Supporting Information

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I. General Remarks:
Unless otherwise stated, all commercial reagents and solvents were used without additional purification. All the reactions were carried out under air atmosphere. $^1$H NMR spectra of compounds 2 were recorded at 25°C on a Bruker Ascend™ 400 spectrometer. Chemical shifts (in ppm) were referenced TMS in CDCl$_3$ (0 ppm). $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ ($\delta = 77.00$ ppm). Melting points were obtained with a micro melting point XT4A Beijing Keyi electrooptic apparatus and are uncorrected. HRMS data were obtained on a Waters LCT Premierxe™ (USA). All reactions were monitored by TLC with Taizhou GF254 silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure.

II. Synthesis procedure for compounds 2 (2a as an example).

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\text{Acetophenone 1a (36.0 mg, 0.3 mmol), KSeCN (52.2 mg, 0.36 mmol), I}_2 \, (38.1 \, \text{mg, 0.15 mmol), TBHP (108.1 mg, 1.2 mmol), KOAc (58.8 mg, 0.6 mmol in CH}_3\text{CN (3.0 mL). The mixture was stirred at 90 °C for 12.0 h (monitored by TLC), quenched with water, extracted with dichloromethane (5×3 ml), and dried over anhydrous Na}_2\text{SO}_4. \text{The solvent was removed under reduced pressure, and the residue was purified by a shot flash silica gel column chromatography (EtOAc/petro ether = 1:9) to give compound 2a as a white solid (55.3 mg, 82%).}
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IV. Analytical data of products obtained in this study

**1-phenyl-2-selenocyanatoethanone 2a**
White solid, melting point: 48-49 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 4.95$ (s, 2H), 7.54 (t, $J = 8.0$ Hz, 2H), 7.69 (t, $J =7.6$ Hz, 1H), 7.98 (d, $J =7.2$ Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 34.8, 101.7, 128.7, 129.1, 133.8, 193.1$. HRMS (ESI-TOF) Calcd for C$_9$H$_8$NOSe, [M+H]$^+$ 225.9773; Found 225.9777.

**2-selenocyanato-1-(o-tolyl)ethanone 2b**
White solid, melting point: 101-102 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 2.57$ (s, 3H), 4.96 (s, 2H), 7.35 (q, $J = 7.6$ Hz, 2H), 7.52 (t, $J =6.8$ Hz, 1H), 7.80 (d, $J =8.0$ Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 22.0, 40.8, 101.1, 126.2, 130.4, 132.8, 134.3, 186.9$. HRMS (ESI-TOF) Calcd for C$_{10}$H$_{10}$NOSe, [M+H]$^+$ 239.9926; Found 239.9921.
2-selenocyanato-1-(m-tolyl)ethanone 2c
White solid, melting point: 43-44 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 2.44 (s, 3H), 4.93 (s, 2H), 7.42 (t, $J$ = 7.2 Hz, 2H), 7.50 (t, $J$ = 7.2 Hz, 1H), 7.76 (d, $J$ = 8.4 Hz, 1H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 21.3, 38.5, 101.8, 125.9, 129.0, 129.1, 133.8, 135.6, 139.1, 193.3. HRMS (ESI-TOF) Calcd for C$_{10}$H$_{10}$NOSe, [M+H]$^+$ 239.9926; Found 239.9923.

2-selenocyanato-1-(p-tolyl)ethanone 2d
White solid, melting point: 122-123 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 2.46 (s, 3H), 4.93 (s, 2H), 7.32 (d, $J$ = 8.0 Hz, 2H), 7.85 (d, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 21.8, 38.5, 101.9, 128.8, 129.8, 131.3, 146.1, 192.7. HRMS (ESI-TOF) Calcd for C$_{10}$H$_{10}$NOSe, [M+H]$^+$ 239.9926; Found 239.9922.

1-(2,4-dimethylphenyl)-2-selenocyanatoethanone 2e
White solid, melting point: 82-83 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 2.40 (s, 3H), 2.54 (s, 3H), 4.96 (s, 2H), 7.13 (d, $J$ = 10.4 Hz, 2H), 7.39 (d, $J$ = 8.0 Hz, 1H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 21.6, 22.2, 41.2, 102.4, 126.9, 130.1, 131.0, 133.6, 141.0, 144.9, 194.5. HRMS (ESI-TOF) Calcd for C$_{11}$H$_{12}$NOSe, [M+H]$^+$ 254.0085; Found 254.0089.

1-(3,4-dimethylphenyl)-2-selenocyanatoethanone 2f
White solid, melting point: 107-108 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 2.35 (s, 3H), 2.36 (s, 3H), 4.93 (s, 2H), 7.29 (d, $J$ = 8.0 Hz, 1H), 7.70 (d, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 19.7, 20.2, 38.6, 102.0, 126.4, 129.7, 130.3, 131.7, 137.7, 144.9, 192.9. HRMS (ESI-TOF) Calcd for C$_{11}$H$_{12}$NOSe, [M+H]$^+$ 254.0085; Found 254.0091.
1-(3-methoxyphenyl)-2-selenocyanatoethanone 2g
White solid, melting point: 85-86 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 3.87 (s, 3H), 4.92 (s, 2H), 7.20-7.23 (m, 1H), 7.42-7.46 (m, 2H), 7.52 (d, $J$ = 7.6 Hz, 1H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 38.4, 55.5, 101.9, 112.6, 121.4, 130.1, 135.0, 160.0, 193.0. HRMS (ESI-TOF) Calcd for C$_{10}$H$_{10}$NO$_2$Se, [M+H]$^+$ 255.9876; Found 259.9873.

1-(4-cyclohexylphenyl)-2-selenocyanatoethanone 2h
White solid, melting point: 102-103 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 1.26-1.49 (m, 5H), 1.71-1.89 (m, 5H), 2.60 (d, $J$ = 8.4 Hz, 1H), 4.93 (s, 2H), 7.35 (d, $J$ = 8.0 Hz, 2H), 7.87 (d, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 25.9, 26.6, 33.9, 38.7, 44.8, 102.1, 127.6, 129.0, 131.6, 155.9, 192.8. HRMS (ESI-TOF) Calcd for C$_{15}$H$_{18}$NOSe, [M+H]$^+$ 308.0554; Found 308.0559.

1-(3-chlorophenyl)-2-selenocyanatoethanone 2i
White solid, melting point: 67-68 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 4.88 (s, 2H), 7.50 (t, $J$ = 8.0 Hz, 1H), 7.67 (dd, $J_1$ = 1.2 Hz, $J_2$ = 8.0 Hz, 1H), 7.85 (d, $J$ = 8.0 Hz, 1H), 7.94 (s, 1H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 37.6, 101.2, 126.7, 128.7, 130.4, 134.7, 135.2, 135.6, 191.9. HRMS (ESI-TOF) Calcd for C$_9$H$_7$NClOSe, [M+H]$^+$ 259.9383; Found 259.9381.

1-(3-bromophenyl)-2-selenocyanatoethanone 2j
White solid, melting point: 90-91 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 4.89 (s, 2H), 7.43 (t, $J$ = 8.0 Hz, 1H), 7.79-7.89 (m, 2H), 8.09 (s, 1H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 37.7, 101.5, 123.4, 127.2, 130.7, 131.6, 135.4, 137.7, 192.0. HRMS (ESI-TOF) Calcd for C$_9$H$_7$NBrOSe, [M+H]$^+$ 303.8876; Found 303.8872.
1-(4-fluorophenyl)-2-selenocyanatoethanone 2k
White solid, melting point: 112-113 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 4.90$ (s, 2H), 7.21 (t, $J = 8.4$ Hz, 2H), 7.99-8.02 (m, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 37.9$, 101.6, 116.3, 116.6, 130.3, 131.5, 131.6, 166.7 (d, $J = 257$ Hz), 191.5. HRMS (ESI-TOF) Calcd for C$_9$H$_7$NFOSe, [M+H]$^+$ 243.9665; Found 243.9669.

1-(4-bromophenyl)-2-selenocyanatoethanone 2l
White solid, melting point: 144-145 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 4.88$ (s, 2H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.82 (d, $J = 8.4$ Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 37.3$, 101.3, 130.0, 130.4, 132.5, 192.1. HRMS (ESI-TOF) Calcd for C$_9$H$_7$NBrOSe, [M+H]$^+$ 303.8876; Found 303.8873.

1-(4-iodophenyl)-2-selenocyanatoethanone 2m
White solid, melting point: 143-144 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 4.88$ (s, 2H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.91 (d, $J = 8.8$ Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 37.7$, 101.4, 103.4, 129.8, 133.0, 138.5, 192.5. HRMS (ESI-TOF) Calcd for C$_9$H$_7$NIOSe, [M+H]$^+$ 351.8738; Found 351.8733.

1-(naphthalen-2-yl)-2-selenocyanatoethanone 2n
White solid, melting point: 118-119 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 5.07$ (s, 2H), 7.62-7.71 (m, 2H), 7.91-8.01 (m, 4H), 8.48 (s, 1H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 38.4$, 101.8, 123.3, 127.4, 127.9, 129.1, 129.5, 129.7, 131.1, 131.2, 132.3, 136.2, 193.0. HRMS (ESI-TOF) Calcd for C$_{13}$H$_{10}$NOSe, [M+H]$^+$ 275.9926; Found 275.9931.

1-phenyl-2-selenocyanatopropan-1-one 2o
White solid, melting point: 68-69 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 2.06$ (d, $J =$
7.2 Hz, 3H), 5.40 (q, J = 7.2 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.68 (t, J = 7.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 21.3, 49.0, 101.7, 128.9, 129.2, 134.6, 197.0. HRMS (ESI-TOF) Calcd for C$_{10}$H$_{10}$NOSe, [M+H]$^+$ 239.9928; Found 239.9923.

![2-selenocyanato-1-(p-tolyl)propan-1-one 2p](image)

**2-selenocyanato-1-(p-tolyl)propan-1-one 2p**
White solid, melting point: 71-72 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 2.05 (d, J = 7.2 Hz, 3H), 2.46 (s, 3H), 5.40 (q, J = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 21.5, 21.8, 49.4, 129.1, 129.9, 130.2, 145.9, 196.7. HRMS (ESI-TOF) Calcd for C$_{11}$H$_{12}$NOSe, [M+H]$^+$ 254.0084; Found 254.0081.

![1-(4-fluorophenyl)-2-selenocyanatopropan-1-one 2q](image)

**1-(4-fluorophenyl)-2-selenocyanatopropan-1-one 2q**
White solid, melting point: 67-68 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 2.06 (d, J = 7.2 Hz, 3H), 5.35 (q, J = 7.2 Hz, 1H), 7.22 (t, J = 8.4 Hz, 2H), 7.96-7.99 (m, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 21.2, 48.4, 102.3, 116.4, 116.6, 129.2, 131.7, 131.8, 166.6 (d, J = 256 Hz), 195.3. HRMS (ESI-TOF) Calcd for C$_{10}$H$_9$NFOSe, [M+H]$^+$ 257.9832; Found 257.9836.

![1-(4-chlorophenyl)-2-selenocyanatopropan-1-one 2r](image)

**1-(4-chlorophenyl)-2-selenocyanatopropan-1-one 2r**
White solid, melting point: 70-71 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 2.06 (d, J = 7.2 Hz, 3H), 5.32 (t, J = 7.2 Hz, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 21.1, 48.2, 102.2, 129.6, 130.3, 131.1, 141.3, 195.7. HRMS (ESI-TOF) Calcd for C$_{10}$H$_9$NClOSe, [M+H]$^+$ 273.9536; Found 273.9541.

![1-(4-fluorophenyl)-2-selenocyanatopropan-1-one 2s](image)

**1-(4-fluorophenyl)-2-selenocyanatopropan-1-one 2s**
White solid, melting point: 104-105 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 2.06 (t, J =
4.0 Hz, 3H), 5.30-5.36 (m, 1H), 7.81 (d, J = 8.0 Hz, 2H), 8.05 (d, J = 8.0 Hz, 2H). $^1\text{H}$ NMR (100 MHz; CDCl$_3$): $\delta$ = 14.0, 47.5, 101.6, 121.8, 124.6, 126.2 (q, $J_{\text{C-F}}$ = 4.0 Hz), 129.2, 135.5, 135.7, 135.9, 195.7. HRMS (ESI-TOF) Calcd for C$_{11}$H$_9$N$_3$FOSe, [M+H]$^+$ 307.9802; Found 307.9805.

2-selenocyanato-3,4-dihyronaphthalen-1(2H)-one 2t
White solid, melting point: 82-83 °C. $^1\text{H}$ NMR (400 MHz; CDCl$_3$): $\delta$ = 2.53-2.60 (m, 1H), 2.89-2.94 (m, 1H), 3.15-3.22 (m, 2H), 4.99-5.04 (m, 1H), 7.13-7.39 (m, 2H), 7.57-7.60 (m, 1H), 8.01 (d, J = 7.6 Hz, 1H). $^{13}\text{C}$ NMR (100 MHz; CDCl$_3$): $\delta$ = 30.3, 32.5, 53.2, 102.5, 127.3, 127.7, 129.0, 130.4, 135.0, 144.1, 194.2. HRMS (ESI-TOF) Calcd for C$_{11}$H$_{10}$NOSe, [M+H]$^+$ 251.9928; Found 251.9924.

1-(furan-2-yl)-2-selenocyanatoethanone 2u
White solid, melting point: 101-102 °C. $^1\text{H}$ NMR (400 MHz; CDCl$_3$): $\delta$ = 4.60 (s, 2H), 6.65 (dd, $J_1$ = 1.6 Hz, $J_2$ = 7.6 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.69 (s, 1H). $^{13}\text{C}$ NMR (100 MHz; CDCl$_3$): $\delta$ = 35.1, 100.9, 113.2, 119.4, 147.9, 150.3, 181.3. HRMS (ESI-TOF) Calcd for C$_7$H$_6$NOSe, [M+H]$^+$ 215.9562; Found 215.9567.

2-selenocyanato-1-(thiophen-2-yl)ethanone 2v
White solid, melting point: 100-101 °C. $^1\text{H}$ NMR (400 MHz; CDCl$_3$): $\delta$ = 4.75 (s, 2H), 7.21-7.26 (m, 1H), 7.80 (d, J = 2.4 Hz, 2H). $^{13}\text{C}$ NMR (100 MHz; CDCl$_3$): $\delta$ = 36.7, 101.8, 128.7, 134.2, 136.2, 140.2, 185.4. HRMS (ESI-TOF) Calcd for C$_7$H$_8$NSOSe, [M+H]$^+$ 231.9333; Found 231.9337.

1-(5-methylthiophen-2-yl)-2-selenocyanatoethanone 2w
White solid, melting point: 98-99 °C. $^1\text{H}$ NMR (400 MHz; CDCl$_3$): $\delta$ = 2.58 (s, 3H), 4.70 (s, 2H), 6.89 (d, J = 3.6 Hz, 1H), 7.61 (d, J = 4.0 Hz, 1H). $^{13}\text{C}$ NMR (100 MHz; CDCl$_3$): $\delta$ = 16.1, 36.5, 101.6, 127.5, 134.9, 137.9, 152.9, 184.7. HRMS (ESI-TOF) Calcd for C$_8$H$_8$NSOSe, [M+H]$^+$ 245.9492; Found 245.9489.
2-selenocyanato-1-(thiophen-3-yl)ethanone 2x
White solid, melting point: 104-105 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 4.85 (s, 2H), 7.41-7.43 (m, 1H), 7.55 (d, $J$ = 4.2 Hz, 1H), 8.18 (t, $J$ = 2.4 Hz, 1H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 37.9, 101.5, 126.7, 127.5, 134.3, 138.6, 186.9. HRMS (ESI-TOF) Calcd for C$_7$H$_6$NSOSe, [M+H]$^+$ 231.9333; Found 231.9338.

1-(benzo[b]thiophen-2-yl)-2-selenocyanatoethanone 2y
White solid, melting point: 117-118 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 4.78 (s, 2H), 7.46-7.57 (m, 2H), 7.90-7.97 (m, 2H), 8.07 (s, 1H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 36.4, 101.1, 123.0, 125.6, 126.4, 128.5, 131.6, 138.7, 139.4, 143.2, 186.9. HRMS (ESI-TOF) Calcd for C$_{11}$H$_8$NSOSe, [M+H]$^+$ 281.9493; Found 281.9496.

2-selenocyanato-1-(thiophen-2-yl)propan-1-one 2z
White solid, melting point: 97-98 °C. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ = 2.09 (d, $J$ = 7.2 Hz, 3H), 5.14 (q, $J$ = 7.2 Hz, 1H), 7.23 (t, $J$ = 4.0 Hz, 1H), 7.80 (q, $J$ = 4.0 Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 21.4, 48.2, 101.9, 128.7, 133.8, 136.1, 139.4, 189.2. HRMS (ESI-TOF) Calcd for C$_8$H$_8$NSOSe, [M+H]$^+$ 245.9492; Found 245.9494.
IV. $^1$H NMR and $^{13}$C NMR spectra copies of compounds 2

Compounds 2a
Compounds 2b
Compounds 2c
Compounds 2d
Compounds 2e
Compounds 2f
Compounds 2g
Compounds 2h
Compounds 2i
Compounds 2k

![Chemical structure of compound 2k]

![NMR spectrum of compound 2k]
Compounds 2m
Compounds 2n
Compounds 2o
Compounds 2p
Compounds 2q
Compounds 2r
Compounds 2s
Compounds 2t
Compounds 2u
Compounds 2w
Compounds 2x

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\text{\includegraphics[width=0.5\textwidth]{compound_1.png}}
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\text{\includegraphics[width=0.5\textwidth]{compound_2.png}}
\]

32
Compounds 2y
Compounds 2z

[Chemical structure images]

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