Room-Temperature Metal-Free Oxidative Alkoxylation/Amination of Benzofuran-3(2*H*)-ones with Simple Alcohols and Nitriles

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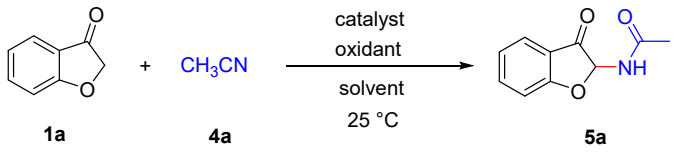
S1 General Information

All chemicals and solvents were purchased from commercial sources and used without further purification. All products were separated by short chromatography on a silica gel (200 to 300 mesh) column using petroleum ether (60 to 90°C) and ethyl acetate, unless stated otherwise. Thin-layer chromatography (TLC) was performed using silica gel plates with fluorescent F254 and visualized with short-wave UV (254 nm). The ^{1}H NMR spectra were recorded on a 400 MHz quantum-iplus FT-NMR spectrometer, and the $^{13}C\{^{1}H\}$ and ^{19}F NMR spectra were determined in $CDCl_3$ solution at 101 and 376 MHz, respectively. The chemical shift reference $CDCl_3$ as internal standard (δ = 7.26 for ^{1}H and δ = 77.16 for ^{13}C) was expressed as ppm. The coupling constant (J) is expressed in hertz (Hz). Mass data were measured using a SCIEX QTOF6600 mass spectrometer. The melting point (M. p.) was determined on a capillary melting point apparatus and was uncorrected. The data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (*s* = singlet, *d* = two-state, *t* = triplet, *q* = quartet, *m* = polymorphic), integration, coupling constant (Hz), and assignment. Data from ^{13}C NMR are reported as chemical shifts. Heating mantles were used as the heat source.

S2 Experimental Section

S2.1 Table S1. Optimization of the reaction conditions for the synthesis of 5a[a, b]



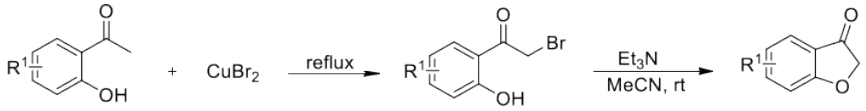
1a **4a** **5a**

Entry	Oxidant	Catalyst	Solvent	Time (h)	Yield (%)
1	PIFA	/	CH_3CN	18	40
2	PIDA	/	CH_3CN	18	28
4	TBHP	/	CH_3CN	18	nr
5	PIFA	/	CH_3CN	18	45 [c]
6	PIFA	/	CH_3CN	18	35 [d]
9	PIFA	/	CH_3CN	18	37 [e]
10	PIFA	/	CH_3CN	18	38 [f]
11	PIFA	/	CH_3CN	12	53
23	PIFA	/	CH_3CN : HFIP = 1 : 1	12	19
24	PIFA	/	CH_3CN : HFIP = 3 : 1	12	24

25	PIFA	/	CH_3CN : HFIP =10 : 1	12	33
26	PIFA	/	CH_3CN : DMF = 1 : 1	12	trace
30	PIFA	/	CH_3CN	12	41[g]
31	PIFA	/	CH_3CN	12	16 [h]
13	PIFA	$Pd(OAc)_2$ (20 mmol%)	CH_3CN	12	33
14	PIFA	$Mn(OAc)_2$ (20 mmol%)	CH_3CN	12	31
15	PIFA	$Mn(OAc)_2 \cdot 2H_2O$ (20 mmol%)	CH_3CN	12	21
16	PIFA	I_2 (0.5 equiv)	CH_3CN	12	nr
17	PIFA	Al_2O_3 (1.0 equiv)	CH_3CN	12	56
33	PIFA	TFA (1.0 equiv)	CH_3CN	12	31
34	PIFA	$BF_3 \cdot Et_2O$ (1.0 equiv)	CH_3CN	12	14

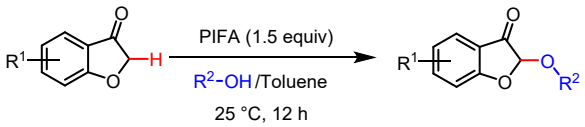
[a] Reaction conditions: **1a** (0.2 mmol), **4a** (1.5 mL), oxidant (0.4 mmol), under air. [b] Yields of isolated product. [c] 1.5 equiv of PIFA was used. [d] 2.5 equiv of PIFA was used. [e] Under oxygen atmosphere. [f] Under nitrogen atmosphere.[ge] at 35 °C. [h] at 50 °C.

S2.2 Preparation of Substrates



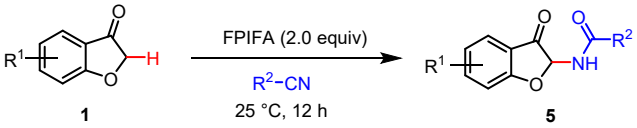
Benzofuran-3(2*H*)-ones were prepared by following the publish procedures [1]. To a solution of *o*-Acetyl phenol (10 mmol, 1 equiv) in $CHCl_3$ was added $CuBr_2$ (11 mmol, 1.1 equiv) dissolved in ethyl acetate, the reaction was kept at reflux until the starting material was consumed. The reaction mixture was concentrated under vacuum and the residue was purified by flash chromatography on silica gel to give the desired compound I. The compound I (5 mmol, 1 equiv) was dissolved in MeCN, then cooled to 0 °C, Et_3N (6.0 mmol, 2 equiv) was slowly added. The solution was quenched with water (30 mL) and extracted with DCM (3×30 mL). The combined organic phase was dried over $NaSO_4$ and concentrated. The residue was purified by flash chromatography on silica gel to afford the product II.

S2.3 General procedure for the synthesis of 3



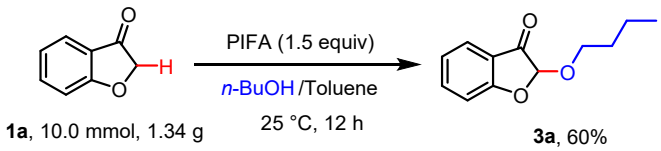
Benzofuran-3(2*H*)-one **1** (0.20 mmol, 1.0 equiv), alcohols **2** (0.75 mL) and PIFA (0.30 mmol, 1.5 equiv) were dissolved in 0.75 mL toluene solution and stirred at room temperature for 12 hours. The solvent was removed under high vacuum and the crude product was purified directly on silica gel (200-300 mesh) (petroleum ether/ethyl acetate = 20:1) by column chromatography to obtain the desired product **3**.

S2.4 General procedure for the synthesis of 5

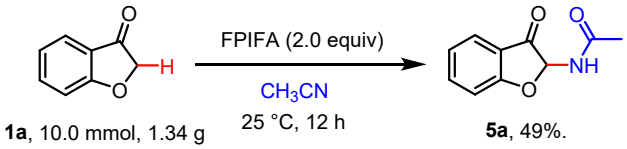


Benzofuran-3(2H)-one **1** (0.15 mmol, 1.0 equiv), nitriles (1.5mL) and FPIFA (0.3 mmol, 2.0 equiv) were mixed and stirred at room temperature for 12 hours. The solvent was removed under high vacuum and the crude product was purified directly on silica gel (200-300 mesh) (petroleum ether / ethyl acetate = 2:1) by column chromatography to obtain the desired product 5.

S2.5 Gram-scale synthesis of 3a and 5a

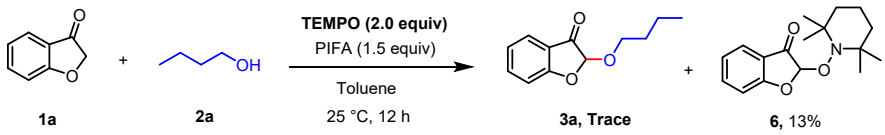


Combined benzofuran-3(2H)-one **1a** (1.34 g, 10.0 mmol, 1.0 equiv), *n*-butanol **2a** (12 mL) and PIFA (6.45 g, 15.0 mmol, 1.5 equiv) were added to 100 mL nightshade bottle in open air. Toluene (12 mL) was then added to the bottle in the air and the mixture was stirred at room temperature for 12 hours. After the reaction was completed, the filtrate was concentrated under vacuum. The crude product was purified by silica gel chromatography (petroleum ether/ ethyl acetate = 20:1, R_f = 0.3) to obtain the desired product **3a** (1.24 g, 60%) as a yellow oil.

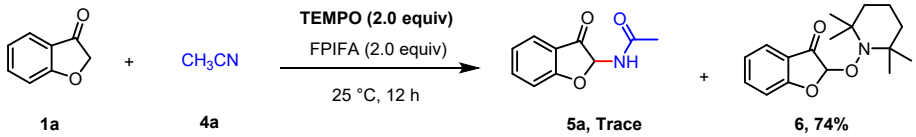


Benzofuran-3(2*H*)-one **1a** (1.34 g, 10.0 mmol, 1.0 equiv), acetonitrile **4a** (24 mL) and FPIFA (10.40 g, 20 mmol, 2.0 equiv) were added to 100 mL nightshade bottle under open conditions. The mixture was stirred at room temperature for 12 hours. After the reaction was completed, the filtrate was concentrated under vacuum. The crude product was purified by silica gel chromatography (petroleum ether/ ethyl acetate = 2:1, R_f = 0.3) to obtain the desired product **5a** (0.94 g, 49%) as a white solid.

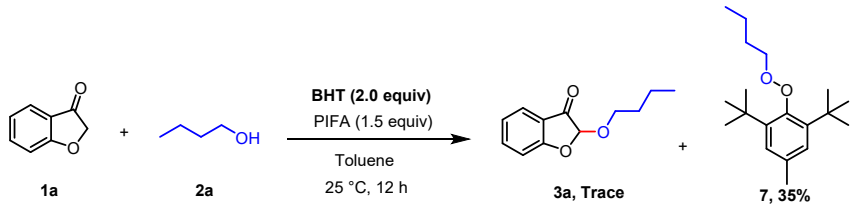
S3 Mechanism Study



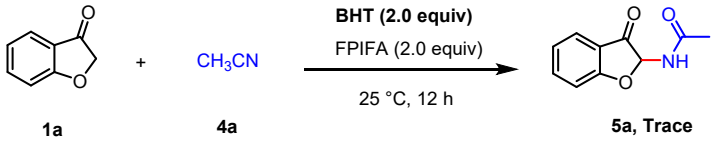
Benzofuran-3(2*H*)-one **1a** (26.8 mg, 0.2 mmol, 1.0 equiv), *n*-butanol **2a** (0.75 mL), PIFA (129.0 mg, 0.30 mmol, 1.5 equiv), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv) and toluene (0.75 mL) were successively added to an overdried 15 mL pressure tube equipped with a magnetic stir rod. The mixture was stirred at room temperature for 12 hours.



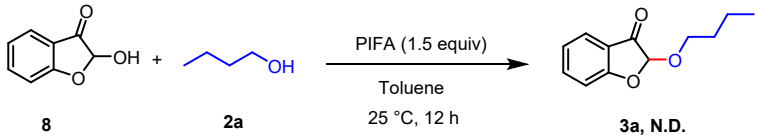
Benzofuran-3(2*H*)-one **1a** (22.1 mg, 0.15 mmol, 1.0 equiv), acetonitrile **4a** (1.5 mL), FPIFA (155.9 mg, 0.3 mmol, 2.0 equiv) and TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv) were successively added to an overdried 15 mL pressure tube fitted with a magnetic stirring rod. The mixture was stirred at room temperature for 12 hours.



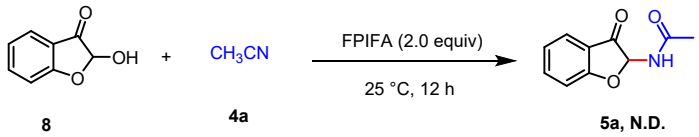
Benzofuran-3(2*H*)-one **1a** (26.8 mg, 0.2 mmol, 1.0 equiv), *n*-butanol **2a** (0.75 mL), PIFA (129.0 mg, 0.30 mmol, 1.5 equiv), BHT (88.1 mg, 0.4 mmol, 2.0 equiv) and toluene (0.75 mL) were successively added to an overdried 15 mL pressure tube equipped with a magnetic stir rod. The mixture was stirred at room temperature for 12 hours.



Benzofuran-3(2*H*)-one **1a** (22.1 mg, 0.15 mmol, 1.0 equiv), acetonitrile **4a** (1.5 mL), FPIFA (155.9 mg, 0.3 mmol, 2.0 equiv) and BHT (88.1 mg, 0.4 mmol, 2.0 equiv) were successively added to an overdried 15 mL pressure tube fitted with a magnetic stirring rod. The mixture was stirred at room temperature for 12 hours.



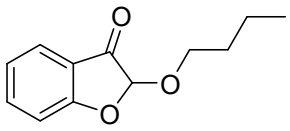
2-hydroxybenzofuran-3(2*H*)-one **8** (30.0 mg, 0.2 mmol, 1.0 equiv), *n*-butanol (0.75 mL) **2a** and PIFA (129.0 mg, 0.30 mmol, 1.5 equiv) and toluene (0.75 mL) were successively added to an overdried 15 mL pressure tube equipped with a magnetic stir rod. The mixture was stirred at room temperature for 12 hours.



2-hydroxybenzofuran-3(2*H*)-one **8** (22.5 mg, 0.15 mmol, 1.0 equiv), acetonitrile **4a** (1.5 mL) and FPIFA (155.9 mg, 0.3 mmol, 2.0 equiv) were successively added to an overdried 15 mL pressure tube fitted with a magnetic stirring rod. The mixture was stirred at room temperature for 12 hours.

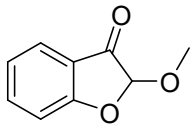
S4 Characterization data for compounds

2-butoxybenzofuran-3(2*H*)-one (3a)



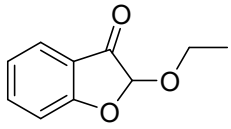
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 30:1), 29.4 mg (71% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.09 – 7.05 (m, 2H), 5.32 (s, 1H), 3.90 – 3.84 (m, 1H), 3.·79 – 3.73 (m, 1H), 1.71 – 1.63 (m, 2H), 1.46 – 1.36 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 171.6, 139.0, 124.9, 122.3, 119.8, 101.8, 70.2, 69.8, 31.5, 19.1, 13.8. HRMS (ESI): Calculated for $C_{12}H_{14}O_3$ $[M + H]^+$: 207.1016, found: 207.1016.

2-methoxybenzofuran-3(2*H*)-one (3b)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 19.5 mg (59% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, J = 8.0 Hz, 2H), 7.09 (q, J = 4.5 Hz, 2H), 5.27 (s, 1H), 3.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 171.7, 139.1, 124.9, 122.5, 119.7, 113.5, 102.3, 57.2. HRMS (ESI): Calculated for $C_9H_8O_3$ $[M + H]^+$: 165.0546, found: 165.0546. [2]

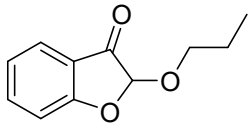
2-ethoxybenzofuran-3(2*H*)-one (3c)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 30:1), 26.9 mg (75% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.09 – 7.05 (m, 2H), 5.33 (s, 1H), 4.00 – 3.80 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 171.7, 139.0, 124.9, 122.3, 119.7, 113.5, 101.6, 66.2, 15.1. HRMS (ESI): Calculated for $C_{10}H_{10}O_3$

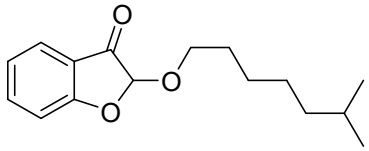
$[M + H]^+$: 179.0703, found: 179.0703.

2-propoxybenzofuran-3(2*H*)-one (3d)



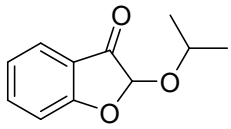
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 30:1), 29.0 mg (75% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.09 – 7.05 (m, 2H), 5.32 (s, 1H), 3.86 – 3.69 (m, 2H), 1.76 – 1.66 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 171.6, 139.0, 124.9, 122.3, 119.8, 113.5, 101.8, 72.1, 22.8, 10.3. HRMS (ESI): Calculated for $C_{11}H_{12}O_3$ $[M + H]^+$: 193.0859, found: 193.0857.

2-((6-methylheptyl)oxy)benzofuran-3(2*H*)-one (3e)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 30:1), 33.2 mg (63% yield), yellow oil. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.06 (q, *J* = 4.4 Hz, 2H), 5.31 (s, 1H), 3.78- 3.59 (m, 2H), 1.62 – 1.57 (m, 1H), 1.44 – 1.27 (m, 8H), 0.88 (q, *J* = 4.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 171.6, 138.9, 124.8, 122.2, 119.9, 113.4, 102.0, 72.7, 39.5, 30.2, 29.0, 23.5, 23.0, 14.1, 11.0. HRMS (ESI): Calculated for $C_{16}H_{22}O_3$ $[M + H]^+$: 263.1642, found: 263.1641.

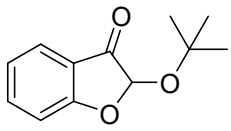
2-isopropoxybenzofuran-3(2*H*)-one (3f)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 25.1 mg (65% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.06 (q, *J* = 4.3 Hz,

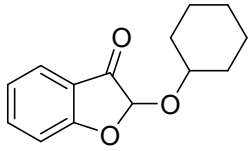
2H), 5.37 (s, 1H), 4.19 – 4.12 (m, 1H), 1.33 (d, J = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 171.6, 138.9, 124.9, 122.2, 119.6, 113.5, 100.7, 74.2, 23.2, 22.0. HRMS (ESI): Calculated for $C_{11}H_{12}O_3$ $[M + H]^+$: 193.0859, found: 193.0856.

2-(tert-butoxy)benzofuran-3(2*H*)-one (3g)



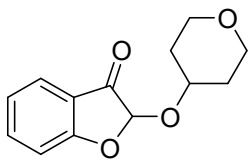
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 25.3 mg (61% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.04 (q, J = 4.3 Hz, 2H), 5.45 (s, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 171.7, 138.7, 124.8, 122.0, 119.5, 113.5, 97.4, 78.2, 28.5. HRMS (ESI): Calculated for $C_{12}H_{14}O_3$ $[M + H]^+$: 207.1016, found: 207.1012.

2-(cyclohexyloxy)benzofuran-3(2*H*)-one (3h)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 23.8 mg (51% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.05 (q, J = 4.7 Hz, 2H), 5.41 (s, 1H), 3.86 – 3.79 (m, 1H), 2.02 (t, J = 12.8 Hz, 2H), 1.82 – 1.76 (m, 2H), 1.55 – 1.44 (m, 3H), 1.37 – 1.21 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 171.6, 138.9, 124.9, 122.1, 119.7, 113.5, 100.6, 79.7, 33.2, 31.9, 25.5, 24.0, 23.9. HRMS (ESI): Calculated for $C_{14}H_{16}O_3$ $[M + H]^+$: 233.1172, found: 233.1167.

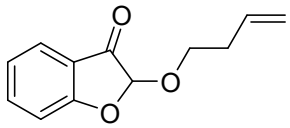
2-((tetrahydro-2*H*-pyran-4-yl)oxy)benzofuran-3(2*H*)-one (3i)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 10:1), 16.9 mg

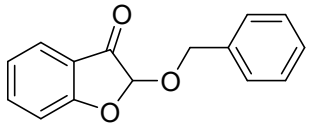
(36% yield), yellow solid, mp = 88.7 – 90.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (q, *J* = 6.7 Hz, 2H), 7.07 (q, *J* = 6.8 Hz, 2H), 5.41 (s, 1H), 4.09 – 4.02 (m, 1H), 4.00 – 3.92 (m, 2H), 3.52 – 3.45 (m, 2H), 2.02 (q, *J* = 4.4 Hz, 2H), 1.85 – 1.73 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 170.4, 137.9, 123.9, 121.3, 118.5, 112.4, 99.3, 74.9, 64.3, 64.2, 32.3, 31.1. HRMS (ESI): Calculated for $C_{13}H_{14}O_4$ $[M + H]^+$: 235.0965, found: 235.0965.

2-(but-3-en-1-yloxy)benzofuran-3(2*H*)-one (3j)



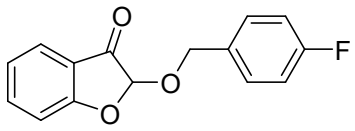
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 21.3 mg (52% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, *J* = 8.2 Hz, 2H), 7.09 – 7.05 (m, 2H), 5.87 - 5.77 (m, 1H), 5.33 (s, 1H), 5.15 – 5.05 (m, 2H), 3.94 – 3.78 (m, 2H), 2.45 (q, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 171.6, 139.0, 134.1, 124.9, 122.4, 119.7, 117.2, 113.5, 101.6, 69.5, 33.9. HRMS (ESI): Calculated for $C_{12}H_{12}O_3$ $[M + H]^+$: 205.0859, found: 205.0859.

2-(benzyloxy)benzofuran-3(2*H*)-one (3k)



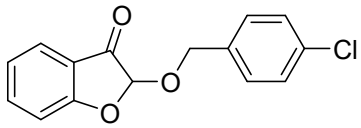
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 25.1 mg (52% yield), yellow solid, mp = 65.5 – 67.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.09 (t, *J* = 8.0 Hz, 2H), 5.39 (s, 1H), 4.89 (q, *J* = 19.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 170.6, 137.9, 134.9, 127.5, 127.3, 123.9, 121.4, 118.7, 112.4, 99.3, 70.5. HRMS (ESI): Calculated for $C_{15}H_{12}O_3$ $[M + H]^+$: 241.0859, found: 241.0859.

2-((4-fluorobenzyl)oxy)benzofuran-3(2*H*)-one (3l)



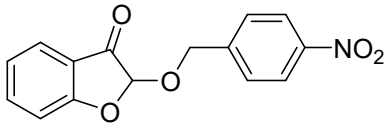
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 26.4 mg (51% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, *J* = 8.4 Hz, 2H), 7.40 (q, *J* = 4.7 Hz, 2H), 7.11 – 7.03 (m, 4H), 5.38 (s, 1H), 4.84 (q, *J* = 18.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 171.6, 162.8 (d, *J* = 247.5 Hz), 139.1, 131.8 (d, *J* = 3.0 Hz), 130.3 (d, *J* = 8.1 Hz), 125.0, 122.5, 119.8 , 115.5 (d, *J* = 21.2 Hz), 113.5, 100.3, 70.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.58. HRMS (ESI): Calculated for $C_{15}H_{11}FO_3$ $[M + H]^+$: 259.0765, found: 259.0765.

2-((4-chlorobenzyl)oxy)benzofuran-3(2*H*)-one (3m)



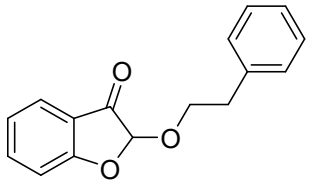
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 26.4 mg (48% yield), yellow solid, mp = 58.4 – 60.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, *J* = 8.6 Hz, 2H), 7.37 – 7.32 (m, 4H), 7.12 – 7.08 (m, 2H), 5.38 (s, 1H), 4.84 (q, *J* = 18.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 171.6, 139.1, 134.5, 134.2, 129.6, 128.8, 125.0, 122.6, 119.7, 113.5, 100.4, 70.7. HRMS (ESI): Calculated for $C_{15}H_{11}ClO_3$ $[M + H]^+$: 275.0469, found: 275.0469.

2-((4-nitrobenzyl)oxy)benzofuran-3(2*H*)-one (3n)



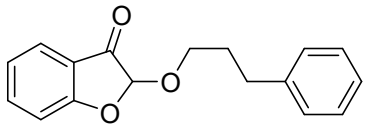
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 20.0 mg (35% yield), yellow solid, mp = 100.9 – 102.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.67 (t, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.12 (q, *J* = 7.1 Hz, 2H), 5.43 (s, 1H), 4.97 (q, *J* = 16.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 171.5, 147.8, 143.6, 139.3, 128.2, 125.1, 123.8, 122.8, 119.6, 113.5, 100.6, 70.1. HRMS (ESI): Calculated for $C_{15}H_{11}NO_5$ $[M + H]^+$: 286.0710, found: 286.0703.

2-phenethoxybenzofuran-3(2*H*)-one (3o)



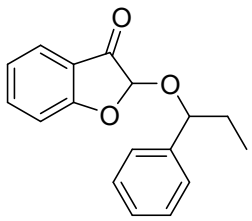
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 35.2 mg (69% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (q, *J* = 6.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.26 (q, *J* = 6.4 Hz, 3H), 7.12 (t, *J* = 7.6 Hz, 2H), 5.39 (s, 1H), 4.12 (q, *J* = 8.0 Hz, 1H), 4.01 (q, *J* = 8.1 Hz, 1H), 3.06 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 170.5, 138.0, 136.7, 127.9, 127.4, 125.5, 123.8, 121.3, 118.7, 112.4, 100.5, 69.9, 35.0. HRMS (ESI): Calculated for $C_{16}H_{14}O_3$ $[M + H]^+$: 255.1016, found: 255.1016.

2-(3-phenylpropoxy)benzofuran-3(2*H*)-one (3p)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 33.4 mg (62% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (q, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 8.6 Hz, 3H), 7.09 (q, *J* = 4.1 Hz, 2H), 5.32 (s, 1H), 3.94 – 3.88 (m, 1H), 3.80 – 3.74 (m, 1H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.05 – 1.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 171.5, 141.3, 138.9, 128.4, 128.3, 125.8, 124.8, 122.2, 119.6, 113.4, 101.7, 69.4, 31.8, 31.0. HRMS (ESI): Calculated for $C_{17}H_{16}O_3$ $[M + H]^+$: 269.1172, found: 269.1172.

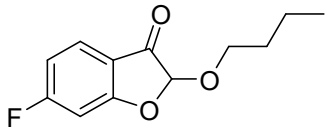
2-(1-phenylpropoxy)benzofuran-3(2*H*)-one (3q)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 30:1), 19.4 mg

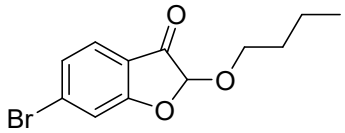
(36% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (q, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.08 – 7.04 (m, 2H), 5.13 (s, 1H), 4.80 (t, *J* = 6.8 Hz, 1H), 1.99 – 1.92 (m, 1H), 1.84 – 1.76 (m, 1H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 171.6, 139.8, 138.7, 128.7, 128.3, 127.5, 124.9, 122.2, 119.9, 113.5, 99.0, 83.3, 30.7, 10.1. HRMS (ESI): Calculated for $C_{17}H_{16}O_3$ $[M + H]^+$: 269.1172, found: 269.1169.

2-butoxy-6-fluorobenzofuran-3(2*H*)-one (3r)



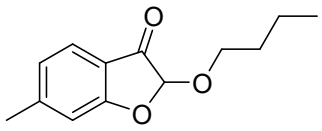
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 40:1), 33.8 mg (75% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, *J* = 7.2 Hz, 1H), 6.77 (q, *J* = 9.7 Hz, 2H), 5.35 (s, 1H), 3.87 (q, *J* = 7.5 Hz, 1H), 3.76 (q, *J* = 7.5 Hz, 1H), 1.70 – 1.62 (m, 2H), 1.46 – 1.36 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 173.2 (d, *J* = 14.1 Hz), 169.9 (d, *J* = 260.6 Hz), 127.0 (d, *J* = 12.1 Hz), 116.4 (d. *J* = 2.0 Hz), 111.0 (d, *J* = 24.2 Hz), 102.9, 101.0 (d, *J* = 26.3 Hz), 70.5, 31.5, 19.0, 13.8. ^{19}F NMR (376MHz, $CDCl_3$) δ -94.93. HRMS (ESI): Calculated for $C_{12}H_{13}FO_3$ $[M + H]^+$: 225.0921, found: 225.0921.

6-bromo-2-butoxybenzofuran-3(2*H*)-one (3s)



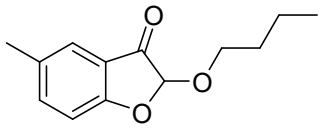
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 36.5 mg (64% yield), yellow oil. ^{1}H (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 5.33 (d, *J* = 0.8 Hz, 1H), 3.90 – 3.75 (m, 2H), 1.70 – 1.62 (m, 2H), 1.46 – 1.36 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C (101 MHz, $CDCl_3$) δ 194.9, 171.7, 133.8, 126.1, 125.7, 118.7, 117.1, 102.4, 70.5, 31.5, 19.0, 13.8. HRMS (ESI): Calculated for $C_{12}H_{13}BrO_3$ $[M + H]^+$: 285.0121, found: 285.0121.

2-butoxy-6-methylbenzofuran-3(2*H*)-one (3t)



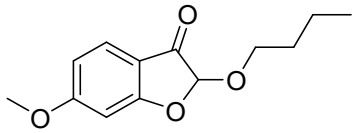
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 15:1), 26.5 mg (60% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 8.4 Hz, 2H), 5.30 (s, 1H), 3.88 – 3.81 (m, 1H), 3.77 – 3.71 (m, 1H), 2.42 (s, 3H), 1.69 – 1.62 (m, 2H), 1.45 – 1.35 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 172.1, 151.3, 124.5, 123.8, 117.4, 113.5, 102.1, 70.0, 31.6, 22.7, 19.1, 13.8. HRMS (ESI): Calculated for $C_{13}H_{16}O_3$ [M + H]$^+$: 221.1172, found: 221.1172.

2-butoxy-5-methylbenzofuran-3(2*H*)-one (3u)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 30:1), 30.5 mg (69% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.4 Hz, 1H), 5.30 (s, 1H), 3.88 – 3.71 (m, 2H), 2.33 (s, 3H), 1.70 – 1.62 (m, 2H), 1.45 – 1.36 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 170.1, 140.2, 131.9, 124.3, 119.6, 113.1, 102.0, 70.0, 31.6, 20.8, 19.1, 13.8. HRMS (ESI): Calculated for $C_{13}H_{16}O_3$ [M + H]$^+$: 221.1172, found: 221.1172.

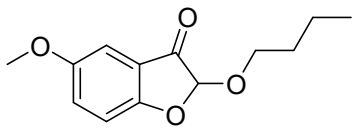
2-butoxy-6-methoxybenzofuran-3(2*H*)-one (3v)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 34.6 mg (73% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 1H), 6.59 (q, J = 3.5 Hz, 1H), 6.47 (d, J = 1.6 Hz, 1H), 5.31 (s, 1H), 3.86 (s, 3H), 3.84 – 3.69 (m, 2H), 1.68 – 1.60 (m, 2H), 1.44 – 1.36 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 174.1, 169.9, 126.1, 112.9, 111.6, 102.8, 96.4, 70.0, 56.0, 31.5, 19.0, 13.8. HRMS (ESI): Calculated for $C_{13}H_{16}O_4$

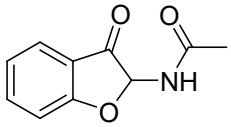
$[M + H]^+$: 237.1121, found: 237.1121.

2-butoxy-5-methoxybenzofuran-3(2*H*)-one (3w)



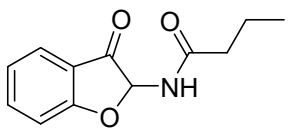
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 20:1), 30.4 mg (64% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (q, *J* = 3.9 Hz, 1H), 7.03 (d, *J* = 2.8 Hz, 1H), 6.99 (d, *J* = 9.2 Hz, 1H), 5.31 (s, 1H), 3.88 – 3.81 (m, 1H), 3.78 (s, 3H), 3.75 – 3.71 (m, 1H), 1.70 – 1.62 (m, 2H), 1.45 – 1.35 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 166.9, 155.1, 128.8, 119.6, 114.4, 104.8, 102.5, 70.1, 55.9, 31.5, 19.1, 13.8. HRMS (ESI): Calculated for $C_{13}H_{16}O_4$ $[M + H]^+$: 237.1121, found: 237.1121.

***N*-(3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide(5a)**



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 30:1), 17.9 mg (62% yield), yellow solid, mp = 168.4 – 170.2 ℃.. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (t, *J* = 8.2 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.52 (d, *J* = 7.2 Hz, 1H), 5.83 (d, *J* = 8.4 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 171.4, 170.9, 139.0, 124.5, 122.5, 119.9, 113.5, 82.7, 22.9. HRMS (ESI): Calculated for $C_{10}H_9NO_3$ $[M + H]^+$: 192.0655, found: 192.0655.

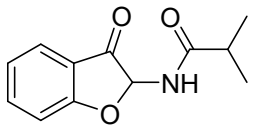
***N*-(3-oxo-2,3-dihydrobenzofuran-2-yl)butyramide (5b)**



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 2:1), 22.4 mg (68% yield), white solid, mp = 122.2 – 124.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 2H), 6.66 (d, *J* = 7.6 Hz, 1H), 5.77 (d, *J* = 8.4 Hz, 1H), 2.28 (t, *J* = 7.6 Hz, 2H),

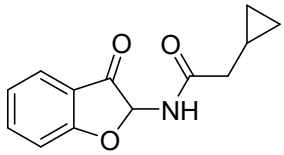
1.73 – 1.63 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 173.9, 171.3, 138.8, 124.4, 122.3, 120.0, 113.5, 82.8, 37.8, 18.5, 13.7. HRMS (ESI): Calculated for $C_{12}H_{13}NO_3$ $[M + H]^+$: 220.0968, found: 220.0968.

_N_-(3-oxo-2,3-dihydrobenzofuran-2-yl)isobutyramide (5c)



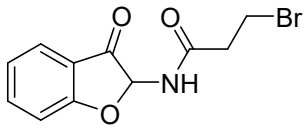
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 3:1), 16.5 mg (50% yield), yellow solid, mp = 96.8 – 98.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, J = 9.0 Hz, 2H), 7.08 (q, J = 4.4 Hz, 2H), 6.57 (d, J = 7.6 Hz, 1H), 5.77 (d, J = 8.0 Hz, 1H), 2.52 - 2.45 (m, 1H), 1.20 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 177.8, 171.3, 138.8, 124.5, 122.3, 120.0, 113.5, 82.9, 35.2, 19.3, 19.2. HRMS (ESI): Calculated for $C_{12}H_{13}NO_3$ $[M + H]^+$: 220.0968, found: 220.0968.

2-cyclopropyl-_N_-(3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5d)



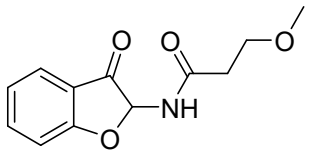
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 1:1), 20.5 mg (59% yield), yellow solid, mp = 111.6 – 113.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (q, J = 6.7 Hz, 2H), 7.09 (t, J = 7.4 Hz, 2H), 6.93 (d, J = 7.6 Hz, 1H), 5.81 (d, J = 8.0 Hz, 1H), 2.27 (d, J = 7.2 Hz, 2H), 1.06 – 0.96 (m, 1H), 0.63 (d, J = 8.0 Hz, 2H), 0.23 (d, J = 4.4 Hz,2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.80, 173.3, 171.3, 138.8, 124.5, 122.4, 120.0, 113.5, 82.7, 41.0, 6.7, 4.8, 4.8. HRMS (ESI): Calculated for $C_{13}H_{13}NO_3$ $[M + H]^+$: 232.0968, found: 232.0969.

3-bromo-_N_-(3-oxo-2,3-dihydrobenzofuran-2-yl)propanamide (5e)



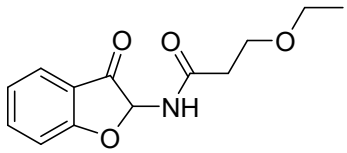
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 2:1), 31.1 mg (73% yield), yellow solid, mp = 100.2 – 102.0 ℃. ^{1}H NMR (400 MHz, DMSO) δ 9.40 (d, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.20 – 7.12 (m, 2H), 5.78 (t, *J* = 10.2 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.85 (t, *J* = 6.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 196.8, 170.9, 138.8, 124.3, 122.4, 120.8 113.6, 83.4, 38.3, 28.6. HRMS (ESI): Calculated for $C_{11}H_{10}BrNO_3$ [M + H]$^+$: 283.9917, found: 283.9917.

3-methoxy-*N*-(3-oxo-2,3-dihydrobenzofuran-2-yl)propanamide (5f)



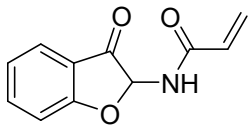
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 1:1), 17.7 mg (50% yield), white solid, mp = 101.6 – 102.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (q, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.09 (q, *J* = 7.8 HZ, 2H), 5.77 (d, *J* = 8.4 Hz, 1H), 3.66 (t, *J* = 5.6 Hz, 2H), 3.38 (s, 3H), 2.58 (t, *J* = 5.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 172.6, 171.3, 138.7, 124.5, 122.3, 120.1, 113.5, 82.7, 67.9, 58.9, 36.4. HRMS (ESI): Calculated for $C_{12}H_{13}NO_4$ [M + H]$^+$: 236.0917, found: 236.0920.

3-ethoxy-*N*-(3-oxo-2,3-dihydrobenzofuran-2-yl)propanamide (5g)



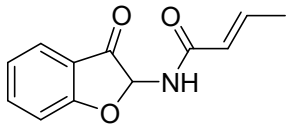
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 2:1), 18.8 mg (50% yield), white solid, mp = 102.2 – 103.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 2H), 5.78 (d, *J* = 8.0 Hz, 1H), 3.70 (t, *J* = 5.6 Hz, 2H), 3.57 – 3.51 (m, 2H), 2.58 (t, *J* = 5.8 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 172.8, 171.3, 138.7, 124.5, 122.3, 120.0, 113.5, 82.7, 66.7, 65.7, 36.6, 15.1. HRMS (ESI): Calculated for $C_{13}H_{15}NO_4$ [M + H]$^+$: 250.1074, found: 250.1076.

***N*-(6-fluoro-3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5h)**



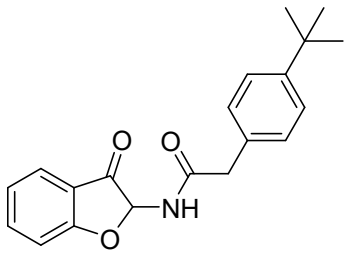
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 3:1), 18.1 mg (59% yield), white solid, mp = 159.1 – 160.7 ℃. ^{1}H NMR (400 MHz, DMSO) δ 9.50 (d, *J* = 7.6 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.19 – 7.12 (m, 2H), 6.29 – 6.14 (m, 2H), 5.84 – 5.75 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 196.9, 170.9, 165.7, 138.8, 130.4, 128.9, 124.3, 122.4, 121.0, 113.5, 83.6. HRMS (ESI): Calculated for $C_{11}H_9NO_3$ $[M + H]^+$: 204.0655, found: 204.0655.

_N_-(3-oxo-2,3-dihydrobenzofuran-2-yl)but-2-enamide (5i)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 4:1), 16.4 mg (50% yield), yellow solid, mp = 160.4 – 162.1 ℃. ^{1}H NMR (400 MHz, DMSO) δ 9.27 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.62 (d, *J* = 7.6 Hz , 1H), 7.14 (q, *J* = 8.0 Hz, 2H), 6.77 – 6.67 (m, 1H), 5.94 (q, *J* = 5.7 Hz, 1H), 5.78 (d, *J* = 7.6 Hz, 1H), 1.83 (q, *J* = 2.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 197.0, 170.8, 165.9, 142.2, 138.7, 124.4, 124.2, 122.3, 121.0, 113.5, 83.8, 18.1. HRMS (ESI): Calculated for $C_{12}H_{11}NO_3$ $[M + H]^+$: 218.0812, found: 218.0812.

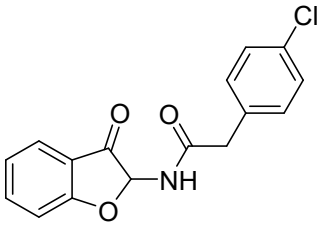
2-(4-(tert-butyl)phenyl)-_N_-(3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5j)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 2:1), 28.7 mg (59% yield), yellow solid, mp = 168.2 – 170.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (q, *J* = 6.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.09 – 7.03 (m, 2H), 6.50 (d, *J* = 7.6 Hz, 1H), 5.68 (d, *J* = 8.0 Hz, 1H), 3.64 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 172.0,

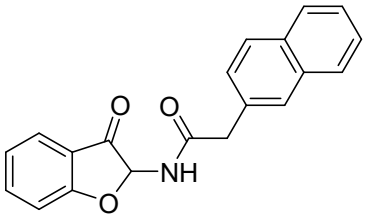
171.2, 150.7, 138.7, 130.3, 129.3, 126.2, 124.5, 122.3, 120.0, 113.4, 82.7, 42.6, 34.6, 31.3. HRMS (ESI): Calculated for $C_{20}H_{21}NO_3$ $[M + H]^+$: 324.1594, found: 324.1594.

2-(4-chlorophenyl)-*N*-(3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5k)



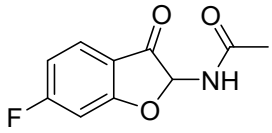
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 2:1), 15.4 mg (34% yield), yellow solid, mp = 220.8 – 221.9 ℃. ^{1}H NMR (400 MHz, DMSO) δ 9.46 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.13 (q, *J* = 8.0 Hz, 2H), 5.74 (d, *J* = 8.0 Hz, 1H), 3.55 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 196.9, 171.4, 170.8, 138.7, 134.5, 131.9, 131.6, 128.7, 124.2, 122.3, 120.9, 113.5, 83.6, 41.1. HRMS (ESI): Calculated for $C_{16}H_{12}ClNO_3$ $[M + H]^+$: 302.0578, found: 302.0578.

2-(naphthalen-2-yl)-*N*-(3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5l)



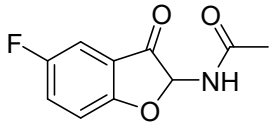
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 5:1), 16.2 mg (34% yield), white solid, mp = 207.1 – 208.9 ℃. ^{1}H NMR (400 MHz, DMSO) δ 9.51 (d, *J* = 7.6 Hz, 1H), 7.87 (q, *J* = 6.1 Hz, 3H), 7.76 (s, 1H), 7.71 – 7.66 (m, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.40 (q, *J* = 3.3 Hz, 1H), 7.13 (q, *J* = 8.0 Hz, 2H), 5.76 (d, *J* = 7.6 Hz, 1H), 3.72 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 196.9, 171.7, 170.8, 138.7, 133.4, 133.2, 132.4, 128.2, 128.1, 128.1, 128.0, 127.9, 126.7, 126.2, 124.2, 122.3, 121.0, 113.5, 83.7, 42.1. HRMS (ESI): Calculated for $C_{20}H_{15}NO_3$ $[M + H]^+$: 318.1125, found: 318.1125.

***N*-(6-fluoro-3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5m)**



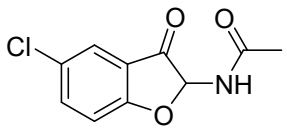
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 1:1), 22.4 mg (71% yield), white solid, mp = 139.8 – 141.3 ℃. ^{1}H NMR (400 MHz, DMSO) δ 9.32 (d, *J* = 7.6 Hz, 1H), 7.70 (q, *J* = 4.9 Hz, 1H), 7.11 (q, *J* = 3.9 Hz, 1H), 7.00 – 6.95 (m, 1H), 5.77 (d, *J* = 7.6 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 196.7 (d, *J* = 2.0 Hz), 170.9, 167.0, 157.5 (d, *J* = 241.4 Hz), 125.9 (d, *J* = 25.3), 121.5 (d, *J* = 7.1 Hz), 115.0 (d, *J* = 8.1 Hz), 109.5 (d, *J* = 23.2 Hz), 84.7, 22.5. ^{19}F NMR (376 MHz, DMSO) δ -98.40. HRMS (ESI): Calculated for $C_{10}H_8FNO_3$ $[M + H]^+$: 210.0561, found: 210.0561.

***N*-(5-fluoro-3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5n)**



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 1:1), 19.2 mg (61% yield), white solid, mp = 178.8 – 180.2 ℃. ^{1}H NMR (400 MHz, DMSO) δ 9.31 (d, *J* = 7.6 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.46 (q, *J* = 3.3 Hz, 1H), 7.21 (q, *J* = 4.1 Hz, 1H), 5.73 (d, *J* = 7.2 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 196.7 (d, *J* = 3.0 Hz), 170.9, 167.0, 157.5 (d, *J* = 240.4 Hz), 125.9 (d, *J* = 25.3), 121.5 (d, *J* = 8.1 Hz), 115.0 (d, *J* = 8.1 Hz), 109.5 (d, *J* = 24.2 Hz), 84.7, 22.5. ^{19}F NMR (376 MHz, DMSO) δ -121.59. HRMS (ESI): Calculated for $C_{10}H_8FNO_3$ $[M + H]^+$: 210.0561, found: 210.0561.

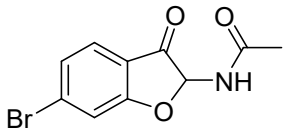
***N*-(3-oxo-2,3-dihydrobenzofuran-2-yl)acrylamide (5o)**



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 2:1), 21.4 mg (63% yield), white solid, mp = 183.8 – 185.7 ℃. ^{1}H NMR (400 MHz, DMSO) δ 9.35 (d, *J* = 7.2 Hz, 1H),

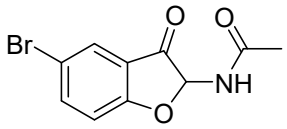
7.73 (q, *J* = 3.7 Hz, 1H), 7.67 (d, *J* = 2.4 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 5.74 (d, *J* = 9.2 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 195.9, 170.9, 169.1, 138.0, 126.3, 123.4, 122.4, 115.4, 84.6, 22.4. HRMS (ESI): Calculated for $C_{10}H_8ClNO_3$ $[M + H]^+$: 226.0265, found: 226.0265.

_N_-(6-bromo-3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5p)



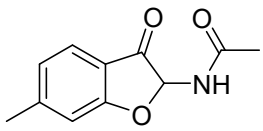
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 2:1), 23.1 mg (57% yield), white solid, mp = 195.4 – 197.0 °C. ^{1}H NMR (400 MHz, DMSO) δ 9.33 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 0.8 Hz, 1H), 7.30 (q, *J* = 3.1 Hz, 1H), 5.72 (d, *J* = 7.2 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 195.9, 171.0, 131.9, 125.6, 120.4, 116.7, 84.4, 22.5. HRMS (ESI): Calculated for $C_{10}H_8BrNO_3$ $[M + H]^+$: 269.9760, found: 269.9760.

_N_-(5-bromo-3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5q)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 2:1), 27.9 mg (69% yield), yellow solid, mp = 171.0 – 172.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.0 Hz, 1H), 7.70 (q, *J* = 3.7 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 5.73 (d, *J* = 8.0 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 170.9, 169.9, 141.3, 127.0, 121.7, 115.2, 115.0, 83.5, 22.8. HRMS (ESI): Calculated for $C_{10}H_8BrNO_3$ $[M + H]^+$: 269.9760, found: 269.9760.

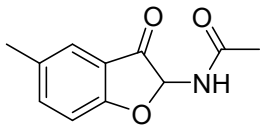
_N_-(6-methyl-3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5r)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 2:1), 19.2 mg (62% yield), yellow solid, mp = 164.0 – 165.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 1H),

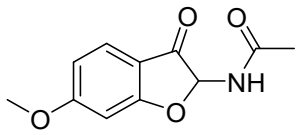
6.88 (t, *J* = 7.2 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.83 (d, *J* = 8.4 Hz, 1H), 2.42 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 172.0, 171.2, 151.4, 124.1, 124.0, 117.5, 113.5, 82.9, 22.9, 22.7. HRMS (ESI): Calculated for $C_{11}H_{11}NO_3$ $[M + H]^+$: 206.0812, found: 206.0812.

***N*-(5-methyl-3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5s)**



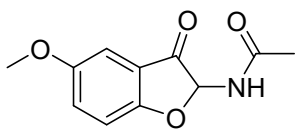
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 2:1), 16.7 mg (54% yield), white solid, mp = 162.1 – 164.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 1H), 7.39 (s, 1H), 6.97 (d, *J* = 8.8 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.80 (d, *J* = 8.4 Hz, 1H), 2.33 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 171.0, 169.9, 140.3, 132.1, 123.8, 119.7, 113.1, 83.0, 22.9, 20.6. HRMS (ESI): Calculated for $C_{11}H_{11}NO_3$ $[M + H]^+$: 206.0812, found: 206.0812.

***N*-(6-methoxy-3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5t)**



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 2:1), 18.3 mg (55% yield), yellow solid, mp = 195.2 – 197.1 ℃. ^{1}H NMR (400 MHz, DMSO) δ 9.20 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 6.72 – 6.67 (m, 2H), 5.77 (t, *J* = 5.6 Hz, 1H), 3.86 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 194.5, 173.5, 171.0, 168.5, 125.5, 113.8, 111.5, 96.9, 84.2, 56.7, 22.7. HRMS (ESI): Calculated for $C_{11}H_{11}NO_4$ $[M + H]^+$: 222.0761, found: 220.0761.

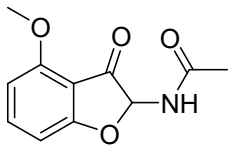
***N*-(5-methoxy-3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5u)**



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 1:1), 14.0 mg (42%

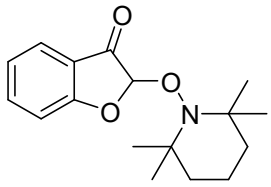
yield), white solid, mp = 163.3 – 165.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 4.6 Hz, 1H), 7.04 (t, *J* = 6.6 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.85 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 170.8, 166.8, 155.3, 128.9, 119.7, 114.5, 104.3, 83.4, 56.0, 22.9. HRMS (ESI): Calculated for $C_{11}H_{11}NO_4$ $[M + H]^+$: 222.0761, found: 222.0761.

***N*-(4-methoxy-3-oxo-2,3-dihydrobenzofuran-2-yl)acetamide (5v)**



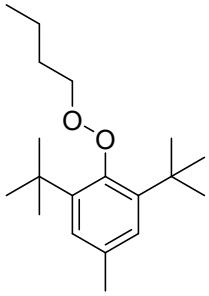
Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 1:1), 15.3 mg (46% yield), white solid, mp = 200.8 – 202.7 °C. ^{1}H NMR (400 MHz, DMSO) δ 9.17 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.2 Hz, 1H), 6.65 (q, *J* = 4.3 Hz, 2H), 5.67 (d, *J* = 8.2 Hz, 1H), 3.87 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 193.7, 171.8, 170.9, 158.0, 140.4, 109.8, 105.1, 104.3, 83.2, 56.4, 22.7. HRMS (ESI): Calculated for $C_{11}H_{11}NO_4$ $[M + H]^+$: 222.0761, found: 222.0762.

2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)benzofuran-3(2*H*)-one (6)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 30:1), 43 mg (74% yield), white solid, mp = 66.3 – 67.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (q, *J* = 6.9 Hz, 2H), 7.04 (q, *J* = 4.5 Hz, 2H), 5.73 (s, 1H), 1.54 (s, 5H), 1.45 (s, 3H), 1.35 (s, 4H), 1.23 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 171.3, 138.8, 124.8, 121.9, 119.9, 113.4, 106.4, 61.8, 59.8, 40.5, 40.3, 33.9, 32.3, 20.5, 20.2, 17.3. HRMS (ESI): Calculated for $C_{17}H_{23}NO_3$ $[M + H]^+$: 290.1751, found: 290.1751.[3]

1,3-di-*tert*-butyl-2-(butylperoxy)-5-methylbenzene (7)



Purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc = 30:1), 35 mg (30% yield), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (s, 2H), 3.20 (t, *J* = 6.4 Hz, 2H), 1.50 – 1.33 (m, 7H), 1.22 (s, 18H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.2, 148.0, 143.4, 71.8, 64.2, 34.8, 32.6, 29.6, 27.4, 19.3, 13.9. HRMS (ESI): Calculated for $C_{19}H_{32}O_2$ $[M + H]^+$: 293.2475, found: 293.2475.[4]

S5 References

[1] Qi, J.; Tang, H.; Chen, C.; Cui, S.; Xu, G. Reductive coupling of alkenes with unsaturated imines via a radical pathway. *Org. Chem. Front.* **2019**, 6, 2760–2764.

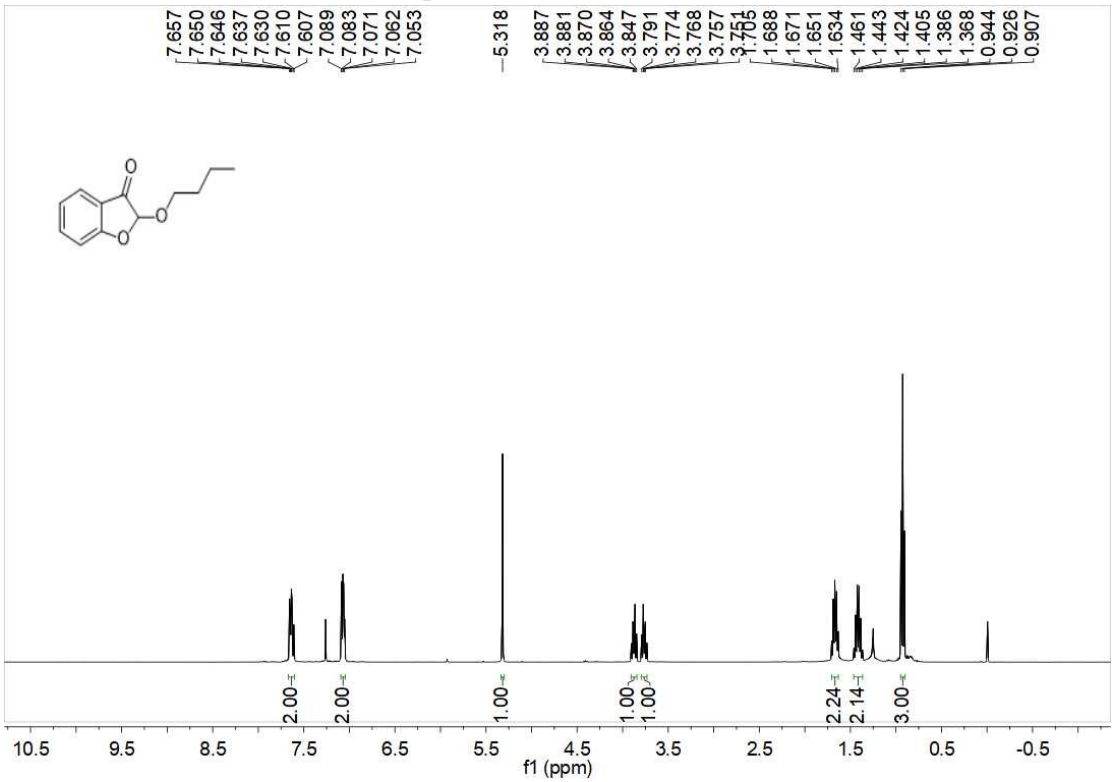
[2] Antus, S.; Baitz-Gacs, E.; Boross, F.; Nogradi, M; Solyom, A. Oxidation of 1,3-diphenyl-1,3-propanediones with thallium(III) nitrate in methanol. *Liebigs Ann. Chem*, **1980**, 8, 1271-1282.

[3] Fan, Y.; Zhou, K.; Luo, X.; Zheng, X.; Yuan, C.; Gui, K.; Cai, Y.; Xia, Q. Iodide Salt-catalyzed oxidative coupling of benzofuran-3(2*H*)-ones with acids and amines using air as the oxidant. *J. Org. Chem*, **2025,** 90, 9636-9642.

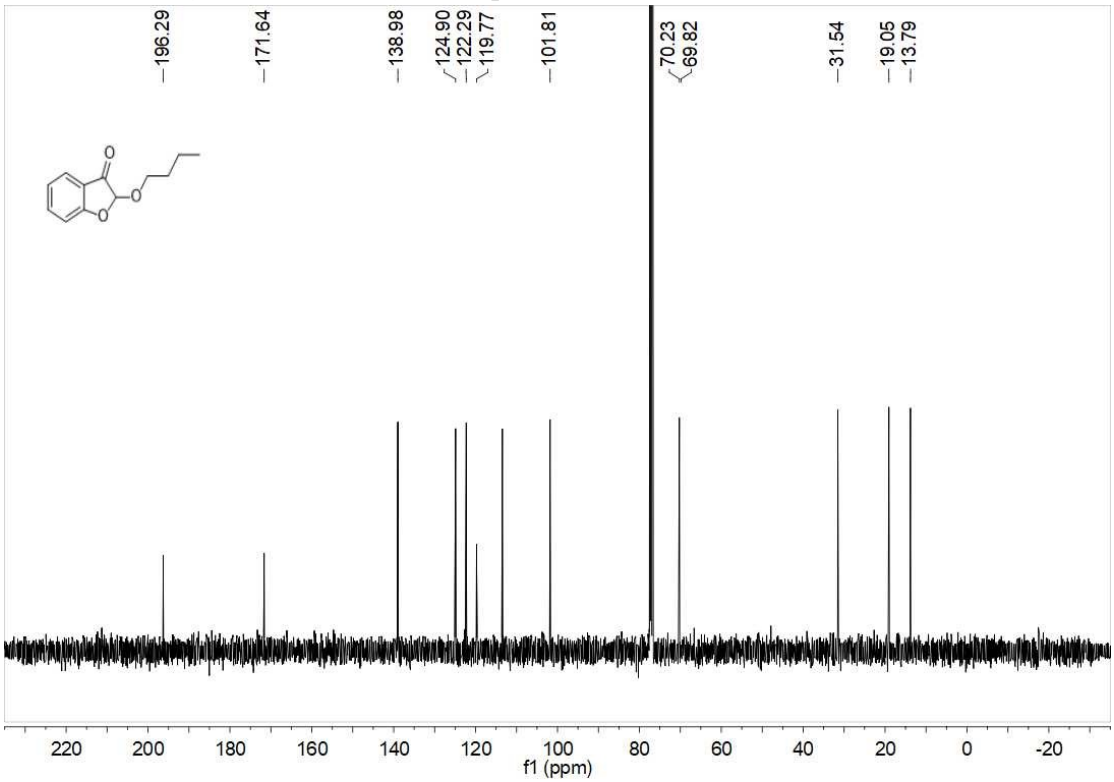
[4] Zheng, M.; Zhuang, X.; Jia, Q.; Ren, Q.; Wu, J. Photoredox-catalyzed multicomponent α-sulfonylation of terminal alkynes. *Org. Lett.* **2024**, 26, 9978-9983.

S6 Copies of ^{1}H, ^{13}C and ^{19}F Spectra

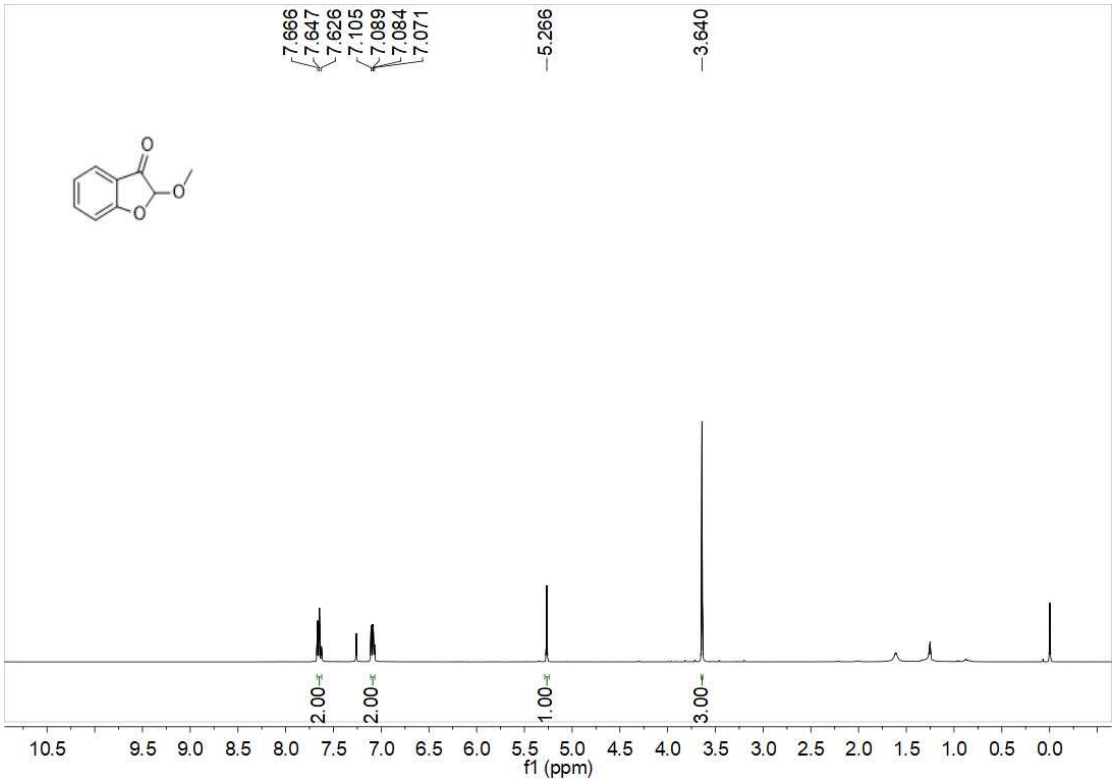
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3a



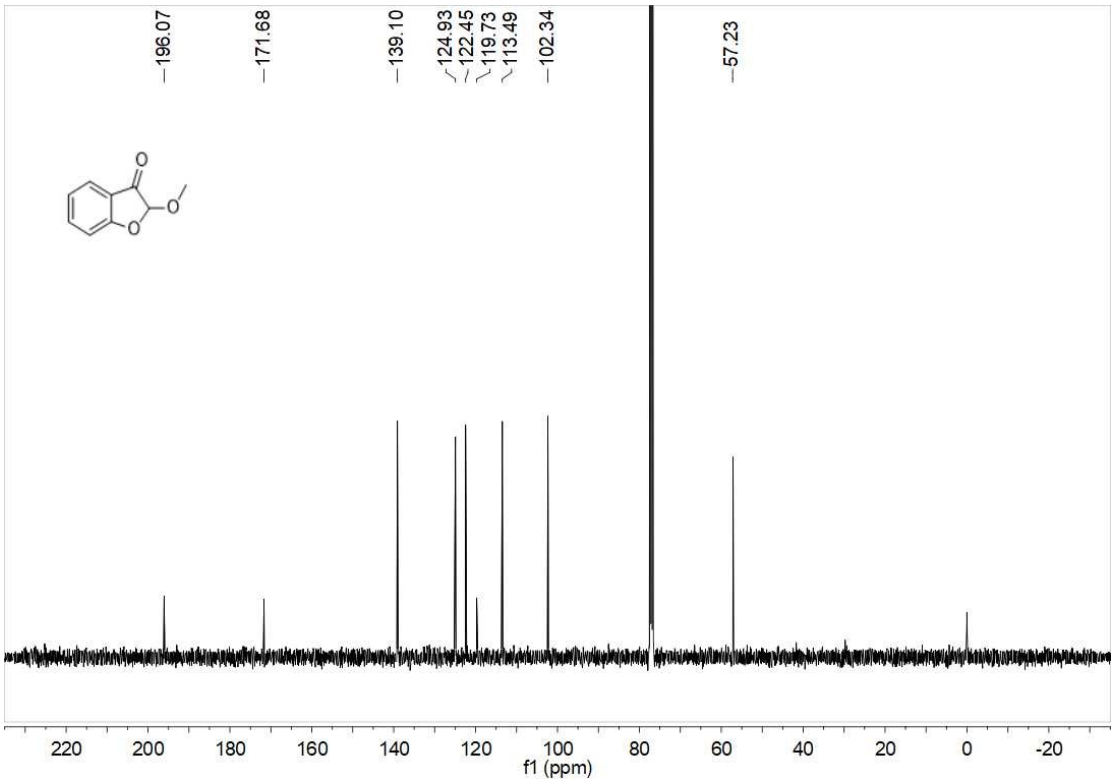
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3a



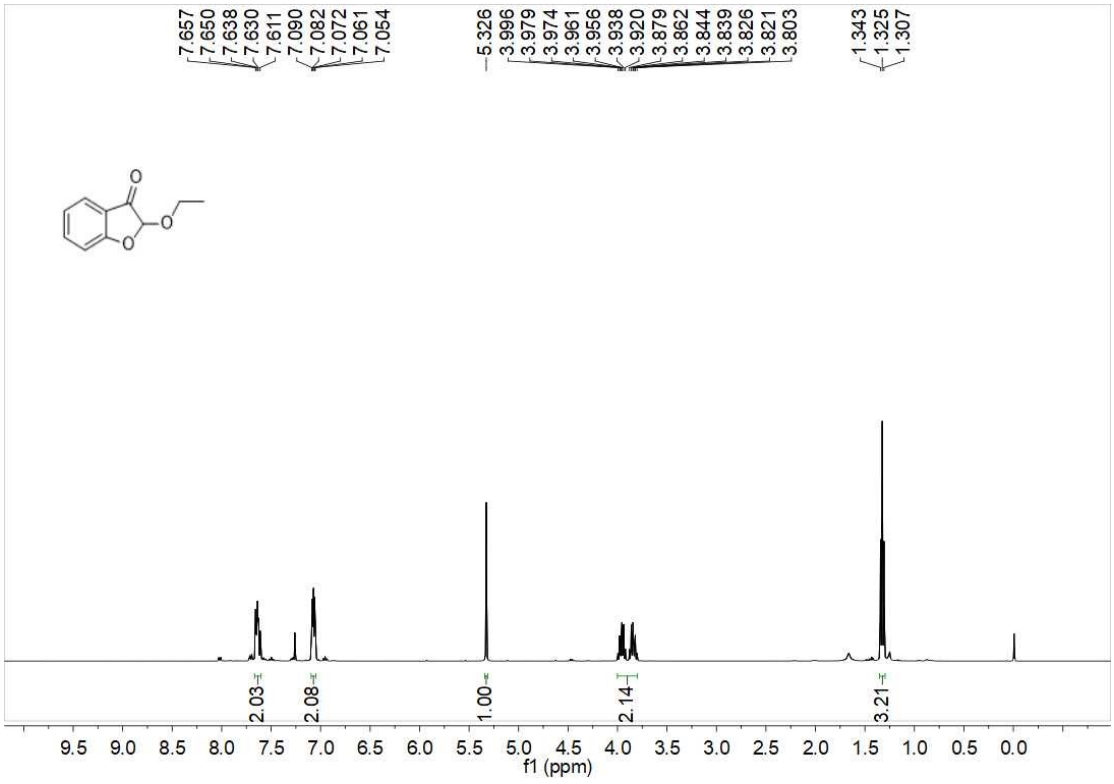
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3b



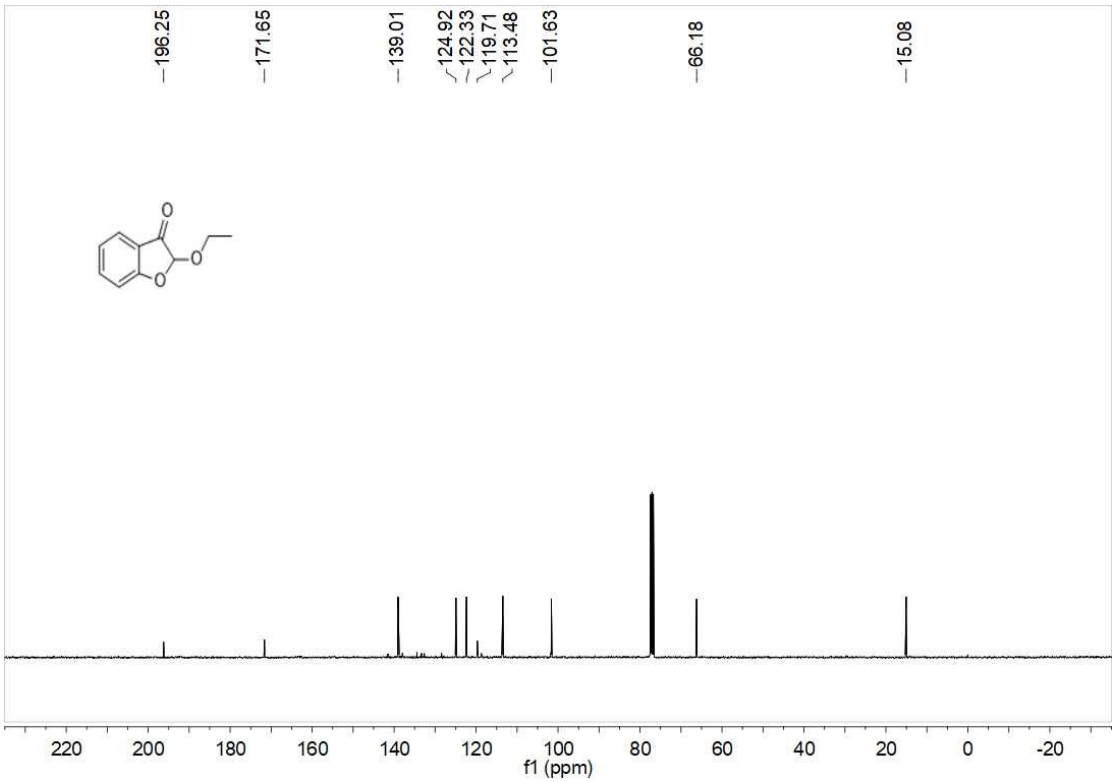
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3b



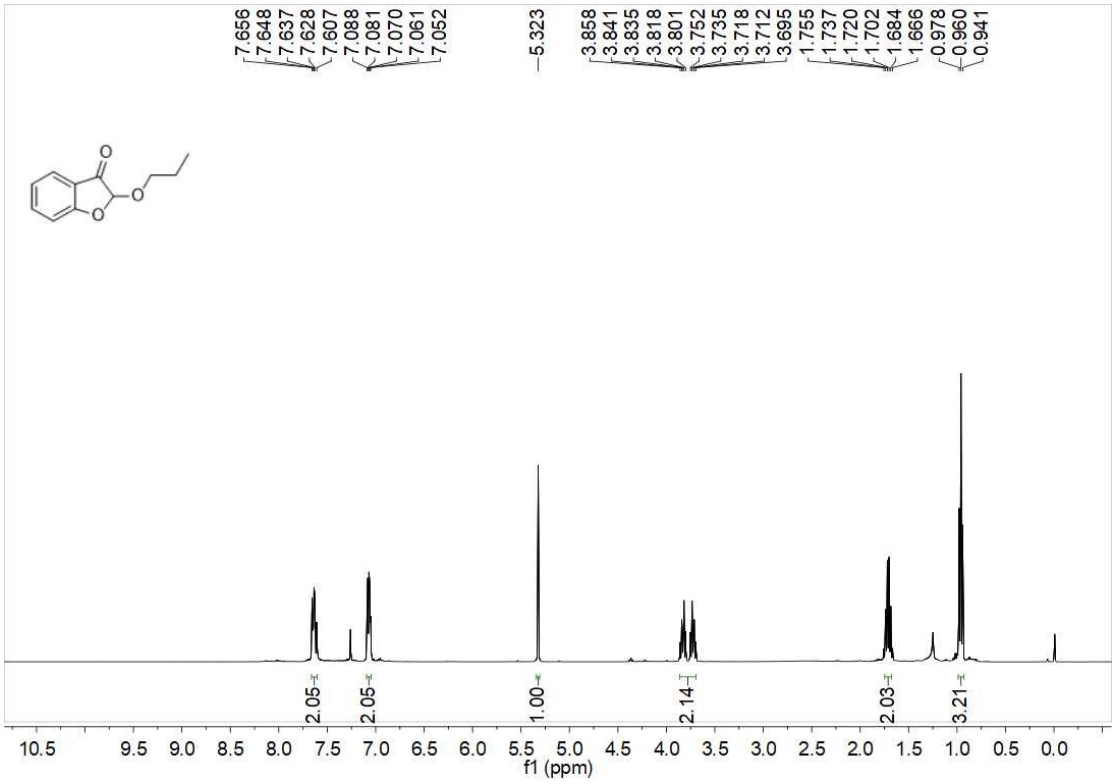
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3c



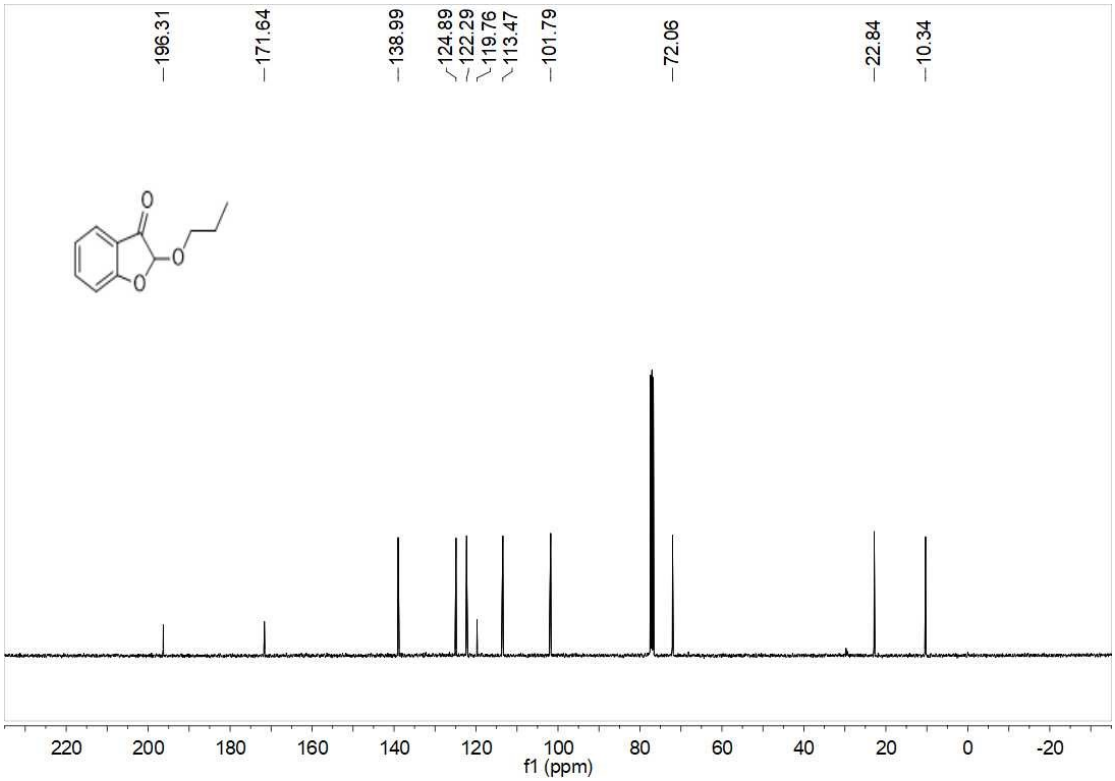
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3c



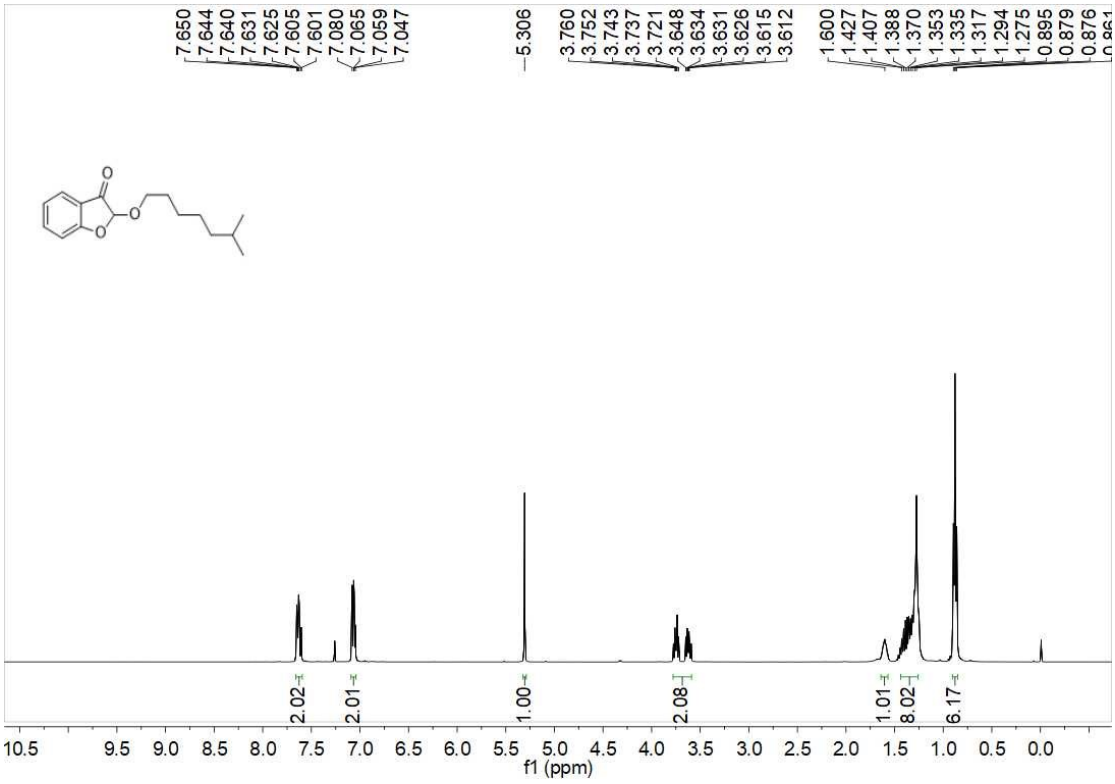
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3d



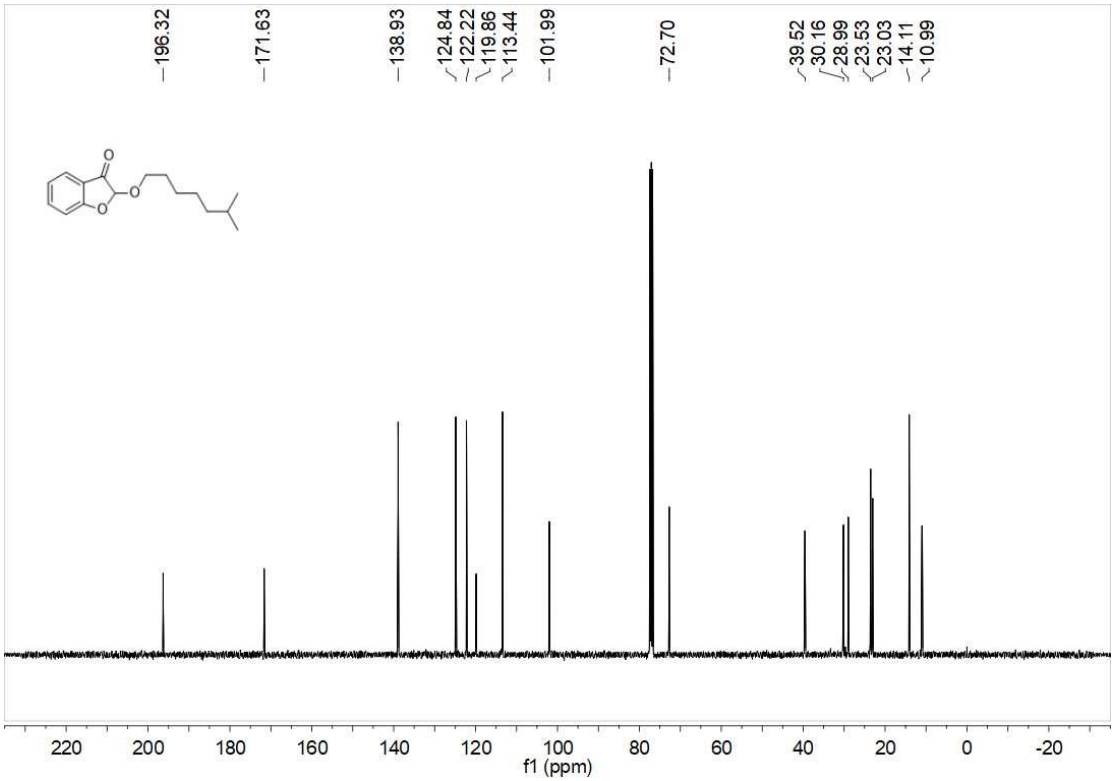
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3d



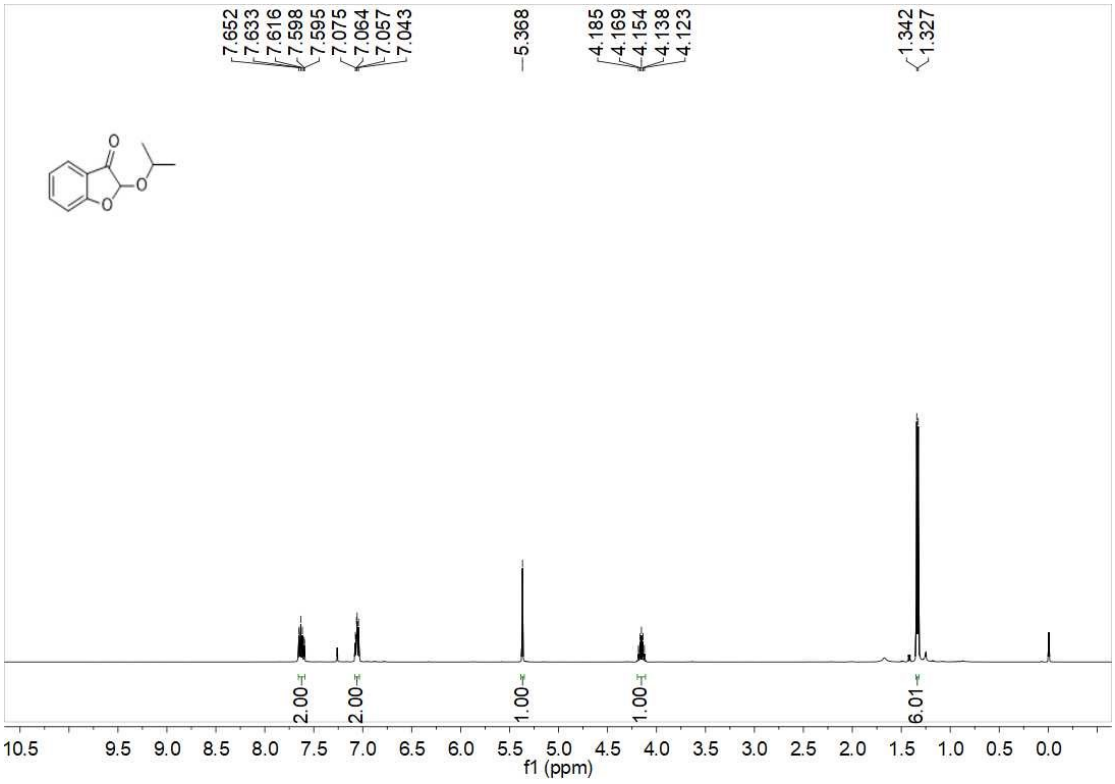
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3e



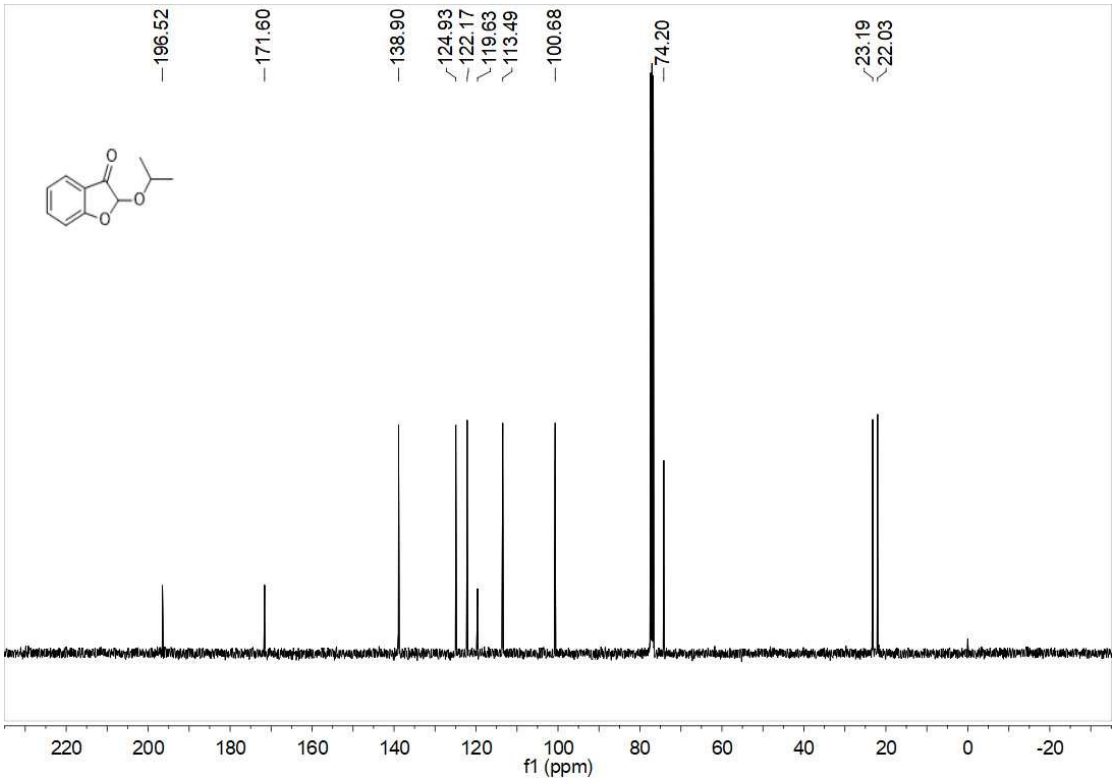
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3e



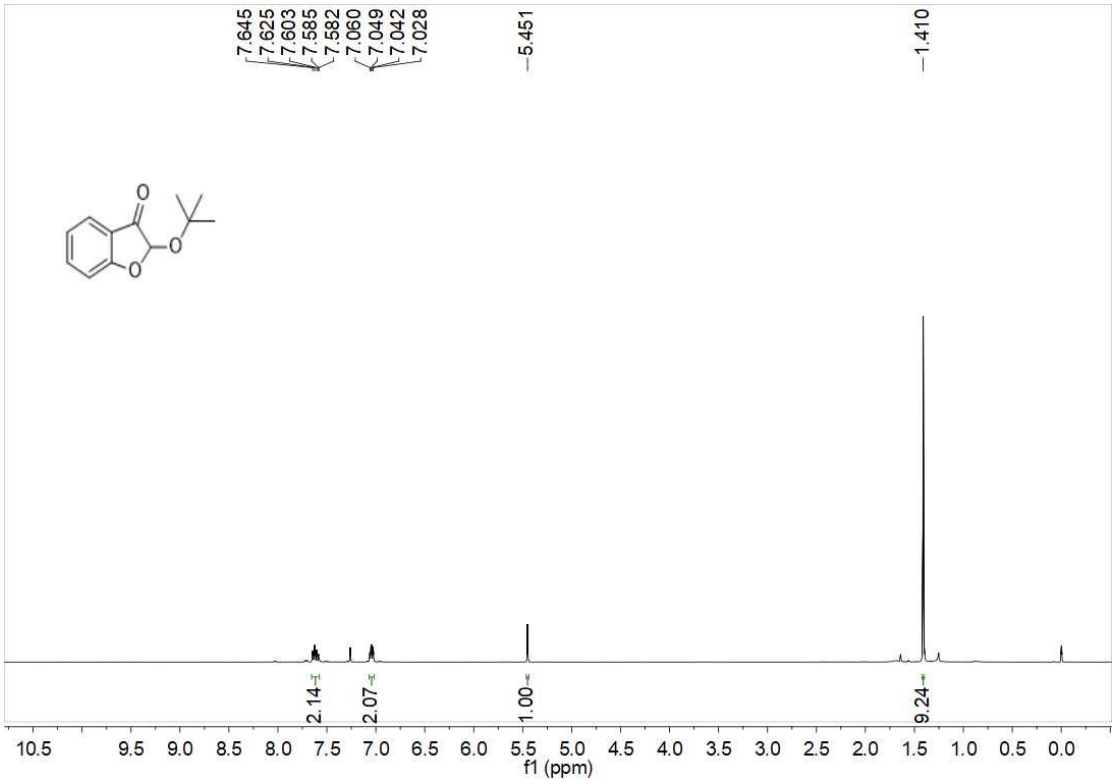
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3f



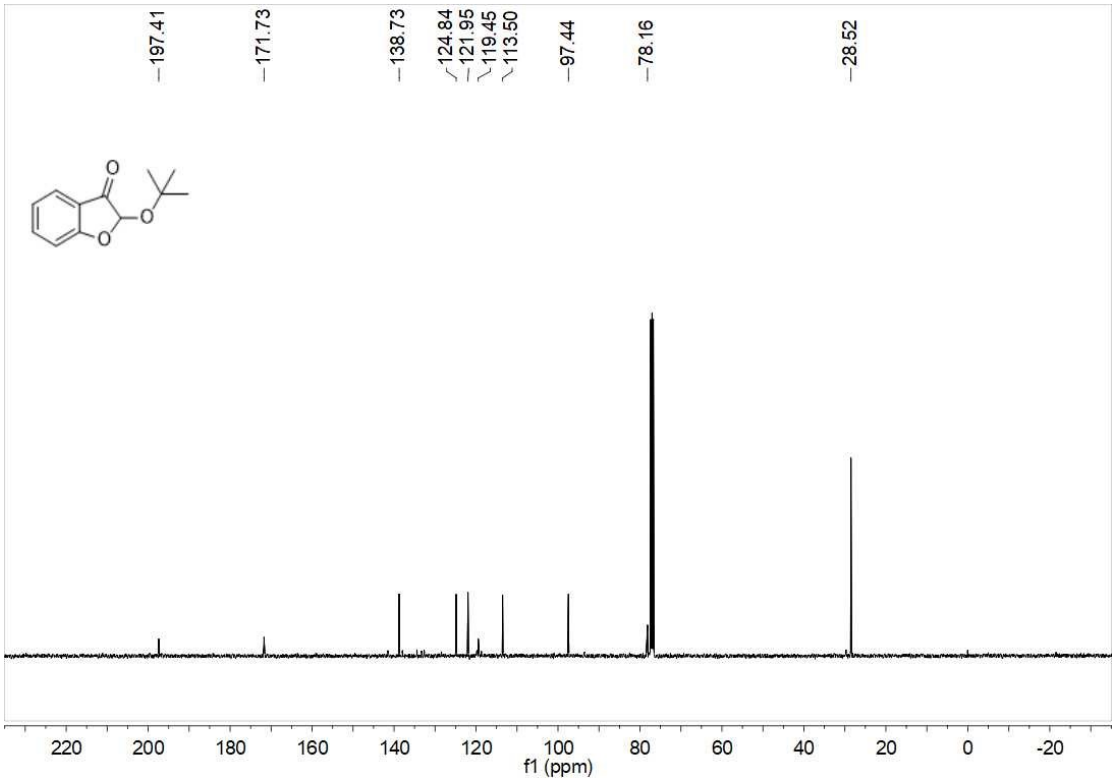
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3f



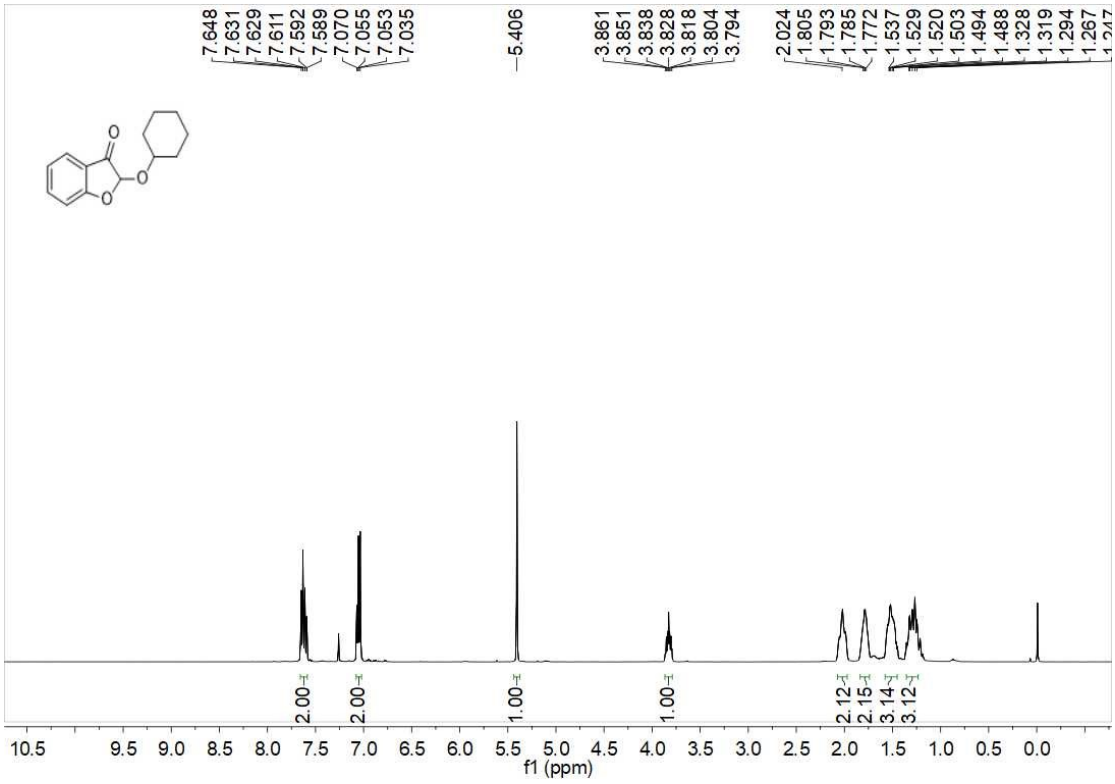
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3g



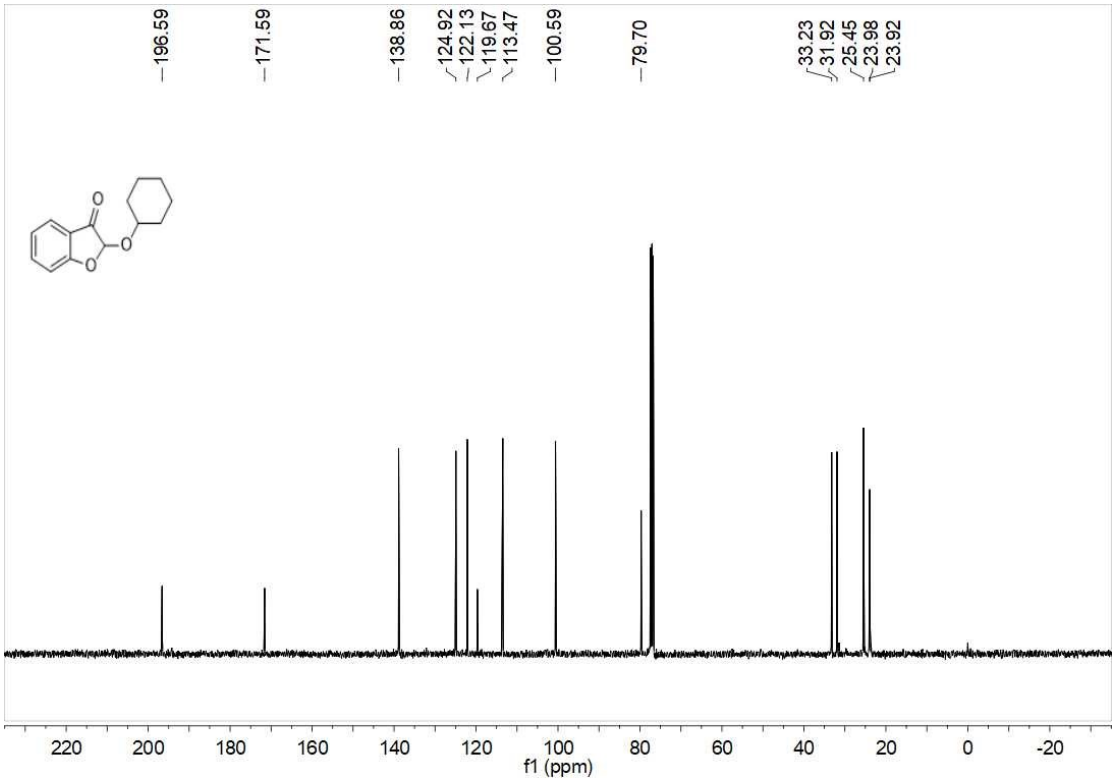
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3g



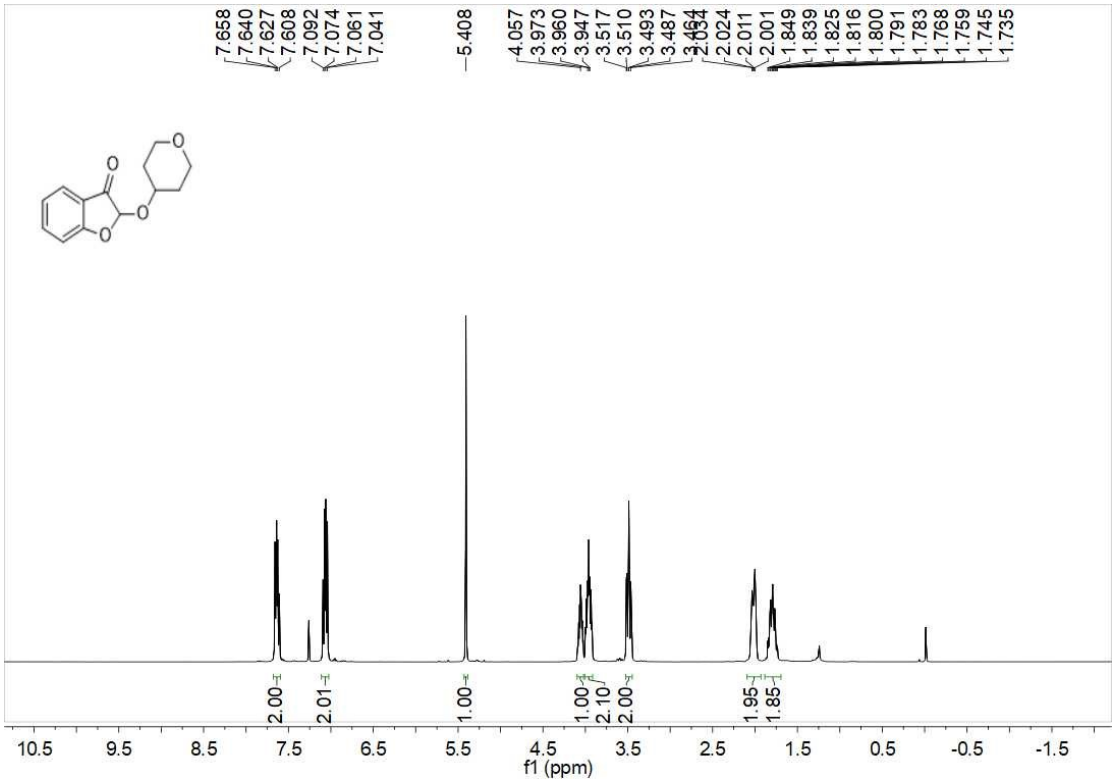
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3h



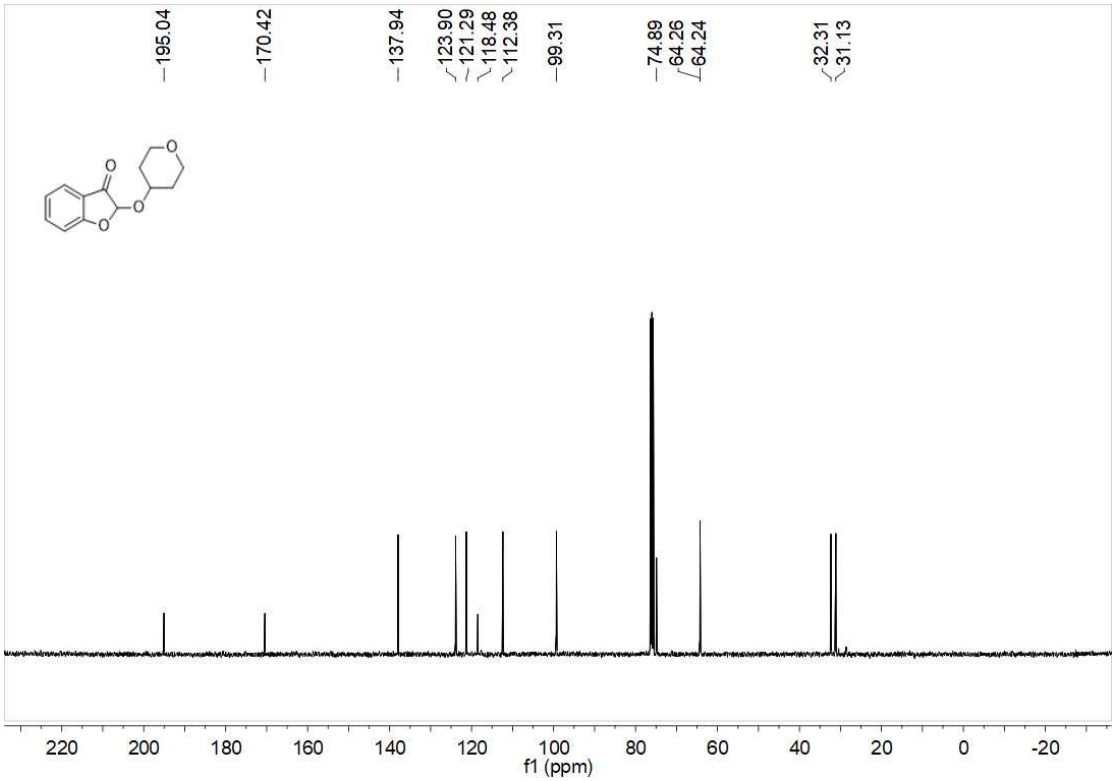
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3h



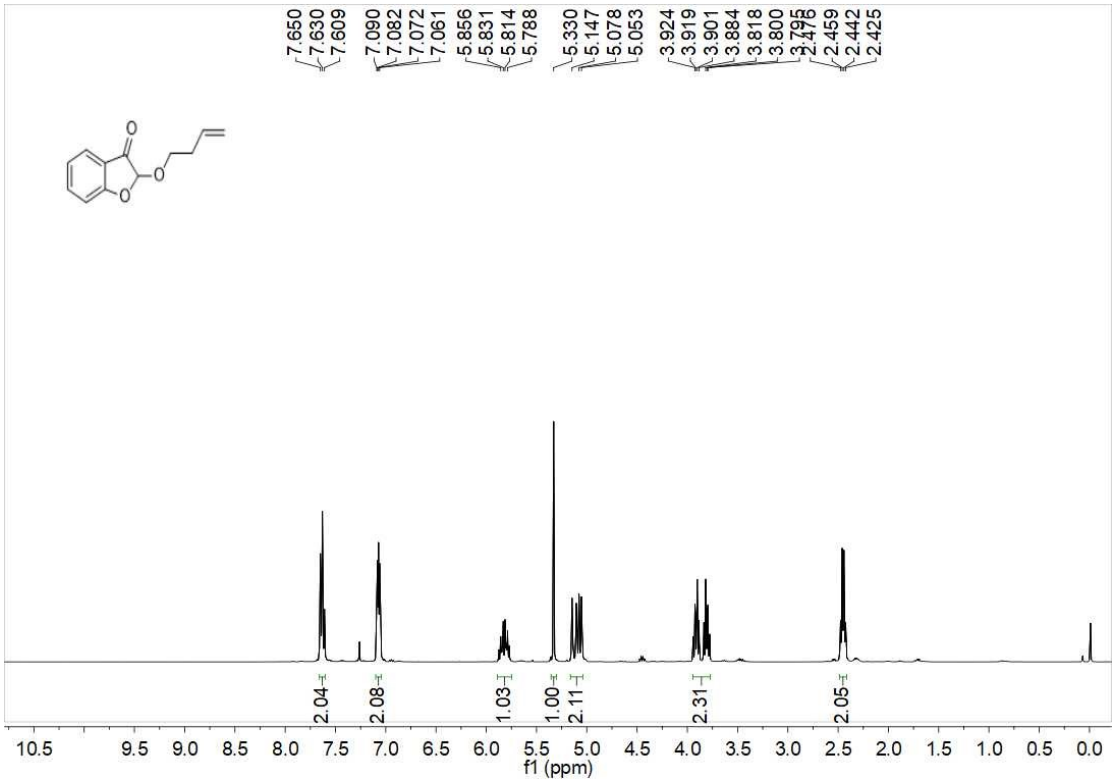
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3i



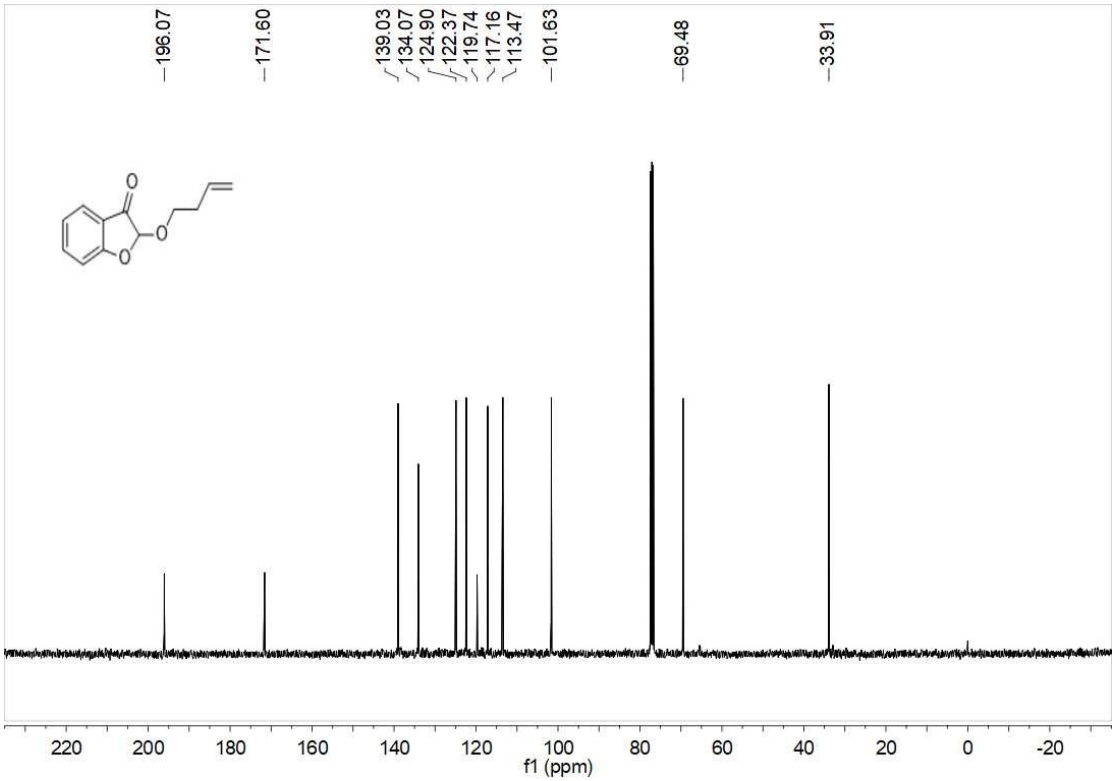
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3i



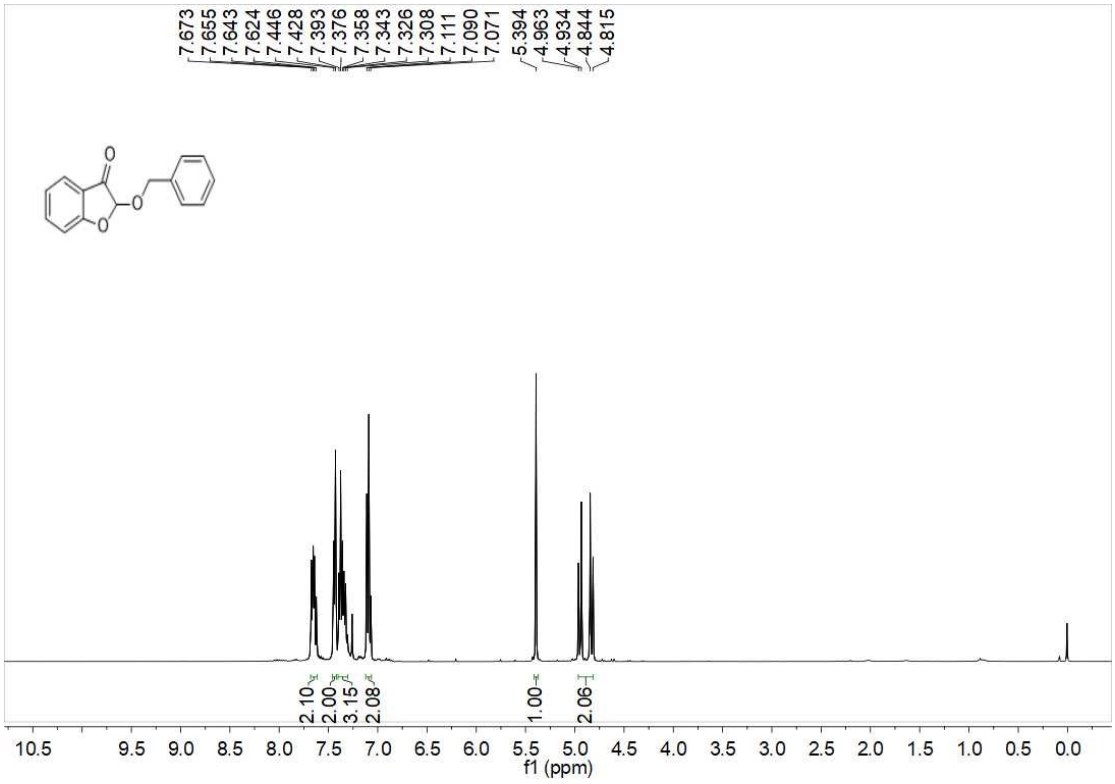
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3j



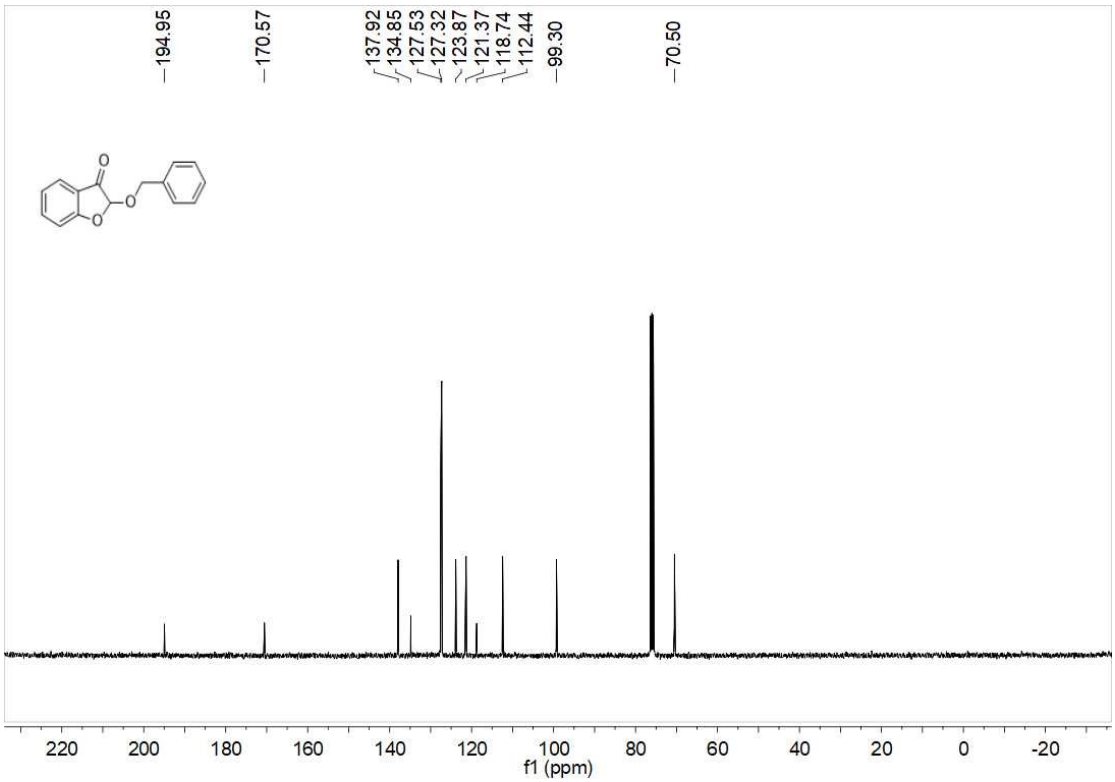
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3j



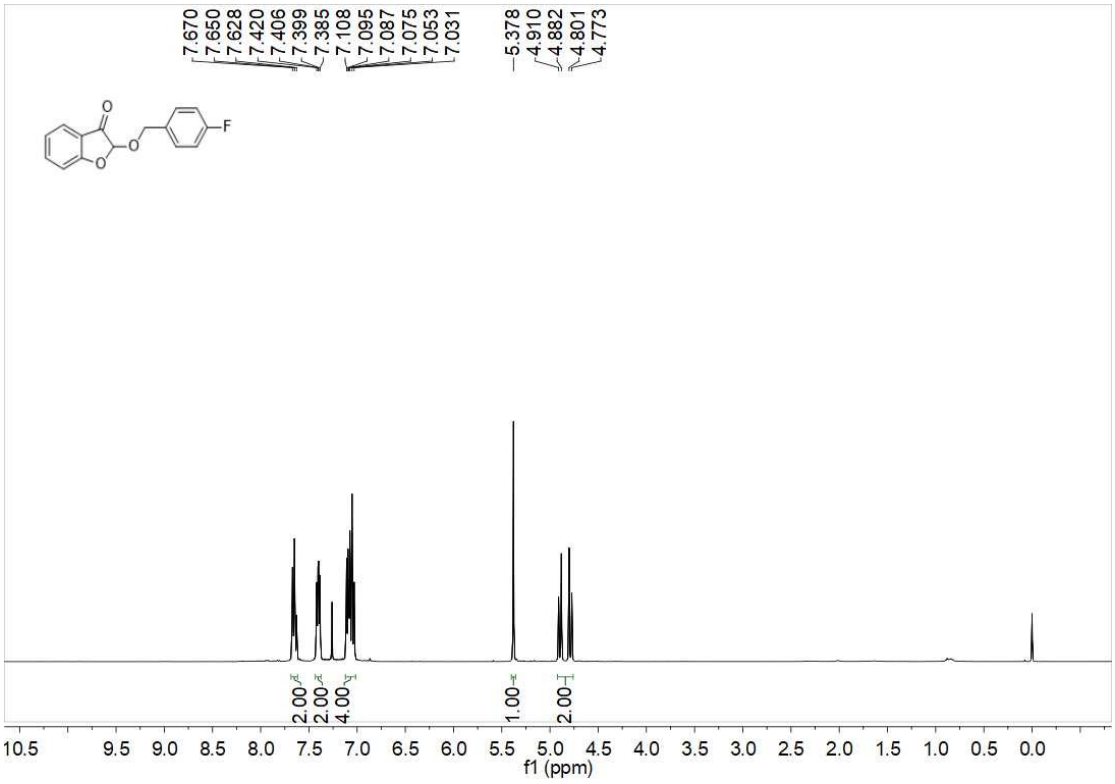
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3k



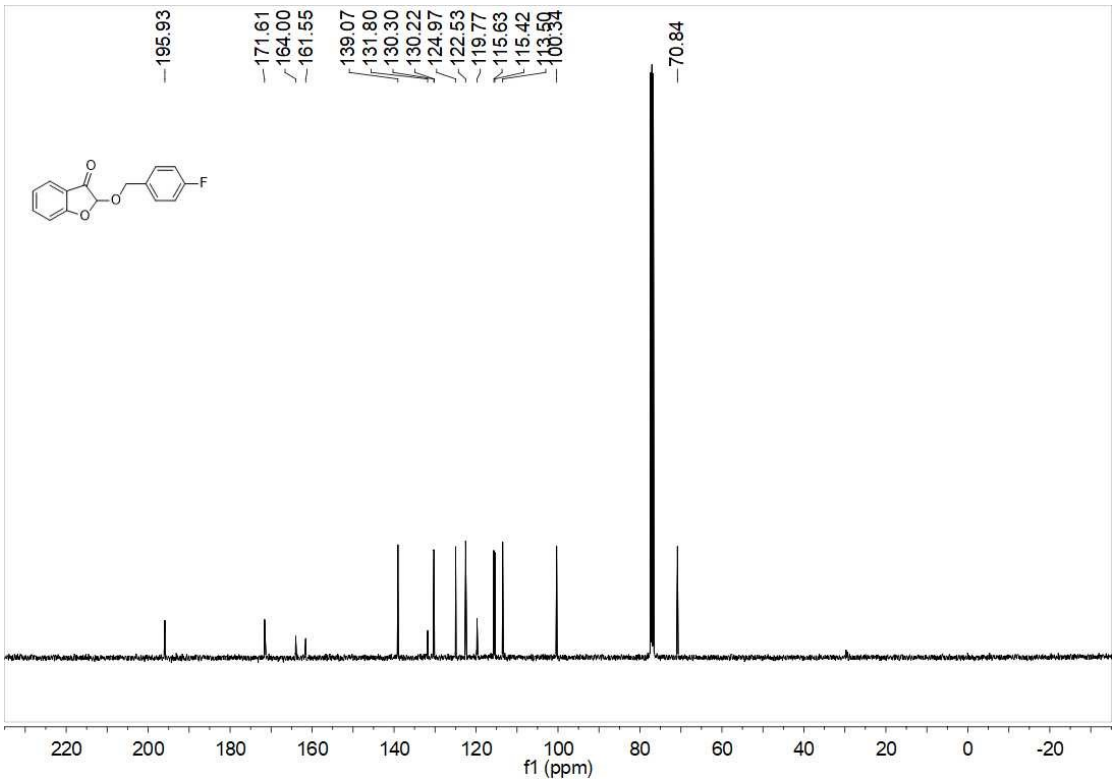
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3k



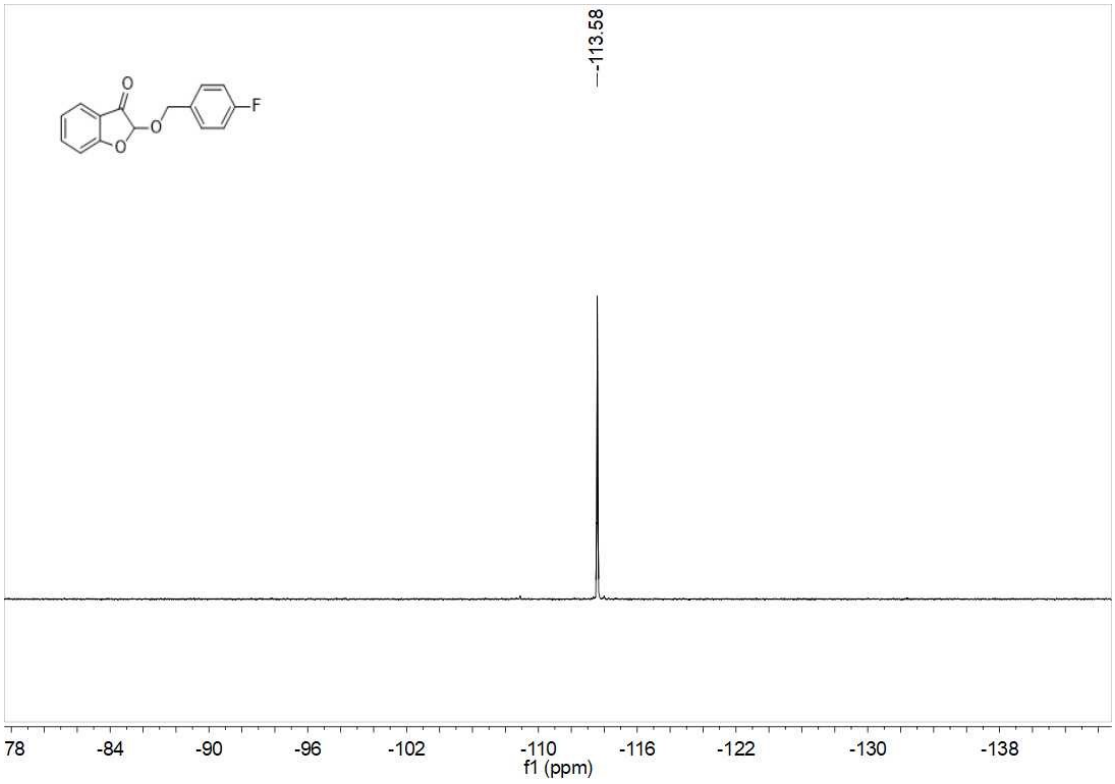
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3l



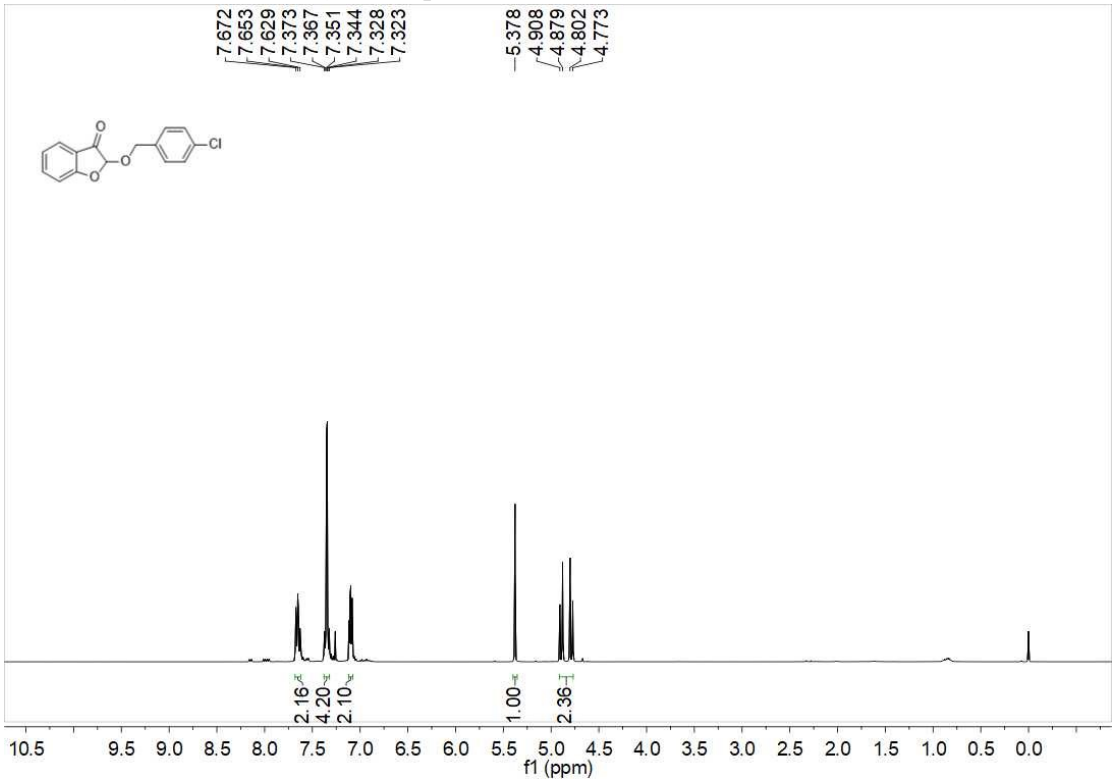
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3l



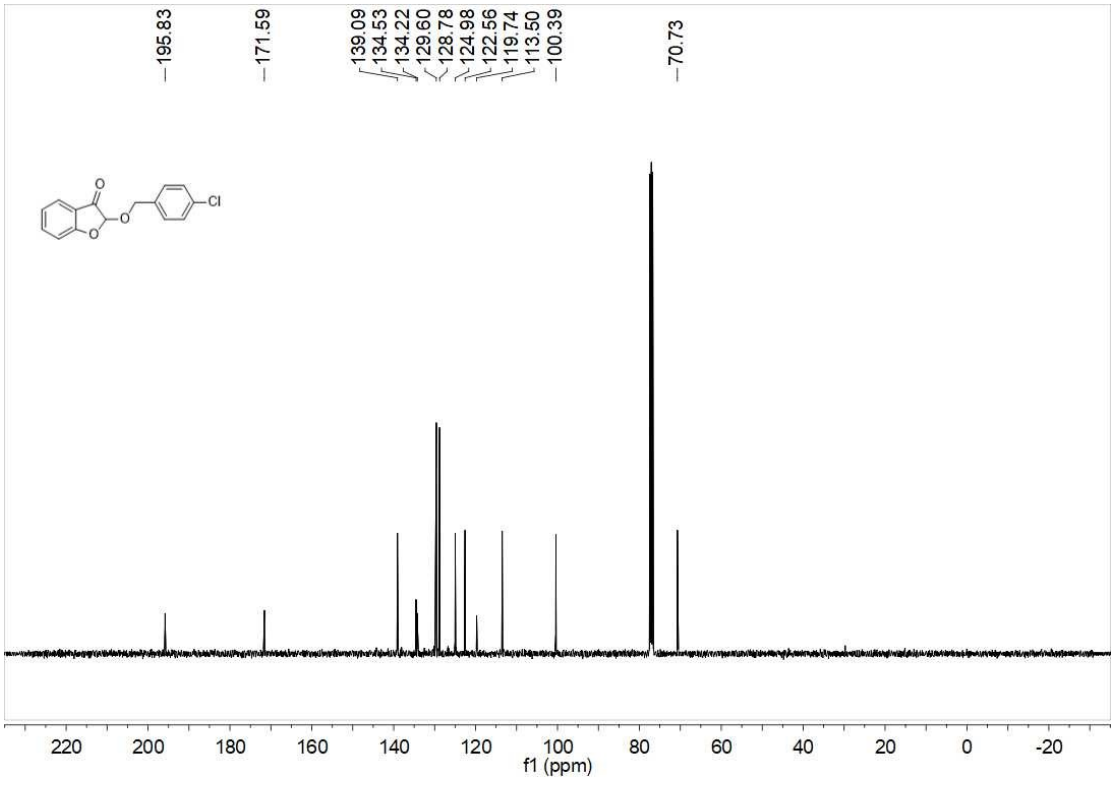
^{19}F NMR (376 MHz, $CDCl_3$) of compound 3l



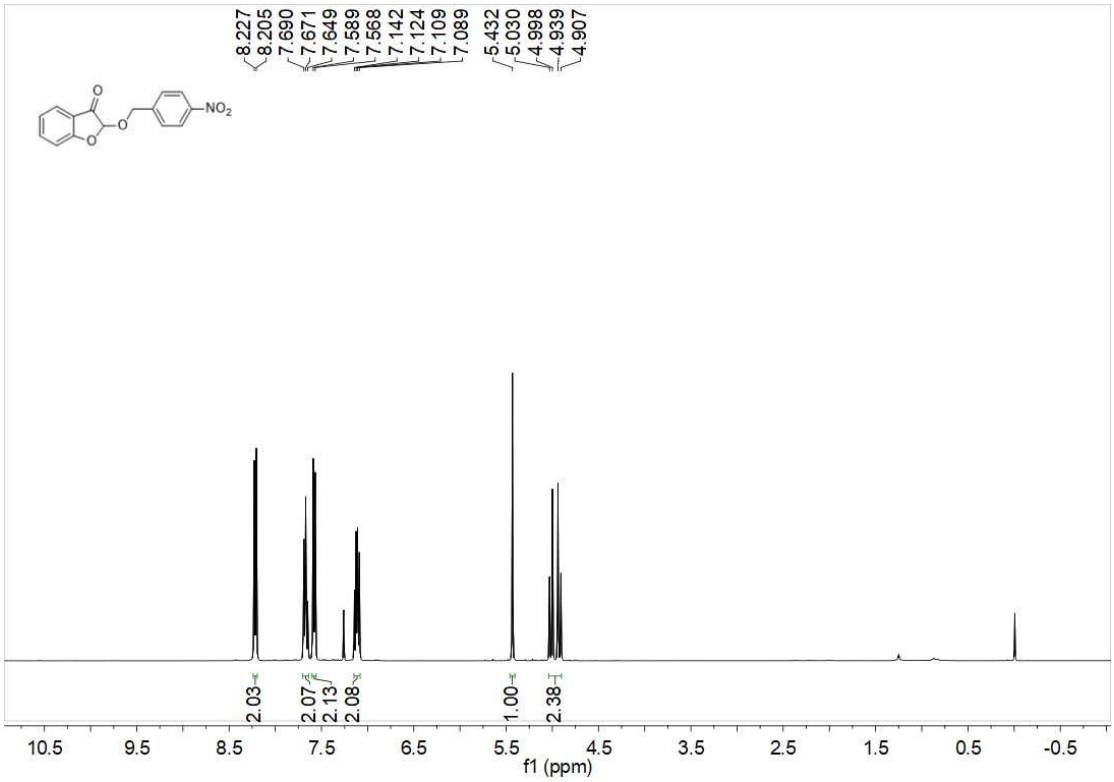
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3m



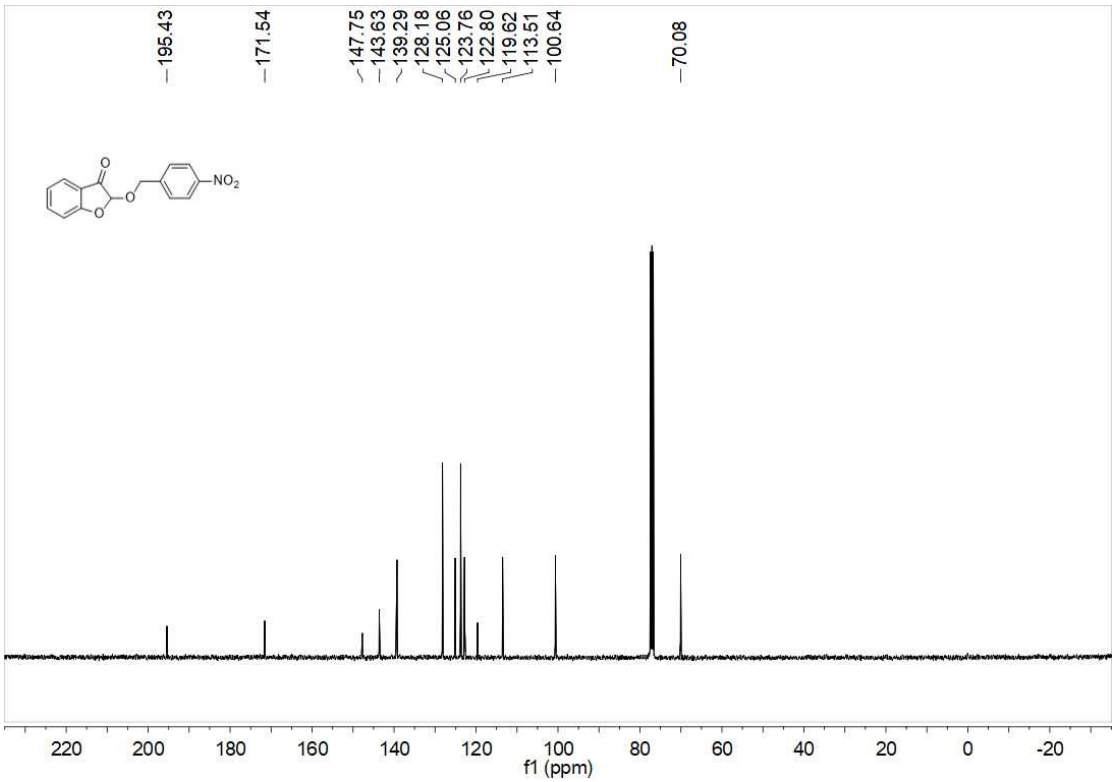
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3m



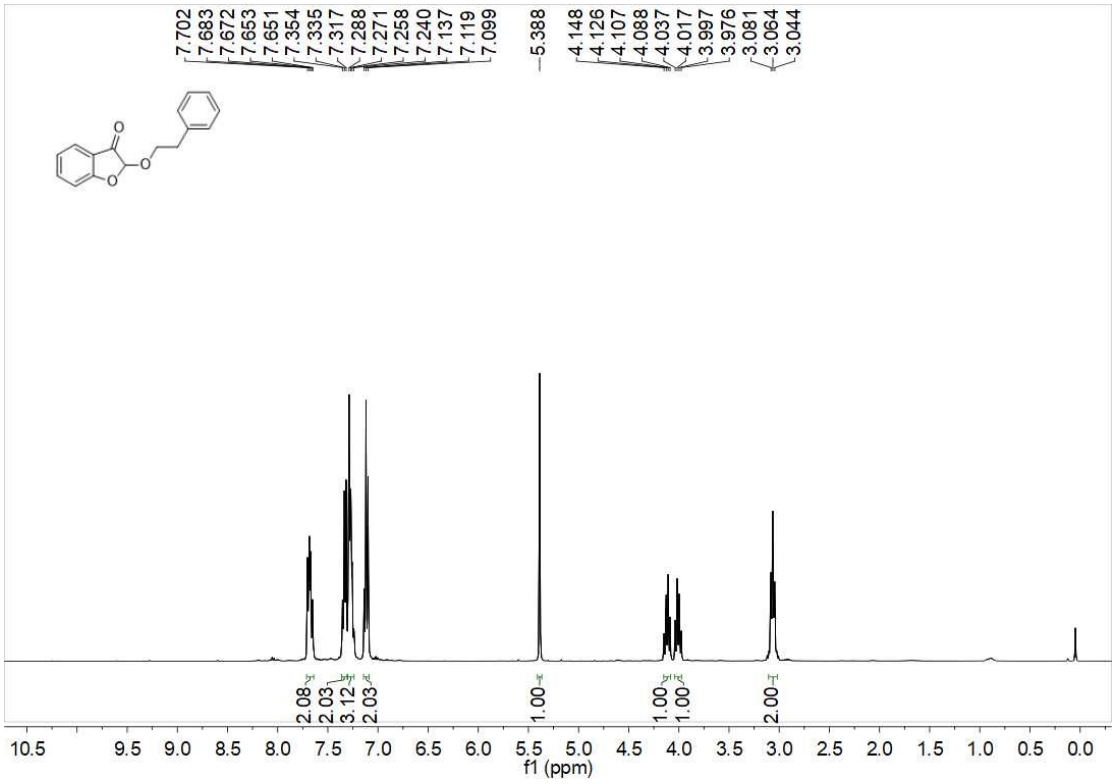
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3n



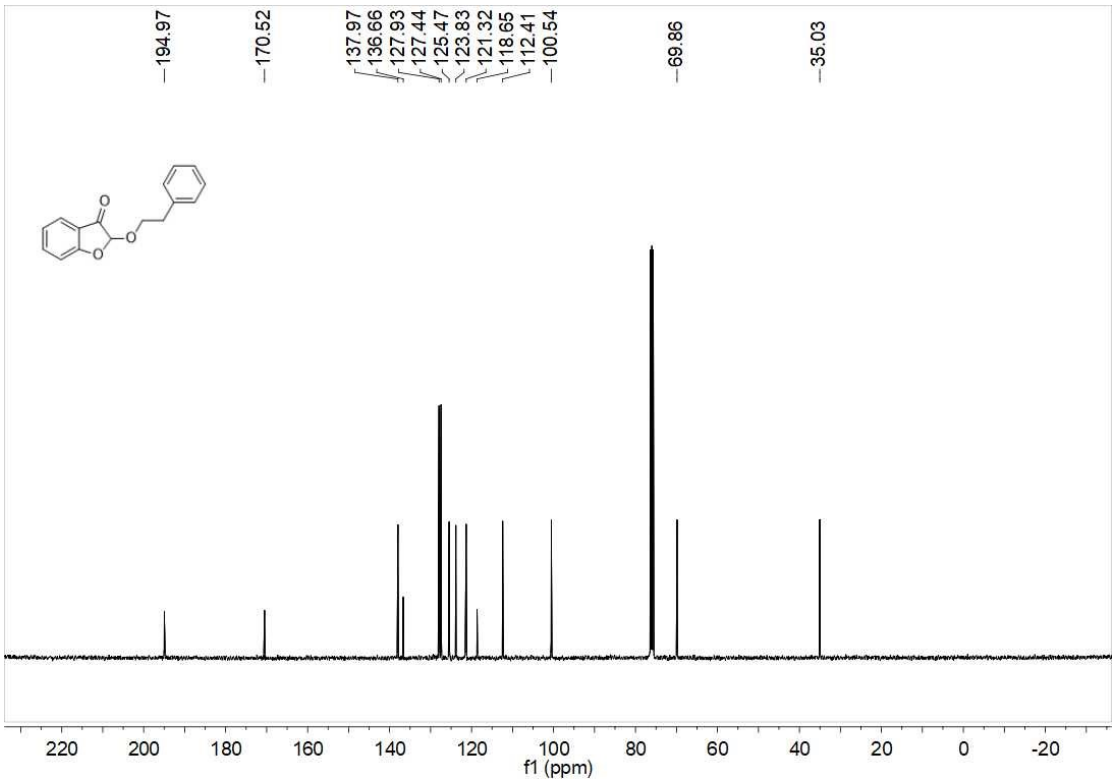
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3n



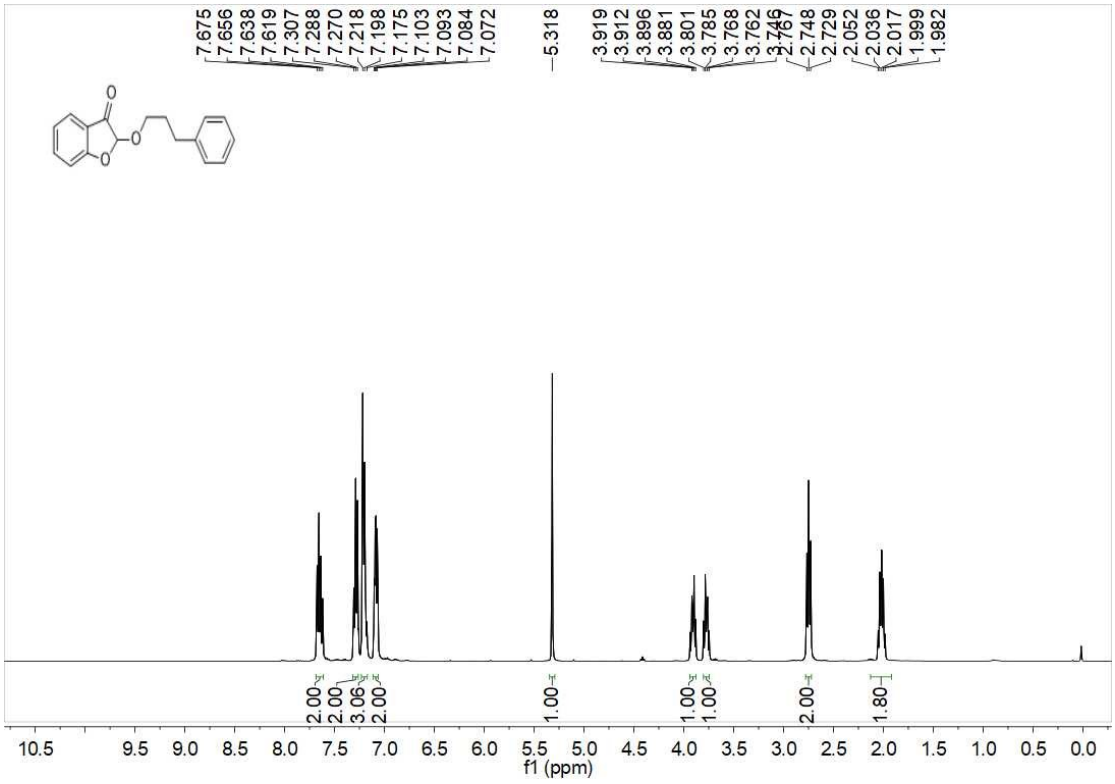
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3o



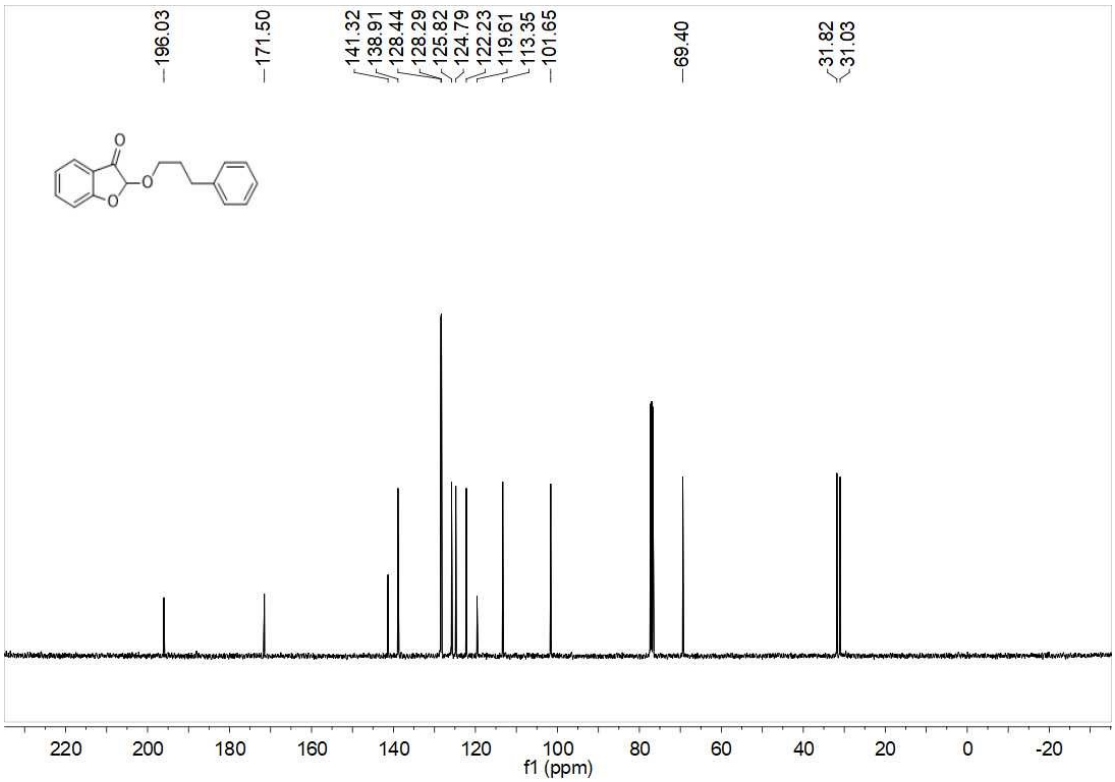
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3o



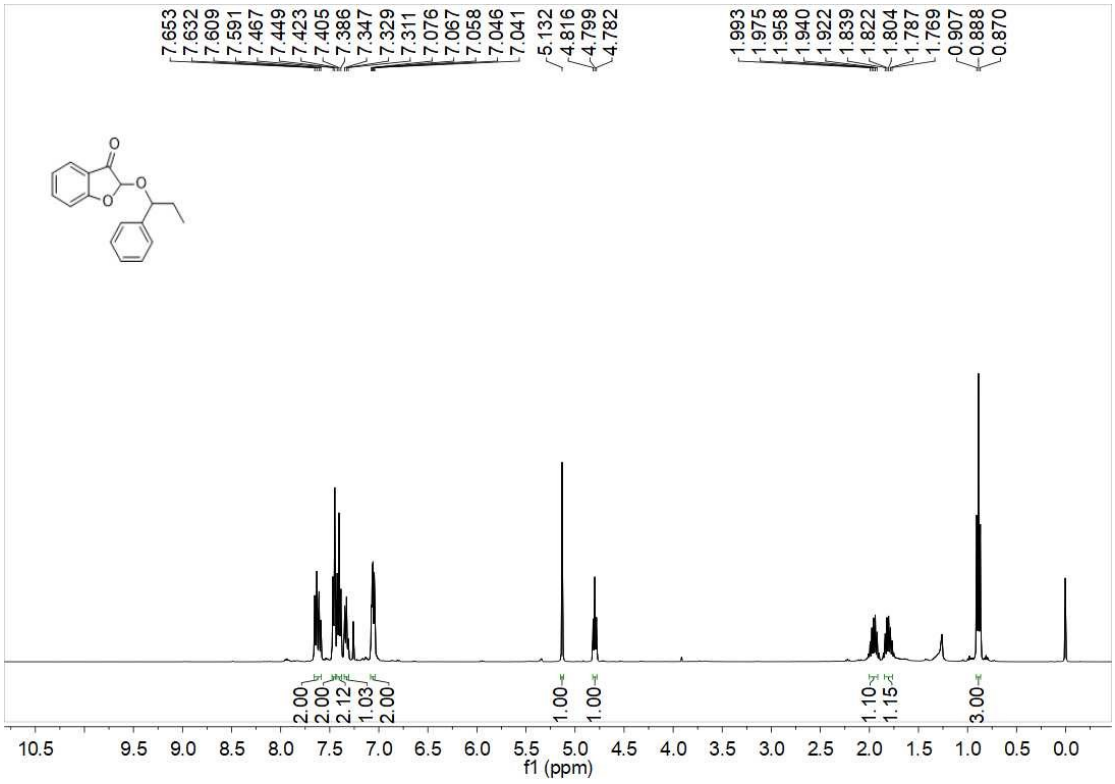
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3p



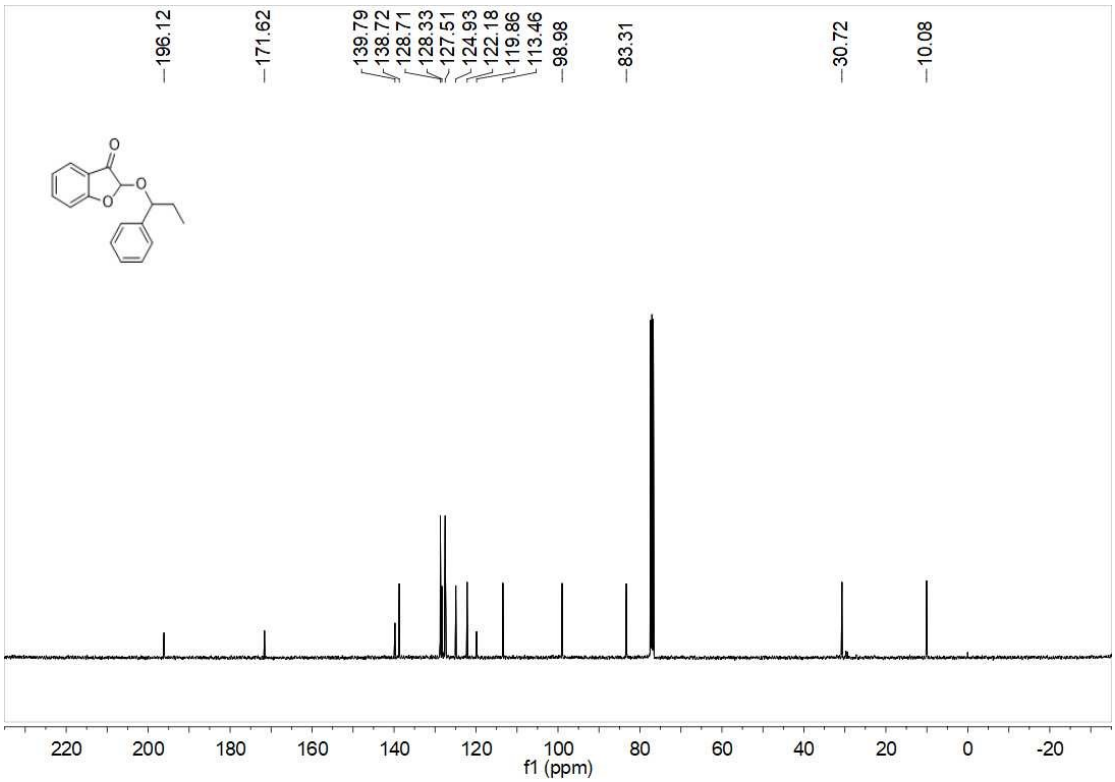
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3p



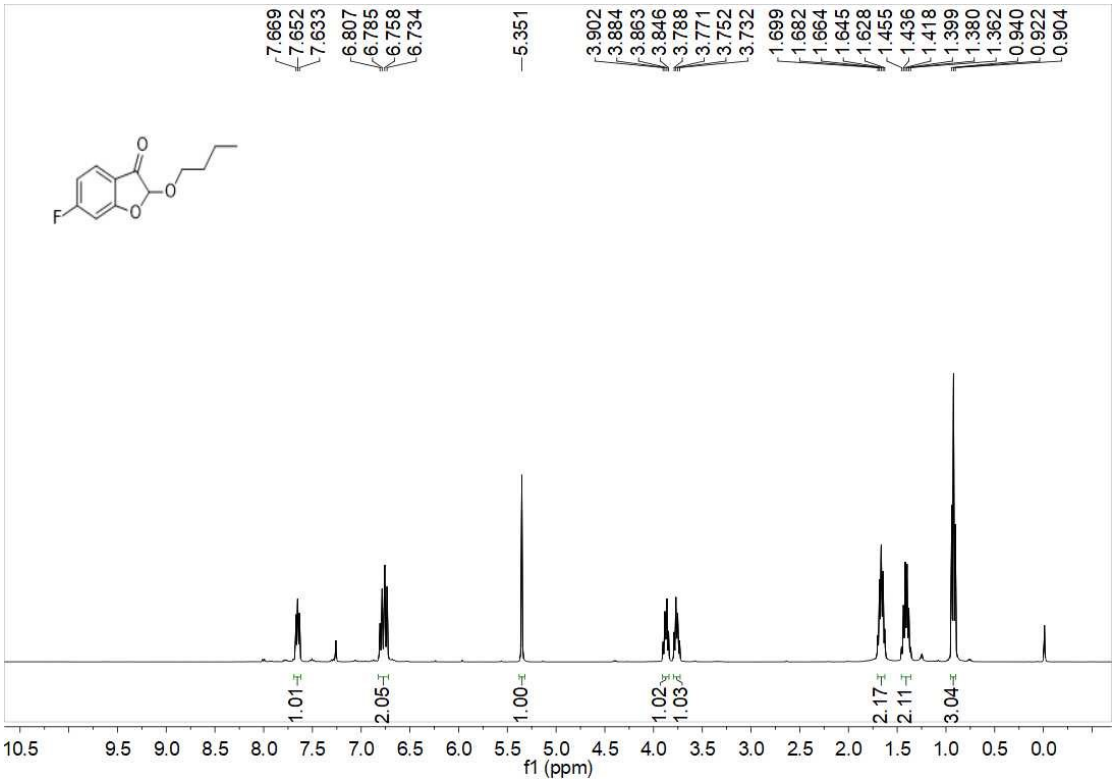
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3q



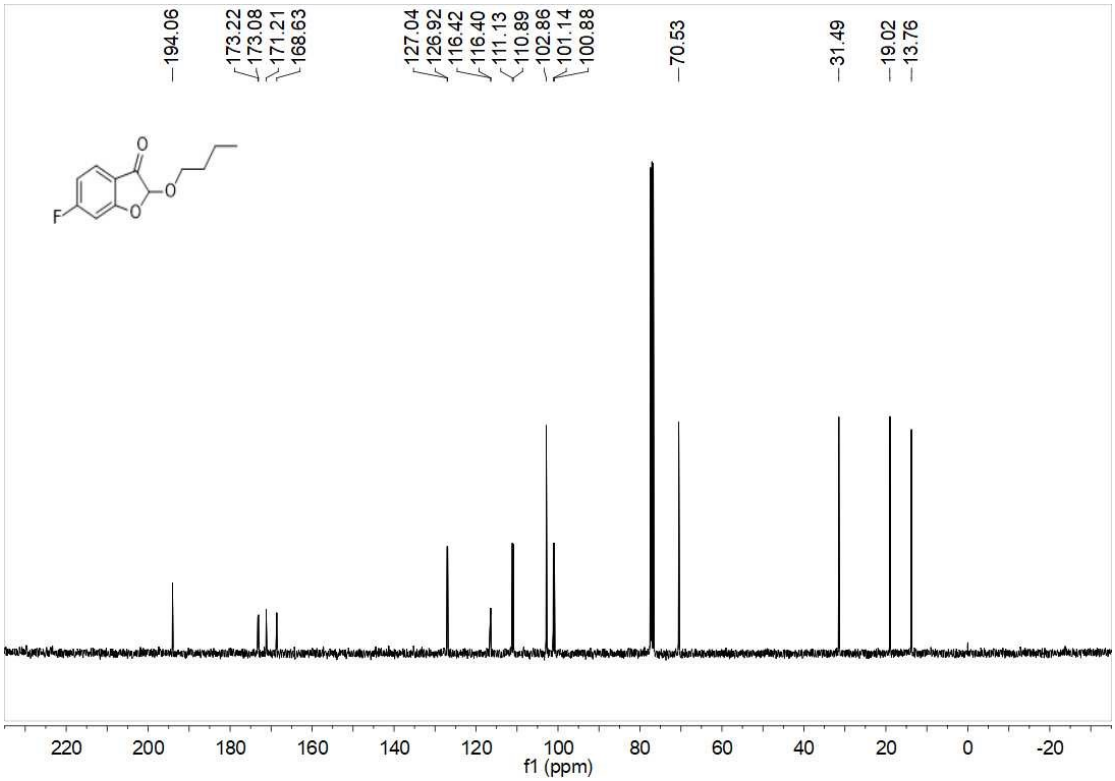
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3q



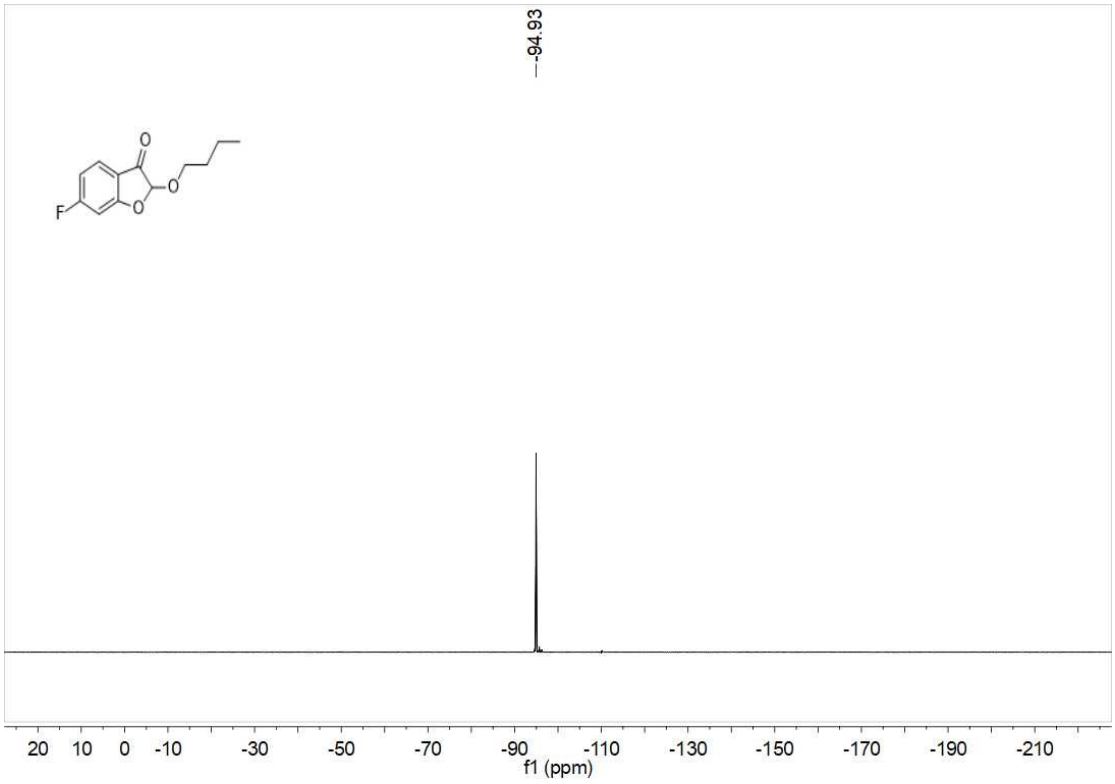
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3r



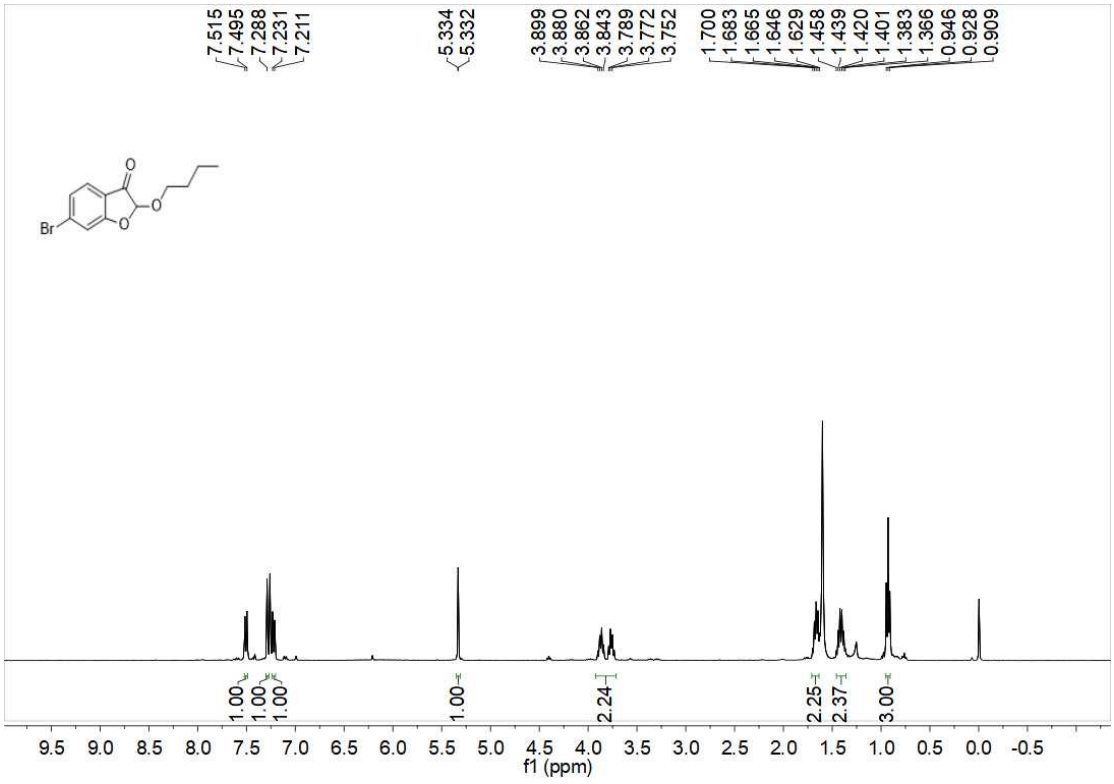
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3r



^{19}F NMR (376 MHz, $CDCl_3$) of compound 3r



^{1}H NMR (400 MHz, $CDCl_3$) of compound 3s



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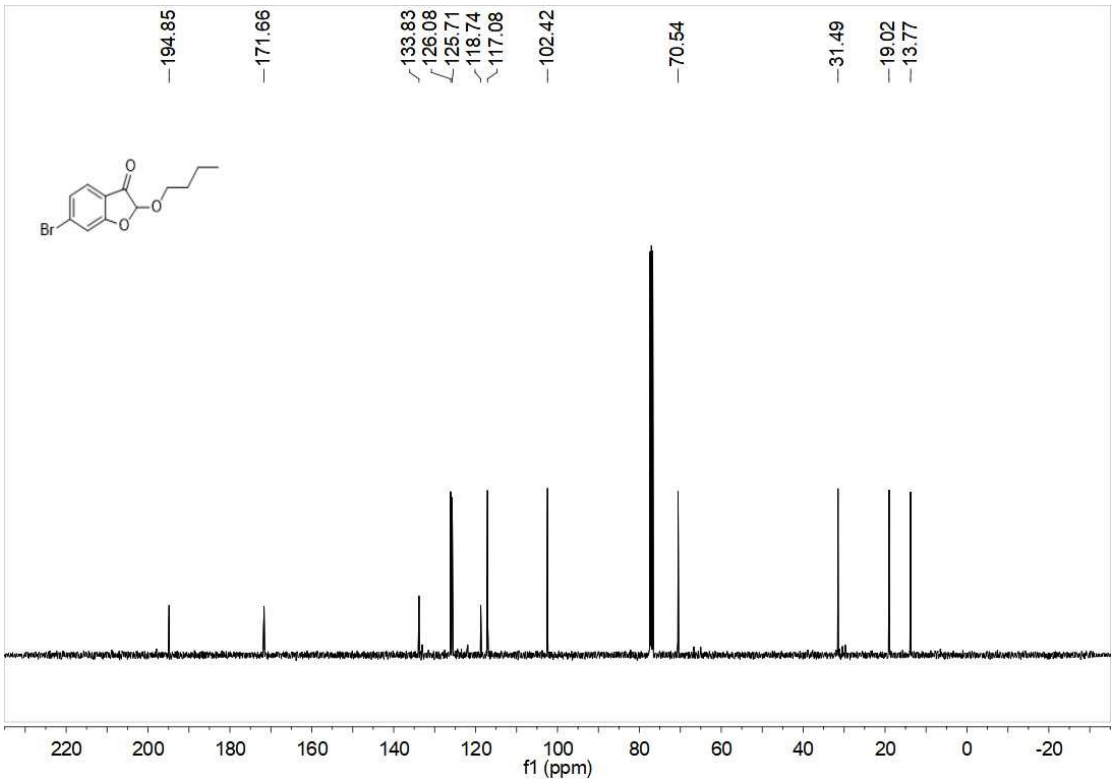
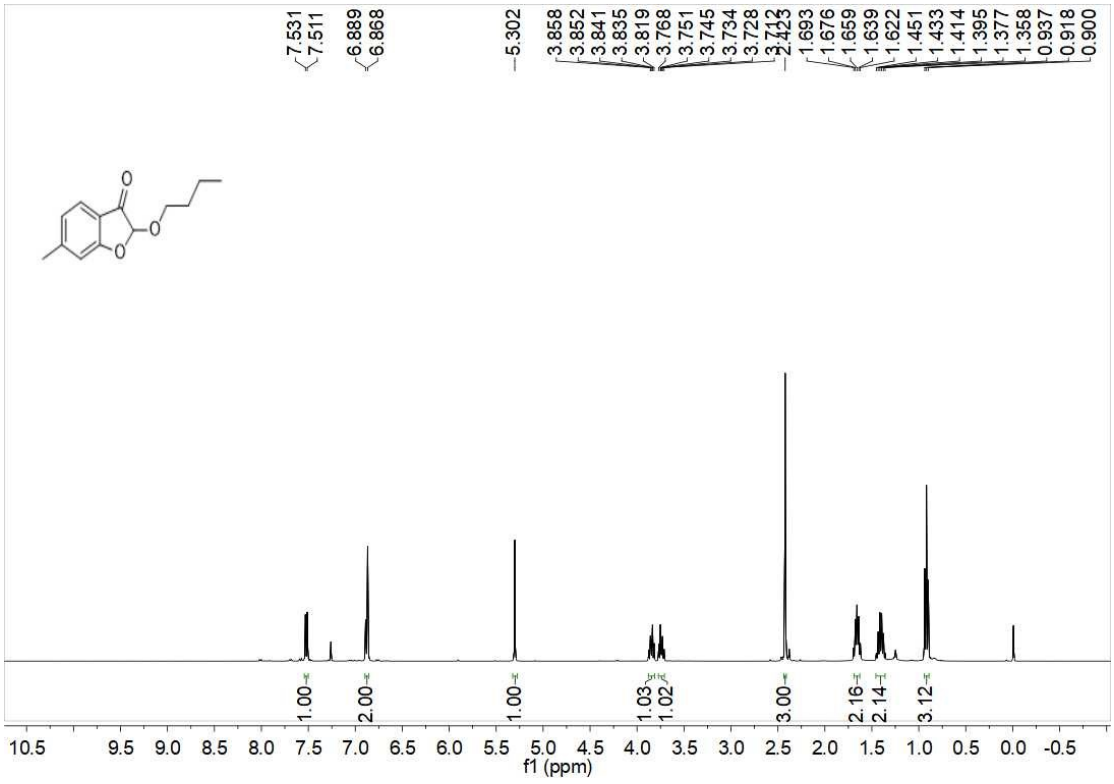


^{1}H NMR (400 MHz, $CDCl_3$) of compound 3t



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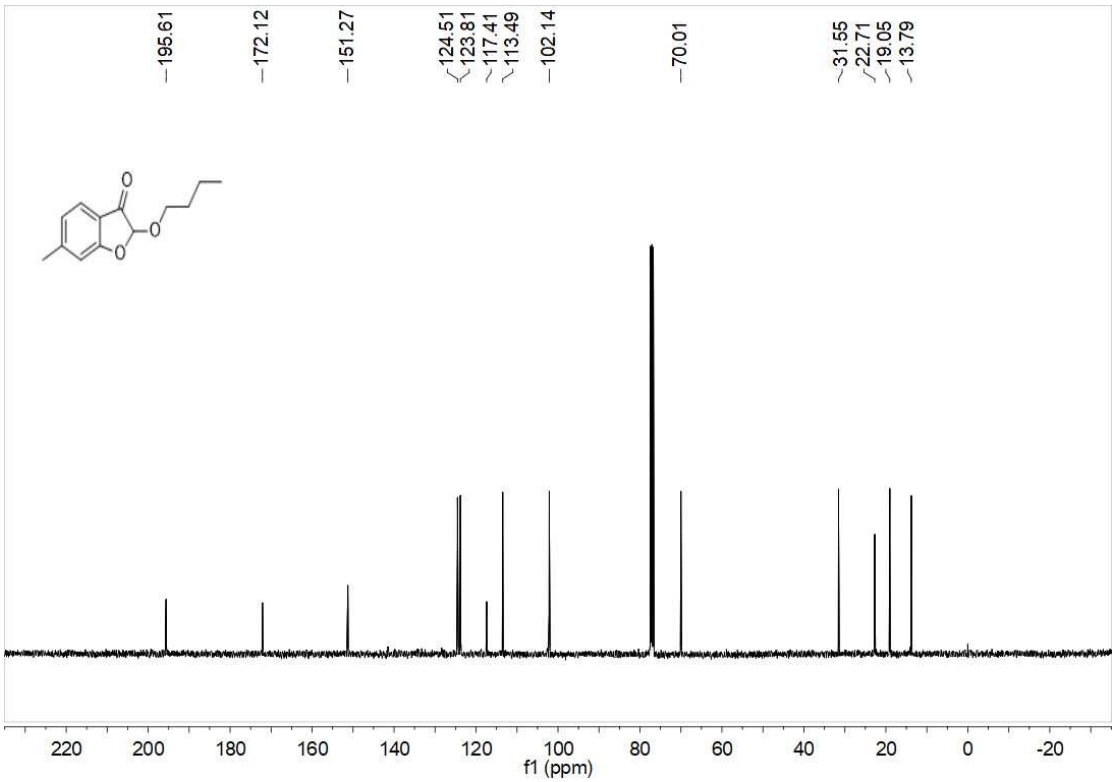
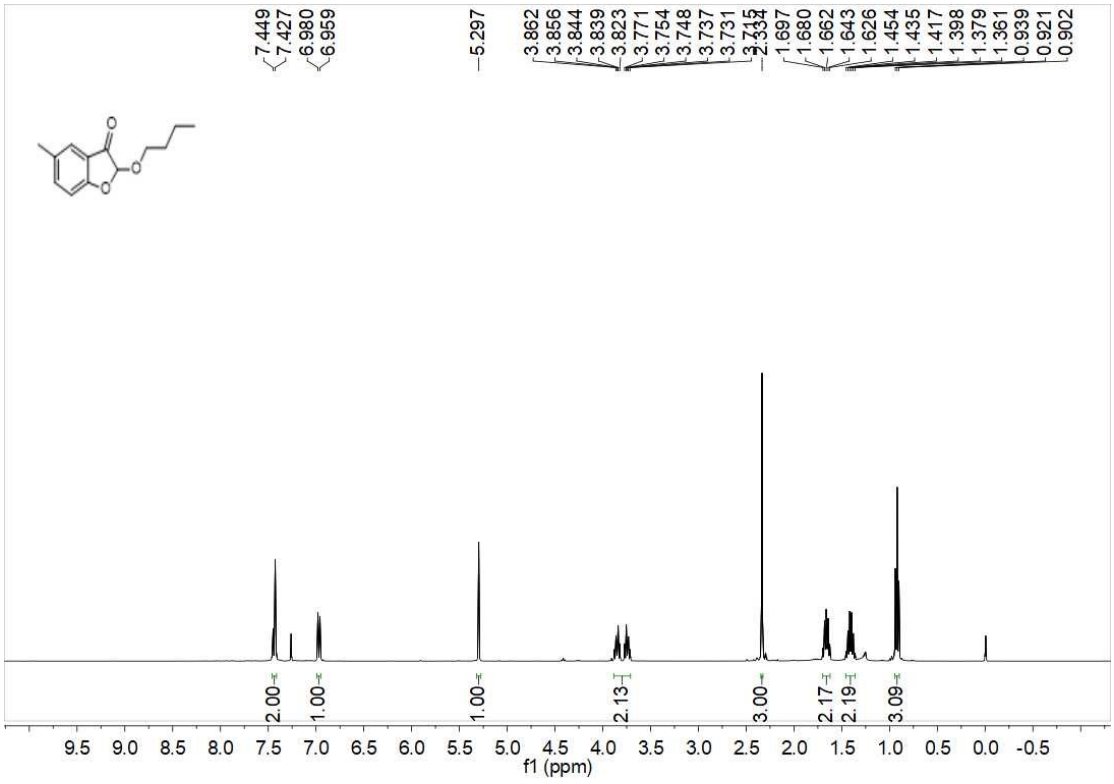
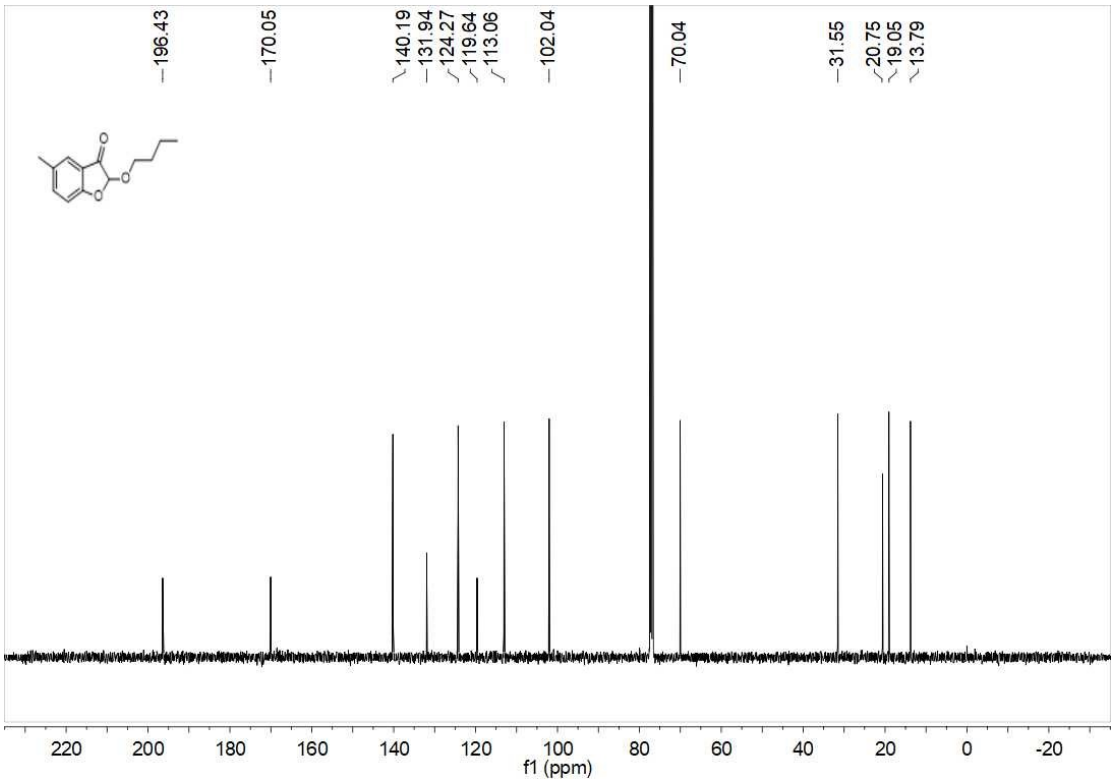


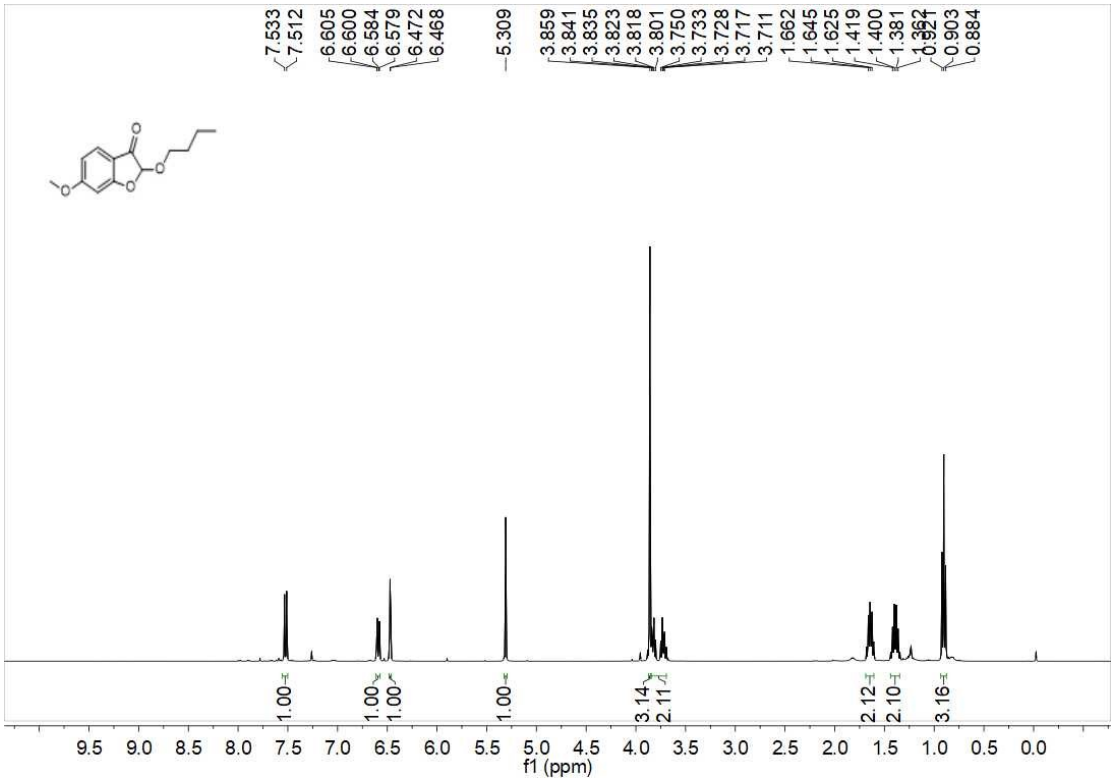
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3u



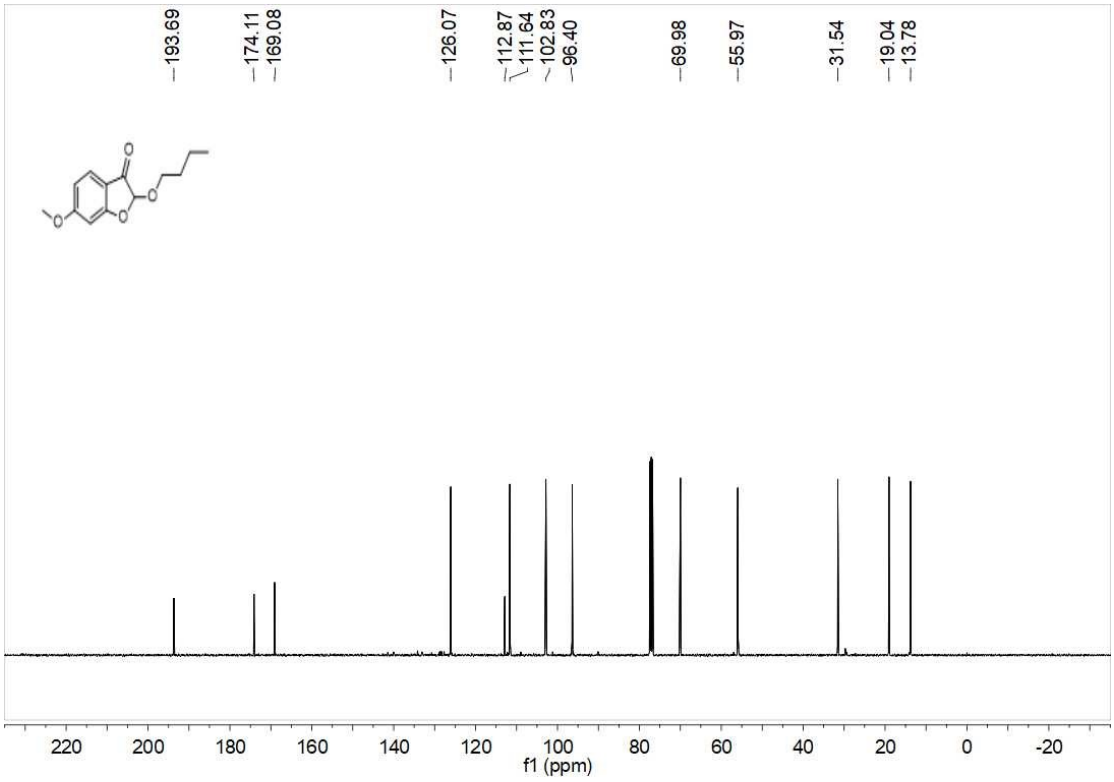
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3u



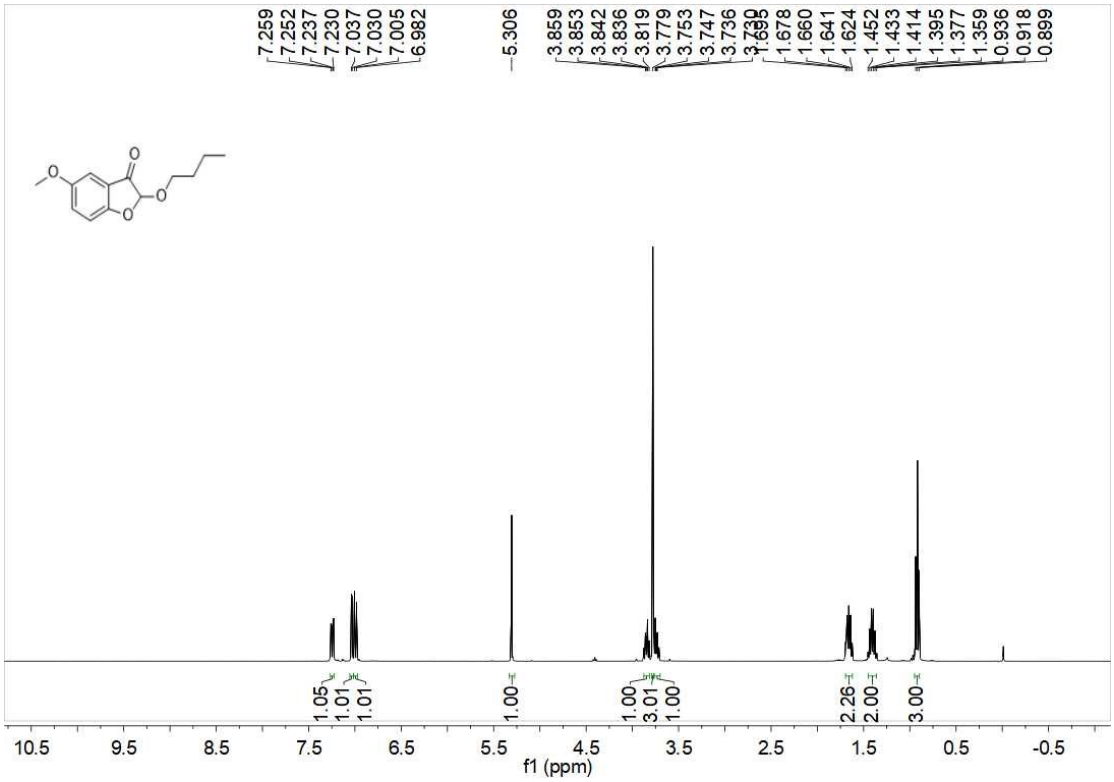
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3v



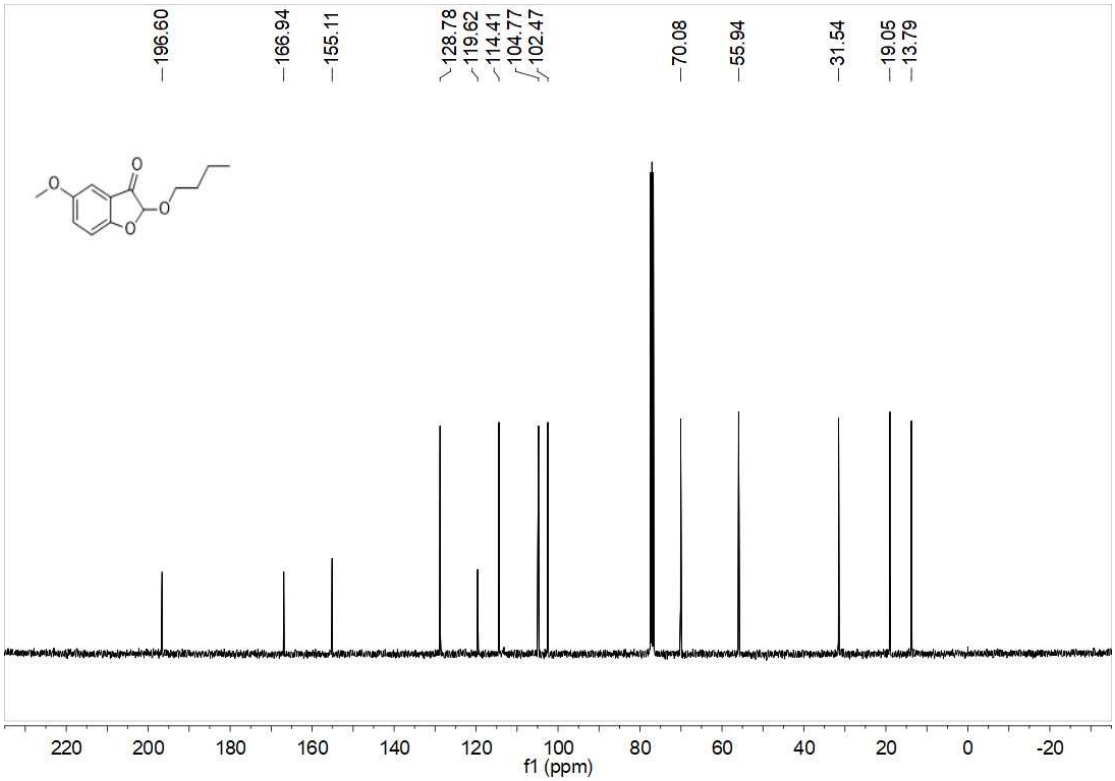
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3v



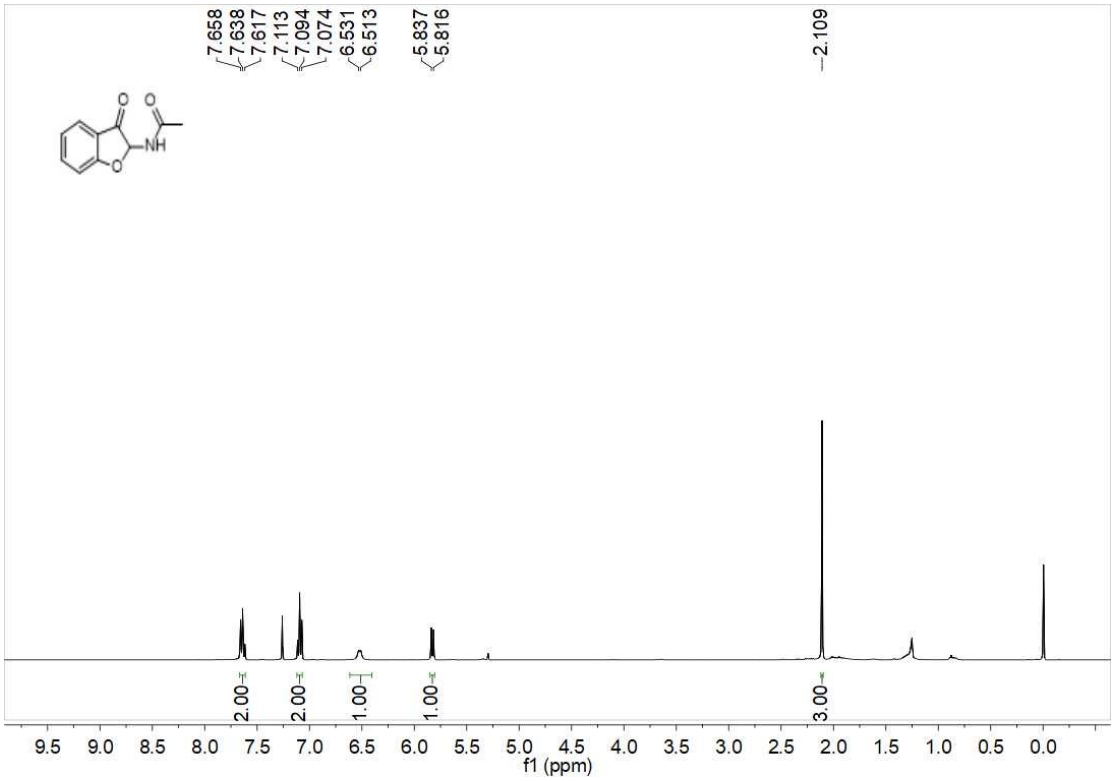
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3w



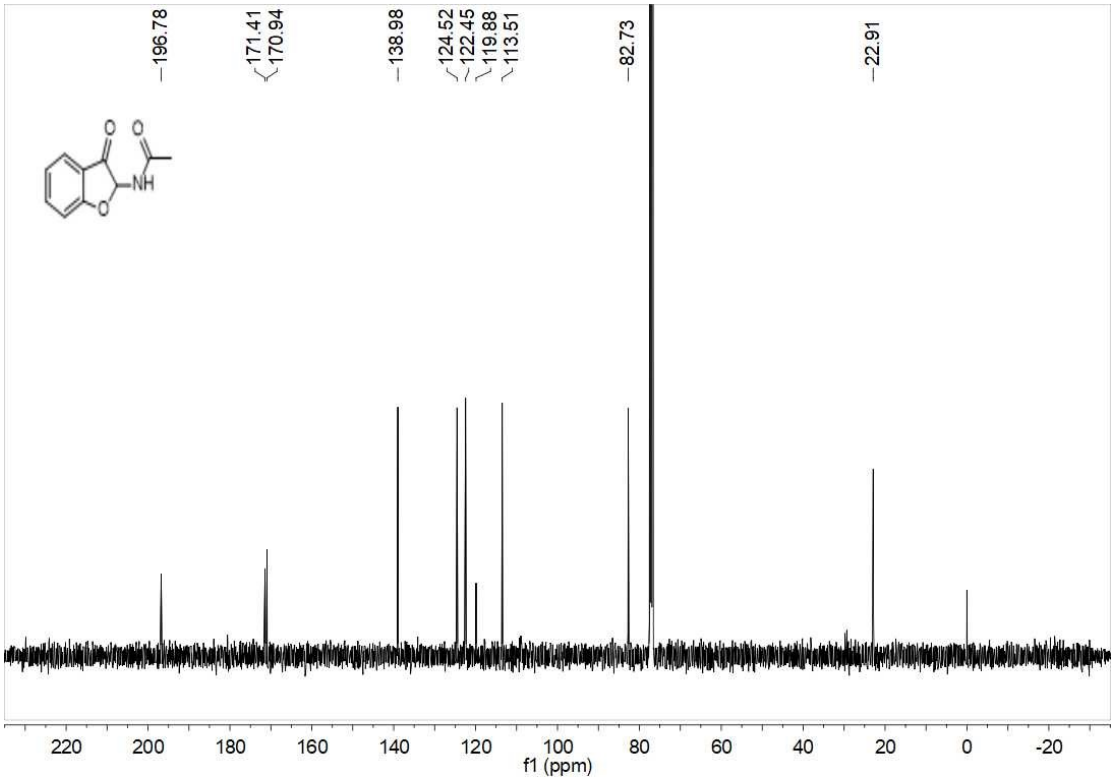
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3w



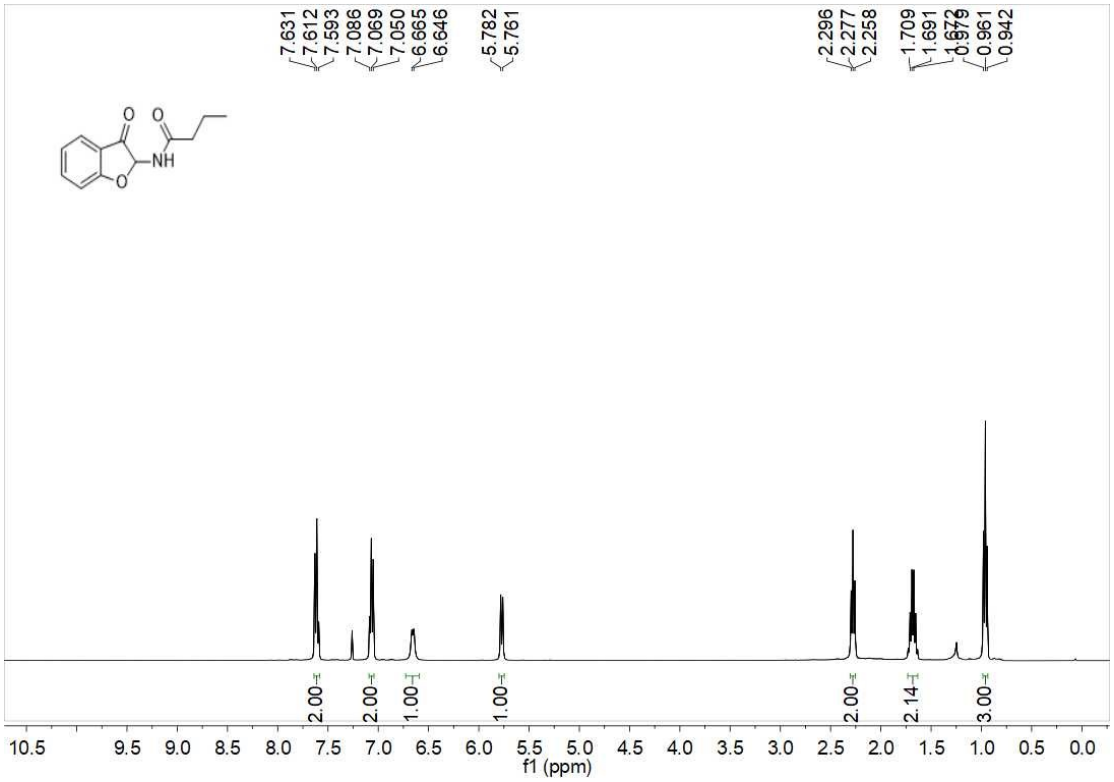
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5a



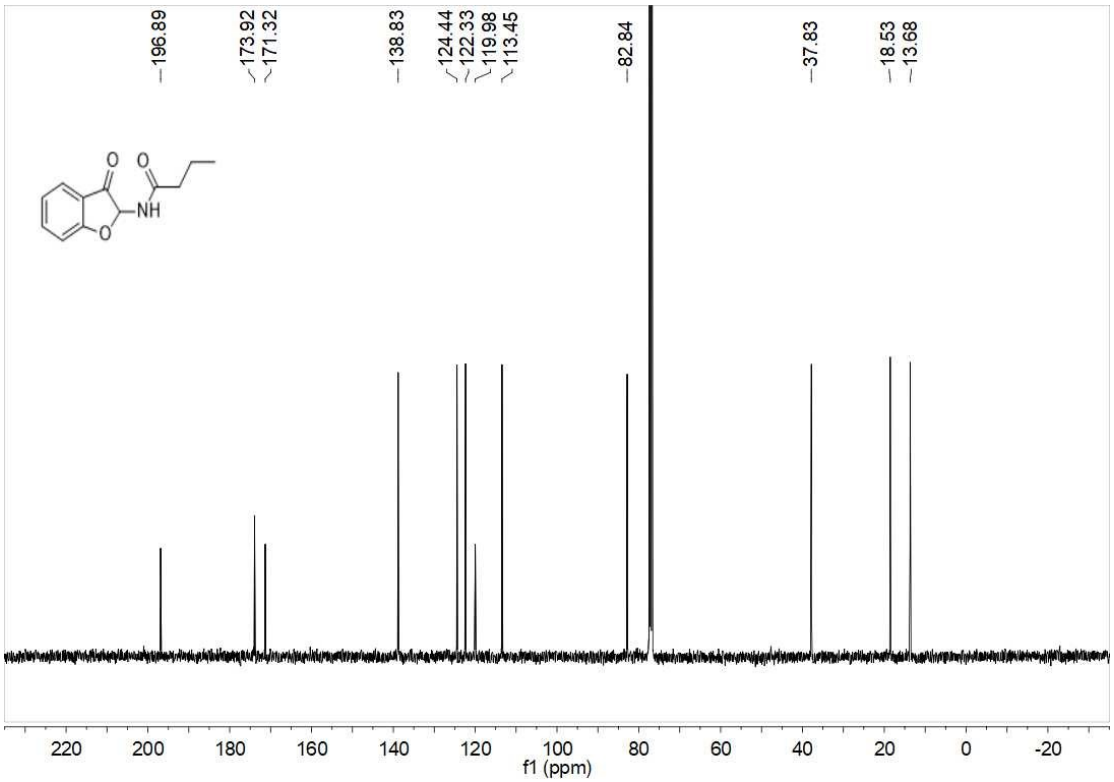
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5a



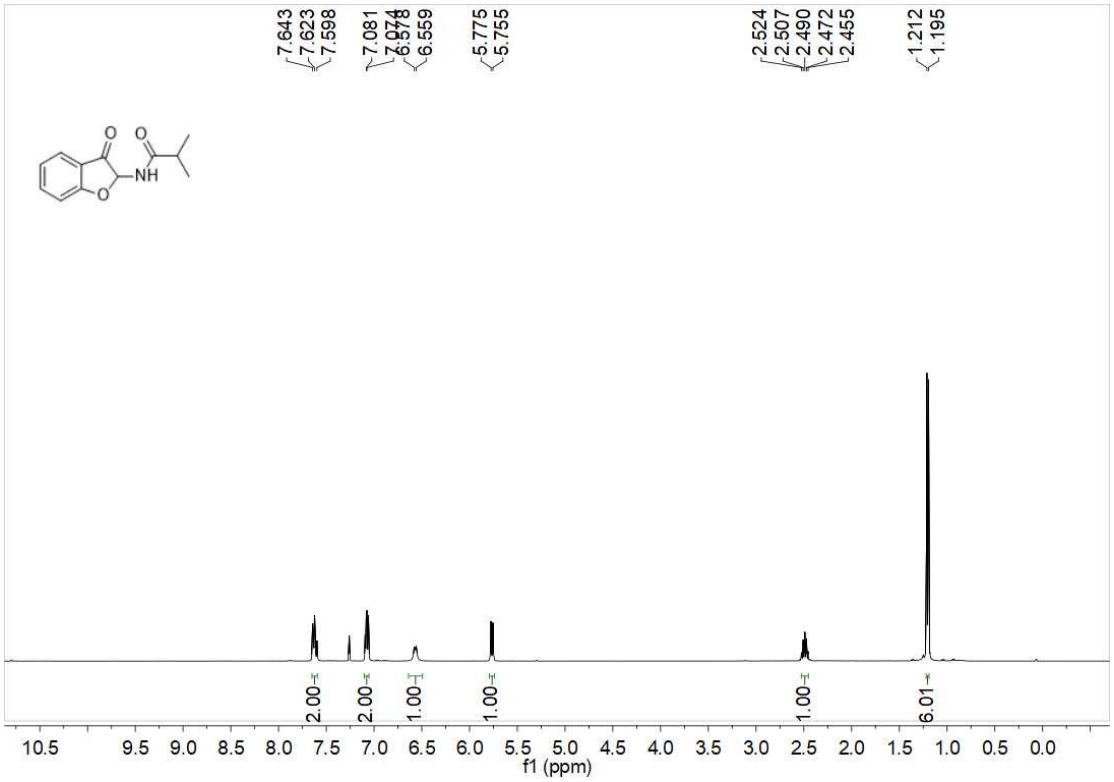
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5b



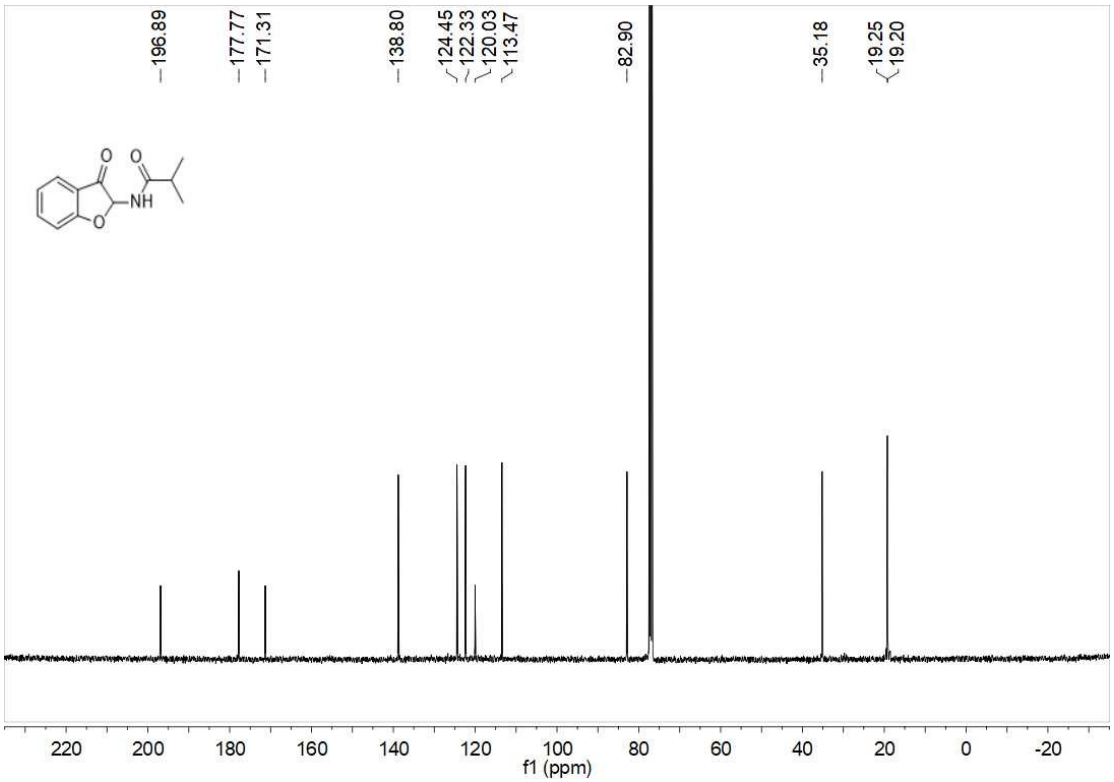
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5b



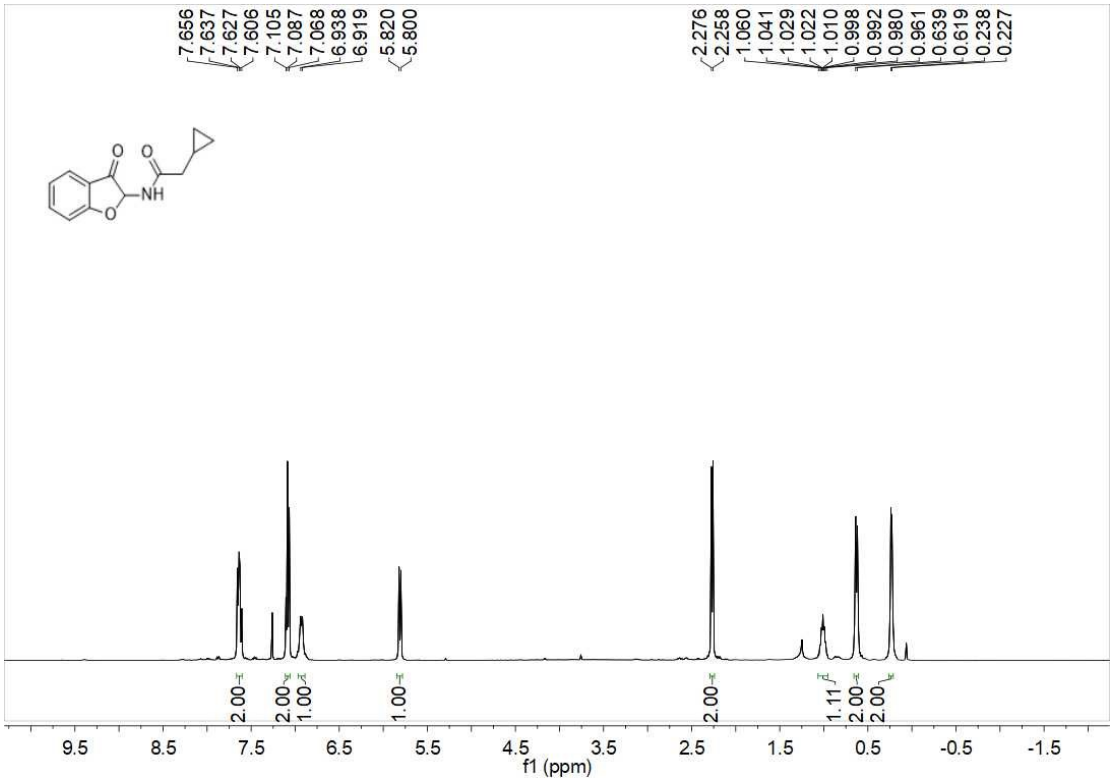
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5c



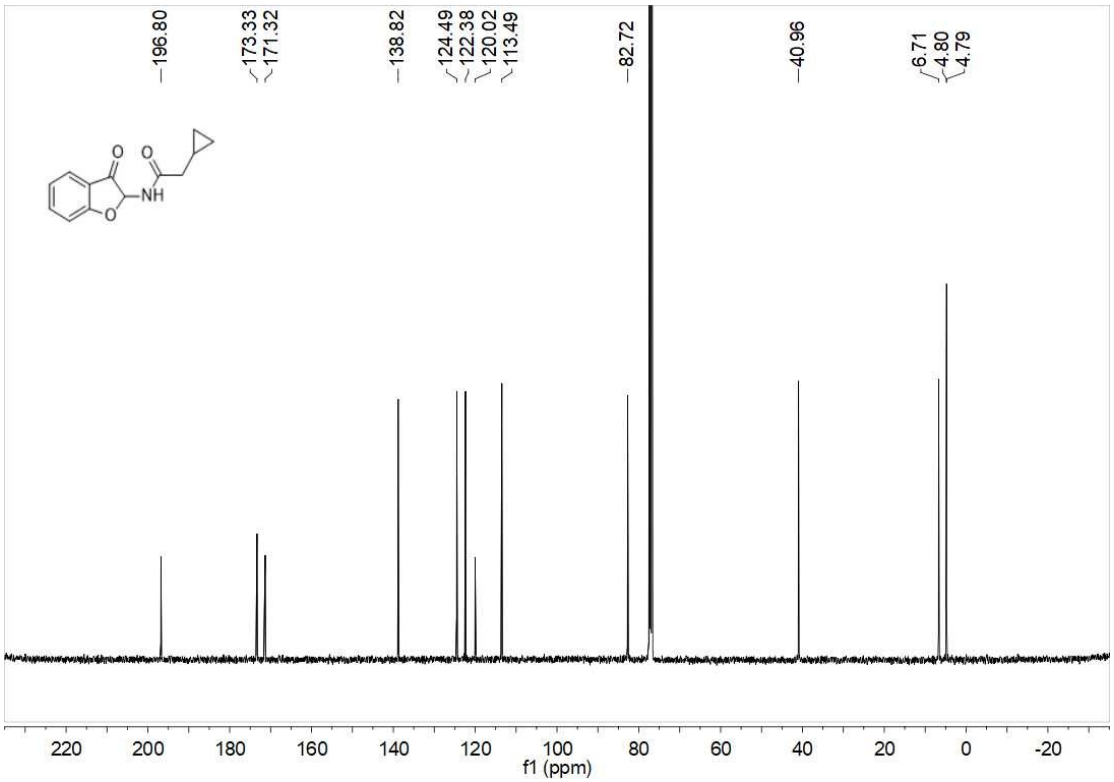
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5c



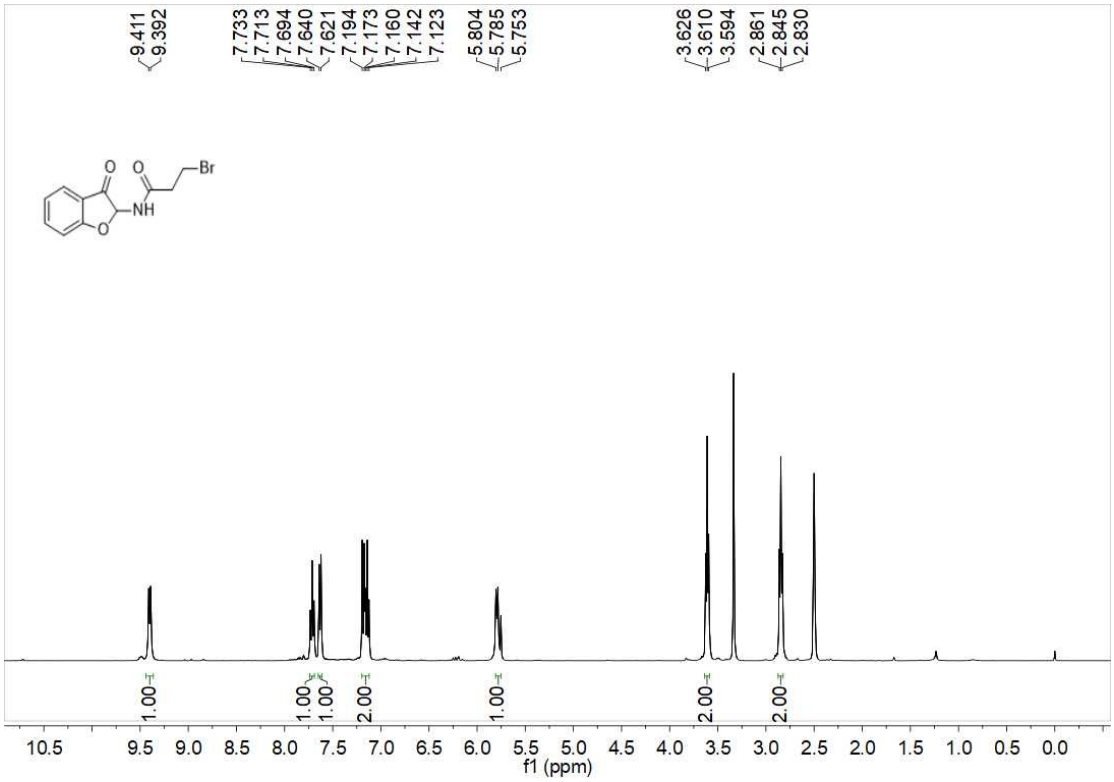
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5d



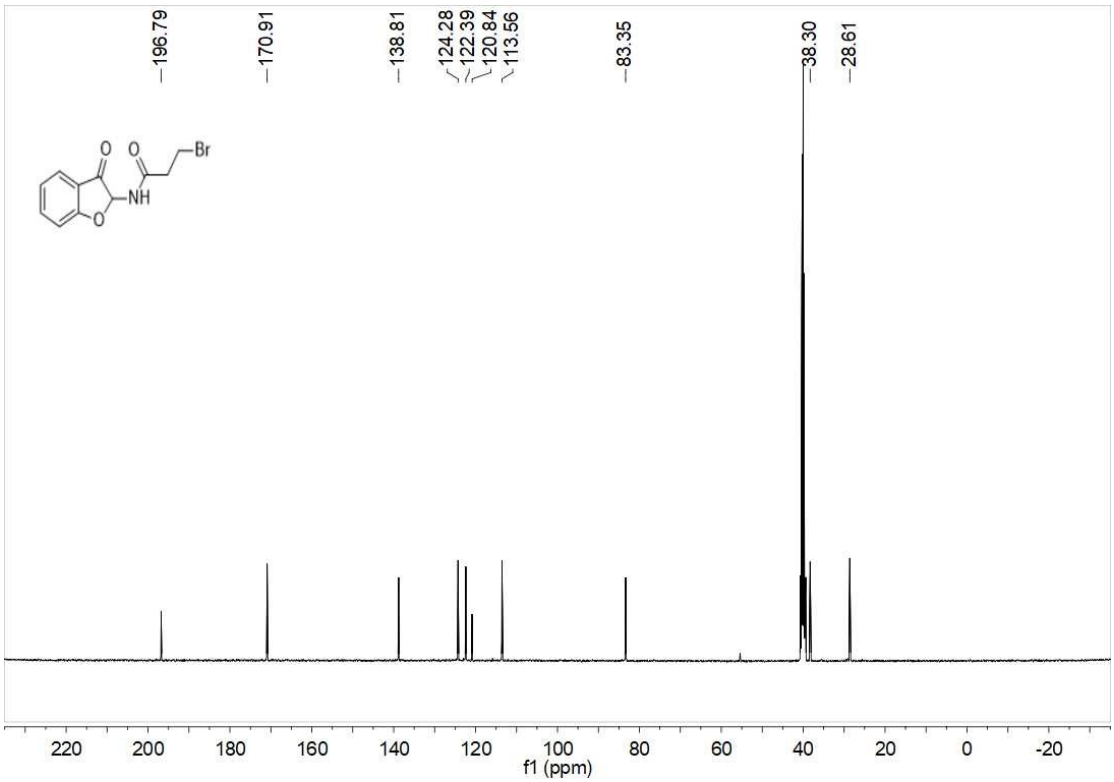
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5d



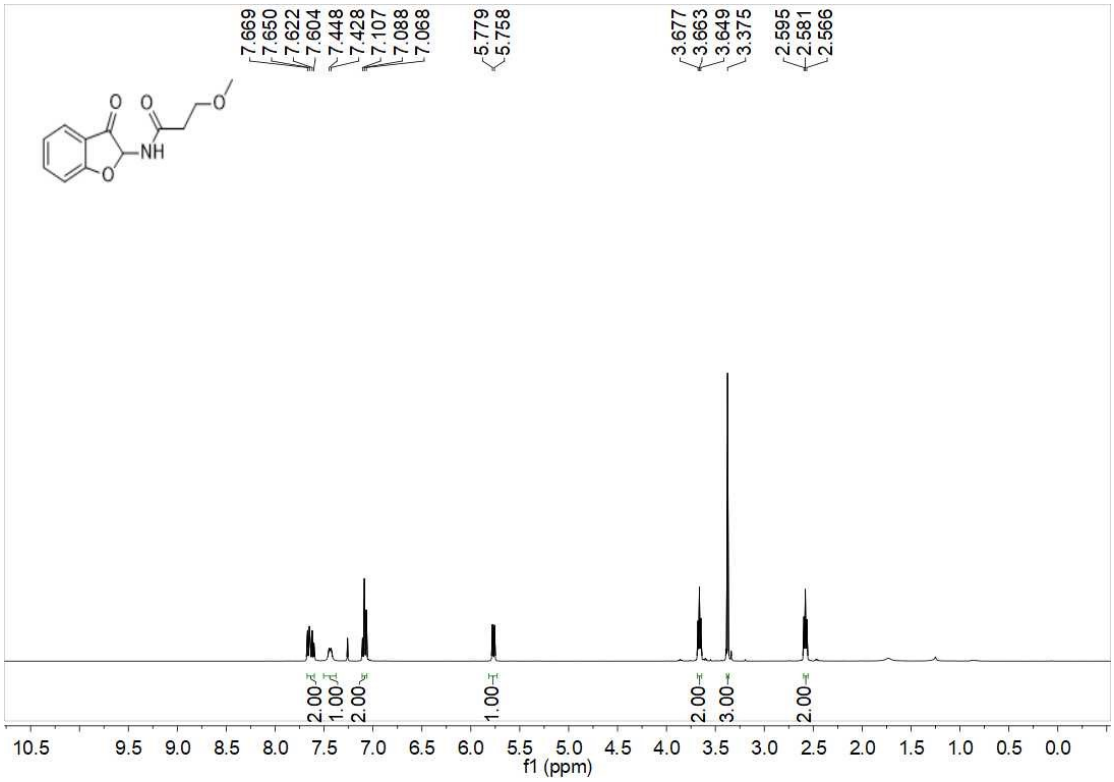
^{1}H NMR (400 MHz, DMSO) of compound 5e



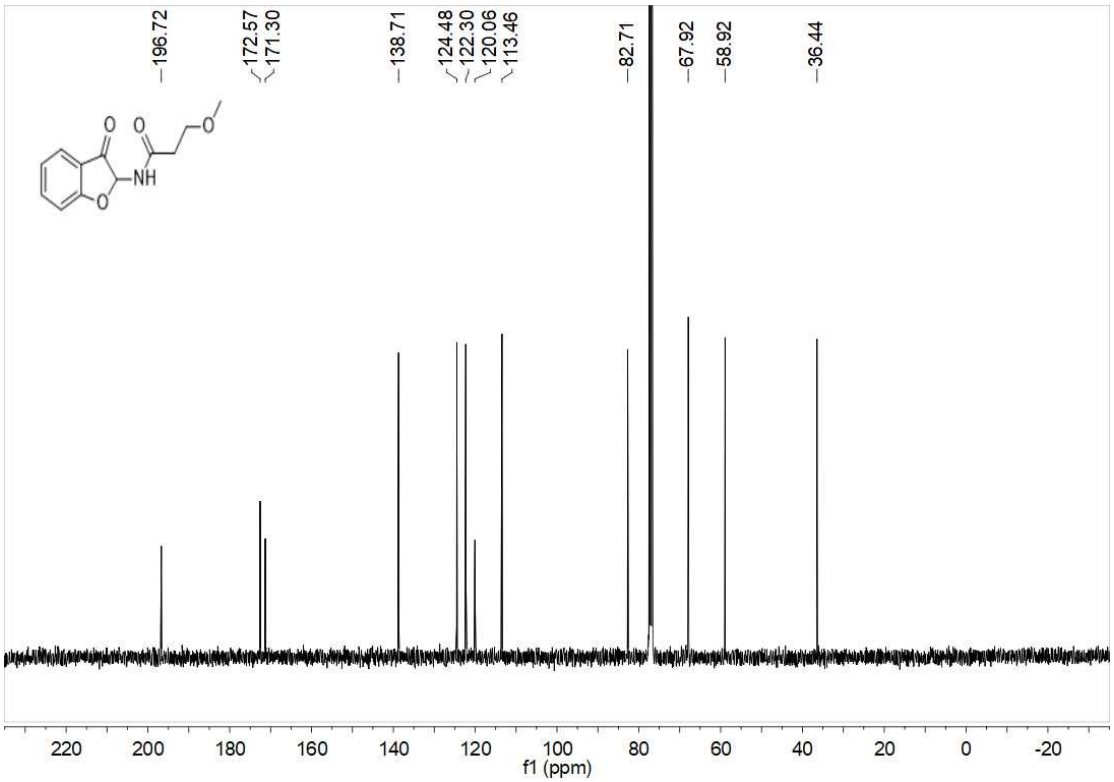
^{13}C {^{1}H} NMR (101 MHz, DMSO) of compound 5e



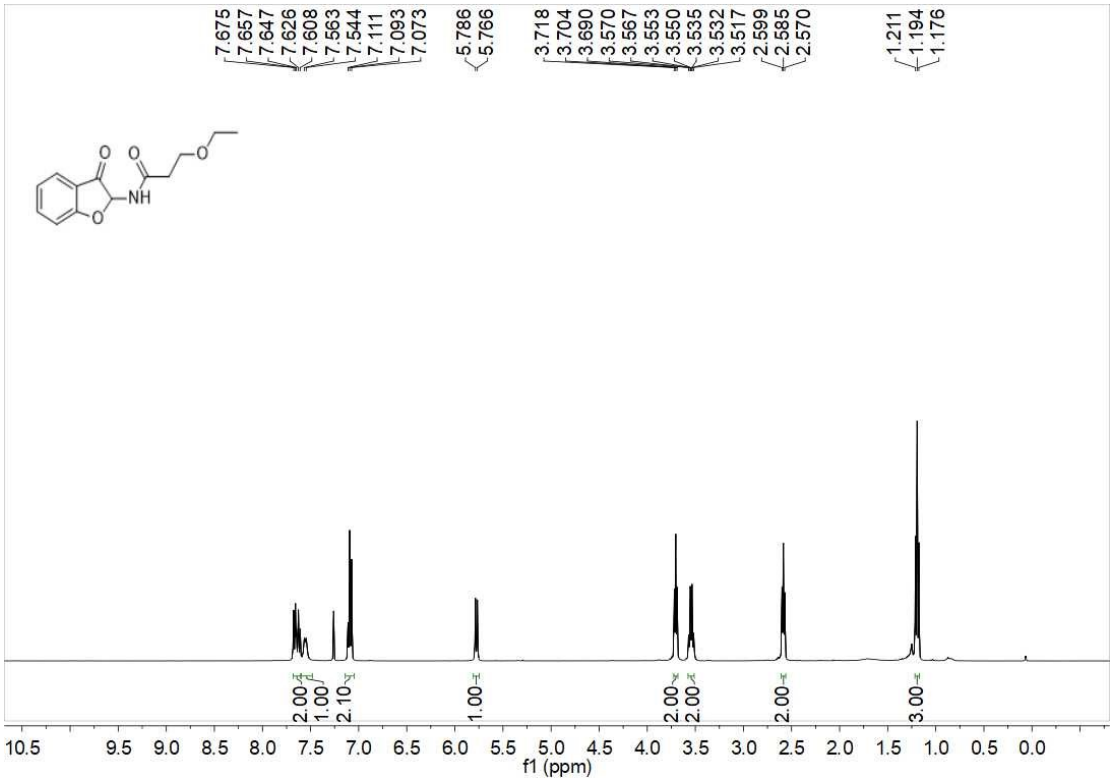
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5f



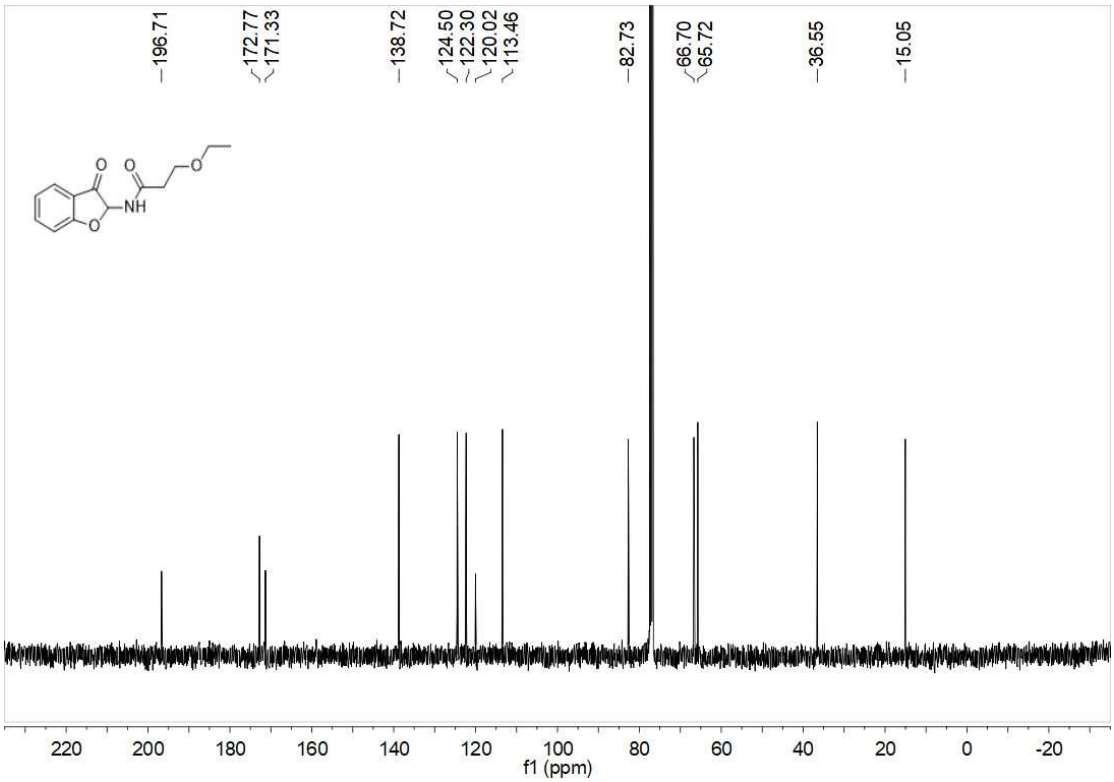
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5f



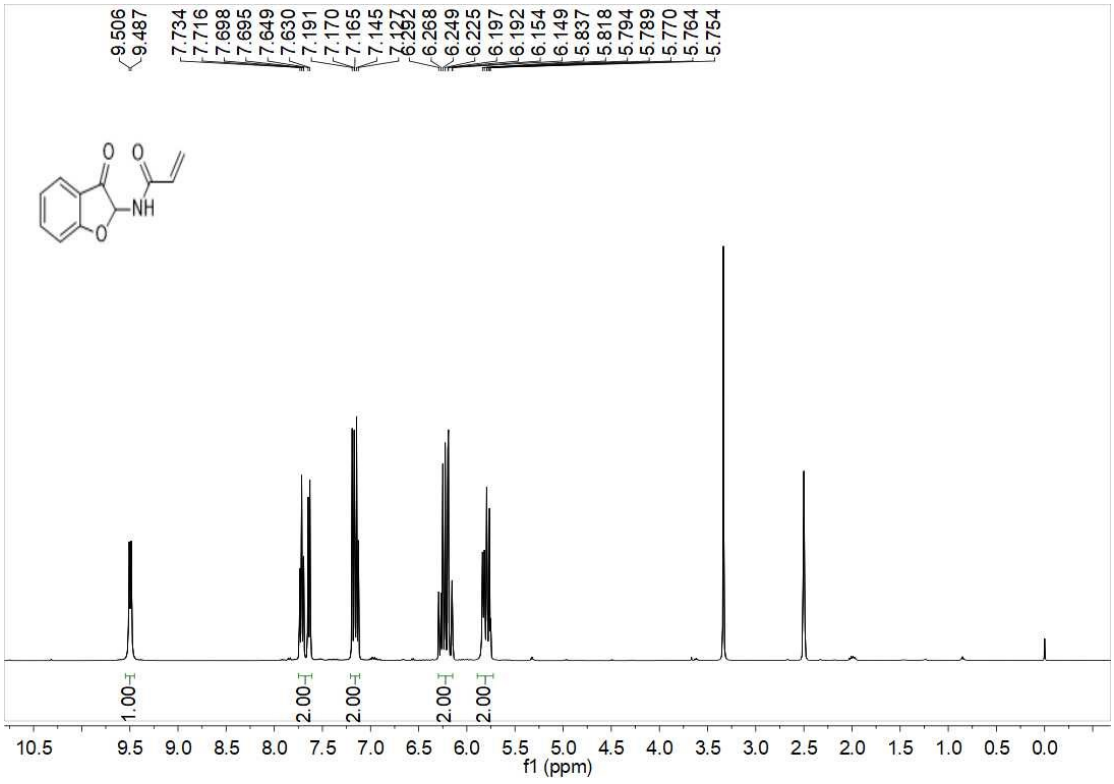
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5g



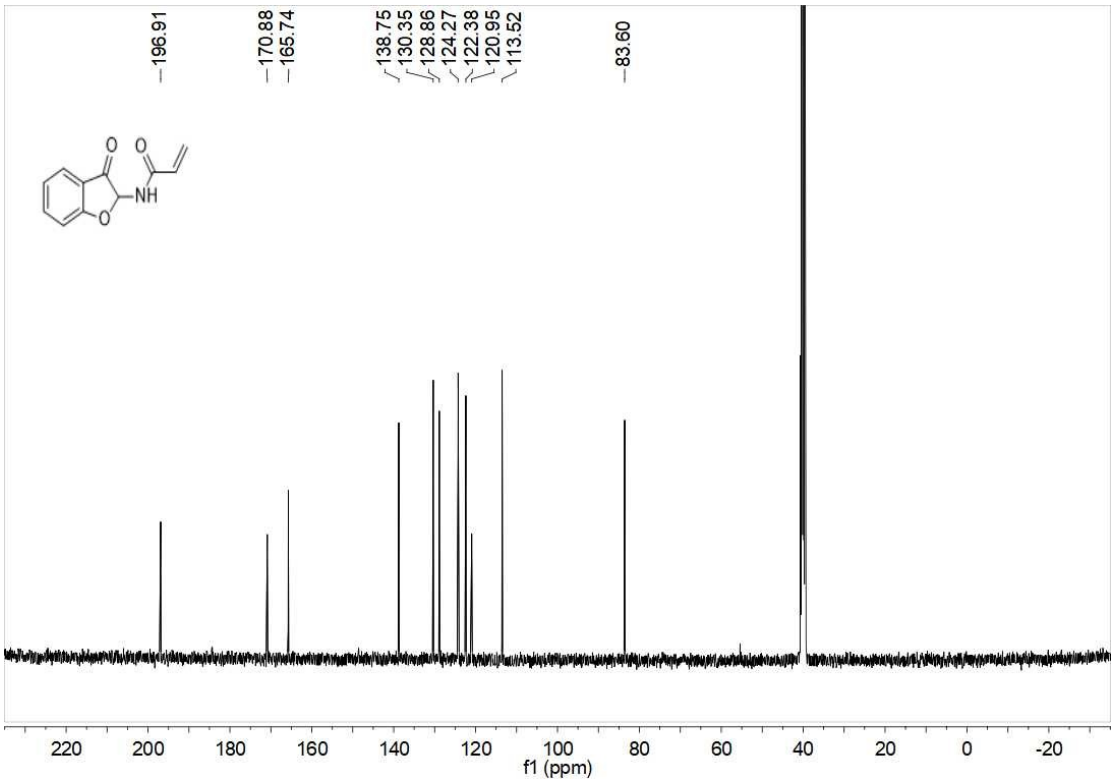
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5g



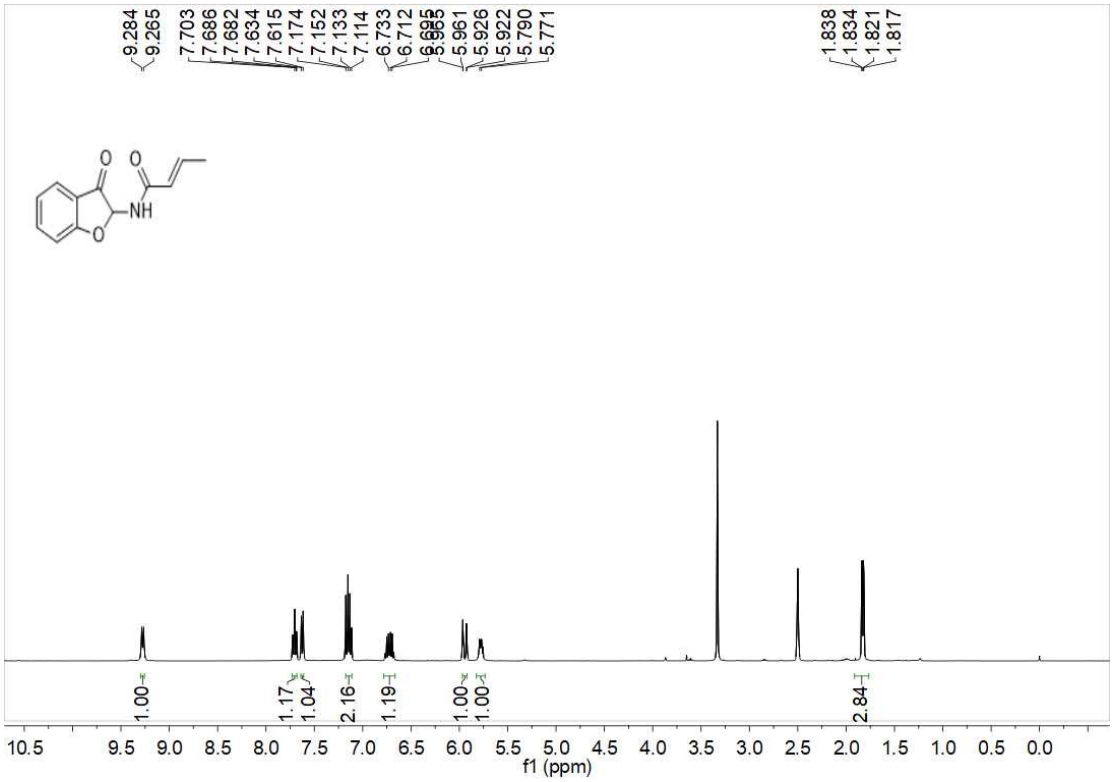
^{1}H NMR (400 MHz, DMSO) of compound 5h



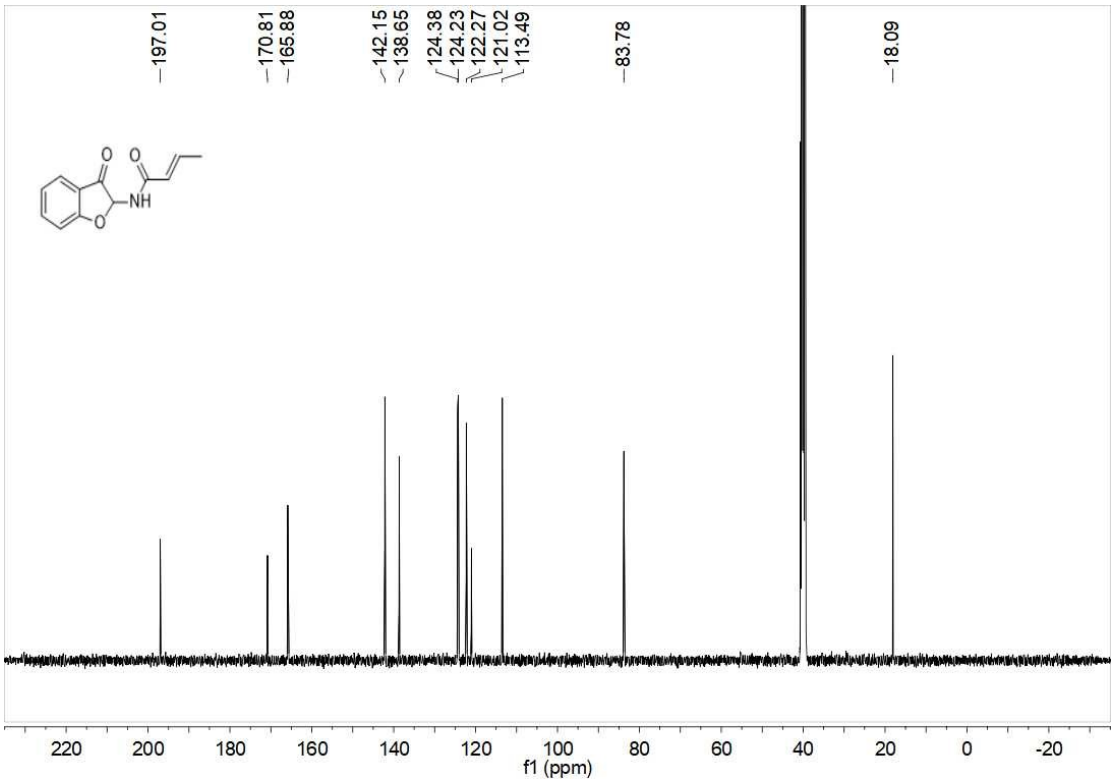
^{13}C {^{1}H} NMR (101 MHz, DMSO) of compound 5h



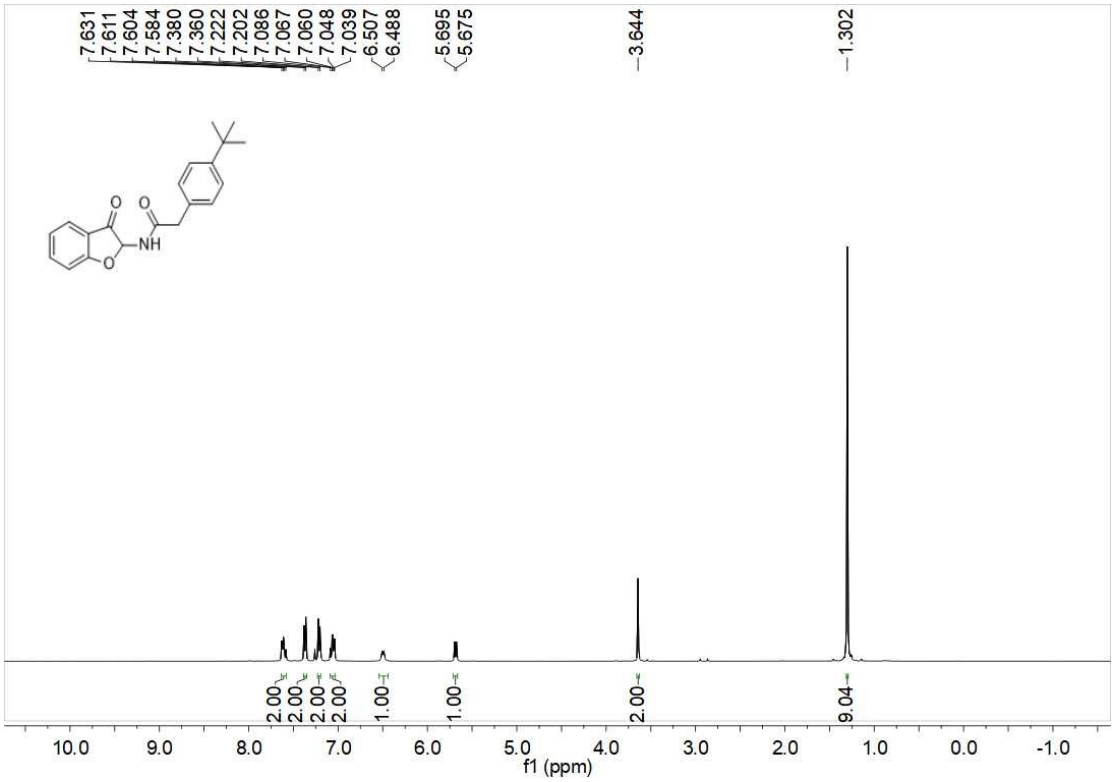
^{1}H NMR (400 MHz, DMSO) of compound 5i



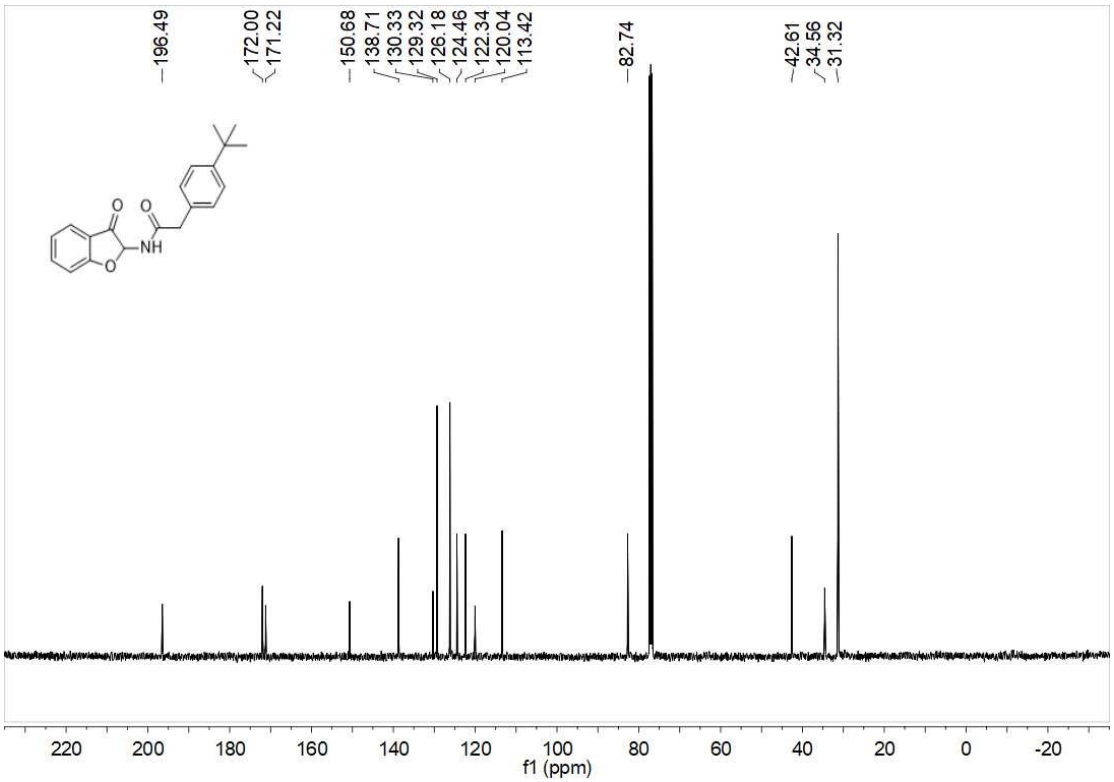
^{13}C {^{1}H} NMR (101 MHz, DMSO) of compound 5i



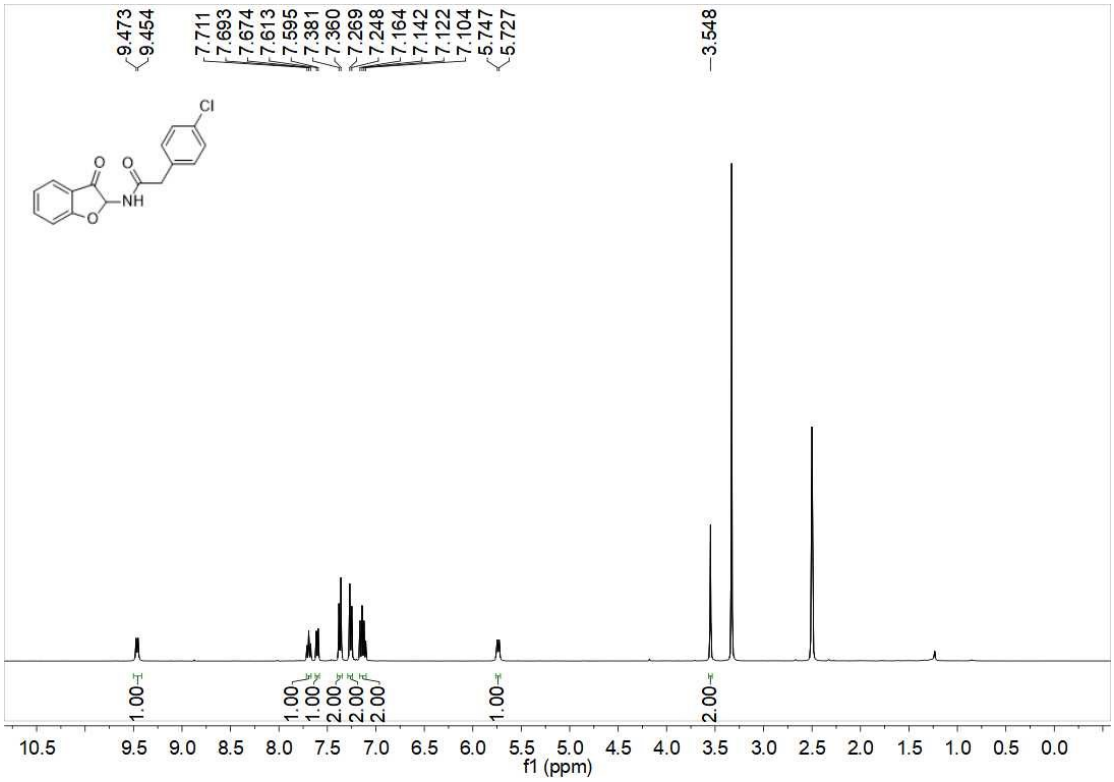
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5j



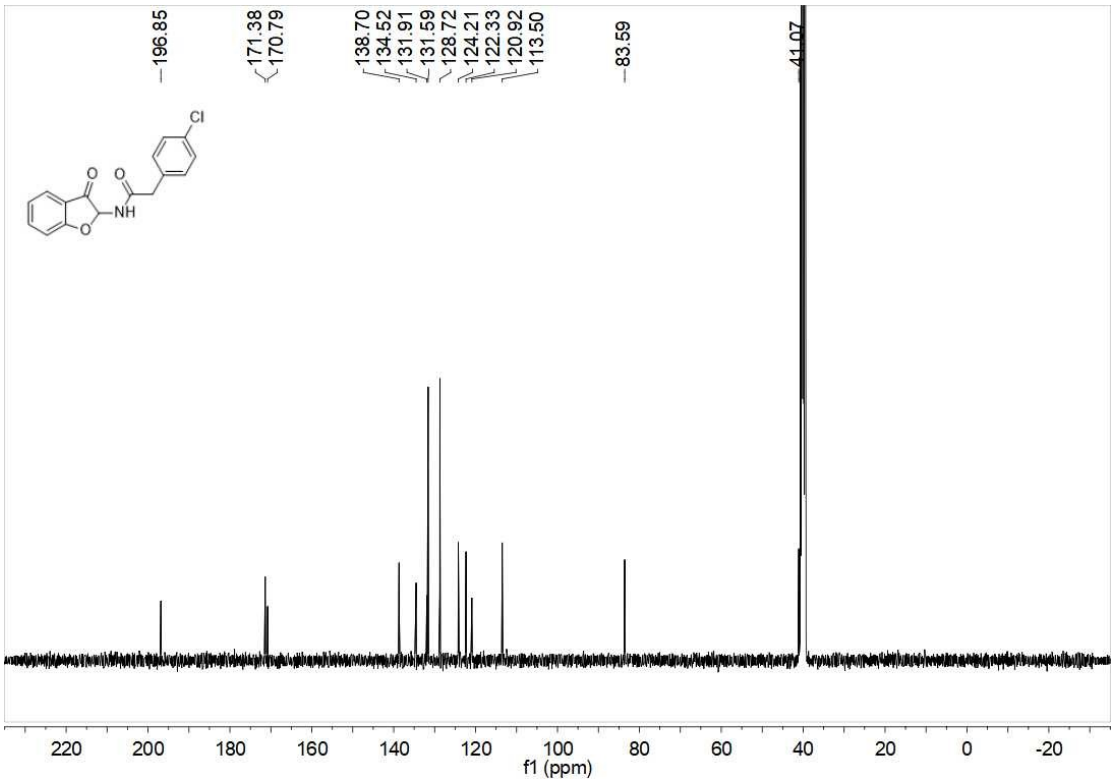
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5j



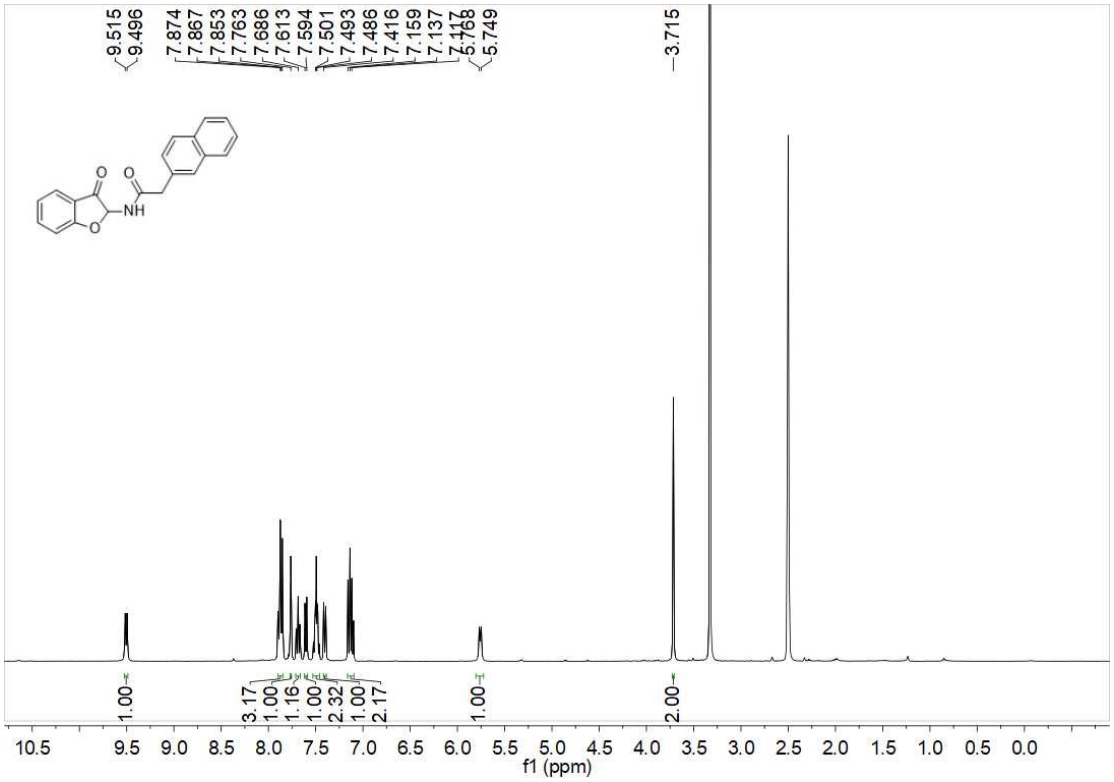
^{1}H NMR (400 MHz, DMSO) of compound 5k



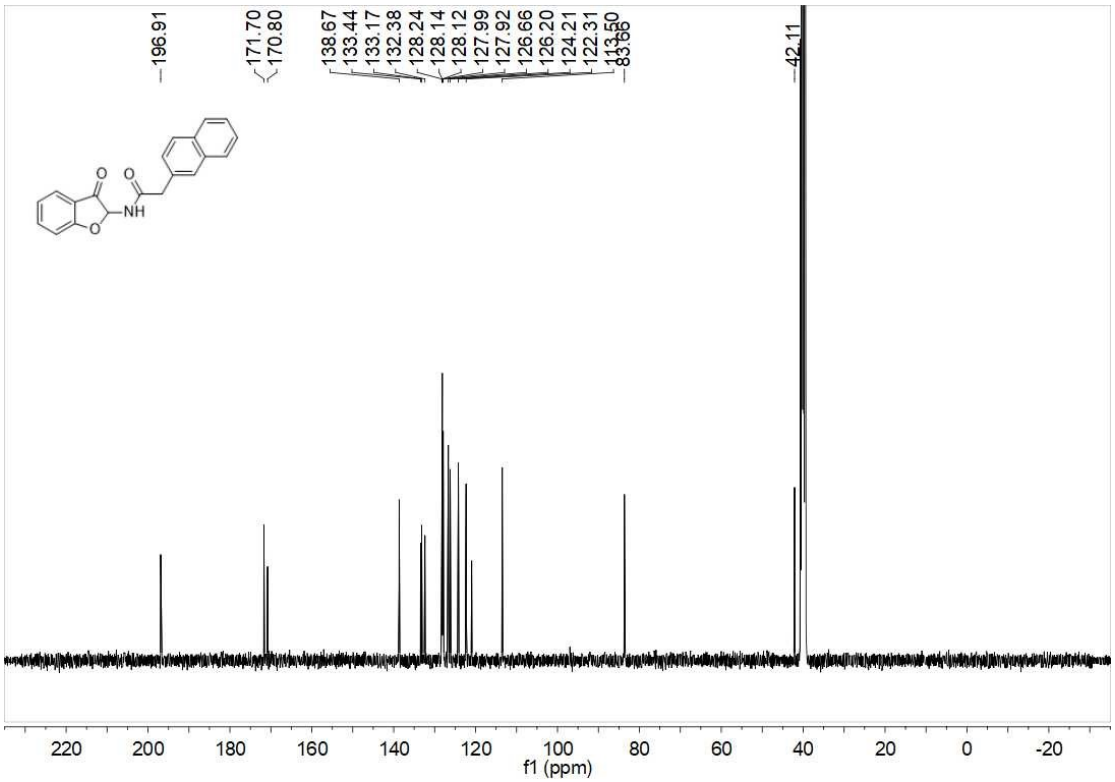
^{13}C {^{1}H} NMR (101 MHz, DMSO) of compound 5k



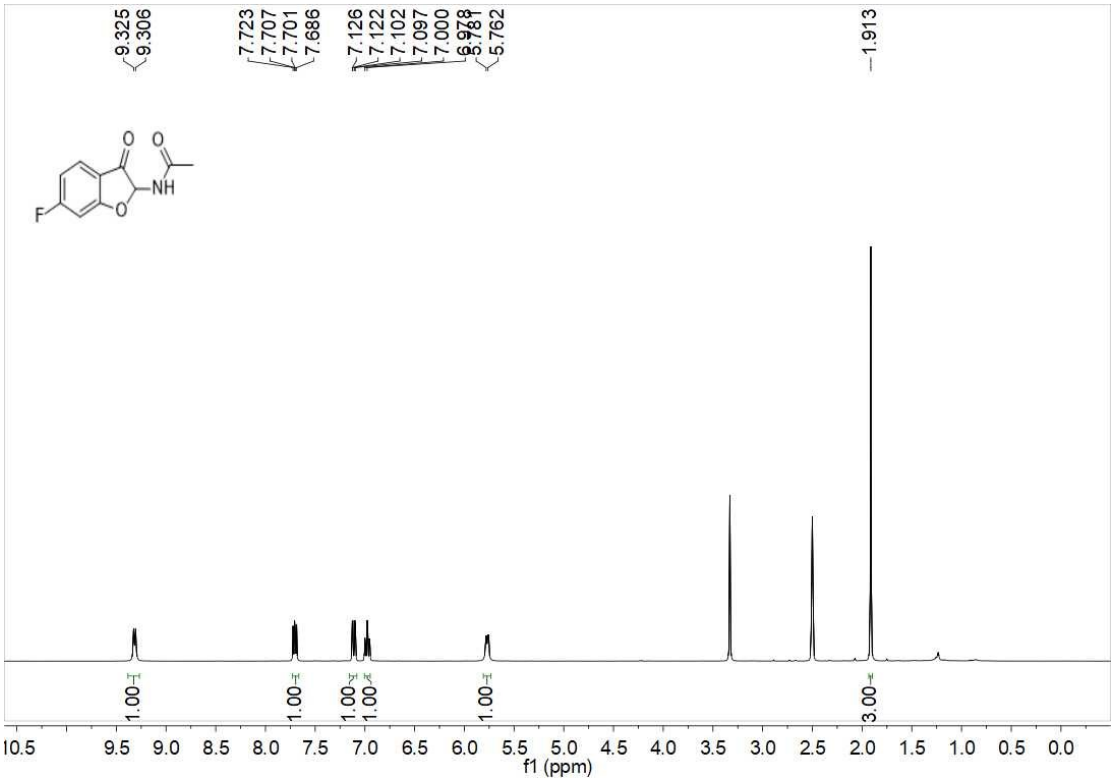
^{1}H NMR (400 MHz, DMSO) of compound 5l



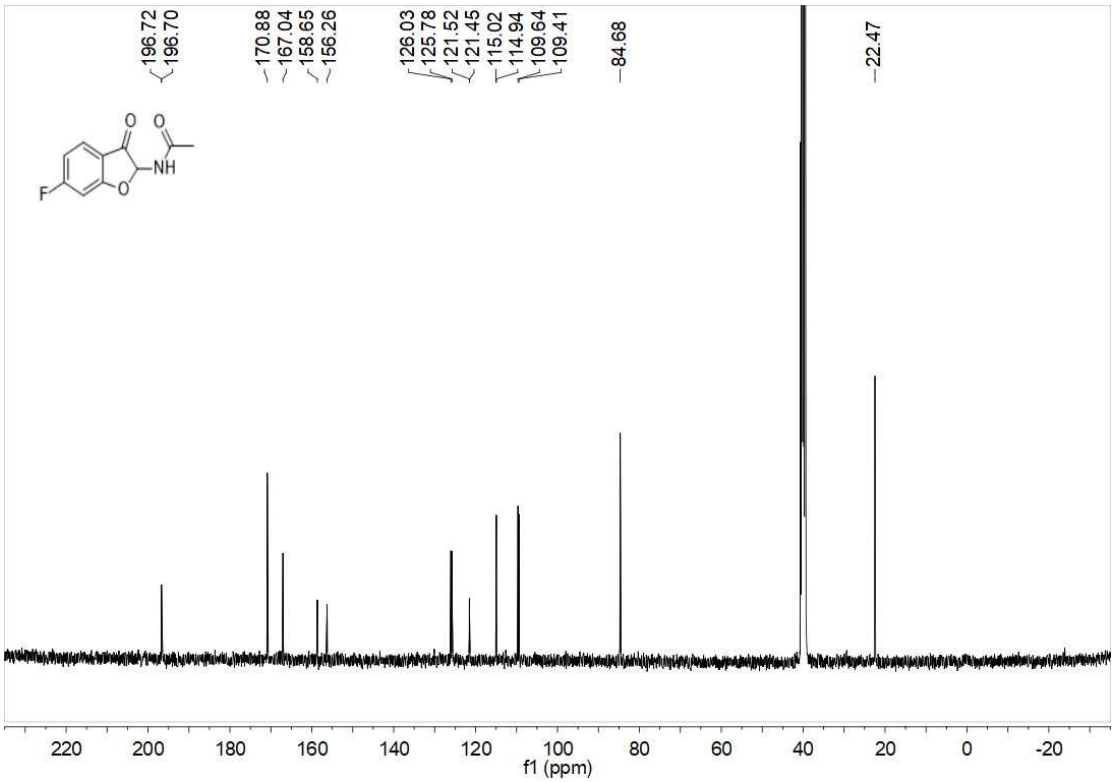
^{13}C {^{1}H} NMR (101 MHz, DMSO) of compound 5l



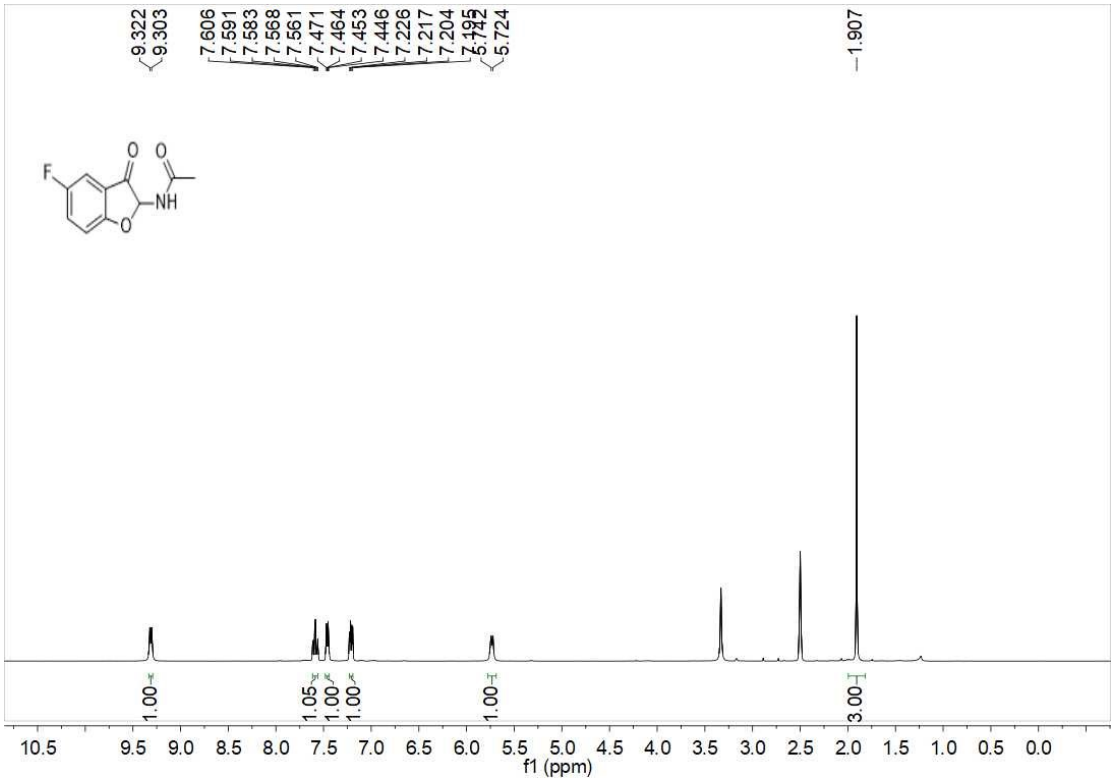
^{1}H NMR (400 MHz, DMSO) of compound 5m



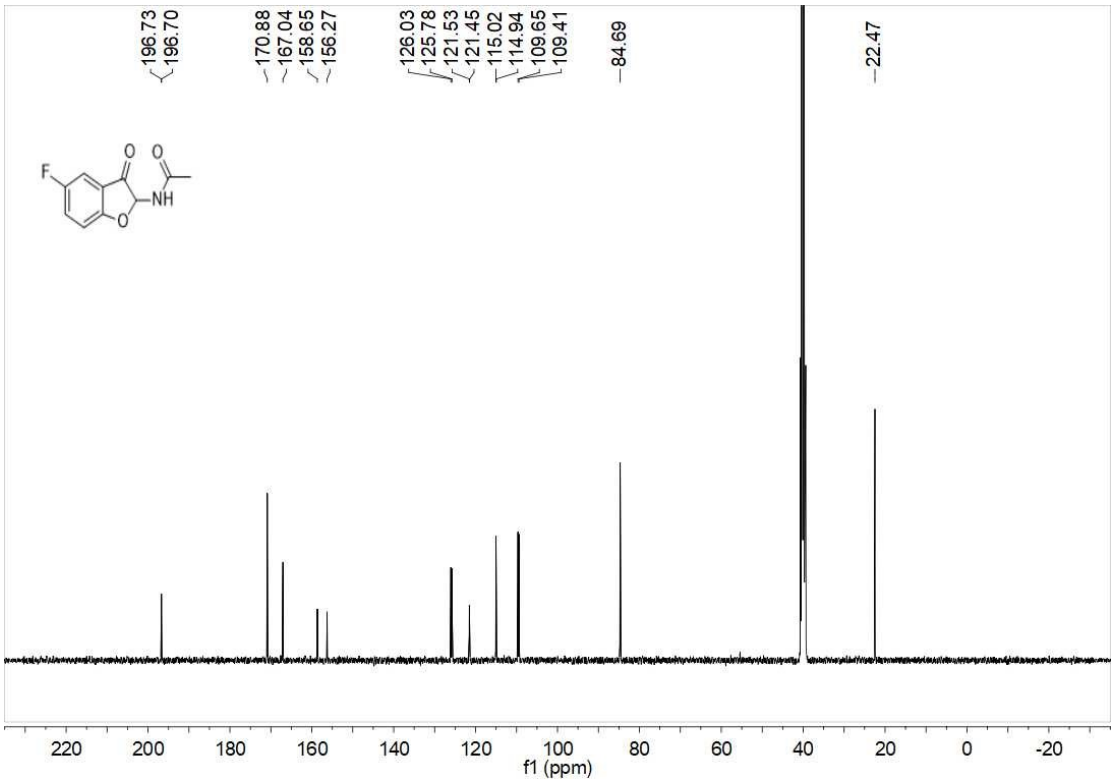
^{13}C {^{1}H} NMR (101 MHz, DMSO) of compound 5m



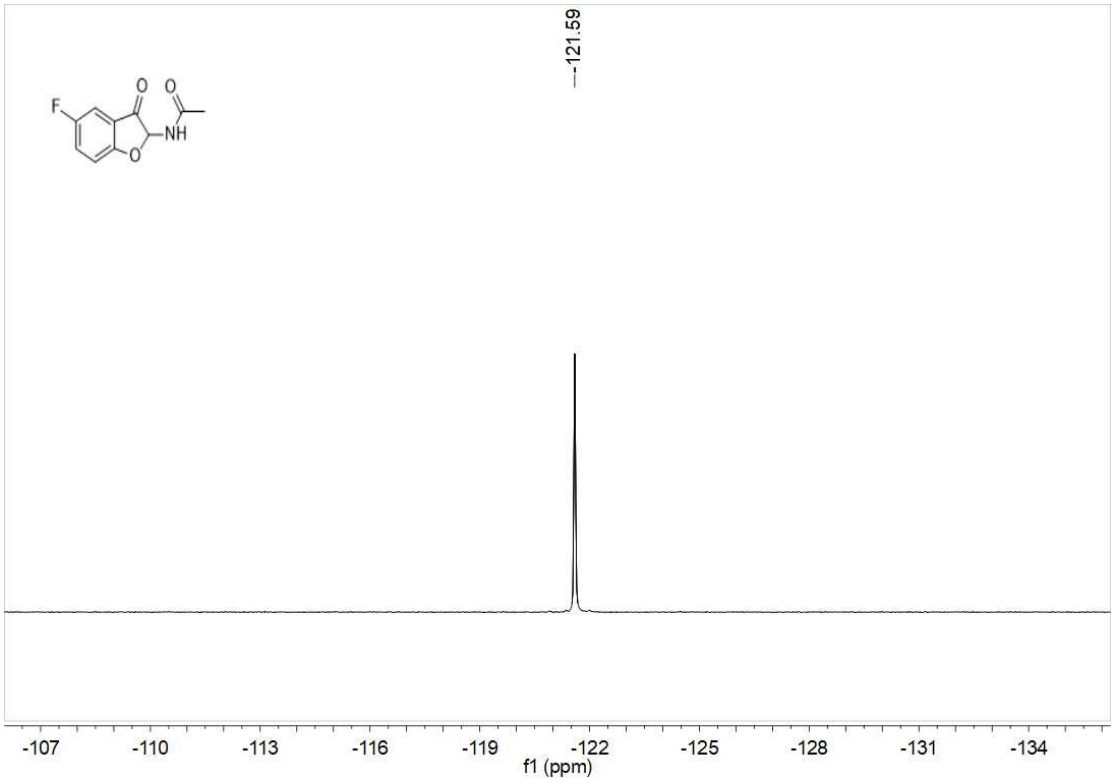
^{1}H NMR (400 MHz, DMSO) of compound 5n



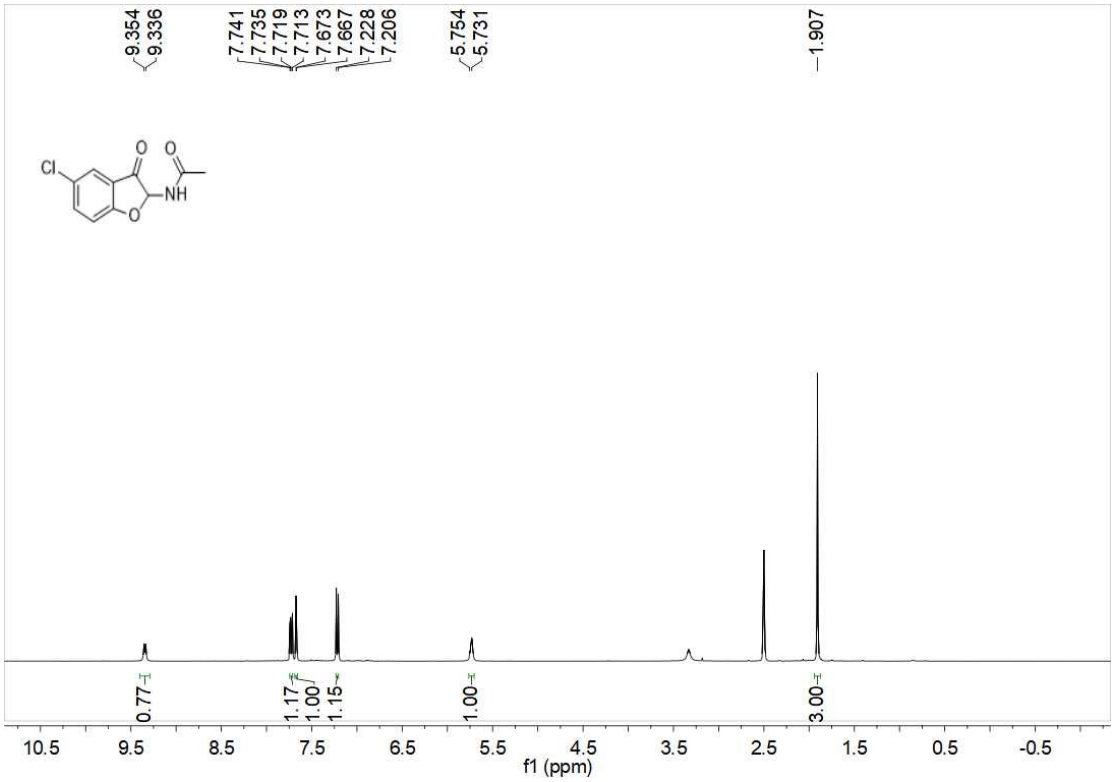
^{13}C {^{1}H} NMR (101 MHz, DMSO) of compound 5n



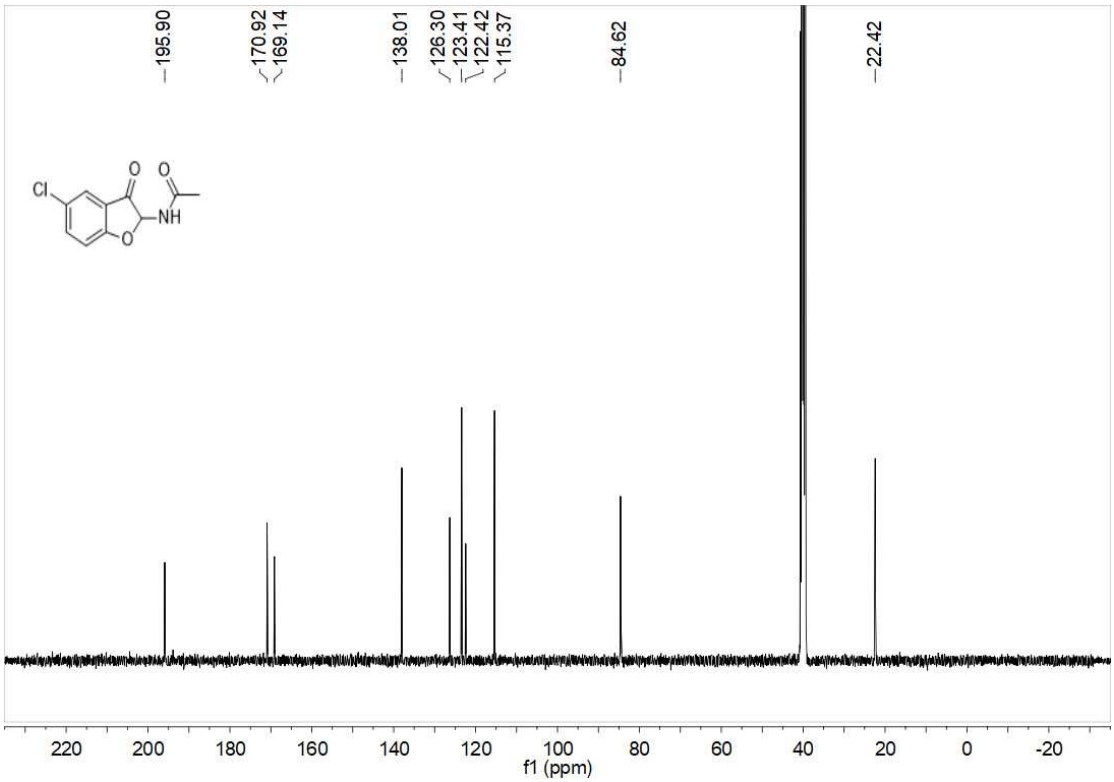
^{19}F NMR (376 MHz, DMSO) of compound 5n



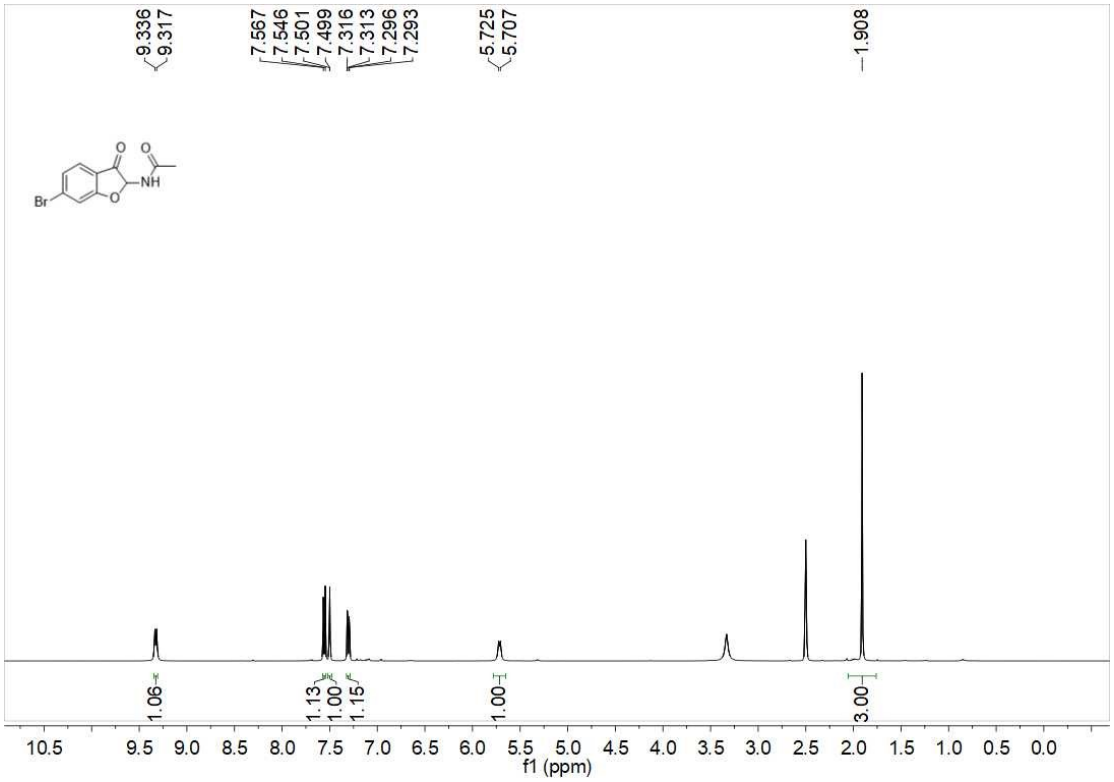
^{1}H NMR (400 MHz, DMSO) of compound 5o



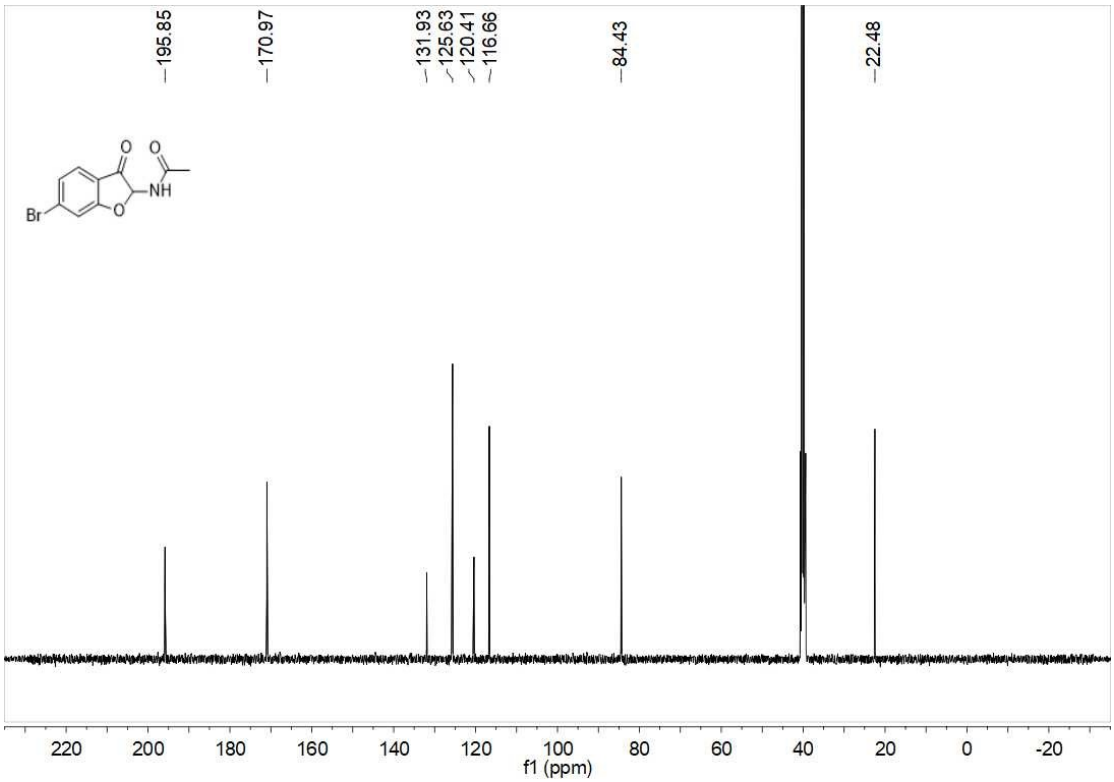
^{13}C {^{1}H} NMR (101 MHz, DMSO) of compound 5o



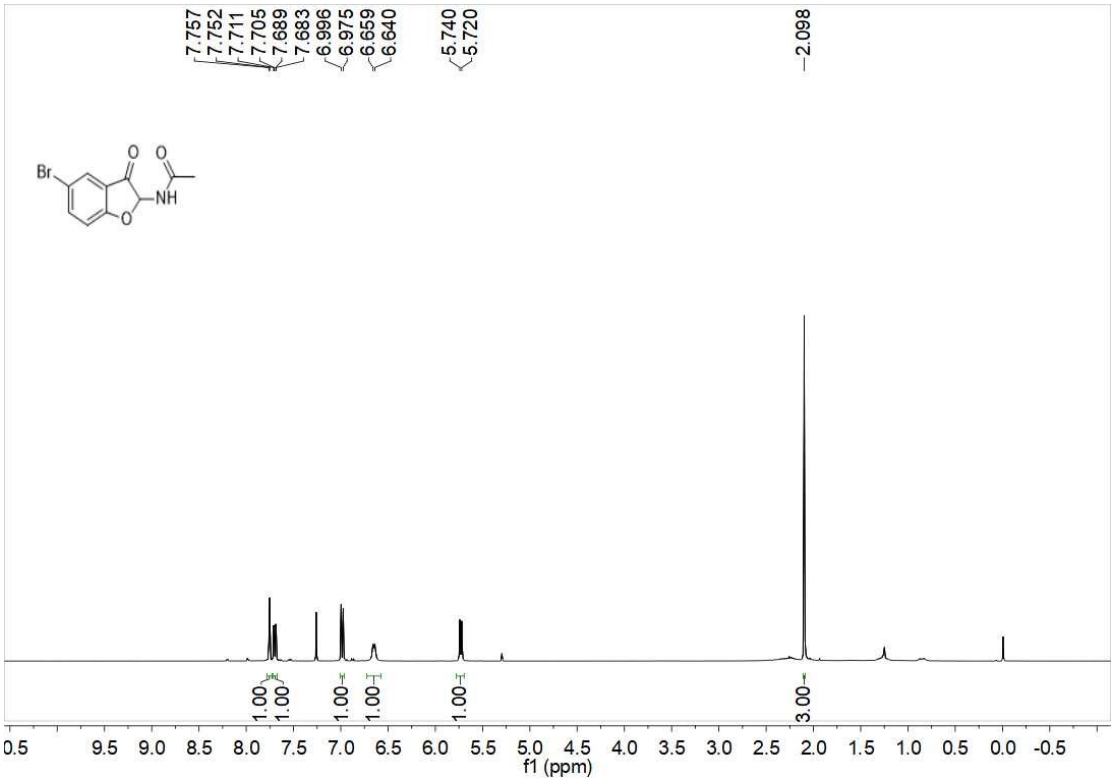
^{1}H NMR (400 MHz, DMSO) of compound 5p



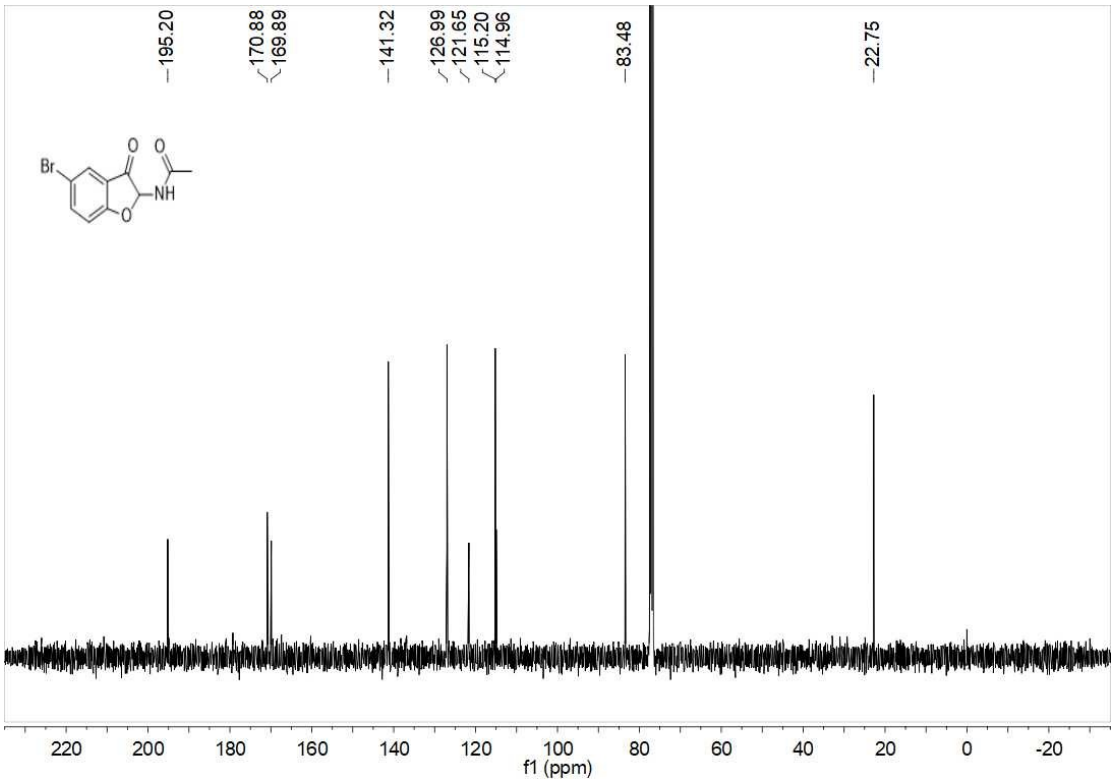
^{13}C {^{1}H} NMR (101 MHz, DMSO) of compound 5p



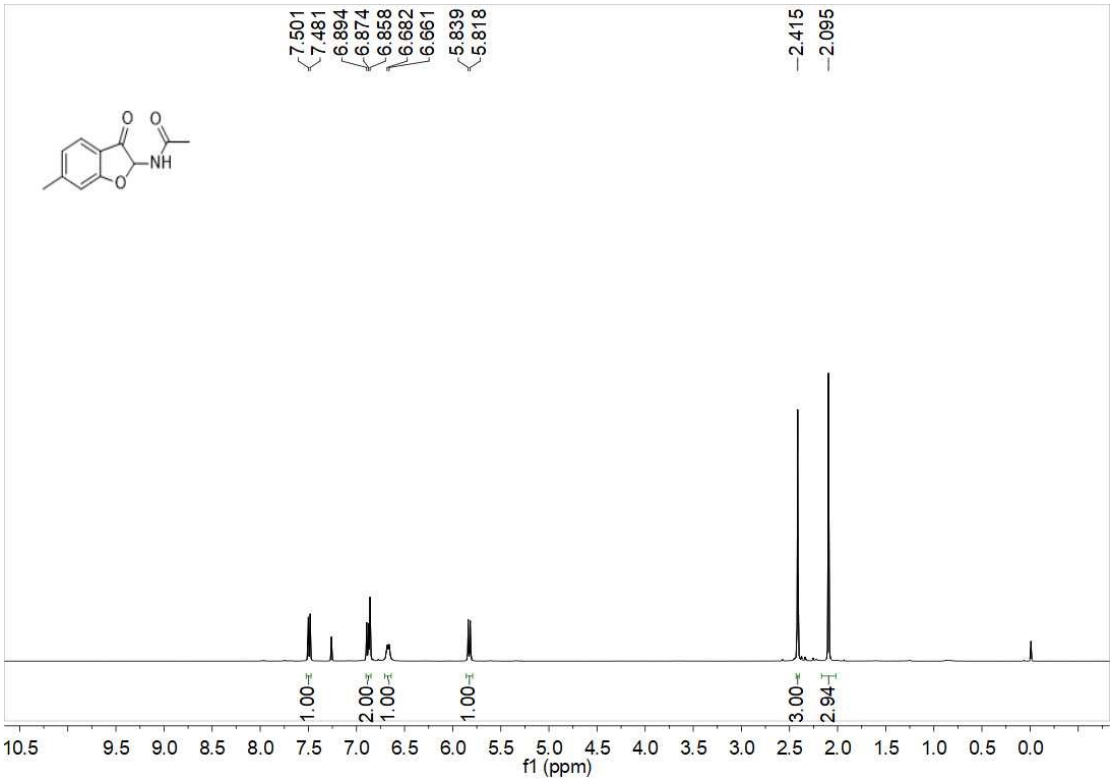
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5q



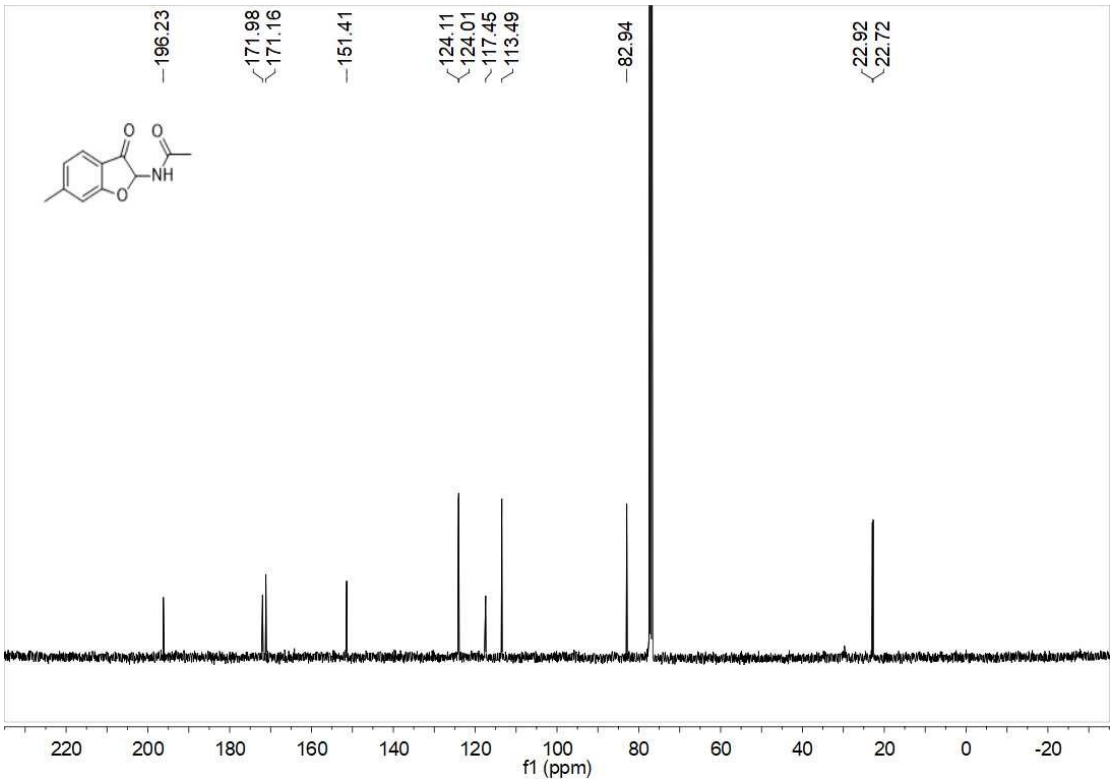
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5q



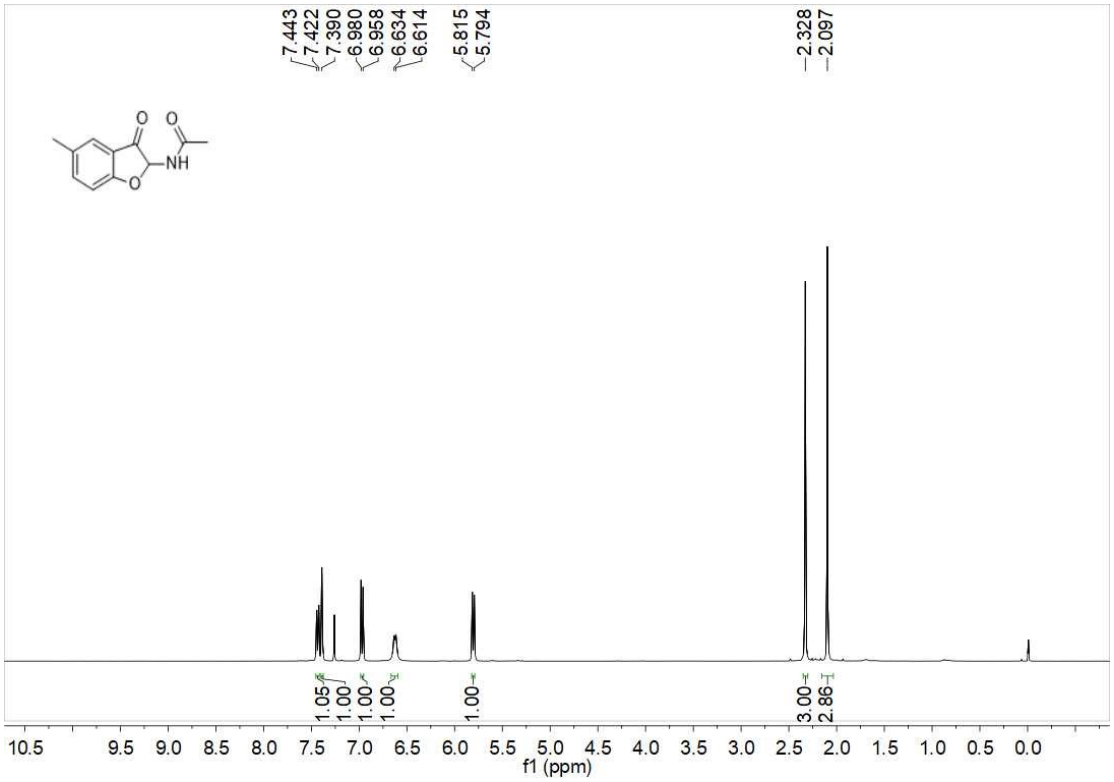
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5r



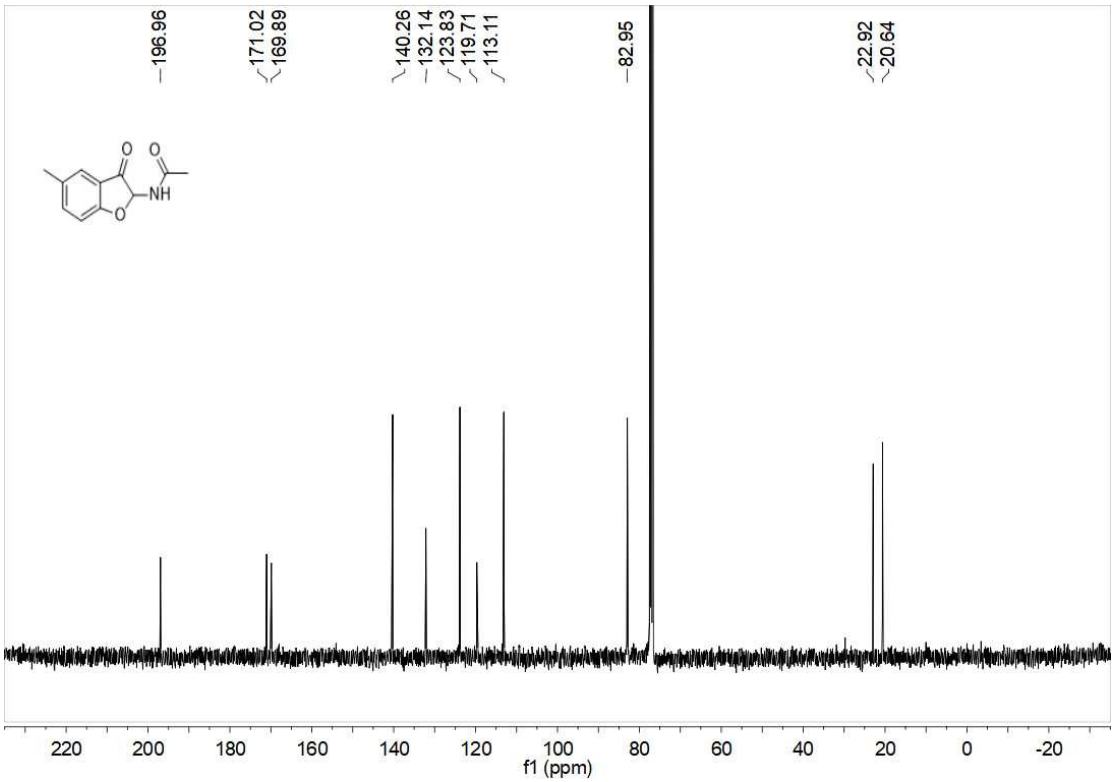
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5r



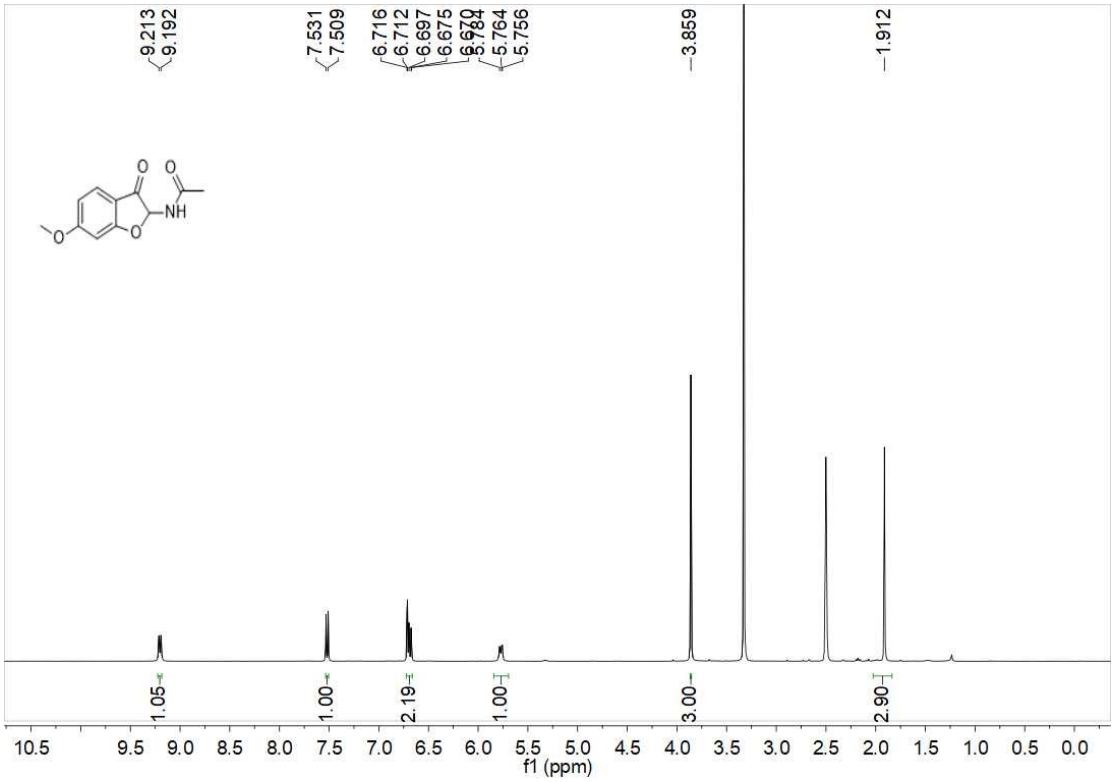
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5s



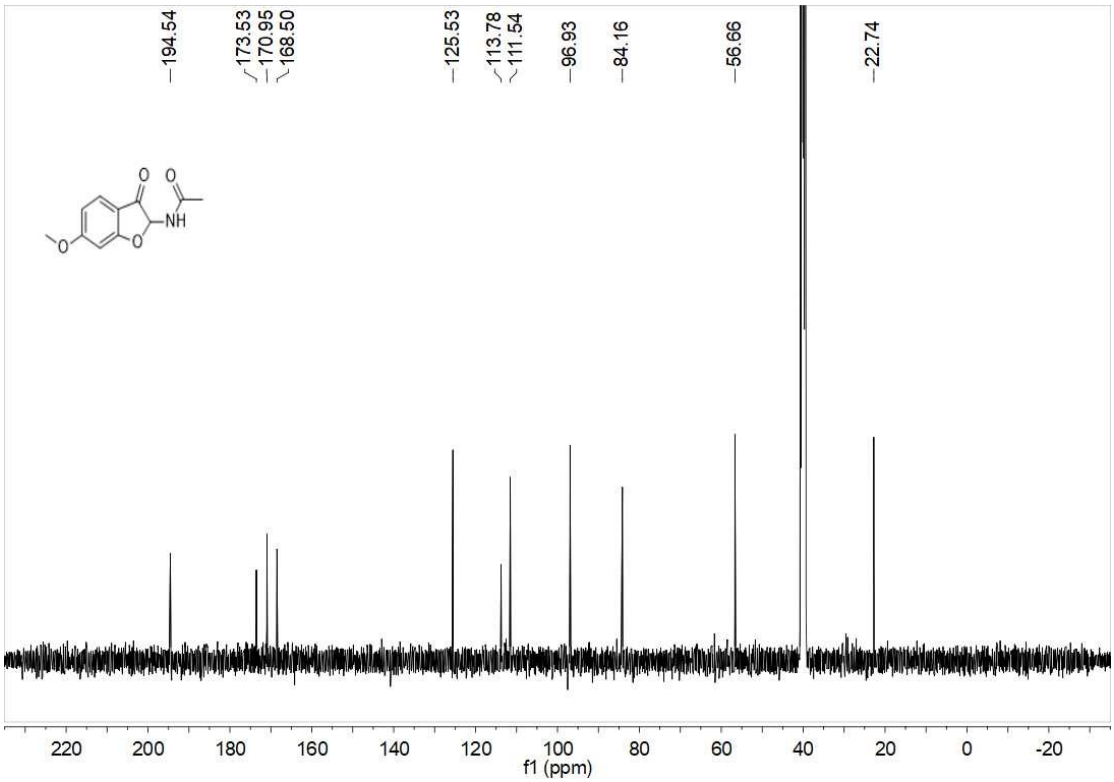
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5s



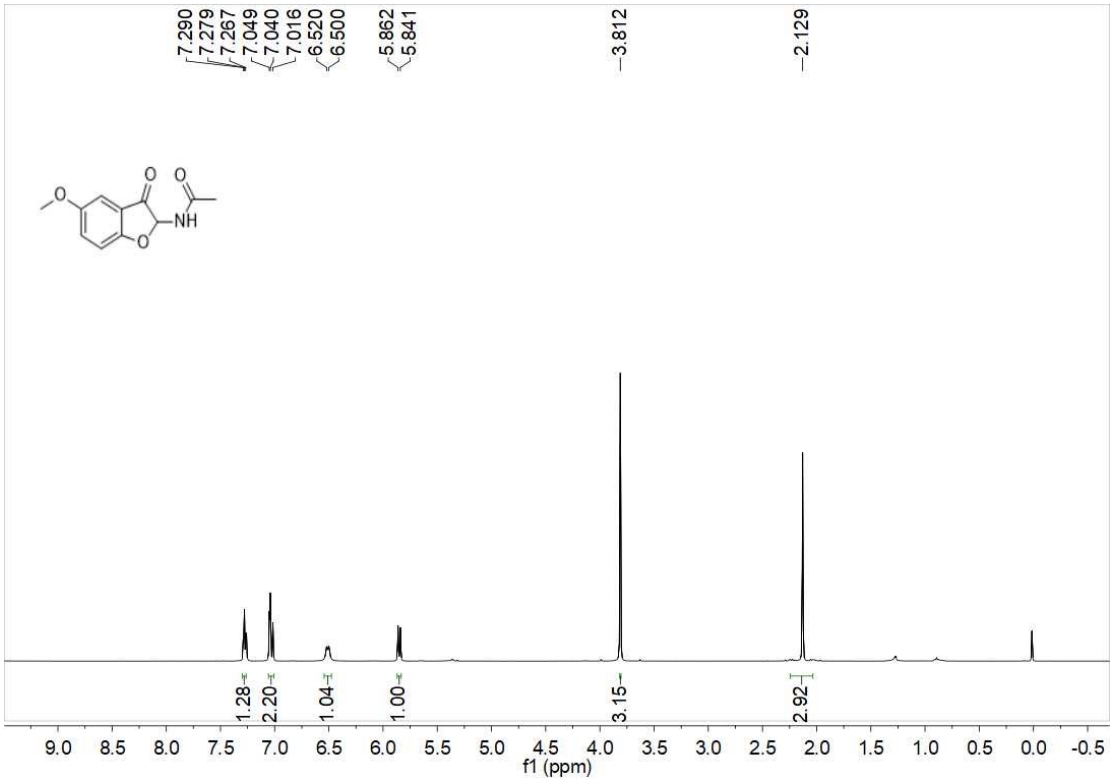
^{1}H NMR (400 MHz, DMSO) of compound 5t



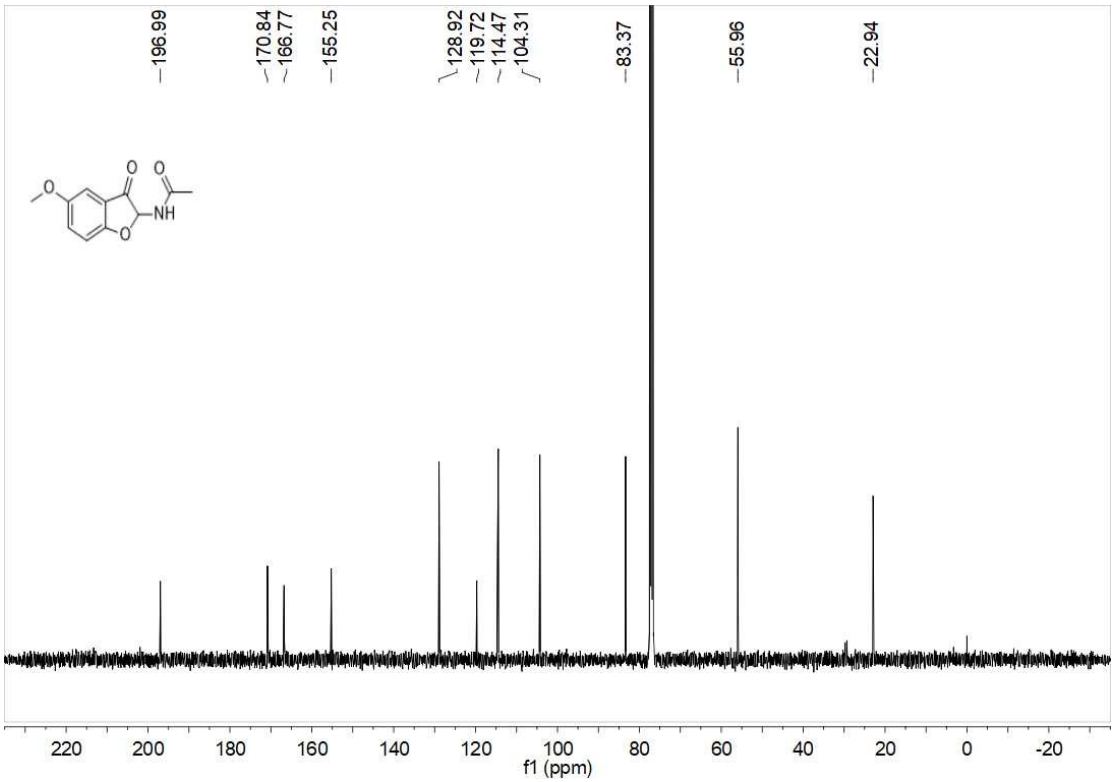
^{13}C {^{1}H} NMR (101 MHz, DMSO) of compound 5t



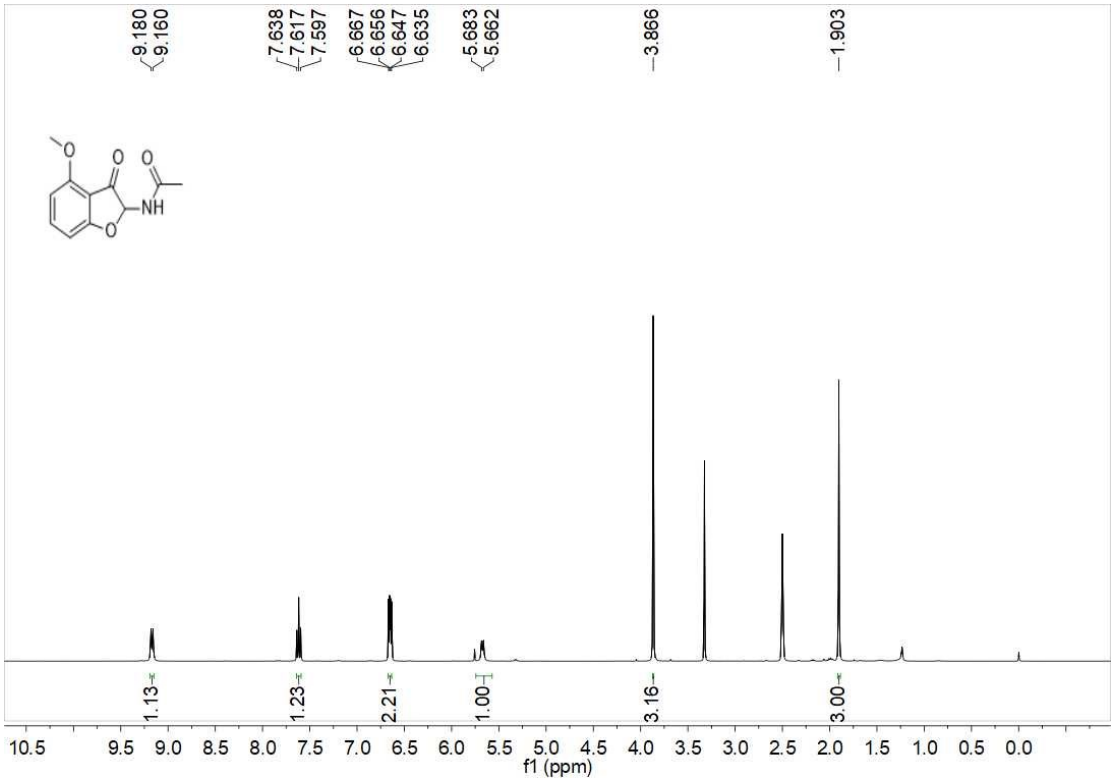
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5u



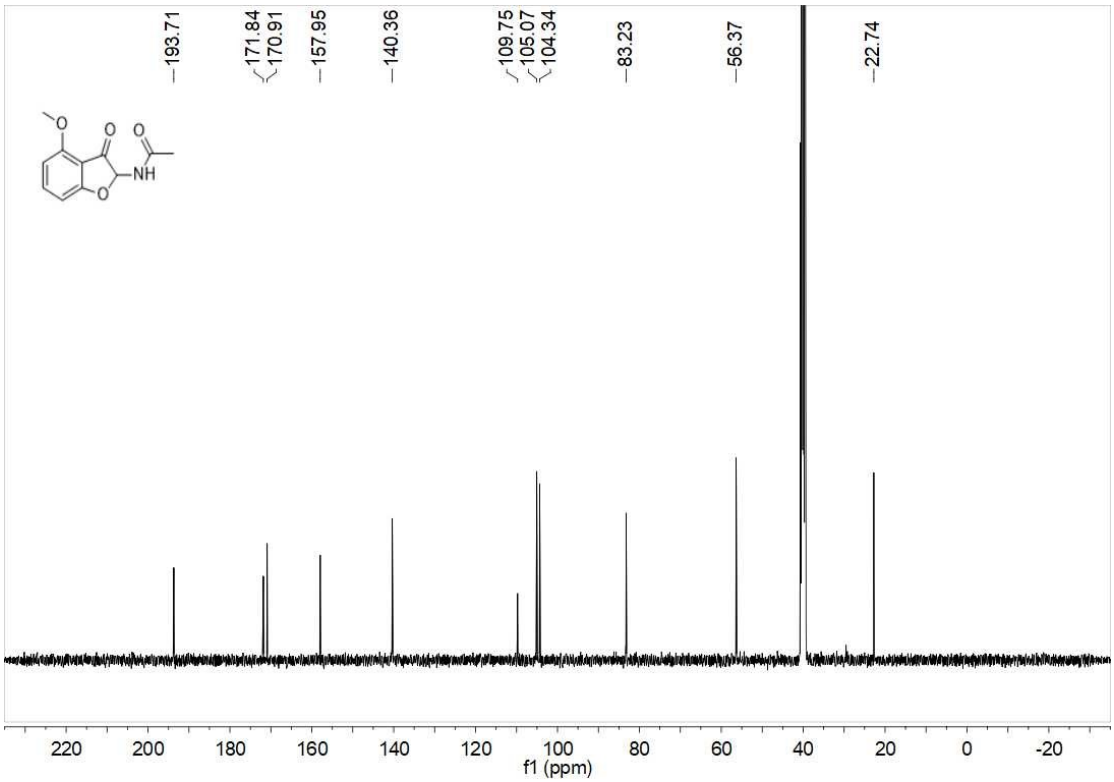
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5u



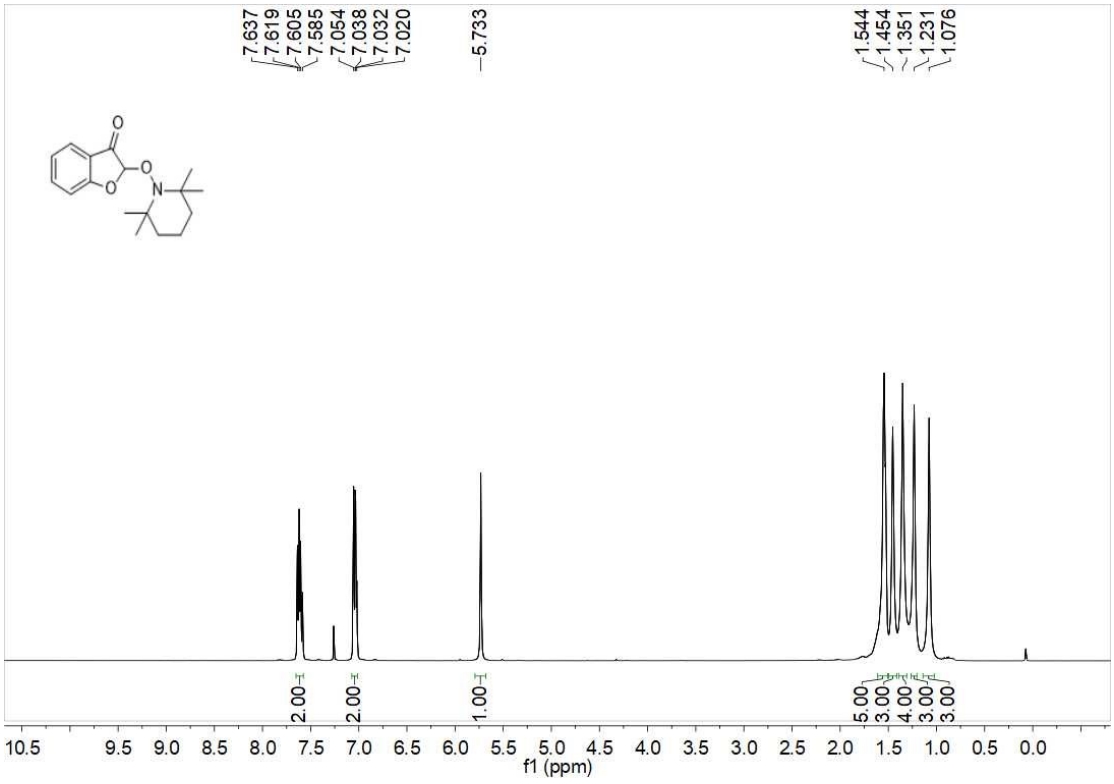
^{1}H NMR (400 MHz, DMSO) of compound 5v



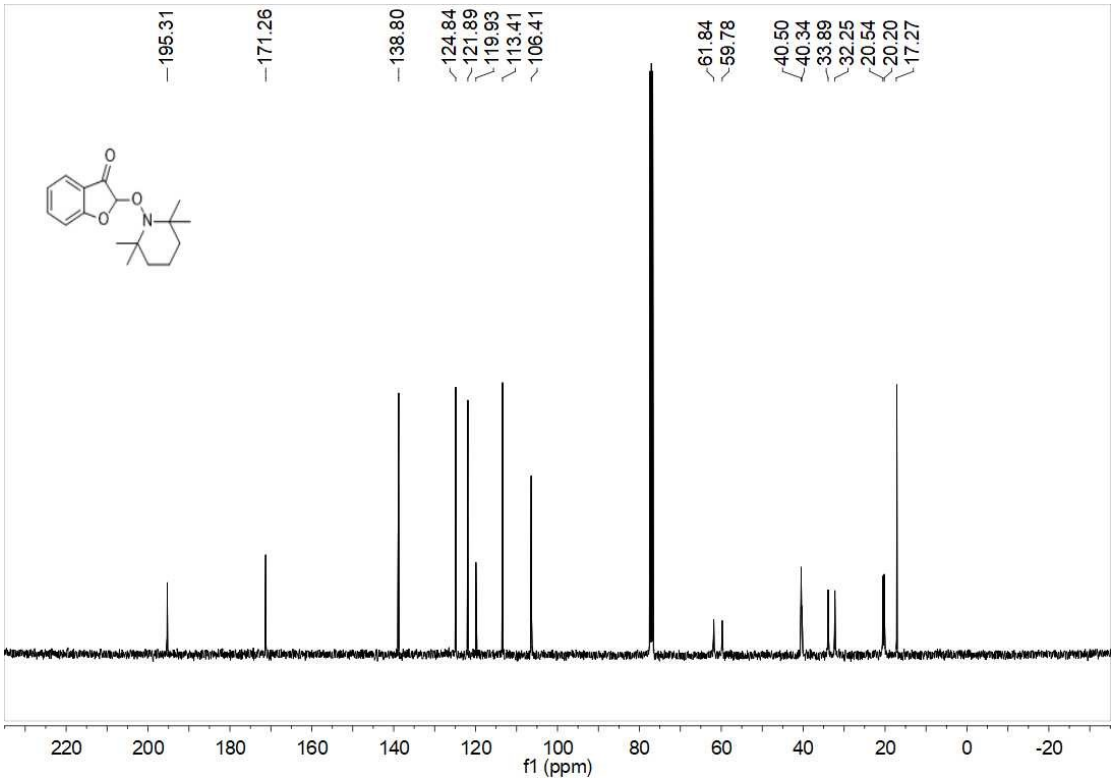
^{13}C {^{1}H} NMR (101 MHz, DMSO) of compound 5v



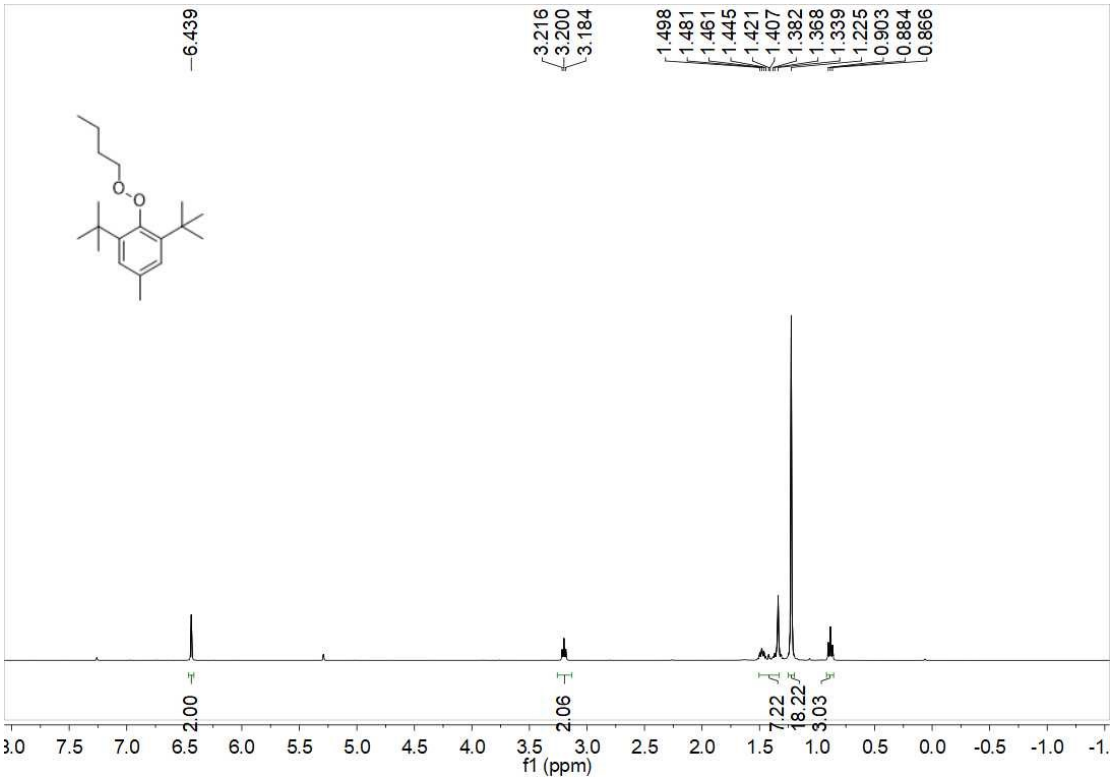
^{1}H NMR (400 MHz, $CDCl_3$) of compound 6



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 6



^{1}H NMR (400 MHz, $CDCl_3$) of compound 7



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 7