Accessing benzooxadiazepines via formal [4+3] cycloadditions of aza-*o*-quinone methides with nitrones

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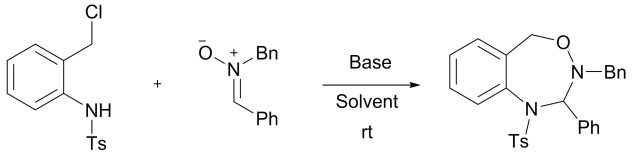
Supporting Information

A. General information

Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere in anhydrous conditions. All chemicals which are commercially available were used without further purification unless otherwise noted. All the solvents were purified according to the standard procedures. Analytical thin-layer chromatography (TLC) was performed on silica gel plates (GF-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (200-300 mesh). ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature in $CDCl_3$ on a Bruker AMX600 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm). Infrared spectra (IR) recorded on a SHIMADZU IRTracer-100 spectrometer are reported in cm^{-1}. All high resolution mass spectra were obtained on a Agilent 6200 Q-TOF MS. The substrates were prepared by know methods. *N*-(ortho-chloromethyl)aryl amides **1a-1i** were prepared according to the literature procedures.[1] Nitrones **2a-2r** were synthesized from corresponding hydroxylamines hydrochloride with aldehydes according to literature methods.[2]

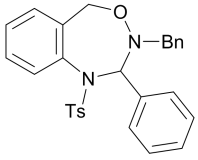
B. Typical experimental Procedures and Characterizations of Products



To a round bottle flask with a magnetic stirring bar were added **1a** (0.60 mmol) and nitrone **2a** (0.40 mmol), followed by the addition of Na_2CO_3 (0.6 mmol). Then dioxane (4.00 mL) was introduced by syringe, and the mixture was stirred at room temperature for 36 h. Then the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (petroleum: ethyl acetate = 20:1) to afford **3aa** (177 mg, 94% yield) as a colourless syrup.

C. Analytical data of the products

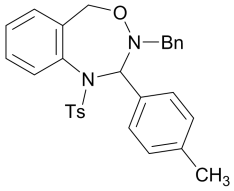
3-benzyl-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3aa)



Foam, 176.8 mg, 94% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.2 Hz, 2H), 7.30-7.13 (m, 12H), 7.11 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 7.6 Hz, 1H), 6.80 (d, J = 7.5 Hz, 1H), 6.00 (s, 1H), 4.29 (d, J = 14.5 Hz, 1H), 3.78 (d, J = 14.1 Hz, 1H), 3.66 (d, J = 14.4 Hz, 1H), 3.61 (d, J = 14.2 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.2, 138.7, 137.8, 137.3, 137.0, 134.5, 131.2, 129.0, 129.0, 128.9, 128.8, 128.7, 128.3, 128.2, 127.7, 127.3, 127.0, 125.5, 83.6, 75.3, 58.3, 21.7; IR (NaCl film): 2918, 1598, 1494,

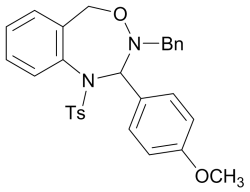
1454, 1350, 1170, 1095, 1068, 698, 580 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{27}N_2O_3S$ $[M+Na]^+$ = 471.1737, found = 471.1738.

3-benzyl-2-(p-tolyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ab)



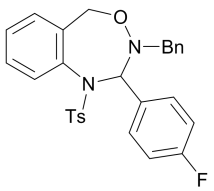
White solid; 176.3 mg, 88% yield, mp 178.1-179.5 ℃; ^1H NMR (600 MHz, $CDCl_3$): δ = δ = 7.43 (d, J = 8.2 Hz, 2H), 7.27-7.19 (m, 4H), 7.18-7.16 (m, 2H), 7.15-7.09 (m, 4H), 7.07 (d, J = 7.9 Hz, 1H), 7.03-6.99 (m, 1H), 6.80 (d, J = 7.5 Hz, 1H), 5.97 (s, 1H), 4.28 (d, J = 14.5 Hz, 1H), 3.79 (d, J = 14.1 Hz, 1H), 3.67 (d, J = 14.4 Hz, 1H), 3.60 (d, J = 14.1 Hz, 1H), 2.33 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.1, 138.8, 138.7, 137.4, 137.1, 134.9, 134.5, 131.3, 129.4, 129.0, 128.8, 128.2, 128.1, 127.6, 127.3, 126.9, 125.5, 83.5, 75.3, 58.3, 21.6, 21.4; IR (NaCl film): 2918, 1492, 1450, 1350, 1168, 1093, 815, 744, 709, 667 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{29}N_2O_3S$ $[M+H]^+$ = 485.1893, found = 485.1894.

3-benzyl-2-(4-methoxyphenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ac)



Syrup; 188.6 mg, 94% yield; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.34 (d, J = 8.2 Hz, 2H), 7.21-7.11 (m, 4H), 7.10-7.06 (m, 5H), 7.04 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 7.8 Hz, 1H), 6.73-6.70 (m, 3H), 5.87 (s, 1H), 4.20 (d, J = 14.4 Hz, 1H), 3.71 (d, J = 14.1 Hz, 1H), 3.68 (s, 3H), 3.58 (d, J = 14.4 Hz, 1H), 3.52 (d, J = 14.2 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.9, 143.0, 137.4, 134.4, 130.0, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.3, 126.9, 125.4, 113.9, 83.2, 75.2, 58.2, 55.3, 21.6; IR (NaCl film): 2926, 1610, 1512, 1346, 1249, 1165, 1091, 1029, 748, 667 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{29}N_2O_4S$ $[M+H]^+$ = 501.1843, found = 501.1840.

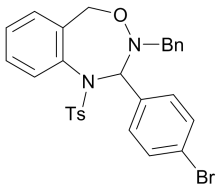
3-benzyl-2-(4-fluorophenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ad)



White solid, 166.1 mg, 85% yield, mp 144.1-146.2 ℃; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.33 (d, J = 8.3 Hz, 2H), 7.21-7.11 (m, 7H), 7.08-7.06 (m, 3H), 7.04 (d, J = 8.0 Hz, 2H),

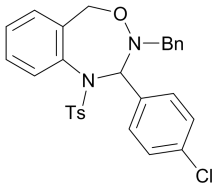
6.91 (dd, J = 7.8, 0.9 Hz, 1H), 6.87 (t, J = 8.7 Hz, 2H), 6.72 (d, J = 7.5 Hz, 1H), 5.90 (s, 1H), 4.20 (d, J = 14.5 Hz, 1H), 3.67 (d, J = 14.1 Hz, 1H), 3.57 (d, J = 14.4 Hz, 1H), 3.52 (d, J = 14.1 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.8, 162.1, 143.2, 138.6, 137.0, 134.4, 129.5, 129.4, 129.0, 128.9, 128.2, 127.4, 127.1, 125.5, 115.7, 115.6, 82.7, 75.3, 58.3, 21.6; IR (NaCl film): 2902, 1602, 1508, 1492, 1350, 1222, 1168, 1091, 746, 669 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{26}FN_2O_3S$ $[M+H]^+$ = 489.1643, found = 489.1647.

3-benzyl-2-(4-bromophenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ae)



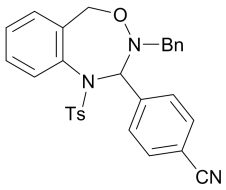
White solid, 207.2 mg, 95% yield, mp 186.3-185.7 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32-7.30 (m, 4H), 7.17-7.12 (m, 4H), 7.06-7.02 (m, 7H), 6.90 (d, J = 7.8 Hz, 2H), 6.71 (d, J = 7.5 Hz, 2H), 5.86 (s, 1H), 4.20 (d, J = 14.5 Hz, 1H), 3.67 (s, 1H), 3.57 (d, J = 13.6 Hz, 1H), 3.51 (d, J = 14.1 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.3, 138.6, 136.9, 136.8, 134.4, 131.9, 130.8, 129.4, 129.1, 129.0, 128.9, 128.2, 128.2, 127.5, 127.1, 125.6, 123.0, 82.7, 75.3, 58.3, 21.7; IR (NaCl film): 2926, 1490, 1454, 1346, 1168, 1089, 1068, 754, 702, 665 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{26}BrN_2O_3S$ $[M+H]^+$ = 549.0842, found = 549.0845.

3-benzyl-2-(4-chlorophenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3af)



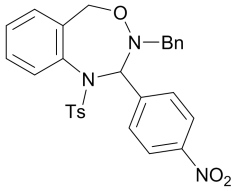
Syrup; 157.4 mg, 78% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.2 Hz, 2H), 7.19-7.12 (m, 6H), 7.11-7.03 (m, 7H), 6.90 (d, J = 7.8 Hz, 1H), 6.72 (d, J = 7.5 Hz, 1H), 5.88 (s, 1H), 4.20 (d, J = 14.5 Hz, 1H), 3.66 (d, J = 14.1 Hz, 1H), 3.57 (d, J = 14.4 Hz, 1H), 3.52 (d, J = 14.1 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.1, 137.4, 135.7, 135.6, 135.1, 133.6, 133.2, 129.7, 127.9, 127.8, 127.8, 127.7, 127.1, 126.3, 125.9, 124.4, 81.5, 74.1, 57.1, 20.5; IR (NaCl film): 2960, 2926, 2856, 1490, 1460, 1377, 1168, 1091, 1016, 665 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{26}ClN_2O_3S$ $[M + H]^+$ = 505.1347, found = 505.1350.

4-(3-benzyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepin-2-yl)benzonitrile (3ag)



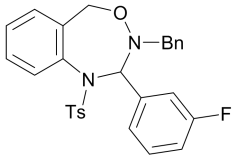
White solid, 193.0 mg, 95% yield, mp 137.6-139.6 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.32-7.25 (m, 5H), 7.20-7.15(m, 5H), 6.96 (d, J = 7.8 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 6.02 (s, 1H), 4.32 (d, J = 14.5 Hz, 1H), 3.72 (d, J = 14.1 Hz, 1H), 3.64 (dd, J = 14.3, 4.3 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.5, 142.6 138.3, 136.4, 136.3, 134.2, 132.5, 130.4, 129.1, 129.0, 128.8, 128.3, 128.2, 128.1, 127.5, 127.2, 125.6, 118.5, 112.7, 82.4, 75.2, 58.3, 21.6; IR (NaCl film): 2918, 1714, 1600, 1496, 1450, 1344, 1166, 1091, 748, 667- cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{26}N_3O_3S$ $[M+H]^+$ = 496.1689, found = 496.1692.

3-benzyl-2-(4-nitrophenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ah)



White solid, 203.1 mg, 99% yield, mp 129.1-131.9 ℃; ^{1}H NMR (600 MHz, CDCl3): δ = 8.15 (d, J = 8.9 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.31 (td, J = 7.5, 1.1 Hz, 1H), 7.29-7.25 (m, 3H), 7.19-7.16 (m, 5H), 6.96-6.95 (m, 1H), 6.85 (d, J = 7.5 Hz, 1H), 6.08 (s, 1H), 4.34 (d, J = 14.6 Hz, 1H), 3.73 (d, J = 14.1 Hz, 1H), 3.68-3.64 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 148.1, 144.5, 143.5, 138.3, 136.3, 136.2, 134.2, 130.4, 129.2, 129.0, 128.9, 128.5, 128.2, 128.1, 127.6, 127.2, 125.6, 123.9, 82.0, 75.2, 58.3, 21.6; IR (NaCl film): 2922, 1492, 1348, 1168, 1097, 864, 767, 704, 665, 582 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{26}N_3O_5S$ $[M+H]^+$ = 516.1588, found = 516.1589.

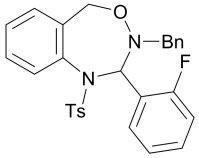
3-benzyl-2-(3-fluorophenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ai)



White solid; 195.6 mg, 94% yield, mp 132.5-134.2 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.2 Hz, 2H), 7.31-7.24 (m, 5H), 7.20-7.17 (M, 3H), 7.15 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 7.02-6.99 (m, 2H), 6.90 (d, J = 9.4 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 5.97 (s, 1H), 4.29 (d, J = 14.5 Hz, 1H), 3.78 (d, J = 14.1 Hz, 1H), 3.64 (d, J = 10.0 Hz, 1H), 3.62 (d, J = 9.7 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.6 (d, J = 246.6 Hz), 143.2, 140.1 (d, J = 7.0 Hz), 138.4, 136.9, 136.7, 134.3, 130.8, 130.3,

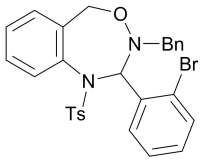
130.2, 128.9, 128.9, 128.2, 128.1, 127.3, 127.1, 125.4, 123.4, 115.9, 115.8, 114.32 (d, J = 22.3 Hz), 82.6, 75.2, 58.3, 21.6; IR (NaCl film): 2929, 1593, 1485, 1454, 1350, 1168, 1095, 734, 665, 576 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{26}FN_2O_3S$ $[M+H]^+$ = 489.1643, found = 489.1647.

3-benzyl-2-(2-fluorophenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3aj)



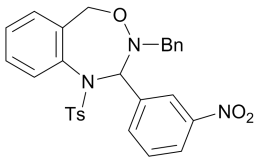
White solid, 193.3 mg, 99% yield, mp 163.3-165.1 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.47 (d, J = 8.0 Hz, 2H), 7.31-7.16 (m, 8H), 7.16-7.07 (m, 4H), 6.95-6.86 (m, 3H), 6.84 (d, J = 7.5 Hz, 1H), 6.50 (s, 1H), 4.33 (d, J = 14.4 Hz, 1H), 3.87 (d, J = 14.4 Hz, 1H), 3.72 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.14 (d, J = 249.8 Hz), 143.1,138.9, 137.1, 136.8, 133.9, 131.3, 130.4, 130.3, 128.9, 128.9, 128.8, 128.6, 128.5, 128.2, 128.1, 127.2, 126.9, 125.5, 124.9, 124.8, 124.0, 123.9, 115.8 (d, J = 22.5 Hz), 75.4, 57.9, 21.5; IR (NaCl film): 2897, 1587, 1487, 1452, 1350, 1228, 1170, 1080, 748, 667 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{26}FN_2O_3S$ $[M+H]^+$ = 489.1643, found = 489.1647.

3-benzyl-2-(2-bromophenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ak)



White solid, 193.9 mg, 89% yield, mp 178.5-179.9 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.9 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.23-7.19 (m, 1H), 7.16-7.12 (m, 3H), 7.09-7.04 (m, 6H), 6.97 (t, J = 7.3 Hz, 1H), 6.80-6.77 (m, 3H), 6.59 (s, 1H), 4.24 (d, J = 14.5 Hz, 1H), 3.90 (d, J = 14.4 Hz, 1H), 3.72 (d, J = 14.0 Hz, 1H), 3.56 (d, J = 13.9 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.2, 139.3, 137.3, 136.7, 136.6, 134.0, 133.2, 131.5, 130.2, 129.7, 128.9, 128.8, 128.7, 128.4, 128.0, 127.2, 126.8, 125.6, 123.8, 81.4, 75.6, 57.6, 21.5; IR (NaCl film): 2933, 1496, 1342, 1166, 1087, 1074, 813, 754, 704, 661 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{26}BrN_2O_3S$ $[M+H]^+$ = 549.0842, found = 549.0845.

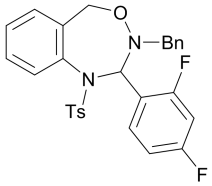
3-benzyl-2-(3-nitrophenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3al)



Yellow solid, 195.3 mg, 95% yield, mp 166.9-168.2 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.16-8.05 (m, 1H), 7.99 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.43-7.37 (m, 1H), 7.33 (d, J

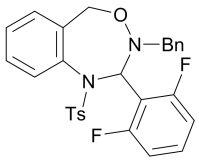
= 8.2 Hz, 2H), 7.22 (td, *J* = 7.5, 1.0 Hz, 1H), 7.19-7.15 (m, 3H), 7.09-7.06 (m, 5H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.00 (s, 1H), 4.25 (d, *J* = 14.6 Hz, 1H), 3.66 (d, *J* = 14.1 Hz, 1H), 3.59 (d, *J* = 5.9 Hz, 1H), 3.57 (d, *J* = 5.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 148.3, 143.6, 139.8, 138.4, 136.4, 136.3, 134.2, 133.8, 130.4, 129.9, 129.3, 129.1, 128.9, 128.3, 128.2, 127.6, 127.3, 125.8, 123.9, 122.6, 82.2, 75.3, 58.4, 21.6; IR (NaCl film): 2914, 1598, 1537, 1492, 1350, 1166, 1078, 960, 813, 665 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{26}N_3O_5S$ $[M+H]^+$ = 516.1588, found = 516.1592.

3-benzyl-2-(2,4-difluorophenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3am)



White solid, 165.8 mg, 82% yield, mp 111.0-112.5 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.2 Hz, 1H), 7.31-7.21 (m, 4H), 7.19-7.09 (m, 4H), 6.92-6.88 (m, 2H), 6.88-6.84 (m, 2H), 6.72-6.61 (m, 1H), 6.44 (s, 1H), 4.32 (d, *J* = 14.4 Hz, 1H), 3.85 (d, *J* = 14.4 Hz, 1H), 3.72 (s, 2H), 2.36 (s, 2H) ; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.8, 163.7, 162.2, 162.1, 161.3, 161.2, 159.6, 159.5, 143.3, 138.9, 136.9, 136.7, 133.8, 133.4, 131.1, 129.0, 128.9, 128.8, 128.4, 128.2, 128.2, 128.1, 127.3, 127.0, 125.6, 121.2, 121.2, 121.1, 121.1, 121.1, 121.1, 111.4, 111.4, 111.2, 111.2, 104.3, 104.2, 104.0, 75.4, 58.0, 21.5; IR (NaCl film): 2897, 1506, 1350, 1165, 1089, 968, 813, 746, 667, 578 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{25}F_2N_2O_3S$ $[M+H]^+$ = 507.1548, found = 507.1549.

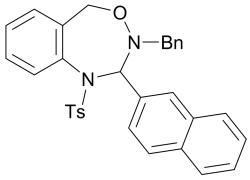
3-benzyl-2-(2,6-difluorophenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3an)



White solid, 201.0 mg, 99% yield, mp 185.3-186.7 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.3 Hz, 1H), 7.34 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.31-7.16 (m, 8H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 8.3 Hz, 1H), 6.79-6.75 (m, 1H), 6.72 (t, *J* = 8.6 Hz, 1H), 6.53 (s, 1H), 4.24 (d, *J* = 14.5 Hz, 1H), 3.77 (d, *J* = 13.9 Hz, 1H), 3.71 (d, *J* = 14.0 Hz, 1H), 3.62 (d, *J* = 14.4 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.9, 161.7, 161.6, 160.2, 160.0, 159.9, 143.3, 138.0, 136.9, 136.1, 133.8, 132.7, 131.0, 130.9, 130.8, 128.9, 128.7, 128.2, 128.0, 126.8, 124.9, 114.4, 114.2, 114.1, 112.6, 112.5, 111.8, 111.7, 76.3, 75.1, 58.6, 21.5; IR (NaCl film): 2889, 1620, 1593, 1471, 1352, 1168, 1012, 786, 740, 665 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{25}F_2N_2O_3S$ $[M+H]^+$ = 507.1548, found = 507.1550.

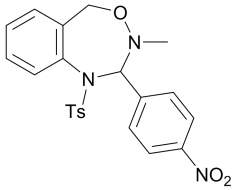
3-benzyl-2-(naphthalen-2-yl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine

(3ao)



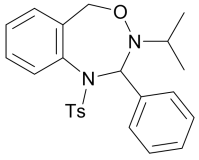
White solid, 206.0 mg, 99% yield, mp 197.9-199.0 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72 (s, 1H), 7.67 (dd, *J* = 8.8, 3.0 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.40-7.31 (m, 4H), 7.24-7.04 (m, 7H), 7.02-7.01 (m, 3H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.08 (s, 1H), 4.24 (d, *J* = 14.5 Hz, 1H), 3.71 (d, *J* = 14.1 Hz, 1H), 3.60 (d, *J* = 14.4 Hz, 1H), 3.55 (d, *J* = 14.2 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.1, 138.6, 137.1, 136.8, 135.1, 134.4, 133.5, 133.1, 131.1, 128.9, 128.8, 128.7, 128.4, 128.2, 128.1, 128.0, 127.6, 127.2, 127.1, 126.9, 126.4, 126.1, 125.4, 124.8, 83.5, 75.2, 58.3, 21.5; IR (NaCl film): 2897, 1600, 1490, 1328, 1159, 1091, 860, 752, 713, 696 cm^{-1}; HRMS (ESI) m/z calcd for $C_{32}H_{29}N_2O_3S$ $[M+H]^+$ = 521.1893, found = 521.1894.

3-methyl-2-(4-nitrophenyl)-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ap)



White solid, 165.7 mg, 94% yield, mp 178.1-179.2 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.38-7.32 (m, 3H), 7.21-7.20 (m, 3H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 5.83 (s, 1H), 4.79 (d, *J* = 14.5 Hz, 1H), 3.74 (d, *J* = 14.4 Hz, 1H), 2.48 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 148.1, 144.5, 143.6, 138.1, 136.4, 134.3, 130.6, 129.2, 129.1, 128.5, 128.2, 127.4, 125.7, 123.9, 84.4, 74.3, 42.4, 21.6; IR (NaCl film): 2933, 1597, 1529, 1348, 1159, 1083, 810, 734, 667, 586 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{22}N_3O_5S$ $[M+H]^+$ = 440.1275, found = 440.1275.

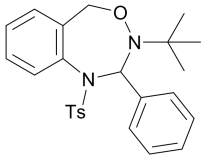
3-isopropyl-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3aq)



White solid, 152.0 mg, 87% yield, mp 158.2-159.9 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 7.7 Hz, 2H), 7.20-7.16 (m, 2H), 7.13 (t, *J* = 7.0 Hz, 2H), 7.07-7.06 (m, 5H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.3 Hz, 1H), 6.02 (s, 1H), 4.48 (d, *J* = 14.4 Hz, 1H), 3.71 (d, *J* = 14.3 Hz, 1H), 2.81-2.53 (m, 1H), 2.29 (s, 3H), 0.96 (d, *J* = 6.0 Hz, 3H), 0.93 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.9, 137.6, 136.7, 135.9, 133.4, 130.1, 127.8, 127.6, 127.5, 127.4, 127.0, 126.4, 125.7, 124.2, 79.3, 74.8, 49.9, 20.5, 20.1,

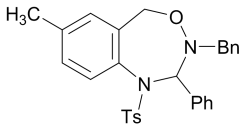
12.1; IR (NaCl film): 2922, 1492, 1344, 1170, 1091, 1051, 763, 731, 667, 580 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{27}N_2O_3S$ $[M+H]^+$ = 423.1737, found = 423.1741.

3-(tert-butyl)-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ar)



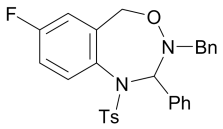
White solid, 43.6 mg, 25% yield, mp 174.8-175.4 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40 (d, J = 6.9 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.22-7.20 (m, 1H), 7.16-7.13 (m, 1H), 7.09-7.04 (m, 3H), 6.92 (t, J = 7.5 Hz, 1H), 6.84-6.81 (m, 2H), 6.67 (d, J = 9.5 Hz, 1H), 6.60 (d, J = 7.7 Hz, 1H), 6.23 (s, 1H), 4.59 (t, J = 10.9 Hz, 1H), 3.91 (d, J = 14.8 Hz, 1H), 2.28 (s, 3H), 0.86 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.9, 140.4, 138.6, 137.3, 134.3, 131.7, 128.7, 128.7, 128.2, 128.2, 128.1, 127.1, 126.7, 125.0, 79.5, 75.7, 59.2, 26.6; IR (NaCl film): 2976, 1490, 1456, 1344, 1168, 1053, 761, 713, 667, 586 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{29}N_2O_3S$ $[M+H]^+$ = 437.1893, found = 437.1895.

3-benzyl-7-methyl-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ba)



White solid, 154.7 mg, 80% yield, mp 170.0-171.4 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.2 Hz, 2H), 7.30-7.15 (m, 10H), 7.12 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 7.7 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.60 (s, 1H), 5.97 (s, 1H), 4.25 (d, J = 14.4 Hz, 1H), 3.78 (d, J = 14.1 Hz, 1H), 3.64 (d, J = 14.4 Hz, 1H), 3.60 (d, J = 14.2 Hz, 1H), 2.33 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.9, 138.7, 138.1, 137.8, 137.2, 136.9, 133.9, 128.8, 128.7, 128.5, 128.3, 128.1, 128.0, 127.6, 127.5, 127.1, 125.9, 83.4, 75.1, 58.2, 21.5, 21.2; IR (NaCl film): 2922, 1494, 1456, 1348, 1166, 1070, 813, 748, 698, 667 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{29}N_2O_3S$ $[M+H]^+$ = 485.1893, found = 485.1894.

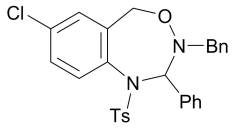
3-benzyl-7-fluoro-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ca)



White solid, 118 mg, 80% yield, mp 156.6-157.9 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 (d, J = 8.2 Hz, 2H), 7.26-7.12 (m, 8H), 7.09 (dd, J = 12.8, 7.4 Hz, 4H), 6.89 (dd, J = 8.7, 5.4 Hz, 1H), 6.77 (td, J = 8.3, 2.8 Hz, 1H), 6.44 (dd, J = 8.8, 2.8 Hz, 1H), 5.90 (s, 1H), 4.13 (d, J = 14.7 Hz, 1H), 3.71 (d, J = 14.1 Hz, 1H), 3.53 (d, J = 10.1 Hz, 1H), 3.51 (d, J = 10.5 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.4 (d, J = 249.4 Hz), 142.2, 139.9 (d, J = 7.6 Hz), 136.4, 135.9, 135.6, 135.2 (d, J = 8.8 Hz), 127.9, 127.9,

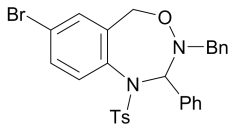
127.7, 127.1, 127.1, 126.5, 126.3, 126.0, 125.9, 112.9 (d, J = 22.1 Hz), 111.2 (d, J = 23.2 Hz), 82.3, 73.9, 57.1, 20.5; IR (NaCl film): 2929, 1598, 1492, 1350, 1209, 1166, 1093, 1074, 702, 667 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{26}FN_2O_3S$ $[M+H]^+$ = 489.1643, found = 489.1644.

3-benzyl-7-chloro-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3da)



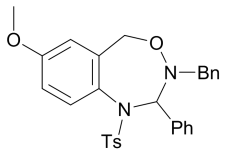
White solid, 197.3 mg, 98% yield, mp 157.6-158.9 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.2 Hz, 2H), 7.34-7.19 (m, 8H), 7.18-7.13 (m, 5H), 6.94 (d, J = 8.4 Hz, 1H), 6.81 (d, J = 2.3 Hz, 1H), 5.97 (s, 1H), 4.21 (d, J = 14.7 Hz, 1H), 3.78 (d, J = 14.1 Hz, 1H), 3.60 (d, J = 14.1 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.3, 140.3, 137.3, 136.9, 136.6, 135.7, 134.6, 129.8, 129.0, 128.9, 128.7, 128.1, 127.5, 127.3, 127.1, 125.5, 83.4, 74.7, 58.2, 21.5; IR (NaCl film): 2926, 1600, 1481, 1352, 1168, 1072, 873, 817, 665, 584 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{26}ClN_2O_3S$ $[M+Na]^+$ = 505.1347, found = 505.1351.

3-benzyl-7-bromo-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ea)



White solid, 199.1 mg, 91% yield, mp 172.5-173.9 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.2 Hz, 2H), 7.38-7.20 (m, 9H), 7.20-7.13 (m, 4H), 6.96 (d, J = 2.1 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 5.96 (s, 1H), 4.20 (d, J = 14.7 Hz, 1H), 3.78 (d, J = 14.1 Hz, 1H), 3.60 (dd, J = 14.4, 3.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.3, 140.7, 137.3, 136.9, 136.6, 135.9, 129.0, 128.9, 128.1, 128.1, 122.8, 83.4, 74.6, 67.1, 58.2, 21.6; IR (NaCl film): 2922, 1598, 1477, 1354, 1165, 1074, 740, 704, 663, 582 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{26}BrN_2O_3S$ $[M+Na]^+$ = 549.0842, found = 549.0840.

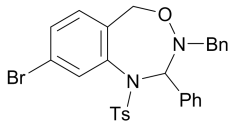
3-benzyl-7-methoxy-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3fa)



White solid, 188.4 mg, 94% yield, mp 163.5-164.9 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.3 Hz, 2H), 7.31-7.20 (m, 8H), 7.20-7.17 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.7 Hz, 1H), 6.68 (dd, J = 8.7, 2.9 Hz, 1H), 6.32 (d, J = 2.9 Hz, 1H), 5.96 (s,

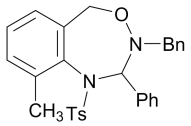
1H), 4.22 (d, J = 14.5 Hz, 1H), 3.79-3.76 (m, 4H), 3.60 (dd, J = 14.3, 8.9 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.5, 142.9, 139.9, 137.7, 137.2, 136.8, 135.4, 128.8, 128.8, 128.6, 128.2, 128.0, 123.6, 111.6, 110.8, 83.4, 75.2, 58.2, 55.3, 21.5; IR (NaCl film): 2900, 1500, 1348, 1288, 1163, 1074, 1039, 866, 700, 663 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{29}N_2O_4S$ $[M+H]^+$ = 501.1843, found = 501.1845.

3-benzyl-8-bromo-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ga)



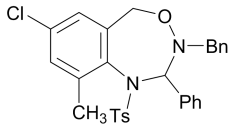
White solid, 184.2 mg, 84% yield, mp 144.6-145.9 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.2 Hz, 2H), 7.40 (dd, J = 8.2, 2.0 Hz, 1H), 7.34-7.28 (m, 3H), 7.25-7.21 (m, 5H), 7.20-7.19 (d, J = 1.9 Hz, 1H), 7.16-7.14 (m, 4H), 6.69 (d, J = 8.2 Hz, 1H), 5.96 (s, 1H), 4.21 (d, J = 14.6 Hz, 1H), 3.78 (d, J = 14.1 Hz, 1H), 3.60-3.55 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.4, 137.8, 137.4, 137.0, 136.9, 136.6, 132.6, 131.9, 129.2, 129.1, 128.9, 128.8, 128.2, 128.1, 127.5, 127.4, 126.7, 119.5, 83.6, 74.9, 58.2, 21.6; IR (NaCl film): 2910, 1597, 1494, 1452, 1350, 1170, 1068, 815, 740, 667 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{25}BrN_2NaO_3S$ $[M+Na]^+$ = 571.0661, found = 571.0661.

3-benzyl-9-methyl-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ha)



White solid, 166.1 mg, 86% yield, mp 142.3-143.1 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 7.1 Hz, 1H), 7.28-7.20 (m, 5H), 7.19-7.14 (m, 6H), 7.03 (d, J = 7.3 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 5.98 (s, 1H), 4.28 (d, J = 14.6 Hz, 1H), 3.83 (d, J = 14.3 Hz, 1H), 3.62 (d, J = 14.3 Hz, 1H), 3.59 (d, J = 14.5 Hz, 1H), 2.37 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.0, 142.5, 139.2, 137.2, 136.9, 129.9, 129.2, 128.9, 128.8, 128.6, 128.5, 128.0, 127.2, 123.1, 83.2, 75.3, 58.1, 21.5, 18.2; IR (NaCl film): 2922, 1598, 1496, 1456, 1340, 1161, 1097, 810, 696, 590 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{29}N_2O_3S$ $[M+H]^+$ = 485.1893, found = 485.1893.

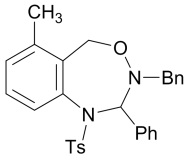
3-benzyl-7-chloro-9-methyl-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ia)



White solid, 164.6 mg, 79% yield, mp 187.3-188.9 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.49 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.1 Hz, 1H), 7.27-7.23 (m, 4H), 7.17-7.16 (m, 2H),

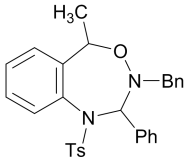
7.03 (d, J = 2.1 Hz, 1H), 6.65 (d, J = 2.0 Hz, 1H), 5.96 (s, 1H), 4.20 (d, J = 14.8 Hz, 1H), 3.82 (d, J = 14.2 Hz, 1H), 3.61 (d, J = 14.3 Hz, 1H), 3.52 (d, J = 14.7 Hz, 1H), 2.37 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.6, 143.3, 140.9, 136.9, 136.8, 136.6, 134.1, 129.1, 129.0, 128.9, 128.8, 128.8, 128.7, 128.6, 128.1, 127.3, 123.2, 83.1, 74.9, 58.1, 21.6, 18.2; IR (NaCl film): 2910, 1577, 1454, 1340, 1215, 1166, 1070, 869, 700, 594 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{27}ClN_2NaO_3S$ $[M+Na]^+$ = 541.1323, found = 541.1327.

3-benzyl-6-methyl-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ja)



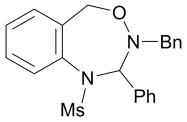
White solid, 180.5 mg, 93% yield, mp 130.1-132.5 ℃;^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.2 Hz, 2H), 7.30-7.19 (m, 10H), 7.12 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 7.4 Hz, 1H), 7.04 (t, J = 7.7 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.02 (s, 1H), 4.34 (d, J = 15.0 Hz, 1H), 3.79 (d, J = 14.1 Hz, 1H), 3.62 (d, J = 14.1 Hz, 1H), 3.52 (d, J = 15.0 Hz, 1H), 2.35 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.9, 137.5, 137.2, 136.8, 136.7, 134.3, 132.3, 131.1, 130.7, 128.9, 128.8, 128.7, 128.5, 128.2, 128.0, 127.7, 127.2, 126.3, 83.3, 73.6, 58.2, 21.5, 18.8; IR (NaCl film): 2924, 1600, 1496, 1467, 1454, 1344, 1163, 1083, 702, 588 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{29}N_2O_3S$ $[M+H]^+$ = 485.1893, found = 485.1893.

3-benzyl-5-methyl-2-phenyl-1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3la)



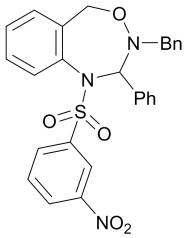
White solid, 164.6 mg, 85% yield, dr = 3/2, mp 132.3-133.7 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (major+minor) = 7.51 (d, J = 8.2 Hz, 1.2 H), 7.39 (d, J = 8.2 Hz, 0.8 H), 7.32-7.20 (m, 10 H), 7.16 (d, J = 8.1 Hz, 1.2 H), 7.11 (dd, J = 10.1, 4.3 Hz, 2 H), 7.09-7.03 (m, 0.6 H), 6.90 (d, J = 7.8 Hz, 0.4 H), 6.86-6.85 (m, 0.8 H), 6.83-6.82 (m, 0.8 H), 6.07 (s, 0.6 H), 5.96 (s, 0.4 H), 4.55 (q, J = 6.8 Hz, 0.6 H), 3.93 (q, J = 6.5 Hz, 0.4 H), 3.85 (dd, J = 13.9, 9.0 Hz, 0.4 H), 3.75 (d, J = 13.7 Hz, 0.6 H), 3.68 (d, J = 13.7 Hz, 0.6 H), 3.54 (d, J = 13.9 Hz, 0.4 H), 2.37 (s, 1.2 H), 2.34 (s, 1.8 H), 0.87 (d, J = 6.6 Hz, 1.2 H), 0.70 (d, J = 6.8 Hz, 1.8 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (major+minor) = 142.2, 142.0, 141.8, 141.4, 137.0, 136.8, 136.6, 136.3, 136.2, 135.7, 133.2, 132.4, 129.9, 129.5, 129.4, 128.3, 128.1, 127.9, 127.8, 127.8, 127.7, 127.5, 127.4, 127.3, 127.1, 127.0, 126.9, 126.8, 126.8, 126.7, 126.4, 126.2, 125.9, 125.6, 125.4, 125.2, 81.7, 81.7, 81.4, 76.7, 57.9, 57.2, 20.5, 20.4, 19.3; IR (NaCl film): 2881, 1597, 1494, 1350, 1168, 1091, 813, 763, 665, 578 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{29}N_2O_3S$ $[M+H]^+$ = 485.1893, found = 485.1893.

4-benzyl-1-(methylsulfonyl)-2-phenyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3ma)



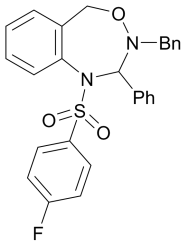
White solid, 148.2 mg, 94% yield, mp 146.3-148.7 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28-7.16 (m, 9H), 7.15-7.14 (m, 2H), 7.10 (t, J = 7.4 Hz, 1H), 6.92 (t, J = 7.8 Hz, 2H), 5.76 (s, 1H), 4.95 (d, J = 15.0 Hz, 1H), 4.63 (d, J = 15.0 Hz, 1H), 3.75 (d, J = 13.9 Hz, 1H), 3.61 (d, J = 15.0 Hz, 1H), 2.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 136.3, 136.0, 133.5, 130.1, 127.9, 127.6, 127.2, 126.5, 126.4, 126.2, 124.6, 82.5, 74.7, 57.5, 38.1; IR (NaCl film): 1492, 1452, 1338, 1155, 1070, 970, 748, 723, 700, 547 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{23}N_2O_3S$ $[M+H]^+$ = 395.1424, found = 395.1425.

3-benzyl-1-((3-nitrophenyl)sulfonyl)-2-phenyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3na)



Foam, 188.4 mg, 94% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.38 (s, 1H), 8.27 (dd, J = 8.2, 1.1 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.28-7.20 (m, 4H), 7.20-7.11 (m, 6H), 7.08-6.96 (m, 2H), 6.95 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 7.6 Hz, 1H), 5.89 (s, 1H), 4.24 (d, J = 14.8 Hz, 1H), 3.74 (d, J = 14.1 Hz, 1H), 3.55-3.51 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.7, 140.8, 136.7, 135.7, 135.4, 133.3, 132.5, 129.2, 128.5, 128.3, 128.2, 128.1, 127.7, 127.1, 126.6, 126.4, 126.3, 125.8, 124.5, 122.4, 82.6, 74.0, 57.1; IR (NaCl film): 1606, 1531, 1496, 1456, 1352, 1174, 1072, 761, 698, 596 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{24}N_3O_5S$ $[M+H]^+$ = 502.1431, found = 502.1431.

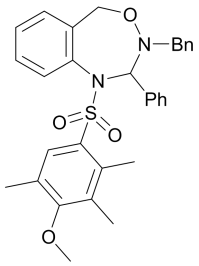
3-benzyl-1-((4-fluorophenyl)sulfonyl)-2-phenyl-1,2,3,5-tetrahydrobenzo[e][1,2,4]oxadiazepine (3oa)



Foam, 168.8 mg, 89% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 (dd, J = 8.7, 5.1 Hz, 2H), 7.29-7.13 (m, 9H), 7.11-7.09 (m, 3H), 6.96-6.93 (m, 3H), 6.75 (d, J = 7.5 Hz, 1H), 5.90 (s, 1H), 4.24 (d, J = 14.6 Hz, 1H), 3.72 (d, J = 14.1 Hz, 1H), 3.61 (d, J = 14.5 Hz, 1H), 3.52 (d, J = 14.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.9 (d, J = 254.3 Hz), 137.3, 136.3, 135.8, 134.8 (d, J = 3.0 Hz), 133.4, 129.8 (d, J = 8.8 Hz), 128.0, 127.9,

127.9, 127.6, 127.1, 126.6, 126.3, 126.0, 124.4, 114.4 (d, J = 22.3 Hz), 82.5, 74.1, 57.2; IR (NaCl film): 1591, 1492, 1456, 1352, 1170, 1093, 1072, 840, 700, 578 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{24}FN_2O_3S$ $[M+H]^+$ = 475.1486, found = 475.1487.

3-benzyl-1-((4-methoxy-2,3,5-trimethylphenyl)sulfonyl)-2-phenyl-1,2,3,5-tetrahydro benzo[e][1,2,4]oxadiazepine (3pa)



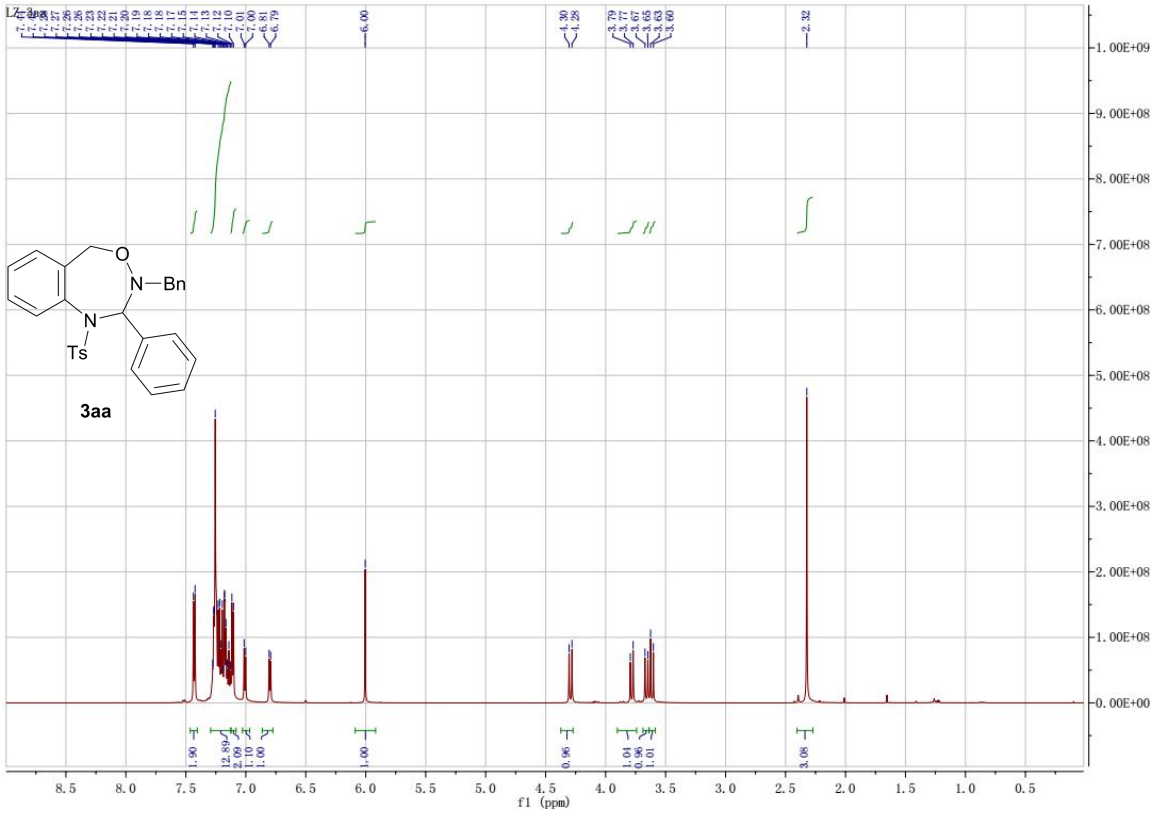
Foam, 181.7 mg, 86% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ = ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33-7.21 (m, 10H), 7.19 (d, J = 7.4 Hz, 2H), 6.97 (d, J = 7.6 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.38 (s, 1H), 6.29 (d, J = 7.7 Hz, 1H), 6.20 (s, 1H), 4.82 (d, J = 14.2 Hz, 1H), 4.51 (d, J = 14.3 Hz, 1H), 3.78 (s, 3H), 2.23 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.2, 140.9, 140.4, 140.3, 137.7, 137.5, 134.0, 131.6, 129.0, 128.9, 128.8, 128.7, 128.4, 128.2, 128.0, 127.1, 126.4, 125.7, 124.6, 111.6, 82.5, 76.1, 58.0, 55.4, 24.3, 18.1, 11.9; IR (NaCl film): 2937, 1585, 1456, 1307, 1149, 1118, 1064, 698, 655, 570 cm^{-1}; HRMS (ESI) m/z calcd for $C_{31}H_{33}N_2O_4S$ $[M+H]^+$ = 529.2156, found = 529.2159.

D. References

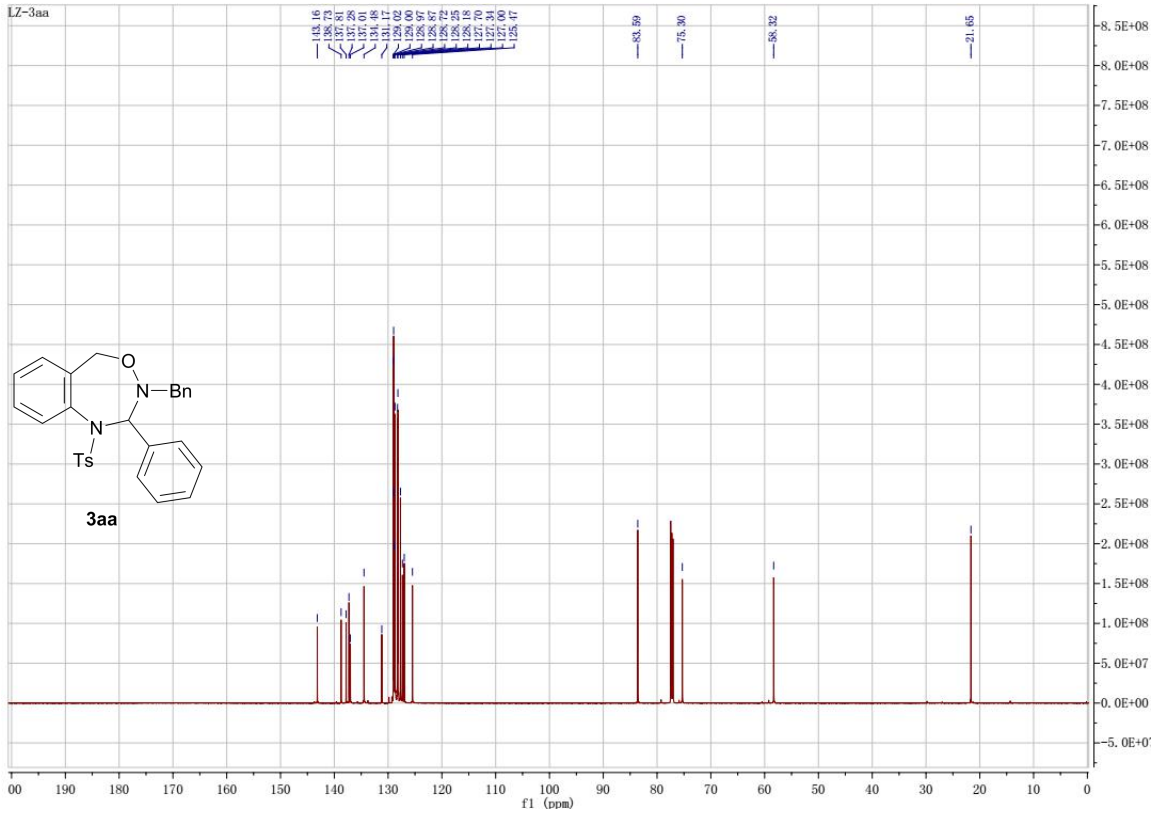
[1] (a) Q. Q. Yang, C. Xiao, L. Q. Lu, J. An, F. Tan, B. J. Li and W. J. Xiao, *Angew. Chem., Int. Ed.*, 2012, **51**, 9137; (b) M. T. Hovey, C. T. Check, A. F. Sipher and K. A. Scheidt, *Angew. Chem., Int. Ed.*, 2014, **53**, 9603; (c) G. Zhan, M. L. Shi, Q. He, W. Du and Y. C. Chen, *Org. Lett.*, 2015, **17**, 4750.

[2] (a) R. Herrera, A. Nagarajan, M. A. Morales, F. Méndez, H. A. Jiménez-Vázquez, L. G. Zepeda and J. Tamariz*, J. Org. Chem.*,2001, **66**, 1252; (b) P. Aschwanden, L. Kværnø, R. W. Geisser, F. Kleinbeck and E. M. Carreira, *Org. Lett.*, 2005, **7**, 5741; (c) T. Sakai, T. Soeta, K. Endo, S. Fujinami and Y. Ukaji, *Org. Lett.*, 2013, **15**, 2422.

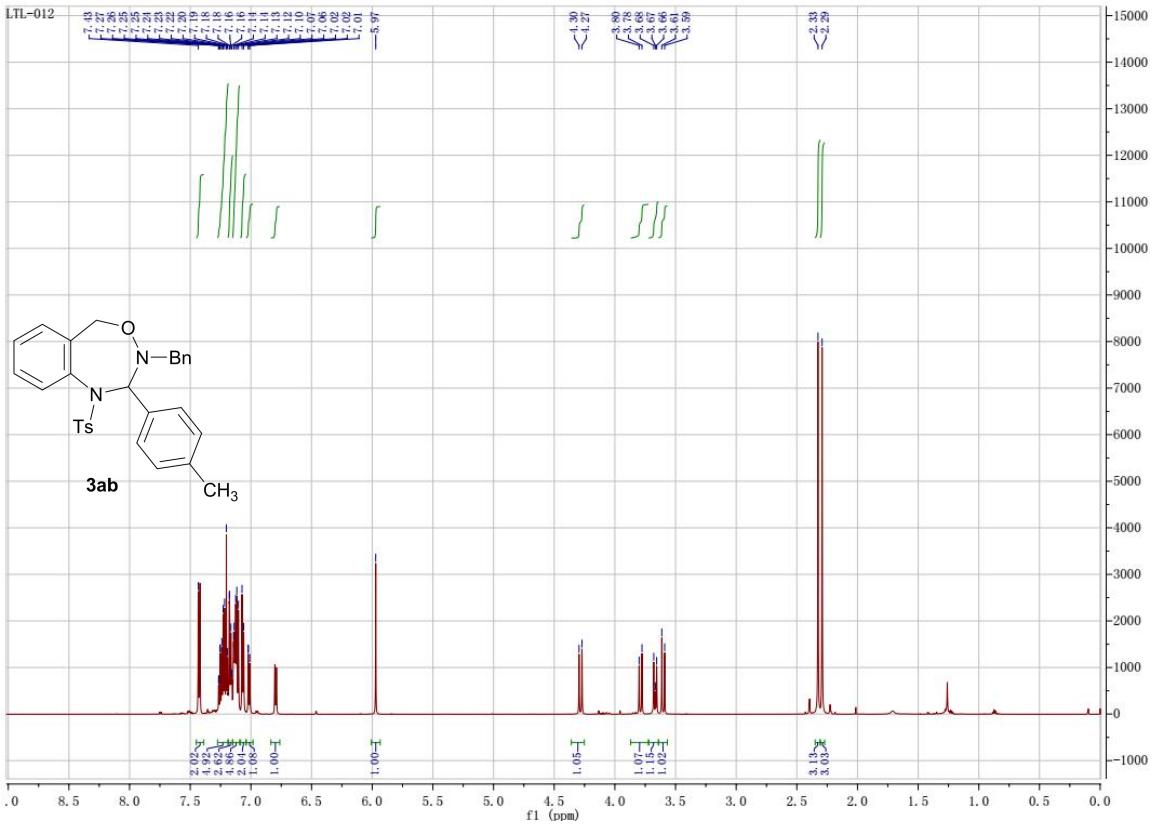
E. Copies of ^{1}H and ^{13}C NMR spectra of the products



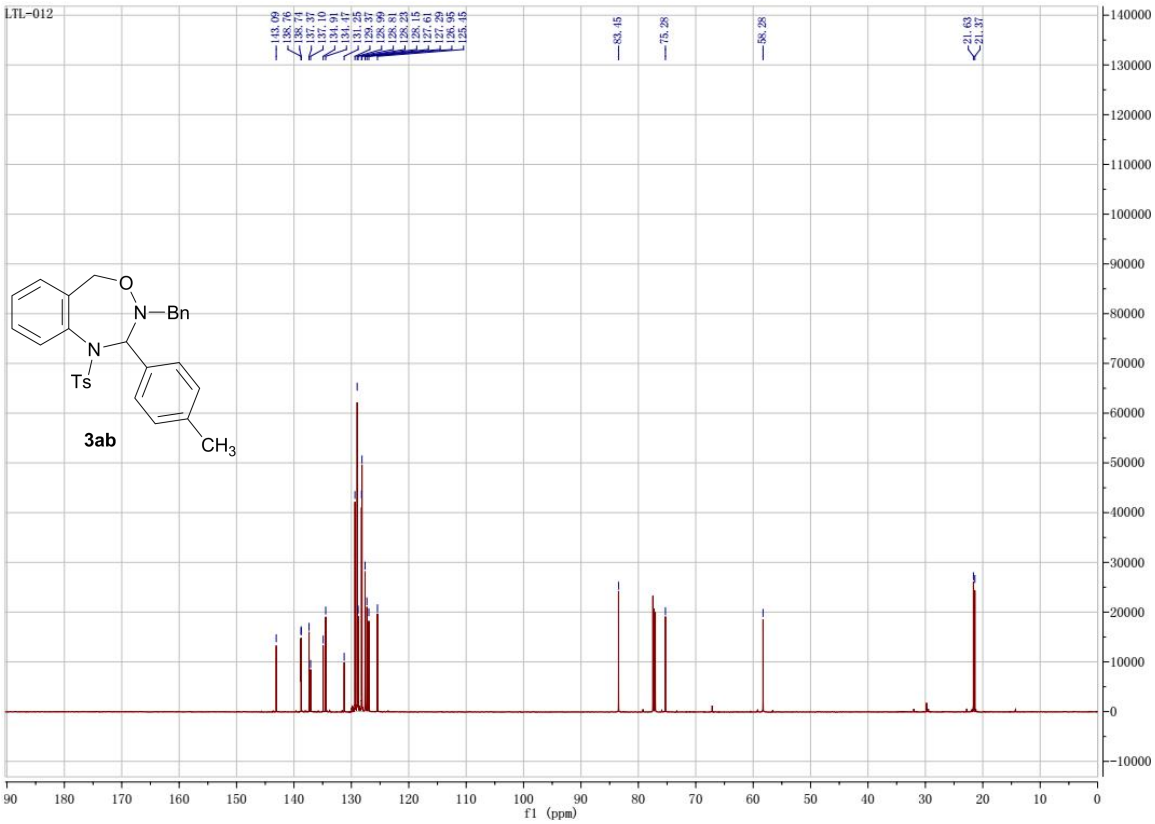
^{1}H NMR (600 MHz, $CDCl_3$)



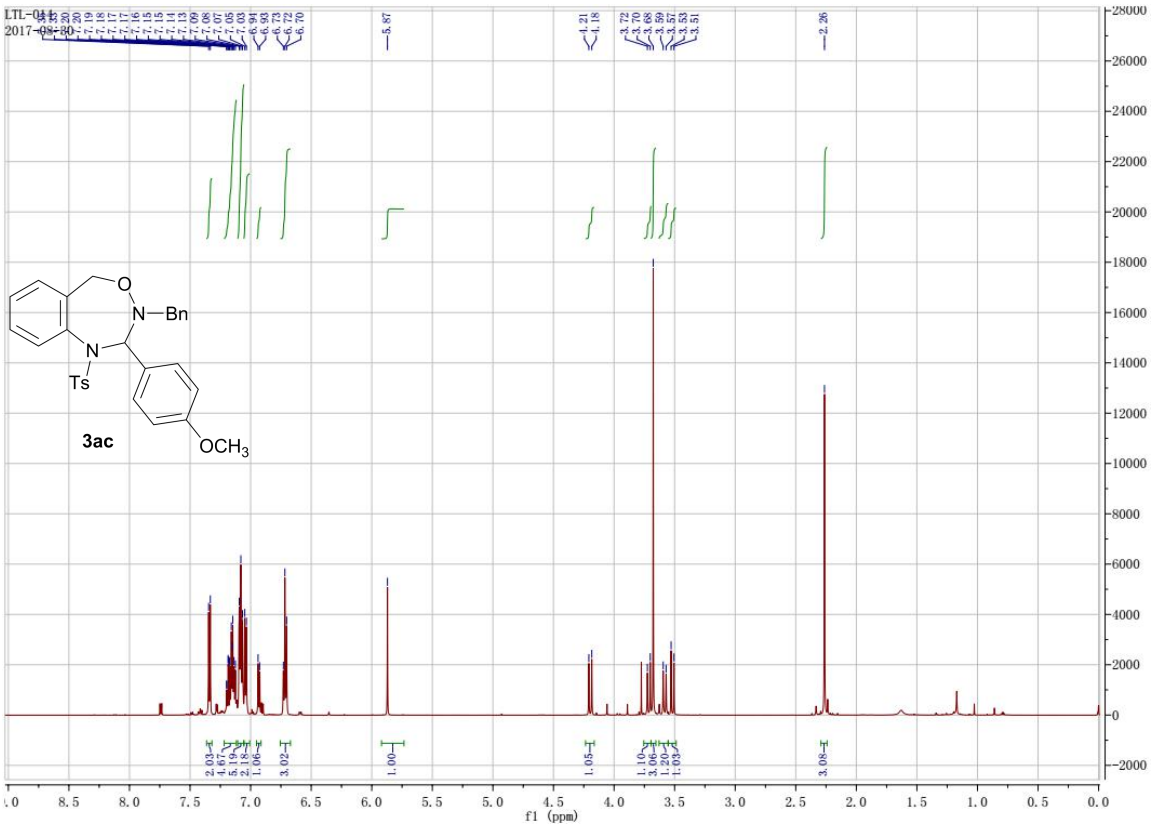
^{13}C NMR (150 MHz, $CDCl_3$)



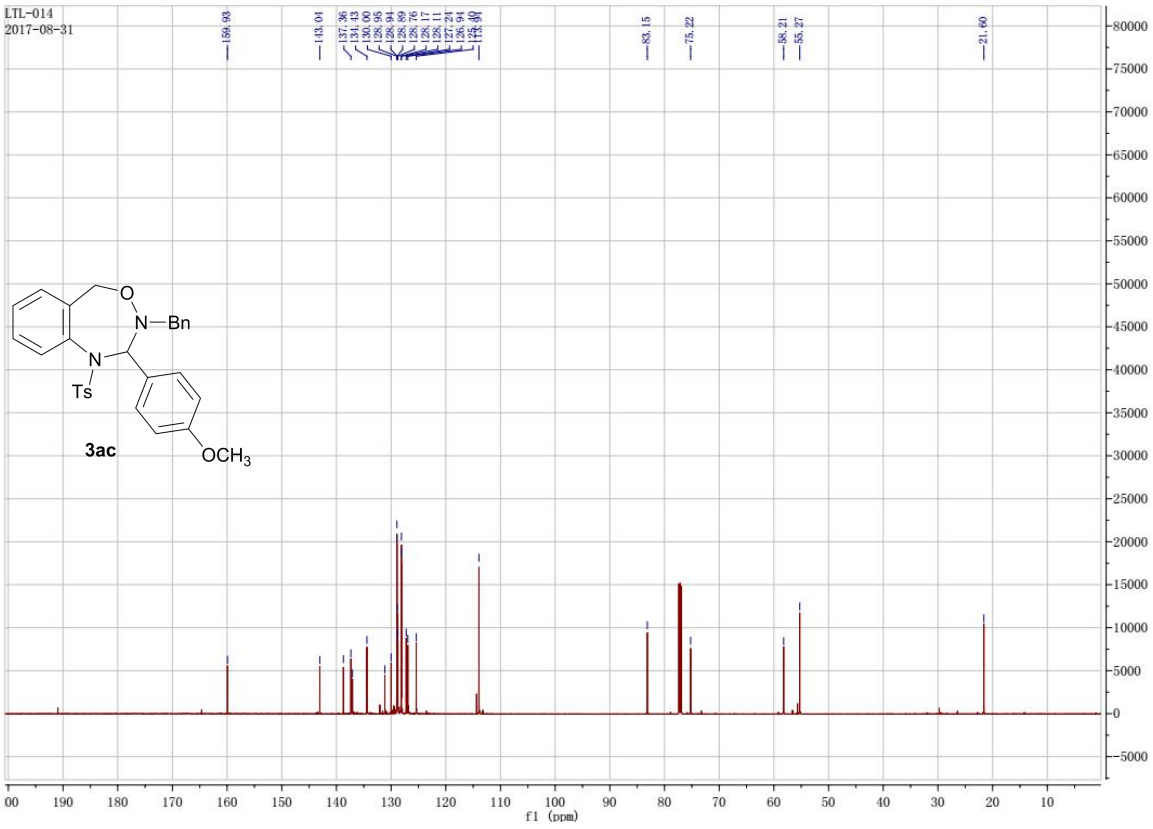
^{1}H NMR (600 MHz, $CDCl_3$)



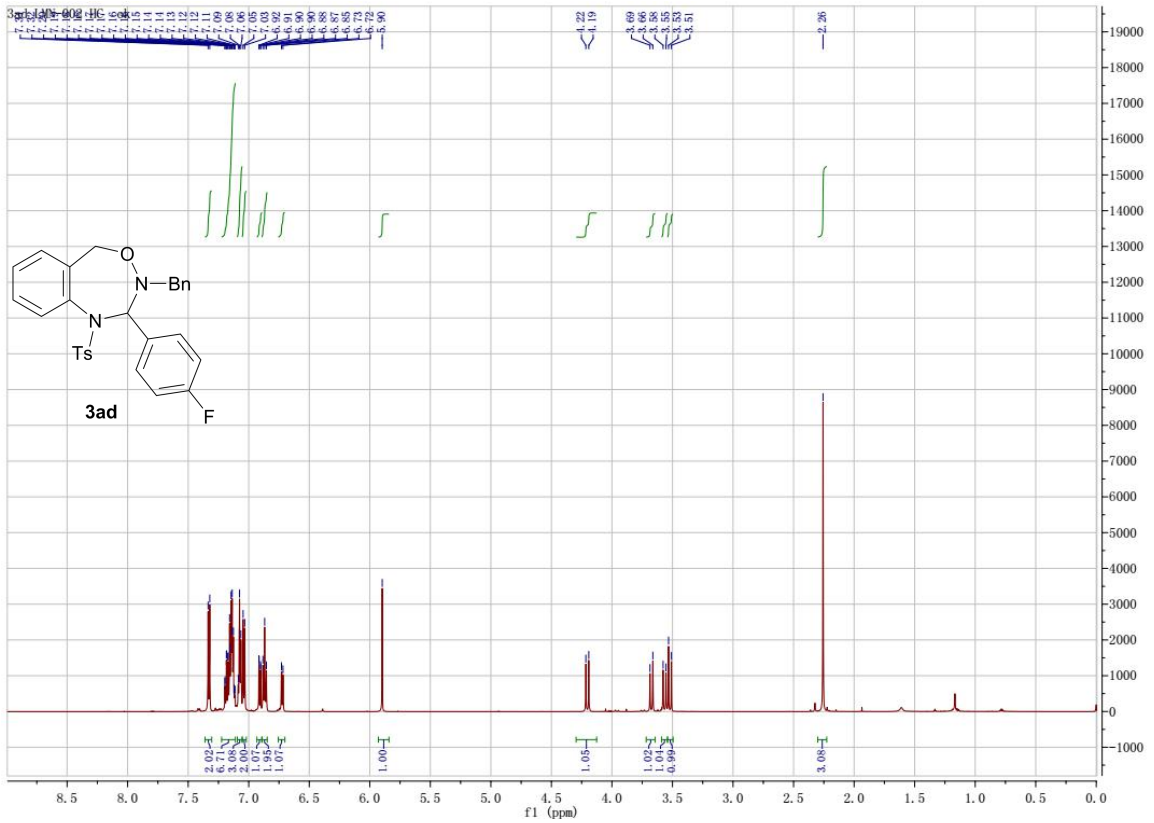
^{13}C NMR (150 MHz, $CDCl_3$)



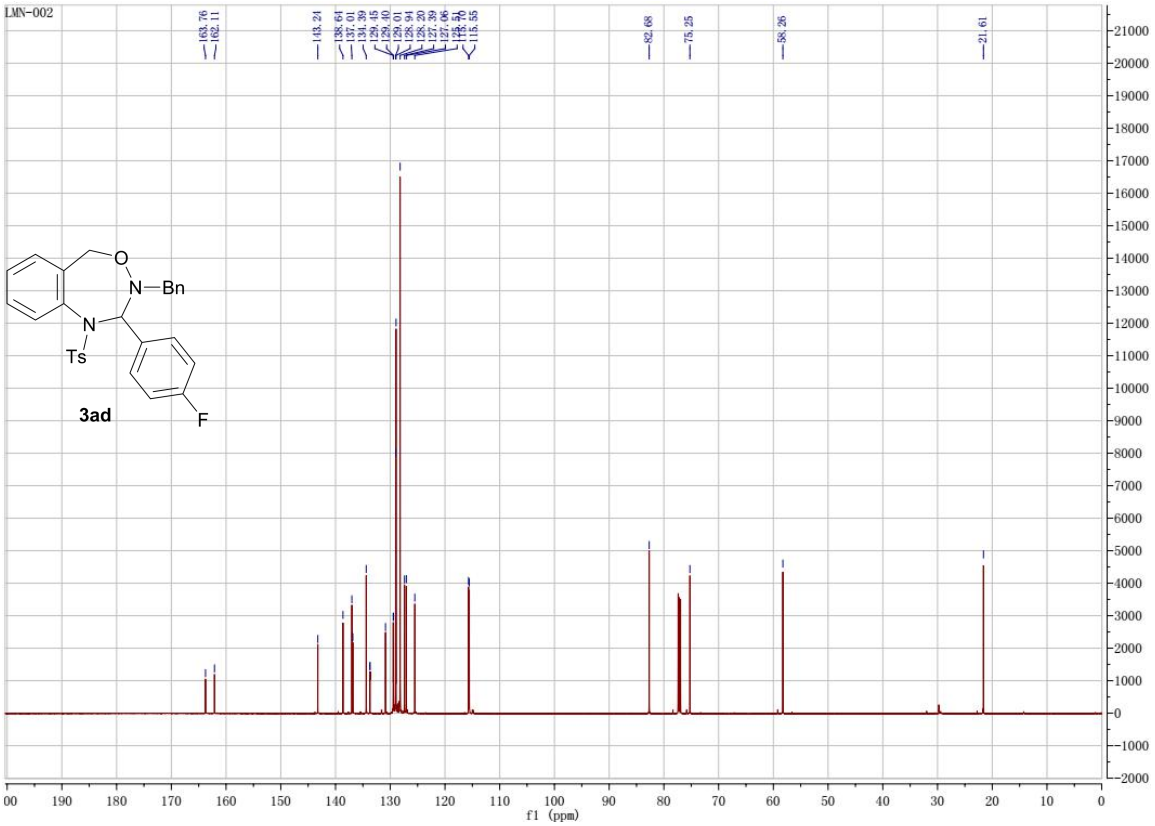
^{1}H NMR (600 MHz, $CDCl_3$)



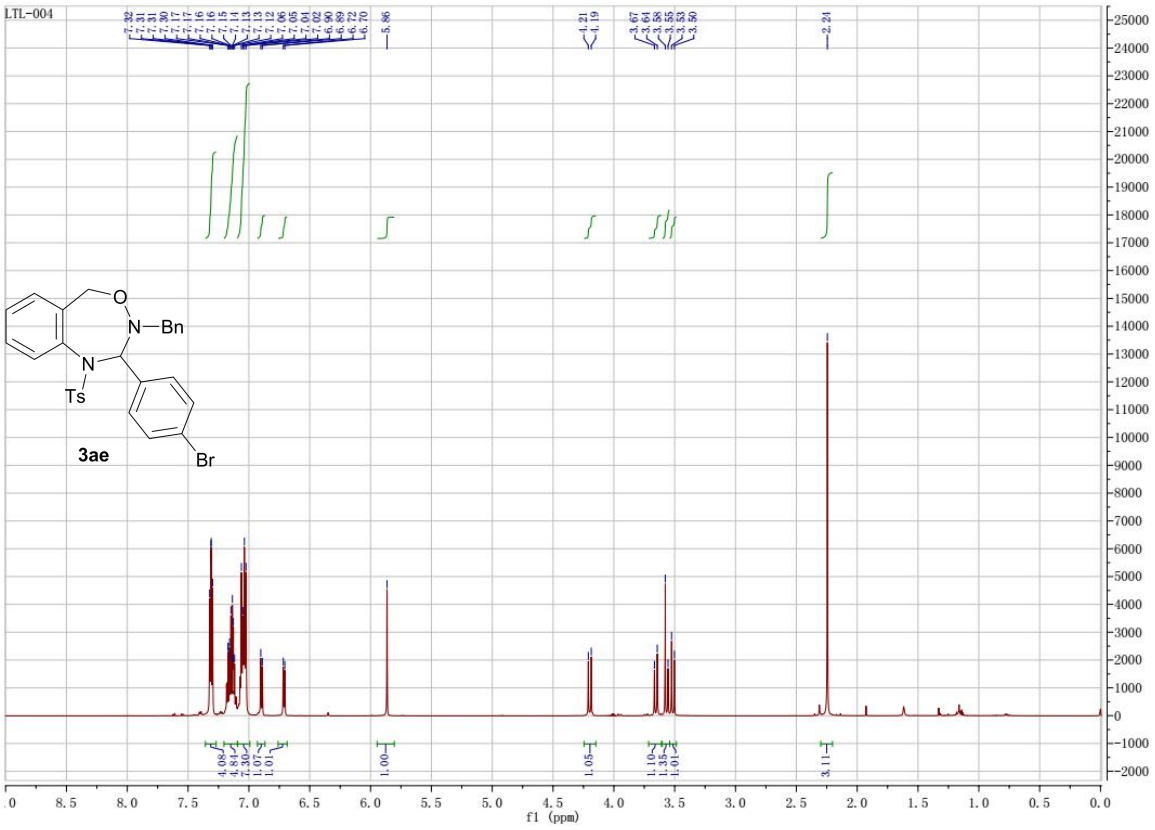
^{13}C NMR (150 MHz, $CDCl_3$)



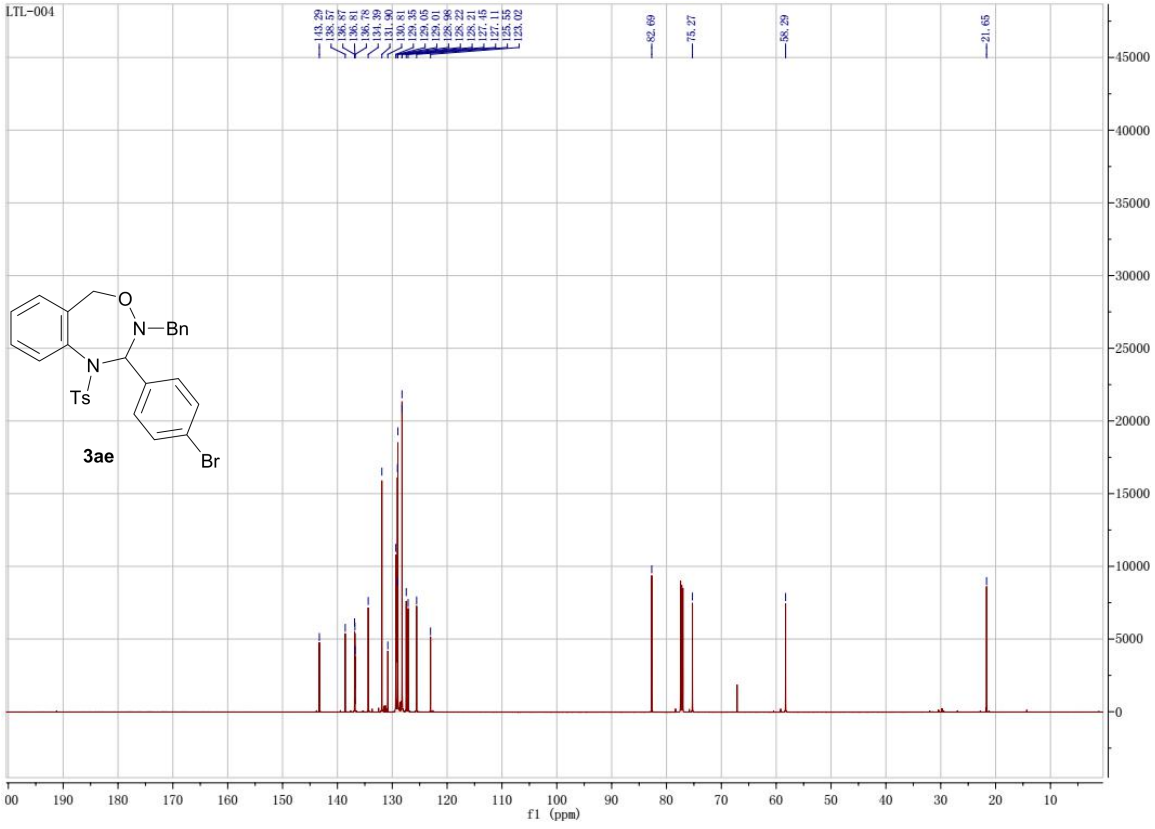
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)



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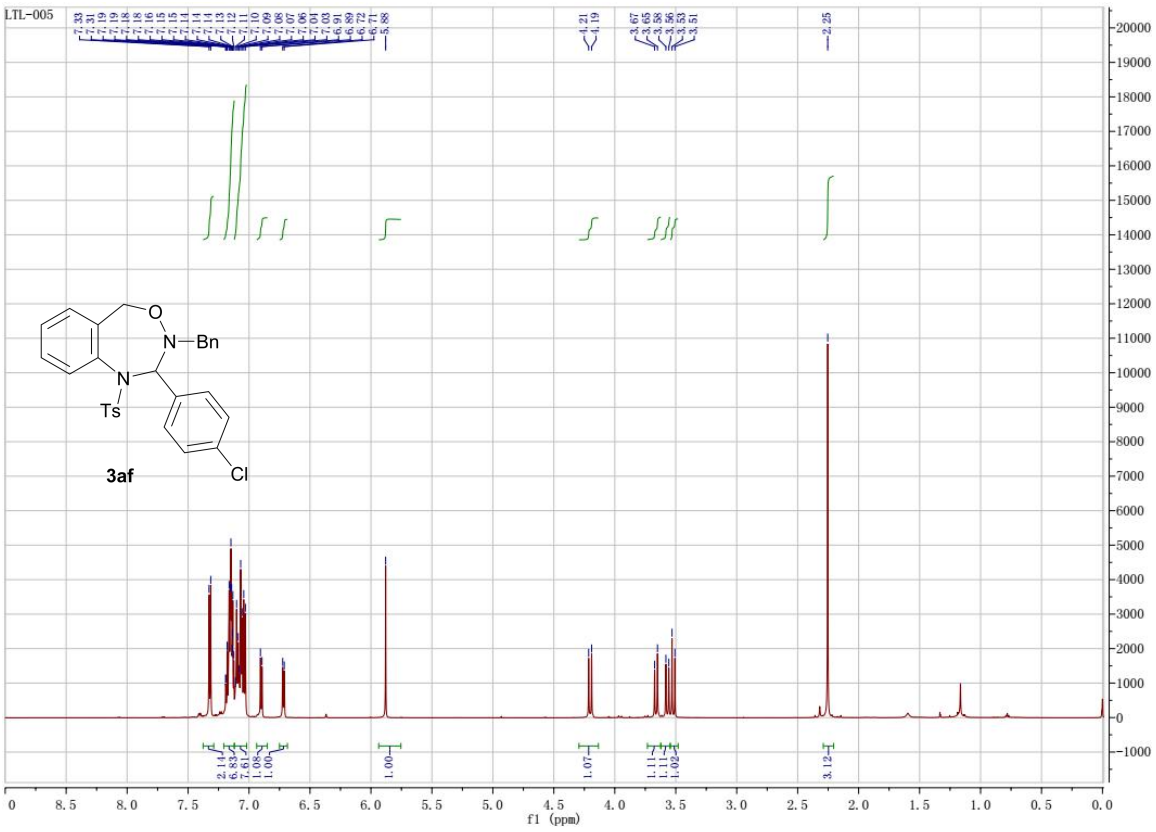
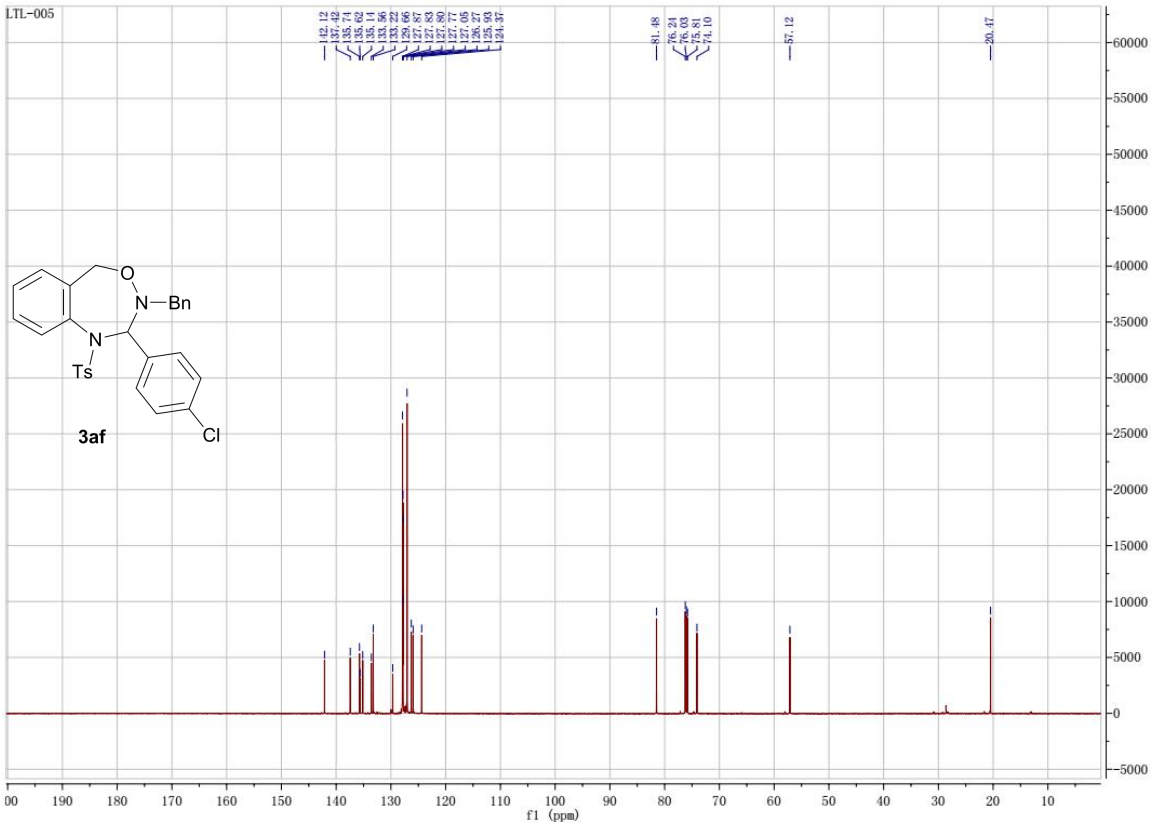
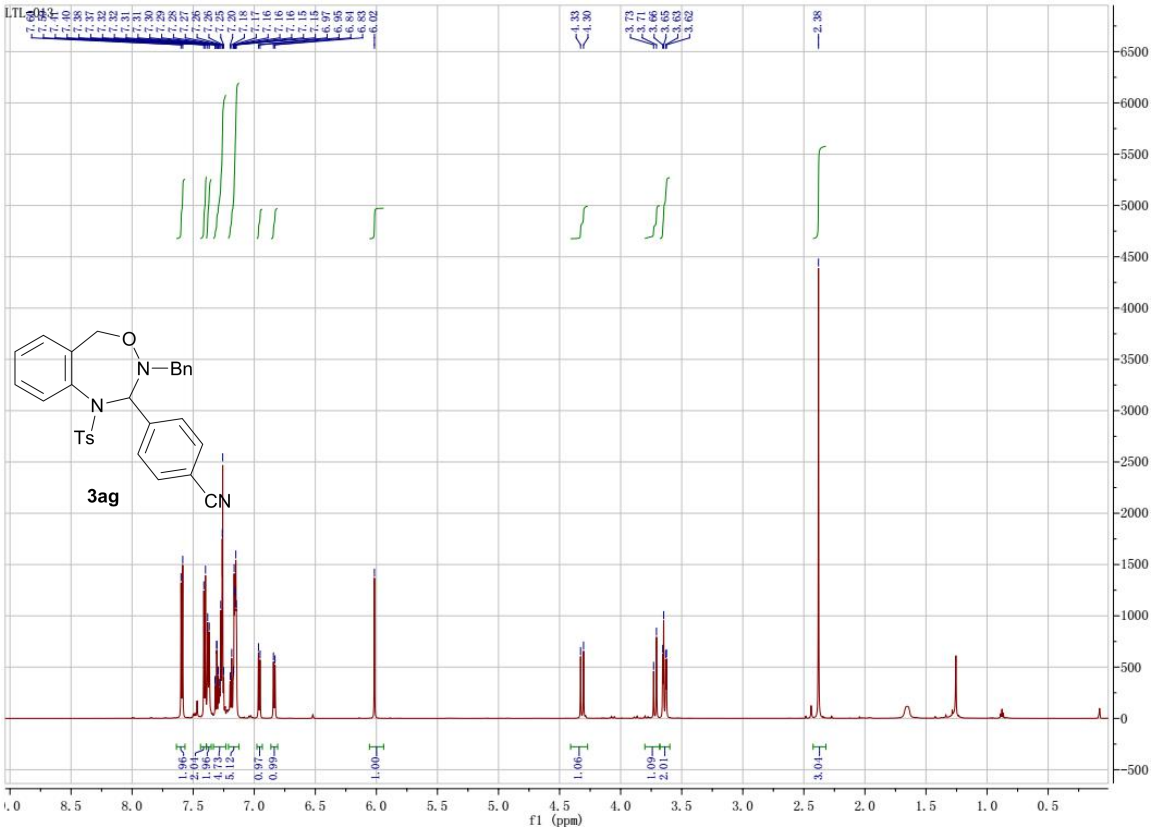


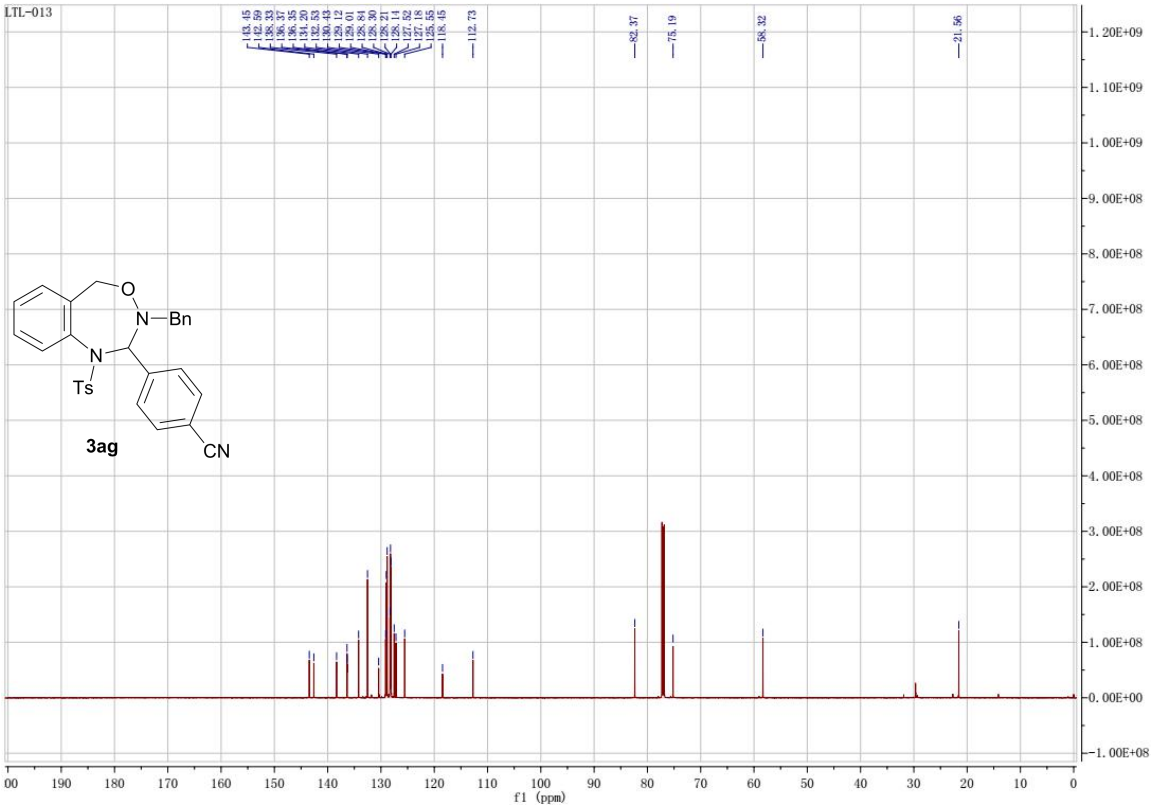
^{1}H NMR (600 MHz, $CDCl_3$)



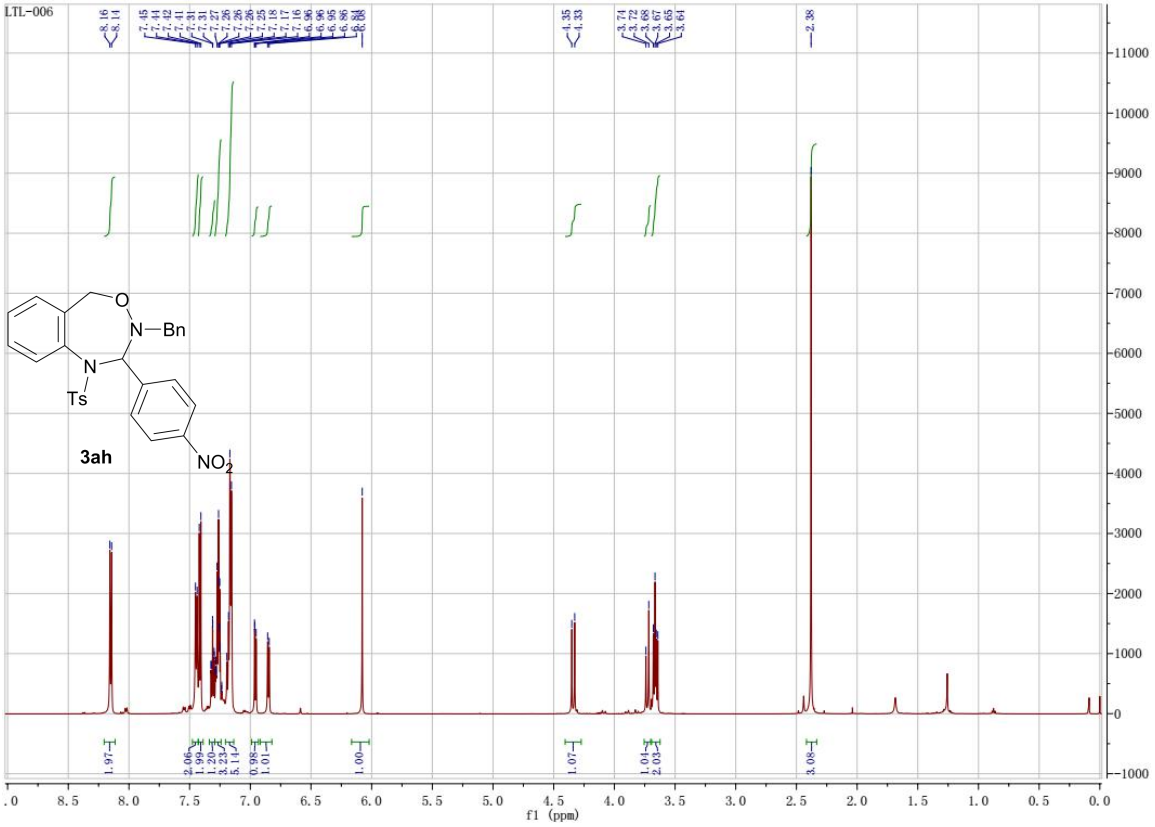
^{13}C NMR (150 MHz, $CDCl_3$)



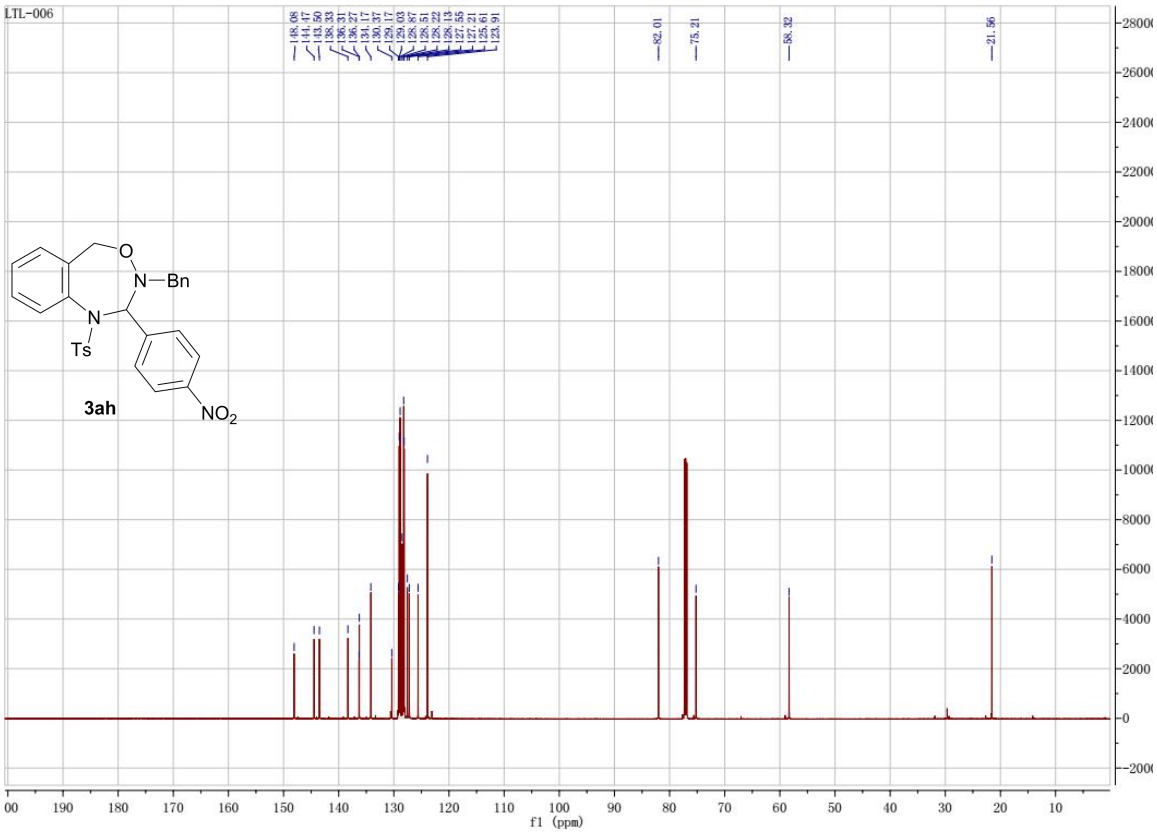
^{1}H NMR (600 MHz, $CDCl_3$)



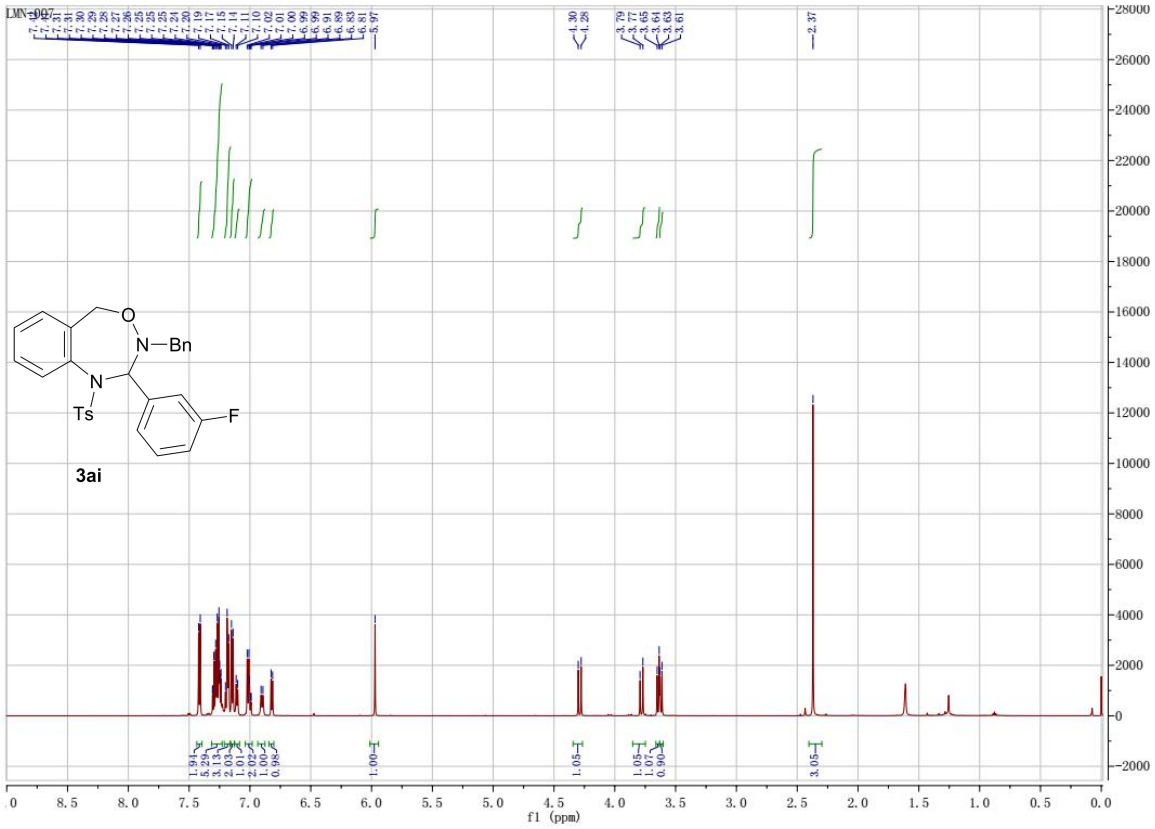
^{13}C NMR (150 MHz, $CDCl_3$)



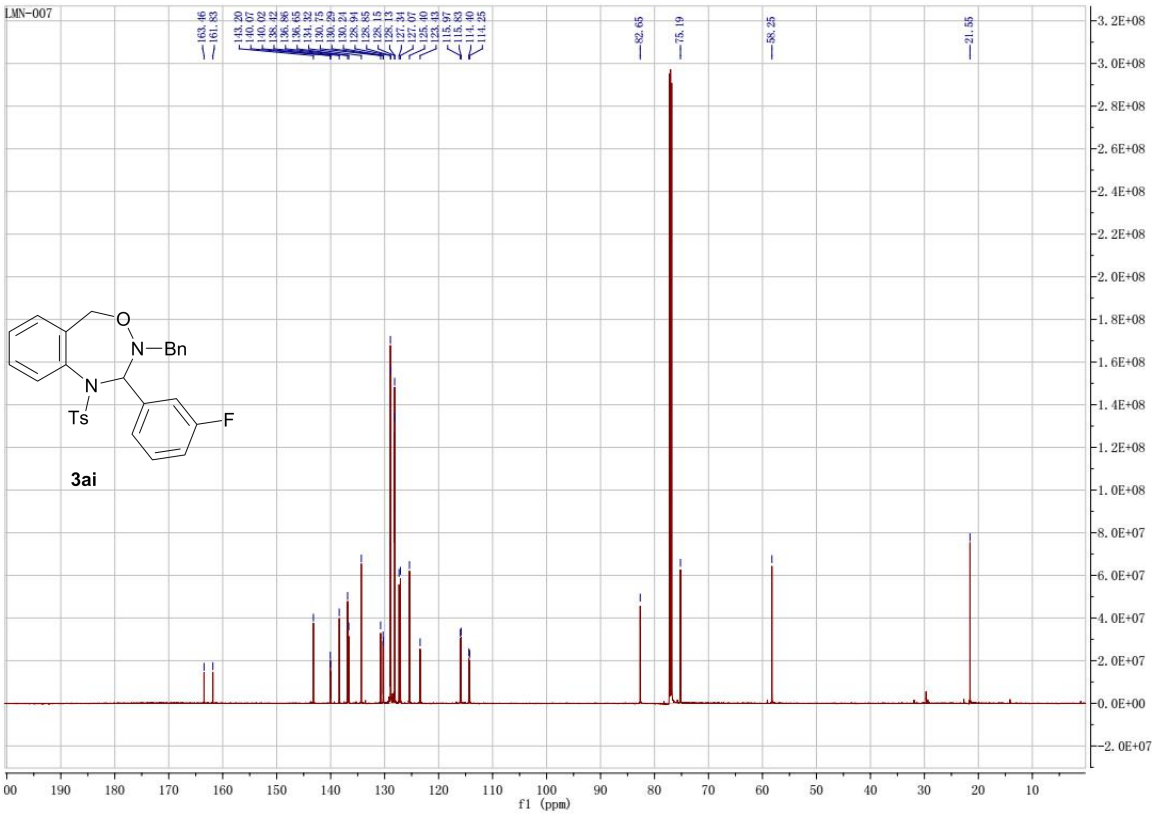
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)



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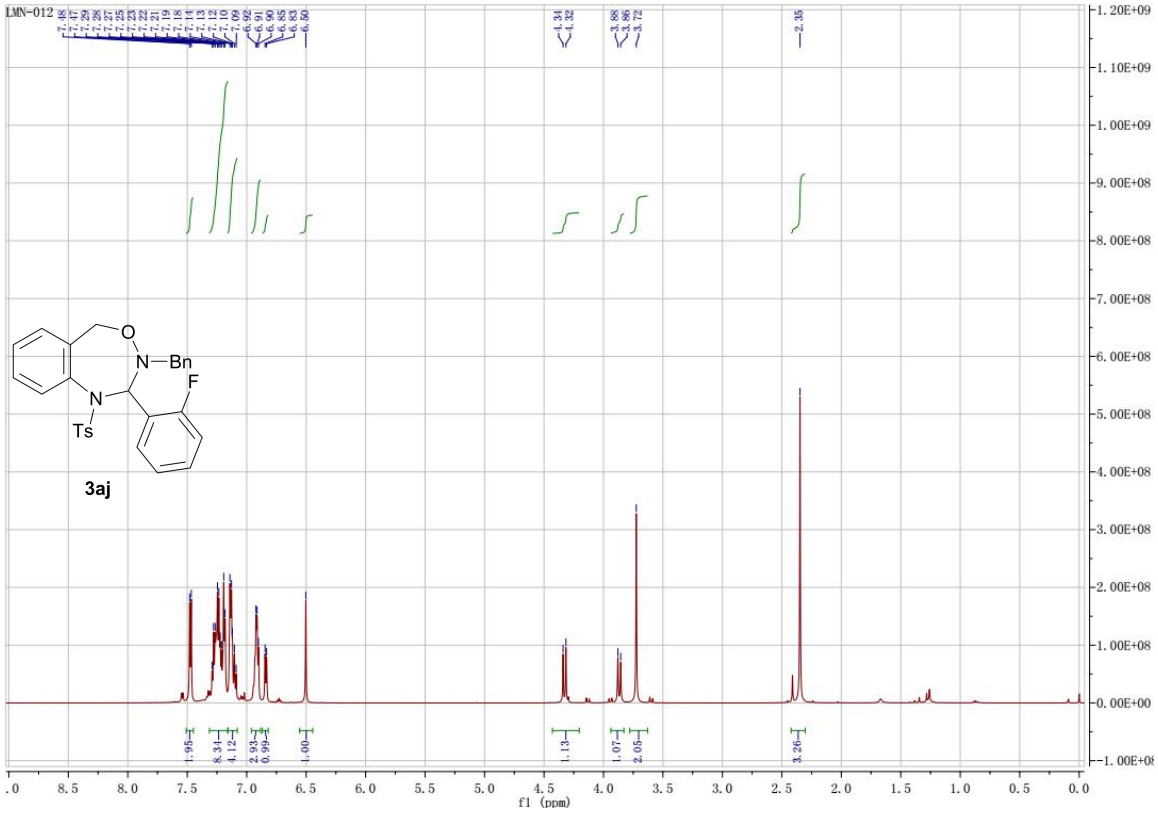
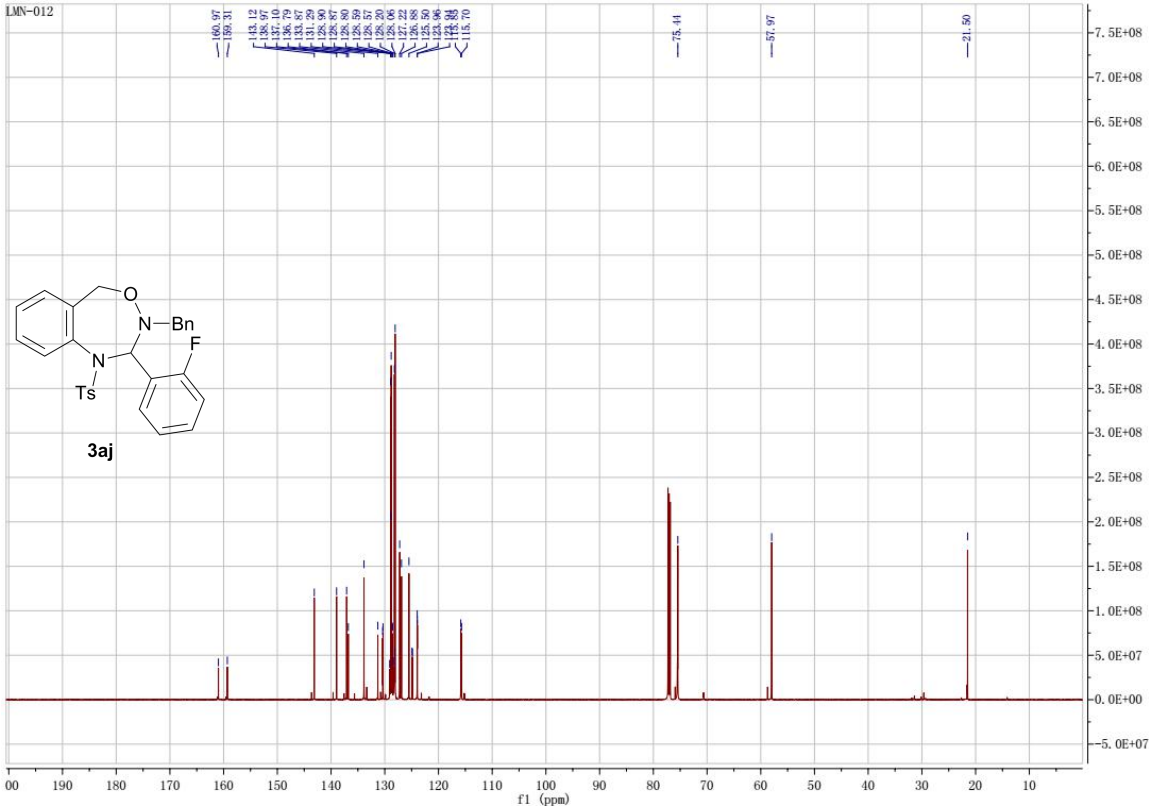


^{1}H NMR (600 MHz, $CDCl_3$)



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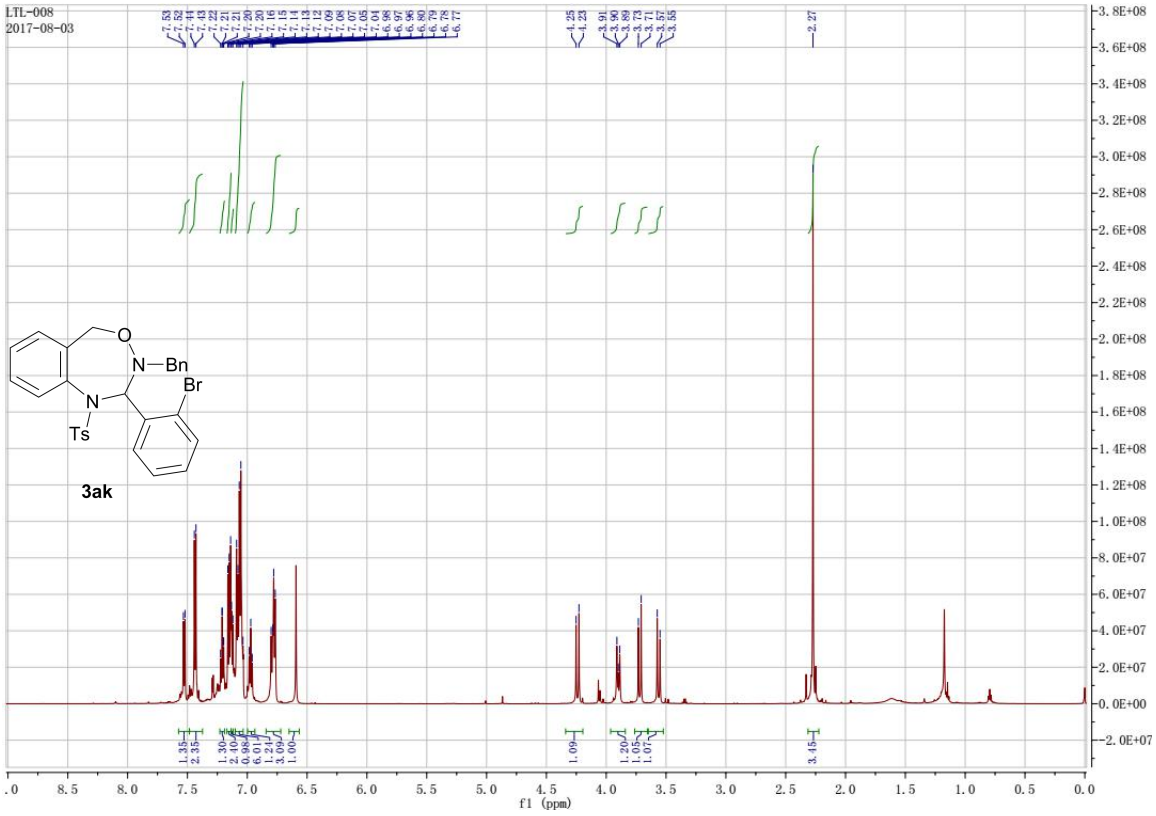
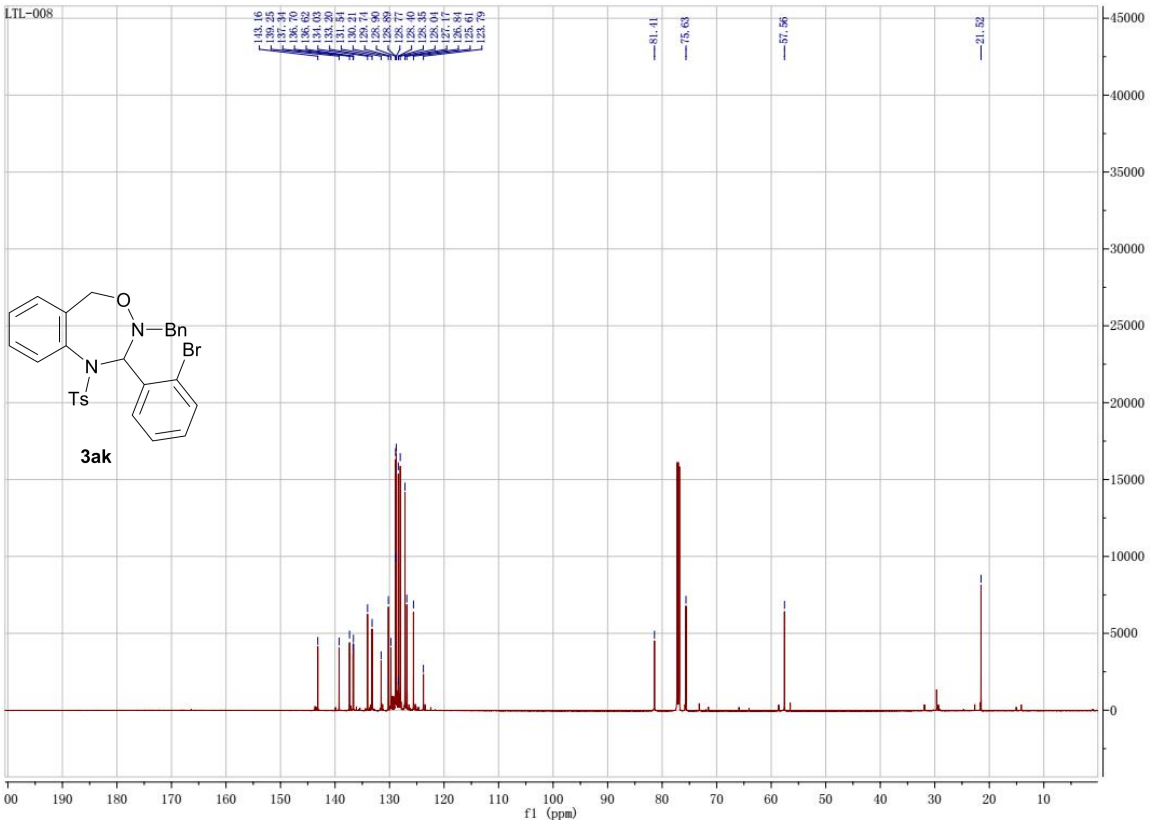
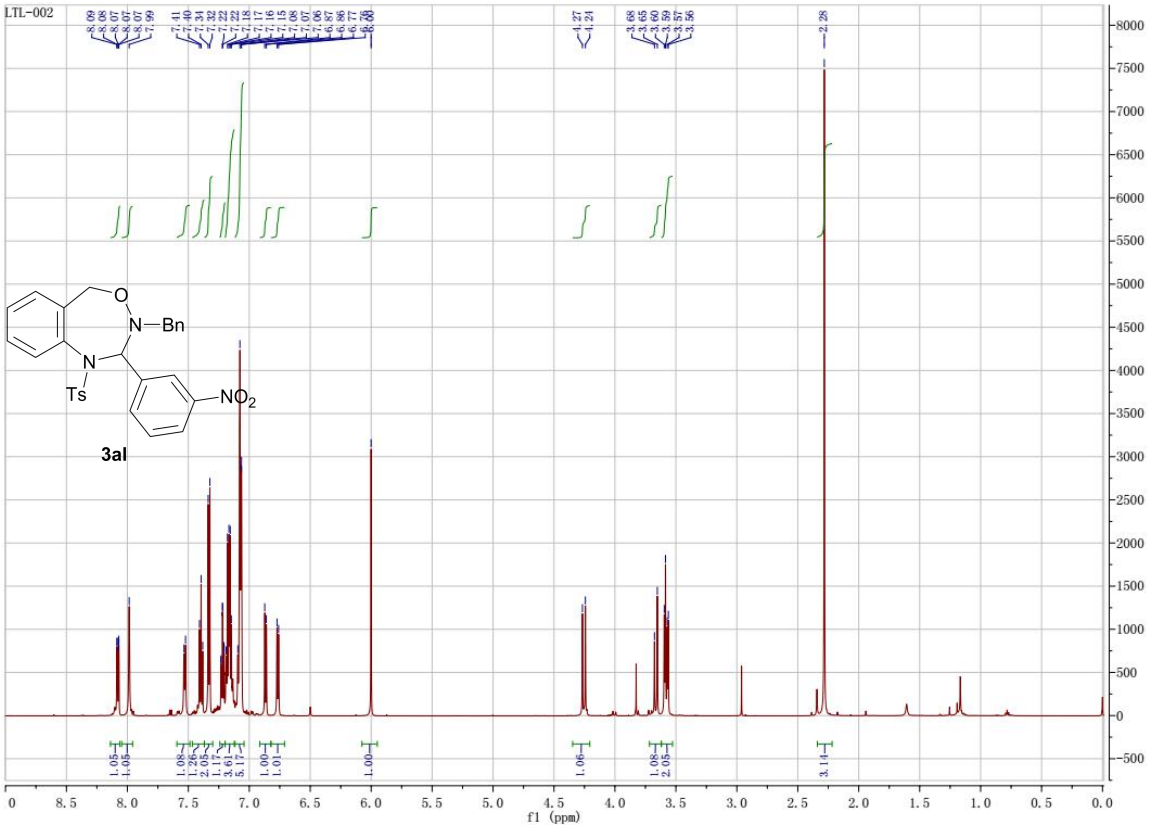


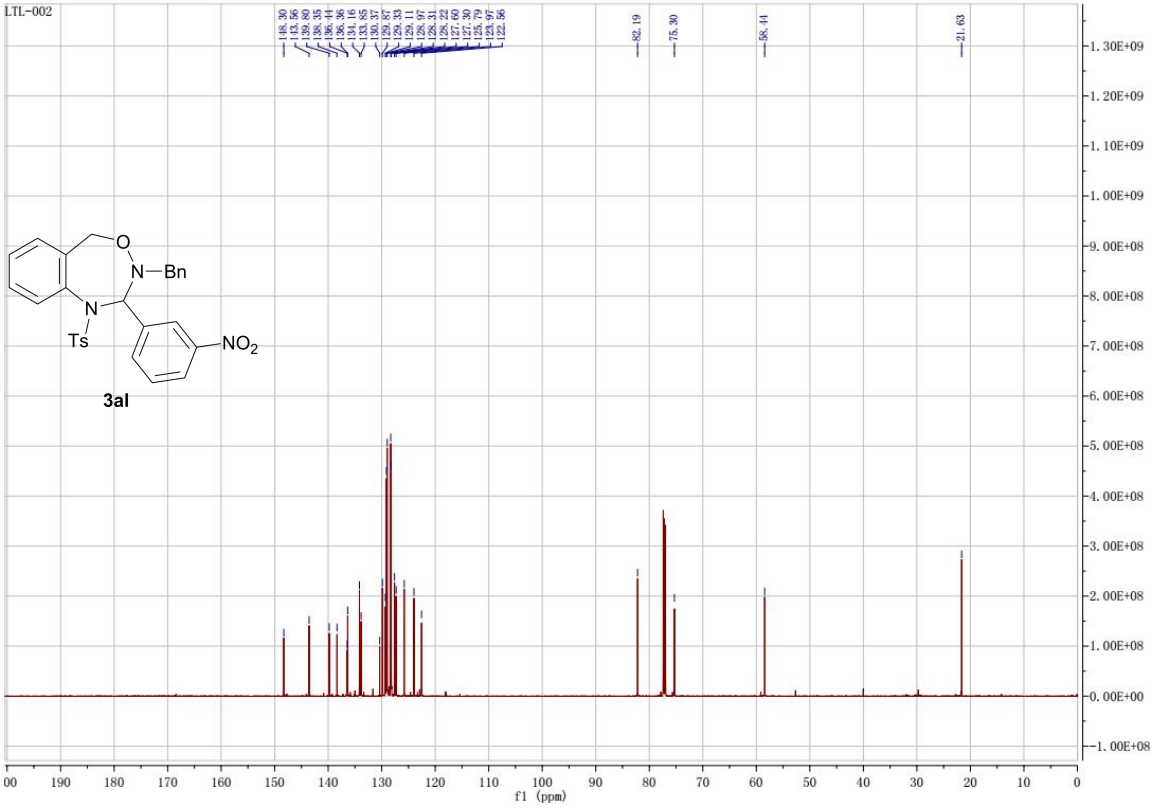
^{1}H NMR (600 MHz, $CDCl_3$)



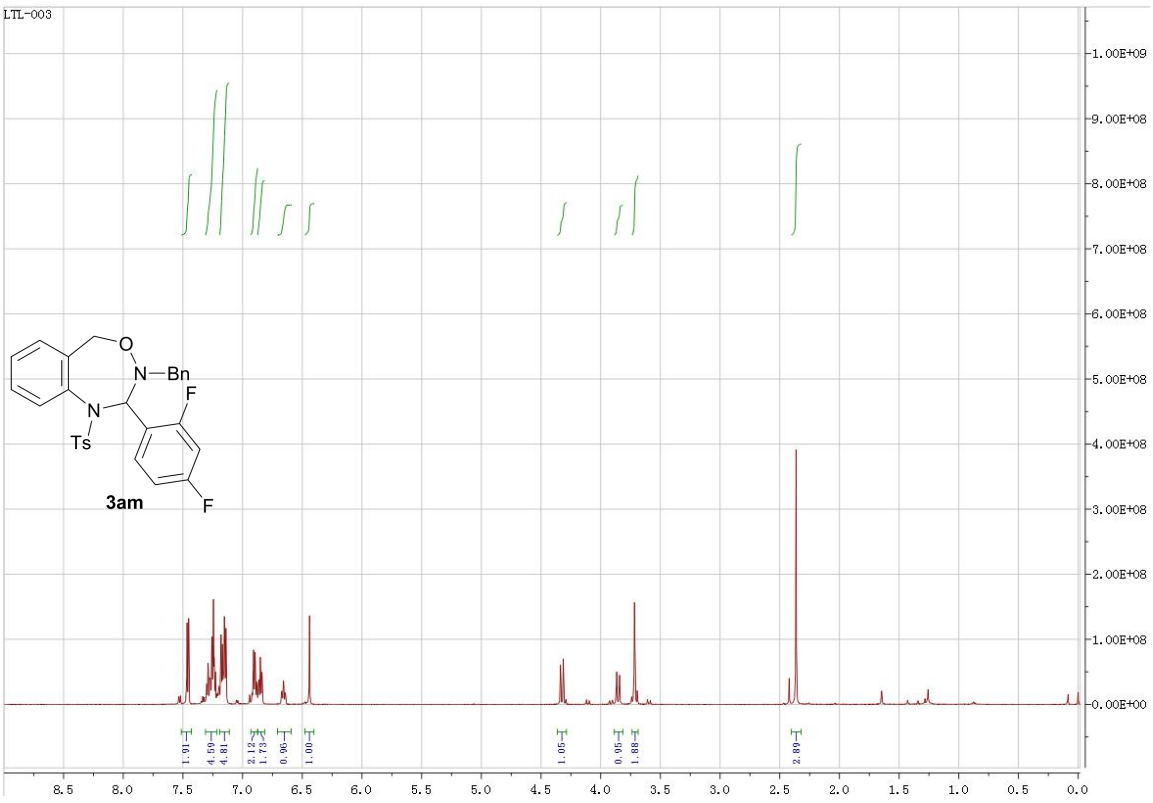
^{13}C NMR (150 MHz, $CDCl_3$)



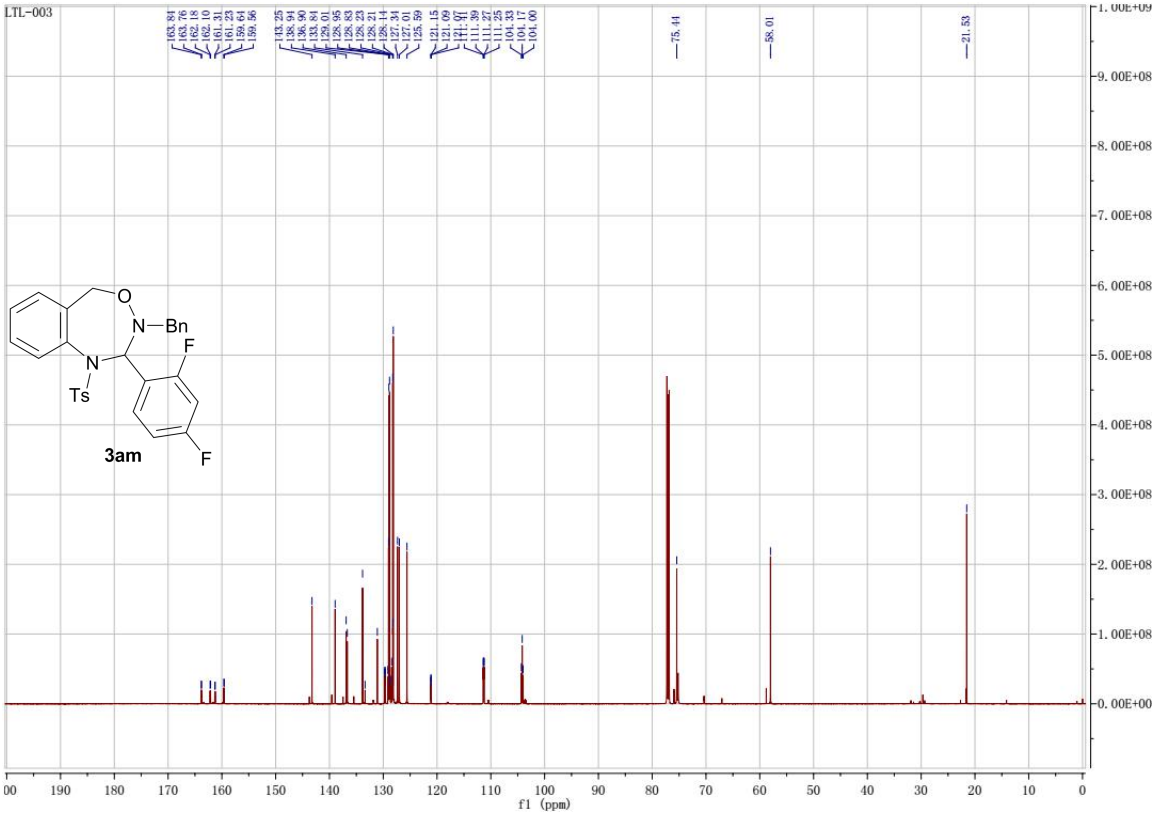
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)



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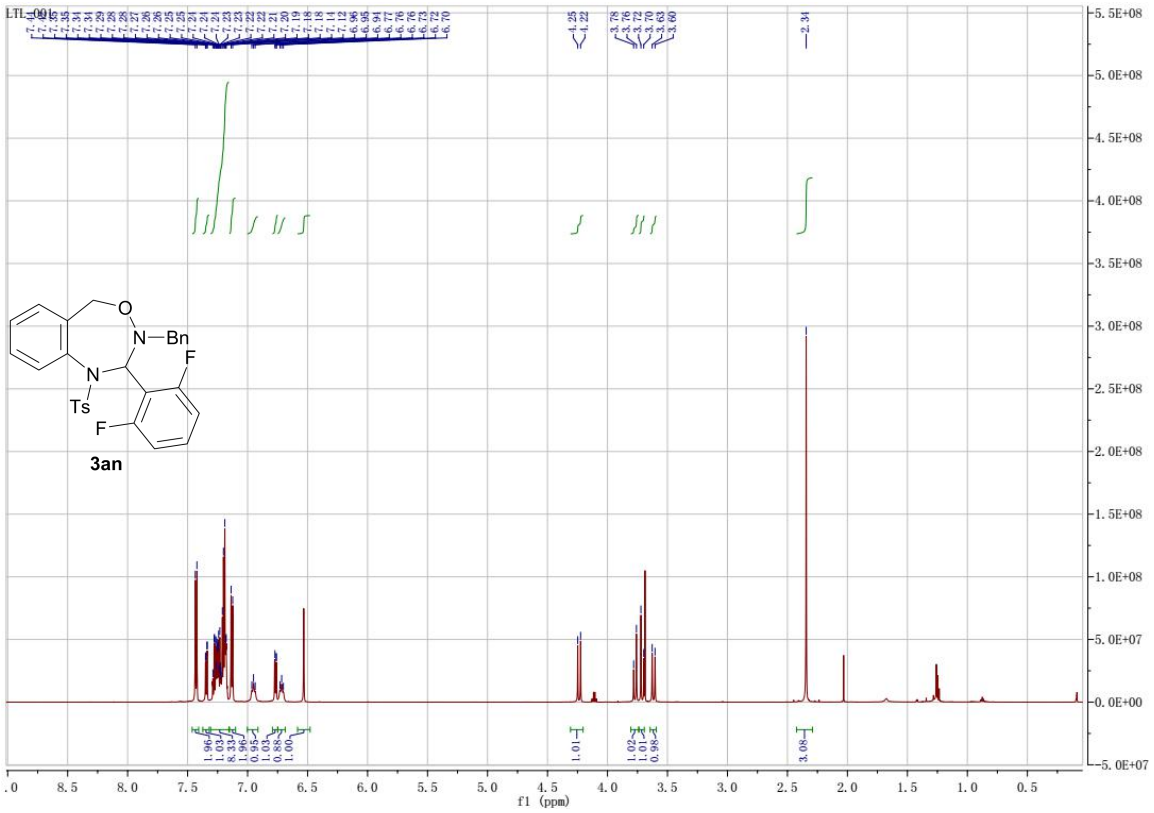

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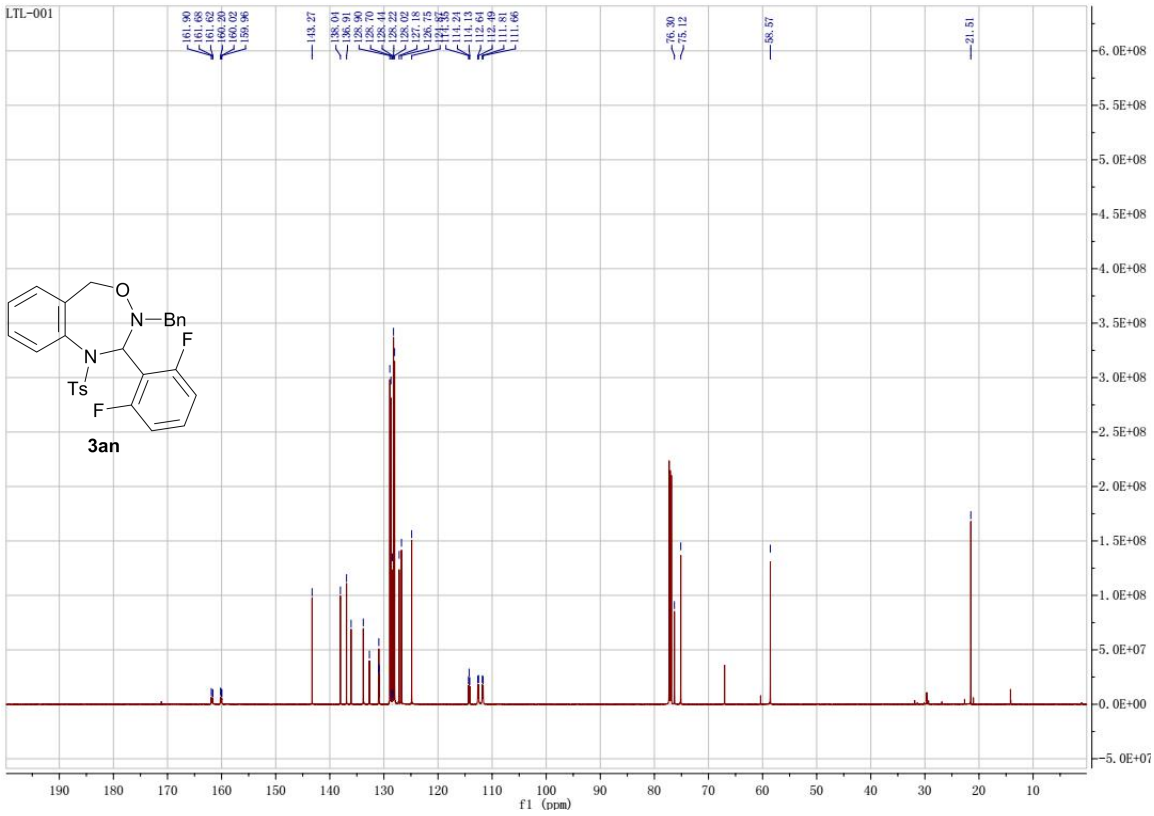

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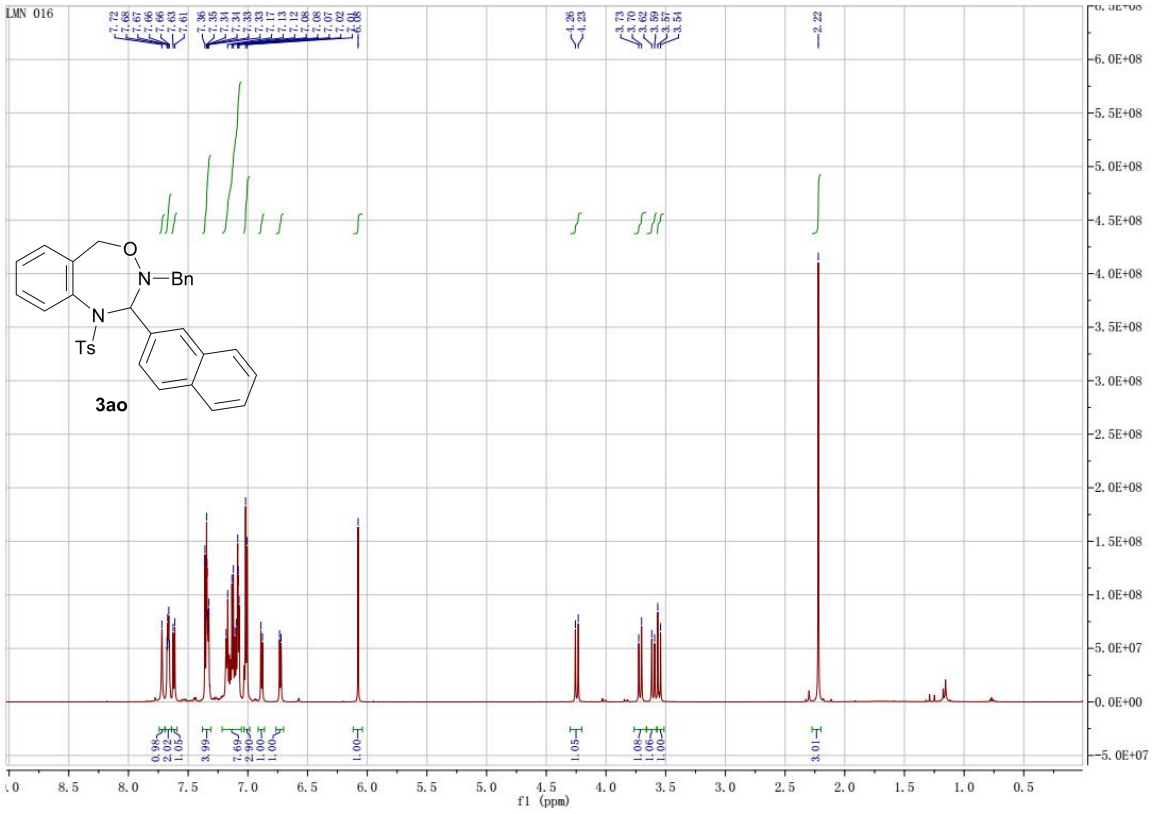

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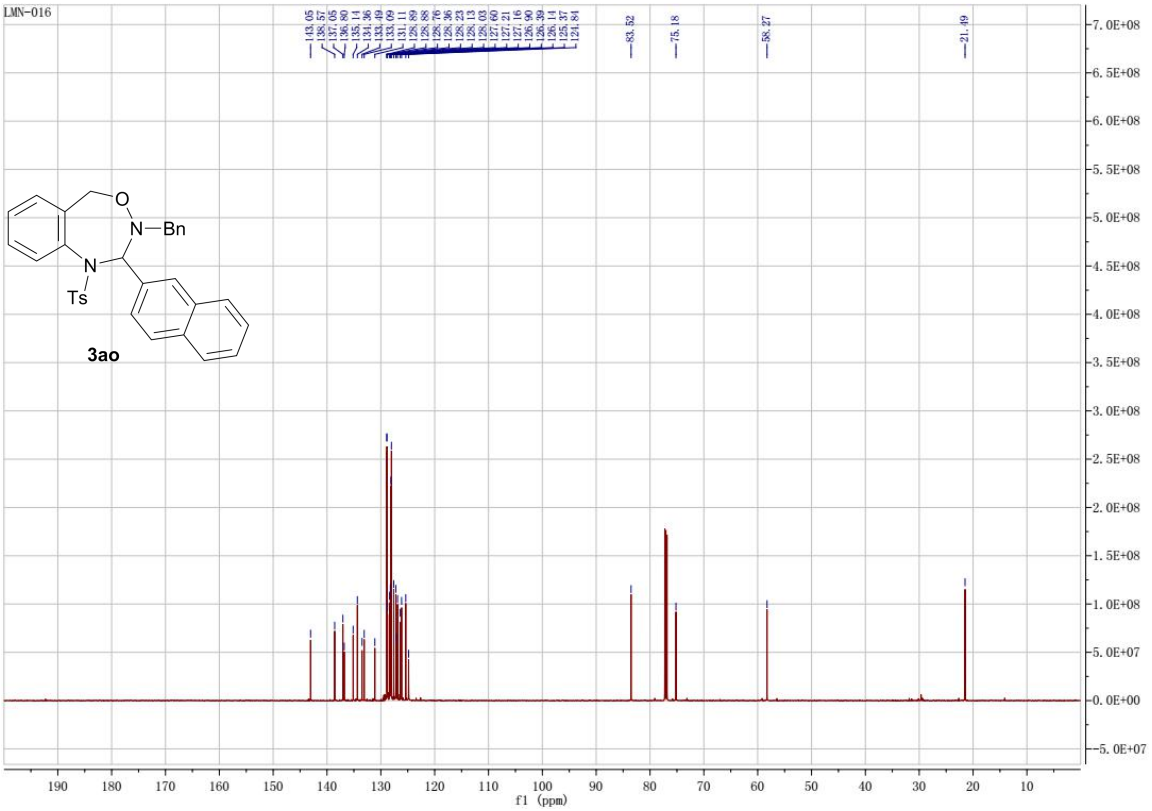

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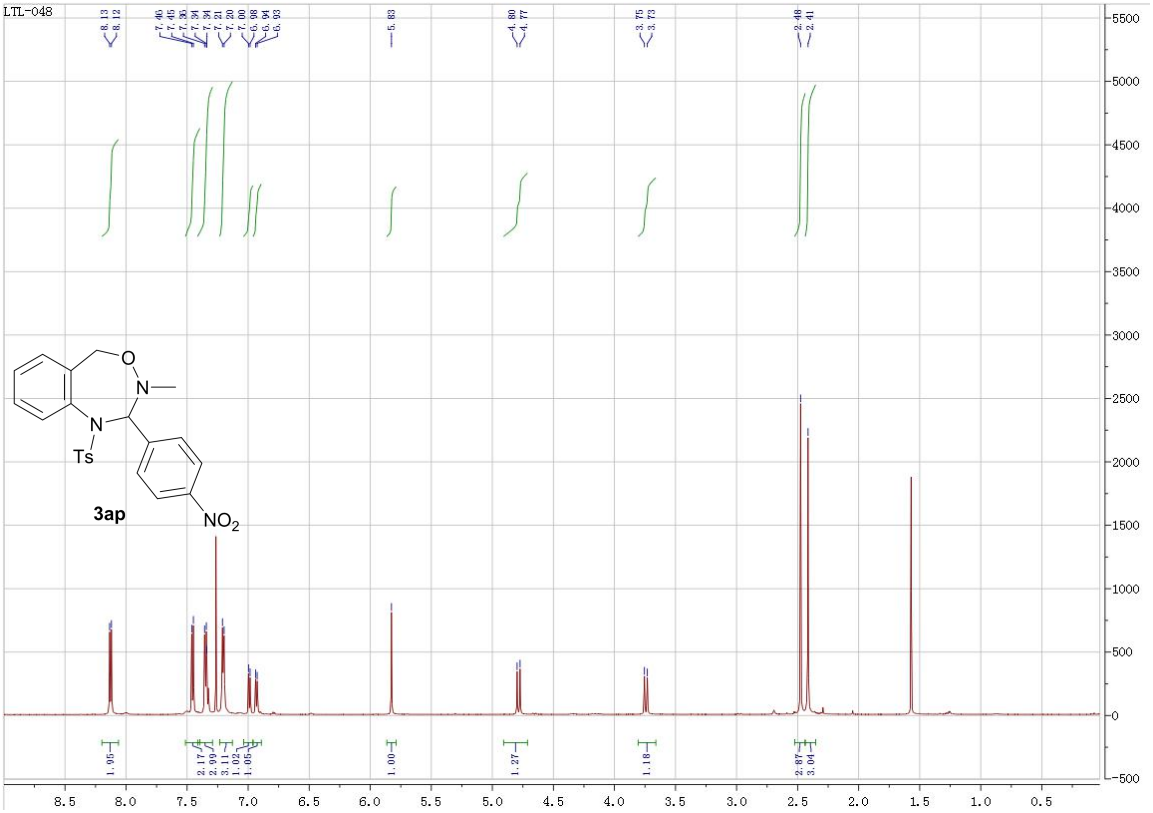

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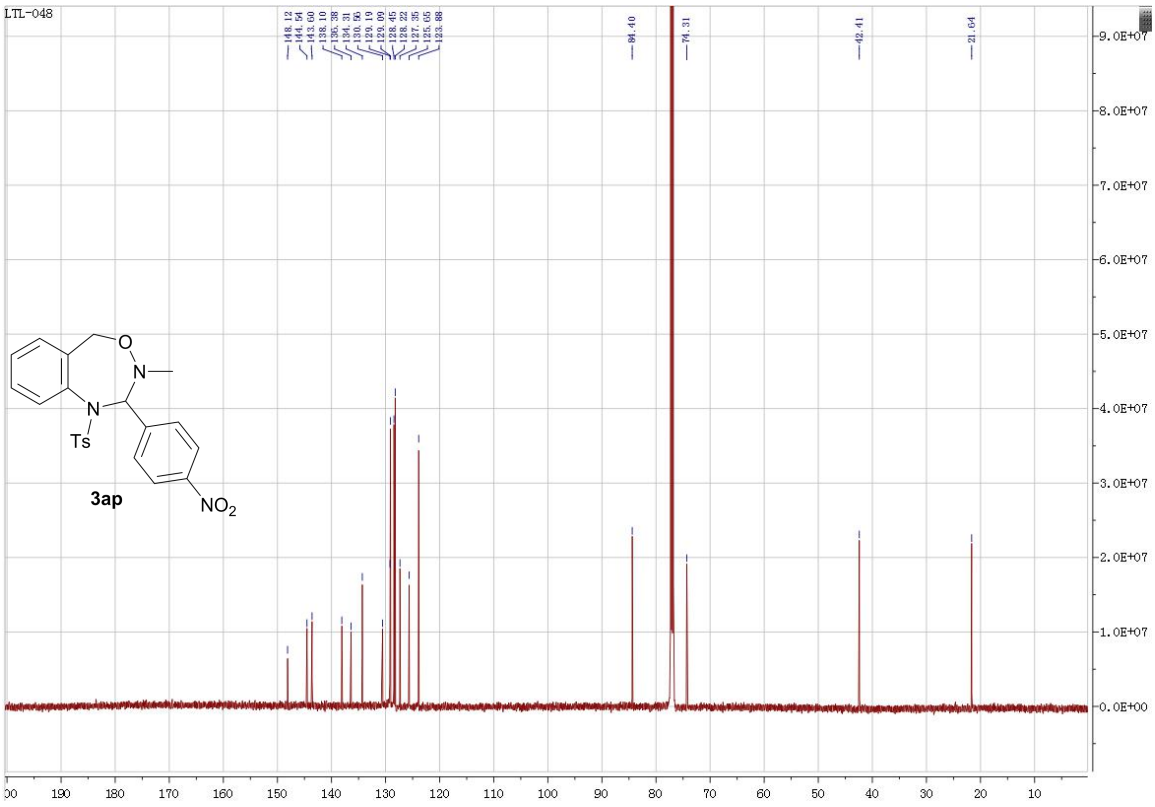

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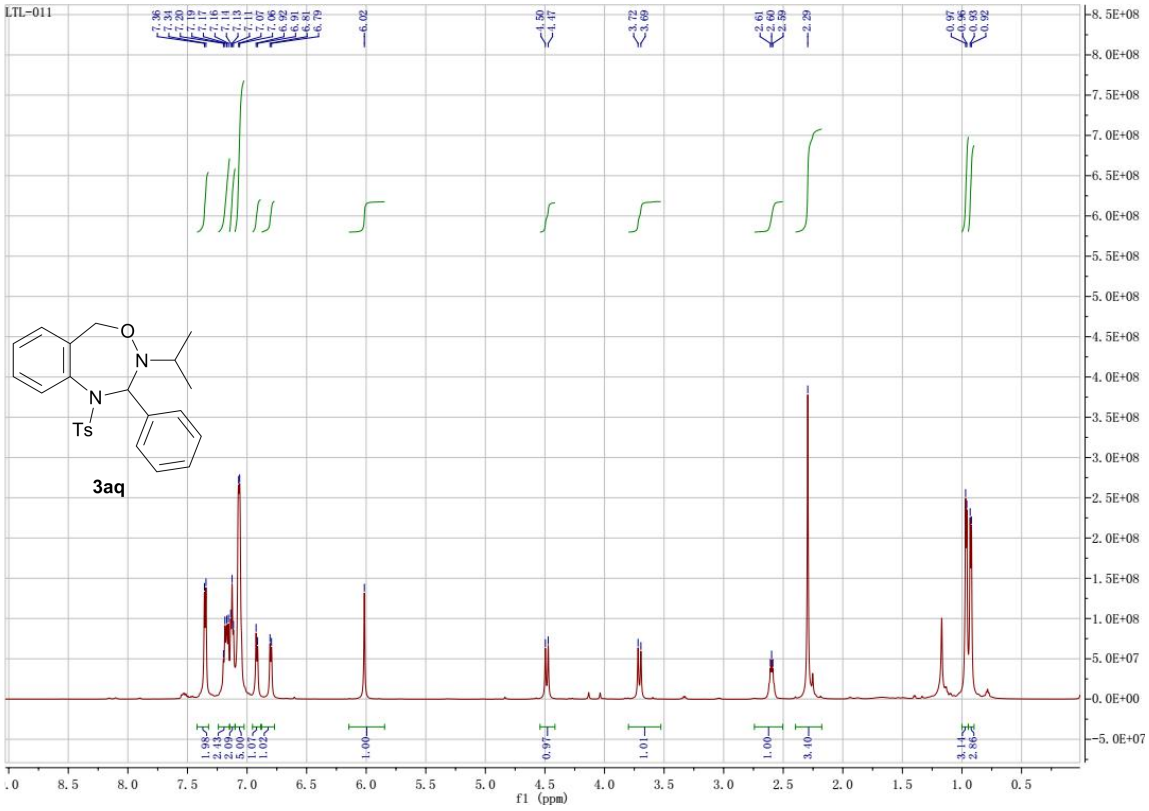

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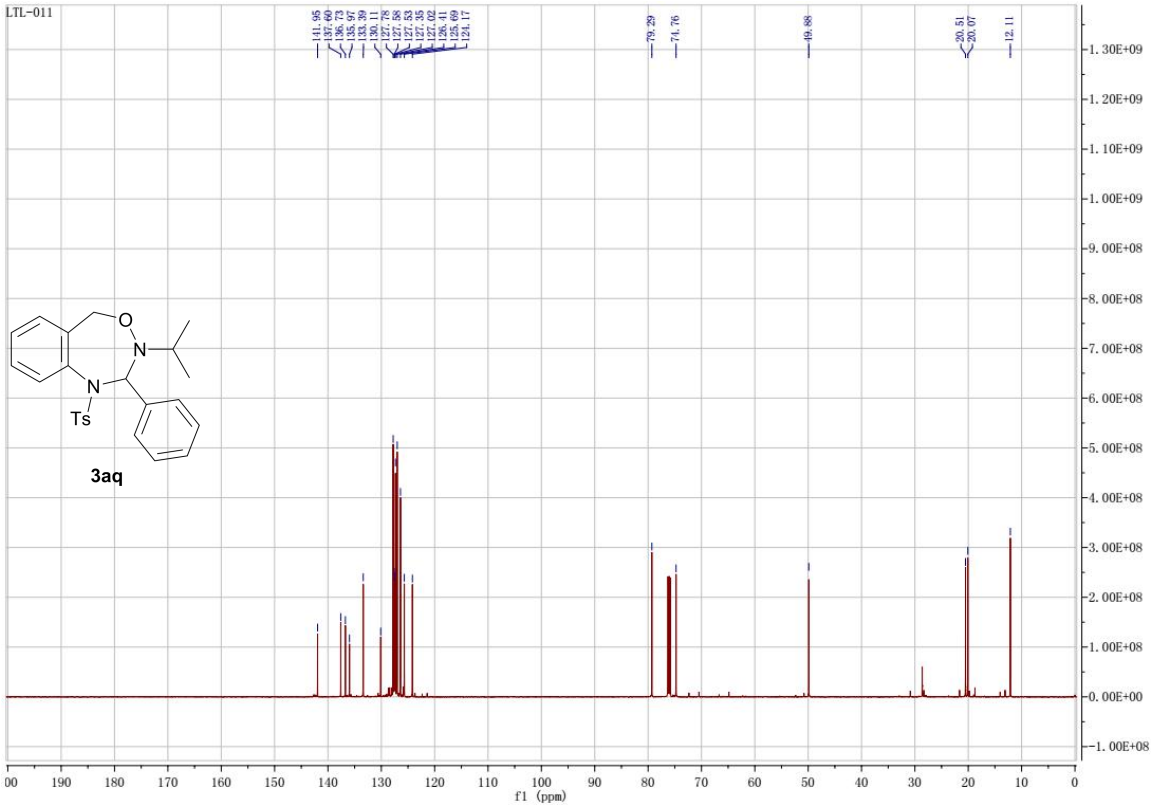

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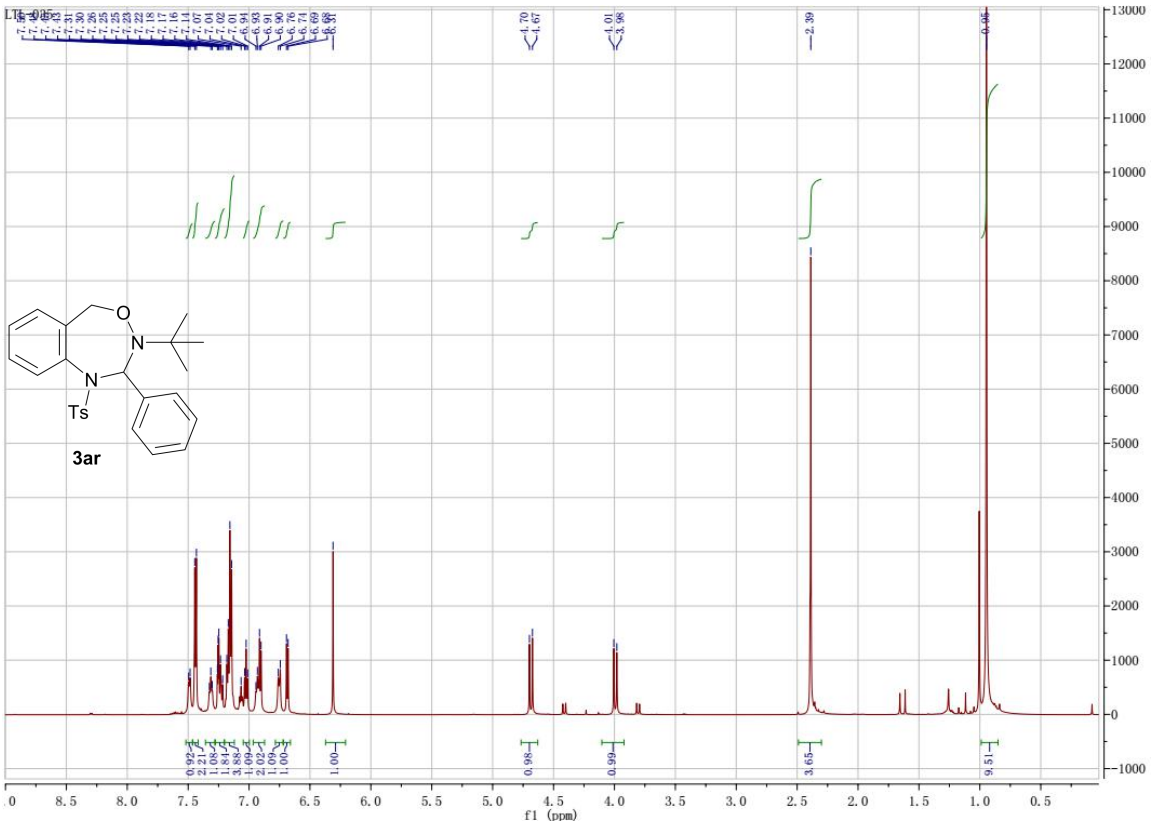

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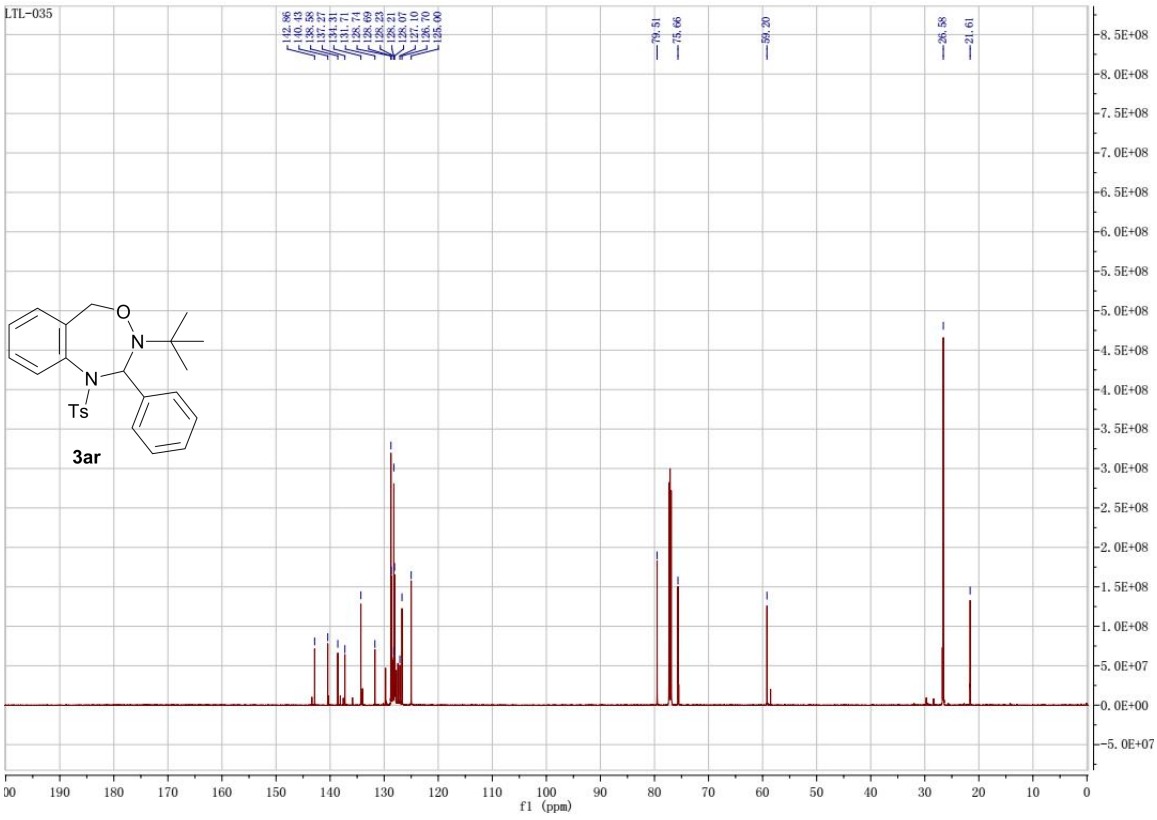

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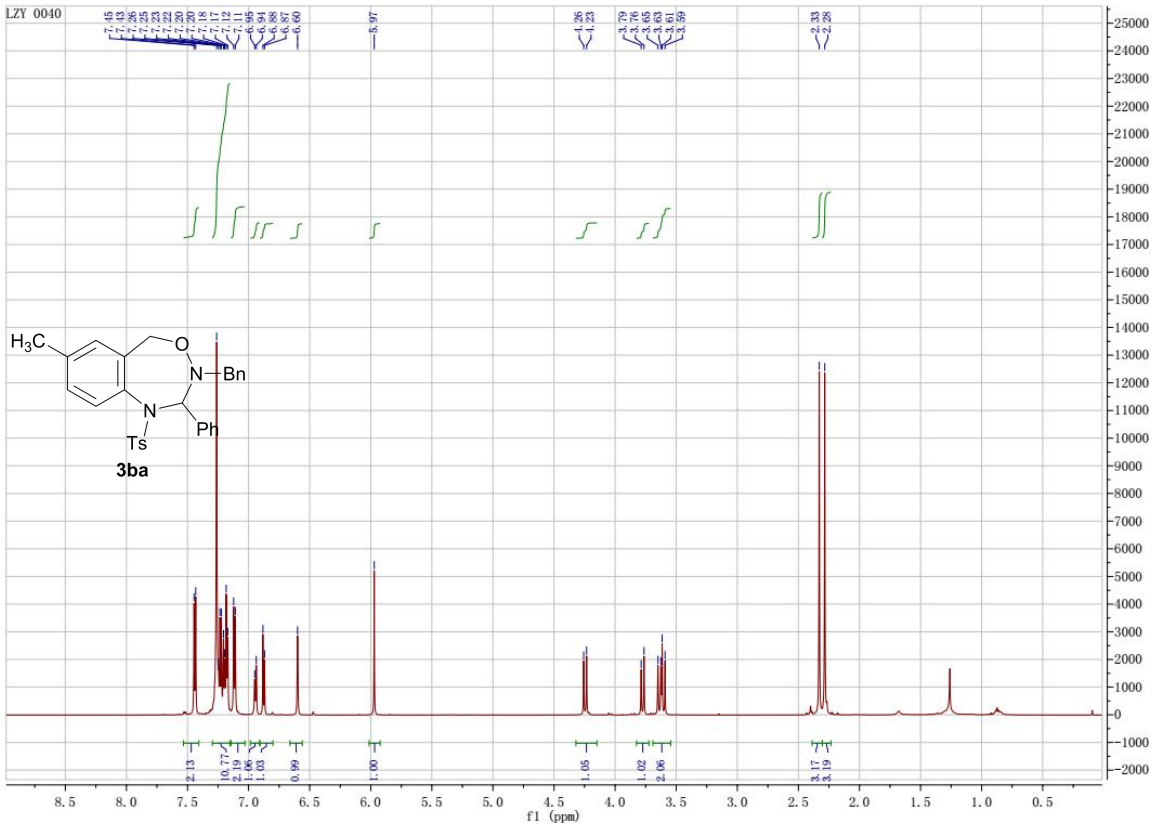

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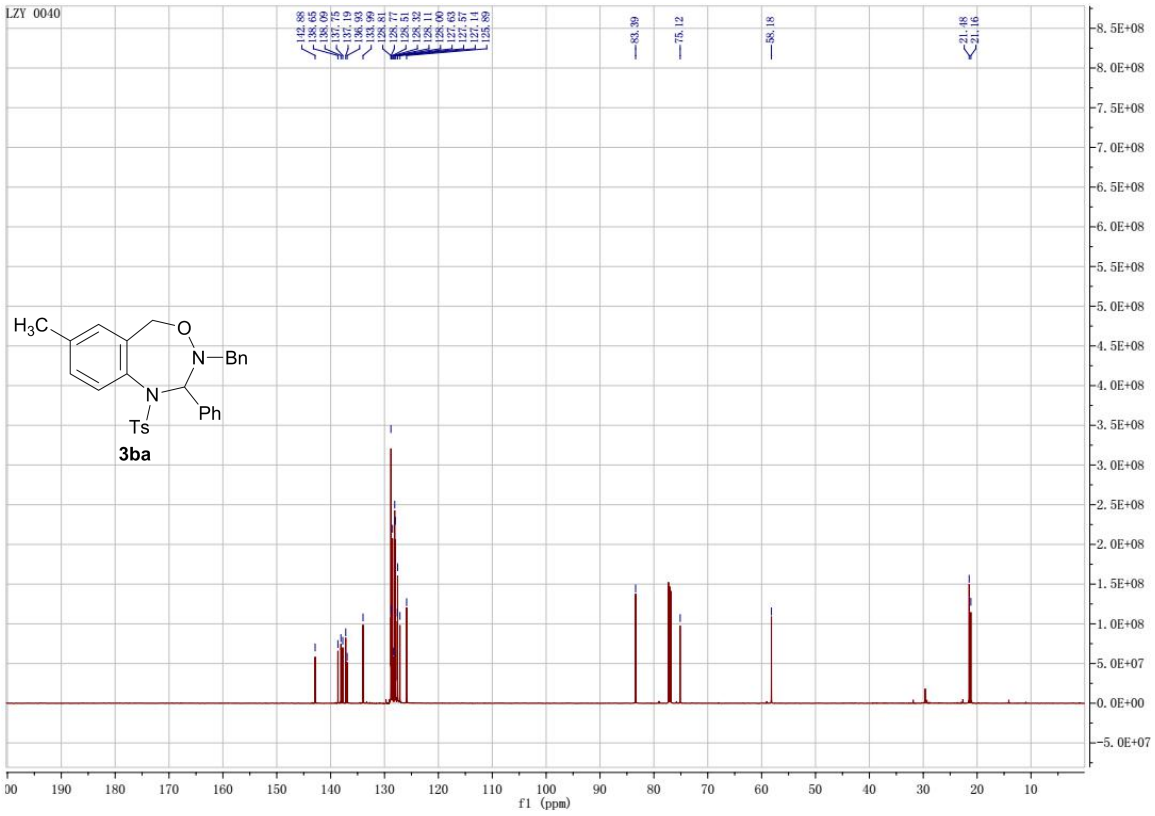

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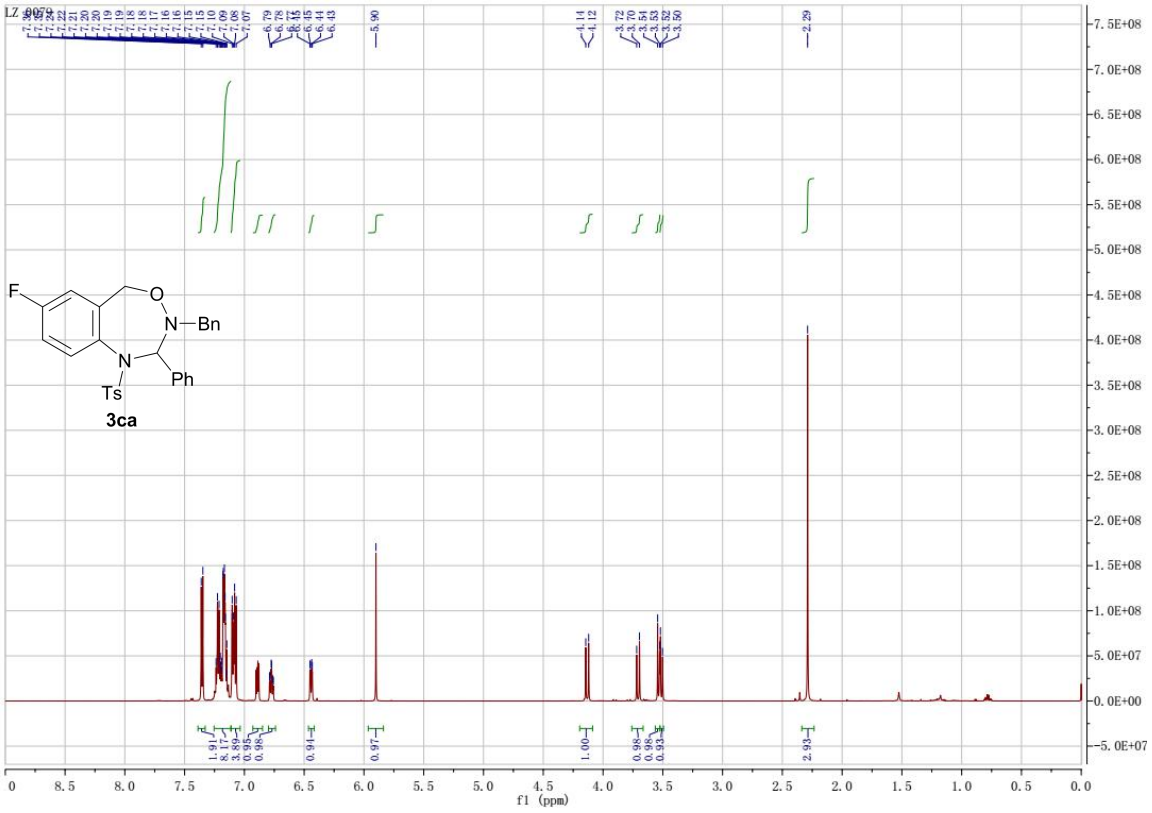

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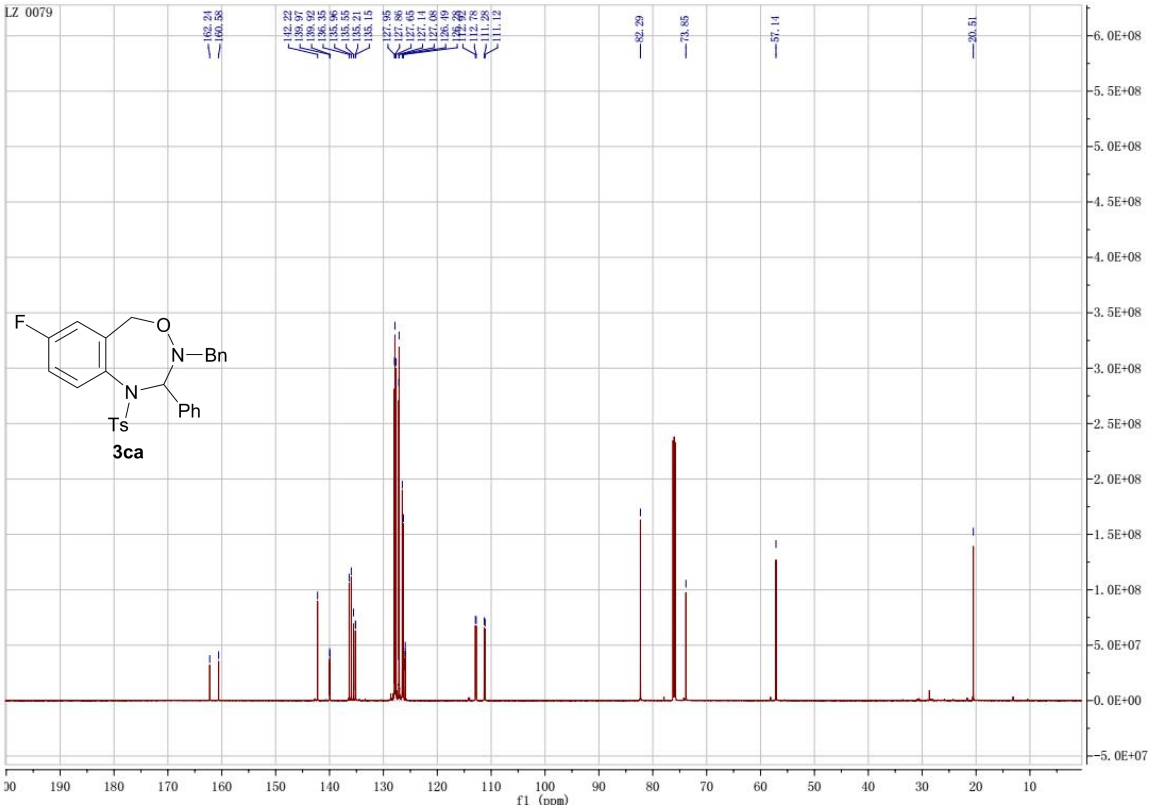

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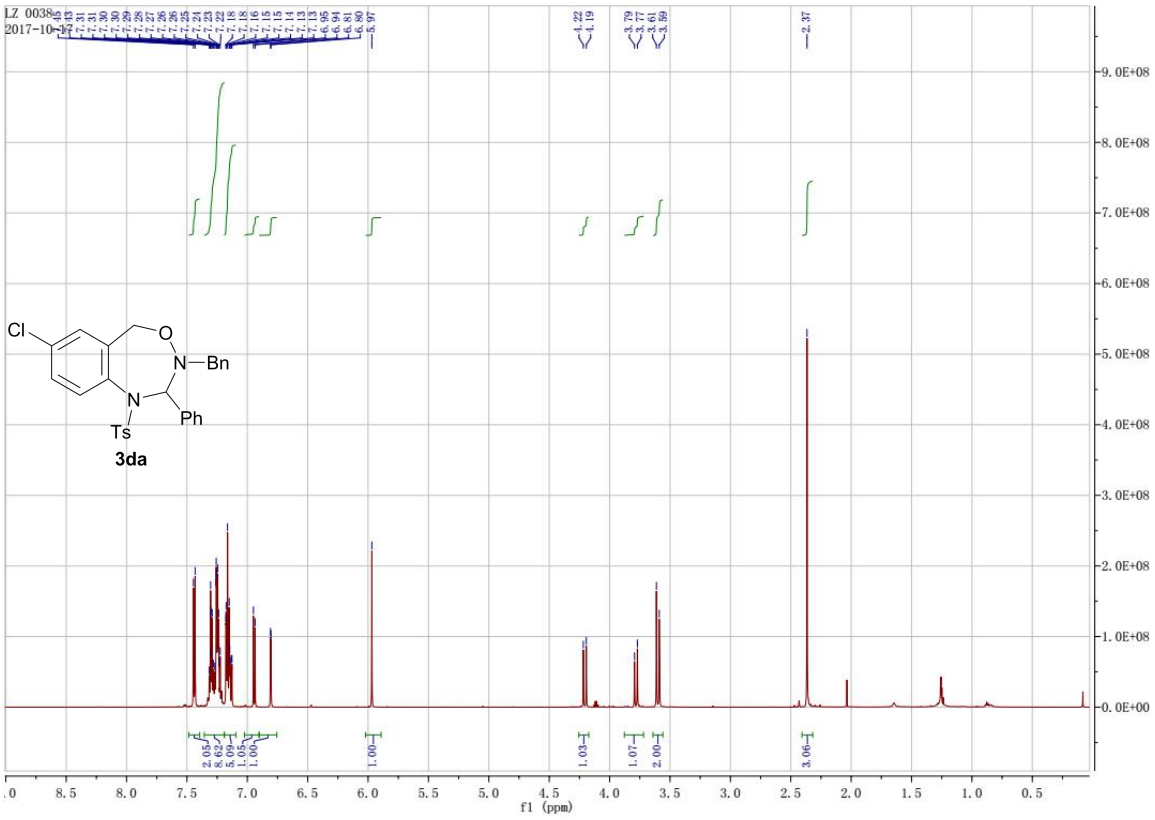

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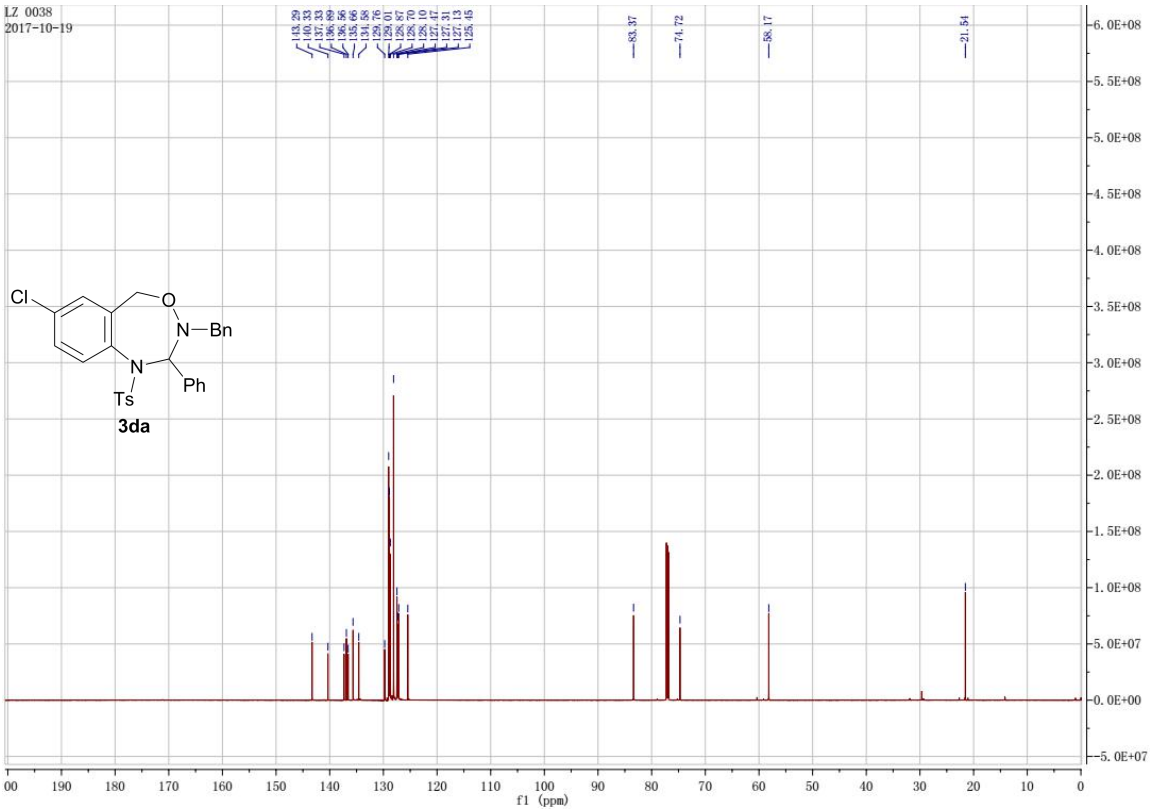

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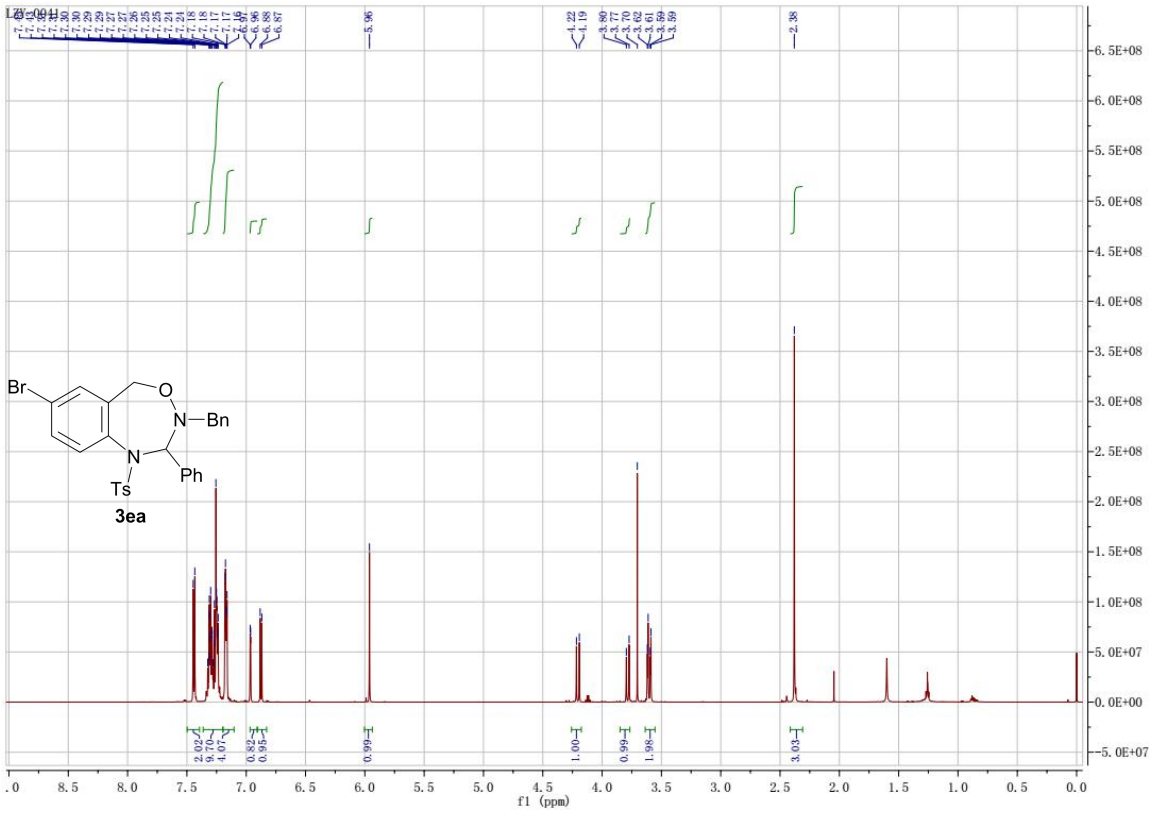

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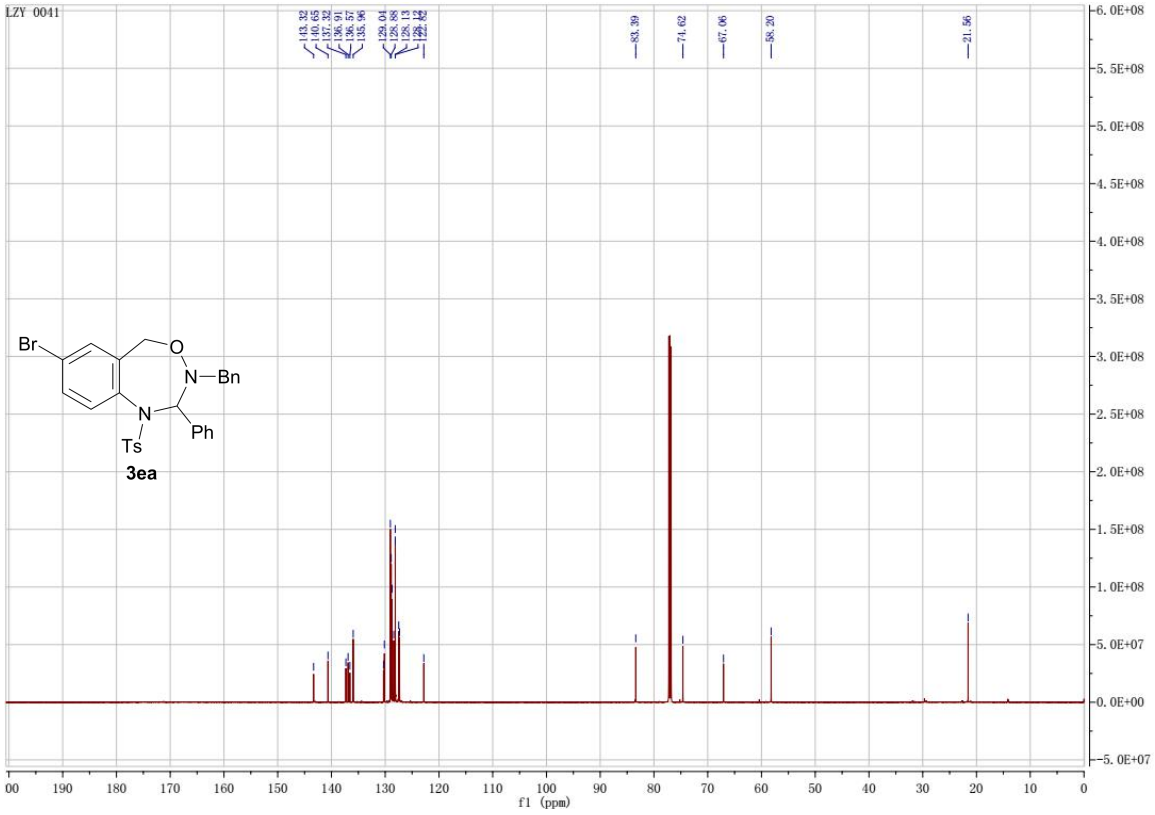

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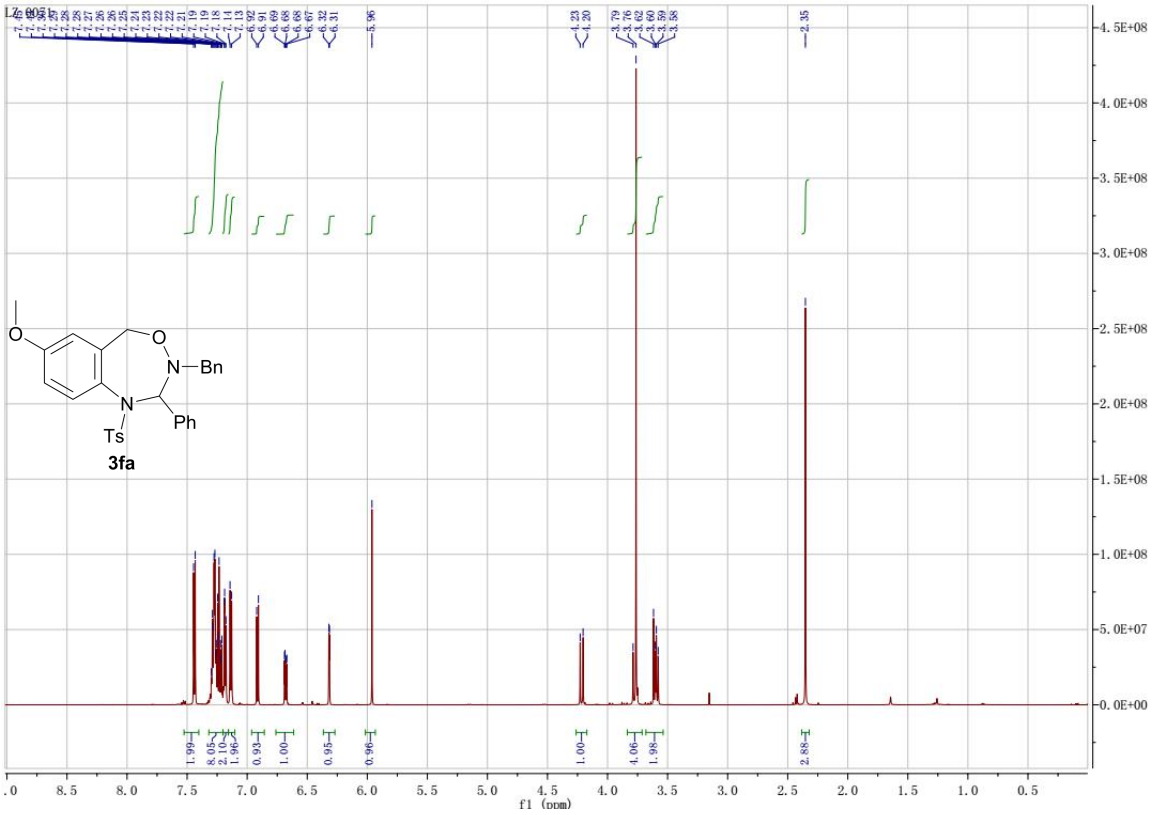

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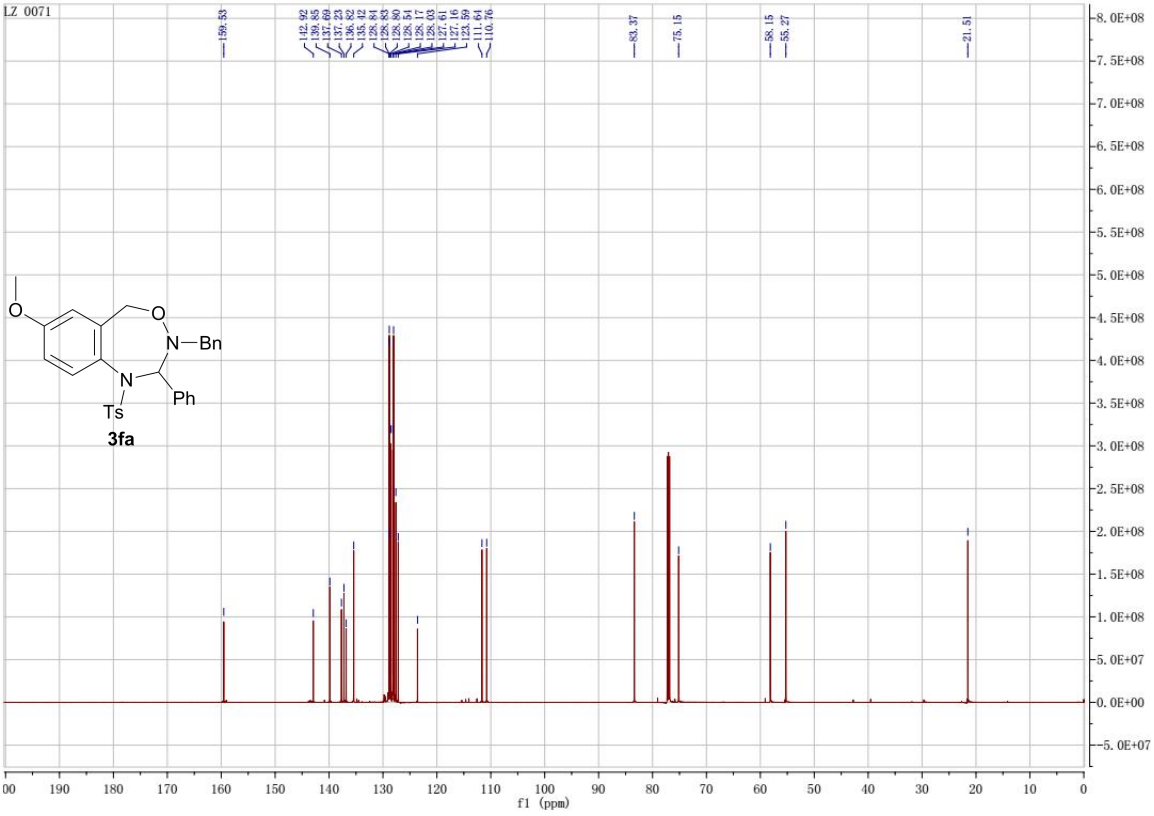

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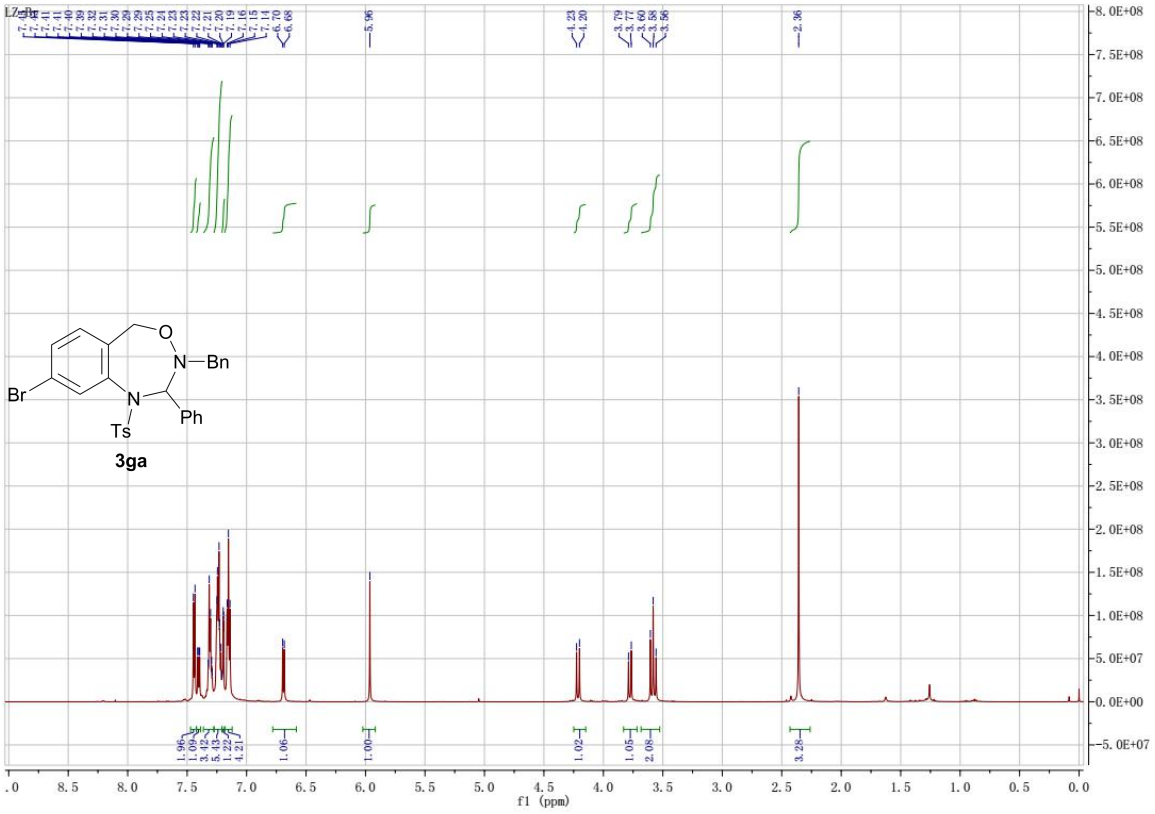

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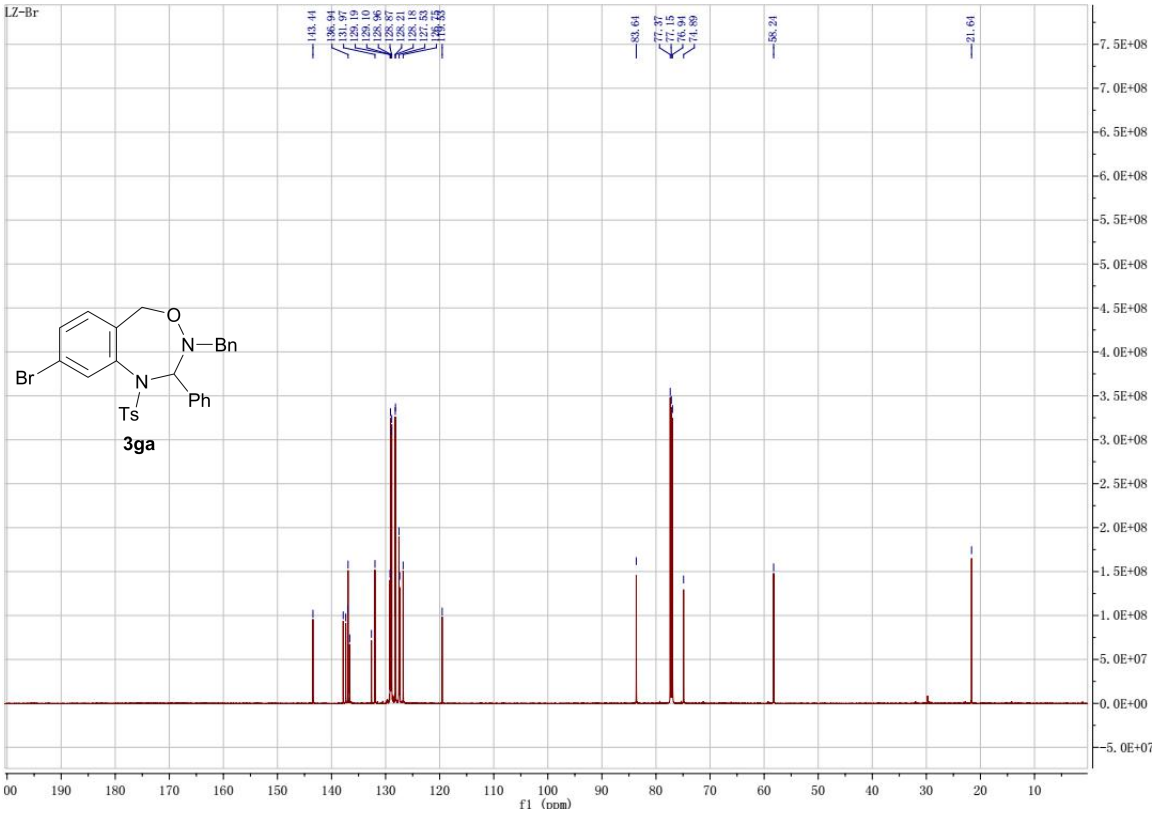

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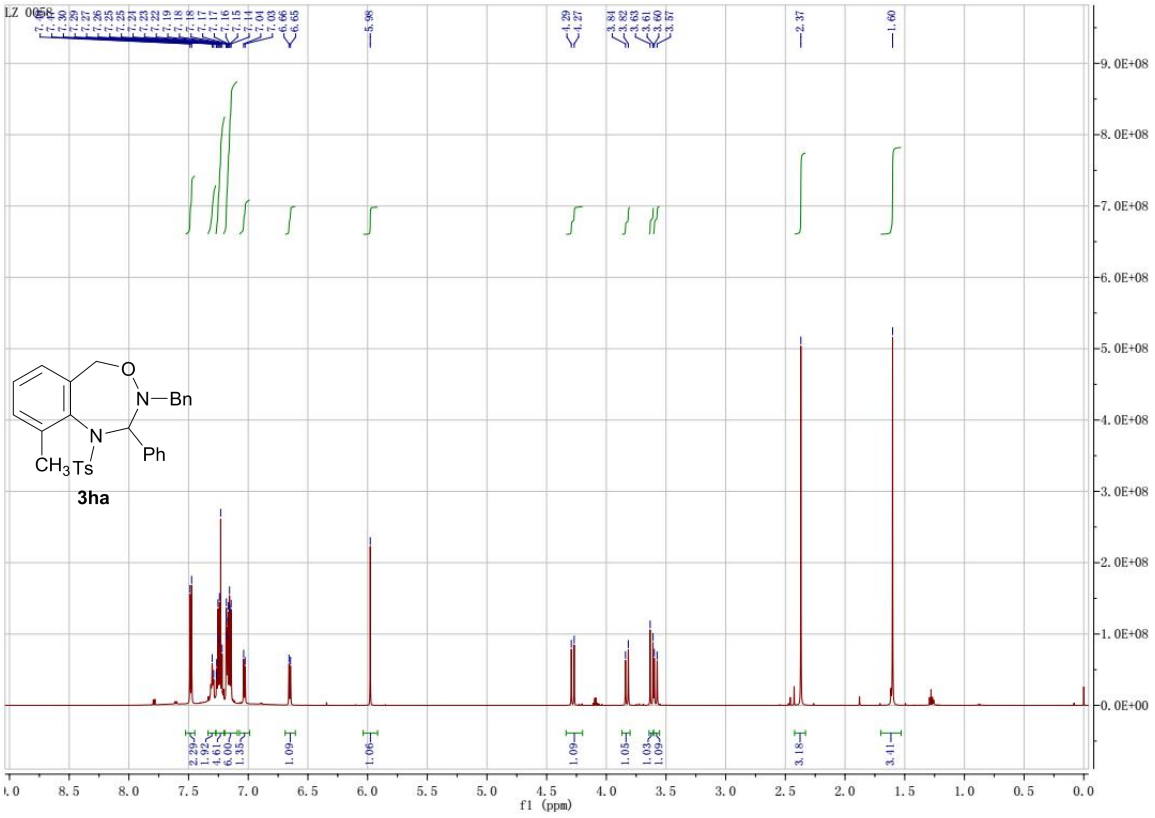

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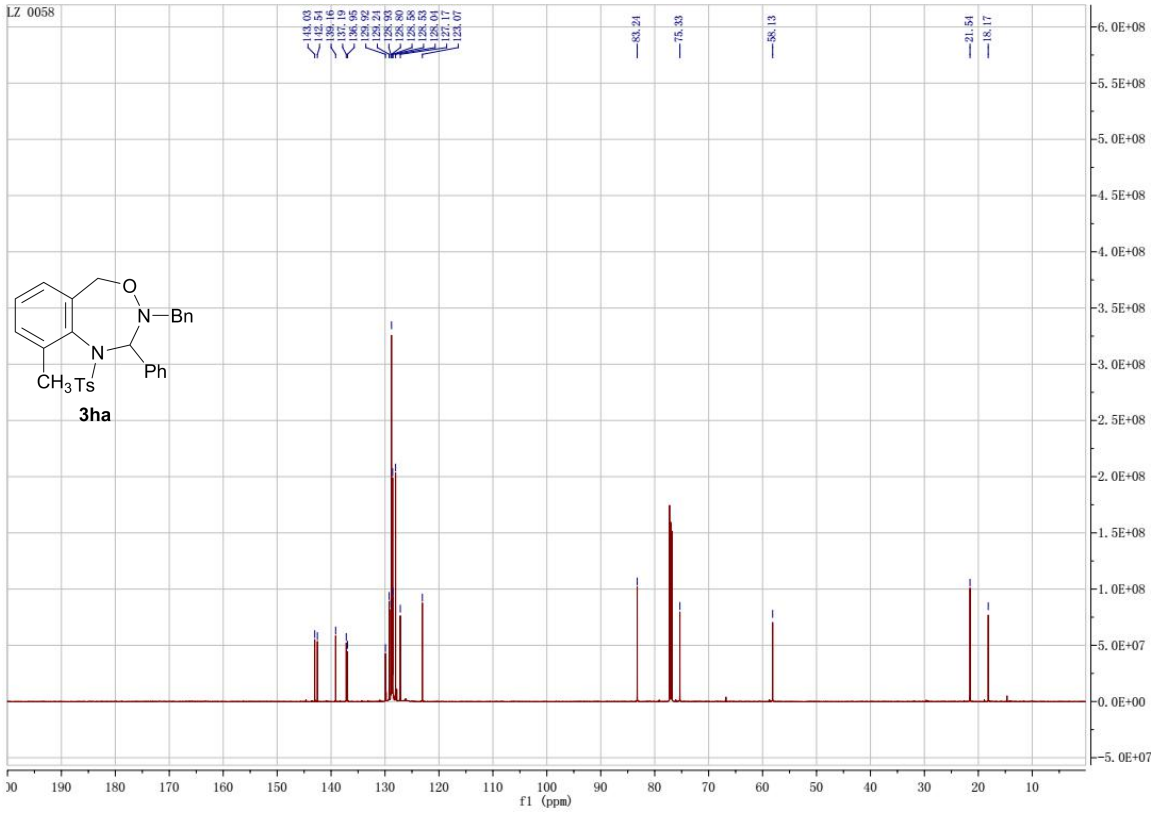

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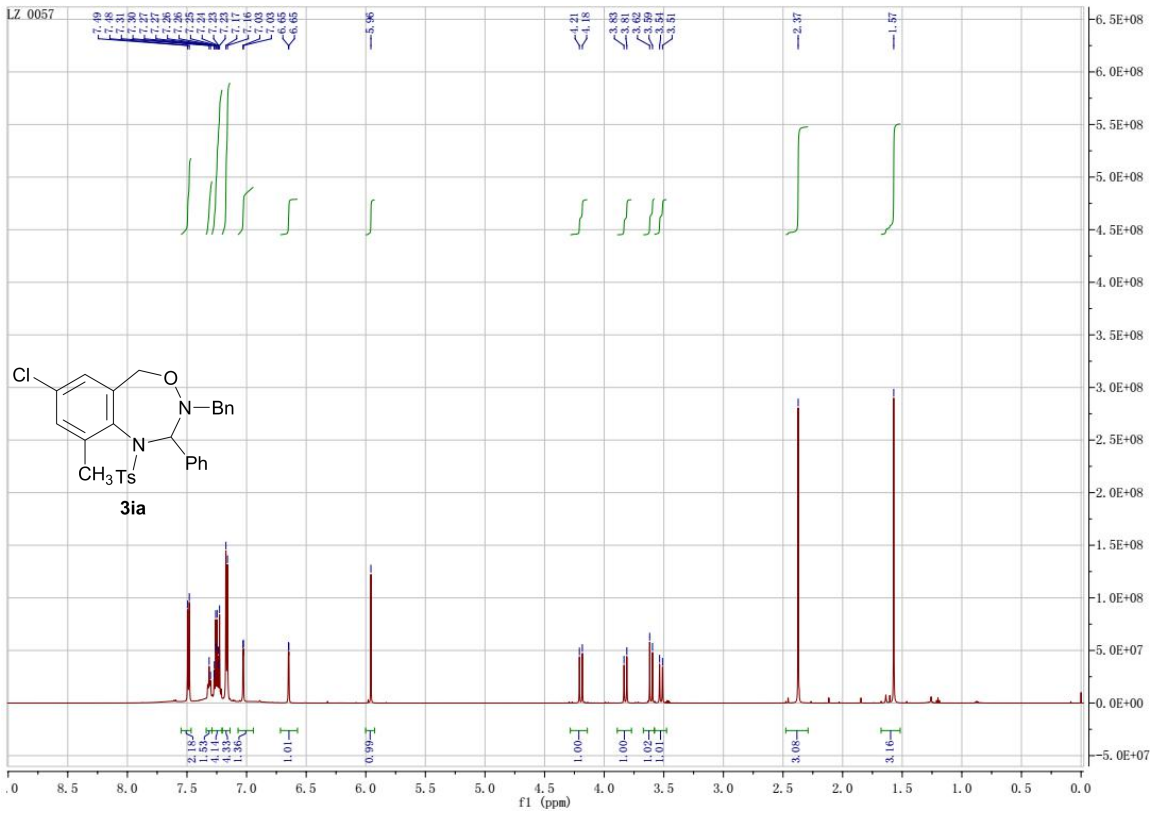

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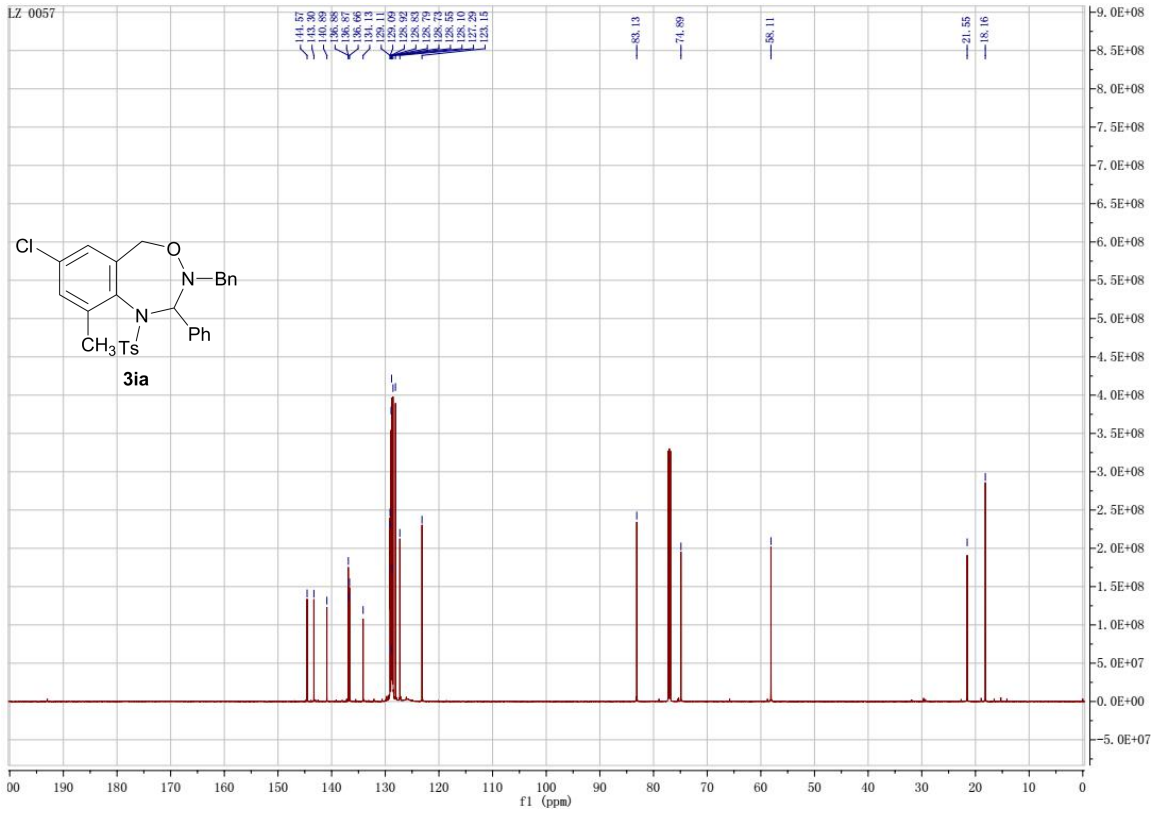

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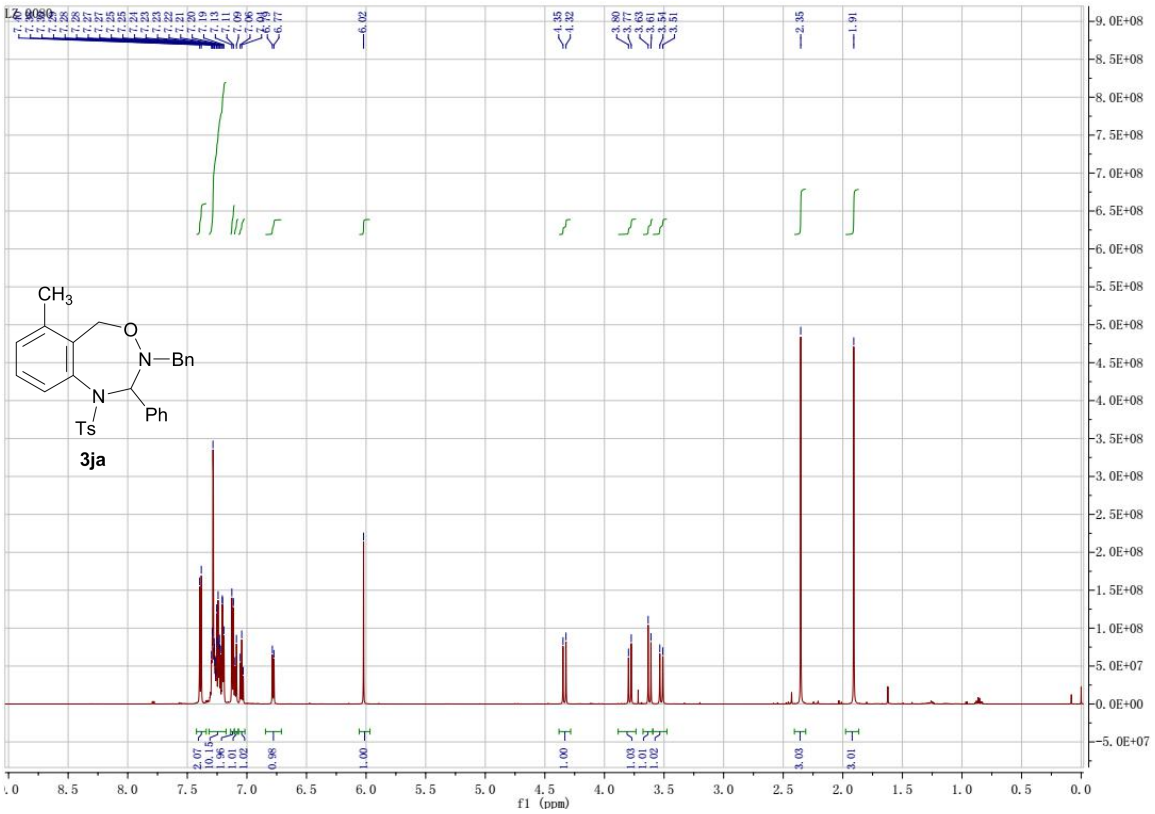

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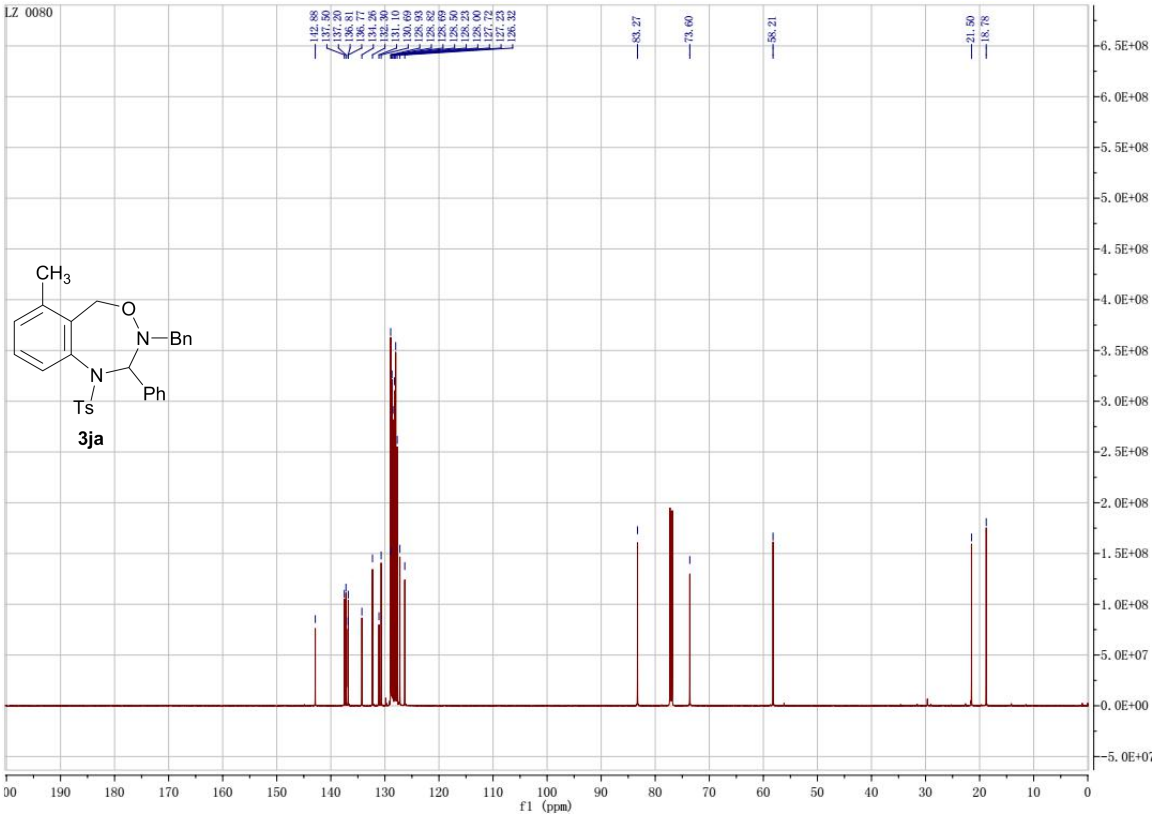

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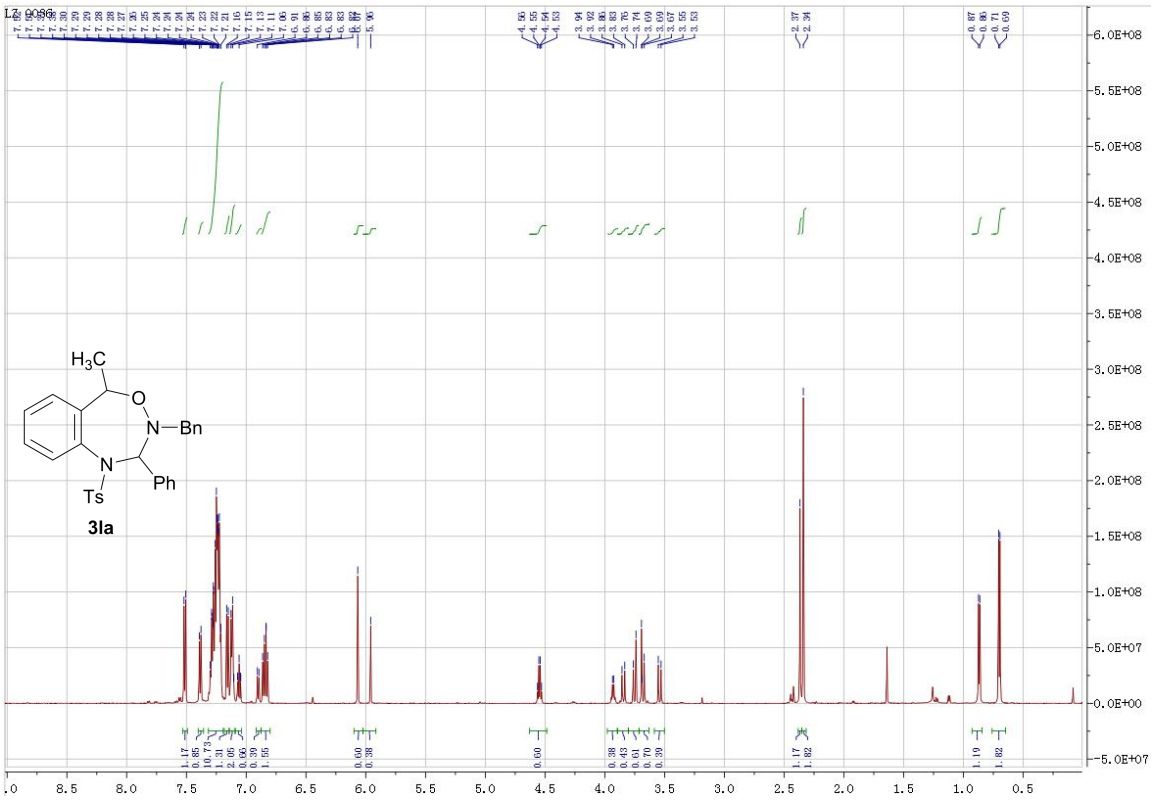

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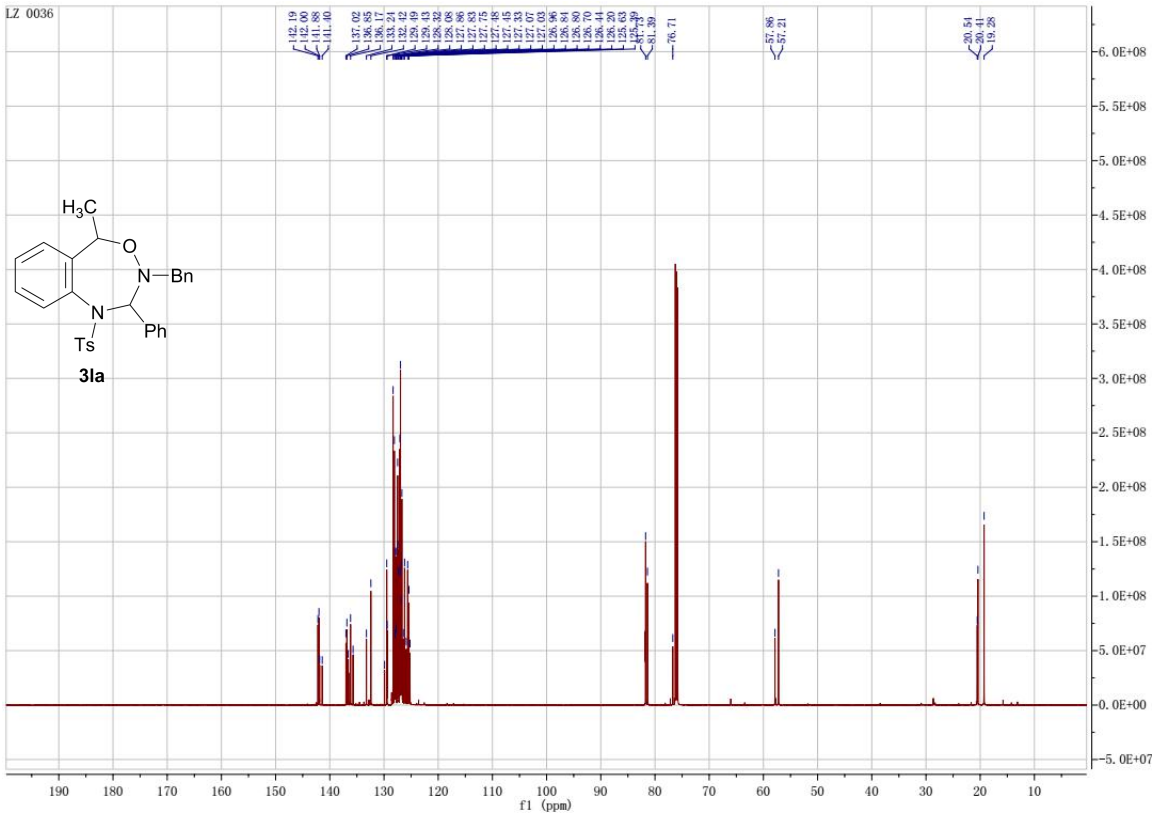

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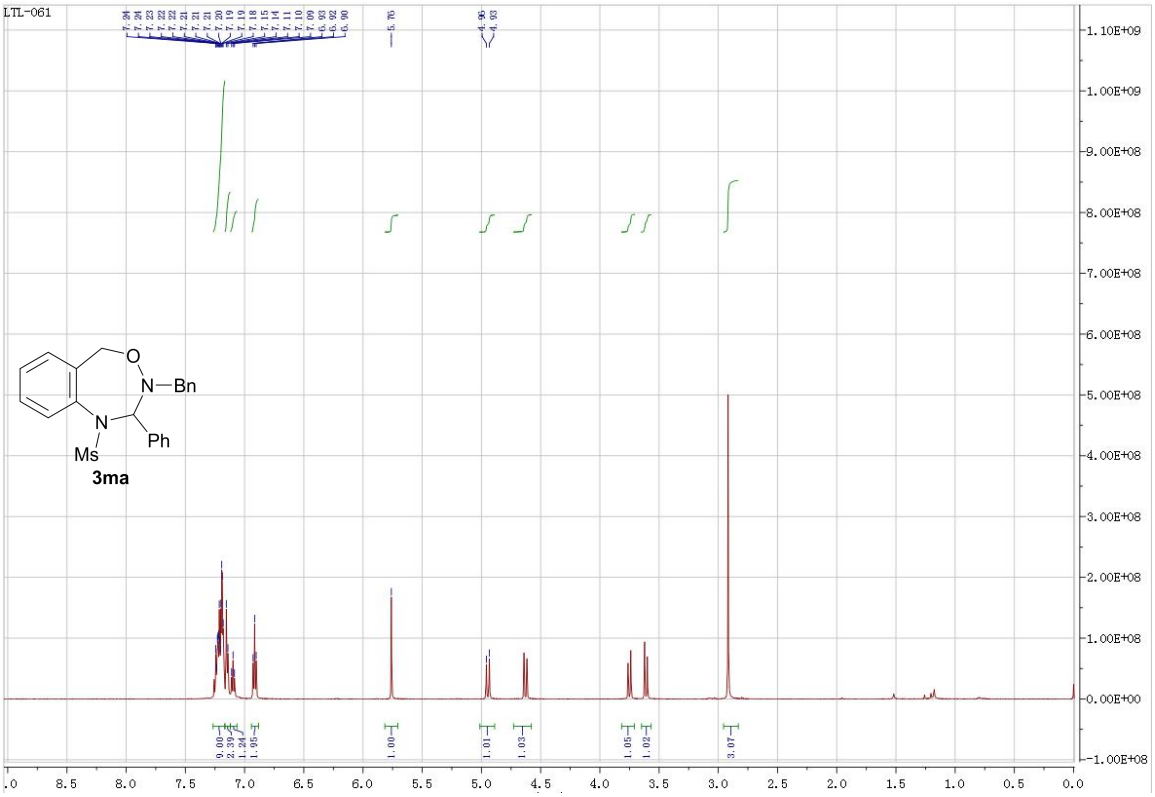

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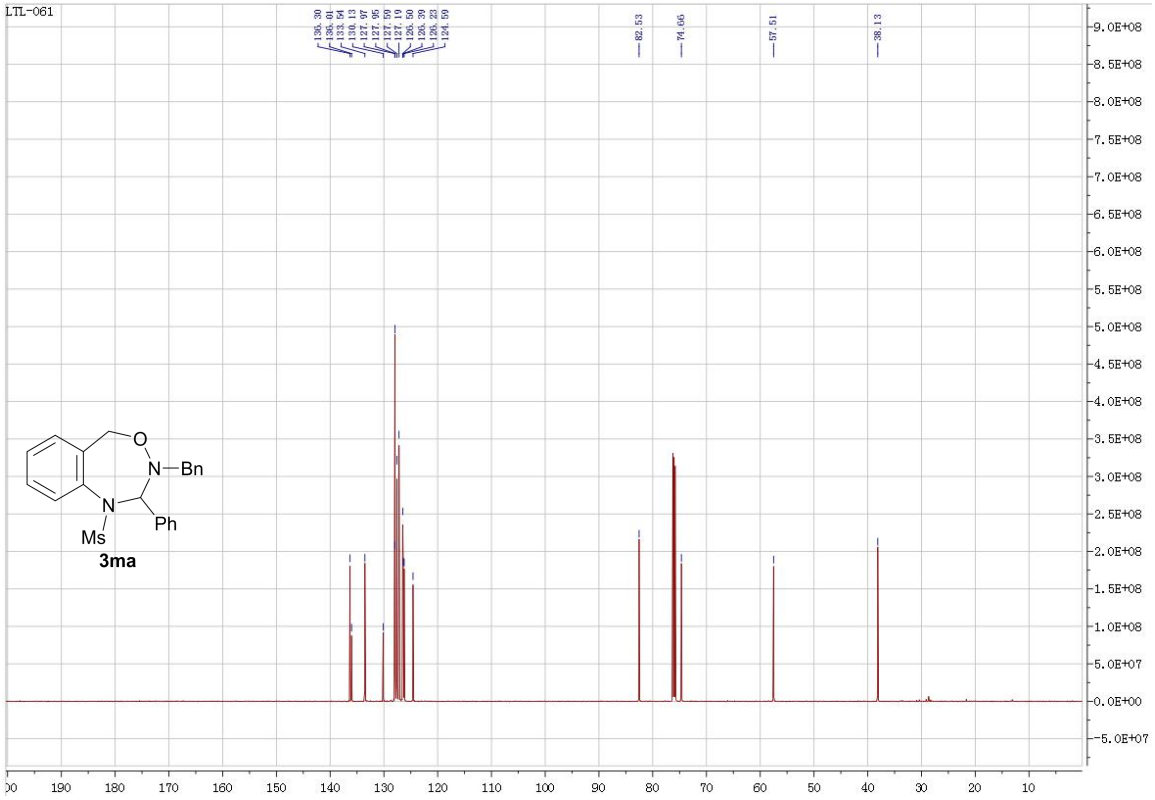

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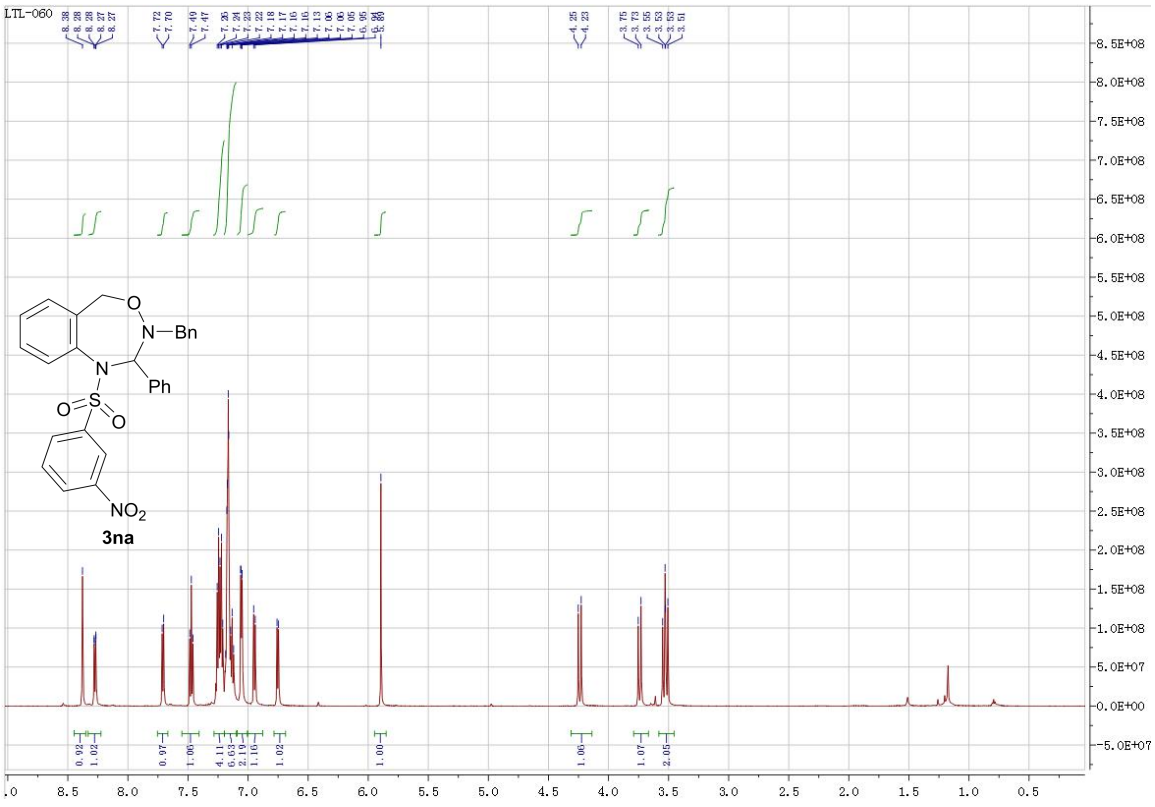

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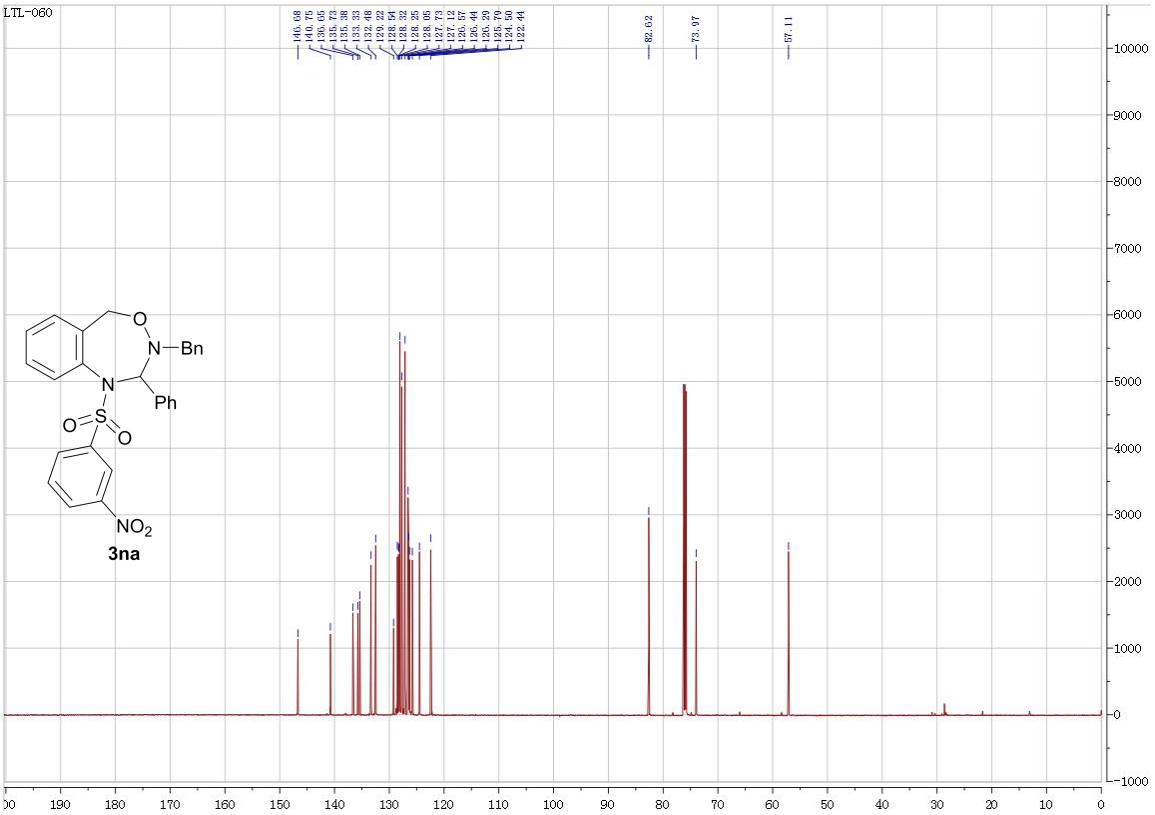

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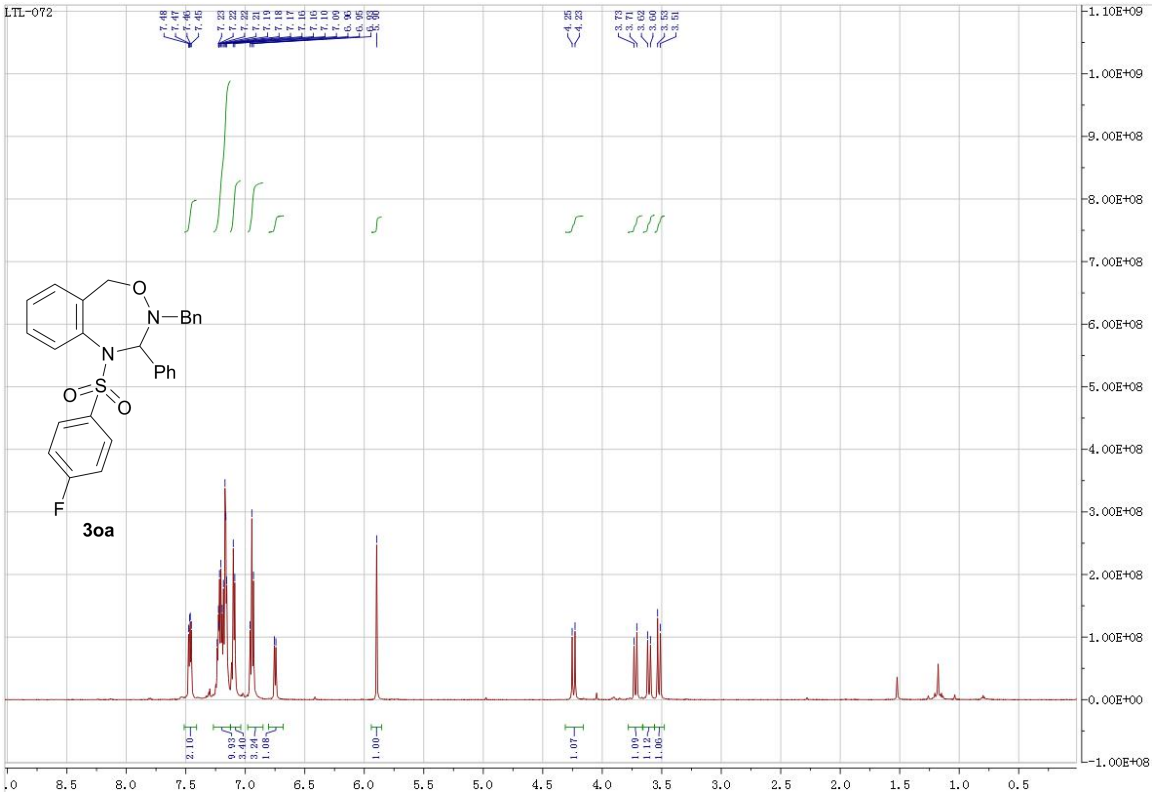

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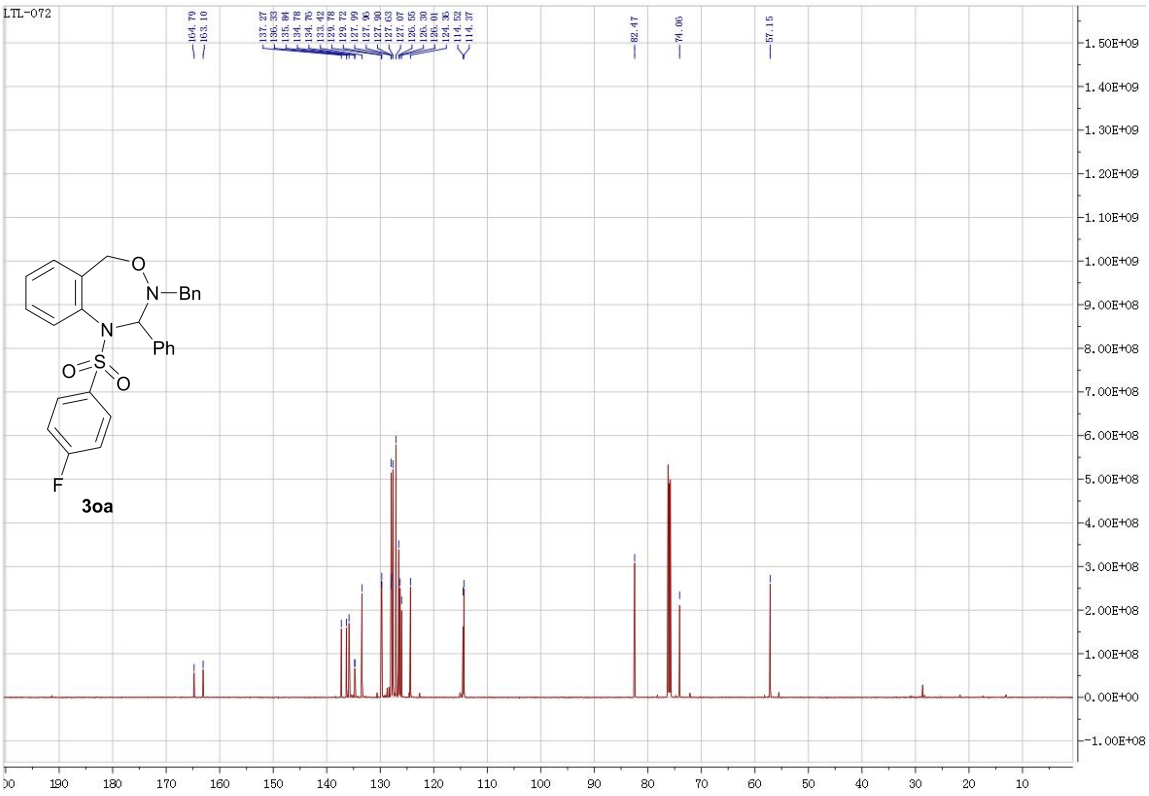

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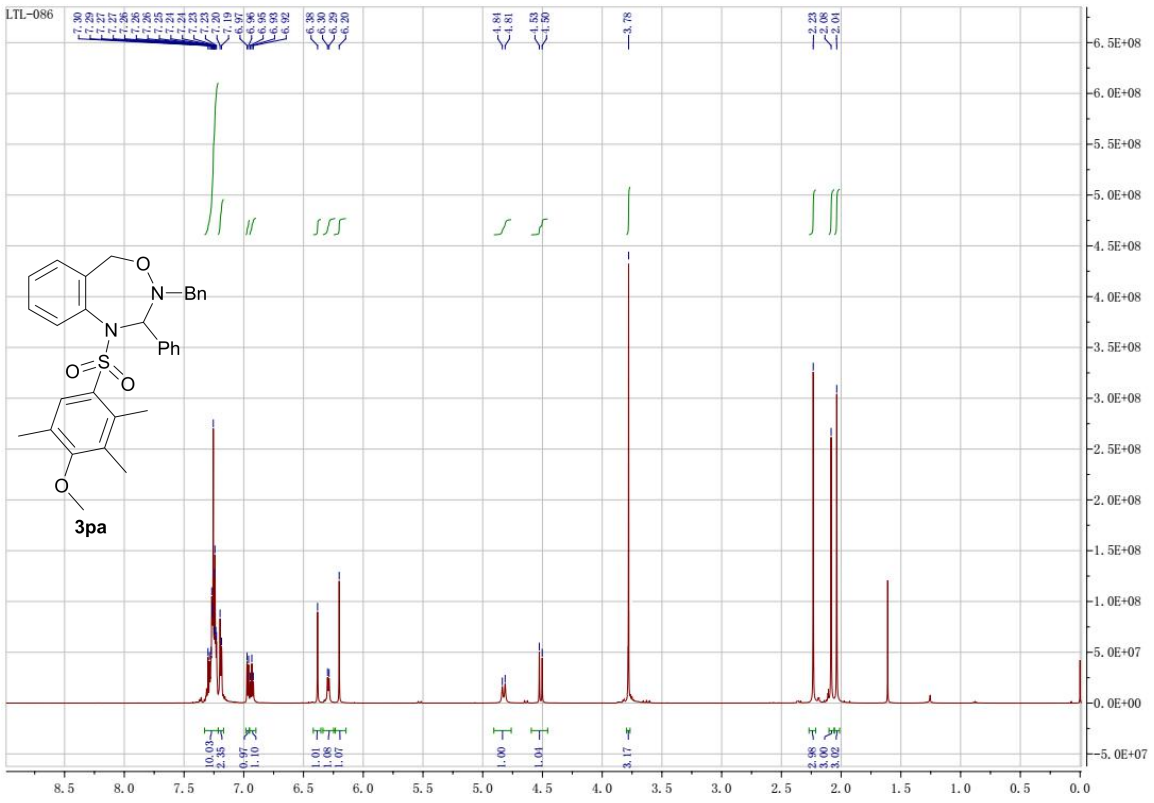

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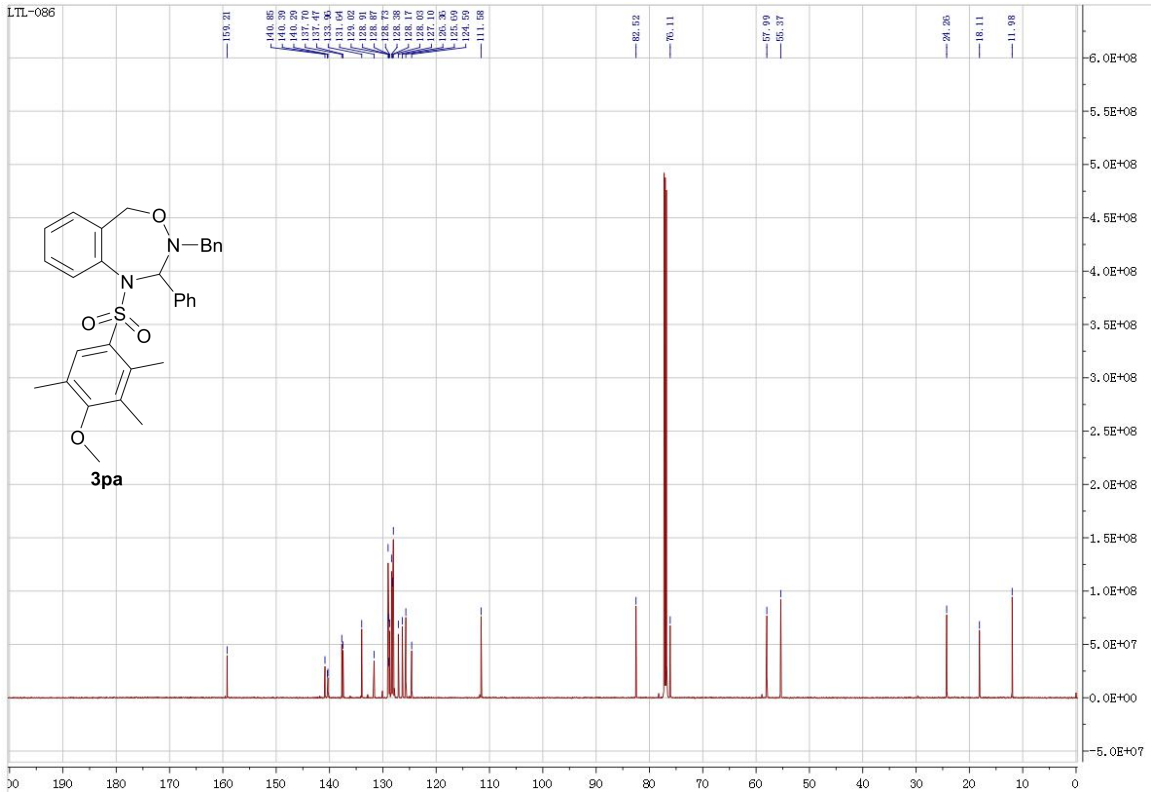

^{13}C NMR (150 MHz, $CDCl_3$)