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Cyclization of 1-(2-Alkynylphenyl)-3,3-dialkyltriazenes: A Convenient, High-Yield Synthesis of Substituted Cinnolines and Isoindazoles

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A new route to isoindazoles and cinnolines through the cyclization of (2-alkynylphenyl)triazenes under neutral conditions is presented. The products that result from heating the starting triazenes depend on both the type of alkyne ortho to the triazene functionality and the temperature used. Butadiyne moieties ortho to dialkyltriazenes yield bis-isoindazole dimers when heated to 150 °C in MeI. A requirement for cyclization in MeI is that the (2-alkynylphenyl)triazene must contain a suitably electron-withdrawing substituent on the phenyl ring to deactivate the triazene toward methylation-induced decomposition to an iodoarene. Ethynyl moieties ortho to dialkyltriazenes yield both isoindazole dimers as well as 3-formylisoindazoles when subjected to the same conditions. Replacing MeI with 1,2-dichlorobenzene as solvent allows for the general cyclization of (2-ethynylphenyl)dialkyltriazenes. Heating to 170 °C results in a mixture of isoindazole and cinnoline products, whereas the cinnolines are produced exclusively in high yield at 200 °C. Alternatively, the isoindazoles can be obtained in good to excellent yield by stirring a 1,2-dichloroethane solution of the starting triazene with CuCl overnight at 50 °C.

Introduction

Aryltriazenes[1] have been used extensively in the preparation of a large variety of phenylacetylene-based systems.[2,3] Triazene preparation can be done efficiently from commercially available anilines, and heating in iodomethane at 100−150 °C produces the corresponding iodoarenes in high yield.[4] Combined with Pd-catalyzed cross-coupling methodology,[5] the ability to mask and unmask a reactive iodoarene provides great control over aromatic substitution patterns. The high-yielding conversion to such a versatile synthon makes aryltriazenes indispensable in the preparation of large phenylacetylene oligomers and polymers requiring multiple synthetic steps.[2]

Our group has used aryltriazenes with great success in the synthesis of numerous dehydrobenzoannulenes (DBAs, e.g., **1**), most of which would be difficult or impossible using other methods.[2c,d,6] The success of our strategies has relied on the use of trimethylsilyl-protected 1-phenyl-1,3-butadiyne moieties (e.g., **2**, Scheme 1), which are synthesized in good overall yield from commercially available anilines via triazene intermediates.

In cases where a strongly electron-withdrawing group is para to the triazene, decomposition to the iodoarene with iodomethane must be done at higher temperatures. Since nitro or cyano substituents on the phenyl ring pull electron density away from the distal dialkylamine, nucleophilic attack on iodomethane, the first step in decomposition, is less favored.[7] In our experience, it has been necessary to heat cyanophenyltriazenes to ca. 150 °C for the aryl iodide to form in high yield in less than 24 h. In most instances, the phenylacetylene/triazene starting materials were stable at elevated temperatures and the iodoarenes could be generated in nearly quantitative yield.

Until recently, our research has focused on triazenes that were ortho to monoacetylenes protected by $SiMe_3$ or Si*i*-Pr_3 groups that rarely contained electron-with-

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(3) Inter alia: (a) Mongin, O.; Papamicaël, C.; Hoyler, N.; Gossauer, A. *J. Org. Chem.* **1998**, *63*, 5568−5580. (b) Förster, B.; Bertran, J.; Teixidor, F.; Viñas, C. *J. Organomet. Chem.* **1999**, *587*, 67−73.

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(7) For analogous decomposition using reagents other than iodomethane, see: (a) Wu, Z.; Moore, J. S. *Tetrahedron Lett.* **1994**, *35*, 5539−5542. (b) Khalaj, A.; Beiki, D.; Rafiee, H.; Najafi, R. *J. Label. Comput. Radiopharm.* **2001**, *44*, 235−240.

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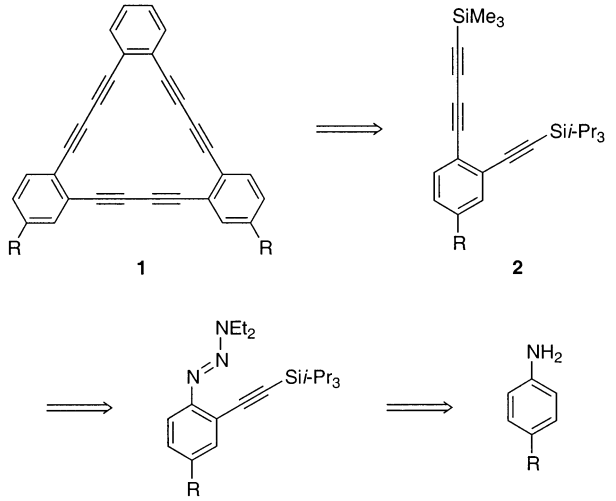
SCHEME 1



drawing substituents. An attempt to react a triazene ortho to a 1,3-butadiyne moiety and para to a cyano group (**3**, Scheme 2), however, gave the desired aryl iodide **4** in very low yield (ca. 10%) along with an unexpected side product in 33% yield. ^{1}H NMR analysis of the new compound revealed that although the aromatic resonances had changed, the diethylamino signals were still present but were upfield relative to the starting material. Combining these results with evidence presented by the ^{13}C NMR and mass spectra suggested that the chemical nature of both the butadiyne unit and the triazene had changed. An X-ray structure analysis (see the Supporting Information) revealed that concurrent cyclization and dimerization had produced a 2*H*-indazole (isoindazole) dimer, compound **5**. A review of the literature revealed no examples of the formation of an isoindazole from a triazene ortho to an acetylene under neutral conditions. Although the majority of indazoles are synthesized using a similar type of ring closure (i.e., ring closure with bond formation between the 2−3 positions on the indazole), acidic conditions or more reactive functional groups (azides, electrophilic carbon functionalities) must be employed.[8] Recent examples of indazole synthesis have utilized monoacetylenes,[9] but the more reactive azide in place of the triazene was necessary for cyclization.

Inspired by the surprising formation of **5**, we decided to explore the cyclization reactions of (2-alkynylphenyl)-triazenes. Our interest in such systems is 3-fold: (1) our extensive use of triazenes compels us to determine under what conditions the aryl iodide will form in preference to this new isoindazole dimer; (2) since this reaction is done under neutral conditions, establishing the presence of a novel cyclization mechanism could help develop new synthetic methods using acetylenes; (3) 2*H*-indazoles have received moderate attention in recent literature regarding their medicinal properties,[10] and finding new and versatile methods for their synthesis could gain increased importance. Since our initial report,[11] we have elucidated the complex mechanistic pathways for triazene cyclization.[12] The following report contains the full details of this new synthesis and represents our efforts to determine its scope.[13]

Results and Discussion

Cyclization of Diyne Triazenes. Our first task was to determine if this cyclization could be repeated with similar starting materials. Thus, unfunctionalized phenyltriazene **6** and 4-nitrophenyltriazene **7** (Scheme 2) were synthesized for comparison with **3**. The synthesis of **3** provides a representative example. 4-Aminobenzonitrile was iodinated using BTEA·ICl_2 and $CaCO_3$,[14] the product of which was first treated with HCl and aqueous $NaNO_2$ at −5 °C and then quenched with Et_2NH and K_2CO_3 to generate triazene **8** in 89% yield. Triazene **9** was obtained similarly starting from 2-iodoaniline.[6b] (Trimethylsilyl)butadiyne was then cross-coupled to **8** and **9** under Sonogashira conditions[15] to produce **3** and **6** in 94% and 36% yield, respectively. Compound **7** followed similarly from triazene **10**, which had been synthesized previously for the study of donor−acceptor annulenes and was readily available.[6a]

Since the nitro functionality has electron-withdrawing ability comparable to the cyano group, we expected **7** to cyclize/dimerize in the same fashion as **3**. This proved to be the case as heating **7** in MeI at 145 °C for 48 h in a sealed glass pressure tube gave dimer **11** in 36% yield along with iodoarene **12** (27%, Scheme 2). In stark contrast, transformation to iodoarene **13** was rapid above 120 °C when triazene **6** was used and occurred in nearly quantitative yield.

Attempts to repeat these reactions at both lower and higher temperatures revealed an interesting temperature window. Using **3**, **6**, and **7**, no reaction occurred below 110 °C. At 140−150 °C, **3** and **7** formed isoindazole dimers **5** and **11**, respectively, along with the corresponding iodoarenes as a minor products. Cyclization/dimerization of **6** could not be accomplished in MeI since triazene decomposition occurred well below 145 °C. If **3** or **7** was heated above 160 °C, however, the iodoarenes were obtained in excellent yield. These results indicate that in order for cyclization/dimerization to occur in MeI, suitably electron-withdrawing substituents must be present to deactivate the dialkylamino nitrogen in the triazene toward nucleophilic attack.

Cyclization of Monoyne Triazenes. To determine whether monoalkynes could be used in place of butadiynyl moieties, **14** and **15** (Scheme 3) were synthesized for

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(9) (a) Prikhodko, T. A.; Vasilevsky, S. F. *Mendeleev Cummun.* **1996**, 98−99. (b) Prikhodko, T. A.; Vasilevsky, S. F. *Mendeleev Commun.* **1998**, 149−150. (c) Prikhodko, T. A.; Vasilevsky, S. F. *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 1268−1273.

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(11) Kimball, D. B.; Hayes, A. G.; Haley, M. M. *Org. Lett.* **2000**, *2*, 3825−3827.

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(13) Complete mechanistic details of the triazene cyclizations will be outlined in a forthcoming full paper.

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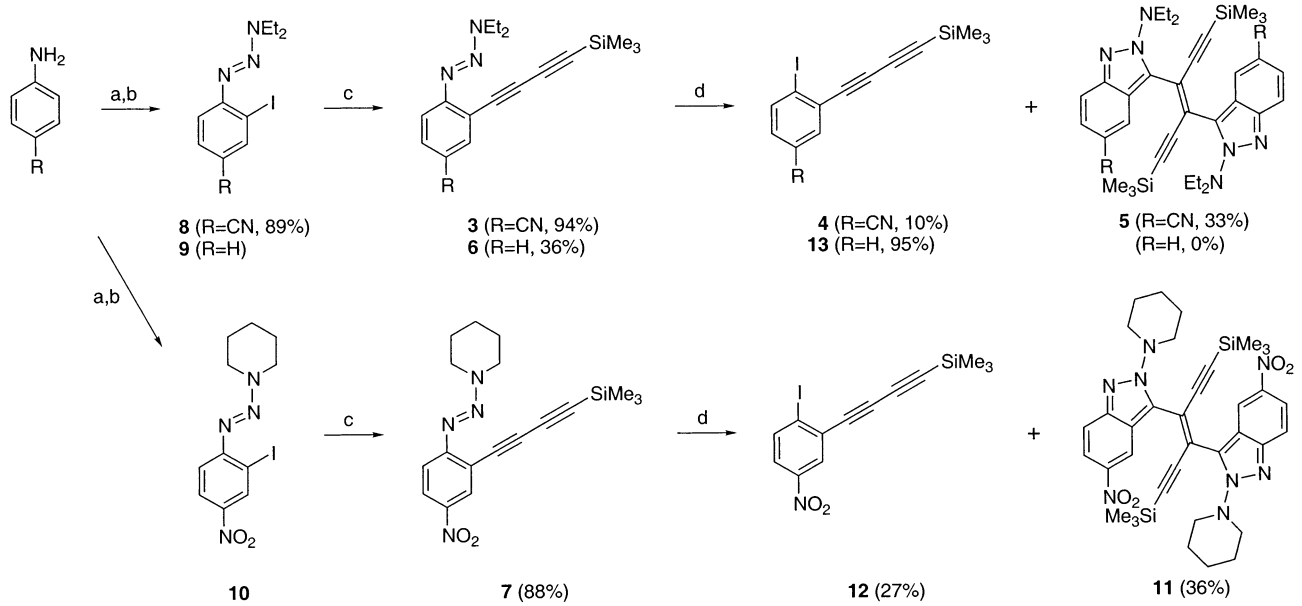
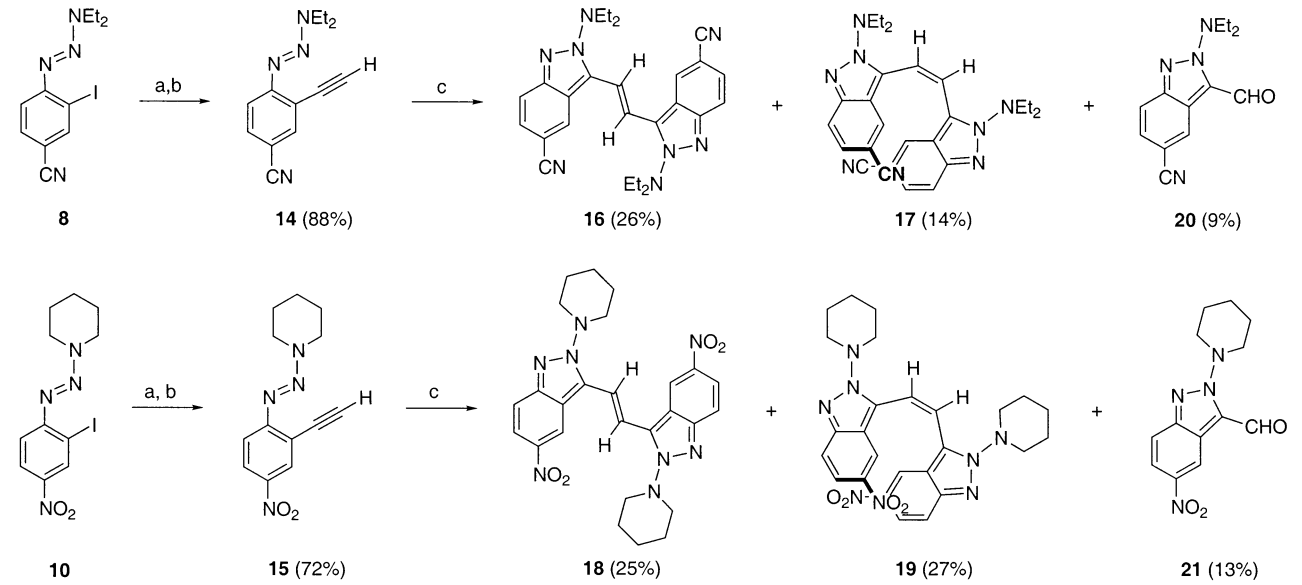
(15) Sonogashira, K. In ref 5b, pp 203−229.

SCHEME 2[a]



[a] Reagents and conditions: (a) BTEA·ICl_2, $CaCO_3$, MeOH, THF; (b) (i) HCl, $NaNO_2$, (ii) Et_2NH or piperidine, K_2CO_3, H_2O, MeCN; (c) $Me_3SiC{\equiv}CC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, NEt_3; (d) MeI, 145 °C.

SCHEME 3[a]



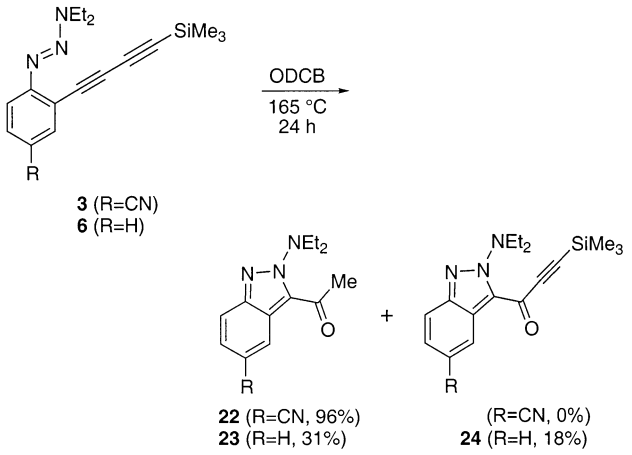
[a] Reagents and conditions: (a) $Me_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, NEt_3; (b) K_2CO_3, MeOH, THF; (c) MeI, 145 °C.

comparison. Ethyne units are both readily available and easier to work with compared to butadiynes. The corresponding (2-iodophenyl)triazenes were first treated with (trimethylsilyl)acetylene under Sonogashira conditions, then cleavage of the trimethylsilyl group was accomplished with K_2CO_3 in MeOH/THF. Compounds **14** and **15** were stable under ambient conditions and could be kept on the benchtop for weeks without apparent decomposition.

Switching to a monoalkyne on the phenyltriazene produced slightly different results upon heating in MeI. When **14** was used in place of **3**, the 2*H*-indazole dimer was produced in 40% yield as a ca. 2:1 ratio of trans (**16**) and cis isomers (**17**), respectively (Scheme 3). Similarly, cyclization of **15** gave a ca. 1:1 ratio of dimers **18** and **19**. Recrystallization from EtOH of both sets of dimers resulted in total conversion to the trans isomers, as confirmed for **16** by X-ray analysis (see the Supporting Information). Another unexpected side product, an isoindazole aldehyde (**20**, **21**), was also obtained in low yield in both reactions. This result suggested that the reactive intermediate, most likely a carbene,[12] could also be trapped by an oxygen atom source before dimerization occurred.

Solvent Studies. Since MeI as solvent severely limited the scope of this unusual transformation, we began exploring different media. Heating cyanophenyltriazene **3** to 160−170 °C for 48 h in several common solvents

SCHEME 4

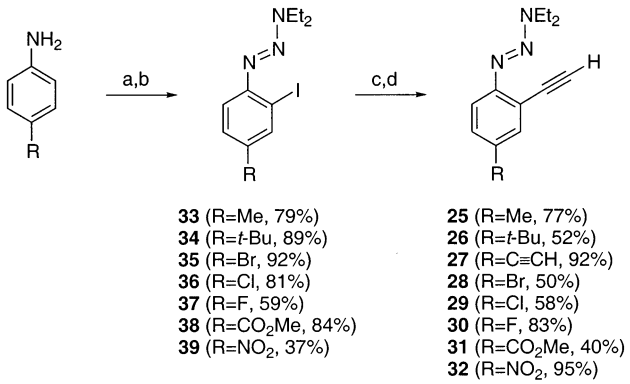


resulted either in no reaction (EtOAc, $CHCl_3$, benzene, toluene, MeCN) or a complex mixture of byproducts (DMF, DMSO). Since the reaction consistently gave isoindazole products close to 145 °C, we then focused on solvents with boiling points above this temperature and with polarity similar to MeI. We found that heating **3** in *o*-dichlorobenzene (ODCB) successfully gave an isoindazole product, but not the expected dimer. Instead, acyl-2*H*-indazole **22** (Scheme 4) was produced in high yield. Repeating this experiment with compound **6** gave the corresponding indazole **23** along with the likely intermediate in the acylindazole formation, propioloylindazole **24** (Scheme 4). NMR and mass spectral analysis corroborated the structure of these acyl products. Although inclusion of oxygen in these molecules was consistent with the aldehydes obtained previously, loss of the $SiMe_3$ protecting group as well as one methine unit from **22** and **23** was curious; a reasonable mechanism for this transformation is not readily obvious.

Thermolysis Studies. The results using ODCB encouraged us to begin a systematic study of the thermal cyclization of (2-ethynylphenyl)triazenes. This type of system was used in preference to butadiynyl moieties as (trimethylsilyl)acetylene is more readily available than (trimethylsilyl)buta-1,3-diyne. Also, given the unusual formation of **22** and **23**, monoyne-containing systems seemed to be the better choice. Compounds **25**−**32** (Scheme 5) were synthesized in four steps in moderate to excellent overall yield from the corresponding 4-substituted anilines via iodotriazenes **33**−**39**. The parent (2-ethynylphenyl)triazene (R = H) was prepared as previously described.[6b] The reaction sequence shown in Scheme 5 is a remarkably efficient process in that purification needed after each step was minimal. The compounds formed are stable to ambient conditions, and 6−8 g quantities of **25**−**32** have been synthesized.

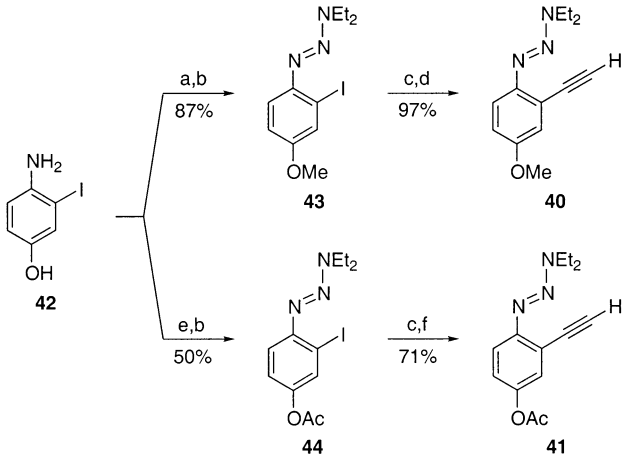
To study compounds with more electron-donating substituents on the phenyl ring, methoxy- and acetoxyphenyltriazenes **40** and **41**, respectively, were prepared from 4-amino-3-iodophenol[16] (**42**, Scheme 6). After the phenol was converted to the methyl ether or the acetyl ester, the corresponding iodotriazenes **43** and **44** were prepared by the usual method in good yield. Subsequent cross-coupling with (trimethylsilyl)acetylene and desilylation with K_2CO_3 in MeOH or Bu_4NF gave triazenes **40** and **41** in 84% and 36% overall yield, respectively.

SCHEME 5[a]



[a] Reagents and conditions: (a) BTEA·ICl_2, $CaCO_3$, MeOH, THF; (b) (i) HCl, $NaNO_2$, (ii) Et_2NH, K_2CO_3, H_2O, MeCN; (c) $Me_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, NEt_3; (d) K_2CO_3, MeOH, THF.

SCHEME 6[a]



[a] Reagents and conditions: (a) MeI, Cs_2CO_3, DMF; (b) (i) HCl, $NaNO_2$, (ii) Et_2NH, K_2CO_3, H_2O, MeCN; (c) $Me_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, NEt_3; (d) K_2CO_3, MeOH, THF; (e) Ac_2O, pyr; (f) Bu_4NF, EtOH, THF.

Unlike their butadiynyl counterparts, the (2-ethynylphenyl)triazenes typically gave a mixture of two different heterocycles when heated to 170 °C in ODCB for 24 h (Table 1). In most cases, both 5-substituted 3-formyl-2-diethyl-2*H*-indazoles (**20**, **45**−**53**) and 6-substituted cinnolines (**56**−**65**) were isolated (Scheme 7). Two notable exceptions are the (2-ethynylphenyl)triazenes with electron-donating oxygen groups, i.e., **40** and **41**. No cinnoline products were observed after heating to 170 °C, and the isoindazole products were obtained in surprisingly high yield (Table 1, entries k and l).

Interestingly, the above conditions are atypical of traditional syntheses of cinnolines.[17] Strong acids and polar solvents are usually necessary to produce a diazonium species susceptible to nucleophilic attack by an activated ortho-carbon nucleophile. Diazonium salts are either formed from anilines or regenerated from triazenes. Acyl groups are common nucleophiles (through enols), although the most prevalent syntheses involve an acetylene. The latter is known as a Richter cyclization and occurs by nucleophilic attack by an oxygen or halogen

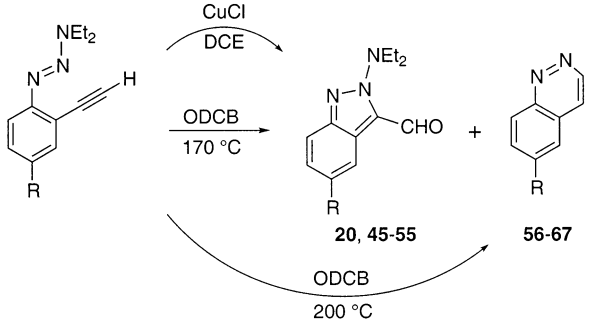
(16) Kvalnes, D. E. *J. Am. Chem. Soc.* **1934**, *56*, 667−670.

TABLE 1. Yields of Isoindazoles and Cinnolines

entry	R	isoindazole[a,b]	cinnoline[a,c]
a	H	**45**, 55% [95%]	**56**, 35% (99%)
b	Me	**46**, 20% [90%]	**57**, 51% (97%)
c	*t*-Bu	**47**, 22% [96%]	**58**, 61% (98%)
d	C≡CH	**48**, 36% [91%]	**59**, 39% (83%)
e	Br	**49**, 15% [98%]	**60**, 70% (98%)
f	Cl	**50**, 14% [95%]	**61**, 58% (97%)
g	F	**51**, 25% [94%]	**62**, 35% (90%)
h	CO_2Me	**52**, 63% [83%]	**63**, 28% (96%)
i	CN	**20**, 50% [85%][d]	**64**, 45% (98%)
j	NO_2	**53**, 60% [78%][e]	**65**, 25% (93%)
k	OMe	**54**, 85% [98%]	**66**, 0% (0%)[f]
l	OAc	**55**, 89% [86%]	**67**, 0% (0%)[f]

[a] Yield at 170 °C. [b] Yield of CuCl-promoted reaction in brackets. [c] Yield at 200 °C in parentheses. [d] Reaction run at rt; at 50 °C, the yield of **20** dropped to 60% and was accompanied by 34% yield of dimer **16**. [e] Reaction run at rt; at 50 °C, the yield of **53** dropped to 54% and was accompanied by 37% yield of dimer **18′** (Et_2N in place of piperidine). [f] Only isoindazole was generated under all reaction conditions.

SCHEME 7



source on the acetylene, inducing cyclization with the nearby electron-deficient diazonium species similar to a Michael addition.[18] A similar mechanism is unlikely in our system since no strong proton donor is available to regenerate the diazonium salt. Also, the cinnolines formed do not incorporate oxygen or nitrogen nucleophiles even when these are present in reaction mixtures.[13]

For all triazenes, the isoindazole dimers seen in cyclizations performed in MeI were either not produced or obtained only in trace amounts. Examination of the ratio of cinnoline to isoindazole for each system showed a difference in the yield of each heterocycle depending on the electronic nature of the para substituent (Table 1). For most of the compounds, the cinnoline product was generated in preference to or in equal quantities to the isoindazole. The largest yields of isoindazole resulted from the starting phenyltriazenes with either strongly donating or strongly withdrawing groups on the benzene ring. The product ratio could be controlled with temperature. Heating the reaction to 195−205 °C furnished only the cinnoline for entries a−j. Under these conditions, the cinnolines were generated in excellent yield. Heating **40** or **41** (entries k and l) to 200 °C in ODCB, however, again did not give the cinnoline products in observable amounts. Interestingly, more than half of the 6-substituted cinnolines are new compounds despite their simple structures. Aside from the parent heterocycle, which is commercially available, our method permits much easier access to the known cinnolines (**60**,[19] **61**,[20] **65**[21]) and in considerably higher overall yields. Compounds **63** and **64** reflect the versatility of this cyclization as their acid-sensitive functionalities would not survive the harsh conditions typical of previous cinnoline syntheses.[17]

TABLE 2. Cyclization of 26 in the Presence of Various Metal Salts[a]

metal salt	yield of **47**[a] (%)	metal salt	yield of **47**[a] (%)
CuI	75	Cu_2O	71
CuCl	87	$Rh_2(OAc)_4$	32
$CuCl_2$	71	$ZnCl_2$	43
$Cu(OAc)_2$	67		

[a] Conditions: **26** (1 equiv), metal salt (1 equiv), CH_2Cl_2 (25 mL), 48 h, rt.

Optimizing Isoindazole Formation. The above observations suggest that, of the two heterocycles that result from the thermal cyclization of (2-ethynylphenyl)-triazenes, the cinnoline is the thermodynamically favored product. Encouraged by the high yields of **56**−**65**, we sought to find conditions suitable for the facile production of the "kinetic" heterocycles **20** and **45**−**54**. Several factors pointed to a carbene mechanism for isoindazole formation,[11−13] such as neutral conditions, relatively high temperatures, alkene dimers (e.g., **5**, **18**), and oxygen-trapped products (e.g., **20**, **24**).

Copper salts have been known for some time to stabilize carbene intermediates and allow their reactions to be performed at lower temperatures.[22] Thus, the cyclization of **14** in the presence of CuI was examined as a test case. Heating a solution of **14** in ODCB to 120−130 °C in the presence of CuI did produce a slightly higher yield of isoindazole **20**; however, several new products were also generated.[23] Lowering the temperature further to 50 °C gave a higher yield of **20**; more importantly, cinnoline **64** was no longer detected. Stirring **26** in the presence of copper salts resulted in isoindazole formation in good yield at room temperature (Table 2). Rhodium and zinc salts resulted in some isoindazole formation, but the material contained numerous other products. Whereas the reaction mixture would eventually become discolored as the isoindazole was generated over 16−30 h using copper salts, rhodium and zinc salts caused immediate discoloration, with the starting material consumed in less than 30 min (as monitored by NMR spectroscopy). Optimization of the conditions led to the

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(18) von Richter, V. *Chem. Ber.* **1883**, *16*, 677−683.

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(23) One of these products was isolated and a suitable crystal was grown for X-ray analysis. The compound was a multi-ring trimeric heterocycle that further implicated a carbene intermediate in isoindazole formation. This compound will be published in the full mechanistic paper.

use of 5 equiv of CuCl as the carbene (carbenoid) stabilizer, 1,2-dichloroethane as the solvent, and a reaction temperature of 50 °C for complete conversion to the isoindazole in 12−36 h. Excellent yields were obtained in most instances (Table 1). The exceptions were with strongly electron-withdrawing systems (**20**, **53**), where dimer formation (**16**, **18′**) was a competitive side reaction at 50 °C; however, if the cyclization was conducted for 3 d at room temperature, the yields of **20** and **53** increased to 85 and 78%, respectively, along with trace amounts of dimer. Although using 5 equiv of CuCl gives complete, exclusive production of isoindazole, the reaction can be done in the presence of catalytic amounts of CuCl using longer reaction times. For example, stirring a mixture of **28** and 10 mol % CuCl for 3 d resulted in nearly quantitative formation of **49**.

Conclusions

A novel route for the selective synthesis of 2*H*-indazoles and cinnolines from (2-alkynylphenyl)triazenes has been developed. Unlike previous methods, these cyclizations are done under neutral conditions that allow for greater versatility and functional group tolerance. The ability to generate both the isoindazole and the cinnoline from the same starting material under the same conditions is unique to our system. This reaction is also temperature sensitive, allowing for either heterocycle to be synthesized in excellent yield by increasing the reaction temperature or adding CuCl. We are currently working on extending this new methodology for the construction of other heterocyclic compounds.

Experimental Section

General Methods. Reagents and instrumentation used have been described previously.[6d,e]

General Iodination Procedure A. The starting aniline (1 equiv), BTEA·ICl_2 (1.15 equiv), and $CaCO_3$ (1.5 equiv) were dissolved in 5:1 $CHCl_3$/MeOH (0.1 M) and either stirred at rt or heated to reflux under N_2 for 24 h. The resulting mixture was filtered, and the solvent was evaporated. The crude product was redissolved in Et_2O and washed successively with $NaHSO_3$ (5% by weight) and water. The combined organics were dried ($MgSO_4$), filtered, and concentrated to afford the desired product in sufficiently pure form for further use.

General Triazene Formation Procedure B. The iodoaniline (1 equiv) was dissolved in a minimum amount of MeCN, after which HCl (12 M, 8 equiv) and ice (∼2 g) were added. The suspension was cooled to −5 °C, and a solution of $NaNO_2$ (2.2 equiv) in 3:1 water/MeCN (2 M) was added slowly such that the temperature remained between −5 and −2 °C. Once the addition was complete, the solution was stirred at −5 °C for 30 min, after which time it was transferred slowly via cannula to a quench solution of Et_2NH (10 equiv), K_2CO_3 (5 equiv), and 3:1 water/MeCN (0.1 M) cooled to 0 °C. Once the transfer was complete, the mixture was allowed to gradually warm to rt overnight. The mixture was diluted with water and extracted with Et_2O. The combined organics were dried ($MgSO_4$), filtered, and concentrated. Column chromatography on silica gel gave the desired product.

General Acetylene Coupling Procedure C. The (2-iodophenyl)triazene (1 equiv), $PdCl_2(PPh_3)_2$ (0.04 equiv), CuI (0.07 equiv), and either (trimethylsilyl)-1,3-butadiyne or (trimethylsilyl)acetylene (TMSA, 1.5 equiv) were dissolved in NEt_3 (0.1 M solution based on triazene). The mixture was immediately degassed by three successive freeze−pump−thaw cycles, and the flask was charged with N_2. The mixture was heated to 50 °C and stirred under N_2 overnight. After cooling, the solvent was evaporated and the crude product was redissolved in 10−50% CH_2Cl_2 in hexanes and vacuum filtered through a pad of silica gel. The solvent was evaporated to yield the product that was either purified by column chromatography on silica gel (butadiynes) or immediately desilylated as below (ethynes).

General Desilylation Procedure D. The [2-(trimethylsilyl)ethynylphenyl]triazene (1 equiv) and K_2CO_3 (10 equiv) were dissolved in THF/MeOH (5:1 v/v, 0.1 M) and the mixture was stirred at rt for 4 h. The reaction was diluted with Et_2O and washed with saturated NH_4Cl solution. The organic layer was dried ($MgSO_4$), filtered, and concentrated. Column chromatography on silica gel gave the desired product.

General Cinnoline Formation Procedure E. To a sealable glass pressure tube was added the (2-ethynylphenyl)triazene in 1,2-dichlorobenzene (0.05 M). The tube was sealed and heated to 200 °C with stirring overnight. After cooling, the solvent was evaporated and the crude product was purified by preparative TLC to yield the cinnoline.

General Isoindazole Formation Procedure F. The (2-ethynylphenyl)triazene (0.2 mmol) was dissolved in 1,2-dichloroethane (30 mL), and CuCl (1 mmol) was added. The mixture was heated to 50 °C for 12−36 h. After cooling, the metal salts were removed by vacuum filtration through a pad of silica gel, eluting with 1:1 hexanes/CH_2Cl_2. The solvent was evaporated, and the crude product was purified by preparative TLC to yield the isoindazole.

1-(4-Cyano-2-iodophenyl)-3,3-diethyl-1-triazene (8). Aminobenzonitrile (5 g, 42.3 mmol), BTEA·ICl_2 (30 g, 76.9 mmol), and $CaCO_3$ (8.5 g, 84.9 mmol) were reacted using general procedure A (done at reflux). The product was immediately combined with HCl (9 mL, 110 mmol), $NaNO_2$ (1.78 g, 25.8 mmol), Et_2NH (14 mL, 135 mmol), and K_2CO_3 (6.87 g, 52 mmol) using general procedure B. Concentration of the organic layer furnished **8** (3.62 g, 89%) as a brown solid in sufficiently pure form for further elaboration: mp 78.1−79.8 °C; ^{1}H NMR ($CDCl_3$) δ 8.09 (d, J = 1.8 Hz, 1H), 7.53 (dd, J = 7.8, 1.8 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 3.85 (q, J = 7.2 Hz, 4H), 1.37 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 153.85, 142.62, 132.32, 118.07, 117.13, 108.91, 95.82, 49.87, 42.99, 14.38, 10.78; IR (KBr) 3083, 2224 cm^{-1}; HRMS calcd for $C_{11}H_{13}IN_4$ 329.0263, found 329.0263. Anal. Calcd for $C_{11}H_{13}IN_4$ (328.15): C, 40.26; H, 3.99; N, 17.07. Found: C, 40.36; H, 3.83; N, 16.81.

1-[4-Cyano-2-[(4-trimethylsilyl)buta-1,3-diynyl]phenyl]-3,3-diethyl-1-triazene (3). Iodide **8** (1.67 g, 5.10 mmol), 1-(trimethylsilyl)-1,3-butadiyne (810 mg, 6.63 mmol), $PdCl_2(PPh_3)_2$ (215 mg, 0.31 mmol), and CuI (136 mg, 0.71 mmol) were reacted using general procedure C. Chromatography on silica gel (6:1 hexanes/EtOAc, R_f = 0.21) gave **3** (1.54 g, 94%) as a dark red oil: ^{1}H NMR ($CDCl_3$) δ 7.72 (t, J = 0.9 Hz, 1H), 7.48 (d, J = 1.2 Hz, 2H), 3.85 (q, J = 7.2 Hz, 4H), 1.37 (t, J = 7.5 Hz, 3H), 1.30 (t, J = 6.9 Hz, 3H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 157.17, 137.74, 132.74, 118.60, 117.68, 117.15, 107.41, 91.78, 87.80, 79.39, 73.22, 49.84, 42.75, 14.35, 10.63, −0.42; IR (neat) 3069, 2226, 2201, 2101, 1593 cm^{-1}; HRMS calcd for $C_{18}H_{23}N_4Si$ 323.1692, found 323.1695.

3,3-Diethyl-1-[2-[(4-trimethylsilyl)buta-1,3-diynyl]phenyl]-1-triazene (6). Iodide **9**[6b] (1.02 g, 3.36 mmol), 1-(trimethylsilyl)-1,3-butadiyne (523 mg, 4.28 mmol), $PdCl_2(PPh_3)_2$ (144 mg, 0.21 mmol), and CuI (72 mg, 0.38 mmol) were reacted using general procedure C. Chromatography on silica gel (5:1 hexanes/CH_2Cl_2, R_f = 0.18) gave **6** (361 mg, 36%) as a tan oil: ^{1}H NMR ($CDCl_3$) δ 7.47 (dd, J = 7.8, 1.2 Hz, 1H), 7.37 (dd, J = 8.1, 0.9 Hz, 1H), 7.28 (td, J = 7.2, 1.5 Hz, 1H), 7.03 (td, J = 7.8, 1.5 Hz, 1H), 3.80 (q, J = 7.2 Hz, 4H), 1.32 (t, J = 6.6 Hz, 6H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 154.45, 133.85, 129.80, 124.55, 117.29, 116.02, 90.15, 88.59, 77.76, 75.91, 49.08, 41.88, 14.46, 10.78, −0.30; IR (neat) 3066, 2200, 2100 cm^{-1}; HRMS calcd for $C_{17}H_{24}N_3Si$ 298.1740, found 298.1740.

1-[4-Nitro-2-[(4-trimethylsilylbuta-1,3-diynyl]phenyl]-azopiperidine (7). Iodide **10**[6a] (200 mg, 0.56 mmol), 1-(trimethylsilyl)-1,3-butadiyne (85 mg, 0.69 mmol), $PdCl_2(PPh_3)_2$ (23 mg, 0.03 mmol), and CuI (15 mg, 0.08 mmol) were reacted using general procedure C. Chromatography on silica gel (3:1 hexanes/CH_2Cl_2, R_f = 0.33) provided **7** (173 mg, 88%) as a bright yellow powder: mp 161.3−163.6 °C; ^{1}H NMR ($CDCl_3$) δ 8.36 (d, J = 2.7 Hz, 1H), 8.10 (dd, J = 9.3, 2.4 Hz, 1H), 7.57 (d, J = 9.0 Hz, 1H), 4.04 (br s, 2H), 3.90 (br s, 2H), 1.78 (br s, 6H), 0.24 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 158.61, 144.20, 130.23, 125.15, 117.39, 116.88, 92.37, 80.06, 79.70, 73.46, 53.99, 44.66, 26.75, 24.84, 24.34, −0.14; IR (KBr) 3080, 2200, 2098, 1600, 1571, 1332, 1097 cm^{-1}; HRMS calcd for $C_{18}H_{23}N_4O_2Si$ 355.1590, found 355.1589.

Cyano Dimer 5. To a sealable glass pressure tube were added **3** (1.10 g, 3.41 mmol) and MeI (40 mL). The tube was sealed and heated overnight at 145 °C. After cooling, the solvent was evaporated, and the crude product was purified by chromatography on silica gel (5:1 hexanes/EtOAc, R_f = 0.31) to give **5** (363 mg, 33%) as a light yellow solid: mp 239.8−241.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.22 (br s, 2H), 7.80 (d, J = 9.0 Hz, 2H), 7.48 (dd, J = 9.0, 1.5 Hz, 2H), 3.38 (q, J = 6.9 Hz, 8H), 1.02 (t, J = 6.6 Hz, 12H), −0.23 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 146.16, 132.96, 129.49, 126.77, 123.13, 119.87, 119.39, 117.39, 108.88, 105.25, 101.23, 51.97, 12.21, −1.16; IR (KBr) 3068, 2226, 2155, 1629 cm^{-1}; HRMS calcd for $C_{36}H_{45}N_8Si_2$ 645.3306, found 645.3308. Anal. Calcd for $C_{36}H_{44}N_8Si_2$ (644.96): C, 67.04; H, 6.88; N, 17.37. Found: C, 66.79; H, 6.86; N, 17.45. Isolation of an earlier band afforded iodide **4** (11 mg, 10%) as a white solid: mp 109.2−110.9 °C; ^{1}H NMR ($CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 2.1 Hz, 1H), 7.26 (dd, J = 8.2, 2.1 Hz, 1H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 139.94, 136.48, 132.17, 130.23, 117.27, 112.46, 106.90, 94.72, 86.76, 79.86, 75.46, −0.54; IR (KBr) 3060, 2232, 2099 cm^{-1}; HRMS calcd for $C_{14}H_{13}INSi$ 349.9862, found 349.9869. Anal. Calcd for $C_{14}H_{12}INSi$ (349.24): C, 48.15; H, 3.46; N, 4.01. Found: C, 48.32; H, 3.51; N, 3.82.

4-Iodo-3-[(4-trimethylsilyl)buta-1,3-diynyl]benzonitrile (4). A solution of **3** (250 mg, 0.78 mmol) in MeI (10 mL) was heated at 160 °C overnight in a sealed glass pressure tube. After cooling, the solvent was evaporated and the residue purified by chromatography on silica gel (3:2 hexanes/CH_2Cl_2, R_f = 0.36) to give **4** (268 mg, 98%) as a white solid. The spectral data were identical to those given above.

Nitro Dimer 11. To a sealable glass pressure tube were added **7** (50 mg, 0.14 mmol) and MeI (5 mL). The tube was sealed and heated at 145 °C with stirring for 48 h. After cooling, the solvent was evaporated, and the crude product was purified by chromatography on silica gel (1:1 hexanes/CH_2Cl_2, R_f = 0.05) to give **11** (18 mg, 36%) as a pale yellow solid: mp 247−249 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.93 (d, J = 2.1 Hz, 2H), 8.18 (dd, J = 9.6, 2.1 Hz, 2H), 7.81 (d, J = 9.3 Hz, 2H), 3.40 (br s, 8H), 1.97 (br s, 8H), 1.70 (br s, 4H), −0.22 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 147.05, 143.03, 132.94, 121.95, 120.68, 120.37, 118.98, 116.88, 108.09, 100.44, 56.42, 26.01, 23.36, −1.07; IR (KBr) 3103, 2155, 1326 cm^{-1}; HRMS calcd for $C_{36}H_{45}N_8O_4Si_2$ 709.3102, found 709.3097. Anal. Calcd for $C_{36}H_{44}N_8O_4Si_2$ (708.97): C, 60.99; H, 6.26; N, 15.81. Found: C, 60.88; H, 6.16; N, 15.97. Isolation of an earlier band afforded iodide **12** (14 mg, 27%) as a beige solid: mp 185.1−186.4 °C; ^{1}H NMR ($CDCl_3$) δ 8.27 (d, J = 2.6 Hz, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.84 (dd, J = 8.8, 2.6 Hz, 1H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 147.74, 139.97, 130.31, 128.16, 124.08, 109.11, 94.91, 86.71, 79.97, 75.54, −0.55; IR (KBr) 3095, 2100, 1348 cm^{-1}. Anal. Calcd for $C_{13}H_{12}INO_2Si$ (369.24): C, 42.29; H, 3.28; N, 3.79. Found: C, 42.34; H, 3.25; N, 3.68.

1-Iodo-4-nitro-2-[(4-trimethylsilyl)buta-1,3-diynyl]benzene (12). A solution of **7** (300 mg, 0.85 mmol) in MeI (10 mL) was heated to 160 °C overnight in a sealed glass pressure tube. After cooling, the solvent was evaporated and the residue purified by chromatography on silica gel (3:2 hexanes/CH_2Cl_2, R_f = 0.25) to give **12** (306 mg, 98%) as beige needles. The spectral data were identical to those given above.

1-Iodo-2-[(4-trimethylsilyl)buta-1,3-diynyl]benzene (13). To a sealable glass pressure tube were added **6** (400 mg, 1.34 mmol) and MeI (10 mL). The tube was sealed and heated to 125 °C overnight. After cooling, the solvent was evaporated and the residue purified by chromatography on silica gel (9:1 hexanes/CH_2Cl_2, R_f = 0.30) to give **13** (429 mg, 95%) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.83 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 7.9 Hz, 1H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.81, 134.13, 130.26, 128.30, 127.80, 100.81, 92.56, 87.50, 77.79, 77.52, −0.43; IR (KBr) 3062, 2205, 2102 cm^{-1}.

1-(4-Cyano-2-ethynylphenyl)-3,3-diethyltriazene (14). Iodide **8** (250 mg, 0.76 mmol), TMSA (0.14 mL, 0.95 mmol), $PdCl_2(PPh_3)_2$ (43 mg, 0.06 mmol), and CuI (20 mg, 0.11 mmol) were reacted using general procedure C. The crude product was immediately treated with K_2CO_3 (1.3 g, 9.8 mmol) using general procedure D. Chromatography on silica gel (9:1 hexanes/EtOAc, R_f = 0.35) gave **14** (152 mg, 88%) as a yellow powder: mp 47.1−48.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.76 (s, 1H), 7.51−7.49 (m, 2H), 3.84 (q, J = 7.0 Hz, 4H), 3.32 (s, 1H), 1.36 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 156.02, 137.52, 132.53, 118.76, 117.95, 117.49, 107.40, 82.62, 79.91, 49.72, 42.53, 14.36, 10.67; IR (neat) 3292, 3070, 2226, 2108 cm^{-1}; HRMS calcd for $C_{13}H_{15}N_4$ 227.1297, found 227.1298. Anal. Calcd for $C_{13}H_{14}N_4$ (226.28): C, 69.00; H, 6.24; N, 24.76. Found: C, 68.77; H, 6.07; N, 24.50.

1-(2-Ethynyl-4-nitrophenyl)azopiperidine (15). Iodide **10** (300 mg, 0.83 mmol), TMSA (0.15 mL, 1.08 mmol), $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol), and CuI (19 mg, 0.10 mmol) were reacted using general procedure C. The crude product was vacuum filtered through a pad of silica gel eluting with CH_2Cl_2. The solvent was evaporated, and the residue was immediately treated with K_2CO_3 (1.65 g, 12.5 mmol) using general procedure D. Chromatography on silica gel (3:2 hexanes/CH_2Cl_2, R_f = 0.24) furnished **15** (154 mg, 72%) as a yellow solid: mp 96−98.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.35 (d, J = 2.7 Hz, 1H), 8.09 (dd, J = 9.3, 2.4 Hz, 1H), 7.57 (d, J = 9.0 Hz, 1H), 4.01 (br s, 2H), 3.87 (br s, 2H), 3.36 (s, 1H), 1.74 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 157.53, 144.16, 129.69, 124.85, 117.63, 117.07, 83.21, 80.07, 53.90, 44.51, 26.69, 24.76, 24.33; IR (KBr) 3300, 3111, 2109, 1599, 1324 cm^{-1}; HRMS calcd for $C_{13}H_{15}N_4O_2$ 259.1195, found 259.1201. Anal. Calcd for $C_{13}H_{14}N_4O_2$ (258.28): C, 60.45; H, 5.46; N, 21.69. Found: C, 60.27; H, 5.65; N, 21.78.

Cyano Dimer 16. To a sealable glass pressure tube were added **14** (50 mg, 0.22 mmol) and MeI (8 mL). The tube was sealed and stirred at 125 °C for 48 h. After cooling, the solvent was evaporated and the crude product was purified by preparative TLC (7:3 hexanes/EtOAc) to give a 2:1 mixture of **16** and **17** (20 mg, 40%) as a light yellow solid. Recrystallization of the mixture from EtOH yielded trans dimer **16** exclusively: mp 224.6−226.4 °C; ^{1}H NMR ($CDCl_3$) δ 8.41−8.40 (m, 2H), 7.93 (s, 2H), 7.82 (dd, J = 8.7, 0.9 Hz, 2H), 7.53 (dd, J = 8.7, 1.5 Hz, 2H), 3.48 (s, 2H), 3.36 (s, 2H), 0.90 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 146.66, 135.41, 128.08, 127.41, 120.02, 119.58, 118.16, 116.66, 106.03, 52.68, 12.15; IR (KBr) 3071, 2220, 1620 cm^{-1}; HRMS calcd for $C_{26}H_{28}N_8$ 452.2437, found 452.2437. Anal. Calcd for $C_{26}H_{28}N_8$ (452.55): C, 69.00; H, 6.24; N, 24.67. Found: C, 68.95; H, 6.16; N, 24.49. Isolation of a second band furnished aldehyde **20** (5 mg, 9%) as a yellow powder: mp 165.8−167.2 °C; ^{1}H NMR ($CDCl_3$) δ 10.41 (s, 1H), 8.66 (t, J = 1.1 Hz, 1H), 7.88 (dd, J = 8.7, 0.9 Hz, 1H), 7.56 (dd, J = 8.7, 1.5 Hz, 1H), 3.46−3.34 (m, 4H), 0.90 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 180.99, 146.03, 133.62, 128.67, 128.22, 119.70, 118.75, 109.68, 52.81, 11.98; IR (KBr) 3077, 3026, 2227, 1670, 1627 cm^{-1}; HRMS calcd for $C_{13}H_{15}N_4O$ 243.1246, found 243.1245. Anal. Calcd for $C_{13}H_{14}N_4O$ (242.28): C, 64.18; H, 6.21; N, 23.03. Found: C, 64.20; H, 5.94; N, 22.91.

Nitro Dimer 18. To a sealable glass pressure tube were added **15** (52 mg, 0.20 mmol) and MeI (5 mL). The tube was sealed and stirred overnight at 150 °C. After cooling, the solvent was evaporated and the crude product was purified by preparative TLC (1:1 hexanes/CH_2Cl_2) to give a 1:1 mixture of **18** and **19** (26 mg, 52%) as an orange solid. Recrystallization of the mixture from EtOH yielded trans dimer **18** exclusively: mp 351−352 °C dec; ^{1}H NMR ($CDCl_3$) δ 9.12 (d, J = 2.4 Hz, 2H), 8.23 (dd, J = 9.6, 2.1 Hz, 2H), 8.11 (s, 2H), 7.82 (d, J = 9.3 Hz, 2H), 3.39−3.35 (m, 8H), 2.06−1.98 (m, 8H), 1.72 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 147.65, 143.80, 134.05, 121.07, 119.67, 119.28, 118.03, 116.55, 56.90, 26.39, 23.57; IR (KBr) 3099, 3080, 1616, 1327 cm^{-1}; HRMS calcd for $C_{26}H_{28}N_8O_4$ 516.2234, found 516.2235. Anal. Calcd for $C_{26}H_{28}N_8O_4$ (516.55): C, 60.45; H, 5.46; N, 21.69. Found: C, 60.34; H, 5.38; N, 21.88. Isolation of a second band furnished aldehyde **21** (7 mg, 13% yield) as a dark orange powder: mp 172.9−173.7 °C; ^{1}H NMR ($CDCl_3$) δ 10.44 (s, 1H), 9.11 (d, J = 1.5 Hz, 1H), 8.19 (dd, J = 9.3, 2.1 Hz, 1H), 7.86 (d, J = 9.3 Hz, 1H), 3.39 (t, J = 5.7 Hz, 4H), 1.95−1.87 (m, 4H), 1.69−1.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 180.30, 146.53, 146.00, 131.45, 121.27, 119.44, 119.36, 118.49, 57.50, 25.70, 23.02; IR (KBr) 3099, 3084, 1668, 1624, 1339 cm^{-1}; HRMS calcd for $C_{13}H_{15}N_4O_3$ 275.1144, found 275.1143. Anal. Calcd for $C_{13}H_{14}N_4O_3$ (274.28): C, 56.93; H, 5.14; N, 21.69. Found: C, 56.48; H, 5.10; N, 21.88.

3-Acyl-5-cyano-2-diethylamino-2*H*-indazole (22). To a sealable glass pressure tube were added **3** (50 mg, 0.16 mmol) and ODCB (5 mL). The tube was sealed and stirred at 165 °C overnight. After cooling, the solvent was evaporated and the crude product was purified by preparative TLC (4:1 hexanes/EtOAc, R_f = 0.25) to give **22** (26 mg, 96%) as a tan oil: ^{1}H NMR ($CDCl_3$) δ 8.70−8.69 (m, 1H), 7.79 (dd, J = 8.7, 0.9 Hz, 1H), 7.50 (dd, J = 8.7, 1.5 Hz, 1H), 3.39 (br d, 4H), 2.86 (s, 3H), 0.93 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 189.35, 145.71, 134.24, 130.33, 127.76, 120.30, 119.42, 119.16, 108.93, 52.77, 30.78, 11.79; IR (neat) 3104, 3080, 2253, 2225, 1661, 1625 cm^{-1}; HRMS calcd for $C_{14}H_{17}N_4O$ 257.1402, found 257.1403.

3-Acyl-2-diethylamino-2*H*-indazole (23) and 2-Diethylamino-3-(3-trimethylsilyl-2-propyn-1-oyl)-2*H*-indazole (24). To a sealable glass pressure tube were added **6** (63 mg, 0.21 mmol) and ODCB (5 mL). The tube was sealed and stirred at 155 °C for 48 h. After cooling, the solvent was evaporated and the crude product was purified by chromatography on silica gel (1:1 hexanes/CH_2Cl_2) to give **23** (15 mg, 31% yield, R_f = 0.1) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 8.25 (d, J = 8.7 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.42−7.30 (m, 2H), 3.47 (br s, 2H), 3.31 (br s, 2H), 2.86 (s, 3H), 0.94 (t, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 189.68, 145.63, 133.22, 126.89, 125.72, 122.43, 121.39, 117.74, 52.63, 30.83, 11.86; IR (neat) 3072, 3056, 1659, 1625 cm^{-1}; HRMS calcd for $C_{13}H_{18}N_3O$ 232.1450, found 232.1452. Isolation of an earlier band (R_f = 0.18) furnished **24** (12 mg, 18% yield) as an unstable tan oil: ^{1}H NMR ($CDCl_3$) δ 8.30 (d, J = 7.5 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.45−7.33 (m, 2H), 3.44 (br s, 2H), 3.28 (br s, 2H), 0.95 (t, J = 7.2 Hz, 6H), 0.32 (s, 9H); IR (neat) 3058, 2153, 1737, 1599, 846 cm^{-1}; HRMS calcd for $C_{17}H_{24}N_3OSi$ 314.1689, found 314.1694.

3,3-Diethyl-1-(2-iodo-4-methylphenyl)-1-triazene (33). *p*-Toluidine (0.63 g, 5.88 mmol), BTEA·ICl_2 (2.63 g, 6.75 mol), and $CaCO_3$ (0.84 g, 8.41 mmol) were reacted using general procedure A (rt). The crude product was immediately treated with HCl (4 mL, 48 mmol), $NaNO_2$ (0.93 g, 13.4 mmol), Et_2-NH (6.21 mL, 60 mmol), and K_2CO_3 (4 g, 30 mmol) using general procedure B. Chromatography on silica gel (9:1 hexanes/CH_2Cl_2, R_f = 0.2) gave **33** (1.48 g, 79%) as a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 7.68 (d, J = 1.3 Hz, 1H), 7.25 (d, J = 8.2 Hz, 1H), 7.08 (dd, J = 8.2, 1.3, 1H), 3.78 (q, J = 7.0 Hz, 4H), 2.29 (s, 3H), 1.32 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 148.14, 139.22, 136.34, 129.46, 117.02, 96.45, 49.00 (br), 42.06 (br), 20.34, 14.10 (br), 11.09 (br); IR (neat) 3057, 3023 cm^{-1}; HRMS calcd for $C_{11}H_{17}N_3I$ 318.0467, found 318.0470.

1-(4-*tert*-Butyl-2-iodophenyl)-3,3-diethyl-1-triazene (34). 4-*tert*-Butylaniline (0.96 mL, 6.0 mmol) was reacted using general procedure A (rt) and general procedure B using the same quantities of reagents described for **33**. After workup, **34** (1.93 g, 89%) was obtained as a yellow oil in sufficiently pure form for further elaboration: ^{1}H NMR ($CDCl_3$) δ 7.81 (d, J = 1.7 Hz,1H), 7.29 (dd, J = 8.4, 1.7, 2H), 7.25 (d, J = 8.4 Hz, 1H), 3.76 (q, J = 7.2 Hz, 4H), 1.29 (t, J = 7.2 Hz, 6H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 149.80, 136.82, 135.86, 125.91, 116.91, 96.62, 49.15 (br), 41.96 (br), 34.29, 31.32, 14.54 (br), 11.22 (br); IR (neat) 3067 cm^{-1}; HRMS calcd for $C_{14}H_{23}N_3I$ 360.0937, found 360.0938.

1-(4-Bromo-2-iodophenyl)-3,3-diethyl-1-triazene (35). 4-Bromoaniline (1.01 g, 5.88 mmol) was reacted using general procedure A (rt) and general procedure B using the same quantities of reagents described for **33**. After workup, **35** (2.06 g, 92%) was obtained as a red oil in sufficiently pure form for further elaboration: ^{1}H NMR ($CDCl_3$) δ 7.96 (d, J = 2.1 Hz, 1H), 7.38 (dd, J = 8.7, 2.1 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 3.79 (q, J = 7.2 Hz, 4H), 1.31 (br s, 6H); ^{13}C NMR ($CDCl_3$) δ 149.52, 140.68, 131.54, 118.19, 118.13, 96.86, 49.29, 42.32, 14.49, 10.87; IR (neat) 3061 cm^{-1}; HRMS calcd for $C_{10}H_{13}N_3{}^{79}$-BrI 380.9338, found 380.9337.

1-(4-Chloro-2-iodophenyl)-3,3-diethyl-1-triazene (36). 4-Chloroaniline (0.75 g, 5.88 mmol) was reacted using general procedure A (rt) and general procedure B using the same quantities of reagents described for **33**. After workup, **36** (1.61 g, 81%) was obtained as a red oil in sufficiently pure form for further elaboration: ^{1}H NMR ($CDCl_3$) δ 7.81 (d, J = 2.1 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.24 (dd, J = 8.4, 1.2 Hz, 1H), 3.79 (q, J = 7.5 Hz, 4H), 1.32 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 149.12, 138.03, 130.45, 128.68, 117.69, 96.28, 49.25, 42.25, 14.49, 10.88; IR (neat) 3062 cm^{-1}; HRMS calcd for $C_{10}H_{13}N_3{}^{35}$-ClI 336.9843, found 336.9838.

3,3-Diethyl-1-(4-fluoro-2-iodophenyl)-1-triazene (37). 4-Fluoroaniline (0.56 mL, 5.88 mmol) was reacted using general procedure A (rt) and general procedure B using the same quantities of reagents described for **33**. After workup, **37** (1.12 g, 59%) was obtained as a red oil: ^{1}H NMR ($CDCl_3$) δ 7.56 (dd, J = 7.9, 2.6 Hz, 1H), 7.31 (dd, J = 9.1, 5.9 Hz, 1H), 7.01 (ddd, J = 9.1, 7.9, 3.0 Hz, 1H), 3.79 (q, J = 7.1 Hz, 4H), 1.32 (t, J = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 159.90 (d, J = 248.8 Hz), 147.03, 125.34 (d, J = 24.1 Hz), 117.57 (d, J = 8.3 Hz), 115.62 (d, J = 22.2 Hz), 95.55 (d, J = 8.3 Hz), 49.11, 42.17, 14.53, 10.98; IR (neat) 3068 cm^{-1}; HRMS calcd for $C_{10}H_{14}N_3$-FI 322.0217, found 322.0226.

1-(4-Carbomethoxy-2-iodophenyl)-3,3-diethyl-1-triazene (38). Methyl 4-aminobenzoate (5.00 g, 33.1 mmol), BTEA·ICl_2 (22.1 g, 56.2 mol), $CaCO_3$ (5.00 g, 49.6 mmol), and CH_2Cl_2/MeOH (300 mL, 2:1 v:v) were combined using general procedure A. The solvent volume was reduced in half by rotary evaporation, and the solution was washed with saturated $Na_2S_2O_3$ solution and dried ($MgSO_4$). Removal of the solvent yielded 9.16 g (~99% yield) of product as a brown powder. The crude product (1.52 g, 5.5 mmol) was immediately dissolved in MeCN (5.0 mL) and treated with concd HCl (1.35 mL, 44.0 mmol), $NaNO_2$ (759 mg, 11.0 mmol), Et_2NH (5.7 mL, 55.0 mmol), and K_2CO_3 (4.60 g, 33.0 mmol) using general procedure B. This mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and filtered. Concentration of the solution furnished **38** (1.67 g, 84%) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 8.52 (d, J = 1.8 Hz, 1H), 7.94 (dd, J = 8.7, 1.8 Hz, 1H), 7.39 (d, J = 8.7 Hz, 1H), 3.90 (s, 3H), 3.84 (q, J = 7.2 Hz, 4H), 1.37 (t, J = 7.5 Hz, 3H), 1.33 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 165.88, 153.87, 140.70, 140.67, 130.08, 127.54, 116.64, 95.75, 52.07, 49.60, 42.65, 14.43, 10.88; IR (neat) 3067, 1708 cm^{-1}; HRMS calcd for $C_{12}H_{16}N_3O_2I$ 361.0287, found 361.0289.

3,3-Diethyl-1-(2-iodo-4-nitrophenyl)-1-triazene (39). 4-Nitroaniline (0.94 g, 6.79 mmol), BTEA·ICl_2 (3.04 g, 7.79 mmol), and $CaCO_3$ (0.97 g, 9.71 mmol) were reacted using general procedure A (reflux). Chromatography on silica gel (2:1 hex-

anes/EtOAc, $R_f = 0.4$) gave the iodinated product (0.94 g). This compound was treated with HCl (2.4 mL, 29 mmol), $NaNO_2$ (0.56 g, 8.12 mmol), Et_2NH (3.5 mL, 34 mmol), and K_2CO_3 (2.4 g, 20 mmol) using general procedure B. Chromatography on silica gel (1:1 hexanes/CH_2Cl_2, $R_f = 0.4$) provided **39** (875 mg, 37%) as an orange solid: mp 71.8−73.4 °C; ^{1}H NMR ($CDCl_3$) δ 8.71 (d, $J = 2.3$ Hz, 1H), 8.14 (dd, $J = 8.8$, 2.3 Hz, 1H), 7.44 (d, $J = 8.8$ Hz, 1H), 3.88 (q, $J = 7.0$ Hz, 4H), 1.39 (t, $J = 7.3$ Hz, 3H), 1.33 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 155.31, 144.50, 134.81, 124.17, 116.26, 95.02, 50.06, 43.20, 14.34, 10.73; IR (KBr) 3088, 3069, 1320 cm^{-1}; HRMS calcd for $C_{10}H_{14}IN_4O_2$ 349.0162, found 349.0167.

3,3-Diethyl-1-(2-ethynyl-4-methylphenyl)-1-triazene (25). Iodide **33** (1.40 g, 4.41 mmol), TMSA (0.91 mL, 6.42 mmol), $PdCl_2(PPh_3)_2$ (235 mg, 0.34 mmol), and CuI (128 mg, 0.67 mmol) were reacted using general procedure C. The crude product was immediately treated with K_2CO_3 (10 g, 76 mmol) using general procedure D. Chromatography on silica gel (4:1 hexanes/CH_2Cl_2, $R_f = 0.15$) gave **25** (730 mg, 77%) as a deep red oil: ^{1}H NMR ($CDCl_3$) δ 7.31 (d, $J = 2.3$ Hz, 1H), 7.29 (d, $J = 8.4$ Hz, 1H), 7.09 (dd, $J = 8.5$, 2.1 Hz, 1H), 3.78 (q, $J = 7.0$ Hz, 4H), 3.23 (s, 1H), 2.30 (s, 3H), 1.30 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 150.88, 134.15, 133.69, 130.29, 116.85, 116.61, 82.22, 80.35, 48.52 (br), 41.65 (br), 20.67, 14.03 (br), 10.78 (br); IR (neat) 3292, 3062, 3024, 2103 cm^{-1}; HRMS calcd for $C_{13}H_{18}N_3$ 216.1501, found 216.1500.

1-(4-*tert*-Butyl-2-ethynylphenyl)-3,3-diethyl-1-triazene (26). Iodide **34** (1.93 g, 5.37 mmol), TMSA (1.9 mL, 13.6 mmol), $PdCl_2(PPh_3)_2$ (252 mg, 0.36 mmol), and CuI (137 mg, 0.72 mmol) were reacted using general procedure C. The crude product was immediately treated with K_2CO_3 (14 g, 100 mmol) using general procedure D. Chromatography on silica gel (4:1 hexanes/CH_2Cl_2, $R_f = 0.13$) gave **26** (720 mg, 52%) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.51 (br s, 1H), 7.32 (br s, 2H), 3.78 (q, $J = 7.0$ Hz, 4H), 3.23 (s, 1H), 1.31 (s, 9H), 1.30 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 150.79, 147.51, 130.17, 126.73, 116.68, 116.21, 82.69, 80.00, 48.66 (br), 41.71 (br), 34.29, 31.23, 14.09, 10.95; IR (neat) 3314, 3293, 3097, 3067, 3032, 2106 cm^{-1}; HRMS calcd for $C_{16}H_{24}N_3$ 258.1970, found 258.1977.

3,3-Diethyl-1-(2,4-diethynylphenyl)-1-triazene (27). Bromide **35** (500 mg, 1.3 mmol), TMSA (0.47 mL, 2.9 mmol), $PdCl_2(PPh_3)_2$ (36 mg, 0.05 mmol), and CuI (35 mg, 0.18 mmol) were reacted using general procedure C. The crude product was immediately treated with K_2CO_3 (2.9 g, 22 mmol) using general procedure D. Chromatography on silica gel (3:1 hexanes/CH_2Cl_2, $R_f = 0.21$) gave **27** (270 mg, 92%) as a yellow solid: mp 93.7−96.4 °C; ^{1}H NMR ($CDCl_3$) δ 7.64 (d, $J = 1.2$ Hz, 1H), 7.39−7.37 (m, 2H), 3.78 (q, $J = 7.2$ Hz, 4H), 3.26 (s, 1H), 3.07 (s, 1H), 1.29 (br s, 6H); ^{13}C NMR ($CDCl_3$) δ 153.02, 137.21, 132.91, 117.92, 117.07, 116.85, 83.15, 81.26, 81.01, 77.12, 49.20 (br), 41.99 (br), 14.44 (br), 10.78 (br); IR (KBr) 3286, 3261, 3065, 3031, 2104 cm^{-1}; HRMS calcd for $C_{12}H_{16}N_3$ 202.1344, found 202.1341. Anal. Calcd for $C_{14}H_{15}N_3$ (225.29): C, 74.64; H, 6.71; N, 18.65. Found: C, 74.52; H, 6.47; N, 18.67.

1-(4-Bromo-2-ethynylphenyl)-3,3-diethyl-1-triazene (28). Bromide **35** (2.13 g, 5.58 mmol), TMSA (0.91 mL, 6.42 mmol), $PdCl_2(PPh_3)_2$ (186 mg, 0.26 mmol), and CuI (101 mg, 0.53 mmol) were reacted using general procedure C (stirred at rt after degassing). The crude product was immediately treated with K_2CO_3 (10 g, 76 mmol) using general procedure D. Chromatography on silica gel (4:1 hexanes/CH_2Cl_2, $R_f = 0.15$) gave **28** (780 mg, 50%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.61 (d, $J = 2.3$ Hz, 1H), 7.37 (dd, $J = 9.7$, 2.2 Hz, 1H), 7.28 (d, $J = 9.8$ Hz, 1H), 3.78 (q, $J = 7.5$ Hz, 4H), 3.28 (s, 1H), 1.30 (br s, 6H); ^{13}C NMR ($CDCl_3$) δ 152.07, 135.69, 132.33, 118.65, 118.41, 116.97, 81.90, 80.59, 49.16 (br), 41.85 (br), 14.47 (br), 10.77 (br); IR (neat) 3298, 3064, 2107 cm^{-1}; HRMS calcd for $C_{12}H_{15}N_3{}^{79}Br$ 280.0449, found 280.0444.

1-(4-Chloro-2-ethynylphenyl)-3,3-diethyl-1-triazene (29). Chloride **36** (1.61 g, 4.77 mmol), TMSA (0.94 mL, 6.68 mmol), $PdCl_2(PPh_3)_2$ (201 mg, 0.29 mmol), and CuI (109 mg, 0.57 mmol) were reacted using general procedure C. The crude product was immediately treated with K_2CO_3 (12.6 g, 95 mmol) using general procedure D. Chromatography on silica gel (4:1 hexanes/CH_2Cl_2, $R_f = 0.21$) gave **29** (650 mg, 58%) as a yellow liquid: ^{1}H NMR ($CDCl_3$) δ 7.45 (d, $J = 2.4$ Hz, 1H), 7.35 (d, $J = 9.0$ Hz, 1H), 7.22 (dd, $J = 8.7$, 2.4 Hz, 1H), 3.79 (q, $J = 7.2$ Hz, 4H), 3.28 (s, 1H), 1.30 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 151.65, 132.78, 129.48, 129.39, 118.21, 118.12, 81.81, 80.73, 49.14, 41.82, 14.42, 10.79; IR (neat) 3300, 3067, 2108 cm^{-1}; HRMS calcd for $C_{12}H_{14}N_3{}^{35}Cl$ 235.0876, found 235.0874.

3,3-Diethyl-1-(2-ethynyl-4-fluorophenyl)-1-triazene (30). Fluoride **37** (1.12 g, 3.49 mmol), TMSA (0.641 mL, 4.53 mmol), $PdCl_2(PPh_3)_2$ (147 mg, 0.21 mmol), and CuI (80 mg, 0.42 mmol) were reacted using general procedure C. The crude product was immediately treated with K_2CO_3 (5.0 g, 37.8 mmol) using general procedure D. After workup, chromatography on silica gel (4:1 hexanes/CH_2Cl_2, $R_f = 0.32$) gave **30** (0.64 g, 83%) as a dark red oil: ^{1}H NMR ($CDCl_3$) δ 7.36 (dd, $J = 8.7$, 5.6 Hz, 1H), 7.17 (dd, $J = 9.1$, 2.9 Hz, 1H), 6.99 (ddd, $J = 9.0$, 8.2, 3.0 Hz, 1H), 3.78 (q, $J = 7.5$ Hz, 4H), 3.27 (s, 1H), 1.30 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 159.59 (d, $J = 243.2$ Hz), 149.68, 119.35 (d, $J = 24.1$ Hz), 118.31 (d, $J = 9.3$ Hz), 117.96 (d, $J = 9.3$ Hz), 116.72 (d, $J = 22.2$ Hz), 81.66, 80.91, 48.96 (br), 41.68 (br), 14.74 (br), 10.72 (br); IR (neat) 3302, 3074, 2108, 1602, 1578 cm^{-1}; HRMS calcd for $C_{12}H_{15}N_3F$ 220.1250, found 220.1247.

1-(4-Carbomethoxy-2-ethynylphenyl)-3,3-diethyl-1-triazene (31). Ester **38** (600 mg, 1.66 mmol), TMSA (0.33 mL, 2.33 mmol), $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol), and CuI (38 mg, 0.20 mmol) were reacted using general procedure C. The crude product was purified by chromatography on silica gel (1:1 hexanes/CH_2Cl_2, $R_f = 0.3$) and subsequently treated with K_2CO_3 (6.02 g, 46 mmol) using general procedure D. Chromatography on silica gel (1:1 hexanes/CH_2Cl_2, $R_f = 0.13$) gave **31** (170 mg, 40%) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 8.17 (d, $J = 2.1$ Hz, 1H), 7.91 (dd, $J = 8.8$, 2.1 Hz, 1H), 7.44 (d, $J = 8.8$ Hz, 1H), 3.87 (s, 3H), 3.79 (q, $J = 6.9$ Hz, 4H), 3.27 (s, 1H), 1.36−1.22 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 166.30, 156.22, 135.23, 130.42, 125.77, 116.84, 116.56, 81.30, 81.06, 51.89, 49.37, 42.12, 14.31, 10.63; IR (neat) 3294, 3073, 2107, 1718 cm^{-1}; HRMS calcd for $C_{14}H_{18}N_3O_2$ 260.1399, found 260.1399.

3,3-Diethyl-1-(2-ethynyl-4-nitrophenyl)-1-triazene (32). Nitro **39** (800 mg, 2.30 mmol), TMSA (0.49 mL, 3.45 mmol), $PdCl_2(PPh_3)_2$ (65 mg, 0.09 mmol), and CuI (39 mg, 0.21 mmol) were reacted using general procedure C. The crude product was immediately treated with K_2CO_3 (4.56 g, 35 mmol) using general procedure D. Chromatography on silica gel (1:1 hexanes/CH_2Cl_2, $R_f = 0.35$) gave **32** (540 mg, 95%) as a yellow powder: mp 106.5−108.7 °C; ^{1}H NMR ($CDCl_3$) δ 8.36 (d, $J = 2.6$ Hz, 1H), 8.10 (dd, $J = 9.1$, 2.6 Hz, 1H), 7.53 (d, $J = 9.1$ Hz, 1H), 3.87 (q, $J = 7.3$ Hz, 4H), 3.33 (s, 1H), 1.38 (t, $J = 7.3$ Hz, 3H), 1.30 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 157.61, 143.72, 129.31, 124.56, 117.39, 116.85, 82.64, 79.89, 49.90, 42.75, 14.33, 10.64; IR (neat) 3295, 3101, 3082, 2111, 1603, 1326 cm^{-1}; HRMS calcd for $C_{12}H_{15}N_4O_2$ 247.1195, found 247.1194. Anal. Calcd for $C_{12}H_{14}N_4O_2$ (246.27): C, 58.53; H, 5.73; N, 22.75. Found: C, 58.41; H, 5.50; N, 22.58.

3,3-Diethyl-1-(2-iodo-4-methoxyphenyl)-1-triazene (43). To a mixture of 4-amino-3-iodophenol[12] (1.8 g, 7.7 mmol) and Cs_2CO_3 (6.2 g, 19 mmol) in DMF (50 mL) was added MeI (0.45 mL, 7.2 mmol) in ca. 75 μL portions over 6 h. The mixture was stirred at ambient temperature for 48 h, diluted with water, and extracted with Et_2O. The combined organics were washed with water, dried ($MgSO_4$), filtered, and concentrated to give a light brown oil: ^{1}H NMR ($CDCl_3$) δ 7.21 (d, $J = 2.6$ Hz, 1H), 6.77 (dd, $J = 8.8$, 2.6 Hz, 1H), 6.70 (d, $J = 8.8$ Hz, 1H), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 152.67, 140.77, 123.45, 116.09, 115.37, 84.24, 55.91.

The above methyl ether (1.72 g, 6.9 mmol) was immediately reacted with HCl (0.88 mL, 10.5 mmol), $NaNO_2$ (230 mg, 3.3 mmol), Et_2NH (1.57 mL, 15 mmol), and K_2CO_3 (992 mg, 7.5 mmol) using general procedure B. After workup, column chromatography on silica gel (3:1 hexanes/CH_2Cl_2, $R_f = 0.4$)

gave **43** (2.22 g, 87% from 4-amino-3-iodophenol) as a tan oil: ^{1}H NMR ($CDCl_3$) δ 7.38 (d, J = 2.6 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 6.87 (dd, J = 8.8, 2.6 Hz, 1H), 3.78 (s, 3H), 3.76 (q, J = 7.0 Hz, 4H), 1.31 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 157.50, 144.38, 123.14, 117.53, 115.29, 96.65, 55.66, 48.00 (br), 42.22 (br), 12.00 (br); IR (neat) 3067, 1104, 1037 cm^{-1}; MS (ESI) m/z 334.0 (20, $M^+ + H$), 261.0 (10, $M^+ - C_4H_{10}N$).

3,3-Diethyl-1-(2-ethynyl-4-methoxyphenyl)-1-triazene (40). Iodoether **43** (430 mg, 1.3 mmol), TMSA (0.26 mL, 1.8 mmol), $PdCl_2(PPh_3)_2$ (36 mg, 0.05 mmol), and CuI (27 mg, 0.14 mmol) were reacted using general procedure C. The crude product was immediately treated with K_2CO_3 (859 mg, 6.5 mmol) using general procedure D. After workup, **40** (290 mg, 97%) was obtained as a dark oil: ^{1}H NMR ($CDCl_3$) δ 7.35 (d, J = 9.1 Hz, 1H), 7.01 (d, J = 2.9 Hz, 1H), 6.87 (dd, J = 9.1, 2.9 Hz, 1H), 3.79 (s, 3H), 3.76 (q, J = 7.3 Hz, 4H), 3.25 (s, 1H), 1.29 (t, J = 7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 156.56, 147.23, 118.05, 117.45, 116.77, 116.69, 81.97, 80.71, 55.51, 48.00 (br s), 43.00 (br s), 13.00 (br s); IR (neat) 3287, 2104, 1037 cm^{-1}; MS (ESI) m/z 232.1 (100, $M^+ + H$), 161.1 (70, $M^+ - C_4H_{10}N$).

1-(4-Acetoxy-2-iodophenyl)-3,3-diethyl-1-triazene (44). 4-Amino-3-iodophenol[12] (705 mg, 3.0 mmol) was treated with Ac_2O (3.0 mL, 3.0 mmol) in pyridine (50 mL) according to the method of Theobold.[24] Evaporation of the solvent and purification by chromatography on silica gel (3:2 hexanes/EtOAc) gave the corresponding ester (650 mg, 73%) as an off-white solid: ^{1}H NMR ($CDCl_3$) δ 7.37 (d, J = 2.6 Hz, 1H), 6.89 (dd, J = 8.5, 2.6 Hz, 1H), 6.71 (d, J = 8.5 Hz, 1H), 4.05 (br s, 2H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.80, 144.84, 142.29, 131.34, 122.51, 114.26, 82.76, 20.92.

The above ester (370 mg, 1.3 mmol), HCl (0.55 mL, 6.6 mmol), $NaNO_2$ (138 mg, 2.0 mmol), Et_2NH (1.4 mL, 13.3 mmol), and K_2CO_3 (1.4 g, 10.6 mmol) were reacted using general procedure B. After workup, product **44** (330 mg, 69%) was obtained as a light yellow oil in sufficiently pure form for further elaboration: ^{1}H NMR ($CDCl_3$) δ 7.58 (d, J = 2.3 Hz, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.04 (dd, J = 8.8, 2.3 Hz, 1H), 3.79 (q, J = 7.0 Hz, 4H), 2.27 (s, 3H), 1.31 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 169.30, 148.29, 147.82, 131.53, 121.89, 117.15, 95.59, 49.14 (br), 42.21 (br), 21.02, 14.53 (br), 10.99 (br); IR (neat) 3065, 1761, 1108 cm^{-1}; MS (ESI) MS m/z 362.0 (100, $M^+ + H$), 320.0 (20, $M^+ - C_2H_2O$), 246.9 (90, $M^+ - C_6H_{12}NO$).

1-(4-Acetoxy-2-ethynylphenyl)-3,3-diethyl-1-triazene (41). Iodoester **44** (315 mg, 0.87 mmol), TMSA (0.17 mL, 1.2 mmol), $PdCl_2(PPh_3)_2$ (24 mg, 0.035 mmol), and CuI (18 mg, 0.096 mmol) were reacted using general procedure C. The crude product was immediately treated with Bu_4NF (1.0 mL, 1.0 M in THF) and EtOH (0.5 mL) in THF. After the mixture was stirred for 24 h under N_2, the solvent was evaporated and the crude product was purified by chromatography (5:1 hexanes/EtOAc) to give **38** (160 mg, 71%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.40 (d, J = 8.8 Hz, 1H), 7.22 (d, J = 2.6 Hz, 1H), 7.01 (dd, J = 8.8, 2.6 Hz, 1H), 3.77 (q, J = 7.3 Hz, 4H), 3.26 (s, 1H), 2.27 (s, 3H), 1.29 (t, J = 7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 169.32, 150.89, 147.11, 125.81, 122.79, 117.69, 117.59, 81.46, 81.09, 49.02 (br), 41.68 (br), 21.02, 14.38 (br), 10.76 (br); IR (neat) 3289, 2580, 2106, 1764 cm^{-1}; MS (ESI) m/z 260.1 (100, $M^+ + H$), 218.1 (40, $M^+ - C_2H_2O$), 145.0 (90, $M^+ - C_6H_{12}NO$).

2-Diethylamino-3-formyl-2*H*-indazole (45). Obtained from 3,3-diethyl-1-(2-ethynylphenyl)-1-triazene[6b] using general procedure F (yellow oil, 95%): ^{1}H NMR ($CDCl_3$) δ 10.42 (s, 1H), 8.22 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.53−7.36 (m, 2H), 3.39 (br s, 4H), 0.89 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 181.42, 145.84, 132.81, 127.22, 126.40, 121.24, 119.85, 118.24, 52.68, 12.02; IR (neat) 3068, 1669, 1627 cm^{-1}; HRMS calcd for $C_{12}H_{16}N_3O$ 218.1293, found 218.1294.

2-Diethylamino-3-formyl-5-methyl-2*H*-indazole (46). Obtained from **25** using general procedure F (tan solid, 90%): mp 27−28.5 °C; ^{1}H NMR ($CDCl_3$) δ 10.38 (s, 1H), 8.01 (s, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 3.43 (br s, 2H), 3.30 (br s, 2H), 2.49 (s, 3H), 0.88 (t, J = 4.5 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 181.46, 144.63, 136.67, 132.28, 129.94, 120.24, 119.63, 117.90, 52.64, 21.98, 12.02; IR (KBr) 3061, 3028, 1671, 1631 cm^{-1}; HRMS calcd for $C_{13}H_{18}N_3O$ 232.1450, found 232.1448. Anal. Calcd for $C_{13}H_{17}N_3O$ (231.29): C, 67.51; H, 7.41; N, 18.17. Found: C, 67.58; H, 7.37; N, 17.94.

5-*tert*-Butyl-2-diethylamino-3-formyl-2*H*-indazole (47). Obtained from **26** using general procedure F (colorless oil that solidifies on standing, 96%): mp 79−81.5 °C; ^{1}H NMR ($CDCl_3$) δ 10.40 (s, 1H), 8.15 (d, J = 1.2 Hz, 1H), 7.74 (d, J = 9.1 Hz, 1H), 7.55 (dd, J = 9.1, 1.7 Hz, 1H), 3.37 (br s br, 4H), 1.40 (s, 9H), 0.88 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 181.52, 149.77, 144.51, 132.79, 126.76, 119.97, 117.76, 115.71, 52.64, 35.27, 31.22, 12.02; IR (neat) 3071, 3034, 1669 cm^{-1}; HRMS calcd for $C_{16}H_{24}N_3O$ 274.1919, found 274.1916.

2-Diethylamino-5-ethynyl-3-formyl-2*H*-indazole (48). Obtained from **27** using general procedure F (orange solid, 91%): mp 97−98.2 °C; ^{1}H NMR ($CDCl_3$) δ 10.39 (s, 1H), 8.42 (s, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 8.9 Hz, 1H), 3.36 (br s, 4H), 3.15 (s, 1H), 0.89 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 181.17, 145.13, 132.85, 130.47, 125.94, 120.12, 119.40, 118.38, 83.82, 77.89, 52.69, 12.00; IR (KBr) 3253, 3074, 2983, 2938, 2855, 2103, 1672, 1620; HRMS calcd for $C_{14}H_{16}N_3O$ 242.1293, found 242.1295.

5-Bromo-2-diethylamino-3-formyl-2*H*-indazole (49). Obtained from **28** using general procedure F (tan oil, 98%): ^{1}H NMR ($CDCl_3$) δ 10.37 (s, 1H), 8.42 (d, J = 1.8 Hz, 1H), 7.68 (d, J = 9.2 Hz, 1H), 7.51 (dd, J = 9.2, 2.0 Hz, 1H), 3.39 (br s, 4H), 0.88 (t, J = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 181.09, 144.27, 132.30, 131.08, 123.62, 120.89, 120.55, 119.88, 52.72, 11.99; IR (KBr) 3073, 1667, 1620 cm^{-1}; HRMS calcd for $C_{12}H_{15}N_3O^{79}Br$ 296.0399, found 296.0394.

5-Chloro-2-diethylamino-3-formyl-2*H*-indazole (50). Obtained from **29** using general procedure F (tan oil that solidifies slowly on standing, 95%): mp 92−93.5 °C; ^{1}H NMR ($CDCl_3$) δ 10.37 (s, 1H), 8.23 (d, J = 2.1 Hz, 1H), 7.73 (d, J = 9.2 Hz, 1H), 7.37 (dd, J = 9.2, 2.1 Hz, 1H), 3.39 (br s, 4H), 0.88 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 181.10, 144.15, 132.53, 128.72, 120.27, 119.73, 52.72, 12.00; IR (neat) 3086, 1671, 1624 cm^{-1}; HRMS calcd for $C_{12}H_{15}N_3O^{35}Cl$ 252.0904, found 252.0898.

2-Diethylamino-5-fluoro-3-formyl-2*H*-indazole (51). Obtained from **30** using general procedure F (light green oil, 94%): ^{1}H NMR ($CDCl_3$) δ 10.37 (s, 1H), 7.83 (dd, J = 8.5, 2,4 Hz, 1H), 7.78 (dd, J = 9.1, 4.4 Hz, 1H), 7.22 (dt, J = 8.9, 2.6 Hz, 1H), 3.42 (br s, 4H), 0.89 (t, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 181.13, 161.46 (d, J = 246 Hz), 143.01, 133.35 (d, J = 8.3 Hz), 120.50 (d, J = 9.3 Hz), 120.00 (d, J = 12 Hz), 118.54 (d, J = 27.8 Hz), 104.67 (d, J = 25 Hz), 52.70, 12.01; IR (neat) 3082, 1726, 1670, 1634 cm^{-1}; HRMS calcd for $C_{12}H_{15}N_3OF$ 236.1199, found 236.1203.

5-Carbomethoxy-2-diethylamino-3-formyl-2*H*-indazole (52). Obtained from **31** using general procedure F (yellow solid, 83%): mp 90.1−90.8 °C; ^{1}H NMR ($CDCl_3$) δ 10.43 (s, 1H), 8.97 (t, J = 1.2 Hz 1H), 8.05 (dd, J = 9.1, 1.5 Hz, 1H), 7.80 (dd, J = 9.1, 0.9 Hz, 1H), 3.95 (s, 3H), 3.39 (br s, 4H), 0.89 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 181.17, 166.94, 147.22, 134.16, 128.05, 127.28, 125.07, 118.99, 118.20, 52.72, 52.25, 12.00; IR (KBr) 3067, 3036, 1719, 1665, 1629 cm^{-1}; HRMS calcd for $C_{14}H_{18}N_3O_3$ 276.1348, found 276.1352; Anal. Calcd for $C_{14}H_{17}N_3O_3$ (275.30): C, 61.08; H, 6.22; N, 15.26. Found: C, 60.82; H, 6.23; N, 15.38.

5-Cyano-2-diethylamino-3-formyl-2*H*-indazole (20). Obtained from **14** using general procedure F (60%) along with isoindazole dimer **16** (34%). The spectral data were identical to those given above. The yield of **20** could be improved to 85% using general procedure F for 3 d at rt.

2-Diethylamino-3-formyl-5-nitro-2*H*-indazole (53). Obtained from **32** using general procedure F (yellow solid, 54%). The yield of **53** could be improved to 78% using general procedure F for 3 d at rt: mp 175.7−177.3 °C; ^{1}H NMR ($CDCl_3$)

(24) Theobold, D. W. *Tetrahedron* **1983**, *39*, 1605−1607.

δ_10.44 (s, 1H), 9.20 (d, J = 2.1 Hz, 1H), 8.25 (dd, J = 9.4, 2.3 Hz, 1H), 7.89 (d, J = 9.4 Hz, 1H), 3.46−3.37 (m, 4H), 0.91 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ_180.85, 147.03, 146.14, 135.39, 121.58, 119.74, 119.44, 118.17, 52.81, 11.96; IR (KBr) 3432, 3325, 3106, 1668, 1343 cm^{-1}; HRMS calcd for $C_{12}H_{15}N_4O_3$ 263.1144, found 263.1149. Anal. Calcd for $C_{12}H_{14}N_4O_3$ (262.26): C, 54.96; H, 5.38; N, 21.36. Found: C, 55.08; H, 5.34; N, 21.06. Isolation of a second band provided isoindazole dimer **18′** (37%) as an orange solid: mp 271−272.4 °C; ^{1}H NMR ($CDCl_3$) δ 9.07 (d, J = 1.8 Hz, 2H), 8.22 (dd, J = 9.9, 2.1 Hz, 2H), 8.06 (s, 2H), 7.81 (d, J = 9.3 Hz, 2H), 3.42 (br s, 8H), 0.96 (t, J = 6.9 Hz, 12H); ^{13}C NMR ($CDCl_3$) δ 147.77, 143.65, 137.59, 120.98, 119.56, 119.05, 118.53, 115.94, 52.61, 12.15; IR (KBr) 3076, 1618, 1327 cm^{-1}; MS (ESI) m/z 493.2 (100, M^+ + H), 391.3.1 (30, $M^+ - C_4H_{11}N_3$). Anal. Calcd for $C_{24}H_{28}N_8O_4$ (492.53): C, 58.53; H, 5.73; N, 22.75. Found: C, 58.35; H, 5.77; N, 22.55.

2-Diethylamino-3-formyl-5-methoxy-2*H*-indazole (54). Obtained from **40** using general procedure F (yellow oil, 98%): ^{1}H NMR ($CDCl_3$) δ 10.36 (s, 1H), 7.68 (d, J = 9.1 Hz, 1H), 7.48 (d, J = 2.3 Hz, 1H), 7.10 (dd, J = 9.1, 2.3 Hz, 1H), 3.90 (s, 3H), 3.40 (br s, 2H), 3.25 (br s, 2H), 0.88 (t, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 181.48, 159.04, 142.05, 132.54, 121.79, 120.86, 119.70, 97.87, 55.66, 52.60, 12.04; IR (neat) 3087, 1662, 1627, 1217 cm^{-1}; MS (ESI) m/z 270.1 (80, M^+ + Na + H), 248.1 (100, M^+ + H).

5-Acetoxy-2-diethylamino-3-formyl-2*H*-indazole (55). Obtained from **41** using general procedure F (clear oil, 86%): ^{1}H NMR ($CDCl_3$) δ 10.37 (s, 1H), 7.91 (d, J = 2.1 Hz, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.16 (dd, J = 9.1, 2.1 Hz, 1H), 3.36 (br s, 4H), 2.34 (s, 3H), 0.88 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 181.11, 169.75, 149.10, 143.88, 133.32, 123.37, 119.84, 119.66, 112.51, 52.69, 21.04, 11.96; IR (neat) 3079, 1761, 1669, 1632, 1211 cm^{-1}; MS (ESI) m/z 322.2 (100, M^+ + 2Na), 276.1 (18, M^+ + H).

Cinnoline (56). Obtained from 3,3-diethyl-1-(2-ethynylphenyl)-1-triazene[6b] using general procedure E (dark oil, 99%): ^{1}H NMR ($CDCl_3$) δ 9.33 (d, J = 5.9 Hz, 1H), 8.56 (dd, J = 8.5, 0.9 Hz, 1H), 7.92−7.83 (m, 3H), 7.80−7.74 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 150.91, 145.05, 131.18, 130.67, 129.93, 126.61, 126.06, 122.54. NMR data matched those of commercially available samples.

6-Methylcinnoline (57). Obtained from **25** using general procedure E (dark oil, 97%): ^{1}H NMR ($CDCl_3$) δ 9.23 (d, J = 5.9 Hz, 1H), 8.41 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 5.9 Hz, 1H), 7.67 (dd, J = 8.8, 1.7 Hz, 1H), 7.57 (s, 1H), 2.58 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 149.98, 145.04, 141.92, 133.22, 129.51, 126.32, 124.93, 121.99, 22.08; IR (KBr) 3053, 1627 cm^{-1}; HRMS calcd for $C_9H_9N_2$ 145.0766, found 145.0768.

6-*tert*-Butylcinnoline (58). Obtained from **26** using general procedure E (dark oil, 98%): ^{1}H NMR ($CDCl_3$) δ 9.25 (d, J = 5.9 Hz, 1H), 8.45 (d, J = 9.1 Hz, 1H), 7.94 (dd, J = 9.1, 2.1 Hz, 1H), 7.82 (d, J = 5.6 Hz, 1H), 7.70 (d, J = 1.8 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 154.53, 149.91, 145.10, 130.05, 129.28, 126.13, 122.70, 121.10, 35.48, 30.79; IR (neat) 3062, 1623 cm^{-1}; HRMS calcd for $C_{12}H_{15}N_2$ 187.1235, found 187.1233.

6-Ethynylcinnoline (59). Obtained from **27** using general procedure E (tan solid, 83%): mp 145−146 °C; ^{1}H NMR ($CDCl_3$) δ 9.34 (d, J = 5.6 Hz, 1H), 8.50 (d, J = 9.1 Hz, 1H), 7.99 (d, J = 1.5 Hz, 1H), 7.87 (dd, J = 8.8, 1.8 Hz, 1H), 7.81 (d, J = 5.5 Hz, 1H), 3.34 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 149.82, 145.66, 133.36, 130.68, 130.05, 125.65, 125.27, 121.94, 82.30, 81.17; IR (neat) 3453, 3152, 3040, 2095, 1618 cm^{-1}; HRMS calcd for $C_{10}H_7N_2$ 155.0609, found 155.0610.

6-Bromocinnoline (60). Obtained from **28** using general procedure E (yellow solid, 98%): mp 127−128.1 °C (lit.[19] mp 129−130 °C); ^{1}H NMR ($CDCl_3$) δ 9.31 (d, J = 5.9 Hz, 1H), 8.40 (d, J = 9.1 Hz, 1H), 8.02 (d, J = 2.1 Hz, 1H), 7.90 (dd, J = 9.1, 2.1 Hz, 1H), 7.77 (d, J = 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 149.33, 145.51, 134.49, 131.60, 128.71, 126.95, 126.13, 121.25; IR (KBr) 3071, 3057, 3028, 1606 cm^{-1}.

6-Chlorocinnoline (61). Obtained from **29** using general procedure E (yellow solid, 97%): mp 128.8−129.9 °C (lit.[20] mp 131−131.5 °C); ^{1}H NMR ($CDCl_3$) δ 9.30 (d, J = 6.2 Hz, 1H), 8.47 (dd, J = 9.1, 0.6 Hz, 1H), 7.82 (d, J = 2.1 Hz, 1H), 7.77 (d, J = 6.2 Hz, 1H), 7.76 (dd, J = 9.1, 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 149.16, 145.50, 137.45, 131.97, 131.66, 126.59, 125.21, 121.44; IR (KBr) 3061, 3034 cm^{-1}.

6-Fluorocinnoline (62). Obtained from **30** using general procedure E (dark semisolid oil, 90%): ^{1}H NMR ($CDCl_3$) δ 9.29 (d, J = 5.9 Hz, 1H), 8.59 (q, J = 9.4, 5.3 Hz, 1H), 7.84 (d, J = 5.9 Hz, 1H), 7.64 (td, J = 8.6, 2.7 Hz, 1H), 7.44 (dd, J = 8.3, 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 162.90 (d, J = 255.5 Hz), 148.59, 145.16, 133.41 (d, J = 9.3 Hz), 122.11 (d, J = 5.6 Hz), 121.89 (d, J = 26.8 Hz), 109.31 (d, J = 22.2 Hz); IR (neat) 3044, 1626 cm^{-1}; HRMS calcd for $C_8H_6N_2F$ 149.0515, found 149.0516.

6-Carbomethoxycinnoline (63). Obtained from **31** using general procedure E (dark solid, 96%): mp 130.4−131.2 °C; ^{1}H NMR ($CDCl_3$) δ 9.41 (d, J = 5.9 Hz, 1H), 8.60 (d, J = 2.1 Hz, 1H), 8.59 (d, J = 9.1 Hz, 1H), 8.40 (dd, J = 9.1, 1.8 Hz, 1H), 7.96 (d, J = 5.9 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.64, 151.29, 145.73, 132.16, 130.32, 129.99, 129.94, 125.15, 123.41, 52.84; IR (KBr) 3063, 1716 cm^{-1}; HRMS calcd for $C_{10}H_9N_2O_2$ 189.0664, found 189.0667.

6-Cyanocinnoline (64). Obtained from **14** using general procedure E (light orange oil that solidifies on standing, 98%): mp 129−131 °C; ^{1}H NMR ($CDCl_3$) δ 9.50 (d, J = 5.9 Hz, 1H), 8.70 (d, J = 8.8 Hz, 1H), 8.30 (d, J = 1.5 Hz, 1H), 7.99 (dd, J = 8.8, 1.8 Hz, 1H), 7.94 (dd, J = 5.9, 0.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 149.98, 146.29, 133.52, 131.70, 130.95, 125.05, 122.20, 117.40, 115.11; IR (neat) 3449, 3070, 3040, 2224 cm^{-1}; HRMS calcd for $C_9H_6N_3$ 156.0562, found 156.0563.

6-Nitrocinnoline (65). Obtained from **32** using general procedure E (light tan powder, 95%): mp 194−195 °C (lit.[21] mp 205−206 °C); ^{1}H NMR ($CDCl_3$) δ 9.54 (d, J = 6.2 Hz, 1H), 8.84 (d, J = 2.3 Hz, 1H), 8.77 (d, J = 9.1 Hz, 1H), 8.60 (dd, J = 9.4, 2.3 Hz, 1H), 8.09 (d, J = 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 150.69, 146.29, 132.49, 124.96, 124.02, 123.93, 123.72; IR (KBr) 3447, 3101, 3035, 1526, 1347 cm^{-1}.

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Supporting Information Available: ^{13}C NMR spectra for compounds **5**, **11**, **14**, **16**, **18**, **20**, **25**−**32**, **40**, **41**, **45**−**55**, and **57-65**; X-ray structures of **5** and **16**, structure refinement details, tables of atomic coordinates, thermal parameters, bond lengths, bond angles, torsion angles, and mean planes. This material is available free of charge via the Internet at http://pubs.acs.org.

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