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One-Pot Multicatalytic Approaches for the Synthesis of Cyclohepta[*b*]indoles, Indolotropones, and Tetrahydrocarbazoles

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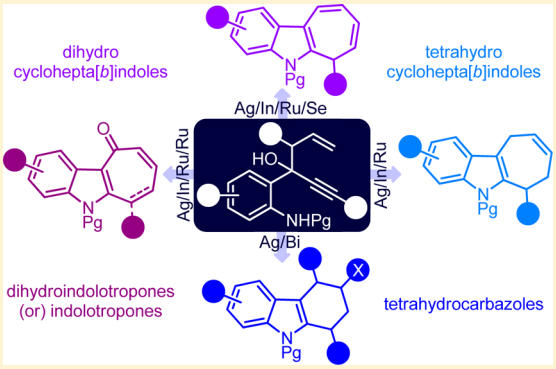
Supporting Information

ABSTRACT: Diversity oriented one-pot synthesis of cyclohepta[*b*]-indoles, indolotropones, and tetrahydrocarbazoles (THCs) have been reported. Readily accessible 3-(2-aminophenyl)-5-hexenyn-3-ols under a one-pot trimetallic orthogonal catalysis furnish tetrahydrocyclohepta-[*b*]indoles, and a one-pot quadruple reaction sequence of the enynols generates dihydrocyclohepta[*b*]indoles and indolotropones. During this study, formation of THCs was realized to be a reason for the yield loss in certain cases, this observation led to the development of a one-pot bimetallic approach for the synthesis of 1,3-disubstituted THCs.



INTRODUCTION

The cyclohepta[*b*]indole scaffold is frequently encountered in numerous natural and non-natural pharmaceutical products, Figure 1.[1] Presence of intricate molecular architectures

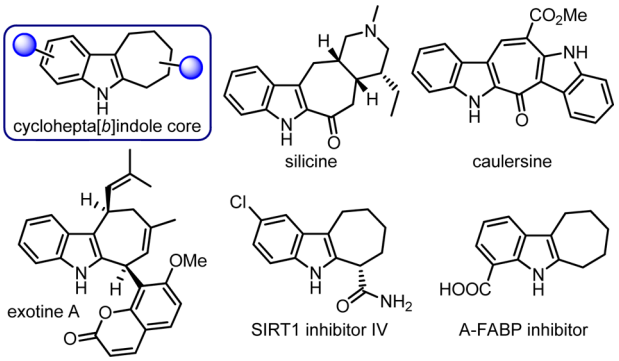


Figure 1. Representative natural products and medicinally important compounds possessing the cyclohepta[*b*]indole skeleton.

associated with a broad spectrum of biological activity profiles attracted the development of numerous synthetic efforts to efficiently access this structural motif.[1,2] However, it often requires multistep sequences involving laborious isolation and purification procedures, which limit the generality and synthetic utility of majority of the methods. Herein, we propose sequential one-pot multicatalytic approaches leading to the synthesis of a diverse range of cyclohepta[*b*]indoles.

Orthogonal tandem catalysis has attracted tremendous attention recently, and is being applied to increasingly challenging synthetic problems.[3] However, the development of such processes is not always straightforward. Compatibility between different catalytic systems and control over the selectivity issues complicate the evolution of such methods. In this direction, we have recently reported the successful development of a few one-pot bi- and trimetallic orthogonal catalytic approaches for the synthesis of complex indole derivatives.[4] With this background, we planned to establish diversity oriented one-pot synthesis of cyclohepta-fused indoles and indolotropones, which otherwise require multistep synthesis.

Diversity oriented synthesis (DOS)[5] coupled with one-pot orthogonal tandem catalysis can be a powerful synthetic tool to access structurally diverse and novel drug-like molecules, necessitated for the study of important biological processes.

For the one-pot synthesis of cyclohepta[*b*]indoles, it was envisioned that a silver(I)-catalyzed 5-*exo*-dig cyclization of 3-(2-aminophenyl)-5-hexenyn-3-ols **A** could provide indolines **B**, Scheme 1.[4d,6] A catalyst C2-promoted 1,3-allylic alcohol isomerization (1,3-AAI) and dehydrative nucleophilic allylation cascade of **B** was considered for the synthesis of **C**. A ring closing metathesis (RCM) reaction catalyzed by a catalyst C3 could generate tetrahydrocyclohepta[*b*]indoles **D**.[4d] Since a straightforward three-step synthesis of enynols **A** has already been established starting from 2-aminobenzaldehydes,[4] this method thus can serve as a short and efficient alternative to access functionalized heptannulated indoles.

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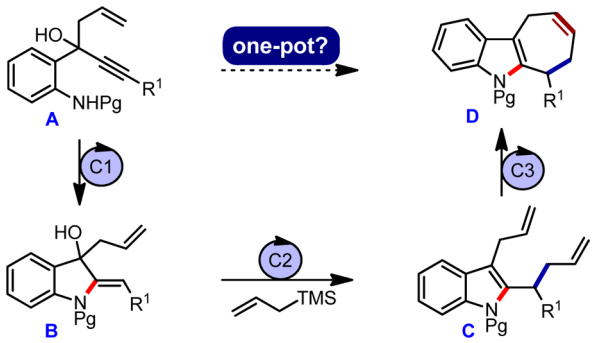
Scheme 1. Hypothesis for the Synthesis of Cyclohepta[*b*]indoles Based on a One-Pot Multicatalytic Approach



RESULTS AND DISCUSSION

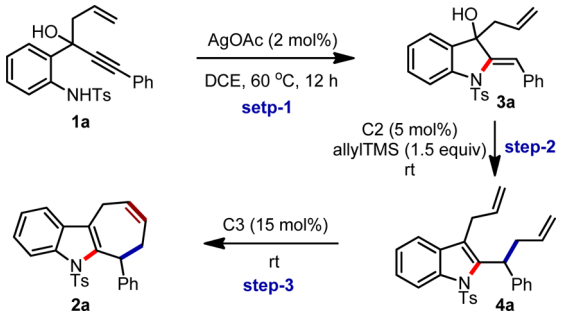
In order to substantiate the hypothesis presented in Scheme 1, we initiated optimization studies with the enynol **1a** as the model substrate.[4d] Various catalyst and solvent combinations were evaluated and the results are summarized in Table 1.

In order for the transformation of **1a** to **3a**, AgOAc was identified as the catalyst of choice.[4c,d,6] Next, for the cascade 1,3-AAI/nucleophilic allylation (conversion of **3a** to **4a**), our initial attempts with the Lewis acids, such as $In(OTf)_3$ or $FeCl_3$, were unsuccessful (Table 1, entries 1 and 2). However, to our delight, formation of **4a** was observed when $Bi(OTf)_3$ was employed as the catalyst. Subsequent RCM reaction of **4a** with Grubbs' first generation catalyst (G-I) resulted in the formation of **2a** in 34% yield (entry 3, yield over 3 steps). In order to improve the yield, several Lewis acids as well as Brønsted acids were evaluated in step-2. Among them, $BiCl_3$, $InCl_3$, and $ZnCl_2$-catalyzed reactions afforded the desired product **2a** in good yields (entries 4−11).

Interestingly, **4a** remained as such when lower loading of either G-I or G-II was explored in step-3 (entries 12−14). On the other hand, the RCM reaction with the purified sample of **4a** generated **2a** in excellent yields (entries 15 and 16), indicating that catalyst poisoning or deactivation would have occurred during a one-pot process, which could be the most likely reason for the nonformation of **2a** in the cases where lower amounts of either G-I or G-II were employed. So, an amount slightly higher than the combined amount of C1 and C2 was realized to be the optimal quantity of C3.

The optimized conditions were then applied to various substrates (Table 2, **1a**−**1m**). The reaction appeared to be practical and straightforward, however, during the course of the investigation, certain interesting electronic and steric influences attracted our attention. For example, reaction of the substrates possessing electron-donating groups (EDGs) on the alkyne (**1g** and **1h**) furnished the respective products (**2g** and **2h**) in less yields than expected, due to the formation of a side product (*vide infra*). On the other hand, the enynol with the 1-methylallyl system failed to undergo RCM reaction despite several of our efforts (**2m**). Nevertheless, the synthetic utility of an orthogonal tandem reaction that integrated silver, indium, and ruthenium in one-pot for the synthesis of novel cyclohepta-fused indoles could be demonstrated.

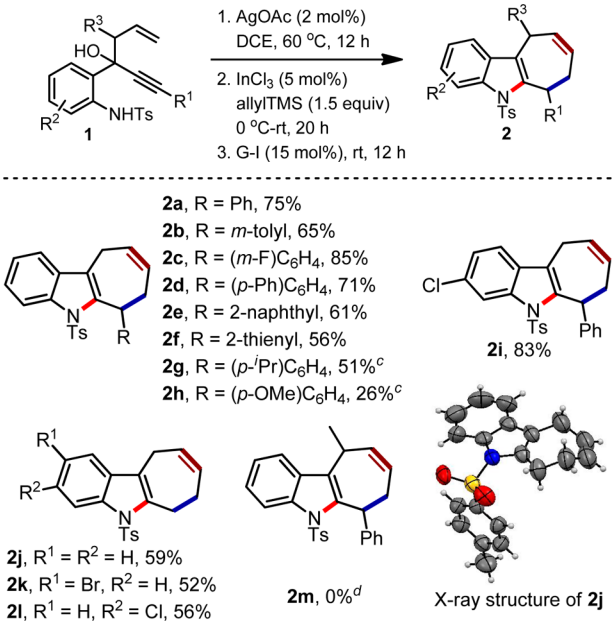
Table 1. Optimization of the Reaction Parameters[a,b]



entry	C2/conditions	C3/conditions	yield (%)[c]
1[d]	$In(OTf)_3$/22 h	–	–
2[d]	$FeCl_3$/25 h	–	–
3[e]	$Bi(OTf)_3$/20 h	G-I/16 h	34
4	TMSOTf/22 h	G-I/12 h	47
5	$Sc(OTf)_3$/21 h	G-I/15 h	53
6	$BiCl_3$/23 h	G-I/13 h	55
7	$InCl_3$/20 h	G-I/12 h	67
8	$ZnCl_2$/24 h	G-I/10 h	70
9	$BiCl_3$/0 °C-rt/25 h	G-I/12 h	74
10	**$InCl_3$/0 °C-rt/21 h**	**G-I/10 h**	**75**
11	$ZnCl_2$/0 °C-rt/26 h	G-I/12 h	71
12[f]	$InCl_3$/0 °C-rt/20 h	G-I (5 mol%)/12 h	–
13[f]	$InCl_3$/0 °C-rt/20 h	G-I (10 mol%)/12 h	–
14[fg]	$InCl_3$/0 °C-rt/20 h	G-II (5 mol%)/10 h	–
15[h]	$InCl_3$/0 °C-rt/20 h	G-I (5 mol%)/1 h	93
16[h]	$InCl_3$/0 °C-rt/20 h	G-II (5 mol%)/1 h	95

[a]See the Experimental Section for detailed reaction conditions. [b]Either step-1 or step-2 or step-3 did not work in toluene, trifluorotoluene, chlorobenzene, and nitromethane solvents. [c]Isolated yields over three steps. [d]Either **3a** decomposed or was as such. [e]G-I, Grubbs' 1st generation catalyst. [f]**4a** was as such. [g]G-II, Grubbs' 2nd generation catalyst. [h]Reaction with the purified **4a**; yield of step-3 alone.

Table 2. One-Pot Trimetallic Orthogonal Catalysis for the Synthesis of Tetrahydrocyclohepta[*b*]indoles[a,b]



[a]See the Experimental Section for detailed reaction condition. [b]Yields reported herein are over three steps. [c]20−25% of a side product formation was observed (*vide infra*). [d]Step-3 failed.

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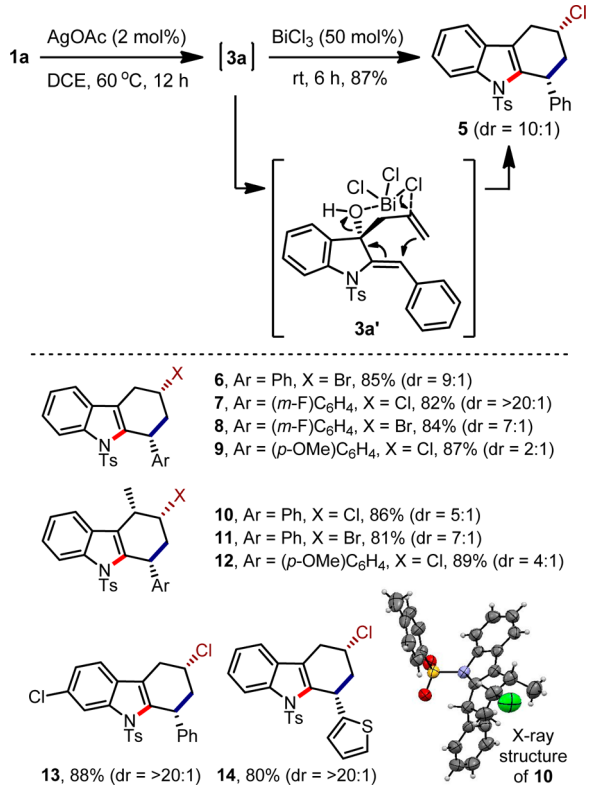
Next, we turned our attention to the side product which was isolated during the synthesis of the indoles **2g** and **2h**. Upon characterization, it was identified to be the tetrahydrocarbazole (THC) **5**, Table 3. Formation of **5** can be conveniently

Table 3. One-Pot Bimetallic Orthogonal Catalysis for the Synthesis of 1,3-Di- and 1,3,4-Trisubstituted THCs[a,b,c]

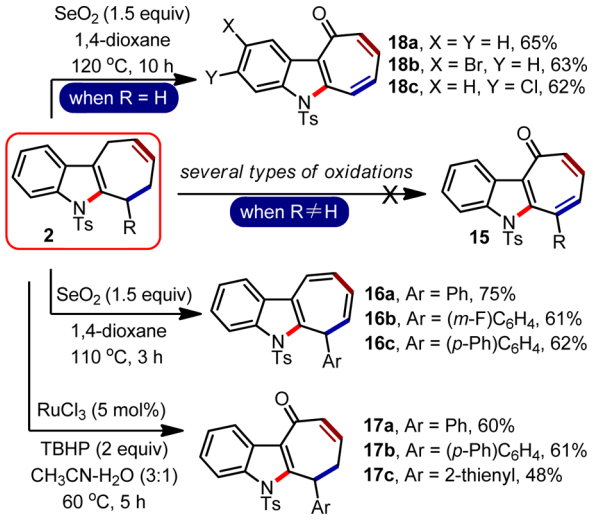


[a]See the Experimental Section for detailed reaction conditions. [b]*E*/*Z* ratios were determined from the ^{1}H NMR analysis of the purified samples. [c]Yields reported herein are over two steps.

interpreted as the halo-Prins-type annulation of **3a** (as depicted in **3a**′).[7] Similar carbocyclizations of unactivated olefins onto stabilized carbocationic intermediates are known,[8] but to the best of our knowledge, not for the synthesis of annulated indoles. In this instance, it is especially appealing since an efficient one-pot access to a new class of 1,3-disubstituted THCs is established. The lack of general methods for the synthesis of 1-aryl-3-halo-THCs prompted us to consider the synthesis of few other analogs **6**−**14** (Table 3).[9] In general, consistent turnaround times and excellent yields were achieved. Under the optimized conditions, 50 mol% of $BiCl_3$ and $BiBr_3$ provided access to chloro- and bromo-incorporated THCs, respectively. This method was also extended for the synthesis of 1,3,4-trisubstituted THCs (**10**−**12**). Interestingly, the major diastereomers exhibited the formation of *cis*-isomers, as revealed by the X-ray diffraction analysis of **10**.[10,11]

After successfully establishing tri- and bimetallic one-pot approaches, respectively, for the synthesis of cyclohepta[*b*]-indoles and THCs, the feasibility of the transformation of the former class to indolotropones was investigated, Scheme 2. Several of our attempts to oxidatively transform tetrahydrocyclohepta[*b*]indoles **2** to indolotropones **15** remained unsuccessful.[11] But, to our delight, dihydrocyclohepta[*b*]indoles (**16a**−**16c**) were formed exclusively under SeO_2-mediated

Scheme 2. Synthetic Approaches for the Dihydrocyclohepta[*b*]indoles, Dihydroindolotropones, and Indolotropones[a]

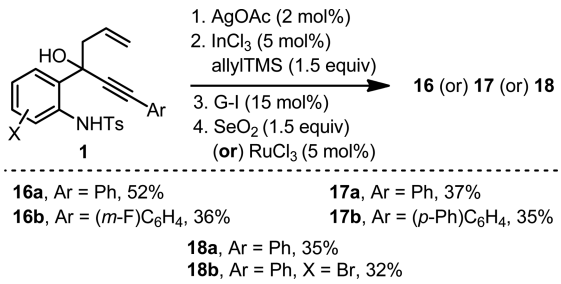


[a]See the Experimental Section for detailed reaction conditions.

reaction,[12,13] and only the dihydroindolotropones (**17a**−**17c**) were obtained under $RuCl_3$-catalyzed oxidation conditions. On the other hand, SeO_2-oxidation of the unsubstituted tetrahydrocyclohepta[*b*]indoles **2j**−**2l** generated unexpectedly the respective cyclohepta[*b*]indol-10-ones **18a**−**18c**, Scheme 2.[14,15]

At this stage, we intended to establish one-pot quadruple reaction cascades for the synthesis of **16**, **17**, and **18** starting from the enynols **1**, Scheme 3. Indeed, we could successfully

Scheme 3. One-Pot Quadruple Reaction Cascade for the Synthesis of Cyclohepta[*b*]indoles 16, 17, and 18[a]



[a]Yields reported herein are over four steps

integrate Ag/In/Ru/Se-promoted reactions in one-pot for the synthesis of **16** or **18**, and Ag/In/Ru(II)/Ru(III)-catalyzed reactions for the synthesis of **17**, thereby validating the first one-pot tetrametallic orthogonal tandem processes involving four distinct catalytic cycles.[16]

CONCLUSIONS

In summary, we have described diversity-oriented bi-, tri-, and tetrametallic one-pot orthogonal processes for the synthesis of a cyclohepta[*b*]indoles, indolotropones, and THCs. We believe that our findings pave the way for the conception of new multicatalytic one-pot processes. Attempts to apply the methodologies described herein for the synthesis of biologically active natural products is currently underway in our laboratory. These results will be communicated shortly.

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EXPERIMENTAL SECTION

General Experimental Methods. All the starting compounds and catalysts employed in this study were procured and were used without further purification. For thin layer chromatography (TLC), silica coated aluminum foils with fluorescent indicator 254 nm were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating. Column chromatography was performed using neutral alumina. Dry THF was obtained by distillation over sodium and stored over sodium wire. IR spectra were recorded on a FT IR spectrometer as thin films or KBr pellet, as indicated, with ν_{max}^{-1}. Melting points were recorded on a digital melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). The following abbreviations are utilized to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Proton chemical shifts are given in δ relative to tetramethylsilane (δ 0.00 ppm) in $CDCl_3$ or in $(CD_3)_2SO$ (δ 2.50 ppm) or in $(CD_3)_2CO$ (δ 2.05 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm) or in $(CD_3)_2SO$ (δ 39.5 ppm) or in $(CD_3)_2CO$ at δ 29.9 and 206.7. Single crystal X-ray analysis was carried on a AXS KAPPA APEX II system or XtaLAB mini X-ray diffractometer. High-resolution mass spectra were recorded on a QTOF mass spectrometer.

*General Procedure for the Preparation of 3-(2-aminophenyl)hex-5-en-1-yn-3-ols (**1a**–**1m**).* All the 3-(2-aminophenyl)hex-5-en-1-yn-3-ols (**1**) employed in this study were prepared following a three-step protocol described in the literature.[4]

Representative Procedure-1: Optimization of the Reaction Parameters (Table 1). A 5 mL glass vial was charged with **1a** (0.1 mmol), AgOAc (2 mol%) in DCE (1 mL), and stirred at 60 °C. After the disappearance of **1a**, allyl-TMS (1.5 equiv) and C2 (5 mol%) were introduced at an appropriate temperature (see Table 1S) and left stirring at room temperature until the intermediate **3a** disappeared (by TLC). Upon complete formation of the intermediate **4a**, C3 (Grubbs' first or second generation catalysts) was introduced at room temperature (see Table 1S) and continued stirring at room temperature until intermediate **4a** disappeared (by TLC). The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2 × 2 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexanes) to afford **2a**.

Representative Procedure-2: One-Pot Synthesis of Tetrahydrocyclohepta[b]indoles (Scheme 2). A 5 mL glass vial was charged with 3-(2-aminophenyl)hex-5-en-1-yn-3-ol **1** (0.1 mmol), AgOAc (2 mol%) in DCE (1 mL) and stirred at 60 °C. After the disappearance of **1**, allyl-TMS (1.5 equiv) and $InCl_3$ (5 mol%) were introduced at 0 °C and continued stirring at room temperature until intermediate **3** disappeared as monitored by TLC. After complete formation of **4**, Grubbs' first generation catalyst (15 mol%) was added to the reaction mixture at room temperature and continued stirring at room temperature until the intermediate **4** disappeared (by TLC). The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2 × 2 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexanes) to afford **2**.

*6-Phenyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (**2a**).* This compound was isolated as colorless viscous liquid. Following the reaction procedure-2, 40 mg of **1a** afforded 29.5 mg of **2a** (75% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 3029, 1737, 1493, 1453, 1170, 747. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25–8.22 (m, 1H), 7.49–7.47 (m, 1H), 7.37–7.29 (m, 2H), 7.22–7.16 (m, 5H), 7.07 (dd, J = 6.6 and 2.9 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 5.93–5.90 (m, 1H), 5.55 (dt, J = 5.1 and 2.7 Hz, 1H), 5.38 (brs, 1H), 3.58–3.54 (m, 2H), 2.95–2.91 (m, 1H), 2.69 (ddd, J = 14.6, 8.4, and 5.6 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144, 142.7, 138, 136, 130.6, 129.3 (2CH), 128.7 (2CH), 128.5 (2CH), 128.2, 127.7 (2CH), 126.3 (2CH), 125.9, 124.5, 123.2, 119.3, 118, 115.2, 41.3, 34.1, 24.8, 21.4. HRMS (ESI): m/z calcd for $C_{26}H_{24}NO_2S$ $(M+H)^+$: 414.1528, Found: 414.1512.

*4-Methyl-N-(2-(3-(m-tolyl)propioloyl)phenyl)benzenesulfonamide (**1b1**).* This compound was isolated as pale yellow solid. mp = 147–150 °C. R_f = 0.5 (hexane/EtOAc = 6/4). IR (thin film, neat): ν_{max}/cm^{-1} 3200, 2924, 2193, 1611, 1490, 1158, 754. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (dd, J = 7.8 and 1.5 Hz, 1H), 7.80 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.3 Hz, 1H), 7.56–7.46 (m, 3H), 7.34 (d, J = 5.1, 2H), 7.29–7.24 (m, 3H), 7.16 (t, J = 7.7 Hz, 1H), 2.41 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.5, 144.1, 140.9, 138.7, 136.4, 135.7, 134.8, 133.6, 132.2, 130.3, 129.8 (2CH), 128.7, 127.3 (2CH), 122.6, 122.5, 119.4, 118.4, 95.7, 86.4, 21.6, 21.2. HRMS (ESI): m/z calcd for $C_{23}H_{20}NO_3S$ $(M+H)^+$: 390.1164, Found: 390.1148.

*N-(2-(3-Hydroxy-1-(m-tolyl)hex-5-en-1-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (**1b**).* This compound was isolated as colorless liquid. R_f = 0.5 (hexane/EtOAc = 6.5/2.5). IR (thin film, neat): 3451, 2964, 2231, 1588, 1494, 1333, 1160, 749. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.4 (brs, 1H), 7.8 (d, J = 8.3 Hz, 2H), 7.76–7.69 (m, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.31 (s, 1H), 7.27–7.14 (m, 5H), 7.09–6.98 (m, 1H), 5.90–5.78 (m, 1H), 5.19 (dd, J = 10.3 and 1.2 Hz, 1H), 5.06 (d, J = 17.1 Hz, 1H), 3.8 (brs, 1H), 2.68–2.53 (m, 2H), 2.37 (brs, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 138.2, 137.2, 135.7, 132.3, 132.2, 130.0, 129.8, 129.7 (2CH), 129.1, 128.9, 128.5, 128.3, 127.2 (2CH), 123.4, 121.6, 120.8, 120.1, 88.9, 88.3, 74.8, 47.5, 21.5, 21.2. HRMS (ESI): m/z calcd for $C_{26}H_{25}NNaO_3S$ $(M+Na)^+$: 454.1453; Found: 454.1437.

*6-(m-Tolyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (**2b**).* This compound was isolated as pale yellow solid. Following the reaction procedure-2, 40 mg of **1b** afforded 26.5 mg **2b** (65% yield). mp = 90–92 °C. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2926, 1737, 1453, 1368, 1170,746. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.8 Hz, 1H), 7.58–7.56 (m, 1H), 7.37–7.33 (m, 4H), 7.17 (d, J = 8.3 Hz, 2H), 7.12–7.07 (m, 1H), 6.97 (d, J = (7.6 Hz, 1H), 6.96–6.79 (m, 2H), 5.88–5.84 (m, 1H), 5.48–5.47 (m, 1H), 5.25 (brs, 1H), 3.54–3.52 (m, 2H), 2.84–2.81 (m, 1H), 2.70–2.65 (m, 1H), 2.26 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 142.5, 138.6, 137.1, 136, 130, 129.3, 129.2 (2CH), 128.8, 128.1 (2CH), 127.6, 126.6, 126.3 (2CH), 125.6, 124.4, 123.2, 119.1, 118, 115.2, 41.2, 34.2, 24.8, 21.4 (2CH). HRMS (ESI): m/z calcd for $C_{27}H_{26}NO_2S$ $(M+H)^+$: 428.1684, Found: 428.1678.

*6-(3-Fluorophenyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (**2c**).* This compound was isolated as pale brown solid. Following the reaction procedure-2, 40 mg of **1c** afforded 34 mg **2c** (85% yield). mp = 104–106 °C. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2926, 1736, 1589, 1452, 1369, 748. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29–8.27 (m, 1H), 7.5 (dd, J = 7.6 and 1 Hz, 1H), 7.35 (m, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.15 (td, J = 7.9 and 6.1 Hz, 1H), 6.98 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 7.8 Hz, 1H), 6.84 (td, J = 8.4 and 2.6 Hz, 1H), 6.62 (dd, J = 10.3 and 1.7 Hz, 1H), 5.92 (dd, J = 6.5 and 4.3 Hz, 1H), 5.53 (dt, J = 5.1 and 2.7 Hz, 1H), 5.37 (brs, 1H), 3.63–3.50 (m, 2H), 2.96–2.92 (m, 1H), 2.67 (ddd, J = 14.5, 8.3, and 5.7 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.51 (d, J = 243.0 Hz), 145.4 (d, J = 6.7 Hz), 144.3, 137.7, 136.1 (d, J = 17.6 Hz), 130.4, 129.5, 129.4 (2CH), 129.2 (d, J = 8.2 Hz), 128.4 (d, J = 1.1 Hz), 126.1 (2CH), 124.8, 124.2 (d, J = 2.7 Hz), 123.4, 119.7, 118.2, 115.6, 115.4, 115.3, 112.7 (d, J = 21.1 Hz), 41.1 (d, J = 1.3 Hz), 34.0, 24.7, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −114.2. HRMS (ESI): m/z calcd for $C_{26}H_{21}FNO_2S$ $(M-H)^+$: 430.1277, Found: 430.1258.

*6-([1,1′-Biphenyl]-4-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (**2d**).* This compound was isolated as colorless solid. Following the reaction procedure-3, 40 mg of **1d** (R^1 = (*p*-Ph)C_6H_4, R^2 = H) afforded 28.7 mg of **2d** (71% yield). mp = 169–171 °C. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2927, 1736, 1486, 1454, 1367, 1169, 758. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30–8.25 (m, 1H), 7.61–7.55 (m, 2H), 7.53–7.49 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.40–7.31 (m, 5H), 7.22 (d, J = 8.3 Hz, 2H), 7.10 (d, J

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= 8.3 Hz, 2H), 6.91 (d, J = 8.3 Hz, 2H), 6.01−5.93 (m, 1H), 5.59 (td, J = 5.2 and 2.6 Hz, 1H), 5.42 (brs, 1H), 3.68−3.53 (m, 2H), 2.98 (dd, J = 14.7 and 2, 1H), 2.72 (ddd, J = 14.5, 8.3, and 5.9 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 141.9, 140.9, 138.7, 138.5, 136.24, 136.21, 130.5, 129.3 (2CH), 129.1 (2CH), 128.9, 128.7 (2CH), 128.5, 127.1, 126.9 (2CH), 126.4 (2CH), 126.2 (2CH), 124.6, 123.3, 119.2, 118.1, 115.3, 41.0, 34.1, 24.7, 21.4. HRMS (ESI): m/z calcd for $C_{32}H_{28}NO_2S$ $(M+H)^+$: 490.1841, Found: 490.1820.

*6-(Naphthalen-2-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]-indole (**2e**).* This compound was isolated as pale yellow oil. Following the reaction procedure-2, 40 mg of **1e** afforded 24.3 mg of **2e** (61% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 1454, 1365, 1169, 1126, 809, 746, 664. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36−8.29 (m, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.60−7.52 (m, 1H), 7.49−7.31 (m, 6H), 7.11 (s, 1H), 7.04 (d, J = 8.6 Hz, 2H), 6.54 (d, J = 8.1 Hz, 2H), 5.99−5.89 (m, 1H), 5.54−5.44 (m, 2H), 3.69−3.56 (m, 2H), 3.08−3.98 (m, 1H), 2.77 (ddd, J = 14.5, 8.3, and 5.6 Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 139.9, 138.3, 136.3, 136, 133, 132, 130.4, 128.9 (2CH), 128.5, 127.7, 127.4, 127.3, 127.27, 127.23, 125.8 (2CH), 125.4, 125.2, 124.6, 123.2, 119.1, 118.1, 115.2 (2CH), 41.4, 33.9, 24.6, 21.2. HRMS (ESI): m/z calcd for $C_{30}H_{26}NO_2S$ $(M+H)^+$: 464.1684, Found: 464.1668.

*4-Methyl-N-(2-(3-(thiophen-2-yl)propioloyl)phenyl)benzene-sulfonamide (**1f1**).* This compound was isolated as pale yellow solid. mp = 166−168 °C. R_f = 0.5 (hexane/EtOAc = 6/4). IR (thin film, neat): ν_{max}/cm^{-1} 3109, 2916, 2187, 1609, 1489, 1260, 1157, 914. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.25 (s, 1H), 8.21 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.1 Hz, 2H), 7.74 (d, J = 8.6 Hz, 1H), 7.63−7.57 (m, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.25 (d, J = 7.6 Hz, 2H), 7.20−7.12 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180, 144.1, 140.8, 137.3, 136.4, 135.7, 134.5, 132.4, 129.8 (2CH), 128, 127.3 (2CH), 122.7, 122.4, 119.3, 118.5, 91.4, 89.4, 21.5. HRMS (ESI): m/z calcd for $C_{20}H_{16}NO_3S_2$ $(M+H)^+$: 382.0572, Found: 382.0555.

*N-(2-(3-Hydroxy-1-(thiophen-2-yl)hex-5-en-1-yn-3-yl)phenyl)-4 methylbenzenesulfonamide (**1f**).* This compound was isolated as pale yellow liquid. R_f = 0.5 (hexane/EtOAc = 6.5/2.5). IR (thin film, neat): ν_{max}/cm^{-1} 3432, 3228, 2221, 1704, 1584, 1337, 1160, 661. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21 (s, 1H), 7.80 (d, J = 7.3 Hz, 2H), 7.60 (dd, J = 11.1 and 8.2 Hz, 2H), 7.33 (d, J = 4.9 Hz, 1H), 7.30−7.22 (m, 4H), 7.08−7.00 (m, 2H), 5.89−5.77 (m, 1H), 5.23 (d, J = 10.3 Hz, 1H), 5.10 (d, J = 17.1 Hz, 1H), 3.32 (s, 1H), 2.66−2.55 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 137.2, 135.7, 132.9, 131.9, 129.7 (2CH), 129.6, 129.2, 128.5, 128, 127.2 (2CH), 127.1, 123.5, 121.5, 121.2, 120.2, 92.9, 81.5, 75, 47.3, 21.5. HRMS (ESI): m/z calcd for $C_{23}H_{21}NNaO_3S_2$ $(M+Na)^+$: 446.0861, Found: 446.0855.

*6-(Thiophen-2-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (**2f**).* This compound was isolated as pale yellow liquid. Following the reaction procedure-2, 40 mg of **1f** afforded 22.3 mg of **2f** (56% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 1735, 1597, 1367, 1170, 662. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29−8.24 (m, 1H), 7.45 (dt, J = 7.7 and 0.8 Hz, 1H), 7.40−7.35 (m, 3H), 7.35−7.30 (m, 1H), 7.12 (dd, J = 5.1 and 1.2 Hz, 1H), 7.04 (d, J = 7.8 Hz, 2H), 6.8 (dd, J = 5 and 3.5 Hz, 1H), 6.6 (dt, J = 3.5 and 1 Hz, 1H), 5.89−5.83 (m, 1H), 5.75−5.63 (m, 2H), 3.63−3.45 (m, 2H), 2.93−2.85 (m, 1H), 2.79−2.70 (m,1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 144.3, 138.9, 136.1, 136.0, 130.5, 129.5 (2CH), 127.9, 127.3, 126.4 (2CH), 126.1, 125.3, 124.7, 123.7, 123.4, 119.5, 118.2, 115.4, 37, 34.5, 25.5, 21.5. HRMS (ESI): m/z calcd for $C_{24}H_{22}NO_2S_2$ $(M+H)^+$: 420.1092, Found: 420.1076.

*6-(4-Isopropylphenyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]-indole (**2g**).* This compound was isolated as colorless liquid. Following the reaction procedure-2, 40 mg of **1g** afforded 20.4 mg of **2g** (51% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2920, 1602, 1451, 1172, 1090, 673. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 7.5 Hz, 1H), 7.48−7.46 (m, 1H), 7.35−7.30 (m, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.03−6.98 (m, 4H), 6.94 (d, J = 8.2 Hz, 2H), 5.95−5.89 (m, 1H), 5.59−5.54 (m, 1H), 5.36 (brs, 1H), 3.58−3.54 (m, 1H), 2.92−2.84 (m, 2H), 2.69−2.62 (m, 1H), 2.27 (s, 3H), 1.6 (s, 1H), 1.26 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 Hz, $CDCl_3$): δ 146.3, 143.9, 140, 139, 136.1, 136, 130.6, 129.2 (2CH), 128.8, 128.4 (2CH), 128, 126.4 (2CH), 125.7 (2CH), 124.4, 123.2, 119.1, 118, 115.2, 40.9, 34.2, 33.5, 24.9, 24.15, 24.10, 21.4. HRMS (ESI): m/z calcd for $C_{29}H_{30}NO_2S$ $(M+H)^+$: 456.1997, Found: 456.1980.

*6-(4-Methoxyphenyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]-indole (**2h**).* This compound was isolated as pale yellow liquid. Following the reaction procedure-2, 40 mg of **1h** afforded 10.4 mg of **2h** (26% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2929, 1453, 1374, 1171, 704, 665, 583. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26−8.22 (m, 1H), 7.50−7.46 (m, 1H), 7.38−7.30 (m, 2H), 7.25−7.20 (m, 2H), 6.99−6.94 (m, 4H), 6.71−6.66 (m, 2H), 5.97−5.89 (m, 1H), 5.56 (dt, J = 5.1 and 2.7 Hz, 1H), 5.32 (brs, 1H), 3.79 (s, 3H), 3.60−3.52 (m, 2H), 2.95−2.87 (m, 1H), 2.64 (ddd, J = 14.5, 8.3, and 5.9 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 143.9, 138.9, 136.2, 136.1, 134.9, 130.5, 129.5 (2CH), 129.2 (2CH), 128.9, 128.2, 126.3 (2CH), 124.4, 123.2, 119, 118, 115.2, 113.1 (2CH), 55.1, 40.5, 34.2, 24.7, 21.4. HRMS (ESI): m/z calcd for $C_{27}H_{26}NO_3S$ $(M+H)^+$: 444.1633, Found: 444.1614.

*3-Chloro-6-phenyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]-indole (**2i**).* This compound was isolated as colorless oil. Following the reaction procedure-2, 40 mg of **1i** afforded 33 mg of **2i** (83% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2925, 1597, 1452, 1370, 1172, 811, 745, 667. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.38 (d, J = 8.3 Hz, 1H), 7.29 (d, J = 8.3 Hz, 1H), 7.24−7.13 (m, 5H), 7.07−6.94 (m, 4H), 5.95−5.84 (m, 1H), 5.54 (d, J = 2.2 Hz, 1H), 5.34 (brs, 1H), 3.62−3.42 (m, 2H), 2.91 (d, J = 13.7 Hz, 1H), 2.73−2.61 (m, 1H), 2.3 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 142.4, 139.3, 136.4, 135.8, 130.5, 129.5 (2CH), 129.1, 128.8, 128.5 (2CH), 127.9, 127.8 (2CH), 126.4 (2CH), 126, 123.8, 118.9, 118.8, 115.4, 41.3, 34.1, 24.7, 21.5. HRMS (ESI): m/z calcd for $C_{26}H_{23}ClNO_2S$ $(M+H)^+$: 448.1138, Found: 448.1121.

*5-Tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (**2j**).* This compound was isolated as colorless solid. Following the reaction procedure-2, 40 mg of **1j** afforded 23.5 mg of **2j** (59% yield). mp = 85−87 °C. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 1597, 1453, 1369, 1170, 747. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 8.6 Hz, 2H), 7.40−7.38 (m, 1H), 7.31−7.24 (m, 2H), 7.19 (d, J = 8.3 Hz, 2H), 6.00−5.97 (m, 2H), 3.41 (d, J = 1.5 Hz, 2H), 3.24 (ddd, J = 6.2, 4.3, and 1.7 Hz, 2H), 2.48−2.44 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 137, 136.3, 135.7, 131.3, 130.7, 129.7 (2CH), 129.1, 126.2 (2CH), 124, 123.2, 118.3, 117.7, 114.8, 26.4, 25.2, 22.9, 21.5. HRMS (ESI): m/z calcd for $C_{20}H_{20}NO_2S$ $(M+H)^+$: 338.1215, Found: 338.1202.

*N-(4-bromo-2-propioloylphenyl)-4-methylbenzenesulfonamide (**1k1**).* This compound was isolated as yellow solid. Following the reaction procedure-1, 100 mg of **B** (R^1 = Br, R^2 = H) afforded 80 mg of **2k** (80% yield). mp = 144−145 °C. R_f = 0.5 (hexane/EtOAc = 6/4). IR (thin film, neat): ν_{max}/cm^{-1} 2925, 2100, 1626, 1479, 1388, 1215, 1165, 660. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.91 (s, 1H), 8.31 (dd, J = 2 and 0.4 Hz, 1H), 7.80−7.72 (m, 2H), 7.66−7.59 (m, 2H), 7.30−7.25 (m, 2H), 3.64 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 144.6, 139.9, 138.9, 137.1, 135.9, 129.9 (2CH), 127.3 (2CH), 123.1, 120.0, 115.1, 83.1, 79.2, 21.6. HRMS (ESI): m/z calcd for $C_{16}H_{11}BrNO_3S$ $(M-H)^+$: 375.9641, Found: 375.9626.

*N-(4-bromo-2-(3-hydroxyhex-5-en-1-yn-3-yl)phenyl)-4-methyl-benzenesulfonamide (**1k**).* This compound was isolated as pale yellow liquid. Following the reaction procedure-1, 80 mg of **1k1** afforded 74 mg of **1k** (83% yield). R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 2925, 2113, 1597, 1486, 1384, 1335, 1163, 660. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (s, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 2.4 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.37−7.30 (m, 1H), 7.26 (d, J = 8.3 Hz, 2H), 5.79−5.66 (m, 1H), 5.18 (dd, J = 10.3 and 1.2 Hz, 1H), 4.99 (dd, J = 17.1 and 1.2 Hz, 1H), 3.7 (brs, 1H), 2.82 (s, 1H), 2.51−2.40 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 136.7, 134.8, 132.0, 131.6, 131.3, 131.2, 129.8 (2CH), 127.1 (2CH), 121.8, 121.3, 116.4, 83.4, 76.9, 73.7, 46.9, 21.5. HRMS (ESI): m/z calcd for $C_{19}H_{17}BrNO_3S$ $(M-H)^+$: 418.0111, Found: 418.0095.

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*2-Bromo-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (**2k**).* This compound was isolated as colorless solid. Following the reaction procedure-4, 40 mg of **1k** afforded 20.5 mg of **2k** (52% yield). mp = 176−178 °C. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2925, 1596, 1451, 1370, 1161, 913, 744. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.8 Hz, 1H), 7.59 (dd, J = 6.8 and 1.6 Hz, 2H), 7.51 (d, J = 2.0 Hz, 1H), 7.35 (dd, J = 8.8 and 2 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 6.01−5.91 (m, 2H), 3.37−3.32 (m, 2H), 3.21 (ddd, J = 6.1, 4.3, and 1.8 Hz, 2H), 2.48−2.39 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 138.5, 136.0, 134.5, 132.5, 131.4, 129.9 (2CH), 128.9, 126.7, 126.3 (2CH), 120.6, 117.6, 116.8, 116.2, 26.4, 25.1, 22.8, 21.6. HRMS (ESI): m/z calcd for $C_{20}H_{17}BrNO_2S$ $(M-H)^+$: 414.0168, Found: 414.0151.

*N-(5-Chloro-2-propioloylphenyl)-4-methylbenzenesulfonamide (**1l1**).* This compound was isolated as a pale green solid. mp = 142−143 °C. R_f = 0.5 (hexane/EtOAc = 6/4). IR (thin film, neat): ν_{max}/cm^{-1} 3190, 2923, 2100, 1622, 1598, 1562, 1164, 938. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.13 (s, 1H), 8.16 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 1.7 Hz, 1H), 7.31 (d, J = 8.3 Hz, 2H), 7.08 (dd, J = 8.6 and 2 Hz, 1H), 3.58 (s,1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.8, 144.6, 142.9, 142.1, 136.2, 136, 129.9 (2CH), 127.3 (2CH), 122.9, 119.9, 117.9, 83.2, 79.5, 21.6. HRMS (ESI): m/z calcd for $C_{16}H_{13}ClNO_3S$ $(M+H)^+$: 334.0305, Found: 334.0290.

*N-(5-Chloro-2-(3-hydroxyhex-5-en-1-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (**1l**).* This compound was isolated as pale yellow liquid. R_f = 0.5 (hexane/EtOAc = 7.5/2.5). IR (thin film, neat): ν_{max}/cm^{-1} 3445, 2982, 2116, 1658, 1599, 1493, 1164, 661. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.17 (s,1H), 7.78 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 2.2 Hz, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 6.99 (dd, J = 8.6 and 2.2 Hz, 1H), 5.80−5.69 (m, 1H), 5.20 (dd, J = 10.3 and 1 Hz, 1H), 5.02 (d, J = 17.1 Hz, 1H), 3.37 (d, J = 4.4 Hz, 1H), 2.81 (s, 1H), 2.54−2.42 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 136.8, 136.7, 134.9, 131.3, 129.8 (2CH), 129.5, 127.7, 127.2 (2CH), 123.3, 121.4, 119.9, 83.6, 76.6, 73.9, 47, 21.5. HRMS (ESI): m/z calcd for $C_{19}H_{18}ClNNaO_3S$ $(M+Na)^+$: 398.0594, Found: 398.0577.

*3-Chloro-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (**2l**).* This compound was isolated as a pale brown solid. Following the reaction procedure-2, 40 mg of **1l** afforded 22.3 mg of **2l** (56% yield). mp = 95−97 °C. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2926, 1737, 1598, 1460, 1371, 1166, 811. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 1.7 Hz, 1H), 7.65−7.60 (m, 2H), 7.31−7.28 (m, 1H), 7.26−7.23 (m, 2H), 7.23−7.21 (m,1H), 6.0−5.94 (m,2H), 3.38 (dd, J = 2.9 and 1.5 Hz, 2H), 3.19 (ddd, J = 6.2, 4.3, and 2 Hz, 2H), 2.49−2.41 (m,2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 137.7, 136.2, 136.1, 131.3, 129.94 (2CH), 129.90, 129.2, 128.9, 126.3 (2CH), 123.8, 118.5, 117.8, 114.9, 26.3, 25.1, 22.8, 21.6. HRMS (ESI): m/z calcd for $C_{20}H_{17}ClNO_2S$ $(M-H)^+$: 370.0667; Found: 370.0656.

Representative Procedure-3: One-Pot Synthesis of 1,3-Di- and 1,3,4-Trisubstituted Tetrahydrocarbazoles (Scheme 3). A 5 mL glass vial was charged with **1** (0.1 mmol), AgOAc (2 mol%) in DCE (1 mL) and stirred at 60 °C. After the disappearance of **1**, BiX_3 (X = Cl, Br; 50 mol%) was introduced at room temperature and continued stirring at room temperature until intermediate **3** disappeared (by TLC). The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2 × 2 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexanes) to afford product **5**.

*3-Chloro-1-phenyl-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (**5**).* This compound was isolated as colorless oil. Following the reaction procedure-3, 40 mg of **1a** afforded 36.5 mg of **5** (87% yield). R_f = 0.3 (hexane/EtOAc = 4/6). IR (thin film, neat): ν_{max}/cm^{-1} 2927, 1597, 1493, 1453, 1370, 1172, 746, 667. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.1 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.37−7.29 (m, 3H),7.23−7.19 (m, 4H), 7.07−7.04 (m, 2H), 7.03−7.01 (d, J = 8.2 Hz, 2H), 4.81 (t, J = 8.3 Hz, 1H), 4.32−4.25 (m, 1H), 3.38−3.33 (m, 1H), 3 (ddd, J = 15.5, 10.3, and 2.8 Hz, 1H), 2.91−2.86 (m, 1H), 2.31 (s, 3H), 2.07 (td, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 144.1, 137.7, 136.4, 135.5, 129.3 (2CH), 129.1, 128.4 (2CH), 127.6 (2CH), 126.4, 126.3 (2CH), 124.9, 123.6, 120.3, 118.4, 115.4, 54.2, 46.1, 42.5, 33, 21.5. HRMS (ESI): m/z calcd for $C_{25}H_{23}ClNO_2S$ $(M+H)^+$: 436.1138, Found: 436.1124.

*3-Bromo-1-phenyl-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (**6**).* This compound was isolated as colorless viscous liquid. Following the reaction procedure-3, 40 mg of **1a** afforded 39.2 mg of **6** (85% yield). R_f = 0.3 (hexane/EtOAc = 4/6). IR (thin film, neat): ν_{max}/cm^{-1} 2925, 1456, 1282, 1172, 768, 751, 708, 669. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 7.8 Hz, 1H), 7.46−7.44 (m, 1H), 7.46−7.31 (m, 2H), 7.23−7.19 (m, 5H), 7.07−7.01 (m, 4H), 4.81 (t, J = 7.9 Hz, 1H), 4.39−4.31 (m, 1H), 3.47−3.42 (m, 1H), 3.16 (ddd, J = 15.5, 10.7, and 2.9 Hz, 1H), 3.01 (ddt, J = 13.2, 7.4, and 2.8 Hz, 1H), 2.32 (s, 3H), 2.19 (td, J = 13.1 and 9.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 144.1, 137.5, 136.3, 135.5, 129.4 (2CH), 128.9, 128.5 (2CH), 127.6 (2CH), 126.4, 126.3 (2CH), 124.9, 123.7, 121.1, 118.4, 115.3, 47, 44.8, 43.3, 33.9, 21.5. HRMS (ESI): m/z calcd for $C_{25}H_{22}BrNNaO_2S$ $(M+Na)^+$: 502.0452, Found: 502.0430.

*3-Chloro-1-(3-fluorophenyl)-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (**7**).* This compound was isolated as a colorless solid. Following the reaction procedure-3, 40 mg of **1c** afforded 34.5 mg of **7** (82% yield). mp = 152−154 °C. R_f = 0.3 (hexane/EtOAc = 4/6). IR (thin film, neat): ν_{max}/cm^{-1} 2932, 1595, 1452, 1369, 1172, 740, 577, 538. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.40−7.36 (m, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.30−7.28 (m, 2H), 7.20−7.14 (m, 1H), 7.05 (d, J = 8.3 Hz, 2H), 6.89−6.86 (m, 1H), 6.85−6.82 (m, 1H), 6.65 (d, J = 9.9 Hz, 1H), 4.8 (t, J = 8.4 Hz, 1H), 4.31−4.24 (m, 1H), 3.38−3.33 (m, 1H), 3 (ddd, J = 15.7, 10.1, and 2.8 Hz, 1H), 2.86 (ddq, J = 10.5, 7.6, and 2.5 Hz, 1H), 2.33 (s, 3H), 2.04 (td, J = 12.7 and 9.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (d, J = 244.1 Hz), 147.2 (d, J = 7 Hz), 144.3, 137.8, 135.5, 135.4, 129.9 (d, J = 8.2 Hz), 129.4 (2CH), 128.9, 126.1 (2CH), 125.2, 123.8, 123.4 (d, J = 2.7 Hz), 120.7, 118.5, 115.5, 114.4 (d, J = 21.7 Hz), 113.3 (d, J = 21.0 Hz), 53.9, 45.6, 42.1 (d, J = 1.3 Hz), 32.8, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −113.1. HRMS (ESI): m/z calcd for $C_{25}H_{21}ClFNNaO_2S$ $(M+Na)^+$: 476.0863, Found: 476.0850.

*3-Bromo-1-(3-fluorophenyl)-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (**8**).* This compound was isolated as colorless viscous liquid. Following the procedure-3, 40 mg of **1c** afforded 38.5 mg of **8** (84% yield). R_f = 0.3 (hexane/EtOAc = 4/6). IR (thin film, neat): ν_{max}/cm^{-1} 2926, 1614, 1591, 1487, 747, 706, 666, 577. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.1 (d, J = 8.1 Hz, 1H), 7.48−7.45 (m, 1H), 7.40−7.36 (m, 1H), 7.33 (dd, J = 7.4 and 1 Hz, 1H), 7.30−7.28 (m, 2H), 7.20−7.13 (m, 1H), 7.05 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 7.9 Hz, 1H), 6.85−6.83 (m, 1H), 6.66 (dt, J = 9.8 and 1.9 Hz, 1H), 4.8 (t, J = 8.2 Hz, 1H), 4.36−4.30 (m, 1H), 3.46−3.41 (m, 1H), 3.15 (ddd, J = 15.6, 10.6 and 10.9 Hz, 1H), 2.99 (ddt, J = 13.2, 10.6, and 2.9 Hz, 1H), 2.33 (s, 3H), 2.15 (td, J = 13.1 and 9.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (d, J = 244.3 Hz), 147.1 (d, J = 7.0 Hz), 144.3, 137.7, 135.5 (d, J = 15.3 Hz), 129.9 (d, J = 8.1 Hz), 129.5, 129.4 (2CH), 128.8, 126.1 (2CH), 125.3, 123.9, 123.4 (d, J = 2.7 Hz), 121.5, 118.5, 115.5, 114.5 (d, J = 21.7 Hz), 113.3 (d, J = 21.0 Hz), 46.5, 44.4, 43.0 (d, J = 1.3 Hz), 33.7, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −113.0. HRMS (ESI): m/z calcd for $C_{25}H_{22}BrFNO_2S$ $(M+H)^+$: 498.0539; Found: 498.0521.

*3-Chloro-1-(4-methoxyphenyl)-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (**9**).* This compound was isolated as a colorless solid. Following the reaction procedure-3, 40 mg of **1h** afforded 36.5 mg of **9** (87% yield). mp = 180−182 °C R_f = 0.3 (hexane/EtOAc = 4/6). IR (thin film, neat): ν_{max}/cm^{-1} 2925, 1510, 1460, 1171, 751, 665. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (dd, J = 7.5 and 0.8 Hz, 1H), 7.47−7.45 (m, 2H), 7.25−7.23 (m, 2H), 7.03−6.99 (m, 3H), 6.94−6.91 (m, 2H), 6.66 (d, J = 8.7 Hz, 2H), 4.75−4.73 (m, 1H), 4.32−4.26 (m, 1H), 3.78 (s, 3H), 3.38−3.32 (m, 1H), 3.03−2.93 (m, 2H), 2.33 (s, 3H), 2.08−1.99 (ddd, J = 13.3, 12.4, and 9.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 148.8, 137.8, 136.8, 135.8, 135.1, 129.2 (2CH), 128.7 (2CH), 126.1 (2CH), 124.9 (2CH), 123.4, 118.3 (2CH), 114.8, 113.7 (2CH), 55.1, 54.2, 46.2, 41.6, 33, 21.5. HRMS (ESI): m/z calcd for $C_{26}H_{24}ClNNaO_3S$ $(M+Na)^+$: 488.1063; Found: 488.1044.

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*3-Chloro-4-methyl-1-phenyl-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (**10**).* This compound was isolated as a colorless solid. Following the reaction procedure-3, 40 mg of **1m** afforded 36 mg of **10** (86% yield). mp = 175−177 °C. R_f = 0.3 (hexane/EtOAc = 4/6). IR (thin film, neat): ν_{max}/cm^{-1} 2929, 1453, 1370 1171, 1089, 743, 665. ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 7.9 Hz, 1H), 7.50−7.48 (m, 1H), 7.37−7.31 (m, 3H), 7.22−7.19 (m, 4H), 7.05−7.01 (m, 4H), 4.8 (t, J = 9 Hz, 1H), 4.48 (dt, J = 13.6 and 4 Hz, 1H), 3.45−3.42 (m, 1H), 2.69−2.63 (m, 1H), 2.32 (s, 3H), 2.18 (td, J = 13.5 and 9.8 Hz, 1H), 1.48 (d, J = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 144, 137.8, 135.6, 135.4, 129.3 (2CH), 128.7, 128.5 (2CH), 127.3 (2CH), 126.4, 126.3 (2CH), 126, 124.8, 123.6, 118.2, 115.4, 58.7, 42.5, 39.7, 33.5, 21.5, 14.8. HRMS (ESI): m/z calcd for $C_{26}H_{25}ClNO_2S$ $(M+H)^+$: 450.1295, Found: 450.1284.

*3-Bromo-4-methyl-1-phenyl-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (**11**).* This compound was isolated as a viscous transparent liquid. Following the reaction procedure-3, 40 mg of **1m** afforded 37.5 mg of **11** (81% yield). R_f = 0.3 (hexane/EtOAc = 4/6). IR (thin film, neat): ν_{max}/cm^{-1} 2967, 1598, 1453, 1370, 1174, 738, 660, 578. ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 7.6 Hz, 1H), 7.48−7.46 (m, 1H), 7.37−7.36 (m, 1H), 7.33−7.31 (m, 1H), 7.22−7.18 (m, 5H), 7.04−7.01 (m, 4H), 4.82 (t, J = 8.9 Hz, 1H), 4.63−4.58 (m, 1H), 3.48−3.45 (m, 1H), 2.82−2.76 (m, 1H), 2.32 (s, 3H), 2.31−2.27 (m, 1H), 1.48 (d, J = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 144, 137.6, 135.6, 135.2, 129.4 (2CH), 128.63, 128.60 (2CH), 127.3, 126.4, 126.37 (2CH), 126.33, 125.9, 124.8, 123.6, 118.2, 115.4, 51.4, 43.3, 40.5, 33.8, 21.5, 16.1. HRMS (ESI): m/z calcd for $C_{26}H_{25}BrNO_2S$ $(M+H)^+$: 494.0789; Found: 494.0772.

*3-Chloro-1-(4-methoxyphenyl)-4-methyl-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (**12**).* This compound was isolated as colorless viscous liquid. Following the reaction procedure-3, 40 mg of **1m** afforded 37.3 mg of 12 (89% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2969, 1614, 1511, 1369, 1171, 1037, 739. ^1H NMR (400 MHz, $CDCl_3$): δ 8.08(d, J = 7.9 Hz, 1H), 7.50−7.48 (m, 1H), 7.37−7.31 (m, 2H), 7.24−7.22 (m, 2H), 7.04−6.99 (m, 3H), 6.92−6.88 (m, 2H), 6.67 (d, J = 8.4 Hz, 2H), 4.76−4.72 (m, 1H), 4.47 (dt, J = 13.6 and 4 Hz, 1H), 3.78 (s, 3H), 3.45−3.42 (m, 1H), 2.65−2.59 (m, 1H), 2.33 (s, 3H), 2.15 (td, J = 13.5, 9.8 Hz, 1H), 1.48 (d, J = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 143.8, 137.9, 137, 135.9, 135.8, 129.2 (2CH), 128.6, 128.4 (2CH), 126.1 (2CH), 125.6, 124.8, 123.5, 118.2, 115.4, 113.8 (2CH), 58.7, 55.1, 41.6, 34.9, 335, 21.5, 14.8. HRMS (ESI): m/z calcd for $C_{27}H_{27}ClNO_3S$ $(M+H)^+$: 480.1400; Found: 480.1381

*3,7-Dichloro-1-phenyl-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (**13**).* This compound was isolated as a colorless solid. Following the reaction procedure-3, 40 mg of **1i** afforded 37 mg of **13** (88% yield). mp = 213-214 °C. R_f = 0.3 (hexane/EtOAc = 4/6). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 1371, 1172, 810, 659, 582, 541. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.40−7.36 (m, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.30−7.28 (m, 2H), 7.20−7.14 (m, 1H), 7.05 (d, J = 8.3 Hz, 2H), 6.89−6.86 (m, 1H), 6.85−6.82 (m, 1H), 6.65 (d, J = 9.9 Hz, 1H), 4.8 (t, J = 8.4 Hz, 1H), 4.31−4.24 (m, 1H), 3.38−3.33 (m, 1H), 3 (ddd, J = 15.6, 10.2, and 2.9 Hz, 1H), 2.87 (ddt, J = 13.3, 7.5, and 2.8 Hz, 1H), 2.33 (s, 3H), 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.47, 144.41, 138, 137.1, 135.3, 130.9, 129.5 (2CH), 128.5 (2CH), 127.6 (2CH), 127.5, 126.5, 126.3 (2CH), 124.2, 119.8, 119.1, 115.5, 53.9, 45.9, 42.4, 32.8, 21.5. HRMS (ESI): m/z calcd for $C_{25}H_{22}Cl_2NO_2S$ $(M+H)^+$: 470.0748, Found: 470.0759.

*3-Chloro-1-(thiophen-2-yl)-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (**14**).* This compound was isolated as viscous transparent liquid. Following the reaction procedure-3, 40 mg of **1f** afforded 33.5 mg of **14** (80% yield). R_f = 0.3 (hexane/EtOAc = 4/6). IR (thin film, neat): ν_{max}/cm^{-1} 2927, 1598, 1454, 1171, 749, 664. ^1H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.3 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.41−7.36 (m, 1H), 7.36- 7.31 (m, 3H), 7.16 (dd, J = 5.1 and 1.1 Hz, 1H), 7.06 (d, J = 8.5 Hz, 2H), 6.82 (dd, J = 5.1 and 3.5 Hz, 1H), 6.53 (d, J = 3.5 Hz, 1H), 5.33 (t, J = 3.7 Hz, 1H), 4.53−4.45 (m, 1H), 3.45 (dd, J = 16.2 and 5.9 Hz, 1H), 2.95 (dd, J = 16.2 and 10.3 Hz, 1H), 2.57−2.54 (m, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 144.4, 136.8, 135.6, 134.7, 129.5 (2CH), 126.5, 126.6, 126.4 (2CH), 125.7, 125.1, 123.5, 118.5, 117.9, 114.9, 51.5, 42.9, 36.1, 32.2, 21.5. HRMS (ESI): m/z calcd for $C_{23}H_{21}ClNO_2S_2$ $(M+H)^+$: 442.0702; Found: 442.0690.

*Representative Procedure-4: Synthesis of Dihydrocyclohepta[b]-indoles **16** (Scheme 2).* Tetrahydrocyclohepta[b]indole **2a** (0.11 mmol) was dissolved in 1,4-dioxane in an oven-dried round-bottom flask and SeO_2 (1.5 equiv) was added to the reaction mixture at room temperature. The reaction mixture was then stirred at 110 °C until the reactant **2a** disappeared as monitored by TLC. The reaction mixture was filtered through Celite and washed with DCM (2−3 mL). The combined organic layers were concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexane) to afford **16**.

*Representative Procedure-5: Synthesis of Dihydroindolotropones **17** (Scheme 2).* Tetrahydrocyclohepta[b]indole **2a** (0.11 mmol) was dissolved in CH_3CN-H_2O (3:1) mixture in a round-bottom flask, and aq. TBHP (2 equiv) was added to the reaction mixture followed by $RuCl_3$ (5 mol%). The reaction mixture was stirred at 60 °C until the reactant **2a** disappeared (by TLC). The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2 × 2 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexanes) to afford **17**.

*Representative Procedure-6: Synthesis of Indolotropones **18** (Scheme 2).* The reaction was performed as in the procedure described for dihydrocyclohepta[b]indoles **16** [representative procedure-4].

*Representative Procedure-7: One-Pot Synthesis of Dihydrocyclohept[b]indoles **16** (Scheme 3).* A 5 mL glass vial was charged with **1** (0.09 mmol), AgOAc (2 mol%) in DCE (1 mL) and stirred at 60 °C. After disappearance of **1**, allyl-TMS (1.5 equiv) and $InCl_3$ (5 mol%) were introduced at 0 °C and continued stirring at 0 °C-rt until intermediate **3** disappeared. On complete formation of intermediate **4**, G-I (15 mol%) was introduced and continued stirring at room temperature until intermediate **4** disappeared. After complete formation of **2**, the solvent DCE was removed by reduced pressure and then 1,4-dioxane solvent was added to the residue and SeO_2 (1.5 equiv) was added to the reaction mixture and stirred at 110 °C until the intermediate **2** disappeared. The reaction mixture was filtered through Celite with DCM. The combined organic layers were concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexane) to afford **16**.

*Representative Procedure-8: One-Pot Synthesis of Dihydroindolotropones **17** (Scheme 3).* A 5 mL glass vial was charged with **1** (0.1 mmol), AgOAc (2 mol%) in DCE (1 mL) and stirred at 60 °C. After disappearance of **1**, allyl-TMS (1.5 equiv) and $InCl_3$ (5 mol%) were introduced at 0 °C and continued stirring at 0 °C-rt until intermediate **3** disappeared. On complete formation of intermediate **4**, G-I (15 mol %) was introduced and continued stirring at room temperature until intermediate **4** disappeared. After complete formation of **2**, the solvent DCE was removed by reduced pressure and CH_3CN-H_2O (3:1) was added to the residue, TBHP (aqueous, 2 equiv) and then $RuCl_3$ (5 mol%) was added to the reaction mixture. The reaction mixture was then stirred at 60 °C until the reactant **2** disappeared. The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2 × 2 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexane) to afford **17**.

*Representative Procedure-9: One-Pot Synthesis of Indolotropones **18** (Scheme 3).* The reaction was performed as in the procedure described for the one-pot synthesis of dihydrocyclohepta-[b]indoles **16** [representative procedure-7].

*6-Phenyl-5-tosyl-5,6-dihydrocyclohepta[b]indole (**16a**).* This compound was isolated as a pale brown liquid. Following the procedure-4, 40 mg of **2a** afforded 31 mg of **16a** (75% yield). R_f = 0.4 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 1735, 1492, 1372, 1170, 747. ^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (d,

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J = 8.1 Hz, 1H), 7.65−7.61 (m, 1H), 7.54−7.50 (m, 2H), 7.43−7.33 (m, 2H), 7.05 (dd, J = 19.9 and 7.5 Hz, 5H), 6.98−6.92 (m, 3H), 6.39−6.29 (m, 2H), 6.22 (d, J = 9.5 Hz, 1H), 6.08−6.03 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 140.2, 136.8, 135.2, 133.3, 129.6 (2CH), 128.5, 128.2, 127.7, 127.6 (2CH), 127.4, 126.9 (2CH), 126.5 (2CH), 126, 124.8, 123.8, 121.7, 120.2, 118.6, 115.6, 39.7, 21.5. HRMS (ESI): m/z calcd for $C_{26}H_{22}NO_2S$ $(M+H)^+$: 412.1371, Found: 412.1376.

*6-(3-Fluorophenyl)-5-tosyl-5,6-dihydrocyclohepta[b]indole (**16b**).* This compound was isolated as a pale brown oil. Following the reaction procedure-4, 40 mg of **2c** afforded 24.2 mg of **16b** (61% yield). R_f = 0.4 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 3026, 1734, 1588, 1372, 1170, 754. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, J = 8.3 Hz, 1H), 7.67−7.63 (m, 1H), 7.54 (d, J = 8.6 Hz, 2H), 7.46−7.34 (m, 2H), 7.07−7.01 (m, 3H), 6.98 (d, J = 10.8 Hz, 1H), 6.80−6.74 (m, 2H), 6.48 (d, J = 10.5 Hz, 1H), 6.41−6.31 (m, 2H), 6.21 (d, J = 9.5 Hz, 1H), 6.07−6.01 (m, 1H), 2.3 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3 (d, J = 243.2 Hz), 145.1, 142.8 (d, J = 6.6 Hz), 136.9, 135.3, 132.5, 129.6 (2CH), 128.9 (d, J = 8.1 Hz), 128.6, 128.4, 127.7, 126.6, 126.4 (2CH), 125.1, 123.9, 122.7 (d, J = 2.7 Hz), 121.9, 120.3, 118.7, 115.6, 113.9 (d, J = 22.4 Hz), 112.8 (d, J = 21.1 Hz), 39.4 (d, J = 1.4 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −114.0. HRMS (ESI): m/z calcd for $C_{26}H_{19}FNO_2S$ $(M-H)^+$: 428.1119, Found: 428.1107.

*6-([1,1′-Biphenyl]-4-yl)-5-tosyl-5,6-dihydrocyclohepta[b]indole (**16c**).* This compound was isolated as a pale yellow solid. Following the reaction procedure-4, 40 mg of **2d** afforded **16c** (62% yield). mp = 173−175 °C. R_f = 0.4 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 3028, 1734, 1597, 1451, 1169, 747. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41−8.38 (m, 1H), 7.68−7.65 (m, 1H), 7.56−7.51 (m, 4H), 7.45−7.31 (m, 7H), 7.05−6.98 (m, 5H), 6.44−6.38 (m, 1H), 6.37−6.31 (m, 1H), 6.26 (d, J = 9.3 Hz, 1H), 6.12−6.06 (m, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 140.8, 139.4, 138.9, 136.9, 135.3, 133.2, 129.5 (2CH), 128.7 (2CH), 128.5, 128.2, 127.6, 127.4 (2CH), 127.3, 127, 126.9 (2CH), 126.5 (2CH), 126.3 (2CH), 124.9, 123.8, 121.8, 120.2, 118.6, 115.6, 39.5, 21.5. HRMS (ESI): m/z calcd for $C_{32}H_{26}NO_2S$ $(M+H)^+$: 488.1684, Found: 488.1666.

*6-Phenyl-5-tosyl-6,7-dihydrocyclohepta[b]indol-10(5H)-one (**17a**).* This compound was isolated as a pale brown liquid. Following the reaction procedure-5, 40 mg of **2a** afforded 24.6 mg of **17a** (60% yield). R_f = 0.3 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 1657, 1452, 1370, 1172, 750. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (dt, J = 8.3 and 1.0 Hz, 1H), 7.75−7.69 (m, 1H), 7.49−7.40 (m, 3H), 7.28−7.25 (m, 2H), 7.20−7.13 (m, 3H), 6.99−6.92 (m, 4H), 6.17 (dd, J = 12.2 and 1.7 Hz, 5.68 (dd, J = 6.0 and 3.3 Hz, 1H), 3.37−3.22 (m, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 145.3, 144.2, 136.4, 135.9, 135.1, 131.8, 129.6 (2CH), 129.3, 128.8 (2CH), 128.5, 127.5 (2CH), 127.1, 126.6 (2CH), 125.6, 124.3, 118.2, 117.9, 115.3, 47.6, 36.8, 21.5. HRMS (ESI): m/z calcd for $C_{26}H_{22}NO_3S$ $(M+H)^+$: 428.1320; Found: 428.1303.

*6-([1,1′-Biphenyl]-4-yl)-5-tosyl-6,7-dihydrocyclohepta[b]indol-10(5H)-one (**17b**).* This compound was isolated as a pale yellow solid. Following the reaction procedure-5, 40 mg of **2d** afforded 25 mg of **17b** (61% yield). mp = 167−168 °C. R_f = 0.3 (hexane/EtOAc = 7/3). IR (thin film, neat): 2917, 1729, 1596, 1443, 1168, 1090, 760. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67−8.63 (m, 1H), 8.36−8.31 (m, 1H), 7.59−7.54 (m, 2H), 7.50−7.41 (m, 4H), 7.42−7.36 (m, 3H), 7.24 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 8.3 Hz, 2H), 6.28 (d, J = 4.2 Hz, 2H), 5.88 (t, J = 4.2 Hz, 1H), 3.31−3.24 (m, 1H), 3.07−2.99 (m, 1H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.3, 146.9, 145.3, 140.4, 139.7, 138.9, 136.9, 136.4, 135.2, 134.6, 129.5 (2CH), 128.9 (2CH), 128.8 (2CH), 127.9, 127.4, 126.97 (2CH), 126.90 (2CH), 126.6 (2CH), 125.9, 125.1, 123.1, 123, 114.7, 39.7, 34.7, 21.5. HRMS (ESI): m/z calcd for $C_{32}H_{26}NO_3S$ $(M+H)^+$: 504.1633, Found: 504.1642.

*6-(Thiophen-2-yl)-5-tosyl-6,7-dihydrocyclohepta[b]indol-10(5H)-one (**17c**).* This compound was isolated as a pale brown solid. Following the reaction procedure-7, 40 mg of **2f** afforded 19.7 mg of **17c** (48% yield). mp = 138−140 °C. R_f = 0.3 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 2925, 1732, 1657, 1374, 1171, 749. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.3 (d, J = 8.4 Hz, 1H), 7.7 (d, J = 7.3 Hz, 1H), 7.51−7.38 (m, 5H), 7.11 (dd, J = 5.1 and 1.2 Hz, 1H), 7.05 (d, J = 8.1 Hz, 2H), 6.76 (dd, J = 5.1 and 3.4 Hz, 1H), 6.56 (d, J = 3.4 Hz, 1H), 6.21 (d, J = 12.2 Hz, 1H), 5.96 (s, 1H), 3.29 (d, J = 4.2 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 145.4, 143.8, 139.5, 135.8, 135.3, 131.5, 129.7 (2CH), 129.3, 128.4, 126.8, 126.6 (2CH), 125.8, 125.7, 124.9, 124.4, 118.1, 117.6, 115.4, 48.2, 32.5, 21.6. HRMS (ESI): m/z calcd for $C_{24}H_{20}NO_3S_2$ $(M+H)^+$: 434.0885, Found: 434.0868.

*5-Tosylcyclohepta[b]indol-10(5H)-one (**18a**).* This compound was isolated as a pale brownish solid. Following the reaction procedure-6, 30 mg of **2j** afforded 20.3 mg of **18a** (65% yield). mp = 169−171 °C. R_f = 0.3 (hexane/EtOAc = 5/5). IR (thin film, neat): ν_{max}/cm^{-1} 2925, 1733, 1620, 1514, 1377, 1175, 747. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, J = 12.7 Hz, 1H), 8.44 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 8 Hz, 1H), 7.86 (d, J = 12 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.61 (ddd, J = 8.5, 7.2, and 1.2 Hz, 1H), 7.51−7.45 (m, 1H), 7.22 (d, J = 8.3 Hz, 2H), 7.14 (dd, J = 12.7 and 2.7 Hz, 1H), 7.08 (dd, J = 12 and 2.7 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 146.1, 138.8, 137.7, 137.2, 136.7, 134.8, 130.2 (2CH), 129.5, 128.7, 127.3, 126.6, 126.5 (2CH), 126.4, 125.1, 119.5, 115.9, 21.7. HRMS (ESI): m/z calcd for $C_{20}H_{16}NO_3S$ $(M+H)^+$: 350.0851, Found: 350.0834.

*2-Bromo-5-tosylcyclohepta[b]indol-10(5H)-one (**18b**).* This compound was isolated as brownish solid. Following the reaction procedure-8, 30 mg of **2k** afforded 20 mg of **18b** (63% yield). mp = 218−220 °C. R_f = 0.3 (hexane/EtOAc = 5/5). IR (thin film, neat): ν_{max}/cm^{-1} 2925, 1623, 1517, 1380, 1172, 749. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, J = 12.8 Hz, 1H), 8.32 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 2 Hz, 1H), 7.75 (d, J = 12.4 Hz, 1H), 7.70−7.64 (m, 3H), 7.24 (d, J = 8 Hz, 2H), 7.14 (dd, J = 12.8 and 2.8 Hz, 1H), 7.06 (dd, J = 12.2 and 2.8 Hz, 1H), 2.36 (3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.2, 146.4, 139.3, 138.4, 136.9, 135.8, 134.5, 131.5, 130.3 (2CH), 129.0, 128.9, 126.5 (2CH), 126.0, 125.2, 122.3, 118.6, 117.4, 21.7. HRMS (ESI): m/z calcd for $C_{20}H_{15}BrNO_3S$ $(M+H)^+$: 427.9956, Found: 427.9939.

*3-Chloro-5-tosylcyclohepta[b]indol-10(5H)-one (**18c**).* This compound was isolated as a pale brownish solid. Following the reaction procedure-8, 30 mg of **2l** afforded 19.4 mg of **18c** (62% yield). mp = 212−214 °C. R_f = 0.3 (hexane/EtOAc = 5/5). IR (thin film, neat): ν_{max}/cm^{-1} 2925, 1732, 1612, 1514, 1415, 1171, 659. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, J = 13 Hz, 1H), 8.47 (d, J = 1.7 Hz, 1H), 7.80 (s, 1H), 7.77 (d, J = 4.8 Hz, 1H), 7.70 (d, J = 8.6 Hz, 2H), 7.46 (dd, J = 8.6 and 1.7 Hz, 1H), 7.26 (d, J = 8.3 Hz, 2H), 7.12 (dd, J = 13 and 2.7 Hz, 1H), 7.07 (dd, J = 12 and 2.7 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.2, 146.4, 138.9, 138.0, 137.5, 137.0, 134.8, 134.6, 130.4 (2CH), 129.0, 126.6 (2CH), 126.1, 125.8 (2CH), 125.7, 120.3, 115.9, 21.7. HRMS (ESI): m/z calcd for $C_{20}H_{15}ClNO_3S$ $(M+H)^+$: 384.0461; Found: 384.0446.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00865.

^{1}H and ^{13}C NMR data of all new compounds (PDF)

X-ray crystallographic data of compound **2j** (CIF)

X-ray crystallographic data of compound **10** (CIF)

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Notes

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(11) See the Supporting Information for details.

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