Supporting Information

Facile Synthesis of 4-Alkyl (and aryl)-2-aryl-6-diazo-4*H*-thieno[3,2-*b*]pyridine-5,7-diones

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General Methods. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz in CDCl_3 solution containing Me_4Si as an internal standard, respectively, unless otherwise stated. J values are given in Hz. IR spectra were obtained in KBr or as thin films on KBr plates. Column chromatography was performed using silica gel (70 - 230 mesh, ASTM). Melting points are uncorrected.

General Procedure for the Preparation of Ethyl 3-{3-alkyl (and aryl)amino-5-arylthieno-2-yl}-2-diazo-3-oxopropanoate (8).

To a mixture of **11** (0.500 mmol) and 2-diazo-3-trimethylsilyloxy-3-butenate **12** (0.600 mmol) in CH_2Cl_2 (20 mL) was added $\text{Hg}(\text{OAc})_2$ (0.750 mmol). The reaction mixture was stirred for 1 h (for alkylamino derivatives) or 12 - 72 h (for arylamino derivatives) and filtered to remove $\text{Hg}(0)$ and unreacted $\text{Hg}(\text{OAc})_2$. Removal of the solvent *in vacuo*, followed by chromatography of the residue on a silica gel (3.5 x 10) using a mixture of EtOAc and *n*-hexane (1 : 9) as eluent gave **8**.

General Procedure for the Preparation of 1-Aryl-3-bis(methylthio)propen-1-ones (10).

N,N-dimethylformamide (40 mL) was added dropwise to a mixture of substituted acetophenones (10.0 mmol), sodium hydride (20.0 mmol) and carbon disulfide (15.0 mmol) in benzene (200 mL). To the whole mixture cooled in an ice bath was dropwise added methyl iodide (30.0 mmol). The mixture was stirred for an additional 1 h, followed by addition of benzene (200 mL) and ice water (500 mL). The benzene layer was separated and dried with anhydrous magnesium sulfate. After removal of benzene *in vacuo*, the crude product was recrystallized from ethanol.

General Procedure for the Preparation of (*E*)-3-Alkylamino-1-aryl-3-(methylthio)propenethiones (11a-d).

A mixture of **10** (2.00 mmol) and alkylamine (10.0 mmol) in ethanol (20 mL) was heated for 3 h at reflux. After removal of ethanol *in vacuo*, the crude product was recrystallized from ether to give 3-alkylamino-1-aryl-3-(methylthio)prop-2-en-1-ones. To the compound (1.00 mmol) in benzene (20 mL) was added Lawesson's reagent (0.500 mmol). The reaction mixture was refluxed for 30 min. Removal of the solvent *in vacuo*, followed by chromatography of the residue on a silica gel (3.5 x 10) using a mixture of EtOAc and *n*-hexane (1 : 6) as eluent gave **11a-d**.

General Procedure for the Preparation of (*E*)-1-Aryl-3-arylamino-3-

(methylthio)propenethiones (11e-m).

A mixture of **10** (2 mmol), arylamine (3 mmol) and $\text{BF}_3 \cdot \text{OEt}$ (0.2 mmol) in dried toluene (10 mL) was refluxed for 2 h and then cooled to room temperature. The reaction mixture was washed with 10% hydrochloric acid (10 mL), followed by water (10 mL) and dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo*, followed by chromatography of the residue on a silica gel (4.5 x 10) using a mixture of EtOAc and *n*-hexane (1 : 6) as eluent gave 1-aryl-3-aryl-amino-3-(methylthio)prop-2-en-1-ones. To the compound (1 mmol) in benzene (20 mL) was added Lawesson's reagent (0.5 mmol). The reaction mixture was refluxed for 30 min. Removal of the solvent *in vacuo*, followed by chromatography of the residue on a silica gel (3.5 x 10) using a mixture of EtOAc and *n*-hexane (1 : 6) as eluent gave **11e-m**.

General Procedure for the Synthesis of 4-Alkyl (and aryl)-2-aryl-6-diazo-4H-thieno[3,2-*b*]pyridine-5,7-diones (14).

(A) method: To a mixture of ethyl 3-{3-alkyl (and aryl)amino-5-arylthieno-2-yl}-2-diazo-3-oxopropanoates **8** (0.200 - 0.400 mmol) and Et_3N (1.20 - 2.40 mmol) in CH_2Cl_2 (20 - 30 mL) was added TMSOTf (0.600 - 1.20 mmol). The mixture was stirred for 1 h at room temperature. Removal of the solvent *in vacuo*, followed by chromatography of the residue on a silica gel (2.0 x 10) using a mixture of EtOAc and *n*-hexane (1 : 3) as eluent gave **14**. Yields are given in Table 2.

(B) method: To a mixture of **8** (0.200 - 0.400 mmol) and di-*tert*-butyl dicarbonate (BOC_2O) (0.600 - 1.20 mmol) in THF (20 - 30 mL) was added 4-(dimethylamino)pyridine (DMAP) (0.040 - 0.080 mmol). The mixture was stirred at room temperature or heated at reflux for an appropriate time. Removal of the solvent *in vacuo*, followed by chromatography of the residue on a silica gel (2.0 x 10) using a mixture of EtOAc and *n*-hexane (1 : 3) as eluent gave unreacted **8**, **14**, and ethyl 3-[(3-(aryl)(*tert*-butoxycarbonyl)amino)-5-arylthieno-2-yl]-2-diazo-3-oxopropanoates **15h** and **15k**. Yields of recovered **8** and **14** are given in Table 2.

General Procedure for the Synthesis 4-Alkyl (and aryl)-2-aryl-5,6-dihydro-4H-thieno[3,2-*b*]pyrrol-5-ones (16).

To a solution of **14** (0.100 - 0.200 mmol) in PhH (20 - 50 mL) was added Rh(II) catalyst (0.002 - 0.006 mmol) ($\text{Rh}_2(\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2)_4$ in (C) method and $\text{Rh}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$ in (D) method). The mixture was heated for an appropriate time at reflux. Removal of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel (2.0 x 10) with a mixture of EtOAc and *n*-hexane (1 : 6) as eluent to give **16**.

Yields are given in Table 2.

Ethyl 2-diazo-3-(3-methylamino-5-phenylthiophen-2-yl)-3-oxopropanoate 8a

: yellow solid; mp 77-78 °C (Et₂O – *n*-hexane); IR (neat) 3312, 2960, 2112, 1705, 1568, 1356, 1292, 1104, 755 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.34 (t, *J* = 7.1 Hz, 3H), 3.04 (d, *J* = 5.2 Hz, 3H), 4.33 (q, *J* = 7.1 Hz, 2H), 6.82 (s, 1H), 7.37-7.42 (m, 3H), 7.64-7.67 (m, 2H), 8.54 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 13.4, 30.4, 60.3, 106.1, 109.4, 125.3, 127.9, 128.4, 132.2, 152.1, 159.8, 161.1, 174.4. Anal. Calcd for C₁₆H₁₅N₃O₃S: C, 58.34; H, 4.59; N, 12.76; S, 9.74. Found: C, 58.01; H, 4.54; N, 12.63; S, 9.57. The ¹³C NMR absorption of diazomethylene carbon was invisible.

Ethyl 2-diazo-3-(3-ethylamino-5-phenylthiophen-2-yl)-3-oxopropanoate 8b

: yellow solid; mp 68-69 °C (Et₂O – *n*-hexane); IR (neat) 3296, 2976, 2112, 1705, 1564, 1369, 1331, 1292, 1104, 755 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.28-1.36 (m, 6H), 3.34-3.43 (m, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 6.82 (s, 1H), 7.37-7.41 (m, 3H), 7.64-7.67 (m, 2H), 8.60 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 13.4, 14.1, 38.6, 60.4, 105.9, 109.6, 125.3, 127.9, 128.5, 132.2, 152.1, 158.8, 161.1, 173.4. Anal. Calcd for C₁₇H₁₇N₃O₃S: C, 59.46; H, 4.99; N, 12.24; S, 9.34. Found: C, 59.61; H, 4.92; N, 12.17; S, 9.14. The ¹³C NMR absorption of diazomethylene carbon was invisible.

Ethyl 2-diazo-3-(3-isopropylamino-5-phenylthiophen-2-yl)-3-oxopropanoate 8c

: yellow liquid; IR (neat) 2969, 2134, 1714, 1569, 1375, 1334, 1295, 1108, 906, and 761 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.24-1.37 (m, 9H), 3.73-3.84 (m, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 6.83 (s, 1H), 7.35-7.42 (m, 3H), 7.62-7.66 (m, 2H), 8.66 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.3, 23.2, 46.3, 61.3, 106.9, 110.8, 126.3, 128.9, 129.4, 133.2, 153.0, 158.9, 161.3, 174.3. Anal. Calcd for C₁₈H₁₉N₃O₃S: C, 60.49; H, 5.36; N, 11.76; S, 8.97. Found: C, 60.55; H, 5.24; N, 11.56; S, 8.99. The ¹³C NMR absorption of diazomethylene carbon was invisible.

Ethyl 2-diazo-3-(3-methylamino-5-(4-tolyl)thiophen-2-yl)-3-oxopropanoate 8d

: yellow solid; mp 96-98°C (Et₂O – *n*-hexane); IR (neat) 3312, 2928, 2112, 1702, 1568, 1526, 1353, 1289, 1104, 1014, 937, and 796 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.31 (t, *J* = 7.1 Hz, 3H), 2.32 (s, 3H), 2.98 (d, *J* = 5.2 Hz, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 6.73 (s, 1H), 7.13-7.15 (m, 2H), 7.50-7.53 (m, 2H), 8.56 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.4, 21.2, 31.3, 61.2, 106.6, 109.7, 126.0, 129.5, 130.3, 139.6, 153.3, 160.9, 162.0, 174.1. Anal. Calcd for C₁₇H₁₇N₃O₃S: C, 59.46; H, 4.99; N, 12.24; S, 9.34. Found: C,

59.33; H, 4.87; N, 12.31; S, 9.21. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

Ethyl 2-diazo-3-{3-(4-methoxyphenylamino)-5-phenylthiophen-2-yl}-3-oxopropanoate 8e

: yellow solid; mp 100-102°C (Et₂O – *n*-hexane); IR (neat) 2960, 2128, 1705, 1558, 1504, 1360, 1289, 1235, 1174, 1107, 1030, 915, and 755 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 1.35 (t, J = 7.1 Hz, 3H), 3.80 (s, 3H), 4.35 (q, J = 7.1 Hz, 2H), 6.88-6.91 (m, 2H), 7.06 (s, 1H), 7.16-7.19 (m, 2H), 7.33-7.35 (m, 3H), 7.57-7.60 (m, 2H), 10.33 (br, s, 1H); ^{13}C NMR (75 MHz, CDCl₃) δ 14.4, 55.4, 61.4, 109.1, 112.2, 114.6, 124.3, 126.3, 128.8, 129.4, 133.0, 133.6, 152.5, 156.7, 156.9, 161.8, 175.2. Anal. Calcd for C₂₂H₁₉N₃O₄S: C, 62.69; H, 4.54; N, 9.97; S, 7.61. Found: C, 62.56; H, 4.50; N, 9.88; S, 7.32. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

Ethyl 2-diazo-3-{5-phenyl-3-(2-tolylamino)thiophen-2-yl}-3-oxopropanoate 8f

: yellow solid; mp 114-116°C (Et₂O – *n*-hexane); IR (neat) 2112, 1702, 1548, 1353, 1289, 1244, 1110, 1014, 918, and 745 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 1.37 (t, J = 7.1 Hz, 3H), 2.35 (s, 3H), 4.37 (q, J = 7.1 Hz, 2H), 7.06-7.11 (m, 2H), 7.20-7.27 (m, 2H), 7.34-7.38 (m, 4H), 7.59-7.62 (m, 2H), 10.32 (br, s, 1H); ^{13}C NMR (75 MHz, CDCl₃) δ 14.4, 18.1, 61.5, 109.8, 112.6, 122.3, 124.5, 126.3, 126.7, 128.9, 129.5, 130.9, 131.0, 133.0, 139.3, 152.4, 156.1, 161.8, 175.5. Anal. Calcd for C₂₂H₁₉N₃O₃S: C, 65.17; H, 4.72; N, 10.36; S, 7.91. Found: C, 65.16; H, 4.71; N, 10.48; S, 7.76. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

Ethyl 3-{3-(4-chlorophenylamino)-5-phenylthiophen-2-yl}-2-diazo-3-oxopropanoate 8g

: yellow solid; mp 128-129°C (Et₂O – *n*-hexane); IR (neat) 2112, 1708, 1552, 1353, 1292, 1248, 1174, 1107, 1008, 915, and 755 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 1.35 (t, J = 7.1 Hz, 3H), 4.34 (q, J = 7.1 Hz, 2H), 6.85-6.88 (m, 3H), 7.12-7.38 (m, 5H), 7.57-7.59 (m, 2H), 10.41 (br, s, 1H); ^{13}C NMR (75 MHz, CDCl₃) δ 14.4, 61.5, 111.0, 112.3, 122.6, 125.9, 126.3, 128.9, 129.0, 129.5, 133.0, 139.6, 152.6, 154.7, 161.5, 175.9. Anal. Calcd for C₂₁H₁₆ClN₃O₃S: C, 59.22; H, 3.79; N, 9.87; S, 7.53. Found: C, 59.34; H, 3.81; N, 9.69; S, 7.44. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

Ethyl 3-{3-(2-cyanophenylamino)-5-phenylthiophen-2-yl}-2-diazo-3-oxopropanoate 8h

: yellow solid; mp 142-143°C (Et₂O – *n*-hexane); IR (neat) 2208, 2128, 1712, 1542, 1500, 1417, 360, 1289, 1254, 1158, 1110, 1008, 915, and 752 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.36 (t, *J* = 7.1 Hz, 3H), 4.35 (q, *J* = 7.1 Hz, 2H), 7.06-7.09 (m, 1H), 7.32-7.39 (m, 4H), 7.52-7.64 (m, 5H), 10.90 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.3, 61.6, 103.4, 112.8, 113.6, 116.8, 119.4, 122.6, 126.3, 129.0, 129.6, 132.7, 133.4, 144.8, 144.2, 151.7, 152.4, 16.3, 176.8. Anal. Calcd for C₂₂H₁₆N₄O₃S: C, 63.45; H, 3.87; N, 13.45; S, 7.70. Found: C, 63.43; H, 3.90; N, 13.32; S, 7.56. The ¹³C NMR absorption of diazomethylene carbon was invisible.

Ethyl 2-diazo-3-{5-(4-methoxyphenyl)-3-(4-methoxyphenylamino)thiophen-2-yl}-3-oxopropanoate 8i

: yellow solid; mp 108-110°C (Et₂O – *n*-hexane); IR (neat) 2944, 2128, 1702, 1542, 1507, 1449, 1356, 1292, 1244, 1174, 1107, 1027, and 819 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.35 (t, *J* = 7.1 Hz, 3H), 3.80 (s, 6H), 4.35 (q, *J* = 7.1 Hz, 2H), 6.85-6.97 (m, 5H), 7.16-7.19 (m, 2H), 7.51-7.54 (m, 2H), 10.37 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.4, 55.3, 55.4, 61.4, 108.4, 111.0, 114.2, 114.5, 124.3, 125.6, 127.6, 133.7, 152.7, 156.6, 157.1, 160.7, 161.9, 174.8. Anal. Calcd for C₂₃H₂₁N₃O₅S: C, 61.18; H, 4.69; N, 9.31; S, 7.10. Found: C, 61.00; H, 4.71; N, 9.35; S, 6.96. The ¹³C NMR absorption of diazomethylene carbon was invisible.

Ethyl 3-{3-(4-bromophenylamino)-5-(4-methoxyphenyl)thiophen-2-yl}-2-diazo-3-oxopropanoate 8j

: yellow solid; mp 104-105°C (Et₂O – *n*-hexane); IR (neat) 2128, 1705, 1542, 1513, 1468, 1433, 1360, 1286, 1248, 1174, 1107, 1027, and 745 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.35 (t, *J* = 7.1 Hz, 3H), 3.80 (s, 3H), 4.34 (q, *J* = 7.1 Hz, 2H), 6.85-6.88 (m, 2H), 7.06-7.10 (m, 3H), 7.41-7.53 (m, 4H), 10.49 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.3, 55.3, 61.4, 110.1, 110.9, 114.2, 116.1, 122.7, 125.4, 127.6, 132.3, 139.9, 152.8, 154.7, 160.8, 161.6, 175.4. Anal. Calcd for C₂₂H₁₈BrN₃O₄S: C, 52.81; H, 3.63; N, 8.40; S, 6.41. Found: C, 52.88; H, 3.61; N, 8.40; S, 6.11. The ¹³C NMR absorption of diazomethylene carbon was invisible.

Ethyl 3-{3-(4-cyanophenylamino)-5-(4-methoxyphenyl)thiophen-2-yl}-2-diazo-3-oxopropanoate 8k

: yellow solid; mp 158-159°C (Et₂O – *n*-hexane); IR (neat) 2219, 2129, 1715, 1556, 1521, 1359, 1299, 1253, 1176, 1109, and 747 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.36 (t, *J* = 7.1 Hz, 3H), 3.83 (s, 3H), 4.35 (q, *J* = 7.1 Hz, 2H), 6.85-6.99 (m, 2H), 7.19-7.25

(m, 3H), 7.49-7.58 (m, 4H), 10.69 (br, s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.8, 55.8, 62.1, 105.2, 112.0, 113.0, 114.0, 114.8, 119.5, 125.6, 128.1, 134.0, 145.4, 152.3, 153.3, 161.4, 161.7, 176.7. Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_4\text{S}$: C, 61.87; H, 4.06; N, 12.55; S, 7.18. Found: C, 61.66; H, 4.01; N, 12.50; S, 7.16. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

Ethyl 3-{5-(4-bromophenyl)-3-(phenylamino)thiophen-2-yl}-2-diazo-3-oxopropanoate 8l

: yellow solid; mp 98-99°C (Et_2O – *n*-hexane); IR (neat) 2128, 1712, 1545, 1353, 1286, 1244, 1174, 1104, 1004, 915, and 745 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.35 (t, J = 7.1 Hz, 3H), 4.33 (q, J = 7.1 Hz, 2H), 7.07-7.29 (m, 4H), 7.31-7.47 (m, 6H), 10.49 (br, s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.4, 61.5, 110.3, 112.5, 121.4, 123.5, 123.9, 127.6, 129.4, 131.8, 131.9, 140.6, 150.8, 155.1, 161.5, 175.6. Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{BrN}_3\text{O}_3\text{S}$: C, 53.63; H, 3.43; N, 8.93; S, 6.82. Found: C, 53.42; H, 3.40; N, 8.85; S, 6.58. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

Ethyl 3-{5-(4-bromophenyl)-3-(4-methoxyphenylamino)thiophen-2-yl}-2-diazo-3-oxopropanoate 8m

: yellow solid; mp 84-85°C (Et_2O – *n*-hexane); IR (neat) 2128, 1705, 1555, 1504, 1363, 1280, 1235, 1174, 1110, 1024, and 742 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.35 (t, J = 7.1 Hz, 3H), 3.81 (s, 3H), 4.34 (q, J = 7.1 Hz, 2H), 6.88-6.91 (m, 2H), 7.02 (s, 1H), 7.14-7.17 (m, 2H), 7.41-7.48 (m, 4H), 10.33 (br, s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.7, 55.9, 61.8, 109.5, 112.8, 115.0, 123.9, 124.7, 128.0, 132.4, 133.9, 151.3, 157.3, 162.1, 175.7. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{BrN}_3\text{O}_4\text{S}$: C, 52.81; H, 3.63; N, 8.40; S, 6.41. Found: C, 52.90; H, 3.71; N, 8.33; S, 6.28. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

(*E*)-3-Methylamino-3-methylthio-1-phenylpropenethione 11a

: yellow solid; mp 92-93°C (EtOAc – *n*-hexane); IR (neat) 1574, 1475, 1290, 1027, 931, and 755 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.48 (s, 3H), 3.14 (d, J = 5.2, 3H), 6.52 (s, 1H), 7.25-7.35 (m, 3H), 7.66- 7.70(m, 2H), 14.40 (br, s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 30.3, 106.9, 126.8, 128.0, 129.0, 149.0, 172.8, 196.4. Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{NS}_2$: C, 59.15; H, 5.87; N, 6.27; S, 28.71. Found: C, 59.21; H, 5.90; N, 6.32; S, 28.63.

(*E*)-3-Ethylamino-3-methylthio-1-phenylpropenethione 11b

: yellow solid; mp 74-75°C (EtOAc – *n*-hexane); IR (neat) 1561, 1482, 1289, 1222, 960, 758, and 714 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.35 (t, *J* = 7.2 Hz, 3H), 2.41 (s, 3H), 3.49-3.58 (m, 2H), 6.50 (s, 1H), 7.33-7.36 (m, 3H), 7.64-7.69 (m, 2H), 14.48 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.0, 14.4, 39.5, 106.7, 126.8, 128.0, 128.9, 149.2, 171.3, 196.3. Anal. Calcd for C₁₂H₁₅NS₂: C, 60.71; H, 6.37; N, 5.90; S, 27.02. Found: C, 60.60; H, 6.22; N, 5.83; S, 26.96.

(*E*)-3-Isopropylamino-3-methylthio-1-phenylpropenethione 11c

: yellow solid; mp 102-104°C (EtOAc – *n*-hexane); IR (neat) 1565, 1477, 1294, 1207, 1157, 929, and 755 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.41 (d, *J* = 6.39 Hz, 6H), 2.47 (s, 3H), 4.02-4.09 (m, 1H), 6.46 (s, 1H), 7.31-7.33 (m, 3H), 7.63-7.67 (m, 2H), 14.56 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.5, 22.7, 47.5, 106.6, 126.8, 127.9, 128.8, 149.2, 169.8, 196.1. Anal. Calcd for C₁₃H₁₇NS₂: C, 62.10; H, 6.82; N, 5.57; S, 25.51. Found: C, 62.35; H, 6.79; N, 5.44; S, 25.42.

(*E*)-3-Methylamino-3-methylthio-1-(4-tolyl)propenethione 11d

: yellow solid; mp 98-100°C (EtOAc – *n*-hexane); IR (neat) 1577, 1482, 1292, 1270, 1024, 931, and 777 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.34 (s, 3H), 2.48 (s, 3H), 3.13 (d, *J* = 4.9 Hz, 3H), 6.51 (s, 1H), 7.12-7.15 (m, 2H), 7.59-7.62 (m, 2H), 14.38 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.3, 21.2, 30.3, 106.4, 126.8, 128.6, 139.2, 146.2, 172.6, 195.9. Anal. Calcd for C₁₂H₁₅NS₂: C, 60.71; H, 6.37; N, 5.90; S, 27.02. Found: C, 60.65; H, 6.39; N, 5.88; S, 26.86.

(*E*)-3-(4-Methoxyphenylamino)-3-methylthio-1-phenylpropenethione 11e

: red solid; mp 148-149°C (EtOAc – *n*-hexane); IR (neat) 1554, 1508, 1473, 1292, 1243, 1195, 1178, 1027, 948, and 755 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.40 (s, 3H), 3.81 (s, 3H), 6.66 (s, 1H), 6.91-6.94 (m, 2H), 7.25-7.37 (m, 5H), 7.72-7.74 (m, 2H), 15.79 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.8, 55.4, 107.5, 114.3, 126.8, 127.0, 128.0, 129.2, 149.0, 158.9, 170.9, 198.8. Anal. Calcd for C₁₇H₁₇NOS₂: C, 64.73; H, 5.43; N, 4.44; S, 20.33. Found: C, 64.69; H, 5.56; N, 4.30; S, 20.49. The ¹³C NMR absorption of one aryl carbon was invisible.

(*E*)-3-Methylthio-1-phenyl-3-(2-tolylamino)propenethione 11f

: red solid; mp 95-96°C (EtOAc – *n*-hexane); IR (neat) 1544, 1471, 1274, 1182, 948, and 757 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.37 (s, 3H), 2.40 (s, 3H), 6.69 (s, 1H), 7.25-7.38 (m, 7H), 7.74-7.77 (m, 2H), 15.76 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ

14.7, 18.3, 107.4, 126.5, 126.8, 127.0, 128.0, 128.4, 129.3, 131.0, 134.5, 135.7, 148.8, 171.4, 199.5. Anal. Calcd for C₁₇H₁₇NS₂: C, 68.18; H, 5.72; N, 4.68; S, 21.42. Found: C, 68.00; H, 5.65; N, 4.47; S, 21.58.

(E)-3-(4-Chlorophenylamino)-3-methylthio-1-phenylpropenethione 11g

: red solid; mp 113-114°C (EtOAc – *n*-hexane); IR (neat) 1585, 1550, 1490, 1469, 1288, 1195, 1089, 948, and 829 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.44 (s, 3H), 6.68 (s, 1H), 7.28-7.39 (m, 7H), 7.70-7.73 (m, 2H), 15.94 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.9, 107.7, 126.8, 126.9, 128.1, 129.4, 129.5, 133.2, 135.2, 148.8, 169.8, 200.4. Anal. Calcd for C₁₆H₁₄ClNS₂: C, 60.08; H, 4.41; N, 4.38; S, 20.05. Found: C, 60.14; H, 4.33; N, 4.26; S, 20.21.

(E)-3-(2-Cyanophenylamino)-3-methylthio-1-phenylpropenethione 11h

: red solid; mp 126-128°C (EtOAc – *n*-hexane); IR (neat) 2224, 1539, 1452, 1264, 1244, 1200, 1177, 944, and 755 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.48 (s, 3H), 6.75 (s, 1H), 7.37-7.75 (m, 9H), 16.04 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 15.0, 108.2, 110.7, 116.2, 126.8, 127.9, 128.0, 128.1, 129.8, 133.5, 133.7, 139.9, 148.5, 169.6, 203.6. Anal. Calcd for C₁₇H₁₄N₂S₂: C, 65.77; H, 4.55; N, 9.02; S, 20.66. Found: C, 65.87; H, 4.52; N, 9.09; S, 20.55.

(E)-1-(4-Methoxyphenyl)-3-(4-methoxyphenylamino)-3-(methylthio)propenethione 11i

: yellow solid; mp 164-166°C (EtOAc – *n*-hexane); IR (neat) 1540, 1473, 1245, 1169, 948, and 755 and cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.44 (s, 3H), 3.81 (s, 3H), 3.85 (s, 3H), 6.66 (s, 1H), 6.88-6.95 (m, 4H), 7.26-7.28 (m, 2H), 7.52-7.55 (m, 2H), 15.79 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.8, 55.3, 55.4, 107.4, 114.1, 126.1, 127.2, 128.0, 128.1, 129.2, 149.0, 158.9, 170.9, 198.6. Anal. Calcd for C₁₈H₁₉NO₂S₂: C, 62.58; H, 5.54; N, 4.05; S, 18.56. Found: C, 62.49; H, 5.51; N, 4.22; S, 18.35.

(E)-3-(4-Bromophenylamino)-1-(4-methoxyphenyl)-3-(methylthio)propenethione 11j

: red solid; mp 157-158°C (EtOAc – *n*-hexane); IR (neat) 1548, 1471, 1245, 1170, 1029, 1008, and 831 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.48 (s, 3H), 3.85 (s, 3H), 6.68 (s, 1H), 6.88-6.91 (m, 2H), 7.25-7.27 (m, 2H), 7.53-7.56 (m, 2H), 7.75-7.78 (m, 2H), 15.89 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 15.0, 55.4, 102.7, 106.8, 113.3, 121.0, 127.2, 128.6, 132.4, 136.0, 161.2, 169.1, 199.7. Anal. Calcd for C₁₇H₁₆BrNOS₂: C, 51.78; H,

4.09; N, 3.55; S, 16.26. Found: C, 51.81; H, 4.12; N, 3.34; S, 16.01.

(*E*)-3-(4-Cyanophenylamino)-1-(4-methoxyphenyl)-3-(methylthio)propenethione 11k

: red solid; mp 158-160°C (EtOAc – *n*-hexane); IR (neat) 2219, 1594, 1473, 1245, 1176, 1020, 950, 836, 823, and 771 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.52 (s, 3H), 3.85 (s, 3H), 6.72 (s, 1H), 6.88-6.91 (m, 2H), 7.50-7.53 (m, 2H), 7.67-7.78 (m, 4H), 16.10 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 15.1, 55.4, 107.4, 109.7, 113.4, 118.3, 125.1, 128.6, 133.1, 141.1, 141.5, 161.5, 167.3, 201.6. Anal. Calcd for C₁₈H₁₆N₂OS₂: C, 63.50; H, 4.74; N, 8.23; S, 18.84. Found: C, 63.55; H, 4.79; N, 8.11; S, 18.67.

(*E*)-1-(4-Bromophenyl)-3-methylthio-3-(phenylamino)propenethione 11l

: yellow solid; mp 136-138°C (EtOAc – *n*-hexane); IR (neat) 1536, 1471, 1172, 1068, 1002, 943, and 784 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.43 (s, 3H), 6.64 (s, 1H), 7.34-7.62 (m, 9H), 15.91 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.9, 107.5, 123.7, 125.5, 127.7, 128.4, 129.3, 131.1, 136.5, 147.5, 170.5, 197.4. Anal. Calcd for C₁₆H₁₄BrNS₂: C, 52.75; H, 3.87; N, 3.84; S, 17.60. Found: C, 52.54; H, 3.92; N, 3.68; S, 17.45.

(*E*)-1-(4-Bromophenyl)-3-(4-methoxyphenylamino)-3-(methylthio)propenethione 11m

: red solid; mp 160-162°C (EtOAc – *n*-hexane); IR (neat) 1536, 1506, 1471, 1290, 1241, 1176, 1006, 831, and 779 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.44 (s, 3H), 3.83 (s, 3H), 6.62 (s, 1H), 6.93-6.96 (m, 2H), 7.26-7.29 (m, 2H), 7.42-7.62 (m, 4H), 15.74 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.9, 55.5, 107.3, 114.4, 123.6, 127.1, 128.4, 129.1, 131.1, 147.6, 159.0, 171.3, 196.8. Anal. Calcd for C₁₇H₁₆BrNOS₂: C, 51.78; H, 4.09; N, 3.55; S, 16.26. Found: C, 51.63; H, 4.15; N, 3.68; S, 16.04.

(*E*)-1-(4-Chlorophenyl)-3-methylamino-3-(methylthio)propenethione 11n

: yellow solid; mp 120-121°C (EtOAc – *n*-hexane); IR (KBr) 1558, 1484, 1216, 1078, 921, and 780 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.48 (s, 3H), 3.13 (d, *J* = 5.2 Hz, 3H), 6.46 (s, 1H), 7.25-7.30 (m, 2H), 7.59-7.63 (m, 2H), 14.35 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.4, 30.3, 106.7, 128.0, 128.2, 134.9, 147.2, 173.0, 194.4. Anal. Calcd for C₁₁H₁₂ClNS₂: C, 51.25; H, 4.69; N, 5.43; S, 24.88. Found: C, 51.16; H, 4.81; N, 5.33; S, 22.12.

(*E*)-3-Methylamino-3-methylthio-1-(4-nitrophenyl)propenethione 11o

: red solid; mp 167-168°C (EtOAc – *n*-hexane); IR (KBr) 1571, 1491, 1337, 1286, 1219, 1104, 1017, 928, and 851 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.53 (s, 3H), 3.18 (d, *J* = 5.2 Hz, 3H), 6.51 (s, 1H), 7.74-7.78 (m, 2H), 8.14-8.19 (m, 2H), 14.37 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.4, 30.5, 107.7, 123.3, 127.6, 147.6, 154.3, 173.6, 192.4. Anal. Calcd for C₁₁H₁₂N₂O₂S₂: C, 49.23; H, 4.51; N, 10.44; S, 23.90. Found: C, 49.30; H, 4.54; N, 10.42; S, 23.97.

(*E*)-3-Ethylamino-1-(4-methoxyphenyl)-3-(methylthio)propenethione 11p

: yellow solid; mp 72-73°C (EtOAc – *n*-hexane); IR (KBr) 1590, 1552, 1468, 1203, 1162, 1027, 953, and 832 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.40 (t, *J* = 7.2 Hz, 3H), 2.48 (s, 3H), 3.46-3.55 (m, 2H), 3.80 (s, 3H), 6.48 (s, 1H), 6.81- 6.86 (m, 2H), 7.67-7.72 (m, 2H), 14.42 (br, s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.1, 14.4, 39.4, 55.3, 105.6, 113.2, 128.4, 141.7, 160.7, 170.8, 195.8. Anal. Calcd for C₁₃H₁₇NOS₂: C, 58.39; H, 6.41; N, 5.24; S, 23.98. Found: C, 58.27; H, 6.35; N, 5.15; S, 23.85.

6-Diazo-4-methyl-2-phenyl-4*H*-thieno[3,2-*b*]pyridine-5,7-dione 14a

: pale yellow solid; mp (dec.) 219-225°C (CH₂Cl₂ – *n*-hexane); IR (KBr) 2128, 1644, 1600, 1456, 1331, and 838 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.58 (s, 3H), 7.15 (s, 1H), 7.42-7.49 (m, 3H), 7.64-7.67 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 31.6, 113.1, 117.2, 126.6, 129.7, 130.4, 132.8, 147.3, 153.9, 161.1, 170.0. Anal. Calcd for C₁₄H₉N₃O₂S: C, 59.35; H, 3.20; N, 14.83; S, 11.32. Found: C, 59.22; H, 3.09; N, 14.79; S, 11.51. The ¹³C NMR absorption of diazomethylene carbon was invisible.

6-Diazo-4-ethyl-2-phenyl-4*H*-thieno[3,2-*b*]pyridine-5,7-dione 14b

: pale yellow solid; mp (dec.) 200-206°C (CH₂Cl₂ – *n*-hexane); IR (KBr) 2121, 1610, 1467, 1319, and 759 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.36 (t, *J* = 7.0 Hz, 3H), 4.13 (q, *J* = 7.0 Hz, 2H), 7.13(s, 1H), 7.43-7.45 (m, 3H), 7.63-7.65 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 12.7, 39.0, 111.7, 116.3, 125.4, 128.5, 129.2, 131.6, 145.3, 152.7, 159.5, 168.8. Anal. Calcd for C₁₅H₁₁N₃O₂S: C, 60.59; H, 3.73; N, 14.13; S, 10.78. Found: C, 60.46; H, 3.71; N, 14.01; S, 10.55. The ¹³C NMR absorptions of diazomethylene carbon was invisible.

6-Diazo-4-isopropyl-2-phenyl-4*H*-thieno[3,2-*b*]pyridine-5,7-dione 14c

: pale yellow solid; mp (dec.) 210-218°C (CH₂Cl₂ – *n*-hexane); IR (KBr) 2150, 1629, 1450, 1326, 1205, and 759 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.61 (d, *J* = 7.0 Hz, 6H), 5.15 (br, s, 1H), 7.31 (s, 1H), 7.37-7.47 (m, 3H), 7.64-7.73 (m, 2H); ¹³C NMR (75 MHz,

CDCl₃) δ 20.1, 46.2, 113.6, 115.2, 126.2, 129.3, 129.9, 132.6, 145.3, 152.7, 160.9, 169.6. Anal. Calcd for C₁₆H₁₃N₃O₂S: C, 61.72; H, 4.21; N, 13.50; S, 10.30. Found: C, 61.59; H, 4.33; N, 13.43; S, 10.04. The ¹³C NMR absorptions of diazomethylene carbon was invisible.

6-Diazo-4-methyl-2-(4-tolyl)-4H-thieno[3,2-*b*]pyridine-5,7-dione 14d

: pale yellow solid; mp (dec.) 210-215°C (CH₂Cl₂ – *n*-hexane); IR (KBr) 2912, 2112, 1644, 1603, 1459, 1331, and 809 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.40 (s, 3H), 3.58 (s, 3H), 7.10 (s, 1H), 7.24-7.26 (m, 2H), 7.53-7.56 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 21.4, 31.2, 112.1, 116.2, 126.0, 129.6, 129.9, 140.4, 146.9, 153.8, 160.7, 169.5. Anal. Calcd for C₁₅H₁₁N₃O₂S: C, 60.59; H, 3.73; N, 14.13; S, 10.78. Found: C, 60.67; H, 3.70; N, 14.32; S, 10.70. The ¹³C NMR absorption of diazomethylene carbon was invisible.

6-Diazo-4-(4-methoxyphenyl)-2-phenyl-4H-thieno[3,2-*b*]pyridine-5,7-dione 14e

: pale yellow solid; mp (dec.) 210-214°C (CH₂Cl₂ – *n*-hexane); IR (KBr) 2128, 1641, 1619, 1504, 1446, 1324, 1244, 1020, and 838 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.89 (s, 3H), 6.54 (s, 1H), 7.06-7.09 (m, 2H), 7.27-7.30 (m, 2H), 7.36-7.39 (m, 3H), 7.50-7.53 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 55.6, 114.5, 115.3, 116.6, 126.2, 129.2, 129.3, 129.4, 129.9, 132.4, 147.9, 152.8, 160.1, 160.9, 169.7. Anal. Calcd for C₂₀H₁₃N₃O₃S: C, 63.99; H, 3.49; N, 11.19; S, 8.54. Found: C, 64.00; H, 3.43; N, 11.08; S, 8.50. The ¹³C NMR absorption of diazomethylene carbon was invisible.

6-Diazo-2-phenyl-4-(2-tolyl)-4H-thieno[3,2-*b*]pyridine-5,7-dione 14f

: pale yellow solid; mp (dec.) 205-211°C (CH₂Cl₂ – *n*-hexane); IR (KBr) 2128, 1651, 1619, 1542, 1449, 1324, 1190, 889, and 825 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.19 (s, 3H), 6.38 (s, 1H), 7.27-7.50 (m, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 17.5, 113.9, 116.4, 126.1, 127.7, 128.5, 129.1, 129.91, 129.94, 131.7, 132.2, 135.7, 136.4, 147.1, 153.1, 160.0, 169.6. Anal. Calcd for C₂₀H₁₃N₃O₂S: C, 66.84; H, 3.65; N, 11.69; S, 8.92. Found: C, 66.65; H, 3.44; N, 11.73; S, 8.83. The ¹³C NMR absorption of diazomethylene carbon was invisible.

4-(4-Chlorophenyl)-6-diazo-2-phenyl-4H-thieno[3,2-*b*]pyridine-5,7-dione 14g

: pale yellow solid; mp (dec.) 212-215°C (CH₂Cl₂ – *n*-hexane); IR (KBr) 2144, 1648, 1619, 1539, 1446, 1321, 1193, 1084, 838, and 816 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.52 (s, 1H), 7.32-7.38 (m, 5H), 7.49-7.57 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 114.0, 116.9, 129.2, 129.2, 129.8, 130.0, 130.4, 132.2, 135.2, 135.6, 146.9, 153.1, 160.4, 169.4.

Anal. Calcd for $C_{19}H_{10}ClN_3O_2S$: C, 60.08; H, 2.65; N, 11.06; S, 8.44. Found: C, 60.00; H, 2.61; N, 11.24; S, 8.31. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

4-(2-Cyanophenyl)-6-diazo-2-phenyl-4*H*-thieno[3,2-*b*]pyridine-5,7-dione 14h

: pale yellow solid; mp (dec.) 220-225°C (CH_2Cl_2 – *n*-hexane); IR (KBr) 2220, 2128, 1660, 1622, 1542, 1449, 1420, 1321, 1193, 892, and 812 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 6.41 (s, 1H), 7.37-7.39 (m, 3H), 7.49-7.70 (m, 4H), 7.87-7.93 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 113.1, 113.7, 115.2, 117.3, 126.2, 129.2, 130.0, 130.1, 130.3, 132.1, 134.3, 134.2, 139.1, 145.6, 153.7, 160.0, 169.2. Anal. Calcd for $C_{20}H_{10}N_4O_2S$: C, 64.86; H, 2.72; N, 15.13; S, 8.66. Found: C, 64.79; H, 2.67; N, 15.12; S, 8.45. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

6-Diazo-2,4-di(4-methoxyphenyl)-4*H*-thieno[3,2-*b*]pyridine-5,7-dione 14i

: pale yellow solid; mp (dec.) 202-210°C (CH_2Cl_2 – *n*-hexane); IR (KBr) 2128, 1651, 1616, 1504, 1446, 1328, 1296, 1248, 1177, 1024, and 832 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.89 (s, 3H), 6.42 (s, 1H), 6.86-6.90 (m, 2H), 7.06-7.10 (m, 2H), 7.26-7.31 (m, 2H), 7.43-7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.4, 55.5, 113.2, 114.5, 115.3, 125.0, 127.6, 129.3, 129.4, 148.0, 152.9, 160.0, 161.0, 169.5. Anal. Calcd for $C_{21}H_{15}N_3O_4S$: C, 62.21; H, 3.73; N, 10.36; S, 7.91. Found: C, 62.00; H, 3.62; N, 10.43; S, 7.70. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

4-(4-Bromophenyl)-6-diazo-2-(4-methoxyphenyl)-4*H*-thieno[3,2-*b*]pyridine-5,7-dione 14j

: pale yellow solid; mp (dec.) 211-215°C (CH_2Cl_2 – *n*-hexane); IR (KBr) 2143, 1624, 1605, 1488, 1455, 1334, 1256, 1177, and 818 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.41 (s, 1H), 6.87-6.90 (m, 2H), 7.27-7.29 (m, 2H), 7.43-7.45 (m, 2H), 7.70-7.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.4, 112.7, 114.5, 115.7, 123.6, 124.8, 127.6, 130.1, 133.3, 135.7, 146.9, 153.2, 180.4, 181.1, 169.1. Anal. Calcd for $C_{20}H_{12}BrN_3O_3S$: C, 52.88; H, 2.66; N, 9.25; S, 7.06. Found: C, 52.81; H, 2.64; N, 9.27; S, 7.00. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

4-(4-Cyanophenyl)-6-diazo-2-(4-methoxyphenyl)-4*H*-thieno[3,2-*b*]pyridine-5,7-dione 14k

: pale yellow solid; mp (dec.) 214-220°C (CH_2Cl_2 – *n*-hexane); IR (KBr) 2350, 2153, 1601, 1455, 1337, 1253, 1172, 1024, and 820 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 3.82

(s, 3H), 6.39 (s, 1H), 6.85-6.88 (m, 2H), 7.26-7.32 (m, 2H), 7.42-7.57 (m, 2H), 7.88-7.90 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 55.8, 112.7, 114.0, 115.0, 118.0, 125.1, 28.1, 130.1, 133.4, 134.3, 141.1, 146.4, 154.1, 160.7, 161.7, 169.4. Anal. Calcd for $\text{C}_{21}\text{H}_{12}\text{N}_4\text{O}_3\text{S}$: C, 62.99; H, 3.02; N, 13.99; S, 8.01. Found: C, 62.89; H, 3.00; N, 13.84; S, 7.88. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

2-(4-Bromophenyl)-6-diazo-4-phenyl-4H-thieno[3,2-*b*]pyridine-5,7-dione 14l

: pale yellow solid; mp (dec.) 236-240°C (CH_2Cl_2); IR (KBr) 2140, 1665, 1628, 1459, 1330, and 815 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 6.49 (s, 1H), 7.01-7.60 (m, 9H). Anal. Calcd for $\text{C}_{19}\text{H}_{10}\text{BrN}_3\text{O}_2\text{S}$: C, 53.79; H, 2.38; N, 9.90; S, 7.56. Found: C, 53.75; H, 2.32; N, 9.76; S, 7.33. The ^{13}C NMR spectrum could not be taken because of solubility problem.

2-(4-Bromophenyl)-6-diazo-4-(4-methoxyphenyl)-4H-thieno[3,2-*b*]pyridine-5,7-dione 14m

: pale yellow solid; mp (dec.) 213-219°C (CH_2Cl_2); IR (KBr) 2141, 1649, 1626, 1460, 1332, 1250, and 816 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 3.89 (s, 3H), 6.52 (s, 1H), 6.94-7.61 (m, 8H); ^{13}C NMR (75 MHz, CDCl_3) δ 55.5, 114.7, 115.3, 124.1, 125.8, 127.6, 129.1, 129.3, 131.3, 132.3, 147.8, 151.2, 160.1, 160.7, 169.3. Anal. Calcd for $\text{C}_{20}\text{H}_{12}\text{BrN}_3\text{O}_3\text{S}$: C, 52.88; H, 2.66; N, 9.25; S, 7.06. Found: C, 52.81; H, 2.64; N, 9.25; S, 6.89. The ^{13}C NMR absorption of diazomethylene carbon was invisible.

Ethyl 3-[3-{*tert*-butoxycarbonyl-(2-cyanophenyl)amino}-5-phenylthiophen-2-yl]-2-diazo-3-oxopropanoate 15h

: pale yellow sticky; IR (neat) 2944, 2224, 2128, 1718, 1596, 1440, 1385, 1363, 1308, 1248, 1155, 1113, 1011, and 755 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.35 (t, $J = 7.1$ Hz, 3H), 1.47 (s, 9H), 4.32 (q, $J = 7.1$ Hz, 2H), 7.00 (s, 1H), 7.31-7.40 (m, 4H), 7.52-7.57 (m, 4H), 7.68-7.70 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.3, 27.9, 61.7, 83.2, 112.4, 116.9, 122.6, 125.9, 127.2, 128.1, 128.6, 129.0, 132.6, 133.0, 133.7, 144.6, 145.6, 160.5, 161.6, 176.4. Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{N}_4\text{O}_5\text{S}$: C, 62.78; H, 4.68; N, 10.85; S, 6.21. Found: C, 62.65; H, 4.45; N, 10.70; S, 6.05. ^{13}C NMR absorptions of two aryl carbons were invisible.

Ethyl 3-[3-{*tert*-butoxycarbonyl-(4-cyanophenyl)amino}-5-(4-methoxyphenyl)thiophen-2-yl]-2-diazo-3-oxopropanoate 15k

: pale yellow sticky; IR (neat) 2930, 2226, 2138, 1724, 1604, 1508, 1320, 1297, 1254,

1178, 2038, 1029, and 832 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.32 (t, $J = 7.1$ Hz, 3H), 1.47 (s, 9H), 3.84 (s, 3H), 4.25 (q, $J = 7.1$ Hz, 2H), 6.87-6.97 (m, 3H), 7.39-7.58 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.7, 28.4, 55.8, 62.1, 83.4, 108.7, 114.9, 119.1, 122.6, 125.6, 125.7, 127.7, 129.1, 132.8, 142.9, 146.6, 148.3, 152.5, 160.9, 161.0, 176.5. Anal. Calcd for $\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}_6\text{S}$: C, 61.53; H, 4.79; N, 10.25; S, 5.87. Found: C, 61.43; H, 4.60; N, 10.17; S, 5.66.

5,6-Dihydro-4-methyl-2-phenyl-4*H*-thieno[3,2-*b*]pyrrol-5-one 16a

: white solid; mp 114-115°C ($\text{Et}_2\text{O} - n\text{-hexane}$); IR (KBr) 2912, 1705, 1590, 1542, 1481, 1334, 1081, 988, and 758 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 3.27 (s, 3H), 3.62 (s, 2H), 6.97 (s, 1H), 7.26-7.41 (m, 3H), 7.52-7.58 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 28.0, 36.4, 107.3, 113.1, 125.3, 127.8, 129.0, 134.2, 146.1, 147.7, 177.0. Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{NOS}$: C, 68.09; H, 4.84; N, 6.11; S, 13.98. Found: C, 67.92; H, 4.76; N, 6.23; S, 13.80.

5,6-Dihydro-4-ethyl-2-phenyl-4*H*-thieno[3,2-*b*]pyrrol-5-one 16b

: white solid; mp 105-106°C ($\text{Et}_2\text{O} - n\text{-hexane}$); IR (neat) 2925, 1706, 1550, 1484, 1338, 1074, and 755 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.31 (t, $J = 7.2$ Hz, 3H), 3.65 (s, 2H), 3.76 (q, $J = 7.2$ Hz, 2H), 6.97 (s, 1H), 7.26-7.46 (m, 3H), 7.56-7.59 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.6, 36.4, 36.5, 107.5, 113.5, 125.4, 127.8, 129.0, 134.3, 146.2, 146.9, 176.6. Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{NOS}$: C, 69.10; H, 5.39; N, 5.76; S, 13.18. Found: C, 69.19; H, 5.32; N, 5.65; S, 13.02.

5,6-Dihydro-4-isopropyl-2-phenyl-4*H*-thieno[3,2-*b*]pyrrol-5-one 16c

: white solid; mp 147-149°C ($\text{Et}_2\text{O} - n\text{-hexane}$); IR (neat) 2925, 1700, 1496, 1475, 1450, 1317, 1302, 1045, 852, and 752 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.42 (d, $J = 6.9$ Hz, 6H), 3.60 (s, 2H), 4.67 (m, 1H), 7.07 (s, 1H), 7.26-7.44 (m, 3H), 7.56-7.59 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 20.4, 36.4, 43.4, 109.1, 114.5, 125.5, 127.8, 129.0, 134.2, 145.1, 145.9, 176.3. Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NOS}$: C, 70.01; H, 5.87; N, 5.44; S, 12.46. Found: C, 69.96; H, 5.68; N, 5.23; S, 12.39.

5,6-Dihydro-4-methyl-2-(4-tolyl)-4*H*-thieno[3,2-*b*]pyrrol-5-one 16d

: white solid; mp 107-108°C ($\text{Et}_2\text{O} - n\text{-hexane}$); IR (KBr) 2912, 1696, 1542, 1504, 1481, 1433, 1395, 1334, 1078, 992, and 931 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.30 (s, 3H), 3.26 (s, 3H), 3.61 (s, 2H), 6.93 (s, 1H), 7.18-7.26 (m, 2H), 7.45-7.48 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.1, 28.0, 36.4, 106.9, 112.5, 125.3, 129.7, 131.6, 137.8, 146.4,

147.8, 177.1. Anal. Calcd for C₁₄H₁₃NOS: C, 69.10; H, 5.39; N, 5.76; S, 13.18. Found: C, 69.15; H, 5.42; N, 5.71; S, 13.01.

5,6-Dihydro-4-(4-methoxyphenyl)-2-phenyl-4*H*-thieno[3,2-*b*]pyrrol-5-one 16e

: white solid; mp 133-135°C (Et₂O – *n*-hexane); IR (KBr) 1078, 1539, 1504, 1459, 1331, 1289, 1244, 1158, 1068, 1027, and 816 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.79 (s, 2H), 3.85 (s, 3H), 6.95 (s, 1H), 7.00-7.03 (m, 2H), 7.28-7.42 (m, 5H), 7.53-7.56 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 36.0, 55.5, 108.6, 113.7, 114.6, 125.4, 125.7, 127.8, 128.6, 128.9, 134.1, 145.8, 147.3, 158.4, 176.0. Anal. Calcd for C₁₉H₁₅NO₂S: C, 71.00; H, 4.70; N, 4.36; S, 9.98. Found: C, 71.23; H, 4.73; N, 4.55; S, 9.74.

5,6-Dihydro-2-phenyl-4-(2-tolyl)-4*H*-thieno[3,2-*b*]pyrrol-5-one 16f

: white solid; mp 128-129°C (Et₂O – *n*-hexane); IR (neat) 1712, 1590, 1539, 1484, 1414, 1324, 1222, 1158, 1116, and 1068 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.27 (s, 3H), 3.82 (s, 2H), 6.69 (s, 1H), 7.25-7.38 (m, 7H), 7.50-7.52 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 18.1, 36.6, 108.4, 113.4, 125.3, 127.1, 127.8, 128.7, 128.9, 131.5, 134.1, 134.4, 135.9, 146.0, 147.6, 175.8. Anal. Calcd for C₁₉H₁₅NOS: C, 74.72; H, 4.95; N, 4.59; S, 10.50. Found: C, 74.58; H, 4.82; N, 4.47; S, 10.31. The ¹³C NMR absorption of one aryl carbon was invisible.

4-(4-Chlorophenyl)-5,6-dihydro-2-phenyl-4*H*-thieno[3,2-*b*]pyrrol-5-one 16g

: white solid; mp 130-131°C (Et₂O – *n*-hexane); IR (KBr) 1712, 1587, 1542, 1491, 1465, 1395, 1328, 1155, 1088, 1065, 1011, and 816 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.80 (s, 2H), 7.00 (s, 1H), 7.25-7.56 (m, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 36.6, 108.5, 114.2, 125.0, 125.4, 128.0, 129.0, 129.5, 132.3., 133.9, 134.3, 146.1, 146.2, 175.6. Anal. Calcd for C₁₈H₁₂ClNOS: C, 66.35; H, 3.71; N, 4.30; S, 9.84. Found: C, 66.24; H, 3.79; N, 4.26; S, 9.78.

4-(2-Cyanophenyl)-5,6-dihydro-2-phenyl-4*H*-thieno[3,2-*b*]pyrrol-5-one 16h

: white solid; mp (dec.) 189-195°C (Et₂O – *n*-hexane); IR (neat) 2230, 1731, 1495, 1449, 1330, 1155, 1057, and 769 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.88 (s, 2H), 6.84 (s, 1H), 7.29-7.39 (m, 3H), 7.51-7.56 (m, 4H), 7.74-7.85 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 36.4, 108.2, 111.2, 114.4, 116.2, 125.5, 126.7, 128.1, 128.2, 129.0, 133.9, 134.0, 134.1, 138.2, 145.5, 146.4, 175.3. Anal. Calcd for C₁₉H₁₂N₂OS: C, 72.13; H, 3.82; N, 8.85; S, 10.14. Found: C, 72.01; H, 3.73; N, 8.66; S, 10.32.

5,6-Dihydro-2,4-di(4-methoxyphenyl)-4H-thieno[3,2-*b*]pyrrol-5-one 16i

: white solid; mp 136-137°C (Et₂O – *n*-hexane); IR (neat) 2928, 1705, 1600, 1542, 1504, 1492, 1331, 1286, 1244, 1174, 1107, 1065, 1027, and 822 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.77 (s, 2H), 3.82 (s, 3H), 3.85 (s, 3H), 6.84 (s, 1H), 6.88-6.91 (m, 2H), 7.00-7.03 (m, 2H), 7.38-7.48 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 36.6, 55.3, 55.5, 107.7, 112.4, 114.3, 114.6, 125.6, 126.7, 127.0, 128.6, 145.9, 147.1, 158.3, 159.4, 176.1. Anal. Calcd for C₂₀H₁₇NO₃S: C, 68.36; H, 4.88; N, 3.99; S, 9.12. Found: C, 68.19; H, 4.76; N, 4.08; S, 9.36.

4-(4-Bromophenyl)-5,6-dihydro-2-(4-methoxyphenyl)-4H-thieno[3,2-*b*]pyrrol-5-one 16j

: white solid; mp (dec.) 211-217°C (Et₂O – *n*-hexane); IR (neat) 1713, 1512, 1488, 1335, 1247, 1175, 1070, 1030, and 814 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.78 (s, 2H), 3.83 (s, 3H), 6.88-6.92 (m, 3H), 7.40-7.48 (m, 4H), 7.59-7.62 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 36.6, 55.3, 107.7, 113.1, 114.4, 120.0, 125.3, 126.8, 132.5, 134.9, 145.9, 146.2, 159.6, 175.7. Anal. Calcd for C₁₉H₁₄BrNO₂S: C, 57.01; H, 3.53; N, 3.50; S, 8.01. Found: C, 57.21; H, 3.45; N, 3.65; S, 8.19. The ¹³C NMR absorption of one aryl carbon was invisible.

4-(4-Cyanophenyl)-5,6-dihydro-2-(4-methoxyphenyl)-4H-thieno[3,2-*b*]pyrrol-5-one 16k

: white solid; mp 160-161°C (Et₂O – *n*-hexane); IR (KBr) 2923, 1728, 1604, 1512, 1333, 1251, 1180, and 828 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.82 (s, 2H), 3.84 (s, 3H), 6.90-6.97 (m, 2H), 7.00 (s, 1H), 7.47-7.54 (m, 2H), 7.69-7.80 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 36.6, 55.4, 107.7, 109.6, 114.0, 114.4, 118.4, 123.3, 126.6, 126.9, 133.3, 133.9, 144.7, 146.7, 159.8, 175.5. Anal. Calcd for C₂₀H₁₄N₂O₂S: C, 69.35; H, 4.07; N, 8.09; S, 9.26. Found: C, 69.12; H, 4.01; N, 8.00; S, 9.44.

2-(4-Bromophenyl)-6-dihydro-4-phenyl-4H-thieno[3,2-*b*]pyrrol-5-one 16l

: white solid; mp 176-178°C (Et₂O – *n*-hexane); IR (neat) 1725, 1494, 1471, 1329, 1156, 1081, 1009, and 803 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.79 (s, 2H), 6.99 (m, 1H), 7.31-7.53 (m, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 36.6, 109.1, 114.5, 121.7, 123.9, 126.6, 127.6, 129.4, 132.0, 133.0, 135.7, 144.5, 146.8, 175.5. Anal. Calcd for C₁₈H₁₂BrNOS: C, 58.39; H, 3.27; N, 3.78; S, 8.66. Found: C, 58.17; H, 3.16; N, 3.60; S, 8.53.

2-(4-Bromophenyl)-5,6-dihydro-4-(4-methoxyphenyl)-4H-thieno[3,2-*b*]pyrrol-5-one 16m

: white solid; mp 180-182°C (Et₂O – *n*-hexane); IR (neat) 2923, 2226, 1724, 1493, 1329, 1155, 1081, 1009, and 803 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.76 (s, 2H), 3.84 (s, 3H), 6.92 (s, 1H), 6.99-7.02 (m, 2H), 7.37-7.47 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 36.6, 55.5, 108.9, 114.2, 114.7, 121.6, 125.7, 126.8, 128.5, 132.0, 133.1, 144.4, 147.5, 158.5, 175.8. Anal. Calcd for C₁₉H₁₄BrNO₂S: C, 57.01; H, 3.53; N, 3.50; S, 8.01. Found: C, 57.15; H, 3.43; N, 3.63; S, 8.15.

2-(4-Chlorophenyl)-5,6-dihydro-4-methyl-4H-thieno[3,2-*b*]pyrrol-5-one 16n

: white solid; mp 138-140°C (Et₂O – *n*-hexane); IR (KBr) and 2923, 1698, 1494, 1344, 1091, and 815 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.25 (s, 3H), 3.60 (s, 2H), 6.93 (s, 1H), 7.32-7.35 (m, 2H), 7.46-7.49 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 28.0, 36.4, 107.6, 113.6, 126.5, 129.1, 132.8, 133.5, 144.7, 147.9, 177.0. Anal. Calcd for C₁₃H₁₀ClNOS: C, 59.20; H, 3.82; N, 5.31; S, 12.16. Found: C, 59.26; H, 3.77; N, 5.33; S, 12.23.

5,6-Dihydro-4-methyl-2-(4-nitrophenyl)-4H-thieno[3,2-*b*]pyrrol-5-one 16o

: yellow solid; mp (dec.) 180-200°C (Et₂O – *n*-hexane); IR (KBr) 2921, 1702, 1580, 1495, 1108, and 850 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.29 (s, 3H), 3.65 (s, 2H), 7.12 (s, 1H), 7.68-7.72 (m, 2H), 8.22-8.25 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 28.0, 36.4, 109.3, 116.8, 124.5, 125.3, 140.4, 143.0, 146.7, 148.6, 176.5. Anal. Calcd for C₁₃H₁₀N₂O₃S: C, 56.92; H, 3.67; N, 10.21; S, 11.69. Found: C, 56.90; H, 3.62; N, 10.24; S, 11.76.

5,6-Dihydro-4-ethyl-2-(4-methoxyphenyl)-4H-thieno[3,2-*b*]pyrrol-5-one 16p

: white solid; mp 100-102°C (Et₂O – *n*-hexane); IR (KBr) 2912, 1700, 1540, 1504, 1481, 1395, 1078, 992, and 825 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.29 (t, *J* = 7.2 Hz, 3H), 3.58 (s, 2H), 3.72 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 6.86 (s, 1H), 6.89-6.92 (m, 2H), 7.46-7.53 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.6, 36.4, 36.5, 55.4, 106.7, 112.3, 114.4, 126.8, 127.2, 146.2, 146.8, 159.4, 176.7. Anal. Calcd for C₁₅H₁₅NO₂S: C, 65.91; H, 5.53; N, 5.12; S, 11.73. Found: C, 65.98; H, 5.50; N, 5.03; S, 11.67.