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Utility Of 2-Amino-4,5,6,7-Tetrahydrobenzo[b]Thiophene-3-Carboxylic Acid In The Synthesis Of Novel Thieno[2,3-b] [1,2,4]Triazepinones And Thieno[2,3-d][1,3,4]Thiadiazolo [2,3-b]Pyrimidinones

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Abstract
A new series of thienothiadiazolopyrimidinone **4** was prepared *via* the reaction of hydrazonoyl chlorides **2** with 2-amino-tetrahydrobenzo[b]thiophene-3-carboxylic acid **1** followed by cyclization with 1,1`-carbonyldiimidazole. Furthermore, benzothienothiadiazolo pyrimidinone derivatives **11a-c** were prepared. The structure of the newly synthesized compounds were established on the basis of spectral data (Mass, IR, ^{1}H and ^{13}C NMR) and elemental analyses.

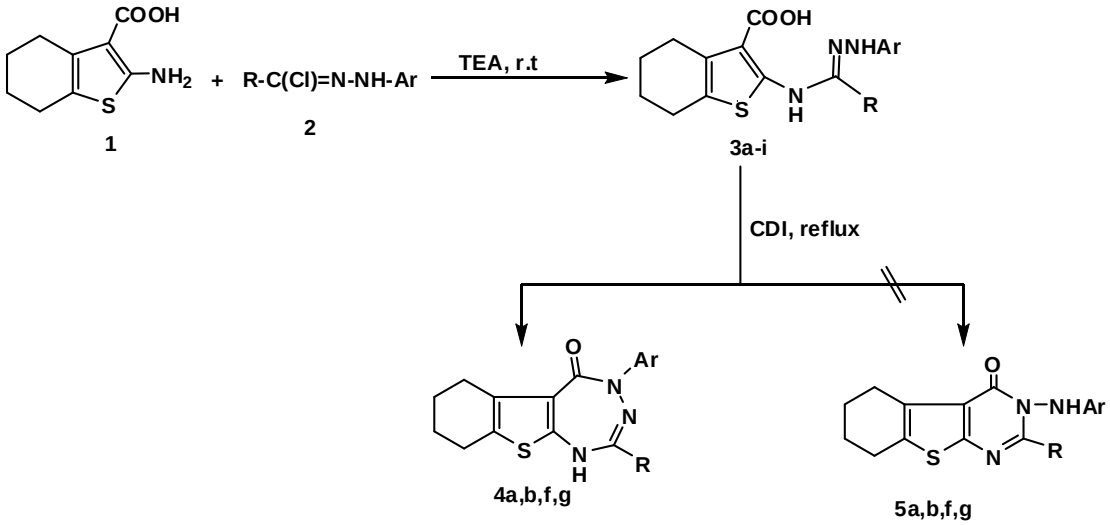
Key words: Hydrazonoyl halides, 2-amino-tetrahydrobenzo[b]thiophene-3-carboxylic acid, thienothiadiazolo-pyrimidinone, thienothiadiazolopyrimidinone.

I. Introduction

Hydrazonoyl halides have been widely employed in the synthesis of heterocyclic derivatives.[1-5] Condensed thienopyrimidines exhibit interesting biological activities like antibacterial,[6] antihistaminic,[7] analgesic and anti-inflammatory [8-10] and antimalarial.[11] Various condensed thienopyrimidine systems were studied for their biological activities.[12-16] All the above findings encouraged us to synthesize a new series of tetrahydrobenzothienothiadiazolopyrimidinone **4** *via* the reaction of hydrazonoyl chlorides **2** with 2-amino-tetrahydrobenzo[b]thiophene-3-carboxylic acid **1**.

II. Results and discussion

Reaction of 2-Amino-tetrahydrobenzo[b] thiophene-3-carboxylic acid **1**[17] with hydrazonoyl halides **2** in the presence of TEA under heating resulted in the formation of the respective amidrazone derivatives **3a-i** (Scheme 1)**.** The structure of compounds **3a-i** was evidenced by its microanalysis and spectral data (mass, IR, ^{1}H NMR) (see Experimental).

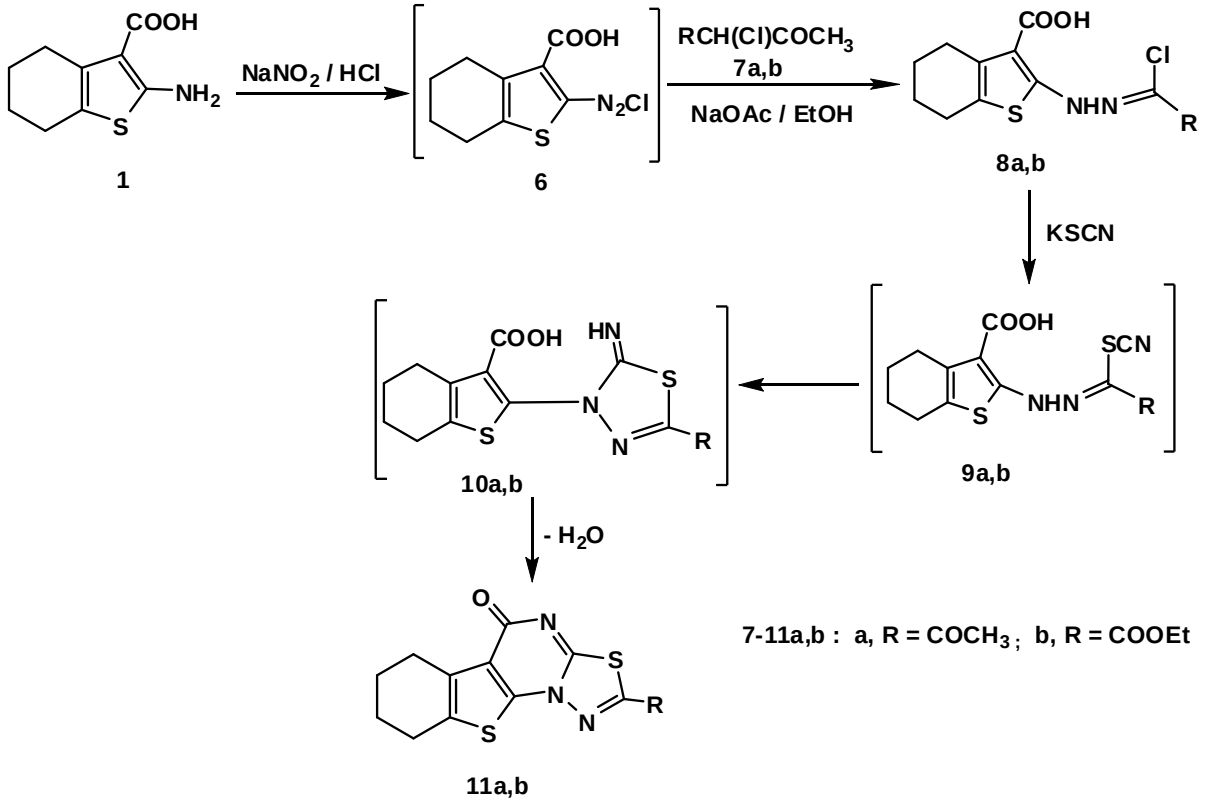


Ar = XC_6H_4
R / X : a, CH_3CO / H; b, CH_3CO / 4-CH_3; c, CH_3CO / 4-Cl; d, CH_3CO / 4-NO_2; e, CH_3CO / 4- OCH_3; f, EtOCO / H; g, EtOCO / 4-CH_3; h, EtOCO / 4-Cl; i, EtOCO / 4-NO_2

Scheme 1. Synthesis of fused triazepinone derivatives **4a-i**

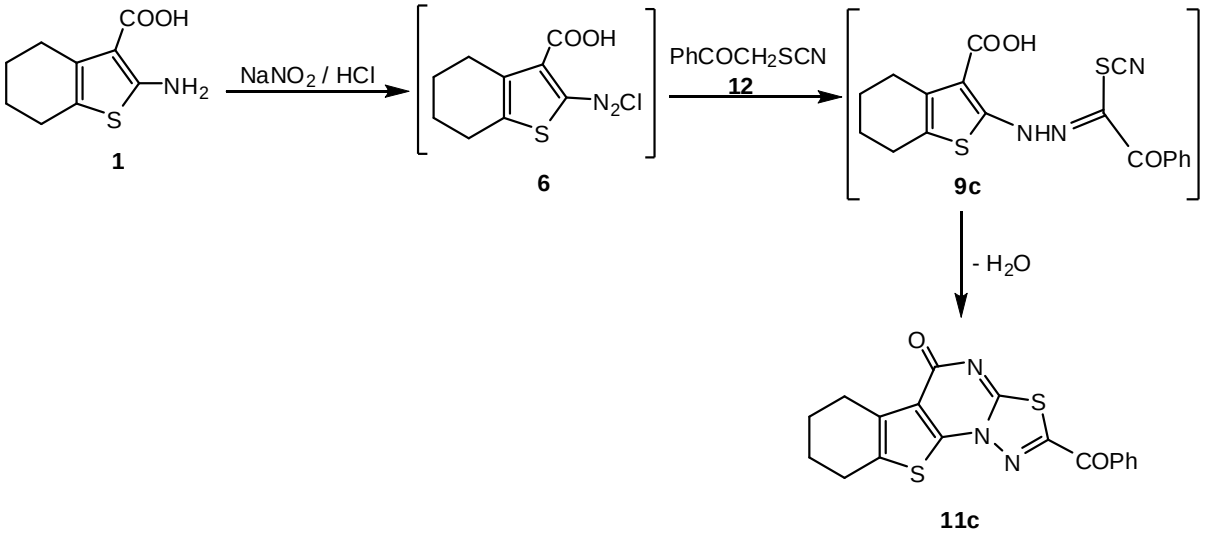
Treatment of the latter products, **3a,b,f,g** with 1,1`-carbonyldiimidazole in dioxane yielded the corresponding triazepinone derivatives **4a,b,f,g** rather than the pyrimidinone derivatives **5a,b,f,g** (Scheme 1).

The actual structures of these products were assigned **4** rather than **5** based on their ^{1}H NMR spectra which showed characteristic singlet signals at δ 8.64-8.73 ppm assigned for the triazepinone-NH of compounds **4** rather than the aniline-NH for compound **5**. The formation of the triazepinones in the line with previous reports.[18, 19] Attempted X-ray of the products are failed.



Scheme 2. Synthesis of 6,7,8,9-tetrahydrobenzo[4,5]thieno[2,3-d][1,3,4] thiadiazolo[2,3-b] pyrimidin-5(4*H*)-one **11a,b**

Diazodization of **1** in the presence of hydrochloric acid in acetic acid solution afforded diazonium chloride **6** that readily coupled with active chloromethylene compounds **7a,b** to yield the corresponding hydrazonoyl chlorides **8a,b**. Reacting **8a,b** with potassium thiocyanate gave the respective thiaziazolooyrimidinone derivatives **11a,b**. It is assumed that compound **11** is formed *via* initial nucleophilic displacement of halide with thiocyanate group forming the non-isolable products **9a**,**b** which undergo *in situ* nucleophilic addition of hydrazone-NH into the thiocyanate group to give the iminothiadiazoine derivatives **10a,b** followed by elimination of water molecule to give the final isolable products **11a,b**. [20] Similarly, coupling of phenacyl thiocyanate **12** with diazonium chloride **6** give the non- isolable acid **9c** which undergoes cyclization *via* dehydration to give compound **11c**. [20]



Scheme 3. Synthesis of 2-benzoyl-6,7,8,9-tetrahydrobenzo[4,5]thieno[2,3-d] [1,3,4]thiadiazolo [2,3-b]pyrimidin-5(4*H*)-one **11c**

III. Experimental

Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra were recorded in a Pye-Unicam SP300 instrument in potassium bromide discs. ^{1}H NMR and ^{13}C NMR spectra were recorded in a Varian Mercury VXR-300 spectrometer 300 MHz in $CHCl_3$ and the chemical shifts were related to TMS as standard solvent. Mass spectra were recorded in a GCMS-QP 1000 EX Shimadzu spectrometer, the ionizing voltage was 70 eV. Elemental analyses were carried out at the Microanalytical Laboratory of Cairo University, Giza, Egypt. 2-Amino-tetrahydrobenzo[b]thiophene-3-carboxylic acid **1**[17] and hydrazonoyl halides **2** [21, 22] and were prepared as reported in the literature.

Reaction of 2-amino-tetrahydrobenzo[b]thiophene-3-carboxylic acid (1) with hydrazonoyl halides (2). A mixture of 2-amino-tetrahydrobenzo[b]thiophene-3-carboxylic acid **1** (0.394g, 2 mmol) and hydrazonoyl halides **2** (2 mmol) in dioxane (20 mL) in the presence of TEA (0.3 mL) was stirred at room temperature till complete reaction (4 h, monitored by TLC). The mixture was evaporated under reduced pressure and the residue was collected by filtration and purified by crystallization from the proper solvent to give pure **3a-i**.

2-(2-Oxo-N'-phenylpropylhydrazonamido)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylic acid **(3a).** Yield 82%; yellow solid; mp 216 °C (from ethanol); ^{1}H NMR ($CDCl_3$): δ 1.37 (m, 4H), 2.50 (m, 4H), 2.61 (s, 3H, $COCH_3$), 7.21-7.37 (m, 5H, Ar-H), 8.24 (s, 1H, NH), 9.09 (s, 1H, NH), 12.35 (s, 1H, OH) ppm; IR (KBr): ν_{max} 3447-3149 (2NH, OH), 1708, 1674 (2C=O) cm^{-1}; MS, m/z (%) 357 (M^+, 100), 339 (50), 179 (25), 77 (80). Anal. Calcd. For $C_{18}H_{19}N_3O_3S$ (357.43): C, 60.49; H, 5.36; N, 11.76. Found: C, 60.25; H, 5.29; N, 11.48%.

2-(2-Oxo-N'-p-tolylpropylhydrazonamido)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylic acid **(3b).** Yield 78%; yellow solid; mp 136 °C (from ethanol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (m, 4H), 2.40 (s, 3H, Ar-CH_3), 2.52 (m, 4H), 2.68 (s, 3H, $COCH_3$), 7.13-7.27 (m, 4H, Ar-H), 8.25 (s, 1H, NH), 9.04 (s, 1H, NH), 12.24 (s, 1H, OH) ppm; IR (KBr): ν_{max} 3448-3242 (2NH, OH), 1706, 1662 (2C=O) cm^{-1}; MS, *m/z* (%) 371 (M^+, 28), 353 (30), 248 (23), 179 (25), 106 (100), 91 (70). Anal. Calcd. For $C_{19}H_{21}N_3O_3S$ (371.13): C, 61.44; H, 5.70; N, 11.31. Found: C, 61.37; H, 5.74; N, 11.22%.

2-(N'-(4-Chlorophenyl)-2-oxopropylhydrazonamido)-4,5,6,7-tetrahydrobenzo[b] thiophene-3-carboxylic acid **(3c).** Yield 84%; yellow solid; mp 146 °C (from dioxane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.36 (m, 4H), 2.53 (m, 4H), 2.71 (s, 3H, $COCH_3$), 7.23-7.31 (m, 4H, Ar-H), 8.21 (s, 1H, NH), 9.12 (s, 1H, NH), 12.29 (s, 1H, OH) ppm; IR (KBr): ν_{max} 3486-3244 (2NH, OH), 1743, 1665 (2C=O) cm^{-1}; MS, *m/z* (%) 393 (M^++2, 10), 391 (M^+, 25) 373 (38), 302 (23), 247 (58), 179 (70), 99 (87), 63 (100). Anal. Calcd. For $C_{18}H_{18}ClN_3O_3S$ (391.08): C, 55.17; H, 4.63; N, 10.72. Found: C, 55.09; H, 4.69; N, 10.48%.

2-(N'-(4-Nitrophenyl)-2-oxopropylhydrazonamido)-4,5,6,7-tetrahydrobenzo[b] thiophene-3-carboxylic acid **(3d).** Yield 86%; yellow solid; mp 187 °C (from dioxane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.40 (m, 4H), 2.41 (m, 4H), 2.83 (s, 3H, $COCH_3$), 7.26-8.27 (m, 4H, Ar-H), 8.61 (s, 1H, NH), 9.32 (s, 1H, NH), 12.19 (s, 1H, NH) ppm; IR (KBr): ν_{max} 3446-3175 (2NH, OH), 1699, 1653 (2C=O) cm^{-1}; MS, *m/z* (%) 402 (M^+, 50), 384 (65), 204 (48), 179 (48), 122 (50), 64 (100). Anal. Calcd. For $C_{18}H_{18}N_4O_5S$ (402.10): C, 53.72; H, 4.51; N, 13.92. Found: C, 53.56; H, 4.43; N, 13.77%.

2-(N'-(4-Methoxyphenyl)-2-oxopropylhydrazonamido)-4,5,6,7-tetrahydrobenzo[b] thiophene-3-carboxylic acid **(3e).** Yield 80%; dark yellow solid; mp 132 °C (from ethanol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.36 (m, 4H), 2.50 (s, 3H, Ar-OCH_3), 2.58 (m, 4H), 2.76 (s, 3H, $COCH_3$), 6.89-7.27 (m, 4H, Ar-H), 8.15 (s, 1H, NH), 9.01 (s, 1H, NH), 12.20 (s, 1H, OH) ppm; IR (KBr): ν_{max} 3446-3146 (2NH, OH), 1739, 1655 (2C=O) cm^{-1}; MS, *m/z* (%) 387 (M^+, 25), 369 (5), 204 (7) 179 (25), 122 (100), 65 (32). Anal. Calcd. For $C_{19}H_{21}N_3O_4S$ (387.13): C, 58.90; H, 5.46; N, 10.85. Found: C, 58.67; H, 5.46; N, 10.69%.

2-(2-Ethoxy-2-oxo-N'-phenylacetohydrazonamido)-4,5,6,7-tetrahydrobenzo[b] thiophene-3-carboxylic acid **(3f).** Yield 82%; yellow solid; mp 128 °C (from ethanol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.38 (t, 3H, CH_3), 1.85 (m, 4H), 2.70 (m, 4H), 4.31 (q, 2H, CH_2), 7.27-7.36 (m, 5H, Ar-H), 11.00 (s, 1H, NH), 11.24 (s, 1H, NH), 12.16 (s, 1H, OH) ppm; IR (KBr): ν_{max} 3445-3238 (2NH, OH), 1707, 1652 (2C=O) cm^{-1}; MS, *m/z* (%) 387 (M^+, 21), 369 (35), 296 (29), 204 (18), 105 (20), 65 (100). Anal. Calcd. For $C_{19}H_{21}N_3O_4S$ (387.13): C, 58.90; H, 5.46; N, 10.85. Found: C, 58.76; H, 5.34; N, 10.76%.

2-(2-Ethoxy-2-oxo-N'-p-tolylacetohydrazonamido)-4,5,6,7-tetrahydrobenzo[b] thiophene-3-carboxylic acid **(3g).** Yield 78%; yellow solid; mp 120 °C (from ethanol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, 3H, CH_3), 1.77

(m, 4H), 2.32 (s, 3H, Ar-H), 2.83 (m, 4H), 4.33 (q, 2H, CH_2), 7.12-7.27 (m, 4H, Ar-H), 11.01 (s, 1H, NH), 11.20 (s, 1H, NH), 12.23 (s, 1H, OH) ppm; IR (KBr): ν_{max} 3468-3170 (2NH, OH), 1699, 1652 (2C=O) cm^{-1}; MS, *m/z* (%) 401 (M^+, 18), 383 (51), 204 (26), 106 (100), 77 (64). Anal. Calcd. For $C_{20}H_{23}N_3O_4S$ (401.14): C, 59.83; H, 5.77; N, 10.47. Found: C, 59.69; H, 5.59; N, 10.32%.

2-(N'-(4-Chlorophenyl)-2-ethoxy-2-oxoacetohydrazon-amido)-4,5,6,7-tetrahydrobenzo [b]thiophene-3-carboxylic acid **(3h).** Yield 82%; yellow solid; mp 174 ^oC (from dioxane); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, 3H, CH_3), 1.81 (m, 4H), 2.69 (m, 4H) 4.33 (q, 2H, CH_2), 7.16 (d, 2H, Ar-H) 7.29 (d, 2H, Ar-H), 10.98 (s, 1H, NH), 11.28 (s, 1H, NH), 12.29 (s, 1H, OH) ppm; IR (KBr): ν_{max} 3447-3184 (2NH, OH), 1707, 1650 (2C=O) cm^{-1}; MS, *m/z* (%) 423 (M^++2, 10), 421 (M^+, 25), 403 (30), 330(44), 205 (24), 179 (41), 99 (100), 63 (53). Anal. Calcd. For $C_{19}H_{20}ClN_3O_4S$ (421.09): C, 54.09; H, 4.78; N, 9.96. Found: C, 54.00; H, 4.59; N, 9.78%.

2-(2-Ethoxy-N'-(4-nitrophenyl)-2-oxoacetohydrazon-amido)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylic acid **(3i).** Yield 80%; dark yellow solid; mp 174 ^oC (from ethanol); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, 3H, CH_3), 1.81 (m, 4H), 2.69 (m, 4H) 4.33 (q, 2H, CH_2), 7.16 (d, 2H, Ar-H) 7.29 (d, 2H, Ar-H), 10.98 (s, 1H, NH), 11.28 (s, 1H, NH), 12.16 (s, 1H, OH) ppm; IR (KBr): ν_{max} 3468-3274 (2NH, OH), 1701, 1680 (2C=O) cm^{-1}; MS, *m/z* (%) 434 (M^++2, 10), 432 (M^+, 25), 403 (30), 111 (100). Anal. Calcd. For $C_{19}H_{20}N_4O_6S$ (432.11): C, 52.77; H, 4.66; N, 12.96. Found: C, 52.63; H, 4.43; N, 12.76%.

Cyclization of 3a,b,f,g

A mixture of **3a,b,f,g** (1 mmol) and 1,1`-carbonyldiimidazole (0.2g) in dioxane (10 mL) was refluxed for 2 h. Progress of the reaction was monitored by TLC. The reaction mixture was cooled and poured into crushed ice, acidified with dilute hydrochloric acid. The precipitate so obtained was filtered, washed with water, dried and recrystallized from the proper solvent to give **4a,b,f,g.**

2-Acetyl-4-phenyl-6,7,8,9-tetrahydro-1H-benzo[4,5] thieno[2,3-e][1,2,4]triazepin-5(4H)-one **(4a).** Yield 80%; yellow solid; mp 186 ^oC (from ethanol); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.37 (m, 4H), 2.51 (m, 4H), 2.61 (s, 3H, $COCH_3$), 7.13-7.27 (m, 5H, Ar-H), 9.12 (s, 1H, NH) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.5, 19.6, 20.1, 20.8, 22.3 101.5, 113.2, 116.0, 120.8, 124.6, 131.0, 138.3, 141.8, 147.6, 168.2, 186.5 ppm; IR (KBr): ν_{max} 3323 (NH), 1702, 1652 (2C=O) cm^{-1}; MS, m/z (%) 339 (M^+, 24), 179 (25), 93 (43), 77 (86), 65 (100). Anal. Calcd. For $C_{18}H_{17}N_3O_2S$ (339.10): C, 63.70; H, 5.05; N, 12.38. Found: C, 63.56; H, 5.12; N, 12.23%.

2-Acetyl-4-(p-tolyl)-6,7,8,9-tetrahydro-1H-benzo[4,5] thieno[2,3-e][1,2,4]triazepin-5(4H)-one **(4b).** Yield 77%; yellow solid; mp 177 ^oC (from ethanol \ dioxane); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.32 (m, 4H), 2.40 (s, 3H, Ar-CH_3), 2.52 (m, 4H), 2.61 (s, 3H, $COCH_3$), 7.17-7.43 (m, 4H, Ar-H), 9.13 (s, 1H, NH) ppm; IR (KBr): ν_{max} 3273 (NH), 1703, 1663 (2C=O) cm^{-1}; MS, *m/z* (%) 353 (19), 179 (16), 106 (100), 77 (60). Anal. Calcd. For $C_{19}H_{19}N_3O_2S$ (353.12): C, 64.57; H, 5.42; N, 11.89. Found: C, 64.35; H, 5.48; N, 11.77%.

2-Ethoxycarbonyl-4-phenyl-6,7,8,9-tetrahydro-1H-benzo [4,5]thieno[2,3-e][1,2,4] triazepin-5(4H)-one **(4f).** Yield 78%; yellow solid; mp 172 ^oC (from ethanol \ dioxane); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.39 (t, 3H, CH_3), 1.85 (m, 4H), 2.70 (m, 4H), 4.31 (q, 2H, CH_2), 7.27-7.36 (m, 5H, Ar-H), 11.00 (s, 1H, NH) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.7, 19.4, 20.6, 20.9, 22.1, 58.4, 113.5, 114.6, 117.3, 123.9, 125.4, 135.0, 138.0, 141.8, 147.6, 167.5, 173.0 ppm; IR (KBr): ν_{max} 3286 (NH), 1707, 1651 (2C=O) cm^{-1}; MS, *m/z* (%) 369 (M^+, 10), 296 (26), 204 (16), 92 (56), 65 (100). Anal. Calcd. For $C_{19}H_{19}N_3O_3S$ (369.11): C, 61.77; H, 5.18; N, 11.37. Found: C, 61.54; H, 5.10; N, 11.15%.

2-Ethoxycarbonyl-4-(p-tolyl)-6,7,8,9-tetrahydro-1H-benzo[4,5]thieno[2,3-e][1,2,4] triazepin-5(4H)-one **(4g).** Yield 80%; yellow solid; mp 192 ^oC (from dioxane); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, 3H, CH_3), 1.77 (m, 4H), 2.32 (s, 3H, Ar-H), 2.83 (m, 4H), 4.33 (q, 2H, CH_2), 7.12-7.27 (m, 4H, Ar-H), 11.01 (s, 1H, NH) ppm; IR (KBr): ν_{max} 3298(NH), 1698, 1652 (2C=O) cm^{-1}; MS, *m/z* (%) 383 (M^+, 14), 278 (24), 204 (28), 106 (100), 51 (20). Anal. Calcd. For $C_{20}H_{21}N_3O_3S$ (383.13): C, 62.64; H, 5.52; N, 10.96. Found: C, 62.43; H, 5.42; N, 10.69%.

IV. General procedures for preparation of compounds 8a,b and 11c

A solution of **1** (0.394g, 2 mmol) in acetic acid (8 mL), was treated with concentrated hydrochloric acid (6 mL) and sodium nitrite (0.69 g, 2 mmol) at 0 °C, This mixture was added gradually with stirring, to a cooled solution of active chloromethylene compounds **7a,b** or phenacyl thiocyanate **12** (2 mmol) in ethanol (10 mL) and sodium acetate (1.0 g). After complete addition, the reaction mixture was kept at room temperature for one hour. The solid product, so formed, was collected by filtration.

2-(2-(1-Chloro-2-oxopropylidene)hydrazinyl)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylic acid **(8a).** Yield 74%; yellow solid; mp 143 ^oC (from ethanol); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.85 (m, 4H), 2.31 (t, 3H, CH_3), 2.70 (m, 4H), 11.00 (s, 1H, NH), 12.03 (s, 1H, OH)

ppm; IR (KBr): ν_{max} 3482 - 3341 (NH, OH), 1718, 1703 (2C=O) cm^{-1}; MS, *m/z* (%) 300 (M^+, 100), 197(50), 105 (20), 53 (73). Anal. Calcd. For $C_{12}H_{13}ClN_2O_3S$ (300.03): C, 47.92; H, 4.36; N, 9.31. Found: C, 47.75; H, 4.47; N, 9.12%.

2-(2-(1-Chloro-2-ethoxy-2-oxoethylidene)hydrazinyl)-4,5,6,7-tetrahydrobenzo[b] thiophene-3-carboxylic acid **(8b).** Yield 82%; yellow solid; mp 135 ^oC (dioxane); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.33 (t, 3H, CH_3), 1.82 (m, 4H), 2.73 (m, 4H), 4.21 (q, 2H, CH_2), 11.04 (s, 1H, NH), 11.83 (s, 1H, OH) ppm; IR (KBr): ν_{max} 3479 - 3338 (NH, OH), 1712, 1698 (2C=O) cm^{-1}; MS, *m/z* (%) 330 (M^+, 100), 197 (42), 105 (43), 53 (67). Anal. Calcd. For $C_{13}H_{15}ClN_2O_4S$ (330.04): C, 47.20; H, 4.57; N, 8.47. Found: C, 47.12; H, 4.35; N, 8.43%.

2-Benzoyl-6,7,8,9-tetrahydrobenzo[4,5]thieno[2,3-d][1,3,4]thiadiazolo[2,3-b] pyrimidin-5(4H)-one **(11c).** Yield 78%; yellow solid; mp 195 ^oC (from ethanol \ dioxane); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.80 (m, 4H), 2.74 (m, 4H), 7.21-7.41 (m, 5H, Ar-H) ppm; IR (KBr): ν_{max} 1694, 1679 (2C=O) cm^{-1}; MS, *m/z* (%) 367 (M^+, 25), 77 (100). Anal. Calcd. For $C_{18}H_{13}N_3O_2S_2$ (367.04): C, 58.84; H, 3.57; N, 11.44. Found: C, 58.67; H, 3.45; N, 11.24%.

V. Reaction of hydrazonoyl chlorides 9a,b with potassium thiocyanate

To a suspension of **9a,b** (1 mmol mol) in ethanol (20 ml) a solution of potassium thiocyanate (1 g, 1.5 mmol) in water (5 ml) was added. The mixture was stirred for 4 hours at room temperature, and then left overnight. The crude product formed was collected, washed with water and crystallized from ethanol.

2-Acetyl-6,7,8,9-tetrahydrobenzo[4,5]thieno[2,3-d][1,3,4]thiadiazolo[2,3-b] pyrimidin-5(4H)-one **(11a).** Yield 72%; yellow solid; mp 218 ^oC; ^1H NMR ($CDCl_3$, 300 MHz) δ = 2.30 (t, 3H, CH_3), 1.82 (m, 4H), 2.76 (m, 4H), 7.12-7.43 (m, 5H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.2, 18.9, 20.8, 20.9, 22.4, 113.5, 114.6, 123.4, 134.0, 140.8, 147.6, 164.8, 189.4 ppm; IR (KBr): ν_{max} 1703, 1673 (2C=O) cm^{-1}; MS, *m/z* (%) 305 (M^+, 54), 262 (100), 105 (29). Anal. Calcd. For $C_{13}H_{11}N_3O_2S_2$ (305.03): C, 51.13; H, 3.63; N, 13.76. Found: C, 51.04; H, 3.43; N, 13.55%.

Ethyl 6,7,8,9-tetrahydro-5-oxo-4H-benzo[4,5]thieno[2,3-d][1,3,4]thiadiazolo[2,3-b] pyrimidine-2-carboxylate **(11b).** Yield 80%; yellow solid; mp 183 ^oC; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.32 (t, 3H, CH_3), 1.81 (m, 4H), 2.77 (m, 4H), 4.23 (q, 2H, CH_2) ppm; IR (KBr): ν_{max} 1690, 1678 (2C=O) cm^{-1}; MS, *m/z* (%) 335 (M^+, 34), 262 (100), 105 (44). Calcd. For $C_{14}H_{13}N_3O_3S_2$ (335.04): C, 50.13; H, 3.91; N, 12.53. Found: C, 50.10; H, 3.76; N, 12.36%.

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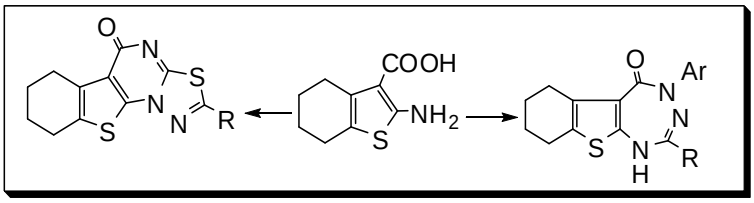
Graphical Abstract

Utility of 2-amino-4,5,6,7-tetrahydrobenzo[b] thiophene-3-carboxylic acid in the synthesis of novel thieno[2,3-b][1,2,4]triazepinones and thieno[2,3-d] [1,3,4] thiadiazolo[2,3-b]pyrimidinones



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