Supporting Information

Copper-Catalyzed Synthesis of Thiazol-2-yl Ethers from Oxime Acetates and Xanthates under Redox-Neutral Conditions

Zhongzhi Zhu, Xiaodong Tang, Jinghe cen, Jianxiao Li, Wanqing Wu, Huanfeng Jiang*

Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

E-mail: jianghf@scut.edu.cn; Fax and Tel.: (+86) 20-87112906

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**General methods**

Melting points were measured with a melting point instrument and were uncorrected. $^1$H and $^{13}$C NMR spectra were recorded using a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. GC-MS was obtained using electron ionization. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with an infrared Fourier spectrometer. High-resolution mass spectra (ESI) were obtained with a LCMS-IT-TOF mass spectrometer.

**Screening reaction conditions**

**Table 1. Optimization of reaction conditions**

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<th>[Cu] (mol %)</th>
<th>2a (equiv)</th>
<th>T (°C)</th>
<th>solvent</th>
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Reaction conditions: All reactions were performed with 1aa (0.3 mmol), 2a, catalyst, solvent (2.0 mL) in a sealed tube for 6 h. GC-MS yield using n-dodecane as an internal standard. n. d. = not detected. Isolated yield. Under N₂ atmosphere.

Typical procedure for preparation of oxime acetates

General Procedure for oximes: To a solution of aromatic ketones (2 mmol) in the mixture of C₂H₅OH/H₂O (v/v = 1:1) was added hydroxylamine hydrochloride (2.2 mmol), NaOAc (3 mmol) in one portion, and the reaction mixture was stirred at 100 °C (when the substrates are aromatic ketones) or at room temperature (when the substrates are aromatic aldehydes) for 6-8 h. Upon completion of the reaction as indicated by TLC, the reaction mixture was diluted with water, extracted with ethyl acetate, and dried over anhydrous Na₂SO₄. The solvent was removed and concentrated under reduced pressure to give oximes.

General Procedure for oxime acetates: The mixture of ketoximes (2.0 mmol), anhydride (4.0 mmol, 2.0 equiv) was stirred in CH₂Cl₂ (10 mL) at room temperature for 24 h. Upon completion of the reaction as indicated by TLC, the reaction mixture was diluted with EtOAc (25 mL), washed with H₂O (20 mL) and aq. NaHCO₃ (10 mL). Neutralization with NaHCO₃ and dried over anhydrous Na₂SO₄ and evaporated in vacuo. The crude residue was purified by column chromatography using silica gel with hexanes as the eluent to give ketoxime acetates.

Typical procedure for the preparation of potassium xanthates 2

A mixture of alcohol (15 mmol), KOH (560 mg, 10 mmol) was stirred in 10 mL of dry diethyl
ether at room temperature for 1 h. Then carbon disulfide (12 mmol) was added and stirred at room
temperature for 1 h to afford the corresponding potassium xanthates 2 as white or yellow
precipitate. After that, the precipitate was washed and filtered with diethyl ether twice and dried
under vacuum to provide the pure compounds.

**Typical procedure for the preparation 3 and 4**

Oximes acetates 1 (0.3 mmol), potassium xanthates 2 (0.36 mmol), CuBr (13.4 mg, 0.06 mmol),
and 2 mL of dry CH₂Cl₂ were added to a 10 mL screw-capped tube (F891410 reaction tube,
purchased from beijing synthware glass). The reaction mixture was stirred at 115 °C (oil bath) for
6 h. The crude product was cooled to room temperature and filtered to obtain a filtrate. Then, the
filtrate was concentrated in vacuum to give a mixture, which was purified by flash column
chromatography to afford the target product. This operation is potentially dangerous and the
screw-capped tube must be intact.

**Characterization data for all products**

2-Ethoxy-4-phenylthiazole (3aa): as a gray oil (51.1 mg, 83% yield); Rf = 0.5 (petroleum ether);
IR (KBr): 2967, 2925, 1613, 1450, 1343, 945, 691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.87-7.85
(m, 2H), 7.43-7.39 (m, 2H), 7.36-7.28 (m, 1H), 6.85 (s, 1H), 4.57 (q, J = 7.1 Hz, 2H), 1.49 (t, J =
7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 149.2, 134.8, 128.6, 127.8, 125.9, 104.4, 67.8,
14.6; HRMS (ESI) m/z: calcd for C₁₁H₁₂NOS [M+H]⁺ 206.0634; found 206.0633.

2-Ethoxy-4-(p-tolyl)thiazole (3ab): as a yellow solid (55.8 mg, 85% yield); mp 51.3-52.3 °C; Rf
= 0.5 (petroleum ether); IR (KBr): 3114, 2961, 2925, 1650, 1525, 1230, 1018, 819, 730 cm⁻¹; ¹H
NMR (400 MHz, CDCl$_3$) δ 7.73 (d, $J = 8.2$ Hz, 2H), 7.22 (t, $J = 13.0$ Hz, 2H), 6.79 (s, 1H), 4.55 (q, $J = 7.1$ Hz, 2H), 2.38 (s, 3H), 1.48 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.9, 149.3, 137.6, 132.1, 129.3, 125.8, 103.5, 67.8, 21.3, 14.5; HRMS (ESI) m/z: calcd for C$_{12}$H$_{14}$NOS [M+H]$^+$ 220.0791; found 220.0787.

2-Ethoxy-4-(4-ethylphenyl)thiazole (3ac): as a yellow oil (53.1 mg, 76% yield); $R_f$ = 0.5 (petroleum ether); IR (KBr): 2965, 2928, 1526, 1231, 1021, 837, 745; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.73-7.71 (m, 2H), 7.24-7.19 (m, 2H), 6.77 (d, $J = 2.1$ Hz, 1H), 4.55-4.49 (m, 2H), 2.75-2.57 (m, 2H), 1.45 (td, $J = 7.1$, 2.2 Hz, 3H), 1.24 (td, $J = 7.6$, 2.3 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.9, 149.3, 144.0, 132.3, 128.1, 125.9, 103.5, 67.7, 28.7, 15.6, 14.5; HRMS (ESI) m/z: calcd for C$_{13}$H$_{16}$NOS [M+H]$^+$ 234.0947; found 234.0950.

2-Ethoxy-4-(4-methoxyphenyl)thiazole (3ad): as a yellow solid (45.8 mg, 65% yield); mp 49.1-50.0 °C; $R_f$ = 0.3 (petroleum ether); IR (KBr): 2932, 1609, 1528, 1488, 1245, 1174, 1026, 750 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.76 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.70 (s, 1H), 4.53 (q, $J = 7.1$ Hz, 2H), 3.83 (s, 3H), 1.47 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.9, 159.4, 149.0, 127.8, 127.2, 114.0, 102.4, 67.7, 55.3, 14.5; HRMS (ESI) m/z: calcd for C$_{12}$H$_{14}$NO$_2$S [M+H]$^+$ 236.0740; found 236.0738.

2-Ethoxy-4-(4-(methylthio)phenyl)thiazole (3ae): as a gray oil (46.6 mg, 62% yield); $R_f$ = 0.4 (petroleum ether); IR (KBr): 3113, 2982, 2923, 1596, 1526, 1475, 1231, 1018, 829, 741 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, $J = 8.6$ Hz, 2H), 7.26 (d, $J = 8.5$ Hz, 2H), 6.78 (s, 1H), 4.53 (d, $J = 7.1$ Hz, 2H), 2.49 (s, 3H), 1.47 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.7, 154.3, 146.4, 137.7, 129.0, 123.2, 122.6, 121.6, 114.3, 55.5, 18.5; HRMS (ESI) m/z: calcd for C$_{12}$H$_{14}$NOS$_2$ [M+H]$^+$ 252.0511; found 252.0507.
2-Ethoxy-4-(4-fluorophenyl)thiazole (3af): as a yellow solid (46.8 mg, 67% yield); mp 56.5-57.5 °C; R_f = 0.5 (petroleum ether); IR (KBr): 3112, 2981, 2823, 1679, 1525, 1473, 1229, 1018, 826, 739 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.81-7.78 (m, 2H), 7.09-7.05 (m, 2H), 6.76 (s, 1H), 4.54 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 163.7, 161.3, 148.2, 131.0, 131.0, 127.6, 127.6, 115.6, 115.4, 103.9, 67.8, 14.5; HRMS (ESI) m/z: calcd for C₁₁H₁₁FNOS [M+H]⁺ 224.0540; found 224.0537.

4-(4-Chlorophenyl)-2-ethoxythiazole (3ag): as a light yellow solid (50.9 mg, 71% yield); mp 60.5-61.5 °C; R_f = 0.6 (petroleum ether); IR (KBr): 2982, 2925, 1681, 1526, 1233, 1020, 745, 665 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 6.82 (s, 1H), 4.53 (d, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 148.0, 133.5, 133.2, 128.7, 127.1, 104.7, 67.9, 14.5; HRMS (ESI) m/z: calcd for C₁₁H₁₁ClNOS [M+H]⁺ 240.0244; found 240.0235.

4-(4-Bromophenyl)-2-ethoxythiazole (3ah): as a yellow solid (49.9 mg, 59% yield); mp 70.1-71.0 °C; R_f = 0.5 (petroleum ether); IR (KBr): 2982, 2927, 1640, 1523, 1233, 1019, 739, 664; ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 8.6 Hz, 2H), 7.58-7.42 (m, 2H), 6.82 (s, 1H), 4.53 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 148.0, 133.6, 131.7, 127.5, 121.7, 104.9, 67.9, 14.5; HRMS (ESI) m/z: calcd for C₁₁H₁₁BrNOS [M+H]⁺ 283.9739; found 283.9731.

2-Ethoxy-4-(4-iodophenyl)thiazole (3ai): as a light yellow solid (51.4 mg, 51% yield); mp 81.1-81.9 °C; R_f = 0.5 (petroleum ether); IR (KBr): 2982, 2923, 1525, 1229, 1013, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.69 (m, 2H), 7.55 (d, J = 8.6 Hz, 2H), 6.86 (s, 1H), 4.53 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 148.1, 137.7, 134.2, 131.0,
127.7, 105.0, 67.9, 14.5; HRMS (ESI) m/z: calcd for C_{11}H_{11}NOS [M+H]^+ 331.9601; found 331.9596.

2-Ethoxy-4-(4-(trifluoromethyl)phenyl)thiazole (3aj): as a white solid (61.4 mg, 75% yield); mp 148-149 °C; R_f = 0.6 (petroleum ether); IR (KBr): 2982, 2930, 1686, 1529, 1323, 1235, 1020, 820 cm^{-1}; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 7.8 Hz, 2H), 7.63 (d, J = 7.7 Hz, 2H), 6.94 (d, J = 1.7 Hz, 1H), 4.58-4.52 (m, 2H), 1.50-1.46 (t, J = 7.1 Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ 174.2, 147.7, 137.9, 129.5 (q, J = 32.1 Hz), 126.0, 125.6 (q, J = 3.6 Hz), 124.3 (q, J = 270.2 Hz), 106.4, 68.0, 14.4; HRMS (ESI) m/z: calcd for C_{11}H_{11}F_{3}NOS [M+H]^+ 274.0508; found 274.0507.

2-Ethoxy-4-(4-nitrophenyl)thiazole (3ak): as a yellow solid (56.2 mg, 75% yield); mp 143-144 °C; R_f = 0.3 (petroleum ether); IR (KBr): 3100, 2987, 1595, 1526, 1335, 1230, 852, 731 cm^{-1}; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.05 (s, 1H), 4.54 (dd, J = 13.9, 6.9 Hz, 2H), 1.46 (t, J = 7.0 Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ 174.3, 146.9, 146.8, 140.4, 126.3, 124.0, 108.4, 68.2, 14.5; HRMS (ESI) m/z: calcd for C_{11}H_{11}N_{2}O_{3}S [M+H]^+ 251.0485; found 251.0478.

2-Ethoxy-4-(o-tolyl)thiazole (3al): as a yellow oil (53.3 mg, 81% yield); R_f = 0.4 (petroleum ether); IR (KBr): 2927, 1682, 1526, 1322, 1233, 1020, 755 cm^{-1}; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, J = 4.9 Hz, 1H), 7.26-7.20 (m, 3H), 6.60 (s, 1H), 4.51 (q, J = 7.1 Hz, 2H), 2.46 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ 173.2, 136.2, 134.9, 130.9, 129.5, 127.9, 125.8, 107.5, 67.7, 21.2, 14.5; HRMS (ESI) m/z: calcd for C_{12}H_{14}NOS [M+H]^+ 220.0791; found 220.0787.

4-(2-Chlorophenyl)-2-ethoxythiazole (3am): as a yellow oil (40.1 mg, 56% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2923, 1596, 1527, 1230, 1018, 751, 694 cm^{-1}; ^1H NMR (400 MHz,
CDCl$_3$ $\delta$ 7.93-7.90 (m, 1H), 7.44-7.42 (m, 1H), 7.33-7.29 (m, 1H), 7.24-7.20 (m, 2H), 4.54 (q, $J$ = 7.1 Hz, 2H), 1.48 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.0, 145.5, 133.3, 131.8, 131.4, 130.5, 128.6, 126.8, 110.1, 67.8, 14.5; HRMS (ESI) m/z: calcd for C$_{11}$H$_{11}$ClNOS [M+H]$^+$ 240.0244; found 240.0242.

2-Ethoxy-4-($m$-tolyl)thiazole (3an): as a yellow oil (53.1 mg, 81% yield); $R_f$ = 0.5 (petroleum ether); IR (KBr) 2926, 1685, 1527, 1232, 1117, 1020, 754 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (s, 1H), 7.63 (d, $J$ = 7.8 Hz, 1H), 7.29 (t, $J$ = 7.6 Hz, 1H), 7.13 (d, $J$ = 7.5 Hz, 1H), 6.84 (s, 1H), 4.56 (q, $J$ = 7.1 Hz, 2H), 2.41 (s, 3H), 1.49 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.9, 149.3, 138.2, 134.7, 128.6, 128.5, 126.6, 123.0, 104.2, 67.8, 21.5, 14.6; HRMS (ESI) m/z: calcd for C$_{12}$H$_{14}$NOS [M+H]$^+$ 220.0791; found 220.0790.

2-Ethoxy-4-(3-fluorophenyl)thiazole (3ao): as a yellow oil (44.2 mg, 66% yield); $R_f$ = 0.6 (petroleum ether); IR (KBr) 2983, 1588, 1445, 1233, 753, 692 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61-7.53 (m, 2H), 7.38-7.28 (m, 1H), 7.01-6.97 (m, 1H), 6.86 (s, 1H), 4.55 (q, $J$ = 7.1 Hz, 2H), 1.48 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.0, 163.2 (d, $J$ = 243.3 Hz), 147.9, 136.9 (d, $J$ = 21.2 Hz), 114.5 (d, $J$ = 22.8 Hz), 105.4, 67.9, 14.5; HRMS (ESI) m/z: calcd for C$_{11}$H$_{14}$FNOS [M+H]$^+$ 224.0540; found 224.0541.

4-(3-Chlorophenyl)-2-ethoxythiazole (3ap): as a yellow oil (45.2 mg, 63% yield); $R_f$ = 0.4 (petroleum ether); IR (KBr) 3115, 2983, 1595, 1527, 1233, 1018, 725 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (t, $J$ = 1.7 Hz, 1H), 7.71-7.60 (m, 1H), 7.31-7.20 (m, 2H), 6.88-6.66 (m, 1H), 4.56-4.49 (m, 2H), 1.46 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.1, 147.7, 136.4, 134.6,
129.8, 127.7, 126.1, 123.8, 105.5, 67.9, 14.5; HRMS (ESI) m/z: calcd for C_{11}H_{11}ClNOS \([M+H]^+\), 240.0244; found 240.0246.

4-(3,4-Dimethylphenyl)-2-ethoxythiazole (3aq): as a gray oil (57.2 mg, 82% yield); \(R_f = 0.5\) (petroleum ether); IR (KBr): 3115, 2980, 1643, 1527, 1394, 1232, 737 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.66 (s, 1H), 7.60-7.58 (m, 1H), 7.18 (d, J = 7.8 Hz, 1H), 6.80 (s, 1H), 4.58 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 1.51 (t, J = 7.1 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 173.9, 149.4, 136.7, 136.3, 132.5, 129.9, 127.2, 123.4, 103.4, 67.8, 19.9, 19.6, 14.6; HRMS (ESI) m/z: calcd for C_{13}H_{16}NOS \([M+H]^+\) 234.0947; found 234.0948.

2-Ethoxy-5-methyl-4-phenylthiazole (3ar): as a yellow oil (51.9 mg, 79% yield); \(R_f = 0.5\) (petroleum ether); IR (KBr): 3405, 3030, 2923, 1646, 1598, 1218, 819 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.66-7.59 (m, 2H), 7.44-7.40 (m, 2H), 7.32 (d, J = 7.4 Hz, 1H), 4.48 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 170.1, 144.3, 135.3, 128.4, 128.3, 127.2, 119.4, 67.1, 14.5, 12.7; HRMS (ESI) m/z: calcd for C_{13}H_{14}NOS \([M+H]^+\) 220.0791; found 220.0789.

2-Ethoxy-5-ethyl-4-phenylthiazole (3as): as a yellow oil (47.5 mg, 68% yield); \(R_f = 0.4\) (petroleum ether); IR (KBr): 2971, 2930, 1530, 1233, 1020, 850, 696 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.62-7.57 (m, 2H), 7.43-7.40 (m, 2H), 7.33 (d, J = 7.4 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 2.86 (q, J = 7.5 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.5 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 170.5, 143.6, 135.4, 128.5, 128.3, 127.8, 127.3, 76.8, 20.9, 16.6, 14.6; HRMS (ESI) m/z: calcd for C_{13}H_{16}NOS \([M+H]^+\) 234.0947; found 234.0949.

2-Ethoxy-4,5-diphenylthiazole (3at): as a light yellow solid (51.3 mg, 61% yield); mp 96-97 °C; \(R_f = 0.4\) (petroleum ether); IR (KBr): 2928, 1599, 1524, 1240, 1018, 837, 753 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.66-7.59 (m, 2H), 7.43-7.40 (m, 2H), 7.33 (d, J = 7.4 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 2.86 (q, J = 7.5 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.5 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 170.5, 143.6, 135.4, 128.5, 128.3, 127.8, 127.3, 67.1, 20.9, 16.6, 14.6; HRMS (ESI) m/z: calcd for C_{13}H_{16}NOS \([M+H]^+\) 234.0947; found 234.0949.
2-Ethoxy-4,5-dihydronaphtho[1,2-d]thiazole (3au): as a gray oil (58.2 mg, 84% yield); $R_f = 0.35$ (petroleum ether); IR (KBr): 3397, 2927, 1643, 1505, 1327, 1031, 831, 754 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 7.6$ Hz, 1H), 7.26-7.19 (m, 1H), 7.16-7.07 (m, 2H), 4.49 (q, $J = 7.1$ Hz, 2H), 3.00 (t, $J = 7.9$ Hz, 2H), 2.87-2.79 (m, 2H), 1.44 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.4, 143.4, 134.3, 131.6, 127.7, 127.0, 126.8, 122.9, 121.4, 67.5, 28.9, 21.8, 14.6; HRMS (ESI) m/z: calcd for C$_{13}$H$_{14}$NOS [M+H]$^+$ 232.0791; found 232.0789.

2-Ethoxy-4-(furan-2-yl)thiazole (3av): as a white oil (44.5 mg, 76% yield); $R_f = 0.4$ (petroleum ether); IR (KBr): 2925, 1686, 1523, 1239, 1016, 752, 492 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40-7.39 (m, 1H), 6.79 (s, 1H), 6.67 (d, $J = 3.1$ Hz, 1H), 6.44-6.43 (m, 1H), 4.50 (q, $J = 7.1$ Hz, 2H), 1.45 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.4, 150.4, 141.9, 140.9, 111.4, 106.7, 103.8, 68.0, 14.5; HRMS (ESI) m/z: calcd for C$_9$H$_9$NNaO$_2$S [M+Na]$^+$ 218.0246; found 218.0242.

2-Ethoxy-4-(thiophen-2-yl)thiazole (3aw): as a gray oil (46.2 mg, 73% yield); $R_f = 0.4$ (petroleum ether); IR (KBr): 3016, 2981, 1522, 1233, 1018, 705 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J = 3.5$ Hz, 1H), 7.23 (d, $J = 5.0$ Hz, 1H), 7.08-6.96 (m, 1H), 6.71 (s, 1H), 4.53 (q, $J = 7.1$ Hz, 2H), 1.46 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.0, 143.8, 138.9, 127.6, 124.8, 123.7, 103.2, 68.0, 14.5; HRMS (ESI) m/z: calcd for C$_9$H$_9$NNaOS$_2$ [M+Na]$^+$ 234.0018; found 234.0020.
2-Ethoxy-4-(thiophen-3-yl)thiazole (3ax): as a light gray oil (45.5 mg, 72% yield); \( R_f = 0.4 \) (petroleum ether); IR (KBr): 3108, 2926, 1522, 1233, 1017, 789, 706 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.67-7.66 (m, 1H), 7.39-7.38 (m, 1H), 7.32-7.30 (m, 1H), 6.68 (s, 1H), 4.53 (q, \( J = 7.1 \) Hz, 2H), 1.47 (t, \( J = 7.1 \) Hz, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 174.0, 145.3, 136.9, 126.1, 125.4, 121.8, 104.0, 67.8, 14.5; HRMS (ESI) m/z: calcd for C\(_9\)H\(_9\)NNaOS\(_2^+\) [M+Na\(^+\)] 234.0018; found 234.0020.

2-Ethoxy-4-(pyridin-2-yl)thiazole (3ay): as a blue oil (33.4 mg, 54% yield); \( R_f = 0.3 \) (petroleum ether); IR (KBr): 2926, 1528, 1229, 1020, 746, 677 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.63-8.47 (m, 1H), 7.96 (d, \( J = 7.9 \) Hz, 1H), 7.72-7.68 (m, 1H), 7.47 (s, 1H), 7.17-7.14 (m, 1H), 4.53 (q, \( J = 7.1 \) Hz, 2H), 1.45 (t, \( J = 7.1 \) Hz, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 174.1, 152.6, 149.3, 148.8, 136.9, 122.4, 120.9, 108.9, 67.8, 14.5; HRMS (ESI) m/z: calcd for C\(_{10}\)H\(_{10}\)N\(_2^+\)NaOS [M+Na\(^+\)] 229.0406; found 229.0411.

4-(Benzo[b]thiophen-2-yl)-2-ethoxythiazole (3az): as a yellow solid (50.8 mg, 65% yield); mp 87.0-88.0 °C; \( R_f = 0.4 \) (petroleum ether); IR (KBr): 3058, 2982, 1525, 1465, 1234, 1019, 717 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.83 (d, \( J = 7.7 \) Hz, 1H), 7.80-7.71 (m, 1H), 7.64 (s, 1H), 7.40-7.29 (m, 2H), 4.58 (q, \( J = 7.1 \) Hz, 2H), 1.50 (t, \( J = 7.1 \) Hz, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 174.1, 143.9, 140.4, 139.5, 138.5, 124.6, 123.8, 122.3, 120.4, 105.7, 68.1; HRMS (ESI) m/z: calcd for C\(_{13}\)H\(_{11}\)NNaOS\(_2^+\) [M+Na\(^+\)] 284.0174; found 284.0170.

2-Ethoxy-4-(naphthalen-2-yl)thiazole (3ba): as a yellow solid (49.2 mg, 64% yield); mp 95.0-96.0 °C; \( R_f = 0.35 \) (petroleum ether); IR (KBr): 3054, 2982, 1599, 1527, 1233, 1018, 748, 472 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.98-7.91 (m, 2H), 7.87 (d, \( J = 8.7 \) Hz, 2H), 7.56-7.51 (m, 2H), 6.94 (s, 1H), 4.63 (q, \( J = 7.1 \) Hz, 2H), 1.54 (t, \( J = 7.1 \) Hz, 3H); \(^1^3\)C NMR (100 MHz,
CDCl$_3$ $\delta$ 174.1, 149.2, 133.8, 133.1, 132.1, 128.5, 128.3, 127.8, 126.4, 126.1, 125.1, 123.9, 105.0, 68.0, 14.7; HRMS (ESI) m/z: calcd for C$_{13}$H$_{13}$NNaOS [M+Na]$^+$ 278.0610; found 278.0612.

2-Ethoxy-4-ethyl-5-methylthiazole (3bb) as a gray oil (32.3 mg, 63% yield); $R_f = 0.5$ (petroleum ether); IR (KBr): 2923, 2854, 1595, 1455, 1259, 1023, 753, 696 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.35 (q, $J = 7.1$ Hz, 2H), 2.49 (q, $J = 7.5$ Hz, 2H), 2.20 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H), 1.17 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.5, 147.2, 116.3, 66.8, 22.2, 14.5, 13.8, 10.9; HRMS (ESI) m/z: calcd for C$_8$H$_{13}$NNaOS [M+Na]$^+$, 194.0610; found 194.0609.

2-Ethoxy-5-ethyl-4-propylthiazole (3bc): as a light gray oil (40.7 mg, 68% yield); $R_f = 0.5$ (petroleum ether); IR (KBr): 2924, 1724, 1594, 1522, 1232, 1021, 705 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.27 (q, $J = 7.1$ Hz, 2H), 2.54 (q, $J = 7.5$ Hz, 2H), 2.36 (t, $J = 7.5$ Hz, 2H), 1.55 (dd, $J = 14.9, 7.4$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H), 1.11 (t, $J = 7.5$ Hz, 3H), 0.84 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.6, 144.9, 125.2, 66.9, 31.0, 22.8, 19.7, 16.6, 14.5, 13.8; HRMS (ESI) m/z: calcd for C$_{10}$H$_{18}$NOS [M+H]$^+$, 200.1104; found 200.1101.

4-butyl-2-ethoxy-5-propylthiazole (3bd): as a gray oil (49.0 mg, 72% yield); $R_f = 0.45$ (petroleum ether); IR (KBr): 2926, 1808, 1594, 1452, 1021, 753, 488 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.38-4.21 (m, 2H), 2.53 (t, $J = 7.4$ Hz, 2H), 2.47-2.38 (m, 2H), 1.61-1.50 (m, 4H), 1.39-1.29 (m, 5H), 0.95-0.88 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.7, 145.7, 123.1, 66.8, 31.7, 28.8, 28.2, 25.1, 22.4, 14.5, 13.9, 13.6; HRMS (ESI) m/z: calcd for C$_{11}$H$_{22}$NOS [M+H]$^+$, 228.1417; found 228.1420.

2-Ethoxy-4,5,6,7-tetrahydrobenzo[d]thiazole (3be): as a yellow oil (44.3 mg, 81% yield); $R_f = 0.4$ (petroleum ether); IR (KBr): 3780, 2928, 2857, 1721, 1669, 1447, 1263, 751, 694 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.38 (q, $J = 7.1$ Hz, 2H), 2.70-2.51 (m, 4H), 1.81 (dd, $J = 4.0, 2.1$ Hz,
4H), 1.40 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 171.9, 143.6, 119.8, 67.0, 26.6, 23.3, 23.2, 23.0, 14.5; HRMS (ESI) m/z: calcd for C8H12NNaOS [M+Na]+ 206.0610; found 206.0620.

2-Ethoxy-5,6,7,8-tetrahydro-4H-cycloheptad(thiazole (3bf): as a gray oil (44.7 mg, 76% yield); Rf = 0.4 (petroleum ether); IR (KBr): 2923, 2847, 1520, 1442, 1235, 1023, 854 cm\(^{-1}\); 1H NMR (400 MHz, CDCl3) δ 4.30 (q, J = 7.1 Hz, 2H), 2.74-2.65 (m, 2H), 2.63-2.49 (m, 2H), 1.75 (d, J = 5.2 Hz, 2H), 1.70-1.59 (m, 4H), 1.35 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 169.2, 148.2, 122.9, 66.7, 31.9, 31.3, 28.1, 26.6, 26.2, 14.5; HRMS (ESI) m/z: calcd for C10H12NNaOS [M+Na]+, 220.0767; found 220.0766.

2-Ethoxy-4,5,6,7,8,9-hexahydrocyclooctad(thiazole (3bg): as a yellow oil (49.3 mg, 78% yield); Rf = 0.35 (petroleum ether); IR (KBr): 2924, 2851, 1714, 1518, 1233, 1023, 753 cm\(^{-1}\); 1H NMR (400 MHz, CDCl3) δ 4.37 (q, J = 7.1 Hz, 2H), 2.71-2.67 (m, 4H), 1.65-1.68 (m, 4H), 1.46-1.43 (m, 4H), 1.37 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 170.6, 146.4, 121.6, 66.9, 31.2, 29.5, 28.1, 26.1, 25.5, 24.4, 14.5; HRMS (ESI) m/z: calcd for C11H17NOS [M+H]+ 212.1104; found 212.1102.

2-Ethoxy-6,7-dihydrobenzod(thiazole (3bh): as a yellow oil (28.7 mg, 53% yield); Rf = 0.55 (petroleum ether); IR (KBr): 2930, 1667, 1526, 1446, 1233, 1021, 861 cm\(^{-1}\); 1H NMR (400 MHz, CDCl3) δ 6.39 (d, J = 9.8 Hz, 1H), 5.92-5.73 (m, 1H), 4.44-4.32 (m, 2H), 2.75 (t, J = 9.4 Hz, 2H), 2.41 (td, J = 9.6, 4.2 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 172.2, 143.0, 125.6, 122.7, 118.8, 67.3, 23.5, 21.2, 14.5; HRMS (ESI) m/z: calcd for C9H12NOS [M+H]+, 182.0634; found 182.0631.

(E)-2-Ethoxy-4-styrylthiazole (3bi): as a yellow oil (29.1 mg, 42% yield); Rf = 0.5 (petroleum ether); IR (KBr): 2927, 2857, 1667, 1530, 1228, 961, 692 cm\(^{-1}\); 1H NMR (400 MHz, CDCl3) δ
7.49 (d, J = 7.3 Hz, 2H), 7.38-7.33 (m, 2H), 7.31 (d, J = 4.8 Hz, 1H), 7.25 (t, J = 3.0 Hz, 1H), 6.87 (d, J = 15.8 Hz, 1H), 6.53 (s, 1H), 4.53 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 173.9, 148.5, 137.2, 130.7, 128.6, 127.6, 126.6, 121.8, 107.9, 67.8, 14.5; HRMS (ESI) m/z: calcd for C\(_{13}\)H\(_{14}\)NOS[M+H]\(^+\), 232.0791; found 232.0788.

**2-Ethoxy-4-ethyl-5-methylthiazole (3bj):** as a yellow oil (26.2 mg, 51% yield); \(R_f = 0.5\) (petroleum ether); IR (KBr): 2926, 2857, 1670, 1595, 1507, 1460, 1238, 1018, 754 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.33 (d, J = 7.1 Hz, 2H), 2.57 (q, J = 7.5 Hz, 2H), 2.12 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.5 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.6, 140.1, 124.9, 66.8, 19.8, 16.1, 14.7, 14.5; HRMS (ESI) m/z: calcd for C\(_8\)H\(_{14}\)NOS [M+H]\(^+\), 172.0791; found 172.0793.

**2-Ethoxy-4-isopropyl-5-methylthiazole (3bk):** as a yellow oil (35.0 mg, 63% yield); \(R_f = 0.5\) (petroleum ether); IR (KBr): 2974, 2928, 1722, 1529, 1229, 1019, 753, 694 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.33 (q, J = 7.1 Hz, 2H), 3.11-3.00 (m, 1H), 2.14 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H), 1.19 (s, 3H), 1.18 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.6, 138.9, 131.0, 66.8, 27.2, 24.7, 14.9, 14.5; HRMS (ESI) m/z: calcd for C\(_9\)H\(_{15}\)NNaOS [M+Na]\(^+\), 208.0767; found 208.0765.

**4-Butyl-2-ethoxy-5-methylthiazole (3bl):** as a yellow oil (36.5 mg, 61% yield); \(R_f = 0.6\) (petroleum ether); IR (KBr): 2924, 2856, 1719, 1671, 1596, 1456, 1262, 754 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.36 (q, J = 7.1 Hz, 2H), 2.57 (t, J = 7.5 Hz, 2H), 2.15 (s, 3H), 1.51 (dd, J = 15.1, 7.6 Hz, 2H), 1.41-1.29 (m, 5H), 0.92 (t, J = 7.3 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.7, 140.6, 123.3, 66.8, 33.7, 26.0, 22.1, 14.8, 14.5, 13.8; HRMS (ESI) m/z: calcd for C\(_{10}\)H\(_{18}\)NOS [M+H]\(^+\), 200.1104; found 200.1103.

**2-Ethoxy-4-hexyl-5-methylthiazole (3bm):** as a yellow oil (46.3 mg, 68% yield); \(R_f = 0.55\) (petroleum ether); IR (KBr): 2982, 2923, 1521, 1383, 1232, 1021, 698 cm\(^{-1}\); \(^1\)H NMR (400 MHz,
CDCl$_3$ $\delta$ 4.35 (q, $J = 7.1$ Hz, 2H), 2.55 (t, $J = 7.5$ Hz, 2H), 2.14 (s, 3H), 1.57-1.46 (m, 2H), 1.39 (t, $J = 7.1$ Hz, 3H), 1.32-1.25 (m, 6H), 0.88 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.7, 140.6, 123.4, 66.8, 31.5, 31.5, 28.6, 26.3, 22.6, 14.8, 14.5, 14.0; HRMS (ESI) m/z: calcd for C$_{12}$H$_{22}$NOS [M+H]$^+$, 228.1417; found 228.1420.

4-Benzyl-2-ethoxy-5-methylthiazole (3bn): as a yellow oil (51.0 mg, 73% yield); $R_f$ = 0.5 (petroleum ether); IR (KBr): 2982, 2924, 1521, 1383, 1232, 1021, 869, 752, 698 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (t, $J = 7.3$ Hz, 2H), 7.24-7.21 (m, 2H), 4.39 (q, $J = 7.1$ Hz, 2H), 3.95 (s, 2H), 2.26 (s, 3H), 1.42 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.6, 141.8, 140.0, 128.6, 128.2, 126.6, 121.6, 67.0, 32.3, 15.0, 14.5; HRMS (ESI) m/z: calcd for C$_{13}$H$_{15}$NNaOS [M+Na]$^+$, 256.0767; found 256.0768.

2-Ethoxy-4-ethyl-5-pentylthiazole (3bo): as a yellow oil (27.9 mg, 41% yield); $R_f$ = 0.45 (petroleum ether); IR (KBr): 2925, 2857, 1526, 1459, 1399, 1235, 1023, 802 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.35 (q, $J = 7.1$ Hz, 2H), 2.60-2.52 (m, 2H), 2.48 (q, $J = 7.5$ Hz, 2H), 1.57-1.48 (m, 2H), 1.39 (t, $J = 7.1$ Hz, 3H), 1.35-1.28 (m, 4H), 1.16 (t, $J = 7.5$ Hz, 3H), 0.92-0.84 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.9, 146.8, 122.9, 66.9, 31.6, 31.2, 26.1, 22.4, 14.5, 14.2, 14.0; HRMS (ESI) m/z: calcd for C$_{11}$H$_{22}$NOS [M+H]$^+$, 228.1414; found 228.1414.

2-Ethoxy-5-hexyl-4-methylthiazole (3bo'): as a yellow oil (14.5 mg, 22% yield); $R_f$ = 4.5 (petroleum ether); IR (KBr): 2924, 2856, 1526, 1458, 1235, 1023, 757 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.32 (q, $J = 7.1$ Hz, 2H), 2.43 (t, $J = 7.5$ Hz, 2H), 2.17 (s, 3H), 1.58-1.53 (m, 2H), 1.36 (t, $J = 7.1$ Hz, 3H), 1.31-1.23 (m, 6H), 0.86 (t, $J = 6.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.4, 146.1, 116.7, 66.8, 31.7, 29.3, 28.9, 28.9, 22.6, 14.4, 14.0, 11.0; HRMS (ESI) m/z: calcd for C$_{11}$H$_{22}$NOS [M+H]$^+$, 228.1417; found 228.1414.
(E)-2-ethoxy-4-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)vinyl)thiazole (3ap): as a yellow oil (55.6 mg, 67% yield); R_f = 0.4 (petroleum ether); IR (KBr): 2924, 1668, 1526, 1446, 1233, 1021, 861 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.91 (d, J = 15.9 Hz, 1H), 6.44-6.24 (m, 1H), 6.17 (t, J = 15.5 Hz, 1H), 4.48 (q, J = 7.1 Hz, 2H), 2.03 (t, J = 6.0 Hz, 2H), 1.76 (s, 3H), 1.65-1.60 (m, 2H), 1.49 (d, J = 6.1 Hz, 2H), 1.43 (d, J = 7.0 Hz, 3H), 1.06 (d, J = 7.9 Hz, 6H); ¹³C NMR (100MHz, CDCl₃) δ 173.7, 149.1, 137.4, 129.9, 129.7, 125.9, 105.7, 67.7, 39.7, 34.2, 33.1, 28.9, 21.7, 19.3, 14.5; HRMS (ESI) m/z: calcd for C₁₆H₂₄NOS [M+H]^+ 278.1573; found 278.1574.

2-Ethoxy-5,7,7-trimethyl-6,7-dihydrobenzo[de]thiazole (3bq): as a yellow oil (52.2 mg, 78% yield); R_f = 0.5 (petroleum ether: ethyl acetate = 50: 1); IR (KBr): 2959, 2865, 1665, 1522, 1232, 1022, 705, 702, cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.17 (d, J = 1.4 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 2.17 (s, 2H), 1.86 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H), 1.19 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 172.2, 142.7, 134.9, 127.9, 116.9, 67.1, 45.2, 33.5, 29.2, 23.4, 14.5; HRMS (ESI) m/z: calcd for C₁₂H₁₇NOS [M + H]^+ 224.1104, found 224.1105.

2-Ethoxy-4-phenyl-4H-chromeno[4,3-de]thiazole (3br): as a yellow oil (75.1 mg, 81%); R_f = 0.3 (petroleum ether: ethyl acetate = 50: 1); IR (KBr): 3062, 2978, 1742, 1693, 1525, 1462, 1221, 752 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.71-7.66 (m, 1H), 7.45 (dd, J = 7.4, 1.7 Hz, 2H), 7.39-7.32 (m, 3H), 7.16-7.10 (m, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.40 (s, 1H), 4.50 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.9, 152.9, 140.6, 140.2, 129.1, 129.0, 128.8, 127.2, 123.1, 121.9, 119.9, 118.2, 116.5, 77.0, 62.6, 14.5; HRMS (ESI) m/z: calcd for C₁₈H₁₆NO₂S [M + H]^+ 310.0896, found 310.0894.

(7R,8aS,9S)-2-Ethoxy-8a,9-dimethyl-7-(prop-1-en-2-yl)-5,6,7,8,8a,9-hexahydronaphtho[2,3-de]thiazole (3bs): as a yellow oil (47.1 mg, 52%); R_f = 0.3 (petroleum ether: ethyl acetate = 20: 1);
Specific rotation \([\alpha]_D^{22}\) +133.9 deg (0.1, CH\(_2\)Cl\(_2\)); IR (KBr): 2967, 2929, 1644, 1518, 1218, 1019, 884 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.09 (s, 1H), 4.72 (s, 2H), 4.38 (q, \(J = 7.2\) Hz, 2H), 2.88 (q, \(J = 7.1\) Hz, 2H), 2.39-2.36 (m, 2H), 2.20-2.14 (m, 1H), 1.94 (d, \(J = 12.8\) Hz, 1H), 1.85-1.79 (m, 1H), 1.74 (s, 3H), 1.39 (t, \(J = 7.1\) Hz, 3H), 1.34-1.29 (m, 1H), 1.24 (s, 1H), 1.20 (d, \(J = 7.1\) Hz, 3H), 0.88 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 172.4, 149.9, 145.0, 142.2, 123.6, 116.4, 108.8, 67.1, 45.2, 41.3, 41.2, 40.5, 31.7, 31.3, 20.9, 15.3, 14.5, 13.6; HRMS (ESI) m/z: calcd for C\(_{18}\)H\(_{26}\)NOS [M +H]\(^+\) 304.1730, found 304.1728.

1-((3S,10aR,12aS)-8-ethoxy-10a,12a-dimethyl-2,3,3a,3b,4,5,10,10a,10b,11,12,12a-dodecahydro-1H-cyclopenta[7,8]phenanthro[2,3-d]thiazol-1-yl)ethan-1-one (3bt): as a yellow oil (74.1 mg, 62%); \(R_f\) = 0.3 (petroleum ether: ethyl acetate = 20: 1); Specific rotation \([\alpha]_D^{22}\) +189.6 deg (0.1, CH\(_2\)Cl\(_2\)); IR (KBr): 2931, 2903, 1701, 1519, 1229, 1020, 586 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.02 (s, 1H), 4.37 (q, \(J = 7.0\) Hz, 2H), 2.72 (d, \(J = 16.1\) Hz, 1H), 2.62-2.47 (m, 2H), 2.36-2.24 (m, 2H), 2.19-2.14 (m, 1H), 2.09 (s, 3H), 2.03 (d, \(J = 12.0\) Hz, 1H), 1.73 (d, \(J = 9.7\) Hz, 2H), 1.68-1.62 (m, 1H), 1.55-1.45 (m, 2H), 1.42 (d, \(J = 9.8\) Hz, 2H), 1.37 (t, \(J = 7.0\) Hz, 3H), 1.26-1.22 (m, 2H), 1.18-1.10 (m, 2H), 1.00 (s, 3H), 0.63 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 209.4, 172.2, 145.5, 142.3, 115.8, 115.5, 67.2, 63.7, 56.2, 54.3, 44.0, 40.1, 38.9, 36.5, 36.4, 31.4, 31.4, 24.5, 22.9, 21.6, 18.1, 14.5, 13.3; HRMS (ESI) m/z: calcd for C\(_{24}\)H\(_{33}\)NO\(_2\)S [M +H]\(^+\) 400.2305, found 400.2311.

2-Methoxy-4-phenylthiazole (3bu): as a yellow oil (47.6 mg, 83% yield); \(R_f\) = 0.5 (petroleum ether); IR (KBr): 3472, 2930, 1531, 1420, 1237, 1065, 979, 714 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90-7.78 (m, 2H), 7.41 (t, \(J = 7.6\) Hz, 2H), 7.32 (d, \(J = 7.4\) Hz, 1H), 6.87 (s, 1H), 4.16 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.6, 149.2, 134.7, 128.6, 127.9, 125.9, 104.7, 58.5; HRMS (ESI)
m/z: calcd for C_{10}H_{10}NOS [M+H]^+, 192.0478; found 192.0475.

**4-phenyl-2-propoxythiazole (3bv)**: as a yellow oil (49.3 mg, 75% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2966, 1599, 1473, 1229, 713 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.95-7.73 (m, 2H), 7.42-7.38 (m, 2H), 7.32-7.28 (m, 1H), 6.85 (s, 1H), 4.46 (t, \(J = 6.6\) Hz, 2H), 1.96-1.76 (m, 2H), 1.07 (t, \(J = 7.4\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.2, 149.2, 134.7, 128.6, 127.8, 125.9, 104.3, 73.5, 22.3, 10.4; HRMS (ESI) m/z: calcd for C_{12}H_{12}NNaOS [M+Na]^+, 242.0610; found 242.0611.

**2-Butoxy-4-phenylthiazole (3bw)**: as a yellow oil (43.3 mg, 62% yield); R_f = 0.45 (petroleum ether); IR (KBr): 2956, 1597, 1527, 1471, 1228, 711 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93-7.76 (m, 2H), 7.39 (t, \(J = 7.6\) Hz, 2H), 7.30 (s, 1H), 6.85 (s, 1H), 4.49 (t, \(J = 6.6\) Hz, 2H), 1.95-1.74 (m, 2H), 1.51 (dd, \(J = 15.0, 7.5\) Hz, 2H), 1.00 (t, \(J = 7.4\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.2, 149.2, 134.7, 128.6, 127.8, 125.9, 104.3, 71.8, 31.0, 19.1, 13.8; HRMS (ESI) m/z: calcd for C_{13}H_{15}NNaOS [M+Na]^+, 256.0767; found 256.0764.

**2-Isopropoxy-4-phenylthiazole (3bx)**: as a yellow oil (34.2 mg, 52% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2960, 2872, 1595, 1495, 819, 759 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91-7.77 (m, 2H), 7.40 (t, \(J = 7.5\) Hz, 2H), 7.30 (t, \(J = 7.3\) Hz, 1H), 6.84 (s, 1H), 5.30 (dt, \(J = 12.4, 6.2\) Hz, 1H), 1.47 (d, \(J = 6.2\) Hz, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 173.5, 149.1, 134.8, 128.6, 127.8, 125.9, 104.1, 75.7, 21.9; HRMS (ESI) m/z: calcd for C_{12}H_{13}NNaOS [M + Na]^+, 242.0610, found 242.0606.

**2-(Cyclohexyloxy)-4-phenylthiazole (3by)**: as a blue oil (43.5 mg, 56% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2935, 2857, 1601, 1520, 1447, 1227, 1010, 713 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.81 (d, \(J = 7.7\) Hz, 2H), 7.37 (t, \(J = 7.5\) Hz, 2H), 7.28 (d, \(J = 7.2\) Hz, 1H), 6.81 (s,
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92-7.75 (m, 2H), 7.40 (t, $J$ = 7.5 Hz, 2H), 7.32 (d, $J$ = 7.3 Hz, 1H), 6.86 (s, 1H), 4.87 (d, $J$ = 14.2 Hz, 2H), 4.63 (t, $J$ = 6.8 Hz, 2H), 2.58 (t, $J$ = 6.8 Hz, 2H), 1.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.9, 150.3, 118.9, 66.4, 63.2, 30.4, 23.0, 19.1, 14.4; HRMS (ESI) m/z: calcd for C$_{10}$H$_{18}$NOS [M+H]$^+$ 200.1104; found 200.1103.

4-Cyclohexylidene-2-ethoxy-1-thia-3-azaspiro[4.5]dec-2-ene (4b): as a yellow oil (51.1 mg, 61% yield); $R_f$ = 0.45 (petroleum ether); IR (KBr): 2928, 2854, 1709, 1599, 1447, 1259, 1066, 754 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.33 (q, $J$ = 7.1 Hz, 2H), 2.52 (d, $J$ = 5.3 Hz, 2H), 2.36 (s, 2H), 2.15-2.11 (m, 2H), 1.82-1.75 (m, 3H), 1.72-1.69 (m, 1H), 1.58-1.56 (m, 6H), 1.44-1.40 (m, 2H), 1.33 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.7, 147.9, 127.9, 72.7, 66.3, 38.6, 33.1, 30.6, 28.5, 28.1, 26.9, 25.5, 25.1, 14.5; HRMS (ESI) m/z: calcd for C$_{16}$H$_{26}$NOS [M+H]$^+$, 280.1730; found 280.1712.

(E)-S-(Ethoxycarbonothioyl)-N-(1-phenylethylidene)thiohydroxylamine (5a): as a yellow oil
(37.2 mg, 52% yield); \( R_f = 0.3 \) (petroleum ether: ethyl acetate = 20: 1); IR (KBr): 2923, 1767, 1521, 1462, 1376, 1199, 928, 761 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.91-7.83 (m, 2H), 7.45-7.38 (m, 3H), 4.84 (q, \( J = 7.1 \) Hz, 2H), 2.42 (s, 3H), 1.55 (t, \( J = 7.1 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 210.7, 162.7, 138.7, 130.4, 128.5, 126.8, 69.8, 20.5, 13.8; HRMS (ESI) m/z: calcd for C\(_{11}\)H\(_{13}\)NNaOS\(_2\) [M+Na\(^+\)], 262.0331; found 262.0329.

\( (E)\)-S-(ethoxycarbonothioyl)-N-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)thiohydroxylamine (5b): as a white oil (68.4 mg, 78% yield); \( R_f = 0.4 \) (petroleum ether: ethyl acetate = 20: 1); IR (KBr): 2932, 2865, 1769, 1523, 1464, 1376, 1227, 1027, 694 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 4.60-4.47 (m, 2H), 2.71-2.61 (m, 1H), 2.01-1.97 (m, 2H), 1.90-1.85 (m, 1H), 1.79-1.67 (m, 1H), 1.56-1.50 (m, 1H), 1.40 (t, \( J = 7.2 \) Hz, 3H), 1.34-1.29 (m, 1H), 0.99 (d, \( J = 6.0 \) Hz, 3H), 0.96 (s, 3H), 0.86 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 205.2, 185.8, 68.1, 54.4, 48.1, 43.6, 34.9, 31.3, 27.0, 19.5, 19.0, 13.8, 10.6; HRMS (ESI) m/z: calcd for C\(_{13}\)H\(_{21}\)NOS\(_2\) [M+H\(^+\)]\(^+\) 294.0957, found 294.0961.
NMR Spectra for all the compounds

$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-phenylthiazole (3aa)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(p-tolyl)thiazole (3ab)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(4-ethylphenyl)thiazole (3ac)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(4-methoxyphenyl)thiazole (3ad)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(4-(methylthio)phenyl)thiazole (3ae)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(4-fluorophenyl)thiazole (3af)
$^1$H NMR and $^{13}$C NMR of 4-(4-chlorophenyl)-2-ethoxythiazole (3ag)
$^1$H NMR and $^{13}$C NMR of 4-(4-bromophenyl)-2-ethoxythiazole (3ah)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(4-iodophenyl)thiazole (3ai)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(4-(trifluoromethyl)phenyl)thiazole (3aj)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(4-nitrophenyl)thiazole (3ak)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(o-tolyl)thiazole (3a)

![NMR Spectra](image-url)
$^1$H NMR and $^{13}$C NMR of 4-(2-chlorophenyl)-2-ethoxythiazole (3am)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-($m$-tolyl)thiazole (3an)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(3-fluorophenyl)thiazole (3ao)
$^{1}H$ NMR and $^{13}C$ NMR of 4-(3-chlorophenyl)-2-ethoxythiazole (3ap)
$^1$H NMR and $^{13}$C NMR of 4-(3,4-dimethylphenyl)-2-ethoxythiazole (3aq)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-5-methyl-4-phenylthiazole (3ar)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-5-ethyl-4-phenylthiazole (3as)
\(^1\)H NMR and \(^{13}\)C NMR of 2-ethoxy-4,5-diphenylthiazole (3at)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4,5-dihyronaphtho[1,2-$d$]thiazole (3au)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(furan-2-yl)thiazole (3av)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(thiophen-2-yl)thiazole (3aw)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(thiophen-3-yl)thiazole (3ax)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-(pyridin-2-yl)thiazole (3ay)
$^1$H NMR and $^{13}$C NMR of 4-(benzo[b]thiophen-2-yl)-2-ethoxythiazole (3az)
$^{1}H$ NMR and $^{13}C$ NMR of 2-ethoxy-4-(naphthalen-2-yl)thiazole (3ba)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-ethyl-5-methylthiazole (3bb)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-5-ethyl-4-propylthiazole (3bc)
$^1$H NMR and $^{13}$C NMR of 4-butyl-2-ethoxy-5-propylthiazole (3bd)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4,5,6,7-tetrahydrobenzo[$d$]thiazole (3be)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-5,6,7,8-tetrahydro-4H-cyclohepta[α]thiazole (3bf)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4,5,6,7,8,9-hexahydrocycloocta[d]thiazole (3bg)
$^1$H NMR and $^{13}$C NMR of 1-(3,4-dihydroquinolin-1(2$H$)-yl)-N-phenylethan-1-imine (3bh)
$^1$H NMR and $^{13}$C NMR of (E)-2-ethoxy-4-styrylthiazole (3bi)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-ethyl-5-methylthiazole (3bj)
$^{1}H$ NMR and $^{13}C$ NMR of 2-ethoxy-4-isopropyl-5-methylthiazole (3bk)
$^1$H NMR and $^{13}$C NMR of 4-butyl-2-ethoxy-5-methylthiazole (3bl)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-hexyl-5-methylthiazole (3bm)
$^1\text{H} \text{NMR and } ^{13}\text{C} \text{NMR of 4-benzyl-2-ethoxy-5-methylthiazole (3bn)}$
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-ethyl-5-pentylthiazole (3bo)
$^1$H NMR and $^{13}$C NMR of hyl-1-(o-tolyl)-1H-benzo[d]imidazole (3bo')
$^1$H NMR and $^{13}$C NMR of (E)-2-ethoxy-4-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)vinyl)thiazole (3bp)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-5,7,7-trimethyl-6,7-dihydrobenzo[d]thiazole (3bq)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-4-phenyl-4H-chromeno[4,3-d]thiazole (3br)
$^1$H NMR and $^{13}$C NMR of (7R,8aS,9S)-2-ethoxy-8a,9-dimethyl-7-(prop-1-en-2-yl)-5,6,7,8,8a,9-hexahydroptho[2,3-d]thiazole (3bs)
$^1$H NMR and $^{13}$C NMR of 1-((3bS,10aR,12aS)-8-ethoxy-10a,12a-dimethyl-2,3,3a,3b,4,5,10,10a,10b,11,12,12a-dodecahydro-1H-cyclopenta[7,8]phenanthro[2,3-d]thiazol-1-yl)ethan-1-one (3bt)
$^1$H NMR and $^{13}$C NMR of 2-methoxy-4-phenylthiazole (3bu)
$^1$H NMR and $^{13}$C NMR of 4-phenyl-2-propoxythiazole (3bv)
$^1$H NMR and $^{13}$C NMR of 2-butoxy-4-phenylthiazole (3bw)
$^1$H NMR and $^{13}$C NMR of 2-isopropoxy-4-phenylthiazole (3bx)
\(^1\)H NMR and \(^{13}\)C NMR of 2-(cyclohexyloxy)-4-phenylthiazole (3by)
$^1$H NMR and $^{13}$C NMR of 2-((3-methylbut-3-en-1-yl)oxy)-4-phenylthiazole (3bz)
$^1$H NMR and $^{13}$C NMR of 2-ethoxy-5,5-dimethyl-4-(propan-2-ylidene)-4,5-dihydrothiazole (4a)
$^1$H NMR and $^{13}$C NMR of 4-cyclohexylidene-2-ethoxy-1-thia-3-azaspiro[4.5]dec-2-ene (4b)
$^1$H NMR and $^{13}$C NMR of (E)-S-(ethoxycarbonothioyl)-N-(1-phenylethylidene)thiohydroxylamine (5a)
$^1$H NMR and $^{13}$C NMR of (E)-S-(ethoxycarbonothioyl)-N-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)thiohydroxylamine (5b)