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Synthesis of Triazafluoranthenones via Silver(I)-Mediated Nonoxidative and Oxidative Intramolecular Palladium-Catalyzed Cyclizations

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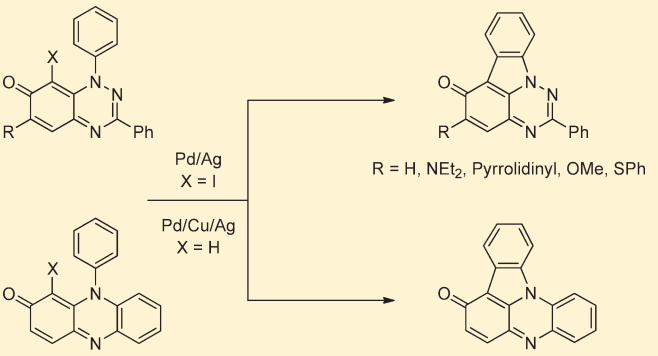
Supporting Information

ABSTRACT: Silver(I) fluoride (AgF)-mediated intramolecular nonoxidative and oxidative palladium-catalyzed cyclizations of 1,3-diphenyl- and 8-iodo-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-ones **6a** (R = H) and **7a** (R = I) afford a new 'alkaloid like' ring system 2-phenyl-6*H*-[1,2,4]triazino[5,6,1-*jk*]carbazol-6-one **8a** (triazafluoranthenone) in 86 and 100% yields, respectively. Furthermore, these cyclization protocols were used to prepare triazafluoranthenone analogues **8b**−**e** bearing dialkylamino, methoxy, and phenylsulfanyl substituents at C-5, which were also independently synthesized from triazafluoranthenone **8a** by regioselective nucleophilic addition. Similar AgF-mediated intramolecular nonoxidative and oxidative palladium-catalyzed cyclizations of 8,10-dihydro-1-iodo-10-phenylphenazin-2(7*H*)-ones **13** gave the new 'alkaloid like' ring system 8*H*-indolo[1,2,3-*mn*]phenazin-8-one **14** in 80 and 18% yields, respectively.



1. INTRODUCTION

Fluoranthene (**1**) (1,2-benzacenaphthene)[1] is an all-carbon polyarene, found naturally in coal tar[2] and as a byproduct of hydrocarbon combustion processes.[3] Several aza analogues of fluoranthene are natural product alkaloids with cytotoxic activities such as the monoaza analogue rufescine (**2**)[4] and the diaza analogues canthin-6-one (**3**)[5] and eupolauridine (**4**)[6] (Figure 1).

We recently reported some chemistry of a potentially useful heterocyclic scaffold 1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**6a**, R = H)[7] that can be prepared in good yield from 1,4-dihydro-1,3-diphenylbenzo[1,2,4]triazin-4-yl (**5**) (Blatter's radical).[8] We now report the silver-mediated palladium-catalyzed nonoxidative and oxidative intramolecular cyclization of the benzotriazinones **6** and **7** to give the first examples of triazafluoranthenes 2-phenyl-6*H*-[1,2,4]triazino[5,6,1-*jk*]carbazol-6-ones **8a**−**e** (Scheme 1).

These new triazafluoranthenes support an important quinonimine moiety which promises to lead to useful redox-sensitive biological activity. Several polycyclic quinonimines have interesting anticancer[9] and antibiotic activity.[10] For example, actinomycin D (**9**), isolated from *Streptomyces parvulus*,[9c] is a strong antitumor agent but has limited use due to side effects such as myelosuppression and cardiotoxicity; the synthetic 7-(benzylamino)-1,3,4,8-tetrahydropyrrolo[4,3,2-*de*]quinolin-8(1*H*)-one (**10**, BA-TPQ) is active against a variety of human cancer cell lines.[11] In addition, several polycyclic quinonimines such as endophenazine B (**11**) [λ_{max}(MeOH) 516 nm (log ε 3.89)],

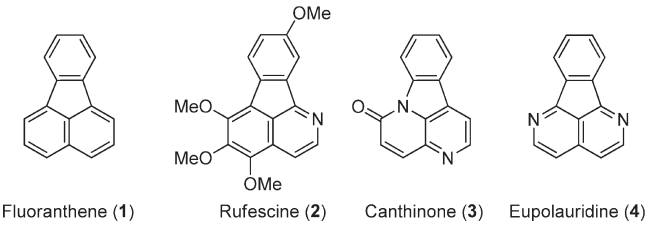
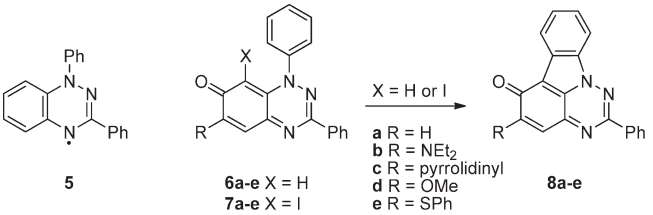


Figure 1. Structure of fluoranthene and selected aza analogues.

Scheme 1



isolated from *Streptomyces anulatus*[12] and 10-phenylphenazin-2(10*H*)-one (**12**, aposafranone),[13] are highly colored. The latter

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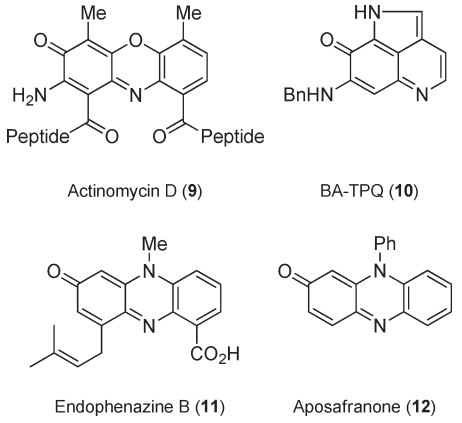

Figure 2. Selected natural and synthetic quinonimines.

have been investigated as dyes and incorporated in organic photovoltaic devices[14] (Figure 2).

2. RESULTS AND DISCUSSION

2.1. Nonoxidative Coupling of Benzotriazinones. The palladium-catalyzed nonoxidative intramolecular cyclization of benzotriazinones **6**, a type of Mizoroki−Heck reaction,[15] required access to the 8-halobenzotriazinones **7** which could be readily prepared by regioselective halogenation using the corresponding *N*-halosuccinimide.[7] Initially the noncatalytic use of $Pd(OAc)_2$ (1−2 equiv) was investigated and some useful observations were quickly made. In the absence of base, ligands, or cocatalysts, 8-iodobenzotriazinone **7a** (R = H) treated with $Pd(OAc)_2$ (2 equiv) in wet or dry DMF or DMA at 100 °C for 3−3.5 h under both air and argon atmospheres afforded the dark brown-colored triazafluoranthenone **8a** (R = H) in 65−70% yields. The use of less $Pd(OAc)_2$ (1−1.5 equiv) or DMSO, or AcOH as solvent, led to complex reaction mixtures and unreacted iodobenzotriazinone **7a**. Because the cyclization involved the loss of HI, the addition of base to the reaction mixture was examined: Performing the cylization in DMF in the presence of inorganic bases (MCO_3, $MHCO_3$, MOH, and MF where M = Cs, K, or Na) or trialkylamines Et_3N and Hünig's base led to low yielding reactions that featured considerable build up of polar baseline material (by TLC), while the use of either pyridine, DMAP, or DBU (entries 1−4, Table 1) gave triazafluoranthenone **8a** in high yields, although the use of DBU together with prolonged reaction times led to reduced yields. Interestingly, a pure sample of triazafluoranthenone **8a** in either DMF or DMA at ca. 100 °C under an argon atmosphere was stable over 16 h but decomposed rapidly in the presence of K_2CO_3, $NaHCO_3$, DMAP, Et_3N, Hünig's base, or DBU; however, under these conditions, triazafluoranthenone **8a** was stable to pyridine and could be recovered unchanged.

With these initial reaction conditions [DMF, 100 °C, pyridine or DBU as base (1 equiv)] both $Pd(Ph_3P)_4$ and $Pd(OAc)_2$ worked well while $Pd(Ph_3P)_2Cl_2$, $(dba)_3Pd_2$, $(MeCN)_2PdCl_2$, and $(dppf)PdCl_2 \cdot DCM$ did not. The stronger base DBU ($pK_b \sim 2$) (entries 2 and 4) did give faster reactions compared to the pyridine base ($pK_b \sim 8.9$) (entries 1 and 3), and in combination with $Pd(Ph_3P)_4$ (entry 4) the reaction was too fast to work up, leading to reduced product yields. Attempts to reduce the quantity of palladium catalyst led to incomplete reactions while the use of 8-bromo or 8-chlorobenzotriazinones gave mainly unreacted starting materials.

In a effort to reduce the need for stoichiometric palladium, the amine base was replaced by silver(I) fluoride (AgF) that has been shown to be beneficial in nonoxidative[16] and Hiyama couplings.[17] AgF not only acts as a mild fluoride base but has been implicated in the reoxidation of the Pd(0) to fulfill the catalytic cycle.[17a,18] Because AgF has excellent solubility in acetonitrile the reactions were re-examined in this solvent, and $Pd(Ph_3P)_2Cl_2$ was shown to be the most promising palladium source. Furthermore, the use of additional Ph_3P (10 mol %) ligand was needed to help the reactions proceed to completion. As such, when 8-iodobenzotriazinone **7a** was reacted with $Pd(Ph_3P)_2Cl_2$ (10 mol %), AgF (1.5−2.5 equiv), and Ph_3P (0.1 equiv) in MeCN at ca. 100 °C under an aerial oxygen (entries 6, 7, and 9), the desired triazafluoranthenone **8a** was obtained in good yields (75−91%), although the reactions did require ca. 1 d to come to completion. The use of less (1.5 equiv) or more (2.5 equiv) AgF was disadvantageous and led to some protodeiodination to give benzotriazinone **6a** in low yields. Attempts to lower the amount of palladium to 5 mol % in MeCN were unsuccesful (entry 10); however, after examining various modifications that included switching to alternative silver(I) salts (AgOAc and Ag_2CO_3), adding inorganic and organic bases to AgF, and introducing various alternative phosphine ligands, it was shown that switching the solvent back to DMF was beneficial (entries 11−15). In fact, in DMF the reaction required no additional phosphine ligand (entries 12, 14, and 15) and both the palladium catalyst and AgF loadings could be reduced to 5 mol % and 1.5 equiv, respectively, to afford the target triazafluoranthenone **8a** quantitatively in only 30 min (entry 15). While these optimized cyclization conditions still failed to work for the 8-bromo- and 8-chlorobenzotriazinones, they did work in most cases well for several 6-substituted benzotriazinones (entries 16−19): 6-diethylamino-, pyrrolidino-, methoxy-, and phenylthio-substituted 8-iodobenzotriazinones **7b**−**e** were readily prepared in two steps from benzotriazinone **6a** via regioselective nucleophilic addition at C-6 to give the 6-substituted benzotriazinones **6b**−**e** followed by iodination using NIS at C-8 with established protocols.[7] C-6 dialkylamino- and methoxy-substituted 8-iodobenzotriazinones **7b**−**d** cyclized faster than the parent system to give the corresponding substituted triazafluoranthenones **8b**−**d** in high yields (83−93%) (entries 16−18); however, the cyclization of 8-iodo-6-phenylthiobenzotriazione **7e** could not be driven to completion and gave only a moderate yield of cyclized product **8e** (53%) together with recovered starting material **7e** (20%) (entry 19).

2.2. Regioselective Nucleophilic Addition of Triazafluoranthenone. The 6-substituted triazafluoranthenones **8b**−**e** were also prepared directly from triazafluoranthenone **8a** by regioselective nucleophilic addition. The selectivity observed was similar to that observed for both benzotriazinone **7a**[7] and aposafranone **12**;[10a] however, nucleophilic addition to triazafluoranthenone required more forceful reaction conditions compared to those needed to functionalize benzotriazinone **7a** (Table 2).

Unlike that for benzotriazinone **7a**, nucleophilic addition of secondary dialkylamines diethylamine and pyrrolidine to triazafluoranthenone **8a** could not be achieved using stoichiometric amounts of amines but required the use of excess amines to give the 5-diethylamino- and 5-pyrrolidinotriazafluoranthenones **8b** and **8c** in 60 and 100% yields, respectively (entries 1 and 2,

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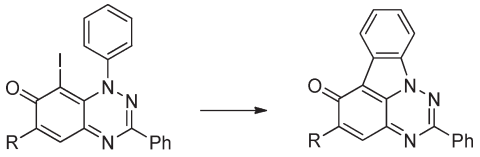
Table 1. Conversion of 8-Iodobenzotriazinones 7a−e (0.1 mmol) into Triazafluoranthenones 8a−e, with Pd Catalyst and Additives in Solvent (1 mL), under an Air Atmosphere Protected by a $CaCl_2$ Tube, at ca. 100 °C

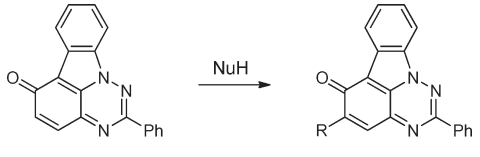


7a-e **8a-e**

entry	R	Pd catalyst (mol %)	solvent	base (equiv)	Ph_3P (equiv)	time (h)	yields (%)
1	H	$Pd(OAc)_2$ (100)	DMF	pyridine (1)	–	3	**8a** (91)
2	H	$Pd(OAc)_2$ (100)	DMF	DBU (1)	–	0.50	**8a** (93)
3	H	$Pd(Ph_3P)_4$ (100)	DMF	pyridine (1)	–	1	**8a** (95)
4	H	$Pd(Ph_3P)_4$ (100)	DMF	DBU (1)	–	0.13	**8a** (73)
5	H	$Pd(Ph_3P)_2Cl_2$ (10)	MeCN	AgF (1)	0.1	24	ir[a]
6	H	$Pd(Ph_3P)_2Cl_2$ (10)	MeCN	AgF (1.5)	0.1	24	**8a** (75)[b]
7	H	$Pd(Ph_3P)_2Cl_2$ (10)	MeCN	AgF (2)	0.1	19	**8a** (91)
8	H	$Pd(Ph_3P)_2Cl_2$ (10)	MeCN	AgF (2)	–	24	ir[a]
9	H	$Pd(Ph_3P)_2Cl_2$ (10)	MeCN	AgF (2.5)	0.1	26	**8a** (82)[c]
10	H	$Pd(Ph_3P)_2Cl_2$ (5)	MeCN	AgF (2)	0.1	24	ir[a]
11	H	$Pd(Ph_3P)_2Cl_2$ (10)	DMF	AgF (2)	0.1	2	**8a** (95)
12	H	$Pd(Ph_3P)_2Cl_2$ (10)	DMF	AgF (2)	–	2	**8a** (93)
13	H	$Pd(Ph_3P)_2Cl_2$ (5)	DMF	AgF (2)	0.1	1.50	**8a** (99)
14	H	$Pd(Ph_3P)_2Cl_2$ (5)	DMF	AgF (2)	–	2	**8a** (99)
15	H	$Pd(Ph_3P)_2Cl_2$ (5)	DMF	AgF (1.5)	–	0.50	**8a** (99)
16	NEt_2	$Pd(Ph_3P)_2Cl_2$ (5)	DMF	AgF (1.5)	–	0.33	**8b** (93)
17	pyrolidinyl	$Pd(Ph_3P)_2Cl_2$ (5)	DMF	AgF (1.5)	–	0.25	**8c** (83)
18	OMe	$Pd(Ph_3P)_2Cl_2$ (5)	DMF	AgF (1.5)	–	0.33	**8d** (89)
19	SPh	$Pd(Ph_3P)_2Cl_2$ (5)	DMF	AgF (1.5)	–	24	**8e** (53)[d]

[a] ir = incomplete reaction. [b] 1,3-Diphenylbenzotriazinone **6a** (6%) recovered. [c] 1,3-Diphenylbenzotriazinone **6a** (3%) recovered. [d] 8-Iodo-6-(phenylthio)benzotriazinone **7e** (20%) recovered.

Table 2. Regioselective Nucleophilic Addition to Triazafluoranthenone 8a



8a **8b,c and e**

entry	R	reagent (equiv)	base (equiv)	solvent	temp (°C)	time (h)	yields (%)
1	NEt_2	Et_2NH (48)	–	EtOH	20	22	**8b** (60)
2	pyrrolidinyl	pyrrolidine (60)	–	EtOH	20	4	**8c** (100)
3	OMe	2N MeONa (1)	–	MeOH	20	5	–[a]
4	OMe	2N MeONa (10)	–	MeOH	60	2	–[a]
5	OH	KOH (2)	–	THF/H_2O 10:1	20	0.5	–[a]
6	SPh	PhSH (2)	i-Pr_2NEt (1.1)	DCM	20	2.5	**8e** (100)

[a] No trace of desired product: only intractable polar materials at baseline on TLC.

Table 2). The reaction of triazafluoranthenone **8a** with alkoxide [2 N MeONa (1 or 10 equiv) at 20 to 60 °C] or with hydroxide [KOH (2 equiv) at 20 °C] gave only intractable polar materials (baseline on TLC) (entries 3−5). This reactivity differed considerably from the analogous nucleophilic addition of methoxide or hydroxide to benzotriazinone **7a** which worked well.[7] While

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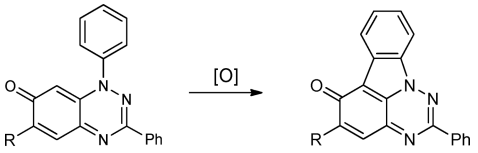
Table 3. Oxidative Cyclization of Benzotriazinones 6a−e (0.1 mmol) into Triazafluoranthenones 8a−e Using $Pd(OAc)_2$, $Cu(OTf)_2$, and AgF in DMSO at ca. 100 °C under O_2 Atmosphere



6a-e **8a-e**

entry	R	$Pd(OAc)_2$ (equiv)	$Cu(OTf)_2$ (equiv)	AgF (equiv)	time (h)	yields of **8** (%)	yields of **6** (%)
1	H	1.0	–	–	4	**8a** (78)	**6a** (0)
2	H	1.0	–	–	12[a]	[b]	[b]
3	H	0.5	–	–	12.5	**8a** (40)	**6a** (31)
4	H	0.1	2	–	7	**8a** (45)	**6a** (54)
5	H	0.1	2	1	8	**8a** (56)	**6a** (42)
6	H	0.1	–	2	18	[c]	[c]
7	H	0.1	2	2	7	**8a** (79)	**6a** (19)
8	H	0.1[d]	2	2	7	**8a** (86)	**6a** (6)
9	H	0.15[d]	2	2	7	**8a** (86)	**6a** (7)
10	H	0.1[d]	3	2	7	**8a** (70)	**6a** (15)
11	H	0.1[d]	2	3	7	**8a** (55)	**6a** (26)
12	NEt_2	0.1[d]	2	2	2	**8b** (67)	**6b** (0)
13	pyrrolidinyl	0.1[d]	2	2	2.5	**8c** (76)	**6c** (0)
14	OMe	0.1[d]	2	2	18	**8d** (19)	**6d** (28)
15	SPh	0.1[d]	2	2	14.5	**8e** (15)	**6e** (44)

[a] In air atmosphere. [b] Decomposition: baseline on TLC. [c] Traces of triazafluoranthenone **8a**, mainly starting material recovered. [d] $Pd(OAc)_2$ freshly recrystallized from AcOH.

the direct regioselective nucleophilic addition of oxygen nucleophiles to triazafluoranthenone **8a** was not successful, we note that these compounds were readily accessible via the above alternative nonoxidative intramolecular cyclization route (entry 18, Table 1). Nevertheless, direct addition favored the introduction of sulfur substituents, because treating the triazafluoranthenone **8a** with thiophenol (2 equiv) in the presence of Hünig's base (1.1 equiv) gave the 5-(phenylthio)triazafluoranthenone **8e** in quantitative yield (entry 6, Table 2) which could not be prepared readily via the nonoxidative intramolecular cyclization route (entry 19, Table 1). These two stratergies were therefore complementary.

We speculate that the observed differences in the ease of nucleophilic addition to the two quinonimines, benzotriazinone **6a** and triazafluoranthenone **8a**, are owed to the ring fusion in the latter. π-Orbital delocalization of the fused ring's electron density could make the quinonimine moiety less electrophilic toward nucleophiles. Furthermore, the planarity of the arene on triazine N-1 can assist the withdrawal of electron density from that nitrogen and thus reduce the zwitterionic resonance contribution, making the carbonyl more prone to attack by hard nucleophiles such as alkoxides.

2.3. Oxidative Coupling of Benzotriazinones. Intramolecular oxidative cyclizations that involve the formation of a new C−C bond have been used for the synthesis of fused heterocycles such as dibenzofurans and carbazoles.[19] Traditionally, the reaction conditions invoked the use of stoichiometric $Pd(OAc)_2$ (1−1.5 equiv), in AcOH, at ca. 100 °C; however, recent efforts to reduce the palladium loading have included the use of co-oxidants such as O_2,[19f] $Cu(OAc)_2$,[20] and *tert*-butyl hydroperoxide.[21]

Oxidative cyclization of benzotriazinones **6** could provide a shorter route to the triazafluoranthenones **8** and bypass the above C-8 iodination step. Treatment of the benzotriazinone **6a** with $Pd(OAc)_2$ (1.5 equiv) in AcOH at ca. 100 °C led only to intractable polar products (baseline on TLC). Interestingly, these conditions can lead to degradation of related oxygenated carbazoles[22] and treatment of triazafluoranthenone **8a** under similar reaction conditions for 1 d also led to consumption and degradation of the tetracycle. In the absence of $Pd(OAc)_2$, however, the triazafluoranthenone **8a** was stable in AcOH at ca. 100 °C. In light of this, the stability of triazafluoranthenone **8a** in the presence of catalytic $Pd(OAc)_2$ (10 mol %) in various solvents (AcOH, DMF, DMSO, and PhMe) at ca. 100 °C under aerial oxygen was screened, and DMSO was found to afford the least decomposition (by TLC). Interestingly, DMSO has been reported to prevent the precipitation of the Pd(0) before further reoxidation[23] and to act as ligand to support the direct oxidation of Pd(0) to Pd(II).[24] Further optimizations were conducted in DMSO (Table 3).

Increasing the $Pd(OAc)_2$ to 1 equiv under an O_2 atmosphere led to complete consumption of the starting material in 4 h and gave triazafluoranthenone **8a** in 78% yield (entry 1, Table 3); however, in an aerial oxygen the reaction was slow, and after 12 h only an intractable mixture was obtained (baseline on TLC) (entry 2). The use of less palladium catalyst (0.5 equiv) in the presence of oxygen failed to consume the benzotriazinone **6a** (entry 3). Similar efforts to catalyze the reaction by using

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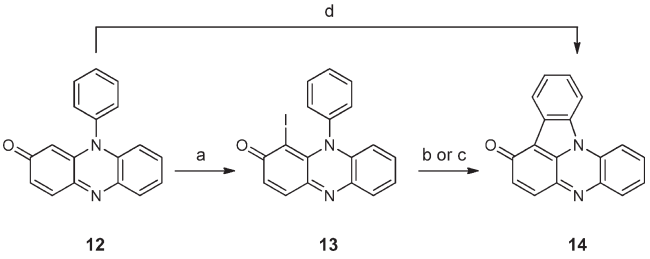
$Cu(II)(OAc)_2 \cdot H_2O$ (2.5 equiv), 1,4-benzoquinone, or *tert*-butyl hydroperoxide as co-oxidants or by switching the solvent (dioxane, AcOH, DMF, and DMA) or the palladium sources [$(dppf)PdCl_2 \cdot DCM$, $(dba)_3Pd_2$, $PdCl_2$, $(MeCN)_2PdCl_2$, PdO, $(PhP_3)_4Pd$, or Pd/C 5 wt %] failed to provide better results. Nevertheless, some success was observed with the use of $Cu(II)(OAc)_2 \cdot H_2O$ in DMSO in the presence of O_2, as such a range of copper salts were examined. Treating benzotriazinone **6a** with $Pd(OAc)_2$ (10 mol %) in DMSO at ca. 100 °C with either $CuSO_4$ or $CuCl_2 \cdot 2H_2O$ (2 equiv) in a O_2 athmosphere gave after 1 d only a trace of triazafluoranthenone **8a**; however, the use of $Cu(OTf)_2$ (2 equiv) gave the desired product **8a** in a 45% yield with 54% of recovered starting material (entry 4, Table 3). In light of our successful use of AgF in the nonoxidative coupling and also because silver(I) salts have been shown to be beneficial in oxidative couplings,[25] we subsequently introduced some AgF (1 equiv) to the reaction mixture and saw an immediate improvement, obtaining the triazafluoranthenone **8a** in a 56% yield with 42% of recovered starting material (entry 5). Increasing the amount of AgF (up to 2 equiv) led to improved yields of triazafluoranthenone **8a** (up to 79%, entry 7), although some benzotriazinone **6a** (19%) remained unreacted even after 7 h. More importantly, in the absence of $Cu(OTf)_2$, the use of AgF (2 equiv) and palladium catalyst gave only traces of the desired product after 18 h (entry 6), supporting the need for both Cu and Ag reagents. Using freshly recrystallized $Pd(OAc)_2$ improved the consumption of benzotriazinone **6a** and raised the yields of triazafluoranthenone **8a** to 86%, leaving only some benzotriazinone **6a** (6%) unreacted (entry 8). Marginal increases of the amount of palladium catalyst (entry 9), Cu (entry 10), and Ag (entry 11) used did not improve these yields and in some cases were detrimental. With these improved conditions, catalyst (0.1 equiv), $Cu(OTf)_2$ (2 equiv), AgF (2 equiv), O_2 atmosphere, and 100 °C, a re-examination of the solvents (PhMe, AcOH, DMF, and DMA) merely confirmed that DMSO was needed because PhMe and AcOH gave no reaction while DMF and DMA only gave a trace of triazafluoranthenone **8a**.

Again, the optimized conditions [freshly recrystallized $Pd(OAc)_2$ (10 mol %), AgF (2 equiv), and $Cu(OTf)_2$ (2 equiv)] were screened for 6-substituted benzotriazinone **6b**−**e**. 6-Diethylamino- and 6-pyrrolidinobenzotriazinone **6b** and **6c** gave the corresponding 5-substituted triazafluoranthenone **8b** and **8c** in a 67 and 76% yield, respectively, in a shorter reaction time if compared with the parent system (entries 12 and 13, Table 3). Unfortunately, the oxidative intramolecular cyclizations of 6-methoxy- and 6-(phenylthio)benzotriazinone **6d** and **6e** could not be driven to completion and gave the desired 5-methoxy- and 5-(phenylthio)triazafluoranthenones **8d** and **8e** in low yields (19 and 15%, respectively) (entries 14 and 15).

2.4. Preparation of 8*H*-Indolo[1,2,3-*mn*]phenazin-8-one (14). Because significant structural similarities exist between the benzotriazinone **6a** and 10-phenylphenazin-2(10*H*)-one **12** (aposafranone) we examined the behavior of the latter in the above intramolecular cyclizations. The anticipated cyclization could lead to the new 8*H*-indolo[1,2,3-*mn*]phenazin-8-one **14** system (Scheme 2). Regioselective iodination at C-1 occurred readily upon treating a solution of aposafranone **12** with NIS (2 equiv) at ca. 20 °C. 1-Iodoaposafranone **13** when treated with $Pd(OAc)_2$ (1.25 equiv) and pyridine (1 equiv) in DMF at 100 °C readily cyclized to the desired indolophenazinone **14** in a 78% yield. Similarly, treatment of 1-iodoaposafranone **13** with $Pd(Ph_3P)_2Cl_2$ (5%) and AgF (1.5 equiv) in DMF at 100 °C gave the indolophenazinone **14** in a 80% yield (Scheme 2). The oxidative cyclization of aposafranone **12** could not, however, be performed using catalytic palladium, and at best the use of $Pd(OAc)_2$ (1 equiv) in DMSO at ca. 100 °C under an oxygen atmosphere gave after 1 d the desired cyclized product **14** in only 18% yield.

Scheme 2



The indolophenazinone **14** was pink-red in color. Differential scanning calorimetry (DSC) under an argon atmosphere revealed that an exothermic reaction occurred in the solid state with onset and peak temperatures of 227 and 229 °C, respectively. As such, no melting point could be recorded. Low resolution (EI) mass spectrometry (*m*/*z* 270 Da, 100%) and elemental analysis (C, 80.05; H, 3.8; N, 10.3%) supported a molecular formula of $C_{18}H_{10}N_2O$. The UV/vis spectra showed a low energy absorption at λ_{max}/nm 495 (log ε 2.91) supporting extended conjugation. The compound showed a mild pink fluorescence to the naked eye when in solution.

3. CONCLUSIONS

8-Iodobenzotriazinones **7a**−**e** undergo palladium-catalyzed nonoxidative intramolecular coupling in the presence of AgF to give the 6*H*-[1,2,4]triazino[5,6,1-*jk*]carbazol-6-ones **8a**−**e** (triazafluorantheones) in moderate to excellent yields while palladium-catalyzed oxidative intramolecular cyclization of benzotriazinones **6a**−**e** required a combination of co-oxidants such as AgF and $Cu(OTf)_2$ in an oxygen atomosphere. Both methods were used to prepare 8*H*-indolo[1,2,3-*mn*]phenazin-8-one (**14**). Additionally, triazafluoranthenone **8a** was shown to suffer regioselective nucleophilic addition at C-5 by amines and thiols but gave intractable polar mixtures with oxygen nucleophiles.

4. EXPERIMENTAL SECTION

4.1. General Methods and Materials. Solvents: DCM was freshly distilled from CaH_2 under argon. DMF was azeotropically distilled with PhH and then distilled under vacum from anhydrous $MgSO_4$ and stored over 4 Å molecular sieves. Acetonitrile was distilled over CaH_2. Reactions were protected by $CaCl_2$ drying tubes. Decomposition points (decomp) and mp >250 °C were determined using a TA Instruments DSC Q1000 with samples hermetically sealed in aluminum pans under an argon atmosphere, using heating rates of 5 °C/min. Anhydrous Na_2SO_4 was used for drying organic extracts, and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass-backed thin layer chromatography (TLC) plates (Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using silica gel 60 (less than 0.063 mm). Melting points were determined using a hotstage microscope apparatus. Solvents used for recrystallization are indicated after the melting point. Inflections

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in the UV spectra are identified by the abbreviation "inf". FTIR spectra were recorded using a Ge ATR accessory and strong, medium and weak peaks are represented by s, m, and w respectively. ^{1}H NMR spectra were recorded at either 300 or 500 MHz and ^{13}C NMR spectra were recorded at either 75 and 125 MHz, respectively. DEPT 135 or APT NMR studies identified quaternary and tertiary carbons, which are indicated by (s) and (d) notations, respectively. Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Low resolution (EI) mass spectra were recorded on a GCMS with direct inlet probe. 1,3-Diphenylbenzo[*e*]-[1,2,4]-triazin-7(1*H*)-one (**6a**),[8a] 6-hydroxy-1,3-diphenylbenzo[*e*][1,2,4]-triazin-7(1*H*)-one (**6f**),[7] 6-(phenylthio)benzo[*e*][1,2,4]triazin-7(1*H*)-one (**6e**),[7] 8-iodo-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**7a**),[7] and 10-phenylphenazin-2(10*H*)-one (**12**) (aposafranone)[13b] were prepared according to literature procedures.

4.2. Preparation of C-6 Substituted Benzotriazinones. *4.2.1. 6-(Diethylamino)-1,3-diphenylbenzo[e][1,2,4]triazin-7(1H)-one (**6b**).* A mixture of 1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**6a**) (36.2 mg, 0.12 mmol) with diethylamine (0.5 mL, 4.81 mmol) was stirred to ca. 20 °C for 25 h until no starting material remained (TLC). The reaction mixture was then diluted (DCM) and washed (5% HCl) to remove unreacted amine. The organic layer was separated, dried (Na_2SO_4), filtered, and adsorbed onto silica. Chromatography (*t*-BuOMe/hexane/DCM, 1:3:6) gave the title compound **6b** (20.4 mg, 46%) as orange needles, mp >300 °C (from EtOH); R_f 0.30 (*t*-BuOMe/hexane, 3:1); (found: C, 74.4; H, 5.9; N, 15.2. $C_{23}H_{22}N_4O$ requires C, 74.6; H, 6.0; N, 15.1%); λ_{max}(DCM)/nm 276 inf (log ε 3.55), 301 (3.67), 321 inf (3.49), 351 inf (3.07), 365 inf (2.96), 435 inf (3.49), 453 (3.56); ν_{max}/cm^{-1} 2970w, 2928w, 1593w, 1585 m, 1537s, 1504 m, 1493 m, 1481 m, 1449 m, 1408w, 1395w, 1377w, 1352w, 1315 m, 1290w, 1265 m, 1173w, 1152w, 1128w, 1082w, 1069w, 1026w, 1003w, 988 m, 926w, 887w, 837w, 822 m, 779 m, 745w; δ_H(300 MHz; $CDCl_3$) 8.28−8.24 (2H, m, Ar *H*), 7.58−7.50 (5H, m, Ar *H*), 7.48−7.42 (3H, m, Ar *H*), 6.70 (1H, s, Ar *H*), 6.02 (1H, s, Ar *H*), 3.82 (4H, q, *J* 6.9, NCH_2), 1.35 (6H, t, *J* 7.0, CH_3); δ_C(75 MHz; $CDCl_3$) 177.0 (s), 153.5 (s), 152.4 (s), 152.2 (s), 142.2 (s), 135.8 (s), 135.3 (s), 130.3 (d), 130.2 (d), 130.0 (d), 129.0 (d), 127.3 (d), 126.4 (d), 101.6 (d), 98.0 (d), 47.8 (NCH_2), 13.6 (CH_3); *m*/*z* (EI) 371 (M^+ + 1, 12%), 370 (M^+, 37), 341 (100), 327 (14), 313 (4), 299 (5), 271 (4), 185 (3), 180 (7), 169 (4), 144 (4), 118 (8), 103 (20), 91 (5), 77 ($C_6H_5^+$, 40), 63 (5), 51 (15).

*4.2.2. 1,3-Diphenyl-6-(pyrrolidin-1-yl)benzo[e][1,2,4]triazin-7(1H)-one (**6c**).* Addition of pyrrolidine (0.4 mL, 3.4 mmol) to 1,3-diphenylbenzo-[*e*][1,2,4]triazin-7(1*H*)-one (**6a**) (30 mg, 0.1 mmol) at ca. 20 °C resulted a very rapid reaction (1 min) and consumption of starting material (TLC). The reaction mixture was then diluted with DCM (15 mL) and washed with 5% HCl (10 mL) to remove unreacted amine. The organic layer was separated, dried (Na_2SO_4) and evaporated in vacuo to afford the title compound **6c** (37 mg, 100%) as orange needles, mp 254−255 °C (from cyclohexane); R_f 0.47 (*t*-BuOMe); (found: C, 74.9; H, 5.6; N, 15.3. $C_{23}H_{20}N_4O$ requires C, 75.0; H, 5.5; N, 15.2%); λ_{max}(DCM)/nm 230 (log ε 3.24), 277 inf (3.45), 300 (3.56), 317 inf (3.43), 348 (2.98), 366 inf (2.88), 452 (3.51); ν_{max}/cm^{-1} 3067w (Ar CH), 2947w, 2930w, 1585 m, 1535s, 1493 m, 1483 m, 1449 m, 1406w, 1395 m, 1371 m, 1312 m, 1292 m, 1229w, 1175w, 1132w, 1069w, 1026w, 1003w, 993w, 916 m, 839 m, 814 m, 799w, 772 m; δ_H(300 MHz; $CDCl_3$) 8.27−8.24 (2H, m, Ar *H*), 7.58−7.48 (5H, m, Ar *H*), 7.46−7.42 (3H, m, Ar *H*), 6.53 (1H, s, Ar *H*), 5.99 (1H, s, Ar *H*), 4.34 (2H, br s, NCH_2), 3.53 (2H, br s, NCH_2), 1.98 (4H, s, CH_2); δ_C(75 MHz; $CDCl_3$) one Ar *C*H missing 176.6 (s), 152.5 (s), 152.1 (s), 152.0 (s), 141.9 (s), 135.7 (s), 135.4 (s), 129.7 (d), 129.5 (d), 128.5 (d), 126.8 (d), 126.0 (d), 100.8 (d), 96.7 (d), 51.9 (CH_2), 50.9 (CH_2), 27.1 (CH_2), 23.7 (CH_2); *m*/*z* (EI) 369 (M^+ + 1, 28%), 368 (M^+, 100), 339 (9), 325 (10), 313 (51), 299 (16), 285 (4), 236 (4), 184 (8), 160 (7), 132 (4), 118 (4), 103 (8), 91 (5), 77 ($C_6H_5^+$, 51), 63 (5), 51 (15).

*4.2.3. 6-Methoxy-1,3-diphenylbenzo[e][1,2,4]triazin-7(1H)-one (**6d**).* To a stirred solution of 1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**6a**) (30 mg, 0.1 mmol) in MeOH (2 mL) was added 2 N MeONa (0.1 mL, 0.2 mmol), and the reaction mixture was heated at reflux for 4 h. TLC (*t*-BuOMe) showed the absence of the starting material and the presence of a new red-purple compound. The mixture was diluted with DCM (10 mL) and adsorbed onto silica gel. Dry flash chromatography (*t*-BuOMe) gave the title compound **6d** (11.4 mg, 35%) as red needles, mp 226−228 °C (from benzene); R_f 0.14 (*t*-BuOMe); (found: C, 72.7; H, 4.6; N, 12.5. $C_{20}H_{15}N_3O_2$ requires C, 72.9; H, 4.6; N, 12.8%); λ_{max}(DCM)/nm 246 (log ε 3.29), 312 (3.58), 358 inf (2.92), 381 inf (2.58), 520 (2.68); ν_{max}/cm^{-1} 3063w (Ar CH), 1611 m, 1587 m, 1555s, 1516 m, 1493 m, 1456w, 1439w, 1385w, 1352w, 1315w, 1285 m, 1244s, 1209 m, 1184 m, 1157w, 1134w, 1067w, 1026w, 999w, 980w, 926w, 856 m, 843 m, 820 m, 773 m, 741 m; δ_H(300 MHz; $CDCl_3$) 8.30−8.27 (2H, m, Ar *H*), 7.61−7.55 (5H, m, Ar *H*), 7.48−7.46 (3H, m, Ar *H*), 7.00 (1H, s, Ar *H*), 6.21 (1H, s, Ar *H*), 4.09 (3H, s, OCH_3); δ_C(75 MHz; $CDCl_3$) 175.1 (s), 164.1 (s), 155.2 (s), 151.5 (s), 141.5 (s), 135.3 (s), 134.4 (s), 130.6 (d), 130.3 (d), 130.1 (d), 128.9 (d), 126.9 (d), 125.9 (d), 104.3 (d), 97.1 (d), 57.0 (OCH_3); *m*/*z* (EI) 330 (M^+ + 1, 23%), 329 (M^+, 91), 300 (100), 286 (10), 283 (5), 271 (4), 195 (3), 180 (5), 168 (7), 155 (4), 144 (5), 128 (4), 116 (6), 103 (7), 89 (4), 77 ($C_6H_5^+$, 45), 63 (4), 51 (12).

*4.2.5. 6-Methoxy-1,3-diphenylbenzo[e][1,2,4]triazin-7(1H)-one (**6d**).* To a stirred solution of 6-hydroxy-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**6f**)[7] (31.5 mg, 0.1 mmol) in MeCN (1 mL) were added MeI (24 μL, 0.4 mmol) and Hünig's base (137 μL, 0.8 mmol). The mixture was stirred at ca. 20 °C for 29 h. TLC (*t*-BuOMe) showed the absence of the starting material and the presence of a faster running compound. Dry flash chromatography (*t*-BuOMe/MeOH, 9:1) of the residue gave the title compound **6d** (26 mg, 78%) as red needles, identical to that described above.

4.3. C-8 Iodination of C-6 Substituted Benzotriazinones 6b−d. *4.3.1. 6-(Diethylamino)-8-iodo-1,3-diphenylbenzo[e][1,2,4]-triazin-7(1H)-one (**7b**).* To a stirred solution of 6-(diethylamino)-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**6b**) (37 mg, 0.1 mmol) in DCM (1 mL) was added NIS (22.4 mg, 0.1 mmol), and the mixture was stirred at ca. 20 °C for 6 h. TLC (*t*-BuOMe/hexane 3:1) showed the absence of the starting material and the presence of a new less polar red compound. The solvent was evaporated in vacuo and the residue crystallized to give the title compound **7b** (36 mg, 73%) as red cubes, mp 185−187 °C (from DCM/MeOH 1:2); R_f 0.41 (*t*-BuOMe); (found: C, 55.6; H, 4.3; N, 11.2. $C_{23}H_{21}IN_4O$ requires C, 55.7; H, 4.3; N, 11.3%); λ_{max}(DCM)/nm 246 (log ε 3.28), 310 (3.42), 334 (3.24), 375 inf (2.84), 463 (3.36); ν_{max}/cm^{-1} 2972w, 2930w, 1601 m, 1585 m, 1557s, 1528 m, 1487s, 1468 m, 1456 m, 1443 m, 1406 m, 1375w, 1352 m, 1312 m, 1292 m, 1260 m, 1231w, 1192w, 1169w, 1152 m, 1125w, 1080w, 1067w, 1028w, 1001w, 982 m, 912 m, 862w, 824 m, 785w, 768 m; δ_H(300 MHz, $CDCl_3$) 8.29−8.26 (2H, m, Ar *H*), 7.55−7.53 (4H, m, Ar *H*), 7.50−7.44 (4H, m, Ar *H*), 6.67 (1H, s, Ar *H*), 3.77 (4H, q, *J* 6.9, NCH_2), 1.39 (6H, t, *J* 7.0, CH_3); δ_C(75 MHz, $CDCl_3$) 173.20 (s), 153.9 (s), 151.9 (s), 150.5 (s), 142.9 (s), 137.5 (s), 135.1 (s), 130.2 (d), 129.2 (d), 129.1 (d), 128.7 (d), 127.2 (d), 127.1 (d), 100.4 (d), 74.1 (s), 47.6 (NCH_2), 13.3 (CH_3); *m*/*z* (EI) 497 (M^+ + 1, 19%), 496 (M^+, 68), 467 (78), 453 (4), 419 (3), 370 (38), 341 (100), 327 (14), 313 (5), 298 (10), 271 (4), 254 (10), 180 (16), 168 (7), 143 (4), 127 (8), 118 (9), 104 (13), 89 (5), 77 ($C_6H_5^+$, 74), 67 (8), 51 (17).

*4.3.2. 8-Iodo-1,3-diphenyl-6-(pyrrolidin-1-yl)benzo[e][1,2,4]triazin-7(1H)-one (**7c**).* To a stirred solution of 1,3-diphenyl-6-(pyrrolidin-1-yl)benzo[*e*][1,2,4]triazin-7(1*H*)-one (**6c**) (37 mg, 0.1 mmol) in DCM (1 mL) was added NIS (22.4 mg, 0.1 mmol), and the mixture was stirred at ca. 20 °C for 7 h. TLC (*t*-BuOMe/hexane, 3:1) showed the absence of the starting material and the presence of a new less polar red compound. The solvent was evaporated in vacuo and the residue crystallized to give the title compound **7c** (32.4 mg, 65%) as red needles, mp >300 °C (from

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DCM/MeOH, 1:2); R_f 0.61 (*t*-BuOMe/hexane, 3:1); (found: C, 55.7; H, 4.0; N, 11.3. $C_{23}H_{19}IN_4O$ requires C, 55.9; H, 3.9; N, 11.3%); λ_{max}(DCM)/nm 212 (log ε 4.30), 305 (3.56), 372 inf (3.10), 458 (3.41); ν_{max}/cm^{-1} 3065w (Ar CH), 2970w, 2920w, 2853w, 1601 m, 1585 m, 1568s, 1524s, 1489s, 1470 m, 1454 m, 1441s, 1400 m, 1371 m, 1342w, 1302s, 1223w, 1196w, 1171w, 1123w, 1105w, 1088w, 1069w, 1047w, 1026w, 1001w, 991w, 934 m, 874w, 839w, 814 m; δ_H(300 MHz, $CDCl_3$) 8.28−8.25 (2H, m, Ar *H*), 7.57−7.52 (4H, m, Ar *H*), 7.48−7.42 (4H, m, Ar *H*), 6.51 (1H, s, Ar *H*), 4.34 (2H, br s, NCH_2), 3.56 (2H, br s, NCH_2), 2.02 (4H, br s, CH_2); δ_C(75 MHz, $CDCl_3$) 173.4 (s), 154.0 (s), 152.0 (s), 149.0 (s), 143.1 (s), 137.8 (s), 135.2 (s), 130.2 (d), 129.2 (d), 129.1 (d), 128.7 (d), 127.3 (d), 127.1 (d), 100.3 (d), 73.3 (s), 52.6 (NCH$_2$), 51.2 (NCH$_2$), 29.9 (CH$_2$), 26.9 (CH$_2$); *m*/*z* (EI) 495 (M^+ + 1, 13%), 494 (M^+, 52), 451 (2), 368 (100), 363 (6), 339 (22), 325 (12), 313 (50), 299 (17), 286 (8), 271 (5), 254 (11), 247 (6), 236 (8), 184 (7), 180 (10), 168 (10), 160 (7), 152 (5), 140 (9), 127 (9), 116 (9), 103 (13), 91 (6), 77 ($C_6H_5^+$, 98), 63 (7), 51 (24).

*4.3.3. 8-Iodo-6-methoxy-1,3-diphenylbenzo[e][1,2,4]triazin-7(1H)-one (**7d**).* To a stirred solution of 6-methoxy-1,3-diphenylbenzo[*e*]-[1,2,4]triazin-7(1*H*)-one (**6d**) (50 mg, 0.15 mmol) in MeOH (3 mL) was added NIS (34 mg, 0.15 mmol), and the mixture was stirred at ca. 20 °C for 7 h. TLC (*t*-BuOMe) showed the absence of the starting material and the presence of a new less polar red compound. The solvent was evaporated in vacuo and the residue crystallized to give the title compound **7d** (58.1 mg, 84%) as purple needles, mp 227−229 °C (from DCM/MeOH, 1:2); R_f 0.24 (*t*-BuOMe/hexane, 3:2); (found: C, 52.6; H, 2.9; N, 9.1. $C_{20}H_{14}IN_3O_2$ requires C, 52.8; H, 3.1; N, 9.2%); λ_{max}(DCM)/nm 251 (log ε 3.37), 324 (3.45), 371 inf (3.04), 537 (2.70); ν_{max}/cm^{-1} 3022w (Ar CH), 2922w, 2853w, 1593s, 1580 m, 1541 m, 1501 m, 1479s, 1454s, 1438 m, 1375w, 1348 m, 1310w, 1285w, 1246s, 1223s, 1188w, 1177 m, 1159w, 1130 m, 1088w, 1072w, 1020w, 1005w, 978w, 903 m, 843 m, 835 m, 785 m, 773 m; δ_H(300 MHz, $CDCl_3$) 8.30−8.27 (2H, m, Ar *H*), 7.58−7.47 (8H, m, Ar *H*), 6.98 (1H, s, Ar *H*), 4.09 (3H, s, OCH_3); δ_C(75 MHz, $CDCl_3$) 172.3 (s), 160.7 (s), 155.8 (s), 151.0 (s), 142.5 (s), 137.0 (s), 133.8 (s), 130.9 (d), 129.6 (d), 129.3 (d), 128.9 (d), 127.0 (d), 127.0 (d), 105.1 (d), 73.3 (s), 57.2 (OCH$_3$); *m*/*z* (EI) 456 (M^+ + 1, 9%), 455 (M^+, 41), 426 (4), 363 (4), 328 (84), 313 (24), 310 (14), 300 (25), 285 (21), 271 (4), 257 (4), 218 (5), 197 (3), 182 (4), 168 (17), 164 (11), 154 (15), 143 (11), 140 (17), 126 (22), 115 (13), 103 (15), 89 (6), 77 ($C_6H_5^+$, 100), 63 (10), 51 (33).

*4.3.4. 8-Iodo-1,3-diphenyl-6-(phenylthio)benzo[e][1,2,4]triazin-7(1H)-one (**7e**).* To a stirred solution of 6-(phenylthio)benzo[*e*][1,2,4]triazin-7(1*H*)-one (**6e**)[7] (40.7 mg, 0.1 mmol) in MeOH (1 mL) was added NIS (22.4 mg, 0.1 mmol), and the mixture was stirred at ca. 20 °C for 18 h. TLC (*t*-BuOMe/hexane, 2:1) showed the absence of the starting material and the presence of a new less polar brown compound. The solvent was evaporated in vacuo and the residue crystallized to give the title compound **7e** (44.6 mg; 84%) as brown needles, mp 218−223 °C (from DCM/MeOH, 1:1); R_f 0.86 (*t*-BuOMe/hexane, 3:1); (found: C, 56.3; H, 2.9; N, 7.7. $C_{25}H_{16}IN_3OS$ requires C, 56.3; H, 3.0; N, 7.9%); λ_{max}(DCM)/nm 218 (log ε 4.23), 267 (3.34), 350 (3.33), 424 (2.99), 547 (1.41); ν_{max}/cm^{-1} 3055w (Ar CH), 2922w, 2849w, 1593 m, 1566w, 1524w, 1501w, 1479s, 1451 m, 1439 m, 1418w, 1364w, 1310w, 1281w, 1254w, 1213w, 1184w, 1136w, 1069w, 1024w, 1011 m, 972w, 947w, 928w, 912w, 883 m, 849w, 829w, 816w, 808w, 783w, 775 m; δ_H(300 MHz, $CDCl_3$) 8.21−8.17 (2H, m, Ar *H*), 7.68−7.65 (2H, m, Ar *H*), 7.59−7.50 (8H, m, Ar *H*), 7.46−7.41 (3H, m, Ar *H*), 6.87 (1H, s, Ar *H*); δ_C(75 MHz, $CDCl_3$) two Ar CH missing 174.1 (s), 157.5 (s), 152.8 (s), 151.2 (s), 142.4 (s), 137.8 (s), 135.8 (d), 133.6 (s), 130.9 (d), 130.5 (d), 129.7 (d), 129.4 (s), 129.3 (d), 128.9 (d). 127.0 (d), 121.3 (d), 72.2 (s); *m*/*z* (EI) 534 (M^+ + 1, 12%), 533 (M^+, 33), 406 (96), 378 (5), 328 (16), 275 (12), 247 (6), 197 (7), 169 (10), 148 (4), 145 (6), 121 (12), 109 (9), 103 (7), 93 (7), 89 (8), 77 ($C_6H_5^+$, 100), 65 (7), 51 (36).

4.4. Nonoxidative Coupling. *4.4.1. 2-Phenyl-6H-[1,2,4]triazino-[5,6,1-jk]carbazol-6-one (**8a**).* To a stirred solution of 8-iodo-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**7a**) (42.5 mg, 0.1 mmol) in DMF (1 mL) were added $Pd(Ph_3P)_2Cl_2$ (3.5 mg, 0.005 mmol, 5 mol %) and AgF (19 mg, 0.15 mmol), and the mixture was heated at 100 °C for 30 min. TLC (*t*-BuOMe/hexane, 3:1) showed the presence of a new more polar compound and the absence of the starting material. The reaction mixture was diluted with Et_2O (5 mL) and washed with H_2O (5 mL). The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo. Dry flash chromatography (*t*-BuOMe/hexane, 1:2) of the residue gave the title compound **8a** (29.5 mg, 99%) as dark brown colored needles, mp (DSC onset) 183 °C (decomp) (from cyclohexane); R_f 0.60 (*t*-BuOMe/hexane, 1:3); (found: C, 76.7; H, 3.8; N, 14.1. $C_{19}H_{11}N_3O$ requires C, 76.8; H, 3.7; N, 14.1%); λ_{max}(DCM)/nm 238 (log ε 3.37), 286 (3.57), 319 inf (3.01), 416 (2.70), 543 (3.46); ν_{max}/cm^{-1} 3064w (Ar CH), 1643 m, 1622s, 1572w, 1541 m, 1506 m, 1483 m, 1452 m, 1436 m, 1402w, 1390w, 1364 m, 1330 m, 1314 m, 1299w, 1266w, 1203w, 1173w, 1161w, 1144 m, 1114w, 1095w, 1072 m, 1025w, 1005w, 989w, 976w, 952w, 932w, 903w, 860w, 855w, 828s; δ_H(300 MHz, $CDCl_3$) 8.55−8.52 (2H, m, Ar *H*), 8.36 (2H, dd, *J* 7.4, 7.4, Ar *H*), 7.68 (1H, d, *J* 9.9, Ar *H*), 7.69−7.55 (5H, m, Ar *H*), 7.23 (1H, d, *J* 9.8, Ar *H*); δ_C(75 MHz, $CDCl_3$) 178.6 (s), 156.5 (s), 153.9 (s), 146.0 (d), 135.0 (s), 134.2 (s), 131.8 (d), 131.5 (d), 129.3 (d), 129.2 (d), 128.2 (d), 126.6 (s), 126.1 (s), 125.8 (d), 123.3 (d), 113.5 (d), 105.2 (s); *m*/*z* (EI) 298 (M^+ + 1, 21%), 297 (M^+, 100), 268 (11), 242 (2), 168 (4), 140 (10), 113 (7), 88 (6), 77 (6), 63 (4).

*4.4.2. 5-(Diethylamino)-2-phenyl-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8b**).* To a stirred solution of 6-(diethylamino)-8-iodo-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**7b**) (49.6 mg, 0.1 mmol) in DMF (1 mL) were added $Pd(Ph_3P)_2Cl_2$ (3.5 mg, 0.005 mmol, 5 mol %) and AgF (19 mg, 0.15 mmol), and the mixture was heated at 100 °C for 20 min. TLC (*t*-BuOMe/hexane, 3:1) showed the presence of a new more polar compound and the absence of the starting material. The reaction mixture was diluted with Et_2O (5 mL) and washed with H_2O (5 mL). The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo. Dry flash chromatography (*t*-BuOMe/hexane, 1:2) of the residue gave the title compound **8b** (34.3 mg, 93%) as red needles, mp 152−154 °C (from EtOH); R_f 0.62 (*t*-BuOMe/hexane, 3:1); (found: C, 75.1; H, 5.4; N, 15.2. $C_{23}H_{20}N_4O$ requires C, 75.0; H, 5.5; N, 15.2%); λ_{max}(DCM)/nm 232 (log ε 3.59), 265 (3.61), 276 (3.62), 303 (3.55), 413 (3.17), 438 (3.35), 461 (3.30); ν_{max}/cm^{-1} 2967w, 2930w, 2907w, 1643 m, 1626 m, 1570w, 1528 m, 1518s, 1499 m, 1476 m, 1450w, 1431w, 1410w, 1395w, 1360w, 1310w, 1292w, 1283 m, 1258 m, 1248 m, 1169w, 1152w, 1123w, 1094w, 1070w, 1028w, 1009w, 986 m, 943 m, 926w, 831w, 814 m, 793 m, 773 m, 758 m; δ_H(300 MHz; $CDCl_3$) 8.49−8.46 (2H, m, Ar *H*), 8.30 (1H, d, *J* 7.8, Ar *H*), 8.25 (1H, d, *J* 8.2), 7.59−7.46 (5H, m, Ar *H*), 6.44 (1H, s, Ar *H*), 3.84 (4H, q, *J* 6.9, NCH_2), 1.44 (6H, t, *J* 7.0, CH_3); δ_C(75 MHz; $CDCl_3$) 174.7 (s), 157.3 (s), 157.2 (s), 152.5 (s), 136.6 (s), 135.2 (s), 130.4 (d), 128.8 (d), 128.0 (d), 127.8 (d), 126.8 (s), 125.7 (s), 124.6 (d), 122.4 (d), 113.2 (d), 104.6 (s), 98.8 (d), 48.2 (NCH$_2$), 13.2 (CH$_3$); *m*/*z* (EI) 369 (M^+ + 1, 13%), 368 (M^+, 47), 339 (100), 325 (14), 297 (8), 269 (3), 193 (2), 165 (4), 151 (4), 140 (5), 125 (4), 114 (4), 77 ($C_6H_5^+$, 6), 51 (3).

*4.4.3. 2-Phenyl-5-(pyrrolidin-1-yl)-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8c**).* To a stirred solution of 8-iodo-1,3-diphenyl-6-(pyrrolidin-1-yl)benzo[*e*][1,2,4]triazin-7(1*H*)-one (**7c**) (49.4 mg, 0.1 mmol) in in DMF (1 mL) were added $Pd(Ph_3P)_2Cl_2$ (3.5 mg, 0.005 mmol, 5 mol %) and AgF (19 mg, 0.15 mmol), and the mixture was heated at 100 °C for 15 min. TLC (*t*-BuOMe/hexane, 3:1) showed the presence of a new more polar compound and the absence of the starting material. The reaction mixture was diluted with Et_2O (5 mL) and washed with H_2O (5 mL). The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo. Dry flash chromatography (*t*-BuOMe/hexane, 1:2) of the residue gave the title compound **8c** (30.2 mg, 83%) as red needles, mp 134−137 °C (from DCM/MeOH, 1:2); R_f 0.71 (*t*-BuOMe/hexane, 3:1); (found: C, 75.1; H, 5.1; N, 15.2. $C_{23}H_{18}N_4O$ requires C, 75.4; H, 5.0; N, 15.3%); λ_{max}(DCM)/nm 231 (log ε 3.38), 267 inf (3.39), 276

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(3.41), 304 (3.30), 371 inf (2.58), 415 inf (3.00) 438 (3.21), 460 (3.06); ν_{max}/cm^{-1} 3049w, 2955w, 2916w, 2870w, 2849w, 1641 m, 1626 m, 1570w, 1510s, 1479w, 1452 m, 1393w, 1368w, 1348w, 1341w, 1321w, 1308w, 1260 m, 1244w, 1229w, 1173w, 1140w, 1105w, 1070w, 1028w, 1007w, 993w, 953w, 937w, 924w, 908w, 858w, 833w, 808w, 785w, 773w; δ_H(300 MHz; $CDCl_3$) 8.46−8.43 (2H, m, Ar *H*), 8.20−8.17 (2H, m, Ar *H*), 7.55−7.41 (5H, m, Ar *H*), 6.17 (1H, s, Ar *H*), 4.35 (2H, br s, NCH_2), 3.52 (2H, br s, NCH_2), 2.01 (4H, br s, CH_2); δ_C(75 MHz; $CDCl_3$) 173.8 (s), 156.8 (s), 155.0 (s), 151.9 (s), 136.5 (s), 135.0 (s), 130.2 (d), 128.5 (d), 127.8 (d), 127.4 (d), 126.3 (s), 125.8 (s), 124.3 (d), 122.1 (d), 112.9 (d), 103.7 (s), 97.9 (d), 52.2 (NCH_2), 29.8 (CH_2); *m*/*z* (EI) 367 (M^+ + 1, 30%), 366 (M^+, 100), 337 (12), 323 (17), 311 (28), 297 (34), 269 (6), 235 (4), 207 (6), 179 (5), 165 (7), 151 (8), 140 (10), 120 (5), 114 (8), 103 (9), 77 ($C_6H_5^+$, 12), 69 (5), 51 (8).

*4.4.4. 5-Methoxy-2-phenyl-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8d**).* To a stirred solution of 8-iodo-6-(methoxy)-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**7d**) (45.5 mg, 0.1 mmol) in DMF (1 mL) were added $Pd(Ph_3P)_2Cl_2$ (3.5 mg, 0.005 mmol, 5 mol %) and AgF (19 mg, 0.15 mmol), and the mixture was heated at 100 °C for 20 min. TLC (*t*-BuOMe/hexane, 3:1) showed the presence of a new more polar compound and the absence of the starting material. The reaction mixture was diluted with Et_2O (5 mL) and washed with H_2O (5 mL). The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo. Dry flash chromatography (*t*-BuOMe/hexane, 1:2) of the residue gave the title compound **8d** (29.2 mg, 89%) as orange plates, mp 245−247 °C (from DCM/MeOH, 1:2); R_f 0.36 (*t*-BuOMe/hexane, 3:1); (found: C, 73.5; H, 4.0; N, 12.5. $C_{20}H_{13}N_3O_2$ requires C, 73.4; H, 4.0; N, 12.8%); λ_{max}(DCM)/nm 235 (log ε 3.27), 270 (3.23), 301 (3.54), 343 (2.83), 395 (2.80), 419 (2.74), 515 (2.27); ν_{max}/cm^{-1} 3006w (Ar CH), 2988w, 2958w, 2923w, 2854w, 1650w, 1631w, 1542 m, 1509w, 1484w, 1467w, 1453w, 1432w, 1407w, 1390w, 1314w, 1276s, 1260s, 1231 m, 1185w, 1177w, 1150w, 1133w, 1104w, 1075w, 1027w, 1002w, 977w, 936w, 917w, 898w, 867w, 822w, 795w; δ_H(300 MHz; $CDCl_3$) 8.52−8.49 (2H, m, Ar *H*), 8.35 (1H, d, *J* 8.3, Ar *H*), 8.27 (1H, d, *J* 8.3, Ar *H*), 7.65−7.50 (5H, m, Ar *H*), 6.76 (1H, s, Ar *H*), 4.11 (3H, s, OCH_3); δ_C(75 MHz; $CDCl_3$) 171.7 (s), 167.1 (s), 156.5 (s), 154.1 (s), 135.3 (s), 134.8 (s), 131.1 (d), 129.0 (d), 128.7 (d), 128.0 (d), 126.3 (s), 125.5 (d), 124.8 (s), 123.2 (d), 113.3 (d), 104.1 (s), 102.4 (d), 57.6 (OCH_3); *m*/*z* (EI) 328 (M^+ + 1, 11%), 327 (M^+, 47), 298 (100), 269 (4), 194 (4), 168 (4), 153 (7), 139 (9), 125 (16), 114 (6), 103 (5), 99 (10), 77 ($C_6H_5^+$, 10), 51 (5).

*4.4.5. 2-Phenyl-5-(phenylthio)-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8e**).* To a stirred solution of 8-iodo-1,3-diphenyl-6-(phenylthio)benzo[*e*][1,2,4]triazin-7(1*H*)-one (**7e**) (53.3 mg, 0.1 mmol) in dry MeCN (1 mL) were added AgF (25 mg, 0.1 mmol), Ph_3P (2.6 mg, 0.01 mmol), and $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol), and the mixture was stirred at reflux for 24 h. TLC (*t*-BuOMe/hexane, 3:1) showed the absence of the starting material and the presence of a less polar product. Dry flash chromatography (*t*-BuOMe/hexane, 1:1) of the residue gave the title compound **8e** (21.6 mg, 53%) as brown needles, mp 279−281 °C (from PhMe); R_f 0.87 (*t*-BuOMe/hexane, 3:1); (found: C, 73.9; H, 3.6; N, 10.3. $C_{25}H_{15}N_3OS$ requires C, 74.1; H, 3.7; N 10.4%); λ_{max}(DCM)/nm 217 (log ε 3.99), 269 (3.34), 284 (3.29), 305 (3.28), 324 (3.14), 387 (1.79), 430 (2.95), 451 (3.02); ν_{max}/cm^{-1} 3053w (Ar CH), 1643s, 1624 m, 1612w, 1574w, 1556w, 1539w, 1502s, 1474 m, 1450w, 1441w, 1433w, 1418w, 1400w, 1385w, 1362w, 1329w, 1315w, 1306w, 1294w, 1265w, 1242w, 1173w, 1155w, 1130w, 1107w, 1069w, 1024w, 1013w, 980w, 972w, 947w, 928w, 868w, 847w, 833w, 806w, 797w; δ_H(300 MHz; $CDCl_3$) 8.44−8.41 (2H, m, Ar *H*), 8.36 (1H, d, *J* 7.9, Ar *H*), 8.30 (1H, d, *J* 8.3, Ar *H*), 7.70−7.65 (3H, m, Ar *H*), 7.63−7.55 (4H, m, Ar *H*), 7.53−7.50 (3H, m, Ar *H*), 6.77 (1H, s, Ar *H*); δ_C(75 MHz; $CDCl_3$) two Ar CH missing 173.8 (s), 165.5 (s), 156.8 (s), 151.5 (s), 135.9 (d), 135.3 (s), 134.9 (s), 131.1 (d), 130.6 (d), 129.5 (s), 129.0 (d), 128.0 (d), 126.9 (s), 126.1 (s), 125.5 (d), 123.1 (d), 120.2 (d), 113.5 (d), 103.4 (s); *m*/*z* (EI) 406 (M^+ + 1, 28%), 405 (M^+, 100), 388 (56), 376 (5), 328 (4), 302 (12), 274 (11), 245 (4), 202 (9), 197 (11), 182 (4), 168 (8), 153 (5), 137 (5), 125 (8), 114 (7), 103 (4), 77 ($C_6H_5^+$,15), 63 (4), 51 (12). Further elution gave unreacted **7e** (10.5 mg, 20%).

4.5. Regioselective Nucleophilic Addition of Triazafluoranthenone. *4.5.1. 5-(Diethylamino)-2-phenyl-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8b**).* To a stirred solution of 2-phenyl-6*H*-[1,2,4]triazino[5,6,1-*jk*]carbazol-6-one (**8a**) (30 mg, 0.1 mmol) in EtOH (0.5 mL) was added diethylamine (0.5 mL, 4.8 mmol), and the mixture was stirred at ca. 20 °C for 22 h. TLC (*t*-ButOMe/hexane, 2:1) showed the absence of the starting material and the presence of a more polar red compound. The solution was diluted with DCM (15 mL) and washed with 5% HCl (10 mL) to remove unreacted amine. The organic layer was separated, dried (Na_2SO_4), evaporated in vacuo, and crystallized to afford the title compound **8b** (22.1 mg, 60%) as red needles, identical to that described above.

*4.5.2. 2-Phenyl-5-(pyrrolidin-1-yl)-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8c**).* To a stirred solution of 2-phenyl-6*H*-[1,2,4]triazino[5,6,1-*jk*]carbazol-6-one (**8a**) (30.6 mg; 0.1 mmol) in EtOH (0.5 mL) was added pyrrolidine (0.5 mL, 6 mmol). The mixture was stirred at ca. 20 °C for 4 h. TLC (*t*-BuOMe/hexane, 2:1) showed the absence of the starting material and the presence of a more polar red compound. The solution was diluted with DCM (15 mL) and washed with 5% HCl (10 mL) to remove unreacted amine. The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo and the residue crystallized to afford the title compound **8c** (37.6 mg, 100%) as red needles, identical to that described above.

*4.5.3. 2-Phenyl-5-(phenylthio)-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8e**).* To a stirred solution of 2-phenyl-6*H*-[1,2,4]triazino[5,6,1-*jk*]carbazol-6-one (**8a**) (30 mg, 0.1 mmol) in DCM (2 mL) were added Hünig's base (18.8 μL; 0.11 mmol) and thiophenyl (20.6 μL, 0.2 mmol). The mixture was stirred at ca. 20 °C for 2.5 h. TLC (*t*-BuOMe/hexane, 3:1) showed the absence of the starting material and the presence of a new less polar compound. The mixture was diluted with DCM (15 mL) and washed with 1 M HCl (10 mL) and then with sat. $NaHCO_3$ (1 × 10 mL). The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo to afford the title compound **8e** (40.4 mg, 100%) as brown needles, identical to that described above.

4.6. Oxidative Coupling. *4.6.1. 2-Phenyl-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8a**).* To a stirred mixture of 1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**6a**) (30 mg, 0.1 mmol) in DMSO (1 mL) were added $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), AgF (25 mg, 0.2 mmol), and $Cu(OTf)_2$ (72 mg, 0.2 mmol), and the solution was heated at ca. 100 °C under an oxygen atmosphere for 7 h. TLC (*t*-BuOMe/hexane 3:1) showed the presence of a less polar red-brown compound. The reaction mixture was then cooled, diluted with DCM (15 mL), and washed with water (3 × 15 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Dry flash chromatography (*t*-BuOMe/hexane, 1:2) of the residue gave the title compound **8a** (25.6 mg, 86%) as dark brown colored needles, identical to that described above.

*4.6.2. 5-(Diethylamino)-2-phenyl-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8b**).* To a stirred solution of 6-(diethylamino)-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**6b**) (37 mg, 0.1 mmol) in DMSO (1 mL) were added $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), AgF (25 mg, 0.2 mmol), and $Cu(OTf)_2$ (72 mg, 0.2 mmol), and the mixture was heated at ca. 100 °C under an oxygen atmosphere for 2 h. TLC (*t*-BuOMe/hexane, 3:1) showed the presence of a less polar red compound. The reaction mixture was then cooled to ca. 20 °C, diluted with DCM (15 mL), and washed with water (3 × 15 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. The residue obtained was dry flash chromatographed (*t*-BuOMe/hexane, 1:2) to afford the title compound **8b** (24.7 mg, 67%) as red needles, identical to that described above.

*4.6.3. 2-Phenyl-5-(pyrrolidin-1-yl)-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8c**).* To a stirred solution of 1,3-diphenyl-6-(pyrrolidin-1-yl)benzo[*e*][1,2,4]triazin-7(1*H*)-one (**6c**) (36.8 mg, 0.1 mmol) in DMSO (1 mL) were added $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), AgF (25 mg, 0.2 mmol), and $Cu(OTf)_2$ (72 mg, 0.2 mmol), and the mixture was heated at ca. 100 °C under an oxygen atmosphere for 2.5 h. TLC (*t*-BuOMe/hexane, 3:1) showed the presence of a less polar red compound. The reaction mixture was then cooled, diluted with DCM (15 mL), and washed with water (3 × 15 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo, and dry flash chromatography (*t*-BuOMe/hexane, 1:2) gave the title compound **8c** (27.8 mg, 76%) as red needles, identical to that described above.

*4.6.4. 5-Methoxy-2-phenyl-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8d**).* To a stirred solution of 6-methoxybenzo-1,3-diphenyl[*e*]-[1,2,4]triazin-7(1*H*)-one (**6d**) (31.5 mg, 0.1 mmol) in DMSO (1 mL) were added $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), AgF (25 mg, 0.2 mmol), and $Cu(OTf)_2$ (72 mg, 0.2 mmol), and the solution was heated at ca. 100 °C under an oxygen atmosphere for 18 h. TLC (*t*-BuOMe/hexane, 3:1) showed the presence of a less polar red compound. The reaction mixture was then cooled to ca. 20 °C, diluted with DCM (15 mL), and washed with water (3 × 15 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo, and dry flash chromatography (*t*-BuOMe/hexane, 1:2) gave the title compound **8d** (6.0 mg, 19%) as orange plates, identical to that described above. Further elution gave unreacted **6d** (9.3 mg, 28%).

*4.6.5. 2-Phenyl-5-(phenylthio)-6H-[1,2,4]triazino[5,6,1-jk]carbazol-6-one (**8e**).* To a stirred solution of 1,3-diphenyl-6-(phenylthio)benzo-[*e*][1,2,4]triazin-7(1*H*)-one (6e) (40.7 mg, 0.1 mmol) in DMSO (1 mL) were added $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), AgF (25 mg, 0.2 mmol), and $Cu(OTf)_2$ (72 mg, 0.2 mmol), and the mixture was heated at ca. 100 °C under an oxygen atmosphere for 14.5 h. TLC (*t*-BuOMe/hexane, 3:1) showed the presence of a less polar brown compound. The reaction mixture was then cooled to ca. 20 °C, diluted with DCM (15 mL), and washed with water (3 × 15 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. The residue obtained was dry flash chromatographed (*t*-BuOMe/hexane, 1:2) to afford the title compound **8e** (6 mg, 15%), as brown needles, identical to that described above. Further elution gave unreacted **6e** (18 mg, 44%)

4.7. Preparation of 8*H*-Indolo[1,2,3-*mn*]phenazin-8-one (14). *4.7.1. 8,10-Dihydro-1-iodo-10-phenylphenazin-2(7H)-one (**13**).* To a stirred solution of 10-phenylphenazin-2(10*H*)-one (**12**) (50 mg, 0.18 mmol) in dry DCM (2 mL) was added NIS (82.7 mg, 0.37 mmol), and the mixture was stirred under Ar atmosphere for 1 d. TLC (EtOAc) showed the absence of the starting material and the presence of a less polar purple colored product. The solvent was evaporated in vacuo, and dry flash chromatography (EtOAc) of the residue gave the title compound **13** (73 mg, 100%) as red needles mp 221−225 °C (cyclohexane); R_f 0.65 (t-BuOMe/hexane, 3:1); (found: C, 54.2; H, 2.7; N, 7.0. $C_{18}H_{11}IN_2O$ requires C, 54.3; H, 2.8; N, 7.0%); λ_{max}(DCM)/nm 287 (log ε 3.63), 355 (2.95), 367 (2.93), 538 (2.97); ν_{max}/cm^{-1} 3005w (Ar CH), 2990w, 1603w, 1585w, 1518s, 1481 m, 1466w, 1456w, 1393w, 1348w, 1315w, 1300w, 1277 m, 1261w, 1240w, 1213w, 1157w, 1146w, 1099w, 1026w, 1003w, 934w, 921w, 893w, 827 m, 754s; δ_H(300 MHz, $CDCl_3$) 7.98−7.94 (1H, m, Ar *H*), 7.63−7.59 (4H, m, Ar *H*), 7.45−7.37 (4H, m, Ar *H*), 7.20 (1H, d, *J* 9.6, Ar *H*), 6.91−6.87 (1H, m, Ar *H*); δ_C(75 MHz, $CDCl_3$) 180.2 (s), 147.6 (s), 138.9 (s), 136.7 (s), 135.1 (d), 134.6 (s), 132.9 (s), 132.4 (d), 131.9 (d), 131.8 (d), 130.6 (d), 130.5 (d), 129.8 (d), 124.8 (d), 116.6 (d), 79.9 (*C*-1); *m*/*z* (EI) 399 (M^+ + 1, 4%), 398 (M^+, 18), 271 (100), 242 (40), 216 (8), 190 (4), 136 (11), 121 (11), 115 (8), 108 (6), 88 (4), 77 (11), 63 (7), 51 (17).

*4.7.2. 8H-Indolo[1,2,3-mn]phenazin-8-one (**14**) via Stochiometric Nonoxidative Coupling.* To a stirred solution of 8,10-dihydro-1-iodo-10-phenylphenazin-2(7*H*)-one (**13**) (32.4 mg; 0.082 mmol) in dry DMF (2 mL) were added pyridine (6.5 mg; 0.082 mmol) and $Pd(OAc)_2$ (22.9 mg; 0.102 mmol), and the mixture was stirred under Ar atmosphere at 100 °C during 40 min. TLC (EtOAc) showed the absence of the starting material and the presence of a new more polar orange product. The mixture was filtered on Celite and extracted with EtOAc (5 × 3 mL). The combined organic extracts were evaporated under reduced pressure and dry flash chromatography (EtOAc) of the residue gave the title compound **14** (17.1 mg; 78%) as pink-red needles (DSC onset) 227 °C (decomp) (from cyclohexane); Found: C, 80.1; H, 3.8; N, 10.3. $C_{18}H_{10}N_2O$ requires C, 80.0; H, 3.7; N, 10.4%); λ_{max} (DCM)/nm 230 (log ε 3.39), 241 (3.50), 265 (3.33), 290 (3.35), 298 (3.41), 341 (3.18), 353 (3.18), 495 (2.91); ν_{max}/cm^{-1} 3129w, 3065 (Ar C−C), 1636 m, 1613s, 1603s, 1570w, 1561w, 1543 m, 1512 m, 1487 m, 1466w, 1447w, 1425w, 1406w, 1368w, 1356w, 1327w, 1302w, 1271w, 1241w, 1221w, 1190w, 1158w, 1131w, 1121w, 1090w, 1048w, 1025w, 953w, 835 m, 797w; δ_H(300 MHz, $CDCl_3$) 8.51−8.46 (2H, m, Ar *H*), 8.33−8.30 (1H, m, Ar *H*), 8.26 (1H, dd, *J* 8.2, 1.5, Ar *H*), 7.87−7.81 (1H, ddd, *J* 8.7, 7.3, 1.5, Ar *H*), 7.66 (1H, ddd, *J* 8.3, 7.4, 1.2, Ar *H*), 7.62−7.51 (3H, m, Ar *H*), 7.00 (1H, d, *J* 9.9, Ar *H*); δ_C(75 MHz, $CDCl_3$) 180.1 (s), 146.9 (s), 138.8 (d), 138.4 (s), 133.9 (s), 133.2 (d), 132.3 (d), 131.5 (d), 128.8 (s), 128.7 (s), 126.9 (s), 126.3 (d), 125.9 (d), 125.5 (d), 123.3 (d), 115.4 (d), 115.1 (d), 108.4 (s); *m*/*z* (EI) 271 (M^+ + 1, 20%), 270 (M^+, 100), 242 (55), (12), 214 (13), 188 (6), 140 (6), 121 (12), 77 ($C_6H_5^+$, 2).

*4.7.3. 8H-Indolo[1,2,3-mn]phenazin-8-one (**14**) via Catalytic Nonoxidative Coupling.* To a stirred solution of 8,10-dihydro-1-iodo-10-phenylphenazin-2(7*H*)-one (**13**) (39.8 mg, 0.1 mmol) in DMF (1 mL) were added $Pd(Ph_3P)_2Cl_2$ (3.5 mg, 0.005 mmol, 5 mol %) and AgF (19 mg, 0.15 mmol), and the mixture was heated at 100 °C for 2 h. The reaction mixture was diluted with Et_2O (5 mL) and washed with H_2O (5 mL). The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo. Dry flash chromatography (EtOAc) of the residue gave the title compound **14** (21.7 mg, 80%) as pink-red crystals, identical to that described above.

■ ASSOCIATED CONTENT

Supporting Information. ^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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