Supporting Information

H₂O-Controlled Selective Thiocyanation and Alkenylation of Ketene Dithioacetals under Electrochemical Oxidation

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1. General information
All glassware was oven dried at 100 °C for hours and cooled down under vacuum. Ketene dithioacetals was prepared according to reported procedures.\textsuperscript{1} All the reaction prepared using a high purity deionized (DI) water with a resistivity of 18.0 MΩ•cm from a Barnstead water purification system and the solvent of CH\textsubscript{3}CN (99.9%, Extra Dry with molecular sieves, Water ≤ 50 ppm) was purchased from Innochem. The deoxygenation of dideionized water and CH\textsubscript{3}CN is through Schlenk technology. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). \textsuperscript{1}H and \textsuperscript{13}C NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively.
2. General procedure for thiocyanation of ketene dithioacetals under electrochemical oxidation.

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, ketene dithioacetal 1 (0.25 mmol), potassium thiocyanate 2a (0.5 mmol, 48.5 mg) and lithium perchlorate (1 mmol, 106 mg) were combined and added. The bottle was equipped with platinum plate (1 × 1 cm$^2$) anode and graphite rod cathode and was then charged with nitrogen. Under the protection by nitrogen, H$_2$O (0.5 mmol, 9 µL) and CH$_3$CN (10 mL) were slowly injected into the reaction tube. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA cm$^{-2}$ under room temperature for 3 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH$_2$Cl$_2$ (10 mL x 3). The organic layers were combined, dried over Na$_2$SO$_4$, and concentrated. The pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl ether = 5:1 - 10:1).

3. Table S1. Optimization of the alkenylation reaction conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>deviation from standard conditions</th>
<th>Yield $^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>without current</td>
<td>n. d.</td>
</tr>
<tr>
<td>3</td>
<td>without KSCN</td>
<td>n. d.</td>
</tr>
<tr>
<td>4</td>
<td>2 equiv of H$_2$O</td>
<td>n. d.</td>
</tr>
<tr>
<td>5</td>
<td>$^{n}$Bu$_4$NBF$_4$ instead of LiClO$_4$</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>$^{n}$Bu$_4$NClO$_4$ instead of LiClO$_4$</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>$^{n}$Bu$_4$NPF$_6$ instead of LiClO$_4$</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td>KSCN (10 mol%) instead of KSCN (2 equiv)</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>KOAc instead of KSCN</td>
<td>trace</td>
</tr>
</tbody>
</table>
a Reaction conditions: 1 (0.25 mmol, 55.5 mg), KSCN (0.5 mmol, 48.5 mg), LiClO₄ (0.1 M, 106 mg), CH₃CN (10 mL), r. t., N₂, 3 h. b Isolated yields.

4. Procedure for gram scale synthesis.

In an oven-dried undivided three-necked bottle (250 mL) equipped with a stir bar, 1-(4-chlorophenyl)-2-(1, 3-dithiolan-2-ylidene)ethan-1-one 1f (5 mmol), potassium thiocyanate 2a (10 mmol) and lithium perchlorate (20 mmol) were combined and added. The bottle was equipped with platinum plate (1 × 1 cm²) anode and graphite rod cathode and was then charged with nitrogen. Under the protection by nitrogen, H₂O (10 mmol) and CH₃CN (200 mL) were slowly injected into the reaction tube. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA cm⁻² under room temperature for 60 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH₂Cl₂ (100 mL × 3). The organic layers were combined, dried over Na₂SO₄, and concentrated. The pure product was obtained in 80% yield by flash column chromatography on silica gel (petroleum: ethyl ether = 5:1).

5. Preliminary mechanistic studies.

(1) The reaction of 1a and 2a with TEMPO or BHT under the standard conditions.

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, ketene dithioacetals 1a (0.25 mmol), 2a (0.5 mmol), LiClO₄ (1 mmol), H₂O (0.5 mmol), TEMPO or BHT (0.5 mmol) and CH₃CN (10 mL) were combined and sealed. The bottle was equipped with platinum electrodes (1 × 1 cm²) as anode and graphite rod as cathode, and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 3 h. When the reaction was finished, the solution was concentrated in vacuum and the yield of 3aa was sharply decreased.

(2) The alkenylation reaction with TEMPO or BHT under the standard conditions.
In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 1a (0.25 mmol), LiClO₄ (1 mmol), KSCN (0.5 mmol), TEMPO or BHT (0.5 mmol) and CH₃CN (10 mL) were combined and sealed. The bottle was equipped with platinum electrodes (1 × 1 cm²) as anode and graphite rod as cathode, and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 3 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH₂Cl₂ (10 mL × 3). The organic layers were combined, dried over Na₂SO₄, and concentrated. The pure product was obtained in 74% and 65% yield by flash column chromatography on silica gel (petroleum: ethyl ether = 2:1).

(3) The reaction of 3ga under the alkenylation conditions.

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 3ga (0.25 mmol), LiClO₄ (1 mmol) and CH₃CN (10 mL) were combined and sealed. The bottle was equipped with platinum electrodes (1 × 1 cm²) as anode and graphite rod as cathode, and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 3 h. When the reaction was finished, the home-coupling product 4d was obtained in 23% isolated yield by flash column chromatography on silica gel (petroleum: ethyl ether = 2:1).

(4) Cyclic Voltammetry of 1a and KSCN.
Figure S1. Cyclic Voltammetry of 1a and KSCN. Glass carbon as working electrode, Pt wire as counter electrode, Ag/AgCl as reference, LiClO₄ (0.1M) as electrolyte in CH₃CN, scan rate: 50 mV/s.

6. References


7. Detail descriptions for products.

2-(1,3-dithiolan-2-ylidene)-1-phenyl-2-thiocyanatoethan-1-one (3aa):² yellow solid was obtained with 96% isolated yield (67.2 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.61 – 7.53 (m, 2H), 7.50 – 7.42 (m, 1H), 7.39 (t, J = 7.4 Hz, 2H), 3.61 (t, J = 6.05 Hz, 2H), 3.49 (t, J = 6.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 189.99, 185.98, 137.98, 131.48, 128.22, 128.15, 109.70, 100.96, 41.42, 36.58. HRMS (EI) calcd for C₁₂H₉NONaS₃ [M+Na]⁺: 307-9738; found: 307.9838.
2-(1,3-dithiolan-2-ylidene)-1-(4-methoxyphenyl)-2-thiocyanatoethan-1-one (3ba): yellow solid was obtained with 96% isolated yield (74.4 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 8.8$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 3.81 (s, 3H), 3.59 (t, $J = 6.5$ Hz, 2H), 3.49 (t, $J = 6.5$ Hz, 2H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 183.94, 179.58, 157.80, 126.19, 125.26, 108.76, 105.02, 96.14, 50.74, 36.47, 31.87. HRMS (EI) calcd for C$_{13}$H$_{11}$NO$_2$NaS$_3$ [M+Na]$^+$: 331.9844; found: 331.9842.

2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(p-tolyl)ethan-1-one (3ca): yellow solid was obtained with 98% isolated yield (66.2 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 6.5$ Hz, 2H), 3.60 (t, $J = 6.6$ Hz, 2H), 3.49 (t, $J = 6.6$ Hz, 2H), 2.35 (s, 3H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 185.01, 180.39, 137.50, 130.30, 124.13, 123.73, 104.97, 96.30, 36.56, 31.82, 16.91. HRMS (EI) calcd for C$_{13}$H$_{11}$NONaS$_3$ [M+Na]$^+$: 315.9895; found: 315.9896.

1-([1,1'-biphenyl]-4-yl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3da): yellow oil was obtained with 88% isolated yield (78.3 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 8.1$ Hz, 2H), 7.69 (d, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 7.7$ Hz, 2H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.40 (t, $J = 7.2$ Hz, 1H), 3.70 (t, $J = 6.6$ Hz, 2H), 3.58 (t, $J = 6.6$ Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 189.55, 185.85, 144.37, 140.03, 136.59, 128.94, 128.08, 127.28, 126.87, 109.72, 100.99, 41.38, 36.58. HRMS (EI) calcd for C$_{18}$H$_{13}$NNaONaS$_3$ [M+Na]$^+$: 378.0051; found: 378.0047.
2-(1,3-dithiolan-2-ylidene)-1-(4-fluorophenyl)-2-thiocyanatoethan-1-one (3ea):\(^2\) yellow solid was obtained with 96% isolated yield (71.5 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.75 – 7.63 (m, 2H), 7.19 – 7.06 (m, 2H), 3.71 (t, \(J = 6.6\) Hz, 2H), 3.59 (t, \(J = 6.6\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 188.58, 186.42, 164.60 (d, \(J = 252.9\) Hz), 134.03, 130.83 (d, \(J = 8.9\) Hz), 115.40 (d, \(J = 22.0\) Hz), 109.58, 100.63, 41.43, 36.62. \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -107.09. HRMS (EI) calcd for C\(_{12}\)H\(_8\)FNNaOS\(_3\) [M+Na\]\(^+\): 319.9644; found: 319.9641.

1-(4-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3fa):\(^2\) yellow solid was obtained with 97% isolated yield (76.1 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.63 (d, \(J = 8.4\) Hz, 2H), 7.46 (d, \(J = 8.4\) Hz, 2H), 3.72 (t, \(J = 6.6\) Hz, 2H), 3.60 (t, \(J = 6.6\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 188.74, 186.85, 137.74, 136.29, 129.67, 128.54, 109.52, 100.60, 41.47, 36.59. HRMS (EI) calcd for C\(_{12}\)H\(_8\)ClNONaS\(_3\) [M+Na\]\(^+\): 335.9349; found: 335.9344.

1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3ga):\(^2\) yellow solid was obtained with 94% isolated yield (83.7 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.53 (d, \(J = 8.5\) Hz, 2H), 7.46 (d, \(J = 8.5\) Hz, 2H), 3.62 (t, \(J = 6.7\) Hz, 2H), 3.50 (t, \(J = 6.7\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 188.83 (s), 186.99, 136.75 (s), 131.50, 129.77, 126.19, 109.54, 100.55, 41.50, 36.61. HRMS (EI) calcd for C\(_{12}\)H\(_8\)BrNONaS\(_3\) [M+Na\]\(^+\): 379.8844; found: 379.8845.

2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3ha):\(^2\) yellow solid was obtained with 88% isolated yield (75.6 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.66 (s, 4H), 3.70 – 3.63 (t, \(J = 6.2\) Hz, 2H), 3.52 (t, \(J = 6.7\) Hz, 2H). \(^{13}\)C NMR (126 MHz, DMSO) \(\delta\) 184.10 (s), 183.29 (s), 136.75 (s), 128.04 (q, \(J = 33.28\) Hz), 124.91, 123.46, 121.18(q, \(J = 273.3\) Hz), 120.55 (q, \(J =
3.6 Hz), 104.67, 95.74, 36.88, 31.84. 19 F NMR (471 MHz, CDCl3) δ -62.93. HRMS (EI) calcd for C13H8F3NONaS3 [M+Na]+: 369.9612; found: 369.9609.

2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(m-tolyl)ethan-1-one (3ia):2 yellow solid was obtained with 83% isolated yield (61.0 mg). 1H NMR (500 MHz, CDCl3) δ 7.36 (d, J = 8.0 Hz, 2H), 7.33 – 7.23 (m, 2H), 3.60 (t, J = 6.1 Hz, 2H), 3.48 (t, J = 6.6 Hz, 2H), 2.34 (s, 1H). 13C NMR (126 MHz, CDCl3) δ 190.25, 185.59, 138.12, 137.95, 132.28, 128.70, 128.05, 125.22, 109.75, 101.07, 41.38, 36.58, 21.39. HRMS (EI) calcd for C13H11NONaS3 [M+Na]+: 315.9895; found: 315.9893.

1-(3-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3ja):2 yellow solid was obtained with 84% isolated yield (65.9 mg). 1H NMR (500 MHz, CDCl3) δ 7.52 (s, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 3.64 (t, J = 6.7 Hz, 2H), 3.51 (t, J = 6.7 Hz, 2H). 13C NMR (126 MHz, CDCl3) δ 188.48, 187.30, 139.69, 134.43, 131.38, 129.54, 128.17, 126.07, 109.43, 100.56, 41.52, 36.61. HRMS (EI) calcd for C12H8ClNONaS3 [M+Na]+: 335.9349; found: 335.9344.

2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(o-tolyl)ethan-1-one (3ka):2 yellow solid was obtained with 85% isolated yield (62.5 mg). 1H NMR (500 MHz, CDCl3) δ 7.33 – 7.24 (m, 1H), 7.21 – 7.12 (m, 3H), 3.66 – 3.59 (t, J = 6.2 Hz, 1H), 3.51 – 3.46 (t, J = 7.2 Hz, 1H), 2.23 (s, 1H). 13C NMR (126 MHz, CDCl3) δ 192.05, 185.63, 138.71, 135.06, 130.74, 129.81, 126.22, 125.50, 109.51, 102.34, 41.68, 36.52, 19.37. HRMS (EI) calcd for C13H11NOS3Na [M+Na]+: 315.9895; found: 315.9893.
2-(1,3-dithiolan-2-ylidene)-1-(2-fluorophenyl)-2-thiocyanatoethan-1-one (3la): yellow solid was obtained with 84% isolated yield (62.5 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.47 – 7.31 (m, 2H), 7.19 (dd, $J = 10.0, 4.9$ Hz, 1H), 7.05 (t, $J = 9.0$ Hz, 1H), 3.63 (t, $J = 6.7$ Hz, 2H), 3.49 (t, $J = 6.7$ Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 186.70, 186.35, 158.78 (d, $J = 248.3$ Hz), 132.71 (d, $J = 8.3$ Hz), 129.54 (d, $J = 3.1$ Hz), 127.12 (d, $J = 16.0$ Hz), 124.69 (d, $J = 3.4$ Hz), 115.75 (d, $J = 21.6$ Hz), 109.55, 102.35, 41.48, 36.58. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -111.82. HRMS (EI) calcd for C$_{12}$H$_8$FNNaOS$_3$Na $[^{[M+Na]}^+]$: 319.9644; found: 319.9641.

1-(2-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3ma): yellow solid was obtained with 83% isolated yield (65.1 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40 – 7.23 (m, 4H), 3.69 – 3.62 (t, $J = 6.4$ Hz, 2H), 3.50 (t, $J = 6.6$ Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 188.65, 186.43, 138.56, 131.01, 130.43, 129.46, 128.07, 127.21, 109.55, 102.16, 41.66, 36.51. HRMS (EI) calcd for C$_{12}$H$_8$ClNONaS$_3$ [M + Na]$^+$: 335.9349; found: 335.9344.

1-(benzo[d][1,3]dioxol-5-yl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3na): yellow solid was obtained with 85% isolated yield (68.9 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.20 (dd, $J = 9.7, 1.6$ Hz, 1H), 7.09 (d, $J = 1.6$ Hz, 1H), 6.80 (d, $J = 8.1$ Hz, 1H), 5.98 (s, 2H), 3.58 (t, $J = 6.5$ Hz, 2H), 3.49 (t, $J = 6.6$ Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 188.37, 184.60, 150.76, 147.64, 131.62, 124.35, 109.63, 108.98, 107.86, 101.80, 100.79, 41.25, 36.67. HRMS (EI) calcd for C$_{13}$H$_9$NO$_3$NaS$_3$ [M+Na]$^+$: 345.9637; found: 345.9639.
2-(1,3-dithiolan-2-ylidene)-1-(naphthalen-2-yl)-2-thiocyanatoethan-1-one (3oa): yellow solid was obtained with 87% isolated yield (71.7 mg). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.26 (s, 1H), 8.06 – 7.98 (m, 3H), 7.62 (t, \(J = 14.7\), 7.0, 1.2 Hz, 2H), 7.52 (t, \(J = 6.5\) Hz, 2H), 3.78 (t, \(J = 6.5\) Hz, 2H). \(^{13}\)C NMR (126 MHz, DMSO) \(\delta\) 189.72, 186.08, 136.09, 134.42, 132.30, 129.37, 128.88, 128.44, 128.22, 128.19, 125.09, 111.49, 101.73, 41.91, 37.20. HRMS (EI) calcd for \(\text{C}_{16}\text{H}_{11}\text{NONaS}_{3}\) [M+Na]: 351.9895; found: 351.9891.

2-(1,3-dithiolan-2-ylidene)-1-(furan-2-yl)-2-thiocyanatoethan-1-one (3pa): yellow solid was obtained with 95% isolated yield (64.1 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.61 (d, \(J = 1.0\) Hz, 1H), 7.47 (d, \(J = 3.5\) Hz, 1H), 6.52 (dd, \(J = 3.6, 1.6\) Hz, 1H), 3.59 (t, \(J = 6.6\) Hz, 2H), 3.46 (t, \(J = 6.5\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 182.28, 169.81, 146.19, 141.92, 115.11, 107.55, 104.97, 93.88, 36.49, 31.35. HRMS (EI) calcd for \(\text{C}_{10}\text{H}_{7}\text{NO}_{2}\text{NaS}_{3}\) [M + Na]: 291.9531; found: 291.9527.

2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(thiophen-2-yl)ethan-1-one (3qa): yellow solid was obtained with 94% isolated yield (67.2 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.04 (dd, \(J = 3.9, 1.0\) Hz, 1H), 7.60 (dd, \(J = 5.0, 1.0\) Hz, 1H), 7.10 (dd, \(J = 4.9, 4.0\) Hz, 1H), 3.59 (t, \(J = 6.6\) Hz, 2H), 3.47 (t, \(J = 6.6\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 187.27, 178.94, 141.3, 134.27, 133.97, 127.89, 109.41, 99.25, 41.35, 36.18. HRMS (EI) calcd for \(\text{C}_{10}\text{H}_{7}\text{NNaOS}_{4}\) [M + Na]: 307.9303; found: 307.9298.
1-(1,3-dithiolan-2-ylidene)-1-thiocyanopropan-2-one (3ra): yellow solid was obtained with 93% isolated yield (50.6 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.69 – 3.62 (t, $J$ = 6.3 Hz, 2H), 3.53 – 3.48 (t, $J$ = 7.1 Hz, 2H), 2.56 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 192.18, 183.68, 109.45, 101.61, 41.66, 36.25, 27.69. HRMS (EI) calcd for C$_7$H$_7$NONaS$_3$ [M + Na]$^+$: 239.9582; found: 239.9578.

2-(1,3-dithian-2-ylidene)-1-phenyl-2-thiocyanatoethan-1-one (3sa): white solid was obtained with 82% isolated yield (60.3 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.71 – 7.64 (m, 2H), 7.49 (t, $J$ = 7.4 Hz, 1H), 7.41 (t, $J$ = 7.6 Hz, 2H), 3.11 (t, $J$ = 7.0 Hz, 2H), 2.88 (t, $J$ = 7.0 Hz, 2H), 2.25 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 189.43, 175.14, 137.79, 132.51, 128.99, 128.48, 109.58, 109.54, 30.80, 30.37, 23.83. HRMS (EI) calcd for C$_{13}$H$_{12}$NONaS$_3$ [M + Na]$^+$: 315.9895; found: 315.9891.

2,3-di(1,3-dithiolan-2-ylidene)-1,4-diphenylbutane-1,4-dione (4a): yellow solid was obtained with 81% isolated yield (44.8 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.61 – 7.53 (m, 4H), 7.50 – 7.42 (m, 2H), 7.39 (t, $J$ = 7.4 Hz, 4H), 3.61 (t, $J$ = 6.1 Hz, 4H), 3.49 (t, $J$ = 6.6 Hz, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 189.98, 185.98, 137.97, 131.48, 128.21, 128.15, 109.70, 41.42, 36.57. HRMS (EI) calcd for C$_{22}$H$_{19}$O$_2$NaS$_4$ [M + Na]$^+$: 465.0082; found: 465.0078.

2,3-di(1,3-dithiolan-2-ylidene)-1,4-di-p-tolylbutane-1,4-dione (4b): yellow solid was obtained with 83% isolated yield (48.8 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J$ = 8.0 Hz, 4H), 7.06 (d, $J$ = 7.9 Hz, 4H), 3.45 (t, $J$ = 6.5 Hz, 4H), 3.35 – 3.29 (t, $J$ = 7.0 Hz, 4H), 2.30 (s, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 191.27, 181.96, 140.82, 136.19, 129.02, 128.08, 114.99, 41.00, 35.65, 21.59. HRMS (EI) calcd
for C_{24}H_{23}O_{5}S_{4} [M+H]^+: 471.0575; found: 471.0578.

2,3-di(1,3-dithiolan-2-ylidene)-1,4-bis(4-fluorophenyl)butane-1,4-dione (4c): yellow solid was obtained with 78% isolated yield (46.7 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.47 (dd, J = 8.5, 5.5 Hz, 4H), 6.95 (t, J = 8.7 Hz, 4H), 3.47 (t, J = 6.5 Hz, 4H), 3.33 (t, J = 6.5 Hz, 4H). ^13C NMR (126 MHz, CDCl_3) δ 189.94, 183.27, 164.03 (d, J = 251.1 Hz), 134.93, 131.38 (d, J = 8.8 Hz), 114.48 (d, J = 21.7 Hz), 114.17, 41.05, 35.71. ^19F NMR (377 MHz, CDCl_3) δ -107.09. HRMS (EI) calcd for C_{22}H_{17}F_{2}O_{2}S_{4} [M+H]^+: 479.0074; found: 479.0078.

1,4-bis(4-bromophenyl)-2,3-di(1,3-dithiolan-2-ylidene)butane-1,4-dione (4d): yellow solid was obtained with 75% isolated yield (56.1 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.50 (d, J = 8.4 Hz, 4H), 7.36 (d, J = 8.4 Hz, 4H), 3.56 (t, J = 6.1 Hz, 4H), 3.43 – 3.38 (t, J = 7.2 Hz, 4H). ^13C NMR (126 MHz, CDCl_3) δ 190.13, 184.20, 137.67, 130.67, 130.54, 124.91, 113.74, 41.18, 35.74. ^19F NMR (377 MHz, CDCl_3) δ -62.82. HRMS (EI) calcd for C_{22}H_{17}Br_{2}O_{2}S_{4} [M+H]^+: 598.8473; found: 598.8478.

1,4-bis(3-chlorophenyl)-2,3-di(1,3-dithiolan-2-ylidene)butane-1,4-dione (4e): yellow solid was obtained with 70% isolated yield (44.7 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.38 (t, J = 1.7 Hz, 2H), 7.33 – 7.28 (m, 4H), 7.23 – 7.18 (m, 2H), 3.49 (t, J = 6.1 Hz, 4H), 3.34 (t, J = 7.2 Hz, 4H). ^13C NMR (126 MHz, CDCl_3) δ 189.86, 184.09, 140.63, 133.53, 130.38, 128.80, 126.84, 114.11, 41.17, 35.71. HRMS (EI) calcd for C_{22}H_{17}Cl_{2}O_{2}S_{4} [M+H]^+: 510.9483; found: 510.9488.
2,3-di(1,3-dithiolan-2-ylidene)-1,4-di(naphthalen-2-yl)butane-1,4-dione (4f): yellow solid was obtained with 84% isolated yield (57.0 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.80 (s, 2H), 7.75 (d, $J$ = 8.0 Hz, 2H), 7.69 (dd, $J$ = 16.1, 8.2 Hz, 4H), 7.48 – 7.35 (m, 6H), 3.34 (t, $J$ = 6.4 Hz, 4H), 3.21 (t, $J$ = 6.4 Hz, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 191.23, 183.16, 136.42, 134.16, 132.21, 129.42, 129.26, 127.61, 127.24, 126.85, 126.13, 125.76, 114.48, 41.01, 35.63. HRMS (EI) calcd for C$_{30}$H$_{23}$O$_2$S$_4$ [M+H]$^+$: 543.0575; found: 543.0578.

$^{Z}$)-cyanic ($^{Z}$)-N-morpholinobenzimidic thioanhydride (5a): yellow solid was obtained with 95% isolated yield (58.6 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.18 (d, $J$ = 7.8 Hz, 2H), 7.51 (t, $J$ = 7.4 Hz, 1H), 7.42 (t, $J$ = 7.7 Hz, 2H), 4.21 (s, 4H), 3.77 – 2.56 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 198.55, 178.02, 133.05, 129.23, 128.74, 127.90, 63.07, 60.16. HRMS (EI) calcd for C$_{12}$H$_{13}$N$_3$NaOS [M+Na]$^+$: 270.0672; found 270.0675.
8. Copies of product NMR Spectra

3aa

$^1$HNMR

$^{13}$CNMR
$^1$HNMR

$^{13}$CNMR
$^{1}$HNMR

$^{13}$CNMR
$^1$HNMR

$^{13}$CNMR
$^1$HNMR

3ea

$^{13}$CNMR
$^{19}\text{FNMR}$
$^{1}$HNMR

$^{13}$CNMR
$^{19}$FNMR
\[ \text{1H NMR} \]

\[
\begin{array}{c}
\text{Cl} \quad \text{O} \\
\text{SCN}
\end{array}
\]

\[ \text{13C NMR} \]
$^{19}$FNMR
$^1$HNMR

$^{13}$CNMR
$^1$HNMR

$^1$CNMR
$^1$HNMR

$^{13}$CNMR
$^1$HNMR

$^{13}$CNMR
$^{1}$HNMR

$^{13}$CNMR
$^{19}$FNMR