

# Electronic Supporting Information

## Quick construction of C-N bond from arylsulfonyl hydrazides and C<sub>sp2</sub>-X compounds promoted by DMAP at room temperature

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## Supplemental Data for Competing Experiments and the Corresponding Discussions

The mixture of 3,4-dibromo-5-methoxy-2(5*H*)-furanone **1a** (0.50 mmol), 3,4-dichloro-5-methoxy-2(5*H*)-furanone **1b** (0.50 mmol), DMAP (2.0 eq. or 4.0 eq), TBAI (3 mol%) and sulfonyl hydrazide **2** (0.60 mmol or 1.2 mmol) in DCM : H<sub>2</sub>O (3 mL, v : v = 5 : 1) was stirred at room temperature for 30 min or 60 min. After the completion of the reaction, the reaction mixture was quenched with H<sub>2</sub>O (15 mL) and extracted with DCM (3 × 15 mL). Then, the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents under reduced pressure, the crude product was simply purified by column chromatography on silica gel to afford the mixed product of **3a** and **4a**. According to the ratio of the <sup>1</sup>H NMR spectra, their yields are calculated.

**Table S1.** The competing experiments of 3,4-dibromo-2(5*H*)-furanones and 3,4-dichloro-2(5*H*)-furanones using **1a** and **1b** as the representatives.

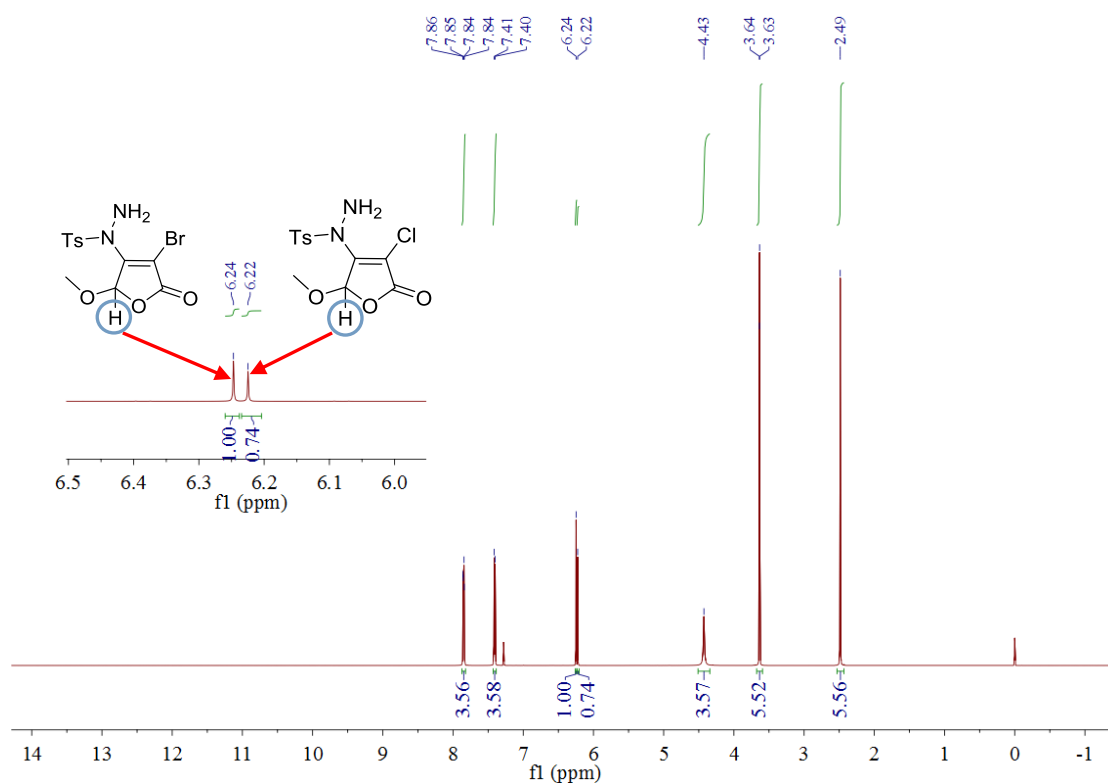
Entry	<b>1a</b> (mmol)	<b>1b</b> (mmol)	<b>2a</b> (mmol)	Other reaction conditions	The <sup>1</sup> H NMR ratio of <b>3a</b> : <b>4a</b>	Yield of <b>3a</b> <sup>a</sup>	Yield of <b>4a</b> <sup>a</sup>
1	0.5	0.5	0.6	1.0 mmol DMAP, 30 min	1.00 : 0.74	48%	36%
2	0.5	0.5	0.6	1.0 mmol DMAP, 60 min	1.00 : 0.75	49%	37%
3	0.5	0.5	1.2	2.0 mmol DMAP, 60 min	1.00 : 1.02	81%	83%

<sup>a</sup>After the crude product was simply purified by column chromatography on silica gel to afford the mixed product of **3a** and **4a**, the yield is calculated as the ratio of the <sup>1</sup>H NMR spectra (**Figs. S1-S3**).

Altering the reaction time and feed ratio, we performed a serial of competition experiments. The results are summarized in **Table S1** according to the ratio of the <sup>1</sup>H NMR spectra (**Figs. S1-S3**). When the reaction time is 30 minutes (**Entry 1**), the yield of **3a** (48%) is obviously higher than that of **4a** (36%). If the reaction time is prolonged to 60 minutes, the yield difference is not altered though there is a little change for the yields of **3a** (49%) and **4a** (37%) respectively (**Entry 2**). These indicate that 3,4-dibromo-2(5*H*)-

furanones have higher activity and faster reaction rate to complete the reaction with a shorter time in comparison of 3,4-dichloro-2(5*H*)-furanones indeed.

However, if using excessive sulfonyl hydrazide (1.2 mmol) to simultaneously react with 3,4-dibromo-5-methoxy-2(5*H*)-furanone **1a** (0.5 mmol) and 3,4-dichloro-5-methoxy-2(5*H*)-furanone **1b** (0.5 mmol) in a competitive reaction system for 60 minutes, the yields of **3a** and **4a** are 81% and 83%, respectively (**Table S1, Entry 3**). There is only a little yield difference indeed. Therefore, the comparable yields can be obtained from the 3,4-dichloro-2(5*H*)-furanones after prolonging reaction time when the amount of sulfonyl hydrazide is enough for it also.



**Fig. S1.** <sup>1</sup>H NMR of products (**Table S1, Entry 1**).

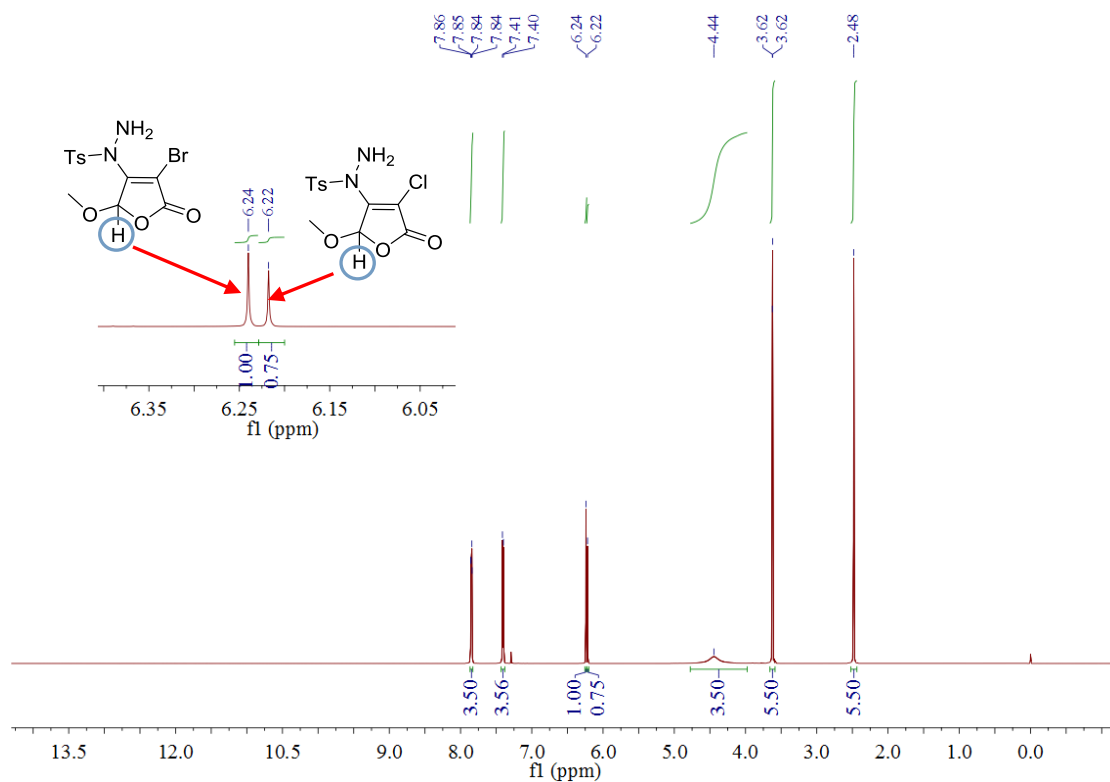


Fig. S2. <sup>1</sup>H NMR of products (Table S1, Entry 2).

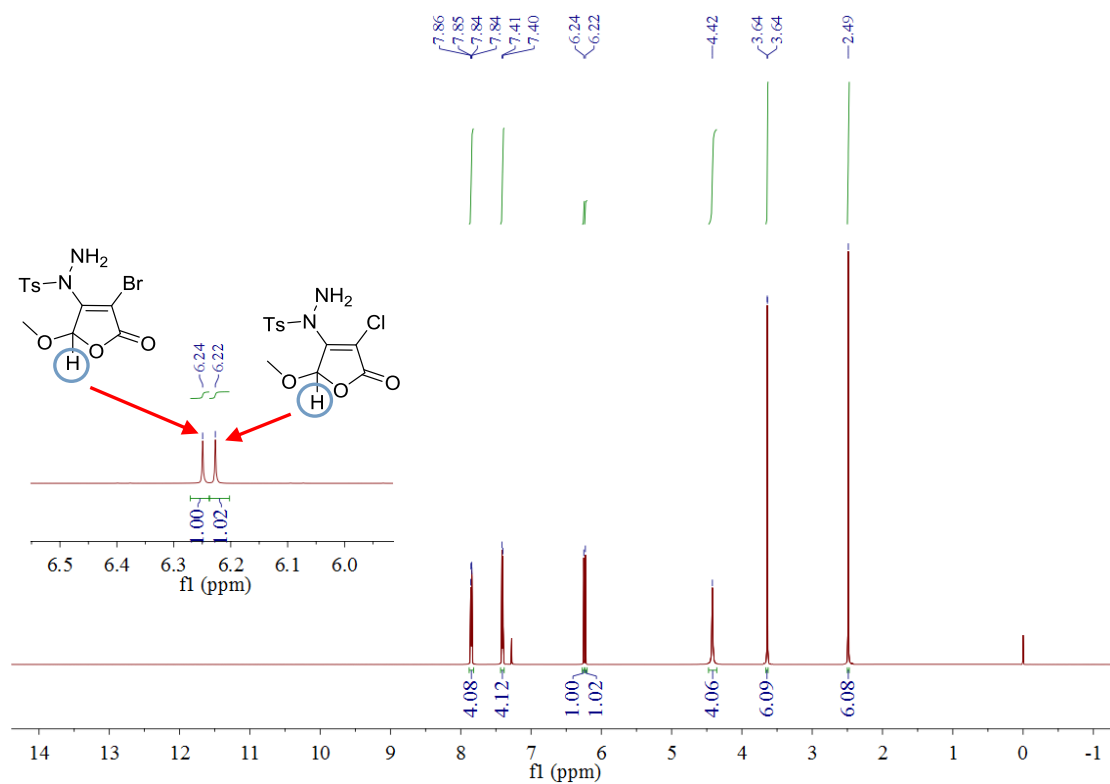
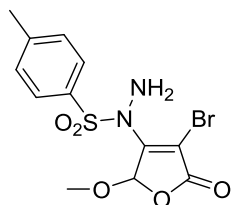


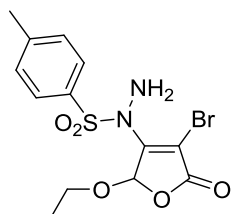
Fig. S3. <sup>1</sup>H NMR of products (Table S1, Entry 3).

## Characterization Data for All Products 3a-4s and Intermediate A



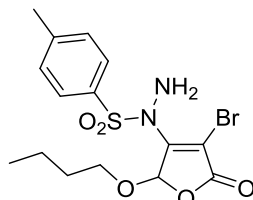
### ***N*-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonylhydrazide (3a)**

White solid (154 mg, 82%); m.p. 135.4-136.9 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ: 2.48 (*s*, 3H, CH<sub>3</sub>), 3.61 (*s*, 3H, OCH<sub>3</sub>), 4.46 (*s*, 2H, NH<sub>2</sub>), 6.24 (*s*, 1H, CH), 7.41 (*d*, *J* = 6.0 Hz, 2H, ArH), 7.85 (*d*, *J* = 6.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ: 21.9, 57.5, 95.3, 101.6, 128.8, 130.2, 132.3, 146.2, 155.7, 165.9; ESI-HRMS, *m/z*: Calcd for C<sub>12</sub>H<sub>14</sub>BrN<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup>, 376.9801, found: 376.9819.



### ***N*-(4-bromo-2-ethoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonylhydrazide (3b)**

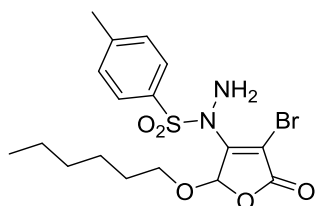
Colorless waxy (152 mg, 78%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ: 1.26 (*t*, *J* = 6.0 Hz, 3H, CH<sub>3</sub>), 2.48 (*s*, 3H, CH<sub>3</sub>), 3.83-3.98 (*m*, 2H, OCH<sub>2</sub>), 4.42 (*s*, 2H, NH<sub>2</sub>), 6.29 (*s*, 1H, CH), 7.40 (*d*, *J* = 6.0 Hz, 2H, ArH), 7.86 (*d*, *J* = 6.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ: 15.0, 21.8, 66.8, 95.7, 100.8, 128.8, 130.1, 132.3, 146.1, 155.9, 166.0; ESI-HRMS, *m/z*: Calcd for C<sub>13</sub>H<sub>16</sub>BrN<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup>, 390.9958, found: 390.9965.



### ***N*-(4-bromo-2-butoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonylhydrazide (3c)**

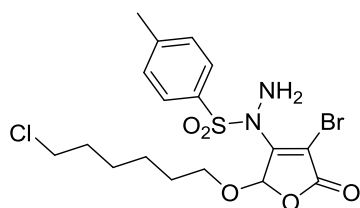
Colorless oil (165 mg, 79%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ: 0.92 (*t*, *J* = 6.0 Hz, 3H, CH<sub>3</sub>), 1.33-1.39 (*m*, 2H, CH<sub>2</sub>), 1.57-1.62 (*m*, 2H, CH<sub>2</sub>), 2.48 (*s*, 3H, CH<sub>3</sub>), 3.76-3.89 (*m*, 2H, OCH<sub>2</sub>), 4.42 (*b*, 2H, NH<sub>2</sub>), 6.27 (*s*, 1H, CH), 7.40 (*d*, *J* = 6.0 Hz, 2H, ArH), 7.86 (*d*, *J* = 6.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ: 13.8, 19.0, 21.8, 31.4, 70.9, 96.0, 101.0, 128.7, 130.1, 132.2, 146.1, 155.9, 166.0; ESI-HRMS,

$m/z$ : Calcd for  $C_{15}H_{20}BrN_2O_5S$   $[M+H]^+$ , 419.0271, found: 419.0273.



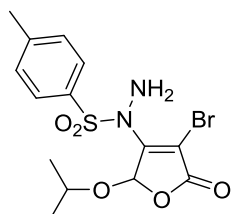
***N*-(4-bromo-2-hexyloxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonylhydrazide (3d)**

Colorless oil (192 mg, 86%);  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 0.89 (*t*,  $J$  = 6.0 Hz, 3H,  $CH_3$ ), 1.26-1.35 (*m*, 6H, 3 $CH_2$ ), 1.58-1.62 (*m*, 2H,  $CH_2$ ), 2.47 (*s*, 3H,  $CH_3$ ), 3.74-3.88 (*m*, 2H,  $OCH_2$ ), 4.19 (*b*, 2H,  $NH_2$ ), 6.26 (*s*, 1H, CH), 7.40 (*d*,  $J$  = 6.0 Hz, 2H, ArH), 7.86 (*d*,  $J$  = 6.0 Hz, 2H, ArH);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ ),  $\delta$ : 14.0, 21.7, 22.5, 25.4, 29.3, 31.5, 71.2, 95.9, 101.0, 128.7, 130.1, 132.2, 146.0, 155.9, 166.0; ESI-HRMS,  $m/z$ : Calcd for  $C_{17}H_{24}BrN_2O_5S$   $[M+H]^+$ , 447.0584, found: 447.0596.



***N*-(4-bromo-2-(6-chlorohexyloxy)-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonylhydrazide (3e)**

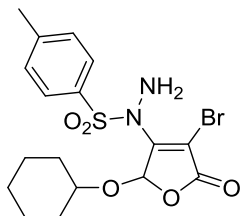
Colorless oil (202 mg, 84%);  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 1.36-1.48 (*m*, 4H, 2 $CH_2$ ), 1.62-1.67 (*m*, 2H,  $CH_2$ ), 1.75-1.80 (*m*, 2H,  $CH_2$ ), 2.48 (*s*, 3H,  $CH_3$ ), 3.54 (*t*,  $J$  = 6.0 Hz, 2H,  $CH_2$ ), 3.77-3.90 (*m*, 2H,  $OCH_2$ ), 4.27 (*b*, 2H,  $NH_2$ ), 6.28 (*s*, 1H, CH), 7.41 (*d*,  $J$  = 6.0 Hz, 2H, ArH), 7.85 (*d*,  $J$  = 6.0 Hz, 2H, ArH);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ ),  $\delta$ : 21.8, 25.1, 26.5, 29.2, 32.5, 45.1, 70.9, 95.9, 101.0, 128.7, 130.2, 132.2, 146.1, 155.9, 165.9; ESI-HRMS,  $m/z$ : Calcd for  $C_{17}H_{23}BrClN_2O_5S$   $[M+H]^+$ , 481.0194, found: 481.0207.



***N*-(4-bromo-2-isopropoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonylhydrazide (3f)**

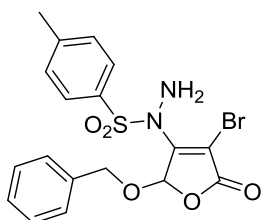
Colorless oil (164 mg, 81%);  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 1.24 (*d*,  $J$  = 6.0 Hz, 3H,  $CH_3$ ), 1.28 (*d*,  $J$  = 6.0 Hz, 3H,  $CH_3$ ), 2.48 (*s*, 3H,  $CH_3$ ), 4.12-4.18 (*m*, 1H, OCH), 4.43 (*s*, 2H,  $NH_2$ ), 6.31 (*s*, 1H, CH), 7.40

(*d*, *J* = 6.0 Hz, 2H, ArH), 7.85 (*d*, *J* = 6.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ : 21.7, 21.9, 23.1, 75.1, 97.2, 100.3, 128.6, 130.1, 132.1, 146.0, 156.4, 166.0; ESI-HRMS, *m/z*: Calcd for C<sub>14</sub>H<sub>18</sub>BrN<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup>, 405.0114, found: 405.0126.



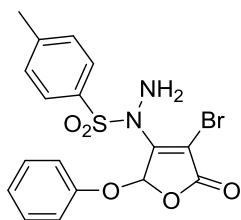
***N*-(4-bromo-2-cyclohexyloxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (3g)**

Colorless oil (173 mg, 78%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ : 1.19-1.55 (*m*, 6H, 3CH<sub>2</sub>), 1.71-1.77 (*m*, 2H, CH<sub>2</sub>), 1.94-2.01 (*m*, 2H, CH<sub>2</sub>), 2.48 (*s*, 3H, CH<sub>3</sub>), 3.82-3.87 (*m*, 1H, OCH), 4.24 (*b*, 2H, NH<sub>2</sub>), 6.35 (*s*, 1H, CH), 7.40 (*d*, *J* = 6.0 Hz, 2H, ArH), 7.85 (*d*, *J* = 6.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ : 21.8, 23.9, 24.0, 25.4, 31.9, 33.3, 80.7, 97.5, 100.4, 128.8, 130.2, 132.3, 146.0, 156.6, 166.1; ESI-HRMS, *m/z*: Calcd for C<sub>17</sub>H<sub>22</sub>BrN<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup>, 445.0427, found: 445.0442.



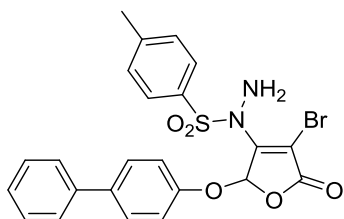
***N*-(2-benzyloxy-4-bromo-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (3h)**

Colorless waxy (181 mg, 80%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.41 (*s*, 3H, CH<sub>3</sub>), 4.31 (*b*, 2H, NH<sub>2</sub>), 4.77-4.94 (*dd*, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 12.0 Hz, 2H, OCH<sub>2</sub>), 6.43 (*s*, 1H, CH), 7.20 (*d*, *J* = 6.0 Hz, 2H, ArH), 7.32-7.36 (*m*, 5H, ArH), 7.76 (*d*, *J* = 6.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ : 21.8, 72.9, 95.3, 100.2, 128.6, 128.7, 128.8, 128.9, 130.0, 132.0, 135.5, 146.0, 155.7, 166.0; ESI-HRMS, *m/z*: Calcd for C<sub>18</sub>H<sub>18</sub>BrN<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup>, 453.0114, found: 453.0115.



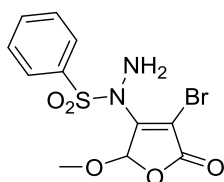
***N*-(4-bromo-5-oxo-2-phenoxy-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (3i)**

Colorless waxy (166 mg, 76%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 2.45 (s, 3H,  $\text{CH}_3$ ), 4.49 (b, 2H,  $\text{NH}_2$ ), 6.82 (s, 1H, CH), 7.08 (d,  $J = 6.0$  Hz, 2H, ArH), 7.13 (t,  $J = 6.0$  Hz, 1H, ArH), 7.32-7.36 (m, 4H, ArH), 7.83 (d,  $J = 6.0$  Hz, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 21.8, 96.4, 98.5, 117.2, 124.3, 128.8, 129.9, 130.2, 132.1, 146.3, 155.6, 155.9, 165.5; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{17}\text{H}_{16}\text{BrN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 438.9958, found: 438.9963.



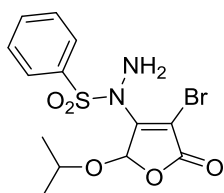
***N*-(2-((1,1'-biphenyl)-4-yloxy)-4-bromo-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonylhydrazide (3j)**

White solid (180 mg, 70%), m.p. 66.2-67.8  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 2.47 (s, 3H,  $\text{CH}_3$ ), 4.47 (b, 2H,  $\text{NH}_2$ ), 6.87 (s, 1H, CH), 7.16 (d,  $J = 6.0$  Hz, 2H, ArH), 7.34 (t,  $J = 6.0$  Hz, 1H, ArH), 7.39 (d,  $J = 6.0$  Hz, 2H, ArH), 7.42-7.44 (m, 2H, ArH), 7.54-7.57 (m, 4H, ArH), 7.86 (d,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 21.9, 96.6, 98.7, 117.7, 127.1, 127.4, 128.7, 129.0, 130.3, 132.2, 137.6, 140.4, 146.4, 155.4, 155.5, 165.5; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{23}\text{H}_{20}\text{BrN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 515.0271, found: 515.0273.



***N*-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonylhydrazide (3k)**

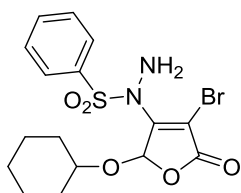
Colorless waxy (147 mg, 81%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.62 (s, 3H,  $\text{OCH}_3$ ), 4.47 (s, 2H,  $\text{NH}_2$ ), 6.24 (s, 1H, CH), 7.61-7.63 (m, 2H, ArH), 7.74 (t,  $J = 6.0$  Hz, 1H, ArH), 7.99 (d,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 57.5, 95.5, 101.5, 128.7, 129.5, 134.8, 135.4, 155.6, 165.8; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{12}\text{H}_{12}\text{BrN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 362.9645, found: 362.9657.





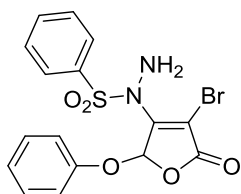
***N*-(4-bromo-2-isopropoxy-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonohydrazide (3l)**

Colorless waxy (164 mg, 84%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.25 (*d*,  $J = 6.0$  Hz, 3H,  $\text{CH}_3$ ), 1.29 (*d*,  $J = 6.0$  Hz, 3H,  $\text{CH}_3$ ), 4.14-4.19 (*m*, 1H, OCH), 4.43 (*s*, 2H,  $\text{NH}_2$ ), 6.32 (*s*, 1H, CH), 7.60-7.64 (*m*, 2H, ArH), 7.74 (*t*,  $J = 6.0$  Hz, 1H, ArH), 7.99 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 22.0, 23.2, 57.3, 97.8, 100.4, 128.7, 129.6, 134.7, 135.4, 156.4, 165.9; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{13}\text{H}_{16}\text{BrN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 390.9958, found: 390.9967.



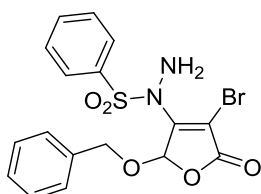
***N*-(4-bromo-2-cyclohexyloxy-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonohydrazide (3m)**

Colorless waxy (161 mg, 75%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.18-1.55 (*m*, 6H,  $3\text{CH}_2$ ), 1.71-1.76 (*m*, 2H,  $\text{CH}_2$ ), 1.95-1.98 (*m*, 2H,  $\text{CH}_2$ ), 3.82-3.86 (*m*, 1H, OCH), 4.09 (*b*, 2H,  $\text{NH}_2$ ), 6.35 (*s*, 1H, CH), 7.60-7.63 (*m*, 2H, ArH), 7.73 (*t*,  $J = 6.0$  Hz, 1H, ArH), 7.98 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 23.8, 23.9, 25.3, 31.8, 33.2, 80.7, 97.8, 100.3, 128.6, 129.5, 134.6, 135.3, 156.4, 165.9; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{13}\text{H}_{16}\text{BrN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 431.0271, found: 431.0263.



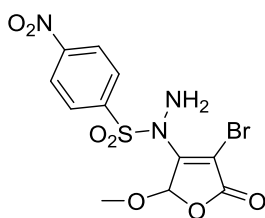
***N*-(4-bromo-5-oxo-2-phenoxy-2,5-dihydrofuran-3-yl)benzenesulfonohydrazide (3n)**

Colorless waxy (153 mg, 72%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 4.52 (*b*, 2H,  $\text{NH}_2$ ), 6.82 (*s*, 1H, CH), 7.06 (*d*,  $J = 6.0$  Hz, 2H, ArH), 7.13 (*t*,  $J = 6.0$  Hz, 1H, ArH), 7.31-7.34 (*m*, 2H, ArH), 7.55-7.57 (*m*, 2H, ArH), 7.70 (*t*,  $J = 6.0$  Hz, 1H, ArH), 7.95 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 96.7, 98.4, 117.2, 124.3, 128.8, 129.6, 129.9, 134.8, 135.2, 155.5, 155.8, 165.4; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{16}\text{H}_{14}\text{BrN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 424.9801, found: 424.9811.



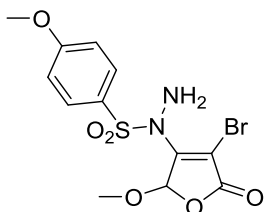
***N*-(2-benzyloxy-4-bromo-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonohydrazide (3o)**

Colorless waxy (173 mg, 79%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 4.34 (*b*, 2H,  $\text{NH}_2$ ), 4.77-4.94 (*dd*,  $J_1 = 12.0$  Hz,  $J_2 = 12.0$  Hz, 2H,  $\text{OCH}_2$ ), 6.43 (*s*, 1H, CH), 7.32-7.36 (*m*, 5H, ArH), 7.39-7.41 (*m*, 2H, ArH), 7.61 (*t*,  $J = 6.0$  Hz, 1H, ArH), 7.88 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 72.9, 95.5, 100.1, 128.6, 128.7, 128.8, 128.9, 129.3, 134.6, 135.0, 135.4, 155.6, 165.9; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{17}\text{H}_{16}\text{BrN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 438.9958, found: 438.9962.



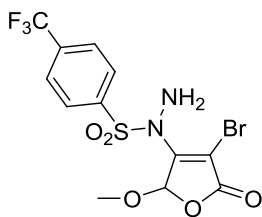
***N*-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-nitrobenzenesulfonohydrazide (3p)**

Colorless waxy (165 mg, 81%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.66 (*s*, 3H,  $\text{OCH}_3$ ), 4.61 (*b*, 2H,  $\text{NH}_2$ ), 6.25 (*s*, 1H, CH), 8.23 (*d*,  $J = 6.0$  Hz, 2H, ArH), 8.44 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 57.9, 95.8, 101.3, 124.4, 130.4, 141.4, 151.1, 155.1, 165.3; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{11}\text{H}_{11}\text{BrN}_3\text{O}_7\text{S}$   $[\text{M}+\text{H}]^+$ , 407.9496, found: 407.9490.



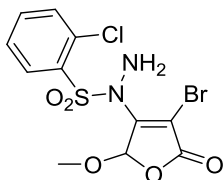
***N*-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methoxybenzenesulfonohydrazide (3q)**

White solid (168 mg, 86%); m.p. 119.8-120.7  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.65 (*s*, 3H,  $\text{OCH}_3$ ), 3.93 (*s*, 3H,  $\text{OCH}_3$ ), 4.42 (*s*, 2H,  $\text{NH}_2$ ), 6.26 (*s*, 1H, CH), 7.07 (*d*,  $J = 6.0$  Hz, 2H, ArH), 7.92 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 55.9, 57.4, 94.7, 101.5, 114.7, 126.2, 131.1, 155.6, 164.6, 165.9; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{12}\text{H}_{14}\text{BrN}_2\text{O}_6\text{S}$   $[\text{M}+\text{H}]^+$ , 392.9750, found: 392.9774.



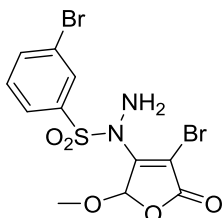
**N-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-trifluoromethylbenzenesulfonylhydrazide (3r)**

Colorless waxy (178 mg, 83%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.67 (*s*, 3H,  $\text{OCH}_3$ ), 4.53 (*s*, 2H,  $\text{NH}_2$ ), 6.26 (*s*, 1H, CH), 7.90 (*d*,  $J = 6.0$  Hz, 2H, ArH), 8.17 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 57.7, 95.7, 101.3, 122.9 (*q*,  $J = 271.5$  Hz), 126.4 (*q*,  $J = 3.0$  Hz), 129.4, 136.1 (*q*,  $J = 33.0$  Hz), 139.2, 155.2, 165.3;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ),  $\delta$ : -63.3; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{12}\text{H}_{11}\text{BrF}_3\text{N}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 430.9519, found: 430.9554.



**N-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-2-chlorobenzenesulfonylhydrazide (3s)**

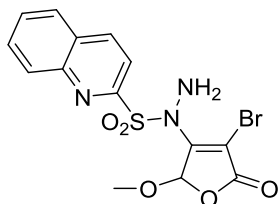
White solid (168 mg, 85%); m.p. 118.5-119.8  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.65 (*s*, 3H,  $\text{OCH}_3$ ), 4.57 (*b*, 2H,  $\text{NH}_2$ ), 6.25 (*s*, 1H, CH), 7.52-7.54 (*m*, 1H, ArH), 7.62 (*d*,  $J = 6.0$  Hz, 1H, ArH), 7.65-7.67 (*m*, 1H, ArH), 8.21 (*d*,  $J = 6.0$  Hz, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 58.0, 94.1, 102.0, 127.6, 132.3, 132.4, 133.4, 133.7, 135.5, 156.5, 165.8; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{11}\text{H}_{11}\text{BrClN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 396.9255, found: 396.9263.



**3-bromo-N-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonylhydrazide (3t)**

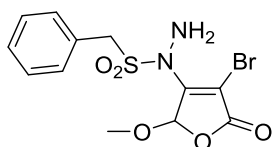
Colorless waxy (180 mg, 82%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.66 (*s*, 3H,  $\text{OCH}_3$ ), 4.51 (*b*, 2H,  $\text{NH}_2$ ), 6.24 (*s*, 1H, CH), 7.48-7.51 (*m*, 1H, ArH), 7.85 (*d*,  $J = 6.0$  Hz, 1H, ArH), 7.94 (*d*,  $J = 6.0$  Hz, 1H, ArH), 8.14 (*s*, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 57.7, 95.4, 101.3, 123.2, 127.4, 130.8, 131.6,

137.3, 137.6, 155.3, 165.5; ESI-HRMS,  $m/z$ : Calcd for  $C_{11}H_{11}Br_2N_2O_5S$   $[M+H]^+$ , 440.8750, found: 440.8771.



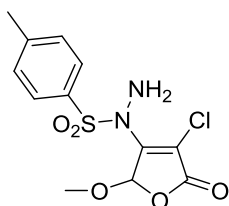
***N*-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)quinoline-2-sulfonohydrazide (3u)**

Colorless waxy (159 mg, 77%);  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 3.27 (*s*, 3H,  $OCH_3$ ), 5.98 (*b*, 2H,  $NH_2$ ), 6.13 (*s*, 1H, CH), 7.65-7.67 (*m*, 1H, ArH), 7.75-7.77 (*m*, 1H, ArH), 8.20 (*d*,  $J = 6.0$  Hz, 1H, ArH), 8.39 (*d*,  $J = 6.0$  Hz, 1H, ArH), 8.58 (*d*,  $J = 6.0$  Hz, 1H, ArH), 9.07 (*d*,  $J = 6.0$  Hz, 1H, ArH);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ ),  $\delta$ : 56.2, 92.8, 100.9, 122.8, 125.7, 129.1, 132.9, 134.9, 137.6, 137.8, 143.1, 151.8, 155.6, 166.6; ESI-HRMS,  $m/z$ : Calcd for  $C_{14}H_{13}BrN_3O_5S$   $[M+H]^+$ , 413.9754, found: 413.9766.



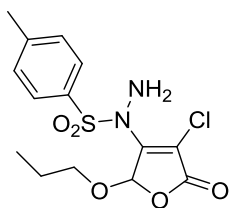
***N*-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-1-phenylmethanesulfonohydrazide (3v)**

White solid (150 mg, 80%); m.p. 146.8-147.9  $^{\circ}C$ ;  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 3.67 (*s*, 3H,  $OCH_3$ ), 4.13 (*b*, 2H,  $NH_2$ ), 4.59-4.82 (*dd*,  $J_1 = 12.0$  Hz,  $J_2 = 12.0$  Hz, 2H,  $CH_2$ ), 6.04 (*s*, 1H, CH), 7.46-7.50 (*m*, 5H, ArH);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ ),  $\delta$ : 57.6, 59.3, 92.3, 100.8, 126.7, 129.5, 129.9, 130.8, 155.2, 166.0; ESI-HRMS,  $m/z$ : Calcd for  $C_{12}H_{14}BrN_2O_5S$   $[M+H]^+$ , 376.9801, found: 376.9832.



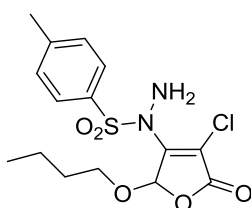
***N*-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (4a)**

Colorless waxy (139 mg, 84%);  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 2.48 (*s*, 3H,  $CH_3$ ), 3.64 (*s*, 3H,  $OCH_3$ ), 4.30 (*b*, 2H,  $NH_2$ ), 6.22 (*s*, 1H, CH), 7.41 (*d*,  $J = 6.0$  Hz, 2H, ArH), 7.85 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ ),  $\delta$ : 21.9, 57.6, 100.6, 106.9, 128.8, 130.2, 132.3, 146.2, 152.0, 165.4; ESI-HRMS,  $m/z$ : Calcd for  $C_{12}H_{14}ClN_2O_5S$   $[M+H]^+$ , 333.0306, found: 333.0327.



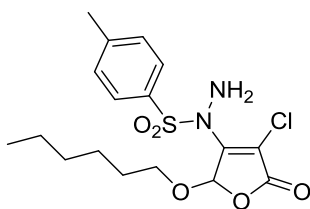
**N-(4-chloro-5-oxo-2-propoxy-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (4b)**

Colorless oil (155 mg, 86%);  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.92 (*t*,  $J = 6.0$  Hz, 3H,  $\text{CH}_3$ ), 1.60-1.66 (*m*, 2H,  $\text{CH}_2$ ), 2.47 (*s*, 3H,  $\text{CH}_3$ ), 3.71-3.85 (*m*, 2H,  $\text{OCH}_2$ ), 4.42 (*b*, 2H,  $\text{NH}_2$ ), 6.24 (*s*, 1H, CH), 7.40 (*d*,  $J = 6.0$  Hz, 2H, ArH), 7.85 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 10.3, 21.7, 22.7, 72.8, 100.1, 107.4, 128.7, 130.1, 132.2, 146.1, 152.1, 165.5; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{14}\text{H}_{18}\text{ClN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 361.0619, found: 361.0630.



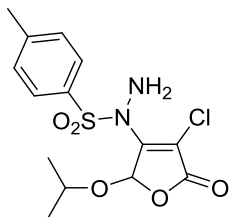
**N-(2-butoxy-4-chloro-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (4c)**

Colorless oil (155 mg, 83%);  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.92 (*t*,  $J = 6.0$  Hz, 3H,  $\text{CH}_3$ ), 1.33-1.40 (*m*, 2H,  $\text{CH}_2$ ), 1.57-1.62 (*m*, 2H,  $\text{CH}_2$ ), 2.48 (*s*, 3H,  $\text{CH}_3$ ), 3.76-3.91 (*m*, 2H,  $\text{OCH}_2$ ), 4.38 (*b*, 2H,  $\text{NH}_2$ ), 6.25 (*s*, 1H, CH), 7.40 (*d*,  $J = 6.0$  Hz, 2H, ArH), 7.85 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 13.9, 19.1, 21.9, 31.5, 71.1, 100.1, 107.6, 128.8, 130.2, 132.3, 146.2, 152.2, 165.6; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{15}\text{H}_{20}\text{ClN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 375.0776, found: 375.0786.



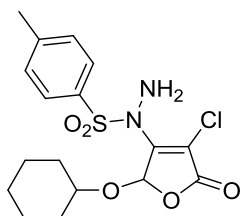
**N-(4-chloro-2-hexyloxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (4d)**

Colorless oil (165 mg, 82%);  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.89 (*t*,  $J = 6.0$  Hz, 3H,  $\text{CH}_3$ ), 1.26-1.36 (*m*, 6H, 3 $\text{CH}_2$ ), 1.59-1.63 (*m*, 2H,  $\text{CH}_2$ ), 2.48 (*s*, 3H,  $\text{CH}_3$ ), 3.75-3.90 (*m*, 2H,  $\text{OCH}_2$ ), 4.39 (*s*, 2H,  $\text{NH}_2$ ), 6.25 (*s*, 1H, CH), 7.40 (*d*,  $J = 6.0$  Hz, 2H, ArH), 7.85 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 14.1, 21.8, 22.6, 25.6, 29.5, 31.6, 71.4, 100.1, 107.6, 128.8, 130.2, 132.3, 146.1, 152.2, 165.6; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{17}\text{H}_{24}\text{ClN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 403.1089, found: 403.1082.



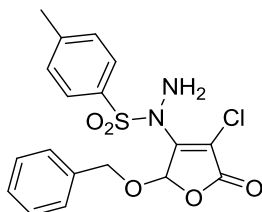
***N*-(4-chloro-2-isopropoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonylhydrazide (4e)**

Colorless oil (149 mg, 83%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.24 (*d*,  $J = 6.0$  Hz, 3H,  $\text{CH}_3$ ), 1.28 (*d*,  $J = 6.0$  Hz, 3H,  $\text{CH}_3$ ), 2.48 (*s*, 3H,  $\text{CH}_3$ ), 4.12-4.18 (*m*, 1H, OCH), 4.40 (*s*, 2H,  $\text{NH}_2$ ), 6.29 (*s*, 1H, CH), 7.40 (*d*,  $J = 6.0$  Hz, 2H, ArH), 7.85 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 21.7, 22.0, 23.2, 75.1, 99.3, 108.5, 128.7, 130.1, 132.2, 146.0, 152.6, 165.6; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{14}\text{H}_{18}\text{ClN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 361.0619, found: 361.0629.



***N*-(4-chloro-2-cyclohexyloxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonylhydrazide (4f)**

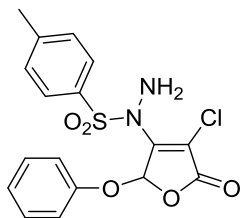
Colorless waxy (156 mg, 78%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.17-1.55 (*m*, 6H,  $3\text{CH}_2$ ), 1.70-1.77 (*m*, 2H,  $\text{CH}_2$ ), 1.94-1.99 (*m*, 2H,  $\text{CH}_2$ ), 2.48 (*s*, 3H,  $\text{CH}_3$ ), 3.82-3.86 (*m*, 1H, OCH), 4.36 (*b*, 2H,  $\text{NH}_2$ ), 6.33 (*s*, 1H, CH), 7.40 (*d*,  $J = 6.0$  Hz, 2H, ArH), 7.85 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 21.9, 24.0, 24.1, 25.4, 32.0, 33.3, 80.7, 99.4, 108.8, 128.8, 130.2, 132.3, 146.1, 152.7, 165.6; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{17}\text{H}_{22}\text{ClN}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ , 401.0932, found: 401.0945.



***N*-(2-benzyloxy-4-chloro-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonylhydrazide (4g)**

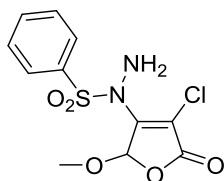
Colorless waxy (151 mg, 74%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 2.40 (*s*, 3H,  $\text{CH}_3$ ), 4.31 (*b*, 2H,  $\text{NH}_2$ ), 4.76-4.94 (*dd*,  $J_1 = 12.0$  Hz,  $J_2 = 12.0$  Hz, 2H,  $\text{OCH}_2$ ), 6.40 (*s*, 1H, CH), 7.20 (*d*,  $J = 6.0$  Hz, 2H, ArH), 7.32-7.36 (*m*, 5H, ArH), 7.75 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 21.8, 72.9, 99.2,

106.9, 128.6, 128.7, 128.8, 128.9, 130.0, 132.0, 135.5, 146.0, 152.0, 165.5; ESI-HRMS,  $m/z$ : Calcd for  $C_{18}H_{18}ClN_2O_5S$   $[M+H]^+$ , 409.0619, found: 409.0630.



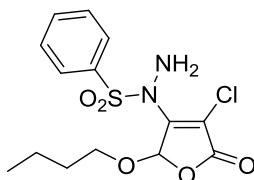
***N*-(4-chloro-5-oxo-2-phenoxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (4h)**

Colorless waxy (148 mg, 75%);  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 2.46 (*s*, 3H,  $CH_3$ ), 4.46 (*s*, 2H,  $NH_2$ ), 6.80 (*s*, 1H, CH), 7.07 (*d*,  $J = 6.0$  Hz, 2H, ArH), 7.13 (*t*,  $J = 6.0$  Hz, 1H, CH), 7.32-7.37 (*m*, 4H, ArH), 7.84 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ ),  $\delta$ : 21.8, 97.5, 108.0, 117.2, 124.3, 128.8, 129.9, 130.2, 132.1, 146.3, 151.8, 155.9, 165.0; ESI-HRMS,  $m/z$ : Calcd for  $C_{17}H_{16}ClN_2O_5S$   $[M+H]^+$ , 395.0463, found: 395.0474.



***N*-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonohydrazide (4i)**

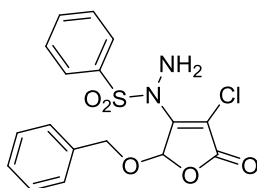
Colorless waxy (130 mg, 82%);  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 3.61 (*s*, 3H,  $OCH_3$ ), 4.51 (*s*, 2H,  $NH_2$ ), 6.22 (*s*, 1H, CH), 7.61-7.63 (*m*, 2H, ArH), 7.74 (*t*,  $J = 6.0$  Hz, 1H, ArH), 7.98 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ ),  $\delta$ : 57.5, 100.5, 106.8, 128.6, 129.5, 134.7, 135.3, 151.9, 165.4; ESI-HRMS,  $m/z$ : Calcd for  $C_{11}H_{12}ClN_2O_5S$   $[M+H]^+$ , 319.0150, found: 319.0164.



***N*-(2-butoxy-4-chloro-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonohydrazide (4j)**

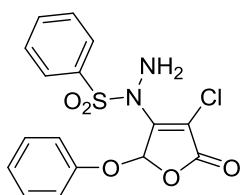
Colorless oil (146 mg, 81%);  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 0.92 (*t*,  $J = 6.0$  Hz, 3H,  $CH_3$ ), 1.33-1.39 (*m*, 2H,  $CH_2$ ), 1.57-1.62 (*m*, 2H,  $CH_2$ ), 3.76-3.91 (*m*, 2H,  $OCH_2$ ), 4.43 (*s*, 2H,  $NH_2$ ), 6.26 (*s*, 1H, CH), 7.60-7.63 (*m*, 2H, ArH), 7.73 (*t*,  $J = 6.0$  Hz, 1H, ArH), 7.99 (*d*,  $J = 6.0$  Hz, 2H, ArH);  $^{13}C$  NMR (150 MHz,

CDCl<sub>3</sub>),  $\delta$ : 13.8, 19.1, 31.5, 71.1, 100.0, 107.8, 128.7, 129.6, 134.7, 135.4, 152.1, 165.5; ESI-HRMS,  $m/z$ :  
Calcd for C<sub>14</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup>, 361.0619, found: 361.0629.



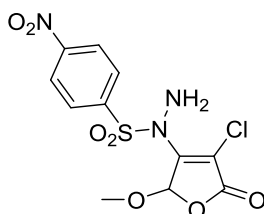
**N-(2-benzyloxy-4-chloro-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonylhydrazide (4k)**

Colorless waxy (152 mg, 77%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ : 4.31 (s, 2H, NH<sub>2</sub>), 4.78-4.97 (dd,  $J_1 = 12.0$  Hz,  $J_2 = 12.0$  Hz, 2H, OCH<sub>2</sub>), 6.42 (s, 1H, CH), 7.34-7.37 (m, 5H, ArH), 7.40-7.43 (m, 2H, ArH), 7.63 (t,  $J = 6.0$  Hz, 1H, ArH), 7.89 (d,  $J = 6.0$  Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ : 73.0, 99.0, 107.1, 128.6, 128.7, 128.8, 128.9, 129.3, 134.6, 135.0, 135.4, 151.9, 165.3; ESI-HRMS,  $m/z$ : Calcd for C<sub>17</sub>H<sub>16</sub>ClN<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup>, 395.0463, found: 395.0472.



**N-(4-chloro-5-oxo-2-phenoxy-2,5-dihydrofuran-3-yl)benzenesulfonylhydrazide (4l)**

White solid (139 mg, 73%); m.p. 129.4-130.8 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ : 4.49 (s, 2H, NH<sub>2</sub>), 6.81 (s, 1H, CH), 7.06 (d,  $J = 6.0$  Hz, 2H, ArH), 7.14 (t,  $J = 6.0$  Hz, 1H, ArH), 7.33-7.35 (m, 2H, ArH), 7.58-7.60 (m, 2H, ArH), 7.73 (t,  $J = 6.0$  Hz, 1H, ArH), 7.97 (d,  $J = 6.0$  Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ : 97.5, 108.4, 117.3, 124.4, 128.8, 129.7, 130.0, 134.9, 135.3, 151.7, 155.9, 164.9; ESI-HRMS,  $m/z$ : Calcd for C<sub>16</sub>H<sub>14</sub>ClN<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup>, 381.0306, found: 381.0316.

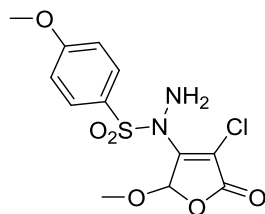


**N-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-nitrobenzenesulfonylhydrazide (4m)**

Colorless waxy (145 mg, 80%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ : 3.67 (s, 3H, OCH<sub>3</sub>), 4.57 (b, 2H, NH<sub>2</sub>), 6.23 (s, 1H, CH), 8.23 (d,  $J = 6.0$  Hz, 2H, ArH), 8.45 (d,  $J = 6.0$  Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz,

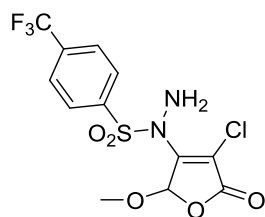


CDCl<sub>3</sub>),  $\delta$ : 57.9, 100.2, 107.2, 124.4, 130.3, 141.3, 151.0, 151.4, 164.7; ESI-HRMS,  $m/z$ : Calcd for C<sub>11</sub>H<sub>11</sub>ClN<sub>3</sub>O<sub>7</sub>S [M+H]<sup>+</sup>, 364.0001, found: 364.0030.



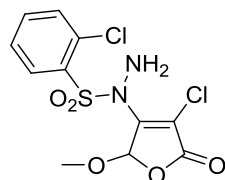
**N-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methoxybenzenesulfonylhydrazide (4n)**

Colorless waxy (143 mg, 82%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ : 3.64 (s, 3H, OCH<sub>3</sub>), 3.92 (s, 3H, OCH<sub>3</sub>), 4.42 (s, 2H, NH<sub>2</sub>), 6.23 (s, 1H, CH), 7.06 (d,  $J$  = 6.0 Hz, 2H, ArH), 7.90 (d,  $J$  = 6.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ : 55.9, 57.5, 100.5, 106.3, 114.7, 126.2, 131.1, 151.9, 164.6, 165.5; ESI-HRMS,  $m/z$ : Calcd for C<sub>12</sub>H<sub>14</sub>ClN<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>, 349.0256, found: 349.0271.



**N-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-(trifluoromethyl)benzenesulfonylhydrazide (4o)**

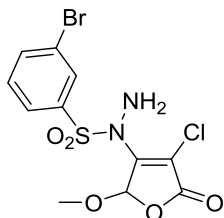
Colorless waxy (162 mg, 84%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ : 3.66 (s, 3H, OCH<sub>3</sub>), 4.54 (b, 2H, NH<sub>2</sub>), 6.23 (s, 1H, CH), 7.90 (d,  $J$  = 6.0 Hz, 2H, ArH), 8.16 (d,  $J$  = 6.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ : 57.8, 100.3, 107.0, 123.0 ( $q$ ,  $J$  = 271.5 Hz), 126.4 ( $q$ ,  $J$  = 3.0 Hz), 129.4, 136.1 ( $q$ ,  $J$  = 34.5 Hz), 139.1, 155.2, 165.0; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>),  $\delta$ : -63.3; ESI-HRMS,  $m/z$ : Calcd for C<sub>12</sub>H<sub>11</sub>ClF<sub>3</sub>N<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup>, 387.0024, found: 387.0044.



**2-chloro-N-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonylhydrazide (4p)**

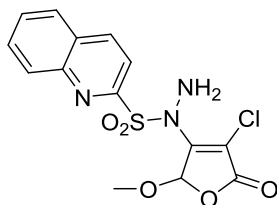
White solid (151 mg, 86%); m.p. 135.4-136.9 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ : 3.65 (s, 3H, OCH<sub>3</sub>), 4.59 (b, 2H, NH<sub>2</sub>), 6.23 (s, 1H, CH), 7.52-7.54 (m, 1H, ArH), 7.62 (d,  $J$  = 6.0 Hz, 1H, ArH), 7.64-7.67 (m, 1H, ArH), 8.21 (d,  $J$  = 6.0 Hz, 1H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ : 58.0, 100.9, 105.8, 127.6, 132.3,

132.4, 133.4, 133.9, 135.5, 152.8, 165.3; ESI-HRMS,  $m/z$ : Calcd for  $C_{11}H_{11}Cl_2N_2O_5S$   $[M+H]^+$ , 352.9760, found: 352.9799.



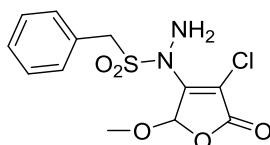
**3-bromo-N-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonylhydrazide (4q)**

Colorless waxy (158 mg, 80%);  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 3.66 (*s*, 3H,  $OCH_3$ ), 4.52 (*b*, 2H,  $NH_2$ ), 6.22 (*s*, 1H, CH), 7.48-7.51 (*m*, 1H, ArH), 7.85 (*d*,  $J = 6.0$  Hz, 1H, ArH), 7.94 (*d*,  $J = 6.0$  Hz, 1H, ArH), 8.14 (*s*, 1H, ArH);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ ),  $\delta$ : 57.7, 100.3, 106.8, 123.2, 127.4, 130.8, 131.6, 137.2, 137.6, 151.6, 165.1; ESI-HRMS,  $m/z$ : Calcd for  $C_{11}H_{11}BrClN_2O_5S$   $[M+H]^+$ , 396.9255, found: 396.9263.



**N-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)quinoline-2-sulfonylhydrazide (4r)**

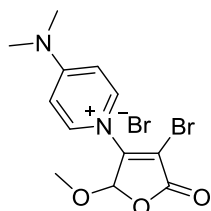
Colorless waxy (138 mg, 75%);  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 3.30 (*s*, 3H,  $OCH_3$ ), 6.00 (*s*, 2H,  $NH_2$ ), 6.08 (*s*, 1H, CH), 7.62-7.65 (*m*, 1H, ArH), 7.72-7.74 (*m*, 1H, ArH), 8.17 (*d*,  $J = 6.0$  Hz, 1H, ArH), 8.37 (*d*,  $J = 6.0$  Hz, 1H, ArH), 8.56 (*d*,  $J = 6.0$  Hz, 1H, ArH), 9.04 (*d*,  $J = 6.0$  Hz, 1H, ArH);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ ),  $\delta$ : 56.3, 100.0, 104.4, 122.8, 125.7, 129.1, 133.0, 134.9, 137.6, 137.7, 143.1, 151.7, 151.9, 166.1; ESI-HRMS,  $m/z$ : Calcd for  $C_{14}H_{13}ClN_3O_5S$   $[M+H]^+$ , 370.0259, found: 370.0287.



**N-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-1-phenylmethanesulfonylhydrazide (4s)**

White solid (134 mg, 81%); m.p. 127.4-128.2 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ ),  $\delta$ : 3.64 (*s*, 3H,  $OCH_3$ ),

4.15 (*b*, 2H, NH<sub>2</sub>), 4.58-4.78 (*dd*, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 12.0 Hz, 2H, CH<sub>2</sub>), 6.00 (*s*, 1H, CH), 7.43-7.48 (*m*, 5H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ: 57.7, 59.3, 99.9, 104.0, 126.8, 129.5, 129.9, 130.8, 151.7, 165.6; ESI-HRMS, *m/z*: Calcd for C<sub>12</sub>H<sub>14</sub>ClN<sub>2</sub>O<sub>5</sub>S [M+H]<sup>+</sup>, 333.0306, found: 333.0349.



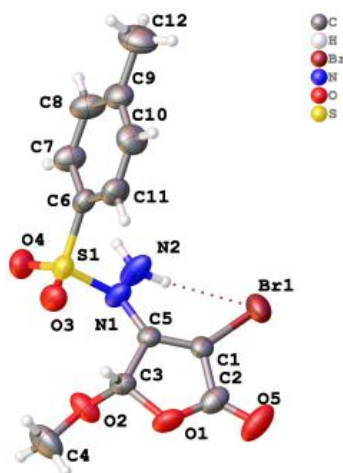
**1-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-dimethylaminopyridin-1-ium bromide  
(intermediate A)**

White solid (186 mg, 95%); m.p. 186.5-186.9 °C; <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O), δ: 3.39 (*s*, 6H, 2CH<sub>3</sub>), 3.69 (*s*, 3H, OCH<sub>3</sub>), 6.57 (*s*, 1H, CH), 7.13 (*d*, *J* = 6.0 Hz, 2H, ArH), 8.42 (*d*, *J* = 6.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, D<sub>2</sub>O), δ: 40.4, 57.4, 101.4, 105.5, 108.2, 138.2, 151.5, 157.0, 166.6; ESI-HRMS, *m/z*: Calcd for C<sub>12</sub>H<sub>15</sub>BrN<sub>2</sub>O<sub>3</sub> [M+H-Br]<sup>+</sup>, 314.0261, found: 314.0279.

## Data of Single-crystal X-ray Analysis

**Table S2.** Crystal data and structure refinement for **3a**.

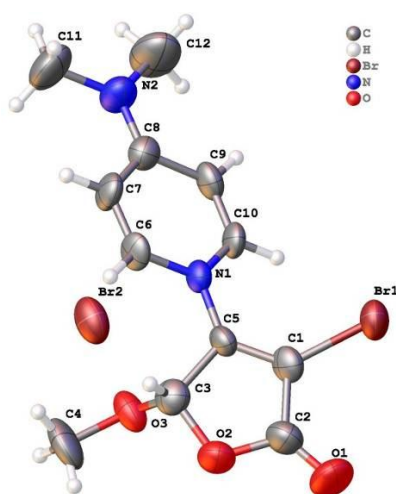
Compound	<b>3a</b>
Empirical formula	C <sub>12</sub> H <sub>13</sub> BrN <sub>2</sub> O <sub>5</sub> S
Formula weight	377.21
Temperature (K)	293.15
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions (Å, °)	$a = 8.4406(6)$ , $b = 12.7982(11)$ , $c = 14.3406(11)$ $\alpha = 90$ , $\beta = 105.550(7)$ , $\gamma = 90$
Volume (Å <sup>3</sup> )	1492.4(2)
Z	4
Density (calculated) (Mg/m <sup>3</sup> )	1.679
Absorption coefficient (mm <sup>-1</sup> )	2.916
F(000)	760
Crystal size (mm <sup>3</sup> )	0.14 x 0.12 x 0.1
Theta range for data collection	3.351 to 29.285 deg
Index ranges	-10 ≤ h ≤ 10, -16 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	7339
Independent reflections	3418 [R(int) = 0.0298]
Completeness to theta = 25.242	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.60038
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3418 / 0 / 192
Goodness-of-fit on F <sup>2</sup>	1.018
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0528, wR <sub>2</sub> = 0.0940
R indices (all data)	R <sub>1</sub> = 0.0969, wR <sub>2</sub> = 0.1100
Extinction coefficient	n/a
Largest diff. peak and hole (e.Å <sup>-3</sup> )	0.506 and -0.556



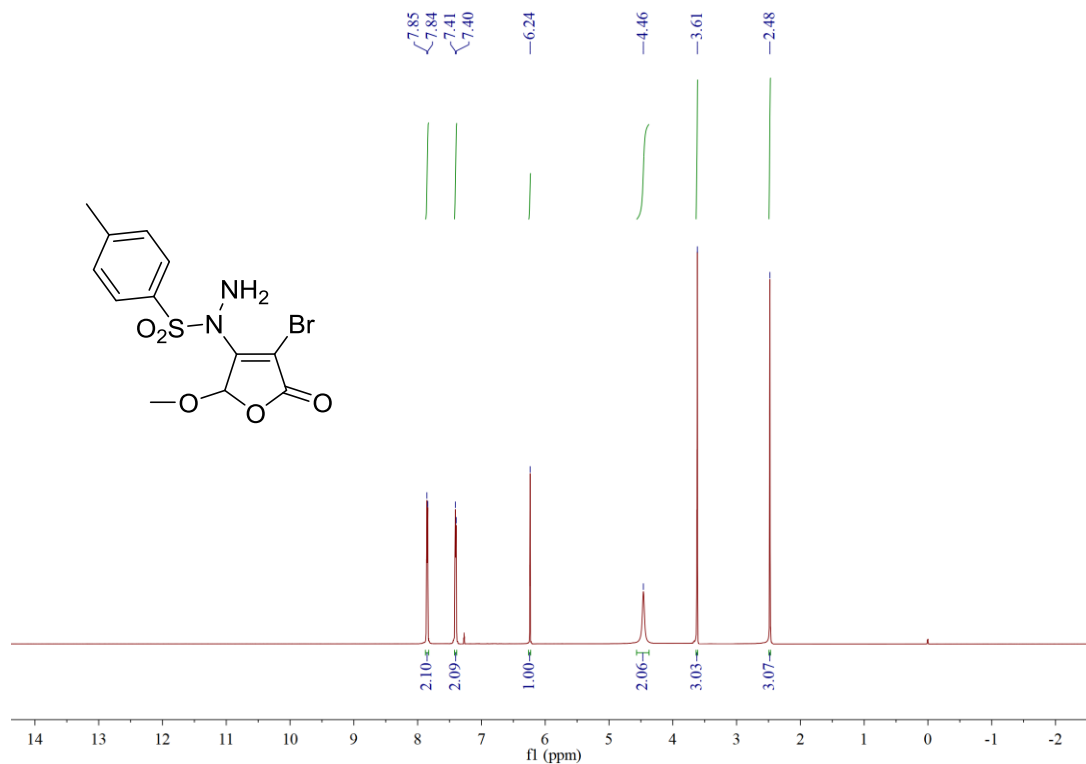
**Fig. S4.** The molecular structure of compound **3a**.

**Table S3.** Crystal data and structure refinement for intermediate **A**.

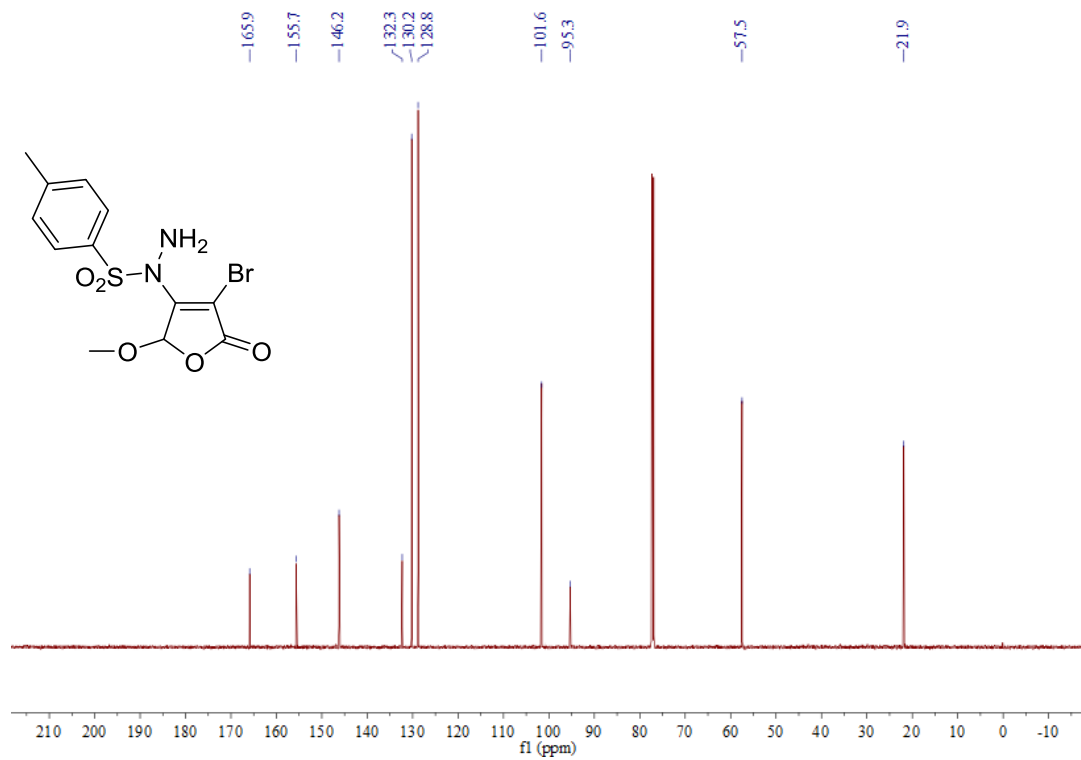
Compound	Intermediate <b>A</b>
Empirical formula	C <sub>12</sub> H <sub>14</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>3</sub>
Formula weight	394.07
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 2 <sub>1</sub> /n
Unit cell dimensions (Å, °)	$a = 8.8741(11)$ , $b = 7.9880(12)$ , $c = 21.034(3)$ $\alpha = 90$ , $\beta = 96.975(12)$ , $\gamma = 90$
Volume (Å <sup>3</sup> )	1480.0(3)
Z	4
Density (calculated) (Mg/m <sup>3</sup> )	1.769
Absorption coefficient (mm <sup>-1</sup> )	5.482
F(000)	776.0
Crystal size (mm <sup>3</sup> )	0.32 x 0.18 x 0.11
Theta range for data collection	7.002 to 53.984 deg
Index ranges	-11 ≤ h ≤ 10, -10 ≤ k ≤ 9, -25 ≤ l ≤ 26
Reflections collected	9145
Independent reflections	3418 [R(int) = 0.0298, R(sigma) = 0.1140]
Completeness to theta	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.24228
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3180 / 1 / 179
Goodness-of-fit on F <sup>2</sup>	0.998
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0611, wR <sub>2</sub> = 0.1076
R indices (all data)	R <sub>1</sub> = 0.1347, wR <sub>2</sub> = 0.1367
Extinction coefficient	n/a
Largest diff. peak and hole (e.Å <sup>-3</sup> )	0.486 and -0.67

**Fig. S5.** The molecular structure of intermediate **A**.

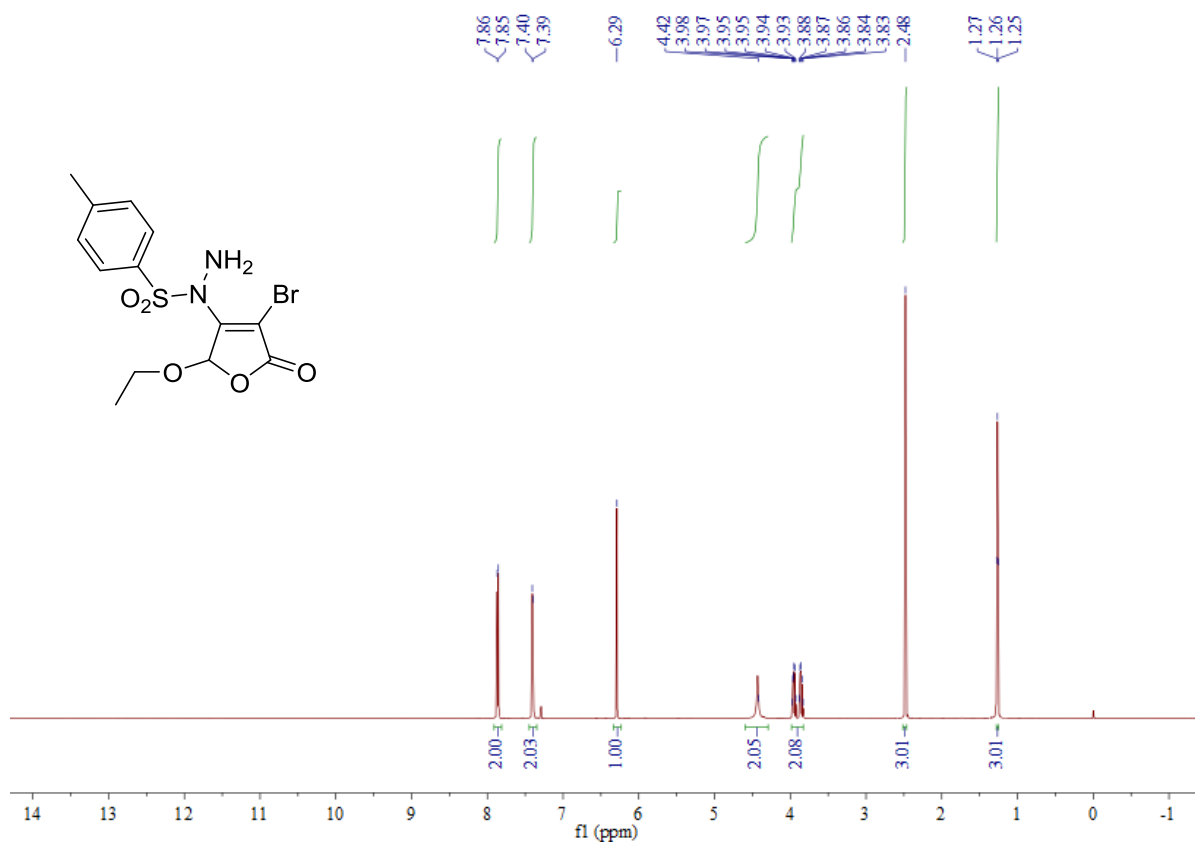
## NMR Spectra for All Compounds 3a-3v, 4a-4s and Intermediate A



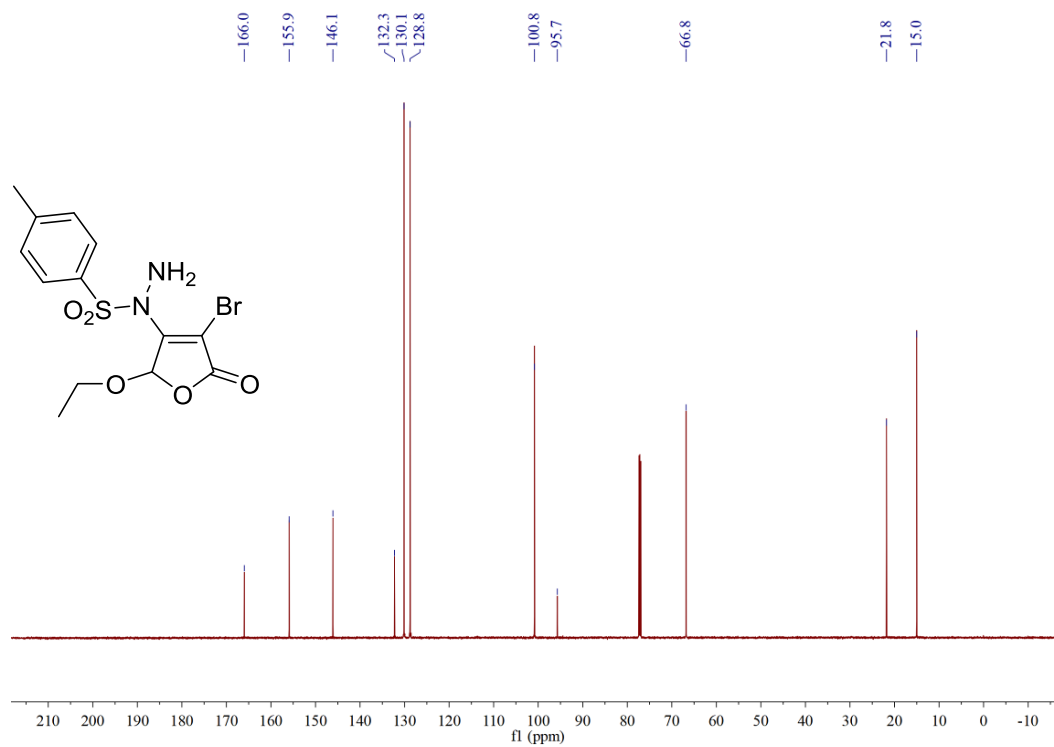
<sup>1</sup>H NMR spectrum of compound 3a



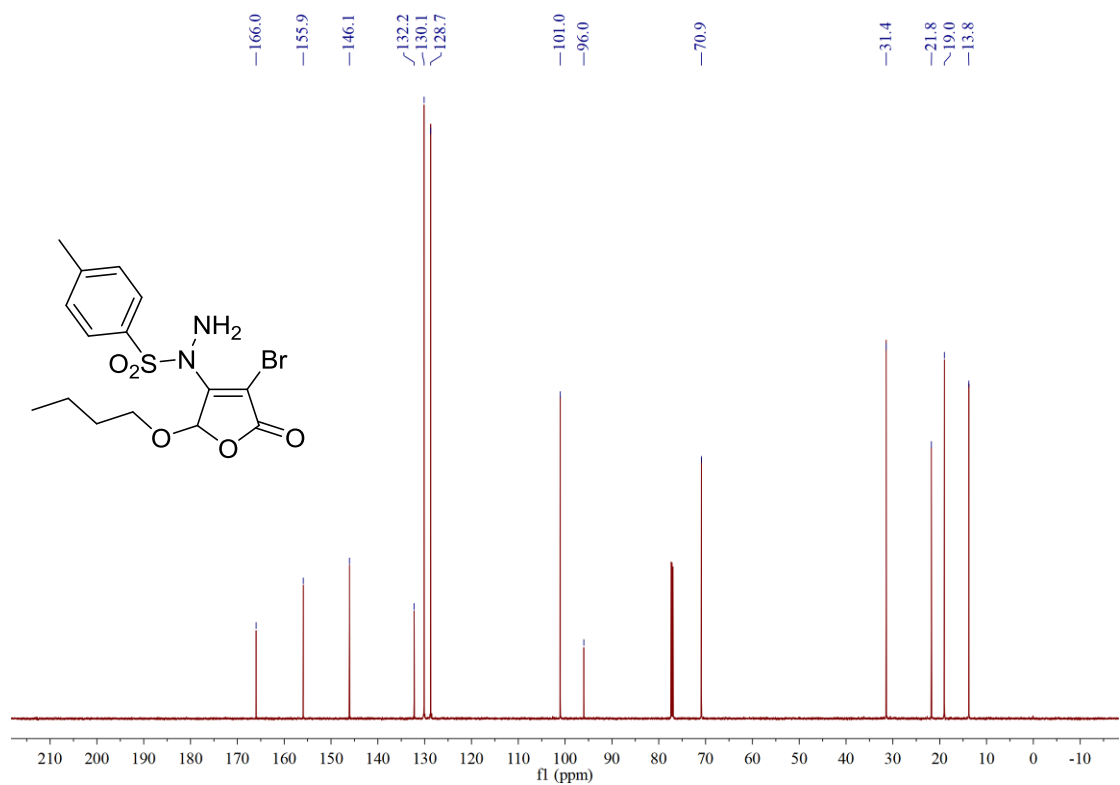
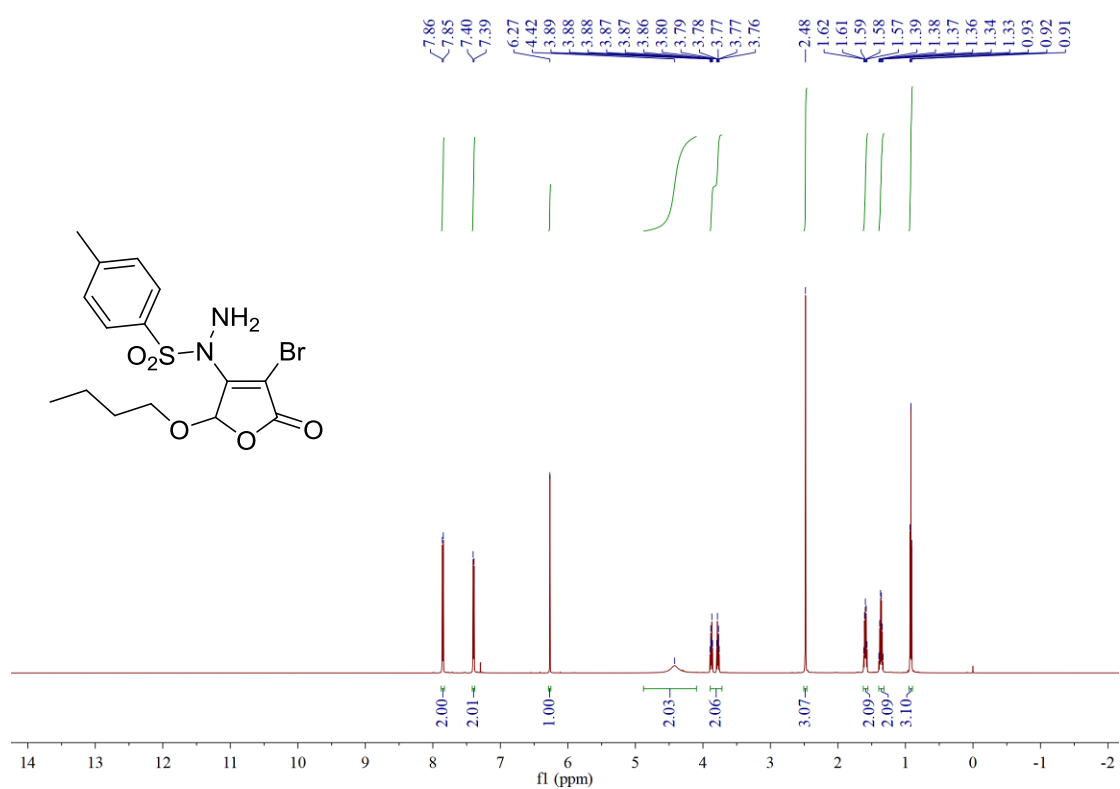
<sup>13</sup>C NMR spectrum of compound 3a



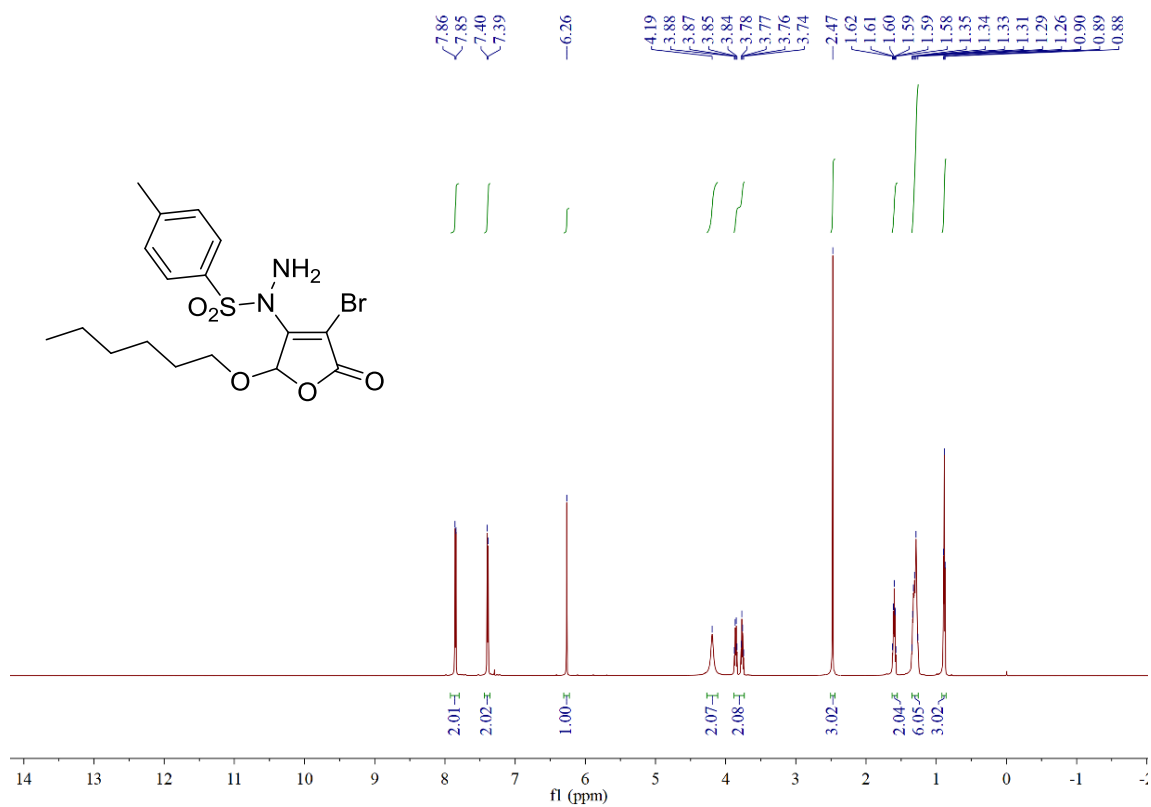
<sup>1</sup>H NMR spectrum of compound **3b**



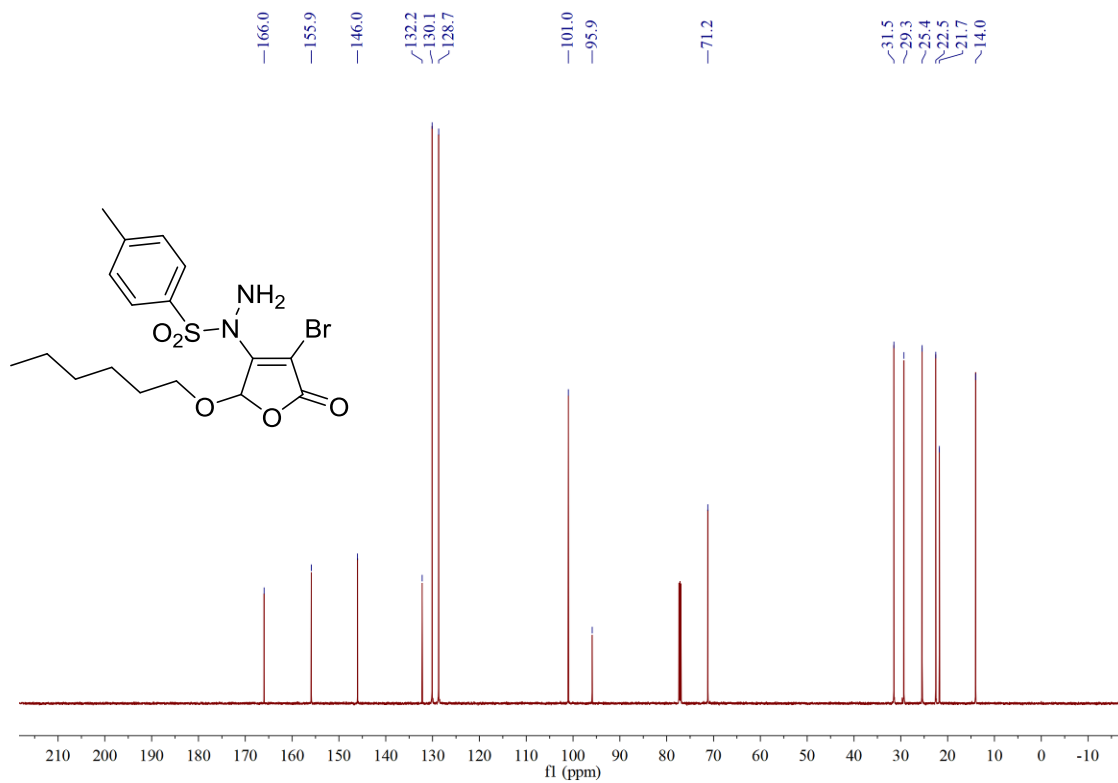
<sup>13</sup>C NMR spectrum of compound **3b**



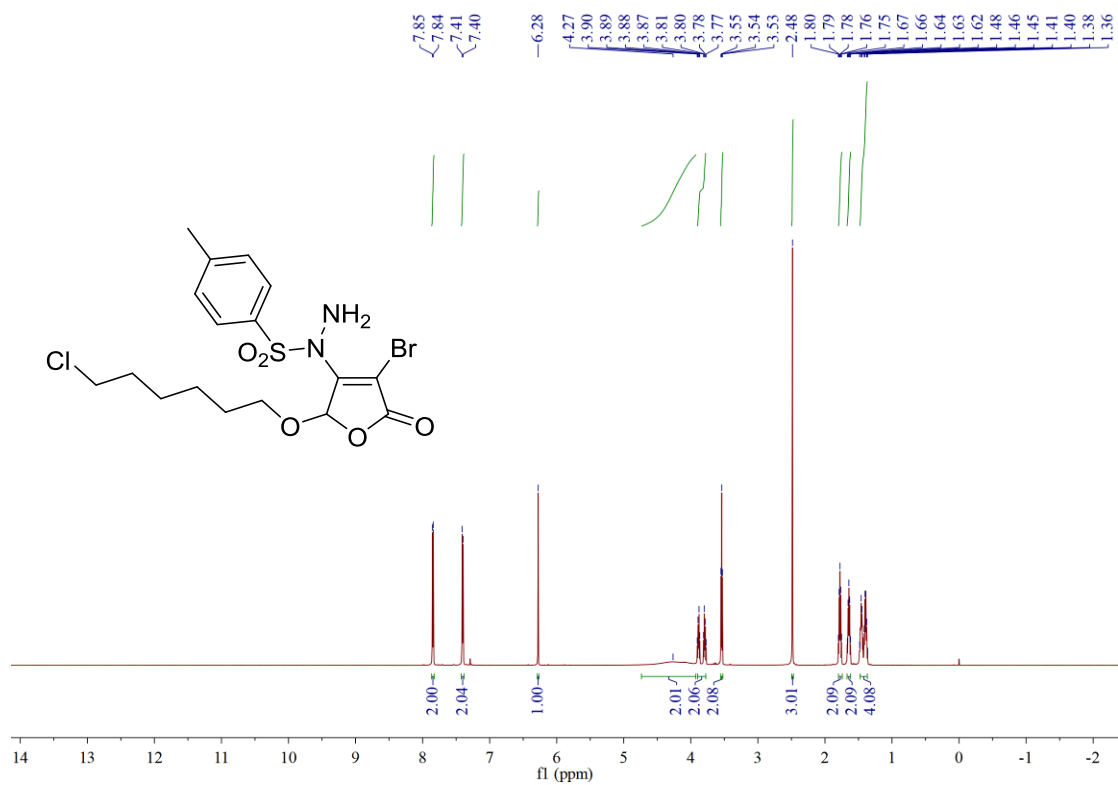




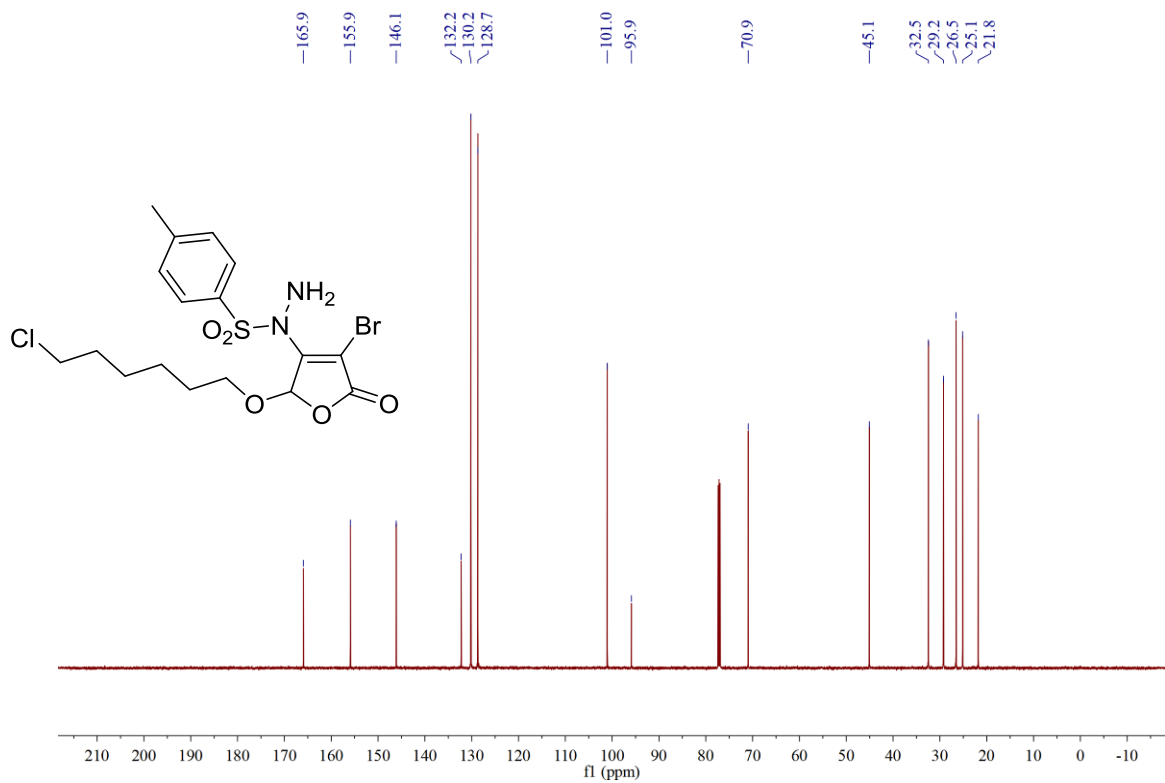
**<sup>1</sup>H NMR spectrum of compound 3d**



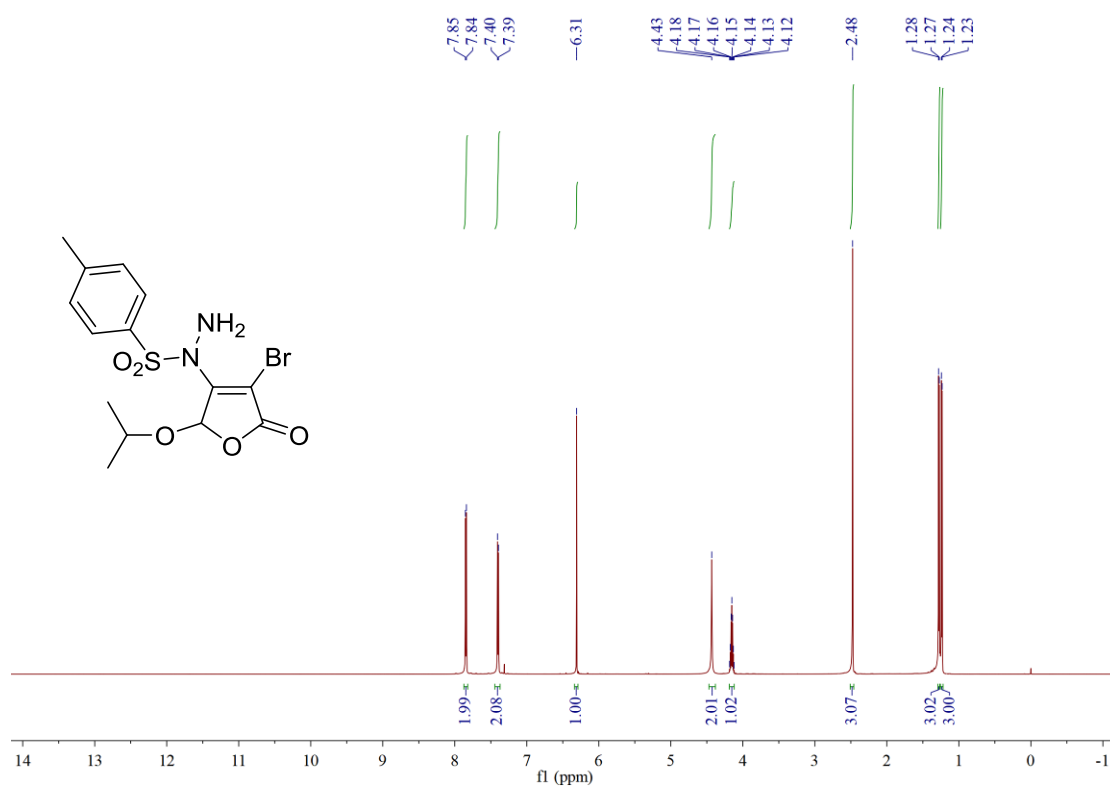
**<sup>13</sup>C NMR spectrum of compound 3d**



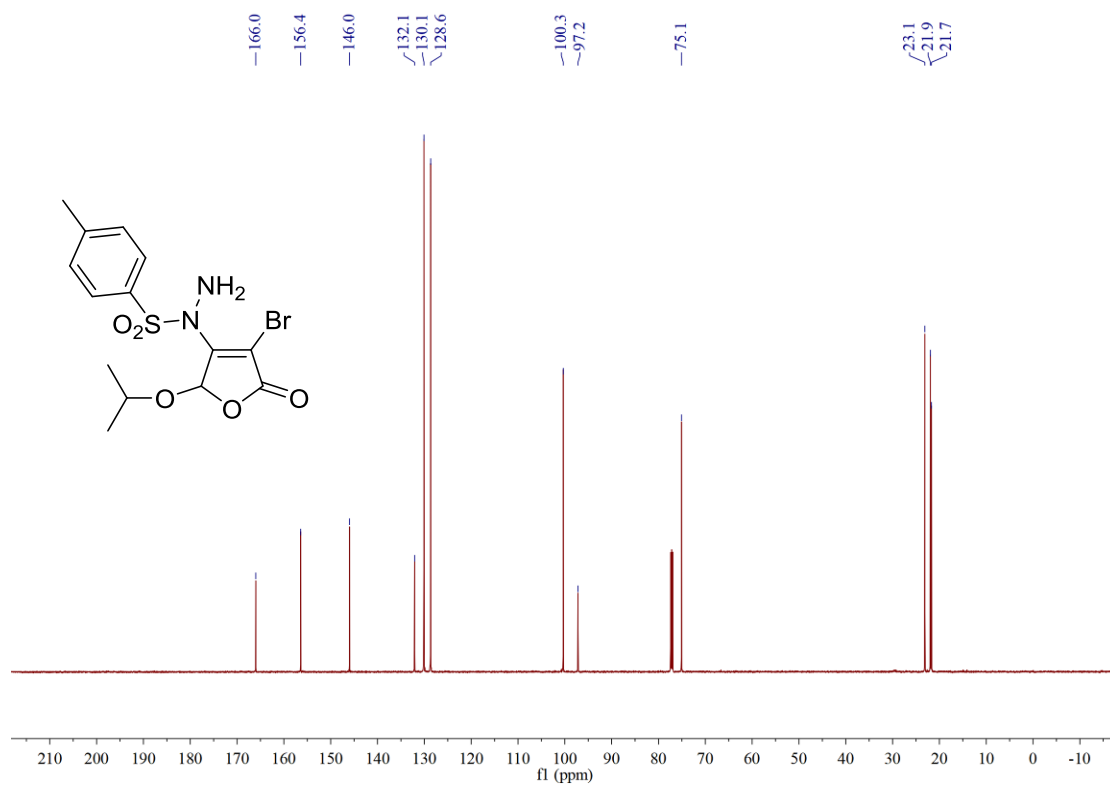
<sup>1</sup>H NMR spectrum of compound 3e



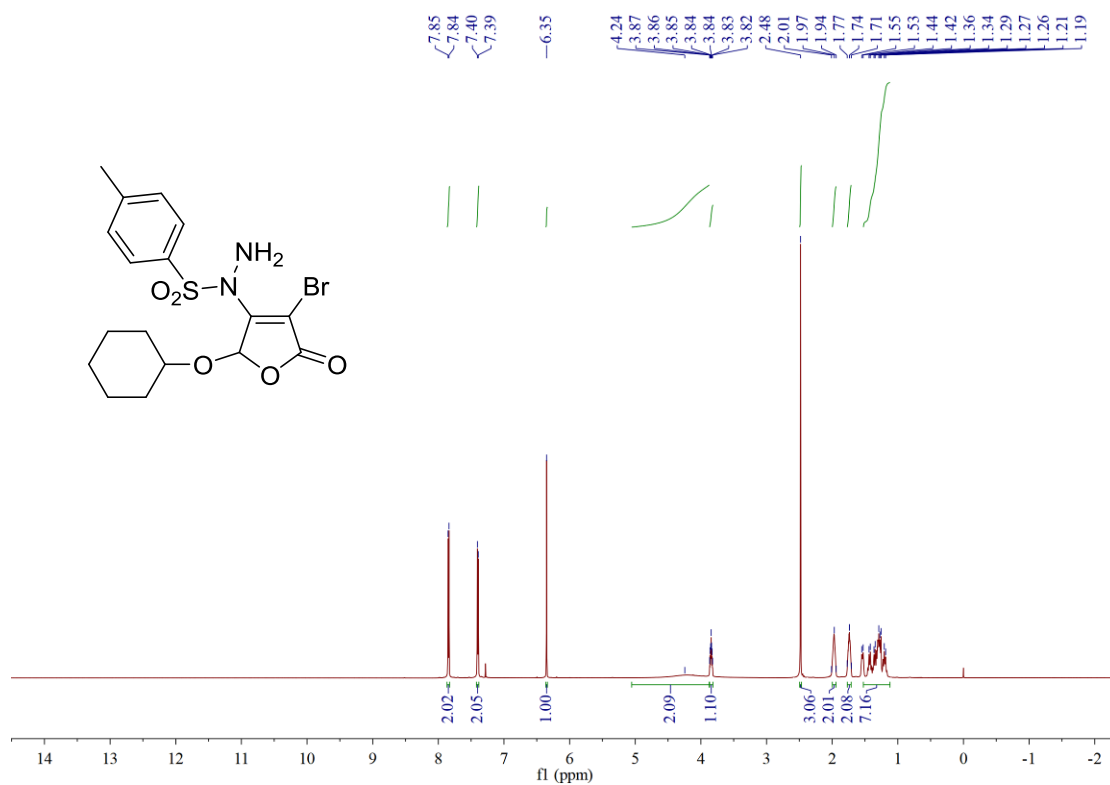
<sup>13</sup>C NMR spectrum of compound 3e



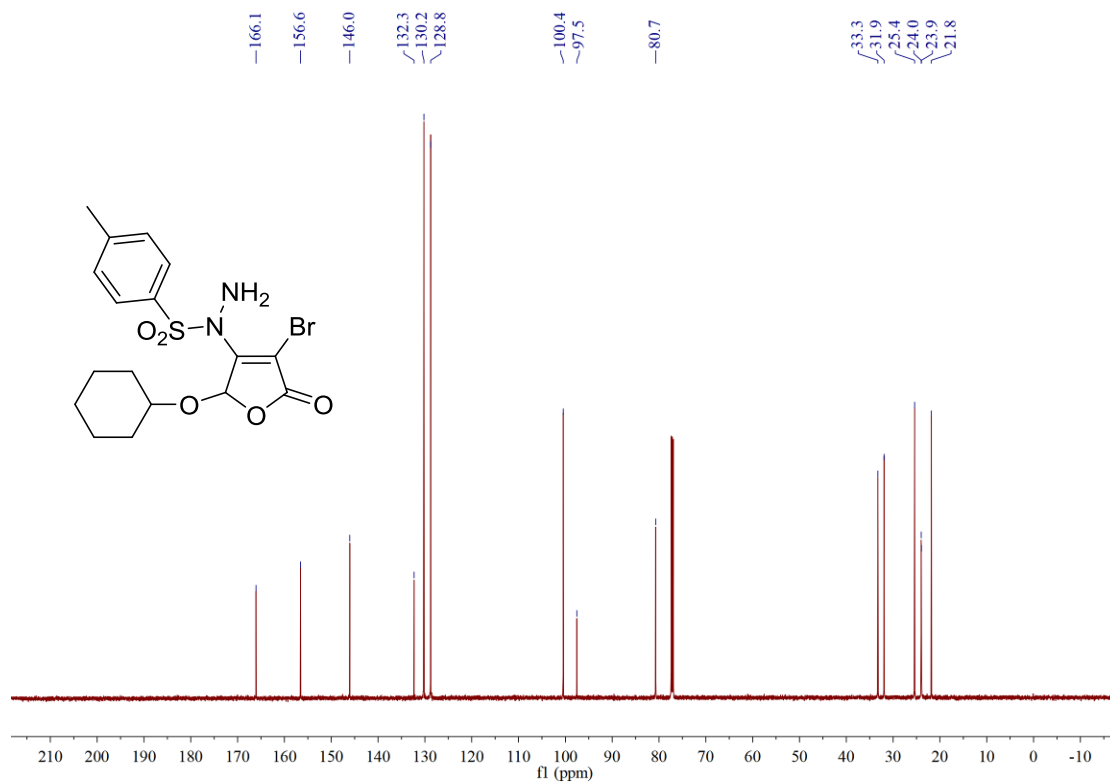
<sup>1</sup>H NMR spectrum of compound **3f**



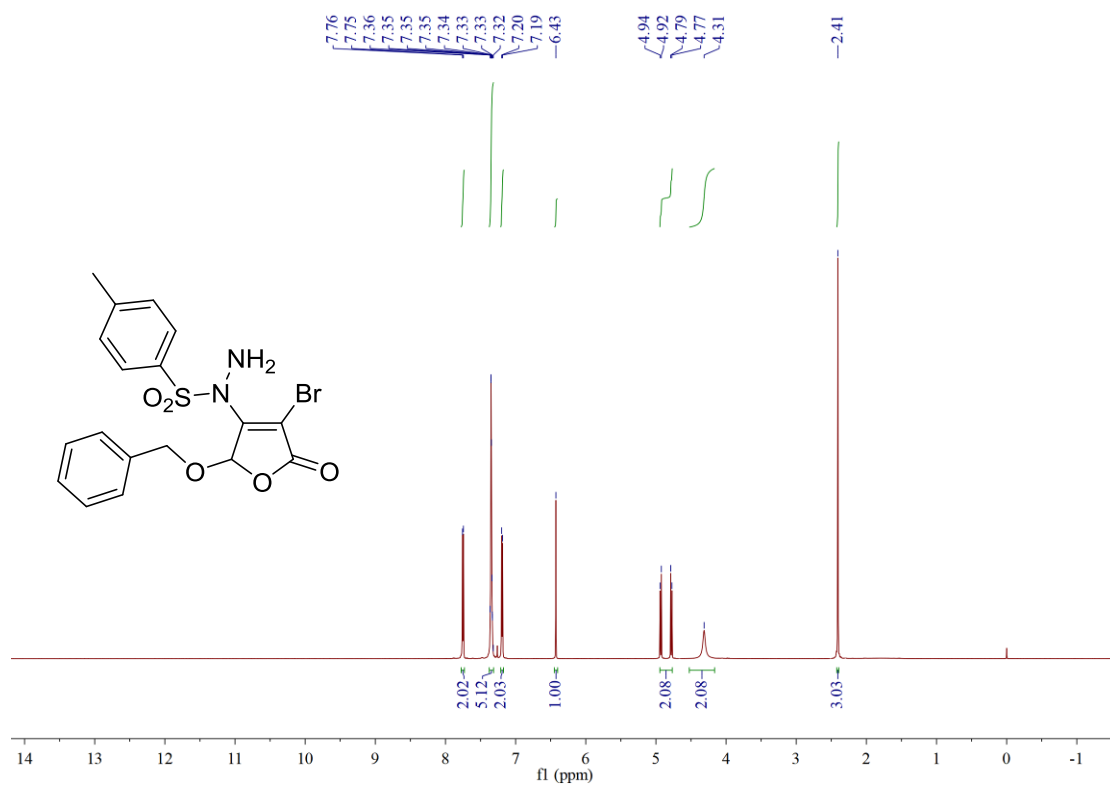
<sup>13</sup>C NMR spectrum of compound **3f**



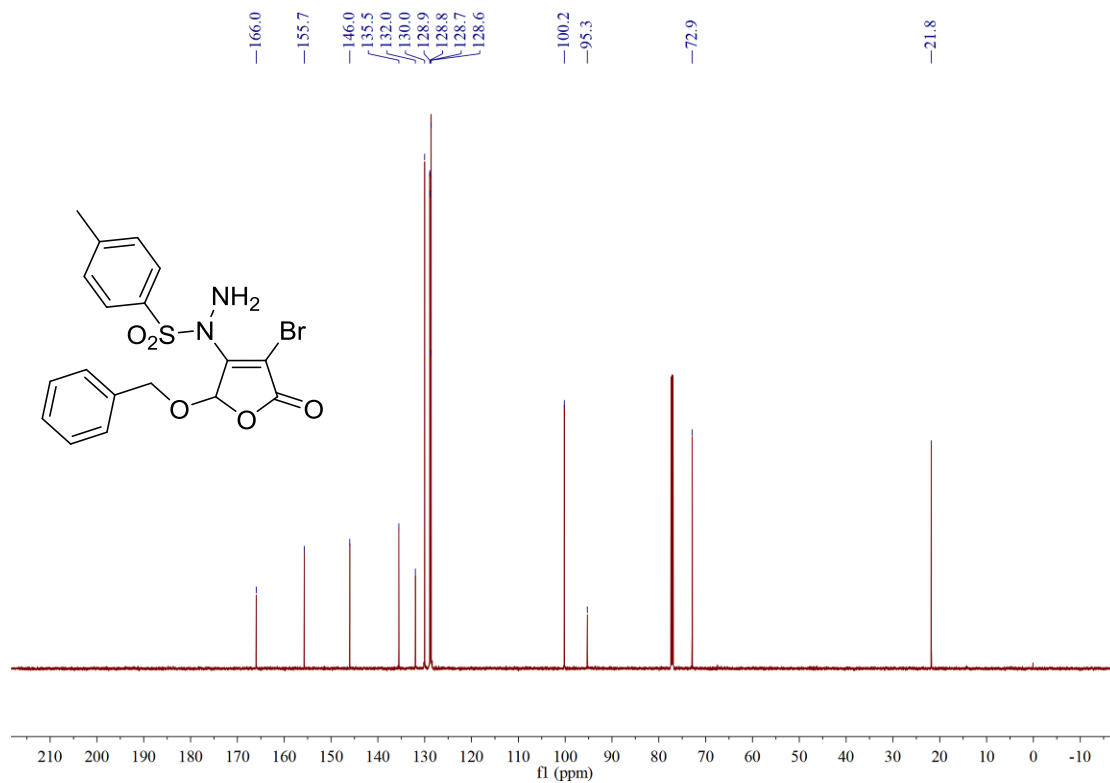
**<sup>1</sup>H NMR spectrum of compound 3g**



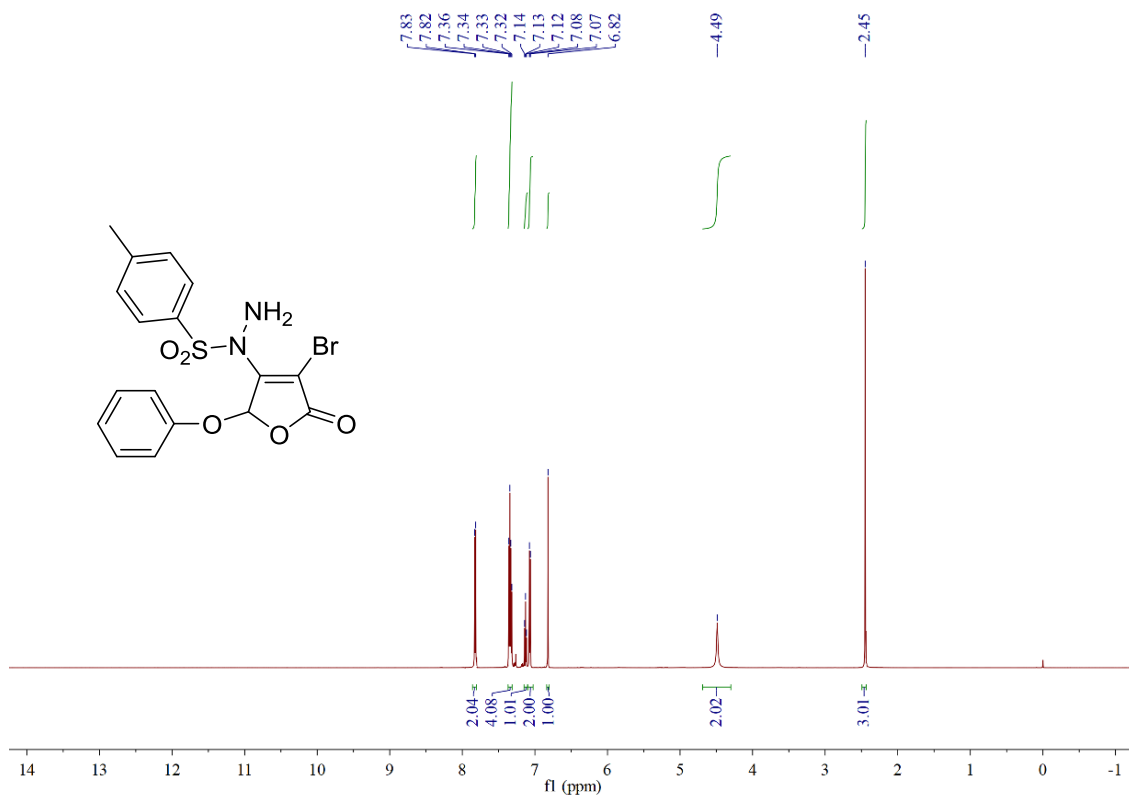
**<sup>13</sup>C NMR spectrum of compound 3g**



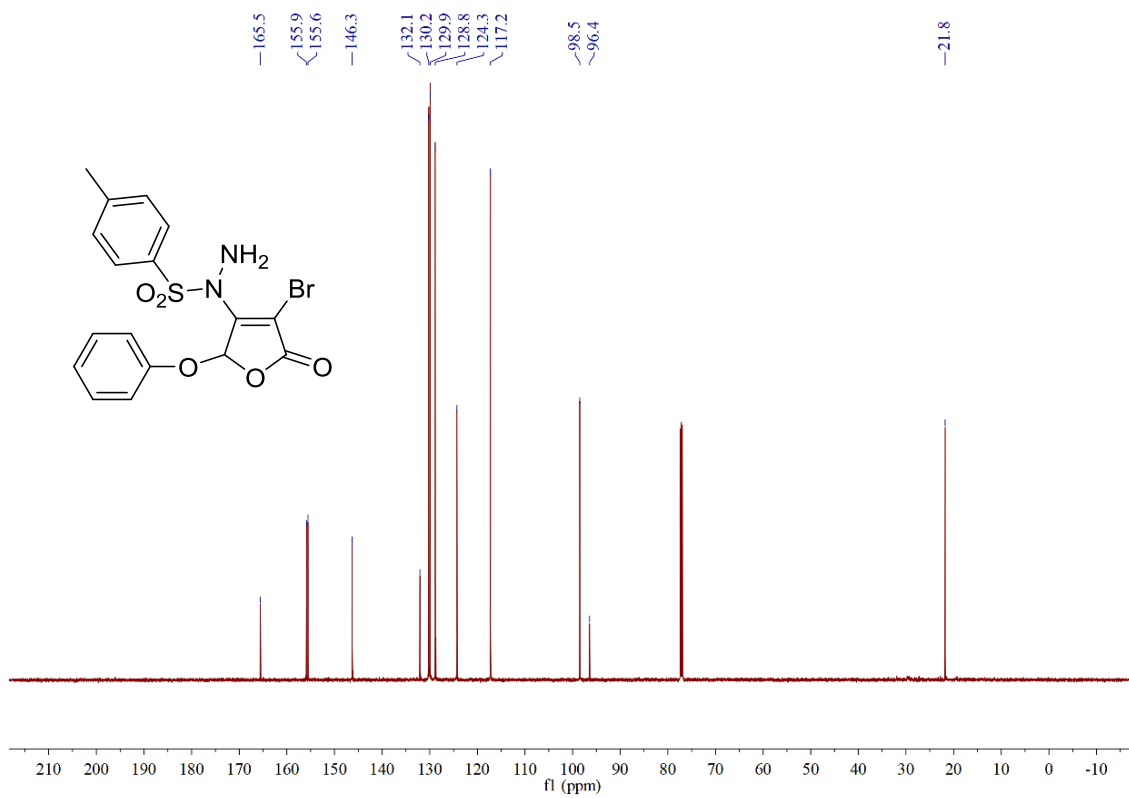
<sup>1</sup>H NMR spectrum of compound **3h**



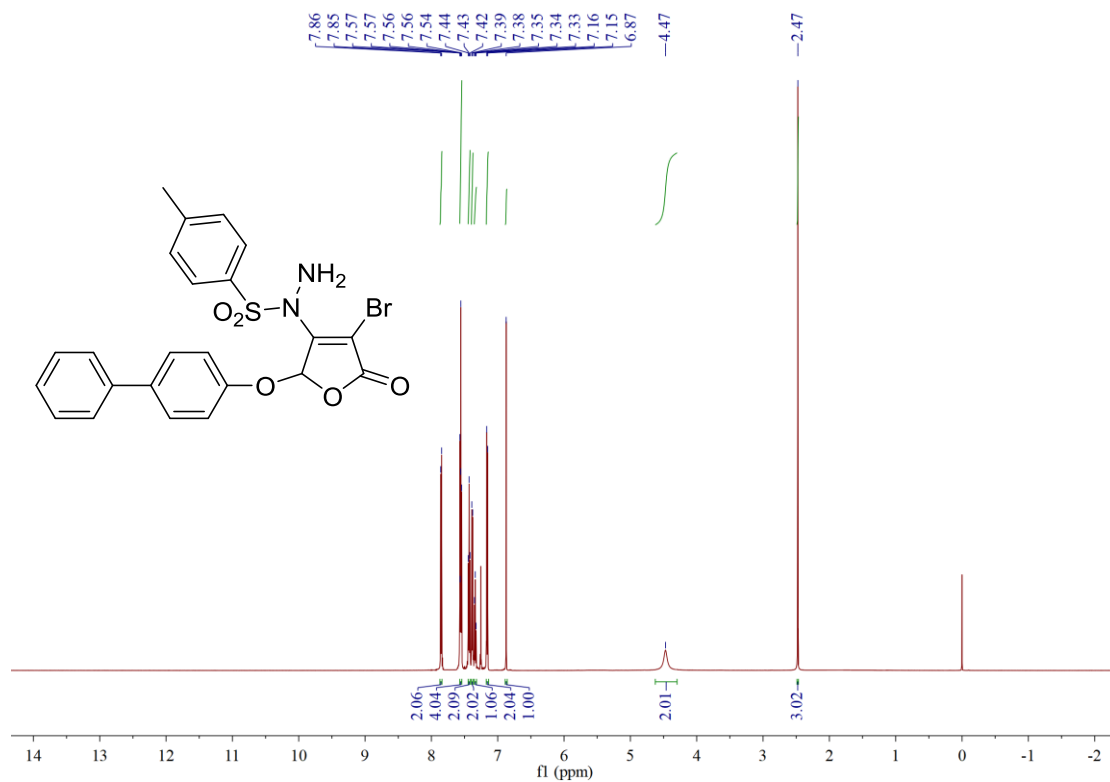
<sup>13</sup>C NMR spectrum of compound **3h**



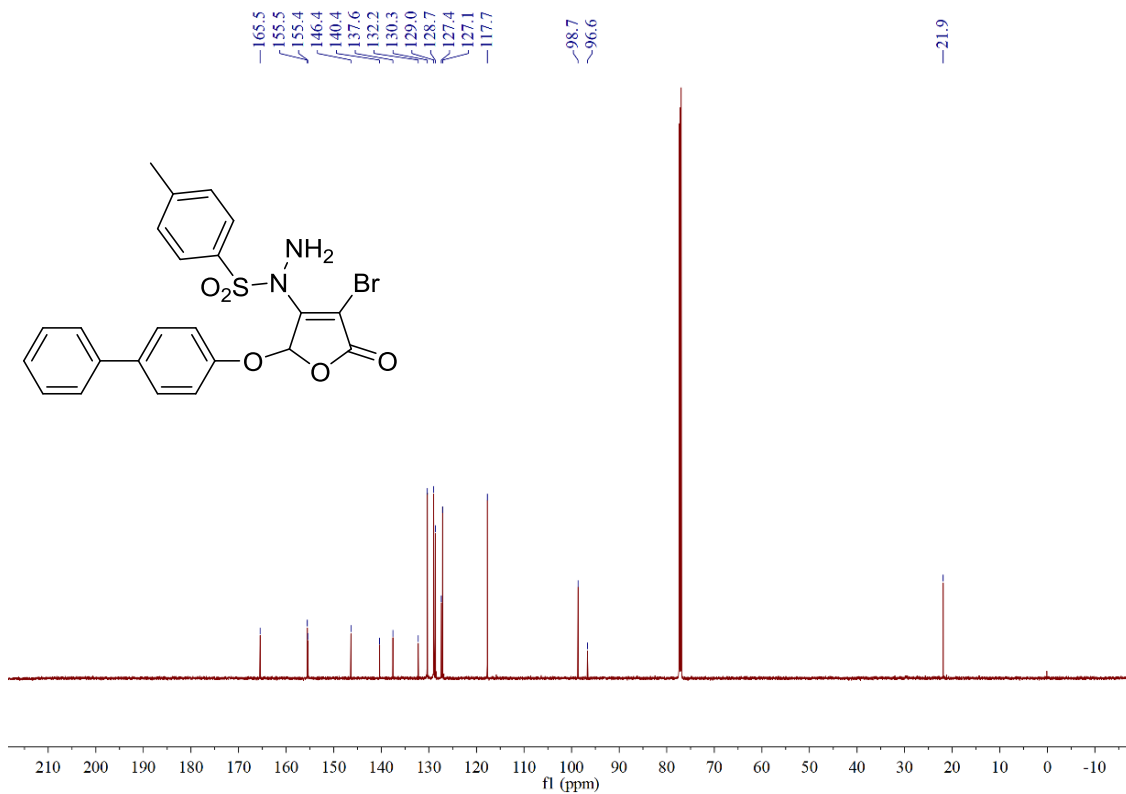
<sup>1</sup>H NMR spectrum of compound 3i



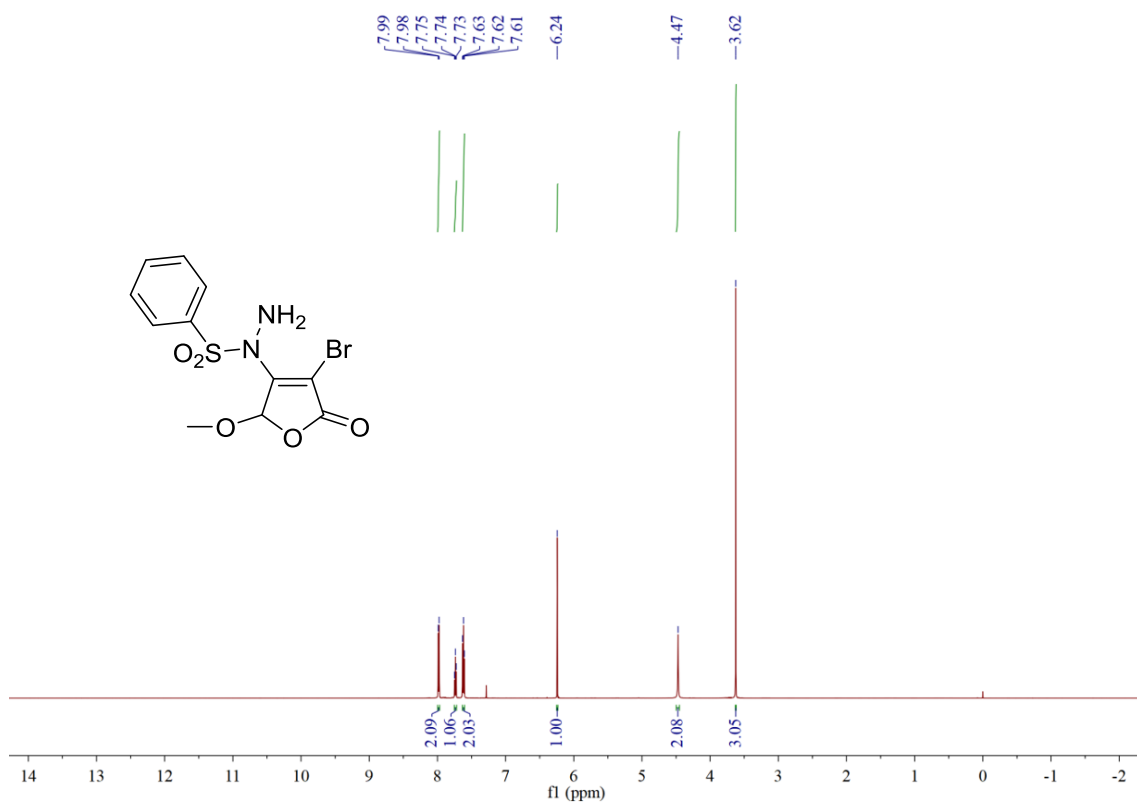
<sup>13</sup>C NMR spectrum of compound 3i



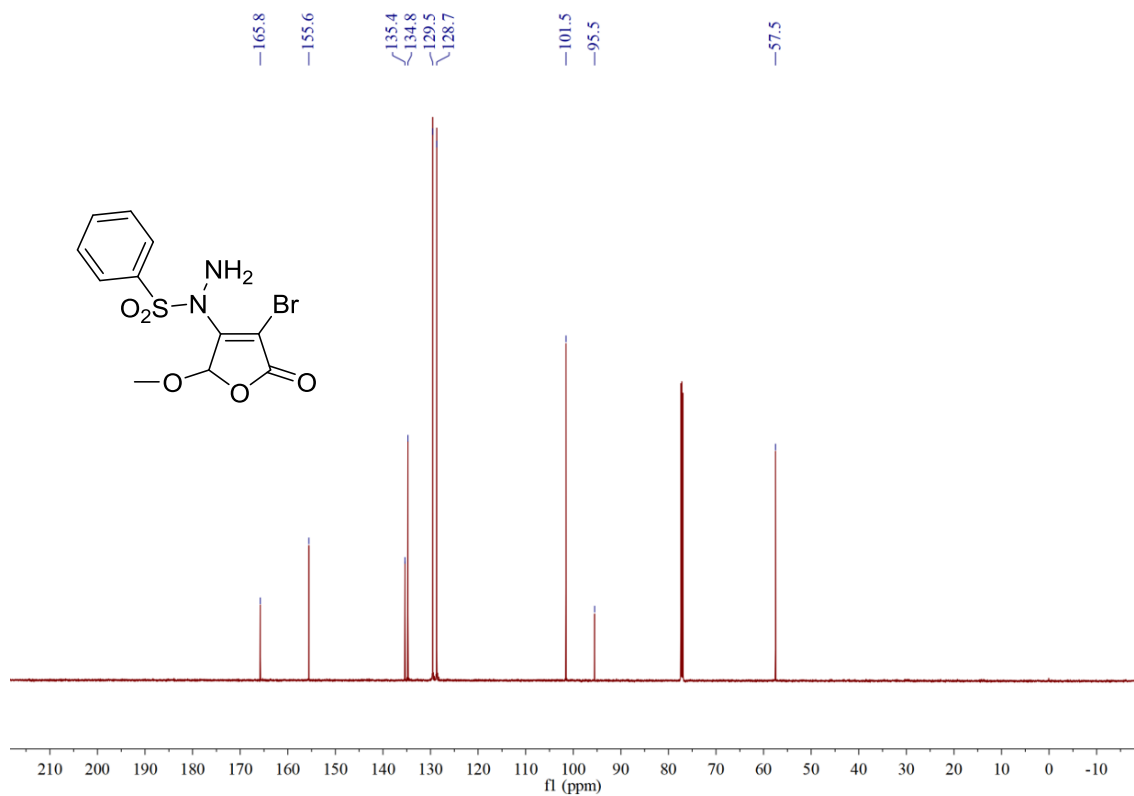
<sup>1</sup>H NMR spectrum of compound 3j



<sup>13</sup>C NMR spectrum of compound 3j

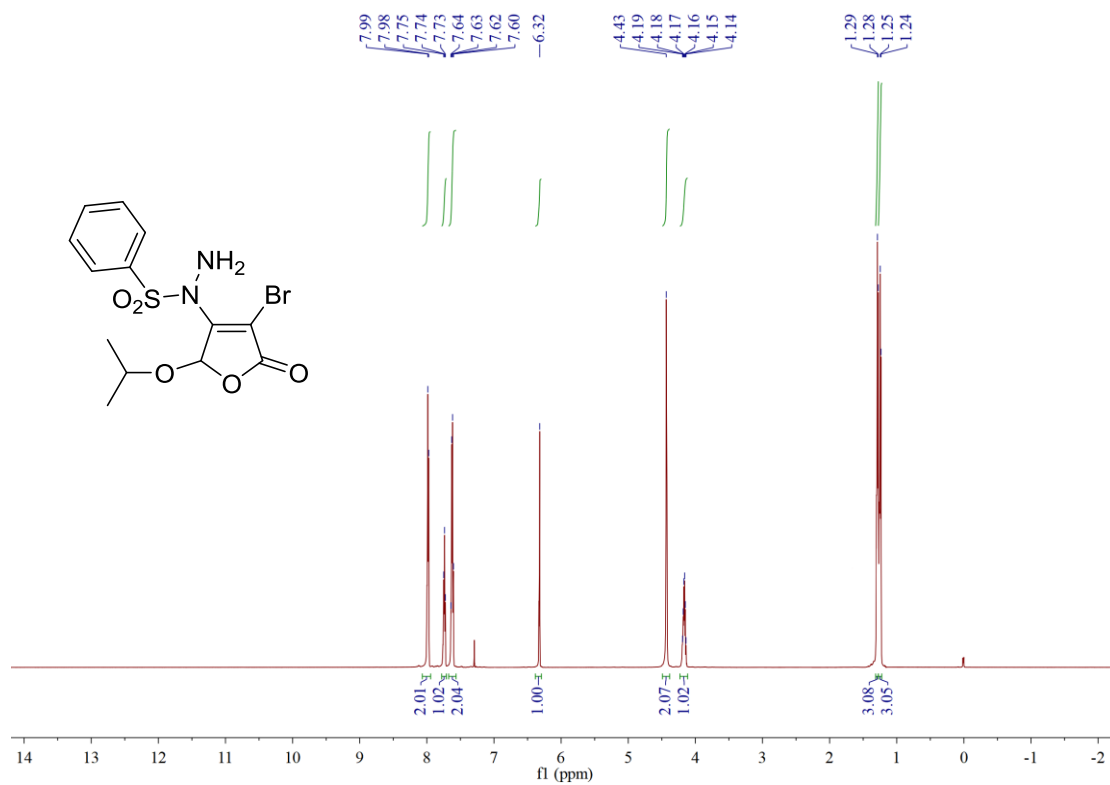


<sup>1</sup>H NMR spectrum of compound **3k**

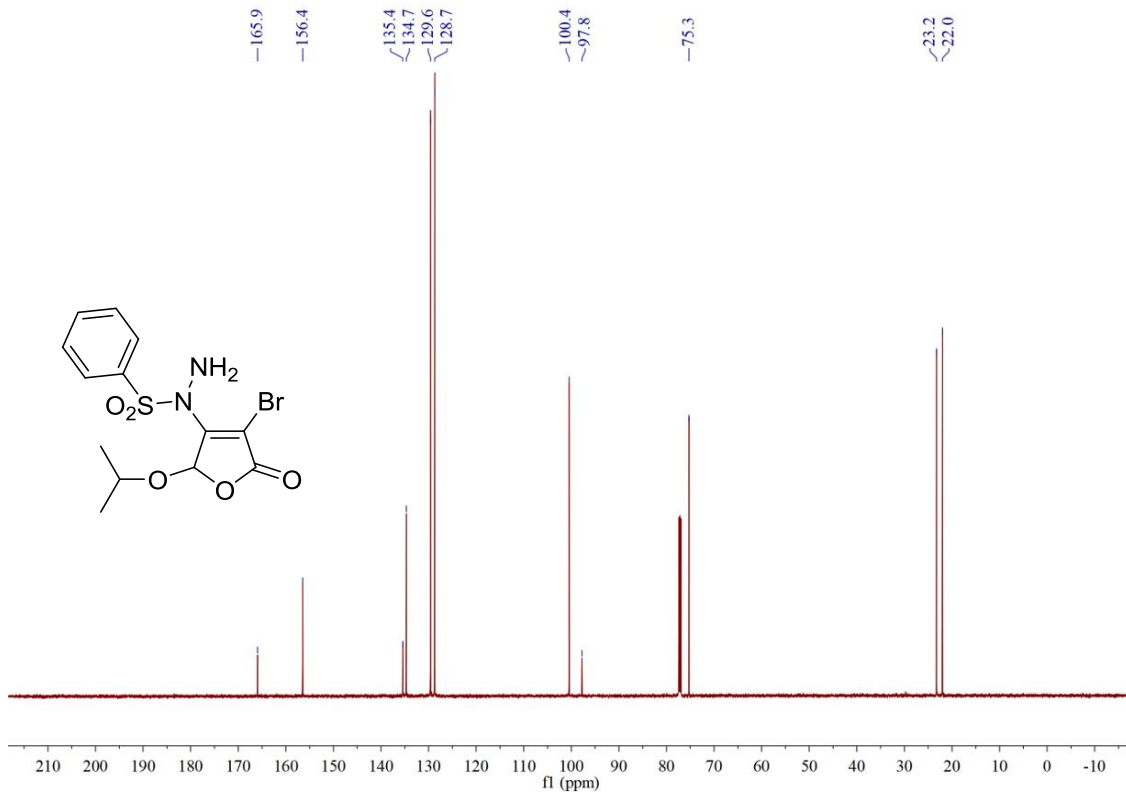


<sup>13</sup>C NMR spectrum of compound **3k**

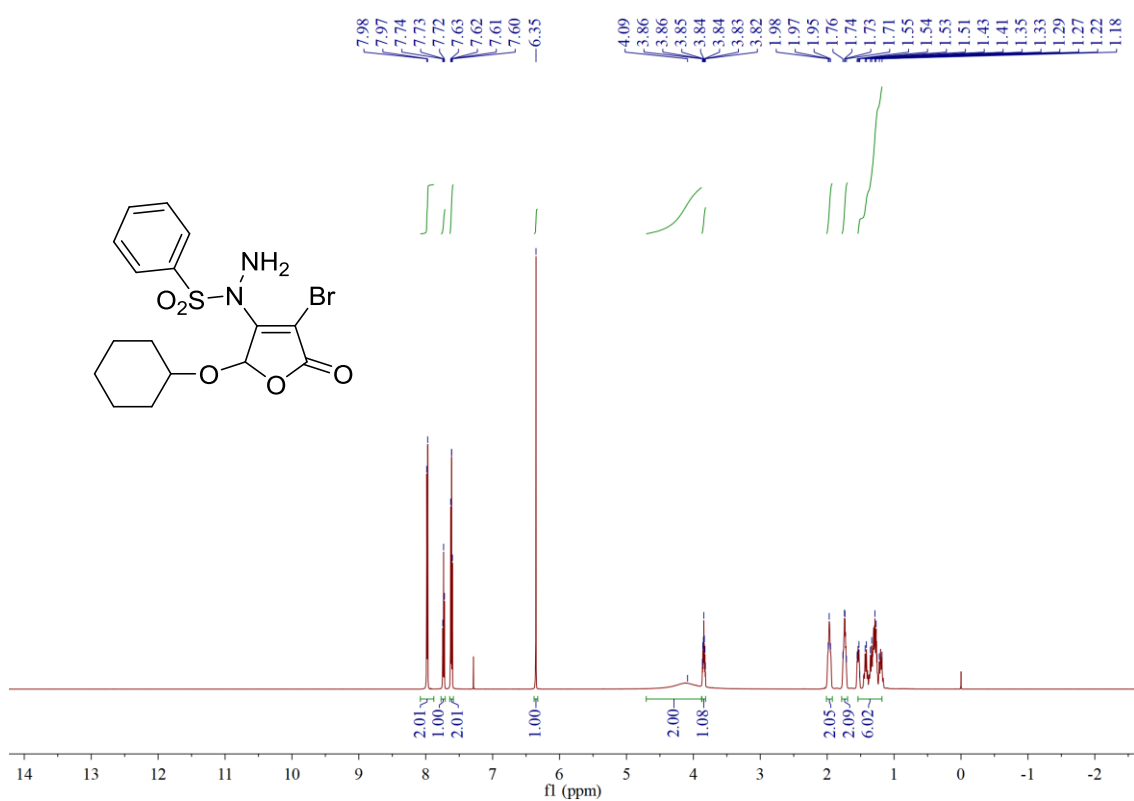




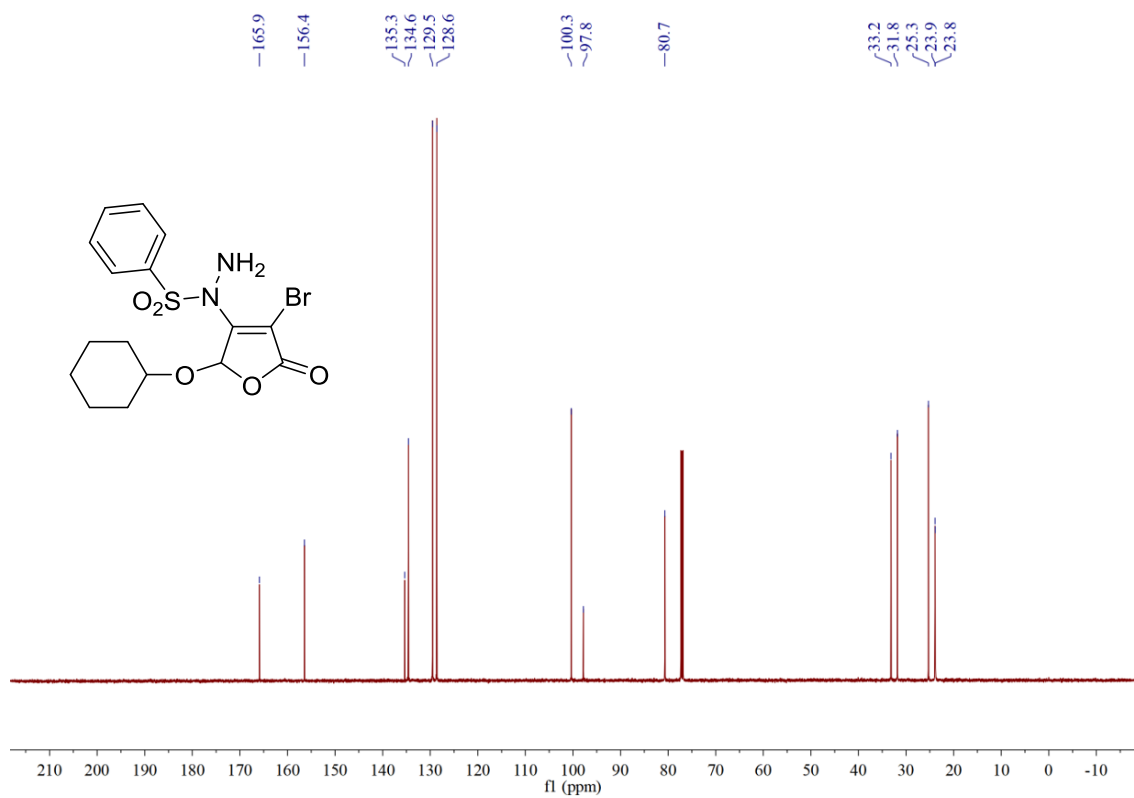
**<sup>1</sup>H NMR spectrum of compound 31**



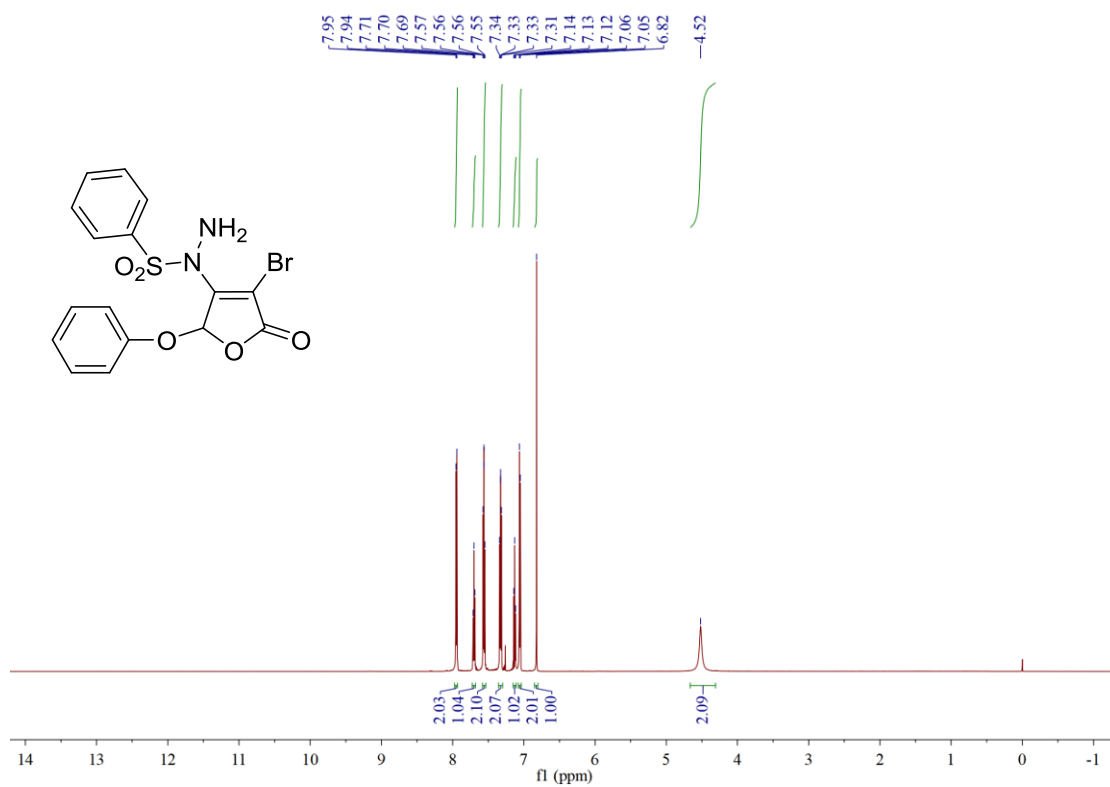
**<sup>13</sup>C NMR spectrum of compound 31**



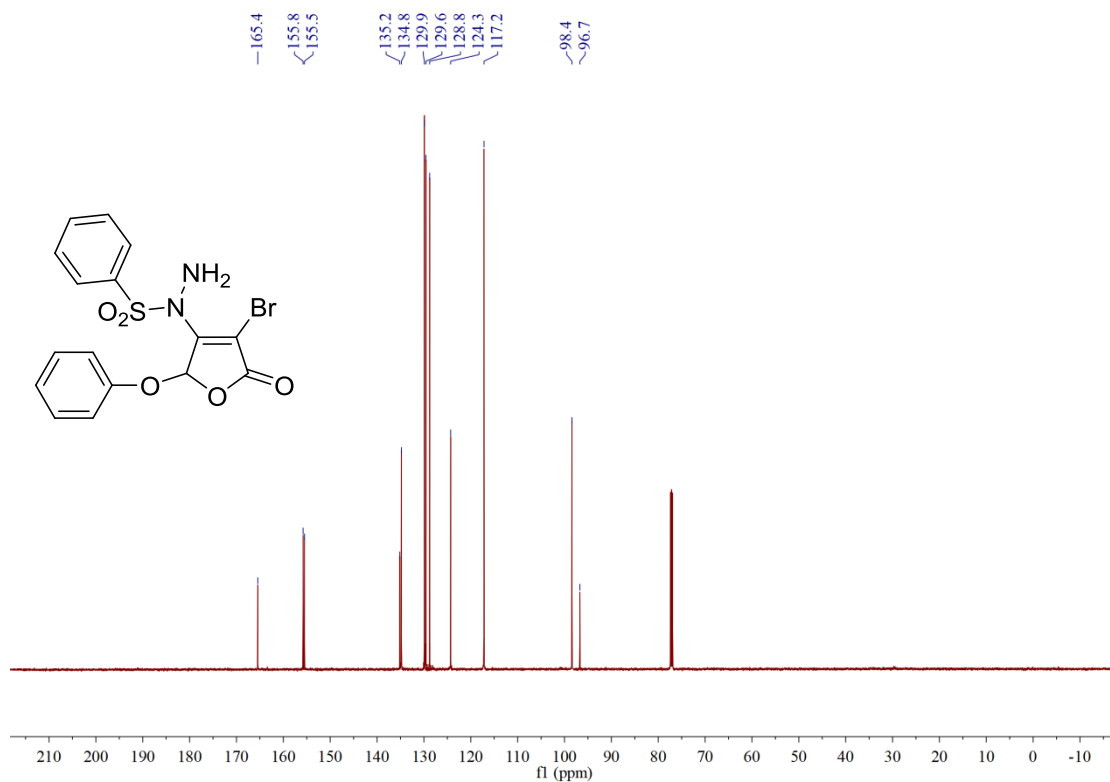
**<sup>1</sup>H NMR spectrum of compound 3m**



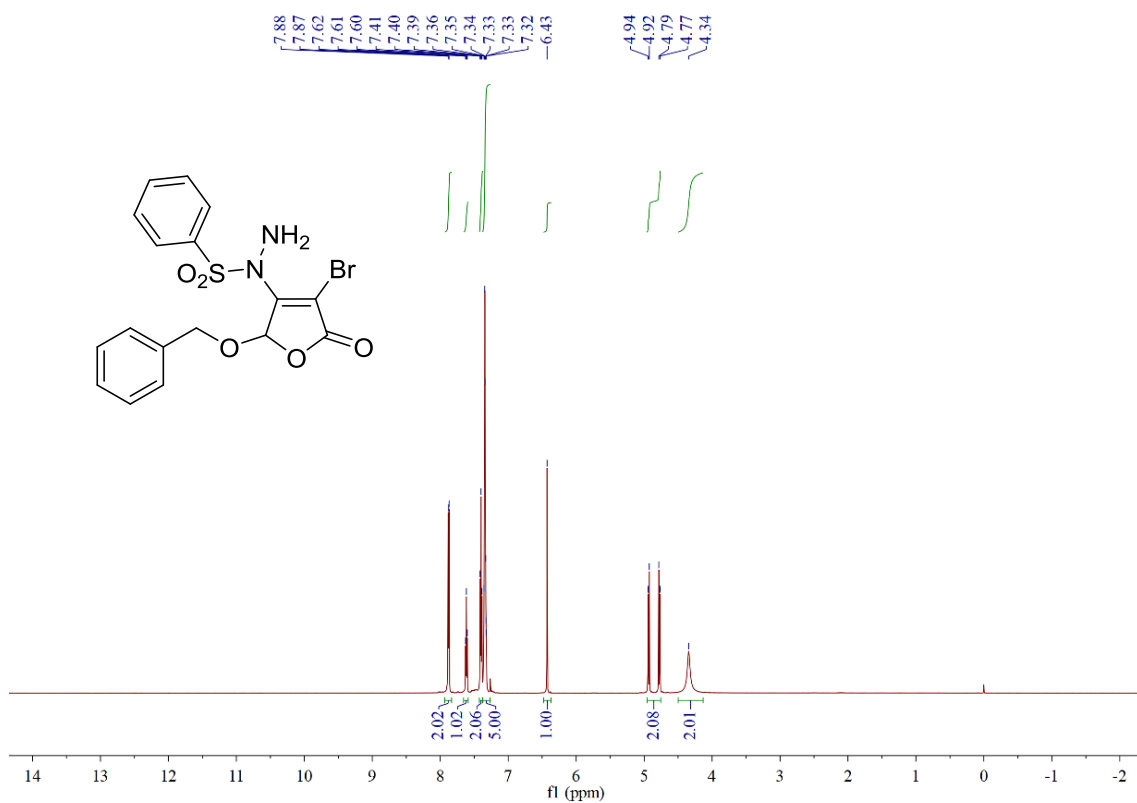
**<sup>13</sup>C NMR spectrum of compound 3m**



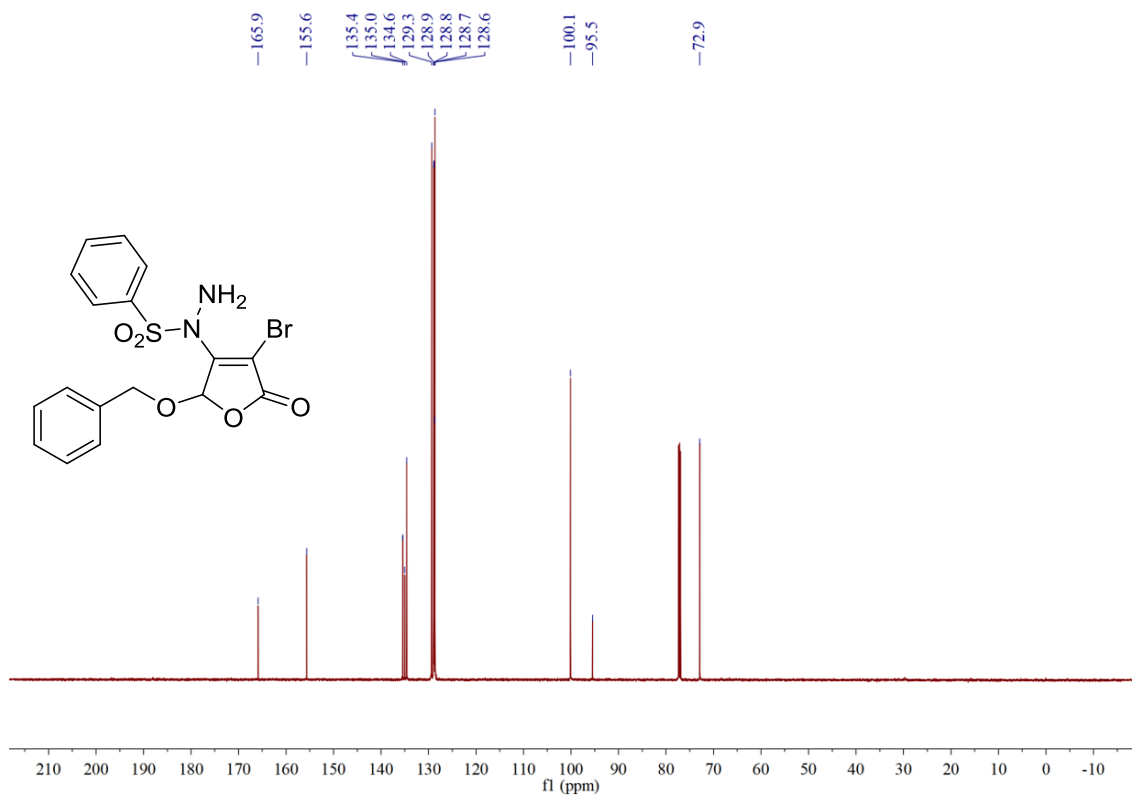
**<sup>1</sup>H NMR spectrum of compound 3n**



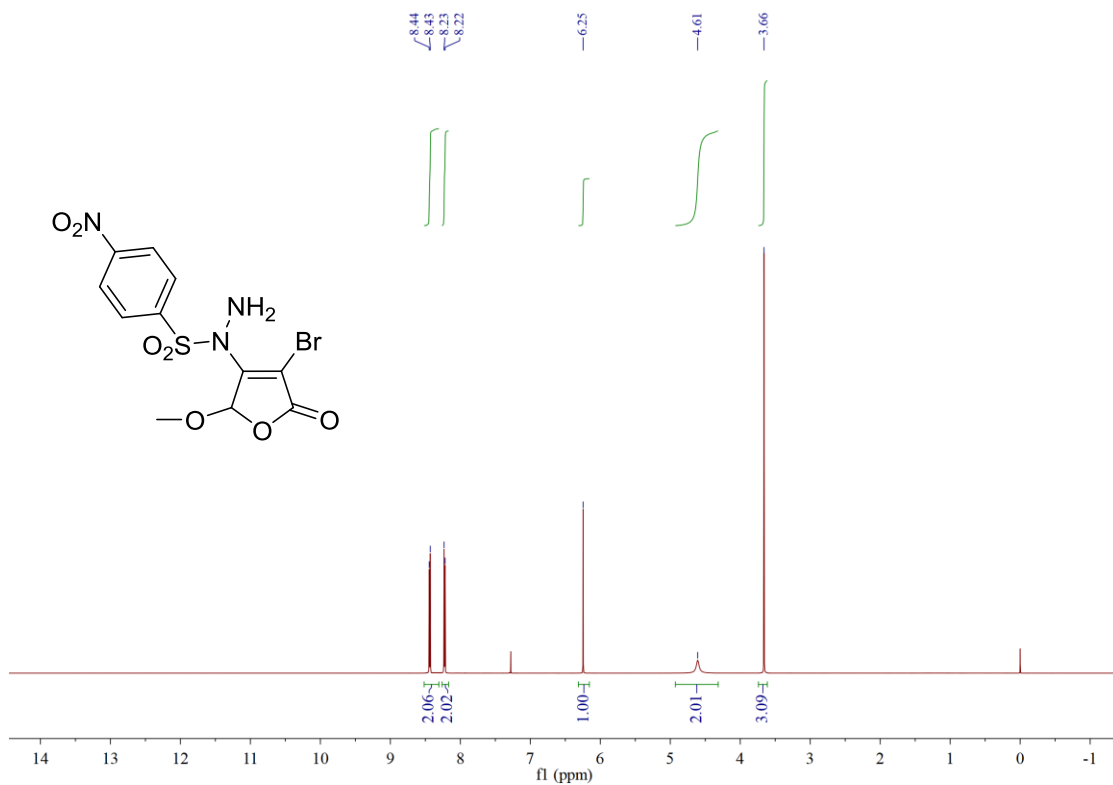
**<sup>13</sup>C NMR spectrum of compound 3n**



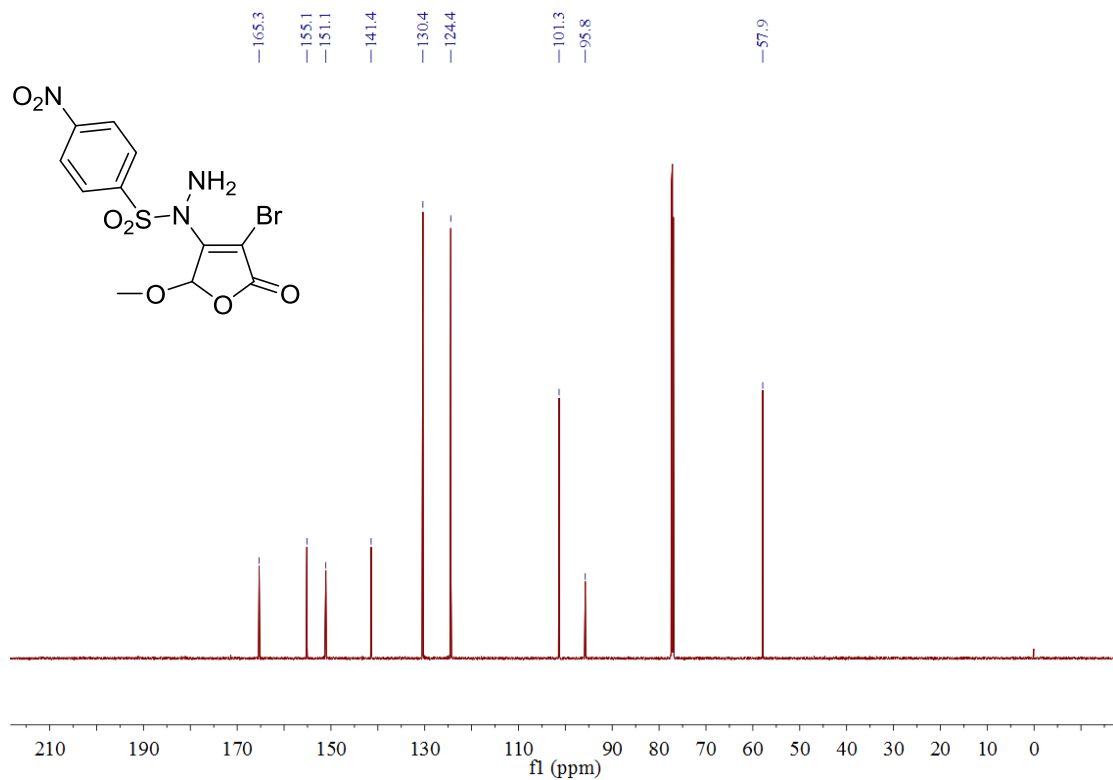
**<sup>1</sup>H NMR spectrum of compound 3o**



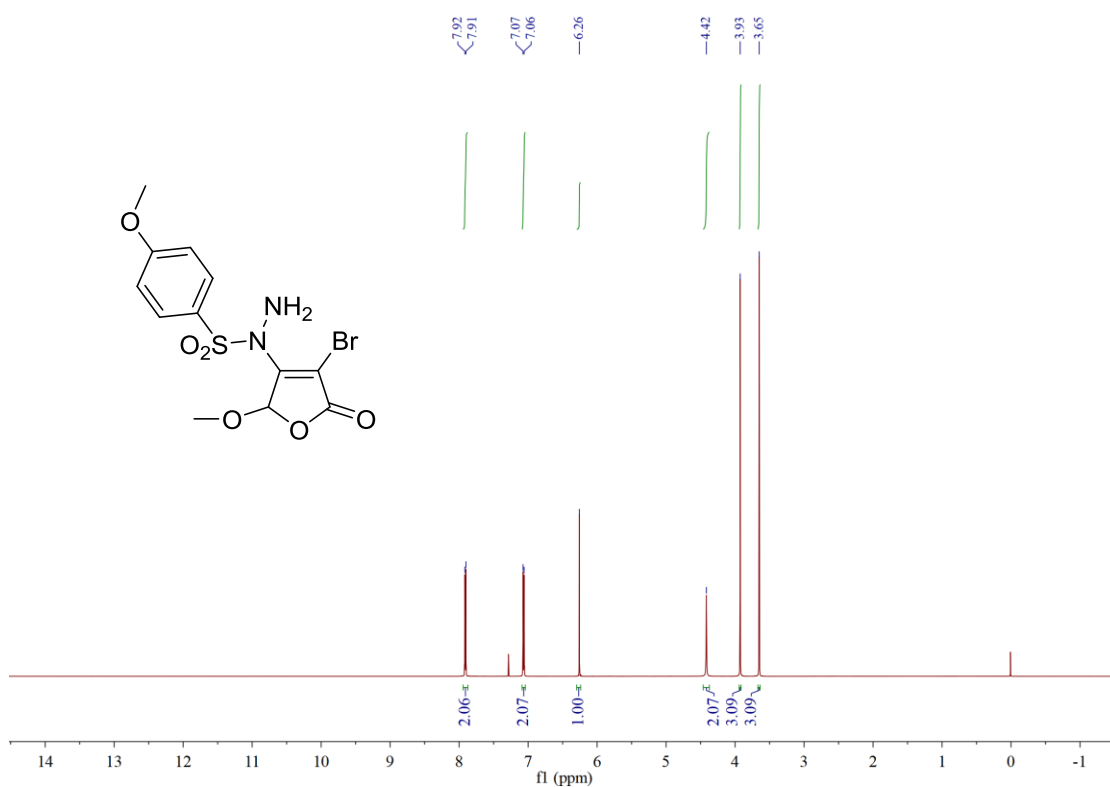
**<sup>13</sup>C NMR spectrum of compound 3o**



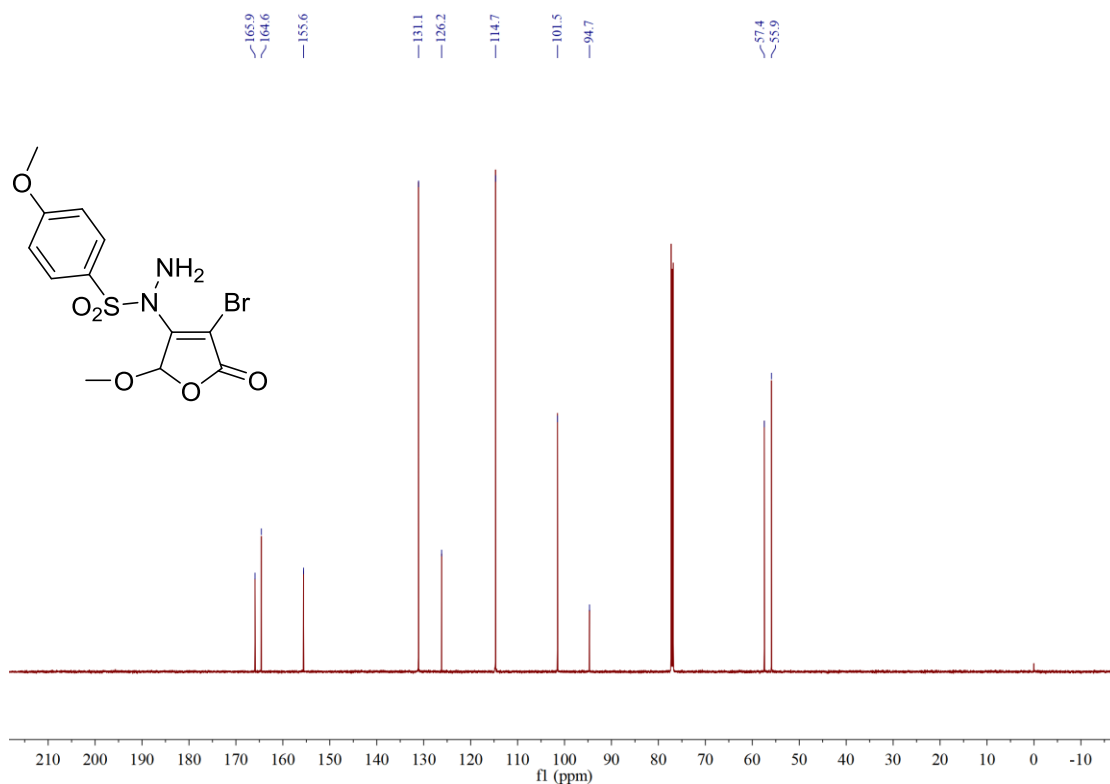
<sup>1</sup>H NMR spectrum of compound **3p**



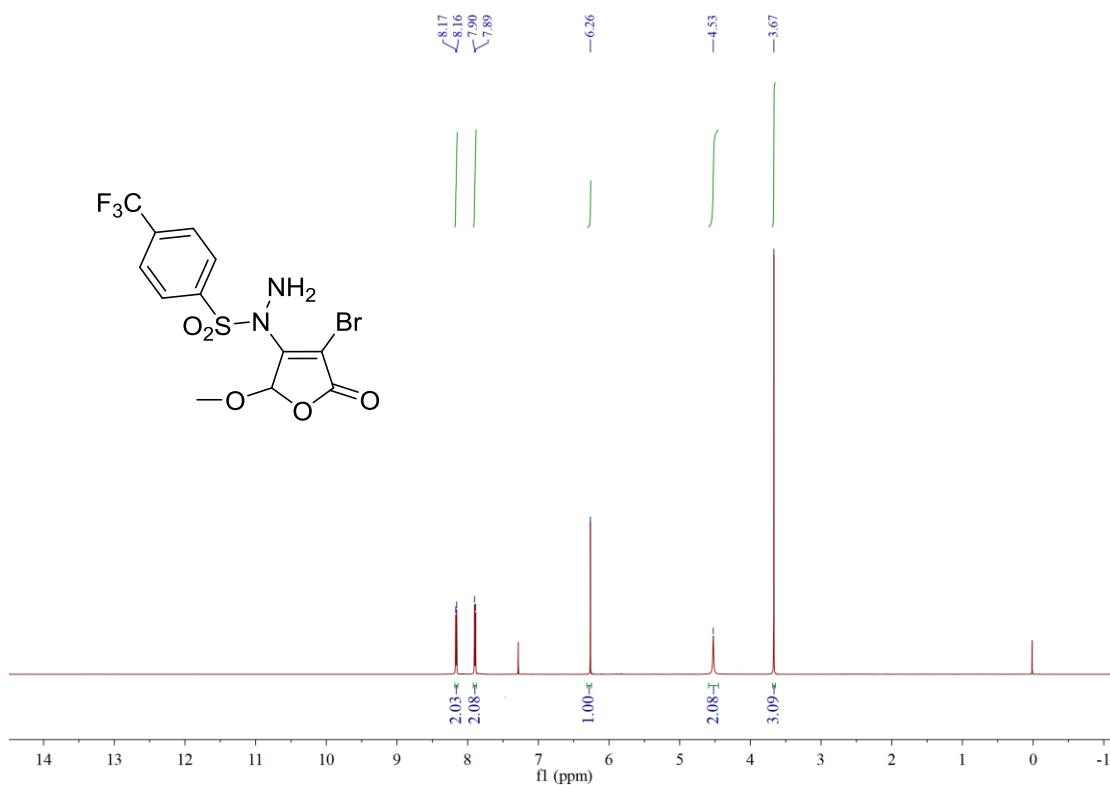
<sup>13</sup>C NMR spectrum of compound **3p**



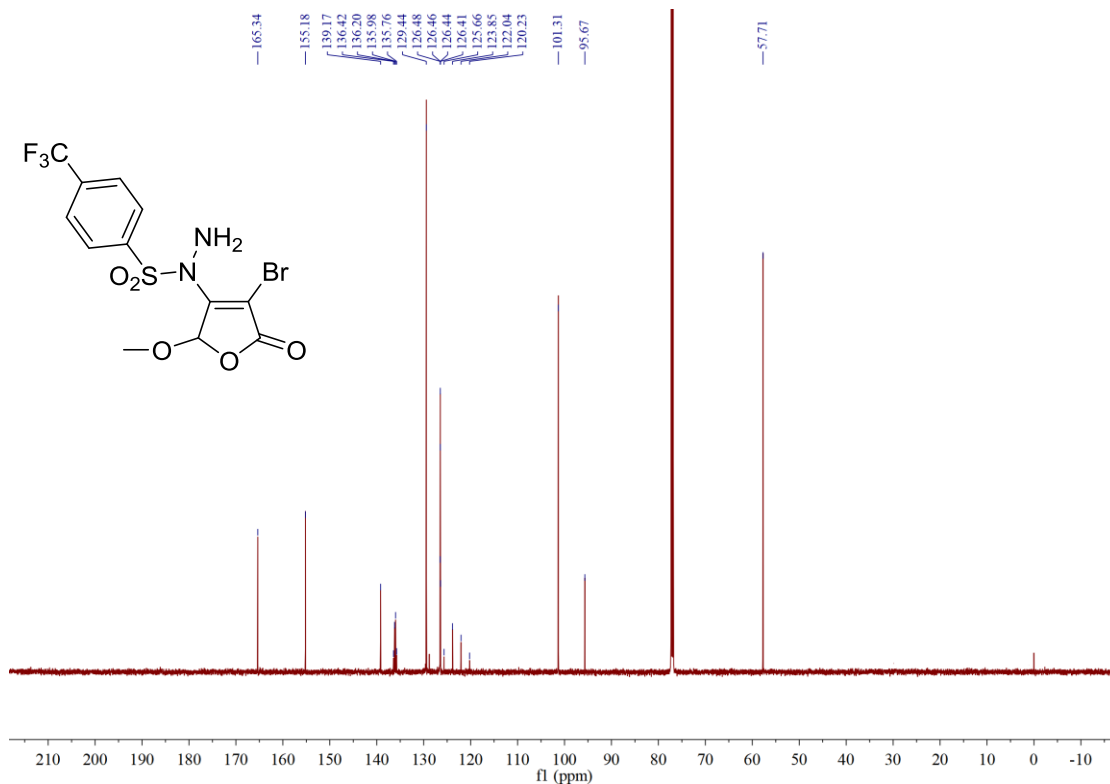
$^1\text{H}$  NMR spectrum of compound **3q**



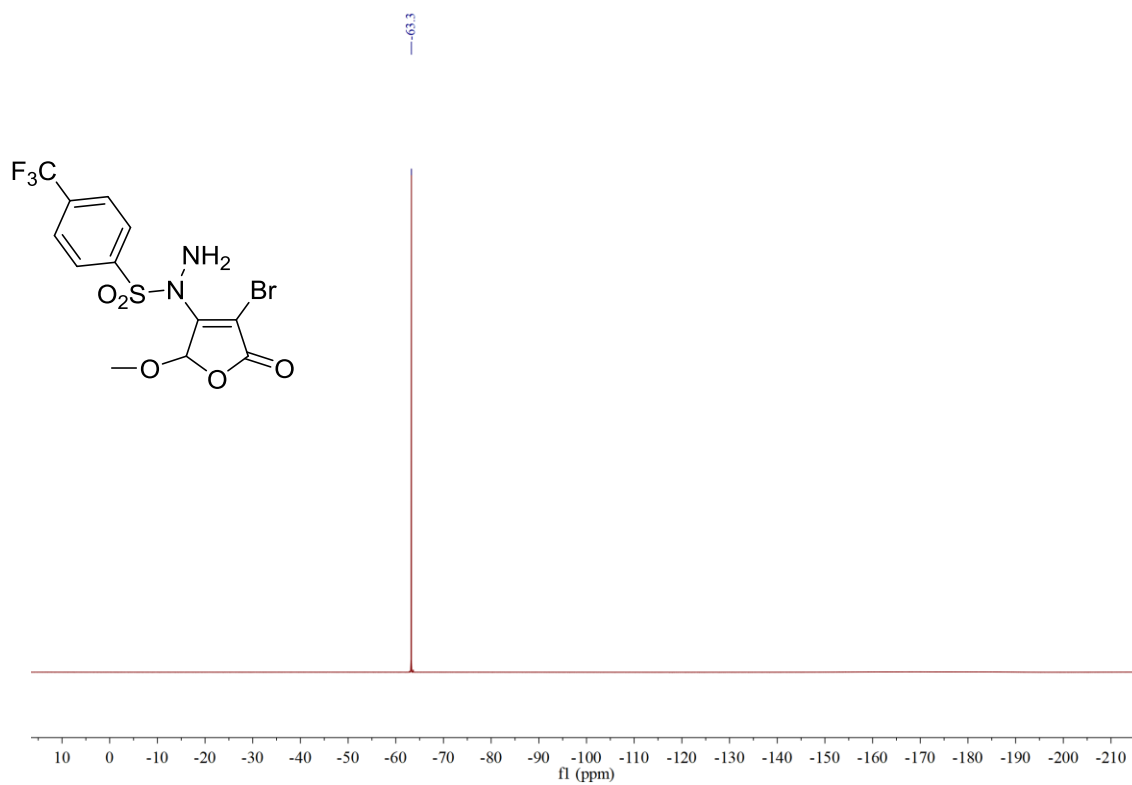
$^{13}\text{C}$  NMR spectrum of compound **3q**



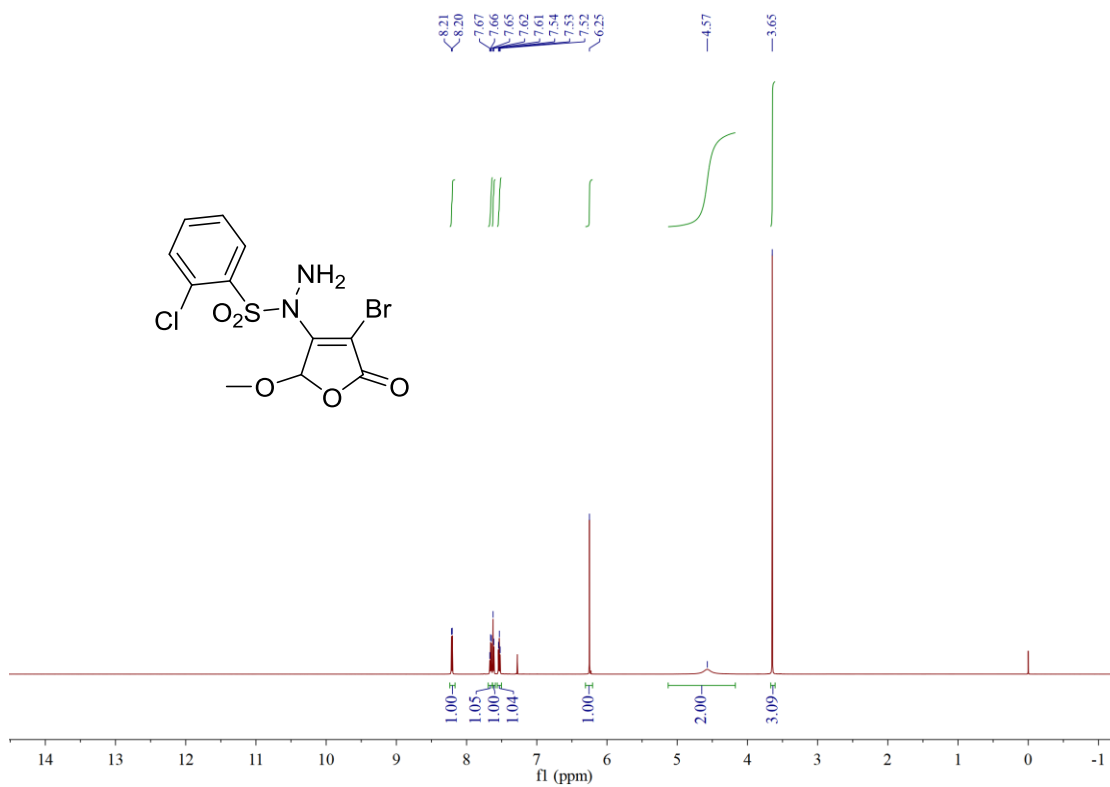
<sup>1</sup>H NMR spectrum of compound **3r**



<sup>13</sup>C NMR spectrum of compound **3r**

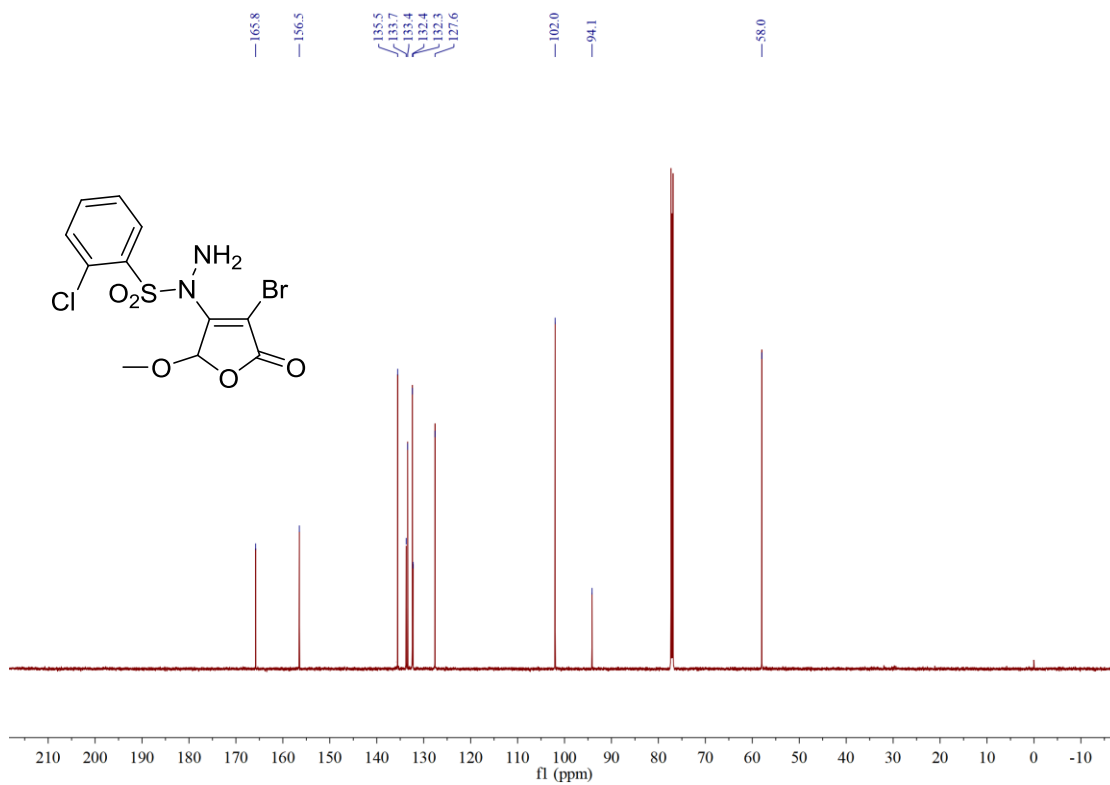


$^{19}\text{F}$  NMR spectrum of compound **3r**

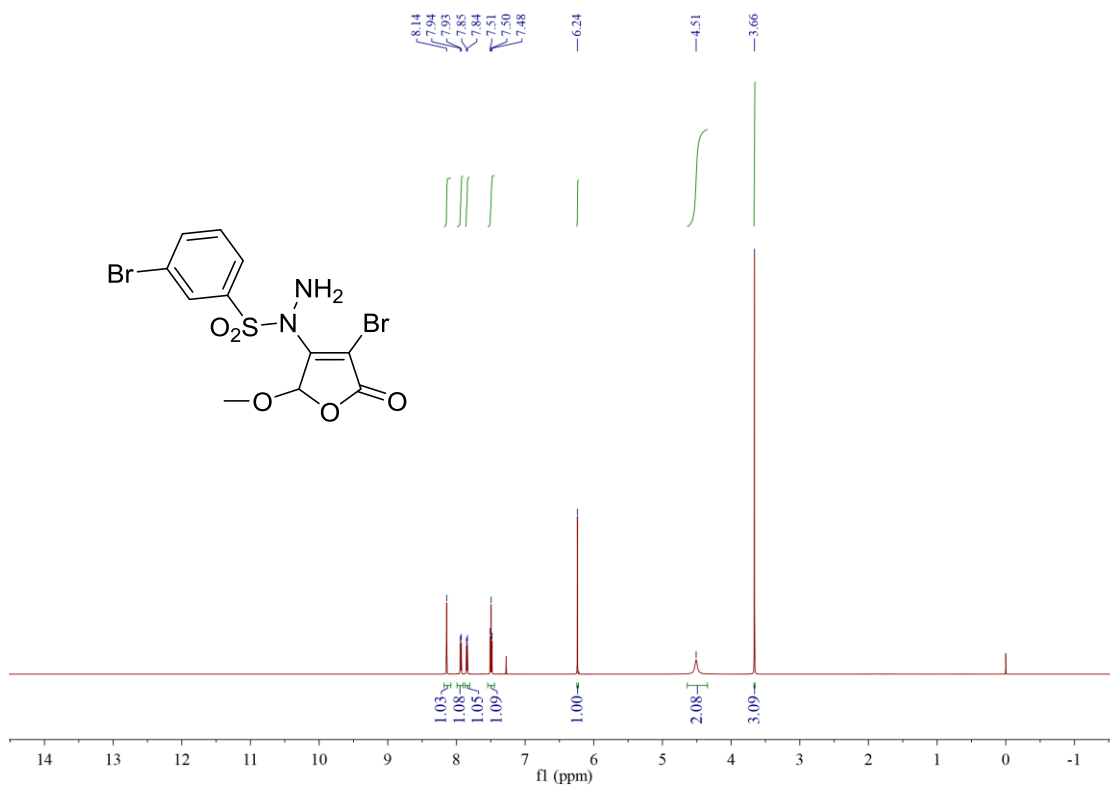


$^1\text{H}$  NMR spectrum of compound **3s**

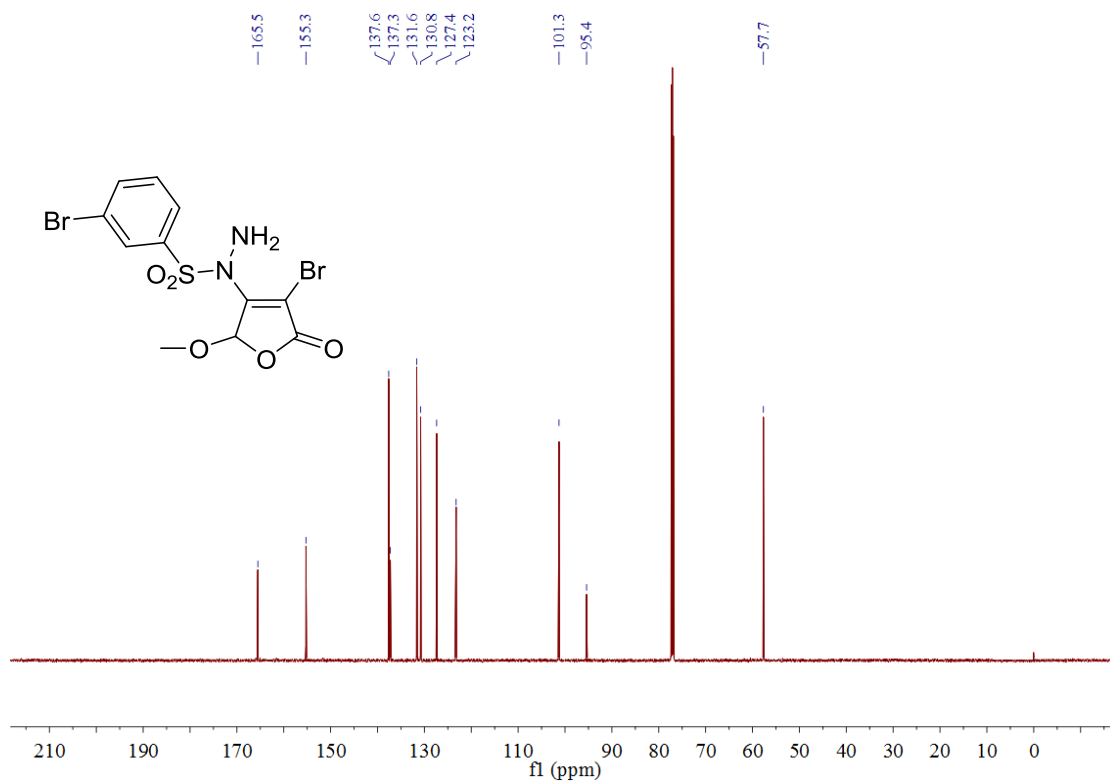




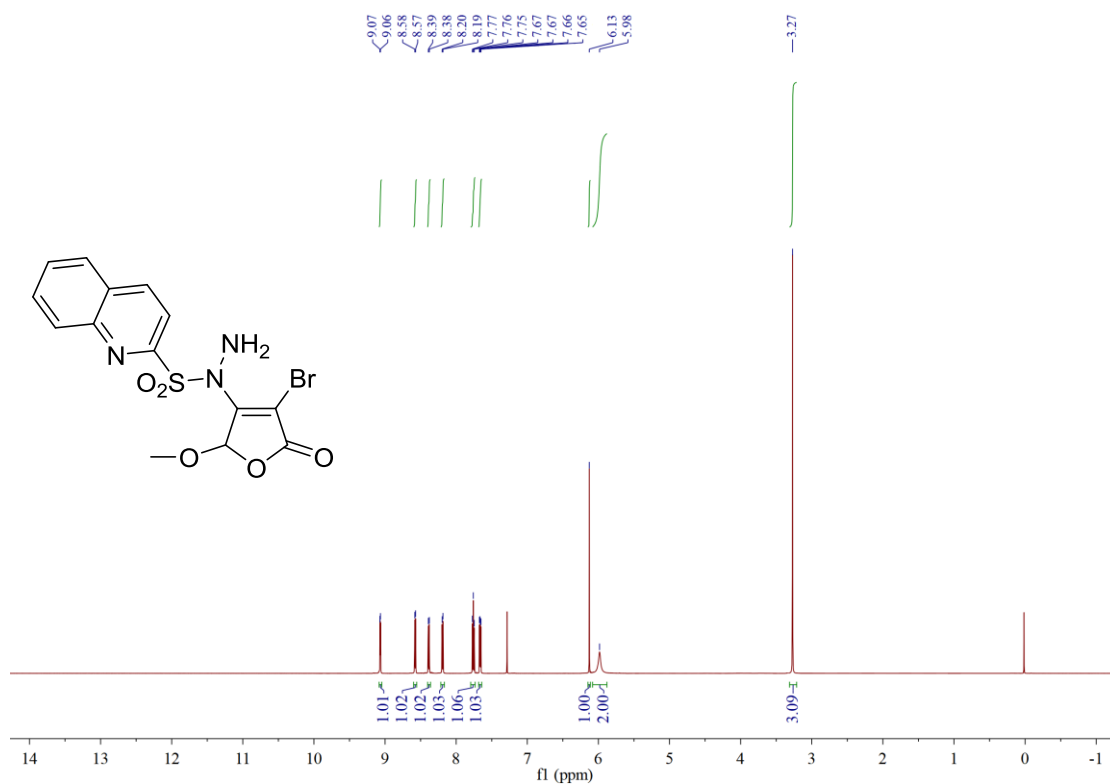
$^{13}\text{C}$  NMR spectrum of compound **3s**



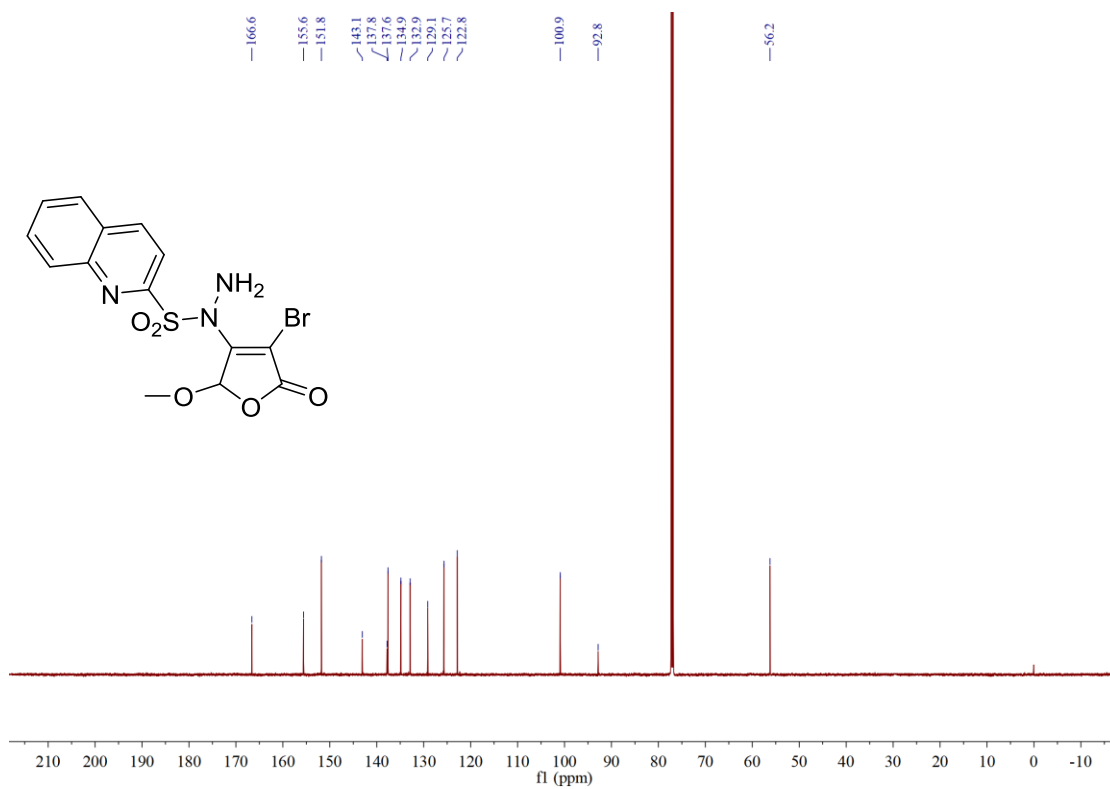
$^1\text{H}$  NMR spectrum of compound **3t**



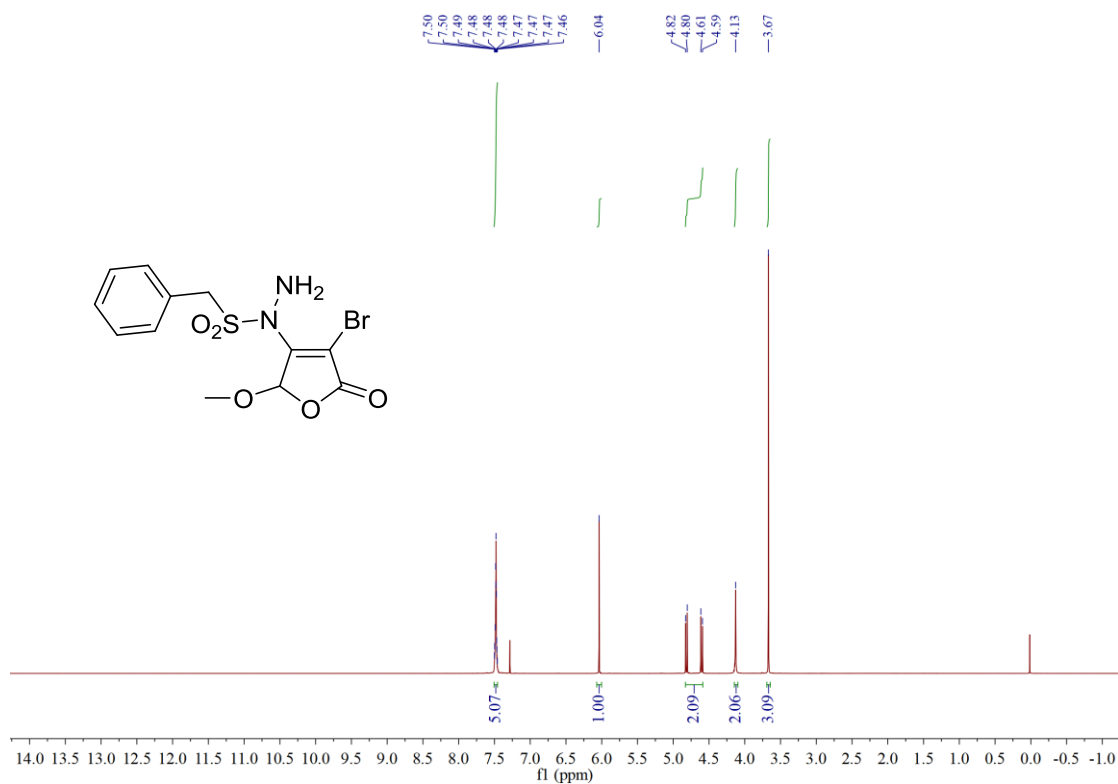
$^{13}\text{C}$  NMR spectrum of compound **3t**



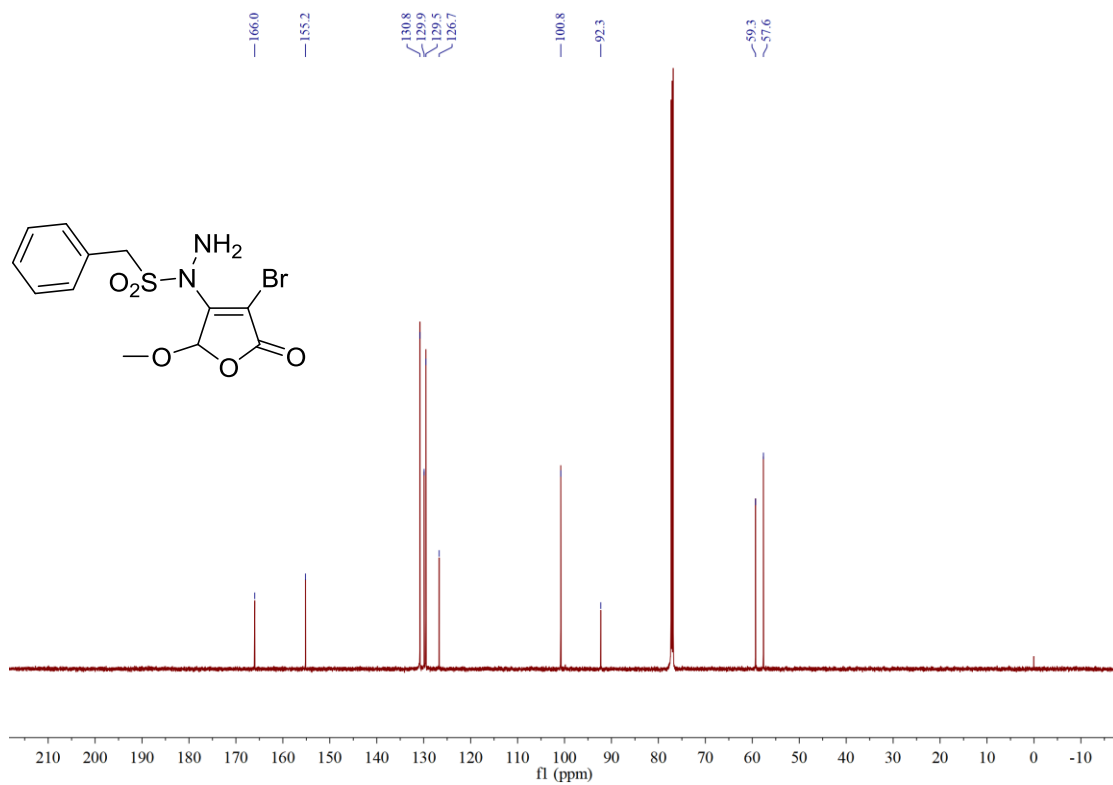
$^1\text{H}$  NMR spectrum of compound **3u**



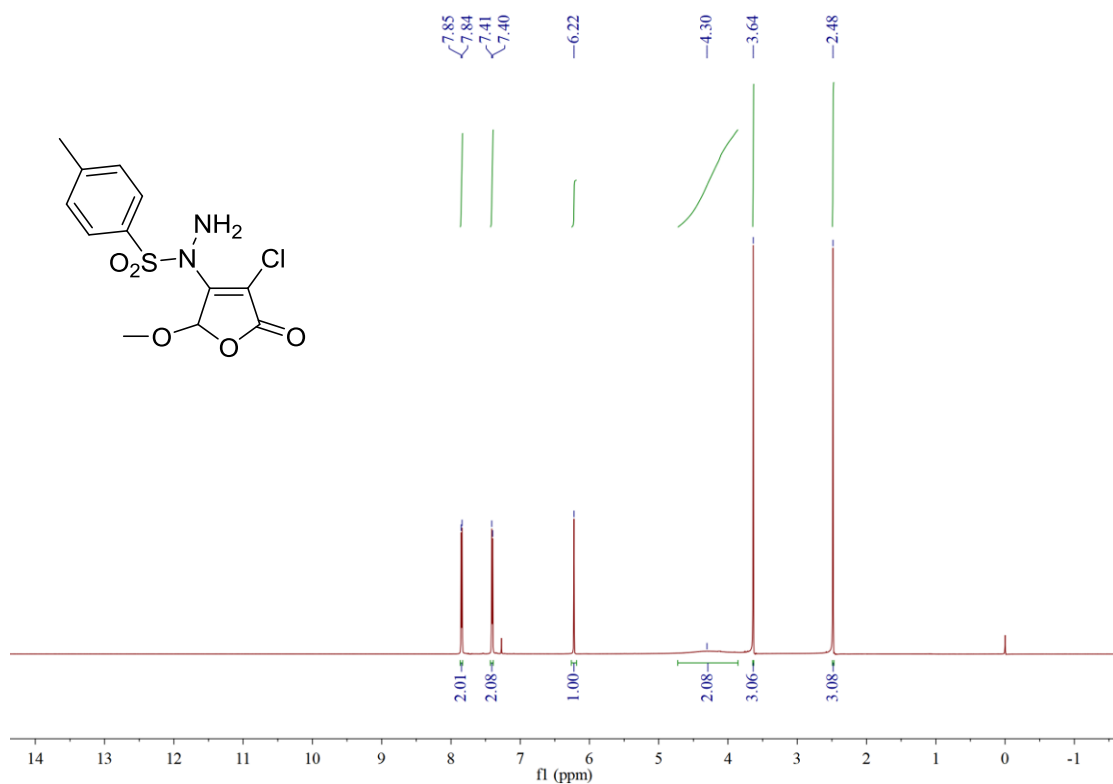
<sup>13</sup>C NMR spectrum of compound **3u**



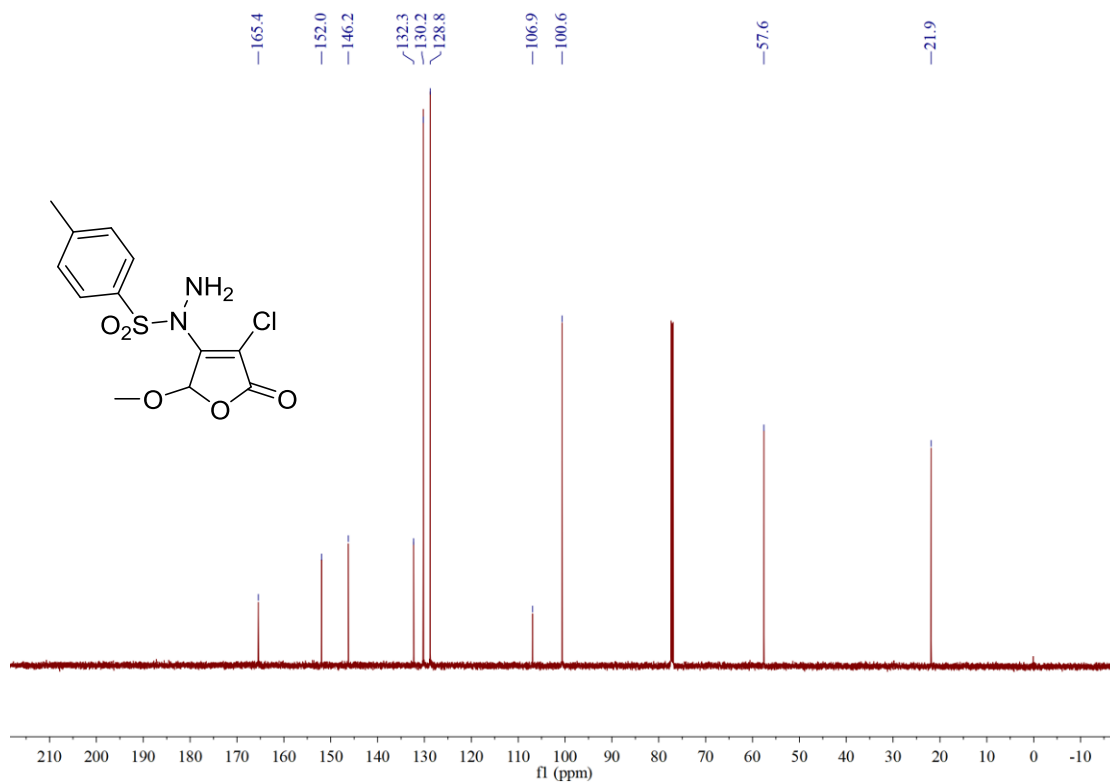
<sup>1</sup>H NMR spectrum of compound **3v**



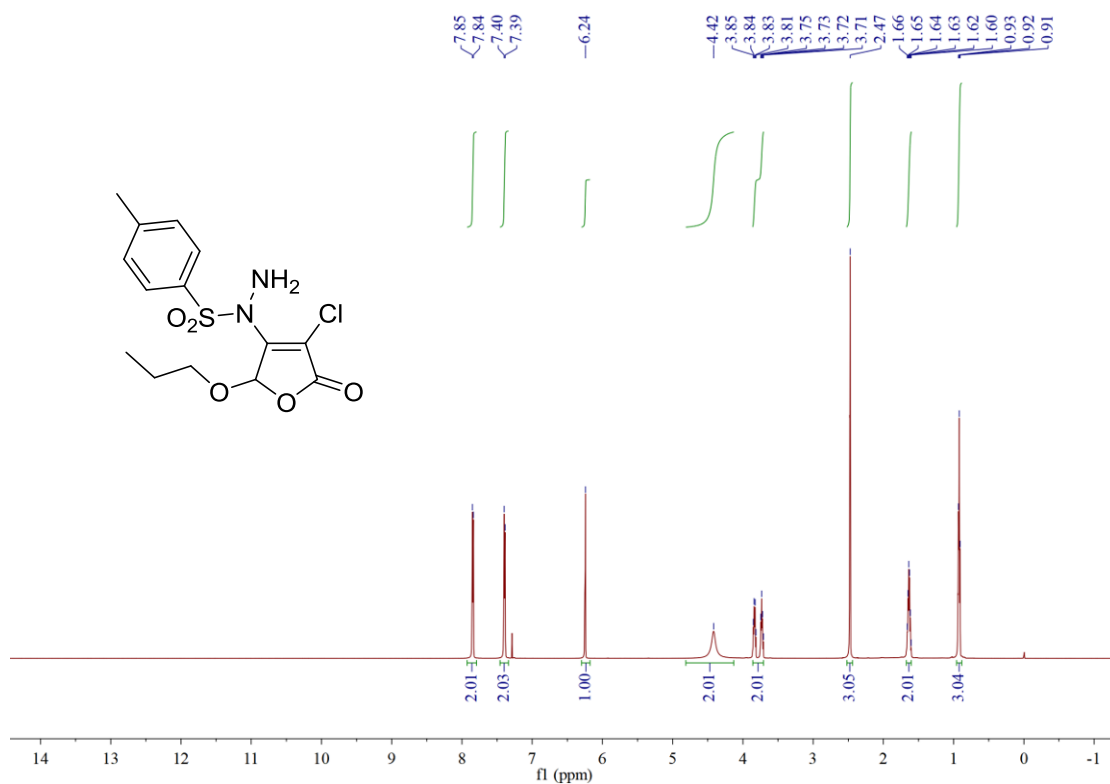
<sup>13</sup>C NMR spectrum of compound **3v**



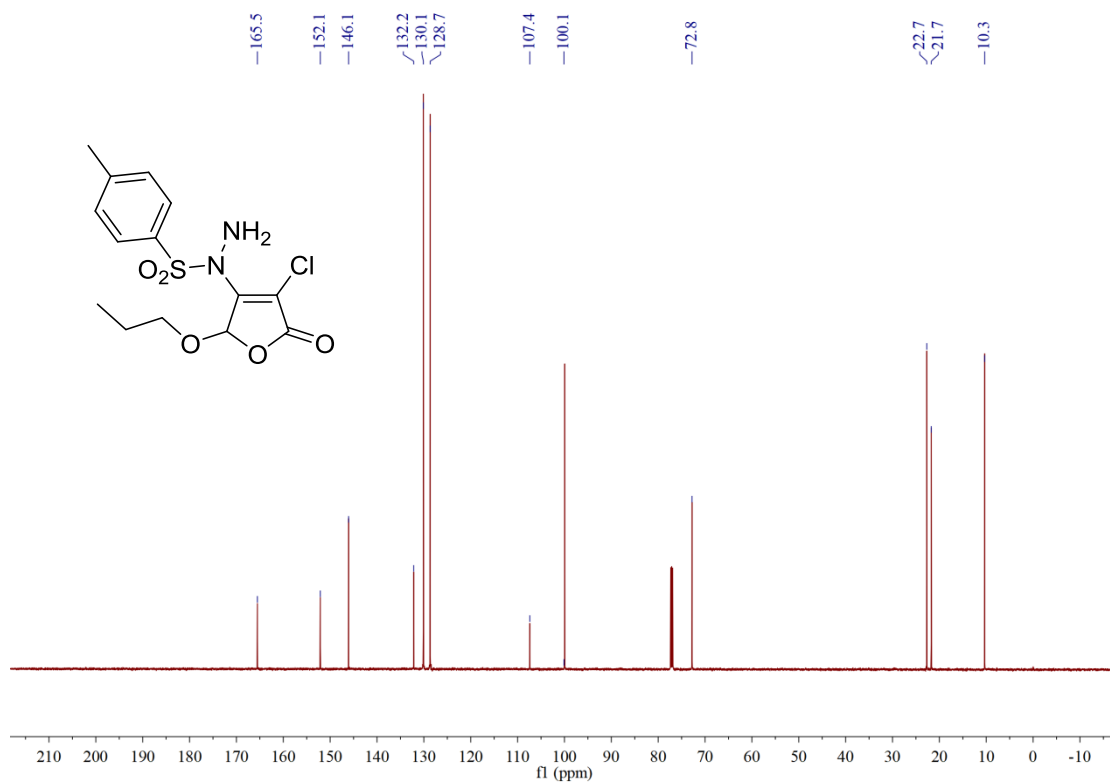
<sup>1</sup>H NMR spectrum of compound **4a**



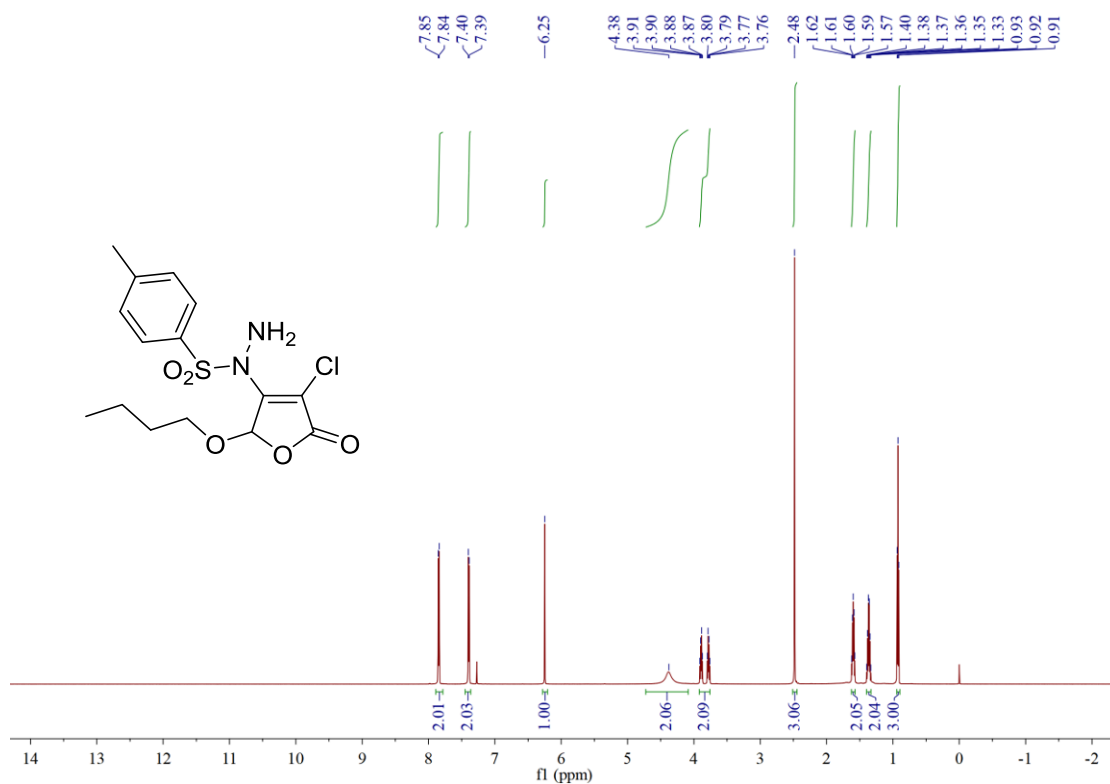
<sup>13</sup>C NMR spectrum of compound **4a**



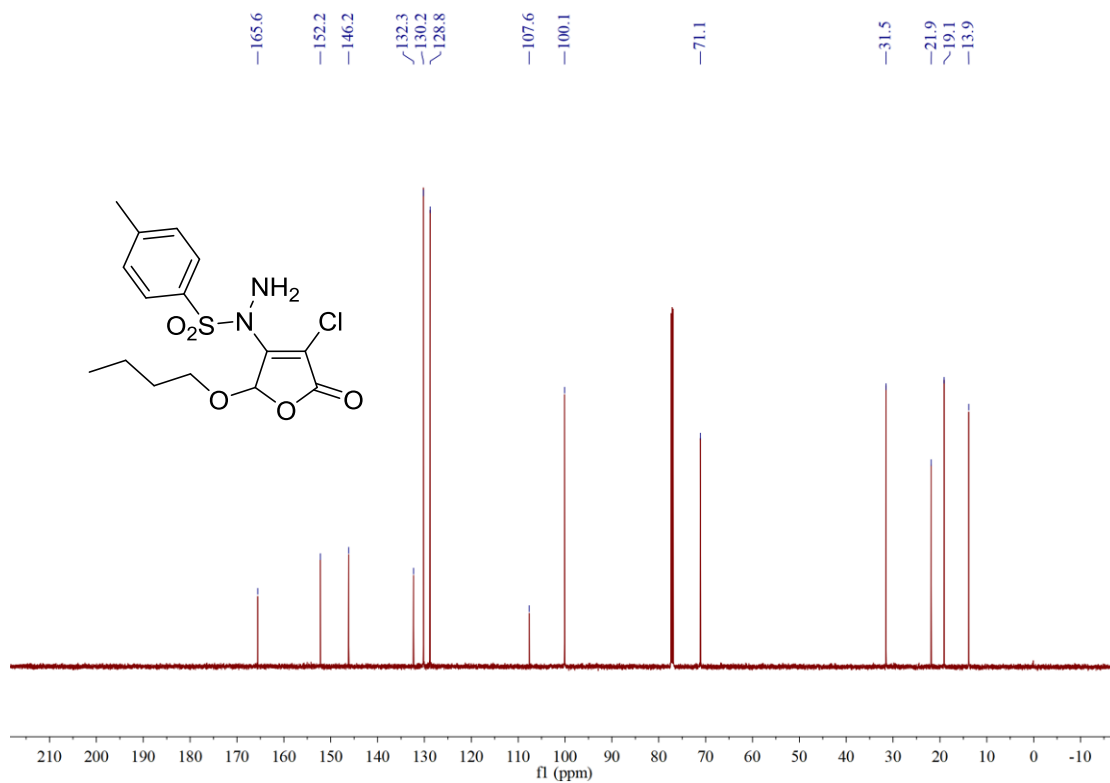
<sup>1</sup>H NMR spectrum of compound **4b**



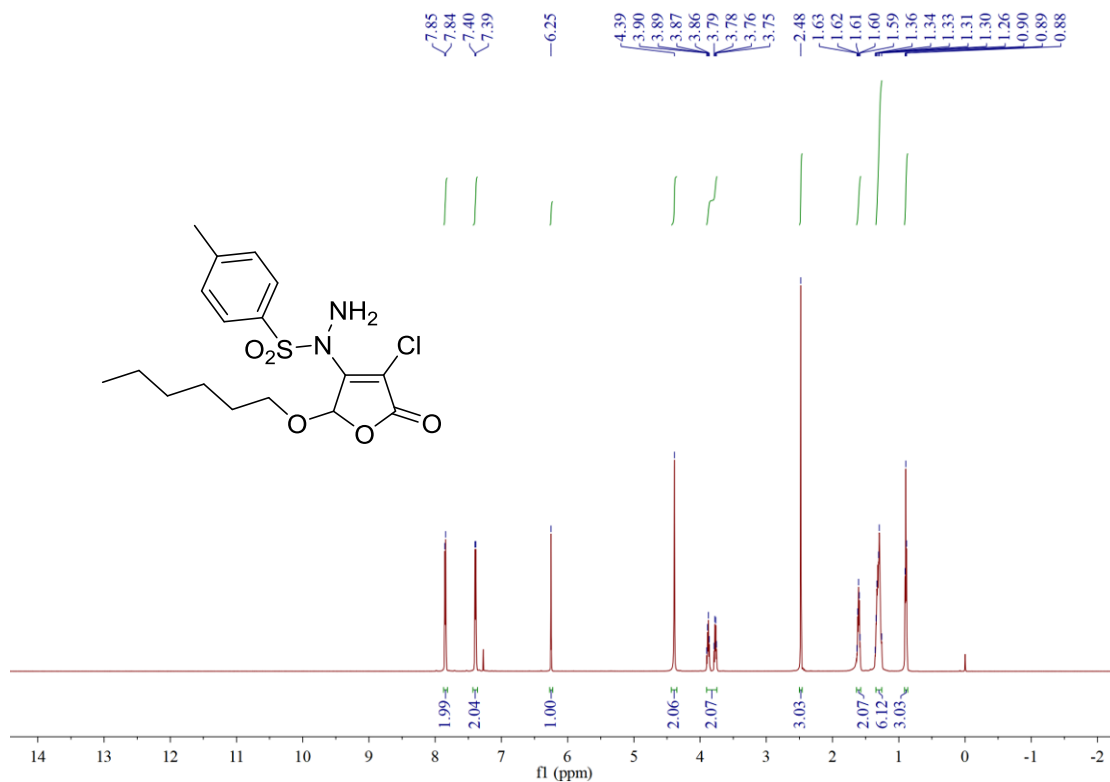
$^{13}\text{C}$  NMR spectrum of compound **4b**



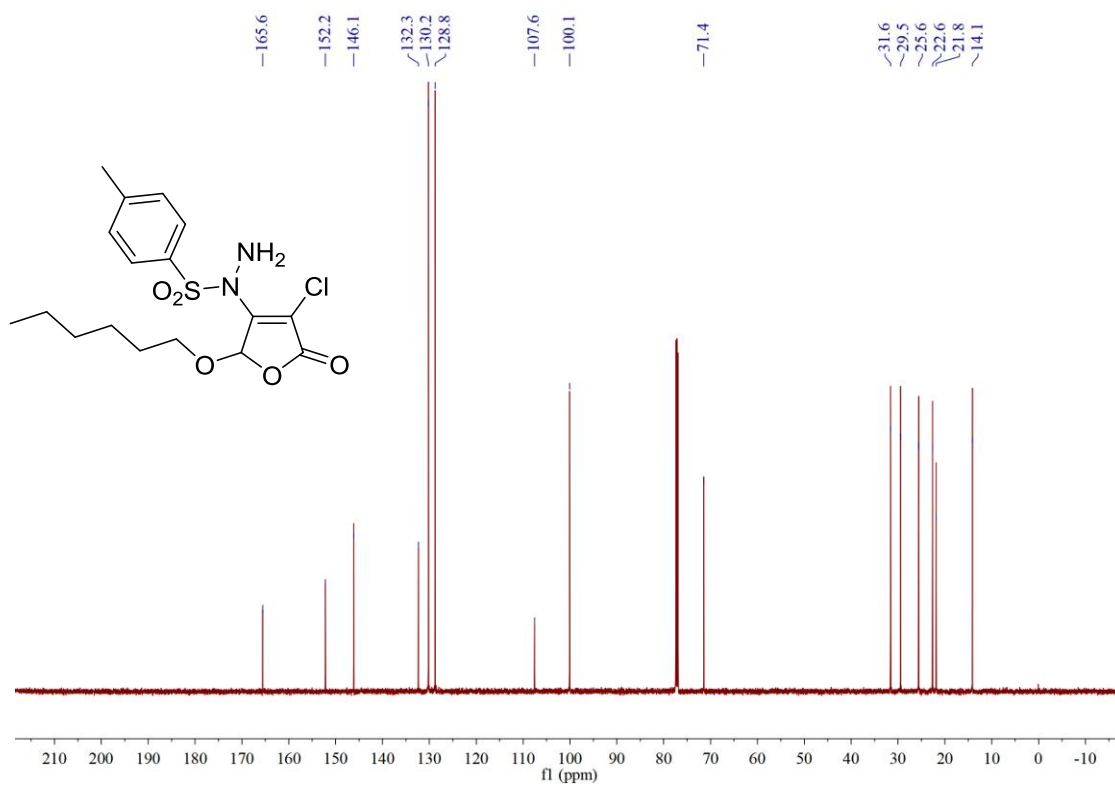
$^1\text{H}$  NMR spectrum of compound **4c**



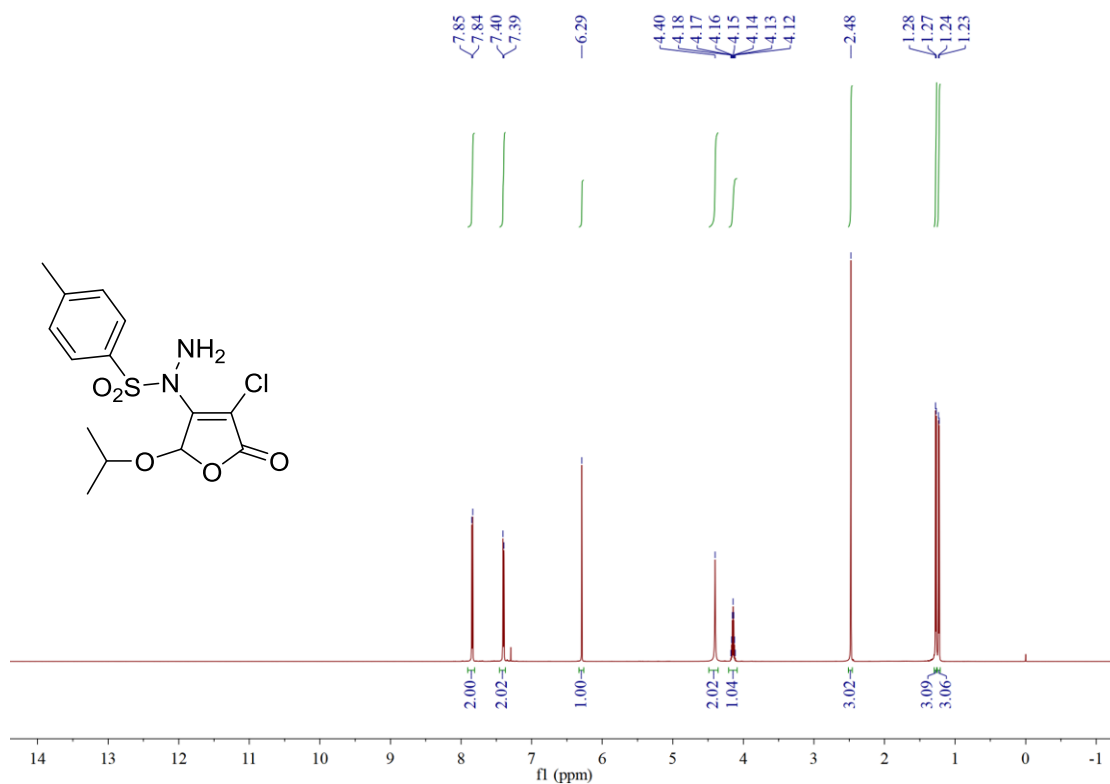
$^{13}\text{C}$  NMR spectrum of compound **4c**



$^1\text{H}$  NMR spectrum of compound **4d**

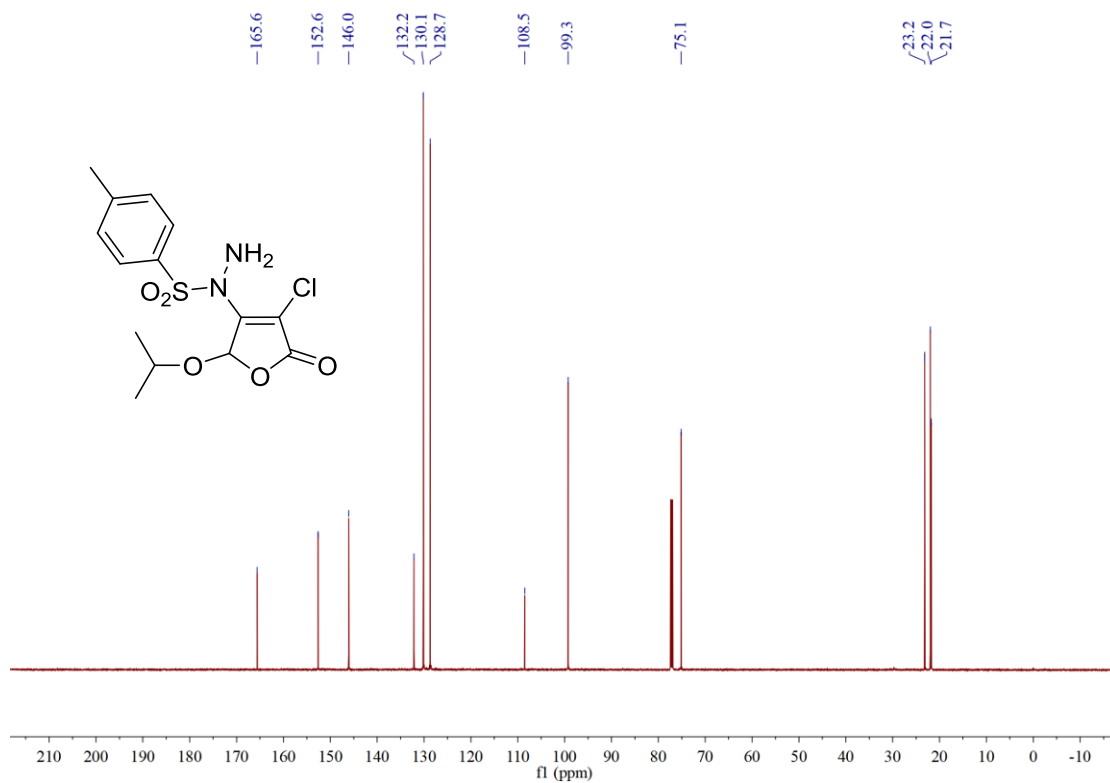


<sup>13</sup>C NMR spectrum of compound **4d**

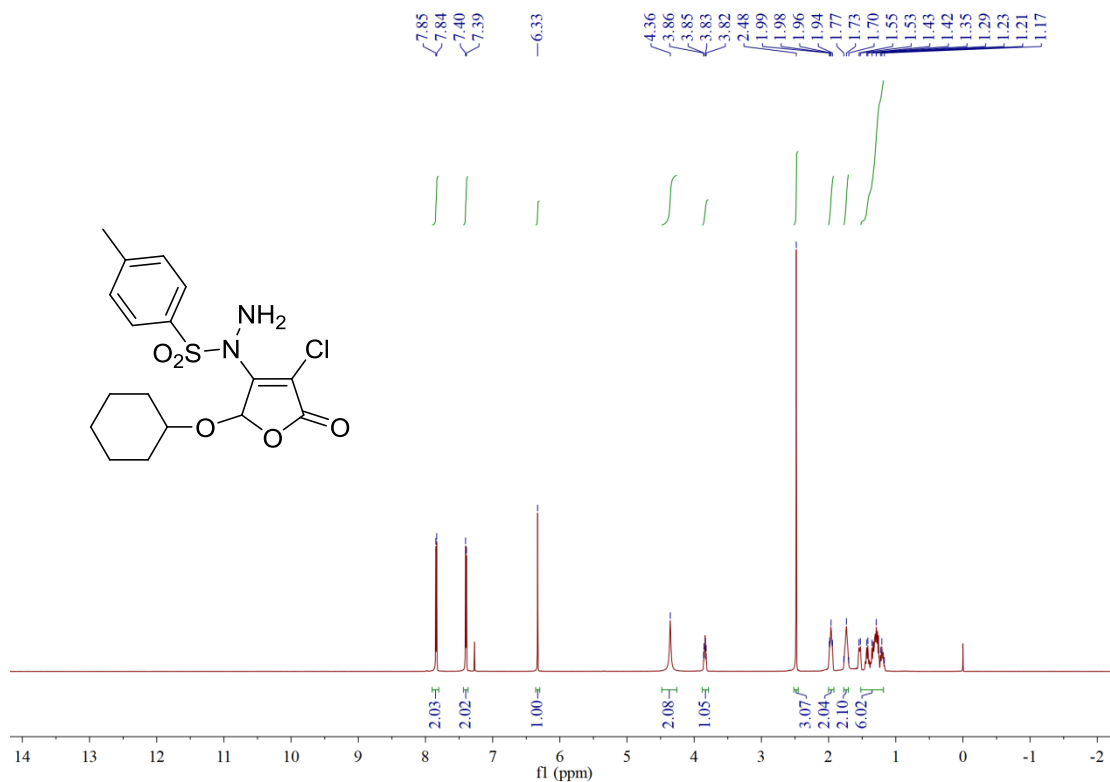


<sup>1</sup>H NMR spectrum of compound **4e**

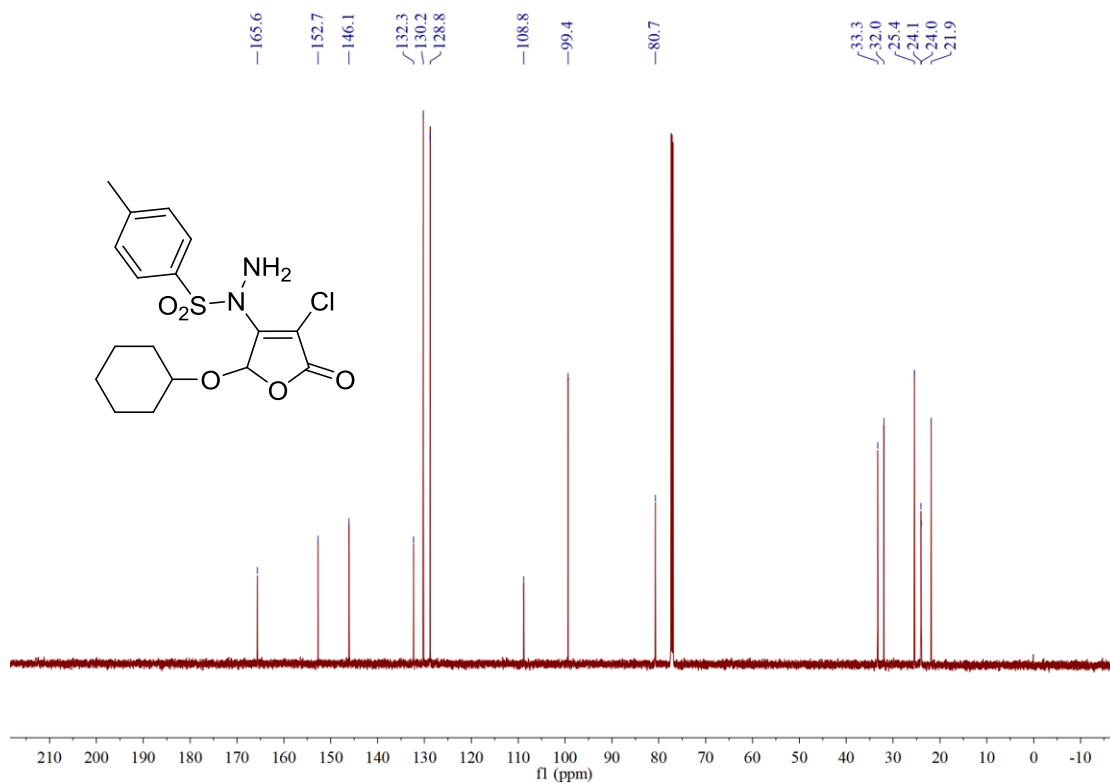




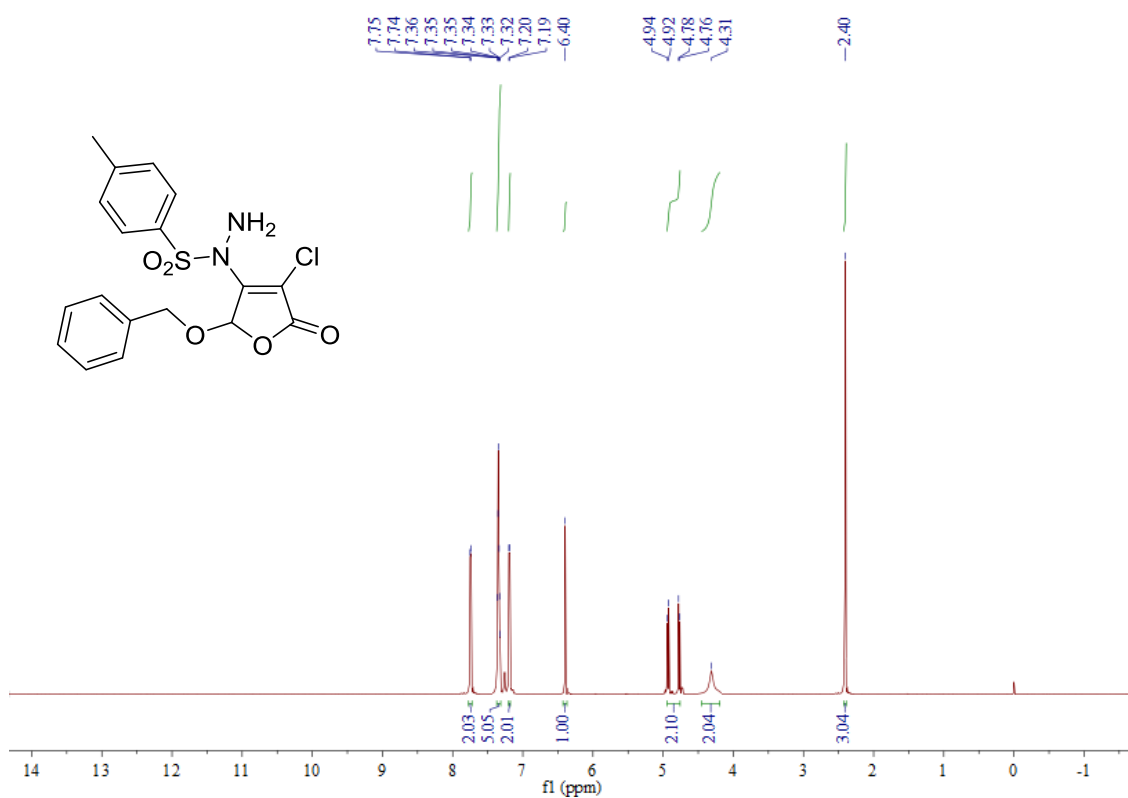
<sup>13</sup>C NMR spectrum of compound **4e**



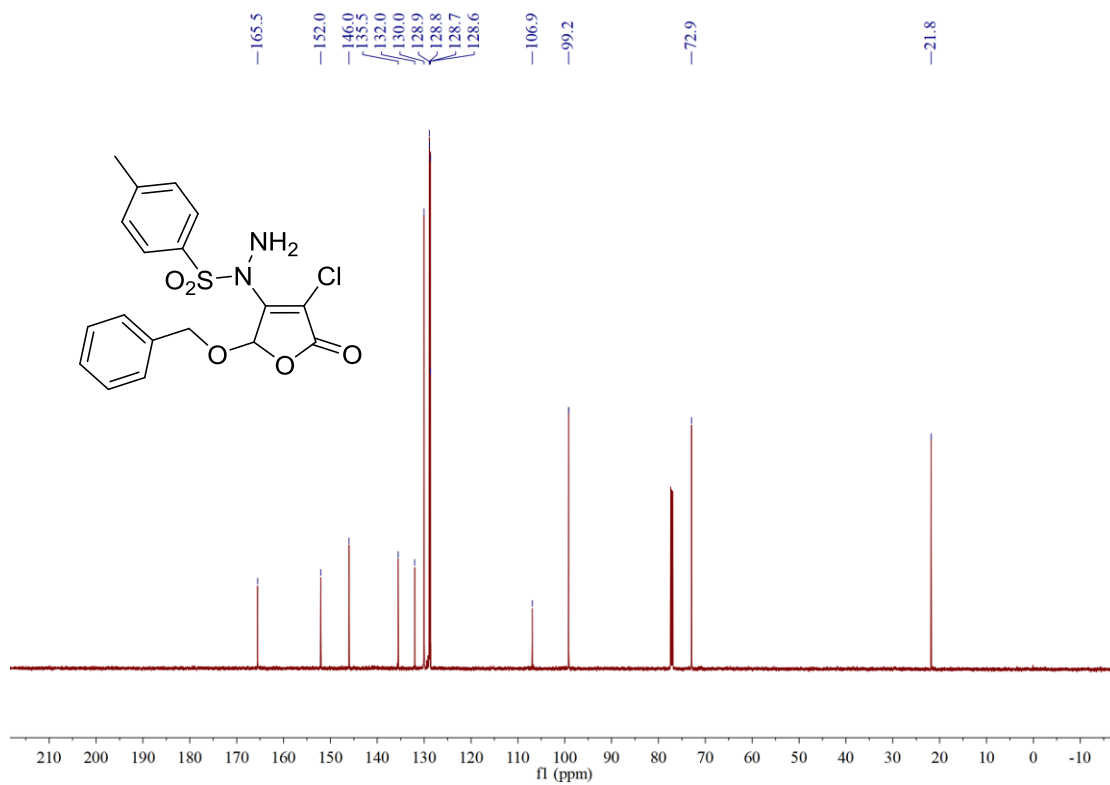
<sup>1</sup>H NMR spectrum of compound **4f**



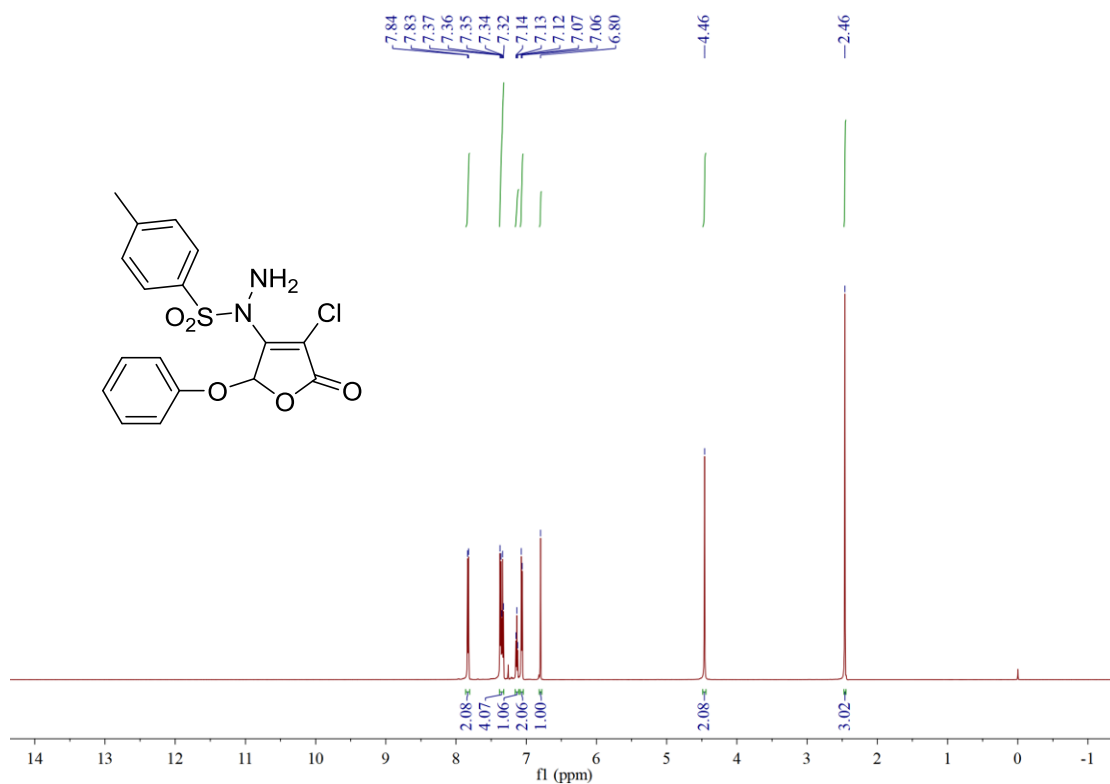
$^{13}\text{C}$  NMR spectrum of compound **4f**



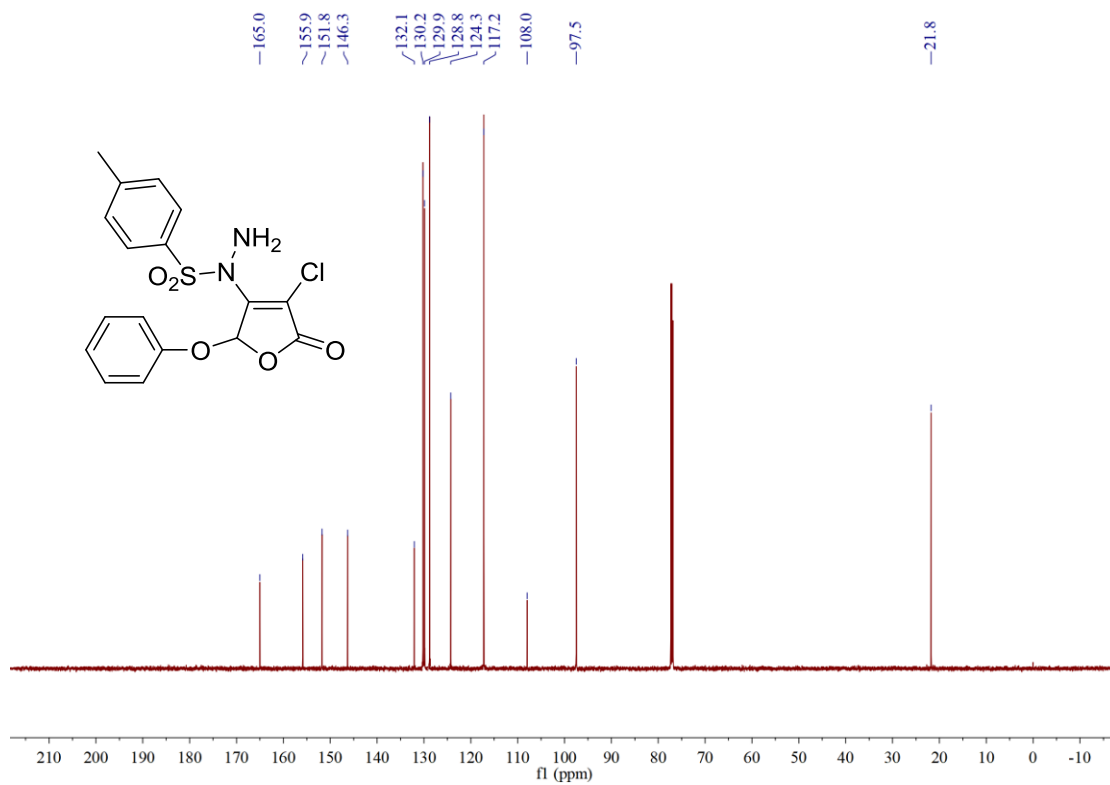
$^1\text{H}$  NMR spectrum of compound **4g**



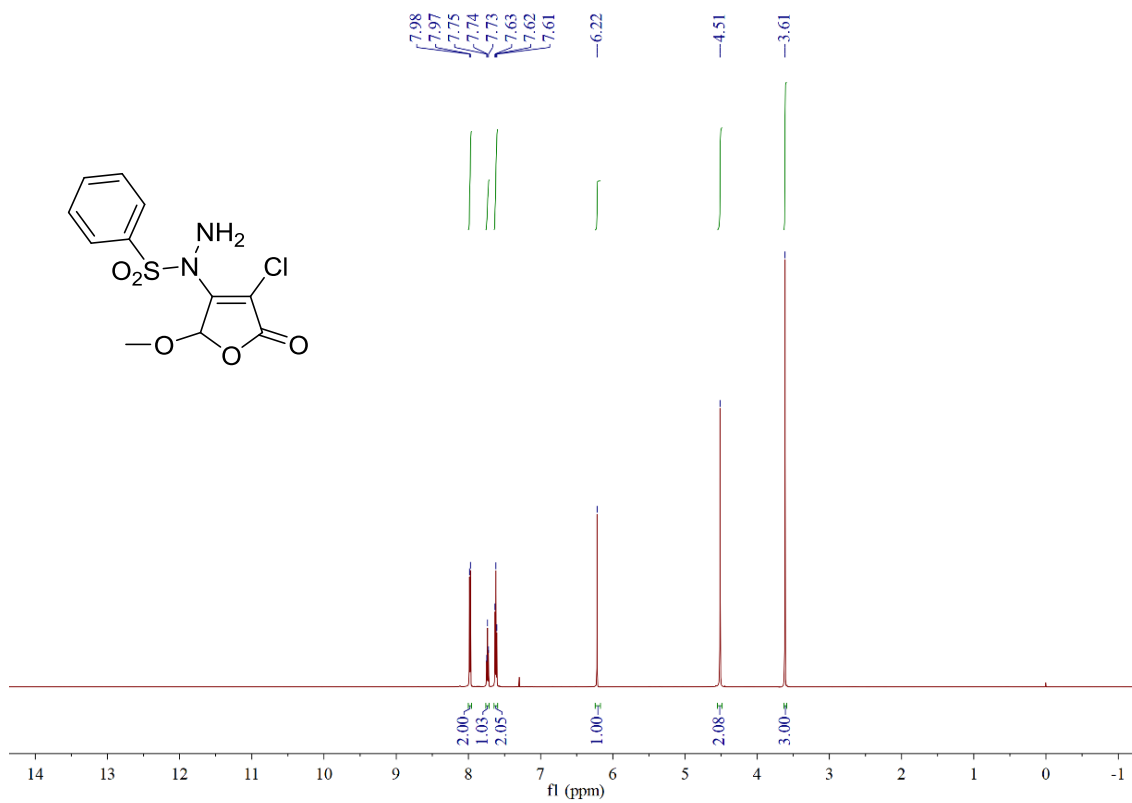
<sup>13</sup>C NMR spectrum of compound **4g**



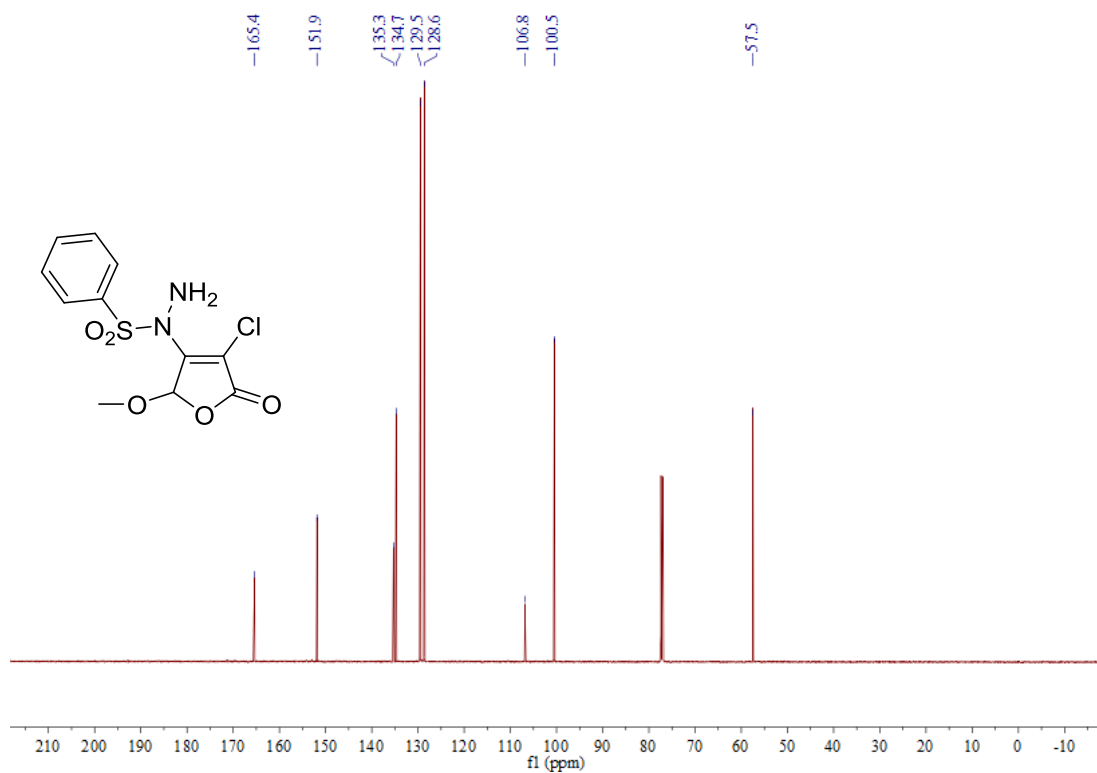
<sup>1</sup>H NMR spectrum of compound **4h**



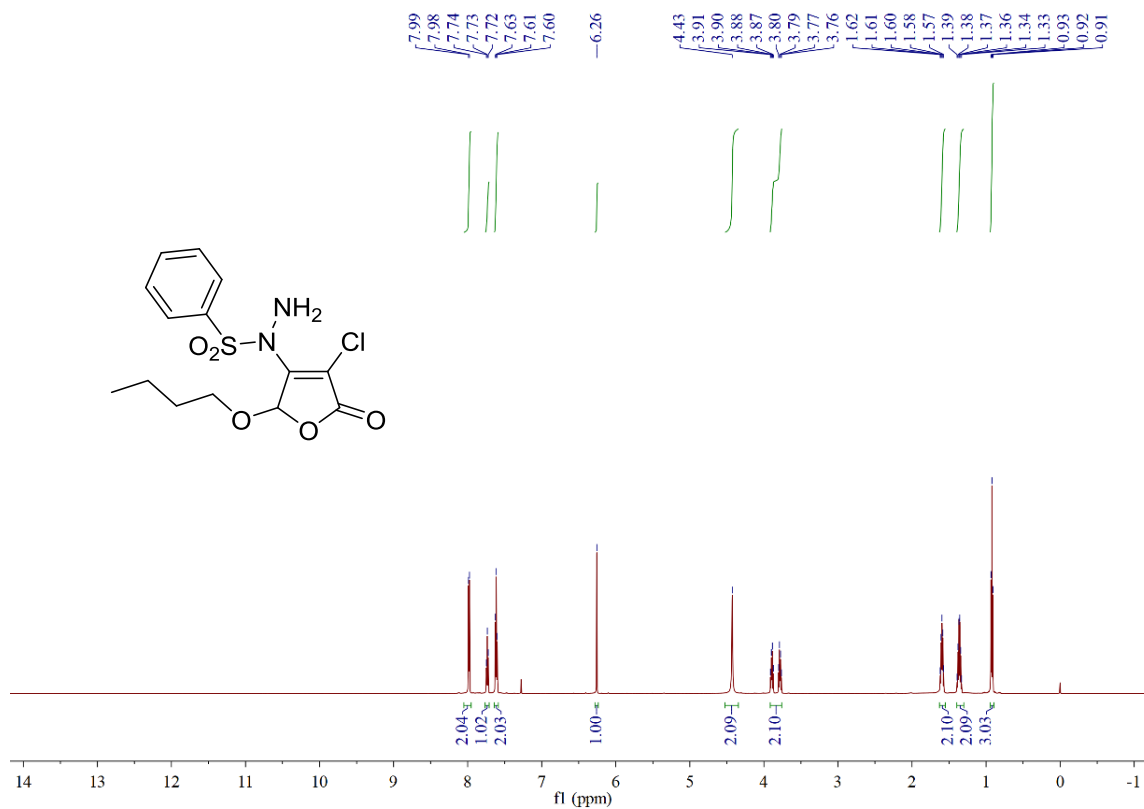
<sup>13</sup>C NMR spectrum of compound **4h**



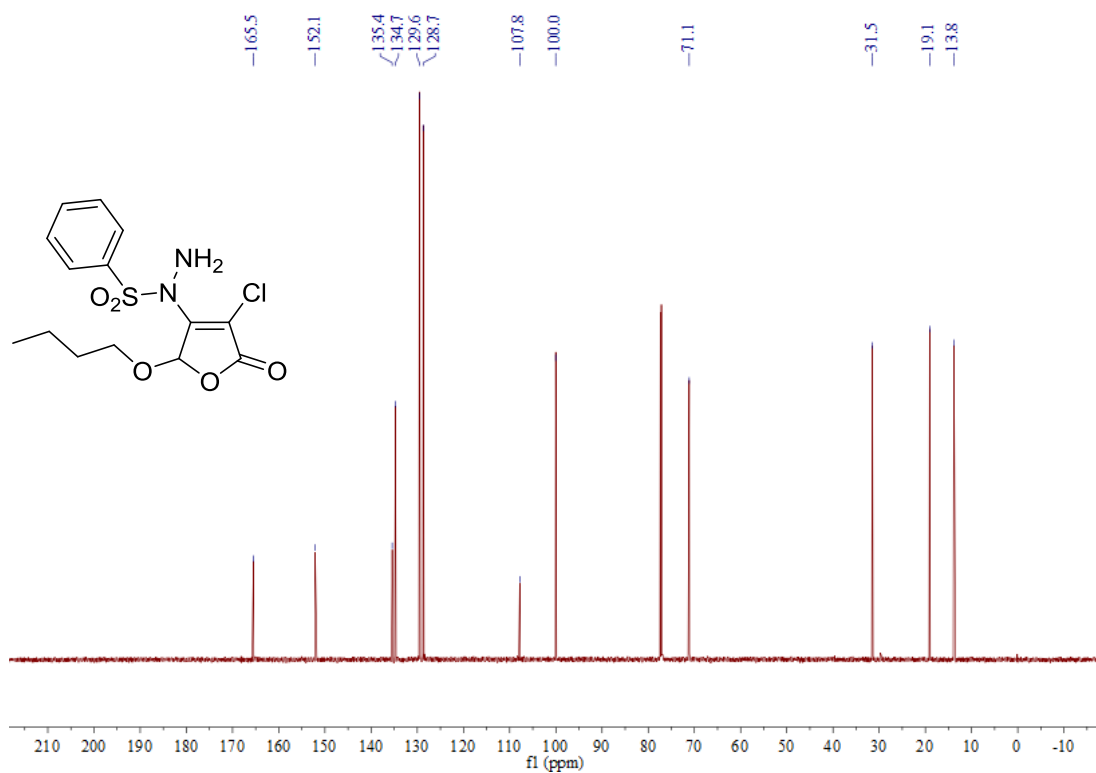
<sup>1</sup>H NMR spectrum of compound **4i**



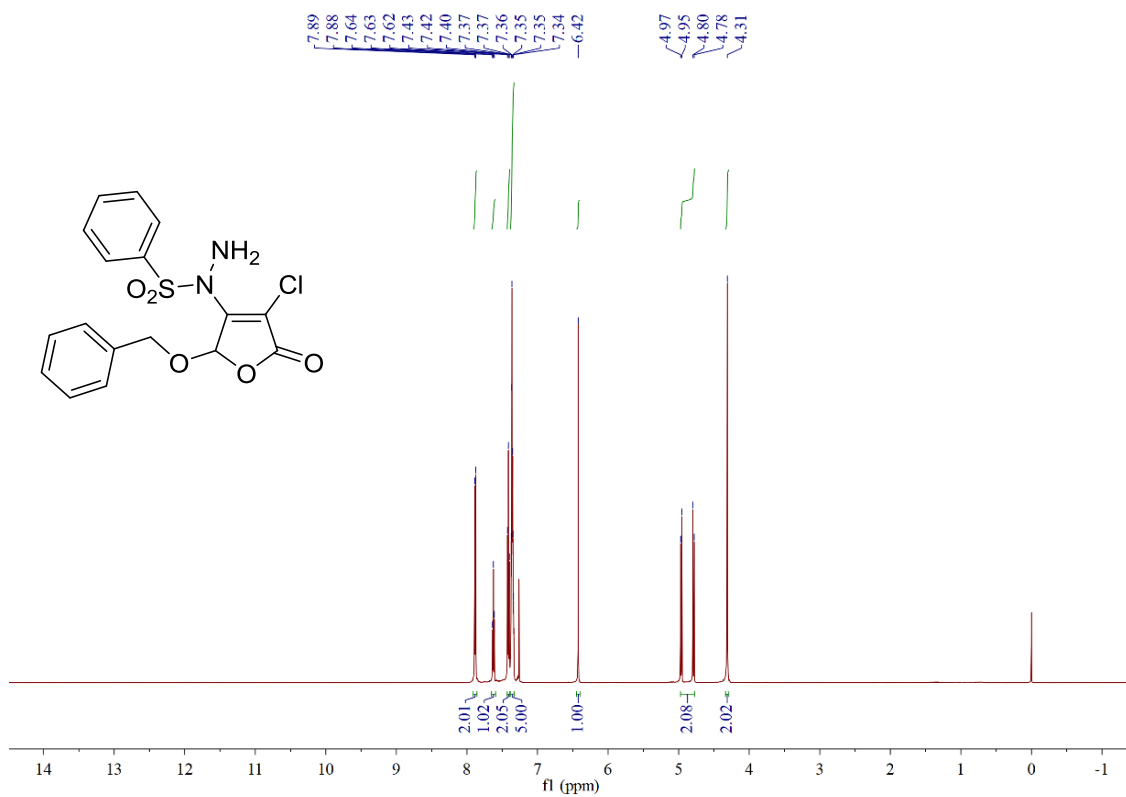
$^{13}\text{C}$  NMR spectrum of compound **4i**



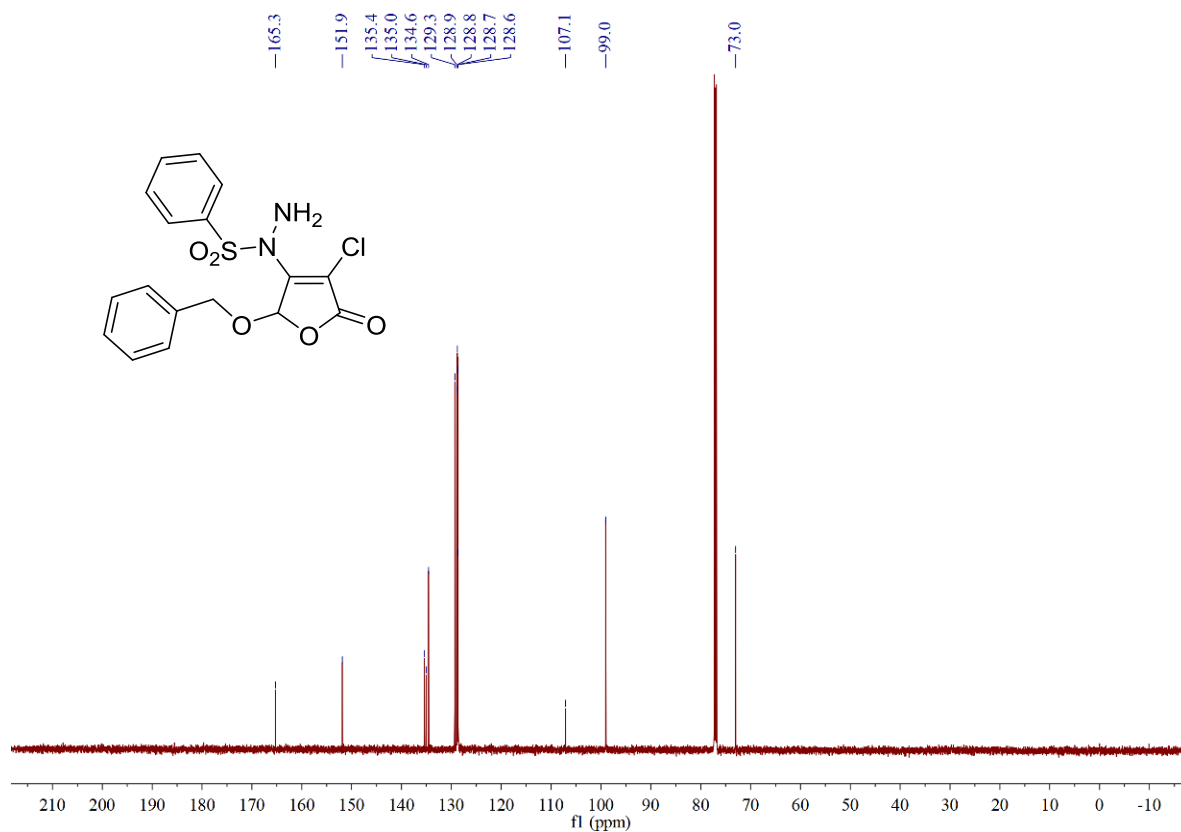
$^1\text{H}$  NMR spectrum of compound **4j**



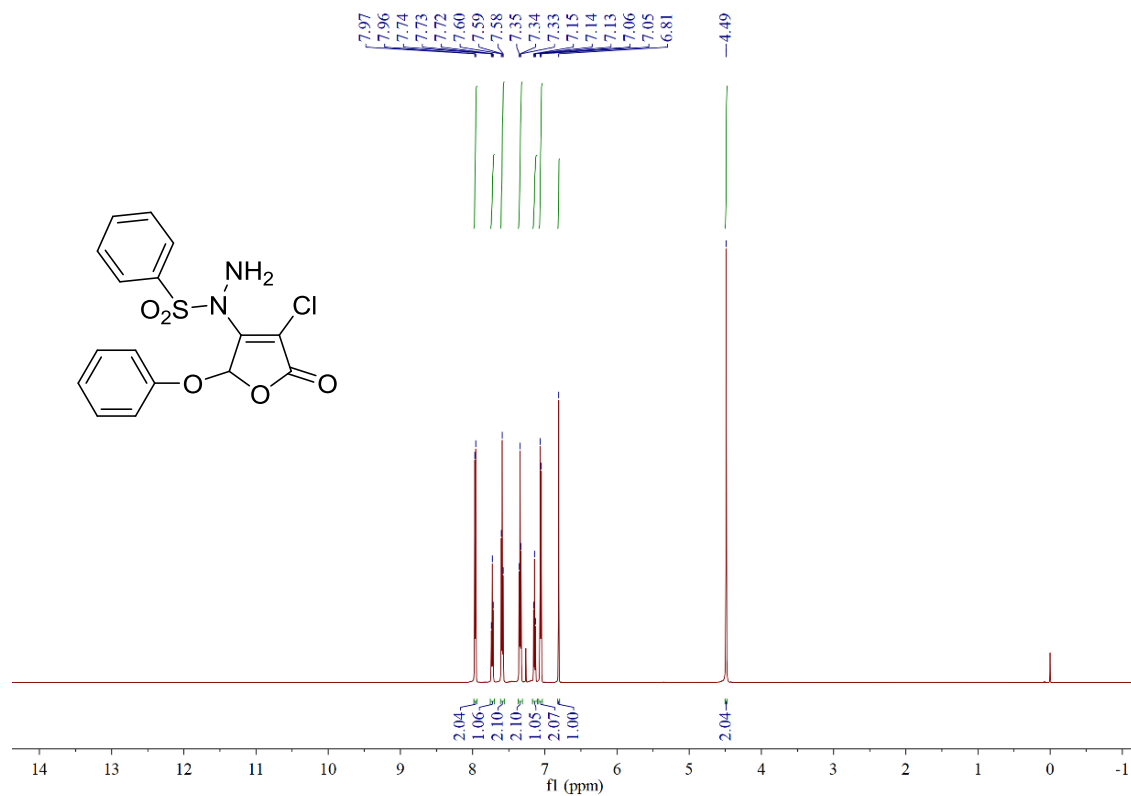
<sup>13</sup>C NMR spectrum of compound **4j**



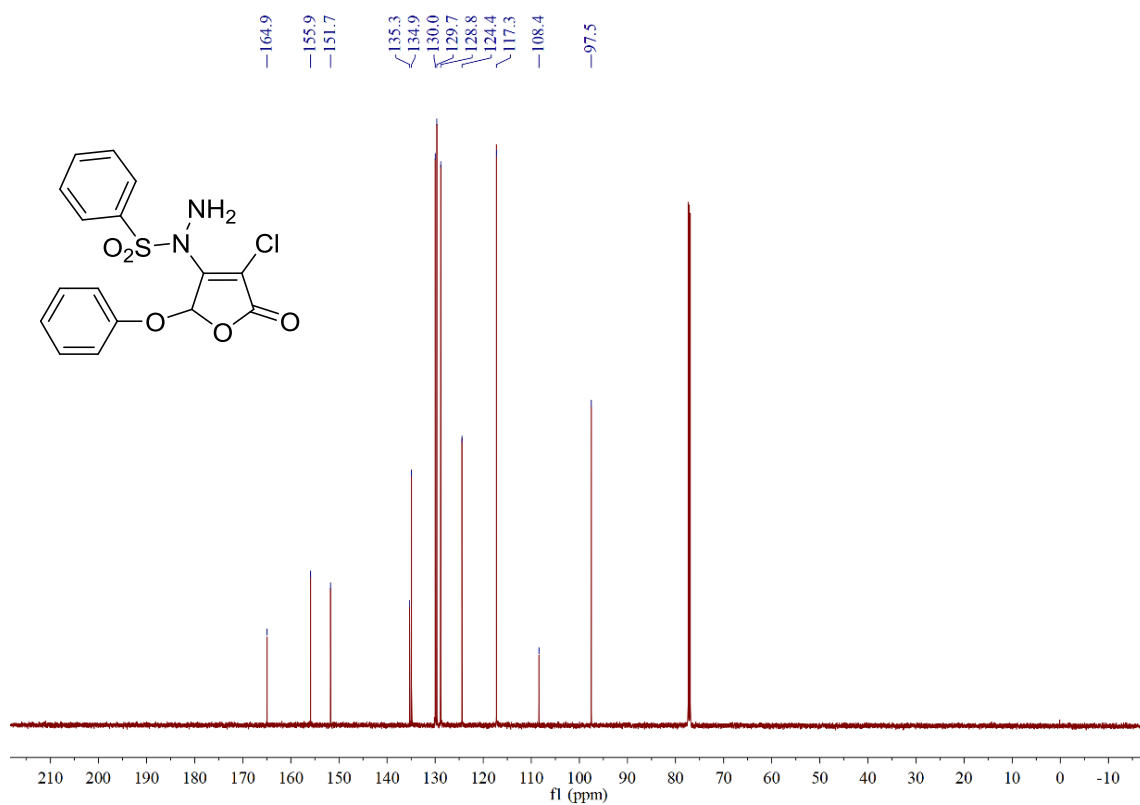
<sup>1</sup>H NMR spectrum of compound **4k**



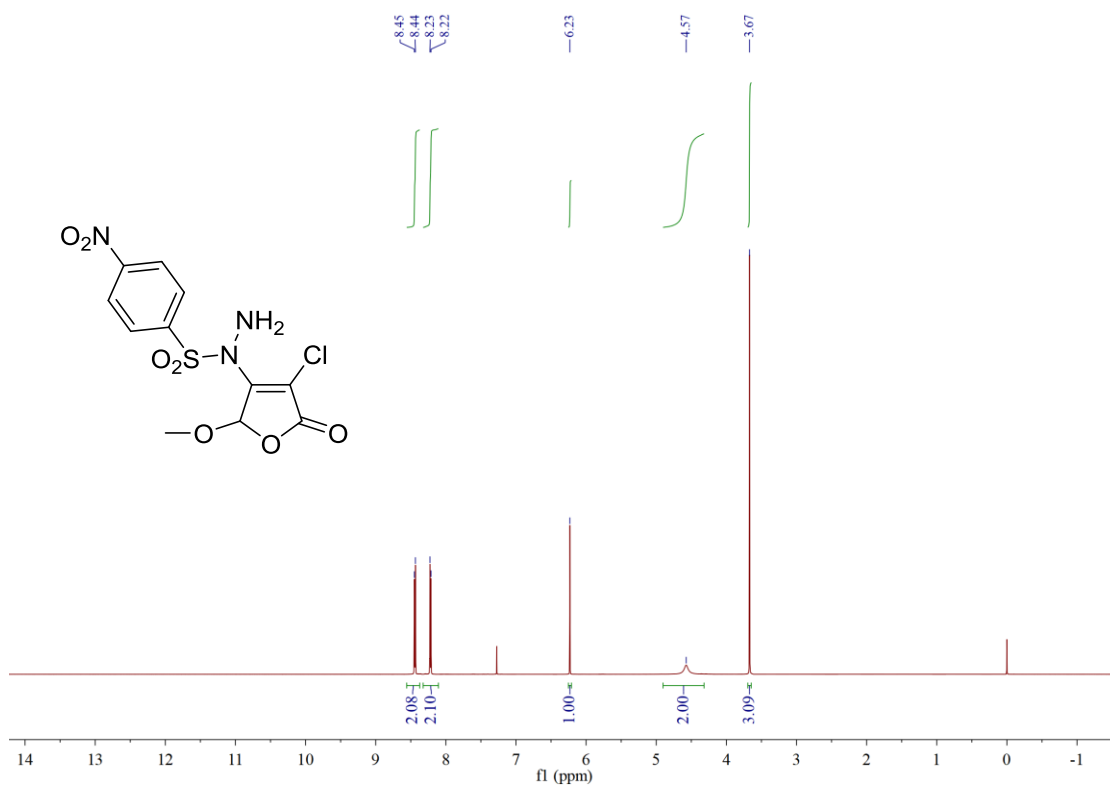
<sup>13</sup>C NMR spectrum of compound 4k



<sup>1</sup>H NMR spectrum of compound 4l

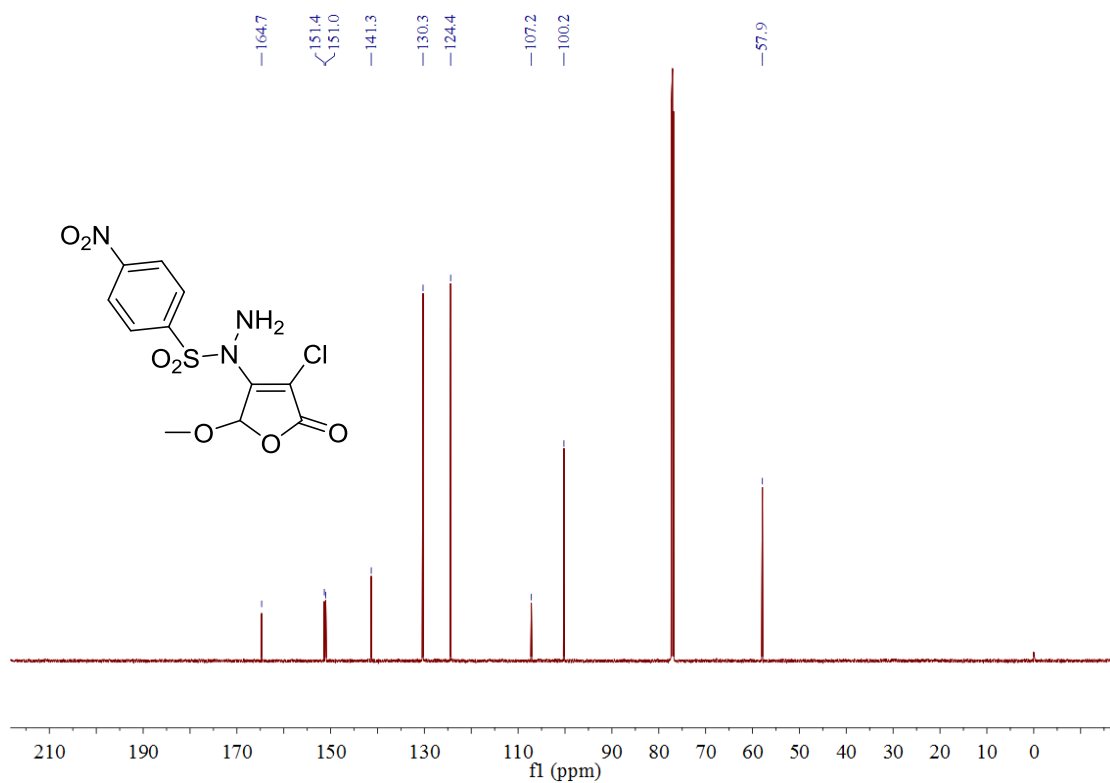


$^{13}\text{C}$  NMR spectrum of compound **4l**

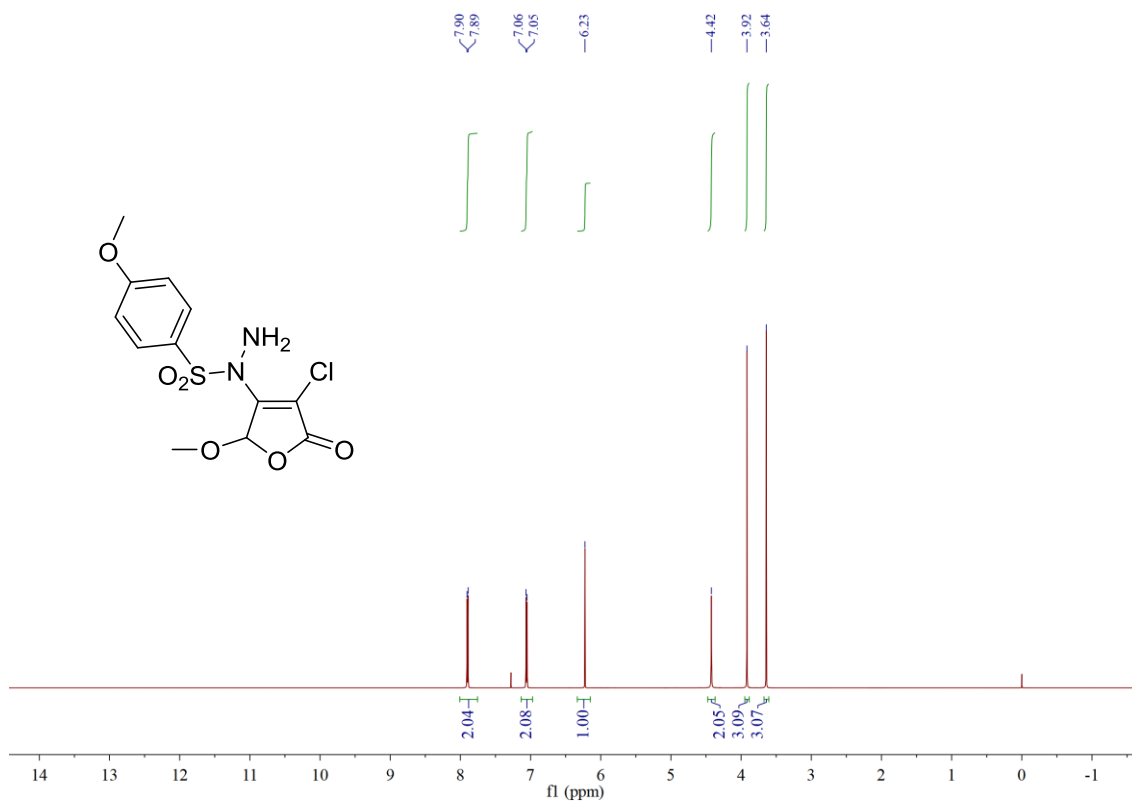


$^1\text{H}$  NMR spectrum of compound **4m**

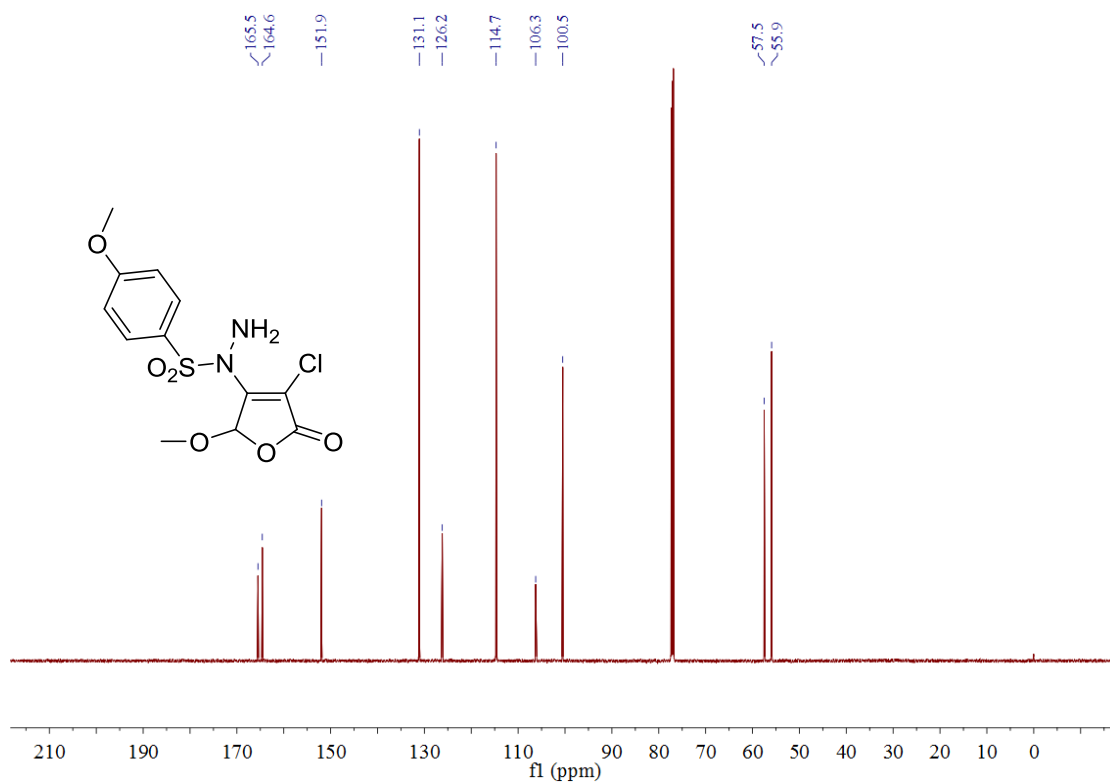




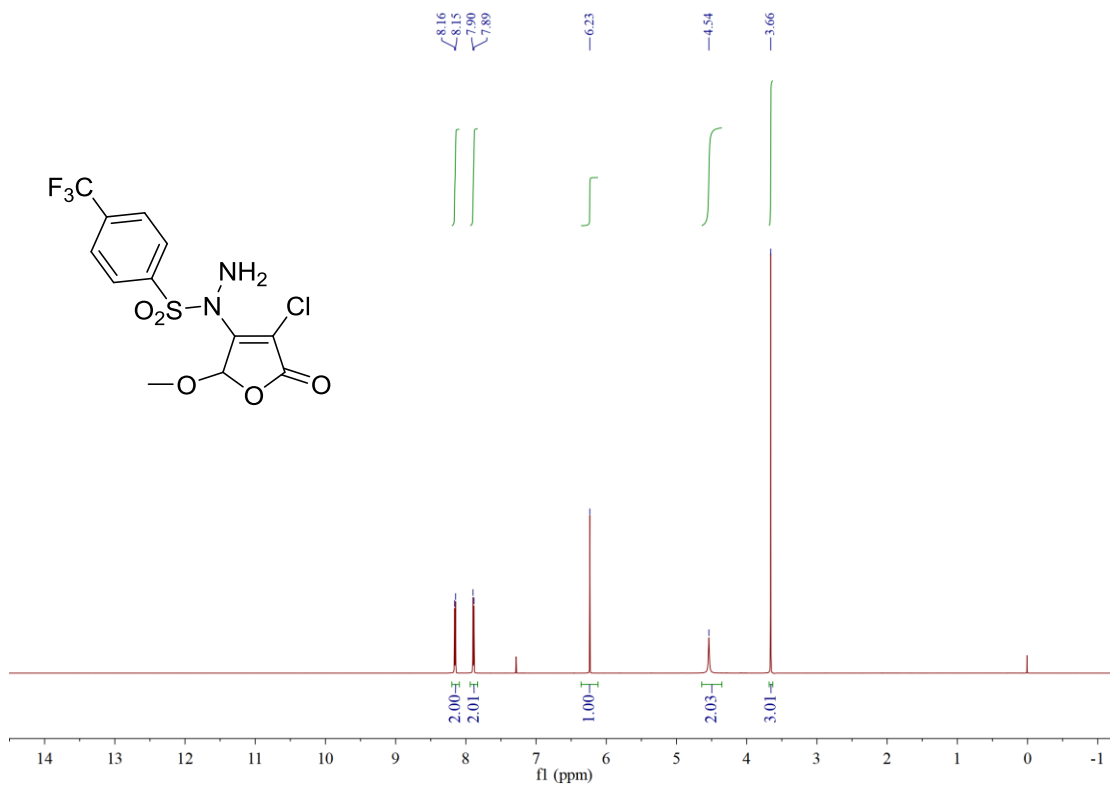
<sup>13</sup>C NMR spectrum of compound **4m**



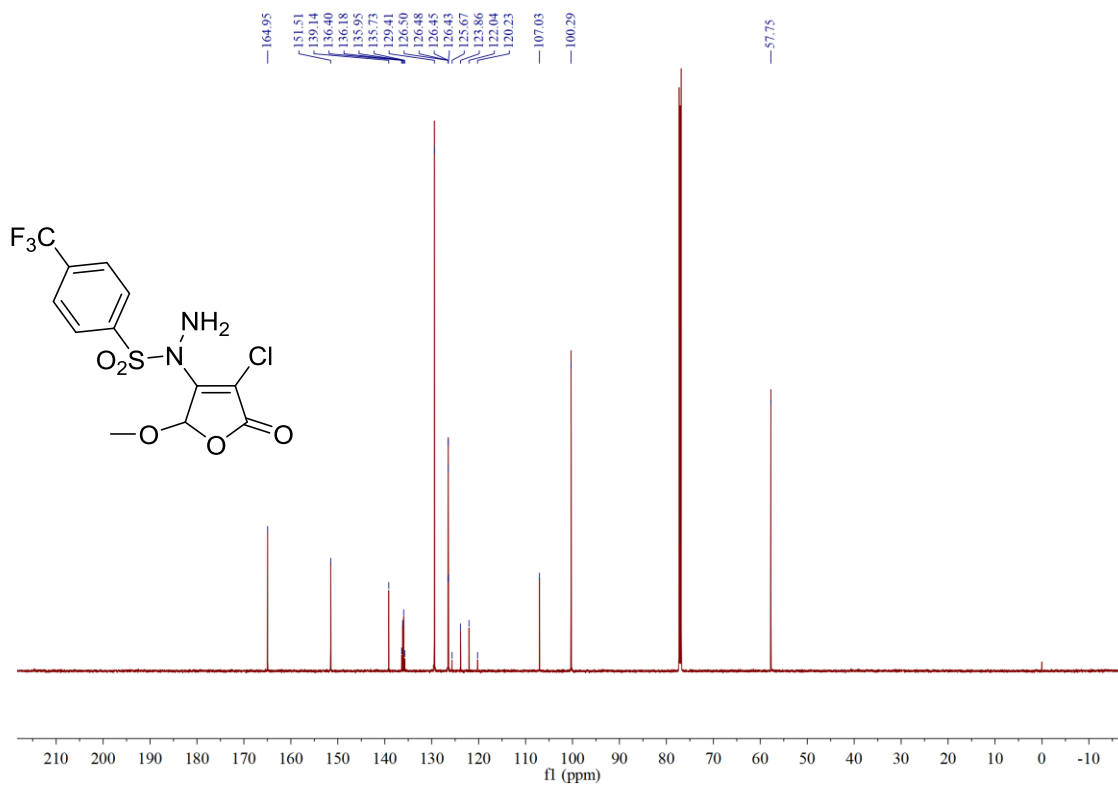
<sup>1</sup>H NMR spectrum of compound **4n**



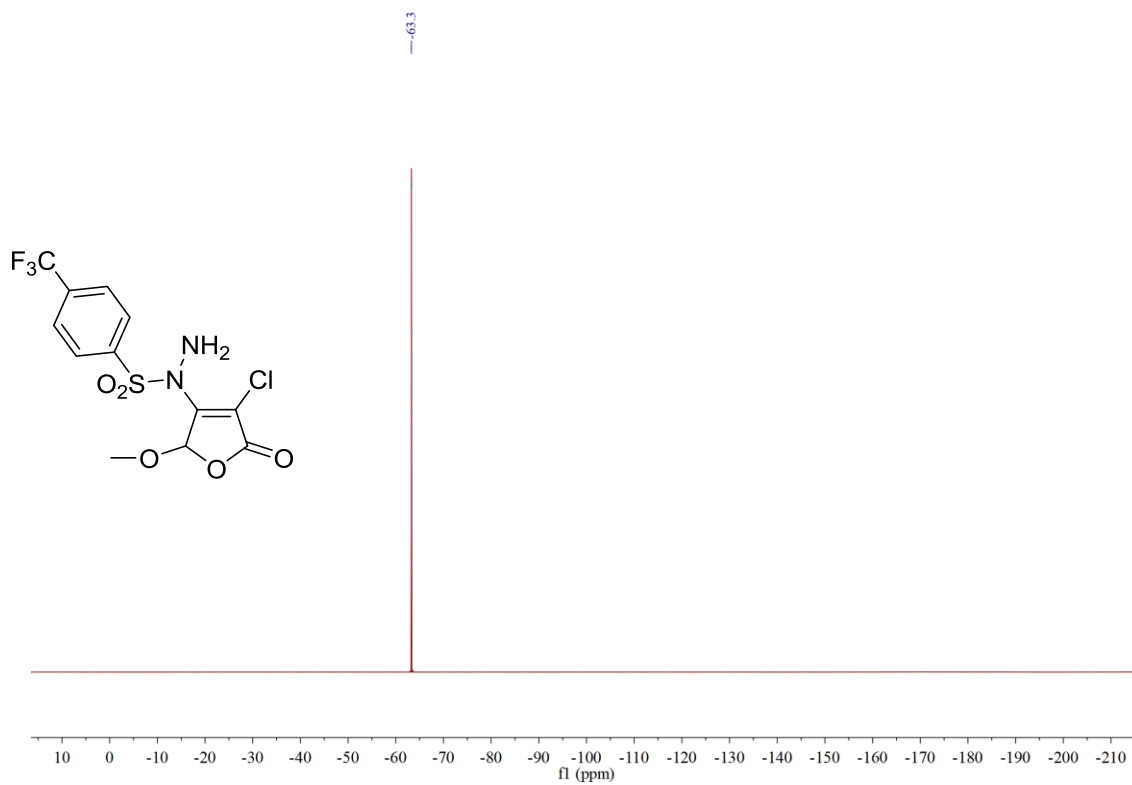
$^{13}\text{C}$  NMR spectrum of compound **4n**



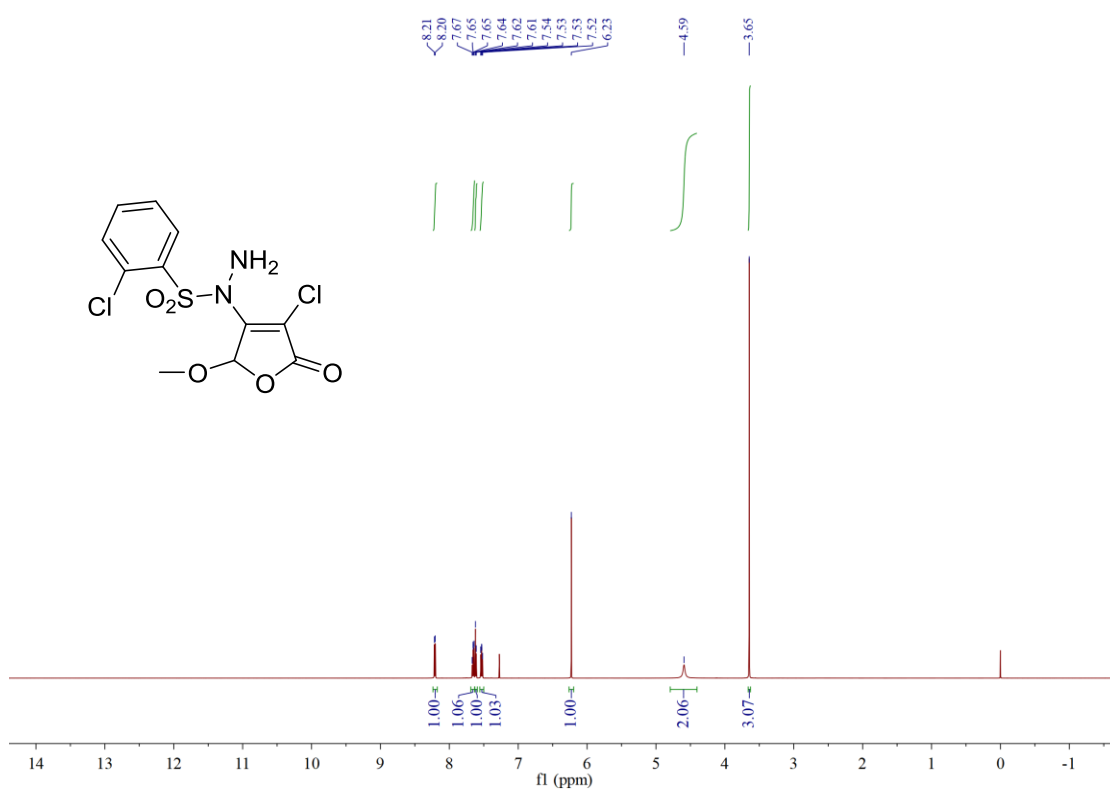
$^1\text{H}$  NMR spectrum of compound **4o**



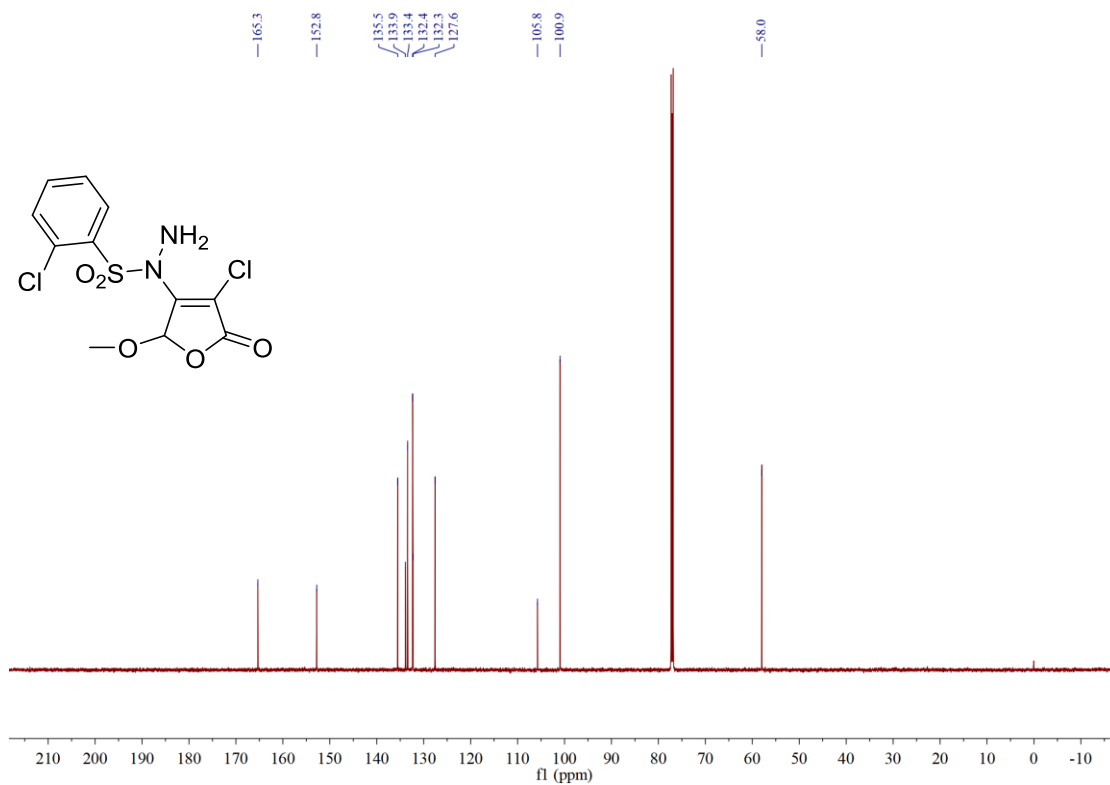
<sup>13</sup>C NMR spectrum of compound **4o**



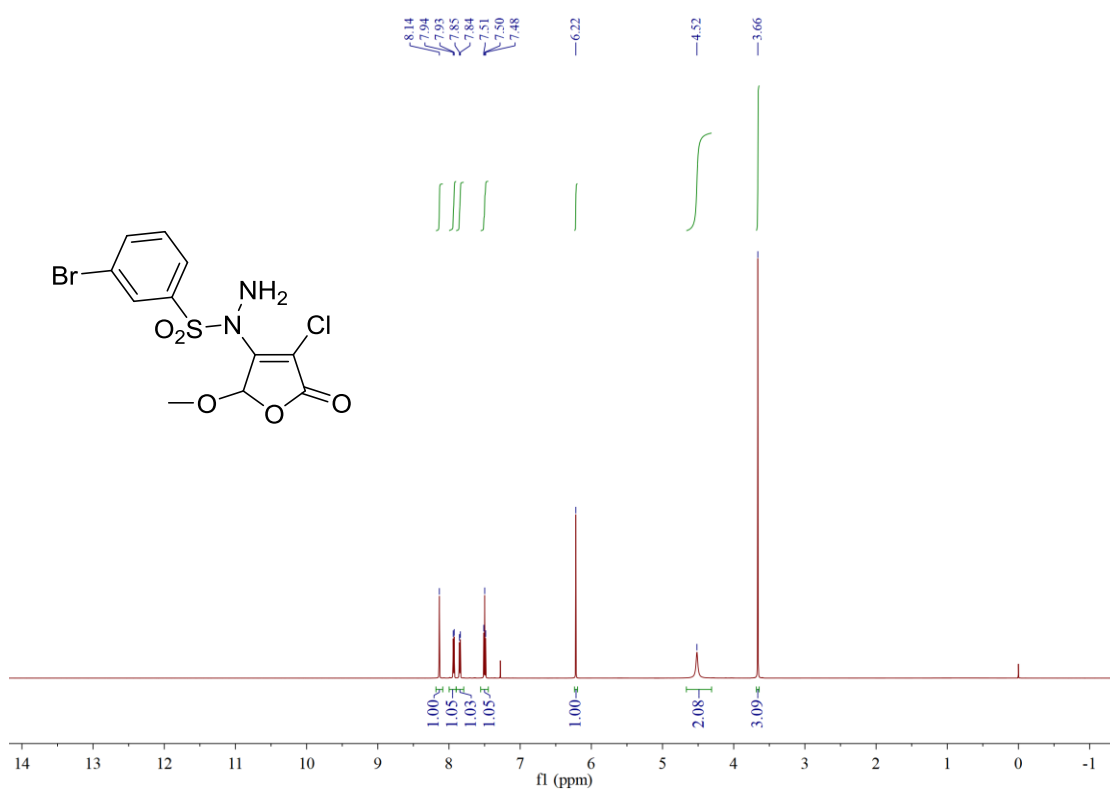
<sup>19</sup>F NMR spectrum of compound **4o**



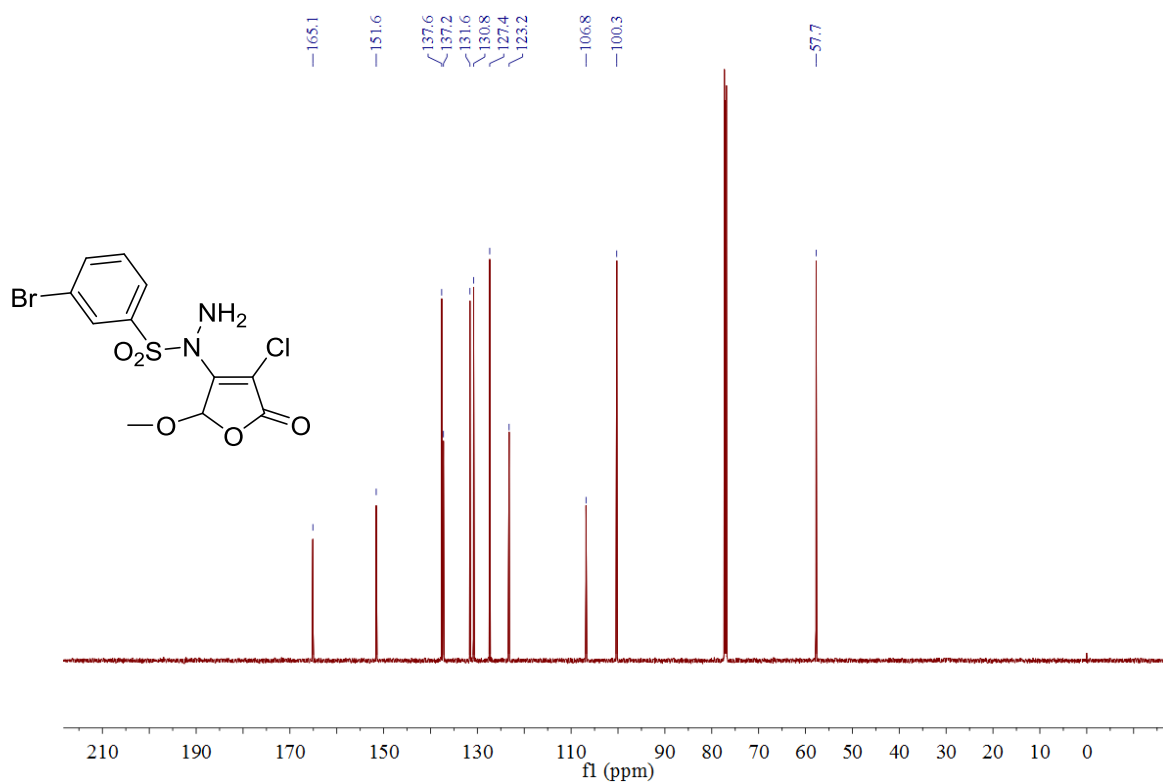
$^1\text{H}$  NMR spectrum of compound **4p**



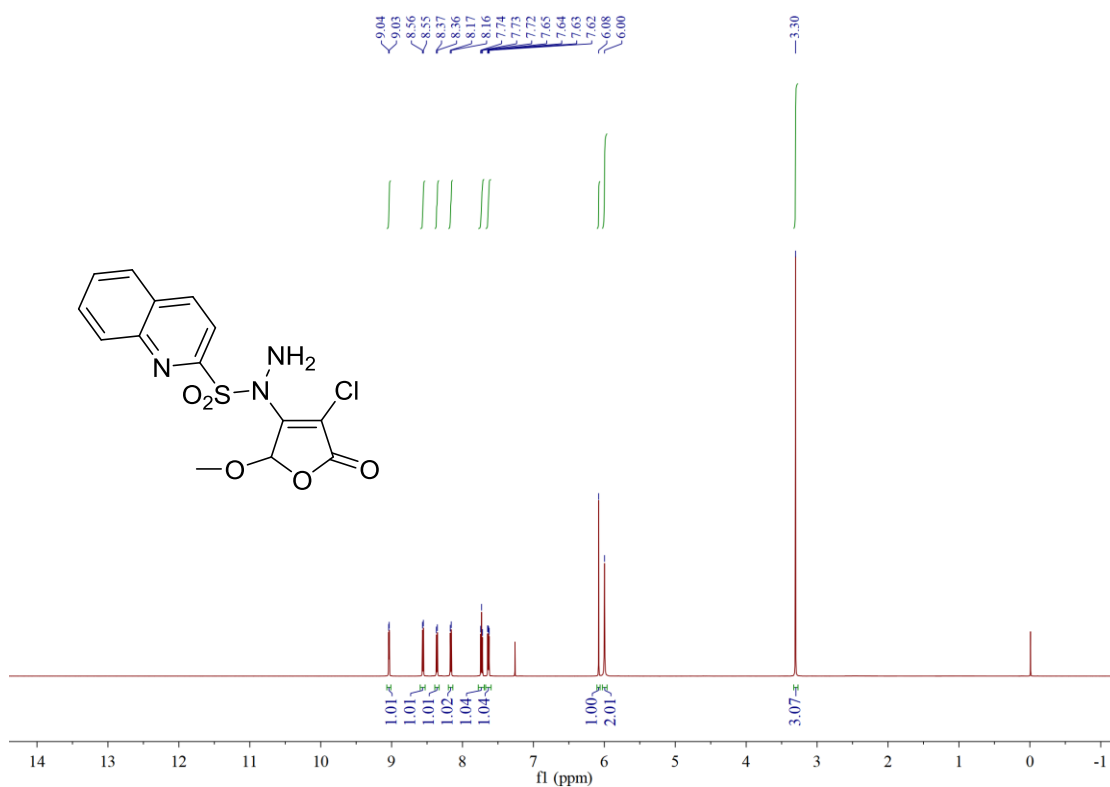
$^{13}\text{C}$  NMR spectrum of compound **4p**



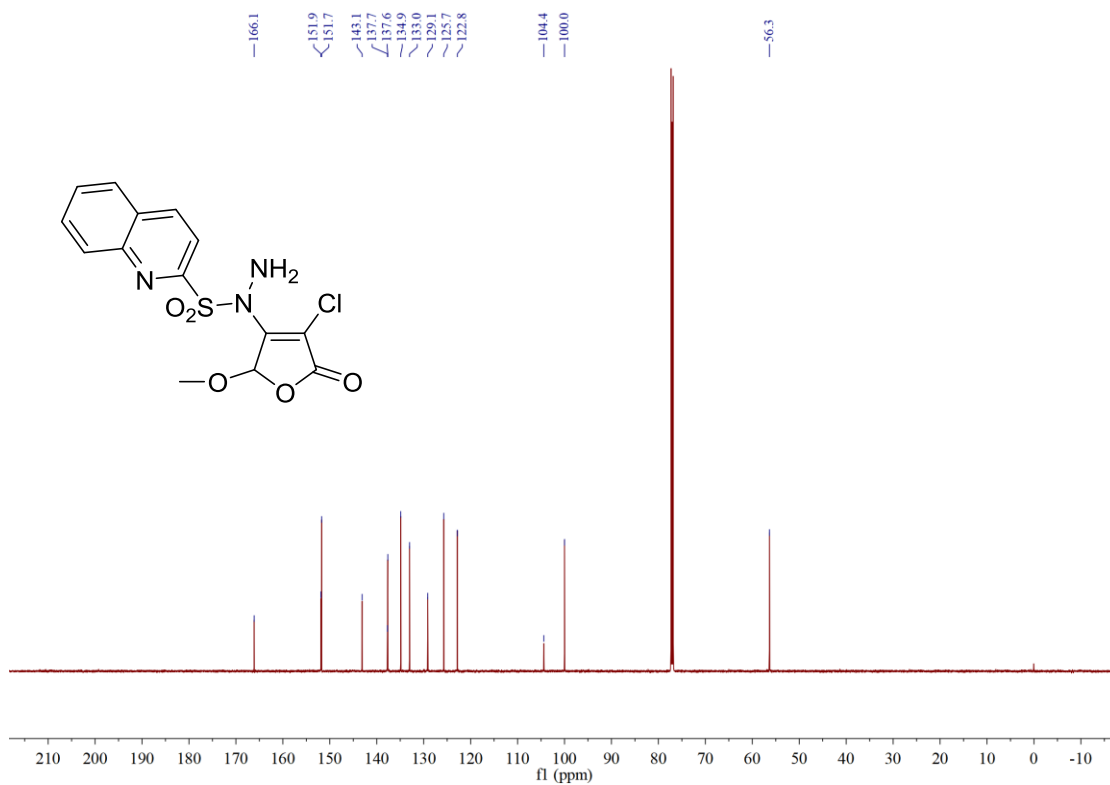
<sup>1</sup>H NMR spectrum of compound **4q**



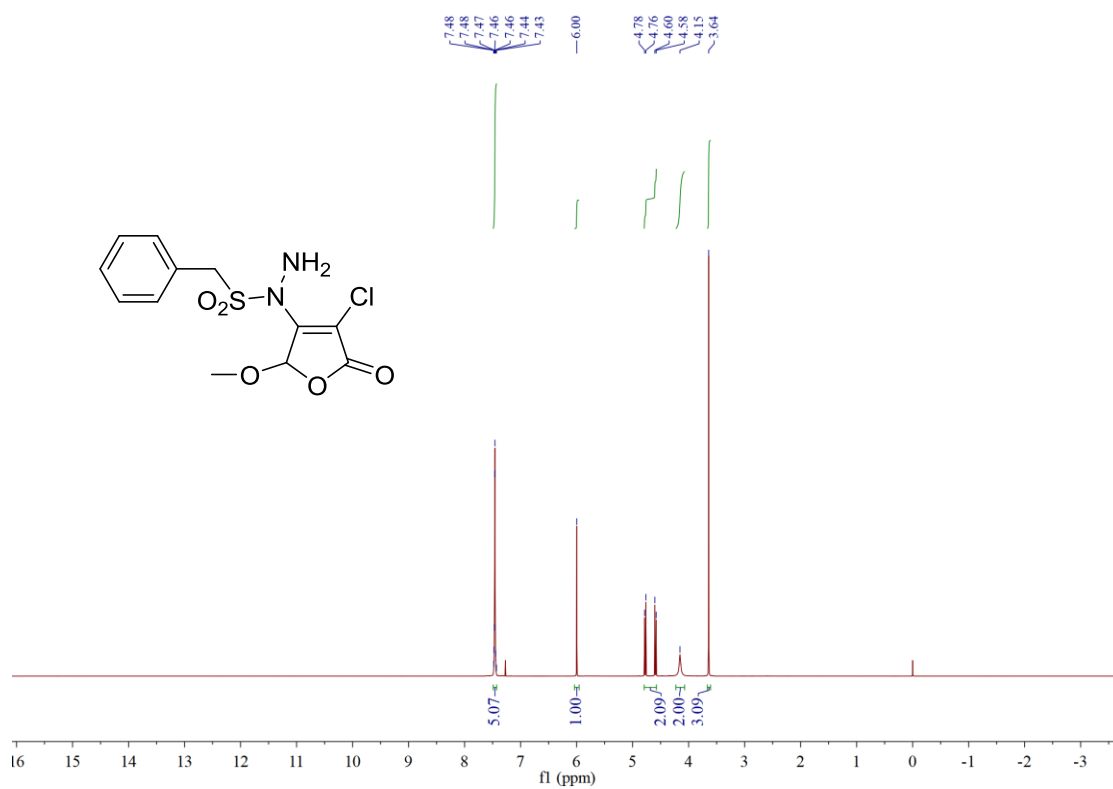
<sup>13</sup>C NMR spectrum of compound **4q**



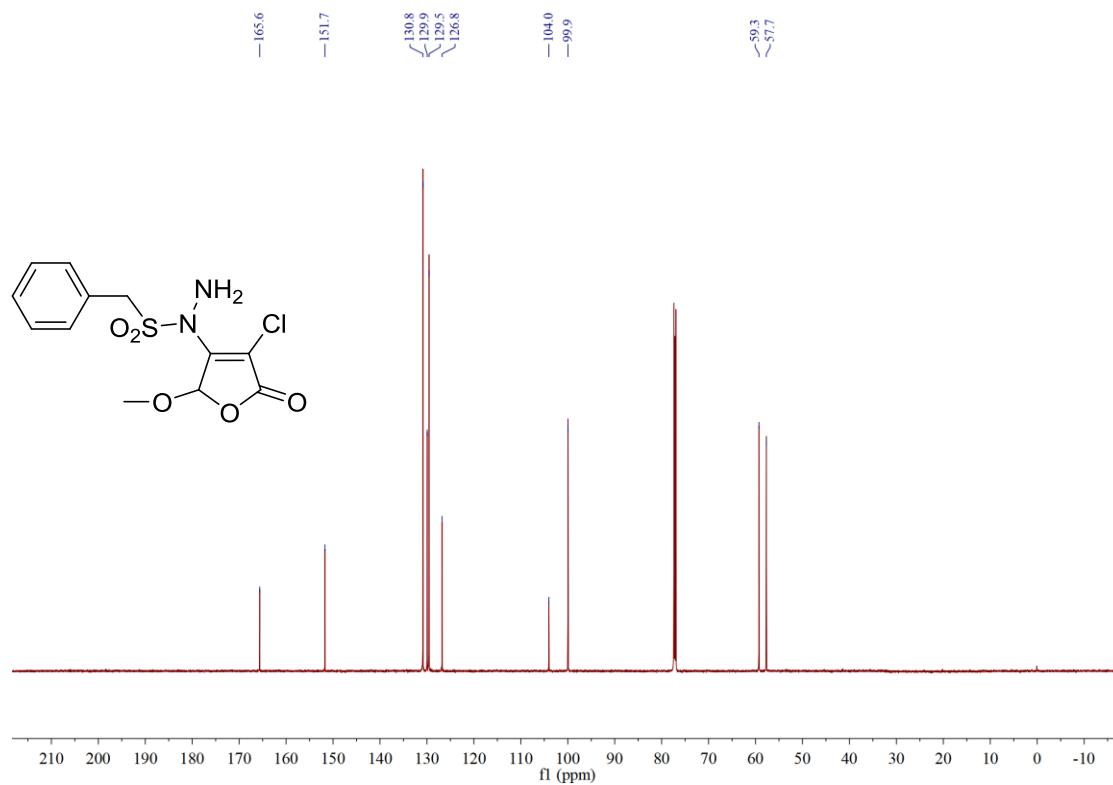
<sup>1</sup>H NMR spectrum of compound **4r**



<sup>13</sup>C NMR spectrum of compound **4r**



<sup>1</sup>H NMR spectrum of compound **4s**



<sup>13</sup>C NMR spectrum of compound **4s**

