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Synthesis of carbazoles by dehydro Diels–Alder reactions of ynamides

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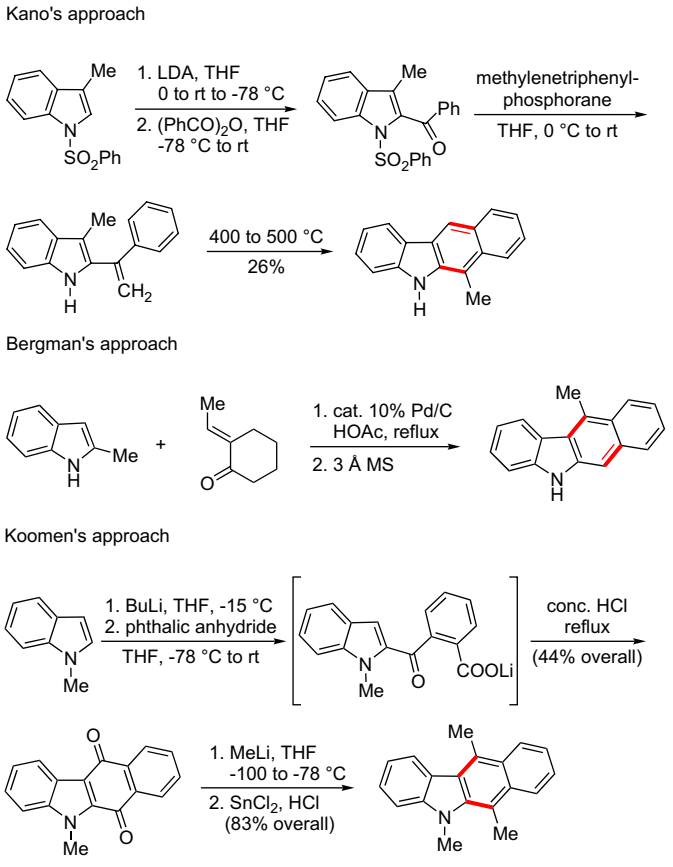
Abstract

A new approach to carbazoles and benzannulated carbazoles by means of intramolecular dehydro Diels–Alder of ynamides is reported. *N*-(*o*-Ethynyl)aryl ynamides and *N*-(*o*-ethynyl) arylynamides were prepared in a few steps starting from *o*-iodoaniline. Thermal cycloaddition of *N*-(*o*-ethynyl)aryl ynamides and *N*-(*o*-ethynyl) arylynamides affords carbazoles and benzannulated and heteroannulated carbazoles in moderate-to-good yields.

1. Introduction

Carbazoles constitute an important class of alkaloids displaying a wide variety of biological activities,[1] and their derivatives are also widely used as building blocks for new organic materials.[2] Accordingly, syntheses of carbazoles and modified carbazoles have been extensively studied.[3,4] One of the most important and well-studied benzo[*b*]carbazoles is the interesting antitumoral agent ellipticine,[5] and the similarity of benzo[*b*]carbazoles in general to this agent suggests their potential for the development of novel antineoplastic agents. Accordingly, several synthetic approaches to benzo[*b*]carbazoles have been developed over the past half century,[6] including benzannulation of indoles (Scheme 1),[7] Fischer indolization of phenylhydrazones (Scheme 2),[8] modified Nenitzescu reaction of *p*-benzoquinones with 2-aminomethylene-1-indanones (Scheme 3),[6] Diels–Alder reactions of pyrano[3,4-*b*]indol-3-ones,[9] 4*H*-furo[3,4-*b*]indoles[10] and 2,4-dihydropyrrolo[3,4-*b*]indoles (Scheme 4)[11] and cycloaromatization of *N*-[2-(1-alkynyl)phenyl]ketenimines (Scheme 5);[12] yields have varied between 22% and 98%. The main failure of these methods is their relative lack of flexibility, since they almost exclusively allow the synthesis of the parent benzo[*b*]carbazole nucleus but not that of benzo[*b*]annulated analogues.



Scheme 1. Benzannulation of indoles.

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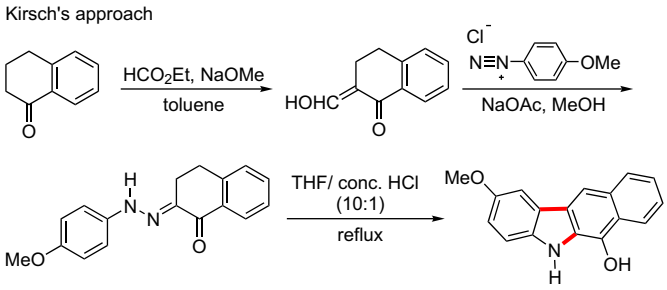
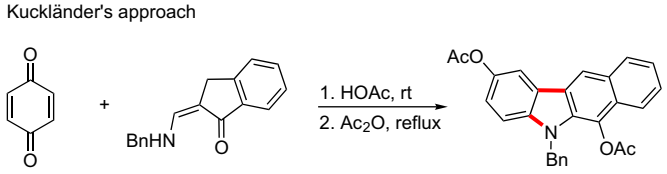


Scheme 2. Fischer indolization of phenylhydrazones.



Scheme 3. Modified Nenitzescu reaction.

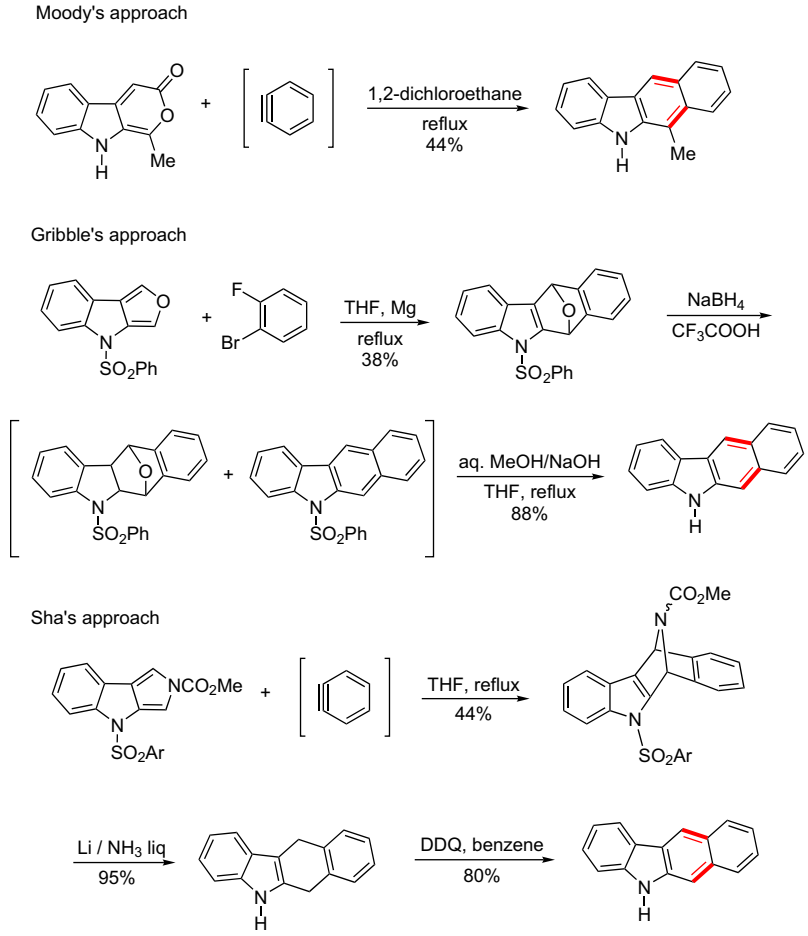
Here, we present a full account of the synthesis of carbazoles and benzannulated carbazoles **3**, which are based on intramolecular dehydro Diels–Alder (IDDA) reactions[13,14] of *N*-(*o*-ethynyl)aryl ynamides **1**[15,16] and *N*-(*o*-ethynyl) arylynamides **2** (Scheme 6).[17,18]

2. Result

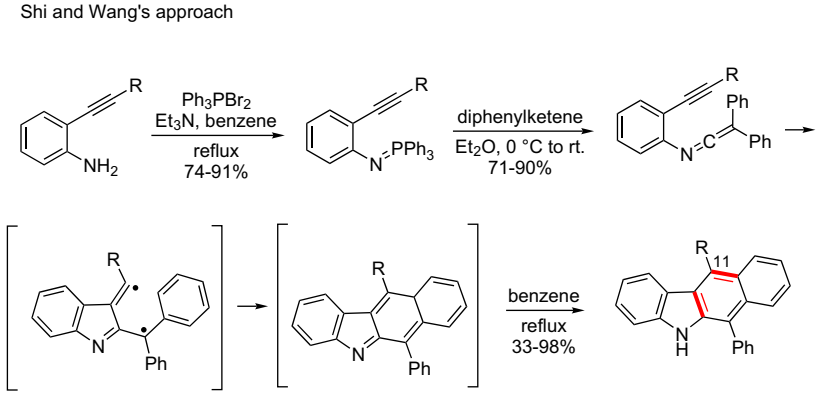
*2.1. Synthesis and intramolecular dehydro Diels–Alder reactions of N-(o-ethynyl)aryl ynamides **1***

Ynamides **1a–f** were synthesized in three steps starting from commercially available 2-iodoaniline (**4**). N-Tosylation of **4** followed by Sonogashira coupling with the appropriate alkyne **5** gave alkynes **6a–f**, and N-ethynylation of these with (trimethylsilyl)ethynyliodonium salt (**7**) gave the desired *N*-(*o*-ethynyl)aryl ynamides **1a–f**, generally in reasonably good overall yield (Scheme 7, Table 1).[16] Using Cs_2CO_3 as the base in the last step afforded desilylated ynamides **1** (R^1=H), using KHMDS retained the TMS group (**1b′,c′**, R^1=TMS).[4a]

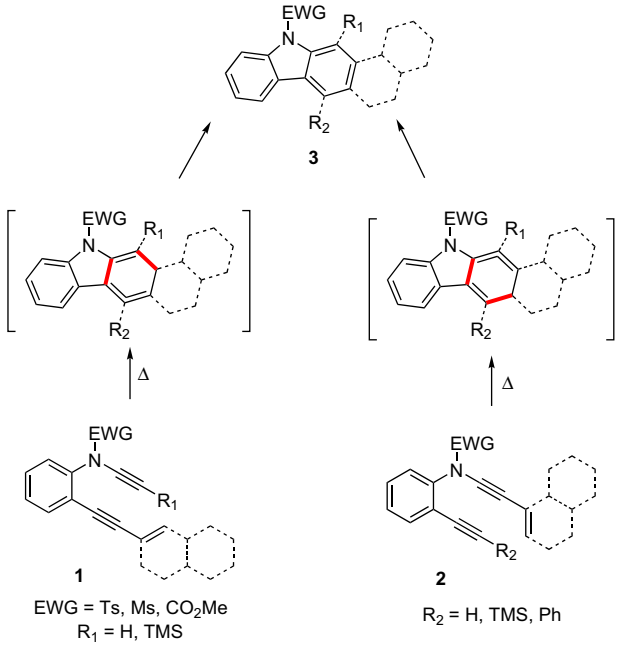
The formation of carbazoles from ynamides **1** generally proceeded best when the IDDA reaction was carried out by heating the ynamides in a mixture of toluene and Et_3N at 150 °C (Table 2). Heating **1a** under these conditions gave 2-methylcarbazole **3a** in only a moderate 40% yield (Table 2, entry 1), but the interesting tetrahydro-5*H*-benzo[*b*]carbazole nucleus **3b**[19] was obtained in 60% yield if Z=Ts (43% yield if Z=CO_2Me, entry 2). Exceptionally, preparation of the silylated analogue **3b′** proceeded best in toluene/MeOH (entry 3).[13] The benzannulated carbazole **3c** was synthesized in low



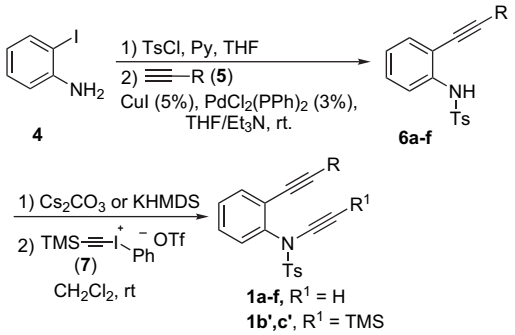
Scheme 4. Diels–Alder reactions.



Scheme 5. Cycloaromatization of ketenimines.



Scheme 6. Synthesis of carbazoles by intramolecular dehydro Diels–Alder of ynamides.



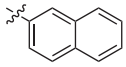
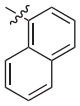
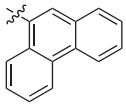
Scheme 7. Synthesis of *N*-(*o*-ethynyl)aryl ynamides **1a–f** and silylated ynamides **1b′**,**c′**.

yield[20] when protected as a tosylate (Z=Ts) but protection as a carbamate (Z=CO_2Me) gave a more satisfactory 50% yield (entry 4). This metal-free IDDA approach to benzannulated carbazoles nicely complements the efficient intermolecular Rh(I)-catalyzed [2+2+2] cycloaddition of ynamides to alkynes, which is not convenient for these targets.[21] Unlike silylated enyne **1b′**, silylated arenyne **1c′** underwent decomposition during all attempted IDDA reactions (entry 5).

Gratifyingly, unlike the methods mentioned above, the ynamide IDDA approach allowed the uneventful preparation of benz[*b*]annulated carbazoles with additional benzene rings: heating ynamides **1d–f** gave the known naphtho[1,2-*b*]carbazole **3d** (90% yield, entry 6),[22] the hitherto unknown naphtho[2,1-*b*]carbazole **3e** (30% yield, entry 7) and the likewise unknown dibenzo[*a*,*c*]carbazole **3f** (60% yield, entry 8).

We next examined the regioselectivity of the dehydro Diels–Alder reaction by installing a second aryl ring in the starting ynamide **1** (R^1=Ar). Heating **1g**[23] gave the 2-nitro-11-phenylbenzo[*b*]carbazole **3g** (though in rather poor yield) by selective cycloaddition to the conjugated arenynamide moiety (Scheme 8), but with the 2-pyrimidinyl ynamide **1h**[23] the cycloaddition occurred regioselectively at the arenyne moiety,

Table 1
Synthesis of *N*-(*o*-ethynyl)aryl ynamides **1a–f** and silylated ynamides **1b′,c′**

Entry	R	R^1	Ynamide	Yield[a] (%)
1		H	**1a**	45[b]
2		H	**1b**	35
3		TMS	**1b′**	38
4		H	**1c**	74
5		TMS	**1c′**	58
6		H	**1d**	20
7		H	**1e**	16
8		H	**1f**	38

[a] Yield for three steps.
[b] Yield for four steps.

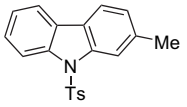
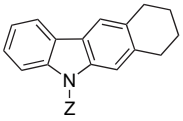
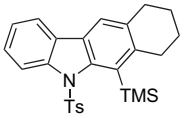
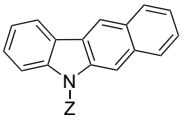
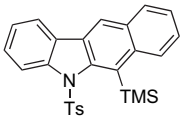
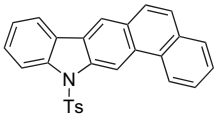
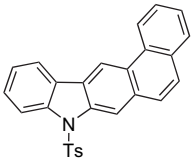
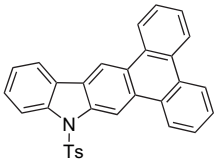
giving 6-pyrimidinylbenzo[*b*]carbazole **3h** (again in poor yield). Interestingly, when the cyclohexenylynamide **1b** was subjected to Sonogashira conditions in the presence of iodobenzene,[24] two carbazoles were isolated, 11-cyclohexenylbenzo[*b*]carbazole **3i** in 8% yield and 6-phenyltetrahydrobenzo[*b*]carbazole **3j** in 16% yield, suggesting that the initial phenylation of **1b** had been followed by the two possible cycloadditions in roughly 1:2 ratio (Scheme 8).

2.2. Synthesis and intramolecular dehydro Diels–Alder reactions of N-(o-ethynyl) arylynamides 2

Given the above results and Danheiser's[17] observation that conjugated enynamides (in our case **2**) give better results than ynamides lacking such conjugation (in our case **1**), we decided to explore in more detail the IDDA reactions of *N*-(*o*-ethynyl) arylynamides **2**. Like ynamides **1**, these were prepared from *o*-iodoaniline (**4**) (Scheme 4). Sonogashira coupling between **4** and alkyne **5i** (R=TIPS), followed by N-tosylation gave the alkyne **6i**, and N-ethynylation of the latter with (trimethylsilyl) ethynyliodonium salt **7** gave the *N*-(*o*-ethynyl)aryl ynamide **1i** in good overall yield. Sonogashira cross-coupling of **1i** with aryl iodides **8** then led to the desired TIPS-substituted arylynamides **2′** in relatively good yields (Table 3).[24]

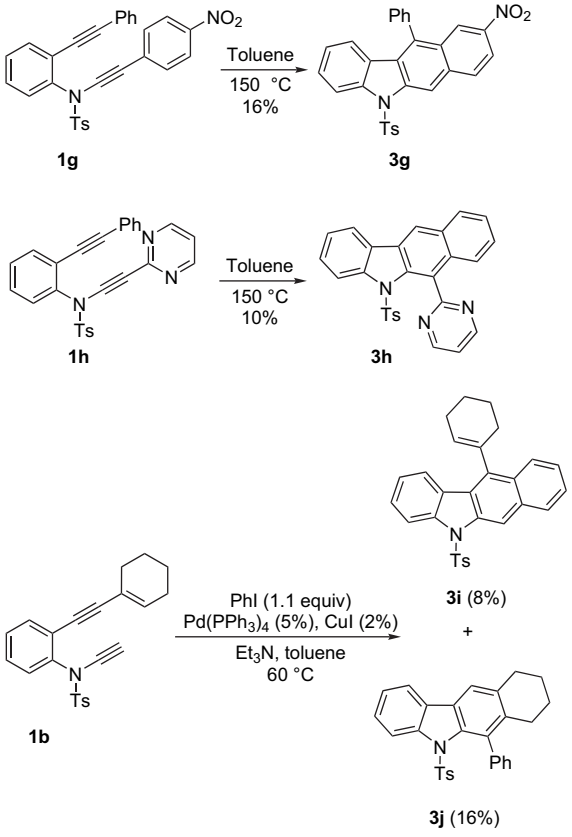
All attempts to cyclize the silylated compounds **2′a–i** led to complex mixtures, probably owing to steric hindrance by the triisopropylsilyl group. Therefore, deprotection was carried out before the IDDA reaction, treatment of alkynes **2′a–i** with TBAF giving the corresponding arylynamides **2a–i** in rather good yields (Scheme 9 and Table 3).

Table 2
Results of intramolecular dehydro Diels–Alder reactions of ynamides **1a–f** and silylated ynamides **1b′,c′**

Entry	Ynamide **1**	Carbazole **3**		Yield[a] (%)
1	**1a**			40
2	**1b**		Z = Ts	60
			Z = CO_2Me	43
3	**1b′**			85[b]
4	**1c**		Z = Ts	12 (15)[b]
			Z = CO_2Me	50
5	**1c′**			—
6	**1d**			90
7	**1e**			30
8	**1f**			60

[a] Conditions: **1** (0.01 M in toluene, typically 6 mL) and 0.5 mL of Et_3N, sealed tube, 150 °C.
[b] MeOH instead Et_3N.

To our delight, heating **2a** in a mixture of toluene and Et_3N afforded **3c** in 50% yield (Table 4, entry 1) instead of the 12% obtained with **1c** (Table 2, entry 4), in keeping with the trend observed by Danheiser.[17] However, naphthylynamide **2b** gave a lower yield of naphthocarbazole **3d** than did **1d**, 73% (Table 4, entry 2) as against 90% (Table 2, entry 6). Surprisingly, the yields of the IDDA reactions of arylynamides **2** did not seem to be influenced by the electronic characteristics of the arylynamide moiety (Table 4, entries 3 and 4), best yields were obtained with halogenated arylynamides (entries 5 and 6). When heteroarylynamides were tried, the 2-pyridylynamide **2g** failed to respond to IDDA conditions (entry 7), and **2h** and **2j** gave low yields of the corresponding heteroarylcarbazoles (entries 8 and 9).[25] Halogen substitution in the non-reactive aryl ring of the ynamide was well tolerated (**2k**, Fig. 1), as was the use of



Scheme 8. Regioselectivity of the IDDA reactions of ynamides **1g**, **1h** and the Sonogashira product of **1b** and iodobenzene.

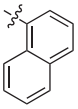
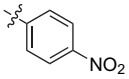
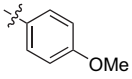
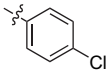
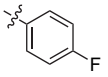
a mesyl nitrogen-protecting group (**2l** and **2m**),[26] since the corresponding carbazoles have been obtained in good-to-excellent yields (entries 10–12).[27] Interestingly, the 11-silylated benzo[*b*]carbazole **3u** was obtained in 31% yield from silylynamide **2″a** (Table 4, entry 13), whereas reaction of **1c′** had failed to afford its 6-silylated isomer **3c′** (Table 2, entry 5) and **2′a** had given a complex mixture.

Gratifyingly, we have also been successful with the application of our methodology to the synthesis of the interesting demethylated derivative of the alkaloid ellipticine (5,11-dimethyl-6*H*-pyrido[4,3-*b*]carbazole),[5] which posseses extraordinary anticancer activity. Owing to the instability of the isolated ynamide **2i** we performed the intramolecular dehydro Diels–Alder reaction with the in situ prepared ynamide. To our delight, TIPS-substituted ynamide **2′i** was subjected to desilylation conditions and then heated at 150 °C to give the pyrido[4,3-*b*]carbazole **3v** in 21% yield (Scheme 10). This result could be considered as one of the most direct approaches to this biological interesting pyridocarbazole nucleus.

3. Conclusions

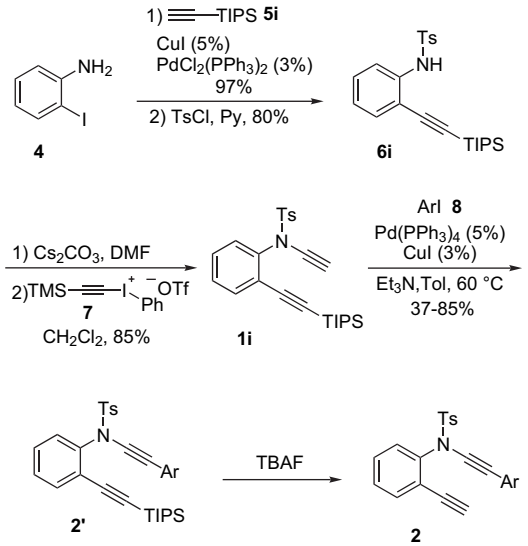
Intramolecular dehydro Diels–Alder reactions of *N*-(*o*-ethynyl)aryl ynamides and *N*-(*o*-ethynyl) arylynamides afford carbazoles and benzannulated and heteroannulated carbazoles in yields that range from poor to excellent but generally exceed 50%. This metal-free IDDA approach to carbazoles

Table 3
Synthesis of *N*-[*o*-(triisopropylsilyl)ethynyl] arylynamides **2′** and *N*-(*o*-ethynyl) arylynamides **2**

Entry	Ar	Arylynamide **2′**	Yield (%)	Arylynamide **2**	Yield (%)
1		**2′a**	85	**2a**	71
2		**2′b**	70	**2b**	81
3		**2′c**	90	**2c**	81
4		**2′d**	60	**2d**	72
5		**2′e**	63	**2e**	95
6		**2′f**	67	**2f**	80
7		**2′g**	47	**2g**	[a]
8		**2′h**	64	**2h**	70
9		**2′i**	95	**2i**	[a]
10		**2′j**	80	**2j**	70

[a] Not isolated.

nicely complements the efficient intermolecular [2+2+2] cycloaddition of ynamides to alkynes. Application to the synthesis of demethylated ellipticine, an interesting antitumoral agent, has also been shown. These results open new perspectives for the application of ynamides in the field of poly- and heterocyclic aromatics with pharmacological interest.

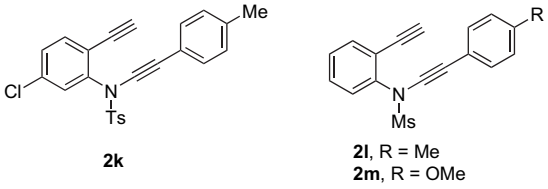


Scheme 9. Synthesis of *N*-(*o*-ethynyl) arylynamides **2** and TIPS-substituted arylynamides **2′**.

Table 4
Results of intramolecular dehydro Diels–Alder reactions of arylynamides **2**

Entry	Arylynamide **2**	Carbazole **3**	Yield (%)
1	**2a**	**3c**	50
2	**2b**	**3d**	73
3	**2c**	**3k**	60
4	**2d**	**3l**	50
5	**2e**	**3m**	82
6	**2f**	**3n**	73
7	**2g**	**3o**	—[a]
8	**2h**	**3p**	21[b]
9	**2j**	**3q**	34[b]
10	**2k**	**3r**	57
11	**2l**	**3s**	95
12	**2m**	**3t**	63
13	**2′′a**[c]	**3u**	31[b]

[a] Not isolated.
[b] Partial decomposition of starting material occurred.
[c] Same structure as **2′a** but with TMS instead of TIPS.



2k **2l**, R = Me; **2m**, R = OMe

Figure 1. Halogen- and mesyl-substituted arylynamides **2k–m**.

4. Experimental

4.1. General

All reactions were carried out under argon atmosphere with magnetic stirring. The solvents were purified and dried using standard procedures. All reagents were purchased and used without further purification. ^{1}H NMR at 250.13 MHz and ^{13}C NMR spectra at 62.89 MHz were determined using $CDCl_3$ as solvent with tetramethylsilane as internal standard. Mass spectra were measured by ionizing the sample at 70 eV. Column chromatographies were made on silica gel 230–240 mesh (flash).

4.1.1. General procedure for the synthesis of N-(o-ethynyl)-aryl ynamides *1*

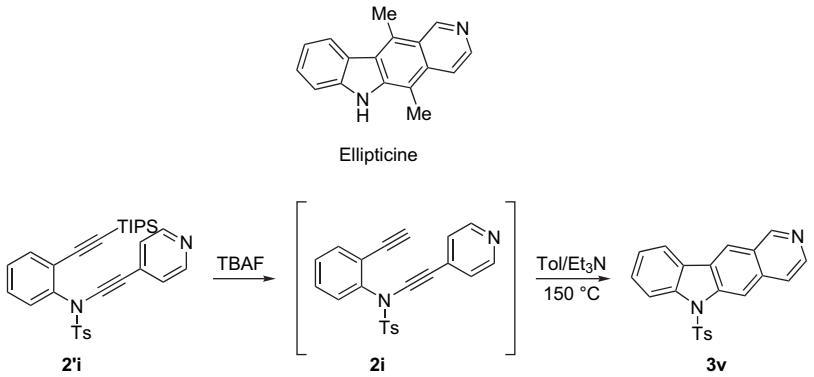
To a stirred solution of *N*-tosylaniline **5** (1 mmol) in dry DMF (20 mL) was added Cs_2CO_3 (1.3 equiv) at rt. After 30 min, a solution of **6** (1.3 mmol) in dry CH_2Cl_2 (8 mL) was added dropwise. Stirring was continued until starting materials disappeared (TLC monitoring, typically 5 h). Then, ether was added (10 mL) and the combined organic layers were extracted with water and brine, dried over anhydrous Na_2SO_4 and concentrated to dryness. Purification of the residue by flash chromatography on silica gel using a gradient mixture of EtOAc/hexanes as eluent afforded ynamides **1** in good yields.

*4.1.1.1. N-Ethynyl-2-((Z)-pent-3-en-1-ynyl)-N-tosylbenzenamine (**1a**).* ^{1}H NMR ($CDCl_3$) δ: 7.71 (d, J=8.3 Hz, 2H, Ar*H*), 7.47–7.44 (m, 1H, Ar*H*), 7.35–7.21 (m, 5H, Ar*H*), 6.07–5.94 (m, 1H, C=C*H*), 5.47 (dd, J=10.7, 1.6 Hz, 1H, C=C*H*), 3.83 (s, 1H, C≡C*H*), 2.41 (s, 3H, CH_3), 1.90 (dd, J=6.9, 1.6 Hz, 3H, CH_3).

*4.1.1.2. 2-(2-Cyclohexenylethynyl)-N-ethynyl-N-tosylbenzenamine (**1b**).* ^{1}H NMR ($CDCl_3$) δ: 7.55 (d, J=8.2 Hz, 2H, Ar*H*), 7.28–7.24 (m, 1H, Ar*H*), 7.14–7.11 (m, 5H, Ar*H*), 5.92 (m, 1H, C=C*H*), 2.70 (s, 1H, CC*H*), 2.27 (s, 3H, CH_3), 1.95–1.89 (m, 4H, CH_2), 1.46–1.44 (m, 4H, CH_2).

*4.1.1.3. Methyl 2-(2-cyclohexenylethynyl) phenylethynylcarbamate (**1b**, Z=CO$_2$Me).* ^{1}H NMR ($CDCl_3$) δ: 7.45 (dd, J=6.5, 2.4 Hz, 1H, ArH), 7.41–7.24 (m, 3H, ArH), 6.22 (m, 1H, C=CH), 3.82 (s, 3H, CH_3), 2.82 (s, 1H, CCH), 2.21–2.18 (m, 4H, CH_2), 1.71–1.60 (m, 4H, CH_2).

*4.1.1.4. 2-(2-Cyclohexenylethynyl)-N-(2-(trimethylsilyl)ethynyl)-N-tosylbenzenamine (**1b′**).* ^{1}H NMR ($CDCl_3$) δ: 7.71 (d,



Scheme 10. Synthesis of demethylated ellipticine derivative **3v** by intramolecular dehydro Diels–Alder of arylynamide **2i**.

J=8.4 Hz, 2H, Ar*H*), 7.42–7.40 (m, 1H, Ar*H*), 7.31–7.27 (m, 5H, Ar*H*), 2.43 (s, 3H, CH_3), 2.09–2.08 (m, 2H, CH_2), 2.02–2.01 (m, 2H, CH_2), 1.62–1.58 (m, 4H, CH_2), 0.13 (s, 3H, Si(CH_3)$_3$).

*4.1.1.5. N-Ethynyl-2-(2-phenylethynyl)-N-tosylbenzenamine (**1c**, Z=Ts).* ^{1}H NMR ($CDCl_3$) δ: 7.68 (d, *J*=7.8 Hz, 2H, Ar*H*), 7.51–7.30 (m, 9H, Ar*H*), 7.07 (d, *J*=7.8 Hz, 2H, Ar*H*), 2.94 (s, 1H, CC*H*), 2.15 (s, 3H, CH_3).

*4.1.1.6. Methyl ethynyl-2-(2-phenylethynyl)phenylcarbamate (**1c**, Z=CO_2Me).* ^{1}H NMR ($CDCl_3$) δ: 7.61 (dd, *J*=7.6, 1.7 Hz, 1H, ArH), 7.57–7.54 (m, 2H, ArH), 7.44–7.39 (m, 2H, ArH), 7.38–7.34 (m, 4H, ArH), 3.85 (s, 3H, CH_3), 2.88 (s, 1H, CCH).

*4.1.1.7. N-(2-(Trimethylsilyl)ethynyl)-2-(2-phenylethynyl)-N-tosylbenzenamine (**1c′**).* ^{1}H NMR ($CDCl_3$) δ: 7.85 (d, *J*=8.2 Hz, 2H, Ar*H*), 7.66–7.61 (m, 9H, Ar*H*), 7.24 (d, *J*=8.2 Hz, 2H, Ar*H*), 2.32 (s, 3H, CH_3), 0.24 (s, 9H, Si(CH_3)$_3$).

*4.1.1.8. N-Ethynyl-2-(2-(naphthalen-3-yl)ethynyl)-N-tosylbenzenamine (**1d**).* ^{1}H NMR ($CDCl_3$) δ: 7.80–7.71 (m, 6H, Ar*H*), 7.54–7.37 (m, 7H, Ar*H*), 7.05 (d, *J*=8.2 Hz, 2H, Ar*H*), 2.98 (s, 1H, CC*H*), 2.01 (s, 3H, CH_3).

*4.1.1.9. N-Ethynyl-2-(2-(naphthalen-1-yl)ethynyl)-N-tosylbenzenamine (**1e**).* ^{1}H NMR ($CDCl_3$) δ: 8.35–8.31 (m, 1H, Ar*H*), 7.84 (d, *J*=7.9 Hz, 2H, Ar*H*), 7.69–7.39 (m, 10H, Ar*H*), 6.87 (d, *J*=7.9 Hz, 2H, Ar*H*), 3.02 (s, 1H, C≡C*H*), 1.83 (s, 3H, CH_3).

*4.1.1.10. N-Ethynyl-2-(2-(phenanthren-9-yl)ethynyl)-N-tosylbenzenamine (**1f**).* ^{1}H NMR ($CDCl_3$) δ: 8.71–8.67 (m, 3H, Ar*H*), 8.44 (d, *J*=7.5 Hz, 1H, Ar*H*), 7.87–7.85 (m, 2H, Ar*H*), 7.72–7.63 (m, 6H, Ar*H*), 7.47–7.43 (m, 3H, Ar*H*), 6.86 (*d*, *J*=8.0 Hz, 2H, Ar*H*), 3.05 (s, 1H, C≡C*H*), 1.74 (s, 3H, CH_3).

*4.1.1.11. N-(2-(4-Nitrophenyl)ethynyl)-2-(2-phenylethynyl)-N-tosylbenzenamine (**1g**).* ^{1}H NMR ($CDCl_3$) δ: 8.10 (d, *J*=8.5 Hz, 2H, Ar*H*), 7.73 (d, *J*=8.5 Hz, 2H, Ar*H*), 7.57–7.52 (m, 2H, Ar*H*), 7.46–7.41 (m, 4H, Ar*H*), 7.28–7.10 (m, 7H, Ar*H*), 2.18 (s, 3H, CH_3).

*4.1.1.12. 2-(2-Phenylethynyl)-N-(2-(pyrimidin-2-yl)ethynyl)-N-tosylbenzenamine (**1h**).* ^{1}H NMR ($CDCl_3$) δ: 8.59 (d, *J*=5.0 Hz, 2H, Ar*H*), 7.78 (d, *J*=8.4 Hz, 2H, Ar*H*), 7.49 (dd, *J*=5.7, 3.5 Hz, 1H, Ar*H*), 7.46 (dd, *J*=5.9, 3.3 Hz, 1H, Ar*H*), 7.37 (d, *J*=3.5 Hz, 1H, Ar*H*), 7.36 (d, *J*=3.5 Hz, 1H, Ar*H*), 7.26–7.21 (m, 3H, Ar*H*), 7.19–7.15 (m, 2H, Ar*H*), 7.10–7.07 (m, 3H, Ar*H*), 2.14 (s, 3H, CH_3).

4.1.2. General procedure for the synthesis of N-(o-ethynyl) arylynamides 2′

To a reaction flask was added 1 mmol ynamide **1i**, 1.1 mmol of aryl iodide, 0.05 mmol of Pd(PPh_3)$_4$, 7.5 mL of Et_3N and 3.7 mL of toluene. The solution was stirred at rt for 10 min, and 0.02 mmol of CuI was then added. After heating the reaction mixture at 60 °C until starting material disappeared (TLC monitoring, 4–8 h), the mixture was diluted with EtOAc, filtered through silica, and concentrated in vacuo. Purification of the residue by flash chromatography on silica gel using a gradient mixture of EtOAc/hexanes as eluent afforded ynamides **2′** in good yields.

*4.1.2.1. 2-(2-(Triisopropylsilyl)ethynyl)-N-(2-phenylethynyl)-N-tosylbenzenamine (**2′a**).* Following the procedure described above and starting with **1i** (300 mg, 0.67 mmol), iodobenzene (82 mg, 0.73 mmol), Pd(PPh_3)$_4$ (38 mg), CuI (2.5 mg) in Et_3N (5 mL) and toluene (2.5 mL), **2′a** was isolated as a clear oil (300 mg, 85%). ^{1}H NMR ($CDCl_3$) δ: 7.79 (d, *J*=8.2 Hz, 2H, Ar*H*), 7.60 (d, *J*=7.4 Hz, 1H, Ar*H*), 7.34–7.25 (m, 9H, Ar*H*), 7.12 (d, *J*=7.5 Hz, 1H, Ar*H*), 2.45 (s, 3H, CH_3), 1.10 (s, 21H, Si(CH(CH_3)$_2$)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 144.7 (*C*), 139.4 (*C*), 134.6 (*C*), 134.5 (*C*H), 131.1 (2×*C*H), 129.5 (2×*C*H), 128.8 (2×*C*H), 128.3 (2×*C*H), 128.0 (*C*H), 127.9 (2×*C*H), 127.4 (*C*H), 124.1 (*C*), 123.0 (*C*), 102.0 (*C*), 97.9 (*C*), 83.0 (*C*), 70.0 (*C*), 21.7 (*C*H_3), 18.6 (Si(CH(*C*H_3)$_2$)$_3$), 11.3 (Si(*C*H(CH_3)$_2$)$_3$); MS FAB *m/z* (%): 528 (M^++1, 2), 231 (43), 137 (100); HRMS: ($C_{32}H_{38}NO_2SSi$) calcd: 528.2392; found: 528.2390.

*4.1.2.2. 2-(2-(Triisopropylsilyl)ethynyl)-N-(2-(naphthalen-1-yl)ethynyl)-N-tosylbenzenamine (**2′b**).* Following the procedure described above and starting with **1i** (100 mg, 0.22 mmol), iodonaphthalene (36 μL, 0.24 mmol), $Pd(PPh_3)_4$ (13 mg), CuI (1 mg) in Et_3N (1.5 mL) and toluene (0.7 mL), **2′b** was isolated as a clear oil (89 mg, 70%). ^1H NMR ($CDCl_3$) δ: 8.26 (d, J=8.0 Hz, 1H, Ar*H*), 7.86–7.17 (m, 14H, Ar*H*), 2.45 (s, 3H, CH_3), 1.09 (s, 21H, Si(C*H*(CH_3)$_2$)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 144.8 (*C*), 144.7 (*C*), 139.5 (*C*), 136.6 (*C*), 134.7 (*C*), 134.6 (*C*H), 13.10 (*C*), 133.06 (*C*), 129.7 (2×*C*H), 129.5 (*C*H), 129.2 (*C*H), 12.1 (*C*H), 129.0 (*C*H), 128.9 (*C*H), 128.4 (2×*C*H), 128.0 (*C*H), 127.8 (*C*H), 126.4 (*C*H), 126.2 (*C*H), 125.0 (*C*H), 102.0 (*C*), 98.1 (*C*), 87.7 (*C*), 68.5 (*C*), 21.6 (*C*H_3), 18.6 (Si(CH(*C*H_3)$_2$)$_3$), 11.3 Si(*C*H(CH$_3$)$_2$)$_3$.

*4.1.2.3. 2-(2-(Triisopropylsilyl)ethynyl)-N-(2-(4-nitrophenyl)-ethynyl)-N-tosylbenzenamine (**2′c**).* Following the procedure described above and starting with **1i** (100 mg, 0.22 mmol), 4-iodonitrobencene (61 mg, 0.24 mmol), $Pd(PPh_3)_4$ (13 mg), CuI (1 mg) in Et_3N (1.5 mL) and toluene (0.7 mL), **2′c** was isolated as a clear oil (113 mg, 90%). ^1H NMR ($CDCl_3$) δ: 8.13 (d, J=8.6 Hz, 2H, Ar*H*), 7.76 (d, J=8.3 Hz, 2H, Ar*H*), 7.60 (dd, J=6.7, 2.5 Hz, 1H, Ar*H*), 7.43–7.32 (m, 6H, Ar*H*), 7.22 (d, J=7.2, 2.9 Hz, 1H, Ar*H*), 2.46 (s, 3H, CH_3), 1.03 (s, 21H, Si(C*H*(CH_3)$_2$)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 146.0 (*C*), 145.2 (*C*), 138.3 (*C*), 134.8 (*C*H), 134.5 (*C*), 130.7 (*C*), 130.5 (2×*C*H), 129.8 (2×*C*H), 129.2 (*C*H), 129.0 (*C*H), 128.4 (*C*H), 128.3 (2×*C*H), 123.6 (*C*), 123.4 (2×*C*H), 101.5 (*C*), 98.5 (*C*), 88.9 (*C*), 70.3 (*C*), 21.7 (*C*H_3), 18.5 (Si(CH(*C*H_3)$_2$)$_3$), 11.2 (Si(*C*H(CH$_3$)$_2$)$_3$).

*4.1.2.4. 2-(2-(Triisopropylsilyl)ethynyl)-N-(2-(4-methoxyphenyl)ethynyl)-N-tosylbenzenamine (**2′d**).* Following the procedure described above and starting with **1i** (150 mg, 0.33 mmol), 4-iodoanisole (86 mg, 0.37 mmol), $Pd(PPh_3)_4$ (19 mg), CuI (1 mg) in Et_3N (2.5 mL) and toluene (1.2 mL), **2′d** was isolated as a clear oil (110 mg, 60%). ^1H NMR ($CDCl_3$) δ: 7.78 (d, J=8.5 Hz, 2H, Ar*H*), 7.59 (d, J=7.5 Hz, 1H, Ar*H*), 7.33–7.27 (m, 6H, Ar*H*), 7.07 (d, J=7.5 Hz, 1H, Ar*H*), 6.79 (d, J=8.5 Hz, 2H, Ar*H*), 3.79 (s, 3H, OCH_3), 2.46 (s, 3H, CH_3), 1.13 (s, 21H, Si(C*H*(CH_3)$_2$)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 159.3 (*C*), 144.5 (*C*), 139.8 (*C*), 134.7 (*C*), 134.5 (*C*H), 133.2 (2×*C*H), 129.5 (2×*C*H), 128.83 (*C*H), 128.77 (*C*H), 128.4 (2×*C*H), 128.0 (*C*H), 124.2 (*C*), 115.0 (*C*), 113.7 (2×*C*H), 102.2 (*C*), 97.7 (*C*), 81.6 (*C*), 69.5 (*C*), 55.2 (OCH_3), 21.7 (*C*H_3), 18.6 (Si(CH(*C*H_3)$_2$)$_3$), 11.3 (Si(*C*H(CH$_3$)$_2$)$_3$); MS FAB *m/z* (%): 558 (M^++1, 5), 384 (24), 154 (34), 121 (100); HRMS: ($C_{33}H_{40}NO_3SSi$) calcd: 558.2498; found: 558.2504.

*4.1.2.5. N-(2-(4-Chlorophenyl)ethynyl)-2-(2-(triisopropylsilyl)-ethynyl)-N-tosylbenzenamine (**2′e**).* Following the procedure described above and starting with **1i** (150 mg, 0.40 mmol), 1-chloro-4-iodobenzene (105 mg, 0.44 mmol), $Pd(PPh_3)_4$ (23 mg), CuI (2 mg) in Et_3N (3 mL) and toluene (1.5 mL), **2′e** was isolated as a clear oil (122 mg, 63%). ^1H NMR ($CDCl_3$) δ: 7.75 (d, J=8.3 Hz, 2H, Ar*H*), 7.58 (dd, J=7.0, 2.2 Hz, 1H, Ar*H*), 7.33–7.23 (m, 8H, Ar*H*), 7.11 (dd, J=7.1, 2.0 Hz, 1H, Ar*H*), 2.44 (s, 3H, CH_3), 1.08 (m, 21H, Si(C*H*(CH_3)$_2$)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 144.8 (*C*), 139.1 (*C*), 134.6 (*C*H), 133.3 (*C*), 132.2 (2×*C*H), 129.6 (2×*C*H), 128.9 (*C*H), 128.3 (2×*C*H), 128.2 (*C*H), 124.0 (*C*), 121.6 (*C*), 101.9 (*C*), 98.0 (*C*), 83.8 (*C*), 69.1 (*C*), 21.7 (*C*H_3), 18.6 (*C*H_3), 11.2 (*C*H). MS ESI-TOF *m/z* (%): 580 (M^++H_2O, 100), 562 (M^+, 3), 428 (29); HRMS: ($C_{32}H_{37}ClNO_2SSi$) calcd: 562.1997; found: 562.1992.

*4.1.2.6. N-(2-(4-Fluorophenyl)ethynyl)-2-(2-(triisopropylsilyl)-ethynyl)-N-tosylbenzenamine (**2′f**).* Following the procedure described above and starting with **1i** (190 mg, 0.55 mmol), 1-iodo-4-fluorbenzene (128 mg, 0.60 mmol), $Pd(PPh_3)_4$ (31 mg), CuI (2 mg) in Et_3N (4 mL) and toluene (2 mL), **2′f** was isolated as a clear oil (145 mg, 62%). ^1H NMR ($CDCl_3$) δ: 7.76 (d, J=8.3 Hz, 2H, Ar*H*), 7.58 (dd, J=7.1, 2.2 Hz, 1H, Ar*H*), 7.33–7.24 (m, 6H, Ar*H*), 7.10 (d, J=7.3 Hz, 1H, Ar*H*), 6.94 (t, J=8.7 Hz, 1H, Ar*H*), 2.44 (s, 3H, CH_3), 1.09 (s, 21H, Si(C*H*(CH_3)$_2$)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 164.0 (*C*), 160.1 (*C*), 144.7 (*C*), 139.3 (*C*), 134.5 (*C*H), 133.2 (*C*H), 133.0 (*C*H), 129.6 (2×*C*H), 128.9 (2×*C*H), 128.3 (2×*C*H), 128.1 (*C*H), 124.0 (*C*), 119.1 (*C*), 115.4 (*C*H), 115.1 (*C*H), 102.0 (*C*), 97.9 (*C*), 82.5 (*C*), 68.9 (*C*), 21.6 (*C*H_3), 18.6 (Si(CH(*C*H_3)$_2$)$_3$), 11.2 (Si(*C*H(CH$_3$)$_2$)$_3$); MS ESI-TOF *m/z* (%): 546 (M^++1, 100), 348 (33); HRMS: ($C_{32}H_{37}FNO_2SSi$) calcd: 546.2293; found: 546.2289.

*4.1.2.7. 2-(2-(Triisopropylsilyl)ethynyl)-N-(2-(pyridin-2-yl)-ethynyl)-N-tosylbenzenamine (**2′g**).* Following the procedure described above and starting with **1i** (100 mg, 0.22 mmol), 2-iodopyridine (36 μL, 0.24 mmol), $Pd(PPh_3)_4$ (13 mg), CuI (1 mg) in Et_3N (3.2 mL) and toluene (1.6 mL), **2′g** was isolated as a clear oil (55 mg, 47%). ^1H NMR ($CDCl_3$) δ: 8.46 (br s, 1H, Ar*H*), 7.77 (d, J=8.3 Hz, 2H, Ar*H*), 7.56 (dd, J=7.6, 1.4 Hz, 1H, Ar*H*), 7.34–7.22 (m, 6H, Ar*H*), 7.12 (t, J=5.2 Hz, 1H, Ar*H*), 7.06 (d, J=7.7 Hz, 1H, Ar*H*), 2.42 (s, 3H, CH_3), 1.06 (s, 21H, Si(C*H*(CH_3)$_2$)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 149.5 (*C*H), 144.9 (*C*), 143.6 (*C*), 138.7 (*C*), 135.7 (*C*H), 134.54 (*C*H), 134.5 (*C*), 129.7 (2×*C*H), 129.1 (*C*H), 128.9 (*C*H), 128.4 (2×*C*H), 128.2 (*C*H), 126.1 (*C*H), 124.2 (*C*), 121.7 (*C*H), 101.8 (*C*), 97.9 (*C*), 83.2 (*C*), 70.4 (*C*), 21.7 (*C*H_3), 18.5 (Si(CH(*C*H_3)$_2$)$_3$), 11.2 (Si(*C*H(CH$_3$)$_2$)$_3$); MS ESI-TOF *m/z* (%): 529 (M^++1, 22), 268 (45), 288 (100); HRMS: ($C_{31}H_{37}N_2O_2SSi$) calcd: 529.2345; found: 529.2340.

*4.1.2.8. 2-(2-(Triisopropylsilyl)ethynyl)-N-(2-(pyridin-3-yl)-ethynyl)-N-tosylbenzenamine (**2′h**).* Following the procedure described above and starting with **1i** (100 mg, 0.22 mmol), 3-iodopyridine (50 mg, 0.24 mmol), $Pd(PPh_3)_4$ (13 mg), CuI (1 mg) in Et_3N (1.5 mL) and toluene (0.7 mL), **2′h** was isolated as a clear oil (74 mg, 64%). ^1H NMR ($CDCl_3$) δ: 8.55 (d, J=1.5 Hz, 1H, Ar*H*), 8.46 (dd, J=4.6, 1.5 Hz, 1H, Ar*H*), 7.78 (d, J=8.3 Hz, 2H, Ar*H*), 7.63–7.59 (m, 2H, Ar*H*), 7.39–7.28 (m, 4H, Ar*H*), 7.22–7.15 (m, 2H, Ar*H*), 2.45 (s, 3H, CH_3), 1.09 (s, 21H, Si(C*H*(CH_3)$_2$)$_3$); ^{13}C NMR/DEPT

($CDCl_3$) δ: 151.6 (*C*H), 147.7(*C*H), 144.9 (*C*), 138.8 (*C*), 137.8 (*C*H), 134.7 (*C*H), 134.5 (*C*), 129.7 (2×*C*H), 129.1 (*C*H), 128.9 (*C*H), 128.4 (2×*C*H), 128.2 (*C*H), 123.9 (*C*), 122.7 (*C*H), 109.0 (*C*), 101.8 (*C*), 98.2 (*C*), 86.0 (*C*), 67.1 (*C*), 21.6 (*C*H_3), 18.5 (Si(CH(*C*H_3)$_2$)$_3$), 11.2 (Si(*C*H(CH$_3$)$_2$)$_3$); MS ESI-TOF *m/z* (%): 529 (M^++1, 100); HRMS: ($C_{31}H_{37}N_2O_2SSi$) calcd: 529.2345; found: 529.2340.

*4.1.2.9. 2-(2-(Triisopropylsilyl)ethynyl)-N-(2-(pyridin-4-yl)-ethynyl)-N-tosylbenzenamine (**2′i**).* Following the procedure described above and starting with **1i** (120 mg, 0.27 mmol), 4-iodopyridine (60 mg, 0.29 mmol), $Pd(PPh_3)_4$ (15 mg), CuI (1 mg) in Et_3N (2.6 mL) and toluene (1.3 mL), **2′i** was isolated as a clear oil (136 mg, 95%). ^{1}H NMR ($CDCl_3$) δ: 8.28 (br s, 2H, Ar*H*), 7.55 (d, *J*=8.3 Hz, 2H, Ar*H*), 7.39 (dd, *J*=5.9, 2.6 Hz, 1H, Ar*H*), 7.16–7.10 (m, 4H, Ar*H*), 7.01–6.94 (m, 3H, Ar*H*), 2.23 (s, 3H, CH_3), 0.84 (s, 21H, Si(C*H*(CH_3)$_2$)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 149.1 (2×*C*H), 145.0 (*C*), 138.2 (*C*), 134.6 (*C*H), 134.3 (*C*), 131.6 (*C*), 129.6 (2×*C*H), 129.1 (*C*H), 128.9 (*C*H), 128.3 (2×*C*H), 128.2 (2×*C*H), 124.0 (*C*H), 123.5 (*C*), 101.4 (*C*), 98.3 (*C*), 88.0 (*C*), 69.1 (*C*), 21.5 (*C*H_3), 18.4 (Si(CH(*C*H_3)$_2$)$_3$), 11.0 (Si(*C*H(CH$_3$)$_2$)$_3$).

*4.1.2.10. 2-(2-(Triisopropylsilyl)ethynyl)-N-(2-(thiophen-2-yl)-ethynyl)-N-tosylbenzenamine (**2′j**).* Following the procedure described above and starting with **1i** (120 mg, 0.27 mmol), 2-iodothiophene (41 μL, 0.37 mmol), $Pd(PPh_3)_4$ (19 mg), CuI (1 mg) in Et_3N (2.5 mL) and toluene (1.2 mL), **2′j** was isolated as a clear oil (140 mg, 80%). ^{1}H NMR ($CDCl_3$) δ: 7.77 (d, *J*=8.3 Hz, 2H, Ar*H*), 7.58 (dd, *J*=7.0, 2.0 Hz, 1H, Ar*H*), 7.34–7.22 (m, 5H, Ar*H*), 7.13 (dd, *J*=3.6, 1.1 Hz, 1H, Ar*H*), 7.04 (dd, *J*=7.5, 1.7 Hz, 1H, Ar*H*), 6.93 (dd, *J*=5.2, 3.7 Hz, 1H, Ar*H*), 2.46 (s, 3H, CH_3), 1.16 (s, 21H, Si(C*H*(CH_3)$_2$)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 144.7 (*C*), 139.4 (*C*), 134.6 (*C*), 134.4 (*C*H), 132.8 (*C*H), 129.6 (2×*C*H), 129.0 (*C*H), 128.9 (*C*H), 128.3 (2×*C*H), 127.9 (*C*H), 127.6 (*C*H), 126.8 (*C*H), 124.2 (*C*), 123.0 (*C*), 102.0 (*C*), 97.8 (*C*), 86.3 (*C*), 63.2 (*C*), 21.7 (*C*H_3), 18.7 (Si(CH(*C*H_3)$_2$)$_3$), 11.3 (Si(*C*H(CH$_3$)$_2$)$_3$).

*4.1.2.11. 5-Chloro-2-(2-(triisopropylsilyl)ethynyl)-N-(2-p-tolyl-ethynyl)-N-tosylbenzenamine (**2′k**).* Following the procedure described above and starting with 5-chloro-*N*-ethynyl-2-(2-(triisopropylsilyl)ethynyl)-*N*-tosylbenzenamine (140 mg, 0.29 mmol), 1-iodo-4-methylbenzene (69 mg, 0.32 mmol), $Pd(PPh_3)_4$ (17 mg), CuI (1 mg) in Et_3N (2 mL) and toluene (1 mL), **2′k** was isolated as a clear oil (90 mg, 54%). ^{1}H NMR ($CDCl_3$) δ: 7.60 (d, *J*=8.3 Hz, 2H, Ar*H*), 7.52 (d, *J*=8.4 Hz, 1H, Ar*H*), 7.34 (d, *J*=8.4 Hz, 1H, Ar*H*), 7.17 (d, *J*=8.0 Hz, 2H, Ar*H*), 7.08–7.04 (m, 3H, Ar*H*), 6.90 (d, *J*=8.0 Hz, 2H, Ar*H*), 2.30 (s, 3H, CH_3), 2.15 (s, 3H,CH_3), 0.93 (s, 21H, Si(C*H*(CH_3)$_2$)$_3$); MS ESI-TOF *m/z* (%): 576 (M^++1, 100), 378 (16); HRMS: ($C_{33}H_{39}ClNO_2SSi$) calcd: 576.2154; found: 576.2152.

*4.1.2.12. N-(2-(4-Methylphenyl)ethynyl)-2-(2-(triisopropylsilyl)-ethynyl)-N-mesylbenzenamine (**2′l**).* Following the procedure described above and starting with *N*-ethynyl-2-(2-(triisopropylsilyl)ethynyl)-*N*-mesylbenzenamine (163 mg, 0.46 mmol), 1-iodo-4-methylbenzene (111 mg, 0.51 mmol), $Pd(PPh_3)_4$ (27 mg), CuI (2 mg) in Et_3N (3.4 mL) and toluene (1.7 mL), **2′l** was isolated as a clear oil (125 mg, 61%). ^{1}H NMR ($CDCl_3$) δ: 7.60 (d, *J*=6.6 Hz, 1H, Ar*H*), 7.50 (d, *J*=6.6 Hz, 1H, Ar*H*), 7.42–7.35 (m, 2H, Ar*H*), 7.28 (d, *J*=7.9 Hz, 2H, Ar*H*), 7.06 (d, *J*=7.9 Hz, 2H, Ar*H*), 3.33 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 1.11 (s, 21H, Si(C*H*(CH_3)$_2$)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 138.4 (*C*), 137.7 (*C*), 134.9 (*C*H), 131.3 (2×*C*H), 130.0 (*C*H), 129.5 (*C*H), 129.2 (*C*H), 128.7 (2×*C*H), 122.8 (*C*), 119.5 (*C*), 102.5 (*C*), 98.4 (*C*), 81.0 (*C*), 70.6 (*C*), 39.8 (*C*H_3), 21.3 (*C*H_3), 18.6 (*C*H_3), 11.2 (Si(*C*H(CH$_3$)$_2$)$_3$); MS ESI-TOF *m/z* (%): 466 (M^++1, 100), 344 (60), 279 (35); HRMS: ($C_{27}H_{36}NO_2SSi$) calcd: 466.2231; found: 466.2231.

*4.1.2.13. N-(2-(4-Methoxyphenyl)ethynyl)-2-(2-(triethylsilyl)-ethynyl)-N-mesylbenzenamine (**2′m**).* Following the procedure described above and starting with *N*-ethynyl-2-(2-(triisopropylsilyl)ethynyl)-*N*-mesylbenzenamine (270 mg, 0.81 mmol), 1-iodo-4-methoxybenzene (209 mg, 0.89 mmol), $Pd(PPh_3)_4$ (47 mg), CuI (3 mg) in Et_3N (6 mL) and toluene (3 mL), **2′m** was isolated as a clear oil (186 mg, 52%). ^{1}H NMR ($CDCl_3$) δ: 7.59 (dd, *J*=6.9, 2.3 Hz, 1H, Ar*H*), 7.51 (dd, *J*=7.0, 2.0 Hz, 1H, Ar*H*), 7.41–7.33 (m, 4H, Ar*H*), 6.81 (d, *J*=8.9 Hz, 2H, Ar*H*), 3.79 (s, 3H, Ar*H*), 3.33 (s, 3H, Ar*H*), 1.03 (t, *J*=7.8 Hz, 9H, Si(CH$_2$CH_3)$_3$), 0.67 (c, 6H, Si(CH_2CH$_3$)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 159.4 (*C*), 138.8 (*C*), 134.6 (*C*H), 133.3 (2×*C*H), 130.2 (*C*H), 129.6 (*C*H), 129.1 (*C*H), 122.4 (*C*), 114.6 (*C*), 113.7 (2×*C*H), 101.8 (*C*), 99.4 (*C*), 80.2 (*C*), 70.3 (*C*), 55.2 (*C*H_3), 39.9 (*C*H_3), 7.5 Si(CH$_2$CH_3)$_3$, 4.2 Si(CH_2CH$_3$)$_3$.

*4.1.3. General procedure for the synthesis of N-(o-ethynyl) arylynamides **2***

Excess of tetrabutylammonium fluoride (1.0 M solution in THF) was added to a solution of TIPS-protected arylynamides **2′a–k** (0.1 mmol) in THF (10 mL), and the resulting mixture was stirred at rt for 10 min. After solvent removal, the residue was dissolved in EtOAc, washed with brine, dried over anhydrous Na_2SO_4 and concentrated to dryness. The residue was purified by flash chromatography on silica gel using a gradient mixture of EtOAc/hexanes as eluent giving arylynamides **2a–k** in good yields.

*4.1.3.1. N-2-Ethynylphenyl-N-2-phenylethynyl tosylamide (**2a**).* ^{1}H NMR ($CDCl_3$) δ: 7.77 (d, *J*=8.3 Hz, 2H, ArH), 7.53 (dd, *J*=6.3, 3.3 Hz, 1H, ArH), 7.41–7.26 (m, 10H, ArH), 3.09 (s, 1H, C≡CH), 2.44 (s, 3H, CH_3).

*4.1.3.2. 2-Ethynyl-N-(2-(naphthalen-1-yl)ethynyl)-N-tosylbenzenamine (**2b**).* ^{1}H NMR ($CDCl_3$) δ: 8.29–8.26 (m, 2H, Ar*H*), 7.83–7.30 (m, 13H, Ar*H*), 3.05 (s, 1H, CC*H*), 2.45 (s, 3H, CH_3).

*4.1.3.3. N-2-Ethynylphenyl-N-2-(4-nitrophenyl)ethynyl tosylamide (**2c**).* ^{1}H NMR ($CDCl_3$) δ: 8.14 (d, *J*=8.9 Hz, 2H,

ArH), 7.75 (d, J=8.3 Hz, 2H, ArH), 7.55 (dd, J=6.6, 2.7 Hz, 1H, ArH), 7.48–7.34 (m, 7H, ArH), 3.05 (s, 1H, C≡CH), 2.47 (s, 3H, CH_3).

*4.1.3.4. N-2-Ethynylphenyl-N-2-(4-methoxyphenyl)ethynyl tosylamide (**2d**).* ^{1}H NMR ($CDCl_3$) δ: 7.75 (d, J=8.4 Hz, 2H, ArH), 7.52 (dd, J=6.9, 2.4 Hz, 1H, ArH), 7.39–7.27 (m, 7H, ArH), 6.81 (d, J=8.9 Hz, 2H, ArH), 3.79 (s, 3H, OCH_3), 3.06 (s, 1H, C≡CH), 2.46 (s, 3H, CH_3).

*4.1.3.5. N-(2-(4-Chlorophenyl)ethynyl)-2-ethynyl-N-tosylbenzenamine (**2e**).* ^{1}H NMR ($CDCl_3$) δ: 7.73 (d, J=8.3 Hz, 2H, Ar*H*), 7.54–7.50 (m, 1H, Ar*H*), 7.38–7.21 (m, 9H, Ar*H*), 3.04 (s, 1H, CC*H*), 2.45 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 145.1 (*C*), 139.6 (*C*), 134.2 (*C*H), 133.9 (*C*), 133.7 (*C*), 132.6 (2×*C*H), 129.6 (*C*H+2×*C*H), 129.1 (*C*H), 129.0 (*C*H), 128.5 (2×*C*H), 122.1 (*C*), 121.3 (*C*), 83.4 (*C*), 83.1 (*C*H), 78.7 (*C*), 69.3 (*C*), 21.7 (*C*H_3).

*4.1.3.6. N-(2-(4-Fluorophenyl)ethynyl)-2-ethynyl-N-tosylbenzenamine (**2f**).* ^{1}H NMR ($CDCl_3$) δ: 7.74 (d, J=8.4 Hz, 2H, Ar*H*), 7.52 (dd, J=7.0, 2.4 Hz, 1H, Ar*H*), 7.40–7.29 (m, 7H, Ar*H*), 6.99–6.95 (m, 2H, Ar*H*), 3.04 (s, 1H, CC*H*), 2.46 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 162.3 (d, J_{C-F}=249 Hz, *C*), 145.0 (*C*), 139.8 (*C*), 134.2 (*C*H), 133.6 (d, J_{C-F}=8 Hz, 2×*C*H), 129.6 (*C*H), 129.6 (2×*C*H), 129.1 (*C*H), 129.0 (*C*H), 128.5 (2×*C*H), 122.1 (*C*), 118.8 (*C*), 118.8 (*C*), 115.4 (d, J_{C-F}=22 Hz, 2×*C*H), 83.0 (*C*H), 82.1 (*C*), 18.8 (*C*), 69.2 (*C*), 21.7 (*C*H_3); MS ESI-TOF *m/z* (%): 390 (M^++1, 12), 245 (100), 149 (84); HRMS: ($C_{27}H_{36}NO_2SSi$) calcd: 390.0959; found: 390.0970.

*4.1.3.7. N-2-Ethynylphenyl-N-2-(pyridin-3-yl)ethynyl tosylamide (**2h**).* ^{1}H NMR ($CDCl_3$) δ: 8.59 (s, 1H, ArH), 8.49 (d, J=4.8 Hz, 1H, ArH), 7.76 (d, J=8.4 Hz, 2H, ArH), 7.66 (dt, J=7.9, 1.7 Hz, 1H, ArH), 7.55 (dd, J=6.9, 2.3 Hz, 1H, ArH), 7.44–7.32 (m, 5H, ArH), 7.22 (dd, J=7.8, 4.8 Hz, 1H, ArH), 3.05 (s, 1H, C≡CH), 2.48 (s, 3H, CH_3).

*4.1.3.8. 5-Chloro-2-ethynyl-N-(2-phenylethynyl)-N-tosylbenzenamine (**2k**).* Clear oil. ^{1}H NMR ($CDCl_3$) δ: 7.34 (d, J=8.3 Hz, 2H, Ar*H*), 7.44 (d, J=8.3 Hz, 1H, Ar*H*), 7.34–7.23 (m, 7H, Ar*H*), 7.07 (d, J=8.0 Hz, 2H, Ar*H*), 3.07 (s, 1H, CC*H*), 2.46 (s, 3H, CH_3), 2.32 (s, 3H, CH_3).

*4.1.3.9. N-(2-(4-Methylphenyl)ethynyl)-2-ethynyl-N-mesylbenzenamine (**2l**).* Clear oil. ^{1}H NMR ($CDCl_3$) δ: 7.61 (dd, J=7.4, 1.8 Hz, 1H, Ar*H*), 7.55 (dd, J=7.6, 1.5 Hz, 1H, Ar*H*), 7.49–7.38 (m, 2H, Ar*H*), 7.34 (d, J=8.1 Hz, 2H, Ar*H*), 7.10 (d, J=8.0 Hz, 2H, Ar*H*), 3.47 (s, 1H, CC*H*), 3.33 (s, 3H, CH_3), 2.34 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 139.4 (*C*), 138.3 (*C*), 134.4 (*C*H), 131.7 (2×*C*H), 130.1 (*C*H), 129.9 (*C*H), 129.2 (*C*H), 129.0 (2×*C*H), 121.3 (*C*), 119.3 (*C*), 84.0 (*C*H), 80.8 (*C*), 79.7 (*C*), 65.6 (*C*), 39.5 (*C*H_3), 21.4 (*C*H_3).

*4.1.3.10. N-(2-(4-Methoxyphenyl)ethynyl)-2-ethynyl-N-mesylbenzenamine (**2m**).* Excess of KOH was added to a solution of arylynamide **2′m** (0.1 mmol) in THF, MeOH and H_2O (5+2+2 mL), and the resulting mixture was stirred at rt for 30 min. After solvent removal, the residue was dissolved in EtOAc, washed with brine, dried over anhydrous Na_2SO_4 and concentrated to dryness. The residue was purified by flash chromatography on silica gel using a gradient mixture of EtOAc/hexanes 70:30 as eluent giving **2m** as clear oil in 58% yield. ^{1}H NMR ($CDCl_3$) δ: 7.59 (dd, J=7.4, 1.9 Hz, 1H, Ar*H*), 7.53 (dd, J=7.9, 1.3 Hz, 1H, Ar*H*), 7.43–7.33 (m, 4H, Ar*H*), 6.80 (d, J=8.9 Hz, 2H, Ar*H*), 3.78 (s, 3H, CH_3), 3.48 (s, 1H, CC*H*), 3.32 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 159.6 (*C*), 139.5 (*C*), 134.4 (*C*H), 133.7 (2×*C*H), 130.0 (*C*H), 129.8 (*C*H), 129.1 (*C*H), 121.1 (*C*), 114.3 (*C*), 113.8 (2×*C*H), 83.9 (*C*H), 80.1 (*C*), 79.7 (*C*), 70.3 (*C*), 55.2 (*C*H_3), 39.4 (*C*H_3).

*4.1.3.11. N-2-(2-Trimethylsilylethynyl)phenyl-N-2-phenylethynyl tosylamide (**2″a**).* ^{1}H NMR ($CDCl_3$) δ: 7.75 (d, J=8.3 Hz, 2H, ArH), 7.52–7.50 (m, 1H, ArH), 7.36–7.24 (m, 10H, ArH), 2.45 (s, 3H, CH_3), 0.08 (s, 9H, $Si(CH_3)_3$).

4.1.4. General procedure for intramolecular dehydro Diels–Alder reaction

A toluene solution of **1** or **2** (0.01 M) and 0.5 mL of Et_3N were placed in a sealed tube and heated overnight at 150 °C in a silicon oil bath. After evaporation of the solvent, the crude material was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc as eluent.

*4.1.4.1. 2-Methyl-9-tosyl-9H-carbazole (**3a**).* ^{1}H NMR ($CDCl_3$) δ: 8.29 (d, J=8.4 Hz, 1H, Ar*H*), 8.14 (s, 1H, Ar*H*), 7.48 (d, J=7.5 Hz, 1H, Ar*H*), 7.77 (d, J=7.8 Hz, 1H, Ar*H*), 7.69 (d, J=8.2 Hz, 2H, Ar*H*), 7.45 (t, J=8.4 Hz, 1H, Ar*H*), 7.33 (t, J=7.5 Hz, 1H, Ar*H*), 7.18 (d, J=7.8 Hz, 1H, Ar*H*), 7.10 (d, J=8.2, 2H, Ar*H*), 2.56 (s, 3H, CH_3), 2.26 (s, 3H, CH_3).

*4.1.4.2. 7,8,9,10-Tetrahydro-5-tosyl-5H-benzo[b]carbazole (**3b**).* ^{1}H NMR ($CDCl_3$) δ: 8.27 (d, J=8.3 Hz, 1H, Ar*H*), 8.02 (s, 1H, Ar*H*), 7.81 (d, J=7.0 Hz, 1H, Ar*H*), 7.69 (d, J=8.3 Hz, 2H, Ar*H*), 7.56 (s, 1H, Ar*H*), 7.43 (t, J=8.3 Hz, 1H, Ar*H*), 7.31 (t, J=7.5 Hz, 1H, Ar*H*), 7.09 (d, J=8.1 Hz, 2H, Ar*H*), 2.99–2.90 (m, 4H, CH_2), 2.25 (s, 3H, CH_3), 1.87–1.84 (m, 4H, CH_2).

*4.1.4.3. 7,8,9,10-Tetrahydro-6-(trimethylsilyl)-5-tosyl-5H-benzo[b]carbazole (**3b′**).* ^{1}H NMR ($CDCl_3$) δ: 8.04 (d, J=8.0 Hz, 1H, Ar*H*), 7.46 (d, J=8.0 Hz, 1H, Ar*H*), 7.34–7.29 (m, 2H, Ar*H*), 7.22–7.15 (m, 2H, Ar*H*), 6.75–6.67 (m, 3H, Ar*H*), 3.18–2.79 (m, 4H, CH_2), 1.94–1.77 (m, 4H, CH_2), 2.14 (s, 3H, (CH_3)), 0.55 (s, 3H, $Si(CH_3)_3$).

*4.1.4.4. 5-Tosyl-5H-benzo[b]carbazole (**3c**).* ^{1}H NMR ($CDCl_3$) δ: 8.69 (d, J=8.6 Hz, 1H, Ar*H*), 8.58 (d, J=9.1, 1H, Ar*H*), 8.51–8.43 (m, 2H, Ar*H*), 7.99 (d, J=8.4 Hz, 1H, Ar*H*), 7.93 (d, J=9.1 Hz, 1H, Ar*H*), 7.70–7.65 (m, 3H, Ar*H*), 7.55–7.45 (m, 3H, Ar*H*), 7.04 (d, J=8.2 Hz, 2H, Ar*H*), 2.22 (s, 3H, CH_3).

*4.1.4.5. 12-Tosyl-12H-naphtho[1,2-b]carbazole (**3d**).* ^{1}H NMR ($CDCl_3$) δ: 9.66 (s, 1H, Ar*H*), 8.93 (d, *J*=8.3 Hz, 1H, Ar*H*), 8.39 (d, *J*=8.4 Hz, 1H, Ar*H*), 8.34 (s, 1H, Ar*H*), 8.03 (d, *J*=7.1 Hz, 1H, Ar*H*), 7.93 (d, *J*=7.8 Hz, 1H, Ar*H*), 7.8 (d, *J*=8.8 Hz, 1H, Ar*H*), 7.78–7.72 (m, 4H, Ar*H*), 7.68 (t, *J*=8.0 Hz, 1H, Ar*H*), 7.55 (t, *J*=7.3 Hz, 1H, Ar*H*), 7.43 (t, *J*=7.6 Hz, 1H, Ar*H*), 7.03 (d, *J*=8.0 Hz, 2H, Ar*H*), 2.20 (s, 3H, CH_3).

*4.1.4.6. 8-Tosyl-8H-naphtho[2,1-b]carbazole (**3e**).* ^{1}H NMR ($CDCl_3$) δ: 9.18 (s, 1H, Ar*H*), 8.80–8.78 (m, 2H, Ar*H*), 7.80–7.41 (m, 10H, Ar*H*), 7.13 (d, *J*=7.6 Hz, 1H, Ar*H*), 7.06 (d, *J*=8.3 Hz, 2H, Ar*H*), 2.22 (s, 3H, CH_3).

*4.1.4.7. 10-Tosyl-10H-phenanthro[9,10-b]carbazole (**3f**).* ^{1}H NMR ($CDCl_3$) δ: 9.56 (s, 1H, Ar*H*), 9.06 (s, 1H, Ar*H*), 8.85 (dd, *J*=8.1, 1.3 Hz, 1H, Ar*H*), 8.71–8.68 (m, 1H, Ar*H*), 8.38 (d, *J*=8.3 Hz, 1H, Ar*H*), 8.08 (d, *J*=7.7 Hz, 1H, Ar*H*), 7.77–7.63 (m, 7H, Ar*H*), 7.57–7.53 (m, 2H, Ar*H*), 7.44 (dt, *J*=7.6, 0.9 Hz, 1H, Ar*H*), 7.04 (d, *J*=8.1 Hz, 2H, Ar*H*), 2.19 (s, 3H, (CH_3)).

*4.1.4.8. 9-Nitro-11-phenyl-5-tosyl-5H-benzo[b]carbazole (**3g**).* ^{1}H NMR ($CDCl_3$) δ: 8.92 (s, 1H, Ar*H*), 8.58 (d, *J*=2.3 Hz, 1H, Ar*H*), 8.35 (d, *J*=8.4 Hz, 1H, Ar*H*), 8.29 (dd, *J*=9.1, 2.3 Hz, 1H, Ar*H*), 8.20 (d, *J*=9.1 Hz, 1H, Ar*H*), 7.80 (d, *J*=8.4 Hz, 2H, Ar*H*), 7.66–7.63 (m, 3H, Ar*H*), 7.48 (t, *J*=8.4 Hz, 1H, Ar*H*), 7.40–7.37 (m, 2H, Ar*H*), 7.16 (d, *J*=8.1 Hz, 2H, Ar*H*), 7.07 (t, *J*=8.1 Hz, 1H, Ar*H*), 6.65 (d, *J*=8.4 Hz, 1H, Ar*H*), 2.29 (s, 3H, (CH_3)).

*4.1.4.9. 6-(Pyrimidin-2-yl)-5-tosyl-5H-benzo[b]carbazole (**3h**).* ^{1}H NMR ($CDCl_3$) δ: 8.90 (d, *J*=4.8 Hz, 2H, Ar*H*), 8.57 (d, *J*=8.3 Hz, 1H, Ar*H*), 8.47 (s, 1H, Ar*H*), 8.34–8.27 (m, 3H, Ar*H*), 8.11 (d, *J*=7.9 Hz, 1H, Ar*H*), 7.11 (t, *J*=7.1 Hz, 1H, Ar*H*), 7.60 (t, *J*=7.3 Hz, 1H, Ar*H*), 7.48–7.41 (m, 3H, Ar*H*), 7.32 (t, *J*=4.8 Hz, 1H, Ar*H*), 7.00 (d, *J*=8.2 Hz, 2H, Ar*H*), 6.74 (d, *J*=8.1 Hz, 2H, Ar*H*), 2.09 (s, 3H, CH_3).

*4.1.4.10. 11-Cyclohexenyl-5-tosyl-5H-benzo[b]carbazole (**3i**).* ^{1}H NMR ($CDCl_3$) δ: 8.69 (s, 1H, Ar*H*), 8.36 (d, *J*=8.4 Hz, 1H, Ar*H*), 8.15 (d, *J*=7.8 Hz, 1H, Ar*H*), 8.08 (d, *J*=8.4 Hz, 1H, Ar*H*), 8.04 (d, *J*=8.1 Hz, 1H, Ar*H*), 7.73 (d, *J*=8.0 Hz, 2H, Ar*H*), 7.56–7.47 (m, 3H, Ar*H*), 7.34 (t, *J*=7.4 Hz, 1H, Ar*H*), 7.07 (d, *J*=8.0 Hz, 2H, Ar*H*), 5.84 (br s, 1H, C=C*H*), 2.38–2.33 (m, 4H, CH_2), 2.24 (s, 3H, CH_3), 1.98–1.93 (m, 4H, CH_2).

*4.1.4.11. 7,8,9,10-Tetrahydro-6-phenyl-5-tosyl-5H-benzo[b]carbazole (**3j**).* ^{1}H NMR ($CDCl_3$) δ: 8.09 (d, *J*=7.6 Hz, 2H, Ar*H*), 7.67 (d, *J*=8.1 Hz, 1H, Ar*H*), 7.51 (s, 1H, Ar*H*), 7.42–7.29 (m, 6H, Ar*H*), 7.05 (d, *J*=8.2 Hz, 2H, Ar*H*), 6.89 (d, *J*=8.2 Hz, 2H, Ar*H*), 2.98–2.95 (m, 2H, CH_2), 2.62–2.59 (m, 2H, CH_2), 2.24 (s, 3H, (CH_3)), 1.85–1.79 (m, 2H, CH_2), 1.74–1.69 (m, 2H, CH_2).

*4.1.4.12. 5-[(4-Methylphenyl)sulfonyl]-9-nitro-5H-benzo[b]carbazole (**3k**).* ^{1}H NMR ($CDCl_3$) δ: 8.95 (s, 1H, Ar*H*), 8.83 (s, 1H, Ar*H*), 8.53 (s, 1H, Ar*H*), 8.35 (d, *J*=8.4 Hz, 1H, Ar*H*), 8.29 (d, *J*=9.1, 1H, Ar*H*), 8.15 (d, *J*=9.1 Hz, 1H, Ar*H*), 8.07 (d, *J*=7.7 Hz, 1H, Ar*H*), 7.74 (d, *J*=8.4 Hz, 2H, Ar*H*), 7.61 (t, *J*=7.3 Hz, 1H, Ar*H*), 7.45 (t, *J*=7.4 Hz, 1H, Ar*H*), 7.11 (d, *J*=8.5 Hz, 2H, Ar*H*), 2.26 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 145.4 (*C*), 140.2 (*C*), 139.8 (*C*), 135.1 (*C*), 134.6 (*C*), 129.9 (*C*H), 129.8 (2×*C*H), 129.6 (*C*), 129.4 (*C*H), 128.7 (*C*), 128.6 (*C*), 126.6 (2×*C*H), 125.1 (*C*), 125.0 (*C*H), 124.5 (*C*H), 121.0 (*C*H), 120.7 (*C*H), 119.1 (*C*H), 115.3 (*C*H), 112.1 (*C*H), 21.5 (*C*H_3); MS (70 eV) *m*/*z* (%): 416 (M^+, 5), 261 (57), 214 (72), 91 (100); HRMS: ($C_{23}H_{16}N_2O_4S$): calcd: 416.0830; found: 416.0831.

*4.1.4.13. 5-[(4-Methylphenyl)sulfonyl]-9-methoxy-5H-benzo[b]carbazole (**3l**).* ^{1}H NMR ($CDCl_3$) δ: 8.65 (s, 1H, Ar*H*), 8.32 (d, *J*=8.4 Hz, 1H, Ar*H*), 8.19 (s, 1H, Ar*H*), 7.96–7.92 (m, 2H, Ar*H*), 7.67 (d, *J*=8.4 Hz, 2H, Ar*H*), 7.50 (t, *J*=8.5 Hz, 1H, Ar*H*), 7.36 (t, *J*=8.4 Hz, 1H, Ar*H*), 7.25–7.20 (m, 2H, Ar*H*), 7.02 (d, *J*=8.1 Hz, 2H, Ar*H*), 3.93 (s, 3H, OCH_3), 2.20 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 157.1 (*C*), 144.7 (*C*), 140.0 (*C*), 135.9 (*C*), 134.7 (*C*), 131.7 (*C*), 129.8 (*C*H), 129.5 (2×*C*H), 128.6 (*C*), 128.2 (*C*H), 127.3 (*C*), 126.5 (2×*C*H), 126.4 (*C*), 124.1 (*C*H), 120.5 (*C*H), 119.3 (*C*H), 116.9 (*C*H), 115.4 (*C*H), 112.4 (*C*H), 105.4 (*C*H), 55.3 (O*C*H_3), 21.4 (*C*H_3); MS (70 eV) *m*/*z* (%): 401 (M^+, 10), 246 (100), 203 (72); HRMS ($C_{24}H_{19}NO_3S$): calcd: 401.1085; found: 401.1082.

*4.1.4.14. 9-Chloro-5-[(4-methylphenyl)sulfonyl]-5H-benzo[b]carbazole (**3m**).* ^{1}H NMR ($CDCl_3$) δ: 8.70 (s, 1H, Ar*H*), 8.33 (d, *J*=8.4 Hz, 1H, Ar*H*), 8.19 (s, 1H, Ar*H*), 7.98–7.95 (m, 2H, Ar*H*), 7.90 (d, *J*=1.7 Hz, 1H, Ar*H*), 7.70 (d, *J*=8.4 Hz, 2H, Ar*H*), 7.54 (td, *J*=8.5, 1.3 Hz, 1H, Ar*H*), 7.46 (dd, *J*=8.8, 2.1 Hz, 1H, Ar*H*), 7.38 (t, *J*=7.6 Hz, 1H, Ar*H*), 7.05 (d, *J*=8.2 Hz, 2H, Ar*H*), 2.22 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 145.0 (*C*), 140.1 (*C*), 137.4 (*C*), 134.6 (*C*), 131.0 (*C*), 131.0 (*C*), 130.8 (*C*), 129.9 (*C*H), 129.6 (2×*C*H), 128.7 (*C*H), 127.7 (*C*), 126.8 (*C*H), 126.5 (2×*C*H), 126.4 (*C*H), 125.8 (*C*), 124.2 (*C*H), 120.7 (*C*H), 117.4 (*C*H), 115.3 (*C*H), 112.2 (*C*H), 21.4 (*C*H_3); MS (70 eV) *m*/*z* (%): 407 (M+Cl 37, 6), 405 (M+Cl 35, 15), 252 (34), 250 (100), 58 (66); HRMS ($C_{23}H_{16}NO_2SCl$): calcd 405.0590; found 405.0592.

*4.1.4.15. 9-Fluoro-5-[(4-methylphenyl)sulfonyl]-5H-benzo[b]carbazole (**3n**).* ^{1}H NMR ($CDCl_3$) δ: 8.73 (s, 1H, Ar*H*), 8.33 (d, *J*=8.4 Hz, 1H, Ar*H*), 8.24 (s, 1H, Ar*H*), 8.03 (dd, *J*=9.0, 5.6 Hz, 1H, Ar*H*), 7.99 (d, *J*=7.2 Hz, 1H, Ar*H*), 7.70 (d, *J*=8.4 Hz, 2H, Ar*H*), 7.57–7.52 (m, 2H, Ar*H*), 7.39 (t, *J*=7.5 Hz, 1H, Ar*H*), 7.33 (td, *J*=8.7, 2.5 Hz, 1H, Ar*H*), 7.06 (d, *J*=8.4 Hz, 2H, Ar*H*), 2.22 (s, 3H, Ar*H*); ^{13}C NMR/DEPT ($CDCl_3$) δ: 160.1 (d, J_{C-F}=245 Hz, *C*), 144.9 (*C*), 140.1 (*C*), 134.6 (*C*), 131.1 (*C*), 131.1 (*C*), 130.7 (d, J_{C-F}=9 Hz, *C*H), 129.9 (*C*), 129.6 (2×*C*H), 128.7 (*C*H), 127.8 (*C*), 126.5 (2×*C*H), 125.9 (*C*), 124.2 (*C*H), 120.7 (*C*H), 117.5 (d, J_{C-F}=6 Hz, *C*H), 116.6 (d, J_{C-F}=26 Hz, *C*H), 115.4 (*C*H), 112.4 (*C*H), 110.6 (d, J_{C-F}=21 Hz, *C*H), 21.4 (*C*H_3); ESI-TOF *m*/*z*

(%): 390 (M^++1, 6), 245 (100), 149 (76); HRMS ($C_{23}H_{17}FNO_2S$): calcd: 390.0959; found: 390.0970.

*4.1.4.16. 10-[(4-Methylphenyl)sulfonyl]-10H-pyrido[3,4-b]-carbazole (**3p**).* ^{1}H NMR ($CDCl_3$) δ: 9.48 (s, 1H, Ar*H*), 8.87 (s, 1H, Ar*H*), 8.53 (d, *J*=5.8 Hz, 1H, Ar*H*), 8.37 (d, *J*=8.4 Hz, 1H, Ar*H*), 8.33 (s, 1H, Ar*H*), 8.07 (d, *J*=8.4 Hz, 1H, Ar*H*), 7.77 (d, *J*=5.8 Hz, 1H, Ar*H*), 7.73 (d, *J*=8.4 Hz, 2H, Ar*H*), 7.61 (t, *J*=8.4 Hz, 1H, Ar*H*), 7.44 (t, *J*=7.9 Hz, 1H, Ar*H*), 7.10 (d, *J*=8.4 Hz, 2H, Ar*H*), 2.25 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 145.0 (*C*), 140.7 (*C*), 134.4 (*C*), 132.6 (*C*), 130.9 (*C*H), 129.9 (*C*H), 129.8 (2×*C*H), 129.7 (*C*), 128.8 (*C*H), 126.6 (2×*C*H), 126.5 (*C*), 125.1 (*C*), 124.5 (*C*H), 121.4 (*C*H), 117.0 (*C*H), 115.4 (*C*H), 112.4 (*C*H), 29.7 (*C*H_3); MS (70 eV) *m/z* (%): 372 (M^+, 21), 217 (100), 190 (12); HRMS: ($C_{22}H_{16}N_2O_2S$): calcd: 372.0932; found: 372.0925.

*4.1.4.17. 9-[(4-Methylphenyl)sulfonyl]-9H-thieno[2,3-b]carbazole (**3q**).* ^{1}H NMR ($CDCl_3$) δ: 8.84 (s, 1H, Ar*H*), 8.33 (d, *J*=8.3 Hz, 1H, Ar*H*), 8.28 (s, 1H, Ar*H*), 7.94 (d, *J*=7.6 Hz, 1H, Ar*H*), 7.69 (d, *J*=8.4 Hz, 2H, Ar*H*), 7.51 (d, *J*=7.3 Hz, 1H, Ar*H*), 7.48 (d, *J*=5.9 Hz, 1H, Ar*H*), 7.41–7.34 (m, 2H, Ar*H*), 7.07 (d, *J*=8.5 Hz, 2H, Ar*H*), 2.23 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 144.9 (*C*), 139.7 (*C*), 139.2 (*C*), 136.6 (*C*), 136.4 (2×*C*), 134.7 (*C*), 129.6 (2×*C*H), 127.5 (*C*H), 126.5 (2×*C*H), 125.2 (*C*), 124.0 (*C*H), 123.4 (*C*H), 119.9 (*C*H), 115.4 (2×*C*H), 114.0 (*C*H), 108.5 (*C*H), 21.5 (*C*H_3); MS (70 eV) *m/z* (%): 377 (M^+, 11), 222 (100), 196 (7); HRMS: ($C_{21}H_{15}NO_2S$): calcd: 377.0544; found: 377.0549.

*4.1.4.18. 3-Chloro-9-methyl-5-[(4-methylphenyl)sulfonyl]-5H-benzo[b]carbazole (**3r**).* ^{1}H NMR ($CDCl_3$) δ: 8.64 (s, 1H, Ar*H*), 8.35 (d, *J*=1.8 Hz, 1H, Ar*H*), 8.16 (s, 1H, Ar*H*), 7.94 (d, *J*=8.5 Hz, 1H, Ar*H*), 7.87 (d, *J*=8.3 Hz, 1H, Ar*H*), 7.72–7.70 (m, 3H, Ar*H*), 7.39 (dd, *J*=8.5, 1.6 Hz, 1H, Ar*H*), 7.34 (d, *J*=8.0, 1.7 Hz, 1H, Ar*H*), 7.08 (d, *J*=8.3 Hz, 2H, Ar*H*), 2.55 (s, 3H, CH_3), 2.24 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 145.1 (*C*), 140.6 (*C*), 136.8 (*C*), 135.0 (*C*), 134.5 (*C*), 133.9 (*C*), 131.3 (*C*), 130.9 (*C*), 129.7 (2×*C*H), 128.6 (*C*H), 128.2 (*C*H), 126.7 (*C*H), 126.6 (2×*C*H), 125.9 (*C*), 125.0 (*C*), 124.5 (*C*H), 121.2 (*C*H), 117.7 (*C*H), 115.6 (*C*H), 112.1 (*C*H), 21.7 (*C*H_3), 21.5 (*C*H_3); ESI-TOF m/z (%): 420 (M^++1, 9), 356 (100), 282 (66); HRMS ($C_{24}H_{19}NO_2SCl$): calcd: 420.0820; found: 420.0836.

*4.1.4.19. 9-Methyl-5-(methylsulfonyl)-5H-benzo[b]carbazole (**3s**).* ^{1}H NMR ($CDCl_3$) δ: 8.51 (s, 1H, Ar*H*), 8.33 (s, 1H, Ar*H*), 8.17 (d, *J*=8.2 Hz, 1H, Ar*H*), 8.10 (d, *J*=8.2 Hz, 1H, Ar*H*), 7.91 (d, *J*=8.4 Hz, 1H, Ar*H*), 7.77 (s, 1H, Ar*H*), 7.53 (td, *J*=7.6, 1.4 Hz, 1H, Ar*H*), 7.45 (td, *J*=7.5, 1.0 Hz, 1H, Ar*H*), 7.39 (dd, *J*=8.4, 1.5 Hz, 1H, Ar*H*), 2.96 (s, 3H, CH_3), 2.57 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 140.0 (*C*), 136.7 (*C*), 134.9 (*C*), 131.3 (*C*), 130.9 (*C*), 128.6 (*C*H), 128.4 (*C*H), 128.1 (*C*H), 126.8 (*C*H), 126.8 (*C*H), 126.7 (*C*), 126.4 (*C*), 124.3 (*C*H), 120.7 (*C*H), 117.9 (*C*H), 111.5 (*C*H), 37.7 (*C*H_3), 21.7 (*C*H_3); ESI-TOF m/z (%): 310 (M^++1, 6), 245 (100), 149 (86); HRMS ($C_{18}H_{16}NO_2S$): calcd: 310.0896; found: 310.0902.

*4.1.4.20. 9-Methoxy-5-(methylsulfonyl)-5H-benzo[b]carbazole (**3t**).* ^{1}H NMR ($CDCl_3$) δ: 8.48 (s, 1H, Ar*H*), 8.33 (s, 1H, Ar*H*), 8.17 (d, *J*=8.0 Hz, 1H, Ar*H*), 8.09 (d, *J*=7.7 Hz, 1H, Ar*H*), 7.89 (d, *J*=9.0 Hz, 1H, Ar*H*), 7.54 (td, *J*=8.1, 1.4 Hz, 1H, Ar*H*), 7.44 (td, *J*=7.5, 1.1 Hz, 1H, Ar*H*), 7.29 (d, *J*=2.4 Hz, 1H, Ar*H*), 7.23 (dd, *J*=9.0, 2.5 Hz, 1H, Ar*H*), 3.97 (s, 3H, CH_3), 2.96 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 157.3 (*C*), 140.0 (*C*), 135.8 (*C*), 131.8 (*C*), 129.8 (*C*H), 128.6 (*C*), 128.5 (*C*H), 127.1 (*C*), 126.3 (*C*), 124.3 (*C*H), 120.7 (*C*H), 119.5 (*C*H), 117.2 (*C*H), 115.0 (*C*H), 111.9 (*C*H), 105.5 (*C*H), 55.3 (*C*H_3), 37.7 (*C*H_3). MS (70 eV) *m/z* (%): 325 (M^+, 19), 246 (100), 203 (50); HRMS ($C_{18}H_{15}NO_3S$): calcd: 325.0773; found: 325.0769.

*4.1.4.21. 5-[(4-Methylphenyl)sulfonyl]-11-(trimethylsilyl)-5H-benzo[b]carbazole (**3u**).* ^{1}H NMR ($CDCl_3$) δ: 8.74 (s, 1H, Ar*H*), 8.35–8.33 (m, 2H, Ar*H*), 8.06 (d, *J*=8.1 Hz, 1H, Ar*H*), 8.01 (d, *J*=7.7 Hz, 1H, Ar*H*), 7.97 (d, *J*=8.1 Hz, 1H, Ar*H*), 7.71 (d, *J*=8.4 Hz, 2H, Ar*H*), 7.57–7.48 (m, 2H, Ar*H*), 7.39 (t, *J*=7.7 Hz, 1H, Ar*H*), 7.05 (d, *J*=8.4 Hz, 2H, Ar*H*), 2.22 (s, 3H, CH_3); 0.07 (s, 9H, Si(CH_3)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ: 144.9 (*C*), 140.1 (*C*), 138.8 (*C*), 137.3 (*C*), 134.7 (*C*), 133.0 (*C*), 130.6 (*C*), 129.6 (2×*C*H), 128.5 (*C*H), 128.4 (*C*H), 128.0 (*C*H), 126.9 (*C*), 126.5 (2×*C*H), 126.3 (*C*), 125.9 (*C*H), 125.1 (*C*H), 124.1 (*C*H), 120.6 (*C*H), 118.3 (*C*H), 115.4 (*C*H), 112.2 (*C*H), 21.5 (*C*H_3), 1.9 (Si(*C*H_3)$_3$); MS FAB *m/z* (%): 444 (M^++1.4), 371 (50), 216 (100); HRMS: ($C_{26}H_{25}NO_2SSiNa$) calcd: 466.1273; found: 466.1267.

*4.1.4.22. 6-Tosyl-6H-pyrido[4,3-b]carbazole (**3v**).* ^{1}H NMR ($CDCl_3$) δ: 9.39 (s, 1H, Ar*H*), 8.71 (s, 1H, Ar*H*), 8.55 (d, *J*=5.9 Hz, 1H, Ar*H*), 8.50 (s, 1H, Ar*H*), 8.36 (d, *J*=8.4 Hz, 1H, Ar*H*), 8.07 (d, *J*=7.2 Hz, 1H, Ar*H*), 7.86 (d, *J*=5.9 Hz, 1H, Ar*H*), 7.74 (d, *J*=8.4 Hz, 2H, Ar*H*), 7.59 (t, *J*=7.2 Hz, 1H, Ar*H*), 7.44 (t, *J*=7.2 Hz, 1H, Ar*H*), 7.11 (d, *J*=8.4 Hz, 2H, Ar*H*), 2.26 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ: 152.7 (*C*H), 145.3 (*C*), 142.3 (*C*H), 140.1 (*C*), 140.0 (*C*), 135.1 (*C*), 134.6 (*C*), 131.1 (*C*), 129.8 (2×*C*H), 129.1 (*C*H), 128.0 (*C*), 126.5 (2×*C*H), 125.5 (*C*), 124.4 (*C*H), 120.8 (*C*H), 118.6 (*C*H), 115.2 (*C*H), 110.4 (*C*H), 21.5 (*C*H_3); MS (70 eV) *m/z* (%): 372 (M^+, 13), 217 (100), 190 (12); HRMS: ($C_{22}H_{16}N_2O_2S$): calcd: 372.0932; found: 372.0937.

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25. Electron-poor and electron-rich heteroaroaromatic substrates (e.g., **2h**, **2j**) gave low yields in IDDA reactions due to partial decomposition of the reacting intermediates. See Ref. 14 for more details.

26. The starting arylynamides **2k**, **2l** and **2m** were obtained following the same procedure as for **2** (Scheme 9) but starting with 2-iodo-5-chloroaniline and the mesyl-protected analogue of **1i** either with TIPS (for **2l**) or TES (for **2m**).

27. Electron-rich and electron-poor *para* substituents on the reacting aryl ring are very well tolerated in IDDA reactions. Herein, halogenated substrates on the reacting and non-reacting aryl ring (e.g., **2e**, **2f** and **2k**) underwent IDDA reactions in rather good yields. Mesyl groups in nitrogen (e.g., **2l** and **2m**) are also very well tolerated in IDDA reactions. See Refs. 14d,h for more details of the IDDA mechanism.