Supporting Information

Electrochemical oxidative dearomatization of 2-arylthiophenes

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1. General Information

All reactions were performed under an atmosphere of argon using standard Schlenk techniques, unless otherwise indicated. All commercial reagents were used without further purification, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) analysis. TLC plates were viewed under UV light and stained with potassium permanganate. Yields refer to products isolated after purification by column chromatography, unless otherwise stated. Proton nuclear magnetic resonance ($^1$H NMR) spectra, carbon nuclear magnetic resonance ($^{13}$C NMR) spectra and fluorine nuclear magnetic resonance ($^{19}$F NMR) were recorded on Bruker AV-400 (400 MHz), JEOL-500 (500 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($\text{CHCl}_3 = \delta 7.26$). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances IR spectra were obtained from Thermo Scientific NICOLET 380 FT-IR (KCl card). HRMS were obtained on an Exactive Plus LC-MS (ESI) mass spectrometer with the use of quadrupole analyzer. Cyclic voltammetry data were measured with a CHI 760E potentiostat (Chinstruments). All chemicals were purchased from Innochem or Energy Chemical and used as received.

Electrolysis experiments were performed using MESTEK DC power supply. Electrode clips (PT-1 or PT-3) and platinum plate (99.99%, 15*15*0.3 mm or 30*30*0.1 mm) was purchased from Gaoss Union. The carbon cloth (CeTech WOS1002) was cut into 15 x 15 x 0.1 mm pieces before use, and was clamped between electrode clips.
Figure S1 Setup of electrochemical synthesis

2. General Procedures

Method A: General procedure for the preparation of 2-phenylthiophene compounds\textsuperscript{1,2}

\[
\begin{array}{c}
R^1\text{S}Br + R^2\text{PhBOH} \xrightarrow{\text{Pd(OAc)}_2 (0.1\% \text{ mmol})}
\text{K}_2\text{CO}_3 (2.0 \text{ equiv})
\text{DMF (10 mL), 120 °C, 12 h}}
\end{array}
\]
Arylboronic acid (6.0 mmol, 1.2 equiv.) and K$_2$CO$_3$ (1.38 g, 10.0 mmol, 2.0 equiv.) were placed in a 100 mL duplex flask, which was filled with nitrogen. 2-Bromo thiophene (5.0 mmol, 1.0 equiv.), Pd(OAc)$_2$ (0.24 mg, 0.1 mmol%), and DMF (10.0 mL) were consequently added to the reaction flask. The reaction mixture was stirred at 120 °C for 12 h. The resulting mixture was quenched with water. Then the suspension solution was extracted by ethyl acetate (3×25 mL), the organic layers were combined, dried over sodium sulfate, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel (petroleum/ethyl acetate = 200:1).

The following chemicals can be purchased commercially.

2-phenylthiophene; 2-(4-fluorophenyl)thiophene; 2-(4-bromophenyl)thiophene; 5-phenylthiophene-2-carbaldehyde; 5-phenylthiophene-2-carboxylic acid; 2-bromo-5-phenylthiophene; 2-(benzo[b]thiophen-2-yl)pyridine; 2,5-diphenylthiophene; 6-methoxy-2-(4-methoxyphenyl)benzo[b]thiophene.

**Method B: General procedure for the preparation of 2-phenylthiophene compounds**

\[
\begin{align*}
\text{PhCO} & + \text{R} & \text{S}_8 (4.0 \text{ equiv}), K_2\text{CO}_3 (3.0 \text{ equiv}) \\
\text{DMF} & \quad 110 ^\circ \text{C}, 16 \text{ h} & \text{Ph} \\
\end{align*}
\]

A 100 mL oven-dried reaction vessel was charged with S$_8$ (512 mg, 16 mmol, 4 equiv.), K$_2$CO$_3$ (1.656 g, 12 mmol, 3.0 equiv.), methyl 2-phenylacetate (900 mg, 6.0 mmol, 1.5 equiv.), substituted benzaldehyde (4.0 mmol, 1.0 equiv.). The reaction vessel was added DMF (20 mL) by syringe. The sealed vessel was stirred at 110 °C for 16 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography on silica gel (petroleum/ethyl acetate = 100:1) to give the desired product.

**Method C: General procedure for the electrochemically induced thiophene dearomatization**
In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, 2-phenylthiophene (0.3 mmol, 1.0 equiv.) and nBu₄NOAc (0.3 mmol, 1.0 equiv.) were added. The glassware was equipped with carbon cloth (15 mm × 15 mm × 0.1 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N₂, CH₃CO₂H (3 mL) and MeCN (7 mL) were injected into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA at an ambient temperature for 5 h. The reaction mixture was concentrated in vacuo and the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

Method D: Scale-up synthesis of compound

In an oven-dried undivided three-necked glassware (100 mL) equipped with a stirring bar, 2-(4-fluorophenyl)thiophene (1.60 g, 9 mmol, 1.0 equiv.) and nBu₄NOAc (2.72 g, 9 mmol, 1.0 equiv.) were added. The glassware was equipped with carbon cloth (30 mm × 30 mm × 0.1 mm) as the anode and platinum plate (30 mm × 30 mm × 0.1
mm) as the cathode. Under the protection of N₂, \( \text{CH}_3\text{CO}_2\text{H} \) (30 mL) and MeCN (70 mL) were injected into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 50 mA at an ambient temperature for 24 h. The reaction mixture was concentrated \textit{in vacuo} and the crude residue was subjected to flash column chromatography on silica gel to give the desired product (1.634 g, 72 % yield).

**Method E: Synthesis of compound 42**

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \\
\text{OAc}
\end{array}
\begin{array}{c}
\text{O} \\
\text{F}
\end{array}
\begin{array}{c}
\text{SH}
\end{array}
+ \begin{array}{c}
\text{Cl}
\end{array}
\begin{array}{c}
\text{OAc}
\end{array}
\begin{array}{c}
\text{F}
\end{array}
\begin{array}{c}
\text{Cl}
\end{array}
\rightarrow
\begin{array}{c}
\text{Cl}
\end{array}
\begin{array}{c}
\text{OAc}
\end{array}
\begin{array}{c}
\text{F}
\end{array}
\begin{array}{c}
\text{H}
\end{array}
\end{align*}
\]

Triethylamine (8 \( \mu \text{L}, 0.057\text{mmol}, 1.0 \text{ equiv.}) was added to the \( \text{CH}_2\text{Cl}_2 \) (5 mL) solution of the 7 (50.4 mg, 0.2 mmol, 3.5 equiv.) and 4-chlorobenzenethiol (28.8 mg, 0.2 mmol, 3.5 equiv.) at 0 °C. After 15 min, the reaction was allowed to warm to rt overnight. The solvent was removed and the product was purified by flash column chromatography (ethyl acetate/hexanes = 10:1) giving 42 (21.1 mg, 27%) as a white solid.

**Method F: Synthesis of compound 43**

\[
\begin{align*}
\begin{array}{c}
\text{OAc}
\end{array}
\begin{array}{c}
\text{O} \\
\text{F}
\end{array}
\begin{array}{c}
\text{F}
\end{array}
\begin{array}{c}
\text{Cl}
\end{array}
\rightarrow
\begin{array}{c}
\text{HN} \\
\text{N}
\end{array}
\begin{array}{c}
\text{O} \\
\text{F}
\end{array}
\begin{array}{c}
\text{F}
\end{array}
\end{align*}
\]

To a solution of 2-(4-fluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate 7 (50.4 mg, 0.2 mmol, 1.0 equiv.) and piperidine (50.0 \( \mu \text{L}, 0.5 \text{ mmol, 2.5 equiv.}) in EtOH (5 mL) and \( \text{NH}_2\text{NH}_2\cdot\text{HCl} \) (27.4 mg, 0.4 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 1 h. Then the solvent was removed and the product was purified by flash column chromatography (ethyl acetate/hexanes = 1:1) giving 14.2 mg (37%) of 43 as a white solid.

**Method G: Synthesis of compound 45**

7
General Procedure for 44

A mixture of compound 43 (28.0 mg, 0.146 mmol, 1.0 equiv.), K$_2$CO$_3$ (60.3 mg, 0.437 mmol, 3.0 equiv.), and ethyl bromoacetate (73.0 mg, 0.437 mmol, 3.0 equiv.) in CH$_3$CN and acetone (1:1 = 20 mL) was refluxed and stirring for 12 h. The mixture was then concentrated in vacuo, diluted with cold water, and extracted with CH$_2$Cl$_2$. The solvent was evaporated in vacuo and then purified by flash column chromatography (cyclohexane/ethyl acetate = 1:1) giving 22.7 mg (56%) of 44 as a white solid.

General Procedure for the hydrolysis of 44a

A suspension of compound 44 (22.7 mg, 0.08 mmol, 1.0 equiv.) in 6 N NaOH (2 mL) was stirred at 80 °C for 5 h. The mixture was diluted with ice-cold water and then acidified with 6 N HCl. The solvent was evaporated in vacuo to give compound 44a, which was used directly in the next step without further purification.

General Procedure for 45

An oven-dried round-bottom flask was charged with crude product 44a (20.0 mg, 0.08 mmol, 1.0 equiv.), 4-chloroaniline (10.2 mg, 0.08 mmol, 1.0 equiv.), DMAP (14.7 mg, 0.12 mmol, 1.5 equiv.) and DCM (5 mL). EDC (18.4 mg, 0.12 mmol, 1.5 equiv.) in DCM was added dropwise to the above solution under a nitrogen atmosphere. The reaction mixture was kept stirring at room temperature for 16 h. The reaction was then quenched by HCl (1 M) and extracted with DCM. The combined organic extracts were washed with brine, dried over MgSO$_4$ and concentrated in vacuo. The product was purified by flash column chromatography (DCM/petroleum = 1:1) giving 22.6 mg (79%) of 45 as a white solid.
3. Characterization of Products

2: 5-oxo-2-phenyl-2,5-dihydrothiophen-2-yl acetate
Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 54.5 mg (78% yield) of 2 as a white solid.

IR (neat, cm⁻¹): 3066 (w), 1756 (m), 1693 (s), 1492 (w), 1447 (w), 1370 (w), 1327 (w), 1218 (s), 1168 (w), 1066 (m), 1013 (w), 968 (w), 797 (w), 761 (m), 710 (w), 527 (w);

$^1$H NMR (500 MHz, Chloroform-d) δ 7.58 – 7.54 (m, 2H), 7.42 (d, $J = 6.1$ Hz, 1H), 7.40 – 7.33 (m, 3H), 6.19 (d, $J = 6.1$ Hz, 1H), 2.18 (s, 3H);

$^{13}$C NMR (126 MHz, Chloroform-d) δ 197.2, 169.1, 156.3, 137.4, 129.5, 129.3, 129.2, 125.6, 96.6, 21.4.

HRMS (ESI) calculated for $\text{C}_{12}\text{H}_{10}\text{NaO}_3\text{S}[\text{M}+\text{Na}^+]$: 257.0243; found: 257.0236.

3: 5-oxo-2-(p-tolyl)-2,5-dihydrothiophen-2-yl acetate
Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 49.3 mg (66% yield) of 3 as a white solid.

IR (neat, cm⁻¹): 2923 (w), 2853 (w), 1753 (m), 1695 (s), 1611 (w), 1369 (w), 1216 (s), 1185 (w), 1067 (m), 1012 (m), 961 (w), 816 (w), 810 (w), 623 (w), 520 (w);

$^1$H NMR (500 MHz, Chloroform-d) δ 7.45 (d, $J = 8.0$ Hz, 2H), 7.42 (d, $J = 6.0$ Hz, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 6.17 (d, $J = 6.1$ Hz, 1H), 2.34 (s, 3H), 2.17 (s, 3H);

$^{13}$C NMR (126 MHz, Chloroform-d) δ 197.3, 169.2, 156.4, 139.4, 134.4, 129.8, 129.3, 125.6, 96.7, 21.5, 21.2.

HRMS (ESI) calculated for $\text{C}_{13}\text{H}_{12}\text{NaO}_3\text{S}[\text{M}+\text{Na}^+]$: 271.0399; found: 271.0392.

4: 2-(4-isopropylphenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate
Followed Method C (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 46.3 mg (56% yield)
of 4 as a white solid.

IR (neat, cm\(^{-1}\)): 2960 (w), 2923 (w), 2852 (w), 1754 (s), 1698 (s), 1463 (w), 1369 (w), 1218 (s), 1170 (w), 1068 (m), 1012 (w), 896 (w), 832 (w), 796 (w), 623 (w); \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.49 – 7.45 (m, 2H), 7.41 (d, \(J = 6.1\) Hz, 1H), 7.25 – 7.22 (m, 2H), 6.17 (d, \(J = 6.1\) Hz, 1H), 2.90 (hept, \(J = 7.0\) Hz, 1H), 2.17 (s, 3H), 1.23 (d, \(J = 6.9\) Hz, 6H); \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 197.4, 169.2, 156.4, 150.2, 134.6, 129.3, 127.3, 125.7, 96.7, 33.9, 23.9, 21.5.

HRMS (ESI) calculated for C\(_{15}\)H\(_{16}\)NaO\(_3\)S [M+Na\(^+\)]: 299.0712; found: 299.0717.

\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{OAc}
\end{array}
\begin{array}{c}
\text{Bu}
\end{array}
\]

5: 2-(4-(tert-butyl)phenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed Method C (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 44.4 mg (51% yield) of 5 as a white solid.

IR (neat, cm\(^{-1}\)): 2960 (w) 2926 (w), 2868 (w), 1754 (m), 1694 (s), 1506 (w), 1367 (m), 1269 (w), 1218 (s), 1066 (m), 1010 (m), 965 (w), 918 (w), 896 (w), 833 (w), 795 (w), 622 (m), 566 (w); \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.48 – 7.45 (m, 2H), 7.40 – 7.37 (m, 2H), 6.17 (d, \(J = 6.1\) Hz, 1H), 2.18 (s, 3H), 1.30 (s, 9H); \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 197.4, 169.2, 156.4, 152.5, 134.2, 129.3, 126.1, 125.4, 96.6, 34.8, 31.3, 21.5.

HRMS (ESI) calculated for C\(_{16}\)H\(_{18}\)NaO\(_3\)S [M+Na\(^+\)]: 313.0869; found: 313.0875.

\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{Ac}
\end{array}
\begin{array}{c}
\text{F}
\end{array}
\]

7: 2-(4-fluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed Method C (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 61.2 mg (81% yield) of 7 as a white solid.

IR (neat, cm\(^{-1}\)): 2955 (w), 2921 (w), 2850 (w), 1754 (m), 1698 (s), 1600 (w), 1507 (w), 1370 (w), 1218 (s), 1162 (m), 1067 (m), 912 (w), 896 (w), 837 (w), 795 (w), 607 (w), 549 (w); \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.58 – 7.52 (m, 2H), 7.40 – 7.37 (m, 2H), 6.17 (d, \(J = 6.1\) Hz, 1H), 7.11 – 7.02 (m, 2H), 6.20 (d, \(J = 6.1\) Hz, 1H), 2.17 (s, 3H); \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 196.7, 169.1, 163.1 (d, \(J = 249.4\) Hz), 156.1, 133.4 (d, \(J = 3.4\) Hz), 126.1, 125.4, 96.6, 34.8, 31.3, 21.5.
Hz), 129.6, 127.7 (d, J = 8.5 Hz), 116.1 (d, J = 22.1 Hz), 96.0, 21.4; $^{19}$F NMR (471 MHz, Chloroform-d) $\delta$ -112.0.

HRMS (ESI) calculated for C$_{12}$H$_9$FNaO$_3$S [M+ Na$^+$]: 275.0149; found: 275.0145.

8: 2-(4-chlorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate
Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 60.1 mg (75% yield) of 8 as a white solid.

IR (neat, cm$^{-1}$): 2924 (w), 1746 (m), 1691 (s), 1594 (w), 1491 (m), 1368 (m), 1212 (s), 1094 (m), 1065 (s), 1010 (s), 913 (m), 896 (m), 827 (m), 795 (m), 619 (s), 532 (m), 466 (w); $^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.51 – 7.48 (m, 2H), 7.38 (d, $J = 6.1$ Hz, 1H), 7.36 – 7.33 (m, 2H), 6.21 (d, $J = 6.1$ Hz, 1H), 2.17 (s, 3H); $^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 196.6, 169.1, 155.9, 136.2, 135.4, 129.8, 129.4, 127.1, 96.0, 21.4.

HRMS (ESI) calculated for C$_{12}$H$_9$FNaO$_3$S [M+Na$^+$]: 290.9853; found: 290.9855.

9: 2-(4-bromophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate
Followed Method C (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 60.7 mg (65% yield) of 9 as a white solid.

IR (neat, cm$^{-1}$): 3073 (w), 2960 (w), 1755 (m), 1691 (s), 1586 (w), 1486 (m), 1369 (m), 1212 (s), 1183 (m), 1066 (s), 1008 (s), 968 (w), 822 (w), 795 (w), 734 (w), 632 (w), 619 (m), 529 (w); $^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.53 – 7.49 (m, 2H), 7.45 – 7.42 (m, 2H), 7.38 (d, $J = 6.1$ Hz, 1H), 6.21 (d, $J = 6.1$ Hz, 1H), 2.18 (s, 3H); $^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 196.6, 169.1, 155.8, 136.7, 132.3, 129.9, 127.4, 123.6, 96.0, 21.4.

HRMS (ESI) calculated for C$_{12}$H$_9$BrNaO$_3$S [M+Na$^+$]: 334.9348; found: 334.9357.

10: 5-oxo-2-(4-(trifluoromethyl)phenyl)-2,5-dihydrothiophen-2-yl acetate
Followed Method C (current = 15 mA), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 47.1 mg (52% yield) of 10 as a white solid.

IR (neat, cm⁻¹): 3076 (w), 2929 (w), 1757 (m), 1695 (s), 1409 (w), 1371 (w), 1323 (s), 1215 (m), 1166 (m), 1065 (s), 917 (w), 896 (w), 840 (m), 796 (w), 679 (w), 634 (w), 620 (w), 526 (w), 447 (w); ¹H NMR (500 MHz, Chloroform-d) δ 7.70 – 7.63 (m, 4H), 7.40 (d, J = 6.1 Hz, 1H), 6.25 (d, J = 6.1 Hz, 1H), 2.20 (s, 3H); ¹³C NMR (126 MHz, Chloroform-d) δ 196.3, 169.6, 155.6, 141.6, 131.3 (q, J = 33.8 Hz), 130.2, 126.2 (q, J = 279.4 Hz), 95.8, 21.2; ¹⁹F NMR (471 MHz, Chloroform-d) δ -62.7 (s).

HRMS (ESI) calculated for C₁₃HₙF₃NaO₃S [M+Na⁺]: 325.0117; found: 325.0137.

11: 2-(4-cyanophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 39.6 mg (51% yield) of 11 as a white solid.

IR (neat, cm⁻¹): 3047 (w), 2924 (w), 2231 (m), 1754 (s), 1709 (s), 1696 (s), 1370 (m), 1217 (s), 1068 (s), 909 (m), 838 (w), 798 (w), 731 (w), 584 (w), 559 (w); ¹H NMR (500 MHz, Chloroform-d) δ 7.68 (d, J = 1.2 Hz, 4H), 7.37 (d, J = 6.1 Hz, 1H), 6.27 (d, J = 6.1 Hz, 1H), 2.21 (s, 3H); ¹³C NMR (126 MHz, Chloroform-d) δ 195.8, 169.1, 155.1, 142.8, 133.0, 130.7, 126.4, 118.1, 113.3, 95.6, 21.3.

HRMS (ESI) calculated for C₁₃HₙKNO₃S [M+K⁺]: 297.9935; found: 297.9943.

12: 2-(4-acetylphenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 62.7 mg (76% yield) of 12 as a white solid.

IR (neat, cm⁻¹): 2924 (w), 1754 (m), 1682 (s), 1603 (m), 1367 (m), 1266 (s), 1212 (s), 1066 (s), 1011 (m), 896 (w), 797 (w), 756 (w), 622 (m), 594 (w), 526 (w); ¹H NMR (500 MHz, Chloroform-d) δ 7.97 – 7.94 (m, 2H), 7.66 – 7.63 (m, 2H), 7.41 (d, J = 6.1 Hz, 1H), 6.24 (d, J = 6.1 Hz, 1H), 2.58 (s, 3H), 2.19 (s, 3H); ¹³C NMR (126 MHz,
Chloroform-<em>d</em>) δ 197.2, 196.4, 169.2, 155.6, 142.4, 137.7, 130.2, 129.2, 125.9, 96.0, 26.8, 21.3.

HRMS (ESI) calculated for C<sub>14</sub>H<sub>12</sub>NaO<sub>4</sub>S [M+Na<sup>+</sup>]: 299.0349; found: 299.0348.

13: methyl 4-(2-acetoxy-5-oxo-2,5-dihydrothiophen-2-yl)benzoate

Followed Method C (current = 15 mA), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 63.2 mg (72% yield) of 13 as a white solid.

IR (neat, cm<sup>-1</sup>): 3071 (w), 2953 (w), 2925 (w), 1756 (m), 1708 (s), 1694 (s), 1608 (w), 1575 (w), 1435 (m), 1406 (w), 1370 (w), 1278 (s), 1212 (s), 1111 (s), 916 (w), 896 (w), 797 (w), 770 (m), 735 (w), 620 (m), 568 (w); <sup>1</sup>H NMR (500 MHz, Chloroform-<em>d</em>) δ 8.06 – 8.01 (m, 2H), 7.64 – 7.60 (m, 2H), 7.40 (d, <em>J</em> = 6.1 Hz, 1H), 6.23 (d, <em>J</em> = 6.1 Hz, 1H), 3.91 (s, 3H), 2.19 (s, 3H); <sup>13</sup>C NMR (126 MHz, Chloroform-<em>d</em>) δ 196.5, 169.1, 166.3, 155.6, 142.3, 131.0, 130.4, 130.2, 125.6, 96.1, 52.4, 21.3.

HRMS (ESI) calculated for C<sub>14</sub>H<sub>13</sub>O<sub>5</sub>S [M+H<sup>+</sup>]: 293.0478; found: 293.0480.

14: 2-(4-nitrophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 21.7 mg (26% yield) of 14 as a white solid.

IR (neat, cm<sup>-1</sup>): 3079 (w), 2925 (w), 1754 (m), 1693 (s), 1606 (w), 1520 (s), 1491 (w), 1606 (w), 1520 (s), 1491 (w), 1347 (s), 1211 (s), 1169 (m), 1066 (s), 1010 (m), 971 (w), 850 (s), 796 (m), 735 (w), 618 (m), 532 (w), 454 (w); <sup>1</sup>H NMR (500 MHz, Chloroform-<em>d</em>) δ 8.25 – 8.22 (m, 2H), 7.76 – 7.72 (m, 2H), 7.40 (d, <em>J</em> = 6.1 Hz, 1H), 6.23 (d, <em>J</em> = 6.1 Hz, 1H), 6.29 (d, <em>J</em> = 6.1 Hz, 1H), 2.22 (s, 3H); <sup>13</sup>C NMR (126 MHz, Chloroform-<em>d</em>) δ 195.7, 169.2, 155.0, 148.3, 144.7, 131.4, 126.8, 124.4, 95.5, 21.3.

HRMS (ESI) calculated for C<sub>12</sub>H<sub>9</sub>NNaO<sub>5</sub>S [M+Na<sup>+</sup>]: 302.0094; found: 302.0102

15: 5-oxo-2-(m-tolyl)-2,5-dihydrothiophen-2-yl acetate
Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 55.0 mg (74% yield) of 15 as a white solid.

IR (neat, cm\(^{-1}\)): 2924 (w), 1750 (s), 1690 (w), 1485 (w), 1430 (w), 1369 (w), 1325 (w), 1215 (s), 1171 (w), 1159 (w), 1067 (m), 1015 (m), 970 (w), 895 (w), 830 (w), 817 (w), 784 (m), 718 (w), 621 (s), 499 (w); \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.40 (d, \(J = 6.1\) Hz, 1H), 7.38 – 7.32 (m, 2H), 7.26 (t, \(J = 7.7\) Hz, 1H), 7.15 (d, \(J = 7.5\) Hz, 1H), 6.16 (d, \(J = 6.1\) Hz, 1H), 2.35 (s, 3H), 2.17 (s, 3H); \(^13\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 197.2, 169.1, 156.4, 138.9, 137.2, 130.1, 129.3, 129.0, 126.2, 122.5, 96.6, 21.6, 21.4.

HRMS (ESI) calculated for C\(_{13}\)H\(_{12}\)NaO\(_3\)S [M+Na\(^+\)]: 271.0399; found: 271.0399.

16: 2-(3-acetylphenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 50.2 mg (61% yield) of 16 as a white solid.

IR (neat, cm\(^{-1}\)): 2925 (w), 1754 (m), 1683 (s), 1598 (w), 1430 (m), 1359 (m), 1268 (m), 1214 (s), 1170 (m), 1067 (m), 1014 (m), 960 (w), 894 (w), 797 (w), 735 (w), 712 (w), 620 (m), 590 (w), 526 (w); \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.13 (t, \(J = 1.7\) Hz, 1H), 7.93 – 7.90 (m, 1H), 7.78 (ddd, \(J = 7.9, 2.1, 1.0\) Hz, 1H), 7.51 – 7.47 (m, 1H), 7.43 (d, \(J = 6.1\) Hz, 1H), 6.23 (d, \(J = 6.1\) Hz, 1H), 2.60 (s, 3H), 2.19 (s, 3H); \(^13\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 197.3, 196.5, 169.2, 155.8, 138.5, 137.9, 130.2, 129.0, 129.6, 129.4, 125.1, 96.1, 26.8, 21.4.

HRMS (ESI) calculated for C\(_{14}\)H\(_{12}\)NaO\(_4\)S [M+Na\(^+\)]: 299.0349; found: 299.0348.

17: 2-(3-fluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed Method C (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 50.6 mg (67% yield) of 17 as a white solid.
IR (neat, cm⁻¹): 3072 (w), 2927 (w), 1749 (w), 1693 (s), 1588 (w), 1566 (w), 1472 (w), 1261 (w), 1065 (m), 1013 (m), 970 (w), 785 (m), 748 (w), 652 (w), 620 (s), 573 (w), 505 (w); \(^1\)H NMR (500 MHz, Chloroform-d) \(\delta\) 7.54 - 7.53 (m, 1H), 7.50 – 7.45 (m, 2H), 7.37 (d, \(J = 6.1\) Hz, 1H), 7.33 – 7.31 (m, 2H), 7.18 (s, 1H), 6.22 (d, \(J = 6.1\) Hz, 1H), 2.18 (s, 3H); \(^1\)C NMR (126 MHz, Chloroform-d) \(\delta\) 198.5, 169.1, 155.8, 139.7, 135.2, 130.5, 130.0, 129.5, 125.9, 123.8, 95.7, 21.4.

HRMS (ESI) calculated for C\(_{12}\)H\(_9\)ClNaO\(_3\)S [M+Na\(^+\)]: 290.9853; found: 290.9859.

18: 2-(3-chlorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 53.7 mg (67% yield) of 18 as a white solid.

IR (neat, cm⁻¹): 3072 (w), 2927 (w), 1749 (w), 1693 (s), 1588 (w), 1566 (w), 1472 (w), 1261 (w), 1065 (m), 1013 (m), 970 (w), 785 (m), 748 (w), 652 (w), 620 (s), 573 (w), 505 (w); \(^1\)H NMR (500 MHz, Chloroform-d) \(\delta\) 7.68 (t, \(J = 1.9\) Hz, 1H), 7.50 – 7.45 (m, 2H), 7.37 (d, \(J = 6.1\) Hz, 1H), 7.25 – 7.22 (m, 1H), 6.21 (d, \(J = 6.1\) Hz, 1H), 2.18 (s, 3H); \(^1\)C NMR (126 MHz, Chloroform-d) \(\delta\) 196.5, 169.1, 155.8, 139.7, 135.2, 130.5, 130.0, 129.5, 125.9, 123.8, 95.7, 21.4.

HRMS (ESI) calculated for C\(_{12}\)H\(_9\)ClNaO\(_3\)S [M+Na\(^+\)]: 275.0158; found: 275.0149.

19: 2-(3-bromophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 41.1 mg (44% yield) of 19 as a white solid.

IR (neat, cm⁻¹): 3069 (w), 2926 (w), 1749 (w), 1693 (s), 1588 (w), 1566 (w), 1472 (w), 1214 (s), 1170 (w), 1065 (m), 1013 (m), 970 (w), 896 (w), 785 (m), 748 (w), 652 (w), 620 (s), 573 (w), 505 (w); \(^1\)H NMR (500 MHz, Chloroform-d) \(\delta\) 7.58 (t, \(J = 1.9\) Hz, 1H), 7.48 – 7.45 (m, 2H), 7.37 (d, \(J = 6.1\) Hz, 1H), 7.25 – 7.22 (m, 1H), 6.21 (d, \(J = 6.1\) Hz, 1H), 2.18 (s, 3H); \(^1\)C NMR (126 MHz, Chloroform-d) \(\delta\) 196.5, 169.1, 155.8,
139.9, 132.5, 130.7, 130.0, 128.7, 124.3, 123.3, 95.6, 21.4.

**HRMS (ESI)** calculated for C_{12}H_{9}BrNaO_{3}S [M+Na^+] : 334.9348; found: 334.9356.

![](image)

**20: 5-oxo-2-(o-tolyl)-2,5-dihydrothiophen-2-yl acetate**
Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 40.8 mg (55% yield) of 20 as a white solid.

**IR (neat, cm^{-1}):** 3069 (w), 2928 (w), 1750 (m), 1689 (s), 1602 (w), 1456 (w), 1367 (m), 1206 (s), 1166 (m), 1055 (w), 1009 (w), 957 (w), 795 (w), 757 (s), 724 (w), 622 (s), 607 (s), 459 (w); ¹H NMR (500 MHz, Chloroform-d) δ 7.98 (d, J = 6.3 Hz, 1H), 7.47 (dd, J = 8.0, 1.3 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.23 (dd, J = 7.6, 1.6 Hz, 1H), 7.20 – 7.16 (m, 1H), 6.37 (d, J = 6.3 Hz, 1H), 2.52 (s, 3H), 2.12 (s, 3H); ¹³C NMR (126 MHz, Chloroform-d) δ 195.9, 168.8, 154.2, 135.9, 135.5, 132.9, 131.7, 129.4, 126.2, 125.7, 98.0, 21.3, 21.2.

**HRMS (ESI)** calculated for C_{13}H_{12}NaO_{3}S [M+ Na^+] : 271.0399; found: 271.0394.

![](image)

**21: 2-(2-fluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate**
Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 33.2 mg (44% yield) of 21 as a white solid.

**IR (neat, cm^{-1}):** 3081 (w), 2928 (w), 1750 (m), 1691 (s), 1602 (w), 1489 (s), 1367 (m), 1206 (s), 1166 (m), 1055 (w), 1009 (w), 957 (w), 795 (w), 757 (s), 724 (w), 622 (s), 607 (s), 459 (w); ¹H NMR (500 MHz, Chloroform-d) δ 7.80 (dd, J = 6.2, 1.4 Hz, 1H), 7.74 (td, J = 8.0, 1.7 Hz, 1H), 7.38 - 7.34 (m, 1H), 7.14 (td, J = 7.7, 1.3 Hz, 1H), 7.09 (ddd, J = 12.0, 8.2, 1.2 Hz, 1H), 6.25 (d, J = 6.2 Hz, 1H), 2.11 (s, 3H); ¹³C NMR (126 MHz, Chloroform-d) δ 196.0, 169.4, 159.8 (d, J = 250.8 Hz), 154.0 (d, J = 4.2 Hz), 131.7 (d, J = 8.6 Hz), 130.8, 129.5 (d, J = 2.3 Hz), 124.4 (d, J = 3.6 Hz), 124.3 (d, J = 9.7 Hz), 116.9 (d, J = 22.3 Hz), 94.8 (d, J = 3.0 Hz), 21.1; ¹⁹F NMR (471 MHz, Chloroform-d) δ -112.2 (m).
HRMS (ESI) calculated for C$_{12}$H$_9$FNaO$_3$S [M+Na$^+$]: 275.0149; found: 275.0154.

![Image of 22](image)

**22: 2-(2-chlorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate**

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 42.5 mg (53% yield) of 22 as a white solid.

IR (neat, cm$^{-1}$): 3076 (w), 1748 (m), 1694 (s), 1568 (w), 1465 (w), 1435 (w), 1368 (m), 1213(s), 1169 (w), 1073 (m), 1010 (w), 965 (w), 797 (w), 758 (m), 718 (w), 621 (m), 606 (w), 464 (w); $^1$H NMR (500 MHz, Chloroform-d) δ 8.08 (d, J = 6.3 Hz, 1H), 7.74 (dd, J = 7.8, 1.8 Hz, 1H), 7.43 (dd, J = 7.8, 1.5 Hz, 1H), 7.31 (td, J = 7.6, 1.8 Hz, 1H), 7.26 (td, J = 7.7, 1.5 Hz, 1H), 6.34 (d, J = 6.2 Hz, 1H), 2.13 (s, 3H); $^{13}$C NMR (126 MHz, Chloroform-d) δ 195.9, 169.3, 153.2, 134.8, 132.1, 131.7, 130.8, 128.7, 127.2, 96.6, 21.0.

HRMS (ESI) calculated for C$_{12}$H$_{10}$ClO$_3$S [M+H$^+$]: 269.0034; found: 269.0038.

![Image of 23](image)

**23: 2-(2-bromophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate**

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 53.3 mg (57% yield) of 23 as a white solid.

IR (neat, cm$^{-1}$): 3075 (w), 2925 (w), 1749 (m), 1694 (s), 1468 (w), 1432 (w), 1368 (w), 1213 (s), 1169 (w), 1073 (w), 1026 (w), 964 (w), 932 (w), 797 (w), 757 (m), 739 (w), 713 (w), 644 (w), 620 (w), 535 (w); $^1$H NMR (500 MHz, Chloroform-d) δ 8.13 (d, J = 6.3 Hz, 1H), 7.67 (ddd, J = 16.4, 7.9, 1.5 Hz, 2H), 7.31 (td, J = 7.7, 1.4 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.36 (d, J = 6.3 Hz, 1H), 2.14 (s, 3H); $^{13}$C NMR (126 MHz, Chloroform-d) δ 196.0, 169.3, 153.3, 136.6, 135.7, 132.1, 130.9, 128.7, 127.7, 121.0, 97.1, 21.2.

HRMS (ESI) calculated for C$_{12}$H$_9$BrNaO$_3$S [M+Na$^+$]: 334.9348; found: 334.9344.
24: 2-(3,5-difluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 55.0 mg (68% yield) of 24 as a white solid.

IR (neat, cm⁻¹): 3088 (w), 2925 (w), 1751 (m), 1695 (s), 1622 (m), 1579 (m), 1437 (m), 1370 (m), 1314 (m), 1208 (s), 1121 (s), 1071 (s), 896 (w), 858 (m), 811 (s), 789 (w), 526 (w), 511 (w);

¹H NMR (500 MHz, Chloroform-d) δ 7.36 (d, J = 6.0 Hz, 1H), 7.12 – 7.07 (m, 2H), 6.81 – 6.71 (m, 1H), 6.24 (d, J = 6.1 Hz, 1H), 2.20 (s, 3H);

¹³C NMR (126 MHz, Chloroform-d) δ 196.0, 169.1, 163.4 (d, J = 250.6 Hz), 163.3 (d, J = 250.4 Hz), 155.2, 141.9 (t, J = 9.2 Hz), 130.3, 109.06 (d, J = 28.2 Hz), 109.06 (d, J = 13.7 Hz), 104.8 (t, J = 25.2 Hz), 95.2, 21.3;

¹⁹F NMR (471 MHz, Chloroform-d) δ -107.1 (m).

HRMS (ESI) calculated for C₁₂H₈F₂NaO₅S [M+Na⁺]: 293.0054; found: 293.0057.

25: 2-(3-chloro-5-fluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 48.9 mg (57% yield) of 25 as a white solid.

IR (neat, cm⁻¹): 3084 (w), 1751 (m), 1695 (s), 1605 (m), 1588 (m), 1582 (m), 1437 (m), 1354 (m), 1211 (s), 1171 (w), 1071 (m), 1020 (m), 956 (w), 888 (m), 860 (m), 800 (m), 769 (w), 703 (w), 622 (m), 526 (w);

¹H NMR (500 MHz, Chloroform-d) δ 7.38 – 7.32 (m, 2H), 7.18 (dq, J = 9.3, 1.5 Hz, 1H), 7.08 (dt, J = 8.1, 2.0 Hz, 1H), 6.24 (dd, J = 6.1, 1.0 Hz, 1H), 2.20 (s, 3H);

¹³C NMR (126 MHz, Chloroform-d) δ 195.9, 169.1, 162.9 (d, J = 252.0 Hz), 155.2, 141.7 (d, J = 8.2 Hz), 136.1 (d, J = 10.6 Hz), 130.4, 121.8 (d, J = 3.3 Hz), 117.2 (d, J = 24.4 Hz), 111.7 (d, J = 23.7 Hz), 95.1 (d, J = 2.0 Hz), 21.3;

¹⁹F NMR (471 MHz, Chloroform-d) δ -108.5 (m).

HRMS (ESI) calculated for C₁₂H₈ClFNaO₅S [M+Na⁺]: 308.9759; found: 308.9766.
26: 5-oxo-2-(pyridin-2-yl)-2,5-dihydrothiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 2:1) to give 49.3 mg (70% yield) of 26 as a white solid.

IR (neat, cm\(^{-1}\)): 3070 (w), 2926 (w), 1746 (m), 1691 (s), 1586 (m), 1464 (w), 1432 (m), 1370 (m), 1221 (s), 1102 (w), 1070 (m), 1017 (m), 801 (w), 781 (m), 747 (m), 623 (m), 528 (m); \(^1\)H NMR (500 MHz, Chloroform-d) \(\delta\) 8.60 – 8.58 (m, 1H), 7.76 (dt, \(J = 8.0, 1.2\) Hz, 1H), 7.74 – 7.69 (m, 1H), 7.66 (d, \(J = 6.1\) Hz, 1H), 7.28 – 7.24 (m, 1H), 6.29 (d, \(J = 6.1\) Hz, 1H), 2.19 (s, 3H); \(^{13}\)C NMR (126 MHz, Chloroform-d) \(\delta\) 196.9, 169.7, 155.8, 155.7, 149.8, 137.5, 130.9, 123.8, 121.7, 96.2, 21.2.

HRMS (ESI) calculated for C\(_{11}\)H\(_9\)NNaO\(_3\)S [M+Na\(^+\)]: 258.0195; found: 258.0192.

27: 5-oxo-2-(quinolin-5-yl)-2,5-dihydrothiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 2:1) to give 33.3 mg (39% yield) of 27 as a white solid.

IR (neat, cm\(^{-1}\)): 3077 (w), 2926 (w), 1751 (m), 1697 (s), 1595 (w), 1500 (m), 1368 (m), 1319 (w), 1205 (s), 1067 (w), 1017 (w), 954 (m), 828 (w), 803 (s), 735 (w), 621 (m), 543 (w), 495 (w); \(^1\)H NMR (500 MHz, Chloroform-d) \(\delta\) 8.98 (dd, \(J = 4.2, 1.6\) Hz, 1H), 8.73 (ddd, \(J = 8.8, 1.6, 0.8\) Hz, 1H), 8.21 (d, \(J = 6.3\) Hz, 1H), 8.15 (dt, \(J = 8.5, 1.0\) Hz, 1H), 7.82 (dd, \(J = 7.4, 1.2\) Hz, 1H), 7.67 - 7.64 (m, 1H), 7.51 (dd, \(J = 8.8, 4.1\) Hz, 1H), 6.45 (d, \(J = 6.3\) Hz, 1H), 2.05 (s, 3H); \(^{13}\)C NMR (126 MHz, Chloroform-d) \(\delta\) 195.0, 168.9, 153.5, 150.5, 149.4, 134.1, 132.6, 132.4, 132.2, 128.5, 125.4, 124.5, 121.6, 97.7, 21.3.

HRMS (ESI) calculated for C\(_{15}\)H\(_{12}\)NO\(_3\)S [M+H\(^+\)]: 286.0532; found: 286.0533.
28: 5-oxo-3-phenyl-2,5-dihydrothiophen-2-yl propionate
Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 39.4 mg (53% yield) of 28 as a white solid.
IR (neat, cm⁻¹): 3066 (w), 2924 (w), 1748 (m), 1492 (w), 1447 (w), 1354 (w), 1152 (m), 1064 (m), 992 (w), 799 (w), 761 (m), 697 (m), 556 (w); ¹H NMR (400 MHz, Chloroform-d) δ 7.56 (d, J = 7.4 Hz, 2H), 7.42 (d, J = 6.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 3H), 6.19 (d, J = 6.4 Hz, 1H), 2.47 (q, J = 7.7 Hz, 2H), 1.16 (t, J = 7.5 Hz, 3H); ¹³C NMR (101 MHz, Chloroform-d) δ 197.3, 172.6, 156.4, 137.5, 129.5, 129.3, 129.2, 125.6, 96.5, 28.0, 8.8.
HRMS (ESI) calculated for C₁₃H₁₂NaO₃S [M+Na⁺]: 271.0399; found: 271.0397.

29: 5-oxo-2-phenyl-2,5-dihydrofuran-2-yl acetate
Following Method C (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 33.0 mg (50% yield) of 29 as a yellow oil.
IR (neat, cm⁻¹): 2985 (w), 1733 (s), 1373 (m), 1266 (m), 1240 (s), 1097 (w), 1045 (m), 911 (w), 847 (w), 734 (s), 704 (m), 608 (w), 461 (w); ¹H NMR (500 MHz, Chloroform-d) δ 7.74 (d, J = 5.6 Hz, 1H), 7.51 – 7.49 (m, 2H), 7.43 – 7.40 (m, 3H), 6.25 (d, J = 5.6 Hz, 1H), 2.11 (s, 3H); ¹³C NMR (126 MHz, Chloroform-d) δ 169.7, 168.3, 153.4, 135.2, 130.1, 129.0, 125.5, 122.2, 106.5, 21.7.
HRMS (ESI) calculated for C₁₂H₁₄O₄ [M+H⁺]: 219.0652; found: 219.0650.

30: 3-oxo-2,5-diphenyl-2,3-dihydrothiophen-2-yl acetate
Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 39.8 mg (43% yield) of 30 as a white solid.
IR (neat, cm⁻¹): 3062 (w), 1761 (m), 1692 (s), 1581 (w), 1552 (m), 1490 (m), 1249 (w), 1223 (m), 1195 (w), 1044 (m), 1000 (w), 926 (w), 767 (m), 755 (m), 703 (m), 489 (w); ¹H NMR (400 MHz, Chloroform-d) δ 7.75 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 7.3 Hz, 2H), 7.56 (d, J = 6.9 Hz, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.0 Hz, 3H),
6.49 (s, 1H), 2.26 (s, 3H); $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 198.1, 173.8, 168.9, 135.9, 132.8, 132.3, 129.3, 128.9, 126.9, 126.8, 125.8, 113.7, 91.8, 21.1.

HRMS (ESI) calculated for C$_{16}$H$_{14}$NaO$_3$S [M+ Na$^+$]: 333.0556; found: 333.0545.

31: 3-oxo-2-phenyl-2,3-dihydrobenzo[b]thiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 52.8 mg (62% yield) of 31 as a white solid.

IR (neat, cm$^{-1}$): 3063 (m), 2925 (w), 1758 (m), 1589 (m), 1574 (w), 1447 (m), 1368 (w), 1308 (w), 1280 (m), 1222 (s), 1196 (m), 1057 (m), 990 (m), 908 (m), 753 (m), 738 (m), 695 (m), 616 (w), 478 (m); $^1$H NMR (500 MHz, Chloroform-$d$) δ 7.77 (dd, $J = 7.7$, 0.9 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.60 (m, 1H), 7.40 (dt, $J = 8.0$, 0.8 Hz, 1H), 7.35 (m, 3H), 7.27 – 7.23 (m, 1H), 2.24 (s, 3H); $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 195.9, 169.0, 149.5, 136.5, 135.9, 129.4, 128.9, 127.9, 127.7, 126.0, 125.7, 123.8, 92.3, 21.0.

HRMS (ESI) calculated for C$_{16}$H$_{12}$NaO$_3$S [M+Na$^+$]: 307.0399; found: 307.0400.

32: 5-fluoro-3-oxo-2-phenyl-2,3-dihydrobenzo[b]thiophen-2-yl acetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 60.7 mg (67% yield) of 32 as a white solid.

IR (neat, cm$^{-1}$): 3065 (w), 1756(m), 1719 (s), 1601 (w), 1464 (s), 1447 (w), 1427 (w), 1370 (w), 1304 (w), 1264 (s), 1221 (s), 1196 (m), 1053 (m), 1002 (m), 888 (w), 867 (w), 821 (s), 795 (w), 734 (s), 694 (s), 502 (w); $^1$H NMR (500 MHz, Chloroform-$d$) δ 7.66 – 7.63 (m, 2H), 7.47 – 7.43 (m, 1H), 7.38 – 7.33 (m, 5H), 2.24 (s, 3H); $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 195.2 (d, $J = 3.2$ Hz) 169.0, 161.1 (d, $J = 248.2$ Hz), 144.3 (d, $J = 2.6$ Hz), 135.5, 129.6, 129.2 (d, $J = 7.2$ Hz), 129.0, 126.0, 124.6 (d, $J = 7.9$ Hz), 124.2 (d, $J = 24.0$ Hz), 113.8 (d, $J = 23.7$ Hz), 93.2, 20.9; $^{19}$F NMR (471 MHz, Chloroform-$d$) δ -116.2.

HRMS (ESI) calculated for C$_{16}$H$_{11}$FKO$_3$S [M+ K$^+$]: 341.0045; found: 341.0040.
33: 3-oxo-2-phenyl-5-(trifluoromethyl)-2,3-dihydrobenzo[b]thiophen-2-yl acetate
Followed Method C (current = 15 mA), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 57.8 mg (55% yield) of 33 as a white solid.

IR (neat, cm⁻¹): 3062 (w), 2926 (w), 1760 (m), 1722 (s), 1613 (s), 1492 (w), 1355 (s), 1195 (s), 1092 (s), 1080 (w), 1049 (w), 737 (m), 720 (w), 707 (m), 541 (w), 523 (m), 450 (w); ¹H NMR (500 MHz, Chloroform-d) δ 8.01 (dt, J = 1.7, 0.8 Hz, 1H), 7.82 (dd, J = 8.4, 2.0 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.52 (d, J = 8.3 Hz, 1H), 7.40 – 7.36 (m, 3H), 2.25 (s, 3H); ¹³C NMR (126 MHz, Chloroform-d) δ 194.8, 169.1, 153.4, 135.1, 132.7 (q, J = 3.7 Hz), 129.8, 129.1, 128.7 (q, J = 33.58 Hz), 128.2, 126.0, 124.8 (q, J = 4.3 Hz), 123.7 (q, J = 271.0 Hz), 124.3, 92.7, 20.9; ¹⁹F NMR (471 MHz, Chloroform-d) δ -62.5.
HRMS (ESI) calculated for C₁₇H₁₁F₃NaO₃S [M+ Na⁺]: 375.0273; found: 375.0264.

34: 3-oxo-2-(pyridin-2-yl)-2,3-dihydrobenzo[b]thiophen-2-yl acetate
Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 37.6 mg (44% yield) of 34 as a white solid.

IR (neat, cm⁻¹): 2924 (w), 2854 (w), 1764 (m), 1587 (m), 1370 (w), 1282 (m), 1210 (s), 1108 (w), 1064 (w), 1006 (w), 767 (w), 740 (w), 699 (w), 531 (w); ¹H NMR (500 MHz, Chloroform-d) δ 8.52 – 8.51 (m, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.73 (td, J = 7.7, 1.8 Hz, 1H), 7.68 (dt, J = 8.1, 1.2 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.29 – 7.21 (m, 2H), 2.26 (s, 3H); ¹³C NMR (126 MHz, Chloroform-d) δ 197.1, 168.0, 156.5, 149.93, 149.88, 137.2, 136.3, 128.4, 127.4, 125.6, 123.83, 123.81, 120.8, 91.5, 21.0.
HRMS (ESI) calculated for C₁₅H₁₂NO₃S [M+H⁺]: 286.0532; found: 286.0534.
**36: 2-oxo-3-phenyl-2,3-dihydrothiophen-3-yl acetate**

Following Method C (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 20.9 mg (30% yield) of 36 as a white solid and 9.0 mg (14% yield) of 37 as a white solid.

**IR (neat, cm⁻¹):** 3060 (w), 2933 (w), 1749 (m), 1702 (m), 1492 (w), 1054 (w), 908 (s), 836 (w), 728 (s), 652 (w), 487 (w); **¹H NMR (500 MHz, Chloroform-d) δ** 7.62 – 7.59 (m, 2H), 7.44 – 7.41 (m, 4H), 6.84 (d, J = 3.1 Hz, 1H), 2.19 (s, 3H); **¹³C NMR (126 MHz, Chloroform-d) δ** 195.3, 170.4, 145.6, 144.9, 130.0, 129.9, 128.8, 128.3, 76.5, 20.8.

**HRMS (ESI) calculated for C₁₂H₁₁O₃S [M+ H⁺]:** 235.0423; found: 235.0419.

**37: 3-phenylthiophen-2-yl acetate**

**IR (neat, cm⁻¹):** 3055 (w), 2928 (w), 1760 (w), 1265 (w), 1204 (w), 907 (m), 728 (s), 652 (m), 508 (w); **¹H NMR (500 MHz, Chloroform-d) δ** 7.55 – 7.52 (m, 2H), 7.44 – 7.39 (m, 2H), 7.33 – 7.29 (m, 1H), 7.04 (d, J = 5.9 Hz, 1H), 6.97 (d, J = 5.9 Hz, 1H), 2.30 (s, 3H); **¹³C NMR (126 MHz, Chloroform-d) δ** 167.9, 146.1, 134.2, 128.7, 128.1, 127.6, 127.3, 125.2, 117.8, 21.0.

**HRMS (ESI) calculated for C₁₂H₁₁O₂S [M+ H⁺]:** 219.0474; found: 219.0487.

**39: 5-oxo-2,3-diphenyl-2,5-dihydrothiophen-2-yl acetate**

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 52.7 mg (56% yield) of 39 as a white solid.
1H NMR (400 MHz, Chloroform-d) δ 7.44 (dd, J = 6.9, 1.5 Hz, 2H), 7.36 – 7.24 (m, 8H), 6.58 (s, 1H), 2.19 (s, 3H); 13C NMR (101 MHz, Chloroform-d) δ 194.8, 168.2, 167.1, 137.9, 131.5, 130.5, 129.0, 128.9, 128.7, 128.6, 128.3, 125.2, 96.7, 21.7.


41: (5-phenylthiophen-2-yl)methylene diacetate

Followed Method C, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 29.9 mg (34% yield) of 41 as a white solid.

1H NMR (500 MHz, Chloroform-d) δ 7.89 (s, 1H), 7.61 – 7.57 (m, 2H), 7.41 – 7.37 (m, 2H), 7.33 – 7.29 (m, 1H), 7.22 – 7.17 (m, 2H), 2.15 (s, 6H);

13C NMR (126 MHz, Chloroform-d) δ 168.7, 146.4, 137.1, 133.9, 129.1, 128.4, 128.2, 126.1, 122.7, 86.7, 21.0.


42: 3-((4-chlorophenyl)thio)-2-(4-fluorophenyl)-5-oxotetrahydrothiophen-2-yl acetate

Following Method E, the desired product was purified using silica gel chromatography (ethyl acetate/hexanes = 10:1) to give 21.1 mg (27% yield) of 42 as a white solid.

IR (neat, cm⁻¹): 2924 (w), 2853 (w), 1757 (s), 1712 (s), 1601 (w), 1508 (s), 1476 (s), 1213 (s), 1162 (m), 1093 (m), 1012 (s), 907 (m), 833 (m), 772 (w), 738 (w), 503 (w);

1H NMR (500 MHz, Chloroform-d) δ 7.56 – 7.51 (m, 2H), 7.16 – 7.12 (m, 2H), 7.10 – 7.05 (m, 2H), 6.93 – 6.90 (m, 2H), 3.65 (dd, J = 12.3, 6.7 Hz, 1H), 3.23 (dd, J = 16.9, 12.3 Hz, 1H), 3.08 (dd, J = 16.8, 6.7 Hz, 1H), 2.24 (s, 3H);

13C NMR (126 MHz, Chloroform-d) δ 200.7, 168.5, 162.9 (d, J = 246.6 Hz), 134.7, 134.1, 133.4 (d, J = 3.5 Hz), 132.1, 129.4, 128.2 (d, J = 8.4 Hz), 115.6 (d, J = 21.9 Hz), 99.0, 61.4, 47.7, 21.7;

19F NMR (471 MHz, Chloroform-d) δ -112.6 (m).

HRMS (ESI) calculated for C18H14ClFO3S2Na [M+Na+] : 418.9949; found: 418.9946
Following **Method F**, the desired product was purified using silica gel chromatography (ethyl acetate/hexanes = 1:1) to give 14.2 mg (37% yield) of 43 as a white solid.

**IR (neat, cm$$^{-1}$$):** 3233 (w), 3103 (w), 2922 (w), 2851 (w), 1684 (s), 1617 (w), 1599 (w), 1512 (m), 1347 (m), 1217 (w), 1158 (w), 840 (m), 817 (w), 770 (w), 520 (w); **$^1$H NMR (400 MHz, Chloroform-d)$\delta$** 8.91 (br s, 1H), 7.74 – 7.69 (m, 2H), 7.12 – 7.06 (m, 2H), 2.97 (dd, $J = 8.9, 7.6$ Hz, 2H), 2.61 (dd, $J = 8.9, 7.5$ Hz, 2H); **$^{13}$C NMR (101 MHz, Chloroform-d)$\delta$** 167.3, 163.9 (d, $J = 252.0$ Hz), 149.7, 131.8 (d, $J = 3.46$ Hz), 127.9 (d, $J = 8.45$ Hz), 115.8 (d, $J = 22.1$ Hz), 26.4, 22.7; **$^{19}$F NMR (471 MHz, Chloroform-d)$\delta$** -110.6 (m).

**HRMS (ESI)** calculated for C$_{10}$H$_{10}$FN$_2$O [M+ H$^+$]: 193.0772; found: 193.0771.

44: ethyl 2-(3-(4-fluorophenyl)-6-oxo-5,6-dihydropyridazin-1(4H)-yl)acetate$^5$

Following **Method G**, the desired product was purified using silica gel chromatography (cyclohexane/ethyl acetate 1:1) to give 22.7 mg (56% yield) of 44 as a white solid.

**$^1$H NMR (400 MHz, Chloroform-d)$\delta$** 7.75 – 7.67 (m, 2H), 7.08 (t, $J = 8.6$ Hz, 2H), 4.58 (s, 2H), 4.22 (q, $J = 7.1$ Hz, 2H), 3.00 (t, $J = 8.1$ Hz, 2H), 2.66 (t, $J = 8.1$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H).

45: N-(4-chlorophenyl)-2-(3-(4-fluorophenyl)-6-oxo-5,6-dihydropyridazin-1(4H)-yl)acetamide$^6$

Following **Method F**, the desired product was purified using silica gel chromatography (DCM/petroleum = 1:1) to give 22.6 mg (79% yield) of 45 as a white solid.

**$^1$H NMR (400 MHz, Chloroform-d)$\delta$** 8.34 (br s, 1H), 7.76 – 7.70 (m, 2H), 7.46 – 7.41 (m, 2H), 7.24 – 7.19 (m, 2H), 7.12 – 7.05 (m, 2H), 4.64 (s, 2H), 3.01 (dd, $J = 9.0, 7.4$ Hz, 2H), 2.69 (dd, $J = 9.0, 7.4$ Hz, 2H).
4. Cyclic Voltammetry Studies

**General information:** Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter), a platinum wire auxiliary electrode and SCE reference electrode. Current was reported in A, while all potentials were reported in V against the Fe⁺/Fe redox couple. The scan rate was 0.1 V/s.

![Cyclic voltammograms](image)

**Figure S2-1.** Cyclic voltammograms.

**Left:** Cyclic voltammograms of 1 (3 mM), AcOH (3 mL), 1 (3 mM) and AcOH (3 mL) in acetonitrile (MeCN) containing 10 mM Bu₄NPF₆ as the electrolyte.

**Right:** Cyclic voltammograms of 1 (3 mM) and 1 (3 mM) with varying concentrations of AcOH in acetonitrile (MeCN) containing 10 mM Bu₄NPF₆ as the electrolyte.
**Figure S2-2.** Cyclic voltammograms.

**Left:** Cyclic voltammograms of **1** (3 mM), \(^*\)Bu\(_4\)NOAc (3 mM), an equivalent mixture of **1** and \(^*\)Bu\(_4\)NOAc in acetonitrile (MeCN) containing 10 mM \(^*\)Bu\(_4\)NPF\(_6\) as the electrolyte.

**Right:** Cyclic voltammograms of **1** (3 mM) and \(^*\)Bu\(_4\)NOAc in acetonitrile (MeCN) containing 10 mM \(^*\)Bu\(_4\)NPF\(_6\) as the electrolyte.
5. References


6. Spectral Data (\(^1\)H, \(^{13}\)C, \(^{19}\)F)

\[ \text{OAc} \]
\[ \text{O} \]
\[ \text{2} \]
\[ \text{\(^1\)H NMR(500 MHz, CDCl\(_3\))} \]

\[ \text{\(^{13}\)C NMR(126 MHz, CDCl\(_3\))} \]
$\text{\[^{1}H\ NMR(500 MHz, CDCl\textsubscript{3})\]}

$\text{\[^{13}C\ NMR(126 MHz, CDCl\textsubscript{3})\]}$
$^1$H NMR (500 MHz, CDCl$_3$)

$^1$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR(500MHz, CDCl$_3$)

5

$^13$C NMR(126 MHz, CDCl$_3$)

5

O=\text{S} \quad \text{OAc} \quad \text{tBu}
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

7

O=S

OAc

F

O=S

OAc

F

NMR(500 MHz, CDCl$_3$)

NMR(126 MHz, CDCl$_3$)
7

$^{19}$F NMR(471 MHz, CDCl$_3$)

8

$^1$H NMR(500 MHz, CDCl$_3$)
\[ \text{O} \begin{array}{c} \text{S} \\ \text{OAc} \end{array} \text{Cl} \]

\[ ^{13}\text{C NMR}(126\text{ MHz, CDCl}_3) \]

\[ \text{H} \begin{array}{c} \text{N} \\ \text{Ac} \end{array} \text{Br} \]

\[ ^1\text{H NMR}(500\text{ MHz, CDCl}_3) \]
9
$^{13}$C NMR(126 MHz, CDCl$_3$)

10
$^1$H NMR(500 MHz, CDCl$_3$)
\[ \text{O=S} \]
\[ \text{OAc} \]
\[ \text{CF}_3 \]

10

$^{13}$C NMR(126 MHz, CDCl$_3$)

\[ \text{O=S} \]
\[ \text{OAc} \]
\[ \text{CF}_3 \]

10

$^{19}$F NMR(471 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}$H NMR(500 MHz, CDCl$_3$)

$^{13}$C NMR(126 MHz, CDCl$_3$)
$^{1}H$ NMR(500 MHz, CDCl$_3$)

$^{13}C$ NMR(126 MHz, CDCl$_3$)
$1^H$ NMR(500 MHz, CDCl$_3$)

$13^C$ NMR(126 MHz, CDCl$_3$)
$^{1}H$ NMR ($500$ MHz, CDCl$_3$)

$^{13}$C NMR ($126$ MHz, CDCl$_3$)
1H NMR (500 MHz, CDCl₃)

13C NMR (126 MHz, CDCl₃)

Chemical shifts (ppm):

- H NMR (500 MHz, CDCl₃)
  - 16.13
  - 16.96
  - 19.31
  - 26.78

- C NMR (126 MHz, CDCl₃)
  - 13.81
  - 13.94
  - 14.38
  - 21.38
  - 26.78
  - 43.04
  - 44.07

$\text{S OAc O}$

$\text{17}$
$^1\text{H NMR (400 MHz, CDCl}_3\text{)}$

$\text{O=S OAc F}$

$\text{17}$
$^{13}\text{C NMR (101 MHz, CDCl}_3\text{)}$
$^{19}\text{F NMR}(471 \text{ MHz, CDCl}_3)$

$^{1}\text{H NMR}(500 \text{ MHz, CDCl}_3)$
$^{13}$C NMR (126 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)
**13C NMR(126 MHz, CDCl₃)**

20

**1H NMR(500 MHz, CDCl₃)**

21
$^{13}$C NMR (126 MHz, CDCl$_3$)

$^{19}$F NMR (471 MHz, CDCl$_3$)
\[ \text{H NMR (500 MHz, CDCl}_3\text{)} \]

\[ \text{Cl} \]

\[ \text{S} \]

\[ \text{OAc} \]

\[ \text{O} \]

\[ \text{22} \]

\[ \text{13C NMR (126 MHz, CDCl}_3\text{)} \]

\[ \text{Cl} \]

\[ \text{S} \]

\[ \text{OAc} \]

\[ \text{O} \]
\[ 1^3C \text{ NMR}(126 \text{ MHz}, \text{CDCl}_3) \]
**1H NMR (500 MHz, CDCl₃)**

![1H NMR spectrum](image)

**13C NMR (126 MHz, CDCl₃)**

![13C NMR spectrum](image)
$^{19}$F NMR (471 MHz, CDCl$_3$)

$^{1}$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (126 MHz, CDCl$_3$)

$^{19}$F NMR (471 MHz, CDCl$_3$)
$^1$H NMR(500 MHz, CDCl$_3$)

$^{13}$C NMR(126 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (126 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
31

$^1$H NMR (500 MHz, CDCl$_3$)

31

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

Chemical shifts for $^1$H NMR:
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- 5.15 ppm
- 1.02 ppm
- 1.98 ppm
- 2.24 ppm
- 7.26 ppm
- 7.34 ppm
- 7.34 ppm
- 7.34 ppm
- 7.35 ppm
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- 7.66 ppm

Chemical shifts for $^{13}$C NMR:
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- 113.93 ppm
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- 124.94 ppm
- 125.00 ppm
- 125.97 ppm
- 128.96 ppm
- 129.13 ppm
- 129.19 ppm
- 129.55 ppm
- 135.45 ppm
- 144.33 ppm
- 144.34 ppm
- 160.10 ppm
- 162.07 ppm
- 169.00 ppm
- 195.19 ppm
- 195.21 ppm

Structure of compound 32:

![Structure](image)
32

$^{19}$F NMR(471 MHz, CDCl$_3$)

33

$^1$H NMR(500 MHz, CDCl$_3$)
$^{13}$C NMR (126 MHz, CDCl$_3$)

$^{19}$F NMR (471 MHz, CDCl$_3$)
$^{1}\text{H NMR}(500 \text{ MHz, CDCl}_3)$

$^{13}\text{C NMR}(126 \text{ MHz, CDCl}_3)$
36

$^1$H NMR (500 MHz, CDCl$_3$)

36

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

petroleum ether
$^{19}$F NMR(471 MHz, CDCl$_3$)

$^{1}$H NMR(400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{19}$F NMR (471 MHz, CDCl$_3$)
44
$^1$H NMR(400 MHz, CDCl$_3$)

45
$^1$H NMR(400 MHz, CDCl$_3$)
7. **X-ray Crystallographic Data**

7.1 The structure of 16 was determined by the X-ray diffraction. Recrystallized from DCM and PE. Further information can be found in the CIF file (Deposition number: CCDC 2106081)

![Figure S3. X-ray structure of 16](image)

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S = 1.032 Npar= 174
7.2 The structure of 27 was determined by the X-ray diffraction. Recrystallized from DCM and PE. Further information can be found in the CIF file (Deposition number: CCDC 2106079)

Figure S4. X-ray structure of 27

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S = 1.037  Npar= 182
7.3 The structure of 30 was determined by the X-ray diffraction. Recrystallized from DCM and PE. Further information can be found in the CIF file (Deposition number: CCDC 2106084)

**Figure S4. X-ray structure of 30**

<table>
<thead>
<tr>
<th>Bond precision:</th>
<th>C-C = 0.0025 Å</th>
<th>Wavelength=0.71073</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell:</td>
<td>a=9.346(5)</td>
<td>b=11.033(5)</td>
</tr>
<tr>
<td>Alpha:</td>
<td>α=77.727(15)</td>
<td>Beta:</td>
</tr>
<tr>
<td>Hall group:</td>
<td>P -1</td>
<td></td>
</tr>
<tr>
<td>Moiety formula:</td>
<td>C18 H14 O3 S</td>
<td></td>
</tr>
<tr>
<td>Sum formula:</td>
<td>C18 H14 O3 S</td>
<td></td>
</tr>
<tr>
<td>Mr</td>
<td>310.35</td>
<td></td>
</tr>
<tr>
<td>Dx, g cm⁻³</td>
<td>1.350</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Mr (mm⁻¹)</td>
<td>0.221</td>
<td></td>
</tr>
<tr>
<td>F000</td>
<td>648.0</td>
<td></td>
</tr>
<tr>
<td>F000’</td>
<td>648.80</td>
<td></td>
</tr>
<tr>
<td>h,k,lmax</td>
<td>13,15,21</td>
<td></td>
</tr>
<tr>
<td>Nref</td>
<td>9089</td>
<td></td>
</tr>
<tr>
<td>Tmin,Tmax</td>
<td>0.895,0.895</td>
<td></td>
</tr>
<tr>
<td>Tmin’</td>
<td>0.895</td>
<td></td>
</tr>
</tbody>
</table>

Correction method= # Reported T Limits: Tmin=0.489 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.994 Theta(max)= 30.245

R(reflections)= 0.0480( 6312) wR2(reflections)= 0.1235( 9037)
S = 1.038 Npar= 399
7.4 The structure of 31 was determined by the X-ray diffraction. Recrystallized from DCM and PE. Further information can be found in the CIF file (Deposition number: CCDC 2106078)

Figure S5. X-ray structure of 31