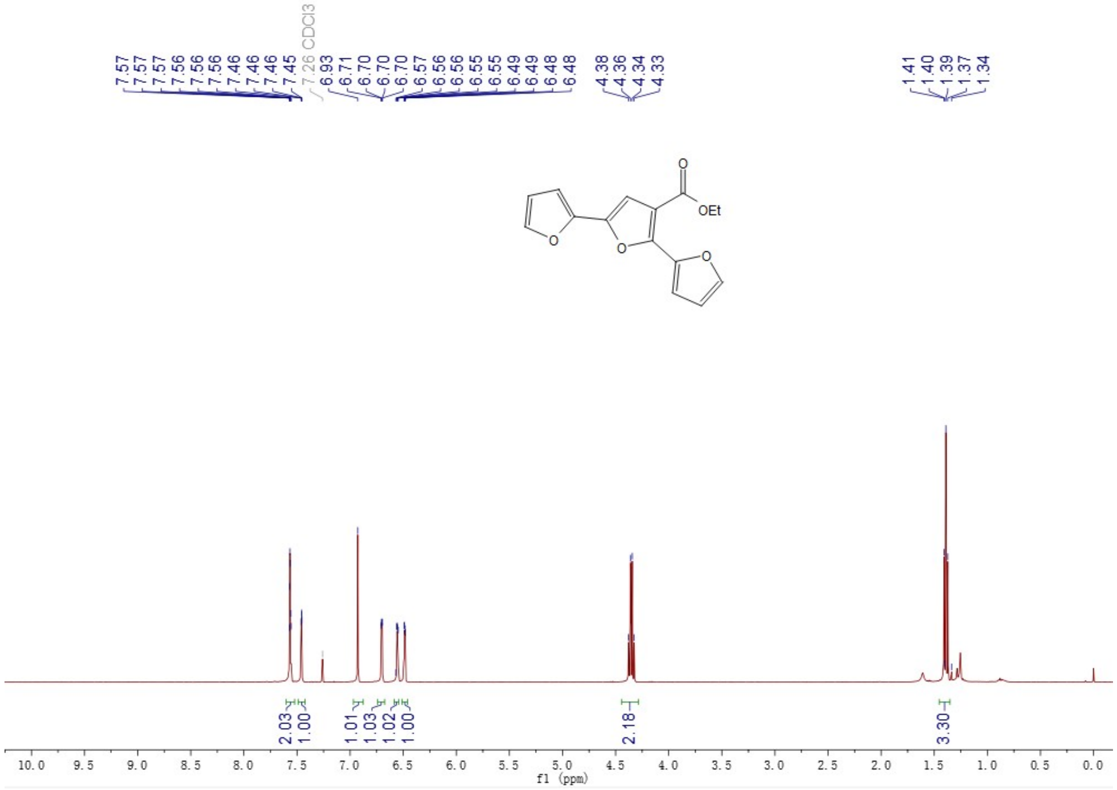
^{1}H NMR (400 MHz, Chloroform-d) of compound **5i.**



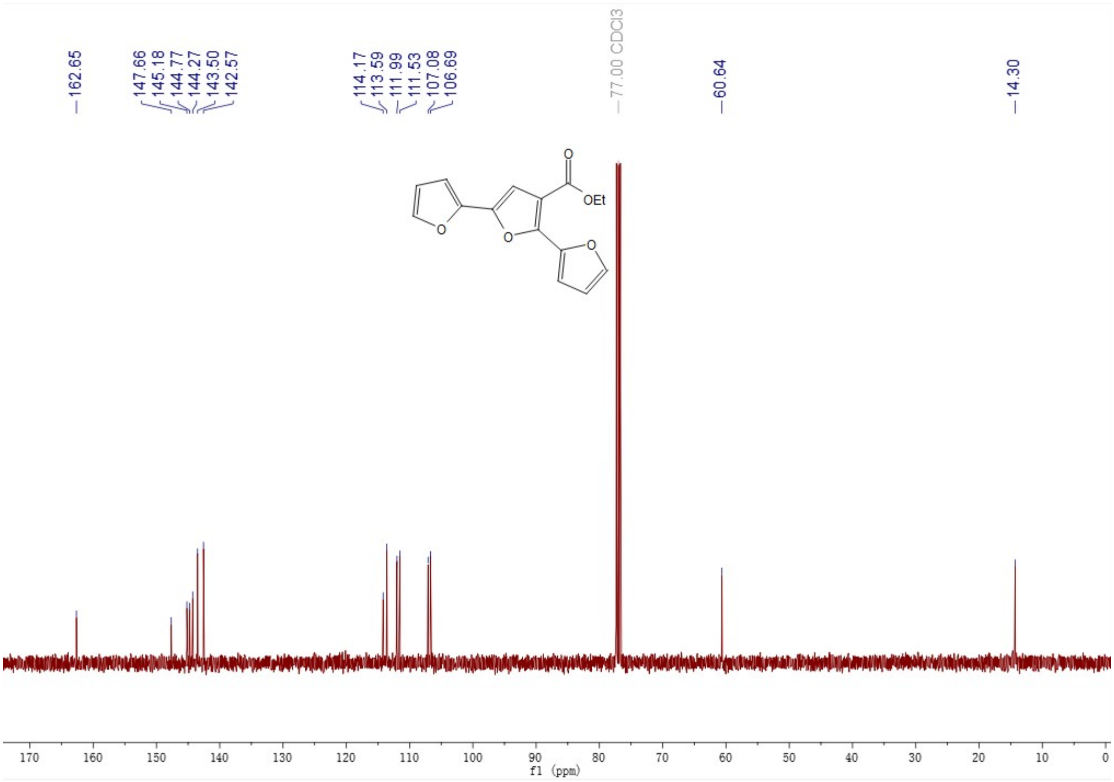
^{13}C NMR (101 MHz, Chloroform-d) of compound **5i.**



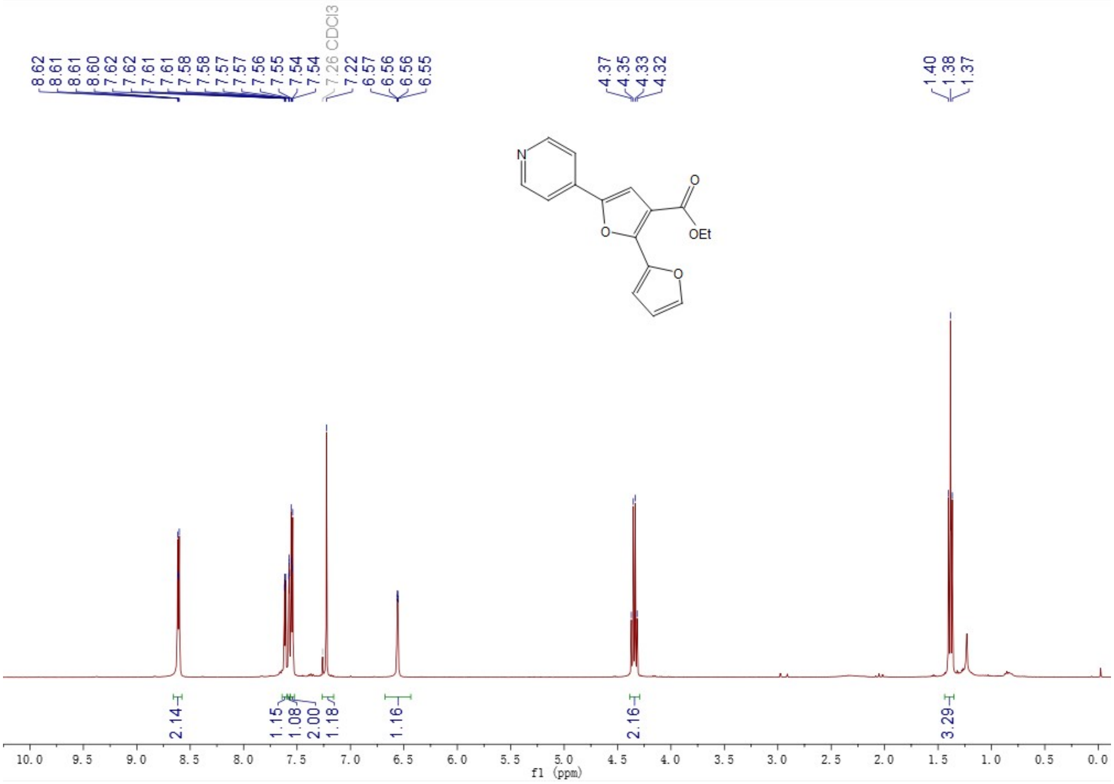
^{1}H NMR (400 MHz, Chloroform-d) of compound **5j.**



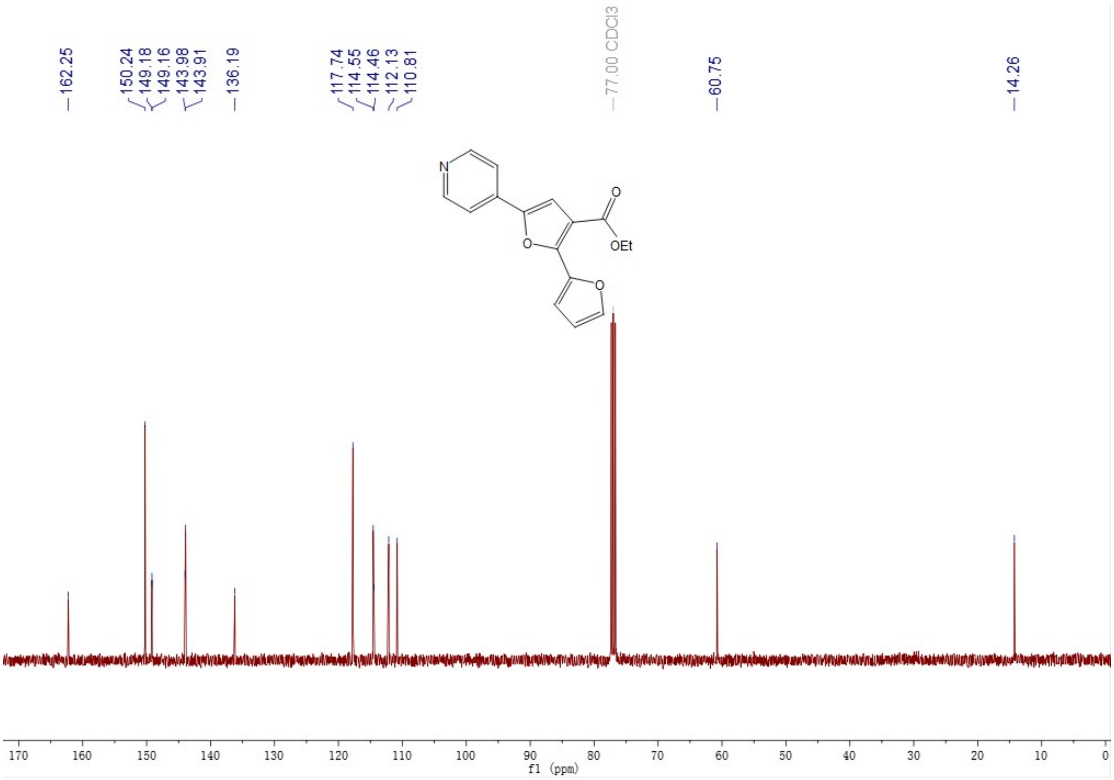
^{13}C NMR (126 MHz, Chloroform-d) of compound **5j.**



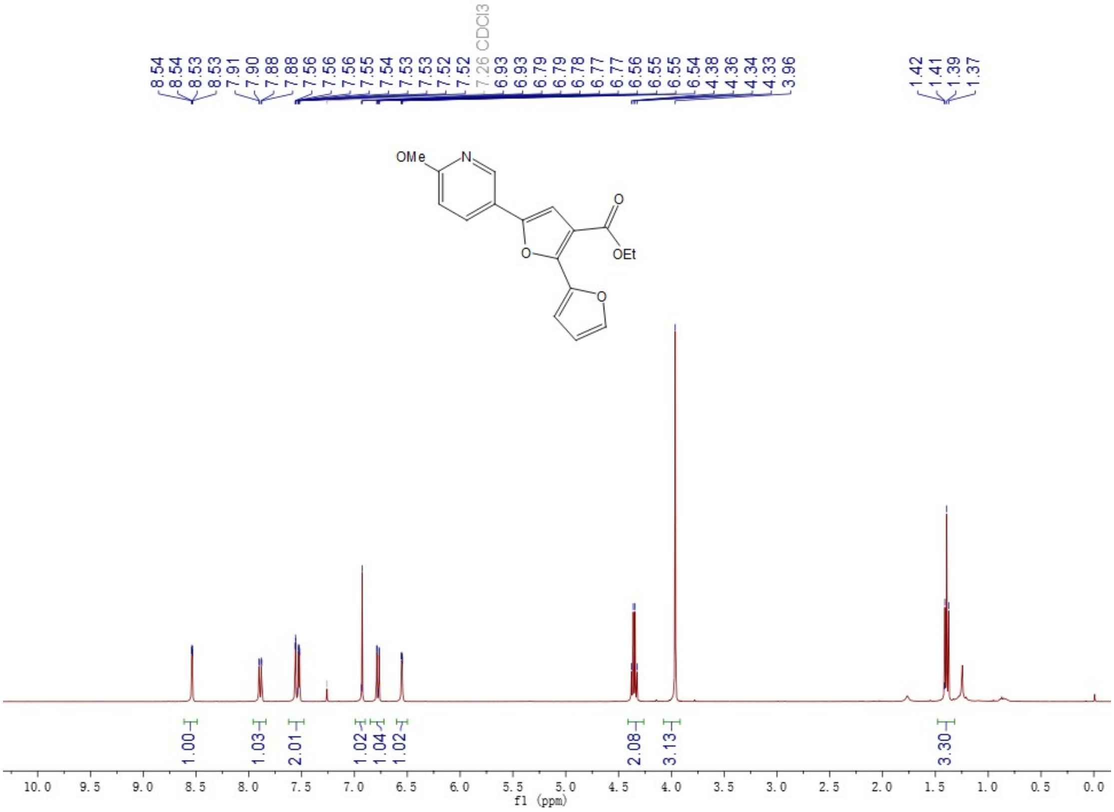
^{1}H NMR (400 MHz, Chloroform-d) of compound **5k.**



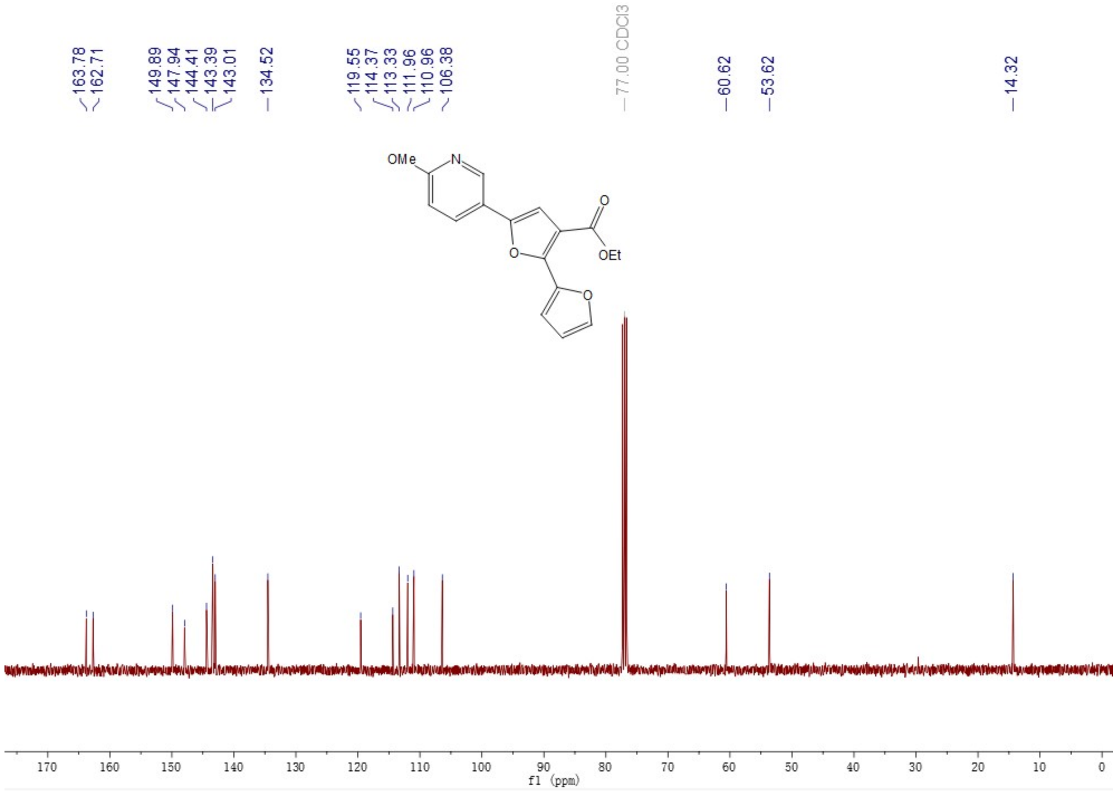
^{13}C NMR (126 MHz, Chloroform-d) of compound **5k.**



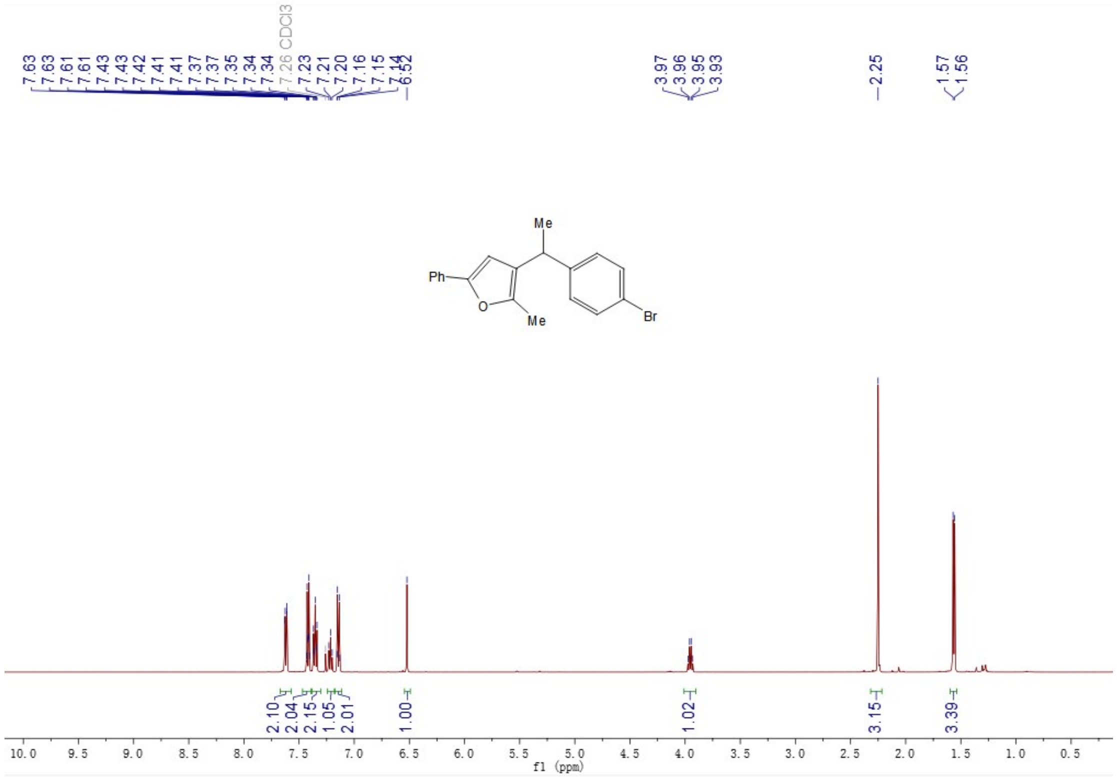
^{1}H NMR (400 MHz, Chloroform-d) of compound **5l.**



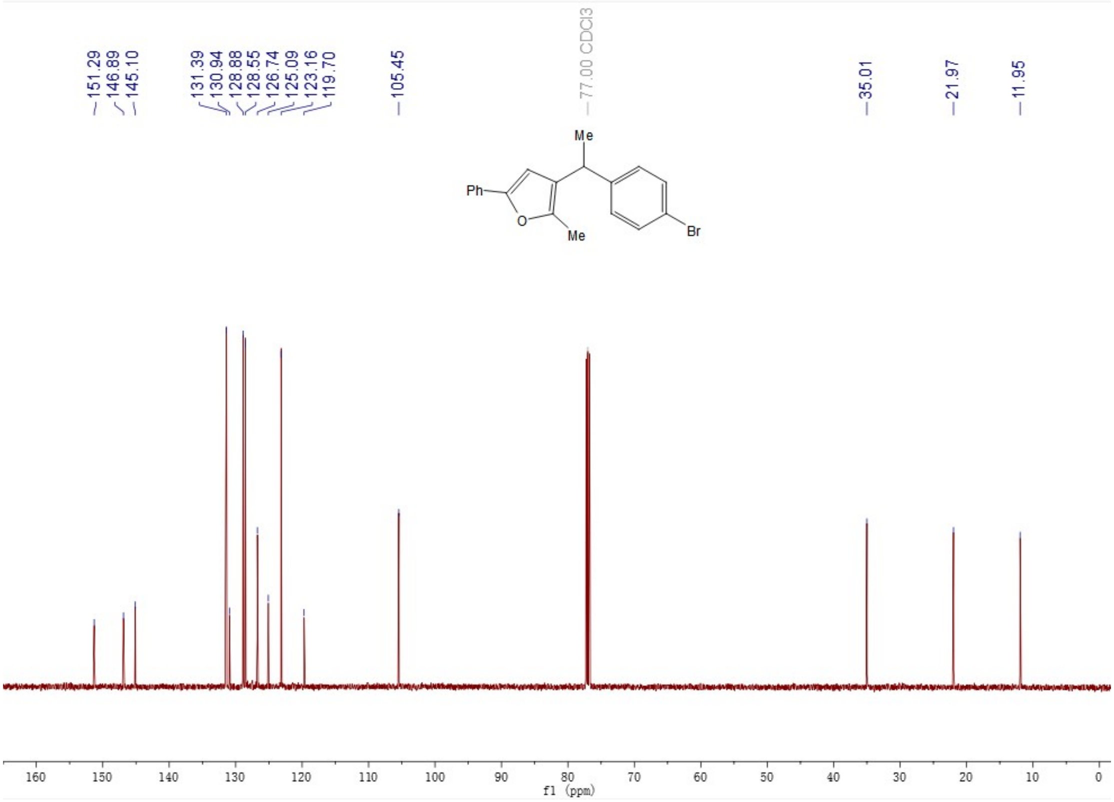
^{13}C NMR (126 MHz, Chloroform-d) of compound **5l.**



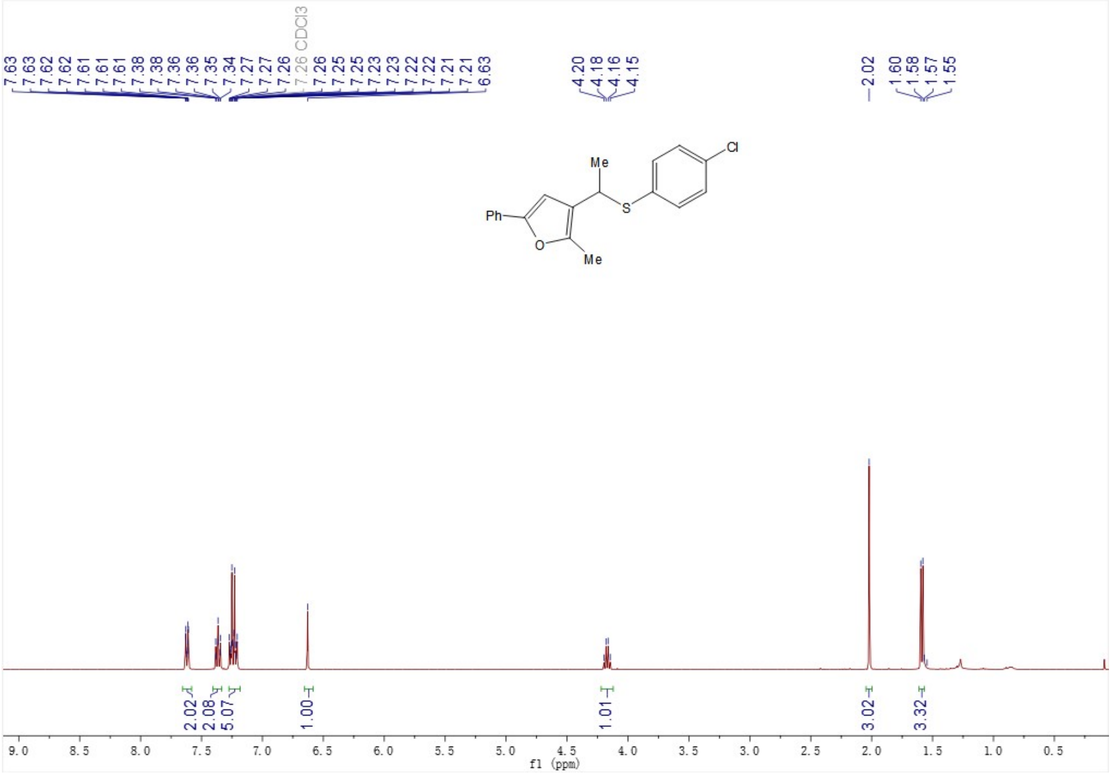
^{1}H NMR (400 MHz, Chloroform-d) of compound **3ab.**



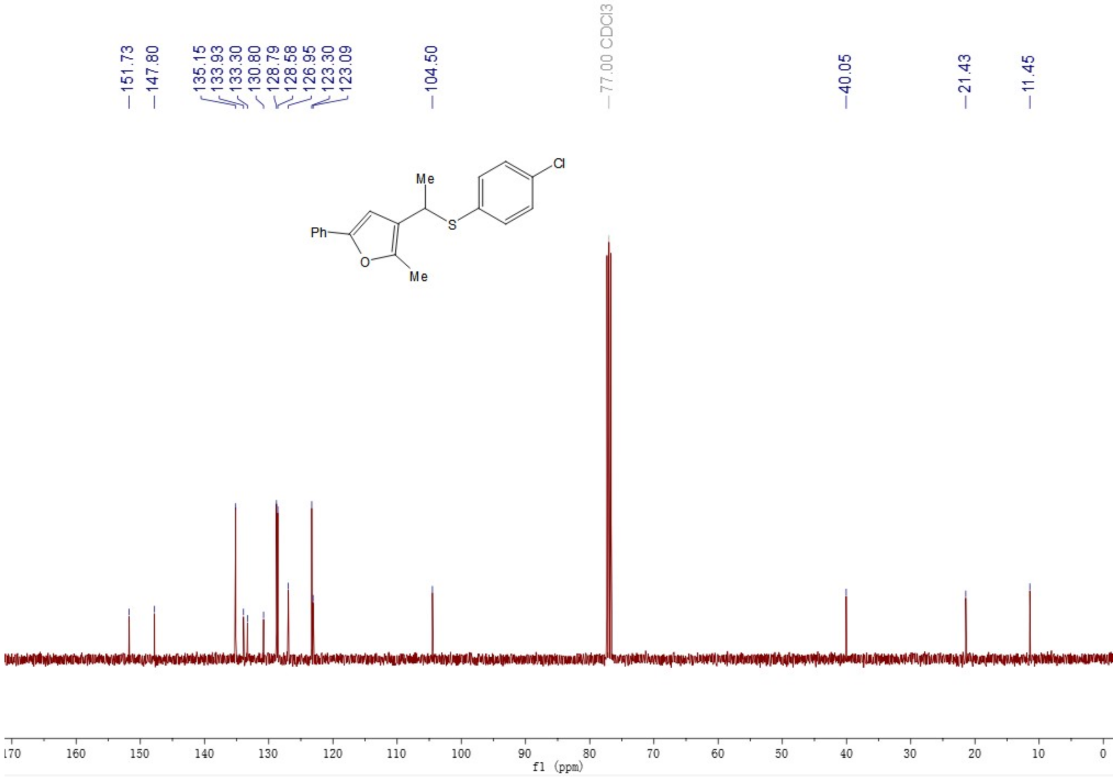
^{13}C NMR (101 MHz, Chloroform-d) of compound **3ab.**



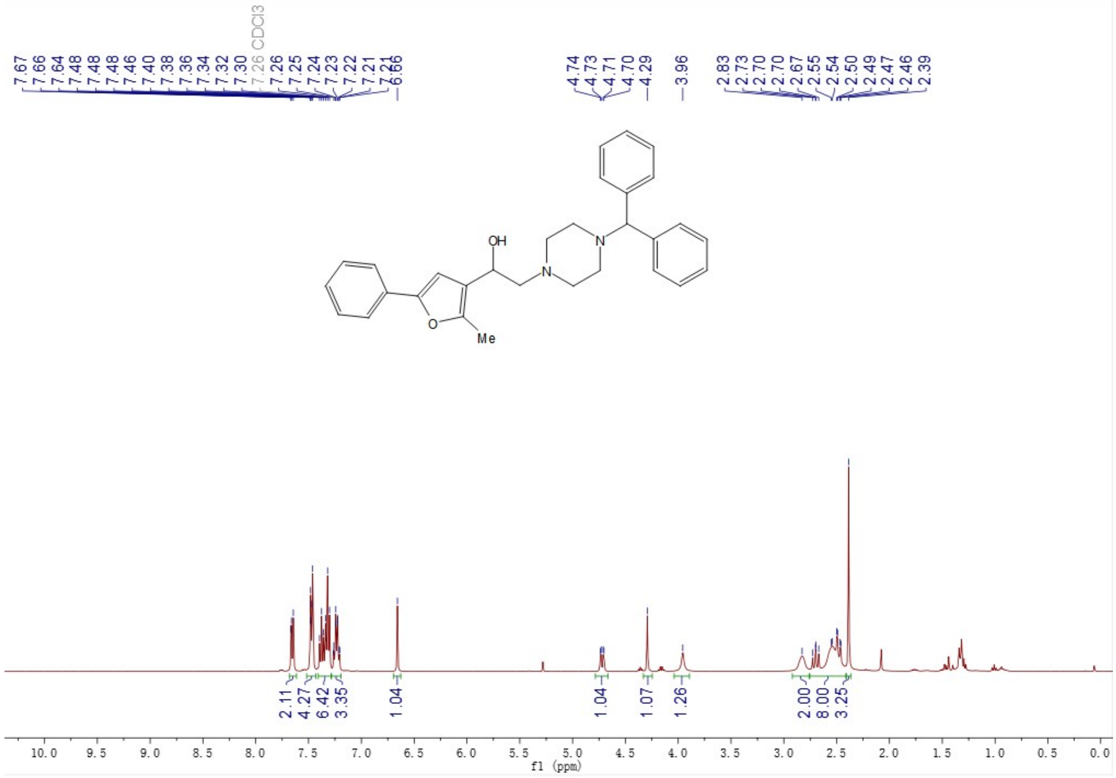
^{1}H NMR (400 MHz, Chloroform-d) of compound **3ac.**



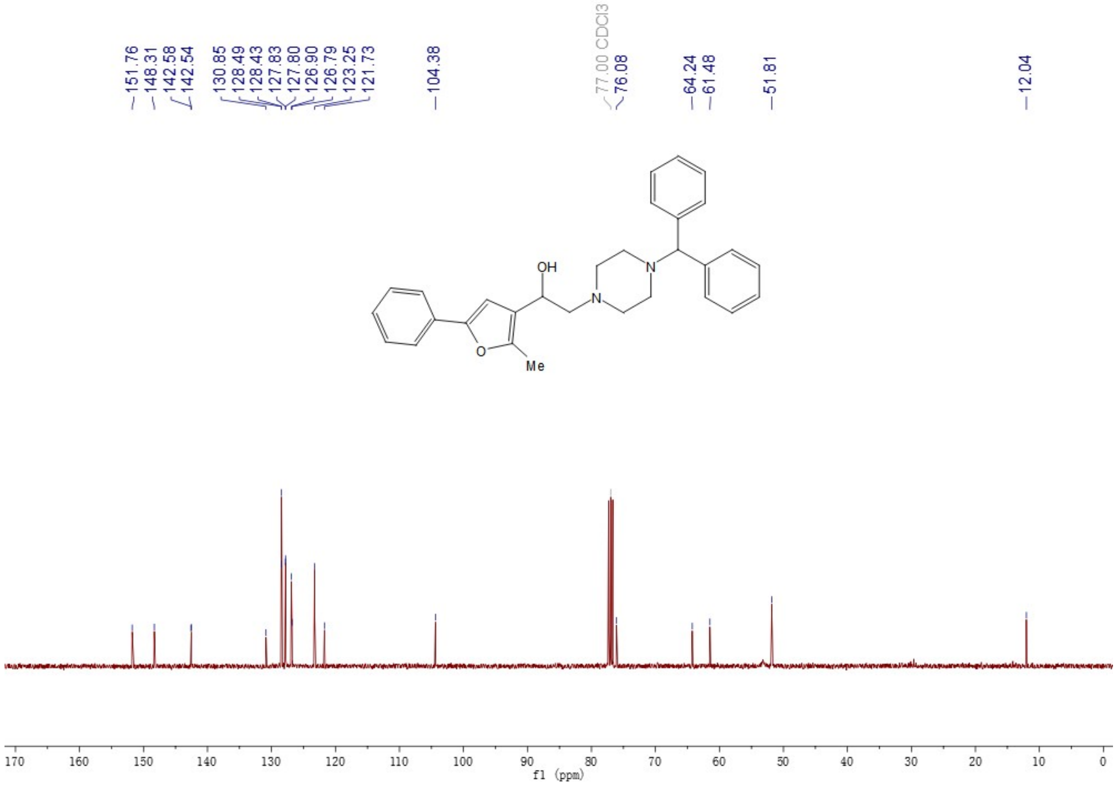
^{13}C NMR (101 MHz, Chloroform-d) of compound **3ac.**



^{1}H NMR (400 MHz, Chloroform-d) of compound **3ad.**



^{13}C NMR (101 MHz, Chloroform-d) of compound **3ad.**


151.76
148.31
142.58
142.54
130.85
128.49
128.43
127.83
127.80
126.90
126.79
123.25
121.73
104.38
77.00 CDCl3
76.08
64.24
61.48
51.81
12.04
OH
N
N
O
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5. References

1. Lu, C.; Li, X.; Chang, S.; Zhang, Y.; Xing, D.; Wang, S.; Lin, Y.; Jiang, H.; Huang, L. *Org. Chem. Front.* **2022,** *9*, 2382-2389.

2. Ouellet, S. G.; Roy, A.; Molinaro, C.; Angelaud, R.; Marcoux, J. F.; O'Shea, P. D.; Davies, I. W. *J. Org. Chem.* **2011,** *76*, 1436-1439.

3. Smadi, M. A.; Ratrout, S. *Molecules.* **2004,** *9*, 957-967.

4. Chen, J.; Jiang, Y.; Yu, J. T.; Cheng, J. *J. Org. Chem.* **2016,** *81*, 271-275.

5. Wang, C.; Geng, X.; Zhao, P.; Zhou, Y.; Wu, Y. D.; Cui, Y. F.; Wu, A. X. *Chem. Commun.* **2019,** *55*, 8134-8137.

6. Yang, X. L.; Guo, J. D.; Xiao, H.; Feng, K.; Chen, B.; Tung, C. H.; Wu, L. Z. *Angew. Chem. Int. Ed.* **2020,** *59*, 5365-5370.

7. Lapointe, D.; Markiewicz, T.; Whipp, C. J.; Toderian, A.; Fagnou, K. *J. Org. Chem.* **2011,** *76*, 749-759.

8. Li, J.; Xing, H. W.; Yang, F.; Chen, Z. S.; Ji, K. *Org. Lett.* **2018,** *20*, 4622−4626.

9. Rao, M. S.; Haritha, M.; Chandrasekhar, N.; Basaveswara Rao, M. V.; Pal, M. *Arab. J. Chem.* **2019,** *12*, 2697-2703.

10. He, C.; Guo, S.; Ke, J.; Hao, J.; Xu, H.; Chen, H.; Lei, A. *J. Am. Chem. Soc.* **2012,** *134*, 5766-5769.

11. Zhao, L.; Wong, W. Y.; Mak, T. C. *Chem. Eur. J.* . **2006,** *12*, 4865-4872.

12. Huang, W.; Liu, C.; Gu, Y. *Adv. Syn.Catal.* **2017,** *359*, 1811-1818.

13. Zhang, X. X.; Dai, W. P.; Wu, W.; Cao, S. *Org. Lett.* **2015,** *17*, 2708−2711.

14. Remizov, Y. O.; Pevzner, L. M.; Petrov, M. L. *Russ. J. Gen. Chem.* **2018,** *88*, 1402-1410.

15. Zheng, M. F.; Huang, L. B.; Wu, W. Q.; Jiang, H. F. *Org. Lett.* **2013,** *15*, 1838–1841.

16. Li, P.; Zhao, J.; Xia, C.; Li, F. *Org. Lett.* **2014,** *16*, 5992-5995.

17. Qian, C. Y. *J. Heterocyclic Chem.* **1994,** *31*, 1219-1227

18. Cao, H.; Zhan, H. Y.; Cen, J. H.; Lin, J. X.; Lin, Y. G.; Zhu, Q. X.; Jiang, H. F. *Org. Lett.* **2013,** *15*, 1080–1083.

19. You, C.; Zhang, Z.; Tu, Y.; Tang, H.; Wang, Y.; Long, D.; Zhao, J. *J. Org. Chem.* **2020,** *85*, 3902-3910.

20. Roslan, I. I.; Sun, J.; Chuah, G.-K.; Jaenicke, S. *Adv.Syn. Catal.* **2015,** *357*, 719-726.

21. Pang, W.; Zhu, S.; Xin, Y.; Jiang, H.; Zhu, S. *Tetrahedron.* **2010,** *66*, 1261-1266.

22. Feng, L.; Yan, H.; Yang, C.; Chen, D.; Xia, W. *J. Org. Chem.* **2016,** *81*, 7008-7022.

23. Koch, R.; Berstermann, H. M.; Wentrup, C. *J. Org. Chem.* **2014,** *79*, 65-71.