Electronic Supporting Information

Quick construction of C-N bond from arylsulfonyl hydrazides and \( \text{C}_{\text{sp}2}-\text{X} \) compounds promoted by DMAP at room temperature

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Table of Contents

Supplemental Data for Competing Experiments and the Corresponding Discussions..............................................................[2-4]
Characterization Data for All Products 3a-4s and Intermediate A.........................................................................................[5-19]
Data of Single-crystal X-ray Analysis........................................................................................................................................[20-21]
NMR Spectra for All Compounds 3a-3v, 4a-4s and Intermediate A.........................................................................................[22-64]
Supplemental Data for Competing Experiments and the Corresponding Discussions

The mixture of 3,4-dibromo-5-methoxy-2(5H)-furanone 1a (0.50 mmol), 3,4-dichloro-5-methoxy-2(5H)-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 : H2O (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 H2O (15 mL) and extracted with DCM (3 × 15 mL). Then, the organic layer was dried over anhydrous Na2SO4. 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 1H NMR spectra, their yields are calculated.

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

| Entry | 1a (mmol) | 1b (mmol) | 2a (mmol) | Other reaction conditions | The 1H NMR ratio of 3a : 4a | Yield of 3a | Yield of 4a |
|-------|-----------|-----------|-----------|--------------------------|-----------------------------|------------|------------|
| 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%        |

*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 1H 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 1H 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(5H)-
furanones have higher activity and faster reaction rate to complete the reaction with a shorter time in comparison of 3,4-dichloro-2(5H)-furanones indeed.

However, if using excessive sulfonyl hydrazide (1.2 mmol) to simultaneously react with 3,4-dibromo-5-methoxy-2(5H)-furanone 1a (0.5 mmol) and 3,4-dichloro-5-methoxy-2(5H)-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(5H)-furanones after prolonging reaction time when the amount of sulfonyl hydrazide is enough for it also.

Fig. S1. $^1$H NMR of products (Table S1, Entry 1).
Fig. S2. $^1$H NMR of products (Table S1, Entry 2).

Fig. S3. $^1$H NMR of products (Table S1, Entry 3).
Characterization Data for All Products 3a-4s and Intermediate A

\[
\text{N-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (3a)}
\]
White solid (154 mg, 82%); m.p. 135.4-136.9 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\): 2.48 (s, 3H, CH\(_3\)), 3.61 (s, 3H, OCH\(_3\)), 4.46 (s, 2H, NH\(_2\)), 6.24 (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, 57.5, 95.3, 101.6, 128.8, 130.2, 132.3, 146.2, 155.7, 165.9; ESI-HRMS, m/z: Calcd for C\(_{12}\)H\(_{14}\)BrN\(_2\)O\(_5\)S [M+H]\(^+\), 376.9801, found: 376.9819.

\[
\text{N-(4-bromo-2-ethoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (3b)}
\]
Colorless waxy (152 mg, 78%); \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\): 1.26 (t, \(J = 6.0\) Hz, 3H, CH\(_3\)), 2.48 (s, 3H, CH\(_3\)), 3.83-3.98 (m, 2H, OCH\(_2\)), 4.42 (s, 2H, NH\(_2\)), 6.29 (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\(_3\)), \(\delta\): 15.0, 21.9, 57.5, 95.7, 100.8, 128.8, 130.2, 132.3, 146.1, 155.9, 166.0; ESI-HRMS, m/z: Calcd for C\(_{13}\)H\(_{16}\)BrN\(_2\)O\(_5\)S [M+H]\(^+\), 390.9958, found: 390.9965.

\[
\text{N-(4-bromo-2-butoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (3c)}
\]
Colorless oil (165 mg, 79%); \(^1\)H 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\(_2\)), 2.48 (s, 3H, CH\(_3\)), 3.76-3.89 (m, 2H, OCH\(_2\)), 4.42 (b, 2H, NH\(_2\)), 6.27 (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\(_3\)), \(\delta\): 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_{2}O_{5}S [M+H]^+, 419.0271, found: 419.0273.

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

Colorless oil (192 mg, 86%); ^1^H NMR (600 MHz, CDCl$_3$), δ: 0.89 (t, J = 6.0 Hz, 3H, CH$_3$), 1.26-1.35 (m, 6H, 3CH$_2$), 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); ^1^C NMR (150 MHz, CDCl$_3$), δ: 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$_2$O$_5$S [M+H]^+, 447.0584, found: 447.0596.

N-(4-bromo-2-(6-chlorohepxyloxy)-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (3e)

Colorless oil (202 mg, 84%); ^1^H NMR (600 MHz, CDCl$_3$), δ: 1.36-1.48 (m, 4H, 2CH$_2$), 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); ^1^C NMR (150 MHz, CDCl$_3$), δ: 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$_2$O$_5$S [M+H]^+, 481.0194, found: 481.0207.

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

Colorless oil (164 mg, 81%); ^1^H NMR (600 MHz, CDCl$_3$), δ: 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); $^{13}$C NMR (150 MHz, CDCl$_3$), \( \delta \): 21.7, 21.9, 23.1, 75.1, 97.2, 100.3, 128.6, 130.1, 132.1, 146.0, 166.0; ESI-HRMS, m/z: Calcd for C$_{14}$H$_{18}$BrN$_2$O$_5$S [M+H]$^+$, 405.0114, found: 405.0126.

$\text{N-(4-bromo-2-cyclohexyloxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonyhydrazide (3g)}$

Colorless oil (173 mg, 78%); $^1$H NMR (600 MHz, CDCl$_3$), \( \delta \): 1.19-1.55 (m, 6H, 3CH$_2$), 1.71-1.77 (m, 2H, CH$_2$), 1.94-2.01 (m, 2H, CH$_2$), 2.48 (s, 3H, CH$_3$), 3.82-3.87 (m, 1H, OCH), 4.24 (b, 2H, NH$_2$), 6.35 (s, 1H, CH), 7.40 (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, 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$_{17}$H$_{22}$BrN$_2$O$_5$S [M+H]$^+$, 445.0427, found: 445.0442.

$\text{N-(2-benzyloxy-4-bromo-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonyhydrazide (3h)}$

Colorless waxy (181 mg, 80%); $^1$H NMR (600 MHz, CDCl$_3$), \( \delta \): 2.41 (s, 3H, CH$_3$), 4.31 (b, 2H, NH$_2$), 4.77-4.94 (dd, J$_1$ = 12.0 Hz, J$_2$ = 12.0 Hz, 2H, OCH$_2$), 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); $^{13}$C NMR (150 MHz, CDCl$_3$), \( \delta \): 21.8, 23.9, 25.4, 31.9, 33.3, 80.7, 97.5, 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$_{18}$H$_{18}$BrN$_2$O$_5$S [M+H]$^+$, 453.0114, found: 453.0115.

$\text{N-(4-bromo-5-oxo-2-phenoxy-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonyhydrazide (3i)}$
Colorless waxy (166 mg, 76%); $^1$H NMR (600 MHz, CDCl$_3$), $\delta$: 2.45 (s, 3H, CH$_3$), 4.49 (b, 2H, 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); $^{13}$C NMR (150 MHz, 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 C$_{17}$H$_{16}$BrN$_2$O$_5$S [M+H]$^+$, 438.9958, found: 438.9963.

\[
\begin{array}{c}
\text{O}_2\text{S}-\text{N} \\
\text{Br} \\
\end{array}
\]

$N$-(2-[[1,1'-biphenyl]-4-yloxy]-4-bromo-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (3j)

White solid (180 mg, 70%), m.p. 66.2-67.8 ºC; $^1$H NMR (600 MHz, CDCl$_3$), $\delta$: 2.47 (s, 3H, CH$_3$), 4.47 (b, 2H, 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); $^{13}$C NMR (150 MHz, 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 C$_{23}$H$_{20}$BrN$_2$O$_5$S [M+H]$^+$, 515.0271, found: 515.0273.

\[
\begin{array}{c}
\text{O}_2\text{S}-\text{N} \\
\text{Br} \\
\end{array}
\]

$N$-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonohydrazide (3k)

Colorless waxy (147 mg, 81%); $^1$H NMR (600 MHz, CDCl$_3$), $\delta$: 3.62 (s, 3H, OCH$_3$), 4.47 (s, 2H, 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); $^{13}$C NMR (150 MHz, 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 C$_{12}$H$_{12}$BrN$_2$O$_5$S [M+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%); \(^1^H\) NMR (600 MHz, CDCl\(_3\)), \(\delta\): 1.25 (d, \(J = 6.0\) Hz, 3H, CH\(_3\)), 1.29 (d, \(J = 6.0\) Hz, 3H, CH\(_3\)), 4.14-4.19 (\(m\), 1H, OCH), 4.43 (s, 2H, 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); \(^{13}\)C NMR (150 MHz, 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, \(m/\ell\): Calcd for C\(_{13}\)H\(_{16}\)BrN\(_2\)O\(_5\)S [M+H]+, 390.9958, found: 390.9967.

![Chemical Structure](https://example.com/structure.png)

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

Colorless waxy (161 mg, 75%); \(^1^H\) NMR (600 MHz, CDCl\(_3\)), \(\delta\): 1.18-1.55 (\(m\), 6H, 3CH\(_2\)), 1.71-1.76 (\(m\), 2H, CH\(_3\)), 1.95-1.98 (\(m\), 2H, CH\(_2\)), 3.82-3.86 (\(m\), 1H, OCH), 4.09 (b, 2H, 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); \(^{13}\)C NMR (150 MHz, 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, \(m/\ell\): Calcd for C\(_{13}\)H\(_{16}\)BrN\(_2\)O\(_5\)S [M+H]+, 431.0271, found: 431.0263.

![Chemical Structure](https://example.com/structure.png)

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

Colorless waxy (153 mg, 72%); \(^1^H\) NMR (600 MHz, CDCl\(_3\)), \(\delta\): 4.52 (b, 2H, 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); \(^{13}\)C NMR (150 MHz, 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, \(m/\ell\): Calcd for C\(_{16}\)H\(_{14}\)BrN\(_2\)O\(_5\)S [M+H]+, 424.9801, found: 424.9811.

![Chemical Structure](https://example.com/structure.png)
**N-(2-benzyloxy-4-bromo-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonohydrazide (3o)**

Colorless waxy (173 mg, 79%); $^1$H NMR (600 MHz, CDCl$_3$), δ: 4.34 (b, 2H, NH$_2$), 4.77-4.94 (dd, J$_1$ = 12.0 Hz, J$_2$ = 12.0 Hz, 2H, 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); $^{13}$C NMR (150 MHz, CDCl$_3$), δ: 72.9, 95.5, 100.1, 128.6, 128.7, 128.8, 128.9, 129.3, 134.6, 135.0, 155.6, 165.9; ESI-HRMS, m/z: Calcd for C$_{17}$H$_{16}$BrN$_2$O$_5$S [M+H]$^+$, 438.9958, found: 438.9962.

![N-(2-benzyloxy-4-bromo-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonohydrazide (3o)](image)

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

Colorless waxy (165 mg, 81%); $^1$H NMR (600 MHz, CDCl$_3$), δ: 3.66 (s, 3H, OCH$_3$), 4.61 (b, 2H, 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); $^{13}$C NMR (150 MHz, CDCl$_3$), δ: 57.9, 95.8, 101.3, 124.4, 130.4, 141.4, 151.1, 155.1, 165.3; ESI-HRMS, m/z: Calcd for C$_{11}$H$_{11}$BrN$_2$O$_5$S [M+H]$^+$, 407.9496, found: 407.9490.

![N-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-nitrobenzenesulfonohydrazide (3p)](image)

**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 °C; $^1$H NMR (600 MHz, CDCl$_3$), δ: 3.65 (s, 3H, OCH$_3$), 3.93 (s, 3H, OCH$_3$), 4.42 (s, 2H, 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); $^{13}$C NMR (150 MHz, CDCl$_3$), δ: 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 C$_{12}$H$_{14}$BrN$_2$O$_6$S [M+H]$^+$, 392.9750, found: 392.9774.
$N$-$(4$-bromo-$2$-methoxy-$5$-oxo-$2,5$-dihydrofuran-$3$-yl)$-4$-trifluoromethylbenzenesulfonohydrazide ($3r$)

Colorless waxy (178 mg, 83%); $^1$H NMR (600 MHz, CDCl$_3$), $\delta$: 3.67 (s, 3H, OCH$_3$), 4.53 (s, 2H, 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); $^{13}$C NMR (150 MHz, 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; $^{19}$F NMR (564 MHz, CDCl$_3$), $\delta$: -63.3; ESI-HRMS, $m/z$: Calcd for C$_{12}$H$_{11}$BrF$_3$N$_2$O$_5$S [M+H]$^+$, 430.9519, found: 430.9554.

$N$-$(4$-bromo-$2$-methoxy-$5$-oxo-$2,5$-dihydrofuran-$3$-yl)$-2$-chlorobenzenesulfonohydrazide ($3s$)

White solid (168 mg, 85%); m.p. 118.5-119.8 °C; $^1$H NMR (600 MHz, CDCl$_3$), $\delta$: 3.65 (s, 3H, OCH$_3$), 4.57 ($b$, 2H, 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); $^{13}$C NMR (150 MHz, 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 C$_{11}$H$_{11}$BrClN$_2$O$_5$S [M+H]$^+$, 396.9255, found: 396.9263.

3-bromo-$N$-$(4$-bromo-$2$-methoxy-$5$-oxo-$2,5$-dihydrofuran-$3$-yl)$benzenesulfonohydrazide ($3t$)

Colorless waxy (180 mg, 82%); $^1$H NMR (600 MHz, CDCl$_3$), $\delta$: 3.66 (s, 3H, OCH$_3$), 4.51 ($b$, 2H, 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); $^{13}$C NMR (150 MHz, 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, \textit{m/z}: Calcd for C\textsubscript{11}H\textsubscript{13}BrN\textsubscript{2}O\textsubscript{5}S [M+H]\textsuperscript{+}, 440.8750, found: 440.8771.

\[
\text{N-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)quinoline-2-sulfonohydrazide (3u)}
\]
Colorless waxy (159 mg, 77\%); \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}), \(\delta\): 3.27 (s, 3H, OCH\textsubscript{3}), 5.98 (b, 2H, NH\textsubscript{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), 8.97 (d, \(J = 6.0\) Hz, 1H, ArH); \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{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, \textit{m/z}: Calcd for C\textsubscript{14}H\textsubscript{13}BrN\textsubscript{2}O\textsubscript{5}S [M+H]\textsuperscript{+}, 413.9754, found: 413.9766.

\[
\text{N-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-1-phenylmethanesulfonohydrazide (3v)}
\]
White solid (150 mg, 80\%); m.p. 146.8-147.9 \textdegree C; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}), \(\delta\): 3.67 (s, 3H, OCH\textsubscript{3}), 4.13 (b, 2H, NH\textsubscript{2}), 4.59-4.82 (dd, \(J_{1} = 12.0\) Hz, \(J_{2} = 12.0\) Hz, 2H, CH\textsubscript{2}), 6.04 (s, 1H, CH), 7.46-7.50 (m, 5H, ArH); \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}), \(\delta\): 57.6, 59.3, 92.3, 100.8, 126.7, 129.5, 129.9, 130.8, 155.2, 166.0; ESI-HRMS, \textit{m/z}: Calcd for C\textsubscript{14}H\textsubscript{13}BrN\textsubscript{2}O\textsubscript{5}S [M+H]\textsuperscript{+}, 376.9801, found: 376.9832.

\[
\text{N-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (4a)}
\]
Colorless waxy (139 mg, 84\%); \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}), \(\delta\): 2.48 (s, 3H, CH\textsubscript{3}), 3.64 (s, 3H, OCH\textsubscript{3}), 4.30 (b, 2H, NH\textsubscript{2}), 6.22 (s, 1H, CH), 7.41 (d, \(J = 6.0\) Hz, 2H, ArH), 7.85 (d, \(J = 6.0\) Hz, 2H, ArH); \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}), \(\delta\): 21.9, 57.6, 100.6, 106.9, 128.8, 130.2, 132.3, 146.2, 152.0, 165.4; ESI-HRMS, \textit{m/z}: Calcd for C\textsubscript{12}H\textsubscript{14}ClN\textsubscript{2}O\textsubscript{5}S [M+H]\textsuperscript{+}, 333.0306, found: 333.0327.
**N-(4-chloro-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (4b)**

Colorless oil (155 mg, 86%); $^1$H NMR (600 MHz, CDCl$_3$), $\delta$: 0.92 (t, $J = 6.0$ Hz, 3H, CH$_3$), 1.60-1.66 (m, 2H, CH$_2$), 2.47 (s, 3H, CH$_3$), 3.71-3.85 (m, 2H, OCH$_2$), 4.42 (b, 2H, 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); $^{13}$C NMR (150 MHz, 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 C$_{14}$H$_{18}$ClN$_2$O$_5$S [M+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%); $^1$H NMR (600 MHz, CDCl$_3$), $\delta$: 0.92 (t, $J = 6.0$ Hz, 3H, CH$_3$), 1.33-1.40 (m, 6H, 3CH$_2$), 1.57-1.62 (m, 2H, CH$_2$), 2.48 (s, 3H, CH$_3$), 3.76-3.91 (m, 2H, OCH$_2$), 4.38 (b, 2H, 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); $^{13}$C NMR (150 MHz, 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 C$_{15}$H$_{20}$ClN$_2$O$_5$S [M+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%); $^1$H NMR (600 MHz, CDCl$_3$), $\delta$: 0.89 (t, $J = 6.0$ Hz, 3H, CH$_3$), 1.26-1.36 (m, 6H, 3CH$_2$), 1.59-1.63 (m, 2H, CH$_2$), 2.48 (s, 3H, CH$_3$), 3.75-3.90 (m, 2H, OCH$_2$), 4.39 (s, 2H, 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); $^{13}$C NMR (150 MHz, 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 C$_{17}$H$_{23}$ClN$_2$O$_5$S [M+H]$^+$, 403.1089, found: 403.1082.
N-(4-chloro-2-isopropoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methylbenzenesulfonohydrazide (4e)

Colorless oil (149 mg, 83%); \(^1\)H 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), 4.40 (s, 2H, 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); \(^{13}\)C NMR (150 MHz, 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 C\(_{14}\)H\(_{18}\)ClN\(_2\)O\(_5\)S [M+H]^+, 361.0619, found: 361.0629.

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

Colorless waxy (156 mg, 78%); \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\): 1.17-1.55 (m, 6H, 3CH\(_2\)), 1.70-1.77 (m, 2H, CH\(_2\)), 1.94-1.99 (m, 2H, CH\(_2\)), 2.48 (s, 3H, CH\(_3\)), 3.82-3.86 (m, 1H, OCH), 4.36 (b, 2H, 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); \(^{13}\)C NMR (150 MHz, 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 C\(_{17}\)H\(_{22}\)ClN\(_2\)O\(_5\)S [M+H]^+, 401.0932, found: 401.0945.

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

Colorless waxy (151 mg, 74%); \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\): 2.40 (s, 3H, CH\(_3\)), 4.31 (b, 2H, NH\(_2\)), 4.76-4.94 (dd, \(J_1 = 12.0\) Hz, \(J_2 = 12.0\) Hz, 2H, 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); \(^{13}\)C NMR (150 MHz, 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_{2}O_{5}S [M+H]^+, 409.0619, found: 409.0630.

![Chemical structure 4h]

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

Colorless waxy (148 mg, 75%); $^1$H 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$_2$O$_5$S [M+H]$^+$, 395.0463, found: 395.0474.

![Chemical structure 4i]

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

Colorless waxy (130 mg, 82%); $^1$H 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$_2$O$_5$S [M+H]$^+$, 319.0150, found: 319.0164.

![Chemical structure 4j]

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

Colorless oil (146 mg, 81%); $^1$H 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$_3$), δ: 13.8, 19.1, 31.5, 71.1, 107.8, 129.6, 134.7, 135.4, 152.1, 165.5; ESI-HRMS, m/z: Calcd for C$_{14}$H$_{18}$ClN$_2$O$_5$S [M+H]$^+$, 361.0619, found: 361.0629.

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

Colorless waxy (152 mg, 77%); $^1$H NMR (600 MHz, CDCl$_3$), δ: 4.31 (s, 2H, NH$_2$), 4.78-4.97 (dd, $J_1$ = 12.0 Hz, $J_2$ = 12.0 Hz, 2H, OCH$_2$), 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); $^{13}$C NMR (150 MHz, CDCl$_3$), δ: 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$_{17}$H$_{16}$ClN$_2$O$_5$S [M+H]$^+$, 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; $^1$H NMR (600 MHz, CDCl$_3$), δ: 4.49 (s, 2H, NH$_2$), 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); $^{13}$C NMR (150 MHz, CDCl$_3$), δ: 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$_{16}$H$_{14}$ClN$_2$O$_3$S [M+H]$^+$, 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%); $^1$H NMR (600 MHz, CDCl$_3$), δ: 3.67 (s, 3H, OCH$_3$), 4.57 (b, 2H, NH$_2$), 6.23 (s, 1H, CH), 8.23 (d, $J$ = 6.0 Hz, 2H, ArH), 8.45 (d, $J$ = 6.0 Hz, 2H, ArH); $^{13}$C NMR (150 MHz,
CDCl₃, δ: 57.9, 100.2, 107.2, 124.4, 130.3, 141.3, 151.0, 151.4, 164.7; ESI-HRMS, m/z: Calcd for C₁₁H₁₁ClN₂O₂S [M+H]⁺, 364.0001, found: 364.0030.

\[ \text{N-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-methoxybenzenesulfonylhydrazide (4n)} \]

Colorless waxy (143 mg, 82%); ¹H NMR (600 MHz, CDCl₃), δ: 3.64 (s, 3H, OCH₃), 3.92 (s, 3H, OCH₃), 4.42 (s, 2H, NH₂), 6.23 (s, 1H, CH), 7.06 (d, J = 6.0 Hz, 2H, ArH), 7.90 (d, J = 6.0 Hz, 2H, ArH); ¹³C NMR (150 MHz, CDCl₃), δ: 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 C₁₂H₁₃ClN₂O₂S [M+H]⁺, 349.0256, found: 349.0271.

\[ \text{N-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-trifluoromethylbenzenesulfonylhydrazide (4o)} \]

Colorless waxy (162 mg, 84%); ¹H NMR (600 MHz, CDCl₃), δ: 3.66 (s, 3H, OCH₃), 4.54 (b, 2H, NH₂), 6.23 (s, 1H, CH), 7.90 (d, J = 6.0 Hz, 2H, ArH), 8.16 (d, J = 6.0 Hz, 2H, ArH); ¹³C NMR (150 MHz, CDCl₃), δ: 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; ¹⁹F NMR (564 MHz, CDCl₃), δ: -63.3; ESI-HRMS, m/z: Calcd for C₁₂H₁₁ClF₂N₂O₂S [M+H]⁺, 387.0024, found: 387.0044.

\[ \text{2-chloro-N-(4-chloro-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)benzenesulfonylhydrazide (4p)} \]

White solid (151 mg, 86%); m.p. 135.4-136.9 °C; ¹H NMR (600 MHz, CDCl₃), δ: 3.65 (s, 3H, OCH₃), 4.59 (b, 2H, NH₂), 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); ¹³C NMR (150 MHz, CDCl₃), δ: 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 C₁₁H₁₄Cl₂N₂O₅S [M+H]^+, 352.9760, found: 352.9799.

![Chemical structure 1](image)

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

Colorless waxy (158 mg, 80%); ¹H NMR (600 MHz, CDCl₃), δ: 3.66 (s, 3H, OCH₃), 4.52 (br, 2H, NH₂), 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); ¹³C NMR (150 MHz, CDCl₃), δ: 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 C₁₁H₁₁BrClN₂O₅S [M+H]^+, 396.9255, found: 396.9263.

![Chemical structure 2](image)

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

Colorless waxy (138 mg, 75%); ¹H NMR (600 MHz, CDCl₃), δ: 3.30 (s, 3H, OCH₃), 6.00 (s, 2H, NH₂), 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); ¹³C NMR (150 MHz, CDCl₃), δ: 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 C₁₄H₁₁ClN₂O₅S [M+H]^+, 370.0259, found: 370.0287.

![Chemical structure 3](image)

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

White solid (134 mg, 81%); m.p. 127.4-128.2 °C; ¹H NMR (600 MHz, CDCl₃), δ: 3.64 (s, 3H, OCH₃),
4.15 (b, 2H, NH₂), 4.58-4.78 (dd, J₁ = 12.0 Hz, J₂ = 12.0 Hz, 2H, CH₂), 6.00 (s, 1H, CH), 7.43-7.48 (m, 5H, ArH); ¹³C NMR (150 MHz, CDCl₃), 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 C₁₂H₁₄ClN₂O₅ [M+H]⁺, 333.0306, found: 333.0349.

\[ \text{1-(4-bromo-2-methoxy-5-oxo-2,5-dihydrofuran-3-yl)-4-dimethylaminopyridin-1-ium bromide} \]

(Intermediate A)

White solid (186 mg, 95%); m.p. 186.5-186.9 °C; ¹H NMR (600 MHz, D₂O), δ: 3.39 (s, 6H, 2CH₃), 3.69 (s, 3H, OCH₃), 6.57 (s, 1H, CH), 7.13 (d, J = 6.0 Hz, 2H, ArH), 8.42 (d, J = 6.0 Hz, 2H, ArH); ¹³C NMR (150 MHz, D₂O), 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 C₁₂H₁₃BrN₂O₃ [M+H-Br]⁺, 314.0261, found: 314.0279.
Data of Single-crystal X-ray Analysis

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

| Compound          | 3a          |
|-------------------|-------------|
| Empirical formula | C_{12}H_{13}BrN_{2}O_{5}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, °) | \(a = 8.4406(6), b = 12.7982(11), c = 14.3406(11)\) \(a = 90, \beta = 105.550(7), \gamma = 90\) |
| Volume (Å³)       | 1492.4(2)   |
| Z                 | 4           |
| Density (calculated) (Mg/m³) | 1.679 |
| Absorption coefficient (mm⁻¹) | 2.916 |
| F(000)            | 760         |
| Crystal size (mm³) | 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 F² |
| Data / restraints / parameters | 3418 / 0 / 192 |
| Goodness-of-fit on F² | 1.018         |
| Final R indices [I>2sigma(I)] | R₁ = 0.0528, wR₂ = 0.0940 |
| R indices (all data) | R₁ = 0.0969, wR₂ = 0.1100 |
| Extinction coefficient | n/a          |
| Largest diff. peak and hole (e.Å⁻³) | 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 A |
|----------|----------------|
| Empirical formula | C$_{12}$H$_{14}$Br$_2$N$_2$O$_3$ |
| Formula weight | 394.07 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | P 2$_1$/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$^3$) | 1480.0(3) |
| Z | 4 |
| Density (calculated) (Mg/m$^3$) | 1.769 |
| Absorption coefficient (mm$^{-1}$) | 5.482 |
| F(000) | 776.0 |
| Crystal size (mm$^3$) | 0.32 x 0.18 x 0.11 |
| Theta range for data collection | 7.002 to 53.984 deg |
| Index ranges | $-11 \leq h \leq 10$, $-10 \leq k \leq 9$, $-25 \leq l \leq 26$ |
| 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$^2$ |
| Data / restraints / parameters | 3180 / 1 / 179 |
| Goodness-of-fit on F$^2$ | 0.998 |
| Final R indices [I>2sigma(I)] | R$_1$ = 0.0611, wR$_2$ = 0.1076 |
| R indices (all data) | R$_1$ = 0.1347, wR$_2$ = 0.1367 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole (e.Å$^3$) | 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

$^1$H NMR spectrum of compound 3a

$^{13}$C NMR spectrum of compound 3a
$^{1}H$ NMR spectrum of compound 3b

$^{13}C$ NMR spectrum of compound 3b
$^1$H NMR spectrum of compound 3c

$^{13}$C NMR spectrum of compound 3c
$^1$H NMR spectrum of compound 3d

$^{13}$C NMR spectrum of compound 3d
H NMR spectrum of compound 3e

$^1$H NMR spectrum of compound 3e

$^{13}$C NMR spectrum of compound 3e
$^1$H NMR spectrum of compound 3f

$^{13}$C NMR spectrum of compound 3f
$^1$H NMR spectrum of compound 3g

$^{13}$C NMR spectrum of compound 3g
$^{1}H$ NMR spectrum of compound 3h

$^{13}C$ NMR spectrum of compound 3h
$^1$H NMR spectrum of compound 3i

$^{13}$C NMR spectrum of compound 3i
$^1$H NMR spectrum of compound 3j

$^{13}$C NMR spectrum of compound 3j
$^1$H NMR spectrum of compound 3k

$^{13}$C NMR spectrum of compound 3k
$^{1}H$ NMR spectrum of compound 3l

$^{13}C$ NMR spectrum of compound 3l
$^{1}$H NMR spectrum of compound 3m

$^{13}$C NMR spectrum of compound 3m
$^1$H NMR spectrum of compound 3n

$^{13}$C NMR spectrum of compound 3n
$^1$H NMR spectrum of compound 3o

$^{13}$C NMR spectrum of compound 3o
$^1$H NMR spectrum of compound 3p

$^{13}$C NMR spectrum of compound 3p
$^1$H NMR spectrum of compound 3q

$^{13}$C NMR spectrum of compound 3q
$^1$H NMR spectrum of compound 3r

$^{13}$C NMR spectrum of compound 3r
$^{19}$F NMR spectrum of compound 3r

$^1$H NMR spectrum of compound 3s
$^{13}$C NMR spectrum of compound 3s

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

$\text{H NMR spectrum of compound 3u}$
$^{13}$C NMR spectrum of compound 3u

$^1$H NMR spectrum of compound 3v
$^{13}$C NMR spectrum of compound 3v

$^1$H NMR spectrum of compound 4a
\[ \text{CNMR spectrum of compound 4a} \]

\[ \text{\textsuperscript{1}H NMR spectrum of compound 4b} \]
$^{13}$C NMR spectrum of compound 4b

$^1$H NMR spectrum of compound 4c
$^{13}$C NMR spectrum of compound 4c

$^1$H NMR spectrum of compound 4d
$^{13}$C NMR spectrum of compound 4d

$^1$H NMR spectrum of compound 4e
$^{13}$C NMR spectrum of compound 4e

$^1$H NMR spectrum of compound 4f
$\text{C NMR spectrum of compound 4f}$

$\text{H NMR spectrum of compound 4g}$
$^{13}$C NMR spectrum of compound 4g

$^1$H NMR spectrum of compound 4h
$^{13}$C NMR spectrum of compound 4h

$^1$H NMR spectrum of compound 4i
$^{13}$C NMR spectrum of compound 4i

$^1$H NMR spectrum of compound 4j
$^{13}$C NMR spectrum of compound 4j

$^1$H NMR spectrum of compound 4k
$^{13}$C NMR spectrum of compound 4k

$^1$H NMR spectrum of compound 4l
$^{13}$C NMR spectrum of compound 4l

$^1$H NMR spectrum of compound 4m
$^{13}$C NMR spectrum of compound 4m

$^1$H NMR spectrum of compound 4n
$^{13}$C NMR spectrum of compound 4n

$^1$H NMR spectrum of compound 4o
$^{13}$C NMR spectrum of compound 4o

$^{19}$F NMR spectrum of compound 4o
$\text{H NMR spectrum of compound 4p}$

$\text{13C NMR spectrum of compound 4p}$
$^1$H NMR spectrum of compound 4q

$^{13}$C NMR spectrum of compound 4q
$^1$H NMR spectrum of compound 4r

$^{13}$C NMR spectrum of compound 4r
**H NMR spectrum of compound 4s**

**C NMR spectrum of compound 4s**
$^1$H NMR spectrum of intermediate A

$^{13}$C NMR spectrum of intermediate A