Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 80 (4) S119–S121 (2015) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Novel one-pot process for the synthesis of ethyl 2-imino-4--methyl-2,3-dihydrothiazole-5-carboxylates

HAMID BEYZAEI*, REZA ARYAN and HADI MOGHADAS

Department of Chemistry, Faculty of Science, University of Zabol, Zabol 9861335856, Iran

J. Serb. Chem. Soc. 80 (4) (2015) 453–458

PHYSICAL, ANALYTICAL AND SPECTRAL DATA OF THE SYNTHESIZED COMPOUNDS

Ethyl 3-amino-2-imino-4-methyl-2,3-dihydrothiazole-5-carboxylate ***(4a)***. Yield: 50 %; white crystals; m.p.: 285–286 °C; Anal. Calcd. for $C_7H_{11}N_3O_2S$: C, 41.78; H, 5.51; N, 20.88; S, 15.93 %. Found: C, 41.82; H, 5.56; N, 20.86, S, 15.85 %; IR (KBr, cm^{-1}): 1585 (C=C stretching of thiazole ring), 1623 (C=N stretching of imine group), 1693 (C=O stretching of CO_2Et group), 3467, 3434 (NH stretching of imine and primary amine groups); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.24 (3H, *t*, *J* = 7.1 Hz, CH_3), 2.07 (3H, *s*, =CCH_3), 4.16 (2H, *q*, *J* = 7.1 Hz, OCH_2), 7.91 (2H, *s*, NH_2, D_2O exchangeable), 10.16 (1H, *s*, NH, D_2O exchangeable); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 169.91 (C=O), 161.32 (=**C**CH_3), 159.99 (C=NH), 106.65 (**C**=CCH_3), 59.73 (OCH_2), 19.91 (C=C**C**H_3), 14.44 (CH_2**C**H_3).

Ethyl 2-imino-4-methyl-3-(phenylamino)-2,3-dihydrothiazole-5-carboxylate ***(4b)***. Yield: 55 %; white crystals; Decomp. 280–281 °C; Anal. Calcd. for $C_{13}H_{15}N_3O_2S$: C, 56.30; H, 5.45; N, 15.15; S, 11.56 %. Found: C, 56.24; H, 5.52; N, 15.18, S, 11.48 %; IR (KBr, cm^{-1}): 1406, 1545 (C=C stretching of aromatic ring), 1611 (C=C– stretching of thiazole ring), 1666 (C=N stretching of imine group), 1709 (C=O stretching of CO_2Et group), 3349 (NH stretching of imine and secondary amine); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.30 (3H, *t*, *J* = 7.1 Hz, CH_3), 2.09 (3H, *s*, =CCH_3), 4.27 (2H, *q*, *J* = 7.1 Hz, OCH_2), 7.43, 7.72 (3H, *m*, 2H, *d*, *J* = 10.1 Hz, aromatic), 7.81 (1H, *s*, N**H**Ph, D_2O exchangeable), 10.06 (1H, *s*, C=NH, D_2O exchangeable); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 162.44 (C=O), 161.44 (=**C**CH_3), 157.06 (C=NH), 145.85, 130.72, 123.05, 115.79 (aromatic), 106.93 (**C**=CCH_3), 60.96 (OCH_2), 17.31 (=C**C**H_3), 14.13 (CH_2**C**H_3).

* Corresponding author. E-mail: hbeyzaei@yahoo.com

*Ethyl 3-((2,4-dinitrophenyl)amino)-2-imino-4-methyl-2,3-dihydrothiazole-5-carboxylate (**4c**)*. Yield: 83 %; red crystals; Decomp. 218–219 °C; Anal. Calcd. for $C_{13}H_{13}N_5O_6S$: C, 42.51; H, 3.57; N, 19.07; S, 8.73 %. Found: C, 42.55; H, 3.53; N, 19.14, S, 8.67 %; IR (KBr, cm^{-1}): 1338, 1427 (N–O stretching of NO_2 group), 1498, 1594 (C=C stretching of aromatic and thiazole rings), 1613 (C=N stretching of imine group), 1715 (C=O stretching of CO_2Et group), 3089, 3305 (NH stretching of imine and secondary amine); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.26 (3H, *t*, *J* = 7.1 Hz, CH_3), 2.55 (3H, *s*, =CCH_3), 4.26 (2H, *q*, *J* = 7.1 Hz, OCH_2), 8.30, 8.33, 9.03 (1H, *d*, *J* = 2.6 Hz, 1H, *d*, *J* = 2.6 Hz, 1H, *d*, *J* = 9.3 Hz, aromatic), 8.95 (1H, *s*, N**H**Ph, D_2O exchangeable), 11.44 (1H, *s*, C=NH, D_2O exchangeable); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 168.65 (C=O), 161.83 (C=**C**CH_3), 159.11 (C=NH), 148.99, 143.07, 138.47, 130.25, 122.79, 116.27 (aromatic), 107.95 (**C**=CCH_3), 62.81 (OCH_2), 14.00 (CH_2**C**H_3), 11.31 (=C**C**H_3).

*Ethyl 3-benzamido-2-imino-4-methyl-2,3-dihydrothiazole-5-carboxylate (**4d**)*. Yield: 68 %; white crystals; m.p.: 200–201 °C; Anal. Calcd. for $C_{14}H_{15}N_3O_3S$: C, 55.07; H, 4.95; N, 13.76; S, 10.50 %. Found: C, 55.00; H, 5.01; N, 13.79, S, 10.45 %; IR (KBr, cm^{-1}): 1463, 1509 (C=C stretching of aromatic and thiazole rings), 1601 (C=N stretching of imine group), 1647 (C=O stretching of CONH group), 1669 (C=O stretching of CO_2Et group), 3442 (NH stretching of imine and amide); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.23 (3H, *t*, *J* = 7.0 Hz, CH_3), 2.12 (3H, *s*, =CCH_3), 4.15 (2H, *q*, *J* = 7.0 Hz, OCH_2), 7.53–7.98 (5H, *m*, aromatic), 10.72 (1H, *s*, C=NH, D_2O exchangeable), 11.00 (1H, *s*, CONH, D_2O exchangeable); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 168.47 (CO_2Et), 165.11 (CONH), 161.35 (=**C**CH_3), 159.72 (C=NH), 132.14, 131.92, 128.53, 127.60 (aromatic), 106.08 (**C**=CCH_3), 59.67 (OCH_2), 16.96 (=C**C**H_3), 14.44 (CH_2**C**H_3).

*Ethyl 3-(4-hydroxybenzamido)-2-imino-4-methyl-2,3-dihydrothiazole-5-carboxylate (**4e**)*. Yield: 48 %; yellow crystals; m.p.: 185–186 °C; Anal. Calcd. for $C_{14}H_{15}N_3O_4S$: C, 52.33 %; H, 4.71; N, 13.08; S, 9.98 %. Found: C, 52.39; H, 4.66; N, 13.15, S, 9.90 %; IR (KBr, cm^{-1}): 1472, 1506 (C=C– stretching of aromatic and thiazole rings), 1609 (C=N stretching of imine group), 1674 (C=O stretching of CONH group), 1702 (C=O stretching of CO_2Et group), 3419 (NH stretching of imine and amide); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.24 (3H, *t*, *J* = 7.0 Hz, CH_3), 2.16 (3H, *s*, =CCH_3), 4.17 (2H, *q*, *J* = 7.0 Hz, OCH_2), 6.93, 7.80 (2H, *d*, *J* = 8.2 Hz, 2H, *d*, *J* = 8.2 Hz, aromatic), 8.15 (1H, *s*, OH, D_2O exchangeable), 10.13 (1H, *s*, C=NH, D_2O exchangeable), 10.59 (1H, *s*, CONH, D_2O exchangeable); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 169.85 (CO_2Et), 167.73 (CONH), 163.03 (=**C**CH_3), 161.58 (C=NH), 159.73, 132.32, 129.41, 114.93 (aromatic), 106.63 (**C**=CCH_3), 60.40 (OCH_2), 22.41 (=C**C**H_3), 14.35 (CH_2**C**H_3).

*Ethyl 3-acetamido-2-imino-4-methyl-2,3-dihydrothiazole-5-carboxylate (**4f**)*. Yield: 60 %; white crystals; m.p.: 179–180 °C; Anal. Calcd. for $C_9H_{13}N_3O_3S$: C, 44.43; H, 5.39; N, 17.27; S, 13.18 %. Found: C, 44.39; H, 5.37; N, 17.33, S, 13.14 %; IR (KBr, cm^{-1}): 1590 (C=C stretching of aromatic and thiazole rings), 1616 (C=N stretching of imine group), 1673 (C=O stretching of CONH group), 1703 (C=O stretching of CO_2Et group), 3253, 3382 (NH stretching of imine and amide); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.23 (3H, *t*, J = 7.1 Hz, CH_3), 1.91 (3H, *s*, $=CCH_3$), 2.43 (3H, *s*, $COCH_3$), 4.16 (2H, *q*, J = 7.1 Hz, OCH_2), 10.02 (1H, *s*, C=NH, D_2O exchangeable), 10.39 (1H, *s*, CONH, D_2O exchangeable); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 168.99 (CO_2Et), 167.72 (CONH), 161.79 ($=\mathbf{C}CH_3$), 161.49 (C=NH), 106.86 ($\mathbf{C}=CCH_3$), 60.03 (OCH_2), 20.45 ($=C\mathbf{C}H_3$), 17.29 ($CO\mathbf{C}H_3$), 14.24 ($CH_2\mathbf{C}H_3$).