JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.6b01764 • Publication Date (Web): 28 Sep 2016

ACS Publications

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Synthesis of 6,12-Epiminodibenzo[*b,f*][1,5]diazocines via an Ytterbium Triflate-Catalyzed, AB_2 Three-Component Reaction

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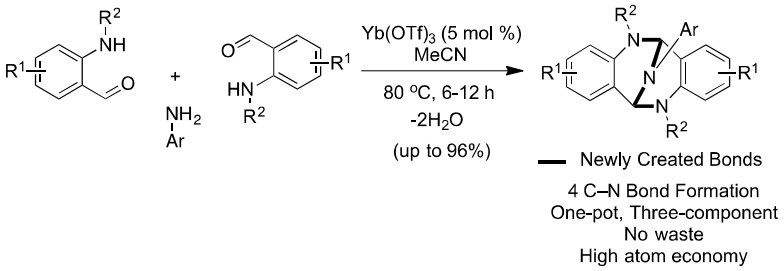
GRAPHICAL ABSTRACT



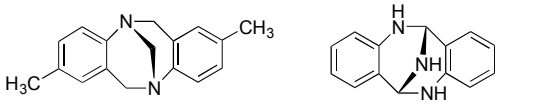
ABSTRACT

An efficient and selective procedure for the synthesis of epiminodibenzo[*b,f*][1,5]diazocines involving a AB_2 three-component reaction is developed. Two equivalents of suitably substituted 2-aminoarylaldehydes reacted with arylamines in the presence of $Yb(OTf)_3$ to afford the desired products in high yields. The reaction is highly atom-economic and waste-free, in addition to allowing the generation of two heterocyclic rings and four C–N bonds in a single operation. Significantly, this approach is a complementary to the existing literature procedures, affording arylamine-derived products that could not be accessed previously. A

plausible mechanism is proposed involving an imine formation-intermolecular annulation-intramolecular iminium ion cyclization sequence.

INTRODUCTION

Tröger's base **1** and its analogs are recognized as a very important class of nitrogen heterocycles with potential applications in various areas of supramolecular chemistry.[1] The presence of two stereogenic nitrogen atoms and its unique V-shaped rigid structure with a hydrophobic cavity between the aryl rings explains its role in asymmetric catalysis, molecular recognition, self-assembly, sensors, optoelectronics and enzyme inhibition.[2,3] Consequently, considerable effort has been devoted to the synthesis, functionalization and chiral resolution of Tröger's base-related compounds.[4] Likewise, one of the most closely related analogs of Tröger's base, epiminodibenzo[*b,f*][1,5]diazocine **2**, was also found to possess similar applications owing to its structural resemblance (Figure 1).[5-7] Consequently, development of efficient synthetic procedures for this class of compounds is an essential task. Very few methodologies to access epiminodibenzo[*b,f*][1,5]diazocines are known in the literature, that include a porous grapheme oxide-catalyzed tandem reaction of 2-aminobenzylamine,[5] a TMSOTf/Et_3N catalyzed domino process starting from *N*-alkyl-aldimines[6] and a metal-free cyclization of 2-aminophenyl ketimines.[7]

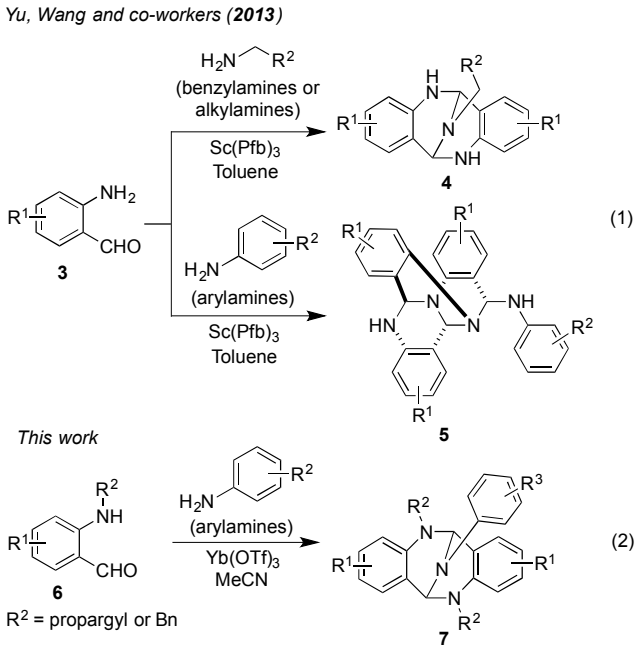


1: Tröger's base **2**: 6,12-Epiminodibenzo[*b,f*][1,5]-diazocine

Figure 1. Structures of Tröger's base and 6,12-epiminodibenzo[*b,f*][1,5]diazocine

Although epiminodibenzo[*b,f*][1,5]diazocines may seem, in principle, easy to access from two equivalents of 2-aminoarylaldehydes and a primary amine, this approach presents a major limitation associated with the low stability of these aldehydes, where the presence of

two highly reactive adjacent functionalities often affords trimerization products rather than the desired compounds, especially in the presence of nucleophiles.[8] For this reason, functionalized 2-aminoarylaldehydes including iminophosphoranes[9] and *N*-Ts/Ms derivatives[10] have been employed as precursors for the synthesis of epiminodibenzo[*b*,*f*][1,5]diazocines combined with primary amines, albeit in low yields. Recently, Yu, Wang and co-workers reported a simple cascade reaction between 2-aminoarylaldehydes **3** and primary amines in the presence of scandium pentafluorobenzoate.[11] This reaction afforded the expected epiminodibenzo[*b*,*f*][1,5]diazocine derivatives **4** in good yields, but worked exclusively for benzylamines and other alkylamines. On the other hand, 2-aminoarylaldehydes reacted with arylamines furnishing the ring-fused quinazoline derivatives **5** (Scheme 1, eq 1). In this context, we envisioned to develop a simple procedure for the synthesis of epiminodibenzo[*b*,*f*][1,5]diazocines **7** starting from 2-aminoarylaldehydes **6** and arylamines with an aim to provide a complementary approach to the existing Lu and Wang's protocol (Scheme 1, eq 2).



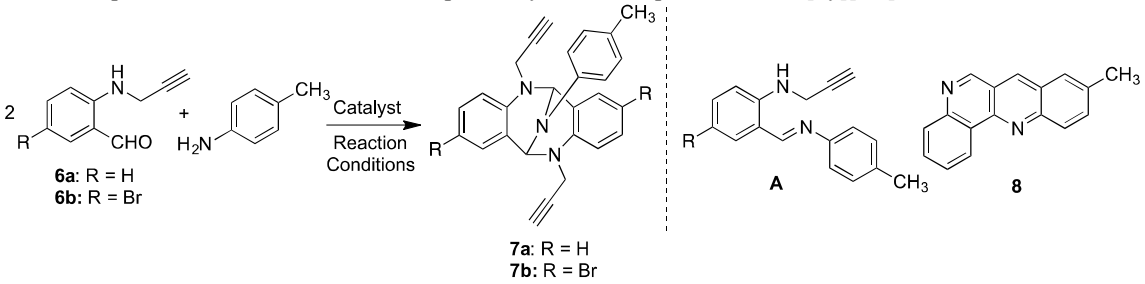
Scheme 1. Reactivity of 2-aminoarylaldehydes with primary amines

RESULTS AND DISCUSSION

Recently, we have reported the synthesis of 5,6-dihydrodibenzo[*b,h*][1,6]naphthyridines via copper(II) bromide catalyzed intramolecular [4+2] hetero-Diels–Alder reactions from 2-(*N*-propargylamino-*N*-tosyl)benzaldehydes and arylamines.[12] During this investigation, we were drawn to study whether the reaction between 2-(*N*-propargylamino)benzaldehyde **6a** and *p*-toluidine would afford the completely aromatized dibenzo[*b,h*][1,6]naphthyridine **8**. However, under our experimental conditions, in the presence of 10 mol % of $CuBr_2$ in toluene at 25 ^{o}C we observed only the imine intermediate **A**. On the other hand, at 80 ^{o}C, 15% of dibenzo[*b,h*][1,6]naphthyridine **8** was isolated together with unreacted aldehyde and imine **A** (Table 1, entries 1 and 2). Surprisingly, switching the reaction solvent to acetonitrile, under similar experimental conditions, the reaction furnished 58% of epiminodibenzo[*b,f*][1,5]diazocines **7a** via an AB_2 three-component reaction, together with the imine intermediate **A** (Table 1, entry 3). Among the other tested copper catalysts, $CuCl_2$ furnished comparable yield, nonetheless, in the presence of CuCl, complete decomposition of starting material **6a** was observed (entries 4 and 5). In an effort to improve the reaction yield, subsequently, we moved to screen some Lewis acids. As shown in entries 6-9, with the exception of $InCl_3$, other tested catalysts cerium(IV) ammonium nitrate (CAN), $Sc(OTf)_3$ and $Yb(OTf)_3$ furnished the product **7a** in good yields. The reaction was completed in 8 h in the presence of 10 mol % of $Yb(OTf)_3$ at 80 ^{o}C and a maximum yield of 75% was observed (entry 9). Decreasing the catalyst loading to 5 mol % did not affect the rate of the reaction significantly and delivered 74% of the product under similar reaction time (entry 10). It should be highlighted here that all the tested catalysts, including the copper salts, afforded only the imine intermediate **A** at 25 ^{o}C and in no case the [4+2] cycloaddition product **8** was isolated. Further screening of solvents including DCM, DCE, THF, toluene and ethanol

reveled that DCM gave comparable yield and in the cases of toluene and ethanol the reaction was not completed even after 24 h (entries 11-15). Inferior outcomes were observed when the reaction was carried out in green solvents such as water, PEG-200 and glycerol (entries 16-18). Remarkably, the bromo derivative **7b** was obtained in 95% yield under optimized reaction conditions (entry 19).

Table 1. Optimization of the AB_2 three-component synthesis of epiminodibenzo[*b,f*][1,5]diazocines[a]



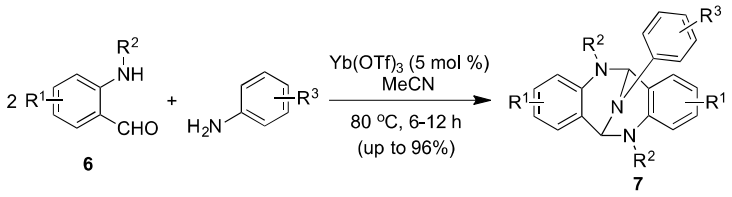
entry	compd	catalyst	mol %	solvent	temperature (^oC)	reaction time (h)	yield of **7a**/**7b**[b] (%)
1	**7a**	$CuBr_2$	10	Toluene	25	24	-[c]
2	**7a**	$CuBr_2$	10	Toluene	80	24	-[d]
3	**7a**	$CuBr_2$	10	MeCN	80[c]	12	58[e]
4	**7a**	$CuCl_2$	10	MeCN	80[c]	16	55[e]
5	**7a**	CuCl	10	MeCN	80[c]	24	-[f]
6	**7a**	$InCl_3$	10	MeCN	80[c]	24	21[e]
7	**7a**	CAN	10	MeCN	80[c]	8	63
8	**7a**	$Sc(OTf)_3$	10	MeCN	80[c]	16	69[e]
9	**7a**	$Yb(OTf)_3$	10	MeCN	80[c]	8	75
10[g]	**7a**	$Yb(OTf)_3$	5	MeCN	80	8	74
11	**7a**	$Yb(OTf)_3$	5	DCM	45	12	65
12	**7a**	$Yb(OTf)_3$	5	DCE	80	24	57
13	**7a**	$Yb(OTf)_3$	5	THF	70	12	55
14	**7a**	$Yb(OTf)_3$	5	Toluene	80	24	51[e]
15	**7a**	$Yb(OTf)_3$	5	EtOH	80	24	25[e]
16	**7a**	$Yb(OTf)_3$	5	Water	80	24	-[h]
17	**7a**	$Yb(OTf)_3$	5	PEG-200	80	24	40[e]
18	**7a**	$Yb(OTf)_3$	5	Glycerol	80	24	28[e]
19[g]	**7b**	$Yb(OTf)_3$	5	MeCN	80	8	95

[a] All reactions were carried out with **6a**/**6b** (1.0 mmol) and *p*-toluidine (0.5 mmol) with catalyst in 2 mL of solvent. [b] Isolated yield. [c] Only imine **A** was observed at 25 ^oC. [d] 15% of compound **8** was isolated together with unreacted **6a** and intermediate **A**. [e] Unreacted imine **A** was noticed in the crude ^{1}H-NMR spectra. [f] Decomposition of compound **6a** was observed. [g] Optimized reaction conditions. [h] Only imine **A** was formed.

With the optimized reaction conditions in hand, we next turned out attention to investigate the scope and limitations of the AB_2 three-component synthesis of

epiminodibenzo[*b,f*][1,5]diazocines **7**. Unlike Yu and Wang's methodology,[11] our conditions worked very well for all the tested arylamines to afford the target compounds in good to excellent yields (Scheme 2). Initially, we examined the effect of the substituents on the aldehyde component **6**, it revealed that the presence of electron-withdrawing substituents including bromine and chlorine afforded the products in excellent yields compared to the unsubstituted aldehyde, presumably due to the stability and controlled reactivity of aldehydes **6** (eg. **7b**, **7g**-**7n**). These electron-withdrawing groups decrease the nucleophilicity of the nitrogen atom thus confirms the smooth reactivity of compounds **6**. The nitrogen atom also bears propargyl and benzyl substituents. We then investigated the nature of the substituents on the arylamines. All moderately electron-releasing groups including *p*-methyl (**7a** and **7b**), *m*-methyl (**7j**, **7k** and **7o**) and 3,5-dimethyl (**7i** and **7p**), strongly electron-releasing *p*- and *m*-methoxy (**7d**, **7l** and **7q**) arylamines furnished the products in high yields. Similarly, electron-deficient arylamines including fluoro- (**7f**), chloro- (**7h** and **7r**), bromo- (**7e** and **7m**) substituted analogs also reacted smoothly to yield the corresponding epiminodibenzo[*b,f*][1,5]diazocines **7** in comparable yields. Notably, *m*-nitroaniline, bearing a strong electron-withdrawing group also yielded the product **7n** in 87% yield albeit in a longer reaction time. In order to show the generality of the protocol, we then investigated the reactivity of benzylamine and butylamine under the optimized reaction conditions. Interestingly, benzylamine tolerated the reaction conditions to afford the product **7s** in 81% yield. However, the reaction was sluggish and needed longer reaction time (20 h) than arylamines. On the other hand, the reaction failed to yield the desired product in the case of butylamine presumably due to the poor stability of the intermediate imine. Thus this methodology allows general and direct access to arylamine-derived epiminodibenzo[*b,f*][1,5]diazocines **7**, which could not be obtained by the existing procedure. Furthermore, this AB_2 three-component approach generates two heterocyclic rings and four

new C–N bonds in a single operation. In addition, the reaction is highly atom economic and no waste is produced except two molecules of water. The reaction between 2-aminobenzaldehyde and *p*-toluidine under our optimized conditions afforded a mixture of epiminodibenzo[*b,f*][1,5]diazocine **7u**[9a] and quinazoline derivative **5a**.[11] Thus the presence of *N*-alkyl group on the 2-aminoarylaldehyde is essential to yield the desired products in a controlled manner.



6 7

7a (8 h, 74%) **7b** (8 h, 96%) **7c** (6 h, 72%) **7d** (8 h, 77%)

7e (8 h, 80%) **7f** (8 h, 71%) **7g** (10 h, 84%) **7h** (8 h, 91%)

7i (8 h, 95%) **7j** (8 h, 94%) **7k** (8 h, 93%) **7l** (6 h, 79%)

7m (8 h, 95%) **7n** (12 h, 87%) **7o** (8 h, 72%) **7p** (8 h, 74%)

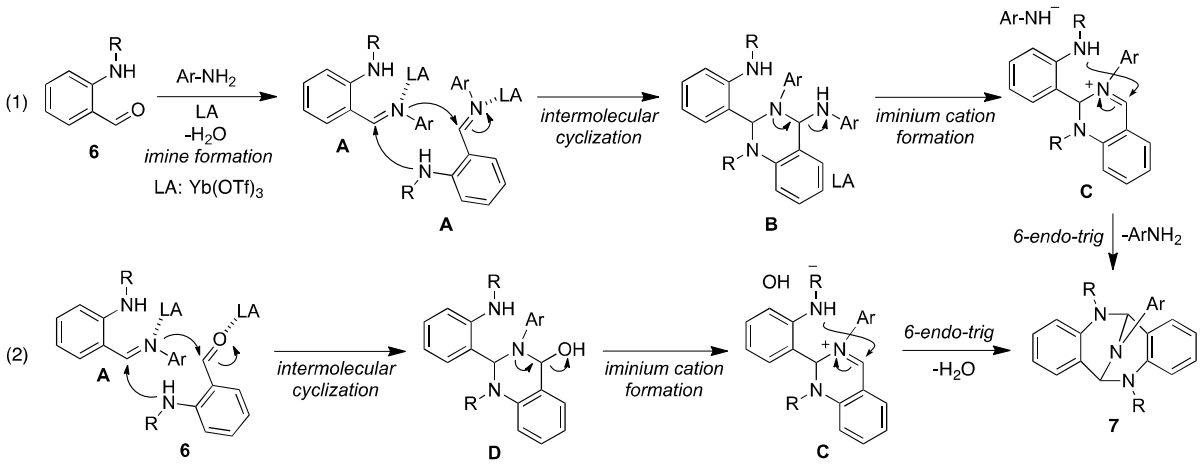
7q (10 h, 69%) **7r** (8 h, 71%) **7s** (20 h, 81%) **7t** (24 h, 0%)

7u (3 h, 16%)[9a] **5a** (3 h, 42%)[11]

Reaction conditions: aldehydes **6** (1.0 mmol), arylamines (0.5 mmol), $Yb(OTf)_3$ (5 mol %), MeCN (2 mL), 80 °C, 6-12 h.

Scheme 2. Synthesis of epiminodibenzo[*b,f*][1,5]diazocines **7**

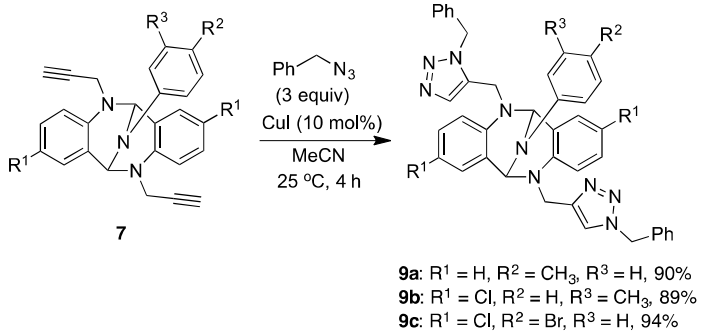
As shown in Scheme 3, eq 1, this reaction is proposed to proceed via imine intermediate **A** generated from aldehyde **6** and arylamines, as the imine formation was observed immediately after the addition arylamines to the aldehydes and confirmed by crude ^{1}H-NMR analysis. Subsequent intermolecular self-cyclization of two molecules of imine **A** would generate the aminal **B**, which could eliminate a molecule of arylamine followed by intramolecular *6-endo-trig* cyclization to afford compound **7** through the intermediacy of iminium cation **C**. This mechanism is supported by the observation that, in some occasions, the initially formed imine **A** was converted into the product **7** in the absence of aldehyde **6**. Alternatively, as shown in eq 2, Lewis acid catalyzed reaction between imine **A** and a second equivalent of aldehyde **6** would afford 1,2,3,4-tetrahydroquinazolin-4-ol intermediate **D**, which subsequently generates the iminium cation **C** triggered by the Lewis acid. A final intramolecular cyclization of intermediate **C** furnishes the product **7**.



Scheme 3. Proposed Mechanism

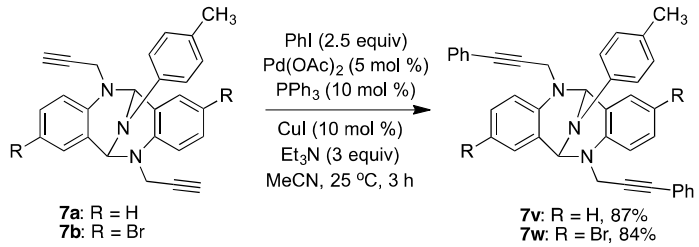
We next sought to showcase the usefulness of the terminal alkyne group in many of our compounds to introduce an additional diversity point. 1,2,3-Triazoles are important class of nitrogen heterocycles known to exhibit broad-spectrum pharmacological activities exemplified by anti-influenza A agents,[13] σ_2 receptor ligands,[14] Nrf2–Keap1 protein–protein

interaction inhibitors[15] and many others. The Cu(I) catalyzed 1,3-dipolar reaction between alkyne and azide, popularly known as the 'click reaction' is a well-explored protocol to access 1,2,3-triazoles.[16] Consequently, we envisioned to utilize the terminal alkynes of the synthesized epiminodibenzo[*b,f*][1,5]diazocines **7** to introduce the triazole moiety by the reaction with benzyl azide. As expected, bis-triazole tethered epiminodibenzo[*b,f*][1,5]diazocines **9** were obtained in excellent yields under mild experimental conditions in the presence of CuI (Scheme 4). Owing to the biological interest of both 1,2,3-triazole and epiminodibenzo[*b,f*][1,5]diazocines, this approach could be used to generate a library of compounds bearing both heterocycles.



Scheme 4. Synthesis of bis-triazole tethered epiminodibenzo[*b,f*][1,5]diazocines **8**

Finally, we derivatized the terminal alkynes under Sonogashira reaction conditions as shown in Scheme 5. Under standard conditions, phenyl group was successfully introduced to epiminodibenzo[*b,f*][1,5]diazocines **7a** and **7b** to obtain compounds **7v** and **7w** in high yields.



Scheme 5. Sonogashira reaction of epiminodibenzo[*b,f*][1,5]diazocines **7a** and **7b**

In conclusion, we have demonstrated the synthesis of Tröger's base analogs epiminodibenzo[*b,f*][1,5]diazocines from readily available starting materials involving a $Yb(OTf)_3$ catalyzed AB_2 three-component reaction in high yields. The reaction generates two heterocyclic rings and four C–N bonds in a single operation in addition to its high atom economy. This methodology is complementary to the existing procedure since this reaction is completely selective for arylamines whereas the literature method works only for benzylamines and alkyl amines. We have also proposed a plausible mechanism to explain the product formation involving imine formation-intermolecular annulation-intramolecular iminium ion cyclization steps.

EXPERIMENTAL SECTION

General Information. Commercially available reagents were used without further purification and the reaction solvents (THF, MeCN, DCM etc) were purified using standard procedures. The reactions were monitored by thin-layer chromatography visualized by UV detection or using *p*-anisaldehyde or 2,4-DNP stains or molecular iodine. Flash column chromatography was performed with silica gel (230-400 mesh). Melting points were recorded on a melting point apparatus in capillaries and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at room temperature in a spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C. Chemical shifts (δ) are expressed in ppm using TMS as internal standard, and coupling constants (*J*) are given in hertz. Infrared (IR) spectra were obtained in a FTIR spectrometer with a diamond ATR accessory for solid and liquid samples, requiring no sample preparation, and the major frequencies were reported in cm^{-1}. Elemental analyses were determined by using a CHNS combustion microanalyzer.

General Procedure for the Synthesis of 2-(prop-2-yn-1-ylamino)arylaldehyde 6a-d. To a stirred solution of suitably substituted 2-aminobenzyl alcohol (30 mmol) in acetonitrile (80

mL) were added K_2CO_3 (45 mmol) and propargyl bromide (40 mmol) and stirring was continued for 6-8 hours at 75 ^oC. The reaction mixture was diluted with water, extracted with ethyl acetate (3 x 30 mL) and washed with brine solution. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether-ethyl acetate mixture as eluent (70:30 v/v). Subsequently, a solution of 2-(prop-2-ynylamino)benzylamine obtained in the previous step in CH_2Cl_2 (150 mL) was added MnO_2 (10 equiv) and the mixture was stirred at room temperature for 12-16 hours. The reaction mixture was filtered and washed with CH_2Cl_2 (3 x 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether-ethyl acetate mixture as eluent (96:4 v/v) to yield the products **6a-c**. Compound **6d** was prepared by using the literature procedure.[17]

*2-(Prop-2-ynylamino)benzaldehyde (**6a**).* Yellow viscous liquid; yield: 2.29 g, 48%; IR (neat) 3331.9, 3287.5, 3047.3, 2830.8, 2111.5, 1655.3, 1575.3, 1515.7, 1335.5, 1199.3 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.44 (t, *J* = 2.4 Hz, 1H), 4.06 (dd, *J* = 6.0, 2.4 Hz, 2H), 6.77-6.83 (m, 2H), 7.47 (td, *J* = 7.8, 1.5 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.44 (br s, 1H), 9.85 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.1, 71.6, 79.8, 111.2, 116.1, 119.1, 135.8, 136.6, 149.4, 194.2. Anal Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.09; H, 5.80; N, 8.87.

*5-Bromo-2-(prop-2-ynylamino)benzaldehyde (**6b**).* Yellow solid; mp: 112-115 ^oC; yield: 3.64 g, 51%; IR (neat) 3314.2, 3244.8, 3050.0, 2849.6, 2109.3, 1654.6, 1562.5, 1504.4, 1303.5, 1174.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.19 (s, 1H), 3.96 (d, *J* = 5.7 Hz, 2H), 6.66 (d, *J* = 9.0 Hz, 1H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.54 (s, 1H), 8.36 (br s, 1H), 9.70 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.2, 71.9, 79.2, 107.3, 113.4, 120.4, 138.3, 138.4, 148.3, 192.9. Anal Calcd for $C_{10}H_8BrNO$: C, 50.45; H, 3.39; N, 5.88. Found: C, 50.14; H, 3.31; N, 6.06.

*5-Chloro-2-(prop-2-yn-1-ylamino)benzaldehyde (**6c**).* Yellow solid; mp: 105-108 ^{o}C; yield: 3.25 g, 56%; IR (neat) 3318.2, 3267.3, 3027.0, 2820.0, 1577.8, 1555.7, 1340.3, 1161.1 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (t, *J* = 2.4 Hz, 1H), 4.04 (dd, *J* = 6.0, 2.4 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 1H), 7.40 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.49 (d, *J* = 2.7 Hz, 1H), 8.42 (br s, 1H), 9.78 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.2, 71.9, 79.3, 113.0, 119.7, 120.7, 135.2, 135.7, 147.9, 193.0. Anal Calcd for $C_{10}H_8ClNO$: C, 62.03; H, 4.16; N, 7.23. Found: C, 61.94; H, 4.21; N, 7.29.

General procedure for the AB$_2$ three-component synthesis of epiminodiazocines 7. To a stirred solution of *N*-substituted-2-aminoarylaldehyde **6** (1.0 mmol) and primary amines (0.5 mmol) in acetonitrile (2 mL) was added $Yb(OTf)_3$ (5 mol %) and stirring was continued until completion of the reaction (6 to 12 hours) at 80 ^{o}C. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified through silica gel column chromatography using petroleum ether-ethyl acetate (97:5, v/v) as eluent.

*5,11-Di(prop-2-yn-1-yl)-13-(p-tolyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7a**).* Colourless solid; mp: 139-142 ^{o}C; yield: 144 mg, 74%; IR (neat) 3286.3, 3258.1, 2988.5, 2120.2, 1602.2, 1493.1, 1458.4, 1325.1, 1225.6, 1165.5, 1098.4 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H), 2.46 (t, *J* = 2.4 Hz, 2H), 4.07 (dd, *J* = 17.1, 2.4 Hz, 2H), 4.29 (dd, *J* = 17.1, 2.4 Hz, 2H), 5.97 (s, 2H), 6.77-6.85 (m, 4H), 7.01-7.09 (m, 4H), 7.15 (td, *J* = 7.5, 1.5 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6, 40.4, 69.7, 73.6, 79.9, 115.2, 118.3, 119.1, 123.3, 128.2, 128.9, 129.8, 130.6, 142.4, 144.7. Anal Calcd for $C_{27}H_{23}N_3$: C, 83.26; H, 5.95; N, 10.79. Found: C, 82.98; H, 6.06; N, 10.61.

*2,8-Dibromo-5,11-di(prop-2-yn-1-yl)-13-(p-tolyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7b**).* Pale brown solid; mp: 73-75 ^{o}C; yield: 262 mg, 96%; IR (neat) 3280.8, 3255.2, 2977.0, 2116.7, 1605.9, 1485.5, 1344.6, 1234.6, 1157.3, 1088.2 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H), 2.45 (t, *J* = 2.4 Hz, 2H), 4.03 (dd, *J* = 17.4, 2.4 Hz, 2H), 4.26 (dd, *J* = 17.4, 2.4 Hz, 2H), 5.83 (s, 2H), 6.65 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 7.24 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.45 (d, *J* = 2.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5, 40.5, 69.6, 74.1, 79.0, 111.4, 116.9, 118.5, 124.9, 129.9, 130.7, 131.4, 131.8, 141.1, 143.9. Anal Calcd for $C_{27}H_{21}Br_2N_3$: C, 59.25; H, 3.87; N, 7.68. Found: C, 58.97; H, 3.80; N, 7.74.

*13-Phenyl-5,11-di(prop-2-yn-1-yl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7c**).* Colourless solid; mp: 133-136 ^{o}C; yield: 135 mg, 72%; IR (neat) 3288.1, 3257.5, 3037.5, 2950.1, 2113.2, 1597.7, 1490.7, 1227.4, 1148.5, 1097.2 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (t, *J* = 2.1 Hz, 2H), 3.98 (dd, *J* = 17.4, 2.1 Hz, 2H), 4.21 (dd, *J* = 17.4, 2.1 Hz, 2H), 5.95 (s, 2H), 6.69-6.80 (m, 4H), 6.82 (t, *J* = 7.2 Hz, 1H), 7.04-7.21 (m, 6H), 7.28 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.4, 69.4, 73.8, 79.8, 115.3, 118.1, 119.2, 121.1, 123.3, 128.2, 129.0, 129.3, 142.4, 147.0. Anal Calcd for $C_{26}H_{21}N_3$: C, 83.17; H, 5.64; N, 11.19. Found: C, 82.80; H, 5.75; N, 11.02.

*13-(4-Methoxyphenyl)-5,11-di(prop-2-yn-1-yl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7d**).* Colourless solid; mp: 128-132 ^{o}C; yield: 156 mg, 77%; IR (neat) 3280.5, 3245.0, 2932.2, 2118.6, 1601.2, 1506.1, 1453.8, 1356.4, 1236.4, 1094.5, 1026.1 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (t, *J* = 2.4 Hz, 2H), 3.76 (s, 3H), 4.06 (dd, *J* = 17.1, 2.4 Hz, 2H), 4.28 (dd, *J* = 17.1, 2.4 Hz, 2H), 5.86 (s, 2H), 6.78-6.85 (m, 6H), 7.05 (d, *J* = 9.0 Hz, 2H), 7.16 (td, *J* = 8.7, 1.5 Hz, 2H), 7.36 (dd, *J* = 7.5, 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.4, 55.5, 70.4, 73.5, 79.9, 114.5, 115.1, 119.7, 120.3, 123.3,

128.2, 128.9, 140.9, 142.4, 154.6. Anal Calcd for $C_{27}H_{23}N_3O$: C, 79.97; H, 5.72; N, 10.36. Found: C, 79.66; H, 5.78; N, 10.20.

*13-(4-Bromophenyl)-5,11-di(prop-2-yn-1-yl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7e**).* Colourless solid; mp: 96-98 ^oC; yield: 182 mg, 80%; IR (neat) 3285.9, 3025.8, 2824.9, 2185.9, 1601.2, 1584.0, 1490.1, 1366.4, 1232.9, 1097.4 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.47 (t, *J* = 2.7 Hz, 2H), 4.04 (dd, *J* = 17.1, 2.7 Hz, 2H), 4.28 (dd, *J* = 17.1, 2.7 Hz, 2H), 5.97 (s, 2H), 6.77(d, *J* = 8.1 Hz, 2H), 6.82 (td, *J* = 7.5, 1.2 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 7.15 (td, *J* = 8.1, 1.5 Hz, 2H), 7.33-7.36 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.3, 69.3, 74.0, 79.6, 113.5, 115.3, 119.4, 119.8, 122.9, 128.2, 129.2, 132.1, 142.2, 146.2. Anal Calcd for $C_{26}H_{20}BrN_3$: C, 68.73; H, 4.44; N, 9.25. Found: C, 68.51; H, 4.39; N, 9.02.

*13-(4-Fluorophenyl)-5,11-di(prop-2-yn-1-yl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7f**).* Colourless solid; mp: 143-146 ^oC; yield: 140 mg, 71%; IR (neat) 3293.4, 3275.3, 3070.4, 2825.2, 2115.0, 1600.8, 1491.0, 1363.4 1231.6, 1091.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.44 (t, *J* = 2.4 Hz, 2H), 4.04 (dd, *J* = 17.1, 2.4 Hz, 2H), 4.27 (dd, *J* = 17.1, 2.4 Hz, 2H), 5.89 (s, 2H), 6.78 (d, *J* = 8.1 Hz, 2H), 6.82 (td, *J* = 7.2, 1.2 Hz, 2H), 6.94 (t, *J* = 9.0, Hz, 2H), 7.02-7.09 (m, 2H), 7.15 (td, *J* = 9.0, 1.8 Hz, 2H), 7.34 (dd, *J* = 7.5, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.3, 70.1, 73.8, 79.7, 115.2, 115.8 (d, *J* = 21.8 Hz), 119.3, 120.1 (d, *J* = 8.25 Hz), 123.1, 128.2, 129.1, 142.3, 143.5 (d, *J* = 2.3 Hz), 157.9 (d, *J* = 239.3 Hz). Anal Calcd for $C_{26}H_{20}FN_3$: C, 79.37; H, 5.12; N, 10.68. Found: C, 79.01; H, 5.18; N, 10.72.

*2,8-Dibromo-13-phenyl-5,11-di(prop-2-yn-1-yl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7g**).* Colourless solid; mp: 148-151 ^oC; yield: 224 mg, 84%; IR (neat) 3276.8, 3037.7, 2827.0, 2118.9, 1593.7, 1488.3, 1355.9, 1233.8, 1113.8 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.40 (t, *J* = 2.4 Hz, 2H), 3.97 (dd, *J* = 17.4, 2.4 Hz, 2H), 4.15

(dd, *J* = 17.4, 2.4 Hz, 2H), 5.83 (s, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 7.16-7.22 (m, 4H), 7.39 (d, *J* = 2.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.6, 69.4, 74.3, 79.0, 111.6, 117.1, 118.3, 121.9, 125.0, 129.4, 130.8, 131.9, 141.2, 146.4. Anal Calcd for $C_{26}H_{19}Br_2N_3$: C, 58.56; H, 3.59; N, 7.88. Found: C, 58.29; H, 3.63; N, 7.86.

*2,8-Dibromo-13-(4-chlorophenyl)-5,11-di(prop-2-yn-1-yl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7h**).* Pale yellow solid; mp: 150-153 ^{o}C; yield: 259 mg, 91%; IR (neat) 3289.4, 3264.8, 2923.6, 2837.4, 2153.6, 1593.6, 1479.2, 1346.2, 1232.8, 1058.2 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.48 (t, *J* =2.4 Hz, 2H), 4.04 (dd, *J* = 17.4, 2.4 Hz, 2H), 4.22 (dd, *J* = 17.4, 2.4 Hz, 2H), 5.85 (s, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 9.0, Hz, 2H), 7.20-7.30 (m, 4H), 7.44 (d, *J* = 2.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.5, 69.4, 74.5, 78.8, 111.7, 117.1, 119.7, 124.6, 126.9, 129.4, 130.8, 132.1, 141.0, 145.0. Anal Calcd for $C_{26}H_{18}Br_2ClN_3$: C, 55.01; H, 3.20; N, 7.40. Found: C, 54.80; H, 3.32; N, 7.18.

*2,8-Dibromo-13-(3,5-dimethylphenyl)-5,11-di(prop-2-yn-1-yl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7i**).* Pale brown solid; mp: 191-194 ^{o}C; yield: 267 mg, 95%; IR (neat) 3296.6, 2915.8, 2843.4, 2121.5, 1588.9, 1484.1, 1367.1, 1268.4 1155.9, 1058.2 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 6H), 2.48 (t, *J* =2.4 Hz, 2H), 4.05 (dd, *J* = 17.4, 2.4 Hz, 2H), 4.23 (dd, *J* = 17.4, 2.4 Hz, 2H), 5.89 (s, 2H), 6.58-6.68 (m, 5H), 7.24 (dd, *J* = 9.0, 2.1 Hz, 2H), 7.44 (d, *J* = 2.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 40.5, 69.3, 74.2, 79.1, 111.4, 115.8, 117.1, 123.5, 125.1, 130.8, 131.9, 139.0, 141.2, 146.2. Anal Calcd for $C_{28}H_{23}Br_2N_3$: C, 59.91; H, 4.13; N, 7.49. Found: C, 59.66; H, 4.18; N, 7.53.

*2,8-Dibromo-5,11-di(prop-2-yn-1-yl)-13-(m-tolyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7j**).* Colourless solid; mp: 163-167 ^{o}C; yield: 258 mg, 94%; IR (neat) 3283.9, 3235.4, 2966.2, 2845.9, 2114.9, 1601.3, 1489.2, 1353.9, 1255.2, 1190.8, 1091.8 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.30 (s, 3H), 2.47 (t, *J* =2.4 Hz, 2H),

4.05 (dd, *J* = 17.4, 2.4 Hz, 2H), 4.23 (dd, *J* = 17.4, 2.4 Hz, 2H), 5.89 (s, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.83 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.90 (s,1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.24 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.45 (d, *J* = 8.7, 2.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 40.5, 69.3, 74.2, 79.0, 111.5, 115.2, 117.1, 119.0, 122.6, 125.0, 129.2, 130.8, 131.9, 139.2, 141.2, 146.3. Anal Calcd for $C_{27}H_{21}Br_2N_3$: C, 59.25; H, 3.87; N, 7.68. Found: C, 58.88; H, 3.89; N, 7.61.

*2,8-Dichloro-5,11-di(prop-2-yn-1-yl)-13-(m-tolyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7k**).* Colourless solid; mp: 159-161^{o}C; yield: 213 mg, 93%; IR (neat) 3302.0, 3039.7, 2919.5, 2829.6, 2132.2, 1599.3, 1492.8, 1368.8, 1255.0, 1180.2, 1034.2 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (s, 3H), 2.48 (t, *J* = 2.4 Hz, 2H), 4.04 (dd, *J* = 17.4, 2.4 Hz, 2H), 4.23 (dd, *J* = 17.4, 2.4 Hz, 2H), 5.91 (s, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.84 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.91 (s, 1H), 7.12 (dd, *J* = 9.0, 2.4 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 40.7, 69.3, 74.3, 79.2, 115.2, 116.8, 118.9, 122.6, 124.3, 124.7, 127.9, 129.1, 129.3, 139.2, 140.8, 146.4. Anal Calcd for $C_{27}H_{21}Cl_2N_3$: C, 70.75; H, 4.62; N, 9.17. Found: C, 70.37; H, 4.58; N, 9.11.

*2,8-Dichloro-13-(3-methoxyphenyl)-5,11-di(prop-2-yn-1-yl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7l**).* Pale brown solid; mp: 154-157 ^{o}C; yield: 188 mg, 79%; IR (neat) 3306.3, 3025.1, 2932.6, 2122.0, 1597.2, 1488.7, 1322.6, 1188.9, 1078.5 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.50 (t, *J* = 2.4 Hz, 2H), 3.78 (s, 3H), 4.04 (dd, *J* = 17.4, 2.4 Hz, 2H), 4.23 (dd, *J* = 17.4, 2.4 Hz, 2H), 5.93 (s, 2H), 6.49 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.62-6.68 (m, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 7.11 (dd, *J* = 8.7, 2.7 Hz, 2H), 7.17 (t, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.7, 55.3, 69.2, 74.3, 79.1, 104.5, 106.7, 110.6, 117.0, 124.5, 124.6, 127.9, 129.1, 130.1, 140.8, 147.8, 160.6. Anal Calcd for $C_{27}H_{21}Cl_2N_3O$: C, 68.36; H, 4.46; N, 8.86. Found: C, 68.02; H, 4.39; N, 8.81.

*13-(4-Bromophenyl)-2,8-dichloro-5,11-di(prop-2-yn-1-yl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7m**).* Pale yellow solid; mp: 183-186 ^{o}C; yield: 249 mg, 95%; IR (neat) 3286.2, 3044.5, 2993.2, 1599.6, 1497.2, 1366.1, 1159.1, 1021.5 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.49 (t, *J* = 2.4 Hz, 2H), 4.02 (dd, *J* = 17.4, 2.4 Hz, 2H), 4.22 (dd, *J* = 17.4, 2.4 Hz, 2H), 5.87 (s, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 7.12 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.31 (d, *J* = 2.4 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.6, 69.2, 74.5, 78.9, 114.2, 116.8, 120.0, 124.2, 124.6, 127.9, 129.3, 132.3, 140.6, 145.5. Anal Calcd for $C_{26}H_{18}BrCl_2N_3$: C, 59.68; H, 3.47; N, 8.03. Found: C, 59.32; H, 3.37; N, 8.01.

*2,8-dichloro-13-(3-nitrophenyl)-5,11-di(prop-2-yn-1-yl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7n**).* Pale yellow solid; mp: 169-171 ^{o}C; yield: 213 mg, 87%; IR (neat) 3294.9, 3108.7, 2924.5, 2849.0, 2124.6, 1602.9, 1520.8, 1493.8, 1351.4, 1246.2, 1118.0, 1006.5 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.66 (t, *J* = 2.4 Hz, 2H), 4.07 (dd, *J* = 17.4, 2.4 Hz, 2H), 4.30 (dd, *J* = 17.4, 2.4 Hz, 2H), 6.08 (s, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 7.14 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.34 (d, *J* = 2.4 Hz, 2H), 7.36-7.50 (m, 2H), 7.76 (dt, *J* = 7.5, 1.5 Hz, 1H), 8.04 (t, *J* = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.4, 68.6, 75.1, 78.5, 112.3, 115.9, 117.0, 123.1, 123.9, 124.9, 127.9, 129.5, 130.2, 140.5, 147.3, 149.3. Anal Calcd for $C_{26}H_{18}Cl_2N_4O_2$: C, 63.82; H, 3.71; N, 11.45. Found: C, 63.62; H, 3.60; N, 11.32.

*5,11-Dibenzyl-13-(m-tolyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7o**).* Colourless solid; mp: 141-143 ^{o}C; yield: 178 mg, 72%; IR (neat) 3033.7, 2969.9, 2916.7, 1599.0, 1489.1, 1449.5, 1353.1, 1248.5, 1099.0 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.22 (s, 3H), 4.65 (s, 4H), 5.67 (s, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.65-6.75 (m, 5H), 7.01-7.11 (m, 5H), 7.25-7.30 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 55.2, 71.1, 114.7, 115.5, 117.8, 119.5, 122.1, 123.1, 127.1, 127.3, 127.7, 128.6, 128.7, 129.0, 138.6, 138.9, 143.7,

147.3. Anal Calcd for $C_{35}H_{31}N_3$: C, 85.16; H, 6.33; N, 8.51. Found: C, 85.20; H, 6.39; N, 8.43.

*5,11-Dibenzyl-13-(3,5-dimethylphenyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7p**).* Colourless solid; mp: 110-113 ^{o}C; yield: 188 mg, 74%; IR (neat) 3019.8, 2911.8, 2842.6, 1595.2, 1490.8, 1448.8, 1357.4, 1119.1, 1050.8 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 6H), 4.62 (d, *J* = 16.2 Hz, 2H), 4.69 (d, *J* = 16.2 Hz, 2H), 5.67 (s, 2H), 6.52 (s, 2H), 6.55 (s, 1H), 6.61 (d, *J* = 8.1 Hz, 2H), 6.69 (td, *J* = 7.5, 0.9 Hz, 2H), 7.03 (td, *J* = 8.7, 1.5 Hz, 2H), 7.10 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.25-7.33 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 55.2, 70.9, 114.8, 116.2, 117.8, 122.9, 123.3, 127.2, 127.5, 127.7, 128.7, 128.8, 138.7, 138.9, 143.8, 147.2. Anal Calcd for $C_{36}H_{33}N_3$: C, 85.17; H, 6.55; N, 8.28. Found: C, 84.90; H, 6.39; N, 8.17.

*5,11-Dibenzyl-13-(4-methoxyphenyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7q**).* Colourless solid; mp: 168-172 ^{o}C; yield: 189 mg, 69%; IR (neat) 3055.4, 3021.9, 2947.5, 1599.8, 1492.2, 1352.3, 1242.3, 1095.9 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75 (s, 3H), 4.62 (s, 4H), 5.51 (s, 2H), 6.61 (d, *J* = 8.1 Hz, 2H), 6.70 (td, *J* = 7.5, 1.2 Hz, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 7.01-7.09 (m, 4H), 7.20-7.31 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4, 55.6, 72.2, 114.5, 114.7, 117.9, 121.2, 123.3, 127.2, 127.4, 127.7, 128.6, 128.8, 138.8, 141.4, 143.8, 155.0. Anal Calcd for $C_{35}H_{31}N_3O$: C, 82.48; H, 6.13; N, 8.25. Found: C, 82.11; H, 6.02; N, 8.14.

*5,11-Dibenzyl-13-(3-chlorophenyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7r**).* Colourless solid; mp: 129-131 ^{o}C; yield: 183 mg, 71%; IR (neat) 3043.1, 2944.5, 1599.2, 1467.8, 1379.3, 1158.1, 1034.9 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.64 (s, 4H), 5.63 (s, 2H), 6.65 (d, *J* = 8.1 Hz, 2H), 6.69-6.75 (m, 3H), 6.87-6.90 (m, 2H), 7.03-7.12 (m, 5H), 7.28-7.36 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2, 70.7, 114.9, 116.3, 118.1, 118.7, 121.2, 122.7, 127.3, 127.4, 127.7, 128.7, 128.9, 130.1,

134.8, 138.3, 143.5, 148.5. Anal Calcd for $C_{34}H_{28}ClN_3$: C, 79.44; H, 5.49; N, 8.17. Found: C, 79.17; H, 5.41; N, 8.01.

*13-Benzyl-2,8-dibromo-5,11-di(prop-2-yn-1-yl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7s**).* Colourless solid; mp: 78-80 ^oC; yield: 222 mg, 81%; IR (neat) 3256.5, 3028.7, 2857.0, 2135.5, 1603.8, 1488.3, 1365.3, 1213.8, 1123.4, 1032.2 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.31 (t, *J* = 2.4 Hz, 2H), 3.62 (d, *J* = 12.9 Hz, 1H), 3.70 (d, *J* = 12.9 Hz, 1H), 4.03 (dd, *J* = 17.7, 2.4 Hz, 2H), 4.17 (dd, *J* = 17.7, 2.4 Hz, 2H), 4.90 (s, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 7.25 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.29-7.38 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.0, 54.2, 70.7, 73.6, 79.0, 110.6, 115.8, 124.0, 127.7, 128.6, 129.3, 131.1, 131.7, 136.9, 140.5. Anal Calcd for $C_{27}H_{21}Br_2N_3$: C, 59.25; H, 3.87; N, 7.68. Found: C, 58.96; H, 3.81; N, 7.54.

*9-Methyldibenzo[b,h][1,6]naphthyridine (**8**).* Pale brown solid; mp: 172-175 ^oC; yield: 37 mg, 15%; IR (neat) 3057.8, 3006.8, 2919.7, 2857.8, 1600.9, 1491.6, 1382.5, 1294.2, 1036.2 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.62 (s, 3H), 7.75-7.88 (m, 4H), 8.18 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.28 (d, *J* = 8.7 Hz, 1H), 8.75 (s, 1H), 9.31 (dd, *J* = 7.8, 1.5 Hz, 1H), 9.37 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 119.5, 124.1, 125.3, 126.9, 127.0, 127.6, 129.3, 129.4, 130.4, 134.5, 135.9, 136.5, 145.8, 147.0, 148.9, 154.0. Anal Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.19; H, 5.07; N, 11.31.

General Procedure for the Synthesis of Triazoles 9. To a solution of epiminodiazocine **7** (0.5 mmol) and benzyl azide (1.5 mmol) in acetonitrile (3 mL) was added CuI (10 mol %) under nitrogen atmosphere at 25 ^oC and stirred for 4 h. After completion of reaction, the mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was separated, dried over Na_2SO_4 and solvent removed under reduced pressure. The residue was purified through silica gel column chromatography using 40-60% ethyl acetate in petroleum ether as eluent.

*5-((1-Benzyl-1H-1,2,3-triazol-4-yl)methyl)-11-((1-benzyl-1H-1,2,3-triazol-5-yl)methyl)-13-(p-tolyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**9a**).* Colourless solid; mp: 96-98 ^{o}C; yield: 295 mg, 90%; IR (neat) 3134.4, 3028.8, 2918.9, 1602.1, 1493.7, 1454.1, 1324.0, 1214.2, 1045.2 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.19 (s, 3H), 4.72 (d, *J* = 16.8 Hz, 2H), 4.82 (d, *J* = 16.8 Hz, 2H), 5.33 (d, *J* = 15.0 Hz, 2H), 5.39 (d, *J* = 15.0 Hz, 2H), 5.61 (s, 2H), 6.55-6.61 (m, 4H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.77 (s, 2H), 6.85 (d, *J* = 8.1 Hz, 2H), 7.01 (td, *J* = 7.8, 1.5 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 2H), 7.10-7.14 (m, 4H), 7.30-7.36 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6, 47.0, 54.0, 71.8, 113.8, 117.9, 119.0, 122.4, 122.8, 127.8, 128.6, 128.9, 129.0, 129.7, 131.0, 134.8, 142.2, 144.7, 146.4. Anal Calcd for $C_{41}H_{37}N_9$: C, 75.09; H, 5.69; N, 19.22. Found: C, 74.83; H, 5.70; N, 18.91. One aromatic carbon is merged with others.

*5-((1-Benzyl-1H-1,2,3-triazol-4-yl)methyl)-11-((1-benzyl-1H-1,2,3-triazol-5-yl)methyl)-2,8-dichloro-13-(m-tolyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**9b**).* Colourless solid; mp: 95-98 ^{o}C; yield: 323 mg, 89%; IR (neat) 3136.9, 3033.8, 2924.0, 2855.5, 1602.6, 1495.1, 1357.2, 1252.5, 1115.5, 1047.4 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.13 (s, 3H), 4.63 (d, *J* = 16.2 Hz, 2H), 4.80 (d, *J* = 16.2 Hz, 2H), 5.34 (d, *J* = 15.0 Hz, 2H), 5.43 (d, *J* = 15.0 Hz, 2H), 5.61 (s, 2H), 6.51-6.57 (m, 3H), 6.67-6.74 (m, 4H), 6.93 (t, *J* = 7.8 Hz, 1H), 7.00 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.06 (d, *J* = 2.4 Hz, 2H), 7.14-7.17 (m, 4H), 7.32-7.40 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 47.4, 54.1, 71.3, 115.8, 115.9, 119.9, 122.1, 123.0, 123.2, 124.3, 127.4, 127.9, 128.2, 128.7, 129.0, 129.1, 134.6, 139.2, 140.9, 145.6, 146.6. Anal Calcd for $C_{41}H_{35}Cl_2N_9$: C, 67.95; H, 4.87; N, 17.40. Found: C, 67.67; H, 4.98; N, 17.31.

*5-((1-Benzyl-1H-1,2,3-triazol-4-yl)methyl)-11-((1-benzyl-1H-1,2,3-triazol-5-yl)methyl)-13-(4-bromophenyl)-2,8-dichloro-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**9c**).* Colourless solid; mp: 215-218 ^{o}C; yield: 372 mg, 94%; IR (neat) 3302.4, 3039.6,

2921.5, 2852.1, 1599.6, 1493.2, 1369.1, 1255.2, 1180.4, 1034.6 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.61 (d, *J* = 16.2 Hz, 2H), 4.77 (d, *J* = 16.2 Hz, 2H), 5.43 (s, 4H), 5.56 (s, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 6.87 (s, 2H), 7.02 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.07 (d, *J* = 2.4 Hz, 2H), 7.14 (d, *J* = 9.0 Hz, 2H), 7.18-7.21 (m, 4H), 7.35-7.37 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 46.8, 54.1, 70.3, 114.1, 116.0, 120.5, 122.2, 123.3, 124.0, 127.4, 127.9, 128.7, 129.1, 132.0, 134.5, 140.7, 145.5. Anal Calcd for $C_{40}H_{34}BrCl_2N_9$: C, 60.69; H, 4.33; N, 15.93. Found: C, 60.37; H, 4.20; N, 15.81. Two aromatic carbons are merged with others.

Sonogashira coupling of epiminodibenzo[*b,f*][1,5]diazocines 7. To a stirred solution of epiminodiazocine **7** (0.5 mmol) in acetonitrile (2 mL) under nitrogen atmosphere were added iodobenzene (1.25 mmol), triethylamine (1.5 mmol), palladium acetate (5 mol %), triphenylphosphine (10 mol %) and copper(I) iodide (10 mol %). Stirring was continued at 25 ^oC until the completion of the reaction (3 h), and then the reaction mixture was diluted with ethyl acetate and washed with water. The organic layer was separated, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified through silica gel column chromatography using petroleum ether-ethyl acetate (98:2, v/v) as eluent.

*5,11-Bis(3-phenylprop-2-yn-1-yl)-13-(p-tolyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7v**).* Pale brown solid; mp: 132-134 ^oC; yield: 236 mg, 87%; IR (neat) 3031.3, 2923.9, 2245.0, 1603.5, 1513.4, 1491.5, 1359.8, 1237.6, 1097.5 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 3H), 4.26 (d, *J* = 17.1 Hz, 2H), 4.51 (d, *J* = 17.1 Hz, 2H), 6.10 (s, 2H), 6.78-6.83 (m, 4H), 7.02-7.17 (m, 6H), 7.31-7.36 (m, 6H), 7.40-7.48 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6, 41.0, 69.7, 85.3, 85.6, 115.2, 118.3, 119.0, 122.8, 123.4, 128.2, 128.4, 128.5, 128.9, 129.8, 130.4, 131.8, 142.6, 144.8. Anal Calcd for $C_{39}H_{31}N_3$: C, 86.47; H, 5.77; N, 7.76. Found: C, 86.17; H, 5.69; N, 7.71.

*2,8-Dibromo-5,11-bis(3-phenylprop-2-yn-1-yl)-13-(p-tolyl)-5,6,11,12-tetrahydro-6,12-epiminodibenzo[b,f][1,5]diazocine (**7w**).* Pale brown solid; mp: 93-95 ^{o}C; yield: 294 mg, 84%; IR (neat) 3042.1, 2918.8, 2221.4, 1597.5, 1477.7, 1367.3, 1247.9, 1161.0, 1045.3 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24 (s, 3H), 4.28 (d, *J* = 17.4 Hz, 2H), 4.44 (d, *J* = 17.4 Hz, 2H), 5.95 (s, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.25 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.31-7.35 (m, 6H), 7.43-7.47 (m, 4H), 7.53 (d, *J* = 2.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.4, 40.1, 68.7, 83.2, 84.8, 110.0, 115.6, 117.4, 121.3, 123.9, 127.2, 127.5, 128.8, 129.7, 130.2, 130.7, 140.1, 142.9. Anal Calcd for $C_{39}H_{29}Br_2N_3$: C, 66.97; H, 4.18; N, 6.01. Found: C, 66.62; H, 4.12; N, 5.88. One aromatic carbon is merged with others.

ASSOCIATED CONTENT

Supporting information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Copies of ^{1}H and ^{13}C NMR spectra.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

Financial support from the Department of Science and Technology, DST (No. SB/FT/CS-006/2013 & No. INT/AUA/BMWF/P-26/2015) and the Council of Scientific and Industrial Research, CSIR (No. 02(0219)/14/EMR-II) is gratefully acknowledged. JCM acknowledges financial support from MINECO, grant CTQ2012-33272-BQU.

This article is dedicated to Professor S. Sivasubramanian on the occasion of his 75th birthday

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