Another Way to the Synthesis of 1,2,3-Triazoles

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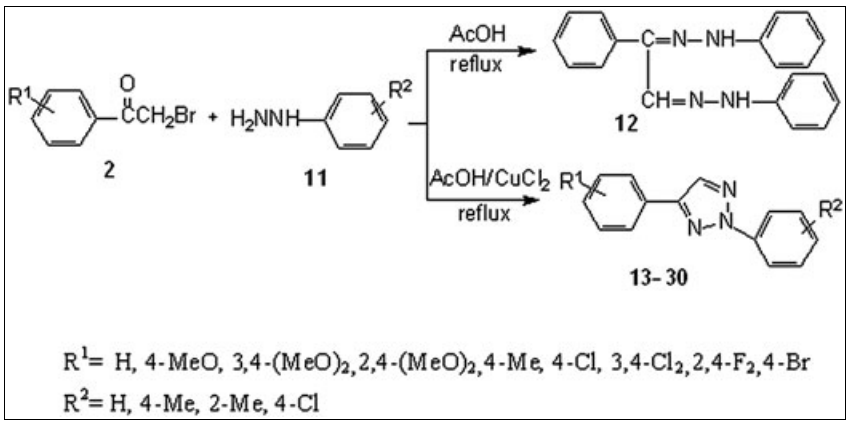

The reactions of α-bromoacetophenones with methylhydrazine in refluxing acetic acid generated 2-methyl-4-aryl-2*H*-[1,2,3]triazoles in good yields. The method was developed by the reactions of α-bromoacetophenones with phenylhydrazines in the presence of cupric ion, leading to 2,4-diary-2*H*-[1,2,3]triazoles. The structures were established on the basis of corresponding IR, ^{1}H NMR, and elemental analysis data.

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INTRODUCTION

1,2,3-Triazoles have a broad range of biological activity, and there are numerous examples in the literature including antibacterial activity [1, 2], antiviral activity [3], anti-convulsant [4], selective β3-adrenergic receptor agonism [5], and so on. A few methods for the preparation of 1,2,3-triazole derivatives have been developed. Among them, 1,3-dipolar cycloaddition between an azide and an alkyne is the classical and extensively used method [6–8], leading to the 1*H*-[1,2,3]triazole derivatives. Other methods, such as the reaction of nitriles with CH_2N_2 [9] and the intramolecular condensation of bisarylhydrazones [10–12], have not been developed further. The strict reaction conditions or monotonous products may be responsible for their unpopularity today. Herein we report a one-pot synthesis of 2,4-disubstituted-2*H*-[1,2,3]triazoles via the coupling of α-bromoacetophenones with hydrazines.

RESULTS AND DISCUSSION

We studied the reaction of *N*-phenacylisoquinolinium bromide (**1**) with methylhydrazine in refluxing acetic acid. Unexpectedly 2-methyl-4-phenyl-2*H*-[1,2,3]triazole (**3**) was obtained. Then α-bromoacetophenone (**2**), a more simple material than the quaternary salt (**1**), was employed to react with methylhydrazine, yielding the same product (**3**). In order to investigate this reaction, a series of substituted α-bromoacetophenones were applied in the same reaction condition, and the corresponding 2-methyl-4-aryl-2*H*-[1,2,3]triazoles (**4**-**10**) (Table 1) were obtained in moderate to high yields (Scheme 1).

The possible mechanism is proposed here (**Scheme** 2). In this scheme, C1 and C2 of α-bromoacetophenone(**2**) underwent nucleophilic attack of methylhydrazine, respectively, which afforded intermediate (**a**). The loss of an amino moiety from intermediate (**b**) gave rise to intermediate (**c**). Then, C2 of (**c**) underwent nucleophilic attack of another methylhydrazine, with the result of methylimino group being replaced by methyl hydrazono group. Further loss of a proton from intermediate (**d**) led to the intermediate (**e**). In the end, through the loss of methylamine under thermal condition, compound **3** was obtained.

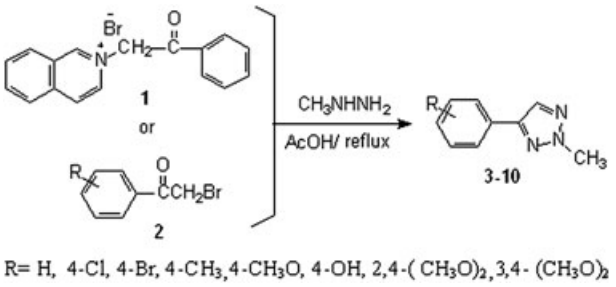
To extend the utility of this method, phenylhydrazine was employed as the starting material to react with α-bromoacetophenone in refluxing acetic acid. The reaction appeared to be limited. Little triazole, but bisphenylhydrazone (**12**), was obtained in low yield. To obtain the desired product, an addition of catalyzer was necessary. Some catalysts were tried, and cupric ion was found to be more efficient to promote the cyclization than the others. Therefore, 2,4-diaryl-2*H*-[1,2,3]triazoles (**13**-**30**) (Table 2) were prepared by cupric ion mediated

Table 1

Analytical and spectroscopic data for compounds **3-10**.

No	R	Yield %	m.p./_C	IR(KBr)/m (cm_1)	^{1}H NMR: (deuteriochloroform): δ	Calculated (found) (%) C	H	N
3	H	60	56	3035,1476, 1457, 1385, 764, 691	7.81(s,1H), 7.78–7.76(m,2H), 7.45–7.41(m,2H), 7.36–7.32(m,1H), 4.23(s,3H)	67.91 (68.12)	5.70 (5.65)	26.40 (26.60)
4	4-Cl	47	96–98	1471,1377, 829	7.79(s,1H), 7.70(dd,2H, *J* = 2.0,6.7 Hz), 7.39(dd,2H, *J* = 2.0, 6.7 Hz), 4.23(s,3H)	55.83 (55.69)	4.16 (4.01)	21.70 (21.45)
5	4-Br	41	120–122	1473, 1379, 832	7.80(s,1H), 7.65-7.63(m,2H), 7.57-7.54(m,2H), 4.23(s,3H)	45.40 (45.16)	3.39 (3.43)	17.65 (17.46)
6	4-CH3	56	64–66	3035,1485,1385,821	7.77(s,1H), 7.65(d, 2H, *J* = 8.1 Hz), 7.23(t, 2H, *J* = 8.0 Hz), 4.21 (s,3H), 2.37 (s,3H)	69.34 (69.01)	6.40 (6.17)	24.26 (24.04)
7	4-CH3O	73	104–106	1613,1578,1483, 1383, 837	7.74(s,1H), 7.71-7.68(m,2H), 6.97-6.94(m,2H), 4.21(s,3H), 3.84(s,3H)	63.48 (63.34)	5.86 (5.99)	22.21 (21.98)
8	4-OH	81	126–128	3195,1617,1591,1492, 1452, 843	7.75(s,1H), 7.65-7.62(m,2H), 6.91-6.87 (m, 2H), 4.22(s,3H)	61.70 (61.52)	5.18 (5.23)	23.99 (23.85)
9	3,4-(MeO)2	58	94–96	1607,1590,1500,1380, 862, 841	7.76(s,1H),7.34(d,1H, *J* = 1.8 Hz), 7.31-7.27(m,1H), 6.92(d,1H, J ¼ 8.3 Hz), 4.23(s,3H), 3.97(s,3H), 3.92(s,3H)	60.27 (60.02)	5.94 (5.98)	19.18 (19.05)
10	2,4-(MeO)2	58	80	1615,1581,1384, 834	7.95(s,1H), 7.86(d, 1H, J ¼ 8.5 Hz), 6.59-6.54(m,2H), 4.21(s,3H), 3.90(s,3H), 3.84 (s,3H)	60.27 (60.12)	5.94 (5.85)	19.18 (19.07)

Scheme 1. The synthesis of 2-methyl-4-aryl-2H-[1,2,3]triazoles (**3-10**).



R= H, 4-Cl, 4-Br, 4-CH3, 4-CH3O, 4-OH, 2,4-(CH3O)2, 3,4-(CH3O)2

cyclization of phenylhydrazines and α-bromoacetophenones (**Scheme** 3).

A possible mechanism for the reaction of α-bromoacetophenone with phenylhydrazine was offered here (**Scheme** 4). After α-bromoacetophenone underwent a similar process to Scheme 2, bisphenylhydrazone (**12**) was obtained. However, (**12**) was not active enough to undergo intramolecular cyclization as the radical intermediate (**d**). It is assumed that the bulk, electron-attracting phenyl ring rendered its neighboring nitrogen harder to attack imino-nitrogen of phenylhydrazono residue on C1. Therefore,

Scheme 2. The possible mechanism for the synthesis of 2-methyl-4-phenyl-2H-[1,2,3]triazole (**3**).

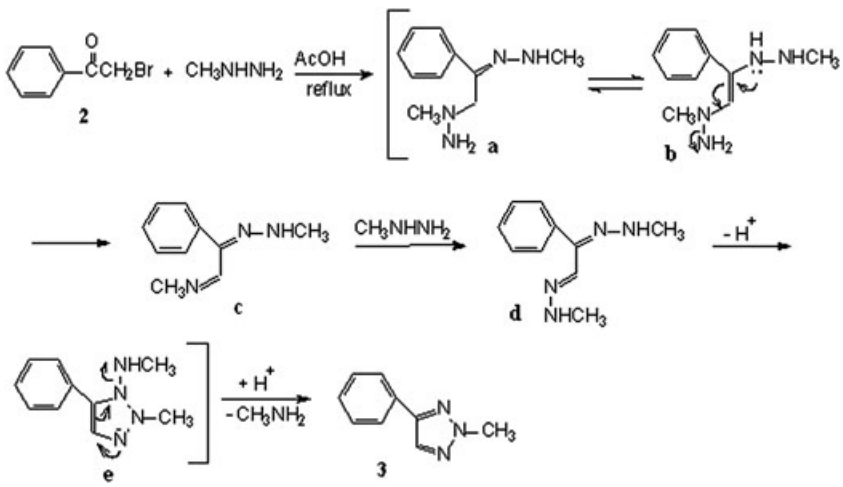
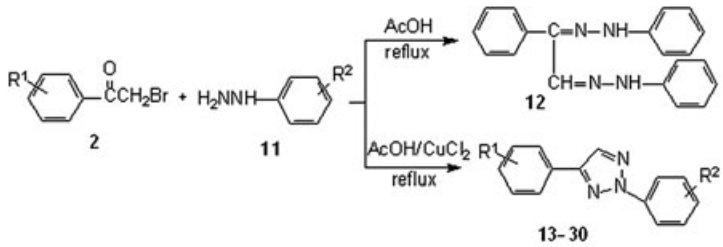


Table 2

Analytical and spectroscopic data for compounds **13-30**.

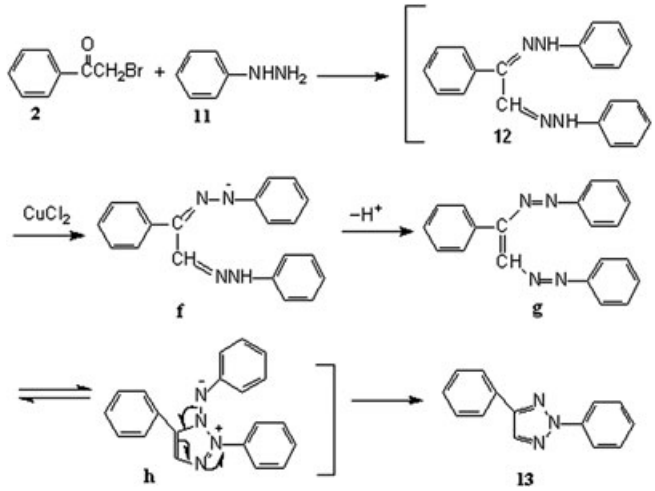
No	R^1	R^2	Yield %	m.p./°C	IR(KBr)/ν (cm^{-1})	^{1}H NMR: (deuteriochloroform): δ	Calculated (found) (%) C	H	N
13	H	H	50	34–36	3035,1598,1497,1457,757,693	8.14 (d, 2H, *J* = 8.2 Hz), 8.05 (s,1H), 7.90 (dd, 2H, *J* = 1.0, 8.2 Hz), 7.52-7.45 (m,4H), 7.41-7.34 (m,2H)	76.02 (75.88)	4.98 (4.90)	19.00 (19.14)
14	4-MeO	H	58	92–94	2966,1597,1500,1488,1464,835,762,693	8.12 (dd, 2H, *J* = 1.0, 8.6 Hz), 7.98(s,1H), 7.85-7.82(m,2H), 7.51-7.47(m,2H), 7.36-7.34(m,1H), 7.02-6.99(m,2H), 3.86(s,3H)	71.71 (71.66)	5.18 (5.03)	16.73 (16.65)
15	3,4-$(MeO)_2$	H	44	96–97	1598,1503,1464,764,692	8.12(d, 2H, *J* = 8.4 Hz), 7.98(s,1H), 7.51-7.45(m,3H), 7.41(d,1H, *J* = 8.4 Hz), 7.35-7.31(m,1H), 6.94(d,1H,*J* = 8.4 Hz), 3.98(s,3H), 3.92(s,3H)	68.33 (68.49)	5.34 (5.07)	14.95 (14.82)
16	2,4-$(MeO)_2$	H	46	75–76	1613,1594,1483,1461,758,701	8.23(s,1H), 8.15(dd,2H, *J* = 1.0,8.6 Hz), 8.08(d,1H,*J* = 8.4 Hz),7.52-7.49(m,2H), 7.37-7.33(m,1H), 6.65(dd,1H, *J* = 2.4,8.4 Hz), 6.59(d,1H,*J* = 2.8 Hz), 3.97(s,3H), 3.89(s,3H)	68.33 (68.28)	5.34 (5.16)	14.95 (15.08)
17	4-Me	H	51	64–66	1596,1496,1460,821,753,703	8.14-8.12(m,2H), 8.02(s,1H), 7.79(d, 2H, *J* = 8.1 Hz), 7.51-7.47(m,2H), 7.36-7.34(m,1H), 7.28-7.25(m,2H), 2.40(s,3H)	76.60 (76.44)	5.53 (5.42)	17.87 (17.72)
18	4-Cl	H	48	98–100	1597,1499,1460, 827,753,687	8.14-8.11(m,2H), 8.03(s,1H), 7.83(dd, 2H, *J* = 2.0,6.7 Hz), 7.50(t, 2H, *J* = 7.9 Hz), 7.44(dd, 2H, *J* = 2.0,6.7 Hz), 7.38-7.36 (m,1H)	65.77 (65.85)	3.91 (3.73)	16.44 (16.25)
19	3,4-Cl_2		39	108–110	1595, 1496, 1454, 762, 697;	8.10(d, 2H, *J* = 8.4 Hz), 8.00(d, 2H, *J* = 11.6 Hz), 7.69(dd, 1H, *J* = 2.2,8.2 Hz), 7.52-7.48(m,3H), 7.36(t,1H, *J* = 7.2 Hz)	57.95 (57.83)	3.10 (3.02)	14.49 (14.38)
20	2,4-F_2	H	59	82–84	1597,1500,1459, 749,702	8.17-8.13(m,4H), 7.53(t,2H, *J* = 7.6 Hz), 7.39(t,1H, *J* = 7.2 Hz), 7.08-6.95(m,2H)	65.37 (65.19)	3.50 (3.62)	16.34 (16.49)
21	4-Br	H	52	100–102	1599,1500,1461, 825,751, 687	8.13(d,2H, *J* = 7.7 Hz), 8.04(s,1H), 7.78(d,2H, *J* = 8.4 Hz), 7.60(d,2H, *J* = 8.4 Hz), 7.51(t,2H, *J* = 8.0 Hz), 7.37(t,1H, *J* = 7.4 Hz)	56.02 (55.86)	3.33 (3.25)	14.00 (14.11)
22	H	2-Me	28	73–74	2965, 1611, 1514, 1455, 764, 693	8.08-8.04(m,3H), 7.92-7.90(m,2H), 7.51-7.47(m,2H), 7.42-7.38(m,1H), 7.04-7.01(m,2H), 3.89(s,3H)	76.60 (76.74)	5.53 (5.50)	17.87 (17.74)
23	4-MeO	2-Me	32	64-65	2964, 1613, 1580, 1497, 1461, 839, 761	8.01(s,1H), 7.83-7.80(m,2H), 7.64-7.62(m,1H), 7.36-7.33(m,3H), 7.01-6.98(m,2H), 3.86(s,3H), 2.44(s,3H)	72.45 (72.26)	5.66 (5.29)	15.85 (15.68)
24	4-Cl	2-Me	35	67–69	2962, 1496, 824, 756	8.08(s,1H), 7.85-7.83(m,2H), 7.65-7.63(m,1H), 7.47-7.45(m,2H), 7.39-7.37(m,3H), 2.46(s,3H)	66.80 (66.87)	4.45 (4.28)	15.59 (15.34)
25	H	4-Me	46	74–76	3035,1605,1510,1456,812,767,692	8.06-8.03(m,3H), 7.94-7.91(m,2H), 7.51-7.48(m,2H), 7.43-7.39(m,1H), 7.32(d,2H, *J* = 8.0 Hz), 2.44(s,3H)	76.60 (76.42)	5.53 (5.38)	17.87 (18.03)
26	4-MeO	4-Me	58	115–117	3032,1614,1511,833,823	8.03-8.01(m,2H), 7.98(s,1H), 7.86-7.84(m,2H), 7.30(t,2H, *J* = 7.6 Hz), 7.03-7.01(m,2H), 3.89(s,3H), 2.44(s,3H)	72.45 (72.62)	5.66 (5.54)	15.85. (15.66)
27	4-Cl	4-Me	55	143–145	3036,1603,825,	8.03-8.00 (m,3H), 7.87-7.84 (m,2H), 7.48-7.44 (m,2H), 7.32 (d, 2H, *J* = 8.0 Hz), 2.44 (s,3H)	66.80 (66.72)	4.45 (4.30)	15.59 (15.36)
28	H	4-Cl	44	112–113	1494,1455,828,767,692	8.12-8.08 (m,3H), 7.93-7.90 (m,2H), 7.52-7.47 (m,4H), 7.45-7.42 (m,1H)	65.77 (65.59)	3.91 (3.62)	16.44 (16.25)
29	4-MeO	4-Cl	38	144–146	2963,1614,1494,459,837	8.10-8.08 (m,2H), 8.00 (s,1H), 7.85-7.83 (m,2H), 7.49-7.46 (m,2H), 7.03-7.01 (m,2H), 3.89 (s,3H)	63.06 (63.28)	4.20 (4.12)	14.71 (14.66)
30	4-Cl	4-Cl	26	134–135	1604,1493,827	8.11-8.08 (m,3H), 8.05 (s,1H), 7.86-7.83 (m,2H), 7.50-7.46 (m,4H)	57.95 (57.82)	3.10 (2.98)	14.49 (14.58)

Scheme 3. The synthesis of 2,4-diaryl-2H-[1,2,3]triazole derivatives (**13-30**).



R^1= H, 4-MeO, 3,4-$(MeO)_2$, 2,4-$(MeO)_2$, 4-Me, 4-Cl, 3,4-Cl_2, 2,4-F_2, 4-Br
R^2= H, 4-Me, 2-Me, 4-Cl

Scheme 4. The possible mechanism for the synthesis of 2,4-diphenyl-2H-[1,2,3]triazole (**13**).



the oxidation agent was needed to promote this cyclization. The mechanism proposed here was quite similar to the report by K.S. Balachandran [11]. It was said that the oxidation agent abstracts a proton from bisphenylhydrazone (**12**), giving rise to a radical intermediate (**f**). Further loss of a proton leads to the bis-azoolefin (**g**). And it is proved that bis-azoolefin can exist in the mesoionic form, which can be converted to 1,2,3-triazole, through the loss of phenylnitrene, both under thermal and photochemical conditions. In the absence of any catalysts, the intermediate (**12**) was the main product of the reaction of α-bromoacetophenone(**2**) with phenylhydrazine (**11**) in the acetic acid, which appeared as a kind of bright yellow solid. mp: 148°C (Lit. [12] 148°C), m/z 314 (calculated m/z 314).

EXPERIMENTAL

General procedure for the reaction of α-bromoacetophenones with methylhydrazine, yielding 2-methyl-4-aryl-2*H*-[1,2,3]triazoles(3-10). Methylhydrazine (1.7 mL,30 mmol) was added slowly to the solution of α-bromoacetophenone (1.2 g, 6 mmol) in acetic acid (2 mL).The mixture was heated to reflux over an oil bath for about 3 hours. After being cooled to room temperature, the reaction mixture was neutralized with 20% NaOH solution and then extracted twice with chloroform. The combined organic extracts were washed with water and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel using ethyl acetate: petroleum ether (1:15) as eluant to afford 2-methyl-4-phenyl-2*H*-[1,2,3]triazole (**3**) (60% yield) as white solid. mp 56°C (Lit. [9] 58°C); IR(KBr)/v (cm^{-1}) 3035, 1476, 1457, 1385, 764, 691; ^{1}H NMR: (deuteriochloroform): δ 7.81(s, 1H), 7.78–7.76(m, 2H), 7.45–7.41(m, 2H), 7.36–7.32 (m, 1H), 4.23 (s, 3H); Anal. Calcd. for $C_9H_9N_3$: C, 67.92; H, 5.66; N, 26.42. Found: C, 68.12; H, 5.65; N, 26.60.

4-(4-Chloro-phenyl)-2-methyl-2H-[1,2,3]triazole (4). Yield (%) 47; m.p. 96–98°C; IR/v (cm^{-1}) 1471, 1377, 829; ^{1}H NMR: δ 7.79 (s, 1H), 7.70 (dd, 2H, *J* = 2.0, 6.7 Hz), 7.39 (dd, 2H, *J* = 2.0, 6.7 Hz), 4.23 (s, 3H); Anal. Calcd. for $C_9H_8N_3Cl$: C, 55.83; H, 4.14; N, 21.71. Found: C, 55.69; H, 4.01; N, 21.45.

4-(4-Bromo-phenyl)-2-methyl-2H-[1,2,3]triazole (5). Yield (%) 41; m.p. 120–122°C; IR/v (cm^{-1}) 1473, 1379, 832; ^{1}H

NMR: δ 7.80 (s, 1H), 7.65–7.63 (m, 2H), 7.57–7.54 (m, 2H), 4.23 (s, 3H); Anal. Calcd. for $C_9H_8N_3Br$: C, 45.40; H, 3.36; N, 17.65. Found: C, 45.16; H, 3.43; N, 17.46.

2-Methyl-4-p-tolyl-2H-[1,2,3]triazole (6). Yield (%) 56; m.p. 64–66°C; IR/v (cm^{-1})3035, 1485, 1385, 821; ^1H NMR: δ 7.77 (s, 1H), 7.65 (d, 2H, *J* = 8.1 Hz), 7.23 (t, 2H, *J* = 8.0 Hz), 4.21 (s, 3H), 2.37 (s, 3H); Anal. Calcd. for $C_{10}H_{11}N_3$: C, 69.36; H, 6.36; N, 24.28. Found: C, 69.01; H, 6.17; N, 24.04.

4-(4-Methoxy-phenyl)-2-methyl-2H-[1,2,3]triazole (7). Yield (%) 73; m.p. 104–106°C; IR/v (cm^{-1})1613, 1578, 1483, 1383, 837; ^1H NMR: δ 7.74 (s, 1H), 7.71–7.68 (m, 2H), 6.97–6.94 (m, 2H), 4.21 (s, 3H), 3.84 (s, 3H); Anal. Calcd. for $C_{10}H_{11}N_3O$: C, 63.49; H, 5.82; N, 22.22. Found: C, 63.34; H, 5.99; N, 21.98.

4-(2-Methyl-2H-[1,2,3]triazol-4-yl)-phenol (8). Yield (%) 81; m.p. 126–128°C; IR/v (cm^{-1}); 3195, 1617, 1591, 1492, 843; ^1H NMR: δ 7.75 (s, 1H), 7.65–7.62 (m, 2H), 6.91–6.87 (m, 2H), 4.22 (s, 3H); m/z: 175$(M)^+$; Anal. Calcd. for $C_9H_9N_3O$: C,61.71; H, 5.14; N, 24.00. Found: C, 61.52; H, 5.23; N, 23.85.

4-(3,4-Dimethoxy-phenyl)-2-methyl-2H-[1,2,3]triazole (9). Yield (%) 58; m.p. 94–96°C; IR/v (cm^{-1}) 1607, 1590, 1500, 1380, 862, 841; ^1H NMR: δ 7.76 (s, 1H), 7.34 (d, 1H, *J* = 1.8 Hz), 7.31–7.27 (m, 1H), 6.92 (d, 1H, *J* = 8.3 Hz), 4.23 (s, 3H), 3.97 (s, 3H), 3.92 (s, 3H); Anal. Calcd. for $C_{11}H_{13}N_3O_2$: C, 60.27; H, 5.94; N, 19.18. Found: C, 60.02; H, 5.98; N, 19.05.

4-(2,4-Dimethoxy-phenyl)-2-methyl-2H-[1,2,3]triazole (10). Yield (%) 58; m.p. 80°C; IR/v (cm^{-1}) 1615, 1581, 1384, 834; ^1H NMR: δ 7.95 (s, 1H), 7.86 (d, 1H, *J* = 8.5 Hz), 6.59–6.54 (m, 2H), 4.21 (s, 3H), 3.90 (s, 3H), 3.84 (s, 3H); Anal. Calcd. for $C_{11}H_{13}N_3O_2$: C, 60.27; H, 5.94; N, 19.18. Found: C, 60.12; H, 5.85; N, 19.07.

General procedure for the reaction of α-bromoacetophenones with phenylhydrazines, yielding 2,4-diaryl-2*H*-[1,2,3]triazoles (13-30). Cupric chloride (0.2 g 1.5 mmol) was added to the mixture solution of α-bromoacetophenone (0.30 g 1.5 mmol) and phenylhydrazine (0.71 mL 6 mmol) in acetic acid (4 mL). The above mixture was heated to reflux over an oil bath for about 2 hours. After being cooled to room temperature, the reaction mixture was filtered by cotton, washed with dichloride methane until only the insoluble solid was left. The filtered solution was neutralized by 20% NaOH solution, then extracted, washed with NaCl saturated water, and dried over anhydrous Na_2SO_4. The solution was concentrated and the residue was purified by column chromatography on silica gel using ethyl acetate: petroleum ether = 1:30 as eluant, affording 2,4-diphenyl-2*H*-[1,2,3] triazole (**13**) (50 % yield) as light yellow solid. m.p. 36°C (Lit. [12] 40°C); IR/v (cm^{-1}) 3035, 1598, 1497, 1457, 757, 693; ^1H NMR: δ 8.14 (d, 2H, *J* = 8.2 Hz), 8.05 (s, 1H), 7.90 (dd, 2H, *J* = 1.0, 8.2 Hz), 7.52–7.45 (m, 4H), 7.41–7.34 (m, 2H); Anal. Calcd. for $C_{14}H_{11}N_3$: C,76.02; H, 4.98; N, 19.00. Found: C, 75.88; H, 4.90; N, 19.14.

4-(4-Methoxy-phenyl)-2-phenyl-2H-[1,2,3]triazole (14). Yield (%) 58; m.p. 92–94°C; IR/v (cm^{-1}) 2966, 1597, 1500, 1488, 1464, 835, 762, 693; ^1H NMR: δ 8.12 (dd, 2H, *J* = 1.0, 8.6 Hz), 7.98 (s, 1H), 7.85–7.82 (m, 2H), 7.51–7.47 (m, 2H), 7.36–7.34 (m, 1H), 7.02–6.99 (m, 2H), 3.86 (s, 3H); Anal. Calcd. for $C_{15}H_{13}N_3O$: C, 71.71; H, 5.18; N, 16.73. Found: C, 71.66; H, 5.03; N, 16.65.

4-(3,4-Dimethoxy-phenyl)-2-phenyl-2H-[1,2,3]triazole (15). Yield (%) 44; m.p. 96–97°C; IR/v (cm^{-1}) 1598, 1503, 1464, 764, 692; ^1H NMR: δ 8.12 (d, 2H, *J* = 8.4 Hz), 7.98 (s, 1H), 7.51–7.45 (m, 3H), 7.41 (d, 1H, *J* = 8.4 Hz), 7.35–7.31 (m, 1H), 6.94 (d, 1H, *J* = 8.4 Hz), 3.98 (s, 3H), 3.92 (s, 3H); Anal. Calcd. for $C_{16}H_{15}N_3O_2$: C, 68.33; H, 5.34; N, 14.95. Found: C, 68.49; H, 5.07; N, 14.82.

4-(2,4-Dimethoxy-phenyl)-2-phenyl-2H-[1,2,3]triazole (16). Yield (%) 46; m.p. 75–76°C; IR/v (cm^{-1})1613, 1594, 1483, 1461, 758, 701; ^1H NMR: δ 8.23 (s, 1H), 8.15 (dd, 2H, *J* = 1.0, 8.6 Hz), 8.08 (d, 1H, *J* = 8.4 Hz), 7.52–7.49 (m, 2H), 7.37–7.33 (m, 1H), 6.65 (dd, 1H, *J* = 2.4, 8.4 Hz), 6.59 (d, 1H, *J* = 2.8 Hz), 3.97 (s, 3H), 3.89 (s, 3H); Anal. Calcd. for $C_{16}H_{15}N_3O_2$: C, 68.33; H, 5.34; N, 14.95. Found: C, 68.28; H, 5.16; N, 15.08.

2-Phenyl-4-p-tolyl-2H-[1,2,3]triazole (17). Yield (%) 51; m.p. 64–66°C; IR/v (cm^{-1}) 1596, 1496, 1460, 821, 753, 703; ^1H NMR: δ 8.14–8.12 (m, 2H), 8.02 (s, 1H), 7.79 (d, 2H, *J* = 8.1 Hz), 7.51–7.47 (m, 2H), 7.36–7.34 (m, 1H), 7.28–7.25 (m, 2H), 2.40(s, 3H); Anal. Calcd. for $C_{15}H_{13}N_3$: C, 76.60; H, 5.53; N, 17.87. Found: C, 76.44; H, 5.42; N, 17.72.

4-(4-Chloro-phenyl)-2-phenyl-2H-[1,2,3]triazole (18). Yield (%) 48; m.p. 98–100°C; IR/v (cm^{-1})1597, 1499, 1460, 827, 753, 687; ^1H NMR: δ 8.14–8.11 (m, 2H), 8.03 (s, 1H), 7.83 (dd, 2H, *J* = 2.0, 6.7 Hz), 7.50 (t, 2H, *J* = 7.9 Hz), 7.44 (dd, 2H, *J* = 2.0, 6.7 Hz), 7.38–7.36 (m, 1H); Anal. Calcd. for $C_{14}H_{10}N_3Cl$: C, 65.77; H, 3.91; N, 16.44. Found: C, 65.85; H, 3.73; N, 16.25.

4-(3,4-Dichloro-phenyl)-2-phenyl-2H-[1,2,3]triazole (19). Yield (%) 39; m.p. 108–110°C; IR/v (cm^{-1})1595, 1496, 1454, 762, 697; ^1H NMR: δ 8.10 (d, 2H, *J* = 8.4 Hz), 8.00 (d, 2H, *J* = 11.6 Hz), 7.69 (dd, 1H, *J* = 2.2, 8.2 Hz), 7.52–7.48 (m, 3H), 7.36 (t, 1H, *J* = 7.2 Hz); Anal. Calcd. for $C_{14}H_9N_3Cl_2$: C, 57.95; H, 3.10; N, 14.49. Found: C, 57.83; H, 3.02; N, 14.38.

4-(2,4-Difluoro-phenyl)-2-phenyl-2H-[1,2,3]triazole (20). Yield (%) 59; m.p. 82–84°C; IR/v (cm^{-1})1597, 1500, 1459, 749, 702; ^1H NMR: δ 8.17–8.13 (m, 4H), 7.53 (t, 2H, *J* = 7.6 Hz), 7.39 (t, 1H, *J* = 7.2 Hz), 7.08–6.95 (m, 2H); Anal. Calcd. for $C_{14}H_9N_3F_2$: C, 65.37; H, 3.50; N, 16.34. Found: C, 65.19; H, 3.62; N, 16.49.

4-(4-Bromo-phenyl)-2-phenyl-2H-[1,2,3]triazole (21). Yield (%) 52; m.p. 100–102°C; IR/v (cm^{-1}) 1599, 1500, 1461, 825, 751, 687; ^1H NMR: δ 8.13 (d, 2H, *J* = 7.7 Hz), 8.04 (s, 1H), 7.78 (d, 2H, *J* = 8.4 Hz), 7.60 (d, 2H, *J* = 8.4 Hz), 7.51 (t, 2H, *J* = 8.0 Hz), 7.37(t, 1H, *J* = 7.4 Hz); Anal. Calcd. for $C_{14}H_{10}N_3Br$: C, 56.02; H, 3.33; N, 14.00. Found: C, 55.86; H, 3.25; N, 14.11.

4-Phenyl-2-o-tolyl-2H-[1,2,3]triazole (22). Yield (%) 28; m.p. 73–74°C; IR/v (cm^{-1}) 2965, 1611, 1514, 1455, 764, 693; ^1H NMR: δ 8.08–8.04 (m, 3H), 7.92–7.90 (m, 2H), 7.51–7.47 (m, 2H), 7.42–7.38 (m, 1H), 7.04–7.01 (m, 2H), 3.89 (s, 3H); Anal. Calcd. for $C_{15}H_{13}N_3$: C, 76.60; H,5.53; N,17.87. Found: C, 76.74; H, 5.50; N, 17.74.

4-(4-Methoxy-phenyl)-2-o-tolyl-2H-[1,2,3]triazole (23). Yield (%) 32; m.p. 64–65°C; IR/v (cm^{-1}) 2964, 1613, 1580, 1497, 1461, 839, 761; ^1H NMR: δ 8.01 (s, 1H), 7.83–7.80 (m, 2H), 7.64–7.62 (m, 1H), 7.36–7.33 (m, 3H), 7.01–6.98 (m, 2H), 3.86 (s, 3H), 2.44 (s, 3H); Anal. Calcd. for $C_{16}H_{15}N_3O$: C,72.45; H, 5.66; N, 15.85. Found: C, 72.26; H, 5.29; N, 15.68.

4-(4-Chloro-phenyl)-2-o-tolyl-2H-[1,2,3]triazole (24). Yield (%) 35; m.p. 67–69°C; IR/v (cm^{-1}) 2962, 1496, 824, 756; ^1H NMR: δ 8.08 (s, 1H), 7.85–7.83 (m, 2H), 7.65–7.63 (m, 1H), 7.47–7.45 (m, 2H), 7.39–7.37 (m, 3H), 2.46 (s, 3H);

Anal. Calcd. for $C_{15}H_{12}N_3Cl$: C, 66.80; H, 4.45; N, 15.59. Found: C, 66.87; H, 4.28; N, 15.34.

4-Phenyl-2-p-tolyl-2H-[1,2,3]triazole (25). Yield (%) 46; m.p. 74–76°C; IR/v (cm^{-1}) 3035, 1605, 1510, 1456, 812, 767, 692; ^1H NMR: δ 8.06–8.03 (m, 3H), 7.94–7.91 (m, 2H), 7.51–7.48 (m, 2H), 7.43–7.39 (m, 1H), 7.32 (d, 2H, J = 8.0 Hz), 2.44 (s, 3H); Anal. Calcd. for $C_{15}H_{13}N_3$: C, 76.60; H,5.53; N,17.87. Found: C, 76.42; H, 5.38; N, 18.03.

4-(4-Methoxy-phenyl)-2-p-tolyl-2H-[1,2,3]triazole (26). Yield (%) 58; m.p. 115–117°C; IR/v (cm^{-1}) 3032, 1614, 1511, 833, 823; ^1H NMR: δ 8.03–8.01 (m, 2H), 7.98 (s, 1H), 7.86–7.84 (m, 2H), 7.30 (t, 2H, J = 7.6 Hz), 7.03–7.01 (m, 2H), 3.89 (s, 3H), 2.44 (s, 3H); Anal. Calcd. for $C_{16}H_{15}N_3O$: C,72.45; H, 5.66; N, 15.85. Found: C, 72.62; H, 5.54; N, 15.66.

4-(4-Chloro-phenyl)-2-p-tolyl-2H-[1,2,3]triazole (27). Yield (%) 55; m.p. 143–145°C; IR/v (cm^{-1}) 3036, 1603, 825; ^1H NMR: δ 8.03–8.00 (m, 3H), 7.87–7.84 (m, 2H), 7.48–7.44 (m, 2H), 7.32 (d, 2H, J = 8.0 Hz), 2.44 (s, 3H); Anal. Calcd. for $C_{15}H_{12}N_3Cl$: C, 66.80; H, 4.45; N, 15.59. Found: C, 66.72; H, 4.30; N, 15.36.

2-(4-Chloro-phenyl)-4-phenyl-2H-[1,2,3]triazole (28). Yield (%) 44; m.p. 112–113°C; IR/v (cm^{-1}) 1494, 1455, 828, 767, 692; ^1H NMR: δ 8.12–8.08 (m, 3H), 7.93–7.90 (m, 2H), 7.52–7.47 (m, 4H), 7.45–7.42 (m, 1H); Anal. Calcd. for $C_{14}H_{10}N_3Cl$: C, 65.77; H, 3.91; N, 16.44. Found: C, 65.59; H, 3.62; N, 16.25.

2-(4-Chloro-phenyl)-4-(4-methoxy-phenyl)-2H-[1,2,3] triazole (29). Yield (%) 38; m.p. 144–146°C; IR/v (cm^{-1}) 2963, 1614, 1494, 459, 837; ^1H NMR: δ 8.10–8.08 (m, 2H), 8.00 (s, 1H), 7.85–7.83 (m, 2H), 7.49–7.46 (m, 2H), 7.03–7.01 (m, 2H), 3.89 (s, 3H); Anal. Calcd. for $C_{15}H_{12}N_3ClO$: C, 63.06; H, 4.20; N, 14.71. Found: C, 63.28; H, 4.12; N, 14.66.

2,4-Bis-(4-chloro-phenyl)-2H-[1,2,3]triazole (30). Yield (%) 26; m.p. 134–135°C; IR/v (cm^{-1}) 1604, 1493, 827; ^1H NMR: δ 8.11–8.08 (m, 3H), 8.05 (s, 1H), 7.86–7.83 (m, 2H), 7.50–7.46 (m, 4H); Anal. Calcd. for $C_{14}H_9N_3Cl_2$: C, 57.95; H, 3.10; N, 14.49. Found: C, 57.82; H, 2.98; N, 14.58.

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