

## Supporting Information

### Divergent Synthesis of Indole-fused Polycycles via Rh(II)-Catalyzed Intramolecular [3+2] Cycloaddition of Indolyltriazaoles

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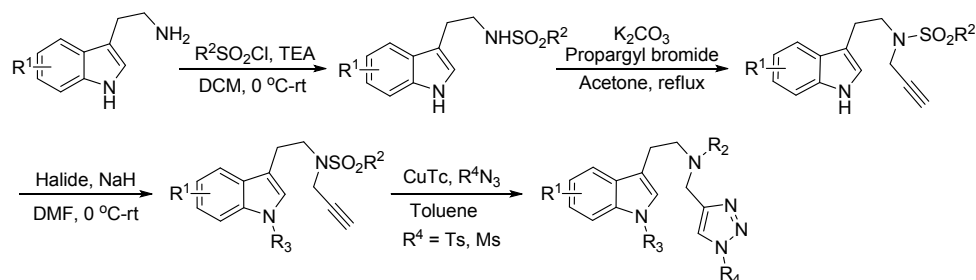
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#### CONTENTS

|  |         |
|--|---------|
| 1. General remarks.....  | S2      |
| 2. General procedure for the synthesis of triazoles <b>1</b> ..... | S3-S5   |
| 3. General procedure for the synthesis of <b>2</b> .....           | S5      |
| 4. General procedure for the synthesis of triazoles <b>3</b> ..... | S5      |
| 5. General procedure for the synthesis of <b>4</b> .....           | S5-S6   |
| 6. Deprotection of Products <b>2</b> .....                         | S5-S6   |
| 7. Characterization and spectra charts.....                        | S6-S59  |
| 8. Crystallographic information of <b>2a</b> and <b>4a</b> .....   | S60-S61 |
| 9. Reference.....  | S62     |

**1. General Remarks.** MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected.  $^1\text{H}$  NMR spectra were recorded for solution in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as internal standard or  $\text{DMSO}-d_6$ .  $J$ -values are in Hz. HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF<sub>254</sub> silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques.

## 2. General procedure for the synthesis of triazoles 1

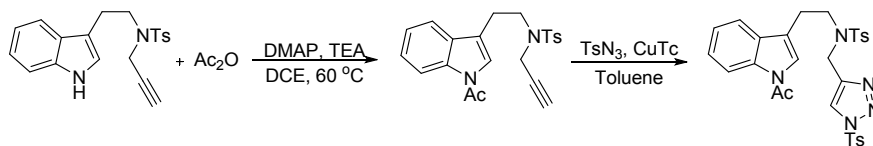


Tryptamine (10.0 mmol, 1.0 equiv) was suspended in DCM (30 mL), followed by addition of TEA (20.0 mmol, 2.0 equiv). The suspension was cooled to 0 °C, and then  $R^2SO_2Cl$  (10.0 mmol, 1.0 equiv) in DCM (10 mL) was added dropwise at this temperature. The reaction mixture was stirred overnight at room temperature. Then the reaction was quenched by water, and diluted with DCM. After extraction, the organic layers were dried over  $Mg_2SO_4$ , filtered and concentrated *in vacuo*. The crude product was used to the next step without further purification.

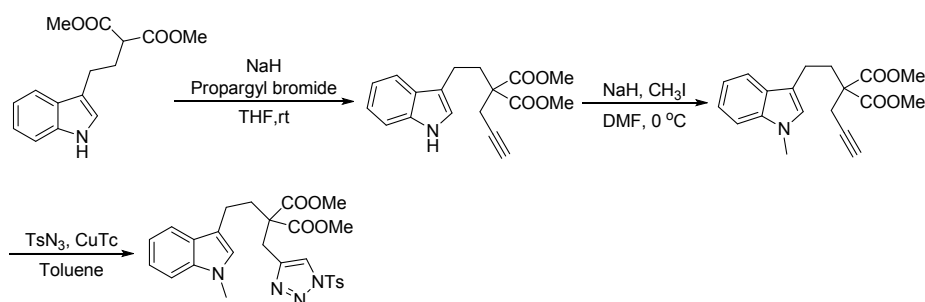
The obtained NTs-tryptamine was dissolved in acetone (20 mL), to the solution were added  $K_2CO_3$  (20.0 mmol, 2.0 equiv) and propargyl bromide (15.0 mmol, 1.5 equiv) at room temperature. The reaction mixture was reflux for 6 h, whereupon a deep-yellow mixture was obtained. The precipitate was filtered off and the solution was concentrated to give the crude product, which was used to the next steps without further purification.

The obtained intermediate was dissolved in DMF (20 mL), and NaH (10 mmol, 1.0 eq) was added to the solution at 0 °C, followed by addition of halide ( $CH_3I$ , BnBr,  $CH_3CH_2I$ , *n*-iodobutane, allyl bromide) (12 mmol, 1.2 eq) at 0 °C. The reaction was stirred for 15 min and then quenched by addition of water, the mixture was extracted by EA, and the organic layers were washed by water, brine and dried over  $MgSO_4$ , concentrated to give the crude product, which were purified by silica gel chromatography to get the alkyne intermediate.

CuTc (0.2 mmol, 0.04 equiv) was added into a solution of the obtained alkyne (5.0 mmol, 1.0 equiv) in toluene (10 mL). The reaction mixture was stirred for 3 min at room temperature, followed by addition of  $TsN_3$  (6 mmol, 1.2 equiv) or  $MsN_3$  (6 mmol, 1.2 equiv) via a syringe. The reaction mixture was stirred for 5 h at room temperature and the resulting mixture was directly subjected to a flash column chromatography to afford the desired product as a white solid.



To a 50 mL reaction tube were added N-(2-(1H-indol-3-yl)ethyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (10 mmol, 1.0 equiv), Ac<sub>2</sub>O (40 mmol, 4.0 equiv), DMAP (2 mmol, 0.2 equiv) and TEA (15 mmol, 1.5 equiv), followed by addition of DCE (25 mL). The reaction mixture was stirred for 24 h at 60 °C and then quenched by water, the mixture was extracted with DCM, and the organic layers were washed with water, brine and dried over MgSO<sub>4</sub>, concentrated to give the crude product, which was purified by silica gel chromatography to give the intermediate alkyne in 90% yield. The obtained intermediate was used to the next step following the same procedure depicted above.

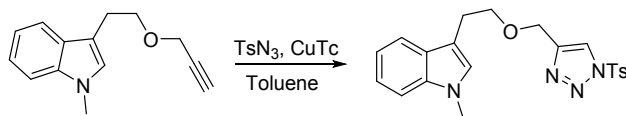


Dimethyl 2-(2-(1H-indol-3-yl)ethyl)malonate<sup>[1]</sup> was synthesized according to the previously reported procedure. To a solution of dimethyl 2-(2-(1H-indol-3-yl)ethyl)malonate (10 mmol, 1.0 equiv) in distilled THF was added NaH (11 mmol, 1.1 equiv) at 0 °C, after stirring for 30 min, propargyl bromide (11 mmol, 1.1 equiv) was added dropwise. The reaction mixture was stirred for 3h at room temperature and then quenched by water, the mixture was extracted by DCM, and the organic layers were washed by water, brine and dried over MgSO<sub>4</sub>, concentrated to give the crude product, which was used to the next step without further purification.

The obtained intermediate was dissolved in DMF (20 mL), and NaH (10 mmol, 1.0 eq) was added to the solution at 0 °C, followed by addition of CH<sub>3</sub>I (12 mmol, 1.2 eq) at 0 °C. The reaction was stirred for 15 min and then quenched by addition of water, the mixture was extracted by EA, and the organic layer was washed by water, brine and dried over MgSO<sub>4</sub>, and concentrated to give the crude product, which

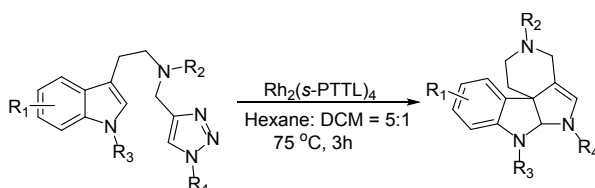
were purified by silica gel chromatography to get the intermediate alkyne.

The obtained intermediate was used to the next step following the same procedure depicted above.



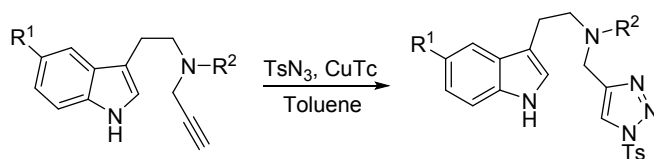
1-methyl-3-(2-(prop-2-yn-1-yloxy)ethyl)-1H-indole<sup>[2]</sup> was synthesized according to the previously reported procedure. The obtained alkyne was used to the next step following the same procedure depicted above.

### 3. General procedure for the synthesis of 2.



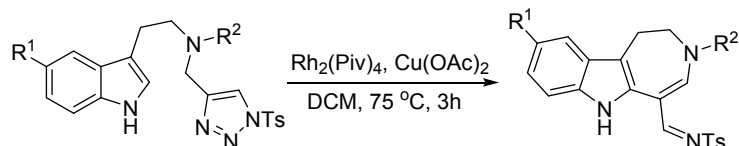
To a flame-dried flask were added the triazole (0.2 mmol, 1.0 equiv),  $\text{Rh}_2(\text{s-PTTL})_4$  (0.004 mmol, 0.02 equiv), the flask was evacuated and backfilled with Ar for 3 times. Solvent (6 ml, hexane:DCM = 5:1) were added to this flask via a syringe under Ar. The reaction mixture was stirred for 3 hours at 75 °C. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under vacuum, the crude product was purified by silica gel chromatography (PE:EA = 5:1) to give the desired product 2.

### 4. General procedure for the synthesis of 3



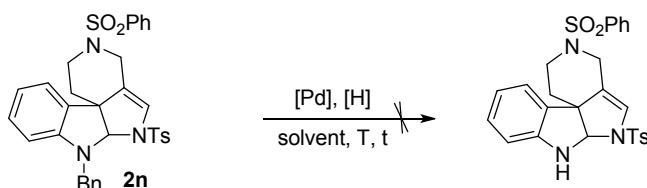
The obtained alkyne was used to the next step following the same procedure depicted above.

## 5. General procedure for the synthesis of 4



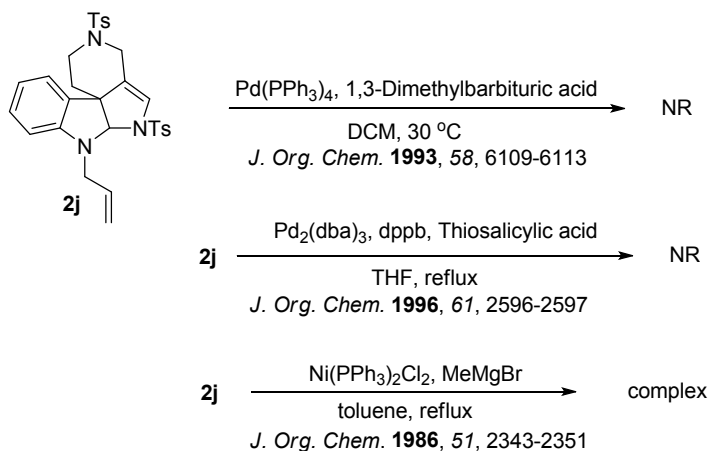
To a flame-dried flask was added **3** (0.2 mmol, 1.0 equiv),  $\text{Rh}_2(\text{Piv})_4$  (0.004 mmol, 0.02 equiv) and  $\text{Cu}(\text{OAc})_2$  (0.2 mmol, 1.0 equiv), the flask was evacuated and backfilled with Ar for 3 times. DCM (2.0 mL) was added to this flask via a syringe under Ar. The reaction mixture was stirred for 3 hours at 75 °C. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under vacuum, the crude product was purified by silica gel chromatography (PE:EA = 4:1) to give the desired product **4**.

## 6. Deprotection of products 2

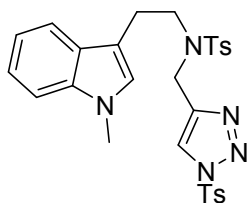


Conditions:

- $\text{Pd}(\text{OH})_2/\text{C}$ ,  $\text{H}_2$  (1 atm), EA, 50 °C, 12 h. NR
- $\text{Pd}/\text{C}$ ,  $\text{H}_2$  (1 atm), MeOH, 50 °C, 12 h. NR
- $\text{Pd}(\text{OH})_2/\text{C}$ ,  $\text{H}_2$  (30 atm), EA, 50 °C, 12 h. NR
- $\text{Pd}/\text{C}$ ,  $\text{H}_2$  (30 atm), MeOH, AcOH (1 drop), 50 °C, 12 h, complex

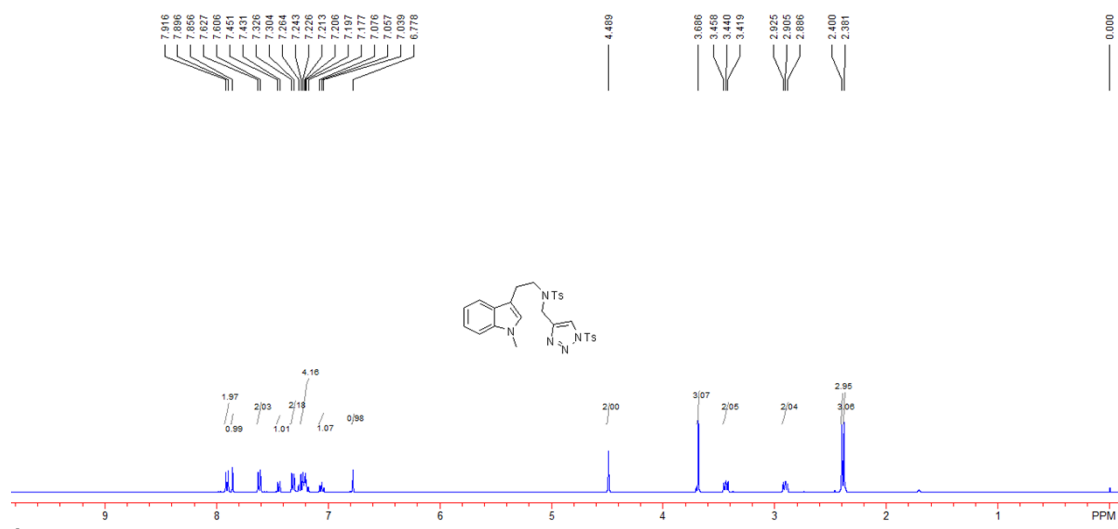


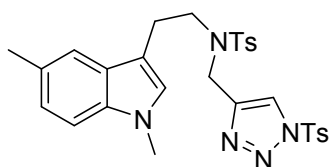
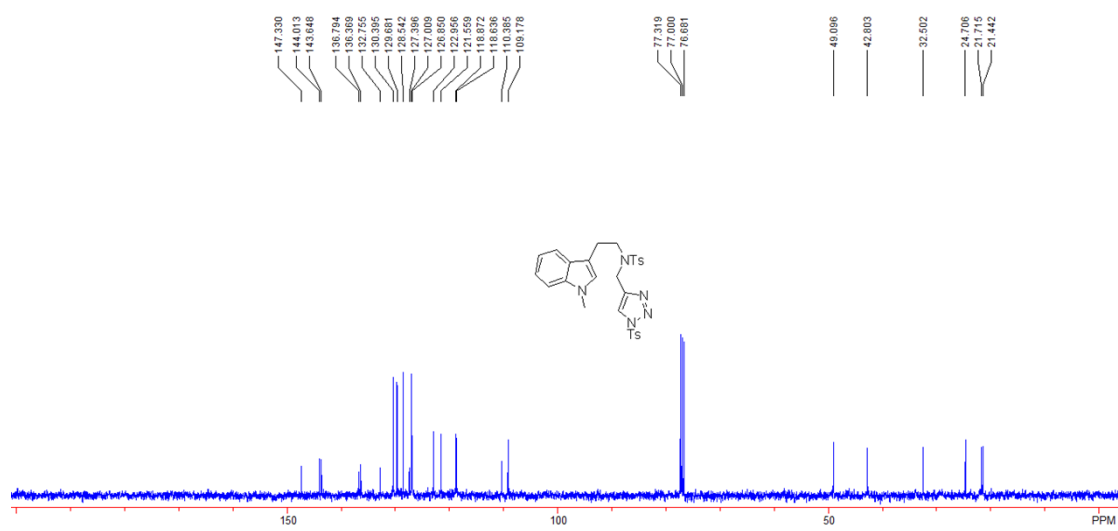
## 7. Characterization and spectra charts.



**4-methyl-N-(2-(1-methyl-1H-indol-3-yl)ethyl)-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 1a.**

5.0 mmol scale, 2.11 g, a white solid, 75% yield. m.p.: 88-90 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.38 (s, 3H, CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 2.90 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.44 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.69 (s, 3H, CH<sub>3</sub>), 4.49 (s, 2H, CH<sub>2</sub>), 6.78 (s, 1H, CH=), 7.06 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.19-7.27 (m, 4H, Ar), 7.31 (d, *J* = 8.4 Hz, 2H, Ar), 7.44 (d, *J* = 8.0 Hz, 1H, Ar), 7.62 (d, *J* = 8.4 Hz, 2H, Ar), 7.86 (s, 1H, CH=), 7.91 (d, *J* = 8.4 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.4, 21.7, 24.7, 32.5, 42.8, 49.1, 109.2, 110.4, 118.6, 118.9, 121.6, 122.9, 126.8, 127.0, 127.4, 128.5, 129.7, 130.4, 132.8, 136.4, 136.8, 143.6, 144.0, 147.3. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3142, 2926, 1594, 1553, 1392, 1331, 1194, 1178, 1156, 1090, 1009, 970, 896, 812, 740, 701, 668 cm<sup>-1</sup>. HRMS (MALDI) Calcd. for C<sub>28</sub>H<sub>30</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 564.1734, found: 564.1721.

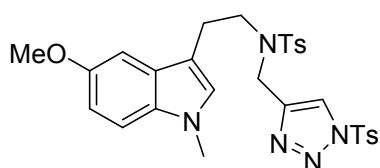
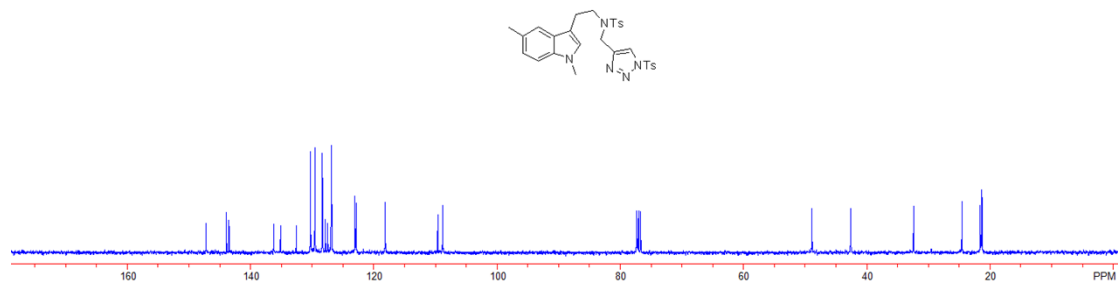
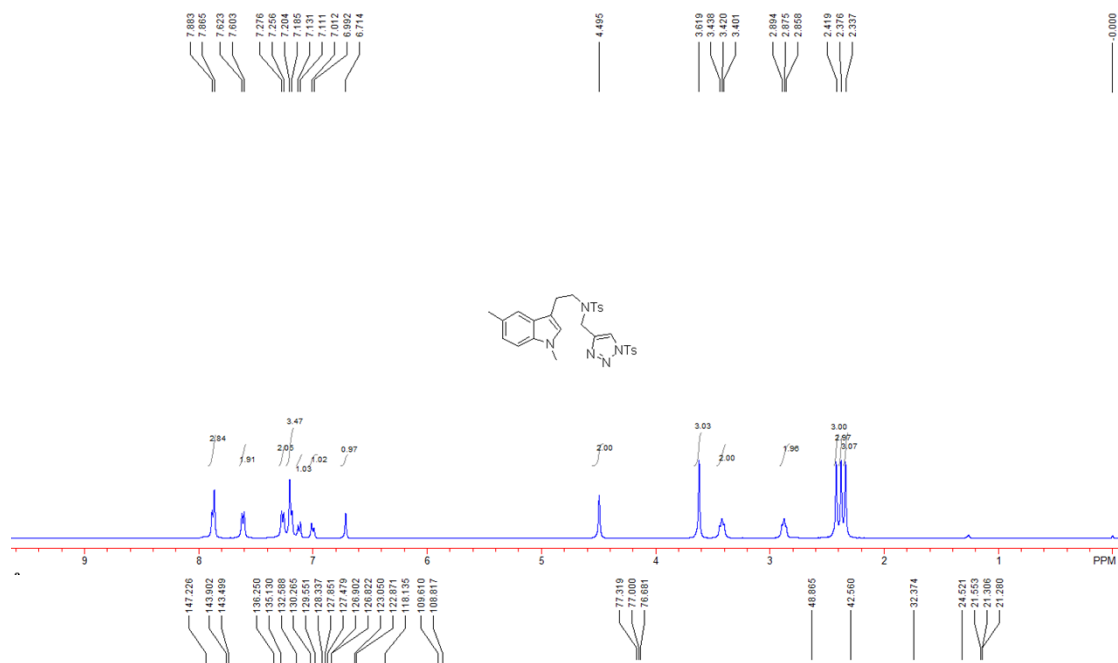




**N-(2-(1,5-dimethyl-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 1b.**

5.0 mmol scale, 2.34 g, a white solid, 81% yield. m.p.: 98-100 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.34 (s, 3H, CH<sub>3</sub>), 2.38 (s, 3H, CH<sub>3</sub>), 2.42 (s, 3H, CH<sub>3</sub>), 2.88 (t, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 3.42 (t, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 3.62 (s, 3H, CH<sub>3</sub>), 4.49 (s, 2H, CH<sub>2</sub>), 6.71 (s, 1H, CH=), 7.00 (d, *J* = 8.0 Hz, 1H, Ar), 7.12 (d, *J* = 8.0 Hz, 1H, Ar), 7.19 (d, *J* = 8.0 Hz, 3H, Ar), 7.27 (d, *J* = 8.0 Hz, 2H, Ar), 7.61 (d, *J* = 8.0 Hz, 2H, Ar), 7.86 (s, 1H, CH=), 7.87 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.28, 21.31, 21.6, 24.5, 32.4, 42.6, 48.9, 108.8, 109.6, 118.1, 122.9, 123.0, 126.8, 126.9, 127.5, 127.8, 128.3, 129.6, 130.3, 132.6, 135.1, 136.2, 143.5, 143.9, 147.2. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3151, 2914, 2848, 1592, 1489, 1442, 1382, 1335, 1194, 1178, 1155, 1090, 1010, 972, 791, 749, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>29</sub>H<sub>32</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>++</sup>H) requires 578.1890, found: 578.1887.

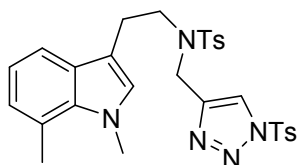
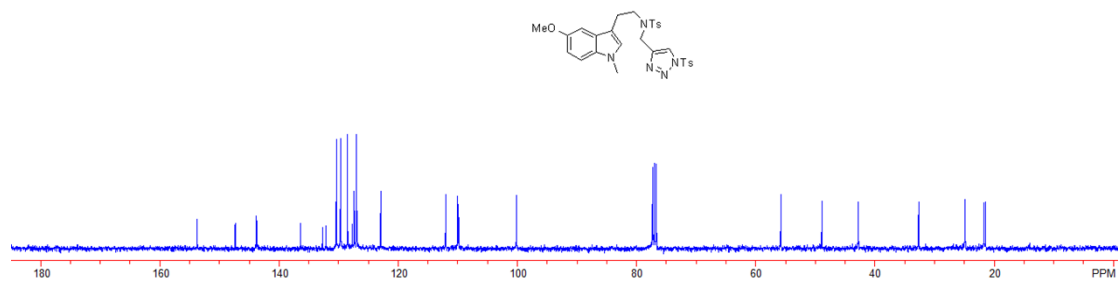
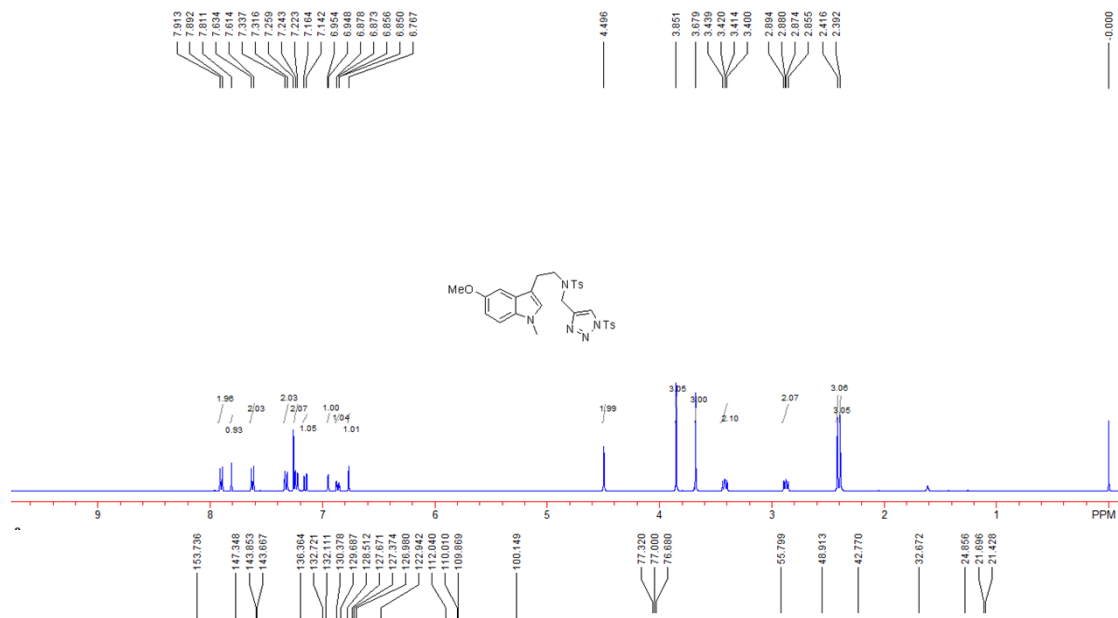




**N-(2-(5-methoxy-1-methyl-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide **1c**.**

5.0 mmol scale, 2.52 g, a white solid, 85% yield. m.p.: 79-81 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.39 (s, 3H, CH<sub>3</sub>), 2.42 (s, 3H, CH<sub>3</sub>), 2.88 (dd, *J* = 8.0 Hz, *J* = 10.0 Hz, 2H, CH<sub>2</sub>), 3.42 (dd, *J* = 8.0 Hz, *J* = 10.0 Hz, 2H, CH<sub>2</sub>), 3.68 (s, 3H, CH<sub>3</sub>), 3.85 (s, 3H, CH<sub>3</sub>), 4.50 (s, 2H, CH<sub>2</sub>), 6.77 (s, 1H, CH=), 6.86 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 1H, Ar), 6.95 (d, *J* = 2.4 Hz, 1H, Ar), 7.15 (d, *J* = 8.8 Hz, 1H, Ar), 7.23 (d, *J* = 8.0 Hz, 2H, Ar), 7.33 (d, *J* = 8.0 Hz, 2H, Ar), 7.62 (d, *J* = 8.0 Hz, 2H, Ar), 7.81 (s, 1H, CH=), 7.90 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)

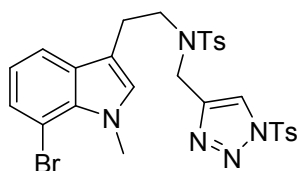
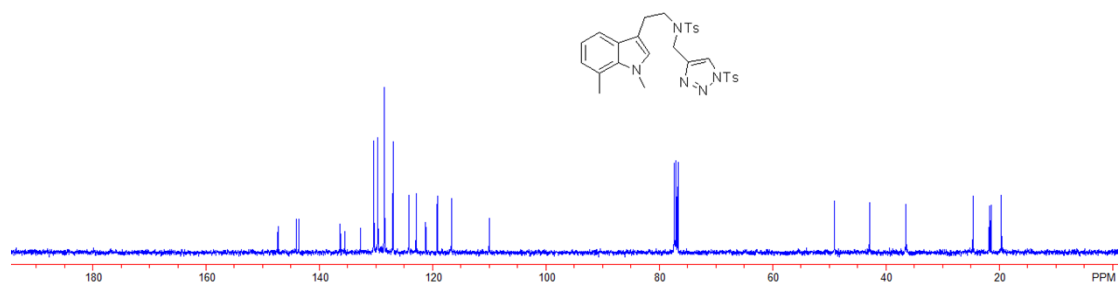
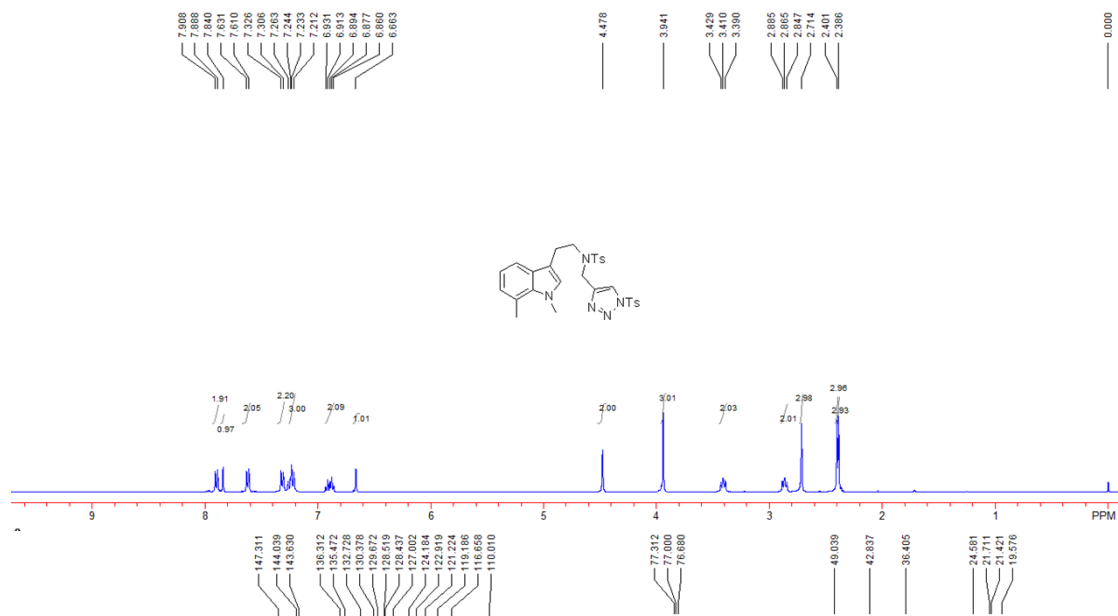
$\delta$  21.4, 21.7, 24.8, 32.7, 42.8, 48.9, 55.8, 100.1, 109.9, 110.0, 122.0, 122.9, 127.0, 127.4, 127.7, 128.5, 129.7, 130.4, 132.1, 132.7, 136.4, 143.7, 143.8, 147.3, 153.7. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  3153, 2923, 1595, 1491, 1453, 1392, 1335, 1304, 1194, 1178, 1154, 1120, 1090, 972, 909, 811, 731, 686, 668 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>29</sub>H<sub>32</sub>N<sub>5</sub>O<sub>5</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 594.1839, found: 594.1836.



**N-(2-(1,7-dimethyl-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 1d.**

5.0 mmol scale, 2.68 g, a white solid, 93% yield. m.p.: 100-102 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  2.39 (s, 3H, CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 2.71 (s, 3H, CH<sub>3</sub>), 2.86 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.41 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.94 (s, 3H, CH<sub>3</sub>), 4.48 (s, 2H, CH<sub>2</sub>), 6.67 (s, 1H, CH=), 6.86-6.94 (m, 2H, Ar), 7.21-7.25 (m, 3H, Ar), 7.32 (d, *J*

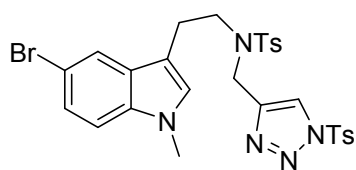
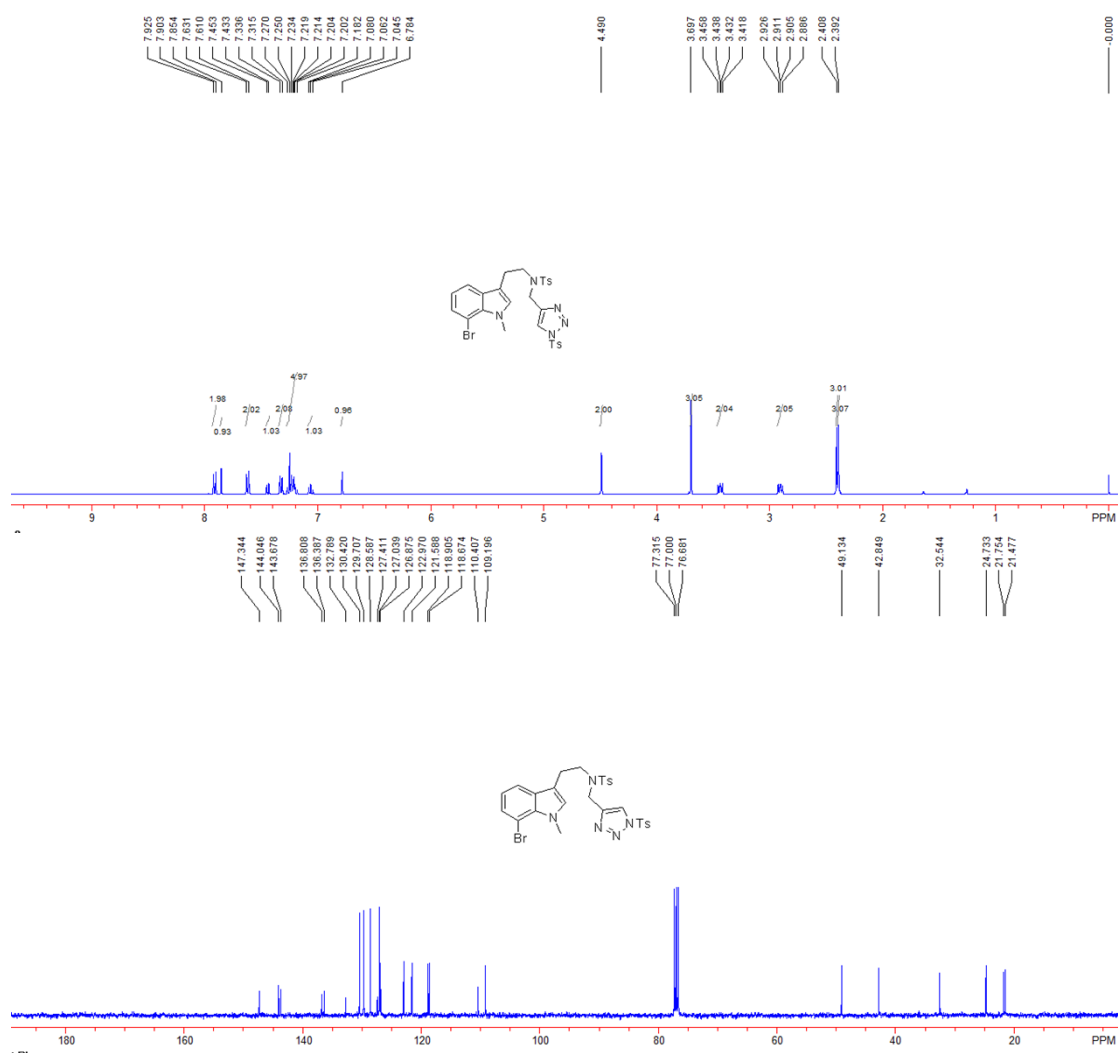
= 8.0 Hz, 2H, Ar), 7.62 (d,  $J$  = 8.0 Hz, 2H, Ar), 7.84 (s, 1H, CH=), 7.90 (d,  $J$  = 8.0 Hz, 2H, Ar).  
 $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  19.6, 21.4, 21.7, 24.6, 36.4, 42.8, 49.0, 110.0, 116.6, 119.2, 121.2, 122.9, 124.2, 127.0, 128.4, 128.5, 129.7, 130.4, 132.7, 135.5, 136.3, 143.6, 144.0, 147.3.  
 IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu$  3150, 2922, 1734, 1593, 1453, 1392, 1335, 1194, 1178, 1155, 1090, 1010, 972, 812, 746, 667, 654  $\text{cm}^{-1}$ . HRMS (ESI) Calcd. for  $\text{C}_{29}\text{H}_{32}\text{N}_5\text{O}_4\text{S}_2^+$  ( $\text{M}^++\text{H}$ ) requires 578.1890, found: 578.1886.



**N-(2-(7-bromo-1-methyl-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide **1e**.**

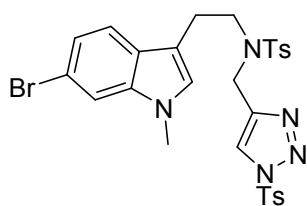
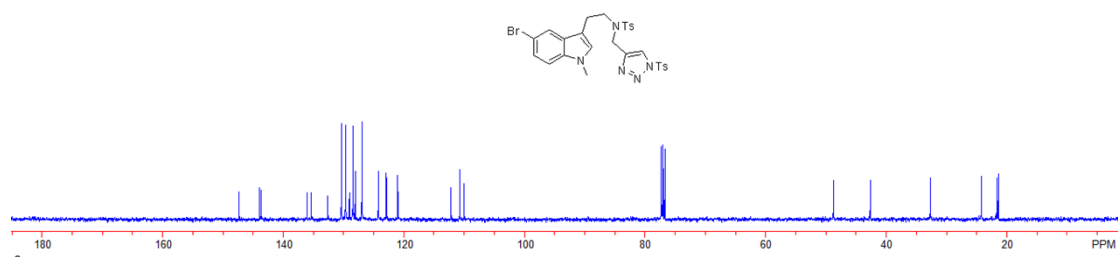
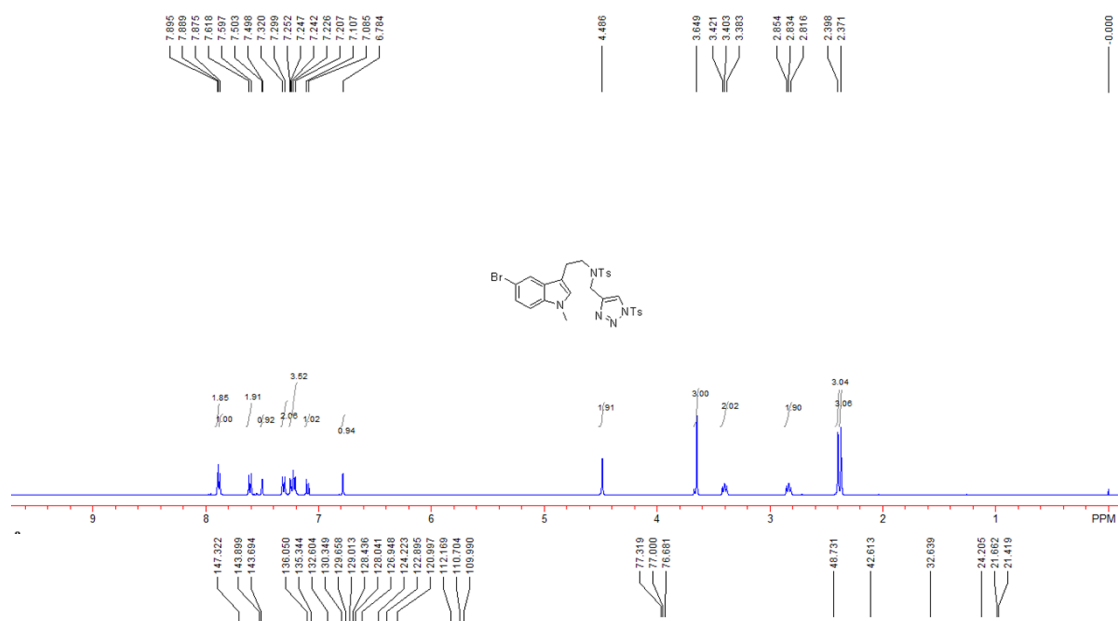
5.0 mmol scale, 2.95 g, a white solid, 92% yield. m.p.: 97-99 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  2.39 (s, 3H,  $\text{CH}_3$ ), 2.41 (s, 3H,  $\text{CH}_3$ ),

2.91 (dd,  $J = 8.0$  Hz,  $J = 10.4$  Hz, 2H, CH<sub>2</sub>), 3.43 (dd,  $J = 8.0$  Hz,  $J = 8.0$  Hz, 2H, CH<sub>2</sub>), 3.70 (s, 3H, CH<sub>3</sub>), 4.49 (s, 2H, CH<sub>2</sub>), 6.78 (s, 1H, CH=), 7.06 (dd,  $J = 7.2$  Hz, 2H, Ar), 7.18-7.27 (m, 3H, Ar), 7.33 (d,  $J = 8.4$  Hz, 2H, Ar), 7.44 (d,  $J = 8.0$  Hz, 1H, Ar), 7.62 (d,  $J = 8.4$  Hz, 2H, Ar), 7.85 (s, 1H, CH=), 7.91 (d,  $J = 8.4$  Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  21.5, 21.8, 24.7, 32.5, 42.8, 49.1, 109.2, 110.4, 118.7, 118.9, 121.6, 123.0, 126.9, 127.0, 127.4, 128.6, 129.7, 130.4, 132.8, 136.4, 136.8, 143.7, 144.0, 147.3. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  3153, 2914, 2862, 1732, 1682, 1596, 1477, 1451, 1393, 1327, 1194, 1179, 1155, 1090, 1010, 973, 812, 739, 701, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>28</sub>H<sub>29</sub>BrN<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 642.0839, found: 642.0835.



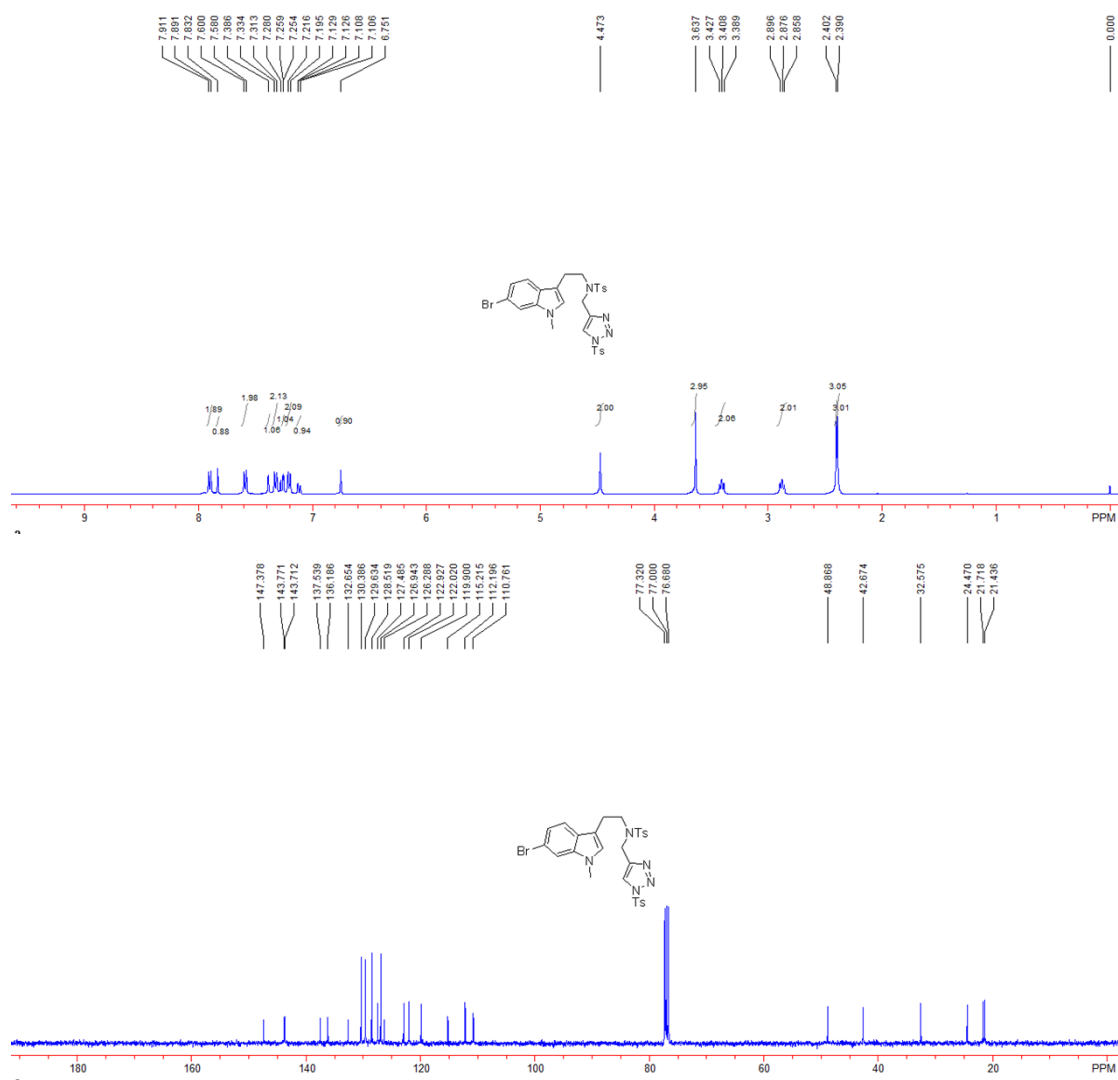
**N-(2-(5-bromo-1-methyl-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 1f.**

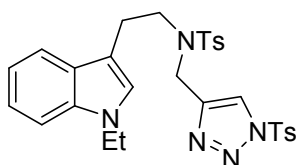
5.0 mmol scale, 2.69 g, a white solid, 84% yield. m.p.: 105-107 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.37 (s, 3H, CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 2.83 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.40 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.65 (s, 3H, CH<sub>3</sub>), 4.49 (s, 2H, CH<sub>2</sub>), 6.78 (s, 1H, CH=), 7.10 (d, *J* = 8.8 Hz, 1H, Ar), 7.20-7.26 (m, 3H, Ar), 7.31 (d, *J* = 8.4 Hz, 2H, Ar), 7.50 (d, *J* = 1.6 Hz, 1H, Ar), 7.61 (d, *J* = 8.4 Hz, 2H, Ar), 7.88 (d, *J* = 8.4 Hz, 2H, Ar), 7.89 (s, 1H, CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.4, 21.6, 24.2, 32.6, 42.6, 48.7, 110.0, 110.7, 112.2, 121.0, 122.9, 124.2, 126.9, 128.0, 128.4, 129.0, 129.6, 130.3, 132.6, 135.3, 136.0, 143.7, 143.9, 147.3. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3143, 2930, 1595, 1477, 1392, 1335, 1304, 1194, 1179, 1155, 1090, 1010, 973, 812, 793, 749, 701, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>28</sub>H<sub>29</sub>BrN<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 642.0839, found: 642.0834.



**N-(2-(6-bromo-1-methyl-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 1g.**

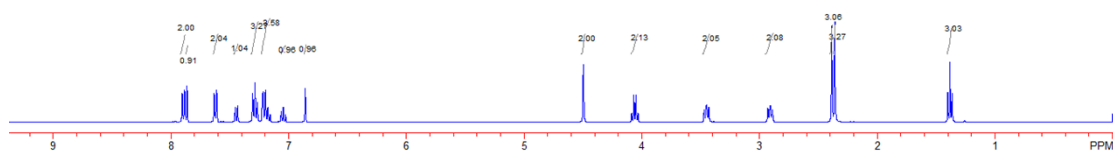
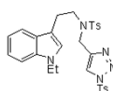
5.0 mmol scale, 2.95 g, a white solid, 92% yield. m.p.: 111-113 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.39 (s, 3H, CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 2.88 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.41 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.64 (s, 3H, CH<sub>3</sub>), 4.47 (s, 2H, CH<sub>2</sub>), 6.75 (s, 1H, CH=), 7.12 (dd, *J* = 0.8 Hz, *J* = 8.0 Hz, 1H, Ar), 7.21 (d, *J* = 8.4 Hz, 2H, Ar), 7.25 (d, *J* = 2.0 Hz, 1H, Ar), 7.32 (d, *J* = 8.4 Hz, 2H, Ar), 7.38 (s, 1H, Ar), 7.59 (d, *J* = 8.0 Hz, 2H, Ar), 7.83 (s, 1H, CH=), 7.90 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.4, 21.7, 24.5, 32.6, 42.7, 48.9, 110.8, 112.2, 115.2, 119.9, 122.0, 122.9, 126.3, 126.9, 127.5, 128.5, 129.6, 130.4, 132.7, 136.2, 137.5, 143.7, 143.8, 147.4. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3142, 2926, 1593, 1471, 1447, 1392, 1324, 1305, 1194, 1178, 1155, 1090, 1010, 974, 833, 811, 749, 701, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>28</sub>H<sub>29</sub>BrN<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 642.0839, found: 642.0835.

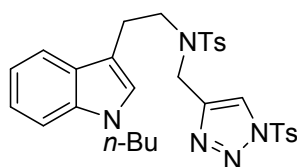
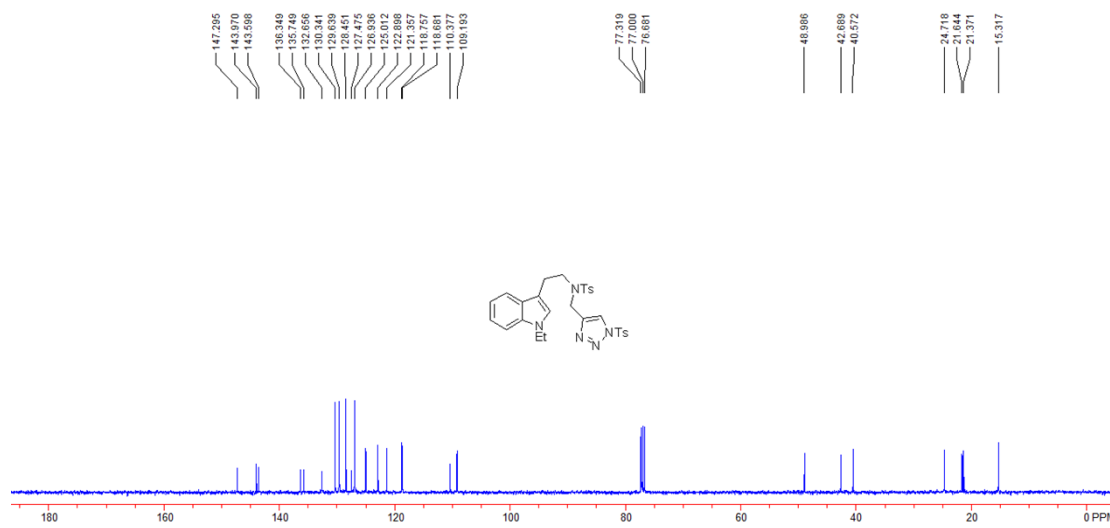




**N-(2-(1-ethyl-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 1h**

5.0 mmol scale, 2.54 g, a white solid, 88% yield. m.p.: 75-77 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 1.38 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 2.36 (s, 3H, CH<sub>3</sub>), 2.39 (s, 3H, CH<sub>3</sub>), 2.91 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.45 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 4.06 (q, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 4.50 (s, 2H, CH<sub>2</sub>), 6.86 (s, 1H, CH=), 7.04 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.15-7.23 (m, 3H, Ar), 7.29 (dd, *J* = 8.0 Hz, 3H, Ar), 7.44 (d, *J* = 8.0 Hz, 1H, Ar), 7.62 (d, *J* = 8.0 Hz, 2H, Ar), 7.86 (s, 1H, CH=), 7.89 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 15.3, 21.4, 21.6, 24.7, 40.6, 42.7, 49.0, 109.2, 110.4, 118.7, 118.8, 121.4, 122.9, 125.0, 126.9, 127.5, 128.5, 129.6, 130.3, 132.7, 135.7, 136.3, 143.6, 144.0, 147.3. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3150, 2981, 2930, 1594, 1461, 1393, 1332, 1305, 1216, 1194, 1178, 1154, 1090, 1010, 972, 910, 812, 737, 701, 666 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>28</sub>H<sub>29</sub>BrN<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 578.1890, found: 578.1887.

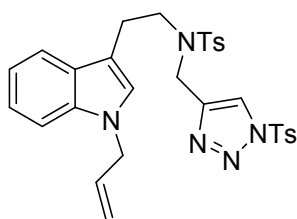
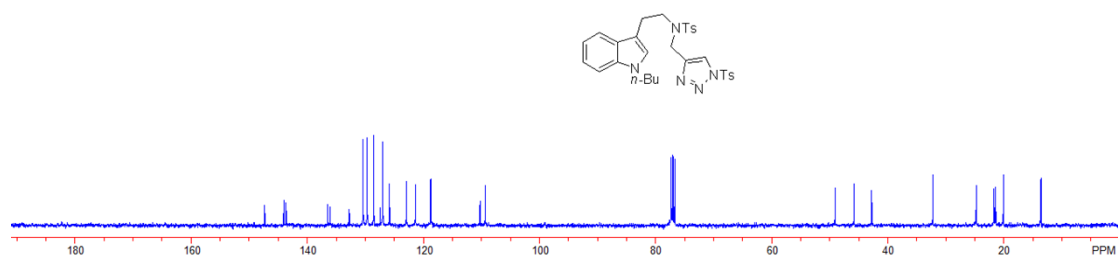
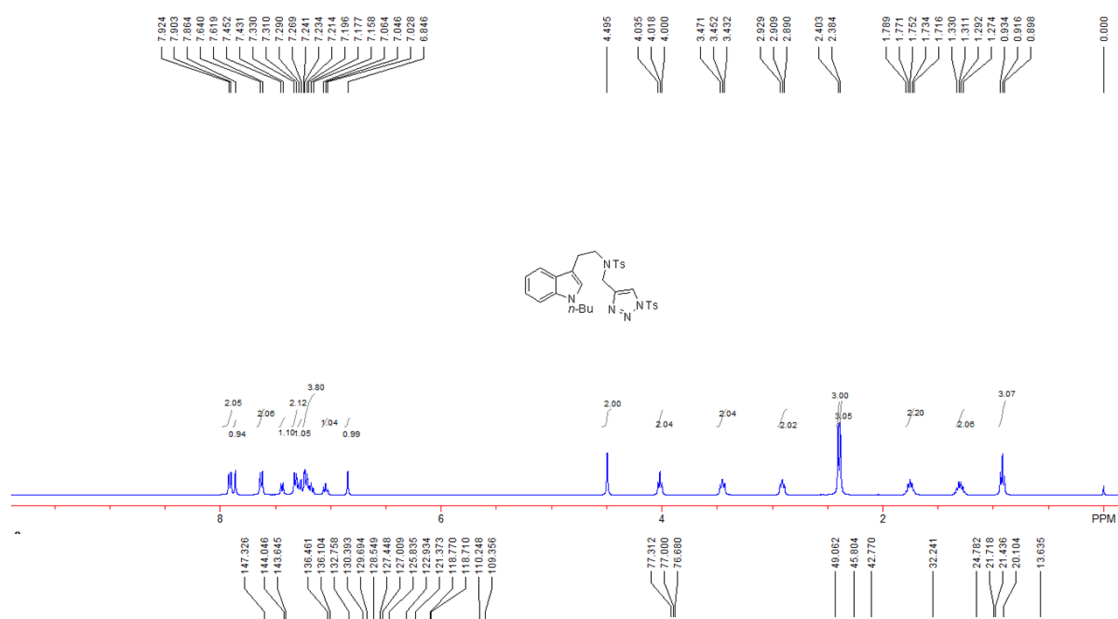




**N-(2-(1-butyl-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 1i**

5.0 mmol scale, 2.34 g, a white solid, 78% yield. m.p.: 68-70 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 0.92 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 1.27-1.33 (m, 2H, CH<sub>2</sub>), 1.71-1.79 (m, 2H, CH<sub>2</sub>), 2.38 (s, 3H, CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 2.91 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.45 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 4.02 (t, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 4.50 (s, 2H, CH<sub>2</sub>), 6.85 (s, 1H, CH=), 7.05 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H, Ar), 7.15-7.25 (m, 3H, Ar), 7.28 (d, *J* = 8.4 Hz, 1H, Ar), 7.32 (d, *J* = 8.0 Hz, 2H, Ar), 7.44 (d, *J* = 8.4 Hz, 1H, Ar), 7.63 (d, *J* = 8.4 Hz, 2H, Ar), 7.86 (s, 1H, CH=), 7.91 (d, *J* = 8.4 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 13.6, 20.1, 21.4, 21.7, 24.8, 32.2, 42.8, 45.8, 49.1, 109.4, 110.2, 118.7, 118.8, 121.4, 122.9, 125.8, 127.0, 127.4, 128.5, 129.7, 130.4, 132.8, 136.1, 136.5, 143.6, 144.0, 147.3. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 2955, 2931, 2826, 1590, 1461, 1451, 1394, 1333, 1194, 1179, 1154, 1090, 1010, 971, 812, 737, 701, 666 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>36</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 606.2203, found: 606.2219.

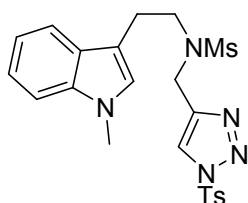
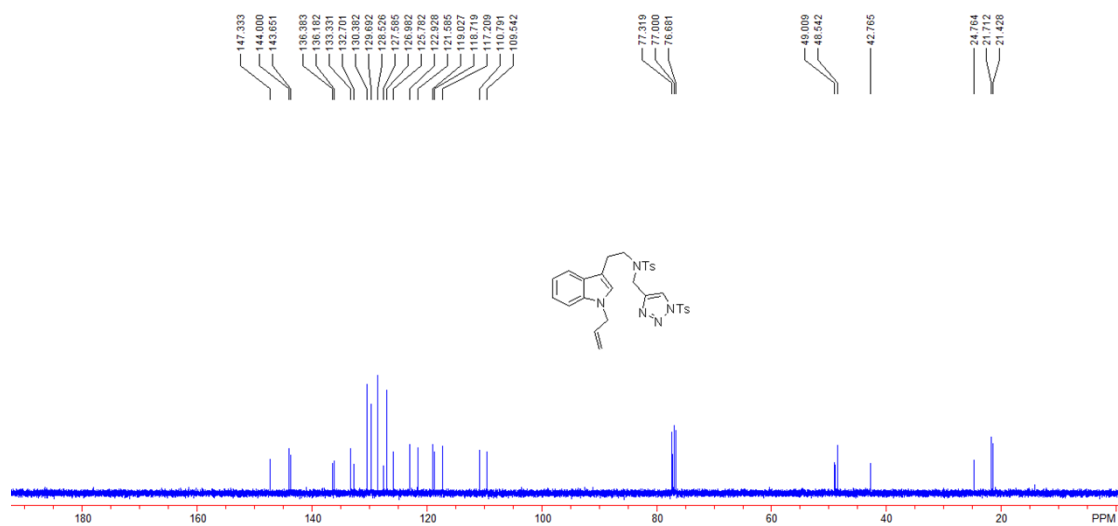
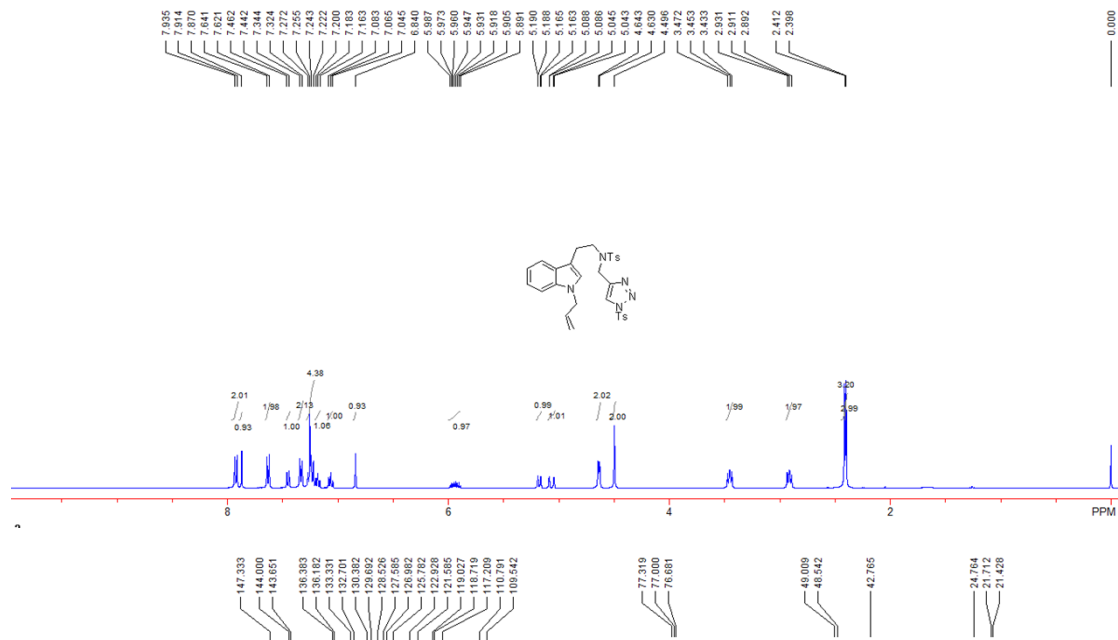




**N-(2-(1-allyl-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 1j**

5.0 mmol scale, 2.41 g, a white solid, 82% yield. m.p.: 75-77 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.40 (s, 3H, CH<sub>3</sub>), 2.41 (s, 3H, CH<sub>3</sub>), 2.91 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.45 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 4.50 (s, 2H, CH<sub>2</sub>), 4.64 (d, *J* = 5.2 Hz, 2H, CH<sub>2</sub>), 5.07 (dd, *J* = 17.2 Hz, *J* = 0.8 Hz, 1H, CH<sub>2</sub>=), 5.18 (dd, *J* = 0.8 Hz, *J* = 10.0 Hz, 1H, CH<sub>2</sub>=), 5.89-5.99 (m, 1H, CH=), 6.84 (s, 1H, CH=), 7.06 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H, Ar), 7.18 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H, Ar), 7.22-7.28 (m, 3H, Ar), 7.33 (d, *J* = 8.0 Hz, 2H, Ar), 7.45 (d, *J* = 8.0 Hz, 1H, Ar), 7.63 (d, *J* = 8.0 Hz, 2H, Ar), 7.87 (s, 1H, CH=), 7.92 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ

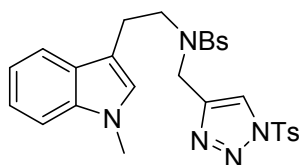
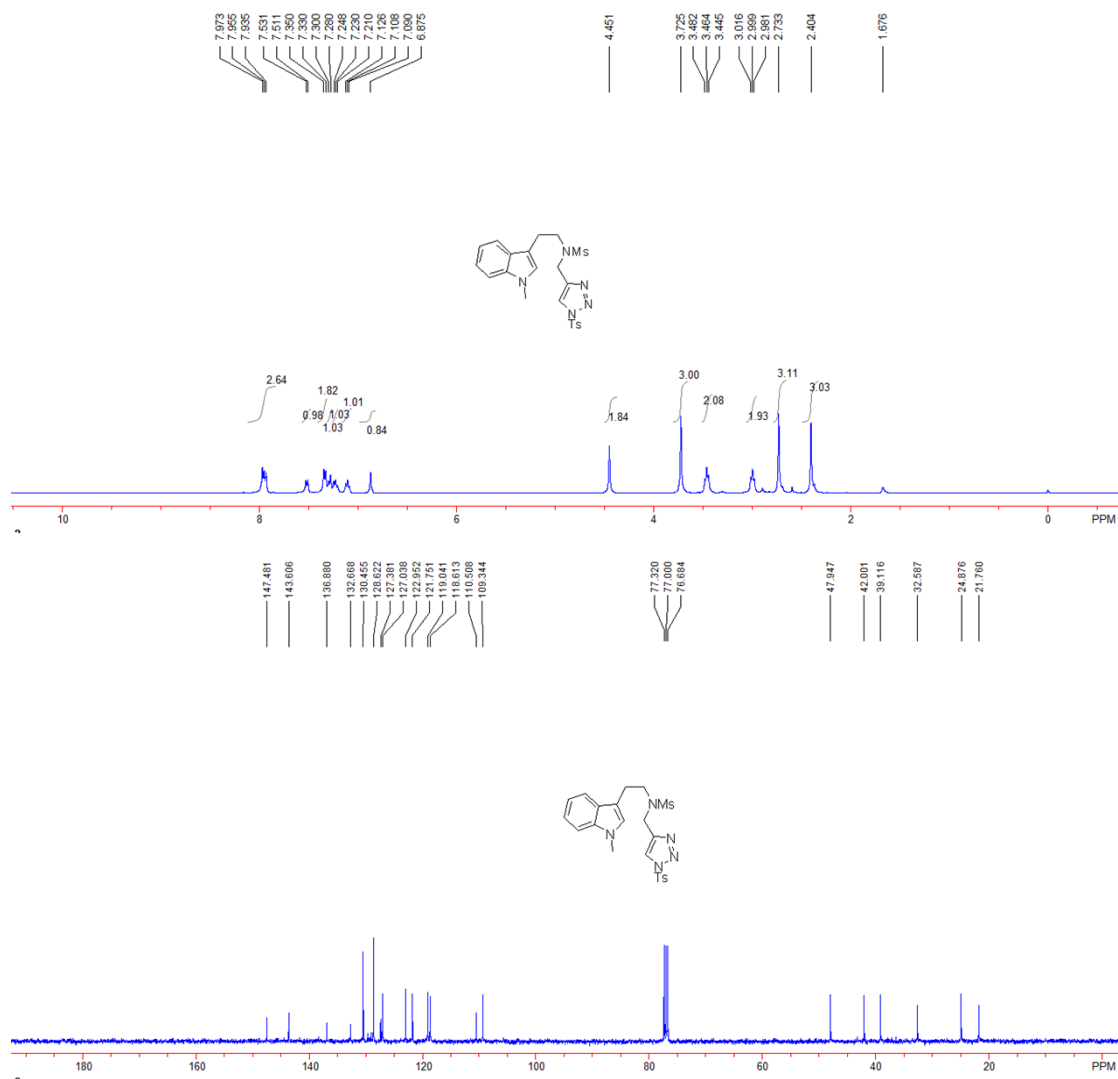
21.4, 21.7, 24.8, 42.8, 48.5, 49.0, 109.5, 110.8, 117.2, 118.7, 119.0, 121.6, 122.9, 125.8, 127.0, 127.6, 128.5, 129.7, 130.4, 132.7, 133.3, 136.2, 136.4, 143.7, 144.0, 147.3. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  2930, 1599, 1467, 1392, 1331, 1304, 1194, 1178, 1154, 1089, 1010, 973, 919, 812, 739, 700, 686, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>30</sub>H<sub>32</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 590.1890, found: 590.1886.



**N-(2-(1-methyl-1H-indol-3-yl)ethyl)-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)methanesulfonamide 1k**

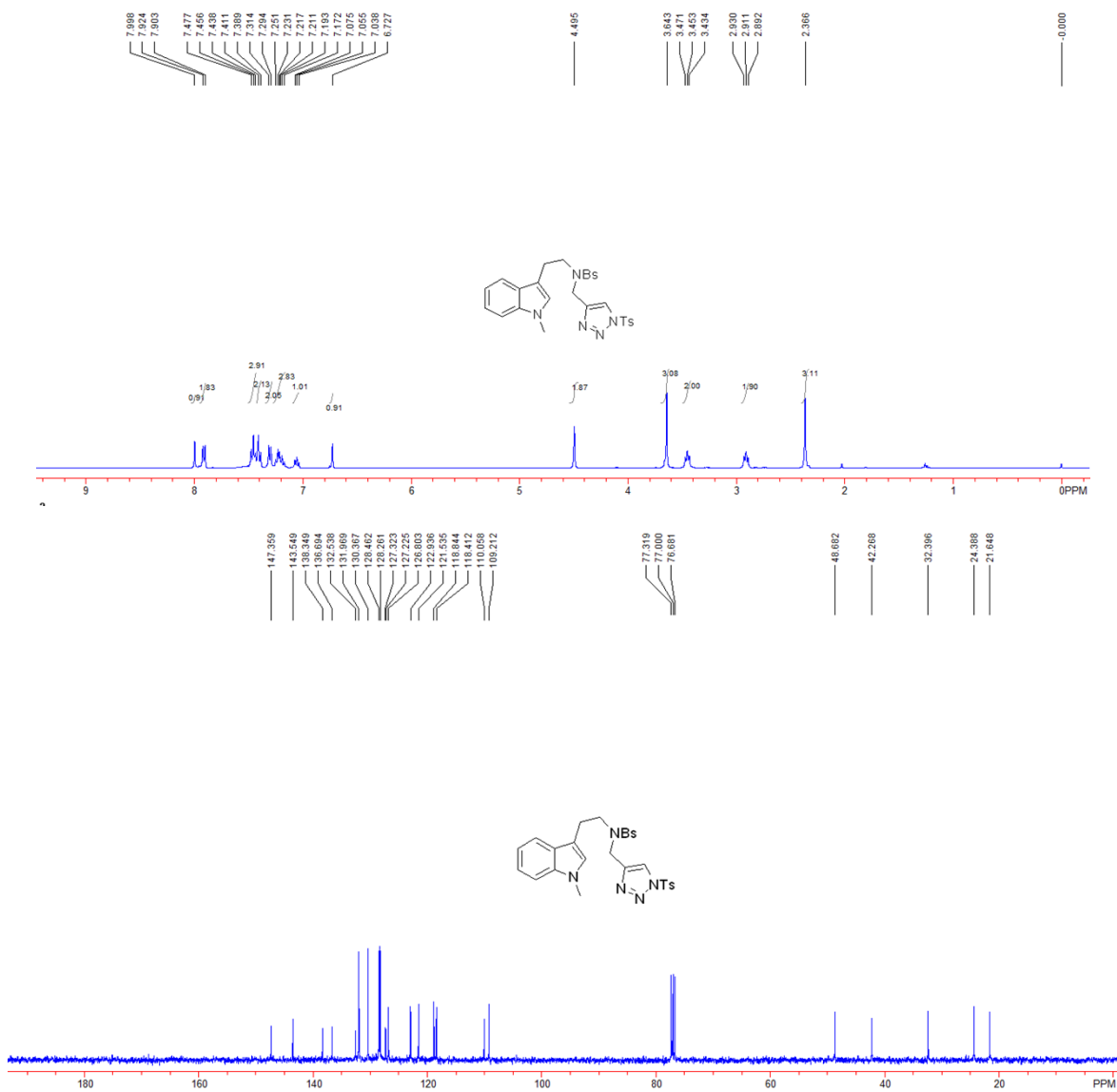
5.0 mmol scale, 1.73 g, a white solid, 71% yield. m.p.: 118-120 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  2.40 (s, 3H, CH<sub>3</sub>), 2.73 (s, 3H, CH<sub>3</sub>), 3.00 (t, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 3.46 (t, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 3.72 (s, 3H, CH<sub>3</sub>), 4.45 (s, 2H,

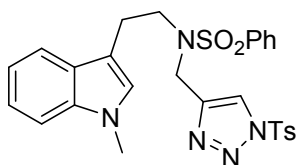
CH<sub>2</sub>), 6.88 (s, 1H, CH=), 7.11 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H, Ar), 7.23 (dd, *J* = 7.2 Hz, *J* = 8.0 Hz, 1H, Ar), 7.29 (d, *J* = 8.0 Hz, 2H, Ar), 7.34 (d, *J* = 8.0 Hz, 2H, Ar), 7.52 (d, *J* = 8.0 Hz, 1H, Ar), 7.94 (d, *J* = 8.0 Hz, 2H, Ar), 7.97 (s, 1H, CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.8, 24.9, 32.6, 39.1, 42.0, 47.9, 109.3, 110.5, 118.6, 119.0, 121.8, 122.9, 127.0, 127.4, 128.6, 130.4, 132.7, 136.9, 143.6, 147.5. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3142, 2927, 1596, 1487, 1385, 1324, 1176, 1137, 989, 971, 900, 821, 738, 703, 683 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>22</sub>H<sub>26</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 488.1421, found: 488.1418.



**4-bromo-N-(2-(1-methyl-1H-indol-3-yl)ethyl)-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 11**

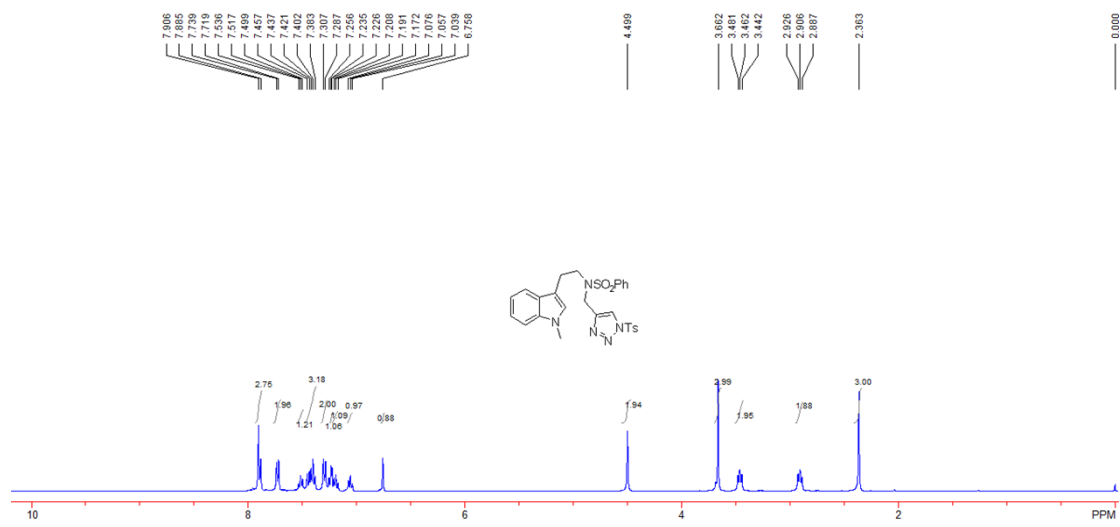
5.0 mmol scale, 2.35 g, a white solid, 75% yield. m.p.: 111-113 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.37 (s, 3H, CH<sub>3</sub>), 2.91 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>), 3.45 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>), 3.64 (s, 3H, CH<sub>3</sub>), 4.50 (s, 2H, CH<sub>2</sub>), 6.73 (s, 1H, CH=), 7.06 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H, Ar), 7.17-7.26 (m, 2H, Ar), 7.30 (d, *J* = 8.0 Hz, 2H, Ar), 7.40 (d, *J* = 8.0 Hz, 2H, Ar), 7.46 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 3H, Ar), 7.91 (d, *J* = 8.0 Hz, 2H, Ar), 8.00 (s, 1H, CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.6, 24.4, 32.4, 42.3, 48.7, 109.2, 110.0, 118.4, 118.8, 121.5, 122.9, 126.8, 127.2, 127.3, 128.3, 128.5, 130.4, 132.0, 132.5, 136.7, 138.3, 143.5, 147.4. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3093, 2914, 1735, 1573, 1427, 1388, 1327, 1194, 1178, 1156, 1089, 1068, 1009, 974, 813, 741, 700, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>27</sub>H<sub>27</sub>BrN<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>++</sup>H) requires 628.0682, found: 628.0679.

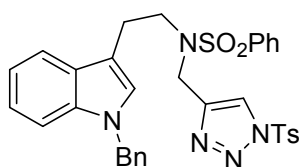
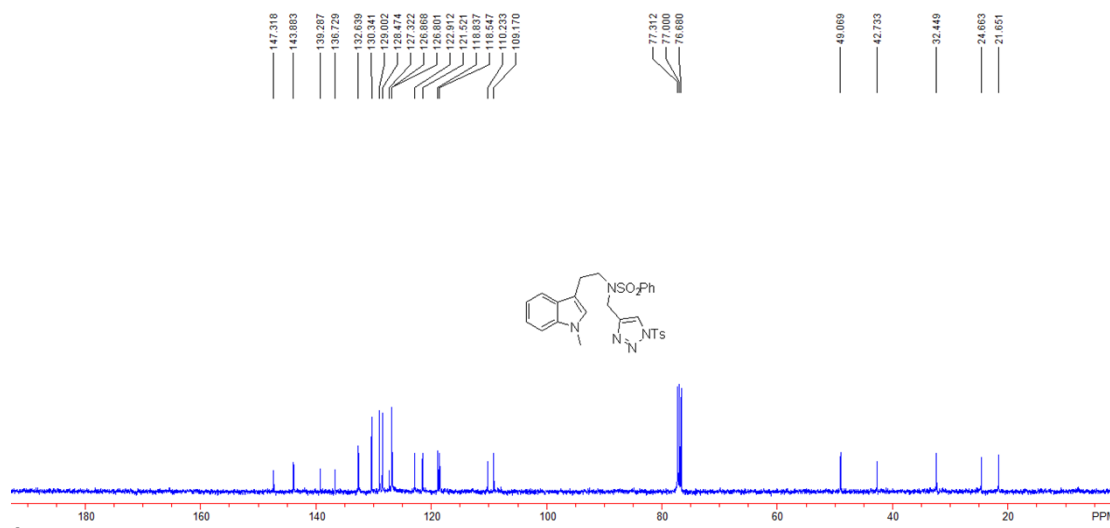




**N-(2-(1-methyl-1H-indol-3-yl)ethyl)-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 1m**

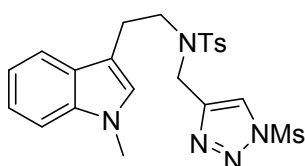
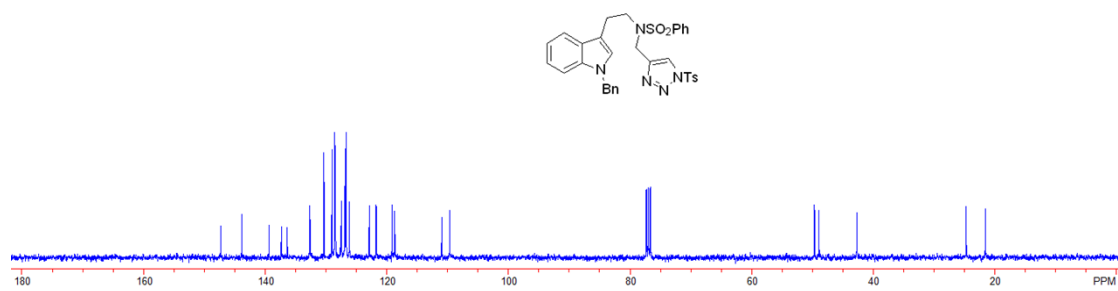
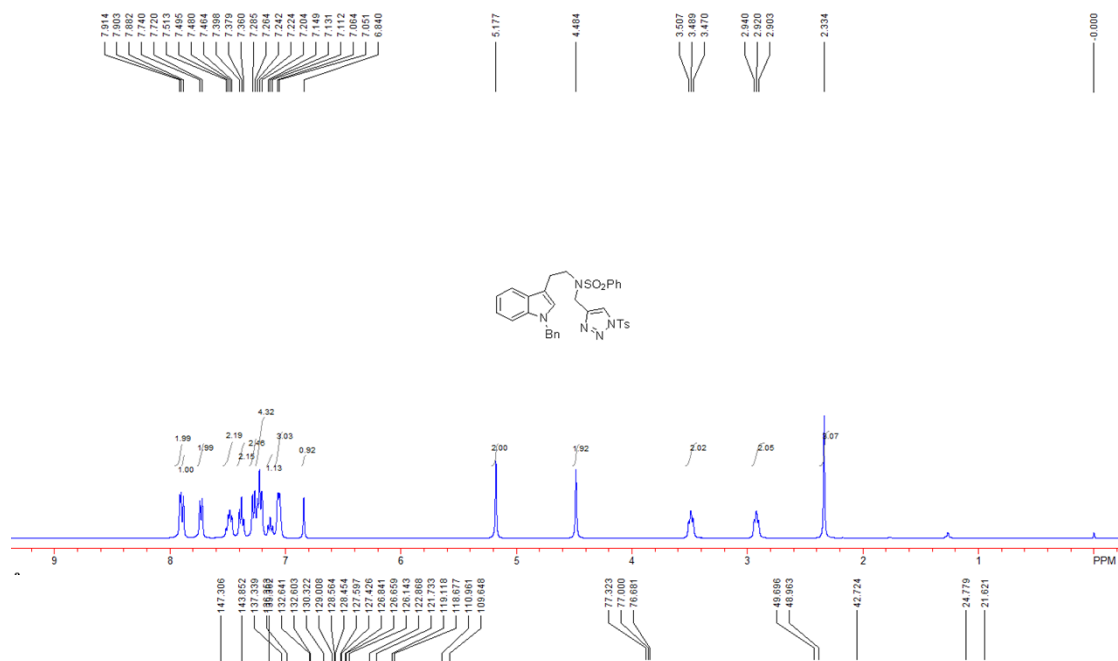
5.0 mmol scale, 2.20 g, a white solid, 80% yield. m.p.: 93-95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.36 (s, 3H, CH<sub>3</sub>), 2.91 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.46 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.66 (s, 3H, CH<sub>3</sub>), 4.50 (s, 2H, CH<sub>2</sub>), 6.76 (s, 1H, CH=), 7.06 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.19 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 2H, Ar), 7.23 (d, *J* = 7.6 Hz, 1H, Ar), 7.30 (d, *J* = 8.0 Hz, 2H, Ar), 7.38-7.46 (m, 3H, Ar), 7.52 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.73 (d, *J* = 8.0 Hz, 2H, Ar), 7.89 (d, *J* = 8.0 Hz, 2H, Ar), 7.91 (s, 1H, CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.6, 24.7, 32.4, 42.7, 49.1, 109.2, 110.2, 118.5, 118.8, 121.5, 122.9, 126.8, 126.9, 127.3, 128.5, 129.0, 130.3, 132.6, 136.7, 139.3, 143.9, 147.3. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3145, 2931, 1702, 1590, 1445, 1391, 1327, 1194, 1178, 1155, 1090, 1010, 972, 700, 688, 666 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>27</sub>H<sub>28</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 550.1577, found: 550.1578.





**N-(2-(1-benzyl-1H-indol-3-yl)ethyl)-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 1n**

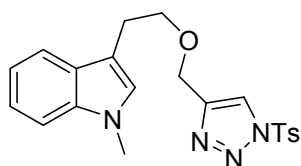
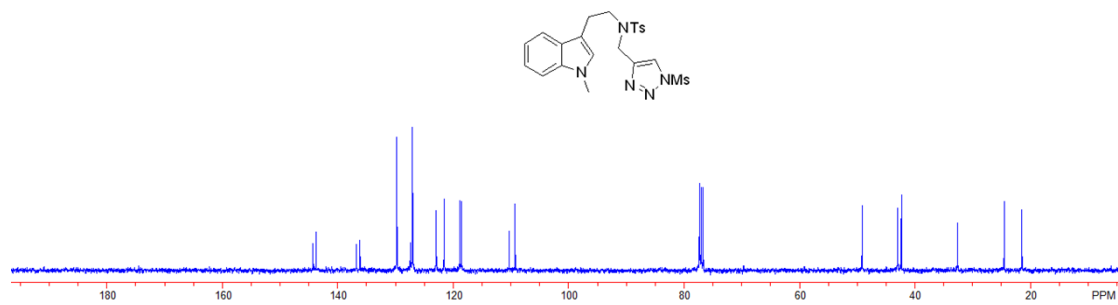
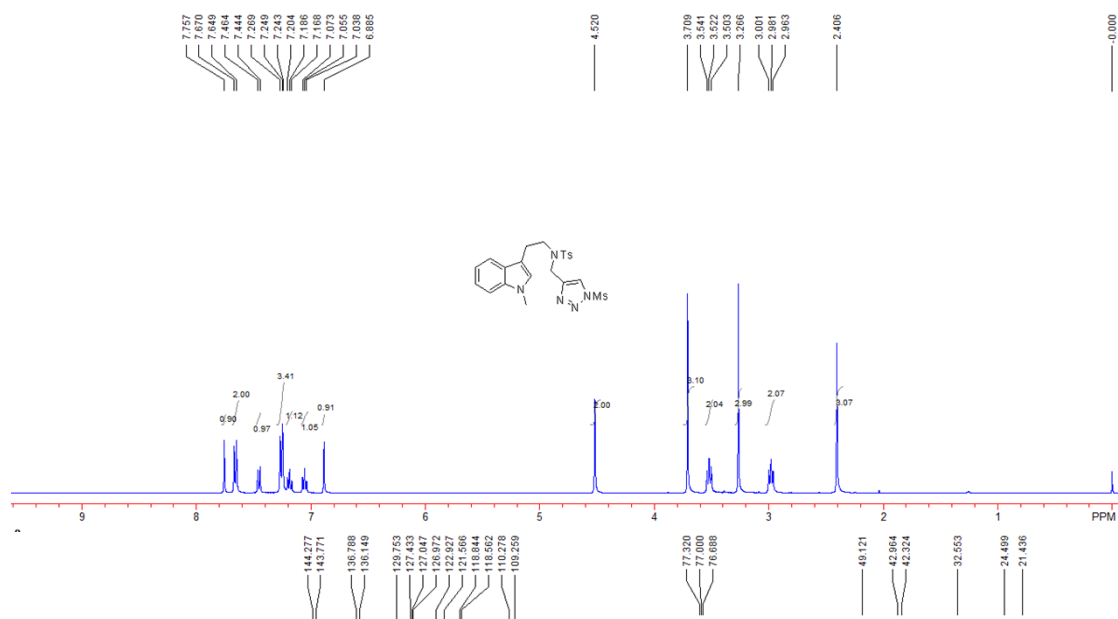
5.0 mmol scale, 2.75 g, a white solid, 88% yield. m.p.: 80-82 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.33 (s, 3H, CH<sub>3</sub>), 2.92 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.49 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 4.48 (s, 2H, CH<sub>2</sub>), 5.18 (s, 2H, CH<sub>2</sub>), 6.84 (s, 1H, CH=), 7.06 (d, *J* = 5.2 Hz, 3H, Ar), 7.13 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.22 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 4H, Ar), 7.27 (d, *J* = 8.4 Hz, 2H, Ar), 7.38 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 2H, Ar), 7.46-7.52 (m, 2H, Ar), 7.73 (d, *J* = 8.4 Hz, 2H, Ar), 7.89 (d, *J* = 8.4 Hz, 2H, Ar), 7.91 (s, 1H, CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.6, 24.8, 42.7, 49.0, 49.7, 109.6, 111.0, 118.7, 119.1, 121.7, 122.9, 126.1, 126.6, 126.8, 127.4, 127.6, 128.4, 128.6, 129.0, 130.3, 132.60, 132.64, 136.4, 137.3, 139.4, 143.8, 147.3. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3153, 3056, 2919, 1590, 1446, 1392, 1194, 1177, 1155, 1090, 1011, 972, 812, 737, 690, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>33</sub>H<sub>32</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 626.1890, found: 626.1887.



**4-methyl-N-(2-(1-methyl-1H-indol-3-yl)ethyl)-N-((1-(methylsulfonyl)-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 10**

5.0 mmol scale, 1.95 g, a white solid, 80% yield. m.p.: 109-110 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.41 (s, 3H, CH<sub>3</sub>), 2.98 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.27 (s, 3H, CH<sub>3</sub>), 3.52 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.71 (s, 3H, CH<sub>3</sub>), 4.52 (s, 2H, CH<sub>2</sub>), 6.88 (s, 1H, CH=), 7.06 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H, Ar), 7.19 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H, Ar), 7.24-7.27 (m, 3H, Ar), 7.46 (d, *J* = 8.0 Hz, 1H, Ar), 7.66 (d, *J* = 8.0 Hz, 2H, Ar), 7.76 (s, 1H, CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.3, 24.5, 32.6, 42.3, 43.0, 49.1, 109.2, 110.3, 118.6, 118.8, 121.6, 122.9, 126.9, 127.0, 127.4,

129.7, 136.1, 136.8, 143.8, 144.3. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  3144, 3023, 2926, 1721, 1596, 1474, 1375, 1326, 1182, 1153, 1091, 1012, 984, 951, 814, 769, 736, 687, 668 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>22</sub>H<sub>26</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 488.1421, found: 488.1419.

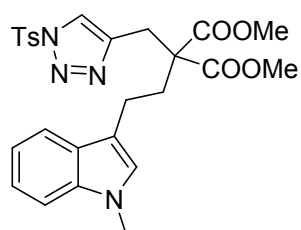
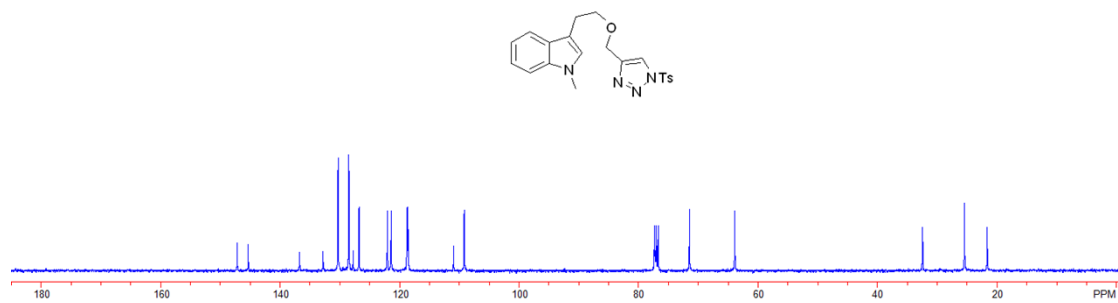
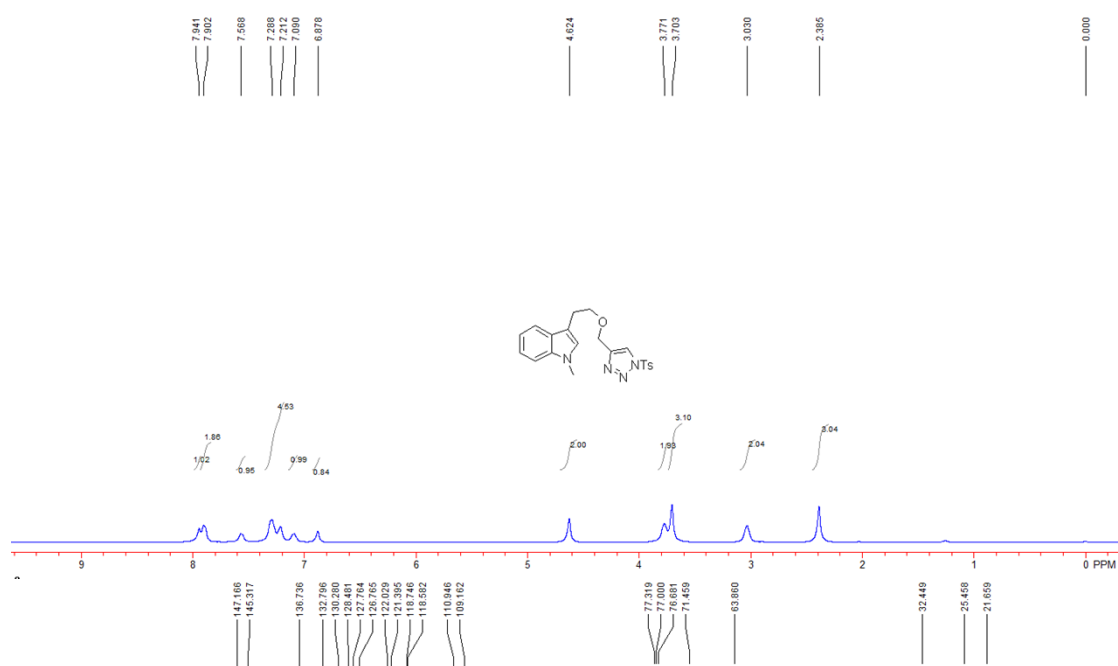


### 1-Methyl-3-(2-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)ethyl)-1H-indole **1p**

5.0 mmol scale, 1.89 g, a white solid, 92% yield. m.p.: 68-70 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  2.44 (s, 3H, CH<sub>3</sub>), 3.05 (t, *J* = 6.8 Hz, 2H, CH<sub>2</sub>), 3.75 (s, 3H, CH<sub>3</sub>), 3.79 (s, *J* = 6.8 Hz, 2H, CH<sub>2</sub>), 4.65 (s, 2H, CH<sub>2</sub>), 6.90 (s, 1H, Ar), 7.10 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H, Ar), 7.23 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H, Ar), 7.30 (d, *J* = 8.0 Hz, 1H, Ar), 7.35 (d, *J* = 8.0 Hz, 1H, Ar), 7.57 (d, *J* = 8.0 Hz, 1H, Ar), 7.93 (d, *J* = 8.0 Hz, 2H, Ar), 7.76 (s, 1H, CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  21.6, 25.4, 32.4, 63.9, 71.4, 109.2, 110.9, 118.6, 118.7, 121.4, 122.0, 126.8, 127.8,



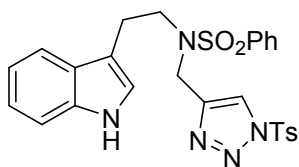
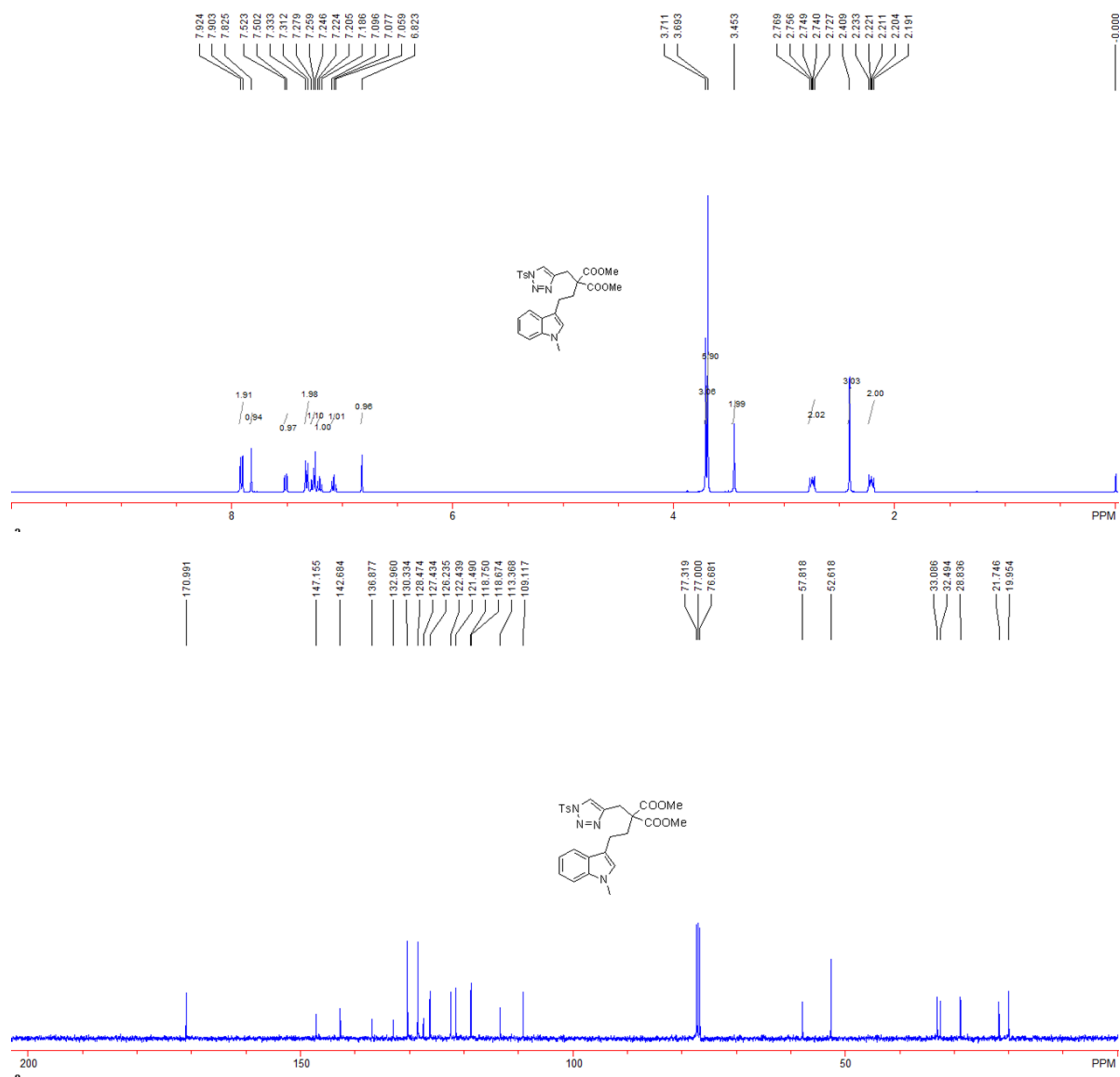
128.5, 130.3, 132.8, 136.7, 145.3, 147.2. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  3199, 3056, 2874, 1592, 1471, 1390, 1307, 1194, 1175, 1090, 1009, 964, 908, 733, 701, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>22</sub>H<sub>26</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 411.1485, found: 411.1484.



**Dimethyl 2-(2-(1-methyl-1H-indol-3-yl)ethyl)-2-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)malonate 1q**

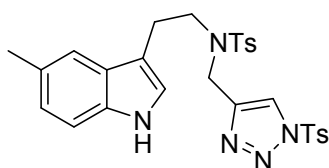
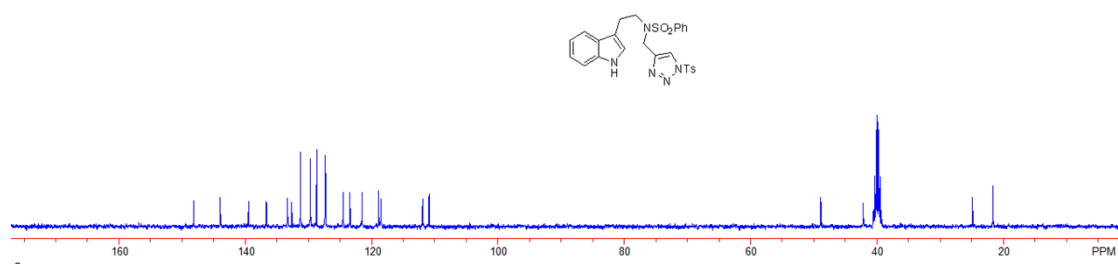
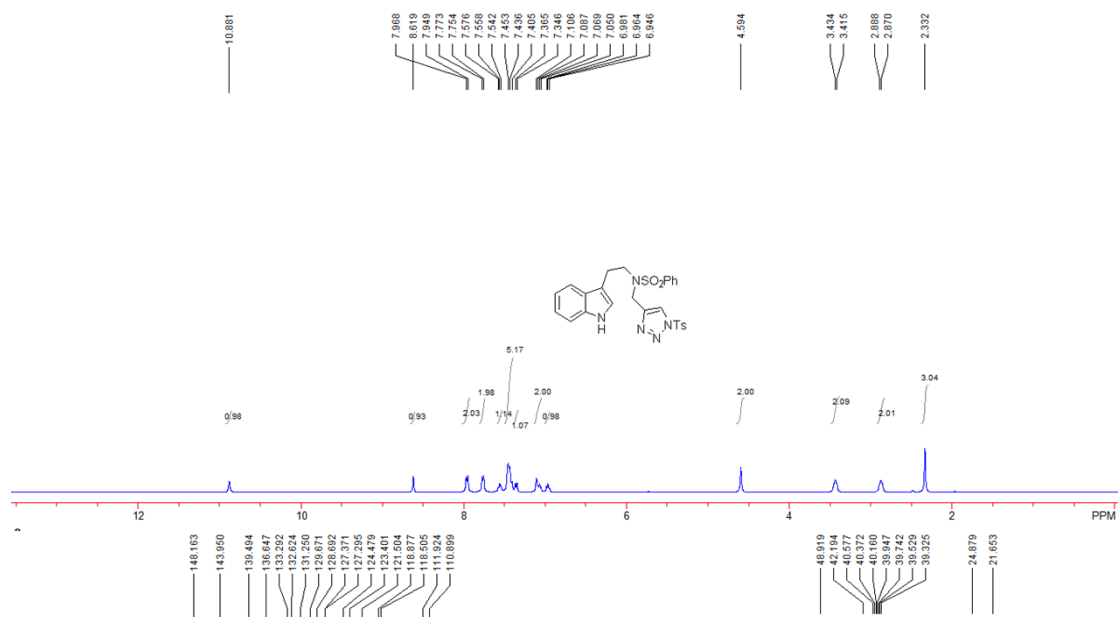
5.0 mmol scale, 2.07 g, a white solid, 79% yield. m.p.: 79-81 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  2.19-2.24 (m, 2H, CH<sub>2</sub>), 2.41 (s, 3H, CH<sub>3</sub>), 2.72-2.77 (m, 2H, CH<sub>2</sub>), 3.45 (s, 2H, CH<sub>2</sub>),

3.69 (s, 6H, CH<sub>3</sub>), 3.71 (s, 3H, CH<sub>3</sub>), 6.82 (s, 1H, Ar), 7.08 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.20 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.27 (d, *J* = 7.6 Hz, 1H, Ar), 7.32 (d, *J* = 8.4 Hz, 2H, Ar), 7.51 (d, *J* = 7.6 Hz, 1H, Ar), 7.82 (s, 1H, CH=), 7.91 (d, *J* = 8.4 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 19.9, 21.7, 28.8, 32.5, 33.1, 52.6, 57.8, 109.1, 113.4, 118.7, 118.8, 121.5, 122.4, 126.2, 127.4, 128.5, 130.3, 133.0, 136.9, 142.7, 147.2, 171.0. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3161, 2959, 1729, 1596, 1445, 1194, 1174, 1091, 1010, 968, 812, 740, 701, 669 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>26</sub>H<sub>29</sub>N<sub>4</sub>O<sub>6</sub>S<sup>+</sup> (M<sup>+</sup>+H) requires 525.1802, found: 525.1801.



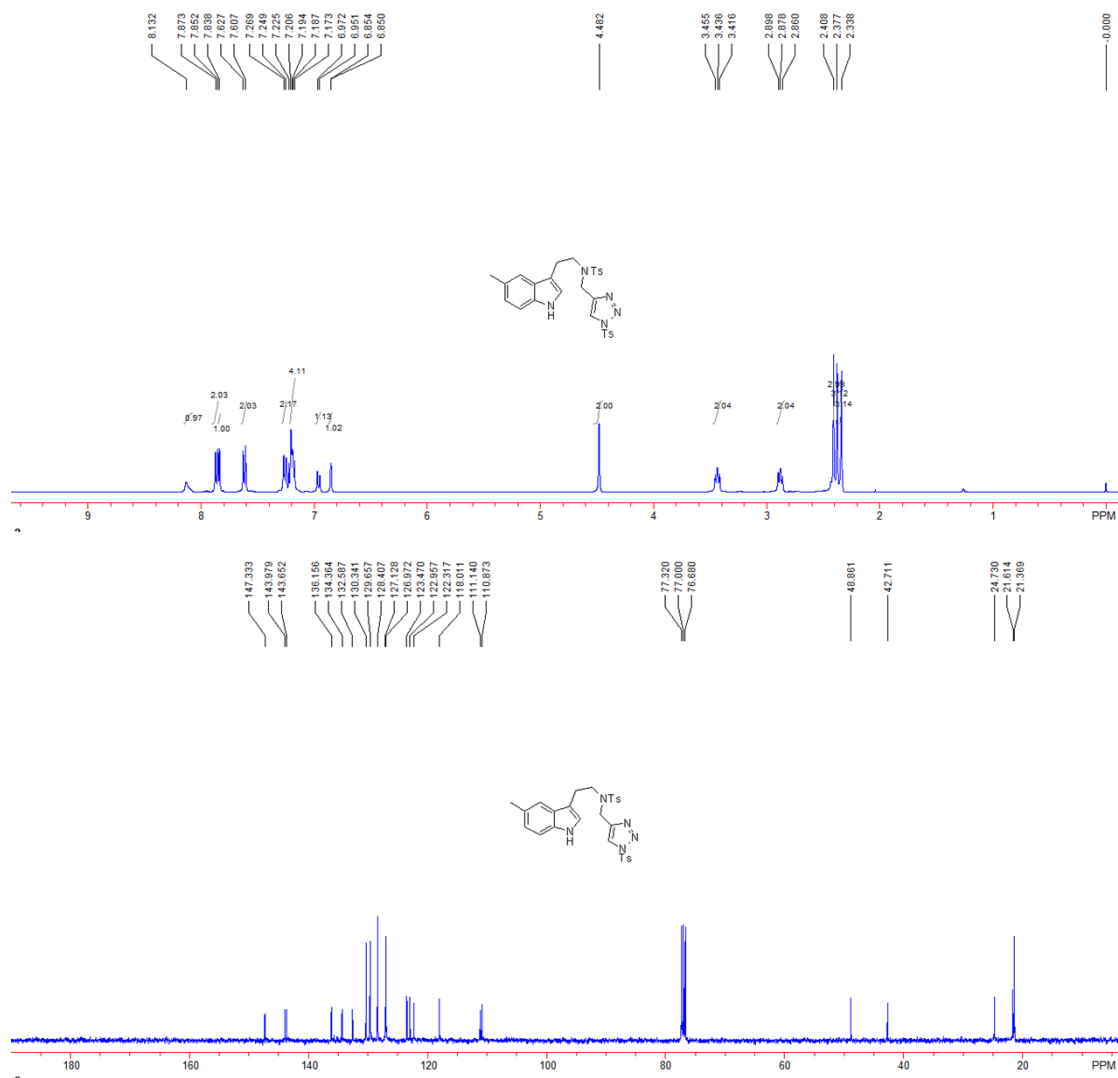
**N-(2-(1H-indol-3-yl)ethyl)-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 3a**

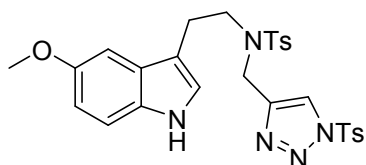
5.0 mmol scale, 2.42 g, a white solid, 88% yield. m.p.: 145-148 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, TMS) δ 2.33 (s, 3H, CH<sub>3</sub>), 2.87 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>), 3.42 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>), 4.59 (s, 2H, CH<sub>2</sub>), 6.96 (dd, *J* = 6.8 Hz, *J* = 6.8 Hz, 1H, Ar), 7.05-7.11 (m, 2H, Ar), 7.35 (d, *J* = 7.6 Hz, 1H, Ar), 7.40-7.46 (m, 5H, Ar), 7.56 (dd, *J* = 6.8 Hz, *J* = 6.8 Hz, 1H, Ar), 7.76 (d, *J* = 7.6 Hz, 2H, Ar), 7.96 (d, *J* = 7.6 Hz, 2H, Ar), 8.62 (s, 1H, CH=), 10.88 (s, 1H, NH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz, TMS) δ 21.6, 24.9, 42.2, 48.9, 110.9, 111.9, 118.5, 118.9, 121.5, 123.4, 124.4, 127.3, 127.4, 128.7, 129.7, 131.2, 132.6, 133.3, 136.6, 139.5, 143.9, 148.2. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3408, 3121, 1592, 1445, 1395, 1183, 1180, 1117, 1088, 977, 925, 818, 797, 752, 687, 668 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>26</sub>H<sub>26</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 536.1421, found: 536.1422.



**4-Methyl-N-(2-(5-methyl-1H-indol-3-yl)ethyl)-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 3b**

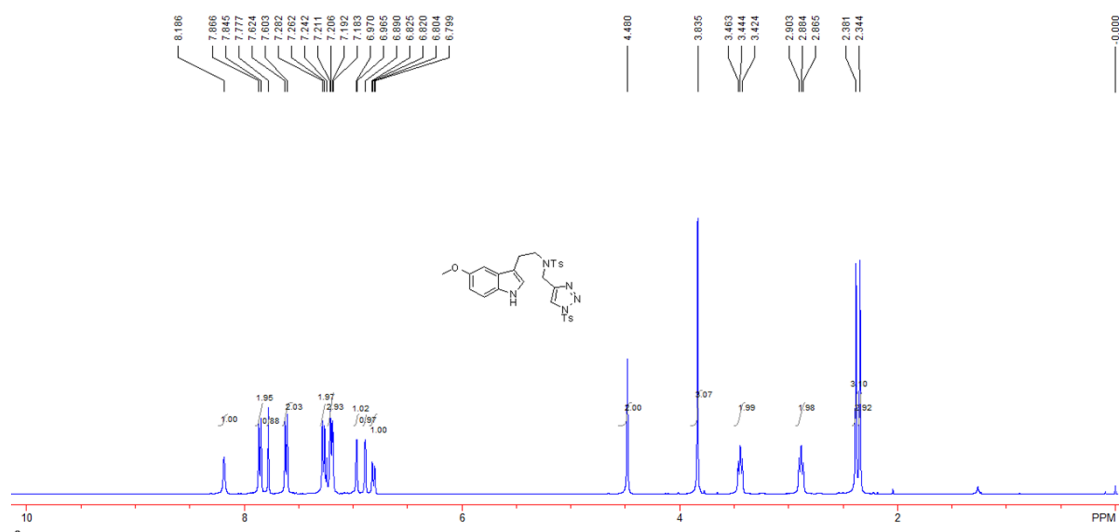
5.0 mmol scale, 2.6 g, a white solid, 92% yield. m.p.: 118-120 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.34 (s, 3H, CH<sub>3</sub>), 2.38 (s, 3H, CH<sub>3</sub>), 2.41 (s, 3H, CH<sub>3</sub>), 2.88 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.44 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 4.48 (s, 2H, CH<sub>2</sub>), 6.85 (d, 1H, *J* = 1.6 Hz, Ar), 6.96 (d, *J* = 8.0 Hz, 1H, Ar), 7.17-7.21 (m, 4H, Ar), 7.26 (d, *J* = 8.0 Hz, 2H, Ar), 7.62 (d, *J* = 8.0 Hz, 2H, Ar), 7.84 (s, 1H, CH=), 7.86 (d, *J* = 8.0 Hz, 2H, Ar), 8.13 (s, 1H, NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.4, 21.6, 24.7, 42.7, 48.9, 110.9, 111.1, 118.0, 122.3, 122.9, 123.5, 127.0, 127.1, 128.4, 129.6, 130.3, 132.6, 134.4, 136.2, 143.6, 144.0, 147.3. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3412, 2919, 2850, 1594, 1394, 1332, 1178, 1154, 1090, 1009, 975, 812, 798, 732, 668 cm<sup>-1</sup>. HRMS (MALDI) Calcd. for C<sub>28</sub>H<sub>30</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 564.1734, found: 564.1737.

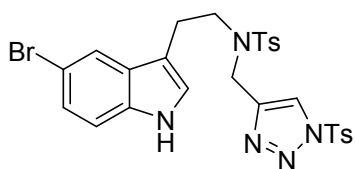
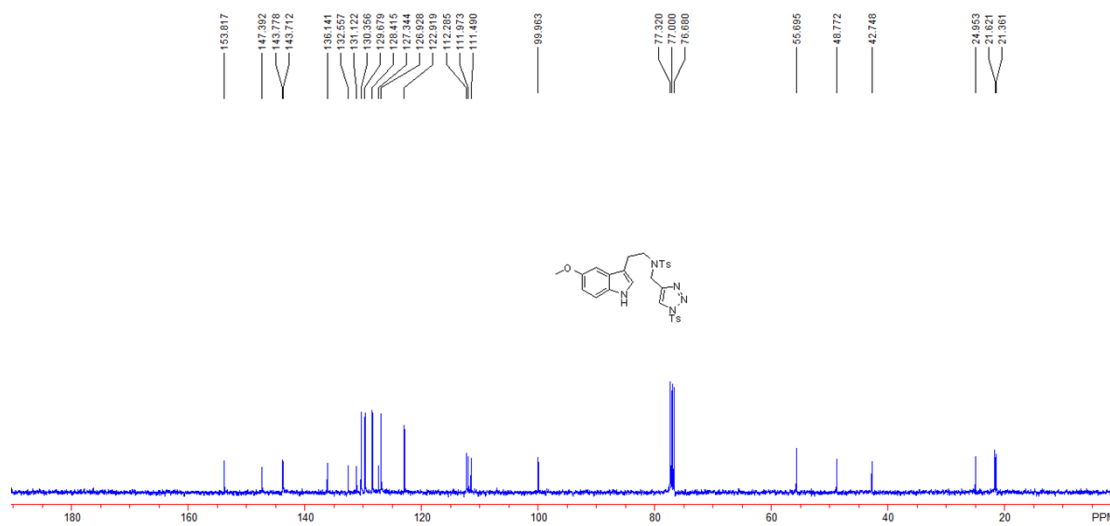




**N-(2-(5-methoxy-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 3c**

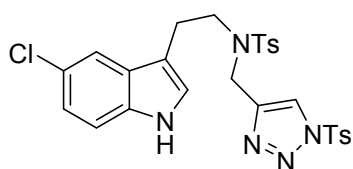
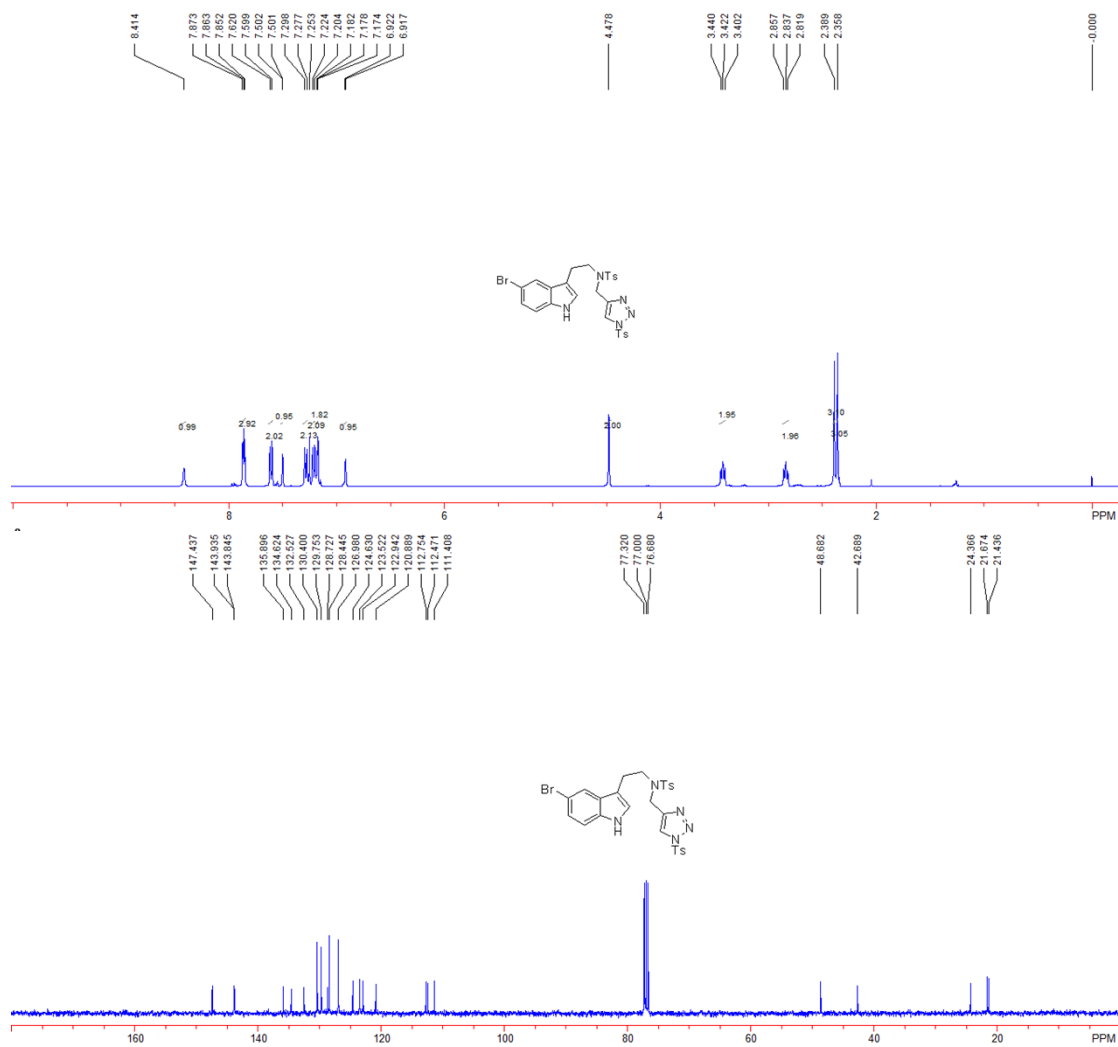
5.0 mmol scale, 2.20 g, a white solid, 77% yield. m.p.: 99-111 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  2.34 (s, 3H,  $\text{CH}_3$ ), 2.38 (s, 3H,  $\text{CH}_3$ ), 2.88 (t,  $J = 8.0$  Hz, 2H,  $\text{CH}_2$ ), 3.44 (t,  $J = 8.0$  Hz, 2H,  $\text{CH}_2$ ), 4.48 (s, 2H,  $\text{CH}_2$ ), 6.81 (dd,  $J = 8.4$  Hz,  $J = 2.0$  Hz, 1H, Ar), 6.89 (s, 1H, Ar), 6.97 (d,  $J = 2.0$  Hz, 1H, Ar), 7.18-7.23 (m, 3H, Ar), 7.27 (d,  $J = 8.0$  Hz, 2H, Ar), 7.61 (d,  $J = 8.4$  Hz, 2H, Ar), 7.78 (s, 1H, CH=), 7.85 (d,  $J = 8.4$  Hz, 2H, Ar), 8.19 (s, 1H, NH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  21.4, 21.6, 25.0, 42.7, 48.8, 55.7, 100.0, 111.5, 112.0, 112.3, 122.9, 126.9, 127.3, 128.4, 129.7, 130.4, 131.1, 132.6, 136.1, 143.7, 143.8, 147.4, 153.8. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu$  3421, 2923, 1593, 1554, 1393, 1331, 1194, 1178, 1154, 1090, 1011, 974, 911, 811, 700, 668  $\text{cm}^{-1}$ . HRMS (MALDI) Calcd. for  $\text{C}_{28}\text{H}_{30}\text{N}_5\text{O}_5\text{S}_2^+$  ( $\text{M}^++\text{H}$ ) requires 580.1683, found: 580.1685.





**N-(2-(5-bromo-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 3d**

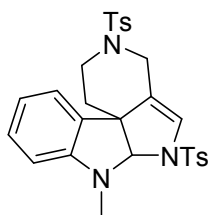
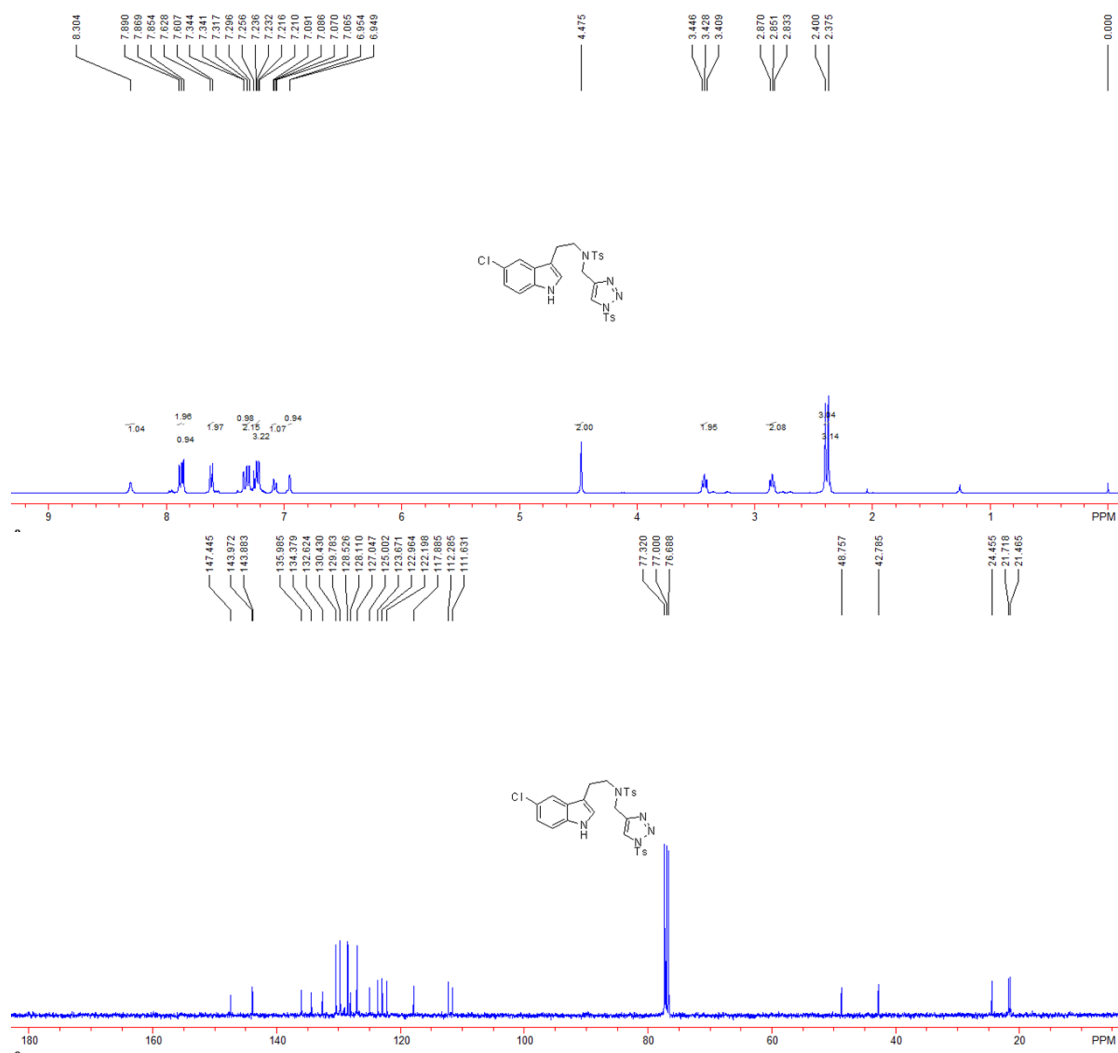
5.0 mmol scale, 2.35 g, a white solid, 75% yield. m.p.: 138-140 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.36 (s, 3H, CH<sub>3</sub>), 2.39 (s, 3H, CH<sub>3</sub>), 2.84 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 3.42 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 4.48 (s, 2H, CH<sub>2</sub>), 6.92 (d, *J* = 2.0 Hz, 1H, Ar), 7.17-7.19 (m, 2H, Ar), 7.21 (d, *J* = 8.0 Hz, 2H, Ar), 7.29 (d, *J* = 8.0 Hz, 2H, Ar), 7.50 (d, *J* = 0.4 Hz, 1H, Ar), 7.61 (d, *J* = 8.4 Hz, 2H, Ar), 7.862 (d, *J* = 8.4 Hz, 2H, Ar), 7.863 (s, 1H, CH=), 8.41 (s, 1H, NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.4, 21.7, 24.4, 42.7, 48.7, 111.4, 112.5, 112.8, 120.9, 122.9, 123.5, 124.6, 127.0, 128.4, 128.7, 129.8, 130.4, 132.5, 134.6, 135.9, 143.8, 143.9, 147.4. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3417, 2927, 1702, 1596, 1453, 1394, 1332, 1178, 1153, 1089, 1011, 975, 811, 700, 667 cm<sup>-1</sup>. HRMS (MALDI) Calcd. for C<sub>27</sub>H<sub>27</sub>BrN<sub>5</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 628.0682, found: 628.0681.



**N-(2-(5-chloro-1H-indol-3-yl)ethyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 3e**

5.0 mmol scale, 2.24 g, a white solid, 77% yield. m.p.: 133-135 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.38 (s, 3H, CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 2.85 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>), 3.43 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>), 4.48 (s, 2H, CH<sub>2</sub>), 6.95 (d, *J* = 2.0 Hz, 1H, Ar), 7.08 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H, Ar), 7.21-7.24 (m, 3H, Ar), 7.31 (d, *J* = 8.4 Hz, 2H, Ar), 7.34 (d, *J* = 2.0 Hz, 1H, Ar), 7.62 (d, *J* = 8.4 Hz, 2H, Ar), 7.85 (s, 1H, CH=), 7.88 (d, *J* = 8.4 Hz, 2H, Ar), 8.30 (s, 1H, NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.5, 21.7, 24.4, 42.8, 48.8, 111.6, 112.3, 117.9, 122.2, 123.0, 123.7, 125.0, 127.0, 128.1, 128.5, 129.8, 130.4, 132.6, 134.4, 136.0, 143.9, 144.0, 147.4. IR (CH<sub>2</sub>Cl<sub>2</sub>) v

3421, 2923, 1716, 1593, 1461, 1379, 1333, 1178, 1156, 1092, 990, 971, 912, 802, 754, 702, 668  $\text{cm}^{-1}$ . HRMS (MALDI) Calcd. for  $\text{C}_{27}\text{H}_{27}\text{ClN}_5\text{O}_4\text{S}_2^+$  ( $\text{M}^++\text{H}$ ) requires 584.1187, found: 584.1188.

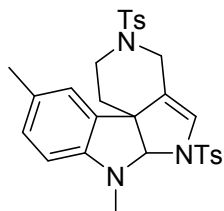
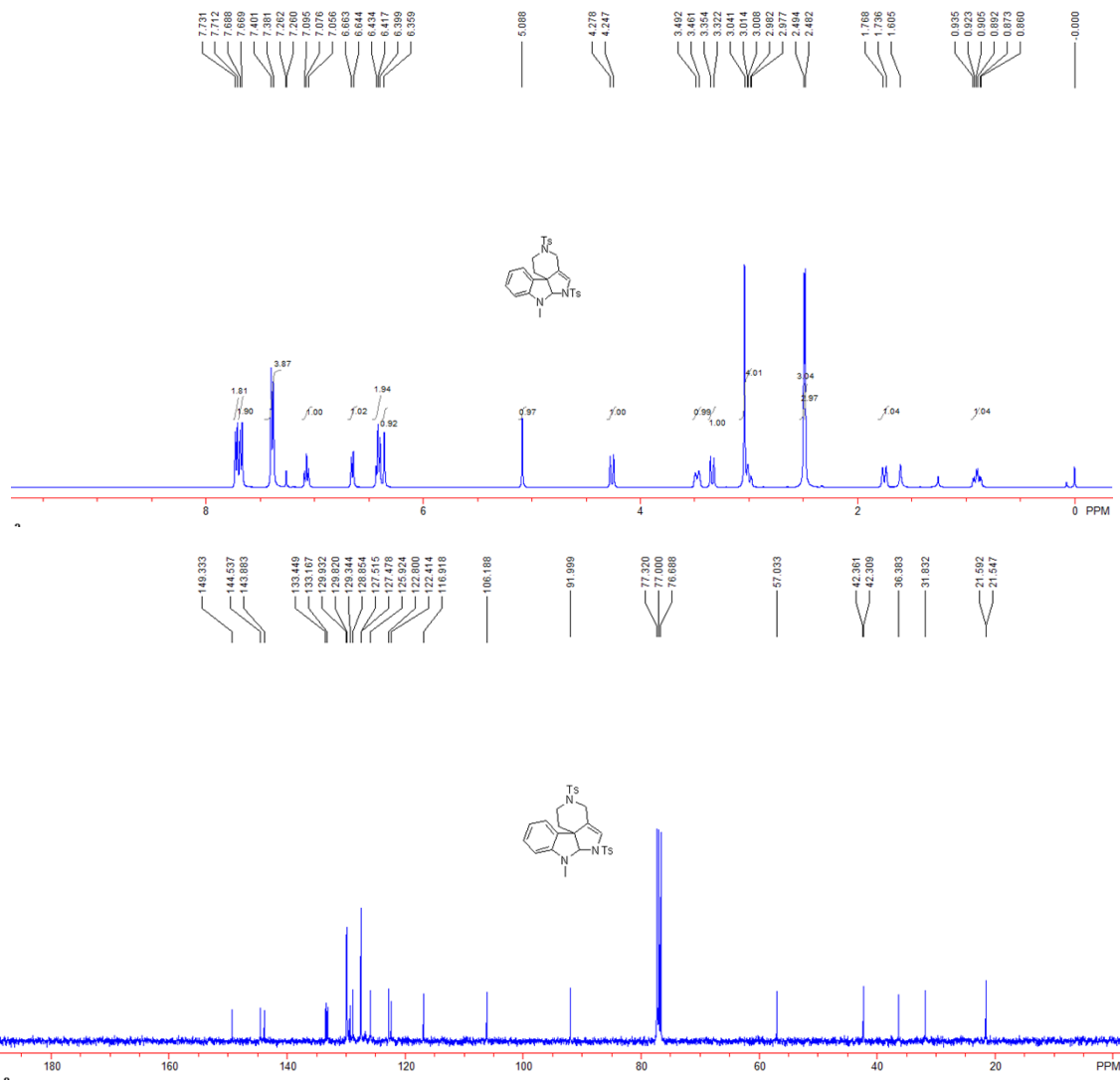


### 7-Methyl-3,6-ditosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2a

0.2 mmol scale, 82 mg, a white solid, 77% yield. m.p.: 152-154 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 0.90 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 5.2 Hz, 1H, CH<sub>2</sub>), 1.75 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 2.48 (s, 3H, CH<sub>3</sub>), 2.49 (s, 3H, CH<sub>3</sub>), 2.97-3.05 (m, 4H), 3.33 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 3.48 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 4.26 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 5.09 (s, 1H, CH), 6.36 (s, 1H), 6.42 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 2H, Ar), 6.65 (d, *J* = 7.6 Hz, 1H, Ar), 7.08 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.39 (d, *J* = 8.0 Hz, 4H, Ar), 7.68 (d, *J* = 8.0 Hz, 2H, Ar), 7.72 (d, *J* = 8.0 Hz,

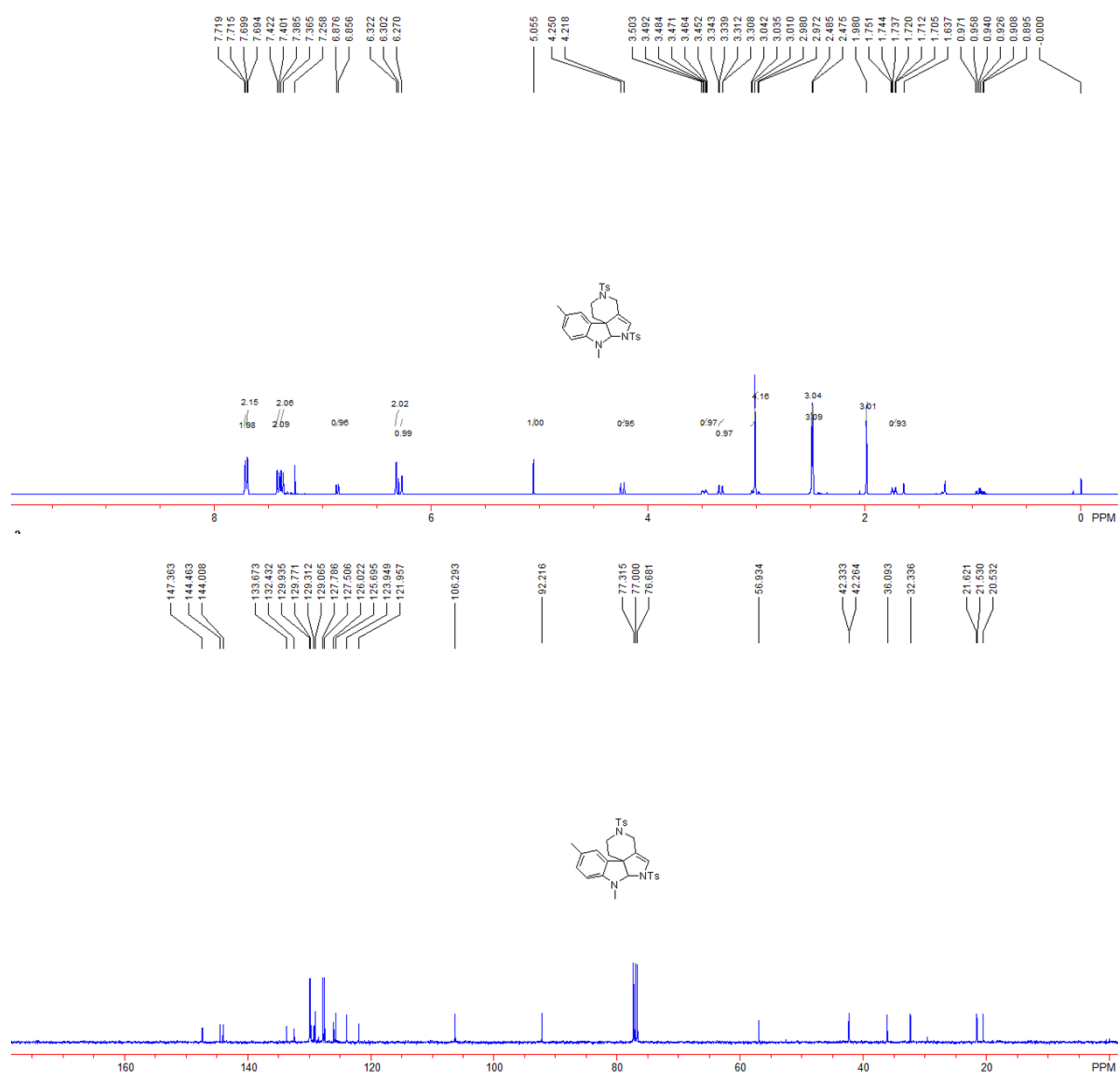


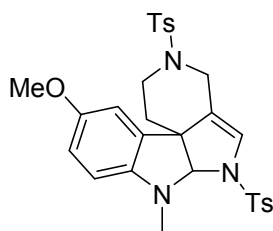
2H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  21.5, 21.6, 31.8, 36.4, 42.3, 42.4, 57.1, 92.0, 106.2, 116.9, 122.4, 122.8, 126.0, 127.50, 127.54, 128.9, 129.4, 129.8, 130.0, 133.2, 133.5, 143.9, 144.6, 149.4. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu$  3132, 2922, 1699, 1595, 1451, 1385, 1330, 1247, 1194, 1179, 1155, 1091, 1011, 974, 812, 748, 701, 666  $\text{cm}^{-1}$ . HRMS (ESI) Calcd. for  $\text{C}_{28}\text{H}_{30}\text{N}_3\text{O}_4\text{S}_2^+$  ( $\text{M}^+\text{H}$ ) requires 536.1672, found: 536.1670.



**7,10-Dimethyl-3,6-ditosyl-2,3,4,4a,5,6,6a,7-octahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2b**

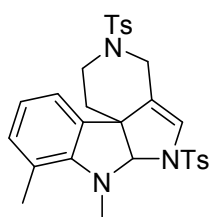
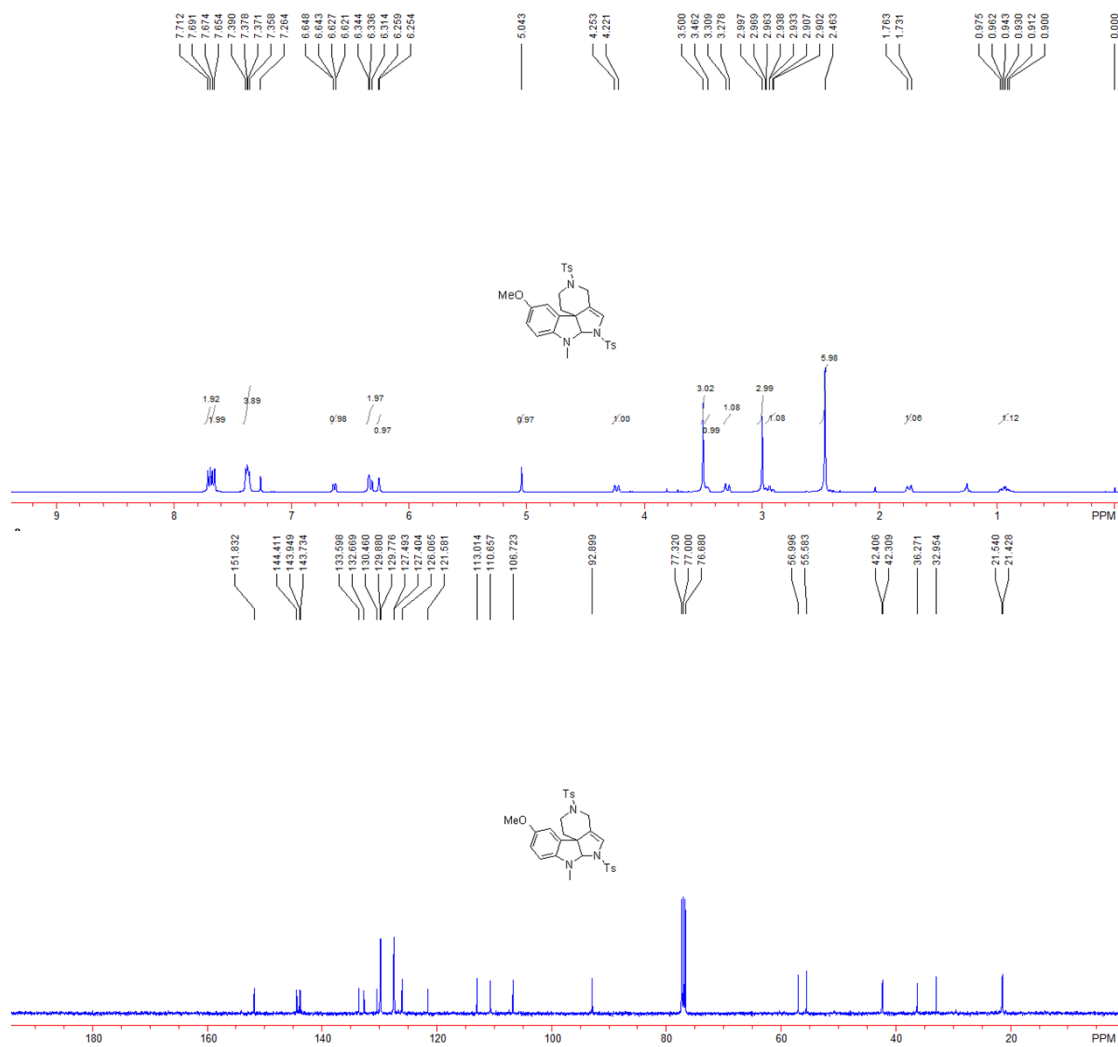
0.2 mmol scale, 78 mg, a white solid, 71% yield. m.p.: 161-163 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 0.93 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 5.2 Hz, 1H, CH<sub>2</sub>), 1.73 (ddd, *J* = 12.8 Hz, *J* = 2.8 Hz, *J* = 2.8 Hz, 1H, CH<sub>2</sub>), 1.98 (s, 3H, CH<sub>3</sub>), 2.47 (s, 3H, CH<sub>3</sub>), 2.48 (s, 3H, CH<sub>3</sub>), 2.97-3.05 (m, 4H), 3.33 (dd, *J* = 12.8 Hz, *J* = 1.6 Hz, 1H, CH<sub>2</sub>), 3.48 (ddd, *J* = 12.8 Hz, *J* = 2.8 Hz, *J* = 2.8 Hz, 1H, CH<sub>2</sub>), 4.23 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 5.06 (s, 1H, CH), 6.27 (s, 1H), 6.31 (d, *J* = 8.0 Hz, 2H, Ar), 6.87 (d, *J* = 8.0 Hz, 1H, Ar), 7.38 (d, *J* = 8.0 Hz, 2H, Ar), 7.41 (d, *J* = 8.0 Hz, 2H, Ar), 7.70 (d, *J* = 8.0 Hz, 2H, Ar), 7.71 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 20.5, 21.5, 21.6, 32.3, 36.1, 42.26, 42.33, 56.9, 92.2, 106.3, 121.9, 123.9, 125.7, 126.0, 127.5, 127.8, 129.1, 129.3, 129.8, 129.9, 132.4, 133.7, 144.0, 144.5, 147.4. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 2919, 2846, 1678, 1597, 1455, 1352, 1306, 1290, 1162, 1118, 1089, 920, 863, 767, 681, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>29</sub>H<sub>32</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 550.1829, found: 550.1821.





**10-methoxy-7-methyl-3,6-ditosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2c**

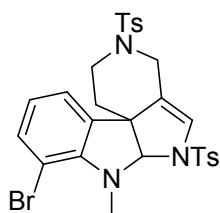
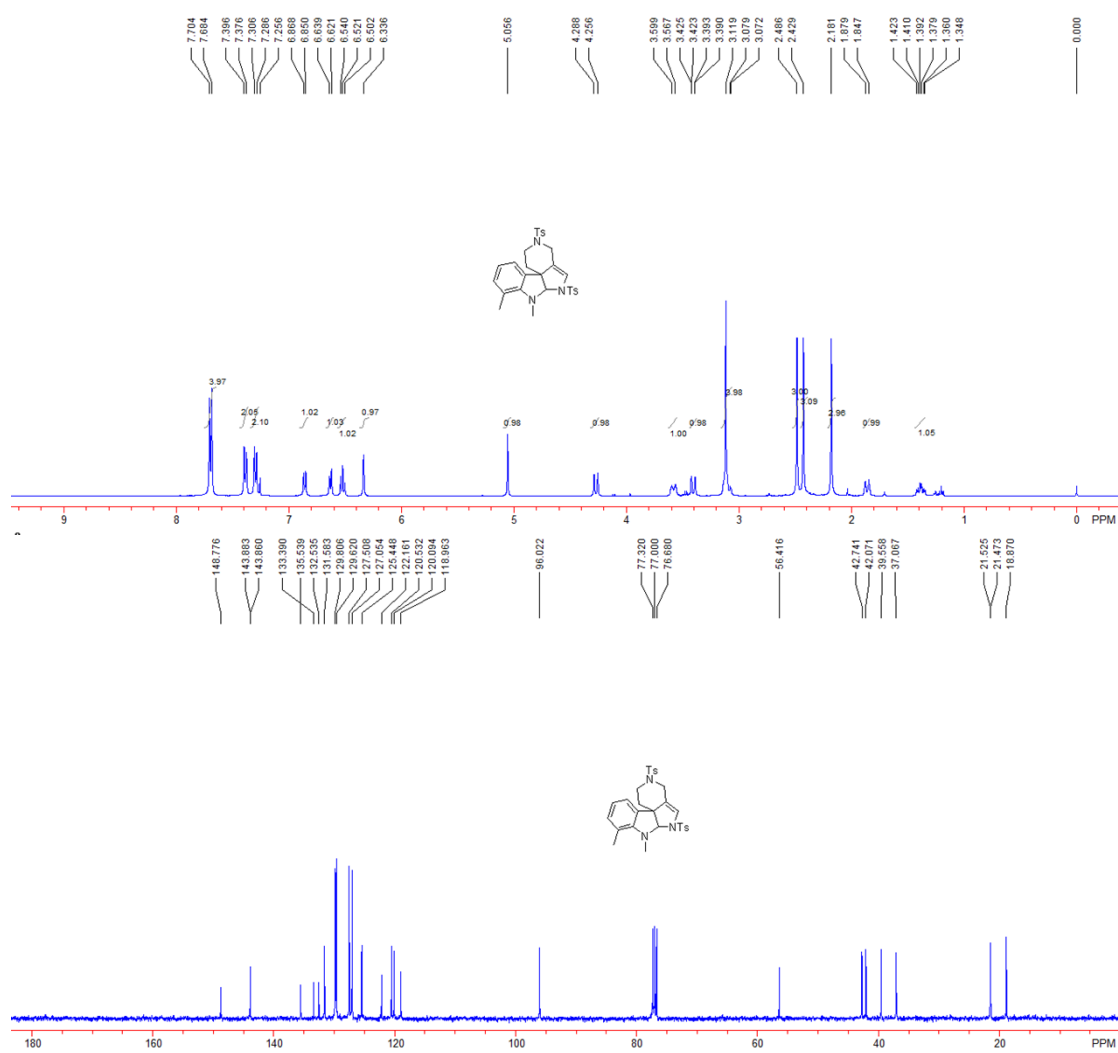
0.2 mmol scale, 88 mg, a white solid, 78% yield. m.p.: 119-121 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 0.94 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 4.8 Hz, 1H, CH<sub>2</sub>), 1.75 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 2.46 (s, 6H, CH<sub>3</sub>), 2.94 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 4.8 Hz, 1H, CH<sub>2</sub>), 3.00 (s, 3H, CH<sub>3</sub>), 3.29 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 3.48 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 3.50 (s, 3H, CH<sub>3</sub>), 4.24 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 5.04 (s, 1H, CH), 6.26 (d, 1H, *J* = 2.0 Hz), 6.31-6.35 (m, 2H, Ar), 6.63 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H, Ar), 7.35-7.39 (m, 4H, Ar), 7.66 (d, *J* = 8.0 Hz, 2H, Ar), 7.70 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.4, 21.5, 32.9, 36.3, 42.3, 42.4, 55.6, 57.0, 92.9, 106.7, 110.6, 113.0, 121.6, 126.1, 127.4, 127.5, 129.8, 129.9, 130.5, 132.7, 133.6, 143.7, 143.9, 144.4, 151.8. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 2923, 2829, 1677, 1596, 1497, 1453, 1348, 1284, 1216, 1162, 1088, 998, 919, 813, 706, 667, 656 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>29</sub>H<sub>32</sub>N<sub>3</sub>O<sub>5</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 566.1778, found: 566.1775.



**7,8-dimethyl-3,6-ditosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2d**

0.2 mmol scale, 91 mg, a white solid, 83% yield. m.p.: 155-157 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 1.38 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 5.2 Hz, 1H, CH<sub>2</sub>), 1.86 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 2.18 (s, 3H, CH<sub>3</sub>), 2.43 (s, 3H, CH<sub>3</sub>), 2.49 (s, 3H, CH<sub>3</sub>), 3.07-3.12 (m, 4H), 3.41 (dd, *J* = 12.8 Hz, *J* = 1.2 Hz, 1H, CH<sub>2</sub>), 3.58 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 4.27 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 5.06 (s, 1H, CH), 6.34 (s, 1H), 6.52 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H, Ar), 6.63 (d, *J* = 7.2 Hz, 1H, Ar), 6.86 (d, *J* = 7.2 Hz, 1H, Ar), 7.30 (d, *J* = 8.0 Hz, 2H, Ar), 7.39 (d, *J* = 8.0 Hz, 2H, Ar), 7.69 (d, *J* = 8.0 Hz, 4H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 18.9, 21.47, 21.52, 37.1, 39.6, 42.1, 42.7, 56.4, 96.0, 119.0, 120.1, 120.5, 122.2, 125.4, 127.0, 127.5, 129.6, 129.8, 131.6, 132.5,

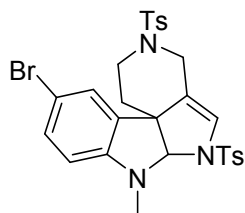
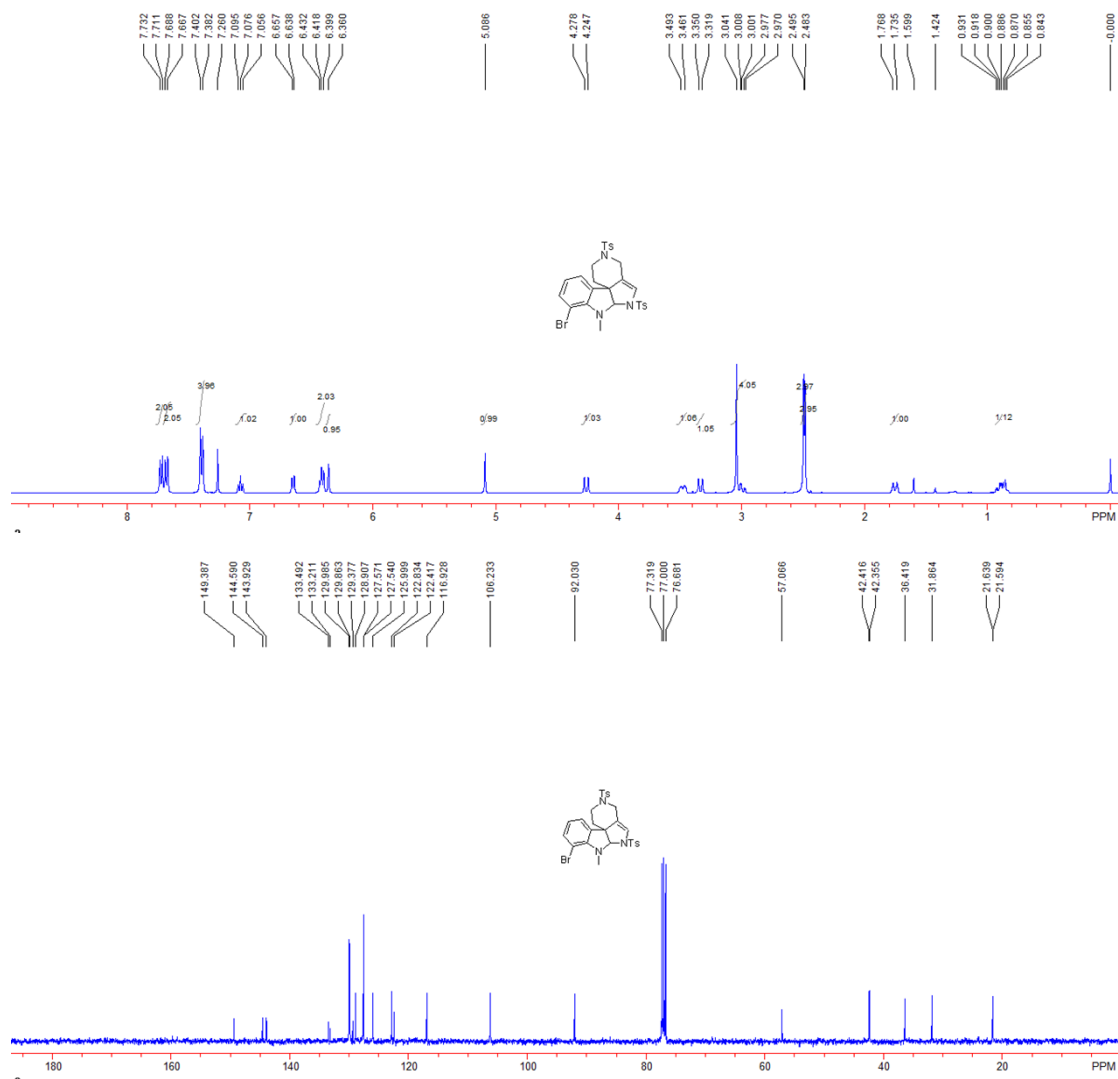
133.4, 135.5, 143.86, 143.88, 148.8. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  2923, 2850, 1665, 1594, 1472, 1348, 1299, 1159, 998, 956, 928, 815, 748, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>29</sub>H<sub>32</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 550.1829, found: 550.1826.



### 8-bromo-7-methyl-3,6-ditosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2e

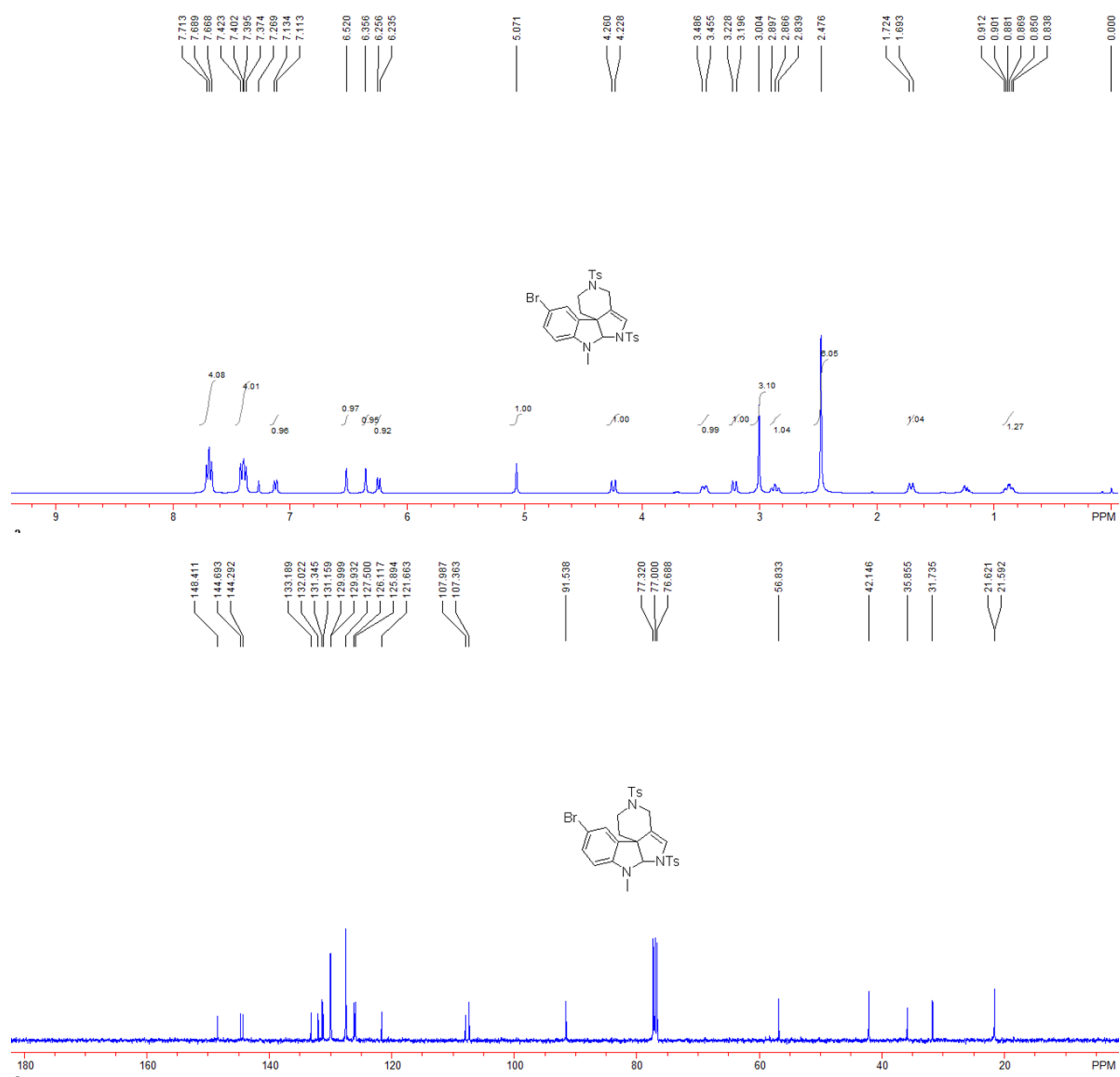
0.2 mmol scale, 89 mg, a white solid, 73% yield. m.p.: 189-191 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  0.89 (ddd,  $J = 12.8$  Hz,  $J = 12.8$  Hz,  $J = 5.2$  Hz, 1H, CH<sub>2</sub>), 1.75 (d,  $J = 12.8$  Hz, 1H, CH<sub>2</sub>), 2.48 (s, 3H, CH<sub>3</sub>), 2.50 (s, 3H, CH<sub>3</sub>), 2.97-3.06 (m, 4H), 3.33 (d,  $J = 12.8$  Hz, 1H, CH<sub>2</sub>), 3.48 (d,  $J = 12.8$  Hz, 1H, CH<sub>2</sub>), 4.26 (d,  $J = 12.8$  Hz, 1H, CH<sub>2</sub>), 5.09 (s, 1H, CH), 6.36 (s, 1H),

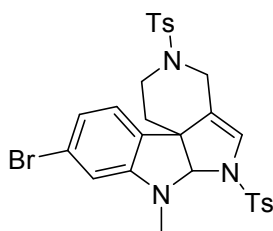
6.39-6.44 (m, 2H, Ar), 6.65 (d,  $J = 7.6$  Hz, 1H, Ar), 7.08 (dd,  $J = 7.6$  Hz,  $J = 7.6$  Hz, 1H, Ar), 7.39 (d,  $J = 8.4$  Hz, 4H, Ar), 7.68 (d,  $J = 8.4$  Hz, 2H, Ar), 7.72 (d,  $J = 8.4$  Hz, 2H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  21.59, 21.64, 31.9, 36.4, 42.3, 42.4, 57.1, 92.0, 106.2, 116.9, 122.4, 122.8, 126.0, 127.5, 127.6, 128.9, 129.4, 129.9, 130.0, 133.2, 133.5, 143.9, 144.6, 149.4. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu$  3068, 2906, 1661, 1598, 1494, 1430, 1342, 1303, 1159, 1089, 1011, 994, 911, 817, 751, 707, 669  $\text{cm}^{-1}$ . HRMS (ESI) Calcd. for  $\text{C}_{28}\text{H}_{29}\text{BrN}_3\text{O}_4\text{S}_2^+$  ( $\text{M}^++\text{H}$ ) requires 614.0777, found: 614.0773.



**10-bromo-7-methyl-3,6-ditosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2f**

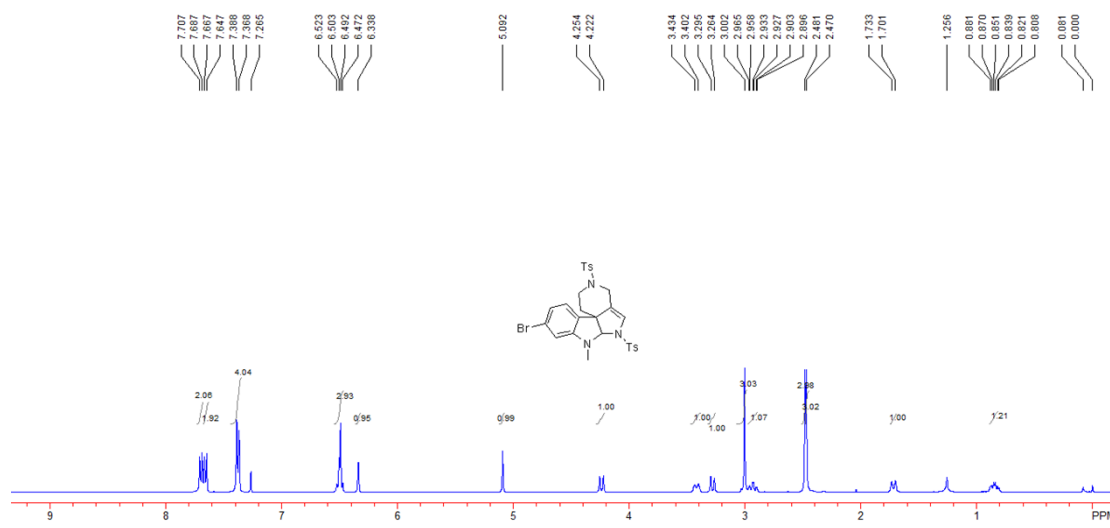
0.2 mmol scale, 97 mg, a white solid, 79% yield. m.p.: 150-152 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  0.87 (ddd,  $J = 12.4$  Hz,  $J = 12.4$  Hz,  $J = 4.8$  Hz, 1H,  $\text{CH}_2$ ), 1.71 (d,  $J = 12.8$  Hz, 1H,  $\text{CH}_2$ ), 2.48 (s, 6H,  $\text{CH}_3$ ), 2.87 (dd,  $J = 12.4$  Hz,  $J = 12.4$  Hz, 1H,  $\text{CH}_2$ ), 3.00 (s, 3H,  $\text{CH}_3$ ), 3.21 (d,  $J = 12.8$  Hz, 1H,  $\text{CH}_2$ ), 3.47 (d,  $J = 12.4$  Hz, 1H,  $\text{CH}_2$ ), 4.24 (d,  $J = 12.8$  Hz, 1H,  $\text{CH}_2$ ), 5.07 (s, 1H, CH), 6.24 (d,  $J = 8.4$  Hz, 1H, Ar), 6.36 (s, 1H), 6.52 (s, 1H, Ar), 7.12 (d,  $J = 8.4$  Hz, 1H, Ar), 7.37-7.43 (m, 4H, Ar), 7.69 (dd,  $J = 8.4$  Hz,  $J = 8.4$  Hz, 4H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  21.59, 21.62, 31.7, 35.8, 42.1, 56.8, 91.5, 107.4, 108.0, 121.7, 125.9, 126.1, 127.5, 129.9, 130.0, 131.2, 131.3, 132.0, 133.2, 144.3, 144.7, 148.4. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu$  3109, 2914, 2850, 1597, 1492, 1349, 1306, 1161, 1088, 996, 950, 906, 812, 765, 707, 669, 655  $\text{cm}^{-1}$ . HRMS (ESI) Calcd. for  $\text{C}_{28}\text{H}_{29}\text{BrN}_3\text{O}_4\text{S}_2^+$  ( $\text{M}^+\text{+H}$ ) requires 614.0777, found: 614.0774.



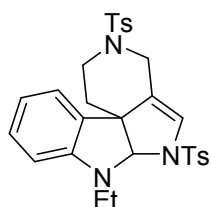
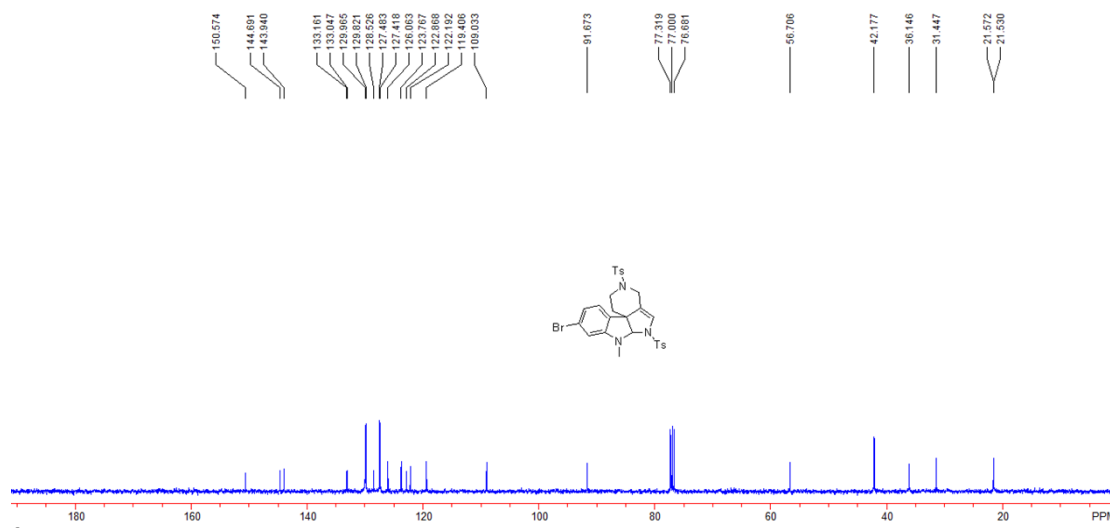


**9-bromo-7-methyl-3,6-ditosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2g**

0.2 mmol scale, 98 mg, a white solid, 80% yield. m.p.: 212-214 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 0.84 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 5.2 Hz, 1H, CH<sub>2</sub>), 1.72 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 2.47 (s, 3H, CH<sub>3</sub>), 2.48 (s, 3H, CH<sub>3</sub>), 2.93 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 2.8 Hz, 1H, CH<sub>2</sub>), 3.00 (s, 3H, CH<sub>3</sub>), 3.28 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 3.42 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 4.24 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 5.09 (s, 1H, CH), 6.34 (s, 1H), 6.47-6.53 (m, 3H, Ar), 7.38 (d, *J* = 8.0 Hz, 4H, Ar), 7.66 (d, *J* = 8.0 Hz, 2H, Ar), 7.70 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.5, 21.6, 31.4, 36.1, 42.2, 56.7, 91.7, 109.0, 119.4, 122.2, 122.9, 123.8, 126.1, 127.4, 127.5, 128.5, 129.8, 130.0, 133.0, 133.2, 143.9, 144.7, 150.6. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3101, 2939, 2846, 1686, 1596, 1495, 1438, 1414, 1352, 1305, 1161, 1090, 996, 901, 885, 800, 791, 756, 747, 707, 668, 658 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>28</sub>H<sub>29</sub>BrN<sub>3</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 614.0777, found: 614.0773.

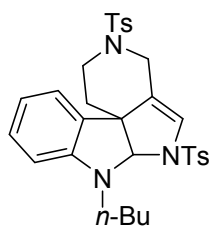
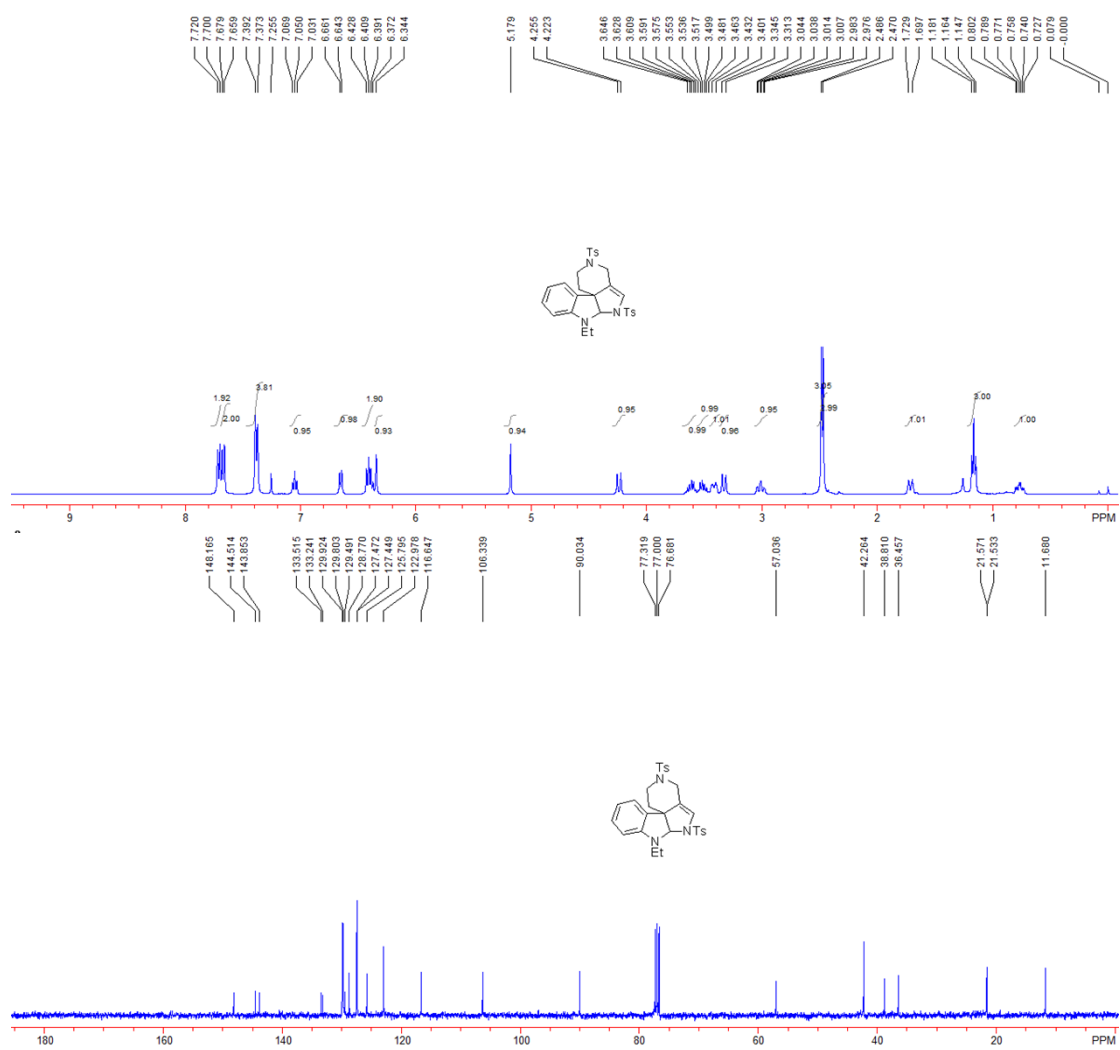






**9-bromo-7-methyl-3,6-ditosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2h**

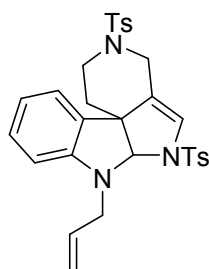
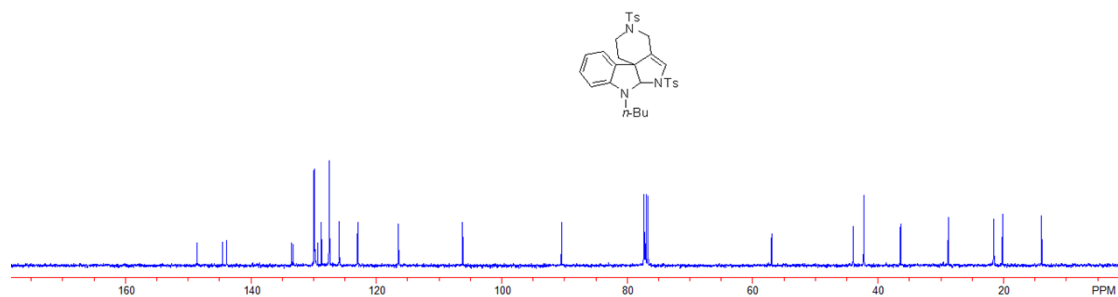
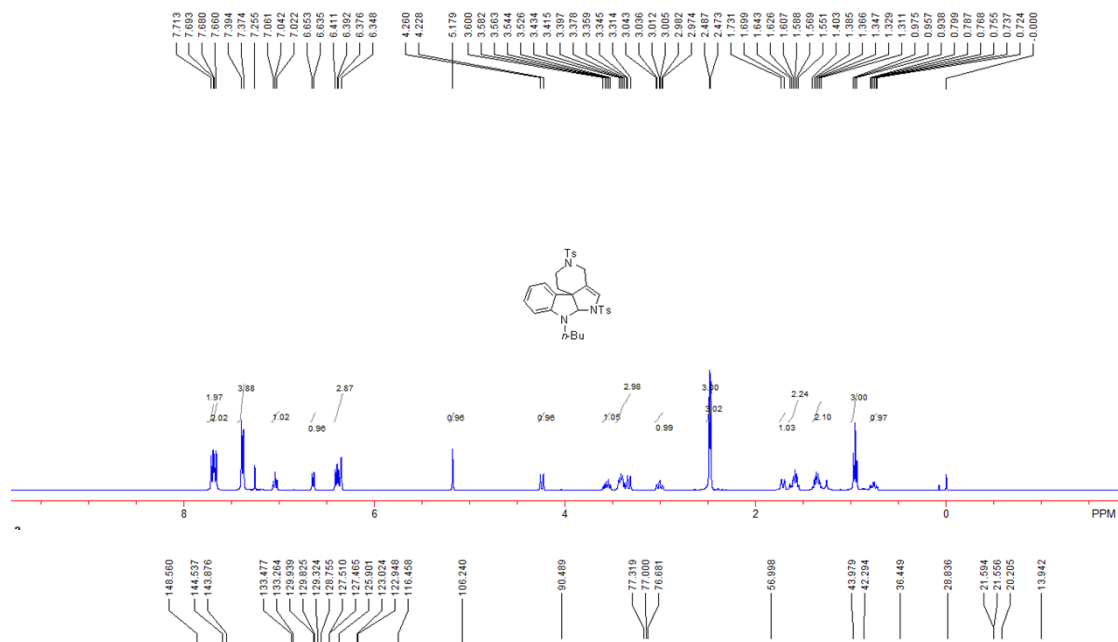
0.2 mmol scale, 76 mg, a white solid, 70% yield. m.p.: 135-137 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  0.76 (ddd,  $J = 12.8$  Hz,  $J = 12.8$  Hz,  $J = 5.2$  Hz, 1H,  $\text{CH}_2$ ), 1.16 (t,  $J = 6.8$  Hz, 3H,  $\text{CH}_3$ ), 1.71 (d,  $J = 12.8$  Hz, 1H,  $\text{CH}_2$ ), 2.47 (s, 3H,  $\text{CH}_3$ ), 2.49 (s, 3H,  $\text{CH}_3$ ), 3.01 (ddd,  $J = 12.8$  Hz,  $J = 12.8$  Hz,  $J = 2.8$  Hz, 1H,  $\text{CH}_2$ ), 3.33 (d,  $J = 12.8$  Hz, 2H,  $\text{CH}_2$ ), 3.42 (d,  $J = 12.8$  Hz, 1H,  $\text{CH}_2$ ), 3.46-3.56 (m, 1H,  $\text{CH}_2$ ), 3.57-3.65 (m, 1H,  $\text{CH}_2$ ), 4.24 (d,  $J = 12.8$  Hz, 1H,  $\text{CH}_2$ ), 5.18 (s, 1H, CH), 6.34 (s, 1H), 6.37-6.43 (m, 2H, Ar), 6.65 (d,  $J = 7.6$  Hz, 1H, Ar), 7.05 (dd,  $J = 7.6$  Hz,  $J = 7.6$  Hz, 1H, Ar), 7.38 (d,  $J = 8.0$  Hz, 4H, Ar), 7.68 (d,  $J = 8.0$  Hz, 2H, Ar), 7.71 (d,  $J = 8.0$  Hz, 2H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  11.7, 21.5, 21.6, 36.5, 38.8, 42.3, 57.0, 90.0, 106.3, 116.6, 123.0, 125.8, 127.4, 127.5, 128.8, 129.5, 129.8, 129.9, 133.2, 133.5, 143.9, 144.5, 148.2. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu$  2979, 2919, 2854, 1673, 1594, 1490, 1349, 1305, 1162, 1088, 1019, 998, 945, 906, 741, 706, 669, 654  $\text{cm}^{-1}$ . HRMS (ESI) Calcd. for  $\text{C}_{29}\text{H}_{32}\text{N}_3\text{O}_4\text{S}_2^+$  ( $\text{M}^++\text{H}$ ) requires 550.1829, found: 550.1827.



### 7-butyl-3,6-ditosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole **2i**

0.2 mmol scale, 61 mg, a white solid, 53% yield. m.p.: 95-97 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 0.76 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 5.2 Hz, 1H, CH<sub>2</sub>), 0.96 (t, *J* = 7.6 Hz, 3H, CH<sub>3</sub>), 1.31-1.41 (m, 2H, CH<sub>2</sub>), 1.55-1.65 (m, 2H, CH<sub>2</sub>), 1.71 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 2.47 (s, 3H, CH<sub>3</sub>), 2.49 (s, 3H, CH<sub>3</sub>), 3.01 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 3.2 Hz, 1H, CH<sub>2</sub>), 3.33 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 3.59-3.44 (m, 2H, CH<sub>2</sub>), 3.52-3.60 (m, 1H, CH<sub>2</sub>), 4.24 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 5.18 (s, 1H, CH), 6.35 (s, 1H, Ar), 6.39 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 2H, Ar), 6.64 (d, *J* = 7.6 Hz, 1H, Ar), 7.04 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.38 (d, *J* = 8.0 Hz, 4H, Ar), 7.67 (d, *J* = 8.0 Hz, 2H, Ar), 7.70 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 13.9, 20.2,

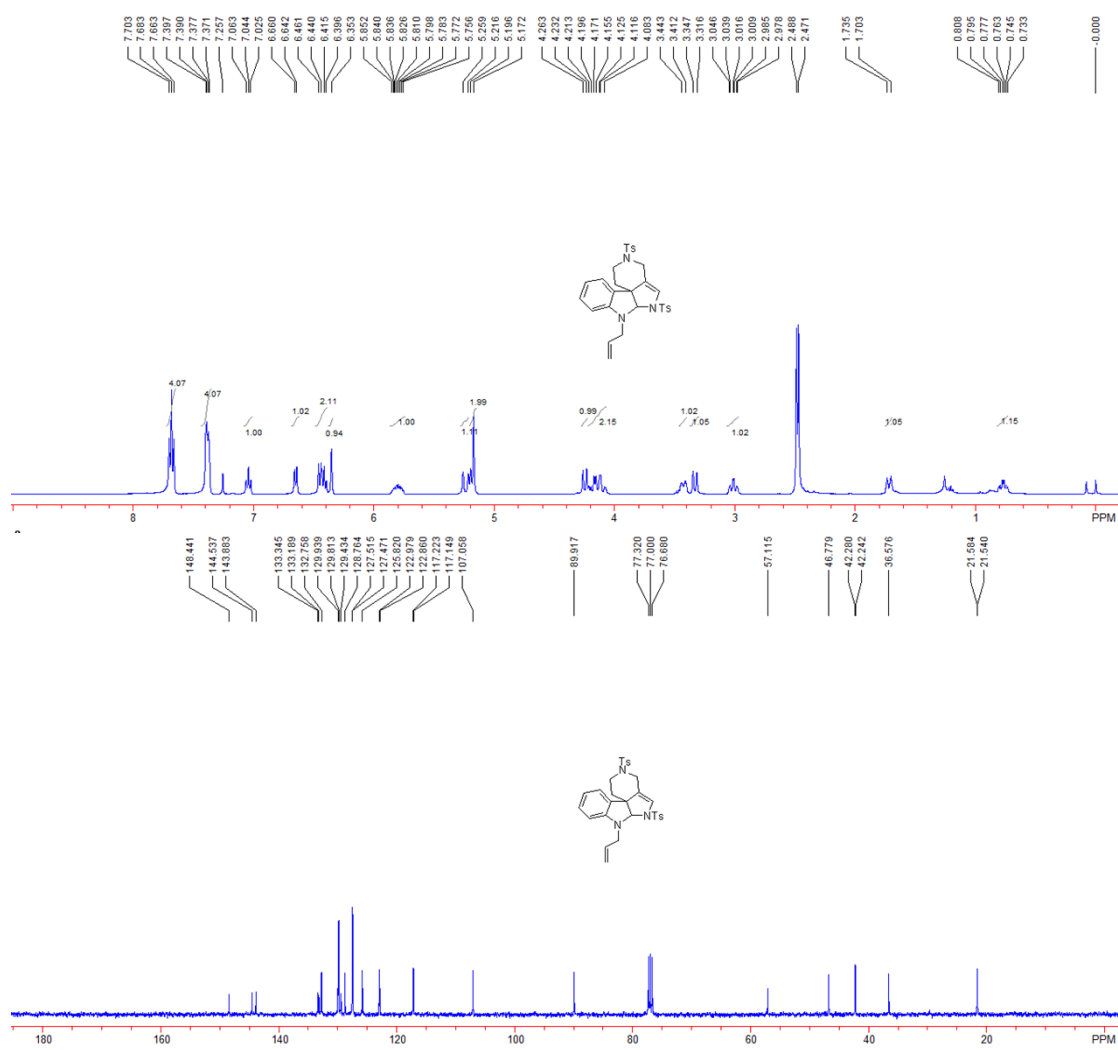
21.5, 21.6, 28.8, 36.4, 42.3, 44.0, 57.0, 90.5, 106.2, 116.4, 122.9, 123.0, 125.9, 127.46, 127.51, 128.8, 129.3, 129.8, 129.9, 133.3, 133.5, 143.9, 144.5, 148.6. IR (CH<sub>2</sub>Cl<sub>2</sub>) v 2955, 2854, 1675, 1599, 1451, 1349, 1305, 1161, 1088, 1020, 997, 908, 813, 736, 706, 669 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>36</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 578.2142, found: 578.2139.

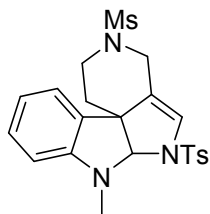


**7-Allyl-3,6-ditosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2j**

0.2 mmol scale, 61 mg, a white solid, 53% yield. m.p.: 95-97 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 0.77 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 5.2 Hz, 1H, CH<sub>2</sub>), 1.72 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 2.47 (s, 3H, CH<sub>3</sub>), 2.49 (s, 3H, CH<sub>3</sub>),

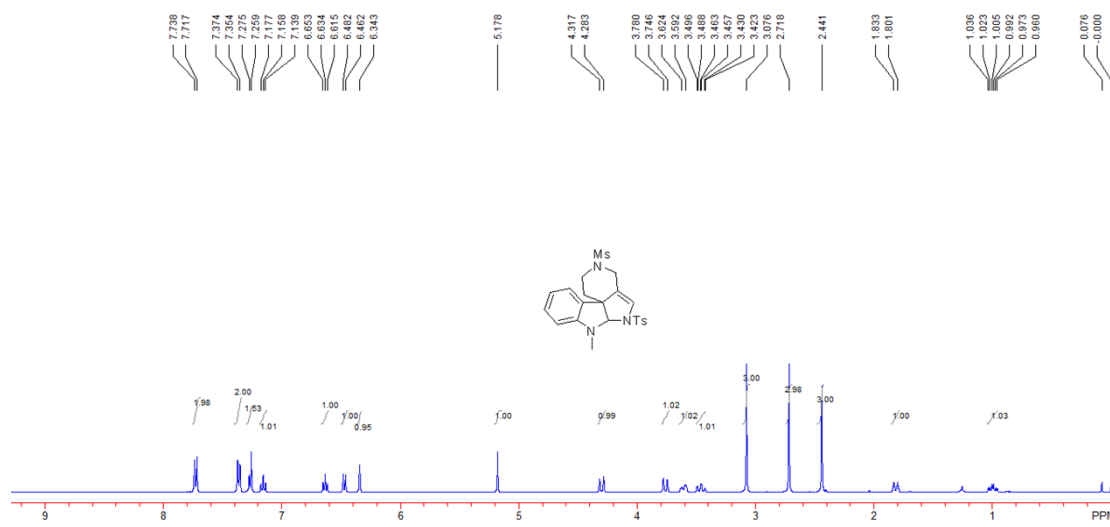
3.01 (ddd,  $J = 12.8$  Hz,  $J = 12.8$  Hz,  $J = 2.8$  Hz, 1H, CH<sub>2</sub>), 3.33 (d,  $J = 12.8$  Hz, 1H, CH<sub>2</sub>), 3.43 (d,  $J = 12.8$  Hz, 1H, CH<sub>2</sub>), 4.08-4.22 (m, 2H, CH<sub>2</sub>), 4.25 (d,  $J = 12.8$  Hz, 1H, CH<sub>2</sub>), 5.17 (s, 1H, CH), 5.19 (d,  $J = 9.6$  Hz, 1H, CH<sub>2</sub>=), 5.23 (d,  $J = 17.2$  Hz, 1H, CH<sub>2</sub>=), 5.75-5.86 (m, 1H, CH=), 6.35 (s, 1H), 6.39-6.47 (m, 2H, Ar), 6.65 (d,  $J = 7.2$  Hz, 1H, Ar), 7.04 (dd,  $J = 7.2$  Hz,  $J = 7.2$  Hz, 1H, Ar), 7.37-7.40 (m, 4H, Ar), 7.68 (dd,  $J = 8.0$  Hz,  $J = 8.0$  Hz, 4H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  21.5, 21.6, 36.6, 42.2, 42.3, 46.8, 57.1, 89.9, 107.0, 107.1, 117.1, 117.2, 122.9, 123.0, 125.8, 127.47, 127.52, 128.8, 129.4, 129.8, 129.9, 132.8, 133.2, 133.3, 143.9, 144.5, 148.4. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  3105, 2919, 2838, 1667, 1486, 1447, 1352, 1344, 1162, 1119, 1087, 1019, 976, 914, 744, 705, 671 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>30</sub>H<sub>32</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 562.1829, found: 562.1825.

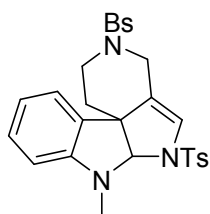
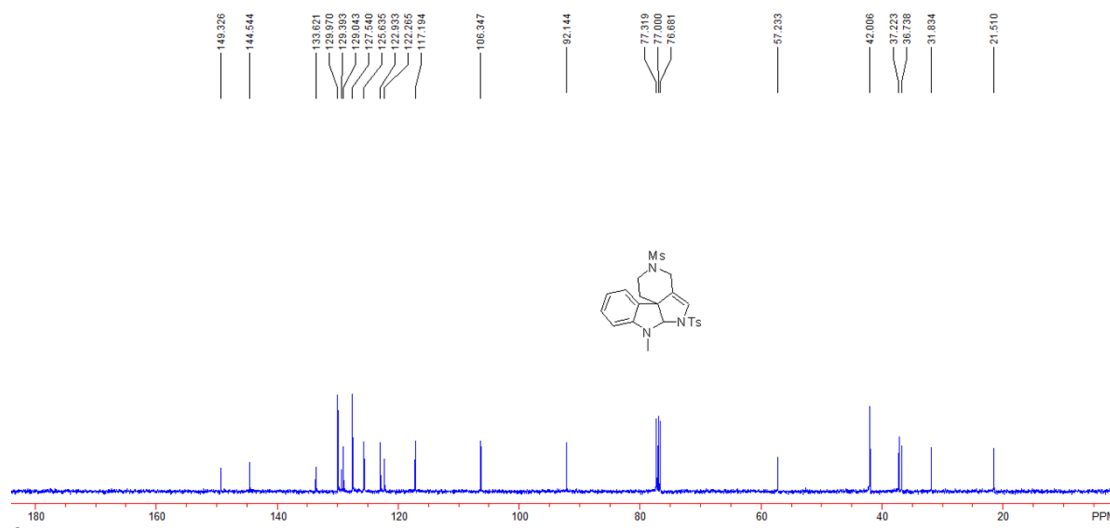




**7-Methyl-3-(methylsulfonyl)-6-tosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2k**

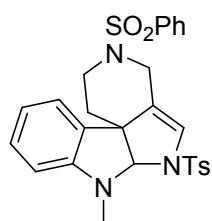
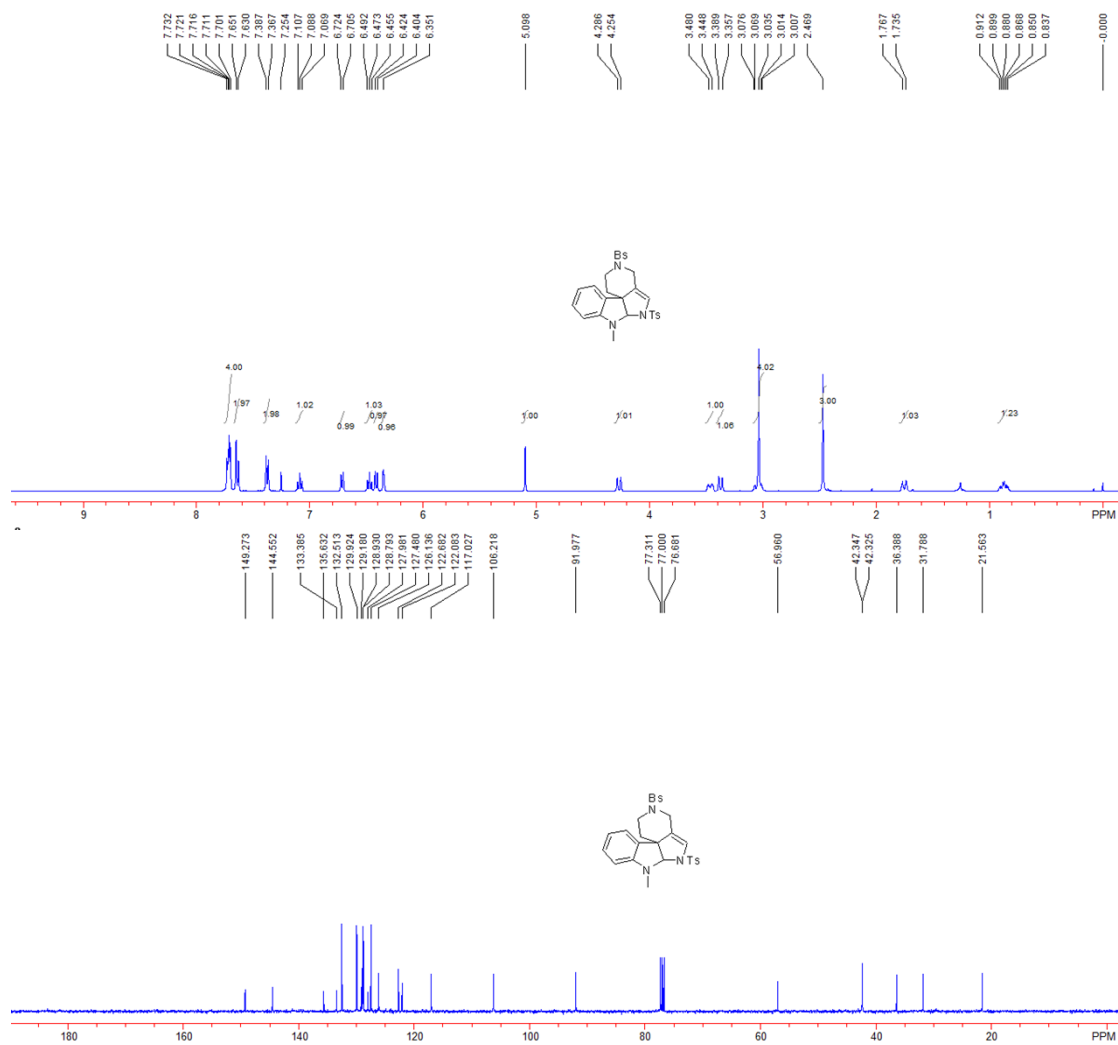
0.2 mmol scale, 84 mg, a white solid, 92% yield. m.p.: 185-188 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.00 (ddd,  $J = 12.8$  Hz,  $J = 12.8$  Hz,  $J = 5.2$  Hz, 1H,  $\text{CH}_2$ ), 1.82 (d,  $J = 12.8$  Hz, 1H,  $\text{CH}_2$ ), 2.44 (s, 3H,  $\text{CH}_3$ ), 2.72 (s, 3H,  $\text{CH}_3$ ), 3.08 (s, 3H,  $\text{CH}_3$ ), 3.46 (ddd,  $J = 12.8$  Hz,  $J = 12.8$  Hz,  $J = 2.8$  Hz, 1H,  $\text{CH}_2$ ), 3.61 (d,  $J = 12.8$  Hz, 1H,  $\text{CH}_2$ ), 3.76 (d,  $J = 12.8$  Hz, 1H,  $\text{CH}_2$ ), 4.29 (d,  $J = 12.8$  Hz, 1H,  $\text{CH}_2$ ), 5.18 (s, 1H, CH), 6.34 (s, 1H), 6.47 (d,  $J = 7.6$  Hz, 1H, Ar), 6.63 (dd,  $J = 7.6$  Hz,  $J = 7.6$  Hz, 1H, Ar), 7.16 (dd,  $J = 7.6$  Hz,  $J = 7.6$  Hz, 1H, Ar), 7.27 (d,  $J = 7.6$  Hz, 1H, Ar), 7.36 (d,  $J = 8.0$  Hz, 2H, Ar), 7.73 (d,  $J = 8.0$  Hz, 2H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  21.5, 31.8, 36.7, 37.2, 42.0, 57.2, 92.1, 106.3, 117.2, 122.3, 122.9, 125.6, 127.5, 129.0, 129.4, 130.0, 133.6, 144.5, 149.3. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu$  3069, 2923, 1663, 1600, 1492, 1337, 1303, 1150, 1087, 1005, 908, 873, 767, 707, 665  $\text{cm}^{-1}$ . HRMS (ESI) Calcd. for  $\text{C}_{22}\text{H}_{26}\text{N}_3\text{O}_4\text{S}_2^+$  ( $\text{M}^+\text{H}$ ) requires 460.1359, found: 460.1358.





**3-((4-Bromophenyl)sulfonyl)-7-methyl-6-tosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2l**

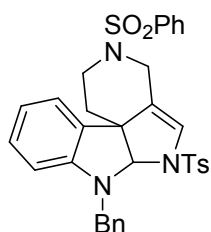
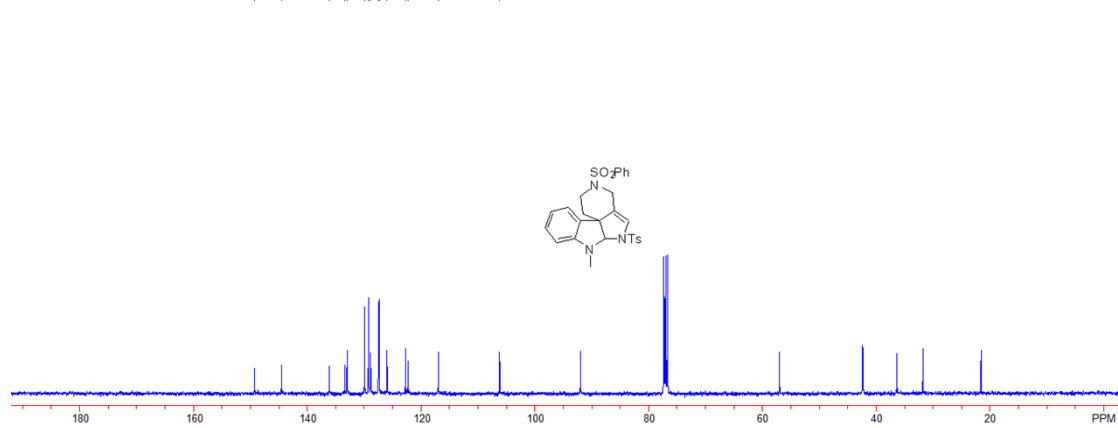
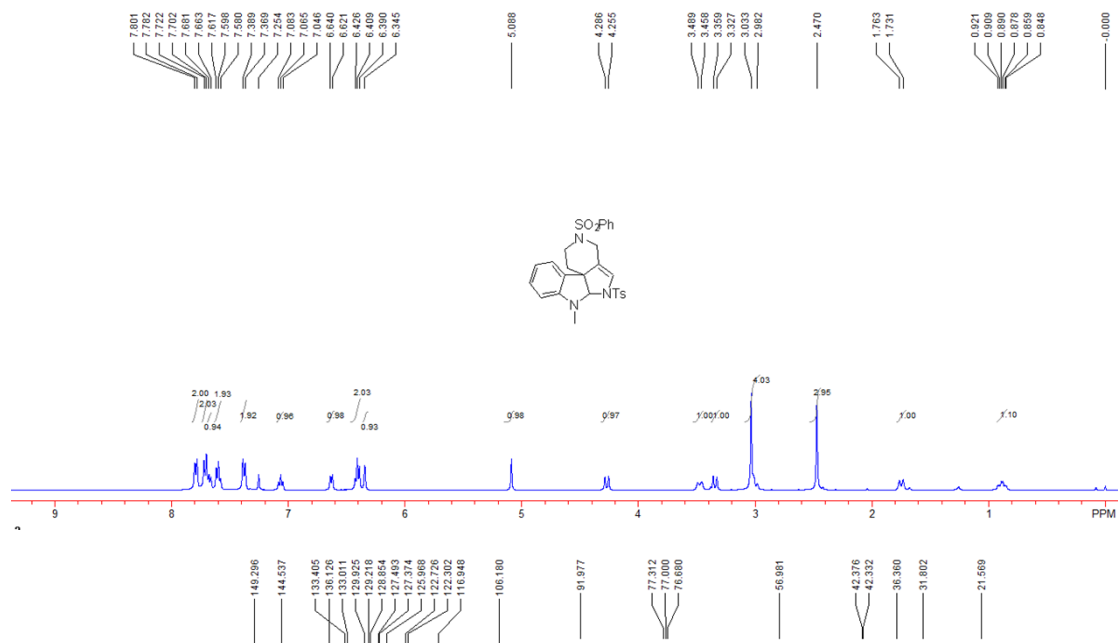
0.2 mmol scale, 92 mg, a white solid, 77% yield. m.p.: 272-274 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 1.00 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 5.2 Hz, 1H, CH<sub>2</sub>), 1.75 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 2.47 (s, 3H, CH<sub>3</sub>), 3.00-3.08 (m, 4H), 3.37 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 3.46 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 4.27 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 5.10 (s, 1H, CH), 6.35 (s, 1H), 6.41 (d, *J* = 7.6 Hz, 1H, Ar), 6.47 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 6.71 (d, *J* = 7.6 Hz, 1H, Ar), 7.09 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.38 (d, *J* = 8.0 Hz, 2H, Ar), 7.64 (d, *J* = 8.0 Hz, 2H, Ar), 7.70-7.74 (m, 4H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.6, 31.8, 36.4, 42.32, 42.35, 57.0, 92.0, 106.2, 117.0, 122.1, 122.7, 126.1, 127.5, 128.0, 128.8, 128.9, 129.2, 129.9, 132.5, 133.4, 135.6, 144.6, 149.3. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3101, 2914, 2842, 1678, 1599, 1572, 1347, 1303, 1161, 1087, 1070, 997, 946, 906, 813, 748, 704, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>27</sub>H<sub>27</sub>BrN<sub>3</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 600.0621, found: 600.0617.



**7-Methyl-3-(phenylsulfonyl)-6-tosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2m**

0.2 mmol scale, 72 mg, a white solid, 69% yield. m.p.: 168-170 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 0.88 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 4.4 Hz, 1H, CH<sub>2</sub>), 1.75 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 2.47 (s, 3H, CH<sub>3</sub>), 2.98-3.04 (m, 4H), 3.34 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 3.47 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 4.27 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 5.09 (s, 1H, CH), 6.34 (s, 1H), 6.39-6.43 (m, *J* = 7.6 Hz, 2H, Ar), 6.42 (d, *J* = 7.6 Hz, 1H, Ar), 6.63 (d, *J* = 7.6 Hz, 1H, Ar), 7.06 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.38 (d, *J* = 8.0 Hz, 2H, Ar), 7.60 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 2H, Ar), 7.67 (d, *J* = 7.6 Hz, 1H, Ar), 7.71 (d, *J* = 8.0 Hz, 2H, Ar), 7.79 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100

MHz, TMS)  $\delta$  21.6, 31.8, 36.4, 42.3, 42.4, 57.0, 92.0, 106.2, 117.0, 122.3, 122.7, 126.0, 127.4, 127.5, 128.8, 129.2, 129.9, 133.0, 133.4, 136.1, 144.5, 149.3. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  3072, 2906, 2829, 1598, 1491, 1443, 1338, 1165, 1089, 994, 954, 905, 741, 704, 667 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>27</sub>H<sub>28</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 522.1516, found: 522.1510.

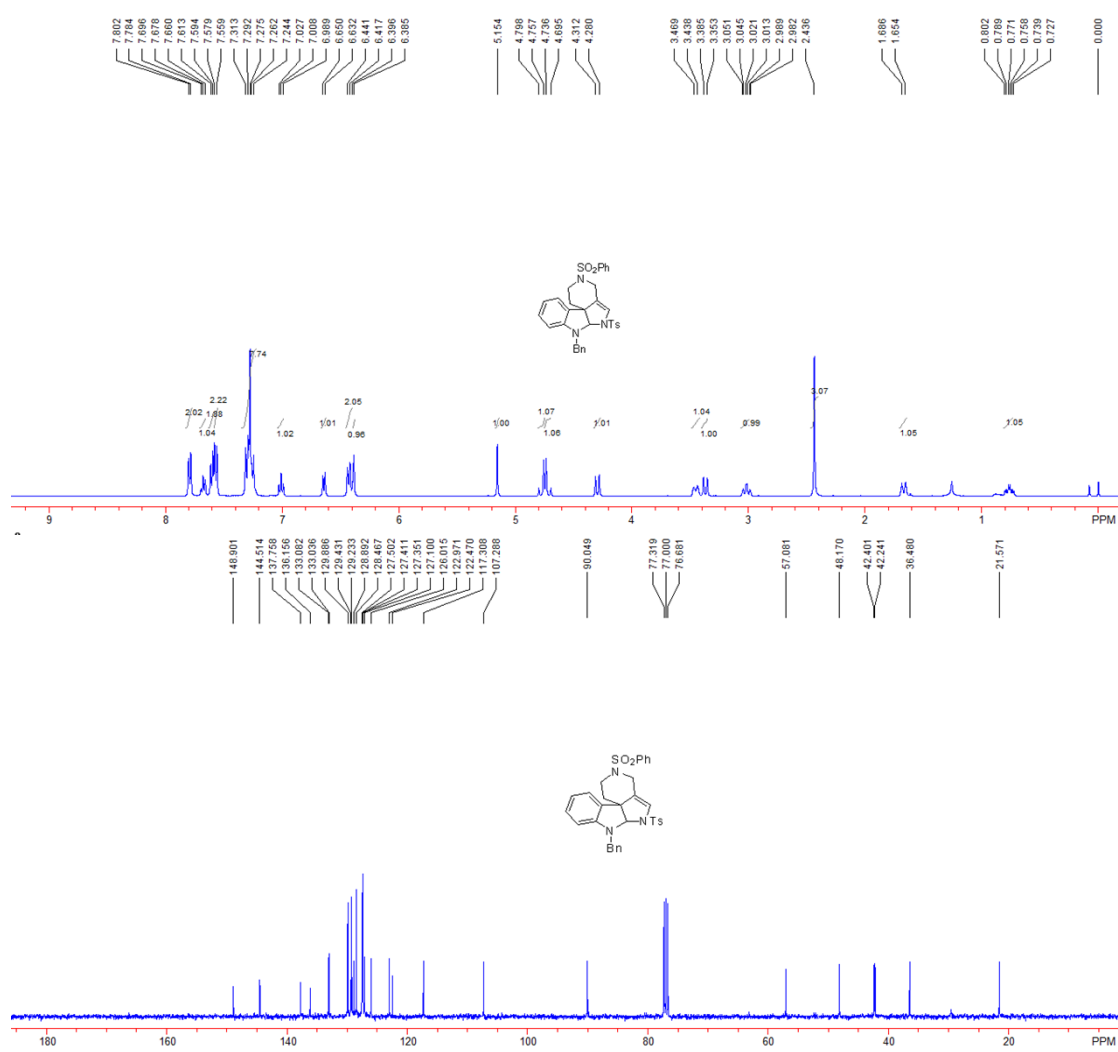


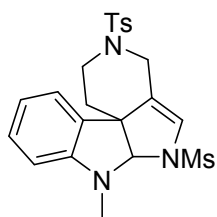
**7-Benzyl-3-(phenylsulfonyl)-6-tosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2n**

0.2 mmol scale, 74 mg, a white solid, 62% yield. m.p.: 115-117 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  0.76 (ddd,  $J$  = 12.8 Hz,  $J$  = 12.8 Hz,  $J$  = 5.2 Hz, 1H, CH<sub>2</sub>), 1.67 (d,  $J$  = 12.8 Hz, 1H,



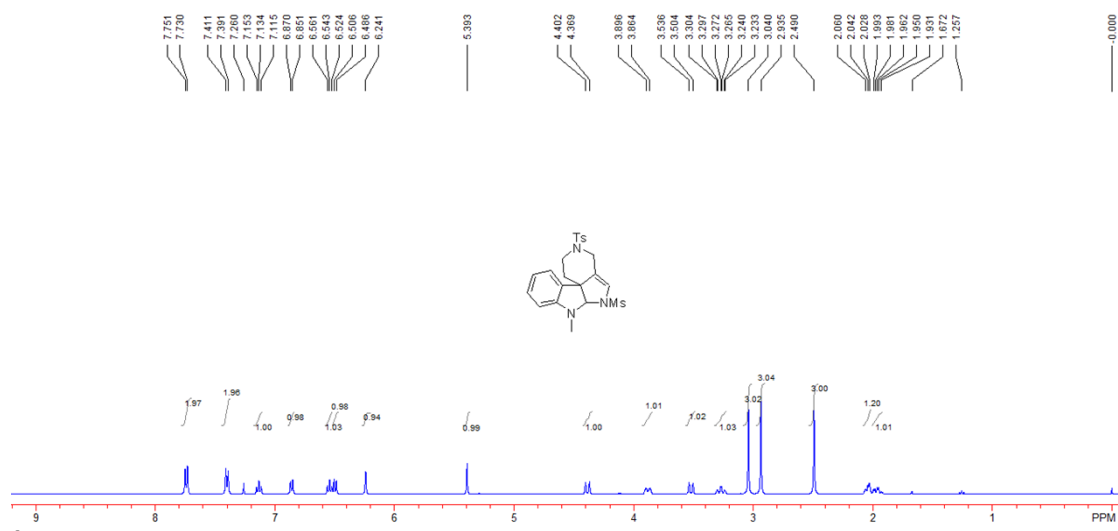
CH<sub>2</sub>), 2.44 (s, 3H, CH<sub>3</sub>), 3.02 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 2.8 Hz, 1H, CH<sub>2</sub>), 3.37 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 3.45 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 4.30 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 4.72 (d, *J* = 16.4 Hz, 1H, CH<sub>2</sub>), 4.77 (d, *J* = 16.4 Hz, 1H, CH<sub>2</sub>), 5.15 (s, 1H, CH), 6.38 (s, 1H), 6.39-6.45 (m, 2H, Ar), 6.64 (d, *J* = 7.6 Hz, 1H, Ar), 7.01 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.24-7.32 (m, 7H, Ar), 7.57 (d, *J* = 8.0 Hz, 2H, Ar), 7.60 (d, *J* = 8.0 Hz, 2H, Ar), 7.68 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H, Ar), 7.79 (d, *J* = 7.2 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.6, 36.5, 42.2, 42.4, 48.2, 57.1, 90.0, 107.3, 117.3, 122.5, 123.0, 126.0, 127.1, 127.3, 127.4, 127.5, 128.5, 128.9, 129.2, 129.4, 129.9, 133.0, 133.1, 136.2, 137.8, 144.5, 148.9. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3052, 2919, 2838, 1594, 1446, 1358, 1342, 1303, 1168, 1087, 995, 974, 910, 815, 746, 694, 669 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>33</sub>H<sub>32</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 598.1829, found: 598.1825.

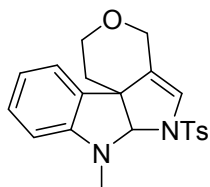
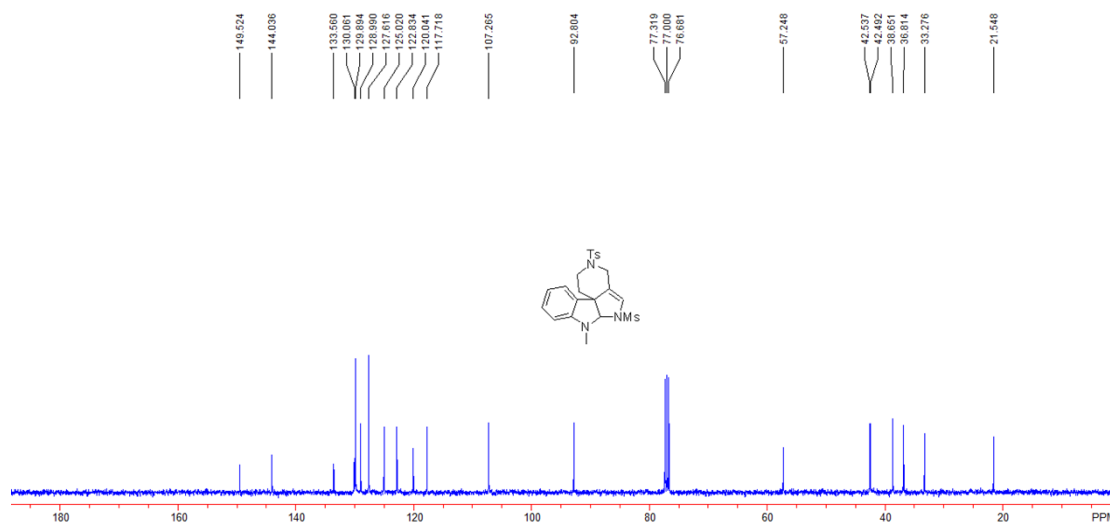




**7-Methyl-6-(methylsulfonyl)-3-tosyl-2,3,4,6,6a,7-hexahydro-1H-pyrido[4',3':3,4]pyrrolo[2,3-b]indole 2o**

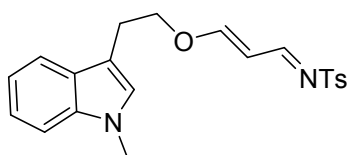
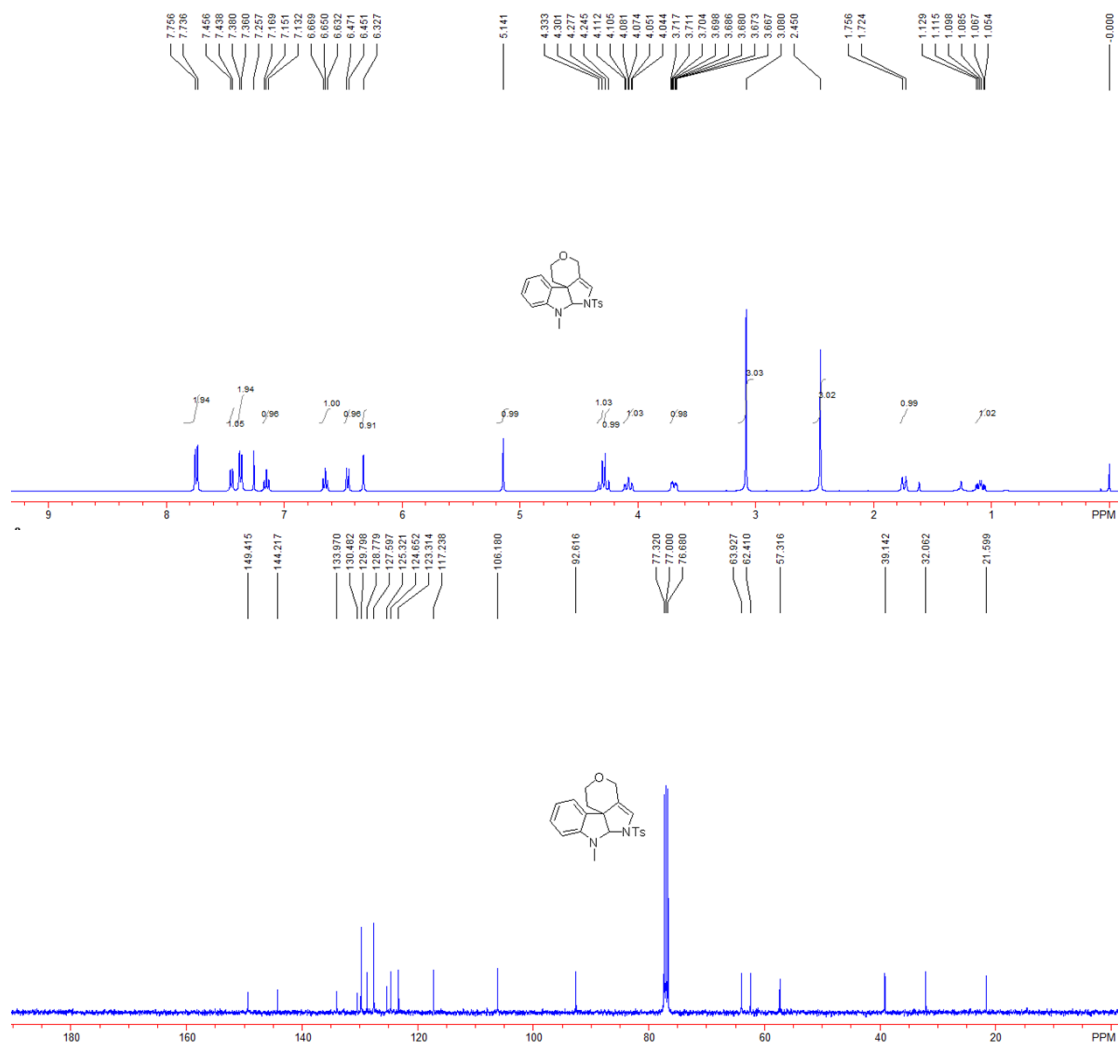
0.2 mmol scale, 61 mg, a white solid, 66% yield. m.p.: 241-243 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 1.96 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 4.8 Hz, 1H, CH<sub>2</sub>), 2.04 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 2.49 (s, 3H, CH<sub>3</sub>), 2.94 (s, 3H, CH<sub>3</sub>), 3.04 (s, 3H, CH<sub>3</sub>), 3.27 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 2.8 Hz, 1H, CH<sub>2</sub>), 3.52 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 3.88 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 4.38 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 5.39 (s, 1H, CH), 6.24 (s, 1H), 6.50 (d, *J* = 7.6 Hz, 1H, Ar), 6.54 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 6.86 (d, *J* = 7.6 Hz, 1H, Ar), 7.13 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.40 (d, *J* = 8.0 Hz, 2H, Ar), 7.74 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.5, 33.3, 36.8, 42.49, 42.54, 57.2, 92.8, 107.3, 117.7, 120.0, 122.8, 125.0, 127.6, 129.0, 129.9, 130.1, 133.6, 144.0, 149.5. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3089, 2919, 2829, 1675, 1599, 1493, 1347, 1314, 1300, 1155, 1008, 951, 906, 887, 746, 732, 678, 654 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>22</sub>H<sub>26</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 460.1359, found: 460.1359.





### 7-methyl-6-tosyl-1,2,4,6,6a,7-hexahydropyrano[4',3':3,4]pyrrolo[2,3-b]indole 2q

0.2 mmol scale, 34 mg, a white solid, 45% yield. m.p.: 206-208 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 1.09 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 5.2 Hz, 1H, CH<sub>2</sub>), 1.74 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 2.45 (s, 3H, CH<sub>3</sub>), 3.08 (s, 3H, CH<sub>3</sub>), 3.66-3.72 (m, 1H, CH<sub>2</sub>), 4.08 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 2.8 Hz, 1H, CH<sub>2</sub>), 4.26 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 4.32 (d, *J* = 12.8 Hz, 1H, CH<sub>2</sub>), 5.14 (s, 1H, CH), 6.33 (s, 1H), 6.46 (d, *J* = 7.6 Hz, 1H, Ar), 6.65 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.15 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.37 (d, *J* = 8.0 Hz, 2H, Ar), 7.45 (d, *J* = 7.6 Hz, 1H, Ar), 7.74 (d, *J* = 8.0 Hz, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.6, 32.1, 39.1, 57.3, 62.4, 63.9, 92.6, 106.2, 117.2, 123.3, 124.6, 125.3, 127.6, 128.8, 129.8, 130.5, 134.0, 144.2, 149.4. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3064, 2919, 2850, 1661, 1601, 1492, 1349, 1299, 1162, 1084, 1010, 975, 938, 814, 746, 737, 708, 669 cm<sup>-1</sup>. HRMS (ESI) Calcd. for C<sub>21</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>S<sup>+</sup> (M<sup>+</sup>+H) requires 383.1424, found: 383.1422.

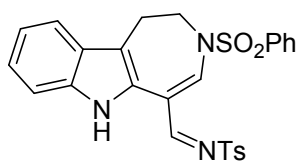
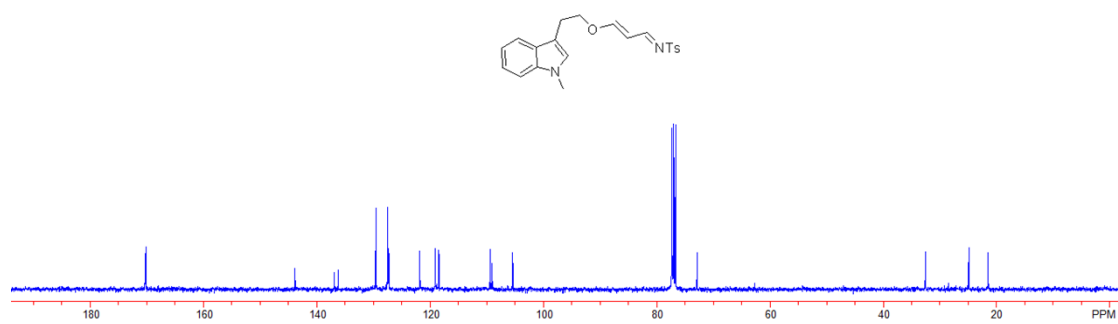
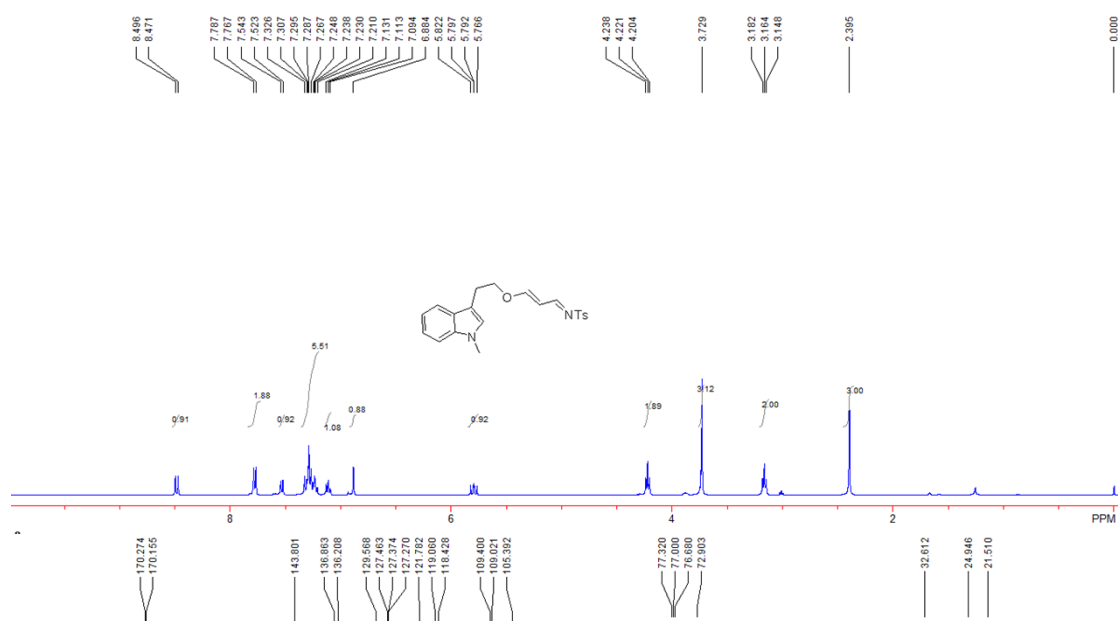


#### 4-Methyl-N-((1Z,2E)-3-(2-(1-methyl-1H-indol-3-yl)ethoxy)allylidene)benzenesulfonamide

##### 2q'

0.2 mmol scale, 30 mg, a white solid, 40% yield. m.p.: 88-90 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.40 (s, 3H, CH<sub>3</sub>), 3.16 (t, *J* = 6.8 Hz, 2H, CH<sub>2</sub>), 3.73 (s, 3H, CH<sub>3</sub>), 4.22 (d, *J* = 6.8 Hz, 2H, CH<sub>2</sub>), 5.79 (dd, *J* = 10.0 Hz, *J* = 10.4 Hz, 1H, CH=), 6.88 (s, 1H, Ar), 7.13 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.21-7.33 (m, 5H, Ar, CH=), 7.53 (d, *J* = 8.0 Hz, 1H, Ar), 7.78 (d, *J* = 8.0 Hz, 2H, Ar), 8.48 (d, *J* = 10.0 Hz, 1H, CH=N). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.5, 24.9, 32.6, 72.9, 105.4, 109.0, 109.4, 118.4, 119.1, 121.8, 127.3, 127.4, 127.5, 129.6, 136.2, 136.9, 143.8, 170.2, 170.3. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3048, 2935, 2858, 1653, 1596, 1550, 1470, 1327, 1156, 1122, 1034,

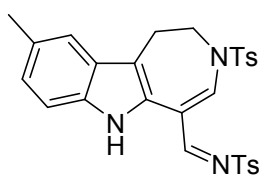
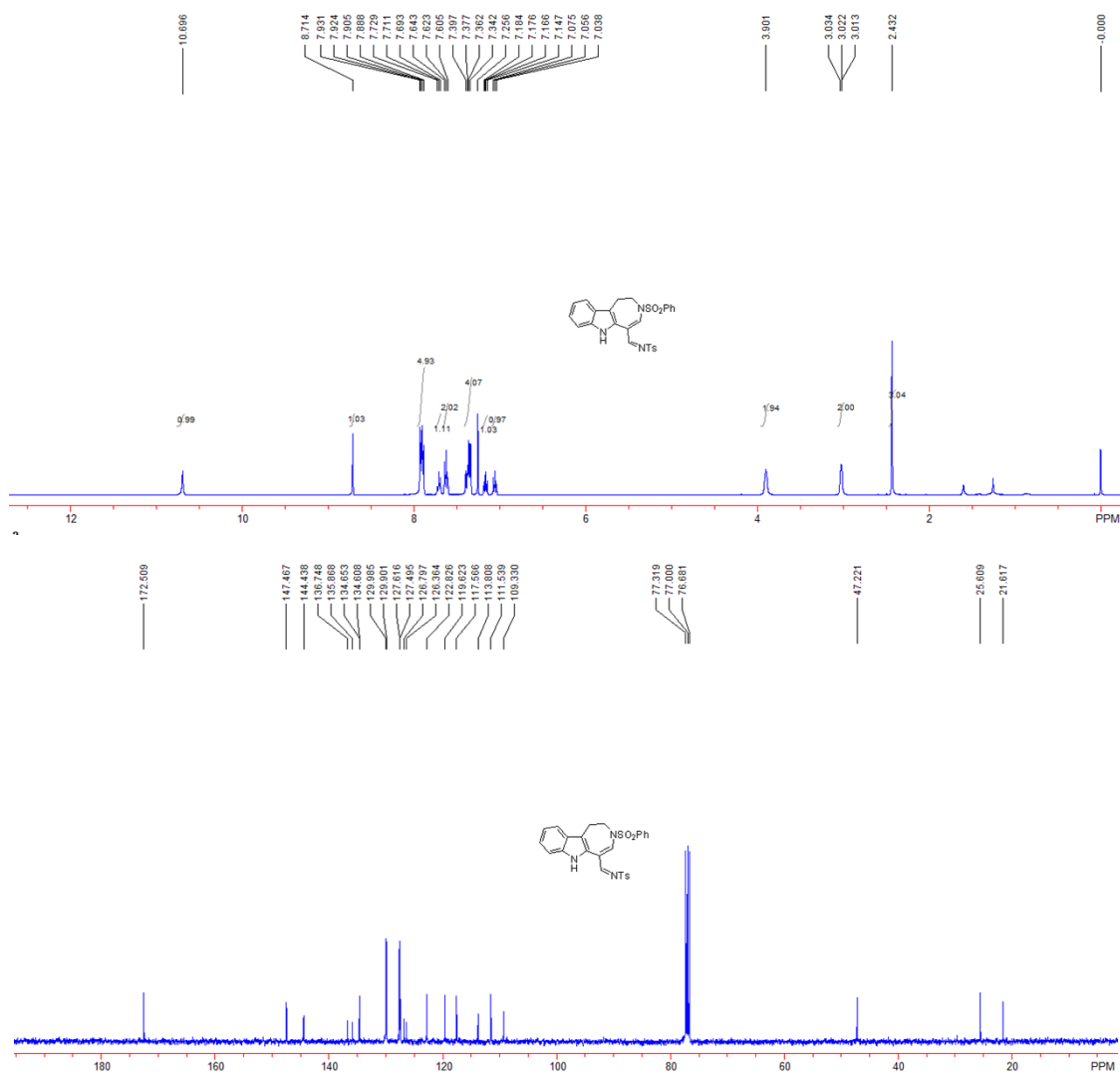
1010, 812, 741, 662  $\text{cm}^{-1}$ . HRMS (ESI) Calcd. for  $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_3\text{S}^+$  ( $\text{M}^++\text{H}$ ) requires 383.1424, found: 383.1422.



**(E)-4-methyl-N-((3-(phenylsulfonyl)-1,2,3,6-tetrahydroazepino[4,5-b]indol-5-yl)methylene)benzenesulfonamide 4a**

0.2 mmol scale, 48 mg, a yellow solid, 47% yield. m.p.: 249-251  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  2.43 (s, 3H,  $\text{CH}_3$ ), 3.02 (t,  $J = 3.6$  Hz, 2H,  $\text{CH}_2$ ), 3.90 (br s, 2H,  $\text{CH}_2$ ), 7.06 (dd,  $J = 7.6$  Hz, 1H, Ar), 7.17 (dd,  $J = 7.6$  Hz,  $J = 7.6$  Hz, 1H, Ar), 7.34-7.40 (m, 4H, Ar), 7.62 (dd,  $J = 7.6$  Hz,  $J = 7.6$  Hz, 2H, Ar), 7.71 (dd,  $J = 7.6$  Hz,  $J = 7.6$  Hz, 1H, Ar), 7.88-7.94 (m, 5H, Ar), 8.71 (s, 1H,  $\text{CH}=\text{N}$ ), 10.70 (s, 1H, NH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  21.6, 25.6, 47.2, 109.3, 111.5, 113.8, 117.6, 119.6, 122.8, 126.4, 126.8, 127.5, 127.6, 129.9, 130.0, 134.6, 134.7, 135.9,

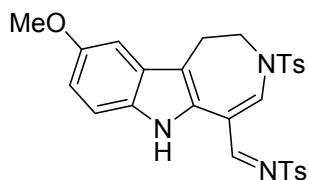
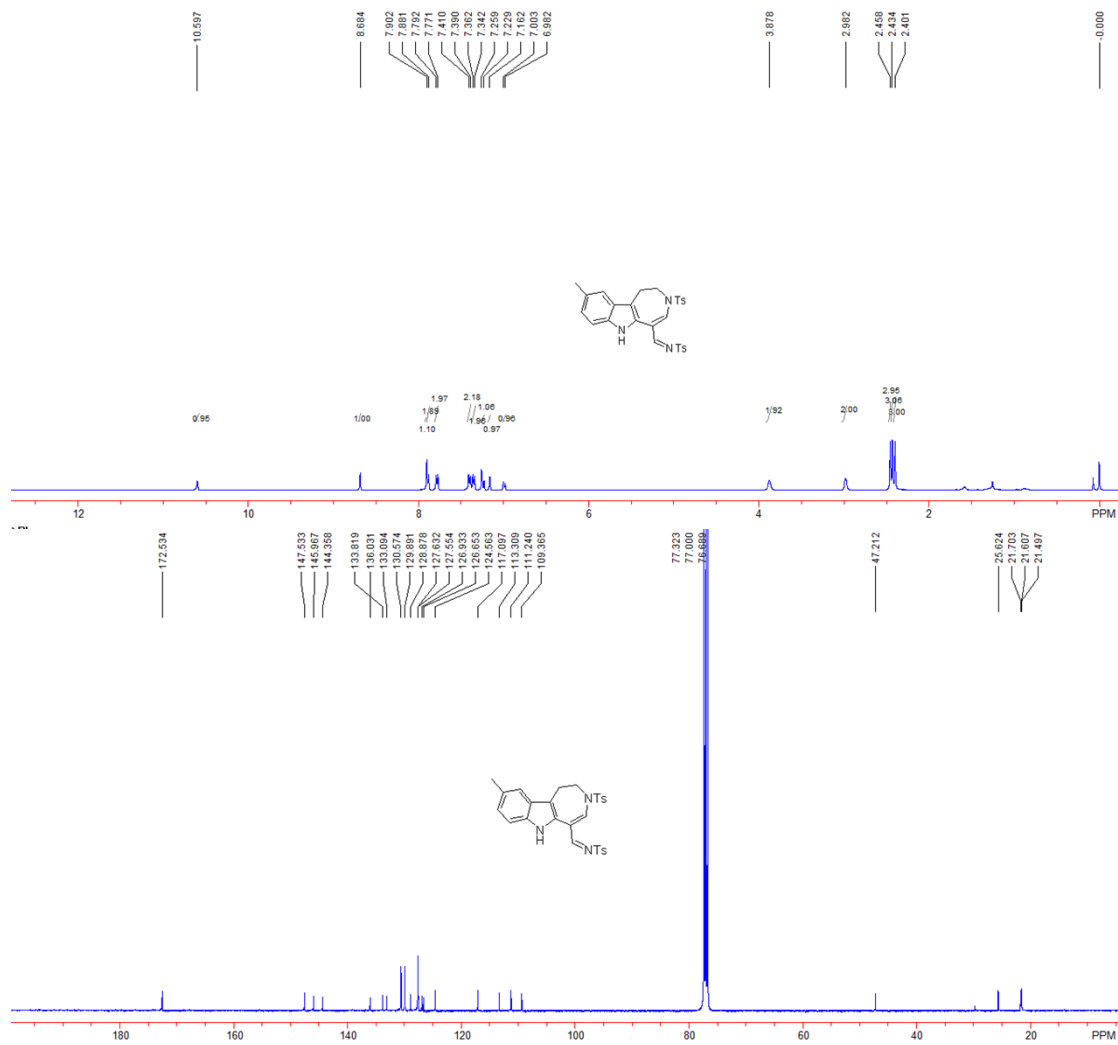
136.7, 144.4, 147.5, 172.5. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  3376, 3064, 2910, 1621, 1559, 1445, 1351, 1336, 1319, 1271, 1157, 1082, 1016, 919, 832, 742, 726, 705, 679 cm<sup>-1</sup>. HRMS (MALDI) Calcd. for C<sub>26</sub>H<sub>24</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 506.1203, found: 506.1193.



**(E)-4-methyl-N-((9-methyl-3-tosyl-1,2,3,6-tetrahydroazepino[4,5-b]indol-5-yl)methylene)benzenesulfonamide 4b**

0.2 mmol scale, 45 mg, a white solid, 43% yield. m.p.: 139-141 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  2.41 (s, 3H, CH<sub>3</sub>), 2.43 (s, 3H, CH<sub>3</sub>), 2.46 (s, 3H, CH<sub>3</sub>), 2.98 (s, 2H, CH<sub>2</sub>), 2.88 (s, 2H, CH<sub>2</sub>), 6.99 (d, *J* = 8.4 Hz, 1H, Ar), 7.16 (s, 1H, Ar), 7.24 (d, *J* = 8.4 Hz, 1H, Ar), 7.35 (d, *J* = 8.0 Hz, 2H, Ar), 7.40 (d, *J* = 8.0 Hz, 2H, Ar), 7.78 (d, *J* = 8.0 Hz, 2H, Ar), 7.89 (d, *J* = 8.0 Hz, 2H,

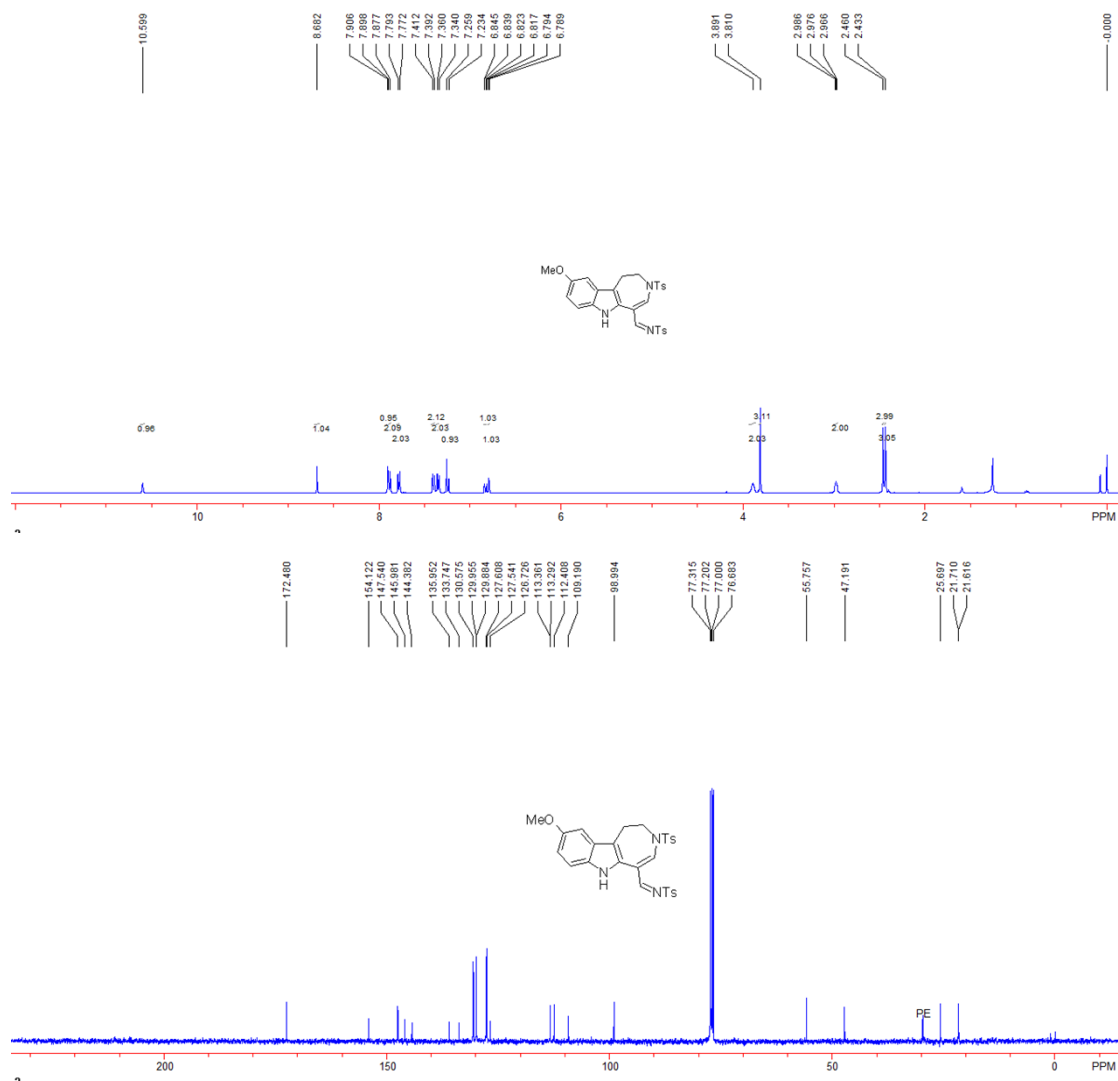
Ar), 7.90 (s, 1H, CH=), 8.68 (s, 1H, CH=N), 10.60 (s, 1H, NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.5, 21.6, 21.7, 25.6, 47.2, 109.4, 111.2, 113.3, 117.1, 124.6, 126.6, 126.9, 127.5, 127.6, 128.9, 129.9, 130.6, 133.1, 133.8, 136.0, 144.4, 146.0, 147.5, 172.5. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3373, 2919, 1595, 1557, 1360, 1302, 1169, 1152, 1101, 1085, 837, 794, 684, 665 cm<sup>-1</sup>. HRMS (MALDI) Calcd. for C<sub>28</sub>H<sub>28</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 534.1516, found: 534.1509.



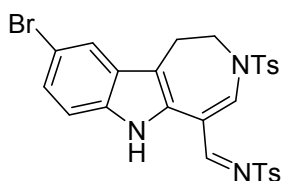
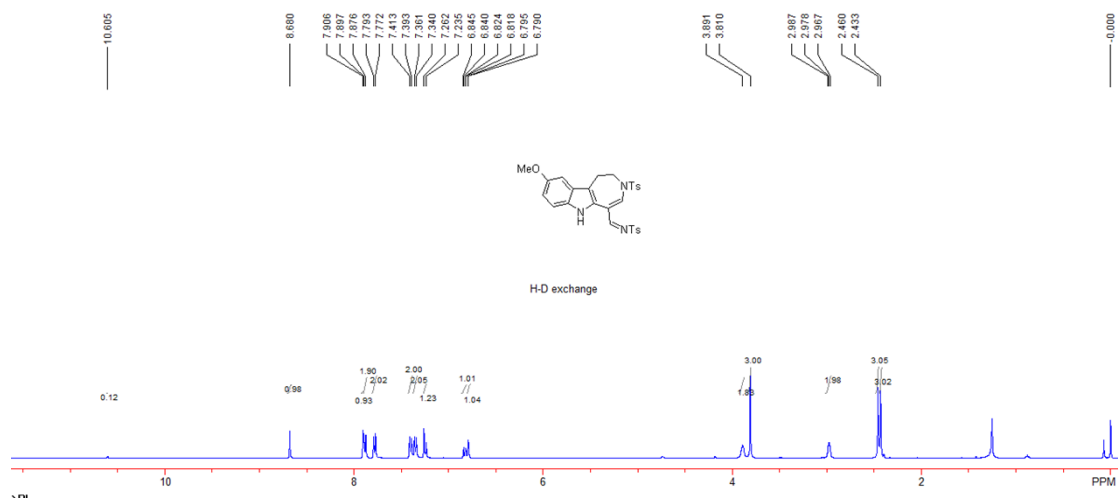
**(E)-N-((9-methoxy-3-tosyl-1,2,3,6-tetrahydroazepino[4,5-b]indol-5-yl)methylene)-4-methylbenzenesulfonamide 4c**

0.2 mmol scale, 35 mg, a white solid, 32% yield. m.p.: 155-157 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.43 (s, 3H, CH<sub>3</sub>), 2.46 (s, 3H, CH<sub>3</sub>), 2.98 (t, *J* = 4.0 Hz, 2H, CH<sub>2</sub>), 3.81 (s, 3H, CH<sub>3</sub>), 3.89 (br s, 2H, CH<sub>2</sub>), 6.79 (d, *J* = 2.0 Hz, 1H,

Ar), 6.83 (dd,  $J = 8.8$  Hz,  $J = 2.0$  Hz, 1H, Ar), 7.24 (d,  $J = 8.0$  Hz, 1H, Ar), 7.35 (d,  $J = 8.0$  Hz, 2H, Ar), 7.40 (d,  $J = 8.0$  Hz, 2H, Ar), 7.78 (d,  $J = 8.4$  Hz, 2H, Ar), 7.89 (d,  $J = 8.4$  Hz, 2H, Ar), 7.91 (s, 1H, CH=), 8.68 (s, 1H, CH=N), 10.60 (s, 1H, NH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  21.6, 21.7, 25.7, 47.2, 55.8, 99.0, 109.2, 112.4, 113.3, 113.4, 126.7, 127.5, 127.6, 129.9, 130.0, 130.6, 133.7, 136.0, 144.4, 146.0, 147.5, 154.1, 172.5. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu$  3376, 2923, 1595, 1552, 1357, 1304, 1274, 1167, 1153, 1082, 1011, 907, 834, 728, 702, 664  $\text{cm}^{-1}$ . HRMS (MALDI) Calcd. for  $\text{C}_{28}\text{H}_{28}\text{N}_3\text{O}_5\text{S}_2^+$  ( $\text{M}^+\text{H}$ ) requires 550.1465, found: 550.1461.

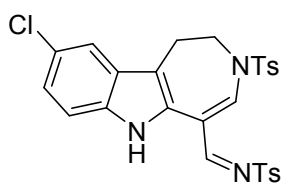
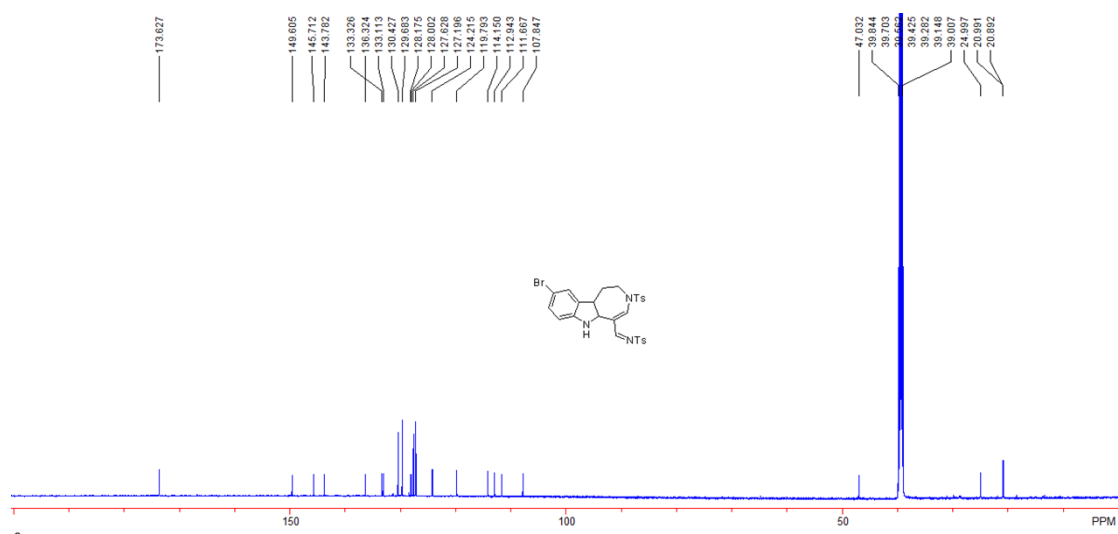
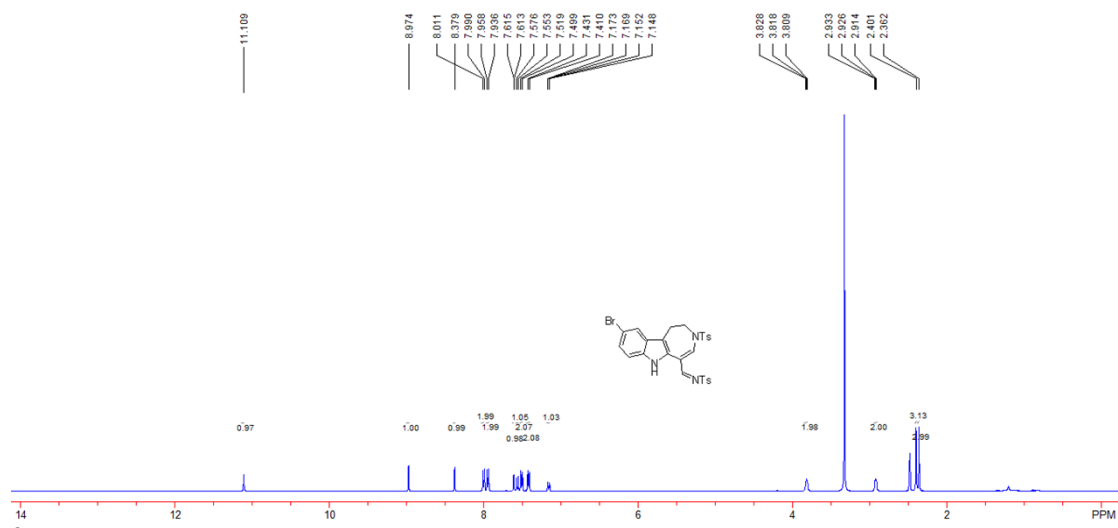






**(*E*)-N-((9-bromo-3-tosyl-1,2,3,6-tetrahydroazepino[4,5-b]indol-5-yl)methylene)-4-methylbenzenesulfonamide 4d**

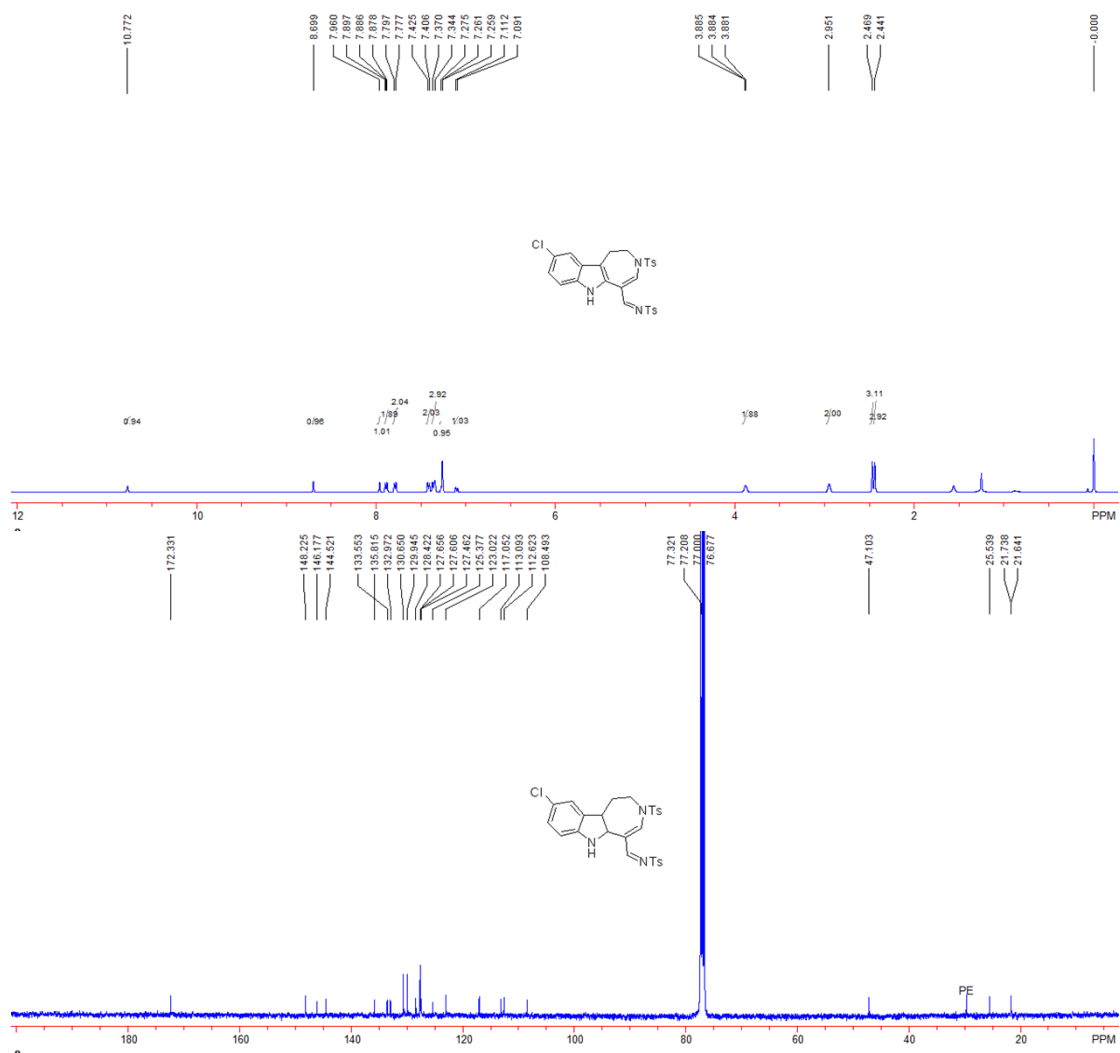
0.2 mmol scale, 31 mg, a white solid, 26% yield. m.p.: 229-231 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ 2.36 (s, 3H, CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 2.93 (t, *J* = 4.0 Hz, 2H, CH<sub>2</sub>), 3.82 (t, *J* = 4.0 Hz, 2H, CH<sub>2</sub>), 7.16 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 1H, Ar), 7.42 (d, *J* = 8.0 Hz, 2H, Ar), 7.51 (d, *J* = 8.0 Hz, 2H, Ar), 7.56 (d, *J* = 8.8 Hz, 1H, Ar), 7.61 (d, *J* = 1.6 Hz, 1H, Ar), 7.95 (d, *J* = 8.4 Hz, 2H, Ar), 8.00 (d, *J* = 8.4 Hz, 2H, Ar), 8.38 (s, 1H, CH=), 8.98 (s, 1H, CH=N), 11.11 (s, 1H, NH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ 20.9, 21.0, 25.0, 47.0, 107.8, 111.7, 112.9, 114.2, 119.8, 124.2, 127.2, 127.6, 128.0, 128.2, 129.7, 130.4, 133.1, 133.3, 136.3, 143.8, 145.7, 149.6, 173.6. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3378, 2900, 1621, 1560, 1458, 1443, 1351, 1335, 1315, 1271, 1158, 1080, 1014, 919, 741, 725, 677 cm<sup>-1</sup>. HRMS (MALDI) Calcd. for C<sub>27</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub>BrS<sub>2</sub><sup>+</sup> (M<sup>+</sup>+H) requires 598.0464, found: 598.0459.



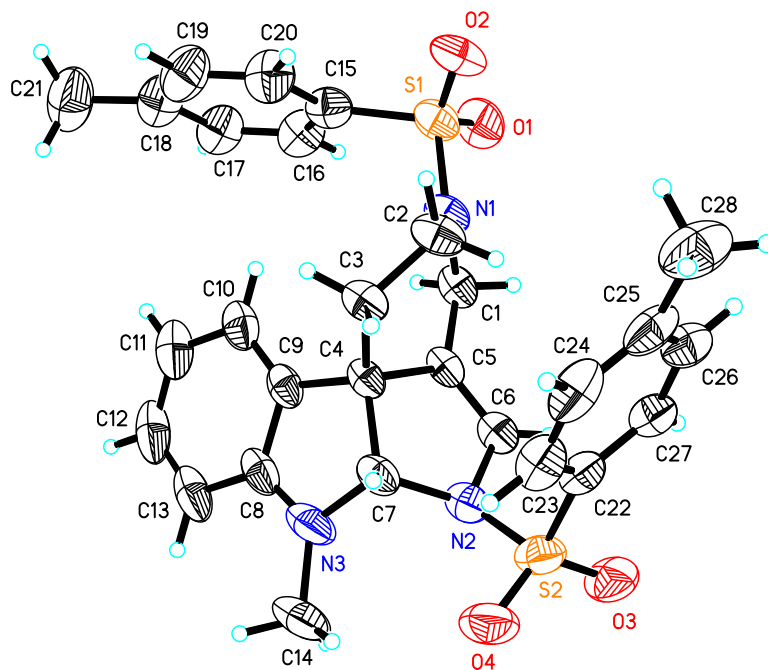
**(E)-N-((9-chloro-3-tosyl-1,2,3,6-tetrahydroazepino[4,5-b]indol-5-yl)methylene)-4-methylbenzenesulfonamide **4e****

0.2 mmol scale, 22 mg, a white solid, 20% yield. m.p.: 255-257 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.44 (s, 3H, CH<sub>3</sub>), 2.47 (s, 3H, CH<sub>3</sub>), 2.95 (br s, 2H, CH<sub>2</sub>), 3.88 (t, *J* = 1.2 Hz, 2H, CH<sub>2</sub>), 7.10 (d, *J* = 8.4 Hz, 1H, Ar), 7.27 (d, *J* = 8.4 Hz, 1H, Ar), 7.34-7.37 (m, 3H, Ar), 7.41 (d, *J* = 8.0 Hz, 2H, Ar), 7.79 (d, *J* = 8.0 Hz, 2H, Ar), 7.89 (d, *J* = 8.0 Hz, 2H, Ar), 7.96 (s, 1H, CH=), 8.70 (s, 1H, CH=N), 10.77 (s, 1H, NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.6, 21.7, 25.5, 47.1, 108.5, 112.6, 113.1, 117.0, 123.0, 125.4, 127.5, 127.6, 127.7, 128.4, 129.9, 130.6, 133.0, 133.6, 135.8, 144.5, 146.2, 148.2, 172.3. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 3364, 2919, 1557, 1319, 1299, 1168, 1159,

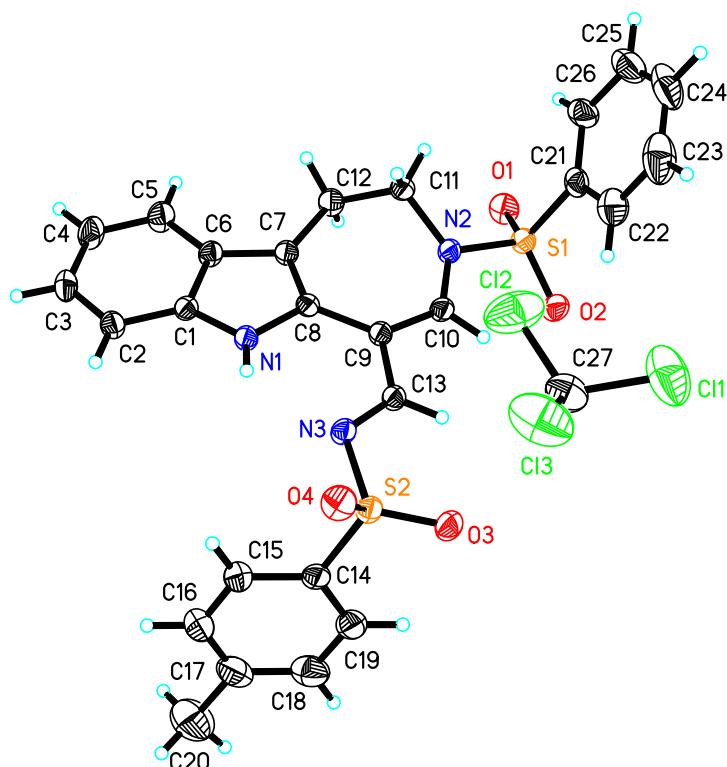
1086, 1022, 924, 830, 814, 795, 706, 688  $\text{cm}^{-1}$ . HRMS (MALDI) Calcd. for  $\text{C}_{27}\text{H}_{25}\text{N}_3\text{O}_4\text{ClS}_2^+$  ( $\text{M}^+\text{H}$ ) requires 554.0970, found: 554.0965.



## 8. Crystallographic information of 2a and 4a



The crystal data of **2a** have been deposited in CCDC with number 1018373. Empirical formula:  $C_{28}H_{29}N_3O_4S_2$ , Formula weight: 535.66, Temperature: 293(2) K, Crystal system: Monoclinic, Space group: P21/n, Unit cell dimensions:  $a = 10.2945(8) \text{ \AA}$ ,  $\alpha = 90^\circ$ ;  $b = 18.1137(16) \text{ \AA}$ ,  $\beta = 105.831(2)^\circ$ ;  $c = 14.6463(12) \text{ \AA}$ ,  $\gamma = 90^\circ$ . Volume:  $2627.5(4) \text{ \AA}^3$ ,  $Z = 4$ , Density (calculated):  $1.354 \text{ Mg/m}^3$ , F(000): 1128, Crystal size:  $0.211 \times 0.175 \times 0.123 \text{ mm}^3$ , Final R indices [ $I > 2\sigma(I)$ ]:  $R1 = 0.0519$ ,  $wR2 = 0.1435$ .



The crystal data of **4a** have been deposited in CCDC with number 1018374. Empirical formula:  $C_{27}H_{24}Cl_3N_3O_4S_2$ , Formula weight: 624.96, Temperature: 293(2) K, Crystal system: Triclinic, Space group: P-1, Unit cell dimensions:  $a = 11.3585(10)$  Å,  $\alpha = 106.420(2)^\circ$ ;  $b = 11.9810(10)$  Å,  $\beta = 108.985(2)^\circ$ ;  $c = 13.4380(12)$  Å,  $\gamma = 104.217(2)^\circ$ . Volume:  $1539.6(2)$  Å<sup>3</sup>,  $Z = 2$ , Density (calculated): 1.348 Mg/m<sup>3</sup>,  $F(000)$ : 644, Crystal size: 0.211 x 0.165 x 0.123 mm<sup>3</sup>, Final R indices [ $I > 2\sigma(I)$ ]:  $R1 = 0.0531$ ,  $wR2 = 0.1487$ .

## 9. Reference

- [1] R.-D. Gao, C. Liu, L.-X. Dai, W. Zhang, S.-L. You, *Org. Lett.* **2014**, *16*, 3919–3921.
- [2] C. Ferrer, C. H. M. Amijs, A. M. Echavarren, *Chem. – Eur. J.* **2007**, *13*, 1358–1373.