Supporting Information for

An atom-economic route to densely functionalized thiophenes via base-catalyzed rearrangement of 5-propargyl-2*H*-thiopyran-4(3*H*)-ones

Chunlin Tang^a, Jian Qin^b, Xingqi Li^{*a}

^a*Department of Chemistry, Northeast Normal University, Changchun 130024, China*

^b*Department of Chemistry and Environmental Science, Jinzhou Teachers Training College, Jinzhou 121000, China*

E-mail: lixq653@nenu.edu.cn

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II. General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. Melting points were determined in an open capillary and were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C at 500 MHz and 125 MHz, respectively, with TMS as internal standard. Mass spectra were recorded on AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on microTof by using ESI method.

III. Synthesis and analytical data for 1a-1f

General Synthetic Procedure (with the synthesis of substrate **1a** as an example):

To a solution of thiopyran-4(3*H*)-one (140 mg, 0.5 mmol) in toluene (1.0 mL) at room temperature, 1,3-diphenylprop-2-yn-1-ol (125 mg, 0.6 mmol) and FeBr_3 (30 mg, 0.10 mmol) were added in succession and the mixture stirred for 5 min at room temperature (20 °C) without exclusion of air. After the reaction was complete (monitored by TLC), the mixture was diluted with CH_2Cl_2 (10 mL) and aqueous NaCl solution (10 mL). The mixture was further stirred for an additional 30 min and the two layers separated. The aqueous layer was extracted with CH_2Cl_2 (5 mL $\times$ 3). The combined organic layers were dried over MgSO_4 , filtered, solvent removed by rotary evaporation, and the residue purified by silica gel column chromatography (petroleum ether : ethyl acetate = 12 :1) to afford the product **1a** (200 mg, 85% yield).

5-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)-6-(ethylthio)-2-phenyl-2*H*-thiop

pyran-4(3*H*)-one (1a, major isomer : minor isomer = 70 : 30)

200 mg (85% yield), Reddish brown liquid; ¹H-NMR (500 MHz, CDCl₃) δ 1.16 (t, *J* = 7.5 Hz, 3H, minor isomer), 1.26 (t, *J* = 7.5 Hz, 3H, major isomer), 2.86-3.09 (m, 3H), 3.13-3.25 (m, 1H), 4.56-4.62 (m, 1H), 6.10 (s, 1H, minor isomer), 6.12 (s, 1H, major isomer), 7.18-7.23 (m, 1H), 7.27-7.36 (m, 9H), 7.45-7.54 (m, 4H); ¹³C-NMR (CDCl₃, 125 MHz) δ 14.6, 14.7, 27.8, 27.9, 34.8, 44.2, 44.3, 44.7, 44.9, 83.3, 83.8, 88.2, 88.3, 123.52, 123.56, 126.0, 126.1, 127.0, 127.2, 127.6, 127.7, 127.8, 127.97, 127.99, 128.7, 128.8, 128.9, 131.3, 131.4, 131.6, 134.11, 134.17, 135.4, 135.5, 139.0, 139.2, 158.62, 158.65, 188.59, 188.62; **HRMS** (ESI) *m/z* calculated for C₂₈H₂₄ClO₂ [M+H]⁺: 475.0957 found 475.0949.

5-(1,3-diphenylprop-2-yn-1-yl)-6-(ethylthio)-2-(p-tolyl)-2*H*-thiopyran-4(3*H*)-one (1b, major isomer : minor isomer = 70 : 30)

230 mg (88% yield), Reddish brown liquid; ¹H-NMR (500 MHz, CDCl₃) δ 1.16 (t, *J* = 7.5 Hz, 3H, minor isomer), 1.29 (t, *J* = 7.5 Hz, 3H, major isomer), 2.37 (s, 3H), 2.86-3.13 (m, 3H), 3.18-3.31 (m, 1H), 4.59-4.65 (m, 1H), 6.15 (s, 1H, minor isomer), 6.17 (s, 1H, major isomer), 7.18-7.25 (m, 3H), 7.28-7.34 (m, 7H), 7.49-7.59 (m, 4H); ¹³C-NMR (CDCl₃, 125 MHz) δ 14.7, 14.9, 21.1, 27.9, 28.0, 34.9, 35.0, 44.8, 45.0, 45.7, 45.8, 83.3, 84.0, 88.5, 88.6, 123.8, 123.9, 126.1, 126.2, 127.3, 127.4, 127.5, 127.67, 127.69, 127.8, 127.9, 128.0, 128.1, 129.64, 129.68, 131.7, 134.13, 134.19, 138.54, 138.59, 139.4, 139.6, 159.5, 189.4, 189.5; **HRMS** (ESI) *m/z* calculated for C₂₉H₂₇OS₂ [M+H]⁺: 455.1503 found 455.1494.

5-(1,3-diphenylprop-2-yn-1-yl)-6-(ethylthio)-2-phenyl-2*H*-thiopyran-4(3*H*)-one (1c, major isomer : minor isomer = 55 : 45)

185 mg (80% yield), Reddish brown liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.32 (t, J = 7.5 Hz, 3H, minor isomer), 1.43 (t, J = 7.5 Hz, 3H, major isomer), 3.01-3.27 (m, 3H), 3.33-3.47 (m, 1H), 4.76-4.81 (m, 1H), 6.34 (s, 1H, minor isomer), 6.37 (s, 1H, major isomer), 7.37-7.42 (m, 1H), 7.46-7.53 (m, 6H), 7.54-7.58 (m, 4H), 7.68-7.78 (m, 4H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 14.8, 15.0, 28.0, 28.1, 35.0, 35.0, 44.7, 44.9, 45.9, 46.1, 83.5, 84.1, 88.6, 88.7, 123.92, 123.97, 126.2, 126.3, 127.3, 127.6, 127.82, 127.83, 127.9, 128.0, 128.22, 128.24, 128.6, 128.7, 129.0, 129.1, 131.4, 134.80, 131.85, 137.2, 137.3, 139.5, 139.6, 159.4, 189.3, 189.4; **HRMS** (ESI) m/z calculated for $\text{C}_{28}\text{H}_{24}\text{OS}_2$ $[\text{M}+\text{H}]^+$: 441.1347 found 441.1343.

2-(4-chlorophenyl)-5-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)-6-(ethylthio)-2H-thiopyran-4(3H)-one (1d, major isomer : minor isomer = 70 : 30)

190 mg (80% yield), Reddish brown liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.20 (t, J = 7.5 Hz, 3H, minor isomer), 1.28 (t, J = 7.5 Hz, 3H, major isomer), 2.89-3.26 (m, 4H), 4.56-4.62 (m, 1H), 6.06 (s, 1H, minor isomer), 6.09 (s, 1H, major isomer), 7.25-7.29 (m, 2H), 7.30-7.37 (m, 7H), 7.40-7.44 (m, 1H), 7.46-7.53 (m, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 14.7, 14.8, 28.0, 28.0, 34.6, 44.5, 44.6, 45.1, 45.2, 83.7, 84.3, 87.7, 87.8, 123.51, 123.56, 127.90, 127.94, 128.0, 128.15, 128.18, 128.7, 128.8, 128.9, 129.1, 129.2, 131.0, 131.3, 131.6, 131.9, 132.0, 134.53, 134.58, 135.5, 135.6, 137.9, 138.0, 159.2, 188.8; **HRMS** (ESI) m/z calculated for $\text{C}_{28}\text{H}_{22}\text{Cl}_2\text{OS}_2$ $[\text{M}+\text{H}]^+$: 509.0567 found 509.0563

2-(4-chlorophenyl)-6-(ethylthio)-5-(3-(4-fluorophenyl)-1-phenylprop-2-yn-1-yl)-2H-thiopyran-4(3H)-one (1e, major isomer : minor isomer = 70 : 30)

195 mg (81% yield), Reddish brown liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.17 (t, J =

7.5 Hz, 3H, minor isomer), 1.27 (t, $J=7.5$ Hz, 3H, major isomer), 2.86-3.12 (m, 3H), 3.14-3.26 (m, 1H), 4.58-4.62 (m, 1H), 6.09 (s, 1H, minor isomer), 6.11 (s, 1H, major isomer), 6.98-7.03 (m, 2H), 7.20-7.25 (m, 1H), 7.27-7.36 (m, 6H), 7.45-7.54 (m, 4H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 14.7, 14.9, 27.9, 28.1, 34.9, 44.5, 44.6, 45.0, 45.2, 82.3, 82.9, 87.9, 88.0, 115.25, 115.27, 115.42, 115.44, 119.81, 119.84, 126.2, 126.3, 127.2, 127.4, 127.8, 127.9, 128.9, 129.1, 129.2, 131.4, 131.7, 133.4, 133.5, 134.4, 134.5, 135.5, 135.6, 139.1, 139.3, 158.8, 161.1, 163.1, 188.85, 188.94; **HRMS** (ESI) m/z calculated for $\text{C}_{28}\text{H}_{22}\text{ClFOS}_2$ $[\text{M}+\text{H}]^+$: 493.0863 found 493.0859.

2-(4-chlorophenyl)-5-(1,3-diphenylprop-2-yn-1-yl)-6-(methylthio)-2*H*-thiopyran-4(3*H*)-one (1f, major isomer : minor isomer = 51 : 49)

210 mg (82% yield), Reddish brown liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 2.43 (s, 3H, minor isomer), 2.48 (s, 3H, major isomer), 3.02-3.09 (m, 1H), 3.13-3.25 (m, 1H), 4.58-4.64 (m, 1H), 6.17(s, 1H, minor isomer), 6.20 (s, 1H, major isomer), 7.22-7.27 (m, 1H), 7.31-7.39 (m, 9H), 7.49-7.59 (m, 4H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 16.3, 16.4, 34.7, 44.31, 44.39, 45.5, 45.6, 83.7, 84.3, 88.0, 88.1, 123.7, 123.8, 126.3, 126.4, 127.3, 127.5, 127.8, 128.02, 128.09, 128.21, 128.23, 128.9, 129.2, 129.3, 130.1, 130.2, 131.76, 131.79, 134.5, 134.6, 135.64, 135.69, 139.0, 139.1, 160.2, 160.3, 188.50, 188.57; **HRMS** (ESI) m/z calculated for $\text{C}_{27}\text{H}_{21}\text{ClOS}_2$ $[\text{M}+\text{H}]^+$: 461.0801 found 461.0809.

IV. Synthesis and analytical data for 2a-2f

General Synthetic Procedure (with the synthesis of **2a** as an example):

To a solution of 5-propargyl-2*H*-thiopyran-4(3*H*)-one (240 mg, 0.5 mmol) in DMSO (1.0 mL) at room temperature, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)

(0.15 mmol, 0.022 mL) was added, and the mixture was stirred for 10 min at room temperature (25 °C) without exclusion of air. After the reaction was completed (monitored by TLC), the reaction mixture was diluted by adding CH₂Cl₂ (10 mL) and aqueous NH₄Cl solution (10 mL). The mixture was stirred for additional 30 min and two layers were separated. The aqueous layer was extracted with CH₂Cl₂ (5 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and the solvent was removed by rotary evaporation, and then the residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20 : 1) to afford the product **2a** (210 mg, 90% yield) as a yellow solid.

(E)-1-(5-Benzyl-2-(ethylthio)-4-phenylthiophen-3-yl)-3-(4-chlorophenyl)prop-2-en-1-one (2a).

210 mg (90% yield), Yellow solid, mp 145-146 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 1.36 (t, *J* = 7.0 Hz, 3H), 2.96 (q, *J* = 7.5 Hz, 2H), 4.00 (s, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.20-7.30 (m, 7H), 7.35-7.40 (m, 4H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 13.84, 30.43, 34.21, 126.38, 126.64, 127.86, 128.43, 128.58, 128.70, 128.85, 129.22, 129.91, 133.50, 135.72, 136.06, 138.83, 139.00, 139.78, 140.89, 187.14; **HRMS** (ESI) *m/z* calculated for C₂₈H₂₃ClOS₂ [M+H]⁺: 475.0957 found: 475.0945.

(E)-1-(5-Benzyl-2-(ethylthio)-4-phenylthiophen-3-yl)-3-p-tolylprop-2-en-1-one (2b)

190 mg (85% yield), Yellow solid, mp 117-118 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 1.34 (t, *J* = 7.5 Hz, 3H), 2.31 (s, 3H), 2.94 (q, *J* = 7.5 Hz, 2H), 4.00 (s, 2H), 6.41 (d,

$J = 16.0$ Hz, 1H), 7.04-7.07 (m, 4H), 7.12 (d, $J = 7.5$ Hz, 2H), 7.21-7.39 (m, 8H), 7.41 (d, $J = 16.0$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 13.96, 21.40, 30.72, 34.24, 109.71, 125.25, 126.59, 127.74, 128.18, 128.44, 128.55, 128.61, 129.36, 129.83, 132.18, 125.95, 139.04, 139.24, 139.86, 140.47, 143.07, 188.27; **HRMS** (ESI) m/z calculated for $\text{C}_{29}\text{H}_{26}\text{OS}_2$ $[\text{M}+\text{H}]^+$: 455.1503 found: 455.1513.

(*E*)-1-(5-Benzyl-2-(ethylthio)-4-phenylthiophen-3-yl)-3-phenylprop-2-en-1-one (2c)

185 mg (86% yield), Yellow solid, mp 99-100 °C; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.34 (t, $J = 7.5$ Hz, 3H), 2.93 (q, $J = 7.0$ Hz, 2H), 4.00 (s, 2H), 6.45 (d, $J = 15.5$ Hz, 1H), 7.12 (s, 4H), 7.21-7.34 (m, 11H), 7.43 (d, $J = 15.5$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 13.89, 30.60, 34.18, 126.05, 126.56, 127.74, 128.09, 128.38, 128.51, 128.54, 128.60, 129.79, 129.93, 134.87, 135.90, 139.02, 139.13, 139.76, 142.78, 187.92; **HRMS** (ESI) m/z calculated for $\text{C}_{28}\text{H}_{24}\text{OS}_2$ $[\text{M}+\text{H}]^+$: 441.1347 found: 441.1334.

(*E*)-1-(5-Benzyl-4-(4-chlorophenyl)-2-(ethylthio)thiophen-3-yl)-3-(4-chlorophenyl)prop-2-en-1-one (2d)

230 mg (92% yield), Yellow solid, mp 117-118 °C; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.36 (t, $J = 7.5$ Hz, 3H), 2.95 (q, $J = 7.0$ Hz, 2H), 3.98 (s, 2H), 6.40 (d, $J = 16.0$ Hz, 1H), 7.07 (d, $J = 8.5$ Hz, 2H), 7.11 (d, $J = 7.5$ Hz, 2H), 7.21-7.31 (m, 8H), 7.31-7.41 (m, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 13.89, 30.66, 34.16, 126.36, 126.74, 128.35, 128.65, 128.85, 129.02, 129.24, 131.20, 133.28, 134.01, 134.39, 136.01, 137.70,

139.16, 139.43, 139.47, 141.48, 144.99, 187.31; **HRMS** (ESI) m/z calculated for $C_{28}H_{22}Cl_2OS_2$ $[M+H]^+$: 509.0567 found: 509.0543.

(*E*)-3-(4-Chlorophenyl)-1-(2-(ethylthio)-5-(4-fluorobenzyl)-4-phenylthiophen-3-yl)prop-2-en-1-one (2e)

235 mg (96% yield), Yellow solid, mp 121-122 °C; **1H -NMR** (500 MHz, $CDCl_3$) δ 1.37 (t, $J = 7.5$ Hz, 3H), 2.97 (q, $J = 7.5$ Hz, 2H), 3.97 (s, 2H), 6.36 (d, $J = 15.5$ Hz, 1H), 6.94-7.01 (m, 4H), 7.06 (t, $J = 7.0$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 7.27 (t, $J = 7.0$ Hz, 2H), 7.36-7.42 (m, 4H); **^{13}C -NMR** ($CDCl_3$, 125 MHz) δ 13.78, 30.37, 33.36, 115.25, 115.42, 126.23, 127.87, 128.70, 128.80, 129.17, 129.79, 129.86, 133.39, 135.36, 135.38, 135.70, 135.91, 138.49, 138.83, 138.99, 140.89, 145.75, 160.57, 162.52, 186.99; **HRMS** (ESI) m/z calculated for $C_{28}H_{22}ClFOS_2$ $[M+H]^+$: 493.0863 found: 493.0861.

(*E*)-1-(5-Benzyl-2-(methylthio)-4-phenylthiophen-3-yl)-3-(4-chlorophenyl)prop-2-en-1-one (2f)

188 mg (82% yield), Yellow solid, mp 121-122 °C; **1H -NMR** (500 MHz, $CDCl_3$) δ 2.58 (s, 3H), 3.98 (s, 2H), 6.29 (d, $J = 15.5$ Hz, 1H), 6.93 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 7.5$ Hz, 2H), 7.19-7.32 (m, 7H), 7.38-7.44 (m, 4H); **^{13}C -NMR** ($CDCl_3$, 125 MHz) δ 18.97, 34.23, 109.74, 125.99, 126.66, 127.94, 128.43, 128.61, 128.79, 128.82, 129.19, 130.03, 133.59, 135.63, 136.36, 136.78, 137.79, 139.27, 139.79, 140.41, 150.42, 186.12; **HRMS** (ESI) m/z calculated for $C_{27}H_{21}ClOS_2$ $[M+H]^+$: 461.0801 found: 461.0833.

V. Copies of ^1H - and ^{13}C -NMR Spectra for 1a-1f and 2a-2f

VI. Figure S1

Figure S1. Hydrogen bonding networks of compound **2a**

VII. Figure S2

Figure S2. Packing diagrams of compound 2a

VIII. Table S1

Table S1. Crystal data and structure refinement of compound **2a**

Formula	C ₂₈ H ₂₃ OCIS ₂
<i>Mr</i>	475.03
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	9.470(5)
<i>b</i> (Å)	9.654(5)
<i>c</i> (Å)	14.067(5)
$\alpha(^{\circ})$	80.869(5)
$\beta(^{\circ})$	80.198(5)
$\gamma(^{\circ})$	72.496(5)
<i>V</i> (Å ³)	1200.7(10)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	1.314
<i>F</i> (000)	496
<i>R</i> _{int}	0.0234
GOF on <i>F</i> ²	1.015
<i>R</i> 1 ^{<i>a</i>} [<i>I</i> >2σ(<i>I</i>)]	0.0483
<i>wR</i> 2 ^{<i>b</i>} (all data)	0.1009