Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Ring-Opening Formal Hetero-[5+2] Cycloaddition of 1-Tosyl-2,3-dihydro-1*H*-pyrroles pyrroles with Terminal Alkynes: Entry to 1-Tosyl-2,3-dihydro 2,3-Dihydro-1*H*-azepines

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(A) Typical Experimental Procedure

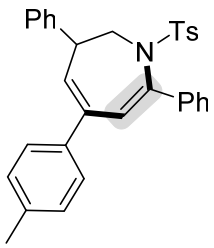
(a) 2,3-Dihydro-1*H*-pyrroles were synthesized according to the known literatures.[1]

(b) Typical Experimental Procedure for the Ring-Opening/Formal Hetero-[5+2] Cycloaddition:

To a Schlenk tube was added 2,3-dihydro-1*H*-pyrroles **1** (0.2 mmol), alkynes **2** (0.8 mmol; 4 equiv), $FeCl_3$ (4 mol%), $BF_3 \cdot Et_2O$ (40 mol%; add by twice), anhydrous CH_2ClCH_2Cl (2 mL). Then the tube was charged with argon, and was stirred at 80 °C (oil bath temperature) for the indicated time (about 24 h) until complete consumption of starting material as monitored by TLC. After the reaction was finished, the reaction mixture was cooled to room temperature, and the resulting residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate) to afford the desired azepines.

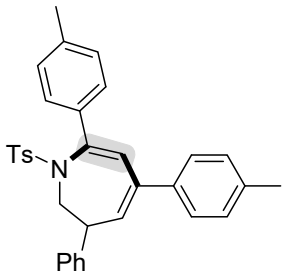
(B) Analytical data

3,7-Diphenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (3):[2]



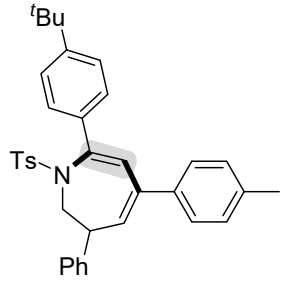
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 4.5 Hz, 2H), 7.41-7.34 (m, 8H), 7.22-7.19 (m, 6H), 6.24 (s, 1H), 6.01 (d, *J* = 2.8 Hz, 1H), 4.60-4.55 (m, 1H), 4.34-4.30 (m, 1H), 3.56-3.50 (m, 1H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.5, 143.3, 141.7, 140.6, 138.8, 137.7, 136.9, 135.7, 134.2, 129.3, 129.0, 128.9, 128.5, 128.2, 127.5, 127.4, 127.3, 126.8, 122.4, 56.9, 48.3, 21.6, 21.1.

3-Phenyl-5,7-*di*-*p*-tolyl-1-tosyl-2,3-dihydro-1*H*-azepine (4):[2]



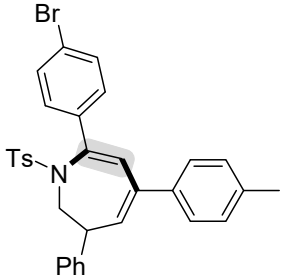
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 8.0 Hz, 2H), 7.36-7.32 (m, 4H), 7.27-7.24 (m, 3H), 7.15-7.10 (m, 8H), 6.13 (s, 1H), 5.88 (s, 1H), 4.52-4.47 (m, 1H), 4.23-4.21 (m, 1H), 3.45 (t, *J* = 12.0 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:143.4, 143.3, 141.7, 140.6, 138.5, 137.7, 136.8, 136.0, 135.8, 133.9, 129.2, 128.9 (2C), 128.8, 128.1, 127.5, 127.2 (2C), 126.8, 121.6, 57.0, 48.1, 21.5, 21.3, 21.1.

7-(4-(*tert*-Butyl)phenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (5):



White solid, mp 162.6-164.9 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 4H), 7.30-7.28 (m, 5H), 7.13 (s, 5H), 7.12 (s, 1H), 6.18 (s, 1H), 5.94 (d, *J* = 3.0 Hz, 1H), 4.54-4.50 (m, 1H), 4.29-4.25 (m, 1H), 3.51-3.46 (m, 1H), 2.37 (s, 3H), 2.36 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:151.5, 143.2, 143.1, 141.6, 140.7, 137.9, 136.7, 135.7, 135.7, 133.9, 129.1, 128.9, 128.1, 127.4, 127.2, 127.0, 126.7, 125.0, 121.8, 57.1, 48.4, 34.6, 31.3, 21.5, 21.0; HRMS *m/z* (ESI) calcd for $C_{36}H_{38}NO_2S$ $[M+H]^+$ 548.2632, found 548.2627.

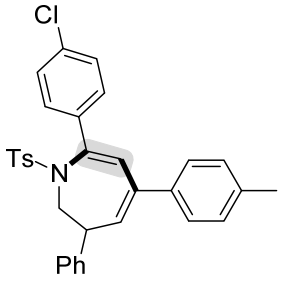
7-(4-Bromophenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (6):



White solid, mp 153.1-154.2 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 8.0 Hz, 2H), 7.41-7.24 (m, 9H), 7.17-7.07 (m, 6H), 6.14 (s, 1H), 5.94 (s, 1H), 4.51-4.46 (m, 1H), 4.21-4.19 (m, 1H), 3.41 (t, *J* = 12.0 Hz, 1H), 2.36 (s, 3H),

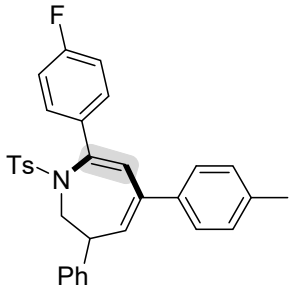
2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:143.8, 142.1, 141.5, 140.4, 137.8, 137.5, 137.0, 135.5, 134.7, 131.3, 129.3, 129.0, 128.9, 128.8, 128.1, 127.5, 127.4, 126.8, 122.6 (2C), 56.7, 48.2, 21.5, 21.1; HRMS *m/z* (ESI) calcd for $C_{32}H_{29}{}^{79}BrNO_2S$ $[M+H]^+$ 570.1097, found 570.1095.

7-(4-Chlorophenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (7):



White solid, mp 147.1-147.9 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 8.0 Hz, 2H), 7.38-7.32 (m, 4H), 7.28-7.25 (m, 5H), 7.17-7.08 (m, 6H), 6.14 (s, 1H), 5.93 (s, 1H), 4.51-4.46 (m, 1H), 4.22-4.19 (m, 1H), 3.42 (t, *J* = 12.0 Hz, 1H), 2.36 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:143.8, 142.1, 141.5, 140.4, 137.5, 137.4, 137.0, 135.5, 134.7, 134.4, 129.3, 129.0, 128.9, 128.5, 128.3, 128.1, 127.5, 127.3, 126.8, 122.6, 56.7, 48.2, 21.5, 21.1; HRMS *m/z* (ESI) calcd for $C_{32}H_{29}{}^{35}ClNO_2S$ $[M+H]^+$ 526.1602, found 526.1615.

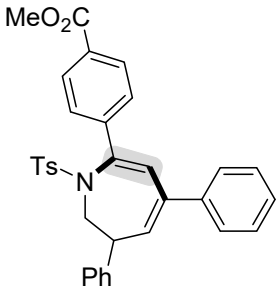
7-(4-Fluorophenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (8):



White solid, mp 154.4-156.0 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 8.0 Hz, 2H), 7.43-7.40 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30-7.27 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.14-7.10 (m, 4H), 6.98 (t, *J* = 9.0 Hz, 2H), 6.10 (s, 1H), 5.94 (d, *J* = 3.0 Hz, 1H), 4.53-4.49 (m, 1H), 4.26-4.22 (m, 1H), 3.47-3.41 (m, 1H), 2.37 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:163.0 (d, *J* = 246.8 Hz, 1C), 143.6, 142.2, 141.6, 140.5, 137.7, 136.9, 134.9, 134.3, 129.0 (d, *J* = 8.3 Hz, 1C), 129.3, 128.9 (d, *J* = 13.4 Hz, 1C), 128.1, 127.4, 127.3, 126.7, 122.0, 115.0 (d, *J* = 21.6

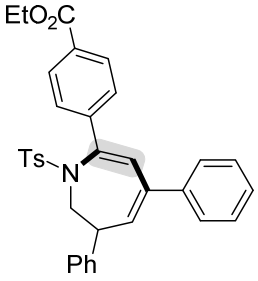
Hz, 1C), 56.7, 48.0, 21.5, 21.0; HRMS *m/z* (ESI) calcd for $C_{32}H_{29}FNO_2S$ $[M+H]^+$ 510.1911, found 510.1907.

Methyl 4-(4,6-diphenyl-1-tosyl-6,7-dihydro-1*H*-azepin-2-yl)benzoate (9):



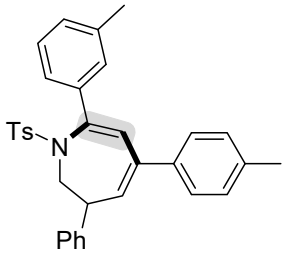
White solid, mp 172.5-174.2 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.37-7.27 (m, 8H), 7.23-7.21 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.27 (s, 1H), 6.00 (d, *J* = 3.0 Hz, 1H), 4.53-4.50 (m, 1H), 4.25-4.21 (m, 1H), 3.93 (s, 3H), 3.47-3.42 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:166.7, 144.2, 143.8, 143.3, 142.4, 140.1, 137.4, 135.8, 135.7, 129.9, 129.5, 129.3, 128.9, 128.3, 128.0, 127.5, 127.4, 127.2, 127.1, 126.9, 123.7, 56.5, 52.1, 48.3, 21.5; HRMS *m/z* (ESI) calcd for $C_{33}H_{30}NO_4S$ $[M+H]^+$ 536.1890, found 536.1895.

Ethyl 4-(4,6-diphenyl-1-tosyl-6,7-dihydro-1H-azepin-2-yl)benzoate (10):



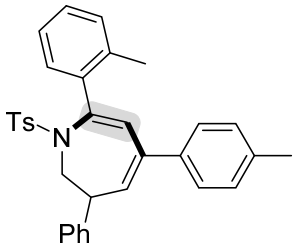
White solid, mp 181.4-183.0 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 6.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 6.5 Hz, 2H), 7.38-7.26 (m, 8H), 7.23-7.21 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.27 (s, 1H), 6.00 (d, *J* = 3.5 Hz, 1H), 4.54-4.50 (m, 1H), 4.42-4.37 (m, 2H), 4.26-4.21 (m, 1H), 3.47-3.42 (m, 1H), 2.37 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:166.3, 144.2, 143.8, 143.4, 142.4, 140.2, 137.4, 137.4, 135.8, 135.7, 130.2, 129.4, 129.3, 128.9, 128.3, 128.0, 127.5, 127.4, 127.2, 127.1, 126.9, 123.6, 61.0, 56.5, 48.2, 21.5, 14.3; HRMS *m/z* (ESI) calcd for $C_{34}H_{32}NO_4S$ $[M+H]^+$ 550.2063, found 550.2055.

3-Phenyl-7-(*m*-tolyl)-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (11):



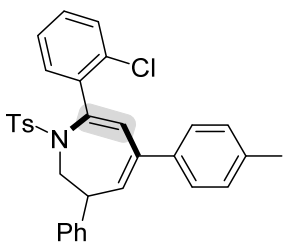
White solid, mp 145.8-147.3 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.0 Hz, 2H), 7.36-7.27 (m, 5H), 7.20-7.03 (m, 10H), 6.14 (s, 1H), 5.95 (s, 1H), 4.51-4.46 (m, 1H), 4.30-4.27 (m, 1H), 3.45 (d, *J* = 12.0 Hz, 1H), 2.34 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.4, 143.3, 141.8, 140.7, 138.6, 137.9, 137.5, 136.8, 135.7, 134.1, 129.3, 129.2, 129.0, 128.9, 128.1 (2C), 128.0, 127.5, 127.3, 126.8, 124.7, 122.2, 57.0, 48.6, 21.5, 21.4, 21.1; HRMS *m/z* (ESI) calcd for $C_{33}H_{32}NO_2S$ $[M+H]^+$ 506.2148, found 506.2159.

3-Phenyl-7-(*o*-tolyl)-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (12):



White solid, mp 144.8-145.3 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 4.0 Hz, 4H), 7.30-7.11 (m, 10H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.15 (s, 1H), 5.79 (s, 1H), 4.46-4.43 (m, 1H), 4.38-4.33 (m, 1H), 3.38-3.32 (m, 1H), 2.34 (s, 3H), 2.34 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.2, 142.5, 142.4, 141.3, 137.6, 137.4, 137.3, 136.7, 135.4, 134.3, 131.3, 129.8, 129.0 (2C), 128.9, 128.3, 128.1, 127.2, 127.1, 127.0, 125.4, 121.1, 55.7, 50.2, 21.5, 21.1, 19.8; HRMS *m/z* (ESI) calcd for $C_{33}H_{32}NO_2S$ $[M+H]^+$ 506.2148, found 506.2155.

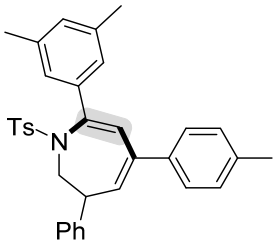
7-(2-Chlorophenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (13):



White solid, mp 147.1-147.7 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 7.2 Hz, 1H), 7.40-7.37 (m, 4H), 7.32-7.25 (m, 4H), 7.23-7.19 (m, 3H), 7.12 (d, *J* = 8.0 Hz,

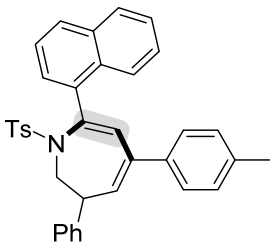
2H), 7.02 (d, *J* = 8.0 Hz, 3H), 6.19 (s, 1H), 5.88 (s, 1H), 4.45-4.41 (m, 1H), 4.38-4.33 (m, 1H), 3.53-3.47 (m, 1H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:143.2, 142.1, 141.1, 140.3, 137.2, 136.9, 136.7, 135.4, 135.1, 134.2, 133.2, 129.5, 129.0 (2C), 128.9, 128.2, 127.2, 127.1, 127.0, 126.5, 122.6, 56.0, 50.2, 21.5, 21.1; HRMS *m/z* (ESI) calcd for $C_{32}H_{29}{}^{35}ClNO_2S$ $[M+H]^+$ 526.1602, found 526.1607.

7-(3,5-Dimethylphenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (14):



White solid, mp 163.1-163.7 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-7.45 (m, 2H), 7.29-7.17 (m, 5H), 7.10-7.05 (m, 5H), 6.87-6.77 (m, 4H), 6.05 (s, 1H), 5.88-5.85 (m, 1H), 4.41-4.36 (m, 1H), 4.26-4.22 (m, 1H), 3.40-3.33 (m, 1H), 2.28 (s, 3H), 2.24 (s, 3H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:143.4, 143.3, 140.8, 138.4, 137.8, 137.5, 136.7, 135.7, 134.1, 130.2, 129.1, 128.9, 128.8, 128.1, 127.5, 127.2, 126.9, 125.3, 124.9, 122.0, 57.0, 48.8, 21.5, 21.4, 21.3, 21.1; HRMS *m/z* (ESI) calcd for $C_{34}H_{34}NO_2S$ $[M+H]^+$ 520.2305, found 520.2309.

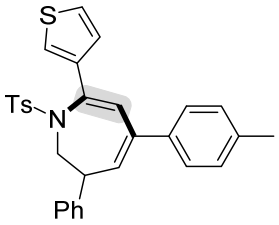
7-(Naphthalen-1-yl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (15):



White solid, mp 168.2-170.5 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.55-7.28 (m, 11H), 7.17-7.14 (m, 3H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 2H), 6.28 (s, 1H), 6.04 (s, 1H), 4.59-4.55 (m, 2H), 3.66-3.60 (m, 1H), 2.35 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:142.5, 142.4, 141.4, 136.8, 136.6, 135.5, 135.2, 134.6, 133.1, 132.2, 129.0, 128.9, 138.8, 138.4, 128.1, 128.0, 127.3, 127.0, 126.5, 126.0, 125.2, 125.0, 124.9, 121.8, 56.1, 50.6,

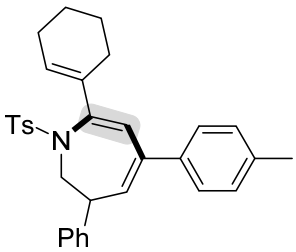
21.1, 21.0; HRMS *m/z* (ESI) calcd for $C_{36}H_{32}NO_2S$ $[M+H]^+$ 542.2146, found 542.2152.

3-Phenyl-7-(thiophen-3-yl)-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (16):



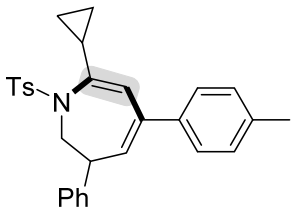
White solid, mp 143.1-144.5 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.0 Hz, 2H), 7.29-7.24 (m, 3H), 7.20-7.13 (m, 4H), 7.08-6.97 (m, 7H), 6.16 (s, 1H), 5.81 (d, *J* = 3.2 Hz, 1H), 4.40-4.35 (m, 1H), 4.15-4.10 (m, 1H), 3.42 (t, *J* = 12.0 Hz, 1H), 2.26 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:143.5, 141.2, 140.5, 138.5, 137.7, 136.9, 135.7, 134.1, 129.3, 128.9, 128.8, 128.1, 127.5, 127.3, 126.7, 126.6, 125.4, 123.8, 121.7, 57.3, 48.0, 21.5, 21.1; HRMS *m/z* (ESI) calcd for $C_{30}H_{28}NO_2S_2$ $[M+H]^+$ 498.1556, found 498.1560.

7-(Cyclohex-1-en-1-yl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (17):



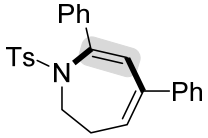
Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26-7.23 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.03 (s, 1H), 5.96 (s, 1H), 5.82 (d, *J* = 3.0 Hz, 1H), 4.34-4.30 (m, 1H), 4.16-4.11 (m, 1H), 3.48 (t, *J* = 7.5 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.12 (br, 2H), 1.70 (br, 3H), 1.60 (br, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:145.3, 143.0, 140.9, 140.6, 138.1, 136.7, 136.2, 135.2, 132.9, 129.1, 129.0, 128.7 (2C), 128.1, 127.4, 127.1, 126.5, 120.0, 58.7, 47.6, 26.6, 25.7, 22.6, 22.1, 21.4, 21.0; HRMS *m/z* (ESI) calcd for $C_{32}H_{34}NO_2S$ $[M+H]^+$ 496.2312, found 496.2320.

7-Cyclopropyl-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (18):



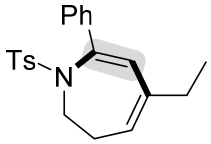
Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 6.5 Hz, 3H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.09 (s, 4H), 5.92 (d, *J* = 3.0 Hz, 1H), 5.59 (s, 1H), 4.33-4.29 (m, 1H), 4.22-4.19 (m, 1H), 3.27-3.21 (m, 1H), 2.37 (s, 3H), 2.34 (s, 3H), 1.92-1.86 (m, 1H), 0.90-0.82 (m, 1H), 0.61-0.57 (s, 2H), 0.53-0.49 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:146.3, 143.3, 141.9, 140.8, 138.5, 136.7, 135.4, 133.2, 129.4, 128.8, 128.7, 128.1, 127.2, 127.1, 126.7, 116.3, 57.5, 48.8, 21.5, 21.0, 16.8, 9.8, 7.4; HRMS *m/z* (ESI) calcd for $C_{29}H_{30}NO_2S$ $[M+H]^+$ 456.1998, found 456.1993.

5,7-Diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (21):



Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54-7.48 (m, 4H), 7.31-7.24 (m, 6H), 7.14-7.10 (m, 4H), 6.15 (s, 1H), 5.88 (t, *J* = 4.5 Hz, 1H), 3.96 (d, *J* = 5.5 Hz, 2H), 2.76-2.73 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:144.4, 143.2, 142.5, 139.2, 137.7, 136.2, 131.5, 129.1, 128.3, 128.2, 128.1, 127.3, 127.1, 126.9, 126.7, 122.9, 50.2, 32.1, 21.4; HRMS *m/z* (ESI) calcd for $C_{25}H_{24}NO_2S$ $[M+H]^+$ 402.1525, found 402.1533.

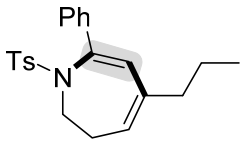
5-Ethyl-7-phenyl-1-tosyl-2,3-dihydro-1*H*-azepine (22):



Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 2.5 Hz, 2H), 7.32 (t, *J* = 2.5 Hz, 3H), 7.20-7.17 (m, 2H), 5.76 (s, 1H), 5.53 (s, 1H), 3.85 (d, *J* = 5.0 Hz, 2H), 2.59 (d, *J* = 4.5 Hz, 2H), 2.41 (s, 3H), 2.06-2.01 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$)

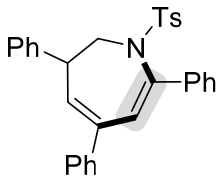
δ:143.0, 141.7, 139.4, 137.9, 135.6, 129.0, 128.0 (2C), 127.7, 127.4, 127.0, 123.3, 49.6, 33.6, 31.9, 21.4, 14.2; HRMS *m/z* (ESI) calcd for $C_{21}H_{24}NO_2S$ $[M+H]^+$ 354.1532, found 354.1542.

7-Phenyl-5-propyl-1-tosyl-2,3-dihydro-1*H*-azepine (23):



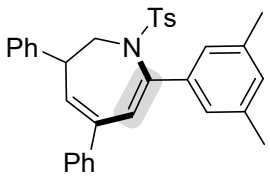
Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.0 Hz, 2H), 7.41-7.39 (m, 2H), 7.29-7.27 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.70 (s, 1H), 5.52 (t, *J* = 4.5 Hz, 1H), 3.82 (d, *J* = 6.0 Hz, 2H), 2.57-2.54 (m, 2H), 2.38 (s, 3H), 1.96 (t, *J* = 7.5 Hz, 2H), 1.37-1.29 (m, 2H), 0.82 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:143.1, 141.6, 139.6, 138.0, 134.0, 129.0, 128.4, 128.0, 127.9, 127.4, 127.2, 123.4, 49.5, 42.9, 32.1, 22.7, 21.5, 13.6; HRMS *m/z* (ESI) calcd for $C_{22}H_{26}NO_2S$ $[M+H]^+$ 368.1692, found 368.1703.

3,5,7-Triphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (24):[3]



^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.0 Hz, 2H), 7.36-7.35 (m, 2H), 7.29-7.13 (m, 13H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.08 (s, 1H), 5.89 (s, 1H), 4.45-4.40 (m, 1H), 4.21-4.16 (m, 1H), 3.42-3.35 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.5, 143.5, 143.4, 140.5, 138.7, 137.7, 135.9, 134.8, 129.2, 128.9, 128.5, 128.3, 128.1, 127.5, 127.4, 127.3, 127.1, 126.9, 122.2, 58.8, 48.4, 21.5.

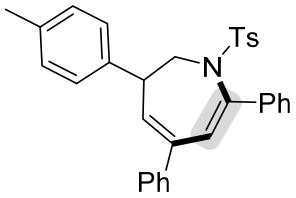
7-(3,5-Dimethylphenyl)-3,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (25):



White solid, mp 166.1-167.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 8.0 Hz, 2H), 7.28-7.14 (m, 10H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 3H), 6.05 (s, 1H),

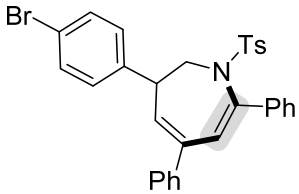
5.90 (s, 1H), 4.41-4.36 (m, 1H), 4.28-4.23 (m, 1H), 3.40-3.34 (m, 1H), 2.26 (s, 3H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.7, 143.6, 143.3, 140.7, 138.3, 138.0, 137.5, 135.9, 134.7, 130.3, 129.1, 128.9, 128.3, 128.2, 127.5, 127.3, 127.1, 127.0, 125.4, 121.8, 56.9, 48.9, 21.5, 21.3; HRMS *m/z* (ESI) calcd for $C_{33}H_{32}NO_2S$ $[M+H]^+$ 506.2148, found 506.2151.

5,7-Diphenyl-3-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (26):[3]



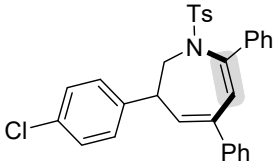
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.0 Hz, 2H), 7.37-7.35 (m, 2H), 7.23-7.20 (m, 6H), 7.13 (d, *J* = 6.8 Hz, 2H), 7.08-7.05 (m, 6H), 6.08 (s, 1H), 5.87 (s, 1H), 4.43-4.38 (m, 1H), 4.18-4.13 (m, 1H), 3.40-3.34 (m, 1H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.5, 143.5, 143.3, 138.8, 137.7, 137.5, 137.0, 129.5, 129.2, 128.5, 128.3, 128.1, 128.0, 127.5, 127.3, 127.1, 126.9, 122.2, 56.9, 48.0, 21.5, 21.1.

3-(4-Bromophenyl)-5,7-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (27):[3]



^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.24-7.05 (m, 12H), 6.06 (s, 1H), 5.82 (s, 1H), 4.41-4.36 (m, 1H), 4.21-4.17 (m, 1H), 3.36-3.29 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.4, 143.6, 143.5, 139.5, 138.5, 137.6, 136.3, 133.9, 132.0, 129.8, 129.3, 128.6, 128.3, 128.1, 127.5, 127.4, 127.2, 126.9, 121.9, 121.2, 56.4, 47.9, 21.5.

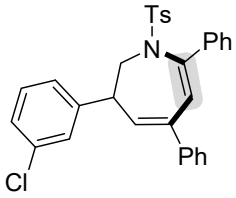
3-(4-Chlorophenyl)-5,7-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (28):[3]



^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 8.0 Hz, 2H), 7.34-7.32 (m, 2H), 7.26-7.18 (m, 8H), 7.15-7.13 (m, 4H), 7.07

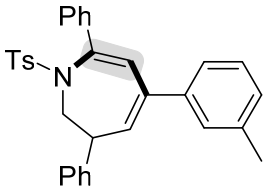
(d, *J* = 8.4 Hz, 2H), 6.06 (s, 1H), 5.83 (s, 1H), 4.42-4.37 (m, 1H), 4.22-4.18 (m, 1H), 3.36-3.30 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.4, 143.6, 143.5, 139.0, 138.5, 137.6, 136.2, 134.0, 133.1, 129.4, 129.2, 129.0, 128.6, 128.3, 128.1, 127.5, 127.4, 127.2, 126.9, 121.9, 56.5, 47.8, 21.5.

3-(3-Chlorophenyl)-5,7-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (29):[3]



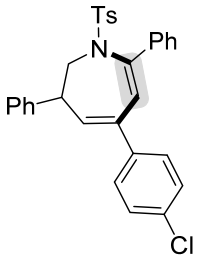
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.25-7.06 (m, 14H), 6.07 (s, 1H), 5.83 (s, 1H), 4.44-4.39 (m, 1H), 4.21-4.16 (m, 1H), 3.39-3.32 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.4, 143.6, 143.5, 142.6, 138.5, 137.6, 136.4, 134.7, 133.7, 130.2, 129.3, 128.6, 128.3, 128.2, 128.1, 127.5 (2C), 127.4, 127.2, 126.9, 126.3, 121.9, 56.4, 48.1, 21.5.

3,7-Diphenyl-5-(*m*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (30):



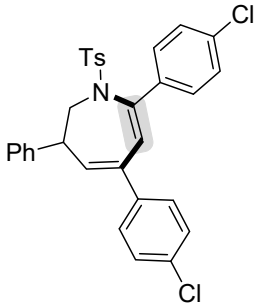
White solid, mp 143.0-144.2 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.0 Hz, 2H), 7.36-7.34 (m, 2H), 7.28-7.17 (m, 9H), 7.14-6.92 (m, 5H), 6.08 (s, 1H), 5.88-5.85 (m, 1H), 4.45-4.39 (m, 1H), 4.20-4.15 (m, 1H), 3.41-3.33 (m, 1H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:144.5, 143.5, 143.2, 140.6, 138.8, 137.9, 137.7, 136.0, 134.6, 129.3, 128.9, 128.5, 128.2, 128.1, 127.8, 127.7, 127.5, 127.4, 127.3, 126.9, 124.0, 122.4, 56.8, 48.4, 21.5; HRMS *m/z* (ESI) calcd for $C_{32}H_{30}NO_2S$ $[M+H]^+$ 492.1992, found 492.1999.

5-(4-Chlorophenyl)-3,7-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (31):



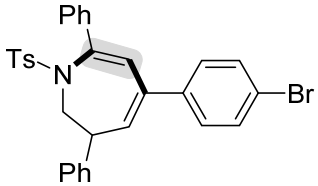
White solid, mp 139.1-139.7 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 8.0 Hz, 2H), 7.33-7.16 (m, 12H), 7.08-7.05 (m, 4H), 5.99 (s, 1H), 5.88 (s, 1H), 4.43-4.38 (m, 1H), 4.23-4.17 (m, 1H), 3.41-3.35 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:143.9, 143.6, 142.9, 140.3, 138.5, 137.6, 135.1, 134.8, 133.0, 129.2, 128.9, 128.7, 128.4, 128.2, 128.1, 128.0, 127.5, 127.4, 121.6, 56.8, 48.5, 21.5; HRMS *m/z* (ESI) calcd for $C_{31}H_{27}{}^{35}ClNO_2S$ $[M+H]^+$ 512.1445, found 512.1458.

5,7-Bis(4-chlorophenyl)-3-phenyl-1-tosyl-2,3-dihydro-1*H*-azepine (32):[2]



^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 8.4 Hz, 2H), 7.29-7.15 (m, 11H), 7.08-7.04 (m, 4H), 5.97 (s, 1H), 5.88 (s, 1H), 4.42-4.37 (m, 1H), 4.18-4.13 (m, 1H), 3.37-3.31 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:143.9, 142.7, 142.7, 140.1, 137.4, 137.1, 135.6, 134.7, 134.6, 133.1, 129.4, 129.0, 128.6, 128.5, 128.4, 128.2, 128.1, 127.5, 121.7, 56.6, 48.4, 21.5.

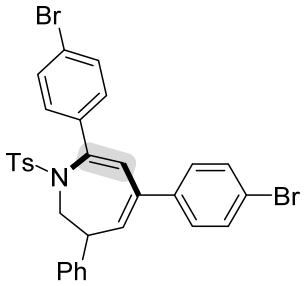
5-(4-Bromophenyl)-3,7-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (33):



White solid, mp 140.1-141.2 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 7.2 Hz, 2H), 7.35-7.18 (m, 12H), 7.07-7.01 (m, 4H), 5.99 (s, 1H), 5.88 (s, 1H), 4.43-4.38 (m, 1H), 4.21-4.18 (m, 1H), 3.41-3.35 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:143.9, 143.6, 143.3, 140.3, 138.5, 137.6, 135.1, 134.9, 131.4, 129.2, 128.9, 128.7, 128.6, 128.2, 128.1, 127.5, 127.4, 126.9, 121.4, 121.1, 56.8, 48.5, 21.5;

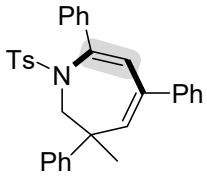
HRMS *m/z* (ESI) calcd for $C_{31}H_{27}BrNO_2S$ $[M+H]^+$ 556.0940, found 556.0944.

5,7-Bis(4-bromophenyl)-3-phenyl-1-tosyl-2,3-dihydro-1*H*-azepine (34):[2]



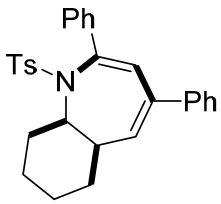
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 8.4 Hz, 2H), 7.37-7.26 (m, 6H), 7.21-7.17 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 5.98 (s, 1H), 5.90 (s, 1H), 4.43-4.38 (m, 1H), 4.18-4.15 (m, 1H), 3.37-3.31 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:143.9, 143.2, 142.8, 140.1, 137.5, 137.4, 135.6, 134.7, 131.4, 131.3, 129.3, 129.0, 128.9, 128.5, 128.0, 127.5, 122.8, 121.6, 121.2, 56.6, 48.4, 21.5.

3-Methyl-3,5,7-triphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (35):[3]



^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.0 Hz, 2H), 7.38-7.31 (m, 9H), 7.27-7.24 (m, 3H), 7.01 (d, *J* = 5.5 Hz, 4H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.12 (s, 1H), 6.75 (s, 1H), 4.47 (d, *J* = 14.0 Hz, 1H), 3.87 (d, *J* = 14.5 Hz, 1H), 2.32 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:145.1, 144.4, 143.4, 142.6, 140.1, 139.2, 137.6, 133.5, 128.9, 128.6, 128.5, 128.3, 126.9, 120.9, 62.6, 48.4, 26.5, 21.4.

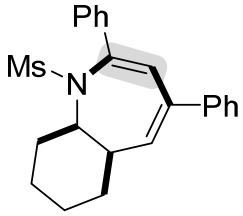
2,4-Diphenyl-1-tosyl-5*a*,6,7,8,9,9*a*-hexahydro-1*H*-benzo[b]azepine (36):



Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52-7.46 (m, 4H), 7.32-7.23 (m, 6H), 7.17-7.13 (m, 4H), 6.23 (s, 1H), 5.63 (s, 1H), 4.46 (t, *J* = 6.0 Hz, 1H), 3.13 (s, 1H), 2.35 (s, 3H), 1.77-1.71 (m, 4H), 1.59-1.44 (m, 3H), 1.21-1.18 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:145.4, 143.2, 140.5, 138.0, 137.5, 136.0, 135.9, 129.0, 128.2, 128.0, 127.9, 127.4 (2C), 126.8,

126.7, 123.7, 56.1, 41.8, 32.0, 26.9, 26.1, 21.4 (2C); HRMS *m/z* (ESI) calcd for $C_{29}H_{30}NO_2S$ $[M+H]^+$ 456.1999, found 456.2003.

1-(Methylsulfonyl)-2,4-diphenyl-5a,6,7,8,9,9a-hexahydro-1*H*-benzo[*b*]azepine (37):



Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.0 Hz, 2H), 7.42-7.30 (m, 8H), 6.40 (s, 1H), 6.00 (d, *J* = 1.5 Hz, 1H), 4.36-4.32 (m, 1H), 3.40 (s, 1H), 2.84 (s, 3H), 1.95-1.76 (m, 4H), 1.70-1.44 (m, 3H), 1.35-1.29 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:145.2, 140.2, 138.0, 136.2, 136.2, 128.4, 128.3, 128.1, 127.3, 127.0, 126.9, 123.8, 56.1, 42.5, 40.9, 32.0, 26.7, 26.0, 21.4; HRMS *m/z* (ESI) calcd for $C_{23}H_{26}NO_2S$ $[M+H]^+$ 380.1692, found 380.1687.

(C) References

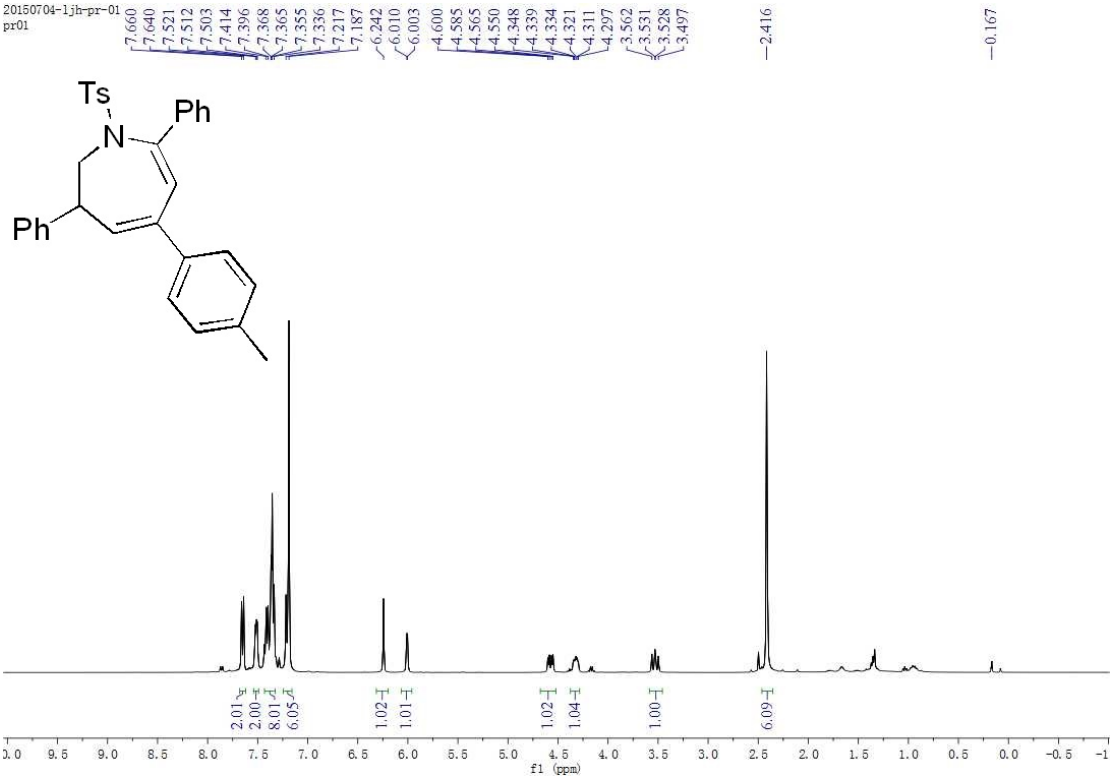
(1) (*a*) K. Hiroya, S. Matsumoto, M. Ashikawa, K. Ogiwara and T. Sakamoto, *Org. Lett.,* 2006, **8**, 5349; (*b*) J.-M. Fan, L.-F. Gao and Z.-Y. Wang, *Chem. Commun.,* 2009, **3**, 5021; (*c*) P.A. Wender and D. Strand, *J. Am. Chem. Soc.,* 2009, **131,** 7528; (*d*) M.-C. Chung, Y.-H. Chan, W.-J. Chang and D.-R. Hou, *Org. Biomol. Chem.,* 2017, **15**, 3783.

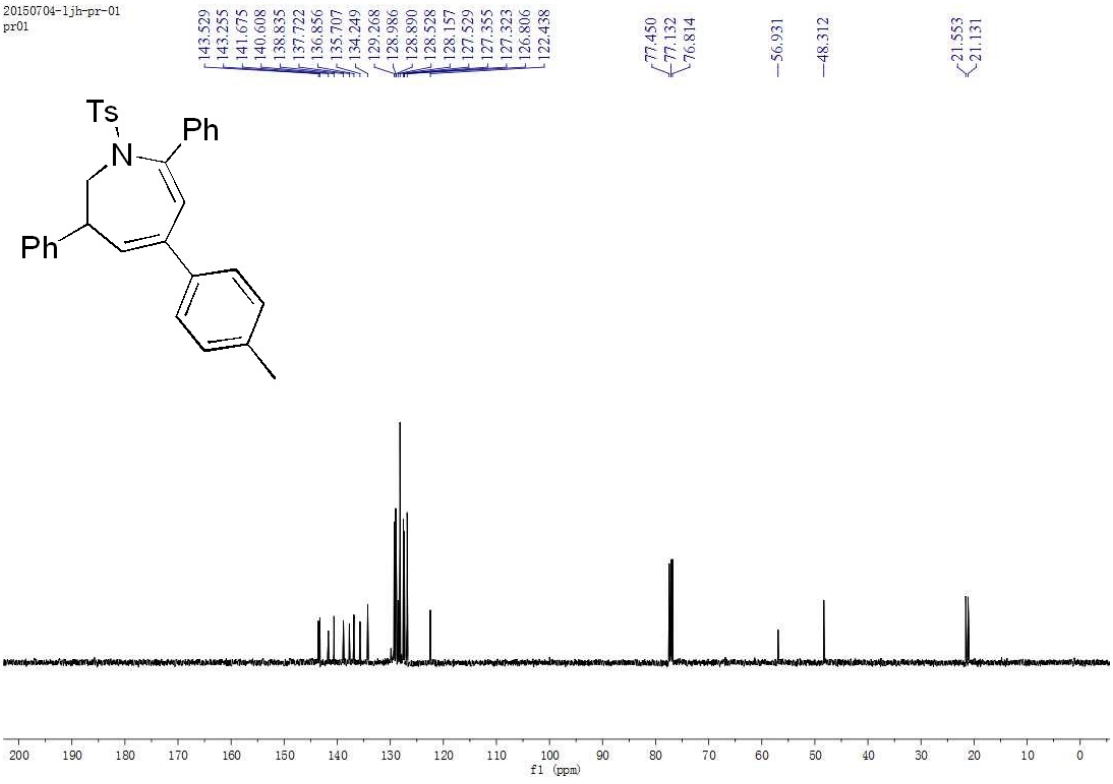
[2] M.-B. Zhou, R.-J. Song and J.-H. Li, *Angew. Chem. Int. Ed.,* 2014, **53**, 4196.

[3] M.-B. Zhou, R.-J. Song, C.-Y. Wang and J.-H. Li, *Angew. Chem. Int. Ed.,* 2013, **52**, 10805.

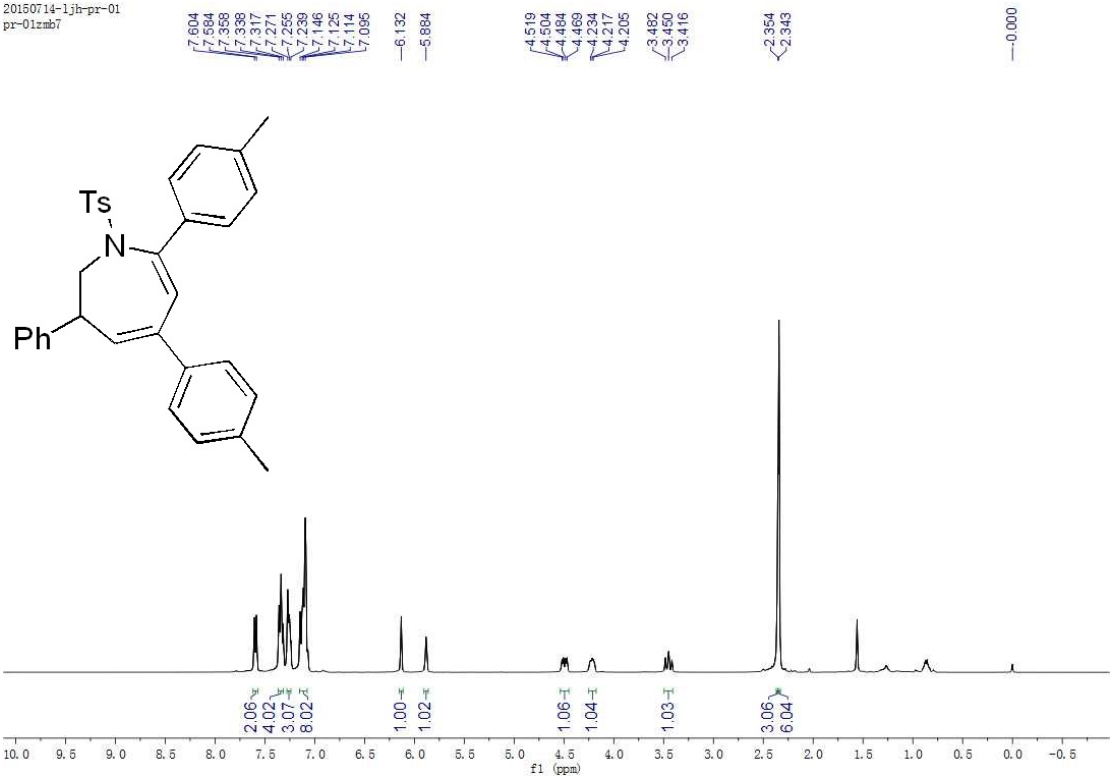
(D) Spectra

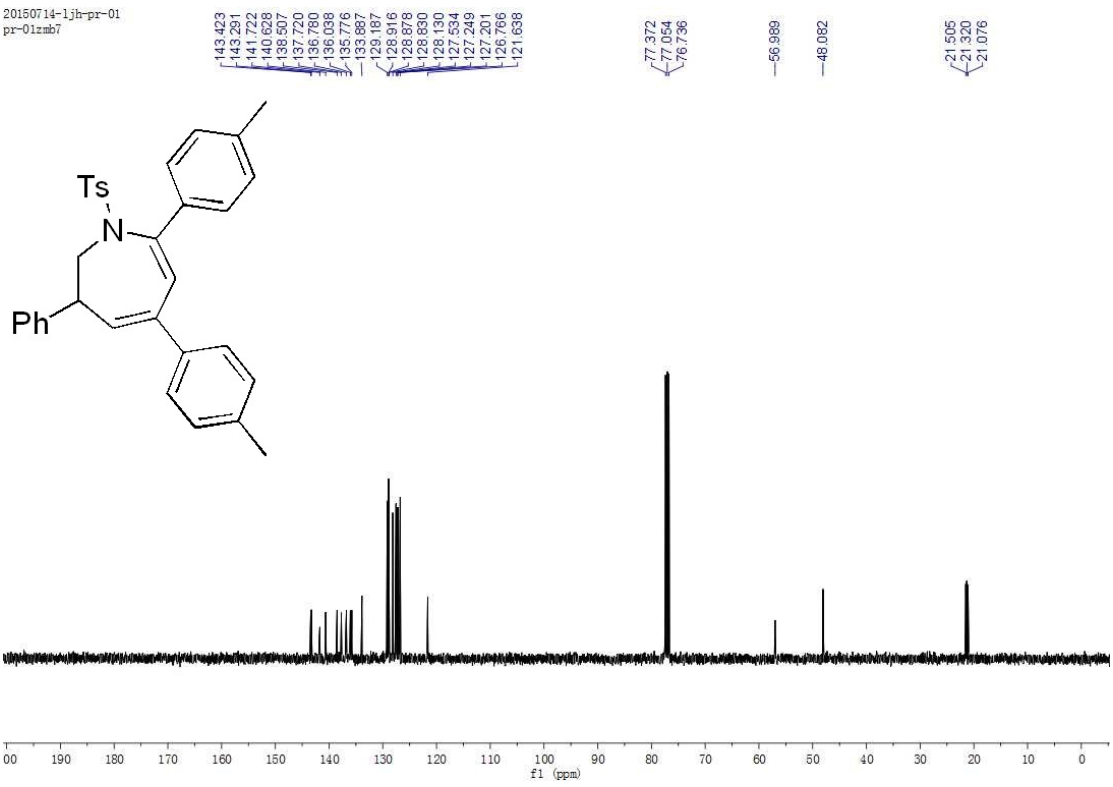
3,7-Diphenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (3)



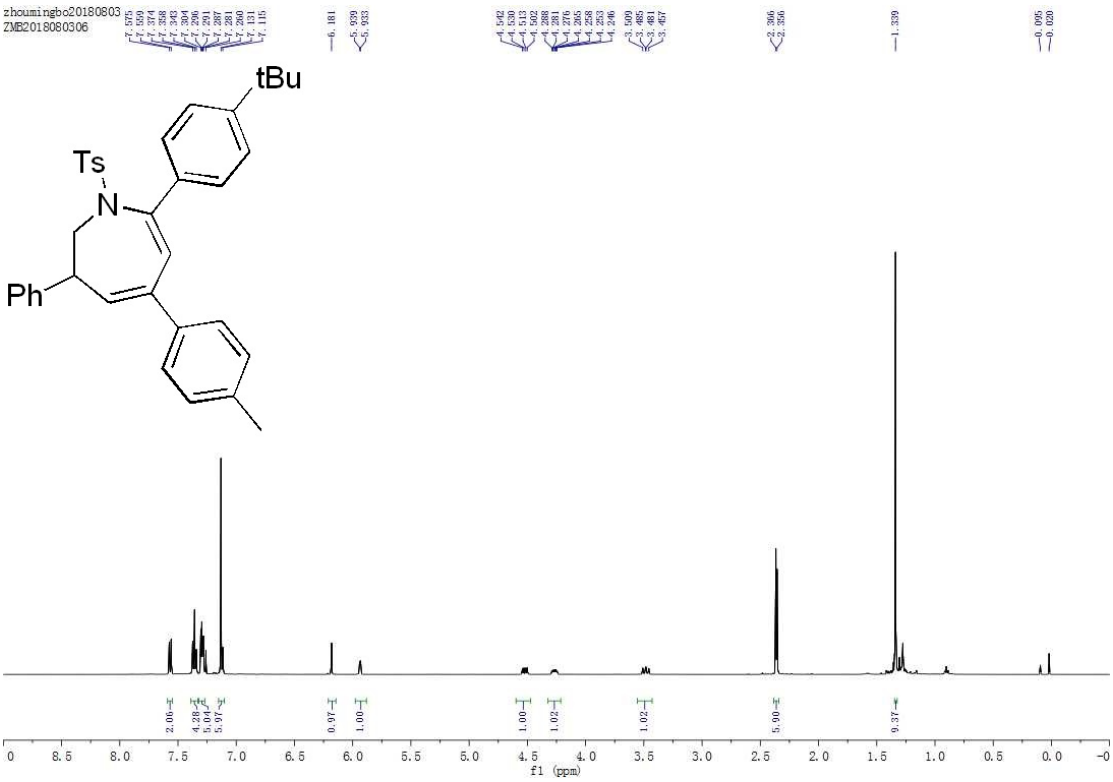


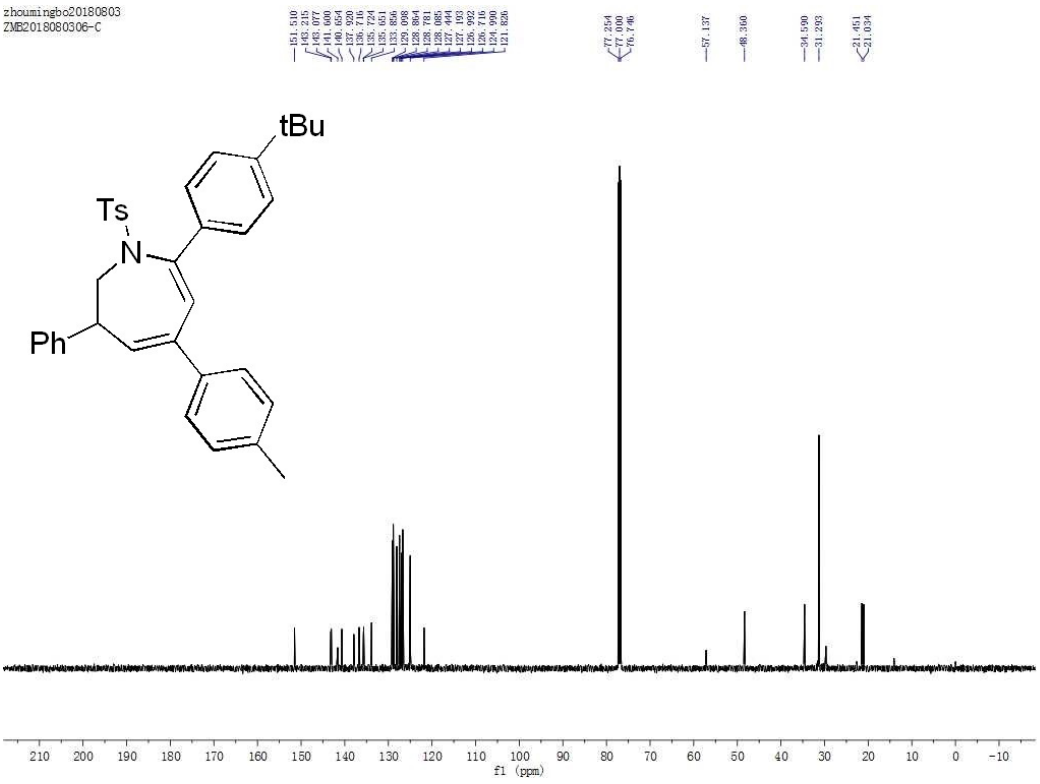
3-Phenyl-5,7-*di*-*p*-tolyl-1-tosyl-2,3-dihydro-1*H*-azepine (4)



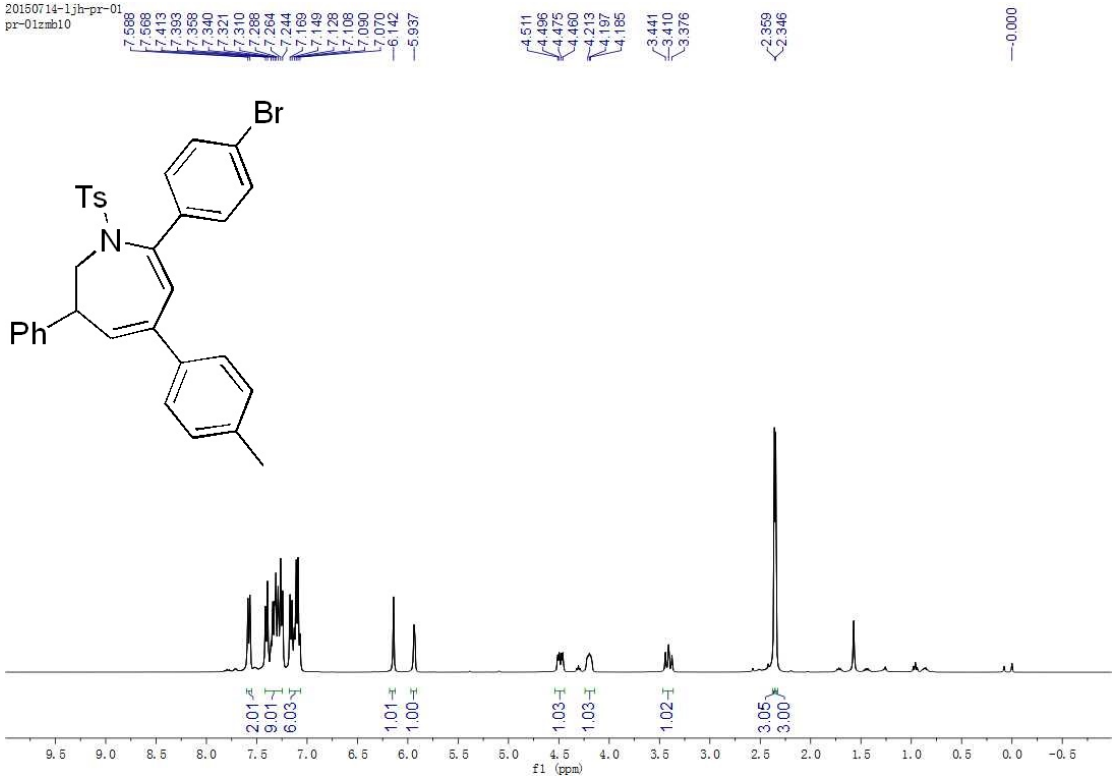


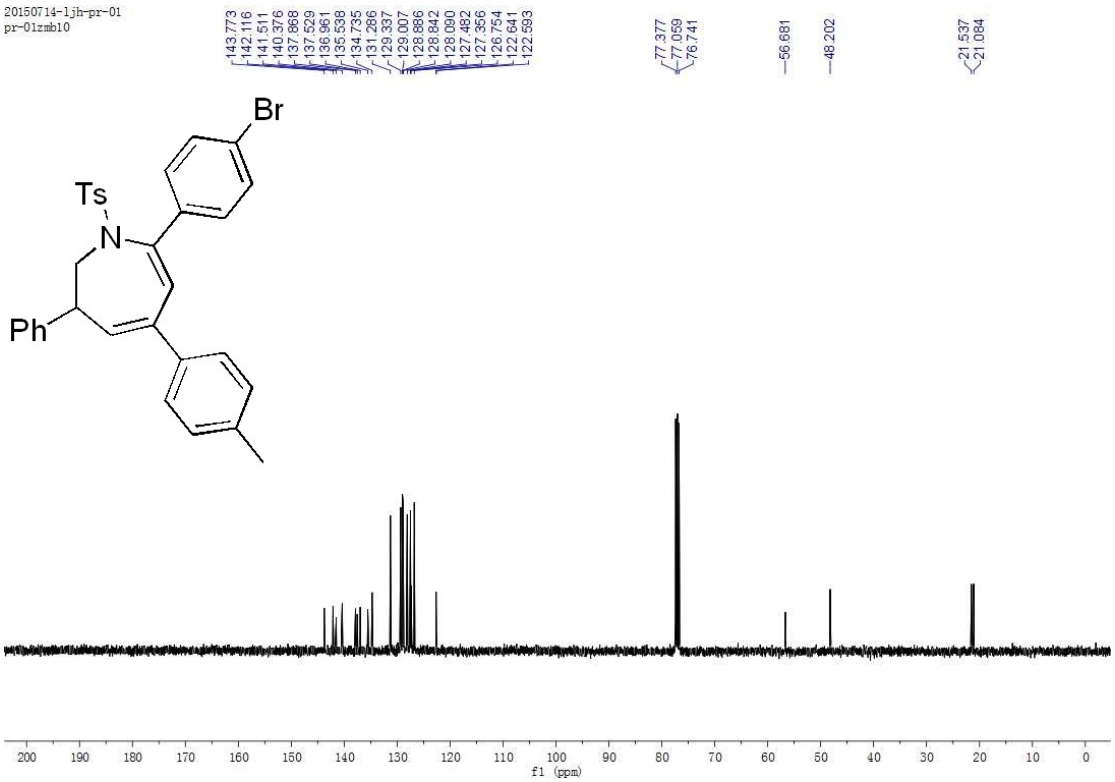
7-(4-(*tert*-Butyl)phenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (5)



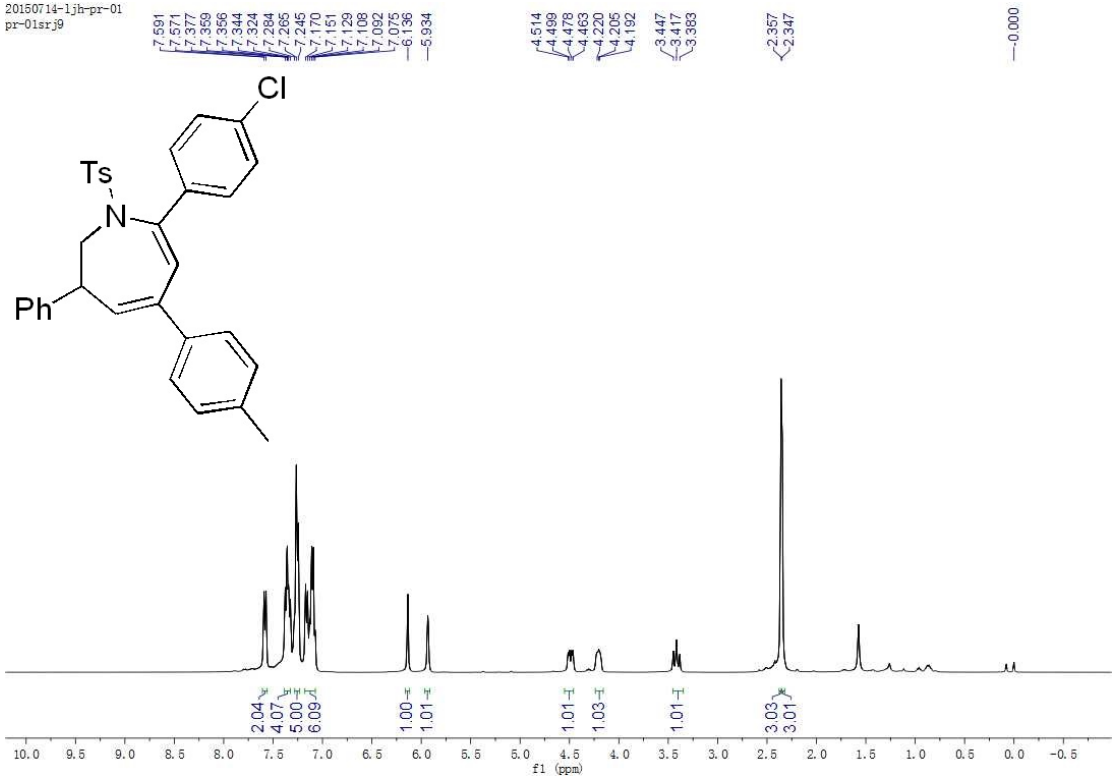


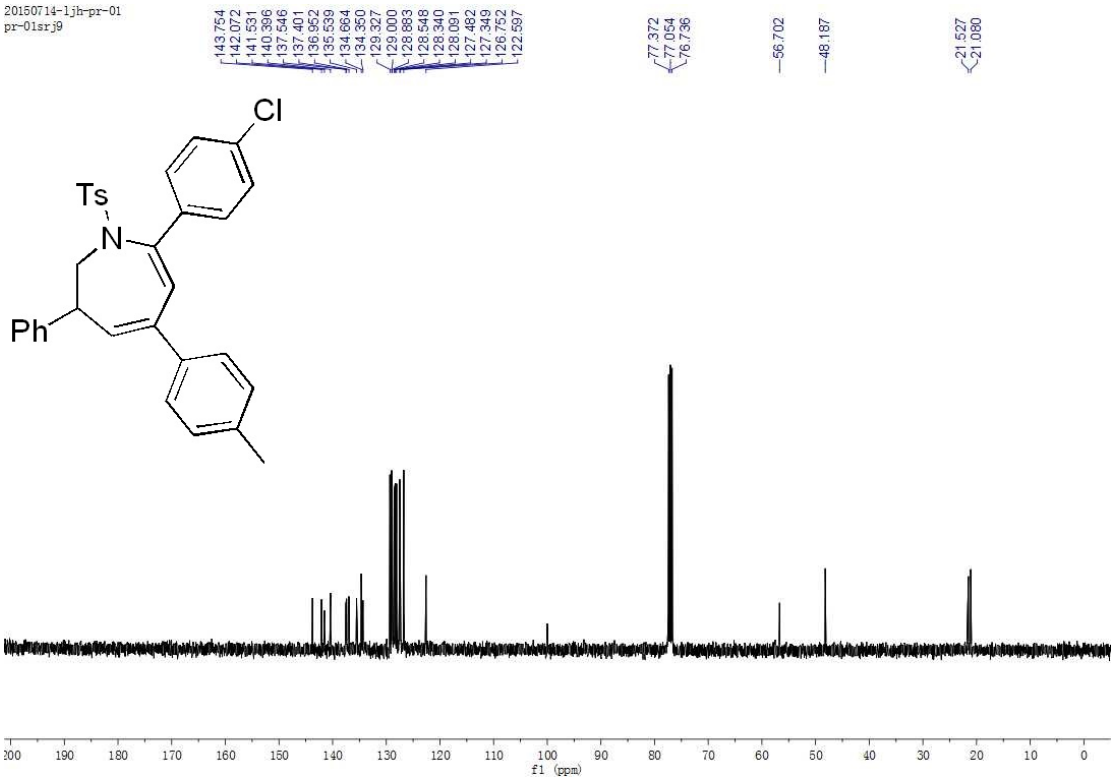
7-(4-Bromophenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (6)



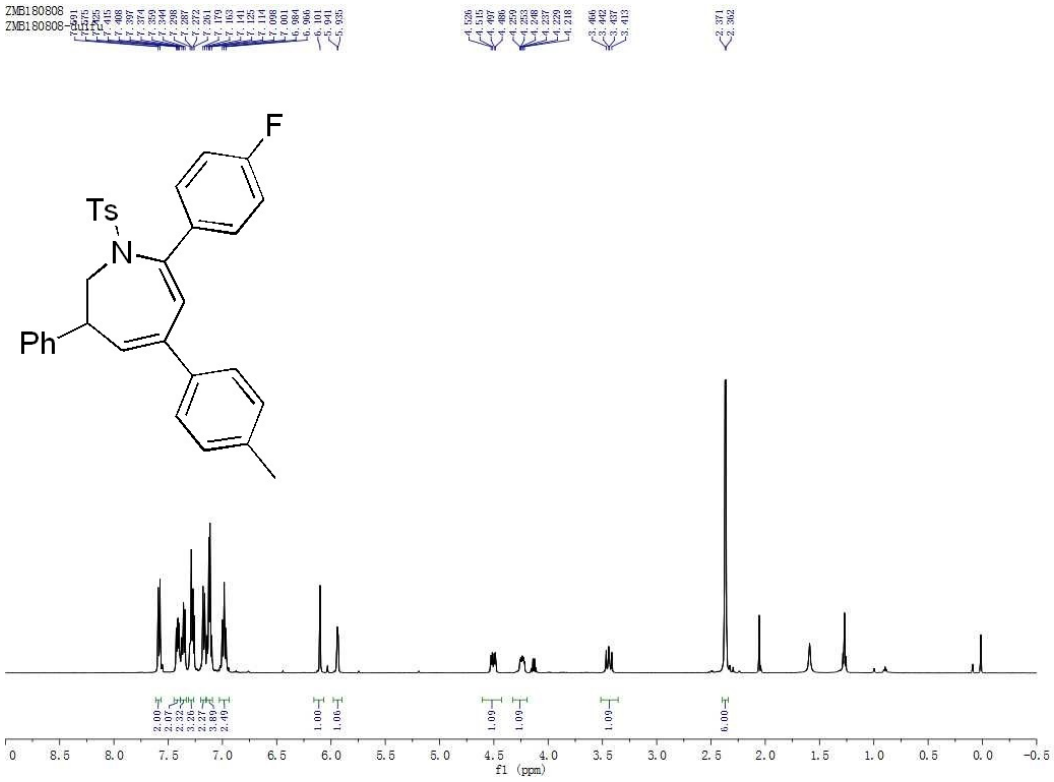


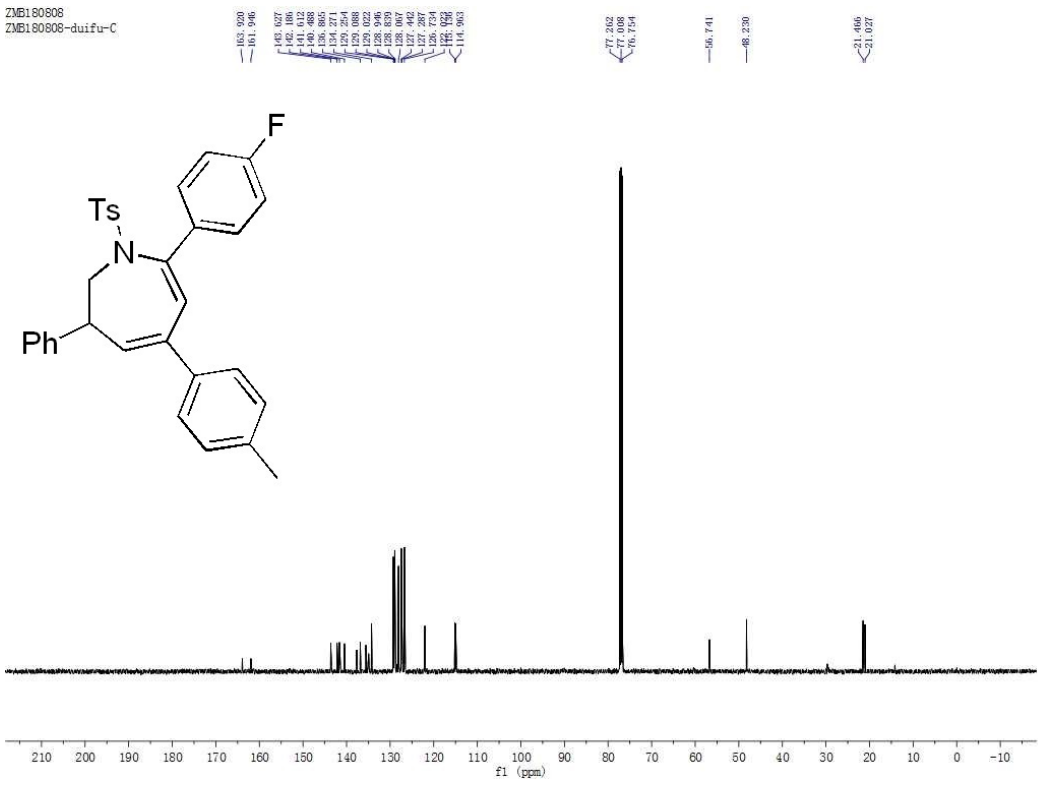
7-(4-Chlorophenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (7)



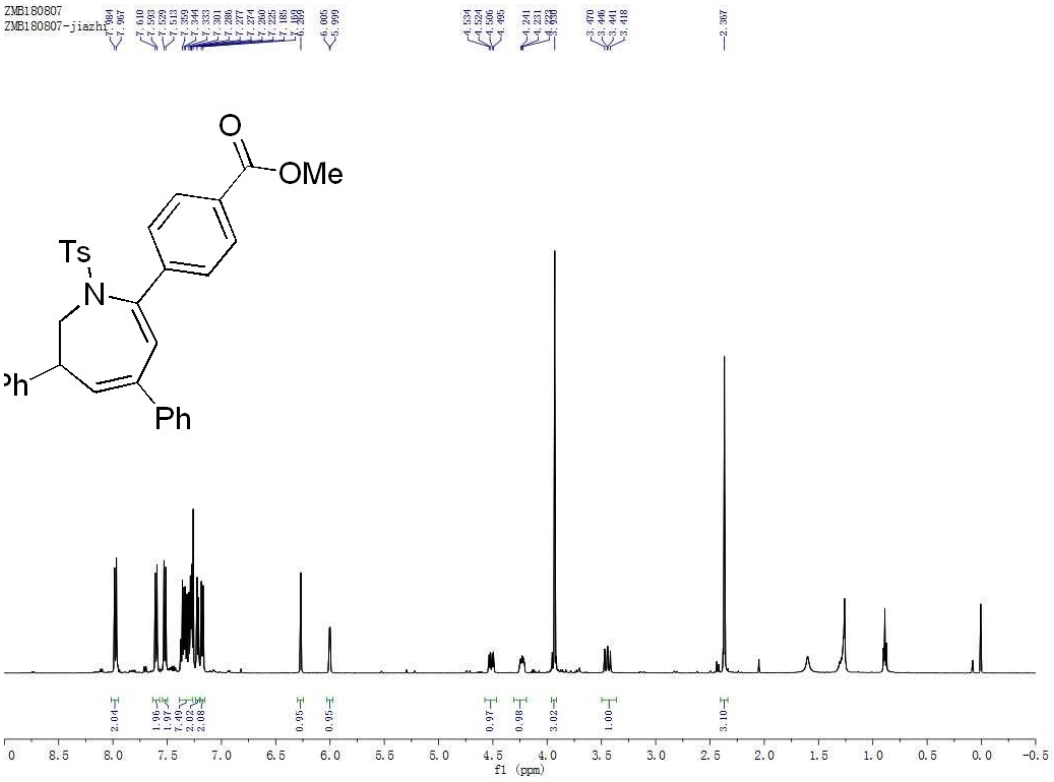


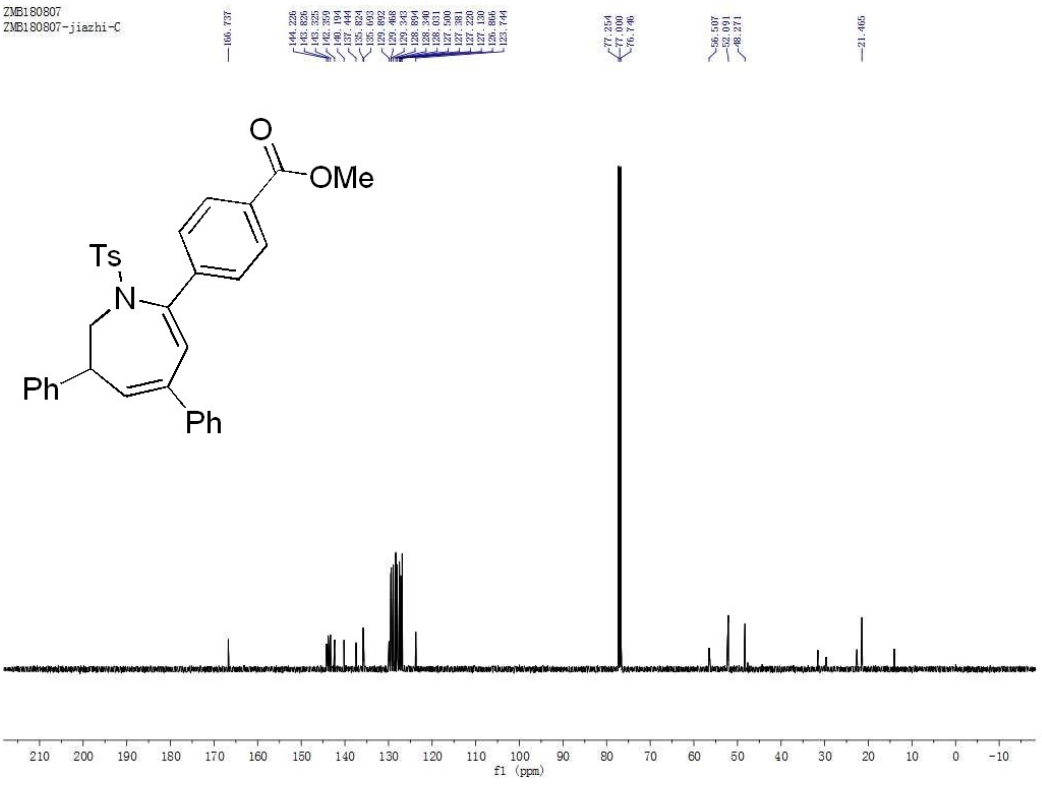
7-(4-Fluorophenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (8)



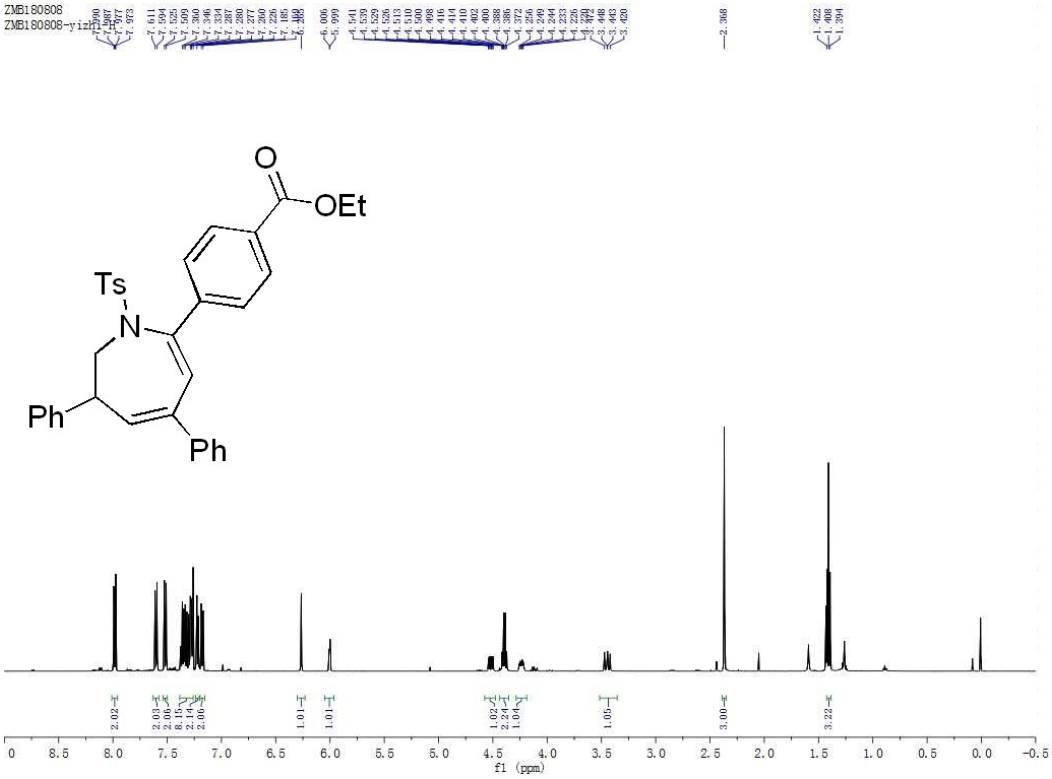


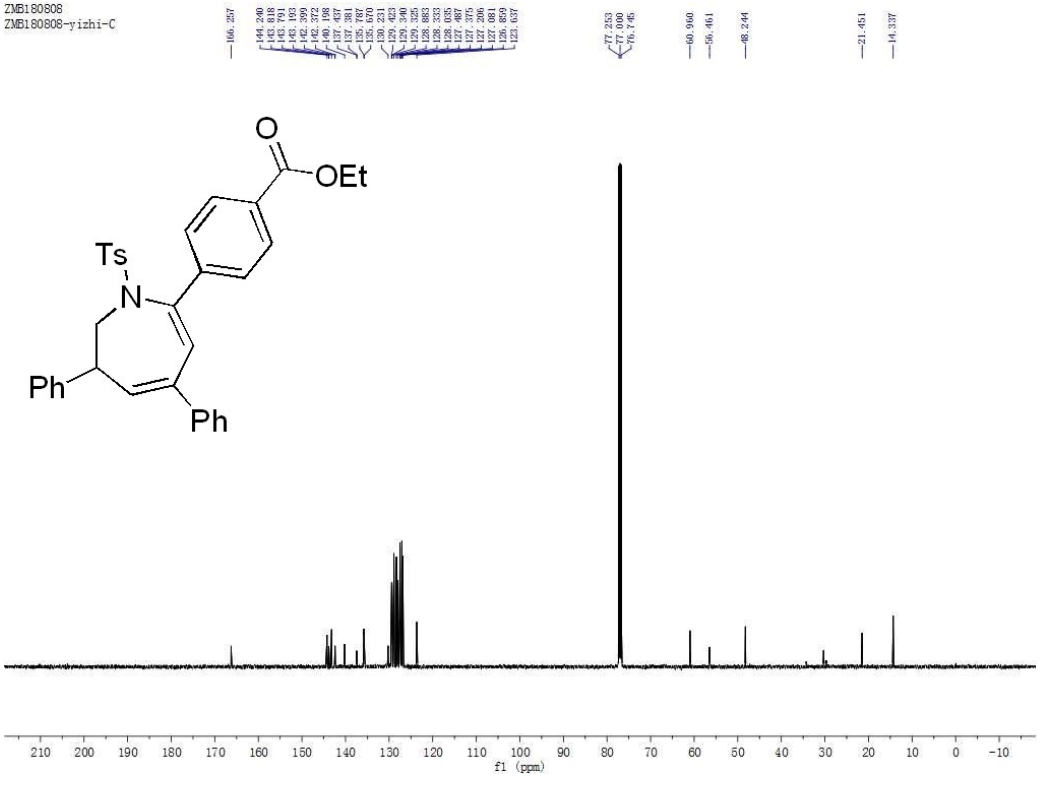
Methyl 4-(4,6-diphenyl-1-tosyl-6,7-dihydro-1*H*-azepin-2-yl)benzoate (9)



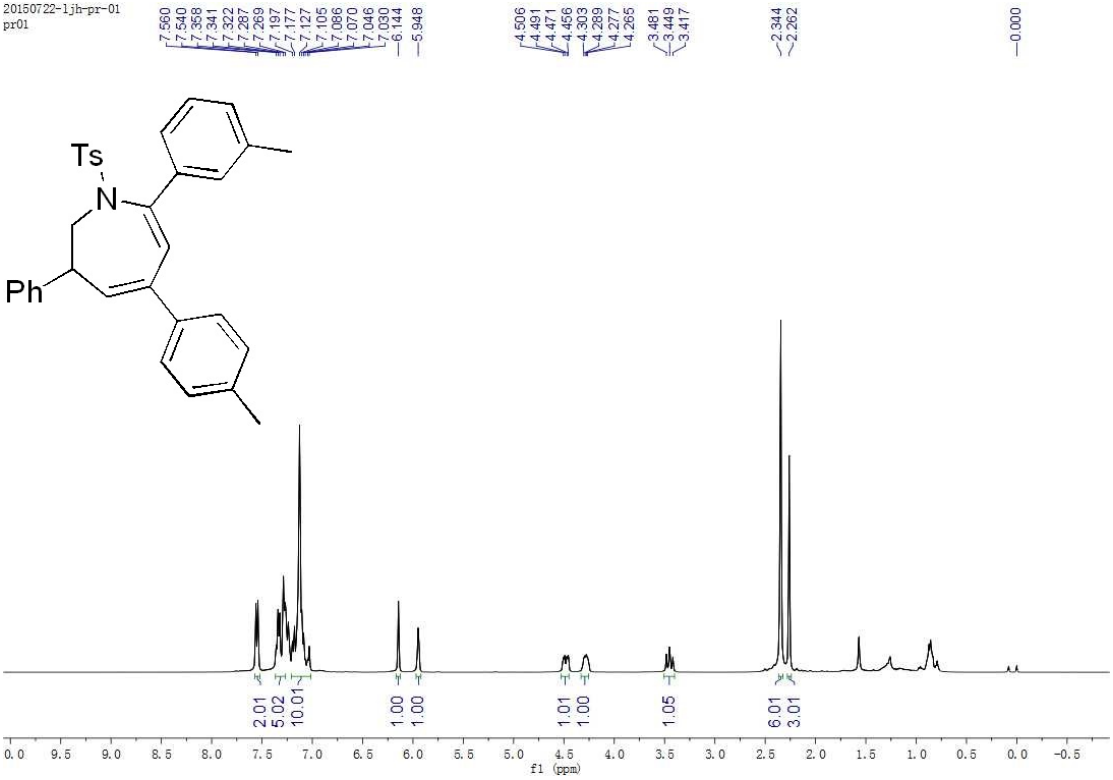


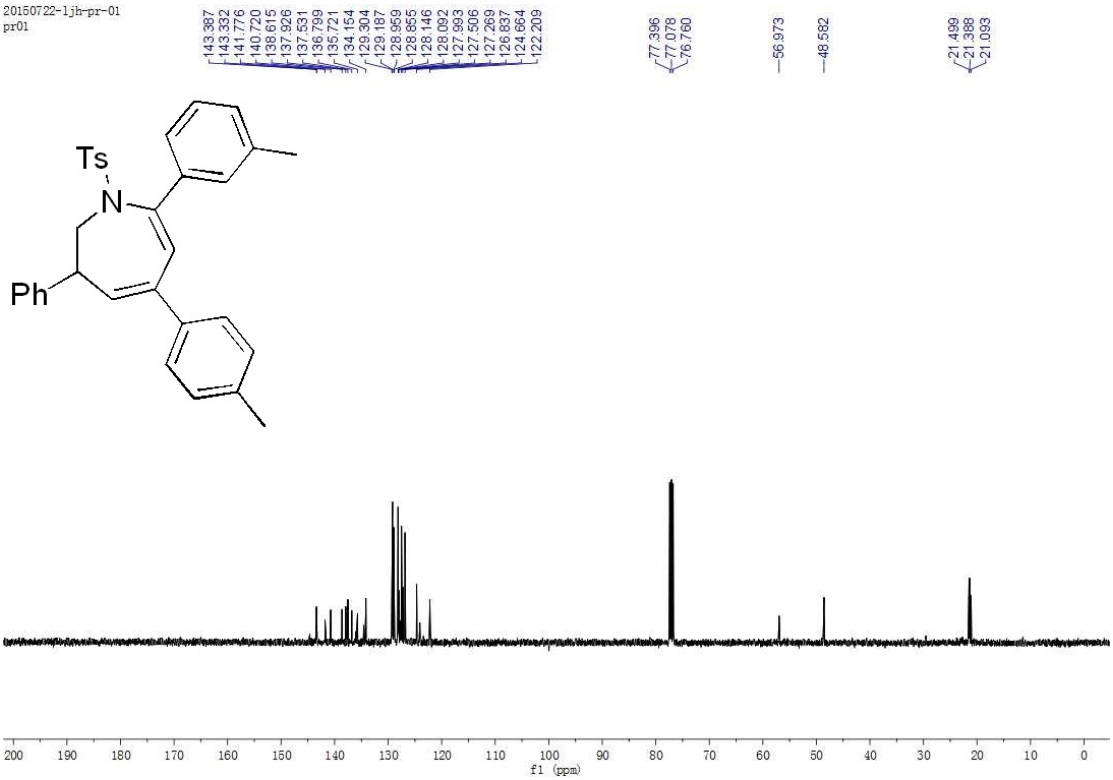
Ethyl 4-(4,6-diphenyl-1-tosyl-6,7-dihydro-1H-azepin-2-yl)benzoate (10)



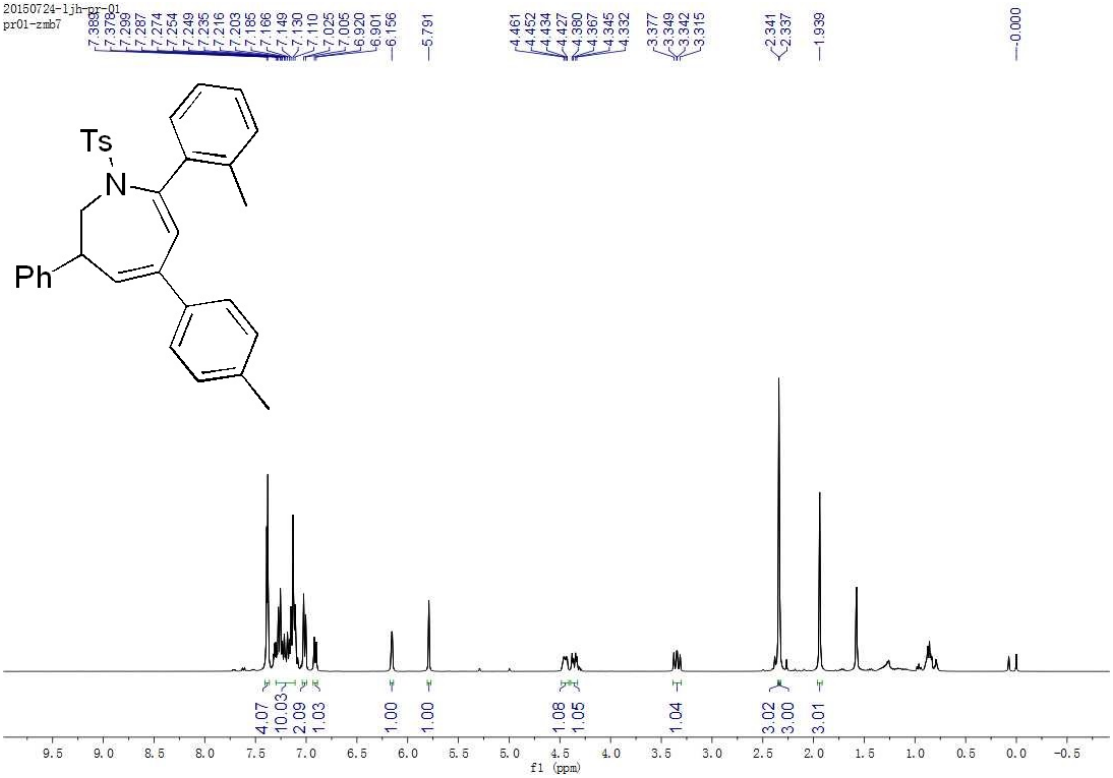


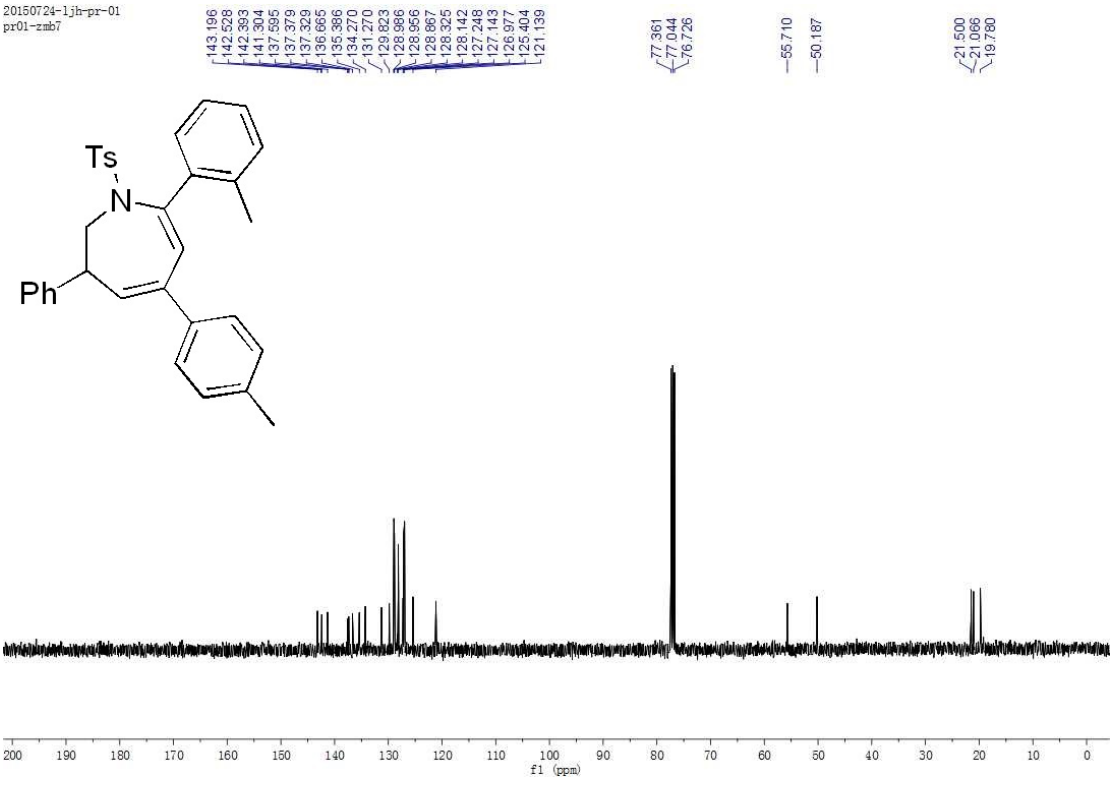
3-Phenyl-7-(*m*-tolyl)-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (11)



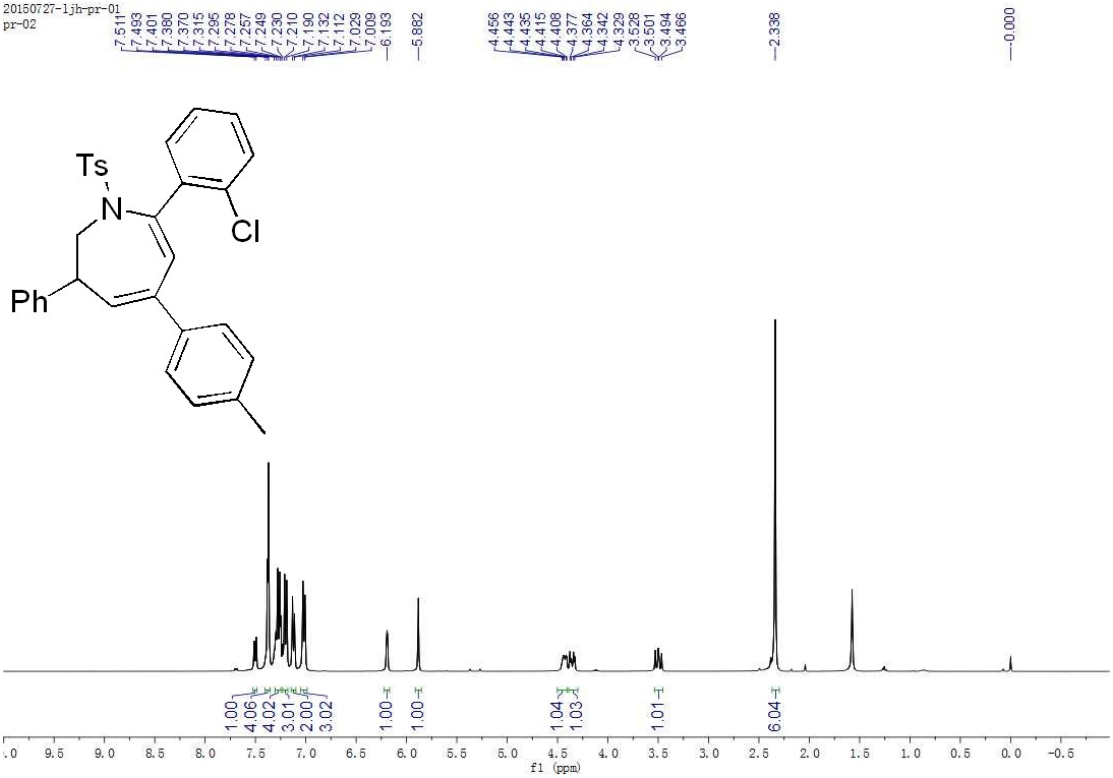


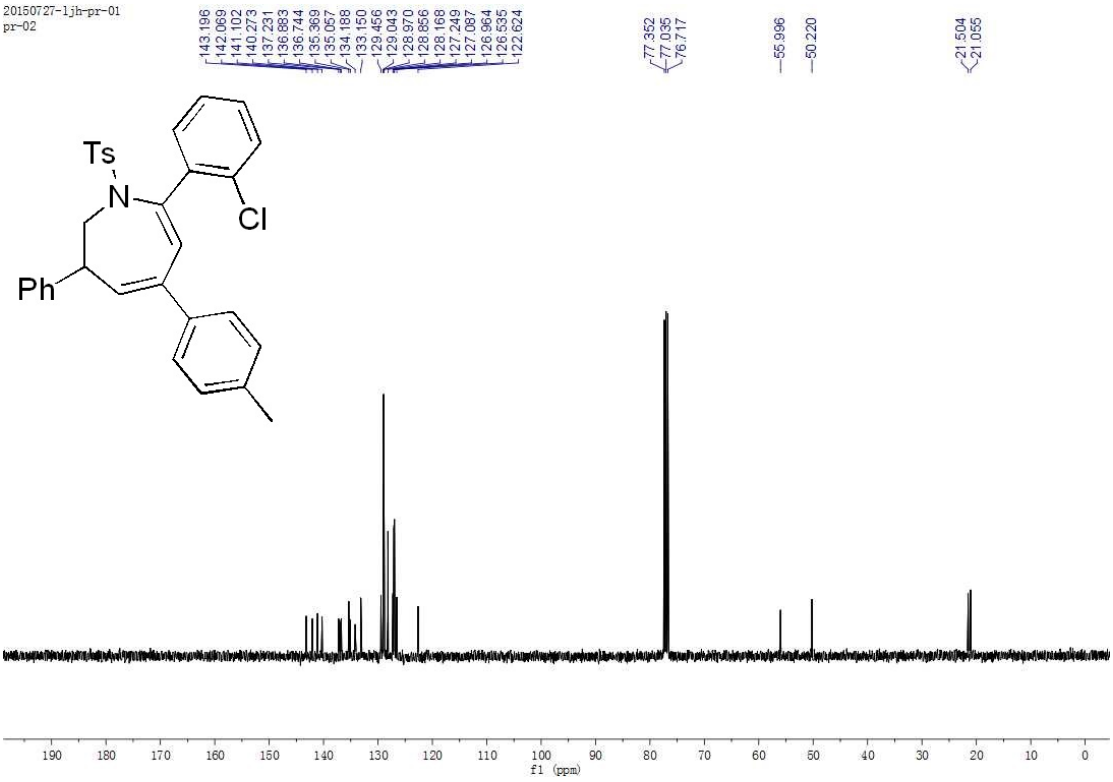
3-Phenyl-7-(*o*-tolyl)-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (12)



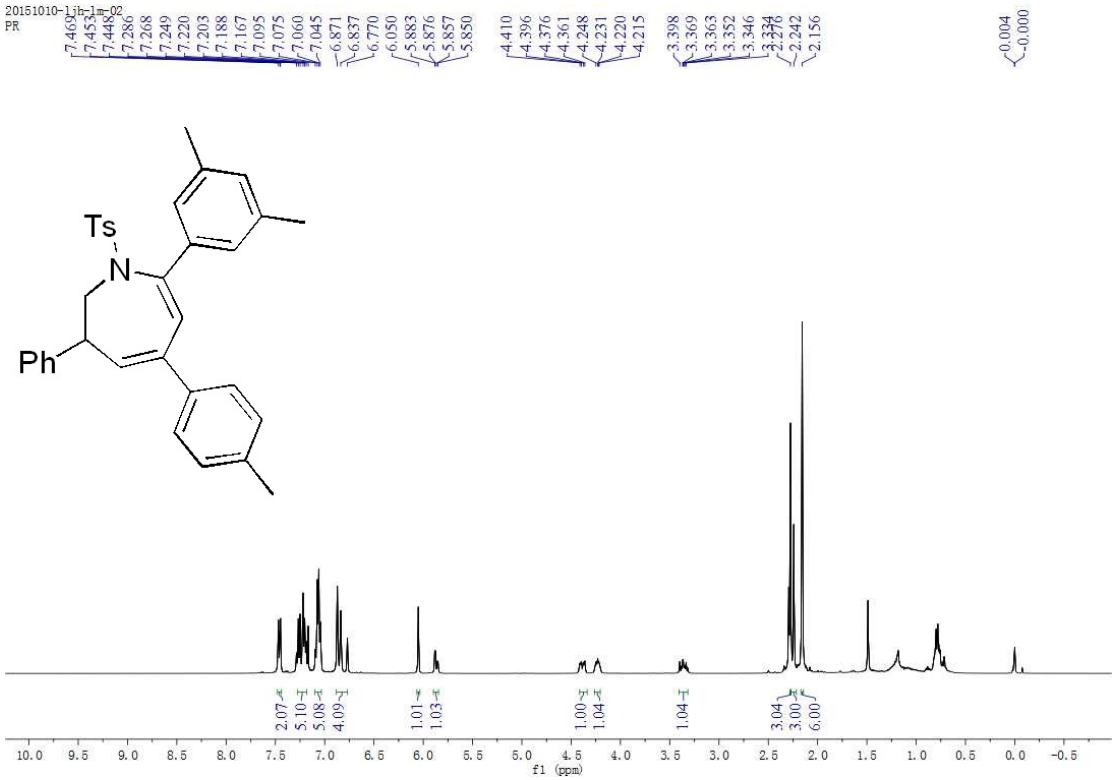


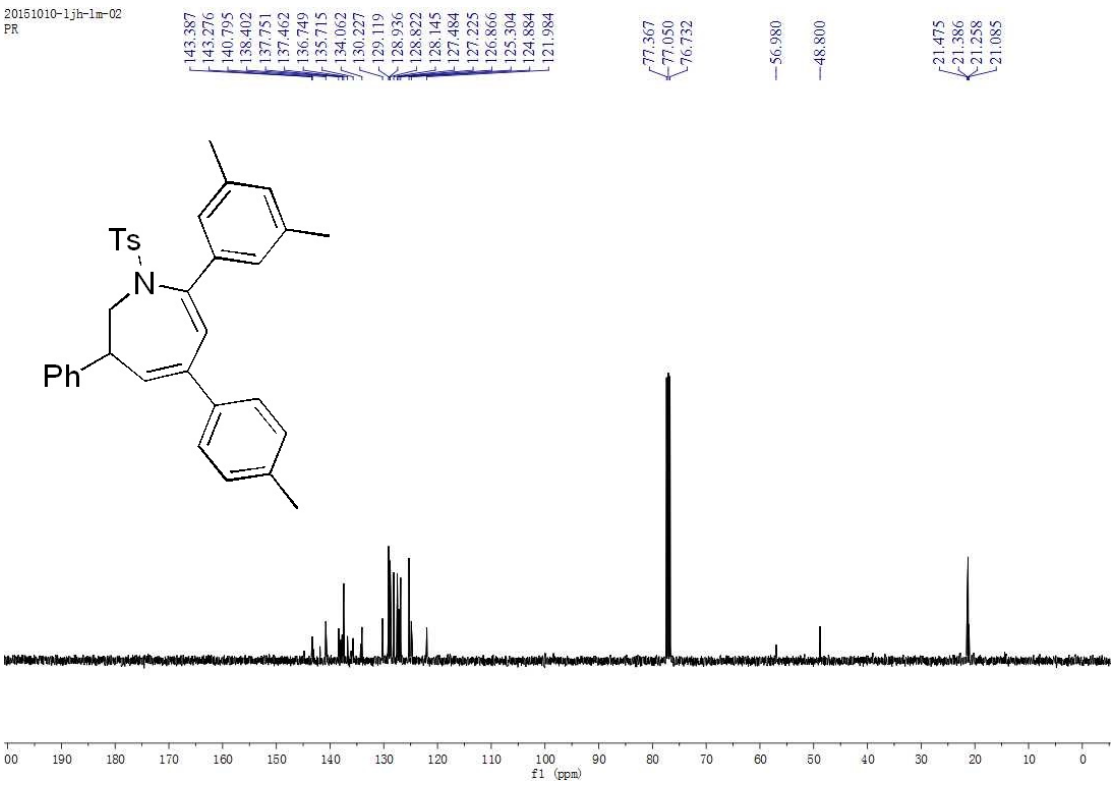
7-(2-Chlorophenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (13)



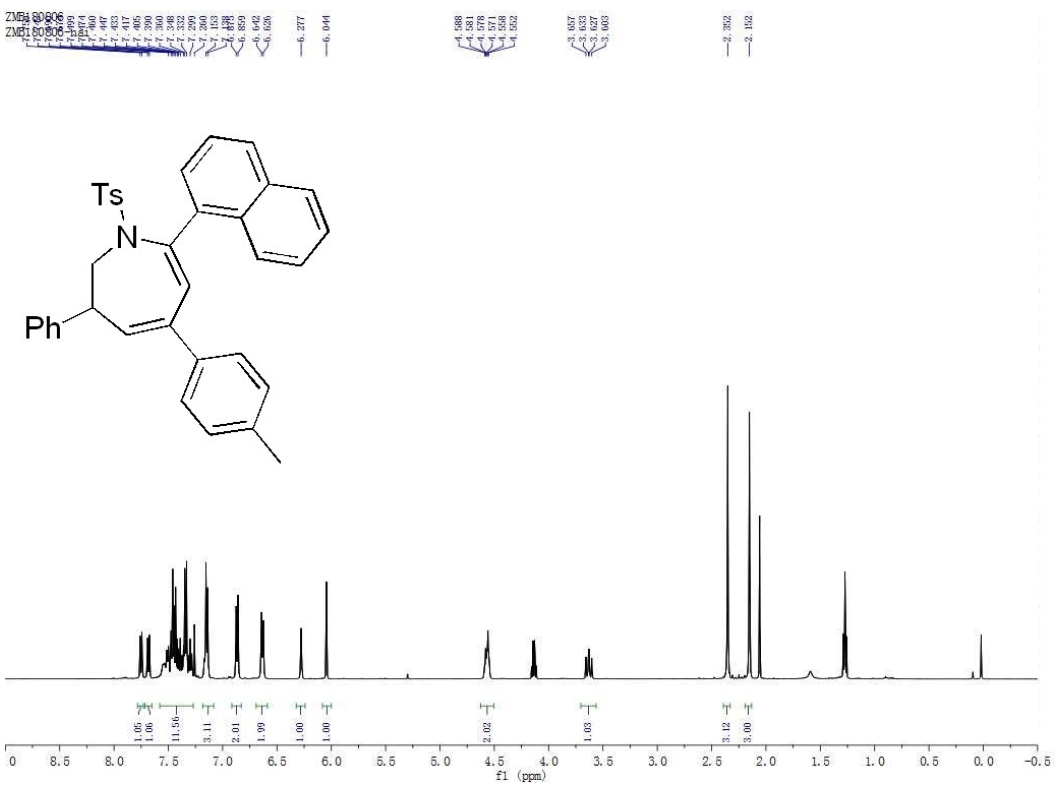


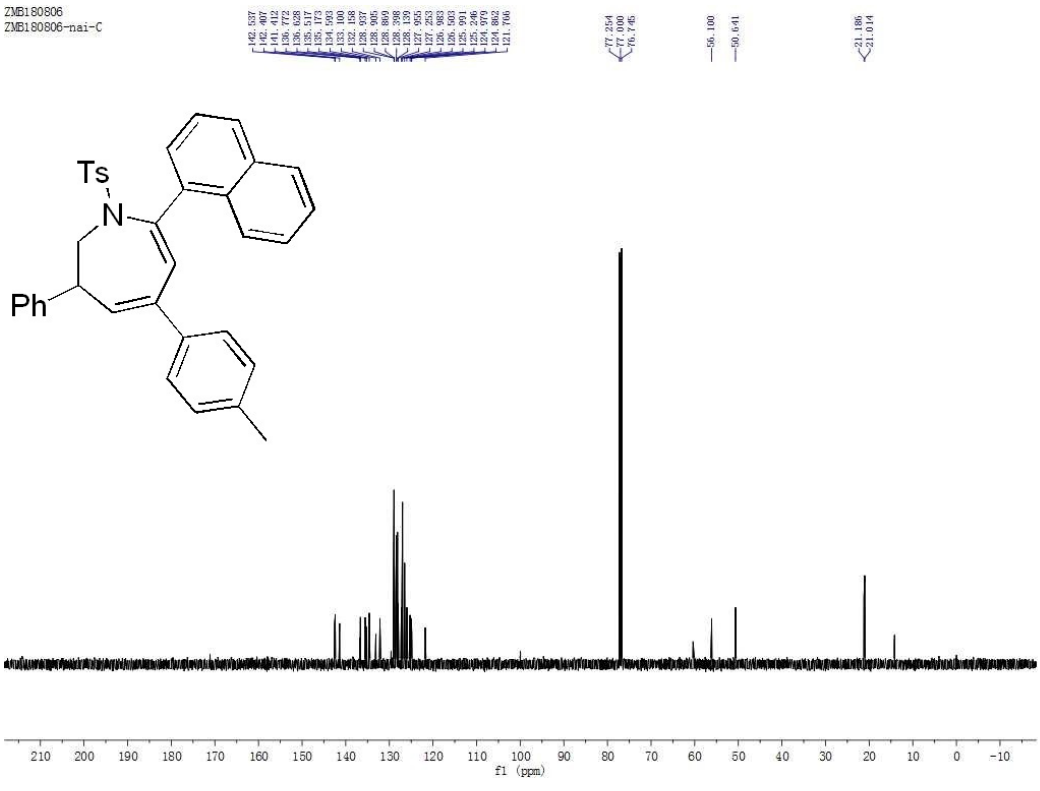
7-(3,5-Dimethylphenyl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (14)



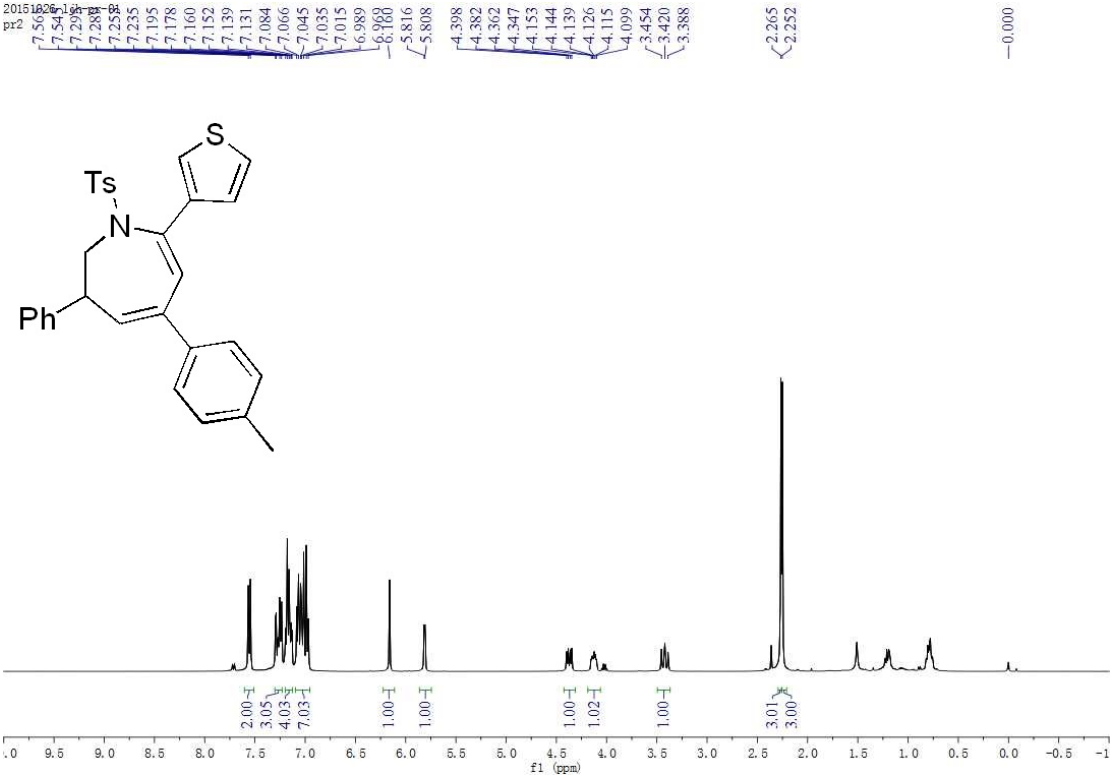


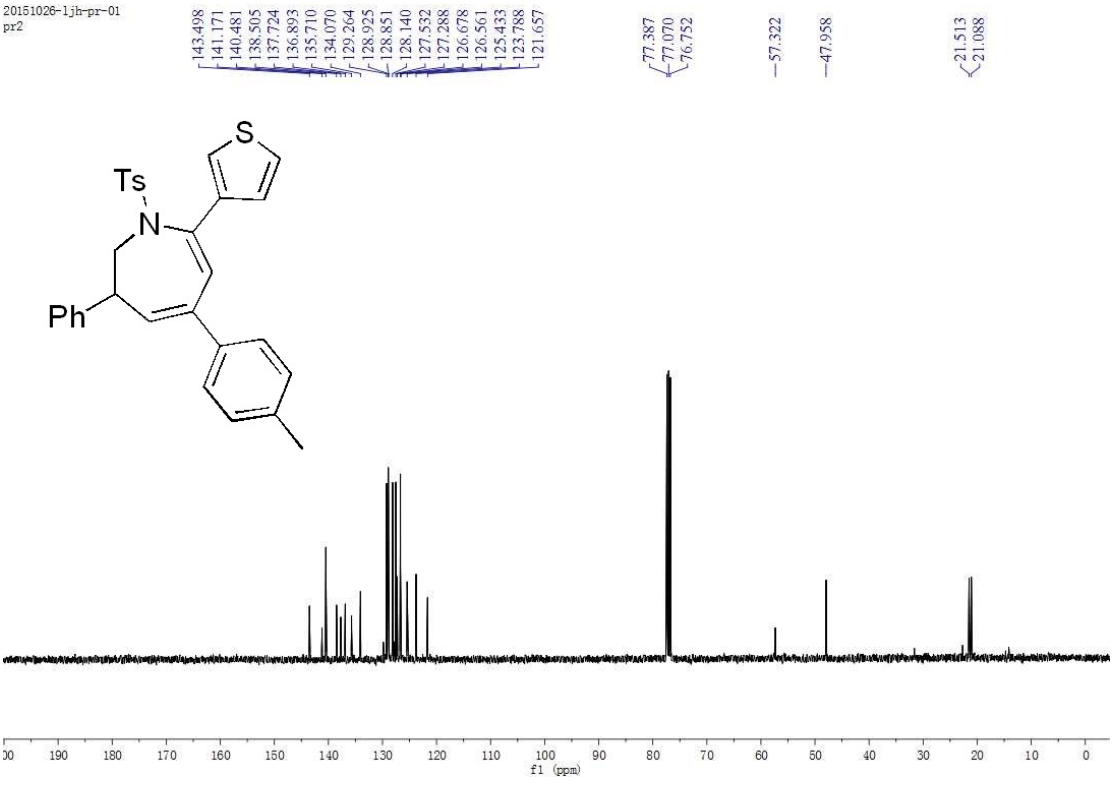
7-(Naphthalen-1-yl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (15)



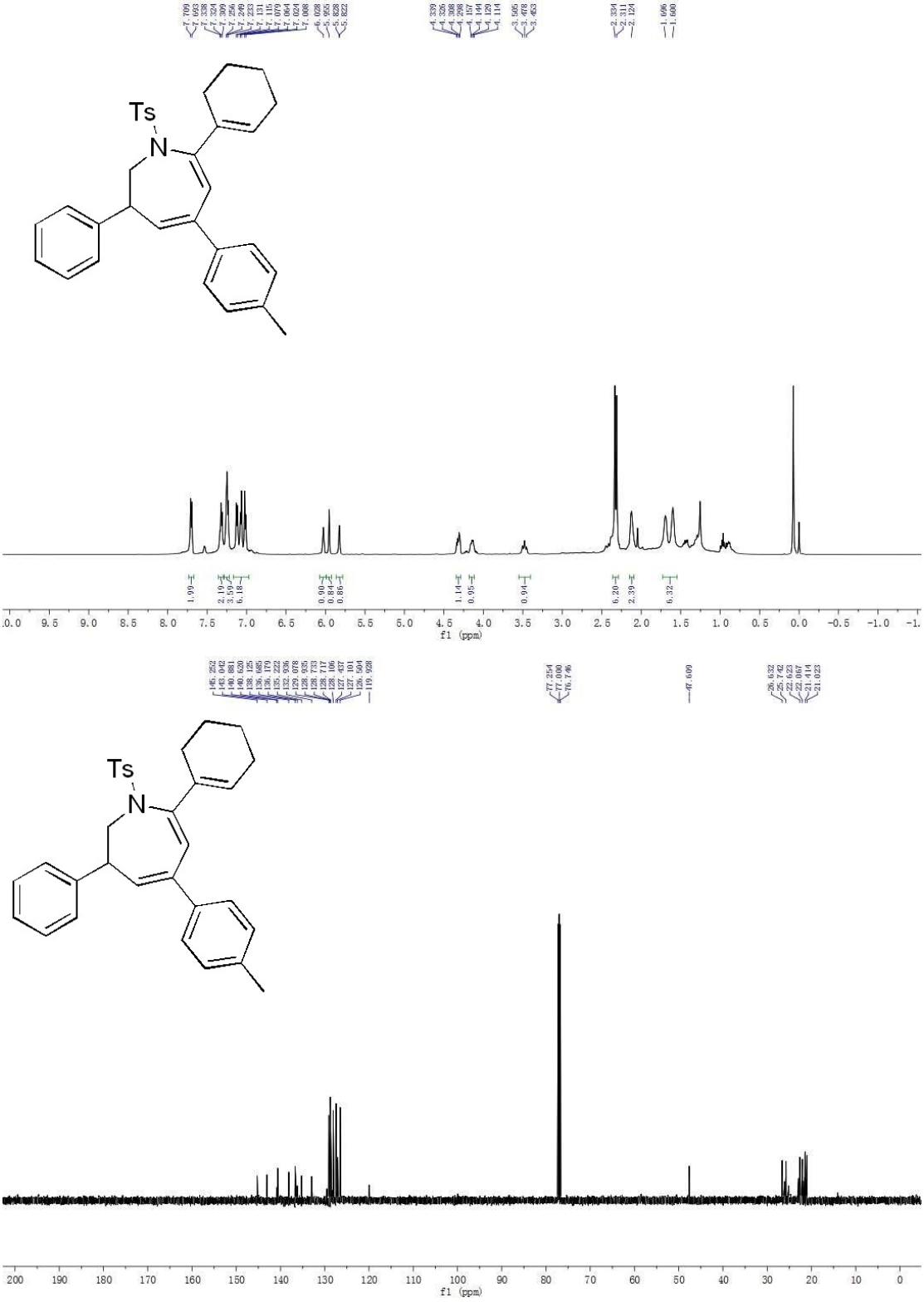


3-Phenyl-7-(thiophen-3-yl)-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (16)

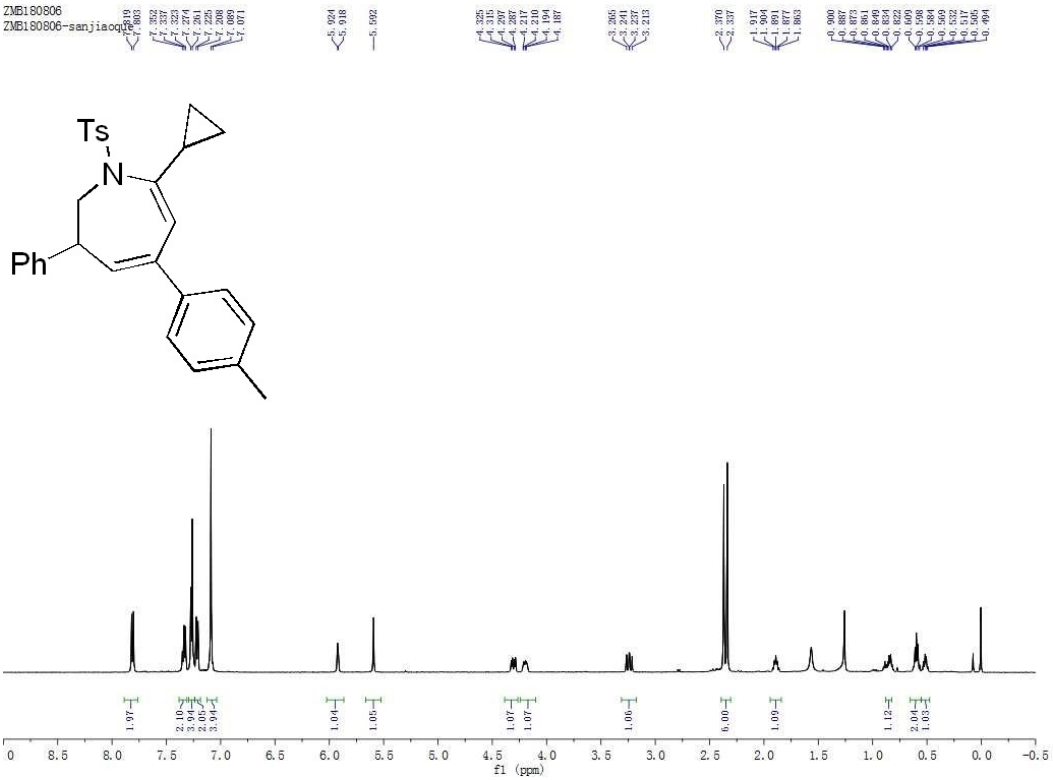


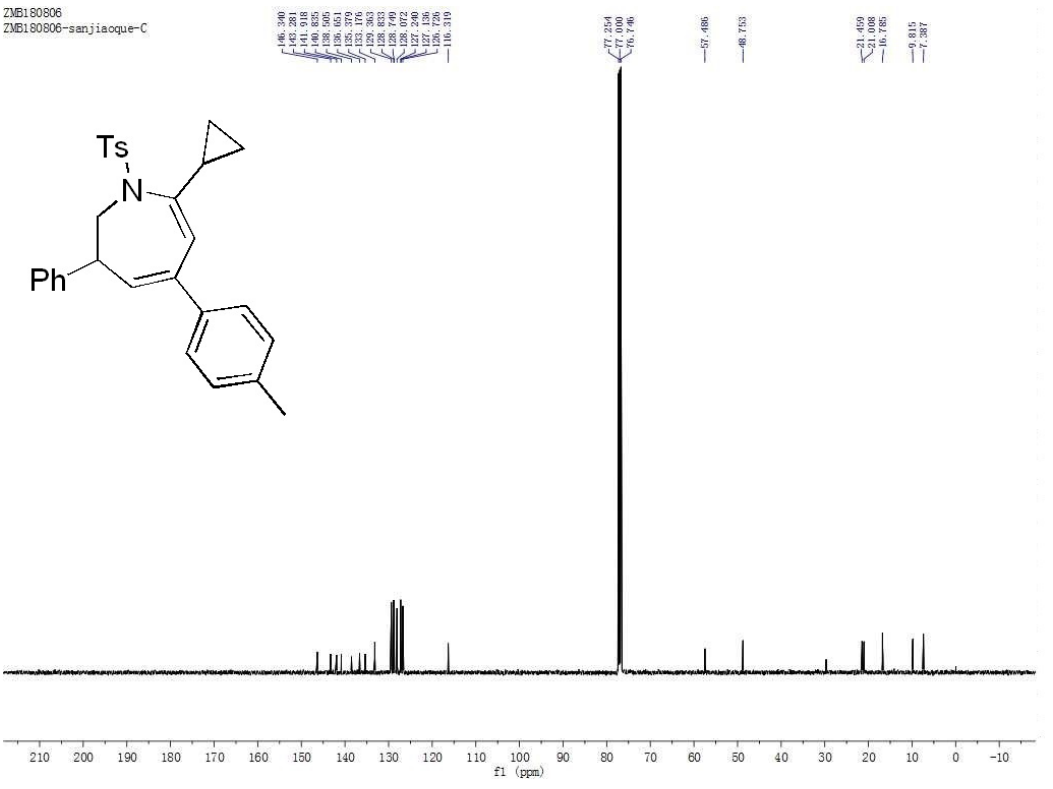


7-(Cyclohex-1-en-1-yl)-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (17)

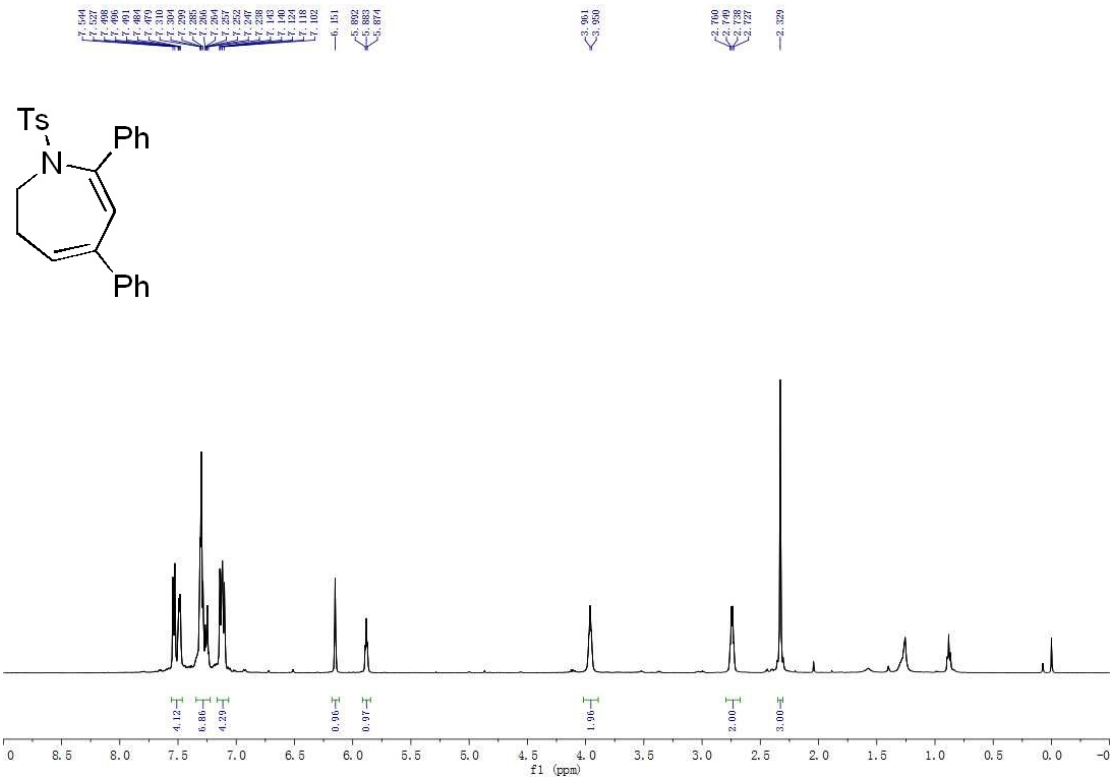


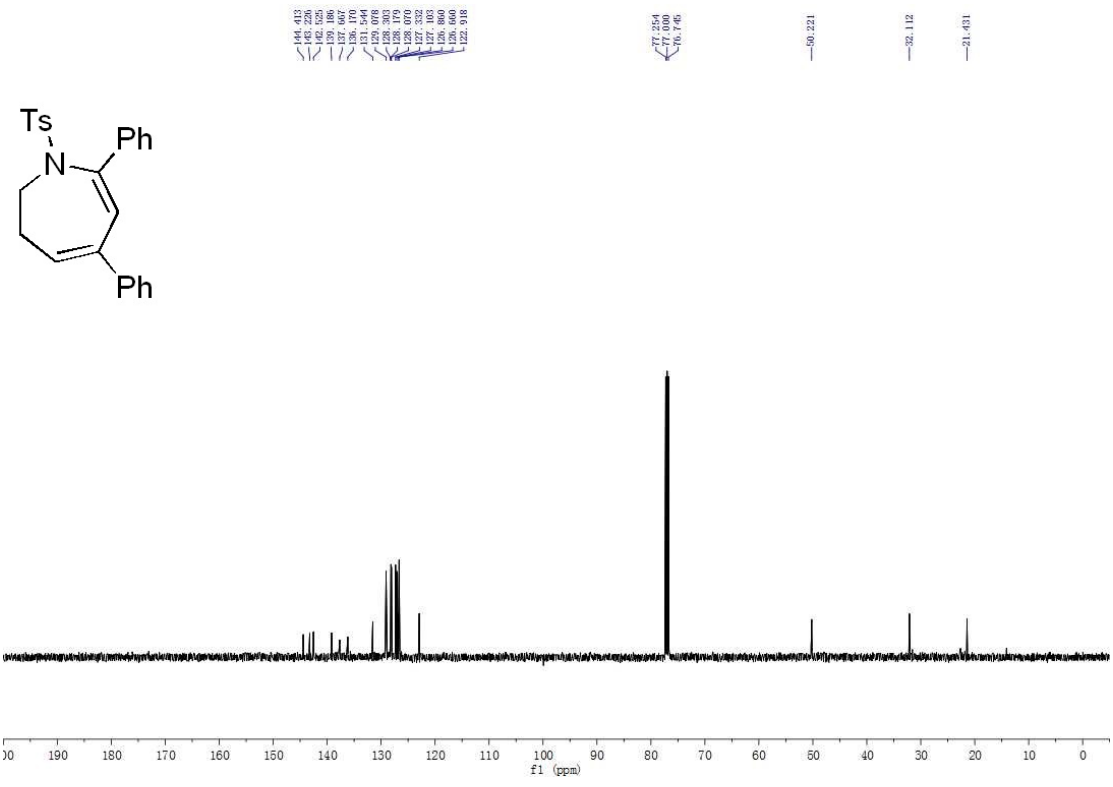
7-Cyclopropyl-3-phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (18)



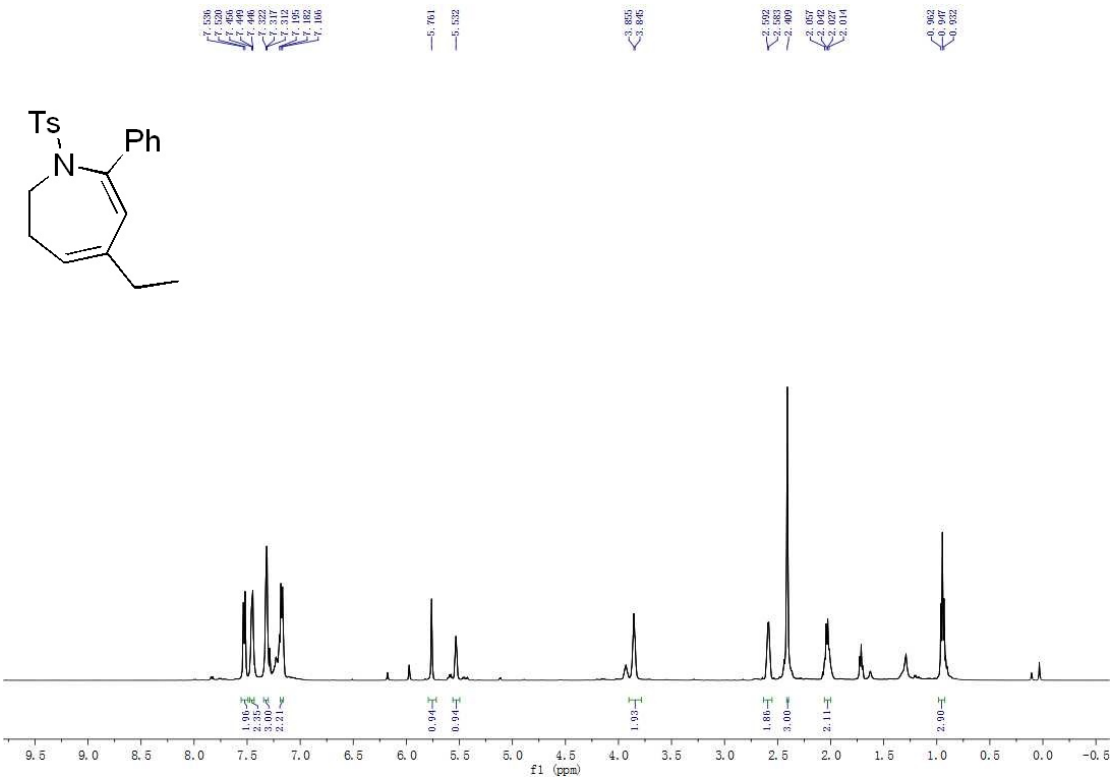


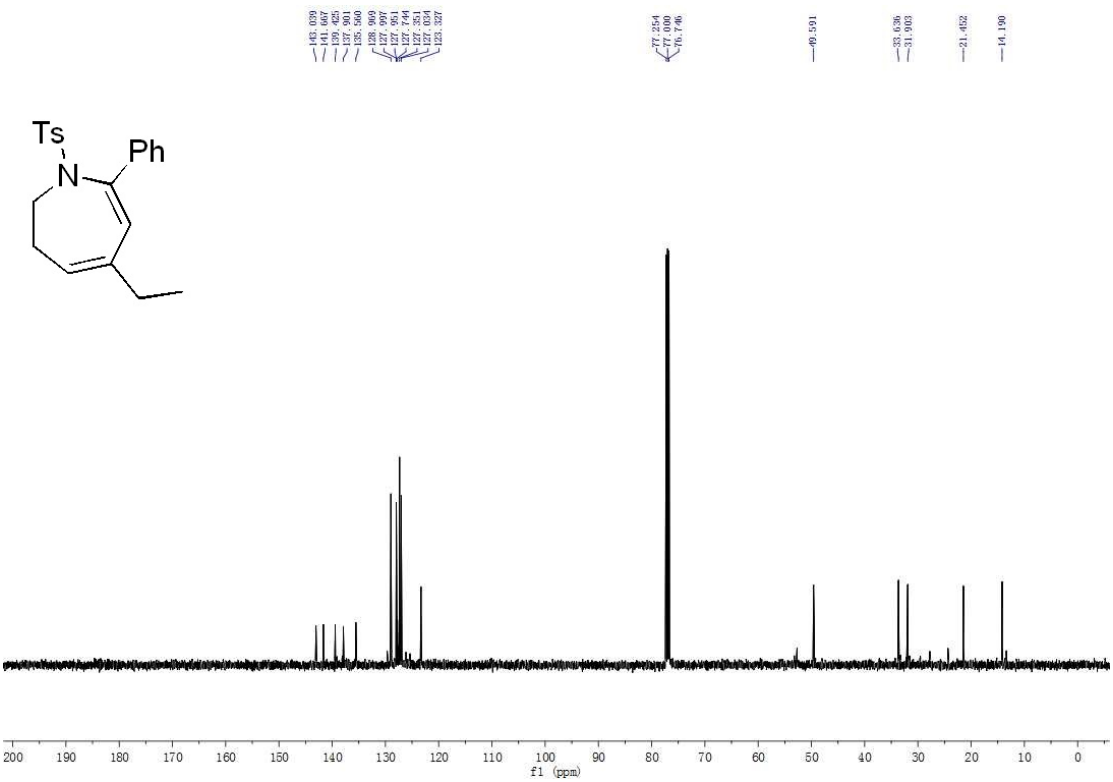
5,7-Diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (20)



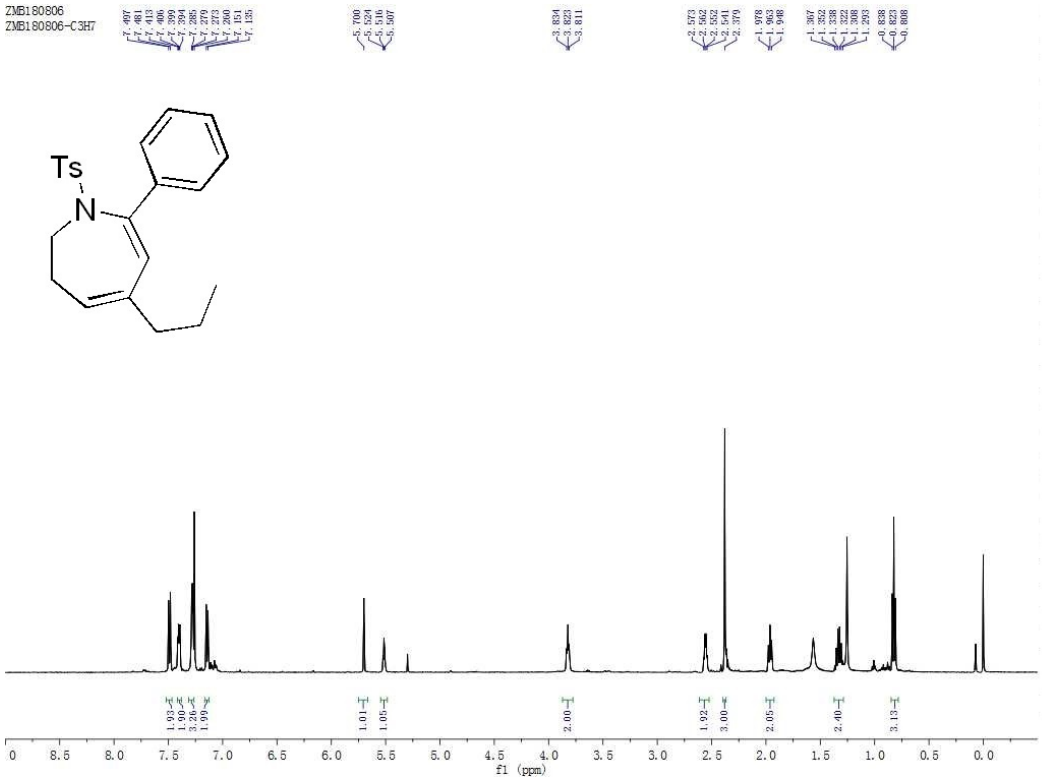


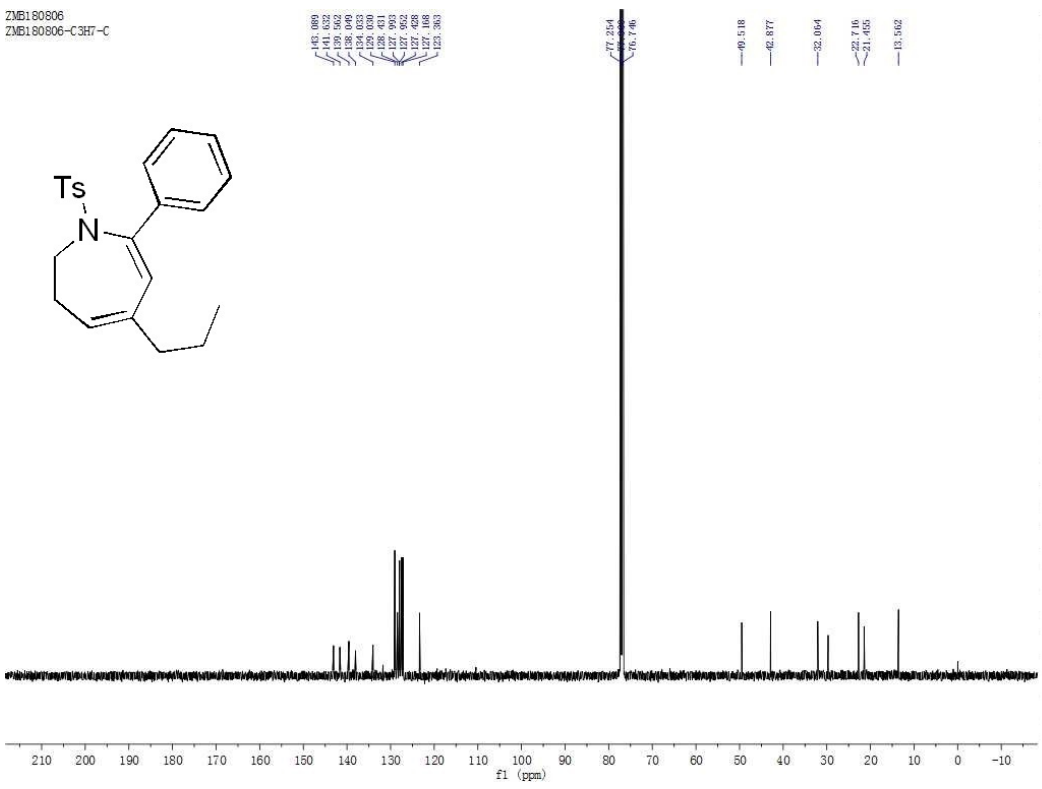
5-Ethyl-7-phenyl-1-tosyl-2,3-dihydro-1*H*-azepine (21)



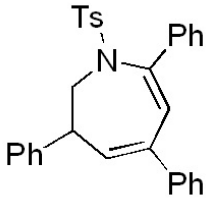


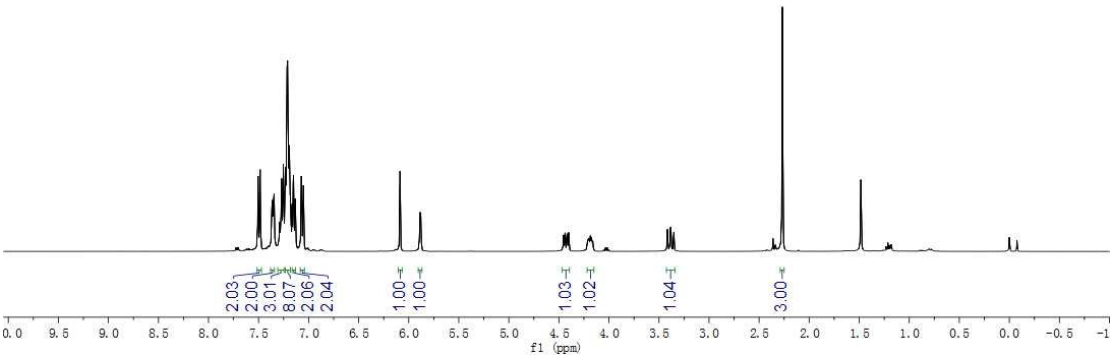
7-Phenyl-5-propyl-1-tosyl-2,3-dihydro-1*H*-azepine (22)

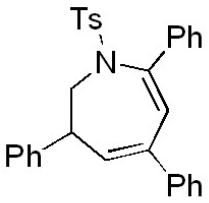


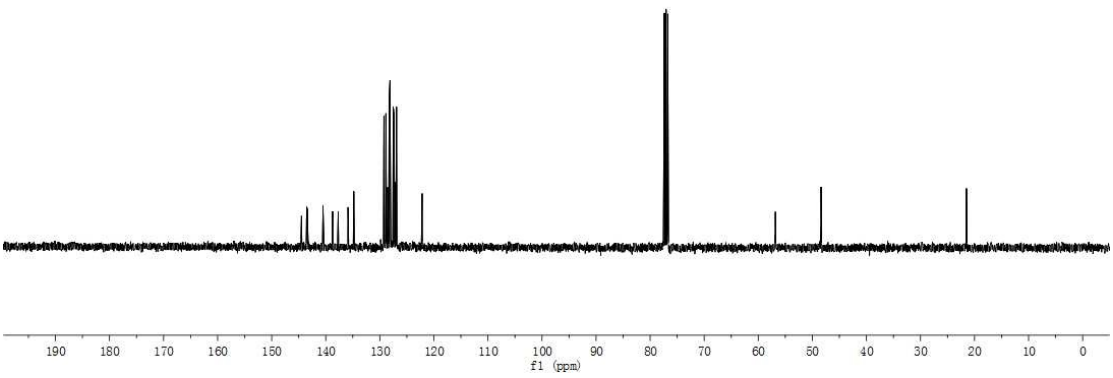


3,5,7-Triphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (23)

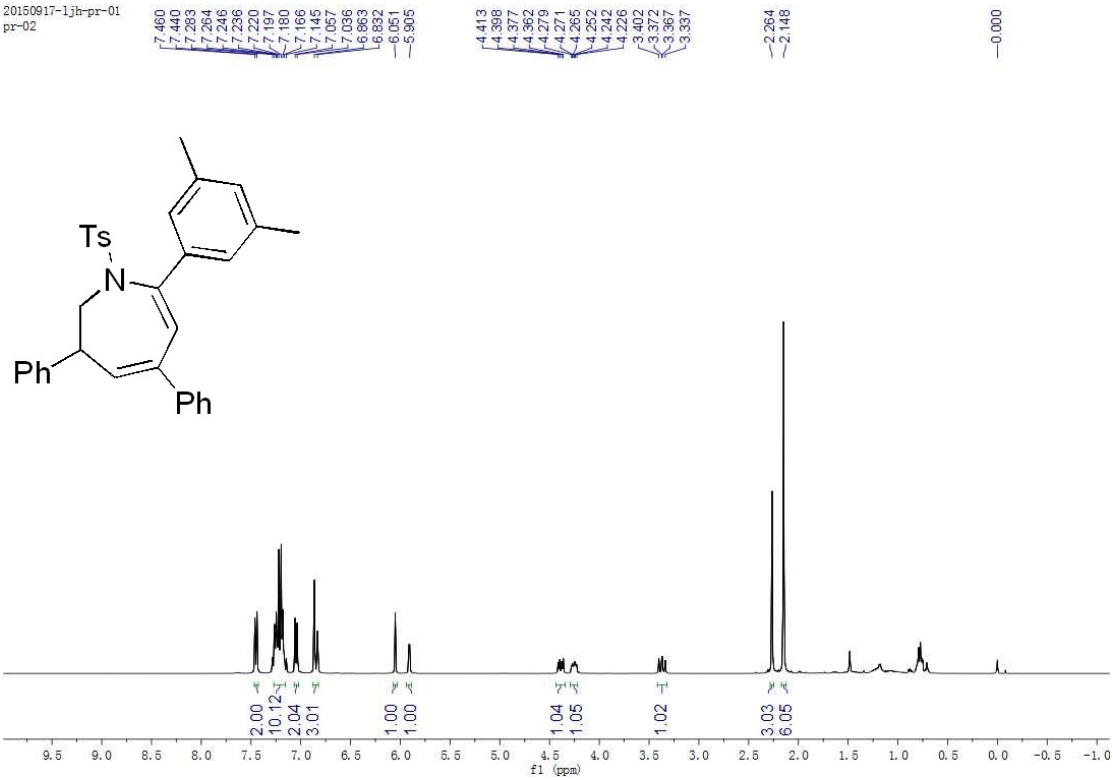


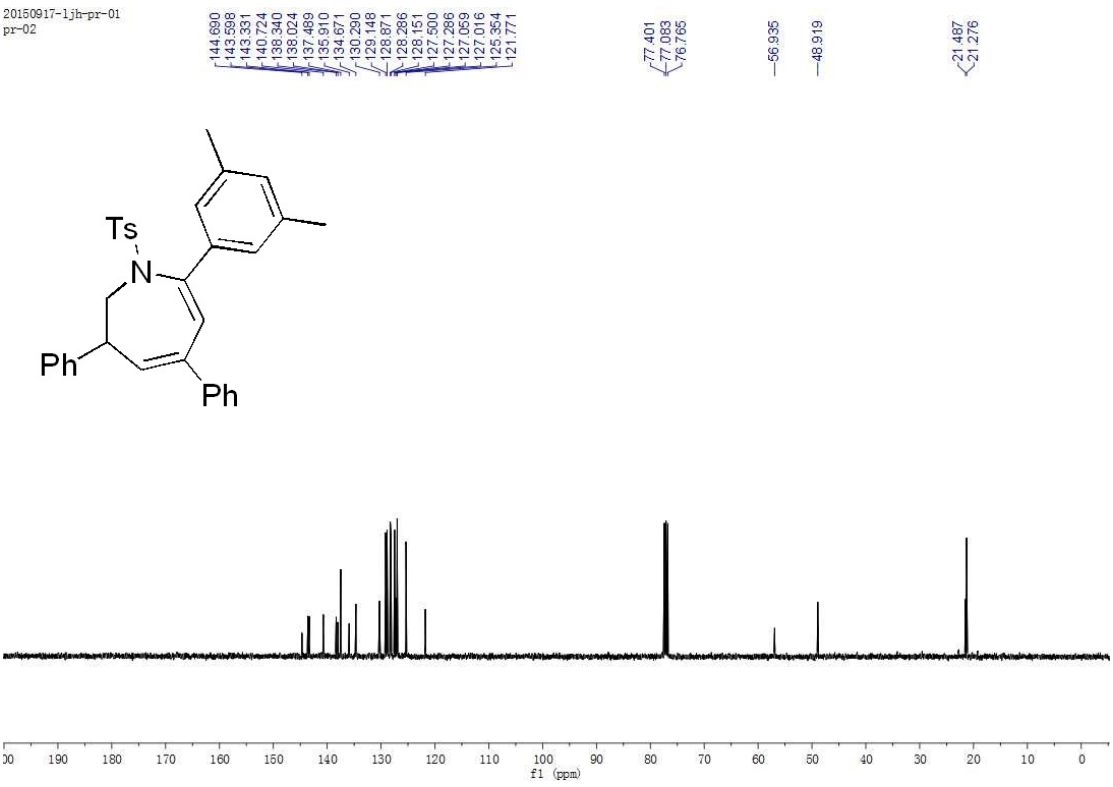




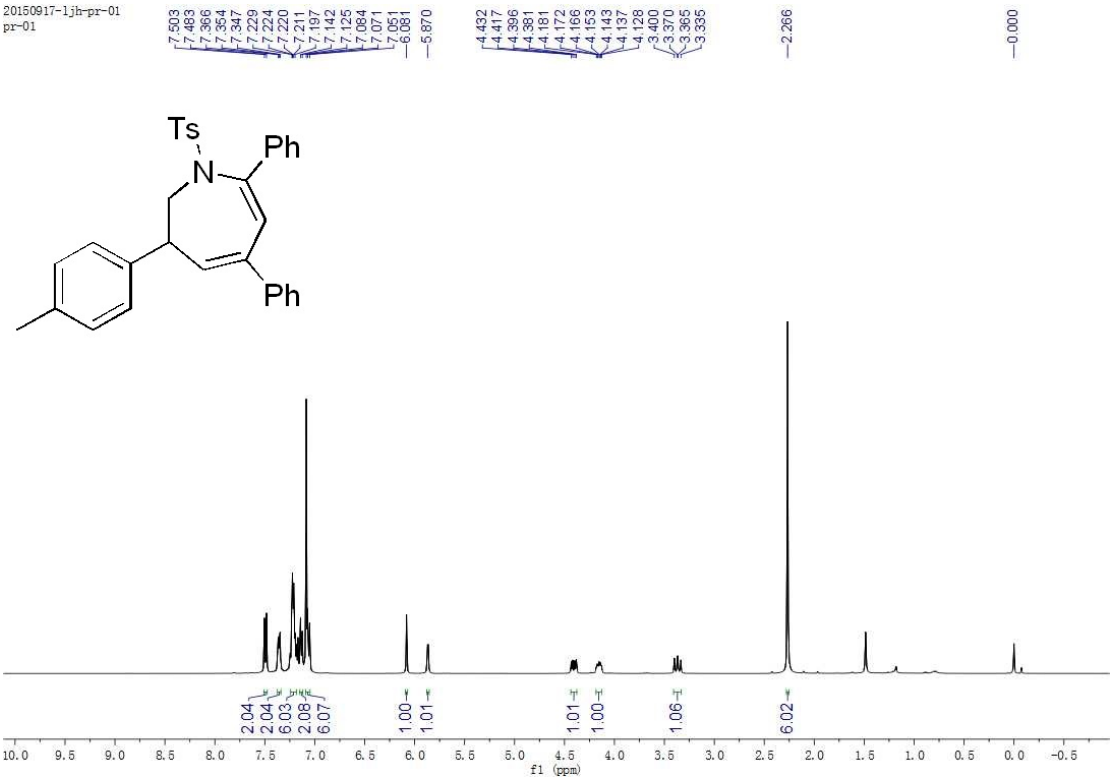


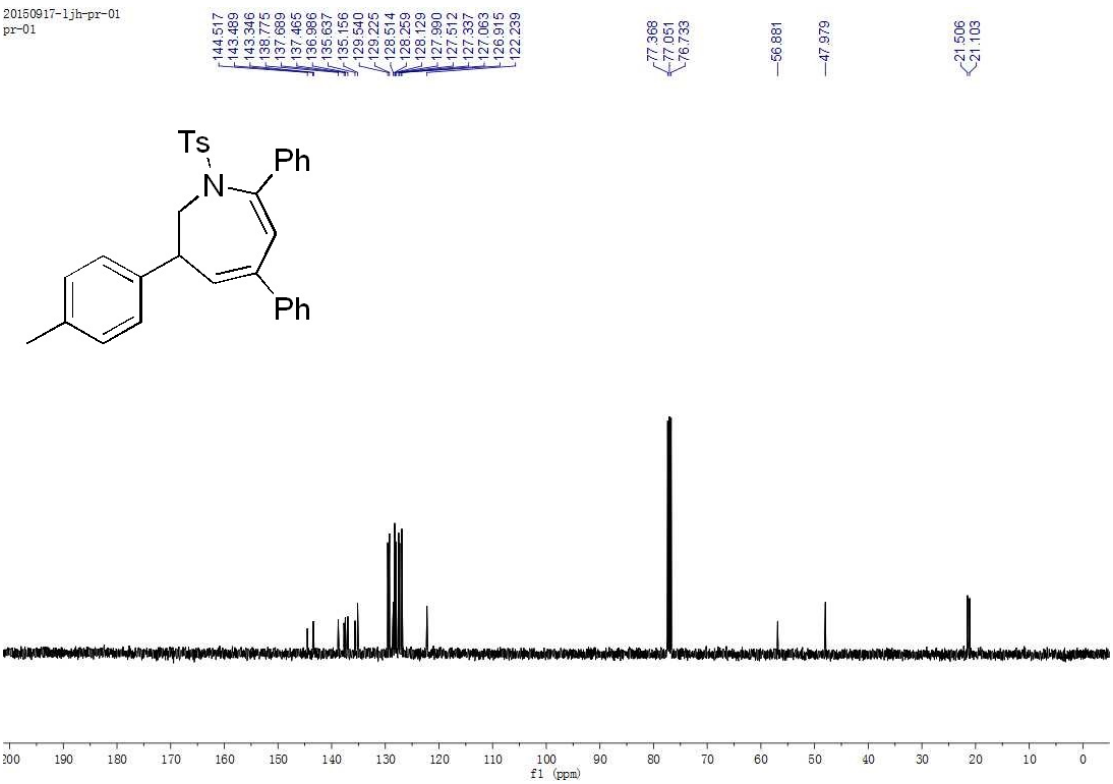
7-(3,5-Dimethylphenyl)-3,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (24)



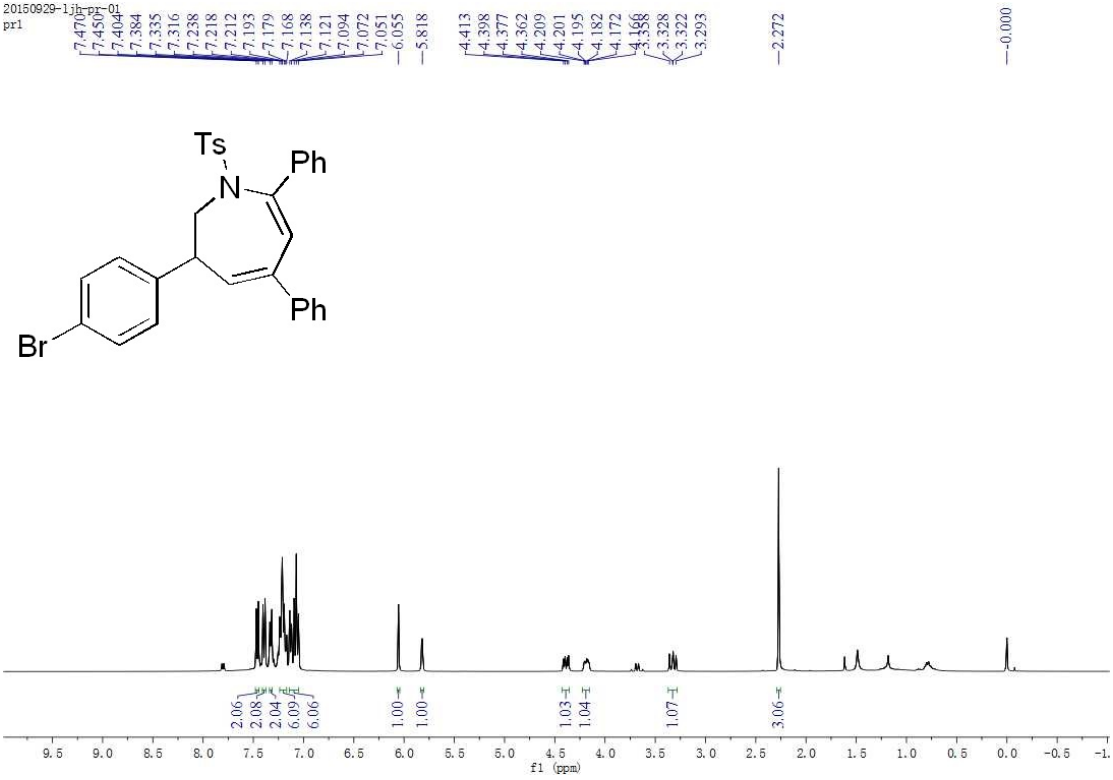


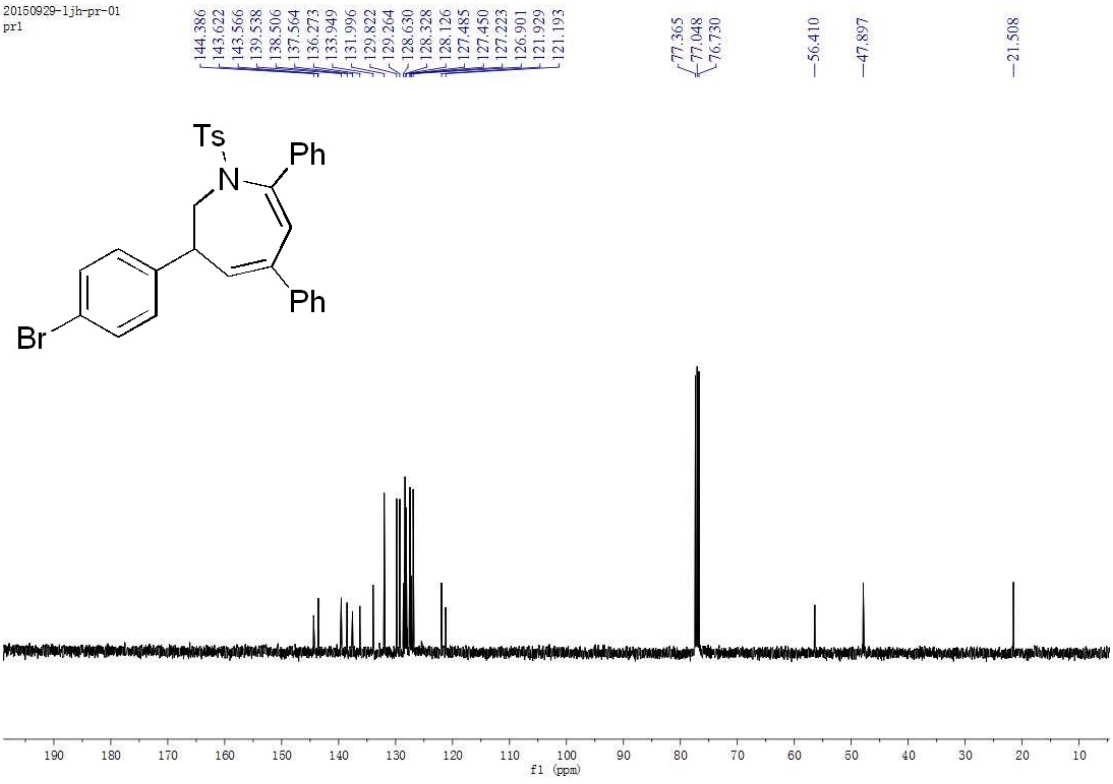
5,7-Diphenyl-3-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (25)



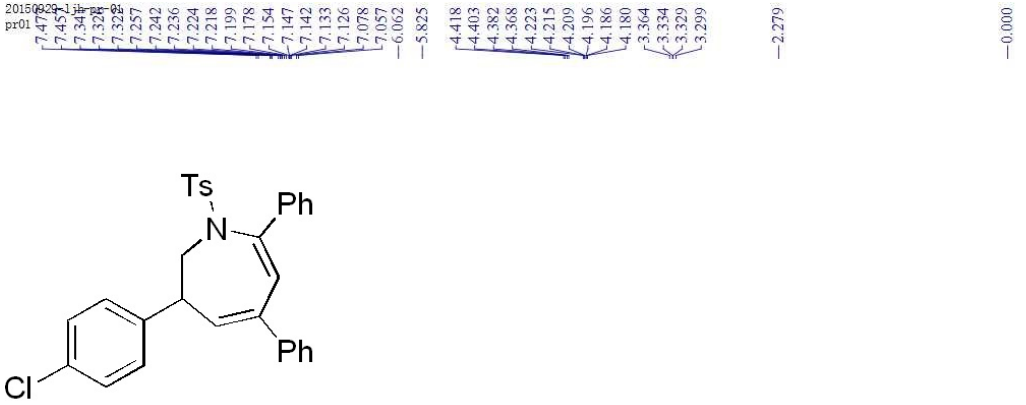


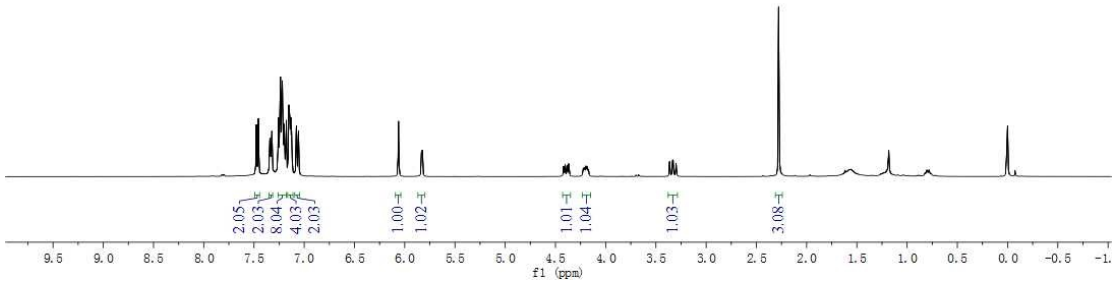
3-(4-Bromophenyl)-5,7-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (26)

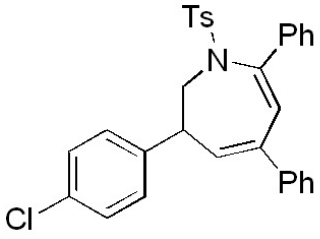


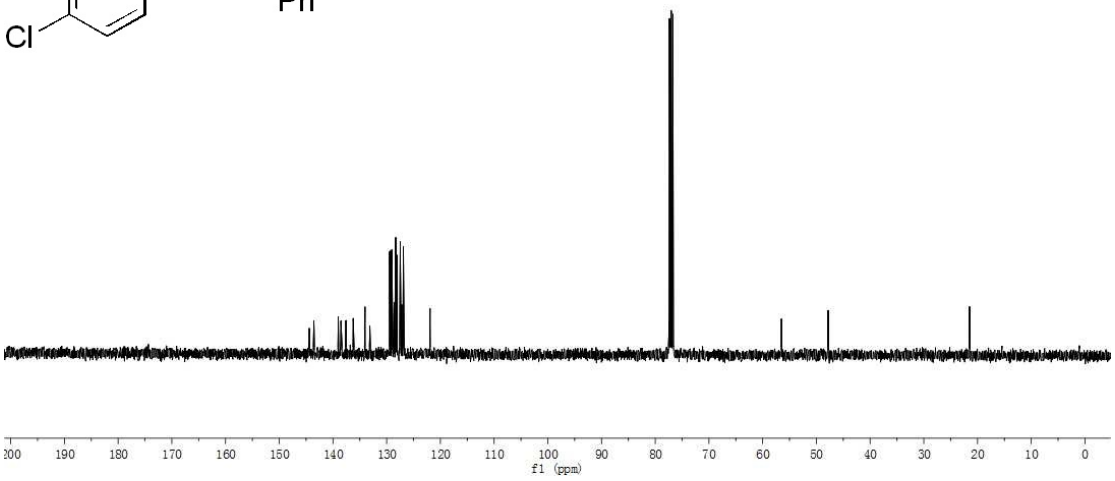


3-(4-Chlorophenyl)-5,7-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (27)

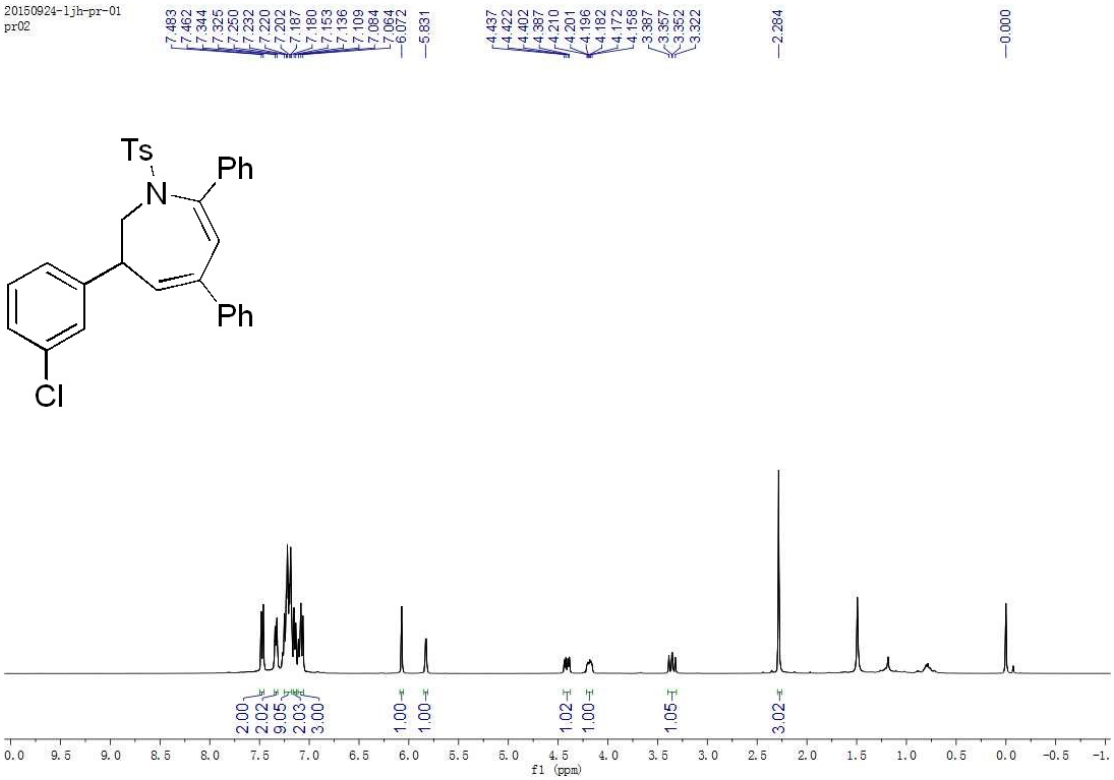


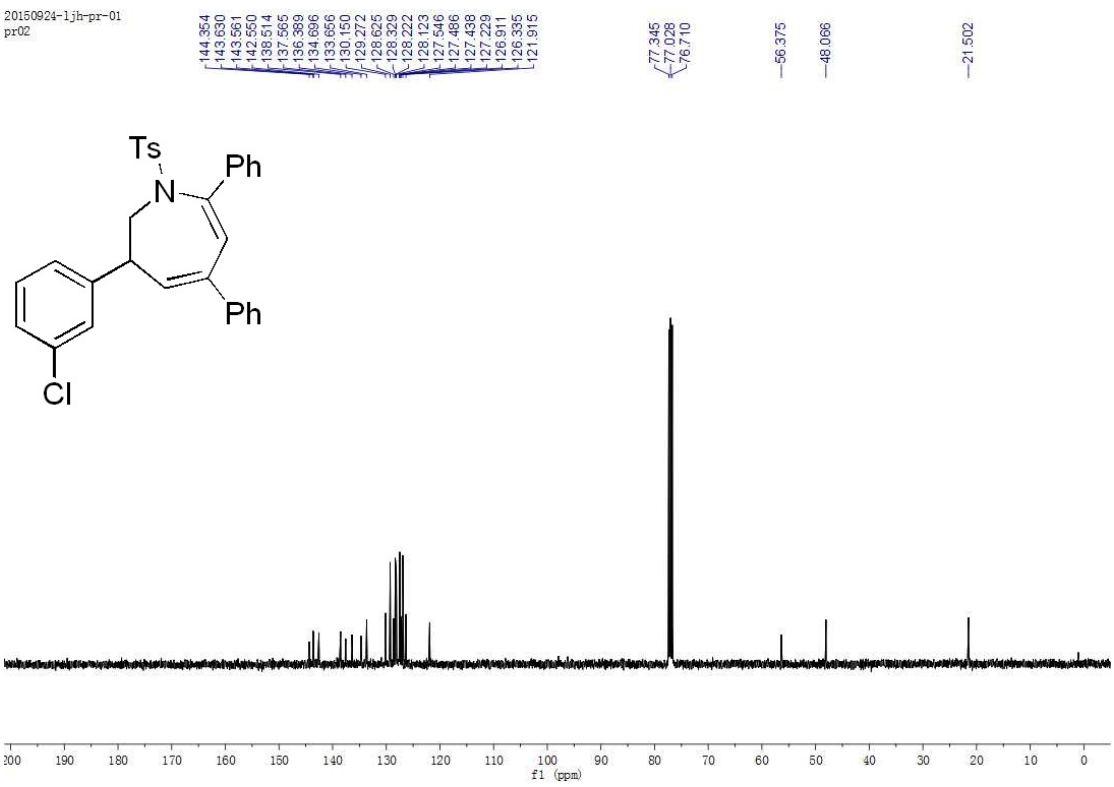




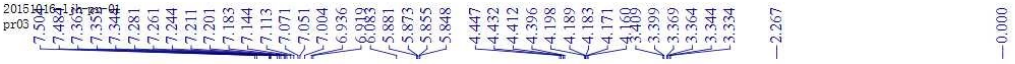


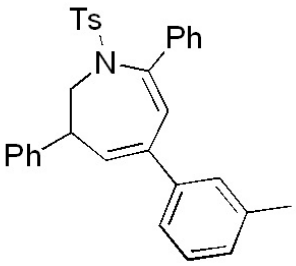
3-(3-Chlorophenyl)-5,7-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (28)

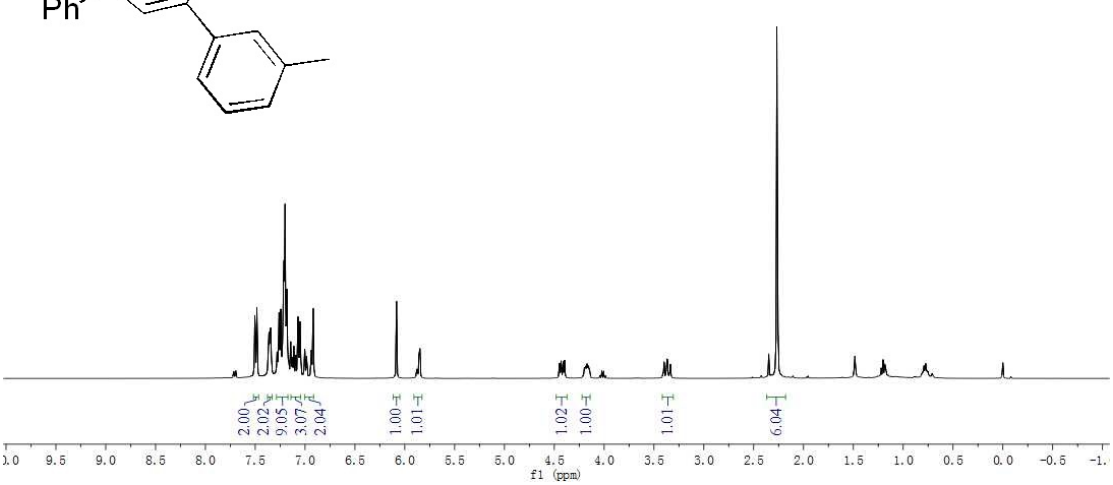


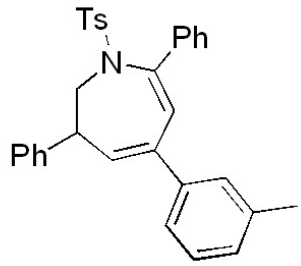


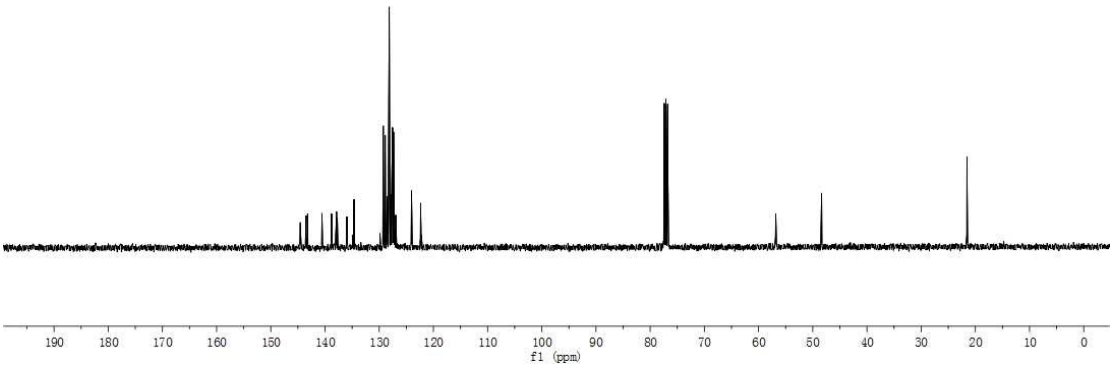
3,7-Diphenyl-5-(*m*-tolyl)-1-tosyl-2,3-dihydro-1*H*-azepine (29)



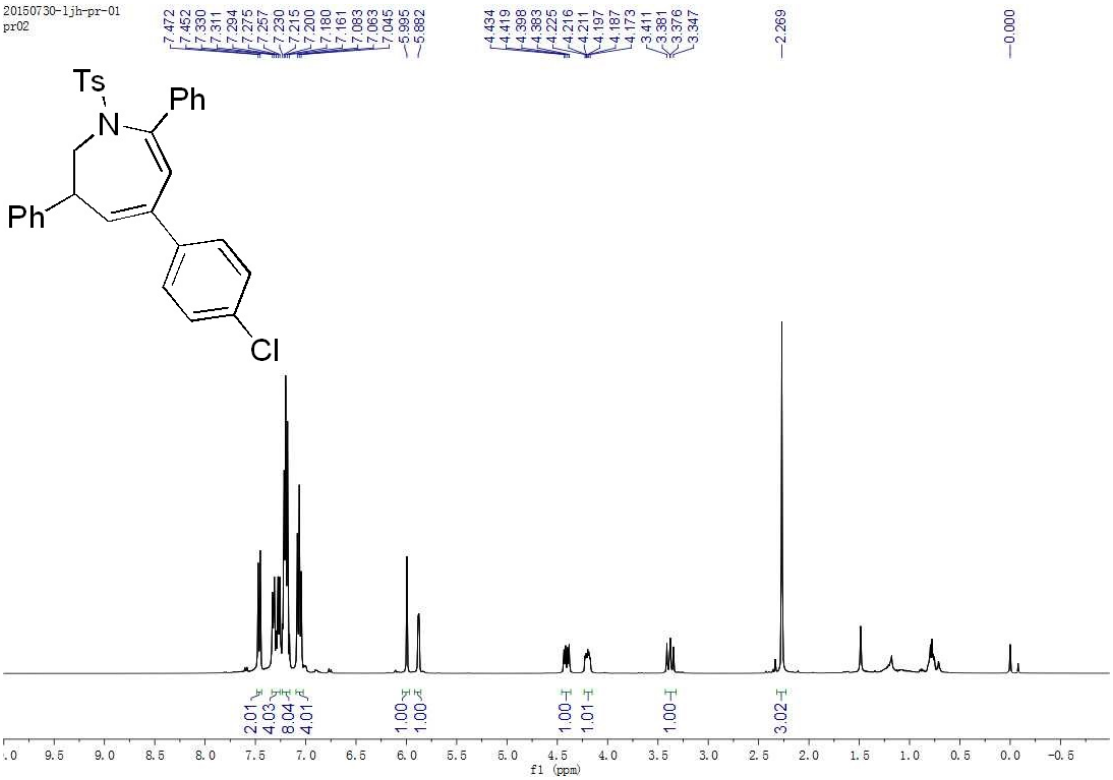


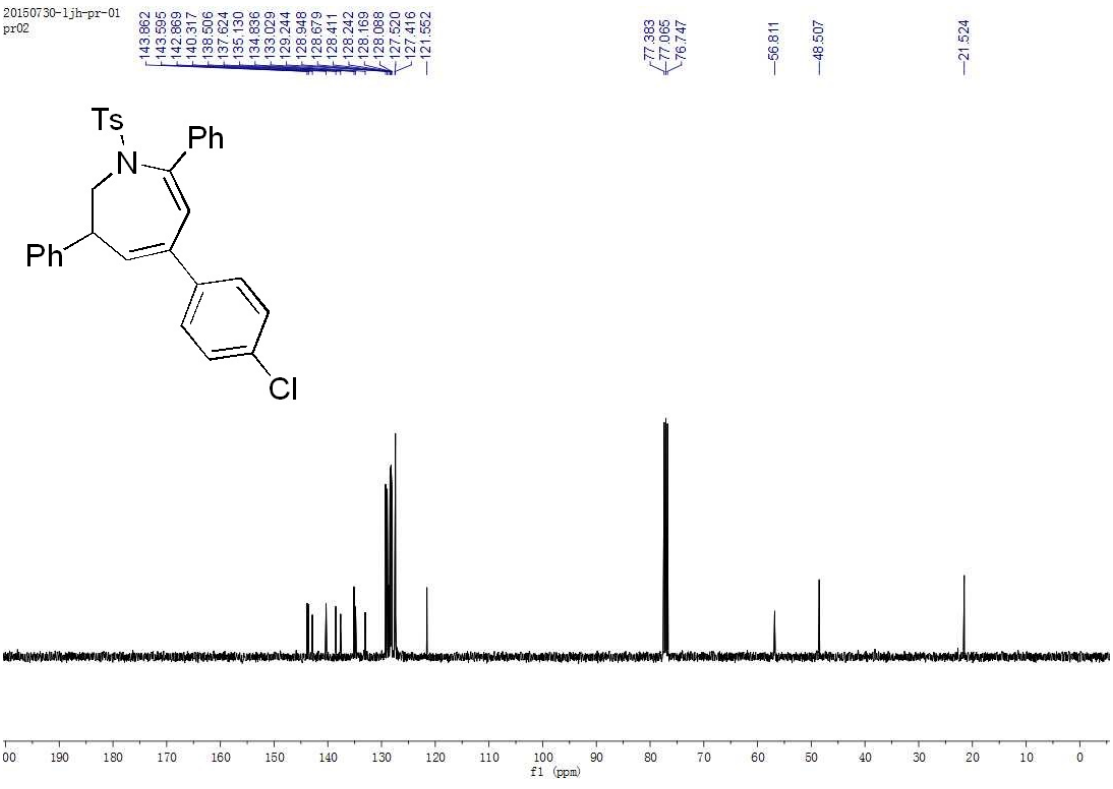




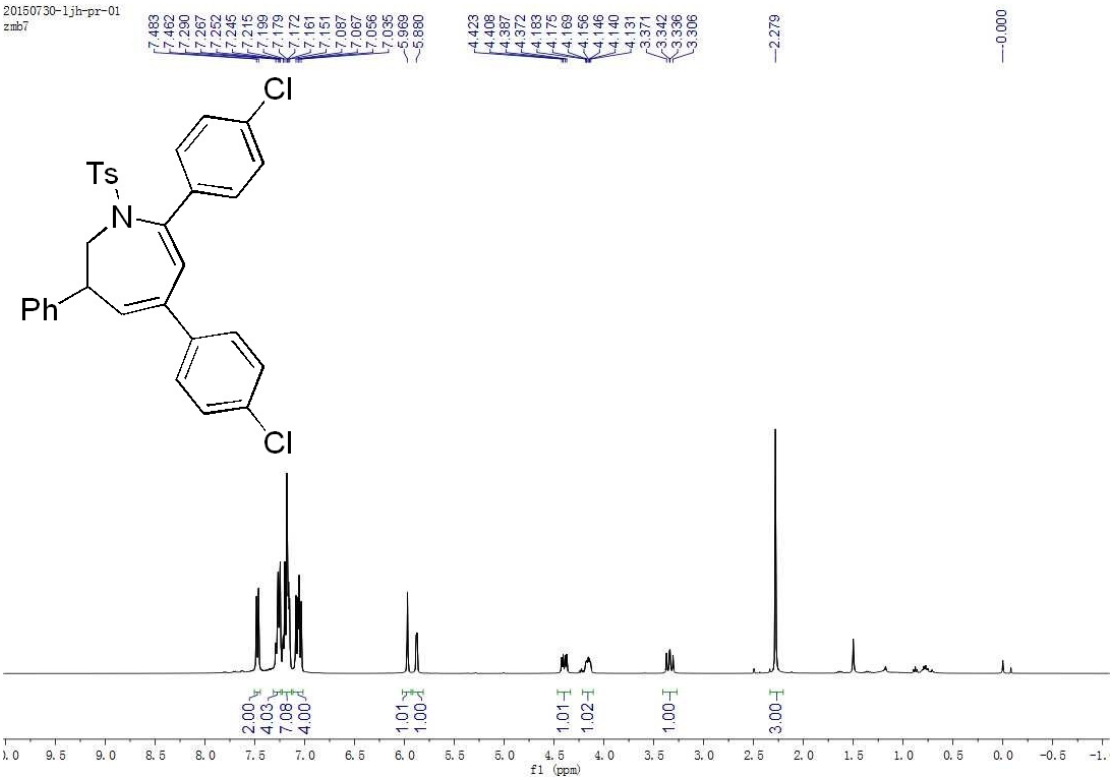


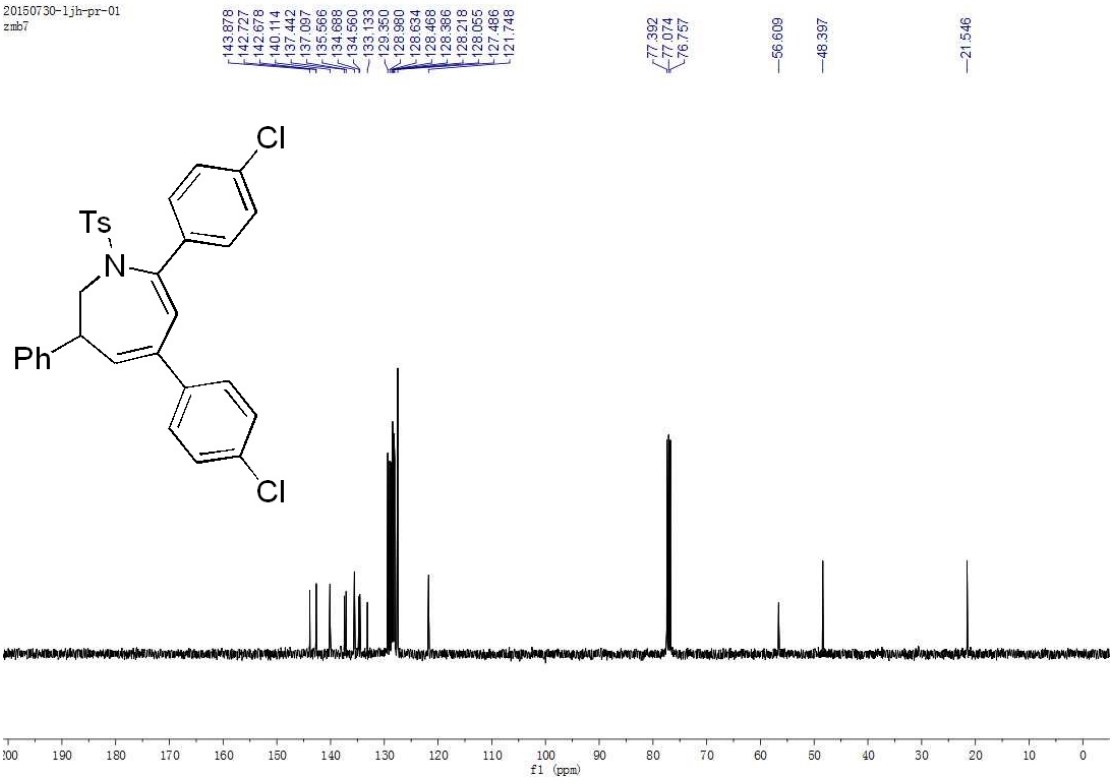
5-(4-Chlorophenyl)-3,7-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (30)



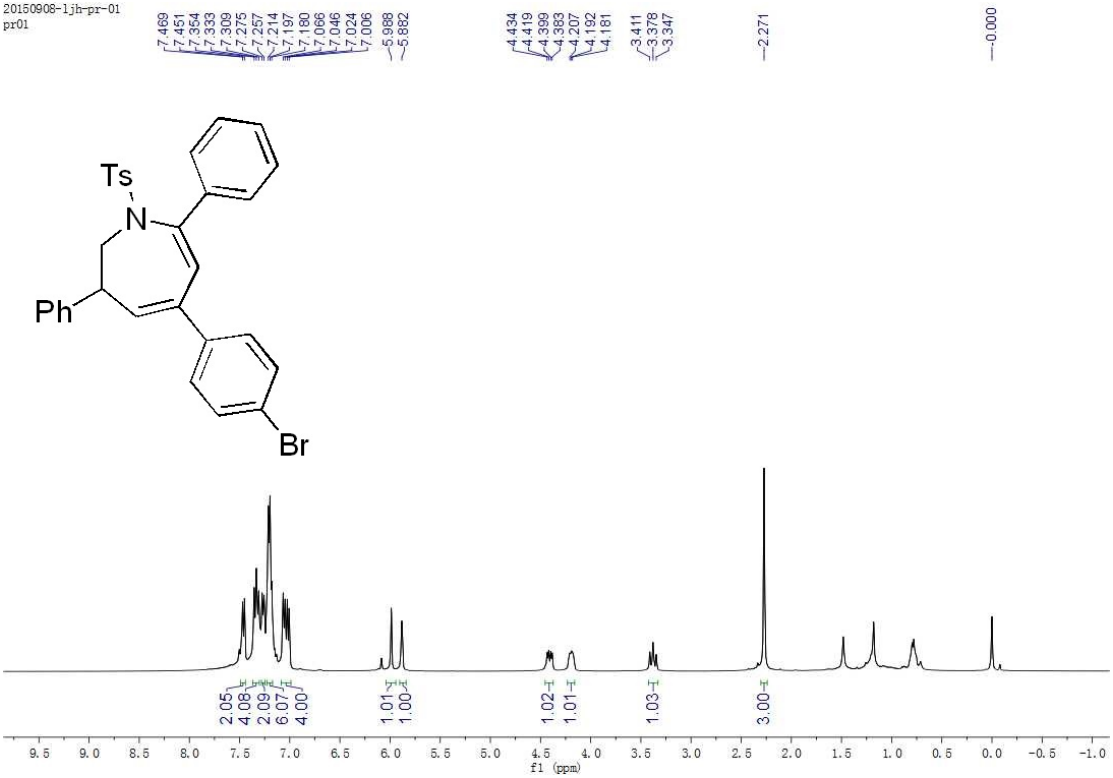


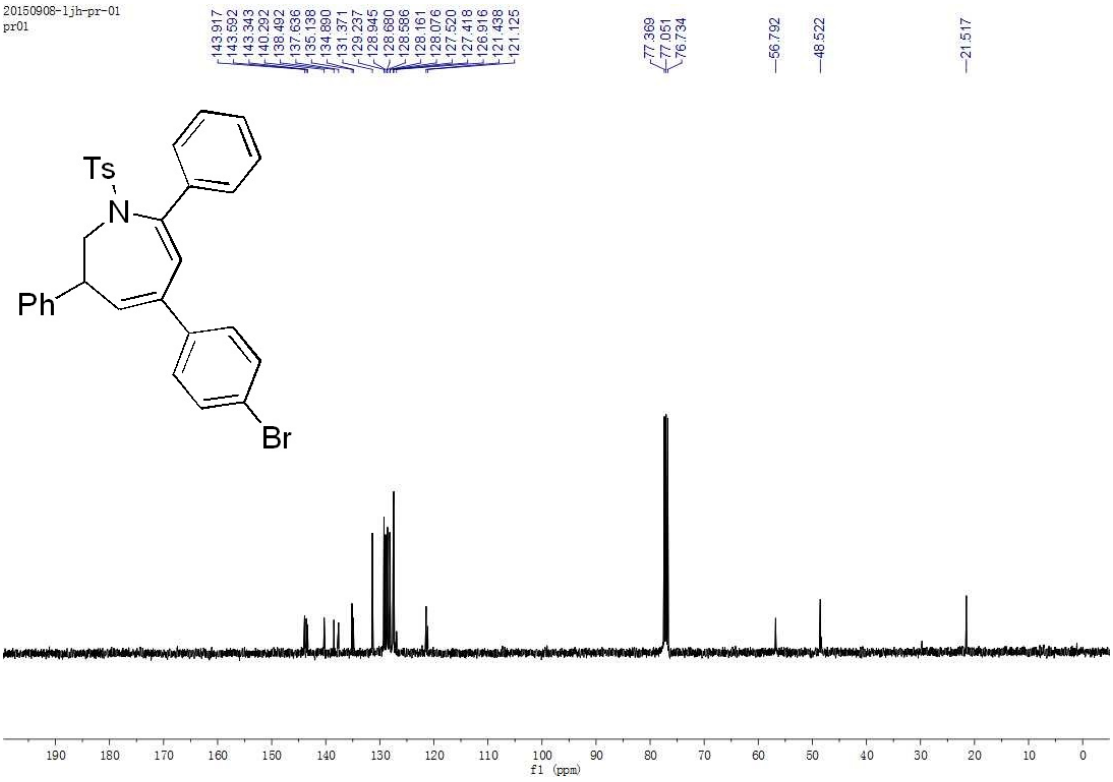
5,7-Bis(4-chlorophenyl)-3-phenyl-1-tosyl-2,3-dihydro-1*H*-azepine (31)



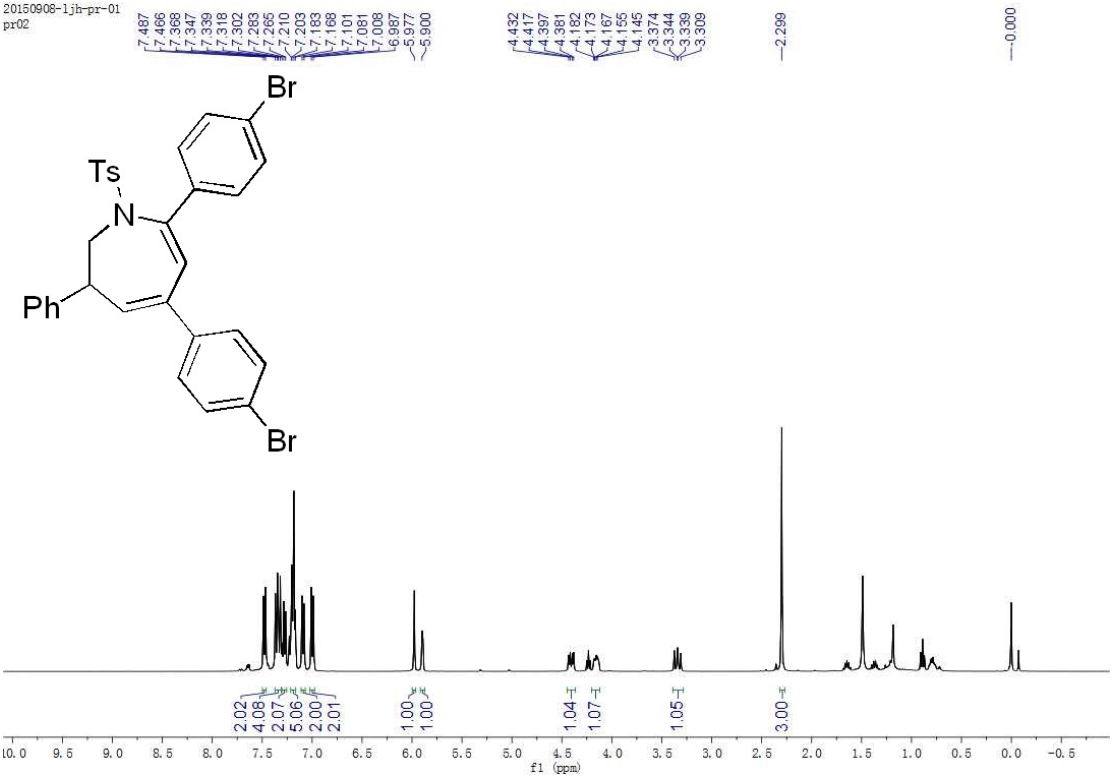


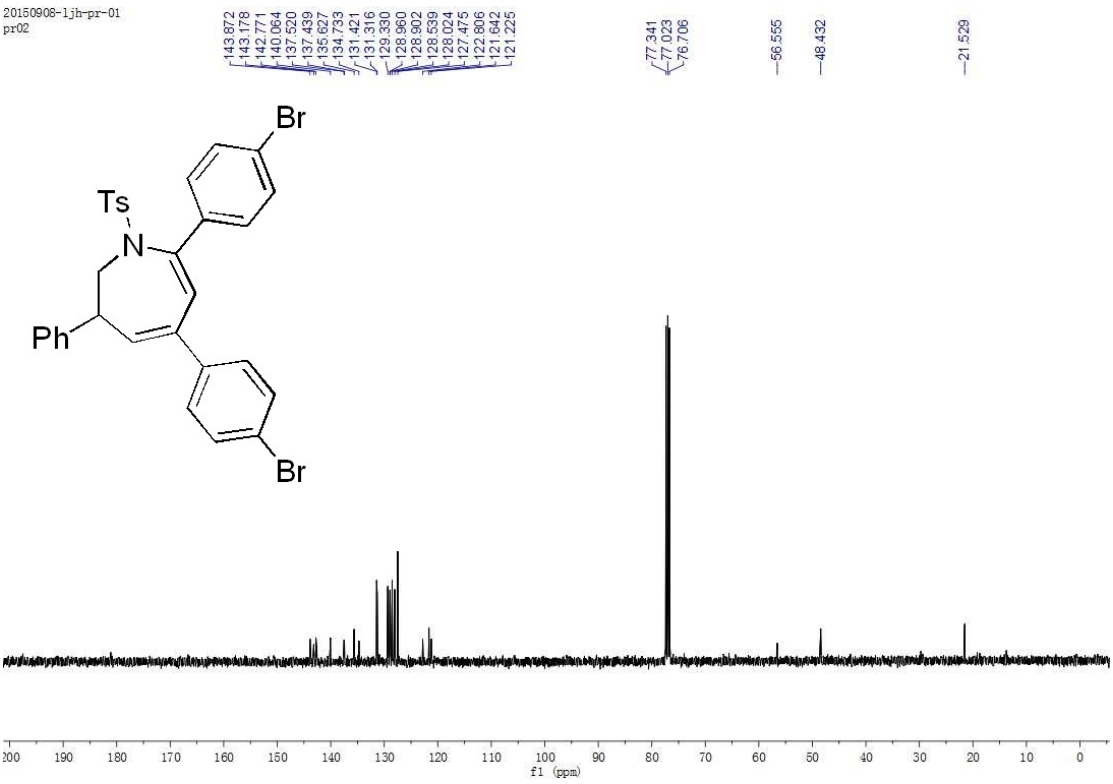
5-(4-Bromophenyl)-3,7-diphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (32)



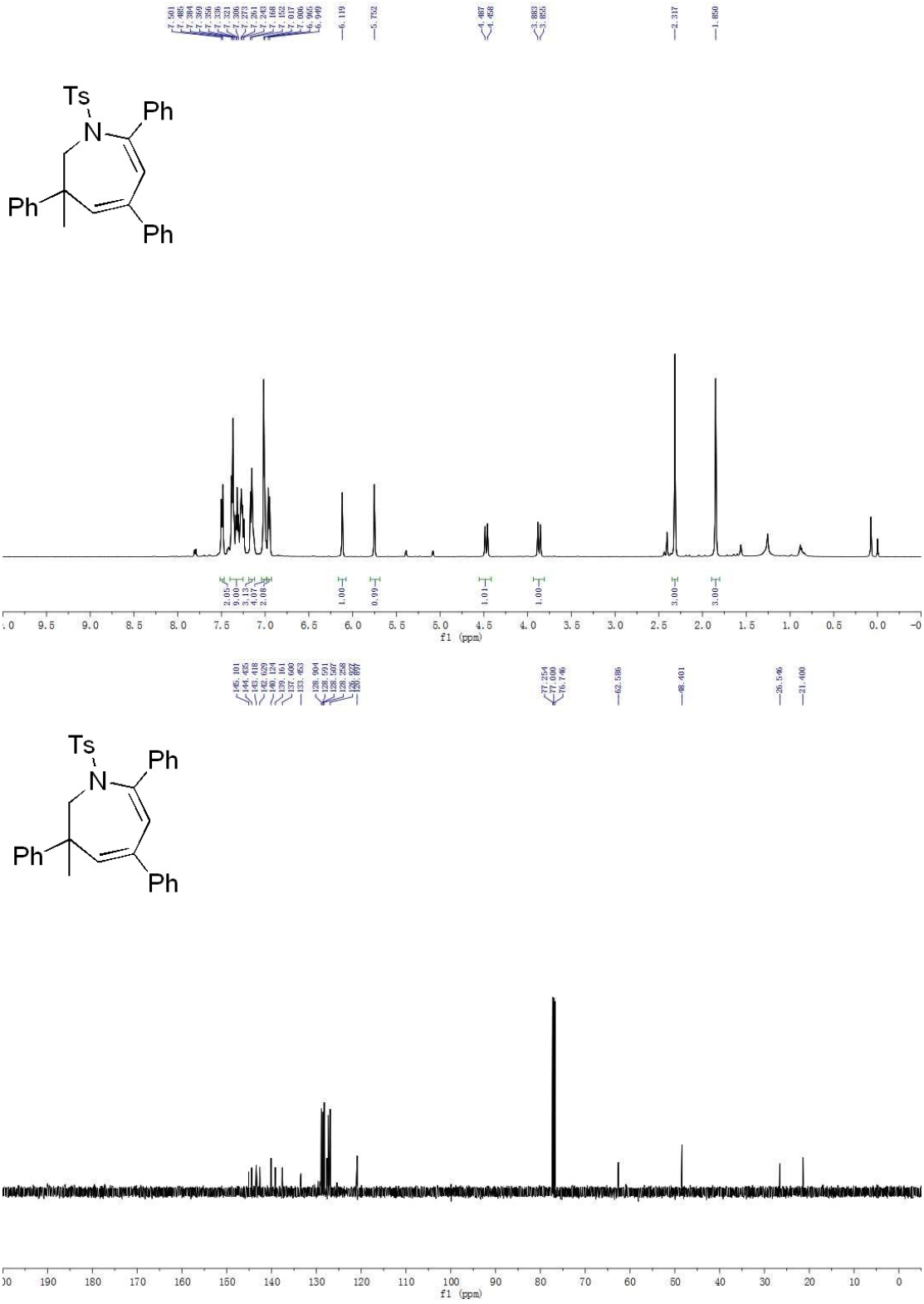


5,7-Bis(4-bromophenyl)-3-phenyl-1-tosyl-2,3-dihydro-1*H*-azepine (33)

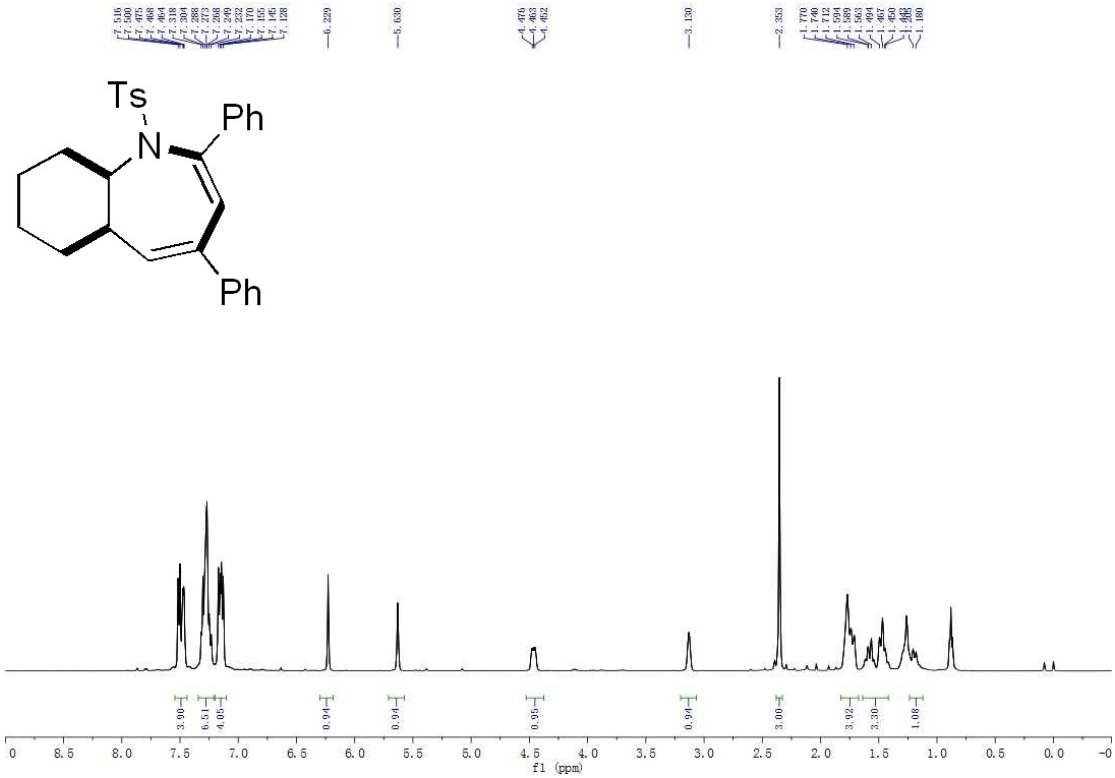


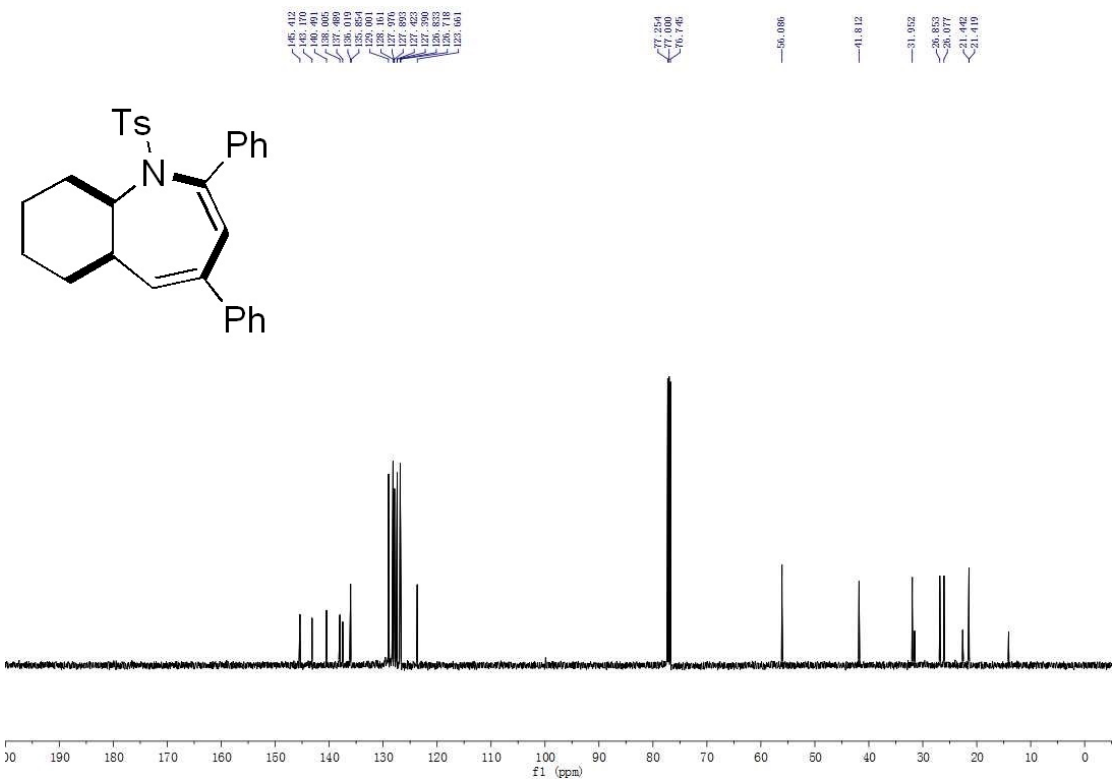


3-Methyl-3,5,7-triphenyl-1-tosyl-2,3-dihydro-1*H*-azepine (34)



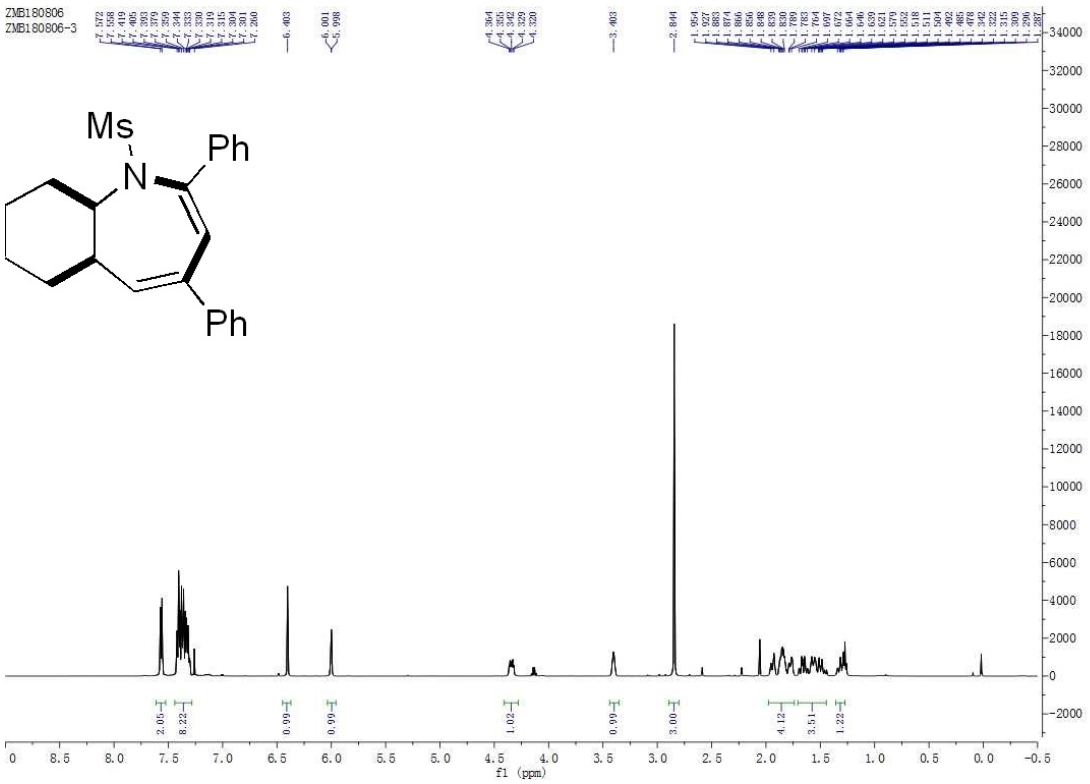
2,4-Diphenyl-1-tosyl-5*a*,6,7,8,9,9*a*-hexahydro-1*H*-benzo[b]azepine (35)

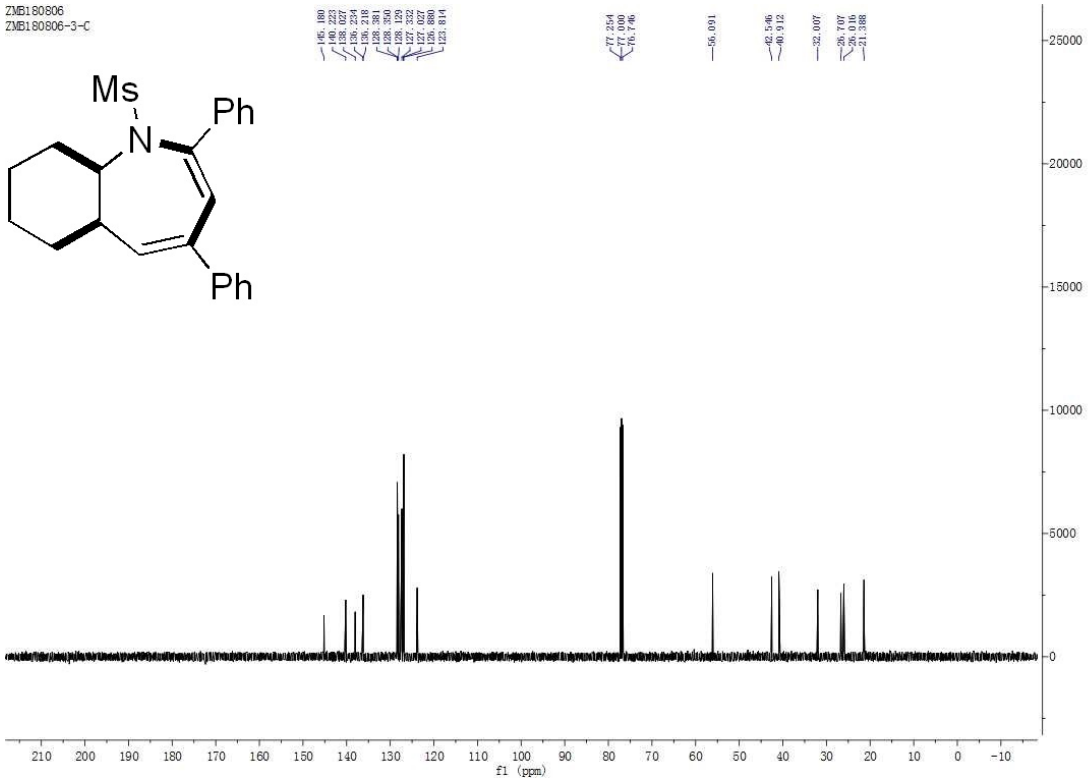




1-(Methylsulfonyl)-2,4-diphenyl-5a,6,7,8,9,9a-hexahydro-1*H*-benzo[*b*]azepine

(36)





(E) The X-ray single-crystal diffraction analysis of 3 (CCDC 1867336)

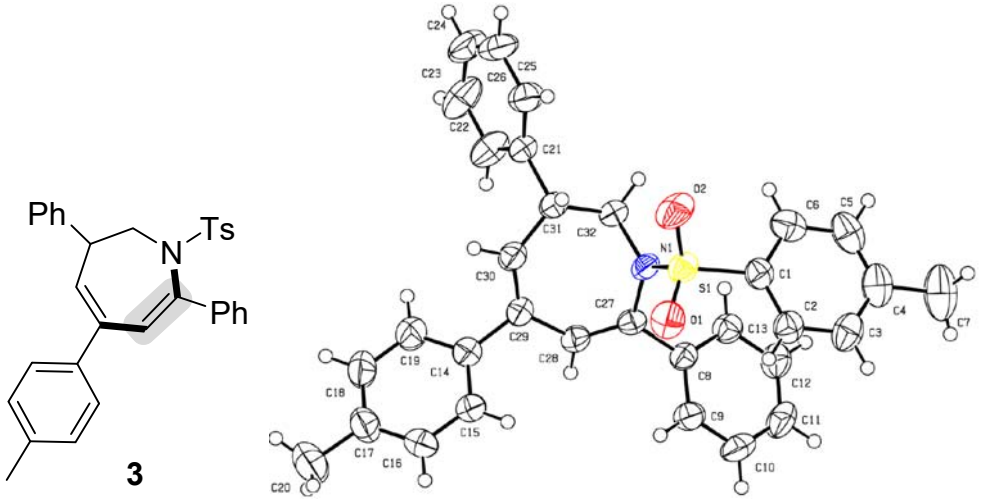


Table S1. Crystal data and structure refinement for 1jh027_0m.

Identification code	1jh027_0m
Empirical formula	C32 H29 N O2 S
Formula weight	491.62
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, Pn
Unit cell dimensions	a = 5.8755(8) A alpha = 90 deg. b = 9.7514(14) A beta = 96.573(2) deg. c = 23.346(3) A gamma = 90 deg.
Volume	1328.8(3) A^3
Z, Calculated density	2, 1.229 Mg/m^3
Absorption coefficient	0.151 mm^-1
F(000)	520
Crystal size	0.21 x 0.20 x 0.15 mm
Theta range for data collection	1.76 to 27.42 deg.
Limiting indices	-6<=h<=7, -12<=k<=12, -30<=l<=25
Reflections collected / unique	7597 / 3989 [R(int) = 0.0221]
Completeness to theta = 27.42	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9777 and 0.9690
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3989 / 2 / 327
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0967
R indices (all data)	R1 = 0.0485, wR2 = 0.1017
Absolute structure parameter	-0.06(8)
Largest diff. peak and hole	0.192 and -0.167 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ljh027_0m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	12812(4)	8685(2)	3280(1)	63(1)
S(1)	10516(1)	9180(1)	3196(1)	47(1)
C(1)	9120(5)	8305(3)	2595(1)	46(1)
N(1)	9232(4)	8727(2)	3756(1)	43(1)
C(2)	10172(5)	7194(3)	2368(1)	50(1)
O(2)	10064(5)	10602(2)	3110(1)	74(1)
C(3)	9012(6)	6469(3)	1912(1)	62(1)
C(4)	6819(6)	6836(4)	1687(1)	65(1)
C(5)	5832(6)	7953(4)	1910(2)	67(1)
C(6)	6943(6)	8709(3)	2368(1)	59(1)
C(7)	5539(8)	5995(5)	1210(2)	100(2)
C(8)	9372(5)	6200(2)	3697(1)	40(1)
C(9)	11026(5)	5190(3)	3669(1)	49(1)
C(10)	10531(6)	4021(3)	3345(1)	58(1)
C(11)	8400(6)	3848(3)	3046(1)	61(1)
C(12)	6749(6)	4839(3)	3072(1)	55(1)
C(13)	7217(5)	6022(3)	3393(1)	46(1)
C(14)	13148(5)	8235(3)	5489(1)	49(1)
C(15)	15087(6)	7452(3)	5430(1)	54(1)
C(16)	16686(6)	7204(3)	5895(2)	65(1)
C(17)	16443(6)	7708(4)	6442(1)	63(1)
C(18)	14502(6)	8471(4)	6497(2)	69(1)
C(19)	12899(6)	8741(4)	6036(2)	66(1)
C(20)	18204(8)	7454(5)	6952(2)	95(1)
C(21)	7816(5)	11653(3)	4753(1)	48(1)
C(22)	6777(6)	11267(3)	5237(2)	66(1)
C(23)	5413(7)	12193(4)	5493(2)	80(1)
C(24)	5110(7)	13518(4)	5271(2)	85(1)
C(25)	6159(9)	13883(4)	4811(2)	94(2)
C(26)	7507(7)	12980(4)	4548(2)	74(1)
C(27)	9888(4)	7467(2)	4040(1)	40(1)
C(28)	10777(5)	7448(3)	4591(1)	45(1)
C(29)	11500(5)	8601(3)	4976(1)	45(1)
C(30)	10887(5)	9921(3)	4908(1)	49(1)
C(31)	9319(5)	10648(3)	4464(1)	45(1)
C(32)	7860(5)	9713(3)	4050(1)	44(1)

Table S3. Bond lengths [A] and angles [deg] for ljh027_0m.

O(1)-S(1)	1.425(2)
S(1)-O(2)	1.422(2)
S(1)-N(1)	1.642(2)
S(1)-C(1)	1.763(3)
C(1)-C(2)	1.383(4)
C(1)-C(6)	1.384(4)
N(1)-C(27)	1.428(3)
N(1)-C(32)	1.474(3)
C(2)-C(3)	1.389(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.382(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.365(5)
C(4)-C(7)	1.513(5)
C(5)-C(6)	1.397(5)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-C(9)	1.390(4)
C(8)-C(13)	1.390(4)
C(8)-C(27)	1.484(3)
C(9)-C(10)	1.381(4)
C(9)-H(9)	0.9300
C(10)-C(11)	1.372(5)
C(10)-H(10)	0.9300
C(11)-C(12)	1.376(5)
C(11)-H(11)	0.9300
C(12)-C(13)	1.386(4)
C(12)-H(12)	0.9300
C(13)-H(13)	0.9300
C(14)-C(15)	1.391(4)
C(14)-C(19)	1.394(5)
C(14)-C(29)	1.494(4)
C(15)-C(16)	1.374(4)
C(15)-H(15)	0.9300
C(16)-C(17)	1.391(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.379(5)
C(17)-C(20)	1.506(5)
C(18)-C(19)	1.372(5)

C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-C(26)	1.384(4)
C(21)-C(22)	1.396(5)
C(21)-C(31)	1.526(4)
C(22)-C(23)	1.388(5)
C(22)-H(22)	0.9300
C(23)-C(24)	1.395(6)
C(23)-H(23)	0.9300
C(24)-C(25)	1.347(7)
C(24)-H(24)	0.9300
C(25)-C(26)	1.375(5)
C(25)-H(25)	0.9300
C(26)-H(26)	0.9300
C(27)-C(28)	1.332(4)
C(28)-C(29)	1.471(4)
C(28)-H(28)	0.9300
C(29)-C(30)	1.341(4)
C(30)-C(31)	1.485(4)
C(30)-H(30)	0.9300
C(31)-C(32)	1.521(4)
C(31)-H(31)	0.9800
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700

O(2)-S(1)-O(1)	120.56(16)
O(2)-S(1)-N(1)	106.20(14)
O(1)-S(1)-N(1)	108.30(13)
O(2)-S(1)-C(1)	107.30(14)
O(1)-S(1)-C(1)	106.97(14)
N(1)-S(1)-C(1)	106.78(12)
C(2)-C(1)-C(6)	120.7(3)
C(2)-C(1)-S(1)	119.8(2)
C(6)-C(1)-S(1)	119.5(2)
C(27)-N(1)-C(32)	118.6(2)
C(27)-N(1)-S(1)	118.46(18)
C(32)-N(1)-S(1)	121.37(18)
C(1)-C(2)-C(3)	119.4(3)
C(1)-C(2)-H(2)	120.3
C(3)-C(2)-H(2)	120.3
C(4)-C(3)-C(2)	120.9(3)

C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(5)-C(4)-C(3)	118.7(3)
C(5)-C(4)-C(7)	121.1(4)
C(3)-C(4)-C(7)	120.2(4)
C(4)-C(5)-C(6)	122.1(3)
C(4)-C(5)-H(5)	119.0
C(6)-C(5)-H(5)	119.0
C(1)-C(6)-C(5)	118.2(3)
C(1)-C(6)-H(6)	120.9
C(5)-C(6)-H(6)	120.9
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(13)	119.3(2)
C(9)-C(8)-C(27)	120.9(2)
C(13)-C(8)-C(27)	119.8(2)
C(10)-C(9)-C(8)	120.4(3)
C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(11)-C(10)-C(9)	120.2(3)
C(11)-C(10)-H(10)	119.9
C(9)-C(10)-H(10)	119.9
C(10)-C(11)-C(12)	119.9(3)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-H(11)	120.0
C(11)-C(12)-C(13)	120.7(3)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	119.6
C(12)-C(13)-C(8)	119.5(3)
C(12)-C(13)-H(13)	120.2
C(8)-C(13)-H(13)	120.2
C(15)-C(14)-C(19)	117.3(3)
C(15)-C(14)-C(29)	121.0(3)
C(19)-C(14)-C(29)	121.5(3)
C(16)-C(15)-C(14)	120.8(3)
C(16)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(15)-C(16)-C(17)	122.1(3)
C(15)-C(16)-H(16)	118.9
C(17)-C(16)-H(16)	118.9

C(18)-C(17)-C(16)	116.6(3)
C(18)-C(17)-C(20)	121.1(4)
C(16)-C(17)-C(20)	122.3(4)
C(19)-C(18)-C(17)	122.2(3)
C(19)-C(18)-H(18)	118.9
C(17)-C(18)-H(18)	118.9
C(18)-C(19)-C(14)	121.1(3)
C(18)-C(19)-H(19)	119.5
C(14)-C(19)-H(19)	119.5
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(26)-C(21)-C(22)	118.6(3)
C(26)-C(21)-C(31)	120.6(3)
C(22)-C(21)-C(31)	120.8(3)
C(23)-C(22)-C(21)	120.1(3)
C(23)-C(22)-H(22)	120.0
C(21)-C(22)-H(22)	120.0
C(22)-C(23)-C(24)	119.9(4)
C(22)-C(23)-H(23)	120.1
C(24)-C(23)-H(23)	120.1
C(25)-C(24)-C(23)	119.4(3)
C(25)-C(24)-H(24)	120.3
C(23)-C(24)-H(24)	120.3
C(24)-C(25)-C(26)	121.7(4)
C(24)-C(25)-H(25)	119.1
C(26)-C(25)-H(25)	119.1
C(25)-C(26)-C(21)	120.3(4)
C(25)-C(26)-H(26)	119.8
C(21)-C(26)-H(26)	119.8
C(28)-C(27)-N(1)	121.0(2)
C(28)-C(27)-C(8)	122.9(2)
N(1)-C(27)-C(8)	116.0(2)
C(27)-C(28)-C(29)	129.3(2)
C(27)-C(28)-H(28)	115.3
C(29)-C(28)-H(28)	115.3
C(30)-C(29)-C(28)	127.3(3)
C(30)-C(29)-C(14)	117.7(2)
C(28)-C(29)-C(14)	115.0(2)
C(29)-C(30)-C(31)	132.6(3)
C(29)-C(30)-H(30)	113.7

C(31)-C(30)-H(30)	113.7
C(30)-C(31)-C(32)	114.7(2)
C(30)-C(31)-C(21)	110.1(2)
C(32)-C(31)-C(21)	110.7(2)
C(30)-C(31)-H(31)	107.0
C(32)-C(31)-H(31)	107.0
C(21)-C(31)-H(31)	107.0
N(1)-C(32)-C(31)	112.9(2)
N(1)-C(32)-H(32A)	109.0
C(31)-C(32)-H(32A)	109.0
N(1)-C(32)-H(32B)	109.0
C(31)-C(32)-H(32B)	109.0
H(32A)-C(32)-H(32B)	107.8

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for ljh027_0m. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	48(1)	77(2)	66(1)	-8(1)	12(1)	-9(1)
S(1)	59(1)	38(1)	46(1)	-1(1)	11(1)	-4(1)
C(1)	55(2)	49(2)	34(1)	6(1)	11(1)	-1(1)
N(1)	57(1)	33(1)	41(1)	-5(1)	8(1)	6(1)
C(2)	50(2)	58(2)	43(2)	-1(1)	12(1)	0(1)
O(2)	123(2)	32(1)	71(2)	3(1)	24(2)	-5(1)
C(3)	76(2)	64(2)	48(2)	-7(2)	21(2)	-10(2)
C(4)	66(2)	86(2)	44(2)	2(2)	13(2)	-24(2)
C(5)	50(2)	98(3)	52(2)	12(2)	1(2)	-12(2)
C(6)	56(2)	65(2)	57(2)	13(2)	14(1)	8(2)
C(7)	93(3)	138(4)	68(3)	-17(3)	1(2)	-50(3)
C(8)	47(2)	36(1)	38(1)	-1(1)	9(1)	-1(1)
C(9)	49(2)	44(2)	55(2)	-3(1)	6(1)	3(1)
C(10)	71(2)	38(1)	66(2)	-6(1)	16(2)	9(1)
C(11)	86(2)	42(2)	56(2)	-14(1)	10(2)	-13(2)
C(12)	59(2)	50(2)	54(2)	-5(1)	2(1)	-13(1)
C(13)	51(2)	40(1)	47(2)	0(1)	7(1)	-2(1)
C(14)	50(2)	46(2)	49(2)	-4(1)	1(1)	3(1)
C(15)	68(2)	47(2)	47(2)	-3(1)	2(1)	13(1)
C(16)	70(2)	62(2)	59(2)	5(2)	-3(2)	22(2)
C(17)	69(2)	68(2)	48(2)	4(2)	-6(2)	1(2)
C(18)	72(2)	87(2)	46(2)	-16(2)	0(2)	9(2)
C(19)	63(2)	80(2)	55(2)	-16(2)	4(2)	16(2)
C(20)	94(3)	119(4)	65(3)	8(2)	-16(2)	15(3)
C(21)	50(2)	43(1)	49(2)	-11(1)	0(1)	9(1)
C(22)	74(2)	48(2)	82(2)	-14(2)	30(2)	-10(2)
C(23)	78(3)	78(3)	92(3)	-35(2)	42(2)	-14(2)
C(24)	78(3)	84(3)	94(3)	-39(2)	10(2)	30(2)
C(25)	141(4)	66(2)	75(3)	-5(2)	10(3)	58(3)
C(26)	115(3)	62(2)	48(2)	6(2)	17(2)	35(2)
C(27)	44(1)	31(1)	45(2)	2(1)	7(1)	1(1)
C(28)	57(2)	32(1)	47(2)	-1(1)	2(1)	2(1)
C(29)	48(2)	44(1)	43(2)	-8(1)	3(1)	2(1)
C(30)	45(2)	48(2)	54(2)	-15(1)	-1(1)	4(1)
C(31)	46(2)	39(1)	50(2)	-8(1)	5(1)	5(1)
C(32)	47(2)	40(1)	46(2)	-6(1)	6(1)	7(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ljh027_0m.

	x	y	z	U(eq)
H(2)	11644	6936	2518	60
H(3)	9720	5725	1757	74
H(5)	4374	8219	1753	80
H(6)	6238	9463	2517	70
H(7A)	5494	6484	852	151
H(7B)	4004	5833	1297	151
H(7C)	6306	5133	1178	151
H(9)	12474	5303	3870	59
H(10)	11645	3348	3330	69
H(11)	8073	3062	2827	73
H(12)	5303	4714	2872	66
H(13)	6096	6691	3406	55
H(15)	15304	7092	5071	65
H(16)	17972	6684	5843	78
H(18)	14273	8813	6857	83
H(19)	11625	9272	6090	79
H(20A)	17899	6591	7126	142
H(20B)	18133	8176	7229	142
H(20C)	19703	7434	6827	142
H(22)	7000	10389	5388	80
H(23)	4701	11931	5812	96
H(24)	4193	14142	5440	102
H(25)	5966	14770	4667	113
H(26)	8215	13263	4232	89
H(28)	10968	6582	4756	55
H(30)	11581	10494	5195	59
H(31)	10278	11193	4234	54
H(32A)	6800	9211	4261	53
H(32B)	6965	10270	3762	53

Table S6. Torsion angles [deg] for 1jh027_0m.

O(2)-S(1)-C(1)-C(2)	141.3(2)
O(1)-S(1)-C(1)-C(2)	10.6(3)
N(1)-S(1)-C(1)-C(2)	-105.2(2)
O(2)-S(1)-C(1)-C(6)	-41.0(3)
O(1)-S(1)-C(1)-C(6)	-171.7(2)
N(1)-S(1)-C(1)-C(6)	72.5(2)
O(2)-S(1)-N(1)-C(27)	-163.1(2)
O(1)-S(1)-N(1)-C(27)	-32.3(2)
C(1)-S(1)-N(1)-C(27)	82.6(2)
O(2)-S(1)-N(1)-C(32)	2.3(2)
O(1)-S(1)-N(1)-C(32)	133.1(2)
C(1)-S(1)-N(1)-C(32)	-112.0(2)
C(6)-C(1)-C(2)-C(3)	-0.9(4)
S(1)-C(1)-C(2)-C(3)	176.8(2)
C(1)-C(2)-C(3)-C(4)	-0.4(5)
C(2)-C(3)-C(4)-C(5)	1.7(5)
C(2)-C(3)-C(4)-C(7)	-177.2(3)
C(3)-C(4)-C(5)-C(6)	-1.8(5)
C(7)-C(4)-C(5)-C(6)	177.1(3)
C(2)-C(1)-C(6)-C(5)	0.8(4)
S(1)-C(1)-C(6)-C(5)	-176.8(2)
C(4)-C(5)-C(6)-C(1)	0.5(5)
C(13)-C(8)-C(9)-C(10)	-0.2(4)
C(27)-C(8)-C(9)-C(10)	-179.5(3)
C(8)-C(9)-C(10)-C(11)	0.2(5)
C(9)-C(10)-C(11)-C(12)	-0.4(5)
C(10)-C(11)-C(12)-C(13)	0.6(5)
C(11)-C(12)-C(13)-C(8)	-0.6(5)
C(9)-C(8)-C(13)-C(12)	0.4(4)
C(27)-C(8)-C(13)-C(12)	179.7(3)
C(19)-C(14)-C(15)-C(16)	-0.4(5)
C(29)-C(14)-C(15)-C(16)	175.1(3)
C(14)-C(15)-C(16)-C(17)	0.5(5)
C(15)-C(16)-C(17)-C(18)	0.1(5)
C(15)-C(16)-C(17)-C(20)	-179.2(4)
C(16)-C(17)-C(18)-C(19)	-0.9(6)
C(20)-C(17)-C(18)-C(19)	178.5(4)
C(17)-C(18)-C(19)-C(14)	1.0(6)
C(15)-C(14)-C(19)-C(18)	-0.3(5)
C(29)-C(14)-C(19)-C(18)	-175.7(3)
C(26)-C(21)-C(22)-C(23)	1.9(5)
C(31)-C(21)-C(22)-C(23)	-179.9(3)

C(21)-C(22)-C(23)-C(24)	-1.0(6)
C(22)-C(23)-C(24)-C(25)	-0.3(6)
C(23)-C(24)-C(25)-C(26)	0.6(7)
C(24)-C(25)-C(26)-C(21)	0.3(7)
C(22)-C(21)-C(26)-C(25)	-1.5(6)
C(31)-C(21)-C(26)-C(25)	-179.7(4)
C(32)-N(1)-C(27)-C(28)	-47.1(4)
S(1)-N(1)-C(27)-C(28)	118.7(3)
C(32)-N(1)-C(27)-C(8)	128.9(3)
S(1)-N(1)-C(27)-C(8)	-65.3(3)
C(9)-C(8)-C(27)-C(28)	-52.1(4)
C(13)-C(8)-C(27)-C(28)	128.6(3)
C(9)-C(8)-C(27)-N(1)	132.0(3)
C(13)-C(8)-C(27)-N(1)	-47.3(4)
N(1)-C(27)-C(28)-C(29)	-8.1(5)
C(8)-C(27)-C(28)-C(29)	176.2(3)
C(27)-C(28)-C(29)-C(30)	19.1(5)
C(27)-C(28)-C(29)-C(14)	-159.2(3)
C(15)-C(14)-C(29)-C(30)	-129.9(3)
C(19)-C(14)-C(29)-C(30)	45.3(4)
C(15)-C(14)-C(29)-C(28)	48.5(4)
C(19)-C(14)-C(29)-C(28)	-136.2(3)
C(28)-C(29)-C(30)-C(31)	2.1(6)
C(14)-C(29)-C(30)-C(31)	-179.6(3)
C(29)-C(30)-C(31)-C(32)	9.9(5)
C(29)-C(30)-C(31)-C(21)	135.5(4)
C(26)-C(21)-C(31)-C(30)	133.7(3)
C(22)-C(21)-C(31)-C(30)	-44.5(4)
C(26)-C(21)-C(31)-C(32)	-98.5(3)
C(22)-C(21)-C(31)-C(32)	83.3(4)
C(27)-N(1)-C(32)-C(31)	85.2(3)
S(1)-N(1)-C(32)-C(31)	-80.2(3)
C(30)-C(31)-C(32)-N(1)	-55.2(3)
C(21)-C(31)-C(32)-N(1)	179.5(2)

Symmetry transformations used to generate equivalent atoms: