

HETEROCYCLES, Vol. 91, No. 1, 2015, pp. 113 - 122. © 2015 The Japan Institute of Heterocyclic Chemistry
Received, 10th November, 2014, Accepted, 9th December, 2014, Published online, 19th December, 2014
DOI: 10.3987/COM-14-13122

ONE-POT, THREE COMPONENT SYNTHESIS OF THIAZOL-2(3*H*)-IMINES USING POLY(4-VINYLPYRIDINE) AS AN EFFICIENT REUSABLE HETEROGENEOUS BASIC CATALYST

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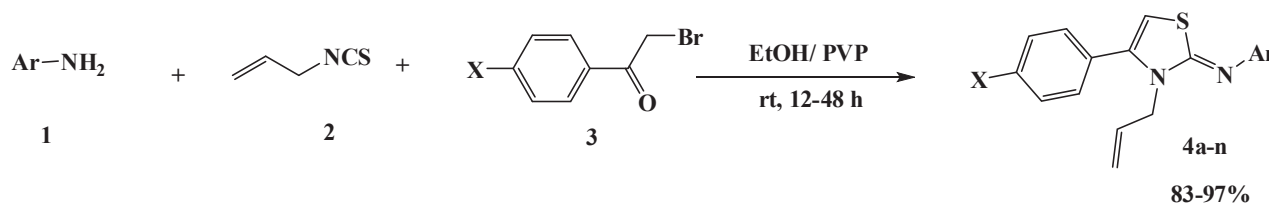
Abstract – Poly(4-vinylpyridine) is reported as a green, efficient and reusable basic catalyst for the synthesis of thiazol-2(3*H*)-imines under one-pot, three component reaction conditions. This simple method produces the products at room temperature in excellent yields (83-97%). Furthermore, this catalyst can be recovered by simple filtration and recycled up to four consecutive runs without any loss of its efficiency

One-pot, multi component reactions (MCR) are highly powerful and useful synthetic tools in synthetic chemistry and drug discovery. MCRs improved economic and environmental aspects of synthetic chemistry as a result of decreasing purification steps without isolating any intermediate.¹⁻⁵ thiazol-2(3*H*)-imines display a central role in agriculture and medicinal chemistry,^{6, 7} which exhibit very biological activities such as antimicrobial,⁸ bleaching herbicidal,⁹ anti-inflammatory,¹⁰ and antidepressant activities.¹¹ Moreover, these moieties have been found in insecticides and plant growth regulators.^{12, 13} Several alternative methods have been developed for synthesis of thiazolidines and thiazolines have been developed, which include intramolecular cyclization of *n*-(2-hydroxyethyl)thiourea derivatives in the presence of diethyl azodicarboxylate,¹⁴ condensation of α -haloketones with thiourea,¹⁵ base-catalyzed cyclization of 1-(fluorobenzoyl)-3-(fluorophenyl)thiourea with 2-bromoacetone in aqueous media¹⁶ and condensation of carbonyl compounds with thiourea and 1,3-disubstituted thiourea using 1,1'-(ethane-1,2-diyl)dipyridinium bistr bromide (EDPBT) as brominating agent.¹⁷ For example, Balalaie *et al.* reported the synthesis of 2-aminothiazole and 2-iminothiazolidine derivatives catalyzed by diammonium hydrogen phosphate (DAP) and 1,4-diazabicyclo[2.2.2]octane (DABCO) in

aqueous-phase.¹⁸ Sravanthi *et al.* reported the synthesis of novel *bis*-thiazol-2-ylidenes derivatives in ultrasonic condition.¹⁹ Also, with excellent regioselectivity, Mamaghani and co-workers have obtained substituted iminothiazolines as the superior regioisomer through cyclization of unsymmetrical thioureas.²⁰ In our previous studies, we have reported the synthesis of 3*H*-thiazoles from allylisothiocyanate, aryl amines and phenacylbromide in the presence of triethylamine under reflux conditions.²¹ On the other hand, heterogeneous basic catalysts are desirable in synthetic organic chemistry and green processes due to some potential advantages such as facile recovery, eco-benign and easy product isolation.^{22, 23}

Poly(4-vinylpyridine)-supported reagents are useful tools for organic reactions including reductions, oxidations and halogenations.²⁴ Bhanage *et al.* have reported the synthesis of dimethyl carbonate *via* transesterification of ethylene carbonate with methanol using poly(4-vinylpyridine) (PVP) as a base catalyst.²⁵ recently, Shirini *et al.* used poly(4-vinylpyridine) in chemoselective *O*-TMS protection of alcohols and phenols and *N*-*boc* protection of amines.²⁶

Herein, we report the application of PVP as an efficient recyclable basic catalyst in the regioselective synthesis of thiazol-2(3*H*)-imines from arylamines, allylisothiocyanate and various phenacyl bromides (Scheme 1).



Ar = 3-MeOC₆H₄, 4-MeOC₆H₄, 3,4-di-MeOC₆H₃, 4-EtOC₆H₄, 4-EtC₆H₄, 1-naphthyl, 2-MeOC₆H₄, 3-OHC₆H₄, 4-MeC₆H₄, 3-ClC₆H₄, 4-ClC₆H₄, 4-IC₆H₄
X = H, OMe, Br

Scheme 1. Synthesis of 3-allyl-2-(arylimino)-4-aryl-3*H*-thiazole derivatives

In order to achieve the optimal reaction conditions for the synthesis of thiazol-2(3*H*)-imines, synthesis of **4b** was chosen as a model, and studied under several conditions (Table 1).

Table 1. Effect of various catalysts in the synthesis of **4b**

Catalyst ^a	Conditions	Time (h)	Yield (%) ^b
triethylamine	reflux	2	76
DBU ^c	reflux	8	60
PVP	room temp.	20	93

^aAmount of the catalyst: 0.02 g/1 mmol substrate. ^bIsolated yields.
^c1,8-Diazabicyclo[5.4.0]undec-7-ene

Among the tested basic catalysts, the best result was achieved by carrying out the reaction in the presence of 0.02 g of PVP at room temperature in ethanol. As shown in Table 2, under the optimized condition, thiazol-2(3*H*)-imines **4a-n** were obtained in high yields (83-97%).

Table 2. Synthesis of thiazol-2(3*H*)-imine derivatives catalyzed by PVP

Product	X	Ar	Time (h)	Yield ^a (%)
4a	H	3-MeOC ₆ H ₄	24	91
4b	H	4-MeOC ₆ H ₄	20	93
4c	H	3,4-diMeOC ₆ H ₃	20	94
4d	H	4-EtOC ₆ H ₄	18	96
4e	H	4-EtC ₆ H ₄	20	90
4f	H	1-naphthyl	30	87
4g	H	3-HOC ₆ H ₄	36	85
4h	OMe	1-naphthyl	48	83
4i	OMe	4-MeC ₆ H ₄	40	85
4j	Br	4-MeC ₆ H ₄	18	89
4k	Br	4-EtOC ₆ H ₄	12	97
4l	Br	4-MeOC ₆ H ₄	15	94
4m	Br	4-IC ₆ H ₄	18	92
4n	Br	4-ClC ₆ H ₄	18	91

^a Isolated yield

The results revealed that an electronic effect by the *p*-substituent (X) of phenacyl bromide was observed. An electron-withdrawing group (Br) enhanced the reaction rate, while the substrate with an electron-donating substituent (OMe) needed longer reaction time.

All products were cleanly isolated by filtration and recrystallization from a mixture of ethanol/water (1: 1 v/v). The structures of compounds (**4a-n**) were fully confirmed by spectral (¹H-NMR, ¹³C-NMR, IR) and elemental analyses. The appearance of a singlet in the region of 5-6 ppm in the ¹H-NMR spectra which correspond to the H at the 5-position of the thiazole ring confirms skeleton of thiazol-2(3*H*)-imines. The structure of **4d** was also confirmed by single-crystal X-ray crystallography.^{27,28} The compound crystallized in monoclinic system with space group P2₁/n, a = 5.7886(4), b = 24.3201(19), c = 12/6329(11)Å, β = 94.450(2)°, Z = 4 and V = 1173.1(2)Å³. The molecular structure with the numbering scheme of the compound is shown in Figure 1.

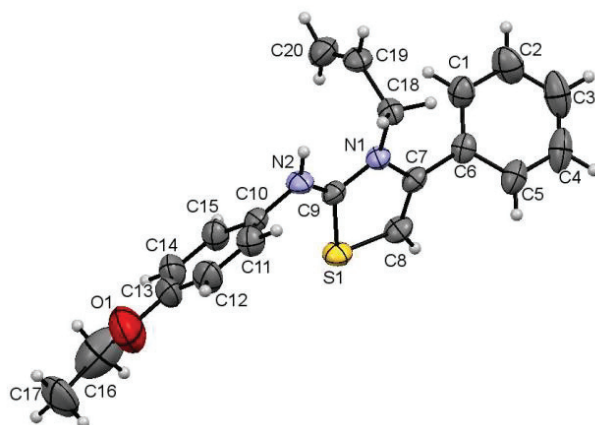


Figure 1. Molecular structure of compound **4d** with numbering scheme drawn at 50% probability ellipsoid

The central five-membered N1/C7/C8/S1/C9 thiazole ring, (C1-C6) and (C10-C15) benzene rings are planar with maximum deviation of 0.016(4)Å for C10 atom from the least square plane of the benzene ring. The central thiazole ring makes dihedral angle with the (C10-C15) ring of 61.6(2)° and 46.5(2)° with (C1-C6) ring. The two benzene rings are perpendicular to each other at an angle of 73.2(2)°. The propenyl group attached at the thiazole N1 atom is also vertical to the thiazole ring with C8-C7-N1-C18 and S1-C9-N1-C18 torsional angles of 165.4(4) and 167.2(3)°, respectively. The C7-C8 and C19-C20 are double bonds with bond length of 1.333(6) and 1.29(7)°, respectively. Other bond lengths and angles are in normal ranges. In the crystal structure the molecule is stabilized by C8-H8A...N2 intermolecular hydrogen bond (D-H=0.93Å, H...A = 2.43Å, D...A = 3.359(5)Å D-H...A = 175°) forming a one dimensional chain along a-axis and C20-H20A...π bond with H20A...(C1-C6),(-1+x, y,z) centroid distance of 2.82Å and D-H...centroid angle 146°.

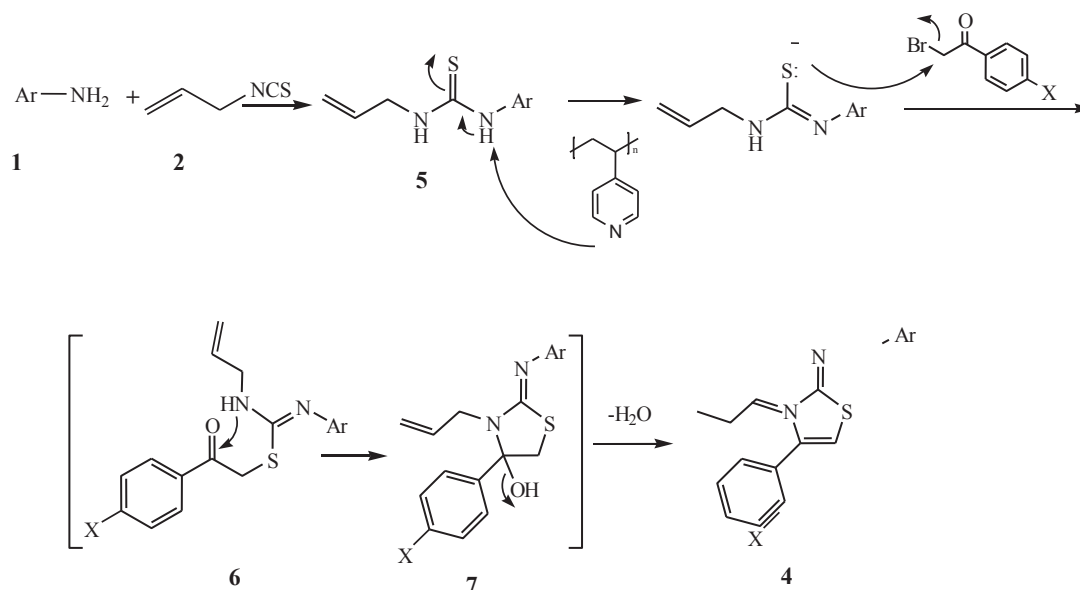
In addition, recyclability of the catalyst is significant. To investigate these properties for PVP as a basic catalyst, the synthesis of **4k** was selected as the model (Table 2). After completion of the reaction, the catalyst was filtered, washed with aqueous Na₂CO₃ (10%), distilled water and hot acetone. Then catalyst was dried and used for another consecutive run. The results showed that during four consecutive runs the activity of PVP was the same as the freshly used catalyst (Table 3).

Table 3. Recyclability of PVP in the synthesis of thiazol-2(3*H*)-imine derivatives

Run	1	2	3	4
Time (h)	24	24	28	36
Yield (%) ^a	97	92	87	87

^a Isolated yield

The plausible mechanism for the formation of 3-allyl-2-(aryl imino)-4-aryl-3*H*-thiazoles (**4a-n**) were outlined in Scheme 2.



Scheme 2. Plausible mechanism for the formation of **4a-n**

EXPERIMENTAL

Materials and methods: All chemicals were purchased from Merck, Fluka and Aldrich chemical companies and used without further purification. All yields refer to isolated products. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. FT-IR spectra were recorded on a Shimadzu 8400S spectrophotometer. The NMR spectra were recorded on a Bruker AVANCE DMX400 spectrometer, operating at 400 MHz (¹H NMR) and 100 MHz (¹³C NMR). The chemical shift values are expressed in ppm relative to TMS as an internal standard. Elemental analyses were recorded with a CHN model 2400 Perkin-Elmer and agreed with the calculated values. Poly(4-vinylpyridine) [~60 mesh, average M_w: 60,000] purchased from Fluka Chemical company.

General procedure for synthesis of 3-allyl-2-(aryl imino)-4-aryl-3*H*-thiazoles. Arylamine (1 mmol), allyl isothiocyanate (AITC) (1 mmol) and various phenacyl bromides (1 mmol) were added to a round-bottom flask containing EtOH (10 mL). Polyvinylpyridine (0.02 g) was added at once to this mixture. The mixture was stirred at room temperature for specified time according to Table 1. The progress of the reaction was monitored by TLC. After completion, PVP was filtered, washed with aqueous Na₂CO₃ (10%), distilled water and hot acetone and recovered to use subsequently. The remained solution was poured into ice bath. Then solid residue was filtered washed with aqueous Na₂CO₃ (10%), distilled water and recrystallized from EtOH/H₂O (1: 1 v/v) to give a pure product.

Recycling of the catalyst. After filtration, the catalyst was washed with aqueous Na₂CO₃ (10%), distilled water and hot acetone and then was dried under vacuum at 50 °C before the next run.

Spectral data of compounds:

3-Allyl-2-(3'-methoxyphenylimino)-4-phenyl-3H-thiazole (4a): Yield 91%; white solid; mp 145-146 °C; ¹H-NMR (CDCl₃, 400 MHz): δ_H: 3.84 (s, 3H), 5.18 (d, 1H, *J* = 17.2 Hz), 5.32 (d, 1H, *J* = 10.4 Hz), 5.42 (d, 2H, *J* = 4.8 Hz), 5.85-5.95 (m, 1H), 6.66 (s, 1H), 6.91 (dd, 1H, *J* = 8.4, 2.4 Hz), 7.19 (dd, 1H, *J* = 7.8, 2.4 Hz), 7.31-7.40 (m, 4H), 7.52 (t, 2H, *J* = 7.2 Hz), 7.58 (dd, 1H, *J* = 8.4, 7.8 Hz) ppm; ¹³C-NMR (CDCl₃, 100 MHz): δ_c: 51.0, 55.7, 104.2, 109.6, 114.8, 115.4, 118.9, 127.8, 129.3, 129.4, 129.6, 130.7, 131.1, 138.8, 143.5, 160.8, 168 ppm; FT-IR (KBr, cm⁻¹): 3108, 2997, 2939, 2835, 1612, 1593, 1576, 1490, 1288, 1157, 1055, 1016, 996, 783, 698. Anal. Calcd for C₁₉H₁₈N₂OS (322.41): C, 70.78; H, 5.62; N, 8.68. Found: C, 70.76; H, 5.65; N, 8.70%.

3-Allyl-2-(4'-methoxyphenylimino)-4-phenyl-3H-thiazole (4b): Yield 93%; white solid; mp 145-146 °C; ¹H-NMR (CDCl₃, 400 MHz): δ_H: 3.83 (s, 3H), 4.45 (d, 2H, *J* = 3.6 Hz), 5.04 (d, 1H, *J* = 17.2 Hz), 5.17 (d, 1H, *J* = 10.4 Hz), 5.78 (s, 1H), 5.89-5.97 (m, 1H), 6.92 (d, 2H, *J* = 8.6 Hz), 7.03 (d, 2H, *J* = 8.6 Hz), 7.40-7.48 (m, 5H) ppm; ¹³C-NMR (CDCl₃, 100 MHz): δ_c: 47.5, 55.4, 95.5, 114.6, 116.4, 122.4, 128.5, 128.9, 129.1, 131.7, 132.8, 140.4, 145.2, 155.0, 159.6 ppm; FT-IR (KBr, cm⁻¹): 3110, 2995, 2939, 2836, 1610, 1592, 1571, 1490, 1361, 1281, 1057, 950, 781. Anal. Calcd for C₁₉H₁₈N₂OS (322.41): C, 70.78; H, 5.62; N, 8.68. Found: 70.80; H, 5.59; N, 8.72%.

3-Allyl-2-(3',4'-dimethoxyphenylimino)-4-phenyl-3H-thiazole (4c): Yield 94%; white solid; mp 145-146 °C; ¹H-NMR (CDCl₃, 400 MHz): δ_H: 3.88 (s, 6H), 4.44 (d, 2H, *J* = 4.4 Hz), 5.04 (d, 1H, *J* = 17.2 Hz), 5.17 (d, 1H, *J* = 10.4 Hz), 5.78 (s, 1H), 5.89-5.98 (m, 1H), 6.66 (d, 1H, *J* = 8.8 Hz), 6.68 (s, 1H), 6.86 (d, 1H, *J* = 8.8 Hz), 7.38-7.46 (m, 5H) ppm; ¹³C-NMR (CDCl₃, 100 MHz): δ_c: 50.1, 51.2, 57.2, 103.4, 116.5, 117.3, 122.4, 128.3, 128.7, 128.9, 130.3, 131.8, 136.7, 141.1, 145.6, 150.1, 155.6, 163.2 ppm; FT-IR (KBr, cm⁻¹): 3096, 2976, 2926, 1614, 1560, 1458, 1238, 1058, 954, 900, 698, 605. Anal. Calcd for C₂₀H₂₀N₂O₂S (352.43): C, 68.16; H, 5.71; N, 7.94. Found: C, 68.19; H, 5.73; N, 7.97%.

3-Allyl-2-(4'-ethoxyphenylimino)-4-phenyl-3H-thiazole (4d): Yield 96%; white solid; mp 145-146 °C; ¹H-NMR (CDCl₃, 400 MHz): δ_H: 1.44 (t, 3H, *J* = 6.8 Hz), 4.05 (q, 2H, *J* = 6.8 Hz), 4.45 (d, 2H, *J* = 4.4 Hz), 5.05 (d, 1H, *J* = 17.2 Hz), 5.17 (d, 1H, *J* = 10.4 Hz), 5.78 (s, 1H), 5.89-5.98 (m, 1H), 6.91 (d, 2H, *J* = 8.4 Hz), 7.02 (d, 2H, *J* = 8.4 Hz), 7.43-7.46 (m, 5H) ppm; FT-IR (KBr, cm⁻¹): 2972, 2922, 1616, 1541, 1506, 1458, 1315, 1236, 1116, 1051, 954. Anal. Calcd for C₂₀H₂₀N₂OS (336.44): C, 71.40; H, 5.99; N, 8.32. Found: C, 71.37; H, 6.04; N, 8.29%.

3-Allyl-2-(4'-ethylphenylimino)-4-phenyl-3H-thiazole (4e): Yield 90%; white solid; mp 145-146 °C; ¹H-NMR (CDCl₃, 400 MHz): δ_H: 1.17 (t, 3H, *J* = 7.6 Hz), 2.57 (q, 2H, *J* = 7.6 Hz), 4.46 (d, 2H, *J* = 3.6 Hz), 5.05 (d, 1H, *J* = 17.2 Hz), 5.17 (d, 1H, *J* = 10.4 Hz), 5.76 (s, 1H), 5.90-5.98 (m, 1H), 6.93 (d, 2H, *J* = 8 Hz), 7.04 (d, 2H, *J* = 8 Hz), 7.41-7.49 (m, 5H) ppm; FT-IR (KBr, cm⁻¹): 3074, 2924, 2861, 1599, 1565,

1481, 1380, 1222, 1073, 918, 701, 533. Anal. Calcd for C₂₀H₂₀N₂S (320.45): C, 74.96; H, 6.29; N, 8.74. Found: C, 75.04; H, 6.21; N, 8.79%.

3-Allyl-2-(1'-naphthylimino)-4-phenyl-3H-thiazole (4f): Yield 87%; white solid; mp 150-152°C; ¹H-NMR (CDCl₃, 400 MHz): δ_H: 4.62-4.63 (m, 2H), 5.19 (dd, 1H, *J* = 17.2, 1.2 Hz), 5.30 (dd, 1H, *J* = 10.4, 1.2 Hz), 5.83 (s, 1H), 6.03-6.11 (m, 1H), 7.44-7.55 (m, 9H), 7.60 (d, 1H, *J* = 8.4 Hz), 7.86 (d, 1H, *J* = 7.8 Hz), 8.27 (d, 1H, *J* = 7.8 Hz) ppm; ¹³C-NMR (CDCl₃, 100 MHz): δ_C: 47.7, 96.0, 114.4, 116.6, 122.9, 123.8, 125.0, 126.0, 126.3, 127.8, 128.6, 128.7, 128.9, 129.2, 131.6, 133.0, 134.7, 140.3, 148.2, 159.4 ppm; FT-IR (KBr, cm⁻¹): 3080, 2922, 1610, 1589, 1577, 1560, 1496, 1413, 1382, 1242, 1230, 1001, 966, 914, 844, 700. Anal. Calcd for C₂₂H₁₈N₂S (342.45): C, 77.16; H, 5.29; N, 8.18. Found: C, 77.09; H, 5.36; N, 8.10%.

3-Allyl-2-(*m*-hydroxyphenylimino)-4-phenyl-3H-thiazole (4g): Yield 85%, white solid; mp 145-147°C; ¹H-NMR (DMSO, 400 MHz): δ_H: 4.70 (s, 2H), 4.94 (d, 1H, *J* = 17.2 Hz), 5.24 (d, 1H, *J* = 10.8 Hz), 5.82-5.91 (m, 1H), 6.83 (d, 1H, *J* = 8.0 Hz), 6.85 (s, 1H), 6.90 (d, 1H, *J* = 8.0 Hz), 7.10 (s, 1H), 7.35 (t, 1H, *J* = 8.0 Hz), 7.49-7.59 (m, 5H), 10.02 (br, 1H) ppm; FTIR (KBr, cm⁻¹) ν_{max} 3157, 3047, 2937, 2881, 1608, 1566, 1500, 1450, 1371, 1213, 1161, 970, 869, 700. Anal. Calcd for C₁₈H₁₆N₂OS (308.41): C, 70.10; H, 5.23; N, 9.08. Found: C, 70.06; H, 5.26; N, 9.10%.

3-Allyl-2-(1'-naphthylimino)-4-(4'-methoxyphenyl)-3H-thiazole (4h): Yield 83%, cream solid; mp 96-97°C; ¹H-NMR (CDCl₃, 400 MHz): δ_H: 4.11 (s, 3H), 4.33 (m, 2H), 5.21 (dd, 1H, *J* = 9.6, 1.4 Hz), 5.28 (dd, 1H, *J* = 10.0, 1.2 Hz), 5.88 (m, 1H), 6.13 (s, 1H), 6.93 (d, 2H, *J* = 8.4 Hz), 7.07 (d, 2H, *J* = 8.4 Hz), 7.43-7.46 (m, 4H), 7.55 (d, 1H, *J* = 8.2 Hz), 7.76 (d, 1H, *J* = 7.6 Hz), 8.01 (d, 1H, *J* = 7.6 Hz) ppm; FTIR (KBr, cm⁻¹) ν_{max} 3055, 2976, 2933, 2837, 1683, 1597, 1508, 1394, 1255, 1176, 1016, 775, 551. Anal. Calcd for C₂₃H₂₀N₂OS (372.48): C, 74.16; H, 5.41; N, 7.52. Found: C, 74.20; H, 5.37; N, 7.49%.

3-Allyl-2-(*p*-tolylimino)-4-(4'-methoxyphenyl)-3H-thiazole (4i): Yield 85%, white solid; mp 107-108°C; ¹H-NMR (CDCl₃, 400 MHz): δ_H: 2.37 (s, 3H), 4.73 (s, 3H), 4.29 (m, 2H), 5.14 (dd, 1H, *J* = 9.6, 1.2 Hz), 5.18 (dd, 1H, *J* = 10.0, 1.2 Hz), 5.85 (m, 1H), 6.01 (s, 1H), 6.93 (d, 2H, *J* = 8.6 Hz), 7.04 (d, 2H, *J* = 8.6 Hz), 7.12 (d, 2H, *J* = 8.6 Hz), 7.24 (d, 2H, *J* = 8 Hz) ppm; ¹³C-NMR (CDCl₃, 100 MHz): δ_C: 21.0, 47.8, 51.4, 97.3, 113.1, 117.0, 120.6, 121.2, 125.6, 128.9, 129.2, 130.0, 133.1, 133.3, 137.7, 148.8 ppm; FTIR (KBr, cm⁻¹) ν_{max} 3080, 3010, 2912, 1550, 1529, 1315, 1236, 1134, 958, 819, 659, 563, 493. Anal. Calcd for C₂₀H₂₀N₂OS (336.45): C, 71.39; H, 5.99; N, 8.32. Found: C, 71.41; H, 5.43; N, 8.36%.

3-Allyl-2-(*p*-methylphenylimino)-4-(4'-bromophenyl)-3H-thiazole (4j): Yield 89%, yellowish solid; mp 117-118°C; ¹H-NMR (CDCl₃, 400 MHz): δ_H: 2.35 (s, 3H), 4.42 (d, 2H, *J* = 4.8 Hz), 5.04 (dd, 1H, *J* = 17.2, 1.2 Hz), 5.18 (dd, 1H, *J* = 10.4, 1.2 Hz), 5.79 (s, 1H), 5.88-5.97 (m, 1H), 6.97 (d, 2H, *J* = 7.4 Hz), 7.16 (d, 2H, *J* = 8.0 Hz), 7.30 (d, 2H, *J* = 8.0 Hz), 7.57 (d, 2H, *J* = 7.4 Hz) ppm; ¹³C-NMR (CDCl₃, 100 MHz): δ_C: 20.9, 47.5, 96.2, 116.5, 120.6, 121.2, 123.4, 125.7, 130.0, 131.8, 132.4, 132.7, 139.2

149.0, 159.1 ppm; FTIR (KBr, cm^{-1}) ν_{max} 3043, 2973, 2902, 1606, 1589, 1506, 1375, 1230, 1126, 1010, 825, 669, 474. Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{SBr}$ (385.32): C, 59.22; H, 4.44; N, 7.26. Found: C, 59.19; H, 4.47; N, 7.29%.

3-Allyl-2-(*p*-ethoxyphenylimino)-4-(4'-bromophenyl)-3*H*-thiazole (4k): Yield 97%, yellow solid; mp 119-121 °C; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ_{H} : 1.43 (t, 3H, $J = 6.8$ Hz), 4.04 (q, 2H, $J = 6.8$ Hz), 4.41 (d, 2H, $J = 4.8$ Hz), 5.05 (dd, 1H, $J = 1.2, 16.0$ Hz), 5.18 (dd, 1H, $J = 1.2, 10.4$ Hz), 5.78 (s, 1H), 5.88-5.97 (m, 1H), 6.90 (d, 2H, $J = 6.8$ Hz), 6.99 (d, 2H, $J = 6.8$ Hz), 7.29 (d, 2H, $J = 9.2$ Hz), 7.57 (d, 2H, $J = 9.2$ Hz) ppm; FTIR (KBr, cm^{-1}) ν_{max} 3053, 2983, 2920, 1612, 1593, 1506, 1467, 1321, 1238, 1114, 1010, 916, 840, 555, 480. Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{SOBr}$ (415.35): C, 58.83; H, 4.61; N, 6.74. Found: C, 58.85; H, 4.59; N, 6.72%.

3-Allyl-2-(*p*-methoxyphenylimino)-4-(4'-bromophenyl)-3*H*-thiazole (4l): Yield 94%, yellow solid; mp 114-116 °C; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ_{H} : 3.82 (s, 3H), 4.42 (d, 2H, $J = 4.8$ Hz), 5.04 (dd, 1H, $J = 1.2, 17.2$ Hz), 5.18 (dd, 1H, $J = 1.2, 9.4$ Hz), 5.79 (s, 1H), 5.88-5.97 (m, 1H), 6.90 (d, 2H, $J = 6.8$ Hz), 7.00 (d, 2H, $J = 7.4$ Hz), 7.29 (d, 2H, $J = 7.4$ Hz), 7.57 (d, 2H, $J = 6.8$ Hz) ppm; $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ_{C} : 47.5, 55.45, 96.2, 114.6, 116.5, 123.4, 127.4, 130.3, 130.5, 131.8, 132.7, 139.2, 144.9, 155.6, 159.3 ppm; FTIR (KBr, cm^{-1}) ν_{max} 3064, 2897, 2831, 1610, 1589, 1506, 1396, 1242, 1033, 840, 756, 669, 491. Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{SOBr}$ (401.32): C, 56.86; H, 6.98; N, 4.26. Found: C, 56.88; H, 7.01; N, 4.24%.

3-Allyl-2-(*p*-iodophenylimino)-4-(4'-bromophenyl)-3*H*-thiazole (4m): Yield 92%, yellow solid; mp 116-118 °C; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ_{H} : 4.41 (d, 2H, $J = 4.8$ Hz), 5.03 (dd, 1H, $J = 1.2, 17.2$ Hz), 5.19 (dd, 1H, $J = 1.2, 10.4$ Hz), 5.83 (s, 1H), 5.86-5.95 (m, 1H), 6.86 (d, 2H, $J = 8.8$ Hz), 7.29 (d, 2H, $J = 8.8$ Hz), 7.58 (d, 2H, $J = 8.8$ Hz), 7.63 (d, 2H, $J = 8.8$ Hz) ppm; $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ_{C} : 47.6, 86.1, 96.4, 116.7, 123.6, 123.8, 130.2, 130.4, 131.8, 132.5, 138.3, 139.3, 151.1, 159.4 ppm; FTIR (KBr, cm^{-1}) ν_{max} 3043, 2920, 2850, 1610, 1568, 1375, 1002, 840, 813, 756, 624, 480. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{SBrI}$ (497.19): C, 43.48; H, 2.83; N, 5.63. Found: C, 43.45; H, 2.85; N, 5.61%.

3-Allyl-2-(*p*-chlorophenylimino)-4-(4'-bromophenyl)-3*H*-thiazole (4n): Yield 91%, yellow solid; mp 109-111 °C; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ_{H} : 4.27-4.30 (m, 2H), 5.01 (dd, 1H, $J = 1.6, 17.2$ Hz), 5.08 (dd, 1H, $J = 1.6, 10.0$ Hz), 5.82-5.92 (m, 1H), 6.00 (s, 1H), 6.95 (d, 2H, $J = 6.8$ Hz), 7.27 (d, 2H, $J = 6.8$ Hz), 7.50 (d, 2H, $J = 7.6$ Hz), 7.57 (d, 2H, $J = 7.6$ Hz) ppm; FTIR (KBr, cm^{-1}) ν_{max} 3043, 1616, 1577, 1483, 1315, 1232, 1087, 1010, 835, 719, 632, 482. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{SBrCl}$ (405.74): C, 53.28; H, 3.47; N, 6.90. Found: C, 53.26; H, 3.45; N, 6.93%.

ACKNOWLEDGEMENTS

We are very grateful to research council of university of guilan for financial support of this work and the instrumentation center (crim) of universiti kebangsaan malaysia (ukm-dip-011-2012) for the x-ray analysis.

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27. X-Ray data for **4d**: (C₂₀H₂₀N₂OS), M = 336.44 g/mol, monoclinic system, space group P 2₁/n, a = 5.7886(4) Å, b = 24.3201(19) Å, c = 12.6329(11) Å, β = 94.450(2)°, V = 1773.1(2) Å³, Z = 4, D_c = 1.320 Mg/m³, μ = 0.205 mm⁻¹, crystal size = 0.500 × 0.220 × 0.140 mm³. The structure was solved by using SHELXS. The structural refinement was carried out with SHELXL. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F² values to final R₁ = 0.0791, wR₂ = 0.1983 and S = 1.095 with 241 parameters using 3106 independent reflection (θ range = 2.988 to 24.993°). The hydrogen atoms were placed in calculated positions. All hydrogen atoms were refined isotropically in riding model with U_{iso}(H) = 1.2 U_{eq}(C) and 1.5U_{eq}(Cmethyl) However the olefinic proton H20A and H20B were located from Fourier map and refined isotropically. Crystallographic data for the structural determination has been deposited with the Cambridge Crystallographic Data Centre, CCDC No 1008333. This information may be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Centre (CCDC), 12 Union Road, Cambridge CB2, 1EZ, UK. Fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.
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