Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Copper-catalyzed radical Heck type cyclization: three-component reaction of DABCO•$(SO_2)_2$, aryldiazonium tetrafluoroborates and dienes toward sulfonated benzo- seven-membered nitrogen heterocycles

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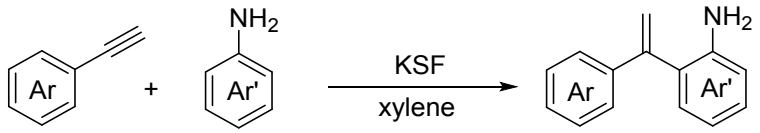
1. General Considerations

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. ^{1}H NMR、^{13}C NMR and ^{19}F spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ^{13}C and 282 MHz for ^{19}F). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hz. High-resolution mass spectra (HRMS) were obtained using a Bruker micro-TOF II focus spectrometer (ESI). Column chromatography was performed using EM Silica gel 60 (300-400 mesh). All melting points were uncorrected.

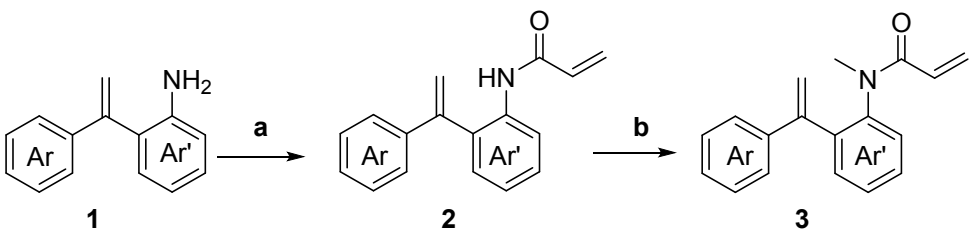
2. Synthesis and Reaction

2.1 Synthesis of 2-(1-Substituted vinyl) anilines:[1]



Under air, anilines (9.0 mmol), phenylacetylenes (18.0 mmol) and 1.7 g of montmorillonite KSF were added to 150 mL of xylene in a round-bottomed flask. The flask was stirred and heated in an oil bath to 140 °C, under a reflux condenser (running cold water as the coolant) that was connected at its top to a paraffin bubbler. After 18 h, the reaction mixture was cooled to room temperature and purified directly by flash chromatography with a gradient of hexane to hexane/ethyl acetate (V_1/V_2 = 60/1), followed by distillation under vacuum to afford corresponding 2-(1-arylvinyl) anilines.

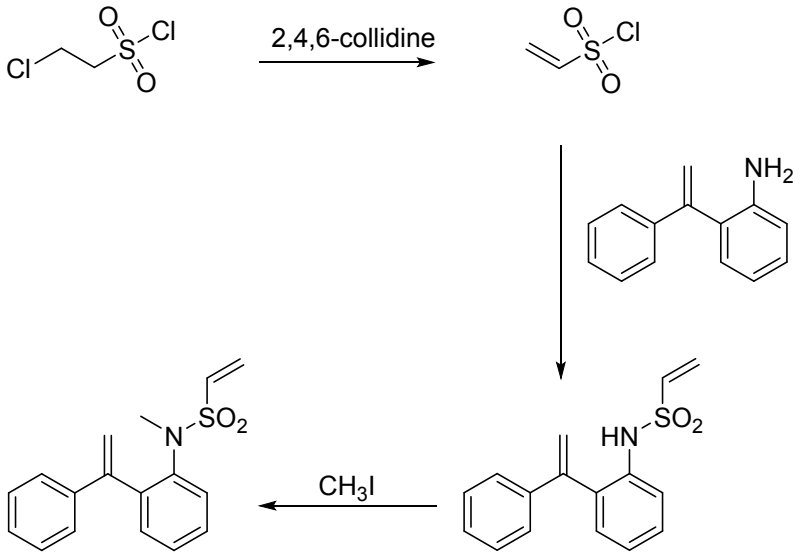
2.2 General Procedure for the Synthesis of Substrates 3:[2]



A solution of compound **1** (2.0 mmol) in CH_2Cl_2 (5.0 mL) was stirred at 0 °C under

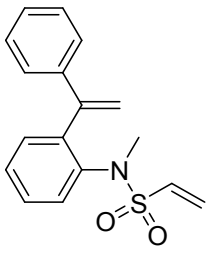
N_2. Then Et_3N (3.0 mmol) and acryloyl chloride (2.4 mmol) were added dropwise respectively and the resulting mixture was warmed to room temperature and stirred overnight. Upon completion, the mixture was evaporated to remove the solvent and excess acryloyl chloride the residue dissolved in THF (5.0 mL) was added to NaH (3.0 mmol) in THF (5.0 mL) at 0 ^oC dropwise and the reaction mixture was stirred for 30 min. Afterward, iodomethane (3.0 mmol) was added and the reaction was stirred overnight at room temperature. The reaction mixture was quenched by water and extracted with DCM for 3 times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel to afford the product **3**.

2.3 Synthesis of *N*-Methyl-*N*-(2-(1-phenylvinyl)phenyl)ethenesulfonamide:[3]



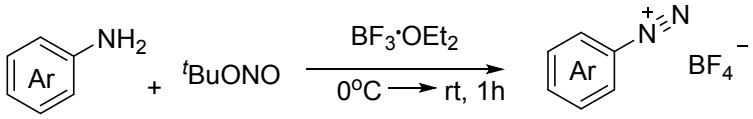
To the solution of 2-chloroethane sulfonyl chloride **1** (18.47 mmol) in 12 mL of Diethyl ether at -55 ^oC added a solution of 2,4,6-collidine in 5 mL of diethyl ether was added in a way that temperature does not rise above 50 ^oC in 10 minutes. Reaction mixture was stirred for 45 minutes and allowed to warm to room temperature. After cooling to 0 ^oC, 5 mL of 1% H_2SO_4 was added with stirring. Organic layer was separated washed with water and brine, and dried over anhydrous Na_2SO_4. Solvent was removed at rotavapor and crude sulfonyl chloride was distilled using kugelrohr apparatus (50-56^oC/10 mmHg) (1.63 g, 69%).

A solution of 2-(1-phenylvinyl)aniline (10 mmol) in CH_2Cl_2 (50 mL) was stirred at 0 °C under N_2. Then Et_3N (12 mmol) and vinyl sulfonyl chloride (12 mmol) were added dropwise respectively and the resulting mixture was warmed to room temperature and stirred overnight. Upon completion, the mixture was evaporated to remove the solvent and excess acryloyl chloride the residue dissolved in THF (50 mL) was added to NaH (11 mmol) at 0 °C dropwise and the reaction mixture was stirred for 30 min. Afterward, iodomethane (12 mmol) was added and the reaction was stirred overnight at room temperature. The reaction mixture was quenched by water and extracted with DCM for 3 times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel to afford the *N*-methyl-*N*-(2-(1-phenylvinyl)phenyl)ethenesulfonamide.



^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34-7.29 (m, 3H), 7.25-7.20 (m, 5H), 6.07-5.75 (m, 3H), 5.66-5.31 (m, 2H), 2.64 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.8, 142.1, 141.2, 139.2, 133.9, 131.7, 128.8, 128.4, 128.2, 127.8, 127.7, 126.8, 116.9, 37.9.

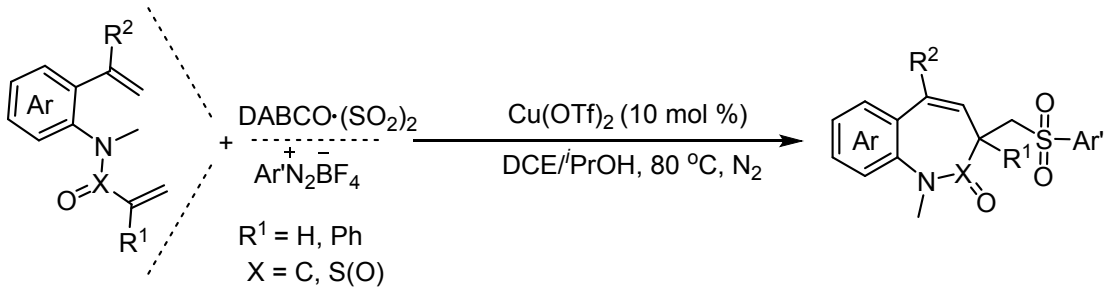
2.4 Preparation of Arenenediazonium Tetrafluoroborate Salts:[4]



To a solution of the appropriately substituted aniline (10 mmol, 1.0 equiv) in 100 mL of CH_2Cl_2 at 0 °C was added $BF_3{\cdot}OEt_2$ (15 mmol, 1.5 equiv) followed by *tert*-butyl nitrite (12 mmol, 1.2 equiv). The resulting reaction mixture was stirred for 1 h at that temperature and then it was allowed to warm to room temperature. After stirring for 1 h, the precipitate was collected on a Büchner funnel and washed with small

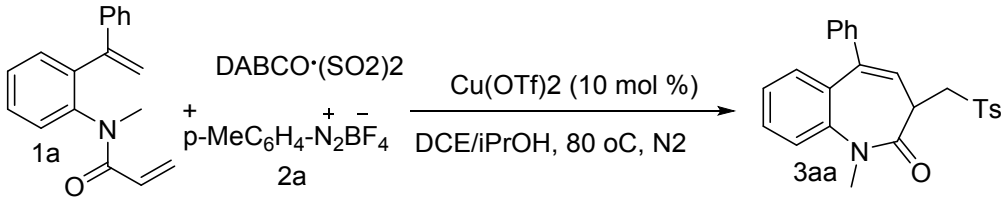
amount of ice-cold distilled water. The solid was dissolved in acetone and precipitated with slow addition of ethyl ether. White crystalline solids were obtained after repeat this trituration two to three times. Yields of the aryldiazonium salts are ranged from 65% to 92%.

3. The Reaction of Dienes, Arenenediazonium Tetrafluoroborate and DABSO



Under N_2, a 20 mL of Schlenk tube equipped with a stir bar was charged with Dienes (0.1 mmol), aryldiazonium tetrafluoroborates (0.15 mmol, 1.5 equiv), DABCO-bis(sulfur dioxide) (0.1 mmol, 1.0 equiv), $Cu(OTf)_2$ (10 mol %), DCE (1.0 mL) and ^{i}PrOH (0.1 mmol). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 80 °C for 12 h in oil bath (**Because of the diazonium salts as initially water-free solids, be careful with the potential hazards of it**). After the completion of the reaction, 6 mL of saturated brines was added to the mixture, and extracted with ethyl acetate (8 mL × 3) with ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4. Subsequently, the solvent was filtered and evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V_1/V_2, 3:1) as the eluent to give the desired products.

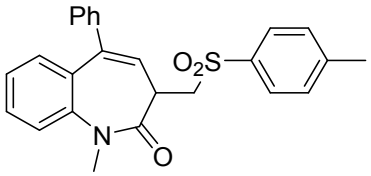
4. 1 mmol Scale Reaction of *N*-Methyl-*N*-(2-(1-phenylvinyl)phenyl)acrylamide 4-Methylbenzenediazonium Tetrafluoroborate and DABSO



Under N_2, *N*-methyl-*N*-(2-(1-phenylvinyl)phenyl)acrylamide (1.0 mmol, 263 mg), 4-methylbenzenediazonium tetrafluoroborate (1.5 mmol, 309 mg), DABSO (1 mmol, 240 mg), $Cu(OTf)_2$ (0.1 mmol, 36.1 mg), DCE (10 mL) and ^{i}PrOH (1.0 mmol). The sealed Schlenk tube was stirred at 80 °C for 12 h in oil bath. After the reaction mixture was cooled to room temperature, saturated brine water (15.0 mL) was added to terminate the reaction. The reaction mixture was diluted with EtOAc and washed with saturated brine water. The organic layer was dried over anhydrous Na2SO4 and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate (3:1) as eluent to give the desired product in 61% yield.

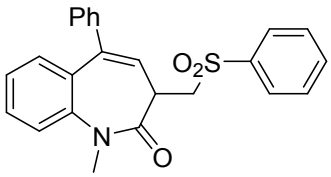
5. Characterization Data for the Products

1-methyl-5-phenyl-3-(tosylmethyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3aa):



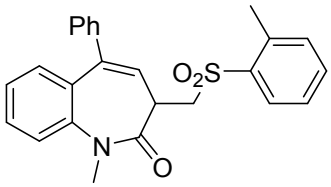
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (28.4 mg, 68% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.77-7.74 (m, 2H), 7.42-7.30 (m, 7H), 7.20-7.10 (m, 4H), 5.83 (d, J = 6.2 Hz, 1H), 3.97-3.91 (m, 1H), 3.68-3.60 (m, 1H), 3.37 (s, 3H), 3.28-3.20 (m, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.1, 145.1, 142.2, 140.5, 139.8, 136.7, 132.6, 130.4, 130.0, 129.1, 128.8, 128.5, 128.4, 128.2, 127.5, 124.9, 122.7, 56.5, 39.4, 36.8, 21.8. MS (EI): 417 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{25}H_{23}NNaO_3S]^+$ 440.1291, found 440.1284.

1-methyl-5-phenyl-3-((phenylsulfonyl)methyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ab):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (26.2 mg, 65% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93-7.85 (m, 2H), 7.69-7.54 (m, 3H), 7.44-7.30 (m, 5H), 7.23-7.15 (m, 4H), 5.90 (d, J = 6.2 Hz, 1H), 3.99-3.95 (m, 1H), 3.70-3.64 (m, 1H), 3.37 (s, 3H), 3.27-3.22 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) 169.9, 142.1, 140.6, 139.8, 139.5, 134.0, 132.5, 130.4, 129.4, 129.2, 128.8, 128.4, 128.3, 128.2, 127.3, 124.9, 122.6, 56.4, 39.2, 36.8. MS (EI): 403 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd. for $[C_{24}H_{21}NNaO_3S]^+$ 426.1134, found 426.1104.

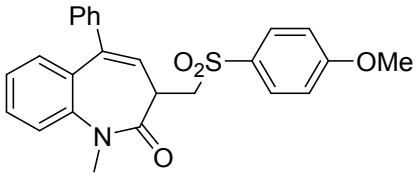
1-methyl-5-phenyl-3-((*o*-tolylsulfonyl)methyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ac):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (17.5 mg, 42% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94-7.86 (m, 1H), 7.56-7.30 (m, 8H), 7.21-7.12 (m, 4H), 5.86 (d, J = 6.1 Hz, 1H), 4.05-4.00 (m, 1H), 3.70-3.64 (m, 1H), 3.36 (s, 3H), 3.27-3.23 (m, 1H), 2.75(s, 3H); ^{13}C

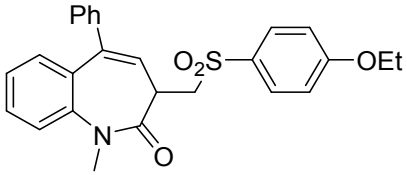
NMR ($CDCl_3$, 100 MHz) δ 170.0, 142.1, 140.6, 139.9, 138.8, 137.6, 134.0, 133.0, 132.6, 130.5, 130.3, 129.2, 128.8, 128.5, 128.2, 127.4, 126.7, 124.9, 122.7, 55.5, 39.2, 36.9, 20.6. MS (EI): 417 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{25}H_{23}NNaO_3S]^+$ 440.1291, found 440.1318.

3-(((4-methoxyphenyl)sulfonyl)methyl)-1-methyl-5-phenyl-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ad):



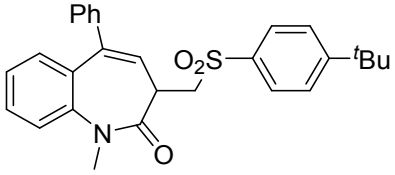
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (30.7 mg, 71% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, J = 8.9 Hz, 2H), 7.43-7.29 (m, 5H), 7.22-7.12 (m, 4H), 6.99 (d, J = 8.8 Hz, 2H), 5.85 (d, J = 6.2 Hz, 1H), 3.96-3.91 (m, 1H), 3.87 (s, 3H), 3.67-3.61 (m, 1H), 3.36 (s, 3H), 3.22-3.18 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 164.0, 142.1, 140.4, 139.7, 132.5, 131.0, 130.4, 130.3, 129.1, 128.7, 128.4, 128.1, 127.5, 124.8, 122.6, 114.5, 56.6, 55.8, 39.4, 36.7. MS (EI): 433 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{25}H_{23}NNaO_4S]^+$ 456.1240, found 456.1264.

3-(((4-ethoxyphenyl)sulfonyl)methyl)-1-methyl-5-phenyl-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ae):



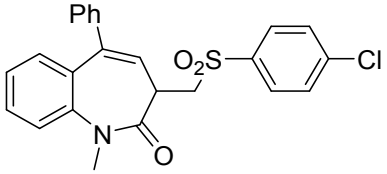
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (29.5 mg, 66% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, J = 8.9 Hz, 2H), 7.43-7.28 (m, 5H), 7.22-7.12 (m, 4H), 6.98 (d, J = 8.9 Hz, 2H), 5.85 (d, J = 6.2 Hz, 1H), 4.12-4.06 (m, 2H), 3.96-3.91 (m, 1H), 3.66-3.60 (m, 1H), 3.36 (s, 3H), 3.23-3.18 (m, 1H), 1.45 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 163.4, 142.2, 140.4, 139.8, 132.5, 130.7, 130.4, 130.3, 129.1, 128.8, 128.4, 128.1, 127.5, 124.8, 122.6, 114.9, 64.2, 56.6, 39.4, 36.8, 14.7. MS (EI): 447 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{26}H_{25}NNaO_4S]^+$ 470.1397, found 470.1405.

3-(((4-(*tert*-butyl)phenyl)sulfonyl)methyl)-1-methyl-5-phenyl-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3af):



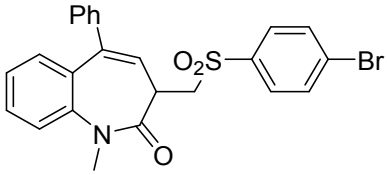
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (34.0 mg, 74% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H) 7.43-7.39 (m, 5H), 7.22-7.13 (m, 4H), 5.87 (d, J = 6.2 Hz, 1H), 3.97-3.92 (m, 1H), 3.70-3.64 (m, 1H), 3.36 (s, 3H), 3.23-3.18 (m, 1H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 157.9, 142.2, 140.4, 139.8, 136.4, 132.6, 130.4, 129.1, 128.7, 128.4, 128.2, 128.2, 127.5, 126.4, 124.8, 122.6, 56.4, 39.4, 36.8, 35.4, 31.2. MS (EI): 459 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{28}H_{29}NNaO_3S]^+$ 482.1760, found 482.1753.

3-(((4-chlorophenyl)sulfonyl)methyl)-1-methyl-5-phenyl-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ag):



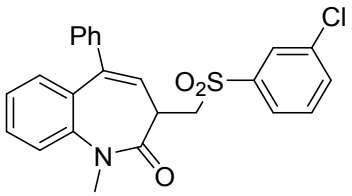
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (29.3 mg, 67% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H) 7.45-7.41 (m, 1H), 7.35-7.31 (m, 4H), 7.21-7.12 (m, 4H), 5.83 (d, J = 6.2 Hz, 1H), 4.02-3.97 (m, 1H), 3.68-3.62 (m, 1H), 3.37 (s, 3H), 3.23-3.21 (m, 1H);^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 142.1, 140.8, 140.8, 139.7, 138.0, 132.5, 130.4, 129.9, 129.7, 129.3, 128.7, 128.5, 128.3, 127.0, 125.0, 122.7, 56.5, 39.3, 36.8. MS (EI): 437 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{24}H_{20}ClNNaO_3S]^+$ 460.0745, found 460.0753.

3-(((4-bromophenyl)sulfonyl)methyl)-1-methyl-5-phenyl-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ah):



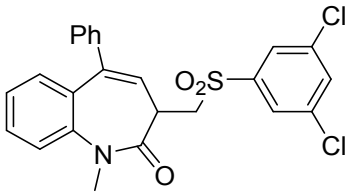
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (30.8 mg, 64% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75-7.69 (m, 4H), 7.45-7.31 (m, 5H), 7.22-7.10 (m, 4H), 5.80 (d, J = 6.2 Hz, 1H), 4.02-3.97 (m, 1H), 3.68-3.62 (m, 1H), 3.36 (s, 3H), 3.23-3.19 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 142.1, 140.8, 139.6, 138.5, 132.7, 132.4, 130.4, 129.9, 129.4, 129.3, 128.7, 128.5, 128.2, 126.9, 124.9, 122.6, 56.4, 39.3, 36.8. MS (EI): 481 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{24}H_{20}BrNNaO_3S]^+$ 504.0239, found 504.0225.

3-(((3-chlorophenyl)sulfonyl)methyl)-1-methyl-5-phenyl-1,3-dihydro-2H-benzo[b]azepin-2-one (3ai):



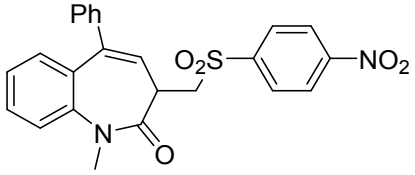
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (24.5 mg, 56% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85-7.79 (m, 2H), 7.65-7.63 (m, 1H), 7.53-7.31 (m, 6H), 7.24-7.15 (m, 4H) 5.90 (d, J = 6.2 Hz, 1H), 4.03-3.98 (m, 1H), 3.68-3.63 (m, 1H), 3.37 (s, 3H), 3.25-3.20 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 142.1, 141.2, 140.9, 139.7, 135.6, 134.2, 132.5, 130.8, 130.5, 129.3, 128.8, 128.5, 128.4, 128.3, 126.9, 126.5, 125.0, 122.7, 56.4, 39.3, 36.8. MS (EI): 437 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{24}H_{20}ClNNaO_3S]^+$ 460.0745, found 460.0755.

3-(((3,5-dichlorophenyl)sulfonyl)methyl)-1-methyl-5-phenyl-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3aj):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (24.0 mg, 51% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78-7.73 (m, 2H), 7.64-7.62 (m, 1H), 7.47-7.32 (m, 5H), 7.24-7.17 (m, 4H); 5.89 (d, J = 6.2 Hz, 1H), 4.05-4.01 (m, 1H), 3.67-3.62 (m, 1H), 3.38 (s, 3H), 3.24-3.19 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.5, 142.3, 142.1, 141.2, 139.7, 136.5, 134.0, 132.5, 130.6, 129.4, 128.8, 128.6, 128.4, 126.8, 126.5, 125.1, 122.8, 56.5, 39.3, 36.9. MS (EI): 471 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{24}H_{19}Cl_2NNaO_3S]^+$ 494.0355, found 494.0367.

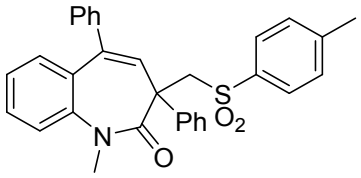
1-methyl-3-(((4-nitrophenyl)sulfonyl)methyl)-5-phenyl-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3ak):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (18.8 mg, 42% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38 (d, J = 8.6 Hz, 2H), 8.09 (d, J = 8.6 Hz, 2H) 7.47-7.31 (m, 5H), 7.24-7.17 (m, 4H), 5.90 (d, J = 6.2 Hz, 1H), 4.10-4.05 (m, 1H), 3.72-3.66 (m, 1H), 3.35 (s, 3H), 3.28-3.23 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ13C NMR (101 MHz, CDCl3) δ 169.5, 151.0, 145.1, 142.0, 141.1, 139.6, 132.4, 130.5, 129.8, 129.4, 128.7, 128.6, 128.4, 126.4, 125.1, 124.5, 122.7, 56.4, 39.1, 36.9. MS (EI): 448 (M^+); HRMS (ESI-TOF)

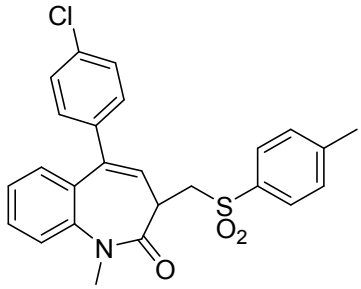
m/z [M + Na]$^+$ calcd. for [$C_{24}H_{20}N_2NaO_5S$]$^+$ 471.0976, found 471.0985.

1-methyl-3,5-diphenyl-3-(tosylmethyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ba):



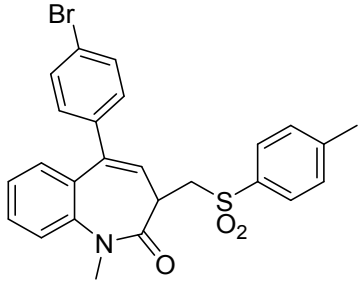
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (21.2 mg, 43% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52-7.39 (m, 7H), 7.15-7.06 (m, 2H), 7.00-6.67 (m, 10H), 4.24-4.13 (m, 2H), 3.42 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.0, 143.8, 141.6, 141.3, 140.7, 138.6, 133.9, 133.8, 130.2, 129.5, 129.2, 129.2, 128.6, 128.5, 128.3, 127.6, 127.5, 127.4, 127.2, 124.1, 122.4, 66.1, 54.9, 38.6, 21.6. MS (EI): 493 (M$^+$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for [$C_{31}H_{27}NNaO_3S$]$^+$ 516.1604, found 516.1593.

5-(4-chlorophenyl)-1-methyl-3-(tosylmethyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ca):



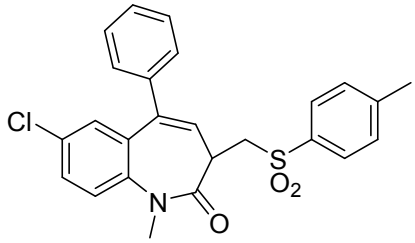
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (30.2 mg, 67% yield) as a yellowish solid. m.p. 182-183 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.79-7.70 (m, 2H), 7.46-7.27 (m, 6H), 7.18-7.14 (m, 2H), 7.10-7.05 (m, 2H), 5.87 (d, J = 6.2 Hz, 1H), 3.94-3.88 (m, 1H), 3.69-3.61 (m, 1H), 3.38 (s, 3H), 3.26-3.19 (m, 1H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.9, 145.1, 142.2, 139.3, 138.3, 136.6, 134.1, 132.1, 130.2, 130.0, 130.0, 129.3, 128.6, 128.3, 127.9, 125.0, 122.7, 56.4, 39.3, 36.8, 21.7. MS (EI): 451 (M$^+$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for [$C_{25}H_{22}ClNNaO_3S$]$^+$ 474.0901, found 474.0929.

5-(4-bromophenyl)-1-methyl-3-(tosylmethyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3da):



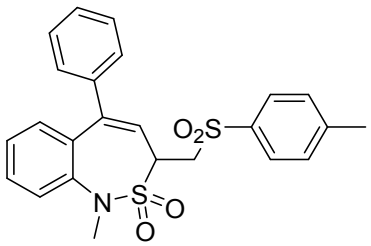
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (27.2 mg, 55% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, J = 8.2 Hz, 2H), 7.44-7.32 (m, 6H), 7.19-7.13 (m, 2H), 7.01 (d, J = 8.4 Hz, 2H), 5.87 (d, J = 6.2 Hz, 1H), 3.92-3.87 (m, 1H), 3.67-3.61 (m, 1H), 3.37 (s, 3H), 3.24-3.19 (m, 1H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 145.1, 142.2, 139.4, 138.8, 136.6, 132.0, 131.6, 130.4, 130.2, 130.0, 129.4, 128.3, 127.9, 125.0, 122.8, 122.3, 56.4, 39.3, 36.9, 21.8. MS (EI): 495 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{25}H_{22}BrNNaO_3S]^+$ 518.0396, found 518.0410.

7-chloro-1-methyl-5-phenyl-3-(tosylmethyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ea):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (28.0 mg, 62% yield) as a yellowish solid. m.p. 171-172 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80-7.72 (m, 2H), 7.39-7.26 (m, 7H), 7.18-7.09 (m, 3H), 5.87 (d, J = 6.2 Hz, 1H), 3.93-3.89 (m, 1H), 3.67-3.60 (m, 1H), 3.34 (s, 3H), 3.21-3.16 (m, 1H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 145.1, 140.6, 139.5, 139.0, 136.5, 134.0, 130.3, 130.0, 129.7, 129.2, 128.7, 128.6, 128.4, 128.4, 128.2, 124.1, 56.3, 39.4, 36.8, 21.7. MS (EI): 451 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{25}H_{22}ClNNaO_3S]^+$ 474.0901, found 474.0939.

1-methyl-5-phenyl-3-(tosylmethyl)-1,3-dihydrobenzo[*c*][1,2]thiazepine 2,2-dioxide (4):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **3a** (16.3 mg, 36% yield) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76-7.71 (m, 2H), 7.53-7.33 (m, 8H), 7.24-7.21 (m, 3H), 6.25 (d, J = 6.7 Hz, 1H), 4.13-4.06 (m, 1H), 3.77-3.63 (m, 2H), 3.17 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.8, 145.7, 140.7, 139.2, 137.5, 136.0, 131.4, 131.0, 130.3, 129.8, 129.1, 128.8, 128.5, 128.2, 120.9, 57.4, 54.3, 40.3, 21.8. One signal may be overlapped. MS (EI): 453 (M^+); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $[C_{24}H_{23}NNaO_4S_2]^+$ 476.0961, found 476.0979.

6. Reference

1 (*a*) Z. Zhang, L.-L. Liao, S.-S. Yan, L. Wang, Y.-Q. He, J.-H. Ye, J. Li, Y.-G. Zhi and D.-G. Yu, *Angew. Chem., Int. Ed.,* 2016, **55**, 7068; (*b*) K. Sasano, J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.,* 2013, **135**, 10954; (*c*) L. Wang, J. Ferguson and F. Zeng, *Org. Biomol. Chem.,* 2015, **13**, 11486; (*d*) A. Arienti, F. Bigi, R. Maggi, E. Marzi, P. Moggi, M. Rastelli, G. Sartori and F. Tarantola, *Tetrahedron* 1997, **53**, 3795; (*e*) J. Ferguson, F.-L. Zeng, N. Alwis and H. Alper, *Org. Lett.,* 2013, **15**, 1998; (f) W.-H. Hu, J-T. Yu, S. Liu, Y. Jiang and J.

Cheng, *Org. Chem. Front.,* 2017, **4**, 22; (*g*) J. Yuan, J.-T Yu, Y. Jiang and J. Cheng, *Org. Biomol. Chem.,* 2017, **15**, 1334.

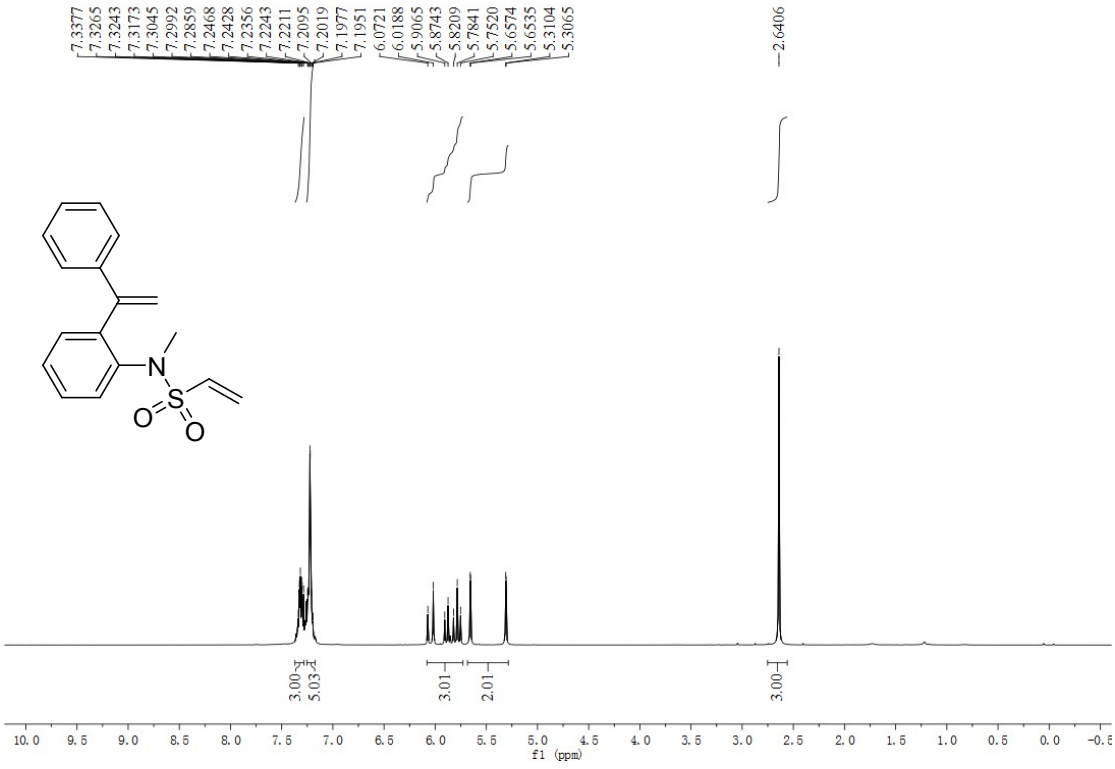
2 (*a*) Q. H. Deng, J. R. Chen, Q. Wei, Q. Q. Zhao, L. Q. Lu and W. J. Xiao, *Chem. Commun.,* 2015, **51**, 3537; (*b*) L.-Z. Yu, Q. Xu, X.-Y. Tang and M. Shi, *ACS Catal.,* 2015, **6**, 526; (*c*) Y. Zhao, J. R. Chen and W. J. Xiao, *Org. Lett*., 2016, **18**, 6304.

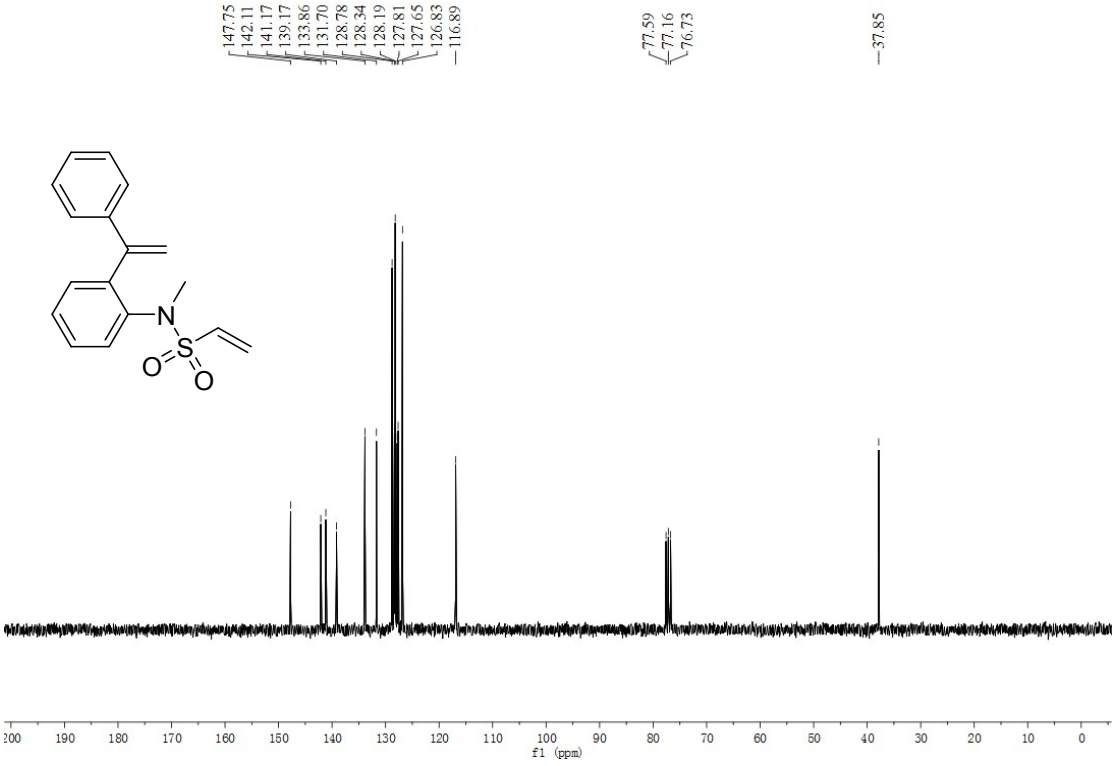
3 R. M. Moriarty and S. Tyagi, *Org. Lett.,* 2010, **12**, 364.

4 (*a*) B. Panda and T. K. Sarkar, *Chem. Commun*., 2010, **46**, 3131; (*b*) R. Cai, M. Lu, E. Y. Aguilera, Y. M. Xi, N. G. Akhmedov, J. L. Petersen, H. Chen and X. D. Shi, *Angew. Chem. Int. Ed.,* 2015, **54**, 8772.

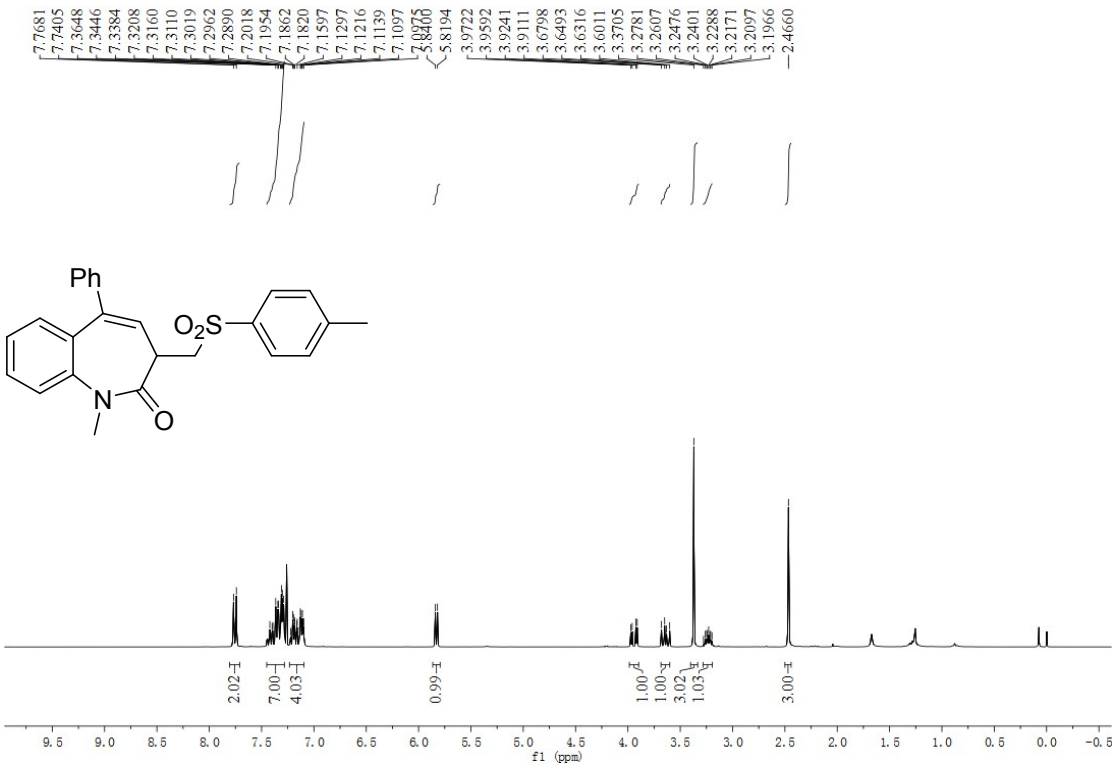
7. Copies of the ^{1}H NMR, ^{13}C NMR Spectras

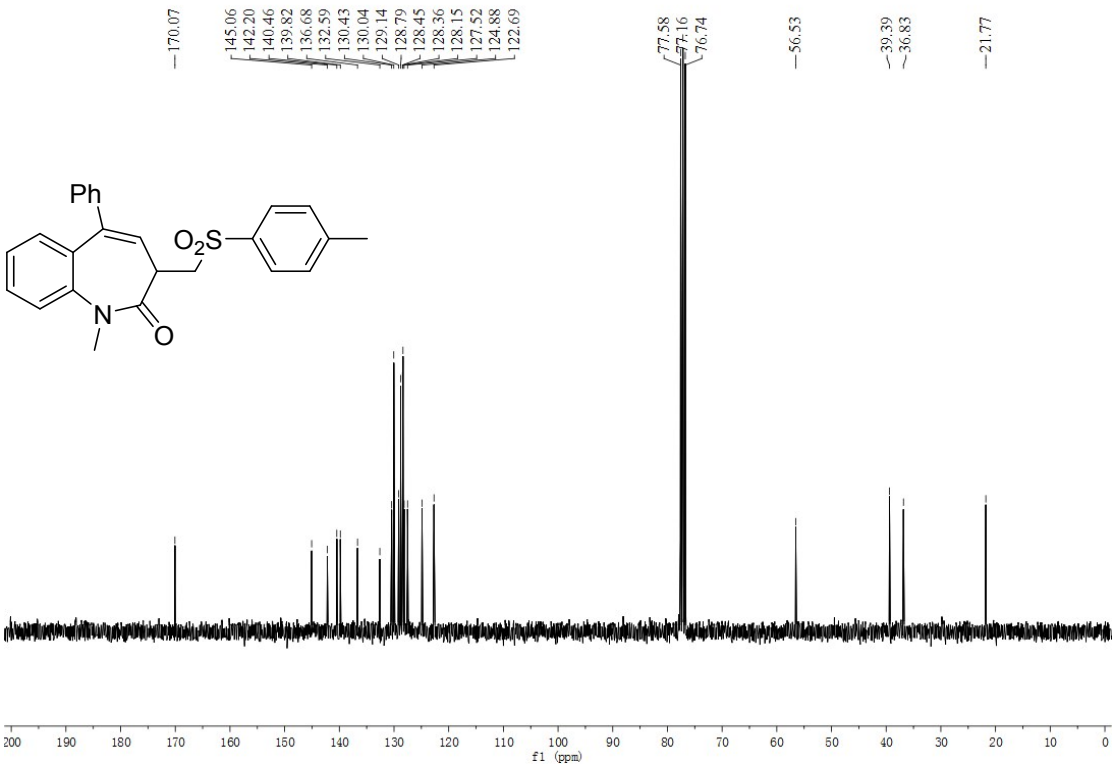
N-methyl-*N*-(2-(1-phenylvinyl)phenyl)ethenesulfonamide





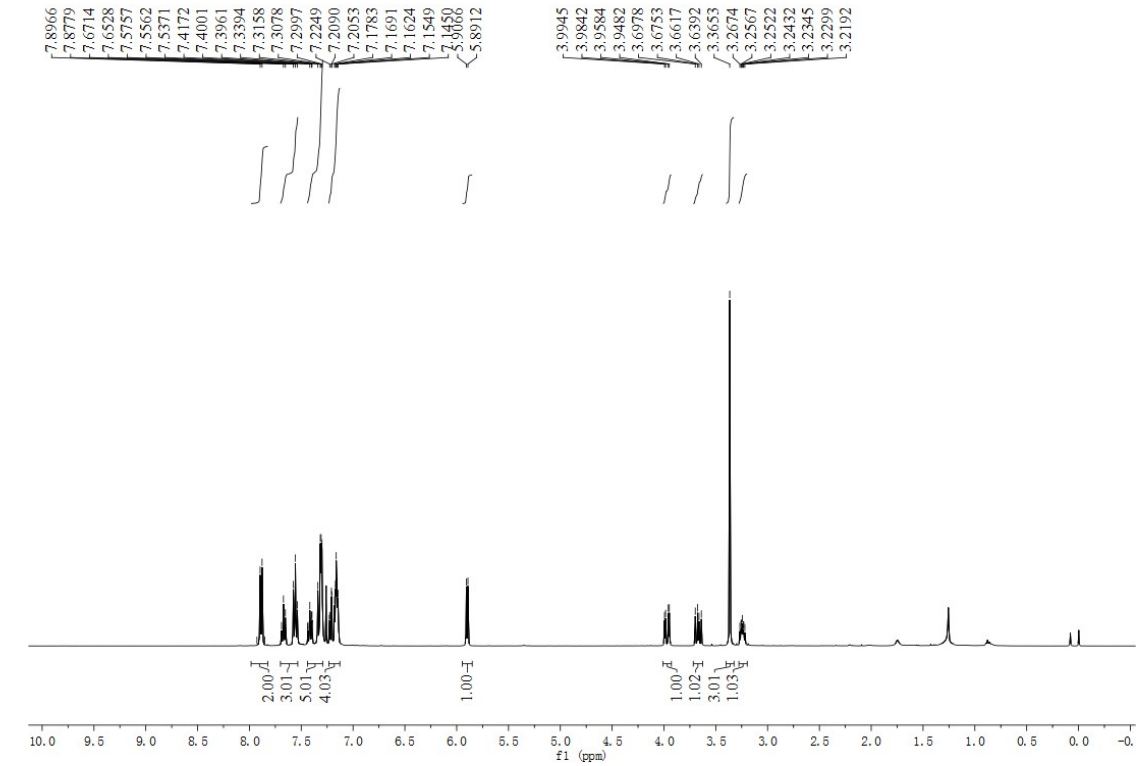
1-methyl-5-phenyl-3-(tosylmethyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3aa):

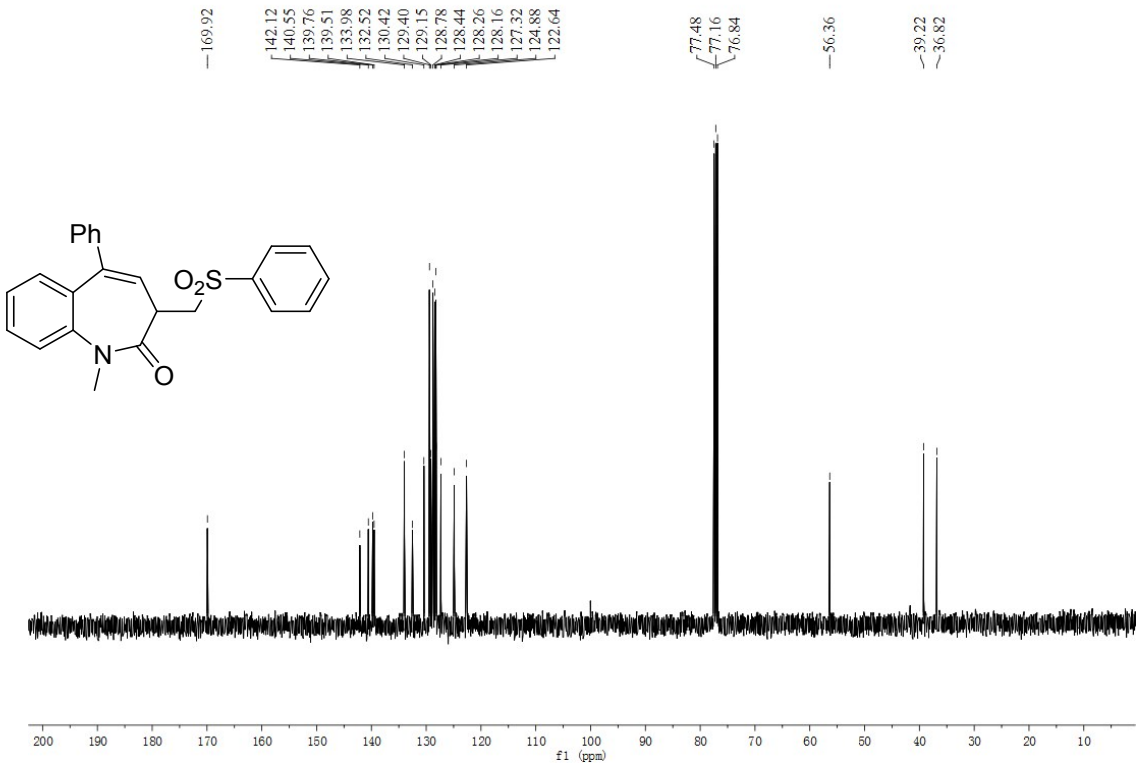




1-methyl-5-phenyl-3-((phenylsulfonyl)methyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-

one (3ab)





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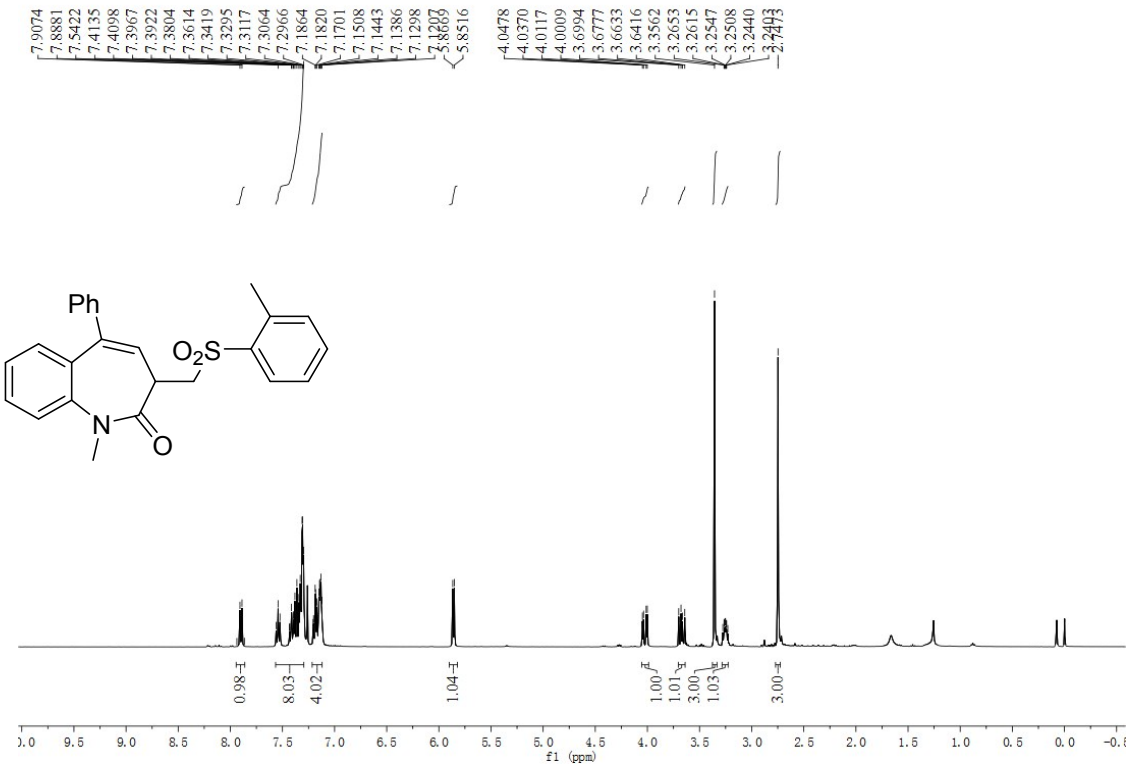
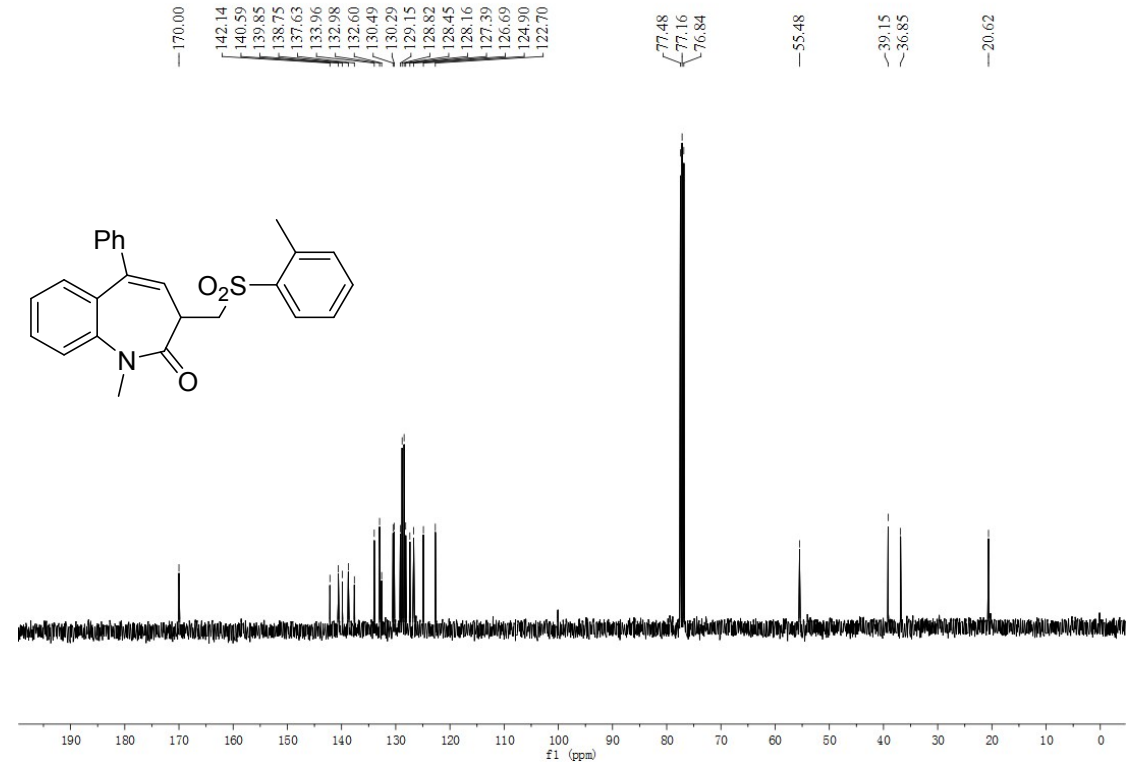
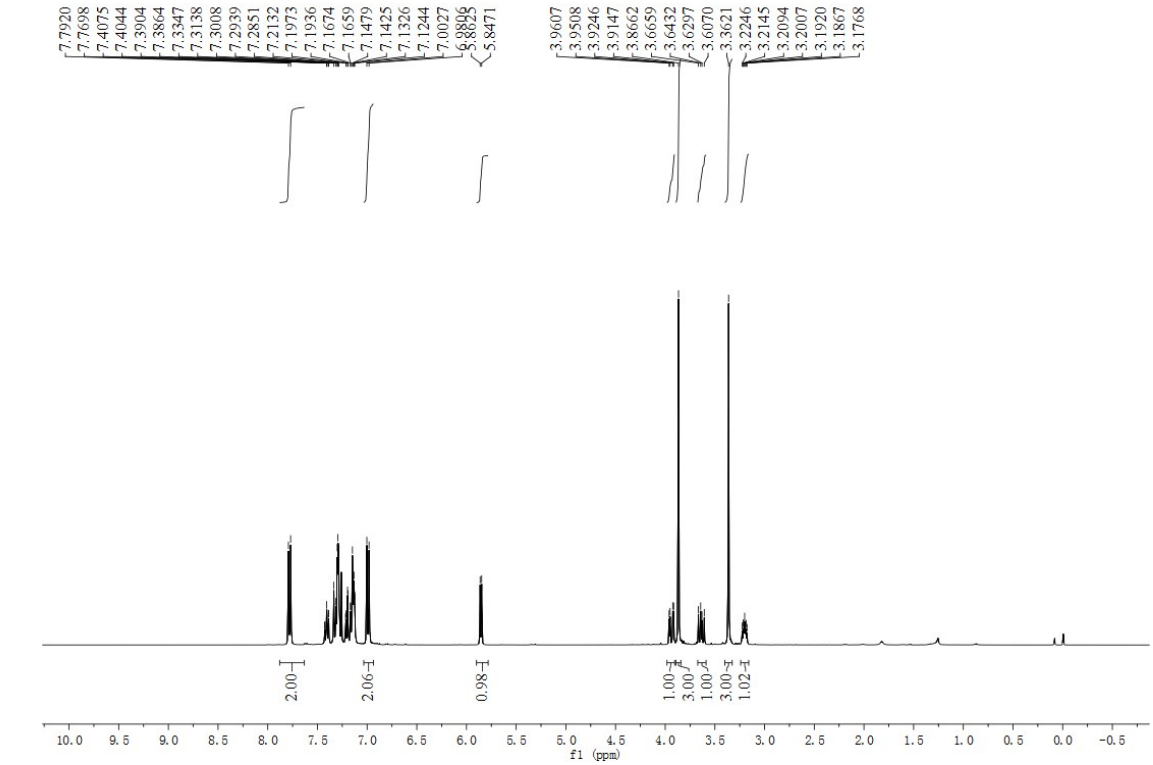
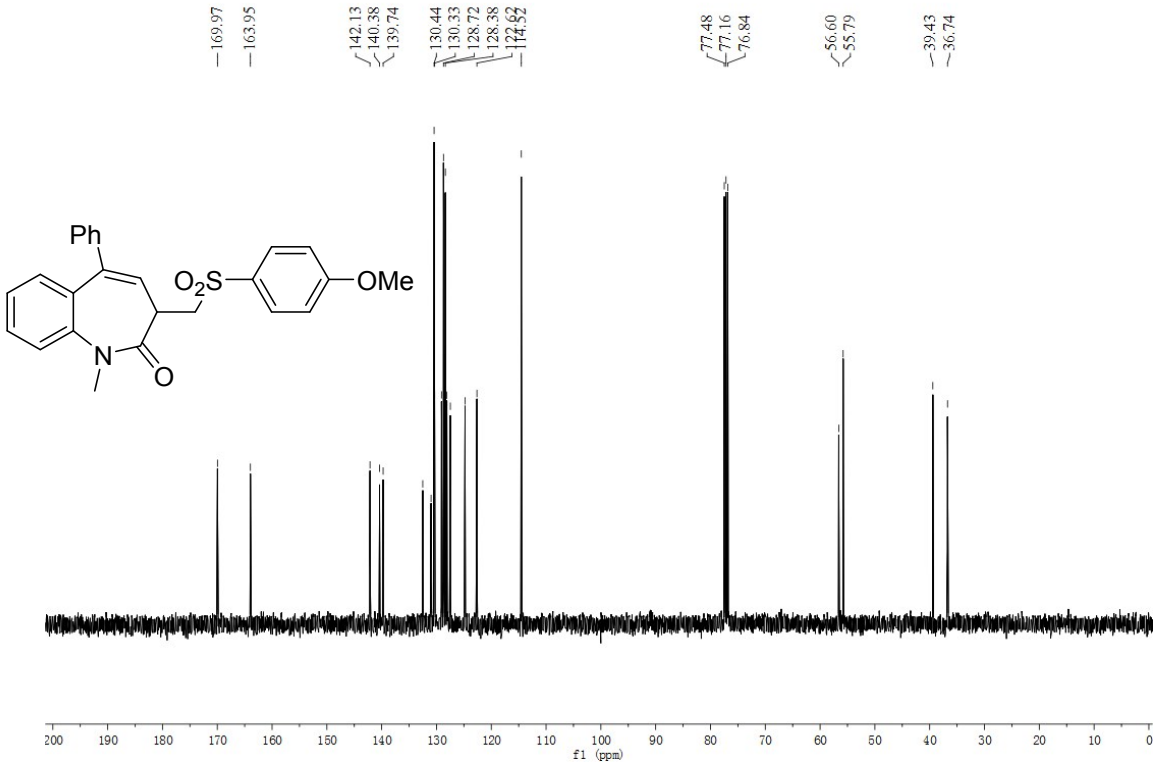




3-(((4-methoxyphenyl)sulfonyl)methyl)-1-methyl-5-phenyl-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ad):





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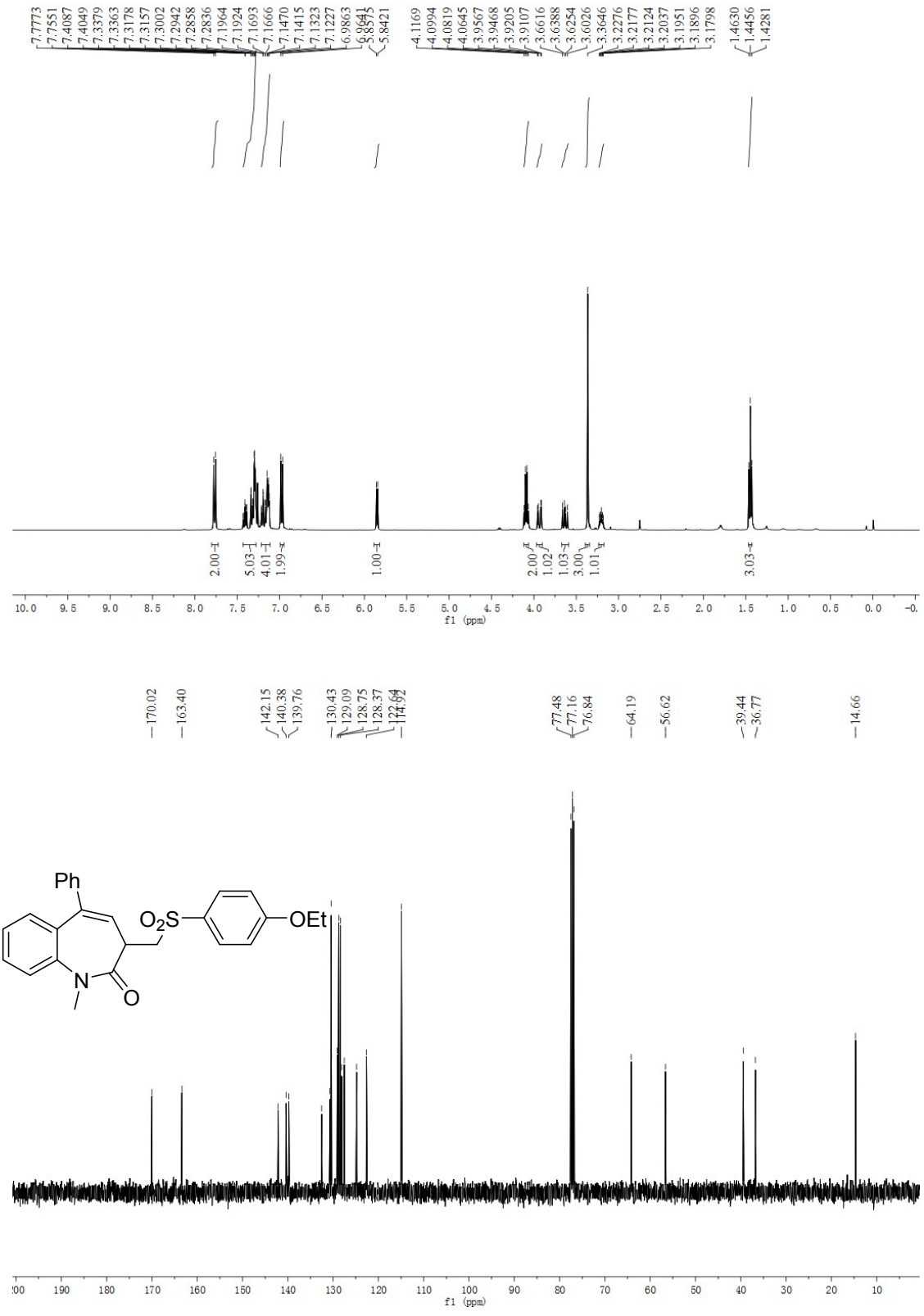
Ph



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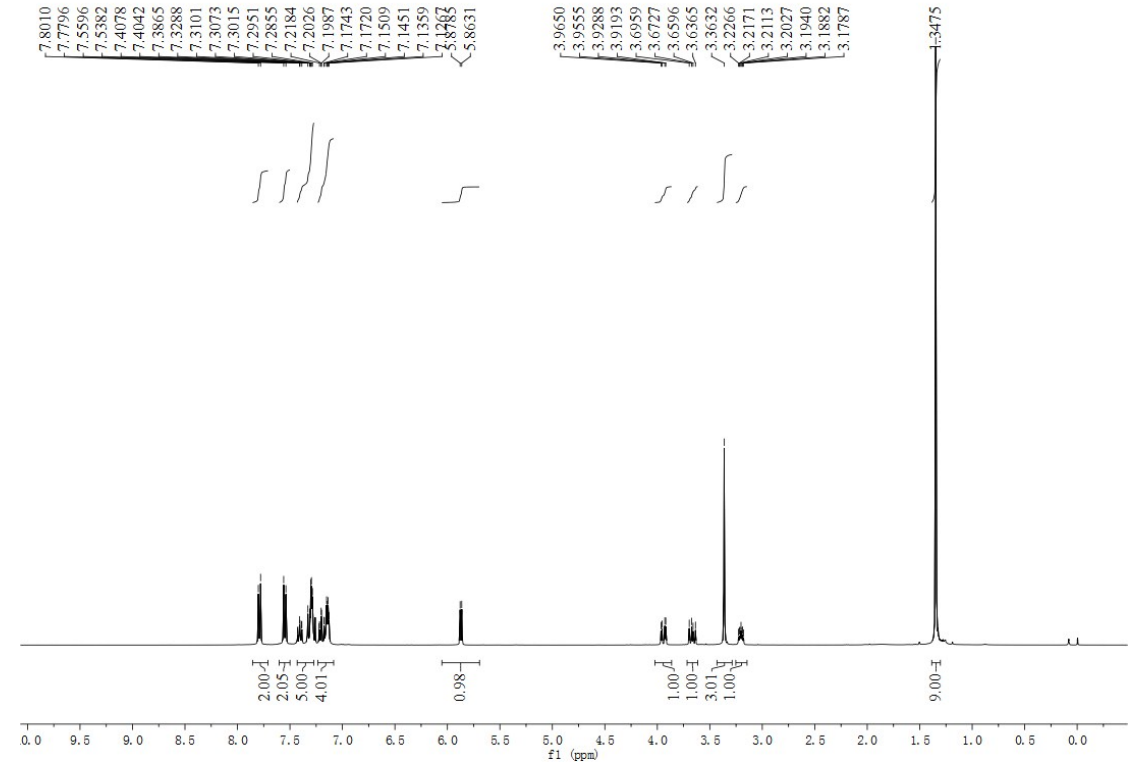

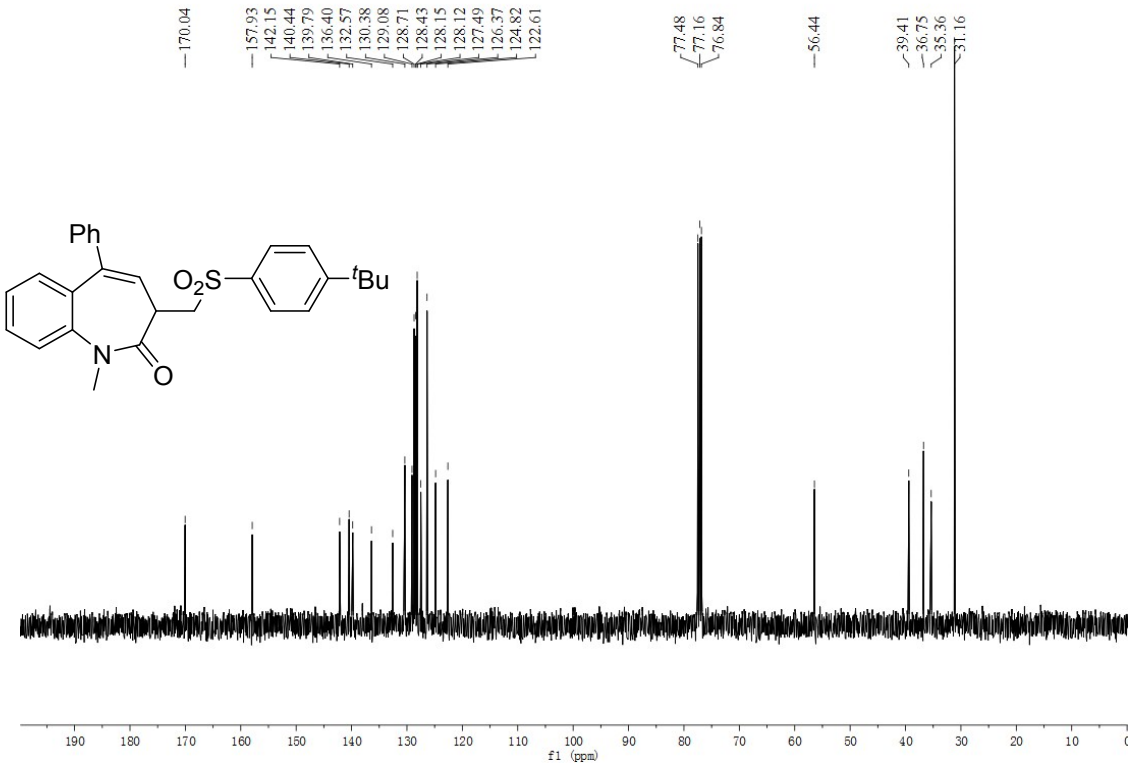

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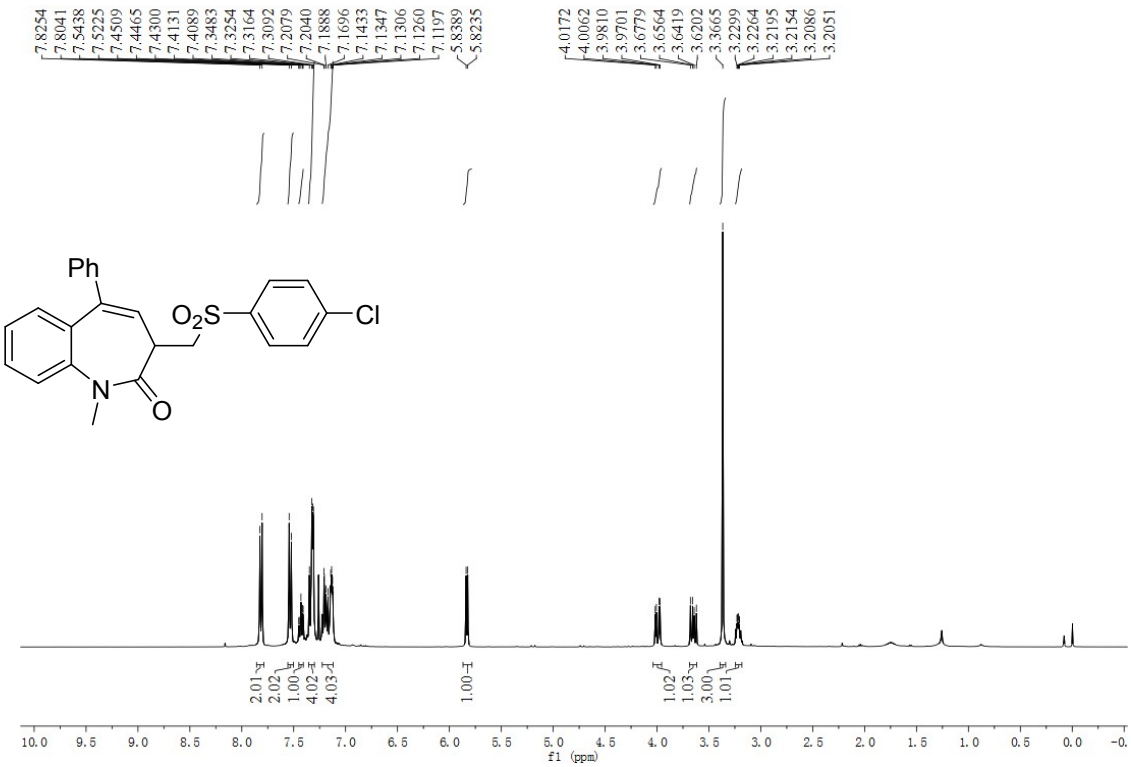
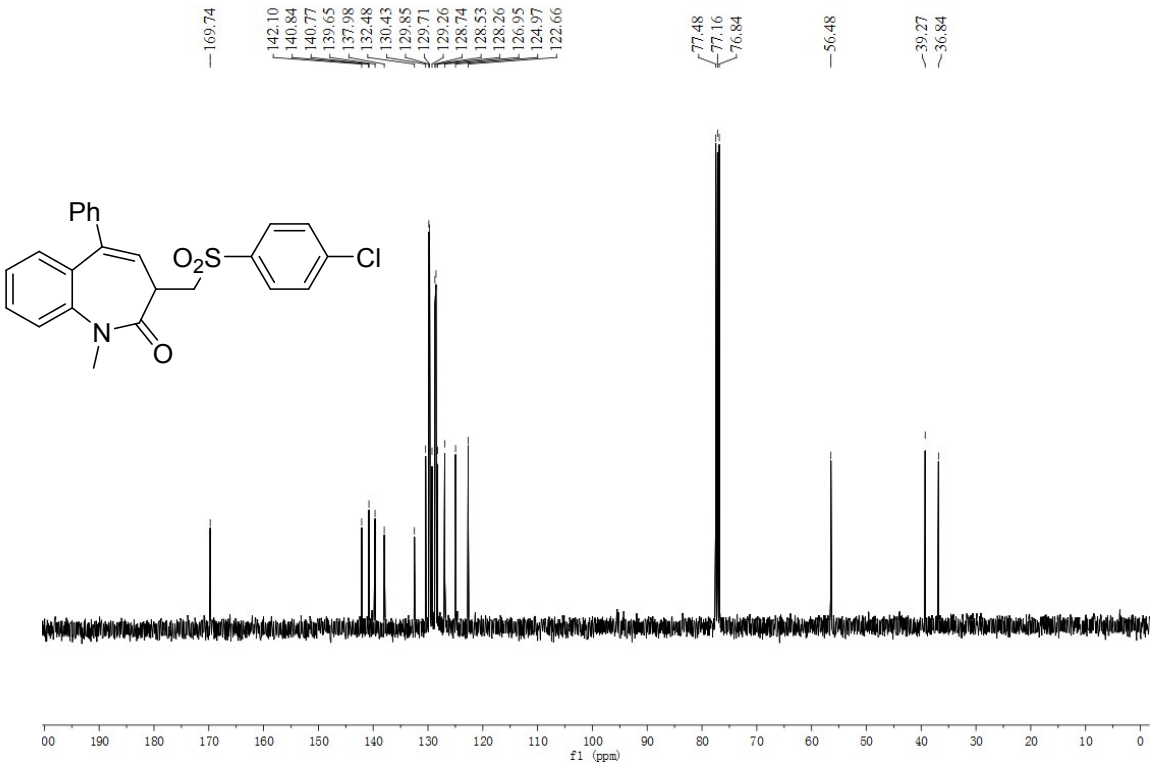
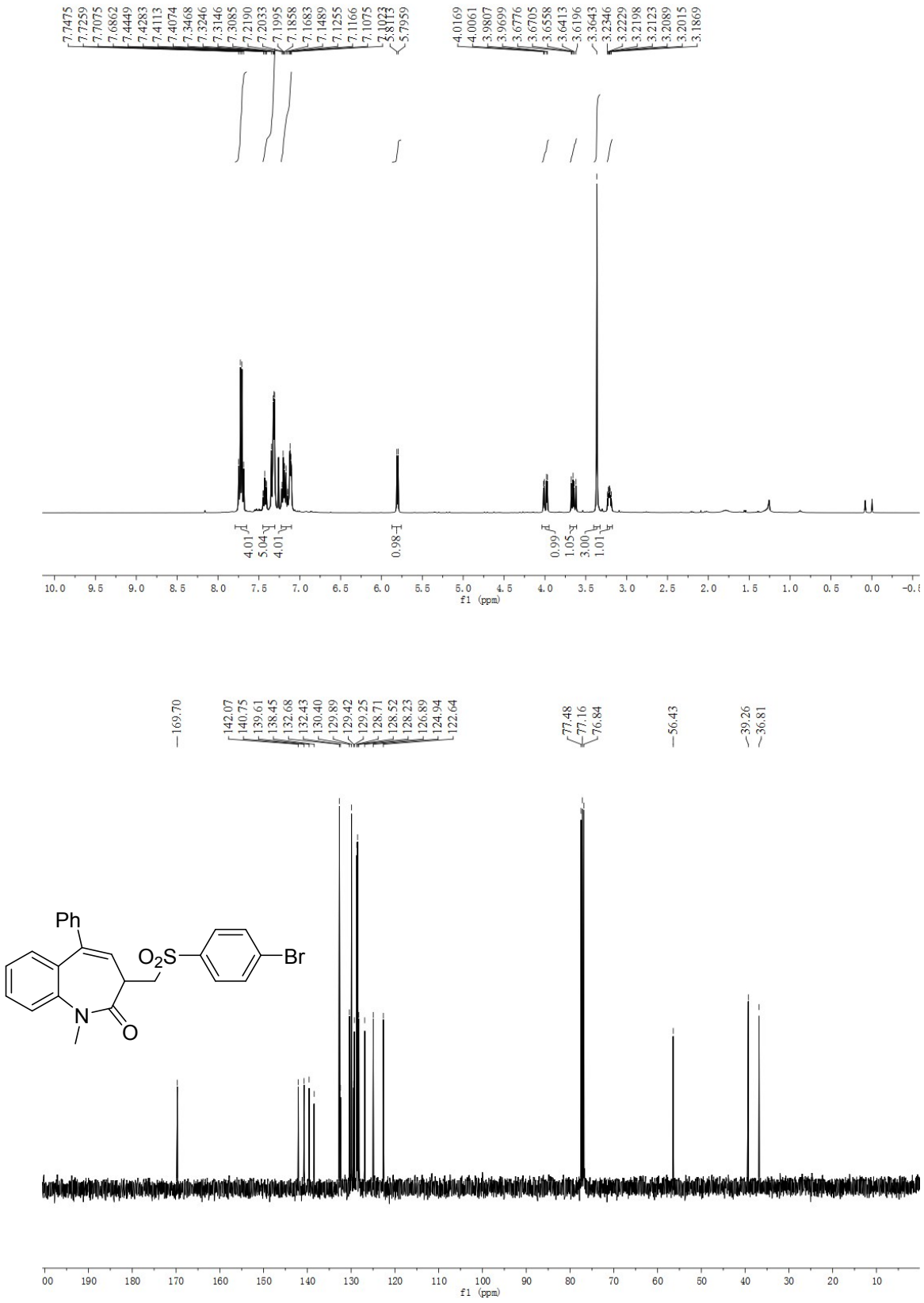




3-(((4-bromophenyl)sulfonyl)methyl)-1-methyl-5-phenyl-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ah):



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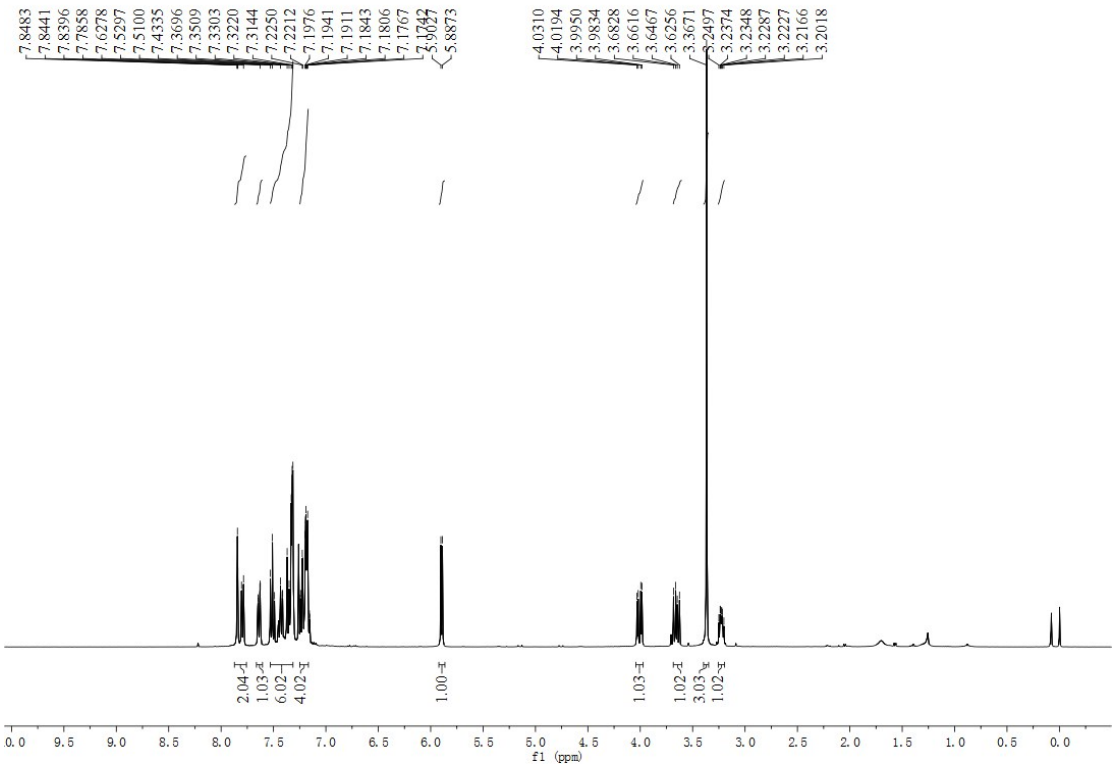
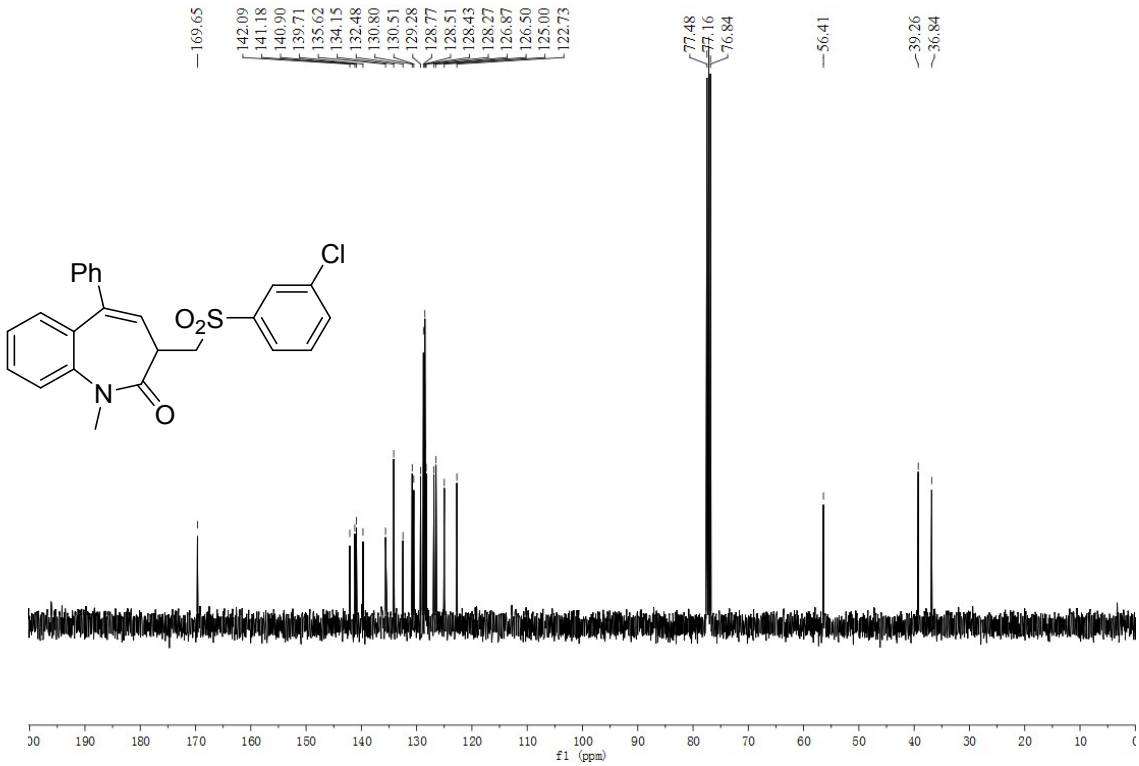
Cl





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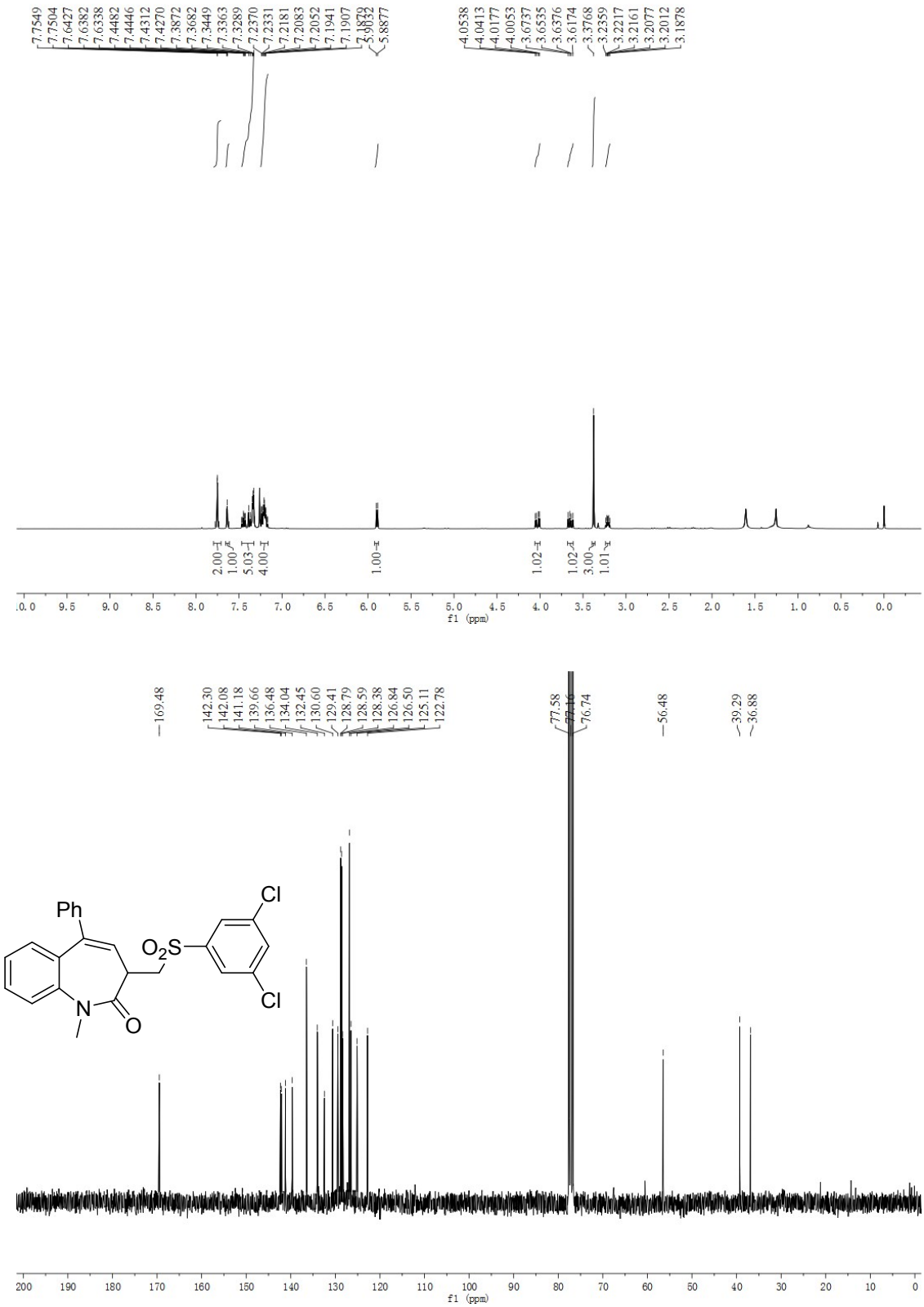
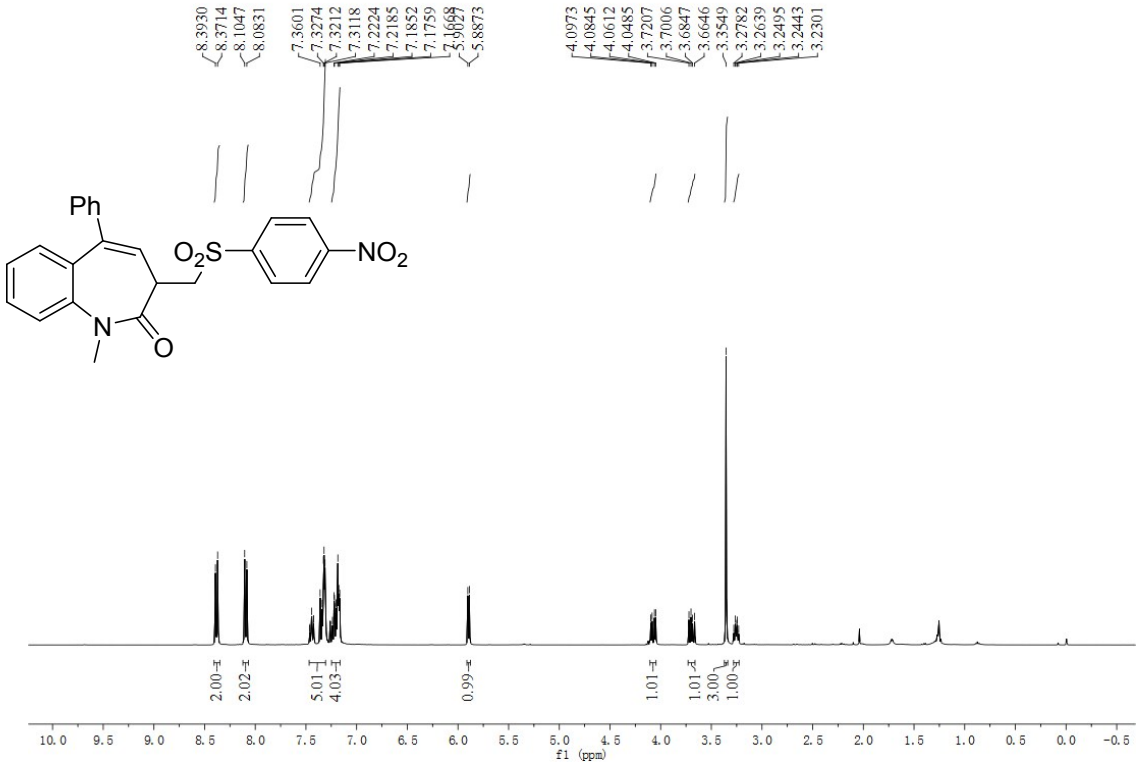
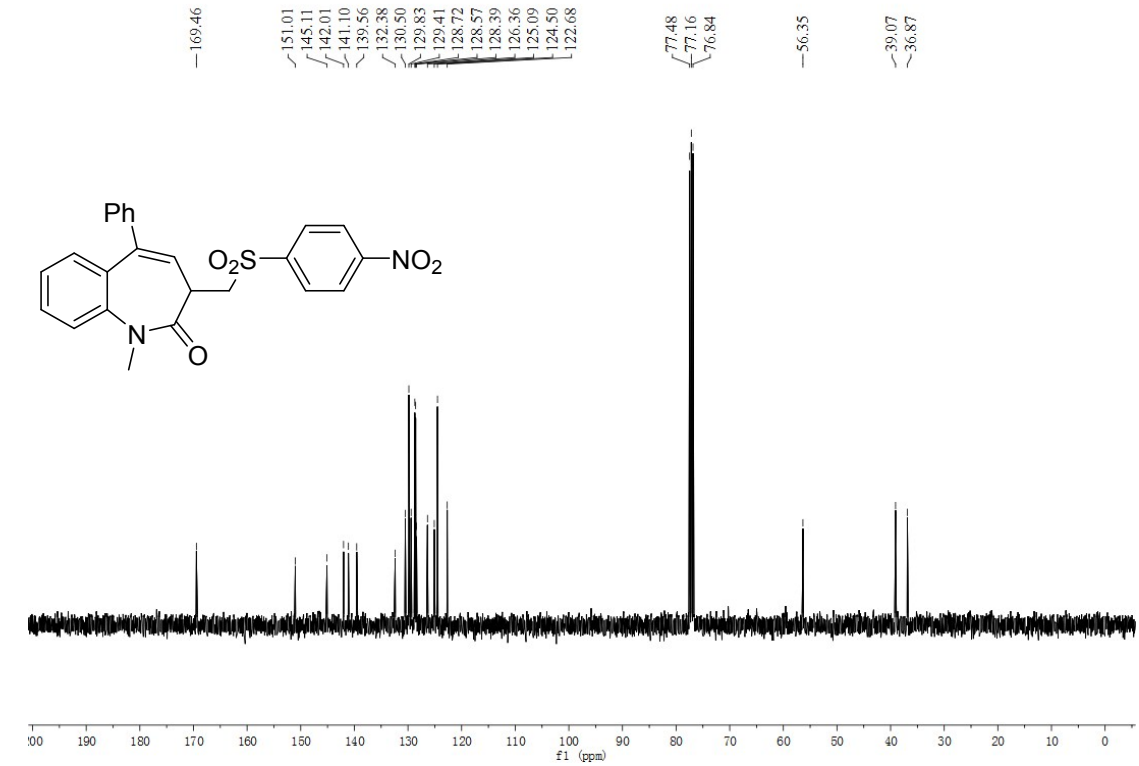


1-methyl-3-(((4-nitrophenyl)sulfonyl)methyl)-5-phenyl-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3ak):





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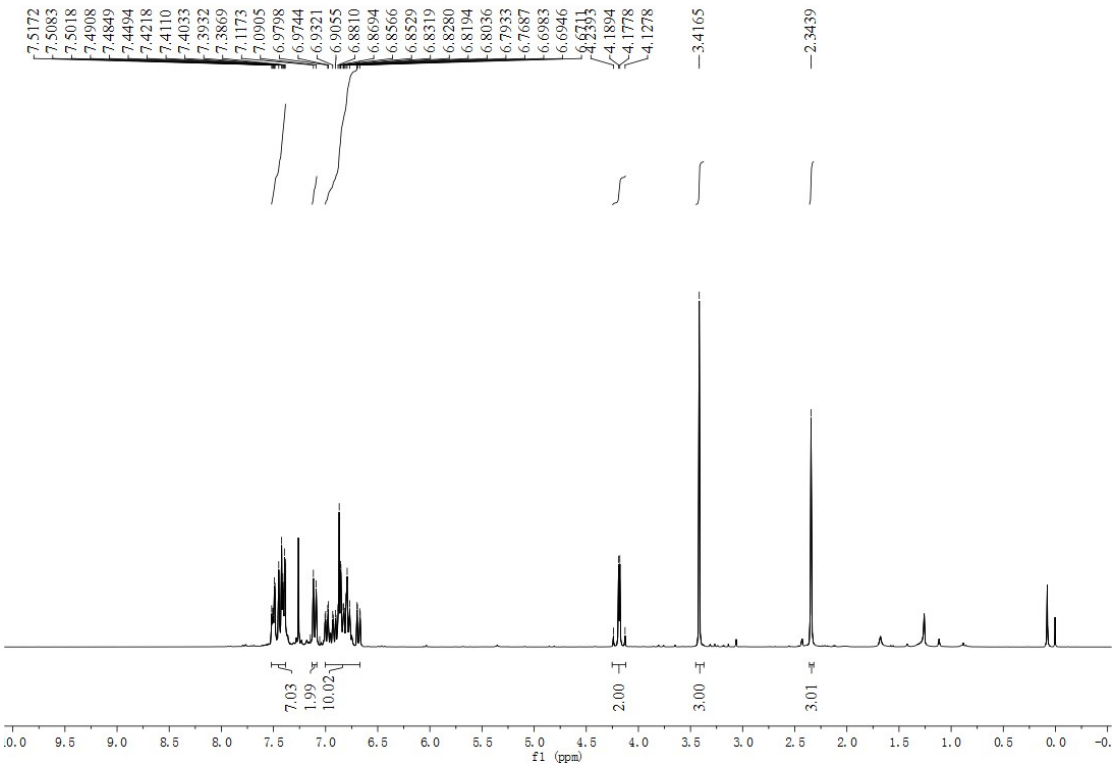
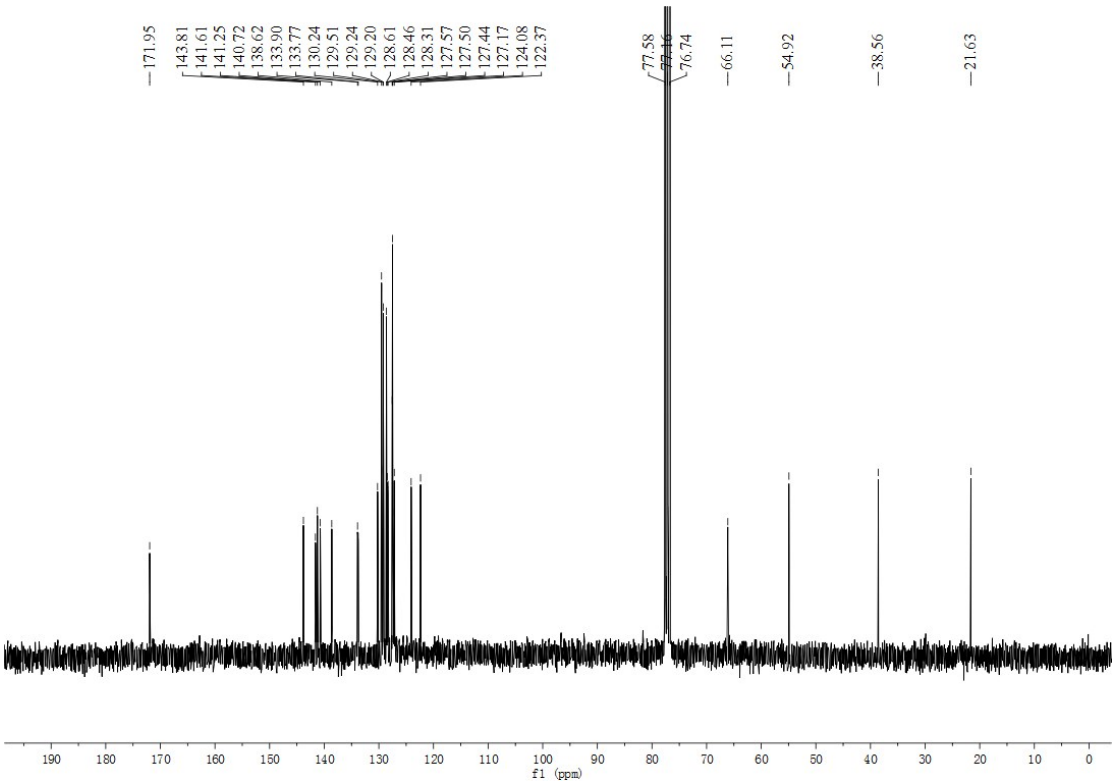
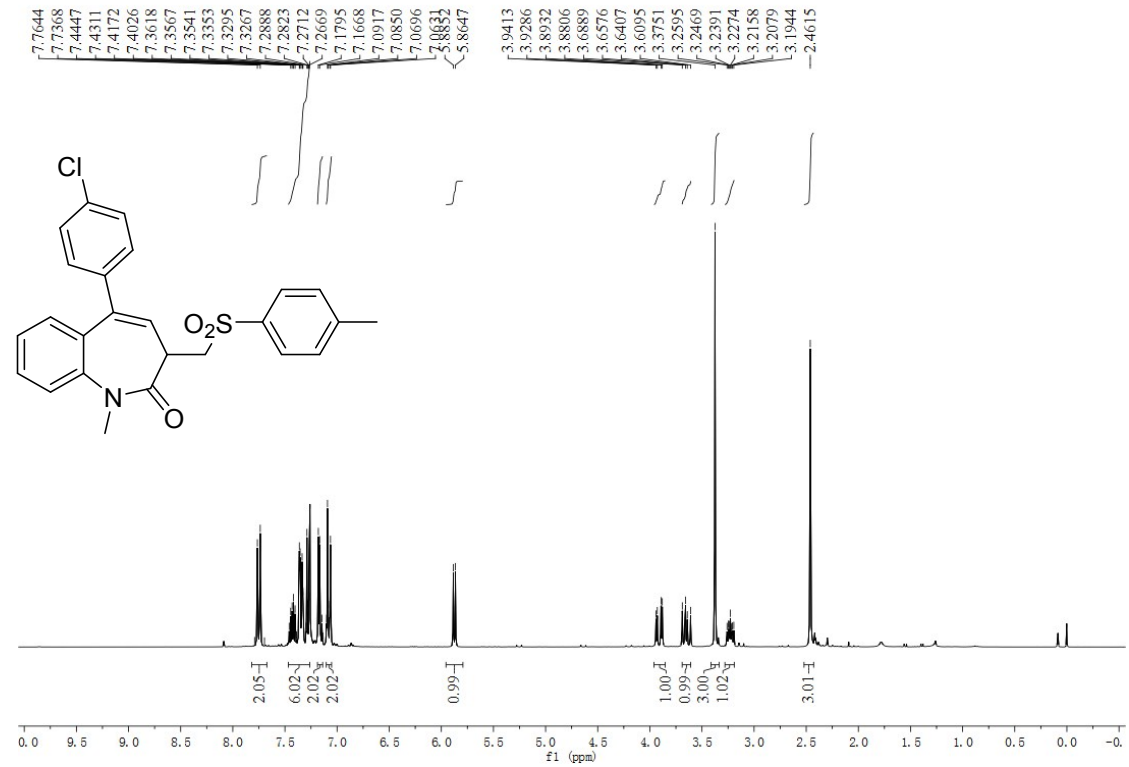
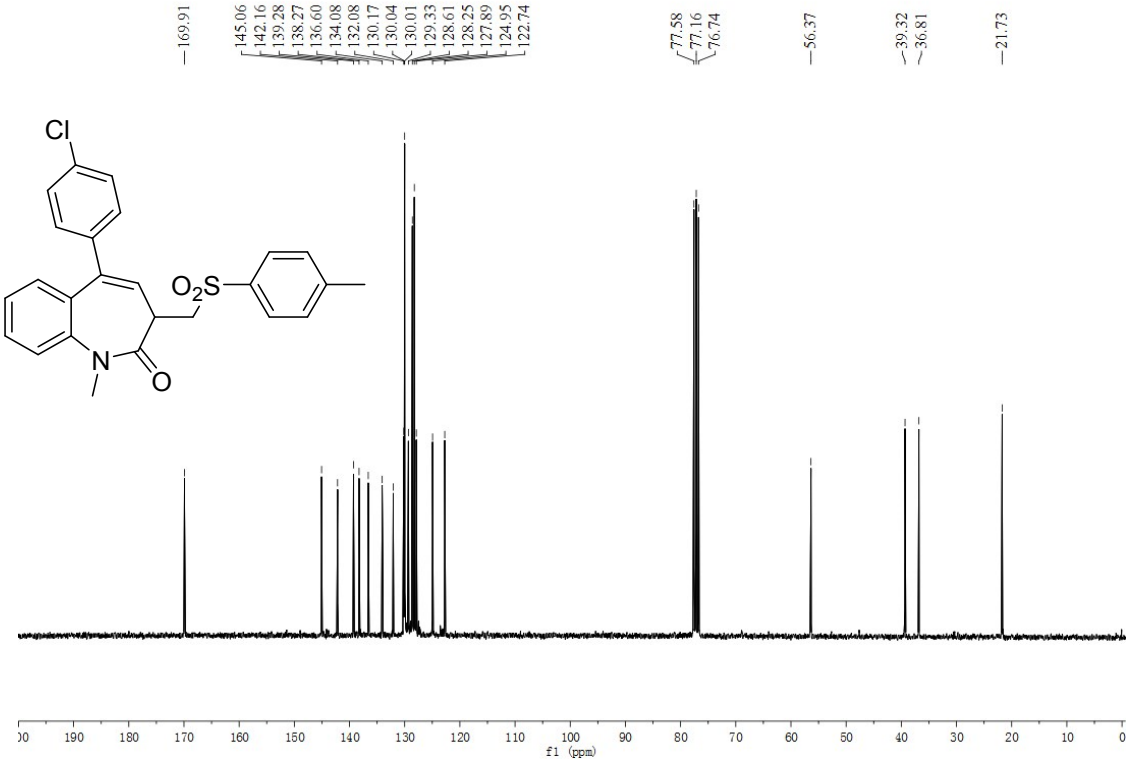


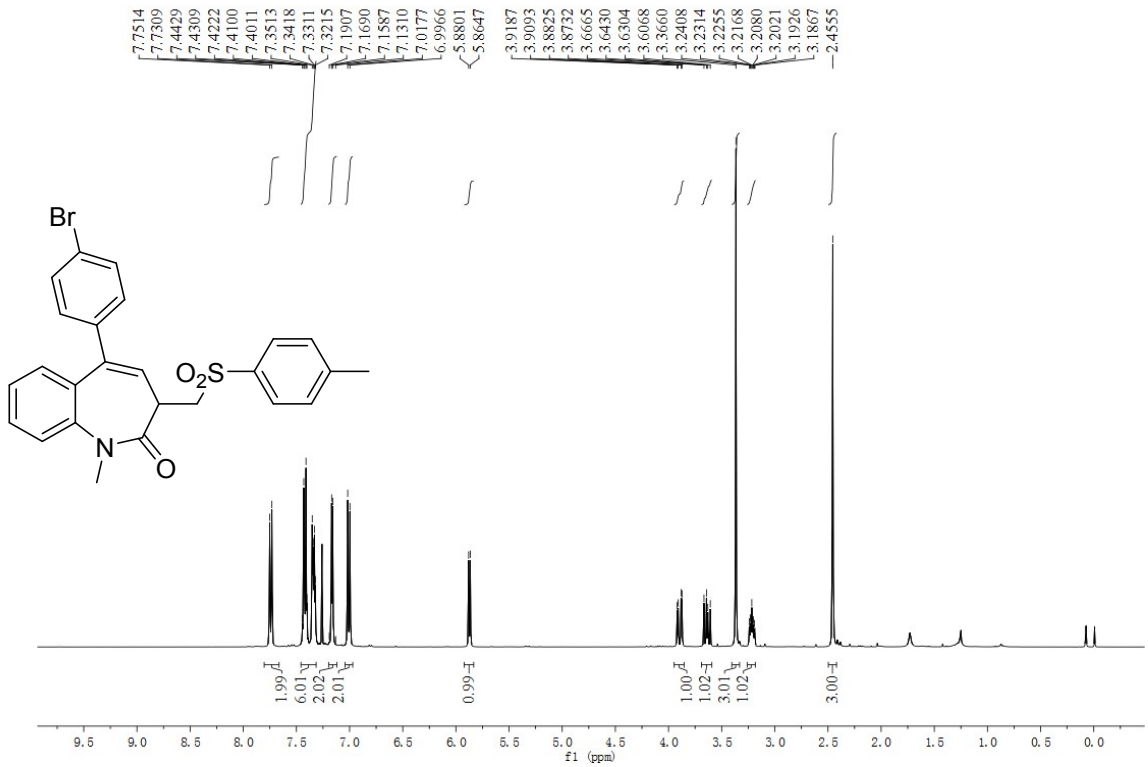


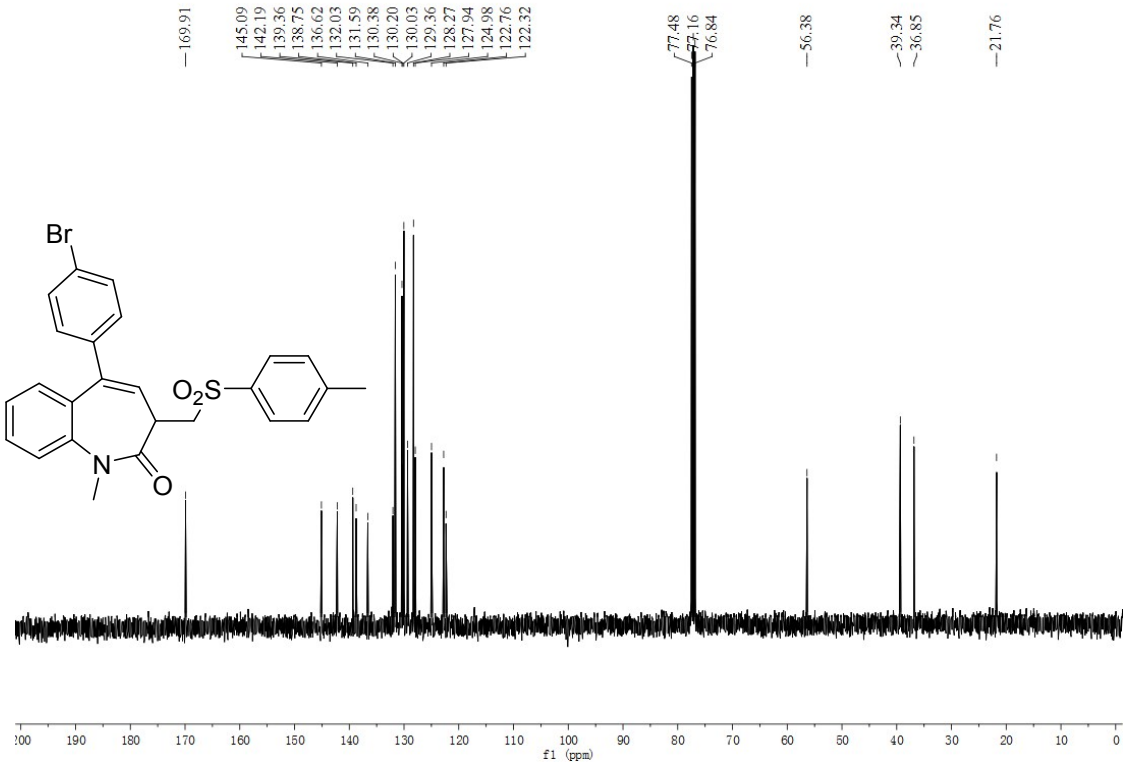
5-(4-chlorophenyl)-1-methyl-3-(tosylmethyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ca):



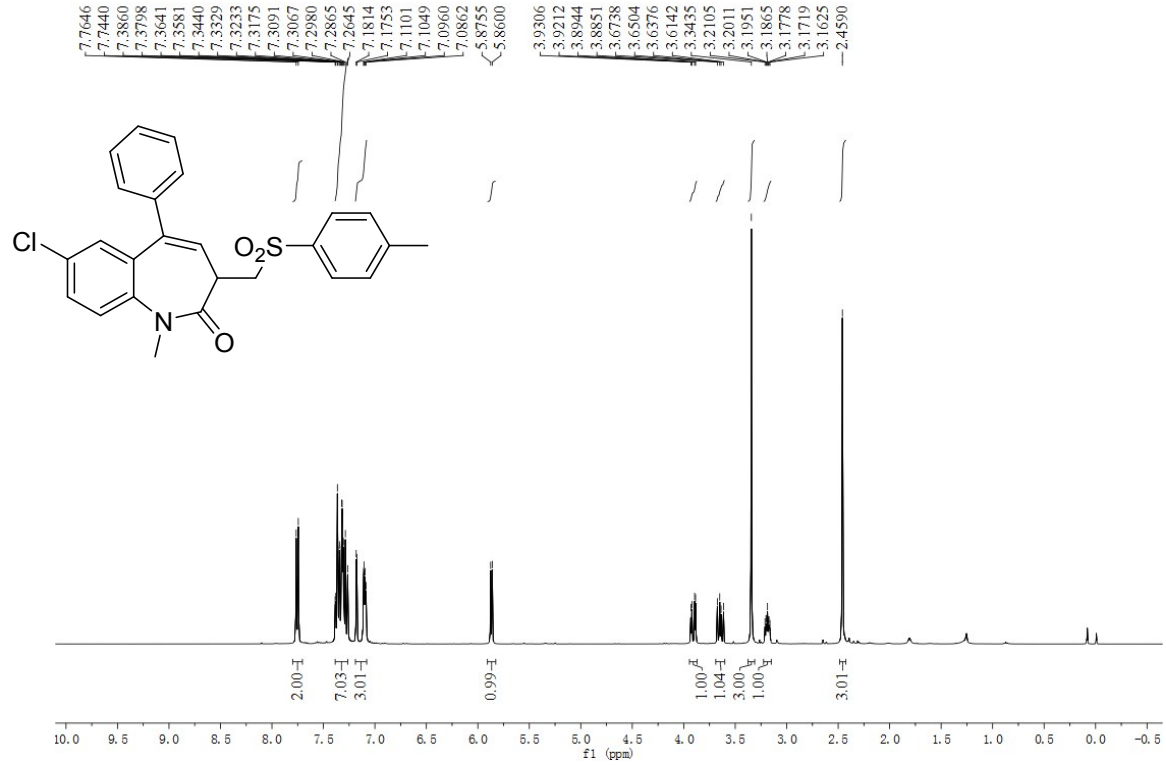


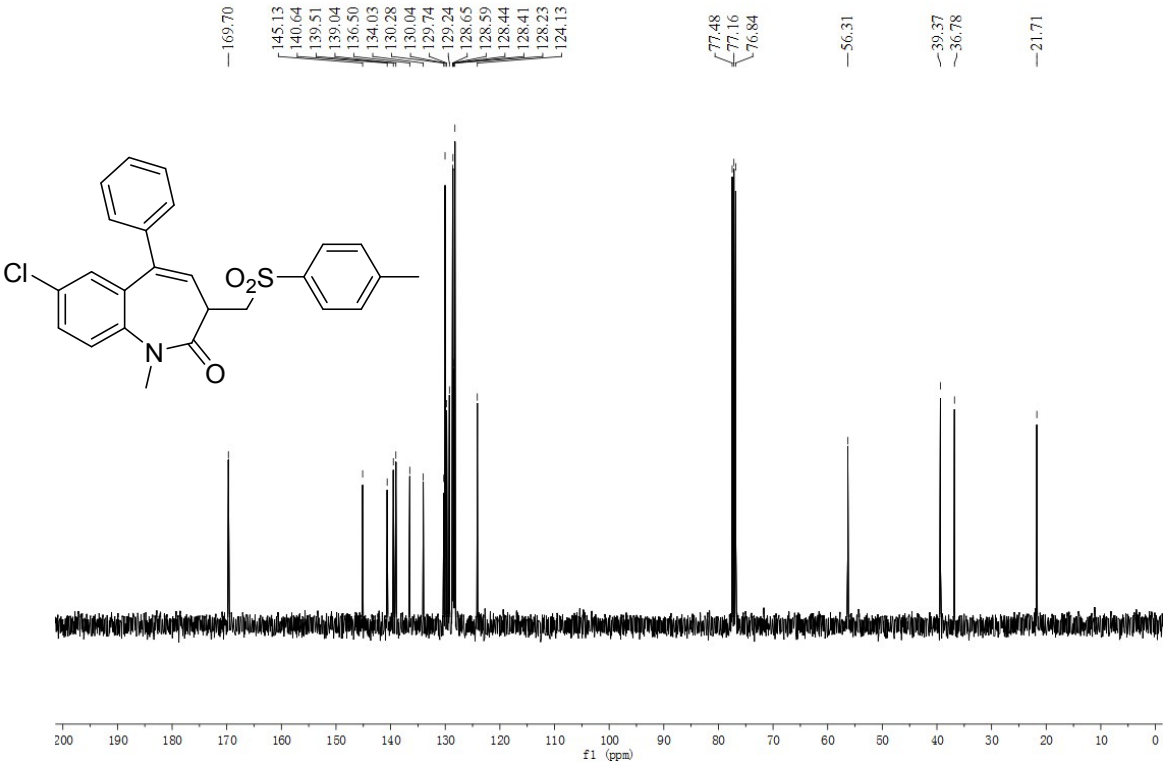
5-(4-bromophenyl)-1-methyl-3-(tosylmethyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3da):



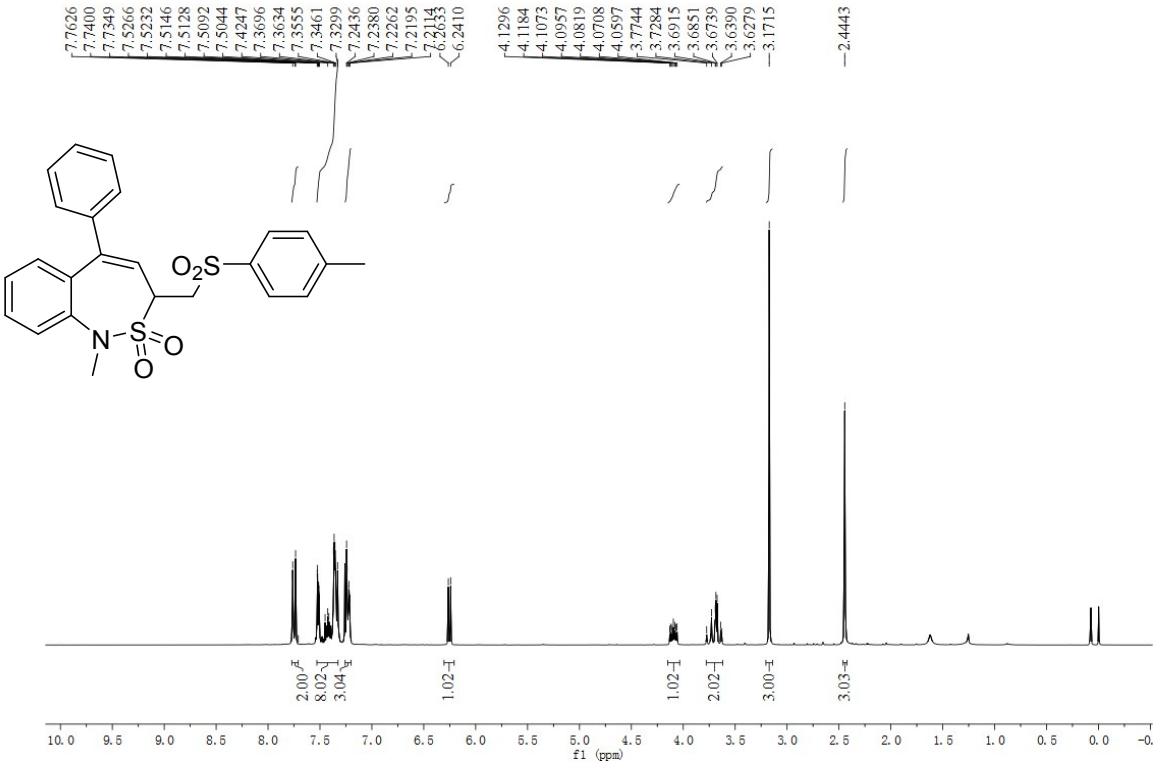


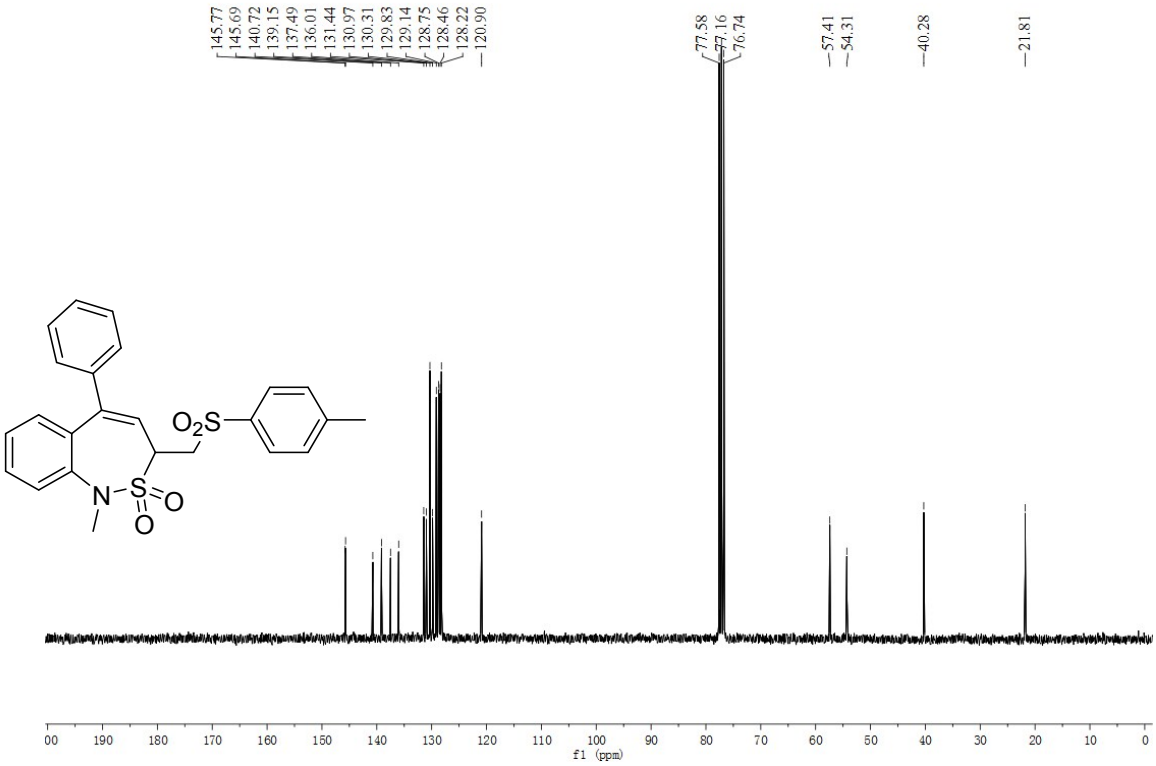
7-chloro-1-methyl-5-phenyl-3-(tosylmethyl)-1,3-dihydro-2*H*-benzo[*b*]azepin-2-one (3ea):





1-methyl-5-phenyl-3-(tosylmethyl)-1,3-dihydrobenzo[*c*][1,2]thiazepine 2,2-dioxide (4):


7.7626
7.7400
7.7349
7.5266
7.5232
7.5146
7.5128
7.5092
7.5044
7.4247
7.3696
7.3634
7.3555
7.3461
7.3299
7.2436
7.2380
7.2262
7.2195
7.2114
6.2633
6.2410
4.1296
4.1184
4.1073
4.0957
4.0819
4.0708
4.0597
3.7744
3.7284
3.6915
3.6851
3.6739
3.6390
3.6279
3.1715
2.4443
O2S
N
S
O
O
2.00
8.02
3.04
1.02
1.02
2.02
3.00
3.03
f1 (ppm)


145.77
145.69
140.72
139.15
137.49
136.01
131.44
130.97
130.31
129.83
129.14
128.75
128.46
128.22
120.90
77.58
77.16
76.74
57.41
54.31
40.28
21.81
O2S
N
S
O
O
f1 (ppm)