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Palladium-Catalyzed Iterative C–H Bond Arylations: Synthesis of Medium-Size Heterocycles with a Bridgehead Nitrogen Atom

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Condensed N-heterocycles were prepared by using iterative C–H bond activation reactions catalyzed by palladium. The first step consists of a palladium-catalyzed direct desulfitative C–H bond arylation of brominated *N*-benzylpyrrole derivatives with benzenesulfonyl chlorides. The presence of the bromine atom allows the formation in the second step of several N-heterocycles with five-, six-, or seven-membered rings by a palladium-catalyzed intramolecular C–H bond arylation.

Introduction

The discovery of new simple and short synthetic strategies for obtaining complex medium-size polycyclic heterocycles is an important research area from both academic and industrial points of views because of the usefulness of these molecules as pharmaceutical precursors or electronic devices. For example, IIK7, in the isoindole molecule class, is a commercial analogue of melatonin with an important physiological ability to reduce intraocular pressure (Figure 1).[1] Lamellarins A4 and G are natural pyrrole alkaloids, which exhibit a wide variety of biological activities (for example, reversal of multidrug resistance, HIV-1 integrase inhibition, and antibiotic activity).[2] Compound **I**, with a pyrrole-fused 6-membered ring, which is a pyrrolo[1,2,*f*]phenanthridine derivative, displays valuable pharmaceutical properties, such as anti-HIV activity and the stimulation of the multiplication of MT-4 cells at low concentrations (Figure 1).[3] Among the dibenzoazepine analogues, molecule **II**, a pyrrole-fused 7-membered ring, is recognized for its anti-hypertensive, anti-psychotic, anti-inflammatory, anaesthetic, anti-ulcer, and vasodilatatory multiproperties (Figure 1).[4] In addition, congested pyrrole structures such as Ullazine and pyrrolo-[1,2-*f*]phenanthridine (**III**) have recently found applications in electronic devices, in which they are used as organic sensitizers for solar-cell applications (Figure 1).[5]

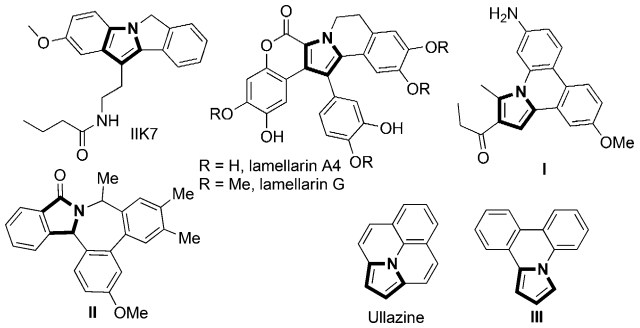

Figure 1. Examples of pyrrole-fused heterocyclic structures.

One of the most reliable and fast approaches for the preparation of such polycyclic molecules involves domino or cascade reactions including multicomponent reactions.[6] More recently, metal-catalyzed C–H bond activation was introduced as one of the most attractive methods for the modification and the synthesis of heterocycles,[7] and sequential approaches involving at least one C–H bond cyclization have been described for the synthesis of fused polycyclic heterocycles.[8] On the other hand, an iterative process, namely the repetition of successive or similar reactions for the stepwise synthesis of molecules, represents a huge advantage for synthesis in few steps and the design of diversity.[9]

Palladium-catalyzed intramolecular arylation of pyrroles is an efficient pathway for the construction of five-membered-ring pyrrolo[1,2,*a*]isoindoles. However, this methodology remains limited to scarce examples.[10] Moreover, to the best of our knowledge, further transformations of the isoindoles, such as direct intermolecular arylations, have not been reported (Figure 2a). Knochel and co-workers reported palladium-catalyzed intramolecular arylation for the construction of condensed N-heterocycles (Figure 2b).[8c,d] From *N*-(2-bromobenzyl)- or *N*-(2-bromobenzoyl)-substituted pyrroles, the six-membered-ring cyclization occurred, with $Pd(OAc)_2$ catalysts in the presence of

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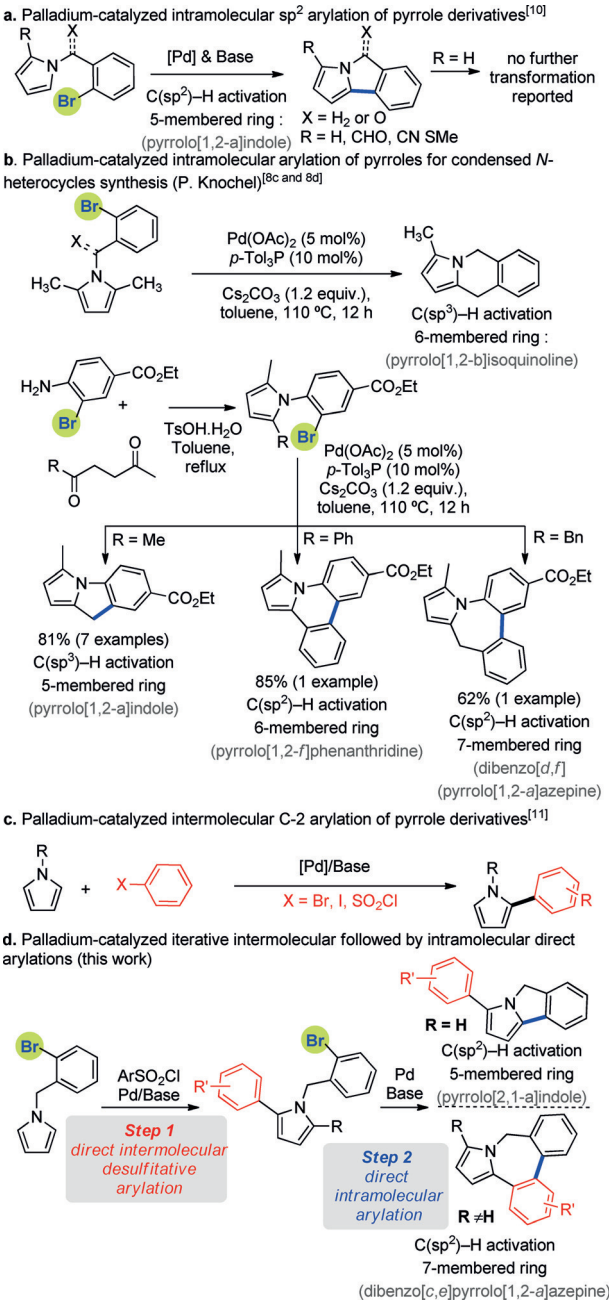


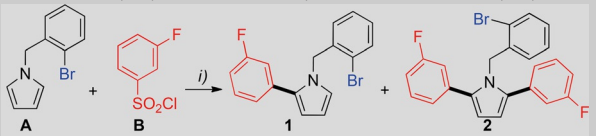
Figure 2. Previous examples of Pd-catalyzed intra- and intermolecular direct arylations of pyrrole derivatives. *p*-Tol: *p*-tolyl; Ts: toluene-4-sulfonyl; Bn: benzyl.

a phosphine and Cs_2CO_3 as base, through a C(sp^3)–H bond activation. In addition, from *N*-(2-bromophenyl)-substituted pyrroles, similar reaction conditions afforded [1,2,*a*]-pyrrole-fused five- or seven-membered or [1,2,*f*]-pyrrole-fused six-membered cyclized products depending on the C2 substituent on the pyrrole unit (that is, R is Me, Ph, or CH_2Ph) through C(sp^3)–H or C(sp^2)–H bond activation. On the other hand, palladium-catalyzed intermolecular C2 arylation of pyrroles is a well-established procedure (Figure 2c).[11] However, palladium-catalyzed intramolecular direct arylation generally proceeds faster than the intermolecular reaction and prevents an orthogonal approach for the synthesis of N-condensed molecules through iterative palladium-catalyzed C–H bond arylation. On the basis of the original report by Dong and co-workers,[12] our group and others have exploited the reactivity of benzenesulfonyl chlorides for direct regioselective arylation of several heteroarenes.[13] This methodology tolerated C–X bonds, which allowed orthogonal functionalizations.[14] Herein, we report a novel approach for the synthesis of pyrrolo[2,1,*a*]isoindole, dibenzo[*c*,*e*]pyrrolo[1,2,*a*]azepine, and pyrrolo[1,2,*f*]phenanthridine derivatives by using two iterative C–H bond arylations and by starting from *N*-(2-bromobenzyl)pyrrole. This uncommon procedure involves firstly a palladium intermolecular arylation, in which benzenesulfonyl chlorides were used as aryl sources, and then a palladium-catalyzed direct cyclization affords the desired N-condensed heterocycles (Figure 2d).

Results and Discussion

We selected *N*-(2-bromobenzyl)pyrrole and 3-fluorobenzenesulfonyl chloride as starting materials and investigated the Pd-catalyzed intermolecular direct pyrrole C2 arylation. With our previous optimized reaction conditions, (that is, 5 mol% of $PdCl_2(CH_3CN)_2$ in the presence of 3 equivalents of Li_2CO_3 in 1,4-dioxane at $T = 140\,^{\circ}C$), a mixture of mono- and diarylated products **1** and **2** was obtained in 85:15 ratio, albeit without full consumption of the starting materials (Table 1, entry 1).[13g] Notably, no side product resulting from an intramolecular arylation by activation of the C–Br bond was detected. A decrease in the amount of pyrrole to 1.2 equivalents allowed full conversion of benzenesulfonyl chloride to be reached with a slightly better ratio of **1**:**2** (87:13), and **1** was isolated in 75% yield

Table 1. Screening conditions for the selective synthesis of 2-arylated *N*-(2-bromobenzyl)pyrrole and 2,5-diarylated *N*-(2-bromobenzyl)pyrrole.



i) **A** (1.5 equiv.), **B** (1 equiv.), $PdCl_2(CH_3CN)_2$ (5 mol%), Li_2CO_3 (3 equiv.), 1,4-dioxane, 140 °C, 16 h

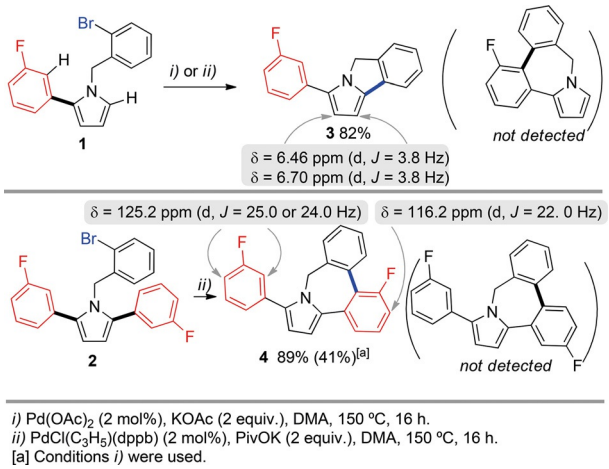
Entry	Modifications to conditions	Conv. [%][a]	1:2[a]
1	–	87	85:15
2	**A** (1.2 equiv.)	100	87:13 (75%)[b]
3	**A** (1.2 equiv.), $Pd_2(dba)_3$[c]	20	95:5
4	**A** (1.2 equiv.), $PdCl_2(PhCN)_2$	100	57:43
5	**A** (1.2 equiv.), $Pd(OAc)_2$	100	57:43
6	**A** (1.2 equiv.), $PdCl_2$	100	62:38
7	**A** (1.2 equiv.), 120 °C, 24 h	40	66:34
8	**A** (1.2 equiv.), Li_2CO_3 (1.5 equiv.)	30	80:20
9	**A** (1.2 equiv.), Na_2CO_3	95	67:33
10	**A** (1.2 equiv.), K_2CO_3	23	95:5
11	**A** (1.2 equiv.), KOAc	59	83:17
12	**A** (1 equiv.), **B** (2.5 equiv.)	100	45:55 (41%)[d]
13	**A** (1 equiv.), **B** (2.5 equiv.), 24 h	100	5:95 (87%)[d, e]

[a] Determined by GC and ^1H NMR spectroscopy, the conversion is based on 3-fluorobenzenesulfonyl chloride. [b] Yield of **1** after isolation. [c] dba: *trans*,*trans*-dibenzylideneacetone. [d] Yield of **2** after isolation. [e] **B** was added in two portions separated by 15 h.

(Table 1, entry 2). $Pd_2(dba)_3$ catalyst affords a higher selectivity in favor of the monoarylated product **1** (95:5), albeit with poor conversion (Table 1, entry 3). Other sources of palladium such as $PdCl_2(PhCN)_2$, $Pd(OAc)_2$, and $PdCl_2$ did not allow improvement of the selectivity in favor of **1** (Table 1, entries 4–6). A lower reaction temperature of 120 °C resulted in a lower conversion of 40% without any improvement of the **1**:**2** ratio (Table 1, entry 7). The same trend was observed with a lower amount of base (1.5 equiv.; Table 1, entry 8). The use of Na_2CO_3, K_2CO_3, or KOAc instead of Li_2CO_3 led to slightly lower yields of **1**, either as a result of lower conversions or poor **1**:**2** selectivities (Table 1, entries 9–11).

On the other hand, we were also interested in the selective synthesis of the C2,C5-diarylated pyrrole **2**. An increase in the amount of 3-fluorobenzenesulfonyl chloride to 2.5 equivalents allowed the formation of diarylated product **2** in only 41% isolated yield (Table 1, entry 12). During this reaction, we observed the formation of a large amount of C2-arylated product **1** and also of a side product resulting from the degradation of the benzenesulfonyl chloride. To prevent this decomposition, we decided to introduce the benzenesulfonyl chloride in two portions separated by 15 h. As a result, **2** was obtained with much higher selectivity (>95%) and isolated in 87% yield (Table 1, entry 13).

Having found the best reaction conditions to synthesize C2-arylated pyrrole **1** or C2,C5-diarylated pyrrole **2**, both in good yields, we turned our attention to the cyclization reactions (Scheme 1). Firstly, we selected pyrrole **1**, which contains two reactive C–H bonds under palladium catalysis. In the presence of 2 mol% of $Pd(OAc)_2$ and KOAc as base, the cyclized product **3**, resulting from activation of the C–H bond at the C5 position on the pyrrole, was obtained in an excellent 82% yield (Scheme 1, top). The potential other regioisomer, which would result from activation of the C–H bond at the *ortho* position with respect to the fluorine atom, was not detected. We also employed the conditions that we had previously described for the synthesis of *ortho*-fluorinated biaryls,[15] (that is, $PdCl(C_3H_5)$(dppb) in the presence of PivOK as base), but again only product **3** was obtained, with a comparable yield. The C2,C5-diarylated pyrrole **2** was then subjected to the same reaction conditions. We were pleased to find that the intramolecular direct arylation occurred to give the seven-membered ring product **4** in 89% yield (Scheme 1, bottom). With the first set of conditions, namely, the $Pd(OAc)_2$/KOAc system, a lower 41% yield of **4** was obtained because of a poor conversion. Moreover, the reaction was fully regioselective because the arylation occurred only at the *ortho* position to the fluorine atom (as determined by analysis of $^{19}F/^{1}H$ and $^{19}F/^{13}C$ coupling constants). Notably, the synthesis of **3** or **4** could not be performed by a "one-pot" procedure from *N*-(2-bromobenzyl)pyrrole and benzenesulfonyl chloride.

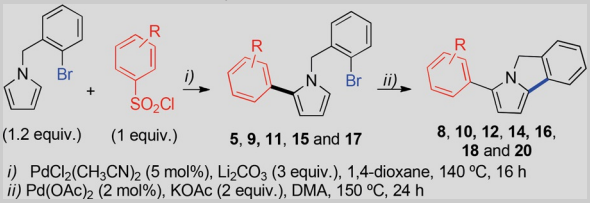


i) $Pd(OAc)_2$ (2 mol%), KOAc (2 equiv.), DMA, 150 °C, 16 h.
ii) $PdCl(C_3H_5)$(dppb) (2 mol%), PivOK (2 equiv.), DMA, 150 °C, 16 h.
[a] Conditions *i)* were used.

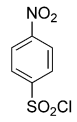
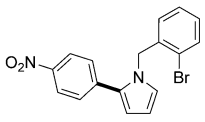
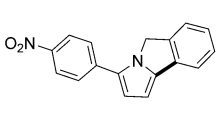
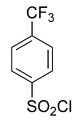
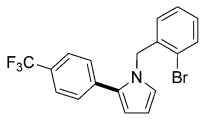
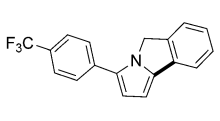
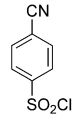
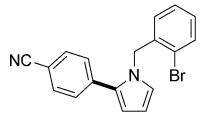
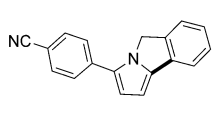
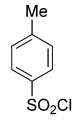
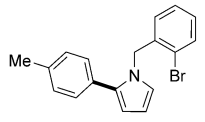
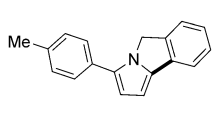
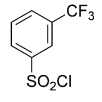
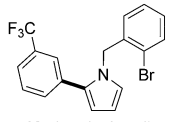
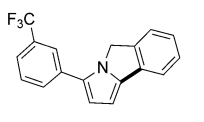
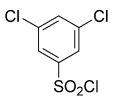
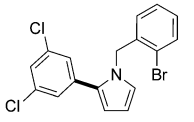
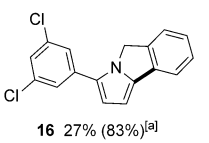
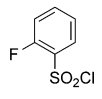
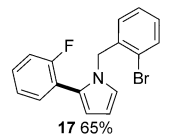
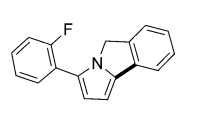
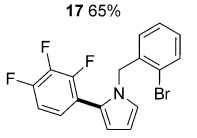
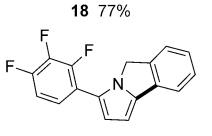
Scheme 1. Palladium-catalyzed direct cyclization reactions of 1-(2-bromobenzyl)-2-(3-fluorophenyl)pyrrole and 1-(2-bromobenzyl)-2,5-bis(3-fluorophenyl)pyrrole. DMA: *N*,*N*-dimethylacetamide; dppb: 1,1′-bis(diphenylphosphanyl)butane; Piv: pivaloyl.

After having developed these iterative processes for the synthesis of five- or seven-membered-ring N-condensed heterocycles, we generalized the protocol. Firstly, we investigated the scope of the iterative C–H arylations for the synthesis of 3-arylated pyrrolo[2,1-*a*]isoindoles with a set of benzenesulfonyl chlorides (Table 2). With 4-nitrobenzenesulfonyl chloride as the coupling partner, the desulfitative arylation of the pyrrole proceed smoothly to afford the desired C2-arylated pyrrole **5** in 78% yield. Compound **5** was then treated with 2 mol% of $Pd(OAc)_2$ in the presence of 2 equivalents of KOAc in DMA for 16 h. Unfortunately, no cyclized product **6** was detected, and only the starting material **5** was recovered. The use of 2 mol% of $PdCl(C_3H_5)$(dppb) in the presence of 2 equivalents of PivOK was also unsuccessful (Table 2, entry 1). A competitive reaction between **1** and **5** revealed that only product **1** was cyclized, to form **3**, whereas **5** remained untouched. This result suggests that the nitro substituent prevents the cyclization as a result of its strong electron-withdrawing character. In contrast, with 4-(trifluoromethyl)benzenesulfonyl chloride as the coupling partner, the pyrrolo[2,1-*a*]isoindole **8** was isolated in 57% overall yield by successive palladium-catalyzed C–H bond arylations (Table 2, entry 2). The C2 arylated pyrrole intermediate **7** was not isolated in pure form because of contamination with the starting materials; therefore, the crude mixture was directly used in the second step. A 4-cyano substituent on the benzenesulfonyl chloride was tolerated with both sets of reaction conditions, and the intermediate **9** was isolated in 71% yield; it was then regioselectively cyclized into **10** in 92% yield (Table 2, entry 3). The first desulfitative arylation of pyrroles was also performed with electron-rich tosyl chloride, although the C2-arylated pyrrole **11** was isolated in a moderate 42% yield. Again, the electronic properties of the arene at the C2 position of the pyrrole unit have a minor influence on the intramolecular arylation, because the pyrrolo[2,1,*a*]isoindole **12** was isolated as a single regioisomer in 88% yield (Table 2, entry 4). Next, we investigated the reactivity of *meta*-substituted benzenesulfonyl chlorides in the iterative process. With 3-(trifluoromethyl)benzenesulfonyl chloride, intermediate **13** was not isolated as a result of contamination, but the iterative process from the crude mixture afforded the desired cyclized product **14** in 68% yield over two steps (Table 2, entry 5). 3,5-Dichlorobenzenesulfonyl chloride was easily coupled through palladium-catalyzed direct desulfitative arylation to give the

Table 2. Synthesis of 3-arylated pyrrolo[2,1-*a*]isoindoles by palladium-catalyzed iterative C–H bond arylations.



i) $PdCl_2(CH_3CN)_2$ (5 mol%), Li_2CO_3 (3 equiv.), 1,4-dioxane, 140 °C, 16 h
ii) $Pd(OAc)_2$ (2 mol%), KOAc (2 equiv.), DMA, 150 °C, 24 h

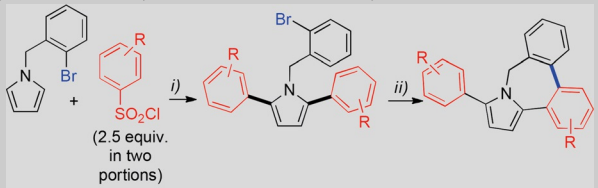
Entry	$ArSO_2$–Cl	Step 1	Step 2
1		 **5** 78%	 **6** 0% (0%)[a]
2		 **7** *(not isolated)*	 **8** 57% over 2 steps
3		 **9** 71%	 **10** 92%
4		 **11** 42%	 **12** 88%
5		 **13** *(not isolated)*	 **14** 68% over 2 steps
6		 **15** 81%	 **16** 27% (83%)[a]
7		 **17** 65%	 **18** 77%
8		 **19** *(not isolated)*	 **20** 66% over 2 steps

[a] $PdCl(C_3H_5)(dppb)$ (2 mol%) and PivOK (2 equiv.) were used instead of $Pd(OAc)_2$ and KOAc.

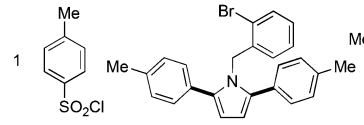
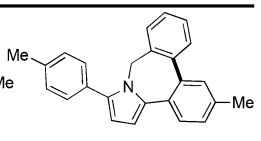
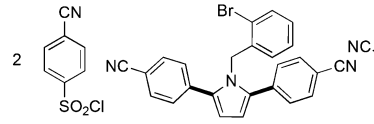
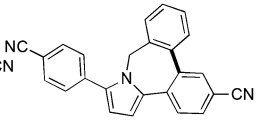
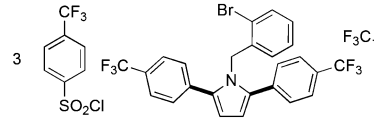
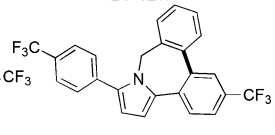
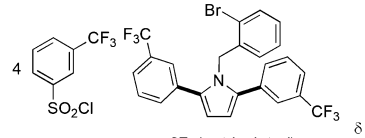
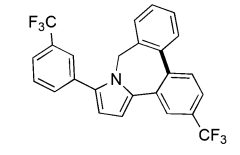
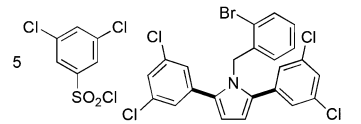
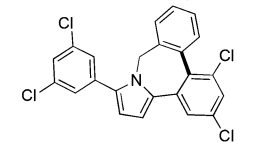
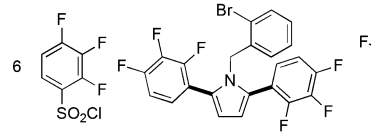
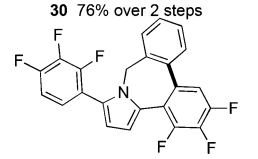
C2-arylated product **15** in an excellent yield. The presence of two chlorine atoms on the C2-arene slightly decreased the yield of the cyclized product **16**. However, the other reaction conditions (that is, 2 mol% of $PdCl(C_3H_5)(dppb)$ in the presence of 2 equivalents of PivOK) led to a complete conversion, and pyrrolo[2,1,*a*]isoindole **16** was isolated in 83% yield as a single regioisomer (Table 2, entry 6). An *ortho*-fluoro substituent on the benzenesulfonyl chloride has no significant effect on both arylations, because 1-(2-bromobenzyl)-2-(2-fluorophenyl)pyrrole (**17**) was obtained in 65% yield and was cyclized into 3-(2-fluorophenyl)pyrrolo[2,1-*a*]isoindole (**18**) in 77% yield (Table 2, entry 7). Finally, we also performed the reaction with 2,3,4-trifluorobenzenesulfonyl chloride as the coupling partner. The C2-arylated pyrrole intermediate **19** was not isolated, and the crude mixture was directly treated with 2 mol% of $PdCl(C_3H_5)(dppb)$ in the presence of 2 equivalents of PivOK to afford the cyclized product **20** in 66% overall yield (Table 2, entry 8). Notably, even in the presence of the highly activated trifluorobenzene, no C–H bond activation on this benzene ring was observed and the cyclization took place exclusively on the pyrrole unit.

We then moved on to study the one-pot preparation of 1-(2-bromobenzyl)-2,5-di(aryl)pyrroles, through a desulfitative diarylation, and their reactivities in palladium-catalyzed direct intramolecular arylation (Table 3). With the optimized conditions described in Table 1 (entry 13), in which tosyl chloride was added in two portions separated by 15 h, 1-(2-bromobenzyl)-2,5-di-*p*-tolylpyrrole (**21**) was isolated in 77% yield. The intramolecular arylation was then performed with $PdCl(C_3H_5)(dppb)$ as the catalyst and PivOK as the base in DMA. The reaction was found to be sensitive to the electronic properties of the aryl groups, because only a moderate yield of 38% of **22** was obtained as a result of a low conversion of **21** (Table 3, entry 1). In contrast, with 4-cyanobenzenesulfonyl chloride, the intermolecular desulfitative arylation and intramolecular arylation both proceeded in high yields, because the diarylated pyrrole **23** was isolated in 76% yield and was converted into the corresponding pyrrolo[2,1,*a*]azepine **24** in 62% yield. Four other examples of pyrrolo[1,2-*a*]azepine syntheses were performed by using the same synthetic scheme. However, as a result of laborious purification issues for the 1-(2-bromobenzyl)-2,5-di(aryl)pyrrole intermediates, the cyclizations were directly performed from the crude mixtures. With 4-(trifluoromethyl)benzenesulfonyl chloride as the aryl source, the iterative C–H bond arylations allowed the formation of the desired heteropolycycle **26** in 77% overall yield (Table 3, entry 3). Both the intermolecular desulfitative and the intramolecular direct C–H bond arylation conditions tolerated an aryl group with a *meta* substituent. For example, 3-(trifluoromethyl)benzenesulfonyl chloride was treated with the pyrrole derivative and then cyclized into pyrrolo[2,1,*a*]azepine **28** in 49% yield over two steps (Table 3, entry 4). The cyclization reaction was completely regioselective, and the product resulted from the activation of the less sterically hindered C–H bond (the configuration of the product was determined by analysis of $^{19}F/^{1}H$ and $^{19}F/^{13}C$ coupling constants). The iterative reaction proceeded smoothly with a benzenesulfonyl chloride bearing two chloro substituents at positions 3 and 5 to give the pyrrolo[2,1,*a*]azepine **30** in 76% yield. Finally, 2,3,4-trifluorobenzenesulfonyl chloride was used as the coupling partner to afford the desired 2,5-diarylpyrrole derivative **31** through a double direct desulfitative

Table 3. Synthesis of 7-aryldibenzo[*c*,*e*]pyrrolo[1,2-*a*]azepine derivatives by palladium-catalyzed iterative C–H bond arylations.

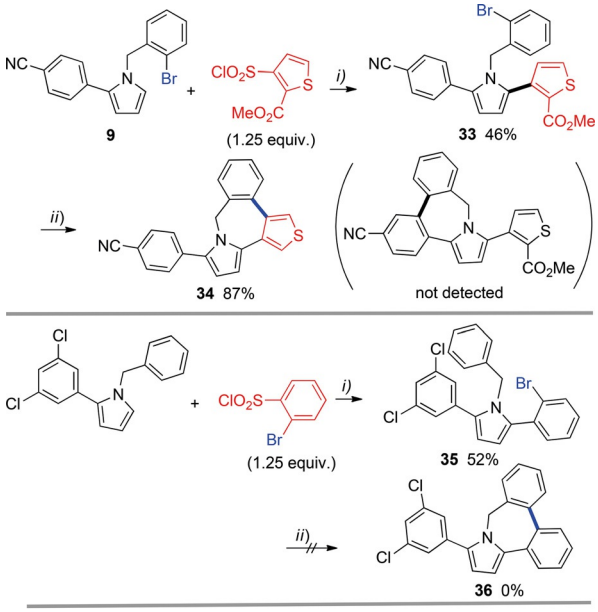


i) $PdCl_2(CH_3CN)_2$ (5 mol%), Li_2CO_3 (3 equiv.), 1,4-dioxane, 140 °C 24 h;
ii) $PdCl(C_3H_5)(dppb)$ (2 mol%), PivOK (2 equiv.), DMA, 150 °C, 24 h

Entry $ArSO_2$–Cl	Step 1	Step 2
1	 **21** 77%	 **22** 38%
2	 **23** 76%	 **24** 62%
3	 **25** (*not isolated*)	 **26** 77% over 2 steps
4	 **27** (*not isolated*)	 δ = 126.2 ppm (q, *J* = 3.7 Hz) δ = 125.9 ppm (q, *J* = 3.7 Hz) δ = 124.1 ppm (q, *J* = 272.0 Hz) δ = 124.0 ppm (q, *J* = 3.7 Hz) **28** 49% over 2 steps
5	 **29** (*not isolated*)	 **30** 76% over 2 steps
6	 **31** (*not isolated*)	 **32** 65% over 2 steps

arylation catalyzed by 5 mol% of $PdCl_2(CH_3CN)_2$. Again, as a result of the purification issue with such a fluorinated molecule, the $PdCl(C_3H_5)(dppb)$-catalyzed intramolecular arylation was directly performed on the crude mixture, after a simple filtration on silica gel, to afford the N-condensed heterocycle **32** in 65% overall yield.

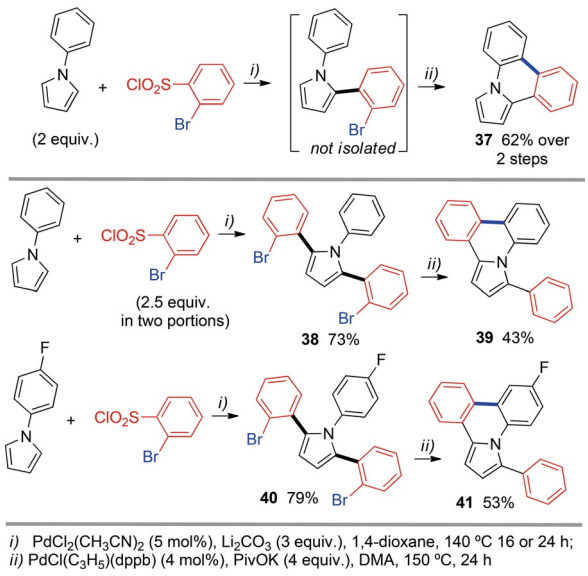
Next, we investigated the reactivity of unsymmetrical 2,5-di(aryl)pyrroles in the palladium-catalyzed direct intramolecular reaction (Scheme 2). From the C2-arylated pyrrole **9**, we performed a second desulfitative arylation with methyl 3-(chlorosulfonyl)thiophene-2-carboxylate as the coupling partner. The previous optimized reaction conditions, namely, 5 mol% of $PdCl_2(CH_3CN)_2$ in the presence of 3 equivalents of Li_2CO_3 in 1,4-dioxane at $T = 140\,^{\circ}C$, led to the unsymmetrical 2,5-di(aryl)pyrrole **33** in a moderate 45% yield. With this substrate in hand, we performed the cyclization reaction with $PdCl(C_3H_5)(dppb)$ as the catalyst in the presence of 2 equivalents of PivOK as the base in DMA. We were pleased to find that the direct intramolecular arylation exclusively occurred at the thienyl C–H bond to afford **34** in 87% yield as a single regioisomer. The reaction conditions also promoted an in situ decarboxylation[16] (Scheme 2, top). The arylation took place at the C4 position of the thiophene, so we assumed that the arylation occurred first, followed by the decarboxylation. We also attempted to perform a reversed seven-membered-ring cyclization with a reactant bearing the bromo substituent on the benzenesulfonyl chloride partner and the C–H bond on the benzyl group (Scheme 2, bottom). Firstly, we synthesized the precursor **35** from 1-benzyl-2-(3,5-dichlorophenyl)pyrrole and 2-bromobenzenesulfonyl chloride by using our standard desulfitative direct arylation conditions. Unfortunately, **35** was found to be unreactive for the direct intramolecular arylation, and **36** was not obtained. We impute this lack of reactivity to the lower degree of freedom of the C(benzyl)–N bond, which prevents a suitable conformation for the cyclization.



i) $PdCl_2(CH_3CN)_2$ (5 mol%), Li_2CO_3 (3 equiv.), 1,4-dioxane, 140 °C;
ii) $PdCl(C_3H_5)(dppb)$ (2 mol%), PivOK (2 equiv.), DMA, 150 °C, 24 h

Scheme 2. Palladium-catalyzed iterative arylations from 1-(2-bromobenzyl)-2-(4-cyanophenyl)pyrrole and 1-benzyl-2-(3,5-dichlorophenyl)pyrrole.

Finally, we investigated the potential of our iterative palladium-catalyzed direct arylations for the synthesis of pyrrolo[1,2,*f*]phenanthridines (that is, six-membered rings; Scheme 3). From *N*-phenylpyrrole and 2-bromobenzenesulfonyl chloride, the desulfitative direct arylation conditions (that is, 5 mol% of $PdCl_2(CH_3CN)_2$, Li_2CO_3, 1,4-dioxane, $T = 140\,^{\circ}C$) allowed the formation of 2-(2-bromophenyl)-1-phenylpyrrole,



Scheme 3. Synthesis of pyrrolo[1,2,*f*]phenanthridine derivatives by iterative palladium-catalyzed direct arylations.

which was not purified. After simple filtration over silica gel to remove inorganic salts, the crude mixture was directly heated in the presence of 2 mol% of $PdCl(C_3H_5)(dppb)$ as the catalyst and PivOK as the base to give pyrrolo[1,2-*f*]phenanthridine **37** in 62% yield over two steps (Scheme 3, top). Then, with similar reaction conditions for the Pd-catalyzed desulfitative arylation but with the addition of 2.5 equivalents of 2-bromobenzenesulfonyl chloride in two portions, 2,5-bis(2-bromophenyl)-1-phenylpyrrole **38** was obtained in 73% yield. Pyrrole **38** was then subjected to intramolecular arylation with our previous best conditions (that is, 4 mol% of $PdCl(C_3H_5)(dppb)$, 4 equivalents of PivOK, DMA, $T=150\,^{\circ}C$). Unfortunately, the expected benzo[7,8]indolizino[6,5,4,3-*def*]phenanthridine resulting from two intramolecular C–H bond arylations was not detected, and only pyrrolo[1,2,*f*]phenanthridine **39** was obtained in 43% yield. This derivative was generated by an intramolecular direct arylation and a debromination. We assume that the second intramolecular direct arylation did not occur because of a too congested structure (Scheme 3, bottom). Similar results were observed with 1-(4-fluorophenyl)pyrrole, which afforded the six-membered-ring fused polycyclic derivative **41** in two steps in 53% yield.

Conclusions

In summary, we have disclosed a novel iterative C–H bond arylation pathway for the synthesis of medium-size N-condensed pyrroles from *N*-(2-bromobenzyl)pyrrole and *N*-phenylpyrrole. These iterative reactions firstly involve an uncommon palladium-catalyzed intermolecular direct arylation followed by a second palladium-catalyzed intramolecular arylation. These intermolecular direct arylations were performed though desulfitative couplings, which tolerate C–Br bonds, with a wide variety of benzenesulfonyl chlorides as arylating agents. Two sets of reaction conditions have been developed for the selective synthesis of C2-arylated pyrroles and C2,C5-diarylated pyrroles. After desulfitative monoarylation, Pd-catalyzed intramolecular arylation led to new five-membered-ring pyrrolo[2,1,*a*]isoindoles in high yields and regioselectivities, whereas diarylated pyrroles allowed the formation of seven-membered-ring dibenzo[*c*,*e*]pyrrolo[1,2,*a*]azepines, also in both high yields and regioselectivities, even with unsymmetrical 2,5-diarylpyrroles. Finally, this iterative process was also employed for an efficient synthesis of six-membered polycyclic pyrroles from simple *N*-phenylpyrrole and 2-bromobenzenesulfonyl chlorides.

Experimental Section

All reactions were carried out under an argon atmosphere with standard Schlenk techniques. 1,4-Dioxane and DMA were purchased from Acros Organics and were not purified before use. ^1H NMR spectra were recorded on Bruker GPX (400 MHz) spectrometer. Chemical shifts (δ) were reported in parts per million relative to residual chloroform ($\delta=7.26$ ppm for ^1H; $\delta=77.0$ ppm for ^{13}C); coupling constants were reported in Hertz. ^1H NMR assignment abbreviations were: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). ^{13}C NMR spectra were recorded at 100 MHz on the same spectrometer and reported in ppm. All reagents were weighed and handled in air.

Procedure A (desulfitative monoarylation): Arylsulfonyl chlorides (1 mmol), heteroarene derivatives (1.2–1.5 mmol), Li_2CO_3 (0.222 g, 3 mmol), 1,4-dioxane (2 mL), and bis(acetonitrile)dichloropalladium(II) (12.9 mg, 0.05 mmol) were successively added to a 5 mL oven-dried Schlenk tube. The reaction mixture was evacuated by vacuum–argon cycles (5 times) and stirred at $T=140\,^{\circ}C$ (oil-bath temperature) for 16–18 h (see tables and schemes). After the reaction mixture was cooled at room temperature and concentrated, the crude mixture was purified by silica column chromatography to afford the desired arylated products.

Procedure B (desulfitative diarylation): Arylsulfonyl chlorides (1.25 mmol), heteroarene derivatives (1.2–1.5 mmol), Li_2CO_3 (0.222 g, 3 mmol), 1,4-dioxane (2 mL), and bis(acetonitrile)dichloropalladium(II) (12.9 mg, 0.05 mmol) were successively added to a 5 mL oven-dried Schlenk tube. The reaction mixture was evacuated by vacuum–argon cycles (5 times) and stirred at $T=140\,^{\circ}C$ (oil-bath temperature) for 16–18 h (see tables and schemes). After 15 h, the solution was cooled down, and arylsulfonyl chloride (1.25 mmol) was added again. The reaction was heated again at $T=140\,^{\circ}C$ for 18 h. After the reaction mixture was cooled at room temperature and concentrated, the crude mixture was purified to afford the desired diarylated products.

Safety information: The reaction vessel should be opened under a fume hood because these desulfitative coupling reactions released sulfur dioxide (SO_2) gas, which is toxic.

Procedure C (cyclization): As a typical experiment, the reaction of the aryl bromide (0.2–0.5 mmol), AcOK (2 equiv.) or PivOK (2 equiv.) at $T=150\,^{\circ}C$ for 16 h in DMA (2 mL) in the presence of $Pd(OAc)_2$ (2 mol%), $PdCl_2$ (2 mol%), or $PdCl(C_3H_5)(dppb)$ (2 mol%) (see tables and schemes) under argon affords the cyclized product after evaporation of the solvent and purification by silica column chromatography.

1-(2-Bromobenzyl)-2-(3-fluorophenyl)pyrrole (1): After following procedure A with 1-(2-bromobenzyl)pyrrole (283 mg, 1.2 mmol)

and 3-fluorobenzenesulfonyl chloride (133 μL, 1 mmol), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **1** (247 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (dd, J = 1.5, 7.9 Hz, 1H), 7.22–7.14 (m, 2H), 7.06 (t, J = 7.7 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 6.94–6.85 (m, 2H), 6.68 (dd, J = 1.9, 2.8 Hz, 1H), 6.55 (d, J = 7.7 Hz, 1H), 6.27 (dd, J = 1.9, 3.6 Hz, 1H), 6.24 (t, J = 3.1 Hz, 1H), 5.12 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9 (d, J = 240.8 Hz), 138.1, 135.3 (d, J = 8.6 Hz), 133.9, 132.9, 130.2 (d, J = 8.5 Hz), 129.2, 128.1, 128.0, 124.2, 123.9, 121.9, 115.5 (d, J = 22.2 Hz), 114.1 (d, J = 21.0 Hz), 110.0, 109.2, 53.1 ppm; elemental analysis: calcd (%) for $C_{17}H_{13}BrFN$ (330.20): C 61.84, H 3.97; found: C 62.06, H 4.02.

1-(2-Bromobenzyl)-2,5-bis(3-fluorophenyl)pyrrole (2): After following procedure B with 1-(2-bromobenzyl)pyrrole (235 mg, 1 mmol) and 3-fluorobenzenesulfonyl chloride (332 μL, 2.5 mmol), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **2** (368 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 7.9 Hz, 1H), 7.21–7.15 (m, 2H), 7.09 (t, J = 7.7 Hz, 1H), 7.01 (d, J = 7.9 Hz, 2H), 6.98–6.92 (m, 3H), 6.88 (dt, J = 2.6, 8.6 Hz, 2H), 6.34 (s, 2H), 6.33–6.31 (m, 1H), 5.17 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7 (d, J = 244.8 Hz), 138.0, 135.8, 135.1 (d, J = 8.2 Hz), 132.5, 129.9 (d, J = 9.3 Hz), 128.7, 127.8, 127.4, 124.3, 120.9, 115.7 (d, J = 22.0 Hz), 114.2 (d, J = 21.5 Hz), 110.6, 49.2 ppm; elemental analysis: calcd (%) for $C_{23}H_{16}BrF_2N$ (424.29): C 65.11, H 3.80; found: C 65.27, H 3.67.

3-(3-Fluorophenyl)pyrrolo[2,1-*a*]isoindole (3): After following procedure C with 1-(2-bromobenzyl)-2-(3-(fluorophenyl)pyrrole (**1**; 165 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **3** (102 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 7.6 Hz, 1H), 7.44–7.32 (m, 5H), 7.23 (t, J = 7.4 Hz, 1H), 6.96 (ddt, J = 1.6, 2.6 and 8.1 Hz, 1H), 6.70 (d, J = 3.8 Hz, 1H), 6.46 (d, J = 3.8 Hz, 1H), 5.14 ppm (s, 2H); ^{3}C NMR (100 MHz, $CDCl_3$): δ = 163.2 (d, J = 245.9 Hz), 140.5, 139.7, 134.9 (d, J = 9.0 Hz), 133.1, 130.2 (d, J = 9.0 Hz), 129.5, 128.1, 125.2, 122.9, 120.1, 118.7, 112.7 (d, J = 21.6 Hz), 112.3, 111.2 (d, J = 21.6 Hz), 99.8, 51.5 ppm; elemental analysis: calcd (%) for $C_{17}H_{12}FN$ (249.29): C 81.91, H 4.85; found: C 82.16, H 4.65.

1-Fluoro-7-(3-fluorophenyl)dibenzo[*c*,*e*]pyrrolo[1,2-*a*]azepine (4): After following procedure C with 1-(2-bromobenzyl)-2,5-bis(3-fluorophenyl)pyrrole (**2**; 212 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **4** (153 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dt, J = 2.9, 5.8 Hz, 1H), 7.47 (t, J = 8.3 Hz, 2H), 7.44–7.35 (m, 3H), 7.34–7.30 (m, 1H), 7.24 (d, J = 7.7 Hz, 1H), 7.19–7.14 (m, 2H), 7.13–7.06 (m, 1H), 6.49 (d, J = 3.7 Hz, 1H), 6.26 (d, J = 3.7 Hz, 1H), 5.04 (d, J = 14.0 Hz, 1H), 4.69 ppm (d, J = 14.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8 (d, J = 249.5 Hz), 160.2 (d, J = 249.5 Hz), 138.0, 135.1 (d, J = 8.1 Hz), 134.7, 133.9, 133.0, 132.2 (d, J = 7.8 Hz), 130.1 (d, J = 8.7 Hz), 129.1, 128.4, 127.5 (d, J = 8.2 Hz), 125.2 (dd, J = 3.3, 24.3 Hz), 123.8, 119.3, 116.4, 116.2, 114.4, 114.3, 114.1, 109.8, 108.0, 47.7 ppm; elemental analysis: calcd (%) for $C_{23}H_{15}F_2N$ (343.38): C 80.45, H 4.40; found: C 80.68, H 4.67.

1-(2-Bromobenzyl)-2-(4-nitrophenyl)pyrrole (5): After following procedure A with 1-(2-bromobenzyl)pyrrole (283 mg, 1.2 mmol) and 4-nitrobenzenesulfonyl chloride (222 mg, 1 mmol), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **5** (278 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.8 Hz, 2H), 7.49 (dd, J = 1.4, 7.9 Hz, 1H), 7.33 (d, J = 8.8 Hz, 2H), 1.19–7.15 (m, 1H), 6.77 (dd, J = 1.8, 2.8 Hz, 1H), 6.58 (dd, J = 1.8, 7.7 Hz, 1H), 6.42 (dd, J = 1.8, 3.7 Hz, 1H), 6.29 (dd, J = 2.8, 3.7 Hz, 1H), 5.16 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ) = 145.2, 141.6, 138.3, 131.9, 131.6, 128.3, 127.1, 127.0, 126.7, 124.8, 123.0, 120.6, 110.8, 108.8, 50.6 ppm; elemental analysis: calcd (%) for $C_{17}H_{13}BrN_2O_2$ (357.21): C 57.16, H 3.67; found: C 57.33, H 3.79.

1-(2-Bromobenzyl)-2-(4-(trifluoromethyl)phenyl)pyrrole (7): After following procedure A with 1-(2-bromobenzyl)pyrrole and 4-(trifluoromethyl)benzenesulfonyl chloride (160 μL, 1 mmol), the residue was filtrated on a silica plug and directly used in the next reaction.

3-(4-(Trifluoromethyl)phenyl)pyrrolo[2,1-*a*]isoindole (8): After following procedure C with the crude mixture of 1-(2-bromobenzyl)-2-(4-(trifluoromethyl)phenyl)pyrrole (**7**), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound 7 (170 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 7.3 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 7.23 (t, J = 7.0 Hz, 1H), 6.75 (d, J = 3.8 Hz, 1H), 6.46 (d, J = 3.8 Hz, 1H), 5.16 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 139.6, 136.2, 132.9, 129.2, 127.6 (q, J = 33.2 Hz), 125.9, 125.8, 125.5, 124.3 (q, J = 270 Hz), 124.3, 123.0, 118.9, 113.1, 100.1, 51.8 ppm; elemental analysis: calcd (%) for $C_{18}H_{12}F_3N$ (299.30): C 72.24, H 4.04; found: C 74.58, H 4.23.

1-(2-Bromobenzyl)-2-(4-cyanophenyl)pyrrole (9): After following procedure A with 1-(2-bromobenzyl)pyrrole (283 mg, 1.2 mmol) and 4-cyanobenzenesulfonyl chloride (201 mg, 1 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 95:5) to afford the desired compound **9** (239 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.56 (m, 3H), 7.38 (d, J = 8.3 Hz, 2H), 7.28–7.24 (m, 1H), 7.17 (ddd, J = 1.6, 7.4, 8.0 Hz, 1H), 6.84 (dd, J = 1.8, 2.8 Hz, 1H), 6.66 (dd, J = 1.8, 7.7 Hz, 1H), 6.46 (dd, J = 1.8, 3.7 Hz, 1H), 6.37 (dd, J = 2.8, 3.7 Hz, 1H), 5.22 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 137.4, 132.9, 132.8, 132.4, 129.2, 128.2, 128.0, 127.8, 125.3, 121.7, 118.9, 111.2, 110.1, 109.6, 51.5 ppm; elemental analysis: calcd (%) for $C_{18}H_{13}BrN_2$ (337.22): C 64.11, H 3.89; found: C 63.38, H 3.86.

3-(4-(Cyanophenyl)pyrrolo[2,1-*a*]isoindole (10): After following procedure C with 1-(2-bromobenzyl)-2-(4-cyanophenyl)pyrrole (**9**; 169 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **10** (118 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.68 (m, 4H), 7.60 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 7.3 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.27–7.24 (m, 1H), 6.83 (d, J = 3.9 Hz, 1H), 6.50 (d, J = 3.9 Hz, 1H), 5.20 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.1, 139.7, 136.9, 132.7, 128.7, 128.3, 125.8, 124.1, 123.0, 119.2, 119.1, 114.1, 108.5, 100.6, 52.0 ppm; elemental analysis: calcd (%) for $C_{18}H_{12}N_2$ (256.31): C 84.35, H 4.72; found: C 84.56, H 4.93.

1-(2-Bromobenzyl)-2-(4-methylphenyl)pyrrole (11): After following procedure A with 1-(2-bromobenzyl)pyrrole (283 mg, 1.2 mmol) and 4-methylbenzenesulfonyl chloride (191 mg, 1 mmol), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **11** (137 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.0 Hz, 1H), 7.27–7.13 (m, 6H), 6.74 (t, J = 2.3 Hz, 1H), 6.66 (dd, J = 1.8, 7.8 Hz, 1H), 6.34–6.30 (m, 2H), 5.19 (s, 2H), 2.36 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 136.8, 135.0, 132.5, 130.1, 129.2, 128.8, 128.5, 128.0, 127.8, 122.7, 121.6, 108.8, 108.7, 51.0, 21.1 ppm; elemental analysis: calcd (%) for $C_{18}H_{16}BrN$ (326.23): C 66.27, H 4.94; found: C 66.49, H 5.11.

3-(4-(Methylphenyl)pyrrolo[2,1-*a*]isoindole (12): After following procedure C with 1-(2-bromobenzyl)-2-(4-methylphenyl)pyrrole (**11**;

163 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **12** (108 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.53 (m, 3H), 7.42 (d, J = 7.4 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 7.6 Hz, 2H), 7.20 (t, J = 7.7 Hz, 1H), 6.63 (d, J = 3.7 Hz, 1H), 6.44 (d, J = 3.7 Hz, 1H), 5.15 (s, 2H), 2.42 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.7, 139.6, 136.0, 133.5, 130.9, 130.2, 129.5, 128.1, 124.9, 124.7, 122.9, 118.5, 110.9, 99.5, 51.4, 21.2 ppm; elemental analysis: calcd (%) for $C_{18}H_{15}N$ (245.33): C 88.13, H 6.16; found: C 88.45, H 6.28.

1-(2-Bromobenzyl)-2-(3-(trifluoromethyl)phenyl)pyrrole (13): After following procedure A with 1-(2-bromobenzyl)pyrrole and 3-(trifluoromethyl)benzenesulfonyl chloride (160 μL, 1 mmol), the residue was filtrated on a silica plug and directly used in the next reaction.

3-(3-(Trifluoromethyl)phenyl)pyrrolo[2,1-*a*]isoindole (14): After following procedure C with the crude mixture of 1-(2-bromobenzyl)-2-(3-(trifluoromethyl)phenyl)pyrrole (**13**), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **14** (203 mg, 68% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (br s, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.49–7.44 (m, 2H), 7.42–7.35 (m, 2H), 7.3 (t, J = 7.4 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.64 (d, J = 3.78 Hz, 1H), 6.37 (d, J = 3.76 Hz, 1H), 5.09 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.9, 139.5, 135.9, 133.6, 133.0, 129.3, 129.2, 128.2, 127.5, 127.5, 125.4, 123.0, 122.5 (q, J = 4.5 Hz), 121.0 (q, J = 4.5 Hz), 118.8, 112.5, 100.0, 51.5 ppm; elemental analysis: calcd (%) for $C_{18}H_{12}F_3N$ (299.30): C 72.24, H 4.04; found: C 74.58, H 4.23.

1-(2-Bromobenzyl)-2-(3,5-dichlorophenyl)pyrrole (15): After following procedure A with 1-(2-bromobenzyl)pyrrole (283 mg, 1.2 mmol) and 3,5-dichlorobenzenesulfonyl chloride (245 mg, 1 mmol), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **15** (308 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (dd, J = 1.4, 7.9 Hz, 1H), 7.28–7.22 (m, 2H), 7.19–7.14 (m, 3H), 6.8 (dd, J = 1.8, 2.8 Hz, 1H), 6.65 (dd, J = 1.8, 7.7 Hz, 1H), 6.38–6.36 (m, 1H), 6.33 (dd, J = 2.7, 3.5 Hz, 1H), 5.2 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 135.8, 134.9, 132.8, 132.0, 129.2, 128.0, 127.9, 126.9, 126.6, 124.5, 121.8, 110.7, 109.2, 51.3 ppm; elemental analysis: calcd (%) for $C_{17}H_{12}BrCl_2N$ (381.09): C 53.58, H 3.17; found: C 53.41, H 2.26.

3-(3,5-Dichlorophenyl)pyrrolo[2,1-*a*]isoindole (16): After following procedure C with 1-(2-bromobenzyl)-2-(3,5-dichlorophenyl)pyrrole (**15**; 191 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **16** (124 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 1.9 Hz, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.31 Hz, 1H), 7.21–7.19 (m, 1H), 6.68 (d, J = 3.9 Hz, 1H), 6.42 (d, J = 3.9 Hz, 1H), 5.10 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3, 139.6, 135.6, 135.4, 132.8, 128.3, 127.8, 125.6, 125.5, 123.0, 122.5, 118.9, 113.2, 100.2, 51.6 ppm; elemental analysis: calcd (%) for $C_{17}H_{11}Cl_2N$ (300.18): C 68.02, H 3.69; found: C 68.31, H 3.85.

1-(2-Bromobenzyl)-2-(2-fluorophenyl)pyrrole (17): After following procedure A with 1-(2-bromobenzyl)pyrrole (283 mg, 1.2 mmol) and 2-fluorobenzenesulfonyl chloride (132 μL, 1 mmol), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **17** (215 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (dd, J = 1.5, 7.9 Hz, 1H), 7.33–7.20 (m, 3H), 7.15–7.09 (m, 3H), 6.79 (t, J = 2.3 Hz, 1H), 6.65 (dd, J = 1.8, 7.8 Hz, 1H), 7.37–7.33 (m, 2H), 5.13 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.0 (d, J = 243.2 Hz), 137.8, 132.4, 132.0, 132.0, 129.5, 129.4, 128.8, 128.3, 127.7, 124.1 (d, J = 5.2 Hz), 123.0, 115.9, 115.7, 110.7, 108.9, 51.2 ppm; elemental analysis: calcd (%) for $C_{17}H_{13}BrFN$ (330.20): C 61.84, H 3.97; found: C 62.08, H 4.11.

3-(2-Fluorophenyl)pyrrolo[2,1-*a*]isoindole (18): After following procedure C with 1-(2-bromobenzyl)-2-(2-fluorophenyl)pyrrole (**17**; 165 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **18** (96 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.55 (m, 2H), 7.42–7.35 (m, 2H), 7.33–7.27 (m, 1H), 7.25–7.17 (m, 3H), 6.65 (dd, J = 1.6, 3.7 Hz, 1H), 6.47 (d, J = 3.7 Hz, 1H), 5.06 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3 (d, J = 242.6 Hz), 140.9 (d, J = 14.3 Hz), 133.4, 128.9 (d, J = 2.9 Hz), 128.2 (d, J = 8.3 Hz), 128.0, 125.2, 125.1, 124.3, 124.2, 122.9, 121.0 (d, J = 13.9 Hz), 118.7, 116.2 (d, J = 22.7 Hz), 114.4 (d, J = 4.4 Hz), 99.4, 51.2 ppm; elemental analysis: calcd (%) for $C_{17}H_{12}FN$ (249.29): C 81.91, H 4.85; found: C 82.16, H 4.65.

1-(2-Bromobenzyl)-2-(2,3,4-trifluorophenyl)pyrrole (19): After following procedure A with 1-(2-bromobenzyl)pyrrole (283 mg, 1.2 mmol) and 2,3,4-trifluorobenzenesulfonyl chloride (141 μL, 1 mmol), the residue was filtrated on a silica plug and directly used in the next reaction.

3-(2,3,4-trifluorophenyl)pyrrolo[2,1-*a*]isoindole (20): After following procedure C with the crude mixture of 1-(2-bromobenzyl)-2-(2,3,4,-trifluorophenyl)pyrrole (**19**), the residue was purified by flash chromatography on silica gel (pentane) to afford the desired compound **20** (188 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, J = 7.6 Hz, 1H), 7.32–7.26 (m, 2H), 7.18–7.10 (m, 2H), 6.96 (ddt, J = 2.0, 7.0, 9.4 Hz, 1H), 6.52 (dd, J = 1.7, 3.8 Hz, 1H), 6.37 (d, J = 3.8 Hz, 1H), 4.93 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.0 (d, J = 250.0 Hz), 149.9 (d, J = 250.0 Hz), 148.3 (d, J = 250.0 Hz), 141.9, 140.6, 139.9, 133.1, 128.1, 125.4, 123.2, 122.9, 121.8 (m), 118.9, 114.8 (dd, J = 3.4, 7.7 Hz), 112.2 (d, J = 3.7 Hz), 99.6, 51.2 ppm; elemental analysis: calcd (%) for $C_{17}H_{10}F_3N$ (285.27): C 71.58, H 3.53; found: C 71.67, H 3.84.

1-(2-Bromobenzyl)-2,5-di-*p*-tolylpyrrole (21): After following procedure B with 1-(2-bromobenzyl)pyrrole (236 mg, 1 mmol) and 4-methylbenzenesulfonyl chloride (476 mg, 2.5 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **21** (321 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.0 Hz, 1H), 7.24–7.17 (m, 5H), 7.12 (d, J = 8.2 Hz, 4H), 7.04 (t, J = 7.9 Hz, 1H), 7.04 (t, J = 7.9 Hz, 1H), 6.39 (s, 2H), 5.24 (s, 2H), 2.34 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9, 136.9, 136.3, 132.2, 130.5, 129.1, 128.7, 128.4, 127.7, 127.6, 120.8, 109.5, 49.1, 21.2 ppm; elemental analysis: calcd (%) $C_{25}H_{22}BrN$ for (416.36): C 72.12, H 5.33; found: C 72.47, H 5.01.

2-Methyl-7-(*p*-tolyl)dibenzo[*c*,*e*]pyrrolo[1,2-*a*]azepine (22): After following procedure C with 1-(2-bromobenzyl)-2,5-di-*p*-tolylpyrrole (**21**; 208 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **30** (64 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, J = 7.4 Hz, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.47 (s, 1H), 7.44–7.38 (m, 3H), 7.34 (d, J = 7.35 Hz, 2H), 7.29–7.25 (m, 1H), 7.18–7.12 (m, 2H), 6.48 (d, J = 3.7 Hz, 1H), 6.26 (d, J = 3.7 Hz, 1H), 5.07 (d, J = 14.1 Hz, 1H), 4.7 (d, J = 14.0 Hz, 1H), 2,50 (s, 3H), 2.47 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 139.5, 137.7, 136.6, 135.9, 134.5, 134.5, 130.9, 130.8, 130.1, 129.8, 129.4, 129.2, 129.0, 128.9, 127.3, 126.7, 125.9, 108.8, 106.6, 47.9, 21.2, 21.1 ppm; elemental analysis: calcd (%) for $C_{25}H_{21}N$ (335.45): C 89.51, H 6.31; found: C 89.76, H 6.12.

4,4′-(1-(2-Bromobenzyl)pyrrole-2,5-diyl)dibenzonitrile (23): After following procedure B with 1-(2-bromobenzyl)pyrrole (236 mg,

1 mmol) and 4-cyanobenzenesulfonyl chloride (504 mg, 2.5 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **23** (333 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.62$ (d, $J = 8.3$ Hz, 4H), 7.47–7.41 (m, 5H), 7.19 (t, $J = 7.4$ Hz, 1H), 7.09 (t, $J = 7.7$ Hz, 1H), 6.55 (s, 2H), 6.42 (d, $J = 7.7$ Hz, 1H), 5.27 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.3$, 137.1, 136.4, 132.8, 132.4, 129.2, 128.8, 128.0, 127.1, 121.0, 118.7, 112.3, 110.9, 49.6 ppm; elemental analysis: calcd (%) for $C_{25}H_{16}BrN_3$ (438.32): C 68.50, H 3.68; found: C 68.64, H 3.89.

7-(4-Cyanophenyl)dibenzo[*c*,*e*]pyrrolo[1,2-*a*]azepine-2-carbonitrile (24): After following procedure C with 4,4′-(1-(2-bromobenzyl)-pyrrole-2,5-diyl)dibenzonitrile (**23**; 219 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **24** (111 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.93$ (s, 1H), 7.79 (t, $J = 8.9$ Hz, 3H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.63 (d, $J = 7.3$ Hz, 1H), 7.57 (d, $J = 8.3$ Hz, 2H), 7.50 (quint., $J = 6.5$ Hz, 2H), 7.34 (d, $J = 7.5$ Hz, 1H), 6.62 (d, $J = 3.9$ Hz, 1H), 6.39 (d, $J = 3.9$ Hz, 1H), 5.02 (d, $J = 14.2$ Hz, 1H), 4.72 ppm (d, $J = 14.3$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 146.4$, 138.3, 137.1, 137.0, 136.8, 135.7, 134.9, 134.4, 132.5, 131.0, 130.4, 129.9, 129.4, 129.2, 129.1, 128.0, 127.5, 118.8, 111.7, 110.9, 110.6, 110.0, 48.2 ppm; elemental analysis: calcd (%) for $C_{25}H_{15}N_3$ (357.41): C 84.01, H 4.23; found: C 83.86, H 4.38.

1-(2-Bromobenzyl)-2,5-bis(4-(trifluoromethyl)phenyl)pyrrole (25): After following procedure B with 1-(2-bromobenzyl)pyrrole (118 mg, 0.5 mmol) and 4-(trifluoromethyl)benzenesulfonyl chloride (306 mg, 1.25 mmol), the residue was filtrated on a silica plug and directly used in the next reaction.

2-(Trifluoromethyl)-7-(4-(trifluoromethyl)phenyl)dibenzo[*c*,*e*]pyrrolo[1,2-*a*]azepine (26): After following procedure C with the crude mixture of 1-(2-bromobenzyl)-2,5-bis(4-(trifluoromethyl)phenyl)pyrrole (**25**), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **26** (171 mg, 77%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.81$ (br s, 1H), 7.75–7.66 (m, 3H), 7.62–7.57 (m, 2H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.40 (qq, $J = 6.7$, 7.4 Hz, 2H), 7.26 (dd, $J = 1.9$, 7.2 Hz, 1H), 6.51 (d, $J = 3.8$ Hz, 1H), 6.27 (d, $J = 3.8$ Hz, 1H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.64 ppm (d, $J = 14.1$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.1$, 137.4, 136.4, 135.1, 134.5, 134.4, 130.3, 129.7, 129.6, 129.4 (q, $J = 30.1$ Hz), 129.3, 129.0 (q, $J = 29.5$ Hz), 128.9, 128.7, 125.6, 125.5 (q, $J = 270.3$ Hz), 124.6 (m), 124.2 (q, $J = 271.3$ Hz), 110.8, 109.0, 48.1 ppm; elemental analysis: calcd (%) for $C_{25}H_{15}F_6N$ (443.38): C 67.72, H 3.41; found: C 67.99, H 3.18.

1-(2-Bromobenzyl)-2,5-bis(3-(trifluoromethyl)phenyl)pyrrole (27): After following procedure B with 1-(2-bromobenzyl)pyrrole (118 mg, 0.5 mmol) and 3-(trifluoromethyl)benzenesulfonyl chloride (306 mg, 1.25 mmol), the residue was filtrated on a silica plug and directly used in the next reaction.

3-(Trifluoromethyl)-7-(3-(trifluoromethyl)phenyl)dibenzo[*c*,*e*]pyrrolo[1,2-*a*]azepine (28): After following procedure C with the crude mixture of 1-(2-bromobenzyl)-2,5-bis(3-(trifluoromethyl)phenyl)pyrrole (**27**), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **28** (109 mg, 49%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (s, 1H), 7.77–7.73 (m, 2H), 7.69–7.64 (m, 4H), 7.63 (s, 1H), 7.52–7.45 (m, 2H), 7.39–7.34 (m, 1H), 6.59 (d, $J = 3.8$ Hz, 1H), 6.35 (d, $J = 3.8$ Hz, 1H), 4.99 (d, $J = 14.3$ Hz, 1H), 4.71 ppm (d, $J = 14.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 139.2$, 139.0, 137.6, 134.3, 134.0, 133.6, 132.5, 131.1 (q, $J = 30.6$ Hz), 131.0, 130.5, 130.31 (q, $J = 30.6$ Hz), 129.2, 128.9, 128.8, 127.5, 126,2 (q, $J = 3.7$ Hz), 125.9 (q, $J = 3.7$ Hz), 124.2 (q, $J = 272.0$ Hz), 124.1 (q, $J = 272.0$ Hz), 124.0 (q, $J = 3.7$ Hz), 123.4 (q, $J = 3.7$ Hz), 110.5, 108.4, 48.0 ppm; elemental analysis: calcd (%) for $C_{25}H_{15}F_6N$ (443.38): C 67.72, H 3.41; found: C 67.51, H 3.59.

1-(2-Bromobenzyl)-2,5-bis(3,5-dichlorophenyl)pyrrole (29): After following procedure B with 1-(2-bromobenzyl)pyrrole (118 mg, 0.5 mmol) and 3,5-dichlorobenzenesulfonyl chloride (306 mg, 1.25 mmol), the residue was filtrated on a silica plug and directly used in the next reaction.

1,3-Dichloro-7-(3,5-dichlorophenyl)dibenzo[*c*,*e*]pyrrolo[1,2-*a*]azepine (30): After following procedure C with the crude mixture of 1-(2-bromobenzyl)-2,5-bis(3,5-dichlorophenyl)pyrrole (**29**; 158 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **30** (122 mg, 91%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.76$ (dd, $J = 2.6$, 6.9 Hz, 1H), 7.57 (d, $J = 2.2$ Hz, 1H), 7.53 (d, $J = 2.2$ Hz, 1H), 7.44–7.38 (m, 3H), 7.34 (d, $J = 2.0$ Hz, 2H), 7.30–7.27 (m, 2H), 6.50 (d, $J = 3.8$ Hz, 1H), 6.26 (d, $J = 3.8$ Hz, 1H), 4.98 (d, $J = 13.9$ Hz, 1H), 4.69 ppm (d, $J = 14.1$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.0$, 135.6, 135.6, 135.1, 134.8, 134.3, 133.7, 133.3, 132.8, 132.7, 132.5, 128.8, 128.8, 128.1, 127.5, 127.3, 127.1, 127.0, 110.5, 108.8, 47.7 ppm; elemental analysis: calcd (%) for $C_{23}H_{13}Cl_4N$ (445.16): C 62.06, H 2.94; found: C 62.01, H 3.07.

1-(2-Bromobenzyl)-2,5-bis(2,3,4-trifluorophenyl)pyrrole (31): After following procedure B with 1-(2-bromobenzyl)pyrrole (236 mg, 1 mmol) and 2,3,4-trifluorobenzenesulfonyl chloride (288 mg, 1.25 mmol), the residue was filtrated on a silica plug and directly used in the next reaction.

2,3,4-Trifluoro-7-(2,3,4-trifluorophenyl)dibenzo[*c*,*e*]pyrrolo[1,2-*a*]azepine (32): After following procedure C with the crude mixture of 1-(2-bromobenzyl)-2,5-bis(2,3,4-trifluorophenyl)pyrrole (**31**), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **32** (270 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.49$ (d, $J = 7.5$ Hz, 1H), 7.41 (dt, $J = 1.6$, 7.5 Hz, 1H), 7.34 (dt, $J = 1.6$, 7.1 Hz, 1H), 7.26–7.21 (m, 1H), 7.12–7.06 (m, 3H), 6.63 (dd, $J = 3.8$, 4.8 Hz, 1H), 6.31 (d, $J = 3.8$ Hz, 1H), 4.75 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 142.9$ (dm, $J = 246.3$ Hz), 141.8 (dm, $J = 246.3$ Hz), 140.4 (dm, $J = 246.3$ Hz), 139.8 (dm, $J = 246.3$ Hz), 137.7, 137.1, 133.2 (m), 130.0, 128.9 (d, $J = 6.7$ Hz), 127.7, 126.5 (dm, $J = 237.2$ Hz), 125.9 (t, $J = 5.9$ Hz), 125.8, 124.4, 123.7 (dm, $J = 246.3$ Hz), 122.4, 118.4 (d, $J = 13.3$ Hz), 118.3 (d, $J = 13.3$ Hz), 113.2 (dd, $J = 3.5$ and 18.6 Hz), 112.2 (dd, $J = 4.2$, 18.6 Hz), 111.7 (d, $J = 7.6$ Hz),111.3, 48.3 ppm; elemental analysis: calcd (%) for $C_{23}H_{11}F_6N$ (415.34): C 66.51, H 2.67; found: C 66.89, H 2.94.

Methyl 3-(1-(2-bromobenzyl)-5-(4-isocyanophenyl)pyrrol-2-yl)-thiophene-2-carboxylate (33): After following procedure A with 1-(2-bromobenzyl)-2-(4-cyanophenyl)pyrrole (337 mg, 1 mmol) and 4-cyanobenzenesulfonyl chloride (300 mg, 1.25 mmol), the residue was purified by flash chromatography on silica gel (pentane-Et_2O, 65-35) to afford the desired compound **33** (220 mg, 46%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.58$ (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 5.1$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.09 (t, $J = 7.6$ Hz, 1H), 6.97 (dd, $J = 7.2$, 8.0 Hz, 1H), 6.85 (d, $J = 5.1$ Hz, 1H), 6.5 (d, $J = 3.7$ Hz, 1H), 6.41 (d, $J = 8.6$ Hz, 1H), 6.38 (d, $J = 3.7$ Hz, 1H), 5.15 (s, 2H), 3.83 ppm (s, 3H); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 161.9$, 138.5, 137.7, 137.6, 134.5, 132.4, 132.3, 131.8, 131.0, 130.5, 129.4, 128.6, 127.6, 121.2, 119.0, 111.6, 111.3, 110.2, 52.2, 49.3 ppm; elemental analysis: calcd (%) for $C_{24}H_{17}BrN_2O_2S$ (477.38): C 60.39, H 3.59; found: C 60.76, H 3.85.

4-(Benzo[*e*]pyrrolo[1,2-*a*]thieno[3,4-*c*]azepin-6-yl)benzonitrile (34): After following procedure C with methyl 3-(1-(2-bromoben-

zyl)-5-(4-isocyanophenyl)pyrrol-2-yl)thiophene-2-carboxylate (**33**; 239 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **34** (172 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 7.4 Hz, 1H), 7.57 (s, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 3.1 Hz, 1H), 7.47–7.36 (m, 3H), 6.49 (d, J = 3.6 Hz, 1H), 6.34 (d, J = 3.6 Hz, 1H), 4.86 ppm (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.9, 137.8, 136.1, 135.1, 133.4, 133.4, 133.0, 132.6, 129.5, 129.2, 129.1, 128.3, 128.2, 123.8, 122.2, 119.2, 111.2, 110.2, 107.6, 48.9 ppm; elemental analysis: calcd (%) for $C_{24}H_{16}N_2O_2S$ (396.09): C 72.71, H 4.07; found: C 73.02, H 3.84.

1-Benzyl-2-(2-bromophenyl)-5-(3,5-dichlorophenyl)pyrrole (35): After following procedure A with 1-benzyl-2-(3,5-dichlorophenyl)-pyrrole (302 mg, 1 mmol) and 2-bromobenzenesulfonyl chloride (319 mg, 1.25 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **35** (238 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (dd, J = 1.8, 7.9 Hz, 1H), 7.32 (dd, J = 1.6, 7.9 Hz, 1H), 7.25 (s, 1H), 7.23 (t, J = 2.3 Hz, 1H), 7.21–7.16 (m, 5H), 7.12 (t, J = 7.3 Hz, 1H), 6.98 (dt, J = 1.7, 7.6 Hz, 1H), 6.44 (d, J = 3.7 Hz, 1H), 6.35 (d, J = 7.5 Hz, 1H), 6.33 (d, J = 3.7 Hz, 1H), 5.11 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 136.0, 135.9, 134.9, 133.8, 133.1, 133.0, 132.8, 132.3, 129.8, 128.6, 127.6, 127.2, 127.0, 126.9, 125.4, 121.2, 110.8, 110.7, 49.0 ppm; elemental analysis: calcd (%) for $C_{23}H_{16}BrCl_2N$ (457.19): C 60.42, H 3.53; found: C 60.62, H 3.73.

Pyrrolo[1,2-*f*]phenanthridine (37): After following procedure A with 1-phenylpyrrole (246 mg, 2 mmol) and 2-bromobenzenesulfonyl chloride (256 mg, 1 mmol), the crude mixture was filtrated on a silica plug and directly used in the next reaction following procedure C. The residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **37** (135 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ) = 8.35 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.78–7.79 (m, 1H), 7.46–7.55 (m, 2H), 7.37–7.44 (m, 2H), 6.97 (dd, J = 1.2, 3.6 Hz, 1H), 6.74 ppm (t, J = 3.2 Hz, 1H); this is a known compound, and the spectral data are identical to those reported in the literature.[17]

2,5-Bis(2-bromophenyl)-1-phenylpyrrole (38): After following procedure B with 1-phenylpyrrole (143 mg, 1 mmol) and 2-bromobenzenesulfonyl chloride (638 mg, 2.5 mmol), the residue was purified by flash chromatography on silica gel (pentane-Et_2O, 85:15) to afford the desired compound **38** (331 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.0 Hz, 2H), 7.21 (dd, J = 2.0, 7.3 Hz, 2H), 7.16 (t, J = 7.6 Hz, 2H), 7.11–7.04 (m, 5H), 7.00–6.94 (m, 2H), 6.50 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 134.9, 133.3, 133.1, 132.7, 130.8, 129.0, 128.2, 128.1, 126.6, 125.5, 110.6 ppm; elemental analysis: calcd (%) for $C_{22}H_{15}Br_2N$ (453.17): C 58.31, H 3.34; found: C 58.62, H 3.18.

3-Phenylpyrrolo[1,2-*f*]phenanthridine (39): After following procedure C with 2,5-bis(2-bromophenyl)-1-phenylpyrrole (**38**; 227 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **39** (63 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 7.8 Hz, 1H), 8.05 (d, J = 7.7 Hz, 1H), 7.53–7.37 (m, 8H), 7.29 (t, J = 7.7 Hz, 1H), 7.13 (t, J = 7.7 Hz, 1H), 7.06 (d, J = 4.0 Hz, 1H), 6.66 ppm (d, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.7, 134.1, 131.6, 131.5, 129.0, 128.6, 128.2, 127.5, 127.1, 126.8, 126.0, 125.3, 124.0, 123.7, 123.1, 122.7, 122.4, 119.1, 116.0, 102.1 ppm; elemental analysis: calcd (%) for $C_{22}H_{15}N$ (293.36): C 90.07, H 5.15; found: C 90.32, H 5.39.

2,5-Bis(2-bromophenyl)-1-(4-fluorophenyl)pyrrole (40): After following procedure B with 1-(4-fluorophenyl)pyrrole (161 mg, 1 mmol) and 2-bromobenzenesulfonyl chloride (638 mg, 2.5 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **40** (372 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.9 Hz, 2H), 7.25–7.17 (m, 4H), 7.11 (dt, J = 1.6, 7.4 Hz, 2H) 6.95 (dd, J = 5.0, 8.9 Hz, 2H), 6.75 (t, J = 8.6 Hz, 2H), 6.48 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9 (d, J = 248.0 Hz), 134.3, 133.9, 133.2, 133.1, 132,6, 129.6, 129.1, 125.6, 125.4 (d, J = 9.0 Hz), 114.8 (d, J = 25.0 Hz), 110.4 ppm; elemental analysis: calcd (%) for $C_{22}H_{14}Br_2FN$ (471.17): C 56.08, H 3.00; found: C 56.17, H 2.83.

7-Fluoro-3-phenylpyrrolo[1,2-*f*]phenanthridine (41): After following procedure C with 2,5-bis(2-bromophenyl)-1-(4-fluorophenyl)pyrrole (**40**; 236 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (pentane–Et_2O, 85:15) to afford the desired compound **41** (83 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 7.9 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.94 (dd, J = 2.8, 10.3 Hz, 1H), 7.54–7.46 (m, 4H), 7.45–4.39 (m, 4H), 7.05 (d, J = 3.9 Hz, 1H), 6.84 (ddd, J = 2.6, 7.8, 9.0 Hz, 1H), 6.65 ppm (d, J = 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7 (d, J = 241.7 Hz), 135.4, 131.6, 131.1, 130.5, 129.0, 128.8, 128.7, 127.7, 127.0, 126.1, 125.1 (d, J = 8.0 Hz), 124.6, 122.7 (d, J = 14.3 Hz), 120.5 (d, J = 8.4 Hz), 115.9, 114.4 (d, J = 23.4 Hz), 109.9, 109.6, 102.3 ppm; elemental analysis calcd (%) for $C_{22}H_{14}FN$ (311.36): C 84.87, H 4.53; found: C 89.13, H 4.75.

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