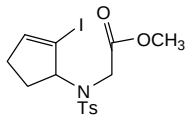
Diels-Alder reactions of 1,2,6,6a-tetrahydro-1-tosyl-cyclopenta[*b*]pyrrol-3(5*H*)-one, 1,2,3,6,7,7a-hexahydro-4*H*-1-tosyl-cyclopenta[*b*]pyridin-4-one and 1,2,5,6,7,7a-hexahydro-3*H*-1-tosyl-indol-3-one: an efficient method to novel nitrogen-containing angular tricyclic skeleton †

Chi-Min Chau*, Kuan-Miao Liu*
cmchau@csmu.edu.tw ; lkm@csmu.edu.tw

General:
Reactions were carried out in oven and flame-dried glassware under a positive pressure of Argon. THF was distilled over sodium/benzophenone. Dichloromethane and xylene was distilled over calcium hydride. Cyclopentadiene was distilled before use. All reagents were purchased commercially and used without further purification. TLC was performed on Merck 5735 DC-plastikfolien Kieselgel 60 F254 precoated plates. Flash column chromatography was performed with silica gel Merck 7736 Kieselgel 60H. 1H-NMR (7.24 ppm for $CDCl_3$ as internal standard) and ^{13}C-NMR (77.0 ppm for $CDCl_3$ as internal standard) spectra were recorded on Varian Unity-400 MHz instrument. Coupling Constants are measured in Hertz. IR spectra was recorded from Bomen MB-100FT spectrometer. Melting point was recorded on Buchi 530 melting-point apparatus and not corrected. HRMS data was obtained from FOEL JMS-HX110 spectrometer. Single crystal X-ray analysis was performed on a Siemens Smart CCD diffractometer.

methyl 2-(N-(2-iodocyclopent-2-enyl)-N-tosylamino)acetate (**3**)

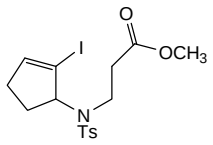


To a solution of compound **1** (50.0 mg, 0.24 mmol) in THF (8 mL) was added triphenyl phosphine (81.0 mg, 0.31 mmol) and methyl 2-(tosylamino)acetate (75.1 mg, 0.31 mmol). After all solid was dissolved completely, DIAD (61 μL, 0.31 mmol) was added slowly to the mixture at 0 °C. The reaction mixture was stirred for additional 1 hour at room temperature (25 °C) followed by removal of the solvent. Purification by flash column chromatography (ethyl acetate/hexane 1:15) afforded compound **3** as a pale yellow solid (88.7 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.35 (brs, 1H), 4.84 (brd, *J* = 6.8 Hz, 1H), 4.03 (AB, *J* = 18.0 Hz, 1H), 3.70 (s, 3H), 3.64 (AB, *J* = 18.0 Hz, 1H), 2.40 (s, 3H), 2.33-2.14 (m, 3H), 2.00-1.92 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1 (C), 146.3 (CH), 143.4 (C), 137.0 (C), 129.3 (CH), 127.7 (CH), 93.4 (C), 70.1 (CH), 52.1 (CH_3), 44.4 (CH_2), 33.0 (CH_2), 27.6 (CH_2), 21.4 (CH_3), 14.0 (C); **IR** (neat) 2977, 2938, 1754, 1737, 1344 cm^{-1}; **MS** (EI) *m/z* 435 (M^+, 6), 308 (39),

249 (56), 94 (100); **HRMS** (EI) *m/z* calcd for $C_{15}H_{18}INO_4S$ 435.0001, found 435.0004; **mp** 155.1~155.9 °C.

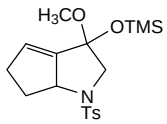
Methyl 3-(*N*-(2-iodocyclopent-2-enyl)-*N*-tosylamino) propanoate (**4**)



To a solution of compound **1** (55.0 mg, 0.26 mmol) in THF (8 mL) was added triphenyl phosphine (89.4 mg, 0.34 mmol) and methyl 3-(tosylamino) propanoate (87.6 mg, 0.34 mmol). After all solid was dissolved completely, DIAD (67 μL, 0.34 mmol) was added slowly to the mixture at 0 °C. The reaction mixture was stirred for additional 1 hour at room temperature (25 °C) followed by removal of the solvent. Purification by flash column chromatography (ethyl acetate/hexane 1:15) afforded compound **4** as a pale yellow solid (96.5 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.30 (brs, 1H), 4.93-4.87 (m, 1H), 3.62 (s, 3H), 3.35-3.25 (m, 1H), 2.99-2.75 (m, 3H), 2.38 (s, 3H), 2.36-2.29 (m, 1H), 2.26-2.16 (m, 1H), 2.09-1.97 (m, 1H), 1.45-1.35 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0 (C), 145.0 (CH), 143.5 (C), 136.6 (C), 129.6 (CH), 127.5 (CH), 95.4 (C), 71.1 (CH), 51.6 (CH_3), 39.5 (CH_2), 36.1 (CH_2), 33.5 (CH_2), 26.1 (CH_2), 21.5 (CH_3); **IR** (neat) 2977, 2938, 1755, 1739, 1343 cm^{-1}; **MS** (EI) *m/z* 449 (M^+, 21), 322 (65), 263 (48), 108 (100), 51 (40); **HRMS** (EI) *m/z* calcd for $C_{16}H_{20}INO_4S$ 449.0158, found 449.0157; **mp** 159.1~160.5 °C.

1,2,3,5,6,6a-Hexahydro-3-methoxy-1-tosyl-3-(trimethylsilyloxy)cyclopenta[b]pyrrole (**6**)

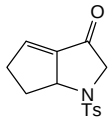


To a stirred solution of substrate **3** (655 mg, 1.51 mmol) in dry THF (10 mL) at -100 °C was added TMSCl (0.38 mL, 3.01 mmol). A solution of *n*-BuLi in *n*-hexane (2.0 M, 1.51 mL, 3.01 mmol) was slowly added at -100 °C, and the reaction mixture was maintained at -100 °C for 30 min. The cooling bath was removed and the reaction mixture was quenched at 0 °C with a solution of NH_4Cl (saturated, 5 mL) and ether (10 mL) and HCl (2N, 5 mL). The mixture was extracted with ether (10 mL x 4). The organic layer was washed with brine (10 mL) and dried over $MgSO_4$. Removal of solvent followed by flash column chromatography (ethyl acetate/hexane 1:25) afforded pure compound **6** as a pale yellow solid (545 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.78

(dd, *J* = 5.2, 2.0 Hz, 1H), 4.36-4.29 (m, 1H), 3.65 (AB, *J* = 10.4 Hz, 1H), 3.59 (AB, *J* = 10.4 Hz, 1H), 3.24 (s, 3H), 2.54-2.42 (m, 3H), 2.38 (s, 3H), 2.06-1.93 (m, 1H), -0.21 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.1 (C), 143.2 (C), 134.6 (C), 129.4 (CH), 127.9 (CH), 125.8 (CH), 98.4 (C), 68.3 (CH), 63.1 (CH_2), 51.0 (CH_3), 35.6 (CH_2), 34.9 (CH_2), 21.4 (CH_3), 0.56 (CH_3); **IR** (neat) 2981, 2936, 1349, 1163 cm^{-1}; **MS** (EI) *m/z* 381 (M^+, 6), 226 (100), 195 (45), 122 (21); **HRMS** (EI) *m/z* calcd for $C_{18}H_{27}NO_4SSi$ 381.1430, found 381.1427; **mp** 157.5~158.3 °C.

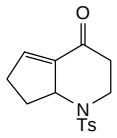
1,2,6,6a-tetrahydro-1-tosyl-cyclopenta[*b*]pyrrol-3(5*H*)-one (**7**)



To a solution of compound **6** (292 mg, 0.77 mmol) in THF (10 mL) was added a solution of acetone (5 mL) and water (5 mL) at 0 °C. *p*TSA (39.5 mg, 0.23 mmol) was then added and the reaction mixture was stirred for 1 hour. The reaction mixture was quenched with water (3 mL) and extracted with ether (10 mL x 4). The organic layer was washed with brine (10 mL) and dried over $MgSO_4$. Concentration and silica gel column chromatography (ethyl acetate/hexane 1:5) gave compound **7** as a white solid (197 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.70 (dd, *J* = 6.0, 2.8 Hz, 1H), 4.40-4.33 (m, 1H), 4.03 (AB, *J* = 16.8 Hz, 1H), 3.52 (AB, *J* = 16.8 Hz, 1H), 2.85-2.78 (m, 2H), 2.70-2.62 (m, 1H), 2.43 (s, 3H), 2.41-2.25 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.1 (C), 144.5 (C), 143.1 (C), 139.6 (CH), 131.4 (C), 129.9 (CH), 128.3 (CH), 68.0 (CH), 61.0 (CH_2), 37.4 (CH_2), 36.7 (CH_2), 21.5 (CH_3); **IR** (neat) 2975, 2880, 1705, 1661 cm^{-1}; **MS** (EI) *m/z* 277 (M^+, 2), 122 (89), 65 (100); **HRMS** (EI) *m/z* calcd for $C_{14}H_{15}NO_3S$ 277.0773, found 277.0770; **mp** 165.3~166.2 °C.

1,2,3,6,7,7a-Hexahydro-4*H*-1-tosyl-cyclopenta[*b*]pyridin-4-one (**8**)

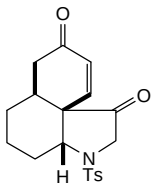


To a stirred solution of substrate **4** (801 mg, 1.78 mol) in dry THF (15 mL) at -100 °C was added TMSCl (0.57 mL, 4.46 mmol). A solution of *n*-BuLi in *n*-hexane (2.0 M, 1.80 mL, 3.57 mmol) was slowly added at -100 °C, and the reaction mixture was maintained at -100 °C for 30 min. The cooling bath was removed and the reaction mixture was quenched at 0 °C with a solution of NH_4Cl (saturated, 8 mL) and ether (10 mL) and HCl (2N, 5 mL). The mixture was extracted with ether (15 mL x 4). The organic layer was washed with brine (20 mL) and dried over $MgSO_4$. Removal of solvent followed by flash

column chromatography (ethyl acetate/hexane 1:3) afforded pure compound **8** as a pale yellow solid (436 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.82 (dd, *J* = 5.4, 2.4 Hz, 1H), 4.39-4.32 (m, 1H), 3.59-3.53 (m, 2H), 2.69 (dt, *J* = 13.2, 6.4 Hz, 1H), 2.56-2.44 (m, 1H), 2.40 (s, 3H), 2.39-2.28 (m, 2H), 2.20-2.02 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.2 (C), 143.7 (C), 142.7 (CH), 139.0 (C), 134.8 (C), 129.8 (CH), 127.1 (CH), 62.0 (CH), 43.0 (CH_2), 38.8 (CH_2), 35.9 (CH_2), 30.2 (CH_2), 21.2 (CH_3); **IR** (neat) 2977, 2880, 1707, 1664 cm^{-1}; **MS** (EI) *m/z* 291 (M^+, 36), 136 (65), 122 (54), 79 (100); **HRMS** (EI) *m/z* calcd for $C_{15}H_{17}NO_3S$ 291.0929, found 291.0925; **mp** 164.3~164.9 °C.

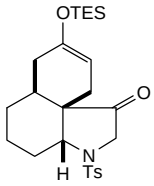
3-tosyl-2,3,3a,4,5,6,6a,7-octahydro-3-aza-cyclopenta[*d*]naphthalene-1,8-dione (**22**)



To a solution of compound **9** (65.0 mg, 0.42 mmol) in toluene (8 mL) was added Danishefsky diene (290 mg, 1.69 mmol). The mixture was refluxed under Ar for 14 hours. After cooling to room temperature, 6N HCl (1 mL) was added, and stirred for additional 1 hour. Addition of water (2 mL) and ether (2 mL) was followed by extraction with ether (5 mL x 4). The combined organic layer was washed with saturated $NaHCO_3$ (5 mL) and brine (5 mL) and dried over $MgSO_4$. After filtration and concentration, purification by flash column chromatography (ethyl acetate/hexane 1:2) afforded compound **22** as a white solid (106 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.12 (d, *J* = 10.2 Hz, 1H), 6.04 (dd, *J* = 10.2, 1.6 Hz, 1H), 4.12 (AB, *J* = 18.2 Hz, 1H), 3.51 (AB, *J* = 18.2 Hz, 1H), 3.37 (brs, 1H), 2.59 (dd, *J* = 17.0, 5.6 Hz, 1H), 2.53-2.45 (m, 2H), 2.44 (s, 3H), 2.17 (dd, *J* = 16.8, 4.4 Hz, 1H), 1.94-1.82 (m, 1H), 1.74-1.50 (m, 3H), 1.44-1.31 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.7 (C), 197.4 (C), 144.8 (C), 141.9 (CH), 132.7 (CH), 131.6 (C), 130.1 (CH), 127.9 (CH), 63.4 (CH), 56.3 (C), 54.5 (CH_2), 39.6 (CH_2), 33.5 (CH), 27.7 (CH_2), 25.4 (CH_2), 21.6 (CH_3), 18.6 (CH_2); **IR** (neat) 1711, 1693, 1672, 1344, 966 cm^{-1}; **MS** (EI) *m/z* 359 (M^+, 7), 155 (37), 148 (79), 106 (41), 91 (100), 65 (44); **HRMS** (EI) *m/z* calcd for $C_{19}H_{21}NO_4S$ 359.1191, found 359.1189.

3-tosyl-8--triethylsilyloxy-3,3a,4,5,6,6a,7,10-octahydro-2*H*-3-aza-cyclopenta[*d*]naphthalen-1-one (**23**)



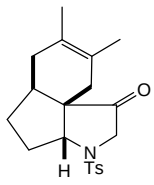
Compound **9** (61.4 mg, 0.21 mmol) and (buta-1,3-dien-2-yloxy)triethylsilane **14** (117 mg, 0.63 mmol) was dissolved in xylene (2 mL). The mixture was transferred into sealed tube and degassed three times under vacuum. The sealed tube was put into the oven which was set at 180 °C for 24 hours. The crude mixyure was purified by flash column chromatography (ethyl acetate/hexane 1:10) to afford compound **23** as a liquid (52.3 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.60 (brs, 1H), 3.93 (AB, *J* = 18.2 Hz, 1H), 3.37 (AB, *J* = 18.2 Hz, 1H), 3.10 (t, *J* = 4.0 Hz, 1H), 2.42 (s, 3H), 2.31-2.22 (m ,1H), 2.20-2.15 (m , 2H), 1.93-1.30 (m , 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.5 (C), 148.4 (C), 144.1 (C), 132.5 (C), 129.8 (CH), 127.6 (CH), 98.3 (CH), 61.8 (CH), 53.3 (CH_2), 50.8 (C), 32.2 (CH_2), 30.3 (CH), 27.7 (CH_2), 25.6 (CH_2), 25.3 (CH_2), 21.5 (CH_3), 19.4 (CH_2), 6.6 (CH_3), 4.8 (CH_2); **IR** (neat) 1715, 1343, 1216, 841 cm^{-1}; **MS** (EI) *m/z* 344 (M^+, 1), 320 (75), 292 (34), 263 (96), 155 (49), 91 (100), 86 (62); **HRMS** (EI) *m/z* calcd for $C_{19}H_{22}NO_3S$ 344.1320, found 344.1322.

General procedure for $BF_3{\cdot}OEt_2$ catalysed cycloadditions:

The enone (1 mmol equiv.) was dissolved in a dichloromethane (3 mL) and cooled to 0°C. $BF_3{\cdot}OEt_2$ (0.3 equiv.) was slowly added to the solution and it was allowed to stir for 10min, followed by the slow addition of diene (2 equiv.). The mixture was stirred for additional 30 min. The solution was quenched with water (3 mL) and ether (6mL), and was extracted with diethyl ether (6 mL x 4) and then washed with brine (6 mL). The combined organic layers were dried over anhydrous sodium sulfate. After filtration and concentration, purification by flash column chromatography afforded the desired product.

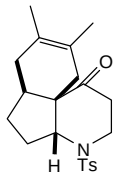
5,6-Dimethyl-1-tosyl-2,3,4,7,7a,8,9,9a-octahydro-1*H*-indeno[1,7a-*b*]pyrrol-3-one (**24**)



The reaction of perhydropyrrolone **7** with 2,3-dimethyl-1,3-butadiene **15** gave the cycloadduct **24** in 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.87 (dd, *J* = 6.0, 5.2 Hz, 1H), 3.80 (AB, *J* = 18.4 Hz, 1H), 3.73 (AB, *J* = 18.4 Hz, 1H), 2.41 (s, 3H), 2.39-2.32 (m, 1H), 2.11-1.94 (m, 3H), 1.86-1.63 (m, 4H), 1.62 (s, 3H), 1.54 (s, 3H), 1.32-1.21 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.2 (C), 144.0 (C), 134.8 (C), 129.9 (CH), 127.5 (CH), 127.0 (C), 123.0 (C), 69.5 (CH), 61.3 (C), 53.4 (CH_2), 39.9 (CH), 34.7 (CH_2), 33.9 (CH_2), 31.7 (CH_2), 31.1 (CH_2), 21.5 (CH_3), 19.6 (CH_3), 19.3 (CH_3); **IR** (neat) 1714, 1374, 1370, 1345 cm^{-1}; **MS** (EI) *m/z* 359 (M^+, 5), 204 (23), 161 (54), 119 (78), 91 (100); **HRMS** (EI) *m/z* calcd for $C_{20}H_{25}NO_3S$ 359.1555, found 359.1553.

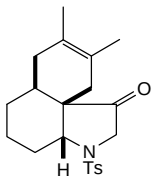
6,7-Dimethyl-1-tosyl-1,2,3,4,5,8,8a,9,10,10a-decahydroindeno[1,7a-*b*]pyridin-4-one (**25**)



The reaction of perhydropyridinone **8** with 2,3-dimethyl-1,3-butadiene **15** gave the cycloadduct **25** in 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 4.14 (t, *J* = 8.4 Hz, 1H), 4.10-4.03 (m, 1H), 3.13 (td, *J* = 12.8, 2.8 Hz, 1H), 2.79-2.62 (m, 2H), 2.39 (s, 3H), 2.31-2.21 (m, 2H), 2.05-1.96 (m, 1H), 1.74 (brd, 1H), 1.63 (s, 6H), 1.50-1.41 (m, 1H), 1.20-0.99 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.1 (C), 143.5 (C), 137.0 (C), 129.8 (CH), 127.1 (CH), 126.2 (C), 123.4 (C), 61.6 (CH), 58.0 (C), 40.3 (CH_2), 38.6 (CH_2), 36.4 (CH_2), 35.0 (CH), 34.6 (CH_2), 28.6 (CH_2), 23.6 (CH_2), 21.5 (CH_3), 19.6 (CH_3), 19.2 (CH_3); **IR** (neat) 1715, 1375, 1371, 1343 cm^{-1}; **MS** (EI) *m/z* 373 (M^+, 4), 218 (53), 161 (33), 119 (63), 91 (100); **HRMS** (EI) *m/z* calcd for $C_{21}H_{27}NO_3S$ 373.1712, found 373.1714.

5,6-Dimethyl-1-tosyl-1,2,3,4,7,7a,8,9,10,10a-decahydrobenzo[*d*]indol-3-one (**26**)

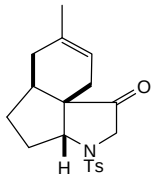


The reaction of perhydroindolone **9** with 2,3-dimethyl-1,3-butadiene **15** gave the cycloadduct **25** in 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 3.93 (AB, *J* = 18.0 Hz, 1H), 3.38 (AB, *J* = 18.0 Hz, 1H), 3.09 (t, *J* = 8.4 Hz, 1H), 2.42 (s, 3H),

2.31-2.22 (m, 1H), 2.08-1.98 (m, 3H), 1.82-1.22 (m, 13H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.3 (C), 144.1 (C), 133.0 (C), 129.9 (CH), 127.6 (CH), 123.9 (C), 120.4 (C), 62.1 (CH), 53.3 (CH_2), 52.3 (C), 34.3 (CH_2), 32.8 (CH_2), 29.8 (CH), 27.5 (CH_2), 25.6 (CH_2), 21.5 (CH_3), 19.4 (CH_2), 19.1 (CH_3), 18.6 (CH_3); **IR** (neat) 1715, 1374, 1371, 1344 cm^{-1}; **MS** (EI) *m/z* 373 (M^+, 5), 218 (14), 161 (75), 119 (34), 91 (100); **HRMS** (EI) *m/z* calcd for $C_{21}H_{27}NO_3S$ 373.1712, found 373.1711.

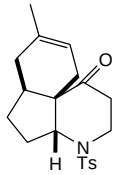
6-Methyl-1-tosyl-2,3,4,7,7a,8,9,9a-octahydro-1*H*-indeno[1,7a-*b*]pyrrol-3-one (**27**)



The reaction of perhydropyrrolone **7** with 2-methyl-1,3-butadiene **16** gave the cycloadduct **27** in 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.29 (brs, 1H), 3.93 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.75 (s, 2H), 2.42 (s, 3H), 2.10-2.00 (m, 2H), 1.88-1.71 (m, 4H), 1.67 (s, 3H), 1.64-1.56 (m, 2H), 1.38-1.28 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.0 (C), 144.1 (C), 135.3 (C), 134.5 (C), 129.9 (CH), 127.6 (CH), 117.2 (CH), 69.5 (CH), 59.9 (C), 53.5 (CH_2), 39.4 (CH), 31.9 (CH_2), 31.7 (CH_2), 30.7 (CH_2), 28.2 (CH_2), 23.8 (CH_3), 21.5 (CH_3); **IR** (neat) 1714, 1665, 1376, 1345, 965 cm^{-1}; **MS** (EI) *m/z* 345 (M^+, 11), 190 (63), 134 (100), 133 (61), 91 (45); **HRMS** (EI) *m/z* calcd for $C_{19}H_{23}NO_3S$ 345.1399, found 345.1396.

7-Methyl-1-tosyl-1,2,3,4,5,8,8a,9,10,10a-decahydroindeno[1,7a-*b*]pyridin-4-one (**28**)

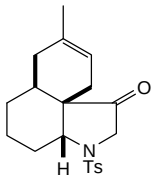


The reaction of perhydropyridinone **8** with 2-methyl-1,3-butadiene **16** gave the cycloadduct **28** in 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 5.29 (brs, 1H), 4.26 (t, *J* = 8.0 Hz, 1H), 4.08-4.01 (m, 1H), 3.15 (td, *J* = 12.4, 2.8 Hz, 1H), 2.76-2.62 (m, 2H), 2.39 (s, 3H), 2.33-2.22 (m, 2H), 1.98 (dd, *J* = 17.2, 7.6 Hz, 1H), 1.80-1.71 (m, 1H), 1.66 (s, 1H), 1.65-1.52 (m, 3H), 1.23-1.07 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.0 (C), 143.5 (C), 136.9 (C), 134.1 (C), 129.7 (CH), 127.1 (CH), 117.5 (CH), 61.3 (CH), 56.6 (C), 40.3 (CH_2), 38.4 (CH_2), 34.5 (CH), 32.5 (CH_2), 30.0

(CH_2), 28.9 (CH_2), 23.7 (CH_3), 23.2 (CH_2), 21.5 (CH_3); **IR** (neat) 1715, 1666, 1376, 1343, 969 cm^{-1}; **MS** (EI) *m/z* 359 (M^+, 5), 204 (55), 148 (100), 147 (57), 91 (68); **HRMS** (EI) *m/z* calcd for $C_{20}H_{25}NO_3S$ 359.1555, found 359.1558.

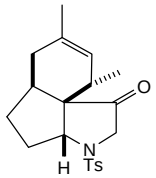
6-Methyl-1-tosyl-1,2,3,4,7,7a,8,9,10,10a-decahydrobenzo[*d*]indol-3-one (**29**)

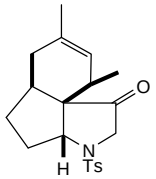


The reaction of perhydroindolone **9** with 2-methyl-1,3-butadiene **16** gave the cycloadduct **29** in 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.19 (brs, 1H), 3.95 (AB, *J* = 17.8 Hz, 1H), 3.35 (AB, *J* = 17.8 Hz, 1H), 3.04 (brs, 1H), 2.42 (s, 3H), 2.39-2.31 (m, 1H), 2.14-2.00 (m, 2H), 1.91-1.21 (m, 8H), 1.62 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.2 (C), 144.1 (C), 132.7 (C), 132.2 (C), 129.9 (CH), 127.7 (CH),115.8 (CH), 62.3 (CH), 53.5 (CH_2),51.0 (C), 32.7 (CH_2), 29.8 (CH), 27.7 (CH_2), 26.6 (CH_2), 25.3 (CH_2), 23.6 (CH_3), 21.5 (CH_3), 19.5 (CH_2); **IR** (neat) 1715, 1664, 1377, 1345, 966 cm^{-1}; **MS** (EI) *m/z* 359 (M^+, 11), 204 (17), 148 (100), 147 (68), 91 (45); **HRMS** (EI) *m/z* calcd for $C_{20}H_{25}NO_3S$ 359.1555, found 359.1553.

4,6-Dimethyl-1-tosyl-2,3,4,7,7a,8,9,9a-octahydro-1*H*-indeno[1,7a-*b*]pyrrol-3-one (**30a**, **30b**)





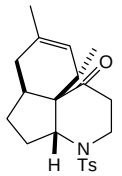
The reaction of perhydropyrrolone **7** with 2-methyl-1,3-pentadiene **17** gave the cycloadduct **30a** and **30b** in 67% and 8% yields.

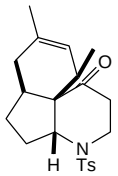
30a: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.16 (brs, 1H), 3.90 (dd, *J* = 6.4, 3.8 Hz, 1H), 3.82 (AB, *J* = 17.8 Hz, 1H), 3.50 (AB, *J* = 17.8 Hz, 1H), 2.43 (s, 3H), 2.42-2.35 (m, 1H), 2.15-2.09 (m, 3H), 1.98-1.86 (m, 2H), 1.76-1.71 (m, 1H), 1.66 (s, 3H), 1.52-1.45 (m ,1H), 0.67 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 210.9 (C), 144.2 (C), 133.3 (C), 132.9 (C), 129.8 (CH), 127.8 (CH), 123.6 (CH), 69.6 (CH), 63.2 (C), 56.1 (CH_2), 40.3 (CH), 32.5 (CH_2), 32.1 (CH), 31.7 (CH_2), 31.0 (CH_2), 23.4 (CH_3), 21.6 (CH_3), 16.0 (CH_3); **IR** (neat) 1715, 1666, 1374, 1373, 1345, 966 cm^{-1}; **MS** (EI) *m/z* 359 (M^+, 8), 204 (40), 147 (36), 91 (100); **HRMS** (EI) *m/z*

calcd for $C_{20}H_{25}NO_3S$ 359.1555, found 359.1552.

30b: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.09 (d, *J* = 1.5 Hz, 1H), 4.13 (dd, *J* = 7.0, 3.8 Hz, 1H), 3.72 (s, 2H), 2.52-2.49 (m, 1H), 2.41 (s, 3H), 2.34-2.31 (m, 1H), 2.17-2.12 (m, 1H), 1.84-1.79 (m, 1H), 1.67 (s, 3H), 1.66-1.55 (m, 3H), 1.29-1.20 (m, 1H), 0.65 (d, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 216.9 (C), 143.9 (C), 136.9 (C), 135.4 (C), 129.8 (CH), 127.4 (CH), 125.2 (CH), 66.2 (C), 64.6 (CH), 54.6 (CH_2), 43.1 (CH), 34.7 (CH), 33.8 (CH_2), 32.5 (CH_2), 32.1 (CH_2), 23.4 (CH_3), 21.6 (CH_3), 16.0 (CH_3); **IR** (neat) 1715, 1665, 1376, 1371, 1343, 966 cm^{-1}; **MS** (EI) *m/z* 359 (M^+, 5), 204 (55), 147 (28), 91 (100); **HRMS** (EI) *m/z* calcd for $C_{20}H_{25}NO_3S$ 359.1555, found 359.1554.

5,7-Dimethyl-1-tosyl-1,2,3,4,5,8,8a,9,10,10a-decahydroindeno[1,7a-*b*]pyridin-4-one (**31a**, **31b**)



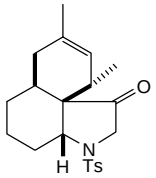
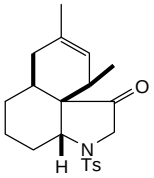


The reaction of perhydropyridinone **8** with 2-methyl-1,3-pentadiene **17** gave the cycloadduct **31a** and **31b** in 62% and 8% yields.

31a: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 5.34-5.31 (brs, 1H), 4.39 (t, *J* = 9.0 Hz, 1H), 4.11-4.06 (m, 1H), 3.10 (td, *J* = 12.7, 2.9 Hz, 1H), 2.69-2.64 (m, 2H), 2.56-2.53 (m, 1H), 2.27 (d, *J* = 14.0 Hz, 1H), 2.09 (dd, *J* = 18.0, 8.4 Hz, 1H), 1.66-1.52 (m, 2H), 1.63 (s, 1H), 1.47 (dd, *J* = 18.0, 8.2 Hz, 1H), 1.19-1.08 (m, 2H), 0.68 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 210.7 (C), 143.5 (C), 136.8 (C), 130.7 (C), 129.7 (CH), 127.1 (CH), 124.0 (CH), 61.4 (CH), 41.0 (CH_2), 39.8 (CH_2), 32.7 (CH_2), 31.9 (CH), 30.6 (CH), 29.2 (CH_2), 60.7 (C), 23.5 (CH_3), 21.9 (CH_2), 21.5 (CH_3), 18.5 (CH_3); **IR** (neat) 1715, 1665, 1377, 1375, 1345, 966 cm^{-1}; **MS** (EI) *m/z* 373 (M^+, 6), 218 (50), 161 (100), 147 (36), 91 (77); **HRMS** (EI) *m/z* calcd for $C_{21}H_{27}NO_3S$ 373.1712, found 373.1712.

31b: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.22-5.20 (brs, 1H), 4.34 (td, *J* = 8.2, 1.4 Hz, 1H), 4.01-3.95 (m, 1H), 3.12 (td, *J* = 12.3, 4.0 Hz, 1H), 2.75-2.64 (m, 1H), 2.63-2.58 (m, 1H), 2.52 (dd, *J* = 16.8, 2.4 Hz, 1H), 2.41 (s, 3H), 2.32-2.28 (m, 1H), 2.05 (dd, *J* = 16.2, 7.3 Hz, 1H), 1.70 (s, 3H), 1.63 (dd, *J* = 16.2, 5.7 Hz, 1H), 1.48-1.39 (m, 2H), 1.24 (d, *J* = 7.5 Hz, 3H), 1.12-0.99 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 213.9 (C), 143.6 (C), 136.3 (C), 135.4 (C), 129.7 (CH), 127.3 (CH), 125.9 (CH), 61.4 (C), 57.9 (CH), 41.7 (CH), 41.0 (CH_2), 38.8 (CH_2), 37.9 (CH), 32.9 (CH_2), 29.5 (CH_2), 24.4 (CH_2), 23.7 (CH_3), 21.5 (CH_3), 17.5 (CH_3); **IR** (neat) 1715, 1664, 1374, 1372, 1345, 967 cm^{-1}; **MS** (EI) *m/z* 373 (M^+, 3), 218 (34), 161 (100), 147 (33), 91 (45); **HRMS** (EI) *m/z* calcd for $C_{21}H_{27}NO_3S$ 373.1712, found 373.1715.

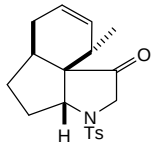
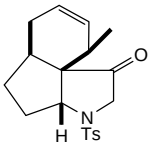
4,6-Dimethyl-1-tosyl-1,2,3,4,7,7a,8,9,10,10a-decahydrobenzo[*d*]indol-3-one (**32a**, **32b**)

The reaction of perhydroindolone **9** with 2-methyl-1,3-pentadiene **17** gave the cycloadduct mixture **32a** and **32b** in a total yield of 70%.

32a: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.09 (brs, 1H), 3.83 (AB, *J* = 18.0 Hz, 1H), 3.43(brs, 1H), 3.33 (AB, *J* = 18.0 Hz, 1H), 2.43 (s, 3H), 2.20-2.04 (m, 4H), 1.70-1.04 (m, 5H), 1.63 (s, 3H), 0.67 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.6 (C), 144.1 (C), 133.3 (C), 131.2 (C), 129.9 (CH), 127.7 (CH), 122.8 (CH), 60.8 (CH), 54.9 (C), 54.1 (CH_2), 32.6 (CH_2), 30.0 (CH), 29.2 (CH), 27.5 (CH_2), 25.9 (CH_2), 23.4 (CH_3), 21.6 (CH_3), 19.3 (CH_2), 16.1 (CH_3); **IR** (neat) 1716, 1664, 1376, 1372, 1343, 965 cm^{-1}; **MS** (EI) *m/z* 373 (M^+, 4), 218 (57), 161 (100), 147 (28), 91 (75); **HRMS** (EI) *m/z* calcd for $C_{21}H_{27}NO_3S$ 373.1712, found 373.1712.

4-Methyl-1-tosyl-2,3,4,7,7a,8,9,9a-octahydro-1*H*-indeno[1,7a-*b*]pyrrol-3-one (**33a**, **33b**)

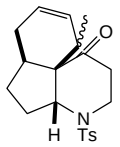
The reaction of perhydropyrrolone **7** with 1,3-pentadiene **18** gave the cycloadduct **33a** and **33b** in 66% and 8% yields.

33a: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.73-5.69 (m, 1H), 5.50-5.46 (m ,1H), 3.93 (dd, *J* = 6.5, 3.8 Hz, 1H), 3.83 (AB, *J* = 17.8 Hz, 1H), 3.51 (AB , *J* = 17.8 Hz, 1H), 2.43 (s, 3H), 2.40-0.81 (m, 8H), 0.67(d, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 210.7 (C), 144.2 (C), 133.0 (C), 129.7 (CH), 127.7 (CH), 127.6 (CH), 125.8 (CH), 69.6 (CH), 63.2 (C), 56.1 (CH_2), 39.8 (CH), 31.7 (CH_2), 31.6 (CH_2), 31.0 (CH), 25.9 (CH_2), 21.7 (CH_3), 15.6 (CH_3); **IR** (neat) 1716, 1645, 1376, 1345, 966 cm^{-1}; **MS** (EI) *m/z* 345 (M^+, 5), 190 (54), 133 (55), 91 (100); **HRMS** (EI) *m/z* calcd for $C_{19}H_{23}NO_3S$ 345.1399, found 345.1396.

33b: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.82-5.78 (m, 1H), 5.42 (brd, *J* = 9.6 Hz, 1H), 4.16 (dd, *J* = 7.1, 3.5 Hz, 1H), 3.72 (s, 2H), 2.53-2.48 (m, 1H), 2.42 (s, 3H), 2.38-2.32 (m, 1H), 2.20-2.13 (m, 1H), 1.91-1.83 (m, 1H), 1.80-1.56 (m, 3H), 1.34-1.29 (m, 1H), 0.68 (d, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 216.6 (C), 143.9 (C), 135.4 (C), 131.6 (CH), 129.8 (CH), 128.6 (CH), 127.3

(CH), 66.2 (C), 64.4 (CH), 54.4 (CH_2), 42.2 (CH), 34.1 (CH), 32.5 (CH_2), 31.7 (CH_2), 28.5 (CH_2), 21.6 (CH_3), 15.9 (CH_3); **IR** (neat) 1715, 1647, 1376, 1343, 968 cm^{-1}; **MS** (EI) *m/z* 345 (M^+, 9), 190 (36), 133 (65), 91 (100); **HRMS** (EI) *m/z* calcd for $C_{19}H_{23}NO_3S$ 345.1399, found 345.1398.

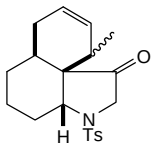
5-Methyl-1-tosyl-1,2,3,4,5,8,8a,9,10,10a-decahydroindeno[1,7a-*b*]pyridin-4-one (**34a**, **34b**)



The reaction of perhydropyridinone **8** with 1,3-pentadiene **18** gave the cycloadduct **34a** and **34b** in a total yield of 66%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.65 (m, 4H), 7.32-7.23 (m, 4H), 5.79-5.76 (m, 1H), 5.64-5.53 (m, 1H), 5.54-5.51 (m, 1H), 5.48-5.45 (m, 1H), 4.43-4.41 (m, 1H), 4.13-4.09 (m, 1H), 4.02-3.97 (m, 1H), 3.11 (td, *J* = 12.0, 4.1 Hz, 1H), 3.05-2.99 (m, 1H), 2.78-2.58 (m, 6H), 2.55-2.45 (m, 2H), 2.44-2.34 (m, 2H), 2.42 (s, 3H), 2.41 (s, 3H), 2.13-2.06 (m, 2H), 2.00-1.94 (m, 1H), 1.89-1.84 (m, 1H), 1.76-1.64 (m, 2H), 1.54-1.37 (m, 2H), 1.27 (s, 3H), 2.26 (s, 3H), 1.17-1.06 (m, 2H), 1.13 (s, 3H), 1.12 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.8 (C), 143.6 (C), 136.3 (C), 134.7 (C), 132.2 (CH), 131.5 (CH), 129.8 (CH), 129.8 (CH), 127.6 (CH), 127.5 (CH), 127.0 (CH), 124.2 (CH), 66.5 (CH), 61.6 (C), 58.5 (C), 57.6 (CH), 48.0 (CH_2), 40.9 (CH_2), ,40.5 (CH), 39.7 (CH_2), 38.8 (CH_2), 37.0 (CH), 35.0 (CH), 29.9 (CH_2), 28.2 (CH), 27.7 (CH_2), 27.1 (CH_2), 27.0 (CH_2), 25.3 (CH_2), 24.3 (CH_2), 21.5 (CH_3), 20.5 (CH_3), 17.5 (CH_3); **IR** (neat) 1715, 1649, 1377, 1342, 968 cm^{-1}; **MS** (EI) *m/z* 359 (M^+, 3), 204 (36), 155 (24), 147 (76), 91 (100); **HRMS** (EI) *m/z* calcd for $C_{20}H_{25}NO_3S$ 359.1555, found 359.1552.

4-Methyl-1-tosyl-1,2,3,4,7,7a,8,9,10,10a-decahydrobenzo[*d*]indol-3-one (**35a**, **35b**)

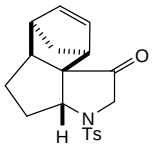


The reaction of perhydroindolone **9** with 1,3-pentadiene **18** gave the cycloadduct mixture **35a** and **35b** in a total yield of 68%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.64 (m, 3.6H), 7.36-7.28 (m, 3.6H), 5.69-5.56 (m, 1.8H), 5.42-5.32 (m, 1.8H), 3.99 (t, *J* = 4.0 Hz, 1H), 3.87 (AB, *J* = 17.4 Hz, 0.8H), 3.86 (AB, *J* = 18.4 Hz, 1H), 3.65 (AB, *J* = 18.4 Hz, 1H), 3.40 (t, *J* = 4.4 Hz, 0.8H), 3.32 (AB,

J = 17.4 Hz, 0.8H), 2.42 (s, 2.4H), 2.41 (s, 3H), 2.32-1.20 (m, 18H), 0.78 (d, *J* = 7.6 Hz, 3H), 0.70 (d, *J* = 7.2 Hz, 2.4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.9 (C), 208.3 (C), 144.1 (C), 143.8 (C), 135.5 (C), 133.0 (C), 130.6 (CH), 129.9 (CH), 129.8 (CH), 128.6 (CH), 127.7 (CH), 127.3 (CH), 126.1 (CH), 124.0 (CH), 60.7 (CH), 59.3 (CH), 55.0 (C), 54.9 (C), 54.5 (CH_2), 54.3 (CH_2), 36.5 (CH), 31.6 (CH), 30.3 (CH_2), 29.3 (CH), 28.9 (CH), 27.7 (CH_2), 27.5 (CH_2), 26.6 (CH_2), 25.6 (CH_2), 25.4 (CH_2), 21.5 (CH_3), 19.4 (CH_2), 16.6 (CH_3), 16.5 (CH_2), 15.7 (CH_3); **IR** (neat) 1717, 1649, 1375, 1343, 969 cm^{-1}; **MS** (EI) *m/z* 359 (M^+, 5), 204 (26), 155 (24), 147 (76), 91 (100); **HRMS** (EI) *m/z* calcd for $C_{20}H_{25}NO_3S$ 359.1555, found 359.1553.

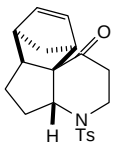
5-tosyl-5-azatetracyclo[8.2.1.$0^{2,6}$.$0^{2,9}$]tridec-11-en-3-one (**36**)



The reaction of perhydropyrrolone **7** with cyclopentadiene **19** gave the cycloadduct **36** in 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.30 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.03 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.88 (AB, *J* = 18.2 Hz, 1H), 3.83 (t, *J* = 6.6 Hz, 1H), 3.79 (AB, *J* = 18.2 Hz, 1H), 2.80-2.73 (m, 2H), 2.42 (s, 3H), 2.26 (brs, 1H), 2.11-1.96 (m, 2H), 2.11-1.96 (m, 2H), 1.83-1.68 (m, 2H), 1.44-1.40 (m, 2H), 1.11-1.01 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.1 (C), 144.0 (C), 139.8 (CH), 136.0 (CH), 134.5 (C), 129.8 (CH), 127.4 (CH), 69.1 (C), 66.3 (CH), 55.0 (CH), 54.1 (CH_2), 50.6 (CH_2), 49.3 (CH), 46.0 (CH), 36.8 (CH_2), 27.6 (CH_2), 21.5 (CH_3); **IR** (neat) 1716, 1666, 1647, 1345, 970 cm^{-1}; **MS** (EI) *m/z* 343 (M^+, 3), 188 (42), 131 (69), 91 (100), 66 (58); **HRMS** (EI) *m/z* calcd for $C_{19}H_{21}NO_3S$ 343.1242, found 343.1240.

6-tosyl-6-azatetracyclo[9.2.1.$0^{2,7}$.$0^{2,10}$]tetradec-12-en-3-one (**37**)

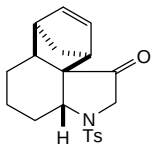


The reaction of perhydropyridinone **8** with cyclopentadiene **19** gave the cycloadduct **37** in 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.28 (dd, *J* = 5.4, 3.0 Hz, 1H), 6.15 (dd, *J* = 5.4, 3.0 Hz, 1H), 4.07-4.00 (m, 1H), 3.88 (dd, *J* = 12.4, 5.2 Hz, 1H), 3.33-3.19 (m, 2H), 2.78-2.68 (m, 2H), 2.62 (brs, 1H), 2.41 (s, 3H),

2.40-2.38 (m, 1H), 1.76 (AB, *J* = 8.0 Hz, 1H), 1.69-1.39 (m, 3H), 1.48 (AB, *J* = 8.0 Hz, 1H), 0.78-0.68 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.3 (C), 143.6 (C), 139.2 (C), 136.9 (C), 136.7 (CH), 129.7 (CH), 127.1 (CH), 66.9 (C), 60.4 (CH), 50.5 (CH_2), 49.1 (CH), 47.3 (CH), 45.3 (CH), 41.0 (CH_2), 39.9 (CH_2), 32.3 (CH_2), 25.1 (CH_2), 21.5 (CH_3); **IR** (neat) 1715, 1665, 1647, 1344, 969 cm^{-1}; **MS** (EI) *m/z* 357 (M^+, 6), 290 (53), 263 (71), 155 (42), 136 (51), 91 (100), 66 (49), 65 (42); **HRMS** (EI) *m/z* calcd for $C_{20}H_{23}NO_3S$ 357.1399, found 357.1402.

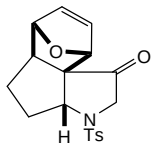
5-tosyl-5-azatetracyclo[9.2.1.0^{2,6}.0^{2,10}]tetradec-12-en-3-one (**38**)



The reaction of perhydroindolone **9** with cyclopentadiene **19** gave the cycloadduct **38** in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.34 (dd, *J* = 6.0, 3.2 Hz, 1H), 5.98 (dd, *J* = 6.0, 3.2 Hz, 1H), 3.97 (AB, *J* = 18.2 Hz, 1H), 3.68 (dd, *J* = 11.0, 6.0 Hz, 1H), 3.67 (AB, *J* = 18.2 Hz, 1H), 2.79 (brs, 1H), 2.59-2.54 (m, 1H), 2.42 (s, 3H), 2.06 (brs, 1H), 2.02-1.93 (m, 1H), 1.61 (brs, 1H), 1.54 (AB, *J* = 8.6 Hz, 1H), 1.52-1.43 (m, 1H), 1.34-1.25 (m, 1H), 1.23-1.12 (m, 1H), 1.09 (AB, *J* = 8.6 Hz, 1H), 1.07-0.94 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 212.3 (C), 143.9 (C), 139.8 (CH), 136.2 (CH), 136.0 (C), 129.8 (CH), 127.2 (CH), 62.0 (CH), 60.5 (C), 51.4 (CH), 51.1 (CH_2), 49.4 (CH), 45.2 (CH_2), 42.0 (CH), 29.9 (CH_2), 25.4 (CH_2), 21.5 (CH_3), 19.9 (CH_2); **IR** (neat) 1715, 1666, 1649, 1343, 969 cm^{-1}; **MS** (EI) *m/z* 357 (M^+, 3), 290 (64), 263 (69), 155 (53), 136 (51), 91 (100), 66 (58), 65 (44); **HRMS** (EI) *m/z* calcd for $C_{20}H_{23}NO_3S$ 357.1399, found 357.1398.

4-(2-furyl)-1-tosyl-perhydrocyclopenta[*b*]pyrrol-3-one (**39**)

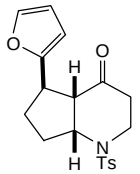


The reaction of perhydropyrrolone **7** with furan **20** gave the cycloadduct **39** in 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 6.49 (dd, *J* = 5.8, 1.6 Hz, 1H), 6.26 (dd, *J* = 5.8, 1.6 Hz, 1H), 4.67 (brs, 1H), 4.36 (brs, 1H), 4.14 (t, *J* = 5.4 Hz, 1H), 3.84 (AB, *J* = 18.2 Hz, 1H), 3.74 (AB, *J* = 18.2 Hz, 1H), 2.43 (s, 3H), 2.28-2.18 (m, 2H), 2.10-1.98 (m, 2H), 1.64-1.54 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 209.9 (C), 144.4 (C), 137.4 (CH), 133.9 (CH), 133.8 (C), 130.0 (CH), 127.8

(CH), 85.4 (CH), 82.5 (CH), 69.5 (C), 67.9 (CH), 55.5 (CH), 55.5 (CH_2), 35.3 (CH_2), 28.6 (CH_2), 21.6 (CH_3); **IR** (neat) 1715,1667, 1346, 1172, 968 cm^{-1}; **MS** (EI) *m/z* 345 (M^+, 21), 190 (41), 133 (71), 91 (100); **HRMS** (EI) *m/z* calcd for $C_{18}H_{19}NO_4S$ 345.1035, found 345.1034.

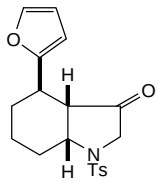
5-(2-furyl)-1-tosyl-perhydrocyclopenta[*b*]pyridin-4-one (**40**)



The reaction of perhydropyridinone **8** with furan **20** gave the product **40** in 40% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 3H), 6.25 (brs, 1H), 6.02 (brd, *J* = 3.2 Hz, 1H), 4.76-4.64 (m, 1H), 4.08-4.00 (m, 1H), 3.91 (ddd, *J* = 8.9, 6.4, 2.4 Hz, 1H), 3.31 (ddd, *J* = 13.5, 10.4, 3.2 Hz, 1H), 2.79 (d, *J* = 7.2 Hz, 1H), 2.52-2.32 (m, 2H), 2.41 (s, 3H), 2.11-2.00 (m, 1H), 1.82-1.74 (m, 1H), 1.70-1.58 (m, 1H), 1.40-1.28 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.6 (C), 156.9 (C), 143.9 (C), 141.3 (CH), 136.1 (C), 129.9 (CH), 127.1 (CH), 110.3 (CH), 105.2 (CH), 59.0 (CH), 57.5 (CH), 41.6 (CH_2), 40.2 (CH_2), 31.5 (CH), 28.4 (CH_2), 27.1 (CH_2), 21.5 (CH_3); **IR** (neat) 3018, 2952, 1715, 1344, 1220 cm^{-1}; **MS** (EI) *m/z* 359 (M^+, 65), 204 (55), 147 (71), 91 (100), 65 (20); **HRMS** (EI) *m/z* calcd for $C_{19}H_{21}NO_4S$ 359.1191, found 359.1189.

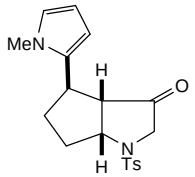
4-(2-furyl)-1-tosyl-perhydro-3-indolone (**41**)



The reaction of perhydroindolone **9** with furan **20** gave the product **41** in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 3H), 6.30-6.28 (m, 1H), 5.95 (brd, *J* = 3.2 Hz, 1H), 4.51-4.43 (m, 1H), 3.87 (AB, *J* = 18.4 Hz, 1H), 3.65 (AB, *J* = 18.4 Hz, 1H), 3.56 (brs, 1H), 2.56 (brd, 1H), 2.41 (s, 3H), 2.12-2.02 (m, 1H), 1.85-1.75 (m, 1H), 1.54-1.04 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.6 (C), 156.3 (C), 144.2 (C), 141.3 (CH), 135.7 (C), 130.1 (CH), 127.2 (CH), 110.2 (CH), 105.3 (CH), 56.7 (CH), 51.4 (CH_2), 51.2 (CH), 31.5 (CH), 29.4 (CH_2), 26.3 (CH_2), 21.5 (CH_3), 18.9 (CH_2); **IR** (neat) 3018, 2952, 1716, 1345, 1218 cm^{-1}; **MS** (EI) *m/z* 359 (M^+, 12), 204 (41), 147 (78), 91 (100), 65 (38); **HRMS** (EI) *m/z* calcd for $C_{19}H_{21}NO_4S$ 359.1191, found 359.1190.

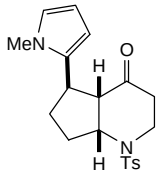
1-tosyl-4-(1-methyl-1*H*-2-pyrrolyl)perhydrocyclopenta[*b*]pyrrol-3-one (**42**)



The reaction of perhydropyrrolone **7** with *N*-methyl pyrrole **21** gave the product **42** in 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.54 (brs, 1H), 6.02 (dd, *J* = 3.6, 2.4 Hz, 1H), 5.79 (brd, *J* = 3.6 Hz, 1H), 4.59-4.53 (m, 1H), 3.82 (AB, *J* = 18.0 Hz, 1H), 3.69 (AB, *J* = 18.0 Hz, 1H), 3.59 (s, 3H), 3.51-3.46 (m, 1H), 2.89 (dd, *J* = 8.8, 2.8 Hz, 1H), 2.46 (s, 3H), 2.34-2.23 (m, 1H), 2.19-2.08 (m, 1H), 2.07-1.96 (m, 1H), 1.89-1.80 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.5 (C), 144.3 (C), 134.1 (C), 133.6 (C), 130.0 (CH), 127.7 (CH), 122.1 (CH), 106.6 (CH), 104.7 (CH), 63.3 (CH), 58.7 (CH), 54.7 (CH_2), 39.9 (CH), 33.8 (CH_3), 33.4 (CH_2), 31.4 (CH_2), 21.5 (CH_3); **IR** (neat) 3021, 2955, 1714, 1345 cm^{-1}; **MS** (EI) *m/z* 358 (M^+, 100), 203 (87), 146 (100), 91 (31); **HRMS** (EI) *m/z* calcd for $C_{19}H_{22}N_2O_3S$ 358.1351, found 358.1350.

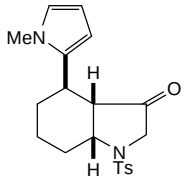
1-tosyl-5-(1-methyl-1*H*-2-pyrrolyl)perhydrocyclopenta[*b*]pyridin-4-one (**43**)



The reaction of perhydropyridinone **8** with *N*-methyl pyrrole **21** gave the product **43** in 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.50 (brs, 1H), 6.02 (dd, *J* = 3.4, 2.4 Hz, 1H), 5.85 (brd, *J* = 3.4 Hz, 1H), 4.75-4.66 (m, 1H), 4.09-4.01 (m, 1H), 3.90 (ddd, *J* = 8.9, 6.5, 2.2 Hz, 1H), 3.32 (ddd, *J* = 13.5, 10.5, 3.2 Hz, 1H), 3.50 (s, 3H), 2.66 (d, *J* = 7.2 Hz, 1H), 2.52-2.34 (m, 2H), 2.41 (s, 3H), 2.11-2.01 (m, 1H), 1.83-1.74 (m, 1H), 1.70-1.59 (m, 1H), 1.40-1.27 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.6 (C), 143.9 (C), 136.4 (C), 136.1 (C), 129.9 (CH), 127.1 (CH), 121.7 (CH), 106.7 (CH), 104.1 (CH), 59.0 (CH), 57.3 (CH), 41.5 (CH_2), 40.3 (CH_2), 33.7 (CH_3), 31.4 (CH), 28.4 (CH_2), 27.0 (CH_2), 21.5 (CH_3); **IR** (neat) 3020, 2956, 1715, 1345 cm^{-1}; **MS** (EI) *m/z* 372 (M^+, 100), 217 (81), 161 (54), 120 (45), 107 (63), 91 (55); **HRMS** (EI) *m/z* calcd for $C_{20}H_{24}N_2O_3S$ 372.1508, found 372.1511.

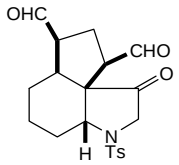
1-tosyl-4-(1-methyl-1*H*-2-pyrrolyl)perhydro-3-indolone (**44**)



The reaction of perhydroindolone **9** with *N*-methyl pyrrole **21** gave the product **44** in 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.52 (brs, 1H), 6.04 (dd, *J* = 3.6, 2.6 Hz, 1H), 5.85 (brd, *J* = 3.6 Hz, 1H), 4.67-4.58 (m ,1H), 3.87 (AB, *J* = 18.2 Hz, 1H), 3.66 (AB, *J* = 18.2 Hz, 1H), 3.58 (brs, 1H), 3.49 (s, 3H), 2.43 (brd, 1H), 2.38 (s, 3H), 2.05-2.01 (m, 1H), 1.65-1.04 (m, 5H); **^{13}C NMR** (100 MHz, d_6-DMSO) δ 208.9 (C), 143.9 (C), 135.1 (C), 133.3 (C), 130.2 (CH), 127.1 (CH), 121.7 (CH), 106.0 (CH), 106.0 (CH), 56.5 (CH), 51.5 (CH), 51.3 (CH_2), 33.1 (CH_3), 28.9 (CH), 28.8 (CH_2), 26.8 (CH_2), 21.0 (CH_3), 17.7 (CH_2); **IR** (neat) 3020, 2957, 1715, 1346 cm^{-1}; **MS** (EI) *m/z* 372 (M^+, 100), 217 (87), 189 (40), 161 (48), 120 (53), 107 (51), 91 (31); **HRMS** (EI) *m/z* calcd for $C_{20}H_{24}N_2O_3S$ 372.1508, found 372.1505.

Decahydro-1-oxo-3-tosyl-1*H*-cyclopenta[*d*]indole-7,9-dicarbaldehyde **(50)**



O_3 gas was introduced into the solution of compound **38** (15 mg, 0.042 mmol) in CH_2Cl_2 (3 mL) at 0°C. After 20 min, the ozone was stopped and the excess ozone was removed by introducing the Ar gas into the solution. Finally, Me_2S (6 ul, 0.084 mmol) was added into the reaction solution and stirred for 20 min. The reaction solvent was removed directly by rotary evaporator to give the crude compound. Purification by flash column chromatography (ethyl acetate/hexane 1:3) afforded compound **50** (16 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (d, *J* = 1.2 Hz, 1H), 9.62 (d, *J* = 2.4 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 4.03 (AB, *J* = 18.4 Hz, 1H), 3.65 (dd, *J* = 4.2, 4.2 Hz, 1H), 3.45 (AB, *J* = 18.4 Hz, 1H), 3.02(dd, *J* = 18.2, 7.8 Hz, 1H), 2.83-2.65 (m, 2H), 2.44 (s, 3H), 2.38-2.27 (m, 1H), 2.06-1.96 (m, 1H), 1.80-1.68 (m, 1H), 1.62-1.53 (m, 1H), 1.48-1.32 (m, 2H), 1.30-1.10 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.2 (C), 201.5 (CH), 200.7 (CH), 144.8 (C), 132.1 (C), 130.1 (CH), 127.8 (CH), 62.5 (C), 57.6 (CH), 53.2 (CH_2), 52.5 (CH), 51.8 (CH), 40.9 (CH), 24.8 (CH_2), 23.7 (CH_2), 23.3 (CH_2), 21.6 (CH_3), 17.7 (CH_2); **IR** (neat) 1725, 1720, 1715, 1343, 1230, 969 cm^{-1}; **MS** (EI) *m/z*

389 (M^+, 3), 360 (60), 331 (62), 176 (100); **HRMS** (EI) *m/z* calcd for $C_{20}H_{23}NO_5S$ 389.4653, found 389.1297.