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[4 + 2] Benzannulation of 3-Alkenylpyrroles/Thiophenes with Propargylic Alcohols: Access to Substituted Indoles, Benzothiophenes, and Aza[5]helicenes

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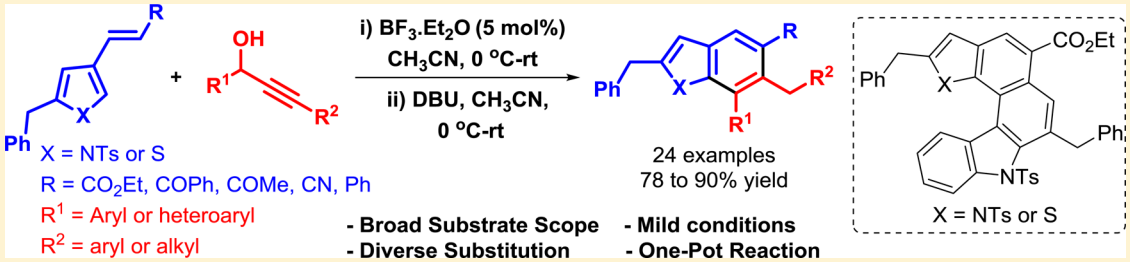
Supporting Information



ABSTRACT: An efficient and practical one-pot [4 + 2] benzannulation method to produce highly substituted indoles and 1-benzothiophenes via sequential acid-catalyzed propargylation/base-mediated cycloisomerization reactions has been developed. This method allows access to differently substituted (mainly on phenyl ring) indoles and 1-benzothiophenes from the reaction of 3-alkenylpyrroles/-thiophenes as C4 synthons with 1-aryl/1-heteroaryl propargylic alcohols as C2 synthons. Interestingly, dialkynyl substrates can undergo tandem benzannulations to give substituted aza[5]helicenes in 82−83% yield.

INTRODUCTION

Indoles and benzothiophenes are an important class of structural motifs among the benzo-fused heteroaromatic compounds due to their presence in numerous bioactive natural products and diverse range of pharmaceutically related small molecules.[1,2] They have also found applications in optoelectronic materials because of their interesting photophysical properties.[3] In addition, these benzannulated heteroaromatics were found in agrochemicals and pigments.[4] Hence, the development of efficient methods for the synthesis of substituted indoles and benzothiophenes has received prominence. Consequently, various heterocyclization methods have been employed for the synthesis of indoles and benzothiophenes through the construction of a five-membered heterocyclic ring on a prefunctionalized benzene ring.[5−7] In these strategies, the diverse substitution on the benzene ring of the indole or benzothiophene is a challenging task. Conventionally, the substitution on the benzene part of benzoheterocycles is achieved via sequential electrophilic substitution and metalation−alkylation reactions.[8] On the other hand, there are synthetic approaches available in the literature to create the diversely substituted benzene ring of indole or benzothiophene via either intermolecular benzannulation (in one pot starting from two or more precursors)[9−11] or intramolecular benzannulations.[12] Among these, [4 + 2] benzannulations have received attention involving the reaction of pyrrole/thiophene as a C2 synthon with various C4 synthons (Scheme 1a) such as 1,3-diynes (**A1**), enalcarbenoids (**A2**), pent-1-en-4-yn-3-ol (**A3**), 2,5-dimethoxytetrahydrofuran (**A4**), and a few others.[9] Alternatively, [4 + 2] benzannulation reactions of 3-alkynylpyrrole-2-carboxaldehyde/3-alkynylthiophene-2-carboxaldehyde (**C1**) with an enol ether/alkene and phenyl(sulfinyl)-methyl-substituted pyrrole (**C2**) with Michael acceptors have also been reported for the synthesis of the corresponding indoles/benzothiophenes (**D1** and **D2**), wherein pyrrole/thiophene derivatives were used as C4 synthons (Scheme 1b).[10] The development of new methods for the synthesis of indoles/benzothiophenes having diverse substitutions on the benzene part from easily accessible starting materials is certainly a valuable addition to the existing benzannulation strategies.

On the basis of our work on the development of novel [4 + 2] benzannulations[13] and the use of 1-aryl propargylic alcohols as handy synthons,[14] we envisioned that 3-alkenylpyrrole/-thiophene derivatives (**C3**) would be suitable C4 synthons in reactions with 1-aryl/heteroaryl propargylic alcohols (C2 synthons) to give the substituted indoles/1-benzothiophenes (**D3**) through acid-catalyzed C2 propargylation followed by base-mediated cycloisomerization (Scheme 1c). This strategy is expected to provide access to indoles/benzothiophenes having substitution at the C5, C6, and C7 positions of the benzene ring, and methods for direct syntheses of such compounds are uncommon. Herein, we report the results of the envisaged

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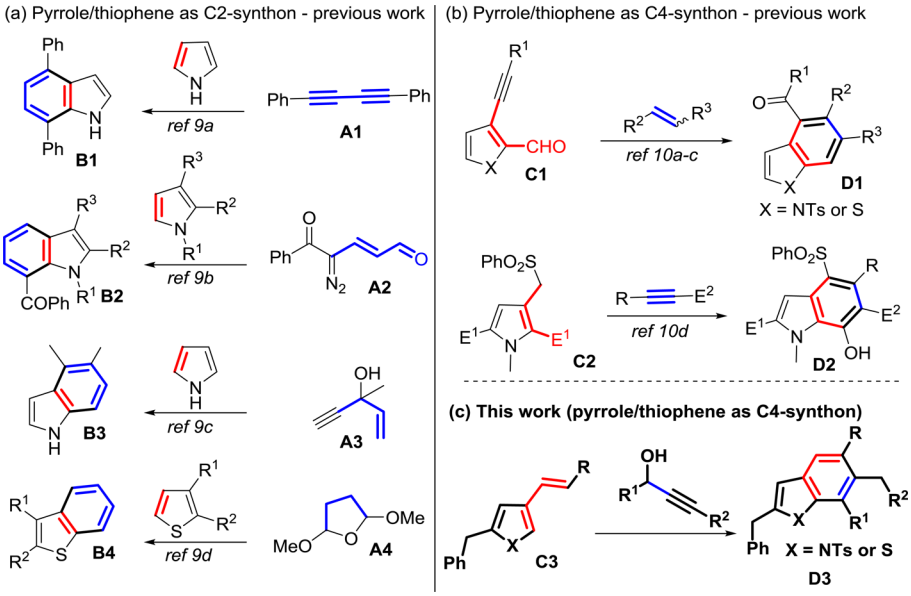
Scheme 1. Selected [4 + 2] Benzannulations for the Synthesis of Indoles and Benzothiophenes

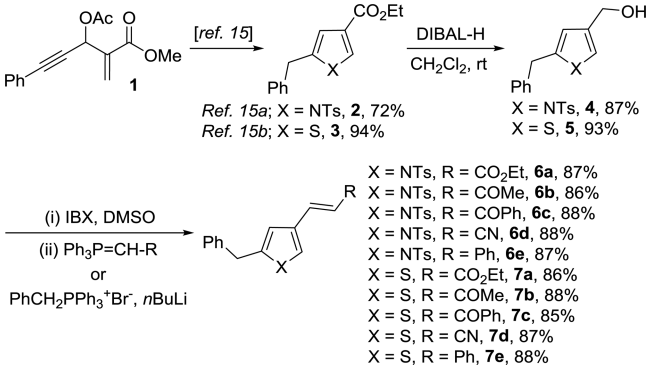


novel [4 + 2] benzannulation approach for the direct synthesis of tetrasubstituted indoles and 1-benzothiophenes.

RESULTS AND DISCUSSION

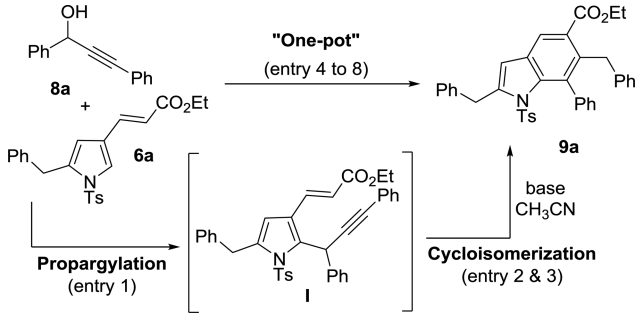
The desired C4 synthons were prepared from Morita–Baylis–Hillman acetate **1**, which was initially converted to the pyrrole **2** or thiophene **3** via our previously reported method.[15] The ester groups of **2** and **3** were reduced using DIBAL-H in CH_2Cl_2 to alcohols **4** and **5**, which were oxidized to aldehydes and subsequently treated with the Wittig ylide to provide the corresponding 2-alkenyl pyrroles **6a–e** and thiophenes **7a–e** in good yield (Scheme 2). The other cyclization component, 1-aryl/heteroaryl propargylic alcohols (**8**, C2 synthon), were obtained by following the literature protocols.[14b,d,16]

Scheme 2. Synthesis of 3-Alkenylpyrrole and -Thiophene Derivatives



The benzannulation of 3-alkenyl pyrrole **6a** with propargylic alcohol **8a** was selected as a model reaction to screen the reaction conditions. First, the propargylation of **6a** with 1,3-diphenylprop-2-yn-1-ol (**8a**) was tested in the presence of $BF_3{\cdot}Et_2O$ (5 mol %) in CH_3CN at room temperature to obtain the 2-propargylated 3-alkenyl pyrrole **I** (entry 1, Table 1). Subsequently, the cycloisomerization was verified in CH_3CN in the presence of two different bases; DBU was found to be the best to obtain the substituted indole **9a** in 95% yield at room temperature in 30 min (entry 3, Table 1), while K_2CO_3 gave **9a** in 73% yield under reflux conditions in 6 h (entry 2, Table 1).

Table 1. Reaction Optimization for [4 + 2] Benzannulation of 6a with 8a



entry	propargylation (acid catalyst (amt (mol %), time (h)))[a]	cycloisomerization (base (temp, time (h)))	product	yield (%)[b]
1	$BF_3{\cdot}Et_2O$ (5, 3)		**I**	91
2[c]		K_2CO_3 (reflux, 6)	**9a**	73
3[c]		**DBU (room temp, 0.5)**	**9a**	**95**
4	**$BF_3{\cdot}Et_2O$ (5, 3)**	**DBU (room temp, 0.5)**	**9a**	**90**
5	$FeCl_3$ (5, 4)	DBU (room temp, 0.5)	**9a**	90
6	*p*TSA (5, 6)	DBU (room temp, 0.5)	**9a**	83
7	I_2 (5, 5)	DBU (room temp, 0.5)	**9a**	64
8	$ZnCl_2$ (5, 3)	DBU (room temp, 0.5)	**9a**	73

[a]Addition of catalyst was carried out at 0 °C, and the mixture was stirred at room temperature. [b]Isolated yields. [c]Starting material used was **I**

Next, the reaction of **6a** with **8a** was carried out in one pot by the successive addition of $BF_3{\cdot}Et_2O$ (5 mol %) and DBU to give ethyl 2,6-dibenzyl-7-phenyl-1-tosyl-1*H*-indole-5-carboxylate (**9a**) in 90% yield. The efficacy of other catalysts, such as $FeCl_3$, *p*TSA, I_2, and $ZnCl_2$ in combination with DBU, was also verified in one-pot reactions, and it was found that the product **9a** was isolated in 64–90% yield (entries 5–8, Table 1).

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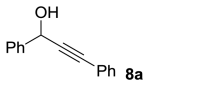
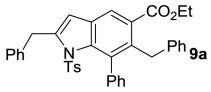
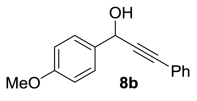
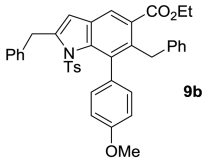
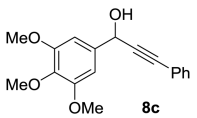
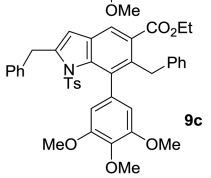
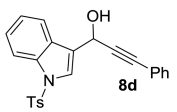
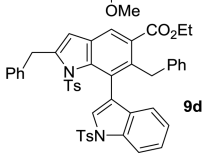
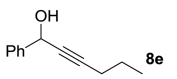
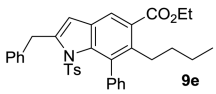
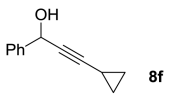
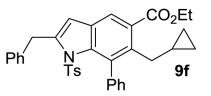
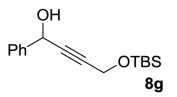
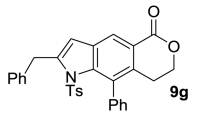
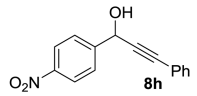
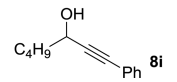
The scope and limitations of this reaction were explored under the optimal conditions, and the results are summarized in Table 2. The [4 + 2] annulation of **6a** with various 1-aryl propargylic alcohols, containing electron-donating phenyl groups such as 4-methoxyphenyl (**8b**) and 3,4,5-trimethoxyphenyl (**8c**) at the C1 position, furnished the corresponding indoles **9b,c** in 87% and 88% yields, respectively (entries 2 and 3, Table 2). A 1-heteroaryl propargylic alcohol, 3-phenyl-1-(1-tosyl-1*H*-indol-3-yl)prop-2-yn-1-ol (**8d**), provided the desired indole product **9d** in 86% yield. 1-Phenyl propargylic alcohols bearing alkyl and cyclopropyl groups on the alkyne, **8e,f**, also successfully participated in [4 + 2] benzannulation with **6a** to give the corresponding 7-phenyl indoles **9e,f**, resepectively (entries 5 and 6, Table 2). The reaction of **6a** with alcohol **8g** underwent desilylative six-membered lactonization during the [4 + 2] benzannulation to give the dihydropyrano[3,4-*f*]indol-5(1*H*)-one **9g** in 79% yield (entry 7, Table 2). The reaction of **6a** with propargylic alcohols **8h**, having electron-withdrawing phenyl group, and **8i**, with an aliphatic group at the C1 position, failed to give the product (entries 8 and 9, Table 2), which demonstrates that the nucleophilic substitution was successful only in the case of propargylic alcohols obtained from electron-rich aromatic aldehydes.

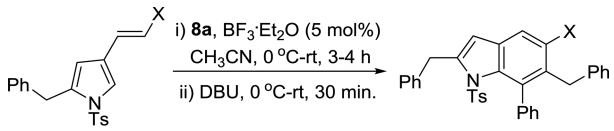
Table 2. [4 + 2] Benzannulation of 2-Alkenylpyrrole 6a with Propargylic Alcohols[a]

entry	propargylic alcohol	reaction time step i/ii(h)	substituted Indole	yield (%)[b]
1	 **8a**	3.0/0.5	 **9a**	90
2	 **8b**	3.0/0.5	 **9b**	87
3	 **8c**	2.0/0.5	 **9c**	88
4	 **8d**	2.5/0.5	 **9d**	86
5	 **8e**	2.5/0.5	 **9e**	85
6	 **8f**	3.0/0.5	 **9f**	89
7	 **8g**	2.5/0.5	 **9g**	79
8[c]	 **8h**	24	-	
9[c]	 **8i**	24	-	

[a]Reaction conditions: **6a** (1 mmol), **8** (1.2 mmol), $BF_3{\cdot}Et_2O$ (5 mol %), CH_3CN, room temperature, and then DBU, room temperature. [b]Isolated yield. [c]Nucleophilic substitution (step i) did not proceed.

Additionally, 2-alkenylpyrroles having different electron-withdrawing groups, **6b−d**, were evaluated in the benzannulation reaction with 1,3-diphenylprop-2-yn-1-ol (**8a**) under optimal conditions (Scheme 3). From these experiments,

Scheme 3. Benzannulation of 2-Alkenylpyrroles 6b−e with 8a



X= COMe, **6b** — X= COMe, **9h**, 87%
X= COPh, **6c** — X= COPh, **9i**, 85%
X= CN, **6d** — X= CN, **9j**, 89%
X= Ph, **6e** — X= Ph, **9k**, 78%

indoles with a 5-carbonyl funtionality, **9h** (87%) and **9i** (85%), and the 5-cyano indole **9j** (89%) were obtained; such structural motifs are found in pharmaceutically important compounds.[17] 2-Alkenylindole **6e** (as an inseparable *E*/*Z* mixture) having weakly electron-withdrawing groups, such as phenyl, also underwent [4 + 2] benzannulation with **8a** to give the corresponding indole **9k** in 78% yield (Scheme 3).

Next, we extended the reaction to the synthesis of substituted 1-benzothiophenes starting from the suitably substituted thiophenes **7a−d**, which were prepared in two steps from the known thiophene **3**, as shown in Scheme 2. The [4 + 2] benzannulation of **7a** with various 1-aryl/1-heteroaryl propargylic alcohols, **8a−g**, were successful in providing a wide variety of substituted 1-benzothiophenes **10a−g** in 80−89% yield (Scheme 4). Similarly, the reactions of 3-alkenyl thiophenes **7b−d** and **7e** (as an inseparable *E*/*Z* mixture) with **8a** also proceeded smoothly to give diversely substituted 1-benzothiophenes **10h−k** (Scheme 5).

We successfully applied the benzannulation of 2-alkenylpyrrole **6a** with a diynyl alcohol, 5-phenyl-1-(1-tosyl-1*H*-indol-3-yl)penta-2,4-diyn-1-ol (**8h**), toward the dibenzannnulation product diaza[5]helicene **11a** (82%) via the monocyclized indole **9l** (81%, Scheme 6). The helicity of **11a** was confirmed by chiral HPLC analysis, which showed the existence of a pair of enanatiomers.[18] Similarly, the reaction of 2-alkenylbenzothiophene **7a** with 2,4-diyn-1-ol **8h** resulted in the formation of **11b** (83%) via benzothiophene **10l** (79%, Scheme 6), through sequential propargylation/benzannulation reactions. The helicene structure of **11b** was determined by X-ray crystallographic analysis (Figure 1), wherein the compound crystallized in the centrosymmetric monoclinic $P2_1/c$ system and exists as a racemic mixture (see the Supporting Information). To our knowledge, there have been no sequential dibenzannulation methods reported in the literature for the synthesis of aza[5]helicenes, which are valuable molecules in materials science.[19]

On the basis of the observed results, a possible reaction mechanism is shown in Scheme 7. Initially, the propargylic alcohol **6a** undergoes nucleophilic substitution with **6a** via carbocation **A** in the presence of acid catalyst to provide **I**, which was isolated and characterized. Next, DBU-promoted

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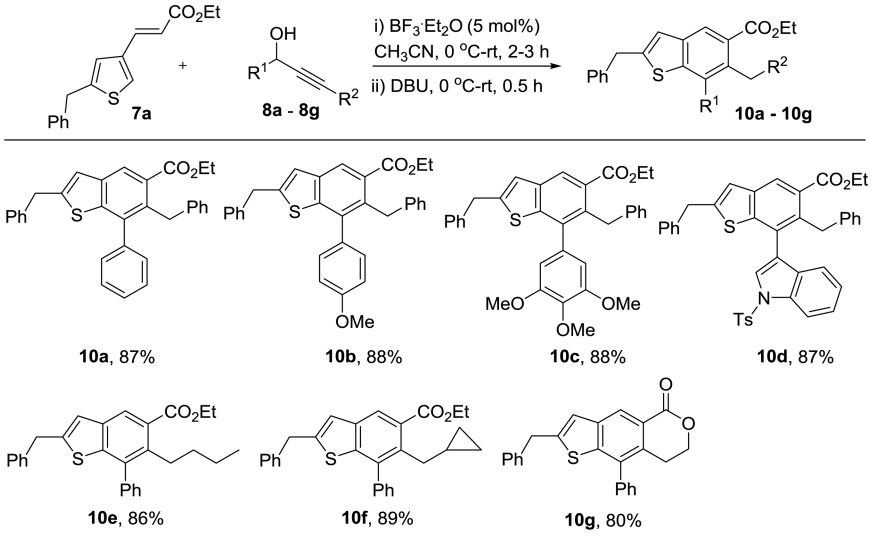
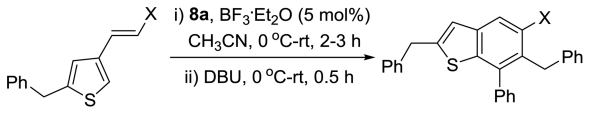
Scheme 4. Benzannulation of 2-Alkenylthiophene 7a with Propargylic Alcohols



Scheme 5. Benzannulation of 2-Alkenylthiophenes 7b−e with 8a



X= COMe, **7b**
X= COPh, **7c**
X= CN, **7d**
X= Ph, **7e**

X= COMe, **10h**, 88%
X= COPh, **10i**, 84%
X= CN, **10j**, 89%
X= Ph, **10k**, 80%

isomerization of **I** gives allene **B**, which cyclizes through 1,3,5-triene electrocyclization to **C** followed by aromatization, leading to the benzannulated product, indole **9a**.

CONCLUSION

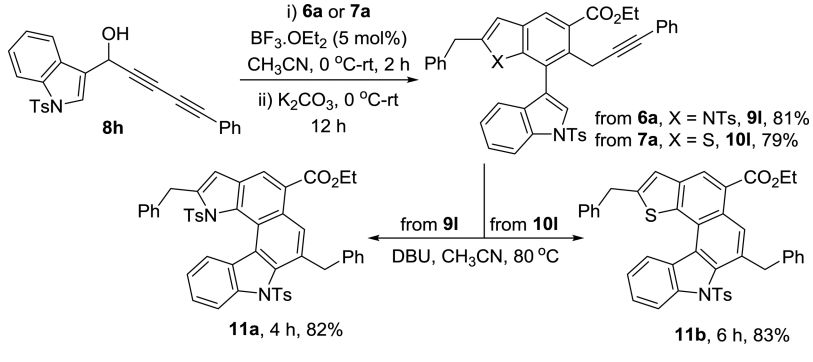
In summary, we have successfully developed a new [4 + 2] benzannulation for the one-pot synthesis of indoles and 1-benzothiophenes from the reaction of 2-alkenyl pyrroles/thiophenes with 1-aryl/1-heteroaryl propargylic alcohols. This powerful methodology, involving propargylation and cycloisomerization reactions, allows the formation of two new C−C bonds to construct diversely substituted benzene rings of indole/benzothiophene. In addition, an efficient dibenzannulation of 2,4-diyn-1-ol was also realized, thus providing a facile access to aza[5]helicenes.

EXPERIMENTAL SECTION

General Information. All air- and moisture-sensitive reactions were carried out under an inert atmosphere (nitrogen or argon). Oven-dried glass apparatus was used to perform all the reactions. Freshly distilled anhydrous solvents were used for air- and moisture-sensitive reactions. Commercially available reagents were used as received. Reactions were monitored by thin-layer chromatography carried out on silica plates using UV light and anisaldehyde for visualization. Column chromatography was performed on silica gel (60−120 mesh) using hexanes and ethyl acetate as eluent. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ solvent on 500, 400, 300, 125, 100, and 75 MHz, respectively, using TMS as an internal standard. Chemical shifts are measured as ppm values relative to internal $CHCl_3$ (δ 7.26) or TMS (δ 0.0) for ^{1}H NMR and $CDCl_3$ (δ 77) for ^{13}C NMR. Chemical shifts δ and coupling constants J are given in ppm (parts per million) and Hz (hertz), respectively. High-resolution mass spectra (HRMS) [ESI+] were obtained using either a TOF or a double-focusing spectrometer.

Experimental Procedures and Analytical Data. *(5-Benzyl-1-tosyl-1H-pyrrol-3-yl)methanol (4).* To a stirred solution of pyrrole **2**[15a] (1 g, 2.71 mmol) in CH_2Cl_2 (20 mL) was added DIBAL-H (25% w/v in toluene, 4.6 mL, 8.13 mmol), at −78 °C, and the mixture was stirred at same temperature for 1 h. Then, the reaction mixture was stirred at 0 °C for 1 h. Next, the reaction mixture was quenched with aqueous saturated sodium potassium tartrate (20 mL) and stirred for 1 h. The aqueous phase was extracted with EA (2 × 10 mL), and the combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, and concentrated using a rotary evaporator. The crude residue was purified by flash column chromatography on silica gel

Scheme 6. Synthesis of Aza[5]helicenes through Dibenzannulation



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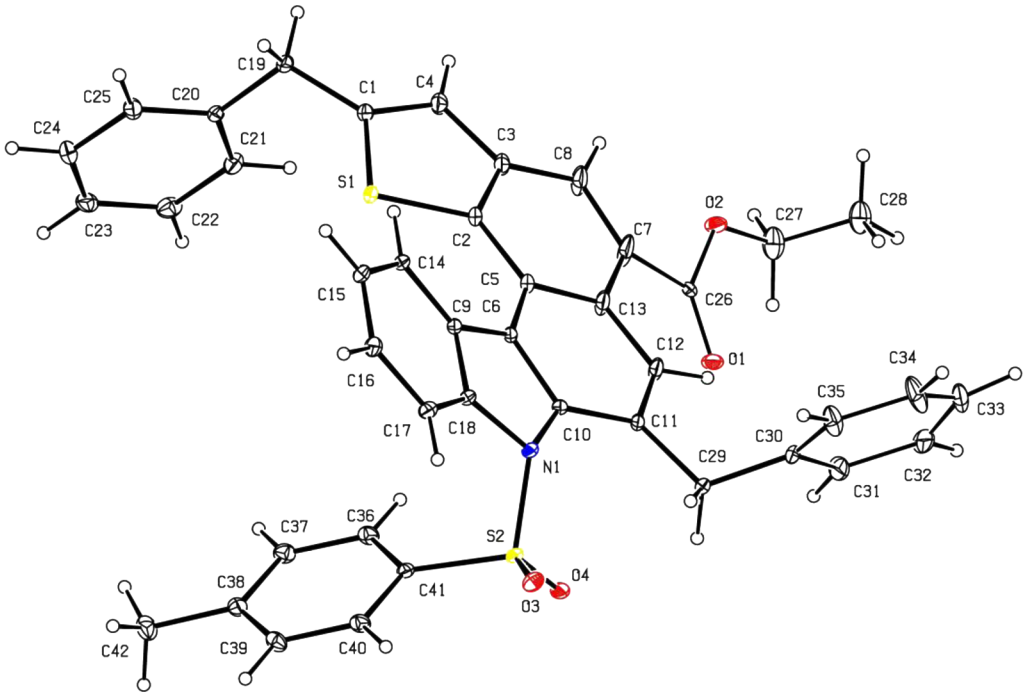
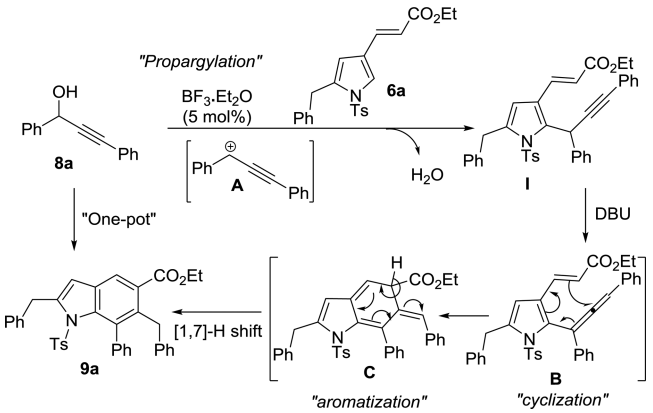


Figure 1. ORTEP diagram of **11b**.

Scheme 7. Plausible Reaction Mechanism



(EtOAc/hexanes) to afford **4**: 804 mg, 87% yield, pale yellow semisolid; R_f = 0.5 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.50 (m, 2H), 7.27 (t, J = 2.4 Hz, 1H), 7.25−7.13 (m, 5H), 7.09−7.00 (m, 2H), 5.78−5.75 (m, 1H), 4.45 (s, 2H), 4.05 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 137.9, 136.0, 135.1, 129.8, 129.0, 128.3, 126.8, 126.3 (2C), 119.7, 113.7, 58.2, 33.5, 21.5; IR (KBr) 3023, 1360, 1256, 1172, 1092, 1021, 743, 664 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{20}O_3NS$ $(M + H)^+$ 342.1158, found 342.1164.

5-Benzyl-1-tosyl-1H-pyrrole-3-carbaldehyde. A solution of (5-benzyl-1-tosyl-1*H*-pyrrol-3-yl)methanol (**4**; 1 g, 2.93 mmol) in THF (4.9 mL) was added to IBX (1.23 g, 4.39 mmol) in DMSO (1.5 mL). The resulting mixture was stirred at room temperature for 1 h and quenched with ice cold water (10 mL), filtered through Celite, extracted with EtOAc (2 × 10 mL) and washed with aqueous saturated $NaHCO_3$ solution (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo.

*Ethyl (E)-3-(5-Benzyl-1-tosyl-1H-pyrrol-3-yl)acrylate (**6a**).* To the above crude 5-benzyl-1-tosyl-1*H*-pyrrole-3-carbaldehyde in CH_2Cl_2 (10 mL) was added phosphonium ylide Ph_3P = CO_2Et (1.52 g, 4.39 mmol), and the mixture was stirred at room temperature for 7 h. The reaction mixture was concentrated using a rotary evaporator, and the residue was purified by flash chromatography on silica gel (EtOAc/hexanes) to give α,β-unsaturated ester **6a** as as pale yellow solid: 1.04 g, 87% yield, R_f = 0.5 (hexanes/EtOAc = 4/1); mp 109−111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−7.54 (m, 2H), 7.51 (d, J = 1.8 Hz, 1H), 7.47 (d, J = 15.8 Hz, trans double bond, 1H), 7.25−7.17 (m, 5H), 7.04 (dt, J = 5.0, 3.9 Hz, 2H), 6.00 (d, J = 15.8 Hz, trans double bond, 1H), 5.90 (d, J = 1.2 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 4.04 (s, 2H), 2.40 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 145.2, 137.3, 136.3, 136.2, 135.4, 130.0, 129.0, 128.4, 126.9, 126.5, 124.4, 122.5, 117.2, 111.3, 60.2, 33.4, 21.6, 14.2; IR (KBr) 3023, 1706, 1637, 1368, 1215, 1173, 742, 665 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{23}NNaO_4S$ $(M + Na)^+$ 432.1240, found 432.1252.

*Procedure for the Preparation of 3-Alkenyl Pyrroles **6b−d**.* A solution of (5-benzyl-1-tosyl-1*H*-pyrrol-3-yl)methanol (**4**; 1 mmol) in THF (for 1 g of IBX, 4 mL of THF) was added to IBX (1.5 mmol) in DMSO (for 1 g of IBX, 1.2 mL of DMSO). The resulting mixture was stirred at room temperature for 1 h, quenched with ice-cold water (5 mL), filtered through Celite, extracted with EtOAc (2 × 10 mL), and washed with aqueous saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated. To this residue in toluene (4 mL) was added the respective phosphonium ylide (Ph_3P=R) (1.5 mmol), and the mixture was refluxed at 120 °C for 12 h. After the mixture was cooled, the solvent was removed and the residue purified by flash chromatography on silica gel (EtOAc/hexanes) to give the corresponding 3-alkenyl pyrroles **6b−d**.

*(E)-4-(5-Benzyl-1-tosyl-1H-pyrrol-3-yl)but-3-en-2-one (**6b**):* 325 mg, 86% yield, pale yellow semisolid; R_f = 0.3 (hexanes/EtOAc = 9/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.49 (m, 3H), 7.32 (d, J = 16.1 Hz, trans double bond, 1H), 7.26−7.19 (m, 5H), 7.10−6.97 (m, 2H), 6.29 (d, J = 16.1 Hz, trans double bond, 1H), 5.92 (d, J = 1.2 Hz, 1H), 4.04 (s, 2H), 2.41 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.0, 145.2, 137.2, 136.4, 135.2, 135.1, 129.9, 128.9, 128.4, 126.9, 126.5, 126.4, 124.8, 122.4, 111.2, 33.3, 27.1, 21.5; IR (KBr) 2927, 2311, 1729, 1362, 1170, 1068, 752, 666 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{21}NNaO_3S$ $(M + Na)^+$ 402.1134, found 402.1116.

*(E)-3-(5-Benzyl-1-tosyl-1H-pyrrol-3-yl)-1-phenylprop-2-en-1-one (**6c**):* 388 mg, 88% yield, pale yellow solid; R_f = 0.5 (hexanes/EtOAc = 7/3); mp 117−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.89 (m, 2H), 7.69−7.50 (m, 5H), 7.46 (t, J = 7.5 Hz, 2H), 7.30−7.18 (m, 5H),

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7.14−7.03 (m, 3H), 6.05 (d, J = 1.0 Hz, 1H), 4.08 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 145.2, 138.1, 137.4, 136.6, 136.3, 135.3, 132.5, 130.0, 129.0, 128.4 (2C), 128.3, 126.9, 126.5, 125.5, 123.0, 121.2, 111.3, 33.4, 21.5; IR (KBr) 2924, 2384, 2311, 1732, 1677, 1364, 1087, 669 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{24}NO_3S$ (M + H)$^+$ 442.1471, found 442.1494.

*(E)-3-(5-Benzyl-1-tosyl-1H-pyrrol-3-yl)acrylonitrile (**6d**):* 318 mg, 88% yield, pale yellow solid; R_f = 0.5 (hexanes/EtOAc = 7/3); mp 96−98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61−7.54 (m, 2H), 7.51 (d, J = 1.9 Hz, 1H), 7.29−7.20 (m, 5H), 7.16 (d, J = 16.4 Hz, trans double bond, 1H), 7.11−6.96 (m, 2H), 5.84 (d, J = 1.2 Hz, 1H), 5.41 (d, J = 16.4 Hz, trans double bond, 1H), 4.03 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 142.1, 137.0, 136.8, 135.1, 130.1, 128.9, 128.5, 127.0, 126.6, 124.3, 121.8, 118.3, 110.2, 94.5, 33.3, 21.6; IR (KBr) 3026, 2217, 1733, 1622, 1368, 1171, 1088, 753 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{18}N_2NaO_2S$ (M + Na)$^+$ 385.0981, found 385.0977.

*(E/Z)-2-Benzyl-4-styryl-1-tosyl-1H-pyrrole (**6e**).* The alcohol **4** was converted to the aldehyde according to the oxidation procedure used for **6a**, as mentioned above. The crude aldehyde was used for a Wittig reaction as follows. *P*-Benzyl triphenyl phosphonium bromide (1.13 g, 2.93 mmol) in THF (8 mL) was cooled to 0 °C, *n*BuLi (1.2 mL, 2.5 M in hexanes, 2.93 mmol) was added dropwise, and the resulting red solution was stirred at 70 °C for 1 h. The mixture was recooled to 0 °C, the above aldehyde in THF (8 mL) was added, and the mixture was stirred at 70 °C for 12 h. After the mixture was cooled, the reaction was quenched with H_2O (5 mL), the aqueous layer was extracted with EtOAc (2 × 10 mL), the combined organic phases were washed with brine (10 mL), dried (Na_2SO_4), and filtered, and the filtrate was concentrated. The residue was purified by flash chromatography on silica gel (EtOAc/hexanes) to give the 3-alkenyl pyrrole **6e** as inseparable *E/Z* mixture (55/45): 1.05 g, 87% yield, pale yellow liquid; R_f = 0.5 (hexanes/EtOAc = 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) for *E/Z* mixture δ 7.51−7.35 (m, 4H), 7.34−7.29 (m, 3H), 7.26−7.18 (m, 3H), 7.15−6.99 (m, 14H), 6.91−6.85 (m, 2H), 6.81 (d, J = 16.3 Hz, trans double bond, 1H), 6.61 (d, J = 16.3 Hz, trans double bond, 1H), 6.40 (d, J = 12.0 Hz, cis double bond, 1H), 6.21 (d, J = 12.0 Hz, cis double bond, 1H), 5.94 (s, 1H), 5.46 (s, 1H), 4.00 (s, 2H), 3.88 (s, 2H), 2.30 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) for *E/Z* mixture δ 144.7, 144.5, 138.0, 137.9, 137.7, 137.3, 135.9, 135.6, 134.0, 129.8, 129.7, 129.2, 129.0, 128.7, 128.5, 128.3, 128.1, 128.0, 127.2, 127.0, 126.8, 126.4, 126.1, 126.0, 125.0, 123.1, 122.0, 121.9, 120.8, 120.1, 114.9, 111.5, 33.5, 33.2, 21.5; IR (KBr) 3027, 1597, 1451, 1363, 1245, 1170, 1089, 1059, 694 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{24}NO_2S$ (M + H)$^+$ 414.1522, found 414.1537.

*Ethyl (E)-3-(5-benzylthiophen-3-yl)acrylate (**7a**).* 3-Alkenyl thiophene **7a** was prepared from **5**[15b] (1 g, 4.90 mmol) according to the oxidation procedure used for **6a** mentioned above, and the reaction time was 8 h: 1.14 g, 86% yield, pale yellow liquid, R_f = 0.6 (hexanes/EtOAc = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 15.9 Hz, trans double bond, 1H), 7.36−7.29 (m, 3H), 7.27−7.22 (m, 3H), 6.96 (d, J = 0.9 Hz, 1H), 6.16 (d, J = 15.9 Hz, trans double bond, 1H), 4.23 (q, J = 7.1 Hz, 2H), 4.12 (s, 2H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 145.8, 139.4, 138.2, 137.2, 128.6, 128.5, 127.2, 126.6, 122.7, 117.4, 60.2, 36.1, 14.2; IR (KBr) 2982, 1704, 1630, 1450, 1271, 1163, 1036, 749 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{17}O_2S$ (M + H)$^+$ 273.0944, found 273.0955.

*Procedure for 3-Alkenyl Thiophenes **7b−d**.* 3-Alkenyl thiophenes **7b−d** were prepared from **5** (1 mmol) following the procedure used for **6b−d**.

*(E)-4-(5-Benzylthiophen-3-yl)but-3-en-2-one (**7b**):* 212 mg, 88% yield, pale yellow solid; R_f = 0.4 (hexanes/EtOAc = 4/1); mp 86−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.29 (m, 4H), 7.29−7.21 (m, 3H), 6.98 (d, J = 0.9 Hz, 1H), 6.45 (d, J = 16.1 Hz, trans double bond, 1H), 4.12 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 146.0, 139.3, 137.3, 137.0, 128.6, 128.5, 127.8, 126.7, 126.5, 122.7, 36.1, 27.2; IR (KBr) 2913, 1661, 1603, 1360, 1257, 973, 744 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{14}NaOS$ (M + Na)$^+$ 265.0658, found 265.0661.

*(E)-3-(5-Benzylthiophen-3-yl)-1-phenylprop-2-en-1-one (**7c**):* 258 mg, 85% yield, pale yellow solid; R_f = 0.5 (hexanes/EtOAc = 4/1); mp 61−63 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01−7.93 (m, 2H), 7.70 (d, J = 15.5 Hz, 1H), 7.62−7.53 (m, 1H), 7.53−7.46 (m, 2H), 7.43 (d, J = 1.3 Hz, 1H), 7.36−7.31 (m, 2H), 7.30−7.22 (m, 4H), 7.12 (d, J = 0.9 Hz, 1H), 4.15 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.7, 145.9, 139.4, 138.5, 138.2, 137.9, 132.5, 128.7, 128.6, 128.5 (2C), 128.3, 126.7, 122.8, 121.4, 36.2; IR (KBr) 3066, 1656, 1588, 1445, 1210, 1018, 974, 694 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{17}OS$ (M + H)$^+$ 305.0995, found 305.0991.

*(E)-3-(5-Benzylthiophen-3-yl)acrylonitrile (**7d**):* inseparable *E/Z* mixture (10/1), 195 mg, 87% yield, yellow liquid, R_f = 0.5 (hexanes/EtOAc = 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) for *E/Z* mixture δ 7.64−7.20 (m, 8H), 6.99 (d, J = 11.9 Hz, cis double bond, 0.2H), 6.90 (s, 1H), 5.57 (d, J = 16.5 Hz, trans double bond, 1H), 5.25 (d, J = 11.9 Hz, cis double bond, 0.1H), 4.15 (s, 0.3H), 4.11 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) for *E/Z* mixture δ 146.7, 145.9, 144.0, 142.1, 139.4, 139.1, 136.5, 135.9, 129.1, 128.7, 128.5, 127.7, 126.8, 126.7, 124.3, 121.7, 118.3, 117.8, 95.1, 92.7, 36.1; IR (KBr) 3029, 2212, 1609, 1448, 1108, 961, 766 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{11}NNaS$ (M + Na)$^+$ 248.0504, found 248.0513.

*(E/Z)-2-Benzyl-4-styrylthiophene (**7e**).* 3-Alkenyl thiophene **7e** was prepared from **5** following the procedure used for **6e**: inseparable *E/Z* mixture (5/4), 1.19 g, 88% yield, pale yellow semisolid, R_f = 0.5 (hexanes/EtOAc = 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) for *E/Z* mixture δ 7.44 (d, J = 7.3 Hz, 2H), 7.38−7.19 (m, 15H), 7.16 (d, J = 8.0 Hz, 2H), 7.11−6.80 (m, 5H). 6.58−6.40 (m, 2H), 4.14 (s, 2H), 3.99 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) for *E/Z* mixture δ 144.9, 143.3, 140.1, 139.9, 139.8, 138.0, 137.7, 137.4, 129.1, 128.7, 128.6, 128.4, 128.3, 128.1, 127.3, 127.0, 126.5, 126.4, 126.2, 124.6, 123.1, 122.9, 121.3, 36.3, 36.1; IR (KBr) 2909, 1599, 1492, 1450, 1075, 958, 693 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{16}S$ (M)$^+$ 276.0972, found 276.0970.

Propargylic alcohols **8a−d**,[14b] **8e**,[16a] **8f**,[16b] **8g**,[16c] **8h**,[14b] and **8i**[14d] were prepared using known protocols.

*5-Phenyl-1-(1-tosyl-1H-indol-3-yl)penta-2,4-diyn-1-ol (**8j**).* To a stirred solution of 1-(1-tosyl-1*H*-indol-3-yl) prop-2-yn-1-ol[20a] (1 g, 3.08 mmol) in dry toluene (15 mL) were added CuCl (15 mol %, 45 mg), $NH_2OH{\cdot}HCl$ (30 mol %, 63 mg), *n*$BuNH_2$ (4.62 mmol, 0.46 mL), and (bromoethynyl)benzene[20b] (4.62 mmol, 0.84 g) at 0 °C; the solution was warmed to room temperature and stirred for 2 h. The reaction mixture was quenched with 3 N HCl and extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and concentrated, and the residue was purified by flash column chromatography on silica gel (EtOAc/hexanes) to afford **8j**: 1.11 g, 85% yield, pale yellow solid; R_f = 0.4 (hexanes/EtOAc = 7/3); mp 72−74 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.77−7.72 (m, 2H), 7.54−7.49 (m, 2H), 7.40−7.36 (m, 1H), 7.36−7.31 (m, 3H), 7.29−7.26 (m, 1H), 7.23 (d, J = 8.1 Hz, 2H), 5.80 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 135.4, 135.0, 132.5, 129.9, 129.4, 128.4, 128.1, 126.8, 125.1, 124.1, 123.4, 121.4, 121.1, 120.3, 113.6, 80.3, 79.5, 73.0, 70.6, 58.4, 21.5; IR (KBr) 3058, 2234, 1600, 1444, 1368, 1171, 1122, 974, 751 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{19}NNaO_3S$ (M + Na)$^+$ 448.0978, found 448.0990.

*Ethyl (E)-3-(5-Benzyl-2-(1,3-diphenylprop-2-yn-1-yl)-1-tosyl-1H-pyrrol-3-yl)acrylate (**I**).* To a stirred solution of alkenyl pyrrole **6a** (1.0 mmol) and propargylic alcohol **8a** (1.2 mmol) in 10 mL of acetonitrile was added $BF_3{\cdot}Et_2O$ (5 mol %) at 0 °C, and the mixture was stirred at room temperature for 3 h. The mixture was quenched with saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with EtOAc (2 × 10 mL), and the organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexanes) to afford **I**: 66 mg, 91% yield, pale brown semisolid; R_f = 0.4 (hexanes/EtOAc = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 15.7 Hz, trans double bond, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.37−7.33 (m, 2H), 7.32−7.29 (m, 2H), 7.25−7.19 (m, 8H), 7.16−7.12 (m, 1H), 7.13−7.07 (m, 4H), 6.45 (s, 1H), 5.80 (s, 1H), 5.76 (d, J = 15.7 Hz, trans double bond, 1H), 4.21−4.07 (m, 2H), 4.03 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.11 (t, J = 7.1 Hz, 3H);

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^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 145.0, 139.5, 137.9, 137.5, 136.3, 135.9, 135.8, 131.5, 129.9, 129.2, 128.4 (2C), 128.0 (2C), 127.0, 126.8, 126.6, 126.5, 122.9, 122.5, 117.5, 111.8, 87.7, 84.8, 60.0, 35.5, 33.9, 21.4, 14.1; IR (KBr) 2980, 1704, 1597, 1263, 1129, 976, 752 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{34}NO_4S$ (M + H)$^+$ 600.2203, found 600.2217.

*General Procedure for the [4 + 2] Benzannulation of 3-Alkenylpyrrole/Thiophene with Propargylic Alcohols: Synthesis of **9a–k** and **10a–k**.* To a stirred solution of 3-alkenyl pyrrole **6** or thiophene **7** (1.0 mmol) and propargylic alcohol **8** (1.2 mmol) in 10 mL of acetonitrile was added $BF_3{\cdot}Et_2O$ (5 mol %) at 0 °C, and the mixture was stirred at room temperature for 1–4 h. Then, DBU (1.0 mmol) was added to the reaction mixture at 0 °C and stirring was continued at room temperature for 30 min. After the completion of the reaction (monitored by TLC), the mixture was concentrated using a rotary vaporator. The crude product was purified by column chromatography on silica gel (EtOAc/hexanes) to afford the corresponding benzannulated products.

*Ethyl 2,6-dibenzyl-7-phenyl-1-tosyl-1H-indole-5-carboxylate (**9a**):* 65 mg, 90% yield, pale yellow semisolid; R_f = 0.4 (hexanes/EtOAc = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.34–7.25 (m, 3H), 7.22–7.14 (m, 3H), 7.14–6.98 (m, 11H), 6.72 (d, J = 7.1 Hz, 2H), 6.17 (t, J = 1.1 Hz, 1H), 4.27 (s, 2H), 4.20 (s, 2H), 4.11 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 146.5, 143.8, 142.0, 141.1, 138.2, 138.1, 135.8, 135.7, 133.7, 131.0, 130.9, 130.2, 129.3, 129.1, 128.5, 128.2, 127.7, 127.1 (2C), 126.7, 125.7, 125.1, 121.8, 114.3, 60.9, 36.7, 35.9, 21.4, 13.9; IR (KBr) 2980, 2926, 1717, 1597, 1367, 1228, 1171, 1014, 699 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{33}NNaO_4S$ (M + Na)$^+$ 622.2023, found 622.2056.

*Ethyl 2,6-dibenzyl-7-(4-methoxyphenyl)-1-tosyl-1H-indole-5-carboxylate (**9b**):* 66 mg, 87% yield, white solid; R_f = 0.5 (hexanes/EtOAc = 7/3); mp 132–134 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.34–7.26 (m, 3H), 7.17 (ddd, J = 6.4, 5.6, 1.5 Hz, 3H), 7.14–6.99 (m, 9H), 6.64–6.62 (m, 3H), 6.17 (t, J = 1.1 Hz, 1H), 4.27 (s, 2H), 4.17–4.11 (m, 4H), 3.72 (s, 3H), 2.34 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 157.2, 146.4, 143.8, 141.1, 138.2, 138.1, 136.1, 135.7, 134.2, 133.6, 132.1, 130.9, 130.2, 129.4, 129.1, 128.5, 128.2, 127.7, 127.2, 127.1, 126.7, 125.8, 121.8, 114.4, 113.2, 61.0, 55.1, 36.7, 35.0, 21.5, 14.0; IR (KBr) 2930, 1718, 1597, 1367, 1245, 1175, 1030, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{39}H_{35}NaNO_5S$ (M + Na)$^+$ 652.2128, found 652.2158.

*Ethyl 2,6-dibenzyl-1-tosyl-7-(3,4,5-trimethoxyphenyl)-1H-indole-5-carboxylate (**9c**):* 74 mg, 88% yield, pale yellow semisolid; R_f = 0.5 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.34–7.27 (m, 3H), 7.24 (s, 2H), 7.18–6.90 (m, 7H), 6.76 (d, J = 7.3 Hz, 2H), 6.39 (s, 1H), 6.03 (s, 2H), 4.37 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 4.05 (s, 2H), 3.81 (s, 3H), 3.37 (s, 6H), 2.33 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 151.6, 146.4, 143.7, 142.5, 140.9, 138.4, 136.8, 136.4, 135.5, 132.9, 132.6, 130.6, 129.9, 129.4, 128.9, 128.5, 128.0, 127.7, 126.7, 125.3, 125.1, 121.8, 114.6, 113.7, 108.5, 61.0, 60.7, 55.3, 36.8, 36.5, 21.4, 13.9; IR (KBr) 2929, 1718, 1589, 1456, 1365, 1237, 1128, 1013, 667 cm^{-1}; HRMS (ESI) m/z calcd for $C_{41}H_{39}NNaO_7S$ (M + Na)$^+$ 712.2339, found 712.2367.

*Ethyl 2′,6′-dibenzyl-1,1′-ditosyl-1H,1′H-[3,7′-biindolyl]-5′-carboxylate (**9d**):* 83 mg, 86% yield, pale yellow semisolid; R_f = 0.5 (hexanes/EtOAc = 7/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 1H), 7.86 (s, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.36–7.28 (m, 3H), 7.23 (d, J = 7.0 Hz, 3H), 7.20–7.07 (m, 9H), 7.03 (d, J = 7.1 Hz, 2H), 6.95 (t, J = 7.6 Hz, 2H), 6.71 (s, 1H), 6.22 (s, 1H), 4.31 (s, 2H), 4.09 (s, 2H), 4.03 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 1.00 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 146.8, 144.5, 144.1, 141.3, 138.1, 138.0, 135.4, 135.2, 135.1, 134.3, 133.4, 131.4, 130.7, 130.5, 129.7, 129.5, 129.4, 129.3, 128.6, 127.2, 127.1, 126.7, 126.6, 125.7, 125.6, 124.5, 124.0, 123.0, 122.5, 119.4, 114.6, 113.6, 61.0, 36.8, 26.6, 21.6, 21.5, 13.8; IR (KBr) 2925, 1716, 1588, 1455, 1364, 1126, 749 cm^{-1}; HRMS (ESI) m/z calcd for $C_{47}H_{41}O_6N_2S_2$ (M + H)$^+$ 793.2400, found 793.2387.

*Ethyl 2-benzyl-6-butyl-7-phenyl-1-tosyl-1H-indole-5-carboxylate (**9e**):* 58 mg, 85% yield, pale brown liquid; R_f = 0.5 (hexanes/EtOAc = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.32–7.25 (m, 3H), 7.21–7.14 (m, 7H), 7.04–6.99 (m, 4H), 6.14 (t, J = 1.1 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 4.24 (s, 2H), 2.77–2.70 (m, 2H), 2.34 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H), 1.26–1.17 (m, 2H), 1.08–1.00 (m, 2H), 0.64 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 145.9, 143.6, 141.0, 139.0, 138.3, 138.1, 136.1, 132.7, 131.1, 130.2, 129.3, 129.2, 129.1, 128.5, 127.0, 126.9, 126.6, 125.7, 121.8, 114.2, 61.0, 36.6, 34.0, 29.9, 22.7, 21.4, 14.2, 13.5; IR (KBr) 2925, 1716, 1598, 1452, 1364, 1221, 1176, 1130, 1088, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{35}H_{35}NNaO_4S$ (M + Na)$^+$ 588.2179, found 588.2196.

*Ethyl 2-benzyl-6-(cyclopropylmethyl)-7-phenyl-1-tosyl-1H-indole-5-carboxylate (**9f**):* 61 mg, 89% yield, pale yellow liquid; R_f = 0.4 (hexanes/EtOAc = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.33–7.21 (m, 8H), 7.18–7.13 (m, 2H), 7.03 (dd, J = 20.5, 8.4 Hz, 4H), 6.13 (s, 1H), 4.36 (q, J = 7.1 Hz, 2H), 4.23 (s, 2H), 2.89 (d, J = 6.5 Hz, 2H), 2.34 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H), 0.53–0.36 (m, 1H), 0.14–0.08 (m, 2H), − 0.30– − 0.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 146.1, 143.7, 141.2, 138.6, 138.1, 138.0, 135.8, 133.0, 131.4, 130.5, 129.6, 129.3, 129.1, 128.5, 127.1, 127.0, 126.6, 125.7, 121.8, 114.4, 61.0, 36.6, 33.1, 21.4, 14.2, 12.2, 4.6; IR (KBr) 2925, 1715, 1596, 1448, 1364, 1224, 1178, 1126, 1015, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{35}H_{33}NNaO_4S$ (M + Na)$^+$ 586.2023, found 586.2056.

*2-Benzyl-9-phenyl-1-tosyl-7,8-dihydropyrano[3,4-f]indol-5(1H)-one (**9g**):* 49 mg, 79% yield, pale yellow solid; R_f = 0.5 (hexanes/EtOAc = 4/1); mp 216–218 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.35–7.26 (m, 6H), 7.22–7.14 (m, 4H), 7.03 (s, 4H), 6.24 (t, J = 1.2 Hz, 1H), 4.33 (t, J = 5.9 Hz, 2H), 4.26 (s, 2H), 2.79 (t, J = 5.9 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 146.6, 144.2, 141.8, 137.7, 137.6, 135.7, 135.0, 132.0, 130.2, 130.1, 129.3 (2C), 128.6, 127.8, 127.4, 126.8, 125.6, 122.7, 122.5, 114.2, 67.2, 36.5, 27.1, 21.5; IR (KBr) 2920, 1719, 1598, 1375, 1182, 982, 754 cm^{-1}; HRMS (ESI) m/z calcd for $C_{31}H_{25}NNaO_4S$ (M + Na)$^+$ 530.1397, found 530.1414.

*1-(2,6-Dibenzyl-7-phenyl-1-tosyl-1H-indol-5-yl)ethan-1-one (**9h**):* 65 mg, 87% yield, pale brown solid; R_f = 0.5 (hexanes/EtOAc = 7/3); mp 151–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.35–7.27 (m, 3H), 7.22–7.13 (m, 7H), 7.12–7.00 (m, 7H), 6.70 (d, J = 6.9 Hz, 2H), 6.15 (t, J = 1.1 Hz, 1H), 4.27 (s, 2H), 4.10 (s, 2H), 2.34 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 146.5, 143.8, 141.9, 140.4, 138.9, 138.3, 138.1, 135.8, 134.8, 133.9, 130.9, 130.6, 129.4, 129.2, 128.8, 128.5, 127.8, 127.2, 127.1, 126.7, 125.7, 125.3, 119.4, 114.1, 36.7, 35.1, 29.9, 21.5; IR (KBr) 3027, 1690, 1597, 1493, 1268, 1090, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{31}NNaO_3S$ (M + Na)$^+$ 592.1917, found 592.1923.

*(2,6-Dibenzyl-7-phenyl-1-tosyl-1H-indol-5-yl)(phenyl)methanone (**9i**):* 60 mg, 85% yield, pale brown solid; R_f = 0.4 (hexanes/EtOAc = 4/1); mp 137–139 °C; ^{1}H NMR (500 MHz, $CDCl_3$); δ 7.58–7.51 (m, 2H), 7.45 (tt, J = 7.4, 3.1 Hz, 1H), 7.34–7.26 (m, 5H), 7.23–7.13 (m, 8H), 7.11–7.02 (m, 4H), 6.93–6.83 (m, 3H), 6.62 (d, J = 7.1 Hz, 2H), 6.11 (s, 1H), 4.28 (s, 2H), 4.03 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 146.5, 143.8, 141.2, 140.2, 138.2, 138.1, 137.7, 137.4, 135.7, 135.5, 133.6, 132.8, 131.0, 130.4, 130.0, 129.4, 129.1, 128.8, 128.5, 127.9, 127.6, 127.2, 127.1, 126.7, 125.8, 125.2, 120.5, 114.2, 36.7, 35.5, 21.5; IR (KBr) 2924, 1663, 1594, 1447, 1238, 1174, 704 cm^{-1}; HRMS (ESI) m/z calcd for $C_{42}H_{33}NNaO_3S$ (M + Na)$^+$ 654.2073, found 654.2087.

*2,6-Dibenzyl-7-phenyl-1-tosyl-1H-indole-5-carbonitrile (**9j**):* 67 mg, 89% yield, brown solid; R_f = 0.4 (hexanes/EtOAc = 4/1); mp 162–164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.35–7.27 (m, 3H), 7.21–7.15 (m, 3H), 7.15–7.06 (m, 5H), 7.02–6.95 (m, 6H), 6.76–6.69 (m, 2H), 6.20 (s, 1H), 4.29 (s, 2H), 4.10 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 144.0, 141.7, 139.5, 138.7, 137.6, 136.9, 135.7, 133.5, 131.5, 130.5, 129.3, 129.2, 128.6, 128.1, 128.0, 127.5, 127.2, 126.8, 125.8, 125.6, 124.9, 118.8, 113.1, 110.9, 37.8, 36.6, 21.4; IR (KBr) 3026, 2222, 1446, 1364, 1084, 758, 703 cm^{-1}; HRMS (ESI) m/z calcd for $C_{36}H_{28}N_2NaO_2S$ (M + Na)$^+$ 575.1764, found 575.1764.

*2,6-Dibenzyl-5,7-diphenyl-1-tosyl-1H-indole (**9k**):* 56 mg, 78% yield, pale brown semisolid; R_f = 0.5 (hexanes/EtOAc = 7/3); ^{1}H

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NMR (400 MHz, $CDCl_3$): δ7.35−7.26 (m, 3H), 7.25−7.19 (m, 6H), 7.15−7.01 (m, 11H), 6.99−6.95 (m, 3H), 6.50 (dd, *J* = 6.5, 3.0 Hz, 2H), 6.16 (t, *J* = 1.1 Hz, 1H), 4.28 (s, 2H), 3.85 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 143.5, 142.4, 142.3, 140.9, 139.0, 138.9, 138.4, 135.9, 133.8, 133.0, 131.3, 130.8, 129.4, 129.2, 129.0, 128.5, 128.0, 127.7, 127.5, 127.4, 126.9, 126.7, 126.6, 125.9, 124.9, 121.5, 114.6, 36.7, 36.5, 21.5; IR (KBr) 2922, 1599, 1493, 1373, 1174, 1030, 885 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{41}H_{33}NNaO_2S$ $(M + Na)^+$ 626.2124, found 626.2133.

*Ethyl 2′-Benzyl-6′-(3-phenylprop-2-yn-1-yl)-1,1′-ditosyl-1H,1′H-[3,7′-biindolyl]-5′-carboxylate (**9l**).* To a stirred solution of alkenyl pyrrole **6a** (1.0 mmol) and propargylic alcohol **8h** (1.2 mmol) in 10 mL of acetonitrile was added $BF_3{\cdot}Et_2O$ (5 mol %) at 0 °C, and the mixture was stirred at room temperature for 2 h. Then, the mixture was cooled to 0 °C and K_2CO_3 (2.0 mmol) was added; this mixture was stirred at room temperature for 12 h and then concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexanes) to afford **9l**: 81 mg, 81% yield, pale yellow semisolid; R_f = 0.4 (hexanes/EtOAc = 4/1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.46 (s, 1H), 7.34−7.26 (m, 3H), 7.25−7.17 (m, 8H), 7.09−7.01 (m, 3H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.41 (s, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.35 (s, 2H), 3.97 (d, *J* = 17.1 Hz, 1H), 3.31 (d, *J* = 17.1 Hz, 1H), 2.31 (s, 3H), 2.21 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 168.1, 146.7, 144.7, 143.8, 142.3, 138.2, 135.8, 135.2, 134.4, 133.9, 131.4 (2C), 130.8, 129.7, 129.3, 129.2, 128.6, 128.5, 128.0, 127.5, 127.0, 126.7, 126.6, 124.6, 124.2, 123.7, 123.3, 123.1, 122.3, 120.7, 118.9, 113.6, 113.3, 89.1, 80.9, 61.3, 36.6, 21.9, 21.5, 21.4, 14.2; IR (KBr) 2924, 1714, 1445, 1172, 1016, 809, 667 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{49}H_{44}O_6N_3S_2$ $(M + NH_4)^+$ 834.2666, found 834.2647.

*Ethyl 2,6-dibenzyl-7-phenyl-1-benzothiophene-5-carboxylate (**10a**):* 73 mg, 87% yield, pale yellow solid; R_f = 0.4 (hexanes/EtOAc = 9/1); mp 130−132 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.38−7.33 (m, 3H), 7.32−7.27 (m, 2H), 7.25−7.18 (m, 5H), 7.15−7.02 (m, 4H), 6.83 (d, *J* = 7.1 Hz, 2H), 4.31 (s, 2H), 4.19−4.11 (m, 4H), 1.17 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 146.9, 145.1, 141.7, 139.2, 139.0, 137.7, 137.6, 132.6, 129.1, 129.0, 128.7, 128.6, 128.5, 128.2, 127.9, 127.8, 126.7, 125.2, 124.4, 121.9, 60.8, 36.9, 35.7, 14.0; IR (KBr) 2922, 2223, 1596, 1445, 1365, 1082, 759 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{31}H_{26}O_2S$ $(M + Na)^+$ 485.1546, found 485.1555.

*Ethyl 2,6-dibenzyl-7-(4-methoxyphenyl)-1-benzothiophene-5-carboxylate (**10b**):* 79 mg, 88% yield, pale yellow liquid; R_f = 0.6 (hexanes/EtOAc = 4/1); ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.35−7.29 (m, 2H), 7.28−7.22 (m, 3H), 7.19−7.05 (m, 6H), 6.93−6.89 (m, 2H), 6.86 (d, *J* = 7.0 Hz, 2H), 4.34 (s, 2H), 4.21−4.13 (m, 4H), 3.84 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 159.1, 146.8, 145.6, 141.8, 139.1, 137.5, 137.4, 132.9, 131.5, 130.2, 129.2, 128.7, 128.6, 128.2, 127.8, 126.7, 125.2, 124.3, 122.0, 113.9, 60.8, 55.1, 36.9, 35.7, 14.0; IR (KBr) 2925, 1713, 1502, 1445, 1236, 1107, 748 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{32}H_{29}O_3S$ $(M + H)^+$ 493.1832, found 493.1853.

*Ethyl 2,6-dibenzyl-7-(3,4,5-trimethoxyphenyl)-1-benzothiophene-5-carboxylate (**10c**):* 89 mg, 88% yield, pale yellow solid; R_f = 0.4 (hexanes/EtOAc = 4/1); mp 97−99 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.29−7.13 (m, 5H), 7.10−6.94 (m, 4H), 6.78 (d, *J* = 7.2 Hz, 2H), 6.28 (s, 2H), 4.24 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.09 (s, 2H), 3.80 (s, 3H), 3.50 (s, 6H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 153.0, 147.0, 145.1, 142.2, 139.0, 137.8, 137.7, 137.4, 134.4, 132.5, 129.2, 128.7, 128.6, 128.1, 127.8, 126.7, 125.2, 124.4, 121.9, 106.0, 60.9, 60.8, 55.8, 37.0, 36.1, 14.0; IR (KBr) 2933, 2311, 1716, 1584, 1456, 1239, 1031, 702 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{34}H_{33}O_5S$ $(M + H)^+$ 553.2043, found 553.2033.

*Ethyl 2,6-dibenzyl-7-(1-tosyl-1H-indol-3-yl)-1-benzothiophene-5-carboxylate (**10d**):* 104 mg, 87% yield, pale yellow solid; R_f = 0.4 (hexanes/EtOAc = 7/3); mp 136−138 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.50 (s, 1H), 7.35−7.28 (m, 3H), 7.28−7.21 (m, 3H), 7.16−7.05 (m, 6H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 6.7 Hz, 2H), 4.49 (d, *J* = 15.7 Hz, 1H), 4.25−4.05 (m, 4H), 3.90 (d, *J* = 15.7 Hz, 1H), 2.29 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 146.8, 146.1, 144.7, 141.4, 138.9, 137.8, 134.8, 134.7, 129.8, 129.7, 129.0, 128.7 (2C), 128.6 (2C), 127.9 (2C), 127.8, 126.8, 126.6, 125.4, 125.3, 125.0, 123.5, 122.0, 120.8, 120.2, 113.7, 60.9, 36.9, 36.1, 21.5, 14.0; IR (KBr) 3024, 1713, 1443, 1370, 1174, 1029, 748 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{40}H_{33}NNaO_4S_2$ $(M + Na)^+$ 678.1743, found 678.1734.

*Ethyl 2-benzyl-6-butyl-7-phenyl-1-benzothiophene-5-carboxylate (**10e**):* 67 mg, 86% yield, pale yellow liquid; R_f = 0.5 (hexanes/EtOAc = 9/1); ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.41−7.31 (m, 3H), 7.25−7.19 (m, 4H), 7.18−7.09 (m, 3H), 6.96 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 2H), 2.77−2.73 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.31−1.21 (m, 2H), 1.11−1.03 (m, 2H), 0.63 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 146.3, 145.2, 139.6, 139.1, 136.9, 136.7, 136.0, 129.2, 128.6, 128.5 (2C), 128.2, 127.7, 126.6, 124.4, 121.9, 60.9, 36.9, 34.2, 30.0, 22.8, 14.3, 13.6; IR (KBr) 2924, 2858, 1716, 1454, 1217, 1034, 699 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{28}H_{29}O_2S$ $(M + H)^+$ 429.1883, found 429.1902.

*Ethyl 2-benzyl-6-(cyclopropylmethyl)-7-phenyl-1-benzothiophene-5-carboxylate (**10f**):* 69 mg, 89% yield, pale yellow liquid; R_f = 0.4 (hexanes/EtOAc = 4/1); ^1H NMR (400 MHz, $CDCl_3$):δ 8.11 (s, 1H), 7.50−7.38 (m, 3H), 7.35−7.26 (m, 4H), 7.25−7.19 (m, 3H), 7.05 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.13 (s, 2H), 2.86 (d, *J* = 6.5 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 0.83−0.70 (m, 1H), 0.28−0.20 (m, 2H), − 0.11 − −0.18 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 146.5, 145.2, 139.8, 139.1, 137.0, 136.7, 135.0, 129.5, 128.7, 128.6 (2C), 128.5, 127.8, 126.6, 124.3, 121.9, 60.9, 36.9, 33.5, 14.2, 12.7, 4.7; IR (KBr) 2989, 1715, 1441, 1243, 1105, 1032, 701 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{28}H_{27}O_2S$ $(M + H)^+$ 427.1726, found 427.1742.

*2-Benzyl-9-phenyl-7,8-dihydro-5H-thieno[2,3-g]isochromen-5-one (**10g**):* 54 mg, 80% yield, pale yellow solid; R_f = 0.5 (hexanes/EtOAc = 7/3); mp 131−133 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.53−7.40 (m, 3H), 7.38−7.34 (m, 2H), 7.33−7.26 (m, 2H), 7.27−7.19 (m, 3H), 7.16 (s, 1H), 4.43 (t, *J* = 5.9 Hz, 2H), 4.17 (s, 2H), 2.92 (t, *J* = 5.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 147.1, 146.3, 138.9, 138.8, 137.5, 133.8, 131.0, 128.9 (2C), 128.7, 128.6, 128.4, 126.8, 124.8, 122.3, 122.2, 67.2, 36.9, 26.3; IR (KBr) 2924, 1721, 1591, 1194, 1111, 754 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{18}NaO_2S$ $(M + Na)^+$ 393.0920, found 393.0895.

*1-(2,6-Dibenzyl-7-phenyl-1-benzothiophen-5-yl)ethan-1-one (**10h**):* 78 mg, 88% yield, pale yellow solid; R_f = 0.4 hexanes/EtOAc = 4/1); mp 130−132 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.42−7.34 (m, 3H), 7.34−7.26 (m, 4H), 7.26−7.21 (m, 3H), 7.16−7.02 (m, 4H), 6.83 (d, *J* = 8.1 Hz, 2H), 4.20 (s, 2H), 4.20 (s, 2H), 4.16 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.5, 147.1, 144.3, 141.7, 139.2, 139.1, 137.9, 137.8, 137.2, 131.8, 129.1, 128.8, 128.7, 128.6 (2C), 128.0, 127.9, 126.7, 125.4, 122.1, 121.8, 37.0, 35.1, 30.0; IR (KBr) 2923, 1686, 1492, 1350, 1107, 885, 702 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{30}H_{24}NaOS$ $(M + Na)^+$ 455.1440, found 455.1433.

*(2,6-Dibenzyl-7-phenyl-1-benzothiophen-5-yl)(phenyl)-methanone (**10i**):* 68 mg, 84% yield, pale yellow semisolid; R_f = 0.5 (hexanes/EtOAc = 4/1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65−7.61 (m, 2H), 7.55 (s, 1H), 7.51−7.44 (m, 2H), 7.43−7.36 (m, 3H), 7.36−7.27 (m, 6H), 7.25−7.20 (m, 2H), 7.00 (s, 1H), 6.97−6.84 (m, 3H), 6.75 (d, *J* = 6.9 Hz, 2H), 4.15 (s, 2H), 4.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 147.0, 143.8, 141.0, 139.2, 139.1, 137.7, 137.4, 137.0, 136.9, 132.8, 132.7, 130.1, 129.2, 129.0, 128.7, 128.6, 128.2, 127.9, 127.7, 126.7, 125.3, 123.0, 121.8, 37.0, 35.2; IR (KBr) 2922, 1725, 1661, 1346, 1035, 710 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{35}H_{27}OS$ $(M + H)^+$ 495.1777, found 495.1768.

*2,6-Dibenzyl-7-phenyl-1-benzothiophene-5-carbonitrile (**10j**):* 82 mg, 89% yield, white solid; R_f = 0.5 (hexanes/EtOAc = 4/1); mp 191−193 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.43−7.35 (m, 3H), 7.35−7.26 (m, 2H), 7.25−7.17 (m, 5H), 7.17−7.09 (m, 3H), 7.07 (s, 1H), 6.90−6.81 (m, 2H), 4.18 (s, 2H), 4.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 146.6, 139.5, 138.7, 138.1, 137.8, 137.5, 135.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 127.3, 126.9,

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126.0, 121.3, 119.1, 110.4, 37.1, 37.0; IR (KBr) 3025, 2223, 1440, 1213, 1081, 749 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{21}NNaS$ $(M + Na)^+$ 438.1287, found 438.1315.

*2,6-Dibenzyl-5,7-diphenyl-1-benzothiophene (**10k**):* 67 mg, 80% yield, pale brown semisolid; R_f = 0.5 (hexanes/EtOAc = 4/1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.34−7.31 (m, 4H), 7.30−7.26 (m, 6H), 7.25−7.23 (m, 2H), 7.22−7.18 (m, 3H), 7.05 (t, J = 0.9 Hz, 1H), 6.97−6.95 (m, 3H), 6.56−6.53 (m, 2H), 4.15 (s, 2H), 3.94 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 142.3, 141.7, 141.2, 140.5, 139.9, 139.4, 138.0, 136.7, 131.5, 129.5, 129.2, 128.7, 128.7, 128.6, 128.5, 128.4, 128.2, 127.7, 127.5, 126.6, 125.0, 123.7, 121.7, 37.0, 35.9; IR (KBr) 2927, 1631, 1488, 1441, 1320, 1199, 749, 698 cm^{-1}; HRMS (EI): m/z calcd for $C_{34}H_{26}S$ $(M)^+$ 466.1755, found 466.1745.

*Ethyl 2-benzyl-6-(3-phenylprop-2-yn-1-yl)-7-(1-tosyl-1H-indol-3-yl)-1-benzothiophene-5-carboxylate (**10l**).* Alkenyl thiophene **7a** (1.0 mmol) was treated with propargylic alcohol **8h** (1.2 mmol) following the procedure used for **9l** to afford **10l**. 98 mg, 79% yield, pale yellow semisolid; R_f = 0.5 (hexanes/EtOAc = 4/1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.87 (s, 1H), 7.81−7.77 (m, 2H), 7.38−7.33 (m, 1H), 7.33−7.26 (m, 5H), 7.24−7.20 (m, 6H), 7.19−7.14 (m, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.09 (s, 1H), 4.44 (q, J = 7.1 Hz, 2H), 4.20−4.08 (m, 3H), 3.73 (d, J = 16.9 Hz, 1H), 2.30 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 147.2, 146.0, 144.9, 138.9, 138.1, 135.0, 134.8, 131.8, 131.4, 129.8, 129.7, 128.7, 128.6, 128.2, 128.0, 127.5, 127.1, 126.8, 125.9, 125.6, 125.2, 123.7, 123.5, 122.1, 120.6, 120.3, 113.8, 89.0, 81.1, 61.3, 36.9, 22.0, 21.5, 14.2; IR (KBr) 2923, 1713, 1595, 1370, 1259, 1125, 753 cm^{-1}; HRMS (ESI) m/z calcd for $C_{42}H_{33}NNaO_4S_2$ $(M + Na)^+$: 702.1743, found 702.1760.

*Ethyl 2,7-Dibenzyl-1,8-ditosyl-1,8-dihydroindolo[6,7-c]carbazole-5-carboxylate (**11a**).* To a stirred solution of **9l** (1.0 mmol) in 10 mL of acetonitrile was added DBU (1.0 mmol) at 0 °C, and the mixture was stirred under reflux (80 °C) for 4 h. The reaction mixture was concentrated, and the residue was purified by column chromatography on silica gel (EtOAc/hexanes) to afford **11a**: 41 mg, 82% yield, pale yellow solid; R_f = 0.5 (hexanes/EtOAc = 4/1); mp 113−115 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.17 (dd, J = 14.8, 8.0 Hz, 2H), 7.90 (s, 1H), 7.43−7.26 (m, 9H), 7.25−7.14 (m, 4H), 7.02−6.90 (m, 3H), 6.76 (d, J = 8.1 Hz, 2H), 6.67 (d, J = 8.3 Hz, 2H), 6.43 (s, 1H), 5.11 (d, J = 16.5 Hz, 1H), 4.77 (d, J = 16.5 Hz, 1H), 4.53 (d, J = 15.8 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.12 (d, J = 15.8 Hz, 1H), 2.30 (s, 3H), 1.85 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 145.5, 144.7, 144.2, 141.1, 140.6, 140.5, 138.4, 137.1, 135.1, 132.8, 132.5, 132.2, 130.9, 129.7, 129.2, 129.0, 128.9, 128.7, 128.5, 128.4, 128.3, 127.9, 127.6, 127.0, 126.7, 126.1, 126.0, 125.9, 124.8, 123.1, 122.4, 119.5, 118.7, 116.8, 61.4, 40.4, 36.4, 21.5, 21.1, 14.2; IR (KBr) 2923, 1709, 1595, 1496, 1224, 1089, 664 cm^{-1}; HRMS (ESI) m/z calcd for $C_{49}H_{44}O_6N_3S_2$ $(M + NH_4)^+$ 834.2666, found 834.2663.

*Ethyl 2,7-Dibenzyl-8-tosyl-8H-thieno[2′,3′:3,4]benzo[1,2-c]-carbazole-5-carboxylate (**11b**).* Compound **10l** (1.0 mmol) was treated with DBU following the procedure used for **11a** to obtain **11b**: 41 mg, 83% yield, pale yellow solid; R_f = 0.5 (hexanes/EtOAc = 4/1); mp 149−151 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, J = 7.9 Hz, 1H), 8.45 (s, 1H), 8.24 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.37−7.33 (m, 1H), 7.29−7.24 (m, 2H), 7.23−7.18 (m, 8H), 7.16−7.09 (m, 1H), 7.08 (s, 1H), 6.82−6.79 (m, 2H), 6.58 (d, J = 8.0 Hz, 2H), 4.78 (s, 2H), 4.28 (q, J = 7.1 Hz, 2H), 4.20 (s, 2H), 1.87 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 144.3, 143.5, 141.8, 141.2, 141.0, 139.0, 138.9, 137.8, 136.8, 133.6, 130.8, 130.1, 129.6, 128.7, 128.6, 128.4, 128.3, 128.0, 127.5, 127.3, 126.8, 126.7, 126.1, 126.0, 125.6, 124.9, 122.9 (2C), 122.5, 120.2, 61.3, 39.5, 36.4, 21.1, 14.2; IR (KBr) 2922, 2855, 2311, 1711, 1368, 1173, 756 cm^{-1}; HRMS (ESI) m/z calcd for $C_{42}H_{34}NO_4S_2$ $(M + H)^+$ 680.1924, found 680.1948.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02637.

^1H and ^{13}C NMR spectra of all new compounds, chiral HPLC chromatogram of **11a**, and X-ray crystallographic analysis for **11b** (PDF)

X-ray crystallographic data for **11b** (CIF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

EA,ethyl acetate; IBX,2-iodoxybenzoic acid

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