

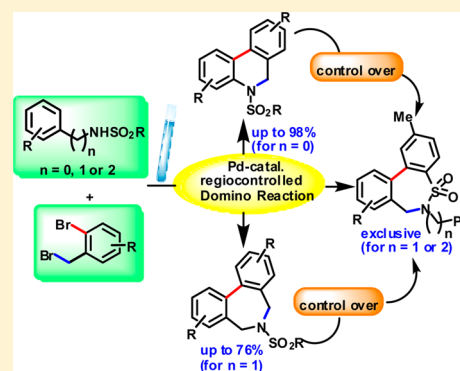
Palladium-Catalyzed Regiocontrolled Domino Synthesis of *N*-Sulfonyl Dihydrophenanthridines and Dihydrodibenzo[*c,e*]azepines: Control over the Formation of Biaryl Sultams in the Intramolecular Direct Arylation

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Supporting Information

ABSTRACT: A palladium-catalyzed domino *N*-benzylation/intramolecular direct arylation involving sulfonanilides and 2-bromobenzyl bromides has been developed for the first time, providing a workable access to *N*-sulfonyl dihydrophenanthridines in good to excellent yields. Under the optimized conditions, the formation of 5,6-dihydrophenanthridines was largely controlled over the formation of biaryl sultams containing a seven member ring. The optimized condition was found extendable to the regiocontrolled domino formation of *N*-sulfonyl-6,7-dihydro-5*H*-dibenzo[*c,e*]azepines over the biaryl sultam formation. Using an appropriate substrate, a biaryl sultam has been obtained exclusively.



INTRODUCTION

Phenanthridines (**1**) and structurally related phenanthridinones (**2**) are largely found in natural sources, exhibiting various biological activities including antibiotic, anti-inflammatory, and anticancer activity (Figure 1).¹ In contrast,

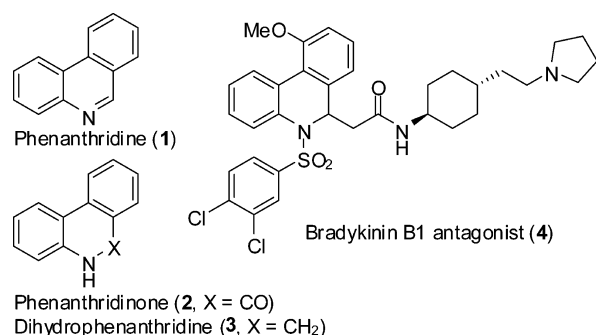


Figure 1. Dihydrophenanthridine and its structurally related compounds.

dihydrogenated phenanthridines at the 5- and 6-positions viz. 5,6-dihydrophenanthridines (**3**), are reported to be poorly natural abundant,² and often exhibit distinct biological properties compared to the phenanthridines owing to the absence of electrophilic C=N bond.³ Compared to the diverse biological profiles of phenanthridines, the biological activity of dihydrophenanthridines⁴ is least investigated probably because of poor accessibility to this skeleton. For example, a

dihydrophenanthridine **4** has recently been identified as bradykinin B1 antagonist.⁵

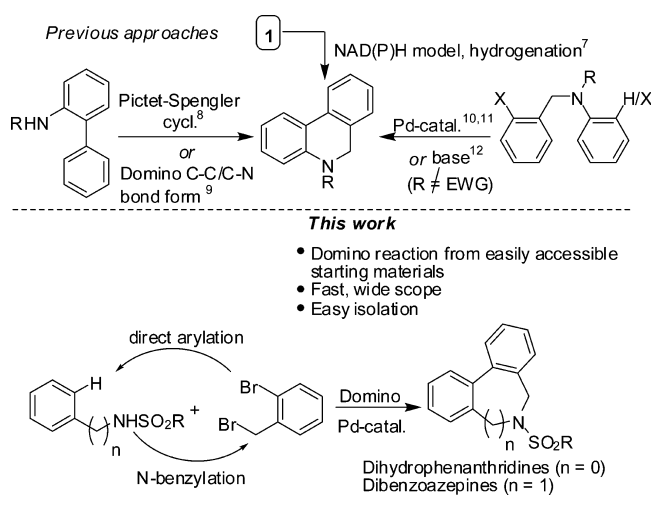
The synthesis of the two important skeletons **1** and **2** merits extensive discussion.⁶ However, less attention has been paid to the synthesis of dihydrophenanthridines **3** or its derivatives. The available procedure includes biomimetic approach,⁷ Pictet–Spengler cyclizations,⁸ domino C–C/C–N reactions,⁹ palladium-catalyzed intramolecular direct arylations,¹⁰ palladium-catalyzed cross-coupling of aryl stannanes with aryl iodides,¹¹ and base-mediated intramolecular radical-cyclizations (Scheme 1).¹² The use of elaborated precursors in many of these approaches, apparently limited substrate scope in the palladium-catalyzed reactions,¹⁰ and inefficiency of precursors containing a *N*-sulfonyl group in the radical cyclizations¹² are particularly noteworthy. Several other methods describing the synthesis of dihydrophenanthridines often produce the product contaminated with phenanthridines, generated in situ by oxidation of dihydrophenanthridines.¹³

A Domino reaction is a process involving two or more bond-forming transformations that occur under one reaction condition without adding additional reagents and catalysts, and subsequent reactions result as a consequence of the functionality formed in the previous step.¹⁴ Transition-metal-catalyzed reactions have expanded the scope of domino reactions for the rapid assembly of molecular scaffolds that are medically important.¹⁵ The development of a transition-

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Scheme 1. Approaches to 5,6-Dihydrophenanthridines or Its Derivatives



metal-catalyzed regiocontrolled domino reaction from a set of substrates that are capable of forming more than one domino product represents a significant challenge. A regiocontrolled domino reaction to the synthesis of 5,6-dihydrophenanthridine using readily available substrates is yet to be realized. Our continued effort to develop domino synthesis of fused nitrogen heterocycles¹⁶ and recent experiences in the synthesis of (NH)-phenanthridinone (3)¹⁷ led us to explore a domino synthesis of dihydrophenanthridines. Herein, we report first example of a palladium-catalyzed regiocontrolled domino reaction involving sulfonanilides and 2-bromobenzyl bromide providing an expedient access to *N*-sulfonyl dihydrophenanthridines with diverse substitution patterns and its application to the synthesis of *N*-sulfonyl-6,7-dihydrodibenzo[*c,e*]azepines in good to excellent yields.

RESULTS AND DISCUSSION

Previously, we demonstrated regioselective *N*-benzylation of indoles^{16c} and C-benzylation of primary benzamides¹⁸ over arylations using 2-bromobenzyl bromide as one of the coupling partners under palladium-catalyzed conditions. On the basis of our previous experiences, sulfonanilides and 2-bromobenzyl bromides were chosen as the two coupling partners for the synthesis of dihydrophenanthridines in the current investigation. The reasons for choosing a sulfonyl group protected anilines as one of coupling partners were two-fold: (a) to prevent the undesired in situ oxidation of dihydrophenanthridines,¹³ and (b) ease of preparation of starting sulfonanilides together with facile deprotection, if necessary. At the outset, we were inclined upon a condition that could offer both *N*-benzylation followed by intramolecular direct arylation. Our investigation on finding an optimized condition for the reaction of sulfonanilide **5** and 2-bromobenzyl bromide (**6**) ultimately secured a reagent blend consisting of Pd(OAc)₂ (10 mol %), PPh₃ (20 mol %), Cs₂CO₃ (2.5 equiv), and dioxane (200 mM) at 110 °C for 16 h, which afforded compound **7**¹⁰ in 78% yield (Table 1, entry 1). Interestingly, a competitive domino product **8**, a biaryl sultam containing a seven member ring obtained by intramolecular arylation of **9** on the benzenesulfonyl ring, was also isolated in 20% yield. Similarly, when *N*-Ts-1-naphthylamine **10**¹⁹ was reacted with substituted 2-bromobenzyl bromide **11**, the two domino

Table 1. Optimization Study^a

N-Ts aniline (**5**)
N-Ts 1-naphthylamine (**10**)
N-Ms aniline (**14**)
N-Ts 2,6-dimethylaniline (**17**)

6 R,R = H,H; X = Br
11 R,R = -O-CH₂O-; X = Br
16 R,R = H,H; X = OTs

↓ reagents and conditions

7 R = Ts
15 R = Ms

8 R², R³, R⁶ = H,H,H
18 R², R⁶ = Me, Me, R³ = H

9

12

13

19

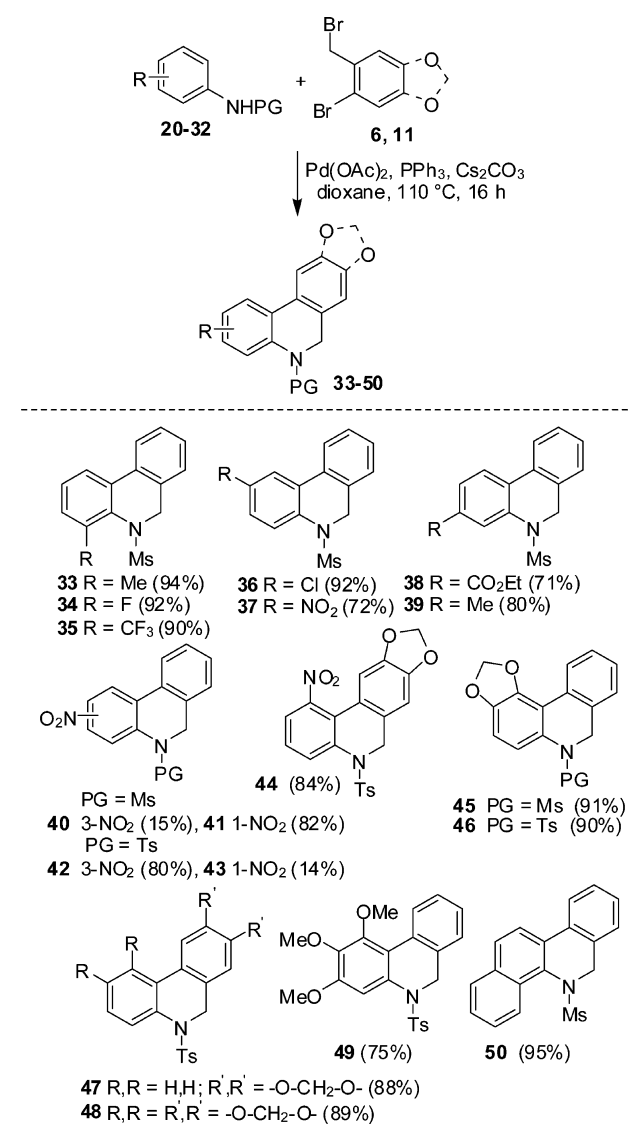
entry	reagents and conditions	substrates	DHP (%) ^b	sultam (%) ^b
1	Pd(OAc) ₂ , PPh ₃ , Cs ₂ CO ₃ , dioxane, 110 °C, 16 h	5 + 6	7 (78)	8 (20)
2		10 + 11	12 (78)	13 (19)
3		14 + 6	15 (96)	
4		14 + 16	15 (95)	
5 ^c		17 + 6		18 (32)

^aSulfonanilide (0.5 mmol), 2-bromobenzyl bromide (0.5 mmol), Pd-source (10 mol %), ligand (20 mol %), base (1.25 mmol), solvent (0.2 M), temp, 16 h. ^bIsolated yield. ^c*N*-Ts-benzyl-2,6-dimethyl aniline **19** formed in 65% yield.

products **12** and **13** were obtained in 78 and 19% yields, respectively (entry 2). The synthesis of biaryl sultam containing a seven member ring has been reported though limited to a few reports.²⁰ However, the formation of biaryl sultam was uncovered in the previous palladium-catalyzed intramolecular direct arylation.¹⁰ Clearly, the conditions developed by us is incongruent from the conditions reported earlier and the results are quite different.¹⁰ Nevertheless, the intramolecular direct arylation on the aniline ring was largely controlled over the biaryl sultam formation under the optimized conditions. Furthermore, we envisaged that the formation of biaryl sultam could be avoided completely by using *N*-Ms anilines. To our delight, reaction of compound **14**²¹ and **6** gave dihydrophenanthridine **15**²² in 96% yield (entry 3). Compound **14** exhibited similar reactivity with a different coupling partner **16**²³ affording **15** in 95% yield (entry 4). Interestingly, when *N*-Tosyl 2,6-dimethylaniline **17**²⁴ was subjected to reaction with **6** under the optimized condition, intramolecular arylation occurred exclusively on the benzenesulfonyl ring leading to the formation of biaryl sultam **18** albeit in poor yield (entry 5, 32% yield).

We next investigated the formation of dihydrophenanthridines using other *N*-Tosyl or *N*-Mesityl derivatives of anilines under the optimized condition. The sulfonamides **20–32** were prepared by reacting anilines and sulfonyl chlorides.²⁵ Under the optimized condition, the sulfonanilides **20**,²⁶ **21**,²⁷ and **22**²⁸ containing an electron-donating or withdrawing group at the 2-position exhibit similar reactivity with **6** affording dihydrophenanthridines **33–35** in excellent yields (Table 2). While the

Table 2. Synthesis of Various Substituted 5,6-Dihydrophenanthridines



sulfonanilide **23**²⁹ containing a substituent at the 4-position sustained similar reactivity with **6** yielding dihydrophenanthridine **36** in 92% yield, compound **24**³⁰ afforded dihydrophenanthridine **37** in somewhat reduced yield. Interestingly, 3-substituted sulfonanilides **25** and **26**²⁷ formed only one regioisomer of dihydrophenanthridines **38** and **39**, resulted from intramolecular direct arylation occurred exclusively at the *para*-position to the concerned group. However, 3-nitro sulfonanilides **27**²⁷ or **28**³¹ exerted good regiocontrol in the formation of regioisomeric dihydrophenanthridines (**40** and **41**) or (**42** and **43**), which upon silica chromatography furnished pure dihydrophenanthridines. A complete regio-

lectivity was observed in the synthesis of **44** that resulted from intramolecular direct arylation occurred exclusively at the *ortho*-position to the NO_2 group. The sulfonanilides with a methylenedioxy ($-\text{OCH}_2\text{O}-$) group in aniline, benzenesulfonyl, or both rings also reacted with **6** or **11** regioselectively resulting in dihydrophenanthridines **45–48** in excellent yields. A trimethoxy substituted dihydrophenanthridine **49** was synthesized from **31**,³² which indicated intramolecular direct arylation occurred at the *ortho*- to a methoxy group. The application of this protocol was also extended to the synthesis of dihydrobenzo[*c*]phenanthridine **50**. A complete regiocontrol observed in the synthesis of many *N*-Tosyl dihydrophenanthridines reported herein is particularly noteworthy. In addition, mild reaction conditions make the protocol especially attractive.

During the course of our current investigation, we also uncovered that the protocol described herein could be extended to the synthesis of 6,7-dihydro-5*H*-dibenzo[*c,e*]-azepines. While the several elegant syntheses of dibenzo[*c,e*]-azepines have been reported,³³ to the best of our knowledge, a domino synthesis is unprecedented. When *N*-Ts benzylamine **51**²⁴ was subjected to reaction with **6** under the optimized condition, dibenzoazepine **52**^{33f} and biaryl sultam **53** were obtained in 42 and 53% yields, respectively (Table 3). It is important to mention here that unlike in dihydrophenanthridine synthesis, the biaryl sultam **53** was found to be the major product in the synthesis of dibenzoazepine **52**. About a 4-fold increase in the ratio of biaryl sultam to dibenzoazepine was observed when *N*-Ts benzhydrylamine **54**³⁴ was reacted with **6** affording dibenzoazepine **55** and biaryl sultam **56** in 14 and 58% yields, respectively. A complete regiocontrol was observed in the reaction of **51** and **11** leading to the formation of biaryl sultam **57** exclusively. While an attempted reaction of **58**³⁵ and **11** to form an eight member ring was unsuccessful, only biaryl sultam **59** was isolated in 78% yield. Interestingly, the presence of an electron-withdrawing group on the benzylamine ring facilitates the intramolecular direct arylation largely on the benzylamine ring. Thus, heating a reaction of *N*-Ts 3-trifluoromethylbenzylamine **60** and **6** in the presence of $\text{Pd}(\text{OAc})_2$, PPh_3 , and Cs_2CO_3 in toluene at 130°C for 16 h gave dibenzoazepine **61** and biaryl sultam **62** in 58 and 40% yields, respectively. Notably, intramolecular direct arylation occurred at the *para*- to the CF_3 group in benzylamine ring. Further improvement in the regioselectivity was demonstrated in the synthesis of optically pure dibenzoazepine **64**. Thus, when *N*-Ts α -methylbenzylamine **63** and **6** were allowed to react, dibenzoazepine **64** and biaryl sultam **65** were obtained in 53 and 30% isolated yields, respectively. Gratifyingly, *N*-Ms 3-trifluoromethylbenzylamine **66** gave dibenzoazepine **67** resulted from intramolecular direct arylation occurred exclusively at the *para*- to the CF_3 group in benzylamine ring. Notably, a palladium-catalyzed intramolecular oxidative coupling involving double $\text{C}(\text{sp}^2)\text{-H}$ bonds to the synthesis of (NH)-biaryl sultam containing a seven member ring was reported by us recently.¹⁷

In line with the mechanism proposed by Fagnou³⁶ and Echavarren³⁷ for intramolecular direct arylation, we also propose the involvement of a similar catalytic cycle as illustrated in Scheme 2. Subsequent to oxidative insertion of palladium (0) into the carbon-bromide bond of *N*-benzylated intermediate **68**, two pathways may be followed in the transformation of **69** to the dihydrophenanthridines or dibenzoazepines. In the first pathway, the carbonate may act as an external base at the C-H bond (H^3) cleaving transition

Table 3. Regioselective Synthesis of *N*-Sulfonyl 6,7-Dihydro-5*H*-dibenzo[*c,e*]azepines

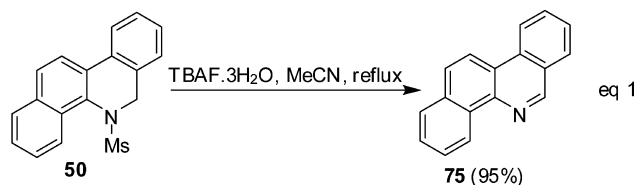
Substrates			Pd(OAc) ₂ , PPh ₃ , Cs ₂ CO ₃ dioxane or toluene, 110 or 130 °C, 16 h		Products
 51 R = H 54 R = Ph + 6	 52 R = H (42%) 55 R = Ph (14%)	 53 R = H (53%) 56 R = Ph (58%)			
 57 n = 1 (68%) 58 n = 2 (78%) + 11	 59 n = 1 (68%) 59 n = 2 (78%)				
 60 PG = Ts 66 PG = Ms + 6	 61 PG = Ts (58%) 67 PG = Ms (76%)	 62 (40%)			
 63 Me + 6	 64 (53%)	 65 (30%)			

state via **70** to form the biaryl palladium(II) intermediate **72**, which would reductively eliminate to give the observed product and regenerate the catalyst. Alternatively, exchange of bromide with carbonate in **69** could give a species **71**, which would undergo a concerted metalation–deprotonation to give the same intermediate **72** of the other pathway.

Subsequent to oxidative insertion into the carbon–bromide bond, **69** could form biaryl sultam following two similar pathways as demonstrated above. The external base will abstract proton (H^b) via transition state **73** to form the biaryl palladium(II) intermediate **74**, which would reductively eliminate to give the biaryl sultam and regenerate the catalyst.

While dihydrophenanthridine **7** is the major product when $n = 0$ in Scheme 2, biaryl sultam **53** is the major product obtained in the synthesis of dibenzoazepine **52**. This reverse regioselectivity observed in the synthesis of dibenzoazepine **52** can be rationalized as follows. When $n = 0$, concerted metalation–deprotonation in **70** may be favored compared to that in **73**, which could drive the formation of energetically favorable six membered dihydrophenanthridine ring. However, the presence of more acidic H^b proton in **73** could facilitate the intramolecular arylation of **73** compared to **70** when $n = 1$ in Scheme 2.

Finally, the synthesis of phenanthridines was achieved by deprotecting dihydrophenanthridines, exemplified with a dihydrophenanthridine **50**. Thus, treatment of **50** with TBAF in acetonitrile at reflux gave nearly quantitative deprotection of Ms group affording **75** in 95% yield.^{6h}



In conclusion, a palladium-catalyzed domino reaction involving sulfonanilides with 2-bromobenzyl bromides to the synthesis of *N*-sulfonyl-5,6-dihydrophenanthridines has been developed, which opens an expedient access to 5,6-dihydrophenanthridines with wide substrate scope. The optimized condition was also found beneficial to the domino synthesis of 6,7-dihydro-5*H*-dibenzo[*c,e*]azepines that are otherwise obtained in several steps using literature procedures. Considering the reaction profiles of NH-Ts amines with **6**, the formation of biaryl sultam was favored as we moved from NH-Ts aniline **5** to NH-Ts aliphatic amine **51**, and biaryl sultam **59** became the exclusive product when NH-Ts aliphatic amine **58** was used.

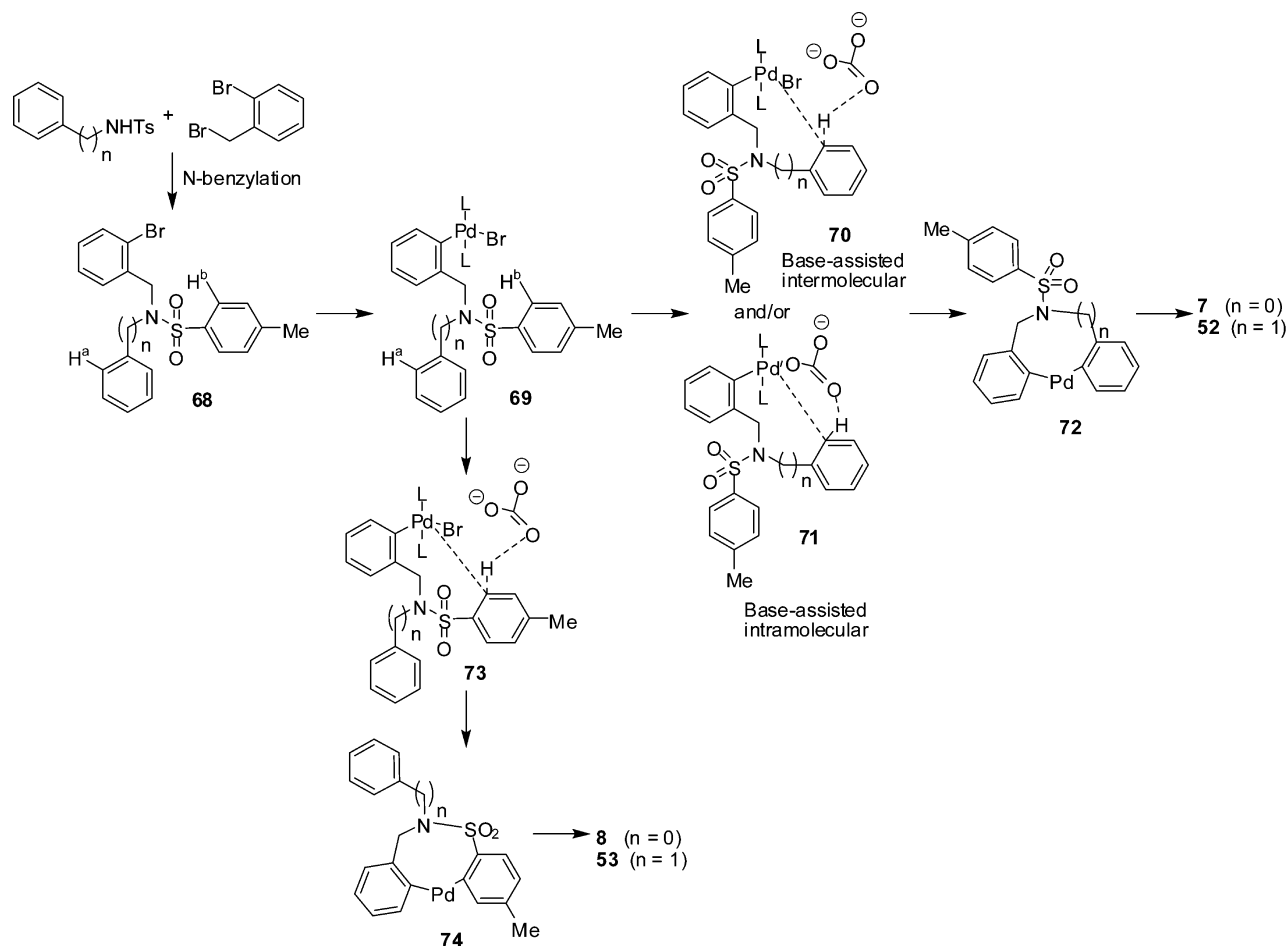
EXPERIMENTAL SECTION

General Methods. Unless noted otherwise, all reagents and solvents were purchased from commercial sources and used as received. All palladium-catalyzed reactions were performed in a screw-cap sealed tube. The ¹H and ¹³C NMR spectra were obtained in CDCl₃ as solvent using a 400 MHz spectrometer with Me₄Si as an internal standard. Coupling constants (*J* values) are reported in Hz. Column chromatography was performed using silica gel (60–120, 100–200, or 230–400 mesh). High resolution mass spectra (HRMS) were obtained using electron spray ionization (ESI) technique and as TOF mass analyzer. All melting points were taken using a melting point apparatus equipped with a calibrated thermometer and are uncorrected. New compounds were characterized by melting point, ¹H and ¹³C NMR, IR, and HRMS data. Compounds **5**, **6**, and **11** were purchased from commercial vendors.

2-Bromobenzyl 4-methylbenzenesulfonate (16).²³ A mortar was charged with anhydrous K₂CO₃ (414 mg, 3 mmol), *p*-toluenesulfonyl chloride (285 mg, 1.5 mmol), and 2-bromobenzyl alcohol (187 mg, 1 mmol), then grinded with a pestle for 5 min. After completion of the reaction, excess tosyl chloride was quenched by the addition of powdered KOH (5 mmol) and a few drops of *tert*-butanol to accelerate the disappearance of tosyl chloride. The reaction mixture was washed with ether (3 × 20 mL). The combined organic layer was evaporated under reduced pressure to obtain an off-white solid that was used in the next step (256 mg, 75%): mp 47–49 °C; IR (KBr, cm^{−1}) 3430, 1593, 1360, 1171, 1032; ¹H NMR δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 5.16 (s, 2H), 2.47 (s, 3H); ¹³C NMR δ 144.9, 132.9, 132.9, 132.8, 130.4, 130.3, 129.8, 128.0, 127.6, 123.3, 71.0, 21.6; HRMS calcd for C₁₄H₁₄BrO₃S [M + H]⁺ 340.9847, found 340.9844.

Typical Procedure for Sulfonylation of Anilines (10, 14, 17, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32). Following a literature procedure,²⁵ a mixture of aniline (1.5 mmol), 4-toluenesulfonyl chloride or methane sulphonyl chloride (1 mmol) and silica gel [1 g (60–120 mesh)] was stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, EtOAc (5 mL) was added, and the mixture was filtered through a sintered funnel. Concentration of the filtrate followed by

Scheme 2. Proposed Mechanism for the Intramolecular Direct Arylation



chromatography [silica, EtOAc–hexanes = 1:9] gave the sulfonanilides.

Typical Procedure for Sulfonylation of Aliphatic Amines (51, 54, 58, 60, 63, 66). Following a literature procedure,³⁴ a solution of benzylamine (1 mmol) and triethylamine (3 mmol) in CH_2Cl_2 (10 mL) was treated with 4-methylbenzene-1-sulfonyl chloride (1 mmol) in small portions at 0 °C. The resulting solution was stirred at room temperature for 4–6 h. Water (50 mL) was added, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layer was dried (Na_2SO_4) and concentrated, which upon chromatography [silica, EtOAc–hexanes = 1:9] gave the sulfonanilides.

General Procedure for the Synthesis of N-Sulfonyl-5,6-dihydrophenanthridines. A mixture of sulfonanilides (0.5 mmol), $\text{Pd}(\text{OAc})_2$ (11 mg, 0.05 mmol), PPh_3 (26 mg, 0.10 mmol), and Cs_2CO_3 (1.25 mmol) in dioxane (2.5 mL) was purged with nitrogen for 5–10 min. 2-Bromobenzyl bromide (0.5 mmol) was added and the mixture was heated at 110 °C for 16 h in a screw-cap sealed tube. Water (20 mL) was added, and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried (Na_2SO_4) and concentrated, which upon chromatography [silica, EtOAc–hexanes = 1:9 to 1:4] gave the dihydrophenanthridines.

Desulfonylation of Dihydrophenanthridine 50. A solution of dihydrophenanthridine 50 (77 mg, 0.25 mmol) in acetonitrile (2 mL) was treated with tetrabutylammonium fluoride trihydrate (157 mg, 0.50 mmol), and then the reaction mixture was refluxed for 6 h. After completion, the mixture was diluted with H_2O and extracted with EtOAc. The organic layer was dried (Na_2SO_4) and concentrated, which upon chromatography [silica, EtOAc–hexanes = 1:9] gave the phenanthridine 75^{6h} (54 mg, 95%).

2-Methyl-6-phenyl-6,7-dihydrodibenzo[d,f][1,2]thiazepine 5,5-dioxide (8). White solid (40 mg, 20%): mp 111–113 °C; IR

(KBr, cm^{-1}) 3423, 2923, 2335, 1593, 1445, 1340, 1162, 1039; ^1H NMR δ 7.87 (d, J = 8.0 Hz, 1H), 7.56–7.55 (m, 2H), 7.49–7.47 (m, 3H), 7.42–7.34 (m, 4H), 7.30–7.29 (m, 2H), 4.35 (s, 2H), 2.56 (s, 3H); ^{13}C NMR δ 144.1, 142.4, 140.8, 139.4, 134.0, 133.4, 130.5, 130.2, 129.6, 129.5, 129.3, 129.2, 129.0, 128.4, 127.7, 127.2, 126.8, 121.7, 55.9, 21.6; HRMS calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$]⁺ 336.1058, found 336.1055.

5-Tosyl-5,6-dihydrobenzo[c][1,3]dioxolo[4,5-j]-phenanthridine (12). Pale yellow solid (167 mg, 78%): mp 147–149 °C; IR (KBr, cm^{-1}) 3395, 2923, 1591, 1481, 1347, 1161, 1035; ^1H NMR δ 8.72 (d, J = 8.56 Hz, 1H), 7.85 (d, J = 6.0 Hz, 2H), 7.64 (t, J = 7.8 Hz, 1H), 7.56–7.50 (m, 2H), 6.90 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.1 Hz, 2H), 6.69 (s, 1H), 6.61 (s, 1H), 5.95 (s, 2H), 5.17 (d, J = 16.4 Hz, 1H), 4.46 (d, J = 16.4 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR δ 147.5, 147.3, 143.0, 133.9, 133.5, 131.6, 131.3, 129.2, 128.5, 128.1, 127.7, 127.3, 126.6, 126.5, 126.4, 126.4, 121.1, 107.0, 104.0, 101.1, 50.9, 21.3; HRMS calcd for $\text{C}_{25}\text{H}_{20}\text{NO}_4\text{S}$ [$\text{M} + \text{H}$]⁺ 430.1113, found 430.1110.

2-Methyl-6-(naphthalen-1-yl)-6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-d]benzo[f][1,2]thiazepine 5,5-dioxide (13). Pale yellow solid (41 mg, 19%): mp 252–254 °C; IR (KBr, cm^{-1}) 3431, 2923, 2252, 1595, 1505, 1335, 1224, 1161, 1035; ^1H NMR δ 8.41 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.60–7.54 (m, 2H), 7.44–7.37 (m, 3H), 7.28 (d, J = 7.2 Hz, 1H), 7.03 (s, 1H), 6.9 (s, 1H), 6.06 (d, J = 8.5 Hz, 2H), 4.24 (s, 2H), 2.54 (s, 3H); ^{13}C NMR δ 148.7, 148.3, 144.1, 139.3, 139.2, 134.8, 134.5, 134.0, 132.3, 130.4, 128.9, 128.7, 128.0, 127.2, 127.0, 126.6, 125.4, 124.1, 123.7, 110.5, 108.9, 101.8, 56.6, 21.7; HRMS calcd for $\text{C}_{25}\text{H}_{20}\text{NO}_4\text{S}$ [$\text{M} + \text{H}$]⁺ 430.1113, found 430.1112.

6-(2,6-Dimethylphenyl)-2-methyl-6,7-dihydrodibenzo[d,f]-[1,2]thiazepine 5,5-dioxide (18). White solid (58 mg, 32%): mp 210–212 °C; IR (KBr, cm^{-1}) 3414, 2913, 1598, 1449, 1315, 1190,

1159, 1030, 769; ^1H NMR δ 8.0 (d, J = 8.0 Hz, 1H), 7.59–7.55 (m, 2H), 7.51–7.47 (m, 2H), 7.45–7.40 (m, 2H), 7.19–7.13 (m, 3H) 4.8 (s, 2H), 2.47 (s, 3H), 1.81 (s, 6H); ^{13}C NMR δ 143.4, 140.7, 139.8, 139.1, 138.9, 135.4, 134.0, 130.6, 130.0, 129.4, 129.2, 128.9, 128.8, 128.7, 128.5, 126.0, 54.3, 21.6, 19.4; HRMS calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 364.1371, found 364.1365.

***N*-(2-Bromobenzyl)-*N*-(2,6-dimethylphenyl)-4-methylbenzenesulfonamide (19).** White solid (143 mg, 65%): mp 133–135 °C; IR (KBr, cm^{-1}) 3434, 2923, 1596, 1437, 1339, 1154, 1024, 861; ^1H NMR δ 7.75 (d, J = 8.2 Hz, 2H), 7.70 (dd, J = 7.7, 1.7 Hz, 1H), 7.40 (dd, J = 8.0, 1.2 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.28 (td, J = 7.6, 1.2 Hz, 1H), 7.13–7.08 (m, 2H), 6.96 (d, J = 7.6 Hz, 2H), 4.89 (s, 2H), 2.47 (s, 3H), 1.81 (s, 6H); ^{13}C NMR δ 143.3, 139.6, 138.3, 135.6, 135.4, 133.0, 132.6, 130.0, 129.6, 129.6, 128.9, 128.3, 128.2, 128.0, 127.6, 127.5, 124.9, 52.9, 21.5, 18.7; HRMS calcd for $\text{C}_{22}\text{H}_{23}\text{BrNO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 444.0633, found 444.0631.

Ethyl 3-(methylsulfonamido)benzoate (25). White solid (194 mg, 80%): mp 112–114 °C; IR (KBr, cm^{-1}) 3246, 2999, 1699, 1339, 1153; ^1H NMR δ 7.97 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.65 (bs, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 7.84 Hz, 1H), 4.40 (q, J = 7.0 Hz, 2H), 3.05 (s, 3H), 1.42 (t, J = 7.0 Hz, 3H); ^{13}C NMR δ 166.2, 137.4, 131.8, 129.8, 126.1, 124.9, 121.6, 61.6, 39.5, 14.2; HRMS calcd for $\text{C}_{10}\text{H}_{14}\text{NO}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 244.0644, found 244.0640.

***N*-(Benzo[d][1,3]dioxol-5-yl)methanesulfonamide (29).** White solid (204 mg, 95%): mp 106–108 °C; IR (KBr, cm^{-1}) 3240, 2901, 1614, 1460, 1342, 1124, 1037, 991; ^1H NMR δ 6.84 (d, J = 2.0 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 6.70–6.68 (m, 2H), 5.98 (s, 2H), 2.97 (s, 3H); ^{13}C NMR δ 148.4, 146.1, 130.2, 116.2, 108.5, 105.0, 101.6, 38.8; HRMS calcd for $\text{C}_8\text{H}_{10}\text{NO}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 216.0331, found 216.0334.

***N*-(Benzo[d][1,3]dioxol-5-yl)-4-methylbenzenesulfonamide (30).** White solid (268 mg, 92%): mp 130–132 °C; IR (KBr, cm^{-1}) 3290, 2904, 1492, 1347, 1160, 936; ^1H NMR δ 7.62 (d, J = 8 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.71 (bs, 1H), 6.68 (s, 1H), 6.61 (d, J = 8.0 Hz, 1H), 6.43 (dd, J = 8.2, 2.1 Hz, 1H), 5.92 (s, 2H), 2.38 (s, 3H); ^{13}C NMR δ 148.0, 145.9, 143.8, 135.8, 130.1, 129.6, 127.3, 116.8, 108.2, 105.5, 101.5, 21.5; HRMS calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 292.0644, found 292.0649.

4-Methyl-5-(methylsulfonyl)-5,6-dihydrophenanthridine (33). White solid (128 mg, 94%): mp 128–130 °C; IR (KBr, cm^{-1}) 3829, 3412, 2928, 2346, 1330, 1150, 960, 762; ^1H NMR δ 7.84 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 7.4 Hz, 1H), 7.42 (t, J = 7.3 Hz, 1H), 7.37–7.27 (m, 4H), 5.06 (d, J = 16.6 Hz, 1H), 4.48 (d, J = 16.5 Hz, 1H), 2.56 (s, 3H), 2.13 (s, 3H); ^{13}C NMR δ 138.6, 134.9, 132.9, 132.4, 131.5, 131.1, 128.8, 128.5, 127.9, 126.2, 123.8, 122.1, 50.5, 37.7, 19.6; HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 274.0902, found 274.0897.

4-Fluoro-5-(methylsulfonyl)-5,6-dihydrophenanthridine (34). White solid (127 mg, 92%): mp 154–156 °C; IR (KBr, cm^{-1}) 3417, 2912, 1561, 1460, 1338, 1152, 964; ^1H NMR δ 7.84 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.48–7.34 (m, 4H), 7.18 (t, J = 8.9 Hz, 1H), 4.79 (s, 2H), 2.62 (s, 3H); ^{13}C NMR δ 159.0 (J = 252 Hz), 133.2, 132.7, 130.7 (J = 3 Hz), 129.1, 128.8, 128.4 (J = 9 Hz), 126.1, 124.1, 119.8, 116.3, 116.1, 49.7, 39.2; HRMS calcd for $\text{C}_{14}\text{H}_{13}\text{FNO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 278.0651, found 278.0661.

5-(Methylsulfonyl)-4-(trifluoromethyl)-5,6-dihydrophenanthridine (35). White solid (147 mg, 90%): mp 140–143 °C; IR (KBr, cm^{-1}) 3416, 2933, 1610, 1497, 1319, 1159, 967; ^1H NMR δ 8.00 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 7.4 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.47–7.39 (m, 2H), 7.34 (d, J = 7.2 Hz, 1H), 5.01 (d, J = 16.8 Hz, 1H), 4.56 (d, J = 16.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR δ 133.7, 133.3, 132.7, 130.8, 129.5 (J = 31 Hz), 129.4, 129.0, 128.3, 128.2 (J = 5 Hz), 127.8, 126.2, 124.8 (J = 273 Hz), 124.0, 49.7, 38.8; HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{F}_3\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 328.0619, found 328.0618.

2-Chloro-5-(methylsulfonyl)-5,6-dihydrophenanthridine (36). Pale yellow semisolid (135 mg, 92%): IR (KBr, cm^{-1}) 3746, 2923, 2361, 1440, 1339, 1155, 965, 779; ^1H NMR δ 7.81 (d, J = 2.36 Hz, 1H), 7.78 (d, J = 7.4 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.47–7.42 (m, 2H), 7.35–7.32 (m, 2H), 4.82 (s, 2H), 2.28 (s, 3H); ^{13}C NMR δ 134.2, 133.4, 132.0, 131.2, 130.1, 129.2, 129.0, 128.6, 126.2, 124.1,

123.8, 49.3, 37.8; HRMS calcd for $\text{C}_{14}\text{H}_{13}\text{ClNO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 294.0356, found 294.0366.

5-(Methylsulfonyl)-2-nitro-5,6-dihydrophenanthridine (37). Yellow solid (109 mg, 72%): mp 162–164 °C; IR (KBr, cm^{-1}) 3730, 3423, 2924, 2343, 1739, 1459, 1340, 1152; ^1H NMR δ 8.75 (s, 1H), 8.23 (dd, J = 8.8, 2.5 Hz, 1H), 7.93–7.90 (m, 2H), 7.54 (td, J = 7.4, 1.4 Hz, 1H), 7.49 (td, J = 7.4, 1.2 Hz, 1H), 7.40 (d, J = 7.2 Hz, 1H), 4.91 (s, 2H), 2.43 (s, 3H); ^{13}C NMR δ 146.5, 141.2, 131.9, 130.5, 130.0, 129.4, 128.1, 126.2, 124.1, 123.3, 119.5, 49.1, 38.8; HRMS calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 305.0596, found 305.0590.

Ethyl 5-(methylsulfonyl)-5,6-dihydrophenanthridine-3-carboxylate (38). White solid (118 mg, 71%): mp 144–146 °C; IR (KBr, cm^{-1}) 3246, 2999, 1698, 1588, 1474, 1339, 1153, 972; ^1H NMR δ 8.35 (s, 1H), 8.07 (dd, J = 8.0, 1.7 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 7.4 Hz, 1H), 7.49–7.41 (m, 2H), 7.36 (d, J = 7.0 Hz, 1H), 4.85 (s, 2H), 4.41 (q, J = 7.1 Hz, 2H), 2.29 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 165.6, 135.7, 133.6, 132.6, 130.8, 130.4, 129.6, 129.0, 128.9, 128.6, 126.2, 124.2, 124.1, 61.3, 49.3, 38.0, 14.3; HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 332.0957, found 332.0950.

3-Methyl-5-(methylsulfonyl)-5,6-dihydrophenanthridine (39). White solid (109 mg, 80%): mp 130–132 °C; IR (KBr, cm^{-1}) 3248, 2929, 1610, 1494, 1316, 772; ^1H NMR δ 7.78 (d, J = 7.7 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.54 (s, 1H), 7.42 (td, J = 7.3, 1.1 Hz, 1H), 7.37–7.31 (m, 2H), 7.21 (d, J = 7.2 Hz, 1H), 4.82 (s, 2H), 2.44 (s, 3H), 2.28 (s, 3H); ^{13}C NMR δ 139.1, 135.7, 131.6, 131.4, 128.7, 128.5, 128.2, 127.0, 126.0, 123.9, 123.3, 49.6, 37.6, 21.3; HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 274.0902, found 274.0908.

5-(Methylsulfonyl)-3-nitro-5,6-dihydrophenanthridine (40). Pale yellow solid (45 mg, 15%): mp 200–202 °C; IR (KBr, cm^{-1}) 3426, 2923, 1333, 1155; ^1H NMR δ 8.57 (s, 1H), 8.24 (dd, J = 8.0, 2.3 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.88–7.86 (m, 1H), 7.53–7.47 (m, 2H), 7.40–7.38 (m, 1H), 4.89 (s, 2H), 2.36 (s, 3H); ^{13}C NMR δ 136.5, 135.4, 132.8, 130.6, 129.4, 129.3, 126.4, 124.8, 124.6, 123.1, 122.2, 49.1, 38.5; HRMS calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 305.0596, found 305.0590.

5-(Methylsulfonyl)-1-nitro-5,6-dihydrophenanthridine (41). Pale yellow solid (124 mg, 82%): mp 174–176 °C; IR (KBr, cm^{-1}) 3730, 2928, 2368, 1527, 1340, 1154; ^1H NMR δ 7.99 (dd, J = 8.2, 1.24 Hz, 1H), 7.71 (dd, J = 1.24, 8.0 Hz, 1H), 7.52–7.39 (m, 5H), 4.86 (s, 2H), 2.16 (s, 3H); ^{13}C NMR δ 138.4, 133.1, 131.0, 129.9, 129.0, 128.4, 126.8, 126.5, 126.1, 123.8, 123.0, 49.8, 38.5; HRMS calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 305.0596, found 305.0595.

3-Nitro-5-tosyl-5,6-dihydrophenanthridine (42). Pale yellow solid (152 mg, 80%): mp 156–158 °C; IR (KBr, cm^{-1}) 3730, 2928, 2368, 1527, 1340, 1154 cm^{-1} ; ^1H NMR δ 8.69 (s, 1H), 8.20 (dd, J = 8.6, 2.3 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.29–7.27 (m, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.17 (d, J = 7.4 Hz, 1H), 7.05 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 4.93 (s, 2H), 2.19 (s, 3H); ^{13}C NMR δ 147.2, 143.6, 136.7, 136.3, 134.4, 132.2, 129.8, 129.1, 128.7, 128.1, 127.0, 126.4, 124.4, 123.8, 123.5, 122.1, 49.4, 21.3; HRMS calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 381.0909, found 381.0904.

1-Nitro-5-tosyl-5,6-dihydrophenanthridine (43). Pale yellow solid (27 mg, 14%): mp 140–142 °C; IR (KBr, cm^{-1}) 3736, 2917, 2346, 1519, 1353, 1163; ^1H NMR δ 7.98 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.8 Hz, 1H), 6.92–6.86 (m, 4H), 6.69 (d, J = 7.8 Hz, 1H), 4.88 (s, 2H), 2.14 (s, 3H); ^{13}C NMR δ 148.1, 143.4, 138.6, 134.4, 132.4, 132.8, 131.4, 129.0, 128.8, 128.0, 127.7, 126.6, 126.5, 126.3, 125.4, 124.5, 122.8, 50.0, 21.3; HRMS calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 381.0909, found 381.0911.

1-Nitro-6-tosyl-5,6-dihydro-[1,3]dioxolo[4,5-*b*]-phenanthridine (44). Yellow solid (178 mg, 84%): mp 220–222 °C; IR (KBr, cm^{-1}) 3423, 2923, 1731, 1354, 1166, 939, 713; ^1H NMR δ 8.06 (dd, J = 8.0, 1.5 Hz, 1H), 7.66 (dd, J = 8.0, 1.2 Hz, 1H), 7.45 (t, J = 8.1 Hz, 1H), 6.99 (d, J = 8.3 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 6.60 (s, 1H), 6.20 (s, 1H), 5.94 (s, 2H), 4.73 (s, 2H), 2.25 (s, 3H); ^{13}C NMR δ 148.5, 147.6, 143.6, 138.2, 134.6, 131.5, 129.9, 128.7, 127.6, 127.3, 127.2, 126.8, 124.8, 123.1, 120.4, 107.2, 105.6, 101.5, 50.0, 21.3; HRMS calcd for $\text{C}_{21}\text{H}_{17}\text{N}_2\text{O}_6\text{S}$ [$\text{M} + \text{H}$] $^+$ 425.0807, found 424.0812.

6-(Methylsulfonyl)-6,7-dihydro-[1,3]dioxolo[4,5-*a*]phenanthridine (45). White solid (138 mg, 91%): mp 166–168 °C; IR (KBr, cm^{-1}) 3432, 2913, 1439, 1324, 1151, 968; ^1H NMR δ 8.1 (d, $J = 8.4$ Hz, 1H), 7.42 (td, $J = 7.3, 1.6$ Hz, 1H), 7.37 (td, $J = 7.4, 1.3$ Hz, 1H), 7.34 (d, $J = 7.3$ Hz, 1H), 7.22 (d, $J = 8.3$ Hz, 1H), 6.84 (d, $J = 8.3$ Hz, 1H), 6.16 (s, 2H), 4.82 (s, 2H), 2.27 (s, 3H); ^{13}C NMR δ 146.9, 144.2, 131.8, 129.6, 128.6, 128.5, 128.5, 126.7, 126.0, 121.3, 113.7, 107.7, 101.8, 49.8, 37.5; HRMS calcd for $\text{C}_{15}\text{H}_{14}\text{NO}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 304.0644, found 304.0648.

6-Tosyl-6,7-dihydro-[1,3]dioxolo[4,5-*a*]phenanthridine (46). White solid (170 mg, 90%): mp 130–132 °C; IR (KBr, cm^{-1}) 2901, 1593, 1436, 1340, 1239, 1158, 1049, 940; ^1H NMR δ 7.51 (d, $J = 7.6$ Hz, 1H), 7.29 (d, $J = 8.3$ Hz, 1H), 7.12–7.06 (m, 3H), 6.96 (d, $J = 6.5$ Hz, 2H), 6.82 (d, $J = 8.3$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 2H), 6.04 (s, 2H), 4.80 (s, 2H), 2.15 (s, 3H); ^{13}C NMR δ 146.7, 143.6, 142.8, 134.4, 131.1, 129.9, 128.3, 128.1, 127.8, 127.2, 127.1, 126.0, 125.9, 121.5, 114.6, 107.4, 101.6, 50.2, 21.3; HRMS calcd for $\text{C}_{21}\text{H}_{18}\text{NO}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 380.0957, found 380.0954.

5-Tosyl-5,6-dihydro-[1,3]dioxolo[4,5-*j*]phenanthridine (47). White solid (168 mg, 88%): mp 145–147 °C; IR (KBr, cm^{-1}) 2914, 1732, 1595, 1480, 1342, 1159, 1032; ^1H NMR δ 7.77 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.42 (dd, $J = 7.1, 2.1$ Hz, 1H), 7.36 (td, $J = 7.4, 1.9$ Hz, 2H), 6.98 (d, $J = 8.2$ Hz, 2H), 6.79 (d, $J = 8.0$ Hz, 2H), 6.69 (s, 1H), 6.52 (s, 1H), 5.92 (s, 2H), 4.73 (s, 2H), 2.23 (s, 3H); ^{13}C NMR δ 147.5, 147.3, 142.9, 135.3, 134.8, 130.7, 128.3, 128.0, 127.7, 127.5, 127.1, 125.5, 125.3, 123.2, 106.6, 103.6, 101.1, 49.7, 21.3; HRMS calcd for $\text{C}_{21}\text{H}_{18}\text{NO}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 380.0957, found 380.0955.

6-Tosyl-6,7-dihydrobis([1,3]dioxolo[4,5-*a*:4',5'-*j*]phenanthridine (48). White solid (188 mg, 89%): mp 196–198 °C; IR (KBr, cm^{-1}) 3434, 2901, 2372, 1596, 1452, 1344, 1159, 1037, 934; ^1H NMR δ 7.30 (d, $J = 8.4$ Hz, 2H), 7.06–7.02 (m, 2H), 6.86 (d, $J = 8.0$ Hz, 1H), 6.82 (s, 1H), 6.80 (s, 1H), 6.59 (s, 1H), 6.06 (s, 2H), 5.93 (s, 2H), 4.72 (s, 2H), 2.25 (s, 3H); ^{13}C NMR δ 147.1, 146.9, 146.6, 143.0, 134.7, 129.3, 128.3, 127.2, 125.5, 122.1, 121.4, 114.7, 106.8, 106.6, 106.5, 101.5, 101.0, 50.1, 21.3; HRMS calcd for $\text{C}_{22}\text{H}_{18}\text{NO}_6\text{S}$ [$\text{M} + \text{H}$] $^+$ 424.0855, found 424.0854.

1,2,3-Trimethoxy-5-tosyl-5,6-dihydrophenanthridine (49). White solid (159 mg, 75%): mp 108–110 °C; IR (KBr, cm^{-1}) 3434, 2928, 2379, 1593, 1348, 1166, 1086, 946; ^1H NMR δ 7.67 (d, $J = 8.0$ Hz, 1H), 7.19 (s, 1H), 7.06–6.99 (m, 3H), 6.91 (d, $J = 8.2$ Hz, 2H), 6.69 (d, $J = 8.0$ Hz, 2H), 4.73 (s, 2H), 3.97 (s, 3H), 3.94 (s, 3H), 3.69 (s, 3H), 2.16 (s, 3H); ^{13}C NMR δ 152.6, 151.2, 142.8, 142.0, 134.4, 132.8, 130.9, 129.2, 128.3, 127.2, 126.9, 126.7, 126.3, 125.8, 117.8, 107.6, 61.2, 60.7, 56.2, 50.4, 21.2; HRMS calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_5\text{S}$ [$\text{M} + \text{H}$] $^+$ 426.1375, found 426.1371.

5-(Methylsulfonyl)-5,6-dihydrobenzo[*c*]phenanthridine (50). Pale yellow solid (147 mg, 95%): mp 170–172 °C; IR (KBr, cm^{-1}) 3427, 2925, 1741, 1333, 1151, 957; ^1H NMR δ 8.60 (d, $J = 8$ Hz, 1H), 7.98 (d, $J = 7.6$ Hz, 2H), 7.95 (s, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.63 (t, $J = 6.9$ Hz, 1H), 7.57–7.50 (m, 2H), 7.44–7.42 (m, 2H), 5.26 (d, $J = 16.5$ Hz, 1H), 4.65 (d, $J = 16.5$ Hz, 1H), 2.20 (s, 3H); ^{13}C NMR δ 134.1, 133.2, 132.4, 132.3, 131.2, 129.0, 128.9, 128.8, 128.1, 127.4, 126.9, 126.6, 126.6, 126.3, 123.9, 121.4, 50.7, 37.2; HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 310.0902, found 310.0912.

6-Benzyl-2-methyl-6,7-dihydrodibenzo[*d,f*][1,2]thiazepine 5,5-dioxide (53). White solid (92 mg, 53%): mp 186–188 °C; IR (KBr, cm^{-1}) 3735, 2923, 2346, 1333, 1160, 957; ^1H NMR δ 7.97 (d, $J = 7.9$ Hz, 1H), 7.50–7.32 (m, 10H), 7.25 (d, $J = 7.4$ Hz, 1H), 4.45 (s, 2H), 3.70 (s, 2H), 2.53 (s, 3H); ^{13}C NMR δ 7.97 (d, $J = 7.9$ Hz, 1H), 7.50–7.32 (m, 10H), 7.25 (d, $J = 7.4$ Hz, 1H), 4.45 (s, 2H), 3.70 (s, 2H), 2.53 (s, 3H); ^{13}C NMR δ 143.9, 140.8, 139.3, 135.9, 133.6, 133.5, 130.5, 130.0, 129.3, 128.9, 128.8, 128.7, 128.6, 128.4, 127.9, 127.1, 54.9, 52.7, 21.6; HRMS calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 350.1215, found 350.1216.

5-Phenyl-6-tosyl-6,7-dihydro-5H-dibenzo[*c,e*]azepine (55). Off-white solid (30 mg, 14%): mp 145–147 °C; IR (KBr, cm^{-1}) 3319, 2922, 1599, 1454, 1338, 1157; ^1H NMR δ 7.44 (d, $J = 8.3$ Hz, 2H), 7.19–7.16 (m, 5H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.07–7.04 (m, 6H), 6.78 (d, $J = 8.2$ Hz, 2H), 6.39 (s, 1H), 4.52 (s, 2H), 2.38 (s, 3H); ^{13}C NMR δ 142.9, 138.8, 138.0, 137.1, 129.2, 129.2, 128.3, 128.2,

127.8, 127.5, 127.3, 126.9, 65.9, 49.8, 21.4; HRMS calcd for $\text{C}_{27}\text{H}_{24}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 426.1528, found 426.1521.

6-Benzhydryl-2-methyl-6,7-dihydrodibenzo[*d,f*][1,2]-thiazepine 5,5-dioxide (56). White solid (123 mg, 58%): mp 173–175 °C; IR (KBr, cm^{-1}) 3435, 2926, 2852, 1594, 1443, 1319, 1164; ^1H NMR δ 7.89 (d, $J = 7.9$ Hz, 1H), 7.46 (d, $J = 4.6$ Hz, 2H), 7.40–7.27 (m, 13H), 7.18 (d, $J = 7.3$ Hz, 1H), 6.82 (s, 1H), 3.61 (s, 2H), 2.44 (s, 3H); ^{13}C NMR δ 143.4, 140.6, 139.1, 138.3, 134.6, 134.1, 130.1, 129.8, 129.1, 129.0, 129.0, 128.6, 128.3, 128.1, 127.6, 126.3, 64.8, 48.6, 21.5; HRMS calcd for $\text{C}_{27}\text{H}_{24}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 426.1528, found 426.1524.

6-Benzyl-2-methyl-6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo-[1,2-*d*]benzo[*f*][1,2]thiazepine 5,5-dioxide (57). White solid (131 mg, 68%): mp 214–216 °C; IR (KBr, cm^{-1}) 3401, 2835, 1597, 1481, 1333, 1227, 1162, 1037, 949; ^1H NMR δ 7.95 (d, $J = 8.4$ Hz, 1H), 7.44–7.31 (m, 7H), 6.95 (s, 1H), 6.70 (s, 1H), 6.03 (s, 2H), 4.42 (s, 2H), 3.58 (s, 2H), 2.51 (s, 3H); ^{13}C NMR δ 148.4, 148.0, 143.9, 139.3, 135.9, 134.6, 133.1, 130.2, 128.7, 128.6, 128.5, 127.9, 127.3, 127.2, 110.4, 108.8, 101.6, 54.5, 52.3, 21.6; HRMS calcd for $\text{C}_{22}\text{H}_{20}\text{NO}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 394.1113, found 394.1111.

2-Methyl-6-phenethyl-6,7-dihydrodibenzo[*d,f*][1,2]-thiazepine 5,5-dioxide (59). White solid (142 mg, 78%): mp 100–102 °C; IR (KBr, cm^{-1}) 3421, 2922, 1598, 1455, 1333, 1162, 1088, 750; ^1H NMR δ 7.92 (d, $J = 7.9$ Hz, 1H), 7.50–7.46 (m, 2H), 7.43–7.40 (m, 2H), 7.36–7.31 (m, 3H), 7.28–7.26 (m, 3H), 6.14 (s, 2H), 3.82 (s, 2H), 3.54 (t, $J = 7.5$ Hz, 2H), 2.99 (t, $J = 7.9$ Hz, 2H), 2.52 (s, 3H); ^{13}C NMR δ 143.7, 140.8, 139.0, 138.7, 134.1, 133.7, 130.4, 130.1, 129.3, 128.9, 128.9, 128.6, 128.4, 126.7, 126.5, 53.9, 53.5, 35.0, 21.5; HRMS calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 364.1371, found 364.1365.

4-Methyl-*N*-(3-(trifluoromethyl)benzyl)benzenesulfonamide (60). Off-white solid (312 mg, 95%): mp 101–103 °C; IR (KBr, cm^{-1}) 3428, 2933, 1631, 1475, 1330, 1169, 1074; ^1H NMR δ 7.74 (d, $J = 8.1$ Hz, 2H), 7.50–7.48 (m, 2H), 7.45 (t, $J = 7.4$ Hz, 1H), 7.39 (s, 1H), 7.29 (d, $J = 7.8$ Hz, 2H), 5.35 (bs, 1H), 4.21 (s, 2H), 2.43 (s, 3H); ^{13}C NMR δ 143.7, 137.5, 136.7, 131.2, 131.0, 129.7, 129.5, 129.1, 127.0, 125.2 (q, $J = 270$ Hz), 124.5 (q, $J = 3$ Hz), 46.6, 21.4; HRMS calcd for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 330.0776, found 330.0770.

6-Tosyl-3-(trifluoromethyl)-6,7-dihydro-5H-dibenzo[*c,e*]azepine (61). White solid (120 mg, 58%): mp 186–188 °C; IR (KBr, cm^{-1}) 3444, 2924, 1597, 1462, 1330, 1157, 1087; ^1H NMR δ 7.74 (d, $J = 8.2$ Hz, 2H), 7.62 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.47–7.34 (m, 4H), 7.27 (d, $J = 7.8$ Hz, 2H), 7.22 (s, 1H), 4.19 (s, 2H), 4.13 (s, 2H), 2.38 (s, 3H); ^{13}C NMR δ 143.9, 139.1, 135.9, 132.3, 132.0, 130.2, 130.1, 129.8, 129.7, 129.2, 129.1, 128.3, 128.0, 127.4, 126.5 (q, $J = 4$ Hz), 125.6 (q, $J = 4$ Hz), 125.1 (q, $J = 270$ Hz), 48.9, 48.5, 21.4; HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{F}_3\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 418.1089, found 418.1084.

2-Methyl-6-(3-(trifluoromethyl)benzyl)-6,7-dihydrodibenzo[*d,f*][1,2]thiazepine 5,5-dioxide (62). White solid (83 mg, 40%): mp 168–170 °C; IR (KBr, cm^{-1}) 3434, 2924, 1599, 1447, 1329, 1165, 1074; ^1H NMR δ 7.97 (d, $J = 7.9$ Hz, 1H), 7.68–7.65 (m, 2H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.54–7.49 (m, 3H), 7.42–7.37 (m, 3H), 7.28 (d, $J = 7.4$ Hz, 1H), 4.52 (s, 2H), 3.72 (s, 2H), 2.53 (s, 3H); ^{13}C NMR δ 144.1, 140.7, 139.2, 137.1, 133.3, 133.3, 131.8, 131.5 (q, $J = 32$ Hz), 130.6, 130.0, 129.4, 129.3, 129.0, 128.9, 128.0 (q, $J = 270$ Hz), 127.0, 125.2 (q, $J = 3$ Hz), 124.8 (q, $J = 3$ Hz), 54.5, 53.0, 21.6; HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{F}_3\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 418.1089, found 418.1090.

(*S*)-5-Methyl-6-tosyl-6,7-dihydro-5H-dibenzo[*c,e*]azepine (64). White solid (96 mg, 53%): mp 179–181 °C; IR (KBr, cm^{-1}) 3428, 2931, 1596, 1449, 1335, 1161; ^1H NMR δ 7.78 (d, $J = 8.0$ Hz, 2H), 7.49–7.35 (m, 6H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 1H), 6.91 (d, $J = 7.5$ Hz, 1H), 5.01 (q, $J = 7.0$ Hz, 1H), 4.68 (d, $J = 11.8$ Hz, 1H), 3.55 (d, $J = 11.8$ Hz, 1H), 2.42 (s, 3H), 0.97 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR δ 143.2, 140.8, 138.6, 137.3, 136.3, 133.1, 129.7, 129.6, 129.4, 129.1, 128.5, 128.4, 128.1, 127.6, 127.1, 59.1, 49.0, 23.9, 21.5; HRMS calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 364.1371, found 364.1378.

(*S*)-2-Methyl-6-(1-phenylethyl)-6,7-dihydrodibenzo[*d,f*]-[1,2]thiazepine 5,5-dioxide (65). White solid (54 mg, 30%): mp 148–150 °C; IR (KBr, cm^{-1}) 3399, 2924, 1736, 1599, 1447, 1328, 1166, 753; ^1H NMR δ 8.00 (d, $J = 7.9$ Hz, 1H), 7.52–7.46 (m, 4H), 7.42–7.33 (m, 6H), 7.08 (d, $J = 7.4$ Hz, 1H), 5.60 (d, $J = 6.9$ Hz, 1H),

3.72 (d, J = 12.0 Hz, 1H), 3.53 (d, J = 12.0 Hz, 1H), 2.52 (s, 3H), 1.60 (d, J = 7.0 Hz, 3H); ^{13}C NMR δ 143.5, 140.6, 139.9, 139.2, 135.1, 134.1, 130.3, 129.8, 129.0, 128.9, 128.9, 128.5, 128.1, 127.7, 127.6, 126.3, 56.4, 46.2, 21.5, 15.7; HRMS calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 364.1371, found 364.1378.

N-(3-(Trifluoromethyl)benzyl)methanesulfonamide (66). Off-white solid (240 mg, 95%): mp 66–68 °C; IR (KBr, cm^{-1}) 3336, 2929, 1330, 1161, 975; ^1H NMR δ 7.60 (s, 1H), 7.57–7.54 (m, 2H), 7.50 (t, J = 7.6 Hz, 1H), 5.28 (bs, 1H), 4.36 (s, 2H), 2.87 (s, 3H); ^{13}C NMR δ 137.9, 131.6 (q, J = 36 Hz), 131.2, 129.3, 125.2 (q, J = 270 Hz), 124.8 (q, J = 4 Hz), 124.5 (q, J = 4 Hz), 46.5, 40.9; HRMS calcd for $\text{C}_9\text{H}_{11}\text{F}_3\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 254.0463, found 254.0460.

6-(Methylsulfonyl)-3-(trifluoromethyl)-6,7-dihydro-5H-dibenzo[*c,e*]azepine (67). White solid (96 mg, 76%): mp 133–135 °C; IR (KBr, cm^{-1}) 3421, 2923, 1621, 1327, 1160; ^1H NMR δ 7.79 (d, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.56–7.54 (m, 2H), 7.49–7.46 (m, 2H), 4.20 (s, 4H), 2.82 (s, 3H); ^{13}C NMR δ 144.2, 139.1, 132.8, 132.2, 130.9, 130.5, 129.9, 129.5, 128.8, 128.5, 126.7 (q, J = 4 Hz), 126.1 (q, J = 4 Hz), 125.1 (q, J = 271 Hz), 48.8, 48.6, 37.4; HRMS calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 342.0776, found 342.0770.

■ ASSOCIATED CONTENT

■ Supporting Information

^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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