Supporting Information

$BF_3 \cdot Et_2O$-mediated annulation of α-keto acids with aliphatic ketones for the synthesis of γ-hydroxy-butenolides and γ- alkylidene-butenolides

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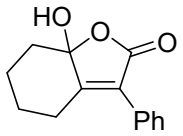
List

1. General Information

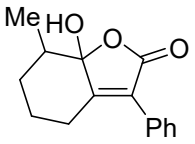
All melting points were determined on a Yanaco melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Nicolet FT-IR 5DX spectrometer. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded in $CDCl_3$. TMS was used as an internal reference and *J* values are given in Hz. HR-MS were obtained on a Bruker microTOF-Q II spectrometer. PE is petroleum ether (60–90 ^{o}C). All α-keto acids[1] and ketones are known compounds, which were purchased directly or were prepared according to the reported procedures.

2. Preparation and characterizations of compounds 3aa-p and 4aa-i

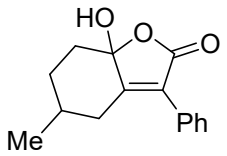


Synthesis of 7a-hydroxy-3-phenyl-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3aa). To a stirred mixture of 2-oxo-2-phenylacetic acid (**1a**, 75 mg, 0.5 mmol) and cyclohexanone (**2a**, 98 mg, 1 mmol) in toluene (2 mL) was added $BF_3{\cdot}Et_2O$ (0.2 equiv., 14 mg) at room temperature. After the reaction system was heated at 40 ^{o}C for 1 h, it was cooled down to room temperature again and was quenched by adding H_2O (15 mL). The resultant mixture was then extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine (2 × 15 mL) and dried over $MgSO_4$. The solvent was removed by vacuum and the residue was purified by flash chromatography (silica gel, 25% EtOAc in PE) to give 99 mg (86%) of the desired product **3aa** as colorless solid, mp 102–104 ^{o}C. IR (KBr) *v* 3414, 1730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.35 (m, 5H), 4.31 (brs, 1H), 2.96 (d, *J* = 13.4 Hz, 1H), 2.53-2.45 (m, 2H), 2.00-1.97 (m, 1H), 1.81-1.78 (m, 2H), 1.62-1.57 (m, 1H), 1.36-1.28 (m, 1H);^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.9, 162.2, 129.2, 128.9, 128.6, 128.5, 124.4, 103.2, 38.3, 26.9, 25.6, 22.0; HRMS *m/z* (ESI) calcd for $C_{14}H_{14}O_3$, $(M+H)^+$ 231.1016; found 231.1014.

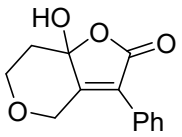
The products **3ab-p** were prepared following the similar procedure above.



7a-hydroxy-7-methyl-3-phenyl-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3ab). 87 mg (71%), white solid, mp 144–146 °C. IR (KBr) *v* 3362, 1748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.35 (m, 5H), 3.64 (s, 1H), 2.98-2.93 (m, 1H), 2.46 (td, *J* = 13.5, 5.7 Hz, 1H), 1.98-1.95 (m, 1H), 1.80-1.74 (m, 1H), 1.70-1.67 (m, 1H), 1.56 (ddd, *J* = 26.1, 13.1, 3.6 Hz, 1H), 1.43-1.32(m, 1H), 1.18 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 162.8, 129.3, 128.9, 128.6, 128.4, 124.2, 104.4, 42.7, 30.2, 26.4, 25.3, 13.8. HRMS *m/z* (ESI) calcd for $C_{15}H_{16}O_3$, $(M+H)^+$ 245.1172; found 245.1170.

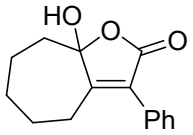


3-Phenyl-6-methyl-7a-hydroxy-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3ac). 104 mg (85%), yellow solid, mp 108–110 °C. IR (KBr) *v* 3364, 1746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 5H), 4.87 (brs, 1H), 2.93-2.89 (m, 1H), 2.58-2.50 (m, 1H), 2.41-2.38 (m, 1H), 2.07-1.98 (m, 1H), 1.93-1.89 (m, 1H), 1.27-1.20 (m, 1H), 1.05-0.98 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 162.2, 129.2, 128.9, 128.5, 128.4, 124.2, 103.6, 45.7, 35.1, 28.8, 25.0, 20.9; HRMS *m/z* (ESI) calcd for $C_{15}H_{16}O_3$, $(M+H)^+$ 245.1172; found 245.1172.

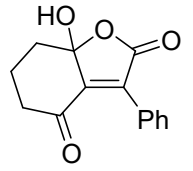


3-Phenyl-7a-hydroxy-7,7a-dihydro-4*H*-furo[3,2-c]pyran-2(6*H*)-one (3ad). 70 mg (60%), colorless oil. IR (KBr) *v* 3421, 1765 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 5H), 4.75 (d, *J* = 13.2 Hz, 1H), 4.41-4.38 (m, 2H), 3.98 (dd, *J* = 11.7, 5.0 Hz, 1H), 3.86-3.80 (m, 1H), 2.37 (d, *J* = 13.4 Hz, 1H), 2.08-2.00 (m, 1H); ^{13}C

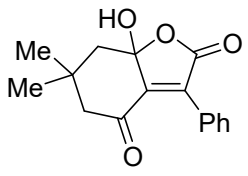
NMR (100 MHz, $CDCl_3$) δ 170.3, 154.8, 129.5, 128.9, 128.7, 128.1, 126.1, 100.9, 64.6, 62.7, 40.0; HRMS *m/z* (ESI) calcd for $C_{13}H_{12}O_4$, $(M+H)^+$ 233.0808; found 233.0808.



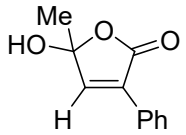
3-Phenyl-8a-hydroxy-4,5,6,7,8,8a-hexahydro-2*H*-cyclohepta[b]furan-2-one (3ae). 96 mg (79%), white solid, mp 84–86 °C. IR (KBr) *v* 3306, 1744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.34 (m, 5H), 4.55 (brs, 1H), 2.82-2.64 (m, 2H), 2.34 (ddd, *J* = 14.2, 6.1, 2.7 Hz, 1H), 1.96-1.55 (m, 6H), 1.45-1.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 164.2, 129.6, 128.9, 128.5, 128.3, 127.1, 107.7, 38.0, 28.5, 26.6, 25.6, 23.5. HRMS *m/z* (ESI) calcd for $C_{15}H_{16}O_3$, $(M+H)^+$ 245.1172; found 245.1171.



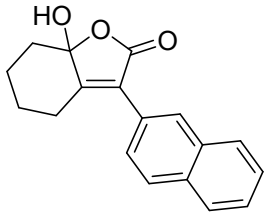
3-Phenyl-7a-hydroxy-5,6,7,7a-tetrahydrobenzofuran-2,4-dione (3af). 71 mg (58%), white solid, mp 172–174 °C. IR (KBr) *v* 3341, 1764, 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87-7.79 (m, 2H), 7.47-7.34 (m, 3H), 4.09 (s, 1H), 2.78-2.68 (m, 1H), 2.68-2.59 (m, 1H), 2.43-2.34 (m, 1H), 2.20-2.01 (m, 2H), 2.00-1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 169.0, 151.3, 130.9, 130.3, 130.2, 128.2, 127.3, 105.4, 42.8, 36.0, 19.6. HRMS *m/z* (ESI) calcd for $C_{14}H_{12}O_4$, $(M+H)^+$ 245.0808; found 245.0808.



3-Phenyl-6,6-dimethyl-7a-hydroxy-5,6,7,7a-tetrahydrobenzofuran-2,4-dione (3ag). 76 mg (56%), white solid, mp 138–140 °C. IR (KBr) *v* 3326, 1763, 1711 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.45-7.36 (m, 3H), 4.18 (s, 1H), 2.60 (dd, *J* = 14.9, 1.7 Hz, 1H), 2.46 (dd, *J* = 14.2, 1.7 Hz, 1H), 2.35 (d, *J* = 14.9 Hz, 1H), 2.01 (d, *J* = 14.2 Hz, 1H), 1.22 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 169.0, 150.7, 131.0, 130.2, 130.1, 128.2, 127.4, 105.4, 56.4, 48.1, 32.8, 32.1, 28.3. HRMS *m/z* (ESI) calcd for $C_{16}H_{16}O_4$, $(M + H)^+$ 273.1121; found 273.1121.

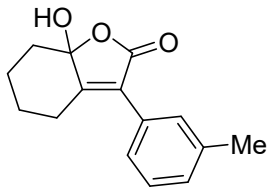


3-Phenyl-4-methyl-5-hydroxyfuran-2(5*H*)-one (3ah). 56 mg (59%), white solid, mp 91–93 °C. IR (KBr) *v* 3362, 2953, 1731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.40-7.33 (m, 3H), 7.30 (s, 1H), 4.41 (s, 1H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 146.4, 132.5, 129.8, 128.6 (2C), 127.4, 103.7, 24.7. HRMS *m/z* (ESI) calcd for $C_{11}H_{10}O_3$, $(M + H)^+$ 191.0703; found 191.0704.

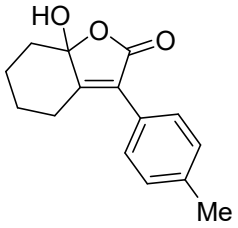


3-(Naphthalen-2-yl)-7a-hydroxy-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3ai). 119 mg (85%), white solid, mp 135–137 °C. IR (KBr) *v* 3399, 1750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.78-7.73 (m, 3H), 7.49-7.41 (m, 3H), 4.70 (s, 1H), 2.98 (d, *J* = 13.7 Hz, 1H), 2.60-2.44 (m, 2H), 2.00-1.89 (m, 1H), 1.82-1.75 (m, 2H), 1.63-1.55 (m, 1H), 1.37-1.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 162.7, 133.0, 132.9, 128.6, 128.2, 128.0, 127.6, 126.6 (2C), 126.2, 126.1, 124.3, 103.5,

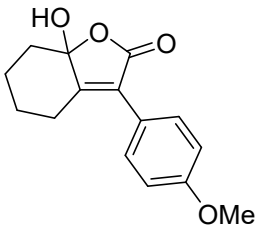
38.2, 26.9, 25.8, 22.0; HRMS *m/z* (ESI) calcd for $C_{18}H_{16}O_3$, $(M+H)^+$ 281.1172; found 281.1170.



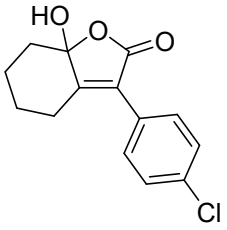
3-(3-Methylphenyl)-7a-hydroxy-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3aj). 96 mg (79%), white solid, mp 104–106 °C. IR (KBr) *v* 3402, 1743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 7.20-7.16 (m, 2H), 4.44 (s, 1H), 2.94 (d, J = 13.6 Hz, 1H), 2.52-2.45 (m, 2H), 2.35 (s, 3H), 1.99-1.96 (m, 1H), 1.79-1.77 (m, 2H), 1.60-1.55 (m, 1H), 1.33-1.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 162.1, 138.1, 129.5, 129.4, 129.1, 128.3, 126.0, 124.4, 103.3, 38.3, 26.9, 25.6, 22.0, 21.4; HRMS *m/z* (ESI) calcd for $C_{15}H_{16}O_3$, $(M+H)^+$ 245.1172; found 245.1171.



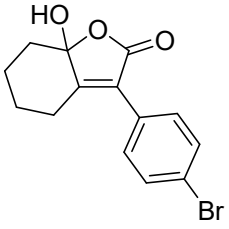
3-(4-Methylphenyl)-7a-hydroxy-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3ak). 102 mg (84%), white solid, mp 131–133 °C. IR (KBr) *v* 3386, 1754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 4.23 (brs, 1H), 2.95 (d, J = 13.7 Hz, 1H), 2.52-2.45 (m, 2H), 2.37 (s, 3H) 1.99-1.96 (m, 1H), 1.81-1.77 (m, 2H), 1.61-1.56 (m, 1H), 1.35-1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 161.5, 138.6, 129.1, 128.8, 126.3, 124.3, 103.2, 38.2, 26.9, 25.6, 22.1, 21.3. HRMS *m/z* (ESI) calcd for $C_{15}H_{16}O_3$, $(M+H)^+$ 245.1172; found 245.1172.



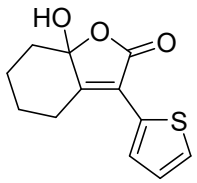
3-(4-Methoxyphenyl)-7a-hydroxy-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3al). 73 mg (56%), white solid, mp 98–100 °C. IR (KBr) *v* 3419, 1746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.25 (s, 1H), 3.82 (s, 3H), 2.94 (d, J = 13.6 Hz, 1H), 2.52-2.45 (m, 2H), 1.99-1.96 (m, 1H), 1.79-1.78 (m, 2H), 1.62-1.56 (m, 1H), 1.34-1.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 160.6, 159.7, 130.3, 123.9, 121.6, 113.9, 103.2, 55.3, 38.2, 26.8, 25.6, 22.1; HRMS *m/z* (ESI) calcd for $C_{15}H_{16}O_4$, $(M+H)^+$ 261.1121; found 261.1123.



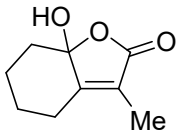
3-(4-Chlorophenyl)-7a-hydroxy-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3am). 100 mg (76%), white solid, mp 156–158 °C. IR (KBr) *v* 3375, 1752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 4H), 4.19 (brs, 1H), 2.91 (d, J = 13.3 Hz, 1H), 2.55-2.46 (m, 2H), 2.03-1.99 (m, 1H), 1.82-1.80 (m, 2H), 1.65-1.57 (m, 1H), 1.38-1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 162.7, 134.8, 130.2, 128.7, 127.5, 123.4, 103.4, 38.2, 26.9, 25.7, 22.0; HRMS *m/z* (ESI) calcd for $C_{14}H_{13}ClO_3$, $(M+H)^+$ 265.0626; found 265.0624.



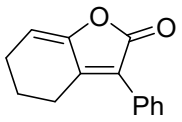
3-(4-Bromophenyl)-7a-hydroxy-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3an). 123 mg (80%), white solid, mp 168–170 °C. IR (KBr) *v* 3263, 1725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.30-7.28 (m, 2H), 3.95 (s, 1H), 2.94-2.90 (m, 1H), 2.55-2.46 (m, 2H), 2.04-1.99 (m, 1H), 1.84-1.80 (m, 2H), 1.66-1.58 (m, 1H), 1.38-1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 162.6, 131.7, 130.5, 128.0, 123.5, 123.1, 103.3, 38.3, 26.9, 25.7, 22.0; HRMS *m/z* (ESI) calcd for $C_{14}H_{13}BrO_3$, $(M+H)^+$ 309.0121; found 309.0121.



3-(Thiophen-2-yl)-7a-hydroxy-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3ao). 85 mg (72%), white solid, mp 70–72 °C. IR (KBr) *v* 3378, 2944, 1731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 3.7 Hz, 1H), 7.39 (d, J = 5.1 Hz, 1H), 7.09-7.07 (m, 1H), 3.92 (brs, 1H), 3.28-3.23 (m, 1H), 2.58-2.45 (m, 2H), 2.07-2.02 (m, 1H), 1.85-1.79 (m, 2H), 1.63-1.55 (m, 1H), 1.43-1.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 158.5, 130.7, 128.5, 127.3, 126.9, 118.2, 103.3, 38.3, 26.7, 26.2, 22.0; HRMS *m/z* (ESI) calcd for $C_{12}H_{12}SO_3$, $(M+H)^+$ 237.0580; found 237.0586.

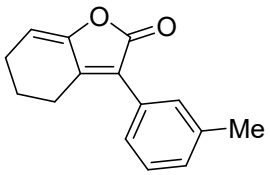


3-Methyl-7a-hydroxy-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3ap). 60 mg (71%), white solid, mp 115–117 °C (lit.[2] 126–128 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 4.71 (brs, 1H), 2.69 (d, J = 13.4 Hz, 1H), 2.45-2.30 (m, 2H), 2.04-2.00 (m, 1H), 1.78-1.73 (m, 5H), 1.53-1.45 (m, 1H), 1.32-1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 161.4, 120.8, 103.9, 38.0, 26.6, 25.0, 22.2, 8.0.

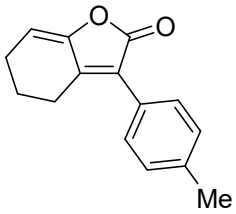


Synthesis of 3-phenyl-5,6-dihydrobenzofuran-2(4*H*)-one (4aa). To a stirred mixture of 2-oxo-2-phenylacetic acid (**1a**, 75 mg, 0.5 mmol) and cyclohexanone (**2a**, 98 mg, 1 mmol) in toluene (2 mL) was added $BF_3 \cdot Et_2O$ (36 mg, 0.25 mmol) at room temperature. After the reaction system was heated at 70 °C for 4 h, it was cooled down to room temperature again and was quenched by adding H_2O (15 mL). The resultant mixture was then extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine (2 × 15 mL) and dried over $MgSO_4$. The solvent was removed by vacuum and the residue was purified by flash chromatography (silica gel, 10% EtOAc in PE) to give 87 mg (82%) of the desired product **4a** as white solid, mp 102–104 °C (lit.[3] yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.61 (m, 2H), 7.45-7.41 (m, 2H), 7.39-7.32 (m, 1H), 5.93 (t, J = 4.7 Hz, 1H), 2.91 (t, J = 6.5 Hz, 2H), 2.44 (dd, J = 10.9, 5.8 Hz, 2H), 1.92-1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 149.2, 147.7, 130.0, 128.5, 128.4 (2C), 121.5, 110.8, 24.3, 23.6, 22.7.

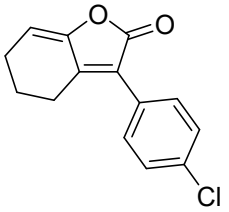
The products **4ab-i** were prepared by the similar procedure.



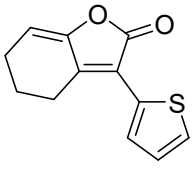
3-(3-Methylphenyl)-5,6-dihydrobenzofuran-2(4*H*)-one (4ab). 86 mg (76%), white solid, mp 80–82 °C. IR (KBr) ν 3341, 1765 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.4 Hz, 1H), 5.92 (t, J = 4.7 Hz, 1H), 2.90 (t, J = 6.5 Hz, 2H), 2.44 (dd, J = 10.7, 5.9 Hz, 2H), 2.39 (s, 3H), 1.92–1.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 149.3, 147.6, 138.2, 129.9, 129.3, 129.0, 128.4, 125.5, 121.7, 110.6, 24.3, 23.6, 22.7, 21.5. HRMS *m/z* (ESI) calcd for $C_{15}H_{14}O_2$, $(M+H)^+$ 227.1067; found 227.1067.



3-(4-Methylphenyl)-5,6-dihydrobenzofuran-2(4*H*)-one (4ac). 91 mg (80%), white solid, mp 96–98 °C. IR (KBr) *v* 3264, 1778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.90 (t, *J* = 4.7 Hz, 1H), 2.89 (t, *J* = 6.5 Hz, 2H), 2.43 (dd, *J* = 10.9, 5.7 Hz, 2H), 2.38 (s, 3H), 1.92-1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 149.3, 146.9, 138.5, 129.2, 128.3, 127.1, 121.5, 110.3, 24.3, 23.6, 22.7, 21.3. HRMS *m/z* (ESI) calcd for $C_{15}H_{14}O_2$, $(M+H)^+$ 227.1067; found 227.1065.

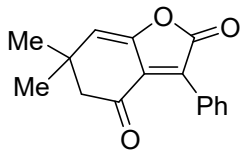


3-(4-Chlorophenyl)-5,6-dihydrobenzofuran-2(4*H*)-one (4ad). 90 mg (73%), white solid, mp 174–176 °C IR (KBr) *v* 3410, 1756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 2H), 7.42-7.39 (m, 2H), 5.97 (t, *J* = 4.7 Hz, 1H), 2.89 (t, *J* = 6.5 Hz, 2H), 2.46 (dd, *J* = 10.8, 5.8 Hz, 2H), 1.94-1.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 149.1, 147.9, 134.5, 129.7, 128.8, 128.5, 120.5, 111.4, 24.3, 23.6, 22.6. HRMS *m/z* (ESI) calcd for $C_{14}H_{11}ClO_2$, $(M+H)^+$ 247.0520; found 247.0520.

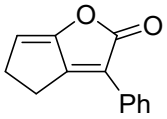


3-(Thiophen-2-yl)-5,6-dihydrobenzofuran-2(4*H*)-one (4ae).[5] 67 mg (61%), yellow solid, mp 56–58 °C. IR (KBr) *v* 3341, 1769 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 3.5 Hz, 1H), 7.44 (dd, *J* = 5.0, 0.7 Hz, 1H), 7.15-7.13(m, 1H), 5.93 (t, *J*

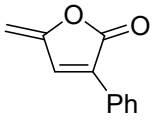
= 4.7 Hz, 1H), 2.95 (t, *J* = 6.6 Hz, 2H), 2.45 (dd, *J* = 10.9, 5.9 Hz, 2H), 1.99-1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 149.3, 143.6, 132.2, 127.7, 127.6, 127.2, 116.5, 110.9, 24.2, 23.4, 22.3.



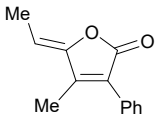
3-Phenyl-6,6-dimethyl-5,6-dihydrobenzofuran-2,4-dione (4af). 71 mg (56%), brown solid, mp 108–110 °C. IR (KBr) *v* 3491, 2965, 1762, 1699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.02 (m, 2H), 7.46-7.44 (m, 3H), 6.04 (s, 1H), 2.70 (s, 2H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 168.1, 148.2, 135.4, 131.0, 130.3, 128.2, 127.9, 127.7, 120.9, 56.3, 36.5, 30.3. HRMS *m/z* (ESI) calcd for $C_{16}H_{14}O_3$, $(M+H)^+$ 255.1016; found 255.1016.



3-Phenyl-4,5-dihydro-2*H*-cyclopenta[b]furan-2-one (4ag). 48 mg (48%), brown solid, mp 100–102 °C (lit.[4] 103 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.87 (m, 2H), 7.44-7.41 (m, 2H), 7.34-7.26 (m, 1H), 5.84 (t, *J* = 3.0 Hz, 1H), 3.09-3.07 (m, 2H), 2.99-2.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 161.6, 153.9, 130.5, 128.7, 128.1, 127.0, 116.3, 112.4, 33.5, 25.4.



3-Phenyl-5-methylene-furan-2(5*H*)-one (4ah). 39 mg (45%), white solid, mp 68–70 °C; IR (KBr) *v* 3324, 1763 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.89 (m, 2H), 7.51 (s, 1H), 7.45-7.39 (m, 3H), 5.23 (d, *J* = 2.5 Hz, 1H), 4.94 (d, *J* = 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 153.4, 134.3, 131.9, 129.9, 128.9, 128.7, 127.2, 97.4. HRMS *m/z* (ESI) calcd for $C_{11}H_8O_2$, $(M+H)^+$ 173.0597; found 173.0597.



(*Z*)-5-ethylidene-4-methyl-3-phenylfuran-2(5H)-one (4ai).[5] 39 mg (39%), colorless oil; IR (KBr) *v* 3324, 1763 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.46-7.42 (m, 2H), 7.39-7.35 (m, 1H), 5.45 (q, J = 7.4 Hz, 1H), 2.23 (s, 3H), 2.00 (d, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 150.6, 146.6, 129.9, 129.0, 128.5, 128.4, 126.3, 107.7, 11.8, 10.8. HRMS *m/z* (ESI) calcd for $C_{13}H_{12}O_2$, $(M+H)^+$ 201.0910; found 201.0910.

3. X-ray crystallographic data of 3af

Sample preparation: Single crystals of **3af** for X-ray diffraction experiment was obtained by slow evaporation of DCM/n-hexane (1:10, v/v) solution containing **3af**. CCDC 2182801 contain the supplementary crystallographic data for this paper, these data can be obtained free of charge from the Cambridge Crystallographic Data Center.

Figure S1. ORTEP Structure of 3af (CCDC 2182801)

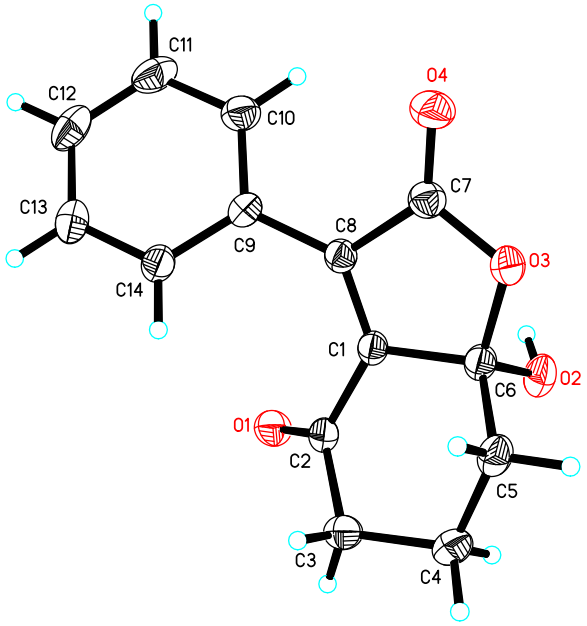


Table 1. Crystal data and structure refinement for 3af (CCDC 2182801).

Identification code	cd16656

Empirical formula	C14 H12 O4
Formula weight	244.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 9.9657(16) Å α= 90°. b = 14.300(2) Å β= 114.989(3)°. c = 9.0367(14) Å γ = 90°.
Volume	1167.3(3) $Å^3$
Z	4
Density (calculated)	1.390 Mg/m^3
Absorption coefficient	0.102 mm^{-1}
F(000)	512
Crystal size	0.200 x 0.170 x 0.120 mm^3
Theta range for data collection	2.255 to 25.498°.
Index ranges	-12<=h<=10, -17<=k<=13, -9<=l<=10
Reflections collected	6549
Independent reflections	2170 [R(int) = 0.0336]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6282
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2170 / 0 / 164
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0481, wR2 = 0.1217
R indices (all data)	R1 = 0.0625, wR2 = 0.1302
Extinction coefficient	n/a
Largest diff. peak and hole	0.704 and -0.152 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 3af (CCDC 2182801). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5548(2)	-567(1)	3083(2)	49(1)
O(2)	2246(2)	593(1)	3662(2)	49(1)
O(3)	3099(2)	2089(1)	3663(2)	47(1)
O(4)	5011(2)	2986(1)	5217(2)	57(1)
C(1)	4439(2)	879(1)	3231(2)	34(1)
C(2)	4575(2)	6(2)	2417(2)	38(1)
C(3)	3441(2)	-90(2)	686(3)	49(1)
C(4)	1898(2)	235(2)	406(3)	51(1)
C(5)	1897(2)	1198(2)	1118(2)	45(1)
C(6)	2892(2)	1174(1)	2918(2)	38(1)
C(7)	4565(2)	2286(2)	4439(2)	41(1)
C(8)	5429(2)	1512(1)	4131(2)	35(1)
C(9)	7045(2)	1537(1)	4723(2)	36(1)
C(10)	7931(2)	1912(2)	6249(3)	49(1)
C(11)	9449(3)	1899(2)	6823(3)	59(1)
C(12)	10113(2)	1512(2)	5908(3)	59(1)
C(13)	9249(2)	1154(2)	4394(3)	51(1)
C(14)	7730(2)	1167(2)	3804(3)	42(1)

Table 3. Bond lengths [Å] and angles [°] for 3af (CCDC 2182801).

O(1)-C(2)	1.216(2)
O(2)-C(6)	1.386(2)
O(2)-H(2)	0.8200
O(3)-C(7)	1.357(2)
O(3)-C(6)	1.446(2)
O(4)-C(7)	1.197(2)
C(1)-C(8)	1.332(3)
C(1)-C(2)	1.485(3)
C(1)-C(6)	1.506(3)
C(2)-C(3)	1.500(3)
C(3)-C(4)	1.522(3)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.519(3)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.506(3)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(7)-C(8)	1.499(3)
C(8)-C(9)	1.467(3)
C(9)-C(14)	1.384(3)
C(9)-C(10)	1.393(3)
C(10)-C(11)	1.377(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.374(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.371(3)
C(12)-H(12)	0.9300
C(13)-C(14)	1.377(3)
C(13)-H(13)	0.9300
C(14)-H(14)	0.9300
C(6)-O(2)-H(2)	109.5
C(7)-O(3)-C(6)	109.79(15)
C(8)-C(1)-C(2)	132.40(18)

C(8)-C(1)-C(6)	111.10(17)
C(2)-C(1)-C(6)	116.33(16)
O(1)-C(2)-C(1)	122.78(18)
O(1)-C(2)-C(3)	123.14(19)
C(1)-C(2)-C(3)	114.04(17)
C(2)-C(3)-C(4)	114.14(18)
C(2)-C(3)-H(3A)	108.7
C(4)-C(3)-H(3A)	108.7
C(2)-C(3)-H(3B)	108.7
C(4)-C(3)-H(3B)	108.7
H(3A)-C(3)-H(3B)	107.6
C(5)-C(4)-C(3)	112.80(18)
C(5)-C(4)-H(4A)	109.0
C(3)-C(4)-H(4A)	109.0
C(5)-C(4)-H(4B)	109.0
C(3)-C(4)-H(4B)	109.0
H(4A)-C(4)-H(4B)	107.8
C(6)-C(5)-C(4)	108.65(18)
C(6)-C(5)-H(5A)	110.0
C(4)-C(5)-H(5A)	110.0
C(6)-C(5)-H(5B)	110.0
C(4)-C(5)-H(5B)	110.0
H(5A)-C(5)-H(5B)	108.3
O(2)-C(6)-O(3)	108.70(16)
O(2)-C(6)-C(1)	112.92(17)
O(3)-C(6)-C(1)	103.47(15)
O(2)-C(6)-C(5)	107.96(16)
O(3)-C(6)-C(5)	112.46(17)
C(1)-C(6)-C(5)	111.34(16)
O(4)-C(7)-O(3)	121.88(19)
O(4)-C(7)-C(8)	128.90(19)
O(3)-C(7)-C(8)	109.22(17)
C(1)-C(8)-C(9)	130.94(18)
C(1)-C(8)-C(7)	106.20(17)
C(9)-C(8)-C(7)	122.84(17)
C(14)-C(9)-C(10)	118.30(19)
C(14)-C(9)-C(8)	121.04(17)
C(10)-C(9)-C(8)	120.64(18)

C(11)-C(10)-C(9)	120.2(2)
C(11)-C(10)-H(10)	119.9
C(9)-C(10)-H(10)	119.9
C(12)-C(11)-C(10)	120.7(2)
C(12)-C(11)-H(11)	119.6
C(10)-C(11)-H(11)	119.6
C(13)-C(12)-C(11)	119.5(2)
C(13)-C(12)-H(12)	120.3
C(11)-C(12)-H(12)	120.3
C(12)-C(13)-C(14)	120.3(2)
C(12)-C(13)-H(13)	119.8
C(14)-C(13)-H(13)	119.8
C(13)-C(14)-C(9)	120.9(2)
C(13)-C(14)-H(14)	119.5
C(9)-C(14)-H(14)	119.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for 3af (CCDC 2182801).

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	44(1)	48(1)	50(1)	-5(1)	14(1)	10(1)
O(2)	37(1)	62(1)	51(1)	7(1)	23(1)	-1(1)
O(3)	36(1)	46(1)	55(1)	-7(1)	17(1)	7(1)
O(4)	57(1)	44(1)	64(1)	-13(1)	21(1)	1(1)
C(1)	29(1)	40(1)	33(1)	2(1)	14(1)	2(1)
C(2)	32(1)	41(1)	42(1)	-3(1)	18(1)	-1(1)
C(3)	43(1)	55(1)	44(1)	-11(1)	13(1)	2(1)
C(4)	38(1)	60(1)	43(1)	-6(1)	7(1)	0(1)
C(5)	32(1)	53(1)	45(1)	5(1)	12(1)	5(1)
C(6)	32(1)	38(1)	45(1)	-2(1)	16(1)	0(1)
C(7)	42(1)	39(1)	42(1)	-1(1)	16(1)	2(1)
C(8)	34(1)	40(1)	32(1)	1(1)	14(1)	1(1)

C(9)	32(1)	37(1)	36(1)	3(1)	12(1)	-2(1)
C(10)	44(1)	50(1)	46(1)	-7(1)	13(1)	-1(1)
C(11)	41(1)	59(2)	56(1)	-6(1)	1(1)	-7(1)
C(12)	31(1)	57(2)	78(2)	9(1)	12(1)	-2(1)
C(13)	40(1)	54(1)	65(2)	5(1)	27(1)	1(1)
C(14)	36(1)	49(1)	42(1)	1(1)	17(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 3af (CCDC 2182801).

	x	y	z	U(eq)
H(2)	2827	507	4616	73
H(3A)	3388	-742	365	59
H(3B)	3764	268	-16	59
H(4A)	1274	249	-758	61
H(4B)	1474	-212	896	61
H(5A)	2252	1660	583	54
H(5B)	899	1367	946	54
H(10)	7495	2173	6882	59
H(11)	10032	2154	7840	71
H(12)	11139	1494	6313	71
H(13)	9693	900	3763	61
H(14)	7156	924	2774	51

Table 6. Torsion angles [°] for 3af (CCDC 2182801).

C(8)-C(1)-C(2)-O(1)	44.9(3)
C(6)-C(1)-C(2)-O(1)	-140.4(2)
C(8)-C(1)-C(2)-C(3)	-133.1(2)
C(6)-C(1)-C(2)-C(3)	41.6(2)
O(1)-C(2)-C(3)-C(4)	142.0(2)
C(1)-C(2)-C(3)-C(4)	-39.9(3)
C(2)-C(3)-C(4)-C(5)	49.3(3)
C(3)-C(4)-C(5)-C(6)	-57.6(2)
C(7)-O(3)-C(6)-O(2)	115.56(17)
C(7)-O(3)-C(6)-C(1)	-4.7(2)
C(7)-O(3)-C(6)-C(5)	-124.95(17)
C(8)-C(1)-C(6)-O(2)	-113.82(19)
C(2)-C(1)-C(6)-O(2)	70.3(2)
C(8)-C(1)-C(6)-O(3)	3.5(2)
C(2)-C(1)-C(6)-O(3)	-172.32(16)
C(8)-C(1)-C(6)-C(5)	124.54(19)
C(2)-C(1)-C(6)-C(5)	-51.3(2)
C(4)-C(5)-C(6)-O(2)	-67.0(2)
C(4)-C(5)-C(6)-O(3)	173.11(16)
C(4)-C(5)-C(6)-C(1)	57.5(2)
C(6)-O(3)-C(7)-O(4)	-176.08(19)
C(6)-O(3)-C(7)-C(8)	4.3(2)
C(2)-C(1)-C(8)-C(9)	-4.3(4)
C(6)-C(1)-C(8)-C(9)	-179.26(18)
C(2)-C(1)-C(8)-C(7)	173.9(2)
C(6)-C(1)-C(8)-C(7)	-1.1(2)
O(4)-C(7)-C(8)-C(1)	178.4(2)
O(3)-C(7)-C(8)-C(1)	-2.0(2)
O(4)-C(7)-C(8)-C(9)	-3.2(3)
O(3)-C(7)-C(8)-C(9)	176.40(17)
C(1)-C(8)-C(9)-C(14)	33.9(3)
C(7)-C(8)-C(9)-C(14)	-144.0(2)
C(1)-C(8)-C(9)-C(10)	-144.3(2)
C(7)-C(8)-C(9)-C(10)	37.8(3)
C(14)-C(9)-C(10)-C(11)	-0.9(3)
C(8)-C(9)-C(10)-C(11)	177.4(2)

C(9)-C(10)-C(11)-C(12)	-0.3(4)
C(10)-C(11)-C(12)-C(13)	1.3(4)
C(11)-C(12)-C(13)-C(14)	-1.0(4)
C(12)-C(13)-C(14)-C(9)	-0.3(3)
C(10)-C(9)-C(14)-C(13)	1.2(3)
C(8)-C(9)-C(14)-C(13)	-177.06(19)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 3af (CCDC 2182801) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3)-H(3A)...O(4)#1	0.97	2.62	3.417(3)	140.1
O(2)-H(2)...O(1)#2	0.82	2.03	2.833(2)	167.4

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y-1/2,-z+1/2 #2 -x+1,-y,-z+1

4. Reference

[1] W. Kuldeep, C. Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Synth. Commun.,* 2008, **38**, 4434–4444.

[2] S. K. Bagal, R. M. Adlington, J. E. Baldwin and R. Marquez, *J. Org. Chem.,* 2004, **69**, 9100-9108.

[3] H. Rudler, A. Parlier, T. Durand-Réville, B. Martin-Vaca, M. Audouin, E. Garrier, V. Certal and J. Vaissermann, *Tetrahedron,* 2000, **56**, 5001–5027.

[4] Y. Harada, Y. Fukumoto, N. Chatani, *Org. Lett.,* 2005, **7**, 4385-4387.

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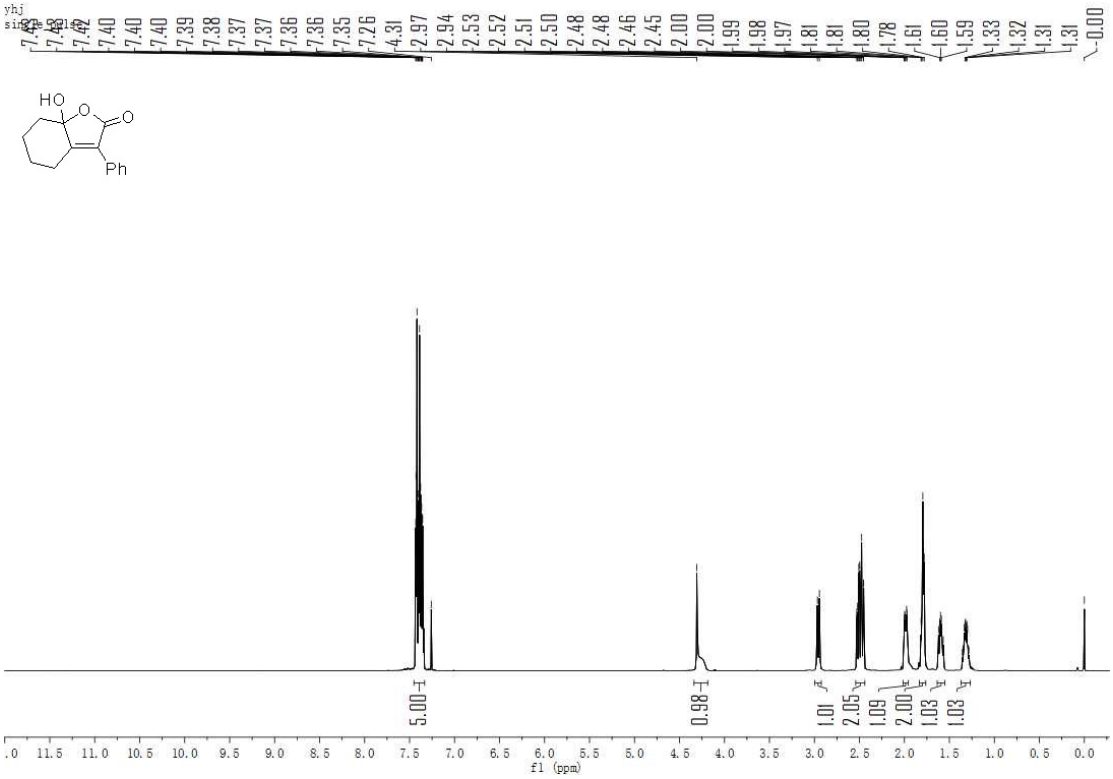
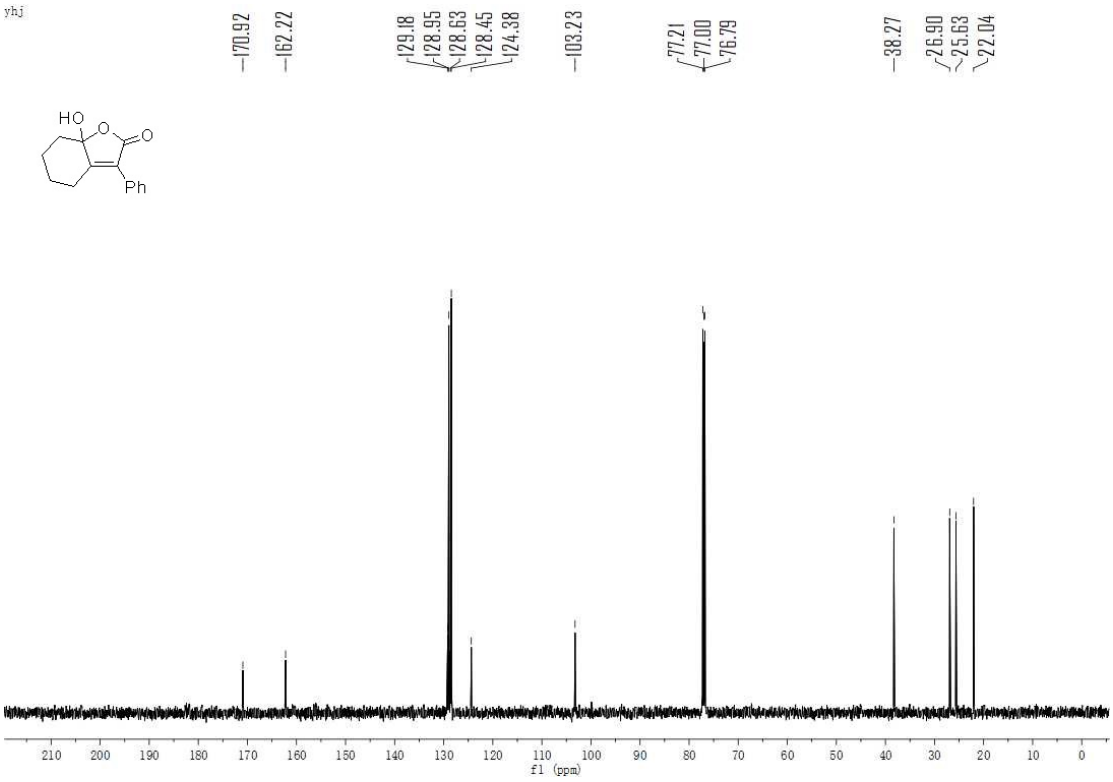
5. ^{1}H-NMR and ^{13}C-NMR spectra of compounds 3aa-p and 4aa-i

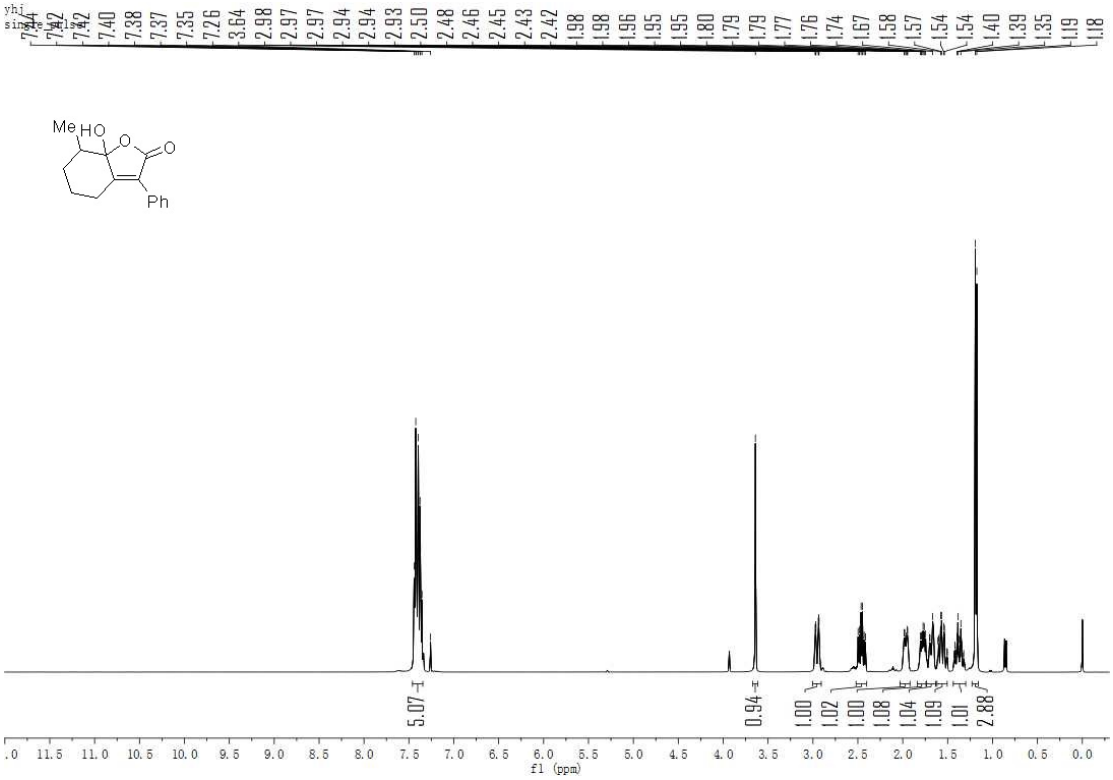
^{1}H NMR spectrum of 3aa



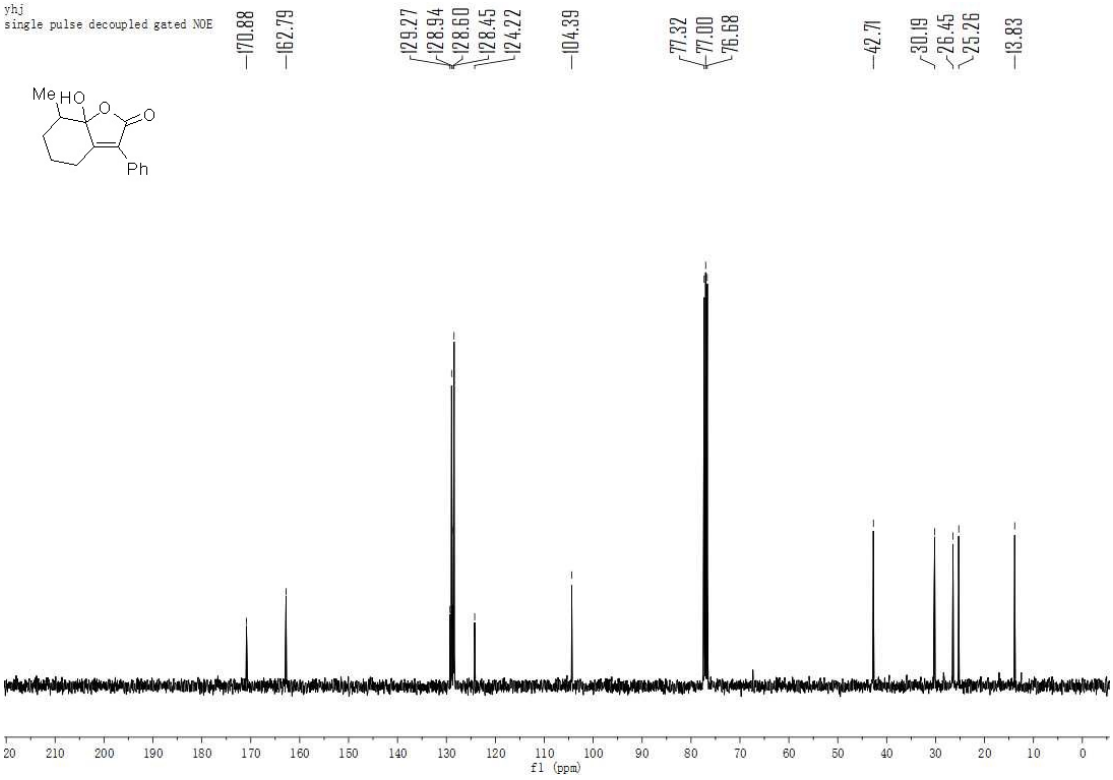
^{13}C NMR spectrum of 3aa



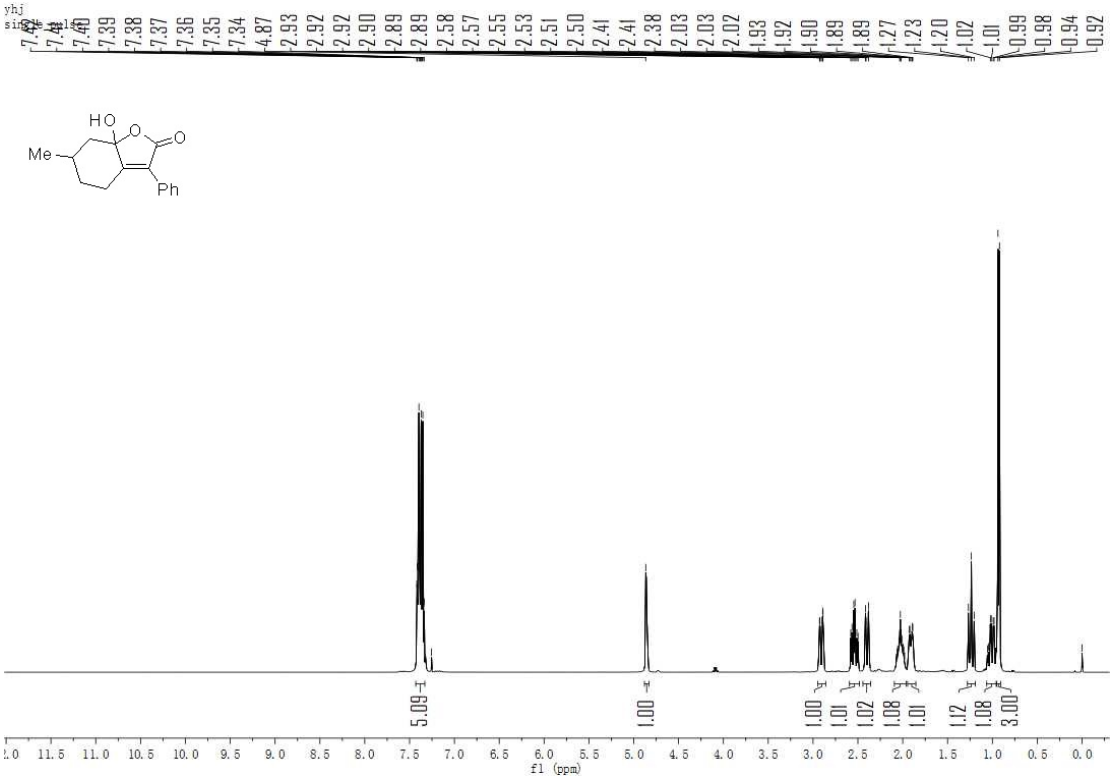
^{1}H NMR spectrum of 3ab



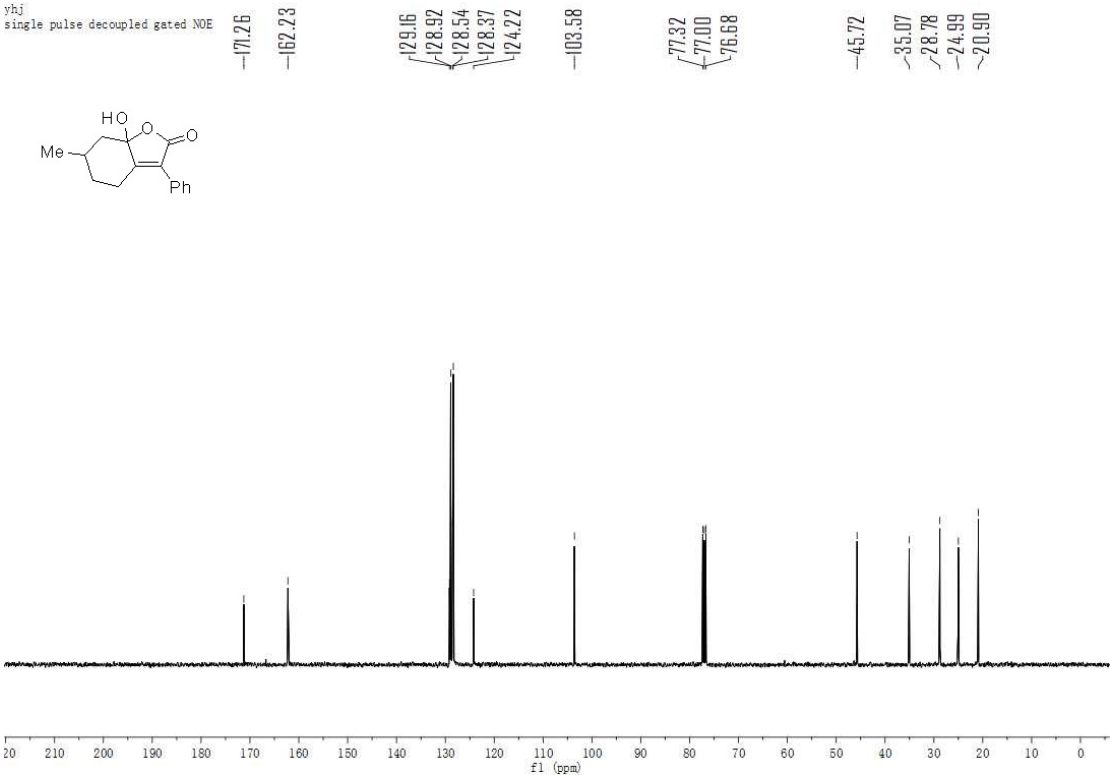
^{13}C NMR spectrum of 3ab



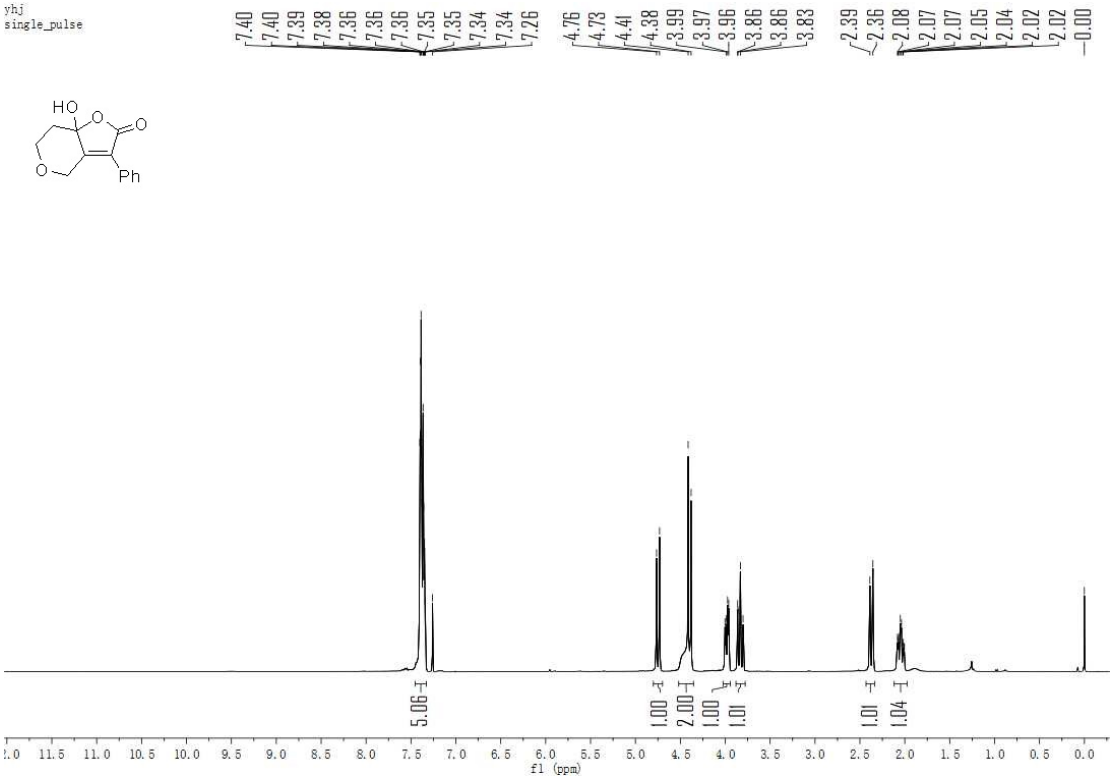
^{1}H NMR spectrum of 3ac



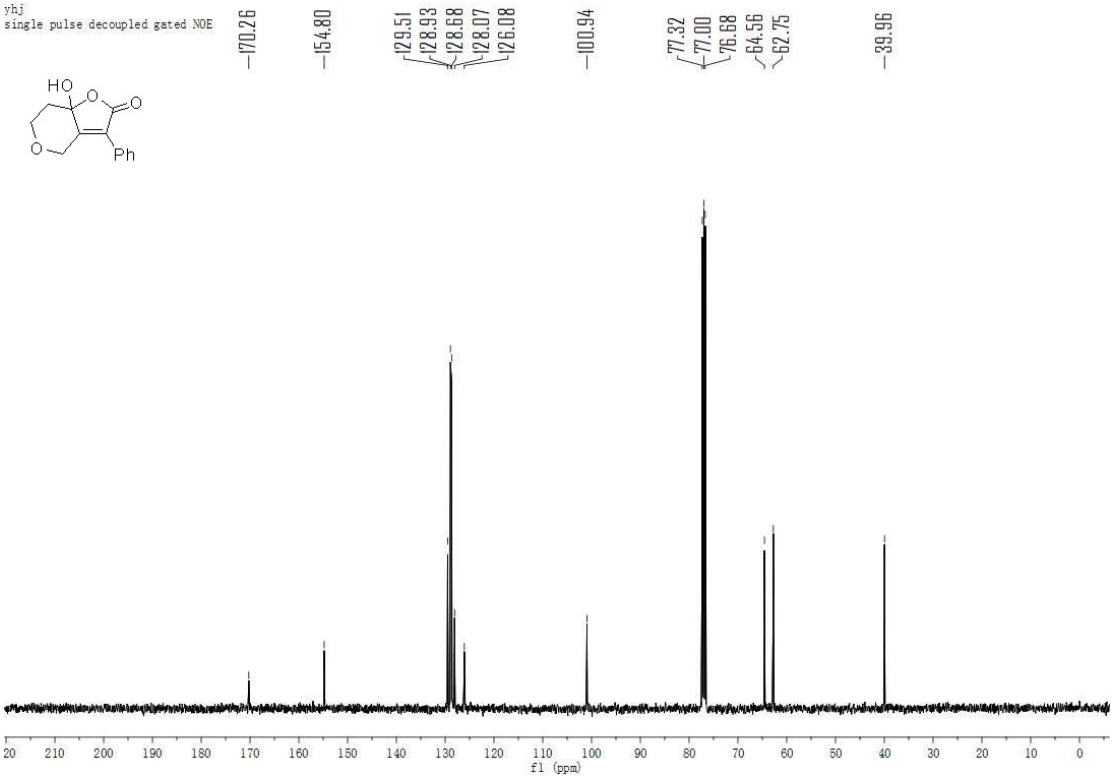
^{13}C NMR spectrum of 3ac



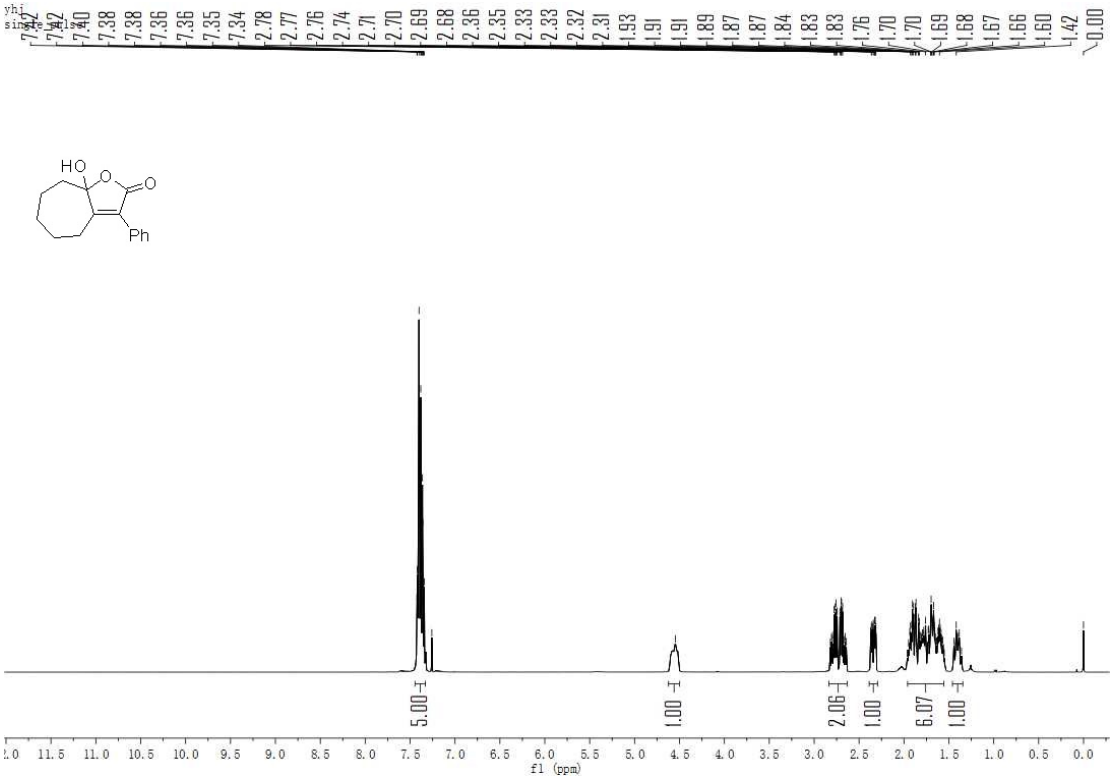
^{1}H NMR spectrum of 3ad



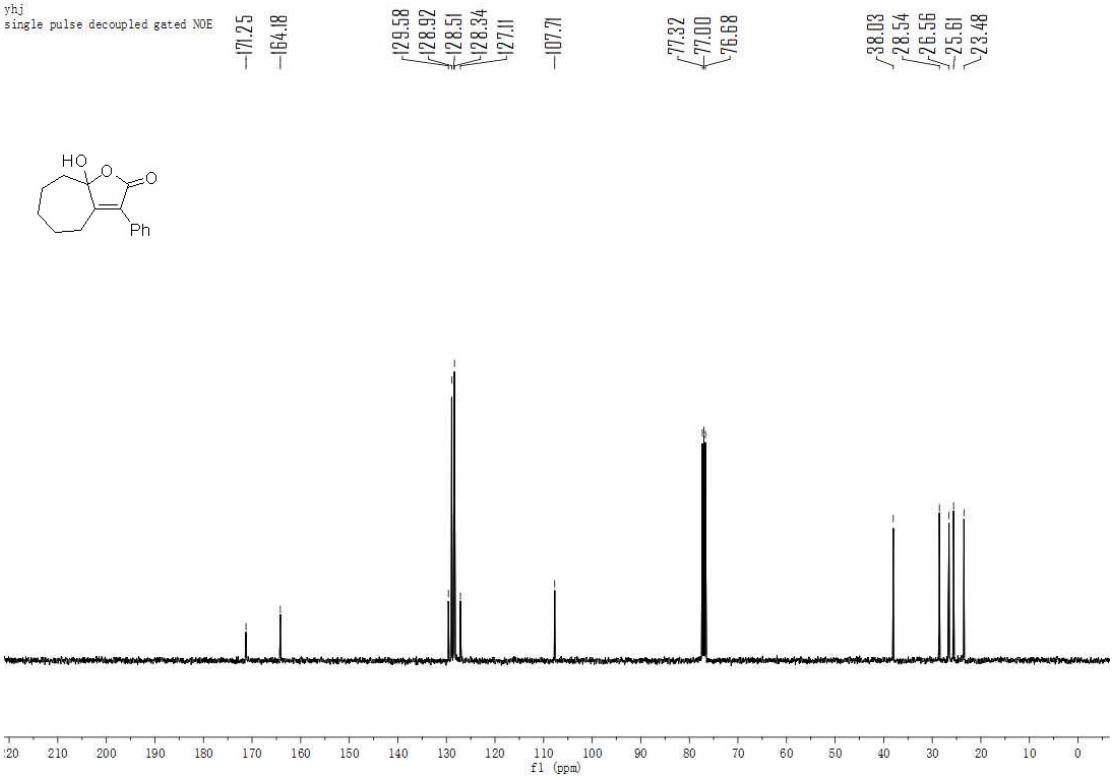
^{13}C NMR spectrum of 3ad



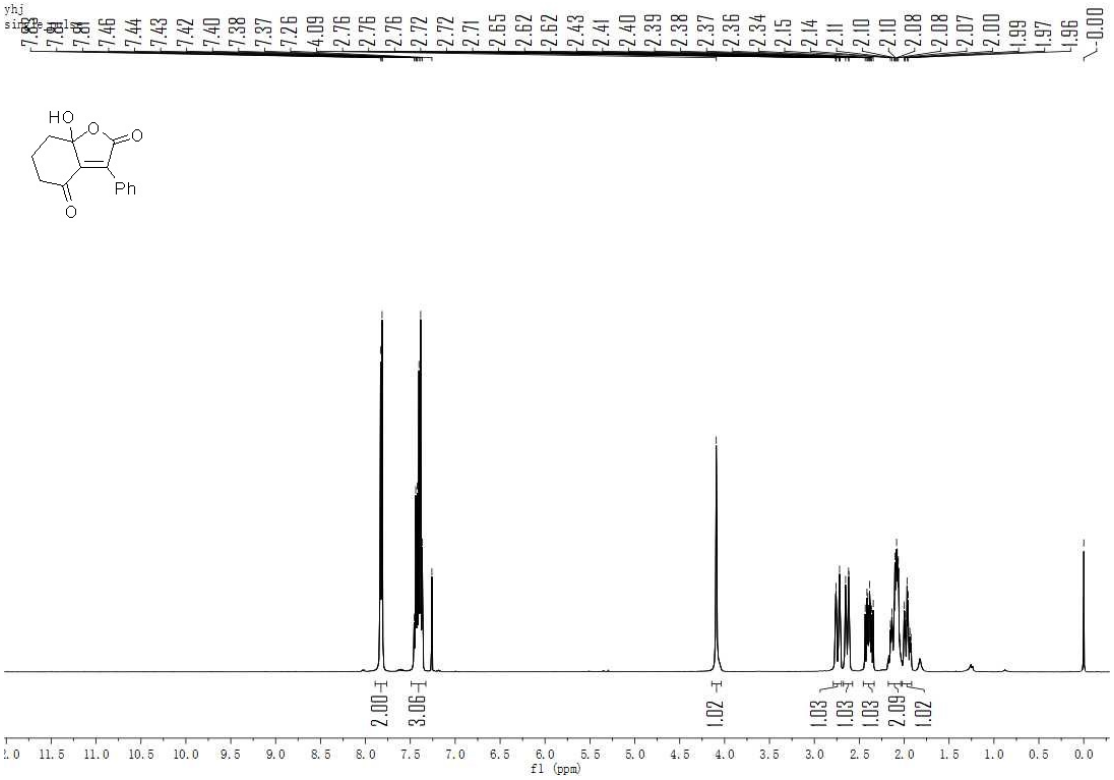
^{1}H NMR spectrum of 3ae



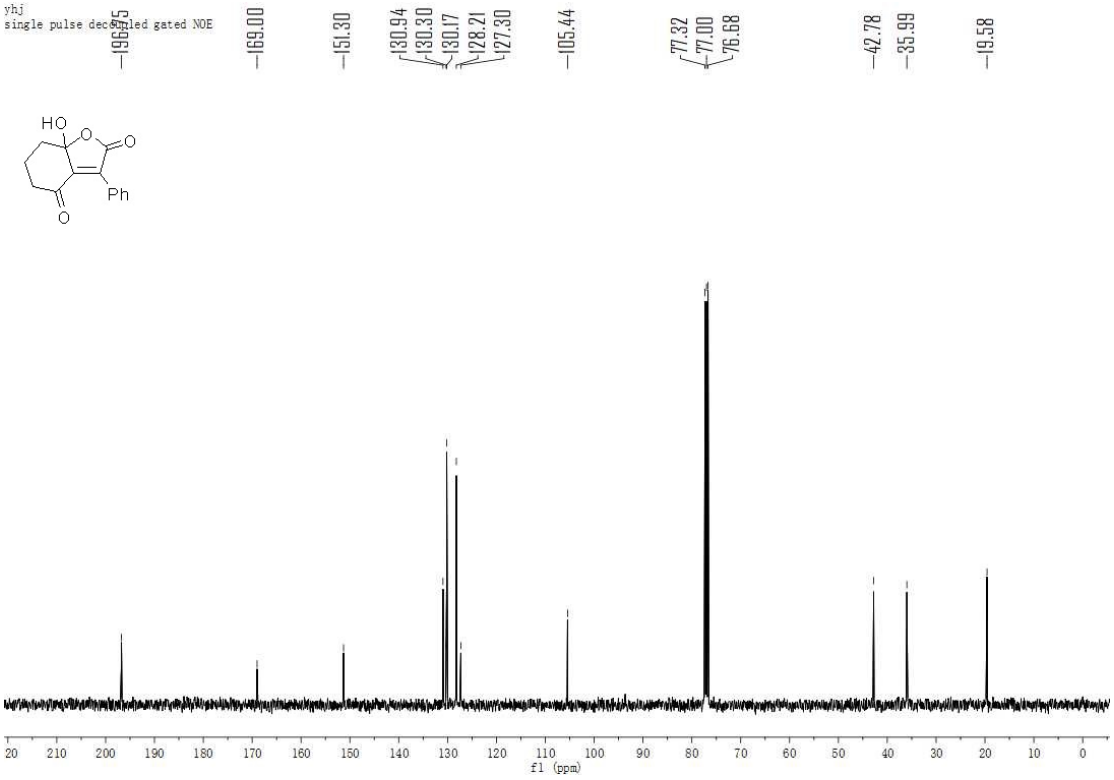
^{13}C NMR spectrum of 3ae



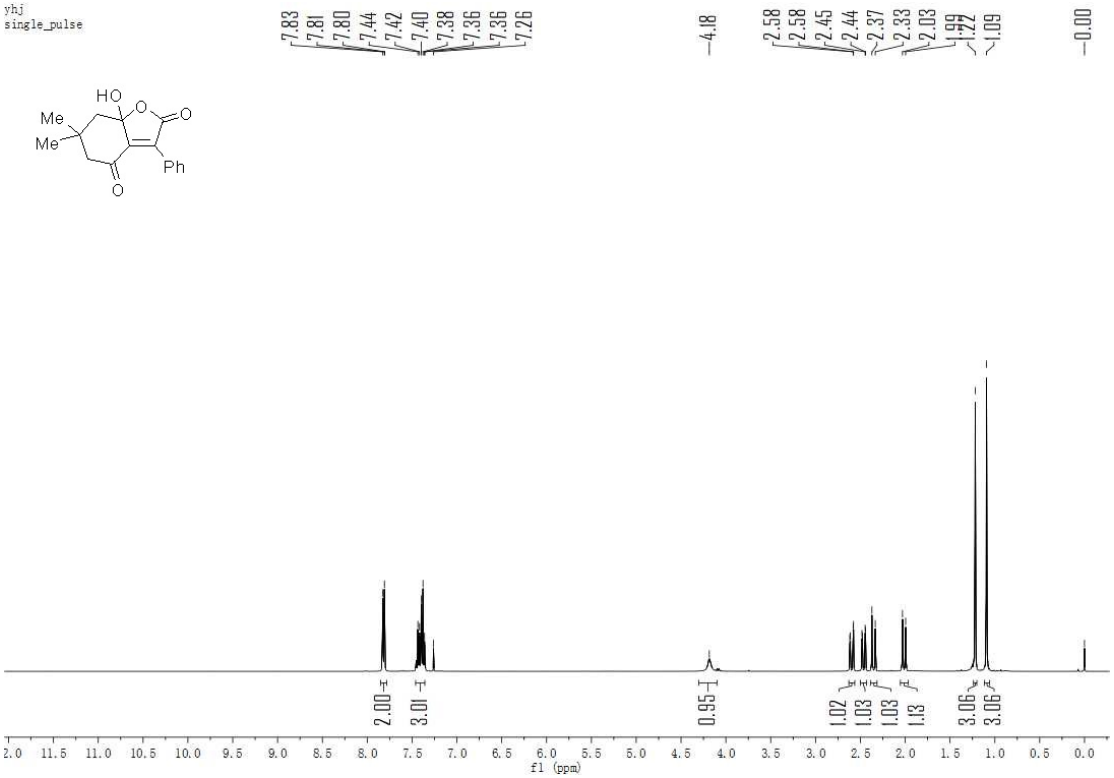
^{1}H NMR spectrum of 3af



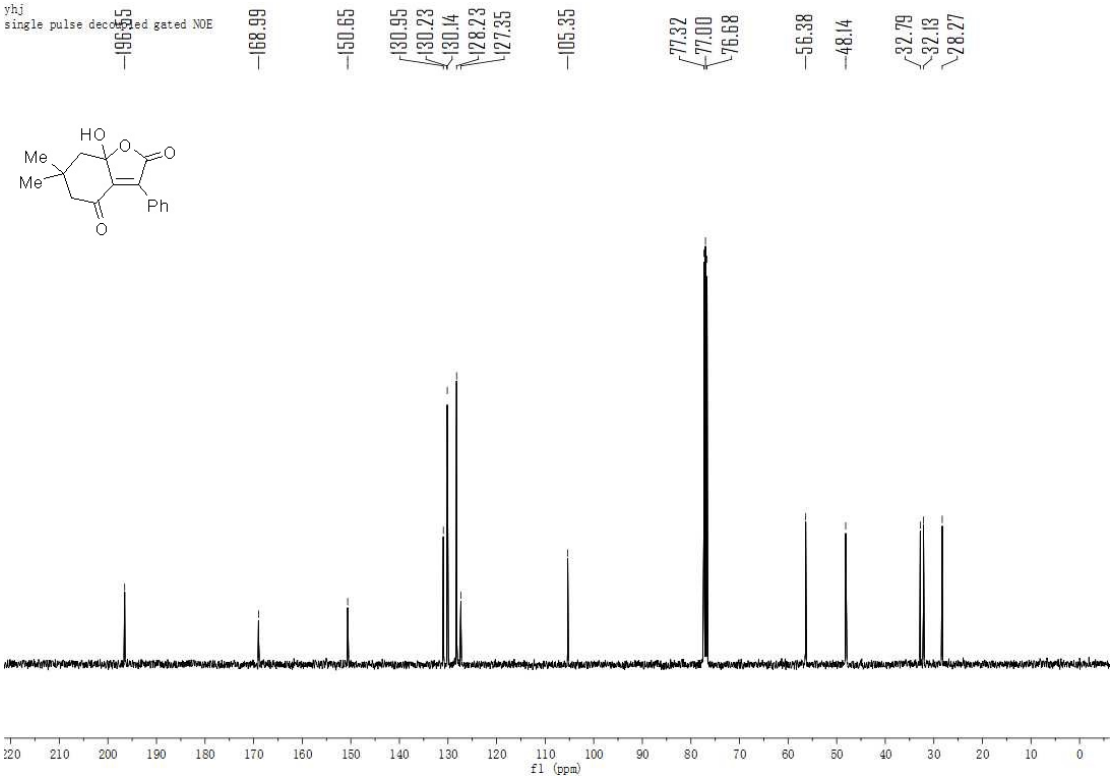
^{13}C NMR spectrum of 3af



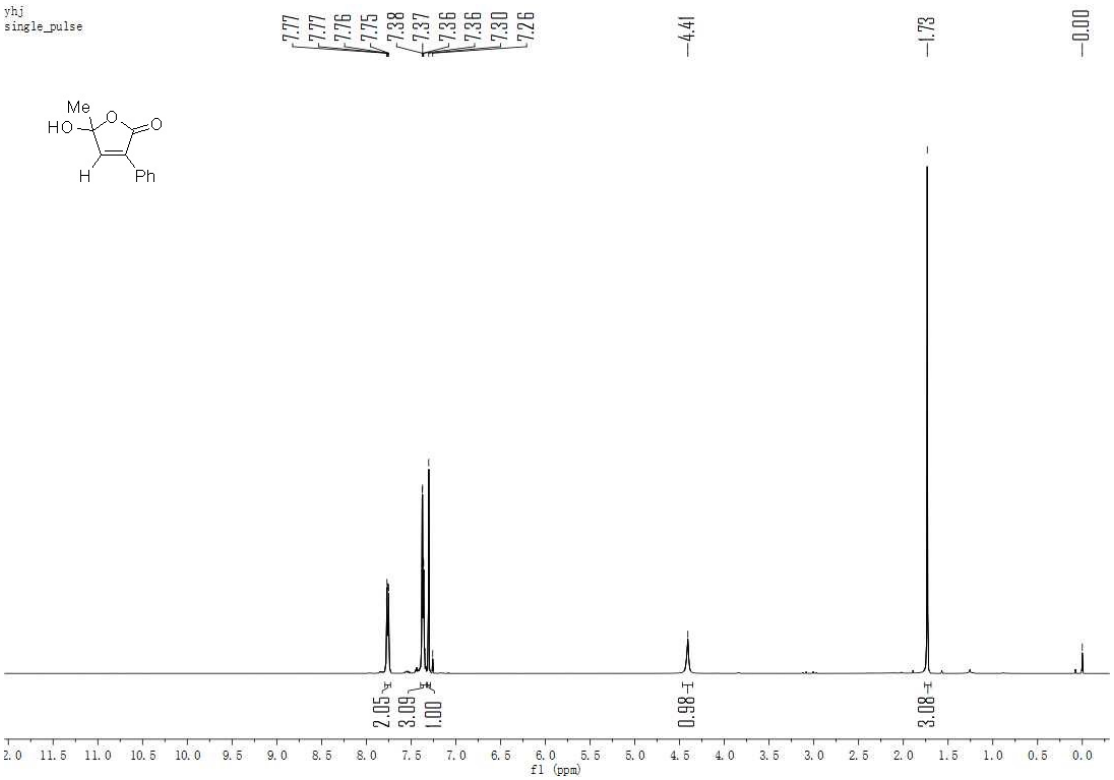
^{1}H NMR spectrum of 3ag



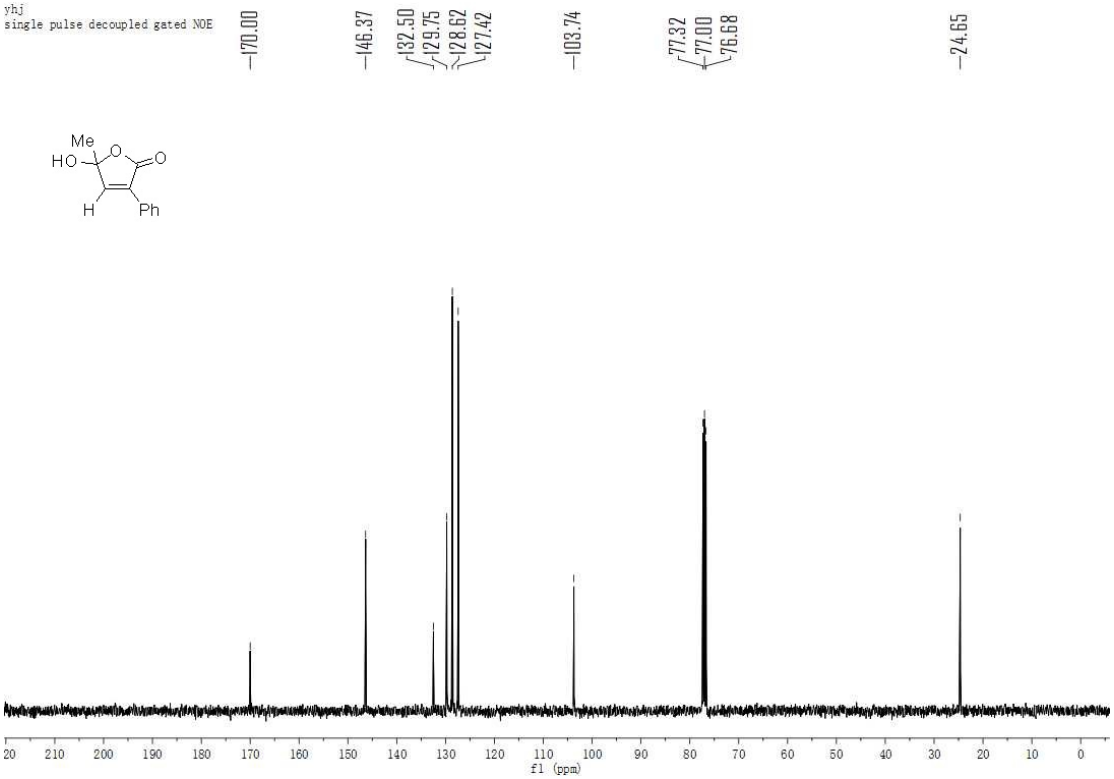
^{13}C NMR spectrum of 3ag



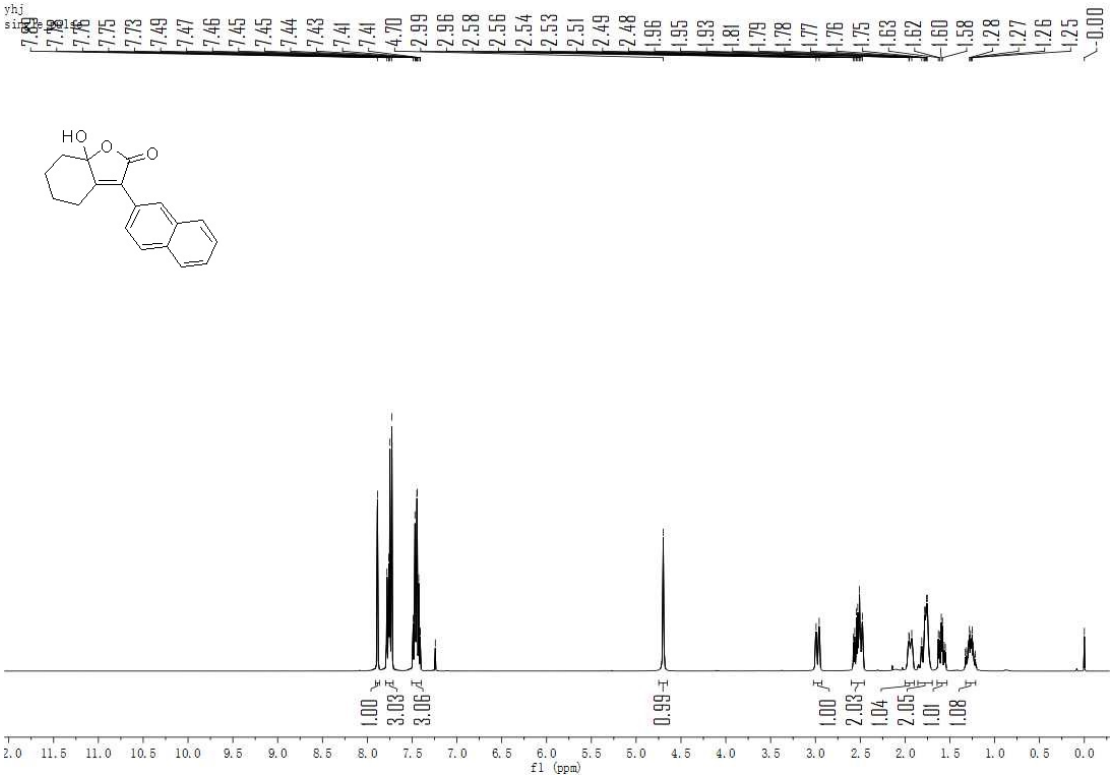
^{1}H NMR spectrum of 3ah



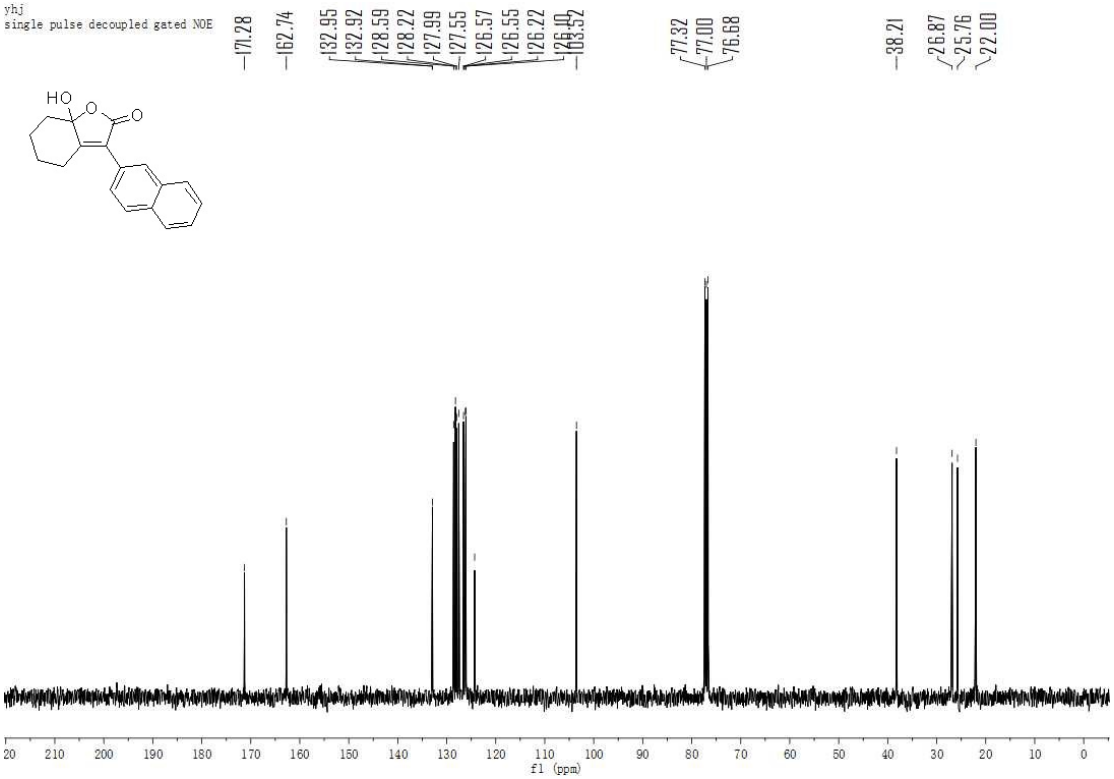
^{13}C NMR spectrum of 3ah



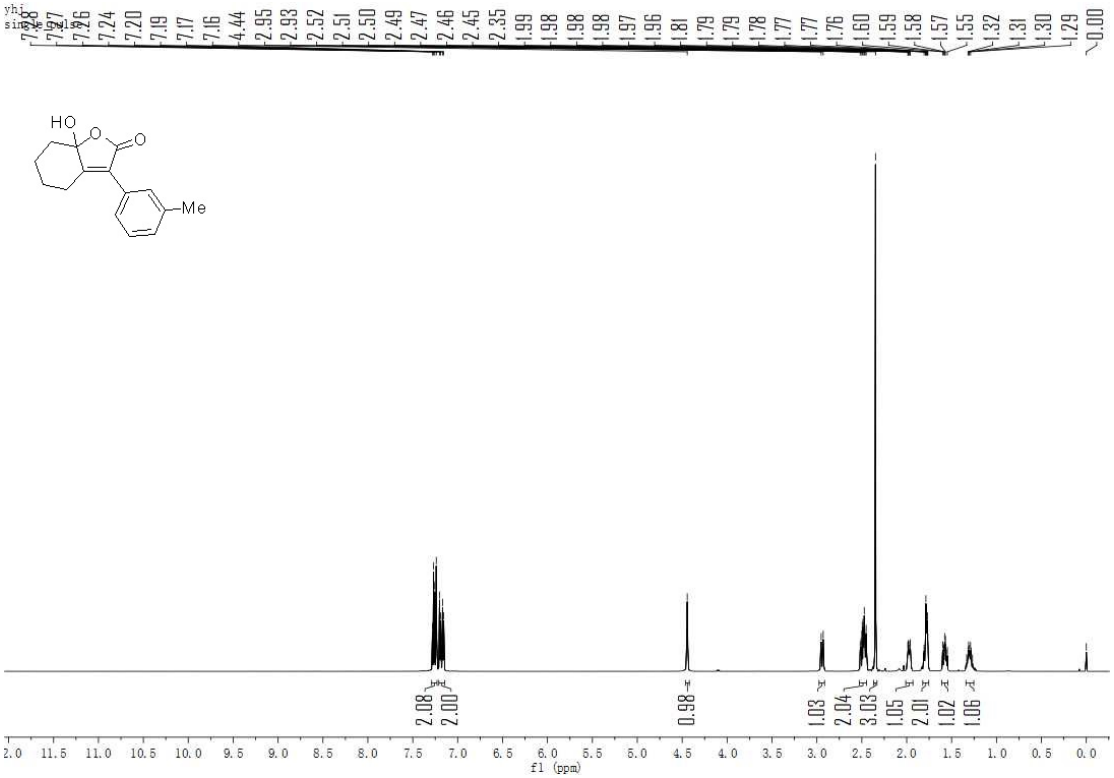
^{1}H NMR spectrum of 3ai



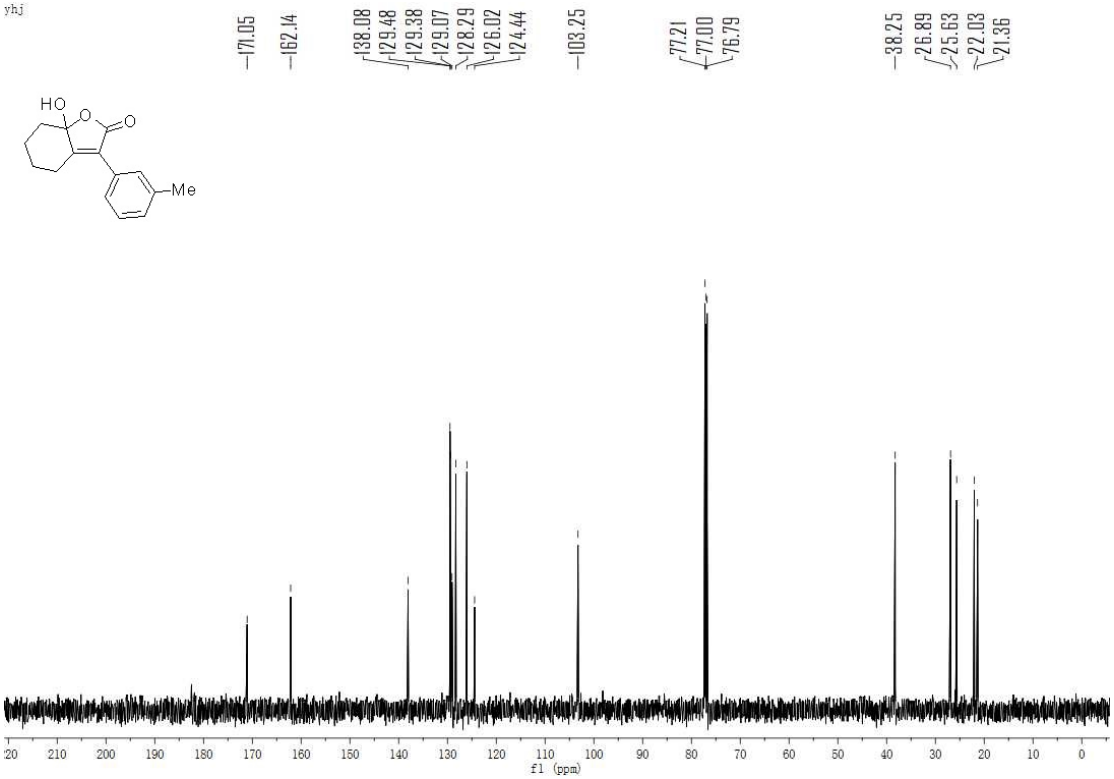
^{13}C NMR spectrum of 3ai



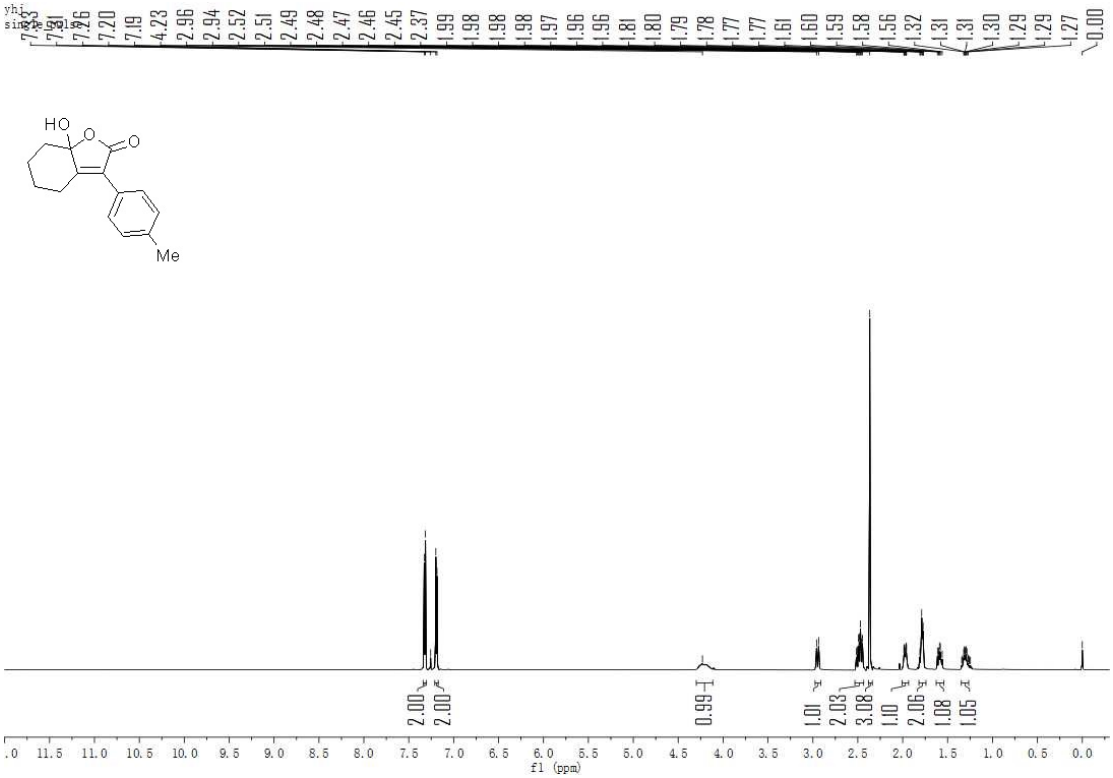
^{1}H NMR spectrum of 3aj



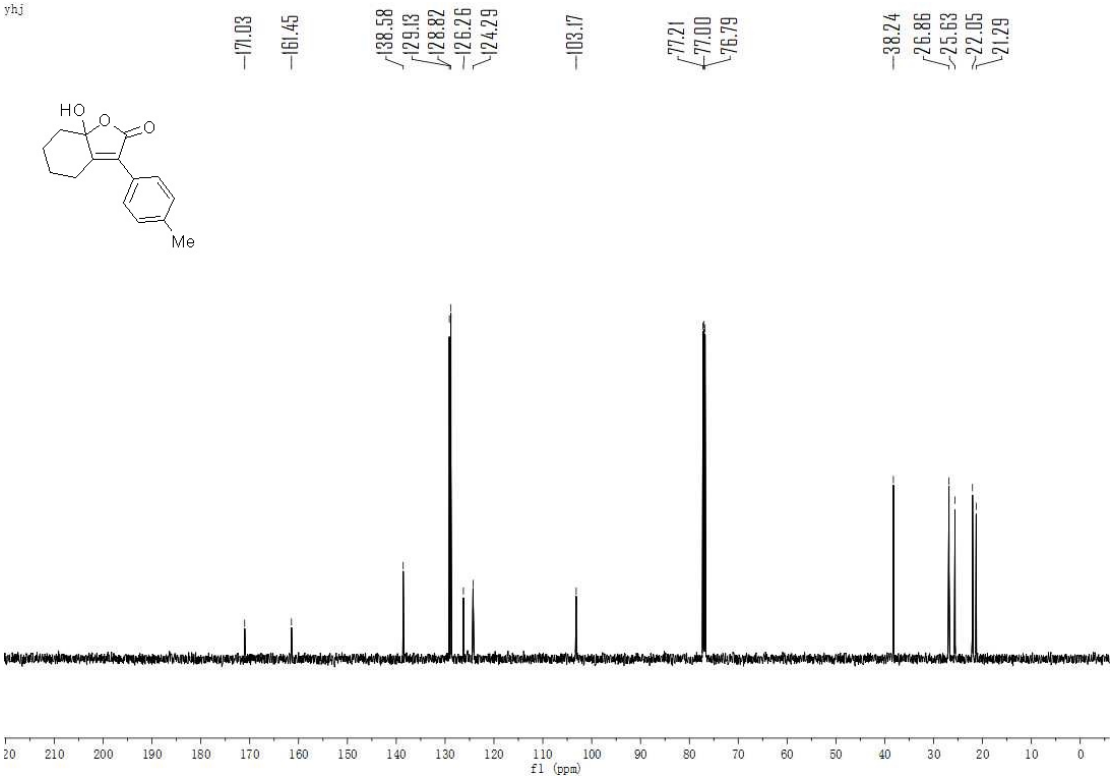
^{13}C NMR spectrum of 3aj



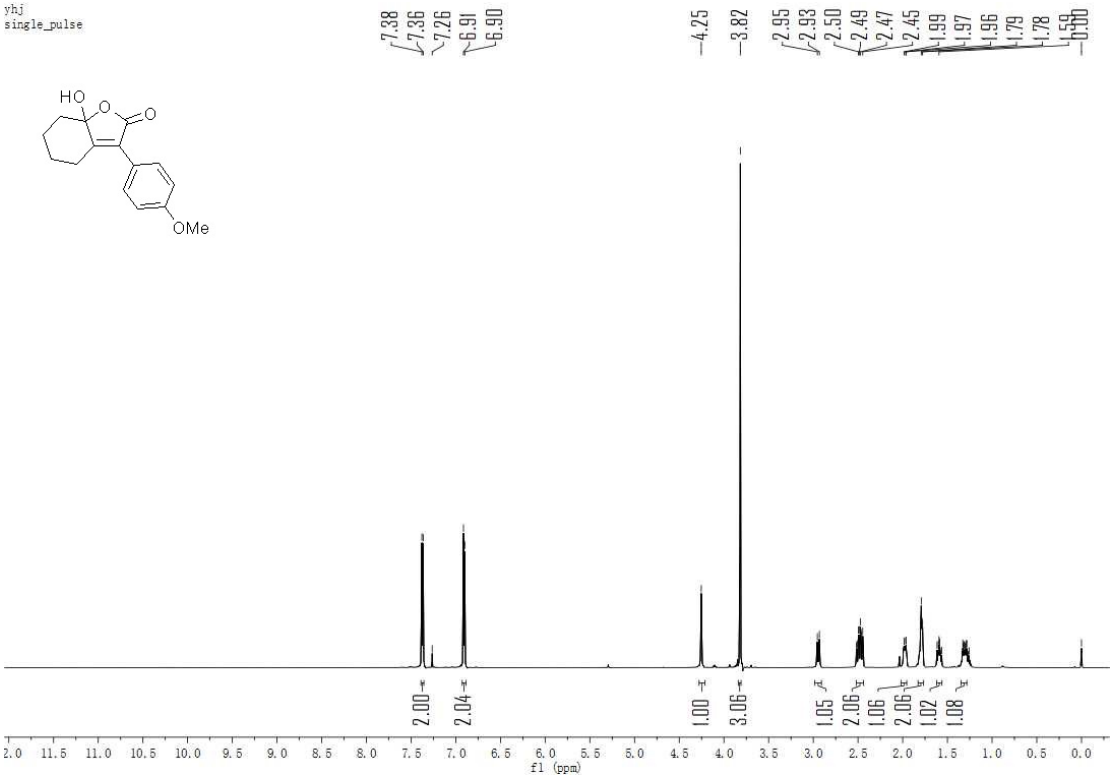
^{1}H NMR spectrum of 3ak



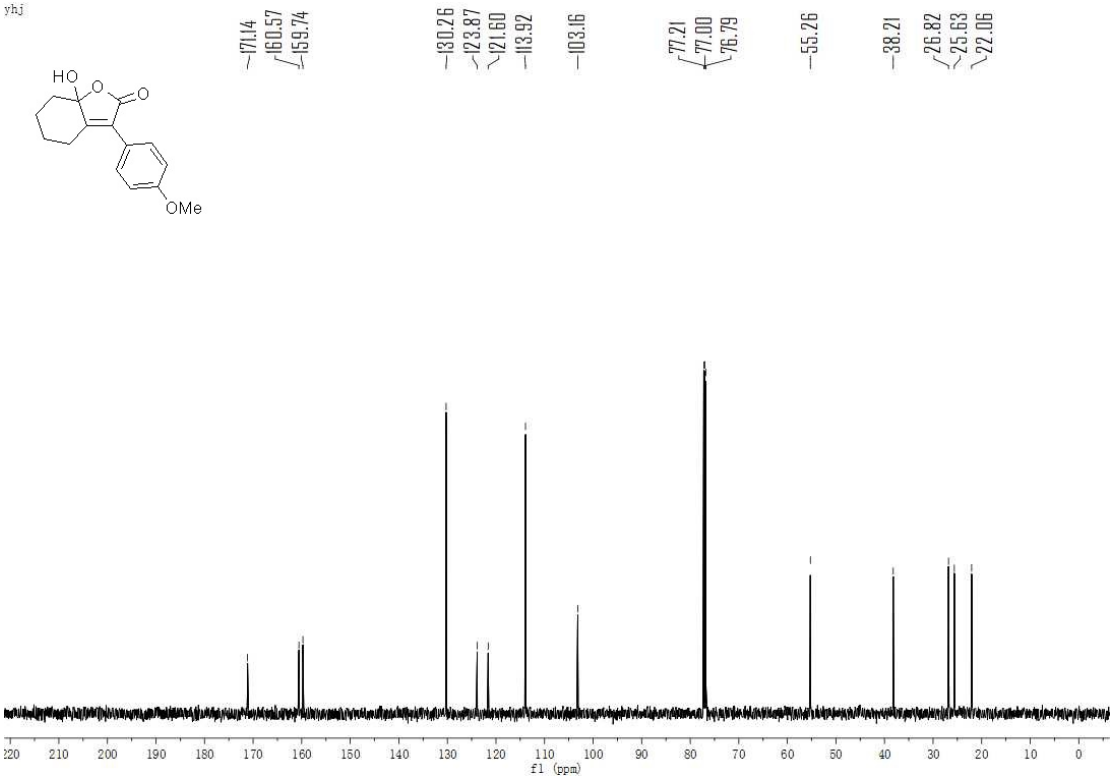
^{13}C NMR spectrum of 3ak



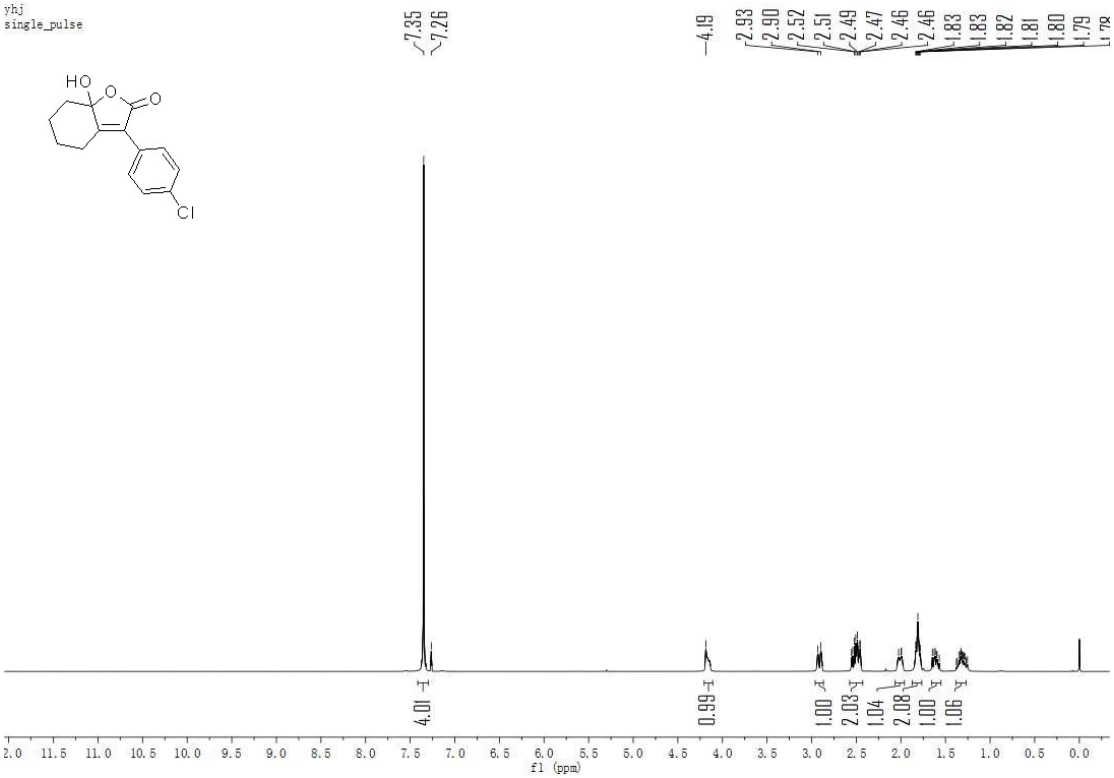
^{1}H NMR spectrum of 3al



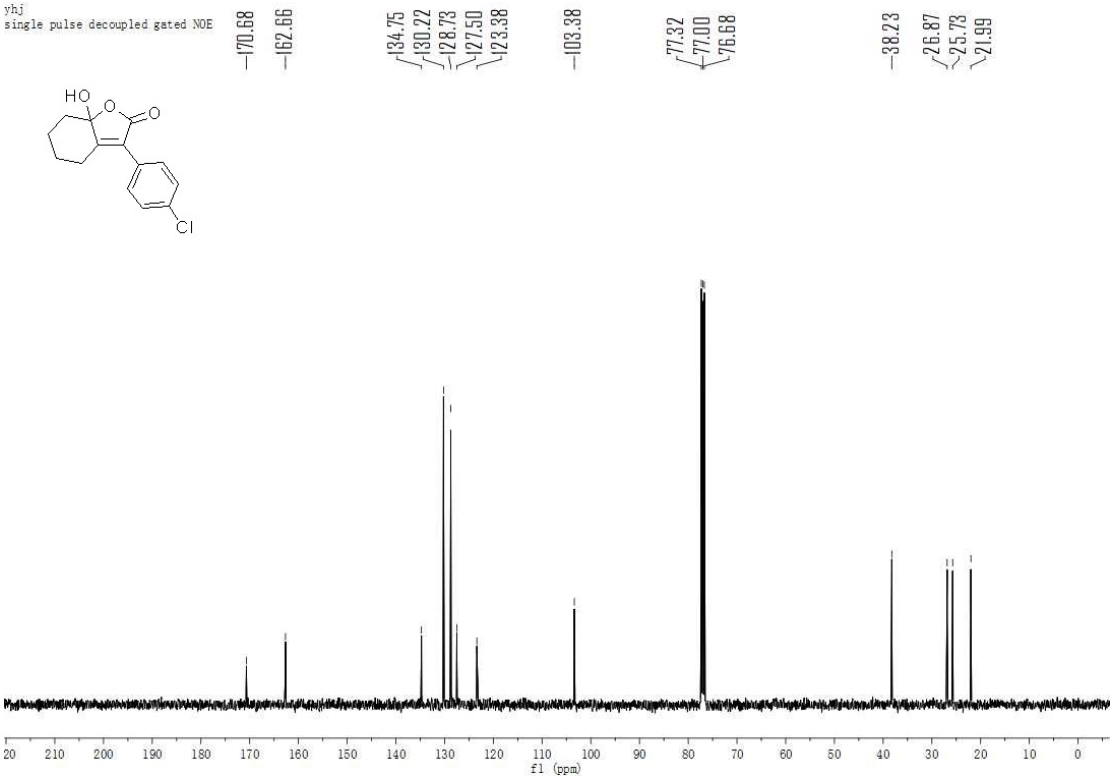
^{13}C NMR spectrum of 3al



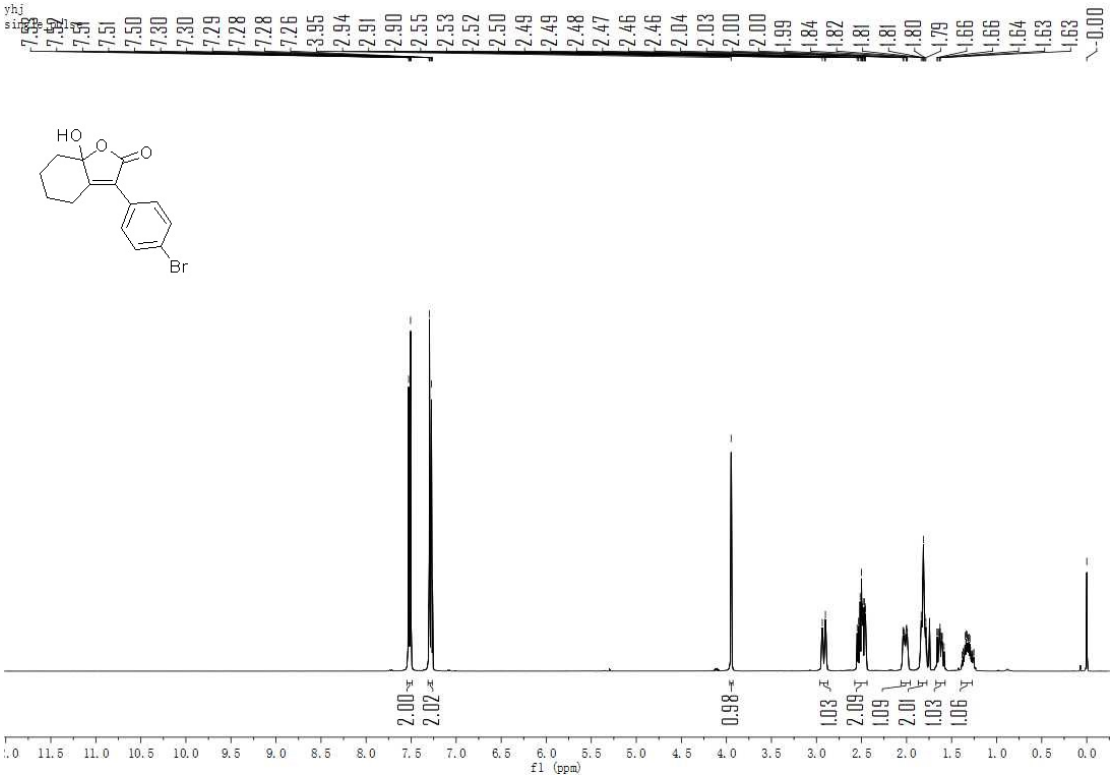
^{1}H NMR spectrum of 3am



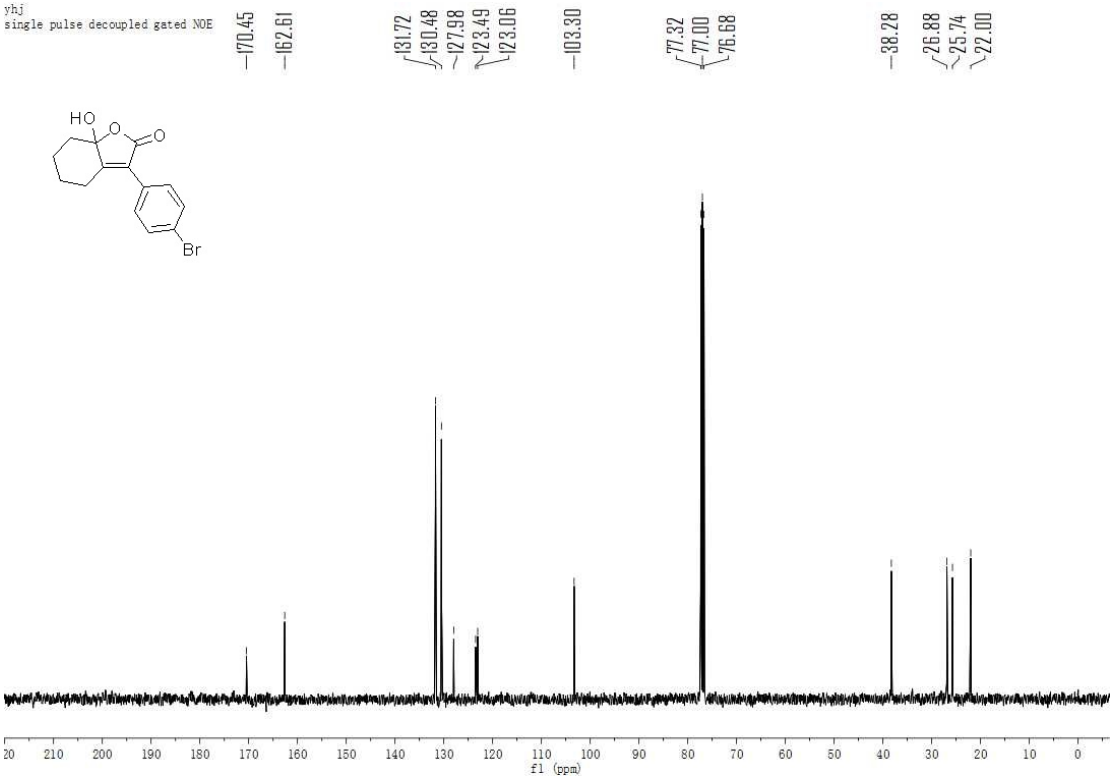
^{13}C NMR spectrum of 3am



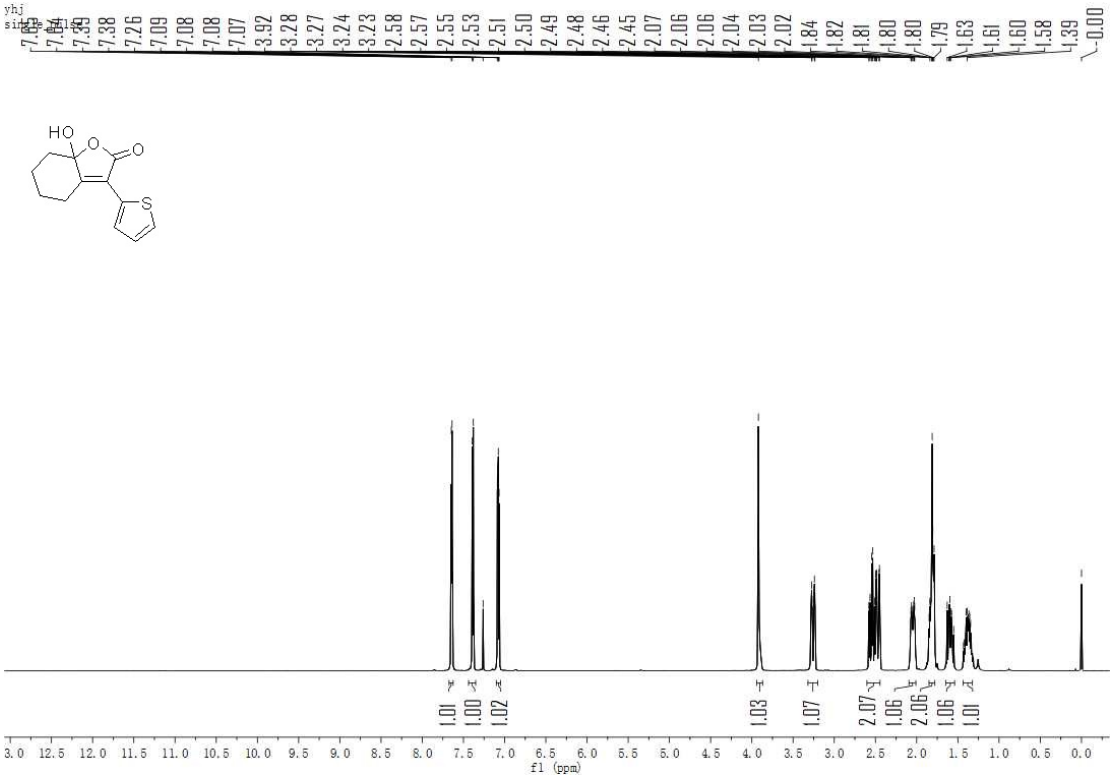
^{1}H NMR spectrum of 3an



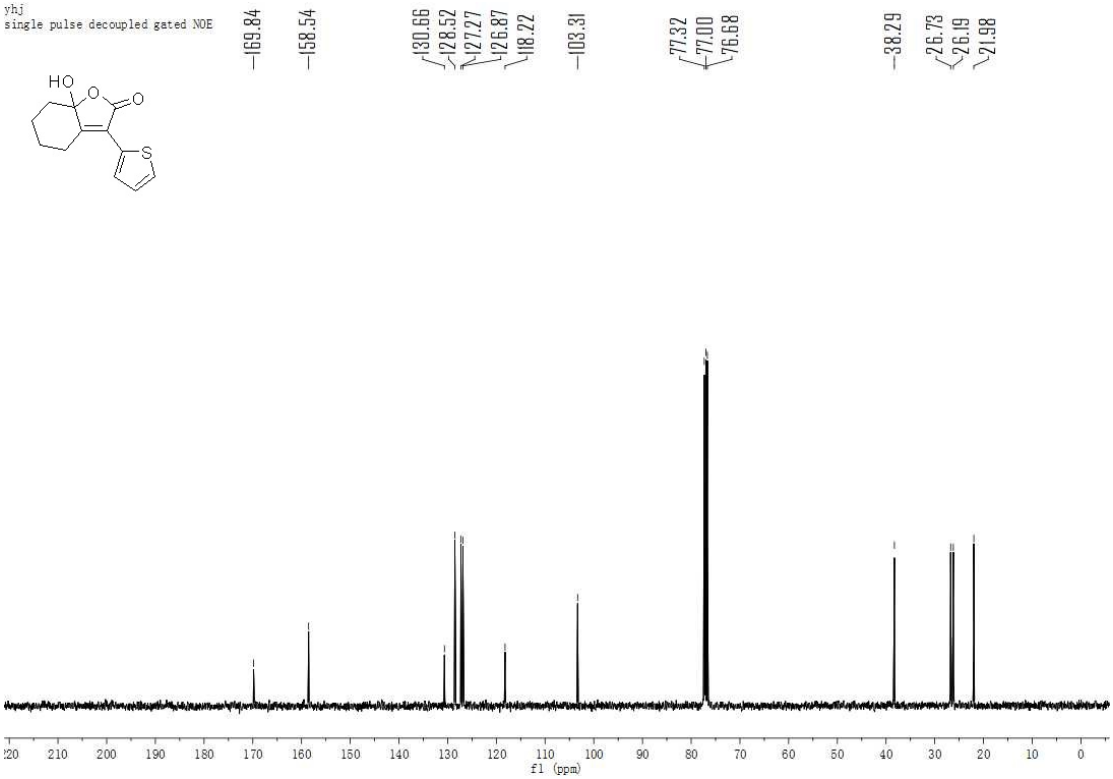
^{13}C NMR spectrum of 3an



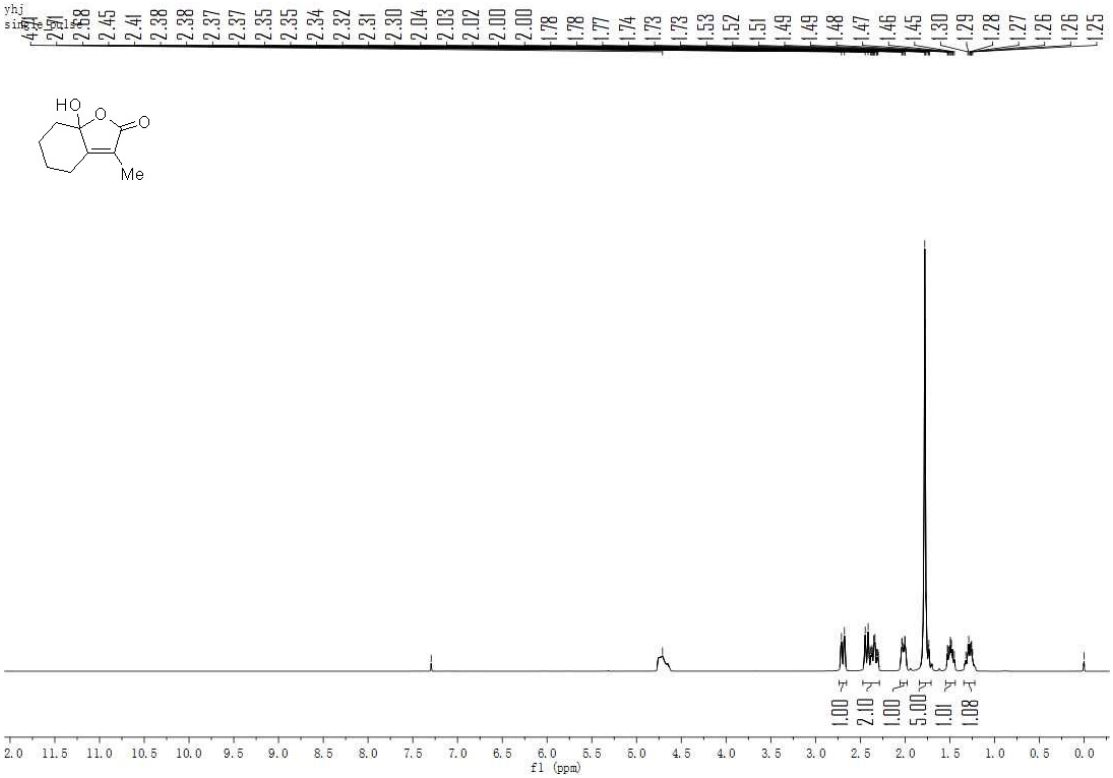
^{1}H NMR spectrum of 3ao



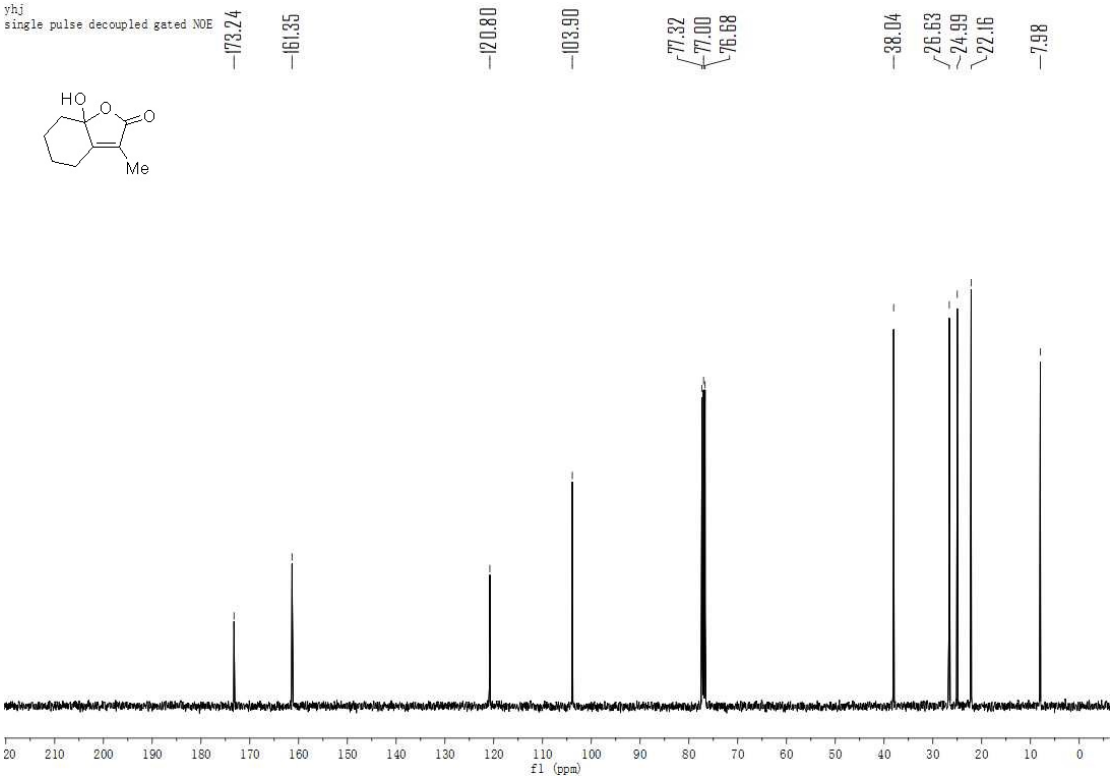
^{13}C NMR spectrum of 3ao



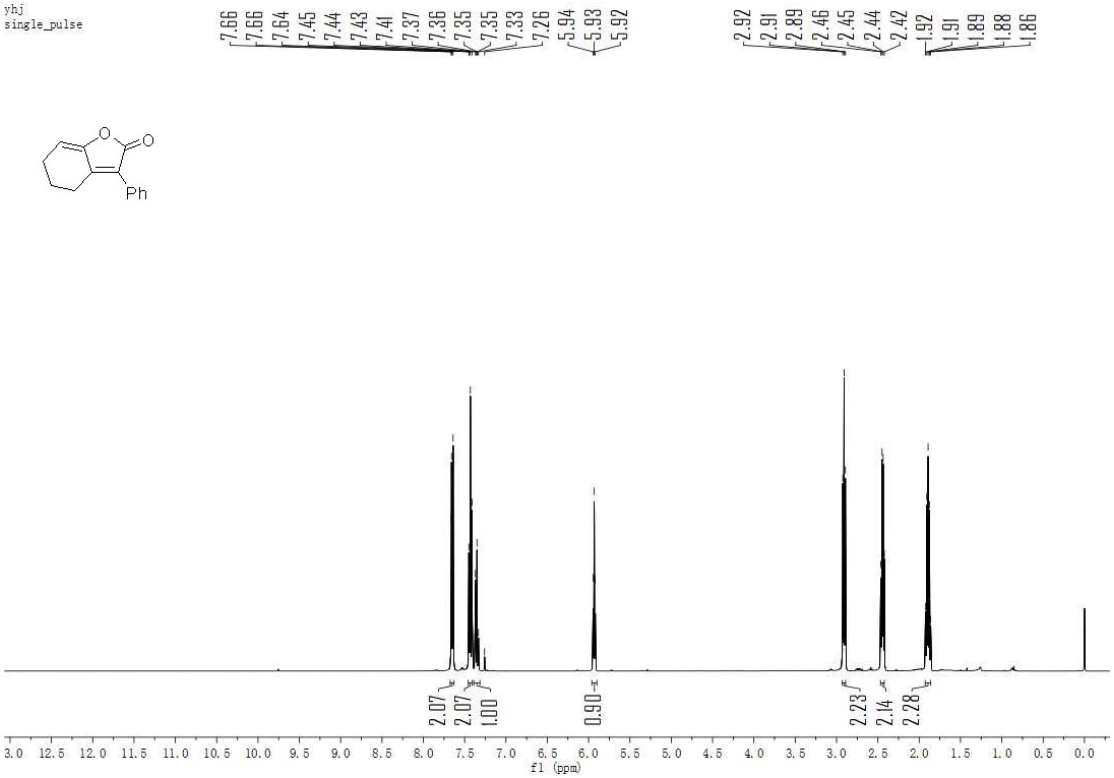
^{1}H NMR spectrum of 3ap



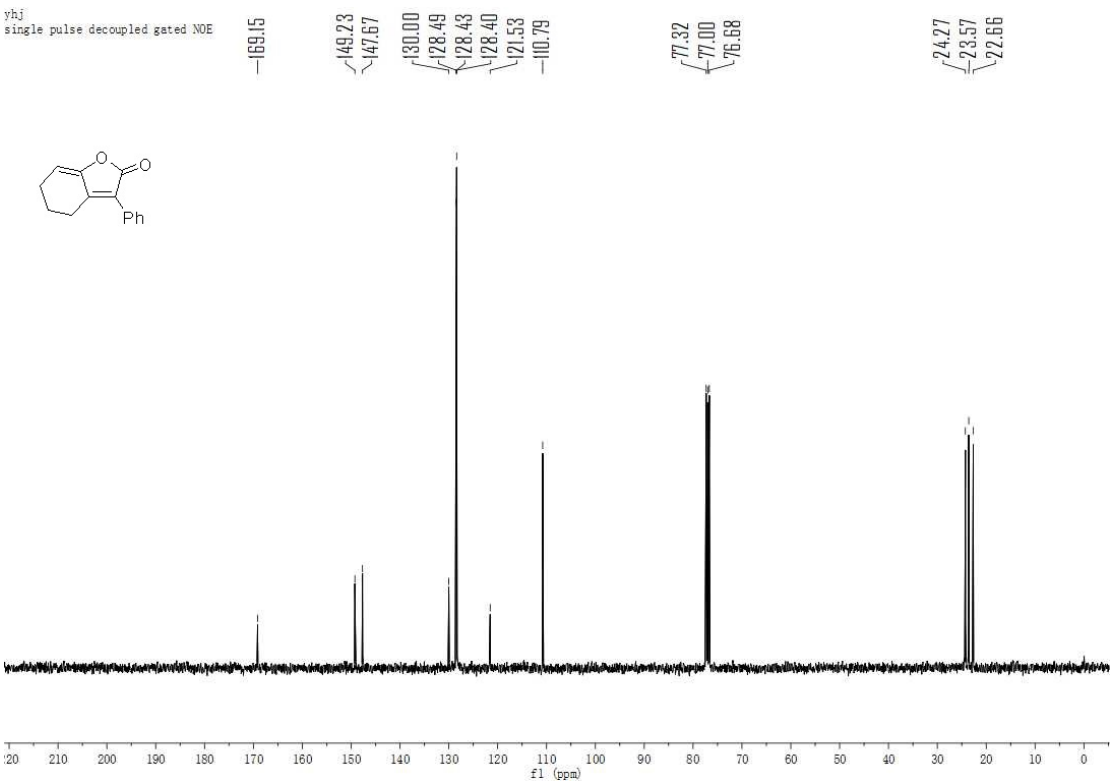
^{13}C NMR spectrum of 3ap



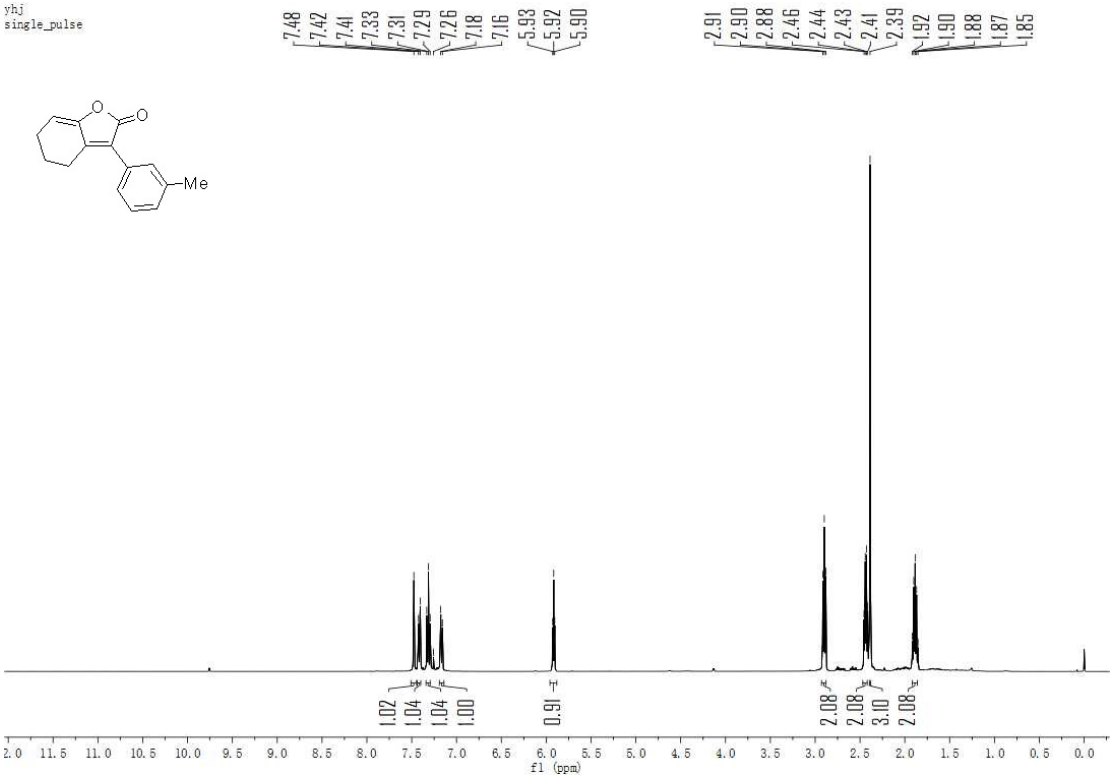
^{1}H NMR spectrum of 4aa



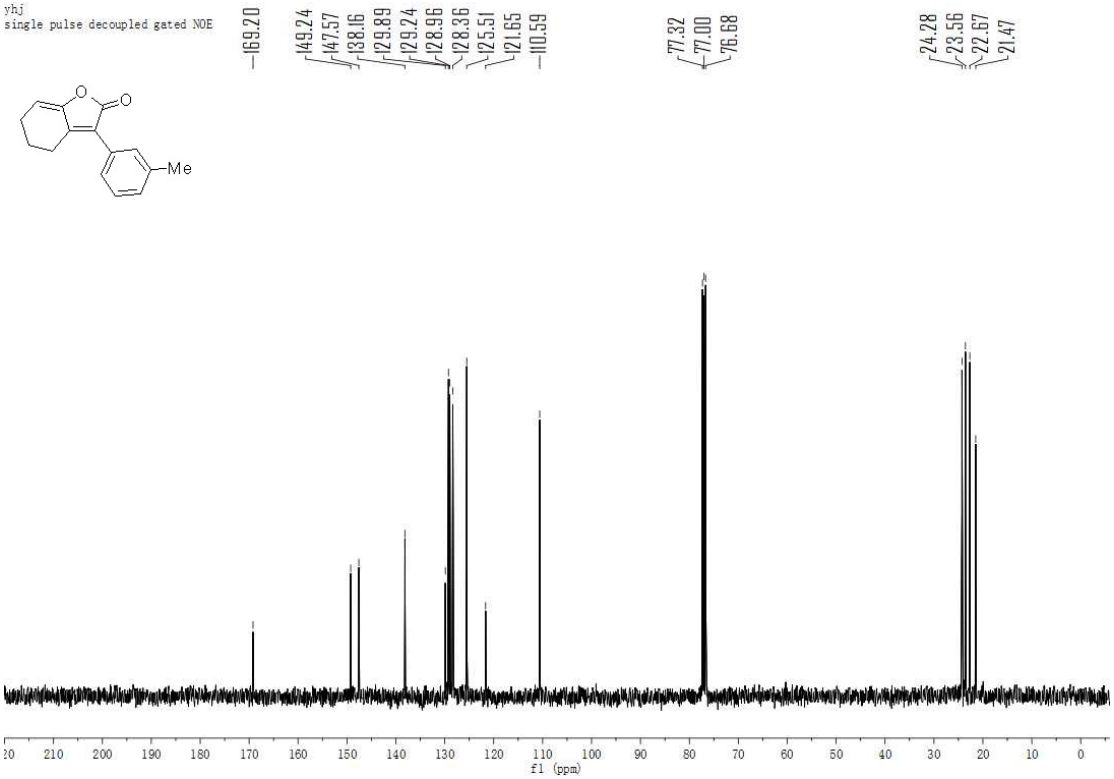
^{13}C NMR spectrum of 4aa



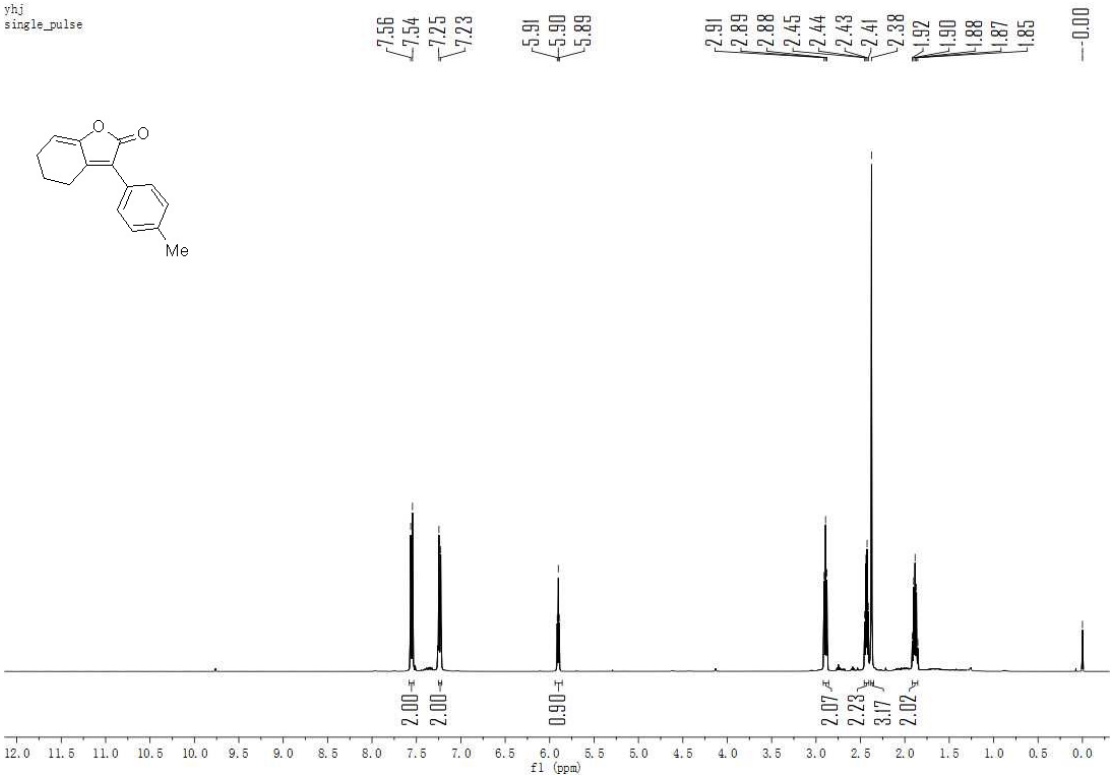
^{1}H NMR spectrum of 4ab



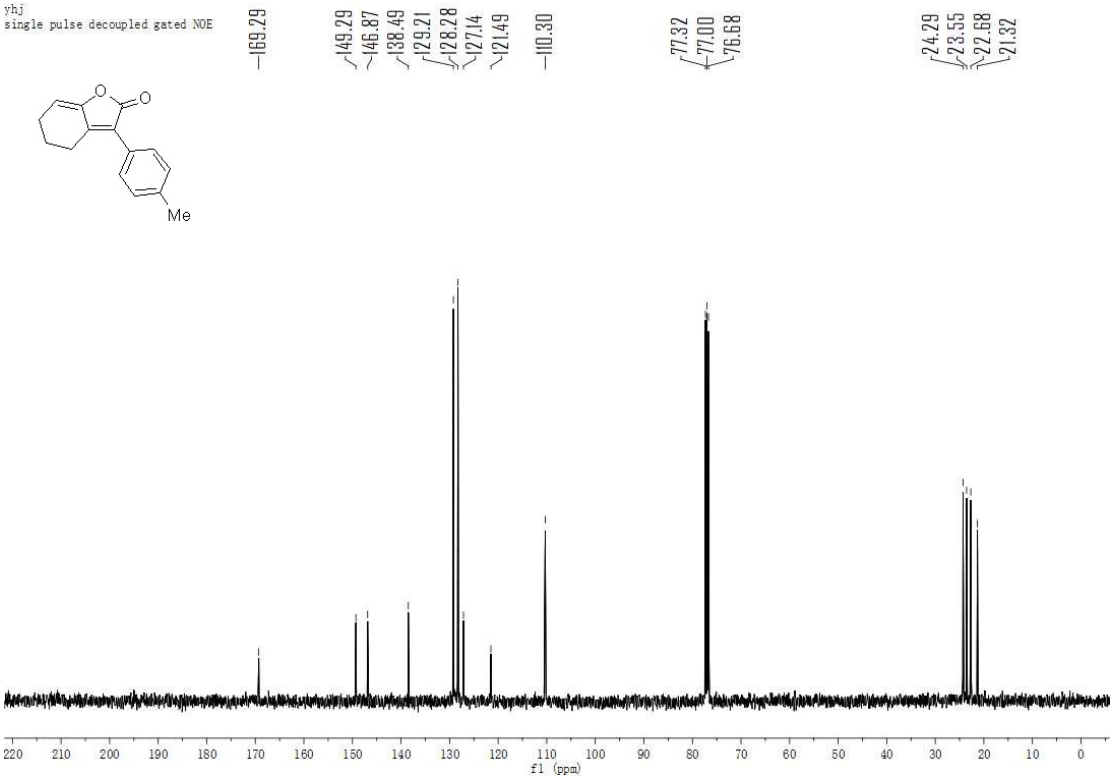
^{13}C NMR spectrum of 4ab



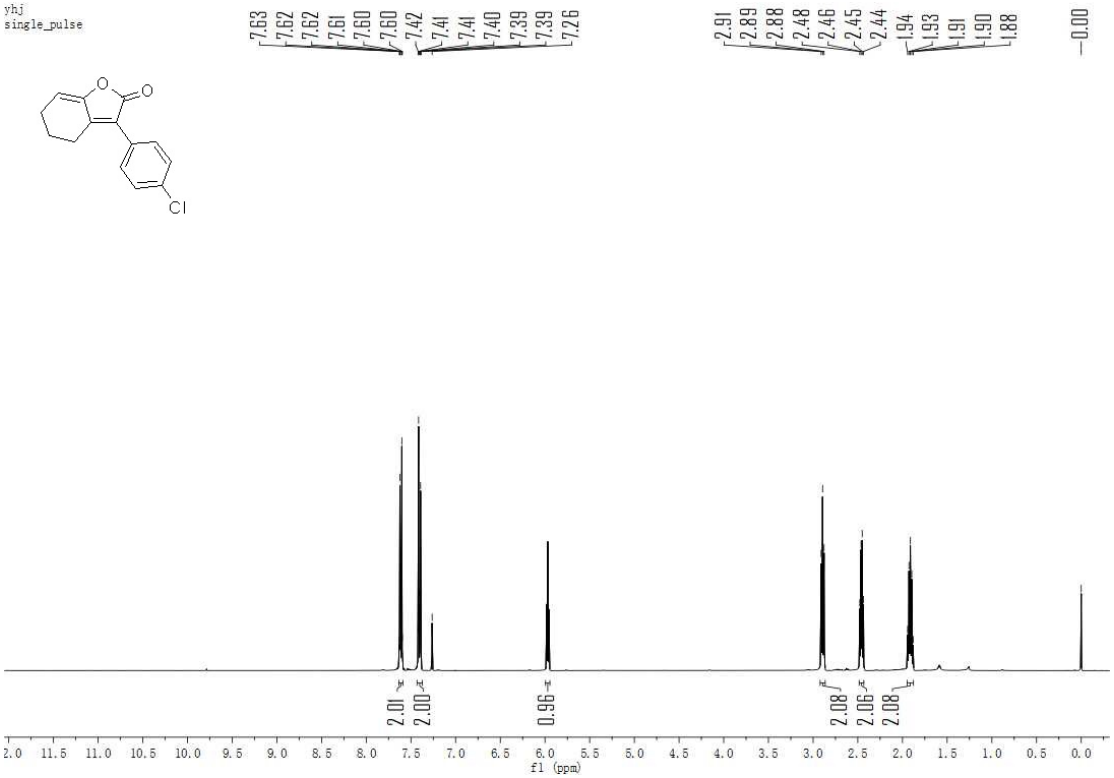
^{1}H NMR spectrum of 4ac



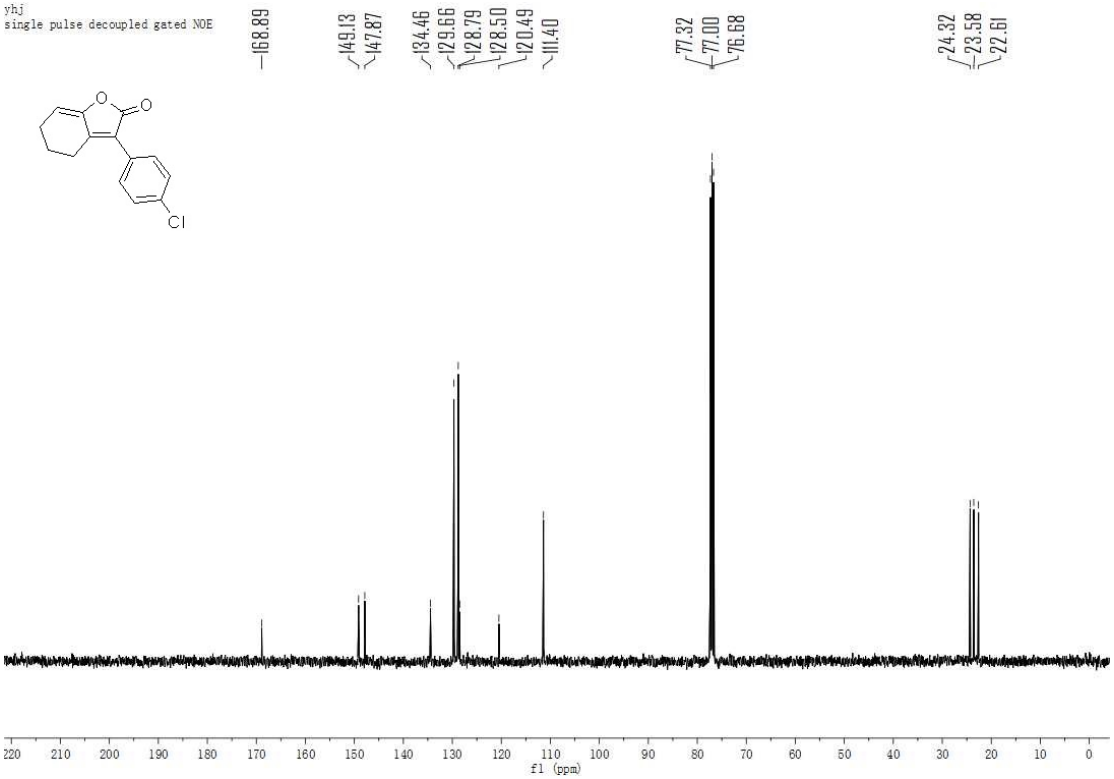
^{13}C NMR spectrum of 4ac



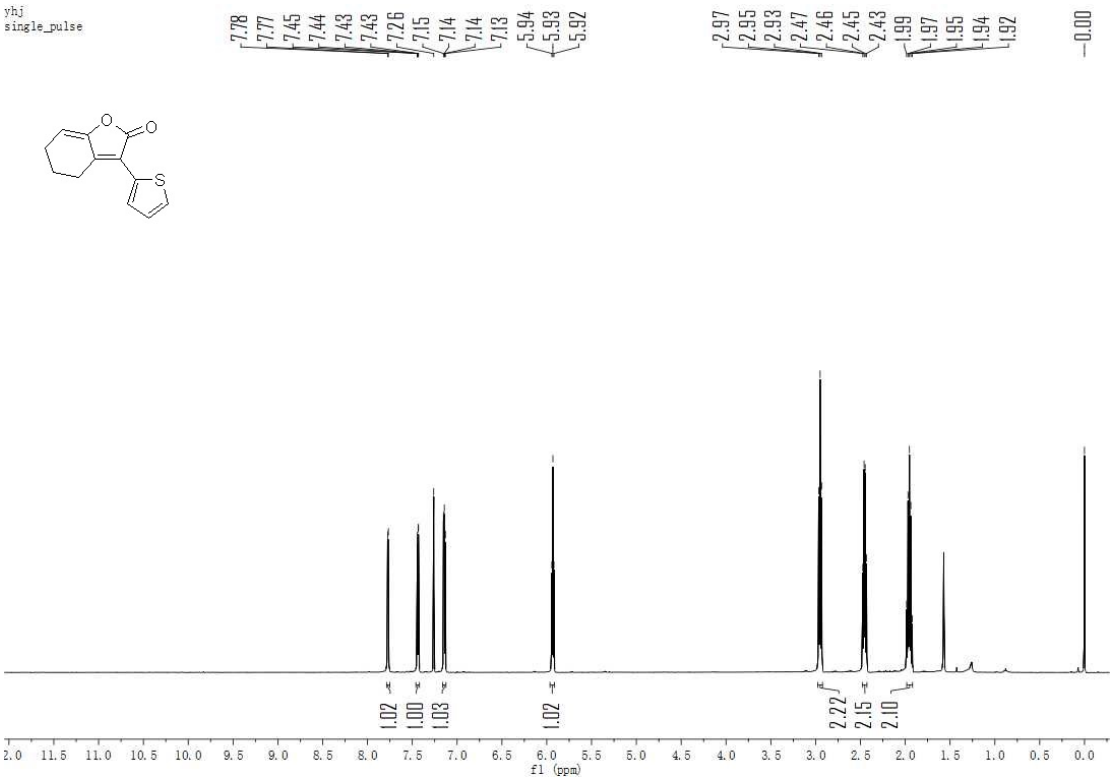
^{1}H NMR spectrum of 4ad



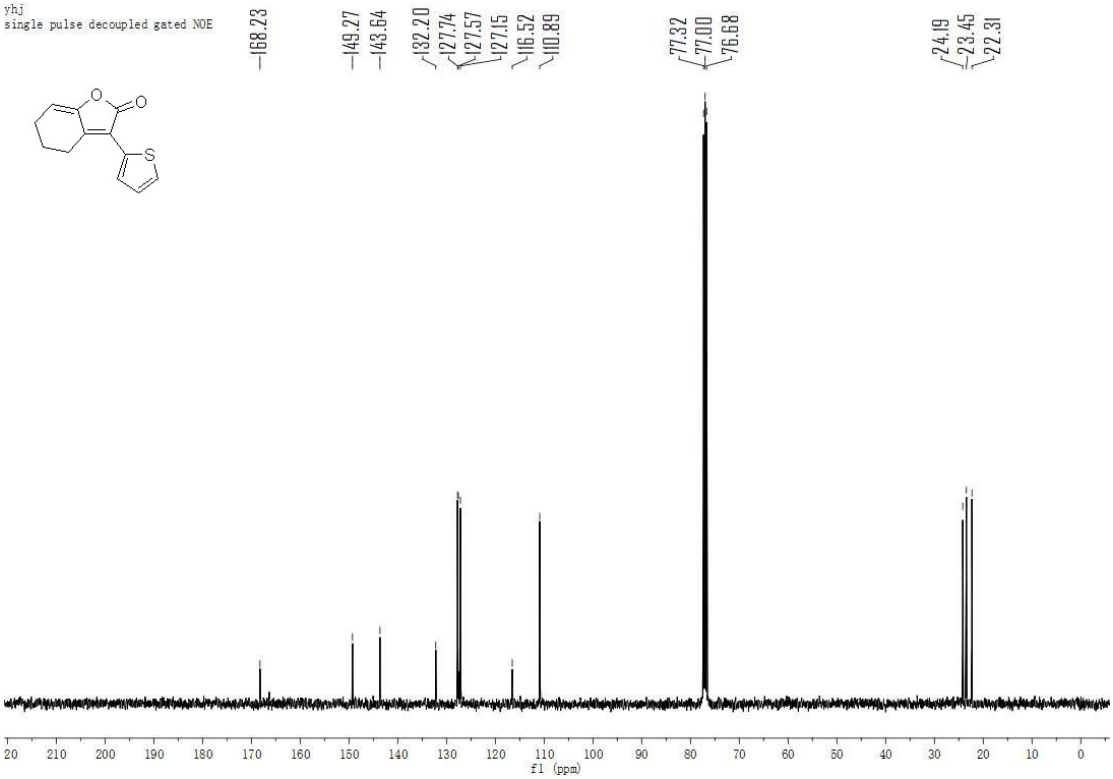
^{13}C NMR spectrum of 4ad



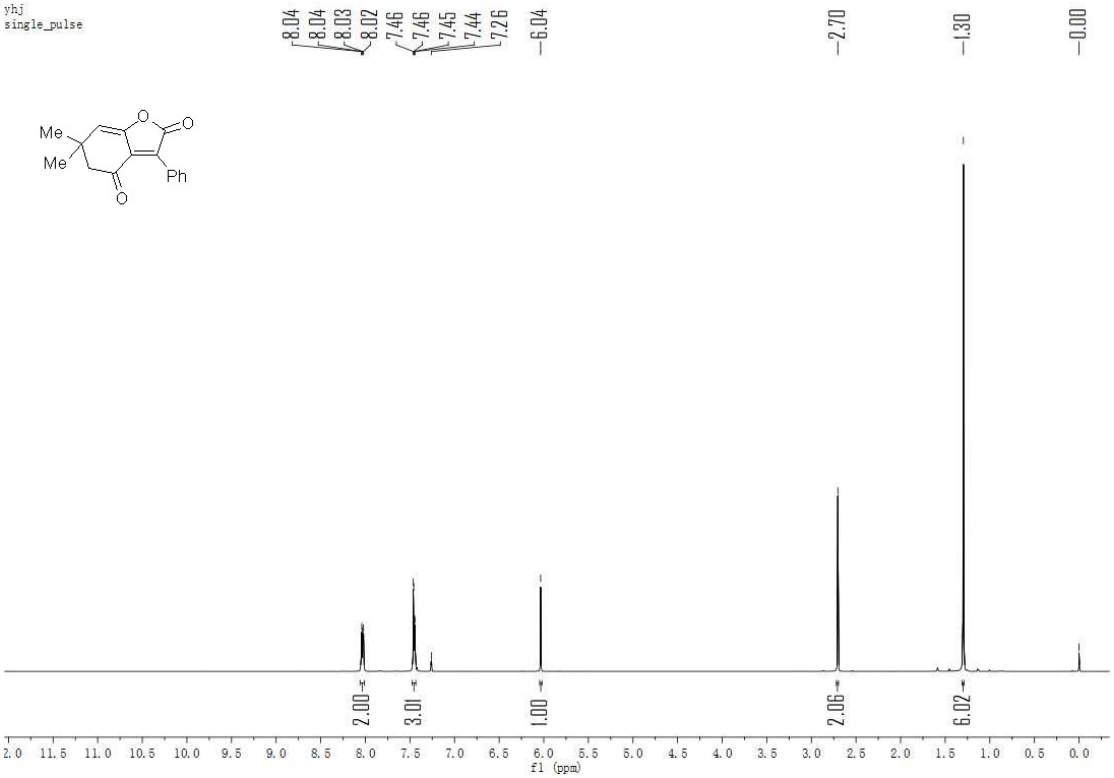
^{1}H NMR spectrum of 4ae



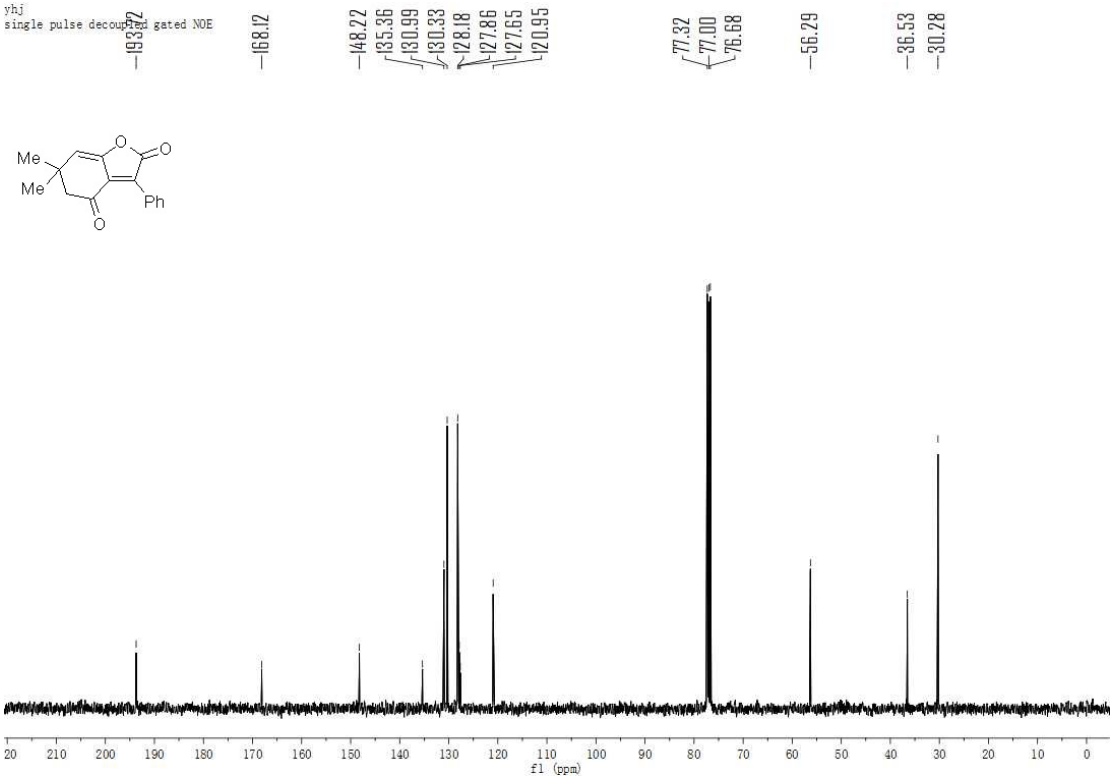
^{13}C NMR spectrum of 4ae



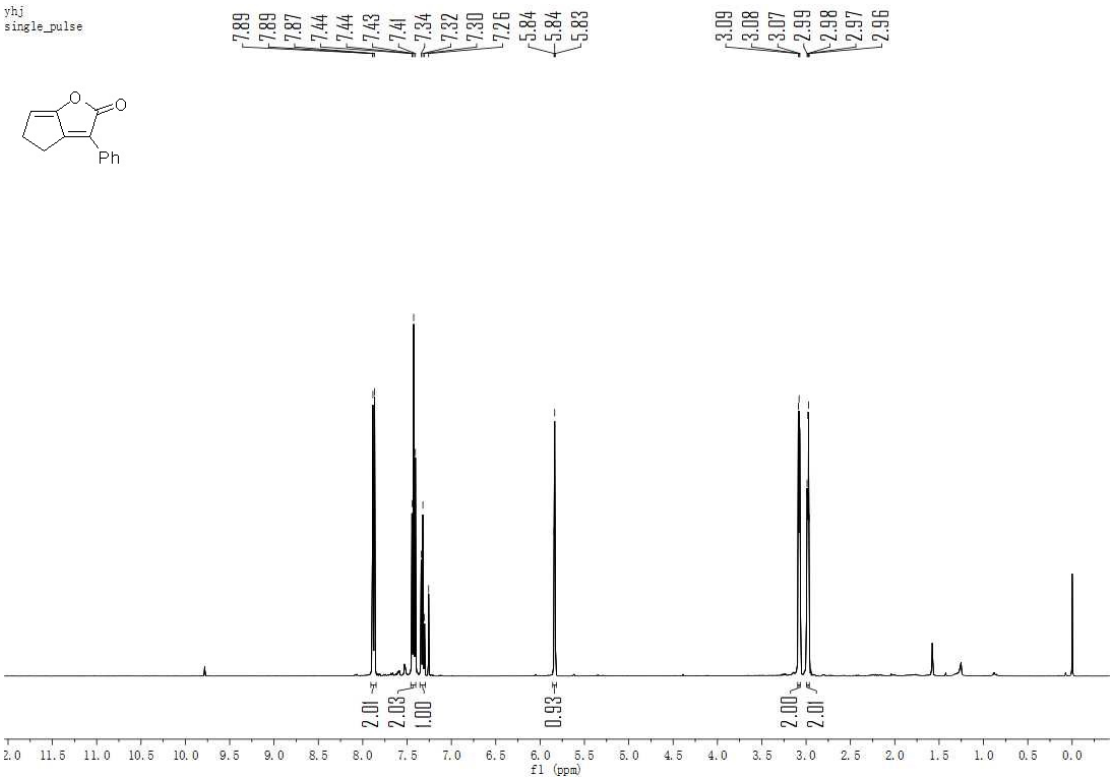
^{1}H NMR spectrum of 4af



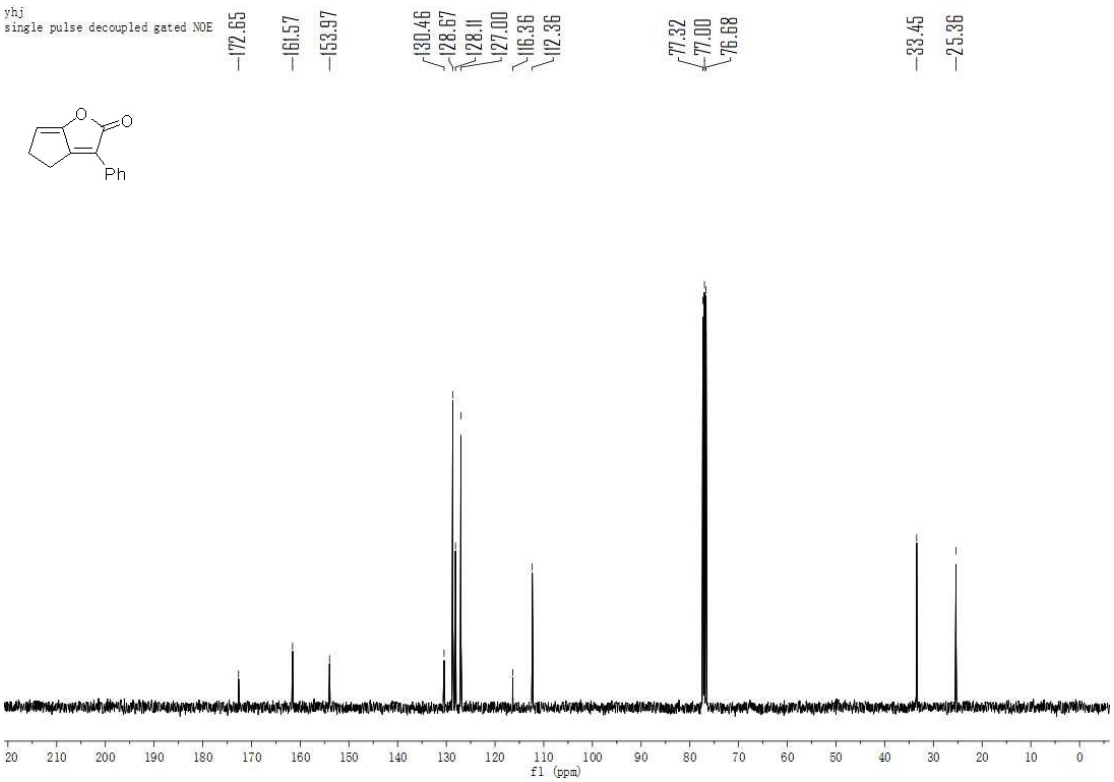
^{13}C NMR spectrum of 4af



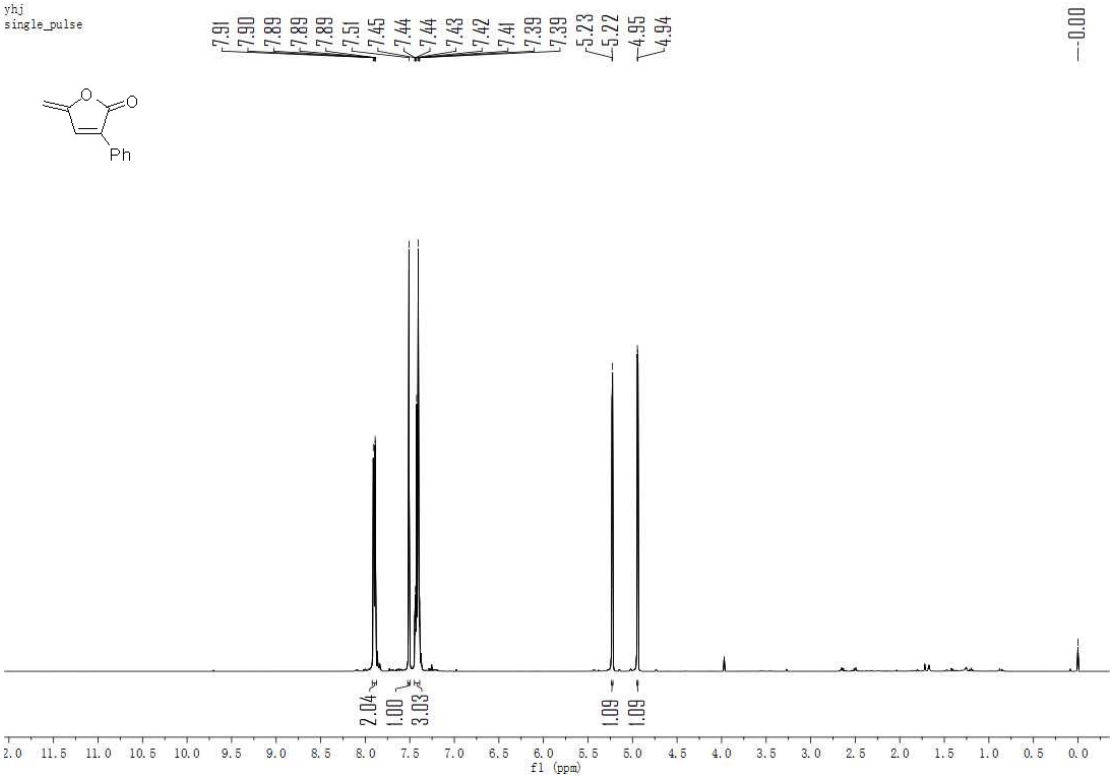
^{1}H NMR spectrum of 4ag



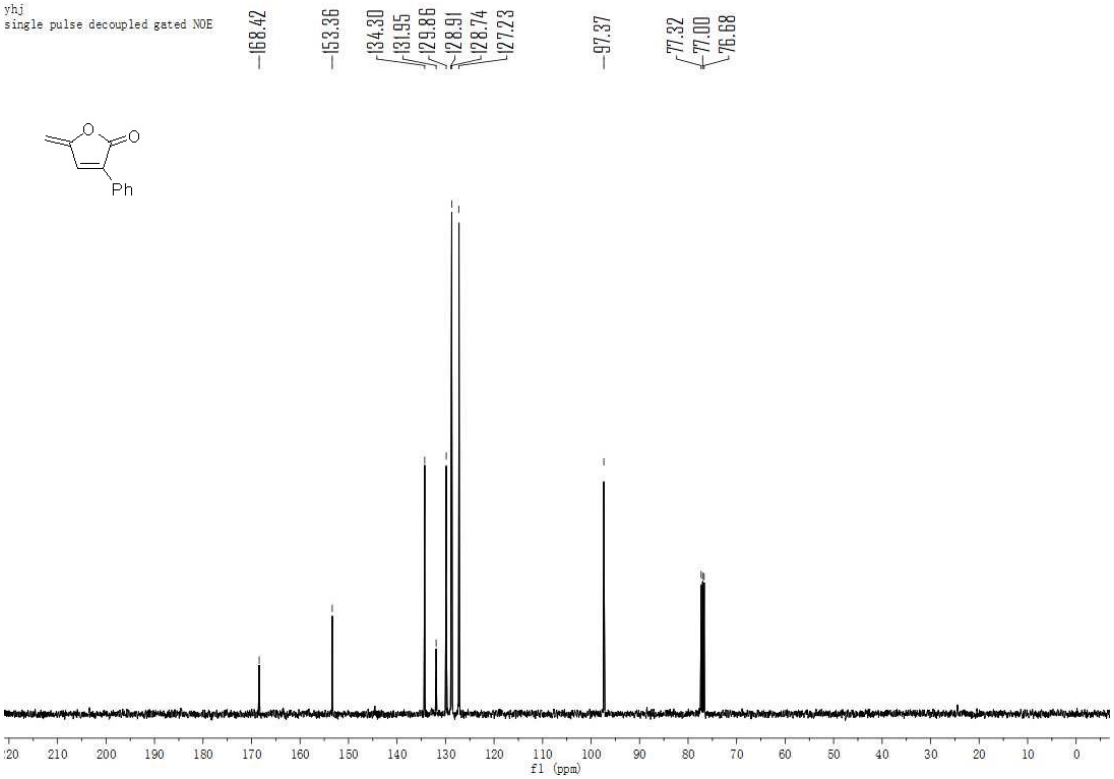
^{13}C NMR spectrum of 4ag



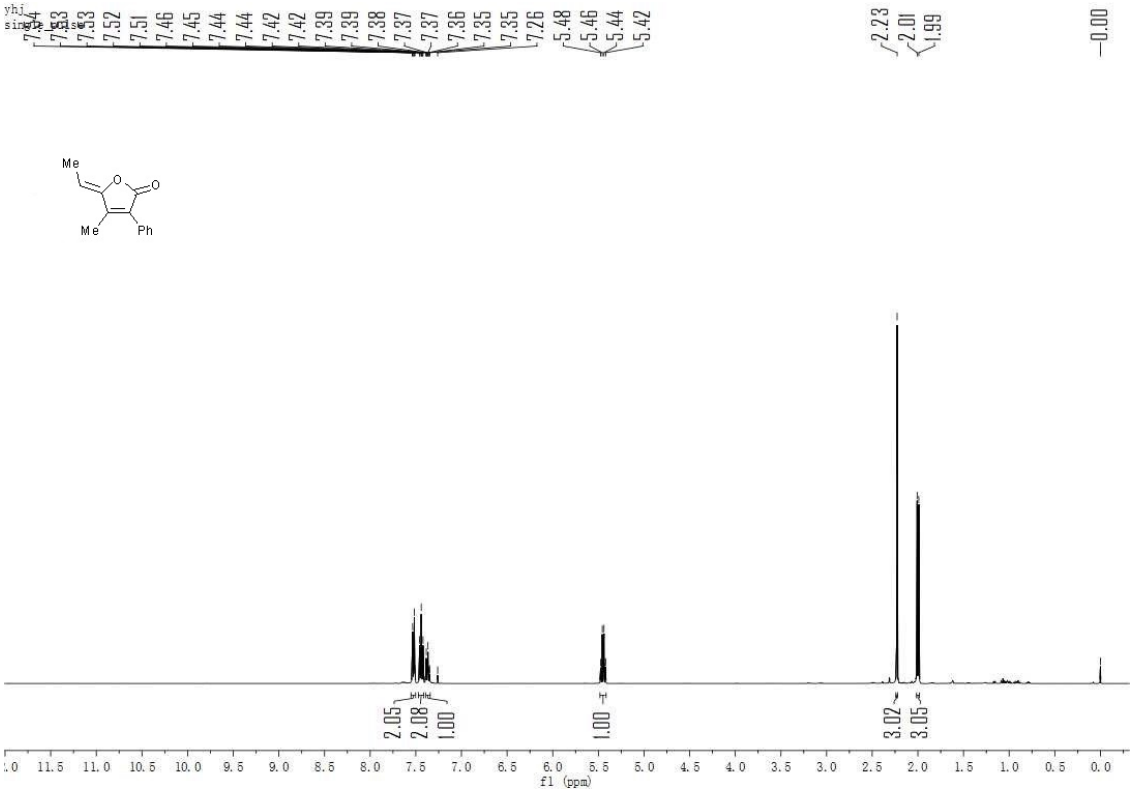
^{1}H NMR spectrum of 4ah



^{13}C NMR spectrum of 4ah



^{1}H NMR spectrum of 4ai



^{13}C NMR spectrum of 4ai