Cycloaddition of phenyltriazolinedione with carbazole-alkynes and yne-carbamates to access diazacyclobutenes

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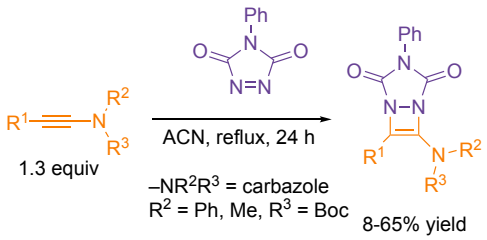
Graphical Abstract

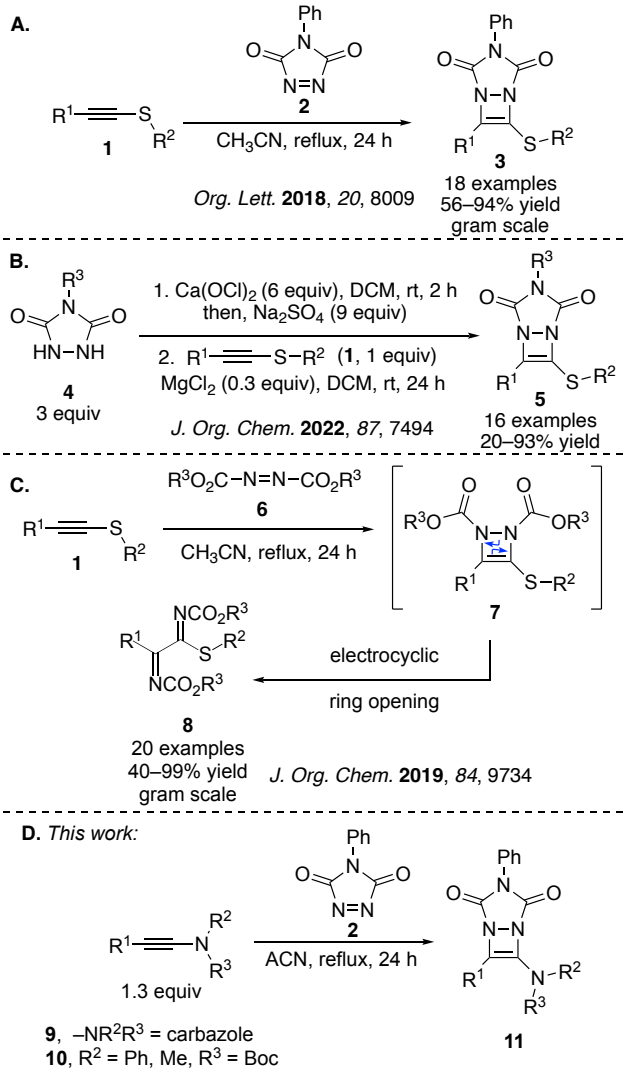


Abstract

Previously, we described the synthesis of stable, bicyclic examples of the rather rare diazacyclobutene motif by means of a cycloaddition between triazolinediones and electron-rich thiolated alkynes. Here, we report the investigation of the cycloaddition of triazolinediones with related electron-rich yne-carbamates and carbazole-alkynes. Bicyclic diazacylobutenes arising from yne-carbamates were isolated in 8-65% yield, while those arising from carbazole-alkynes were isolated in 28-59% yield. Mechanistic studies and characterization of isolable by-products shed light on the underlying issues leading to poor to moderate yields.

Introduction

Recently, our group has been interested in the development of tactics to access the rare diazacyclobutene (DCB) motif for synthetic and biological applications.[1-3] Prior to our efforts in this area, the heterocycle had been studied primarily through computation[4-10] and prepared only infrequently.[11-14] Our initial efforts focused on the union of electron-rich thioalkyne nucleophiles **1** and nitrogenous electrophiles such as triazolinediones **2** (Scheme 1A and B)[1,2] and azodicarboxylates **6** (Scheme 1C).[3] We hypothesized that similar reactivity of nitrogen-containing alkyne nucleophiles (*e.g.* **9** and **10**) might also react productively with triazolinediones to provide stable DCB products **11** (Scheme 1D). The results of these efforts are reported herein.



Scheme 1. A-C. Prior efforts to access diazacyclobutenes. **D.** Synthesis of diazacyclobutenes from carbazole alkynes and yne-carbamates.

Ynamines and ynamides are valuable synthetic tools that are commonly activated using metal-catalysis (*e.g.,* Au(I), Pt(II), Ag(I), Pd(II), and Cu(I)).[15-19] Examples of thermal [2+2] cycloadditions of ynamides are scarce. Ficini [2+2] cycloadditions of ynamines and α,β-unsaturated ketones are by far the most common examples of thermal [2+2]

cycloadditions with nitrogen-bearing alkynes.[20,21] Although the thermal methodology does not translate to ynamides, catalytic methods have recently appeared, which can promote the Ficini reaction of ynamides and α,β-unsaturated ketones.[19,22]

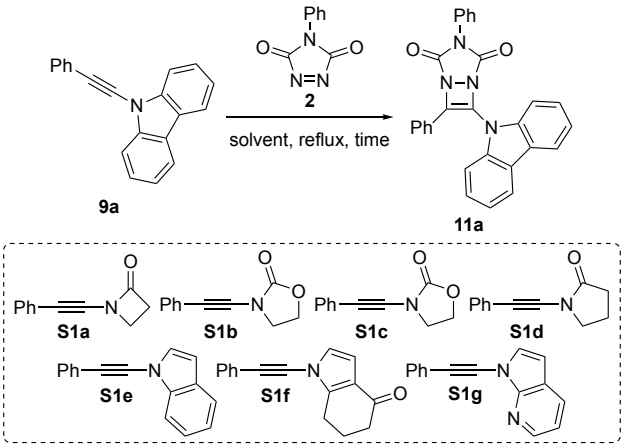
Results and Discussion

To begin our study, we synthesized a series of commonly encountered nitrogen-containing alkynes using established methods (See ESI).[23] Upon subjecting the series to PTAD (**2**) in refluxing acetonitrile, we found that most of these nucleophiles (**S1a**-**S1g**, Table 1 entries 1-9 and dashed box) failed to produce any evidence of the desired bicyclic DCB (*i.e.* **11**, Scheme 1). Alkynes bearing oxazolidinone, thiazolidinone, and pyrrolidinones were unreactive in the presence of PTAD. Substrates bearing nucleophilic heterocycles such as pyrrole and indole produced complex mixtures of products with no spectroscopic evidence suggesting the formation of the desired DCB motif. An alkyne bearing a 2-azetidinone provided the corresponding DCB product (**S2a**) in 10% yield (Table 1, entry 1). The most promising result arose when carbazole-alkyne (**9a**, Table 1, entry 8) provided DCB **11a** in 37% isolated yield after 24 h.

After this initial screen, we decided to move forward with optimization of the reaction **9a** with PTAD to provide DCB **11a** (Table 1). We found that replacing acetonitrile with other solvents (*i.e.* DCM, toluene, THF, and methanol) resulted in diminished yields ranging from 0% to 20% (Table 1, entries 9, 11–13). Methodology that we recently developed using magnesium(II) chloride as a Lewis acid catalyst to facilitate the reaction of thioalkynes at room temperature (see Scheme 1B)[2] did not translate to the use of carbazole-alkyne nucleophiles (Entry 10). Further, optimization of the reaction time (entries 14–18) and revealed an optimal reaction time of 72 h (Entry 16, 54% yield). Lastly,

we found that increasing the equivalents of **9a** to 1.3 equiv. resulted in higher yield of **11a** (Entry 19, 56% yield).

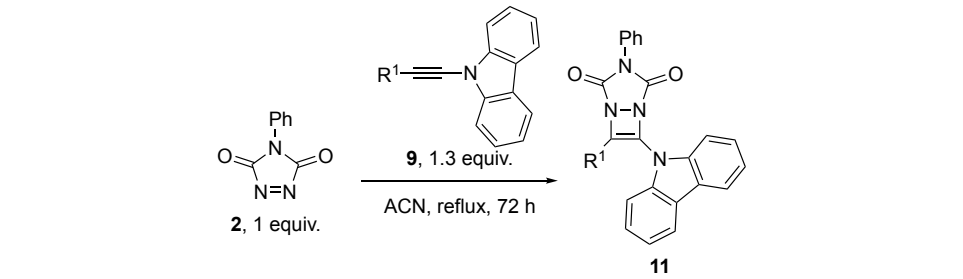
Table 1. Optimization of reaction of PTAD and **9a** to form DCB **11a**



Entry	alkyne equiv.	**2** equiv.	Solvent	Time	Yield (DCB)[a]
1	**S1a**, 1.3	1.0	ACN	24 h	**S2a**, 10%
2	**S1b**, 1.3	1.0	ACN	24 h	**S2b**, 0%
3	**S1c**, 1.3	1.0	ACN	24 h	**S2c**, 0%
4	**S1d**, 1.3	1.0	ACN	24 h	**S2d**, 0%
5	**S1e**, 1.3	1.0	ACN	24 h	**S2e**, 0%[b]
6	**S1f**, 1.3	1.0	ACN	24 h	**S2f**, 0%
7	**S1g**, 1.3	1.0	ACN	24 h	**S2g**, trace
8	**9a**, 1.3	1.0	ACN	24 h	**11a**, 37%
9	**9a**, 1.1	1.0	DCM	24 h	**11a**, 0%
10[c]	**9a**, 1.1	1.0	DCM	24 h	**11a**, 0%
11	**9a**, 1.1	1.0	Toluene	24 h	**11a**, 0%
12	**9a**,1.1	1.0	THF	24 h	**11a**, 14%
13	**9a**, 1.1	1.0	MeOH	24 h	**11a**, 20%
14	**9a**, 1.1	1.0	ACN	24 h	**11a**, 42%
15	**9a**, 1.1	1.0	ACN	48 h	**11a**, 43%
16	**9a**, 1.1	1.0	ACN	72 h	**11a**, 54%
17	**9a**, 1.1	1.0	ACN	120 h	**11a**, 44%
18	**9a**, 1.1	1.0	ACN	168 h	**11a**, 45%
19	**9a, 1.3**	**1.0**	**ACN**	**72 h**	**11a, 56%**

[a]Isolated yields. [b]Complex mixture of products. [c]Room temperature with 30 mol % $MgCl_2$

We next explored the substrate scope of DCB synthesis from carbazole-alkynes (Chart 1). We found that nearly every substrate produced the desired DCB product, albeit in moderate to low isolated yields. Under the optimized conditions, phenyl-bearing compound **11a** was isolated in 56% yield. A *p*-CF_3-phenyl analog, **11b**, was isolated in 35% yield. Products with *para*-situated electron donors such as methyl (**11c**) and methoxy (**11d**) were both isolated in 36% yield. Carbazole-alkyne compounds with halogenated phenyl substituents also provided the desired products (**11e**-**11h**). A *para*-bromo analog



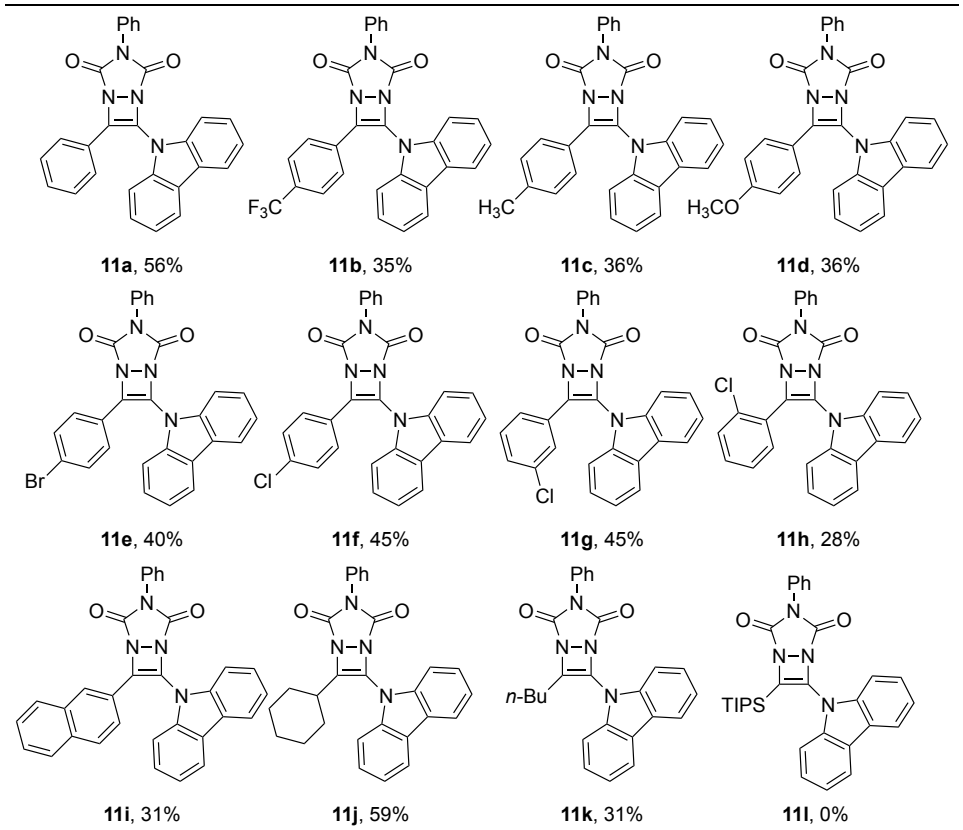
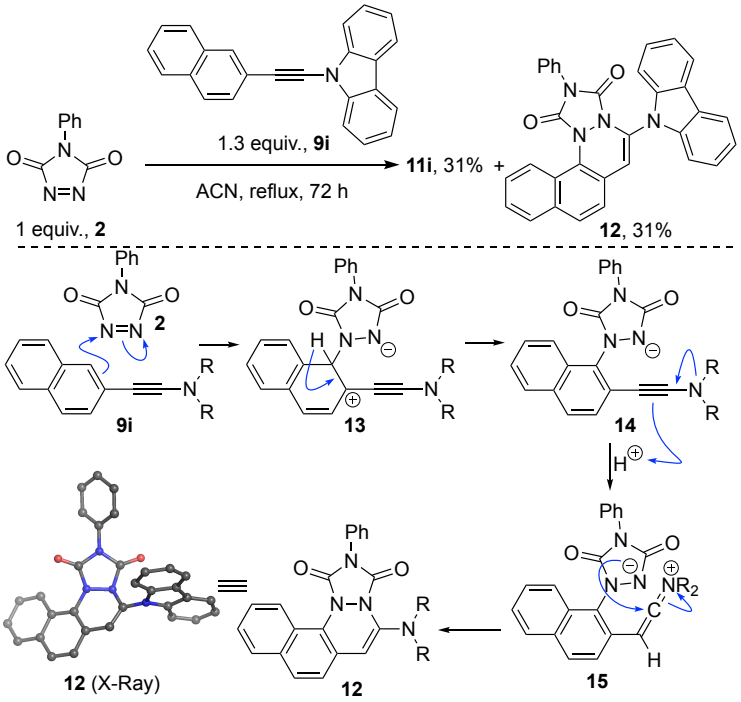


Chart 1. Substrate scope for diazacyclobutene (**11**) synthesis from carbazole-alkynes (**9**).

(**11e**) was isolated in 40% yield, while a series of chlorinated analogs were isolated in 45% (**11f**), 45% (**11g**), and 28% (**11h**) yields respectively. Compounds **11f**, **11g**, and **11h** were all successfully characterized by X-ray crystallography (see ESI). A 2-napthyl carbazole-alkyne provided **11i** in 31% yield. Carbazole-alkynes bearing distal alkyl groups also provided access to the corresponding DCB products upon reaction with PTAD. A cyclohexyl substrate provided **11j** in 59% yield, while *n*-butyl analog **11k** was prepared in 31% yield. Unfortunately, a carbazole-alkyne bearing a TIPS group failed to provide the desired **11l**.

While we were gratified that a series of DCBs (**11**) could be readily prepared from carbazole alkynes (**9**), we were frustrated by the inability to further optimize the yield of the desired products. Interestingly, a significant undesired by-product was isolated along with DCB **11i** upon reaction of a 2-naphthyl carbazole alkyne and PTAD (Scheme 2). In that transformation, compound **12** was isolated in 31% yield along with DCB **11i**. Subsequently **12** was characterized spectroscopically and by single crystal X-ray diffraction. This surprising result may arise from competing electrophilic aromatic substitution of PTAD, **2**, on the naphthalene moiety of



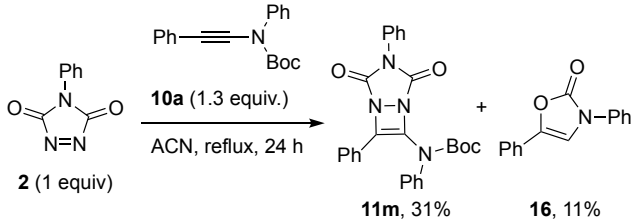
Scheme 2. Top: Isolation of unexpected by-product **12** from reaction of PTAD, **2**, and cabazole-alkyne **9i** leading to DCB **11i**. Bottom: A plausible mechanism leading to **12**; X-ray structure of **12**.

carbazole alkyne **9i** leading to anion **14** by way of elimination of intermediate **13**. Protonation of the carbazole alkyne in **14** could lead to **12** by means of collapse of intermediate **15** by attack of the urazole anion onto the ketene-iminium species. It is noteworthy that we did not observe analogs of **14** in the reaction mixtures of other DCBs **11** arising from carbazole alkynes. Nonetheless, this result serves to highlight the challenges of accessing the desired products from less nucleophilic alkyne congeners like carbazole alkynes as compared to the more reactive thioalkynes that we investigated previously.[1-3] That electrophilic aromatic substitution appears to compete favorably with the desired reaction in some cases highlights the rather sluggish nucleophilicity of the carbazole alkyne moiety.

Next, we transitioned to an investigation of the preparation of DCBs from reaction of PTAD (**2**) and yne-carbamates **10**. In initial grounding experiments (Table 2, entry 1), we found that yne-carbamate **10a** provided access to the desired DCB **11m** in 31% isolated yield along with the oxazolone, **16** (11%). The formation of oxazolones from yne-carbamates such as **10a** is well-documented,[24-26] and presented a problem here because DCB **11m** and **16** were inseparable by flash column chromatography. Thus, we undertook a brief condition screen to minimize formation of **16** and optimize the isolated yield of DCB **11m**. Our initial experiments suggested that longer reaction times led to formation of oxazolone **16** (Entries 1 – 3). Interestingly, **16** was undetected in a control experiment lacking PTAD (**2**), suggesting that the reagent may promote the intramolecular cyclization of yne-carbamate **10a** (Entry 4). The apparent influence of PTAD on the formation of oxazolone **16** induced us to consider the order and rate of addition of reagents in the transformation. We found that the slow addition of PTAD (**2**) to a solution of yne-carbamate **10a** provided

significantly less oxazolone byproduct than the reverse slow addition of **10a** to **2** (*i.e.* 7% of **16** vs. 40% of **16**, respectively (Entries 5 and 6)). With this finding, we reinvestigated longer reaction times with concomitant slow addition of PTAD (**2**) to **10a** (Entries 7 – 9). Interestingly, we found that longer reaction times (*i.e.* 48 h and 72 h) did not produce higher quantities of **11m** (*i.e.* 21%, 20, and 26% yields respectively for 24, 48, and 72 h). Performing the reaction in toluene instead of acetonitrile provided **11m** in 23% isolated yield and in a 94:6 **11m**:**16** ratio (Entry 10). At this point, we noted the gradual

Table 2. Optimization of reaction of PTAD (**2**) and yne-carbamate **10a** to provide DCB **11** and minimize formation of oxazolone **16.**



Entry	**10a** equiv	**2** equiv	Time	**11m:16**[a]	**11m yield**[b]
1	1.3	1.0	24 h	63:37	31%
2	1.3	1.0	48 h	71:29	35%
3	1.3	1.0	72 h	35:65	32%
4	1.3	0	24 h	–	–
5[c]	1.0	1.0	24 h[d]	93:7	22%
6[d]	1.0	1.3	24 h[d]	3:2	6%
7[c]	1.3	1.0	24 h[d]	83:17	21%
8[c]	1.0	1.0	48 h[d]	77:23	20%
9[c,e]	1.0	1.0	72 h[d]	92:8	26%
10[c,e,f]	1.0	1.0	24 h[d]	94:6	23%
11[c,e]	1.0	1.0	24 h[d]	>99:1	31%
12[c,e]	1.5	1.0	24 h[d]	87:13	9%
13[c,e]	2.0	1.0	24 h[d]	25:75	9%
14[c,e]	1.0	1.3	24 h[d]	97:3	41%
15[c,e]	1.0	1.5	24 h[d]	>99:1	38%
16[c,e]	1.0	2.0	24 h[d]	>99:1	45%
17[c,e]	1.0	2.0	48 h[d]	>99:1	36%
18[c,e]	1.0	2.0	72 h[d]	>99:1	47%
19[e]	**1.0**	**2.0**	**24 h**	>99:1	**42%**

[a]Ratio calculated from integration of Boc protons of **11m** and vinylic proton of **16**. [b]Isolated yield after column chromatography. [c]Slow addition of **2** to **10a** at 2 h intervals (0.2 equiv per interval). [d]Slow addition of **10a** to **2** at 2 h intervals (0.2 equiv per interval). [d]Reaction time after first addition of **2**. [e]Glassware joints and septum sealed with Teflon tape to prevent gradual solvent evaporation. [f]Toluene was used as the solvent.

concentration of the reaction over the course of the experiment due to solvent evaporation, a phenomenon that led to increased formation of the undesired oxazolone by-product **16**. Redoubling efforts to prevent solvent evaporation by sealing the round-bottom flask/reflux condenser joint and septum with Teflon tape resulted in the full suppression of the by-product oxazolone **16** (**11m** isolated in 31% yield with a >99:1 **11m**:**16** ratio, Entry 11). In subsequent, adequately sealed experiments, we investigated the effect of varying the equivalence of each reactant. Here, oxazolone **16** was formed in higher quantities as we increased the equivalence of yne-carbamate **10a** (*i.e*, 13% of **7** and 75% of **7**, respectively, Entries 12 and 13). Conversely, increasing the loading of PTAD (**2**) resulted in improved isolated yields of the desired DCB **11m** while completely suppressing formation of oxazolone **16** (*i.e.* 41, 38, and 45% isolated yield of **11m** at 1.3, 1.5, and 2.0 equiv PTAD (**2**), respectively, Entries 14 – 16). This result, in adequately sealed glassware to prevent solvent evaporation, highlighted that the results of the order of addition studies described above (entries 5 and 6) were largely irrelevant to the ultimate outcome of the reaction. Specifically, when solvent evaporation is prevented during the course of the reaction, the order of addition of reagents no longer affects the reaction outcome; undesirable formation of **16** appears to be more favorable when the reaction is conducted at higher concentrations (*i.e.* with less solvent) regardless of the equivalency or order of addition of PTAD. Deploying longer reaction times of 48 h or 72 h while maintaining the 2:1 ratio of PTAD (**2**) to yne-carbamate **10a** did not result in significant increases in yield of DCB **11m** (i.e. 36% and 45% yield for 48 and 72 h, respectively, entries 17 and 18). Finally, after settling on the reaction of 2 equiv PTAD (**2**) and 1 equiv of yne-carbamate **10a** in refluxing acetonitrile for 24 h, we revisited the necessity for slow

addition of the former to the latter (entry 19). In the event, the desired DCB product **11m** was isolated in 42% yield, indicating that the use of 2 equiv of PTAD (**2**) is sufficient to provide the DCB product in comparable isolated yield while also suppressing the formation of the unwanted oxazolone by-product **16**. With these findings, we decided to utilize the conditions outlined in Table 2, entry 19 as our standard conditions.

While the optimization efforts in Table 2 were successful in reducing the prevalence of the undesirable and inseparable oxazolone by-product, they provided **11m** in rather modest isolated yield. Nevertheless, we moved ahead with the optimized conditions in order to evaluate the substrate scope of the formation of DCBs from PTAD (**2**) and yne-carbamate nucleophiles **10** (Chart 2). We found that our optimized conditions were successful at producing near gram quantities of **11m** in comparable yield (45% yield, 0.84 g isolated). An yne-carbamate bearing an electron-withdrawing *p*-CF_3-Ph substituent provided product **11n** in 41% yield. Yne-carbamates substituted with arenes bearing strong electron donors (*i.e. p*-Me-Ph and *p*-MeO-Ph) provided DCBs **11o** and **11p** in slightly lower yields (30% and 14% yields, respectively). A series of yne-carbamates with halogenated arenes provided DCBs **11q** (*p*-Br-Ph, 42%), **11r** (*p*-Cl-Ph, 36%), **11s** (*m*-Cl-Ph, 37%), and **11t** (*o*-Cl-Ph, 39%) in acceptable yields. An *N*-Boc, *N*-Ph DCB bearing a 2-napthyl substituent (**11u**) was isolated in a poor 8% yield. *N*-Boc, *N*-Ph yne-carbamates with alkyl substituents (R^1 = Cy and *n*-Bu) provided DCB products **11v** and **11w** in 51% and 65% isolated yields, respectively. Next, we performed experiments to probe the steric and electronic effects of the carbamate substitution pattern on yne-carbamate **10** (R^1 = Ph). An *N*-Boc, *N*-methyl yne-carbamate provided DCB **11x** in 32% yield while an *N*-methylcarbamate, *N*-phenyl congener provided **11y** in 31% yield. An *N*-

methylcarbamate, *N*-methyl starting material provided compound **11z** in 24% yield. Taken together, and compared to the synthesis of **11m** (*i.e.* Boc, Ph), these results suggest that the steric environment of the nitrogen atom in yne-carbamate **10** does not appreciably affect the outcome of the reaction and likely does not account for the rather modest yields of the DCB products. We also found that ynamides bearing sulfonamide (*i.e.* Ts) groups also provided DCB products, albeit in lower yields (**11aa** and **11ab**, 20% and 37%, respectively). Compounds **11aa** and **11ab** were characterized by single crystal

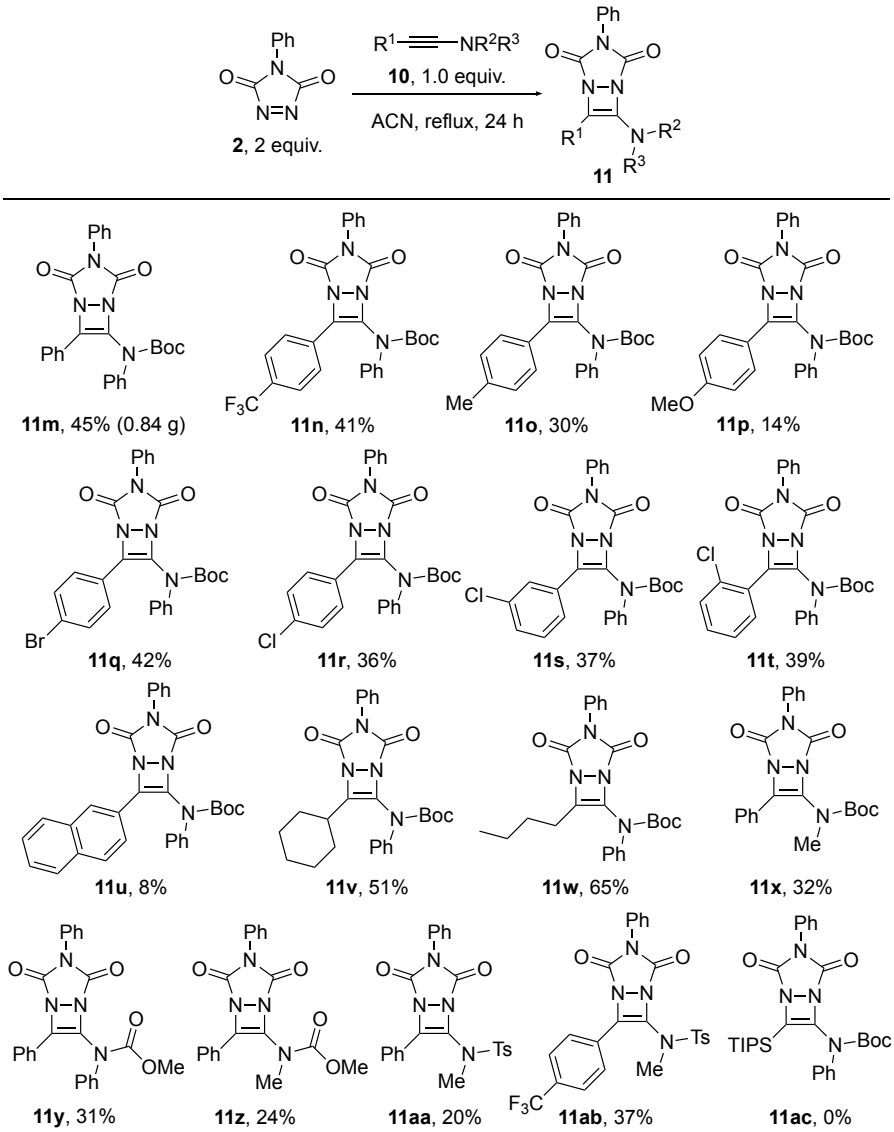
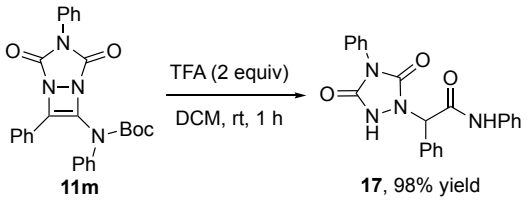


Chart 2. Scope of reaction of PTAD (**2**) and yne-carbamate nucleophiles (**10**) to provide DCBs **11**.

X-ray diffraction (see ESI). Finally – and similar to the results with carbazole alkynes (see Chart 1) – we found that a TIPS-substituted yne-carbamate failed to provide DCB **11ac**.

While we were able to successfully generate a rather large library of DCB products **11** arising from carbazole-alkynes **9** and yne-carbamates **10**, we remained frustrated by the rather poor yield of the transformations despite significant efforts to optimize the reaction conditions. Because many of the DCBs **11** depicted in Chart 2 bear an acid-labile Boc protecting group, we wondered whether the lower yields in the transformation could be due to loss of this group either during the reaction or during purification. We briefly explored attempts to remove the moiety by treatment with trifluoroacetic acid in order to generate an analytical sample of the Boc-deprotected DCB product. During this effort, we discovered that the DCB ring of compound **11m** underwent scission in the presence of TFA to provide phenylglycine derivative **17** in 98% isolated yield (Scheme 3). It is noteworthy that we never observed the formation of **17** in crude reaction mixtures of yne-carbamates **10** and PTAD **2** during the preparation of **11m-z**, nor did we isolate **17** during column chromatography of crude **11m-z**.



Scheme 3. DCB ring cleavage of **11m** with TFA to provide phenylglycine derivative **17**.

The rather low yields for the synthesis of **11** from carbazole-alkynes **9** and yne-carbamates **10** sharply contrast with the generally favorable reactivity of the related thioalkynes **1** that we studied previously for the preparation of thiolated DCBs **3** and **5**, (see Scheme 1A-B).[1,2] To further understand the reactivity differences of electron-rich alkyne nucleophiles with PTAD **2**, we analyzed the energy gaps between frontier molecular orbitals of the PTAD LUMO and the corresponding HOMO of thioalkyne **1**,

carbazole-alkyne **9a** and yne-carbamate **10a** (Figure 1). This was done using the Gaussian 09 suite with DFT calculation[27], employing the B3LYP/6-311G level of theory.[28-30] Frontier molecular orbitals play a significant role in determining the chemical reactivity and kinetic stability of molecules. The HOMO (located in each alkyne moiety) and LUMO (located in the PTAD moiety) energy values were calculated for the PTAD-**1**, PTAD-**9a**, and PTAD-**10a** reactants. As shown in Figure 1, the computed HOMO-LUMO band gap energy for the PTAD/thioalkyne **1** reactant combination is 2.63 eV. In contrast, the PTAD/carbazole-alkyne **10a** and PTAD/yne-carbamate **9a** reactant combinations exhibited significantly higher HOMO-LUMO band gap energies, measuring 4.73 eV and

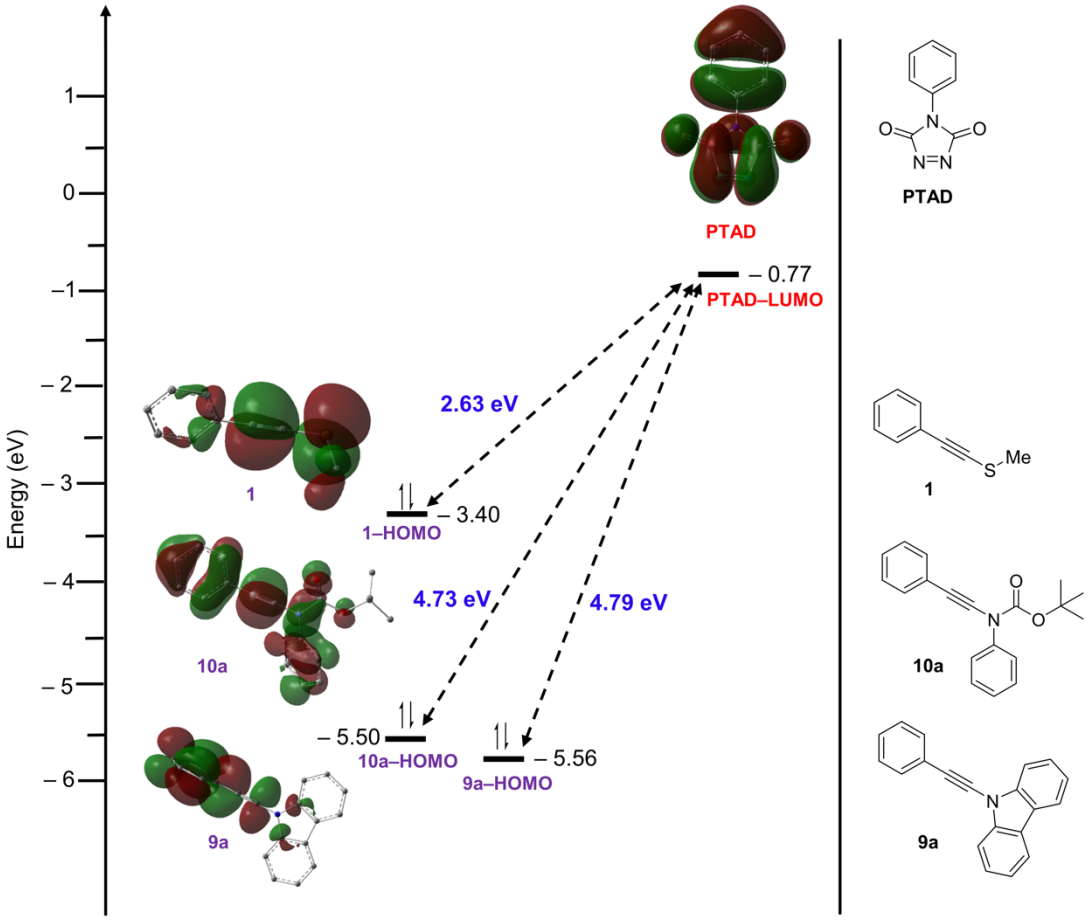


Figure 1. Molecular orbital distribution plots of the ground state LUMO of PTAD (**2**) and the ground state HOMO of thioalkyne **1**, carbazole-alkyne **9a,** and yne-carbamate **10a** at the DFT-B3LYP/6-311G level of theory.

4.79 eV, respectively. The lower HOMO-LUMO band gap for the PTAD/thioalkyne **1** reactant combination is consistent with the observation of higher yielding syntheses of sulfur-containing DCBs (i.e. **3** and **5**)[1,2] as compared to more sluggish reaction of carbazole-alkynes and yne-carbamates described here. This band-gap analysis also suggests that more electron-rich alkynyl amine nucleophiles might fare better in the reaction with PTAD. For example, the HOMO energy of the corresponding *N*,*N*-dimethyl-2-phenylethyn-1-amine is –4.39 eV (i.e. HOMO/ PTAD LUMO band gap = 3.62 eV; See Figure S9). Thus, dialkyl alkyne-amines appear to possess higher HOMO energies, which is more comparable to the energy of HOMO of **1**. Unfortunately, multiple attempts to synthesize dialkyl amino alkynes failed in our hands owing to the propensity for these materials to under rapid hydration to the corresponding *N*,*N*-dialkyl amides during isolation, even due to adventitious humidity in the air.

Conclusion

In conclusion, we have developed robust procedures for the preparation of the DCB heterocycle **11** by reaction of PTAD with carbazole alkynes 9 and yne-carbamates 10, albeit in moderate yields. The analysis of key by-products of these transformations revealed some of the challenges associated with deploying these less-reactive nucleophiles in the transformation. Further studies investigating avenues to increase the reactivity of nitrogen-bearing alkyne nucleophiles with PTAD are ongoing. We are also exploring the chemical reactivity and biological properties of these underexplored heterocycles.

Experimental section

1. General Information.

All reagents were purchased from commercial sources and used without further purification. Dichloromethane and acetonitrile were dried prior to use over phosphorus pentoxide. Acetone was dried over anhydrous calcium sulfate and freshly distilled and stored under argon. ^{1}H and ^{13}C $\{^{1}H\}$ NMR spectra were collected on Bruker Avance 300 and 500 MHz spectrometers using DMSO-d_6 or $CDCl_3$ as solvents. Chemical shifts are reported in parts per million (ppm). Chemical shifts are referenced to residual solvent peaks. Some structural assignments aided by additional information from gHSQC, gHMBC, DEPT-135, and APT experiments. Infrared spectroscopy data were collected using a Shimadzu IRAffinity-1S instrument (with MIRacle 10 single reflection ATR accessory) operating over the range of 400-4000 cm^{-1}. HRMS data were collected using an instrument equipped with electrospray ionization in positive mode (ESI^{+}) and a time-of-flight (TOF) detector. Single crystals of **11f**, **11g**, **11h**, **12**, **11aa**, and **11ab** were grown by slow evaporation of $CHCl_3$ solutions of the respective compounds. Single crystal X-ray diffraction was performed using a Bruker D8 Venture diffractometer with dual Cu and Mo sources and a Photon 2 detector. The structures were refined using SHELXL,[31] and complete crystallographic details are included in the Supporting Information (Tables S1 and S2, Figures S2-S7). Flash silica gel (40–63 μm) was used for column chromatography. All diazacyclobutene products (**11a – 11ab**) were purified by flash chromatography with hexane and ethyl acetate (gradient from 100% hexane to 8:2 hexane/ethyl acetate). All new compounds were characterized by ^{1}H and ^{13}C $\{^{1}H\}$ NMR, ATR-FTIR, HRMS, and melting point (where appropriate). Ynamides (**9**, **10**) were prepared using copper catalyzed coupling of alkynyl bromides and amines or carbamates

(where applicable). Commercially available acetylenes were brominated with NBS to generate alkynyl bromides. (see SI for details).

2. General procedure for synthesis of DCBs from carbazole-alkynes **9**.

To a flame-dried round-bottomed flask equipped with a stir bar was added the corresponding ynamide **9** (1.3 equiv., 1.3 mmol) in dry acetonitrile (5 mL). To the flask was added PTAD **2** (1 equiv., 1 mmol) in dry acetonitrile (5 mL). The reaction mixture was refluxed for 72 h using an oil bath. Upon reaction completion, the mixture was cooled down and the solvent was removed under reduced pressure. The crude mixture was purified via flash chromatography with hexane and ethyl acetate (gradient from 100% hexane to 8:2 hexane/ethyl acetate) (Note: all examples of **11** were purified using this solvent system.)

3. General Procedure for synthesis of DCBs from yne-carbamates **10**.

To a flame-dried round-bottomed flask equipped with a stir bar was added the corresponding ynamide **10** (1 equiv., 1 mmol) in dry acetonitrile (5 mL). To the flask was added PTAD (2 equiv., 2 mmol) in dry acetonitrile (5 mL). The round-bottomed flask was sealed at the joint with a septum and Teflon tape to prevent solvent evaporation. The mixture was refluxed for 24 h using an oil bath. Upon reaction completion, the mixture was cooled down and the solvent was removed under reduced pressure. The crude mixture was purified via flash chromatography with hexane and ethyl acetate (gradient from 100% hexane to 8:2 hexane/ethyl acetate). (Note: all examples of **11** were purified using this solvent system.)

Analytical data for DCBs **11a-11ab.**

11a, 6-(9H-carbazol-9-yl)-3,7-diphenyl-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione; Pale orange solid; Yield: 56% (175 mg); Mp: 161.6-163.4 °C; IR (neat): 1740 (s), 1697 (w), 1493 (w), 1450 (m), 1396 (w), 1373 (m), 1335 (w), 1308 (w), 1265 (w), 1219 (m), 1180 (w), 1142 (m), 1099 (w), 1072 (w), 1015 (w), 961 (w), 899 (w), 775 (w), 764 (w), 748 (s), 721 (m), 702 (m), 687 (m), 667 (m), 633 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16-8.07 (m, 2H), 7.61-7.43 (m, 11H), 7.42-7.29 (m, 5H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.0, 139.4, 138.6, 130.9, 130.1, 129.5, 129.3, 129.0, 126.9, 126.0, 125.4, 125.4, 124.6, 124.1, 122.3, 120.7, 111.2. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{28}H_{18}N_4O_2$ 443.1503; Found 443.1504.

11b, 6-(9H-carbazol-9-yl)-3-phenyl-7-(4-trifluoromethyl)phenyl)-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione; Pale yellow solid; Yield: 35% (149 mg); Mp: 133.6-135.3 °C; IR (neat): 1744 (s), 1447 (w), 1373 (m), 1319 (s), 1261 (w), 1219 (m), 1169 (w), 1126 (m), 1111 (m), 1099 (w), 1072 (w), 1061 (w), 1026 (w), 1015 (w), 957 (w), 841 (w), 775 (w), 745 (m), 721 (m), 710 (w), 687 (w), 667 (w), 633 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.10 (m, 2H), 7.66-7.57 (m, 4H), 7.56-7.44 (m, 9H), 7.44-7.37 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 155.9, 155.2, 139.0, 135.5, 131.3 (q, $^{2}J_{CF}$ = 32.9 Hz), 130.7, 129.5, 129.5, 128.8, 127.1, 126.3, 125.9 (q, $^{3}J_{CF}$ = 4.0 Hz), 125.4, 124.8 (2C – see ESI) , 123.6 (q, $^{1}J_{CF}$ = 272.5 Hz), 122.7, 120.9, 111.2. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{29}H_{17}F_3N_4O_2$ 511.1377; Found 511.1379.

11c, 6-(9H-carbazol-9-yl)-3-phenyl-7-(p-tolyl)-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione; Pale yellow solid; Yield: 36% (163 mg); Mp: 95.6-98.1 °C; IR (neat): 1740 (s), 1721 (m), 1701 (w), 1447 (m), 1373 (s), 1219 (m), 1146 (m), 779 (w), 748 (s), 721 (m), 702 (w), 687 (w), 656 (w), 633 (w), 571 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14-8.09 (m, 2H),

7.57-7.50 (m, 4H), 7.49-7.42 (m, 5H), 7.42-7.35 (m, 4H), 7.16-7.10 (m, 2H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.3, 156.0, 140.6, 139.5, 139.2, 130.9, 129.6, 129.5, 129.3, 126.9, 126.0, 125.4, 124.6, 123.2, 122.6, 122.2, 120.7, 111.1, 21.6. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{29}H_{20}N_4O_2$ 457.1659; Found 457.1656.

11d, 6-(9H-carbazol-9-yl)-7-(4-methoxyphenyl)-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione; Pale orange solid; Yield: 36% (169 mg); Mp: 94.0-97.0 °C; IR (neat): 1740 (s), 1605 (w), 1447 (m), 1377 (s), 1308 (w), 1258 (m), 1219 (s), 1173 (m), 1142 (m), 1115 (w), 1099 (w), 1022 (w), 957 (w), 833 (m), 779 (w), 748 (s), 721 (m), 702 (w), 687 (w), 656 (w), 633 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14-8.08 (m, 2H), 7.59-7.50 (m, 4H), 7.50-7.42 (m, 7H), 7.40-7.34 (m, 2H), 6.88-6.81 (m, 2H), 3.79 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 161.0, 156.6, 156.2, 139.6, 139.4, 130.9, 129.5, 129.3, 127.8, 126.9, 125.5, 124.5, 122.2, 121.9, 120.7, 117.9, 114.5, 111.1, 55.4. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{29}H_{20}N_4O_3$ 473.1608; Found 473.1603.

11e, 6-(4-bromophenyl)-7-(9H-carbazol-9-yl)-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione; Pale yellow solid; Yield: 40% (269 mg); Mp: 174.0-176.3 °C; IR (neat): 1744 (s), 1717 (w), 1697 (w), 1493 (w), 1454 (w), 1443 (w), 1373 (s), 1261 (w), 1219 (m), 1142 (m), 1096 (w), 1076 (w), 1022 (w), 1007 (m), 957 (w), 837 (w), 822 (w), 775 (m), 745 (s), 718 (m), 687 (m), 667 (w), 633 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15-8.10 (m, 2H), 7.58-7.51 (m, 4H), 7.50-7.44 (m, 7H), 7.43-7.33 (m, 4H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.0, 155.7, 139.2, 136.9, 132.2, 130.8, 129.5, 129.4, 127.4, 127.0, 125.4, 124.7, 124.7, 124.4, 124.3, 122.5, 120.8, 111.2. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{28}H_{17}BrN_4O_2$ 521.0608; Found 521.0604.

11f, 6-(9H-carbazol-9-yl)-7-(4-chlorophenyl)-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione; Pale orange solid; Yield: 45% (216 mg); Mp: 169.5-172.6 °C; IR (neat): 1740 (s), 1721 (w), 1701 (w), 1447 (w), 1373 (s), 1219 (m), 1142 (m), 1092 (m), 829 (m), 779 (m), 748 (s), 718 (m), 687 (w), 664 (w), 633 (w), 590 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14-8.10 (m, 2H), 7.57-7.52 (m, 4H), 7.49-7.37 (m, 9H), 7.34-7.28 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.0, 155.7, 139.2, 136.9, 136.1, 130.8, 129.5, 129.4, 129.3, 127.3, 127.0, 125.4, 124.7, 124.5, 123.9, 122.5, 120.8, 111.1. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{28}H_{17}ClN_4O_2$ 477.1113; Found 477.1117.

11g, 6-(9H-carbazol-9-yl)-7-(3-chlorophenyl)-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione; Pale orange solid; Yield: 45% (216 mg); Mp: 155.3-157.5 °C; IR (neat): 1744 (s), 1717 (w), 1697 (w), 1686 (w), 1489 (w), 1447 (w), 1373 (s), 1339 (w), 1258 (w), 1215 (m), 1150 (m), 1142 (m), 1096 (w), 957 (w), 779 (w), 748 (m), 721 (m), 683 (m), 633 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15-8.10 (m, 2H), 7.61-7.58 (m, 1H), 7.57-7.50 (m, 4H), 7.50-7.44 (m, 5H), 7.43-7.37 (m, 2H), 7.35-7.28 (m, 2H), 7.28-7.22 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 155.9, 155.5, 139.2, 136.1, 135.1, 130.8, 130.2, 130.0, 129.5, 129.4, 127.1, 127.0, 125.9, 125.4, 124.8 (2C – see ESI), 124.1, 122.6, 120.8, 111.2. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{28}H_{17}ClN_4O_2$ 477.1113; Found 477.1118.

11h, 6-(9H-carbazol-9-yl)-7-(2-chlorophenyl)-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione; Pale orange solid; Yield: 28% (133 mg); Mp: 196.1-198.5 °C; IR (neat): 1748 (s), 1682 (w), 1493 (w), 1447 (m), 1377 (s), 1335 (w), 1312 (w), 1292 (w), 1258 (w), 1215 (s), 1153 (m), 1142 (m), 1096 (m), 1045 (w), 1018 (m), 1003 (w), 961 (m), 899 (w), 883 (w), 783 (w), 768 (m), 748 (s), 718 (s), 698 (m), 660 (m), 637 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11-8.03 (m, 3H), 7.61-7.52 (m, 4H), 7.50-7.39 (m, 6H), 7.38-7.30 (m,

3H), 7.27-7.22 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.0, 155.7, 140.7, 137.5, 132.1, 131.4, 130.8, 130.5, 129.7, 129.5, 129.4, 127.0, 126.8, 125.4, 125.3, 125.2, 124.2, 122.1, 120.5, 110.9. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{28}H_{17}ClN_4O_2$ 477.1113; Found 477.1114.

11i, 6-(9H-carbazol-9-yl)-7-(naphthalen-2-yl)-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione; Light orange solid; Yield: 31% (153 mg); Mp: 111.8-114.3 °C; IR (neat): 2361 (w), 1782 (w), 1721 (s), 1697 (m), 1616 (w), 1597 (w), 1501 (w), 1493 (w), 1481 (w), 1447 (m), 1400 (m), 1373 (w), 1339 (w), 1300 (w), 1261 (w), 1227 (w), 1192 (w), 1169 (w), 1150 (w), 1096 (w), 1076 (w), 1030 (w), 1011 (w), 837 (w), 806 (w), 741 (w), 721 (m), 691 (m), 671 (w), 660 (w), 640 (w), 613 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28-8.24 (m, 1H), 8.16-8.11 (m, 2H), 7.86-7.80 (m, 1H), 7.80-7.74 (m, 1H), 7.73-7.67 (m, 1H), 7.60-7.44 (m, 11H), 7.43-7.36 (m, 2H), 7.33-7.29 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.1 (2C – see ESI), 139.6, 138.8, 133.6, 132.8, 130.9, 129.5, 129.3, 128.9, 128.8, 127.8, 127.6, 127.1, 127.0, 126.3, 125.4, 124.7, 124.3, 122.7, 122.4, 122.3, 120.7, 111.2. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{32}H_{20}N_4O_2$ 493.1659; Found 493.1658.

11j, 6-(9H-carbazol-9-yl)-7-cyclohexyl-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione; Pale yellow solid; Yield: 59% (277 mg); Mp: 149.3-152.1 °C; IR (neat): 1740 (s), 1721 (m), 1705 (w), 1447 (m), 1377 (m), 1339 (w), 1215 (m), 1146 (w), 748 (s), 721 (m), 706 (w), 687 (w), 671 (w), 633 (w), 613 (w), 579 (w), 563 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12-8.07 (m, 2H), 7.60-7.43 (m, 9H), 7.41-7.35 (m, 2H), 2.79-2.69 (m, 1H), 2.19-1.83 (br. m, 2H), 1.81-1.44 (br. m, 4H), 1.35-1.11 (br. m, 4H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.2, 156.0, 148.5, 140.7, 131.0, 129.4, 129.2, 126.9, 125.6, 125.3,

124.2, 122.0, 120.6, 110.2, 35.7, 25.4, 25.2, 14.1. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{28}H_{24}N_4O_2$ 449.1972; Found 449.1974.

11k, 6-butyl-7-(9H-carbazol-9-yl)-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione; Yellow liquid; Yield: 31% (131 mg); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.13-8.02 (m, 3H), 7.57-7.41 (m, 10H), 7.39-7.32 (m, 2H), 2.74-2.56 (m, 2H), 1.64 (quintet, *J* = 7.6 Hz, 2H), 1.41-1.30 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.2, 156.2, 143.2, 140.3, 129.5, 129.2, 126.9, 125.8, 125.4, 124.3, 122.1, 120.6, 120.3, 119.4, 110.4, 27.8, 25.4, 22.3, 13.5. (NOTE: Further Characterization was not pursued due to significant inseparable impurities (See ^{1}H and ^{13}C NMR in ESI).)

11m, *tert*-butyl (2,4-dioxo-3,7-diphenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate; Pale orange solid; Yield: 45% (845 mg); Mp: 63.1-65.2 °C; IR (neat): 1802 (w), 1732 (s), 1593 (w), 1493 (m), 1451 (w), 1385 (m), 1366 (m), 1292 (m), 1223 (m), 1146 (s), 1072 (w), 961 (w), 914 (w), 837 (w), 756 (m), 710 (m), 687 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.65 (m, 2H), 7.53-7.47 (m, 4H), 7.46-7.35 (m, 8H), 7.30-7.27 (m, 1H), 1.43 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.3, 156.0, 152.1, 138.8, 136.3, 130.9, 129.8, 129.4, 129.3, 129.2, 128.9, 128.6, 127.4, 125.8, 125.6, 125.5, 125.5, 83.9, 27.9. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{27}H_{24}N_4O_4$ 469.1871; Found 469.1871.

11n, *tert*-butyl (2,4-dioxo-3-phenyl-7-(4-trifluoromethyl)phenyl)-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate; Pale yellow solid; Yield 41% (217 mg); Mp: 64.5-66.5 °C; IR (neat): 1802 (w), 1736 (s), 1616 (w), 1597 (w), 1493 (w), 1369 (m), 1319 (s), 1292 (m), 1223 (m), 1150 (s), 1126 (s), 1111 (s), 1065 (m), 1015 (w), 961 (w), 841 (m), 687 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2H), 7.72-7.65

(m, 2H), 7.55-7.37 (m, 9H), 7.33-7.27 (m, 1H), 1.45 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.1, 155.3, 151.8, 138.5, 134.3, 131.2 (q, $^{2}J_{CF}$ = 32.9 Hz), 130.7, 130.3, 129.5, 129.4, 129.3, 129.1, 127.7, 125.9 (q, $^{3}J_{CF}$ = 3.7 Hz), 125.7, 125.5, 122.6 (q, $^{1}J_{CF}$ = 271.9 Hz), 84.3, 27.9. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{28}H_{23}F_3N_4O_4$ 537.1744; Found 537.1745.

11o, *tert*-butyl (2,4-dioxo-3-phenyl-7-(p-tolyl)-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate; Pale orange solid; Yield 30% (145 mg); Mp: 67.5-69.8 °C; IR (neat): 1802 (w), 1732 (s), 1493 (w), 1385 (m), 1369 (m), 1292 (m), 1219 (m), 1150 (s), 1072 (w), 961 (w), 818 (w), 756 (m), 718 (m), 687 (m) cm-1; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.54 (m, 2H), 7.53-7.33 (m, 9H), 7.31-7.20 (m, 3H), 2.38 (s, 3H), 1.44 (s, 9H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 156.3, 156.2, 152.2, 140.3, 138.9, 136.6, 130.9, 129.6, 129.4, 129.3, 129.1, 127.8, 127.3, 125.6, 125.5, 125.5, 123.0, 83.8, 27.9, 21.6. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{28}H_{26}N_4O_4$ 483.2027; Found 483.2027.

11p, *tert*-butyl (7-(4-methoxyphenyl)-2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate; Pale yellow solid; Yield: 14% (81 mg); Mp: 130.6-132.4 °C; IR (neat): 2974 (w), 2361 (w), 1798 (w), 1732 (s), 1605 (m), 1516 (m), 1493 (m), 1385 (m), 1369 (m), 1296 (m), 1258 (m), 1223 (s), 1150 (w), 1115 (w), 1084 (w), 1076 (m), 1022 (m), 961 (m), 837 (w), 779 (w), 768 (w), 756 (w), 745 (w), 718 (m), 687 (m), 660 (w) cm-1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.58 (m, 2H), 7.53-7.46 (m, 4H), 7.46-7.35 (m, 5H), 7.29-7.23 (m, 1H), 6.98-6.92 (m, 2H), 3.84 (s, 3H), 1.44 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 160.8, 156.5, 156.4, 152.3, 139.1, 136.5, 130.9, 129.4, 129.2, 129.1, 127.3, 127.2, 126.8, 125.5, 125.5, 118.4, 114.5, 83.7, 55.4, 27.9. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{28}H_{26}N_4O_5$ 499.1976; Found 499.1976.

11q, *tert*-butyl (7-(4-bromophenyl)-2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate; White solid; Yield: 42% (227 mg); Mp: 82.9-84.8 °C; IR (neat): 1736 (s), 1489 (m), 1385 (m), 1369 (s), 1292 (m), 1258 (w), 1223 (m), 1146 (s), 1072 (m), 1049 (w), 1022 (w), 1007 (w), 961 (w), 914 (w), 899 (w), 826 (w), 783 (w), 756 (m), 741 (w), 714 (m), 691 (m), 633 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.51 (m, 4H), 7.50-7.36 (m, 9H), 7.31-7.26 (m, 1H), 1.44 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.2, 155.6, 151.9, 138.6, 135.0, 132.2, 130.8, 129.4, 129.4, 129.2, 129.0, 127.6, 126.9, 125.6, 125.4, 124.7, 124.1, 84.1, 27.9. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{27}H_{23}BrN_4O_2$ 547.0976; Found 547.0972.

11r, *tert*-butyl (7-(4-chlorophenyl)-2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate; Pale yellow solid; Yield 36% (180 mg); Mp: 71.8-74.7 °C; IR (neat): 1802 (w), 1736 (s), 1593 (w), 1493 (w), 1385 (m), 1366 (m), 1292 (m), 1219 (m), 1146 (m), 1092 (w), 1011 (w), 961 (w), 914 (w), 829 (w), 756 (m), 714 (m), 691 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.55 (m, 2H), 7.54-7.35 (m, 11H), 7.33-7.27 (m, 1H), 1.44 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.2, 155.7, 152.0, 138.7, 135.8, 135.0, 130.8, 129.4, 129.4, 129.3, 129.3, 128.9, 127.6, 126.7, 125.6, 125.5, 124.3, 84.1, 27.9. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{27}H_{23}ClN_4O_4$ 503.1481; Found 503.1482.

11s, *tert*-butyl (7-(3-chlorophenyl)-2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate ; Pale yellow solid; Yield: 37% (121 mg); Mp: 59.7-62.3 °C; IR (neat): 1736 (s), 1493 (w), 1381 (m), 1366 (m), 1292 (m), 1258 (w), 1223 (m), 1146 (s), 1072 (w), 1053 (w), 1026 (w), 961 (w), 918 (w), 837 (w), 772 (m), 756 (m), 714 (m), 687 (s), 633 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.60 (m, 1H), 7.58-7.54 (m, 1H), 7.52-7.38 (m, 9H), 7.37-7.33 (m, 2H), 7.32-7.27 (m, 1H), 1.45 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125

MHz, $CDCl_3$) δ 156.1, 155.5, 151.8, 138.5, 135.0, 134.3, 130.8, 130.2, 129.7, 129.6, 129.4, 129.4, 129.2, 127.7, 127.5, 125.8, 125.4 (2C – See ESI), 123.6, 84.2, 27.9. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{27}H_{23}ClN_4O_4$ 503.1481; Found 503.1482.

11t, *tert*-butyl (7-(2-chlorophenyl)-2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate; Pale yellow solid; Yield: 39% (197 mg); Mp: 85.2-87.6 °C; IR (neat): 1732 (s), 1686 (w), 1493 (m), 1381 (m), 1366 (m), 1292 (m), 1258 (w), 1215 (m), 1150 (s), 1092 (w), 1061 (w), 1042 (w), 1018 (w), 964 (w), 914 (w), 841 (w), 783 (w), 752 (s), 718 (w), 710 (w), 691 (m), 660 (w), 633 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.87-7.82 (m, 1H), 7.54-7.43 (m, 5H), 7.43-7.32 (m, 7H), 7.31-7.26 (m, 1H), 1.34 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.4, 155.3, 151.8, 138.6, 132.4, 131.8, 130.8, 130.7, 130.3, 129.5, 129.4, 129.3, 129.1, 129.1, 127.4, 127.0, 126.3, 126.2, 125.4, 83.6, 27.7. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{27}H_{23}ClN_4O_4$ 503.1481; Found 503.1475.

11u, *tert*-butyl (7-(naphthalen-2-yl)-2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate; Pale yellow solid; Yield: 8% (40 mg); Mp: 153.4-156.1 °C; IR (neat): 2361 (w), 1805 (w), 1755 (s), 1728 (s), 1697 (m), 1597 (w), 1493 (m), 1389 (s), 1366 (m), 1300 (s), 1242 (w), 1215 (m), 1150 (s), 968 (m), 822 (m), 779 (m), 768 (), 756 (m), 718 (m), 687 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.25-8.20 (m, 1H), 7.91-7.80 (m, 3H), 7.70-7.65 (m, 1H), 7.56-7.43 (m, 9H), 7.42-7.36 (m, 2H), 7.30-7.27 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.4, 156.0, 152.2, 138.9, 136.4, 133.5, 132.9, 130.9, 129.4, 129.3, 129.2, 128.9, 128.8, 128.6, 127.9, 127.5, 127.1, 125.7, 125.7, 125.4, 123.1, 122.0, 83.9, 27.9. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{31}H_{26}N_4O_4$ 519.2027; Found 519.2030.

11v, *tert*-butyl (7-cyclohexyl-2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate; Pale yellow solid; Yield: 51% (235 mg); Mp: 116.7-118.2 °C; IR (neat): 2928 (w), 1736 (s), 1493 (m), 1454 (w), 1389 (s), 1369 (m), 1342 (w), 1312 (m), 1292 (m), 1246 (w), 1211 (m), 1150 (s), 1115 (w), 1061 (w), 1015 (w), 964 (w), 934 (w), 910 (w), 887 (w), 841 (w), 826 (w), 814 (w), 783 (w), 768 (m), 748 (m), 710 (m), 691 (m), 633 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.47 (m, 2H), 7.47-7.37 (m, 7H), 7.31-7.26 (m, 1H), 2.62-2.50 (m, 1H), 2.04-1.92 (m, 2H), 1.82-1.70 (m, 2H), 1.70-1.62 (m, 1H), 1.46 (s, 9H), 1.44-1.24 (m, 4H), 1.24-1.12 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.5, 156.1, 152.4, 143.0, 139.9, 131.1, 130.5, 129.3, 129.1, 129.0, 127.1, 125.5, 125.4, 83.4, 35.4, 29.7, 28.6, 27.9 (2C – See ESI), 25.7, 25.4. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{27}H_{30}N_4O_4$ 475.2340; Found 475.2340.

11w, *tert*-butyl (7-butyl-2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate; Orange gel; Yield: 65% (291 mg); IR (neat): 2959 (w), 2361 (w), 1798 (w), 1732 (s), 1597 (w), 1493 (m), 1454 (w), 1385 (s), 1369 (m), 1312 (w), 1292 (w), 1250 (w), 1234 (w), 1207 (w), 1150 (s), 1084 (w), 1061 (w), 1030 (w), 1011 (w), 961 (w), 914 (w), 841 (w), 810 (w), 787 (w), 768 (w), 752 (w), 710 (w), 691 (m), 633 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.47 (m, 2H), 7.46-7.37 (m, 7H), 7.31-7.27 (m, 1H), 2.49 (t, *J* = 7.5 Hz, 2H), 1.65-1.55 (m, 2H), 1.46 (s, 9H), 1.40-1.32 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.5, 156.1, 152.4, 139.8, 139.3, 139.9, 131.0, 129.4, 129.2, 129.0, 127.3, 125.8, 125.4, 83.5, 27.9, 27.6, 24.9, 22.1, 13.6. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{25}H_{28}N_4O_4$ 449.2184; Found 449.2179.

11x, *tert*-butyl (2,4-dioxo-3,7-diphenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(methyl)carbamate; Pale yellow solid; Yield: 32% (128 mg); Mp: 103.0-105.2 °C; IR

(neat): 1736 (s), 1721 (s), 1705 (s), 1493 (w), 1385 (s), 1369 (s), 1323 (s), 1238 (m), 1211 (w), 1146 (m), 1099 (w), 1072 (w), 995 (w), 918 (w), 856 (w), 802 (w), 760 (m), 718 (w), 691 (m), 664 (w), 633 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.58 (m, 2H), 7.53-7.36 (m, 8H), 3.27 (s, 3H), 1.35 (br. s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.5 (2C, C=O), 153.0, 135.1, 130.9, 129.7, 129.6, 129.4, 129.2, 128.8, 126.2, 125.6, 125.5, 82.9, 34.9, 27.8. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{22}H_{22}N_4O_4$ 407.1714; Found 407.1710.

11y, methyl (2,4-dioxo-3,7-diphenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(phenyl)carbamate; Pale yellow solid; Yield: 31% (260 mg); Mp: 63.7-66.3 °C; IR (neat): 1736 (s), 1705 (m), 1543 (w), 1493 (m), 1385 (m), 1366 (m), 1292 (m), 1219 (m), 1142 (w), 1069 (w), 752 (m), 729 (m), 714 (m), 687 (s), 671 (m), 633 (w) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.62 (m, 2H), 7.54-7.27 (m, 13H), 3.85 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.1, 156.0, 154.1, 138.7, 136.5, 130.9, 130.0, 129.5, 129.4, 129.2, 128.9, 127.9, 127.8, 126.7, 125.5, 54.4. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{24}H_{18}N_4O_4$ 427.1401; Found 427.1397.

11z, methyl (2,4-dioxo-3,7-diphenyl-1,3,5-triazabicyclo[3.2.0]hept-6-en-6-yl)(methyl)carbamate; Pale orange solid; Yield: 24% (87 mg); Mp: 98.0-101.3 °C; IR (neat): 1798 (w), 1732 (s), 1705 (m), 1497 (w), 1447 (m), 1377 (m), 1315 (m), 1242 (m), 1204 (m), 1146 (m), 1096 (m), 988 (w), 910 (w), 756 (s), 710 (m), 687 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65-7.57 (m, 2H), 7.55-7.35 (m, 8H), 3.78 (s, 3H), 3.33 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 156.3, 156.3, 154.9, 135.4, 130.8, 129.7, 129.4, 129.2, 128.9 (2C – See ESI), 125.8, 125.7, 125.5, 54.1, 35.7. HRMS (ESI+) m/z: [M+H]+ Calcd for $C_{19}H_{16}N_4O_4$ 365.1245; Found 365.1243.

11aa, Light yellow solid; Yield: 20%; Mp: 167.2-168.2°C; IR (neat): 2927 (w), 2854 (w), 1797 (m), 1739 (s), 1693 (m), 1597 (m), 1492 (m), 1450 (m), 1392 (s), 1350 (s), 1292 (w), 1230 (s), 1188 (m), 1149 (s), 1122 (w), 1083 (m), 1045 (w), 1018 (s), 933 (w), 891 (m), 833 (s), 810 (s), 759 (s), 705 (s), 671 (s), 640 9s), 578 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.70 (m, 4H), 7.60-7.20 (m, 10H), 3.22 (s, 3H), 2.42 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ = 156.1, 155.4, 144.9, 139.7, 133.8, 132.8, 130.7, 130.2, 129.9, 129.2, 129.1, 128.6, 128.2, 126.4, 126.2, 125.3, 36.3, 21.6.

11ab, Light yellow solid; Yield: 37%; Mp: 173.2-174.2°C; IR (neat): 2927(w), 2858 (w), 1801 (w), 1743 (s), 1697 (w), 1616 (w), 1597 (m), 1504 (m), 1458 (m), 1411 (m), 1365 (s), 1350 (s), 1319 (s), 1234 (s), 1157 (s), 1111 (s), 1083 (s), 1064 (s), 1010 (s), 844 (s), 705 (s), 671 (s), 578 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.60-7.37 (m, 5H), 7.34 (d, J = 8.1 Hz, 2H), 3.24 (s, 3H), 2.41 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ = 155.5, 155.4, 145.4, 137.6, 133.5, 131.3, 130.6, 130.1, 129.4, 129.3, 128.8, 128.2, 126.8 ($^{1}J_{CF}$ = 272 Hz, 1C), 126.6, 125.7 ($^{3}J_{CF}$ = 3.96 Hz, 1C), 125.3, 36.2, 21.6.

Associated Content

Data Availability Statement: The data underlying this study are available in the published article and its Supporting Information.

Supporting Information Statement: Data for initial screen of alkynyl amine/amide substrates for cycloaddition with PTAD, general procedure for synthesis of carbazole alkynes (**9**) and yne-carbamates (**10**) from alkynylbromides, characterization data for bromoalkynes, carbazole alkynes (**9**), and yne-carbamates (**10**), XRD data for **11f**, **11g**,

11h, **12**, **11aa**, and **11ab**, computational details, copies of ^{1}H and ^{13}C {^{1}H} NMR spectra for new ynamides, diazacyclobutenes (**11a**-**11ab**), **12**, and **17**.

Author Contributions

B.A.M.: conceptualization, synthesis and compound characterization, writing, and revision; C.J.N.: conceptualization, synthesis and compound characterization; S. K.: computational chemistry; W. B.: synthesis and compound characterization; M. N.: synthesis and compound characterization; E. E. S., A. A. B.; A. S., Y. I., L.U., W.S.: assistance with compound synthesis and characterization under direction of B.A.M.; C.D.M.: X-ray crystallography; B.N.D.: computational chemistry; D.C.W; conceptualization, writing, revision, project direction, and funding acquisition.

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