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PAPER

Silver-catalyzed intramolecular hydroamination of alkynes in aqueous media: efficient and regioselective synthesis for fused benzimidazoles†

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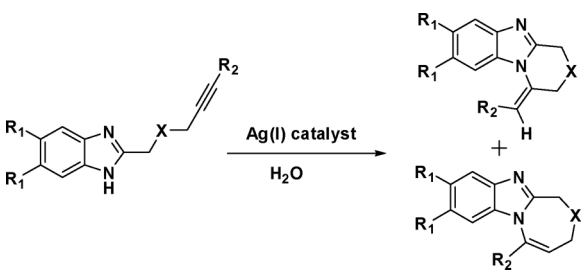
A simple, convenient and green synthetic approach to diverse fused tricyclic benzimidazoles has been developed by Ag(I) complex catalyzed intramolecular hydroamination under the classic method or by microwave irradiation in water. This strategy presents an operationally simple and environmentally friendly transformation, in which various substituted benzimidazoles facilitated efficient cyclization.

Introduction

Fused benzimidazoles are important heterocyclic scaffolds in drug discovery.[1] Various substituted benzimidazoles have been suggested to be potential therapeutic agents involving antiproliferative, antitumor activity and for [1,2-*a*]-fused imidazoles, which have antiulcer, antidepressant and antimicrobial activity.[2] Recently, oxygen- or nitrogen-containing fused benzimidazoles have been successfully synthesized by C–H bond activation,[3] rhodium-catalysed cyclization[4] and radical cyclisation.[5] However, the described methods suffer from a relatively narrow scope of substrates. Thus, it is very important to develop novel and improved protocols for the synthesis of more abundant fused benzimidazoles.

Recently, transition metal-catalyzed transformations have attracted considerable attention because of their remarkable ability to activate π-systems, especially alkynes, towards inter- or intramolecular hydroamination and inter- or intramolecular hydroarylation attacks to construct intriguing fused heterocycles.[6] Among these transition metal catalysts, Ag(I) salts have generally been considered to have a low catalytic efficiency, and only serve as either co-catalysts or Lewis acids. However, in recent years, Ag(I) salts have been demonstrated to be important and versatile catalysts for the synthesis of functionalized heterocycles such as isoquinolines, (2*H*)-isoquinolines, (2*H*)-1,2-oxaphosphorin 2-oxides, 5-substituted proline derivatives, pyrroles, silyl ketene aminals, benzothiazines and other heterocycles in efficient and atom-economic ways.[6,7] In particular, our group has made a contribution by the synthesis of isochromen-1-imines.[8]

Water, an environmentally friendly reaction medium, often has an unpredictable effect on the rate and selectivity of organic reactions through hydrophobic interactions and the enrichment of organic substrates in the local hydrophobic environment.[9] Therefore, as a part of our ongoing efforts to develop new convenient and efficient strategies for the preparation of potential bioactive heterocycles with transition metal catalysts,[8,10] we herein present our findings of the synthesis of fused benzimidazoles by an Ag(I)-catalyzed chemo- and regioselective intramolecular cyclization in aqueous media (Scheme 1).



Scheme 1 Synthesis of fused tricyclic benzimidazoles.

Results and discussion

The requisite cyclization precursors, benzimidazoles (**A**), are readily synthesized from *o*-phenylene diamines through condensation and cyclization reactions with acetic acid. Benzimidazoles are readily synthesized according to the relevant literature.[11]

Initially, 2-(pent-4-ynyl)-1*H*-benzo[*d*]imidazole (**A1**) was chosen as the model substrate for investigating the optimum

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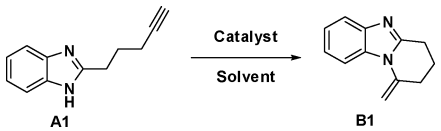
† Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR spectra for the target compounds. See DOI: 10.1039/c0gc00668h

Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst (mmol%)	Solvent	Temp. (°C)	Time	Yield (%)
1	—	Toluene	80	2 h	0
2	$AgSbF_6$ (10)	Toluene	80	2 h	91
3	$AgNO_3$ (10)	Toluene	80	2 h	90
4	AgI (10)	Toluene	80	2 h	15
5	Ag_2CO_3 (10)	Toluene	80	2 h	28
6	AgOTf (10)	Toluene	80	2 h	95
7	Ag_2O (10)	Toluene	80	2 h	trace
8	AgOAc(10)	Toluene	80	2 h	60
9	$AgSO_3CH_3$ (10)	Toluene	80	2 h	94
10	AgOTf (10)	H_2O	80	2 h	65
11	AgOTf (10)	THF	80	2 h	87
12	AgOTf (10)	EtOH	80	2 h	93
13	AgOTf (10)	H_2O	80	8 h	95
14	AgOTf (5)	H_2O	80	8 h	95
15	AgOTf (5)	H_2O	80	10 min	73[b]
16	AgOTf (5)	H_2O	120	10 min	87[b]
17	AgOTf (5)	H_2O	150	15 min	96[b]
18	AgOTf (5)	H_2O	150	15 min	75[b,c]
19	TfOH (10)	H_2O	80	8 h	0
20	TfOH (10)	H_2O	150	15 min	0[b]

[a] **A1** (0.4 mmol), catalyst (5–10 mol %), solvent (3 mL), under N_2 for 2–8 h. [b] The reaction was carried out under microwave irradiation in H_2O. [c] The reaction was carried out under air.

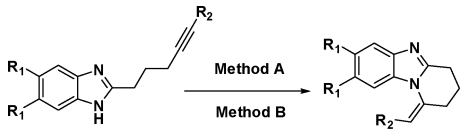
reaction conditions, including different catalysts, various solvents, reaction temperatures and reaction times (Table 1). Under catalyst-free conditions, no reaction took place and only starting material **A1** was recovered (Table 1, entry 1). Various Ag(I) salts (10 mol%) were screened in toluene at 80 °C under an N_2 atmosphere for 2 h. The results demonstrated that these Ag(I) salts displayed distinct catalytic activities (Table 1, entries 2–9). Among them, AgOTf was found to be the most effective catalyst, and the desirable product 1-methylene-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (**B1**) was obtained in 95% yield (Table 1, entry 6). Subsequently, we screened different solvents at 80 °C, and the results show that toluene is the most suitable for this transformation (Table 1, entries 10–12). However, a similar excellent result was also obtained when the transformation was performed in an aqueous medium for a longer time (Table 1, entry 13). Water was thus chosen for further investigations on the basis of it being environmentally benign, abundant, cheap, and often exhibiting a unique reactivity and selectivity that cannot be obtained in conventional organic solvents.[12] In addition, when the AgOTf catalyst loading was decreased from 10 to 5 mol%, an identical good yield of the target compound was also detected (95% yield, Table 1, entry 14). Although microwave irradiation was generally employed to facilitate this reaction, when we treated **A1** with 5 mol% AgOTf under microwave irradiation in water at 80 °C for 10 min, the desired N-annelated product, **B1**, was only formed in 73% yield and a small quantity of starting material **A1** was recovered (Table 1, entry 15). However, when the reaction temperature increased to 120 °C, the yield of the desired product was improved to 87% (Table 1, entry 16). Furthermore, increasing the reaction temperature to 150 °C for 15 min under an N_2 atmosphere resulted in an excellent yield of the desired product (Table 1, entry 17). Without a N_2 atmosphere, the yield of the target compound was drastically affected and decreased to 75% (Table 1, entry 18). Meanwhile, a correlative Brønsted acid was applied and no reaction took place (Table 1, entries 19 and 20). Briefly, the optimum results were achieved when **A1** (0.40 mmol) was treated with 5 mol% of AgOTf in an aqueous medium at 80 °C for 8 h under oil bath heating conditions or at 150 °C for 15 min under microwave irradiation. Owing to the same excellent yields being obtained under both above-mentioned conditions, we chose both of them for subsequent explorations.

To evaluate the scope of the proposed catalytic methods, we attempted to investigate the cyclization of a variety of substituted benzimidazoles (**A**) under the above-mentioned optimized conditions (Table 2). Firstly, we performed these transformations under classic oil bath heating conditions, and the results demonstrated that the protocol was tolerant to substrates with different substituents R_1, including H, methyl and chloro groups (Table 2, entries 1–3). Furthermore, introducing various substituents into the alkynyl groups of various benzimidazoles was investigated (Table 2, entries 4–12). When R_2 was phenyl or several substituted phenyl groups, this reaction was well implemented to form intriguing cyclized products (Table 2, entries 4–7, 9, 11 and 12). However, no products were observed in the cases of 2-(5-(2-(trifluoromethyl)-phenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (**A8**) and 2-(5-(4-(trifluoromethyl)phenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (**A10**), presumably due to electronic effects (Table 2, entries 8 and 10). When we introduced a pyridine moiety as an R_2 substituent, an excellent yield was also obtained. (Table 2, entry 12). Good yields could be obtained irrespective of electron-donating methoxy, halide or heteroaromatic groups. (Table 2, entries 7, 11 and 12). However, the substitution position and type of the R_1 and R_2 substituents were found to be important factors for influencing the yields of the products (Table 2, entries 1–12). Additionally, the replacement of the benzimidazole ring with naphthoimidazole rings also led to good yields (Scheme 2, **A13** and **A14**). However, substitution of the benzimidazole ring with perimidine or benzothiazole heterocycles led to a drastic decrease of yield of the desired products under the optimized reaction conditions (Scheme 2, **A15** and **A16**).

Although some limitations were discovered in these investigations, when the cyclization transformation of substituted benzimidazoles (**A**) was performed under microwave irradiation, as shown in Table 2 and Scheme 2 (method B), better yields were obtained in most cases, irrespective of the type or position of the R_1 and R_2 substituents. Surprisingly, excellent yields were observed in the cases of **A8** and **A10**, respectively (Table 2, entries 8 and 10). However, when we interchanged the benzimidazole ring with perimidine or benzothiazole heterocycles, no reactions occurred under microwave irradiation conditions (Scheme 2, **A15** and **A16**).

Based on the above experimental results, we found that better yields of the target compounds could be achieved under microwave irradiation. Therefore, more experiments were carried out under the microwave-aided optimal reaction conditions, and these further results indicated that the proposed reaction could be extended to the synthesis of oxa-fused benzimidazoles **C17–C27** by using compounds **A17–A27** as starting materials.

Table 2 Synthesis of piperidine[1,2-*a*]benzimidazoles in water[a]



A1-12 B1-12

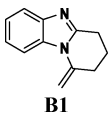
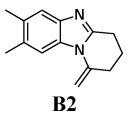
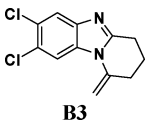
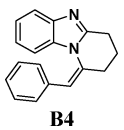
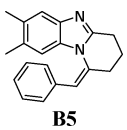
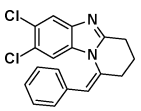
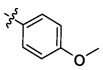
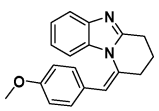
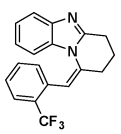
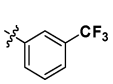
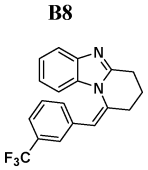
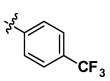
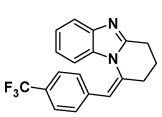
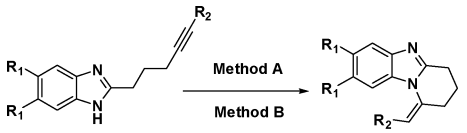
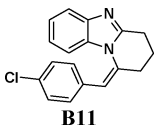
Entry	R_1	R_2	Product	Yield (%) Method A	Method B
1	H	H	 **B1**	94[b]	92
2	CH_3	H	 **B2**	91[b]	88
3	Cl	H	 **B3**	92[b]	89
4	H	Ph	 **B4**	84	81
5	CH_3	Ph	 **B5**	35	86
6	Cl	Ph	 **B6**	43	87
7	H		 **B7**	62	86
8	H		 **B8**	0	84
9	H		 **B9**	87	85
10	H		 **B10**	0	87

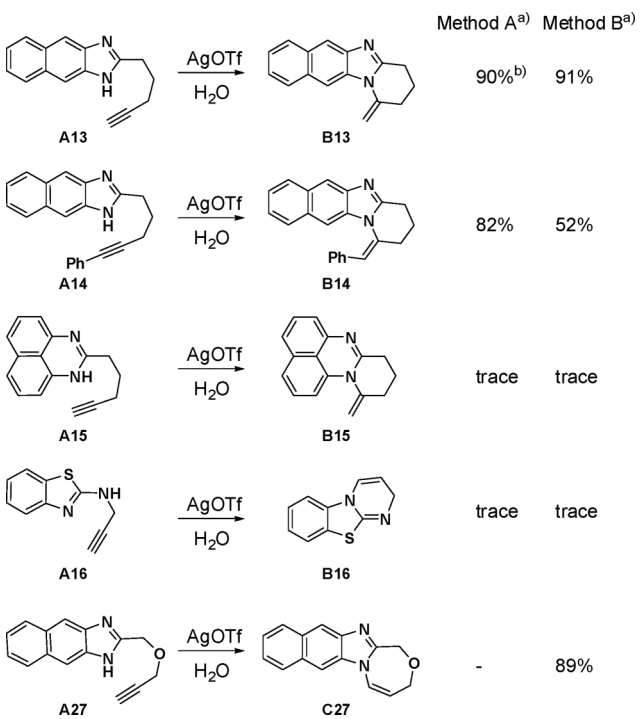
Table 2 *(Contd.)*



A1-12 B1-12

Entry	R_1	R_2	Product	Yield (%) Method A	Method B
11	H		 **B11**	85	73
12	H		 **B12**	92	91

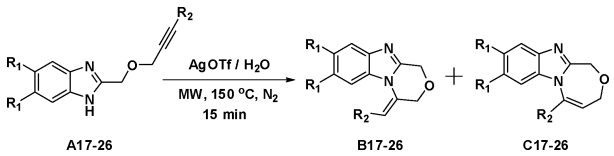
[a] Method A: 80 °C, 60 h, N_2; Method B: MW, 150 °C, 15 min, N_2. [b] 80 °C, 8 h, N_2.



Scheme 2 [a)] Method A: 80 °C, 60 h, N_2; Method B: MW, 150 °C, 15 min, N_2; [b)] 80 °C, 8 h, N_2.

As shown in Table 3, the tolerance of the catalytic system was remarkable, and moderate to excellent yields of the desired products were obtained (Table 3, entries 1–10). Excellent yields were obtained when R_2 was hydrogen and methyl group, respectively, and only seven-membered heterocyclic frameworks, formed *via* a 7-*endo-dig* ring-closing pathway, were generated (Table 3, entries 1–6). However, introducing methyl groups make the transformations require a longer time (50 min) to complete substrate conversion. Hence, we found that the benzimidazoles

Table 3 Synthesis of oxa-fused benzimidazoles under microwave irradiation in water[a]

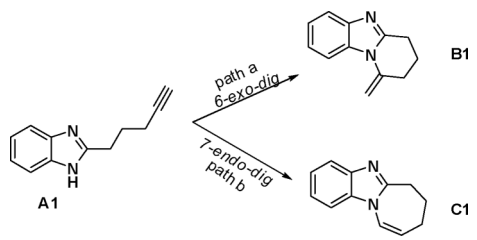


Entry	R_1	R_2	Product/yield (%) B	C
1	H	H	—	**C17** / 80%
2	CH_3	H	—	**C18** / 87%
3	Cl	H	—	**C19** / 88%
4	H	CH_3	—	**C20** / 85%[b]
5	CH_3	CH_3	—	**C21** / 91%[b]
6	Cl	CH_3	—	**C22** / 87%[b]
7	H	Ph	**B23** / 35%	**C23** / 47%
8	H	2-CF_3-Ph	**B24** / 36%	**C24** / 55%
9	H	3-CF_3-Ph	**B25** / 42%	**C25** / 49%
10	H	4-Cl-Ph	**B26** / 43%	**C26** / 49%

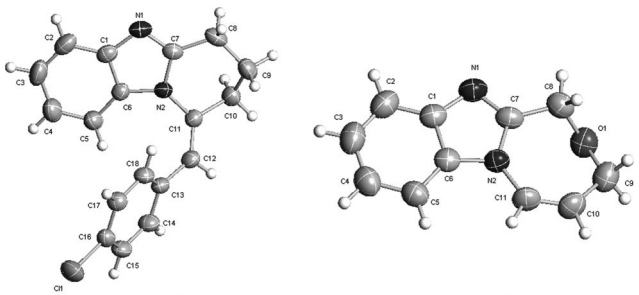
[a] AgOTf, MW, H_2O, 150 °C, 15 min, N_2. [b] AgOTf, MW, H_2O, 150 °C, 50 min, N_2.

of terminal alkynes and alkyl-replaced benzimidazoles have distinctive response characteristics for this cyclization, presumably due to electronic effects and steric hindrance. When introducing aryl groups into the R_2 position, we surprisingly discovered that two main products were formed, namely six-membered and seven-membered ring-closing heterocyclic frameworks (Table 3, entries 7–10), maybe owing to the electronic effects of the oxygen atom and aryl groups. The π–π conjugative effect between the acetylene bond and the aryl groups make the nitrogen atom of benzimidazoles have a similar probability of attacking either carbon of the acetylene bond, generating 6-*exo-dig* and 7-*endo-dig* ring-closure products. In addition, a good yield was obtained when we changed the benzimidazole ring of substrate **A17** into a naphthoimidazole ring, and only a seven-membered product was formed *via* a 7-*endo-dig* ring-closing pathway (Scheme 2, **A27**).

In principle, the cyclization of alkynes possessing a nucleophilic group in proximity to the triple bond can construct various heterocycles *via* different ring-closing pathways. As shown in Scheme 3, there are two possible mechanisms for this transformation to give two possible products: (a) a 6-*exo-dig* cyclization process, leading to the formation of six-membered product **B1** and (b) a 7-*endo-dig* cyclization process, leading the formation of seven-membered product **C1**. All the fused benzimidazoles synthesized were characterized by their ^{1}H NMR, ^{13}C NMR and MS data. Additionally, the structures of **B11** and **C17** were confirmed by X-ray diffraction (XRD) studies (Fig. 1).



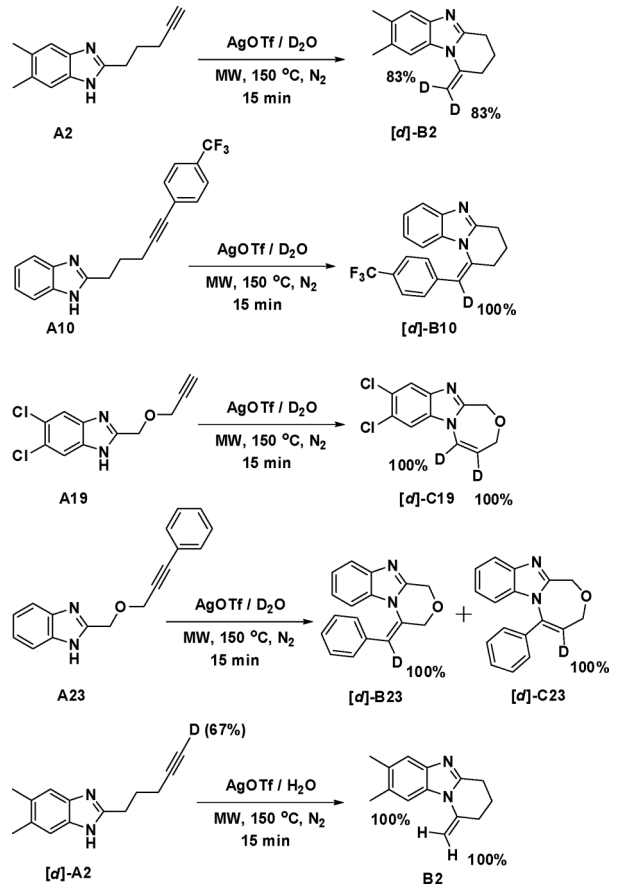
Scheme 3 Two different pathways to fused benzimidazoles **B1** and **C1**.



B11 **C17**

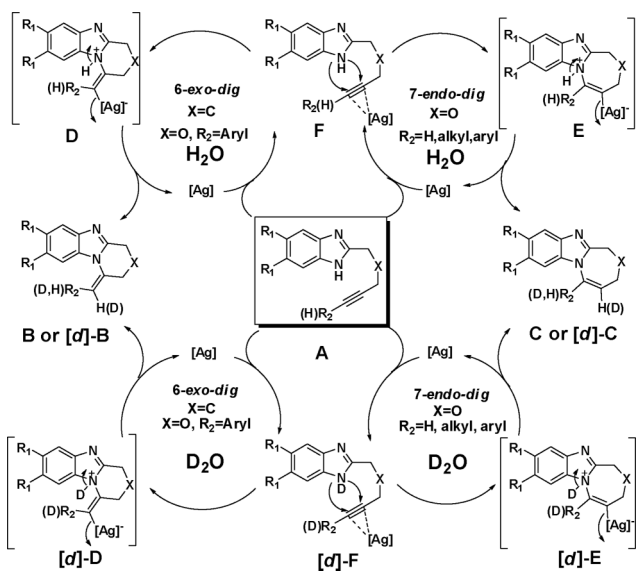
Fig. 1 The X-ray crystal structures of **B11** and **C17**.

To gain insight into the mechanism of the reaction, we performed labelling studies with deuterated starting materials or solvents. The reactions of **A2**, **A10**, **A19** and **A23** in D_2O under the standard conditions afforded the deuterated products [*d*]-**B2**, [*d*]-**B10**, [*d*]-**B19**, [*d*]-**B23** and [*d*]-**C23**, respectively. The reaction of deuterated alkyne [*d*]-**A2** in H_2O led to the formation of non-deuterated product **B2** (Scheme 4).



Scheme 4 Labelling studies with D_2O or deuterated starting materials.

On the basis of our previous knowledge and the results of the present studies, we postulate a plausible mechanism for the construction of polycyclic molecular scaffold fused benzimidazoles (Scheme 5).



Scheme 5 Possible mechanism for intramolecular cyclization.

Firstly, the carbon–carbon triple bonds of **A** are activated by coordination with the transition metal salt to form Ag-alkyne π-complex **F** in H_2O. A subsequent attack of the nitrogen atom at the electron-deficient triple bond leads to intermediates **D** or **E** *via* a 6-*exo-dig* or 7-*endo-dig* ring-closing pathway, respectively, which is followed by proton transfer to produce the final products **B** or **C**.

In addition, the aforementioned labelling experiments indicate that the vinyl protons of the products come from the solvent. Key intermediate [*d*]-**F** could be formed by the treatment of material **A** with D_2O under the catalysis of the Ag salt, which is consistent with the results reported in the literature.[13] A further electrophilic attack of the nitrogen atom towards the electron-deficient triple bond results in the formation of intermediates [*d*]-**D** or [*d*]-**E** by 6-*exo-dig* or 7-*endo-dig* ring-closing pathways, respectively. Subsequently, the resulting intermediates are converted into the final products, [*d*]-**B** or [*d*]-**C**, by deuterium transfer, respectively.

Conclusions

In summary, we have developed an efficient and convenient method for the synthesis of fused tricyclic benzimidazoles *via* Ag(I)-catalyzed intramolecular hydroamination in water. This strategy presents an environmentally friendly transformation that has a good functional group tolerance. Significantly, the strategy affords the important motifs of both useful versatile synthetic intermediates and potent biologically active compounds. It is our expectation that these biologically intriguing structures will be found broad applications in our related medicinal chemistry program. These interesting transformations have motivated us to further investigate their reaction pathway as a part of future endeavours.

Experimental section

General experimental procedures

The reagents were purchased from commercial sources and used without further purification. Analytical thin layer chromatography (TLC) was HSGF 254 (0.15–0.2 mm thickness). All of the microwave-assisted reactions were performed in an Initiator TM EXP microwave system (Biotage, Inc.) at the specified temperature using the standard mode of operation. Column chromatography was performed with CombiFlash® Companion system (Teledyne Isco, Inc.). Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded in $CDCl_3$ as a solvent with tetramethylsilane (TMS) as internal standard (^{1}H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.24 ppm ^{13}C NMR: $CDCl_3$ at 77.0 ppm) or were recorded in DMSO-d_6 as a solvent with tetramethylsilane (TMS) as internal standard (^{1}H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm ^{13}C NMR: DMSO at 40.0 ppm). Low and high-resolution mass spectra (LR MS and HR MS) were measured on Finnigan MAT 95 spectrometer. using tetramethylsilane (TMS).

General procedure for the silver-catalyzed synthesis of diverse substituted fused tricyclic benzimidazoles (compound B1, for example)

Classic method using a thermostate oil bath (Method A). A mixture of **A1** (0.40 mmol) and AgOTf (0.02 mmol) was

stirred in water (3–5 mL) under N_2. The vial was sealed and the mixture stirred at 80 °C with oil bath heating for 8–60 h. After the reaction, the vial was cooled to ambient temperature and the crude reaction mixture extracted three times with ethyl acetate (EA) (15 mL × 3). The combined organic phase was washed with a saturated $NaHCO_3$ solution, brine, dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography to provide desired product **B1**.

Microwave method (Method B)

A mixture of **A1** (0.40 mmol) and AgOTf (0.02 mmol) was stirred in water (3–5 mL) under N_2. The vial was sealed and the mixture irradiated for 15 min at 150 °C. After the reaction, the crude reaction mixture was cooled to ambient temperature and extracted three times with EA (15 mL × 3). The combined organic phase was washed with saturated $NaHCO_3$ solution, brine, dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography on Combiflash to provide desired product **B1**.

The characterization data obtained were as follows: ^{1}H NMR δ (300 MHz, $CDCl_3$): 2.06 (m, 2H, CH_2), 2.07 (t, J = 6.0 Hz, 2H, CH_2), 2.67 (t, J = 6.3 Hz, 2H, CH_2), 4.81 (d, J = 0.9 Hz, 1H, CH), 5.34 (d, J = 0.9 Hz 1H, CH), 7.26–7.29 (m, 2H, ArH), 7.68–7.72 (m, 2H, ArH); ^{13}C NMR δ (100 MHz, $CDCl_3$): 21.3, 25.6, 31.6, 97.0, 112.4, 119.1, 122.8, 123.0, 132.2, 140.7, 143.0, 152.0; EI-MS m/z 184 $[M]^+$; HRMS (EI) calc. for $C_{12}H_{12}N_2$ $[M]^+$ 184.1000, found 184.0995.

Characterization data for other target compounds

7,8-Dimethyl-1-methylene-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (B2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02–2.05 (m, 2H, CH_2), 2.35 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.63 (t, 2H, CH_2), 3.12 (t, 2H, CH_2), 4.75 (s, 1H, CH), 5.29 (s, 1H, CH), 7.43 (s, 1H, ArH), 7.45 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1, 20.6, 21.4, 25.7, 31.7, 96.0, 112.9, 119.4, 130.9, 131.5, 141.0, 142.0, 151.1; EI-MS m/z 212 $[M]^+$; HRMS (EI) calc. for $C_{14}H_{16}N_2$ $[M]^+$ 212.1313, found 212.1308.

7,8-Dichloro-1-methylene-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (B3). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05–2.08 (m, 2H, CH_2), 2.63–2.66 (m, 2H, CH_2), 3.11–3.15 (m, 2H, CH_2), 4.84 (s, 1H, CH), 5.21 (s, 1H, CH), 7.71–7.74 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 25.7, 31.4, 97.6, 113.7, 120.2, 126.5, 126.7, 131.4, 140.4, 142.9, 153.9; EI-MS m/z 252 $[M]^+$; HRMS (EI) calc. for $C_{12}H_{10}Cl_2N_2$ $[M]^+$ 252.0221, found 252.0218.

1-[1-Phenyl-meth-(*Z*)-ylidene]-1,2,3,4-tetrahydropyrido [1,2-*a*]benzimidazole (B4). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (br, 2H, CH_2), 2.68 (t, 2H, CH_2), 3.39 (br, 2H, CH_2), 6.35 (s, 1H, CH), 6.40–6.43 (d, J = 8.1 Hz, 1H, ArH), 6.83 (t, 1H, ArH), 6.97–6.98 (br, 2H, ArH), 7.12–7.14 (m, 4H, ArH), 7.67–7.69 (br, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 24.4, 32.9, 113.7, 115.8, 118.3, 121.9, 122.7, 127.3, 128.3, 128.7, 132.5, 134.9, 140.6, 150.3; EI-MS m/z 260 $[M]^+$; HRMS (EI) calc. for $C_{18}H_{16}N_2$ $[M]^+$ 260.1313, found 260.1304.

7,8-Dimethyl-1-[1-phenyl-meth-(*Z*)-ylidene]-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (B5). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.93 (s, 3H, CH_3), 2.14–2.33 (m, 5H, CH_2, CH_3), 2.63 (t, 2H, CH_2), 3.26 (t, 2H, CH_2), 6.06 (s, 1H, CH), 6.25 (s, 1H, ArH), 6.98–7.01 (m, 2H, ArH), 7.13–7.15 (m, 3H, ArH), 7.38 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.9, 20.0, 21.5, 24.6, 33.2, 114.2, 114.4, 118.5, 126.8, 128.0, 128.7, 129.7, 130.2, 130.8, 133.2, 135.5, 141.7, 151.6; EI-MS m/z 288 $[M]^+$; HRMS (EI) calc. for $C_{20}H_{20}N_2$ $[M]^+$ 288.1626, found 288.1631.

7,8-Dichloro-1-[1-phenyl-meth-(*Z*)-ylidene]-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (B6). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23–2.27 (m, 2H, CH_2), 2.66 (t, 2H, CH_2), 3.27 (t, 2H, CH_2), 6.32 (s, 1H, CH), 6.36 (s, 1H, ArH), 6.94–6.97 (m, 2H, ArH), 7.17–7.19 (m, 3H, ArH), 7.68 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 24.7, 32.7, 115.1, 115.6, 119.6, 125.3, 126.1, 127.7, 128.4, 128.5, 130.0, 132.5, 134.6, 142.6, 154.2; EI-MS m/z 328 $[M]^+$; HRMS (EI) calc. for $C_{18}H_{14}Cl_2N_2$ $[M]^+$ 328.0534, found 328.0536.

1-[1-(4-Methoxy-phenyl)-meth-(*Z*)-ylidene]-1,2,3,4-tetrhydropyrido[1,2-*a*]benzimidazole (B7). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28–2.32 (m, 2H, CH_2), 2.67 (t, 2H, CH_2), 3.51 (t, 2H, CH_2), 3.74 (s, 3H, CH_3), 6.35 (s, 1H, CH), 6.53–6.56 (d, J = 8.1 Hz, 1H, ArH), 6.67–6.70 (d, J = 8.7 Hz, 2H, ArH), 6.91–6.95 (m, 3H, ArH), 7.17–7.27 (t, 1H, ArH), 7.66–7.69 (d, J = 8.1 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 24.7, 32.6, 55.2, 113.7, 114.2, 116.6, 117.9, 122.6, 123.2, 127.0, 130.1, 130.5, 130.6, 141.3, 154.3, 158.8; EI-MS m/z 290 $[M]^+$; HRMS (EI) calc. for $C_{19}H_{18}N_2O$ $[M]^+$ 290.1419, found 290.1416.

1-[1-(2-Trifluoromethyl-phenyl)-meth-(*Z*)-ylidene]-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (B8). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24–2.33 (m, 2H, CH_2), 2.75 (t, 2H, CH_2), 3.31 (t, 2H, CH_2), 6.28–6.31 (d, J = 8.4 Hz, 1H, ArH), 6.50 (s, 1H, CH), 6.72–6.76 (t, 2H, ArH), 6.97–7.02 (t, 1H, ArH), 7.04–7.09 (t, 1H, ArH), 7.18–7.23 (t, 1H, ArH), 7.59–7.62 (d, J = 8.1 Hz, 2H, ArH), 7.70–7.72 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 24.8, 33.2, 110.5, 112.5, 118.7, 121.8, 122.4, 124.4 (d, J = 270.0 Hz), 125.9 (d, J = 5.6 Hz), 127.1, 127.4 (J = 40 Hz), 130.6, 131.2, 131.4, 134.0, 135.3, 143.3, 152.3; EI-MS m/z 328 $[M]^+$; HRMS (EI) calc. for $C_{19}H_{15}F_3N_2$ $[M]^+$ 328.1187, found 328.1182.

1-[1-(3-Trifluoromethyl-phenyl)-meth-(*Z*)-ylidene]-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (B9). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24–2.31 (m, 2H, CH_2), 2.70 (t, 2H, CH_2), 3.30 (t, 2H, CH_2), 6.25 (s, 1H, CH), 6.28 (s, 1H, ArH), 6.78–6.83 (m, 1H, ArH), 7.03–7.09 (t, 1H, ArH), 7.09–7.23 (m, 3H, ArH), 7.35–7.38 (d, J = 7.8 Hz, 1H, ArH), 7.63–7.66 (d, J = 8.1 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 24.6, 33.2, 113.2, 113.3, 119.0, 121.7, 122.5, 123.6 (d, J = 3.7 Hz), 125.5 (d, J = 3.7 Hz), 128.5, 130.5, 131.8, 134.6, 136.0, 143.6, 152.4; EI-MS m/z 328 $[M]^+$; HRMS (EI) calc. for $C_{19}H_{15}F_3N_2$ $[M]^+$ 328.1187, found 328.1173.

1-[1-(4-Trifluoromethyl-phenyl)-meth-(*Z*)-ylidene]-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (B10). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25–2.32 (m, 2H, CH_2), 2.71 (t, 2H, CH_2), 3.31 (t, 2H, CH_2), 6.27–6.30 (m, 2H, CH, ArH), 6.81–6.86 (td, 1H, ArH), 7.05–7.08 (d, J = 7.8 Hz 2H, ArH), 7.11–7,17 (m, 1H, ArH), 7.36–7.39 (d, J = 7.8 Hz, 2H, ArH), 7.65–7.68 (d, J = 8.1 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 25.1, 32.5,

113.8, 116.0, 118.0, 123.2, 123.8 (d, J = 270.6 Hz), 124.0, 125.2, 129.0, 129.3 (d, J = 32.3 Hz), 129.8, 133.9, 138.1, 140.8, 155.3; EI-MS m/z 328 $[M]^+$; HRMS (EI) calc. for $C_{19}H_{15}F_3N_2$ $[M]^+$ 328.1187, found 328.1178.

1-[1-(4-Chloro-phenyl)-meth-(*Z*)-ylidene]-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (B11). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23–2.30 (m, 2H, CH_2), 2.66 (t, 2H, CH_2), 3.29 (t, 2H, CH_2), 6.22 (s, 1H, CH), 6.37–6.40 (d, J = 8.1 Hz, 1H, ArH), 6.85–6.91 (m, 3H, ArH), 7.08–7.17 (m, 3H, ArH), 7.64–7.67 (d, J = 8.1 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 24.4, 33.1, 113.6, 114.0, 118.7, 121.9, 122.6, 128.4, 130.0, 130.8, 132.8, 133.4, 133.6, 143.0, 152.6; EI-MS m/z 294 $[M]^+$; HRMS (EI) calc. for $C_{18}H_{15}ClN_2$ $[M]^+$ 294.0924, found 294.0922.

1-[1-Pyridin-3-yl-meth-(*Z*)-ylidene]-1,2,3,4-tetrahydropyrido-[1,2-*a*]benzimidazole (B12). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17–2.26 (m, 2H, CH_2), 2.66 (t, 2H, CH_2), 3.27 (t, 2H, CH_2), 6.21 (s, 1H, CH), 6.29–6.32 (d, J = 8.4 Hz, 1H, ArH), 6.78–6.83 (t, 1H, ArH), 6.91–6.95 (m, 1H, ArH), 7.02–7.11 (m, 2H, ArH), 7.61–7.64 (d, J = 8.1 Hz, 1H, ArH), 8.34 (br, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 24.2, 32.9, 110.8, 113.2, 118.8, 121.7, 122.4, 122.7, 130.3, 131.0, 135.0, 135.2, 143.2, 147.7, 149.5, 152.4; EI-MS m/z 261 $[M]^+$; HRMS (EI) calc. for $C_{17}H_{15}N_3$ $[M]^+$ 261.1266, found 261.1251.

1-Methylene-1,2,3,4-tetrahydronaphth[2′,3′:4,5]imidazo[1,2-*a*]pyridine (B13). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.07–2.10 (m, 2H, CH_2), 2.69 (t, 2H, CH_2), 3.21 (t, 2H, CH_2), 4.85 (s, 1H, CH), 5.47 (s, 1H, CH), 7.41–7.43 (m, 2H, ArH), 7.91–7.98 (m, 2H, ArH), 8.08 (s, 1H, ArH), 8.13 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 26.2, 31.7, 96.2, 109.1, 115.9, 124.0, 124.4, 127.9, 128.1, 130.4, 130.4, 132.9, 140.8, 143.3, 155.7; EI-MS m/z 234 $[M]^+$; HRMS (EI) calc. for $C_{16}H_{14}N_2$ $[M]^+$ 234.1157, found 234.1150.

1-[1-Phenyl-meth-(*Z*)-ylidene]-1,2,3,4-tetrahydronaphth-[2′,3′:4,5]imidazo[1,2-*a*]pyridine (B14). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25–2.33 (m, 2H, CH_2), 2.72 (t, 2H, CH_2), 3.37 (t, 2H, CH_2), 6.36 (s, 1H, CH), 6.66 (s, 1H, ArH), 7.01–7.04 (m, 2H, ArH), 7.09–7.11 (m, 3H, ArH), 7.23–7.25 (m, 1H, ArH), 7.27–7.40 (m, 2H, ArH), 7.90–7.93 (d, J = 7.8 Hz, 1H, ArH), 8.09 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 25.1, 33.2, 110.7, 114.6, 115.2, 123.6, 123.9, 127.1, 127.9, 127.9, 128.1, 128.5, 128.8, 129.6, 130.0, 132.9, 135.4, 143.3, 156.8; EI-MS m/z 310 $[M]^+$; HRMS (EI) calc. for $C_{22}H_{18}N_2$ $[M]^+$ 310.1470, found 310.1470.

7*H*,9*H*-8-Oxa-4*b*,10-diaza-benz[*a*]azulene (C17). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.61–4.63 (m, 2H, CH_2), 4.99 (s, 2H, CH_2), 5.39–5.44 (m, 1H, CH), 6.94–6.98 (d, J = 9.9 Hz, 1H, CH), 7.29–7.41 (m, 3H, ArH), 7.72–7.75 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 68.2, 71.6, 109.1, 115.5, 119.6, 120.1, 122.9, 123.6, 134.3, 142.2, 153.5; EI-MS m/z 186 $[M]^+$; HRMS (EI) calc. for $C_{11}H_{10}N_2O$ $[M]^+$ 186.0793, found 186.0791.

2,3-Dimethyl-7*H*,9*H*-8-oxa-4*b*,10-diazabenz[*a*]azulene (C18). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 4.60–4.62 (m, 2H, CH), 4.96 (s, 2H, CH_2), 5.33–5.39 (m, 1H, CH), 6.88–6.93 (m, 1H, CH), 7.15 (s, 1H, ArH), 7.48 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.2, 20.6, 68.3, 71.6, 109.4, 114.8, 119.8, 120.1, 131.7, 132.7, 132.9, 140.7, 152.6; EI-MS m/z 214 $[M]^+$; HRMS (EI) calc. for $C_{13}H_{14}N_2O$ $[M]^+$ 214.1106, found 214.1108.

2,3-Dichloro-7*H*,9*H*-8-oxa-4*b*,10-diazabenz[*a*]azulene (C19). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.61–4.62 (m, 2H, CH_2), 4.95 (s, 2H, CH_2), 5.45–5.50 (m, 1H, CH), 6.78–6.83 (m, 1H, CH), 7.48 (s, 1H, ArH), 7.79 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 67.9, 71.6, 110.8, 116.9, 119.0, 121.3, 127.0, 127.7, 133.4, 141.5, 155.4; ESI-MS m/z 255 $[M + H]^+$; HRMS (ESI) calc. for $C_{11}H_9Cl_2N_2O$ $[M + H]^+$ 255.0092, found 255.0089.

5-Methyl-7*H*,9*H*-8-oxa-4*b*,10-diazabenz[*a*]azulene (C20). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.52 (s, 3H, CH_3), 4.07-4.09 (d, J = 6.3 Hz, 2H, CH_2), 4.81 (s, 2H, CH_2), 5.81–5.86 (m, 1H, CH), 7.31–7.34 (m, 2H, ArH), 7.54–7.57 (m, 1H, ArH), 7.80–7.83 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1, 62.9, 63.3, 112.2, 116.7, 120.7, 123.0, 123.5, 133.6, 138.5, 143.2, 152.1; EI-MS m/z 200 $[M]^+$; HRMS (EI) calc. for $C_{12}H_{12}N_2O$ $[M]^+$ 200.0950, found 200.0956.

2,3,5-Trimethyl-7*H*,9*H*-8-oxa-4*b*,10-diazabenz[*a*]azulene (C21). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 4.01–4.03 (d, J = 6.9 Hz, 2H, CH_2), 4.76 (s, 2H, CH_2), 5.76–5.78 (t, 1H, CH), 7.30 (s, 1H, ArH), 7.55 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.0, 20.1, 20.6, 62.8, 63.0, 112.3, 116.0, 120.5, 131.8, 132.1, 132.6, 138.7, 141.7, 151.3; EI-MS m/z 228 $[M]^+$; HRMS (EI) calc. for $C_{14}H_{16}N_2O$ $[M]^+$ 228.1263, found 228.1258.

2,3-Dichloro-5-methyl-7*H*,9*H*-8-oxa-4*b*,10-diazabenz[*a*]azulene (C22). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.46 (s, 3H, CH_3), 4.08–4.10 (d, J = 6.0 Hz, 2H, CH_2), 4.75 (s, 2H, CH_2), 5.77–5.81 (t, 1H, CH), 7.63 (s, 1H, ArH), 7.83 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.3, 62.9, 63.9, 113.5, 117.5, 121.5, 127.0, 127.4, 132.6, 136.9, 142.4, 154.1; EI-MS m/z 268 $[M]^+$; HRMS (EI) calc. for $C_{12}H_{10}Cl_2N_2O$ $[M]^+$ 268.0170, found 268.0179.

4-[1-Phenyl-meth-(*Z*)-ylidene]-3,4-dihydro-1*H*-2-oxa-4*a*,9-diazafluorene (B23). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.46 (s, 2H, CH_2), 5.24 (s, 2H, CH_2), 6.21–6.24 (d, J = 8.4 Hz, 1H, ArH), 6.38 (s, 1H, CH), 6.80–6.86 (t, 1H, ArH), 7.10–7.23 (m, 6H, ArH), 7.66–7.69 (d, J = 8.1 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.3, 70.4, 114.1, 116.2, 119.3, 122.1, 122.9, 128.0, 128.4, 128.5, 129.2, 131.0, 134.4, 143.5, 148.3; EI-MS m/z 262 $[M]^+$; HRMS (EI) calc. for $C_{17}H_{14}N_2O$ $[M]^+$ 262.1106, found 262.1097.

5-Phenyl-7*H*,9*H*-8-oxa-4*b*,10-diazabenz[*a*]azulene (C23). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.18–4.20 (d, J = 6.9 Hz, 2H, CH_2), 4.94 (s, 2H, CH_2), 6.24 (t, 1H, CH), 6.50–6.53 (d, J = 8.1 Hz, 1H, ArH), 7.02–7.07 (t, 1H, ArH), 7.23–7.28 (t, 1H, ArH), 7.34–7.47 (m, 5H, ArH), 7.80–7.83 (d, J = 8.1 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 62.7, 63.0, 112.9, 117.3, 120.5, 123.3, 127.4, 128.9, 130.1, 133.75, 133.84, 142.2, 143.0, 152.8; EI-MS m/z 262 $[M]^+$; HRMS (EI) calc. for $C_{17}H_{14}N_2O$ $[M]^+$ 262.1106, found 262.1104.

4-[1-(2-Trifluoromethyl-phenyl)-meth-(*Z*)-ylidene]-3,4-dihydro-1*H*-2-oxa-4*a*,9-diazafluorene (B24). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.53 (s, 2H, CH_2), 5.24 (s, 2H, CH_2), 6.06–6.09 (d, J = 8.4 Hz, 1H, ArH), 6.57 (s, 1H, CH), 6.75–6.80 (t, 1H, ArH), 6.97–7.10 (d, J = 7.8 Hz, 1H, ArH), 7.10–7.18 (m, 2H, ArH),

7.31–7.36 (t, 1H, ArH), 7.64–7.66 (d, J = 8.4 Hz 1H, ArH), 7.77–7.79 (d, J = 8.1 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.3, 70.3, 111.7, 112.9, 119.3, 122.3, 123.0, 124.1 (d, J = 271.9 Hz), 126.1 (d, J = 5.0 Hz), 127.9, 128.0 (d, J = 29.6 Hz), 130.5, 130.9, 131.2, 131.7, 133.0, 143.3, 148.5; EI-MS m/z 330 $[M]^+$; HRMS (EI) calc. for $C_{18}H_{13}F_3N_2O$ $[M]^+$ 330.0980, found 330.0977.

5-(2-*tert*-Butyl-phenyl)-7*H*,9*H*-8-oxa-4*b*,10-diazabenz[*a*]azulene (C24). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.42–4.44 (d, J = 5.4 Hz, 2H, CH_2), 5.00 (s, 2H, CH_2), 5.91 (t, 1H, CH), 6.15–6.18 (d, J = 8.4 Hz, 1H, ArH), 6.92–6.98 (t, 1H, ArH), 7.17–7.22 (t, 1H, ArH), 7.47–7.50 (m, 1H, ArH), 7.62–7.66 (m, 2H, ArH), 7.73–7.77 (m, 1H, ArH), 7.79–7.82 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 64.2, 65.9, 111.7, 120.4, 120.9, 122.8, 123.46, 123.5 (d, J = 272.3 Hz), 127.2 (d, J = 5.0 Hz), 129.0 (d, J = 30.6 Hz), 129.9, 131.9, 132.3, 134.1, 134.3, 136.7, 142.8, 152.9; EI-MS m/z 330 $[M]^+$; HRMS (EI) calc. for $C_{18}H_{13}F_3N_2O$ $[M]^+$ 330.0980, found 330.0975.

4-[1-(4-Trifluoromethyl-phenyl)-meth-(*Z*)-ylidene]-3,4-dihydro-1*H*-2-oxa-4*a*,9-diazafluorene (B25). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.50 (s, 2H, CH_2), 5.24 (s, 2H, CH_2), 6.17–6.19 (m, 1H, ArH), 6.40 (s, 1H, CH), 6.85–6.90 (t, 1H, ArH), 7.18–7.23 (m, 3H, ArH), 7.47–7.50 (d, J = 8.4 Hz, 2H, ArH), 7.71–7.74 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.3, 70.3, 113.8, 114.4, 119.6, 122.4, 123.3, 125.3 (d, J = 3.3 Hz), 129.4, 129.5 (d, J = 30 Hz), 130.2, 137.9, 142.7, 148.4; EI-MS m/z 330 $[M]^+$; HRMS (EI) calc. for $C_{18}H_{13}F_3N_2O$ $[M]^+$ 330.0980, found 330.0976.

5-(4-Trifluoromethyl-phenyl)-7*H*,9*H*-8-oxa-4*b*,10-diazabenz[*a*]azulene (C25). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.25 (d, J = 6.6 Hz, 2H, CH_2), 4.96 (s, 2H, CH_2), 6.31 (t, 1H, CH), 6.46–6.48 (d, J = 7.8 Hz, 1H, ArH), 7.06–7.12 (t, 1H, ArH), 7.29–7.32 (m, 1H, ArH), 7.48–7.51 (d, J = 8.4 Hz, 2H, ArH), 7.68–7.71 (d, J = 8.1 Hz, 2H, ArH), 7.83–7.85 (d, J = 8.1 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.0, 63.3, 112.6, 119.6, 120.7, 123.3, 123.6, 126.0 (d, J = 3.7 Hz), 127.7, 137.4, 140.5, 143.1, 152.7; EI-MS m/z 330 $[M]^+$; HRMS (EI) calc. for $C_{18}H_{13}F_3N_2O$ $[M]^+$ 330.0980, found 330.0979.

4-[1-(4-Chloro-phenyl)-meth-(*Z*)-ylidene]-3,4-dihydro-1*H*-2-oxa-4*a*,9-diazafluorene (B26). ^{1}H NMR (300 MHz, CDCl3): δ 4.46 (s, 2H, CH_2), 5.24 (s, 2H, CH_2), 6.26–6.28 (d, J = 8.1 Hz, 1H, ArH), 6.32 (s, 1H, CH), 6.90–6.95 (t, 1H, ArH), 7.03–7.06 (d, J = 8.4 Hz, 2H, ArH), 7.18–7.23 (m, 3H, ArH), 7.70–7.72 (d, J = 7.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.3, 70.3, 114.0, 114.9, 119.5, 122.3, 123.1, 128.6, 128.9, 130.5, 132.7, 133.8; EI-MS m/z 296 $[M]^+$; HRMS (EI) calc. for $C_{17}H_{13}ClN_2O$ $[M]^+$ 296.0716, found 296.0718.

5-(4-Chloro-phenyl)-7*H*,9*H*-8-oxa-4*b*,10-diazabenz[*a*]azulene (C26). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.19–4.21 (d, J = 7.2 Hz, 2H, CH_2), 4.94 (s, 2H, CH_2), 6.24 (t, 1H, CH), 6.53–6.55 (d, J = 8.1 Hz, 1H, ArH), 7.06–7.11 (t, 1H, ArH), 7.27–7.33 (m, 3H, ArH), 7.38–7.42 (m, 2H, ArH), 7.82–7.85 (d, J = 8.4 Hz, 1H, ArH); 13 C NMR (100 MHz, $CDCl_3$): δ 62.75, 63.0, 112.8, 117.8, 120.6, 123.2, 123.5, 128.7, 129.3, 132.3, 136.1, 141.0, 143.0; EI-MS m/z 296 $[M]^+$; HRMS (EI) calc. for $C_{17}H_{13}ClN_2O$ [M]+ 296.0716, found 296.0718.

8*H*,10*H*-9-Oxa-5*b*,11-diazanaphth[2,3-*a*]azulene (C27). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.66–4.67 (m, 2H, CH_2), 5.05 (s, 2H, CH_2), 5.41–5.47 (m, 1H, CH), 7.05–7.10 (m, 1H, CH), 7.41–7.50 (m, 2H, ArH), 7.79 (s, 1H, ArH), 7.94–8.02 (m, 2H, ArH), 8.20 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 68.5, 71.9, 105.2, 114.7, 117.3, 119.7, 124.0, 124.9, 127.5, 128.6, 130.5, 130.8; ESI-MS m/z 237 $[M + H]^+$; HRMS (ESI) calc. for $C_{15}H_{13}N_2O$ $[M + H]^+$ 237.1028, found 237.1022.

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