Convenient Access to C10- and C11-(di)arylated dibenzo[b , f]azepines via Palladium-catalyzed C–H Bonds Cleavages

Haoran Li, Thierry Roisnel, Jean-François Soulé, Henri Doucet

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Convenient access to C10- and C11-(di)arylated dibenzo[*b,f*]azepines *via* palladium-catalyzed C-H bonds cleavages

Haoran Li,[a] Thierry Roisnel,[a] Jean-François Soulé,[a]* and Henri Doucet[a]*

[a] Univ Rennes, CNRS, ISCR-UMR 6226, F-35000 Rennes, France.
Tel: +(33) 0223236384, E-mail: jean-francois.soule@univ-rennes1.fr; henri.doucet@univ-rennes1.fr

Received:

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.

Abstract. Conditions allowing the C10- and C11-arylations of dibenzo[*b,f*]azepines *via* successive palladium-catalyzed reactions are reported. Using aryl bromides as the aryl source, the C10-arylation of dibenzo[*b,f*]azepines is very selective. Then, using benzenesulfonyl chlorides as the aryl source, the second arylation at C11-position is achieved affording non-symmetrical C10,C11-diarylated dibenzo[*b,f*]azepines. Both reactions tolerate a variety of substituents on the aryl source.

Keywords: Palladium; Arylation; Azepines; C-C bond formation; C-H bond cleavage

Introduction

Azepine derivatives, and among them 5H-dibenzo[*b,f*]azepines represent an important class of compounds in pharmaceutical and organometallic chemistry.[1] Carbamazepine is employed in the treatment of epilepsy and neuropathic pain and is on the World Health Organization's list of essential medicines; whereas, Opipramol is an anxiolytic and antidepressant drug (Figure 1). Moreover, the phosphoramidite derivative **L** (Figure 1) exhibits important properties as ligand in enantioselective catalysis.[2] Consequently, the development of fast and reliable methods for the preparation of substituted dibenzo[*b,f*]azepines represent an important research topic.

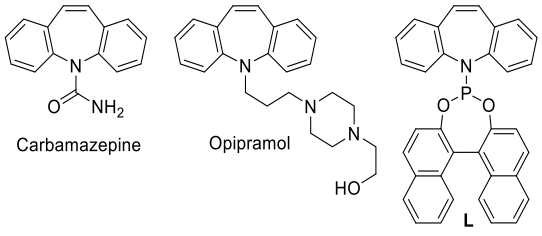
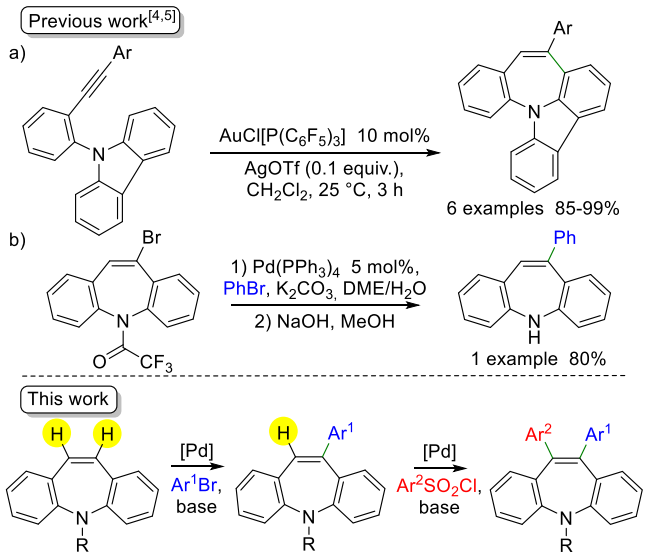


Figure 1. Dibenzo[*b,f*]azepines as units in drugs and ligands.

Dibenzo[*b,f*]azepine is a commercially available compound at an affordable price, which can be prepared by simple heating of 1-phenylindole at 100 °C.[3] Conversely, the preparation of dibenzo[*b,f*]azepines bearing (hetero)aryl-substituents at C10-position is very challenging. They can be prepared *via* Au(I)-catalyzed cycloisomerization reaction, but the preparation of the starting materials requires several steps (Scheme 1, a).[4] A single example of Suzuki coupling using a 10-bromodibenzo[b,f]azepine, prepared in two steps from a dibenzo[*b,f*]azepine has also been reported (Scheme 1, b).[5] Moreover, the access to dibenzo[*b,f*]azepines containing a boron-substituent at C10-position has not yet been reported. Therefore, the arylation of the C-H bonds at C10- and C11-positions of dibenzo[*b,f*]azepines, would represent a very attractive pathway to prepare such (di)arylated dibenzo[*b,f*]azepines.

Since two decades, the Pd-catalyzed arylation of aromatic compounds[6] and of linear alkenes,[7] has emerged as very effective and versatile tool for the simpler access to a wide variety of arylated compounds. Conversely, the Pd-catalyzed arylation of cyclic alkenes has attracted less attention. With cyclic alkenes, the classical Heck type β-H elimination step is not possible as the hydrogen which should be involved in the β-hydride elimination process, is *anti* with respect to the Pd-C bond.[7] With these substrates, a *syn* β'-hydride elimination has been observed in some cases.[8] However, to our knowledge, the arylation of dibenzo[*b,f*]azepines *via* a C-H bond cleavage and the synthesis of C10,C11-diarylated dibenzo[*b,f*]azepines has not been reported yet. Therefore, the discovery of effective procedures allowing the access, *via* C-H bond cleavages, to C10/C11-diarylated dibenzo[*b,f*]azepines using easily available catalysts and aryl sources tolerant to a wide range of functional groups is still needed.



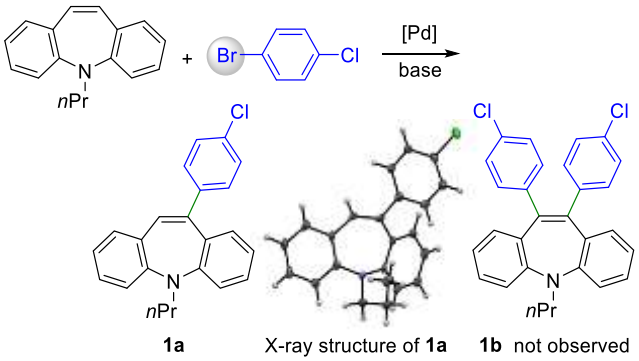
Scheme 1. Access to C10- and C11-arylated azepines.

Herein, we report i) on the influence of the reaction conditions in the Pd-catalyzed arylation at C10-position of dibenzo[b,f]azepines, ii) on the substrate scope of this reaction, and iii) on the programmed synthesis of C10,C11-diarylated dibenzo[b,f]azepines *via* sequential Pd-catalyzed C-H bond cleavages (Scheme 1, bottom).

Results and Discussion

We initially examined the influence of the nature of the base for the arylation of 5-propyldibenzo[*b*,*f*]azepine, based on conditions that we had previously employed for the direct arylation of (hetero)aromatics.[9] The use of 2 mol% $PdCl(C_3H_5)(dppb)$ as catalyst[10] [dppb: 1,4-bis(diphenylphosphino)butane], KOAc as base in DMA with 1.2 equiv. of 5-propyldibenzo[*b*,*f*]azepine and 1 equiv. of 4-bromochlorobenzene as the aryl source resulted in the selective formation of the mono-arylation product **1a** in moderate yield (Table 1, entry 1). The structure of **1a** was confirmed by X-ray analysis. The use of CsOAc, NaOAc, or carbonates as bases did not allow to improve the yield in **1a** (Table 1, entries 2-7). On the other hand, the use of 1 equiv. of 5-propyldibenzo[*b*,*f*]azepine and 1.5 equiv. of 4-bromochlorobenzene provided **1a** in 81% yield (70% isolated) without formation of the diarylated 5-propyldibenzo[*b*,*f*]azepine **1b** according to the GC/MS analysis of the crude mixture. Reactions performed in 1,4-dioxane or xylene gave the coupling product **1a** in very low yields; whereas the polar solvents DMF and NMP afforded **1a** in 50% and 74% yields, respectively (Table 1, entries 11-14). A lower catalyst loading of 0.5 mol% or the use of Pd(OAc) and $PdCl_2(MeCN)_2$ as catalysts also afforded **1a** in lower yields (Table 1, entry 15-17).

Table 1. Influence of the reaction conditions for Pd-catalyzed direct arylation of 5-propyldibenzo[*b*,*f*]azepine with 4-bromochlorobenzene.



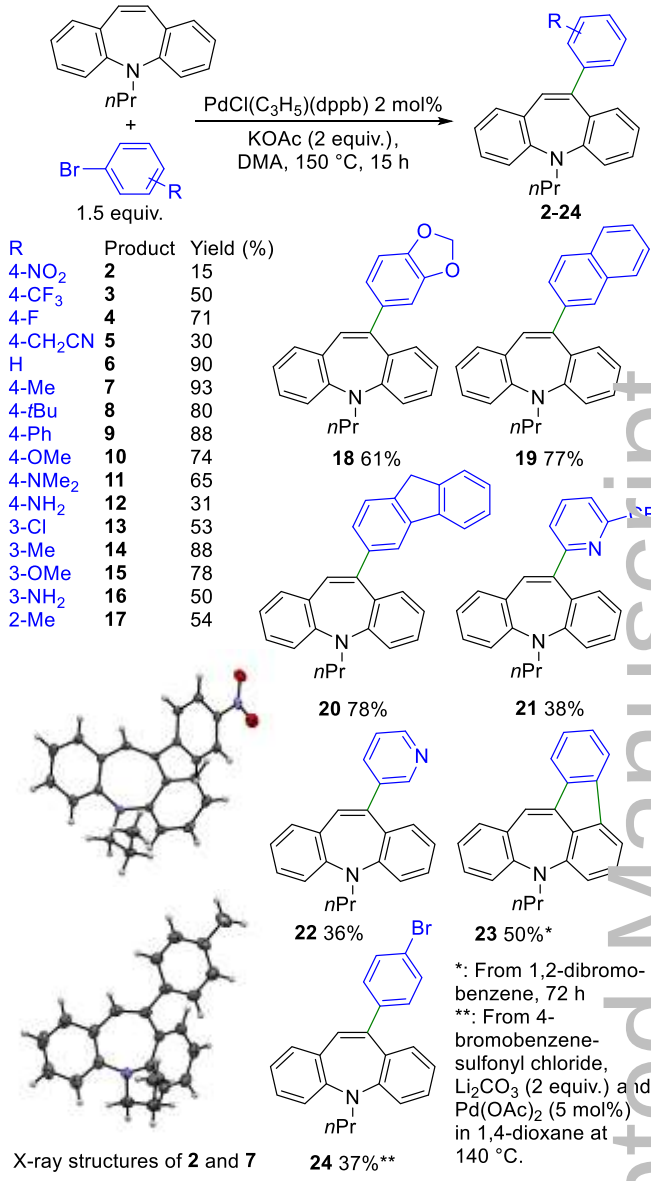
entry	catalyst (mol %)	base	solvent	yield in **1a** (%)
1	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	DMA	56
2	$PdCl(C_3H_5)(dppb)$ (2)	CsOAc	DMA	17
3	$PdCl(C_3H_5)(dppb)$ (2)	NaOAc	DMA	37
4	$PdCl(C_3H_5)(dppb)$ (2)	Li_2CO_3	DMA	5
5	$PdCl(C_3H_5)(dppb)$ (2)	Na_2CO_3	DMA	13
6	$PdCl(C_3H_5)(dppb)$ (2)	K_2CO_3	DMA	44
7	$PdCl(C_3H_5)(dppb)$ (2)	Cs_2CO_3	DMA	2
8	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	DMA	81[a] (70)
9	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	DMA	66[b]
10	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	DMA	72[c]
11	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	1,4-dioxane	15[a,d]
12	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	DMF	50[a]
13	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	NMP	74[a]
14	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	xylene	<5[a]
15	$PdCl(C_3H_5)(dppb)$ (0.5)	KOAc	DMA	31[a]
16	$PdCl_2(MeCN)_2$ (5)	KOAc	DMA	68[a]
17	$Pd(OAc)_2$ (5)	KOAc	DMA	32[a]
18	$PdCl(C_3H_5)(dppb)$ (2)	KOAc	DMA	82[a,e]

Conditions: 5-propyldibenzo[*b*,*f*]azepine (1.2 mmol), 4-bromochlorobenzene (1 mmol), base (2 mmol), argon, 15 h, 150 °C, GC and NMR yields, yield in parenthesis is isolated. [a] 5-propyldibenzo[*b*,*f*]azepine (1 mmol), 4-bromochlorobenzene (1.5 mmol). [b] 5-propyldibenzo[*b*,*f*]azepine (1 mmol), 4-bromochlorobenzene (1.2 mmol). [c] 5-propyldibenzo[*b*,*f*]azepine (1 mmol), 4-bromochlorobenzene (2 mmol). [d] 110 °C. [e] 48 h.

Next, the scope of the C10-arylation of 5-propyldibenzo[*b*,*f*]azepine using 2 mol% $PdCl(C_3H_5)(dppb)$ catalyst, KOAc base in DMA with

various aryl bromides was investigated (Scheme 2). With 4-bromonitrobenzene, a low yield in **2** was obtained due to the formation of several unidentified degradation products. Moderate yields in **3** and **4** were obtained using 4-trifluoromethyl- and 4-fluoro-substituted aryl bromides, and a cyanomethyl substituent on the aryl bromide afforded **5** in only 30% yield. Conversely, from bromobenzene, 4-bromotoluene, 4-*tert*-butylbromobenzene, 4-bromobiphenyl and 4-bromoanisole, the target products **6**-**10** were obtained in 74-93% yields. The lower yields obtained with electron-poor aryl bromides are consistent with the previous report of Hallberg et al. on the arylation of disubstituted alkenes *via* Heck reaction.[11] The structures of product **2** and **7** were confirmed by X-ray analysis. From the electron-rich 4-bromo-*N*,*N*-dimethylaniline, the expected product **11** was isolated in 65% yield. The direct use of unprotected anilines would be useful in organic synthesis as it allows to avoid the protection/deprotection sequence. The reaction of 4-bromoaniline with 5-propyldibenzo[b,f]azepine afforded the desired C10-arylated dibenzo[*b*,*f*]azepine **12** in a moderate yield. However, it should be mentioned that under these reaction conditions, no significant amount of the product arising from Buchwald-Hartwig amination reaction was detected. Then, we examined the reactivity of a few *meta*-substituted aryl bromides. Moderate to high yields in **13**-**16** were obtained from chloro-, methyl-, methoxy- and amino-substituted aryl bromides. The use of more congested 2-bromotoluene provided the desired product **17** in 54% yield. Polyaromatics such as fluorenes continue to attract the attention of synthetic organic chemists, owing to their inherent physical properties. The reaction of 2-bromonaphthalene and 2-bromofluorene with 5-propyldibenzo[*b*,*f*]azepine, under the same reaction conditions, afforded the target products **19** and **20** in 77% and 78% yields, respectively. Pyridines are important motifs embedded in many pharmaceutical compounds and functional materials. Therefore, the coupling of 2-bromo-6-(trifluoromethyl)pyridine and 3-bromopyridine with 5-propyldibenzo[b,f]azepine was also studied. The desired compounds **21** and **22** were obtained in 38% and 36% yield, respectively. Furthermore, using 1,2-dibromobenzene as the aryl source, the formation of the pentacyclic compound **23** was obtained *via* two successive C-H bonds cleavages.

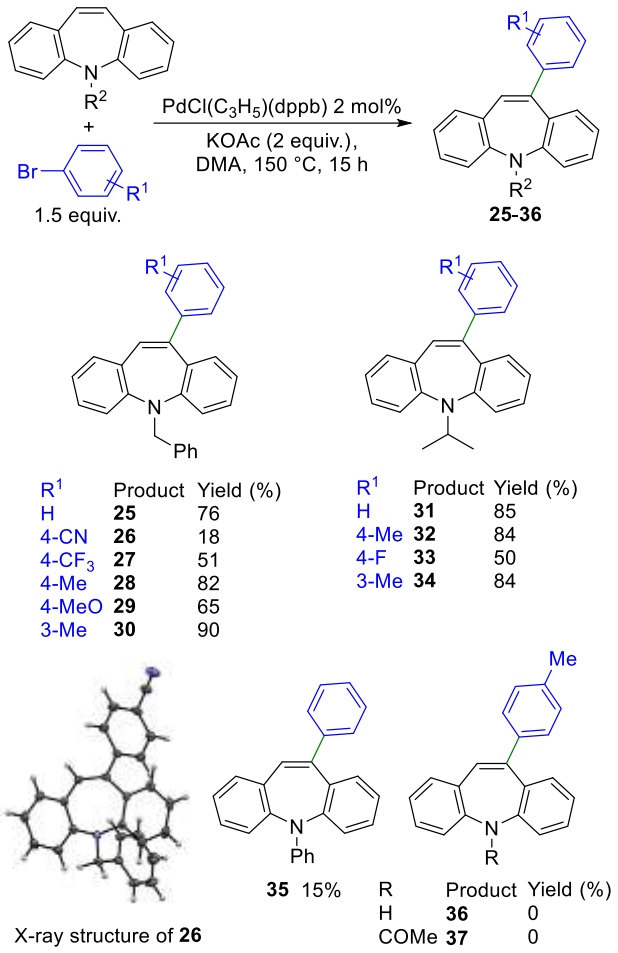
We have recently reported that the Pd-catalyzed direct arylation using $ArSO_2Cl$ as aryl source[12-15] is attractive in some cases, as the reaction likely proceed *via* a different mechanism[16] than with aryl halides and tolerates C-halo bonds. Based on our previous results on Pd-catalyzed desulfitative coupling with $ArSO_2Cl$,[16] the reaction of 5-propyldibenzo[*b*,*f*]azepine with 4-bromobenzenesulfonyl chloride was studied. In the presence of 5 mol% $Pd(OAc)_2$ catalyst and Li_2CO_3 base at 140 °C, the target product **24** was obtained in only 37% yield, but without cleavage of the C-Br bond, allowing further transformations.



Scheme 2. Palladium-catalyzed direct C10-arylation of 5-propyldibenzo[*b*,*f*]azepine with ArBr.

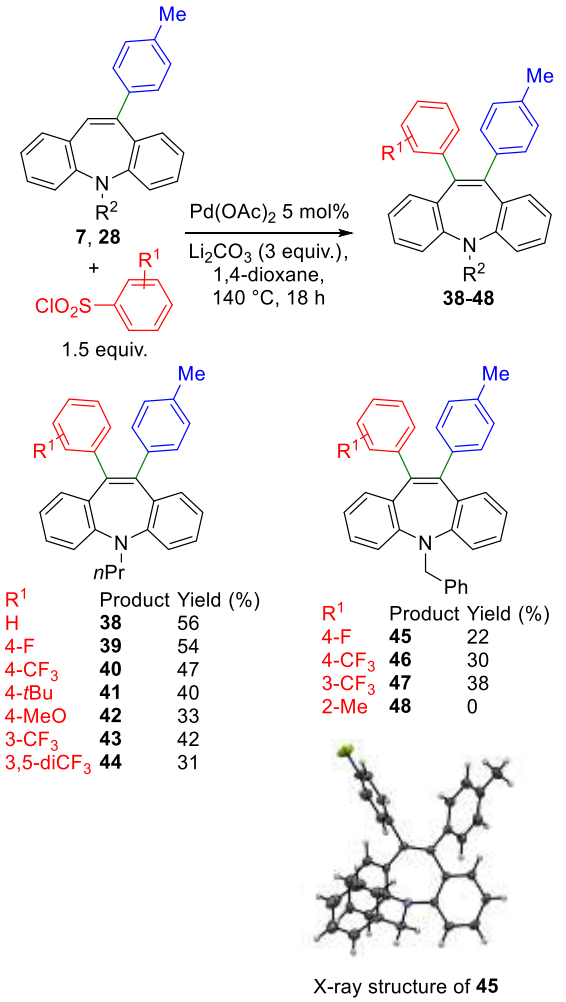
The influence of 5-substituents of dibenzo[*b*,*f*]azepine was also investigated (Scheme 3). Under the same reaction conditions as for C10-arylation of 5-propyldibenzo[*b*,*f*]azepine with aryl bromides, but using a benzyl substituent instead of a propyl substituent, we obtained the desired arylated benzo[*b*,*f*]azepines **25**-**30** in 51-90% yields. The benzyl substituent was stable under these reaction conditions. The structure of **26** was confirmed by X-ray analysis. An isopropyl substituent at 5-position of dibenzo[*b*,*f*]azepine was also tolerated affording the products **31**-**34** in 50-85% yields. Conversely, from 5-phenyldibenzo[*b*,*f*]azepine, product **35** was obtained in only 15% yield, and with dibenzo[*b*,*f*]azepine, and 1-(5H-dibenzo[*b*,*f*]azepin-5-yl)ethan-1-one, no formation of the coupling products **36** and **37** was observed, and the starting materials

were recovered. The result obtained with dibenzo[*b*,*f*]azepine, might be due to the poisoning of the catalyst arising from a deprotonation of the nitrogen atom; whereas, the non-reactivity of 1-(5H-dibenzo[*b*,*f*]azepin-5-yl)ethan-1-one is likely due to electronic factors.



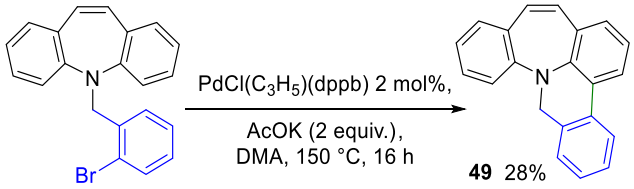
Scheme 3. Palladium-catalyzed direct C10-arylation of dibenzo[*b*,*f*]azepines bearing various substituents at position 5 with ArBr.

As described in table 1 and scheme 2, the formation of C10,C11-diarylated aryldibenzo[*b*,*f*]azepines was never observed, even in the presence of 2 equiv. of the aryl bromide (Table 1, entry 10). Based on our previous results on the arylation of fulvenes and acenaphthylenes,[17] a higher reactivity of $ArSO_2Cl$ *vs* aryl halides for the Pd-catalyzed C11-arylation of 10-aryldibenzo[*b*,*f*]azepines was expected. Moreover, the use of $ArSO_2Cl$ as aryl source for access to such diarylated azepines is attractive as many of them are easily available at an affordable cost and as they are easy to handle. Indeed, the reaction of 5-propyl-10-(*p*-tolyl)dibenzo[*b*,*f*]azepine **7** with $PhSO_2Cl$ in the presence of 5 mol% $Pd(OAc)_2$ catalyst and Li_2CO_3 base at 140 °C afforded the target product **38** in 56% yield (Scheme 4). The reaction tolerated both electron-withdrawing and -donating groups on the benzenesulfonyl chloride such as fluoro, trifluoromethyl, *tert*-butyl and methoxy, affording the non-symmetrical 10,11-diaryldibenzo[*b*,*f*]azepines **39**-**47** in moderate yields; whereas, more congested *o*-toluenesulfonyl chloride was unreactive. The structure of product **45** was unambiguously assigned by X-ray analysis. It should be mentioned that the reaction of 5-propyldibenzo[*b*,*f*]azepine with 3 equiv. of benzenesulfonyl chlorides bearing *para*-chloro or -trifluoromethyl substituents, under the same conditions, afforded the mono-arylated products **1a** and **3** in quite low yields with unidentified side-products; whereas, no formation of di-arylated dibenzo[*b*,*f*]azepines was detected by GC/MS analysis of the crude mixtures.



Scheme 4. Palladium-catalyzed direct C11-arylation of 10-aryl dibenzo[*b*,*f*]azepines with $ArSO_2Cl$.

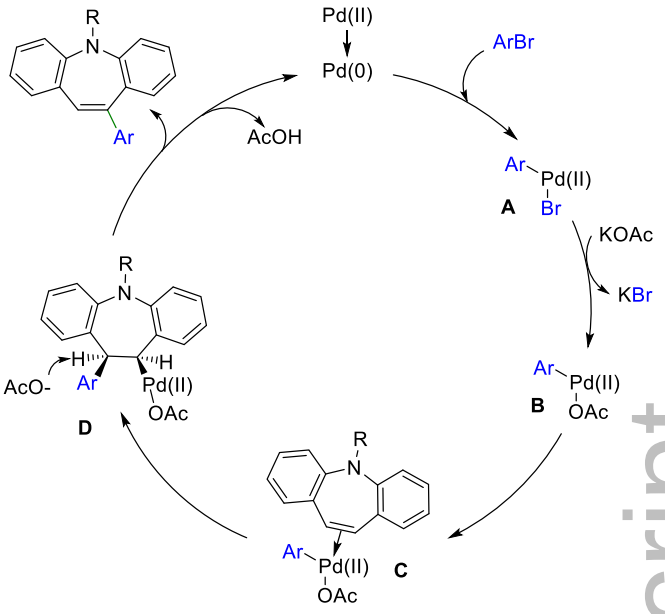
Finally, from a dibenzo[*b*,*f*]azepine bearing a 2-bromobenzyl moiety at 5-position, the formation of the pentacyclic compound **49** was obtained in moderate yield using $PdCl(C_3H_5)(dppb)$ catalyst associated to KOAc base *via* intramolecular C-H bond arylation (Scheme 5).



Scheme 5. Intramolecular palladium-catalyzed direct arylation for access to a benzoazepinophenanthridine.

Although the mechanism of the C10-arylation of dibenzo[*b*,*f*]azepines is not yet elucidated, on the basis of the previous reports,[7] a catalytic cycle can be proposed (Scheme 6). The first step is probably the oxidative addition of ArBr to a Pd(0) species to afford the Pd(II) intermediate **A**. In 2004, de Vries et al. demonstrated that, at elevated temperature, when ligand-free $Pd(OAc)_2$ is employed as catalyst precursor in a polar solvent such as NMP in the presence of a base, soluble palladium(0) colloids or nanoparticles, which are very efficient to promote Suzuki reaction, are formed.[18] Then, **A** affords **B** due to the presence a large amount of AcOK in the reaction mixture. Coordination of the C=C bond of the dibenzo[*b*,*f*]azepine derivative gives **C**; then, insertion of the C=C bond into the Ar-Pd bond affords **D**. An external base such as AcO^- might promote the C-H bond cleavage and releases the C10-arylated dibenzo[*b*,*f*]azepine with regeneration of Pd(0).

Although the mechanism for C11-arylation was not elucidated, the higher reactivity of $ArSO_2Cl$ as aryl sources for such arylations is likely due to a Pd(II)/Pd(IV) mechanism instead of a Pd(0)/Pd(II) mechanism.[15,16] The first step of the catalytic cycle would be the oxidative addition of $ArSO_2Cl$ to Pd(II) affording a Pd(IV) intermediate. Such oxidative addition of $ArSO_2Cl$ on Pd(II) have been reported to proceed at room temperature.[15b] After elimination of SO_2, and coordination of the $C^{10}=C^{11}$ bond of the dibenzo[*b*,*f*]azepine derivative to palladium, an insertion of this double bond into the Ar-Pd bond occurs. Finally, reductive elimination affords the arylated product with regeneration of a Pd(II) species assisted by the base.



Scheme 6. Proposed mechanism for C10-arylation.

Conclusion

In summary, we have demonstrated that the Pd-catalyzed C-H bond arylation at C10-position of dibenzo[*b*,*f*]azepines can be performed using aryl bromides as aryl source in the presence of 2 mol% of a Pd-catalyst. Moreover, we report here the unprecedented access to 10,11-diaryldibenzo[*b*,*f*]azepines. Using $ArSO_2Cl$ as the aryl source instead of aryl bromides, the arylation at C11-position of 10-aryldibenzo[*b*,*f*]azepines proceeded in moderate to good yields giving rise to the non-symmetrical 10,11-diaryldibenzo[*b*,*f*]azepines. The functional group tolerance of both reactions allows the easy tuning of the properties of these dibenzo[*b*,*f*]azepines which might find applications in medicinal chemistry or as new ligands.

Experimental Section

General. All reactions were performed in Schlenk tubes under argon. DMA and DMF analytical grade were not distilled before use. Potassium acetate 99+ was used. Commercial 5H-dibenzo[*b*,*f*]azepine (iminostilbene) (97%) aryl bromides and benzenesulfonyl chlorides were used without purification. ^1H (400 MHz), ^{13}C (100 MHz) spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (^1H: 7.26 and ^{13}C: 77.16). Flash chromatography was performed on silica gel (230-400 mesh). 5-Propyldibenzo[*b*,*f*]azepine and 5-benzyldibenzo[*b*,*f*]azepine were prepared from dibenzo[*b*,*f*]azepine using a reported procedure.[19]

CCDC-1865812, 1865813, 1865815, 1865816, 1865817 and 1865818 contains the supplementary crystallographic data for this paper: compounds **26**, **2**, **45**, **7**, **6**, and **1a**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedure for the synthesis of 5-isopropyldibenzo[*b,f*]azepine and 5-(2-bromobenzyl)dibenzo[*b,f*]azepine: A Schlenk tube equipped with a magnetic stirring bar was charged with dibenzo[*b,f*]azepine (0.386 g, 2 mmol), NaH (reaction with 1-iodopropane) or K_2CO_3 (reaction with 2-bromobenzyl bromide) (3 mmol) and *N*,*N*-dimethylformamide (8 mL). The resulting mixture was cooled in an ice bath for 2 h, then 1-iodopropane or 2-bromobenzyl bromide were added and the mixture was warmed up to room temperature (reaction with 1-iodopropane) or 90°C (reaction with 2-bromobenzyl bromide) for 16 hours. The azepine derivatives were obtained after evaporation of the solvent and purification on silica gel (heptane:CH_2Cl_2 75:25).

5-Isopropyldibenzo[*b,f*]azepine: From 1-iodopropane (0.510 g, 3 mmol), dibenzo[*b,f*]azepine (0.386 g, 2 mmol) and NaH (0.072 g, 3 mmol) at 25 °C, 5-isopropyldibenzo[*b,f*]azepine was obtained in 72% (0.338 g) yield as a green solid: mp 39-41 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.29 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 4H), 7.12 (t, *J* = 7.8 Hz, 2H), 6.89 (s, 2H), 3.97 (sept., *J* = 6.0 Hz, 1H), 1.02 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 135.8, 131.2, 129.1, 128.7, 127.6, 124.6, 48.6, 23.1. Elemental analysis: calcd (%) for $C_{17}H_{17}N$ (235.33): C 86.77, H 7.28; found: C 86.90, H 7.35.

5-(2-Bromobenzyl)dibenzo[*b,f*]azepine: From 2-bromobenzyl bromide (0.624 g, 2.5 mmol), dibenzo[*b,f*]azepine (0.392 g, 2 mmol) and K_2CO_3 (0.417 g, 3 mmol) at 90 °C, 5-(2-bromobenzyl)dibenzo[*b,f*]azepine was obtained in 52% (0.376 g) yield as a green solid: mp 169-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.23-7.15 (m, 5H), 7.10-7.02 (m, 3H), 6.93 (s, 2H), 5.18 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 136.8, 133.9, 132.5, 132.4, 130.1, 129.3, 129.0, 128.3, 127.4, 123.7, 123.6, 120.6, 54.3. Elemental analysis: calcd (%) for $C_{21}H_{16}BrN$ (362.27): C 69.63, H 4.45 found: C 69.50, H 4.65.

Preparation of the PdCl(C_3H_5)(dppb) catalyst:[10] An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane were added, then, the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. ^{31}P NMR (81 MHz, $CDCl_3$) δ = 19.3 (s).

General procedure for the synthesis of 1-23 and 25-36: As a typical experiment, the reaction of the aryl bromide (1.5 mmol), dibenzo[*b,f*]azepine derivative (1 mmol), KOAc (0.196 g, 2 mmol) at 150 °C during 15 h in DMA (5 mL) in the presence of PdCl(C_3H_5)(dppb) (12.2 mg, 0.02 mmol) under argon afford the corresponding arylation product after evaporation of the solvent and purification on silica gel. Solvent heptane:CH_2Cl_2 85:15 for **1-17**; heptane:CH_2Cl_2 95:5 for **18-23** and **25-36**.

General procedure for the synthesis of 24 and 37-46: As a typical experiment, the reaction of the benzenesulfonyl chloride (1.5 mmol), dibenzo[*b,f*]azepine derivative (1 mmol), Li_2CO_3 (0.222, 3 mmol) at 140 °C during 15 h in 1,4-dioxane (5 mL) in the presence of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) under argon, afford the corresponding arylation product after evaporation of the solvent and purification on silica gel. Solvent heptane:CH_2Cl_2 85:15 for **24**; heptane:ethyl acetate 95:5 for **37-46**.

10-(4-Chlorophenyl)-5-propyldibenzo[*b,f*]azepine (1a): From 4-bromochlorobenzene (0.286 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **1a** was obtained in 70% (0.241 g) yield as a yellow solid: mp 179 181 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 4H), 7.31-7.22 (m, 2H), 7.16 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.12 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.00 (td, *J* = 7.5, 1.2 Hz, 1H), 6.98 (s, 1H), 6.91 (td, *J* = 7.5, 1.2 Hz, 1H), 6.82 (dd, *J* = 7.8, 1.7 Hz, 1H), 3.82 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.63 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.64 (sext., *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.2, 142.9, 142.3, 135.4, 133.3, 133.2, 130.8, 130.2, 130.1, 129.4, 129.1, 128.5, 128.4, 123.2, 123.0, 120.5, 119.3, 51.5, 20.8, 11.4. Elemental analysis: calcd (%) for $C_{23}H_{20}ClN$ (345.87): C 79.87, H 5.83; found: C 80.08, H 5.68.

10-(4-Nitrophenyl)-5-propyldibenzo[*b,f*]azepine (2): From 4-bromonitrobenzene (0.303 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **2** was obtained in 15% (0.054 g) yield as a yellow solid: mp 182-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.34-7.24 (m, 2H), 7.18 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.08 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.93 (td, *J* = 7.5, 1.2 Hz, 1H), 6.76 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.83 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.65 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.66 (sext., *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 152.7, 150.5, 147.2, 142.2, 134.8, 133.0, 132.9, 130.2, 129.9, 129.6, 129.5, 129.3, 123.8, 123.6, 123.3, 120.9, 119.6, 51.7, 20.9, 11.5. Elemental analysis: calcd (%) for $C_{23}H_{20}N_2O_2$ (356.43): C 77.51, H 5.66; found: C 77.40, H 5.39.

5-Propyl-10-(4-(trifluoromethyl)phenyl)dibenzo[*b,f*]azepine (3): From 4-(trifluoromethyl)bromobenzene (0.337 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **3** was obtained in 50% (0.190 g) yield as a yellow solid: mp 189-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.34-7.25 (m, 2H), 7.20 (dd, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.10-7.00 (m, 3H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.81 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.85 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.65 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.67 (sext., *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 152.5, 147.5, 142.9, 135.3, 133.3, 132.0, 130.3, 129.7, 129.4 (q, *J* = 32.0 Hz), 129.3, 129.2, 128.9, 125.4 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.9 Hz), 123.4, 123.2, 120.7, 119.5, 51.7, 20.9, 11.5. Elemental analysis: calcd (%) for $C_{24}H_{20}F_3N$ (379.43): C 75.97, H 5.31; found: C 75.79, H 5.50.

10-(4-Fluorophenyl)-5-propyldibenzo[*b,f*]azepine (4): From 4-bromofluorobenzene (0.262 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **4** was obtained in 71% (0.233 g) yield as a yellow solid: mp 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.32-7.22 (m, 2H), 7.16 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.10-7.03 (m, 3H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 6.91 (td, *J* = 7.5, 1.2 Hz, 1H), 6.84 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.83 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.63 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.66 (sext., *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (d, *J* = 246.3 Hz), 152.5, 152.2, 143.2, 140.0, 135.8, 133.6, 130.7, 130.5, 130.4 (d, *J* = 7.8 Hz), 129.5, 129.1, 128.6, 123.3, 123.1, 120.6, 119.4, 115.3 (d, *J* = 21.3 Hz), 51.7, 21.0, 11.5. Elemental analysis: calcd (%) for $C_{23}H_{20}FN$ (329.42): C 83.86, H 6.12; found: C 83.90, H 6.07.

2-(4-(5-Propyldibenzo[*b,f*]azepin-10-yl)phenyl)acetonitrile (5): From 2-(4-bromophenyl)acetonitrile (0.294 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **5** was obtained in 30% (0.105 g) yield as an orange solid: mp 97 99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.33-7.23 (m, 2H), 7.18 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.05-7.00 (m, 2H), 6.93 (td, *J* = 7.5, 1.0 Hz, 1H), 6.84 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.85 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.78 (s, 2H), 3.64 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.66 (sext., *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 152.3, 143.9, 143.3, 135.6, 133.4, 131.1, 130.3, 129.6, 129.5, 129.2, 129.0, 128.7, 128.0, 123.3, 123.1, 120.6, 119.4, 118.0, 51.6, 23.5, 20.9,

11.5. Elemental analysis: calcd (%) for $C_{25}H_{22}N_2$ (350.47): C 85.68, H 6.33; found: C 85.48, H 6.48.

10-Phenyl-5-propyldibenzo[*b,f*]azepine (6): From bromobenzene (0.235 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **6** was obtained in 90% (0.280 g) yield as an orange solid: mp 109-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.45-7.24 (m, 5H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.06-7.00 (m, 2H), 6.97-6.90 (m, 2H), 3.89 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.67 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.70 (sext., *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 152.2, 144.2, 144.0, 136.0, 133.7, 130.7, 130.5, 129.5, 129.0, 128.9, 128.5, 128.4, 127.4, 123.2, 123.1, 120.5, 119.3, 51.7, 21.0, 11.6. Elemental analysis: calcd (%) for $C_{23}H_{21}N$ (311.43): C 88.71, H 6.80; found: C 88.69, H 6.89.

5-Propyl-10-(*p*-tolyl)dibenzo[*b,f*]azepine (7): From 4-bromotoluene (0.256 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **7** was obtained in 93% (0.302 g) yield as a yellow solid: mp 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.33-7.17 (m, 5H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.05-7.00 (m, 2H), 6.97-6.90 (m, 2H), 3.88 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.66 (dt, *J* = 12.4, 7.4 Hz, 1H), 2.43 (s, 3H), 1.68 (sext., *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 152.2, 144.1, 141.1, 137.2, 136.1, 133.8, 130.6, 130.1, 129.5, 129.1, 128.9, 128.8, 128.3, 123.2, 123.0, 120.5, 119.3, 51.7, 21.3, 21.0, 11.5. Elemental analysis: calcd (%) for $C_{24}H_{23}N$ (325.46): C 88.57, H 7.12; found: C 88.68, H 7.20.

10-(4-(*tert*-Butyl)phenyl)-5-propyldibenzo[*b,f*]azepine (8): From 4-*tert*-butylbromobenzene (0.319 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **8** was obtained in 80% (0.294 g) yield as an orange solid: mp 109-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.45 (m, 4H), 7.40-7.26 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.12 (s, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.07-6.97 (m, 2H), 3.94 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.74 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.74 (sext., *J* = 7.4 Hz, 2H), 1.48 (s, 9H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.2, 150.4, 144.0, 141.0, 136.1, 133.9, 130.6, 130.2, 129.5, 128.9, 128.5, 128.3, 125.3, 123.2, 123.0, 120.5, 119.3, 51.6, 34.7, 31.5, 20.9, 11.6. Elemental analysis: calcd (%) for $C_{27}H_{29}N$ (367.54): C 88.24, H 7.95; found: C 88.52, H 8.07.

10-([1,1'-Biphenyl]-4-yl)-5-propyldibenzo[*b,f*]azepine (9): From 4-bromobiphenyl (0.349 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **9** was obtained in 88% (0.340 g) yield as a yellow solid: mp 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.38-7.25 (m, 3H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.15 (s, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.10-6.97 (m, 3H), 3.92 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.71 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.74 (sext., *J* = 7.4 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 152.3, 143.8, 142.9, 140.9, 140.3, 135.9, 133.7, 130.7, 130.6, 129.6, 129.3, 129.0, 128.9, 128.5, 127.4, 127.2, 127.1, 123.3, 123.1, 120.6, 119.3, 51.6, 20.9, 11.6.**:**Elemental analysis: calcd (%) for $C_{29}H_{25}N$ (387.53): C 89.88, H 6.50; found: C 89.99, H 6.34.

10-(4-Methoxyphenyl)-5-propyldibenzo[*b,f*]azepine (10): From 4-bromoanisole (0.280 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **10** was obtained in 74% (0.252 g) yield as a yellow solid: mp 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.31-7.21 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 6.96-6.91 (m, 4H), 3.86 (s, 3H), 3.85 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.65 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.67 (sext., *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 152.5, 152.1, 143.7, 136.5, 136.1, 133.8, 130.6, 130.0, 129.7, 129.4, 128.9, 128.3, 123.2, 123.0, 120.5, 119.3, 113.8, 55.4, 51.6, 21.0, 11.5. Elemental analysis: calcd (%) for $C_{24}H_{23}NO$ (341.45): C 84.42, H 6.79; found: C 84.50, H 6.54.

***N,N*-dimethyl-4-(5-propyldibenzo[*b,f*]azepin-10-yl)aniline (11):** From 4-bromo-*N,N*-dimethylaniline (0.300 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **11** was obtained in 65% (0.230 g) yield as a yellow solid: mp 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.08-7.02 (m, 3H), 6.98 (td, *J* = 7.5, 1.2 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.91 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.69 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.05 (s, 6H), 1.70 (sext., *J* = 7.4 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.1, 150.1, 144.1, 136.3, 134.1, 132.0, 130.7, 129.6, 129.3, 128.8, 128.4, 127.9, 123.1, 122.9, 120.4, 119.1, 112.2, 51.6, 40.7, 20.9, 11.5. Elemental analysis: calcd (%) for $C_{25}H_{26}N_2$ (354.50): C 84.70, H 7.39; found: C 84.47, H 7.10.

4-(5-Propyldibenzo[*b,f*]azepin-10-yl)aniline (12): From 4-bromoaniline (0.258 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **12** was obtained in 31% (0.101 g) yield as a yellow solid: mp 151 153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.20 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.02-6.89 (m, 4H), 6.70 (d, *J* = 8.3 Hz, 2H), 3.86 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.70 (bs, 2H), 3.63 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.66 (sext., *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.1, 145.9, 144.0, 136.2, 134.3, 134.0, 130.7, 129.9, 129.3, 128.8, 128.7, 128.1, 123.1, 123.0, 120.4, 119.2, 114.9, 51.6, 21.0, 11.6. Elemental analysis: calcd (%) for $C_{23}H_{22}N_2$ (326.44): C 84.63, H 6.79; found: C 84.79, H 6.71.

10-(3-Chlorophenyl)-5-propyldibenzo[*b,f*]azepine (13): From 3-bromochlorobenzene (0.286 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **13** was obtained in 53% (0.182 g) yield as an orange solid: mp 82 84 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 1H), 7.33-7.25 (m, 5H), 7.17 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.12 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.00 (td, *J* = 7.5, 1.2 Hz, 1H), 6.98 (s, 1H), 6.91 (td, *J* = 7.5, 1.2 Hz, 1H), 6.83 (dd, *J* = 7.8, 1.6 Hz, 1H), 3.82 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.63 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.66 (sext., *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 152.4, 145.8, 142.9, 135.4, 134.3, 133.4, 131.5, 130.3, 129.6 (m), 129.2, 128.9, 128.8, 127.5, 127.2, 123.4, 123.2, 120.6, 119.4, 51.7, 21.0, 11.6. Elemental analysis: calcd (%) for $C_{23}H_{20}ClN$ (345.87): C 79.87, H 5.83; found: C 80.01, H 5.98.

5-Propyl-10-(*m*-tolyl)dibenzo[*b,f*]azepine (14): From 3-bromotoluene (0.256 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **14** was obtained in 88% (0.286 g) yield as a yellow solid: mp 84-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.32 (m, 5H), 7.31-7.20 (m, 3H), 7.12-7.06 (m, 3H), 7.04-6.98 (m, 2H), 3.95 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.75 (dt, *J* = 12.4, 7.4 Hz, 1H), 2.49 (s, 3H), 1.78 (sext., *J* = 7.4 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.2, 144.3, 144.0, 137.9, 136.1, 133.8, 130.6, 130.5, 129.6, 129.5, 128.9, 128.4, 128.3, 128.2, 126.1, 123.2, 123.0, 120.5, 119.3, 51.7, 21.6, 20.9, 11.6. Elemental analysis: calcd (%) for $C_{24}H_{23}N$ (325.46): C 88.57, H 7.12; found: C 88.41, H 7.02.

10-(3-Methoxyphenyl)-5-propyldibenzo[*b,f*]azepine (15): From 3-bromoanisole (0.280 g, 1.5 mmol) and 5-propyldibenzo[*b,f*]azepine (0.235 g, 1 mmol), **15** was obtained in 78% (0.266 g) yield as an orange solid: mp 61-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.28 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.14-

7.03 (m, 5H), 7.01-6.92 (m, 3H), 3.89 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.88 (s, 3H), 3.69 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.73 (sext., *J* = 7.4 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 152.5, 152.1, 145.4, 144.0, 135.8, 133.6, 130.7, 130.5, 129.5, 129.3, 129.0, 128.5, 123.2, 123.0, 121.5, 120.5, 119.3, 114.8, 112.7, 55.3, 51.6, 20.9, 11.5. Elemental analysis: calcd (%) for $C_{24}H_{23}NO$ (341.45): C 84.42, H 6.79; found: C 84.29, H 6.78.

3-(5-Propyldibenzo[*b*,*f*]azepin-10-yl)aniline (16): From 3-bromoaniline (0.258 g, 1.5 mmol) and 5-propyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), **16** was obtained in 50% (0.163 g) yield as a yellow solid: mp 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.17 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.05-6.83 (m, 5H), 6.76 (s, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 3.85 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.65 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.64 (bs, 2H), 1.68 (sext., *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.1, 146.4, 145.1, 144.3, 136.0, 133.7, 130.7, 130.3, 129.5, 129.2, 128.9, 128.4, 123.2, 123.0, 120.4, 119.5, 119.3, 115.7, 114.3, 51.7, 20.9, 11.6. Elemental analysis: calcd (%) for $C_{23}H_{22}N_2$ (326.44): C 84.63, H 6.79; found: C 84.64, H 6.86.

5-Propyl-10-(*o*-tolyl)dibenzo[*b*,*f*]azepine (17): From 2-bromotoluene (0.256 g, 1.5 mmol) and 5-propyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), **17** was obtained in 54% (0.176 g) yield as a yellow solid: mp 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.33 (m, 1H), 7.29-7.17 (m, 5H), 7.15 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.84 (t, *J* = 7.7 Hz, 1H), 6.81 (s, 1H), 6.65 (dd, *J* = 7.8, 1.6 Hz, 1H), 3.84-3.68 (m, 2H), 2.10 (s, 3H), 1.76-1.53 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 151.5, 143.6, 136.7, 136.2, 133.6, 131.9, 130.2, 130.0, 129.6, 129.0, 128.9, 128.6, 127.6, 125.9, 123.4, 123.1, 120.2, 119.5, 52.1, 21.1, 20.1, 11.9. Elemental analysis: calcd (%) for $C_{24}H_{23}N$ (325.46): C 88.57, H 7.12; found: C 88.67, H 7.25.

10-(Benzo[*d*][1,3]dioxol-5-yl)-5-propyldibenzo[*b*,*f*]azepine (18): From 5-bromobenzo[*d*][1,3]dioxole (0.302 g, 1.5 mmol) and 5-propyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), **18** was obtained in 61% (0.216 g) yield as a yellow solid: mp 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.23 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 7.06-6.93 (m, 6H), 6.87 (d, *J* = 8.6 Hz, 1H), 6.02 (s, 2H), 3.88 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.66 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.69 (sext., *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.1, 147.7, 147.1, 143.7, 138.2, 135.9, 133.6, 130.6, 130.0, 129.4, 129.0, 128.4, 123.2, 123.0, 122.4, 120.4, 119.3, 109.5, 108.2, 101.2, 51.6, 20.9, 11.5. Elemental analysis: calcd (%) for $C_{24}H_{21}NO_2$ (355.44): C 81.10, H 5.96; found: C 81.15, H 6.08.

10-(Naphthalen-2-yl)-5-propyldibenzo[*b*,*f*]azepine (19): From 2-bromonaphthalene (0.311 g, 1.5 mmol) and 5-propyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), **19** was obtained in 77% (0.278 g) yield as an orange solid: mp 149-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.98-7.87 (m, 3H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.60-7.52 (m, 2H), 7.40-7.30 (m, 3H), 7.26-7.21 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 7.04-6.93 (m, 2H), 3.95 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.74 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.79 (sext., *J* = 7.4 Hz, 2H), 1.08 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 152.3, 144.2, 141.4, 135.9, 133.6, 133.5, 132.8, 131.3, 130.6, 129.6, 129.1, 128.5, 128.2, 127.9, 127.8, 127.4 (m), 126.3, 126.0, 123.3, 123.1, 120.6, 119.4, 51.7, 21.0, 11.6. Elemental analysis: calcd (%) for $C_{27}H_{23}N$ (361.49): C 89.71, H 6.41; found: C 89.95, H 6.48.

10-(Fluoren-3-yl)-5-propyldibenzo[b,f]azepine (20): From 2-bromofluorene (0.367 g, 1.5 mmol) and 5-propyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), **20** was obtained in 78% (0.311 g) yield as a yellow solid: mp 219-221 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.77 (m, 2H), 7.62 (s, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.35-7.20 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10-7.05 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.96-6.88 (m, 2H), 3.94 (s, 2H), 3.87 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.66 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.69 (sext., *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.2, 144.5, 143.7, 143.5, 142.7, 141.6, 141.2, 136.2, 133.8, 130.7, 130.5, 129.6, 129.0, 128.4, 127.9, 126.9, 126.8, 125.5, 125.2, 123.3, 123.1, 120.5, 120.0, 119.7, 119.3, 51.7, 37.1, 21.0, 11.6. Elemental analysis: calcd (%) for $C_{30}H_{25}N$ (399.54): C 90.19, H 6.31; found: C 90.00, H 6.14.

5-Propyl-10-(6-(trifluoromethyl)pyridin-2-yl)dibenzo[*b*,*f*]azepine (21): From 2-bromo-6-(trifluoromethyl)pyridine (0.339 g, 1.5 mmol) and 5-propyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), **21** was obtained in 38% (0.144 g) yield as a yellow solid: mp 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.74 (m, 2H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.36-7.25 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.08-6.94 (m, 4H), 3.83 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.63 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.63 (sext., *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 153.0, 152.9, 148.0 (q, *J* = 35.0 Hz), 140.8, 137.5, 134.7, 133.9, 132.9, 130.7, 129.6, 129.2, 126.2, 123.6, 123.2, 121.0, 119.2, 118.6 (q, *J* = 2.9 Hz), 51.6, 20.9, 11.5. Elemental analysis: calcd (%) for $C_{25}H_{19}F_3N_2$ (380.41): C 72.62, H 5.03; found: C 72.80, H 4.87.

5-Propyl-10-(pyridin-3-yl)dibenzo[b,f]azepine (22): From 3-bromopyridine (0.237 g, 1.5 mmol) and 5-propyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), **22** was obtained in 36% (0.112 g) yield as a yellow solid: mp 89-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (bs, 1H), 8.58 (bs, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.35-7.34 (m, 3H), 7.19 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.07-7.00 (m, 3H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.81 (dd, *J* = 7.8, 1.5 Hz, 1H), 3.83 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.64 (dt, *J* = 12.4, 7.4 Hz, 1H), 1.64 (sext., *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 152.6, 149.7, 148.6, 140.8, 139.5, 136.2, 135.1, 133.2, 132.1, 130.1, 129.7, 129.4, 129.0, 123.5, 123.3, 123.2, 120.8, 119.5, 51.7, 20.9, 11.5. Elemental analysis: calcd (%) for $C_{22}H_{20}N_2$ (312.42): C 84.58, H 6.45; found: C 84.30, H 6.68.

13-Propylbenzo[*f*]fluoreno[1,9-*bc*]azepine (23): From 1,2-dibromobenzene (0.357 g, 1.5 mmol) and 5-propyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), during 72 h, **23** was obtained in 50% (0.155 g) yield as a yellow solid: mp 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 8.1 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.85 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.56-7.44 (m, 3H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.06-6.99 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.88 (t, *J* = 7.4 Hz, 2H), 1.90 (sext., *J* = 7.4 Hz, 2H), 1.15 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 140.0, 133.0, 132.4, 129.6, 128.5, 128.2, 127.9, 127.0, 125.2, 123.7, 123.1, 121.9, 121.4, 120.8, 113.6, 113.0, 112.5, 106.5, 48.5, 18.9, 11.2 Elemental analysis: calcd (%) for $C_{23}H_{19}N$ (309.41): C 89.28, H 6.19; found: C 89.20, H 5.94.

10-(4-Bromophenyl)-5-propyldibenzo[*b*,*f*]azepine (24): From 4-bromobenzenesulfonyl chloride (0.383 g, 1.5 mmol), 5-propyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), and Li_2CO_3 (0.222, 3 mmol) in 1,4-dioxane at 140 °C during 15 h, in the presence of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) under argon, after evaporation of the solvent and purification on silica gel, the arylation product **24** was obtained in 37% (0.144 g) yield as a yellow solid: mp 184-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.30-7.22 (m, 2H), 7.17 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.13 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.01 (td, *J* = 7.5, 1.2 Hz, 1H), 6.99 (s, 1H), 6.92 (td, *J* = 7.5, 1.2 Hz, 1H), 6.84 (dd, *J* = 7.8, 1.7 Hz, 1H), 3.84 (dt, *J* = 12.4, 7.4 Hz, 1H), 3.63 (dt, *J* = 12.4, 7.4

Hz, 1H), 1.64 (sext., *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 152.4, 143.0, 142.9, 135.5, 133.4, 131.4, 131.0, 130.6, 130.3, 129.6, 129.2, 128.7, 123.3, 123.2, 121.5, 120.6, 119.4, 51.7, 20.9, 11.5. Elemental analysis: calcd (%) for $C_{23}H_{20}BrN$ (390.32): C 70.78, H 5.16; found: C 71.02, H 5.04.

5-Benzyl-10-phenyldibenzo[*b*,*f*]azepine (25): From bromobenzene (0.235 g, 1.5 mmol) and 5-benzyldibenzo[*b*,*f*]azepine (0.283 g, 1 mmol), **25** was obtained in 76% (0.273 g) yield as an orange solid: mp 72 74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.41-7.25 (m, 5H), 7.20-7.01 (m, 9H), 6.94 (t, *J* = 7.7 Hz, 1H), 6.80-6.75 (m, 2H), 5.04 (d, *J* = 14.4 Hz, 1H), 4.88 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 151.8, 144.3, 143.9, 138.2, 135.9, 133.6, 130.6, 130.4, 129.4, 128.9, 128.8, 128.4, 128.3, 128.2, 128.1, 127.5, 126.9, 123.4, 123.3, 120.4, 119.4, 54.3. Elemental analysis: calcd (%) for $C_{27}H_{21}N$ (359.47): C 90.21 H 5.89; found: C 90.14, H 5.99.

4-(5-Benzyldibenzo[*b*,*f*]azepin-10-yl)benzonitrile (26): From 4-bromobenzonitrile (0.273 g, 1.5 mmol) and 5-benzyldibenzo[*b*,*f*]azepine (0.283 g, 1 mmol), **26** was obtained in 18% (0.069 g) yield as a yellow solid: mp 232-234 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.31-7.12 (m, 9H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.89 (td, *J* = 7.5, 1.2 Hz, 1H), 6.76 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.11 (d, *J* = 14.4 Hz, 1H), 4.96 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.3, 148.5, 142.7, 138.1, 134.9, 132.9, 132.6, 132.4, 130.0, 129.8, 129.5, 129.4, 129.2, 128.4, 128.2, 127.2, 123.7, 123.6, 120.9, 119.8, 119.1, 111.1, 54.4. Elemental analysis: calcd (%) for $C_{28}H_{20}N_2$ (384.48): C 87.47, H 5.24; found: C 87.41, H 5.35.

5-Benzyl-10-(4-(trifluoromethyl)phenyl)dibenzo[*b*,*f*]azepine (27): From 4-(trifluoromethyl)bromobenzene (0.337 g, 1.5 mmol) and 5-benzyldibenzo[*b*,*f*]azepine (0.283 g, 1 mmol), **27** was obtained in 51% (0.218 g) yield as an orange solid: mp 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.33-7.09 (m, 9H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.10 (d, *J* = 14.4 Hz, 1H), 4.95 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.2, 147.5, 143.1, 138.2, 135.4, 133.2, 132.0, 130.2, 129.7, 129.5 (q, *J* = 32.0 Hz), 129.3, 129.1, 129.0, 128.4, 128.2, 127.2, 125.5 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 272.0 Hz), 123.7, 123.6, 120.7, 119.7, 54.4. Elemental analysis: calcd (%) for $C_{28}H_{20}F_3N$ (427.47): C 78.67, H 4.72; found: C 78.60, H 5.02.

5-Benzyl-10-(*p*-tolyl)dibenzo[*b*,*f*]azepine (28): From 4-bromotoluene (0.256 g, 1.5 mmol) and 5-benzyldibenzo[*b*,*f*]azepine (0.283 g, 1 mmol), **28** was obtained in 82% (0.306 g) yield as a yellow solid: mp 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.25-7.11 (m, 10H), 7.10 (s, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.89-6.78 (m, 2H), 5.10 (d, *J* = 14.4 Hz, 1H), 4.94 (d, *J* = 14.4 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 151.9, 144.3, 141.1, 138.4, 137.4, 136.1, 133.8, 130.5, 130.2, 129.5, 129.2, 128.9, 128.7, 128.4, 128.3, 128.2, 127.0, 123.4, 123.3, 120.5, 119.5, 54.4, 21.3. Elemental analysis: calcd (%) for $C_{28}H_{23}N$ (373.50): C 90.04, H 6.21; found: C 90.18, H 5.89.

5-Benzyl-10-(4-methoxyphenyl)dibenzo[*b*,*f*]azepine (29): From 4-bromoanisole (0.280 g, 1.5 mmol) and 5-benzyldibenzo[*b*,*f*]azepine (0.283 g, 1 mmol), **29** was obtained in 65% (0.253 g) yield as an orange solid: mp 56-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.31-7.15 (m, 8H), 7.14 (s, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.95 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.93-6.88 (m, 1H), 5.15 (d, *J* = 14.4 Hz, 1H), 5.00 (d, *J* = 14.4 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 152.3, 151.8, 143.9, 138.3, 136.5, 136.1, 133.8, 130.5, 129.9, 129.7, 129.4, 128.9, 128.3 (*2), 128.2, 127.0, 123.4, 123.3, 120.4, 119.4, 113.8, 55.5, 54.4. Elemental analysis: calcd (%) for $C_{28}H_{23}NO$ (389.50): C 86.34, H 5.95; found: C 86.57, H 5.80.

5-Benzyl-10-(*m*-tolyl)dibenzo[*b*,*f*]azepine (30): From 3-bromotoluene (0.256 g, 1.5 mmol) and 5-benzyldibenzo[*b*,*f*]azepine (0.283 g, 1 mmol), **30** was obtained in 90% (0.336 g) yield as a yellow solid: mp 163-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.35-7.13 (m, 12H), 7.12 (s, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.90-6.82 (m, 2H), 5.12 (d, *J* = 14.4 Hz, 1H), 4.97 (d, *J* = 14.4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 151.8, 144.5, 144.0, 138.4, 138.0, 136.2, 133.8, 130.6, 130.5, 129.6, 129.5, 128.9, 128.4, 128.3 (m), 128.2, 126.0, 123.5, 123.4, 120.5, 119.5, 54.4, 21.7. Elemental analysis: calcd (%) for $C_{28}H_{23}N$ (373.50): C 90.04, H 6.21; found: C 90.01, H 5.99.

5-Isopropyl-10-phenyldibenzo[*b*,*f*]azepine (31): From bromobenzene (0.235 g, 1.5 mmol) and 5-isopropyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), **31** was obtained in 85% (0.264 g) yield as a yellow solid: mp 97-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.49 (m, 2H), 7.47-7.28 (m, 7H), 7.28-7.22 (m, 1H), 7.17-7.10 (m, 2H), 7.05-7.00 (m, 2H), 4.19 (sept., *J* = 6.0 Hz, 1H), 1.16 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 149.9, 143.7, 143.5, 137.1, 135.5, 130.3, 129.5, 129.3, 129.0, 128.9, 128.5, 128.2, 127.5, 126.2, 125.5, 124.1, 47.5, 23.1, 22.9. Elemental analysis: calcd (%) for $C_{23}H_{21}N$ (311.43): C 88.71, H 6.80; found: C 88.97, H 7.03.

5-Isopropyl-10-(*p*-tolyl)dibenzo[*b*,*f*]azepine (32): From 4-bromotoluene (0.256 g, 1.5 mmol) and 5-isopropyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), **32** was obtained in 84% (0.273 g) yield as a yellow solid: mp 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.33-7.17 (m, 7H), 7.12-7.06 (m, 2H), 7.01-6.95 (m, 2H), 4.14 (sept., *J* = 6.0 Hz, 1H), 2.42 (s, 3H), 1.11 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 149.8, 143.3, 140.8, 137.3, 137.2, 135.6, 130.3, 129.3, 129.1, 129.0, 128.9, 128.1, 126.3, 125.5, 124.2, 124.1, 47.5, 23.2, 22.9, 21.3. Elemental analysis: calcd (%) for $C_{24}H_{23}N$ (325.46): C 88.57, H 7.12; found: C 88.42 H 7.40.

10-(4-Fluorophenyl)-5-isopropyldibenzo[*b*,*f*]azepine (33): From 4-bromofluorobenzene (0.262 g, 1.5 mmol) and 5-isopropyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), **33** was obtained in 50% (0.164 g) yield as an orange solid: mp 162-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.37 (m, 2H), 7.34-7.22 (m, 4H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.13-7.05 (m, 4H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 4.16 (sept., *J* = 6.0 Hz, 1H), 1.13 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, *J* = 246.4 Hz), 150.5, 149.9, 142.4, 139.7 (d, *J* = 3.3 Hz), 136.9, 135.3, 130.6 (d, *J* = 8.0 Hz), 130.1, 129.5, 129.2, 129.0, 128.3, 126.0, 125.2, 124.2, 124.1, 115.3 (d, *J* = 21.3 Hz), 47.5, 23.1, 22.9. Elemental analysis: calcd (%) for $C_{23}H_{20}FN$ (329.42): C 83.86, H 6.12; found: C 83.91, H 6.26.

5-Isopropyl-10-(*m*-tolyl)dibenzo[*b*,*f*]azepine (34): From 3-bromotoluene (0.256 g, 1.5 mmol) and 5-isopropyldibenzo[*b*,*f*]azepine (0.235 g, 1 mmol), **34** was obtained in 84% (0.273 g) yield as a yellow solid: mp 119-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.15 (m, 9H), 7.12-7.07 (m, 2H), 7.03-6.97 (m, 2H), 4.16 (sept., *J* = 6.0 Hz, 1H), 2.42 (s, 3H), 1.13 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 149.8, 143.7, 143.6, 138.0, 137.2, 135.6, 130.3, 129.6, 129.4, 129.3, 128.8, 128.4, 128.3, 128.2, 126.3, 126.2, 125.5, 124.1 (m), 47.5, 23.1, 23.0, 21.7. Elemental analysis: calcd (%) for $C_{24}H_{23}N$ (325.46): C 88.57, H 7.12; found: C 88.60 H 7.01.

5,10-Diphenyldibenzo[*b*,*f*]azepine (35): From bromobenzene (0.235 g, 1.5 mmol) and 5-phenyldibenzo[*b*,*f*]azepine (0.269 g, 1 mmol), **35** was obtained in 15% (0.052 g) yield (90% purity) as a yellow solid: mp 208-210 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.55-7.15 (m, 13H), 7.03 (t, *J* = 8.1 Hz, 2H), 6.98 (s, 1H), 6.67 (t, *J* = 8.1 Hz, 1H), 6.41 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 145.1, 144.2, 143.2, 143.0, 138.5, 136.9, 131.9, 130.8, 130.4, 130.2, 130.1, 129.4, 129.0, 128.8, 128.7, 128.4, 127.7, 127.1, 126.9, 118.0, 111.9.

10-Phenyl-5-propyl-11-(*p*-tolyl)-dibenzo[*b,f*]azepine (38): From benzenesulfonyl chloride (0.265 g, 1.5 mmol) and 5-propyl-10-(*p*-tolyl)dibenzo[*b,f*]azepine **7** (0.325 g, 1 mmol), **38** was obtained in 56% (0.224 g) yield as a yellow solid: mp 163-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-6.98 (m, 13H), 6.93 (d, J = 8.0 Hz, 2H), 6.87 (t, *J* = 7.8 Hz, 2H), 3.83 (t, *J* = 7.4 Hz, 2H), 2.22 (s, 3H), 1.74 (sext., *J* = 7.4 Hz, 2H), 1.14 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 152.9, 143.4, 141.8, 141.7, 140.3, 136.6, 136.3, 135.5, 130.8, 130.7, 130.6, 130.5, 128.2, 128.1, 127.5, 126.1, 123.1, 123.0, 118.9, 118.8, 51.1, 21.3, 21.1, 11.8. Elemental analysis: calcd (%) for $C_{30}H_{27}N$ (401.55): C 89.73, H 6.78; found: C 89.80, H 6.59.

10-(4-Fluorophenyl)-5-propyl-11-(*p*-tolyl)dibenzo[*b,f*]azepine (39): From 4-fluorobenzenesulfonyl chloride (0.292 g, 1.5 mmol) and 5-propyl-10-(*p*-tolyl)dibenzo[*b,f*]azepine **7** (0.325 g, 1 mmol), **39** was obtained in 54% (0.226 g) yield as a yellow solid: mp 189-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.16 (m, 2H), 7.14-7.08 (m, 4H), 7.05-6.98 (m, 3H), 6.97-6.93 (m, 3H), 6.90-6.79 (m, 4H), 3.82 (t, *J* = 7.4 Hz, 2H), 2.24 (s, 3H), 1.74 (sext., *J* = 7.4 Hz, 2H), 1.12 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0 (d, *J* = 244.8 Hz), 153.1, 152.9, 142.5, 140.7, 140.1, 139.3, 136.3, 136.2, 135.7, 132.1 (d, *J* = 7.8 Hz), 130.7, 130.6, 130.3, 128.4, 128.2, 123.1, 123.0, 119.0, 118.9, 114.5 (d, *J* = 21.2 Hz), 51.1, 21.3, 21.1, 11.8. Elemental analysis: calcd (%) for $C_{30}H_{26}FN$ (419.54): C 85.89, H 6.25; found: C 85.69, H 6.24.

5-Propyl-10-(*p*-tolyl)-11-(4-(trifluoromethyl)phenyl)dibenzo[*b,f*]azepine (40): From 4-(trifluoromethyl)benzenesulfonyl chloride (0.366 g, 1.5 mmol) and 5-propyl-10-(*p*-tolyl)dibenzo[*b,f*]azepine **7** (0.325 g, 1 mmol), **40** was obtained in 47% (0.220 g) yield as a yellow solid: mp 175-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.25-7.18 (m, 2H), 7.16-7.11 (m, 2H), 7.06-7.00 (m, 3H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.93-6.86 (m, 3H), 3.83 (t, *J* = 7.4 Hz, 1H), 2.25 (s, 3H), 1.76 (sext., *J* = 7.4 Hz, 2H), 1.15 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 152.9, 147.1, 142.7, 140.4, 139.6, 136.1, 136.0, 135.6, 131.0, 130.8, 130.5, 130.3, 128.5, 128.4, 128.2 (q, *J* = 32.0 Hz), 124.6 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.9 Hz), 123.2, 123.1, 119.1, 119.0, 51.1, 21.3, 21.1, 11.8. Elemental analysis: calcd (%) for $C_{31}H_{26}F_3N$ (469.55): C 79.30, H 5.58; found: C 79.02, H 5.50.

10-(4-(*tert*-Butyl)phenyl)-5-propyl-11-(*p*-tolyl)dibenzo[*b,f*]azepine (41): From 4-*tert*-butylbenzenesulfonyl chloride (0.349 g, 1.5 mmol) and 5-propyl-10-(*p*-tolyl)dibenzo[*b,f*]azepine **7** (0.325 g, 1 mmol), **41** was obtained in 40% (0.183 g) yield as a yellow solid: mp 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.02 (m, 11H), 6.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 6.90-6.83 (m, 2H), 3.82 (t, *J* = 7.4 Hz, 1H), 2.23 (s, 3H), 1.75 (sext., *J* = 7.4 Hz, 2H), 1.23 (s, 9H), 1.14 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 152.9, 148.7, 141.7, 141.6, 140.5, 140.3, 136.8, 136.6, 135.4, 130.9, 130.8, 130.6, 130.2, 128.1, 128.0, 127.9, 124.3, 123.0, 118.8, 118.7, 51.0, 34.4, 31.4, 21.2, 21.1, 11.8. Elemental analysis: calcd (%) for $C_{34}H_{35}N$ (457.66): C 89.23, H 7.71; found: C 89.43, H 7.58.

10-(4-Methoxyphenyl)-5-propyl-11-(*p*-tolyl)dibenzo[*b,f*]azepine (42): From 4-methoxybenzenesulfonyl chloride (0.309 g, 1.5 mmol) and 5-propyl-10-(*p*-tolyl)dibenzo[*b,f*]azepine **7** (0.325 g, 1 mmol), **42** was obtained in 33% (0.142 g) yield as a yellow solid: mp 180-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.13 (m, 2H), 7.13-7.03 (m, 6H), 7.02-6.92 (m, 4H), 6.89-6.82 (m, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 3.81 (t, *J* = 7.4 Hz, 2H), 3.72 (s, 3H), 2.23 (s, 3H), 1.75 (sext., *J* = 7.4 Hz, 2H), 1.12 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 153.0, 141.9, 141.3, 140.5, 136.8, 136.6, 136.0, 135.5, 131.7, 130.8, 130.7, 130.4, 128.3, 128.0, 123.1, 123.0, 118.8 (m), 112.9, 55.2, 51.0, 21.3, 21.1, 11.8. Elemental analysis: calcd (%) for $C_{31}H_{29}NO$ (431.58): C 86.27, H 6.77; found: C 86.00, H 6.62.

5-Propyl-10-(*p*-tolyl)-11-(3-(trifluoromethyl)phenyl)-dibenzo[*b,f*]azepine (43) From 3-(trifluoromethyl)benzenesulfonyl chloride (0.366 g, 1.5 mmol) and 5-propyl-10-(*p*-tolyl)dibenzo[*b,f*]azepine **7** (0.325 g, 1 mmol), **43** was obtained in 42% (0.197 g) yield as a yellow solid: mp 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.25-7.20 (m, 2H), 7.17-7.10 (m, 3H), 7.07-7.01 (m, 2H), 6.98-6.91 (m, 3H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.84-6.77 (m, 3H), 3.75 (t, *J* = 7.4 Hz, 2H), 2.13 (s, 3H), 1.68 (sext., *J* = 7.4 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 152.9, 144.0, 143.0, 140.3, 139.6, 136.1, 136.0, 135.7, 133.9, 130.7, 130.5, 130.3, 129.6 (q, *J* = 32.0 Hz), 128.5 (m), 128.4, 128.0, 127.5 (q, *J* = 3.8 Hz), 123.2 (m), 122.9 (q, *J* = 3.8 Hz), 119.2, 119.0, 51.1, 21.2, 21.0, 11.8. Elemental analysis: calcd (%) for $C_{31}H_{26}F_3N$ (469.55): C 79.30, H 5.58; found: C 79.45, H 5.69.

10-(3,5-Bis(trifluoromethyl)phenyl)-5-propyl-11-(*p*-tolyl)dibenzo[*b,f*]azepine (44): From 3,5-bis(trifluoromethyl)benzenesulfonyl chloride (0.468 g, 1.5 mmol) and 5-propyl-10-(*p*-tolyl)dibenzo[*b,f*]azepine **7** (0.325 g, 1 mmol), **44** was obtained in 31% (0.167 g) yield as a yellow solid: mp 154-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.54 (m, 3H), 7.29-7.20 (m, 3H), 7.18-7.10 (m, 2H), 7.07 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.01-6.94 (m, 3H), 6.94-6.86 (m, 2H), 6.78 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.84 (t, *J* = 7.4 Hz, 2H), 2.22 (s, 3H), 1.76 (sext., *J* = 7.4 Hz, 2H), 1.12 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 152.9, 145.2, 144.1, 139.0, 138.9, 136.5, 135.5, 135.0, 130.8 (m), 130.7, 130.4, 130.3, 130.1, 128.9, 128.8, 128.7, 123.4, 123.3, 123.2 (q, *J* = 272.7 Hz), 120.1 (sept., *J* = 3.8 Hz), 119.4, 119.2, 51.1, 21.2, 21.0, 11.7. Elemental analysis: calcd (%) for $C_{32}H_{25}F_6N$ (537.55): C 71.50, H 4.69; found: C 71.35, H 4.68.

5-Benzyl-10-(4-fluorophenyl)-11-(*p*-tolyl)dibenzo[*b,f*]azepine (45): From 4-fluorobenzenesulfonyl chloride (0.292 g, 1.5 mmol) and 5-benzyl-10-(*p*-tolyl)dibenzo[*b,f*]azepine **28** (0.373 g, 1 mmol), **45** was obtained in 22% (0.103 g) yield as a white solid: mp 190-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.24-7.10 (m, 7H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.03-6.91 (m, 4H), 6.89-6.81 (m, 4H), 5.07 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3 (d, *J* = 245.1 Hz), 152.7, 152.6, 142.5, 140.7, 140.0, 139.2, 139.1, 136.2, 136.1, 135.9, 132.2 (d, *J* = 7.8 Hz), 130.8, 130.7, 130.4, 128.5, 128.4 (m), 128.3, 127.3, 123.4, 123.3, 119.1, 119.0, 114.5 (d, *J* = 21.2 Hz), 53.9, 21.3. Elemental analysis: calcd (%) for $C_{34}H_{26}FN$ (467.59): C 87.34, H 5.60; found: C 87.54, H 5.39.

5-Benzyl-10-(*p*-tolyl)-11-(4-(trifluoromethyl)phenyl)dibenzo[*b,f*]azepine (46): From 4-(trifluoromethyl)benzenesulfonyl chloride (0.366 g, 1.5 mmol) and 5-benzyl-10-(*p*-tolyl)dibenzo[*b,f*]azepine **28** (0.373 g, 1 mmol), **46** was obtained in 30% (0.155 g) yield as a white solid: mp 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.45-7.11 (m, 9H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.04-6.92 (m, 3H), 6.91-6.83 (m, 3H), 5.08 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 152.7, 146.9, 142.7, 140.4, 139.5, 138.6, 136.2, 136.0, 135.6, 131.0, 130.8, 130.6, 130.3, 128.6, 128.5 (m), 128.4, 127.4, 124.6 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.9 Hz), 123.5, 123.4, 119.2, 119.1, 53.9, 21.3. Elemental analysis: calcd (%) for $C_{35}H_{26}F_3N$ (517.60): C 81.22, H 5.06; found: C 81.00, H 4.85.

5-Benzyl-10-(*p*-tolyl)-11-(3-(trifluoromethyl)phenyl)dibenzo[*b,f*]azepine (47): From 3-(trifluoromethyl)benzenesulfonyl chloride (0.366 g, 1.5 mmol) and 5-benzyl-10-(*p*-tolyl)dibenzo[*b,f*]azepine **28** (0.373 g, 1 mmol), **47** was obtained in 38% (0.196 g) yield as a yellow solid: mp 125-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.47 (s, 1H), 7.42-7.11 (m, 10H), 7.11-7.01 (m, 3H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.92-6.82 (m, 3H), 5.12 (d, *J* = 14.3 Hz, 1H), 5.05 (d, *J* = 14.3 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 152.6, 143.9, 143.0, 140.4, 139.5, 138.5, 136.1, 135.9, 135.7, 134.0, 130.7, 130.6, 130.3, 128.5, 128.4 (m), 128.0, 127.5 (q, *J* = 3.8 Hz), 127.4, 123.5, 123.1, 123.0, 119.2, 119.1, 53.9, 21.2. Elemental analysis: calcd (%) for $C_{35}H_{26}F_3N$ (517.60): C 81.22, H 5.06; found: C 80.97, H 4.96.

11H-Benzo[6,7]azepino[3,2,1-*de*]phenanthridine (49): The reaction of 5-(2-bromobenzyl)dibenzo[*b,f*]azepine (0.362 g, 1 mmol), KOAc (0.196 g, 2 mmol) at 150 ºC during 16 h in DMA (5 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afford product **49** after evaporation of the solvent and purification on silica gel in 28% (0.079 g) yield as a yellow solid: mp 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.68 (m, 2H), 7.45-7.36 (m, 3H), 7.15-7.01 (m, 4H), 6.90 (td, *J* = 7.5, 1.0 Hz, 1H), 6.83-6.72 (m, 3H), 4.79 (d, *J* = 15.8 Hz, 1H), 4.69 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 145.4, 135.1, 133.4, 133.0, 132.5, 132.4, 131.8, 129.6, 129.4, 129.1, 128.7, 128.3, 128.0, 125.2, 124.5, 124.2, 123.7, 123.1, 121.4, 52.8. Elemental analysis: calcd (%) for $C_{21}H_{15}N$ (281.36): C 89.65, H 5.37; found: C 89.47, H 5.39.

Acknowledgements

We thank China Scholarship Council for a fellowship to HL.

References

[1] L. J. Kricka, A. Ledwith, *Chem. Rev.* **1974**, *74*, 101-123.

[2] a) C. Defieber, M. A. Ariger, P. Moriel, E. M. Carreira, *Angew. Chem., Int. Ed.* **2007**, *46*, 3139-3143; b) R. Mariz, A. Briceno, R. Dorta, R. Dorta, *Organometallics* **2008**, *27*, 6605-6613; c) M. Roggen, E. M. Carreira, *Angew. Chem., Int. Ed.* **2011**, *50*, 5568-5571; d) S. Krautwald, D. Sarlah, M. A. Schafroth, E. M. Carreira, *Science* **2013**, *340*, 1065-1068; e) D. A. Petrone, M. Isomura, I. Franzoni, S. L. Rossler, E. M. Carreira, *J. Am. Chem. Soc.* **2018**, *140*, 4697-4704.

[3] E.-C. Elliott, J. L. Maggs, B. K. Park, P. M. O'Neill, A. V. Stachulski, *Org. Biomol. Chem.* **2013**, *11*, 8426-8434.

[4] a) M. Ito, R. Kawasaki, K. S. Kanyiva, T. Shibata, *Eur. J. Org. Chem.* **2016**, 5234-5237; b) M. Ito, D. Inoue, R. Kawasaki, K. S. Kanyiva, T. Shibata, *Heterocycles* **2017**, *94*, 2229-2246.

[5] A. Herrera, A. Grasruck, F. W. Heinemann, A. Scheurer, A. Chelouan, S. Friess, F. Seidel, R. Dorta, *Organometallics* **2017**, *36*, 714-720.

[6] For reviews on catalyzed C-H bond functionalization: a) L. Ackermann, R. Vicente, A. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792-9826; b) R. Rossi, F. Bellina, M. Lessi, C. Manzini, *Adv. Synth. Catal.* **2014**, *356*, 17-117; c) A. Dey, S. Agasti, D. Maiti, *Org. Biomol. Chem.* **2016**, *14*, 5440-5453; d) T. Gensch, M. J. James, T. Dalton, F. Glorius, *Angew. Chem. Int. Ed.* **2018**, *57*, 2296-2306; e) X. Shi, A. Sasmal, J.-F. Soulé, H. Doucet, *Chem. Asian J.* **2018**, *13*, 143-157.

[7] a) A. H. M. de Vries, J. M. C. A. Mulders, J. H. M. Mommers, H. J. W. Henderickx, J. G. de Vries *Org. Lett.* **2003**, *5*, 3285-32880; b) The Mizoroki–Heck Reaction Ed. by M. Oestreich, 2009, John Wiley & Sons; c) V. Coeffard, P. J. Guiry, *Science of Synthesis, Cross Coupling and Heck-Type Reactions* Vol. 3 2013, 303-344 Edited by G. A. Molander, J. P. Wolfe, M. Larhed.

[8] For Heck reaction with cyclic alkenes: a) R. Larock, B. Baker, *Tetrahedron Lett.* **1988**, *29*, 905-908; b) S. Hillers, S. Sartori, O. Reiser, *J. Am. Chem. Soc.* **1996**, *118*, 2087-2088; c) C. Hartung, K. Koehler, M. Beller, *Org. Lett.* **1999**, *1*, 709-711; d) L. Djakovitch, K. Koehler, *J. Am. Chem. Soc.* **2001**, *123*, 5990-5999; e) F. Berthiol, H. Doucet, M. Santelli, *Tetrahedron Lett.* **2003**, *44*, 1221-1225; f) L. Djakovitch, M. Wagner, C. G. Hartung, M. Beller, K. Koehler, *J. Mol. Catal. A: Chemical* **2004**, *219*, 121-130; g) C. Wu, J. Zhou, *J. Am. Chem. Soc.* **2014**, *136*, 650-652.

[9] L. Zhao, C. Bruneau, H. Doucet, *ChemCatChem* **2013**, *5*, 255-262.

[10] T. Cantat, E. Génin, C. Giroud, G. Meyer A. Jutand, *J. Organomet. Chem.* **2003**, *687*, 365-376.

[11] P. Nilsson, M. Larhed, A. Hallberg, *J. Am. Chem. Soc.* **2001**, *123*, 8217-8225.

[12] K. Yuan, J.-F. Soulé, H. Doucet, *ACS Catal.* **2015**, *5*, 978-991.

[13] L. Wang, W. He, Z. Yu, *Chem. Soc. Rev.* **2013**, *42*, 599-621.

[14] a) M. Miura, H. Hashimoto, K. Itoh, M. Nomura, *Tetrahedron Lett.* **1989**, *30*, 975-976; b) M. Miura, H. Hashimoto, K. Itoh, M. Nomura, *J. Chem. Soc., Perkin Trans. 1* **1990**, 2207-2211.

[15] a) X. Zhao, E. Dimitrijevic, V. M. Dong, *J. Am. Chem. Soc.* **2009**, *131*, 3466-3467; b) X. Zhao, V. M. Dong, *Angew. Chem., Int. Ed.* **2011**, *50*, 932-934.

[16] a) K. Yuan, H. Doucet, *Chem. Sci.* **2014**, *5*, 392-396; b) R. Jin, K. Yuan, E. Chatelain, J.-F. Soulé, H Doucet, *Adv. Synth. Catal.* **2014**, *356*, 3831-3841.

[17] a) M. Brahim, H. Ben Ammar, V. Dorcet, J.-F. Soulé, H. Doucet, *Org. Lett.* **2017**, *19*, 2584-2587; b) X. Shi, T. Roisnel, J.-F. Soulé, H. Doucet, *Org. Chem. Front.* **2018**, *5*, 398-408.

[18] A. Alimardanov, L. Schmieder-van de Vondervoort, A. H. M. de Vries, J. G. de Vries, *Adv. Synth. Catal.* **2004**, *346*, 1812-1817.

[19] T. Ohta, N. Miyata, M. Hirobe, *Chem. Pharm. Bull.* **1981**, *29*, 1221-1230.

Convenient access to C10- and C11-(di)arylated dibenzo[*b*,*f*]azepines *via* palladium-catalyzed C-H bonds cleavages

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Haoran Li,[a] Thierry Roisnel,[a] Jean-François Soulé,[a]* and Henri Doucet[a]*