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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b02023 • Publication Date (Web): 06 Oct 2017

Selective synthesis of 3-arylbenzo-1,2,3-triazin-4(3*H*)-ones and 1-aryl-(1*H*)-benzo-1,2,3-triazoles from 1,3-diaryltriazenes through Pd(0) catalyzed annulation reactions

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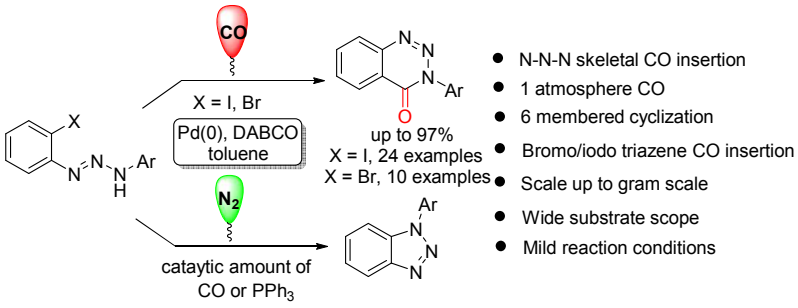


Abstract

Pd(0) catalyzed carbonylative annulation reaction of 1-(2-iodophenyl)-3-aryltriaz-1-enes in the presence of DABCO and 1 atmosphere of carbon monoxide in toluene at 80 ^{o}C gave the corresponding 3-arylbenzo-1,2,3-triazin-4(3*H*)-ones with high selectivity and in excellent yields. Substrate scope of this reaction is demonstrated with 24 examples with various halo, alkyl and alkoxy substituents on either of the aromatic rings. Bromo substituted triazenes were less reactive as starting materials towards the carbonylative annulation reaction and yielded 3-arylbenzo-1,2,3-triazin-4(3*H*)-ones in good to moderate yields only in the presence of xantphos as an additive. In the absence of CO (under N_2 atmosphere) the reaction did not proceed and only starting material was recovered. However, in the presence of catalytic amount of CO or in the presence of Ph_3P in catalytic amounts as additives the reactions proceeded to yield the corresponding 1-aryl-(1*H*)-benzo-1,2,3-triazoles selectively in good yields. Based on control experiments, a plausible reaction mechanism for the selective formation of 3-arylbenzo-1,2,3-

triazin-4(3*H*)-ones in the presence of CO and1-aryl-(1*H*)-benzo-1,2,3-triazoles in the absence of CO through a common intermediate has been proposed.

Introduction

Benzo-1,2,3-triazin-4(3*H*)-one is an important heterocyclic scaffold in medicinal chemistry. Derivatives of benzo-1,2,3-triazin-4(3*H*)-one exhibit a wide variety of biological activities such as sedative,[1] diuretic,[2] anesthetic,[3] antiarthritic,[4] antitubercular[5] and antitumor activities.[6] The structures of a few representative examples of biologically active benzo-1,2,3-triazin-4(3*H)*-ones are shown in Figure 1.

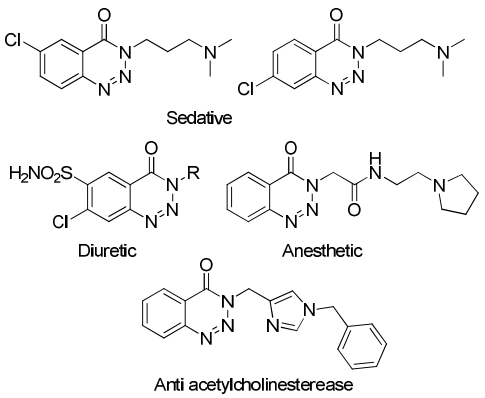
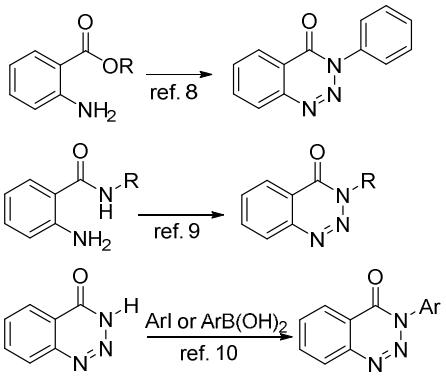


Figure 1.Representative examples of biologically active benzo-1,2,3-triazin-4(3*H*)-ones.

Benzo-1,2,3-triazin-4(3*H*)-ones are also useful starting materials in organic synthesis for the synthesis of isoquinolones by metal catalyzed denitrogenative transannulation reactions with allenes and alkynes.[7] Conventionally benzo-1,2,3-triazin-4(3*H*)-ones were synthesized through a multistep route from methyl anthranilates and anthranilamides using diazotization of the amino functional group (Scheme 1).[8] Recently an oxidative annulation of 2-aminobenzamides with nitromethane using tert-butyl hydroperoxide and KI as oxidant[9] is reported. Copper catalyzed

Ullmann type coupling of benzo-1,2,3-triazin-4(3*H*)-ones with aryl iodides and aryl boronic acids has been reported for the synthesis of 3-arylbenzo-1,2,3-triazin-4(3*H*)-ones.[10] Pd catalyzed denitrogenative carbonylation of aryltriazenes in acidic conditions yields amides.[11]



Scheme 1. Literature methods for the synthesis of benzo-1,2,3-triazin-4(3*H*)-ones.

Although transition metal catalyzed carbonylative annulation reaction has been applied to the synthesis of a variety of heterocyclic scaffolds,[12] it has not been applied to the synthesis of benzo-1,2,3-triazin-4(3*H*)-ones. Our interest in Pd(0) catalyzed carbonylation reactions[13] using carbon monoxide as a one carbon source led us to the investigation of carbonylative annulation of 1-(2-X-phenyl)-3-phenyltriaz-1-ene (X = Br, I). In general carbon monoxide insertion of C-Br bond requires harsher reaction conditions in comparison to insertion to C-I bond and may need high pressure of CO. Especially, CO insertion between aryl bromide and amine has been reported at high pressures of carbon monoxide.[14] Herein we demonstrate the synthesis of 3-arylbenzo-1,2,3-triazin-4(3*H*)-ones from 1-(2-bromophenyl)-3-aryltriaz-1-enes (**4**) under 1 atmosphere CO pressure. Using the carbonylative annulation strategy a facile synthetic method has been developed for the synthesis of 3-arylbenzo-1,2,3-triazin-4(3*H*)-ones. Interestingly in the presence of only catalytic amount of carbon monoxide the reaction led to the formation of 1-aryl-(1*H*)-benzo-1,2,3-triazoles. Cu(I) (*via* C-X activation where X = Br and I)[15] and Pd(II) (via C-H

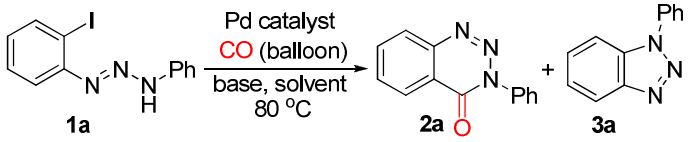
activation)[16] catalyzed synthesis of 1-aryl-(1*H*)-benzo-1,2,3-triazoles from 1,3-diaryltriaz-1-enes is reported in literature.[15,16] A plausible mechanism involving a common intermediate for the selective formation of either 3-arylbenzo-1,2,3-triazin-4(3*H*)-ones or 1-aryl-(1*H*)-benzo-1,2,3-triazoles has been proposed.

Results and discussion

Under basic conditions 1,3-diaryltriaz-1-enes undergo facile *cis-trans* isomerization reaction.[17] We anticipated the *cis* isomer to be particularly useful for Pd(0) catalyzed intramolecular amination and carbonylative amination reactions to yield 1-aryl-(1*H*)-benzo-1,2,3-triazoles and 3-arylbenzo-1,2,3-triazin-4(3*H*)-ones, respectively. We began our investigation on the carbonylative annulation with 1-(2-iodophenyl)-3-phenyltriaz-1-ene **1a** under 1 atmosphere of carbon monoxide in presence of $Pd(PPh_3)_2Cl_2$ in toluene at 80 ^oC in the presence of Et_3N as base (entry 1, Table 1). Under these conditions **2a** was formed in 87%. Reaction also proceeded smoothly to give 95% of **2a** when DABCO was used as the base (entry 4, Table 1). Under these conditions **3a** was not at all formed. The reaction conditions were optimized by screening various Pd source as catalysts, bases and solvents (Scheme 2, Table 1). All the reactions were carried out at 80 ^oC as there was no reaction at room temperature. From entries 2 and 4 (Table 1) it is evident that both Et_3N and DABCO gave good yields of **2a** selectively without the formation of **3a.** Surprisingly no reaction was observed when DBU was used as the base (entry 3, Table 1). When the solvent was changed from toluene to acetonitrile or THF a mixture of **2a** and **3a** was formed and the reaction did not proceed at all in DMF (entries 5-7, Table 1). Both $Pd(OAc)_2$ and $Pd(CH_3CN)_2Cl_2$ (entry 8 and 9, Table 1) were ineffective as catalysts for the above transformation in toluene. When the reaction was carried out with 2 mol% of $Pd(PPh_3)_2Cl_2$ as

catalyst the yield of **2a** dropped to 80%. From entry 4 it is evident that a combination of $Pd(PPh_3)_2Cl_2$ (3 mol%) as the catalyst, DABCO (3 equiv) as base[18] and toluene as solvent at 80 ^oC was most effective for above transformation. Under these conditions **2a** is formed with high selectivity and excellent yield. Therefore subsequent reactions were carried out under these optimized conditions.

Table 1: Optimization of reagents and conditions for Pd catalyzed annulation reaction of 1-(2-iodophenyl)-3-phenyltriaz-1-ene (**1a**).

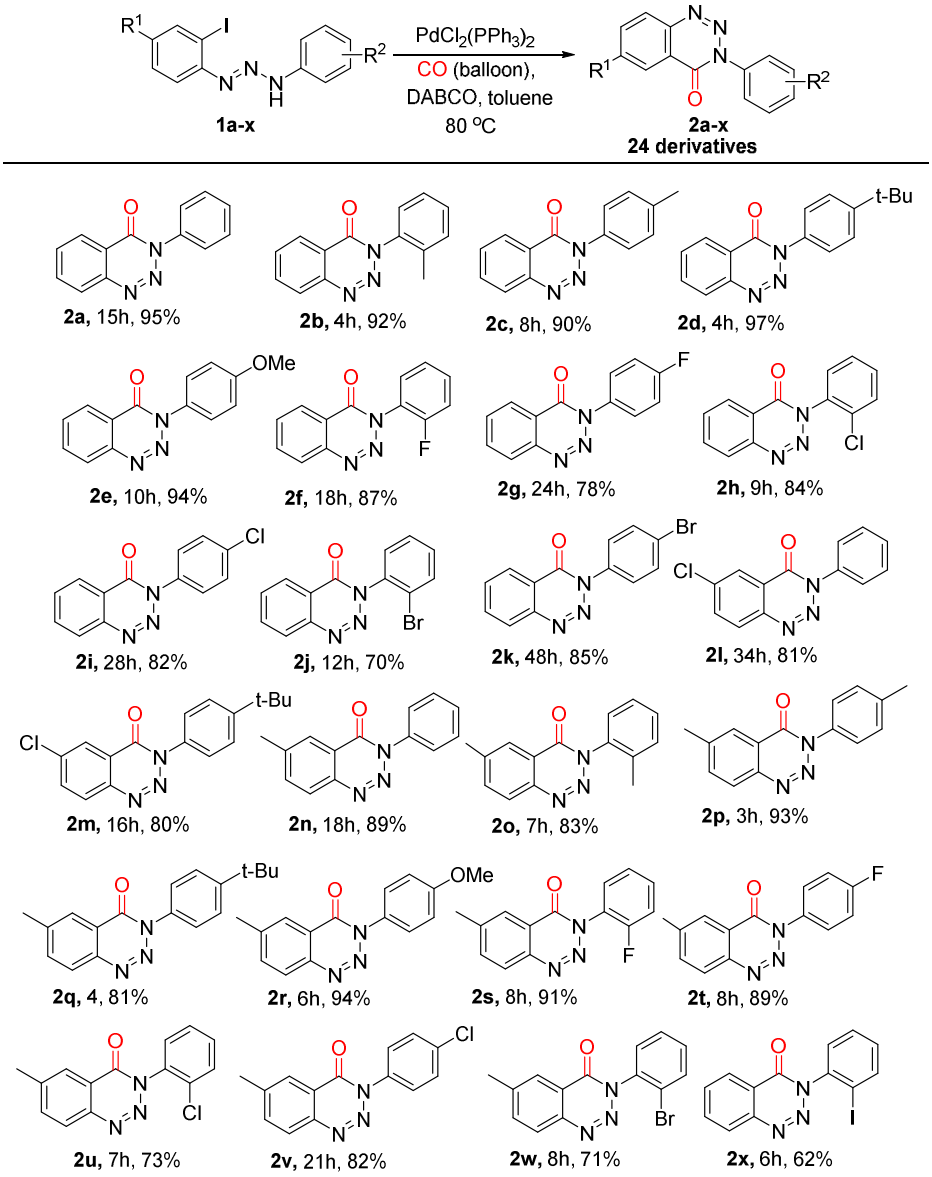


S.No	Pd source[a]	Base	Solvent	Time (h)	Yield(%)	
					2a	**3a**
1	$PdCl_2(PPh_3)_2$	Et_3N	toluene	24	87	0
2	$PdCl_2(PPh_3)_2$	pyridine	toluene	36	trace	0
3	$PdCl_2(PPh_3)_2$	DBU	toluene	36	NR[b]	NR[b]
4	$PdCl_2(PPh_3)_2$	DABCO	toluene	15	95	0
5	$PdCl_2(PPh_3)_2$	DABCO	CH_3CN	24	60	30
6	$PdCl_2(PPh_3)_2$	DABCO	THF	36	40	15
7	$PdCl_2(PPh_3)_2$	DABCO	DMF	15	NR[b]	NR[b]
8	$Pd(OAc)_2$	DABCO	toluene	36	25	0
9	$PdCl_2(CH_3CN)_2$	DABCO	toluene	36	trace	0

Reaction conditions: [a]**1a** (0.5 mmol), Pd cat (3.0 mol%), base (3 equiv), solvent (4 mL)
[b]NR = no reaction

The scope of substrates is amply demonstrated by varying the substituents on both the aryl rings. From the data presented in Scheme 2 the following conclusions can be drawn. Both electron

donating groups (methoxy, methyl and *t*-butyl) as well as electron withdrawing groups (fluoro, chloro, bromo and iodo) are tolerated in the 3-aryl ring. Substrates with electron donating groups reacted faster than the ones with electron withdrawing substituents. *Ortho* and *para* methyl substituents on 3-aryl ring (**1b** and **1c**) showed considerable rate difference. While *para* methyl substituted substrate **1c** took 8 h for the completion of the reaction to give 90% of triazinone **2c**, under similar conditions *ortho* methyl substituted substrate **1b** reacted within 4 h to give 92% of triazinone **2b**. Similarly *ortho* halo substituted triazenes reacted faster than *para* substituted halo triazenes. *Ortho* substituted derivatives are sterically more hindered and hence reacted faster perhaps due to the increased rate of reductive elimination step of the reaction. Diiodo substituted triazene **1x** also reacted cleanly with carbon monoxide under optimized reaction conditions to give mono iodotriazinone **2x** in moderate yield. The products (**2a-x)** were thoroughly characterized by spectroscopic data. In addition, the structures of **2q** and **2w** were established unequivocally by single crystal X-ray data (SI).



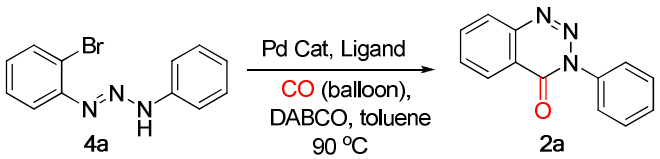
Reaction conditions: 1 (0.5 mmol), $PdCl_2(PPh_3)_2$ (3 mol%), DABCO (3 equiv), toluene (4 mL).

Scheme 2. Pd catalyzed carbonylative annulation of 1-(2-iodophenyl)-3-phenyltriaz-1-ene.

In order to make the methodology more versatile, carbonylative annulation of 1-(2-bromophenyl)-3-aryltriaz-1-enes (**4a-k**) to the corresponding 3-arylbenzo-1,2,3-triazin-4(3*H*)-ones was investigated (Table 2). Firstly 1-(2-bromophenyl)-3-phenyltriaz-1-ene **4a** was treated with CO under optimized reaction conditions of Table 1, yield of the desired product **2a** was

only 12 % after prolonged reaction for 72 h. (Table 2). When the reaction was carried out with 10 mol% of Pd catalyst yield of **2a** improved slightly. Further addition of mono and bi-dentate ligands such as PPh_3 and 1,2-bis(diphenylphosphino)ethane (dppe) (entries 3-5, Table 2) did not improve the yield of **2a**. However, when reaction was carried out in the presence of xantphos as ligand the desired product **2a** was obtained in 60% within 26 h. Only trace amount of **2a** was obtained when $Pd(OAc)_2$ was used as the catalyst. Under optimized reaction conditions (entry 6, Table 2) scope of substrates was demonstrated and results are listed in Table 3. 2-Bromotriazenes substituted both at the *ortho* and *para* positions on the 3-phenyl ring were tolerated under optimized reaction conditions and yielded the corresponding triazinones (**2b-c, 2f-g, 2h-i**) in good to moderate yields. *Ortho* substituted derivatives reacted faster and gave better yields of the corresponding triazinones (**2**) compared to the *para* substituted derivatives. Surprisingly the desired product **2y** was not observed in case of 1- (2-bromophenyl)-3-(3-chlorophenyl)triaz-1-ene (**4y**)**,** the only product obtained was triazole **3y** in 56 % yield. In case of triazene **4z** the expected carbonylated product was obtained in 35% yield.

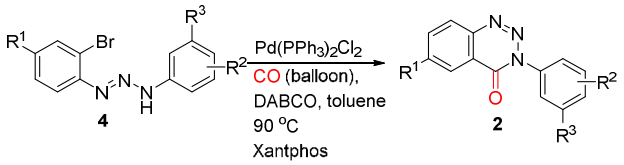
Table 2: Reaction optimization for Pd catalyzed carbonylation of 1-(2-bromophenyl)-3-phenyltriaz-1-ene.



Entry	Pd catalyst[a]	base	Ligand	Time(h)	Yield(%)
1	[b]$PdCl_2(PPh_3)_2$	DABCO	-	72	12
2	$PdCl_2(PPh_3)_2$	DABCO	-	72	23
3	$PdCl_2(PPh_3)_2$	DABCO	PPh_3	72	31
4	$PdCl_2(PPh_3)_2$	DABCO	dppe	68	30
5	$PdCl_2(PPh_3)_2$	K_2CO_3	dppe	72	0
6	$PdCl_2(PPh_3)_2$	DABCO	xantphos	26	60
7	$Pd(OAc)_2$	DABCO	xantphos	26	trace

Reaction conditions: [a]**4a** (0.5 mmol), Pd cat (10 mol%), ligand (10 mol%) base (3 equiv), solvent (3 mL), [b]3 mol% of $PdCl_2(PPh_3)_2$.

Table 3: Pd catalyzed carbonylative annulation of bromotriazene (**4**) derivatives.

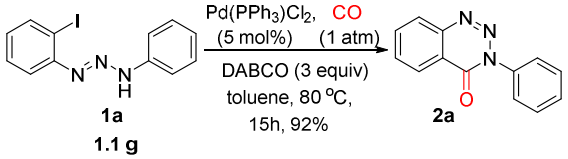


Entry[a]	**4**	R^1	R^2	R^3	Time (h)	**2**, Yield (%)
1	**4a**	H	H	H	26	**2a**, 60
2	**4b**	H	2- Me	H	18	**2b**, 79
3	**4c**	H	4-Me	H	24	**2c**, 62
4	**4f**	H	2-F	H	20	**2f**, 58
5	**4g**	H	4-F	H	26	**2g**, 55
6	**4h**	H	2-Cl	H	22	**2h**, 71
7	**4i**	H	4-Cl	H	28	**2i**, 51[b]
8	**4n**	Me	H	H	26	**2n**, 51

9	**4v**	Me	4-Cl	H	26	**2v**, 53[b]
10	**4y**	H	H	Cl	28	**2y**, 0[b,] **3y**, 56[c]
11	**4z**	H	2- Me	Me	24	**2z**, 35[b]

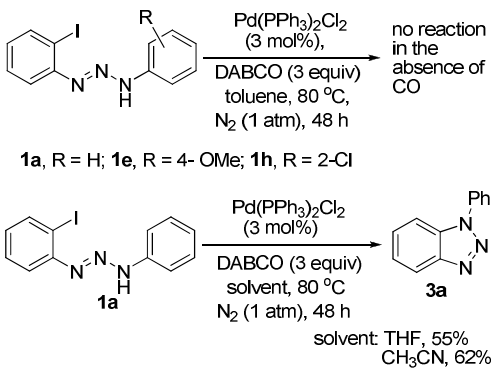
Reaction conditions: [a] **4** (0.5 mmol), $PdCl_2(PPh_3)_2$ cat (10 mol%), ligand (10 mol%), DABCO (3 equiv), toluene (3 mL), [b] $PdCl_2$ was used, [c] non-carbonylated product, triazole **3y** was obtained.

To examine the efficiency of the carbonylation reaction in gram scale, the reaction was carried out with 1.1 g (3.4 mmol) of 1-(2-iodophenyl)-3-phenyltriaz-1-ene **1a** and desired product **2a** obtained in 92% yield (Scheme 3).



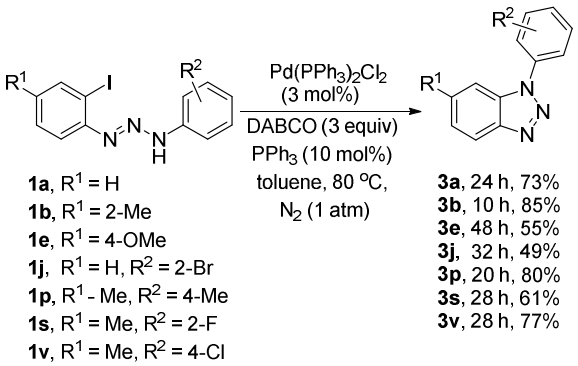
Scheme 3: Synthesis of **2a** in gram scale reaction

In order to understand the reaction mechanism the following control experiments were carried out. When **1a**, **1e** and **1h** were reacted separately in the absence of carbon monoxide (under N_2 atmosphere) but otherwise under identical conditions as in Scheme 2, only starting materials were recovered after 48 h (Scheme 4). The anticipated amination products **3a**, **3e** and **3h**, respectively, were not formed under these reaction conditions. However, when the reaction of **1a** was carried out in THF and acetonitrile the anticipated benzotriazole derivative **3a** was formed in moderate yield.

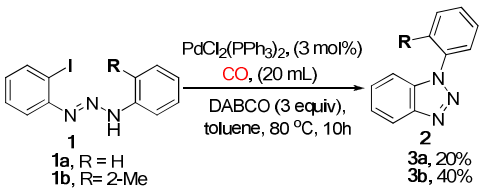


Scheme 4. Effect of solvent polarity on the formation of benzotriazoles in the absence of CO.

In another set of experiments several iodo-1,3-diaryltriazenes (**1**) were reacted separately under optimized conditions with 10 mol% of PPh_3 as an additive. In the presence of PPh_3 as an additive the reaction proceeded smoothly to yield the anticipated amination products, namely the triazoles, (**3**) in good yields (Scheme 5).



Scheme 5. Effect of PPh_3 as additive in the absence of CO towards formation of benzotriazole derivatives.



Scheme 6. Effect of catalytic amount of CO towards formation of benzotriazole derivatives.

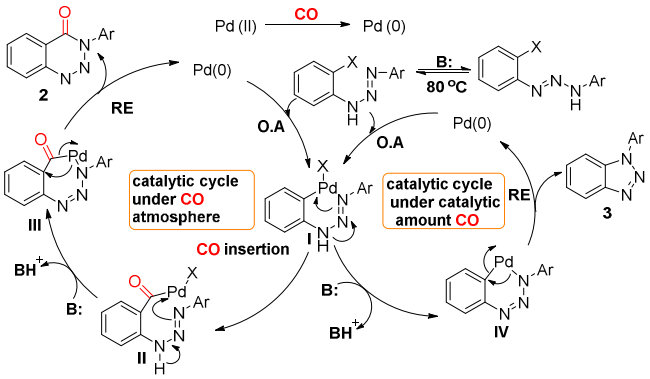
The effect of CO, solvent polarity and PPh_3 as additive in the formation of benzotriazoles was studied. The results of this study are summarized in Table 4. The reaction of **1a** and **1b** in the absence of PPh_3 and in the presence of catalytic amount of CO (20 mL of CO was taken in a syringe and bubbled into the reaction mixture) under otherwise conditions identical to Scheme 2, proceeded to furnish **3a** and **3b** in 20% and 40% yields respectively in 10 h (Scheme 6). From these experiments we conclude that CO acts as the reducing agent in toluene and reduces Pd(II) to Pd(0)[19] which is the catalytically active species. In toluene DABCO does not reduce for Pd(II) to Pd(0). However in acetonitrile and THF the reaction proceeded in the absence of CO indicating that solvent polarity plays a major role in forming the catalytically active Pd(0). In toluene either catalytic amount of PPh_3 or CO was necessary as additives (as reducing agent for Pd(II)) and perhaps as stabilizing ligands for the formation of catalytically active Pd(0) and under these conditions the reaction proceeded to give benzotriazole derivatives (**3**) as the sole product (Table 4).

Table 4. Effect of CO, solvent polarity and PPh_3 as additive in the formation of benzotriazoles

entry	substrate[a]	CO	PPh_3	solvent	Time(h)	Yield(%)
1	**1a**	absent	absent	toluene	48	NR
2	**1e**	absent	absent	toluene	48	NR
3	**1h**	absent	absent	toluene	48	NR
4	**1a**	absent	absent	THF	48	**3a**, 55
5	**1a**	absent	absent	CH_3CN	48	**3a**, 62
6	**1a**	absent	10 mol%	toluene	24	**3a**, 73
7	**1b**	absent	10 mol%	toluene	10	**3b,** 85
8	**1c**	absent	10 mol%	toluene	18	**3r**, 55
9	**1a**	cat. amount[b]	absent	toluene	10	**3a**, 20
10	**1b**	cat. amount[b]	absent	toluene	10	**3b**, 40

Reaction conditions: : [a] **1** (0.5 mmol), $PdCl_2(PPh_3)_2$ (10 mol%), solvent 3 mL, [b]20 mL of CO added from a syringe.

Based on the above observations a plausible mechanism for the formation of benzo-1,2,3-triazin-4(3*H*)-ones (**2**) in the presence of CO and (1*H*)-benzo-1,2,3-triazoles (**3**) in catalytic amount of CO is proposed (Scheme 7). According to literature[20] 1,3-diaryltriazene can undergo *cis-trans* isomerization under basic conditions. Subsequently the *cis* isomer undergoes oxidative addition to *in situ* generated Pd (0) to produce intermediate **I** (Scheme 7). The fact that in the presence of CO, benzotriazinone **2** was formed with high selectivity indicates that intermediate **I** in the catalytic cycle is effectively trapped by CO through insertion reaction. The rate of CO insertion with intermediate **I** must be much faster than the alternative route of Pd-N bond formation leading to the formation of intermediate **IV.** Thus **I** serves as a common intermediate for the formation of **2** and **3** and the presence or absence of CO controls, respectively the rate of CO insertion to form **II** *vs* the rate of Pd-N bond formation to intermediate **IV**. In the case of Pd catalyzed CO insertion of bromotriazenes **4** metal catalyst may get additional stability in presence of xantphos and undergoes oxidative addition[21] with triazene **4** and subsequent reaction of CO followed by reductive elimination of metal produces CO inserted annulated product **2.**



Scheme 7. Catalytic cycle for the formation of **2** and **3**

Conclusion

A new methodology based on Pd(0) catalyzed carbonylative amination of 1-(2-X-phenyl)-3-aryltriaz-1-enes (X = Br and I) (**1**) has been developed for the synthesis of the corresponding 3-arylbenzo-1,2,3-triazin-4(3*H*)-ones (**2**) with high selectivity and in excellent yields under 1 atmosphere of carbon monoxide. The substrate scope for this reaction is amply demonstrated with 24 examples. The less reactive bromo derivatives required catalytic amount of xantphos as ligand for the reaction to proceed to yield **2**. No reaction was observed in the absence of CO (under N_2 atmosphere). However, in the presence of catalytic amount of either CO or triphenylphosphine the reaction of **1** proceeded to give the corresponding benzotriazoles (**3**) in good yields. Thus the methodology developed in the present study allows the synthesis of either 3-arylbenzo-1,2,3-triazin-4(3*H*)-ones (**2**) or 1-aryl-(1*H*)-benzo-1,2,3-triazoles (**3**) in a highly selective manner. Based on some control experiment a mechanism involving a common intermediate (**I** in Scheme 7) for the formation of **2** and **3** is proposed.

Experimental section:

General Procedure for Synthesis of Triazenes (1a-1x, 4)

All the triazenes **(1a-1x, 4)** were synthesized as follows according to reported procedure[16] with minor changes. To a stirred solution of water (7 mL) and conc. HCl (0.7 mL) in 50 mL round bottom was added 2-haloaniline (1 mmol) at room temperature. The resulting mixture was cooled to 0 ^{o}C and then an ice cold solution of $NaNO_2$ (1 equiv) in water (3 mL) was added. After reaction mixture was stirred for 10 min at same temperature was added partner aniline drop wise and the mixture was allowed to stir for 15 min at 0 ^{o}C. To the resulting clear solution (where partner aniline was not completely soluble acetone (1 mL)was added until it became clear

solution) a solution of sodium acetate (1.5 g) in water (6 mL) was added and stirring was continued for next 1h at 0 ^{o}C.The resulting precipitate was filtered through a buchner funnel, washed with ice cold water 3 times and then dried at room temperature. The solid triazenes (**1a-1x**, **4a-4k**) thus obtained were used in further reactions without any purification.

General procedure for the synthesis of benzo-1,2,3-triazine-4-ones (2) from 2-iodotriazenes (1)

To a 10 mL oven dried schlenk round bottom flask kept under N_2 atmosphere was added $PdCl_2(PPh_3)_2$ (3 mol%, 11 mg) and triazene (**1**) (0.5 mmol) followed by DABCO (1.5 mmol, 168 mg) then toluene (4 mL). The reaction mixture was flushed 3 times with CO from a balloon and stirred at 80 ^{o}C under CO (1 atm). Progress of the reaction was monitored by TLC. After stirring for the required period of time (see Scheme 2), the reaction mixture was cooled to room temperature and passed through a celite pad, washed with CH_2Cl_2. The combined filtrate was concentrated under vacuum and the crude product thus obtained was purified by column chromatography on silica gel.

General procedure for Synthesis of benzo-1,2,3-triazine-4(3*H*)-ones (2) from bromotriazenes (4). To an oven dried schlenk reaction tube kept under N_2 atmosphere was added $Pd(PPh_3)_2(Cl)_2$ catalyst (10 mol%), triazene (**4**) (0.5 mmol), DABCO (1.5 mmol, 168 mg) followed by xantphos (10 mol%, 29 mg) then toluene (3 mL). The reaction mixture was flushed 3 times with CO from a balloon and stirred at 90 ^{o}C under CO (1 atm). Progress of the reaction was monitored by TLC. After stirring for the required period of time (Scheme3), the reaction mixture was cooled to room temperature and passed through a celite pad, washed with CH_2Cl_2.

The combined filtrate was concentrated under vacuum and crude product was purified by column chromatography on silica gel.

Synthesis of 2a in gram scale reaction:

To a 50mL oven dried schlenk round bottom flask kept under N_2 atmosphere was added $PdCl_2(PPh_3)_2$ (5 mol%, 120 mg) and triazene (**1a**) (3.4 mmol, 1.1 g) followed by DABCO (10.2 mmol, 1.15 g) then toluene (18 mL). Reaction mixture was flushed 3 times with CO from a balloon and stirred at 80 ^oC under CO (1 atm) for 15h. Progress of the reaction was monitored by TLC. Reaction mixture was cooled to room temperature and passed through a celite pad, washed with CH_2Cl_2. The combined filtrate was concentrated under vacuum and crude the product was purified by column chromatography on silica gel. **2a** was obtained in 92% yield (700 mg).

3-Phenylbenzo-1,2,3-triazin-4(3*H*)-one (2a)[9] :

White solid, yield 105 mg (95%), mp 129 ^oC (lit. 127-129 ^oC), ^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (dd, J = 8 , 1.2 Hz, 1H), 8.22 (d, J = 8 Hz, 1H), 7.98 (dt, J = 7.2, 1.2 Hz, 1H), 7.86-7.82 (m, 1H), 7.67-7.64 (m, 2H), 7.57-7.54 (m, 2H), 7.51-7.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 143.8, 138.9, 135.2, 132.8, 129.1, 129.0, 128.6, 126.1, 125.7, 120.5; IR (KBr): cm^{-1} 1680; HRMS (ESI, m/z) Calcd for $C_{13}H_9N_3ONa$ 246.0643 (M+Na), found 246.0667.

3-(2-Methylphenyl)benzo-1,2,3-triazin-4(3*H*)-one (2b)[9] :

Pale yellow solid, yield 109 mg, (92%), mp 151 ^oC (lit. 153-155 ^oC), ^1H NMR (500 MHz, $CDCl_3$): δ 8.44 (dd, J = 1, 7.5 Hz, 1H), 8.25 (d, J = 8 Hz, 1H), 8.01 (dt, J = 1.5, 7.5 Hz, 1H), 7.87-7.84 (m, 1H), 7.46-7.36 (m, 4H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 144.1, 137.9, 135.6, 135.2, 132.8, 131.3, 130.0, 128.7, 127.8, 127.1, 125.7, 120.4, 17.8.

3-(4-Methylphenyl)benzo-1,2,3-triazin-4(3*H*)-one (2c)[9] :

White solid, yield 106 mg, (90%), mp 139 ^{o}C (lit. 139-141 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 8 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.98 (t, *J* = 7.6 Hz, 1H), 7.83(t, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 143.8, 139.1, 136.4, 135.1, 132.7, 129.8, 128.5, 125.9, 125.7, 120.5, 21.3.

3-(4-*tert*-Butylphenyl)benzo-1,2,3-triazin-4(3*H*)-one (2d)[9] :

White crystalline solid, yield 135 mg, (97%), mp 148 ^{o}C (lit. 144-146 ^{o}C), ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (td, *J* = 1, 8 Hz, 1H), 8.21 (d, *J* = 8 Hz, 1H), 8.00-7.96 (m, 1H), 7.85 - 7.82 (m, 1H), 7.57 (s, 4H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 155.4, 152.2, 143.8, 136.3, 135.1, 132.7, 128.5, 126.2, 125.7, 125.6, 120.5, 34.9, 31.4.

3-(4-Methoxyphenyl)benzo-1,2,3-triazin-4(3*H*)-one (2e)[9] :

Pale yellow solid, yield 118 mg (94%), mp 148 ^{o}C (lit. 151-153 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (dd, *J* = 0.8, 8.8 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.97 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.85-7.81 (m, 1H), 7.56 and 7.05 (AA'BB' pattern *J* = 8.8, 9.2 Hz, 4H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 155.5, 143.8, 135.1, 132.7, 131.8, 128.5, 127.4, 125.7, 120.5, 114.4, 55.7.

3-(2-Fluorophenyl)benzo-1,2,3-triazin-4(3*H*)-one (2f)[22] :

Off white solid, yield 104 mg, (87%), mp 132 ^{o}C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (dd, *J* = 1.5, 8 Hz, 1H), 8.25-8.23 (m, 1H), 8.03-7.99 (m, 1H), 7.88-7.85 (m, 1H), 7.57-7.50 (m, 2H), 7.37-7.29 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.4, 156.4, 154.9, 143.8, 135.4, 133.1, 131.58, 131.52, 129.1, 128.8, 126.7, 126.6, 125.7, 124.93, 124.90, 120.3, 116.9, 116.8.

3-(4-Fluorophenyl)benzo-1,2,3-triazin-4(3*H*)-one (2g)[22] :

White crystalline solid, yield 93 mg (78%), mp 147 ^{o}C (lit. 151-153 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (dd, *J* = 0.4, 7.6 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.02-7.98 (m, 1H), 7.88-7.84 (m, 1H), 7.66-7.63 (m, 2H), 7.26-7.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 143.7, 135.3, 133.0, 128.7, 128.1, 128.0, 125.7, 120.4, 116.2, 116.0.

3-(2-Chlorophenyl)benzo-1,2,3-triazin-4(3*H*)-one (2h)[7] :

Pale yellow solid, yield 107 mg (84%), mp 110 ^{o}C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46-8.44 (m, 1H), 8.26-8.25 (m, 1H), 8.04-8.00 (m, 1H), 7.89-7.85 (m, 1H), 7.63-7.61 (m, 1H), 7.54-7.48 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0, 143.9, 136.6, 135.4, 133.0, 132.4, 131.2, 130.6, 129.6, 128.8, 127.9, 125.7, 120.4.

3-(4-Chlorophenyl)benzo-1,2,3-triazin-4(3*H*)-one (2i)[9] :

White solid, yield 104 mg, (82%), mp 176 ^{o}C (lit. 178-180 ^{o}C), ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (dd, *J* = 1, 7.5 Hz, 1H), 8.22 (d, *J* = 8 Hz, 1H), 8.01-7.98 (m, 1H), 7.87-7.84 (m, 1H), 7.63 and 7.52 (AA'BB' pattern *J* = 9, 9 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 143.7, 137.3, 135.3, 134.9, 133.0, 129.3, 128.7, 127.3, 125.8, 120.3.

3-(2-Bromophenyl)benzo-1,2,3-triazin-4(3*H*)-one (2j):

Yellow solid, yield 105 mg, (70%), mp 110 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (dd, *J* = 7.6, 1.2 Hz 1H), 8.26 (d, *J* = 8 Hz, 1H), 8.04-8.00 (m, 1H), 7.89-7.85 (m, 1H), 7.80 (d, *J* = 8 Hz, 1H), 7.54-7.51 (m, 2H), 7.44- 7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 144.0, 138.2, 135.4, 133.7, 133.0, 131.4, 129.8, 128.9, 128.6, 125.8, 122.3, 120.5; IR (KBr): cm^{-1} 1695; HRMS (ESI, m/z) Calcd for $C_{13}H_9N_3OBr$ 301.9929 (M+H), found 301.9904.

3-(4-Bromophenyl)benzo-1,2,3-triazin-4(3*H*)-one (2k) :

White crystalline solid, yield 128 mg, (85%), mp 187 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 7.6 Hz, 1H), 8.22 (d, *J* = 8 Hz, 1H), 8.00 (t, *J* = 7.2 Hz, 1H), 7.86 (t, *J* = 7.2 Hz, 1H), 7.86 (d,

J = 7.2 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 143.7, 137.8, 135.4, 133.1, 132.3, 128.7, 127.6, 125.8, 122.9, 120.3; IR (KBr): cm^{-1} 1693; HRMS (ESI, m/z) Calcd for $C_{13}H_8N_3OBrNa$ 323.9627 (M+Na), found 323.9637.

6-Chloro-3-phenylbenzo-1,2,3-triazin-4(3*H*)-one (2l)[9] :

Pale yellow solid, yield 100 mg (81%), mp 175 ^{o}C (lit. 175-177 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 2.4 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 7.92 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.65-7.63 (m, 2H), 7.58-7.56 (m, 2H), 7.52-7.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 142.1, 139.3, 138.6, 135.8, 130.3, 129.3, 129.2, 126.1, 125.3, 121.7.

3-(4-*tert*-Butylphenyl)-6-chlorobenzo-1,2,3-triazin-4(3*H*)-one (2m) :

Pale orange solid, yield 124 mg, (80%), mp 161 ^{o}C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (d, *J* = 1.6 Hz, 1H), 8.16 (d, *J* = 6.8 Hz, 1H), 7.91 (dd, *J* = 6.8, 2 Hz 1H), 7.59-7.54 (m, 4H), 1.38 (s , 9H); ^{13}C NMR (125MHz, $CDCl_3$): δ 154.3, 152.4, 142.2, 139.2, 136.0, 135.7, 130.2, 126.3, 125.5, 125.3, 121.7, 34.9, 31.4; IR (KBr): cm^{-1} 1686; HRMS (ESI, m/z) Calcd for $C_{17}H_{17}N_3OCl$ 314.1060 (M+H), found 314.1063.

6-Methyl-3-phenylbenzo-1,2,3-triazin-4(3*H*)-one (2n)[9]:

White crystalline solid, yield 105 mg (89%), mp 155 ^{o}C (lit. 151-153^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s , 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 2H), 7.50-7.46 (m, 1H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 144.2, 142.1, 139.0, 136.5, 129.1, 128.9, 128.5, 126.2, 125.1, 120.3, 22.0.

6-Methyl-3-(2-methylphenyl)benzo-1,2,3-triazin-4(3*H*)-one (2o):

Off white solid, 103 mg, (83%), mp 126 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 0.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.80 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.45-7.35 (m, 4H), 2.60 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 144.2, 142.5, 138.1, 136.5, 135.6, 131.2,

129.9, 128.6, 127.8, 127.1, 125.0, 120.3, 22.0, 17.8; IR (KBr): cm^{-1} 1688; HRMS (ESI, m/z) Calcd for $C_{15}H_{13}N_3ONa$ 274.0956 (M+Na), found 274.0962.

6-Methyl-3-(4-methylphenyl)benzo-1,2,3-triazin-4(3*H*)-one (2p):

White crystalline solid, yield 116 mg (93%), mp 144 ^oC, ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.77 (dd, *J* = 8, 1.2 Hz, 1H), 7.51 (d, *J* = 8 Hz, 2H), 7.34 (d, *J* = 8 Hz, 2H), 2.59 (s, 3H), 2.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 144.0, 142.2, 139.0, 136.5, 136.4, 129.7, 128.4, 126.0, 125.1, 120.3, 22.0, 21.3; ; IR (KBr): cm^{-1} 1680; HRMS (ESI, m/z) Calcd for $C_{15}H_{13}N_3ONa$ 274.0956 (M+Na), found 274.0942.

3-(4-*tert*-Butylphenyl)-6-methylbenzo-1,2,3-triazin-4(3*H*)-one (2q):

White solid, yield 118 mg (81%), mp 184 ^oC, ^1H NMR (500 MHz, $CDCl_3$): 8.22 (s, 1H), 8.10 (d, *J* = 6.8 Hz, 1H), 7.78 (dd, *J* = 6.8, 0.4 Hz, 1H), 7.56 (s, 4H), 2.60 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6, 152.1, 144.0, 142.2, 136.4, 128.5, 126.2, 126.1, 125.6, 125.1, 120.3, 34.9, 31.4, 22.0; IR (KBr): cm^{-1} 1689; HRMS (ESI, m/z) Calcd for $C_{18}H_{20}N_3O$ 294.1606 (M+H), found 294.1617.

3-(4-Methoxyphenyl)-6-methylbenzo-1,2,3-triazin-4(3*H*)-one (2r):

Off white solid, yield 125 mg (94%), mp 152 ^oC, ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 8.09 (d, *J* = 8 Hz, 1H), 7.55 and 7.05 (AA'BB' pattern, *J* = 9.2 Hz, 8.8 Hz, 4H). 7.77 (dd, *J* = 8.4, 2 Hz, 1H), 3.87 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 155.6, 144.0, 142.2, 136.4, 131.9, 128.4, 127.4, 125.1, 120.3, 114.3, 55.7, 22.0; IR (KBr): cm^{-1} 1680; HRMS (ESI, m/z) Calcd for $C_{15}H_{13}N_3O_2Na$ 290.0905 (M+Na), found 290.0912.

3-(2-Fluorophenyl)-6-methylbenzo-1,2,3-triazin-4(3*H*)-one (2s):

Pale orange solid, yield 115 mg (91%), mp 133 ^oC, ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.12 (d, *J* = 8 Hz, 1H), 7.80 (d, *J* = 8 Hz, 1H), 7.57-7.49 (m, 2H), 7.36-7.26 (m, 2H), 2.60 (s,

3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 156.2, 155.1, 144.4, 142.2, 136.6, 131.4, 131.3, 129.1, 128.7, 126.8, 125.1, 124.89, 124.86, 120.1, 116.9, 116.7, 22.0; IR (KBr): cm^{-1} 1693; HRMS (ESI, m/z) Calcd for $C_{14}H_{10}N_3OFNa$ 278.0706 (M+Na), found 278.0685.

3-(4-Fluorophenyl)-6-methylbenzo-1,2,3-triazin-4(3*H*)-one (2t):

White solid, yield 113 mg (89%), mp 156 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.81-7.78 (m, 1H), 7.66-7.61 (m, 2H), 7.26-7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 161.4, 155.5, 144.4, 142.1, 136.6, 135.0, 128.6, 128.1, 128.0, 125.1, 120.2, 116.2, 116.0; IR (KBr): cm^{-1} 1694; HRMS (ESI, m/z) Calcd for $C_{14}H_{10}N_3OFNa$ 278.0706 (M+Na), found 278.0692.

3-(2-Chlorophenyl)-6-methylbenzo-1,2,3-triazin-4(3*H*)-one (2u):

Pale yellow solid, yield 98 mg (73%), mp 152 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.13 (d, *J* = 8 Hz, 1H), 7.81 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.62-7.60 (m, 1H), 7.54-7.47 (m, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 144.4, 142.3, 136.7, 136.6, 132.5, 131.1, 130.5, 129.7, 128.7, 127.9, 125.2, 120.2, 22.0; IR (KBr): cm^{-1} 1694; HRMS (ESI, m/z) Calcd for $C_{14}H_{10}N_3OCl$ 294.0410 (M+Na), found 294.0430.

3-(4-Chlorophenyl)-6-methylbenzo-1,2,3-triazin-4(3*H*)-one (2v):

White solid, yield 110 mg (82%), mp 192 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21(s, 1H), 8.10 (d, *J* = 8 Hz, 1H), 7.79 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 144.4, 142.0, 137.5, 136.6, 134.8, 129.3, 128.6, 127.3, 125.1, 120.2, 22.1; IR (KBr): cm^{-1} 1695; HRMS (ESI, m/z) Calcd for $C_{14}H_{10}N_3OClNa$ 294.0410 (M+Na), found 294.0428.

3-(2-Bromophenyl)-6-methylbenzo-1,2,3-triazin-4(3*H*)-one (2w):

Brown solid, yield 112 mg (71%), mp 142 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (dd, *J* = 1.2, 0.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.83-7.78 (m, 2H), 7.53-7.51 (m, 2H), 7.43-7.39 (m, 1H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 144.4, 142.3, 138.3, 136.7, 133.7, 131.3, 129.8, 128.8, 128.6, 125.2, 122.4, 120.3, 22.0; IR (KBr): cm^{-1} 1694; HRMS (ESI, m/z) Calcd for $C_{14}H_{11}N_3OBr$ 316.0085 (M+H), found 316.0086.

3-(2-Iodophenyl)benzo-1,2,3-triazin-4(3*H*)-one (2x):

White solid, yield 84 mg (62%), mp 175 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47-8.45 (m, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.05-8.01 (m, 2H), 7.90-7.86 (m, 1H), 7.59-7.54 (m, 1H), 7.50-7.48 (m, 1H), 7.28-7.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 144.1, 141.6, 140.1, 135.4, 133.0, 131.4, 129.6, 129.2, 128.9, 125.8, 120.6, 97.5; IR (KBr): cm^{-1} 1694; HRMS (ESI, m/z) Calcd for $C_{13}H_8N_3OINa$ 371.9610 (M+Na), found 371.9595.

3-(2,5-Dimethylphenyl)benzo-1,2,3-triazin-4(3*H*)-one (2z):

White solid, yield 44mg (35%), mp 126 ^{o}C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (dd, *J* = 1, 8 Hz, 1H), 8.25 (d, *J* = 8 Hz, 1H), 8.02-7.99 (m, 1H), 7.87-7.84 (m, 1H), 7.30-7.24 (m, 2H), 7.19 (s, 1H), 2.39 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.3, 144.1, 137.7, 137.0, 135.2, 132.8, 132.3, 131.1, 130.8, 128.6, 128.2, 125.7, 120.4, 20.9, 17.3; IR (KBr): 1680 cm^{-1} ; HRMS (ESI, m/z) Calcd for $C_{15}H_{13}N_3ONa$ 274.0956 (M+Na), found 274.0928.

1-Phenyl-(1*H*)-benzo-1,2,3-triazole (3a)[23] :

White solid, yield 71 mg (73%), mp 93 ^{o}C (lit. 90-92^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 ($AA^{'}BB^{'}$ pattern *J* = 8.4, 1H), 7.80-7.73 (m, 3H), 7.63-7.59 (m, 2H), 7.56-7.48 (m, 2H),7.45-7.41(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 137.1, 132.4, 129.9, 128.7, 128.3, 124.5, 123.0, 120.4, 110.4.

1-(2-Methylphenyl)-(1*H*)-benzo-1,2,3-triazole (3b)[23] :

White solid, yield 89 mg, (85%), mp 61 °C (lit. 60-63°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (AA'BB' pattern J = 8.4, 1H), 7.52-7.33 (m, 7H), 2.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 135.4, 135.3, 134.0, 131.8, 130.1, 128.1, 127.1, 127.0, 124.2, 120.2, 110.2, 17.9.

1-(2-Bromophenyl-(1*H*)-benzo-1,2,3-triazole (3j)[15] :

Pale orange solid, yield 67 mg, (49%), mp 132 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.4 Hz, 1H), 7.84 (dd, J = 8.4, 1.2 Hz, 1H), 7.57-7.41 (m, 5H), 7.36 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 135.8, 134.2, 133.8, 131.6, 129.5, 128.7, 128.2, 124.3, 120.9, 120.3, 110.6.

6-Methyl-1-(4-methylphenyl)-(1*H*)-benzo-1,2,3-triazole (3p)[16] :

Pale yellow solid, 90 mg (80%), mp 90 °C (lit. 92-93 °C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.47 (s, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.24 (dd, J = 8.8, 1.2 Hz, 1H), 2.53 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 138.8, 138.7, 134.7, 133.0, 130.4, 126.6, 123.0, 119.7, 109.6, 22.1, 21.3.;

1-(4-Methoxyphenyl)-6-methyl-(1*H*)-benzo-1,2,3-triazole (3r) :

White solid; yield 62 mg (55%), mp 85 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.4 Hz, 1H), 7.64 and 7.10 (AA'BB' pattern, J = 8.8 Hz, 9.2 Hz, 4H), 7.42 (t, J = 0.8 Hz, 1H), 7.23 (dd, J = 8.8, 1.2 Hz, 1H), 3.90 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 145.0, 138.8, 133.2, 130.2, 126.5, 124.7, 119.7, 115.0, 109.5, 55.7, 22.1; HRMS (ESI, m/z) Calcd for $C_{14}H_{13}N_3ONa$ 262.0956 (M+Na), found 262.0963.

1-(2-Fluorophenyl)-6-methyl-(1*H*)-benzo-1,2,3-triazole (3s) :

Pale yellow solid, 69 mg (61%), mp 89 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.8 Hz, 1H), 7.70-7.66 (m, 1H), 7.56-7.51 (m, 1H), 7.40-7.35 (m, 2H), 7.26-7.24 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 154.5, 144.6, 139.2, 134.1, 131.0, 130.9, 127.9, 126.7,

125.3, 125.2, 124.8, 124.7, 119.6, 117.3, 117.1, 109.8, 109.7, 22.1; HRMS (ESI, m/z) Calcd for 228.0925 (M+H), found 228.0932.

1-(4-Chlorophenyl)-6-methyl-(1*H*)-benzo-1,2,3-triazole (3v)[15] :

White solid, 93 mg (77%), mp 131 ^{o}C (lit. 128-130 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 0.4 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 139.4, 135.8, 134.4, 132.7, 130.1, 126.8, 124.1, 120.0, 109.4, 22.2.

1-(3-Chlorophenyl)-(1*H*)-benzo-1,2,3-triazole (3y)[23]**:**

Pale yellow solid, 64 mg (56%), mp 106 ^{o}C (lit. 108-110 ^{o}C), ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.84 (t, *J* = 2 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.73-7.71 (m, 1H), 7.61-7.54 (m, 2H), 7.50-7.45 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.6, 138.1, 135.7, 132.1, 131.0, 128.8, 128.7, 124.8, 123.0, 120.8, 120.6, 110.2.

Supporting Information

The supporting information is available free of charge on the ACS publication website at DOI:

Copies of ^{1}H and ^{13}C NMR spectra of derivatives of **2** and **3** and CIF files of **2q** and **2w**.

Acknowledgment

We thank the Department of Chemistry, IIT Madras for infrastructure and Mr. Venkatachalam Ramkumar for the XRD data and structure solving. AC thanks UGC, New Delhi for a fellowship.

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Notes:

The authors declare no competing financial interest.

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