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Palladium-Catalyzed Regioselective Synthesis of 1-Benzoazepine Carbonitriles from *o*-Alkynylanilines via 7-*endo*-dig Annulation and Cyanation

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Abstract. We herein report a three-component, one-pot cascade reaction involving an imination/annulation/cyanation sequence for the synthesis of 1-benzoazepine carbonitrile derivatives using readily available *o*-alkynylanilines, cyclic ketones and trimethylsilyl cyanide. This regio- and stereoselective reaction was achieved by combining palladium(II) trifluoroacetate and copper(II) acetate in dimethyl sulfoxide. The important features of this method include a broad substrate scope, the use of trimethylsilyl cyanide as a cyanating agent, the formation of two C-C bonds and one C-N bond, mild reaction conditions and good product yields.

Keywords: Regio- and stereoselective, hydroenamination, cascade, 7-*endo* dig, cyanation, palladium

Introduction

Medium-sized carbocyclic and heterocyclic structures are a pivotal class of compounds because of their presence in many bioactive molecules, pharmaceuticals and natural products.[1] Among these structures, seven membered aza-heterocycles, such as benzoazepines, possess excellent biological activities, such as anti-depressant,[2a,b] methionine aminopeptidase (MetAP) inhibition[2c] and sphingosine kinase I enzyme inhibition (SphK1)[2d] activities (Figure 1). On the other hand, α-aminonitriles are vital bioactive motifs that are used to treat various diseases and are one of the main precursors for synthesizing α-amino acids.[3] In this regard, we envisaged that the incorporation of α-aminonitriles into a benzoazepine core will open a new pathway for identifying potential compounds in medicinal chemistry.

The 1-benzoazepine scaffold has attracted less attention from the synthetic community than those of 2- and 3-benzoazepines, even though compounds with this scaffold possess potential bioactivities.[4g] Very few elegant methods have been reported in the literature for synthesizing the 1-benzoazepine core; however, transition-metal-catalyzed annulation reactions,[4] ring openings of alkylidenecyclopropanes and isoxazolidines,[5] cycloadditions,[6] rearrangement reactions,[7] and others have been reported.[8] Despite the potential advantages of these methods, some of the reported methods require harsh reaction conditions and starting materials that are difficult to synthesize and have poor substrate scope. Thus, the development of new synthetic strategies to construct the benzoazepine core with a broad range of functional groups in a simple and straightforward

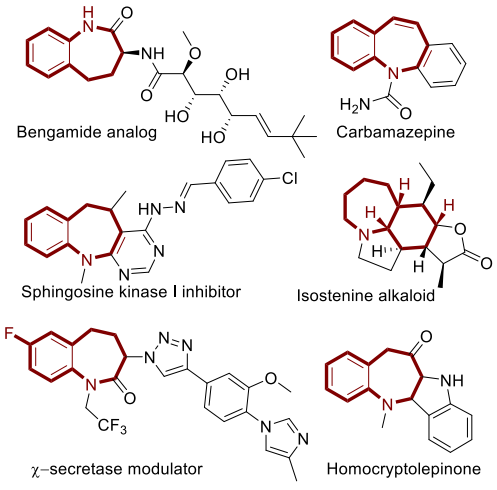

Figure 1. Representative examples of benzoazopines

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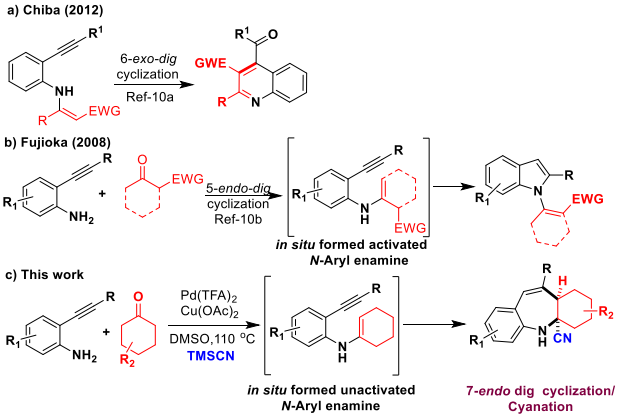
manner, which is an interesting and undeveloped area of research.[9]

Scheme 1. Previous work and this work on cyclization of *N*-aryl enamine

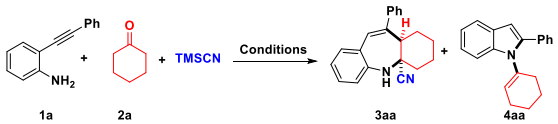


Activated *N*-aryl enamines generated from *o*-alkynylanilines have been used to construct aza-heterocycles such as indoles[10a] and quinolines.[10b,c] For example, Chiba et al. discovered a copper-catalyzed intramolecular aerobic oxidative method to generate multisubstituted quinolines from *N*-aryl enamines (Scheme 1a).[10a] In 2008, Fujioka et al. reported a tandem imination/annulation strategy for the synthesis of *N*-alkylated indoles (Scheme 1b).[10b] To date, the *in situ* generation of *N*-aryl enamines from *o*-alkynylanilines followed by 7-*endo*-dig multicomponent cascade methodologies has not been documented in the literature. Generally, the synthesis of 7-membered rings demands expensive metal catalysts, such as Pt,[11a] Ir,[11b] Rh,[11c] and Au/Ag.[11d] To overcome the above issues and to develop new reaction conditions for the construction of heterocycles and heteroatom-containing acyclic structures,[12] we herein present a new multicomponent reaction (MCR) strategy. The synthesis of benzoazepine-tethered α-aminonitriles was achieved through the *in situ* generation of unactivated cyclic *N*-aryl enamines from *o*-alkynylanilines and cyclohexanone followed by a 7-*endo*-dig cascade reaction sequence involving TMSCN as the cyanating agent (Scheme 1c). To the best of our knowledge, there was only one previous report on 7-*endo*-dig cyclizations of activated β-enamino esters, and that reaction requires a multistep protocol.[13]

Results and Discussion

Our investigation began with 2-(phenylethynyl) aniline **1a**, cyclohexanone **2a** and TMSCN as model substrates using 5 mol% $Pd(OAc)_2$ and 1 equiv of $Cu(OAc)_2$ with DMSO as the solvent at 110 °C. To our surprise, the desired compound, 4a*H*-dibenzo[*b*,*f*] azepine-4a-carbonitrile **3aa,** was obtained as a single stereoisomer in a 55% yield (Table 1, entry 1). Conducting the reaction under an O_2 balloon failed to improve the yield of **3aa** (Table 1, entry 2). To determine the optimal palladium source, we performed the reaction using different Pd catalysts, such as $PdCl_2$, PdI_2, $PdCl_2(PPh_3)_2$, and $Pd(TFA)_2$ (Table 1, entries 3-6). Among them, $Pd(TFA)_2$ afforded the maximum yield (84%, Table 1, entry 6). *In situ* generated Pd(II) failed to produce better results (Table 1, entry 7). Further screening of various copper salts (Table 1, entries 8-14) revealed that $Cu(OAc)_2$ provided the best results. When $Cu(OAc)_2$/CuCN was used, the reaction produced either a mixture of **3aa** and **4aa** or only **4aa** as the major product. These results suggested competition between intramolecular nucleophilic attack of the amine (5-*exo* dig) and the enamine (7-*endo* dig) by the *o*-alkyne. The reaction failed to give the desired product **3aa** when TMSCN was replaced with CuCN (Table 1, entry 15). These results suggested that TMSCN is a key reagent in this reaction process. Interestingly, when the reaction was performed without $Pd(TFA)_2$, we obtained **3aa,** albeit in a low yield (Table 1, entries 17). In contrast, no product

Table 1 Optimization of the reaction conditions[a]



Entry	Pd catalyst	"Cu" Source	Solvent	Yield% [b] **3aa/4aa**
1	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO	55/ --
2[c]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO	45/ --
3	$PdCl_2$	$Cu(OAc)_2$	DMSO	47/--
4	PdI_2	$Cu(OAc)_2$	DMSO	65/--
5	$PdCl_2(PPh_3)_2$	$Cu(OAc)_2$	DMSO	72/--
6	$Pd(TFA)_2$	$Cu(OAc)_2$	DMSO	84/--
7	$Pd(PPh_3)_4$	$Cu(OAc)_2$	DMSO	30/--
8	$Pd(TFA)_2$	$Cu(TFA)_2$	DMSO	25/18
9	$Pd(TFA)_2$	$CuBr_2$	DMSO	--/--
10	$Pd(TFA)_2$	$CuCl_2$	DMSO	33/41
11	$Pd(TFA)_2$	$CuSO_4$	DMSO	Trace/--
12	$Pd(TFA)_2$	CuBr	DMSO	--/--
13[c,d]	$Pd(TFA)_2$	CuBr	DMSO	--/28
14[e]	$Pd(TFA)_2$	CuCN	DMSO	63/--
15[e,f]	$Pd(TFA)_2$	CuCN	DMSO	--/25
16	$Pd(TFA)_2$	--	DMSO	--/59
17	--	$Cu(OAc)_2$	DMSO	44/--
18	$Pd(TFA)_2$	$Cu(OAc)_2$	DMF	62/--
19	$Pd(TFA)_2$	$Cu(OAc)_2$	Dioxane	25/--
20	$Pd(TFA)_2$	$Cu(OAc)_2$	THF	--/--
21	$Pd(TFA)_2$	$Cu(OAc)_2$	CH_3NO_2	--/--
22	$Pd(TFA)_2$	$Cu(OAc)_2$	Toluene	--/--

[a] All reactions were carried out using **1a** (0.5 mmol), **2a** (0.75 mmol), TMSCN (1.0 mmol), Pd catalyst (5 mol %), Cu salt (0.5 mmol) and DMSO solvent (1 mL) at 110 °C and the mixtures were stirred for 3-6h unless otherwise noted.[b] Isolated yield. [c] Reaction was performed under O_2 atmosphere. [d] Reaction was performed in the presence of 0.2 equiv CuBr. [e] Reaction was performed with 1.5 equiv CuCN. [f] Reaction was performed without TMSCN.

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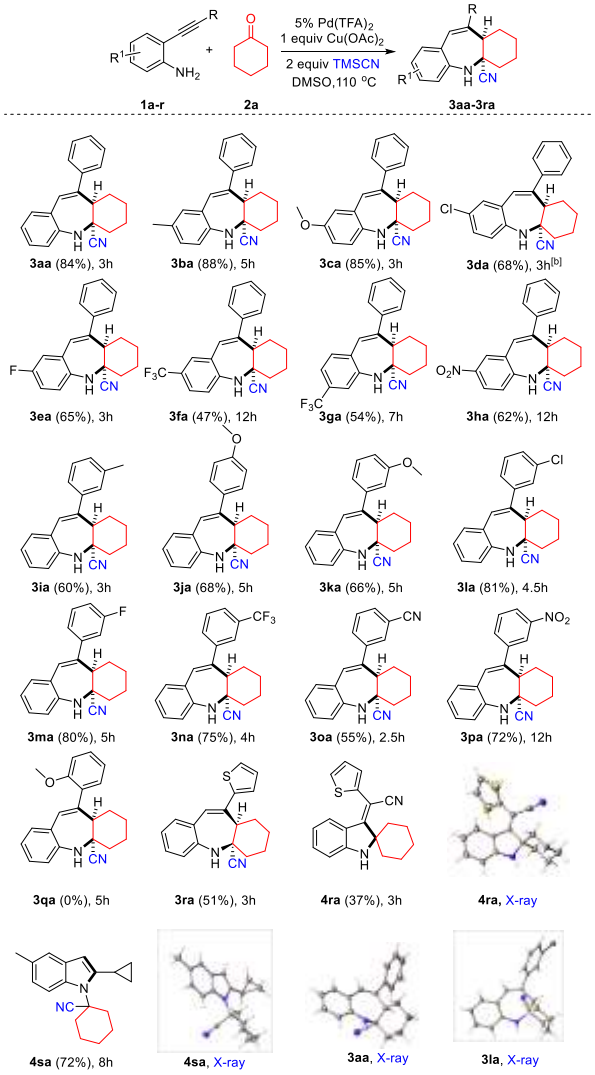
was observed when using $Pd(TFA)_2$ alone (Table 1, entry 16). Changing the solvent from DMSO to other solvents resulted in trace or no product formation, which confirmed that the solvent plays a crucial role in this reaction (Table 1, entries 18-22).

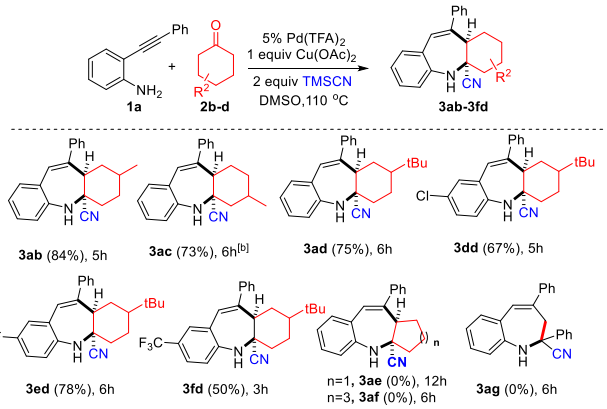
Table 2. Scope and limitations of different *o*-alkyne anilines with cyclohexanone[a,b]



[a] Reaction conditions: compounds **1a-s** (0.5 mmol), **2a** (0.75 mmol), TMSCN (1.0 mmol), Pd catalyst (5 mol %), $Cu(OAc)_2$ (0.5 mmol) and DMSO solvent (1 mL) at 110 °C for the indicated times unless otherwise noted. [b] Reaction was performed with 2.5 mol % Pd catalyst.

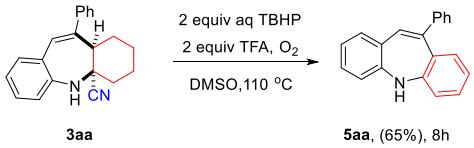
To illustrate the generality and efficiency of our optimized reaction conditions (Table 1, entry 6), we synthesized an array of 4a*H*-dibenzo[*b*,*f*]azepine-4a-carbonitrile derivatives (**3aa-3fd**). Initially, a series of R^1-substituted *o*-alkynylanilines (**1a-1h**) was reacted with cyclohexanone (**2a**) under standard conditions, and all tested substrates provided their respective products in moderate to good yields (Table 2, **3aa-3ha**, 47-88%). The yields were slightly suppressed when R^1 contained an electron-withdrawing group, such as *m*-CF_3, *p*-CF_3 and *p*-NO_2, but the products **3fa-3ha** were still obtained. Next, we explored substrates with R groups bearing electron-donating and electron-withdrawing groups, such as *m*-Me-Ph (**1i**), *p*-OMe-Ph (**1j**), *m*-OMe-Ph (**1k**), *m*-Cl-Ph (**1l**), *m*-F-Ph (**1m**), *m*-CF_3-Ph (**1n**), *m*-CN-Ph (**1o**) and *m*-NO_2-Ph (**1p**). These compounds readily provided the expected products **3ia-3pa** in 55-81% yields. However, the *o*-methoxy-containing substituent (**1q**) failed to give the desired product (**3qa**), which was likely due to steric hindrance. When we tested our reaction with a thiophene substituent (**1r**), we obtained spiro compound **4ra** along with the desired product **3ra**. A plausible mechanism for the formation of **4ra** is shown in the supporting

Table 3. Scope and limitations of *o*-alkyne aniline with different cyclohexanones[a,b]



[a] Reaction conditions: compounds **1a** (0.5 mmol), **2b-d** (0.75 mmol), TMSCN (1.0 mmol), Pd catalyst (5 mol %), $Cu(OAc)_2$ (0.5 mmol) and DMSO solvent (1 mL) at 110 °C for the indicated times unless otherwise noted. [b] Single regioisomer confirmed by NMR analysis.

Scheme 2. Oxidation of 11-phenyl-1,2,3,4,5,11a-hexahydro-4a*H*-dibenzo[*b*,*f*]azepine-4a-carbonitrile



information.[14] This catalytic system did not tolerate alkyl substituents, and these substrates provided only the indole product (**4sa**). The structures of compounds **3aa**, **3la**, **4ra** and **4sa** were confirmed by X-ray crystallography analysis.[15]

Next, we investigated the applicability of this reaction to cyclohexanone derivatives with different R^2 substituents such as 4-Me (**2b**), 3-Me (**2c**) and 4-*t*-Bu (**2d**). The reaction worked well and afforded compounds **3ab-3fd** in 50-84% yields (Table 3). Surprisingly, the reaction with 3-methyl cyclohexanone regioselectively afforded product **3ac** (determined by 2D-NMR analysis), and the cyclopentanone (**2e**), cycloheptanone (**2f**) and

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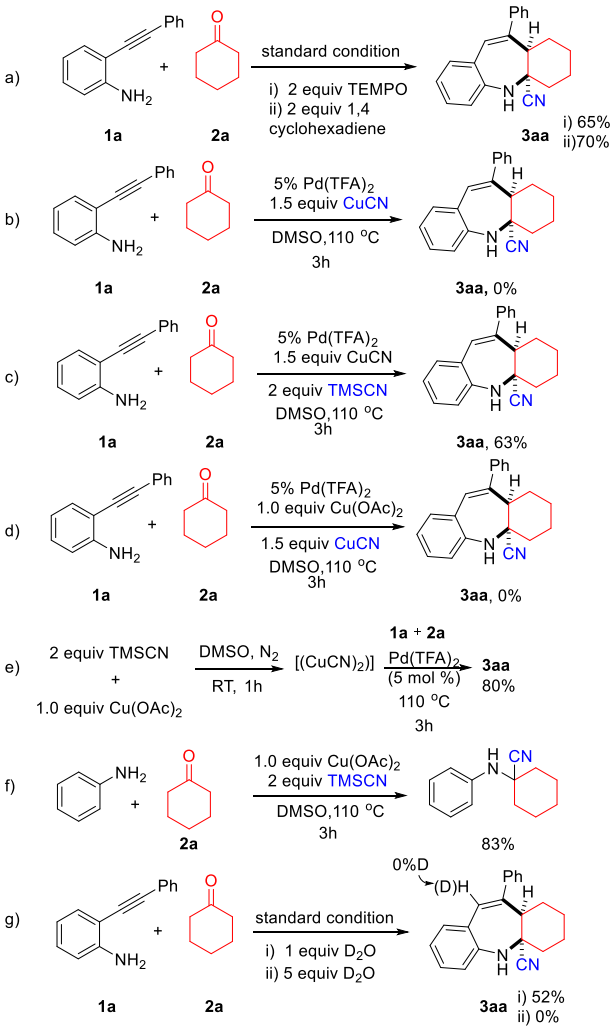
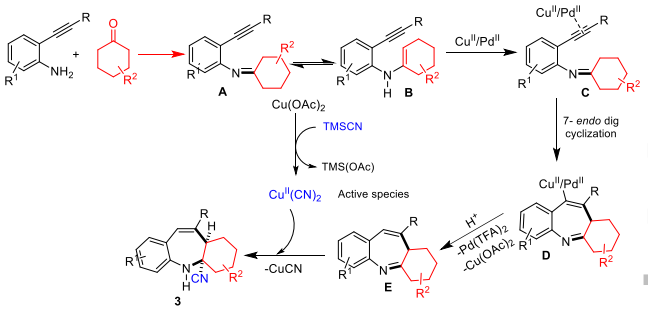
acetophenone (**2g**) derivatives were not compatible with these reaction conditions (Table 3). To show the significance of this synthetic method, we synthesized biologically valuable 10-phenyl-5*H*-dibenzo[*b*,*f*]azepine (**5aa**) by oxidation of 11-phenyl-1,2,3,4,5,11a-hexahydro-4a*H*-dibenzo[*b*,*f*] azepine-4a-carbonitrile (**3aa**, Scheme 2).[12a]

Scheme 3. Control studies



To elucidate the mechanism of this reaction, we conducted various control studies. Recently, Prof Liu et al.[16a-b] proposed a radical mechanism for the *in situ* generation of $Cu(CN)_2$ for various cyanation reactions. Herein, we performed this reaction in the presence of two radical scavengers, TEMPO and 1,4-cyclohexadiene. However, the reaction gave the desired products in yields similar to those achieved in the absence of radical scavengers. These results suggested that the reaction does not occur via a radical pathway (Scheme 3, a). To determine the role of copper in the reaction mechanism, we carried out reactions with CuCN in the presence and absence of TMSCN. The reaction gave the desired product **3aa** in 63% only in the presence of both TMSCN and CuCN. These results support a mechanism involving *in situ* generation of an active $Cu(CN)_2$ species that serves as a cyanating agent (Scheme 3 b and c).[16] Furthermore, to confirm the *in situ* generation of $Cu(CN)_2$, we carried out the reaction with combinations of $Cu(OAc)_2$ and CuCN, which failed to give product **3aa** (Scheme 3, d). In addition, we attempted to *in situ* generate $Cu(CN)_2$ by combining TMSCN and $Cu(OAc)_2$ and reacting that solution with the starting materials **1a** and **2a** in a sequential, one-pot reaction, and this method afforded product **3aa** in an 80% yield (Scheme 3, e).

Next, simple aniline was introduced instead of *o*-alkynylaniline under the optimized reaction conditions to successfully obtain the Strecker product in the presence of $Cu(OAc)_2$. This result confirmed the role of copper salt in the cyanation step (Scheme 3, f).[17] When **1a** and **2a** were treated under the optimized reaction conditions with 1 equiv of D_2O, we did not observe any H/D exchanged product **3aa,** and in the presence of 5 equiv D_2O, the same reaction failed to give the desired product (Scheme 3, g). These results indicate that H_2O was not directly involved in the metal protonation process, and we speculate that acetic acid plays a major role in the protolysis of the palladium complex.[18]



Scheme 4. Plausible reaction mechanism

Based on the literature reports and control studies, a plausible mechanism was proposed, as shown in Scheme 4.[16,19] Initially, the acid-catalyzed imination and consecutive isomerization generated the enamine intermediate **B**. The reaction of enamine **B** with a Pd(II)/Cu(II) catalyst generated active π Pd(II)/Cu(II) species **C**.[18,19] Further intramolecular 7-*endo*-dig cyclization gave metal complex **D**. Then, the acid-promoted protolysis of intermediate **D** regenerated the active Pd(II)/Cu(II) catalysts[18] and produced the highly reactive intermediate **E**. Finally, the active cyanating species $Cu(CN)_2$ will cyanate **E** at the electrophilic imine carbon to afford the final Strecker reaction product.

Conclusion

In summary, we exploited the versatility of *N*-aryl enamine in a regio- and stereoselective annulation reaction to robustly synthesize 2-benzoazepine carbonitrile derivatives. This reaction strategy

involved a tandem imination/annulation/cyanation reaction that was catalyzed/mediated by a Pd(II)/Cu(II) bimetallic system. The mechanistic studies revealed that the reaction occurred via a Pd/Cu-catalyzed/mediated oxidative annulation and $Cu(OAc)_2$/TMSCN-mediated imine cyanation. To the best of our knowledge, this is the first report of a 7-*endo*-dig cyclization/cyanation with an *in situ*-formed *N*-aryl enamine to prepare this valuable motif with a carbonitrile substituent. Further synthetic applications for the developed reactions are currently being developed in our laboratory.

Experimental Section

General procedure for preparation of 11-Phenyl-1,2,3,4,5,11a-hex*aHydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (**3aa):**In an oven dried 15 mL sealed tube 2-(phenylethynyl) aniline **1a** (193 mg, 1.0 mmol) was added in 1 mL of DMSO followed by the sequential addition of $Pd(TFA)_2$ (16 mg, 5.0 mol %), $Cu(OAc)_2$ (181 mg, 1.0 mmol), TMSCN (251 µL, 2.0 mmol) and cyclohexanone **2a** (156 µL, 1.5 mmol). The reaction mixture was allowed to stir at 110 °C for 3h. After the completion, the reaction mixture was cooled to room temperature and diluted with 25.0 mL of cold water. The water layer was extracted with (3X25 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from hexane to 6-10% ethyl acetate/hexane to afford pure 11-phenyl-1,2,3,4,5,11a-hex*aHydro*-4*aH*-dibenzo[*b,f*]azepine-4a-carbonitrile (**3aa**) as an off white solid (252 mg, yield 84%); Mp. 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.38 (m, 2H), 7.37 –7.31 (m, 2H), 7.3–7.25 (m, 1H), 7.17 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.09 (td, *J* = 8, 1.2 Hz, 1H), 6.85 (td, *J* = 7.5, 1.2 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.53 (s, 1H), 4.00 (s, 1H), 3.23–3.12 (m, 1H), 2.37 (d, *J* = 14.9 Hz, 1H), 2.30–2.15 (m, 1H), 1.83–1.63 (m, 5H), 1.46–1.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.45, 142.60, 140.29, 134.20, 129.49, 128.39, 128.22, 127.15, 126.83, 122.29, 120.95, 120.45, 117.86, 52.82, 52.51, 39.22, 28.19, 26.05, 20.05; HRMS (ESI) calcd for $C_{21}H_{21}N_2$ $[M+H]^+$: 301.1695; found: 301.1699.

8-Methyl-11-phenyl-1,2,3,4,5,11*a*-hex*a*hydro-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3ba). Following the general procedure on a 1.0 mmol scale for 5h giving the compound as an yellow solid (276 mg, yield 88%); Mp 174-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.38 (m, 2H), 7.38–7.32 (m, 2H), 7.30–7.26 (m, 1H), 6.99 (s, 1H), 6.91 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.60 (d, *J* = 8.1 Hz, 1H), 6.49 (s, 1H), 3.90 (s, 1H), 3.18 (dd, *J* = 8.7, 4.4 Hz, 1H), 2.36 (d, *J* = 14.4 Hz, 1H), 2.28–2.18 (m, 4H), 1.85–1.66 (m, 5H), 1.41 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.54, 140.33, 140.24, 130.58, 129.59, 129.50, 129.08, 128.36, 127.09, 126.84, 122.21, 121.06, 117.91, 52.89, 52.47, 39.19, 28.18, 26.06, 20.25, 20.07; HRMS (ESI) calcd for $C_{22}H_{23}N_2$ $[M+H]^+$: 315.1852; found: 315.1856.

8-Methoxy-11-phenyl-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3ca). Following the general procedure on a 1.0 mmol scale for 3h giving the compound as a brown solid (280 mg, yield 85%); Mp 142-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.10 (td, *J* = 7.6, 1.2 Hz, 1H), 7.00 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 6.94 (t, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.84 (ddd, *J* = 8.1, 2.6, 0.8 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 6.55 (s, 1H), 4.00 (s, 1H), 3.84 (s, 3H), 3.23–3.14 (m, 1H), 2.38 (d, *J* = 14.9 Hz, 1H), 2.32–2.17 (m, 1H), 1.84–1.66 (m, 5H), 1.48–1.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.57, 146.00, 142.64, 140.14, 134.22, 129.43, 129.34, 128.27, 122.24, 120.90, 120.47, 119.33, 117.86, 113.00, 112.27, 55.30, 52.81, 52.50, 39.22, 28.24, 26.04, 20.05; HRMS (ESI) calcd for $C_{22}H_{23}N_2O$ $[M+H]^+$: 331.1801; found: 331.1805.

8-Chloro-11-phenyl-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3da). Following the general procedure on a 1.0 mmol scale for 4.50h giving the compound as an off-white solid (227 mg, yield 68%); Mp 186-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.33 (m, 4H), 7.33–7.27 (m, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 6.43 (s, 1H), 4.03 (s, 1H), 3.19 (ddd, *J* = 11.4, 3.0, 1.7 Hz, 1H), 2.37 (d, *J* = 12.8 Hz, 1H), 2.24 (ddd, *J* = 14.1, 11.9, 6.0 Hz, 1H), 1.84–1.61 (m, 5H), 1.47–1.33 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.00, 142.00, 141.17, 133.12, 128.47, 128.17, 127.87, 127.46, 126.78, 125.14, 123.74, 120.65, 119.20, 52.80, 52.49, 39.03, 28.22, 25.97, 19.98; HRMS (ESI) calcd for $C_{21}H_{19}N_2Cl$ $[M+H]^+$: 337.1130; found: 357.1129.

8-Fluoro-11-phenyl-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3ea). Following the general procedure on a 1.0 mmol scale for 3h giving the compound as an orange solid (206 mg, yield 65%); Mp 162-163°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.34 (m, 4H), 7.33–7.28 (m, 1H), 6.89 (dd, *J* = 9.8, 2.9 Hz, 1H), 6.84–6.79 (ddd, *J* = 8.7, 7.6, 2.9 Hz, 1H), 6.63 (dd, *J* = 8.7, 4.8 Hz, 1H), 6.42 (s, 1H), 3.92 (s, 1H), 3.18 (ddd, *J* = 11.2, 3.5, 1.7 Hz, 1H), 2.37 (d, *J* = 14.2 Hz, 1H), 2.26 (ddd, *J* = 14.2, 12.3, 5.6 Hz, 1H), 1.82–1.66 (m, 5H), 1.40 (dd, *J* = 10.8, 6.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.19 (d, J_F = 237.7 Hz), 144.10, 142.17, 138.95, 128.46, 128.32 (d, J_F = 1.7 Hz), 127.44, 127.25, 126.85, 123.75 (d, J_F = 7.2 Hz),, 120.77, 119.23 (d, J_F = 22.35 Hz),, 118.99 (d, J_F = 7.8 Hz), 115.24, 115.01, 52.83, 52.53, 39.05, 28.34, 25.98, 20.04; HRMS (ESI) calcd for $C_{21}H_{20}N_2F$ $[M+H]^+$:319.1598; found: 319.1605.

11-(3-(Trifluoromethyl)phenyl)-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3fa). Following the general procedure on a 1.0 mmol scale for 12h giving the compound as an off-white solid (172 mg, yield 47%); Mp 190-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.42–7.39 (m, 2H), 7.39–7.34 (m, 2H), 7.33 –7.26 (m, 2H), 6.74 (d, *J* = 12.0 Hz, 1H), 6.51 (s, 1H), 4.39 (s, 1H), 3.22 (dd, *J* = 9.2, 1.7 Hz, 1H), 2.38 (d, *J* =13.9 Hz, 1H), 2.28–2.13 (m, 1H), 1.86–1.59 (m, 5H), 1.50–1.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.05, 143.77, 142.03, 131.23 (q, J_F = 3.9 Hz), 128.50, 128.37, 127.55, 126.68, 125.67, 124.70 (q, J_F = 3.6 Hz), 122.98, 122.39, 122.06, 121.70, 120.52, 118.01, 52.80, 52.48, 38.91, 28.10, 25.93, 19.87; HRMS (ESI) calcd for $C_{22}H_{20}N_2F_3$ $[M+H]^+$: 369.1570; found: 369.1573.

11-Phenyl-7-(trifluoromethyl)-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3ga). Following the general procedure on a 1.0 mmol scale for 7h giving the compound as an white solid (198 mg, yield 54%); Mp 219-220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.25 (m, 6H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.94 (s, 1H), 6.54 (s, 1H), 4.21 (s,1H), 3.23 (d, *J* = 14.4 Hz, 1H), 2.42 (d, *J* = 14.2 Hz, 1H), 2.30–2.22 (m, 1H), 1.82–1.65 (m, 5H), 1.47–1.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.57 (d, J_F = 79.1 Hz), 142.67, 134.71, 129.92 (d, J_F = 23.8 Hz), 128.47, 128.42, 127.74, 125.24 (q, J_F = 5.7 Hz), 122.63, 120.55 (d, J_F = 6.7 Hz), 116.93 (d, J_F = 3.8 Hz), 114.83 (d, J_F = 3.8 Hz), 52.89, 52.86, 39.07, 28.51, 26.05, 20.14; HRMS (ESI) calcd for $C_{22}H_{20}N_2F_3N_2$ $[M+H]^+$: 369.1572; found: 369.1573.

8-Nitro-11-phenyl-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo [*b,f*]azepine-4*a*-carbonitrile (3ha). Following the general procedure on a 1.0 mmol scale for 12h giving the compound as an yellow solid (213 mg, yield 62%); Mp 237-238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.5 Hz, 1H), 7.96 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.45–7.39 (m, 3H), 7.38–7.29 (m, 2H), 6.74 (d, *J* = 8.9 Hz, 1H), 6.60 (s, 1H),

4.67 (s, 1H), 3.31–3.20 (m, 1H), 2.43 (d, *J* = 14.3 Hz, 1H), 2.33–2.19 (m, 1H), 1.88–1.63 (m, 5H), 1.50–1.39 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.65, 143.31, 143.14, 140.84, 130.07, 128.64, 127.89, 127.67, 126.64, 123.53, 121.47, 120.00, 117.94, 110.00, 53.17, 52.43, 39.03, 27.97, 25.90, 19.89; HRMS (ESI) calcd for $C_{21}H_{20}N_3O_2$ $[M+H]^+$: 346.1551; found: 346.1550.

11-(*m*-Tolyl)-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*] azepine-4*a*-carbonitrile (3ia). Following the general procedure on a 1.0 mmol scale for 3h giving the compound as an off white solid (188 mg, yield 60%); Mp 163-164 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.23 (m, 2H), 7.21–7.14 (m, 2H), 7.13–7.05 (m, 2H), 6.86 (td, *J* = 7.6, 1.2 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.51 (s, 1H), 4.01 (s, 1H), 3.17 (ddd, *J* = 11.2, 3.3, 1.6 Hz, 1H), 2.38 (s, 3H), 2.36–2.35 (m, 1H), 2.24 (td, *J* = 12.8, 4.8 Hz, 1H), 1.79–1.67 (m, 5H), 1.48–1.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.49, 142.58, 140.47, 137.94, 134.14, 129.26, 128.25, 128.13, 127.91, 127.54, 123.97, 122.35, 120.99, 120.41, 117.84, 52.81, 52.53, 39.18, 28.18, 26.03, 21.49, 20.04; HRMS (ESI) calcd for $C_{22}H_{23}N_2$ $[M+H]^+$: 315.1851; found: 315.1856.

11-(4-Methoxyphenyl)-1,2,3,4,5,11a-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3ja). Following the general procedure on a 1.0 mmol scale for 5h giving the compound as an brown solid (224 mg, yield 68%); Mp 156-157 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 8.4 Hz, 1H), 6.87 (m, 3H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.49 (s, 1H), 3.96 (s, 1H), 3.83 (s, 3H), 3.16 (d, *J* = 8.8 Hz, 1H), 2.38 (d, *J* = 15.2 Hz, 1H), 2.25 (td, *J* = 13.6, 4.8 Hz, 1H), 1.81–1.69 (m, 5H), 143–1.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.00, 142.57,139.96, 136.91, 134.16, 128.66, 128.10, 127.98, 122.56, 120.55, 117.90, 113.86, 55.41, 52.97, 52.52, 39.39, 28.30, 26.19, 20.17; HRMS (ESI) calcd for $C_{22}H_{23}N_2O$ $[M+H]^+$: 331.1799; found: 331.1805.

11-(3-Methoxyphenyl)-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*] azepine-4*a*-carbonitrile (3ka). Following the general procedure on a 1.0 mmol scale for 5h giving the compound as an off white solid (217 mg, yield 66%); Mp 140-141 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.9 Hz, 1H), 7.17 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.12–7.05 (m, 1H), 7.00 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 6.94 (t, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.84–6.82 (m 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.55 (s, 1H), 4.05 (s, 1H), 3.83 (s, 3H), 3.21–3.13 (m, 1H), 2.36 (d, *J* = 14.6 Hz, 1H), 2.21 (td, *J* = 13.6, 4.9 Hz, 1H), 1.79–1.65 (m, 5H), 1.44–1.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.52, 145.96, 142.66, 140.08, 134.16, 129.40, 129.32, 128.23, 122.15, 120.94, 120.37, 119.27, 117.84, 112.95, 112.21, 55.27, 52.76, 52.46, 39.07, 28.21, 25.99, 19.99; HRMS (ESI) calcd for $C_{22}H_{23}ON_2$ $[M+H]^+$: 331.1796; found: 331.1805.

11-(3-Chlorophenyl)-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3la). Following the general procedure on a 1.0 mmol scale for 4.50h giving the compound as an off-white solid (270 mg, yield 81%); Mp 185-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.38 (m, 1H), 7.32–7.23 (m, 3H), 7.19 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.11 (td, *J* = 7.2, 1.6 Hz, 1H), 6.87 (td, *J* = 7.5, 1.1 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.53 (s, 1H), 4.03 (s, 1H), 3.17–3.08 (m, 1H), 2.38 (d, *J* = 14.0 Hz, 1H), 2.28 (td, *J* = 12.4, 5.2 Hz, 1H), 1.90–1.66 (m, 5H), 1.48–1.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.31, 142.70, 138.80, 134.36, 134.26, 130.33, 129.64, 128.59, 127.19, 127.00, 125.02, 121.88, 117.92, 52.70, 52.45, 39.10, 28.20, 25.97, 19.99; HRMS (ESI) calcd for $C_{21}H_{20}N_2Cl$ $[M+H]^+$: 335.1306; found: 335.1310.

11-(3-Fluorophenyl)-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3ma). Following the general procedure on a 1.0 mmol scale for 5h giving the compound as an yellow solid (254 mg, yield 80%); Mp 162-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 1H), 7.21–7.17 (m, 2H), 7.14–7.10 (m, 1H), 7.11–7.07 (m, 1H), 7.03–6.95 (m, 1H), 6.87 (td, *J* = 7.6, 1.1 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 6.57 (s, 1H), 4.05 (s, 1H), 3.21–3.08 (m, 1H), 2.38 (d, *J* = 14.0 Hz, 1H), 2.24 (td, *J* = 12.8, 5.2 Hz, 1H), 1.87–1.63 (m, 5H), 1.48–1.35 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.78 (d, J_F = 246.08 Hz), 146.65 (d, J_F = 7.1 Hz), 142.70, 138.86, 138.84, 134.34, 130.16, 129.88, 129.80, 128.55, 122.42 (d, J_F = 2.81 Hz), 121.33 (d, J_F = 106.73Hz), 117.90, 113.93 (d, J_F = 21.24 Hz), 113.77 (d, J_F = 21.54 Hz), 52.70, 52.38, 39.10, 28.23, 25.99, 19.98; HRMS (ESI) calcd for $C_{21}H_{19}N_2FNa$ $[M+Na]^+$: 341.1422; found: 341.1424.

11-(3-(Trifluoromethyl)phenyl)-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3na). Following the general procedure on a 1.0 mmol scale for 7h giving the compound as an off white solid (276 mg, yield 75%); Mp 182-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.57 (dd, *J* = 16.2, 7.7 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.13 (td, *J* = 8.0, 1.6 Hz, 1H), 6.89 (td, *J* = 7.7, 1.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.56 (s, 1H), 4.06 (s, 1H), 3.17 (t, *J* = 6.4 Hz, 1H), 2.40 (d, *J* = 14.3 Hz, 1H), 2.27 (td, *J* = 12.8, 5.2 Hz, 1H), 1.91–1.67 (m, 5H), 1.47–1.39 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.23, 142.75, 138.72, 134.42, 131.01, 130.79, 130.69, 130.13, 128.92, 128.73, 125.44, 123.89 (q, J_F = 3.8 Hz), 123.58 (q, J_F = 3.8 Hz), 121.28 (d, J_F = 106.83 Hz), 119.27 (d, J_F = 260.1 Hz), 52.72, 52.55, 39.06, 28.20, 25.96, 19.98; HRMS (ESI) calcd for $C_{22}H_{20}N_2F_3$ $[M+H]^+$: 369.1572; found: 369.1573.

11-(3-Cyanophenyl)-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*] azepine-4*a*-carbonitrile (3oa). Following the general procedure on a 1.0 mmol scale for 3.50h giving the compound as an brown solid (178 mg, yield 55%); Mp 194-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (t, *J* = 1.5 Hz, 1H), 7.68–7.62 (m, 1H), 7.57 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.14 (td, *J* = 8.4, 1.6 Hz,1H), 6.89 (td, *J* = 7.6, 1.1 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.55 (s, 1H), 4.10 (s, 1H), 3.13 (dd, *J* = 8.8, 4.5 Hz, 1H), 2.41 (d, *J* = 13.5 Hz, 1H), 2.26 td, *J* = 12.0, 5.2 Hz, 1H), 1.89–1.64 (m, 5H), 1.51–1.36 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.61, 142.76, 137.70, 134.49, 131.31, 131.17, 130.58, 130.42, 129.32, 128.96, 121.48, 120.64, 120.56, 118.75, 118.00, 112.65, 52.62, 52.43, 39.01, 28.19, 25.94, 19.92; HRMS (ESI) calcd for $C_{22}H_{19}N_3Na$ $[M+Na]^+$: 348.1471; found: 348.1471.

11-(3-Nitrophenyl)-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3pa). Following the general procedure on a 1.0 mmol scale for 12h giving the compound as an yellow solid (248 mg, yield 72%); Mp 225-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (t, *J* = 2.0 Hz, 1H), 8.15 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 7.75 (ddd, *J* = 7.7, 1.8, 1.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.15(td, *J* = 8.0, 1.6 Hz, 1H), 6.90 (td, *J* = 7.6, 1.1 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.62 (s, 1H), 4.08 (s, 1H), 3.24–3.16 (m, 1H), 2.43 (d, *J* = 14.0 Hz, 1H), 2.35–2.21 (m, 1H), 1.91–1.68 (m, 5H), 1.50–1.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.41, 146.04, 142.84, 137.55, 134.59, 132.81, 131.59, 129.43, 129.07, 122.01, 121.65, 121.50, 120.65, 120.60, 118.04, 52.66, 52.38, 39.04, 28.28, 25.94, 19.96; HRMS (ESI) calcd for $C_{21}H_{19}N_3NaO_2$ $[M+Na]^+$: 368.1369; found: 368.1369.

11-(Thiophen-2-yl)-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*] azepine-4*a*-carbonitrile (3ra). Following the general procedure on a 1.0 mmol scale for 3h giving the compound as a brown solid (156 mg, yield 51%); Mp 201-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.2 Hz, 1H), 7.18 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.11–7.06 (m, 2H), 7.00 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.91– 6.85 (m, 2H), 6.67 (d, *J* = 7.9 Hz, 1H), 4.00 (s, 1H), 3.27 (d, *J* = 11.5 Hz, 1H), 2.39 (d, *J* = 14.1 Hz, 1H), 2.28 (td, *J* = 12.4, 5.6 Hz, 1H), 1.98 (d, *J* = 13.2 Hz, 1H), 1.88–1.74 (m, 4H), 1.54–1.43 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.32, 142.61, 134.35, 132.84, 128.47, 127.70, 127.58, 123.94, 122.72, 121.81, 120.56, 117.82, 52.37, 51.72, 39.31, 28.77, 26.12, 20.08; HRMS (ESI) calcd for $C_{19}H_{19}N_2S$ $[M+H]^+$: 307.1257; found: 307.1263.

3-Methyl-11-phenyl-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3ab). Following the general procedure on a 1.0 mmol scale for 5h giving the compound as an yellow solid (263 mg, yield 84%); Mp 165-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2H), 7.38–7.33 (m, 2H), 7.32–7.26 (m, 1H), 7.18 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.09 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H), 6.86 (td, *J* = 7.6, 1.2 Hz, 1H), 6.68 (dd, *J* = 7.8, 0.8 Hz, 1H), 6.54 (s, 1H), 4.04 (s, 1H), 3.24 (d, *J* = 10.8, 1H), 2.42–2.27 (m, 1H), 2.07–1.97 (m, 1H), 1.97–1.88 (m, 1H), 1.82 –1.68 (m, 3H), 1.22–1.02 (m, 1H), 0.98 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.51, 142.69, 140.03, 134.19, 131.55, 129.44, 128.39, 128.21, 127.15, 126.84, 122.43, 120.78, 120.53, 117.86, 53.28, 52.35, 47.10, 34.89, 28.34, 26.44, 21.72; HRMS (ESI) calcd for $C_{22}H_{23}N_2$ $[M+H]^+$: 315.1854; found: 315.1856.

3-Methyl-11-phenyl-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3ac). Following the general procedure on a 1.0 mmol scale for 6h giving the compound as an yellow solid (229 mg, yield 73%); Mp 150-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2H), 7.38–7.33 (m, 2H), 7.32–7.26 (m, 1H), 7.18 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.09 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H), 6.86 (td, *J* = 7.6, 1.2 Hz, 1H), 6.68 (dd, *J* = 7.8, 0.8 Hz, 1H), 6.54 (s, 1H), 4.04 (s, 1H), 3.20–3.09 (m, 1H), 2.42–2.27 (m, 1H), 2.07–1.97 (m, 1H), 1.97–1.88 (m, 1H), 1.82–1.68 (m, 3H), 1.22–1.02 (m, 1H), 0.98 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.51, 142.69, 140.03, 134.19, 129.44, 128.39, 128.21, 127.15, 126.84, 122.43, 120.78, 120.53, 117.86, 53.28, 52.35, 47.10, 34.89, 28.34, 26.44, 21.72; HRMS (ESI) calcd for $C_{22}H_{23}N_2$ $[M+H]^+$: 315.1850; found: 315.1856.

3-(*Tert*-butyl)-11-phenyl-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3ad). Following the general procedure on a 1.0 mmol scale for 6h giving the compound as an brown solid (267 mg, yield 75%); Mp 196-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.41 (m, 2H), 7.39–7.33 (m, 2H), 7.29 (ddd, *J* = 7.1, 3.7, 1.3 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.10(td, *J* = 8.0, 1.2 Hz, 1H), 6.87 (td, *J* = 7.6, 1.0 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.58 (s, 1H), 4.01 (s, 1H), 3.23 (d, *J* = 11.1 Hz, 1H), 2.44 (dt, *J* = 14.3, 3.4 Hz, 1H), 2.26 (td, *J* = 13.8, 4.2 Hz, 1H), 1.84–1.71 (m, 2H), 1.63–1.44 (m, 2H), 1.26 (tt, *J* = 12.2, 3.4 Hz, 1H), 0.80 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.27, 142.60, 140.13, 134.20, 129.54, 128.40, 128.22, 127.12, 126.65, 122.26, 121.02, 120.42, 117.88, 52.67, 52.36, 48.10, 39.37, 32.41, 29.31, 27.31, 21.08 ; HRMS (ESI) calcd for $C_{21}H_{21}N_2$ $[M+H]^+$: 301.1695; found: 301.1699; HRMS (ESI) calcd for $C_{25}H_{29}N_2$ $[M+H]^+$: 357.2322; found: 357.2325.

2-(*Tert*-butyl)-8-chloro-11-phenyl-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3dd). Following the general procedure on a 1.0 mmol scale for 5h giving the compound as an brown solid (261 mg, yield 67%); Mp 216-217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.25 (m, 5H), 7.16 (d, *J* = 2.0 Hz 1H), 7.03 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.45 (s, 1H), 3.97 (s, 1H), 3.20 (d, *J* = 11.2 Hz, 1H), 2.42 (d, *J* = 14.4 Hz, 1H), 2.25 (td, *J* = 14.0, 4.0 Hz 1H), 1.77 (d, *J* = 13.6 Hz, 2H), 1.51–1.43 (m, 1H), 1.27–1.21 (m, 1H), 0.87 (t, *J* = 6.8 Hz, 1H), 0.83 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.93, 141.98, 141.24, 133.25, 128.61, 128.34, 128.01, 127.57, 126.74, 125.28, 123.84, 120.81, 119.32, 52.73, 52.46, 48.14, 39.36, 32.54, 29.45, 27.40, 21.14; HRMS (ESI) calcd for $C_{25}H_{28}ClN_2$ $[M+H]^+$: 391.1933; found: 391.1935.

2-(T*ert*-butyl)-8-fluoro-11-phenyl-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3ed). Following the general procedure on a 1.0 mmol scale for 6h giving the compound as an off white solid (291 mg, yield 78%); Mp 240-241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.34 (m, 4H), 7.32–7.28 (m, , 1H), 6.90 (dd, *J* = 9.8, 2.9 Hz, 1H), 6.83 (ddd, *J* = 8.7, 7.6, 2.9 Hz, 1H), 6.63 (dd, *J* = 8.7, 4.8 Hz, 1H), 6.45 (s, 1H), 3.89 (s, 1H), 3.21 (dd, *J* = 9.2, 2.0 Hz, 1H), 2.43 (dt, *J* = 14.0, 3.5 Hz, 1H), 2.28 (td, *J* = 13.9, 4.2 Hz, 1H), 1.77 (dd, *J* = 8.3, 5.3 Hz, 2H), 1.56–1.37 (m, 2H), 1.24 (tt, *J* = 12.2, 3.5 Hz, 1H), 0.80 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.18 (d, J_F = 238.6 Hz), 142.96 (d, J_F = 189.2 Hz), 138.93, 128.48, 128.38, 127.44, 126.68, 123.67, 120.83, 119.24 (d, J_F = 22.45 Hz), 119.00 (d, J_F = 8.0 Hz), 115.13 (d, J_F = 22.95 Hz), 52.68, 52.37, 48.01, 39.24, 32.43, 29.46, 27.30, 21.07; HRMS (ESI) calcd for $C_{25}H_{28}FN_2$ $[M+H]^+$: 375.2233; found: 375.2231.

2-(*Tert*-butyl)-11-phenyl-8-(trifluoromethyl)-1,2,3,4,5,11*a*-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile (3fd). Following the general procedure on a 1.0 mmol scale for 3h giving the compound as an off white solid (301 mg, yield 50%); Mp 219-220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 1.6 Hz, 1H), 7.43–7.39 (m, 2H), 7.40–7.35 (m, 2H), 7.34– 7.28 (m, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.58 (s, 1H), 4.31 (s, 1H), 3.31–3.20 (dt, *J* = 9.2, 1.6 Hz, 1H) 2.45 (dt, *J* = 6.7, 3.6 Hz, 1H), 2.25 (td, *J* = 13.9, 4.2 Hz, 1H), 1.80 (ddd, *J* = 12.5, 5.7, 2.0 Hz, 2H), 1.56–1.38 (m, 2H), 1.32–1.24 (m, 1H), 0.81 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.00, 143.63, 141.93, 131.30 (q, J_F = 3.9 Hz) 128.54, 128.46, 127.56, 126.57, 125.67, 124.79 (q, J_F = 3.9 Hz), 122.97, 122.35, 121.73, 120.53, 118.03, 52.64, 52.37, 48.04, 39.20, 32.43, 29.25, 27.28, 20.98; HRMS (ESI) calcd for $C_{26}H_{27}F_3N_2$ $[M+Na]^+$: 447.2017; found: 447.2018.

1-(Cyclohex-1-en-1-yl)-2-phenyl-1*H*-indole (4aa). Following the general procedure on a 1.0 mmol scale for 3h giving the compound as a brown solid; Mp 109-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.57 (m, 3H), 7.43–7.34 (m, 3H), 7.34–7.27 (m, 1H), 7.17 (ddd, *J* = 8.2, 7.1, 1.3 Hz, 1H), 7.10 (td, *J* = 8.0, 1.2 Hz, 1H), 6.66 (s, 1H), 6.08–5.99 (m, 1H), 2.29 (s, 2H), 1.94 (s, 2H), 1.66 (t, *J* = 2.8 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.70, 138.26, 135.80, 133.43, 128.27, 128.06, 127.92, 127.68, 127.44, 121.74, 120.29, 120.08, 110.58, 102.45, 29.24, 24.90, 22.79, 21.76. HRMS (ESI) calcd for $C_{20}H_{20}N$ $[M+H]^+$: 274.1587; found: 274.1590.

((*E*)-2-(spiro[Cyclohexane-1,2'-indolin]-3'-ylidene)-2-(thiophen-2-yl)acetonitrile (4ra). Following the general procedure on a 1.0 mmol scale for 3h giving the compound as a yellow solid (113 mg, yield 37%); Mp 194-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 5.2, 1.3 Hz, 1H), 7.16 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.11 (dd, *J* = 5.1, 3.5 Hz, 1H), 7.07 (dd, *J* = 3.5, 1.3 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 6.42 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 6.33 (dd, *J* = 8.0, 0.8 Hz, 1H), 4.90 (s, 1H), 2.57 (td, *J* = 12.6, 4.4 Hz, 2H), 1.92 (d, *J* = 7.7 Hz, 2H), 1.80 (s, 1H), 1.71 (d, *J* = 11.9 Hz, 2H), 1.51 (t, *J* = 9.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.72, 136.06, 133.83, 128.28, 127.89, 127.69, 126.92, 122.87, 119.21, 118.36, 110.75, 68.02, 33.99, 24.26, 23.08; HRMS (ESI) calcd for $C_{19}H_{19}N_2S$ $[M+H]^+$: 307.1264; found: 307.1263

1-(2-Cyclopropyl-5-methyl-1*H*-indol-1-yl)cyclohexane-1-carbonitrile (4sa). Following the general procedure on a 1.0 mmol scale for 8h giving the compound as an light pink solid (200 mg, yield 72%); Mp 123-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.6 Hz, 1H), 7.27 (s, 1H), 7.00 (dd, *J* = 8.6, 1.5 Hz, 1H), 6.19 (t, *J* = 1.0 Hz, 1H) 2.84 (dd, *J* = 13.1, 1.5 Hz, 2H), 2.49–2.38 (m, 5H), 2.11–2.03 (m, 1H), 2.01–1.95 (m, 3H), 1.95–1.83 (m, 2H), 1.39 –1.25 (m, 1H), 1.05–0.99 (m, 2H), 0.89–0.82 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.73, 134.84, 129.41, 128.58, 123.02, 120.15, 119.09, 112.37, 103.49, 60.73, 36.48, 24.62, 23.69, 21.04, 12.19, 9.53; HRMS (ESI) calcd for $C_{19}H_{22}N_2Na$ $[M+Na]^+$: 301.1677; found: 301.1675.

10-Phenyl-5*H*-dibenzo[*b,f*]azepine (5aa). In an oven dried 15 ml seal tube 11-phenyl-1,2,3,4,5,11a-hex*ahydro*-4*aH*-dibenzo[*b,f*]azepine-4*a*-carbonitrile **4aa** (269 mg, 1.0 mmol) was added in 1 ml of DMSO followed by addition of 2 equiv TFA and 2 equiv 70% aq TBHP. The reaction mixture was allowed to stir at 110 °C for 8h under O_2 atmosphere. After the reaction completion, the reaction

mixture was cooled to room temperature and diluted with 25.0 mL of 10% aqueous $NaHCO_3$ solution. The water layer was extracted with (3X25 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from hexane to 3-6% ethyl acetate/hexane to afford pure 10-phenyl-5*H*-dibenzo[*b*,*f*]azepine (**5aa**) as a pale yellow solid (174 mg, yield 65%); Mp 123-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 2H), 7.80–7.75 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.62–7.58 (m, 3H), 7.46–7.43 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.90, 147.28, 136.06, 135.64, 130.52, 130.01, 129.69, 128.73,128.52, 128.42, 127.99, 126.93, 125.66, 125.23; HRMS (ESI) calcd for $C_{20}H_{16}N$ $[M+H]^+$: 270.1279; found: 270.1277.

1-(phenylamino)cyclohexane-1-carbonitrile. In an oven dried 15 ml seal tube aniline (93 mg, 1.0 mmol) was added in 1 ml of DMSO followed by the addition of $Cu(OAc)_2$ (181 mg, 1.0 mmol), TMSCN (251 µL, 2.0 mmol) and cyclohexanone **2a** (156 µL, 1.5 mmol). The reaction mixture was allowed to stir at 110 °C for 3h. After the reaction completion, the reaction mixture was cooled to room temperature and diluted with 25.0 mL of cooled water. The water layer was extracted with (3X25 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from hexane to 8-10% ethyl acetate/hexane to afford pure 1-(phenylamino)cyclohexane-1-carbonitrile as pale yellow solid (166 mg, yield 83%); Mp 71-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.21 (m, 2H), 6.94–6.87 (m, 3H), 2.35–2.31 (m, 2H), 1.84–1.76 (m, 2H), 1.73–1.62 (m, 5H), 1.39–1.25 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.48, 129.19, 121.10, 120.56, 117.56, 54.36, 36.62, 24.86, 22.17.[17]

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FULL PAPER

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