Supporting Information

for

Copper(I) anchored on covalent triazine framework/ionic liquid as a recyclable catalytic system for cyclization of propargylic amines with CO_2 under ambient conditions

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1. General Information

All commercial reagents were used directly without further purification. Analytical thin-layer chromatography (TLC) was visualized with UV light at 254 nm. Thin-layer chromatography was carried out on TLC aluminum sheets with silica gel 60 F254. Melting points were measured on an X-4 digital melting point apparatus without correction. Infrared (IR) spectra were recorded in the range 4000-600 cm^{-1} using KBr pellets on a Thermo Fisher Nicolet IS50 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Zhongke Niujin AS 400 spectrometer using $CDCl_3$ as the solvent. Chemical shifts are reported as δ (ppm) values relative to TMS as the internal standard and coupling constants (*J*) in Hz. Mass spectra were recorded on an Agilent 6545LC/Q-TOF instrument with an electrospray ionization (ESI) source. Products are purified by flash chromatography column on 200−300 mesh silica gel. Chemical yields refer to pure isolated products.

2. Experimental

2.1. Preparation of CTF:

In a two-necked flask, melamine (1.26 g, 10 mmol) and KOH (1.12 g, 20 mmol) was dissolved in DMSO (100 mL), and the mixture was cooled down to 15 °C under a nitrogen atmosphere. To this cooled solution, cyanuric chloride (1.84 g, 10 mmol) dissolved in anhydrous DMSO (100 mL) was added dropwise over a period of 2 h. Then, the solution was warmed to room temperature and followed by refluxing at 160 °C for 10 h. Finally, the as-prepared precipitate was separated and rinsed with methanol and DI water. white sediment was obtained after drying in an oven at 60 °C overnight.

2.2. Preparation of Cu(I)/CTF:

The Cu(I)/CTF catalyst was prepared by anchoring CuCl onto the CTF support. First, 200 mg of CTF was added to a mixture of 20 mL of ethanol and 158 mg (1.6 mmol) of CuCl. The mixture was sonicated for 0.5 h. Then, it was continuously stirred under reflux for 4 h. Subsequently, the resulting Cu(I)/CTF was filtered and washed three times with 10 mL of ethanol each time. Finally, the obtained sample was dried under vacuum at 60 °C for 8 h.

2.3. Preparation of $[HDBU^+][TFE^-]$:

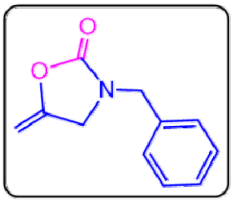
1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (152 g, 1.0 mol) was dropped into the 2,2,2-trifluoroethanol (TFE) (100 g, 1.0 mol) at room temperature in 1 h. After the addition, the reaction mixture was stirred for an addition period of 48 h to ensure the reaction had proceeded to completion.

2.4. General procedure for synthesis of 2-oxazolidinones :

Propargylamine (1.0 mmol), Cu(I)/CTF (30 mg) and $[HDBU^+][TFE^-]$ (0.05 mmol) were successively added into a 25 mL Schlenk flask. The reaction mixture was stirred at room temperature for 6 h under a CO_2 atmosphere (1 atm, using a balloon). After the reaction, excess CO_2 was carefully discharged. The reaction mixture was extracted three times with ethyl acetate (3 × 10 mL). The solvent was removed under reduced pressure, and the crude product was purified by column chromatography, using petroleum ether/EtOAc as eluent. The recovered catalyst and IL were dried for later

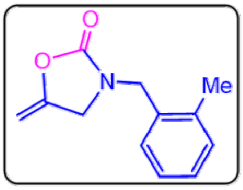
3. Spectra data of all products

3-Benzyl-5-methyleneoxazolidin-2-one **(2a)**



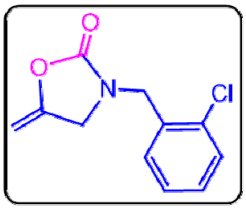
White crystal (180 mg, 0.95 mmol, 95%); m.p.: 51 - 52 ℃; IR(KBr):2923, 1781, 1676, 1425, 1281, 1057, 967, 832, 701, 619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.38 - 7.28 (m, 5H), 4.74 (dd, J = 5.3, 2.6 Hz, 1H), 4.46 (s, 2H), 4.26 - 4.21 (m, 1H), 4.02 (t, J = 2.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.69, 148.97, 134.99, 129.01, 128.21, 86.81, 47.90, 47.26, 29.72. HRMS (ESI-TOF) calculated for $C_{11}H_{11}NO_2$ $[M+H]^+$ *m/z* 190.0863, found 190.0860.

3-(2-Methylbenzyl)-5-methyleneoxazolidin-2-one **(2b)**



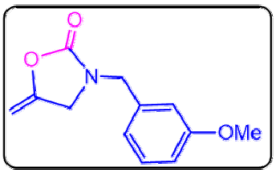
White crystal (187 mg, 0.92 mmol, 92%); m.p.: 59 - 60 ℃; IR(KBr): 2923, 1734, 1675, 1577, 1473, 1383, 1280, 1189, 1061, 966 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.38 - 7.12 (m, 4H), 4.74 (d, J = 2.0 Hz, 1H), 4.50 (s, 2H), 4.23 (s, 1H), 3.96 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.36, 149.01, 136.95, 132.75, 130.95, 129.12, 128.51, 126.36, 86.79, 47.31, 46.07, 19.08. HRMS (ESI-TOF) calculated for $C_{12}H_{13}NO_2$ $[M+H]^+$ *m/z* 204.1019, found 204.1016.

3-(2-Chlorobenzyl)-5-methyleneoxazolidin-2-one **(2c)**



White crystal (194 mg, 0.87 mmol, 87%); m.p.: 59 - 60 ℃; IR(KBr): 2924, 1782, 1676, 1575, 1420, 1317, 1280, 1181, 1066, 966 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.42 - 7.33 (m, 2H), 7.31 - 7.24 (m, 2H), 4.75 (d, J = 2.2 Hz, 1H), 4.62 (s, 2H), 4.26 (d, J = 1.9 Hz, 1H), 4.09 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.61, 148.95, 133.88, 132.71, 130.41, 129.87, 129.74, 127.54, 86.91, 47.69, 45.17. HRMS (ESI-TOF) calculated for $C_{11}H_{10}ClNO_2$ $[M+H]^+$ *m/z* 224.0473, found 224.0470.

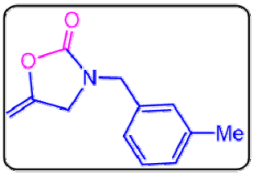
3-(3-Methoxybenzyl)-5-methyleneoxazolidin-2-one **(2d)**



Light yellow oil (208 mg, 0.95 mmol, 95%); IR(KBr): 1782, 1677, 1601, 1420, 1283, 1165, 1063, 971, 913, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.26 - 7.22 (m, 1H), 6.83 - 6.78 (m, 3H), 4.69 (d, J = 2.6 Hz, 1H), 4.39 (s, 2H), 4.21 (d, J = 2.3 Hz, 1H), 4.00 (s, 2H), 3.77 (s, 3H). ^{13}C

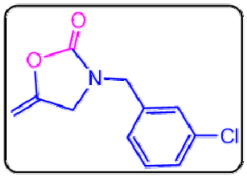
NMR (100 MHz, $CDCl_3$) δ = (ppm) 160.09, 155.66, 149.03, 136.57, 130.04, 120.36, 113.73, 113.61, 86.74, 55.29, 47.78, 47.28. HRMS (ESI-TOF) calculated for $C_{12}H_{13}NO_3$ $[M+H]^+$ *m/z* 220.0968, found 220.0966.

3-(3-Methylbenzyl)-5-methyleneoxazolidin-2-one **(2e)**



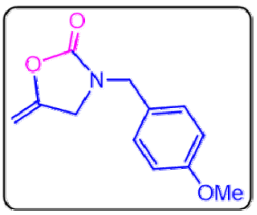
Light yellow oil (189 mg, 0.93 mmol, 93%); IR(KBr): 2922, 1691, 1560, 1473, 1382, 1280, 1166, 1061, 968, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.30 -7.27 (m, 1H), 7.18 - 7.09 (m, 3H), 4.77 (dd, *J* = 5.3, 2.6 Hz, 1H), 4.46 (s, 2H), 4.27 (d, *J* = 2.8 Hz, 1H), 4.05 (t, *J* = 2.2 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.69, 149.07, 138.84, 134.93, 129.04, 128.92, 125.28, 86.73, 47.87, 47.28, 21.39. HRMS (ESI-TOF) calculated for $C_{12}H_{13}NO_2$ $[M+H]^+$ *m/z* 204.1019, found 204.1016.

3-(3-Chlorobenzyl)-5-methyleneoxazolidin-2-one **(2f)**



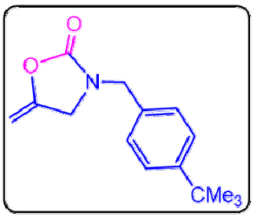
Yellow oil (196 mg, 0.88 mmol, 88%); IR(KBr): 1782, 1693, 1599, 1473, 1319, 1281, 1168, 1064, 969, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.28 - 7.26 (m, 3H), 7.16 (d, *J* = 5.1 Hz, 1H), 4.72 (d, *J* = 2.2 Hz, 1H), 4.42 (s, 2H), 4.26 (s, 1H), 4.05 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.63, 148.79, 137.21, 134.74, 130.34, 128.42, 128.12, 126.29, 87.04, 47.33, 47.24. HRMS (ESI-TOF) calculated for $C_{11}H_{10}ClNO_2$ $[M+H]^+$ *m/z* 224.0473, found 224.0471.

3-(4-Methoxybenzyl)-5-methyleneoxazolidin-2-one **(2g)**



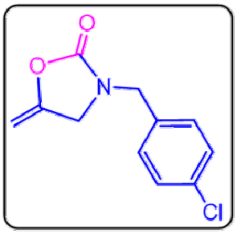
Yellow crystal (208 mg, 0.95 mmol, 95%); m.p.: 55 - 56 °C; IR(KBr): 1783, 1678, 1514, 1419, 1281, 1247, 1176, 1062, 1031, 838 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.23 - 7.21 (m, 2H), 6.92 - 6.90 (m, 2H), 4.74 (dd, *J* = 5.3, 2.5 Hz, 1H), 4.42 (s, 2H), 4.25 (d, *J* = 2.6 Hz, 1H), 4.02 (t, *J* = 2.1 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 159.59, 155.60, 149.08, 129.62, 127.01, 114.34, 86.67, 55.34, 47.27, 47.11. HRMS (ESI-TOF) calculated for $C_{12}H_{13}NO_3$ $[M+H]^+$ *m/z* 220.0968, found 220.0965.

3-(4-(*Tert*-butyl)benzyl)-5-methyleneoxazolidin-2-one **(2h)**



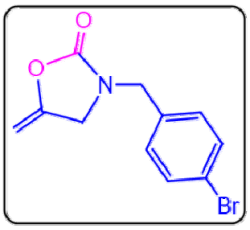
White crystal (228 mg, 0.93 mmol, 93%); m.p.: 111 - 112 °C; IR(KBr): 2962, 2867, 1782, 1654, 1560, 1473, 1315, 1281, 1061, 748cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.42 - 7.40 (m, 2H), 7.25 - 7.23 (m, 2H), 4.76 (d, J = 2.0 Hz, 1H), 4.47 (s, 2H), 4.26 (s, 1H), 4.06 (s, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.65, 151.35, 149.10, 131.93, 128.01, 125.90, 86.67, 47.52, 47.29, 34.62, 31.33. HRMS (ESI-TOF) calculated for $C_{15}H_{19}NO_2$ [M +H]$^+$ *m/z* 246.1489, found 246.1486.

3-(4-Chlorobenzyl)-5-methyleneoxazolidin-2-one **(2i)**



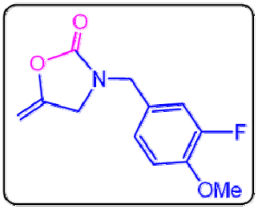
White crystal (198 mg, 0.89 mmol, 89%); m.p.: 89 - 91 °C; IR(KBr): 1778, 1675, 1491, 1407, 1280, 1236, 1060, 967, 876, 831 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.35 - 7.33 (m, 2H), 7.23 - 7.21 (m, 2H), 4.76 (d, J = 2.2 Hz, 1H), 4.43 (s, 2H), 4.26 (d, J = 1.9 Hz, 1H), 4.02 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.65, 148.71, 134.26, 133.55, 129.55, 129.22, 87.10, 47.24. HRMS (ESI-TOF) calculated for $C_{11}H_{10}ClNO_2$ [M +H]$^+$ *m/z* 224.0473, found 224.0471.

3-(4-Bromobenzyl)-5-methyleneoxazolidin-2-one **(2j)**



White crystal (237 mg, 0.89 mmol, 89%); m.p.: 85 - 86 °C; IR(KBr): 2922, 1785, 1629, 1560, 1466, 1383, 1280, 1190, 1067, 968 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.51 - 7.49 (m, 2H), 7.17 - 7.15 (m, 2H), 4.76 (d, J = 2.4 Hz, 1H), 4.42 (s, 2H), 4.26 (s, 1H), 4.02 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 148.68, 134.05, 132.19, 129.87, 122.36, 87.14, 47.31, 47.23. HRMS (ESI-TOF) calculated for $C_{11}H_{10}BrNO_2$ [M +H]$^+$ *m/z* 267.9968, found 267.9965.

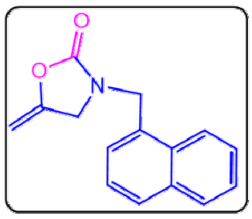
3-(3-Fluoro-4-methoxybenzyl)-5-methyleneoxazolidin-2-one **(2k)**



White crystal (220 mg, 0.93 mmol, 93%); m.p.: 105 - 107 °C; IR(KBr): 1781, 1676, 1518, 1420, 1276, 1223, 1124, 1063, 1024, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.08 - 7.01 (m, 2H), 6.99 - 6.95 (m, 1H), 4.77 (d, J = 2.7 Hz, 1H), 4.41 (s, 2H), 4.28 (d, J = 2.5 Hz, 1H), 4.05 (d, J = 2.0 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.58, 152.42

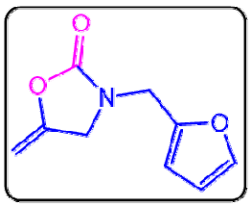
(d, $J_{C\text{-}F}$=246.0), 148.82, 147.71, 147.60, 127.87 (d, $J_{C\text{-}F}$=6.0), 124.16 (d, $J_{C\text{-}F}$=3.0), 116.00 (d, $J_{C\text{-}F}$=19.0), 113.68, 113.67, 86.96, 56.32, 47.17, 47.02. HRMS (ESI-TOF) calculated for $C_{12}H_{12}FNO_3$ $[M+H]^+$ *m/z* 238.0874, found 238.0871.

5-Methylene-3-(naphthalen-1-ylmethyl)oxazolidin-2-one **(2l)**



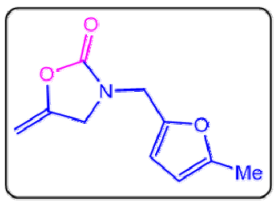
White crystal (224 mg, 0.94 mmol, 94%); m.p.: 112 - 114 ℃; IR(KBr): 1780, 1675, 1510, 1420, 1279, 1057, 964, 875, 792, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 8.14 - 8.12 (m, 1H), 7.90 -7.85 (m, 2H), 7.60 -7.52 (m, 2H), 7.47 - 7.37 (m, 2H), 4.91 (s, 2H), 4.68 (d, J = 2.7 Hz, 1H), 4.14 (d, J = 2.5 Hz, 1H), 3.89 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.30, 149.03, 133.98, 131.48, 130.56, 129.51, 128.87, 127.63, 127.18, 126.37, 125.20, 123.42, 86.79, 47.36, 46.18. HRMS (ESI-TOF) calculated for $C_{15}H_{13}NO_2$ $[M+H]^+$ *m/z* 240.1019, found 240.1017.

3-(Furan-2-ylmethyl)-5-methyleneoxazolidin-2-one **(2m)**



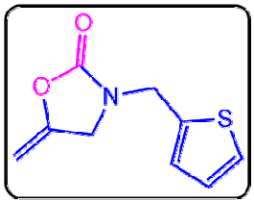
Yellow oil (161 mg, 0.90 mmol, 90%); IR(KBr): 1782, 1677, 1473, 1436, 1280, 1078, 1061, 1002, 967, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.38 - 7.40 (m, 1H), 6.34 - 6.31 (m, 2H), 4.74 (s, 1H), 4.46 (s, 2H), 4.27 (s, 1H), 4.12 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.32, 148.90, 148.72, 143.06, 110.57, 109.25, 86.87, 47.63, 40.39. HRMS (ESI-TOF) calculated for $C_9H_9NO_3$ $[M+H]^+$ *m/z* 180.0655, found 180.0653.

5-Methylene-3-((5-methylfuran-2-yl)methyl)oxazolidin-2-one **(2n)**



Yellow crystal (175 mg, 0.91 mmol, 91%); m.p.: 109 - 111 ℃; IR(KBr): 2922, 1787, 1631, 1555, 1384, 1314, 1112, 913, 779, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 6.19 - 6.18 (m, 1H), 5.92 - 5.91 (m, 1H), 4.74 (s, 1H), 4.40 (s, 2H), 4.27 (s, 1H), 4.12 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 110.18, 106.42, 86.75, 47.58, 40.52, 13.64. HRMS (ESI-TOF) calculated for $C_{10}H_{11}NO_3$ $[M+H]^+$ *m/z* 194.0812, found 194.0810.

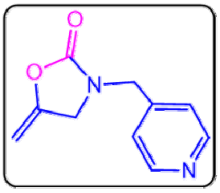
5-Methylene-3-(thiophen-2-ylmethyl)oxazolidin-2-one **(2o)**



Yellow oil (179 mg, 0.92 mmol, 92%); IR(KBr): 1782, 1677, 1420, 1280, 1233, 1136, 1065, 1037, 966, 876 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.30 (d, J = 5.1 Hz, 1H), 7.03 - 6.99 (m, 2H), 4.75 (d,

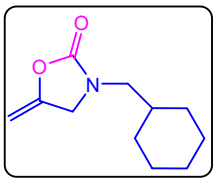
J = 2.6 Hz, 1H), 4.67 (s, 2H), 4.29 (d, J = 2.1 Hz, 1H), 4.13 (d, J = 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.22, 148.86, 137.09, 127.50, 127.20, 126.29, 86.97, 47.10, 42.21. HRMS (ESI-TOF) calculated for $C_9H_9NO_2S$ $[M+H]^+$ *m/z* 196.0427, found 196.0425.

5-Methylene-3-(pyridin-4-ylmethyl)oxazolidin-2-one **(2p)**



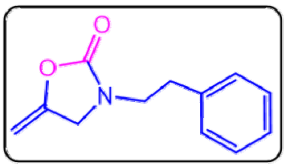
White crystal (169 mg, 0.89 mmol, 89%); m.p.: 62 - 63 ℃; IR(KBr): 1602, 1560, 1442, 1414, 1328, 1115, 1065, 993, 982, 795 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 8.58 (d, J = 4.5 Hz, 2H), 7.34 (d, J = 4.4 Hz, 2H), 3.74 (s, 2H), 3.45 (s, 2H), 2.33 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 149.88, 147.09, 123.93, 78.32, 73.66, 55.85, 42.14. HRMS (ESI-TOF) calculated for $C_{10}H_{10}N_2O_2$ $[M+H]^+$ *m/z* 191.0815, found 191.0811.

3-(Cyclohexylmethyl)-5-methyleneoxazolidin-2-one **(2q)**



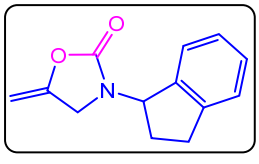
Yellow crystal (179 mg, 0.92 mmol, 92%); m.p.: 33 - 35 ℃; IR(KBr):2924, 2852, 1782, 1690, 1426, 1282, 1129, 1044, 966, 825 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 4.63 (d, J = 2.2 Hz, 1H), 4.22 (d, J = 1.8 Hz, 1H), 4.12 (s, 2H), 3.04 (d, J = 7.3 Hz, 2H), 1.67 - 1.50 (m, 6H), 1.17 - 1.07 (m, 3H), 0.93 - 0.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.83, 149.26, 86.12, 49.99, 48.51, 35.84, 30.45, 26.21, 25.56. HRMS (ESI-TOF) calculated for $C_{11}H_{17}NO_2$ $[M+H]^+$ *m/z* 196.1332, found 196.1330.

5-Methylene-3-phenethyloxazolidin-2-one **(2r)**



Yellow oil (190 mg, 0.94 mmol, 94%); IR(KBr):1782, 1629, 1560, 1455, 1315, 1281, 1061, 1004, 751, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.34 - 7.30 (m, 2H), 7.24 -7.21 (m, 3H), 4.70 (dd, J = 5.3, 2.6 Hz, 1H), 4.21 (d, J = 2.6 Hz, 1H), 3.99 (t, J = 2.1 Hz, 2H), 3.56 (t, J = 7.3 Hz, 2H), 2.89 (t, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.49, 149.03, 137.97, 128.81, 128.62, 126.85, 86.50, 48.44, 45.20, 33.97. HRMS (ESI-TOF) calculated for $C_{12}H_{13}NO_2$ $[M+H]^+$ *m/z* 204.1019, found 204.1015.

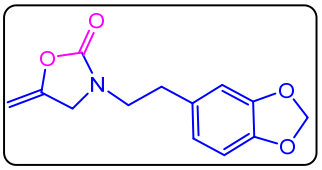
3-(2,3-Dihydro-1*H*-inden-1-yl)-5-methyleneoxazolidin-2-one **(2s)**



Yellow oill (196 mg, 0.91 mmol, 91%); IR(KBr): 2942, 1781, 1691, 1417, 1355, 1281, 1090, 959, 831, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.29 -7.23 (m, 4H), 5.59 (t, J = 7.3 Hz, 1H), 4.74 (s,

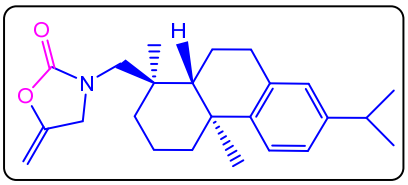
1H), 4.25 (s, 1H), 4.03 -3.99 (m, 1H), 3.84 - 3.80 (m, 1H), 3.08 - 2.90 (m, 2H), 2.52 - 2.43 (m, 1H), 2.06 - 1.97(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 155.46, 149.35, 143.51, 139.17, 128.63, 127.05, 125.20, 124.29, 86.70, 58.10, 43.71, 30.40, 29.13. HRMS (ESI-TOF) calculated for $C_{13}H_{13}NO_2$ $[M+H]^+$ *m/z* 216.1019, found 216.1015.

3-(2-(Benzo[*d*][1,3]dioxol-5-yl)ethyl)-5-methyleneoxazolidin-2-one **(2t)**



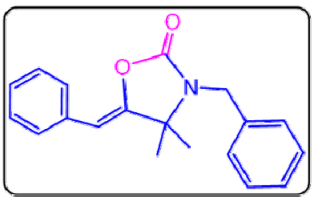
Light yellow crystal (220 mg, 0.89 mmol, 89%); m.p.: 66 - 68 ℃; IR(KBr): 1779, 1691, 1503, 1425, 1281, 1189, 1099, 927, 836, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 6.71 - 6.61 (m, 3H), 5.89 (s, 2H), 4.66 (d, J = 1.2 Hz, 1H), 4.22 - 4.18 (m, 1H), 4.00 (s, 2H), 3.46 (t, J = 7.1 Hz, 2H), 2.76 (t, J = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3) δ = (ppm) 155.46, 149.09, 147.91, 146.40, 131.66, 121.56, 108.90, 108.48, 100.03, 86.47, 48.37, 45.27, 33.60. HRMS (ESI-TOF) calculated for $C_{13}H_{13}NO_4$ $[M+H]^+$ *m/z* 248.0917, found 248.0915.

3-(((1*R*,4a*S*,10a*R*)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-5-methyleneoxazolidin-2-one **(2u)**



White crystal (297 mg, 0.81 mmol, 81%); m.p.: 156 - 158 ℃; IR(KBr): 2927, 1786, 1692, 1497, 1382, 1282, 1067，963, 821, 757 cm^{-1}; ^{1}H NMR (400 MHz, CDCl3) δ = (ppm) 7.18 (d, J = 8.2 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.91 (s, 1H), 4.72 (d, *J* = 2.4 Hz, 1H), 4.25 (d, *J* = 1.8 Hz, 3H), 3.22 - 3.19 (m, 1H), 3.12 - 3.08 (m, 1H), 3.00 - 2.80 (m, 3H), 2.33 - 2.29(m, 1H), 1.96 - 1.91(m, 1H), 1.83 - 1.66 (m, 3H), 1.53 - 1.34 (m, 4H), 1.23 (d, J = 6.5 Hz, 9H), 0.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 157.24, 149.02, 147.03, 145.78, 134.53, 127.02, 124.11, 123.97, 86.36, 57.01, 52.18, 45.19, 39.06, 38.21, 37.52, 37.23, 33.48, 30.06, 25.61, 24.05, 19.07, 18.91, 18.65. HRMS (ESI-TOF) calculated for $C_{24}H_{33}NO_2$ $[M+H]^+$ *m/z* 368.2584, found 368.2581.

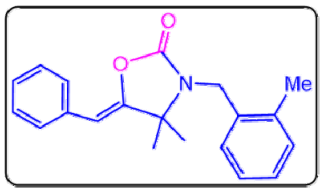
(*E*)-2-Benzyl-4-benzylidene-3,3-dimethylisoxazolidin-5-one **(4a)**



Yellow crystal (267 mg, 0.91 mmol, 91%); m.p.: 88 - 90 ℃; IR(KBr): 2976, 1777, 1689, 1432, 1397, 1190, 1040, 953, 753, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.66 - 7.64 (m, 2H), 7.40 - 7.36 (m, 7H), 7.28 - 7.24 (m, 1H), 5.50 (s, 1H), 4.56 (s, 2H), 1.43 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ = (ppm) 154.84, 153.43, 137.54, 133.61, 128.77,

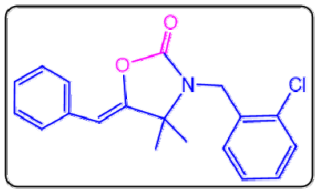
128.54, 128.38, 127.86, 127.79, 126.87, 100.71, 62.49, 44.18, 27.76. HRMS (ESI-TOF) calculated for $C_{19}H_{19}NO_2$ $[M+H]^+$ *m/z* 294.1489, found 294.1486.

(*E*)-4-Benzylidene-3,3-dimethyl-2-(2-methylbenzyl)isoxazolidin-5-one **(4b)**



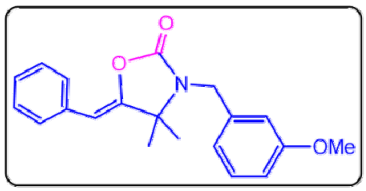
White crystal (286 mg, 0.93 mmol, 93%); m.p.: 95 - 97 °C; IR(KBr): 1780, 1689, 1448, 1396, 1368, 1305, 1192, 1040, 955, 913 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.68 -7.67 (m, 2H), 7.39 - 7.25 (m, 7H), 5.53 (s, 1H), 4.61 (s, 2H), 2.44 (s, 3H), 1.41 (s,6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 154.54, 153.55, 136.05, 134.68, 133.68, 130.80, 128.57, 128.42, 128.17, 127.99, 126.89, 126.29, 100.70, 62.53, 42.56, 27.50, 19.30. HRMS (ESI-TOF) calculated for $C_{20}H_{21}NO_2$ $[M+H]^+$ *m/z* 308.1645, found 308.1642.

(*E*)-4-Benzylidene-2-(2-chlorobenzyl)-3,3-dimethylisoxazolidin-5-one **(4c)**



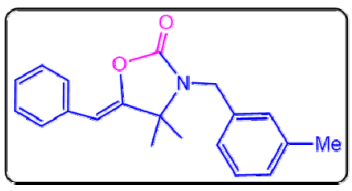
Light yellow crystal (288 mg, 0.88 mmol, 88%); m.p.: 83 - 84 °C; IR(KBr): 1785, 1690, 1599, 1447, 1396, 1309, 1255, 1190, 1046, 957, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.67 -7.65 (m, 2H), 7.52 - 7.50 (m, 1H), 7.42 -7.36 (m, 3H), 7.30 - 7.25 (m, 3H), 5.54 (s, 1H), 4.72 (s, 2H), 1.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 154.84, 153.29, 134.88, 133.54, 132.63, 129.64, 129.46, 129.15, 128.57, 128.41, 127.40, 126.95, 100.98, 62.49, 40.92, 27.48. HRMS (ESI-TOF) calculated for $C_{19}H_{18}ClNO_2$ $[M+H]^+$ *m/z* 328.1099, found 328.1095.

(*E*)-4-Benzylidene-2-(3-methoxybenzyl)-3,3-dimethylisoxazolidin-5-one **(4d)**



Yellow crystal (307 mg, 0.95 mmol, 95%); m.p.:88 - 89°C, IR(KBr): 2926, 1777, 1688, 1586, 1489, 1396, 1282, 1188, 1039, 913cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm)7.65 -7.63 (m, 2H), 7.39 - 7.36 (m, 2H), 7.30 - 7.25 (m, 2H), 6.98 - 6.95 (m, 2H), 6.88 - 6.86 (m, 1H), 5.49 (s, 1H), 4.53 (s, 2H), 3.84 (s, 3H), 1.44 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 159.93, 154.83, 153.39, 139.14, 133.56, 129.78, 128.53, 128.36, 126.87, 120.03, 113.34, 113.29, 100.71, 62.49, 55.30, 44.15, 27.73. HRMS (ESI-TOF) calculated for $C_{20}H_{21}NO_3$ $[M+H]^+$ *m/z* 324.1594, found 324.1590.

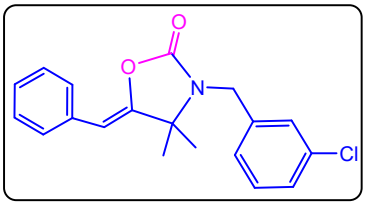
(*E*)-4-Benzylidene-3,3-dimethyl-2-(3-methylbenzyl)isoxazolidin-5-one **(4e)**



Yellow crystal (289 mg, 0.94 mmol, 94%); m.p.:85 - 87°C,

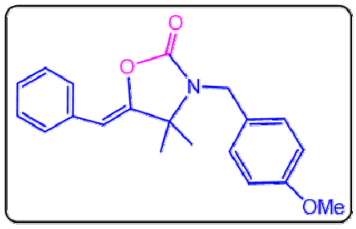
IR(KBr): 1780, 1689, 1491, 1397, 1307, 1275, 1190, 1042, 955, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.69 -7.67 (m, 2H), 7.41 - 7.37 (m, 2H), 7.27 - 7.14 (m, 5H), 5.52 (s, 1H), 4.53 (s, 2H), 2.40 (s, 3H), 1.43 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 154.85, 153.56, 138.49, 137.53, 133.70, 128.65, 128.62, 128.57, 128.46, 128.41, 126.87, 124.85, 100.67, 62.54, 44.14, 27.77, 21.48. HRMS (ESI-TOF) calculated for $C_{20}H_{21}NO_2$ $[M+H]^+$ *m/z* 308.1645, found 308.1641.

(*Z*)-5-Benzylidene-3-(3-chlorobenzyl)-4,4-dimethyloxazolidin-2-one **(4f)**



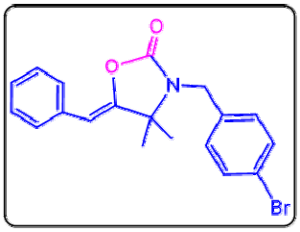
Yellow crystal (291 mg, 0.89 mmol, 89%); m.p.:70 -72℃. IR(KBr): 1778, 1689, 1598, 1396, 1307, 1189, 1043, 954, 755, 693cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.64 (d, J = 7.7 Hz, 2H), 7.41 - 7.35 (m, 3H), 7.32 - 7.22 (m, 4H), 5.52 (s, 1H), 4.51 (s, 2H), 1.44 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ = (ppm) 154.81, 153.10, 139.62, 134.63, 133.46, 130.13, 128.57, 128.40, 128.10, 127.76, 126.98, 125.88, 100.01, 62.49, 43.57, 27.76. HRMS (ESI-TOF) calculated for $C_{19}H_{18}ClNO_2$ $[M+H]^+$ *m/z* 328.1099, found 328.1095.

(*E*)-4-Benzylidene-2-(4-methoxybenzyl)-3,3-dimethylisoxazolidin-5-one **(4g)**



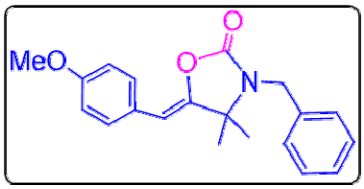
White crystal (307 mg, 0.95 mmol, 95%); m.p.: 108 - 110 °C; IR(KBr): 2929, 1777, 1688, 1613, 1513, 1448, 1396, 1284, 1175, 953 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.64 -7.62 (m, 2H), 7.39 - 7.23 (m, 5H), 6.91 -6.89 (m, 2H), 5.48 (s, 1H), 4.50 (s, 2H), 3.83 (s, 3H), 1.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 159.24, 154.77, 153.52, 133.64, 129.60, 129.20, 128.53, 128.35, 126.83, 114.10, 100.58, 62.44, 55.30, 43.67, 27.80. HRMS (ESI-TOF) calculated for $C_{20}H_{21}NO_3$ $[M+H]^+$ *m/z* 324.1594, found 324.1591.

(*E*)-4-Benzylidene-2-(4-bromobenzyl)-3,3-dimethylisoxazolidin-5-one **(4h)**



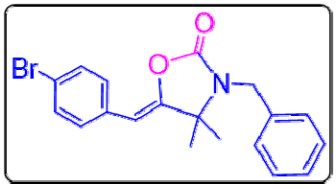
Light yellow crystal (334 mg, 0.90 mmol, 90%); m.p.: 96 - 98 °C; IR(KBr): 1781, 1690, 1488, 1394, 1311, 1190, 1043, 1001, 957, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.65 -7.63 (m, 2H), 7.50 - 7.48 (m, 2H), 7.39 - 7.35 (m, 2H), 7.28 - 7.24 (m, 3H), 5.52 (s, 1H), 4.47 (s, 2H), 1.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 154.79, 153.18, 136.67, 133.53, 131.90, 129.52, 128.58, 128.42, 126.98, 100.96, 62.49, 43.51, 27.77. HRMS (ESI-TOF) calculated for $C_{19}H_{18}BrNO_2$ $[M+H]^+$ *m/z* 372.0594, found 372.0591.

(*Z*)-3-Benzyl-5-(4-methoxybenzylidene)-4,4-dimethyloxazolidin-2-one **(4i)**



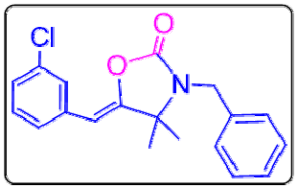
Yellow crystal (300 mg, 0.93 mmol, 93%); m.p.: 109 - 111 °C; IR(KBr): 3432, 1774, 1685, 1607, 1511, 1396, 1249, 1038, 913, 748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.55 - 7.53 (m, 2H), 7.37 - 7.26 (m, 5H), 6.88 - 6.86 (m, 2H), 5.40 (s, 1H), 4.51 (s, 2H), 3.80 (s, 3H), 1.37 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ = (ppm) 158.42, 155.01, 151.66, 137.61, 129.62, 128.74, 127.80, 127.76, 126.32, 113.93, 100.23, 62.37, 55.31, 44.14, 27.80. HRMS (ESI-TOF) calculated for $C_{20}H_{21}NO_3$ $[M+H]^+$ *m/z* 324.1594, found 324.1590.

(*Z*)-3-Benzyl-5-(4-bromobenzylidene)-4,4-dimethyloxazolidin-2-one **(4j)**



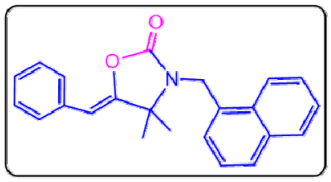
Yellow crystal (334 mg, 0.90 mmol, 90%); m.p.: 108 - 110 ℃; IR(KBr): 2927, 1779, 1686, 1396, 1317, 1038, 1009, 953, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.45 (d, J = 2.1 Hz, 4H), 7.35 - 7.29 (m, 5H), 5.39 (s, 1H), 4.51 (s, 2H), 1.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 154.57, 154.08, 137.37, 132.56, 131.60, 129.88, 128.79, 127.91, 127.78, 120.54, 99.65, 62.57, 44.22, 27.70. HRMS (ESI-TOF) calculated for $C_{19}H_{18}BrNO_2$ $[M+H]^+$ *m/z* 372.0594, found 372.0591.

(*Z*)-3-Benzyl-5-(3-chlorobenzylidene)-4,4-dimethyloxazolidin-2-one **(4k)**



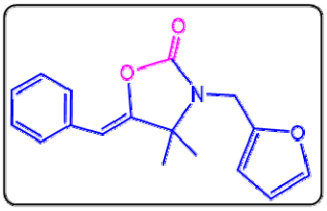
Yellow crystal (301 mg, 0.92 mmol, 92%); m.p.: 107 - 109 ℃; IR(KBr): 1777, 1685, 1625, 1593, 1396, 1368, 1315, 1036, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.59 -7.57 (m, 1H), 7.50 -7.48 (m, 1H), 7.36 -7.34 (m, 4H), 7.26 - 7.24 (m, 2H), 7.19 -7.17 (m, 1H), 5.40 (s, 1H), 4.52 (s, 2H), 1.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = (ppm) 154.63, 154.51, 137.36, 135.38, 134.37, 129.71, 128.80, 128.13, 127.92, 127.78, 126.83, 126.44, 99.51, 62.54, 44.23, 27.72. HRMS (ESI-TOF) calculated for $C_{19}H_{18}ClNO_2$ $[M+H]^+$ *m/z* 328.1099, found 328.1095.

(*E*)-4-Benzylidene-3,3-dimethyl-2-(naphthalen-1-ylmethyl)isoxazolidin-5-one **(4l)**



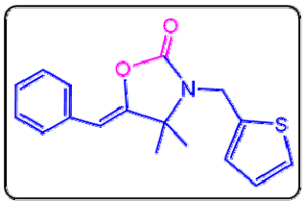
Yellow crystal (322 mg, 0.94 mmol, 94%); m.p.:142 -145 ℃，IR(KBr): 1777, 1689, 1397, 1370, 1274, 1190, 1131, 1044, 792, 694 cm^{-1}; ^1H NMR (400 MHz, CDCl3) δ = (ppm) 8.24 -8.21 (m, 1H), 7.94 - 7.87 (m, 2H), 7.66 - 7.48 (m, 6H), 7.40 - 7.36 (m, 2H), 7.30 - 7.24 (m, 1H), 5.47 (s, 1H), 5.09 (s, 2H), 1.32 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ = (ppm) 154.56, 153.54, 133.89, 133.57, 132.31, 131.41, 129.08, 128.87, 128.55, 128.37, 126.94, 126.89, 126.66, 126.21, 125.15, 123.49, 100.68, 62.65, 43.19, 27.37. HRMS (ESI-TOF) calculated for $C_{23}H_{21}NO_2$ $[M+H]^+$ *m/z* 344.1645, found 344.1642.

(*Z*)-5-Benzylidene-3-(furan-2-ylmethyl)-4,4-dimethyloxazolidin-2-one **(4m)**



Yellow crystal (257 mg, 0.91 mmol, 91%); m.p.:62 - 64 °C. IR(KBr): 1780, 1689, 1492, 1399, 1306, 1183, 1041, 951, 756, 694 cm^{-1}; ^{1}H NMR (400 MHz, CDCl3) δ = (ppm) 7.59 (d, J = 7.8 Hz, 2H), 7.37 -7.31 (m, 3H), 7.21 (t, J = 7.1 Hz, 1H), 6.35 (d, J = 5.6 Hz, 2H), 5.47 (s, 1H), 4.49 (s, 2H), 1.43 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ = (ppm) 154.16, 153.35, 149.77, 142.29, 133.58, 128.53, 128.37, 126.87, 110.85, 109.01, 100.75 , 62.01, 36.97, 27.20. HRMS (ESI-TOF) calculated for $C_{17}H_{17}NO_3$ $[M+H]^+$ *m/z* 284.1281, found 284.1277.

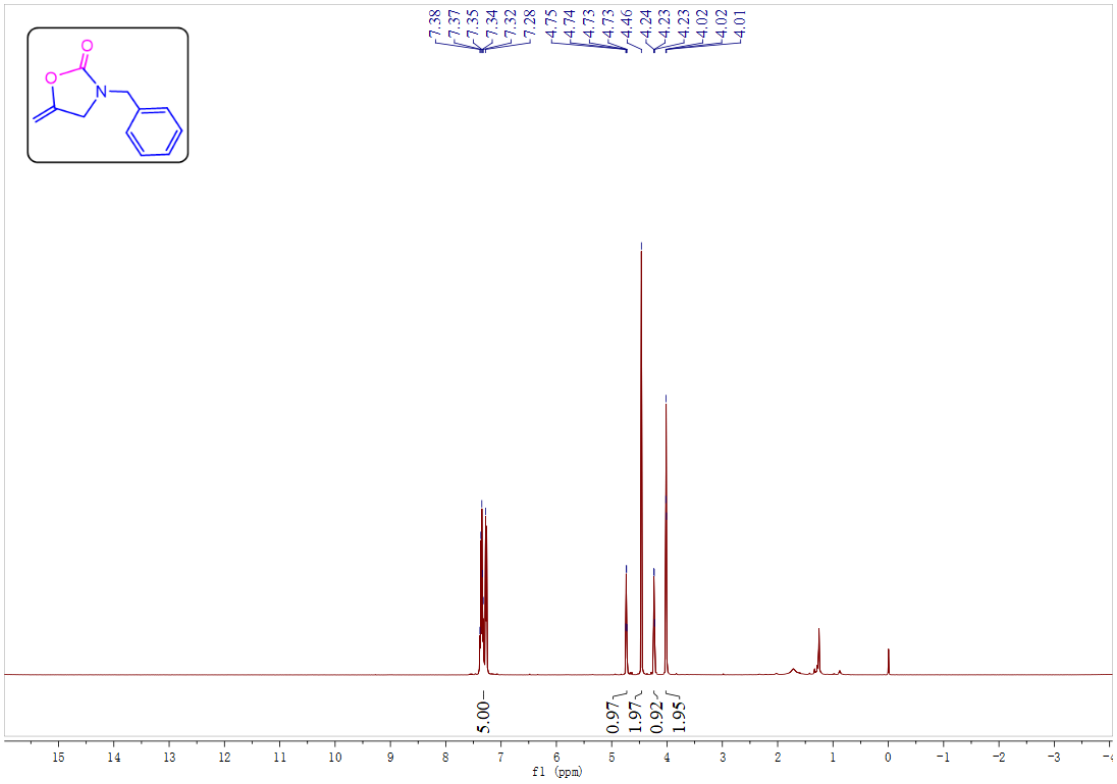
(*Z*)-5-Benzylidene-4,4-dimethyl-3-(thiophen-2-ylmethyl)oxazolidin-2-one **(4n)**

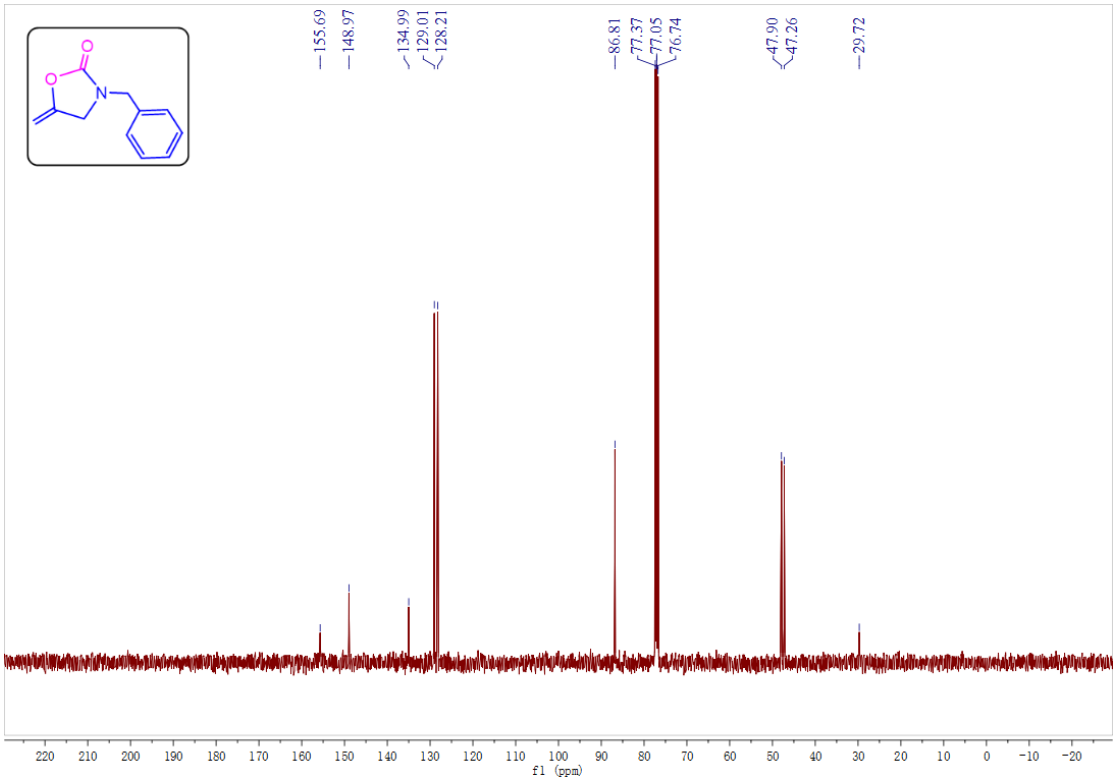


Brown crystal (277 mg, 0.92 mmol, 92%); m.p.: 91 - 93 °C; IR(KBr):2974, 1777, 1688, 1397, 1302, 1256, 1161, 1046, 947, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = (ppm) 7.60 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.25 - 7.20 (m, 2H), 7.07 (s, 1H), 6.99 - 6.94 (m, 1H), 5.48 (s, 1H), 4.67 (s, 2H), 1.47 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ = (ppm) 154.27, 153.25, 139.92, 133.52, 128.55, 128.39, 126.92, 125.84, 100.83, 62.43, 38.95, 27.63. HRMS (ESI-TOF) calculated for $C_{17}H_{19}NO_2S$ $[M+H]^+$ *m/z* 302.1209, found 302.1207.

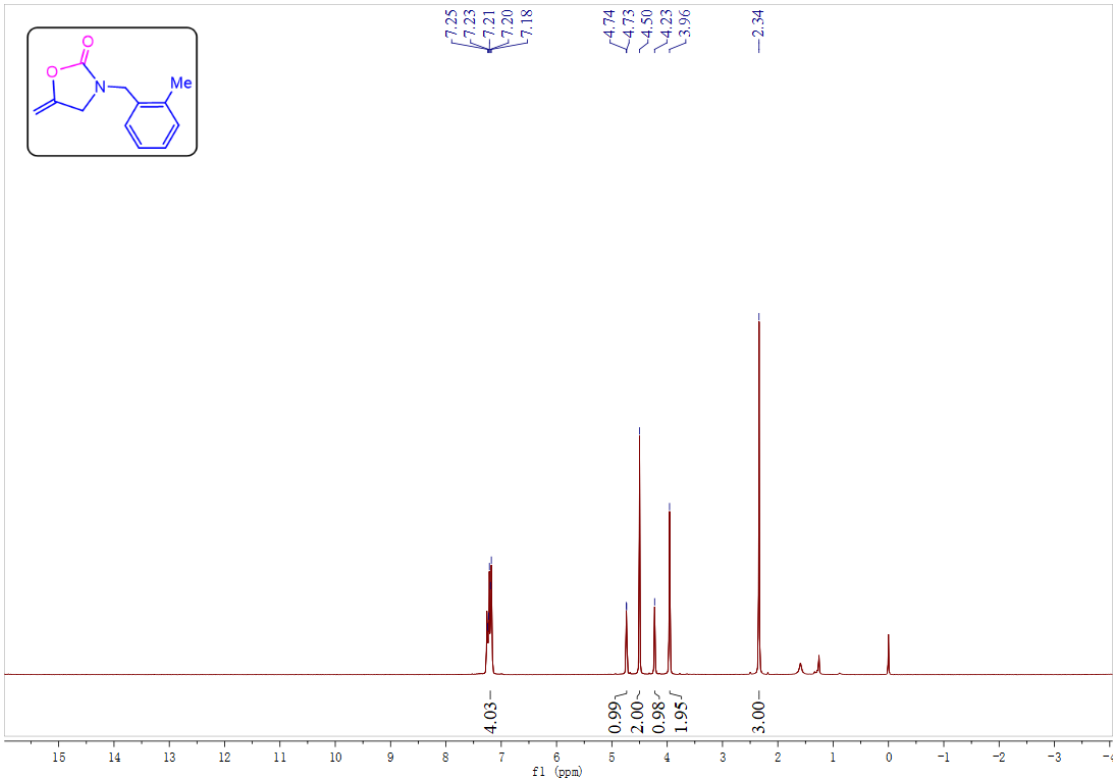
4. Copies of NMR spectra for all products

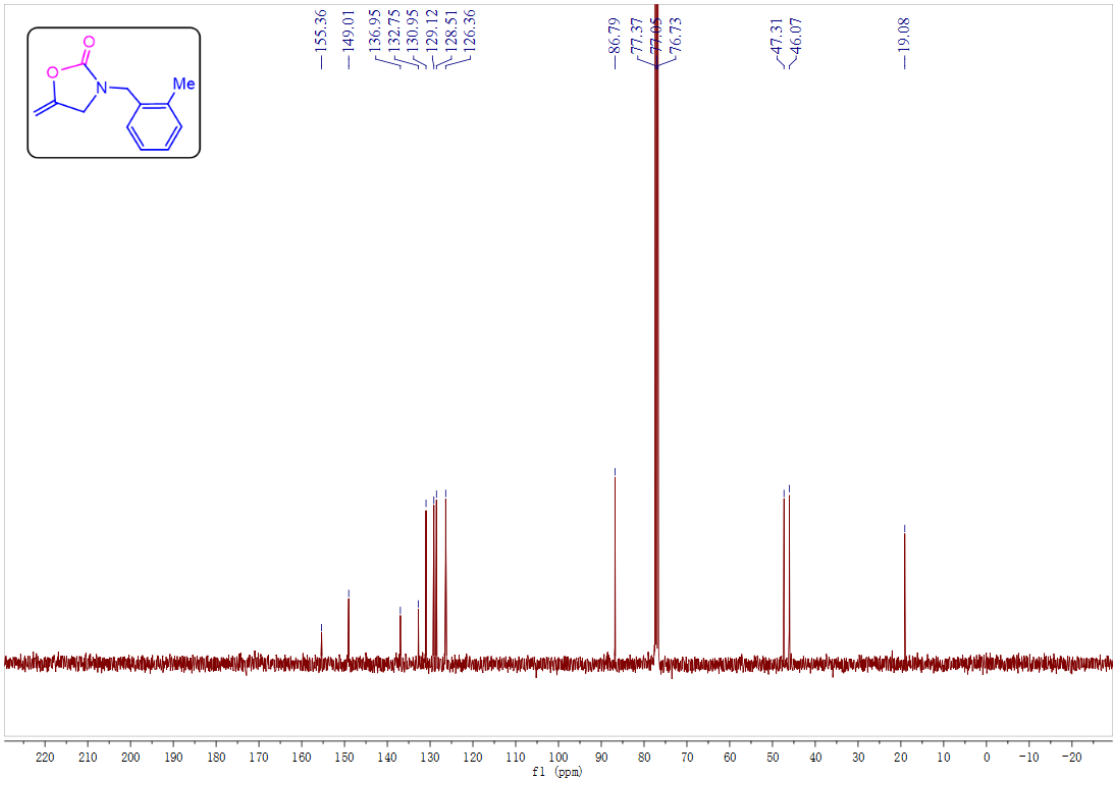
^{1}H NMR and ^{13}C NMR of compound **2a**



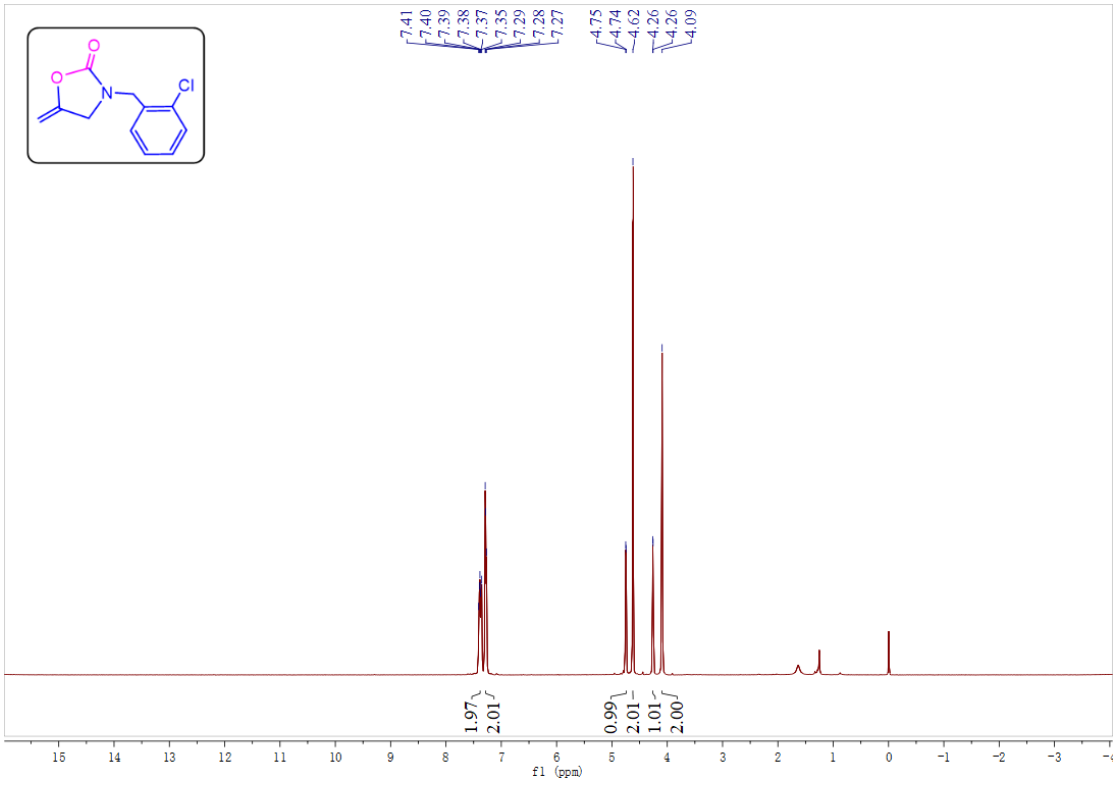


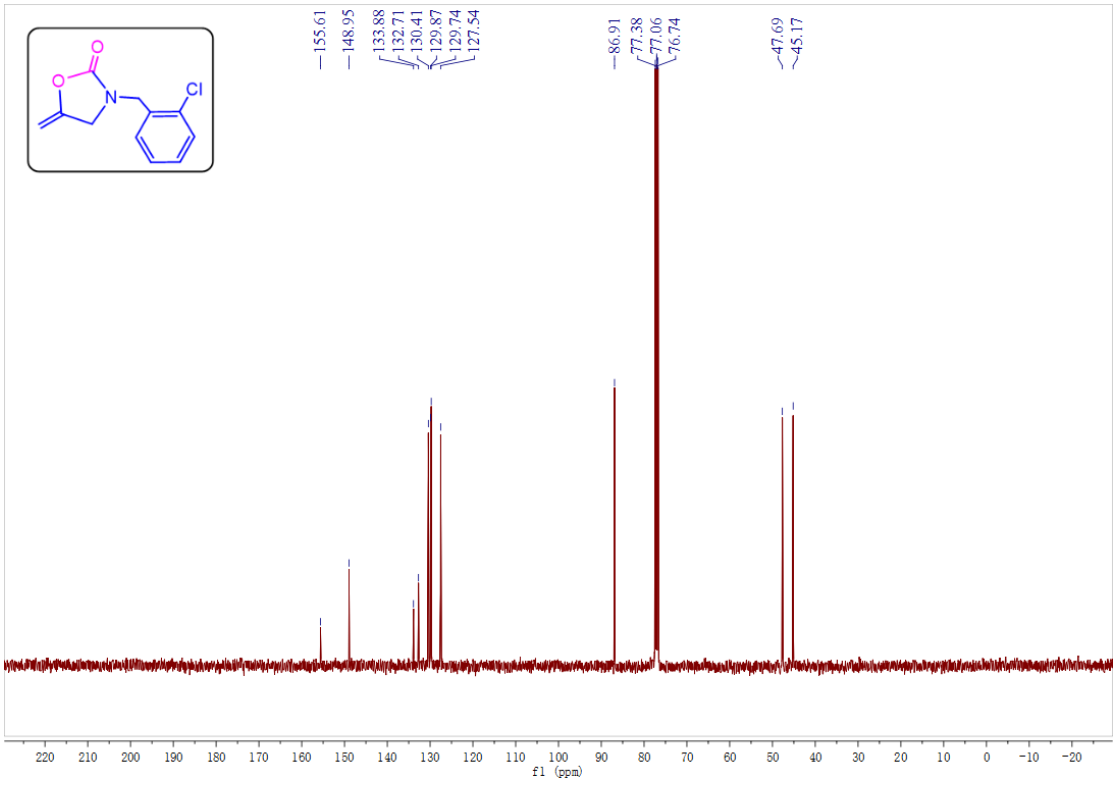
^{1}H NMR and ^{13}C NMR of compound **2b**



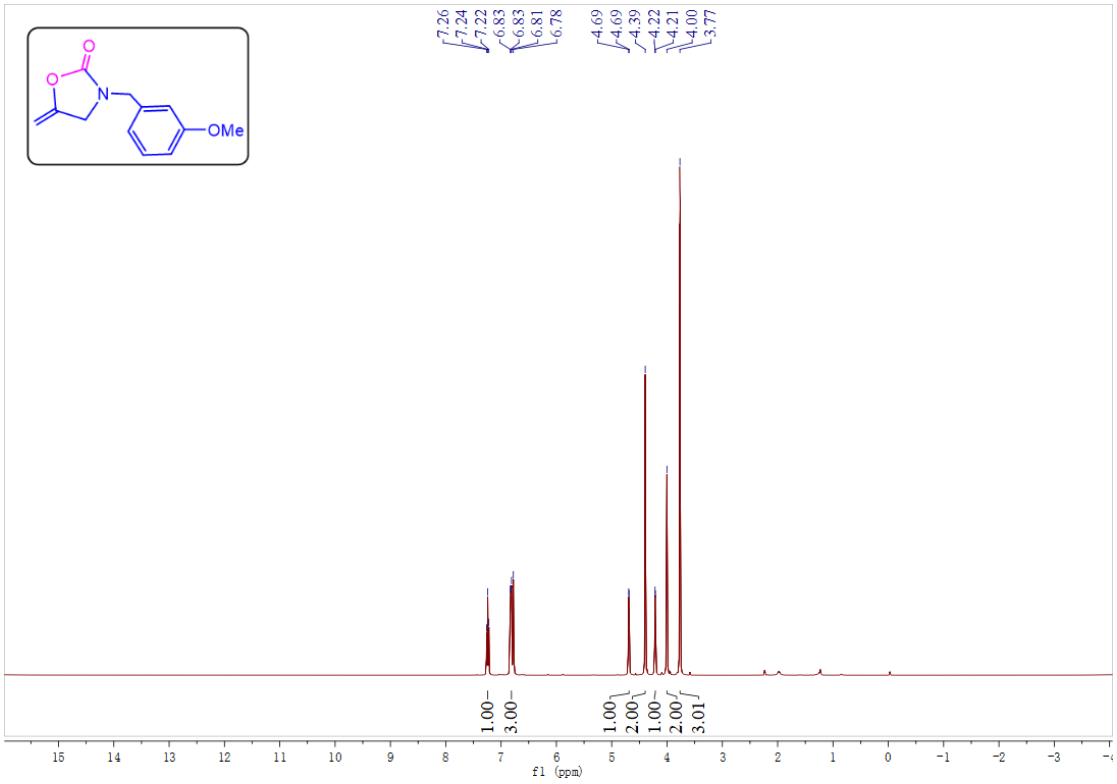


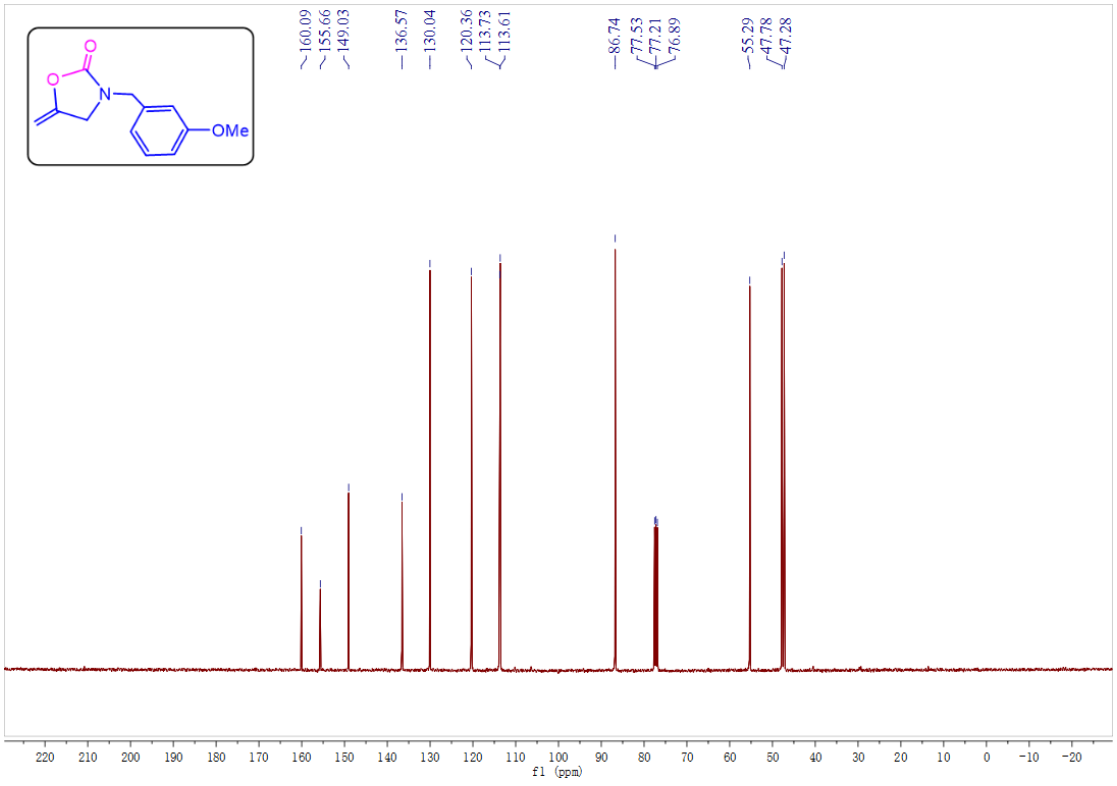
^{1}H NMR and ^{13}C NMR of compound **2c**



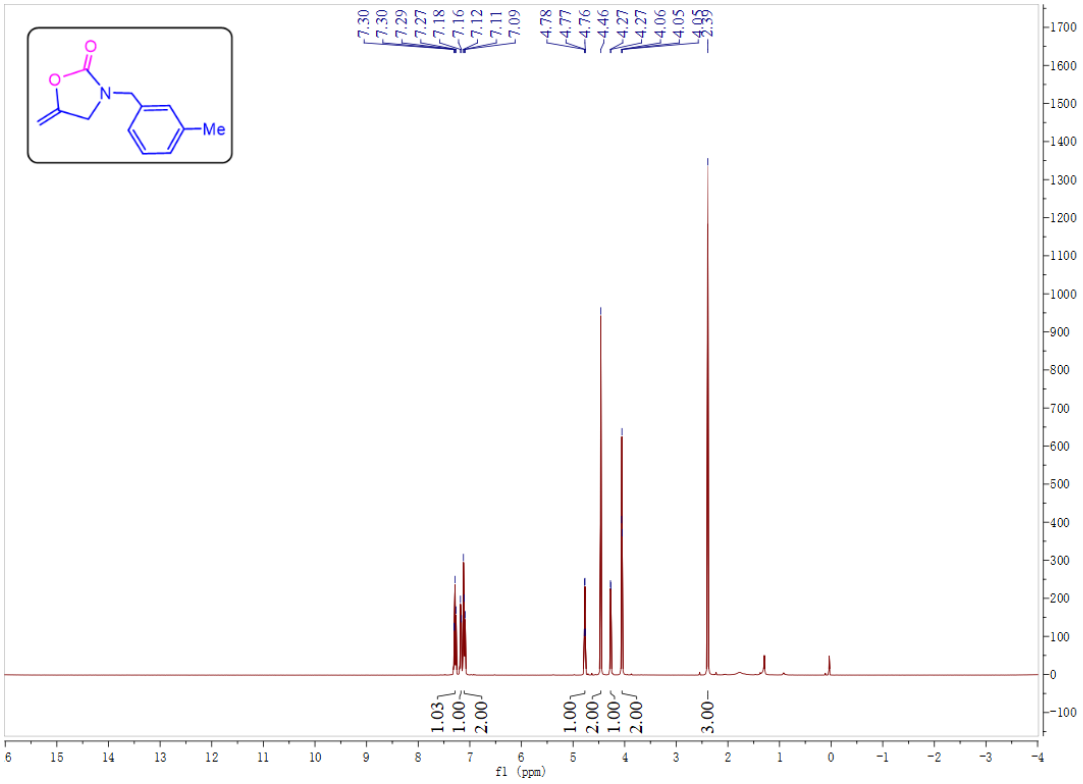


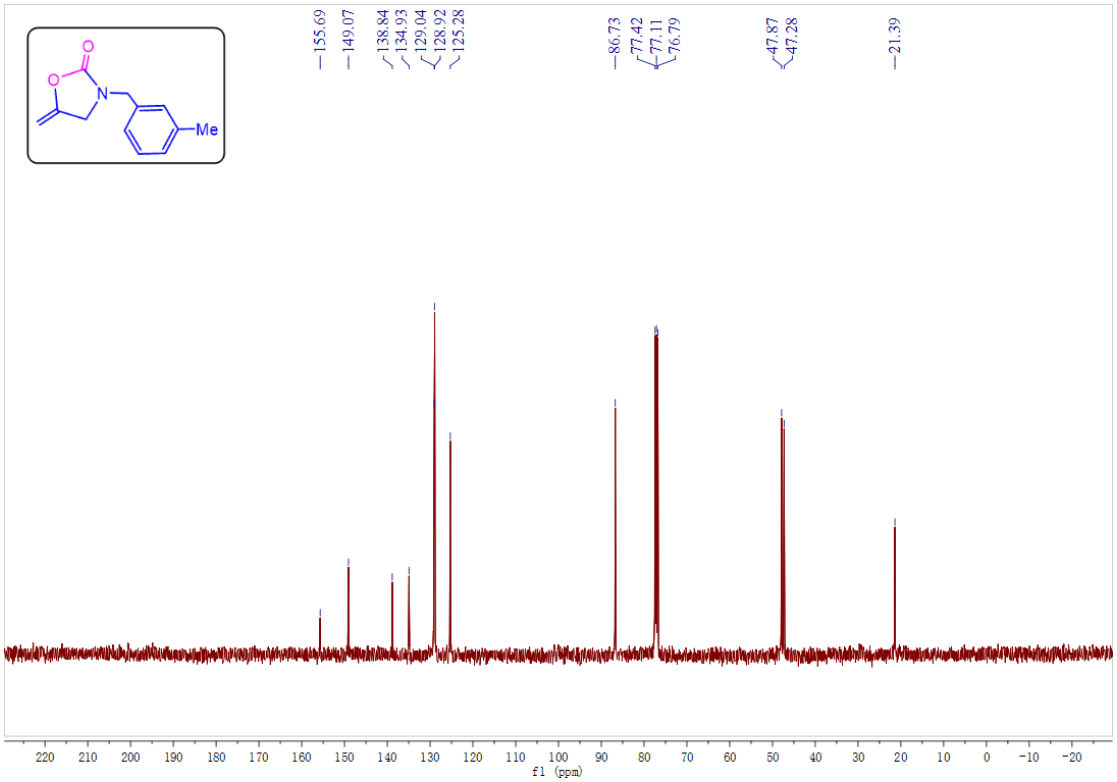
^{1}H NMR and ^{13}C NMR of compound **2d**



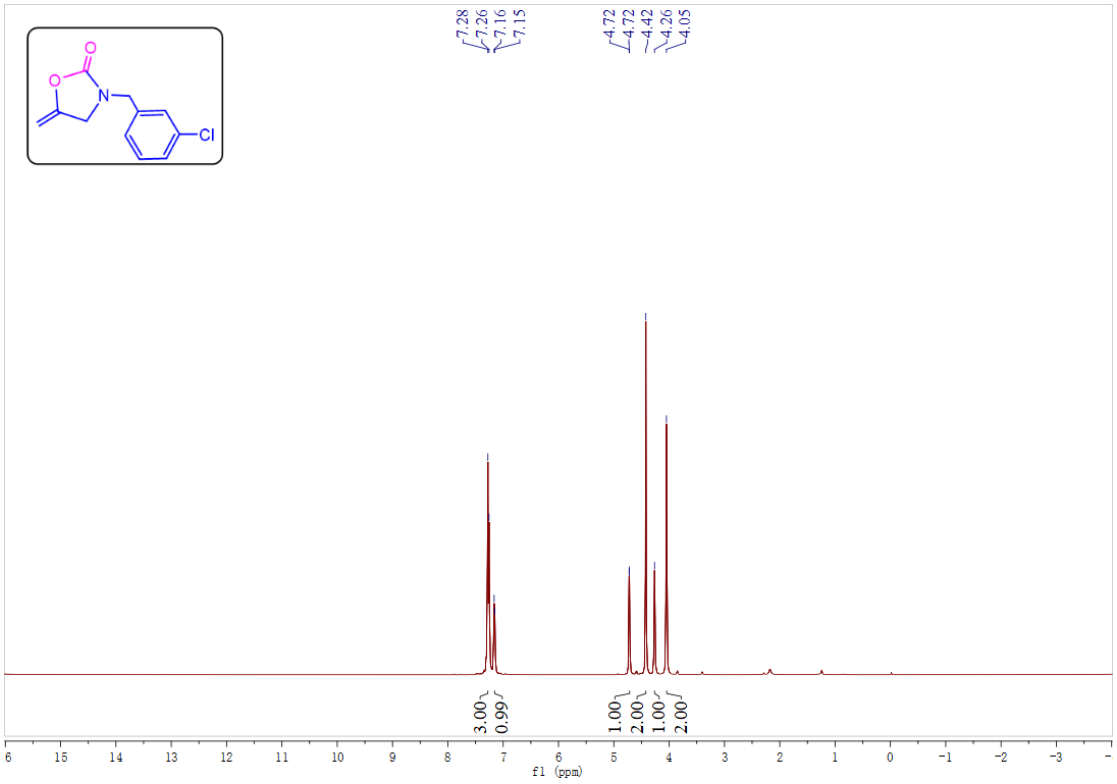


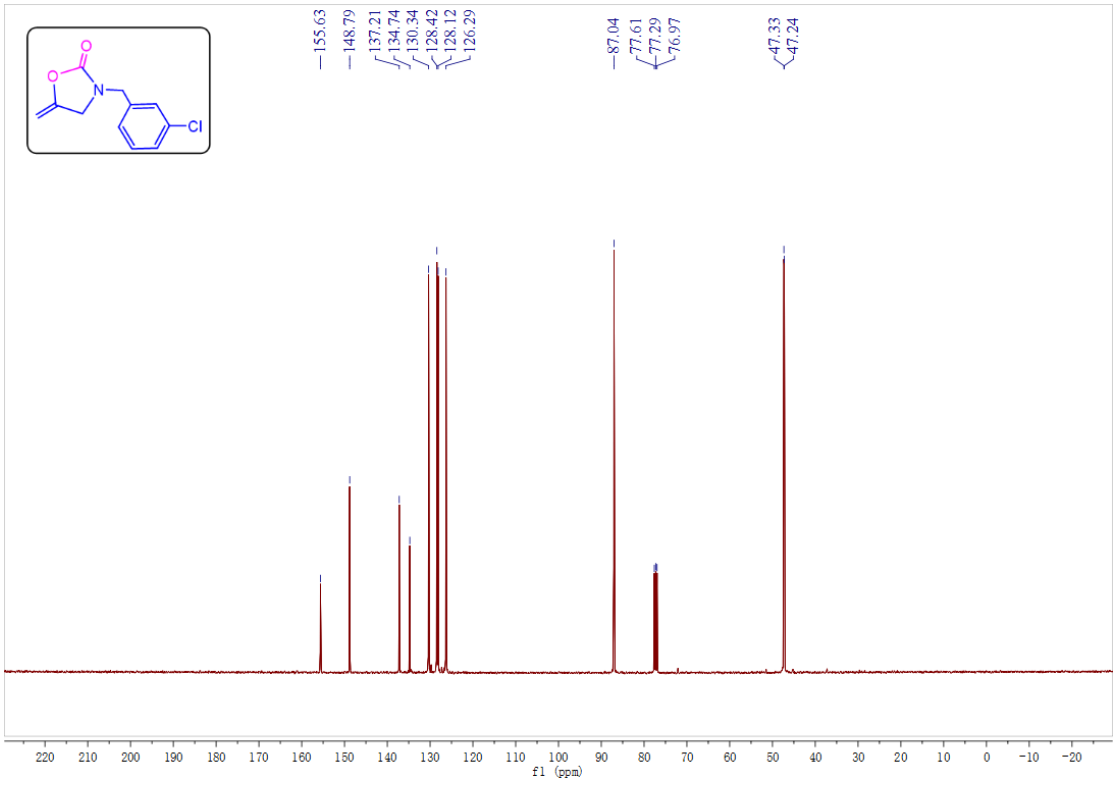
^{1}H NMR and ^{13}C NMR of compound **2e**



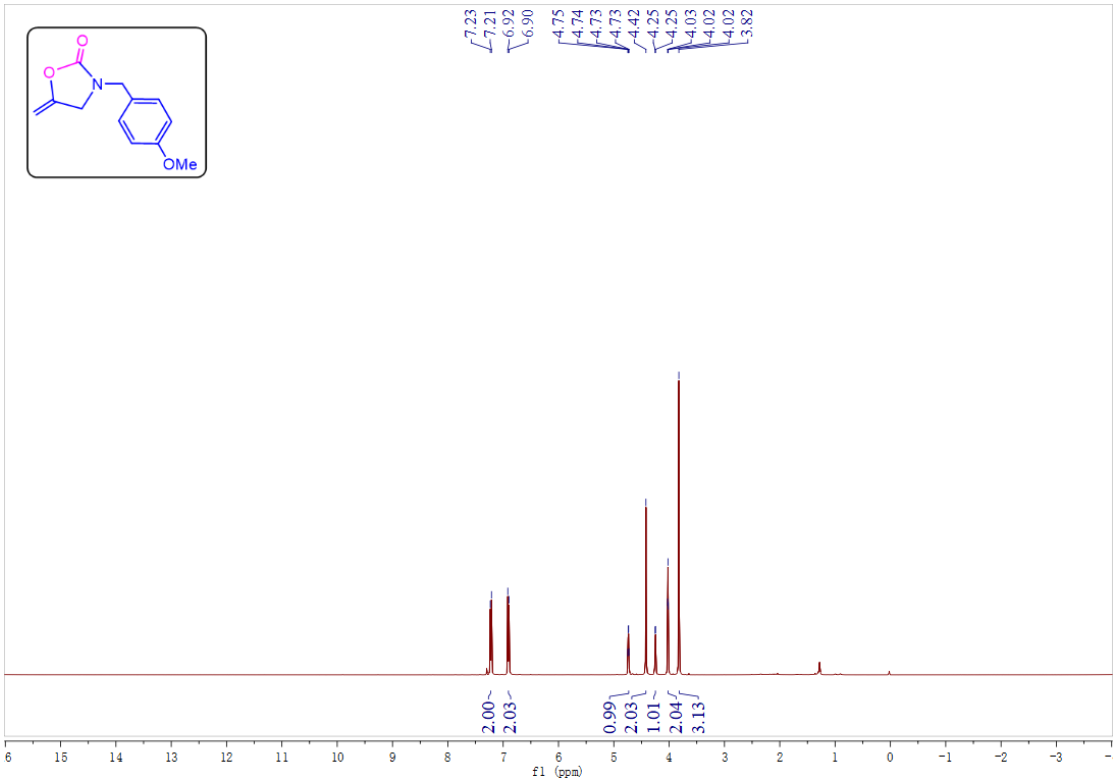


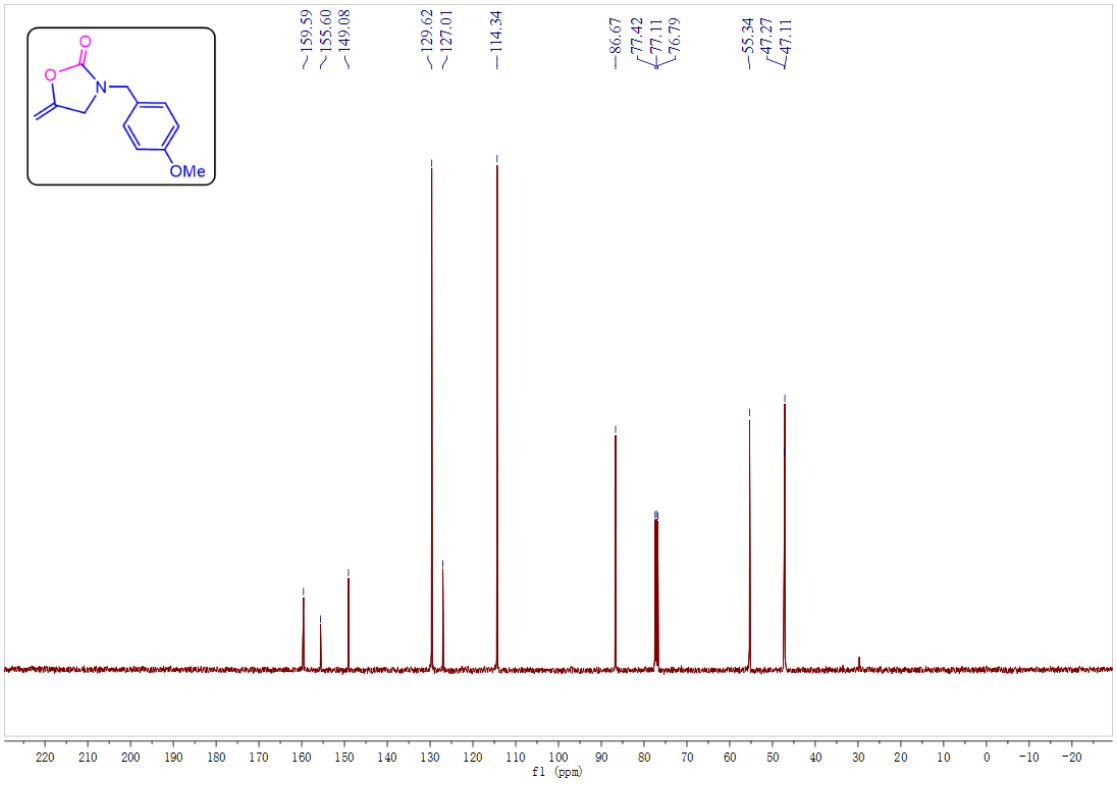
^{1}H NMR and ^{13}C NMR of compound **2f**



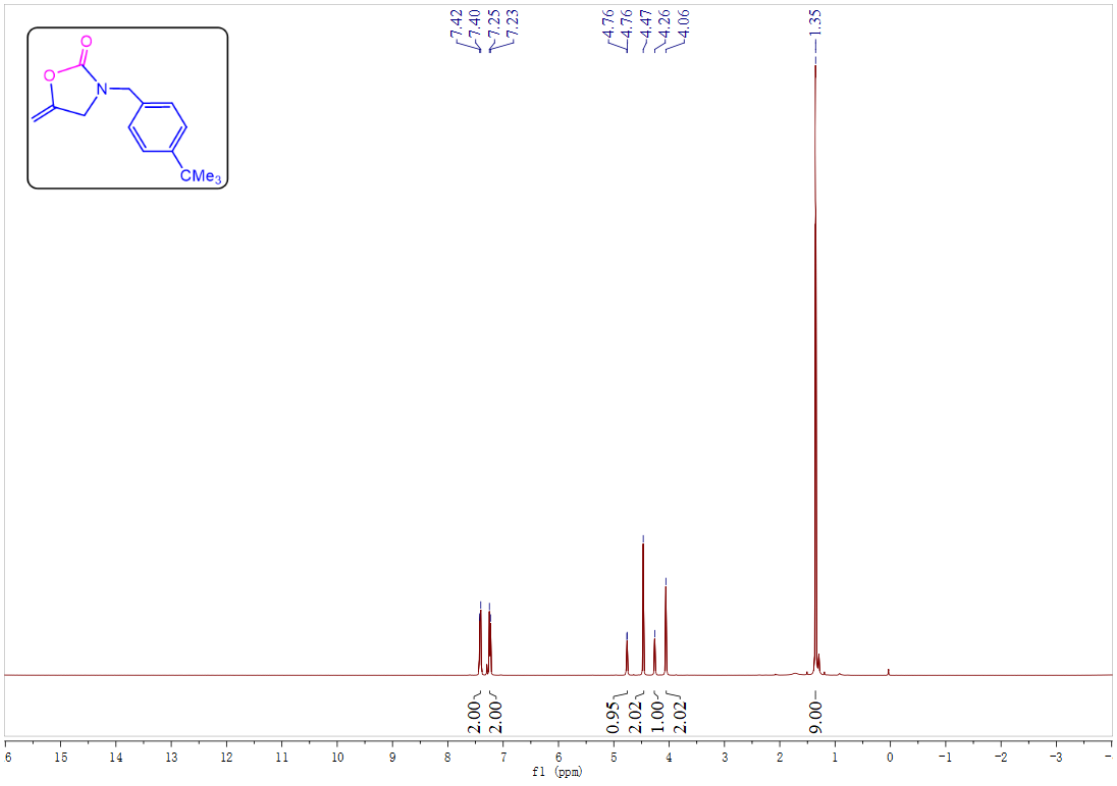


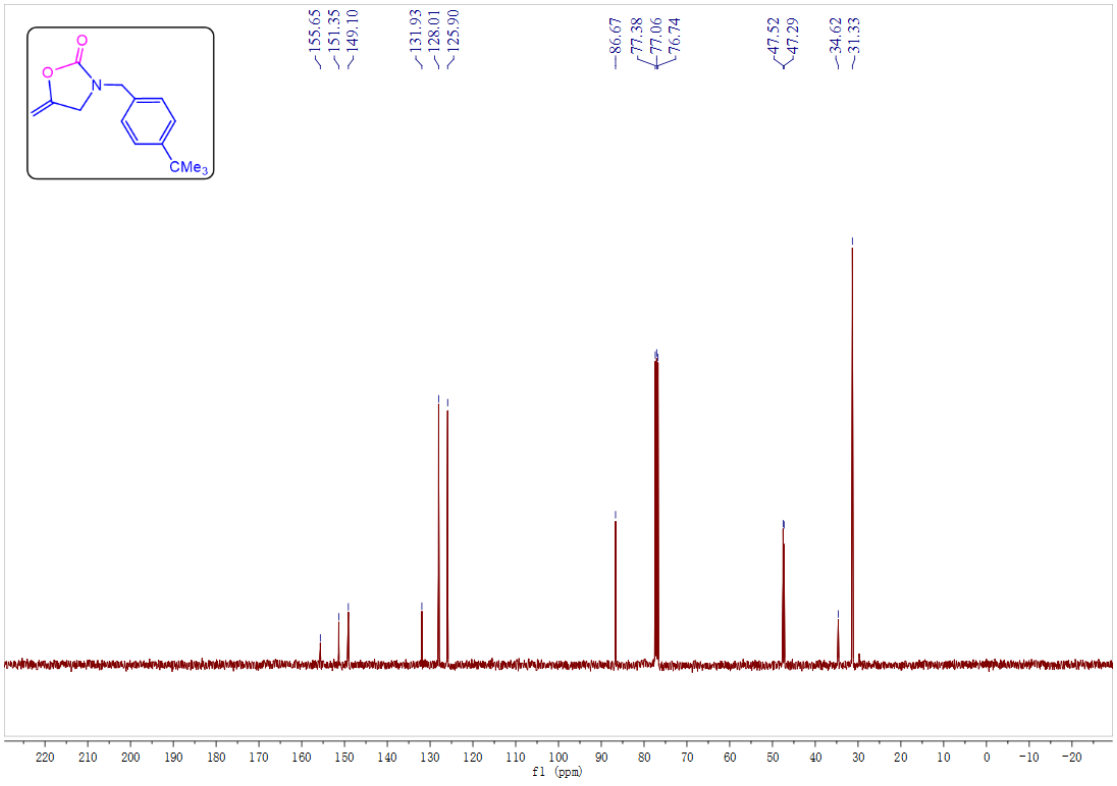
^{1}H NMR and ^{13}C NMR of compound **2g**



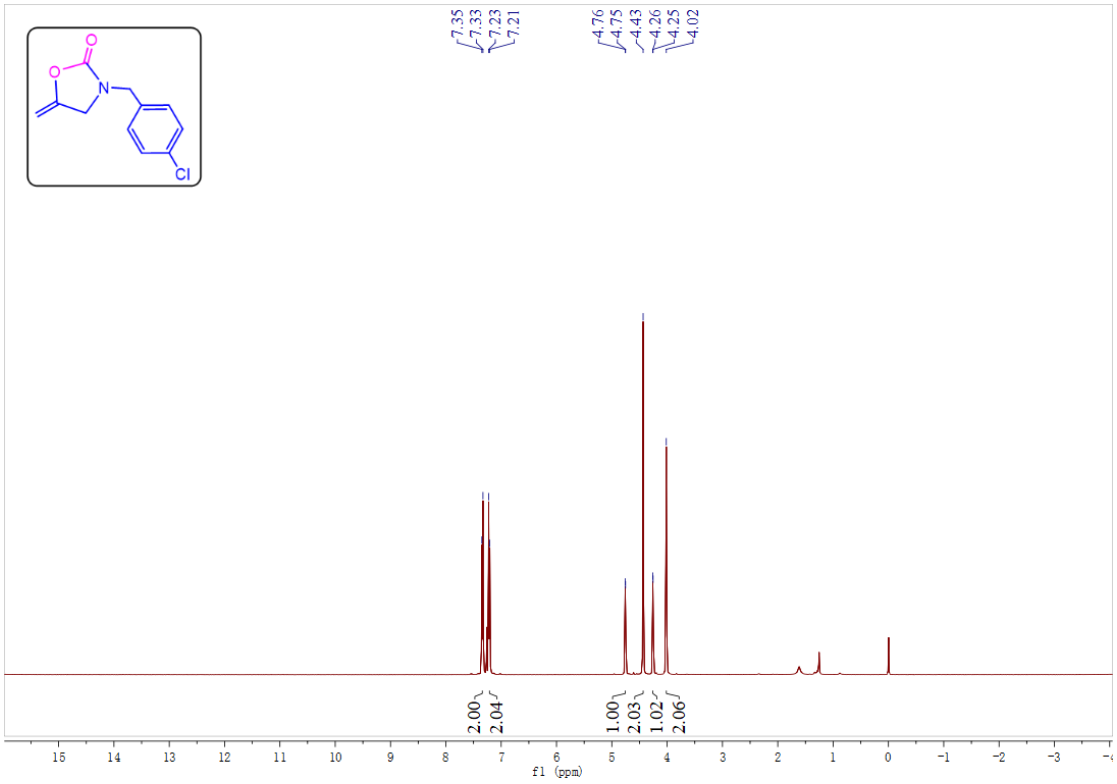


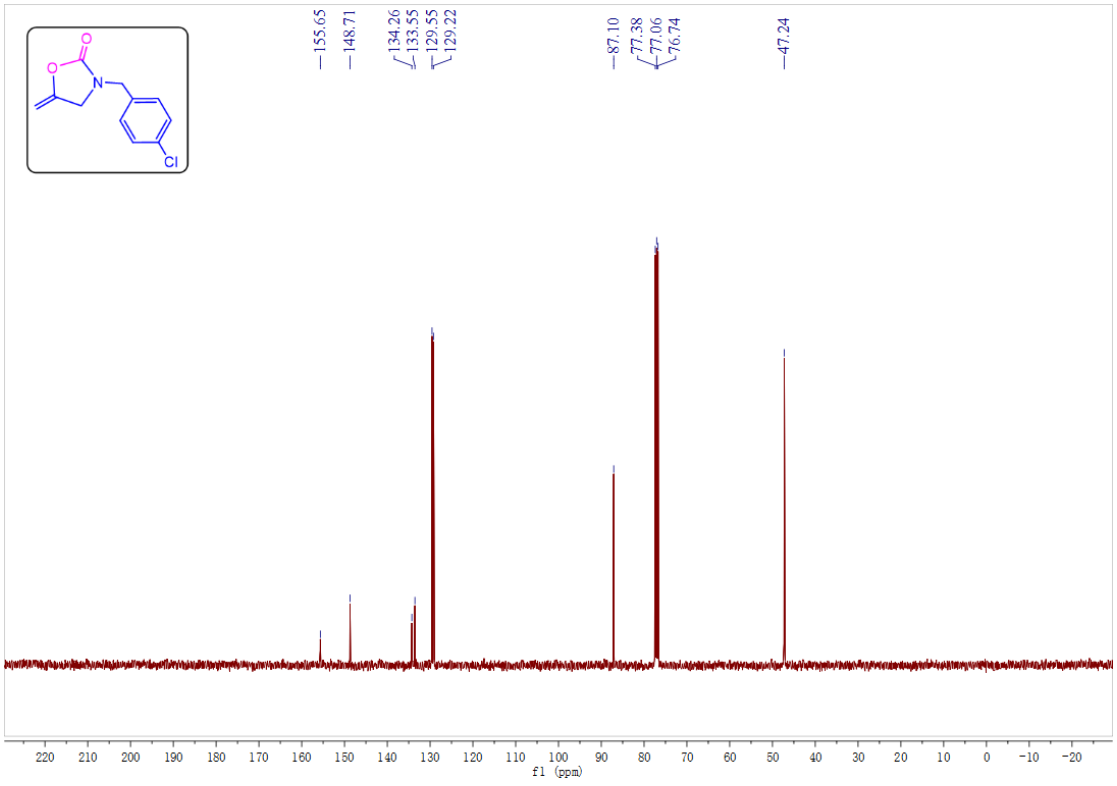
^{1}H NMR and ^{13}C NMR of compound **2h**



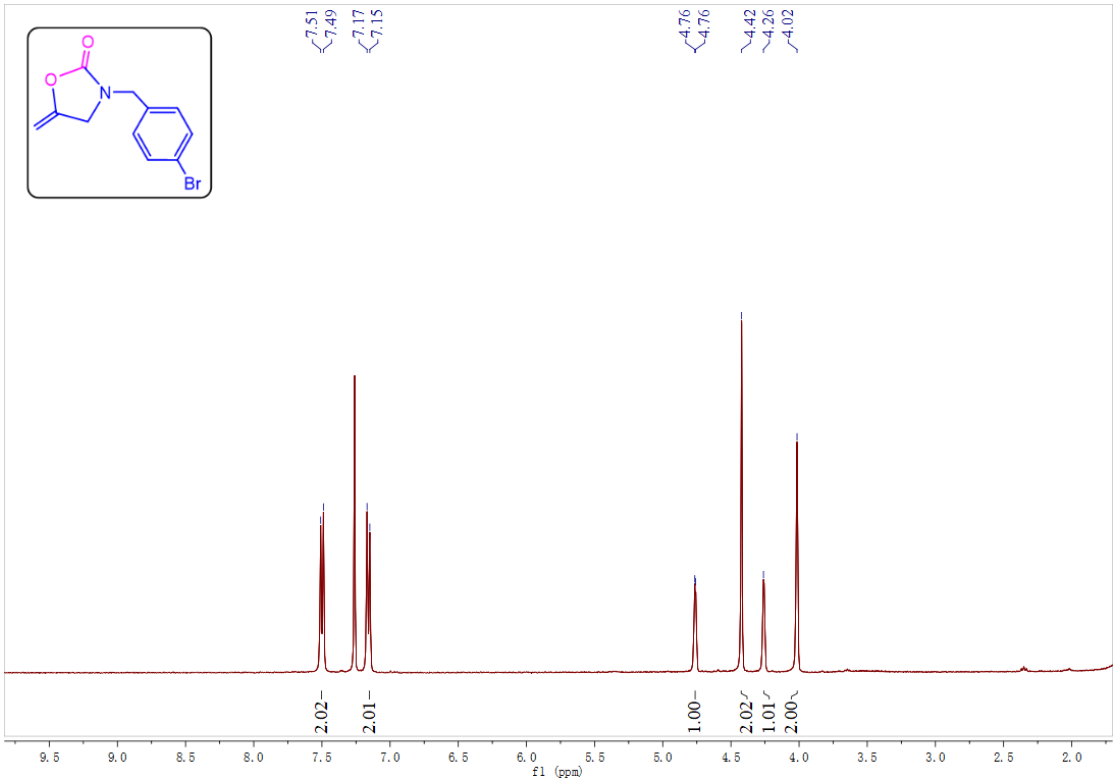


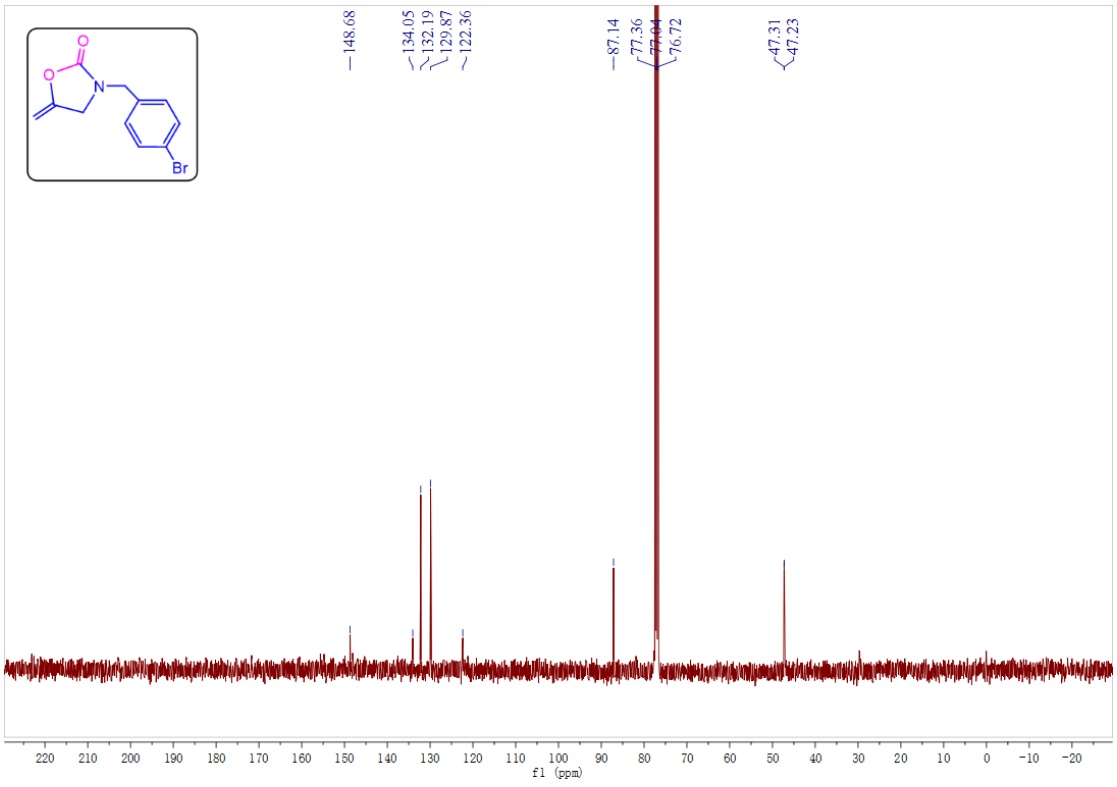
^{1}H NMR and ^{13}C NMR of compound **2i**



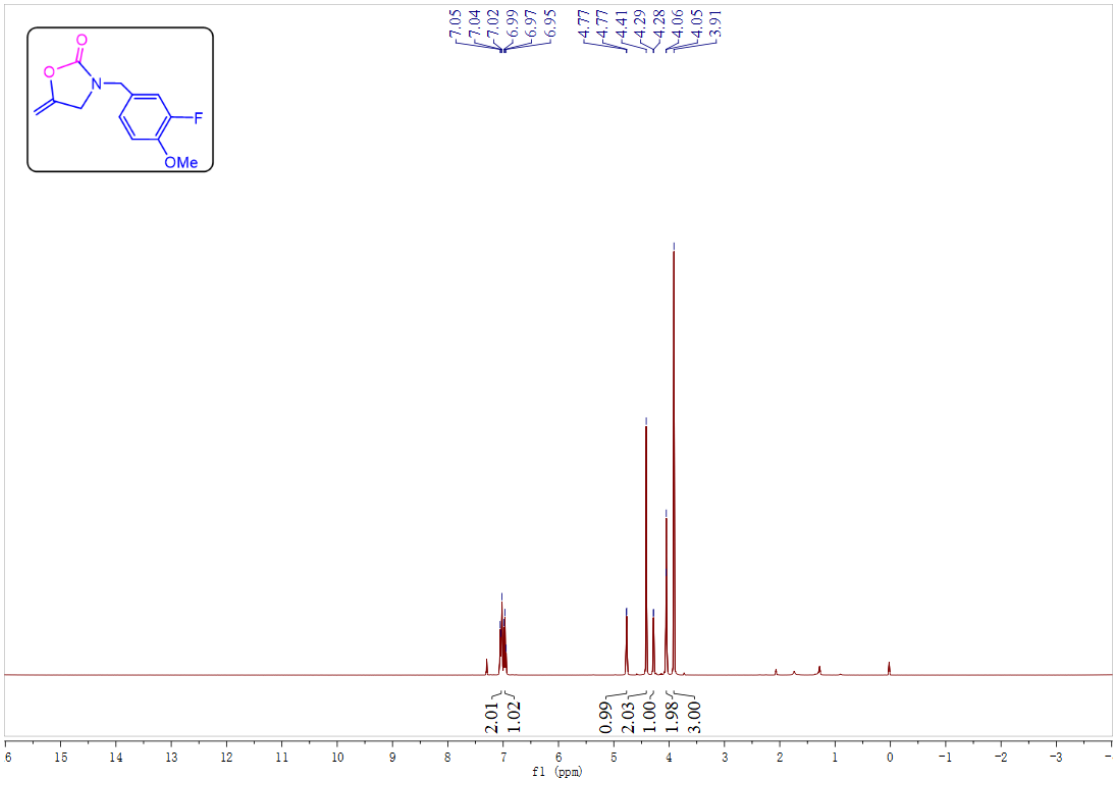


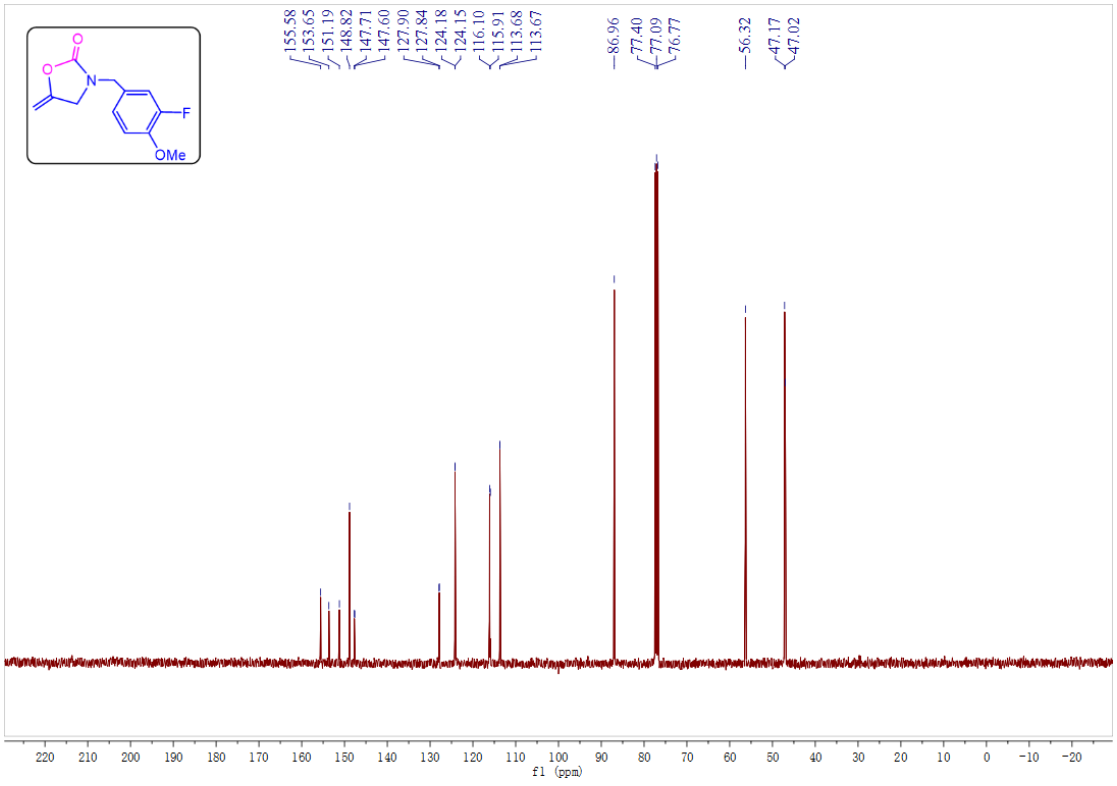
^{1}H NMR and ^{13}C NMR of compound **2j**



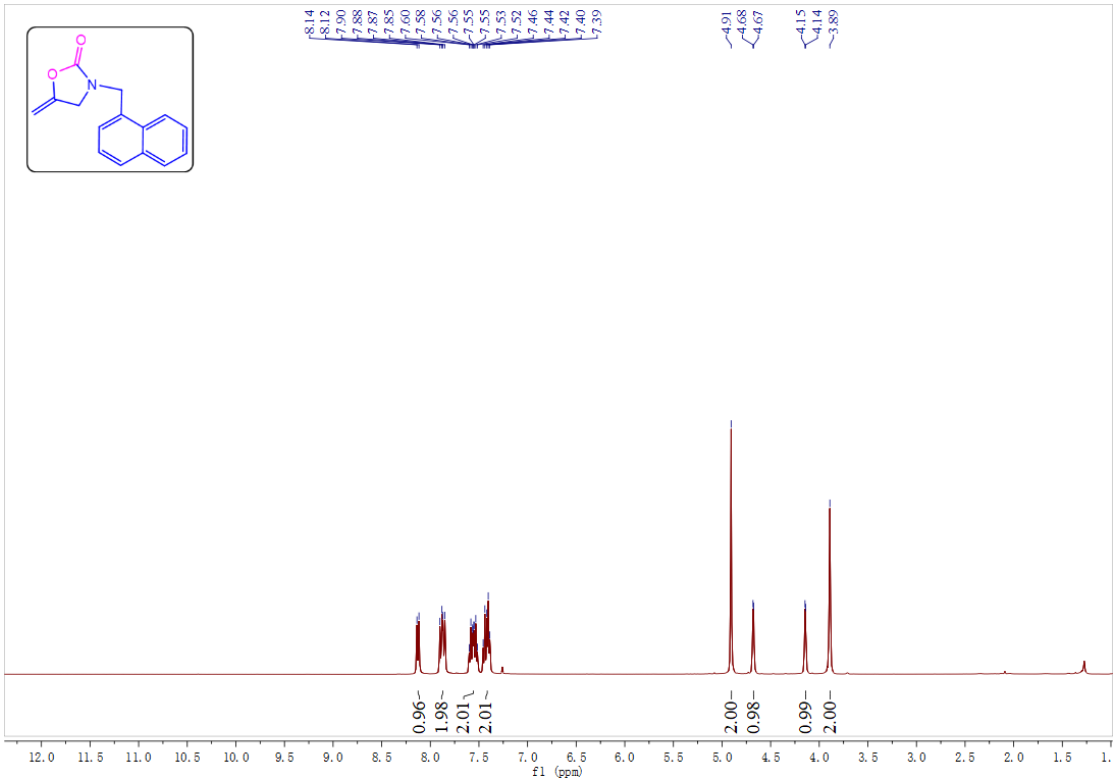


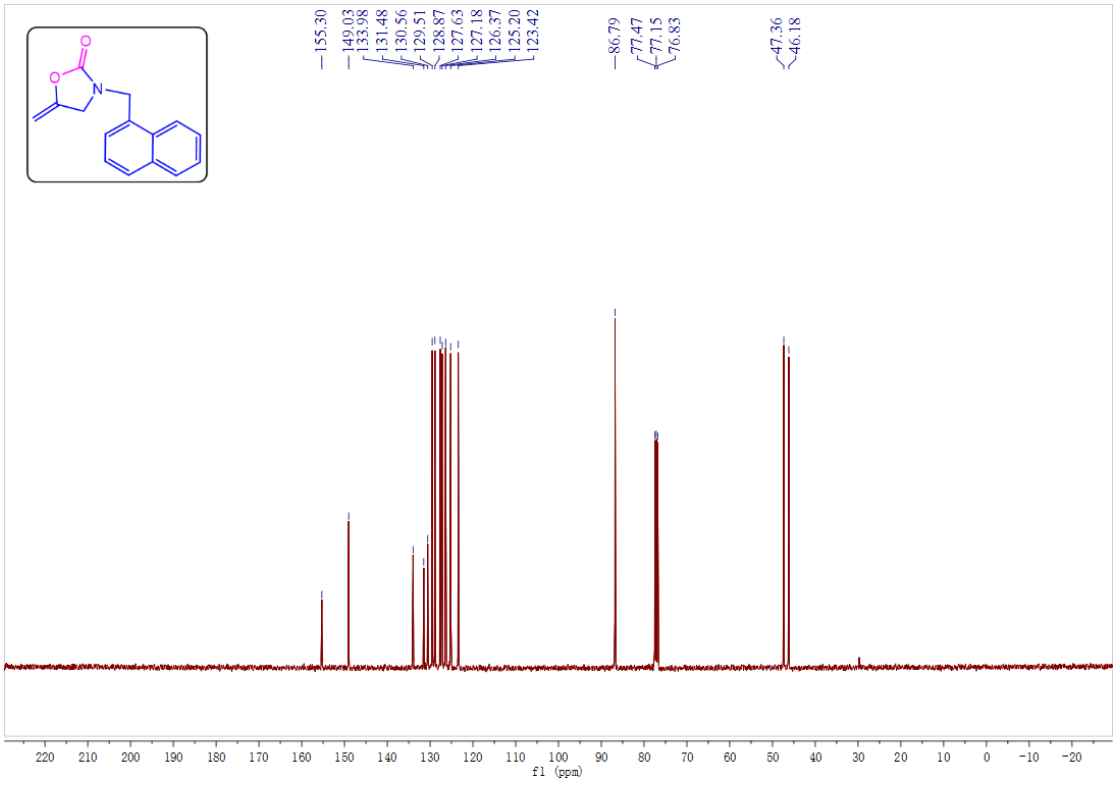
^{1}H NMR and ^{13}C NMR of compound **2k**



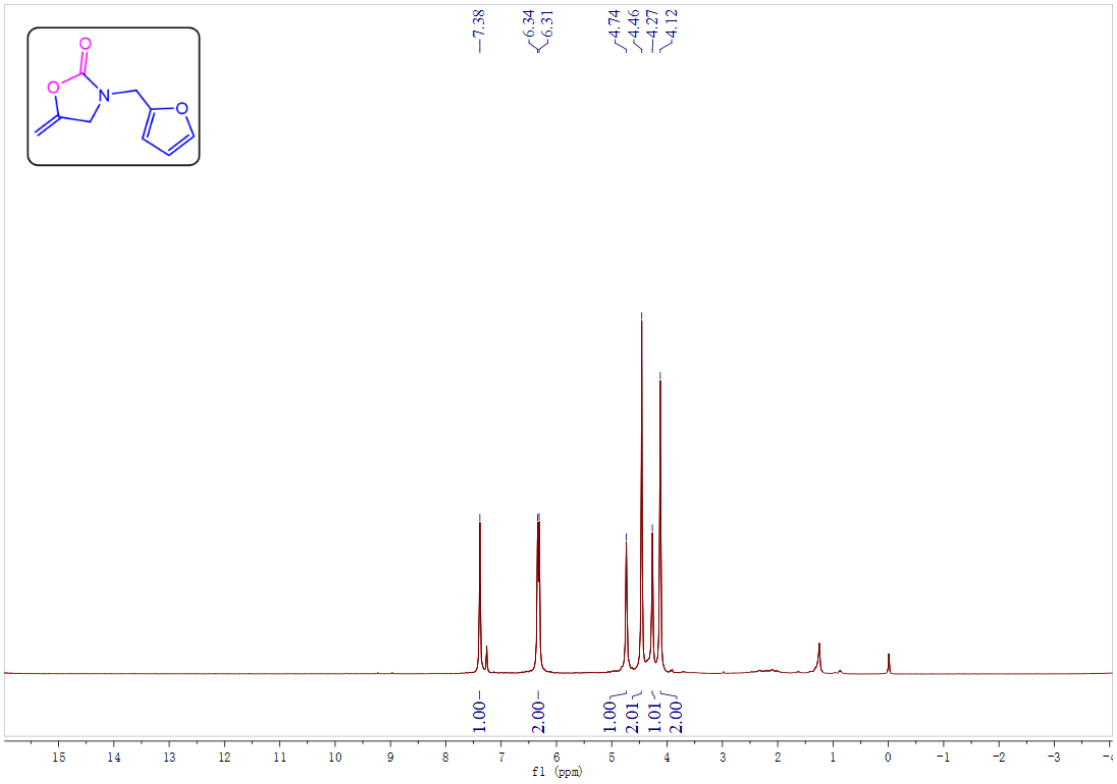


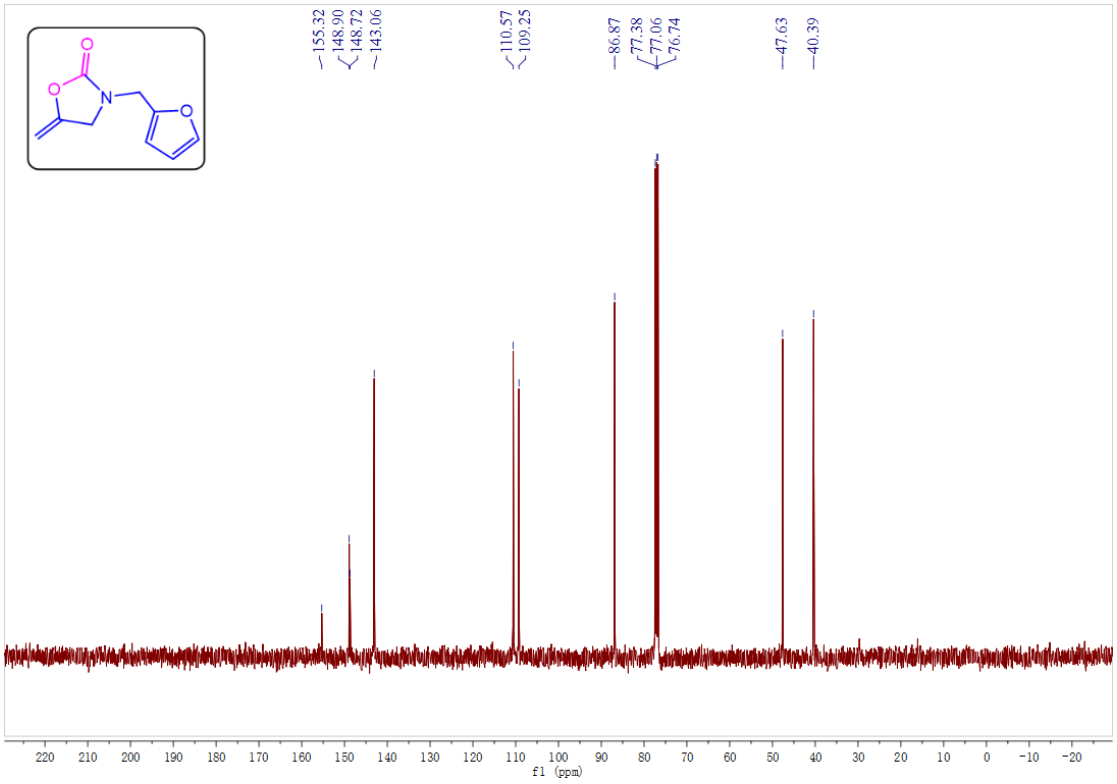
^{1}H NMR and ^{13}C NMR of compound **2l**



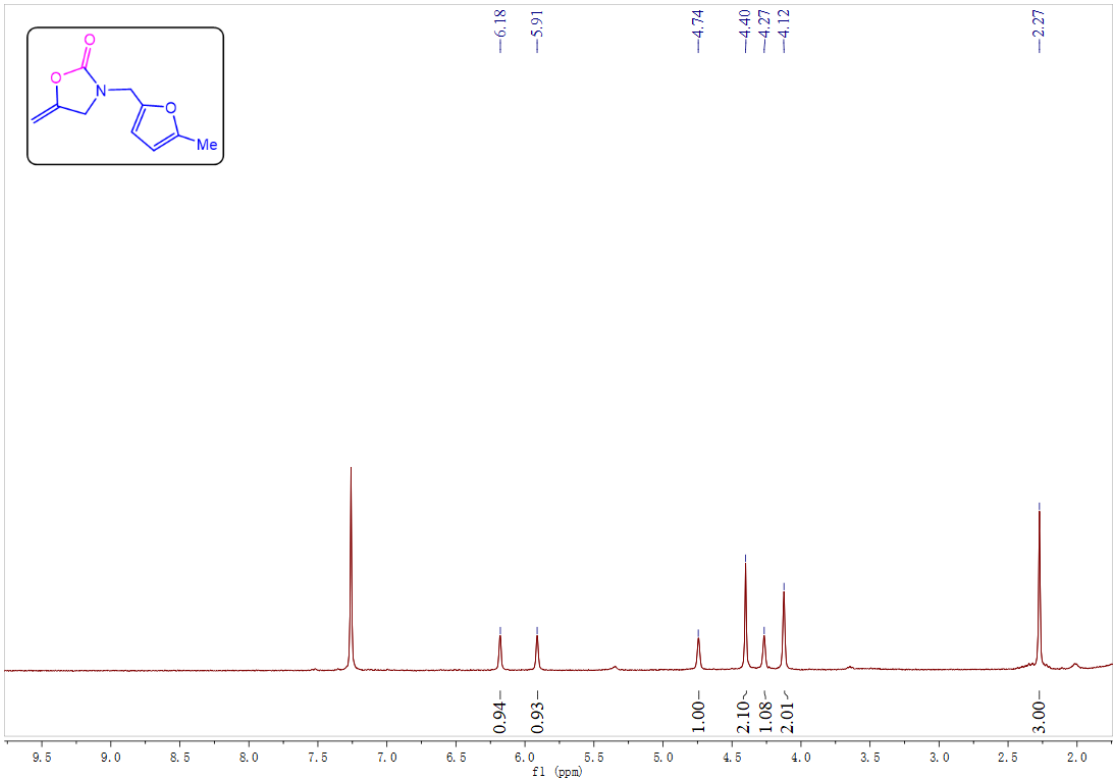


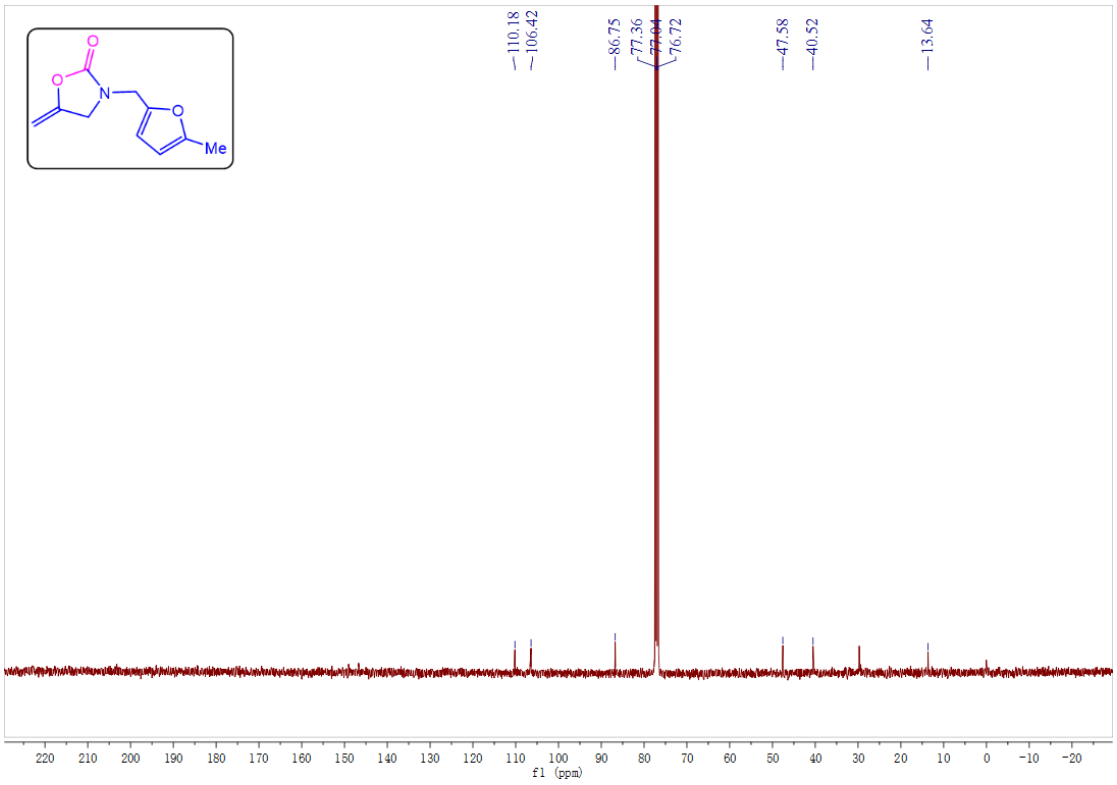
^{1}H NMR and ^{13}C NMR of compound **2m**



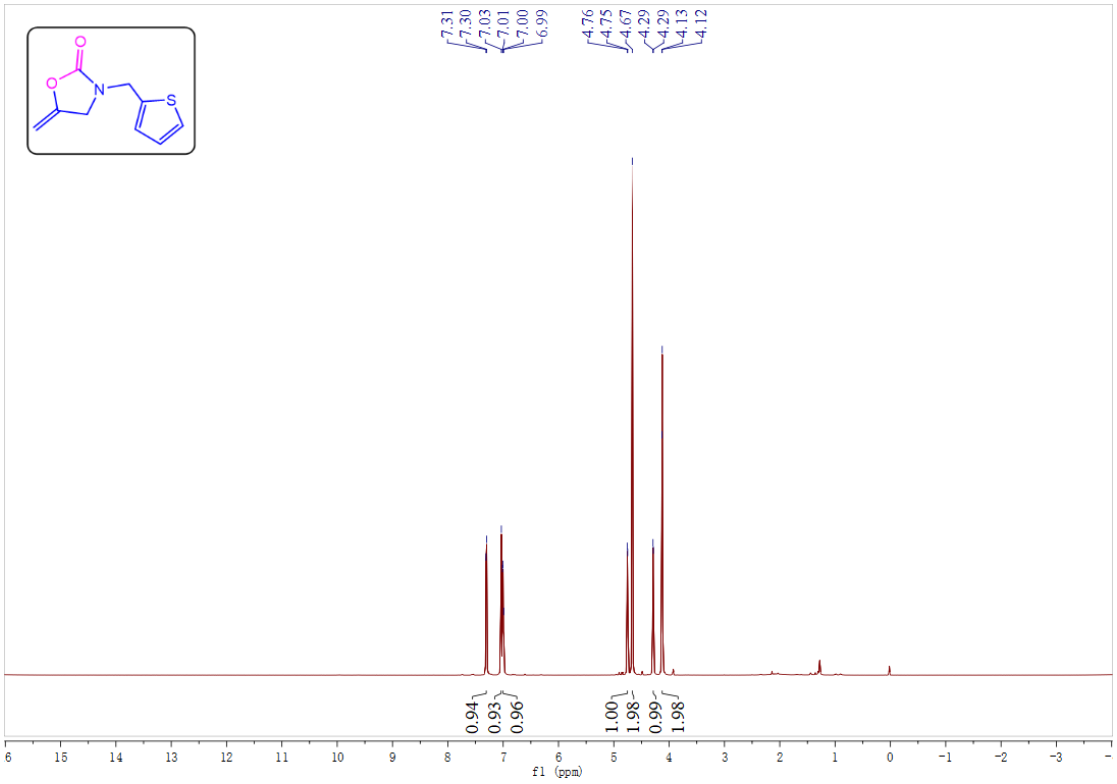


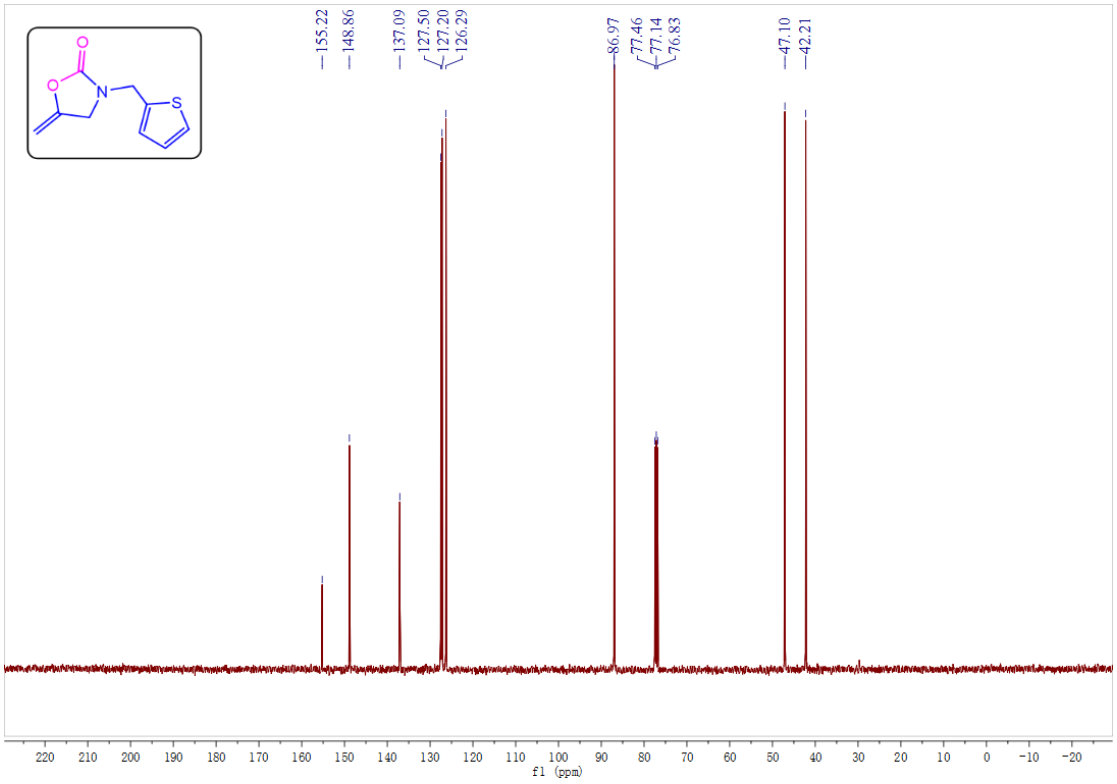
^{1}H NMR and ^{13}C NMR of compound **2n**



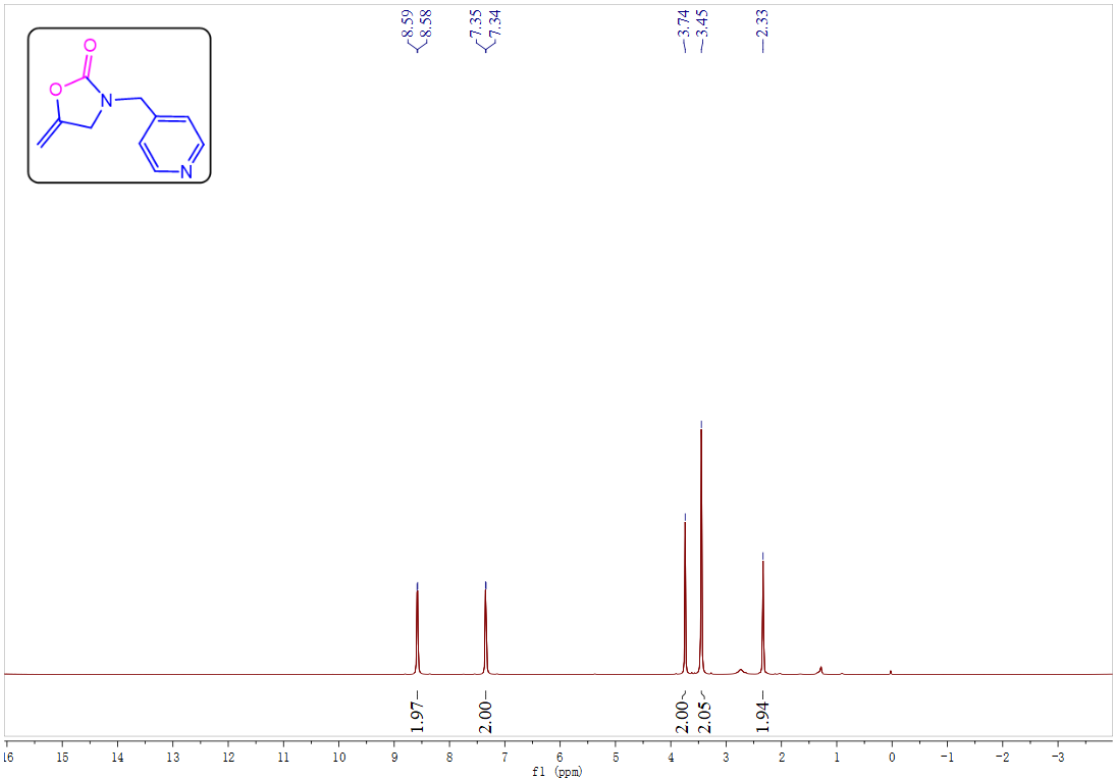


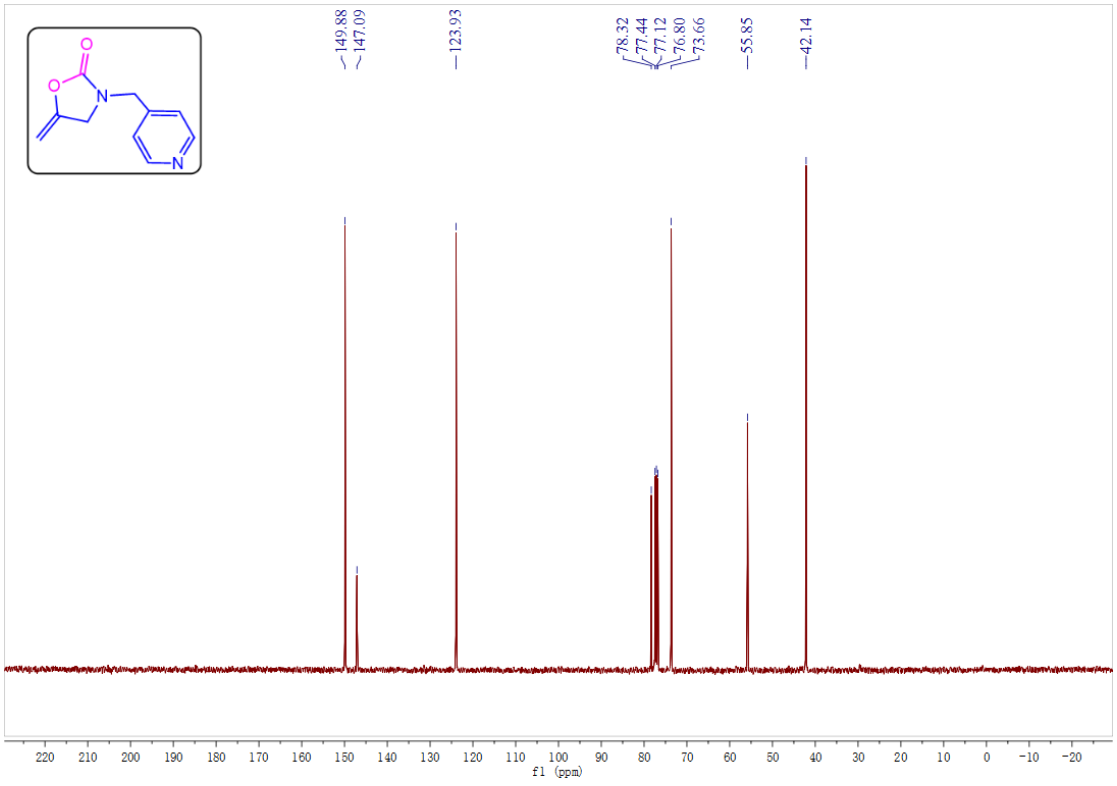
^{1}H NMR and ^{13}C NMR of compound **20**



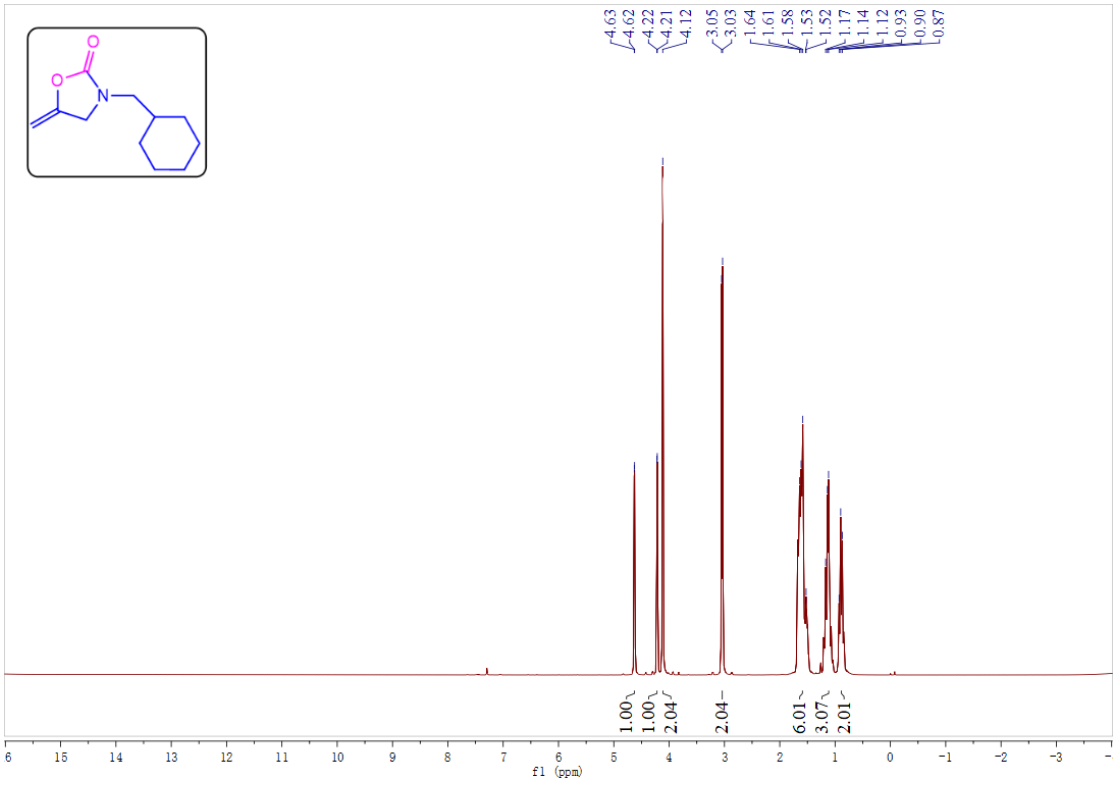


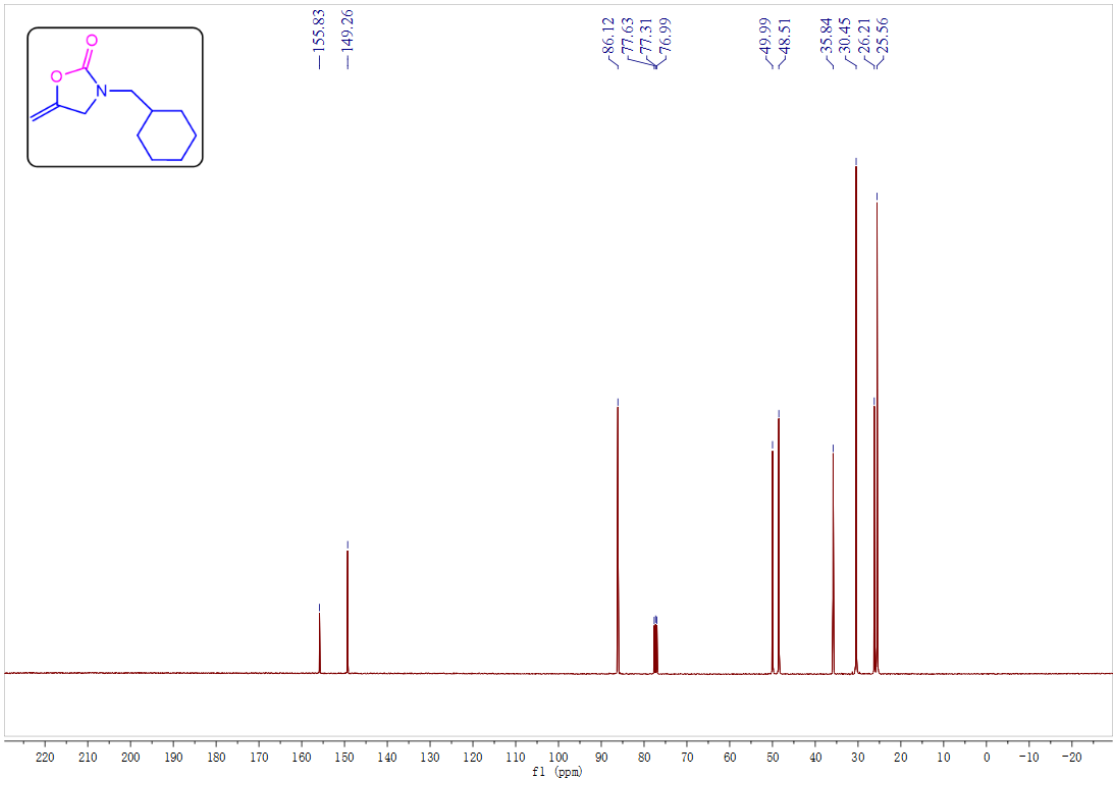
^{1}H NMR and ^{13}C NMR of compound **2p**



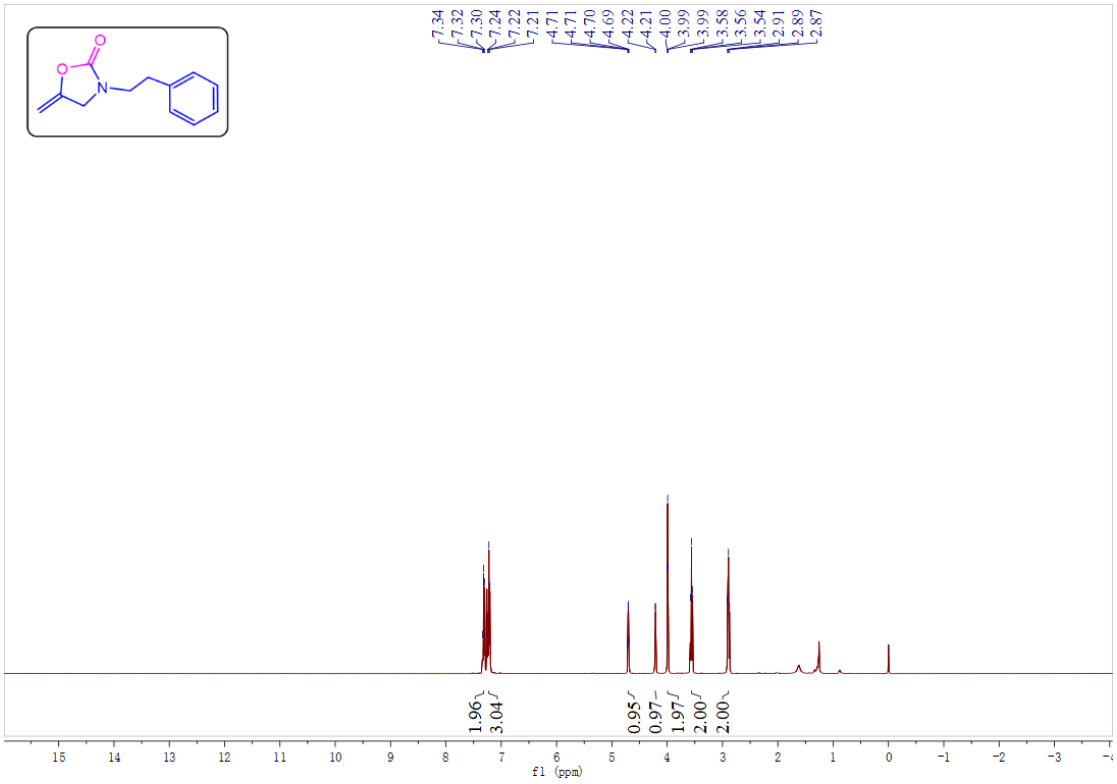


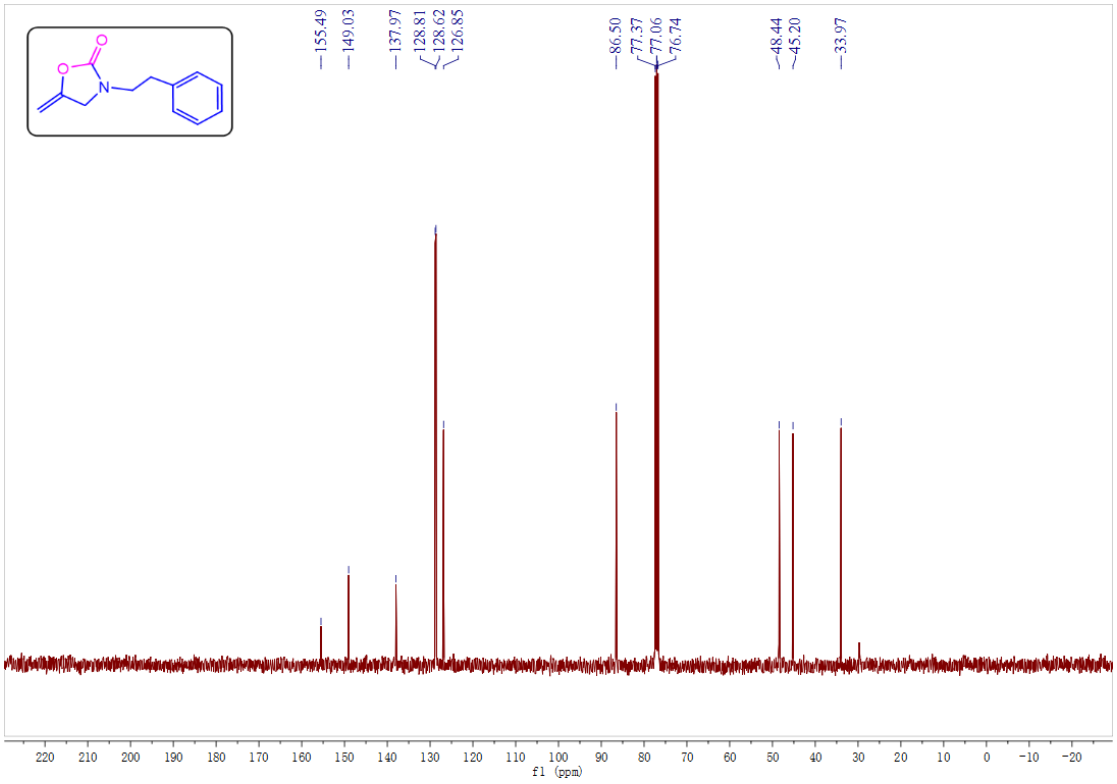
^{1}H NMR and ^{13}C NMR of compound **2q**



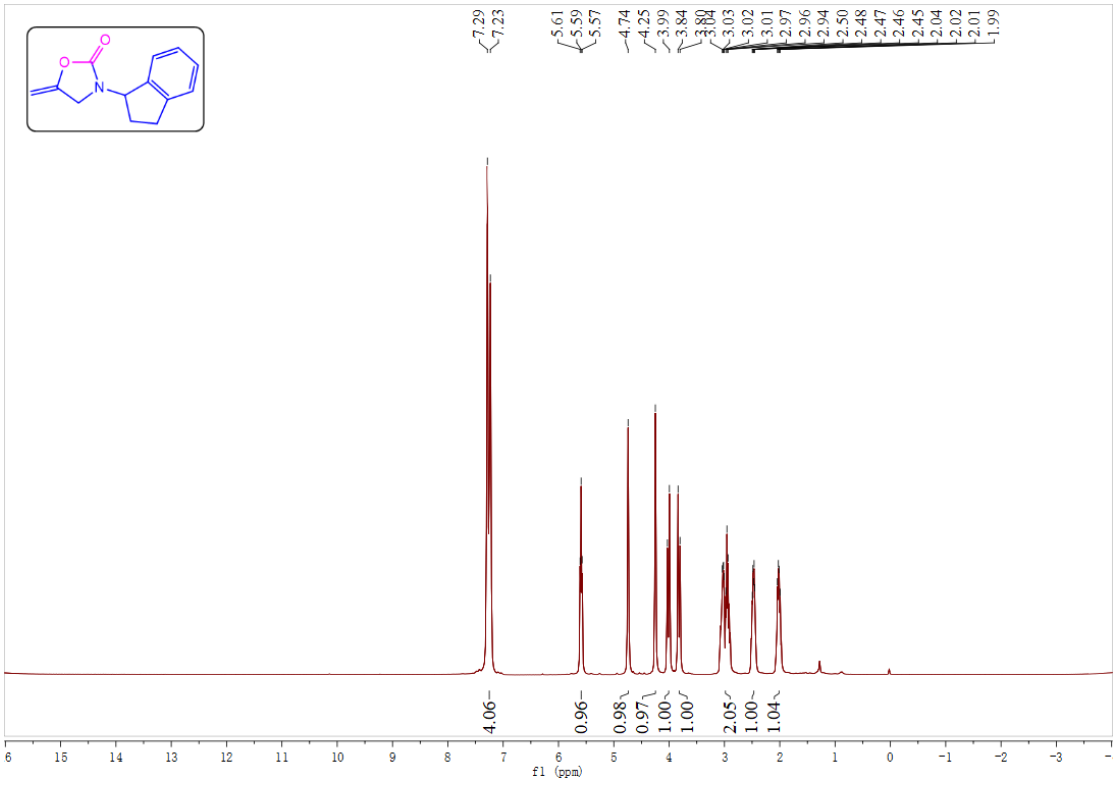


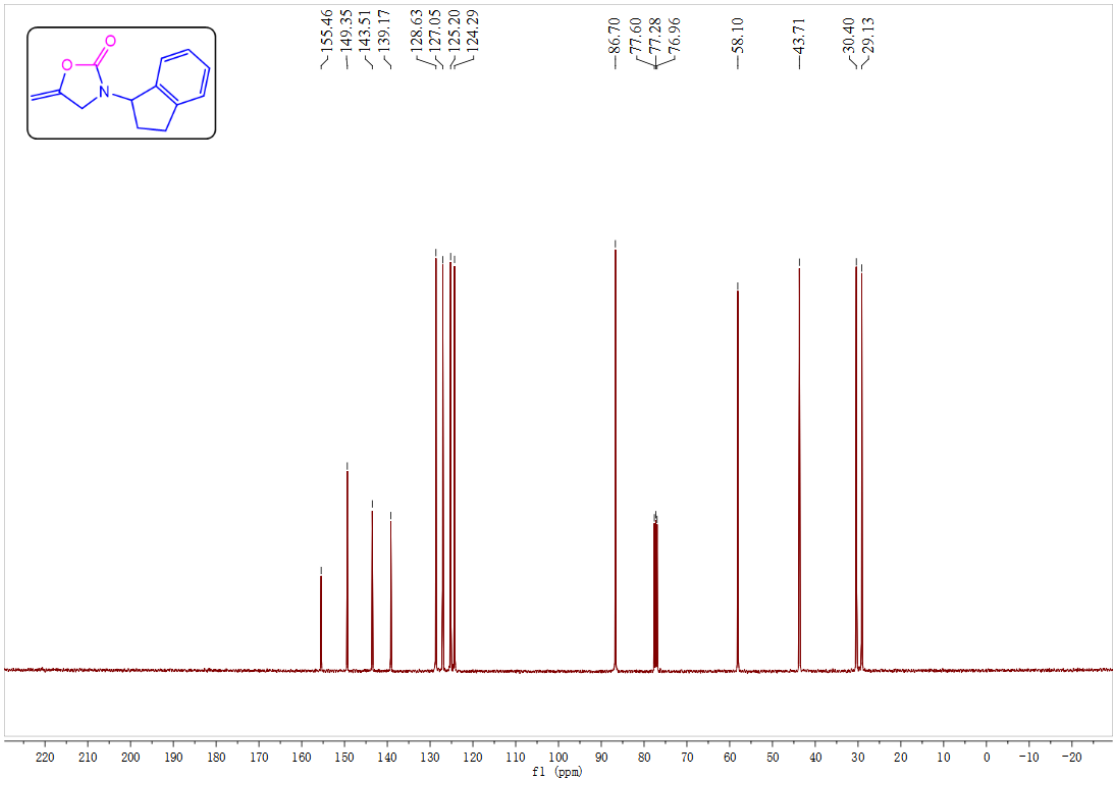
^{1}H NMR and ^{13}C NMR of compound **2r**



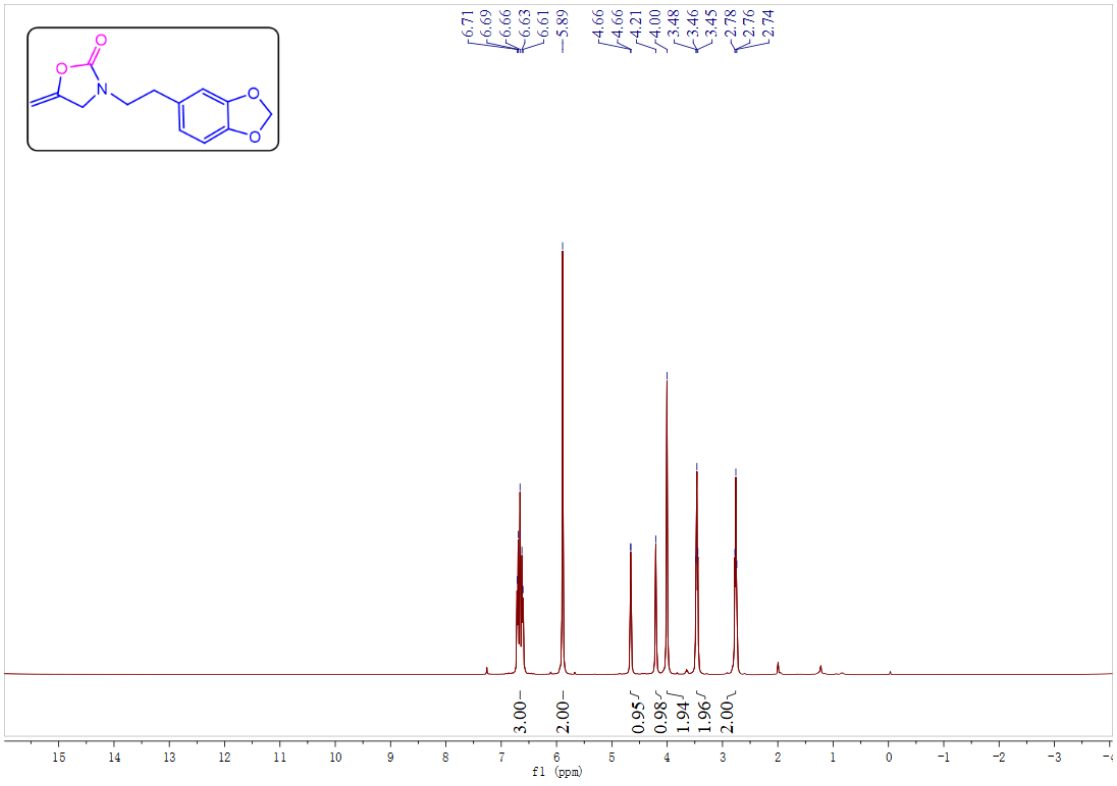


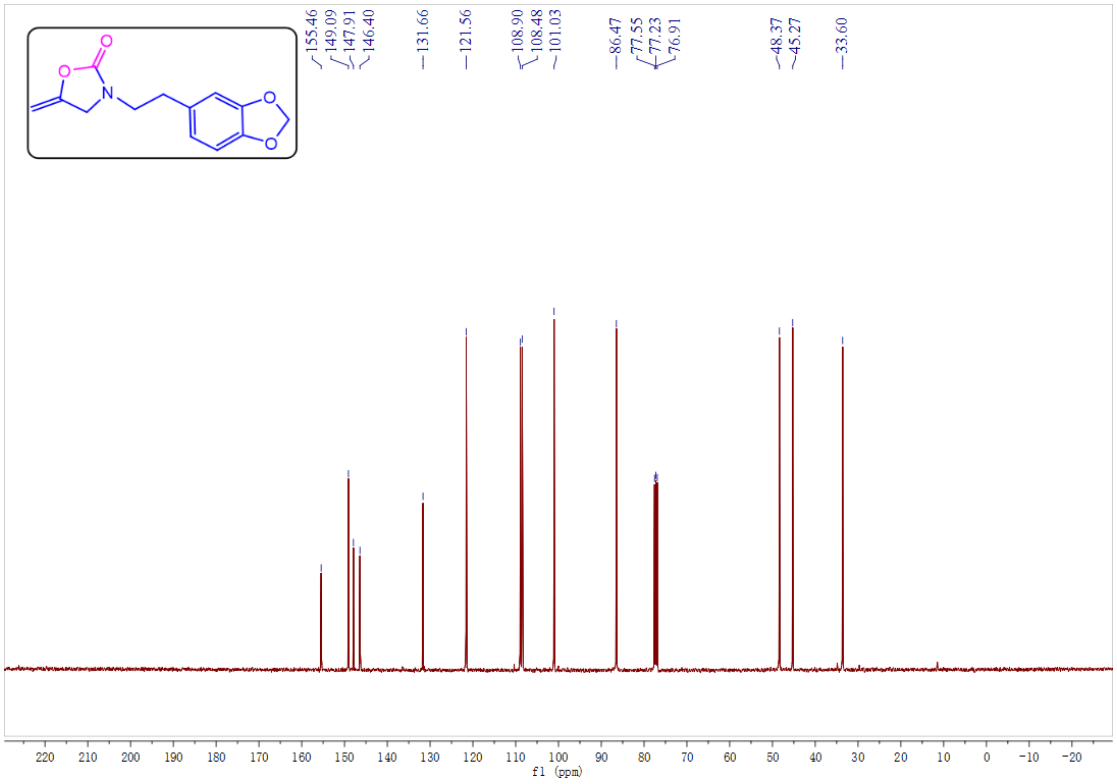
^{1}H NMR and ^{13}C NMR of compound **2s**



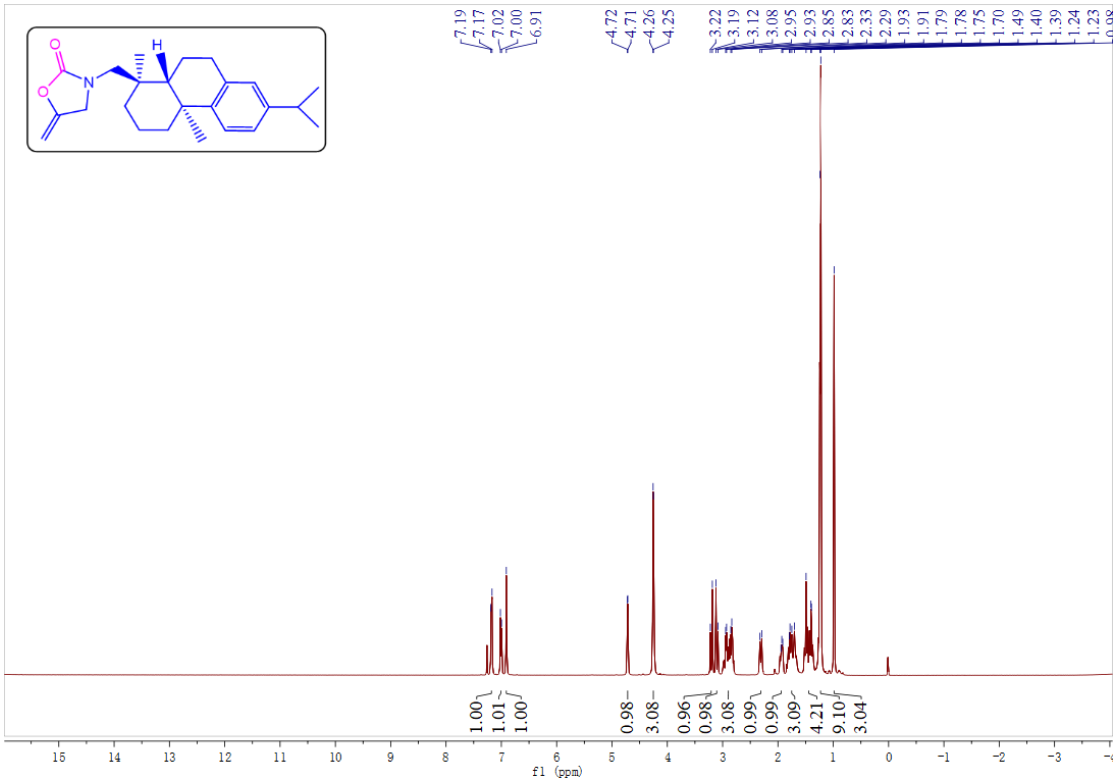


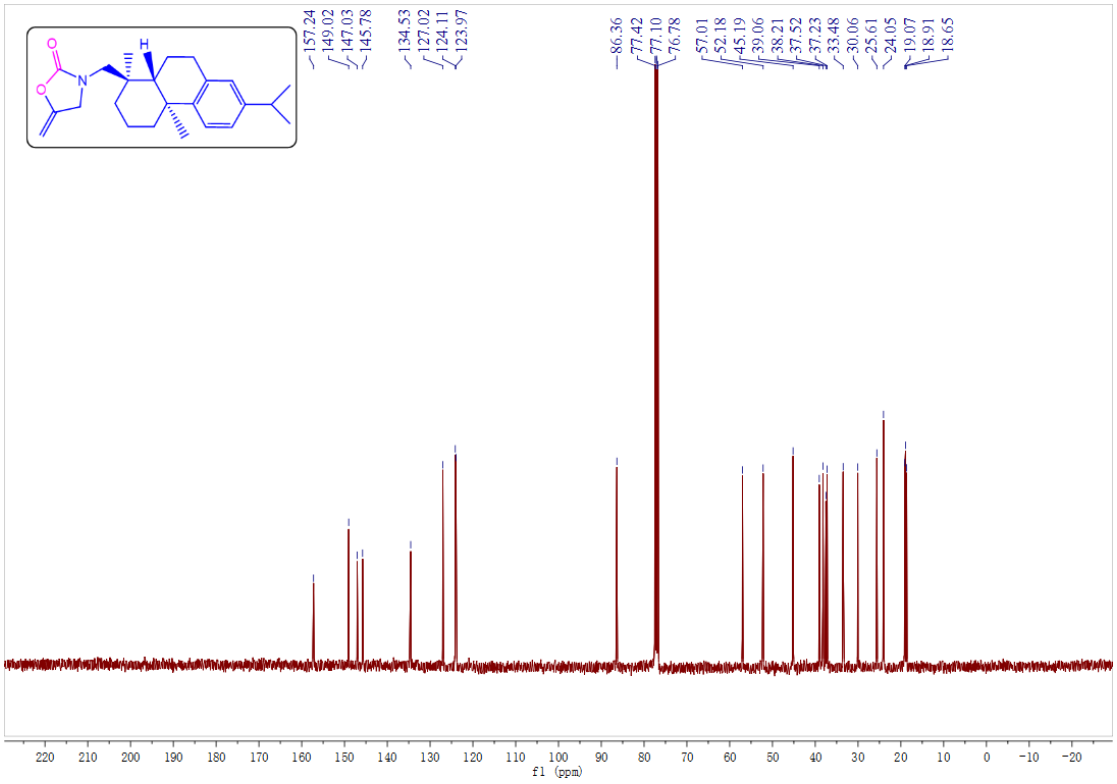
^{1}H NMR and ^{13}C NMR of compound **2t**



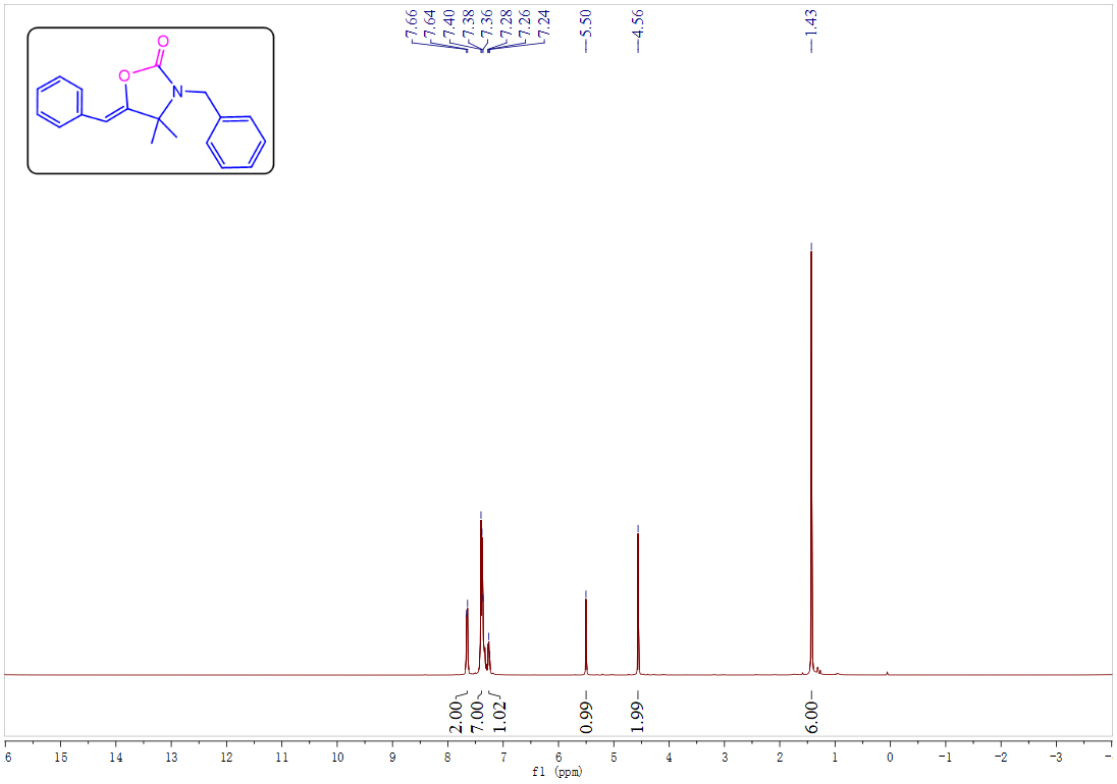


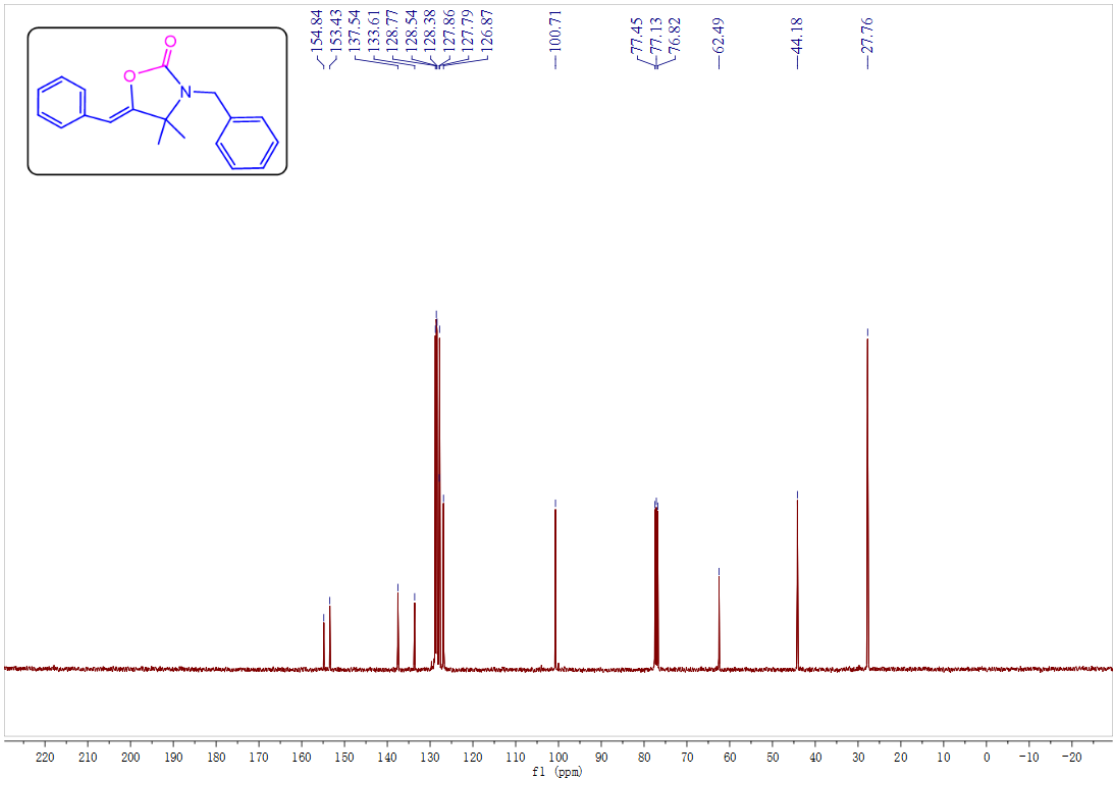
^{1}H NMR and ^{13}C NMR of compound **2u**



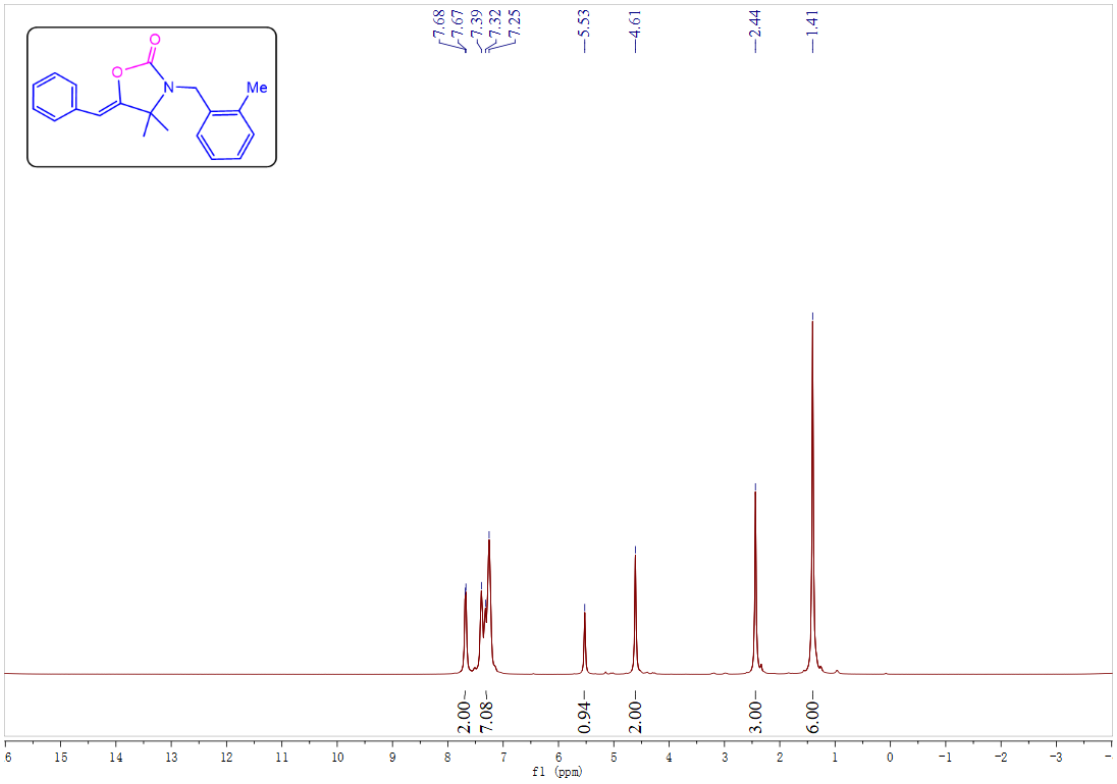


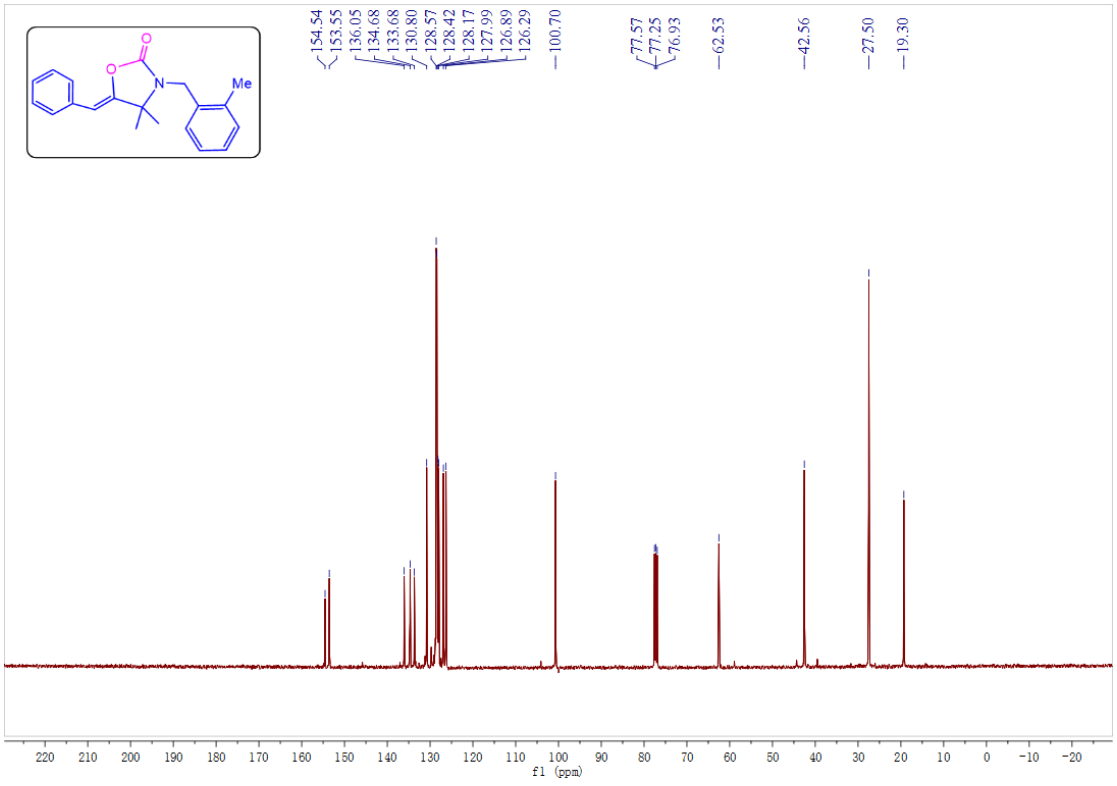
^{1}H NMR and ^{13}C NMR of compound **4a**



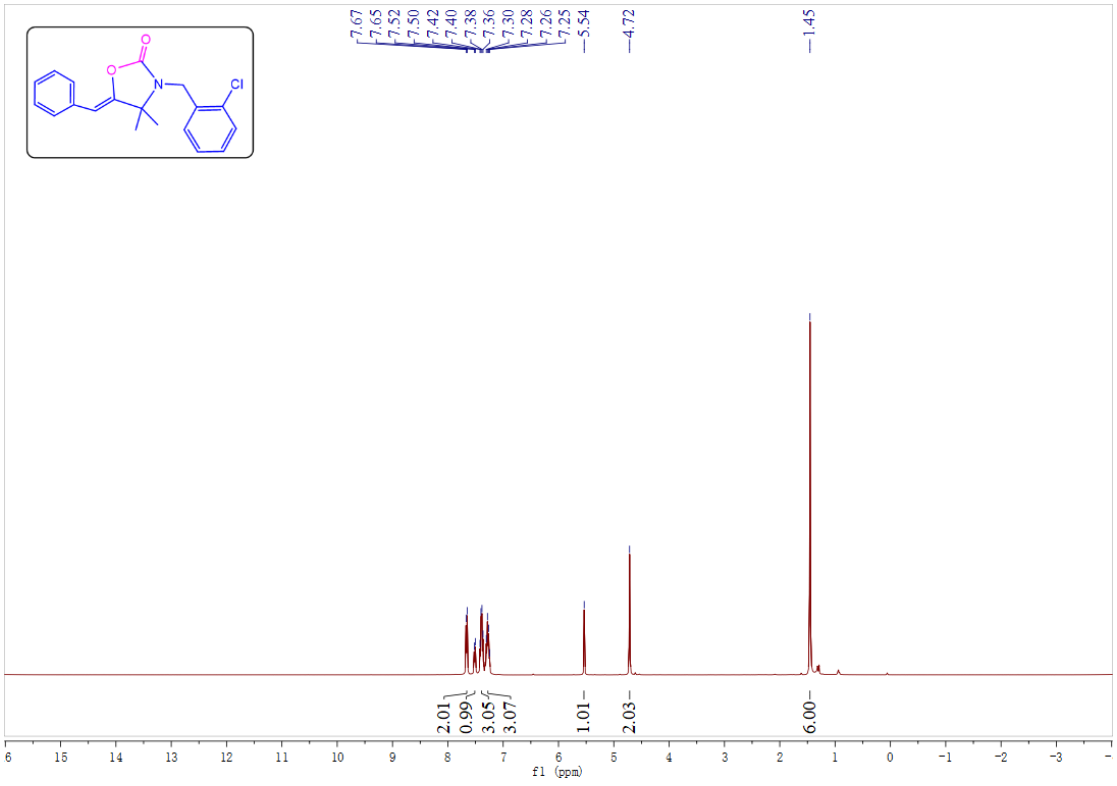


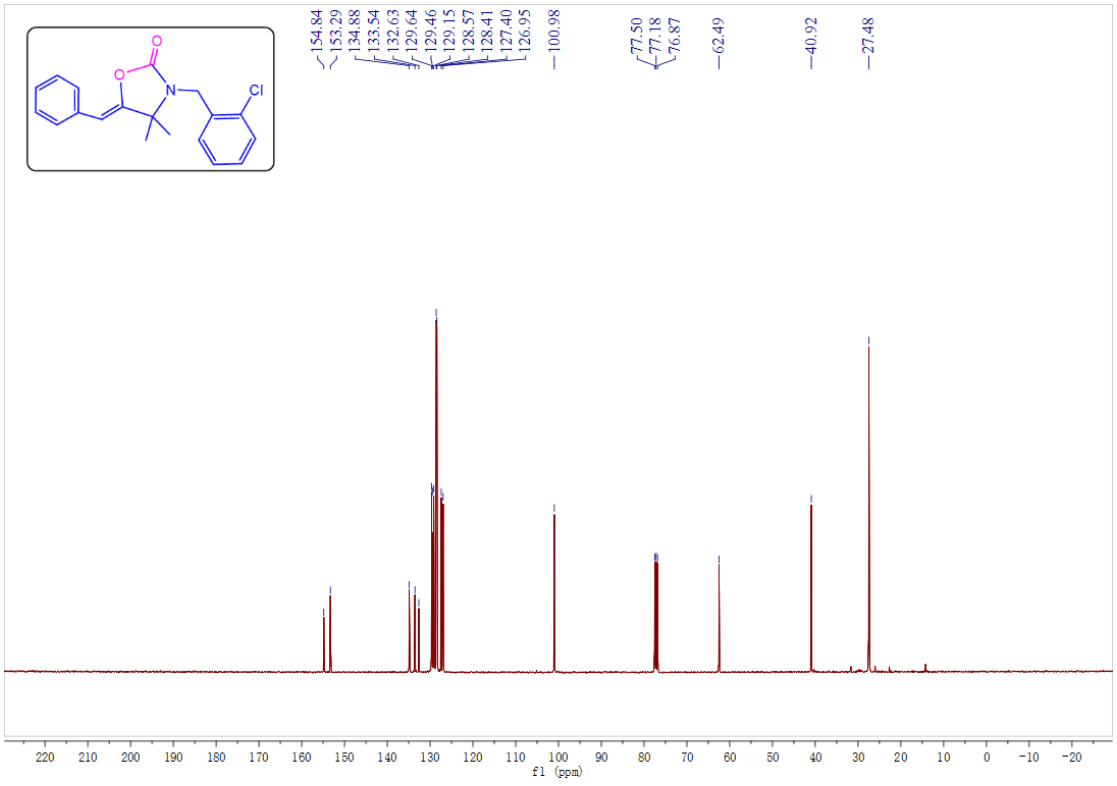
^{1}H NMR and ^{13}C NMR of compound **4b**



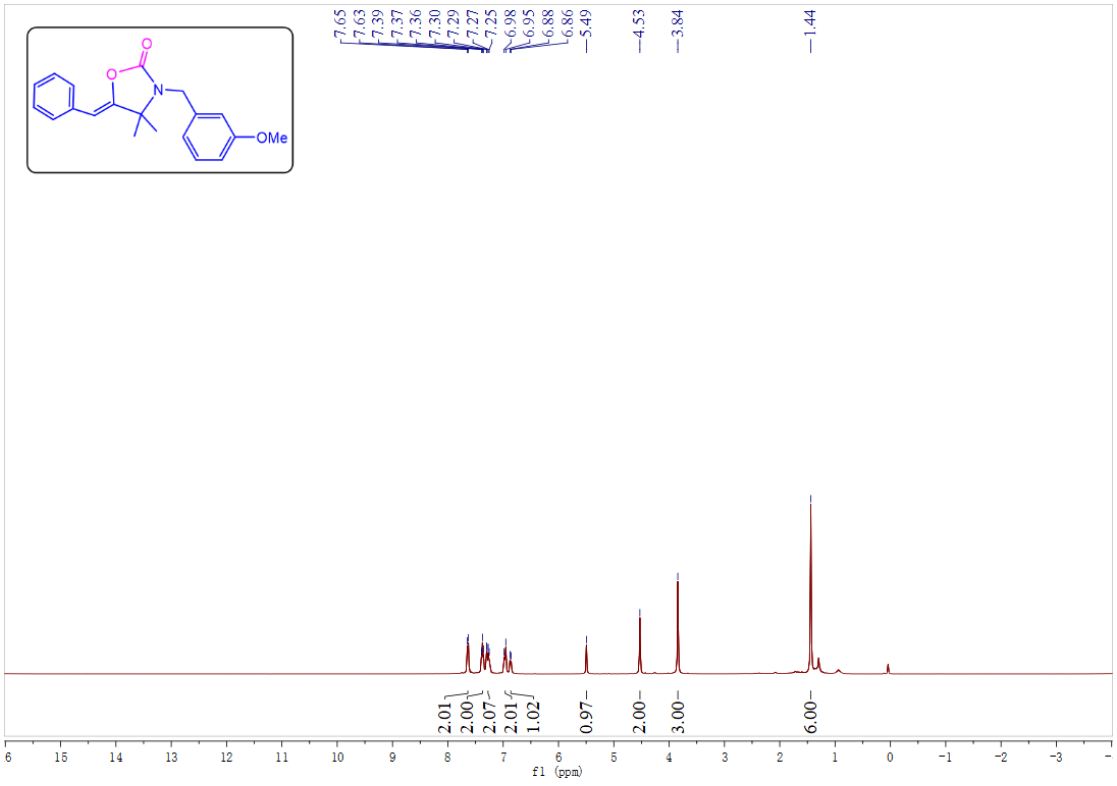


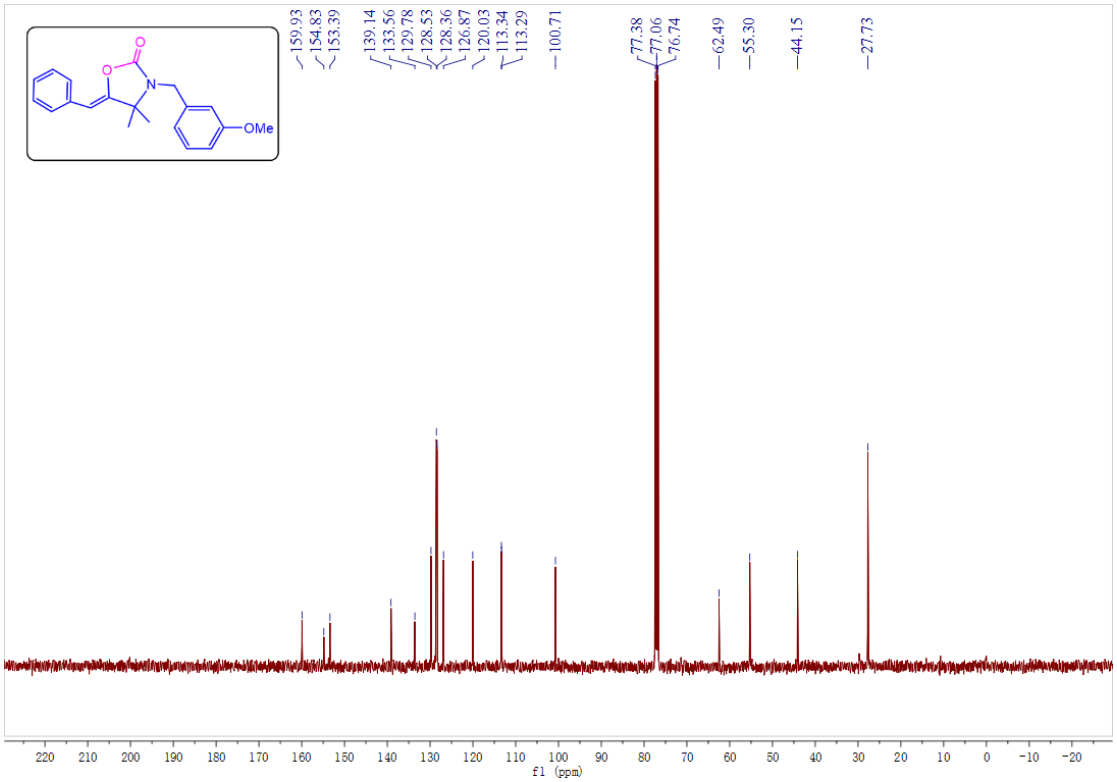
^{1}H NMR and ^{13}C NMR of compound **4c**



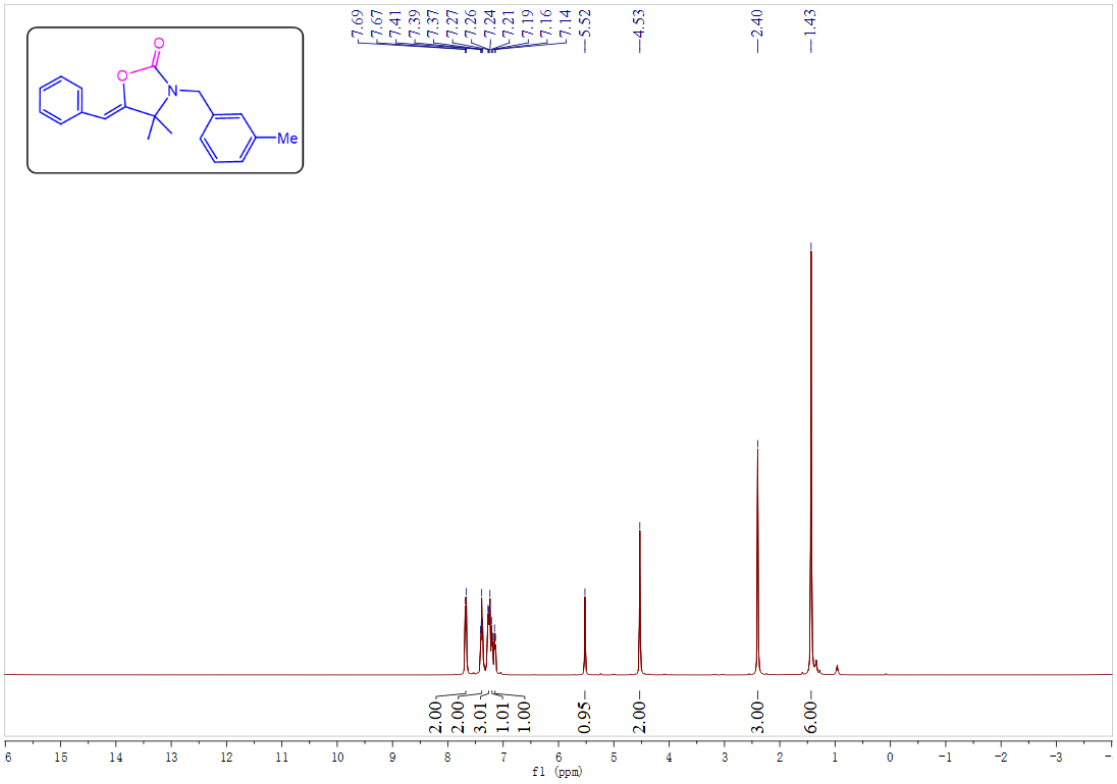


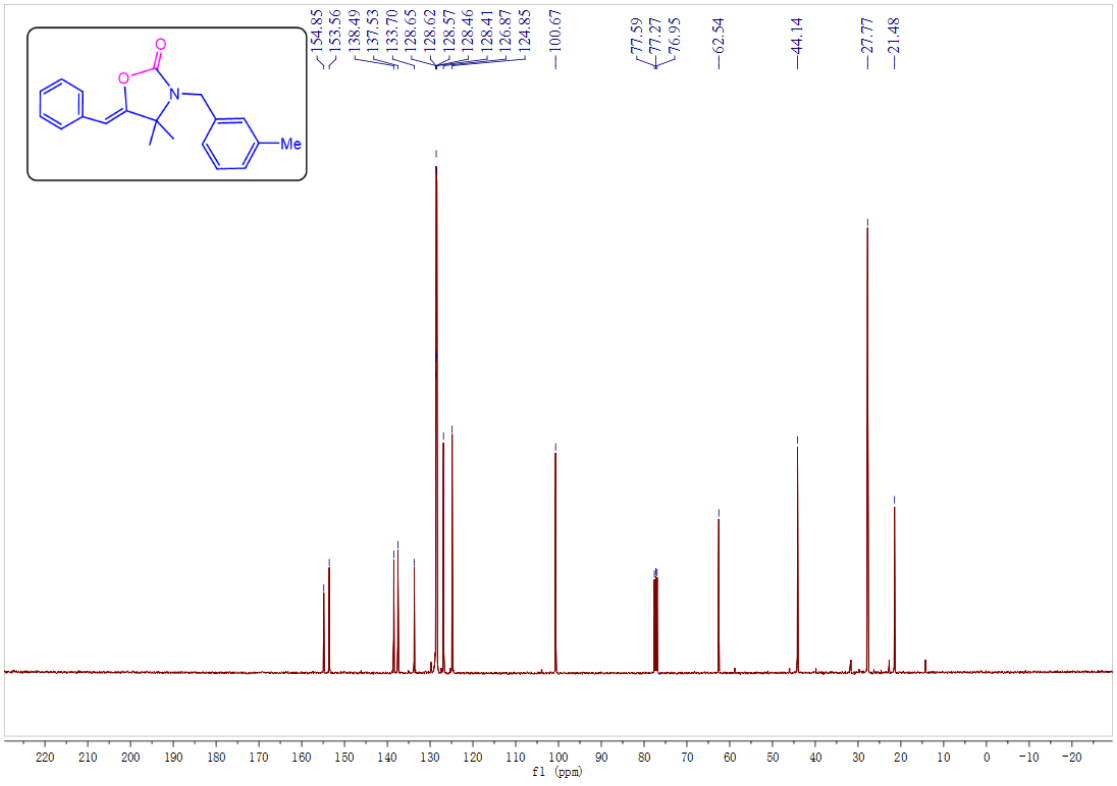
^{1}H NMR and ^{13}C NMR of compound **4d**



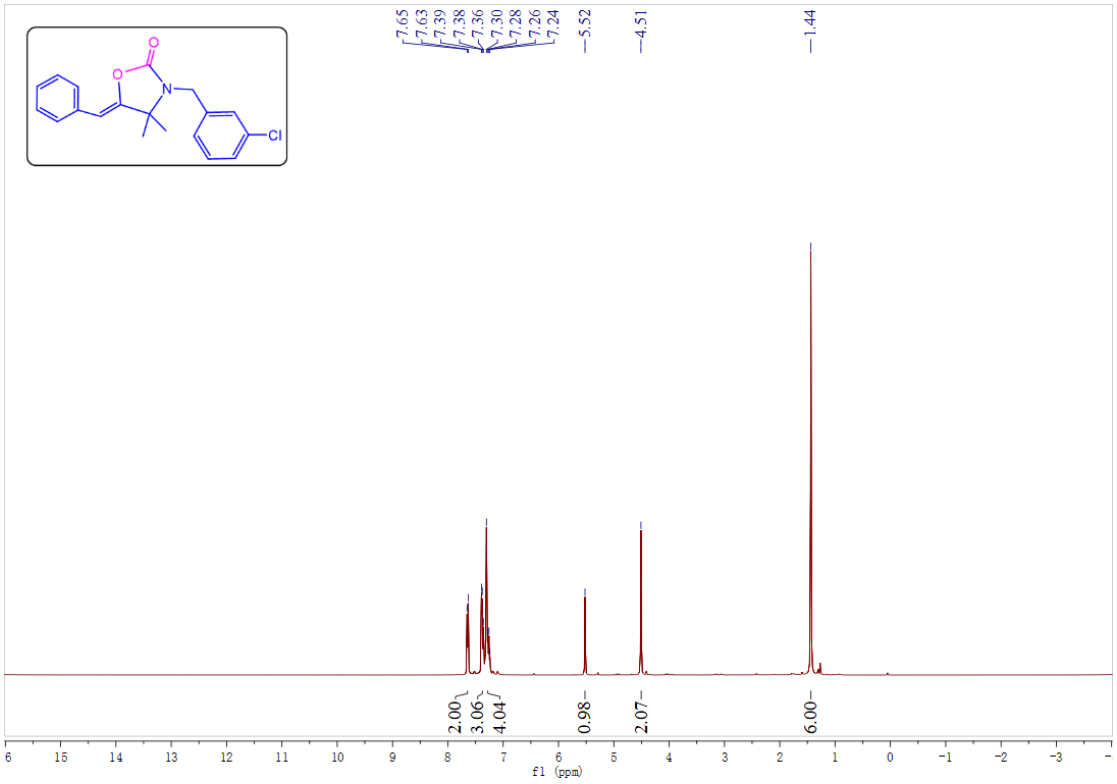


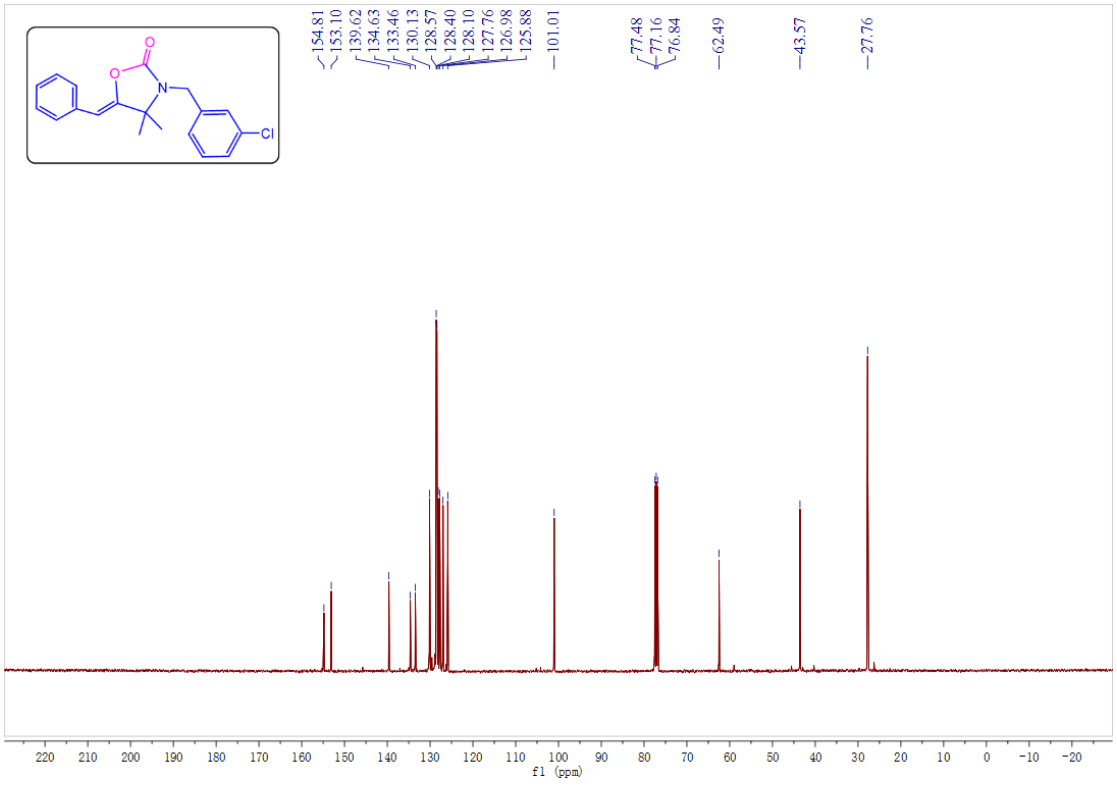
^{1}H NMR and ^{13}C NMR of compound **4e**



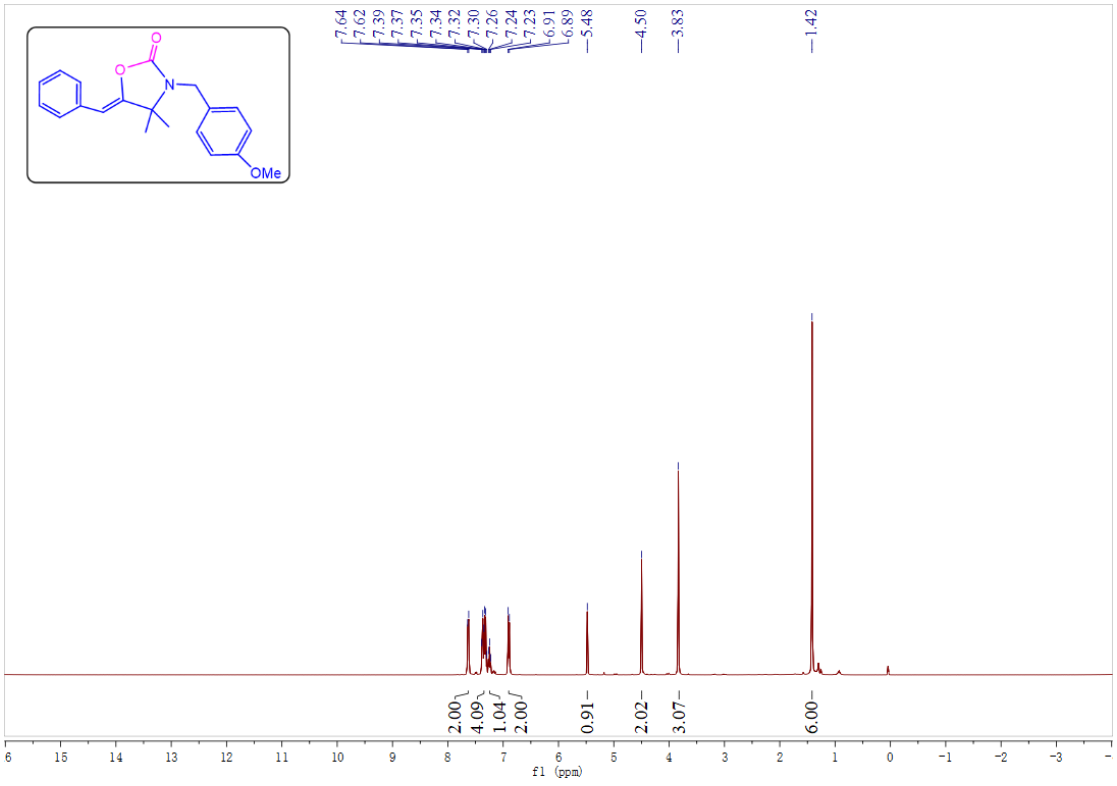


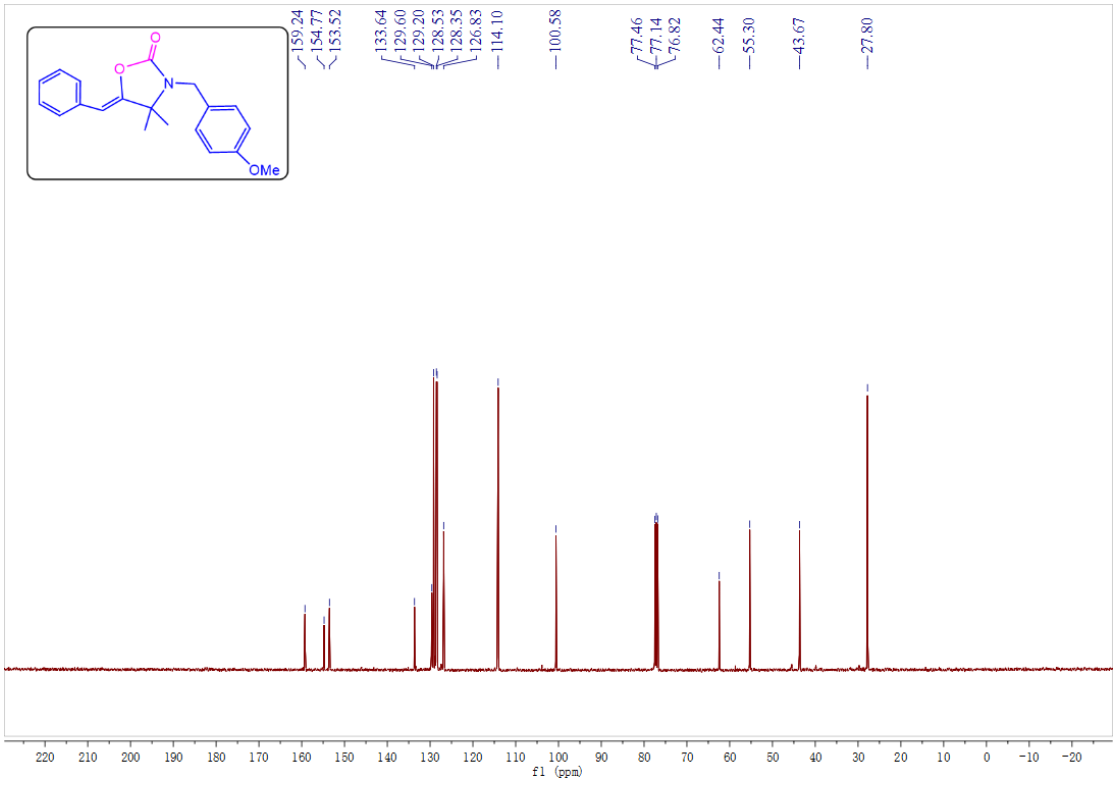
^{1}H NMR and ^{13}C NMR of compound **4f**



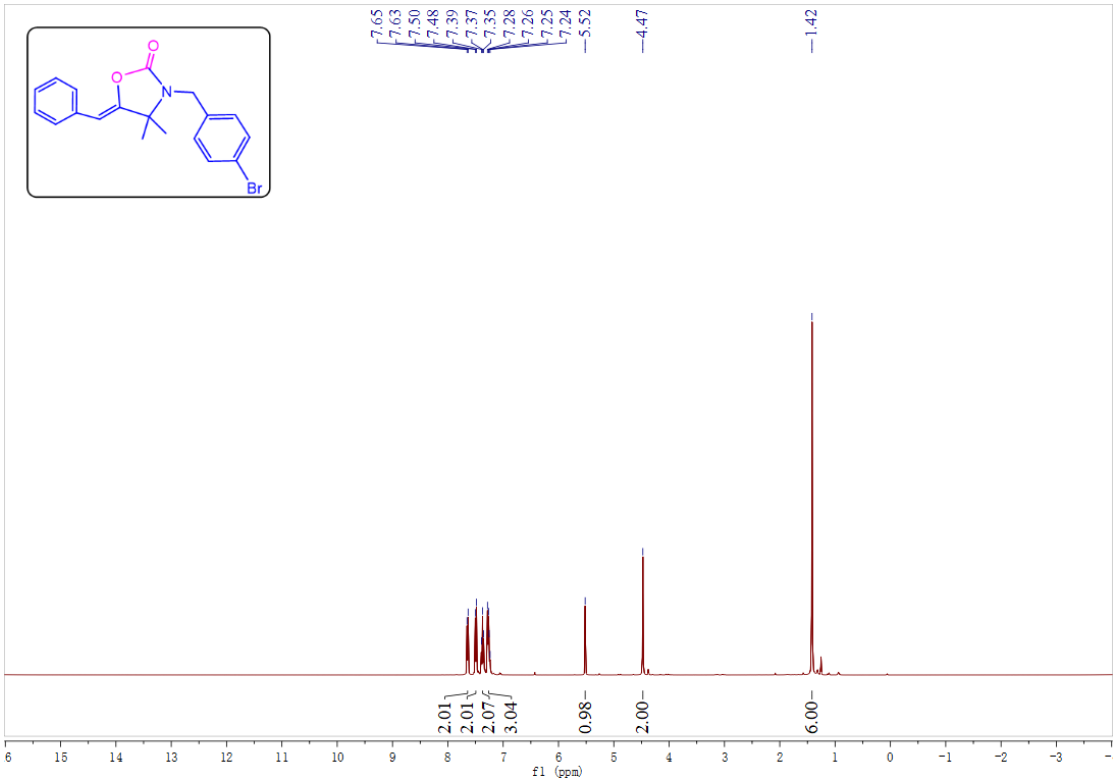


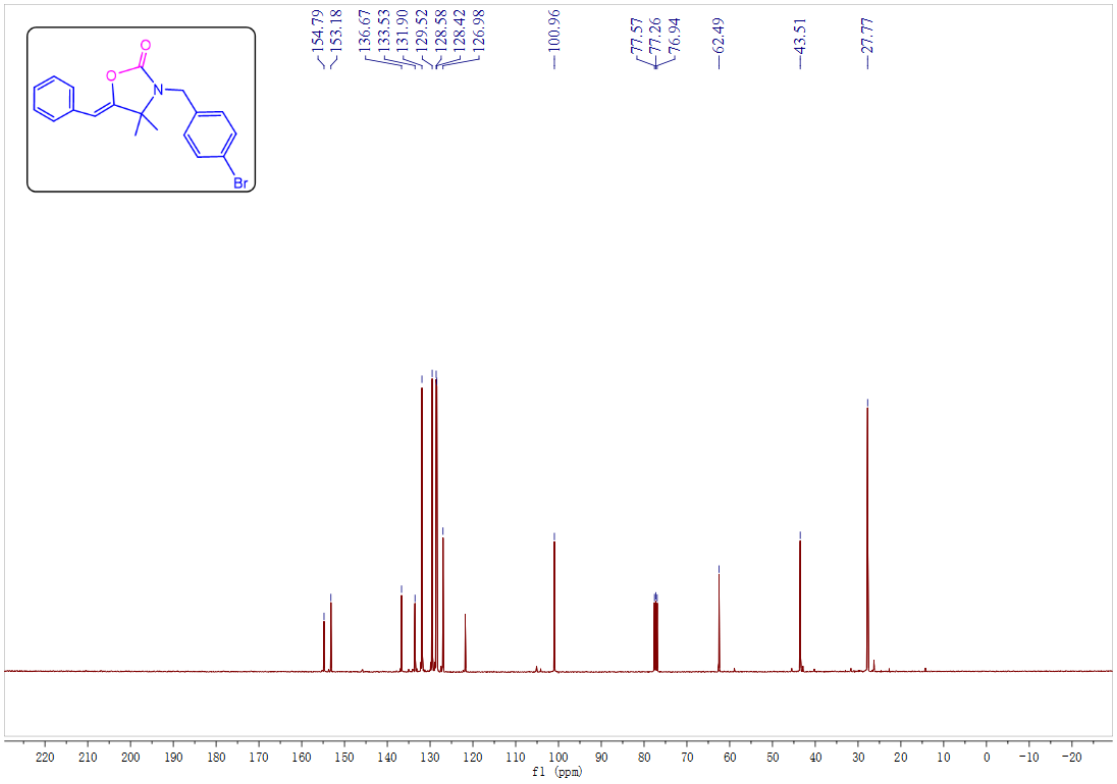
^{1}H NMR and ^{13}C NMR of compound **4g**



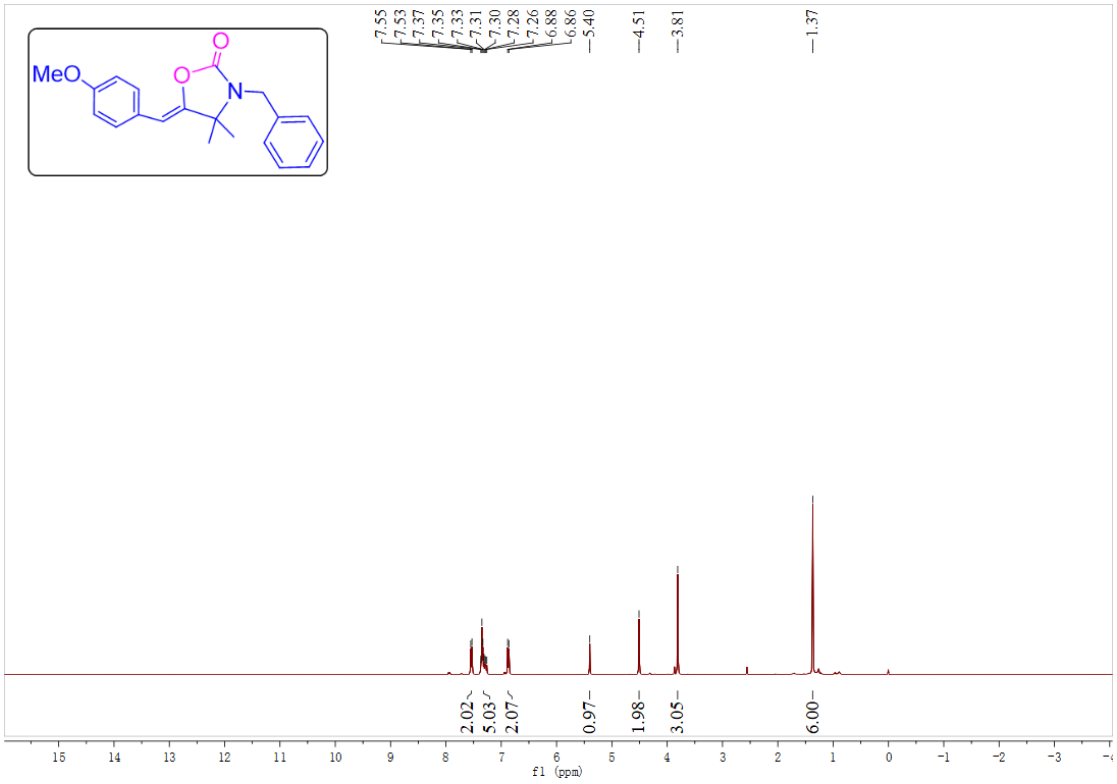


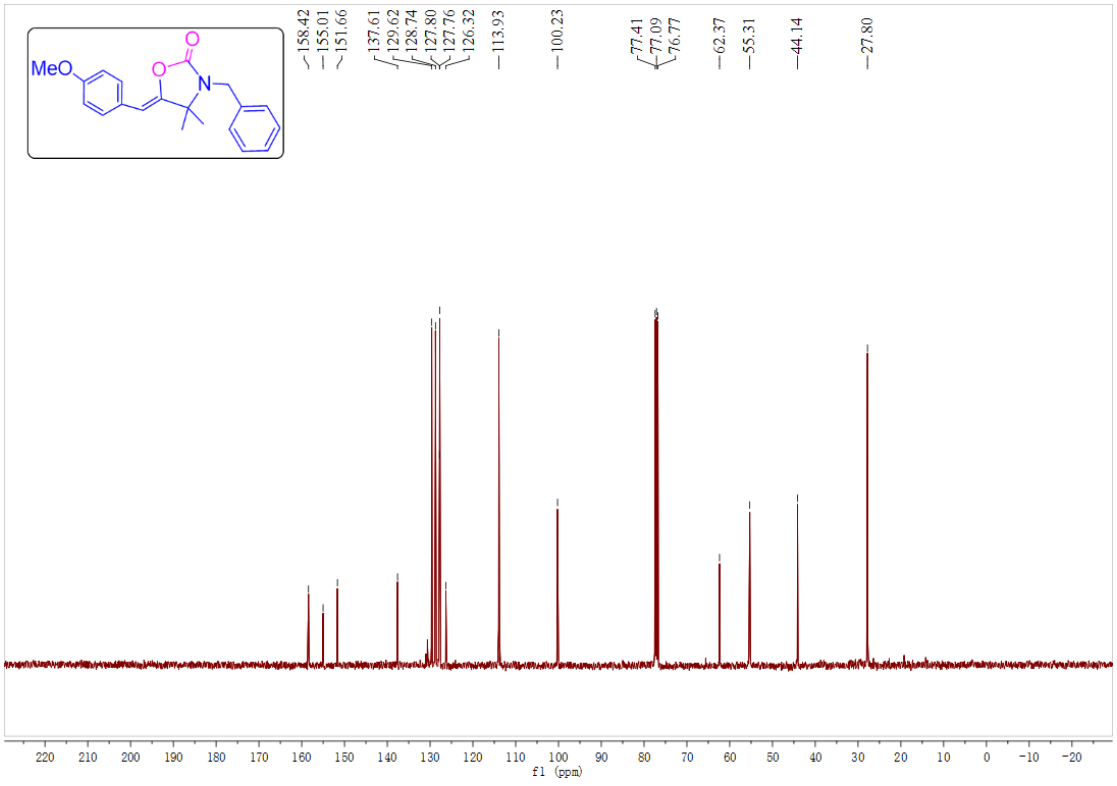
^{1}H NMR and ^{13}C NMR of compound **4h**



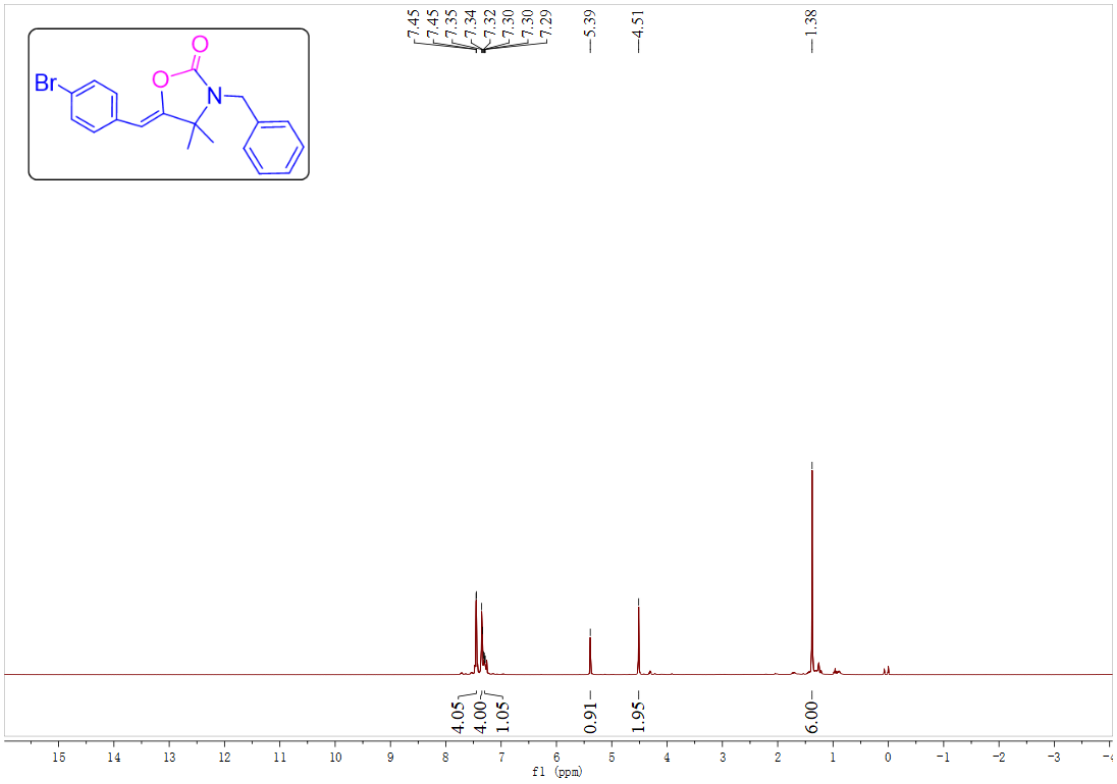


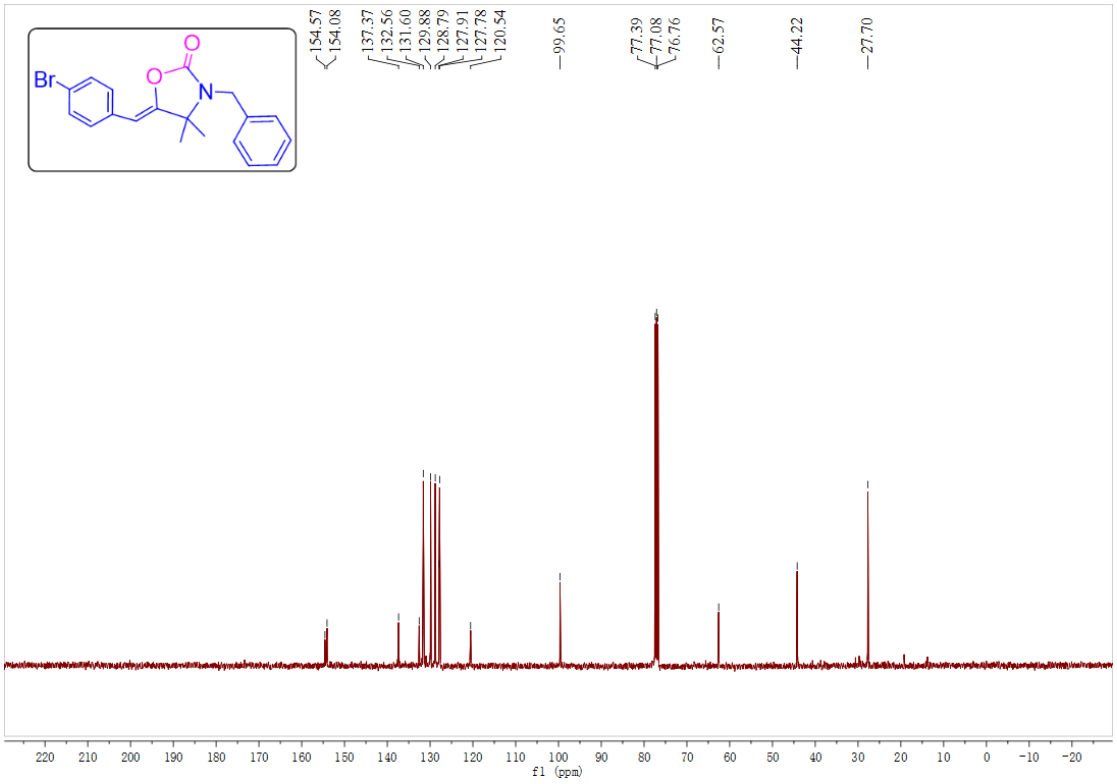
^{1}H NMR and ^{13}C NMR of compound **4i**



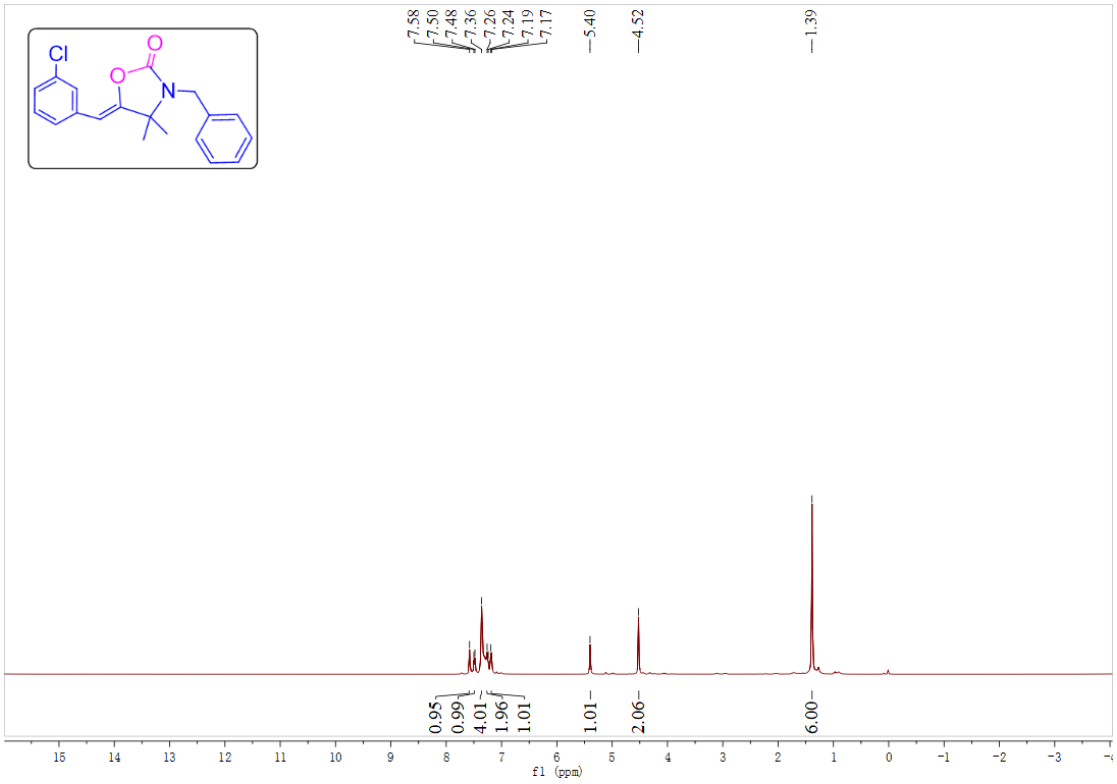


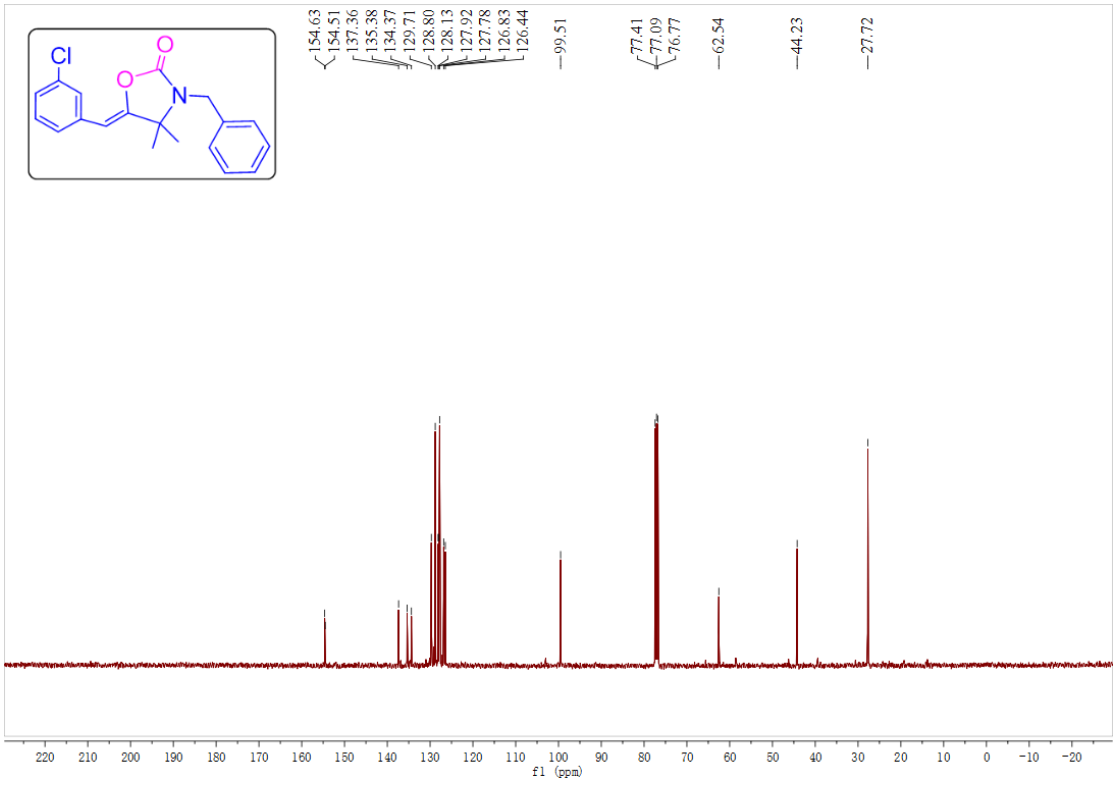
^{1}H NMR and ^{13}C NMR of compound **4j**



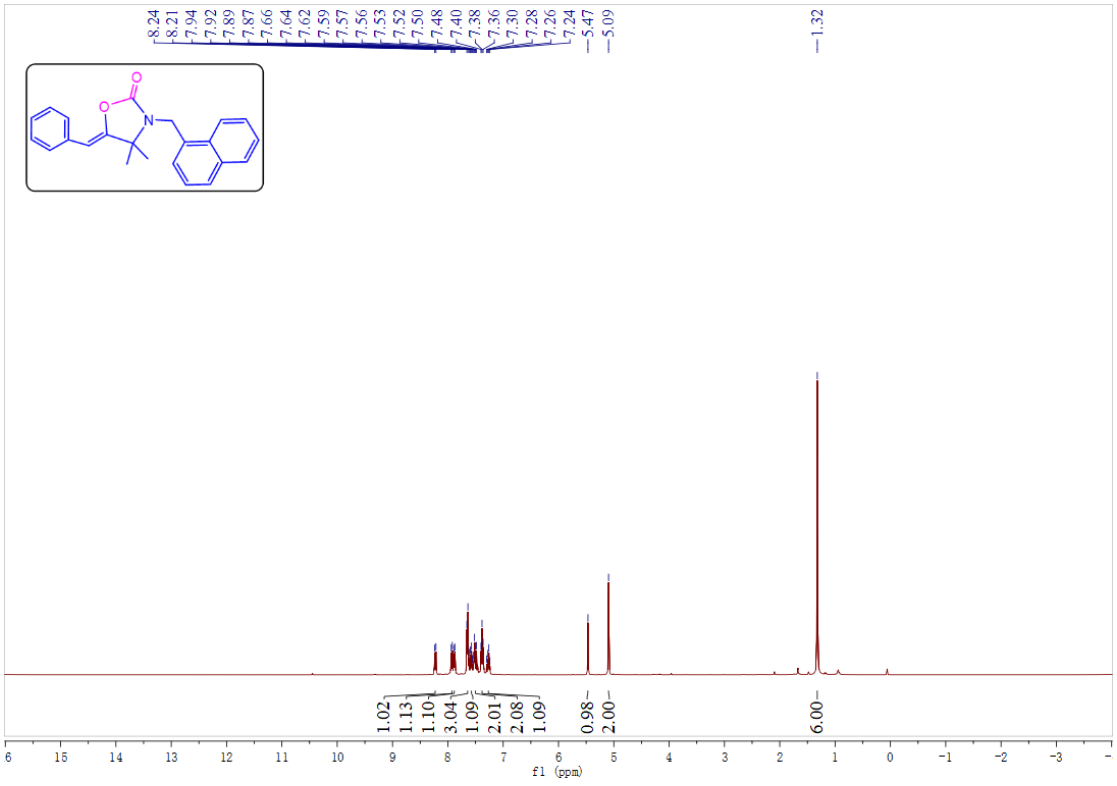


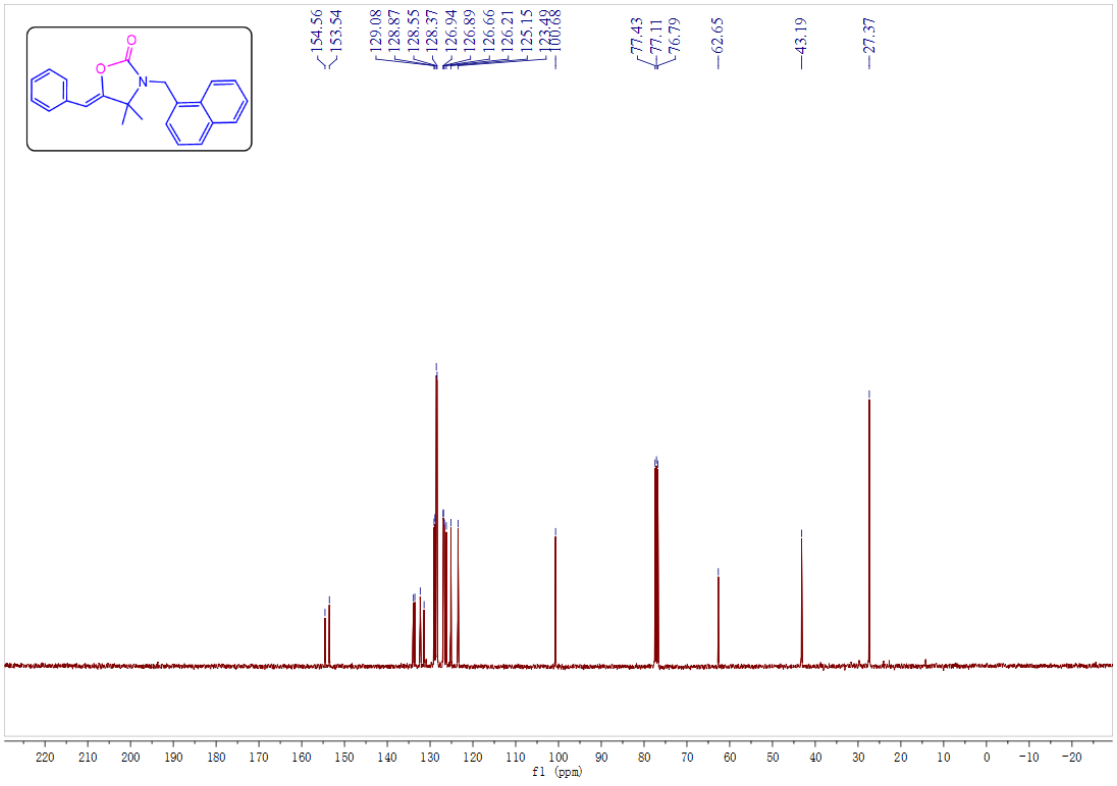
^{1}H NMR and ^{13}C NMR of compound **4k**



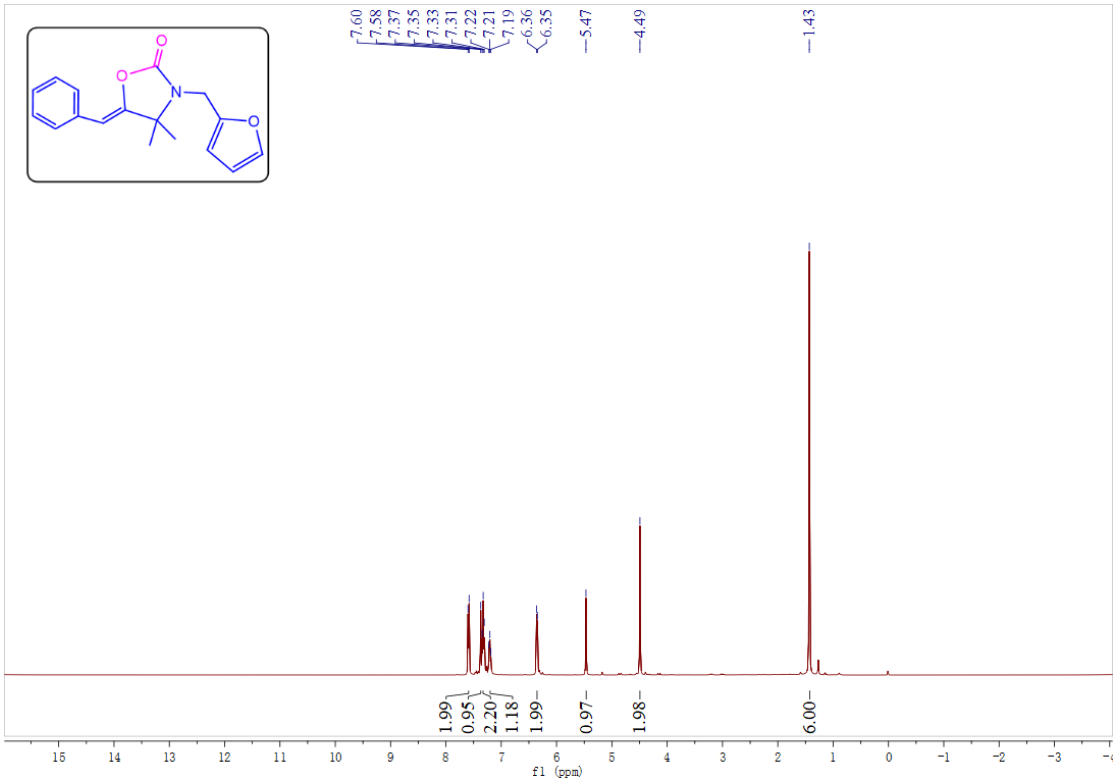


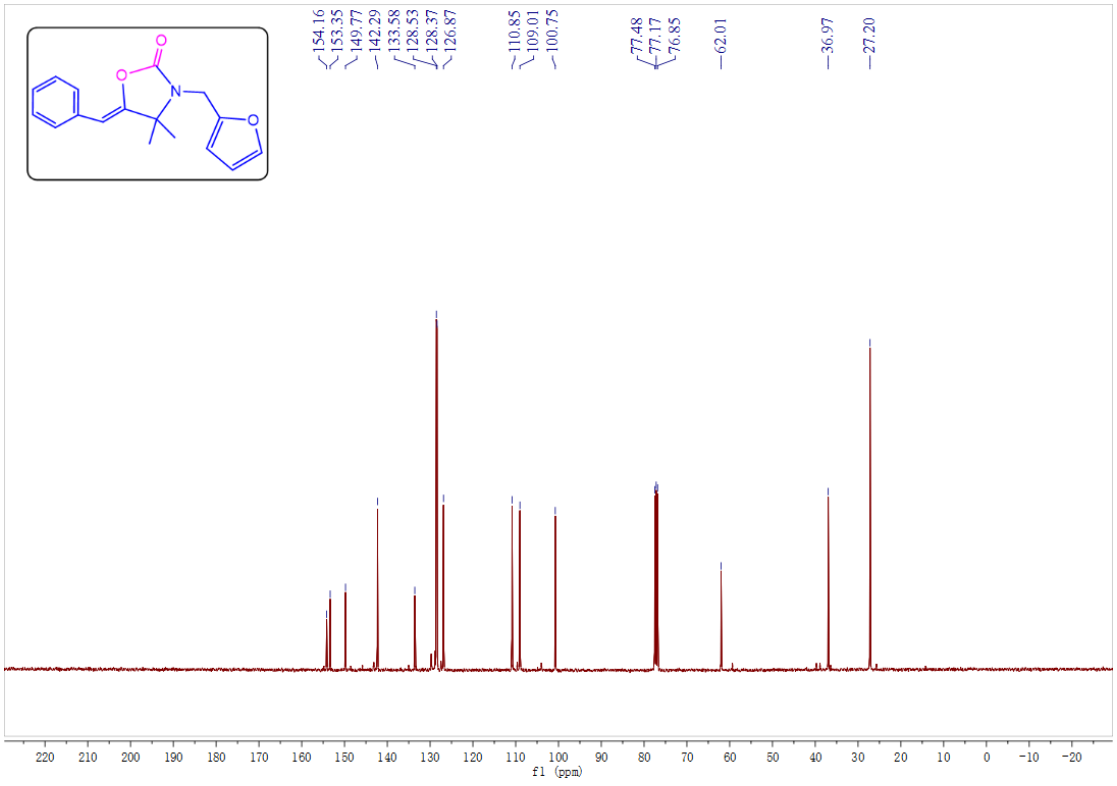
^{1}H NMR and ^{13}C NMR of compound **4l**



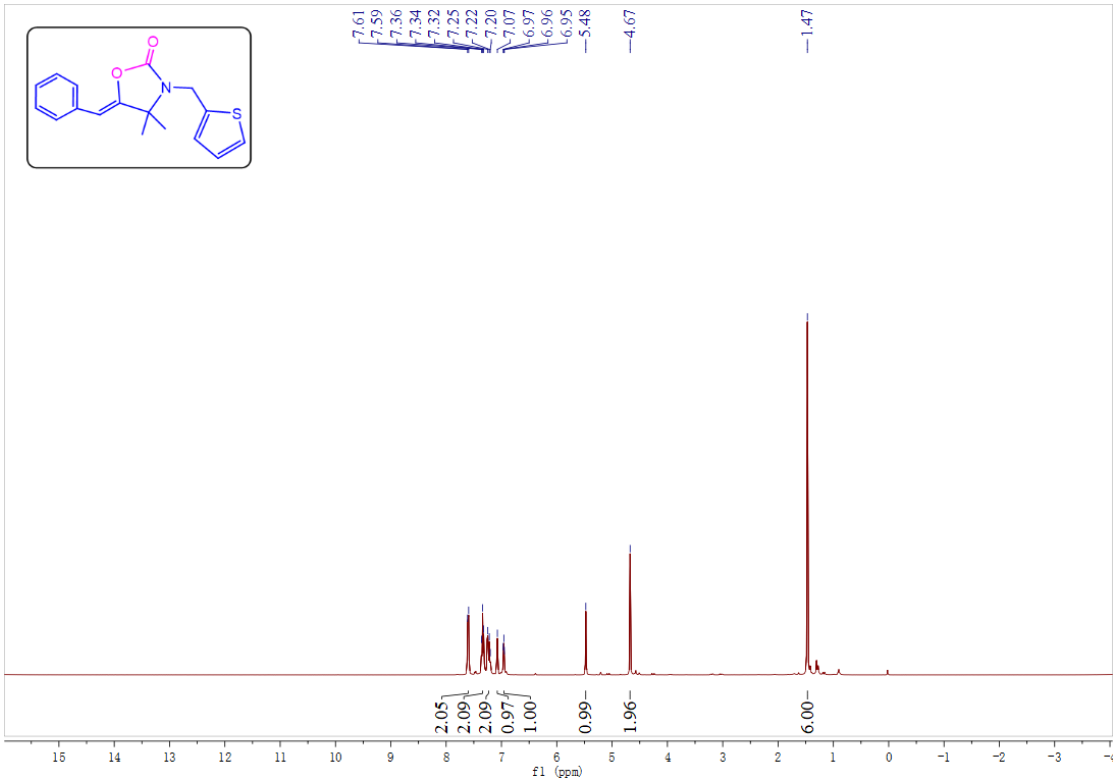


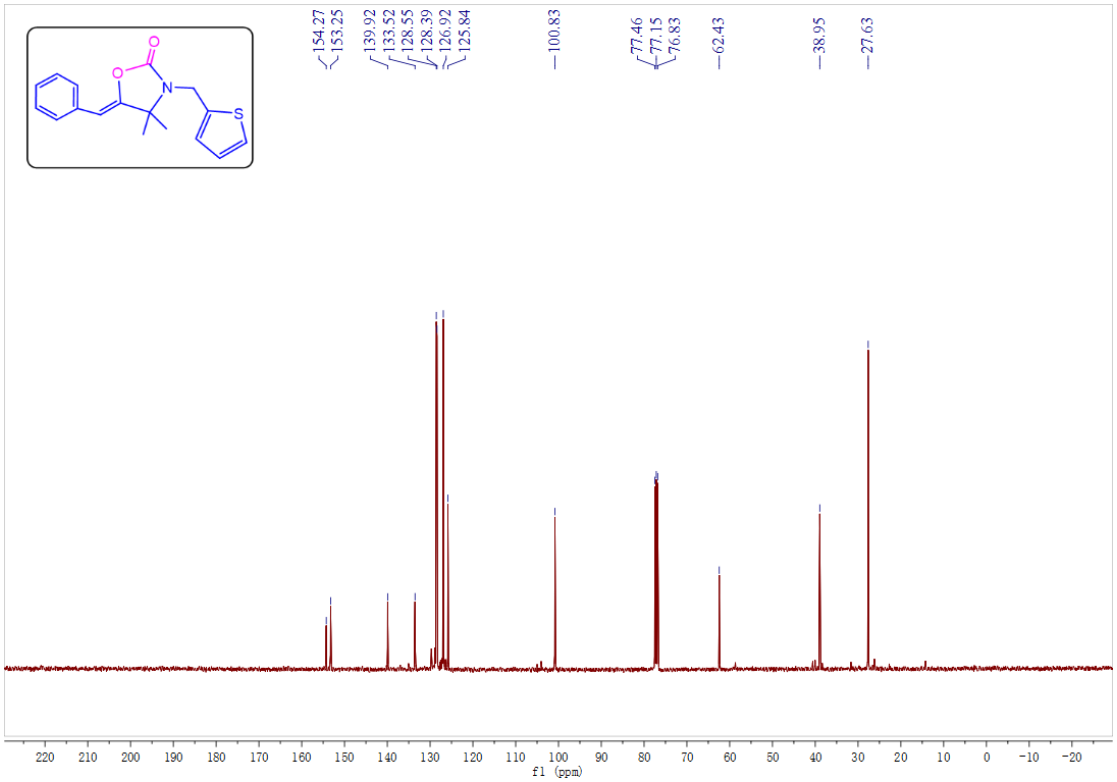
^{1}H NMR and ^{13}C NMR of compound **4m**





^{1}H NMR and ^{13}C NMR of compound **4n**





5. X-Ray Analysis

The crystal structure of **2t** (Fig. S3) was determined by X-Ray structural analysis using XtabLAB Synergy of Rigaku Corporation with Cu Kα radiation. The crystals were kept at 293 K during data collection. Using Olex2, the structures were solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the XL refinement package using Least Squares minimisation.

The crystal was obtained by slow evaporation of solution of 3-(2-(Benzo[*d*][1,3]dioxol-5-yl)ethyl)-5-methyleneoxazolidin-2-one (**2t**) in the dichloromethane-methanol mixture.

Crystal data, data collection, and structure refinement details are summarized in Table S1. The atomic coordinates were deposited at the Cambridge Crystallographic Data Centre. CCDC No. 2662433.

Table S1. Crystal data and structure refinement for **2t**

Identification code	**2t**
CCDC number	**2662433**
Empirical formula	$C_{13}H_{13}NO_4$
Formula weight	247.24
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	23.8084(4)
b/Å	4.61710(10)
c/Å	11.0799(2)
α/°	90
β/°	92.314(2)
γ/°	90
Volume/Å^3	1216.97(4)
Z	4
ρ_{calc}g/cm^3	1.349

μ/mm^{-1}	0.843
F(000)	520.0
Crystal size/mm^3	0.3×0.2×0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.432 to 153.524
Index ranges	-30≤h≤29, -5≤k≤5, -13≤l≤13
Reflections collected	7899
Independent reflections	2447 [R_{int} = 0.0246, R_{sigma} = 0.0278]
Data/restraints/parameters	2447/0/163
Goodness-of-fit on F^2	1.052
Final R indexes [I> = 2σ (I)]	R_1 = 0.0429, wR_2 = 0.1200
Final R indexes [all data]	R_1 = 0.0472, wR_2 = 0.1249
Largest diff. peak/hole / e Å^{-3}	0.17/-0.19

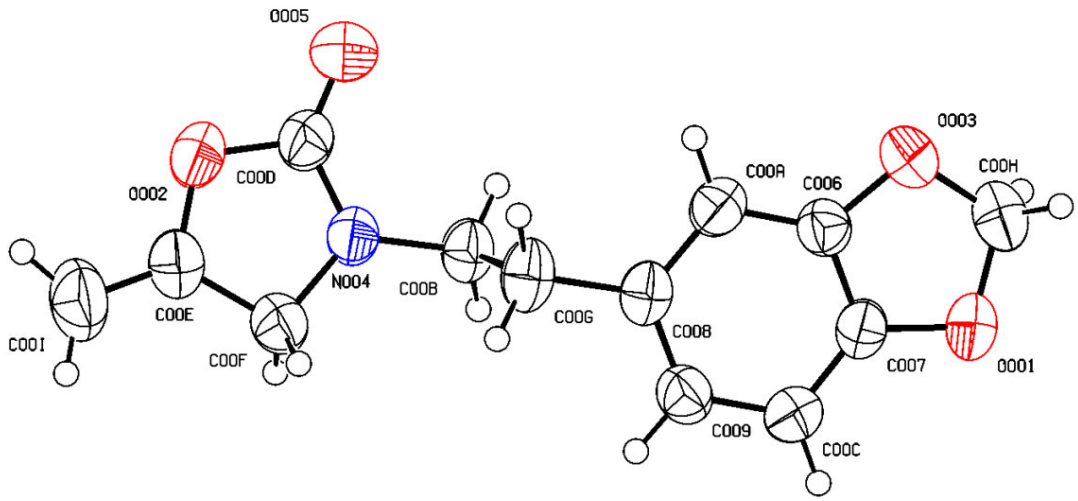


Fig. S1 Molecular structure of **2t**.

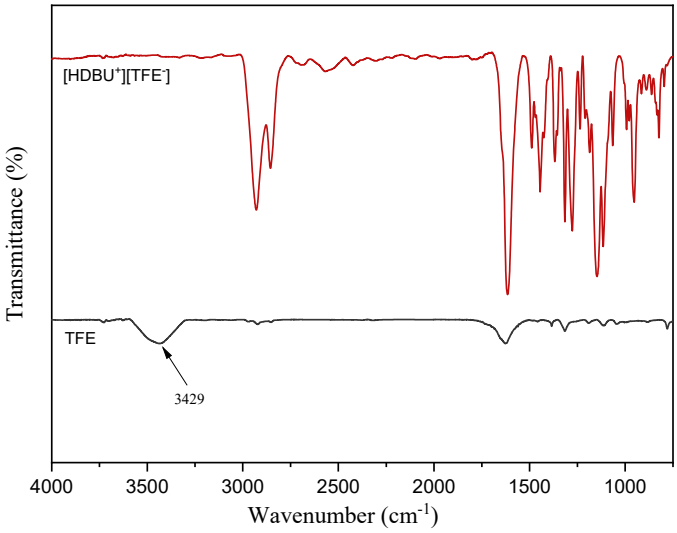


Fig. S2 FTIR spectrum of[$HDBU^+$][TFE^-] and TFE

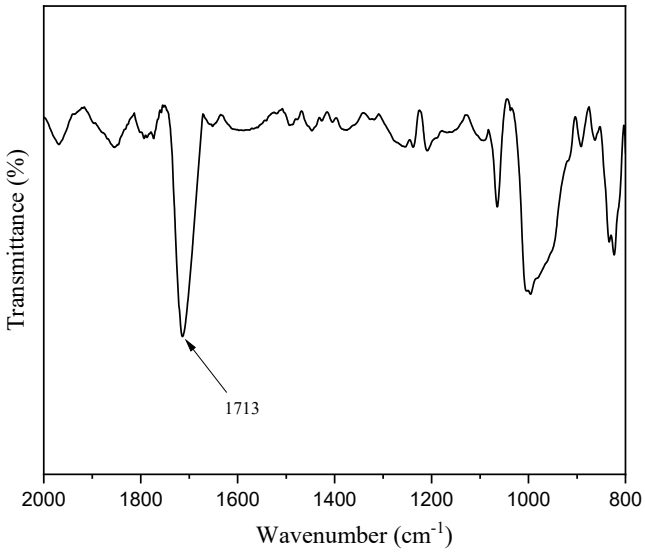


Fig. S3 IR spectra of the intermediate of [$HDBU^+$][TFE^-] exposed to CO_2