Supporting Information

Sulfonium Triggered One-Pot Synthesis of Dihydrofurans via [3+2] Annulation of Alkenes and Active Methylene Compounds

Li Yang [a], Jin-Long Wang [b], Jia Shu [a], Xiang-Qin Xu [a], Shan-Shan Tang [a], and Long-Yong Xie *, [a]

[a] *College of Chemistry and Bioengineering, Hunan University of Science and Engineering, Yongzhou, 425100, China;*

[b] *College of Biological and Pharmaceutical Sciences, China Three Gorges University, 443002, Yichang, China*

E-mail: longyongxie@yeah.net

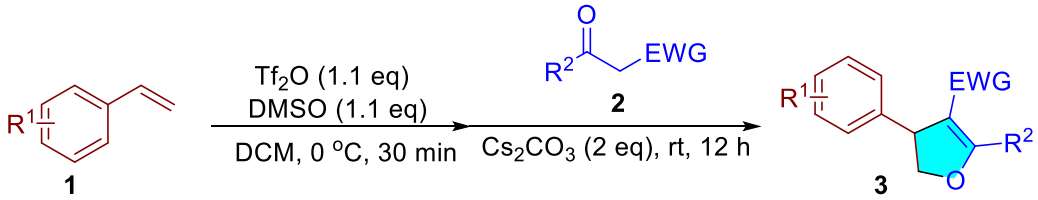
Table of Content

1. General Information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded at 400, 100, 162 and 376 MHz, respectively. Chemical shifts were quoted in ppm relative to $CDCl_3$ (δ_H = 7.26, δ_C = 77.0 ppm). Datas are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. The reactions were monitored by thin-layer chromatography (TLC) using GF_{254} silica gel-coated TLC plates. Mass spectra were performed on a spectrometer operating on ESI-TOF. Melting points were measured on a melting point apparatus and were uncorrected.

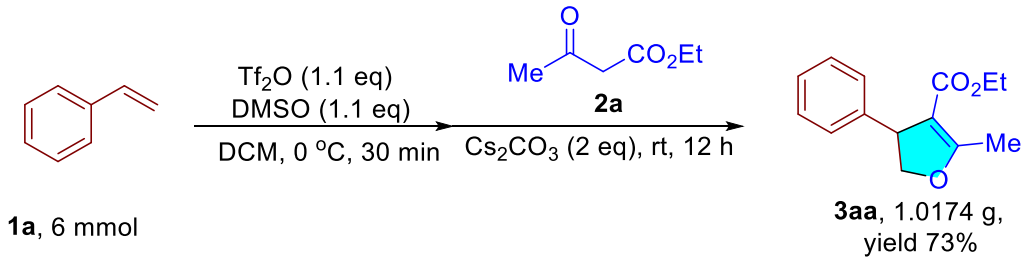
2. Experimental Section

General procedure for the synthesis of 2,3-dihydrofurans



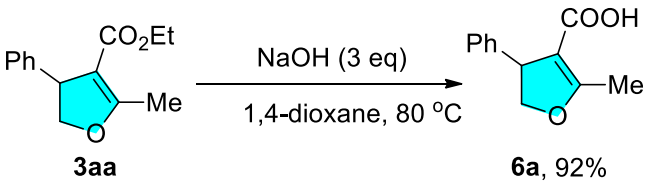
A 10 mL round-bottom flask equipped with a stirring bar was charged with styrene **1** (0.3 mmol, 1eq), and DMSO (0.33 mmol, 1.1 eq) in DCM (3 mL). The mixture was stirred at 0 °C, followed by the dropwise addition of Tf_2O (0.33 mmol, 1.1 eq), and stirred for 0.5 h, then, **2** (0.45 mmol, 1.5 eq), and Cs_2CO_3 (0.6 mmol, 2 eq) was added at room temperature for 12 h, with progress monitored by TLC. Upon completion, 10 mL of H_2O was added to the mixture, followed by extraction with DCM three times (10 mL × 3). The organic phase was subsequently dried over anhydrous sodium sulfate, concentrated under vacuum, and the residue was purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 20:1-10:1) to afford the desired products **3**.

Gram-scale synthesis of 3aa



A 100 mL round-bottom flask equipped with a stirring bar was charged with styrene **1a** (6 mmol, 0.6249 g), and DMSO (6.6 mmol, 0.5157 g) in DCM (60 mL). The mixture was stirred at 0 °C, followed by the dropwise addition of Tf_2O (6.6 mmol, 1.8621 g), and stirred for 0.5 h, then, **2a** (9 mmol, 1.1713 g), and Cs_2CO_3 (12 mmol, 3.9098 g) was added at room temperature for 12 h, with progress monitored by TLC. Upon completion, 30 mL of H_2O was added to the mixture, followed by extraction with DCM three times (30 mL × 2). The organic phase was subsequently dried over anhydrous sodium sulfate, concentrated under vacuum, and the residue was purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 20:1-10:1) to afford 1.0174 g of **3aa** in 73% isolated yield .

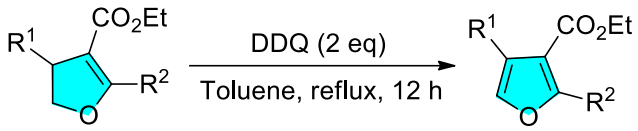
Hydrolysis reaction of 3aa



3aa **6a**, 92%

A 10 mL round-bottom flask equipped with a stirring bar was charged with **3aa** (1 mmol, 232.3 mg), and NaOH (3 mmol, 120 mg) in 1,4-dioxane (10 mL). The reaction mixture was then stirred at 80°C for approximately 12 hours, with progress monitored by TLC. Upon completion, 1M HCl was added to the mixture to adjust pH about 6, followed by extraction with DCM three times (10 mL × 3). The organic phase was subsequently dried over anhydrous sodium sulfate, concentrated under vacuum to afford 187.9 mg of product **6a** in 92% isolated yield.

Dehydrogenation of the cycloaddition products



3aa: R^1= Ph, R^2 = Me **4aa**: R^1= Ph, R^2 = Me, 71%

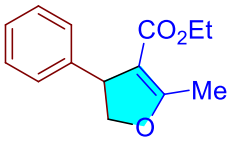
3da: R^1 = 4-ClC_6H_4, R^2 = Me **4da**: R^1 = 4-ClC_6H_4, R^2 = Me, 68%

3an: R^1 = Ph, R^2= furyl **4an**: R^1 = Ph, R^2= furyl, 73%

A 10 mL round-bottom flask equipped with a stirring bar was charged with 2,3-dihydrofuran **3aa**, **3da** or **3an** (0.5 mmol), and DDQ (2 mmol, 454 mg) in toluene (10 mL). The reaction mixture was then stirred at 110°C for approximately 12 hours, with progress monitored by TLC. Upon completion, 10 mL of H_2O was added to the mixture, followed by extraction with EtOAc three times (10 mL × 3). The organic phase was subsequently dried over anhydrous sodium sulfate, concentrated under vacuum, and the residue was purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 50:1-20:1) to afford the desired dehydrogenated products **4aa**, **4da** and **4an** in 71, 68 and 73% yields, respectively.

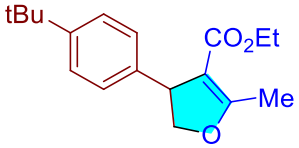
3. Characterization data of products

Ethyl 2-methyl-4-phenylfuran-3-carboxylate (3aa) [1]



Colorless liquid (54.3 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.12 (m, 5H), 4.71 – 4.58 (m, 1H), 4.37 – 4.09 (m, 2H), 3.94 (m, 2H), 2.25 (s, 3H), 1.00 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 165.6, 144.2, 128.4, 127.2, 126.7, 107.3, 78.6, 59.3, 48.3, 14.2, 14.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{17}O_3$: 233.1172; found: 233.1176.

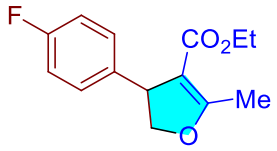
Ethyl 4-(4-(tert-butyl)phenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3ba)



Colorless liquid (56.2 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 4.63 (t, *J* = 9.7 Hz, 1H), 4.48 – 4.12 (m, 2H), 4.12 – 3.72 (m, 2H), 2.23 (s, 3H), 1.23 (s, 9H),

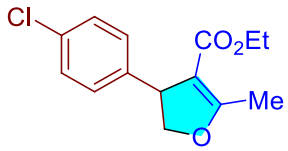
1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.7, 149.4, 141.0, 126.8, 125.3, 107.5, 78.6, 59.3, 47.8, 34.4, 31.4, 14.2, 14.1 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{25}O_3$: 289.1798; found: 289.1801.

Ethyl 4-(4-fluorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3ca) [2]



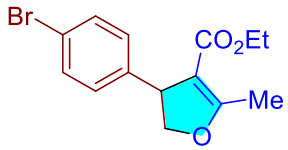
Colorless liquid (59.3mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.00 (m, 2H), 6.90 (t, *J* = 8.8 Hz, 2H), 4.62 (t, 1H), 4.39 – 4.10 (m, 2H), 4.13 – 3.73 (m, 2H), 2.24 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.2, 162.6, 160.2, 139.6, 128.3, 128.2, 115.0, 114.8, 107.0, 78.1, 59.0, 47.3, 13.9, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.2 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{16}FO_3$: 251.1078; found: 251.1080.

Ethyl 4-(4-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3da)



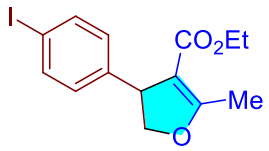
Colorless liquid (53.5 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 47.3, 8.6 Hz, 4H), 4.70 – 4.55 (m, 1H), 4.29 – 4.11 (m, 2H), 4.11 – 3.82 (m, 2H), 2.24 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4 , 165.4, 142.7, 132.4, 128.6, 128.5, 107.1, 78.3, 59.4, 47.8, 14.2, 14.1 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{16}ClO_3$: 267.0782; found: 267.0783.

Ethyl 4-(4-bromophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3ea)



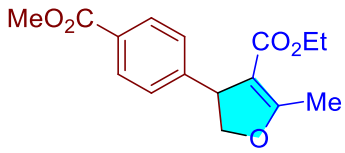
Colorless liquid (67.0 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.64 (t, *J* = 11.2 Hz, 1H), 4.30 – 4.10 (m, 2H), 4.08 – 3.82 (m, 2H), 2.24 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4 , 165.4 , 143.2 , 131.5 , 128.9 , 120.5 , 107.0 , 78.2 , 59.4 , 47.8 , 14.2 , 14.1 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{16}BrO_3$: 311.0277; found: 311.0284.

Ethyl 4-(4-iodophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3fa)



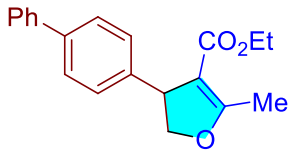
Colorless liquid (66.6 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 7.9 Hz, 2H), 4.71 – 4.57 (m, 1H), 4.26 – 4.12 (m, 2H), 4.03 – 3.87 (m, 2H), 2.23 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.40, 165.39, 143.89, 137.48, 129.23, 106.97, 91.93, 78.20, 59.42, 47.92, 14.18, 14.14 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{16}IO_3$: 359.0139; found: 359.0136.

Ethyl 4-(4-(methoxycarbonyl)phenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3ga)



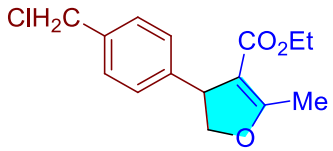
Colorless liquid (47.9 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 4.67 (t, *J* = 9.4 Hz, 1H), 4.47 – 4.16 (m, 2H), 4.14 – 3.74 (m, 5H), 2.26 (s, 3H), 0.99 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7 , 167.0 , 165.4 , 149.4 , 129.8 , 128.7 , 127.2 , 106.9 , 78.1 , 59.4 , 52.0 , 48.3 , 14.2 , 14.1 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{19}O_5$: 291.1227; found: 291.1229.

Ethyl 4-([1,1'-biphenyl]-4-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3ha)



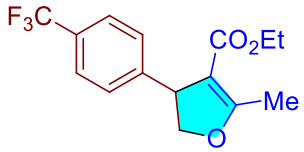
Colorless liquid (51.7 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 20.6, 7.8 Hz, 4H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.22 – 7.17 (m, 2H), 4.73 – 4.63 (m, 1H), 4.38 – 4.24 (m, 2H), 4.04 – 3.89 (m, 2H), 2.27 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.17 , 165.70 , 143.23 , 140.90 , 139.58 , 128.69 , 127.58 , 127.16 , 127.10 , 126.99 , 107.30 , 78.51 , 59.39 , 47.95 , 14.25 , 14.14 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{21}O_3$: 309.1485; found: 309.1489.

Ethyl 4-(4-(chloromethyl)phenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3ia)



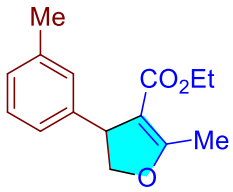
Colorless liquid (45.5 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.11 (m, 4H), 4.64 (t, *J* = 11.1 Hz, 1H), 4.49 (s, 2H), 4.28 -4.20 (m, 2H), 4.02 – 3.87 (m, 2H), 2.24 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3 , 165.5 , 144.5 , 135.9 , 128.7 , 127.6 , 107.2 , 78.4 , 59.4 , 48.0 , 46.1 , 14.2 , 14.1 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{18}ClO_3$: 281.0939; found: 281.0934.

Ethyl 2-methyl-4-(4-(trifluoromethyl)phenyl)-4,5-dihydrofuran-3-carboxylate (3ja)



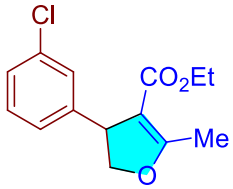
Colorless liquid (54.9 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 4.68 (t, *J* = 9.6 Hz, 1H), 4.33 – 4.20 (m, 2H), 4.03 – 3.86 (m, 2H), 2.26 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7 , 165.3 , 148.2 , 129.0 (q, $J_{C\text{-}F}$ = 32.6 Hz), 127.5 , 125.4 (q, $J_{C\text{-}F}$ = 3.8 Hz) , 124.2 (q, $J_{C\text{-}F}$ = 272.9 Hz), 106.90 , 78.10 , 59.5, 48.2 , 14.2 , 14.1 . ^{19}F NMR (100 MHz, $CDCl_3$) δ -62.37 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{16}F_3O_3$: 301.1046; found: 301.1048.

Ethyl 2-methyl-4-(m-tolyl)-4,5-dihydrofuran-3-carboxylate (3ka)



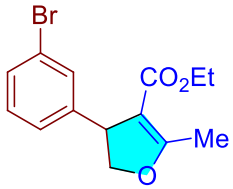
Colorless liquid (53.9 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 6.89 (m, 4H), 4.64 (t, *J* = 9.6 Hz, 1H), 4.47 – 4.12 (m, 2H), 4.11 – 3.80 (m, 2H), 2.25 (s, 6H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0 , 165.7 , 144.1 , 138.0 , 128.3 , 127.9 , 127.4 , 124.2 , 107.3 , 78.6 , 59.3 , 48.2 , 21.4 , 14.2 , 14.1 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{19}O_3$: 247.1329; found: 247.1333.

Ethyl 4-(3-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3la)



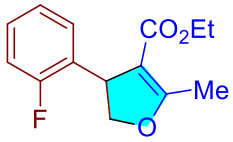
Colorless liquid (59.1 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 6.95 (m, 4H), 4.70 – 4.58 (m, 1H), 4.29 – 4.16 (m, 2H), 4.07 – 3.86 (m, 2H), 2.25 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6 , 165.4 , 146.2 , 134.2 , 129.7 , 127.4 , 126.9 , 125.4 , 106.9 , 78.2 , 59.4 , 48.1 , 14.2 , 14.1 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{16}ClO_3$: 267.0782; found: 267.0784.

Ethyl 4-(3-bromophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3ma)



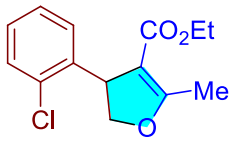
Colorless liquid (67.9 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 2H), 7.17 – 7.02 (m, 2H), 4.64 (t, *J* = 9.5 Hz, 1H), 4.35 – 4.13 (m, 2H), 4.12 – 3.82 (m, 2H), 2.25 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.61 , 165.39 , 146.47 , 130.28 , 130.01 , 129.83 , 125.88 , 122.48 , 106.87 , 78.17 , 59.44 , 48.00 , 14.20 , 14.10 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{16}BrO_3$: 311.0277; found: 311.0274.

Ethyl 4-(2-fluorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3na)



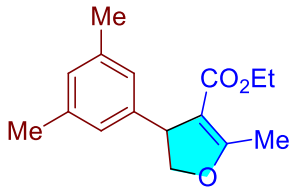
Colorless liquid (51.8 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 6.90 (m, 4H), 4.73 – 4.55 (m, 2H), 4.22 (dd, *J* = 8.7, 4.6 Hz, 1H), 4.04 – 3.87 (m, 2H), 2.26 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0 , 165.5 , 161.6 , 130.7 (d, *J* = 14.0 Hz), 128.5 (d, *J* = 4.3 Hz), 128.2 (d, *J* = 8.3 Hz) , 124.1 (d, *J* = 3.6 Hz), 115.1 (d, *J* = 22.2 Hz), 105.2 , 77.5 , 59.4 , 40.8 , 14.2 , 14.0 . ^{19}F NMR (400 MHz, $CDCl_3$) δ -119.56. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{16}FO_3$: 251.1078; found: 251.1083.

Ethyl 4-(2-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3oa)



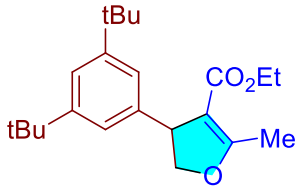
Colorless liquid (59.1 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 6.91 (m, 4H), 4.87 – 4.50 (m, 2H), 4.13 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.05 – 3.83 (m, 2H), 2.27 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5 , 165.6 , 141.3 , 133.2 , 129.3 , 128.0 , 127.9 , 127.0 , 105.1 , 77.6 , 59.4 , 44.6 , 14.3 , 14.1 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{16}ClO_3$: 267.0782; found: 267.0784.

Ethyl 4-(3,5-dimethylphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3pa)



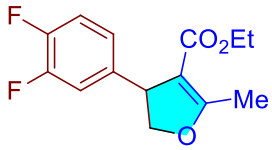
Colorless liquid (50.7 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (s, 1H), 6.74 (s, 2H), 4.63 (t, *J* = 9.8 Hz, 1H), 4.25 (dd, *J* = 9.1, 5.1 Hz, 1H), 4.16 (dd, *J* = 10.2, 5.0 Hz, 1H), 4.04 – 3.86 (m, 2H), 2.25 (s, 3H), 2.21 (s, 6H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.93, 165.79, 144.03, 137.81, 128.33, 107.34, 78.65, 59.29, 48.10, 21.30, 14.24, 14.11. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{21}O_3$: 261.1485; found: 261.1489.

Ethyl 4-(3,5-di-tert-butylphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3qa)



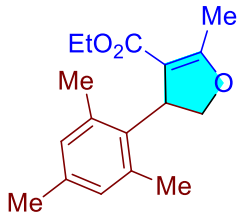
Colorless liquid (70.2 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 6.95 (s, 2H), 4.65 (t, *J* = 9.7 Hz, 1H), 4.43 – 4.09 (m, 2H), 4.08 – 3.76 (m, 2H), 2.25 (s, 3H), 1.23 (s, 18H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0 , 165.9 , 150.6 , 143.2 , 121.3 , 120.6 , 107.5 , 78.8 , 59.1 , 48.7 , 34.8 , 31.5 , 14.1 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{33}O_3$: 345.2424; found: 345.2429.

Ethyl 4-(3,4-difluorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3ra)



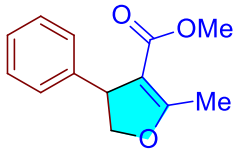
Colorless liquid (57.9 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 6.72 (m, 3H), 4.63 (t, *J* = 11.1 Hz, 1H), 4.39 – 4.13 (m, 2H), 4.10 – 3.76 (m, 2H), 2.24 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 165.3, 150.3 (dd, $J_{C\text{-}F}$ = 249.1 Hz, 12.7 Hz), 149.2 (dd, $J_{C\text{-}F}$ = 247.6 Hz, 12.8 Hz), 141.2 (dd, $J_{C\text{-}F}$ = 4.8 Hz, 3.2 Hz), 123.0 (dd, $J_{C\text{-}F}$ = 6.2 Hz, 3.5 Hz), 117.1(d, $J_{C\text{-}F}$ = 17.2 Hz), 115.9 (d, $J_{C\text{-}F}$ = 17.4 Hz), 106.9, 78.1, 59.5, 47.7, 14.2, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.9, -140.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{15}F_2O_3$: 269.0984; found: 269.10987.

Ethyl 4-mesityl-2-methyl-4,5-dihydrofuran-3-carboxylate (3sa)



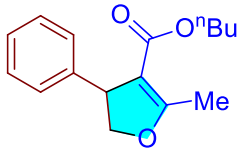
Colorless liquid (41.9 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (d, *J* = 5.3 Hz, 2H), 4.98 – 4.75 (m, 1H), 4.74 – 4.52 (m, 1H), 4.27 (t, *J* = 8.4 Hz, 1H), 4.08 – 3.76 (m, 2H), 2.32 (s, 3H), 2.17 (d, *J* = 10.6 Hz, 9H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5 , 165.8 , 136.9 , 136.5 , 135.7 , 135.3 , 131.2 , 128.9 , 105.4 , 75.4 , 59.2 , 42.4 , 21.3 , 20.7 , 19.1 , 14.1 , 14.0 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{23}O_3$: 275.1642; found: 275.1646.

Methyl 2-methyl-4-phenyl-4,5-dihydrofuran-3-carboxylate (3ab)



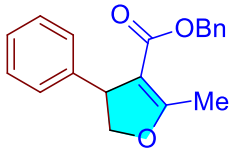
Colorless liquid (48.4 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.08 (m, 5H), 4.73 – 4.59 (m, 1H), 4.35 – 4.18 (m, 2H), 3.49 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5 , 166.1 , 144.1 , 128.5 , 127.0 , 126.7 , 107.0 , 78.7 , 50.7 , 48.2 , 14.2 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_{15}O_3$: 219.1016; found: 219.1018.

Butyl 2-methyl-4-phenyl-4,5-dihydrofuran-3-carboxylate (3ac)



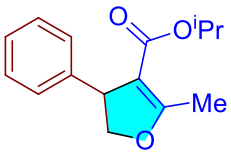
Colorless liquid (56.2 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.11 (m, 5H), 4.65 (t, *J* = 11.2 Hz, 1H), 4.37 – 4.13 (m, 2H), 4.07 – 3.68 (m, 2H), 2.25 (s, 3H), 1.40 – 1.25 (m, 2H), 1.11 – 0.94 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3 , 165.8 , 144.2 , 128.4 , 127.1 , 126.7 , 107.2 , 78.6 , 63.2 , 48.4 , 30.6 , 19.0 , 14.2 , 13.6 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{21}O_3$: 261.1485; found: 261.1488.

Benzyl 2-methyl-4-phenyl-4,5-dihydrofuran-3-carboxylate (3ad)



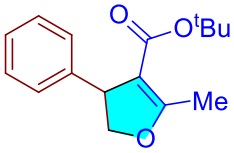
Colorless liquid (61.7 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.09 (m, 8H), 7.01 – 6.80 (m, 2H), 5.03 (d, *J* = 12.7 Hz, 1H), 4.85 (d, *J* = 12.7 Hz, 1H), 4.74 – 4.58 (m, 1H), 4.29-4.23 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 165.4, 144.1, 136.5, 128.6, 128.2, 127.6, 127.5, 127.2, 126.8, 106.8, 78.7, 65.1, 48.2, 14.3 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}O_3$: 295.1329; found: 295.1324.

Isopropyl 2-methyl-4-phenyl-4,5-dihydrofuran-3-carboxylate (3ae)



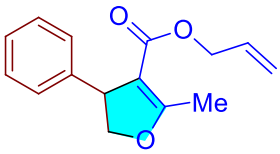
Colorless liquid (52.4 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 5H), 4.88 – 4.73 (m, 1H), 4.72 – 4.54 (m, 1H), 4.36 – 4.14 (m, 2H), 2.24 (s, 3H), 1.08 (d, *J* = 6.2 Hz, 3H), 0.83 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 , 165.2 , 144.3 , 128.3 , 127.3 , 126.6 , 107.6 , 78.5 , 66.4 , 48.4 , 22.0 , 21.5 , 14.1 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{19}O_3$: 247.1329; found: 247.1331.

Tert-butyl 2-methyl-4-phenyl-4,5-dihydrofuran-3-carboxylate (3af)



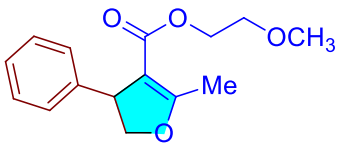
Colorless liquid (48.4 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.10 (m, 5H), 4.63 (t, *J* = 11.5 Hz, 1H), 4.33 – 4.10 (m, 2H), 2.22 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4 , 165.2 , 144.4 , 128.3 , 127.2 , 126.6 , 108.4 , 79.4 , 78.2 , 48.8 , 28.1 , 14.0 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{21}O_3$: 261.1485; found: 261.1488.

Allyl 2-methyl-4-phenyl-4,5-dihydrofuran-3-carboxylate (3ag)



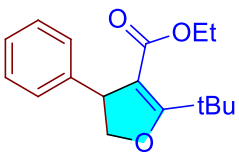
Colorless liquid (54.9 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 5H), 5.79 – 5.58 (m, 1H), 5.06 – 4.86 (m, 2H), 4.70 – 4.62 (m, 1H), 4.54 – 4.33 (m, 2H), 4.31 – 4.22 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8 , 165.3 , 144.0 , 132.6 , 128.5 , 127.1 , 126.8 , 116.9 , 107.0 , 78.7 , 63.9 , 48.2 , 14.3 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{17}O_3$: 245.1172; found: 245.1177.

2-methoxyethyl 2-methyl-4-phenyl-4,5-dihydrofuran-3-carboxylate (3ah)



Colorless liquid (47.9 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 2H), 7.17 – 7.10 (m, 3H), 4.66 (t, *J* = 11.1 Hz, 1H), 4.33 – 4.21 (m, 2H), 4.13 – 3.95 (m, 2H), 3.42 – 3.25 (m, 2H), 3.17 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8 , 165.5 , 144.1 , 128.4 , 127.2 , 126.7 , 107.0 , 78.7 , 70.5 , 62.4 , 58.8 , 48.2 , 14.2 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{19}O_4$: 263.1278; found: 263.1285.

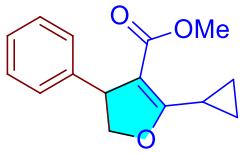
Ethyl 2-(tert-butyl)-4-phenyl-4,5-dihydrofuran-3-carboxylate (3ai)



Colorless liquid (46.0 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.09 (m, 5H), 4.55 (t, *J* = 9.6 Hz, 1H), 4.35 – 4.07 (m, 2H), 4.01 – 3.71 (m, 2H), 1.31 (s, 9H), 0.93 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100

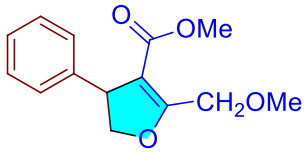
MHz, $CDCl_3$) δ 178.2 , 165.0 , 144.8 , 128.4 , 127.1 , 126.6 , 105.4 , 77.4 , 59.3 , 50.2 , 34.5 , 27.7 , 13.9 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{23}O_3$: 275.1642; found: 275.1644.

Methyl 2-cyclopropyl-4-phenyl-4,5-dihydrofuran-3-carboxylate (3aj)



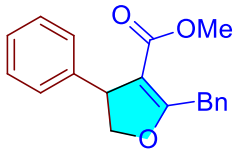
Colorless liquid (49.8 mg, 68%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.09 (m, 5H), 4.54 (t, *J* = 9.2 Hz, 1H), 4.37 – 4.07 (m, 2H), 3.50 (s, 3H), 2.85 – 2.62 (m, 1H), 1.09 – 0.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2 , 166.6 , 144.3 , 128.5 , 127.0 , 126.7 , 106.3 , 78.4 , 50.7 , 48.4 , 9.2 , 8.1 , 7.5 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{17}O_3$: 245.1172; found: 245.1176.

Methyl 2-(methoxymethyl)-4-phenyl-4,5-dihydrofuran-3-carboxylate (3ak)



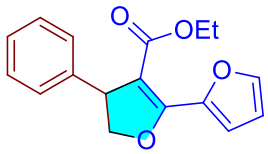
Colorless liquid (45.4 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.14 (m, 5H), 4.75 (t, *J* = 9.9 Hz, 1H), 4.58 (d, *J* = 13.5 Hz, 1H), 4.48 (d, *J* = 13.5 Hz, 1H), 4.40 – 4.34 (m, 1H), 4.32 – 4.26 (m, 1 H), 3.50 (s, 3H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0 , 165.2 , 143.3 , 128.6 , 127.1 , 127.0 , 109.4 , 79.2 , 66.0 , 59.2 , 51.0 , 48.2 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{17}O_4$: 249.1121; found: 249.1126.

Methyl 2-benzyl-4-phenyl-4,5-dihydrofuran-3-carboxylate (3al)



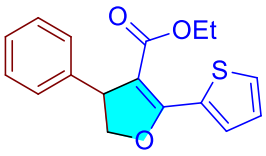
Colorless liquid (54.7 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 4H), 7.22 – 7.17 (m, 3H), 7.15 – 7.06 (m, 3H), 4.62 (t, *J* = 11.0 Hz, 1H), 4.32 – 4.17 (m, 2H), 4.03 (s, 2H), 3.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3 , 165.8 , 143.9 , 136.7 , 129.0 , 128.5, 128.5 , 127.0 , 126.8 , 126.8 , 107.3 , 78.8 , 50.8 , 48.1 , 33.9 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}O_3$: 295.1329; found: 295.1324.

Ethyl 4-phenyl-4,5-dihydro-[2,2'-bifuran]-3-carboxylate (3am)



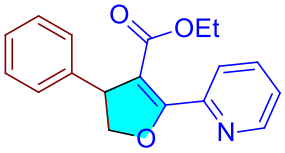
Colorless liquid (41.7 mg, 49%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 3.1 Hz, 1H), 7.50 (s, 1H), 7.28 – 7.11 (m, 5H), 6.71 – 6.30 (m, 1H), 4.88 – 4.71 (m, 1H), 4.56 – 4.26 (m, 2H), 4.14 – 3.83 (m, 2H), 1.10 – 0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 , 155.3 , 144.3 , 144.2 , 143.7 , 128.5 , 127.3 , 126.9 , 118.2 , 112.0 , 106.5 , 78.2 , 59.7 , 49.6 , 14.0 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{17}O_4$: 285.1121; found: 285.1124.

Ethyl 4-phenyl-2-(thiophen-2-yl)-4,5-dihydrofuran-3-carboxylate (3an)



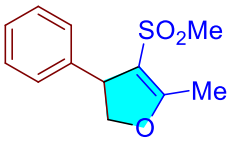
Colorless liquid (40.5 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 3.1 Hz, 1H), 7.46 (d, *J* = 4.9 Hz, 1H), 7.25 – 7.10 (m, 5H), 7.06 (t, *J* = 4.1 Hz, 1H), 4.76 (t, *J* = 8.7 Hz, 1H), 4.51 – 4.28 (m, 2H), 4.10 – 3.83 (m, 2H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9 , 159.5 , 143.9 , 132.6 , 131.2 , 130.4 , 128.5 , 127.3 , 127.2 , 126.8 , 106.0 , 77.7 , 59.7 , 50.0 , 14.0 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{17}O_3S$: 301.0893; found: 301.0890.

Methyl 4-phenyl-2-(pyridin-2-yl)-4,5-dihydrofuran-3-carboxylate (3ao)



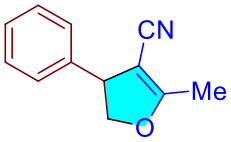
Colorless liquid (27.4 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.0 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.36 (m, 1H), 7.27 – 7.16 (m, 5H), 4.17 – 4.02 (m, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.31 (t, *J* = 6.3 Hz, 1H), 2.63 (dd, *J* = 9.3, 6.6 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3 , 169.1 , 153.3 , 149.0 , 138.4 , 136.9 , 128.6 , 127.2 , 127.0 , 126.7 , 122.1 , 61.0 , 33.3 , 33.0 , 30.8 , 14.1 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{18}NO_3$: 296.1281; found: 296.1285.

5-methyl-4-(methylsulfonyl)-3-phenyl-2,3-dihydrofuran (3ap)



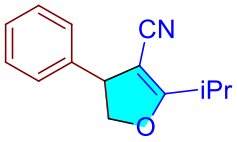
Colorless liquid (37.1 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.24 (d, *J* = 7.2 Hz, 3H), 4.78 (t, *J* = 9.8 Hz, 1H), 4.51 – 4.27 (m, 2H), 2.22 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5 , 141.6 , 129.2 , 127.9 , 127.5 , 114.6 , 78.5 , 49.1 , 45.1 , 13.5 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{15}O_3S$: 239.0736; found: 239.0738.

2-methyl-4-phenyl-4,5-dihydrofuran-3-carbonitrile (3aq)



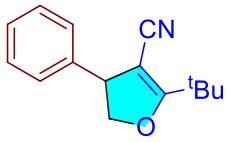
Colorless liquid (35.0 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 3H), 7.20 – 7.16 (m, 2H), 3.05 (t, *J* = 8.7 Hz, 1H), 2.51 (s, 3H), 2.19 – 2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5 , 133.1 , 128.8 , 128.6 , 128.2 , 118.3 , 38.3 , 30.2 , 29.4 , 24.7 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{12}NO$: 186.0913; found: 186.0917.

2-isopropyl-4-phenyl-4,5-dihydrofuran-3-carbonitrile (3ar)



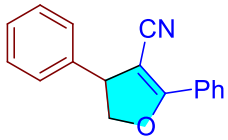
Colorless liquid (35.1 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 3H), 7.18 (d, *J* = 6.8 Hz, 2H), 3.38 – 3.24 (m, 1H), 2.98 (t, *J* = 8.7 Hz, 1H), 2.16 – 2.10 (m, 1H) , 2.05 – 1.99 (m, 1H) , 1.16 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5 , 133.2 , 128.8 , 128.5 , 128.2 , 39.4 , 38.4 , 28.9 , 24.1 , 18.1 , 17.9 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{16}NO$: 214.1226; found: 214.1228.

2-(tert-butyl)-4-phenyl-4,5-dihydrofuran-3-carbonitrile (3as)



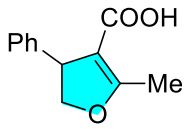
Colorless liquid (41.5 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 3H), 7.22 – 7.15 (m, 2H), 2.89 (t, *J* = 8.6 Hz, 1H), 2.19 (dd, *J* = 8.9, 4.8 Hz, 1H), 1.97 (dd, *J* = 8.0, 4.9 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2 , 133.3 , 128.7 , 128.5 , 128.5 , 45.4 , 39.0 , 26.4 , 26.1 , 24.2 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{18}NO$: 228.1383; found: 228.1379.

2,4-diphenyl-4,5-dihydrofuran-3-carbonitrile (3at)



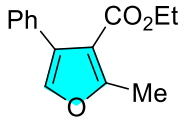
Colorless liquid (43.0 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.57 – 7.27 (m, 8H), 3.09 (t, *J* = 8.7 Hz, 1H), 2.48 (dd, *J* = 9.1, 5.2 Hz, 1H), 2.15 (dd, *J* = 8.3, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6 , 135.5 , 133.7 , 133.1 , 128.9 , 128.8 , 128.7 , 128.7 , 128.2 , 118.6 , 37.9 , 28.7 , 22.4 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{14}NO$: 248.1070; found: 248.1076.

2-methyl-4-phenyl-4,5-dihydrofuran-3-carboxylic acid (6a)



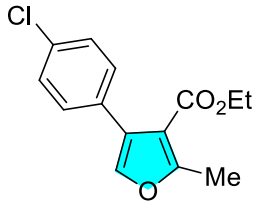
Colorless liquid (56.3 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.4 Hz, 2H), 7.17 – 7.07 (m, 3H), 4.70 – 4.60 (m, 1H), 4.28 – 4.18 (m, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.92 , 171.04 , 143.68 , 128.57 , 127.02 , 126.83 , 106.51 , 79.03 , 47.72 , 14.47 . HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{13}O_3$: 205.0859; found: 205.0866.

Ethyl 2-methyl-4-phenylfuran-3-carboxylate (4aa) [3]



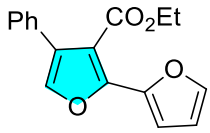
Colorless liquid (49.0 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 5H), 7.19 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.53 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.15, 160.16, 138.18, 132.01, 129.24, 127.72, 127.39, 127.24, 112.78, 60.00, 14.31, 13.99. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{15}O_3$: 231.1016; found: 231.1019.

Ethyl 4-(4-chlorophenyl)-2-methylfuran-3-carboxylate (4da)



Colorless liquid (53.9 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 4H), 7.18 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.53 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.94, 160.45, 138.28, 132.27, 130.57, 130.49, 127.93, 126.38, 112.61, 60.12, 14.38, 14.07. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{14}ClO_3$: 265.0626; found: 265.0630.

Ethyl 4-phenyl-[2,2'-bifuran]-3-carboxylate (4am)



Colorless liquid (48.2 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.37 (s, 1H), 7.33 – 7.24 (m, 5H), 7.23 (d, *J* = 3.4 Hz, 1H), 6.51 – 6.40 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.48, 148.89, 144.38, 143.39, 139.04, 131.40, 128.94, 128.20, 127.92, 127.52, 112.52, 112.19, 111.74, 60.62, 13.77. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{13}O_4$: 221.0808; found: 221.0811.

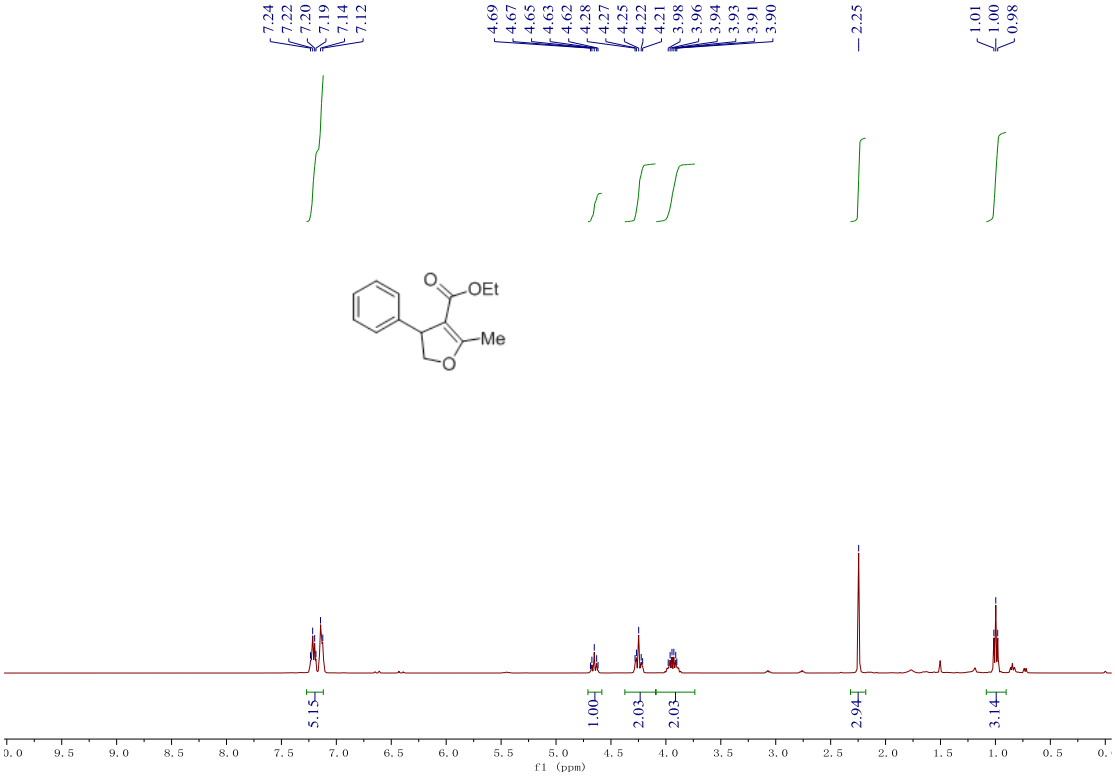
4. References

[1] Chagarovsky, A. O.; Budynina, E. M.; Ivanova, O. A.; Villemson, E. V.; Rybakov, V. B.; Trushkov, I. V.; Melnikov, M. Y., Reaction of Corey Ylide with α,β-Unsaturated Ketones: Tuning of Chemoselectivity toward Dihydrofuran Synthesis. *Org. Lett.* **2014,** *16*, 2830-2833.

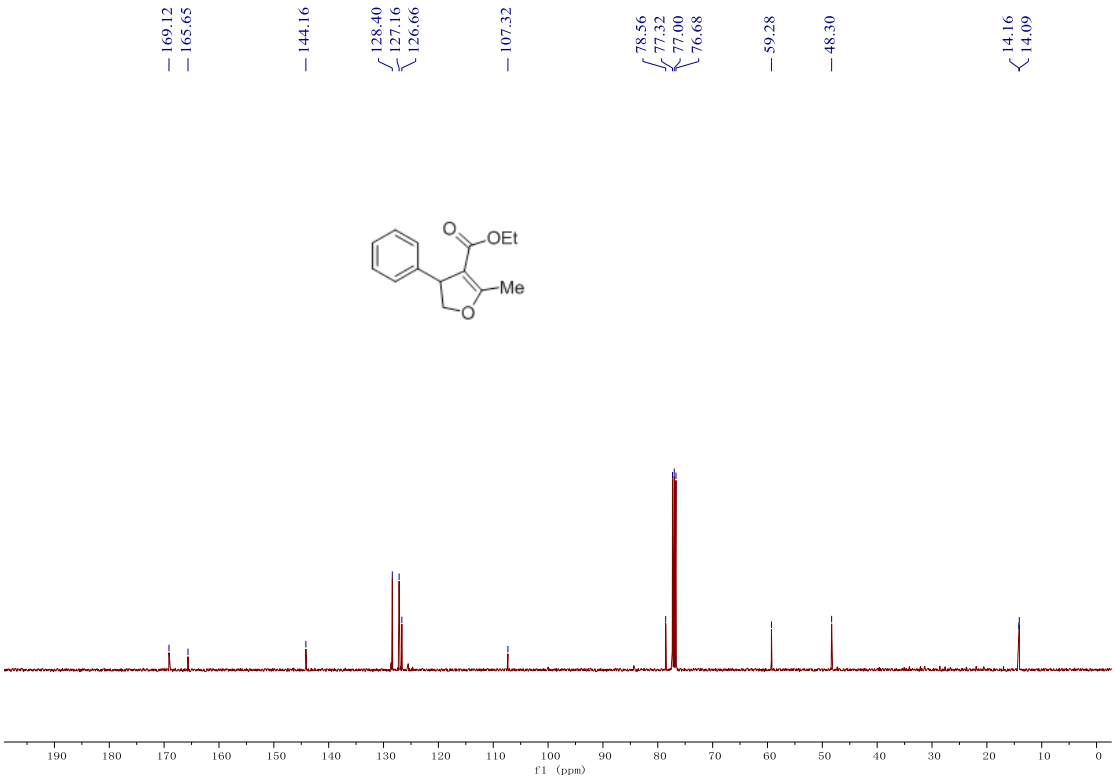
[2] Wang, Z.; Yue, G.; Ji, X.; Song, H.; Yan, P.; Zhao, J.; Jia, X., Tandem Michael Addition–Cyclization of Nitroalkenes with 1,3-Dicarbonyl Compounds Accompanied by Removal of Nitro Group. *J. Org. Chem.* **2021,** *86*, 14131-14143.

[3] Ma, S.; Zhang, J., 2,3,4- or 2,3,5-Trisubstituted Furans: Catalyst-Controlled Highly Regioselective Ring-Opening Cycloisomerization Reaction of Cyclopropenyl Ketones. *J. Am. Chem. Soc.* **2003,** *125*, 12386-12387.

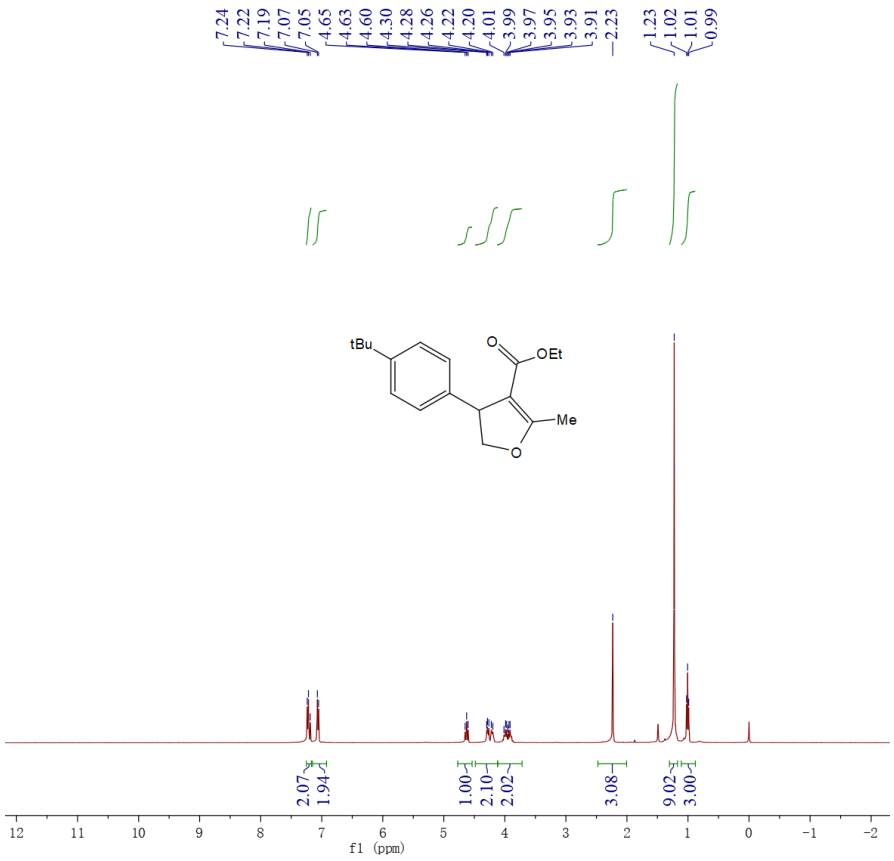
5. NMR spectra of products



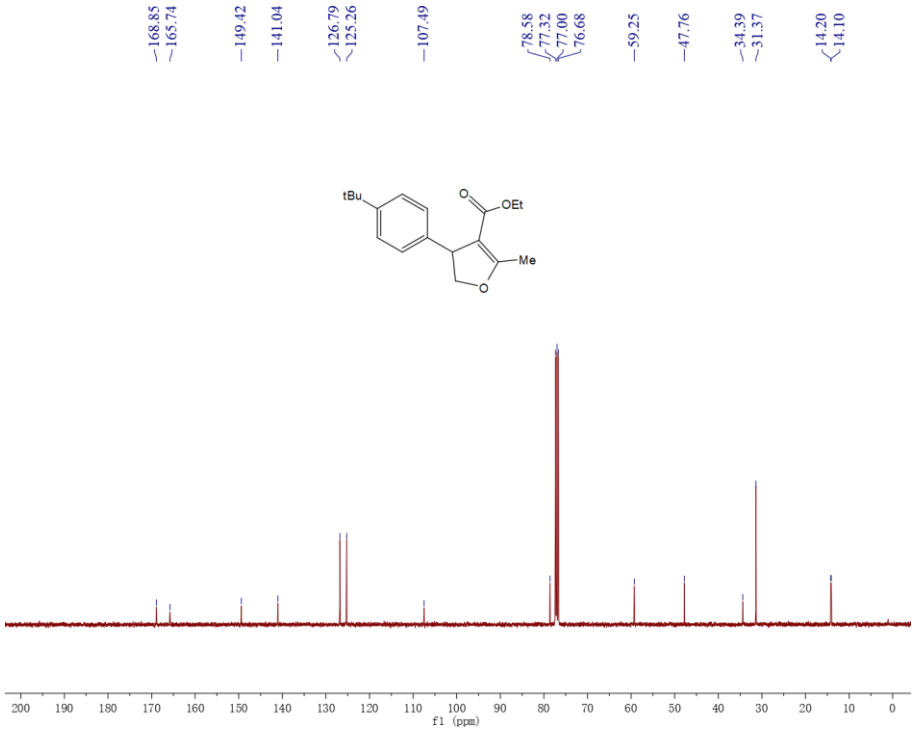
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aa**



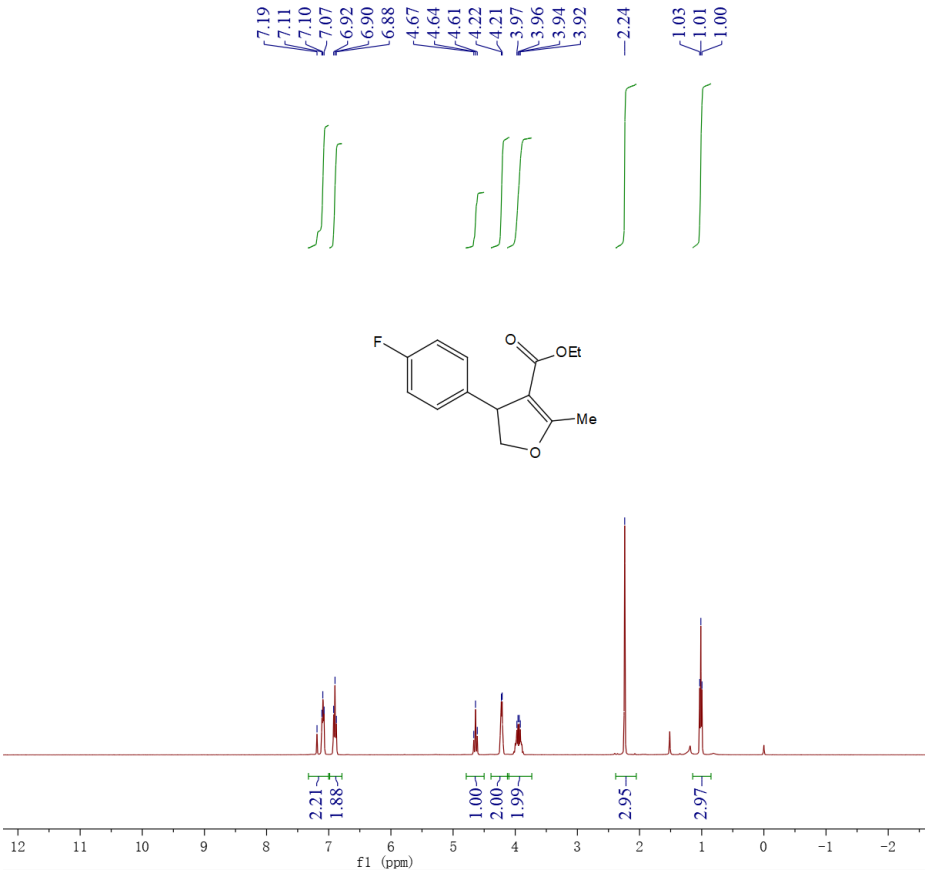
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3aa**



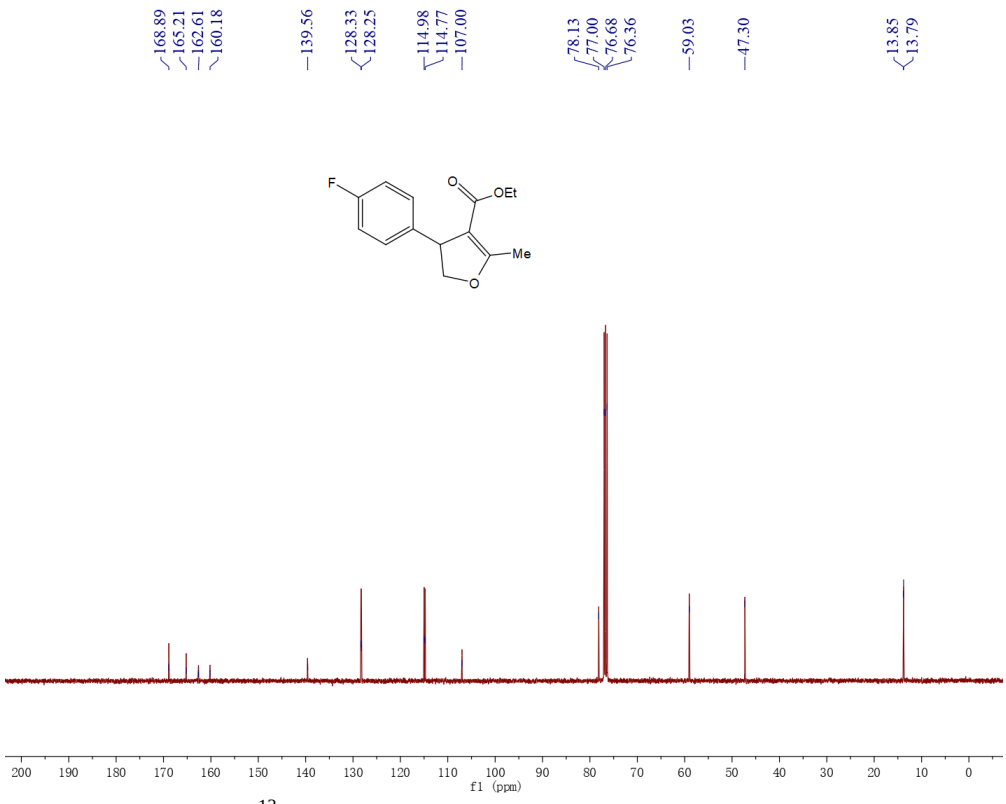
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ba**



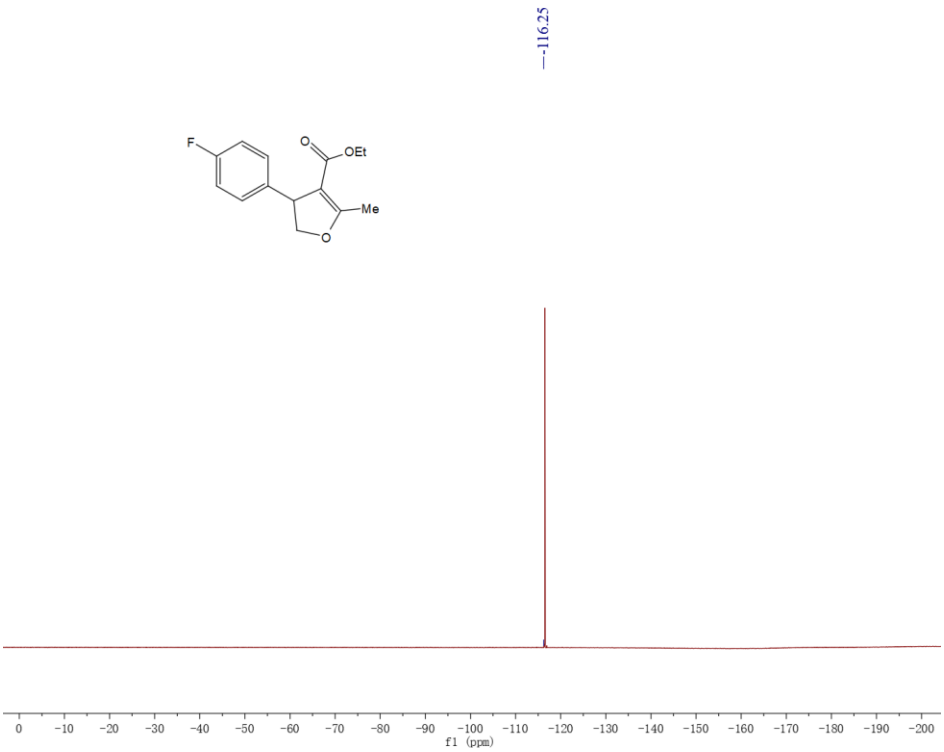
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ba**



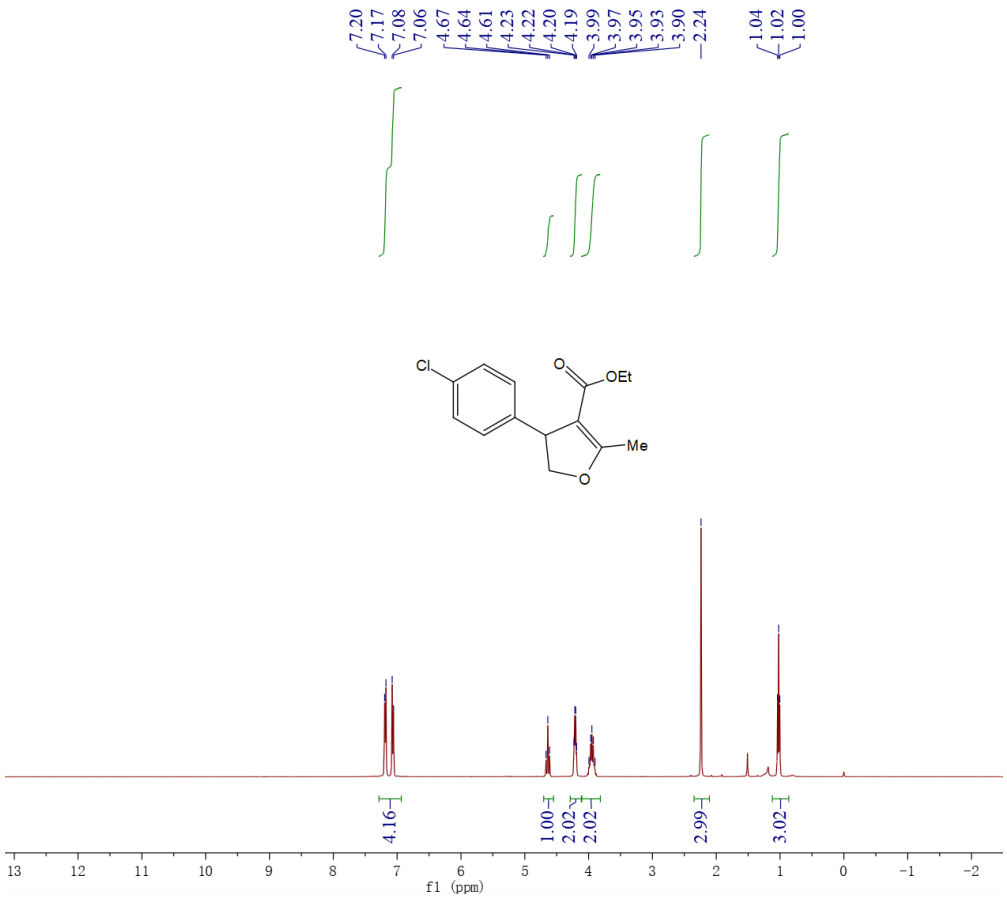
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ca**



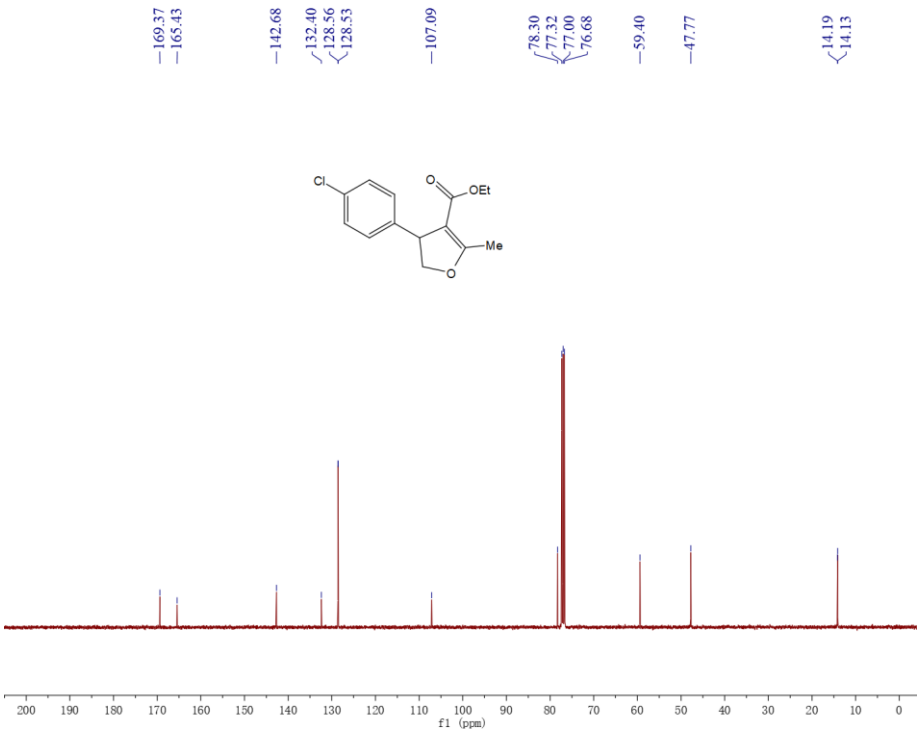
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ca**



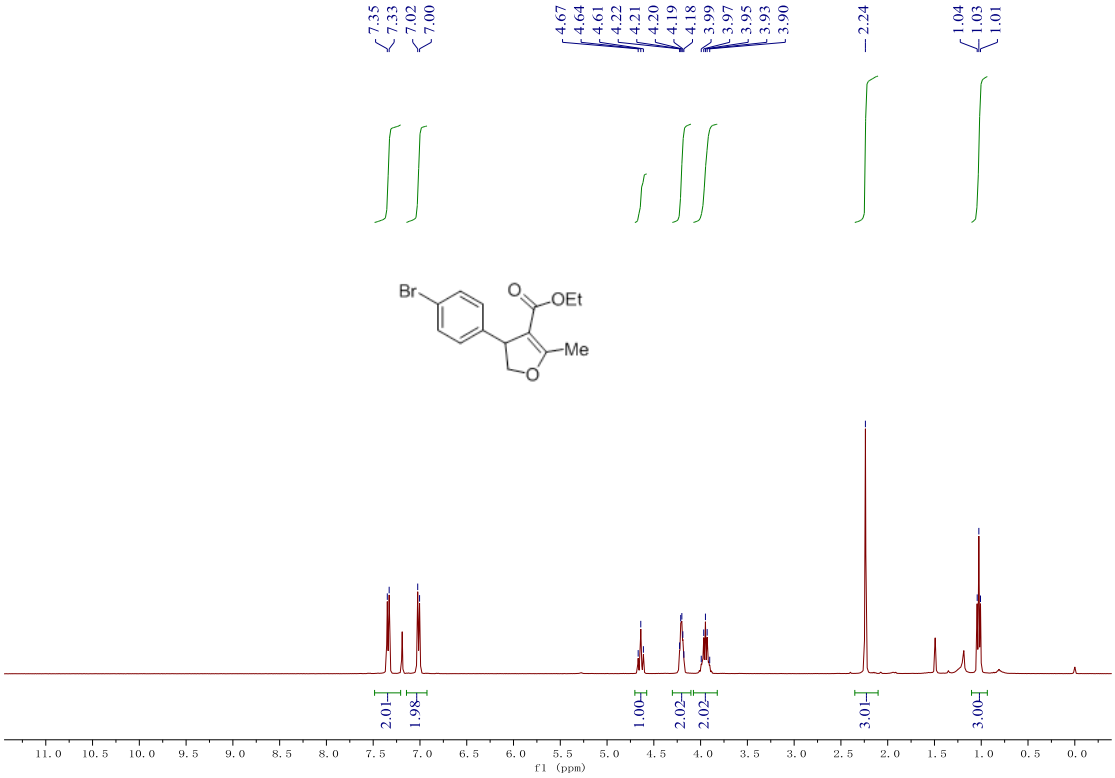
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ca**



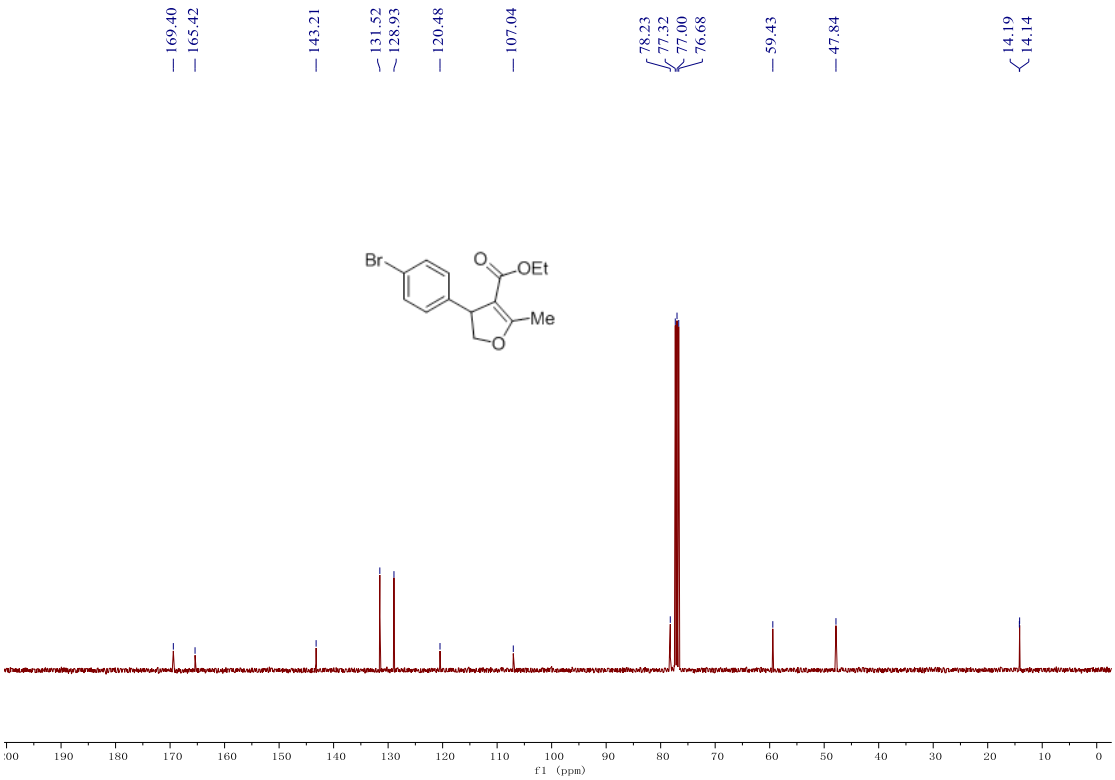
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3da**



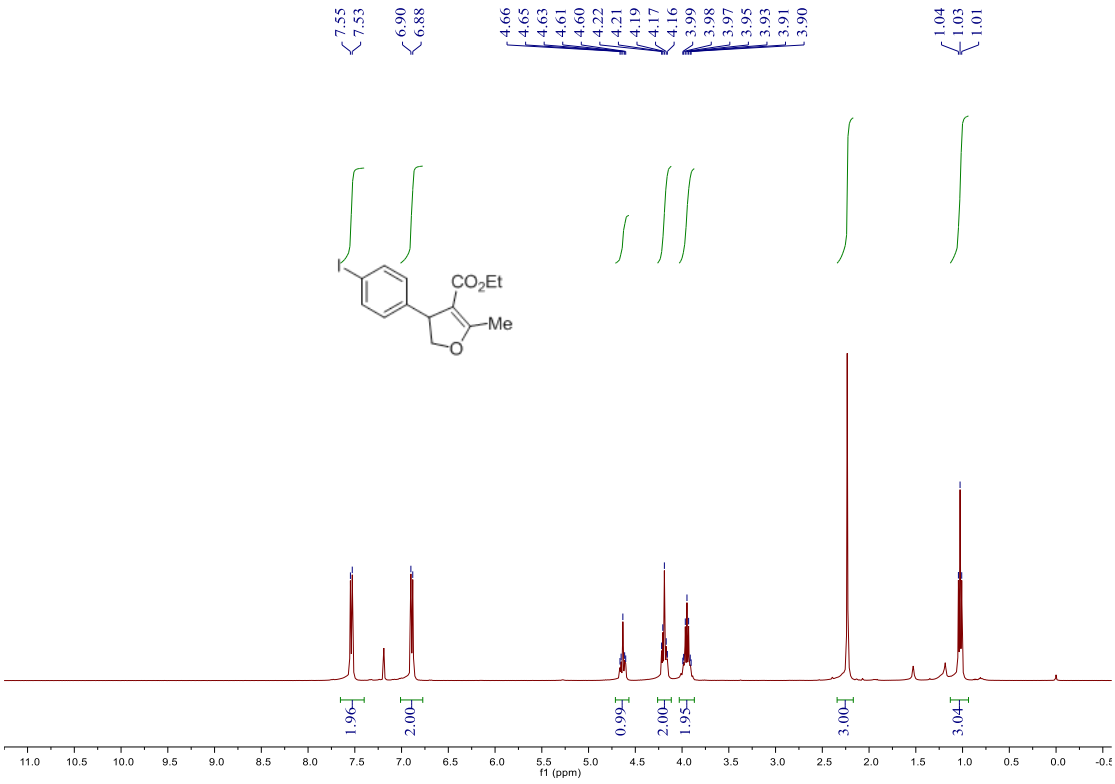
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3da**



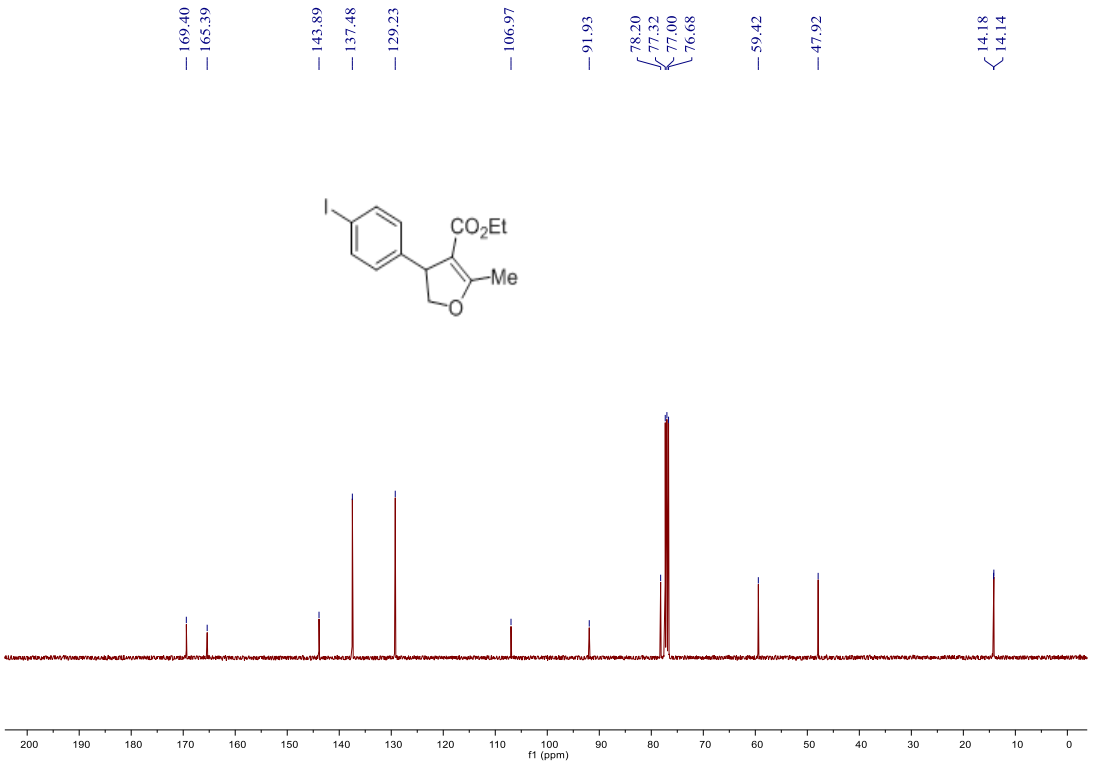
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ea**



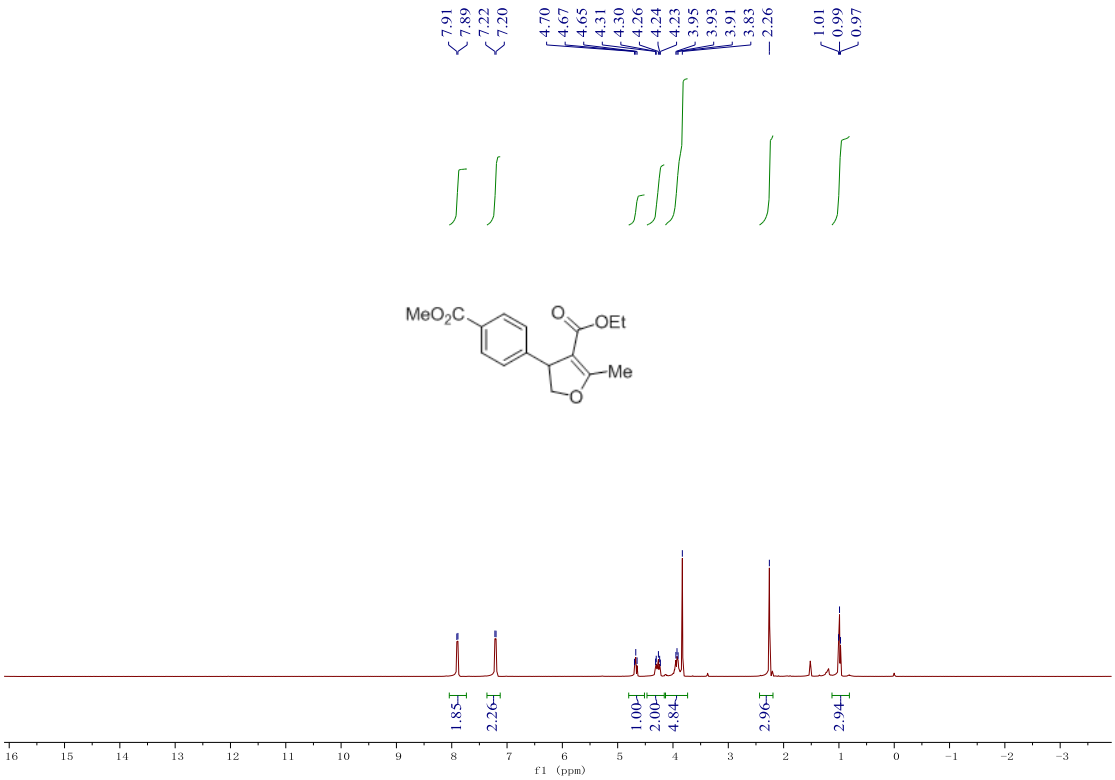
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ea**



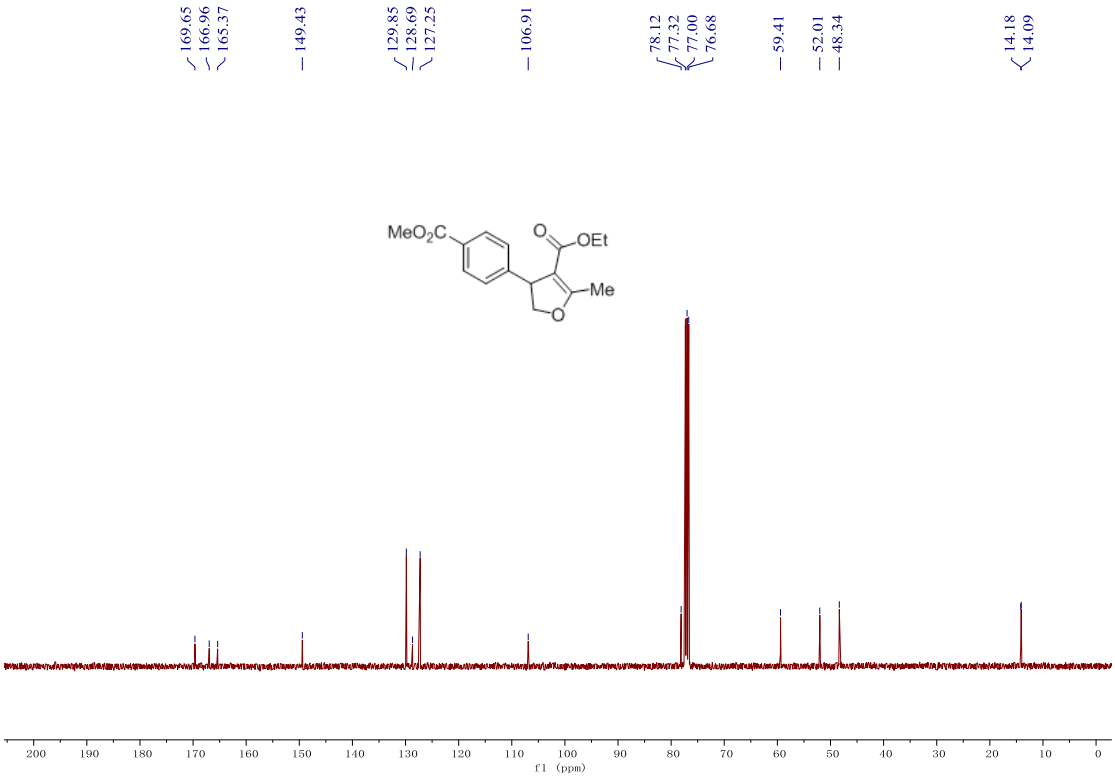
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3fa**



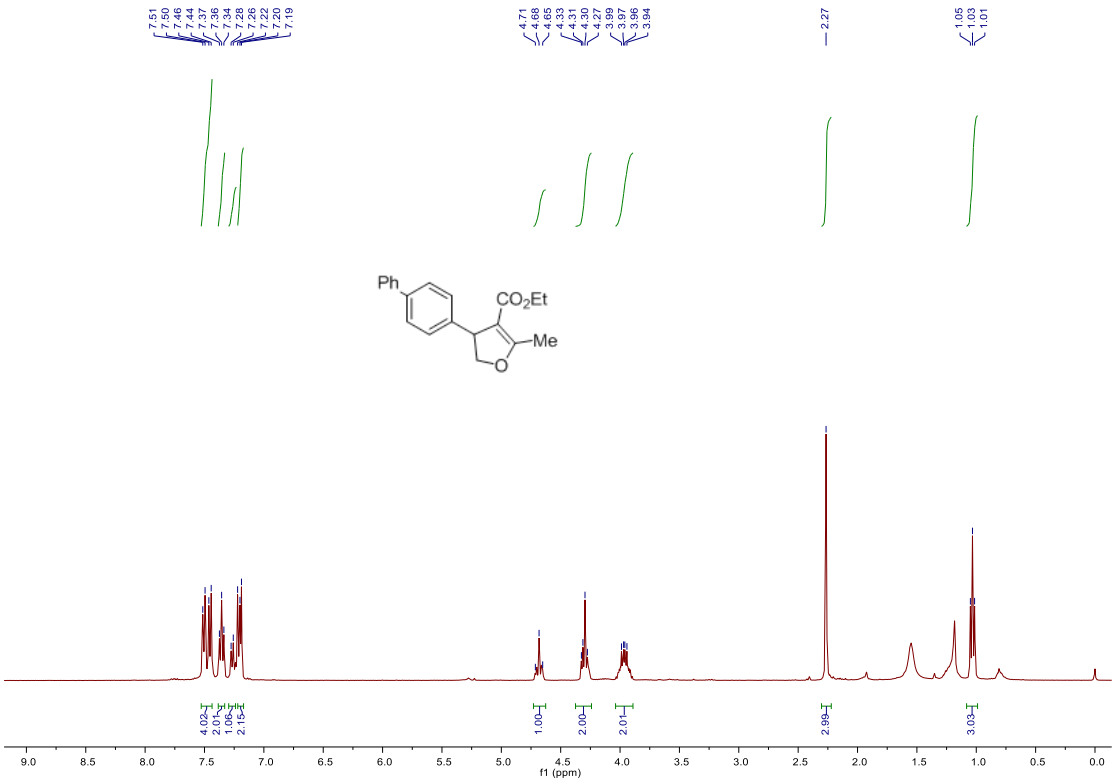
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3fa**



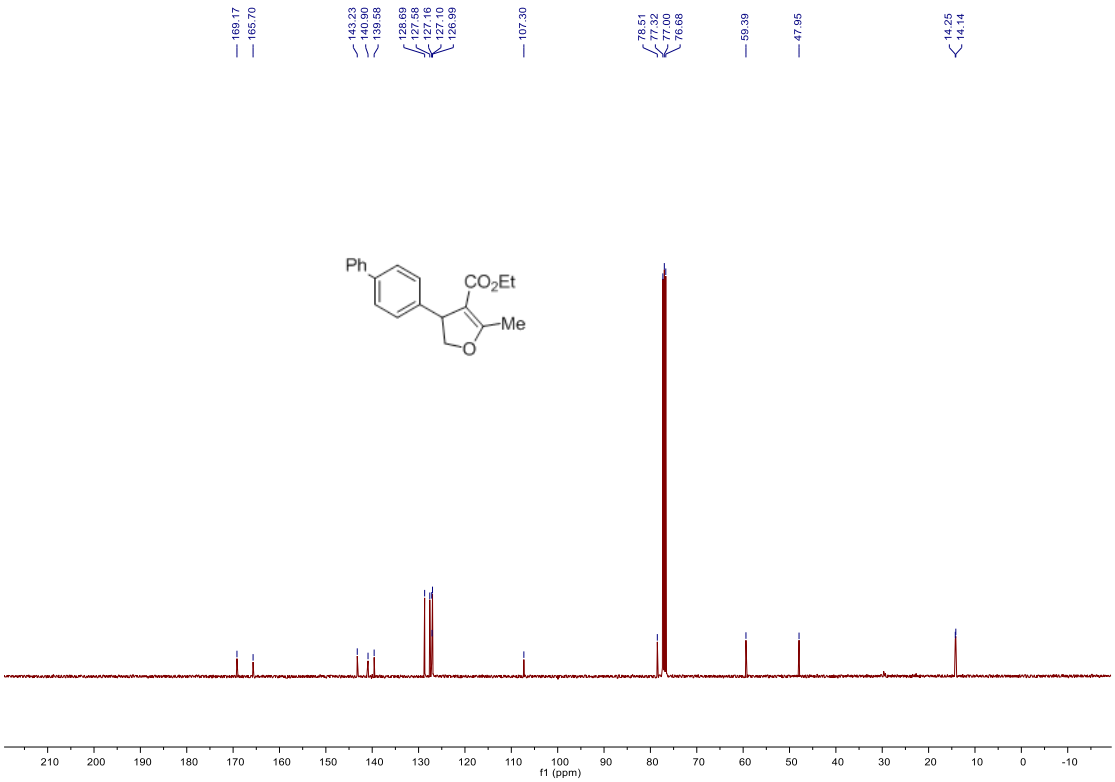
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ga**



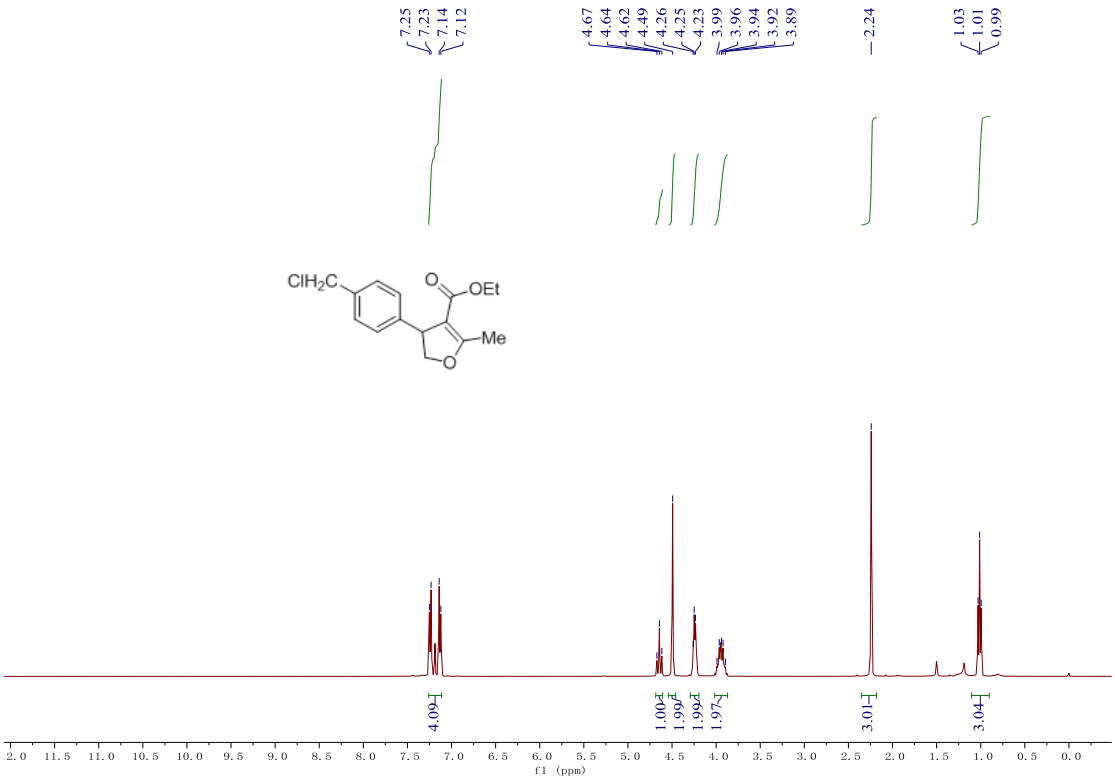
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ga**



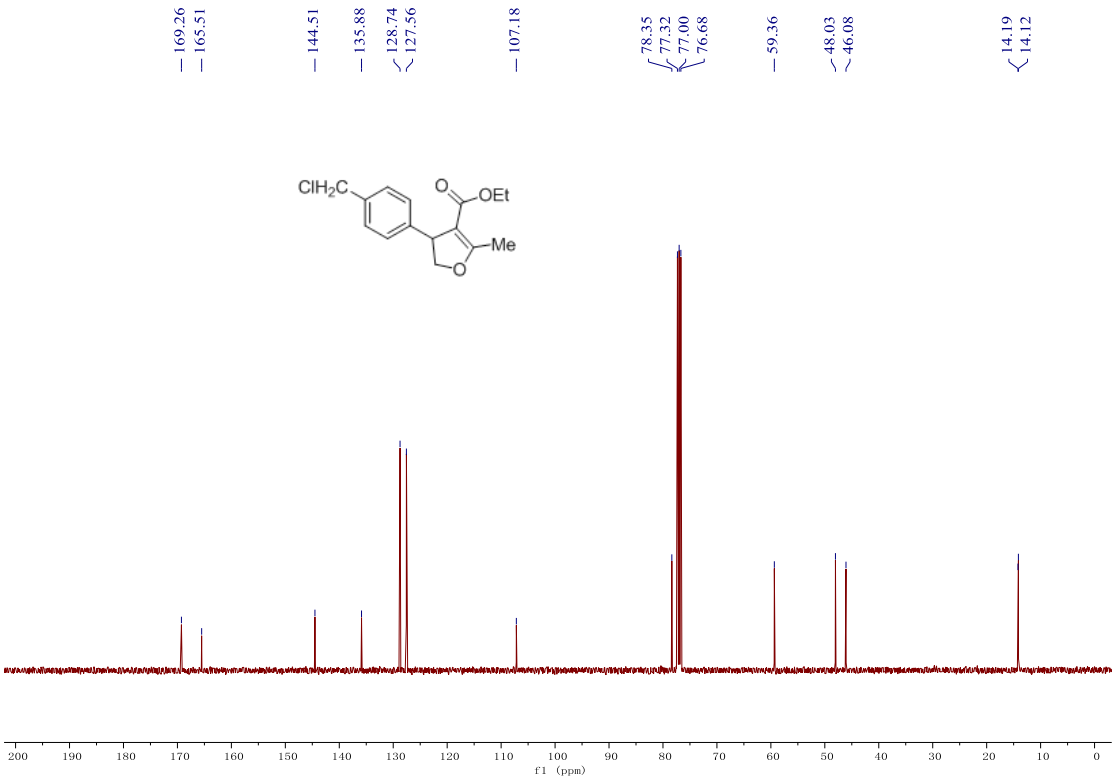
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ha**



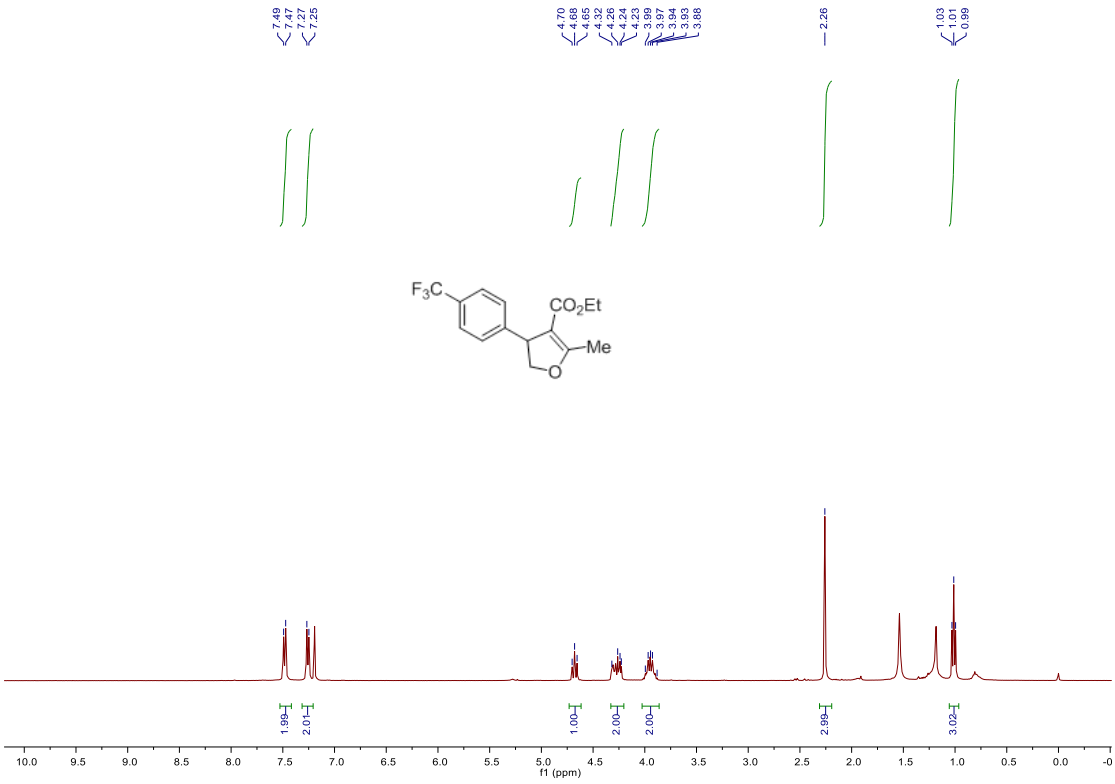
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ha**



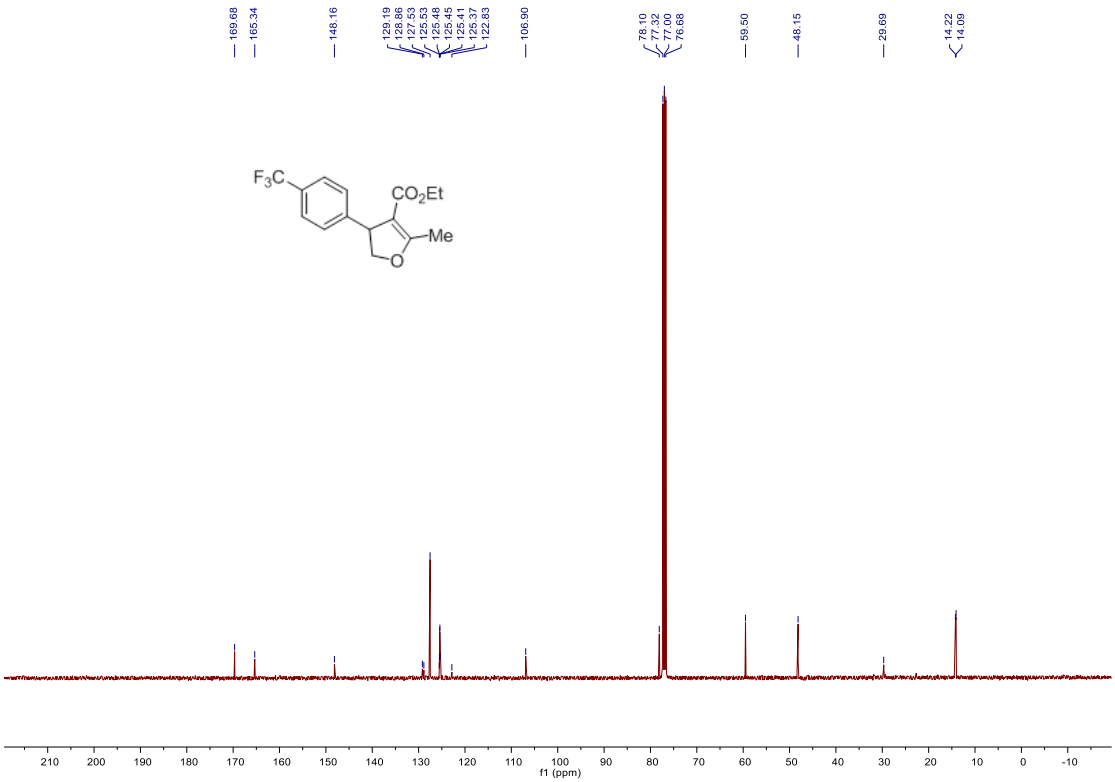
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ia**



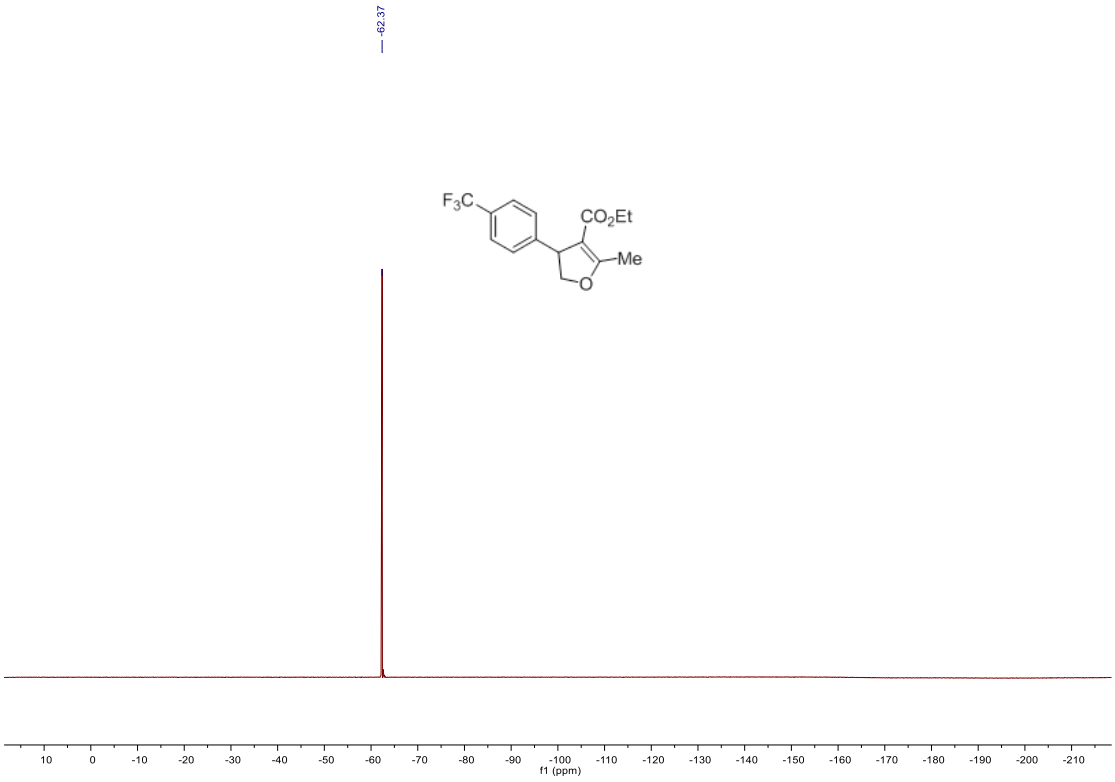
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ia**



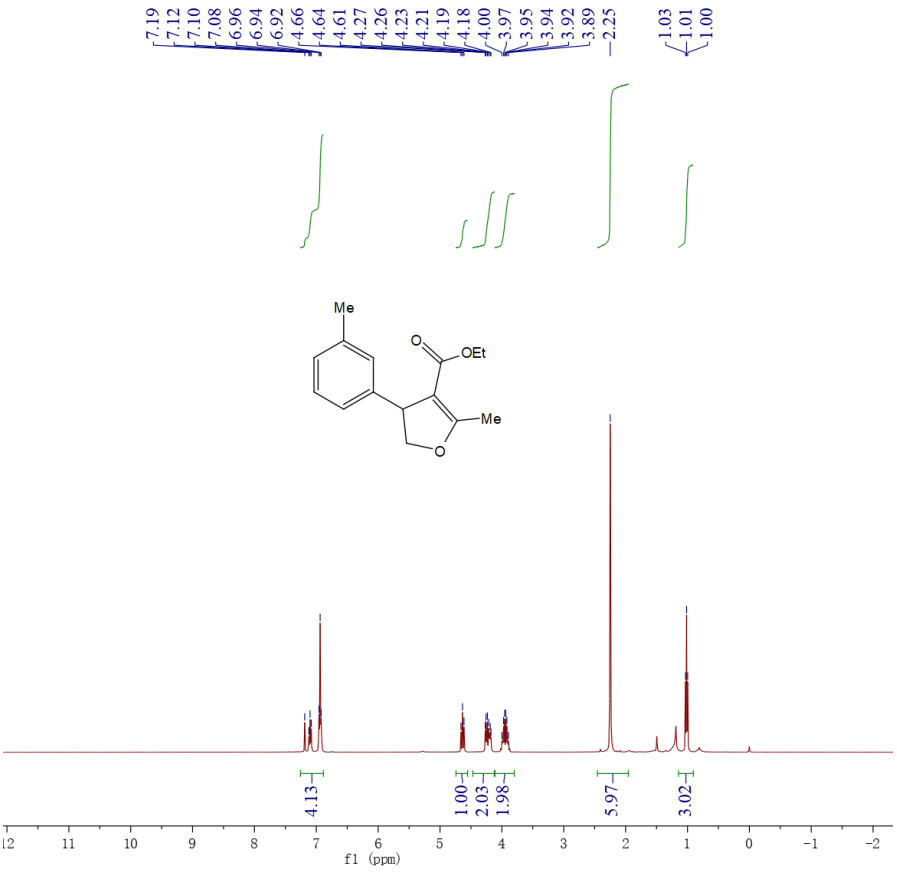
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ja**



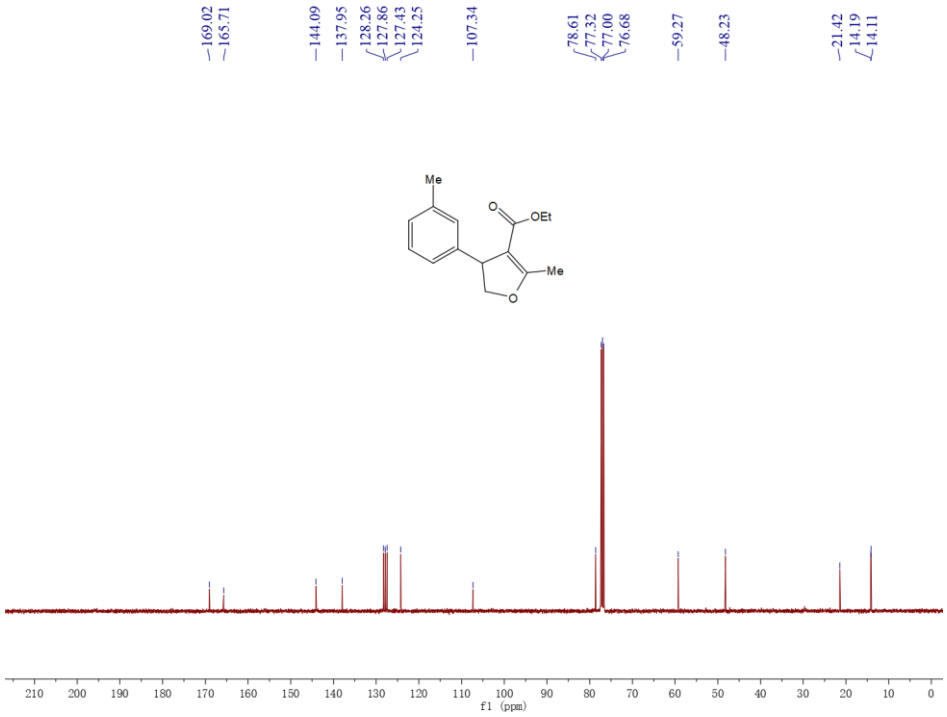
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ja**



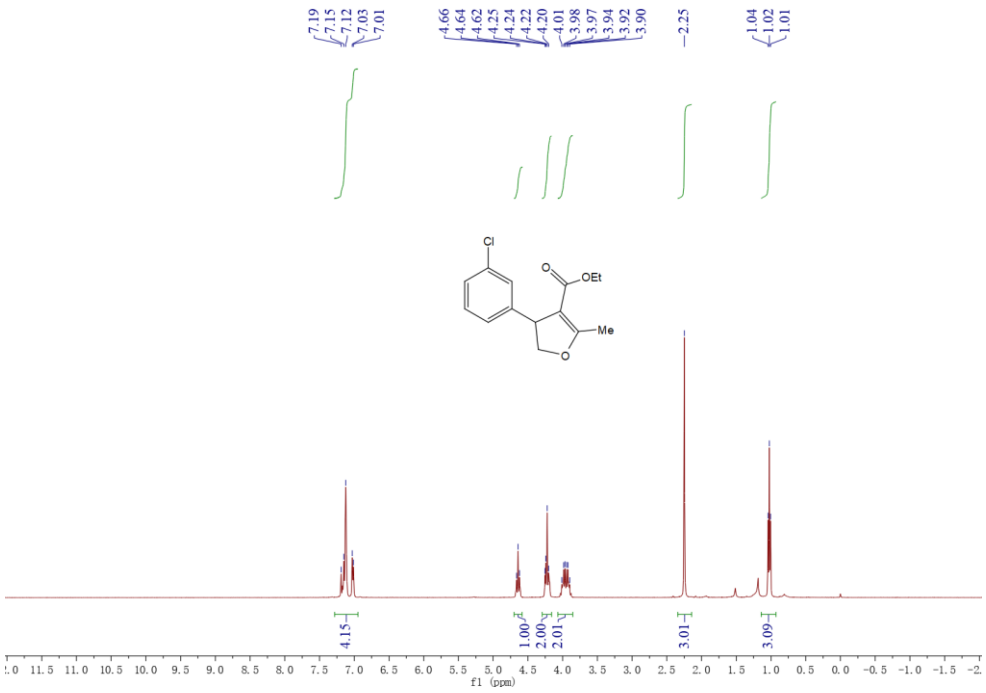
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ja**



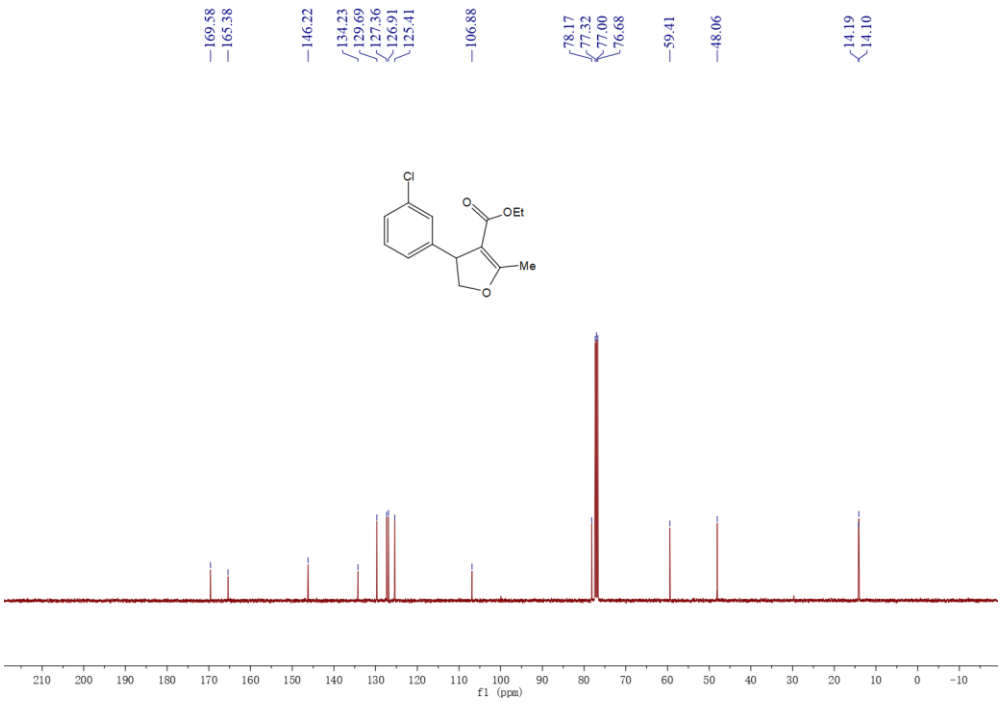
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ka**



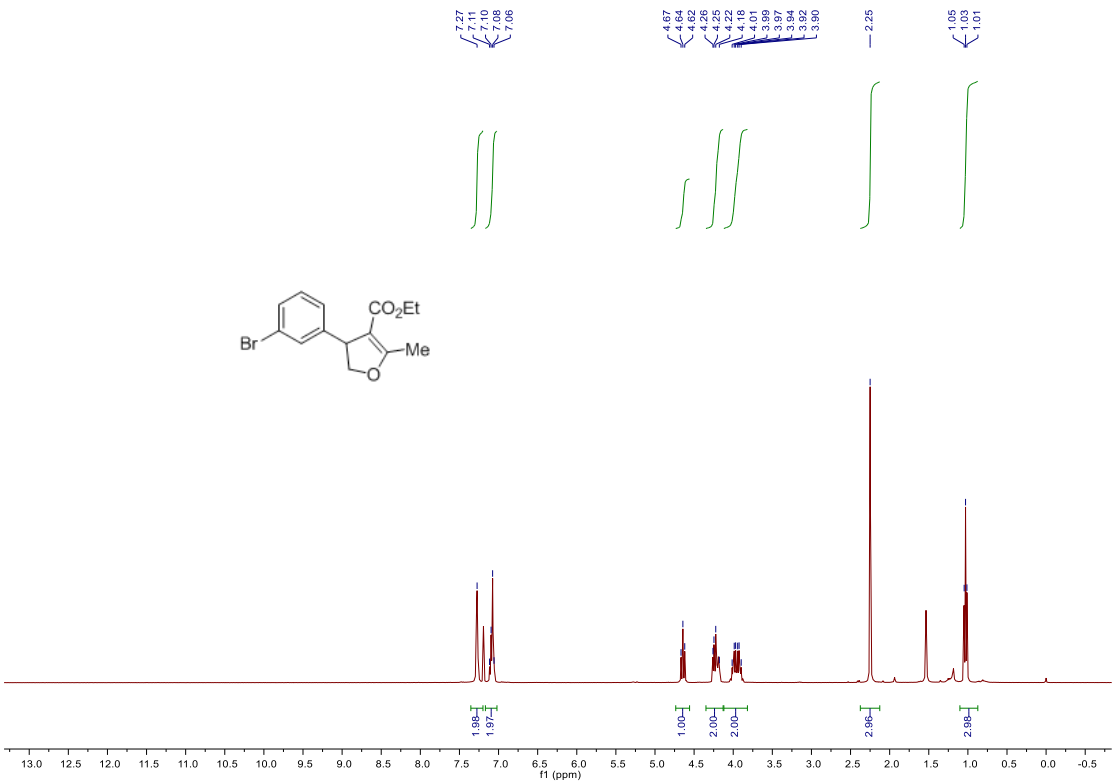
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ka**



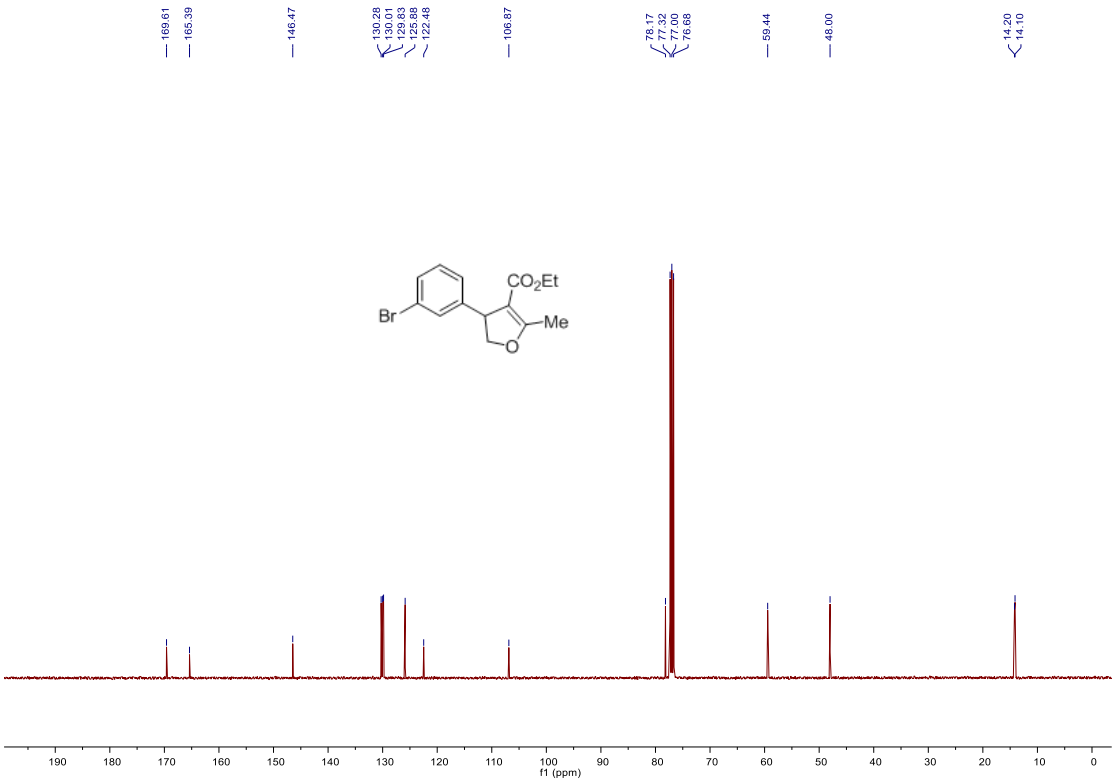
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3la**



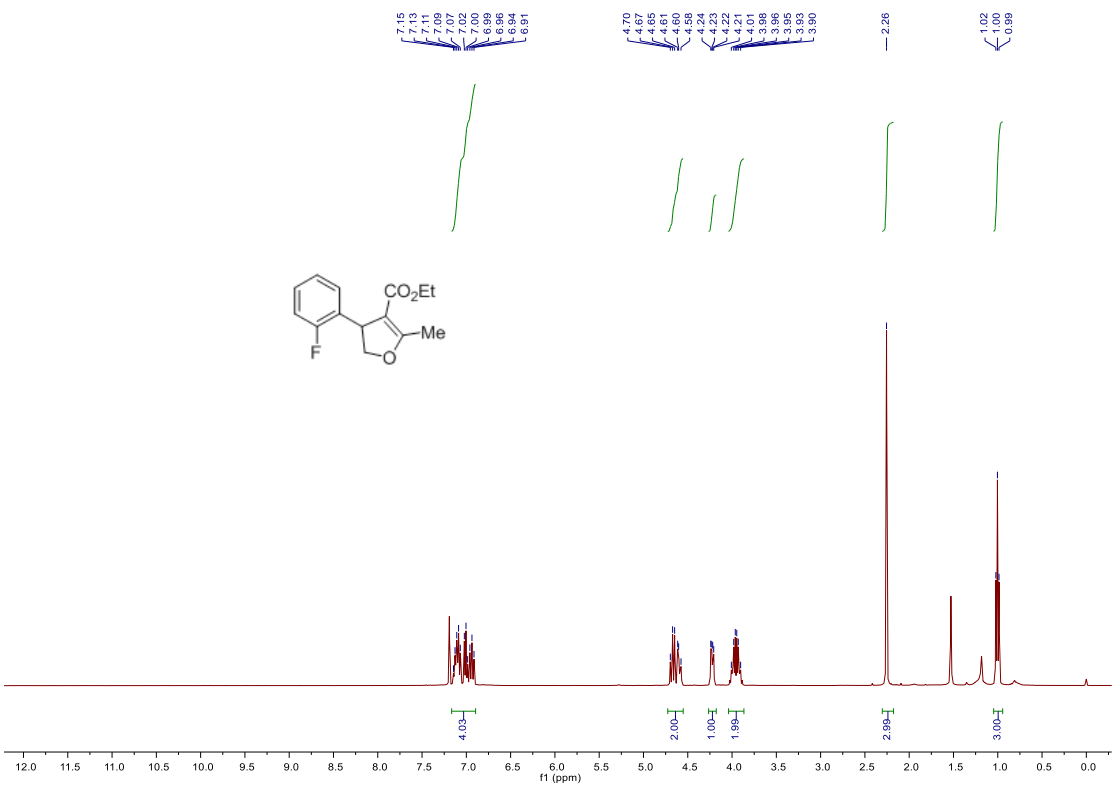
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3la**



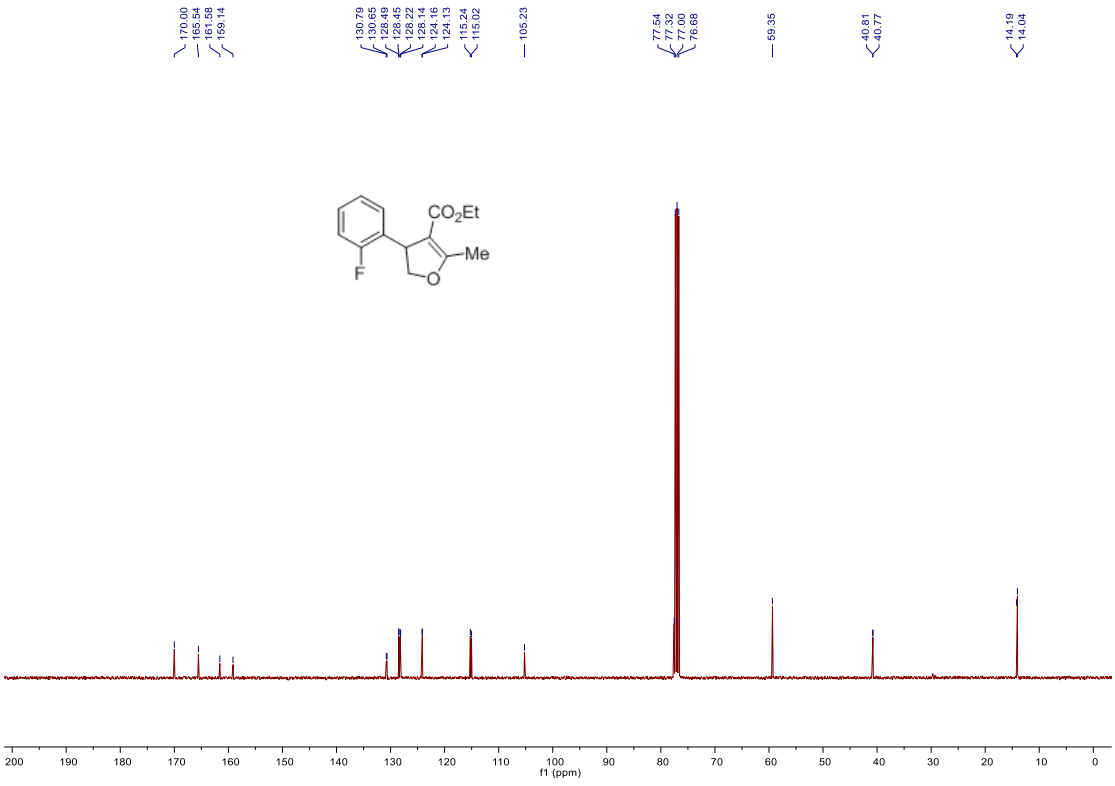
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ma**



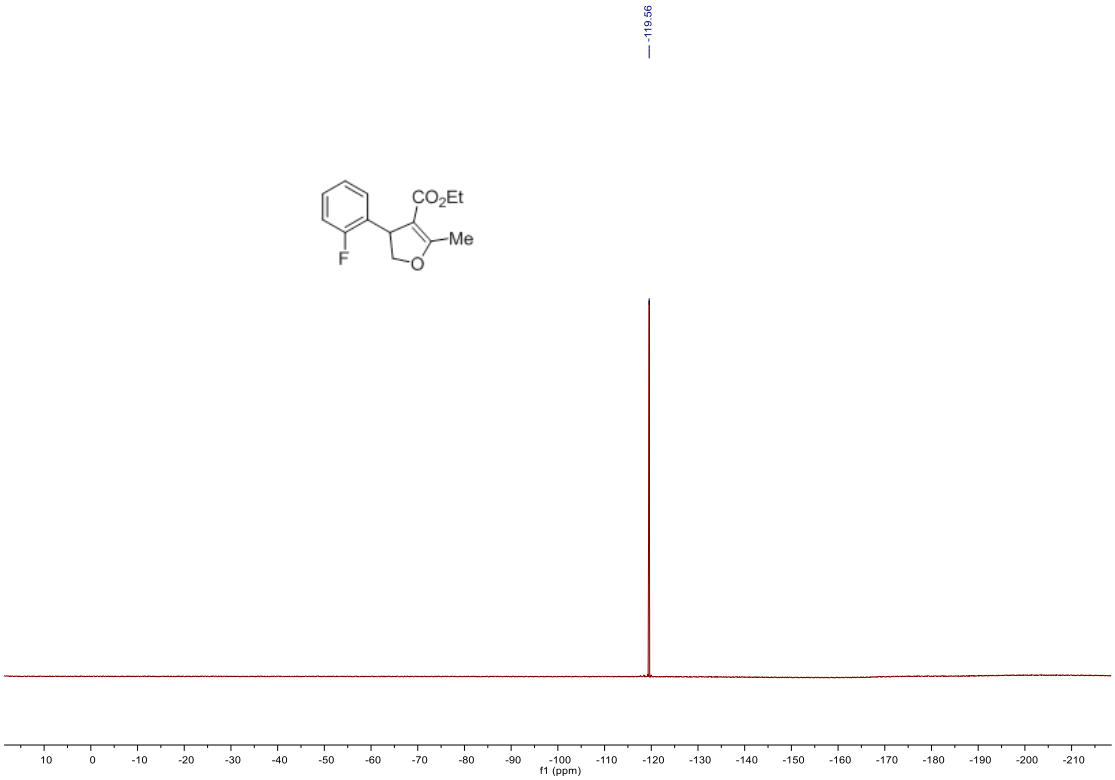
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ma**



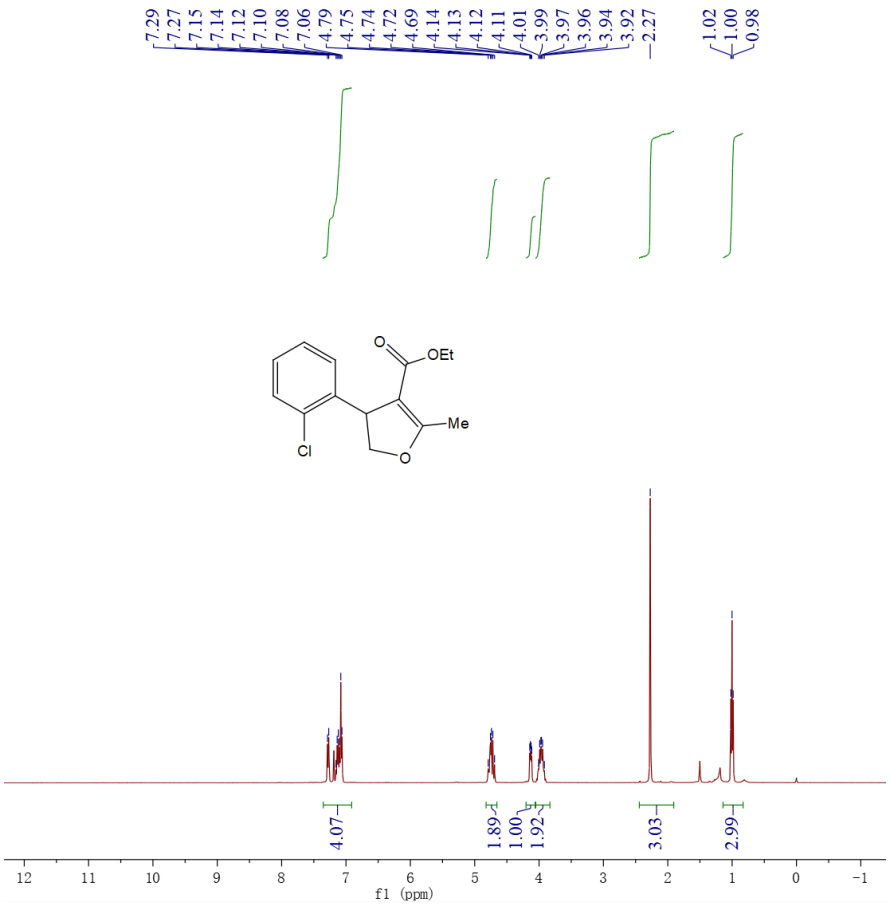
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3na**



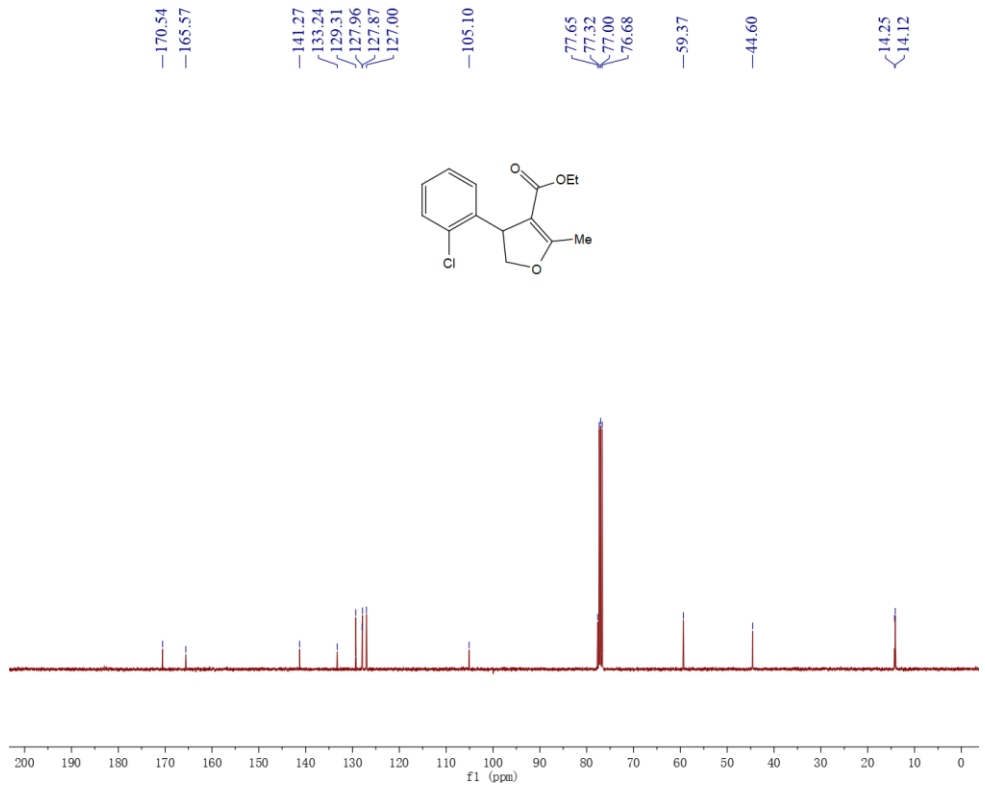
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3na**



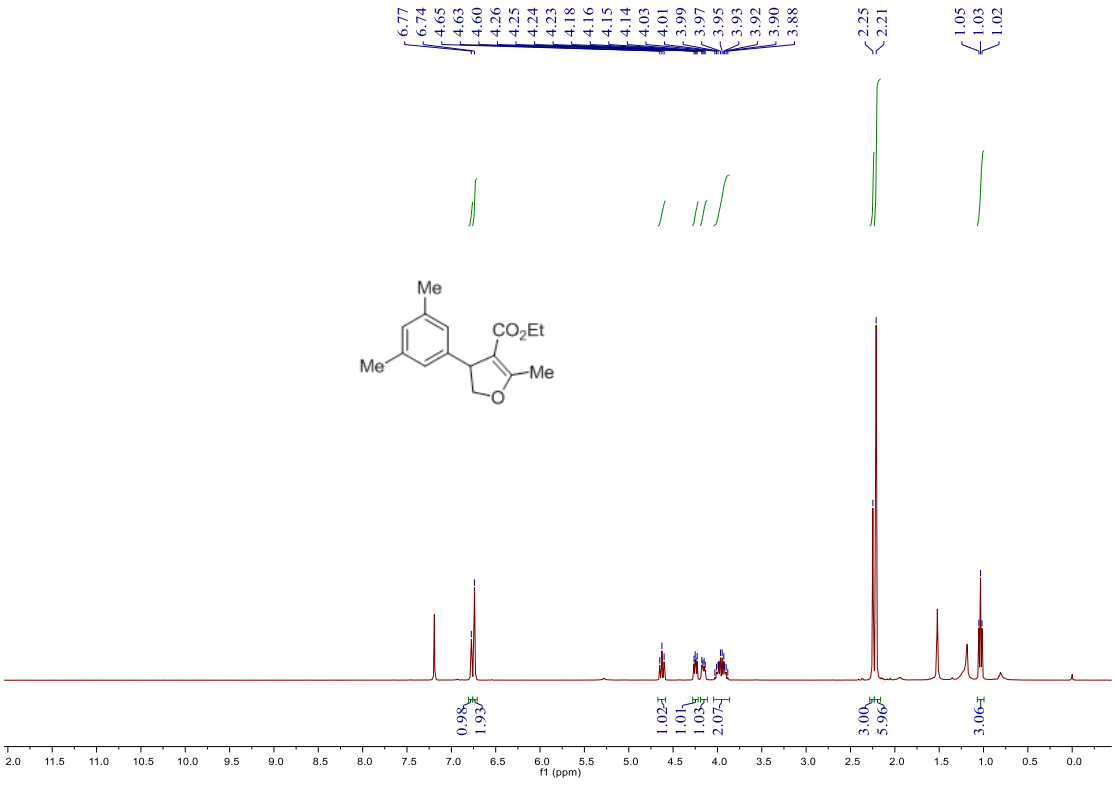
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3na**



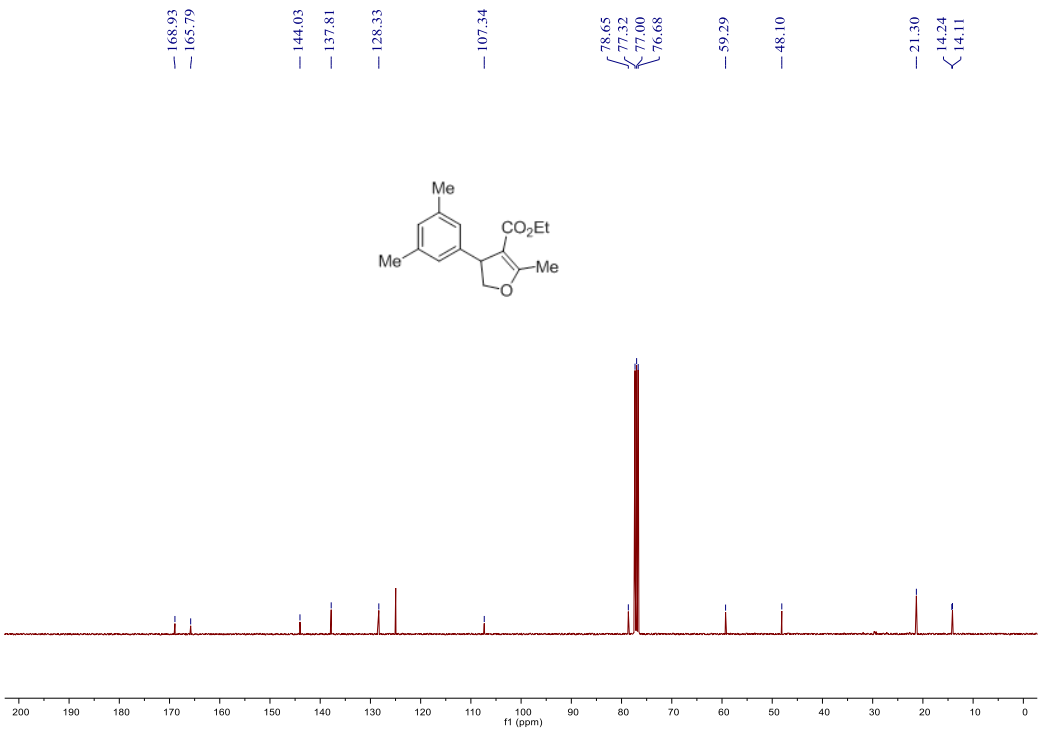
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3oa**



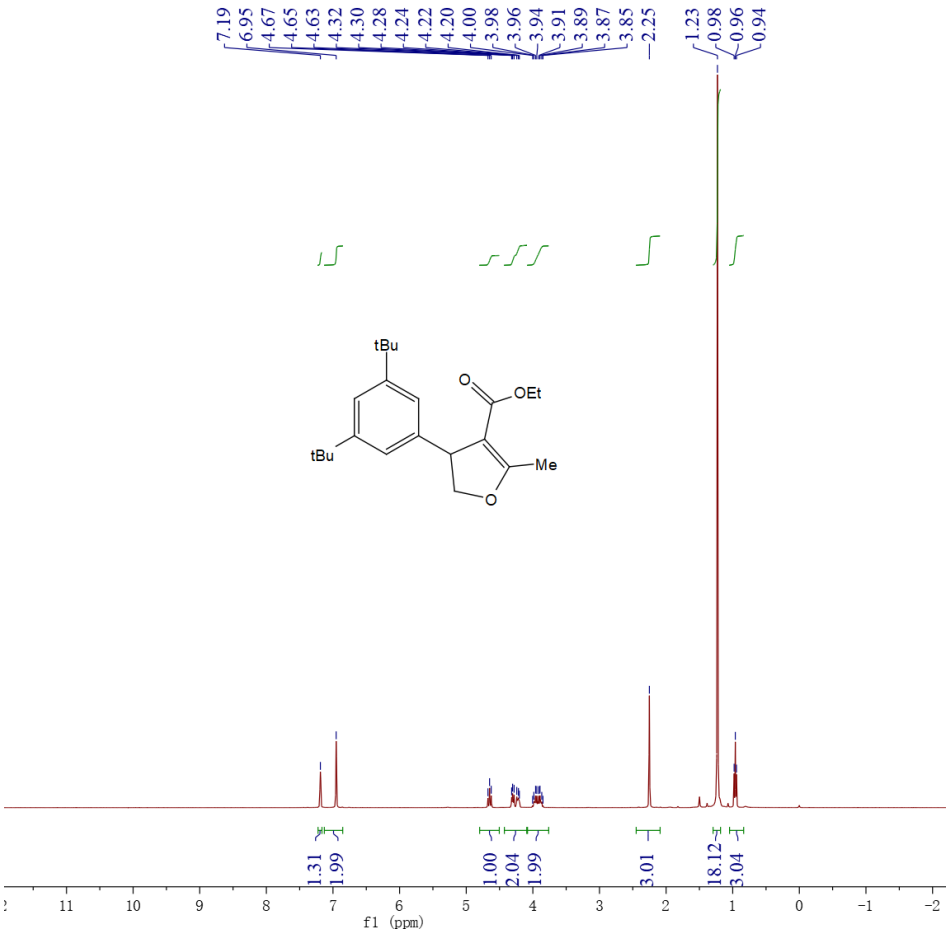
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3oa**



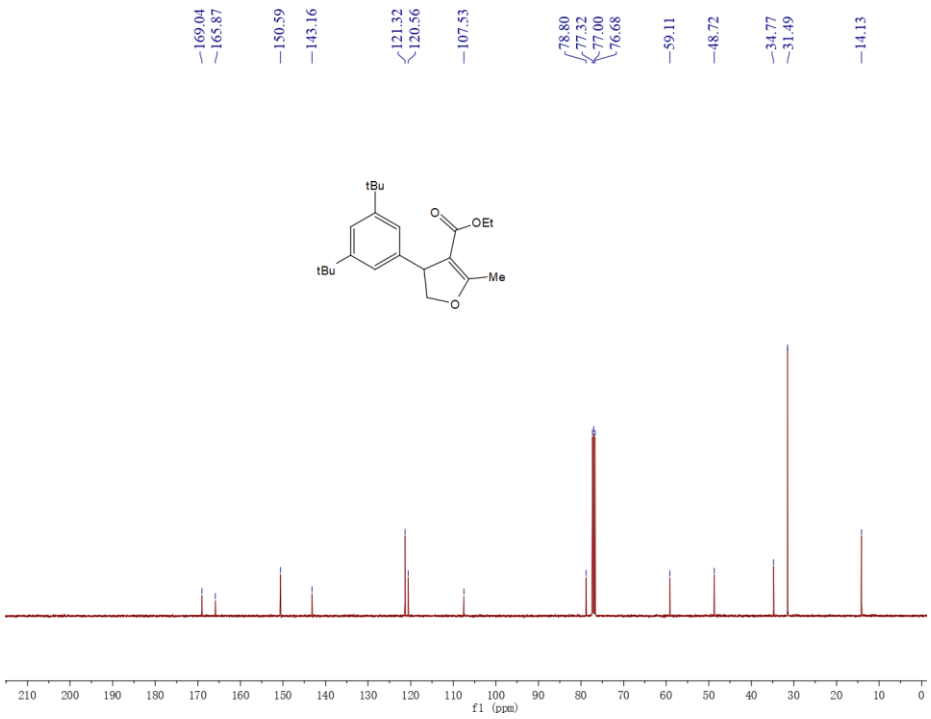
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3pa**



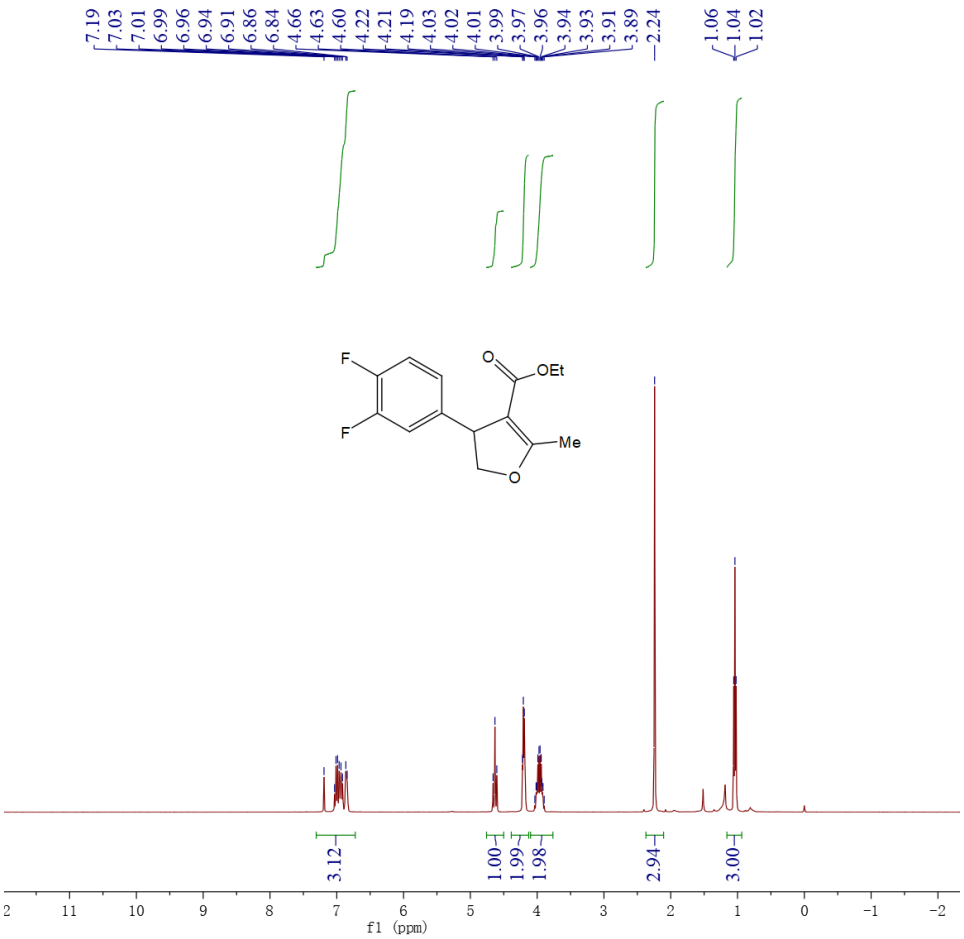
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3pa**



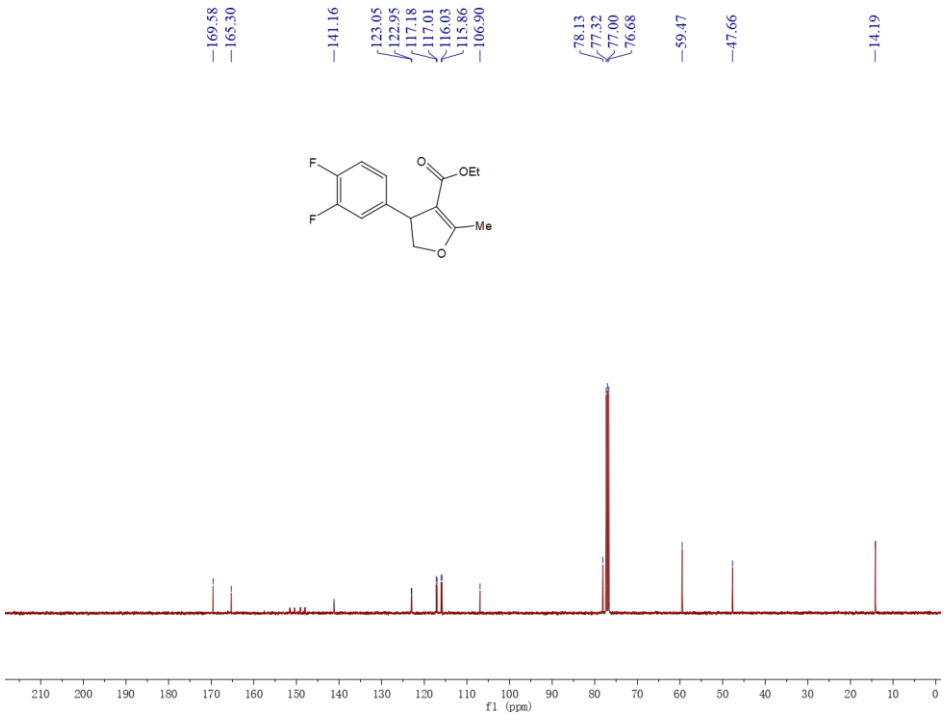
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3qa**



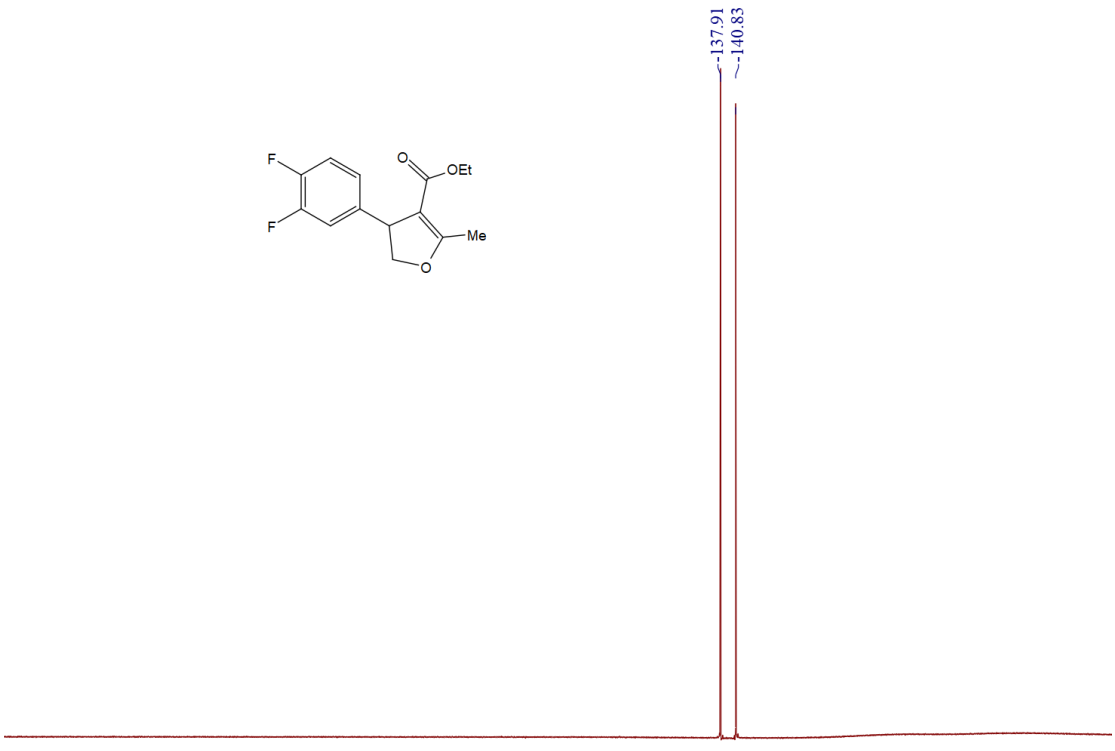
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3qa**



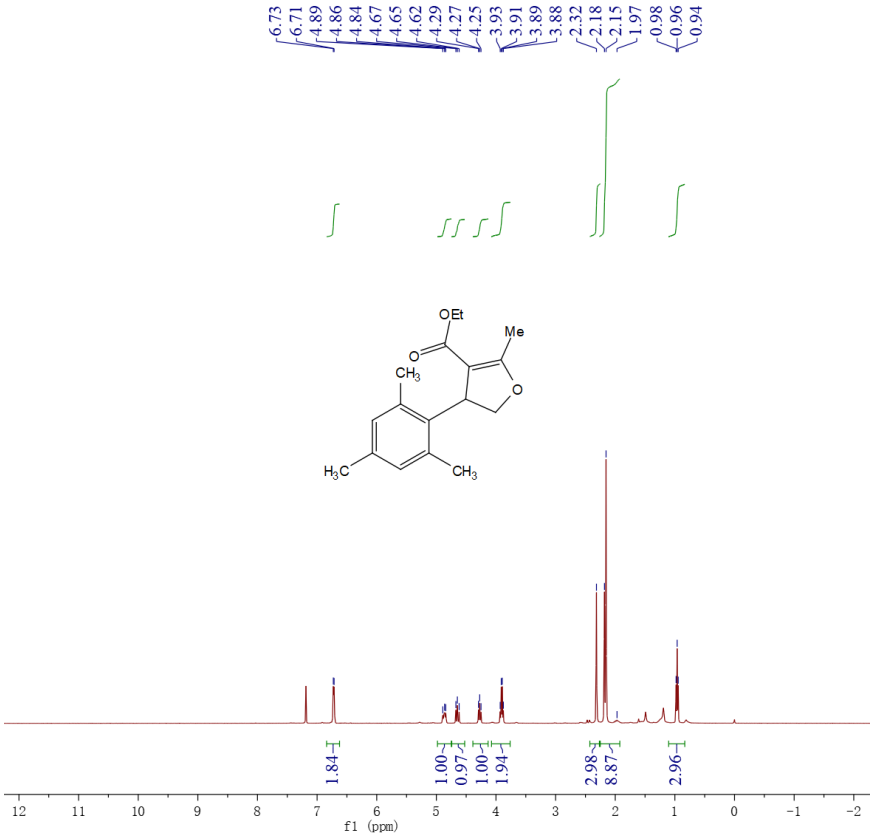
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ra**



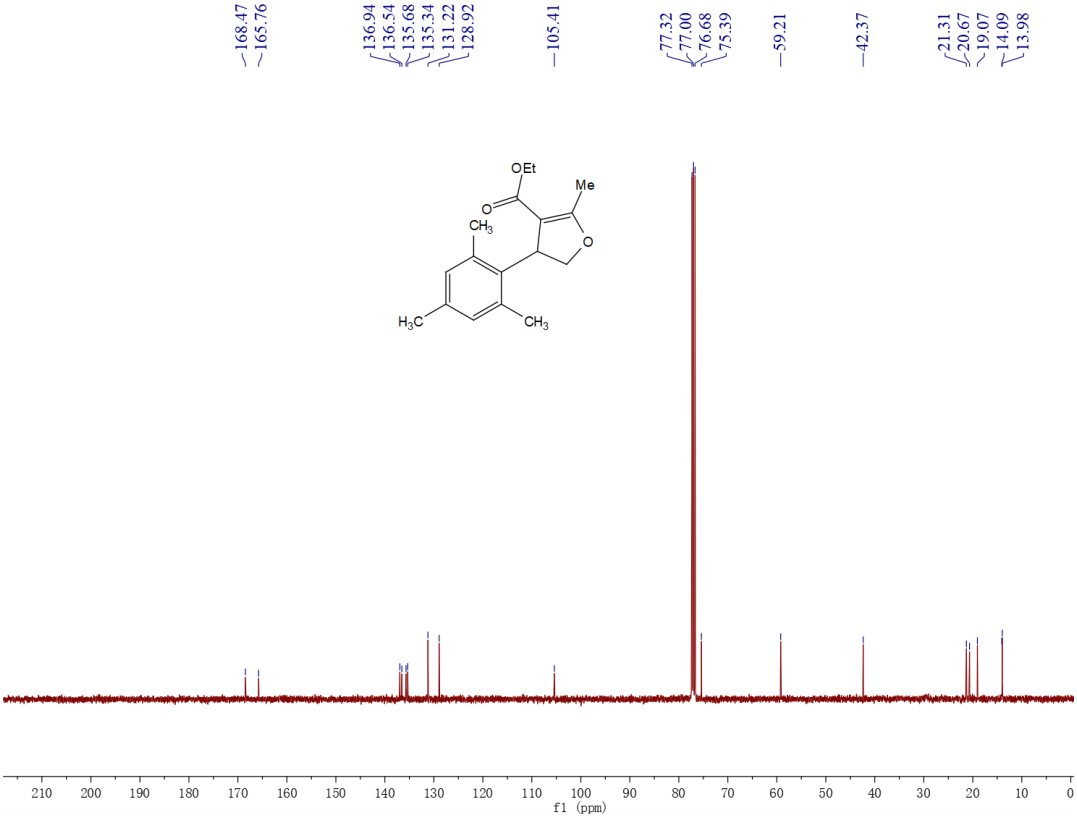
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ra**



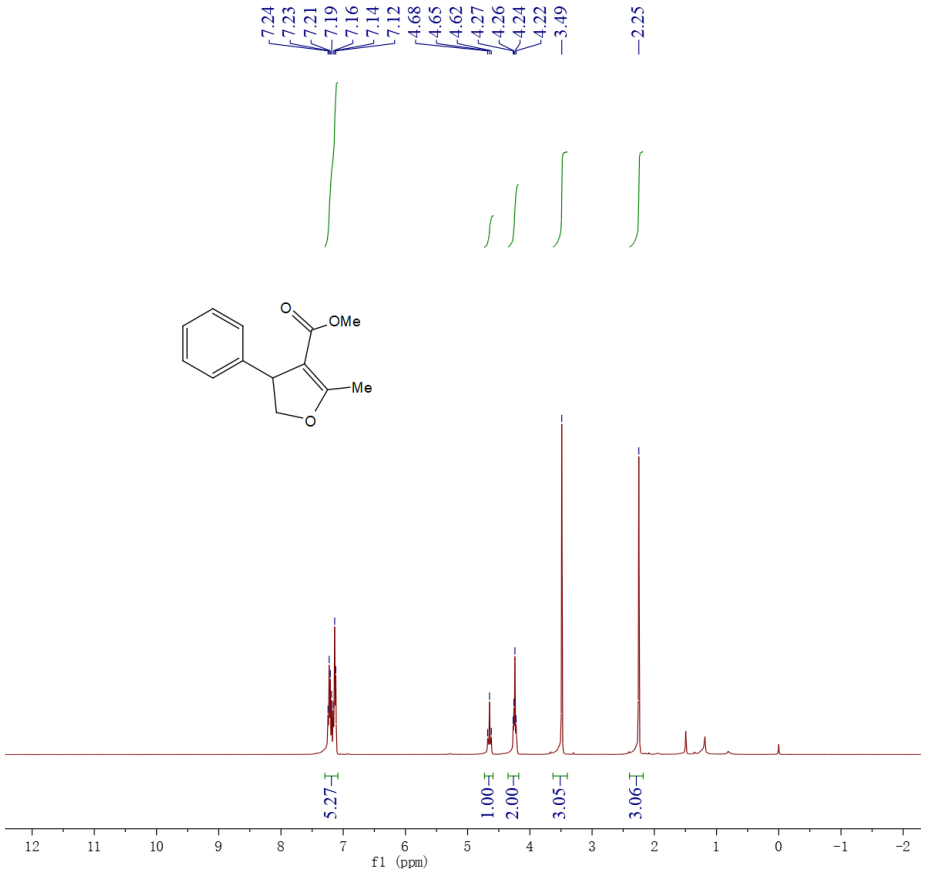
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ra**



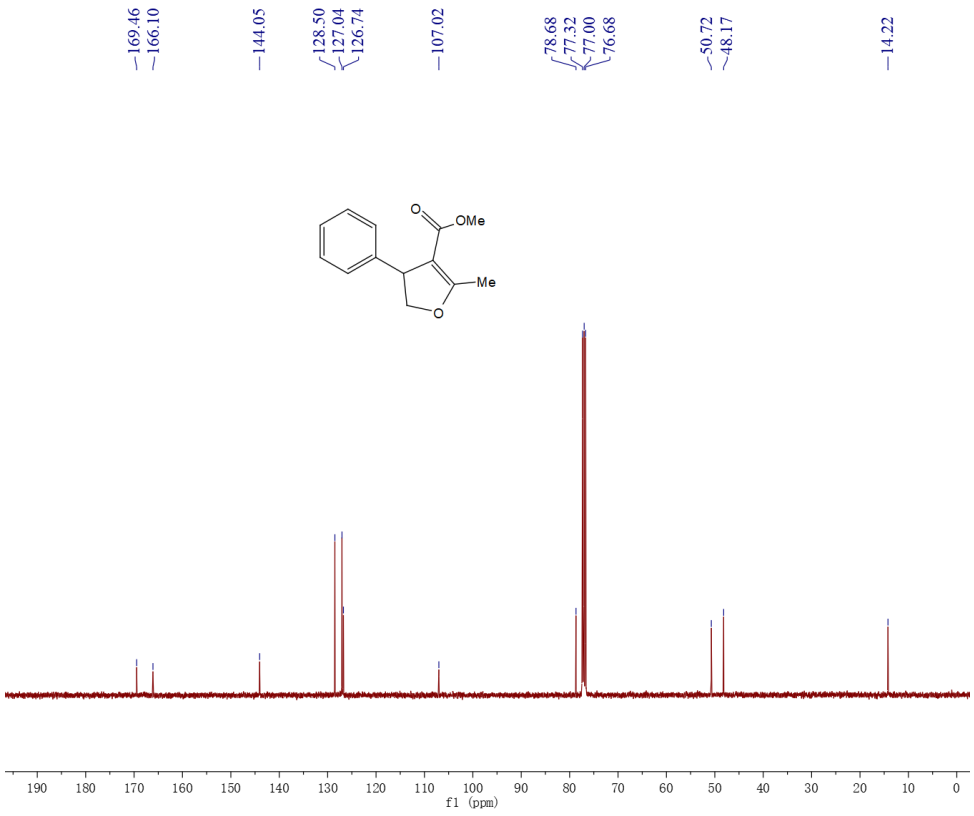
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3sa**



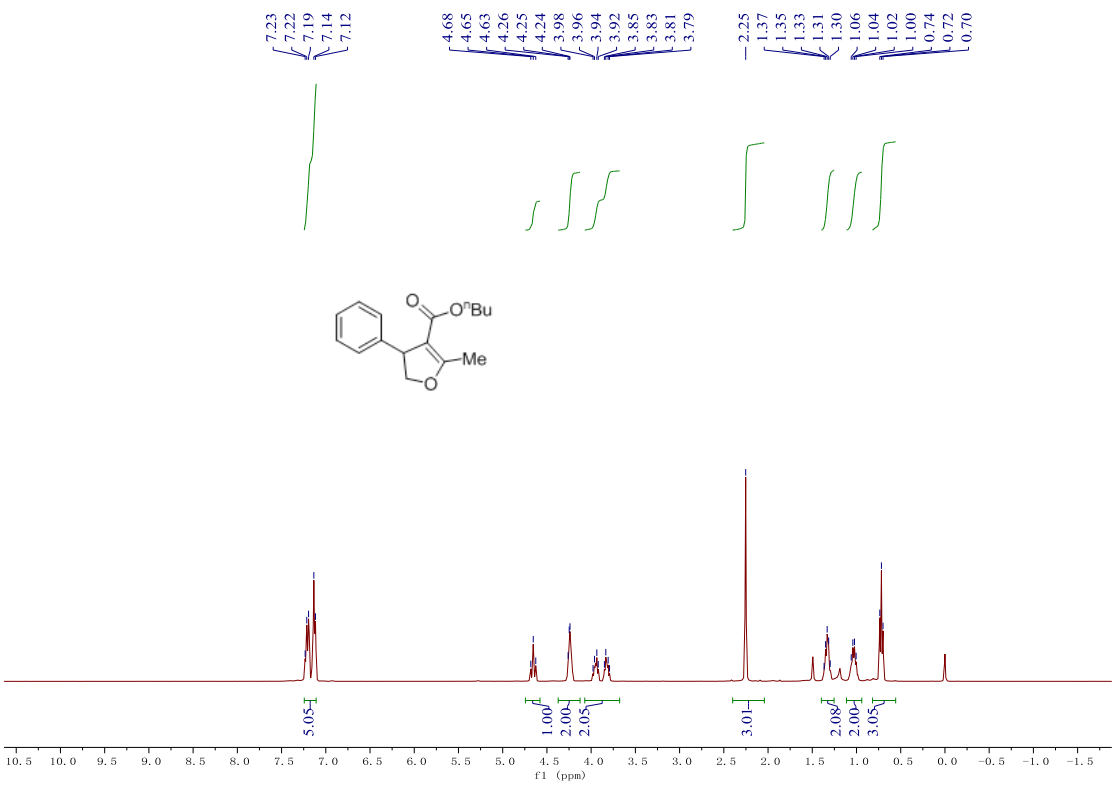
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3sa**



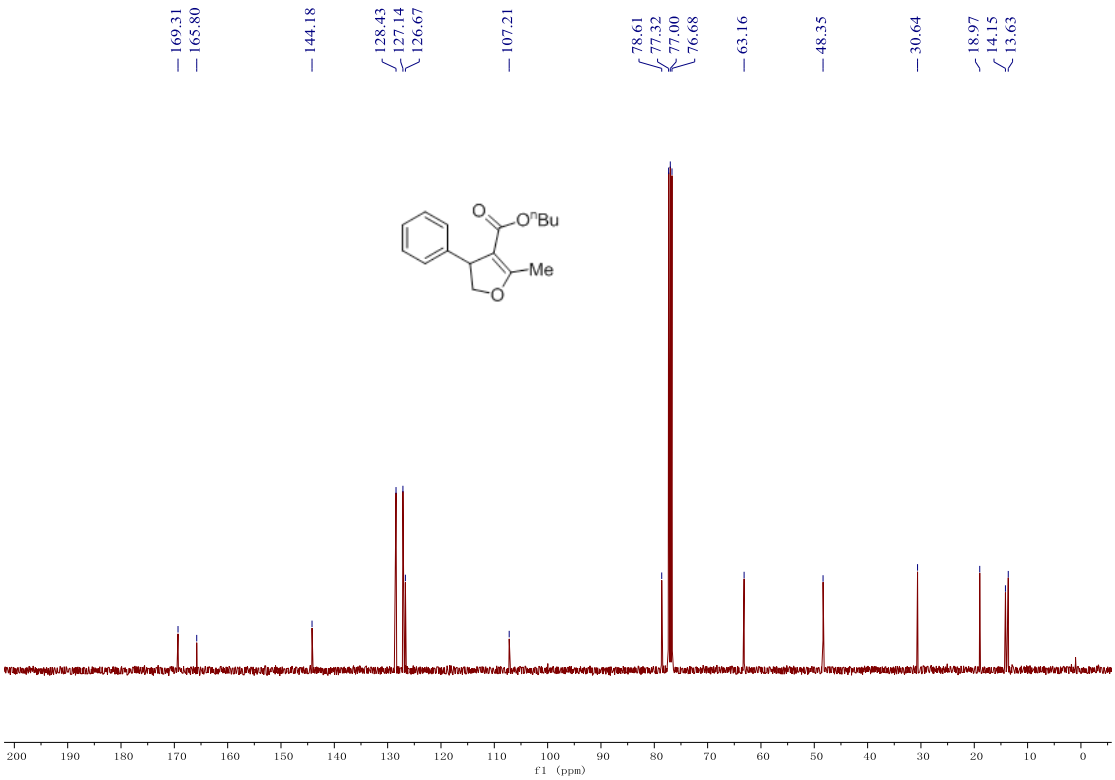
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ab**



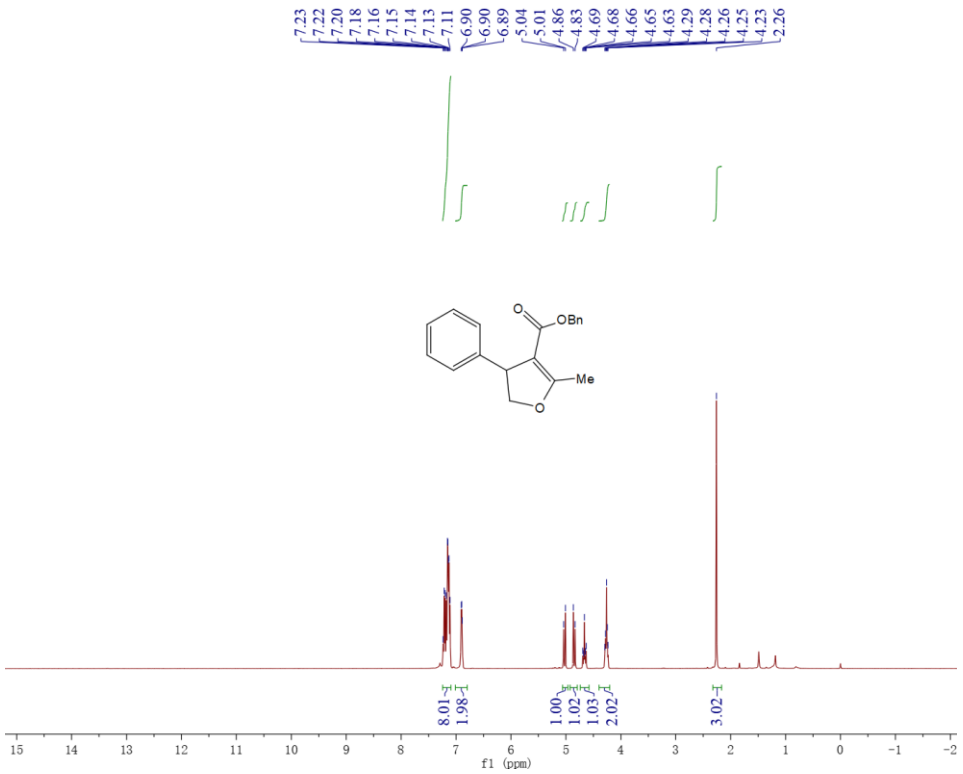
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ab**



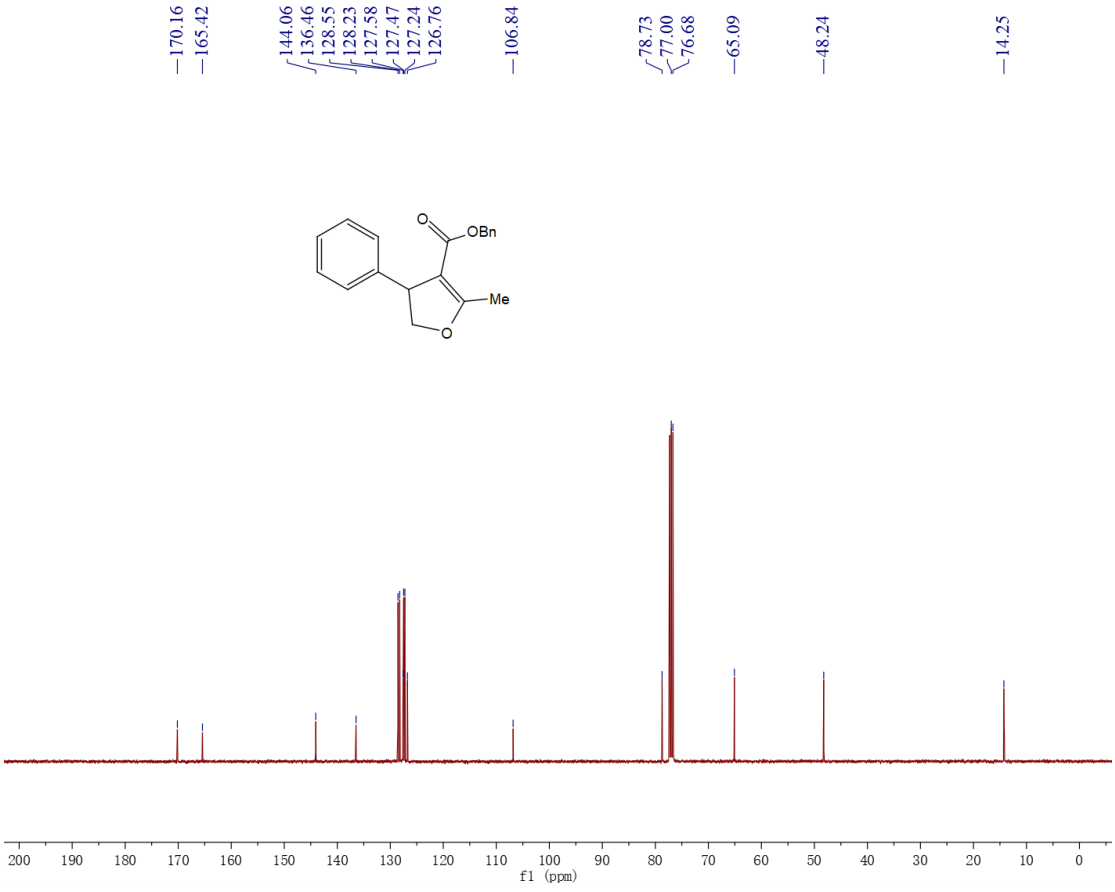
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ac**



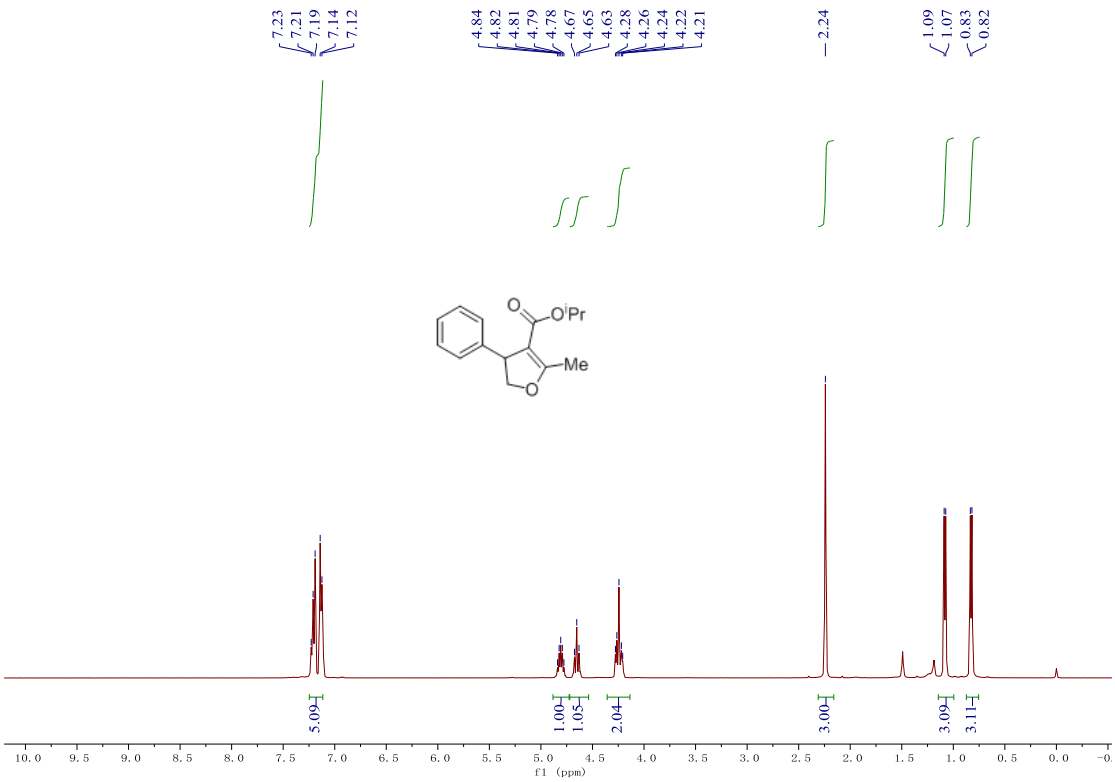
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ac**



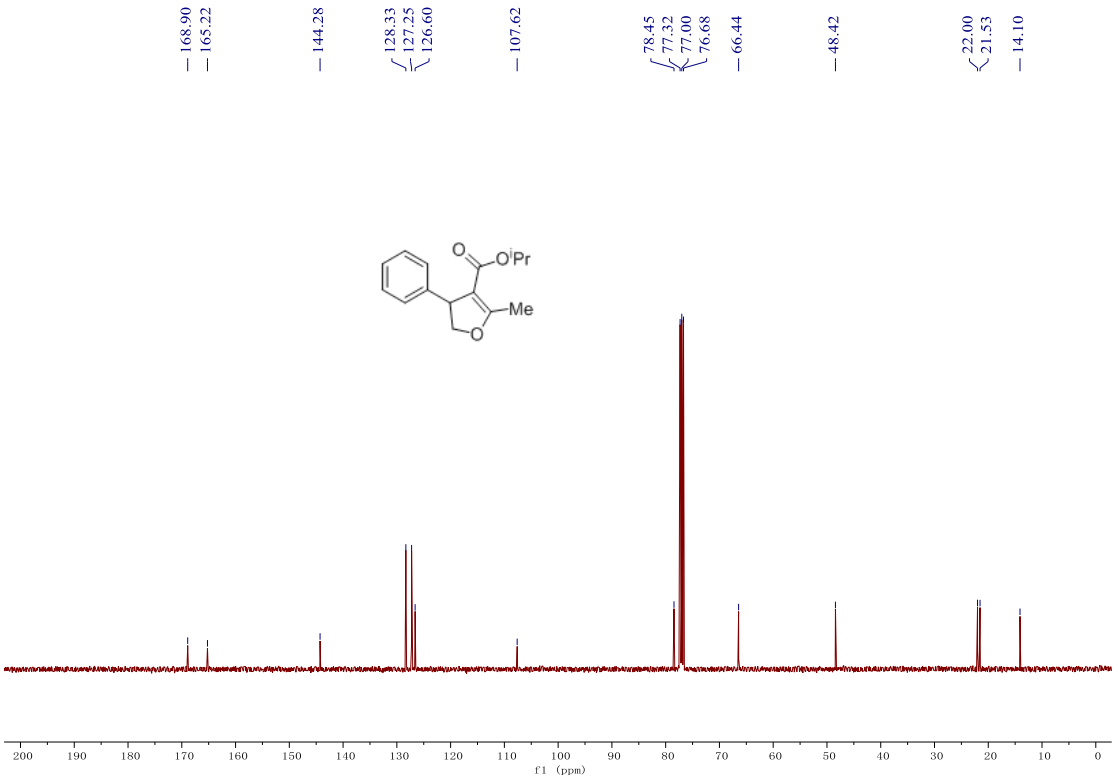
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ad**



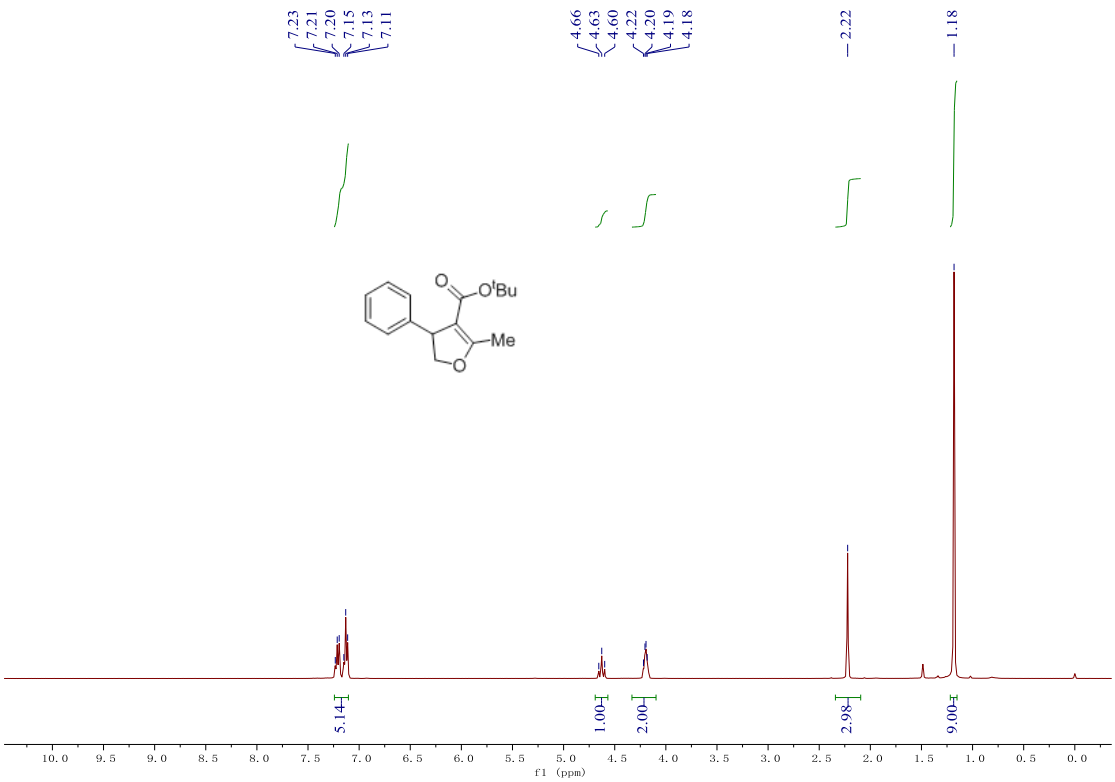
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ad**



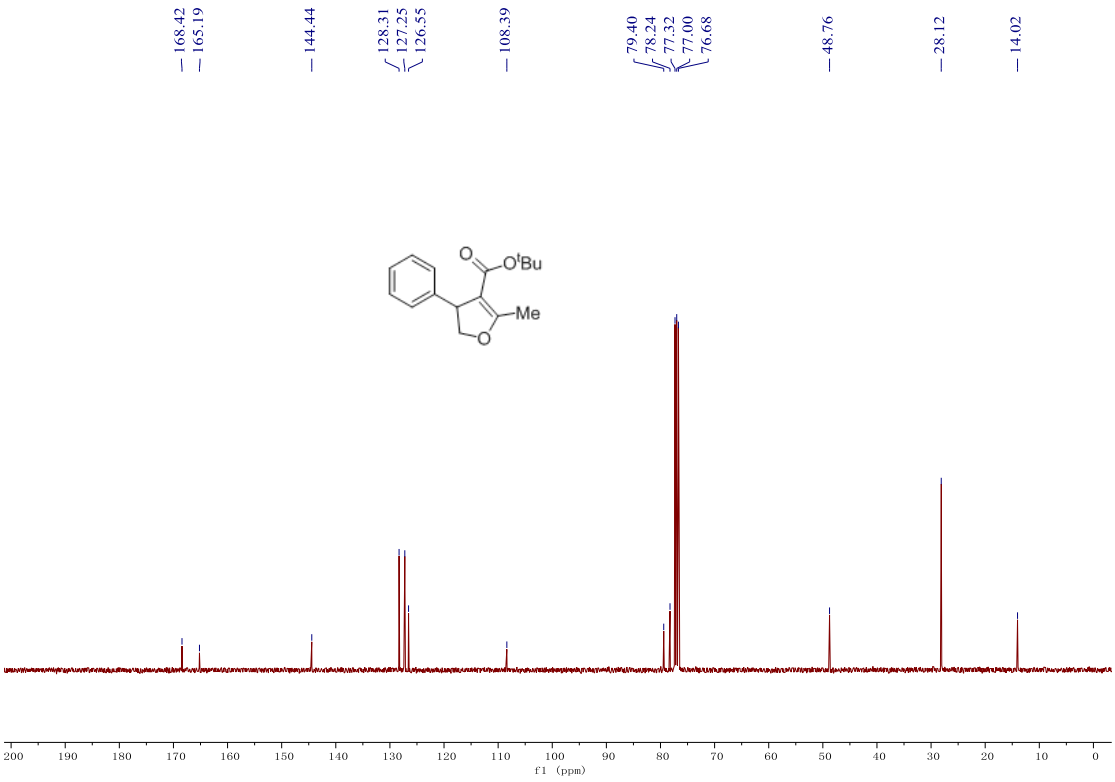
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ae**



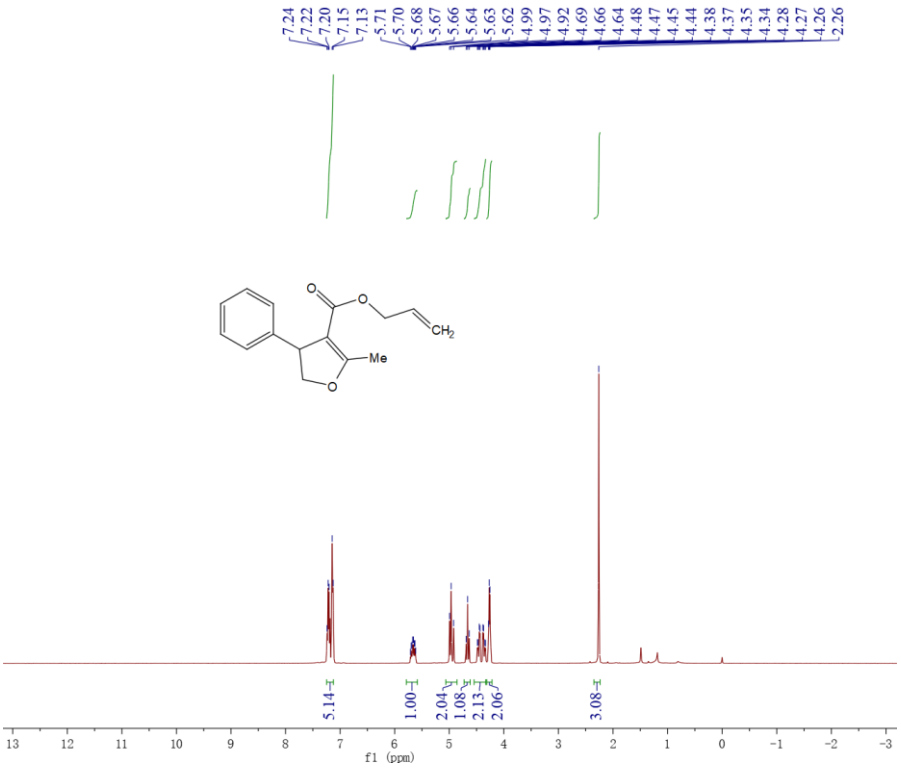
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ae**



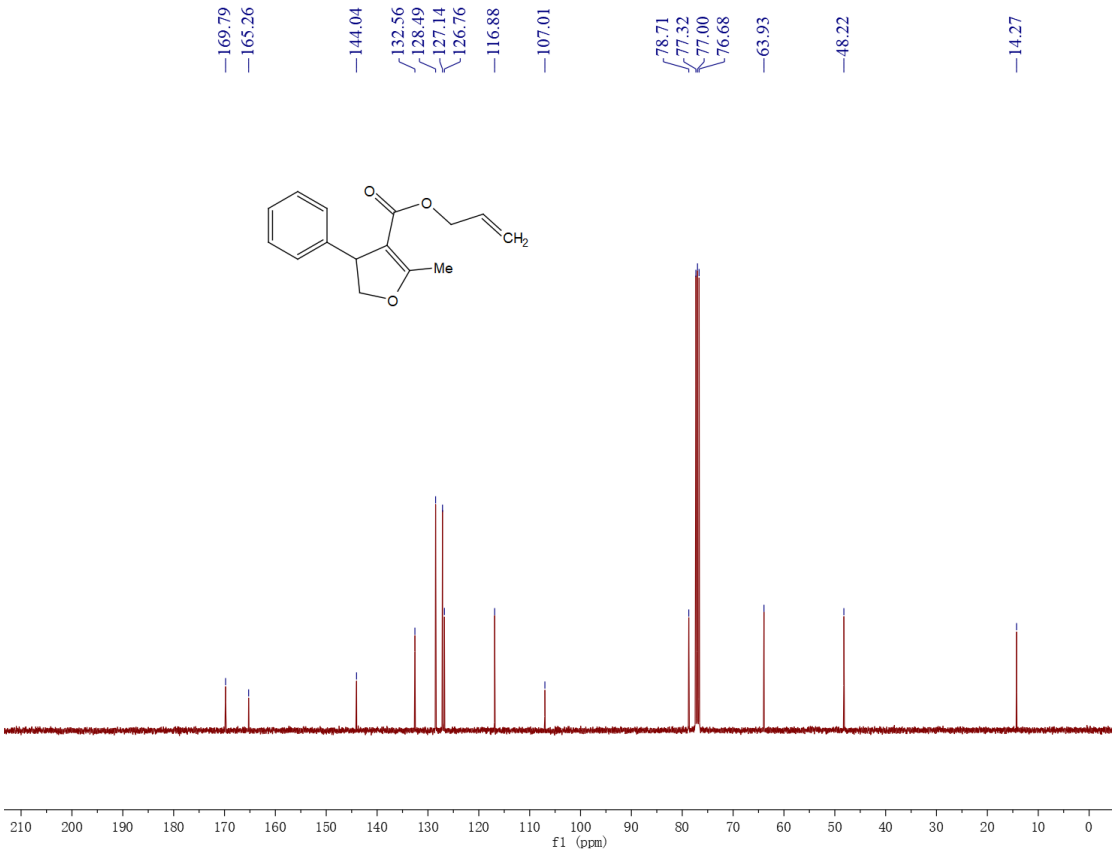
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3af**



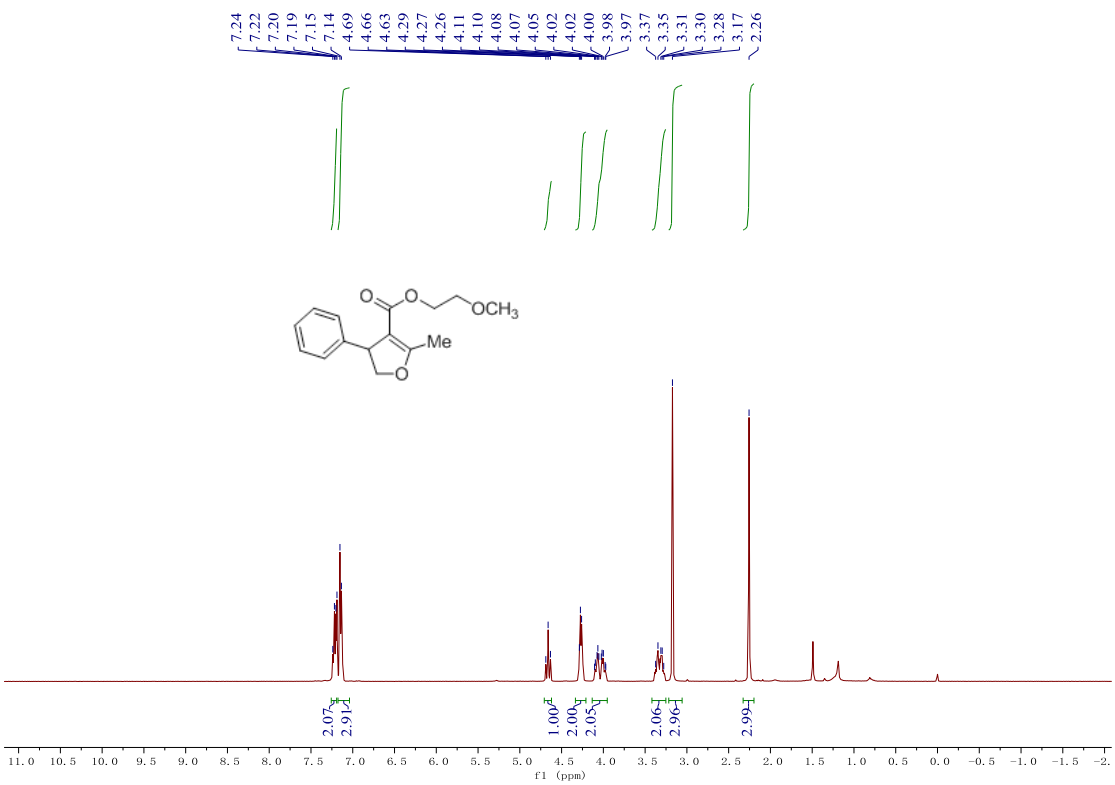
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3af**



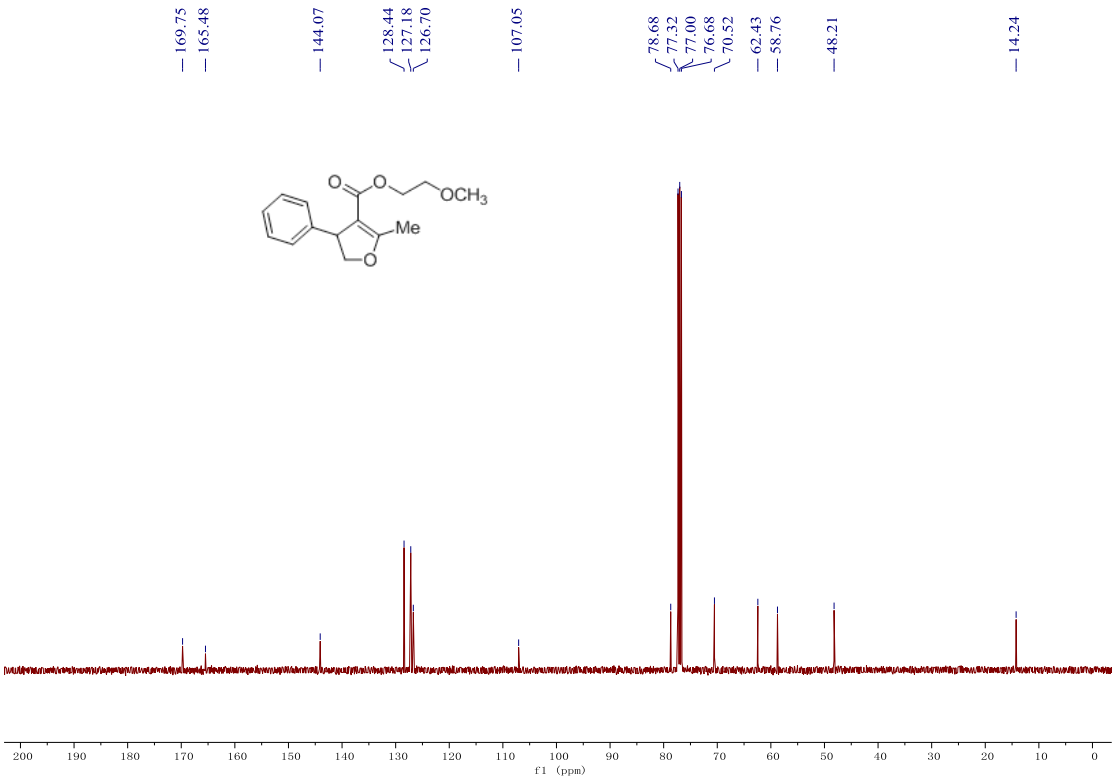
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ag**



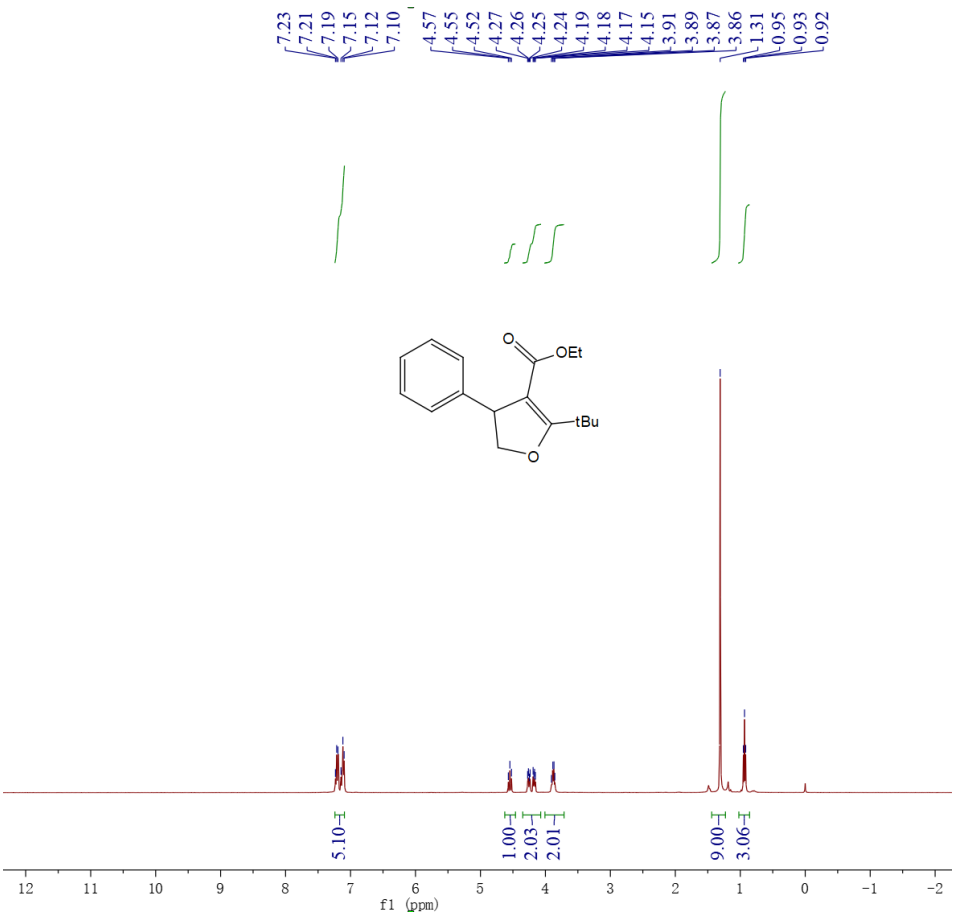
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ag**



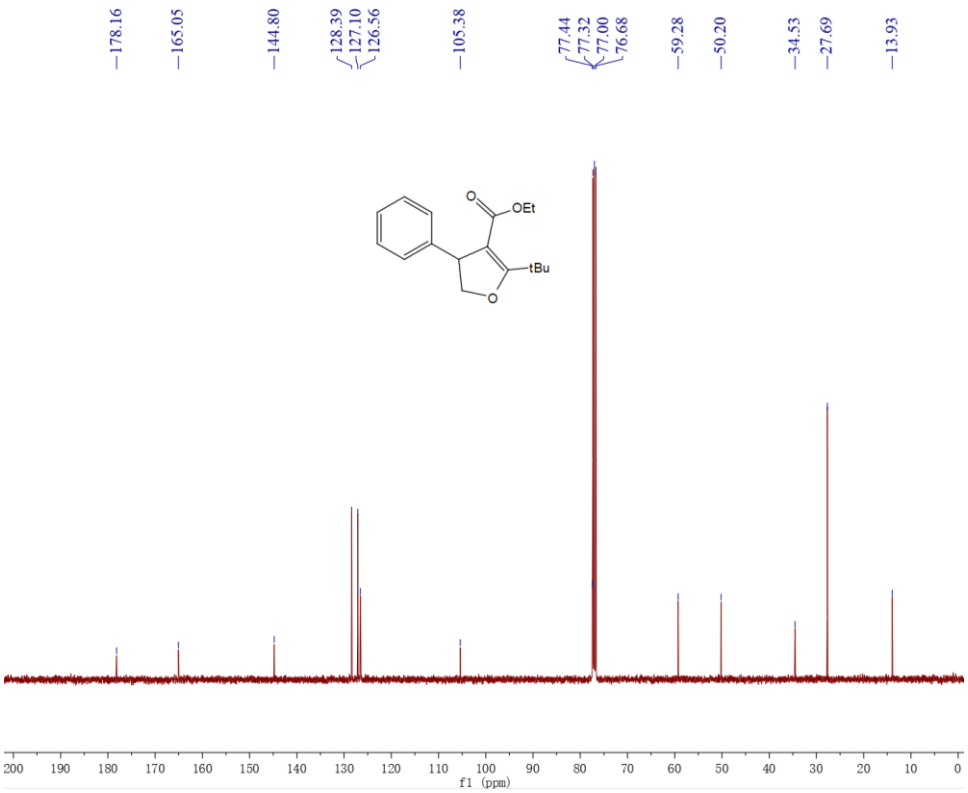
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ah**



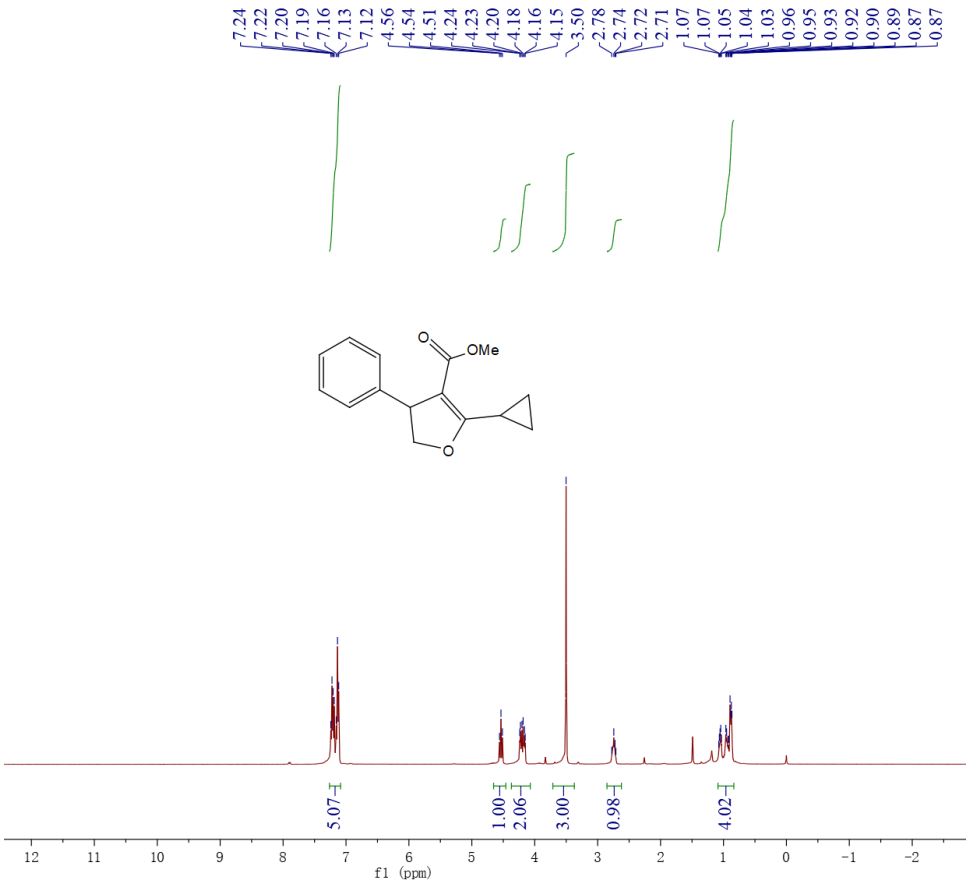
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ah**



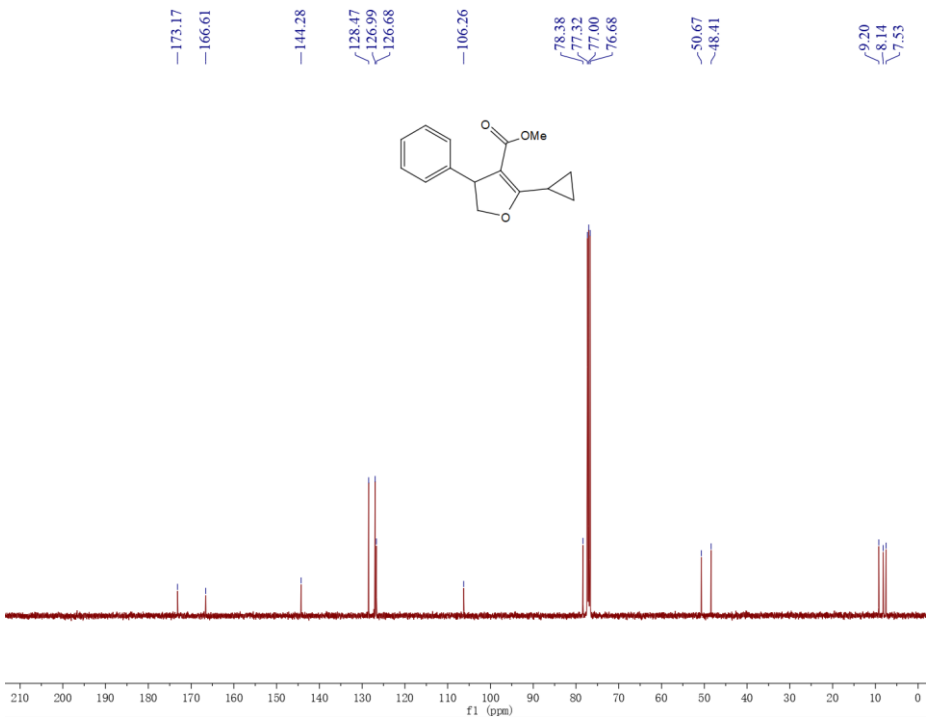
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ai**



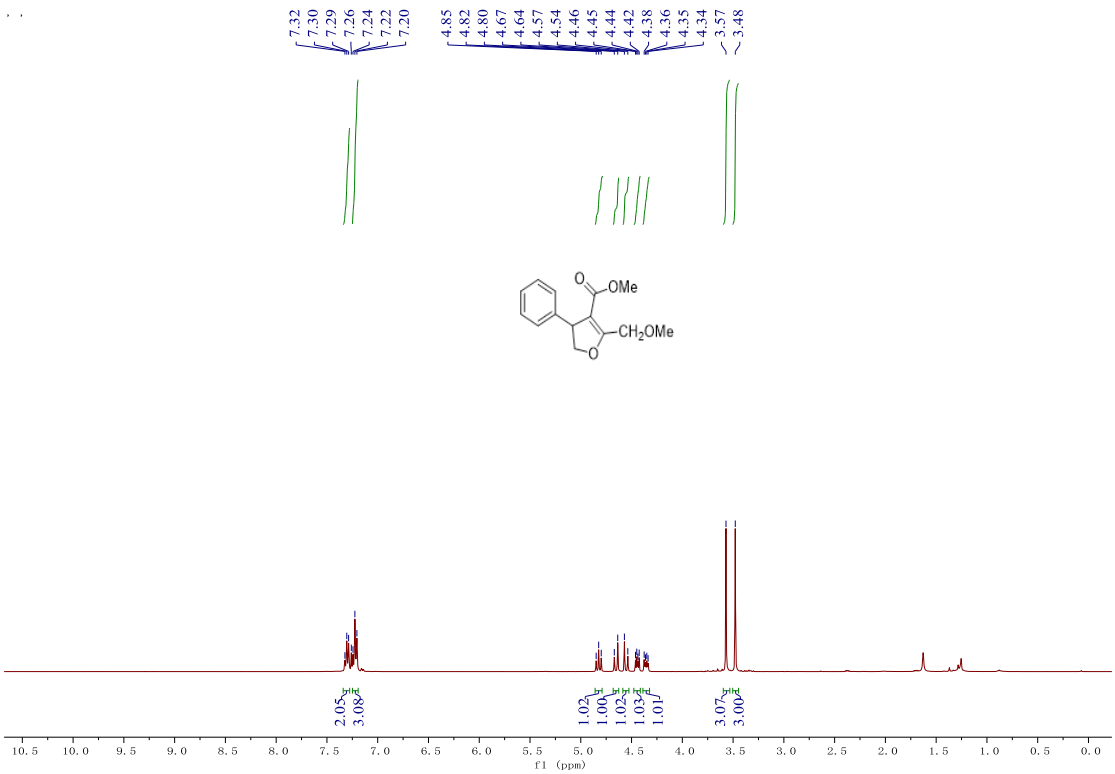
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ai**



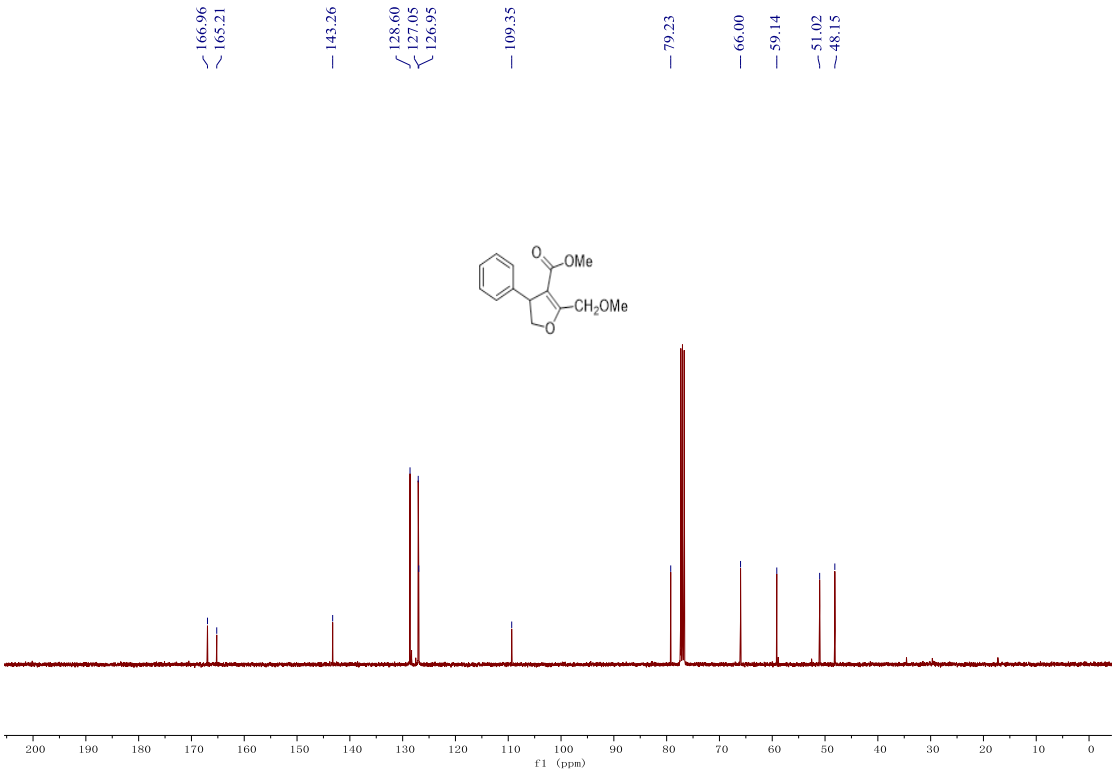
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aj**



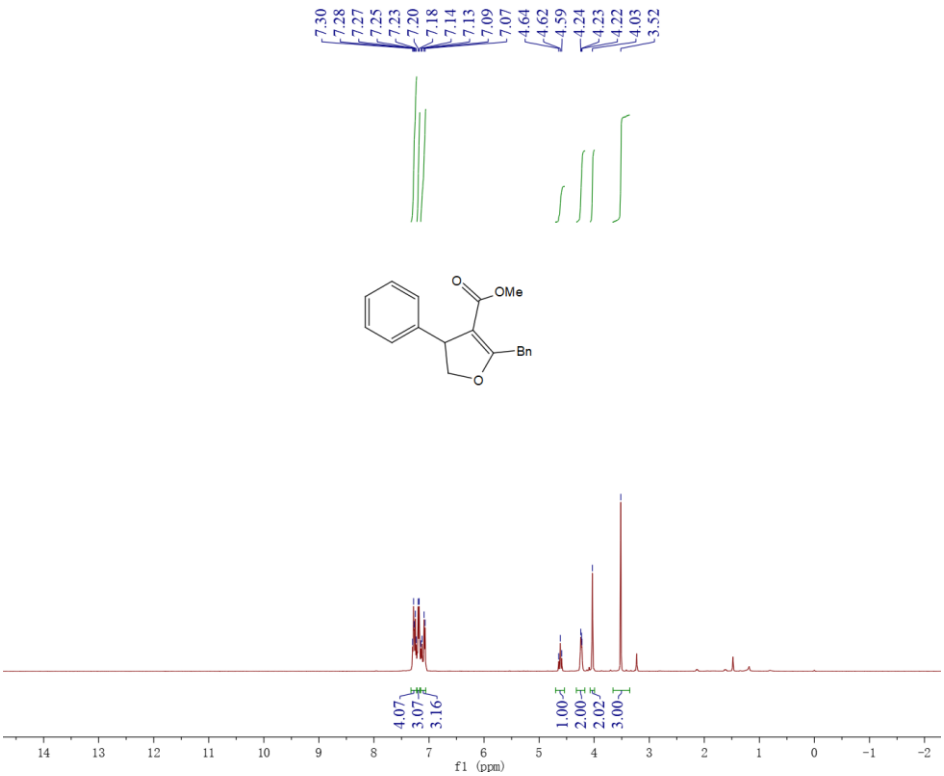
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3aj**



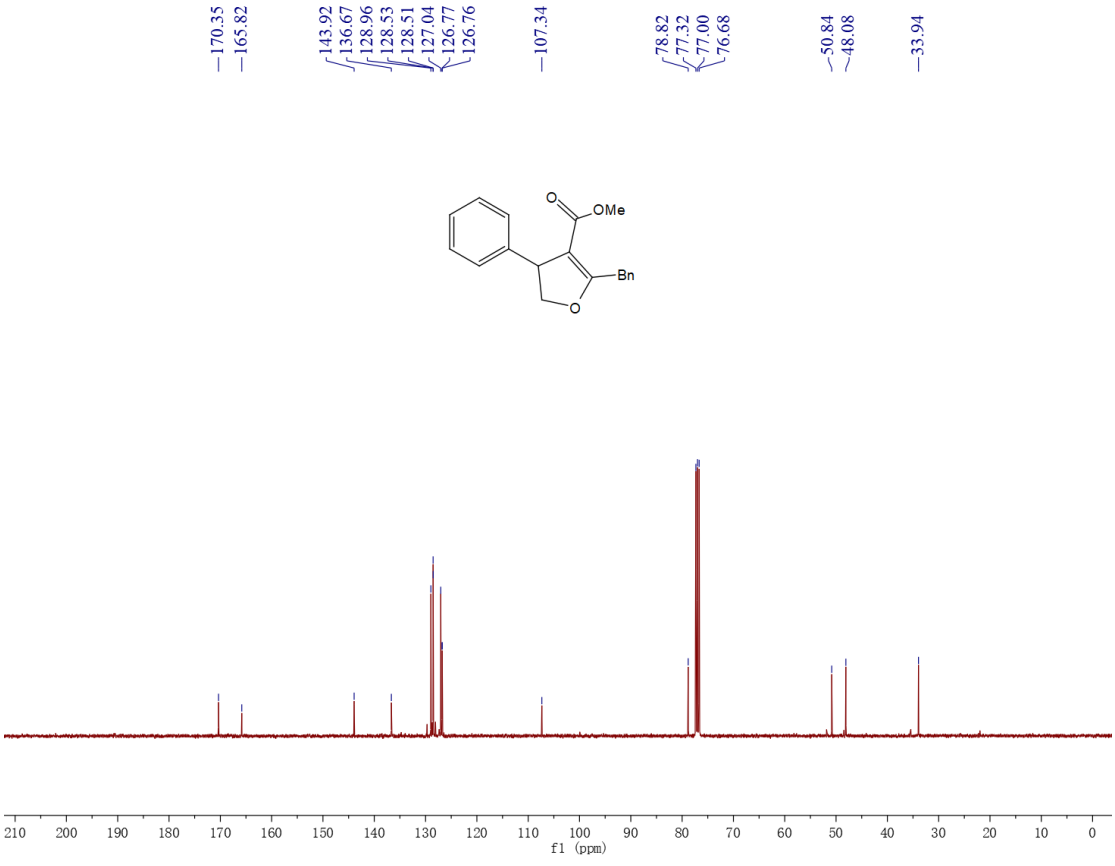
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ak**



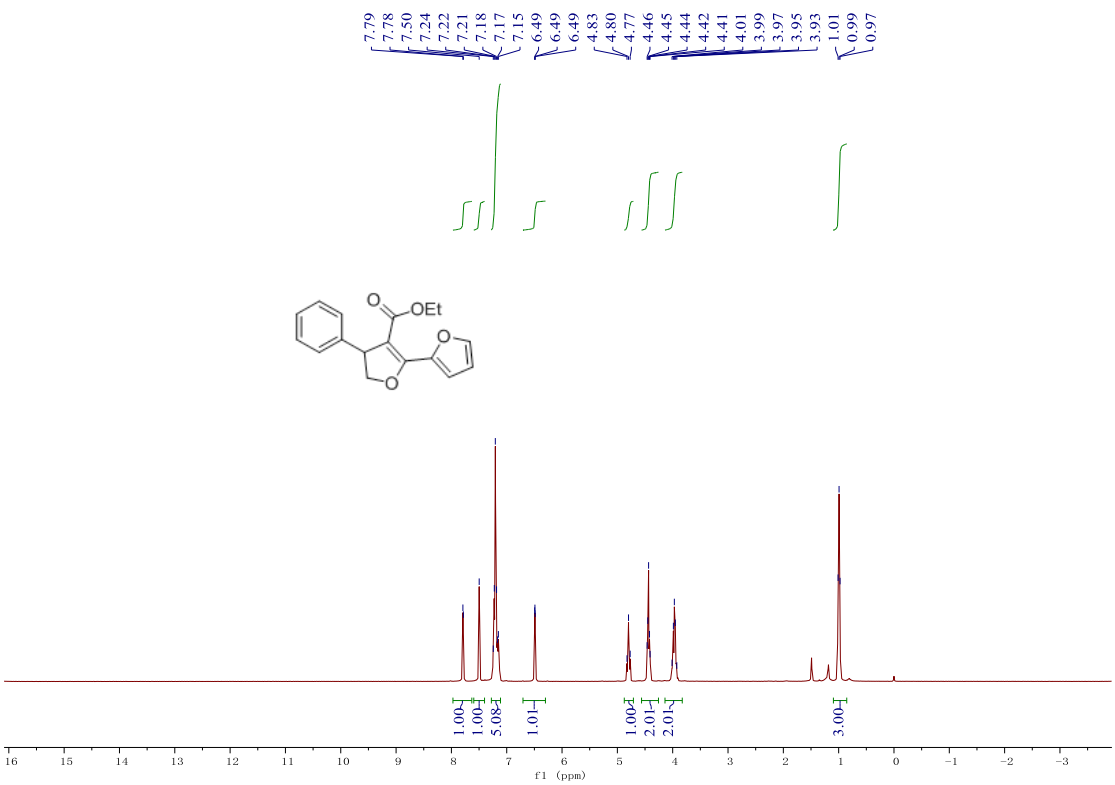
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ak**



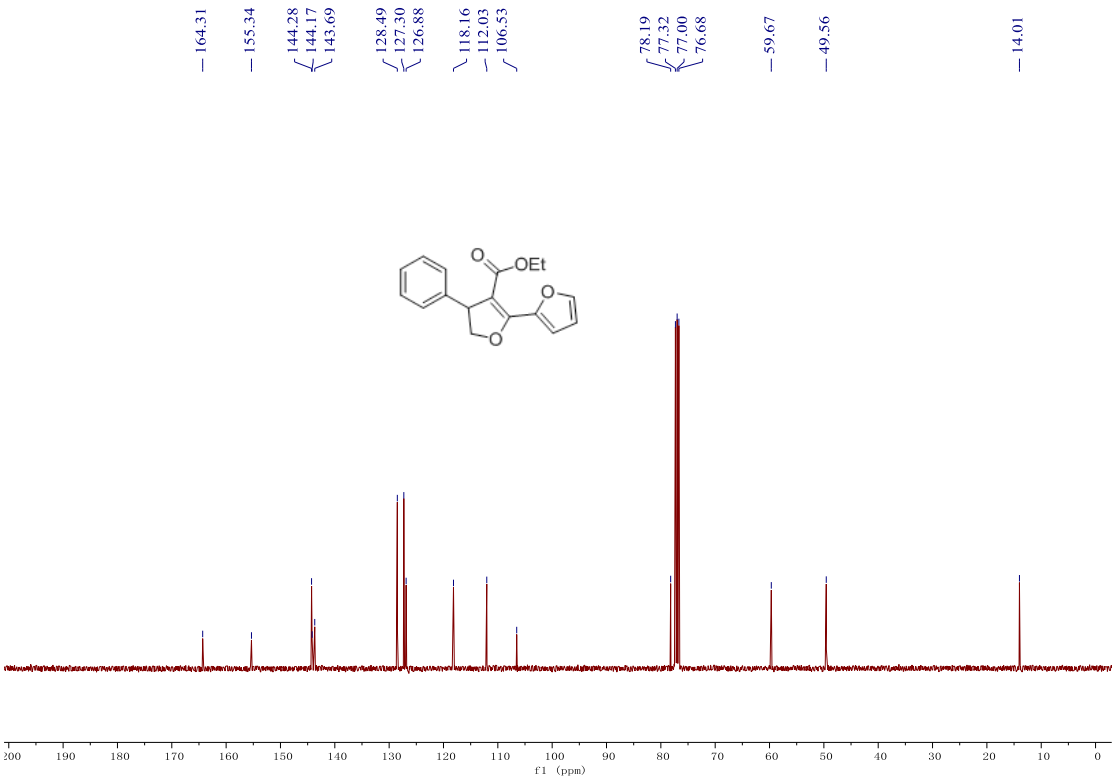
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3al**



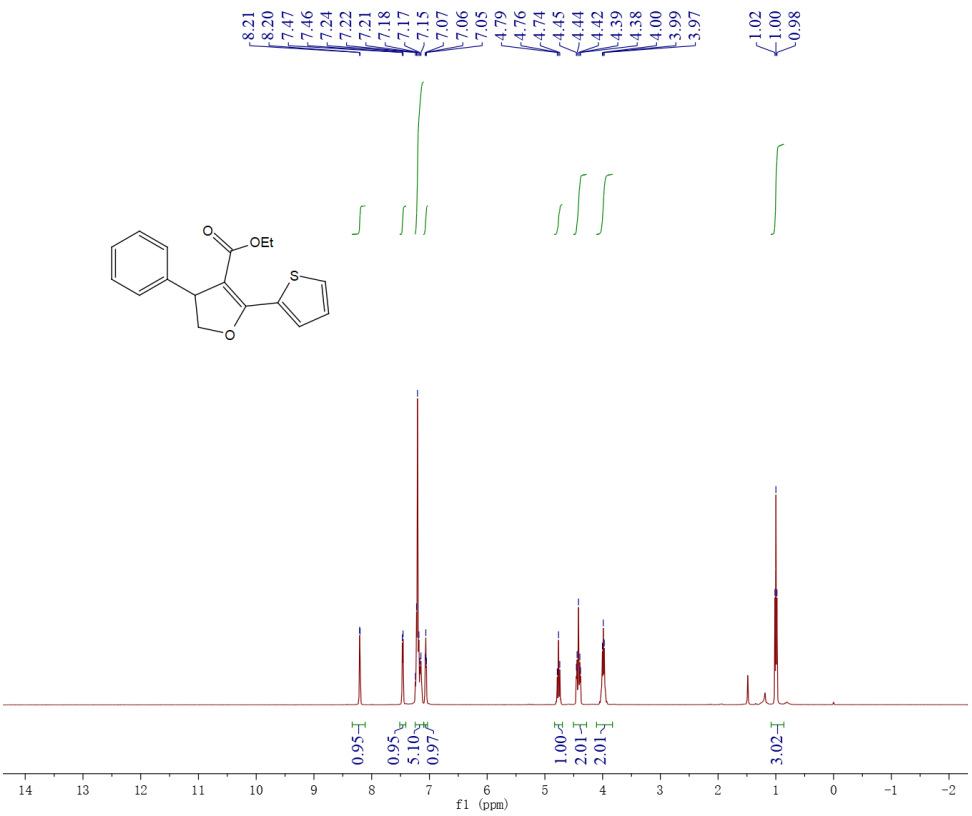
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3al**



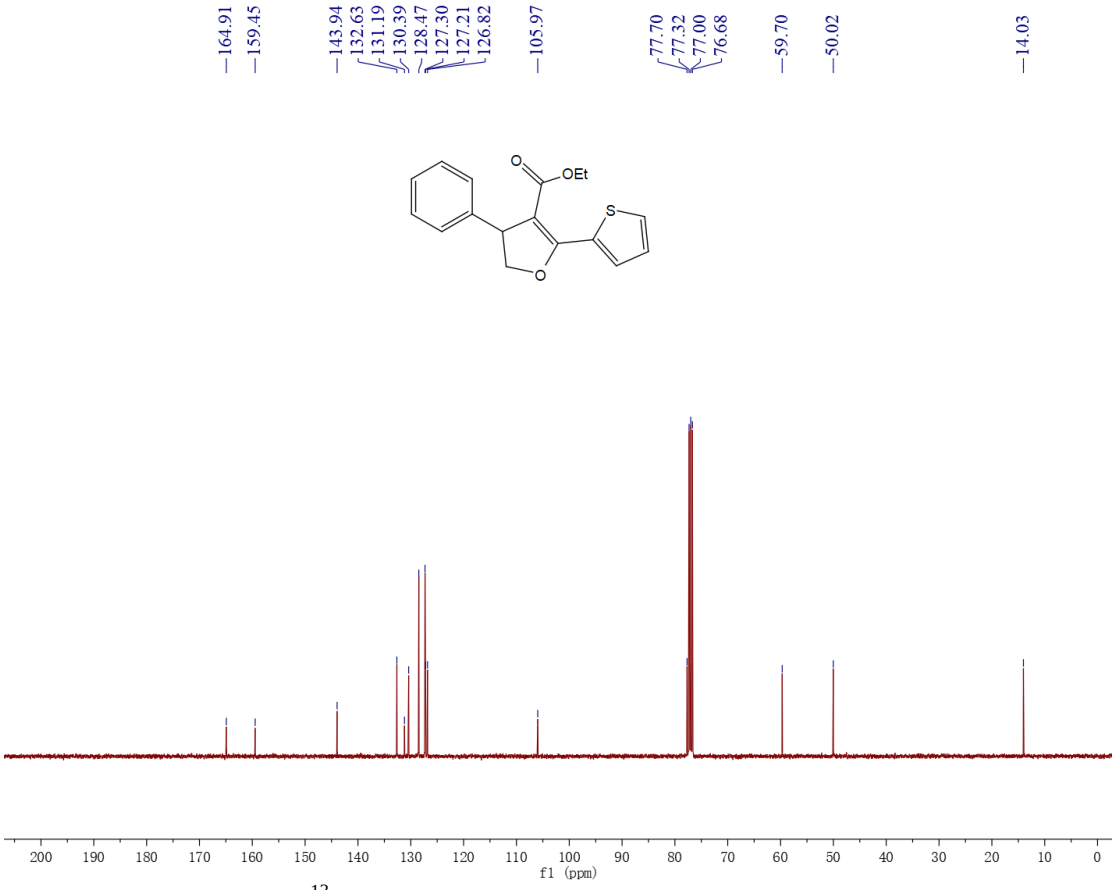
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3am**



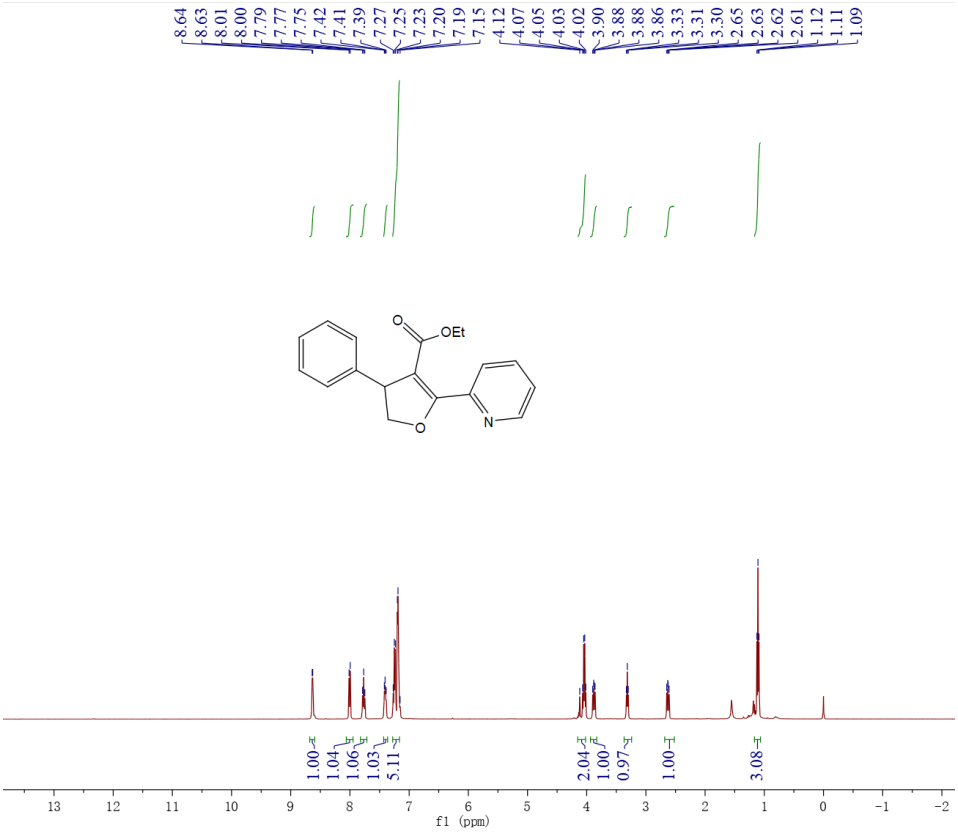
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3am**



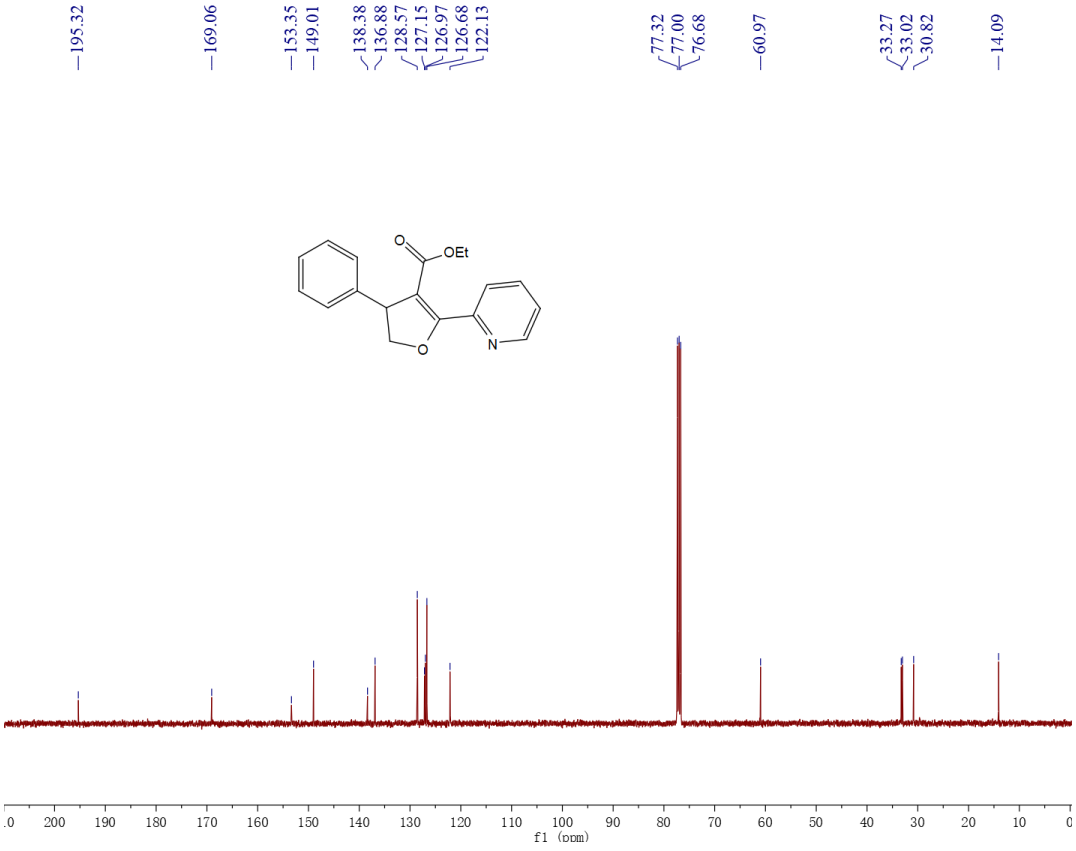
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3an**



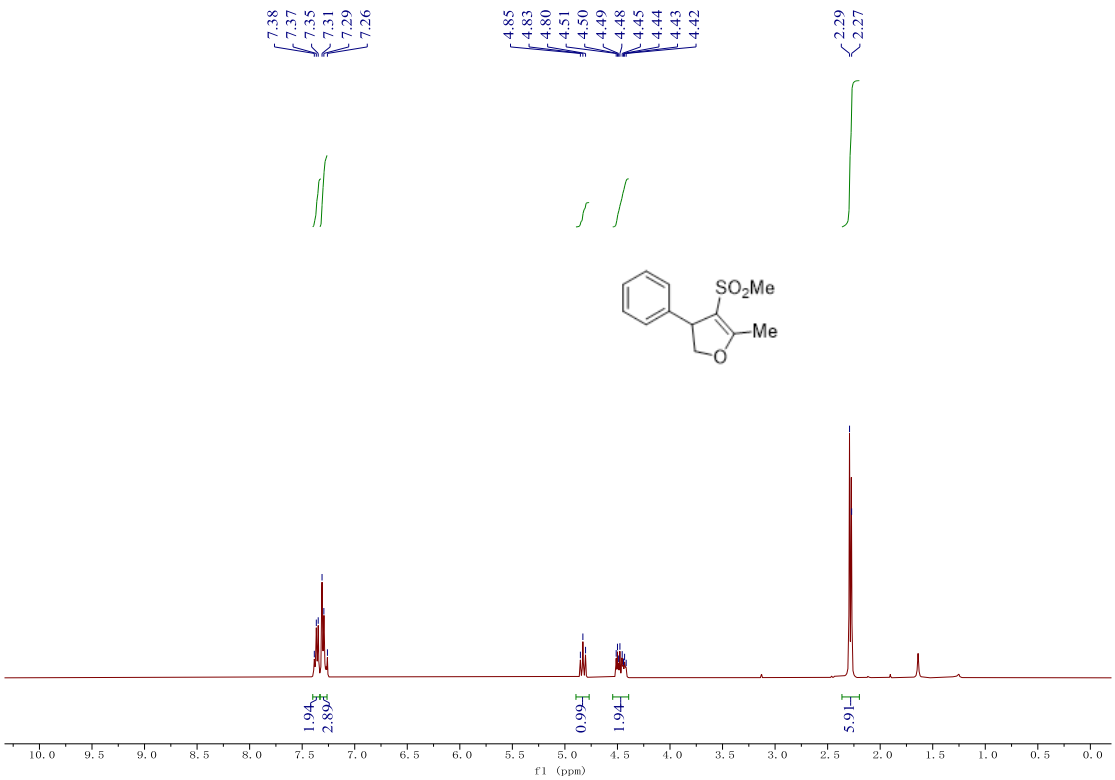
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3an**



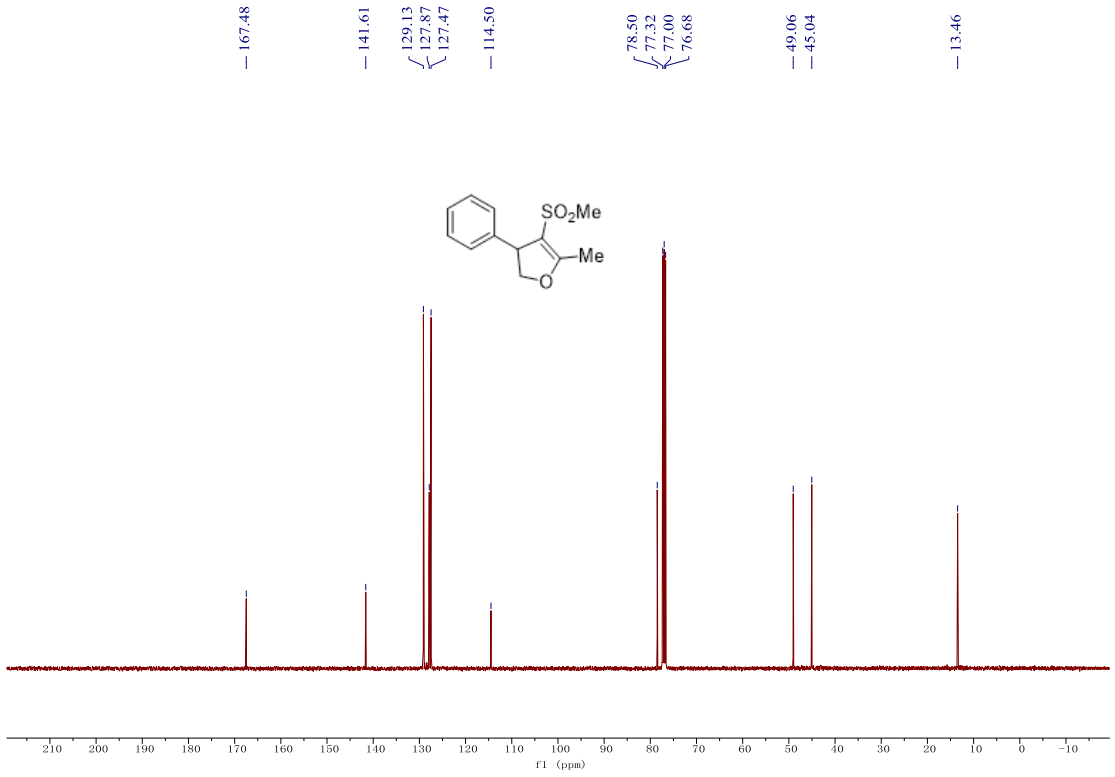
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ao**



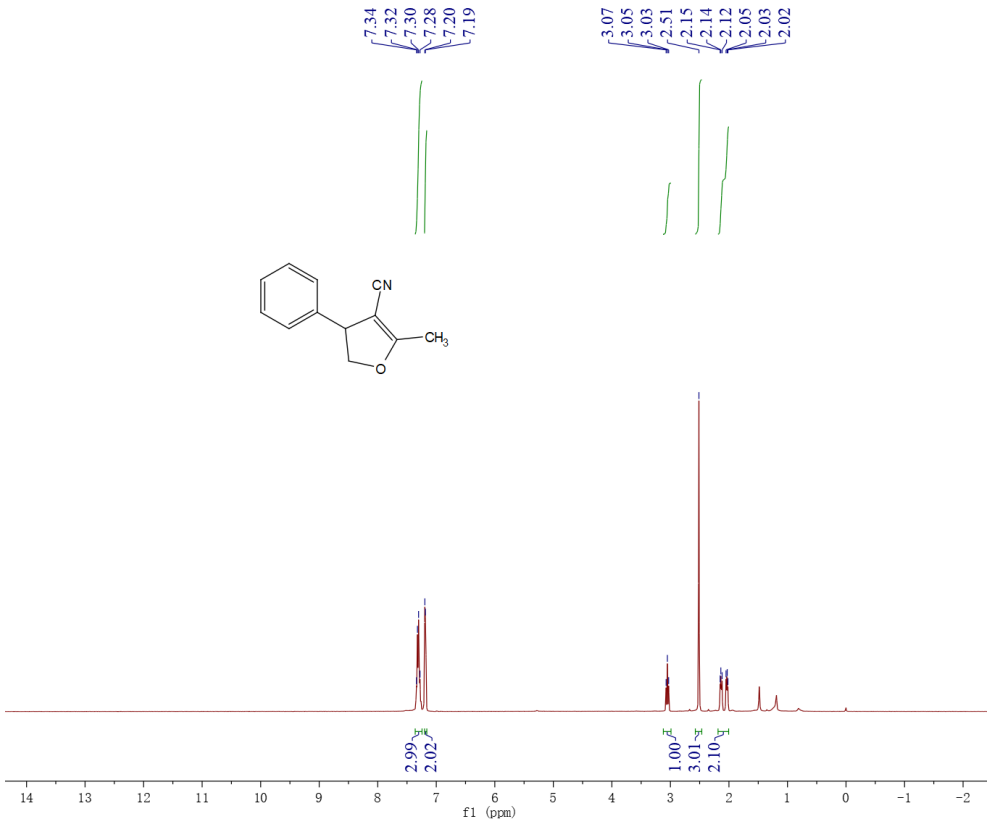
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ao**



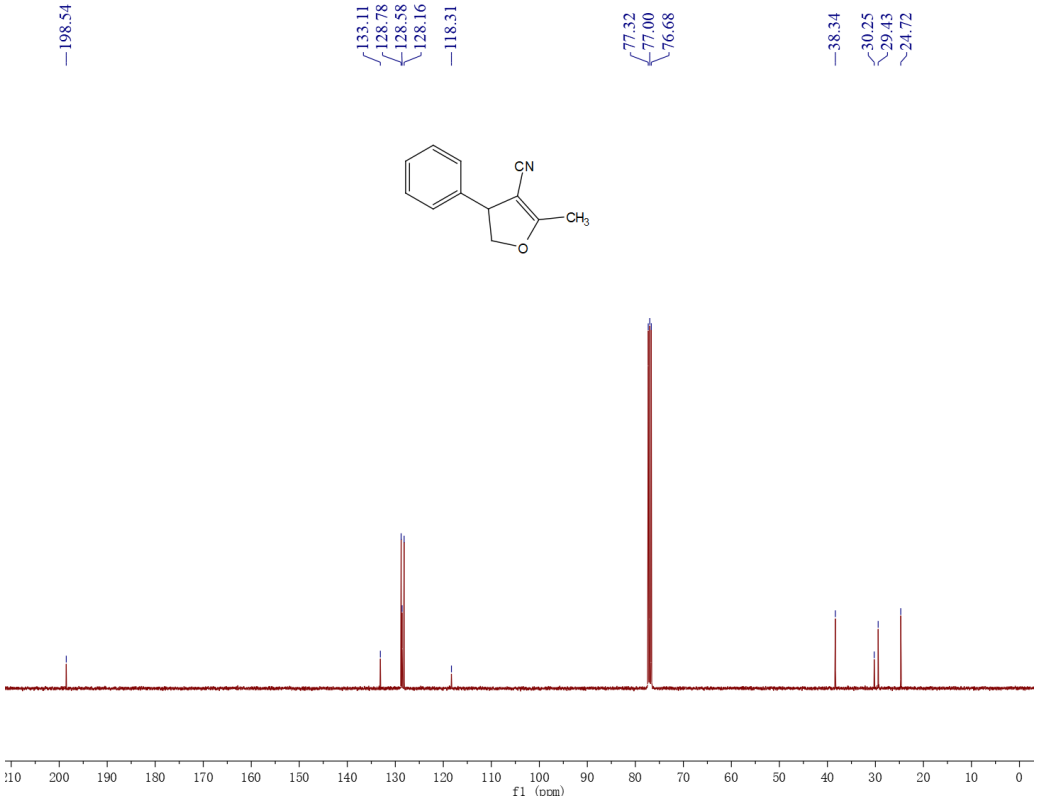
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ap**



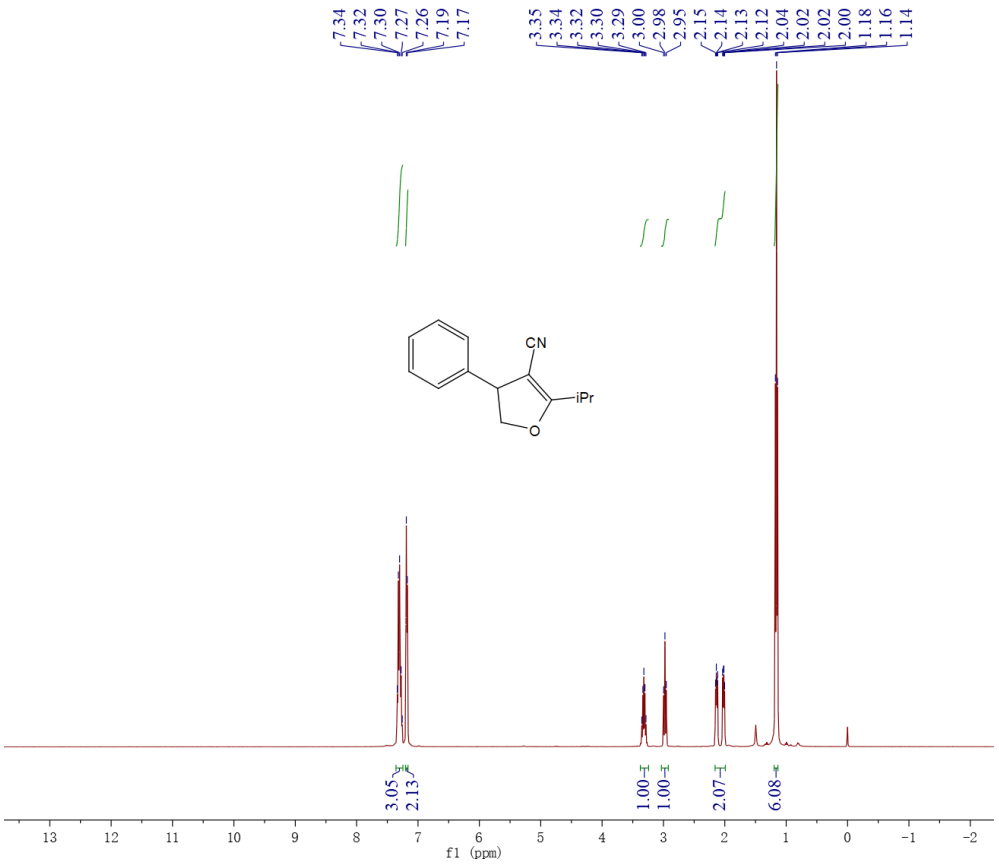
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ap**



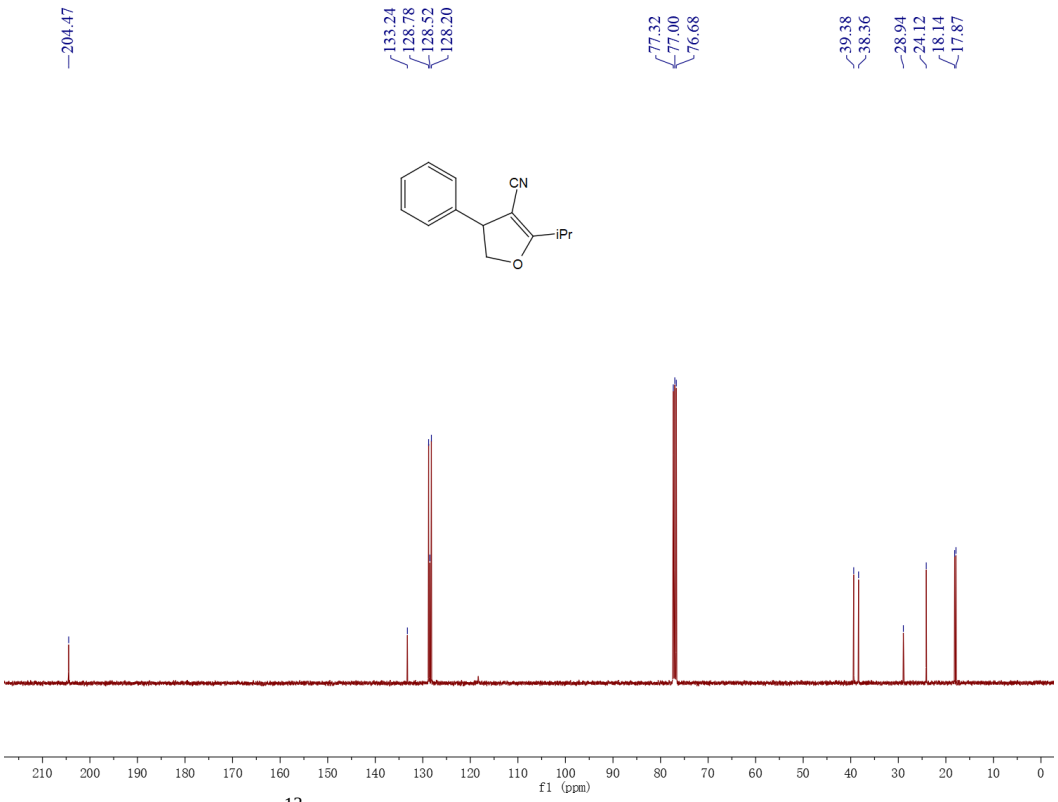
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aq**



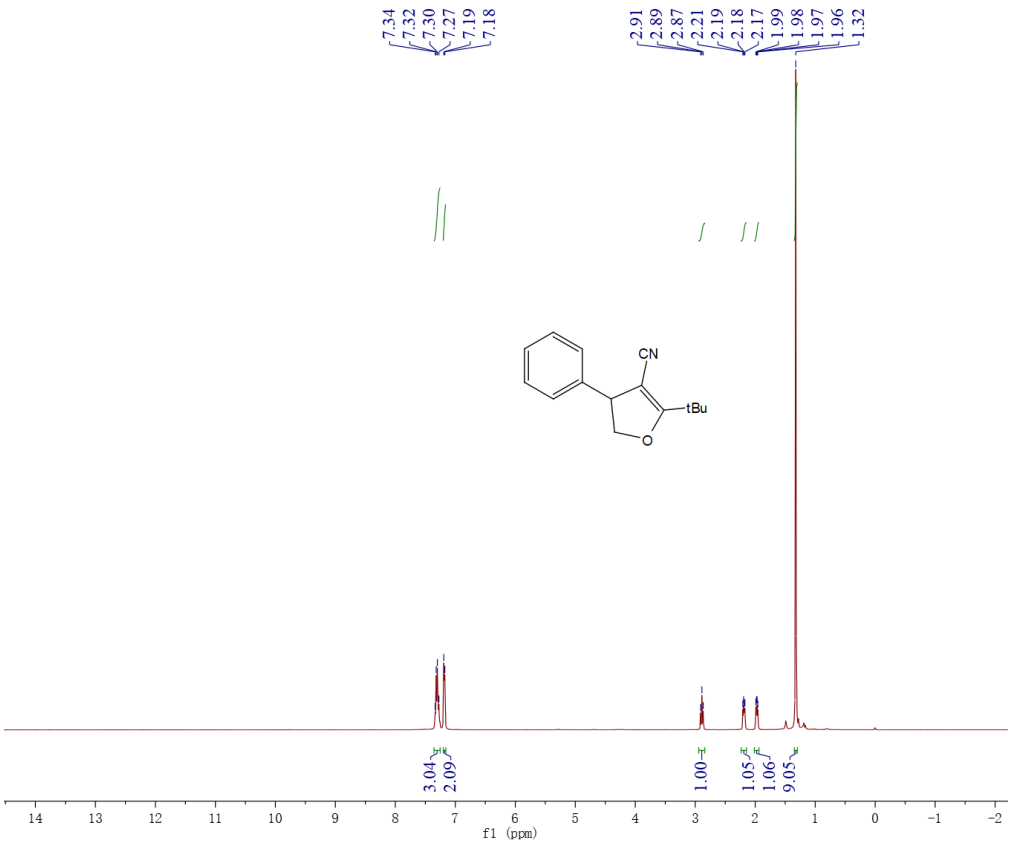
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3aq**



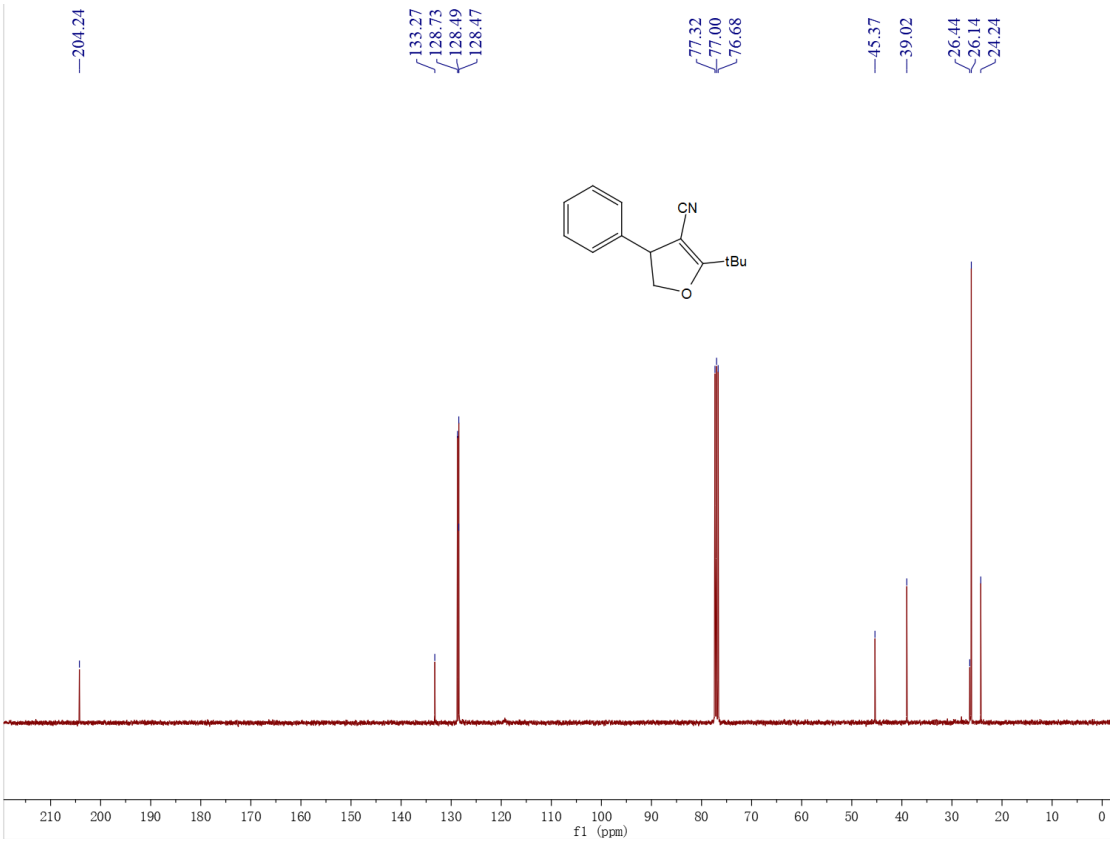
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ar**



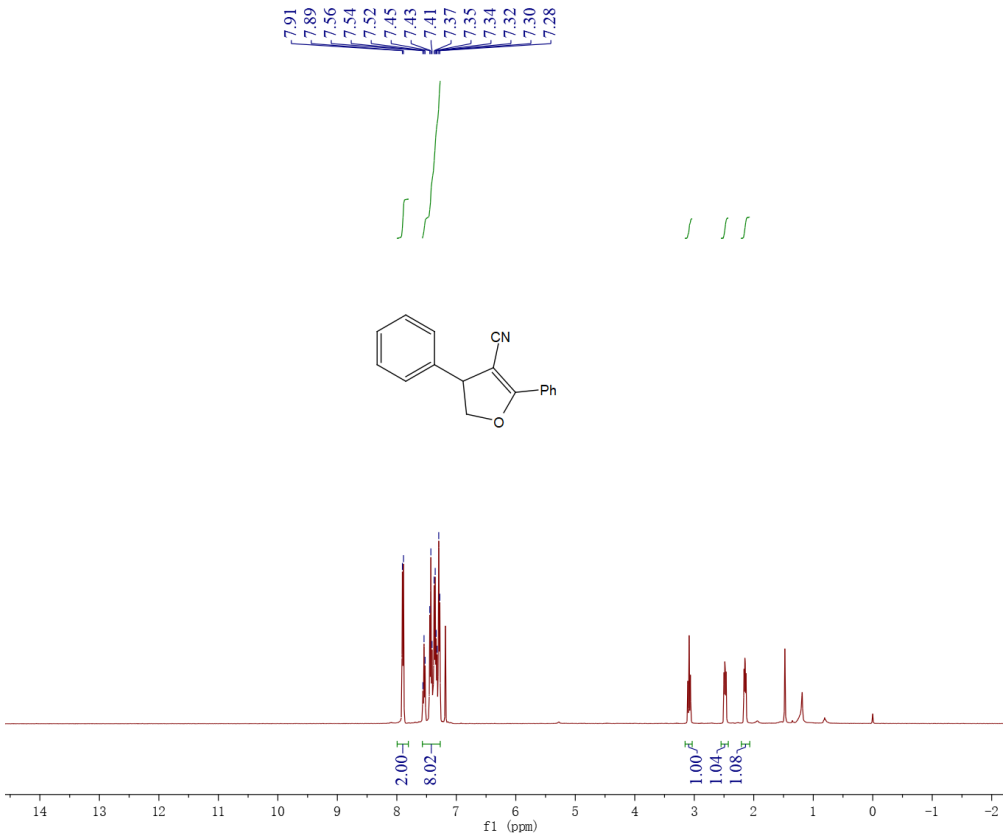
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ar**



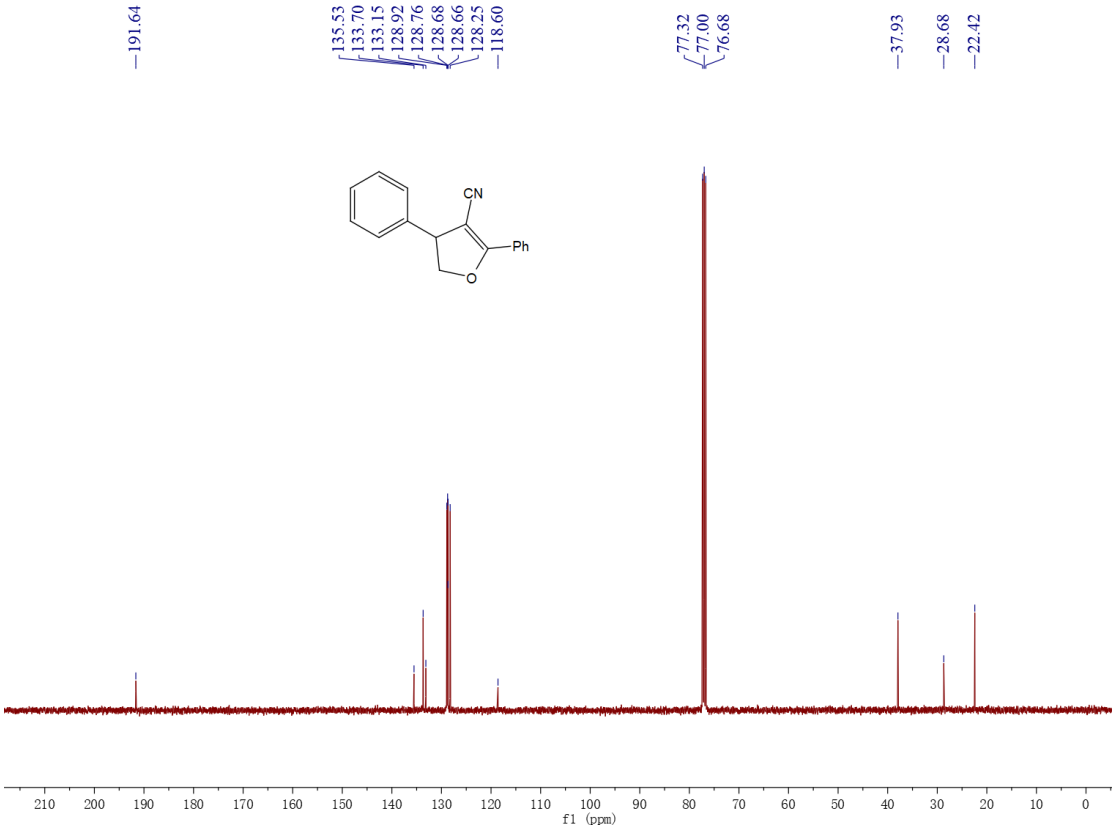
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3as**



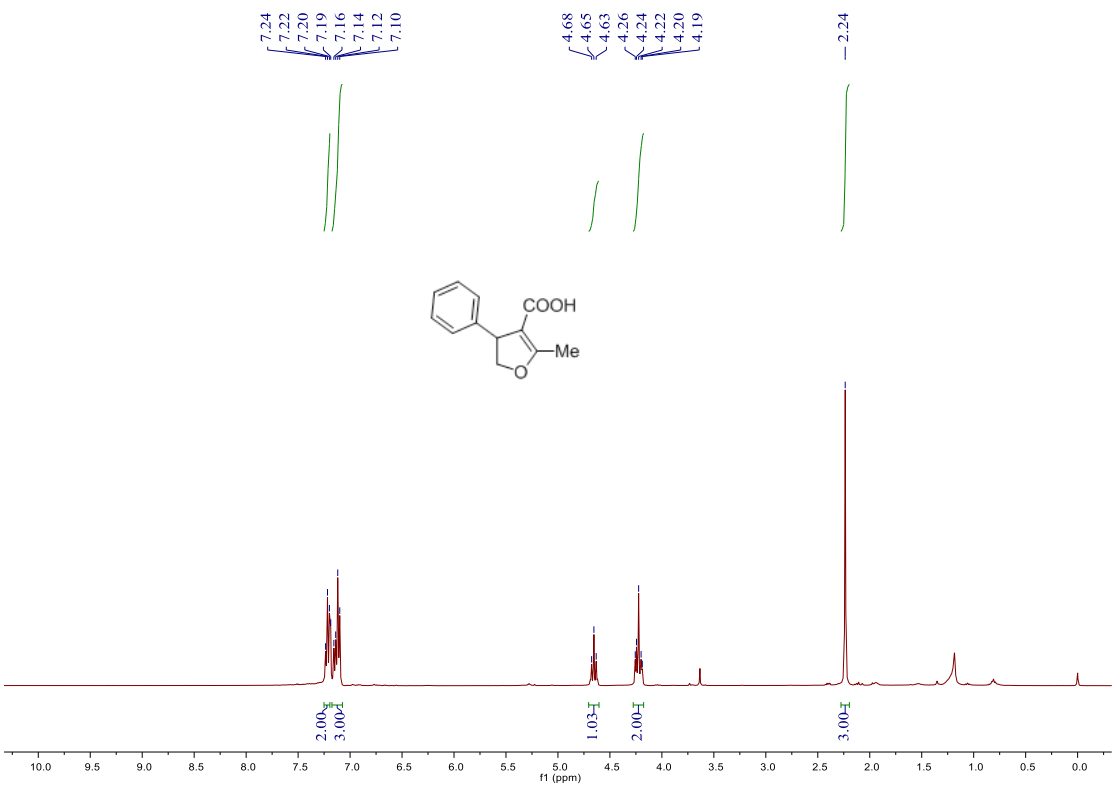
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3as**



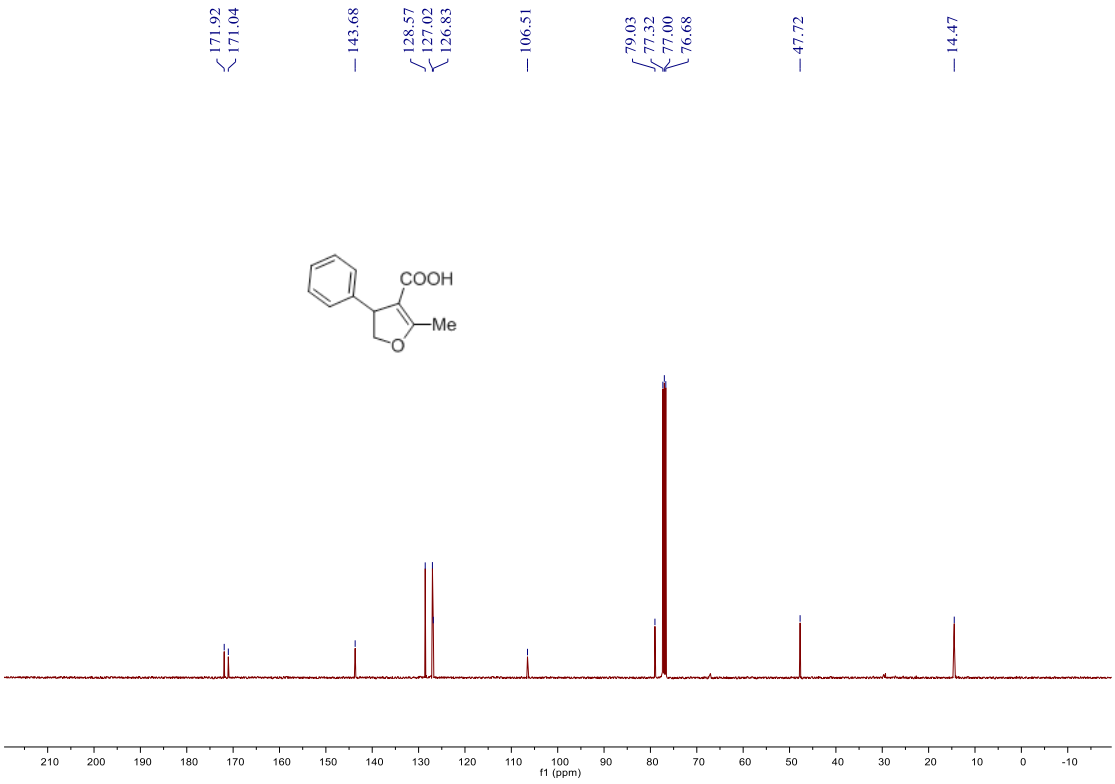
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3at**



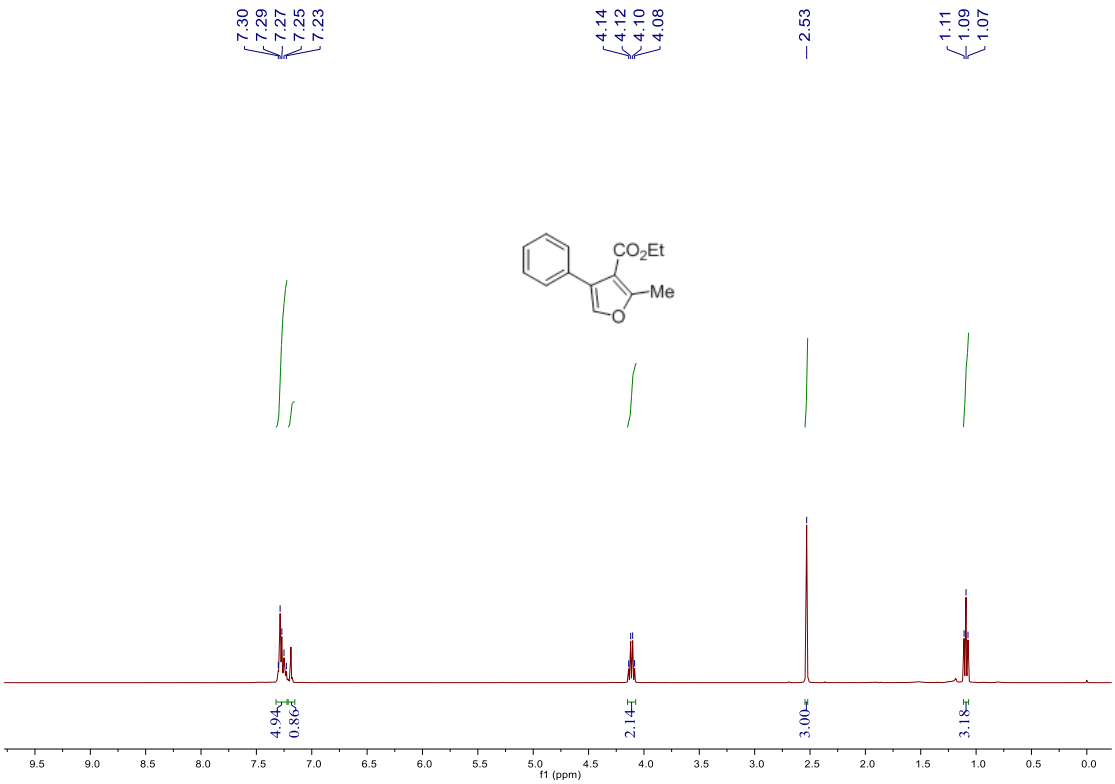
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3at**



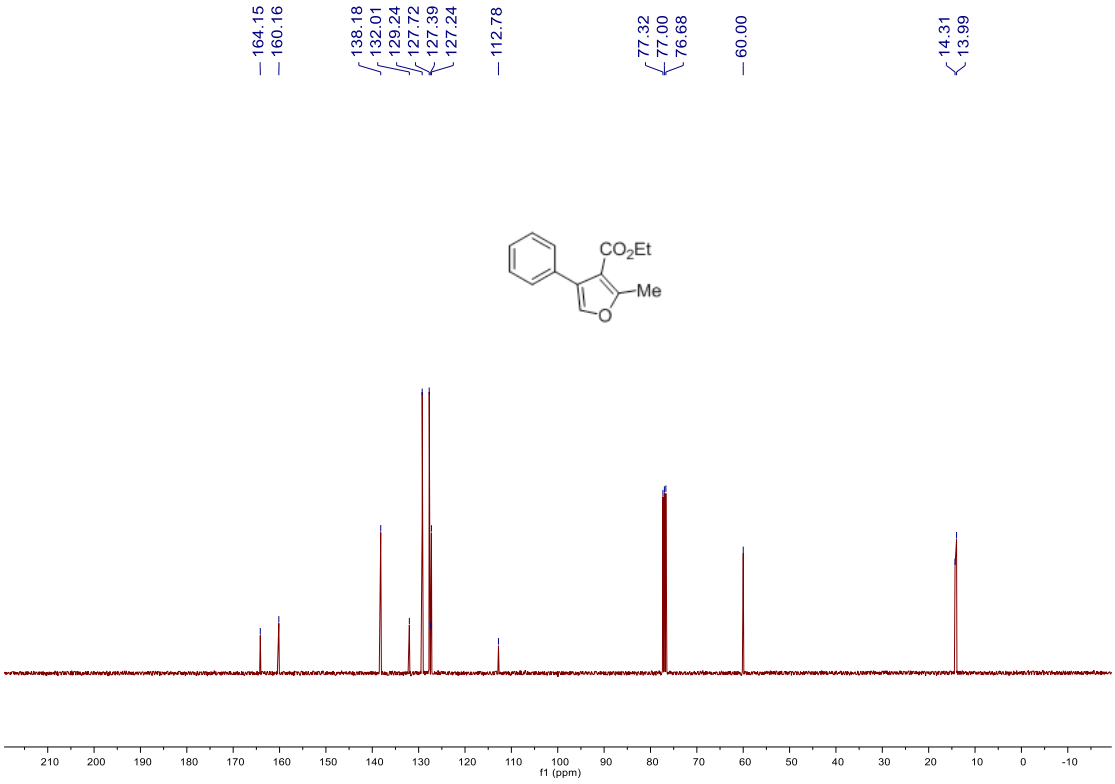
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **6a**



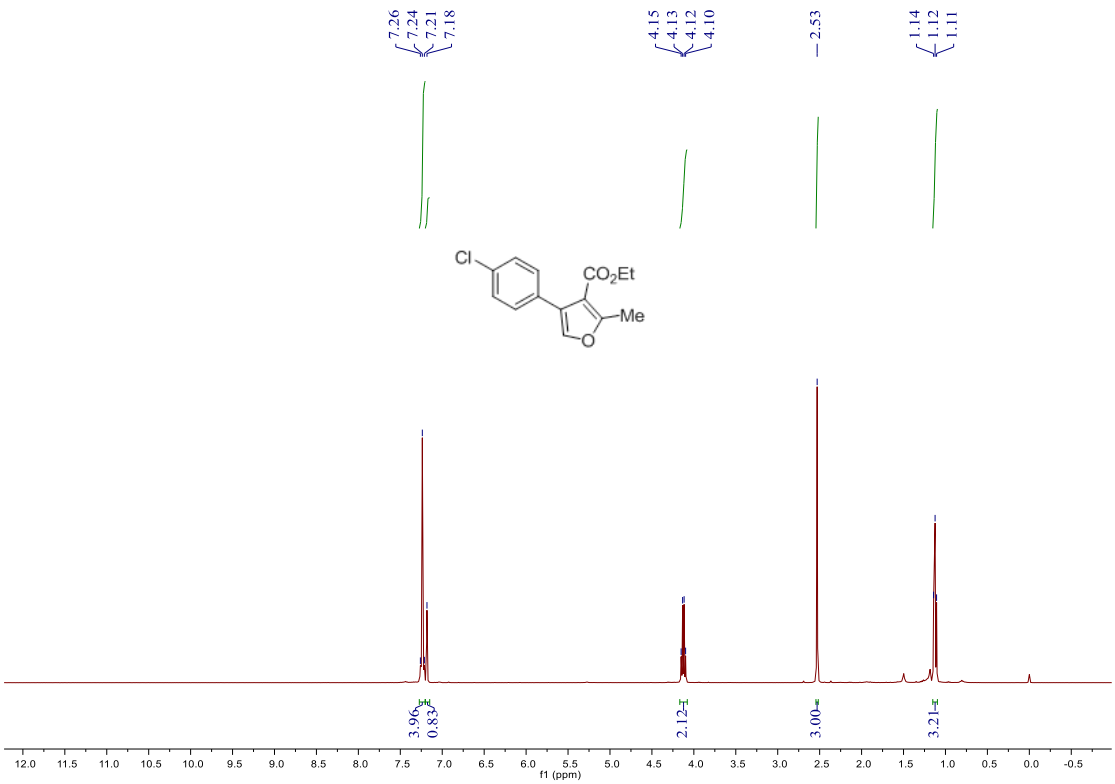
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **6a**



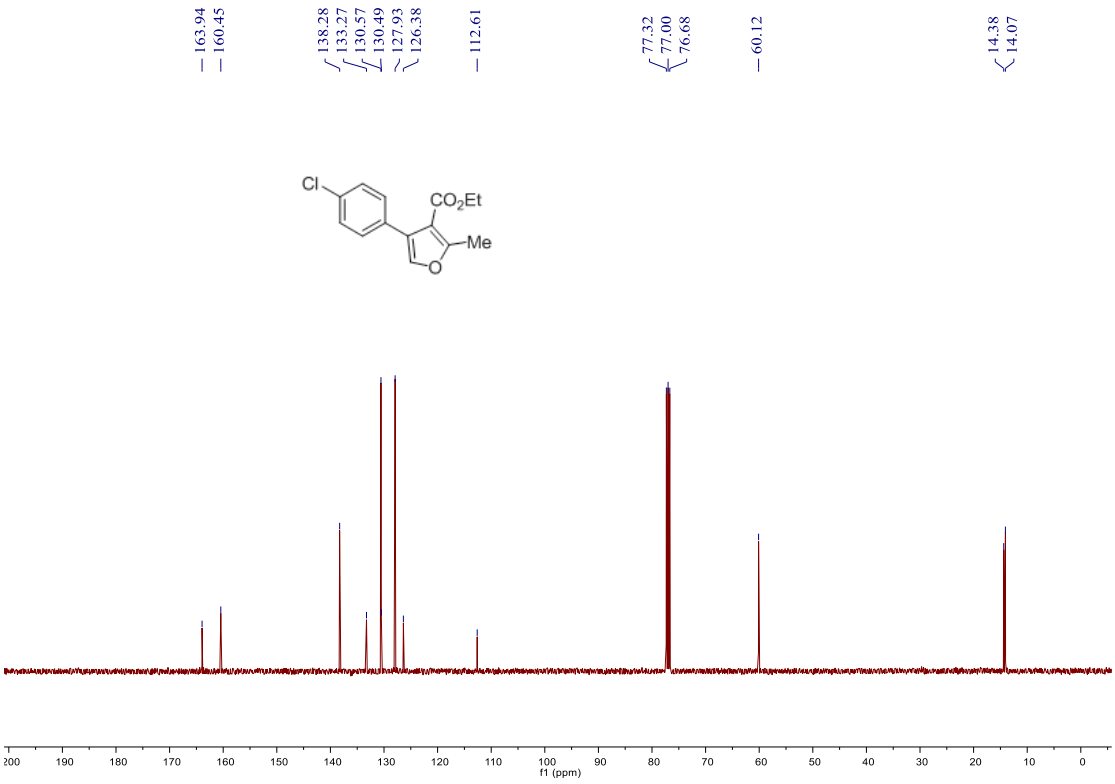
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4aa**



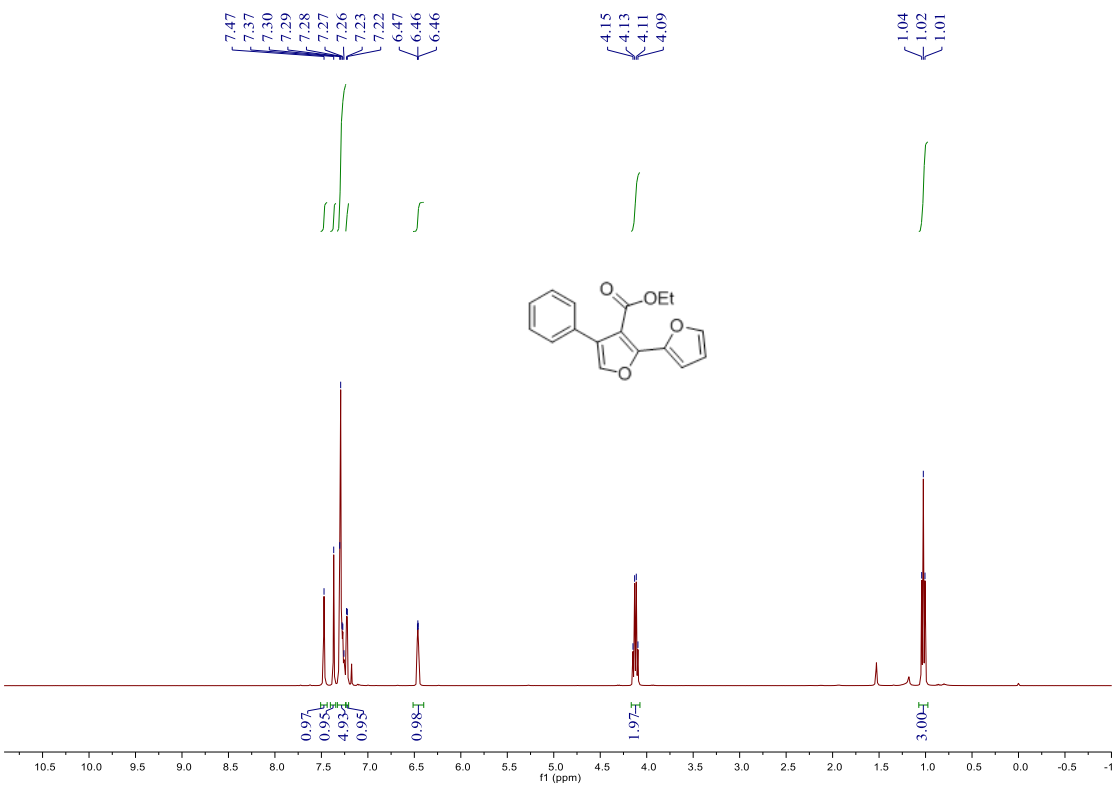
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4aa**



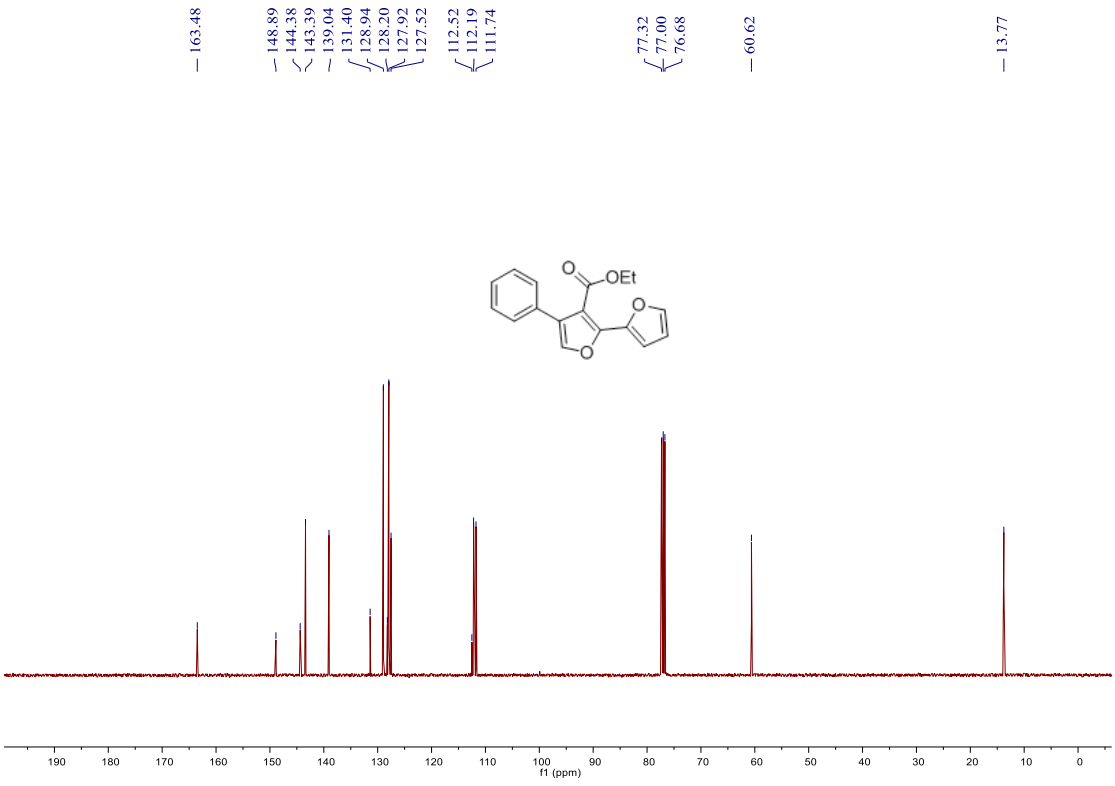
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4da**



^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4da**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4am**



^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4am**