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Supporting Information

Synthesizing Carbonyl Furan Derivatives by Dehydrogenatively Coupling Furfuryl Alcohol with Carbonyl Compounds

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Table of Contents

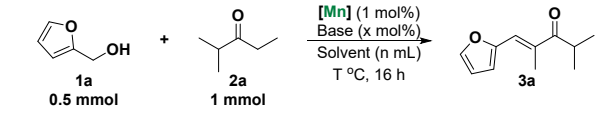
General Considerations

The synthesis of ligands and preparation of catalysts in this work were reported in our previous publication[1]. Air and moisture sensitive reactions were carried out in glovebox or in over-dried glassware sealed with rubber septa using standard schlenk techniques. Most solvents used were dried over solvent purification system (Innovative Technology PS-MD-5) and alcohol solvents were dried over calcium hydride. Deuterated solvents were purchased from Cambridge Isotope Laboratories, vented and distilled over calcium hydride. All chemicals were purchased from commercial sources with purity over 95% and used without further purification. NMR spectra were received using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. GC analysis were carried out on SHIMADAZU GC 2010 PLUS system. (Column: SH-Rtx-200, 30 m x 0.25 mm x 0.25 μm). GC/MS analyses were carried out on an GC-MS-QP2010 SE W system equipped with aSH-Rxi-5Sil MS 30 meter, 0.25 mmID, 0.25 um df. High resolution exact mass measurements (HRMS) were performed on Thermo SCIENTIFIC Q EXACTIVE.

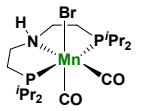
General Procedures for the Optimization of Reaction Conditions

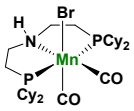
All dehydrogenation experiments were carried out in a 25 mL pressure seal tube. In the argon atmosphere glovebox, furfuryl alcohol **1a** (0.5 mmol), 2-methyl-3-pentanone **2a**, manganese catalysts (0.005 mmol, 1 mol%), base (0.0125–0.0250 mmol, 2.5-5.0 mol%.) solvent (0.5-0.8 mL) were added sequentially to the seal tube equipped with a magnetic stir bar, The reaction mixture was stirred at given temperature for 16 hours and cooled to room temperature. After the gas was released, the yield of product **3a** was determined by GC with biphenyl as the internal standard.

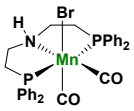
Table S1. Optimization of Reaction Conditions.



Entry	[Mn]	Base	Solvent	n [mL]	x [mol%]	T [°C]	Y_{3a} [%]
1	[Mn]-I	Cs_2CO_3	Toluene	0.5	2.5	140	77
2	[Mn]-II	Cs_2CO_3	Toluene	0.5	2.5	140	70
3	[Mn]-III	Cs_2CO_3	Toluene	0.5	2.5	140	65
4	$Mn(CO)_5Br$	Cs_2CO_3	Toluene	0.5	2.5	140	NP
5	$MnCl_2$	Cs_2CO_3	Toluene	0.5	2.5	140	NP
6	none	Cs_2CO_3	Toluene	0.5	2.5	140	NP
7	[Mn]-I	Cs_2CO_3	dioxane	0.5	2.5	165	24
8	[Mn]-I	Cs_2CO_3	THF	0.5	2.5	140	<5
9	[Mn]-I	KOH	Toluene	0.5	2.5	140	32
10	[Mn]-I	^{t}BuOK	Toluene	0.5	2.5	165	45
11	[Mn]-I	Na_2CO_3	Toluene	0.5	2.5	140	15
12	[Mn]-I	K_2CO_3	Toluene	0.5	2.5	140	<5
13	[Mn]-I	Cs_2CO_3	Toluene	0.5	5.0	140	75
14	[Mn]-I	Cs_2CO_3	Toluene	0.8	2.5	140	47
15[b]	[Mn]-I	Cs_2CO_3	Toluene	0.5	2.5	140	31
16[c]	[Mn]-I	Cs_2CO_3	Toluene	0.5	2.5	140	51
17[d]	[Mn]-I	Cs_2CO_3	Toluene	0.5	2.5	140	77

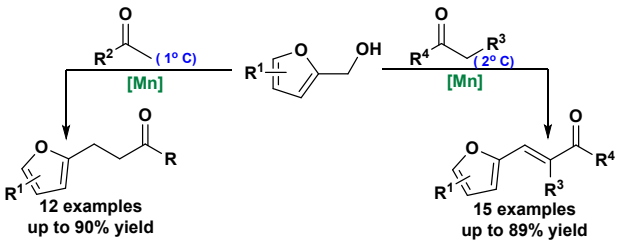






[a] Unless otherwise specified, reactions were performed on a 0.5 mmol scale of furfuryl alcohol 1a, 1.0 mmol 2-methyl-3-pentanone 2a, using 2.5 mol% of base, 1 mol% of Mn-precatalyst, in 0.5 mL toluene at 140 °C for 16 h. The yields were determined by GC using biphenyl as the internal standard. b 0.6 mmol 2a was used. c 0.8 mmol 2a was used. d 1.5 mmol 2a was used.

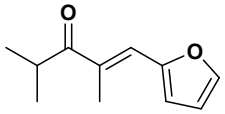
General Experimental Procedures for the Synthesis of Carbonyl Furan Derivatives



All experiments were carried out in a 25 mL pressure seal tube. In the argon atmosphere glovebox, furfuryl alcohol (0.5 mmol), carbonyl compounds (1.0 mmol), **[Mn]-I** (1 mol%), Cs_2CO_3 (2.5 mol%), toluene (0.5 mL) were added sequentially to the seal tube equipped with a magnetic stir bar. The reaction mixture was stirred at given temperature for 16 hours and cooled to room temperature. After the gas was released, the yield of products were purified through column chromatography.

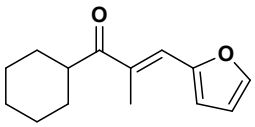
Characterization Data of Products

1-(furan-2-yl)-2,4-dimethylpent-1-en-3-one **3a**



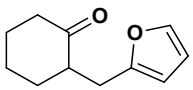
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (66.8mg, 0.38mmol, 75%).^{1}H NMR (400 MHz, CDCl3) δ 7.49 (d, J = 1.5 Hz, 1H), 7.24 (s, 1H), 6.61 (d, J = 3.5 Hz, 1H), 6.46 (dd, J = 3.4, 1.8 Hz, 1H), 3.35 (dt, J = 13.6, 6.8 Hz, 1H), 2.08 (s, 3H), 1.08 (d, J = 6.8 Hz, 6H).^{13}C NMR (101 MHz, CDCl3) δ 205.77 (s), 152.01 (s), 144.18 (s), 132.78 (s), 125.23 (s), 114.98 (s), 112.33 (s), 33.81 (s), 19.74 (s), 13.42 (s). HRMS (EI) calcd. for $C_{11}H_{14}O_2$ [M]: 178.0994; found: 178.0998.

1-cyclohexyl-3-(furan-2-yl)-2-methylprop-2-en-1-one **3c**



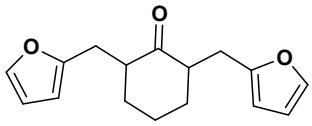
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (97.1mg, 0.44mmol, 89%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 1.6 Hz, 1H), 7.22 (s, 1H), 6.61 (d, J = 3.4 Hz, 1H), 6.46 (dd, J = 3.4, 1.8 Hz, 1H), 3.03 (tt, J = 10.6, 2.7 Hz, 1H), 2.06 (s, 3H), 1.73 (dd, J = 19.1, 8.6 Hz, 5H), 1.22 (dt, J = 24.3, 7.0 Hz, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.10 (s), 152.04 (s), 144.12 (s), 132.93 (s), 125.05 (s), 114.92 (s), 112.34 (s), 44.33 (s), 29.95 (s), 25.95 (s), 13.40 (s). HRMS (EI) calcd. for $C_{14}H_{18}O_2$[M]: 218.1307; found:218.1304.

2-(furan-2-ylmethyl)cyclohexan-1-one **3d**[1][2]



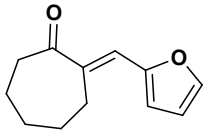
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel colourless oil (31.1mg, 0.18mmol, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 1H), 6.20 (dd, J = 3.1, 1.9 Hz, 1H), 5.94 (dd, J = 3.1, 0.5 Hz, 1H), 3.10 (dd, J = 15.3, 4.8 Hz, 1H), 2.65 – 2.56 (m, 1H), 2.44 (dd, J = 15.3, 8.5 Hz, 1H), 2.40 – 2.32 (m, 1H), 2.31 – 2.21 (m, 1H), 2.02 (tdd, J = 8.7, 5.8, 2.5 Hz, 2H), 1.82 – 1.75 (m, 1H), 1.62 – 1.53 (m, 2H), 1.34 – 1.24 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.94 (s), 154.12 (s), 141.02 (s), 110.20 (s), 106.30 (s), 49.79 (s), 42.11 (s), 33.71 (s), 28.02 (s), 27.81 (s), 25.12 (s).

2,6-bis(furan-2-ylmethyl)cyclohexan-1-one **3d**[2][3]



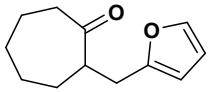
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (25.8mg, 0.10mmol, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 1.0 Hz, 2H), 6.20 (dd, J = 2.9, 1.9 Hz, 2H), 5.94 (d, J = 3.1 Hz, 2H), 3.10 (dd, J = 15.3, 4.9 Hz, 2H), 2.70 – 2.60 (m, 2H), 2.46 (dd, J = 15.3, 8.4 Hz, 2H), 2.09 – 2.02 (m, 2H), 1.83 – 1.53 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 211.69 (s), 154.20 (s), 141.01 (s), 110.21 (s), 106.26 (s), 50.01 (s), 34.91 (s), 27.79 (s), 25.18 (s).

2-(furan-2-ylmethylene)cycloheptan-1-one **3e**[1]



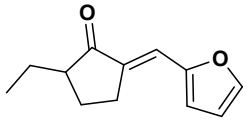
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (30.4mg, 0.16mmol, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 1.6 Hz, 1H), 7.12 (s, 1H), 6.53 (d, J = 3.4 Hz, 1H), 6.40 (dd, J = 3.4, 1.8 Hz, 1H), 2.87 (d, J = 5.7 Hz, 2H), 2.67 – 2.56 (m, 2H), 1.76 – 1.61 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.97 (s), 152.08 (s), 144.01 (s), 137.55 (s), 121.97 (s), 115.76 (s), 111.95 (s), 43.09 (s), 31.34 (s), 29.52 (s), 28.18 (s), 25.30 (s). HRMS (EI) calcd. for $C_{12}H_{14}O_2$[M]: 190.0994; found:190.0987.

2-(furan-2-ylmethyl)cycloheptan-1-one **3e**[2]



The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (49.9mg, 0.26mmol, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 1.6 Hz, 1H), 6.21 – 6.18 (m, 1H), 5.93 (d, J = 3.1 Hz, 1H), 2.97 (dd, J = 15.0, 5.7 Hz, 1H), 2.60 – 2.53 (m, 1H), 2.45 – 2.35 (m, 2H), 1.82 – 1.69 (m, 5H), 1.36 – 1.16 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.91 (s), 154.03 (s), 141.12 (s), 110.17 (s), 106.37 (s), 50.64 (s), 43.26 (s), 30.68 (s), 30.06 (s), 29.25 (s), 28.90 (s), 23.98 (s). HRMS (EI) calcd. for $C_{12}H_{16}O_2$[M]: 192.1150; found:192.1158.

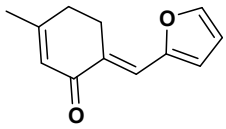
2-ethyl-5-(furan-2-ylmethylene)cyclopentan-1-one **3f**



The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (43.7mg, 0.23mmol, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.10 (t, J = 2.6 Hz,

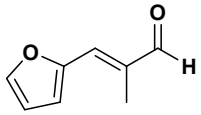
1H), 6.58 (d, J = 3.4 Hz, 1H), 6.43 (dd, J = 3.2, 1.7 Hz, 1H), 2.99 (dd, J = 18.2, 8.4 Hz, 1H), 2.73 – 2.63 (m, 1H), 2.20 (ddd, J = 16.1, 8.7, 3.7 Hz, 2H), 1.82 (ddd, J = 13.4, 7.5, 4.5 Hz, 1H), 1.52 (td, J = 8.7, 2.4 Hz, 1H), 1.31 (dt, J = 21.8, 7.4 Hz, 1H), 0.91 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.88 (s), 152.39 (s), 144.75 (s), 134.04 (s), 118.75 (s), 115.69 (s), 112.42 (s), 50.13 (s), 27.21 (s), 26.10 (s), 23.30 (s), 11.80 (s). HRMS (EI) calcd. for $C_{12}H_{14}O_2$[M]: 190.0994; found:190.0987.

6-(furan-2-ylmethylene)-3-methylcyclohex-2-en-1-one **3h**



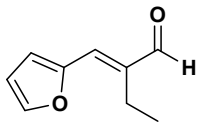
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (19.8mg, 0.11mmol, 21%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 1.5 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.58 (s, 1H), 6.21 (dd, J = 2.9, 2.0 Hz, 1H), 5.96 (d, J = 3.1 Hz, 1H), 5.00 (d, J = 6.6 Hz, 1H), 3.87 (s, 2H), 2.21 (s, 3H), 1.18 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.82 (s), 153.62 (s), 141.59 (s), 138.35 (s), 130.45 (s), 121.82 (s), 121.22 (s), 116.85 (s), 110.42 (s), 106.10 (s), 29.73 (s), 28.99 (s), 21.04 (s). HRMS (EI) calcd. for $C_{12}H_{12}O_2$[M]: 188.0837; found:188.0831.

3-(furan-2-yl)-2-methylacrylaldehyde **5a**[4]



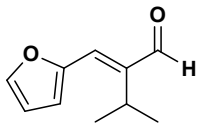
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (32.7mg, 0.24mmol, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 0.8 Hz, 1H), 7.62 (s, 1H), 7.02 (s, 1H), 6.77 (d, *J* = 3.4 Hz, 1H), 6.61 – 6.53 (m, 1H), 2.09 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 194.18 (s), 151.62 (s), 145.34 (s), 135.42 (s), 134.97 (s), 116.52 (s), 112.66 (s), 10.58 (s).

2-(furan-2-ylmethylene)butanal **5b**[5]



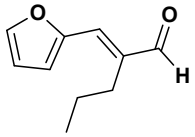
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (66.0mg, 0.44mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.54 (s, 1H), 6.86 (s, 1H), 6.75 – 6.64 (m, 1H), 6.53 – 6.39 (m, 1H), 2.58 (d, J = 7.5 Hz, 2H), 1.04 – 0.98 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.20 (s), 151.26 (s), 145.41 (s), 141.13 (s), 134.84 (s), 116.53 (s), 112.62 (s), 18.14 (s), 12.77 (s).

2-(furan-2-ylmethylene)-3-methylbutanal **5c**[6]



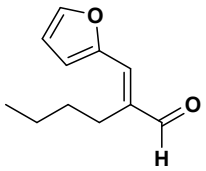
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (20.5mg, 0.13mmol, 25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (d, J = 1.7 Hz, 1H), 7.53 (d, J = 1.5 Hz, 1H), 6.77 (s, 1H), 6.68 (d, J = 3.5 Hz, 1H), 6.48 (dd, J = 3.4, 1.7 Hz, 1H), 3.49 – 3.40 (m, 1H), 1.21 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.81 (s), 151.11 (s), 145.15 (s), 144.20 (s), 134.88 (s), 116.76 (s), 112.46 (s), 27.04 (s), 19.99 (s).

6-(furan-2-ylmethyl)pentanal **5d**[4]



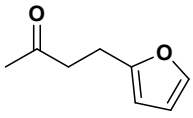
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (46.7mg, 0.29mmol, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.54 (d, J = 1.6 Hz, 1H), 6.89 (s, 1H), 6.69 (d, J = 3.5 Hz, 1H), 6.49 (dd, J = 3.4, 1.8 Hz, 1H), 2.63 – 2.42 (m, 2H), 1.42 (dd, J = 15.3, 7.6 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.43 (s), 151.37 (s), 145.35 (s), 139.76 (s), 135.30 (s), 116.52 (s), 112.61 (s), 26.70 (s), 21.62 (s), 14.22 (s).

2-(furan-2-ylmethylene)hexanal **5e**[4]



The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (42.7mg, 0.24mmol, 48%). 1H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.54 (d, J = 1.2 Hz, 1H), 6.87 (s, 1H), 6.69 (d, J = 3.5 Hz, 1H), 6.49 (dd, J = 3.4, 1.7 Hz, 1H), 2.56 (t, J = 7.4 Hz, 2H), 1.37 – 1.26 (m, 4H), 0.85 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.40 (s), 151.37 (s), 145.33 (s), 140.00 (s), 135.13 (s), 116.47 (s), 112.62 (s), 30.48 (s), 24.59 (s), 22.97 (s), 13.94 (s).

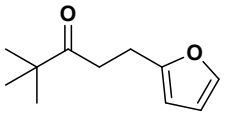
4-(furan-2-yl)butan-2-one **7a**[7]



The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (39.3mg, 0.29mmol, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.13 (m, 1H), 6.22 – 6.14

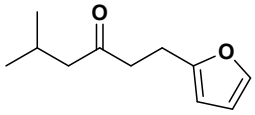
(m, 1H), 5.93 – 5.82 (m, 1H), 2.85 (d, J = 7.4 Hz, 1H), 2.69 (d, J = 7.2 Hz, 1H), 1.19 (s, 3H), 0.83 – 0.76 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.92 (s), 154.47 (s), 141.11 (s), 110.22 (s), 105.25 (s), 40.85 (s), 29.71 (s), 22.14 (s).

1-(furan-2-yl)-4,4-dimethylpentan-3-one **7c**[8]



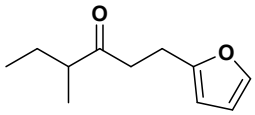
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (57.6mg, 0.32mmol, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 1.0 Hz, 1H), 6.19 (s, 1H), 5.92 (d, J = 0.5 Hz, 1H), 2.78 (ddd, J = 9.9, 6.5, 2.6 Hz, 4H), 1.10 (d, J = 33.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.45 (s), 155.01 (s), 140.98 (s), 110.20 (s), 105.16 (s), 44.16 (s), 34.99 (s), 26.33 (s), 22.48 (s).

1-(furan-2-yl)-5-methylhexan-3-one **7d**[9]



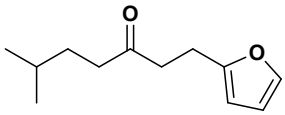
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (72.0mg, 0.40mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 2.0 Hz, 1H), 6.18 (dd, J = 3.0, 1.9 Hz, 1H), 5.95 – 5.85 (m, 1H), 2.83 (t, J = 7.4 Hz, 2H), 2.65 (t, J = 7.4 Hz, 2H), 2.21 (d, J = 7.0 Hz, 2H), 2.07 (dt, J = 13.7, 6.8 Hz, 1H), 0.83 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.30 (s), 154.68 (s), 141.01 (s), 110.20 (s), 105.17 (s), 51.87 (s), 41.26 (s), 24.62 (s), 22.55 (s), 22.10 (s).

1-(furan-2-yl)-4-methylhexan-3-one **7e**



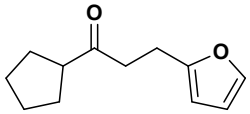
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (77.4mg, 0.43mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 1H), 6.19 (dd, J = 3.0, 1.9 Hz, 1H), 5.93 – 5.89 (m, 1H), 2.84 (t, J = 7.4 Hz, 2H), 2.74 – 2.67 (m, 2H), 2.38 (dd, J = 13.7, 6.9 Hz, 1H), 1.59 (dd, J = 13.9, 6.9 Hz, 1H), 1.35 – 1.28 (m, 1H), 0.99 (d, J = 7.0 Hz, 3H), 0.78 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.20 (s), 154.82 (s), 141.00 (s), 110.21 (s), 105.18 (s), 48.00 (s), 39.21 (s), 25.90 (s), 22.14 (s), 15.80 (s), 11.64 (s). HRMS (EI) calcd. for C11H16O2[M]: 180.1150; found:180.1514

1-(furan-2-yl)-6-methylheptan-3-one **7f**



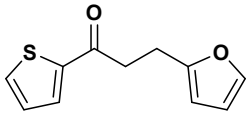
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (56.3mg, 0.29mmol, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 1H), 6.19 (dd, J = 3.0, 1.9 Hz, 1H), 5.92 (dd, J = 5.3, 4.9 Hz, 1H), 2.83 (q, J = 7.2 Hz, 2H), 2.73 – 2.63 (m, 2H), 2.39 – 2.27 (m, 2H), 1.49 – 1.35 (m, 3H), 0.80 (t, J = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.89 (s), 154.69 (s), 141.05 (s), 110.21 (s), 105.17 (s), 40.95 (s), 40.71 (s), 32.59 (s), 27.69 (s), 22.28 (d, J = 11.3 Hz). HRMS (EI) calcd. for $C_{12}H_{18}O_2$[M]: 194.1307; found:194.1315.

1-cyclopentyl-3-(furan-2-yl)propan-1-one **7g**



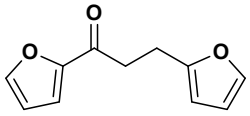
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (75.8mg, 0.39mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 1.2 Hz, 1H), 6.19 (dd, J = 3.0, 1.9 Hz, 1H), 5.91 (d, J = 2.9 Hz, 1H), 2.86 – 2.70 (m, 5H), 1.73 – 1.49 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.72 (s), 154.88 (s), 141.00 (s), 110.21 (s), 105.13 (s), 51.51 (s), 39.82 (s), 28.83 (s), 25.99 (s), 22.29 (s). HRMS (EI) calcd. for $C_{12}H_{16}O_2$[M]: 192.1150; found:192.1514.

1-(furan-2-yl)-1-(thiophen-2-yl)propan-1-one **7h**



The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (65.9mg, 0.32mmol, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 3.8, 1.0 Hz, 1H), 7.56 (dd, J = 4.9, 1.0 Hz, 1H), 7.23 (d, J = 1.2 Hz, 1H), 7.05 (dd, J = 4.9, 3.8 Hz, 1H), 6.20 (dd, J = 3.0, 1.9 Hz, 1H), 5.97 (dd, J = 3.1, 0.6 Hz, 1H), 3.19 (dd, J = 8.5, 6.7 Hz, 2H), 3.04 – 2.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.62 (s), 154.44 (s), 144.02 (s), 141.19 (s), 133.67 (s), 131.91 (s), 128.13 (s), 110.28 (s), 105.48 (s), 37.61 (s), 22.73 (s). HRMS (EI) calcd. for $C_{11}H_{10}O_2S$[M]: 206.0402; found:206.0409.

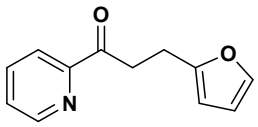
1,3-di(furan-2-yl)propan-1-one **7i**[10]



The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (58.9mg, 0.31mmol, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 1.0 Hz, 1H), 7.23

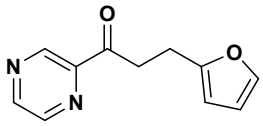
(d, J = 1.1 Hz, 1H), 7.12 (d, J = 3.6 Hz, 1H), 6.46 (dd, J = 3.6, 1.7 Hz, 1H), 6.20 (dd, J = 3.0, 1.9 Hz, 1H), 5.99 – 5.95 (m, 1H), 3.14 – 3.09 (m, 2H), 3.02 – 2.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.88 (s), 154.45 (s), 152.57 (s), 146.40 (s), 141.16 (s), 117.09 (s), 112.24 (s), 110.24 (s), 105.40 (s), 36.71 (s), 22.32 (s).

1-(furan-2-yl)-1-(pyridin-2-yl)propan-1-one **7j**



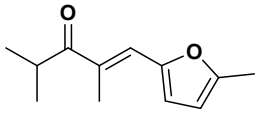
The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (90.5mg, 0.45mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 4.5 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.76 (t, J = 7.7 Hz, 1H), 7.40 (dd, J = 7.4, 4.9 Hz, 1H), 7.22 (s, 1H), 6.20 (s, 1H), 5.98 (d, J = 2.9 Hz, 1H), 3.52 (t, J = 7.5 Hz, 2H), 3.02 (t, J = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.46 (s), 155.02 (s), 153.16 (s), 149.01 (s), 141.01 (s), 136.93 (s), 127.23 (s), 121.82 (s), 110.18 (s), 105.14 (s), 36.18 (s), 22.33 (s). HRMS (EI) calcd. for $C_{12}H_{11}NO_2$[M]: 201.0790; found:201.0784.

1-(furan-2-yl)-1-(pyrazin-2-yl)propan-1-one **7k**



The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (69.7mg, 0.34mmol, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, J = 1.4 Hz, 1H), 8.69 (d, J = 2.5 Hz, 1H), 8.57 (dd, J = 2.4, 1.5 Hz, 1H), 7.22 (dd, J = 1.7, 0.6 Hz, 1H), 6.20 (dd, J = 3.1, 1.9 Hz, 1H), 6.01 – 5.96 (m, 1H), 3.49 (t, J = 7.4 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.86 (s), 154.49 (s), 147.89 (s), 147.37 (s), 143.62 (d, J = 7.4 Hz), 141.15 (s), 110.22 (s), 105.35 (s), 36.32 (s), 22.08 (s). HRMS (EI) calcd. for $C_{11}H_{10}N_2O_2$[M]: 202.0742; found:202.0751.

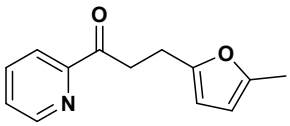
2,4-dimethyl-1-(5-methylfuran-2-yl)pent-1-en-3-one **8a**



The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (52.8mg, 0.27mmol, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 1.3 Hz, 1H), 6.52 (d, J = 3.3 Hz, 1H), 6.07 (d, J = 3.2 Hz, 1H), 3.43 – 3.29 (m, 1H), 2.30 (s, 3H), 2.05 (s, 3H), 1.07 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.71 (s), 154.76 (s), 150.53 (s), 131.19 (s), 125.50 (s),

116.63 (s), 108.91 (s), 33.64 (s), 19.82 (s), 13.90 (s), 13.32 (s). HRMS (EI) calcd. for $C_{12}H_{16}O_2$[M]: 192.1150; found:192.1153.

3-(5-methylfuran-2-yl)-1-(pyridin-2-yl)propan-1-one **8c**



The yield of product was isolated through column chromatography (PE/EA=4:1) on silica gel as colourless oil (79.6mg, 0.37mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 4.6 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.80 – 7.68 (m, 1H), 7.47 – 7.28 (m, 1H), 5.83 (d, J = 2.6 Hz, 1H), 5.74 (s, 1H), 3.48 (t, J = 7.6 Hz, 2H), 2.94 (t, J = 7.5 Hz, 2H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.56 (s), 153.19 (d, J = 12.5 Hz), 150.42 (s), 148.96 (s), 136.87 (s), 127.15 (s), 121.77 (s), 105.80 (d, J = 17.2 Hz), 36.33 (s), 22.42 (s), 13.49 (s). HRMS (EI) calcd. for $C_{13}H_{13}NO_2$[M]: 215.0946; found:215.0951.

Reference

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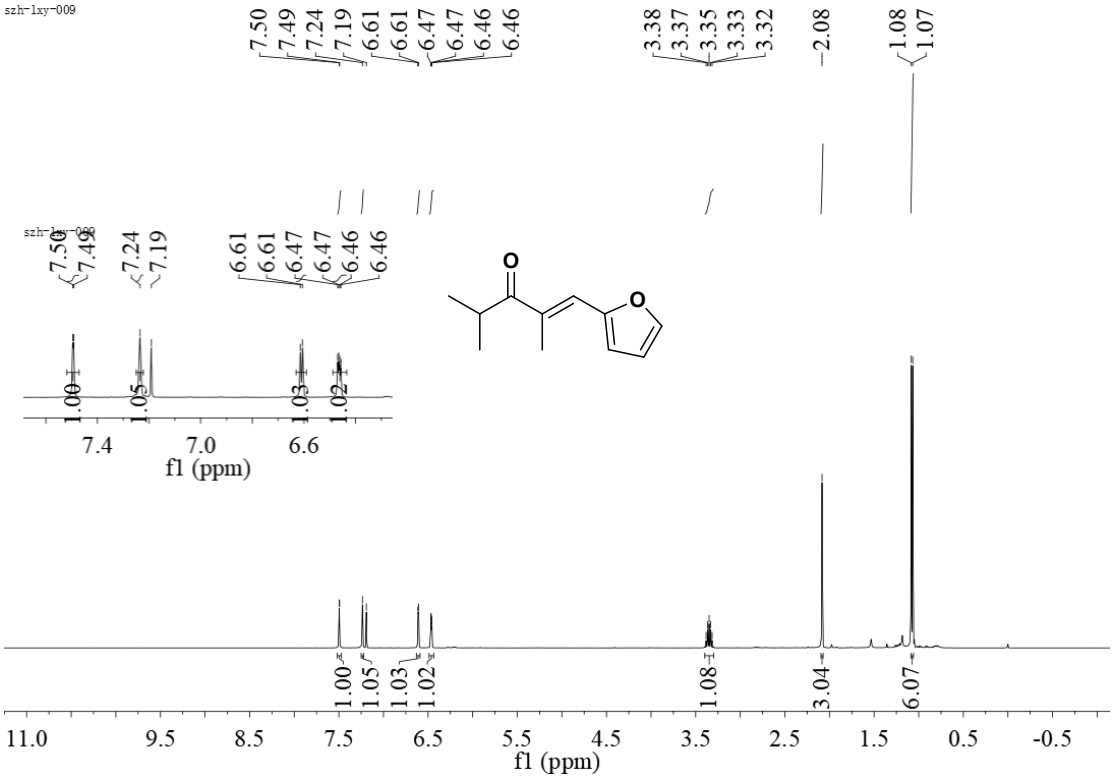
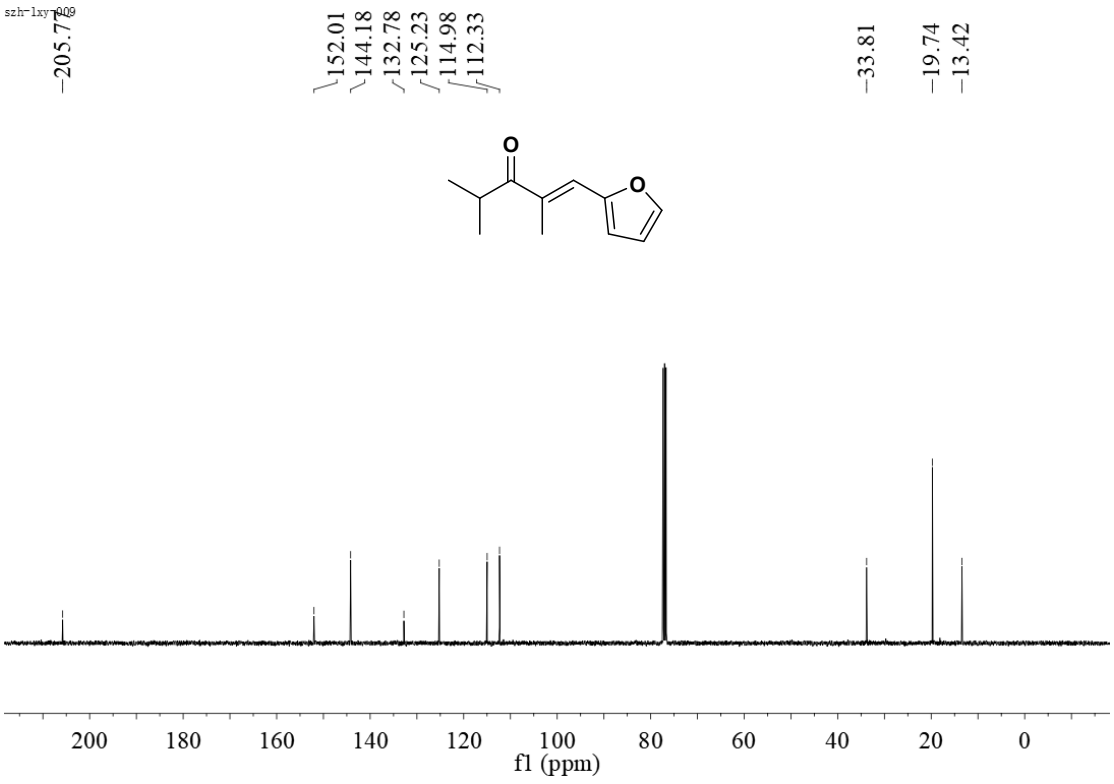
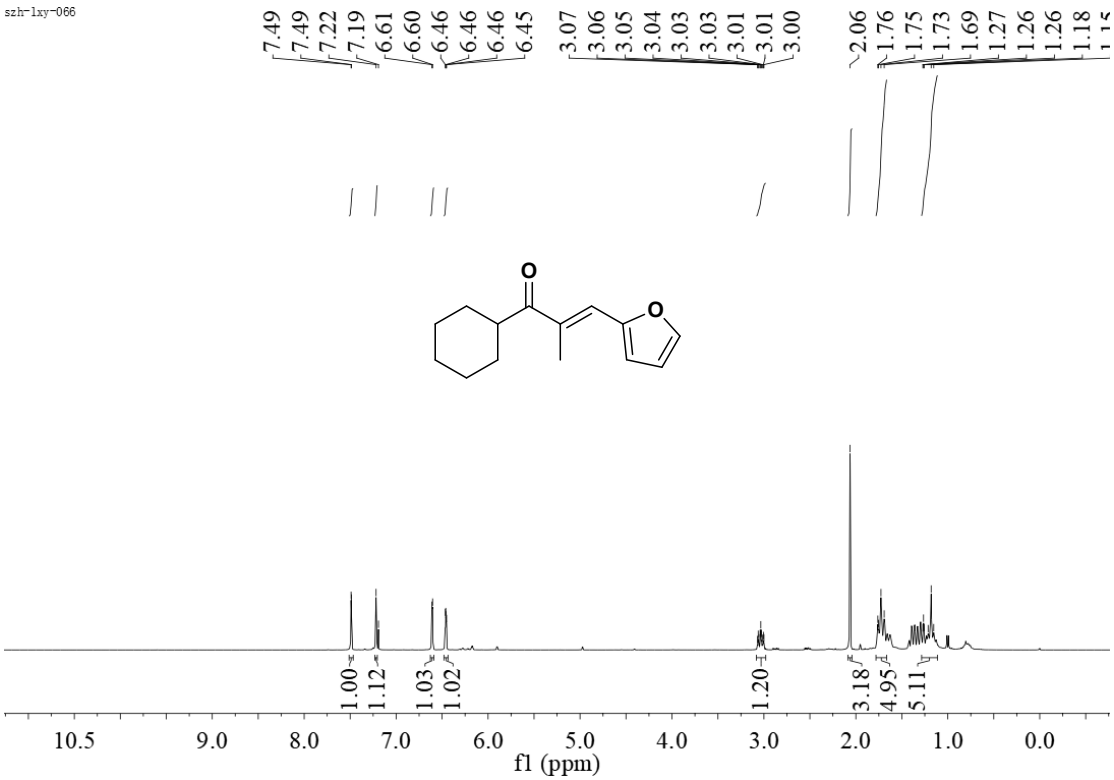
Characterization Data of Products



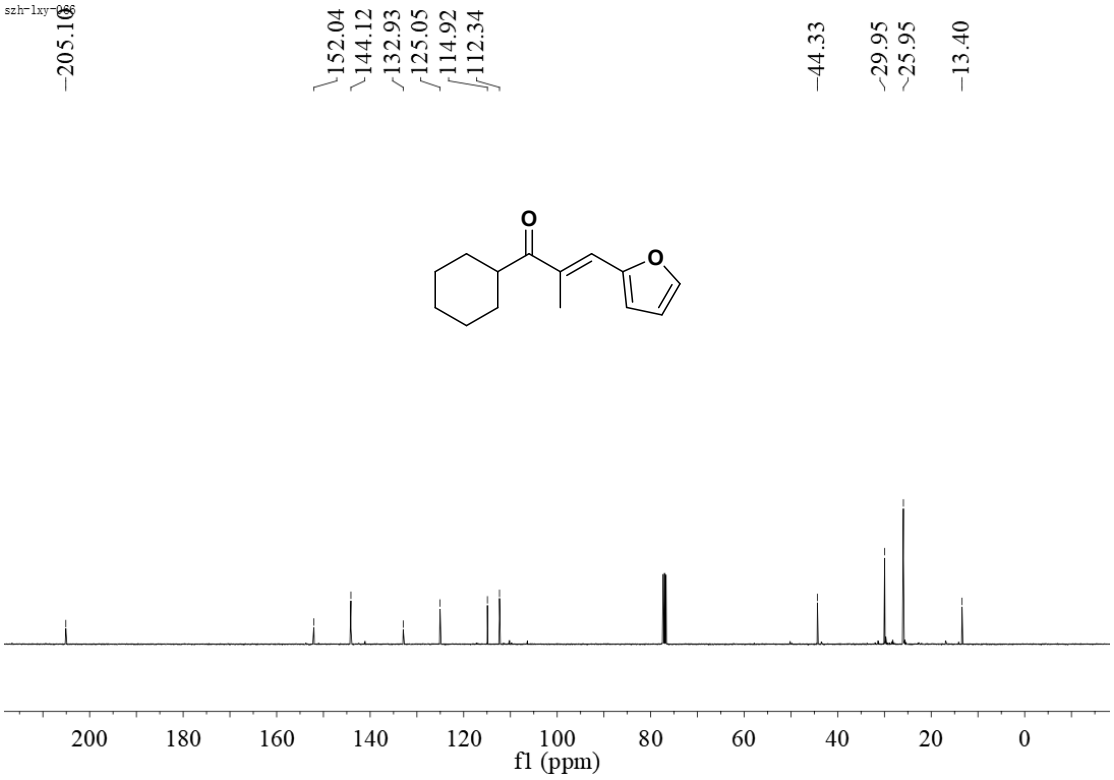
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3a**



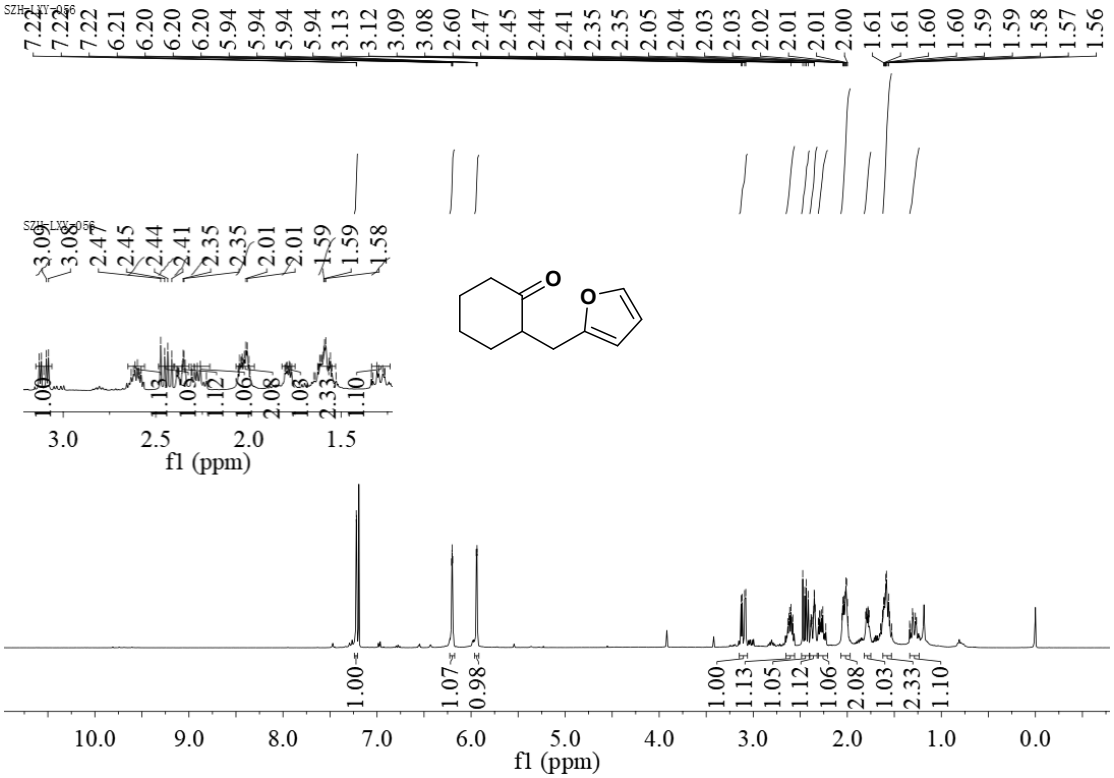
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3a**



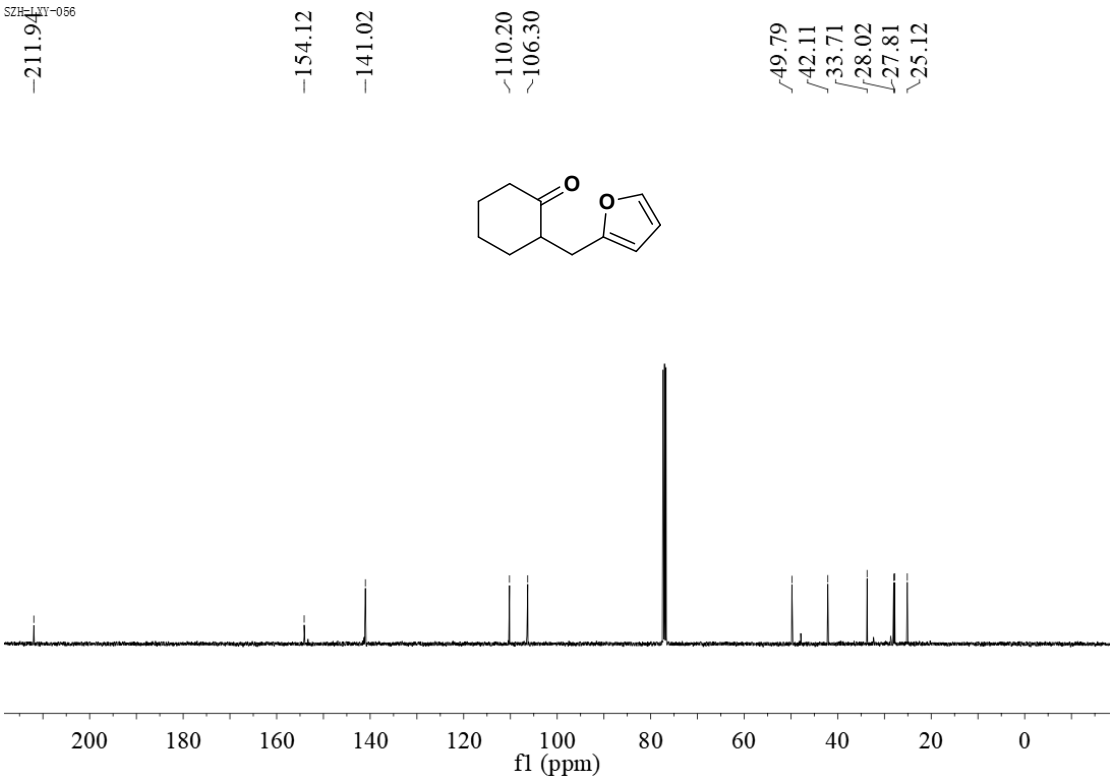
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3c**



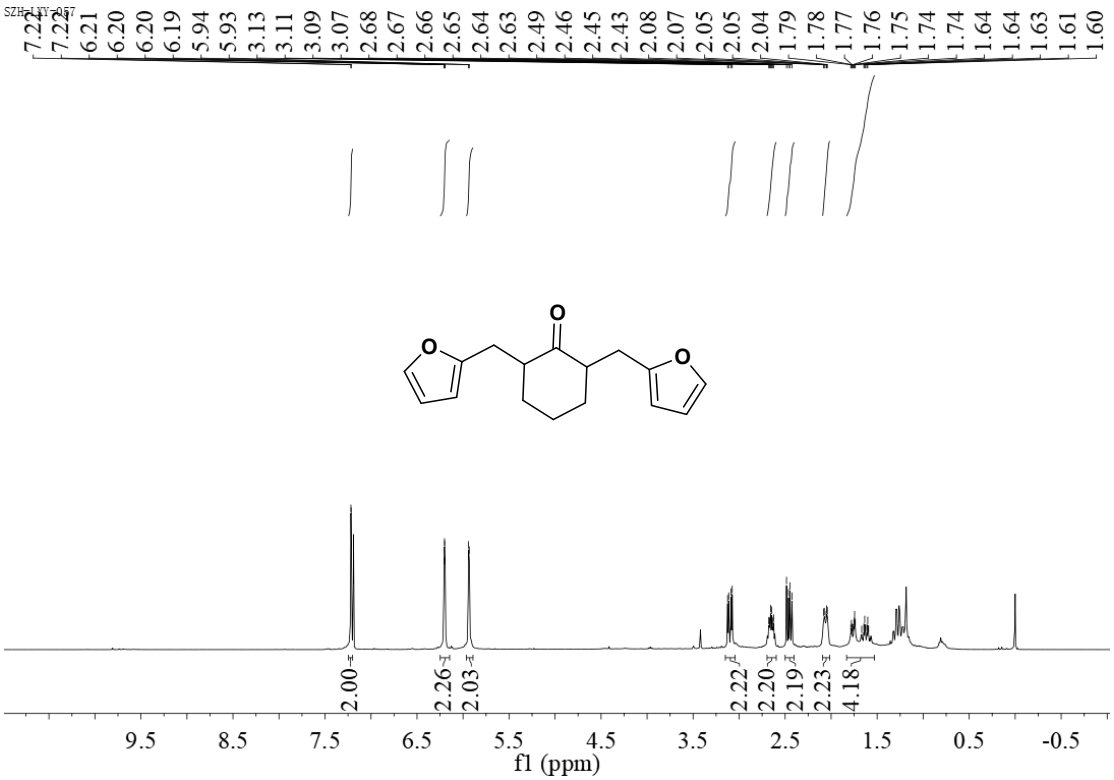
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3c**



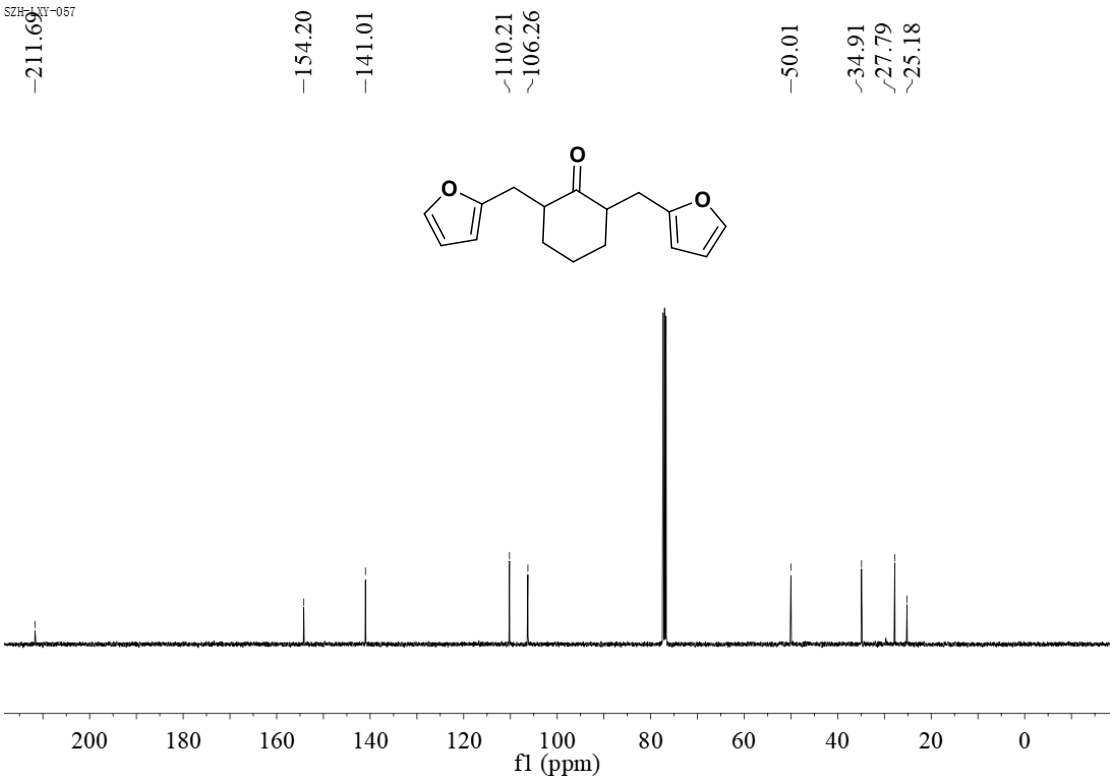
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3d**[1]



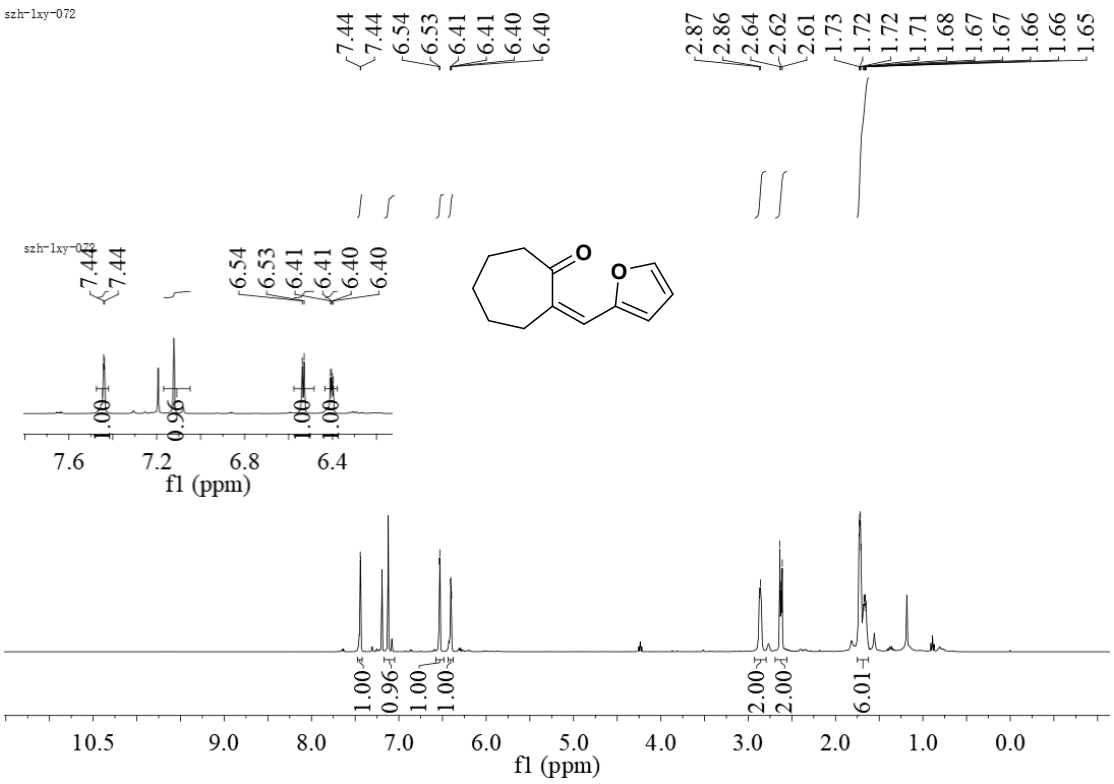
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3d**[1]



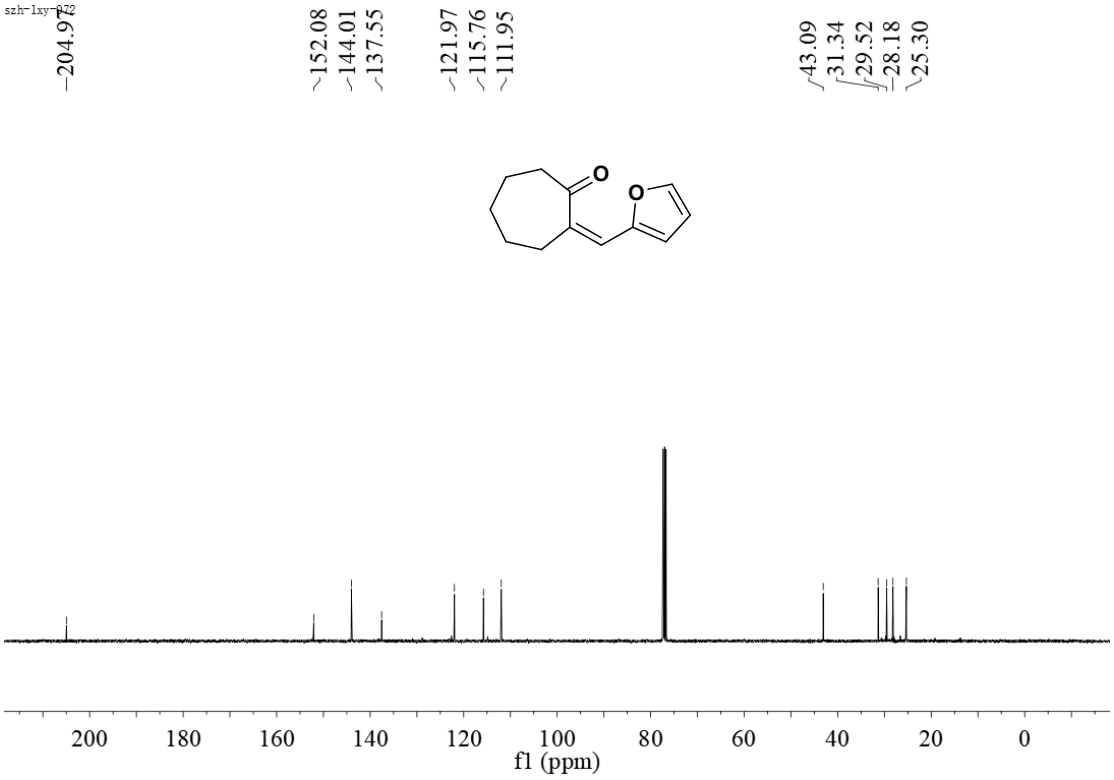
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3d²**



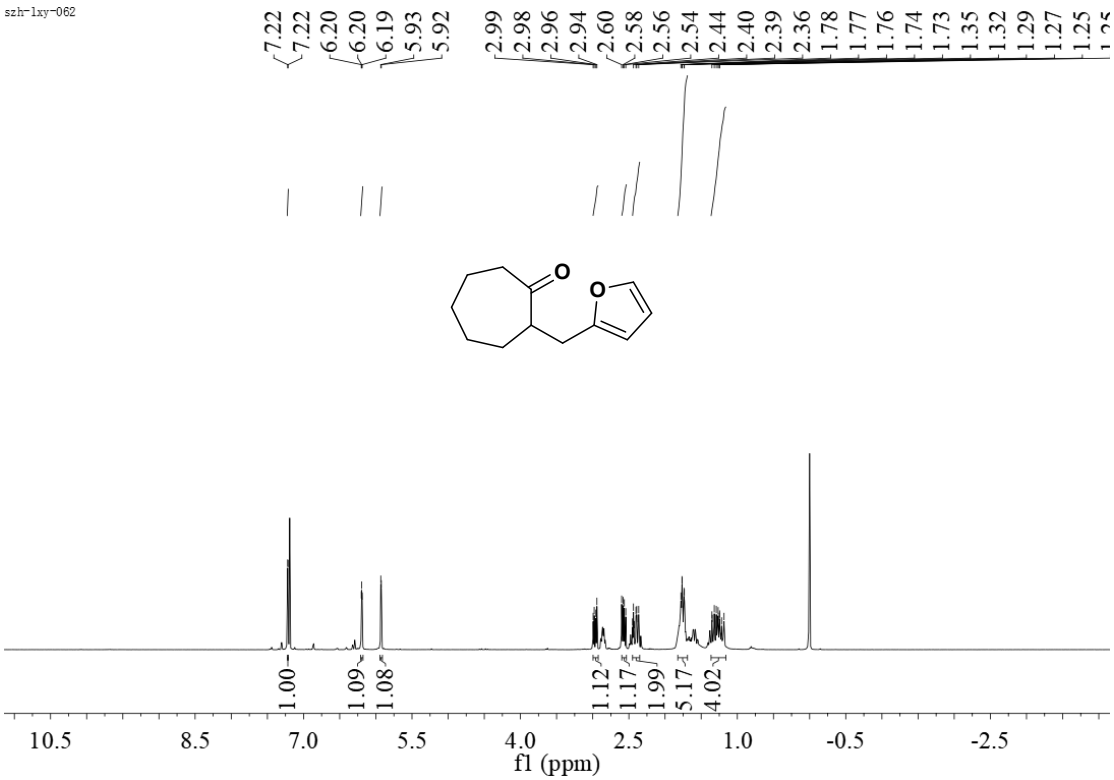
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3d²**



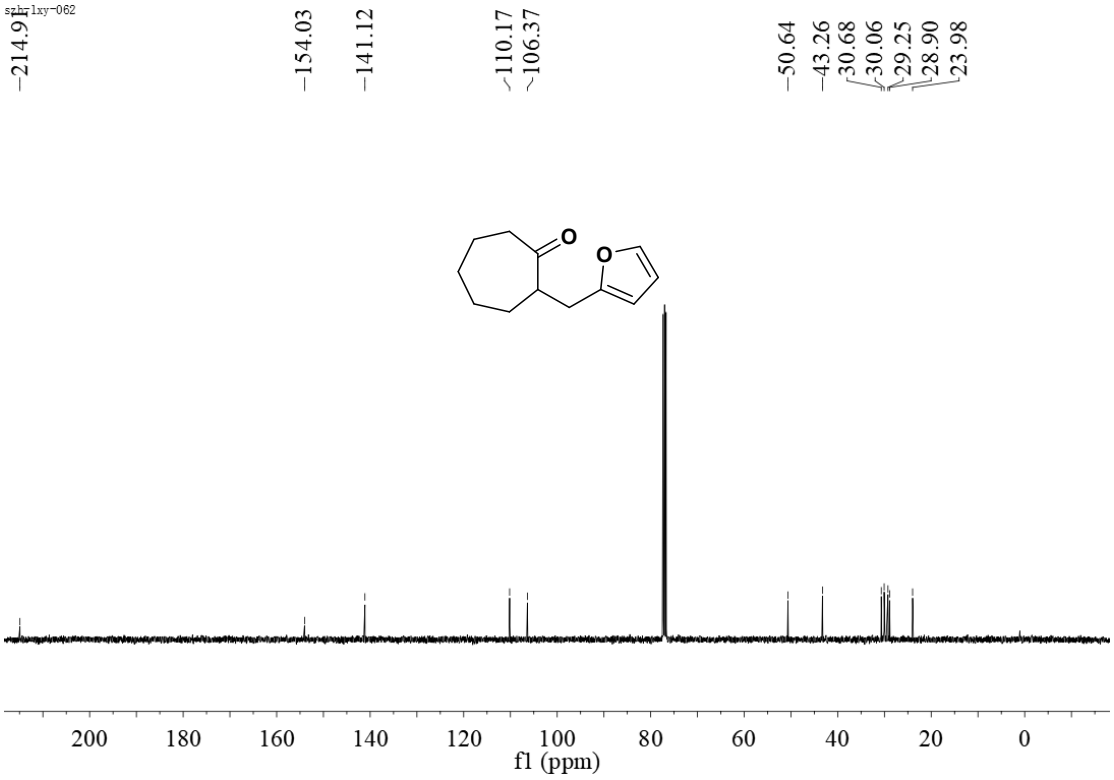
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3e**[1]



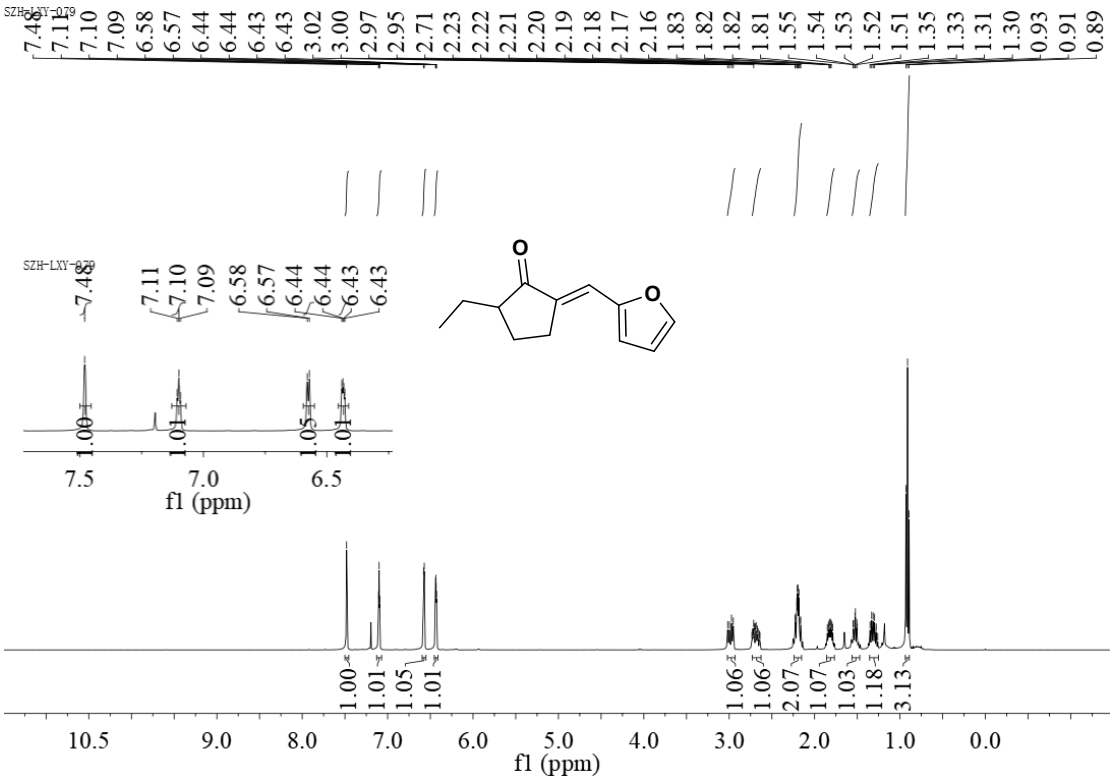
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3e**[1]



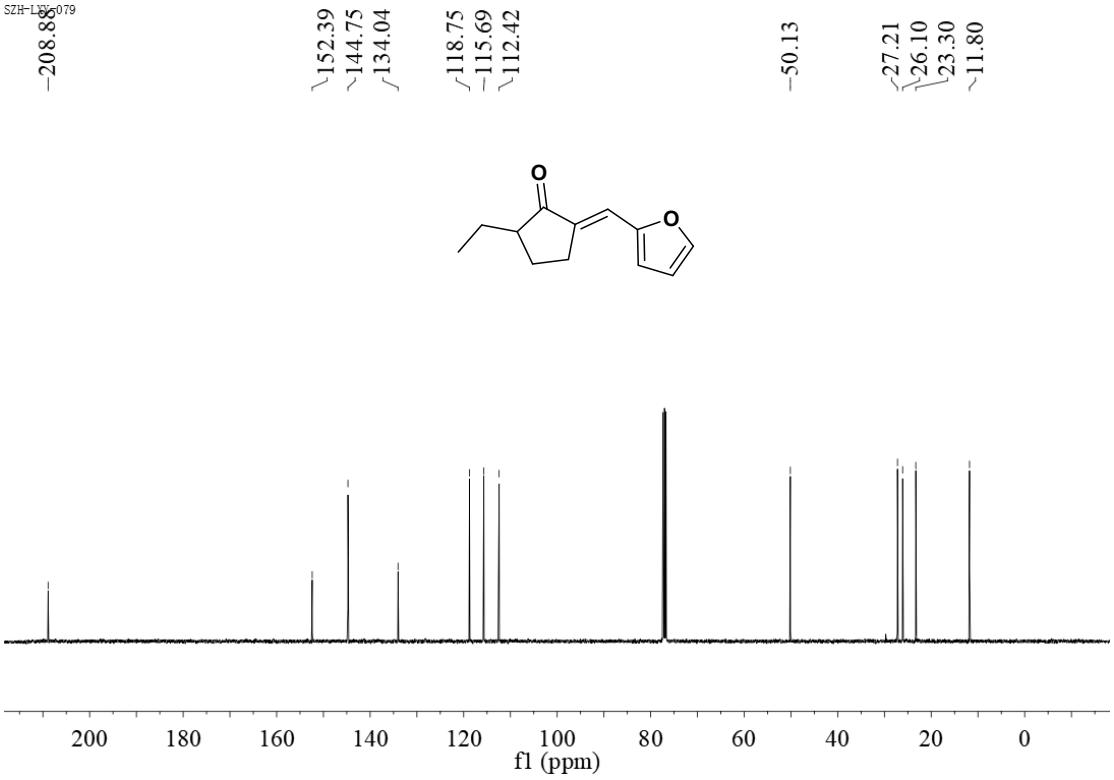
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3e²**



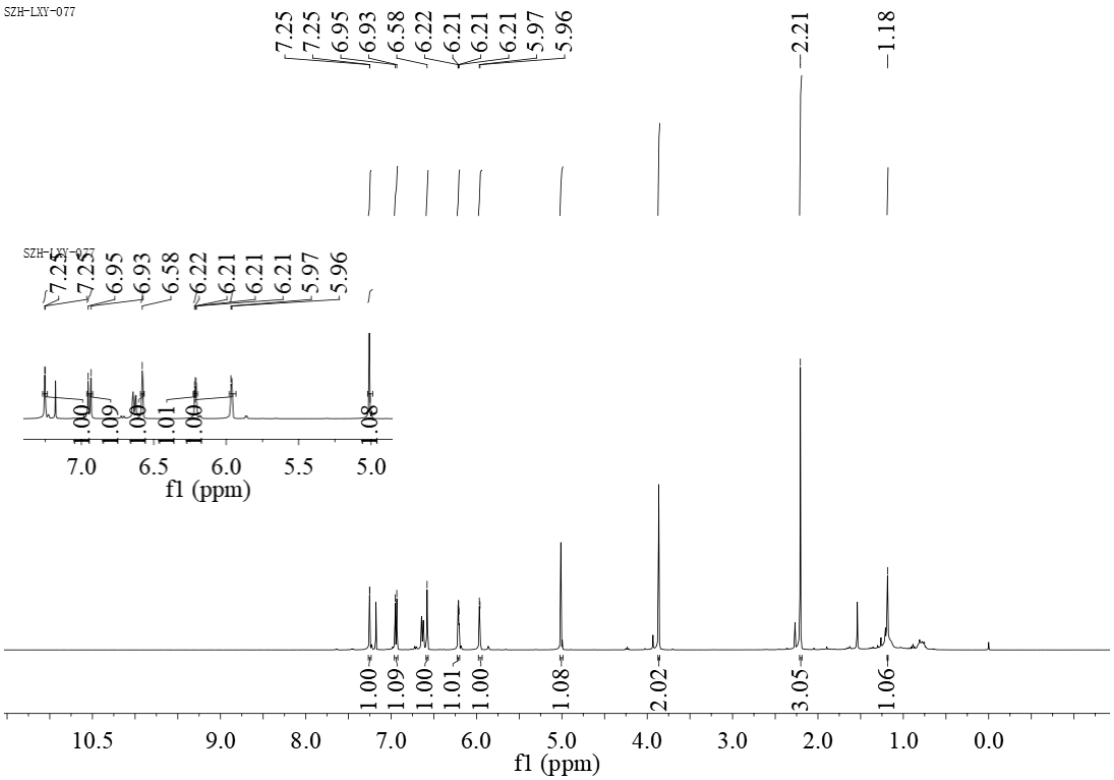
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3e²**



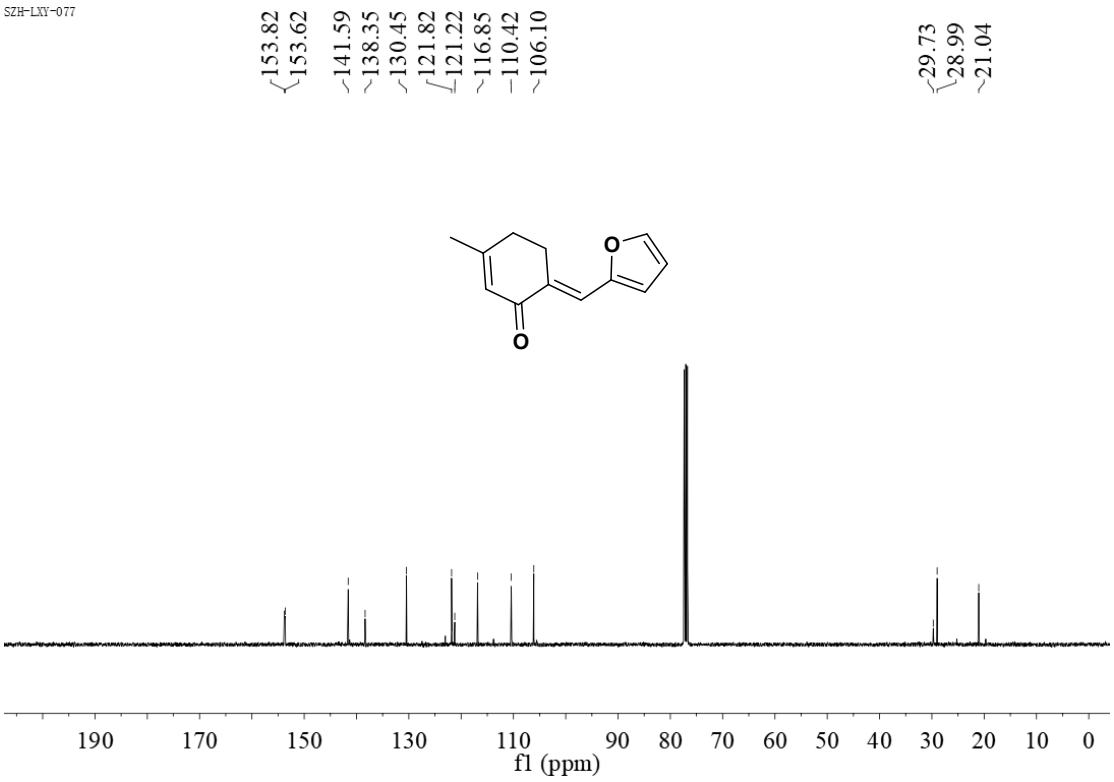
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3f**



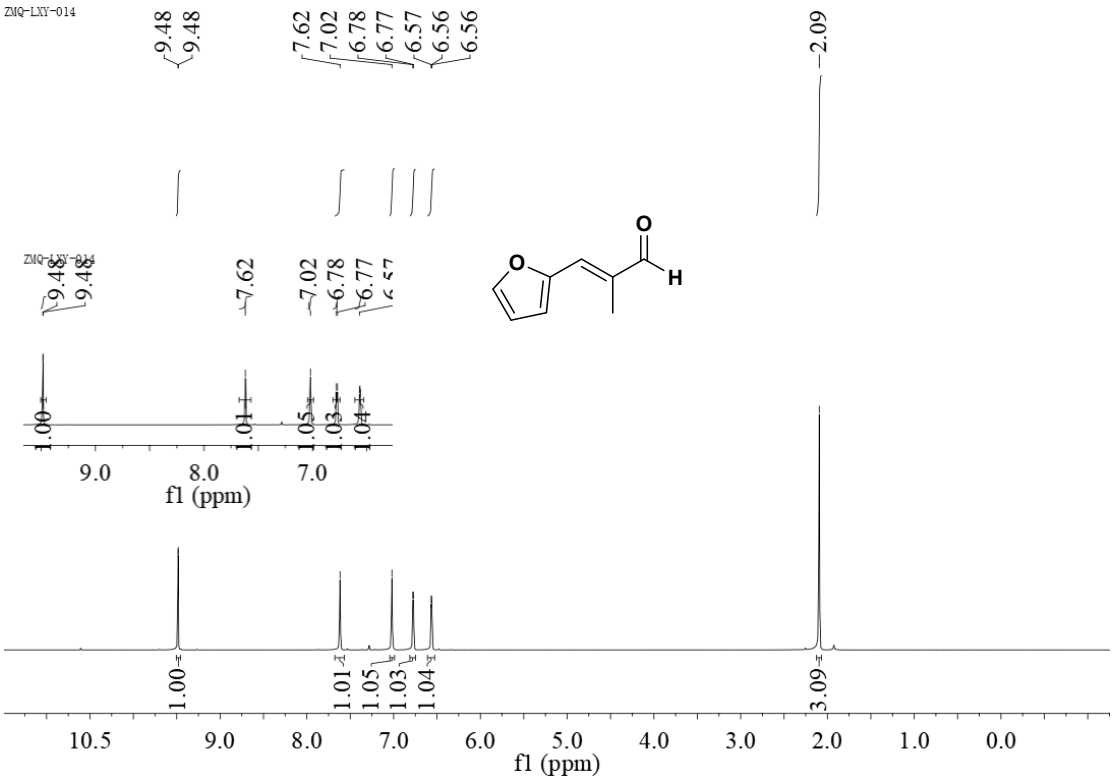
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3f**



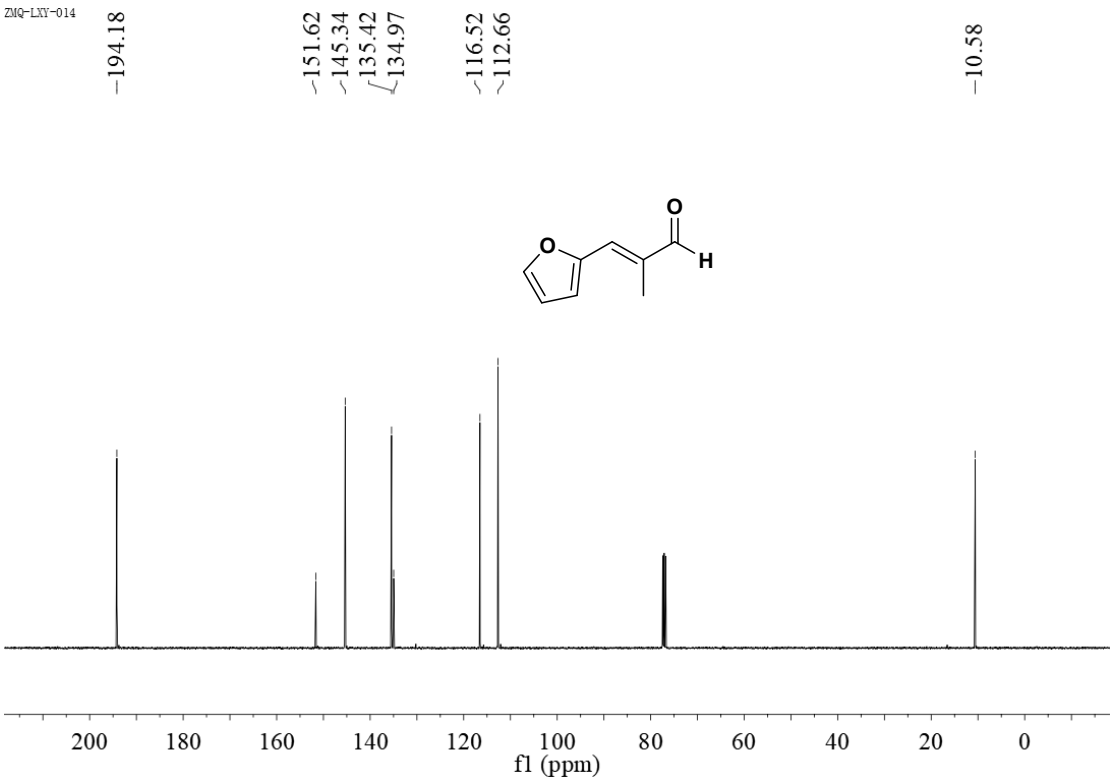
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3h**



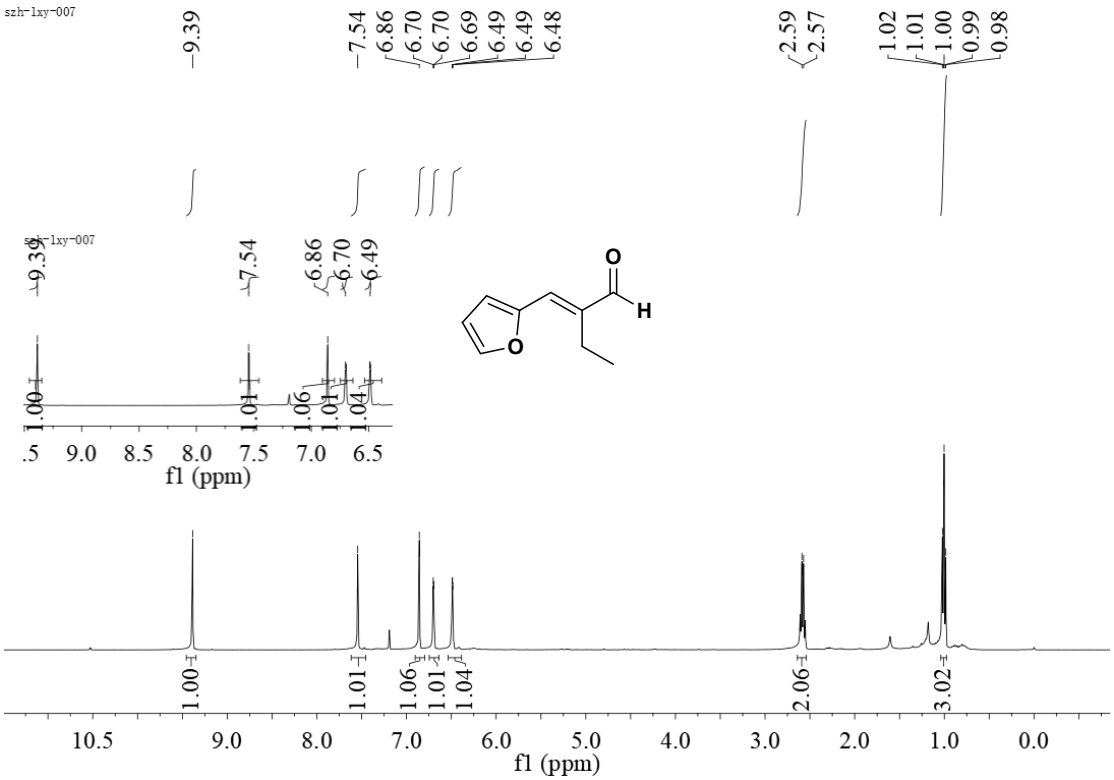
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3h**



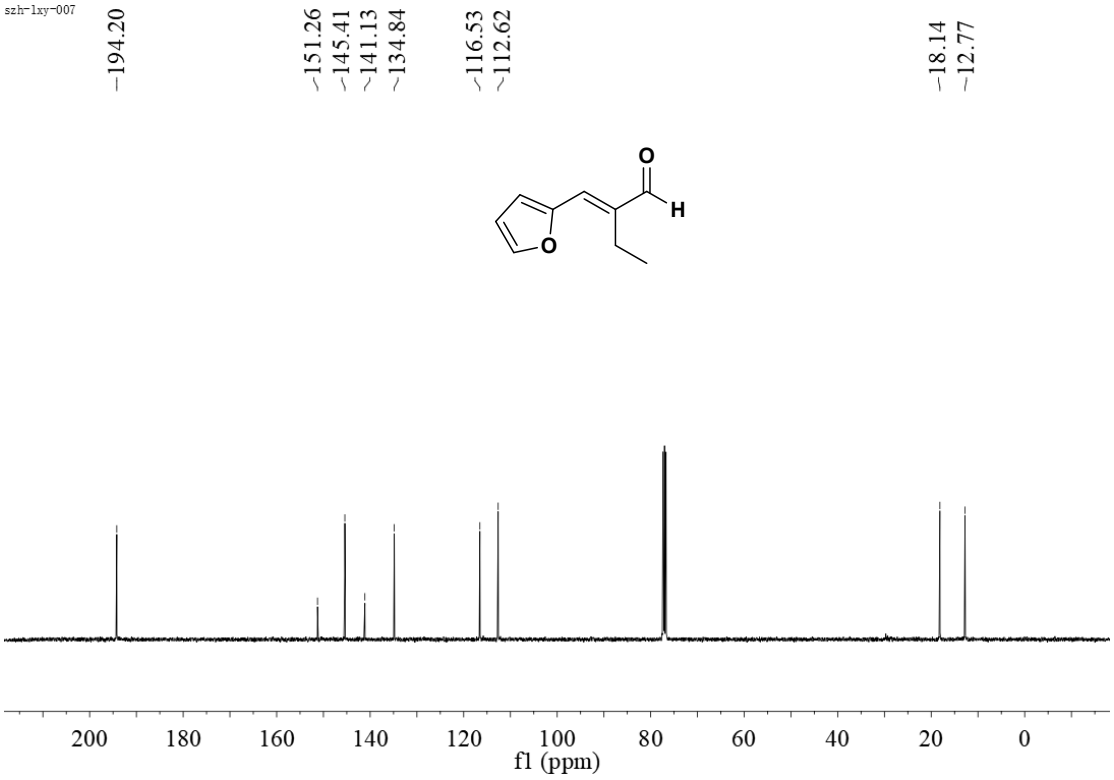
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **5a**



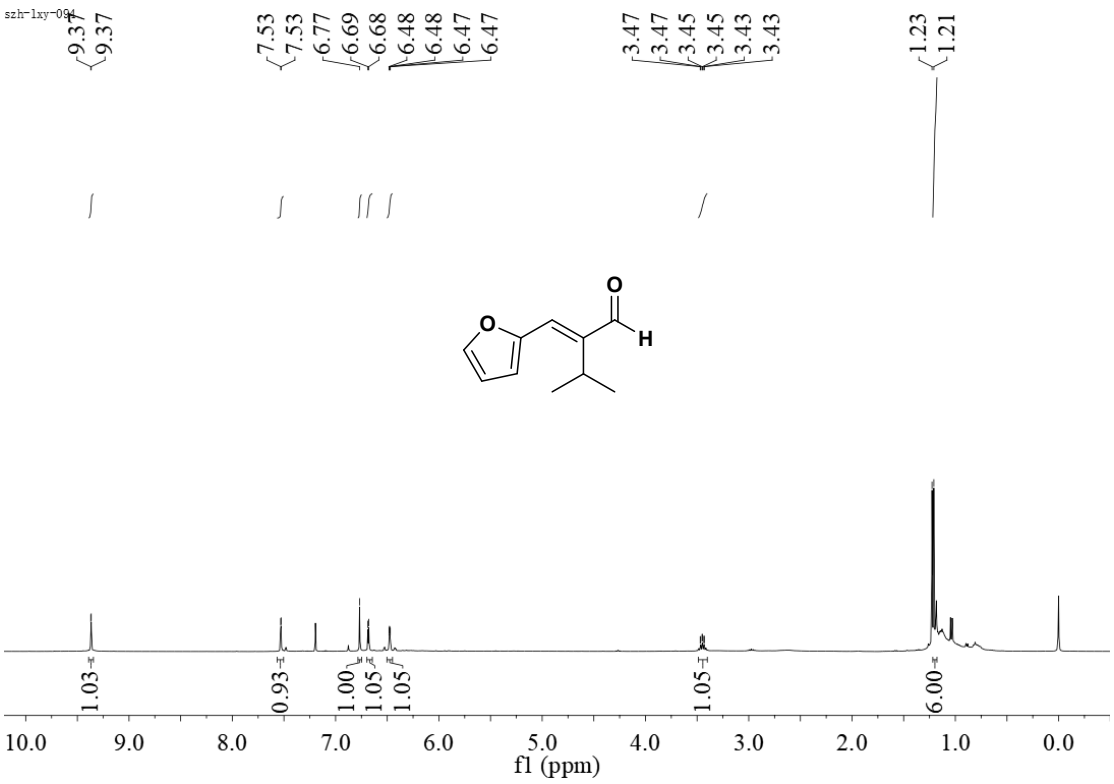
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **5a**



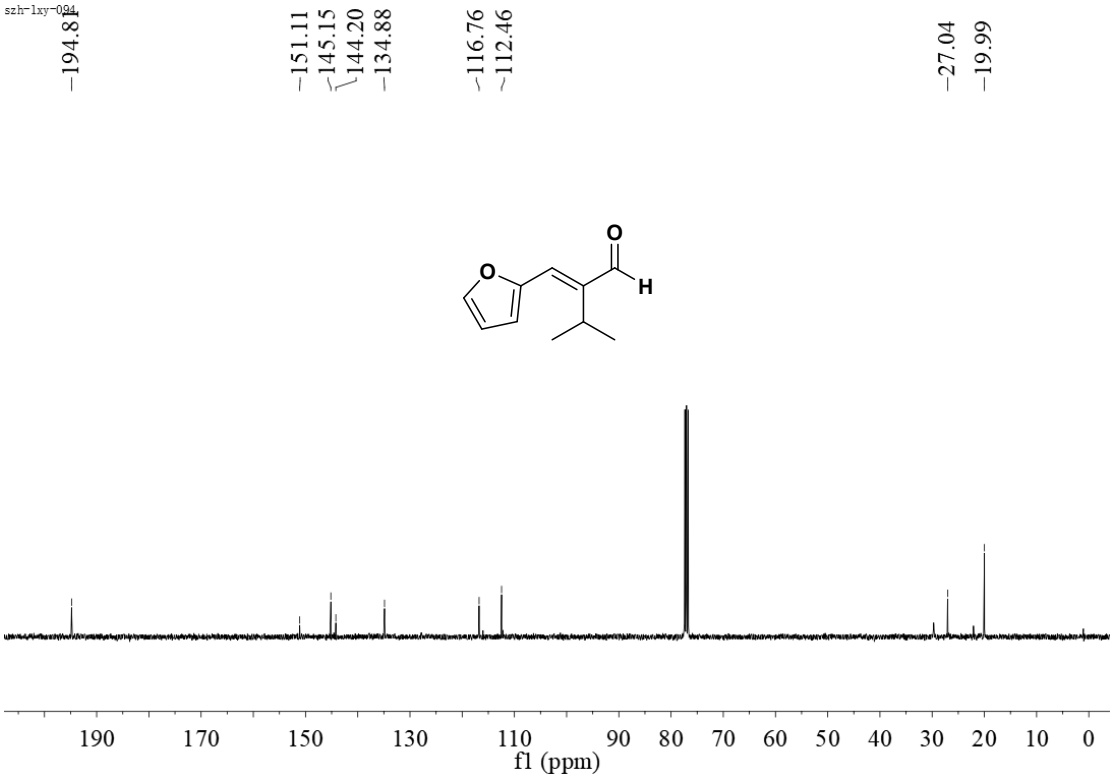
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **5b**



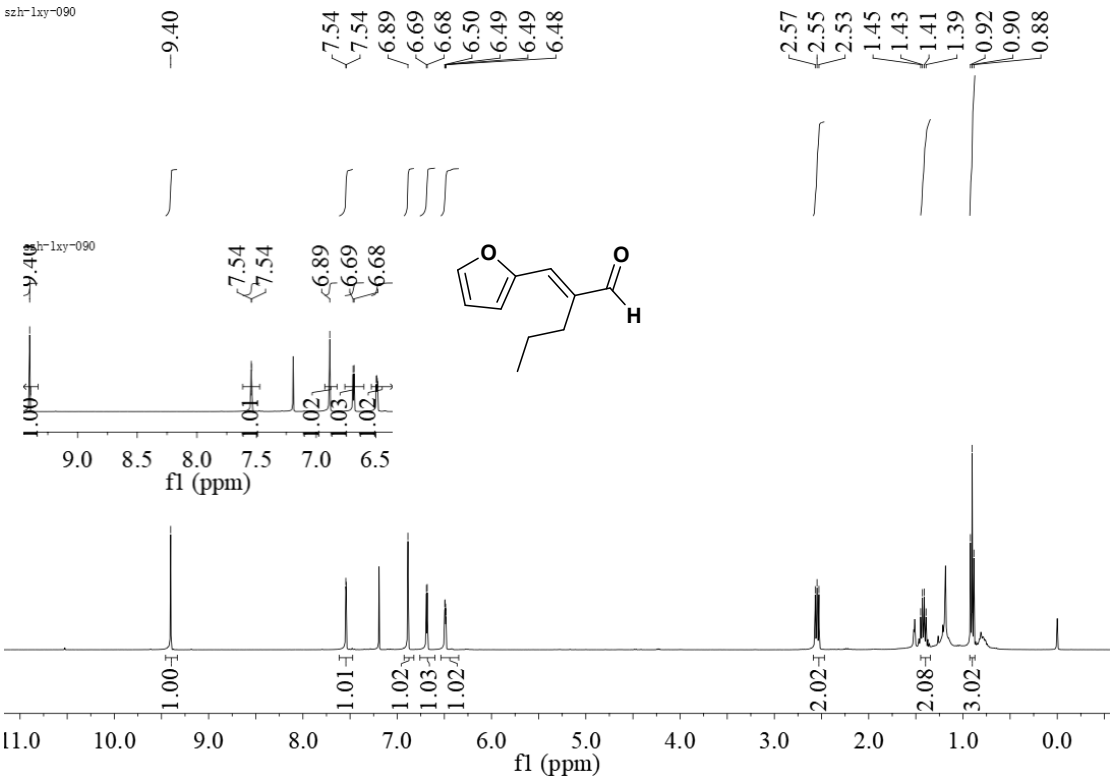
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **5b**



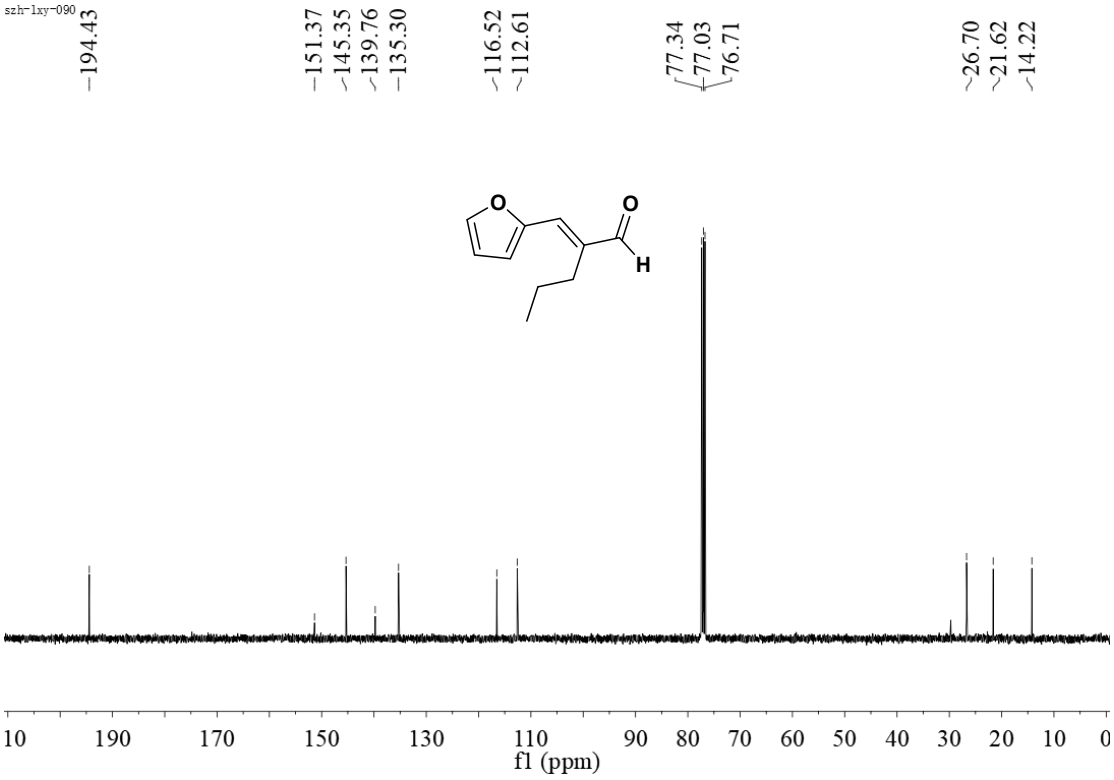
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **5c**



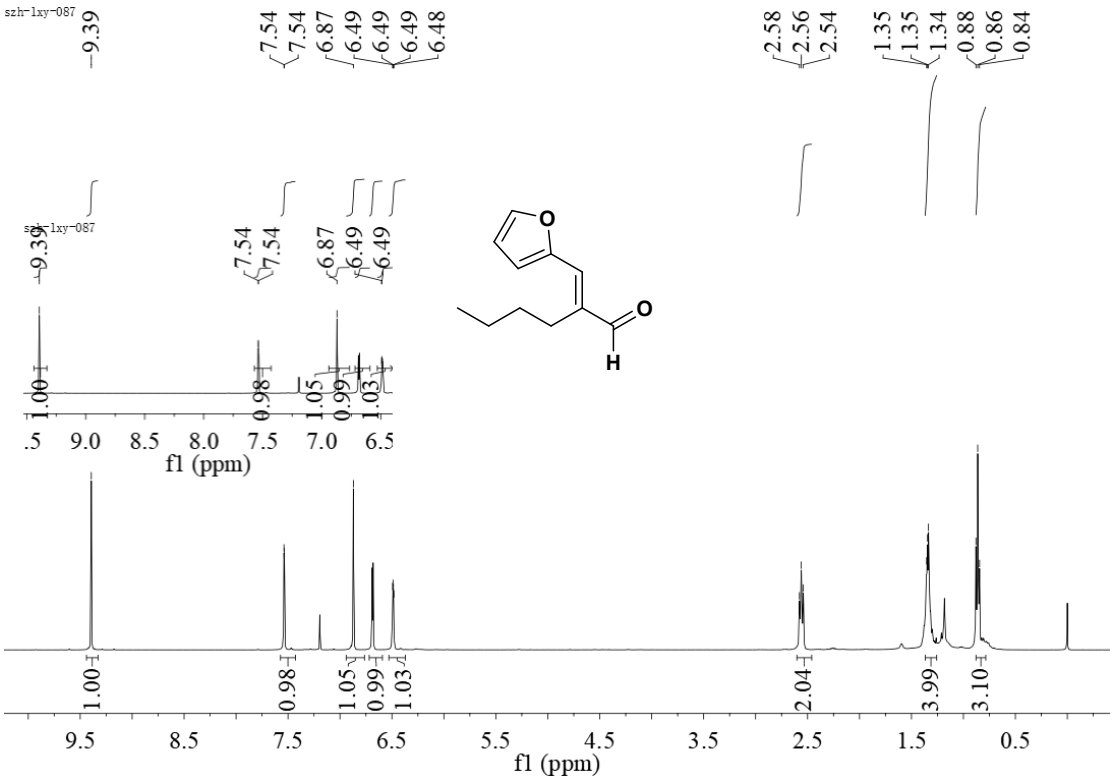
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **5c**



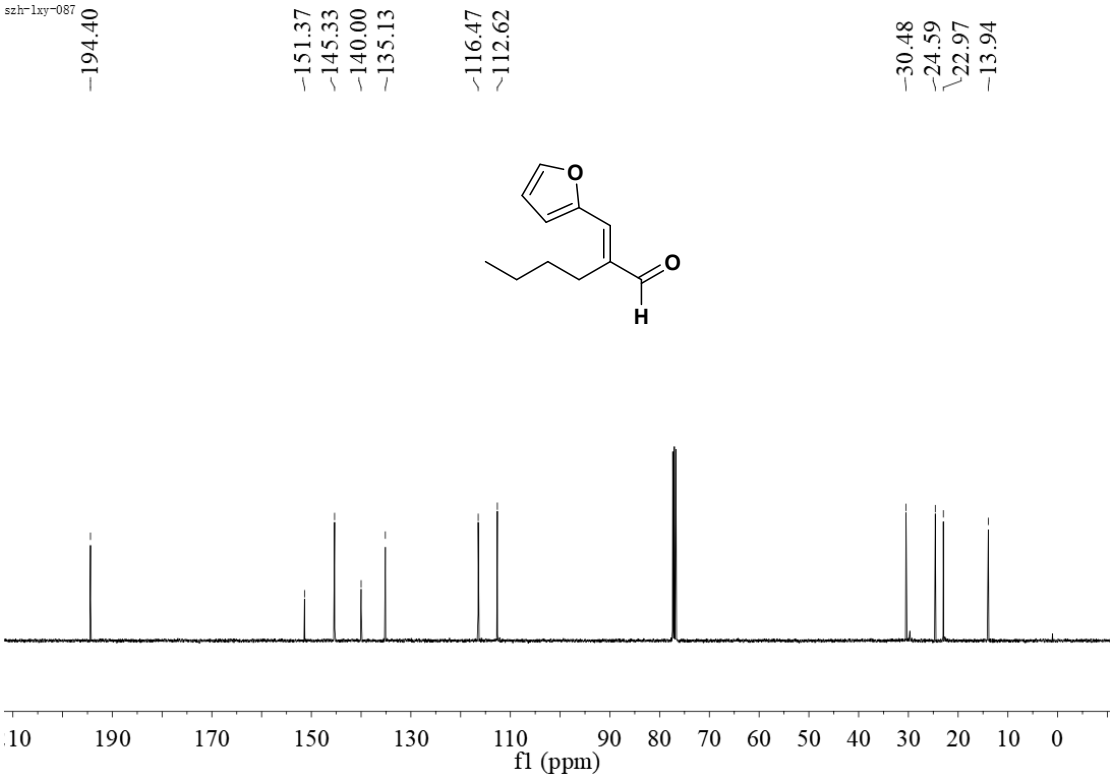
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **5d**



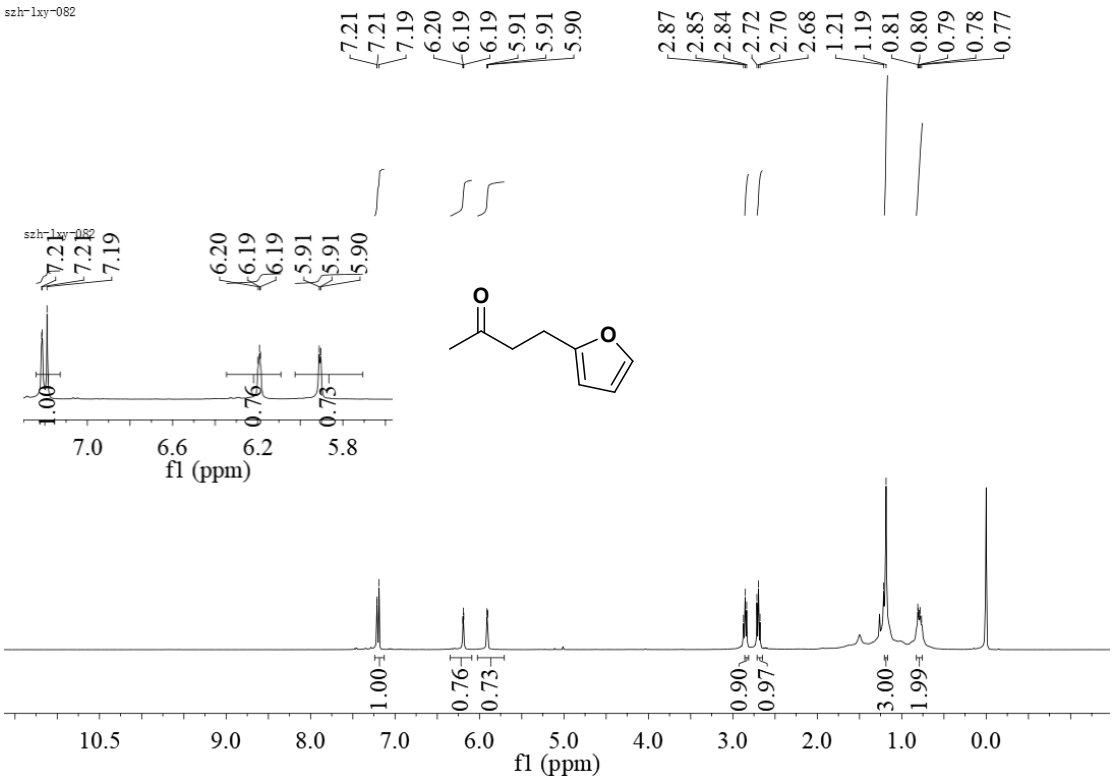
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **5d**



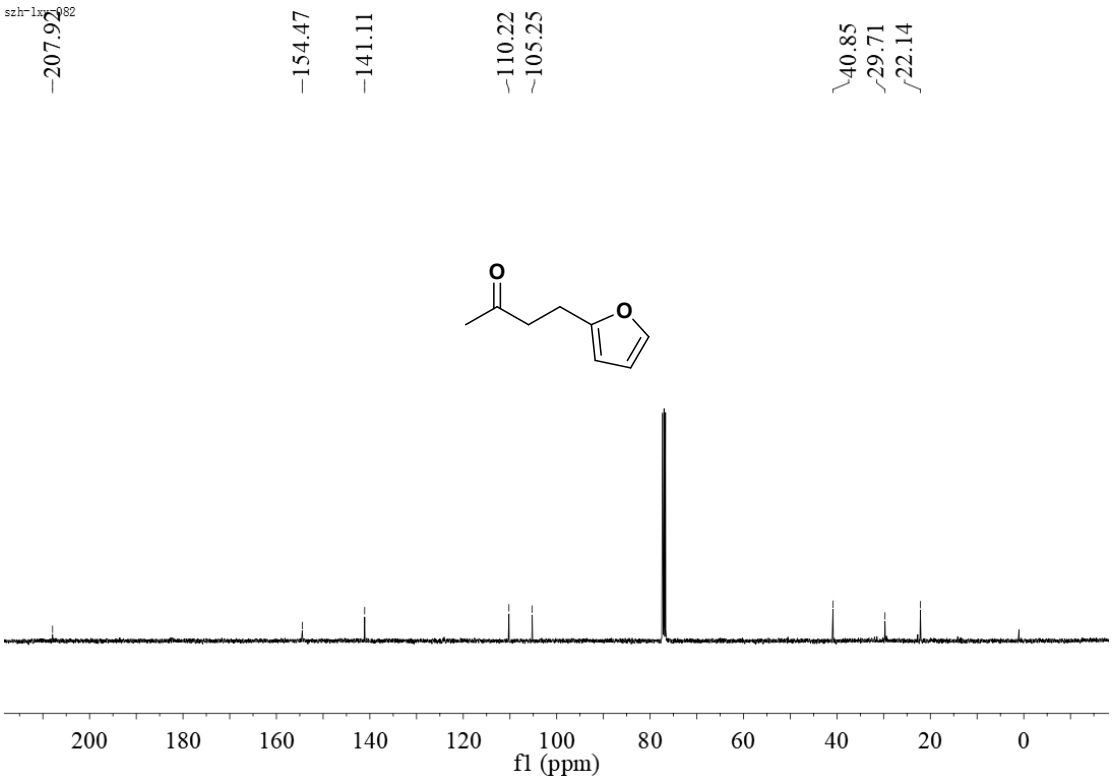
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **5e**



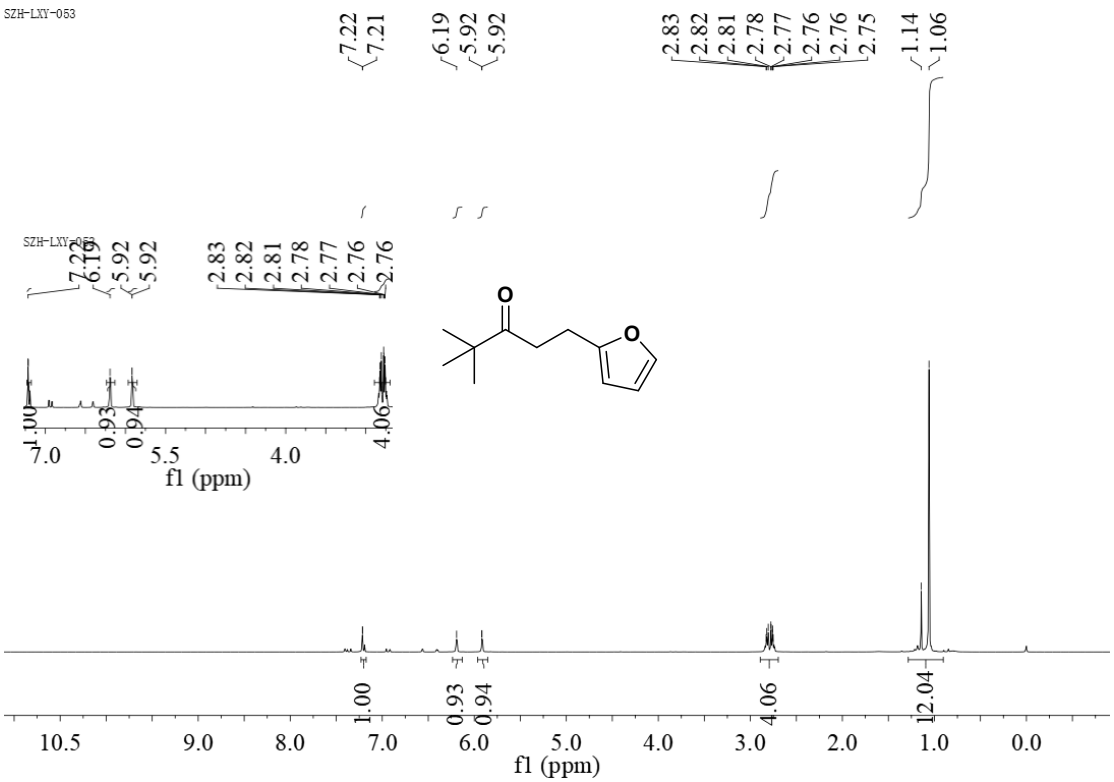
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **5e**



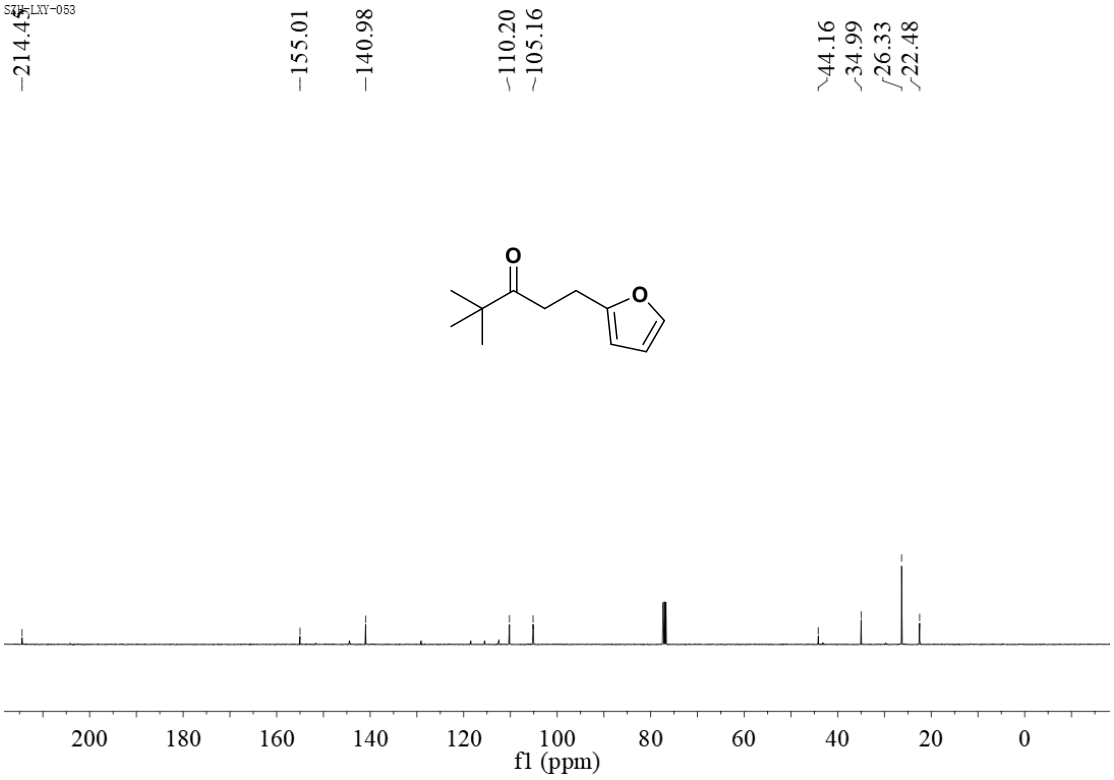
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7a**



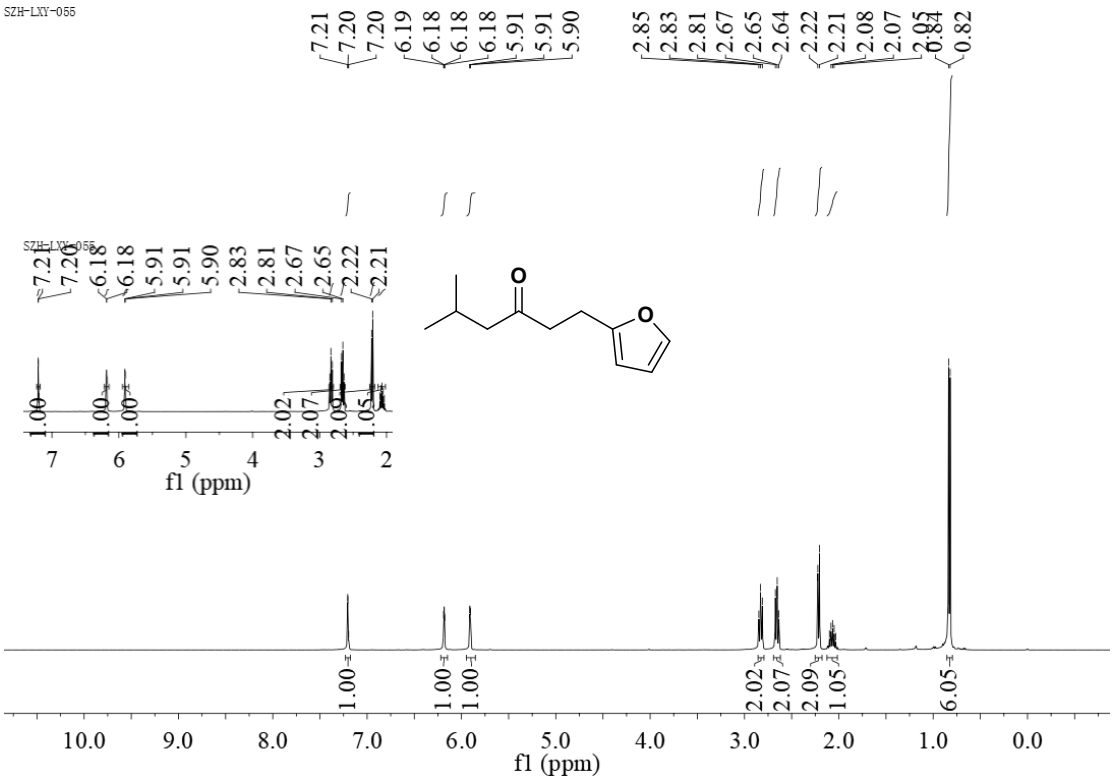
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **7a**



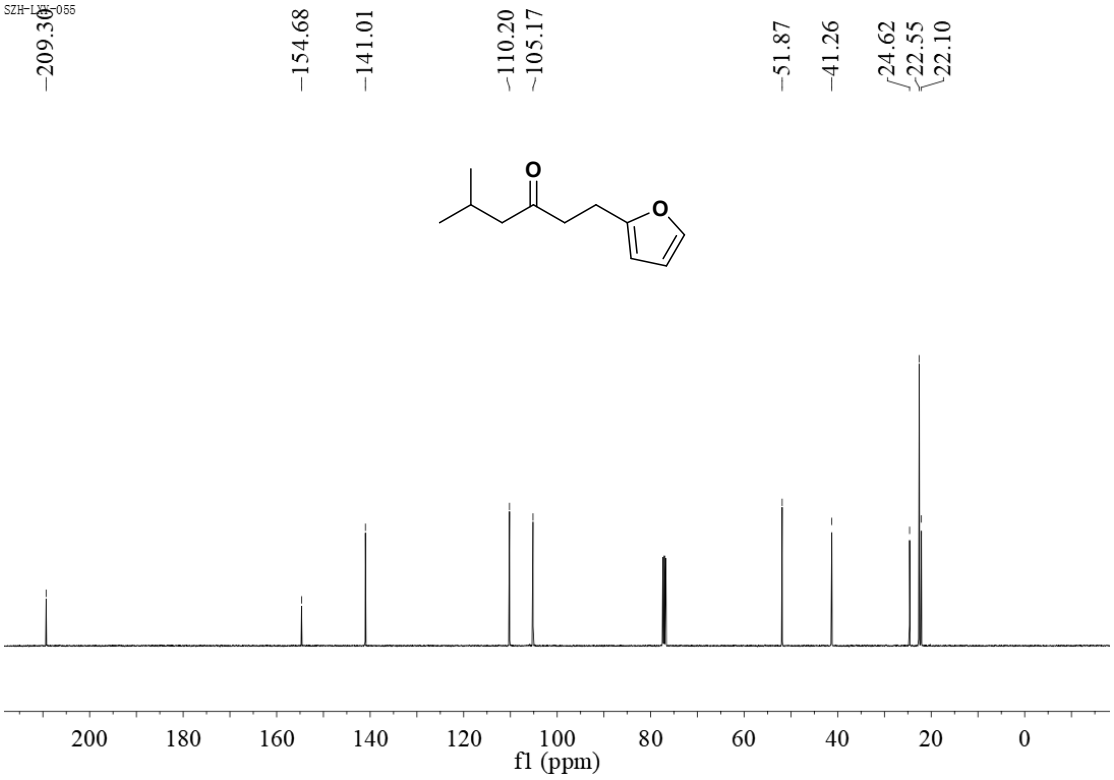
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7c**



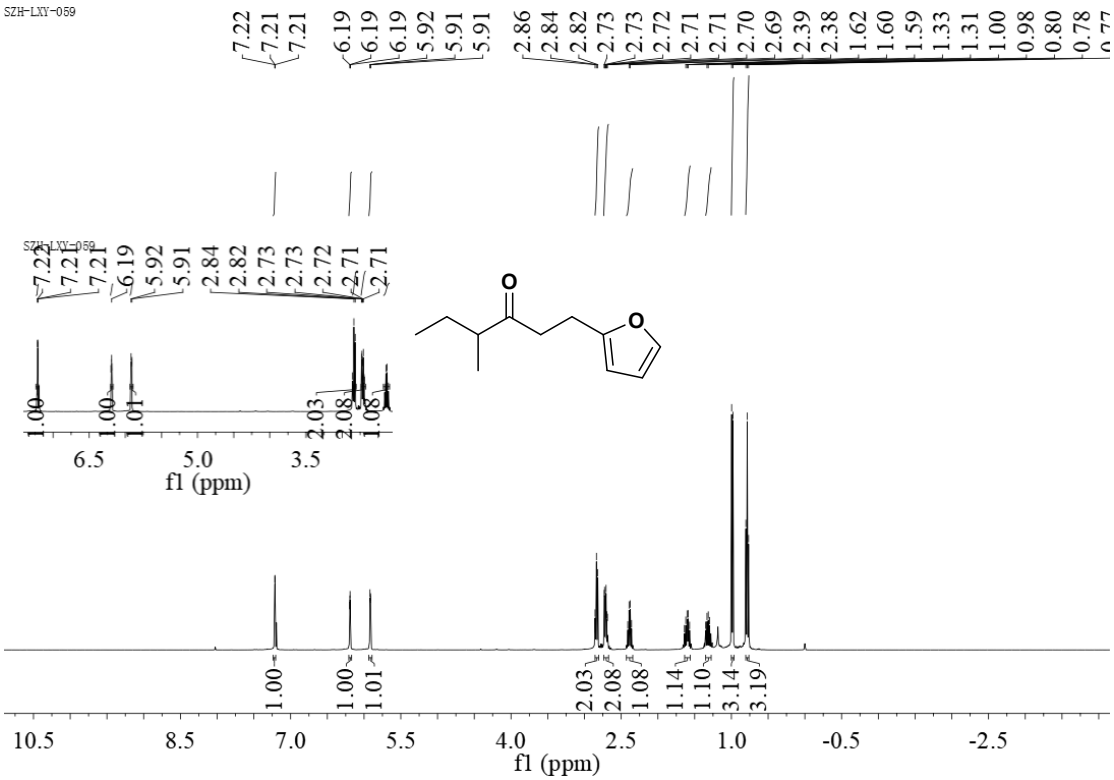
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **7c**



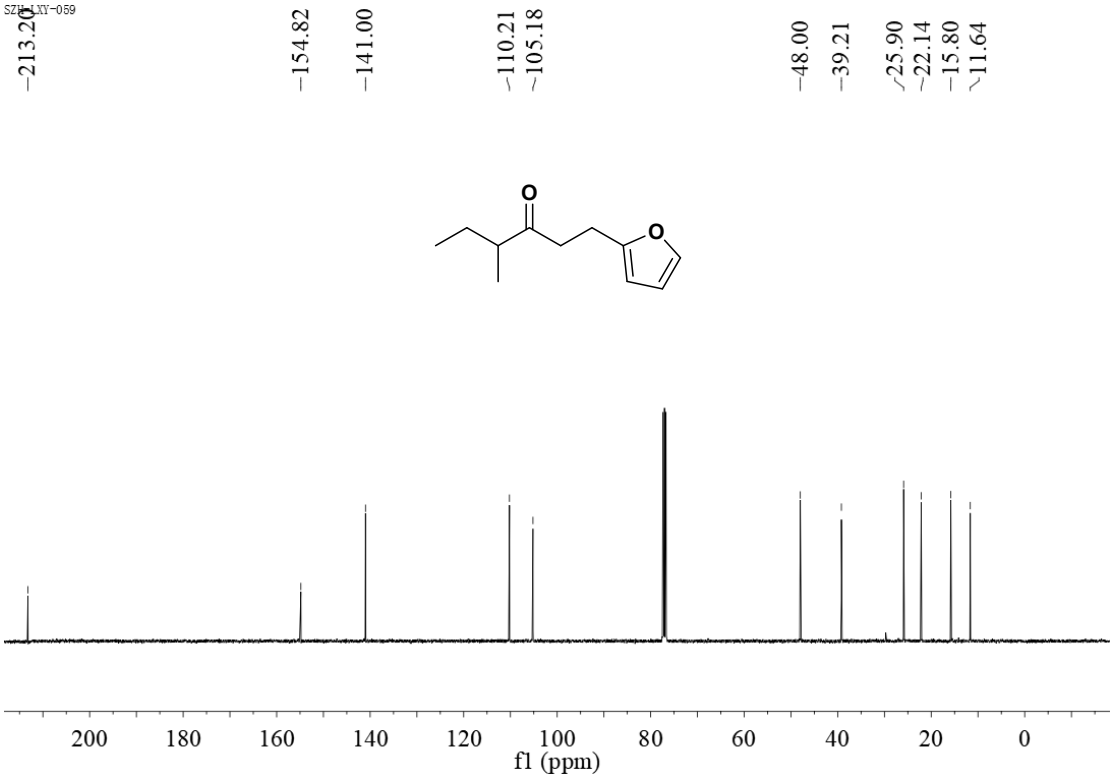
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7d**



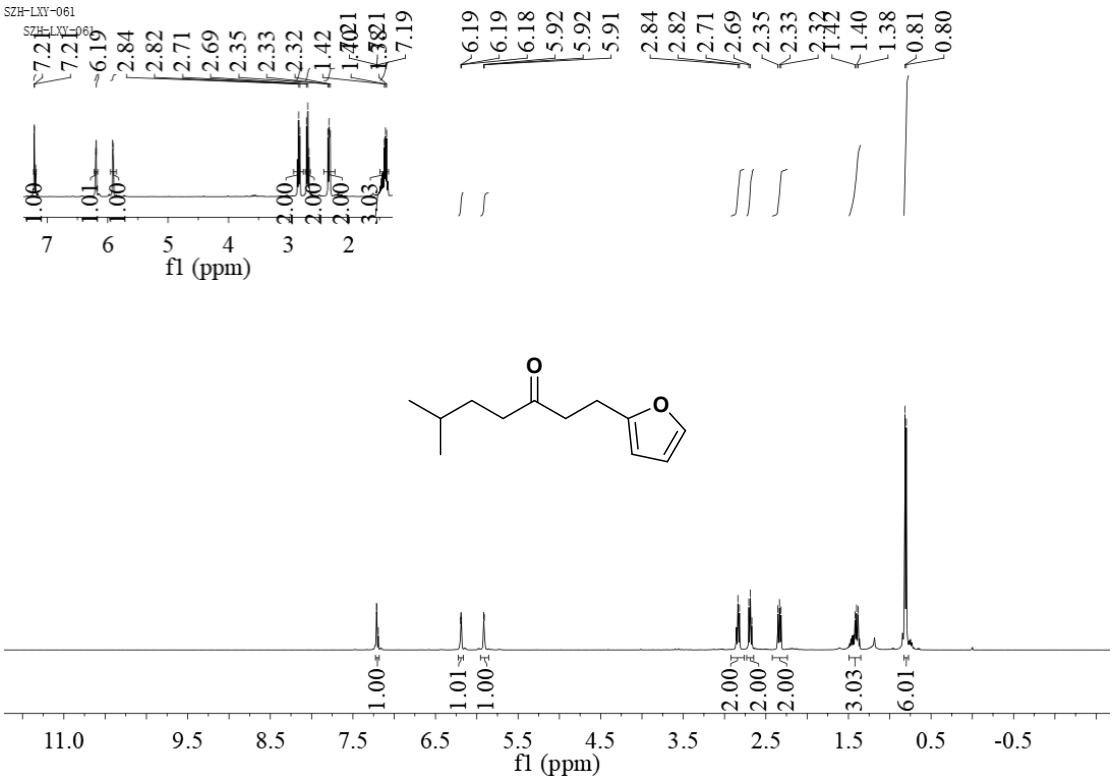
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **7d**



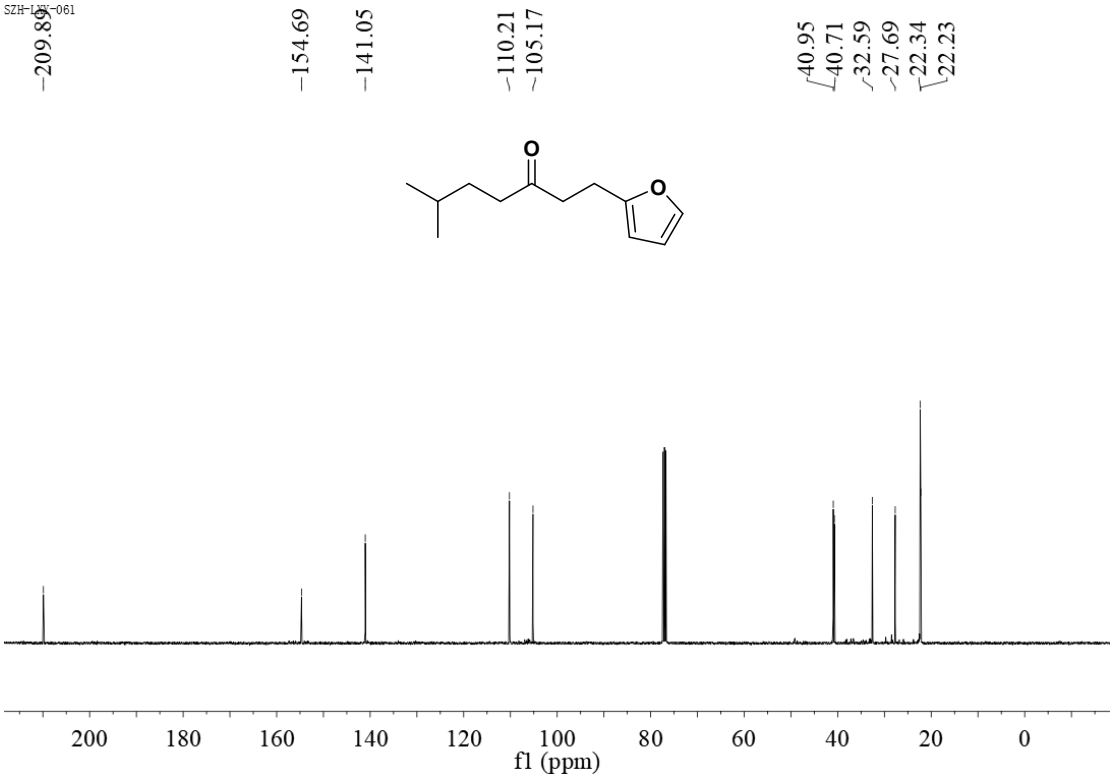
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7e**



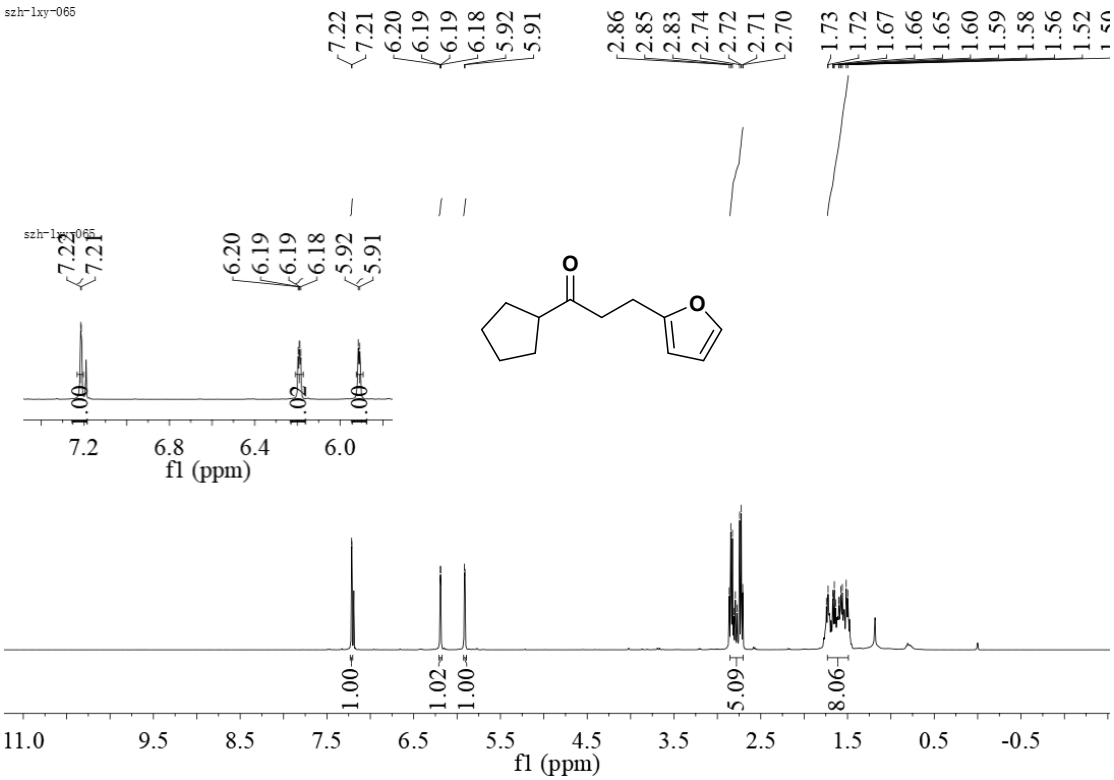
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **7e**



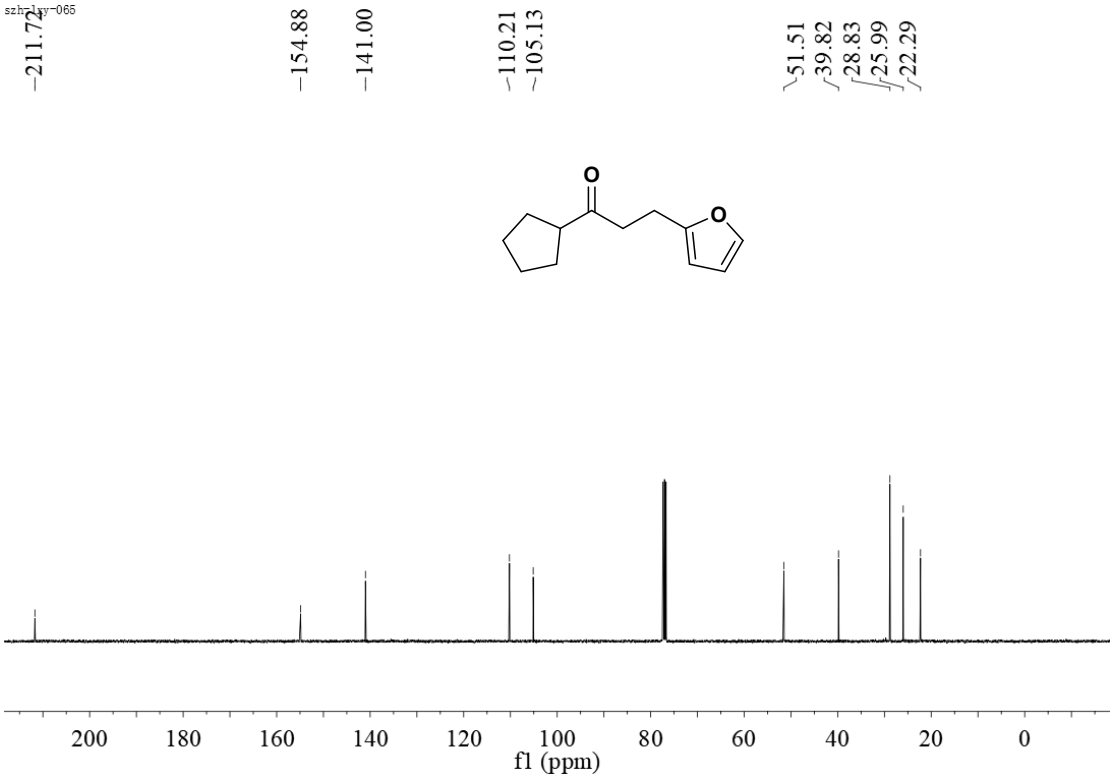
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7f**



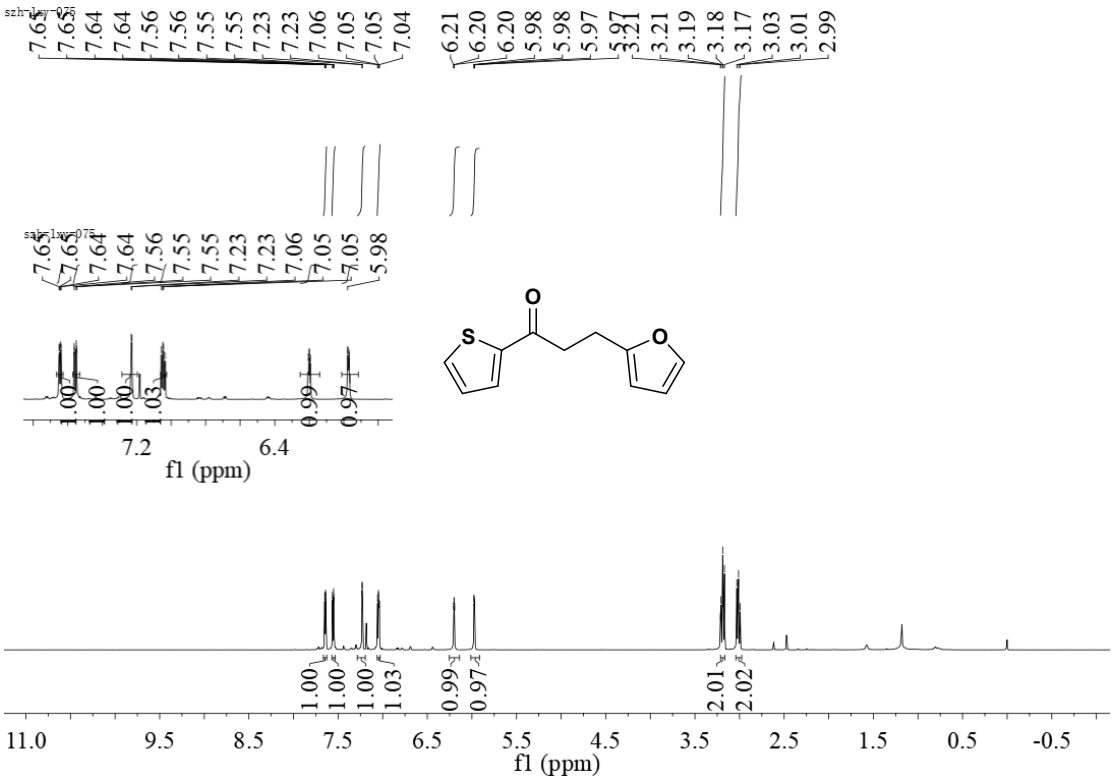
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **7f**



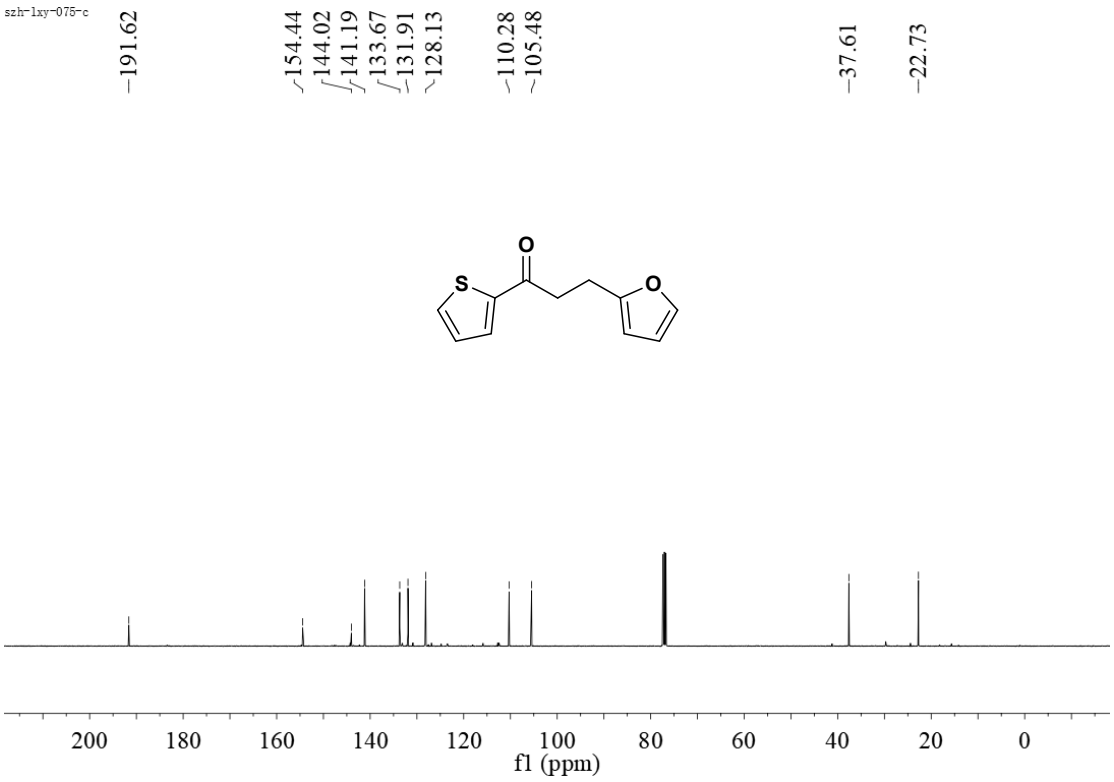
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7g**



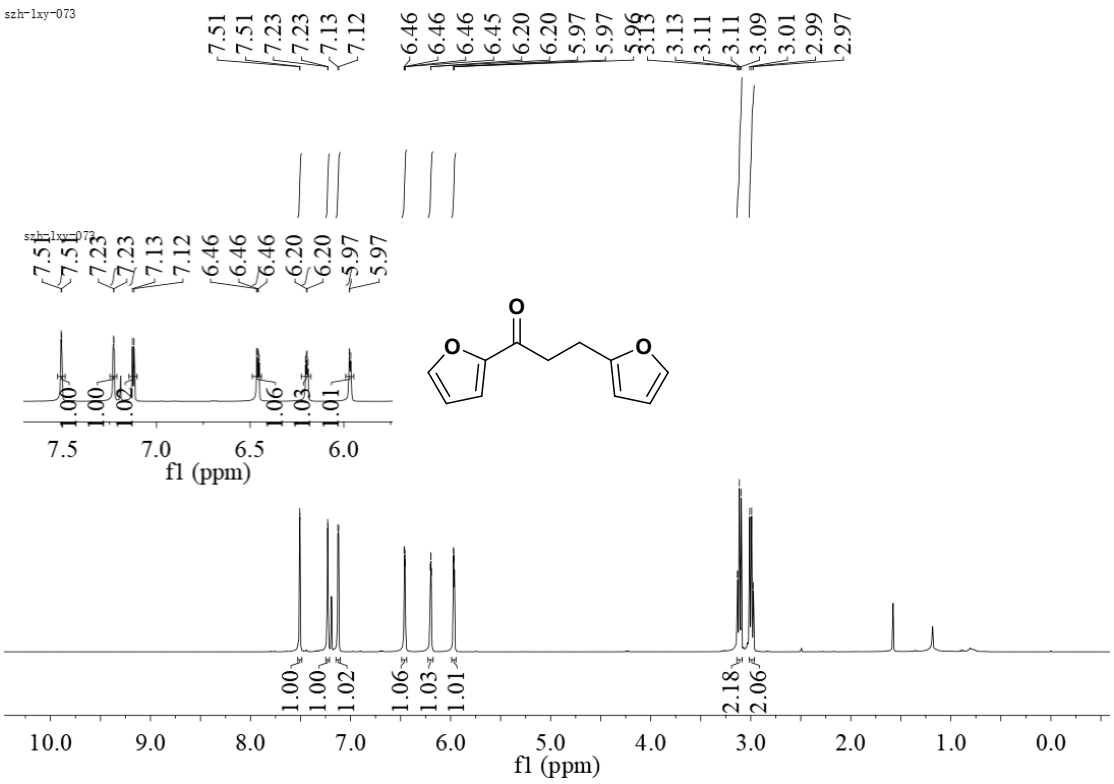
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **7g**



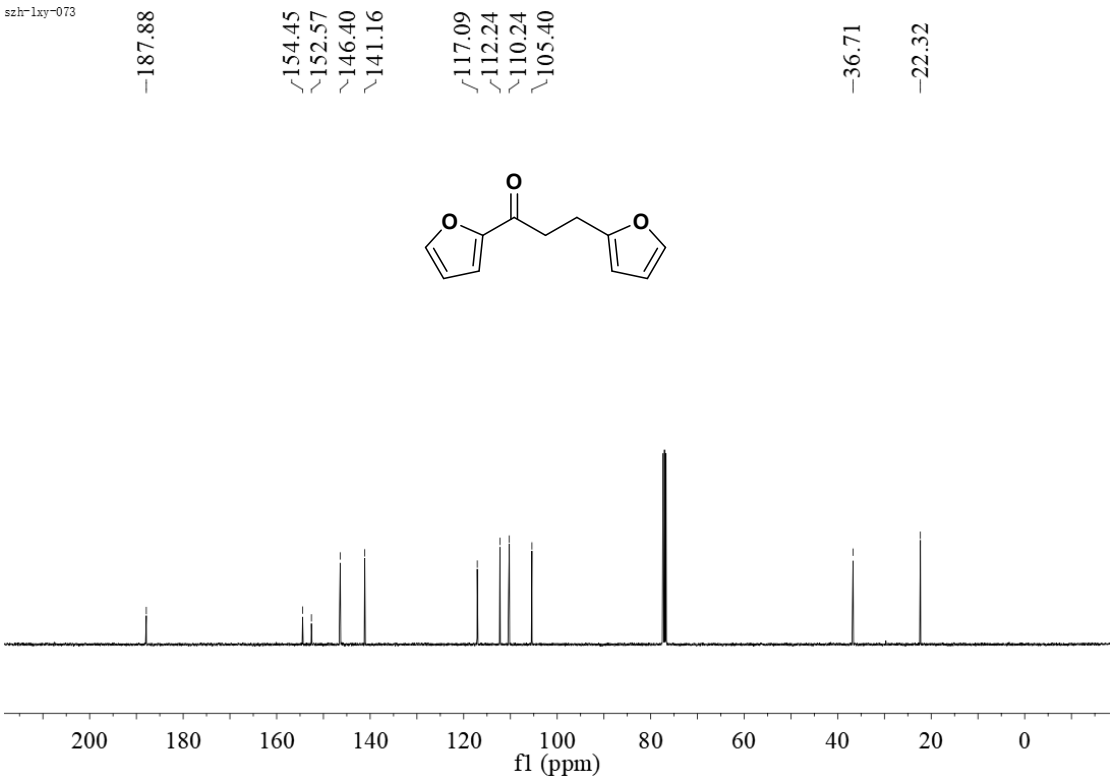
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7h**



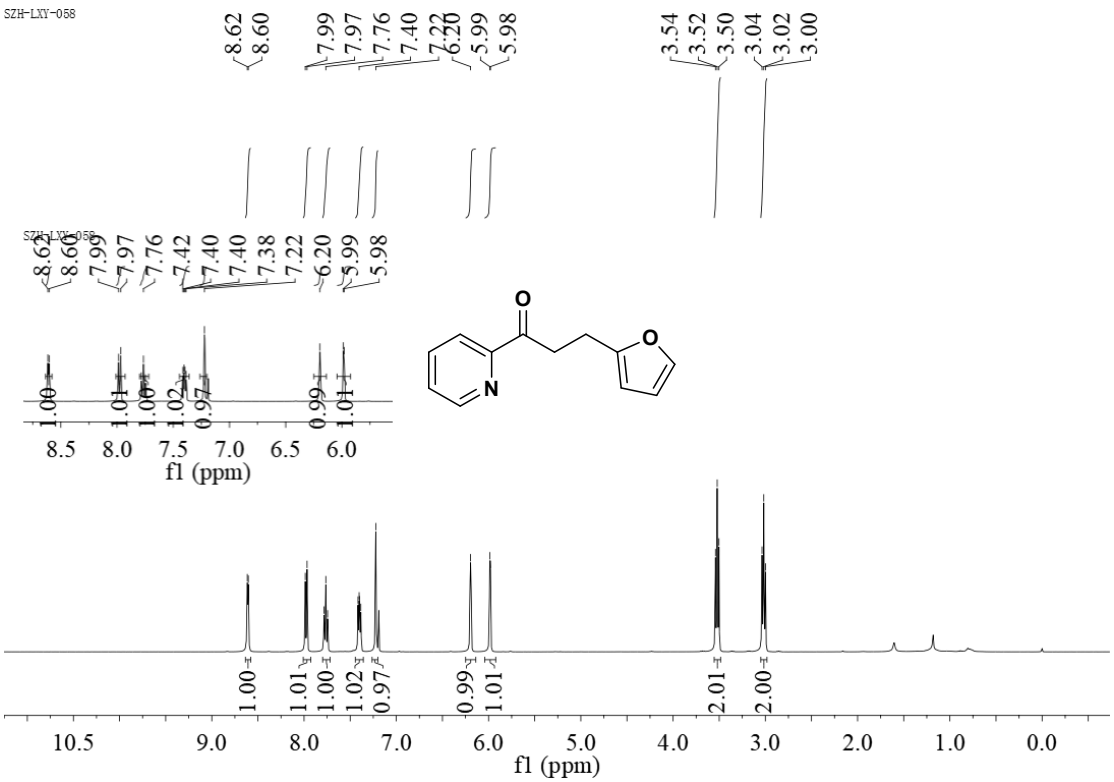
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **7h**



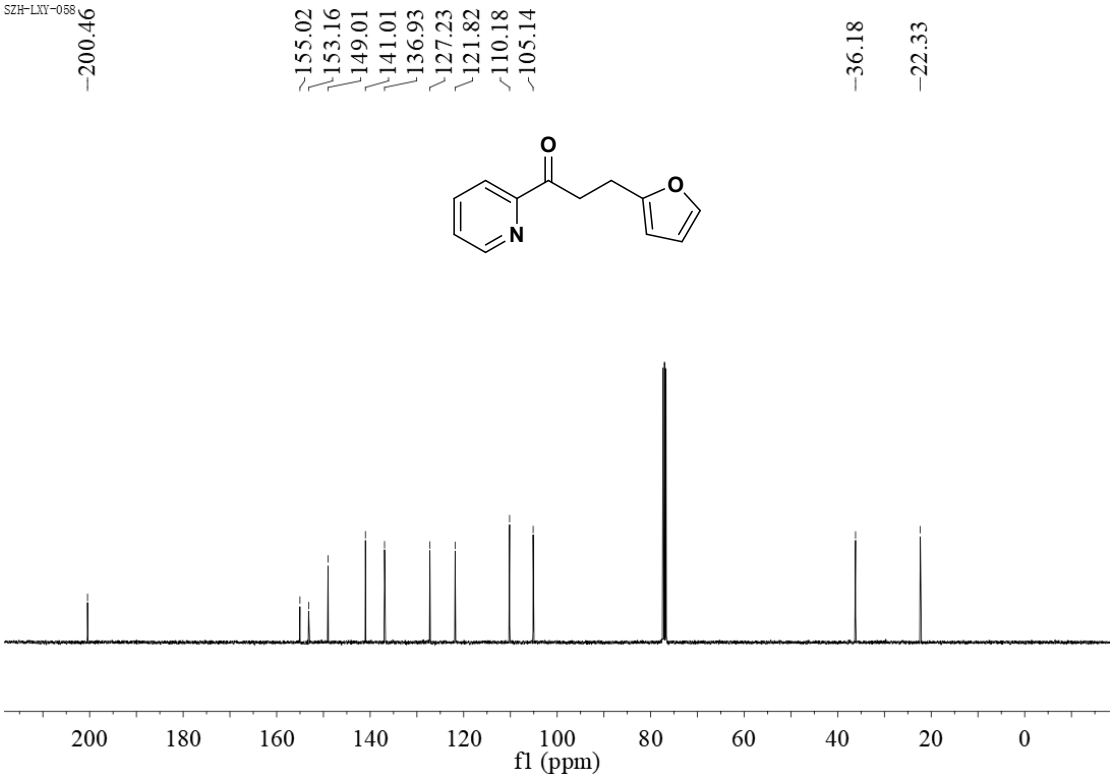
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7i**



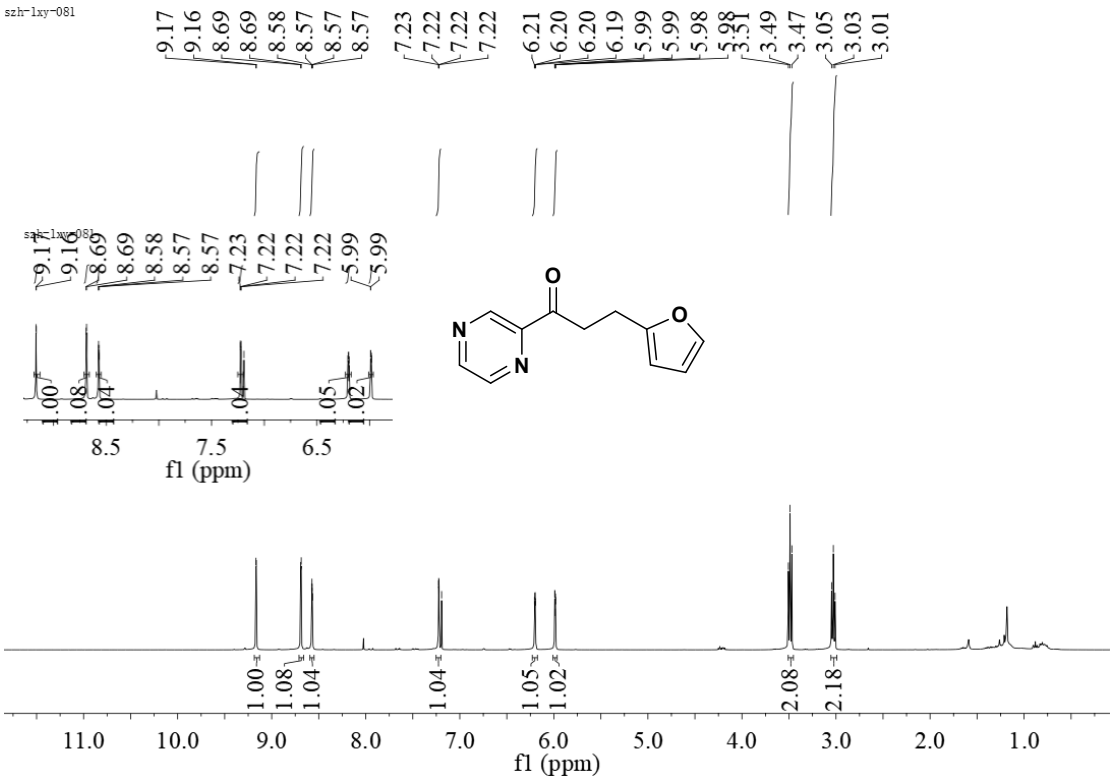
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **7i**



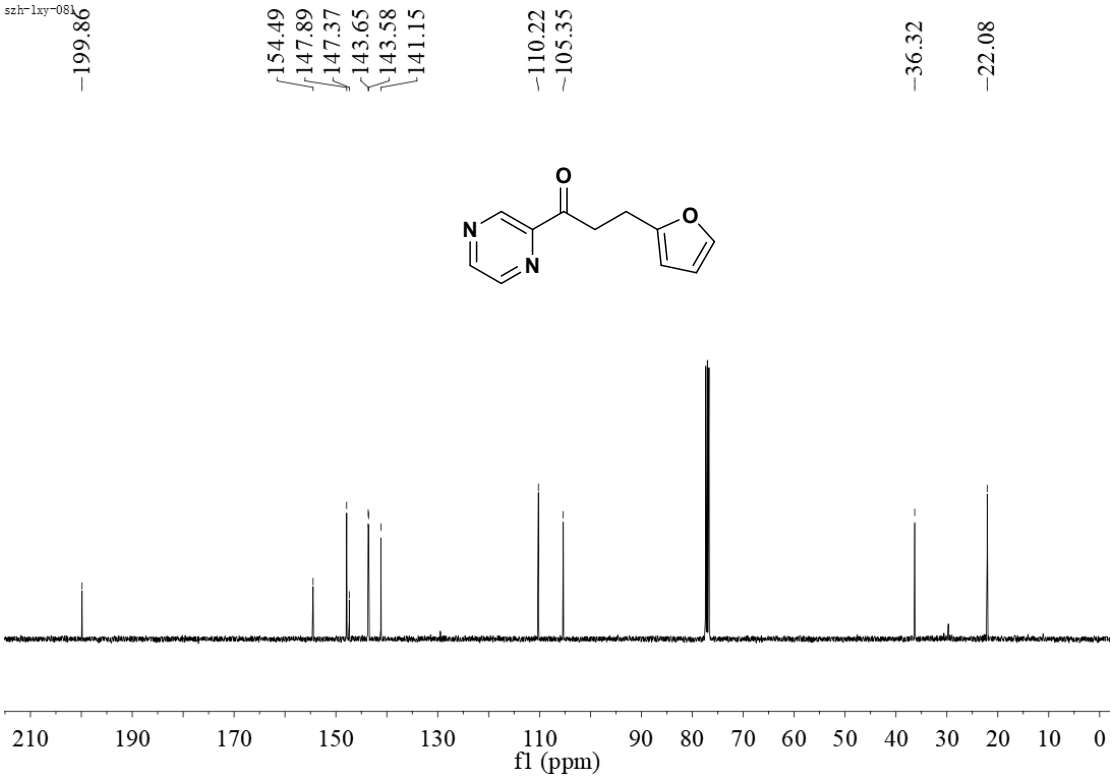
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7j**



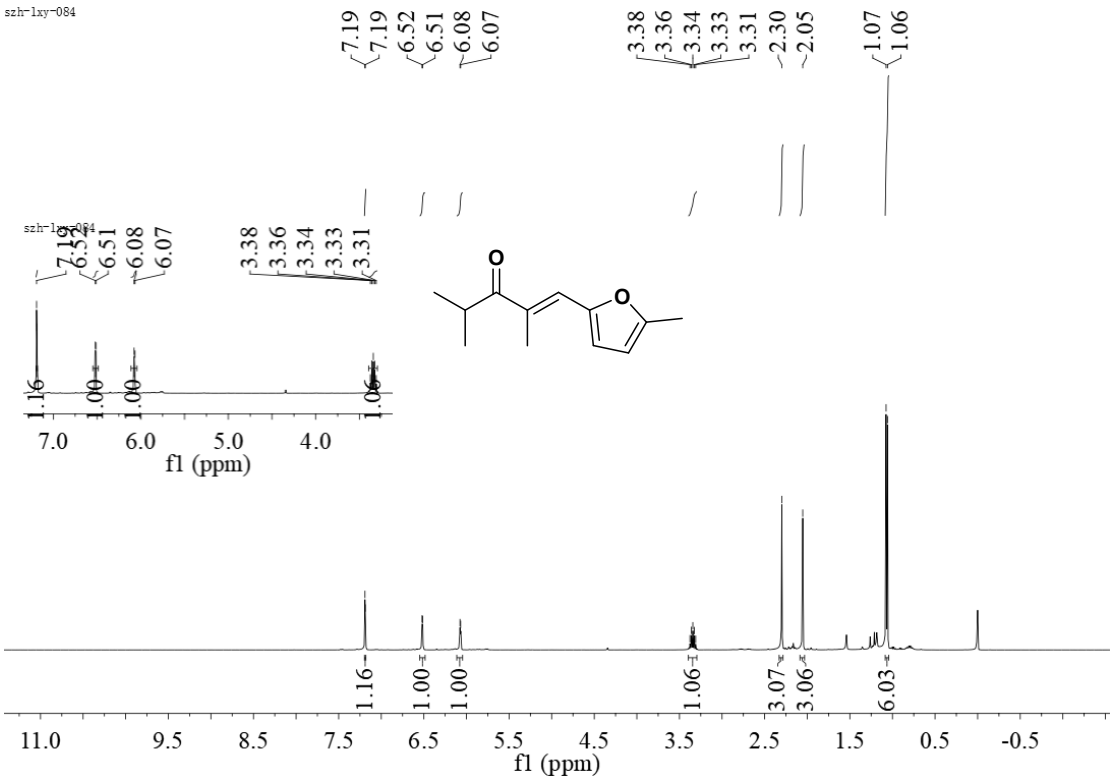
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **7j**



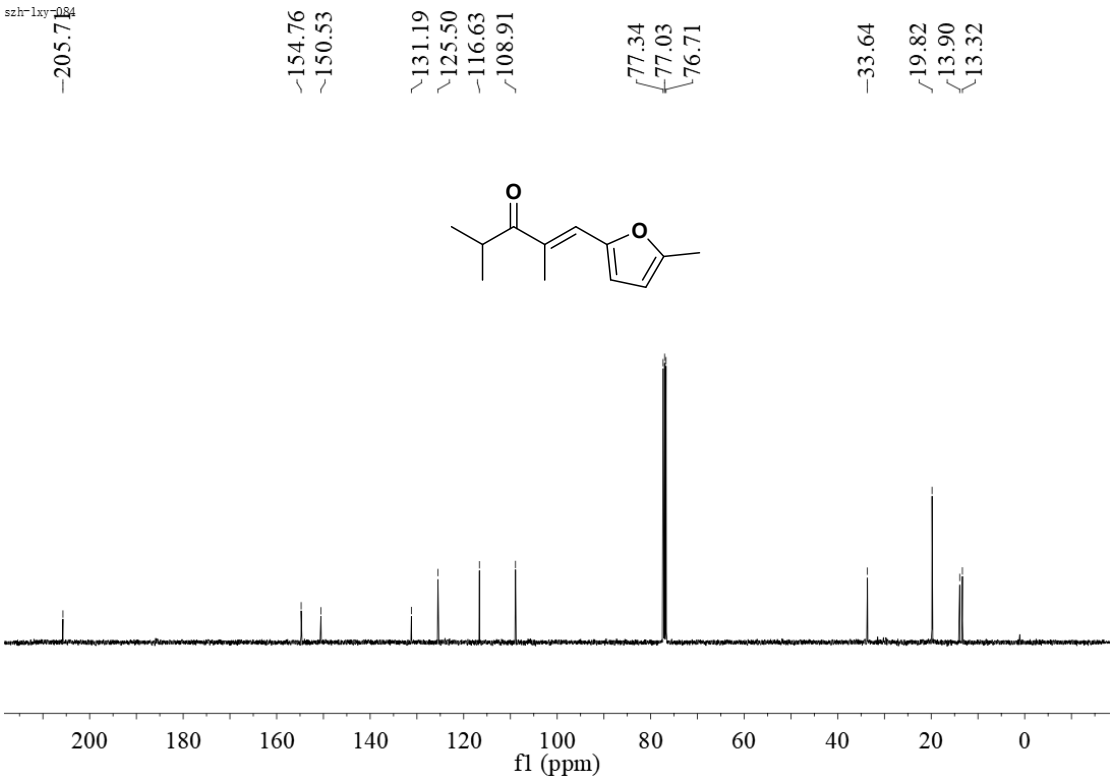
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7k**



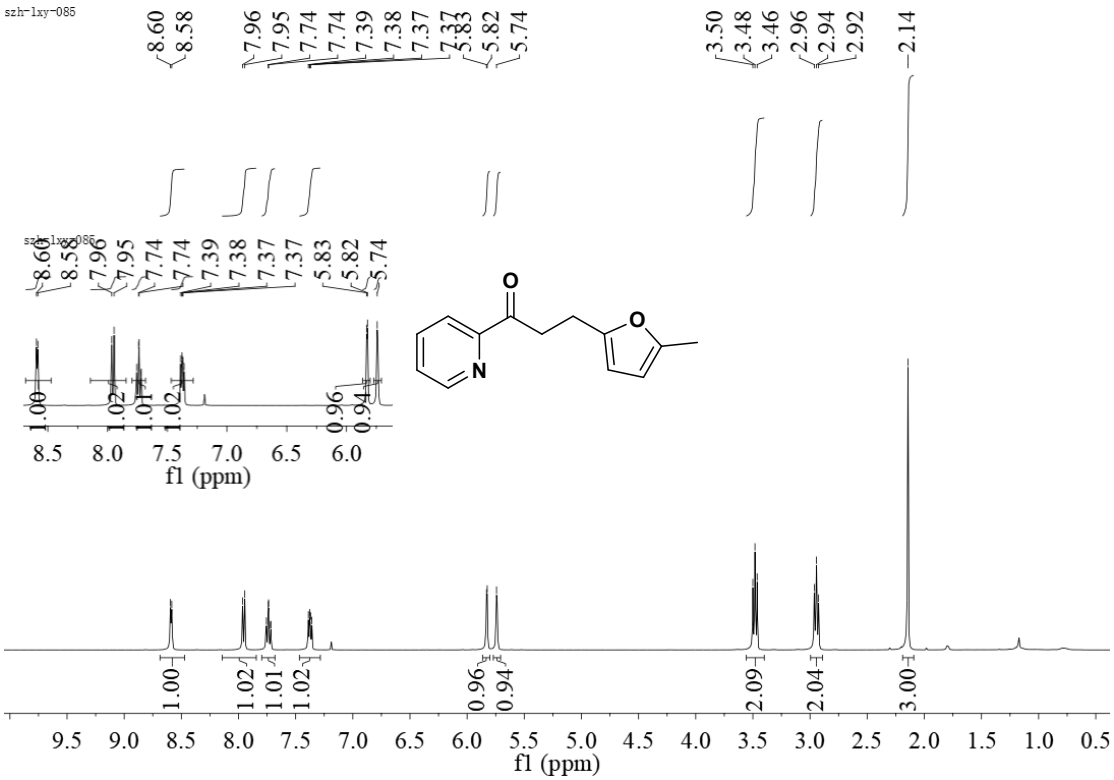
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **7k**



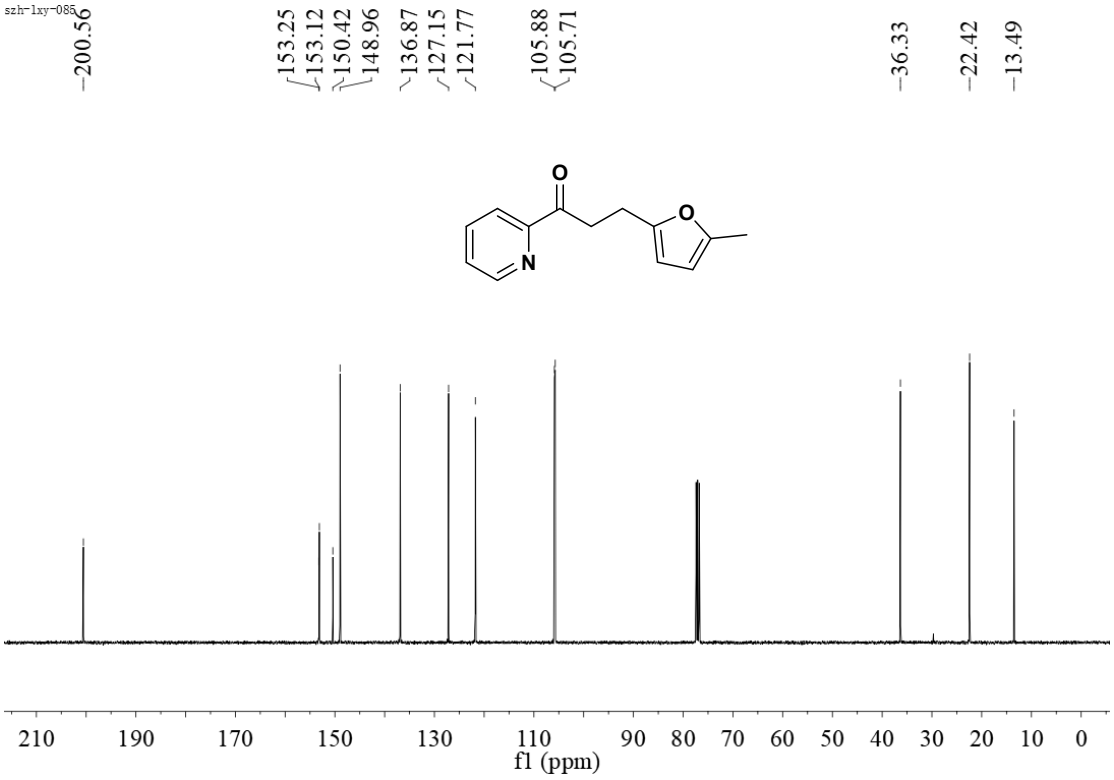
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **8a**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **8a**



^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **8c**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **8c**