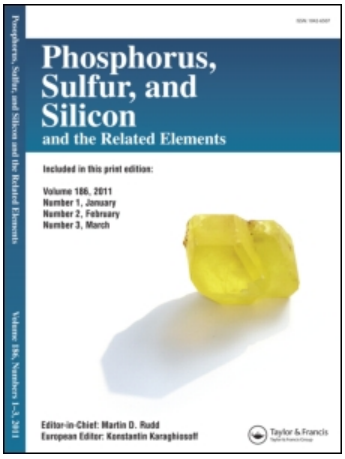

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A One-Pot Synthesis of Functionalized 2,3-Dihydrothiazoles from Isothiocyanates, Primary Alkylamines, and Phenacyl Bromides

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A ONE-POT SYNTHESIS OF FUNCTIONALIZED 2,3-DIHYDROTHIAZOLES FROM ISOTHIOCYANATES, PRIMARY ALKYLAMINES, AND PHENACYL BROMIDES

Issa Yavari, Maryam Ghazvini, Ashraf S. Shahvelayati, and Mohammad M. Ghanbari

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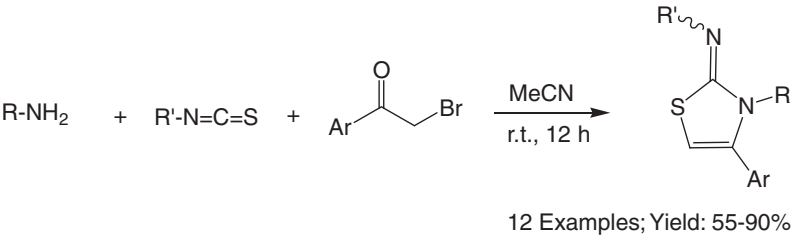
GRAPHICAL ABSTRACT



12 Examples; Yield: 55-90%

Abstract *A simple, one-pot synthesis of N-(4-aryl-3-alkylthiazol-2(3H)-ylidene)anilines and N-(4-aryl-3-alkylthiazol-2(3H)-ylidene)benzamides via the reaction of primary alkylamines, α-bromoketones, and phenylisothiocyanate or benzoylisothiocyanate is described.*

Keywords Benzoylisotiosyanate; α-bromoketones; 2,3-dihydrothiazole; S-nucleophile; phenylisothiocyanate; primary alkylamine

INTRODUCTION

Thiazoles occupy a prominent position among heterocycles. In nature, the thiazolium ring is the chemically active center in the coenzyme derived from vitamin B_1 (thiamin). A large number of thiazoles obtained from microbial and marine origins exhibit important biological effects such as antitumor, antifungal, antibiotic, and antiviral activities.[1] Synthetic thiazoles have also been shown to exhibit a wide variety of biological activities,[2] while others have found application as liquid crystals[3] and cosmetic sunscreens.[4] The classical method for the synthesis of thiazoles is the Hantzsch process, in which a α-haloketone is condensed with a thioamide.[5] This method gives excellent yields for simple thiazoles; however, for some substituted examples, low yields have been reported.[6,7]

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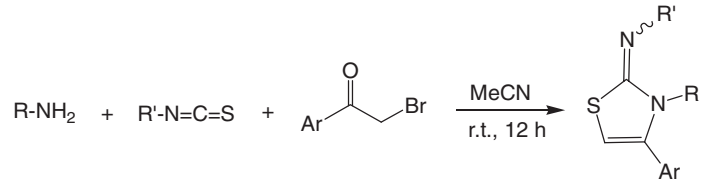
As part of our current studies on the development of new routes in thiazole synthesis,[8–11] we report an efficient procedure for direct synthesis of *N*-(4-aryl-3-alkylthiazol-2(3*H*)-ylidene)anilines **4a–4h** and *N*-(4-aryl-3-alkylthiazol-2(3*H*)-ylidene)benzamides **4i–4l** from primary alkylamines **1**, isothiocyanates **2**, and α-bromoketones **3**, at r.t. (Scheme 1). This catalyst-free and one-pot synthetic method is facile; the work-up procedure is easy and gives pure target compounds.



1	R
a	*n*-Bu
b	*c*-Hexyl
c	Bn
d	*p*-tolylCH$_2$

2	R'
a	Ph
b	Bz

3	Ar
a	4-MeO-C$_6$H$_4$
b	4-Br-C$_6$H$_4$

4	R	R'	Ar	Yiled (%)
a	*n*-Bu	Ph	4-MeO-C$_6$H$_4$	82
b	*n*-Bu	Ph	4-Br-C$_6$H$_4$	90
c	*p*-tolylCH$_2$	Ph	4-MeO-C$_6$H$_4$	75
d	*p*-tolylCH$_2$	Ph	4-Br-C$_6$H$_4$	88
e	Bn	Ph	4-MeO-C$_6$H$_4$	85
f	Bn	Ph	4-Br-C$_6$H$_4$	84
g	*c*-Hexyl	Ph	4-MeO-C$_6$H$_4$	80
h	*c*-Hexyl	Ph	4-Br-C$_6$H$_4$	82
i	*n*-Bu	Bz	4-MeO-C$_6$H$_4$	65
j	*n*-Bu	Bz	4-Br-C$_6$H$_4$	68
k	Bn	Bz	4-MeO-C$_6$H$_4$	66
l	Bn	Bz	4-Br-C$_6$H$_4$	55

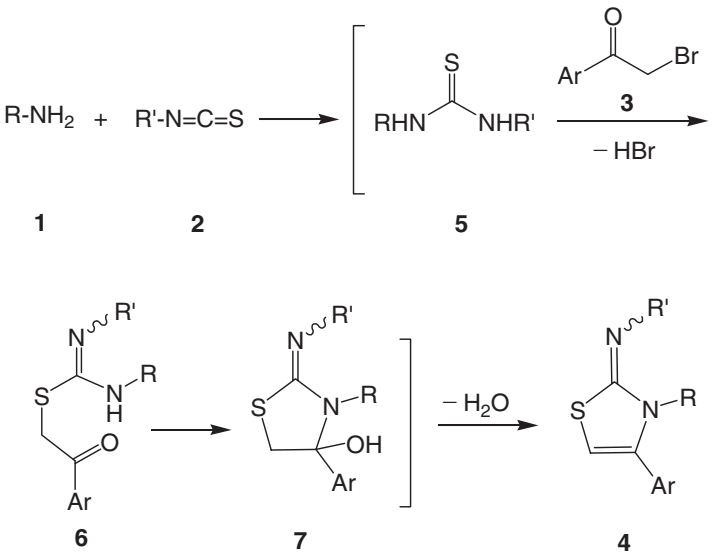
Scheme 1 Synthesis of compounds **4**.

RESULTS AND DISCUSSION

The reaction of **1**, **2**, and **3** proceeds smoothly in MeCN at r.t. to produce *N*-(4-aryl-3-alkylthiazol-2(3*H*)-ylidene)anilines (**4a–4h**) and *N*-(4-aryl-3-alkylthiazol-2(3*H*)-ylidene)benzamides (**4i–4l**) in moderate to good yields (Scheme 1). The structures of compounds **4a–4l** were deduced from their IR, ^{1}H NMR, and ^{13}C NMR spectral data. The mass spectra of these compounds displayed molecular ion peaks at appropriate *m/z* values. The ^{1}H NMR spectrum of **4a** in $CDCl_3$ showed two singlets for the methoxy ($\delta = 3.88$) and methine ($\delta = 5.70$) protons, together with characteristic signals for the *n*-butyl and aryl protons. The ^{13}C NMR spectrum of **4a** showed 16 signals in agreement with the proposed structure. The ^{1}H and ^{13}C NMR spectra of **4b–4l** are similar to those for **4a** except for the alkyl and aryl substituents, which exhibit characteristic signals in the appropriate regions of the NMR spectra.

Although the mechanistic details of the reaction are not known, a plausible rationalization can be advanced to explain the product formation (Scheme 2). Presumably, the initial event is the formation of unsymmetrical thiourea **5** from the amine and heterocumulene **2**. Thiourea **5** is alkylated by bromoketone **3** to furnish intermediate **6**, which undergoes cyclization to generate **7**. Dehydration of intermediate **7** affords product **4**.

In conclusion, we revealed a three-component synthesis of *N*-(4-aryl-3-alkylthiazol-2(3*H*)-ylidene)anilines and *N*-(4-aryl-3-alkylthiazol-2(3*H*)-ylidene)benzamides from primary alkylamines, α-bromoketones, and isothiocyanate. The advantage of the present



Scheme 2 Proposed mechanism for the formation of compounds **4**.

procedure is that the reaction is performed under neutral conditions by simple mixing of the starting materials. This catalyst-free procedure provides an acceptable one-pot method for the preparation of functionalized 2,3-dihydrothiazoles.

EXPERIMENTAL

Compounds **1**, **2**, and **3** were obtained from Merck and were used without further purification; IR spectra: Shimadzu IR-460 spectrometer; ^{1}H and ^{13}C NMR spectra: Bruker DRX-300 Avance instrument; in $CDCl_3$ at 300 MHz and 75 MHz, respectively, δ in ppm J in Hz; EI-MS (70 eV): Finningan-MAT-8430 mass spectrometer, in *m/z*. Elemental analyses (C, H, and N) were performed with a Heraeus CHN-O-Rapid analyzer.

Typical Procedure for the Preparation of Compounds 4

To a stirred solution of alkylamine (**1**, 2 mmol) and isothiocyanate (**2**, 2 mmol) in 10 mL of MeCN, α-bromoketone (**3**, 2 mmol) was added at r.t. After completion of the reaction (1–2 h), as indicated by TLC (AcOEt:hexane, 2:1), the solvent was removed under reduced pressure, and the residue was purified by silica gel (SiO_2; Merck 230–240 mesh) column chromatography (CC) using a 5:1, hexane:AcOEt mixture as eluent to afford **4**.

***N*-(3-Butyl-4-(4-methoxyphenyl)thiazol-2(3*H*)-ylidene)aniline (4a).** Pale yellow oil, yield: 0.55 g (82%). IR (KBr): 1619, 1569, 1480, 1178 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 0.81 (3 H, t, ^{3}J 7.2, Me), 1.20–1.26 (2 H, m, CH_2), 1.62–1.68 (2 H, m, CH_2), 3.78 (2 H, t, ^{3}J 7.1, CH_2), 3.88 (3 H, s, MeO), 5.70 (1 H, s, CH), 6.97 (2 H, d, ^{3}J 8.1, C_6H_4), 7.35 (2 H, d, ^{3}J 8.1, C_6H_4), 7.04–7.38 (5 H, m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): 14.1 (Me), 20.1 (CH_2), 30.5 (CH_2), 45.5 (CH_2), 55.7 (MeO), 98.1 (CH), 114.4 (2 CH), 122.0 (2 CH),129.8 (2 CH), 130.6 (2 CH), 123.3 (CH), 126.2 (C), 138.5 (C), 148.9 (C), 158.1 (C), 160.5 (C=N). Anal. Calcd for $C_{20}H_{22}N_2OS$ (338.47): C, 70.97; H, 6.55;

N, 8.28%. Found: C, 70.30; H, 6.71; N, 8.41%. EI-MS: *m/z* (%): 338 (M^+, 100), 282 (13), 206 (39), 133 (55), 77 (14).

***N*-(4-(4-Bromophenyl)-3-butylthiazol-2(3*H*)-ylidene)aniline (4b).** Colorless powder; mp 239–242°C; 0.69 g (90%). IR (KBr): 1613, 1563, 1479 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 0.75 (3 H, t, ^3J 7.1, Me), 1.26–1.31 (2 H, m, CH_2), 1.66–1.71 (2 H, m, CH_2), 4.63 (2 H, t, ^3J 7.2, CH_2), 6.69 (1 H, s, CH), 7.27 (2 H, d, ^3J 8.0, C_6H_4), 7.66 (2 H, d, ^3J 8.0, C_6H_4), 7.34–7.64 (5 H, m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): 13.9 (Me), 19.6 (CH_2), 30.2 (CH_2), 49.5 (CH_2), 105.8 (CH), 124.7 (2 CH), 125.9 (C), 127.4 (C), 128.9 (CH), 130.5 (2 CH), 131.4 (2 CH), 133.0 (2 CH), 138.1 (C), 142.3 (C), 169.1 (C=N). Anal. Calcd for $C_{19}H_{19}BrN_2S$ (387.34): C, 58.92; H, 4.94; N, 7.23%. Found: C, 59.22; H, 4.76; N, 7.39%. EI-MS: *m/z* (%): 388 ($M^+ + 2$, 100), 386 (M^+, 100), 332 (12.5), 330 (12.5), 256 (41), 254 (41), 133 (58), 77 (17).

***N*-(4-(4-Methoxyphenyl)-3-(4-methylbenzyl)thiazol-2(3*H*)-ylidene)aniline (4c).** Pale yellow oil; 0.58 g (75%). IR (KBr): 1634, 1576, 1471, 1119 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 2.23 (3 H, s, Me), 3.85 (3 H, s, MeO), 5.10 (2 H, s, CH_2), 5.78 (1 H, s, CH), 6.89 (2 H, d, ^3J 8.0, C_6H_4), 7.17 (2 H, d, ^3J 8.0, C_6H_4), 6.98 (2 H, d, ^3J 8.1, C_6H_4), 7.04 (2 H, d, ^3J 7.8, Ph), 7.05–7.16 (3 H, m, Ph), 7.35 (2 H, t, ^3J 7.8, C_6H_4). ^{13}C NMR (75 MHz, $CDCl_3$): 21.5 (Me), 50.1 (CH_2), 55.8 (MeO), 98.3 (CH), 114.6 (2 CH), 124.3 (2 CH), 127.6 (2 CH), 129.5 (2 CH), 129.6 (CH), 130.0 (2 CH), 131.0 (2 CH), 126.2 (C), 129.9 (C), 137.2 (C), 144.7 (C), 149.8 (C), 156.9 (C), 165.7 (C=N). Anal. Calcd for $C_{24}H_{22}N_2OS$ (386.51): C, 74.58; H, 5.74; N, 7.25%. Found: C, 74.72; H, 5.91; N, 7.40%. EI-MS: *m/z* (%): 386 (M^+, 15), 282 (18), 181 (81), 105 (100), 77 (22).

***N*-(4-(4-Bromophenyl)-3-(4-methylbenzyl)thiazol-2(3*H*)-ylidene)aniline (4d).** Colorless powder; mp 163–167°C; 0.77 g (88%). IR (KBr): 1677, 1542, 1466 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 2.30 (3 H, s, Me), 6.04 (2 H, s, CH_2), 6.63 (1 H, s, CH), 7.02 (2 H, d, ^3J 8.0, C_6H_4), 7.09 (2 H, d, ^3J 8.0, C_6H_4), 7.25 (2 H, d, ^3J 7.9, C_6H_4), 7.64 (2 H, d, ^3J 7.8, Ph), 7.36 (1 H, t, ^3J 7.8, Ph), 7.43 (2 H, t, ^3J 7.8, Ph), 7.57 (2 H, d, ^3J 7.8, C_6H_4). ^{13}C NMR (75 MHz, $CDCl_3$): 21.5 (Me), 52.9 (CH_2), 105.0 (CH), 124.4 (2 CH), 127.5 (2 CH), 128.9 (CH), 130.1 (2 CH), 130.6 (2 CH), 131.3 (2 CH), 133.1 (2 CH), 125.9 (C), 130.3 (C), 138.9 (C), 136.2 (C), 138.2 (C), 143.3 (C), 170.0 (C=N). Anal. Calcd for $C_{23}H_{19}BrN_2S$ (435.38): C, 63.45; H, 4.40; N, 6.43%. Found: C, 63.12; H, 4.58; N, 6.59%. EI-MS: *m/z* (%): 436 ($M^+ + 2$, 13), 434 (M^+, 12.5), 344 (11), 342 (11), 250 (14.4), 181 (73), 105 (100), 77 (19).

***N*-(3-Benzyl-4-(4-methoxyphenyl)thiazol-2(3*H*)-ylidene)aniline (4e).** Pale yellow powder; mp 110–119°C; 0.63 g (85%). IR (KBr): 1603, 1573, 1499, 1172 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 3.84 (3 H, s, MeO), 5.14 (2 H, s, CH_2), 6.04 (1 H, s, CH), 6.94 (2 H, d, ^3J 8.0, C_6H_4), 7.28 (2 H, d, ^3J 8.0, C_6H_4), 6.97–7.34 (10 H, m, 2 Ph). ^{13}C NMR (75 MHz, $CDCl_3$): 49.0 (CH_2), 55.7 (MeO), 96.0 (CH), 114.3 (2 CH), 122.0 (2 CH), 133.5 (CH), 124.1 (C), 127.5 (2 CH), 128.7 (2 CH), 129.1 (C), 129.8 (2 CH), 130.8 (2 CH), 137.8 (CH), 140.7 (C), 147.1 (C), 154.3 (C), 160.6 (C=N). Anal. Calcd for $C_{23}H_{20}N_2OS$ (372.48): C, 74.16; H, 5.41; N, 7.52%. Found: C, 74.83; H, 5.64; N, 7.76%. EI-MS: *m/z* (%): 372 (M^+, 33), 268 (35), 181 (76), 105 (100), 77 (22).

***N*-(3-Benzyl-4-(4-bromophenyl)thiazol-2(3*H*)-ylidene)aniline (4f).** Cream powder; mp 132–135°C; 0.71 g (84%). IR (KBr): 1616, 1579, 1483 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 5.16 (2 H, s, CH_2), 5.87 (1 H, s, CH), 7.09–7.28 (5 H, m, Ph), 7.36 (3 H, t, ^3J 7.7, Ph), 7.49 (2 H, d, ^3J 7.9, C_6H_4), 7.66 (2 H, d, ^3J 7.7, Ph), 7.87 (2 H, d, ^3J 7.9, C_6H_4). ^{13}C NMR (75 MHz, $CDCl_3$): 50.2 (CH_2), 104.1 (C), 127.4 (CH), 128.9 (2 CH), 129.2 (CH), 129.9 (2 CH), 130.0 (C), 130.8 (2 CH), 130.9 (2 CH), 131.0 (CH), 132.2

(2 CH), 132.3 (C), 132.6 (2 CH), 132.7 (C), 151.5 (C), 157.1 (C=N). Anal. Calcd for $C_{22}H_{17}BrN_2S$ (421.35): C, 62.71; H, 4.07; N, 6.65%. Found: C, 63.04; H, 4.21; N, 6.79%. EI-MS: *m/z* (%): 422 ($M^+ + 2$, 31), 420 (M^+, 30.6), 330 (19), 328 (19), 237 (38), 181 (73), 105 (100), 77 (17).

***N*-(3-Cyclohexyl-4-(4-methoxyphenyl)thiazol-2(3*H*)-ylidene)aniline (4g).** Pale yellow oil; 0.58 g (80%). IR (KBr): 1644, 1528, 1465, 1180 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 1.13–2.71 (10 H, m, 5 CH_2), 3.80–3.82 (H, m, CH), 3.88 (3 H, s, MeO), 5.61 (1 H, s, CH), 6.97 (2 H, d, ^3J 7.6, C_6H_4), 7.28 (2 H, d, ^3J 7.6, C_6H_4), 7.06–7.38 (5 H, m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): 25.4 (CH_2), 26.6 (2 CH_2), 29.2 (2 CH_2), 47.6 (CH), 55.7 (MeO), 98.3 (CH), 114.3 (2 CH), 122.0 (2 CH), 122.1 (C), 123.5 (C), 125.5 (CH), 129.9 (2 CH), 130.7 (2 CH), 130.8 (C), 141.4 (C), 160.4 (C=N). Anal. Calcd for $C_{22}H_{24}N_2OS$ (364.50): C, 72.49; H, 6.64; N, 7.69%. Found: C, 72.78; H, 6.71; N, 7.81%. EI-MS: *m/z* (%): 364 (M^+, 100), 282 (15), 206 (38), 159 (55), 77 (31).

***N*-(4-(4-Bromophenyl)-3-cyclohexylthiazol-2(3*H*)-ylidene)aniline (4h).** Pale yellow oil; 0.68 g (82%). IR (KBr): 1620, 1588, 1470 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 1.15–2.71 (10 H, m, 5 CH_2), 3.78–3.80 (H, m, CH), 5.69 (H, s, CH), 7.07–7.48 (5 H, m, Ph), 7.27 (2 H, d, ^3J 8.0, C_6H_4), 7.76 (2 H, d, ^3J 8.0, C_6H_4). ^{13}C NMR (75 MHz, $CDCl_3$): 25.7 (CH_2), 26.8 (2 CH_2), 30.7 (2 CH_2), 46.0 (CH), 105.8 (CH), 129.7 (CH), 130.4 (2 CH), 130.8 (2 CH), 131.0 (C), 131.5 (C), 132.2 (2 CH), 132.6 (2 CH), 133.0 (C), 143 (C), 165.8 (C=N). Anal. Calcd for $C_{21}H_{21}BrN_2S$ (413.37): C, 61.02; H, 5.12; N, 6.78%. Found: C, 61.48; H, 5.30; N, 6.90%. EI-MS: *m/z* (%): 414 (M^++2, 100), 412 (M^+, 100), 332 (16.5), 330 (16), 256 (29), 254 (29.5), 159 (48), 77 (26).

***N*-(3-Butyl-4-(4-methoxyphenyl)thiazol-2(3*H*)-ylidene)benzamide (4i).** Cream powder; mp 118–121°C; 0.47 g (65%). IR (KBr): 1591, 1473, 1311 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 0.86 (3 H, t, ^3J 7.3, Me), 1.27–1.29 (2 H, m, CH_2), 1.72–1.74 (2 H, m, CH_2), 4.24 (2 H, t, ^3J 7.2, CH_2), 3.90 (3 H, s, MeO), 6.50 (1 H, s, CH), 7.03 (2 H, d, ^3J 7.8, C_6H_4), 7.33 (2 H, d, ^3J 7.8 Hz, C_6H_4), 7.45–7.48 (3 H, m, Ph). 8.37 (2 H, d, ^3J 8.0, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): 14.0 (Me), 20.2 (CH_2), 30.9 (CH_2), 47.4 (CH_2), 55.8 (MeO), 107.3 (CH), 114.6 (2 CH), 123.4 (C), 128.4 (2 CH), 129.6 (2 CH), 131.2 (2 CH), 131.7 (CH), 137.5 (C), 139.5 (C), 147.0 (C), 160.9 (C=N), 174.3 (C=O). Anal. Calcd for $C_{21}H_{22}N_2O_2S$ (366.48): C, 68.82; H, 6.05; N, 7.64%. Found: C, 69.08; H, 6.21; N, 7.81%. EI-MS: *m/z* (%): 366 (M^+, 28), 310 (31), 105 (100), 77 (50).

***N*-(4-(4-Bromophenyl)-3-butylthiazol-2(3*H*)-ylidene)benzamide (4j).** Cream powder; mp 138–158°C; 0.56 g (68%). IR (KBr): 1599, 1487, 1352 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 0.87 (3 H, t, ^3J 7.3, Me), 1.27–1.29 (2 H, m, CH_2), 1.71–1.73 (2 H, m, CH_2), 4.22 (2 H, ^3J 7.2, CH_2), 6.55 (1 H, s, CH), 7.29 (2 H, d, ^3J 8.0, C_6H_4), 7.67 (2 H, d, ^3J 8.0, C_6H_4), 7.44–7.52 (3 H, m, Ph), 8.35 (2 H, d, ^3J 8.0, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): 14.0 (Me), 20.2 (CH_2), 30.9 (CH_2), 47.4 (CH_2), 108.2 (CH), 124.5 (C), 128.4 (2 CH), 129.6 (2 CH), 130.2 (C), 131.4 (2 CH), 131.8 (CH), 132.5 (2 CH), 137.3 (C), 138.4 (C), 168.8 (C=N), 174.5 (C=O). Anal. Calcd for $C_{20}H_{19}BrN_2OS$ (415.35): C, 57.33; H, 4.61; N, 6.74%. Found: C, 58.11; H, 4.77; N, 6.92%. EI-MS: *m/z* (%): 416 (M^++2, 29), 414 (M^+, 29), 360 (33), 358 (32), 105 (100), 77 (48).

***N*-(3-Benzyl-4-(4-methoxyphenyl)thiazol-2(3*H*)-ylidene)benzamide (4k).** Colorless powder; mp 116–125°C; 0.53 g (66%). IR (KBr): 1607, 1477, 1351, 1167 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 3.86 (3 H, s, MeO), 5.50 (2 H, s, CH_2), 6.53 (1 H, s, CH), 6.90 (2 H, d, ^3J 8.0, C_6H_4), 7.14 (2 H, d, ^3J 8.0, C_6H_4), 7.04–7.28 (5 H, m, Ph), 7.42–7.48 (3 H, m, Ph), 8.30 (2 H, d, ^3J 8.1, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): 50.7 (CH_2), 55.8 (MeO), 107.4 (CH), 114.4 (2 CH), 123.0 (C), 127.6 (2 CH), 128.0 (CH), 128.4 (2 CH), 128.9 (2

CH), 129.7 (2 CH), 131.4 (2 CH), 131.8 (CH), 139.8 (C), 137.3 (C), 139.6 (C), 161.0 (C), 169.5 (C=N), 174.6 (C=O). Anal. Calcd for $C_{24}H_{20}N_2O_2S$ (400.49): C, 71.98; H, 5.03; N, 6.99%. Found: C, 72.12; H, 4.91; N, 7.21%. EI-MS: *m/z* (%): 400 (M^+, 26), 309 (91), 105 (100), 77 (64).

***N*-(3-Benzyl-4-(4-bromophenyl)thiazol-2(3*H*)-ylidene)benzamide (4l).** Colorless powder; mp 140–148°C; 0.49 g (55%). IR (KBr): 1558, 1480, 1351 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 5.50 (2 H, s, CH_2), 6.58 (1 H, s, CH), 7.05 (2 H, d, ^3J 7.8, C_6H_4), 7.53 (2 H, d, ^3J 7.8, C_6H_4), 7.04–7.27 (5 H, m, Ph), 7.42–7.49 (3 H, m, Ph), 8.31 (2 H, d, ^3J 7.9, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): 48.2 (CH_2), 108.7 (CH), 123.9 (C), 127.5 (2 CH), 128.2 (CH), 128.4 (2 CH), 129.1 (2 CH), 129.7 (2 CH), 130.1 (C), 131.5 (2 CH), 131.9 (CH), 132.3 (2 CH), 136.8 (C), 142.2 (C), 152.3 (C), 170.0 (C=N), 178.1 (C=O). Anal. Calcd for $C_{23}H_{17}BrN_2OS$: (449.36): C, 61.48; H, 3.81; N, 6.23%. Found: C, 61.81; H, 3.92; N, 6.38%. EI-MS: *m/z* (%): 450 (M^++2, 23), 448 (M^+, 23), 359 (91), 357 (91), 105 (100), 77 (58).

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