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Gold Catalyzed Concomitant [3+3] Cycloaddition/ Cascade Heterocyclization of Enynones/Enynals with Azides Leading to Furanotriazines

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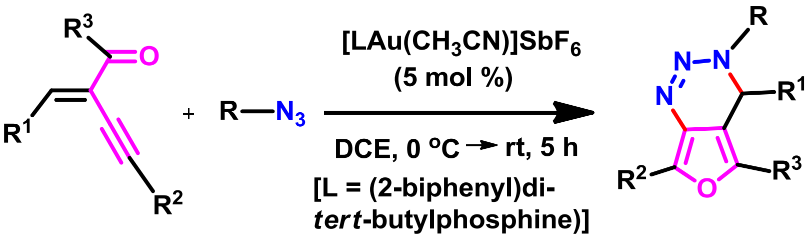


Abstract

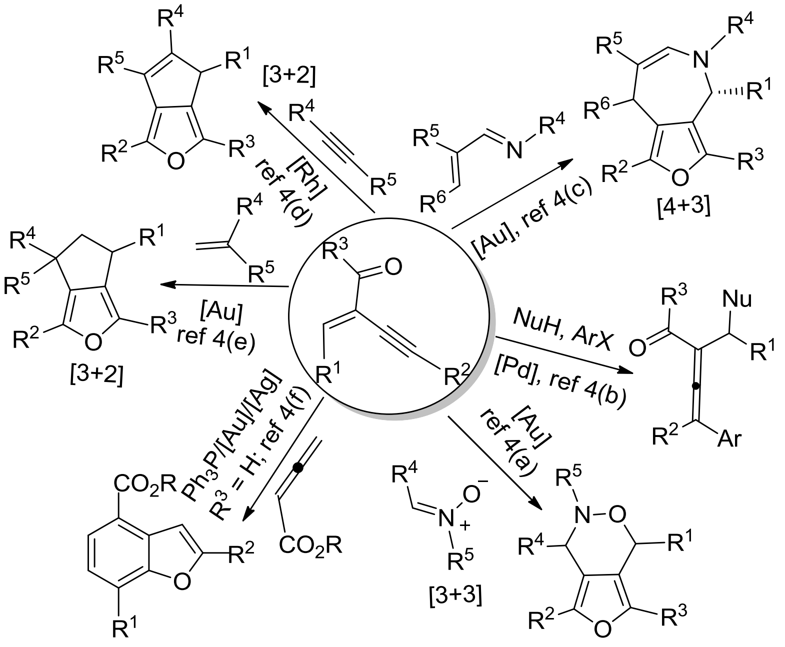
[Au]-catalyzed [3+3] cycloaddition reaction of enynones/enynals with azides, which allows the efficient regioselective synthesis of highly fused furo[3,4-d][1,2,3]triazines in good to excellent yields under mild conditions has been developed. The synthetic utility of furanotriazines was exploited by oxidation with cerium ammonium nitrate (CAN) affording highly functionalized dihydrotriazines. Both furo[3,4-d][1,2,3]triazines and dihydrotriazines exhibit good fluorescence activity.

Introduction

Gold catalysis has now become a powerful synthetic tool thanks to the unique ability of gold(I) to activate carbon-carbon π-systems generating highly complex molecules from simple precursors.[1] Construction of polysubstituted furans via gold catalysis[2] has attracted considerable attention due to the occurrence of furan skeleton in numerous natural products and pharmaceutical ingredients in addition to their importance as building blocks in organic synthesis.[3] Enynones/ enynals, with their multifunctional nature, are versatile synthons for transition metal (including gold) catalyzed transformations as illustrated in Scheme 1.[4] Subsequent to the report by Larock et al in 2004 on gold catalyzed cyclization of enynones to polysubstituted furans,[2a-b] numerous other reports via [Cu],[5a-c] [Ag],[5d] [Pd],[4b, 6a-c] [Pt],[6d-e] and [Rh],[4d] catalyzed annulations as well as electrophilic cyclization[6f-g] have appeared in the literature. Gold catalyzed [3+2] cycloaddition of enynones with diarylethenes is also reported.[4e] Pioneering studies by J. Zhang's group demonstrated the versatility of enynones in [3+3],[4a, 7a] [3+2],[4d, 7b] and [4+3][4c, 8] cycloaddition reactions with various nucleophiles, although [3+3] cycloaddition reactions are rather rare. Gold-catalyzed tandem cyclization of 1,2-bis(alkynyl)-2-en-1-ones with indoles leading to indole-fused polycyclics is also reported recently.[9] An interesting recent work involves aza annulation of enynal azides leading to substituted pyridines.[10] Interestingly, though, phosphorus(III) azides exhibit a different mode of reaction with DMAD (dimethyl acetylenedicarboxylate).[11a-b] The azide-alkyne click reaction leading to 1,2,3-triazoles is well-known; however, additional approaches by using azides and aldehydes are also reported.[11c] Very recently, Luo, Xu and co-workers reported the synthesis of highly functionalized triazines from azides with cyclopropane 1,1-diesters, wherein the cyclopropane ring acts as an alkene equivalent.[11d] Among the three possible triazines systems, 1,2,3-triazines are pharmaceutically useful because of their potent efficacy and minimal side effects.[12] Hence there are a reasonable number of reports on the synthesis and utility of 1,2,3-triazines.[13] To our knowledge, furan fused triazine (furanotriazine) ring system has never been reported till now.

Herein, we report a novel approach to this class of compounds from the regioselective [3+3] cycloaddition of enynones/enynals with azides via gold-catalysis.

Scheme 1. Representative Cycloaddition Reactions of Enynones with Nucleophiles

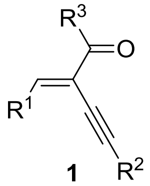


Results and Discussion

(i). Gold catalyzed reaction of enynones **1a-m** *with benzyl azides/alkyl azides/ cinnamyl azides*

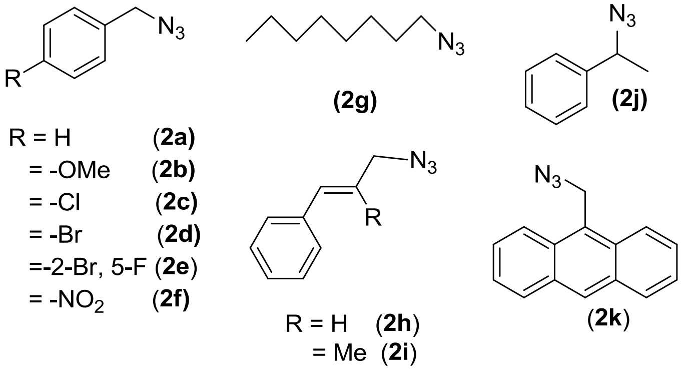
The enynones **1a-m** and the azides **2a-k** used in the present study are shown in Chart 1.

Chart 1. Enynones 1a-m and azides 2a-k



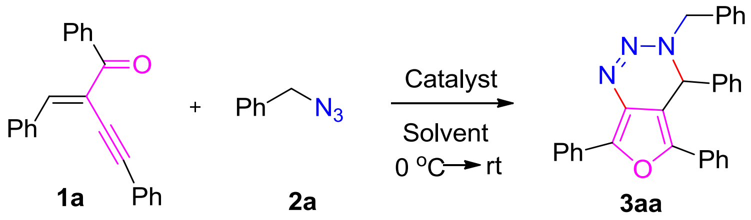
1

R^1 = Ph,	R^2 = Ph,	R^3 = Ph	(**1a**)
R^1 = 4-MeO-C_6H_4,	R^2 = Ph,	R^3 = Ph	(**1b**)
R^1 = 3-F-C_6H_4,	R^2 = Ph,	R^3 = Ph	(**1c**)
R^1 = 4-F-C_6H_4,	R^2 = Ph,	R^3 = Ph	(**1d**)
R^1 = Ph ,	R^2 = 4-MeO-C_6H_4,	R^3 = Ph	(**1e**)
R^1 = Ph ,	R^2 = 4-Me-C_6H_4,	R^3 = Ph	(**1f**)
R^1 = Ph ,	R^2 = 2-Me-C_6H_4,	R^3 = Ph	(**1g**)
R^1 = Ph ,	R^2 = 4-F-C_6H_4,	R^3 = Ph	(**1h**)
R^1 = Ph ,	R^2 = 4-Cl-C_6H_4,	R^3 = Ph	(**1i**)
R^1 = Ph ,	R^2 = -cyclohexenyl	R^3 = Ph	(**1j**)
R^1 = Ph ,	R^2 = Ph,	R^3 = 4-MeO-C_6H_4	(**1k**)
R^1 = Ph ,	R^2 = Ph,	R^3 = 4-Me-C_6H_4	(**1l**)
R^1 = Ph ,	R^2 = Ph,	R^3 = 2-Me-C_6H_4	(**1m**)



Initially, the reaction of (*E*)-2-benzylidene-1,4-diphenylbut-3-yn-1-one **1a** with benzyl azide **2a** in the presence of Ph_3PAuCl/AgOTf (5 mol %) in dichloromethane (DCM) for 5 h led to the [3+3] cycloadduct **3aa** in 35% yield (Table 1, entry 1). The product yield marginally improved by changing the solvent from DCM to DCE (entry 2). Varying the counter-ion or use of IPrAuCl/$AgSbF_6$ did not enhance the yield of **3aa** (entries 3-6). IPrAuCl itself was not effective (entry 7). Other gold catalysts like $NaAuCl_4.2H_2O$, AuCl, $HAuCl_4.3H_2O$ and $AuCl_3$ gave very poor yields (entries 8-11). Surprisingly, the reaction proceeded very smoothly with 5 mol % LAu(CH_3CN)SbF_6 (L = [(2-biphenyl)di-*tert*-butylphosphine]) as the catalyst in DCE solvent affording the product **3aa** in 84% yield (entry 12). It is important to note that enynone in DCE solvent should be added drop-wise at 0 °C to the solution of gold complex and azide; at rt, the reaction is vigorous and reduces the product yield (entry 13). Addition of corresponding silver salt to the above gold catalyst slightly decreases the yield of the desired product (entry 14). Solvents such as DCM, 1,4-dioxane, toluene and $CHCl_3$ were less effective (entries 15-18). In methanol or DMF, enynone did not react with benzyl azide, but other byproducts were formed.[2a-b] Other variations did not improve the yield (entries 19-22). Thus the optimal reaction conditions are: **1a** (1.0 equiv.), **2a** (1.2 equiv) and LAu(CH_3CN)SbF_6 (5 mol %) in DCE (2 mL) as a solvent from 0 °C to rt for 5 h.

Table 1. Survey of Reaction Conditions for the [3+3] Cycloaddition of (*E*)-2-Benzylidene-1,4-diphenylbut-3-yn-1-one 1a with Benzyl Azide 2a[a]



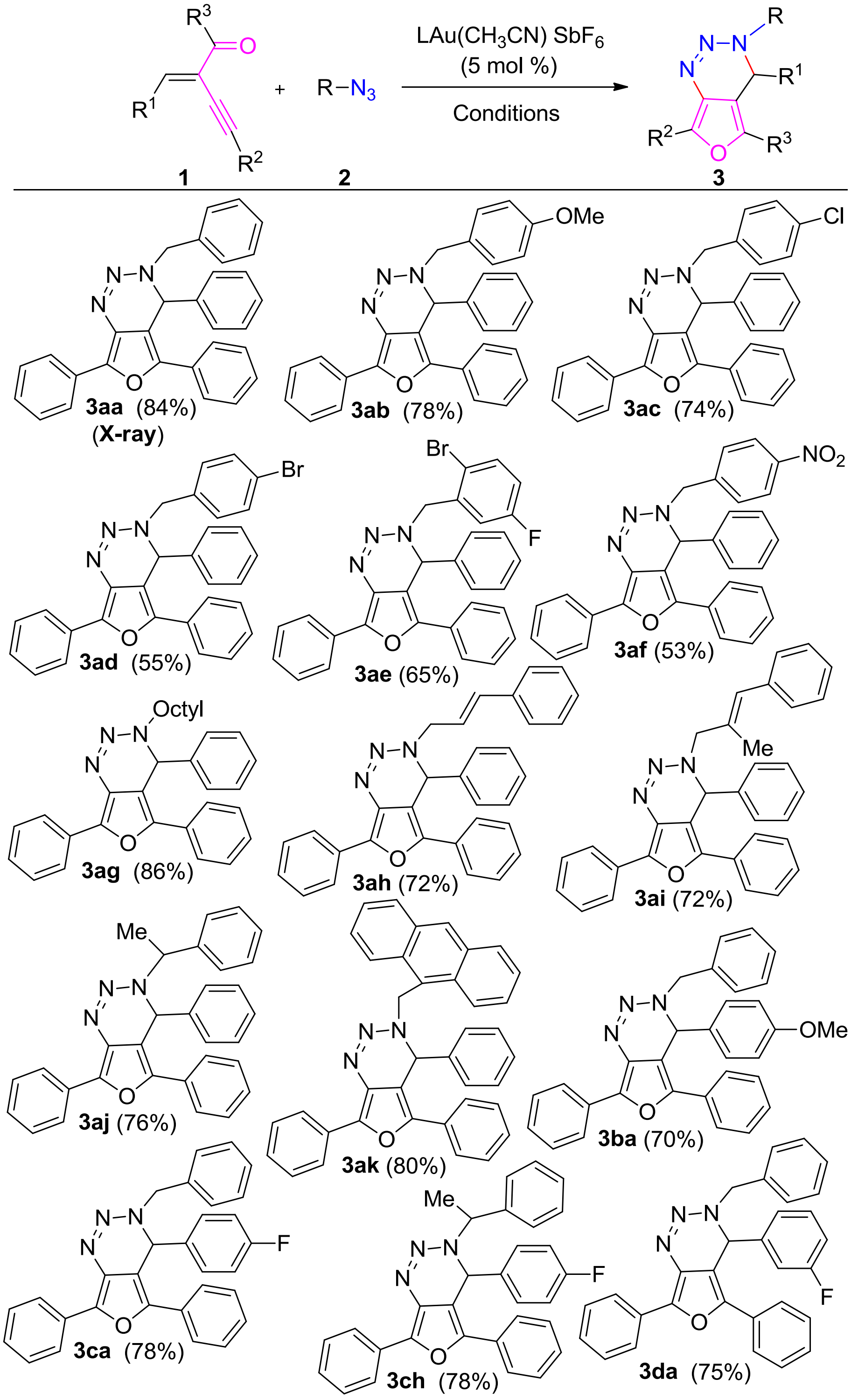
Entry	Catalyst (5 mol %)	Solvent	Yield(%)[b]
1	$Ph_3PAuCl/AgOTf$	DCM	35%
2	$Ph_3PAuCl/AgOTf$	DCE	45%
3	$Ph_3PAuCl/AgSbF_6$	DCE	43%
4	$Ph_3PAuCl/AgBF_4$	DCE	40%
5	$Ph_3PAuCl/AgNTf_2$	DCE	33%

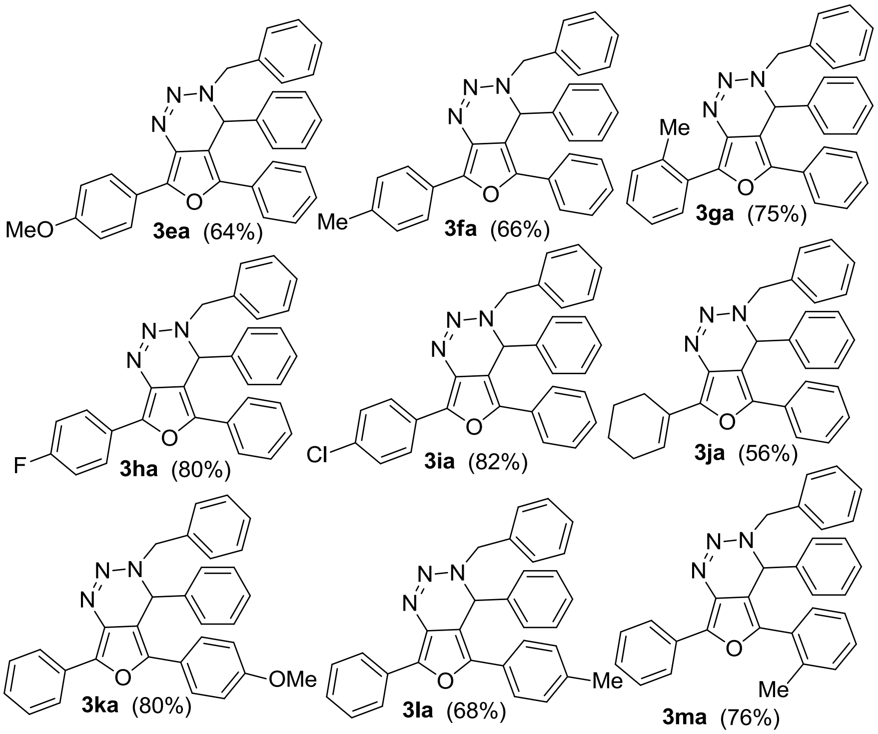
6.	IPrAuCl/AgSbF$_6$	DCM	20%
7.	IPrAuCl	DCM	N.R
8.	NaAuCl$_4$.2H$_2$O/AgOTf	DCE	Trace
9	AuCl/AgOTf	DCE	Trace
10	HAuCl$_4$.3H$_2$O/AgOTf	DCE	10%
11	AuCl$_3$ /AgOTf	DCE	12%
12	**LAu(CH$_3$CN)SbF$_6$**	**DCE**	**84%**
13	LAu(CH$_3$CN)SbF$_6$	DCE	65%[c]
14	LAu(CH$_3$CN)SbF$_6$/AgSbF$_6$	DCE	76%[d]
15	LAu(CH$_3$CN)SbF$_6$	DCM	56%
16	LAu(CH$_3$CN)SbF$_6$	dioxane	45%
17	LAu(CH$_3$CN)SbF$_6$	toluene	55%
18	LAu(CH$_3$CN)SbF$_6$	CHCl$_3$	47%
19	AgSbF$_6$	DCE	30%[d,e]
20	Cu(OTf)$_2$	DCE	N.R
21	LAu(CH$_3$CN)SbF$_6$	DCE	40%[f]
22	-	DCE	N.R.[g]

[a]Standard conditions: Enynone **1a** (0.3 mmol), benzyl azide **2a** (0.36 mmol), catalyst (5 mol %), and solvent (2 mL), rt for 5 h unless otherwise noted. DCM = dichloromethane; DCE = 1,2-dichloroethane, [b]Isolated yields. [c] Addition of **1a** at room temperature. [d] Isolated after 12 h. [e] 20 mol % AgSbF$_6$ was used. [f] 2.5 mol % catalyst was used. [g] Reaction at 80 ^{o}C for 2 d. L = [(2-biphenyl)di-tert-butylphosphine]); IPr = 1,3-Bis(2,6-diisopropyl phenyl-imidazol-2-ylidene). N.R = No reaction.

We then explored the substrate scope of gold catalyzed [3+3] cycloaddition between various 2-(1-alkynyl)-2-alken-1-ones and benzyl azides (Scheme 2). Both electron–donating (**3ab-ac**) and -withdrawing groups (**3ad-af**) on benzyl group of azide gave decent yields, but electron withdrawing groups (–NO_2, -Br) marginally reduced the yield. Dihalo substituted azide (**2e**) also produced the desired product **3ae** in good yield. The generality of this method could be extended to octyl (**2g**), as well as cinnamyl azides like (**2h**) and (**2i**) affording **3ag, 3ah** and **3ai** in 86%, 72%, and 72% yields respectively. Secondary azide [(1-azidoethyl)benzene] **2j** and 9-anthracenylmethyl azide **2k** also worked well offering the corresponding cycloadducts **3aj** and **3ak** in good yields. The reaction was very clean and the corresponding furanotriazines **3ba-ia** and **3ka-ma** were obtained in 53-86% yield with high regioselectivity. This methodology also tolerates the presence of cyclohexenyl moiety (R^2) at the triple bond position resulting in corresponding [3+3] annulation product **3ja**. A limitation though is the case of phenyl azide where multiple products were obtained; this may be due to the delocalization of electron density on azide nitrogen to the benzene ring. The structure of annulation product **3aa** was confirmed by single crystal X-ray diffraction (Figure S1).

Scheme 2. Scope of the Gold Catalyzed [3+3] Annulation Reaction of 2-(1-Alkynyl)-2-alken-1-ones (1a-m) with Azides (2a-k)[a]





3ea (64%) **3fa** (66%) **3ga** (75%)

3ha (80%) **3ia** (82%) **3ja** (56%)

3ka (80%) **3la** (68%) **3ma** (76%)

[a]Conditions: Enynone **1** (0.3 mmol), azide **2** (0.36 mmol), LAu(CH_3CN)SbF_6 (5 mol %), DCE (2 mL), rt for 5 h.

The absorption and fluorescence emission spectra of compounds **3ag** and **3ah** can be compared with that of compound **3ak**. Though compound **3ak** has similar and slightly lower absorbance than compound **3ag** and **3ah** respectively, it shows higher fluorescence emission intensity as expected for an anthracenyl compound (Figure 1 and Figure-S4). Compounds **3aa**, **3ab**, **3ag**, **3ah**, **3ak** and **3ca** are also fluorescence active (cf. Figure 1 and Figures S3-S4). Thus these products could be of use as good fluorescence active materials.

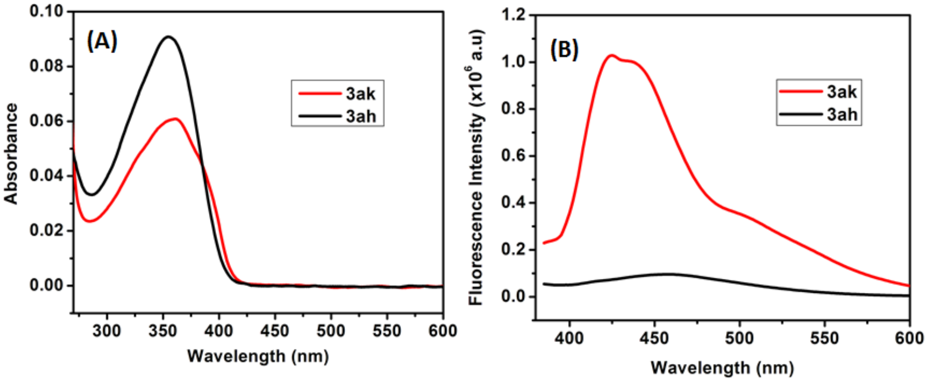
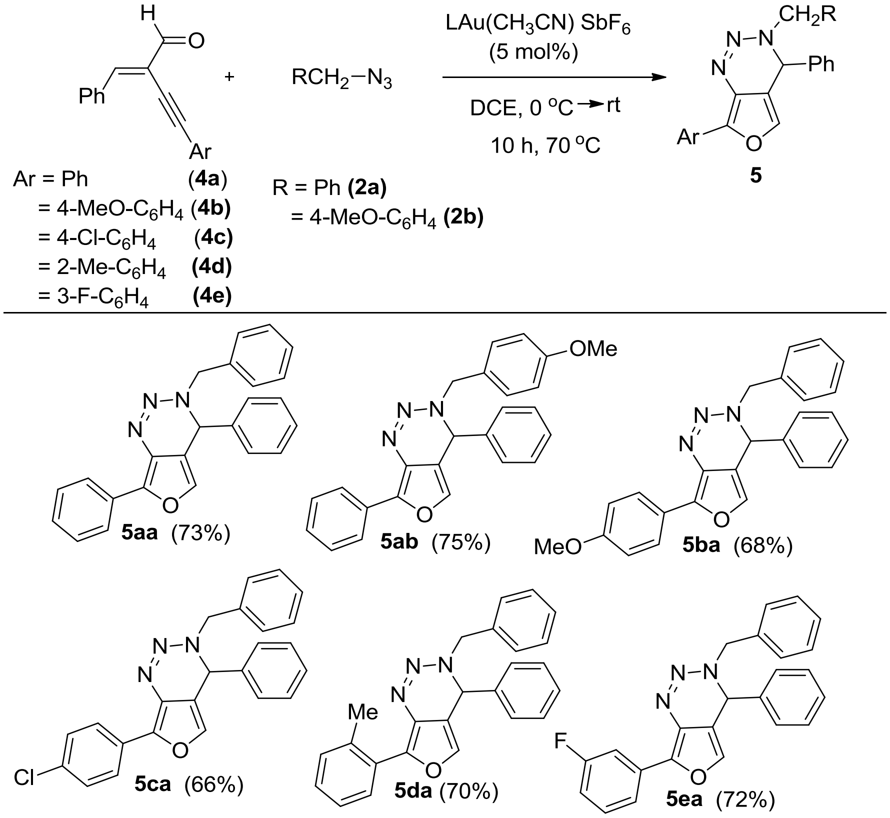


Figure 1. Absorbance (A) and fluorescence emission spectra (B) of compounds **3ah** and **3ak** with c = 1.71x10^{-2} mol/L in THF (upon excitation at 357 nm and 370 nm respectively). Quantum yields for **3ah** and **3ak** are 0.0011 and 0.014, respectively

(ii) Gold catalyzed [3+3] addition of enynals with benzyl azides

In the next step, we expanded the utility of the above reaction to include enynals. Reaction between (*E*)-2-benzylidene-4-phenylbut-3-ynal (**4a**) with benzyl azide (**2a**) by using the above reaction conditions resulting in the desired [3+3] cycloadduct **5aa** in 32% yield with most of the starting material remained even after longer reaction time. Pleasingly, though, upon raising the reaction temperature to 70 ^{o}C compound **5aa** could be obtained in 73% yield after 10 h. At room temperature it took 48 h for completion of the reaction. In an analogous manner, reactions using compounds **4b-e** also proceeded smoothly and resulted in the corresponding [3+3] cycloadducts **5ba-ea** in good yields (Scheme 3).

Scheme 3. Gold Catalyzed [3+3] Cycloaddition of Enynals (4a-e) with Benzyl Azide (2a-b)[a]

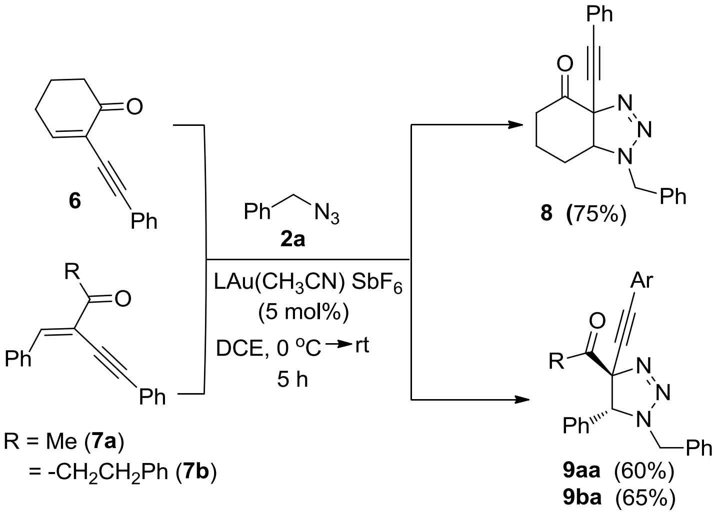


[a]Conditions: Enynal **4** (0.3 mmol), azide **2** (0.36 mmol), $LAu(CH_3CN)SbF_6$ (5 mol%), DCE (2 mL), 70 °C for 10 h.

(iii) Gold catalyzed (3+2) cycloaddition reaction of enynones 6 and 7a-b with benzyl azide (2a)

Interestingly, in contrast to the above, in the presence of above gold catalyst, enynones **6** and **7a-b** underwent [3+2] cycloaddition with benzyl azide **2a**. In these substrates, only ***alkene*** part of the enynones reacts with benzyl azide resulting in the formal [3+2] cycloadducts **8** and **9aa-9ba**, rather than the [3+3] cycloadducts, in 75%, 60% and 65% yields respectively.[14] The difference between this reaction and the one shown in Scheme 2 may be rationalized by realizing that the R^3 group is aryl in the case of **1a-k** (cf. Scheme 2) for [3+3] cycloaddition and alkyl in the case of precursors **6-7a-b** for the [3+2] cycloaddition involving the alkene moiety.

Scheme 4. [3+2] Cycloaddition of Enynones 6 and 7a-b with Benzyl Azide (2a).

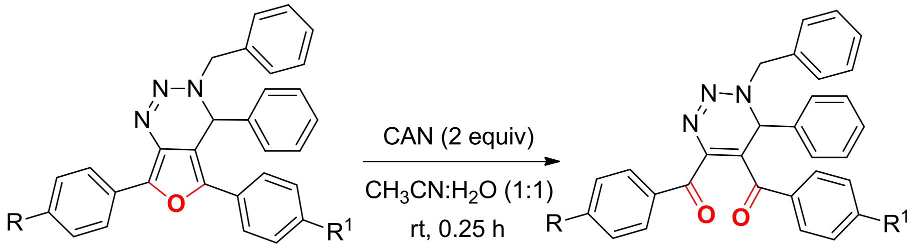


Reaction conditions: Enynone **6**/**7a-b** (0.3 mmol), azide **2** (0.36 mmol), LAu(CH_3CN)SbF_6 (5 mol%), DCE (2 mL), rt for 5 h.

(iv) Synthetic utility of furanotriazines- Selective opening of furan ring leading to 1,2,3-triazines

1,2,3-Triazines constitute an attractive class of compounds to develop new drugs in the future, but synthetic routes to them are rarely reported.[12,13] Keeping this in mind, we performed the furan ring opening reaction of furanotriazine **3aa** with cerium(IV) ammonium nitrate (CAN) at rt/15 min that afforded the desired tetrasubstituted 1,2,3-triazine **10** in 96% yield. The generality of this reaction was explored using furo[3,4-d][1,2,3]triazines **3ea**, **3fa** and **3ka**. Thus we obtained the highly functionalized 1,2,3-triazines (**11-13**) in excellent yields (Scheme 5). The structure of compound **12** was further confirmed by single crystal X-ray analysis (Figure S2). Compounds **10** and **12** are also fluorescence active (Figure S5).

Scheme 5. Highly Substituted [1,2,3]Triazines (10-13) from Ring Opening of Furo[3,4-d][1,2,3]triazines



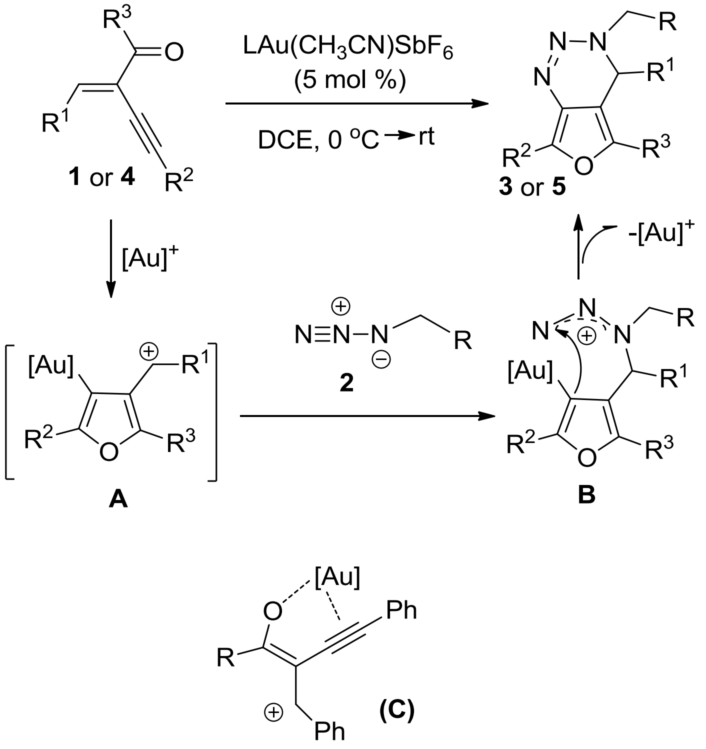
R = H, R^1 = H **3aa**
= OMe, R^1 = H **3ea**
= Me, R^1 = H **3fa**
= H, R^1 = OMe **3ka**

10 (96%)
11 (80%)
12 (83%, **X-ray**)
13 (96%)

(v) ***Plausible pathway for the gold catalyzed*** **cycloaddition of enynones/enynals with benzyl azide**

A plausible pathway for the above [3+3] cycloaddition involves the initial activation of the alkyne end of enynal/enynone **1/4** with gold followed by intramolecular attack of carbonyl oxygen leading to furanyl gold intermediate **A**[4a, 4c-e] which acts as a carbon electrophile (Scheme 6). Intermediate **B** is formed by nucleophilic attack of azide nitrogen on the highly activated species **A**. Intermediate **B** undergoes intramolecular C-N bond formation to furnish the desired [3+3] cycloadduct **3/5** with regeneration of the gold catalyst. In the formation of the [3+2] cycloaddition products [**8**, **9aa**, **9ba**], it is likely that [Au^{I}] is coordinated to both the triple bond and the carbonyl oxygen with an electrophilic carbon center in the intermediate stage such as that shown in (**C**).[15] It is possible that the alkyl group R in **6** and **7a-b** may facilitate the oxygen coordination better than an aryl group at this position.

Scheme 6. Plausible Pathway for the Gold Catalyzed [3+3] Annulation Reaction of Enynones/Enynals with Benzyl Azide



Possible intermediate cation in the formation of **8** and **9aa-9ba**

Summary

In conclusion, we have discovered a new gold catalyzed regioselective [3+3] cycloaddition reaction of enynones with benzyl azides that affords fused heterobicyclic furo[3,4-d][1,2,3]triazines. Our methodology is further elaborated to enynals, providing [3+3] cycloadducts. Interestingly though, enynones with an alkyl group (cf. Scheme 4) tend to undergo [3+2] cycloaddition by using the -ene part and not the -yne part. We have also demonstrated the ring opening of furo[3,4-d][1,2,3]triazines with CAN resulting in highly substituted 1,2,3-triazines in excellent yields. Both furo[3,4-d][1,2,3]triazines and the derived 1,2,3-triazines show good fluorescence activity.

Experimental Section

General Experimental Conditions: Chemicals and solvents were purified when required according to standard procedures.[16] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta = 0$) or $CFCl_3$ ($\delta = 0$). Infrared spectra were recorded neat or by using KBr pellets. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected (not calibrated). Elemental analyses were carried out on a CHN analyzer. For TLC, glass microslides were coated with silica-gel-GF_{254} (mesh size 75μ) and spots were identified using iodine or UV chamber as appropriate. For column chromatography, silica gel of 100-200 mesh size was used. LC-MS or HRMS (ESI-TOF) equipment were used to record mass spectra for isolated compounds where appropriate. UV-Visible absorption spectra and fluorescence spectra (THF solution) were recorded.

(i) Synthesis of functionalized enynones [1a-m], 6 and 7a-b enynals [4a-e]

Enynones [**1a-m**], enynals [**4a-e**], **6** and **7a-b** were prepared based on the literature reports oxidizing 3.5 mmol of the precursor alcohol by MnO_2.[17] Out of these, compounds **1c** and **1d** are new.

(E)-2-(3-fluorobenzylidene)-1,4-diphenylbut-3-yn-1-one (1c). Yellow solid. Yield 1.00 g (84%); mp 60-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.09 (m, 1H), 8.05 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.65-7.61 (m, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.48-7.41 (m, 3H), 7.38-7.35 (m, 3H), 7.19-7.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.0, 162.7 (J = 244.4 Hz), 143.1 (J = 2.8 Hz), 137.0, 136.9, 136.8, 132.8, 131.4, 130.1, 130.0, 129.8, 129.1, 128.5, 128.2, 126.7 (J = 2.7 Hz), 122.3 (J = 42.2 Hz), 117.4 (J = 21.5 Hz), 116.1 (J = 22.7 Hz), 102.0, 86.8; IR

(KBr): 3053, 2192, 1660, 1589, 1496, 1441, 1277, 1222, 1145, 986, 904, 778, 756, 718 cm^{-1}; LC/MS: *m/z* 327 $[M+1]^+$. Anal. Calcd. for $C_{23}H_{15}FO$: C, 84.64; H, 4.63; Found: C, 84.52; H, 4.68.

(E)-2-(4-fluorobenzylidene)-1,4-diphenylbut-3-yn-1-one (1d). Yellow solid. Yield 0.87 g (88%); mp 62-64 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, *J* = 8.8 Hz, 5.6 Hz, 2H), 8.04 (d, *J* = 7.2 Hz, 2H), 7.64-7.60 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.44-7.37 (m, 5H), 7.18 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ.193.2, 163.8 (*J* = 251.4 Hz), 143.7, 137.1, 132.6, 132.5, 132.4, 131.4, 131.2 (*J* = 3.3 Hz), 129.7, 129.0, 128.5, 128.1, 122.7, 120.5, 115.8 (*J* = 21.4 Hz), 101.0, 87.0; IR (KBr): 3052, 2186, 1666, 1605, 1573, 1512, 1452, 1310, 1233, 1156, 959, 827, 751, 690 cm^{-1}; LC/MS: *m/z* 327 $[M+1]^+$. Anal. Calcd. for $C_{23}H_{15}FO$: C, 84.64; H, 4.63; Found: C, 84.75; H, 4.58.

(ii) Synthesis of azides [2a-k]

All these azides were synthesized following known literature procedures.[18a] Thus benzyl and aliphatic bromides were subjected to S_N2 displacement with NaN_3 to afford azides (**2a**-**i**) and **2k**. Azide **2j** was prepared directly from alcohol using trimethylsilyl azide as the azide source.[18b]

(iii) Representative procedure for the preparation of compounds 3aa-ak and 3ba-ma

To an oven dried 5 mL RBF, $LAu(CH_3CN)SbF_6$ (L = [(2-biphenyl)di-*tert*-butylphosphine]) (0.015 mmol) and benzyl azide **2a** (0.36 mmol) in DCE (1 mL) were added, the mixture was kept at 0 ^{o}C and the contents stirred for 5 min. (*E*)-2-Benzylidene-1,4-diphenylbut-3-yn-1-one (**1a**, 0.30 mmol) in DCE was added dropwise to the above mixture. After completion of the reaction, as monitored by TLC, the solvent was evaporated under vacuum. The residue was then purified by silica gel column chromatography by using hexane:EtOAc (49:1) as the eluent to afford 3-benzyl-4,5,7-triphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine **3aa**. Compounds **3ab-ak** and **3ba-ma** were prepared following the same procedure and by using the same molar quantities.

3-benzyl-4,5,7-triphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3aa). Yellow solid. Yield 0.111 g (84%); mp 160-162 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.37 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.45-7.25 (m, 15H), 7.20 (t, *J* = 7.2 Hz, 1H), 5.58 (s, 1H), 5.25 (d, *J* = 15.2 Hz, 1H), 4.39 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.1, 144.5, 139.9, 135.9, 129.7$_0$, 129.6$_6$, 129.0$_2$, 128.9$_7$, 128.8, 128.7, 128.5, 128.3$_4$, 128.2$_8$, 128.2$_5$, 128.1, 127.7, 125.6, 125.0, 107.0, 56.9, 55.9; IR (KBr): 3052, 3030, 2926, 2855, 1600, 1485, 1419, 1364, 1249, 1156, 1074, 942, 910, 762, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{24}N_3O$ [M$^+$+H]: *m/z* 442.1919. Found: 442.1918. X-ray structure has been determined for this compound.

3-(4-methoxybenzyl)-4,5,7-triphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ab). Yellow solid. Yield 0.110 g (78%); mp 154-156 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.37 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.43-7.25 (m, 12H), 7.22-7.18 (m, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.56 (s, 1H), 5.19 (d, *J* = 14.8 Hz, 1H), 4.32 (d, *J* = 14.8 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.5, 144.9, 144.3, 139.9, 129.7, 129.0, 128.7, 128.5, 128.4, 128.2, 127.7, 127.6, 125.6, 125.1, 125.0, 114.4, 107.0, 56.4, 55.6, 55.3; IR (KBr): 3063, 3024, 2827, 1610, 1512, 1484, 1435, 1243, 1166, 1123, 1079, 1029, 947, 766 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{26}N_3O_2$ [M$^+$+H]: *m/z* 472.2025. Found: 472.2025.

3-(4-chlorobenzyl)-4,5,7-triphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ac). Yellow solid. Yield 0.106 g (74%); mp 120-122 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.37-8.35 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.40-7.26 (m, 14H), 7.23-7.19 (m, 1H), 5.52 (s, 1H), 5.17 (d, *J* = 15.2 Hz, 1H), 4.37 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.3, 144.5, 139.6, 134.4, 133.9, 129.6$_3$, 129.5$_9$, 129.5$_6$, 129.2, 129.1, 128.9, 128.8, 128.5, 128.4, 128.3, 127.8, 125.6, 125.0, 124.9, 106.8, 56.2, 56.1; IR (KBr): 3063, 3025, 1589, 1496, 1458, 1436, 1260, 1129, 1074, 1008, 942, 762 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}ClN_3O$ [M$^+$+H]: *m/z* 476.1529. Found: 476.1529.

3-(4-bromobenzyl)-4,5,7-triphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ad). Yellow solid. Yield 0.086 g (55%); mp 160-162 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.37-8.34 (m, 2H), 7.55-7.49 (m, 4H), 7.40-7.32 (m, 6H), 7.30-7.25 (m, 6H), 7.21 (t, *J* = 7.2 Hz, 1H), 5.52 (s, 1H), 5.14 (d, *J* = 15.2 Hz, 1H), 4.35 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.4, 144.6, 139.7, 135.0, 132.1, 129.9, 129.6, 129.1, 128.8, 128.7, 128.5, 128.3, 128.2, 127.8, 125.6, 125.1, 124.9, 122.0, 106.8, 56.3, 56.1; IR (KBr): 3063, 3025, 2921, 1671, 1600, 1485, 1447, 1403, 1266, 1123, 1068, 1008, 948, 767, 685 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}BrN_3O$ [M$^+$+H] and [M$^+$+H+2]: *m/z* 520.1024, 522.1024. Found: 520.1029, 522.1017.

3-(2-bromo-5-fluorobenzyl)-4,5,7-triphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ae). Yellow solid. Yield 0.106 g (65%); mp 162-164 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.37 (d, *J* = 8.0 Hz, 2H), 7.58-7.50 (m, 3H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.41-7.30 (m, 8H), 7.26-7.22 (m, 1H), 7.18-7.15 (m, 1H), 6.96-6.91 (m, 1H), 5.66 (s, 1H), 4.99 (d, *J* = 16.0 Hz, 1H), 4.74 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 162.3 (d, *J* = 246.4 Hz), 145.7, 144.5, 139.7, 138.1 (d, *J* = 6.9 Hz), 134.3 (d, *J* = 7.8 Hz), 129.6 (d, *J* = 2.6 Hz), 129.2, 129.0, 128.8, 128.7, 128.6, 128.2, 127.9, 125.8, 125.0, 124.9, 117.6, 117.0, 116.8, 116.6, 107.0, 57.6, 56.6; ^{19}F NMR (376 MHz, CDCl$_3$): δ -113.48; IR (KBr): 3058, 2921, 1660, 1585, 1490, 1463, 1441, 1266, 1129, 1074, 1030, 942, 773, 690 cm^{-1}; LC/MS: *m/z* 538 [M]$^+$ and 540 [M+2]$^+$. Anal.Calcd. for $C_{30}H_{21}BrFN_3O$: C, 66.92; H, 3.93; N, 7.80; Found: C, 66.85; H, 3.87; N, 7.91.

3-(4-nitrobenzyl)-4,5,7-triphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3af). Yellow solid. Yield 0.077 g (53%); mp 138-140 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.36 (d, *J* = 8.4 Hz, 2H), 7.55-7.50 (m, 4H), 7.40-7.32 (m, 6H), 7.30-7.25 (m, 6H), 7.21 (t, *J* = 7.2 Hz, 1H), 5.52 (s, 1H), 5.14 (d, *J* = 15.2 Hz, 1H), 4.35 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.4, 144.6, 139.7, 135.0, 132.1, 129.9, 129.6$_0$, 129.5$_9$, 129.0, 128.8, 128.7, 128.5, 128.3, 128.2, 127.8, 125.6, 125.1, 124.9, 122.0, 106.8, 56.3, 56.2; IR (KBr): 3068, 2915, 1660, 1595, 1490, 1452, 1397, 1266, 1068, 1008, 942, 926 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}N_4O_3$ [M$^+$+H]: *m/z* 487.1770. Found: 487.1775.

3-octyl-4,5,7-triphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ag). Yellow solid. Yield 0.120 g (86%); mp 92-94 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.35 (d, *J* = 8.0 Hz, 2H), 7.51-7.48 (m, 4H), 7.38-7.27 (m, 8H), 7.25-7.23 (m, 1H), 5.74 (s, 1H), 3.77-3.70 (m, 1H), 3.46-3.39 (m, 1H), 1.83-1.67 (m, 2H), 1.33-1.28 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.7, 144.1, 140.5, 129.9, 129.8, 129.0, 128.7, 128.6$_3$, 128.5$_9$, 128.1, 128.0, 127.7, 125.5, 125.2, 125.0, 107.5, 57.4, 53.5, 31.8, 29.3, 29.2, 27.8, 26.7, 22.7, 14.1; (KBr): 3063, 2921, 2855, 1595, 1485, 1447, 1403, 1310, 1145, 1068, 1019, 948, 756, 690 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{34}N_3O$ [M$^+$+H]: *m/z* 464.2702. Found: 464.2706.

3-cinnamyl-4,5,7-triphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ah). Yellow solid. Yield 0.101 g (72%); mp 156-158 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.36 (d, *J* = 8.2 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.39-7.31 (m, 11H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.32-6.25 (m, 1H), 5.81 (s, 1H), 4.76-4.71 (m, 1H), 4.14-4.08 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.1, 144.4, 140.0, 136.3, 134.4, 129.7, 129.1, 128.7$_3$, 128.6$_9$, 128.6, 128.3, 128.1, 127.8, 126.6, 125.6, 125.1, 124.0, 107.2, 56.4, 55.7; IR (KBr): 3058, 3030, 2909, 1605, 1496, 1447, 1260, 1123, 1074, 948, 767, 690 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{26}N_3O$ [M$^+$+H]: *m/z* 468.2076. Found: 468.2073.

(E)-3-(2-methyl-3-phenylallyl)-4,5,7-triphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ai). Yellow solid. Yield 0.103 g (70%); mp 88-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39-8.37 (m, 2H), 7.54-7.47 (m, 4H), 7.41-7.37 (m, 9H), 7.35-7.30 (m, 4H), 7.26-7.22 (m, 1H), 6.54 (s, 1H), 5.75 (s, 1H), 4.68 (d, *J* = 14.8 Hz, 1H), 4.05 (d, *J* = 14.8 Hz, 1H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 144.5, 140.2, 137.1, 132.9, 129.8, 129.7, 129.1, 128.8, 128.7, 128.5, 128.3_9, 128.3_7, 128.3, 127.9, 127.0, 125.6, 125.1_3, 125.0_8, 107.2, 62.1, 55.9, 15.9; IR (KBr): 3058, 3031, 2921, 1606, 1496, 1425, 1326, 1260, 1129, 1085, 1008, 943, 773, 696 cm^{-1}; LC/MS: *m/z* 482 [M+1]$^+$. Anal.Calcd. for $C_{33}H_{27}N_3O$: C, 82.30; H, 5.65; N, 8.73; Found: C, 82.21; H, 5.63; N, 8.82.

4,5,7-triphenyl-3-(1-phenylethyl)-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3aj). Yellow solid. Yield 0.104 g (76%); mp 180-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.44-7.43 (m, 4H), 7.39-7.32 (m, 9H), 7.23-7.24 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 5.57 (s, 1H), 4.64 (qrt, *J* = 6.8 Hz, 1H), 1.73 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 144.5, 142.1, 140.7, 129.8, 129.7, 129.0_4, 128.9_5, 128.7, 128.4, 128.3, 128.1, 127.9, 127.6, 126.9, 125.5, 125.2, 125.1, 107.1, 61.7, 57.3, 22.6; IR (KBr): 3056, 3025, 2926, 1605, 1490, 1458, 1430, 1271, 1205, 1140, 1079, 1025, 937, 767, 685 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{26}N_3O$ [M$^+$+H] : *m/z* 456.2076. Found: 456.2076.

3-(anthracen-9-ylmethyl)-4,5,7-triphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ak). Yellow solid. Yield 0.132 g (80%); mp 220-222 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.31-8.29 (m, 2H), 8.22-8.20 (m, 2H), 8.07-8.04 (m, 2H), 7.51-7.44 (m, 6H), 7.35-7.30 (m, 6H), 7.25-7.20 (m, 4H), 7.18-7.14 (m, 1H), 6.03 (d, *J* = 14.8 Hz, 1H), 5.64 (d, *J* = 14.8 Hz, 1H), 5.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 143.9, 140.8, 131.5, 131.4, 129.7, 129.6, 129.2, 129.0, 128.9, 128.7, 128.4, 128.2, 127.8, 127.7, 126.4, 125.8, 125.6, 125.1, 124.7, 124.4, 107.8, 56.6, 50.5; IR (KBr): 3068, 3035, 2938, 1605, 1592, 1486, 1448, 1427, 1272, 1150, 1075, 1017, 942, 766, 688 cm^{-1}; HRMS (ESI): Calcd. for $C_{38}H_{28}N_3O$ [M$^+$+H] : *m/z* 542.2232. Found: 542.2225.

3-benzyl-4-(4-methoxyphenyl)-5,7-diphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ba). Yellow solid. Yield 0.099 g (70%); mp 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38-8.36 (m, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.43-7.37 (m, 8H), 7.30-7.18 (m, 5H), 6.88 (d, *J* = 8.0 Hz, 2H), 5.52 (s, 1H), 5.23 (d, *J* = 15.2 Hz, 1H), 4.41 (d, *J* = 15.2 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 144.9, 144.3, 135.9, 132.1, 129.8, 129.7, 129.6, 129.0, 128.7, 128.5, 128.3, 128.2, 128.1, 127.6, 125.6, 125.2, 125.0, 114.3, 107.3, 56.8, 55.3; IR (KBr): 3047, 3019, 2953, 2921, 2833, 1611, 1512, 1496, 1447, 1425, 1255, 1173, 1101, 1068, 948, 822, 762, 685 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{26}N_3O_2$ [M$^+$+H]: *m/z* 472.2025. Found: 472.2024.

3-benzyl-4-(4-fluorophenyl)-5,7-diphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ca). Yellow solid. Yield 0.108 g (78%); mp 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.46-7.35 (m, 8H), 7.30-7.25 (m, 4H), 7.23-7.19 (m, 1H), 7.05 (t, *J* = 8.4 Hz, 2H), 5.58 (s, 1H), 5.25 (d, *J* = 15.2 Hz, 1H), 4.38 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (*J* = 246.7 Hz), 145.3, 144.5, 135.7_3 (*J* = 3.1 Hz), 135.6_5, 130.1 (*J* = 8.4 Hz), 129.6 (*J* = 5.9 Hz), 129.0, 128.8, 128.5, 128.4, 128.2_1, 128.1_8, 127.9, 125.6, 125.0, 124.8, 116.0 (*J* = 21.7 Hz), 106.8, 56.9, 55.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.35; IR (KBr): 3047, 3030, 2926, 2866, 1605, 1490, 1447, 1227, 1156, 1085, 1079, 937, 833, 762, 690 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}FN_3O$ [M$^+$+H]: *m/z* 460.1825. Found: 460.1828.

4-(4-fluorophenyl)-5,7-diphenyl-3-(1-phenylethyl)-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ch). Yellow solid. Yield 0.111 g (78%); mp 174-176 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.38-8.35 (m, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.45-7.24 (m, 12H), 7.21-7.17 (m, 1H), 7.04 (t, *J* = 8.4 Hz, 2H), 5.56 (s, 1H), 4.60 (qrt, *J* = 6.8 Hz, 1H), 1.73 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 162.6 (*J* = 246.9 Hz), 144.6 (*J* = 26.9 Hz), 141.9, 136.5 (*J* = 3.4 Hz), 130.1, 130.0, 129.7, 129.5, 129.1, 128.7, 128.4, 128.2, 128.0, 127.8, 126.8, 125.5, 125.2, 124.9, 116.0 (*J* = 21.8 Hz), 106.9, 61.6, 56.4, 22.6; ^{19}F NMR (376 MHz, CDCl$_3$): δ -112.44; IR (KBr): 3058, 3026, 1606, 1507, 1430, 1233, 1151, 1074, 948, 816, 762, 690 cm^{-1}; LC/MS: *m/z* 475 [M+1]$^+$. Anal.Calcd. for $C_{31}H_{24}FN_3O$: C, 78.63; H, 5.11; N, 8.87; Found: C, 78.53; H, 5.06; N, 8.95.

3-benzyl-4-(3-fluorophenyl)-5,7-diphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3da). Yellow solid. Yield 0.103 g (75%); mp 170-172 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.40-8.38 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.47-7.28 (m, 11H), 7.25-7.21 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.06-7.01 (m, 2H), 5.60 (s, 1H), 5.29 (d, *J* = 15.0 Hz, 1H), 4.41 (d, *J* = 15.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 163.1 (*J* = 247.0 Hz), 145.5, 144.6, 142.2, 142.1, 135.6, 130.6 (*J* = 8.1 Hz), 129.5 (*J* = 5.6 Hz), 129.1, 128.8, 128.6, 128.4, 128.2, 127.9, 125.7, 125.0, 124.7, 124.0 (*J* = 2.7 Hz), 115.9 (*J* = 21.1 Hz), 115.3 (*J* = 21.7 Hz), 106.3, 57.0, 55.3; ^{19}F NMR (376 MHz, CDCl$_3$): δ -111.36; IR (KBr): 3063, 2921, 1595, 1490, 1425, 1364, 1255, 1096, 1074, 942, 910, 762, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}FN_3O$ [M$^+$+H]: *m/z* 460.1825. Found: 460.1829.

3-benzyl-7-(4-methoxyphenyl)-4,5-diphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ea). Yellow solid. Yield 0.091 g (64%); mp 150-152 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.32-8.30 (m, 2H), 7.45-7.24 (m, 14H), 7.19-7.15 (m, 1H), 7.06-7.04 (m, 2H), 5.55 (s, 1H), 5.23 (d, *J* = 14.8 Hz, 1H), 4.37 (d, *J* = 14.8 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.8, 145.5, 143.7, 139.9, 136.0, 129.8, 129.0, 128.9, 128.7, 128.5, 128.3$_2$, 128.2$_7$, 128.0, 127.5, 127.2, 124.8, 123.9, 122.7, 114.3, 107.0, 56.8, 55.9, 55.4; IR (KBr): 3063, 3030, 2932, 2849, 1600, 1490, 1436, 1222, 1074, 942, 827, 762, 690 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{26}N_3O_2$ [M$^+$+H]: *m/z* 472.2025. Found: 472.2026.

3-benzyl-4,5-diphenyl-7-(p-tolyl)-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3fa). Yellow solid. Yield 0.090 g (66%); mp 198-200 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.28 (d, *J* = 8.0 Hz, 2H), 7.46-7.31 (m, 14H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 5.58 (s, 1H), 5.25 (d, *J* = 14.8 Hz, 1H), 4.40 (d, *J* = 14.8 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.5, 144.1, 139.9, 138.4, 136.0, 129.8, 129.5, 129.0$_1$, 128.9$_7$, 128.7, 128.5, 128.4, 128.3, 128.1, 127.6, 127.0, 125.6, 125.0, 124.6, 107.0, 56.9, 55.9, 21.6; IR (KBr): 3063, 3030, 2915, 2860, 1595, 1512, 1447, 1403, 1255, 1068, 959, 811, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{26}N_3O$ [M$^+$+H]: *m/z* 456.2076,. Found: 456.2075.

3-benzyl-4,7-diphenyl-5-(o-tolyl)-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ga). Yellow solid. Yield 0.102 g (75%); mp 96-98 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.39 (d, *J* = 7.6 Hz, 1H), 7.47-7.33 (m, 15H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.22-7.18 (m, 1H), 5.62 (s, 1H), 5.27 (d, *J* = 15.2 Hz, 1H), 4.40 (d, *J* = 15.2 Hz, 1H), 2.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 147.1, 144.7, 140.0, 136.2, 135.9, 131.5, 130.1, 129.8, 129.1, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 127.6, 126.1, 125.3, 124.8, 106.5, 56.9, 55.9, 22.1; IR (KBr): 3063, 3025, 2920, 1600, 1496, 1425, 1348, 1310, 1266, 1101, 1058, 931, 762, 707 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{26}N_3O$ [M$^+$+H]: *m/z* 456.2076. Found: 456.2077.

3-benzyl-7-(4-fluorophenyl)-4,5-diphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ha). Yellow solid. Yield 0.110 g (80%); mp 170-172 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.37-8.33 (m, 2H), 7.45-7.29 (m, 13H), 7.25-7.19 (m, 4H), 5.56 (s, 1H), 5.24 (d, *J* = 15.2 Hz, 1H), 4.39 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 162.7 (*J* = 247.6 Hz), 144.5, 144.3, 139.8, 135.8, 131.5, 129.6, 129.1, 129.0, 128.9, 128.8, 128.5, 128.4, 128.3 (*J* = 3.1 Hz), 128.1, 127.8, 127.5, 127.4, 126.1 (*J* = 3.0 Hz), 125.0, 124.6, 115.9 (*J* = 21.8 Hz), 106.9, 56.9, 55.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.21; IR (KBr): 3068, 3030, 1600, 1501, 1452, 1348, 1227, 1151, 1090, 1068, 948, 833, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}FN_3O$ [M$^+$+H]: *m/z* 460.1825. Found: 460.1827.

3-benzyl-7-(4-chlorophenyl)-4,5-diphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ia). Yellow solid. Yield 0.110 g (80%); mp 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.46-7.25 (m, 14H), 7.21 (t, *J* = 7.2 Hz, 1H), 5.25 (s, 1H), 5.24 (d, *J* = 15.2 Hz, 1H), 4.40 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 143.9, 139.8, 135.7, 133.9, 129.5, 129.0_5, 128.9_8, 128.9_7, 128.8, 128.5, 128.3_0, 128.2_8, 128.2, 128.1, 127.9, 126.7, 125.2, 125.1, 107.0, 57.0, 56.0; IR (KBr): 3058, 3025, 2910, 1595, 1480, 1436, 1414, 1353, 1249, 1090, 1063, 948, 833, 762, 696 cm^{-1}; LC/MS: *m/z* 476 [M+1]$^+$. Anal. Calcd. for $C_{30}H_{22}ClN_3O$: C, 75.70; H, 4.66; N, 8.83; Found: C, 75.58; H, 4.71; N, 8.76.

3-benzyl-7-(cyclohex-1-en-1-yl)-4,5-diphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ja). Yellow solid. Yield 0.075 g (56%); mp 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.29 (m, 11H), 7.25-7.20 (m, 3H), 7.14 (t, *J* = 7.0 Hz, 1H), 6.97 (br, 1H), 5.49 (s, 1H), 5.19 (d, *J* = 15.2 Hz, 1H), 4.33 (d, *J* = 15.2 Hz, 1H), 2.80 (br, 2H), 2.38 (br, 2H), 1.87-1.85 (m, 2H), 1.77-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 143.0, 140.0, 136.1, 129.9, 129.0_1, 128.9, 128.8, 128.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.3, 124.8, 124.1, 106.7, 56.7, 55.8, 25.9, 25.1, 22.4, 22.1; IR (KBr): 3057, 3024, 2920, 2854, 1649, 1599, 1495, 1446, 1177, 1068, 734, 690 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{28}N_3O$ [M$^+$+H]: *m/z* 446.2232. Found: 446.2236.

3-benzyl-5-(4-methoxyphenyl)-4,7-diphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ka). Yellow solid. Yield 0.113 g (80%); mp 80-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32-8.30 (m, 2H), 7.50-7.40 (m, 8H), 7.36-7.34 (m, 1H), 7.26-7.18 (m, 4H), 7.04-7.01 (m, 2H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.70 (s, 1H), 5.35 (d, *J* = 14.8 Hz, 1H), 4.37 (d, *J* = 14.8 Hz, 1H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 145.2, 142.3, 140.9, 136.2, 130.0, 129.7, 129.1, 128.8, 128.7, 128.6, 128.0, 127.9, 127.0, 125.4, 124.9, 120.8, 119.3, 110.8, 109.4, 57.4, 55.4, 54.7; IR (KBr): 3052, 3030, 2921, 2833, 1600, 1584, 1485, 1458, 1430, 1315, 1249, 1107, 1019, 948, 756, 690 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{26}N_3O_2$ [M$^+$+H]: *m/z* 472.2025. Found: 472.2024.

3-benzyl-4,7-diphenyl-5-(p-tolyl)-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3la). Yellow solid. Yield 0.093 g (68%); mp 182-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.44-7.27 (m, 13H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.57 (s, 1H), 5.25 (d, *J* = 14.8 Hz, 1H), 4.40 (d, *J* = 14.8 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 140.0, 137.8, 135.9, 129.8, 129.2, 129.0_1, 128.9_7, 128.7, 128.4, 128.3, 128.1_2, 128.0_9, 126.9, 125.5, 125.1, 125.0, 106.3, 56.9, 55.9, 21.3; IR (KBr): 3068, 3030, 2910, 1605, 1512, 1485, 1452, 1430, 1266, 1112, 1068, 948, 816, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{26}N_3O$ [M$^+$+H]: *m/z* 456.2076. Found: 456.2075.

3-benzyl-4,5-diphenyl-7-(o-tolyl)-3,4-dihydrofuro[3,4-d][1,2,3]triazine (3ma). Yellow solid. Yield 0.103 g (76%); mp 62-64 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30-8.28 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42-7.34 (m, 6H), 7.29-7.26 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.09-7.06 (m, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.38 (s, 1H), 5.26 (d, *J* = 15.2 Hz, 1H), 4.32 (d, *J* = 15.2 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 145.3, 140.6, 137.7, 135.9, 130.5, 129.9, 129.5, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.0_7, 128.0_5, 127.6, 125.3_4, 125.2_5, 123.8, 108.3, 57.1, 55.6, 20.4; IR (KBr): 3057, 3030, 2926, 1605, 1513, 1490, 1436, 1353, 1260, 1156, 1118, 1063, 948, 827, 625 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{26}N_3O$ [M$^+$+H]: *m/z* 456.2076. Found: 456.2074.

(iv) Representative procedure for the synthesis of furo[3,4-d][1,2,3]triazine derivatives (5aa-ea)

Compounds (**5aa-ea)** were prepared following the same procedure and the same molar quantities as described for compounds **3aa**-**ma**. But after the addition of all components, the reaction was continued at 70 °C for 10h.

3-benzyl-4,7-diphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (5aa). Yellow solid. Yield 0.080 g (73%); mp 130-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.64 (m, 2H), 7.46-7.26 (m, 13H), 6.21 (s, 1H), 5.76 (s, 1H), 5.20 (d, *J* = 14.8 Hz, 1H), 4.25 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 149.2, 140.9, 134.8, 129.7, 129.1, 129.0, 128.9, 128.8, 128.6, 128.3, 128.2, 127.6, 124.0, 104.4, 103.3, 60.5, 57.2; IR (KBr): 3053, 3030, 1540, 1485, 1479, 1458, 1392, 1353, 1315, 1255, 1101, 1063, 899, 762 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{20}N_3O$ [M$^+$+H]: *m/z* 366.1606. Found: 366.1605.

3-(4-methoxybenzyl)-4,7-diphenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (5ab). Gummy liquid. Yield 0.089 g (75%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65-7.63 (m, 2H), 7.45-7.34 (m, 6H), 7.30-7.29 (m, 1H), 7.28-7.27 (m, 1H), 7.23 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.20 (s, 1H), 5.74 (s, 1H), 5.13 (d, *J* = 14.5 Hz, 1H), 4.18 (d, *J* = 14.5 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 152.2, 149.2, 141.0, 130.0, 129.7, 129.1, 128.9, 128.7, 128.2, 127.6, 126.5, 124.0, 114.3, 104.3, 103.3, 60.3, 56.7, 55.3; IR (neat): 2920, 2860, 1610, 1517, 1484, 1451, 1397, 1309, 1254, 1183, 1095, 1024, 766. cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{22}N_3O_2$ [M$^+$+H]: *m/z* 396.1712. Found: 396.1710.

3-benzyl-7-(4-methoxyphenyl)-4-phenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (5ba). Yellow solid. Yield 0.081 g (68%); mp 148-150 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.8 Hz, 2H), 7.45-7.37 (m, 5H), 7.33-7.28 (m, 5H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.08 (s, 1H), 5.74 (s, 1H), 5.18 (d, *J* = 14.8 Hz, 1H), 4.23 (d, *J* = 14.8 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 152.5, 148.8, 141.0, 134.9, 129.1, 128.9$_3$, 128.8$_7$, 128.6, 128.2, 127.6, 125.6, 122.7, 114.2, 104.5, 101.7, 60.5, 57.1, 55.3; IR (KBr): 2964, 2932, 2838, 1611, 1496, 1458, 1397, 1255, 1173, 1101, 1068, 937, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{22}N_3O_2$ [M$^+$+H]: *m/z* 396.1712. Found: 396.1720.

3-benzyl-7-(4-chlorophenyl)-4-phenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (5ca). Yellow solid. Yield 0.079 g (66%); mp 140-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.46-7.27 (m, 12H), 6.20 (s, 1H), 5.75 (s, 1H), 5.20 (d, *J* = 14.8 Hz, 1H), 4.25 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 149.3, 140.8, 134.7, 133.9, 129.1$_4$, 129.0$_6$, 129.0, 128.9, 128.6, 128.3, 128.2, 127.6, 125.2, 104.4, 103.7, 60.5, 57.3; IR (KBr): 3063, 3030, 2932, 1622, 1540, 1490, 1468, 1452, 1386, 1315, 1238, 1101, 1068, 1008, 932, 893, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{19}ClN_3O$ [M$^+$+H]: *m/z* 400.1216. Found: 400.1217.

3-benzyl-4-phenyl-7-(o-tolyl)-3,4-dihydrofuro[3,4-d][1,2,3]triazine (5da). Gummy liquid. Yield 0.082 g (70%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.73 (m, 1H), 7.45-7.40 (m, 6H), 7.35-7.29 (m, 5H), 7.23-7.21 (m, 2H), 6.11 (s, 1H), 5.79 (s, 1H), 5.20 (d, *J* = 15.2 Hz, 1H), 4.26 (d, *J* = 15.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 148.8, 140.9, 134.9, 134.8, 131.3, 129.1, 129.0, 128.9, 128.7, 128.3, 128.2, 127.7, 127.1, 126.1, 106.8, 104.0, 60.5, 57.2, 22.1; IR (neat): 3068, 3025, 2926, 2099, 1688, 1600, 1490, 1457, 1392, 1310, 1101, 1074, 1025, 937, 762, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{22}N_3O$ [M$^+$+H]: *m/z* 380.1763. Found: 380.1767.

3-benzyl-7-(3-fluorophenyl)-4-phenyl-3,4-dihydrofuro[3,4-d][1,2,3]triazine (5ea). Gummy liquid. Yield 0.085 g (72%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.38 (m, 8H), 7.35-7.31 (m, 4H), 7.29-7.27 (m, 1H), 7.00-6.95 (m, 1H), 6.23 (s, 1H), 5.75 (s, 1H), 5.20 (d, *J* = 15.2 Hz, 1H), 4.25 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.1 (d, *J* = 244.4 Hz), 150.9 (d, *J* = 3.4 Hz), 149.4, 140.8, 134.7, 131.7 (d, *J* = 8.4 Hz), 130.8, 130.4 (d, *J* = 8.8 Hz), 129.2, 129.1, 128.9, 128.6, 128.3, 127.6, 119.6 (d, *J* = 2.9 Hz), 115.0 (d, *J* = 21.0 Hz), 110.9 (d, *J* = 23.6 Hz), 104.3, 60.5, 57.3; ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.48; IR (neat): 3068, 3030, 2920, 1625, 1605, 1589, 1485, 1457, 1397, 1342, 1266, 1194, 1096, 1025, 948, 778, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{19}FN_3O$ [M$^+$+H]: *m/z* 384.1512. Found: 384.1510.

(v) Synthesis of highly functionalized triazine derivatives 8 and 9aa-9ba

Compounds **8** and **9aa-9ba** were prepared following the same procedure and the same molar quantities as described for compounds **3aa-3ak**.

1-(1-benzyl-5-phenyl-4-(phenylethynyl)-4,5-dihydro-1H-1,2,3-triazol-4-yl)ethanone (8) Gummy liquid. Yield 0.074 g (75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 2H), 7.44-7.31 (m, 8H), 4.17 (d, *J* = 14.0 Hz, 1H), 3.81 (d, *J* = 14.0 Hz, 1H), 2.69-2.63 (m, 2H), 2.20-2.01 (m, 3H), 1.98-1.93 (m, 1H), 1.72-1.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.8, 138.7, 132.1, 128.6, 128.5, 128.3, 127.9, 127.2, 122.4, 86.9, 82.7, 58.6, 52.8, 44.2, 36.8, 23.4, 19.2; IR (Neat): 3063, 2937, 2855, 1704, 1644, 1485, 1452, 1359, 1216, 1096, 1030, 756, 690 cm^{-1}; HRMS (ESI): Calcd. for $C_{21}H_{20}N_3O$ [M$^+$+H]: *m/z* 330.1606. Found: 330.1607.

1-(1-benzyl-5-phenyl-4-(phenylethynyl)-4,5-dihydro-1H-1,2,3-triazol-4-yl)ethanone (9aa)

Gummy liquid. Yield 0.068 g (60%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.39 (m, 3H), 7.35-7.27 (m, 6H), 7.24-7.20 (m, 2H),7.15-7.13 (m, 2H), 7.05-7.03 (m, 2H), 5.28 (d, *J* = 14.8 Hz, 1H), 5.06 (s, 1H), 4.29 (d, *J* = 14.8 Hz, 1H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 134.6, 134.2, 131.5, 128.8_0, 128.7_7, 128.7, 128.5, 128.4, 128.1, 121.7, 93.2, 92.1, 81.9, 63.4, 52.1, 26.8; IR (Neat): 3058, 2926, 2849, 1715, 1666, 1627, 1556, 1501, 1458, 1397, 1266, 1167, 1068, 756, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{22}N_3O$ [M$^+$+H]: *m/z* 380.1763. Found: 380.1763.

1-(1-benzyl-5-phenyl-4-(phenylethynyl)-4,5-dihydro-1H-1,2,3-triazol-4-yl)ethanone (9ba)

Gummy liquid. Yield 0.077 g (65%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.38 (m, 3H), 7.35-7.33 (m, 3H), 7.30-7.26 (m, 6H), 7.23-7.19 (m, 4H), 7.14-7.11 (m, 2H), 7.00-6.98 (m, 2H), 5.27 (d, *J* = 15.2 Hz, 1H), 5.04 (s, 1H), 4.28 (d, *J* = 15.2 Hz, 1H), 3.58-3.40 (m, 2H), 3.00 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 140.6, 134.6, 134.1, 131.5, 128.8, 128.7, 128.5_3, 128.4_6, 128.4_3, 128.3_5, 128.1, 121.6, 93.2, 91.8, 81.9, 63.7, 52.1, 40.8, 29.8; IR (Neat): 3030, 2920, 2214, 1730, 1605, 1506, 1462, 1364, 1271, 1150, 1073, 1024, 761, 706.cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{28}N_3O$ [M$^+$+H]: *m/z* 470.2232. Found: 470.2229.

(vi) General procedure for the synthesis of tetrasubstituted 1,2,3-triazines (10-13)

A solution of cerium(IV) ammonium nitrate (CAN)[19] (124.5 mg, 0.22 mmol) in water (2 mL) was added dropwise to a stirring solution of the **3aa** (50.0 mg 0.11 mmol) in acetonitrile (3 mL). The mixture was stirred at rt for 15 min and then extracted with chloroform (3×20 mL). The combined organic layer was washed with brine solution, dried over anh. sodium sulfate and concentrated in vacuum. The residue was then purified by silica gel column chromatography using ethyl acetate-hexane (1:4) as the eluent to afford (1-benzyl-6-phenyl-1,6-dihydro-1,2,3-triazine-4,5-diyl)bis(phenylmethanone) **10**. Compounds **11-13** were prepared following the same procedure and by using the same molar quantities.

(1-benzyl-6-phenyl-1,6-dihydro-1,2,3-triazine-4,5-diyl)bis(phenylmethanone) (10). Gummy liquid. Yield 0.05 g (96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.47-7.44 (m, 3H), 7.40-7.36 (m, 7H), 7.34-7.27 (m, 5H), 7.08 (t, *J* = 7.6 Hz, 2H), 5.62 (s, 1H), 5.34 (d, *J* = 14.4 Hz, 1H), 4.67 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 191.3, 140.5, 139.0, 136.7, 135.8, 133.6, 133.0, 129.7, 129.5, 129.2, 128.9, 128.7, 128.4, 128.3_0, 128.2_6, 127.1, 119.7, 58.7, 55.1; IR (neat): 3063, 3024, 2926, 2849, 1671, 1599, 1490, 1451, 1402, 1325, 1265, 1210, 1172, 1134, 1024, 920, 695 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}N_3O_2Na$ [M$^+$+Na]: *m/z* 480.1688. Found: 480.1684.

(5-benzoyl-1-benzyl-6-phenyl-1,6-dihydro-1,2,3-triazin-4-yl)(4-methoxyphenyl)methanone (11). Gummy liquid. Yield 0.042 g (80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.46-7.43 (m, 3H), 7.40-7.37 (m, 5H), 7.35-7.28 (m, 5H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.61 (s, 1H), 5.33 (d, *J* = 14.4 Hz, 1H), 4.66 (d, *J* = 14.4 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 189.7, 164.0, 140.8, 139.1, 136.8, 133.6, 132.9, 132.2, 129.4_4, 129.3_9, 129.2, 129.1, 128.8, 128.6, 128.2_4, 128.1_9, 127.1, 119.1, 113.7, 58.7, 55.5, 55.0; IR (neat): 3058, 2937, 2844, 1660, 1595, 1507, 1452, 1326, 1255, 1167, 1118, 1068, 1030, 926, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{25}N_3O_3Na$ [M$^+$+Na]: *m/z* 510.1794. Found: 510.1791.

(5-benzoyl-1-benzyl-6-phenyl-1,6-dihydro-1,2,3-triazin-4-yl)(p-tolyl)methanone (12). Yellow solid. Yield 0.043 g (83%); mp 114-116 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.47-7.44 (m, 3H), 7.40-7.35 (m, 5H), 7.34-7.28 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J*

= 8.0 Hz, 2H), 5.61 (s, 1H), 5.34 (d, *J* = 14.4 Hz, 1H), 4.67 (d, *J* = 14.4 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 190.9, 144.6, 140.7, 139.1, 136.7, 133.6, 133.4, 132.9, 129.9, 129.5, 129.4, 129.2, 129.1, 128.8, 128.6, 128.3, 128.2, 127.1, 119.3, 58.7, 55.1, 21.8; IR (KBr): 3063, 3025, 2926, 1666, 1605, 1496, 1452, 1408, 1321, 1266, 1173, 1112, 926, 690 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{25}N_3O_2Na$ [M$^+$+Na]: *m/z* 494.1845. Found: 494.1843. X-ray structure has been determined for this compound.

(4-benzoyl-1-benzyl-6-phenyl-1,6-dihydro-1,2,3-triazin-5-yl)(4-methoxyphenyl)methanone 13. Gummy liquid. Yield 0.050 g (96%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69-7.67 (m, 2H), 7.52-7.49 (m, 1H), 7.48-7.42 (m, 3H), 7.41-7.32 (m, 7H), 7.29-7.27 (m, 2H), 7.19-7.16 (m, 1H), 6.83 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 6.66-6.63 (m, 1H), 6.42 (d, *J* = 7.5 Hz, 1H), 5.69 (s, 1H), 5.29 (d, *J* = 14.5 Hz, 1H), 4.66 (d, *J* = 14.5 Hz, 1H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 191.8, 157.1, 142.2, 139.7, 135.6, 133.8, 133.4, 132.9, 130.2, 129.2, 129.1$_3$, 129.0$_6$, 129.0, 128.8, 128.7, 128.2, 127.6, 120.3, 117.5, 110.5, 58.8, 54.9, 54.1; IR (neat): 3056, 2936, 1638, 1496, 1452, 1397, 1321, 1282, 1244, 1101, 1014, 926, 696 cm^{-1}; LC/MS: *m/z* 489 [M+1]$^+$. Anal. Calcd. for $C_{31}H_{25}N_3O_3$: C, 76.37; H, 5.17; N, 8.62; Found: C, 76.24; H, 5.21; N, 8.53.

(vi) X-ray Data. X-ray data for compounds **3aa** and **12** was collected using Cu- K_α (λ = 1.54184 Å) and Mo- K_α (λ = 0.71073 Å) radiation respectively. The structures were solved and refined by standard methods.[20] The CCDC numbers are 1426845 and 1434491.

Compound 3aa: $C_{30}H_{23}N_3O$, *M* = 441.51, Monoclinic, Space group P2(1)/n, *a* = 10.3959(14), *b* = 20.556(3), *c* = 11.7549(16) Å, *V* = 2363.2(6) Å^3, β = 109.824(2), *Z* = 4, μ = 0.076 mm^{-1}, data/restraints/parameters: 4210/0/315, R indices (I> 2σ(I)): R1 = 0.0466, *w*R2 (all data) = 0.1397. CCDC No. 1426845.

Compound 12: $C_{31}H_{25}N_3O_2$, *M* = 471.54, Monoclinic, Space group P2(1)/n, *a* = 7.5985(7), *b* = 10.1256(8), *c* = 34.045(3) Å, *V* = 2610.9(4) $Å^3$, β = 94.613(3), *Z* = 4, μ = 0.076 mm^{-1}, data/restraints/parameters: 4470/0/326, R indices ($I > 2\sigma(I)$): R1 = 0.1012, *w*R2 (all data) = 0.3112. The data quality was only moderate. CCDC No. 1434491.

ASSOCIATED CONTENT

Supporting Information

Figures and CIF files giving ORTEPs as shown by X-ray crystallography, Absorption and Fluorescence spectra and copies of $^1H/^{13}C/^{19}F$ NMR spectra of all new products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Selected reviews: (a) Li, Z.; Brouwer, C.; He, C. *Chem. Rev*. **2008**, *108*, 3239. (b) Corma, A.; Leyva-Perez, A.; Sabater, M. J. *Chem. Rev*. **2011**, *111*, 1657. (c) Krause, N.; Winter, C. *Chem. Rev*. **2011**, *111*, 1994. (d) Gulevich, A. V.; Dudnik, A. S.; Chernyak, N.; Gevorgyan, V. *Chem. Rev*. **2013**, *113*, 3084. (e) Zeng, X. *Chem. Rev*. **2013**, *113*, 6864. (f) Qian, D.; Zhang, J. *Chem. Rec.* **2014**, *14*, 280. (g) Dorel, R.; Echavarren, A. M. *Chem. Rev*. **2015**, *115*, 9028 and references cited therein.

(2) Selected articles: (a) Yao, T.; Zhang, X.; Larock, R. C. *J. Am. Chem. Soc*. **2004**, *126*, 11164. (b) Yao, T.; Zhang, X.; Larock, R. C. *J. Org. Chem*. **2005**, *70*, 7679. (c) Suhre, M. H.; Reif, M.; Kirsch, S. F. *Org. Lett.* **2005**, *7*, 3925. (d) Liu, Y.; Song, F.; Song, Z.; Liu, M.; Yan, B. *Org. Lett.* **2005**, *7*, 5409. (e) Egi, M., Azechi, K.; Akai, S. *Org. Lett.* **2009**, *11*, 5002. (f) Kotikalapudi, R.; Kumara Swamy, K. C. *Tetrahedron Lett.* **2012**, 53, 3831. (g) Li, J.; Liu, L.; Ding, D.; Sun, J.; Ji, Y.; Dong, J. *Org. Lett*. **2013**, *15*, 2884. (h) Shiroodi, R. K.; Koleda, O.; Gevorgyan, V. *J. Am. Chem. Soc.* **2014**, *136*, 13146.

(3) Selected recent articles/reviews: (a) Montagnon, T.; Tofi, M.; Vassilikogiannakis, G. *Acc. Chem. Res*. **2008**, *41*, 1001. (b) Wei, H.; Zhai, H.; Xu, P.-F.; *J. Org. Chem.* **2009**, *74*, 2224. (c) Barancelli, D. A.; Mantovani, A. C.; Jesse, C.; Nogueira, C. W.; Zeni, G. *J. Nat. Prod*. **2009**, *72*, 857. (d) Wang, Y.; Luo, Y.-C.; Hu, X.-Q.; Xu, P.-F. *Org. Lett*. **2011**, *13*, 5346. (e) Cho, C.-H.; Shi, F.; Jung, D.-I.; Neuenswander, B.; Lushington, G. H.; Larock, R. C. *ACS Comb. Sci*. **2012**, *14*, 403. (f) Peterson, L. A. *Chem. Res. Toxicol.* **2013**, *26*, 6. (g) Reddy, C. R.; Reddy, M. D. *J. Org. Chem*. **2014**, *79*, 106. (h) Erdenebileg, U.; Hostmark, I.; Polden, K.; Sydnes, L. K. *J. Org. Chem*. **2014**, *79*, 1213. (i) Gandini, A.;

Lacerda, T. M.; Carvalho, A. J. F.; Trovatti, E. *Chem. Rev.* (ASAP, **DOI:** 10.1021/acs.chemrev.5b00264).

(4) (a) Liu, F.; Yu, Y.; Zhang, J. *Angew. Chem. Int. Ed*. **2009**, *48*, 5505. (b) Xiao, Y.; Zhang, J. *Chem. Commun*. **2010**, *46*, 752. (c) Gao, H.; Zhao, X.; Yu, Y.; Zhang, J. *Chem. -Eur. J.* **2010**, *16*, 456. (d) Gao, H.; Zhang, J. *Chem. -Eur. J.* **2012**, *18*, 2777. (e) He, T.; Gao, P.; Qiu, Y.-F.; Yan, X.-B.; Liu, X.-Y.; Liang, Y.-M. *RSC Adv*. **2013**, *3*, 19913. (f) Siva Kumari, A. L.; Kumara Swamy, K. C. *J. Org. Chem*. **2015**, *80*, 4084.

(5) (a) Patil, N. T.; Wu, H.; Yamamoto, Y. *J. Org. Chem*. **2005**, *70*, 4531. (b) Huang, L.; Hu, F.; Ma, Q.; Hu, Y. *Tetrahedron Lett.* **2013**, *54*, 3410. (c) Fu, W.; Xu, F.; Guo, W.; Zhu, M.; Xu, C. *Bull. Korean Chem. Soc*. **2013**, *34*, 887. (d) Chen, W. L.; Li, J.; Zhu, Y. H.; Ye, L. T.; Hu, W.; Moa, W. M. *ARKIVOC* **2011**, *9*, 381.

(6) (a) Xiao, Y.; Zhang, J. *Angew. Chem. Int. Ed*. **2008**, *47*, 1903. (b) Liu, R.; Zhang, J. *Chem. -Eur. J.* **2009**, *15*, 9303. (c) Xiao, Y.; Zhang, J. *Chem. Commun*. **2009**, 3594. (d) Oh, C. H.; Reddy, V. R.; Kim, A.; Rhim, C. Y. *Tetrahedron Lett*. **2006**, *47*, 5307. (e) He, T.; Gao, P.; Zhao, S.-C.; Shi, Y.-D.; Liu, X.-Y.; Liang, Y.-M. *Adv. Synth. Catal.* **2013**, *355*, 365. (f) Liu, Y.; Zhou, S. *Org. Lett*. **2005**, *7*, 4609. (g) Cheng, G.; Hu, Y. *Chem. Commun*. **2007**, 3285.

(7) (a) Liu, F.; Qian, D.; Li, L.; Zhao, X.; Zhang, J. *Angew. Chem. Int. Ed*. **2010**, *49*, 6669. (b) Gao, H.; Wu, X.; Zhang, J. *Chem. -Eur. J.* **2011**, *17*, 2838.

(8) Gao, H.; Wu, X.; Zhang, J. *Chem. Commun*. **2010**, *46*, 8764.

(9) Xie, X.; Du, X.; Chen, Y.; Liu, Y. *J. Org. Chem*. **2011**, *76*, 9175.

(10) Raji Reddy, C.; Panda, S. A.; Damoder Reddy, M. *Org. Lett.* **2015**, *17*, 896.

(11) (a) Bieger, K.; Tejeda, J.; Rèau, R.; Dahan, F.; Bertrand, G. *J. Am. Chem. Soc.* **1994**, 116, 8087. (b) Kumaraswamy, S.; Kommana, P.; Satish Kumar, N.; Kumara Swamy K. C. *Chem. Commun*. **2002**, 40. (c) Ramachary, D. B.; Shashank, A. B.; Karthik, S. *Angew. Chem. Int. Ed.* **2014,** *53*, 10420. (d) Zhang, H.-H.; Luo, Y.–C.; Wang, H.-P.; Chen, W.; Xu, P.–F. *Org. Lett*. **2014**, *16*, 4896.

(12) Selected recent references: (a) Migawa, M. T.; Drach, J. C.; Townsend, L. B. *J. Med. Chem*. **2005**, *48*, 3840. (b) Hunt, J. C. A.; Briggs, E.; Clarke, E. D.; Whittingham, W. G. *Bioorg. Med. Chem. Lett*. **2007**, *17*, 5222. (c) Saravanan, J.; Mohan, S.; Roy, J. J. -*Eur. J. Med. Chem*., **2010**, *45*, 4365. (d) Mueller, R.; Rachwal, S.; Varney, M. A.; Johnson, S. A.; Alisala, K.; Zhong, S.; Li, Y.–X.; Haroldsen, P.; Herbst, T.; Street, L. J. *Bioorg. Med. Chem. Lett*. **2011**, *21*, 7455. (e) Kumar, R.; Singh, A.; Singh, J.; Singh, H.; Roy, R. K.; Chaudhary, A. *Mini-Rev. Med. Chem*. **2014**, *14*, 72. (f) Lauria, A.; Alfio, A.; Bonsignore, R.; Gentile, C.; Martorana, A.; Gennaro, G.; Barone, G.; Terenzi, A.; Almerico, A. M. *Bioorg. Med. Chem. Lett*. **2014**, *24*, 3291.

(13) See for example: (a) Kocienskain, P. J.; Ciabatto, D J. *J. Org. Chem*. **1973**, *38*, 3149. (b) Gompper, R.; Schoenafinger, K. *Chem. Ber*. **1979**, *112*, 1514. (c) Ohsawa, A.; Arai, H.; Ohnishi, H.; Igeta, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1182. (d) Ohsawa, A, Arai, H.; Ohnishi, H.; Igeta, H. *J. Chem. Soc., Chem. Commun.* **1981**, 1174. (e) Schmidt, B. F.; Snyder, E. J.; Carroll, R. M.; Farnsworth, D. W.; Michejda, C. J.; Smith, Jr. R. H. *J. Org. Chem*. **1997**, *62*, 8660. (f) Migawa, M. T.; Townsend, L. B. *J. Org. Chem*. **2001**, *66*, 4776. (g) Butler, R. N.; Fahy, A. M.; Fox, A.; Stephens, J. C.; McArdle, P.; Cunningham, D.; Ryder, A. *J. Org. Chem.* **2006**, *71,* 5679. (h) Miura, T.; Yamauchi, M.; Kosaka, A.;

Murakami, M. *Angew. Chem., Int. Ed*. **2010**, *49*, 4955. (i) Glinkerman, C. M.; Boger, D. L. *Org. Lett*. **2015**, *17*, 4002 and references cited therein.

(14) (a) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett*. **1983**, 1131. (b) Janreddy, D.; Kavala, V.; Kuo, C. –W.; Chen, W. –C.; Ramesh, C.; Kotipalli, T.; Kuo, T. –S.; Chen, M. –L.; He, C. –H.; Yao, C. –F. *Adv. Synth. Catal*. **2013***, 355*, 2918.

(15) For an example of Lewis acid catalyzed [3+2] cycloaddition of alkene with azide, see: Wang, Y.-C.; Xie, Y.-Y.; Qu, H.-E; Wang, H.-S.; Pan, Y.-M.; Huang, F.-P. *J. Org. Chem*. **2014**, *79*, 4463.

(16) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, UK, **1986.**

(17) (a) Yao, T.; Zhang, X.; Larock, R.-C. *J. Am. Chem. Soc*. **2004**, *126*, 11164. (b) Kotikalapudi, R.; Kumara Swamy, K.-C. *Tetrahedron Lett*. **2012**, *53*, 3831. (c) He, T.; Gao, P.; Zhao, S.-C.; Shi, Y.-D.; Liu, X.-Y.; Liang, Y.-M. *Adv. Synth. Catal.* **2013**, *355*, 365.

(18) (a) Chakraborty, A.; Dey, S.; Sawoo, S.; Adarsh, N. N.; Sarkar, A. *Organometallics* **2010**, *29*, 6619. (b) Khedar, P.; Pericherla, K.; Kumar, A. *Synlett* **2014**, *25,* 515.

(19) Lepage, L.; Lepage, Y. *Synthesis* **1983**, 1018.

(20) (a) Sheldrick, G. M. SADABS, *Siemens Area Detector Absorption Correction*; University of Göttingen, Göttingen, Germany, **1996**. (b) Sheldrick, G. M. SHELX-97, *A Program for Crystal Structure Solution and Refinement*; University of Göttingen, Göttingen, Germany, **1997**. (c) Sheldrick, G. M. *SHELXTL NT Crystal Structure Analysis Package*; Bruker AXS, Analytical X-ray System, Madison, WI, **1999**; version 5.10.