Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Stereoselective [4+3] annulation of azadienes and ethyl 4-bromo-3-oxobutanoate: construction of benzindeno-fused azepine derivatives

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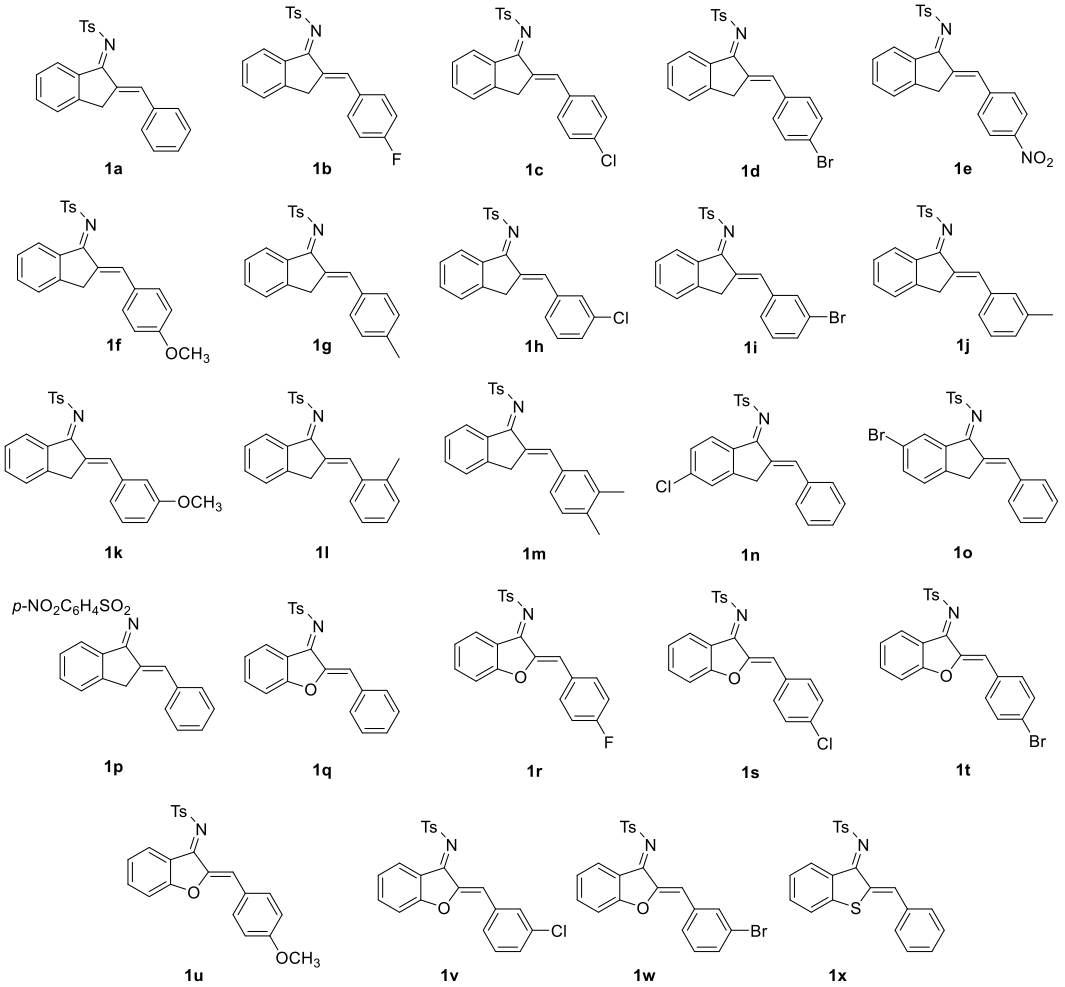
1. General information and materials

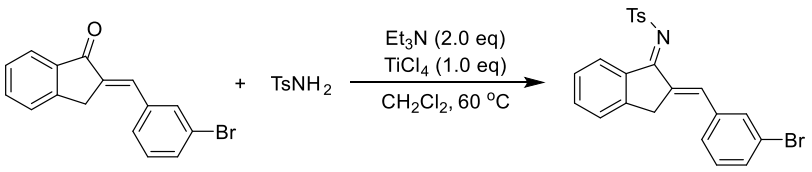
All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers (Aldrich, TCI or Alfa Aesar) and used without further purification. All solvents were purified and dried according to standard methods prior to use. TLC monitored all reactions with silica gel-coated plates. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H- and ^{13}C NMR spectra were recorded at ambient temperature on Bruker 400 instruments. All spectra were referenced to $CDCl_3$ (^{1}H δ 7.26 ppm and ^{13}C NMR δ 77.00 ppm) and DMSO-d_6 (^{1}H NMR, δ 2.50 ppm and ^{13}C NMR, δ 39.52 ppm).. ^{19}F NMR spectrum was recorded on Bruker 400 (376 MHz) spectrometers with $CFCl_3$ as external standard. HRMS were obtained on Waters Xevo Q-TOF MS with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. IR were measured on a Perkin-Elmer 983G apparatus. Compound **1** was synthesized according to the reported method[1-2].

2. The structure of azadienes 1



General procedure for the synthesis of **1**

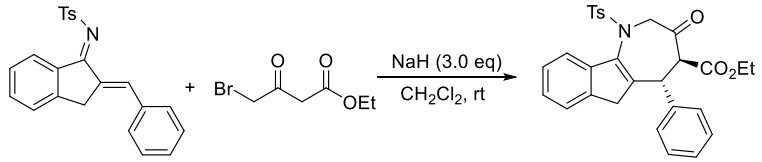
1i as an example



To a stirred solution of *p*-toluenesulfonamide (856.07 mg, 5.00 mmol) and enone (1.50 g, 5.00 mmol) in CH_2Cl_2 (20 mL) were successively added Et_3N (1.01 g, 10.00 mmol) and $TiCl_4$ (0.94 g, 5.00 mmol) at 0 °C with continuous stirring. The resulting mixture was refluxed at 60 °C. After the reaction was complete (monitored by TLC), then cooled to room temperature, quenched with water and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with water (3 × 10 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1:5) to afford **1i**.

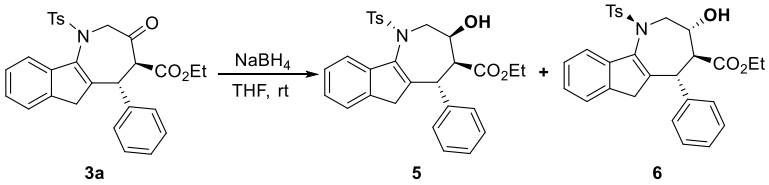
3. General procedure for the synthesis of 3 and 4

3a as an example



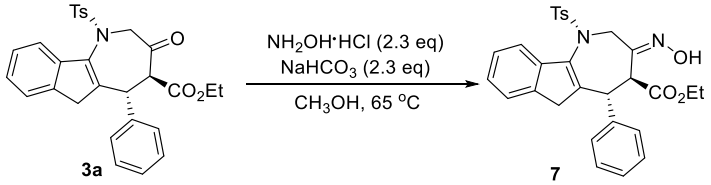
Under Ar atmosphere, **1a** (74.69 mg, 0.20 mmol, 1.0 eq) and **2a** (107.52 mg, 0.50 mmol, 2.5 eq) were dissolved in CH_2Cl_2 4 mL. To the above reaction mixture, NaH (14.40 mg, 0.60 mmol, 3.0 eq) was added. The reaction mixture was stirred at room temperature for 5–14 h. After the reaction was complete (monitored by TLC), the mixture was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The reside was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) to give **3a** (93 mg, 93%) as a white solid.

4. Synthetic procedure for 5 and 6



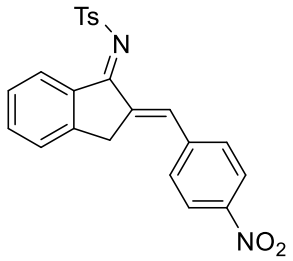
Under an Ar atmosphere, to a THF (4.0 mL) solution of 3a (100.32 mg, 0.20 mmol, 1.0 eq) were added $NaBH_4$ (7.57 mg, 0.20 mmol, 1.0 eq). The reaction mixture was stirred at room temperature for 10 min. After the reaction was complete (monitored by TLC), the solvent was removed in vacuum. The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) to give **5** (55 mg, 55%) and **6** (25 mg, 25%).

5. Synthetic procedure for 7



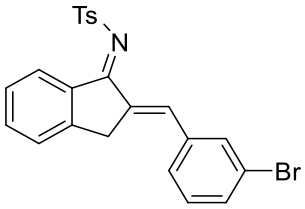
To a solution of **3a** (75.24 mg, 0.15 mmol, 1.0 eq) in 2.0 mL MeOH was added $NaHCO_3$ (28.98 mg, 0.35 mmol, 2.3 eq) and NH_2OH•HCl (23.97 mg, 0.35 mmol, 2.3 eq), the mixture was stirred at 65 °C for 10 h. Then the reaction mixture was allowed to cool to room temperature, the solvent was evaporated and the residue was purified by column chromatography to give **7** (40 mg, 52%) as a white solid.

6. Characterization of all new compounds



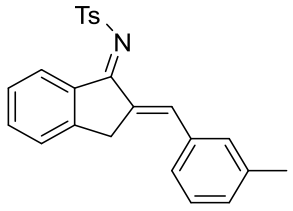
4-methyl-*N*-((*Z*)-2-((*E*)-4-nitrobenzylidene)-2,3-dihydro-1*H*-inden-1-ylidene)benzenesulfonamide (1e)

Yellow solid: 810 mg (yield 39%); mp 162-164 °C; IR (KBr) 3081, 1532, 1313, 1146, 1088, 840, 711, 565 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.27 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.79 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.08 (s, 2H), 2.48 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.7, 149.9, 147.6, 143.3, 141.5, 140.4, 139.5, 135.6, 131.0, 130.8, 129.5, 128.3, 126.9, 125.7, 124.0, 34.1, 21.7 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{23}H_{19}N_2O_4S^+$ 419.1060, found 419.1057.



***N*-((*Z*)-2-((*E*)-3-bromobenzylidene)-2,3-dihydro-1*H*-inden-1-ylidene)-4-methylbenzenesulfonamide (1i)**

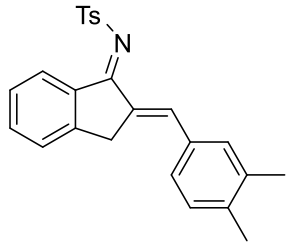
Yellow solid: 650 mg (yield 29%); mp 176-178 °C; IR (KBr) 3056, 1546, 1296, 1145, 1085, 846, 732, 670 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 6.4 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.75 – 7.67 (m, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.47 (m, 5H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 1H), 4.03 (s, 2H), 2.48 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.2, 150.2, 143.1, 139.8, 137.8, 137.4 135.3, 133.2, 132.5, 130.6, 130.4, 129.4, 129.1, 128.1, 126.8, 125.7, 123.0, 34.1, 21.7 ppm. HRMS (ESI-TOF) *m/z* $[M +H]^+$ calcd for $C_{23}H_{19}BrNO_2S^+$ 452.0314, found 452.0325.



4-methyl-*N*-((*Z*)-2-((*E*)-3-methylbenzylidene)-2,3-dihydro-1*H*-inden-1-ylidene)benzenesulfonamide (1j)

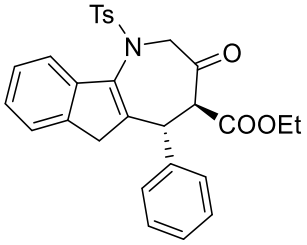
Yellow solid: 435 mg (yield 22%); mp 176-178 °C; IR (KBr) 2915, 1541, 1289, 1139, 1082, 863, 717, 556 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.80 (s, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 4.05 (s, 2H), 2.47 (s, 3H), 2.40 (s,

3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.8, 150.4, 142.9, 140.1, 138.6, 136.1, 135.7, 135.3, 135.0, 134.4, 131.7, 130.7, 130.4, 129.4, 128.8, 127.9, 127.8, 126.8, 125.6, 34.3, 21.6, 21.5 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{22}NO_2S^+$ 388.1366, found 388.1372.



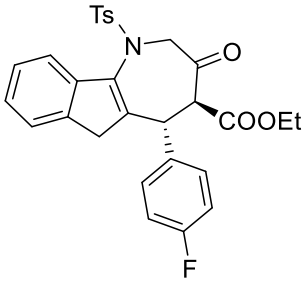
***N*-((*Z*)-2-((*E*)-3,4-dimethylbenzylidene)-2,3-dihydro-1*H*-inden-1-ylidene)-4-methylbenzenesulfonamide (1m)**

Yellow solid: 448 mg (yield 22%); mp 182-184 °C; IR (KBr) 3244, 3124, 1532, 1299, 1147, 1085, 853, 723, 557 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.80 (s, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 4H), 7.19 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 2H), 2.47 (s, 3H), 2.30 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.9, 150.4, 142.8, 140.2, 139.3, 137.2, 135.9, 135.1, 134.9, 134.6, 133.0, 132.4, 130.35, 130.26, 129.4, 128.4, 127.9, 126.8, 125.6, 34.4, 21.6, 19.90, 19.88 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{25}H_{24}NO_2S^+$ 402.1522, found 402.1522.



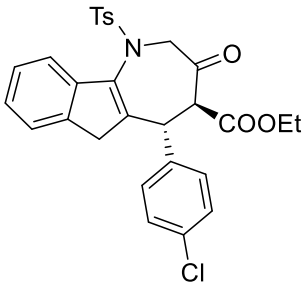
Ethyl 3-oxo-5-phenyl-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3a)

White solid: 94 mg (yield 94%); mp 182-184 °C; 2965, 1748, 1716, 1370, 1340, 1165, 1090, 849, 769, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.34 – 7.25 (m, 2H), 7.26 – 7.21 (m, 2H), 7.20 – 7.12 (m, 2H), 7.06 – 7.00 (m, 1H), 4.90 (d, *J* = 18.4 Hz, 1H), 4.85 (d, *J* = 11.6 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 4.15 (d, *J* = 18.4 Hz, 1H), 4.07 – 3.94 (m, 2H), 3.11 (s, 2H), 2.50 (s, 3H), 1.06 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 202.2, 167.9, 144.8, 143.3, 141.5, 140.8, 140.6, 137.1, 136.7, 130.3, 128.8, 128.7, 127.6, 127.6, 126.4, 125.8, 123.7, 120.1, 61.7, 61.7, 59.8, 46.8, 39.7, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{29}H_{28}NO_5S^+$ 502.1683, found 502.1664.



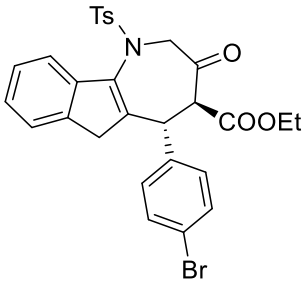
Ethyl 5-(4-fluorophenyl)-3-oxo-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3b)

White solid: 95 mg (yield 91%); mp 154-156 °C; I2981, 1746, 1722, 1408, 1336, 1238, 1160, 846, 815, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.36 (m, 4H), 7.26 – 7.21 (m, 1H), 7.18 – 7.12 (m, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.94 – 6.87 (m, 1H), 4.93 (d, *J* = 5.6 Hz, 1H), 4.89 (s, 1H), 4.31 (d, *J* = 12.0 Hz, 1H), 4.12 (d, *J* = 18.4 Hz, 1H), 4.09 – 3.95 (m, 2H), 3.11 (s, 2H), 2.50 (s, 3H), 1.09 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.05 168.0, 162.1 (d, *J* = 245.1 Hz), 144.8, 143.3, 141.3, 140.7, 137.0 (d, *J* = 40.8 Hz), 136.44, 136.41, 130.5 (d, *J* = 81.0 Hz), 130.3, 127.6, 126.4, 125.9, 123.8, 120.0, 115.7 (d, *J* = 21.3 Hz), 61.7, 61.3, 59.4, 46.0, 39.5, 21.7, 14.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.55 ppm. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{29}H_{27}FNO_5S^+$ 520.1588, found 520.1583.



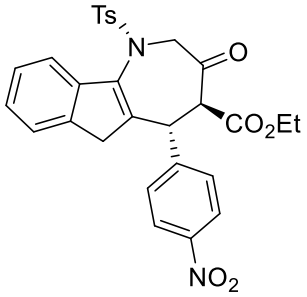
Ethyl 5-(4-chlorophenyl)-3-oxo-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3c)

White solid: 88 mg (yield 82%); mp 153-155 °C; IR (KBr) 2973, 1747, 1718, 1367, 1341, 1161, 1129, 849, 769, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.19 – 7.10 (m, 2H), 6.97 – 6.86 (m, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.88 (d, *J* = 5.2 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 4.13 (d, *J* = 18.4 Hz, 1H), 4.09 – 3.96 (m, 2H), 3.11 (s, 2H), 2.51 (s, 3H), 1.11 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.0, 168.0, 144.9, 142.9, 141.3, 140.7, 139.1, 137.2, 137.0, 133.5, 130.3, 130.2, 129.0, 127.6, 126.4, 126.0, 123.8, 120.0, 61.7, 61.4, 59.2, 46.0, 39.5, 21.7, 14.0 ppm. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{29}H_{27}ClNO_5S^+$ 536.1293, found 536.1287.



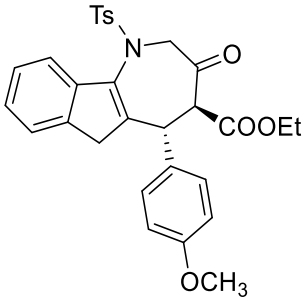
Ethyl 5-(4-bromophenyl)-3-oxo-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3d)

White solid: 96 mg (yield 83%); mp 159-161 °C; IR (KBr) 2983, 1755, 1730, 1711, 1362, 1261, 1163, 1089, 849, 768, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.39 (m, 4H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.19 – 7.12 (m, 2H), 6.96 – 6.89 (m, 1H), 4.92 (d, *J* = 12.8 Hz, 1H), 4.88 (d, *J* = 6.4 Hz, 1H), 4.28 (d, *J* = 12.4 Hz, 1H), 4.13 (d, *J* = 18.4 Hz, 1H), 4.10 – 3.95 (m, 2H), 3.11 (s, 2H), 2.51 (s, 3H), 1.11 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.0, 167.9, 144.9, 142.8, 141.3, 140.7, 139.7, 137.2, 137.1, 132.0, 130.6, 130.3, 127.6, 126.4, 126.0, 123.8, 121.7, 120.0, 61.7, 61.4, 59.1, 46.1, 39.5, 21.7, 14.0 ppm. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{29}H_{27}BrNO_5S^+$ 580.0788, found 580.0784.



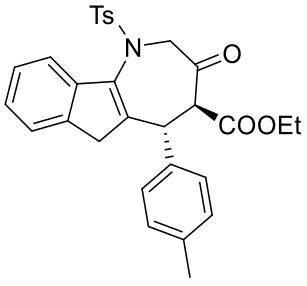
Ethyl 5-(4-nitrophenyl)-3-oxo-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3e)

White solid: 77 mg (yield 70%); mp 169-171 °C; IR (KBr) 2961, 1742, 1519, 1345, 1158, 834, 694, 561 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.19 – 7.10 (m, 2H), 6.79 (d, *J* = 6.8 Hz, 1H), 5.09 (d, *J* = 11.6 Hz, 1H), 4.97 (d, *J* = 18.4 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.17 – 3.97 (m, 3H), 3.20 – 3.02 (m, 2H), 2.52 (s, 3H), 1.12 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.6, 167.9, 147.9, 147.4, 145.0, 141.8, 140.9, 140.6, 137.8, 137.3, 130.3, 130.0, 127.6, 126.6, 126.3, 124.1, 123.9, 119.9, 61.8, 61.7, 58.6, 46.2, 39.4, 21.8, 14.0 ppm. HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{29}H_{27}N_2O_7S^+$ 547.1533, found 547.1548.



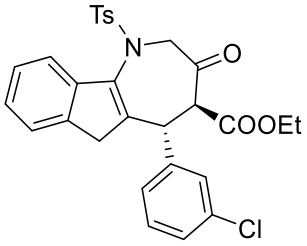
Ethyl-(4-methoxyphenyl)-3-oxo-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3f)

White solid: 64 mg (yield 60%); mp 145-147 °C; IR (KBr) 2930, 1748, 1718, 1511, 1258, 1178, 1161, 816, 671, 548 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.20 – 7.10 (m, 2H), 7.03 – 6.97 (m, 1H), 6.86 – 6.79 (m, 2H), 4.89 (d, *J* = 18.4 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.25 (d, *J* = 11.6 Hz, 1H), 4.13 (d, *J* = 18.4 Hz, 1H), 4.07 – 3.95 (m, 2H), 3.78 (s, 3H), 3.12 (d, *J* = 2.2 Hz, 2H), 2.50 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.0, 168.0, 144.9, 142.9, 141.3, 140.7, 139.1, 137.2, 137.0, 133.5, 130.3, 130.2, 129.0, 127.6, 126.4, 126.02, 125.99, 123.8, 120.0, 61.7, 61.4, 59.2, 46.0, 39.5, 21.7, 14.0 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{30}H_{30}NO_6S^+$ 532.1788, found 532.1797.



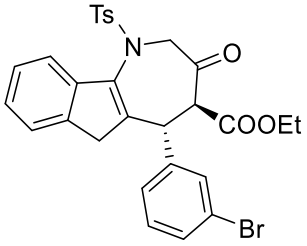
Ethyl 3-oxo-5-(*p*-tolyl)-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3g)

White solid: 100 mg (yield 97%); mp 162-164 °C; IR (KBr) 2981, 1737, 1708, 1370, 1341, 1272, 1162, 1090, 813, 768, 670 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 3H), 7.16 (t, *J* = 6.2 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.2 Hz, 1H), 4.89 (d, *J* = 18.4 Hz, 1H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.25 (d, *J* = 12.0 Hz, 1H), 4.14 (d, *J* = 18.4 Hz, 1H), 4.08 – 3.94 (m, 2H), 3.11 (s, 2H), 2.50 (s, 3H), 2.31 (s, 3H), 1.07 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.3, 168.0, 144.7, 143.6, 141.6, 140.8, 137.6, 137.2, 137.1, 136.4, 130.3, 129.4, 128.5, 127.7, 126.3, 125.8, 123.7, 120.1, 61.6, 61.1, 59.4, 46.4, 39.6, 21.7, 21.1, 13.9 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{30}H_{30}NO_5S^+$ 516.1839, found 516.1840.



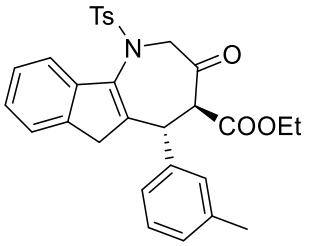
Ethyl 5-(3-chlorophenyl)-3-oxo-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-b]azepine-4-carboxylate (3h)

White solid: 80 mg (yield 75%); mp 195-197 °C; IR (KBr) 2945, 1744, 1711, 1367, 1263, 1169, 1091, 817, 767, 668 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.37 (s, 1H), 7.33 – 7.28 (m, 1H), 7.26 – 7.21 (m, 3H), 7.20 – 7.15 (m, 2H), 7.05 – 6.99 (m, 1H), 4.92 (d, *J* = 18.8 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.26 (d, *J* = 12.0 Hz, 1H), 4.15 (d, *J* = 18.4 Hz, 1H), 4.09 – 3.98 (m, 2H), 3.12 (s, 2H), 2.49 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.9, 167.7, 144.9, 142.5, 142.3, 141.4, 140.7, 137.2, 137.0, 134.5, 130.4, 130.1, 128.7, 127.9, 127.6, 127.1, 126.5, 126.0, 123.8, 120.3, 61.7, 61.4, 59.1, 46.3, 39.5, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{29}H_{27}ClNO_5S^+$ 536.1293, found 536.1271.



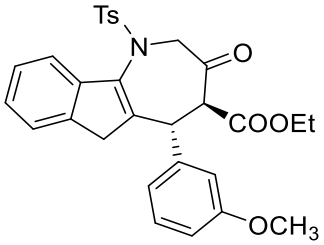
Ethyl 5-(3-bromophenyl)-3-oxo-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3i)

White solid: 62 mg (yield 53%); mp 186-188 °C; IR (KBr) 2945, 1743, 1711, 1367, 1264, 1169, 1092, 767, 668, 573 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.22 – 7.14 (m, 3H), 7.06 – 7.00 (m, 1H), 4.91 (d, *J* = 18.4 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.25 (d, *J* = 12.0 Hz, 1H), 4.15 (d, *J* = 18.8 Hz, 1H), 4.09 – 3.94 (m, 2H), 3.11 (s, 2H), 2.49 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.9, 167.7, 144.9, 142.8, 142.2, 141.4, 140.7, 137.3, 137.0, 131.5, 130.9, 130.4, 127.62, 127.56, 126.5, 126.0, 123.8, 122.7, 120.3, 61.6, 61.4, 59.2, 46.2, 39.5, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{29}H_{27}BrNO_5S^+$ 580.0788, found 580.0801.



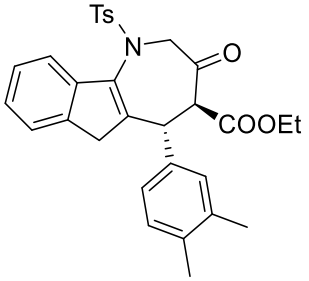
Ethyl 3-oxo-5-(*m*-tolyl)-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3j)

White solid: 100 mg (yield 97%); mp 176-178 °C; IR (KBr) 2911, 1746, 1712, 1367, 1264, 1170, 1093, 768, 702, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 6.8 Hz, 1H), 7.20 – 7.11 (m, 5H), 7.05 (t, *J* = 6.4 Hz, 2H), 4.89 (d, *J* = 18.8 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.24 (d, *J* = 11.6 Hz, 1H), 4.15 (d, *J* = 18.8 Hz, 1H), 4.07 – 3.94 (m, 4H), 3.11 (s, 2H), 2.49 (s, 3H), 2.33 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.3, 167.9, 144.7, 143.4, 141.6, 140.8, 140.5, 138.4, 137.1, 136.5, 130.3, 129.3, 128.6, 128.4, 127.6, 126.4, 125.8, 123.7, 120.1, 61.6, 61.1, 59.4, 46.7, 39.6, 21.7, 21.5, 13.9 ppm. HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{30}NO_5S^+$ 516.1839, found 516.1845.



Eethyl 5-(3-methoxyphenyl)-3-oxo-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3k)

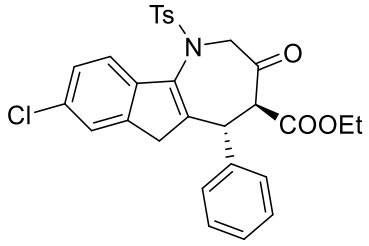
Yellow solid: 76 mg (yield 72%); mp 162-164 °C; IR (KBr) 2909, 1743, 1172, 1367, 1257, 1170, 1091, 770, 668, 579 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.17 – 7.11 (m, 2H), 7.07 (s, 1H), 6.98 – 6.89 (m, 2H), 6.78 (dd, *J* = 7.8, 2.2 Hz, 1H), 4.95 (d, *J* = 11.6 Hz, 1H), 4.90 (d, *J* = 18.4 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 4.12 (d, *J* = 18.4 Hz, 1H), 4.09 – 3.97 (m, 2H), 3.80 (s, 3H), 3.14 (d, *J* = 1.6 Hz, 2H), 2.50 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.3, 168.0, 160.0, 144.8, 143.6, 142.1, 141.5, 140.8, 137.3, 136.6, 130.3, 129.6, 127.6, 126.3, 125.8, 123.8, 121.1, 119.9, 113.8, 113.5, 61.7, 61.3, 59.3, 55.4, 46.7, 39.6, 21.7, 14.0 ppm. HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{30}NO_6S^+$ 532.1788, found 532.1775.



Ethyl 5-(3,4-dimethylphenyl)-3-oxo-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3m)

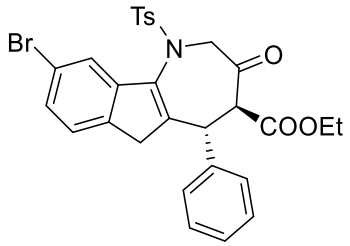
White solid: 99 mg (yield 93%); mp 158-160 °C; IR (KBr) 2912, 1744, 1720, 1369, 1340, 1267, 1162, 826, 815, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz,

2H), 7.24 – 7.12 (m, 4H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.03 (s, 2H), 4.87 (d, *J* = 18.8 Hz, 1H), 4.72 (d, *J* = 11.6 Hz, 1H), 4.21 (d, *J* = 10.8 Hz, 1H), 4.14 (d, *J* = 18.4 Hz, 1H), 4.08 – 3.93 (m, 2H), 3.11 (s, 2H), 2.49 (s, 3H), 2.24 (s, 3H), 2.21 (s, 3H), 1.07 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 202.4, 168.0, 144.7, 143.7, 141.7, 140.8, 138.0, 137.1, 136.9, 136.3, 135.8, 130.3, 129.9, 129.7, 127.6, 126.3, 126.0, 125.7, 123.7, 120.1, 61.6, 61.1, 59.5, 46.3, 39.6, 21.7, 19.9, 19.4, 13.9 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{31}H_{32}NO_5S^+$ 530.1996, found 530.2009.



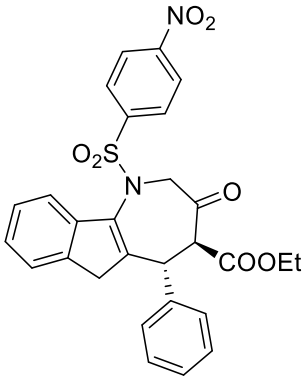
Ethyl 8-chloro-3-oxo-5-phenyl-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3n)

Yellow solid: 96 mg (yield 85%); mp 178-180 °C; IR (KBr) 2922, 1744, 1712, 1365, 1265, 1169, 1092, 817, 668, 594 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.26 – 7.21 (m, 1H), 7.19 (s, 1H), 7.15 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 4.90 (d, *J* = 18.8 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.26 (d, *J* = 12.0 Hz, 1H), 4.14 (d, *J* = 18.4 Hz, 1H), 4.05 – 3.95 (m, 2H), 3.09 (d, *J* = 2.8 Hz, 2H), 2.49 (s, 3H), 1.05 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 202.0, 167.8, 145.0, 143.6, 142.4, 140.3, 140.1, 136.9, 136.1, 131.9, 130.4, 128.8, 128.6, 127.7, 127.6, 126.7, 124.2, 121.1, 61.6, 61.2, 59.3, 46.7, 39.4, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{29}H_{27}ClNO_5S^+$ 536.1293, found 536.1301.



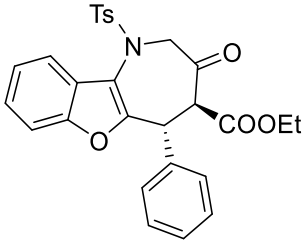
Ethyl 9-bromo-3-oxo-5-phenyl-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3o)

White solid: 110 mg (yield 95%); mp 113-115 °C; IR (KBr) 2974, 1744, 1616, 1360, 1346, 1269, 1161, 699, 672, 552 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.40 (m, 4H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.71 – 6.61 (m, 1H), 5.02 (s, 1H), 4.99 (d, *J* = 8.0 Hz, 1H), 4.30 (d, *J* = 11.6 Hz, 1H), 4.11 (d, *J* = 18.4 Hz, 1H), 4.07 – 3.96 (m, 1H), 3.06 (s, 1H), 2.52 (s, 2H), 1.07 (t, *J* = 7.2 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 202.2, 167.9, 145.7, 145.2, 143.3, 140.3, 139.5, 137.3, 135.6, 130.4, 128.9, 128.8, 128.5, 127.7, 127.6, 125.1, 123.1, 120.4, 61.8, 61.3, 59.2, 46.9, 39.3, 21.8, 13.9 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{29}H_{27}BrNO_5S^+$ 580.0788, found 580.0809.



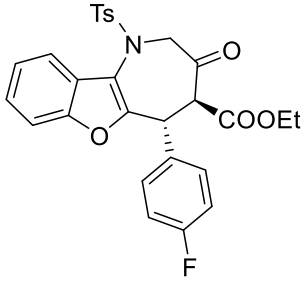
Ethyl 1-((4-nitrophenyl)sulfonyl)-3-oxo-5-phenyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (3p)

White solid: 73 mg (yield 69%); mp 171-173 °C; IR (KBr) 3096, 1737, 1713, 1532, 1371, 1350, 1167, 1091, 737, 626, 599 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.44 (m, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.29 – 7.26 (m, 1H), 7.24 (s, 1H), 7.20 – 7.11 (m, 2H), 6.75 (d, *J* = 7.2 Hz, 1H), 4.96 (d, *J* = 18.4 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 12.0 Hz, 1H), 4.21 (d, *J* = 18.4 Hz, 1H), 4.08 – 3.94 (m, 2H), 3.16 (s, 2H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.2, 167.6, 150.6, 145.7, 144.5, 140.8, 140.8, 140.1, 136.0, 128.9, 128.6, 127.9, 126.5, 126.2, 124.9, 124.1, 119.3, 61.8, 61.5, 59.4, 46.8, 39.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{29}H_{25}N_2O_7S^+$ 533.1377, found 533.1393.



Ethyl 3-oxo-5-phenyl-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine-4-carboxylate (4a)

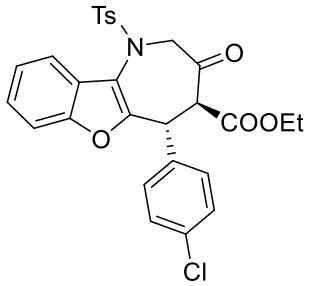
Yellow solid: 85 mg (yield 84%); mp 156-158 °C; IR (KBr) 2962, 1728, 1452, 1363, 1267, 1166, 1101, 755, 670, 544 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 6.8 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.26 (m, 4H), 7.22 – 7.11 (m, 2H), 5.16 (d, *J* = 11.6 Hz, 1H), 5.00 (d, *J* = 18.4 Hz, 1H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.16 (d, *J* = 18.4Hz, 1H), 4.10 – 3.99 (m, 2H), 2.51 (s, 2H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.9, 167.8, 144.9, 143.4, 141.2, 137.24, 137.20, 135.8, 130.3, 128.8, 128.7, 127.9, 127.7, 125.3, 124.4, 122.4, 122.1, 62.0, 61.4, 59.4, 46.1, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{28}H_{26}NO_6S^+$ 504.1475, found 504.1490.



Ethyl 5-(4-fluorophenyl)-3-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine-4-

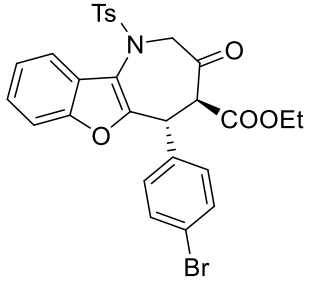
carboxylate (4b)

White solid: 85 mg (yield 81%); mp 174-176 °C; IR (KBr) 2964, 1748, 1606, 1517, 1344, 1235, 1169, 825, 677, 560 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.25 – 7.17 (m, 3H), 7.16 – 7.10 (m, 2H), 6.95 (t, *J* = 8.6 Hz, 2H), 5.12 (d, *J* = 18.8 Hz, 1H), 4.64 (q, *J* = 12.4 Hz, 2H), 4.23 (d, *J* = 18.4 Hz, 1H), 4.14 – 3.99 (m, 2H), 2.51 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.3, 167.0, 162.2 (d, *J* = 245.5 Hz), 153.6, 152.1, 145.1, 136.5, 133.8, 130.5 (d, *J* = 8.2 Hz), 130.4, 127.9, 125.5, 125.0, 123.4, 120.1, 119.2, 115.6 (d, *J* = 21.5 Hz), 111.6, 62.7, 61.7, 58.2, 43.7, 21.8, 14.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.10 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{28}H_{25}FNO_6S^+$ 522.1381, found 522.1384.



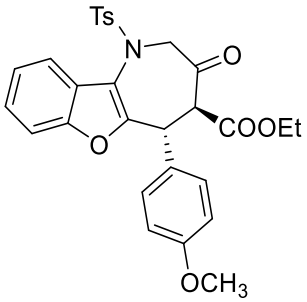
Ethyl 5-(4-chlorophenyl)-3-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine-4-carboxylate (4c)

White solid: 100 mg (yield 93%); mp 154-156 °C; IR (KBr) 2950, 1736, 1337, 1228, 1162, 1083, 814, 748, 672 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.28 (s, 1H), 7.26 – 7.20 (m, 3H), 7.20 – 7.12 (m, 4H), 5.12 (d, *J* = 18.8 Hz, 1H), 4.62 (q, *J* = 12.1 Hz, 2H), 4.24 (d, *J* = 18.58 Hz, 1H), 4.15 – 3.98 (m, 2H), 2.51 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.2, 167.0, 153.6, 151.8, 145.1, 136.6, 136.4, 133.8, 130.4, 130.2, 128.9, 127.9, 125.5, 125.0, 123.4, 120.1, 119.3, 111.6, 62.9, 61.7, 57.9, 43.8, 21.8, 14.0 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{28}H_{25}ClNO_6S^+$ 538.1086, found 538.1072.



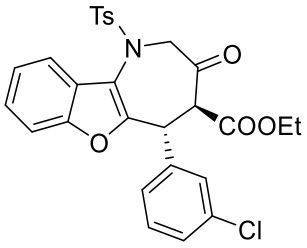
Ethyl 5-(4-bromophenyl)-3-oxo-1-tosyl-2,3,4,5-tetrahydro-1H-benzofuro[3,2-b]azepine-4-carboxylate (4d)

White solid: 105 mg (yield 90%); mp 134-136 °C; IR (KBr) 2953, 1737, 1337, 1288, 1163, 1082, 815, 672, 556 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.35 (m, 4H), 7.30 – 7.26 (m, 1H), 7.26 – 7.21 (m, 1H), 7.19 – 7.13 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 5.12 (d, *J* = 18.4 Hz, 1H), 4.63 (q, *J* = 13.2 Hz, 2H), 4.24 (d, *J* = 18.4 Hz, 1H), 4.16 – 3.98 (m, 2H), 2.51 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.2, 167.0, 153.6, 151.7, 145.1, 137.1, 136.4, 131.8, 130.5, 130.4, 127.8, 125.5, 125.0, 123.5, 122.0, 120.1, 119.3, 111.6, 62.7, 61.7, 57.9, 43.8, 21.8, 14.0 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{28}H_{25}BrNO_6S^+$ 582.0580, found 582.0598.



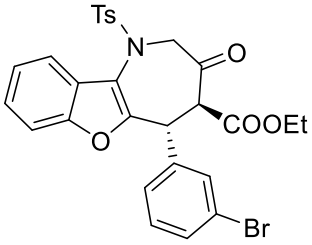
Ethyl 5-(4-methoxyphenyl)-3-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine-4-carboxylate (4e)

White solid: 93 mg (yield 87%); mp 145-147 °C; IR (KBr) 2989, 1742, 1606, 1513, 1257, 1165, 826, 674, 553 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.28 (s, 1H), 7.25 – 7.20 (m, 2H), 7.18 – 7.12 (m, 1H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 5.11 (d, *J* = 18.8 Hz, 1H), 4.65 – 4.50 (m, 2H), 4.23 (d, *J* = 18.4 Hz, 1H), 4.12 – 3.96 (m, 2H), 3.77 (s, 3H), 2.50 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.5, 167.1, 159.0, 153.5, 152.5, 145.0, 136.4, 130.4, 130.1, 129.8, 127.9, 125.3, 125.2, 123.3, 120.1, 118.9, 111.6, 62.7, 61.5, 58.4, 55.2, 43.8, 21.8, 14.0 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{29}H_{28}NO_7S^+$ 534.1581, found 534.1572.



Ethyl 5-(3-chlorophenyl)-3-oxo-1-tosyl-2,3,4,5-tetrahydro-1H-benzofuro[3,2-b]azepine-4-carboxylate (4f)

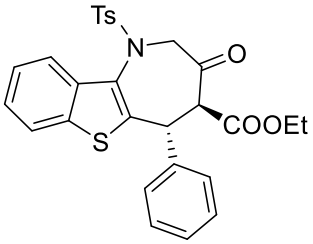
White solid: 92 mg (yield 86%); mp 150-152 °C; IR (KBr) 2980, 1741, 1449, 1346, 1163, 1092, 751, 667, 648 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 3H), 7.28 (d, *J* = 8.4 Hz, 3H), 7.26 – 7.12 (m, 9H), 5.12 (d, *J* = 18.8 Hz, 1H), 4.57 (d, *J* = 12.4 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.26 (d, *J* = 18.4 Hz, 1H), 2.50 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.2, 166.8, 153.6, 151.2, 145.1, 139.9, 136.2, 134.4, 130.5, 129.9, 128.5, 128.2, 127.7, 127.3, 125.6, 125.1, 123.5, 120.4, 119.5, 111.6, 62.6, 61.7, 57.9, 43.9, 21.8, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{28}H_{25}ClNO_6S^+$ 538.1086, found 538.1078.



Ethyl 5-(3-bromophenyl)-3-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine-4-carboxylate (4g)

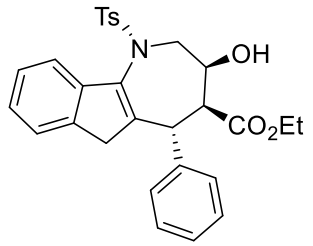
White solid: 90 mg (yield 77%); mp 159-141 °C; IR (KBr) 2991, 1732, 1453, 1365, 1270, 1166, 751, 672, 546 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.41 –

7.36 (m, 2H), 7.33 – 7.26 (m, 2H), 7.26 – 7.23 (m, 1H), 7.22 – 7.14 (m, 3H), 5.10 (d, *J* = 18.8 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.25 (d, *J* = 18.4 Hz, 1H), 4.11 – 3.99 (m, 2H), 2.50 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.1, 166.8, 153.6, 151.2, 145.1, 140.2, 136.2, 131.5, 131.2, 130.6, 130.2, 128.7, 127.72, 127.71, 125.6, 125.1, 123.5, 122.6, 120.4, 119.6, 111.6, 62.6, 61.7, 58.0, 43.9, 21.8, 13.9 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{28}H_{25}BrNO_6S^+$ 582.0580, found 582.0580.



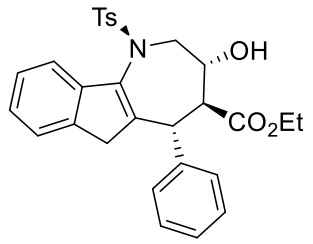
Ethyl 3-oxo-5-phenyl-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[4,5]thieno[3,2-*b*]azepine-4-carboxylate (4h)

White solid: 80 mg (yield 77%); mp 175-177 °C; IR (KBr) 2985, 1737, 1344, 1281, 1163, 1091, 814, 758, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.21 – 7.13 (m, 2H), 5.16 (d, *J* = 12.0 Hz, 1H), 5.00 (d, *J* = 18.4 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.16 (d, *J* = 18.4 Hz, 1H), 4.12 – 3.99 (m, 2H), 2.51 (s, 3H), 1.09 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.9, 167.8, 144.9, 143.4, 141.2, 137.2, 137.2, 135.8, 130.3, 128.8, 128.7, 127.9, 127.7, 125.3, 124.4, 122.4, 122.1, 62.0, 61.4, 59.4, 46.1, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{28}H_{26}NO_5S_2^+$ 520.1247, found 520.1230.



Ethyl 3-hydroxy-5-phenyl-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (5)

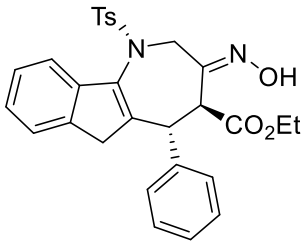
White solid: 55 mg (yield 55%); mp 172-174 °C; IR (KBr) 3530, 2982, 2879, 1709, 1595, 1453, 1341, 1641, 1096, 1024, 770, 701, 673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 39.8, 7.4 Hz, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 3H), 7.24 – 7.21 (m, 4H), 6.86 (s, 1H), 4.40 (d, *J* = 9.2 Hz, 2H), 3.84 – 3.72 (m, 3H), 3.54 (d, *J* = 11.6 Hz, 2H), 3.14 (s, 2H), 2.46 (s, 2H), 0.95 – 0.87 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.8, 144.0, 142.1 141.1, 138.2, 137.6, 129.9, 128.7, 128.6, 128.3, 127.5, 127.2, 126.5, 126.2, 125.2, 123.5, 121.5, 120.6, 68.8, 60.9, 50.5, 44.3, 39.9, 21.6, 13.6 ppm. HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{29}H_{30}NO_5S^+$ 504.1839, found 504.1874.



Ethyl 3-hydroxy-5-phenyl-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (6)

White solid: 25 mg (yield 25%); mp 194-196 °C; IR (KBr) 3452, 2979, 2931, 1704, 1596, 1459,

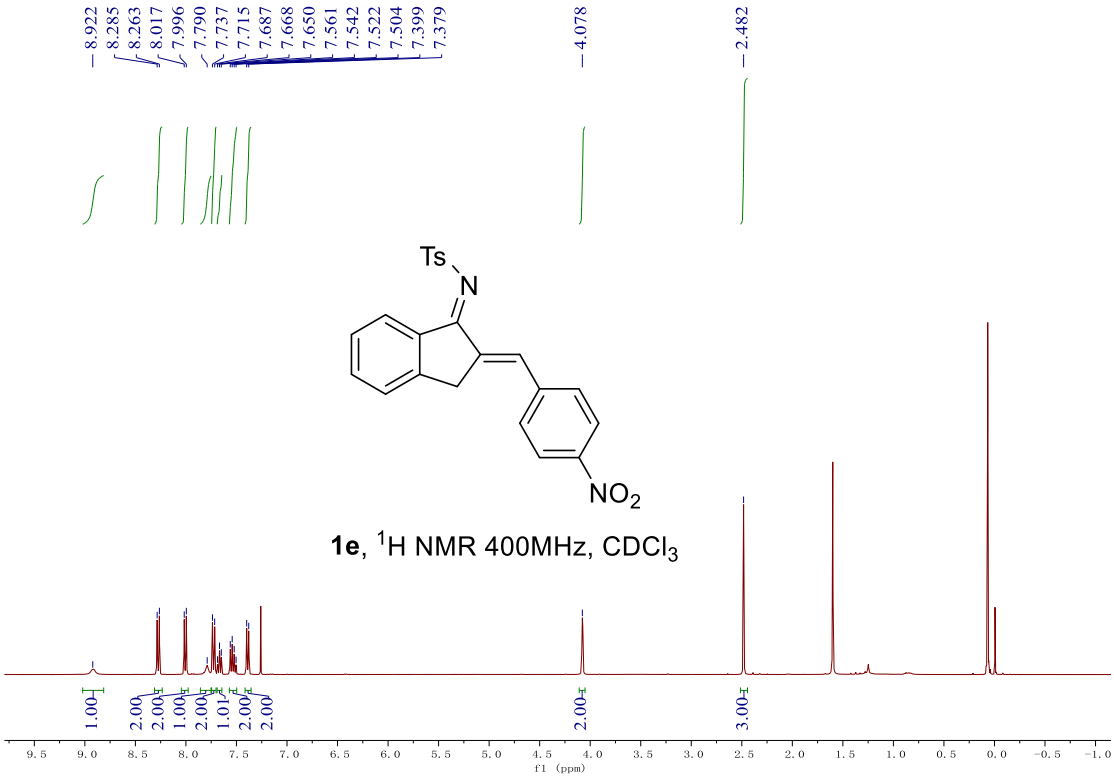
1362, 1166, 1024, 814, 765, 663 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.71 (m, 2H), 7.67 – 7.35 (m, 3H), 7.34 – 7.27 (m, 2H), 7.24 – 6.53 (m, 5H), 4.51 (d, *J* = 14.8 Hz, 1H), 4.41 – 3.93 (m, 2H), 3.81 – 3.63 (m, 2H), 3.26 – 2.80 (m, 3H), 2.69 – 2.42 (m, 5H), 0.79 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.7, 145.2, 144.1, 142.0, 140.5, 139.0, 138.0, 137.5, 129.9, 128.8, 128.3, 127.7, 127.4, 126.5, 125.3, 123.3, 121.0, 71.2, 60.6, 55.3, 53.7, 43.5, 40.2, 21.7, 13.6 ppm. HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{29}H_{30}NO_5S^+$ 504.1839, found 504.1855.



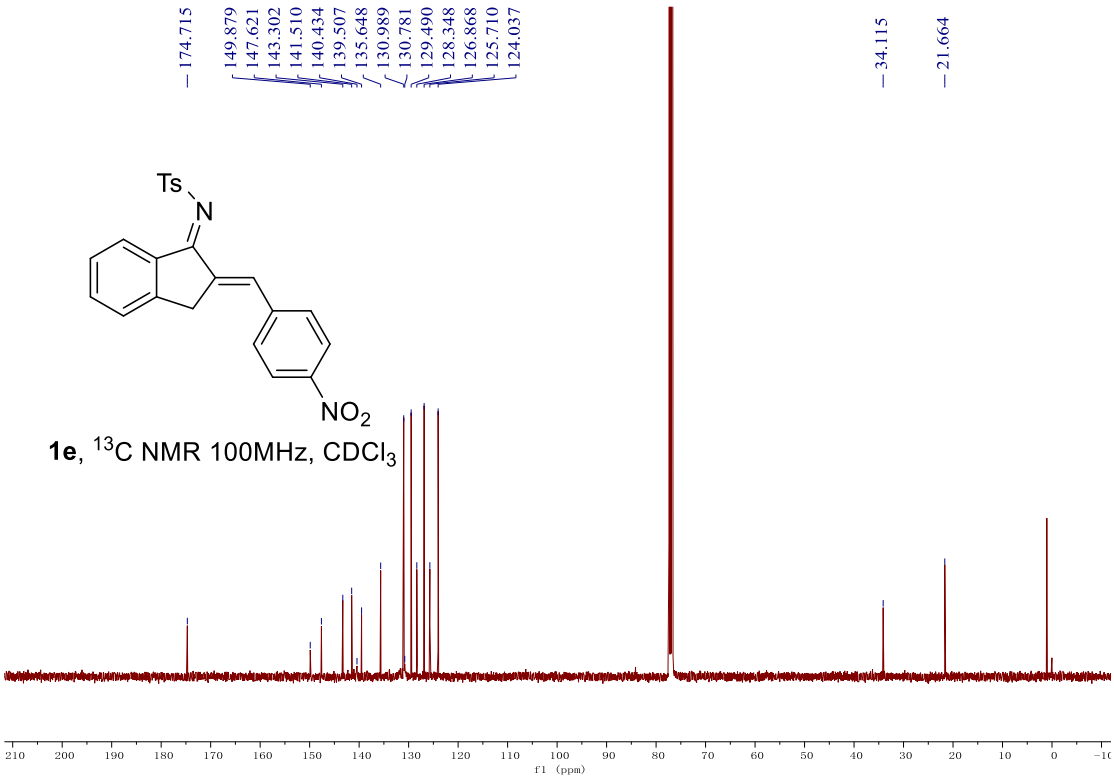
Ethyl (*E*)-3-(hydroxyimino)-5-phenyl-1-tosyl-1,2,3,4,5,6-hexahydroindeno[1,2-*b*]azepine-4-carboxylate (7)

White solid: 40 mg (yield 52%); mp 235-237 °C; IR (KBr) 3308, 2984, 1731, 1338, 1161, 1093, 852, 729, 668 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.48 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.23 (m, 6H), 7.17 – 7.09 (m, 2H), 6.93 – 6.88 (m, 1H), 4.85 (d, *J* = 18.8 Hz, 1H), 4.59 (d, *J* = 18.8 Hz, 1H), 4.29 (d, *J* = 11.6 Hz, 1H), 4.14 (d, *J* = 12.0 Hz, 1H), 3.91 – 3.77 (m, 2H), 3.35 (d, *J* = 23.2 Hz, 1H), 2.81 (d, *J* = 23.2 Hz, 1H), 2.45 (s, 3H), 0.93 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 168.8, 153.2, 144.4, 144.0, 141.8, 141.7, 140.7, 136.9, 135.0, 130.4, 128.5, 128.4, 127.2, 127.2, 126.1, 125.1, 123.7, 119.5, 60.0, 50.5, 50.2, 48.2, 21.1, 13.8 ppm. HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{29}H_{29}N_2O_5S^+$ 517.1792, found 517.1812.

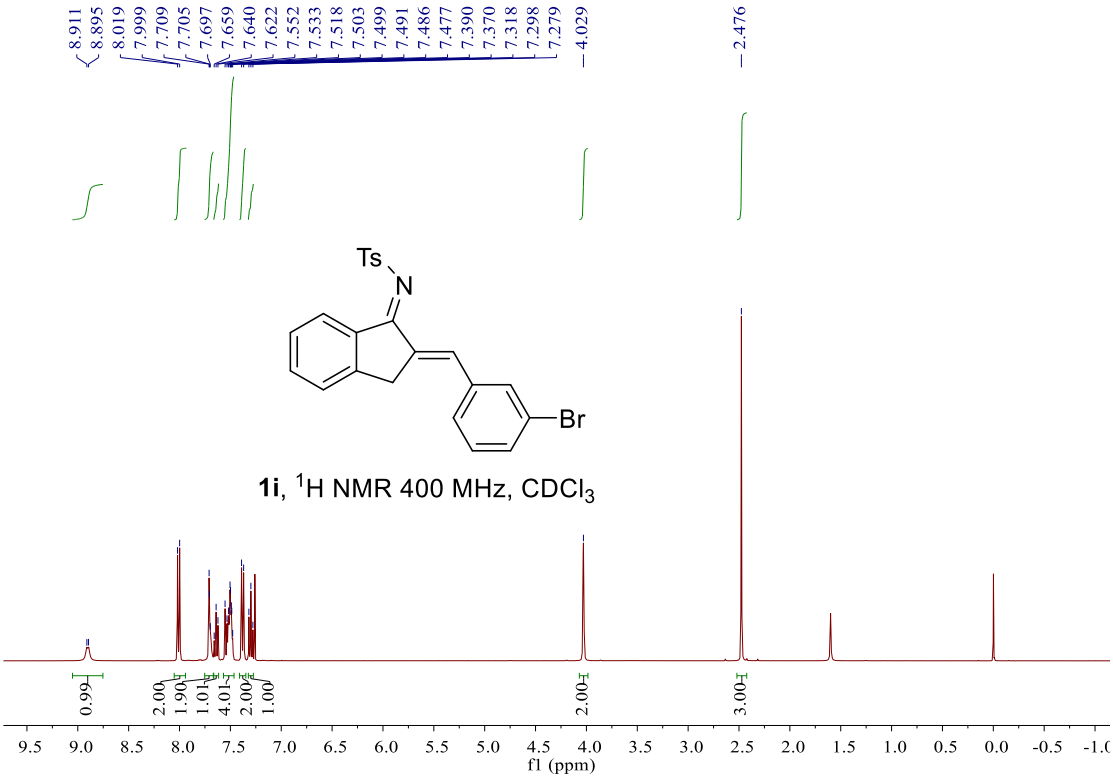
7. NMR spectra of all new compounds



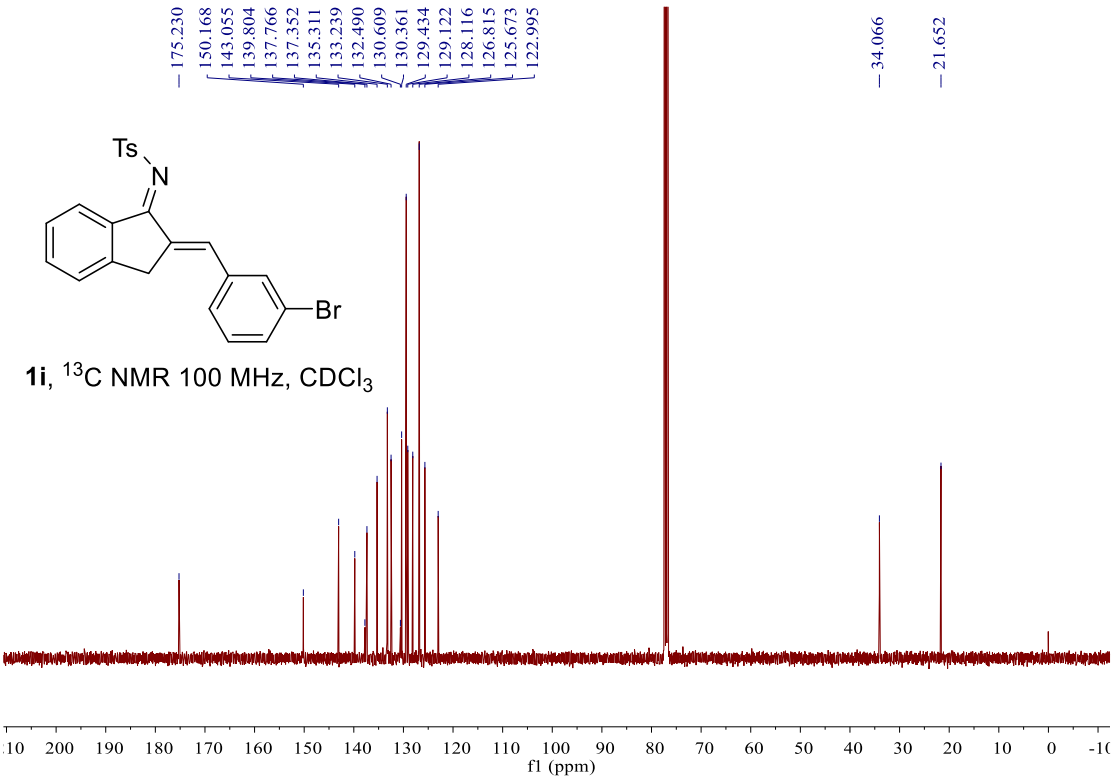
1e, ^{1}H NMR 400MHz, $CDCl_3$



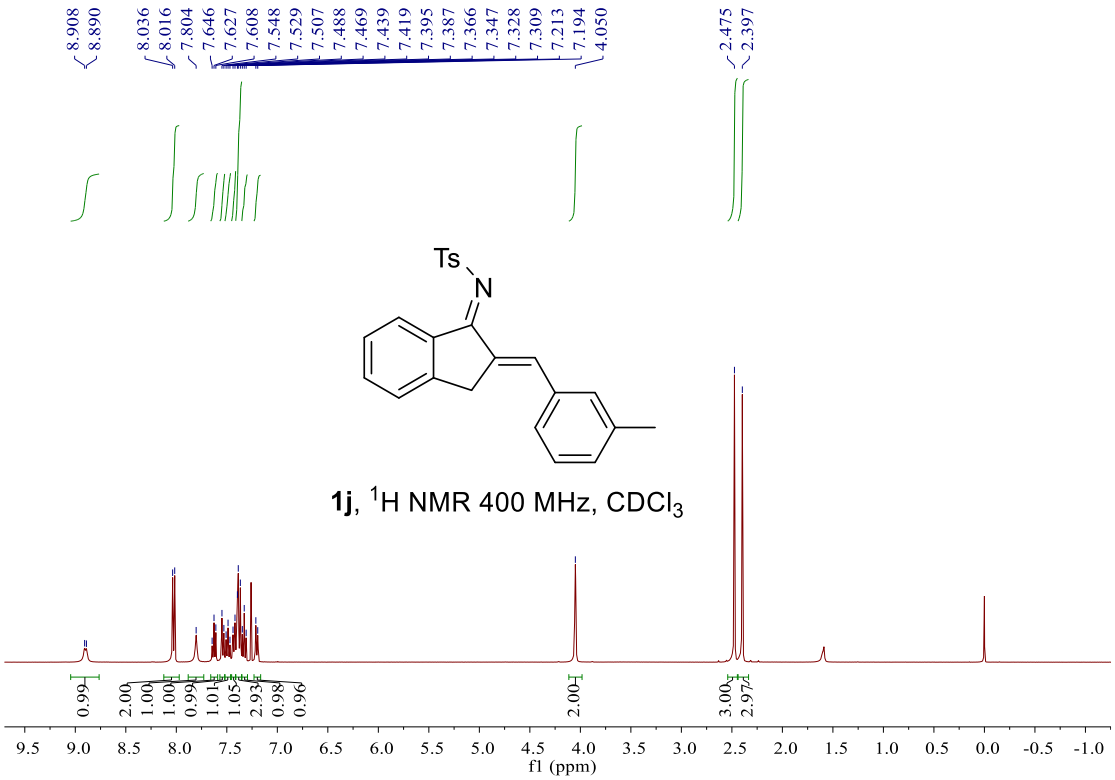
1e, ^{13}C NMR 100MHz, $CDCl_3$



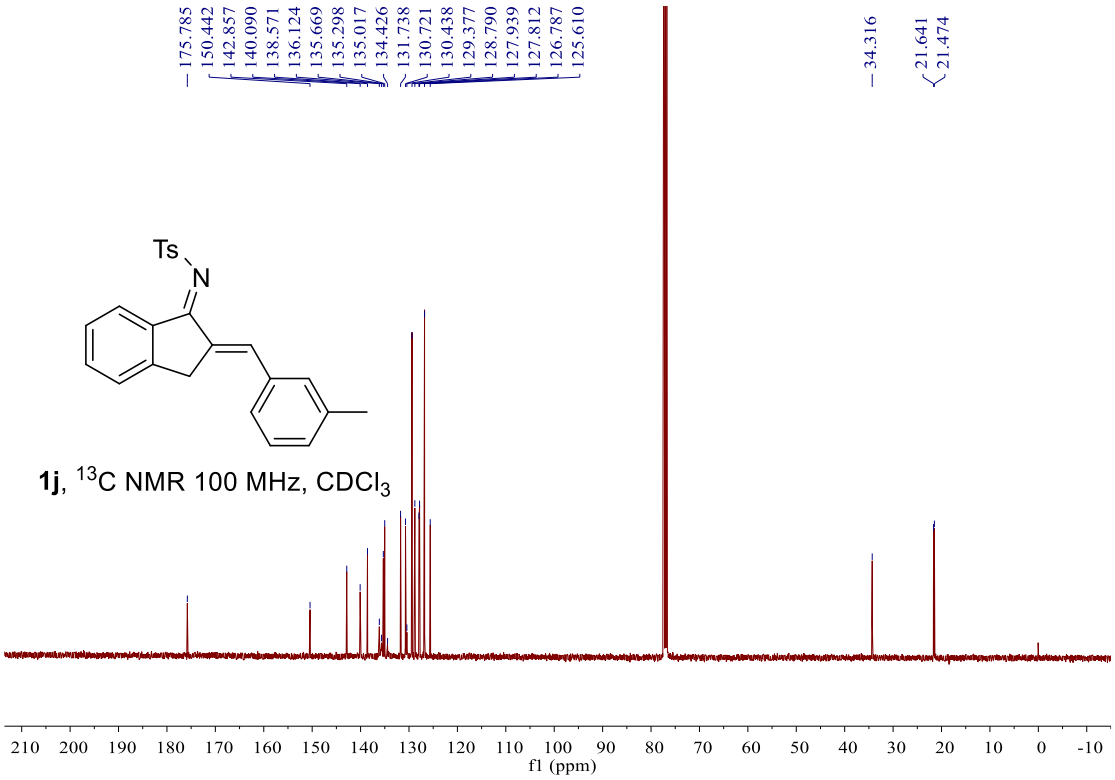
1i, ^{1}H NMR 400 MHz, $CDCl_3$



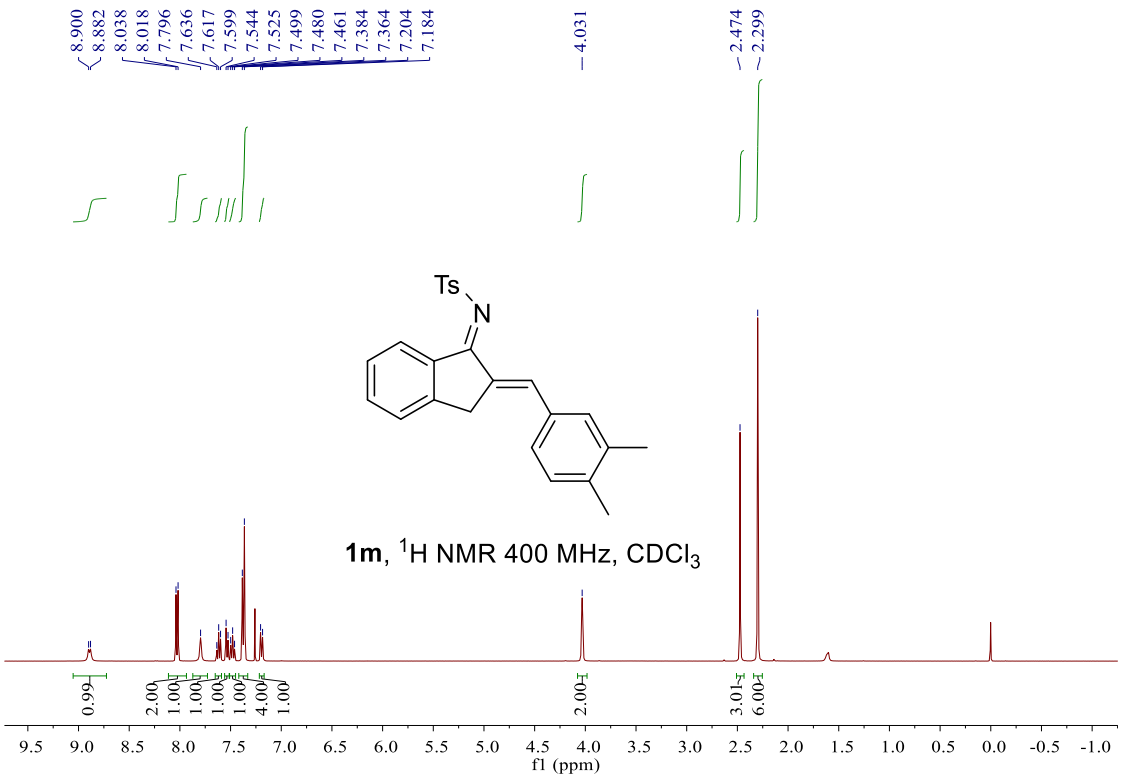
1i, ^{13}C NMR 100 MHz, $CDCl_3$



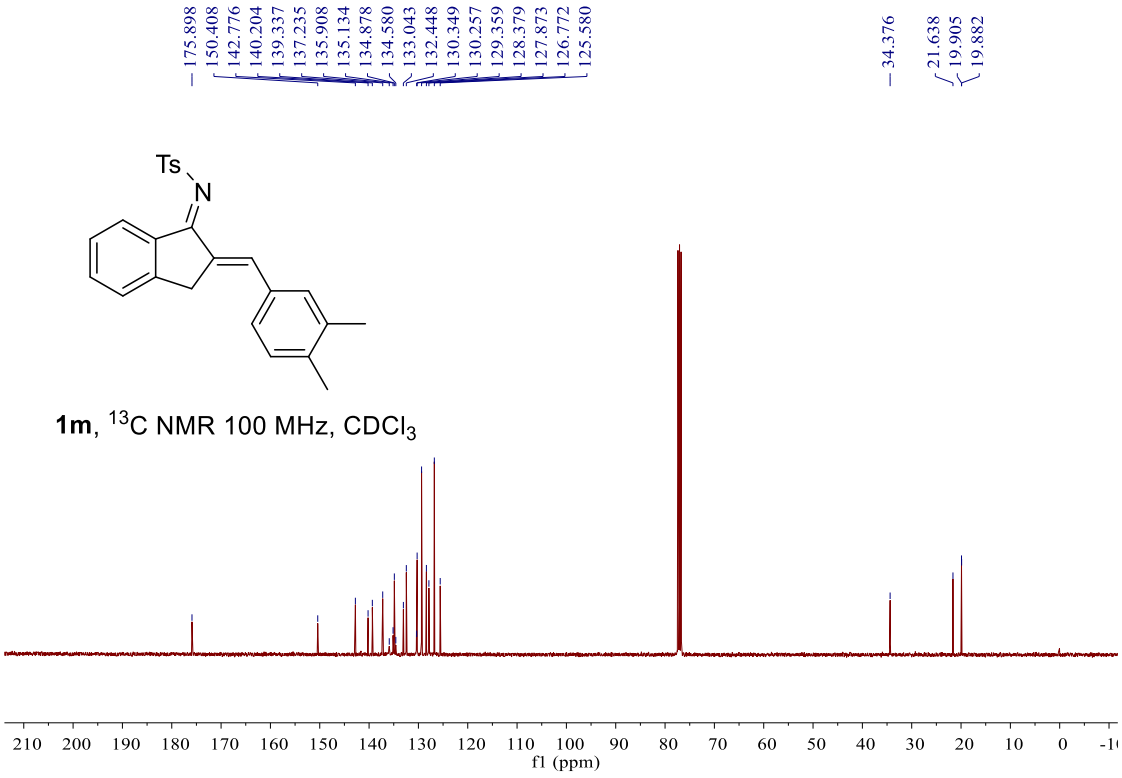
1j, ^{1}H NMR 400 MHz, $CDCl_3$



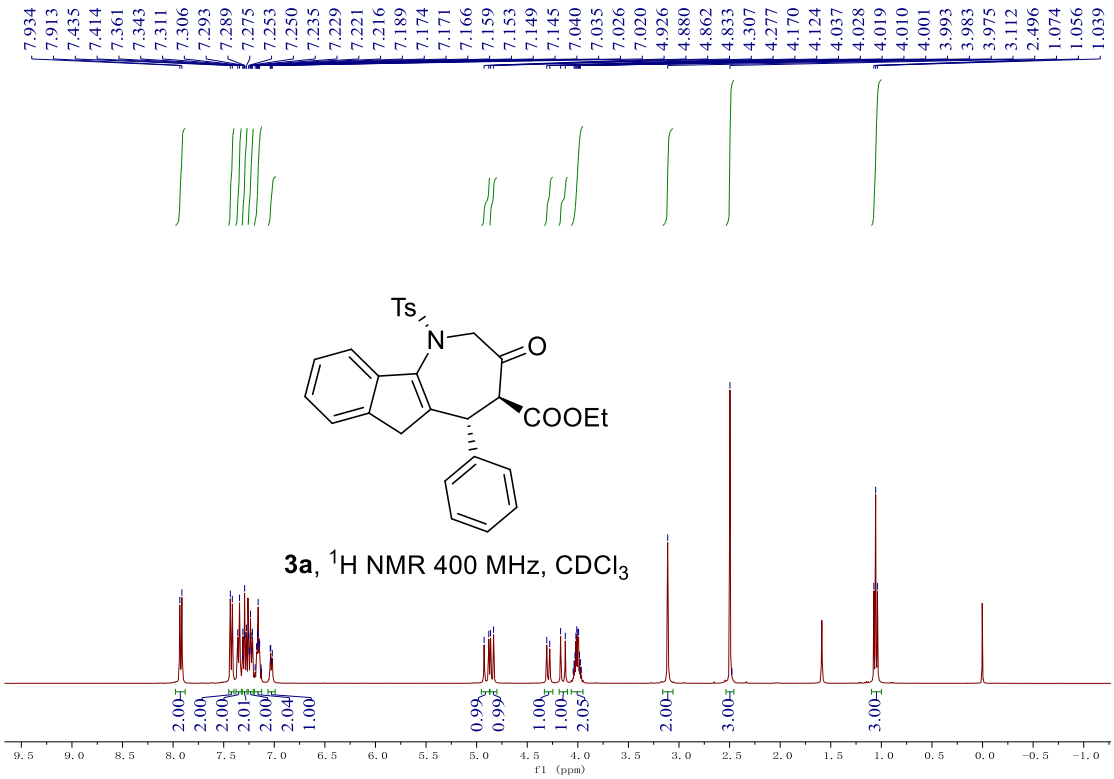
1j, ^{13}C NMR 100 MHz, $CDCl_3$



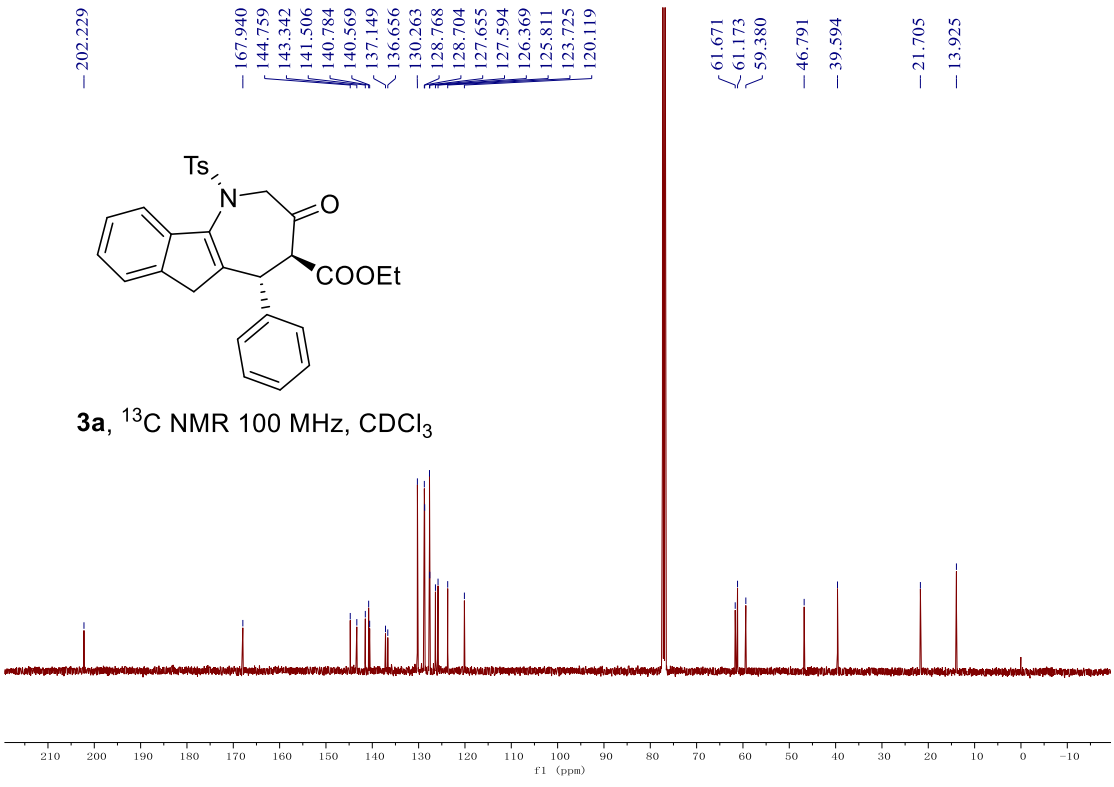
1m, ^{1}H NMR 400 MHz, $CDCl_3$



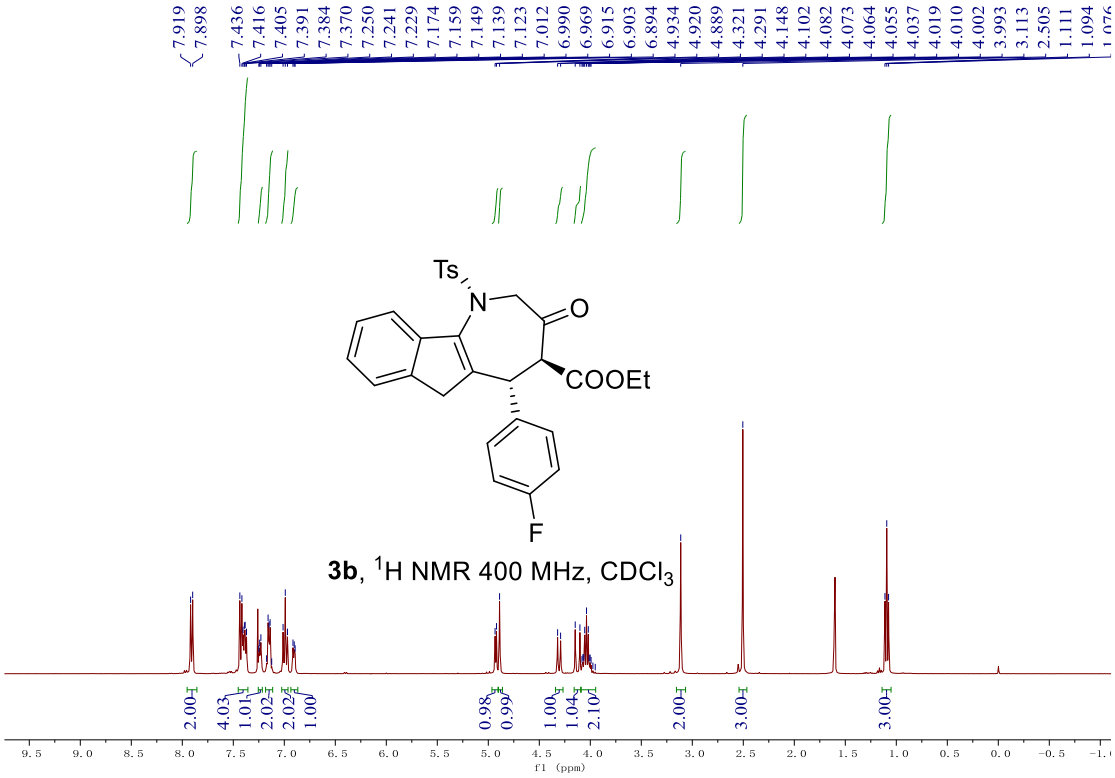
1m, ^{13}C NMR 100 MHz, $CDCl_3$

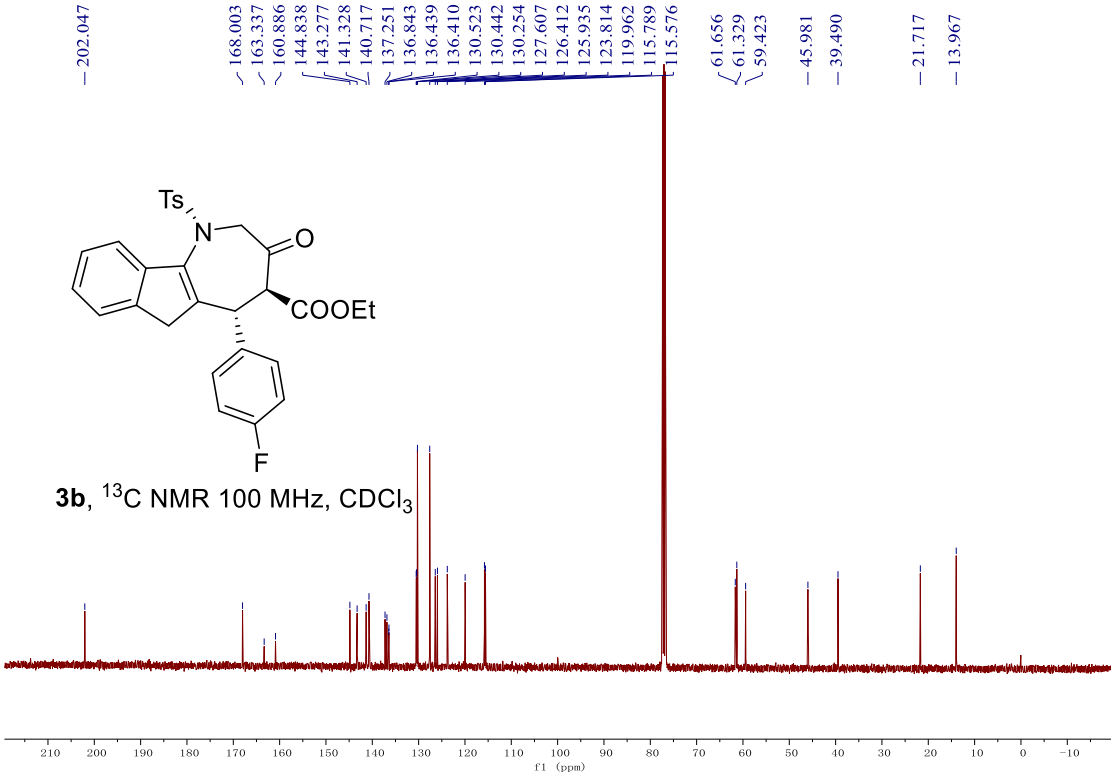


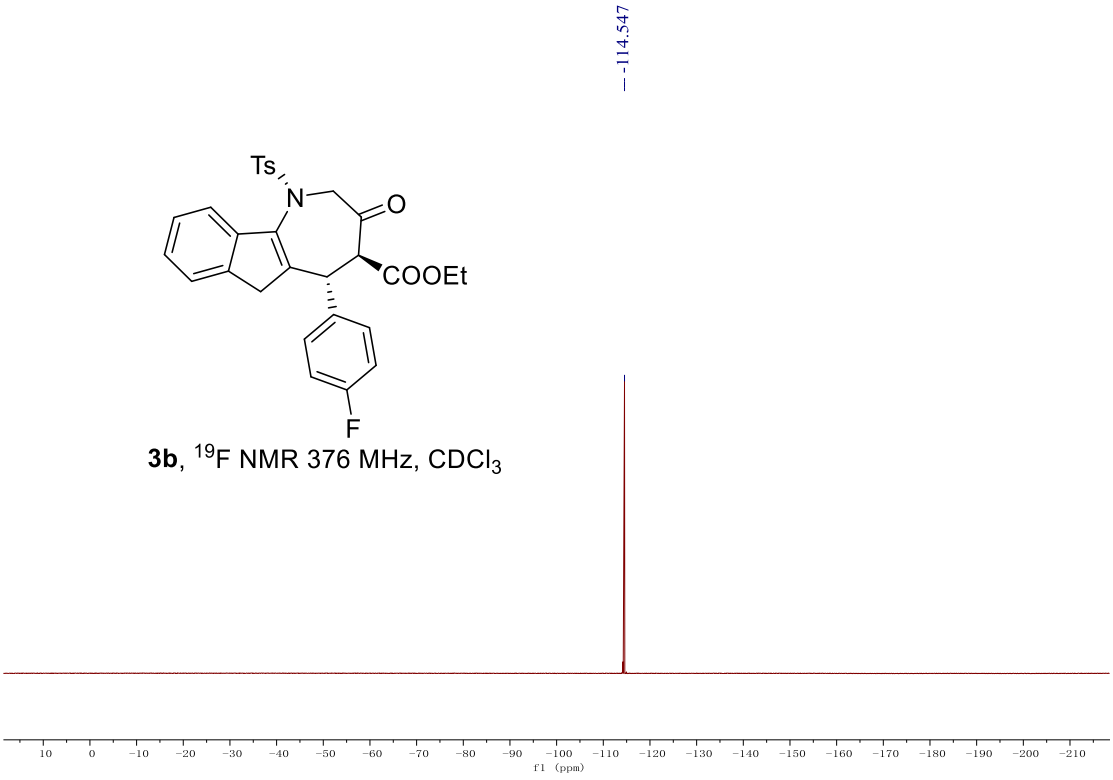
3a, ^{1}H NMR 400 MHz, $CDCl_3$



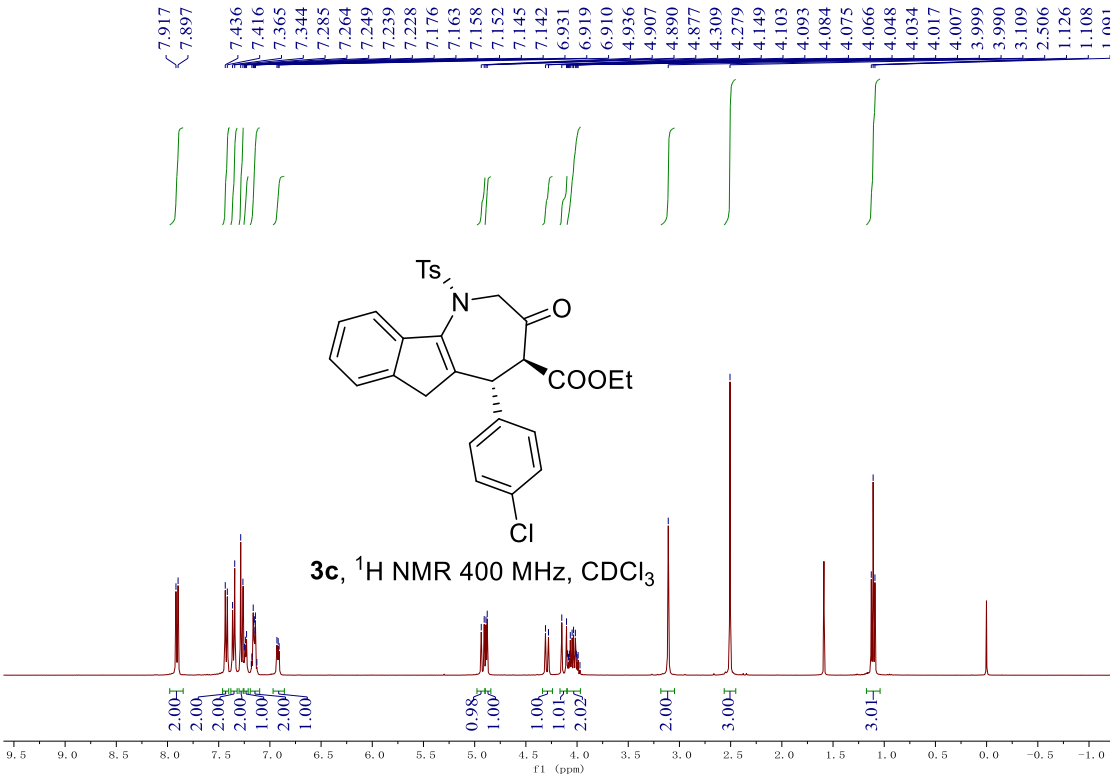
3a, ^{13}C NMR 100 MHz, $CDCl_3$


Ts
N
O
COOEt
F
3b, 1H NMR 400 MHz, CDCl3
f1 (ppm)

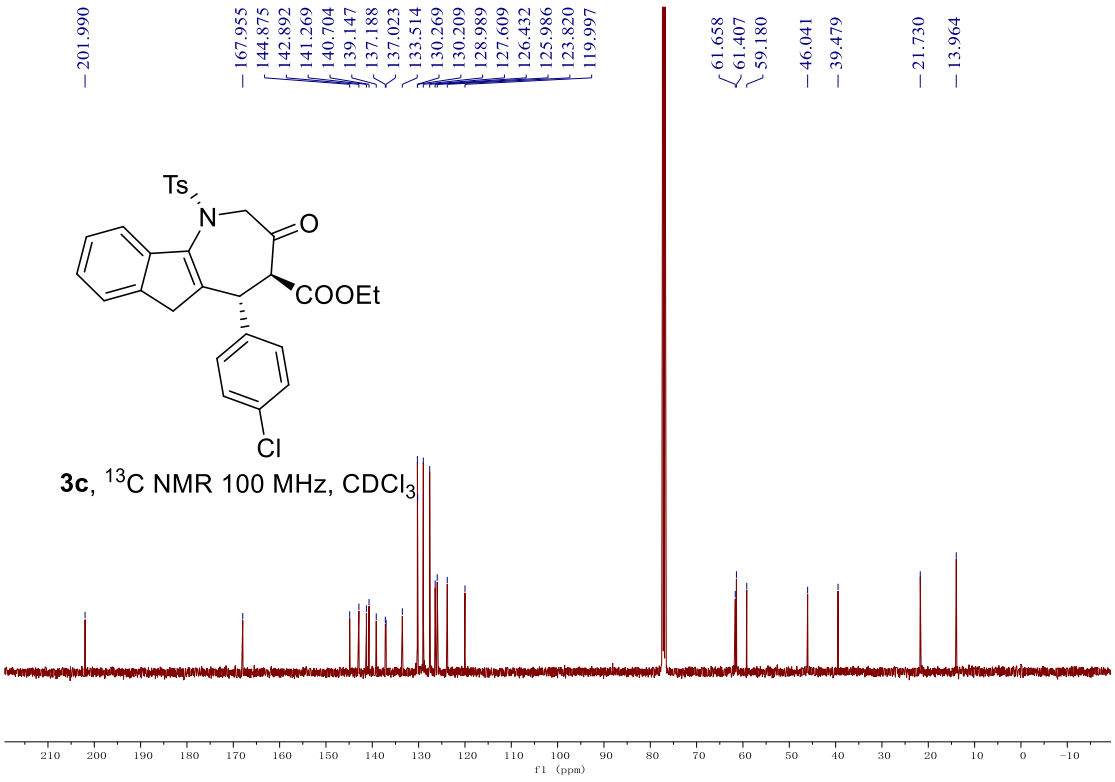

Ts
N
O
COOEt
F
3b, 13C NMR 100 MHz, CDCl3
f1 (ppm)



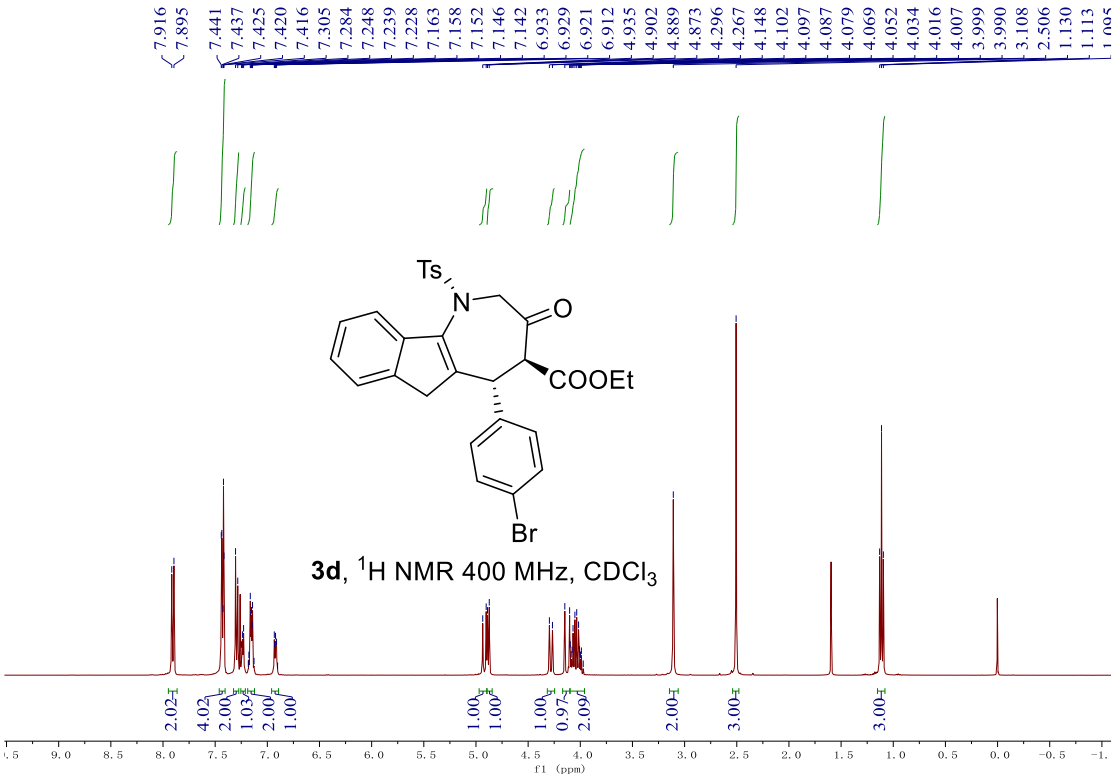
3b, ^{19}F NMR 376 MHz, $CDCl_3$



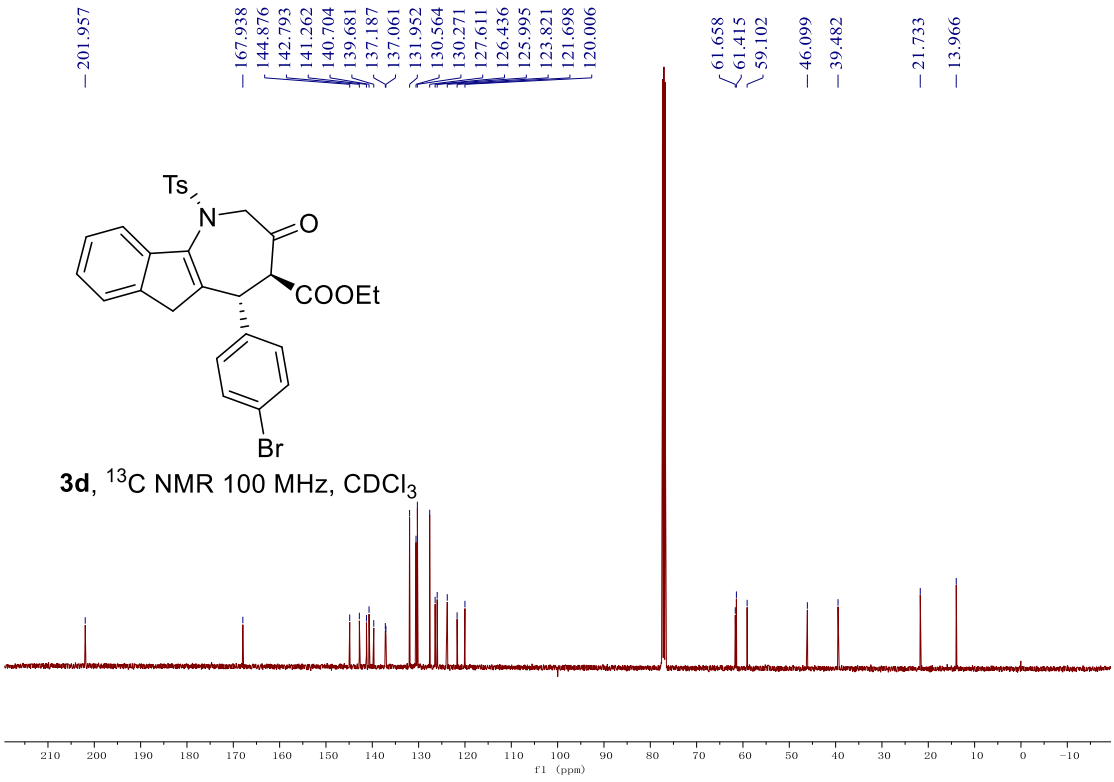
3c, ^{1}H NMR 400 MHz, $CDCl_3$



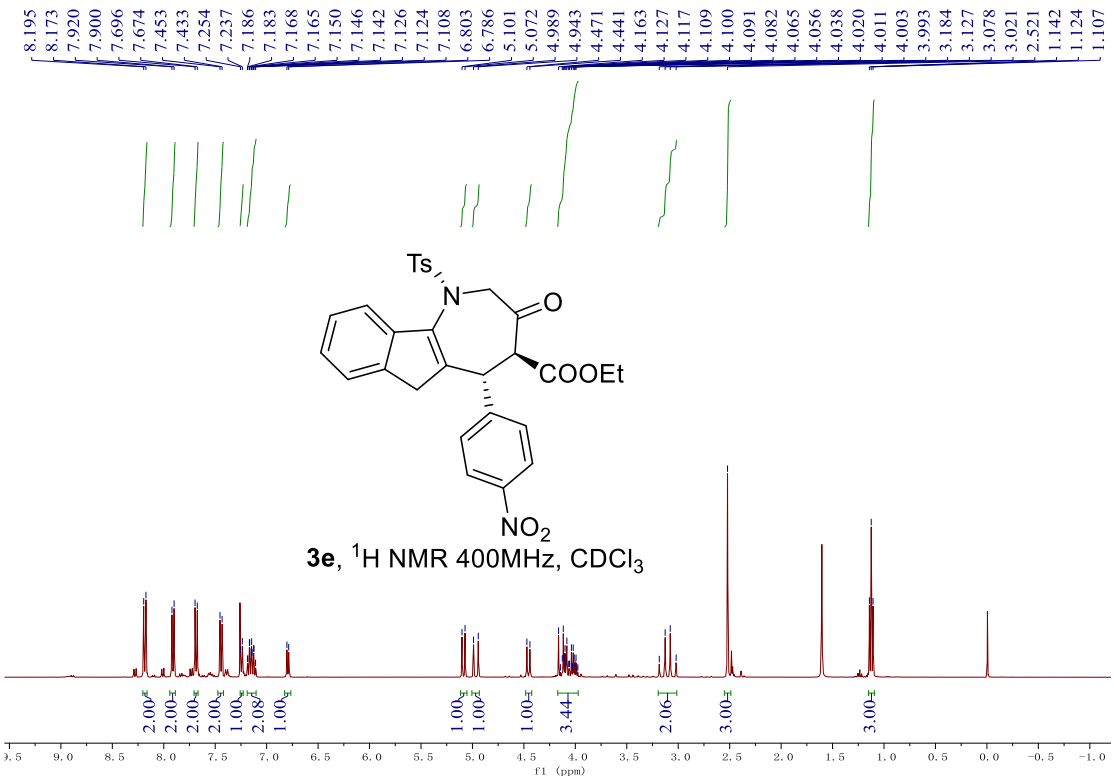
3c, ^{13}C NMR 100 MHz, $CDCl_3$



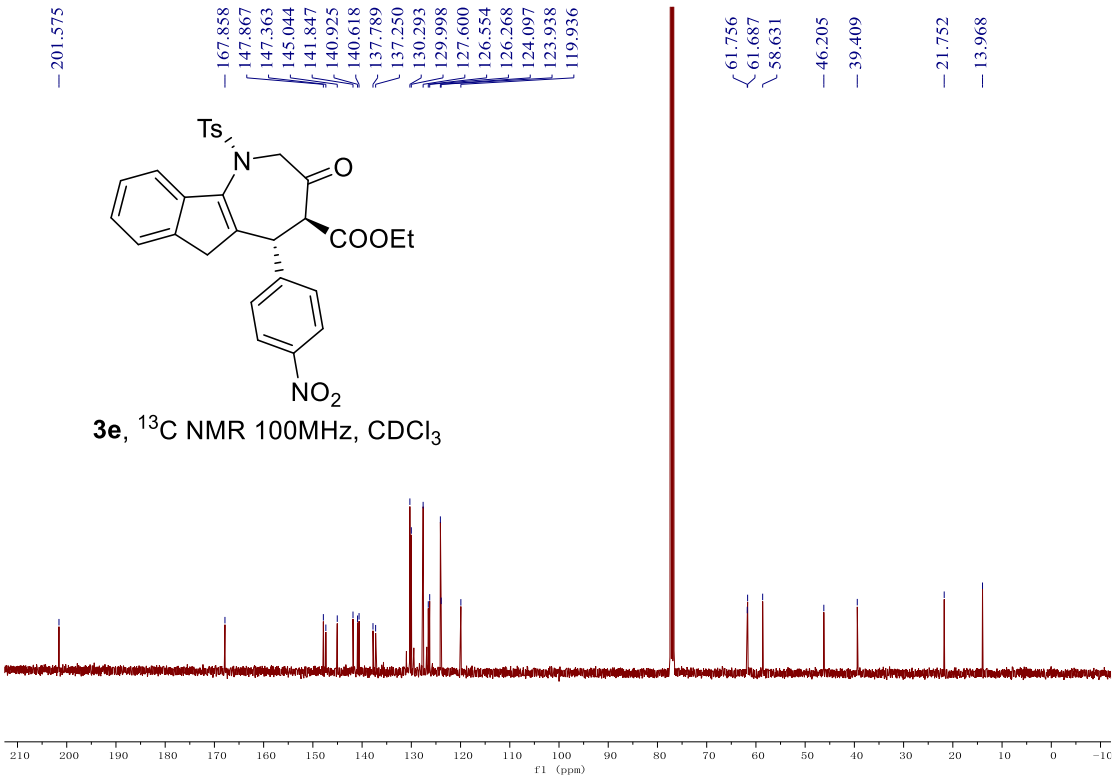
3d, ^{1}H NMR 400 MHz, $CDCl_3$



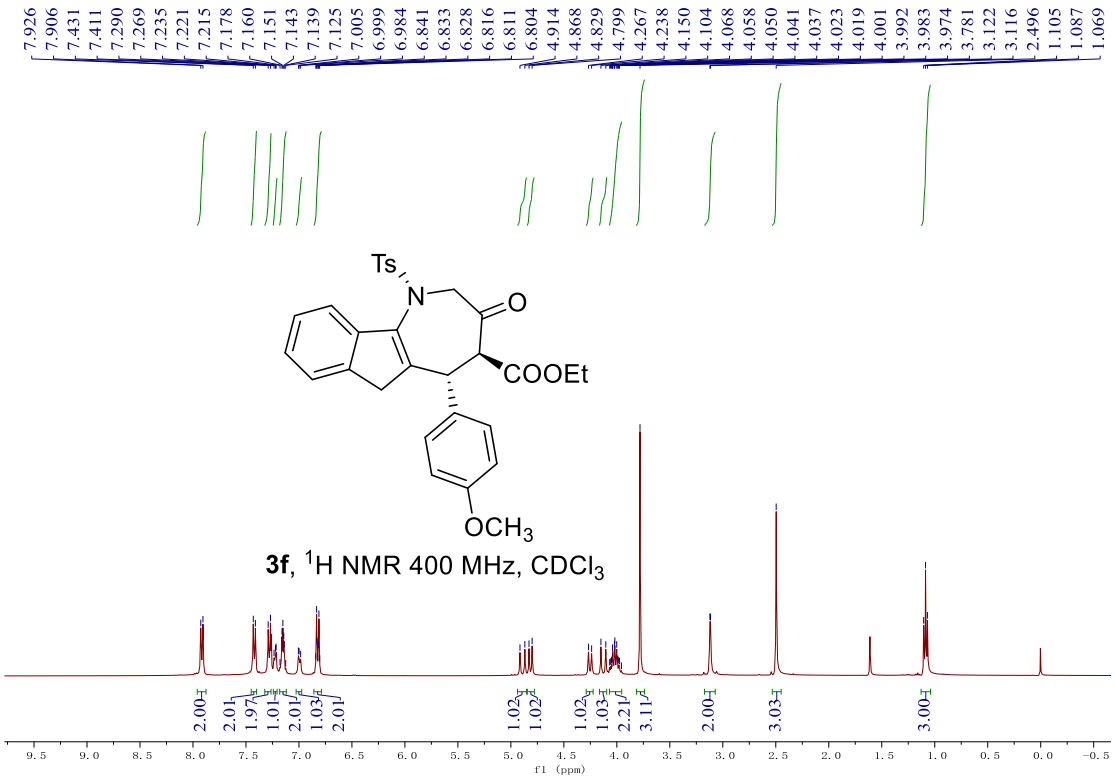
3d, ^{13}C NMR 100 MHz, $CDCl_3$



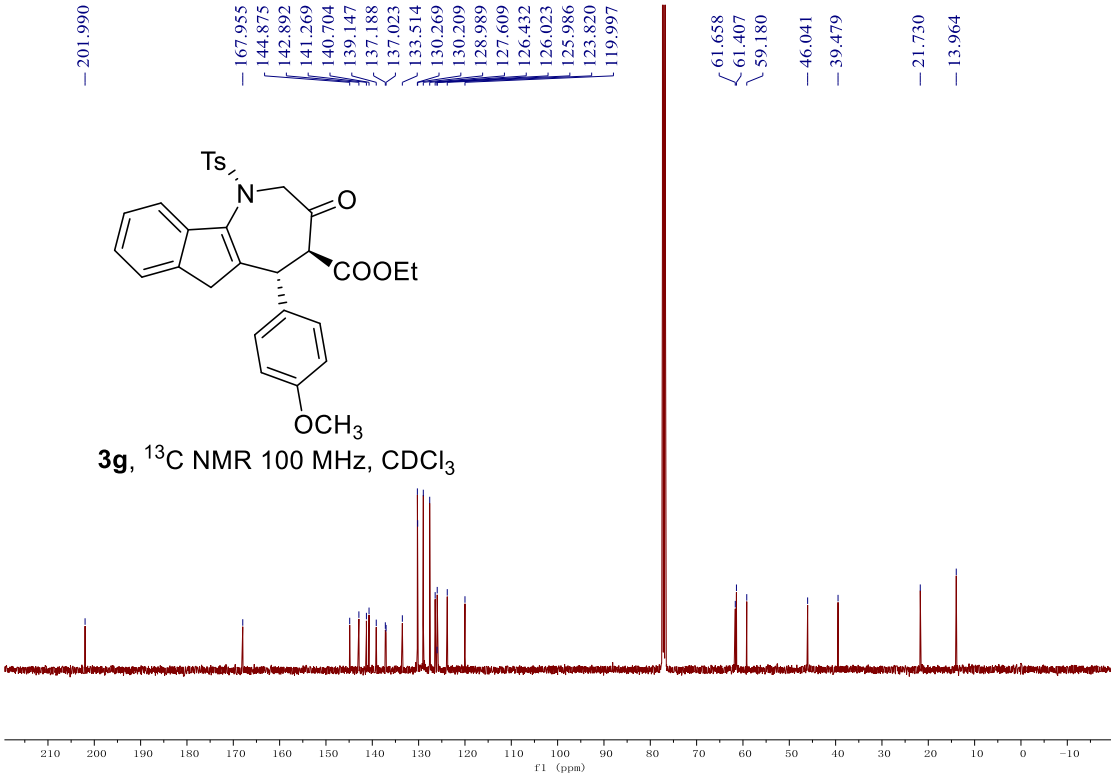
3e, ^{1}H NMR 400MHz, $CDCl_3$



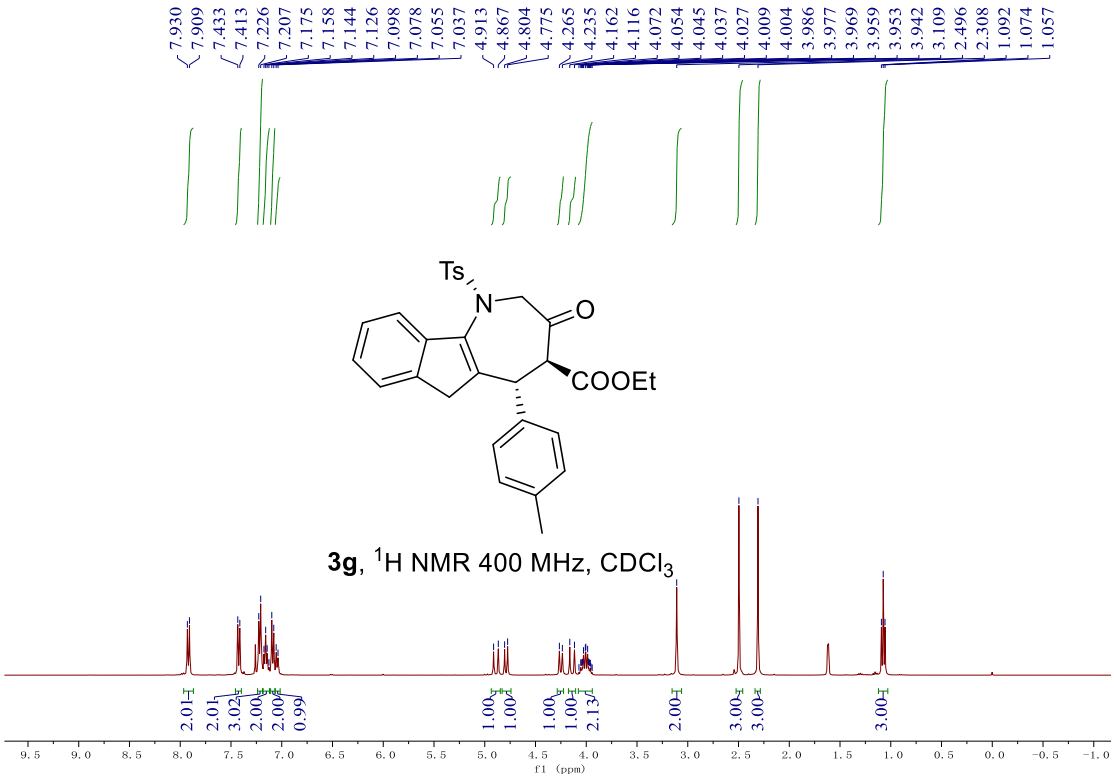
3e, ^{13}C NMR 100MHz, $CDCl_3$



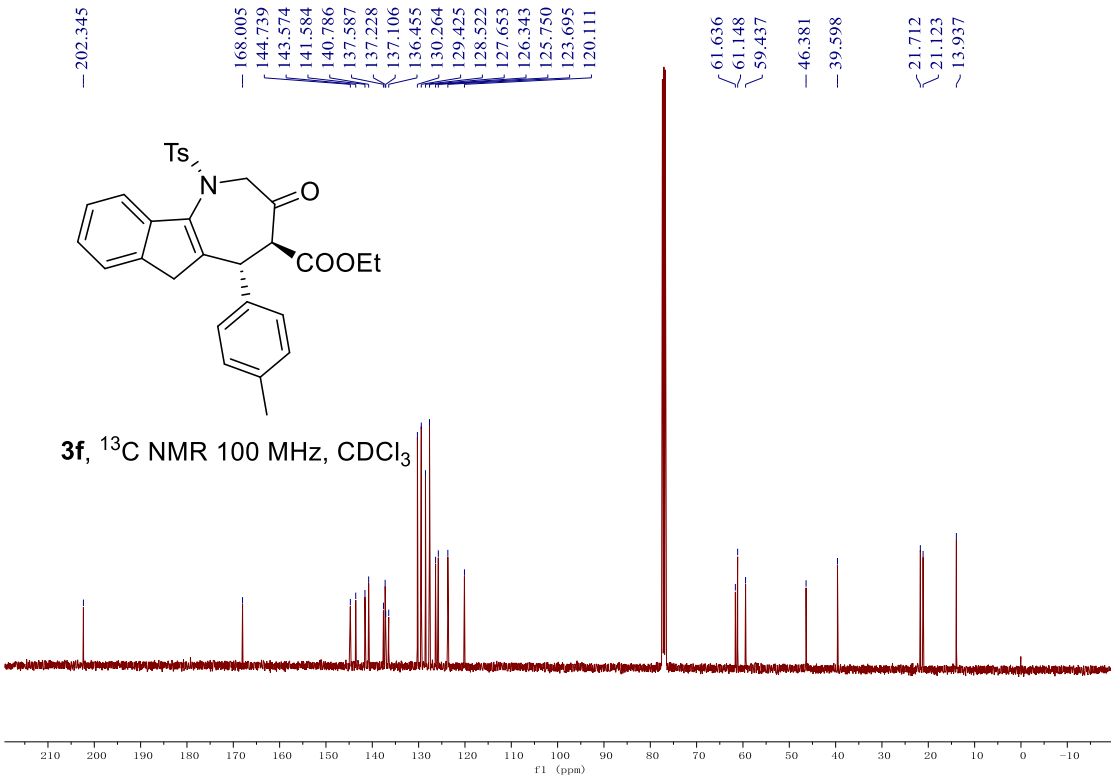
3f, ^{1}H NMR 400 MHz, $CDCl_3$



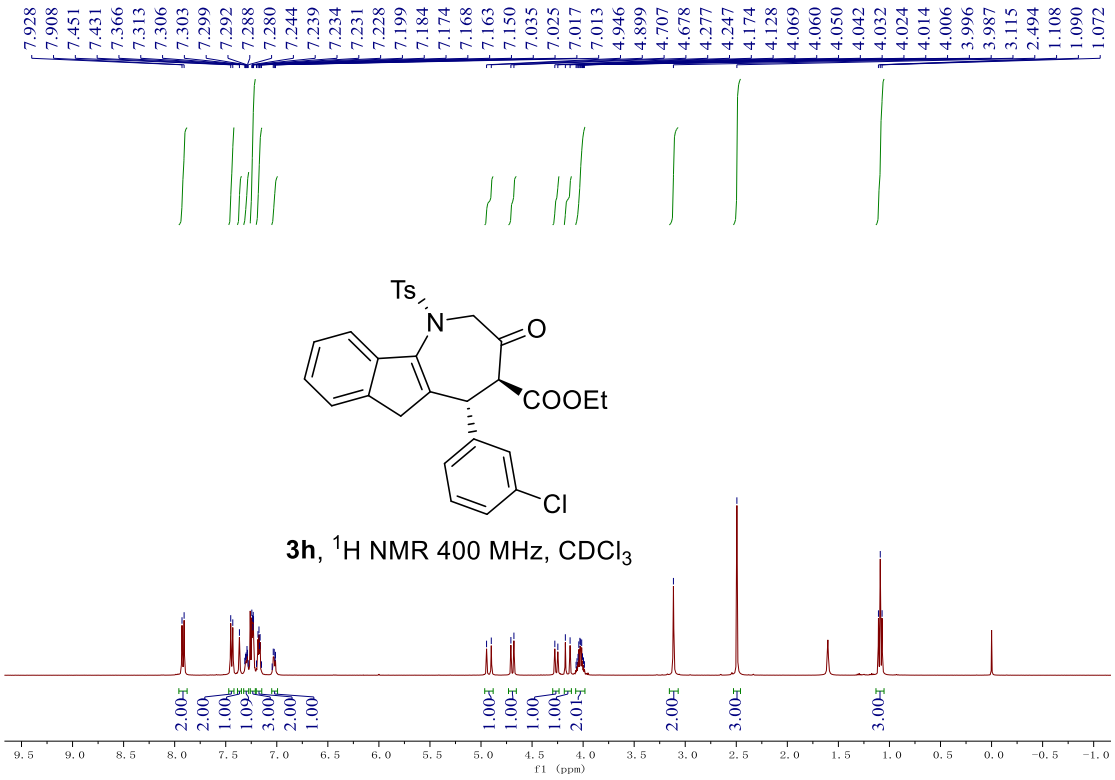
3g, ^{13}C NMR 100 MHz, $CDCl_3$



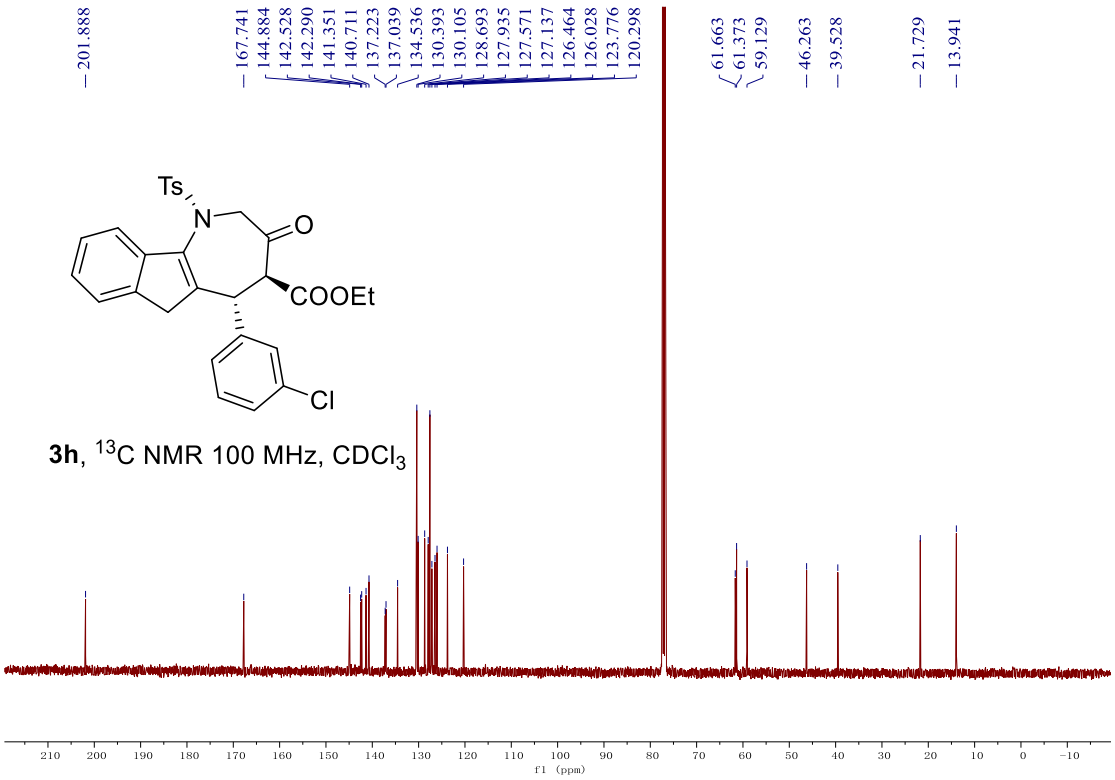
3g, ^{1}H NMR 400 MHz, $CDCl_3$



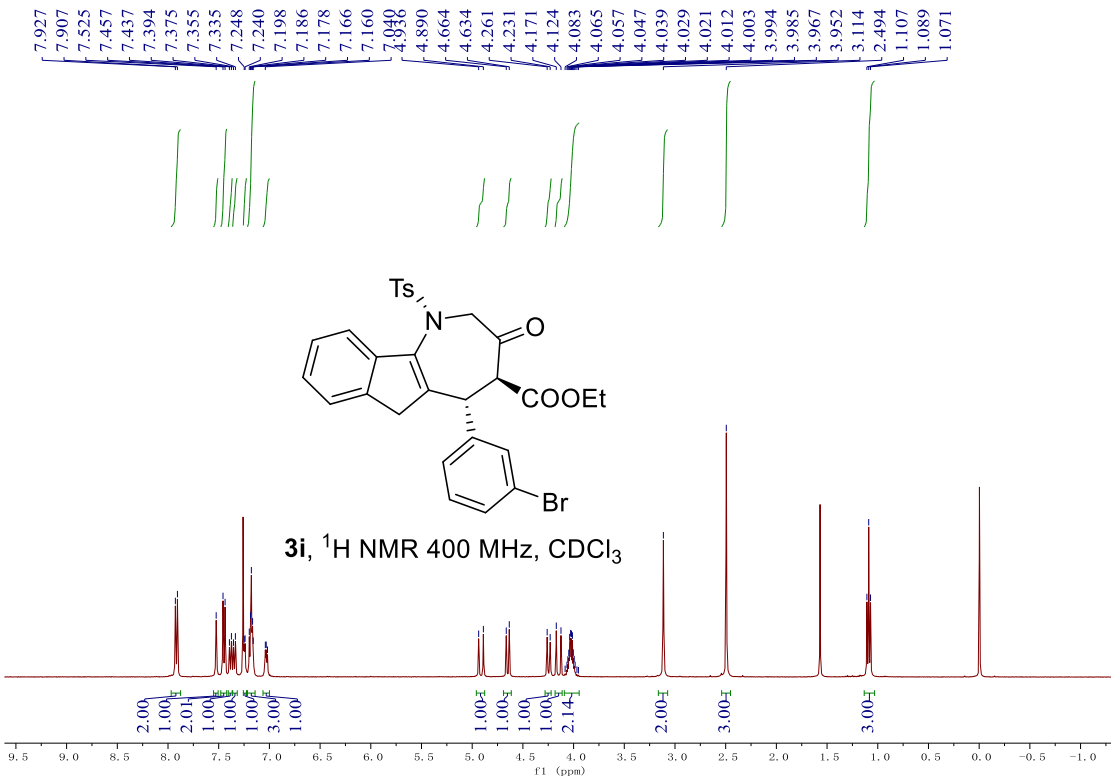
3f, ^{13}C NMR 100 MHz, $CDCl_3$



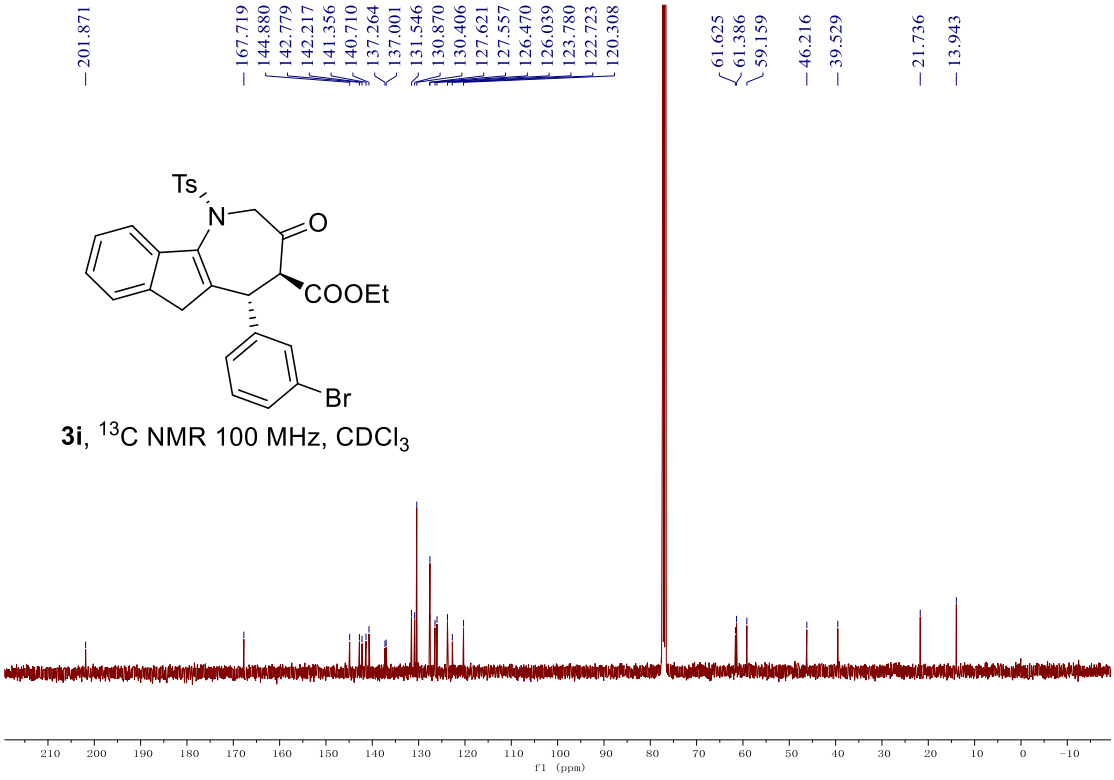
3h, ^{1}H NMR 400 MHz, $CDCl_3$



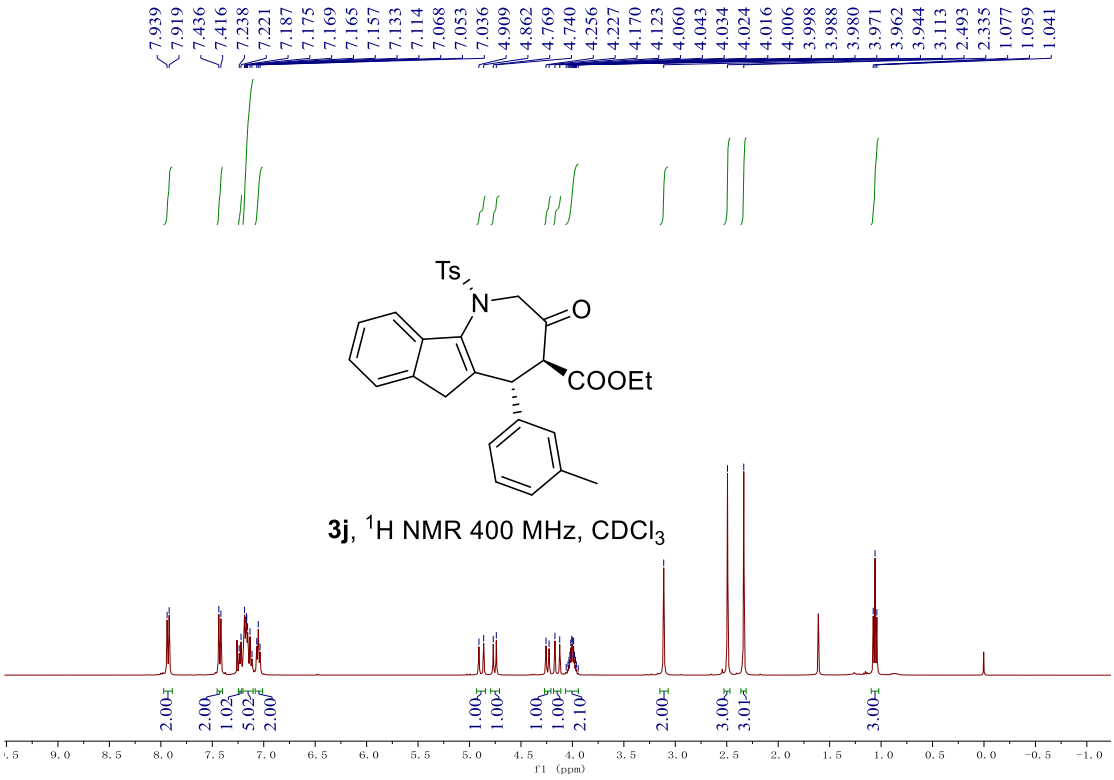
3h, ^{13}C NMR 100 MHz, $CDCl_3$



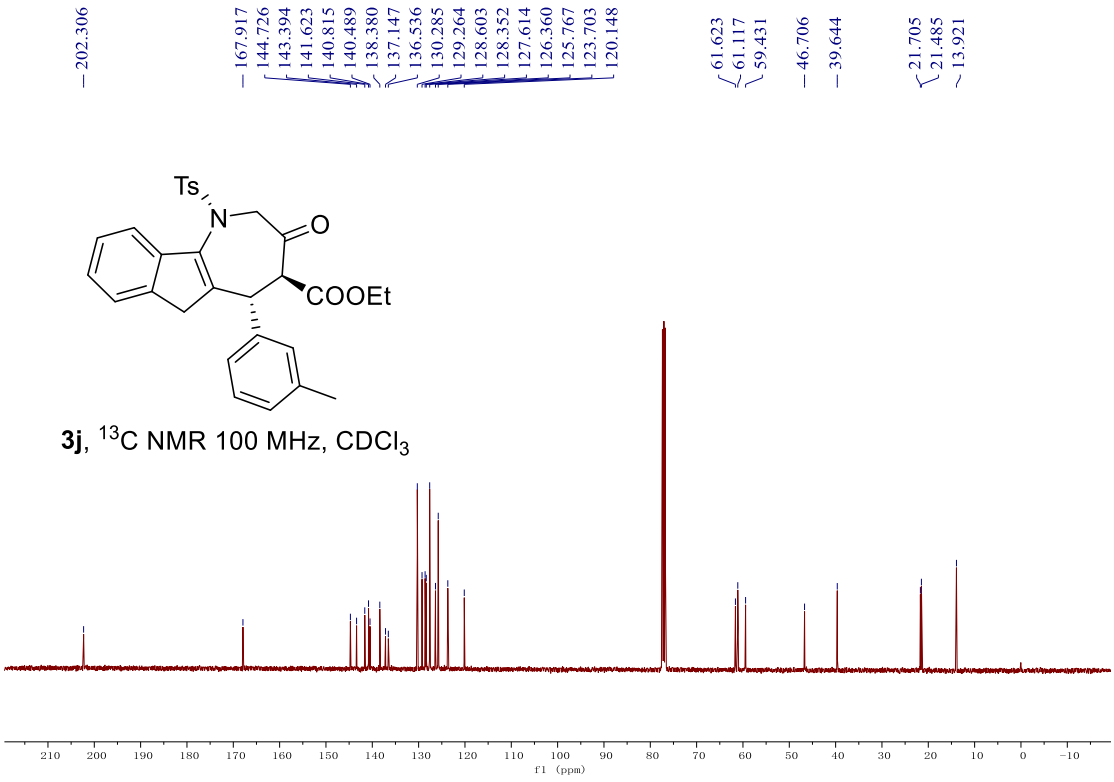
3i, ^{1}H NMR 400 MHz, $CDCl_3$



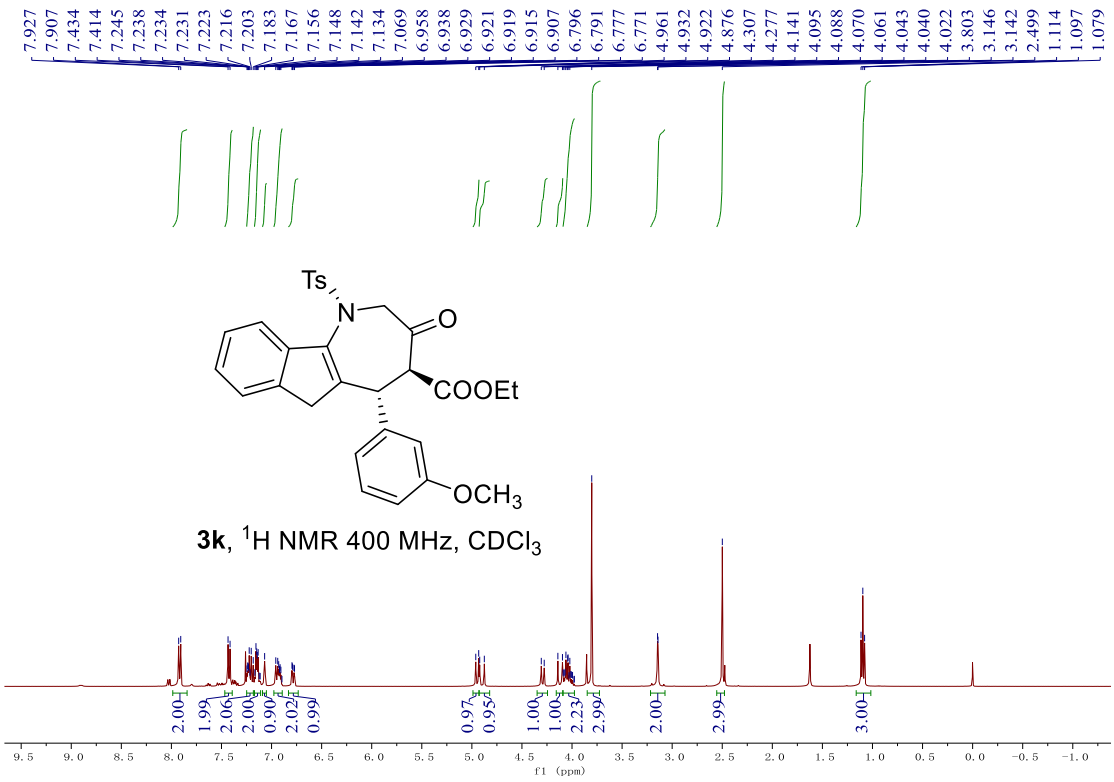
3i, ^{13}C NMR 100 MHz, $CDCl_3$



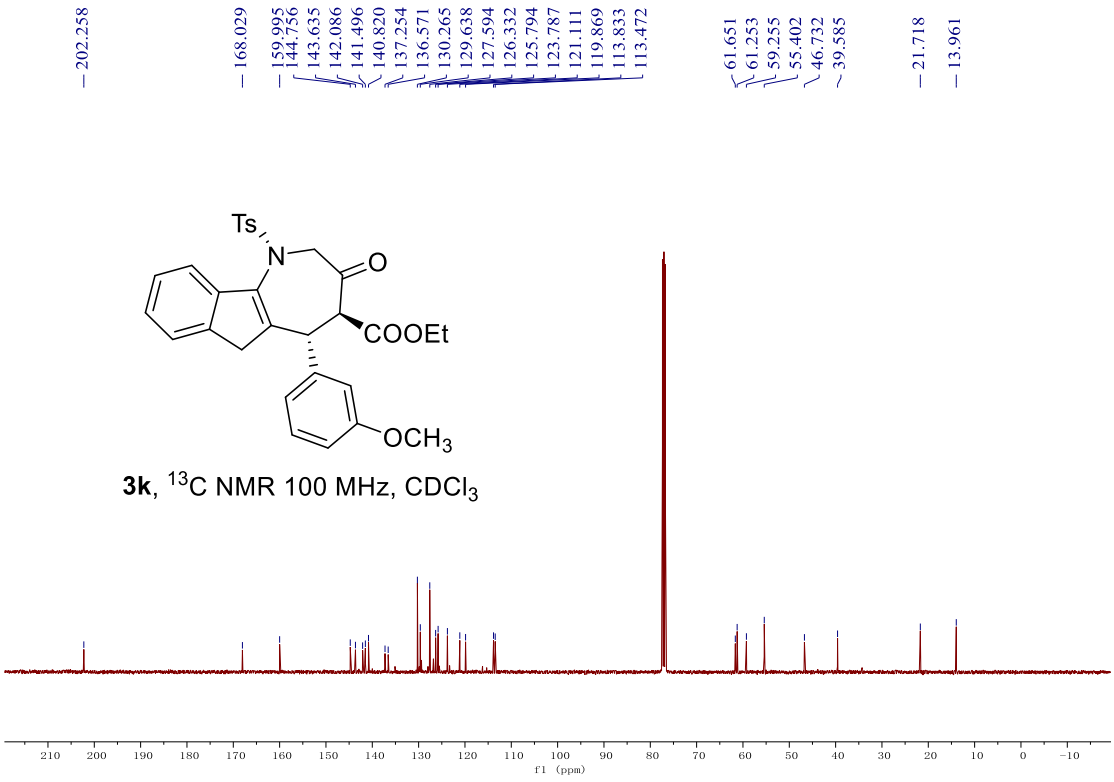
3j, ^{1}H NMR 400 MHz, $CDCl_3$



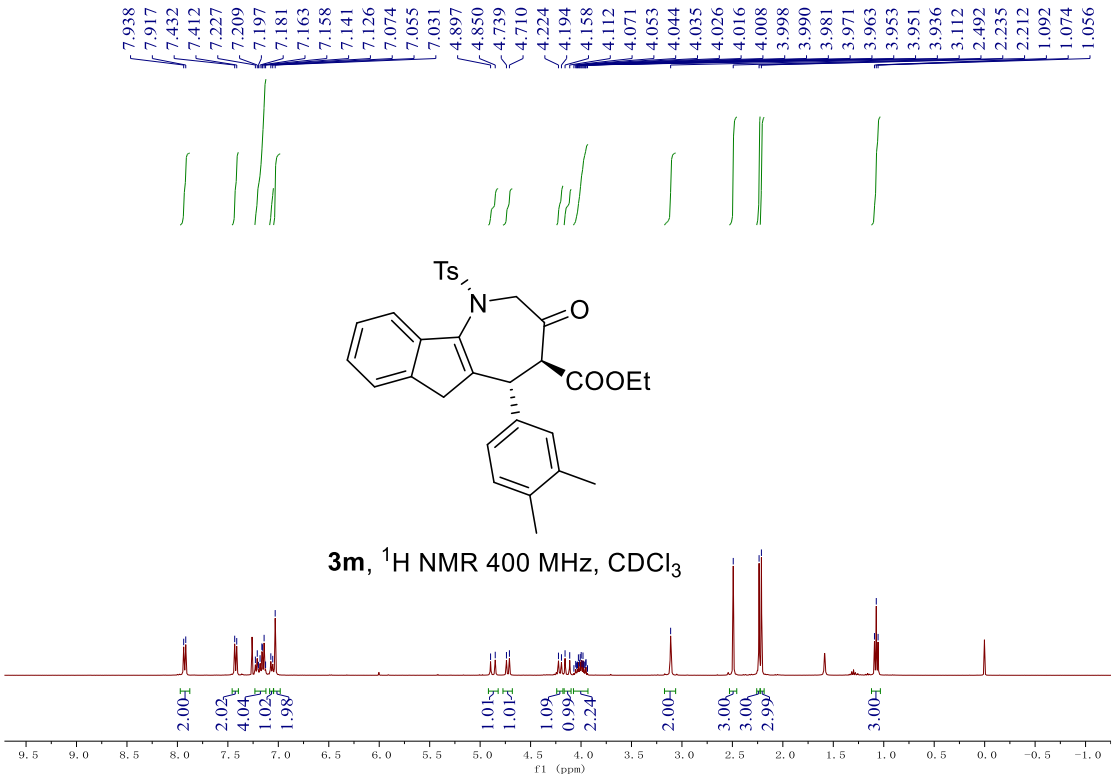
3j, ^{13}C NMR 100 MHz, $CDCl_3$



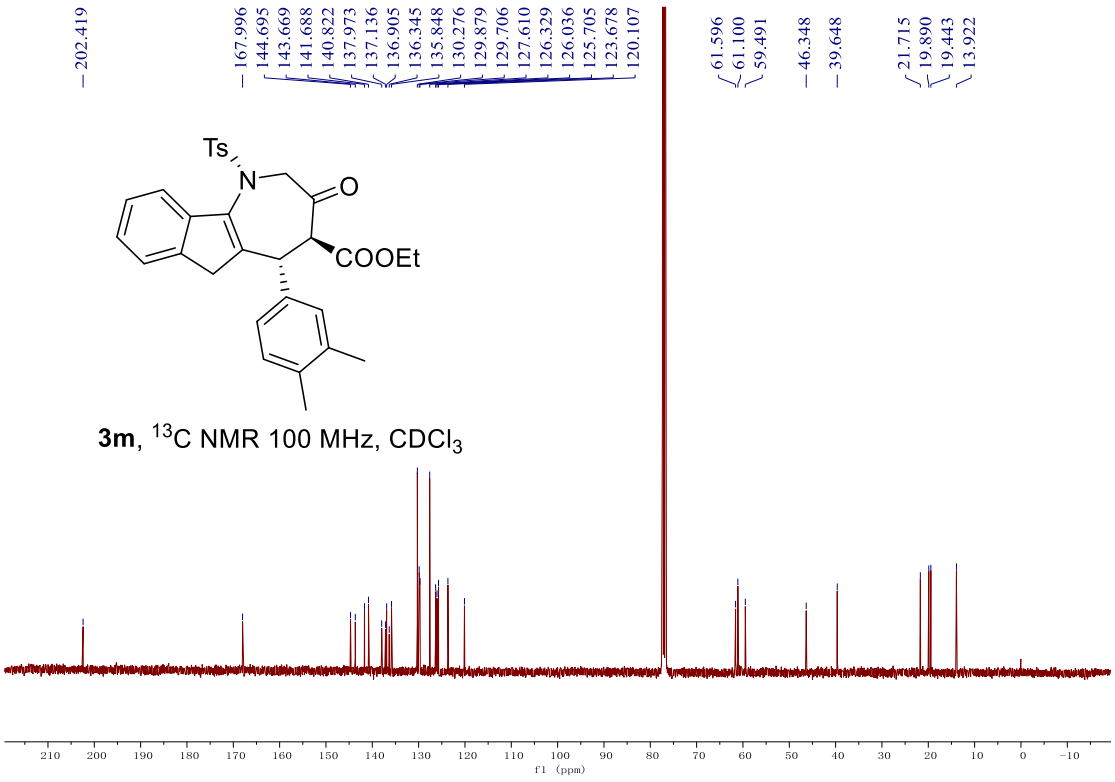
3k, ^{1}H NMR 400 MHz, $CDCl_3$



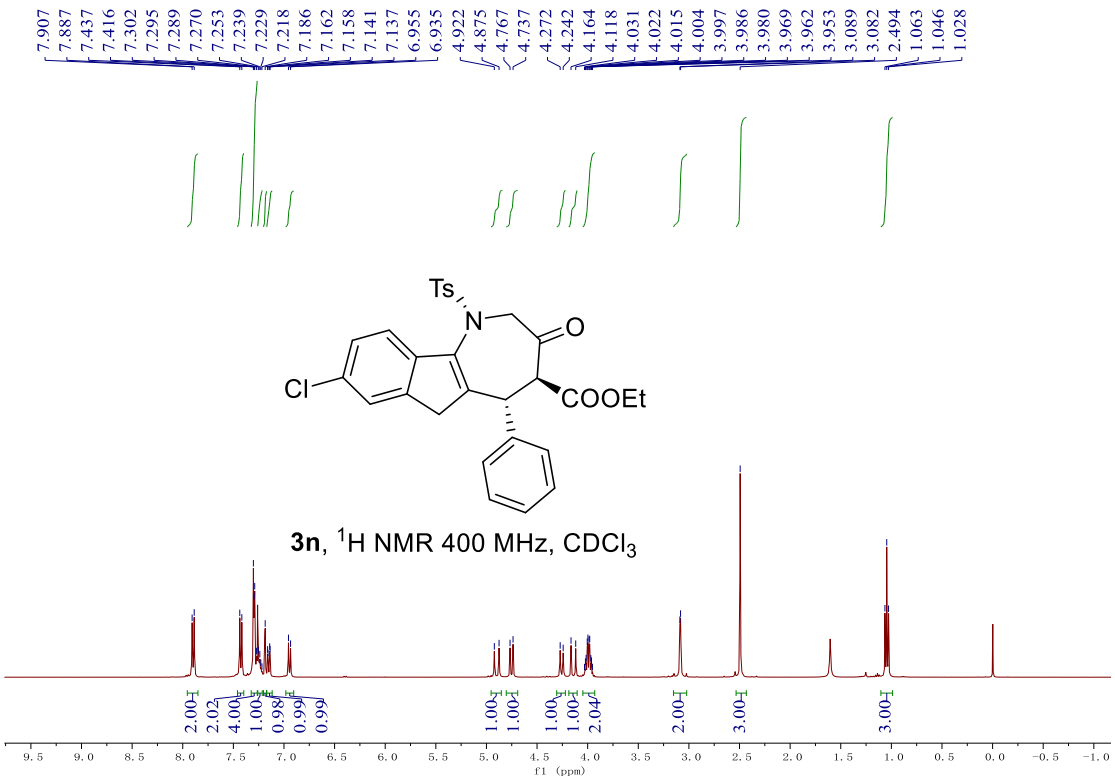
3k, ^{13}C NMR 100 MHz, $CDCl_3$



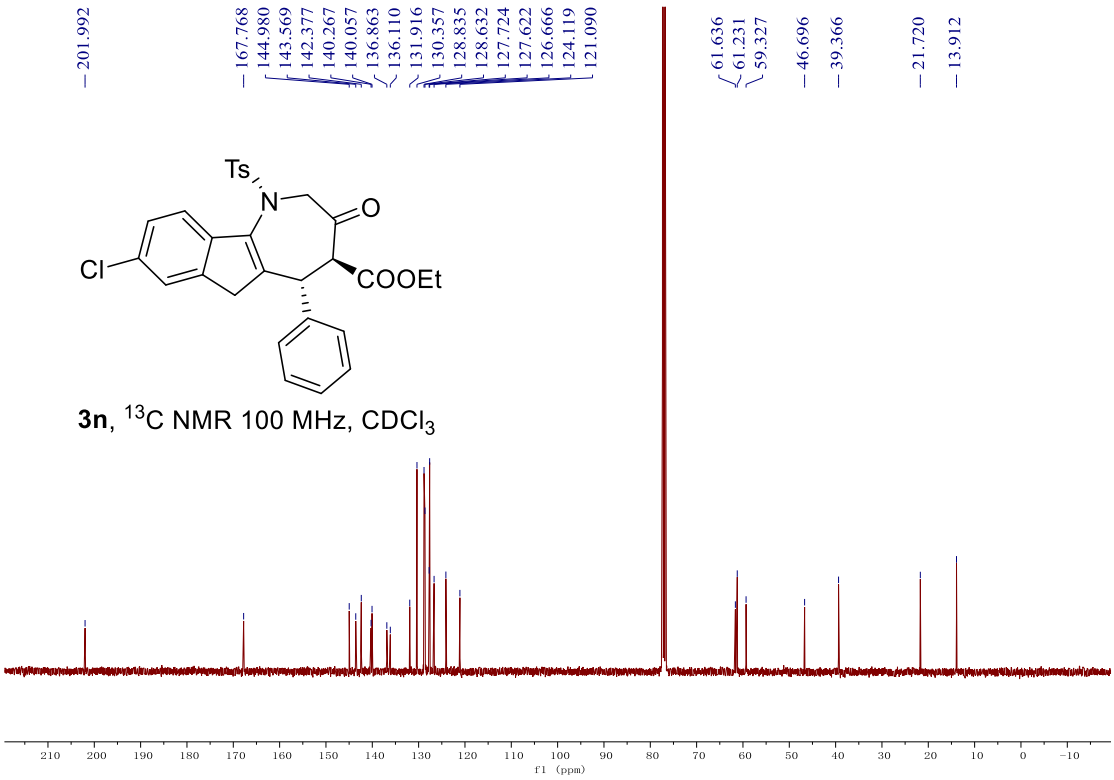
3m, ^{1}H NMR 400 MHz, $CDCl_3$



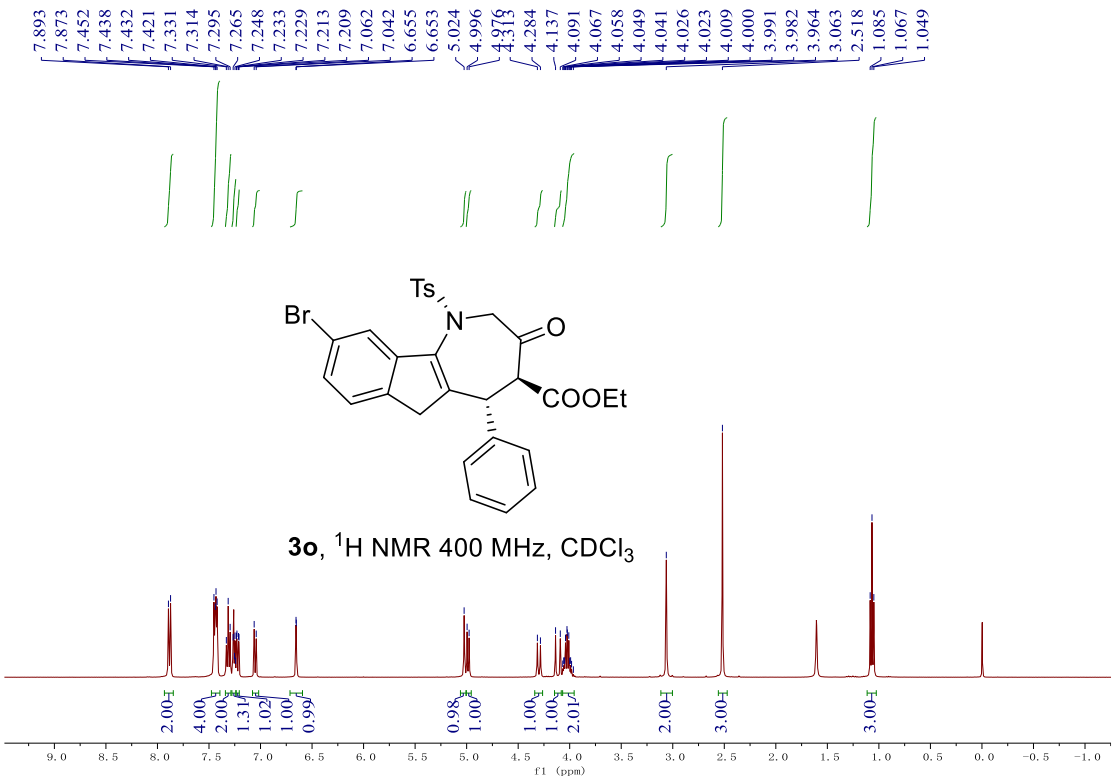
3m, ^{13}C NMR 100 MHz, $CDCl_3$



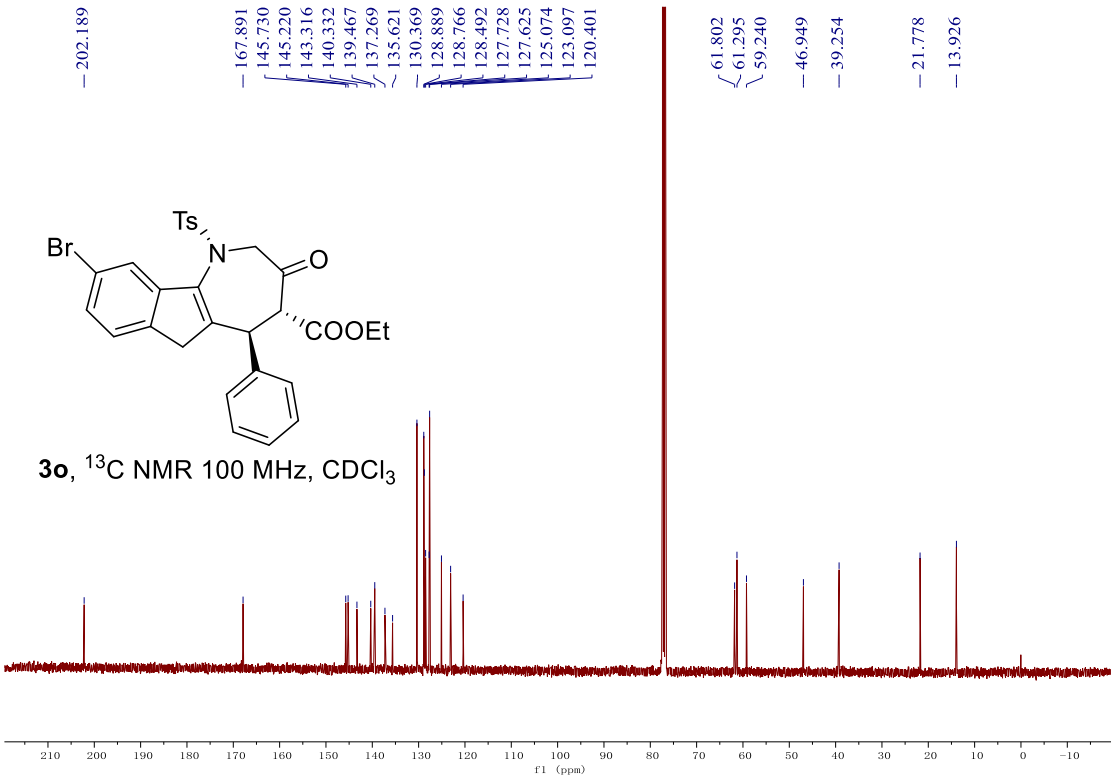
3n, ^{1}H NMR 400 MHz, $CDCl_3$



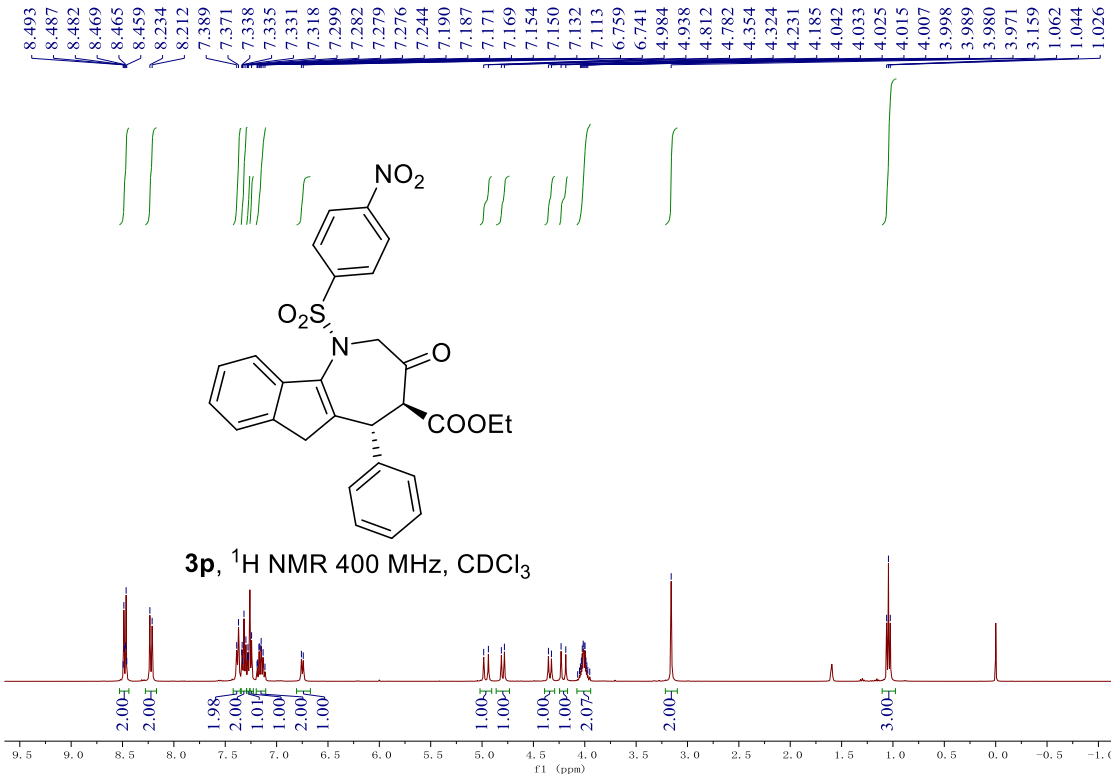
3n, ^{13}C NMR 100 MHz, $CDCl_3$



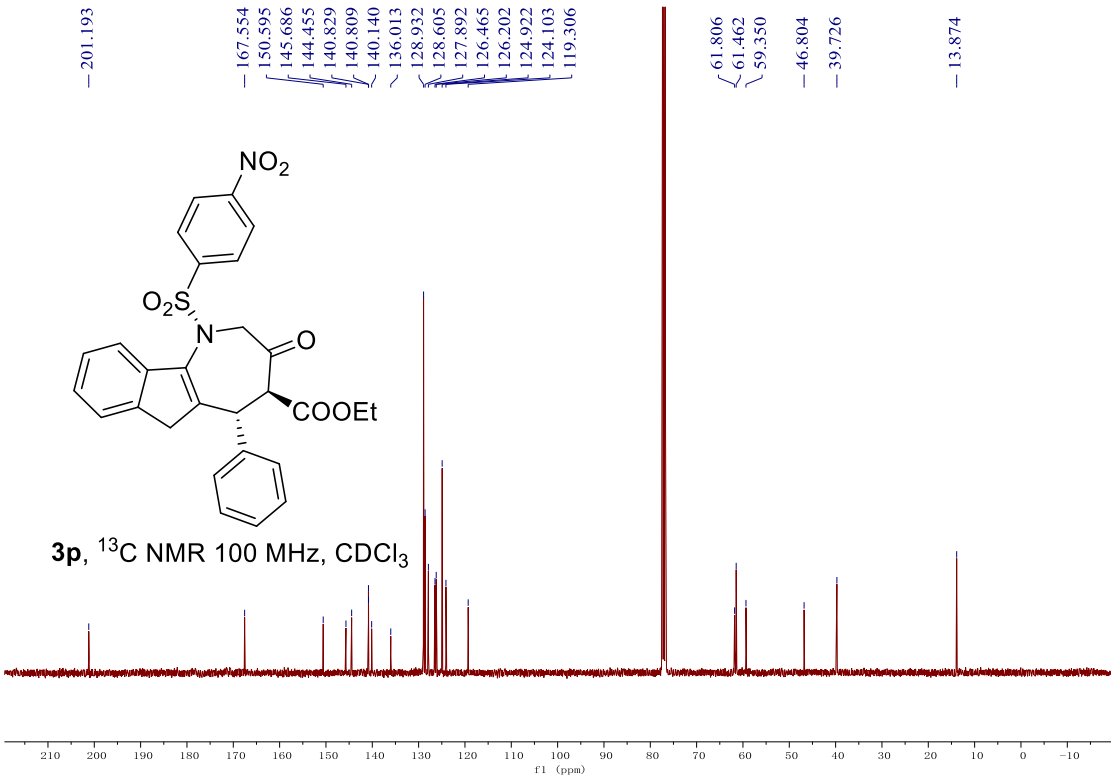
3o, ^{1}H NMR 400 MHz, $CDCl_3$

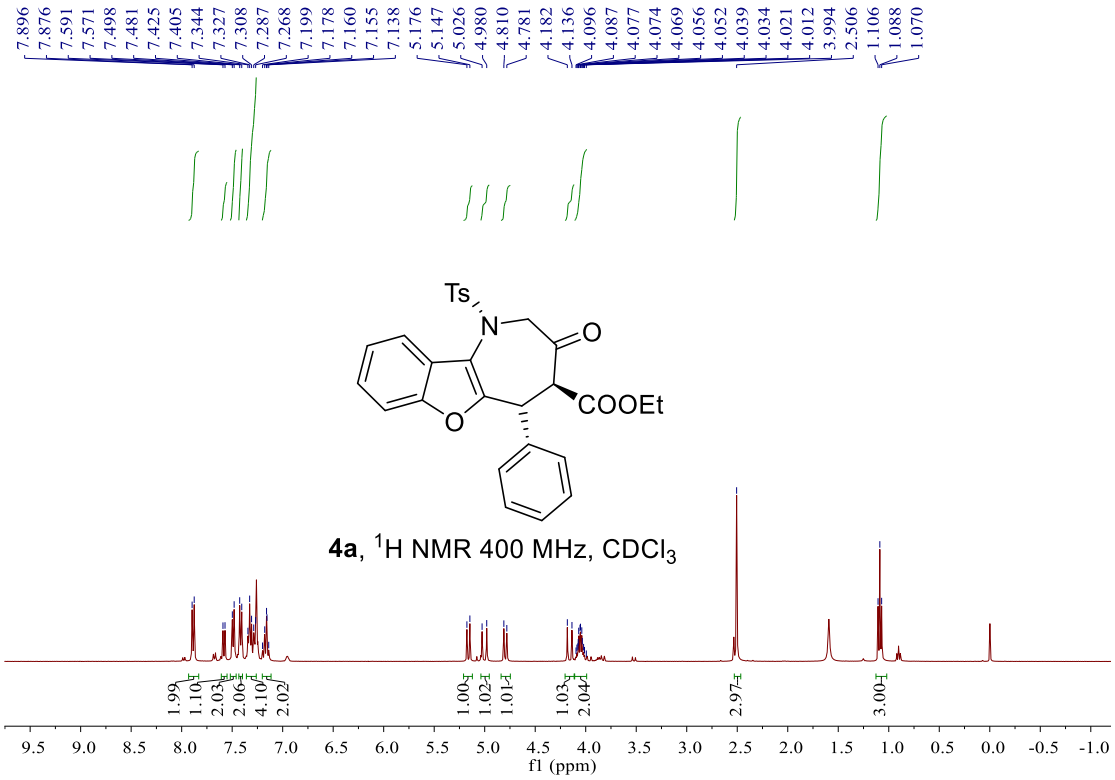


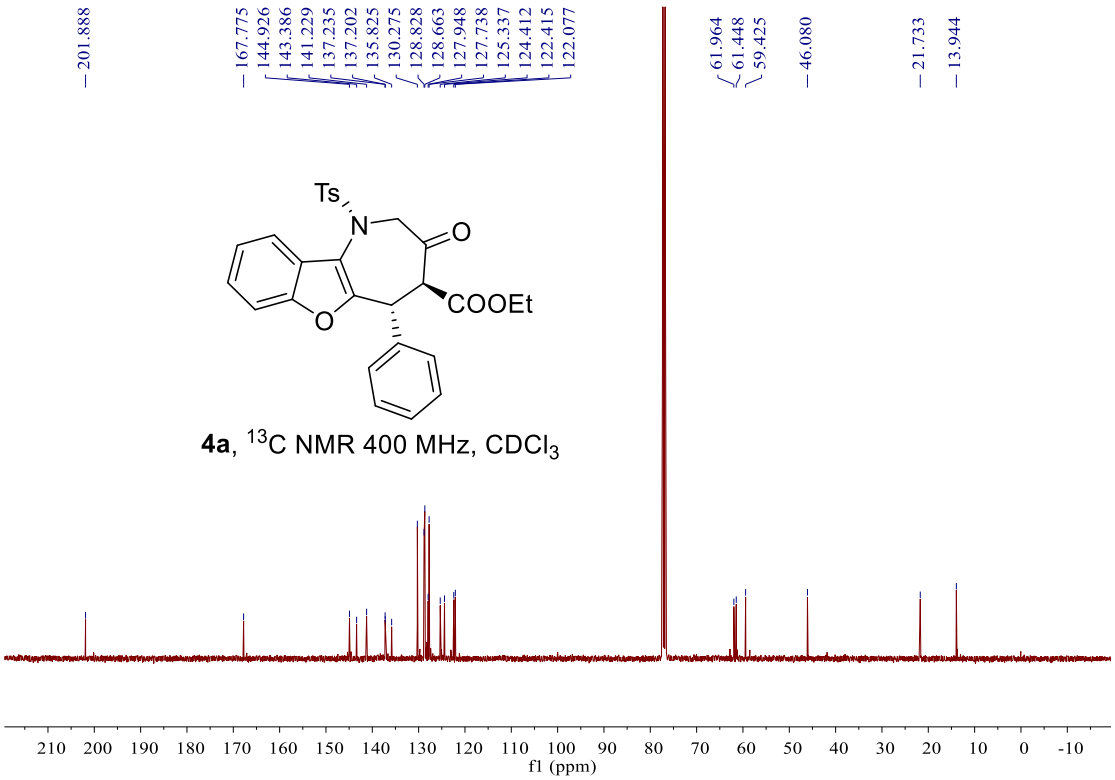
3o, ^{13}C NMR 100 MHz, $CDCl_3$



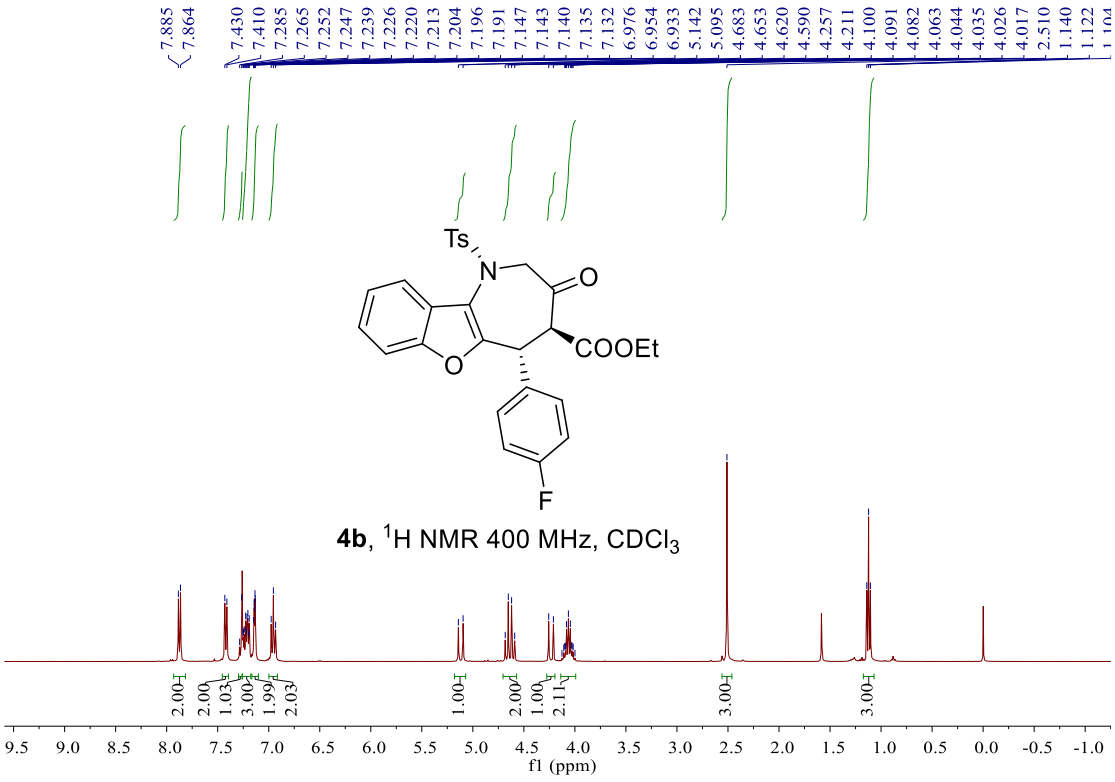
3p, ^{1}H NMR 400 MHz, $CDCl_3$


201.193
167.554
150.595
145.686
144.455
140.829
140.809
140.140
136.013
128.932
128.605
127.892
126.465
126.202
124.922
124.103
119.306
61.806
61.462
59.350
46.804
39.726
13.874
NO2
O2S
N
O
COOEt
3p, 13C NMR 100 MHz, CDCl3
f1 (ppm)

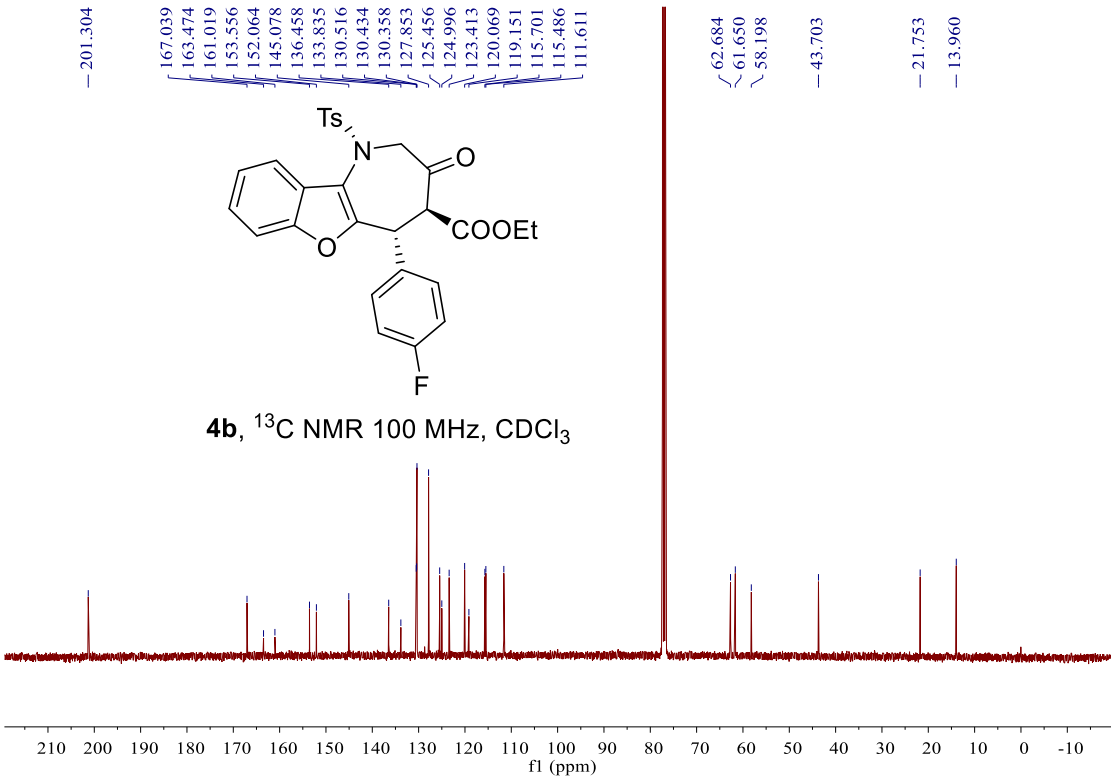

7.896
7.876
7.591
7.571
7.498
7.481
7.425
7.405
7.344
7.327
7.308
7.287
7.268
7.199
7.178
7.160
7.155
7.138
5.176
5.147
5.026
4.980
4.810
4.781
4.182
4.136
4.096
4.087
4.077
4.074
4.069
4.056
4.052
4.039
4.034
4.021
4.012
3.994
2.506
1.106
1.088
1.070
Ts
N
O
O
COOEt
4a, 1H NMR 400 MHz, CDCl3
1.99
1.10
2.03
2.06
4.10
2.02
1.00
1.02
1.01
1.03
2.04
2.97
3.00
f1 (ppm)



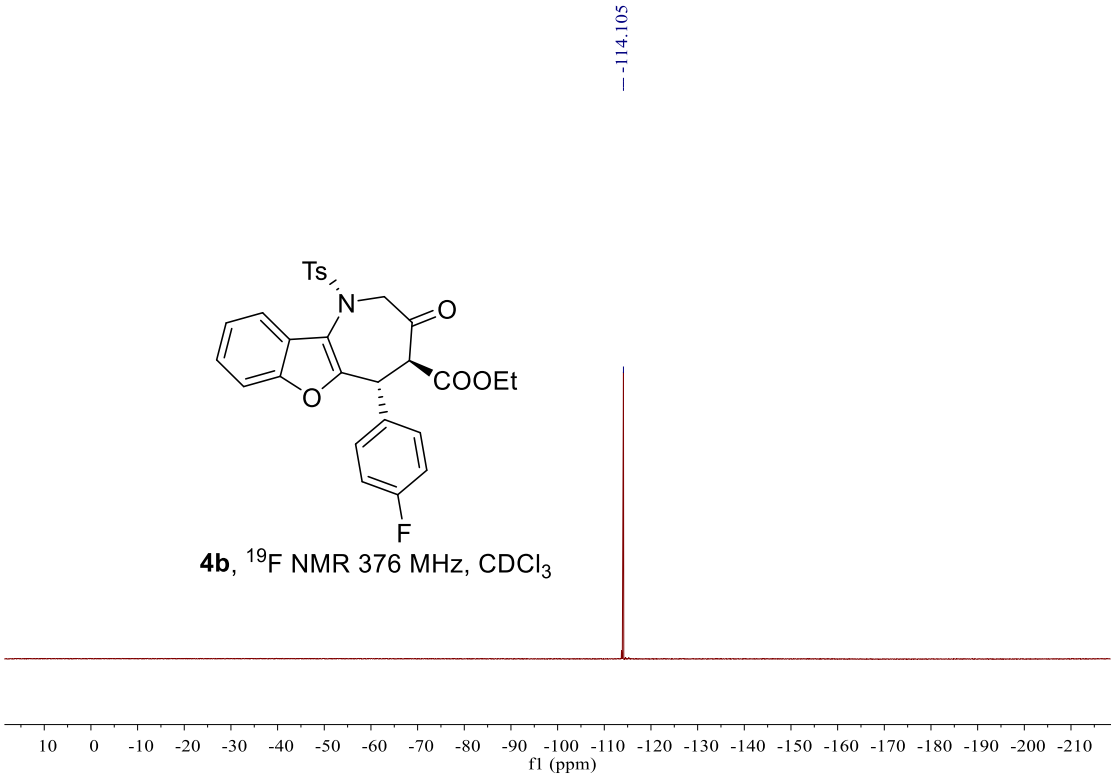
4a, ^{13}C NMR 400 MHz, $CDCl_3$



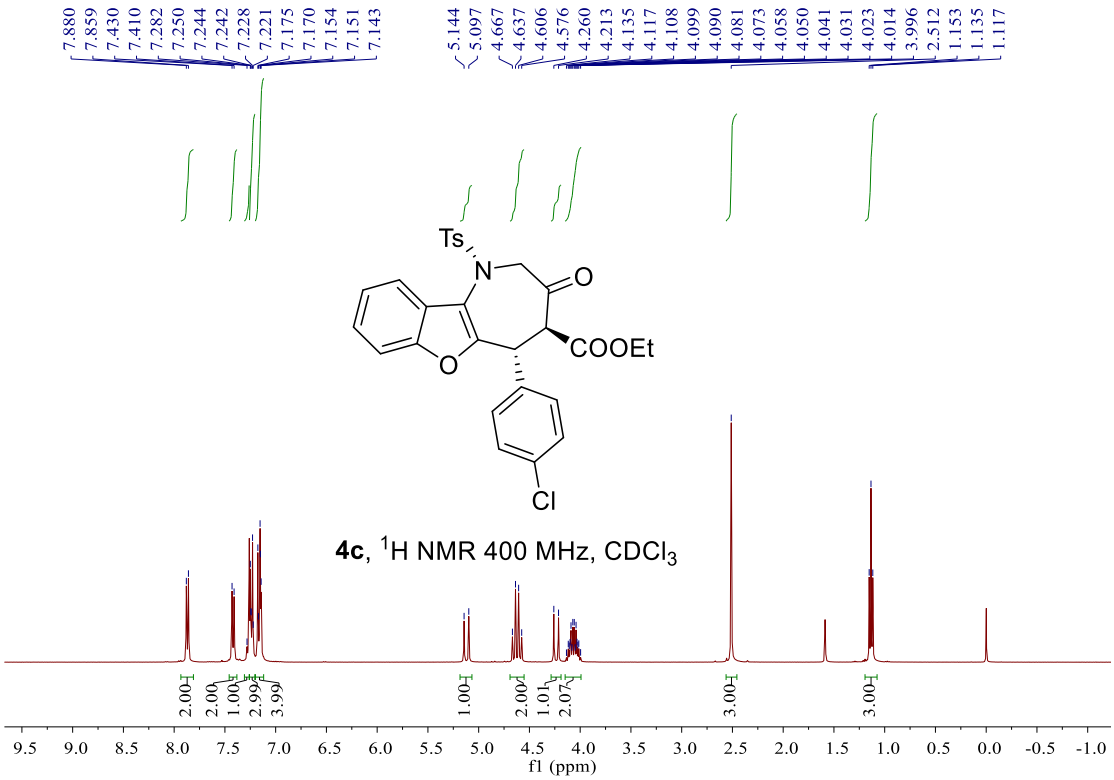
4b, ^{1}H NMR 400 MHz, $CDCl_3$

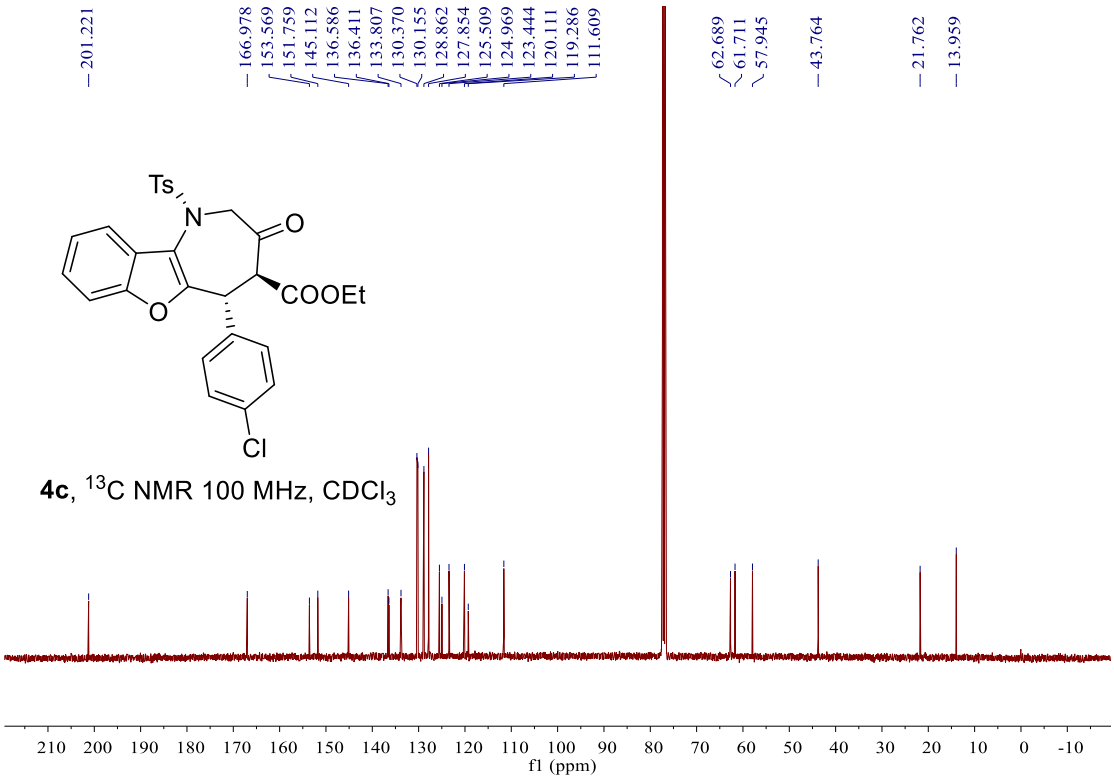


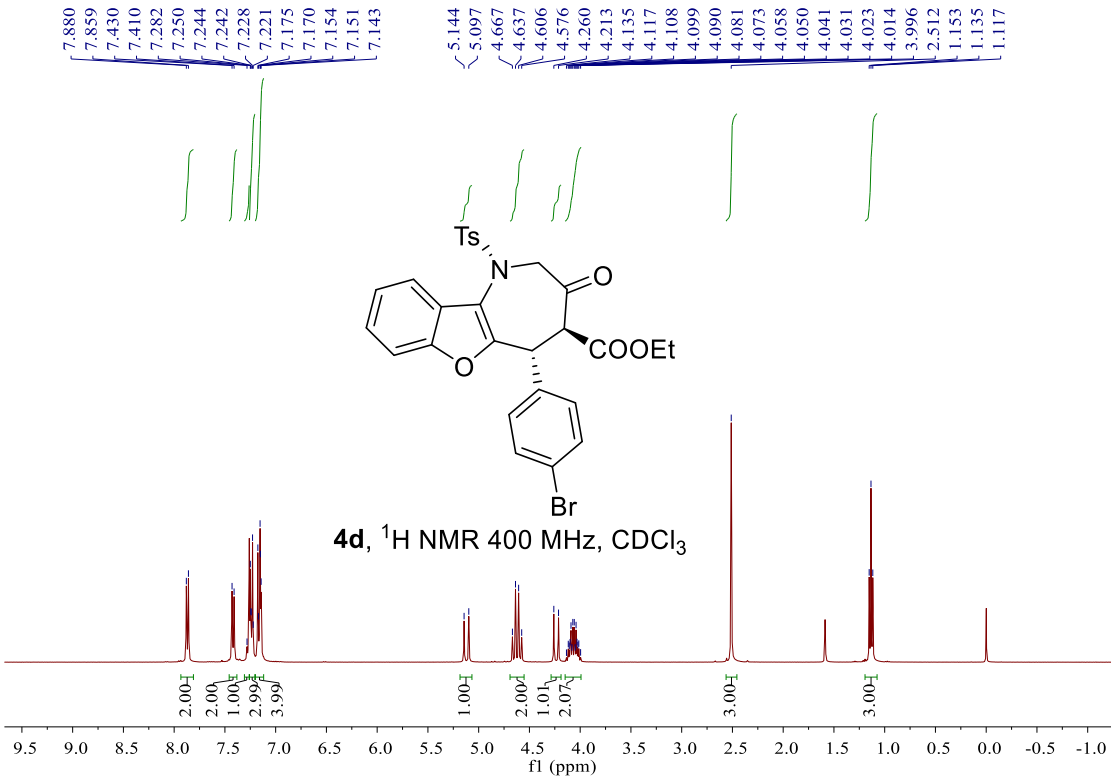
4b, ^{13}C NMR 100 MHz, $CDCl_3$



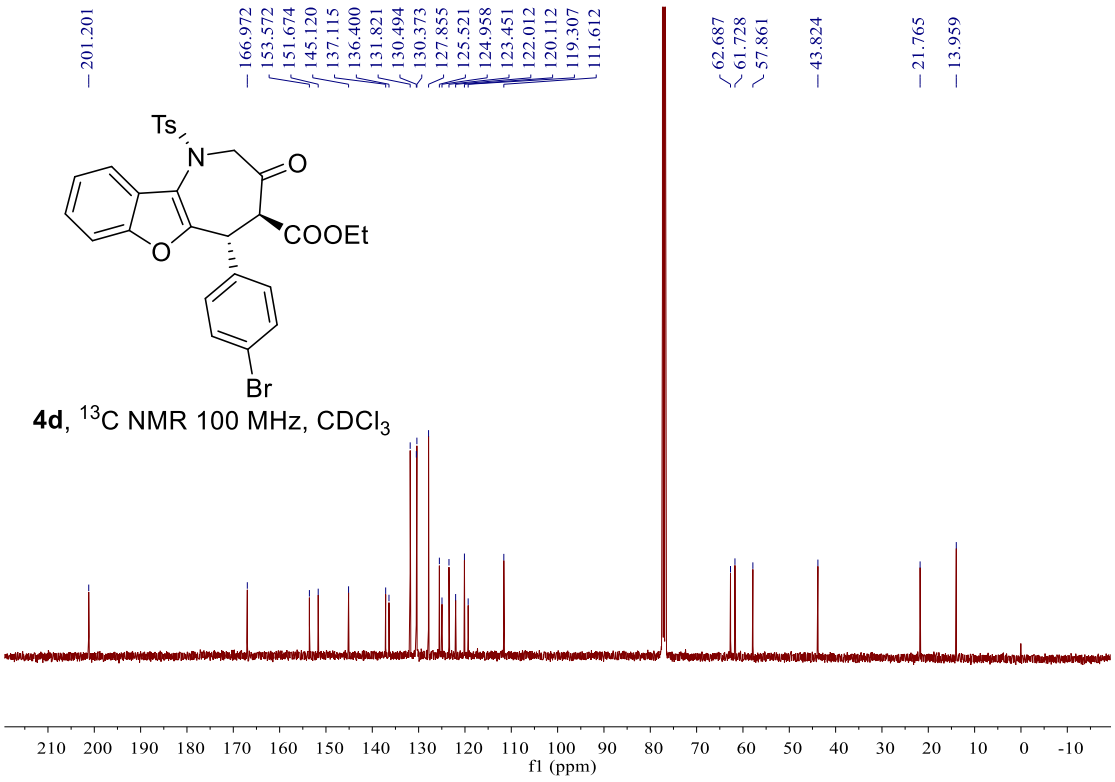
4b, ^{19}F NMR 376 MHz, $CDCl_3$


7.880
7.859
7.430
7.410
7.282
7.250
7.244
7.242
7.228
7.221
7.175
7.170
7.154
7.151
7.143
5.144
5.097
4.667
4.637
4.606
4.576
4.260
4.213
4.135
4.117
4.108
4.099
4.090
4.081
4.073
4.058
4.050
4.041
4.031
4.023
4.014
3.996
2.512
1.153
1.135
1.117
Ts
N
O
O
COOEt
Cl
4c, 1H NMR 400 MHz, CDCl3
2.00
2.00
1.00
2.99
3.99
1.00
2.00
1.01
2.07
3.00
3.00
f1 (ppm)

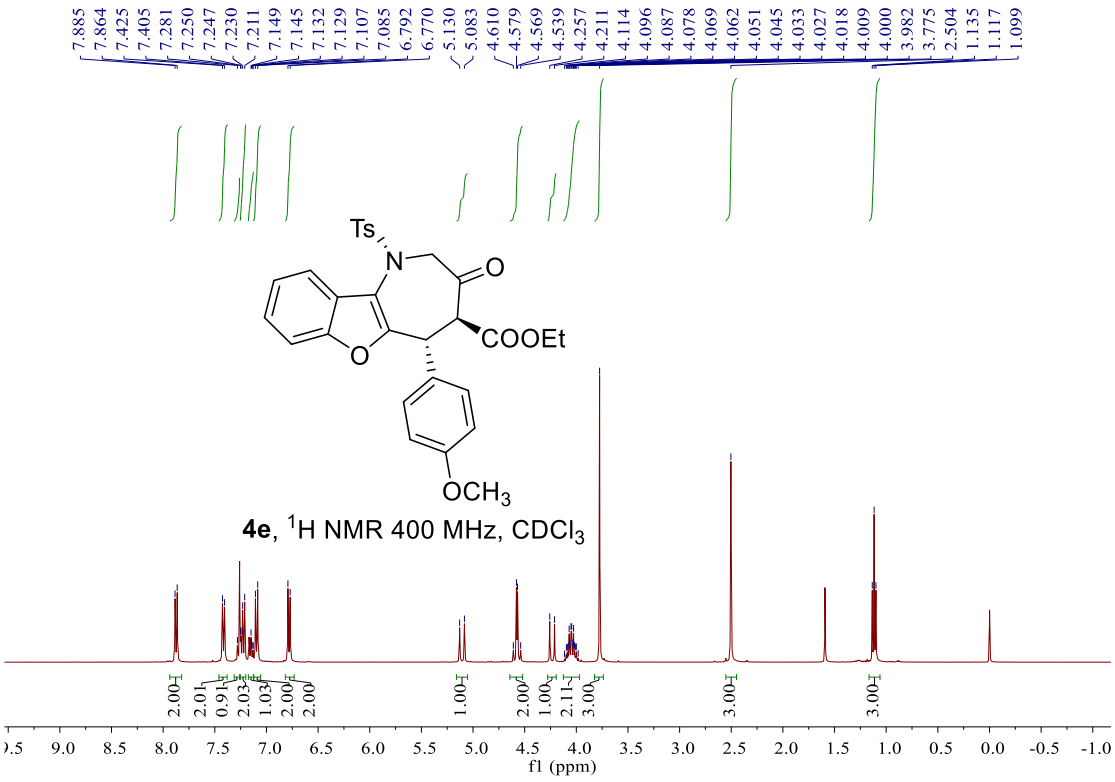

201.221
166.978
153.569
151.759
145.112
136.586
136.411
133.807
130.370
130.155
128.862
127.854
125.509
124.969
123.444
120.111
119.286
111.609
62.689
61.711
57.945
43.764
21.762
13.959
Ts
N
O
O
COOEt
Cl
4c, 13C NMR 100 MHz, CDCl3
f1 (ppm)



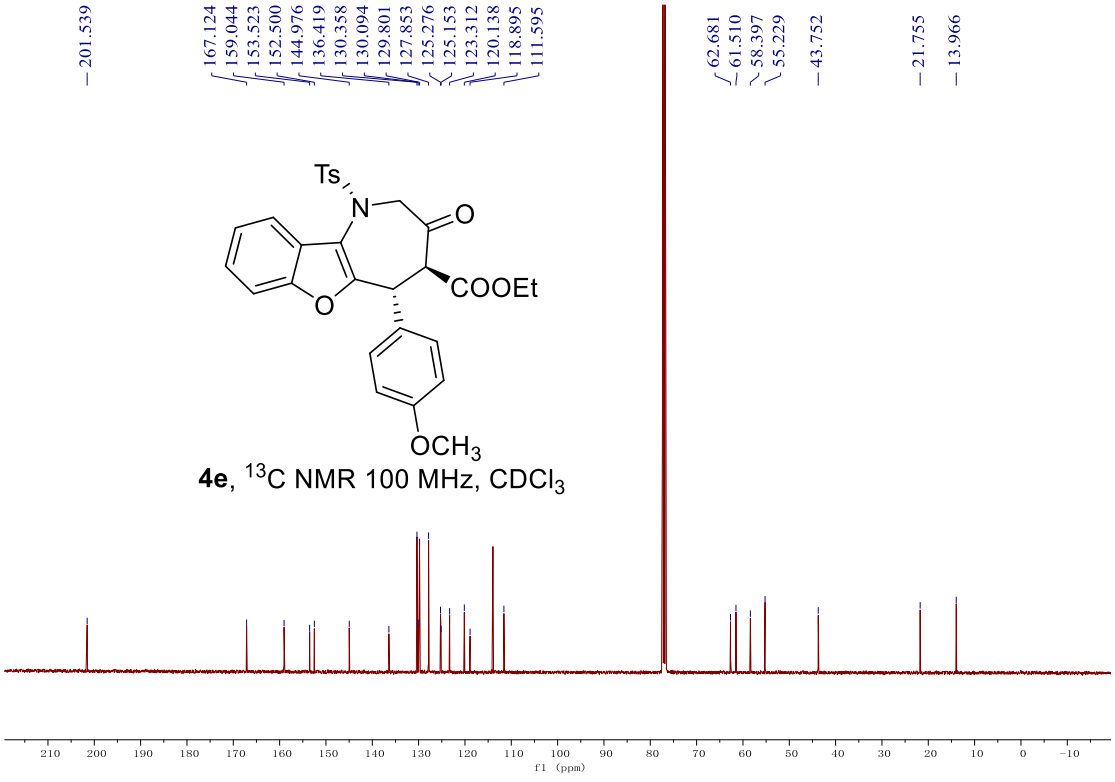
4d, ^{1}H NMR 400 MHz, $CDCl_3$



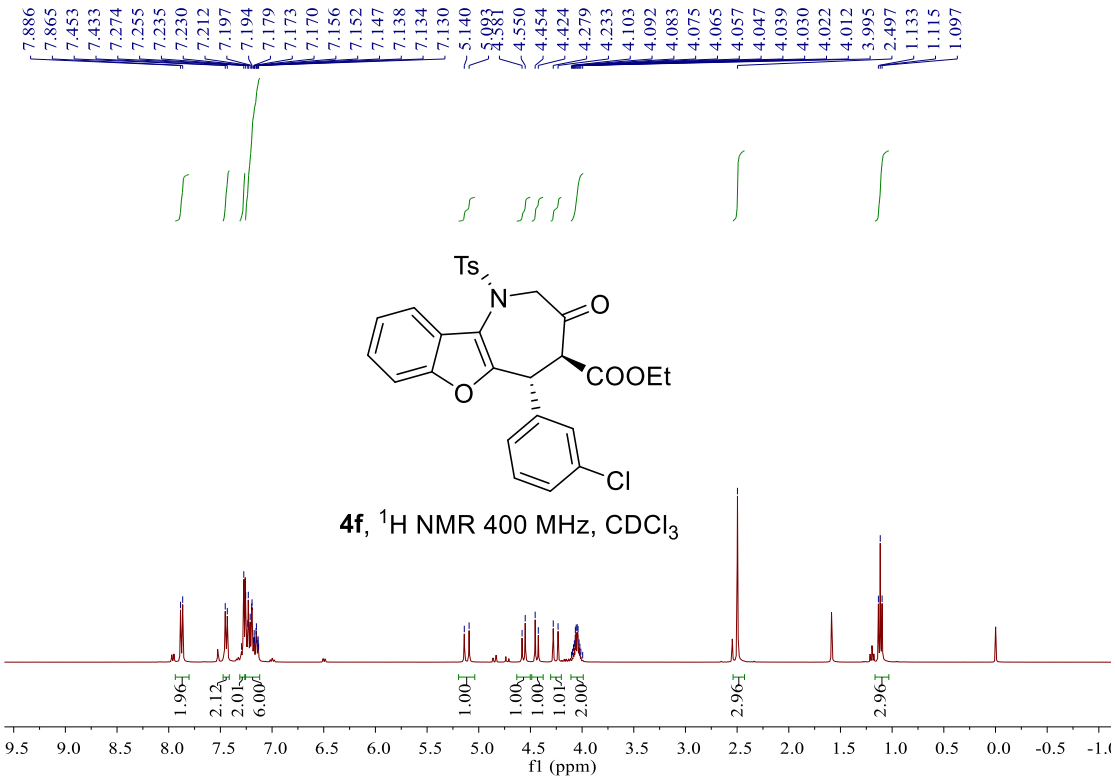
4d, ^{13}C NMR 100 MHz, $CDCl_3$



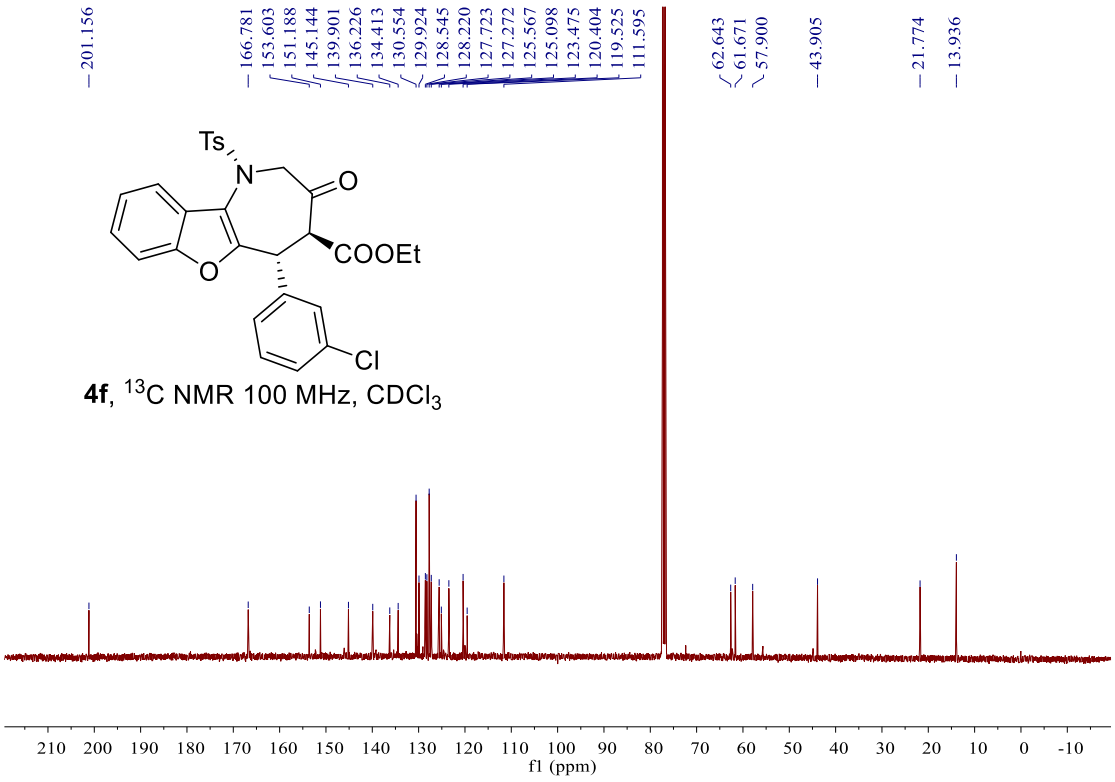
4e, ^{1}H NMR 400 MHz, $CDCl_3$



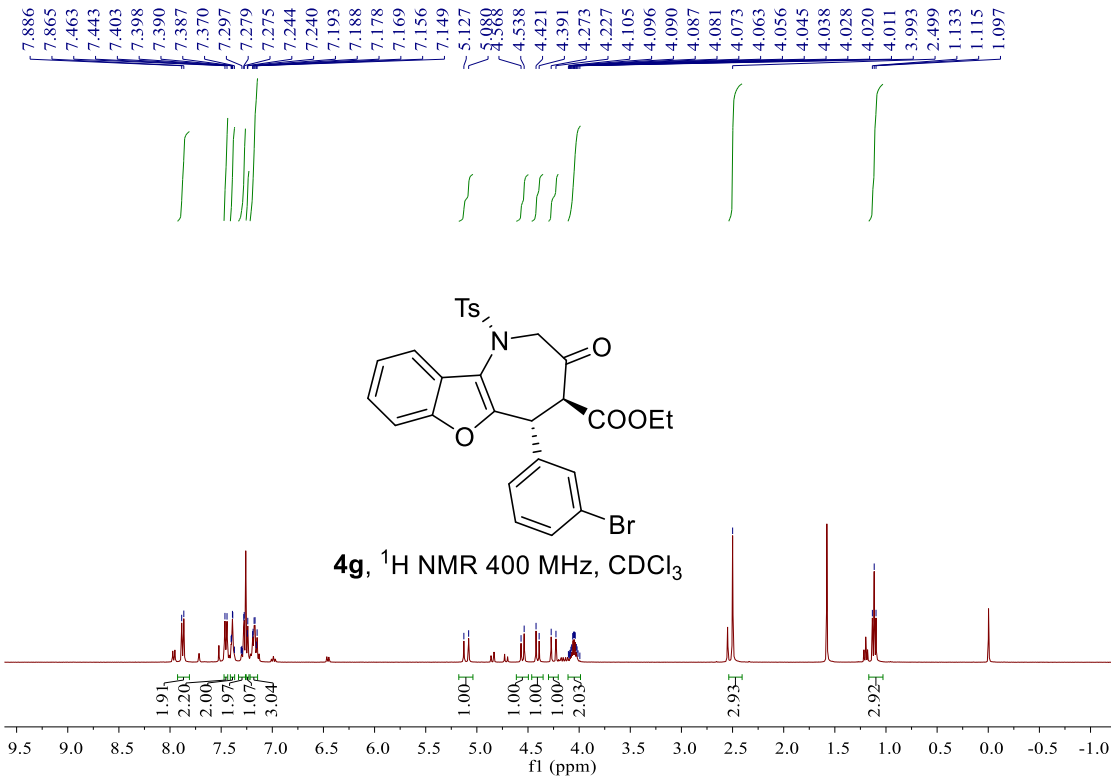
4e, ^{13}C NMR 100 MHz, $CDCl_3$



4f, ^{1}H NMR 400 MHz, $CDCl_3$



4f, ^{13}C NMR 100 MHz, $CDCl_3$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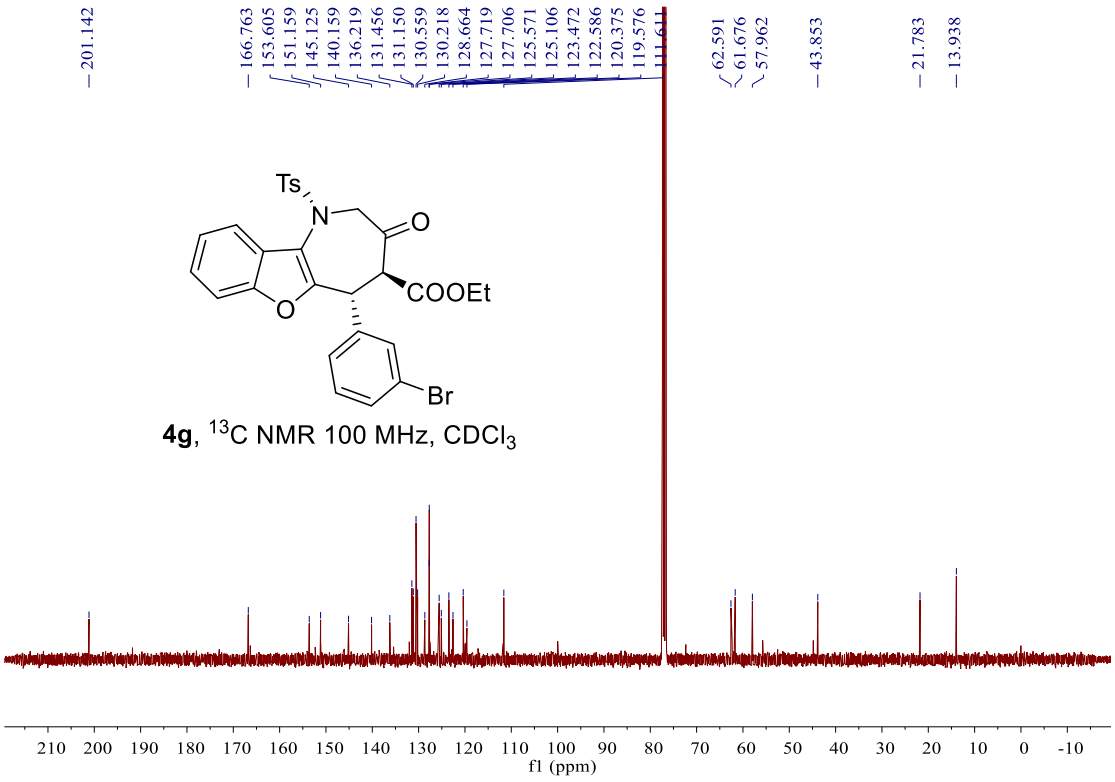
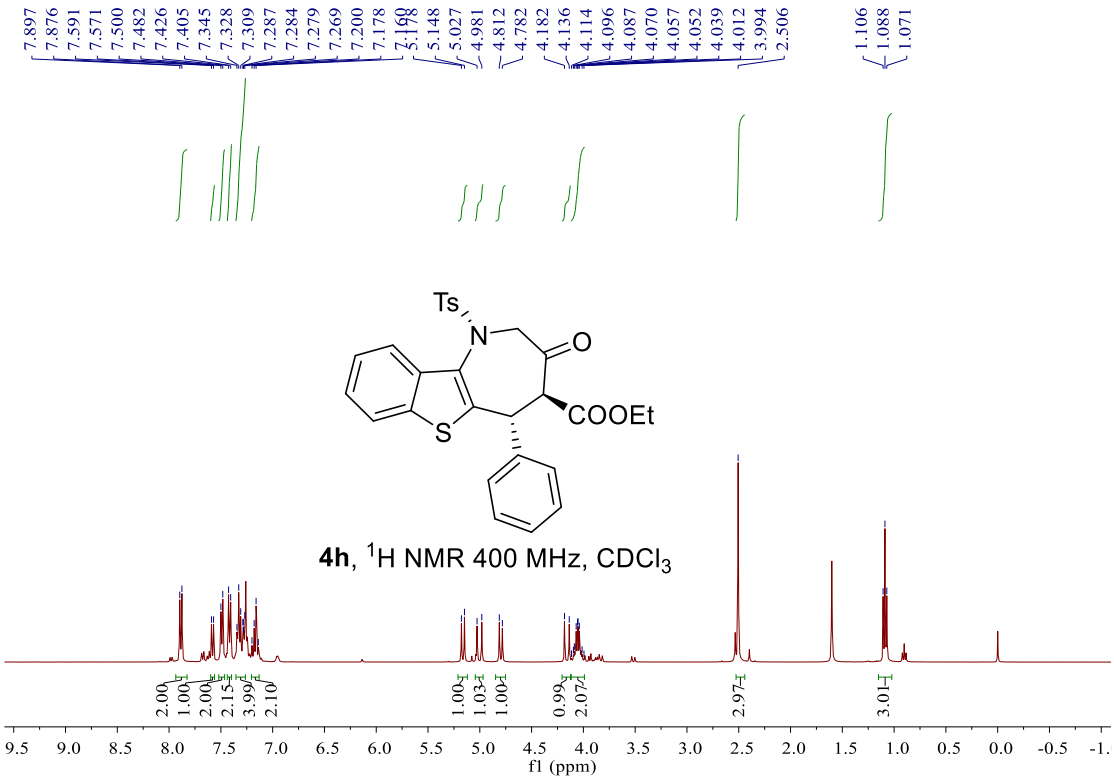
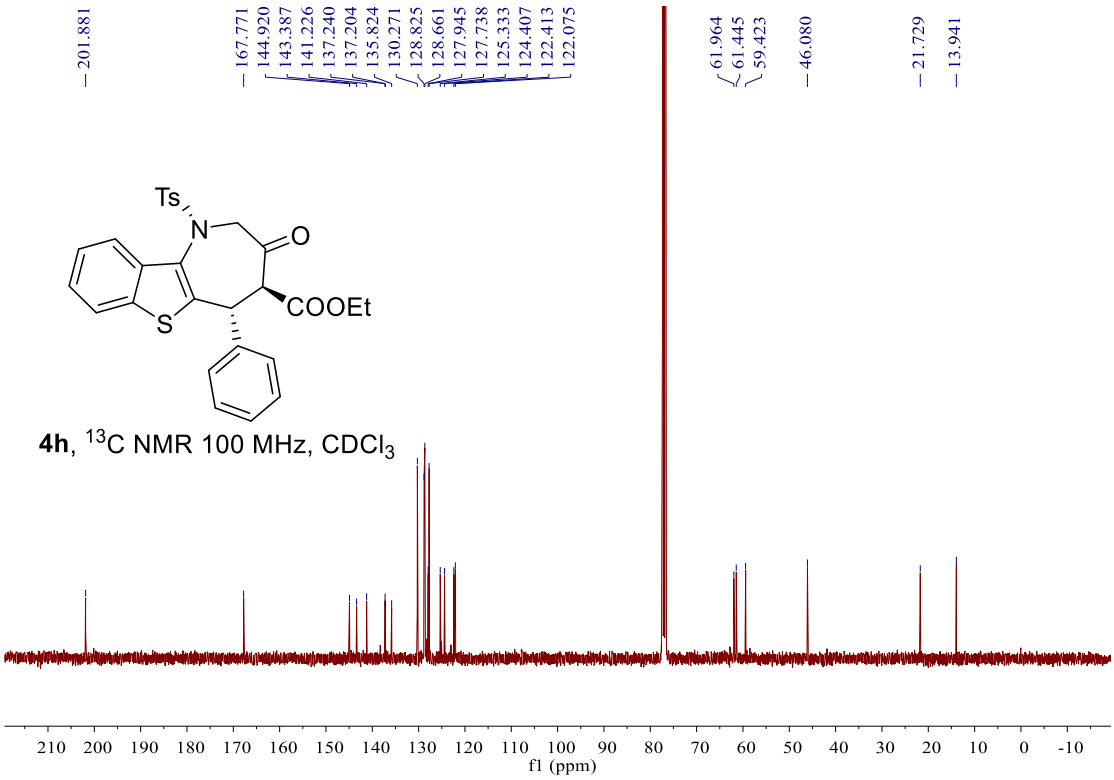
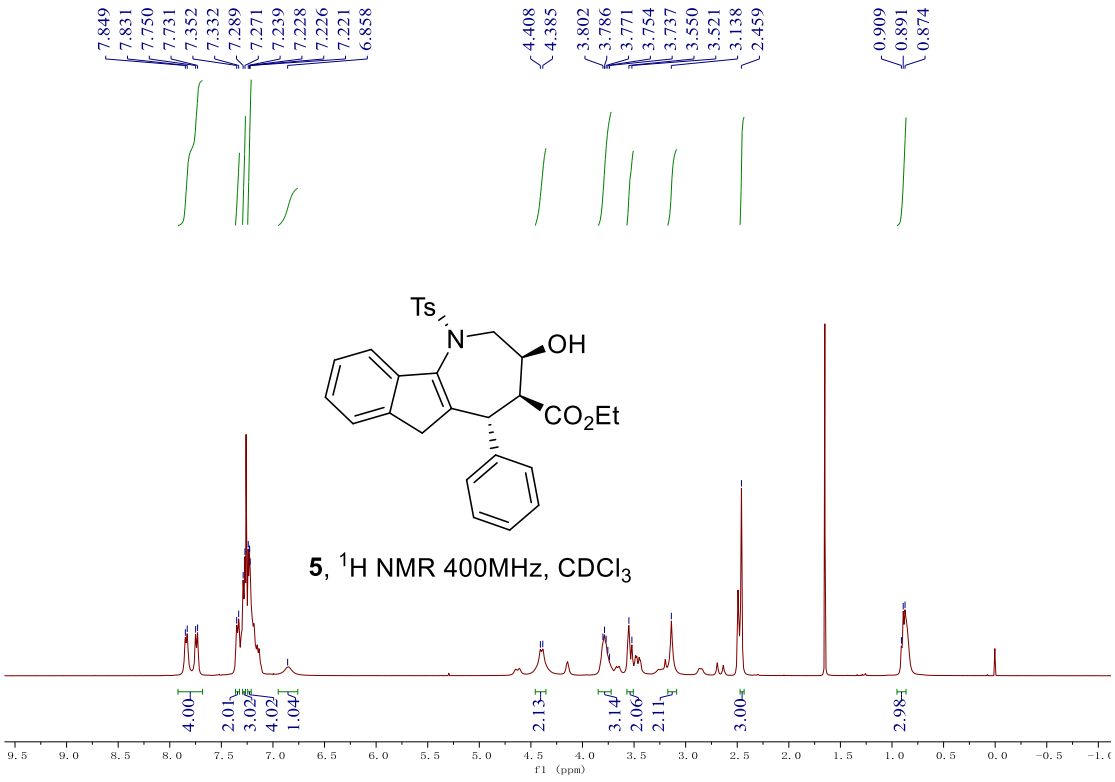
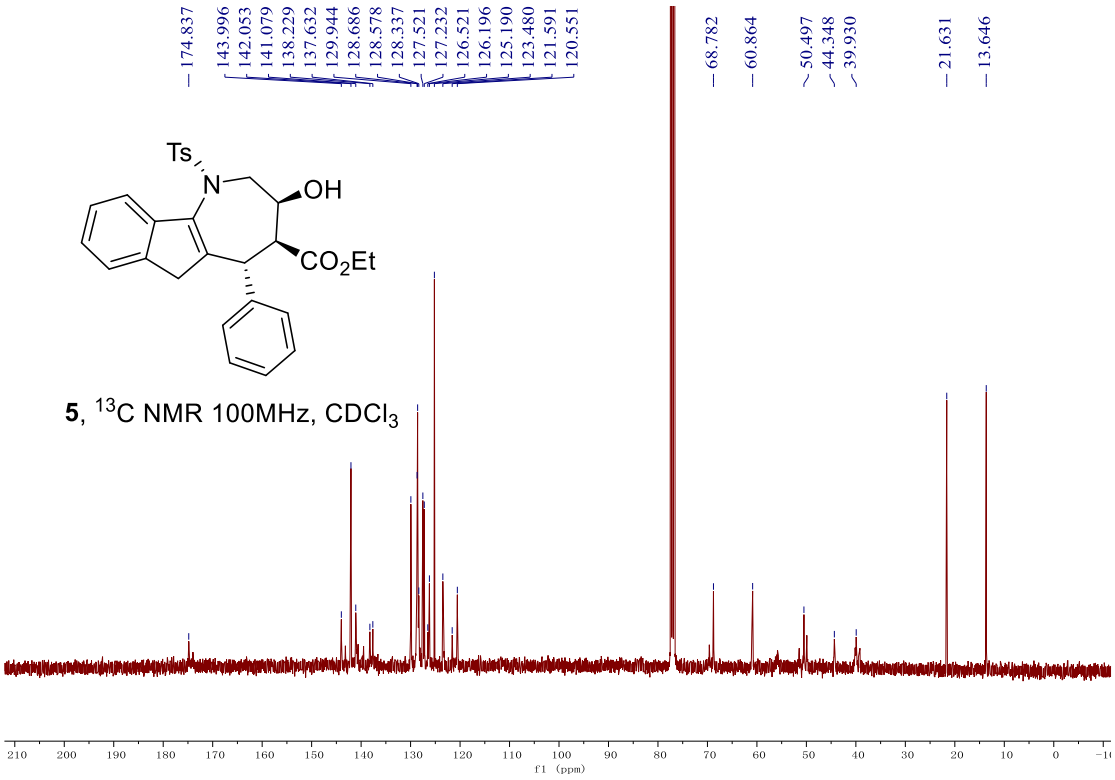
7.865
7.463
7.443
7.403
7.398
7.390
7.387
7.370
7.297
7.279
7.275
7.244
7.240
7.193
7.188
7.178
7.169
7.156
7.149
5.127
5.080
4.568
4.538
4.421
4.391
4.273
4.227
4.105
4.096
4.090
4.087
4.081
4.073
4.063
4.056
4.045
4.038
4.028
4.020
4.011
3.993
2.499
1.133
1.115
1.097
Ts
N
O
O
COOEt
Br
4g, 1H NMR 400 MHz, CDCl3
1.91
2.20
2.00
1.97
1.07
3.04
1.00
1.00
1.00
1.00
2.03
2.93
2.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

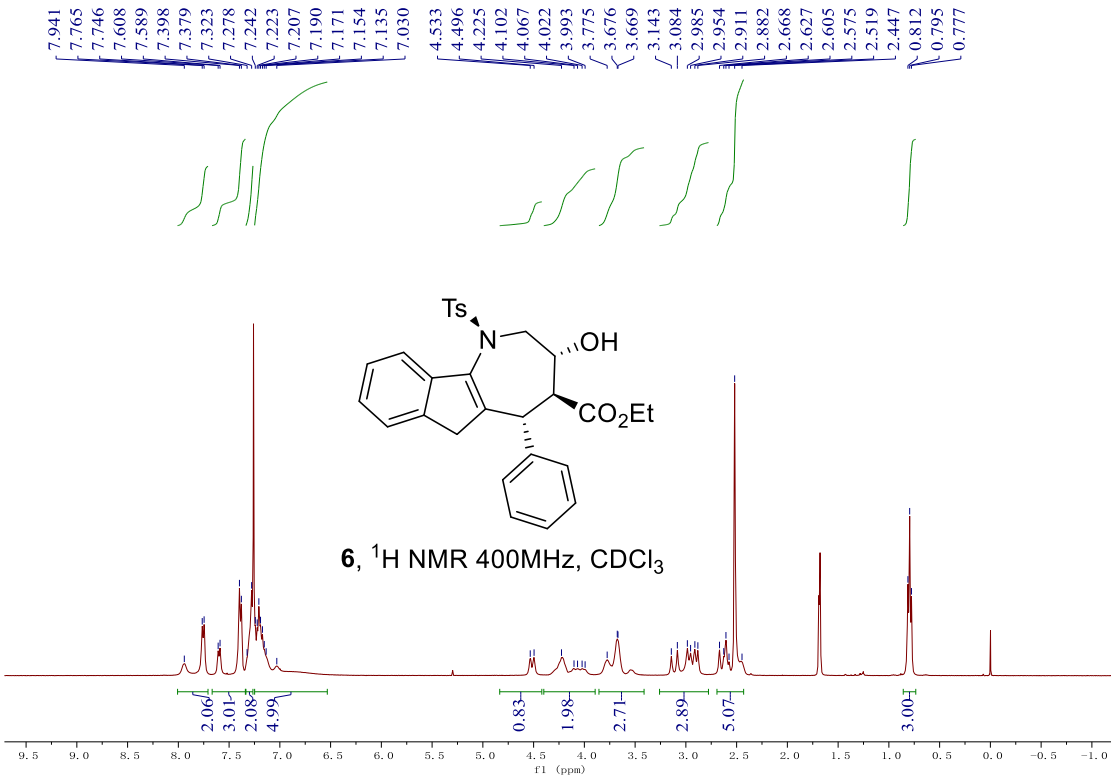

201.142
166.763
153.605
151.159
145.125
140.159
136.219
131.456
131.150
130.559
130.218
128.664
127.719
127.706
125.571
125.106
123.472
122.586
120.375
119.576
111.611
62.591
61.676
57.962
43.853
21.783
13.938
Ts
N
O
O
COOEt
Br
4g, 13C NMR 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

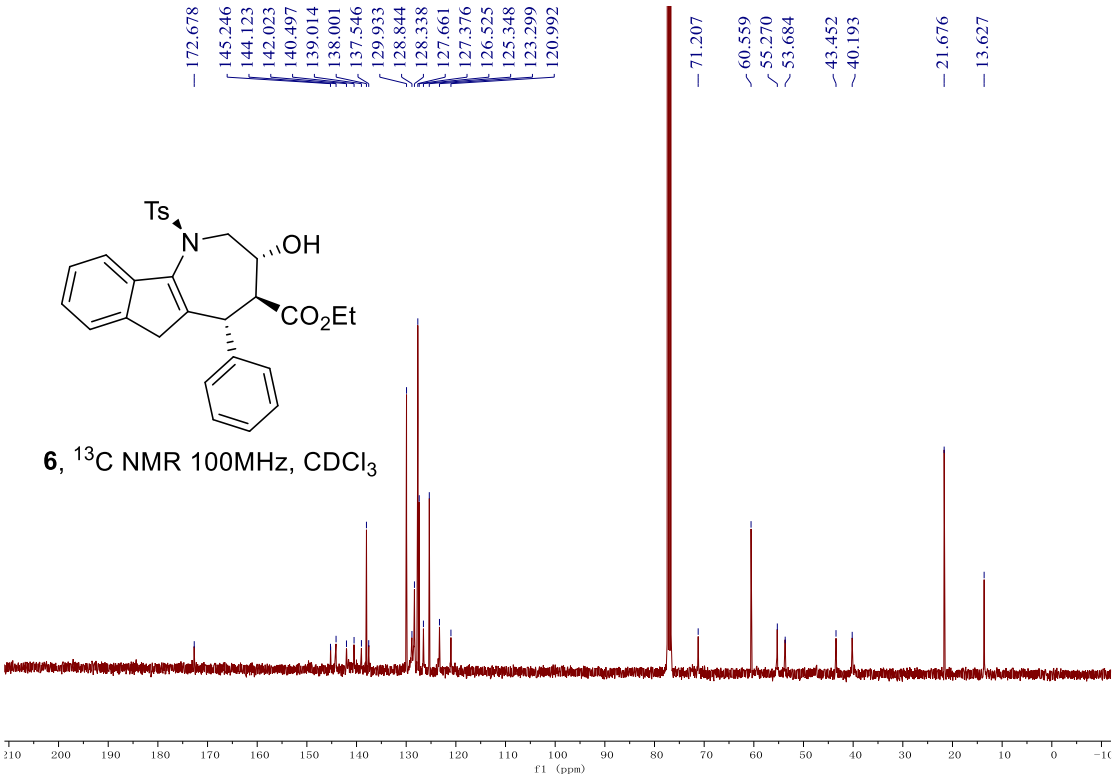

7.897
7.876
7.591
7.571
7.500
7.482
7.426
7.405
7.345
7.328
7.309
7.287
7.284
7.279
7.269
7.200
7.178
5.148
5.027
4.981
4.812
4.782
4.182
4.136
4.114
4.096
4.087
4.070
4.057
4.052
4.039
4.012
3.994
2.506
1.106
1.088
1.071
Ts
N
O
COOEt
S
4h, 1H NMR 400 MHz, CDCl3
2.00
1.00
2.00
2.15
3.99
2.10
1.00
1.03
1.00
0.99
2.07
2.97
3.01
f1 (ppm)

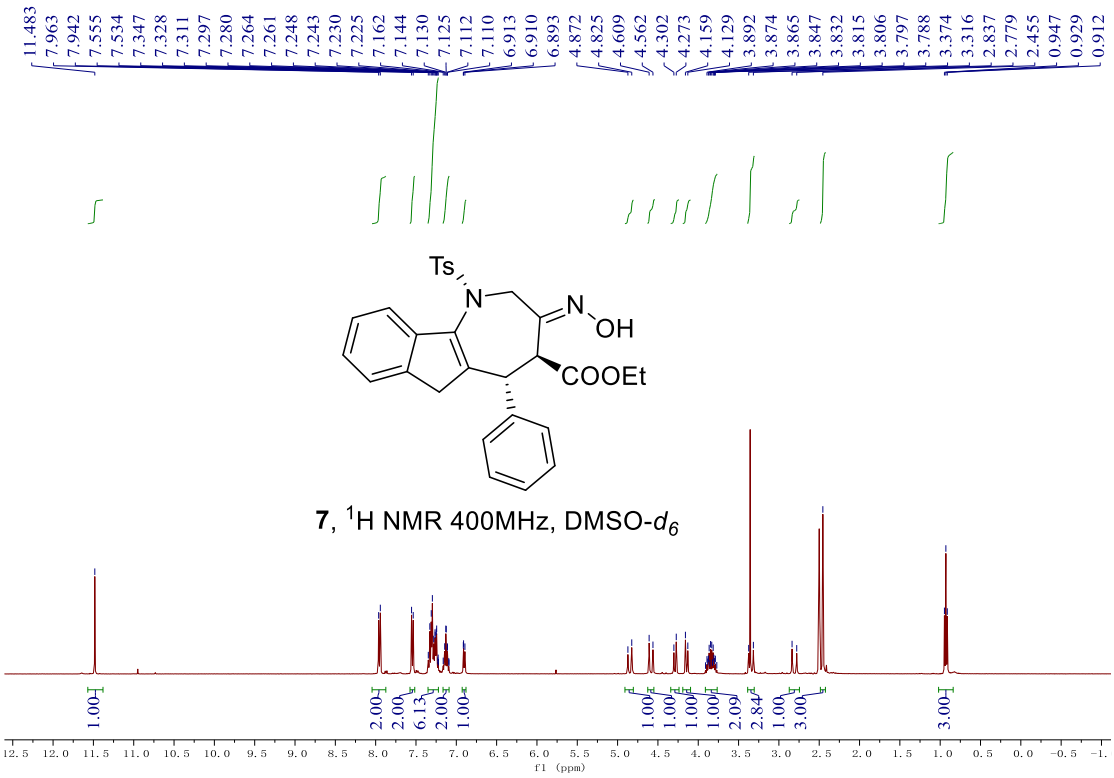

201.881
167.771
144.920
143.387
141.226
137.240
137.204
135.824
130.271
128.825
128.661
127.945
127.738
125.333
124.407
122.413
122.075
61.964
61.445
59.423
46.080
21.729
13.941
Ts
N
O
COOEt
S
4h, 13C NMR 100 MHz, CDCl3
f1 (ppm)


7.849
7.831
7.750
7.731
7.352
7.332
7.289
7.271
7.239
7.228
7.226
7.221
6.858
4.408
4.385
3.802
3.786
3.771
3.754
3.737
3.550
3.521
3.138
2.459
0.909
0.891
0.874
Ts
N
OH
CO2Et
5, 1H NMR 400MHz, CDCl3
4.00
2.01
3.02
4.02
1.04
2.13
3.14
2.06
2.11
3.00
2.98
f1 (ppm)

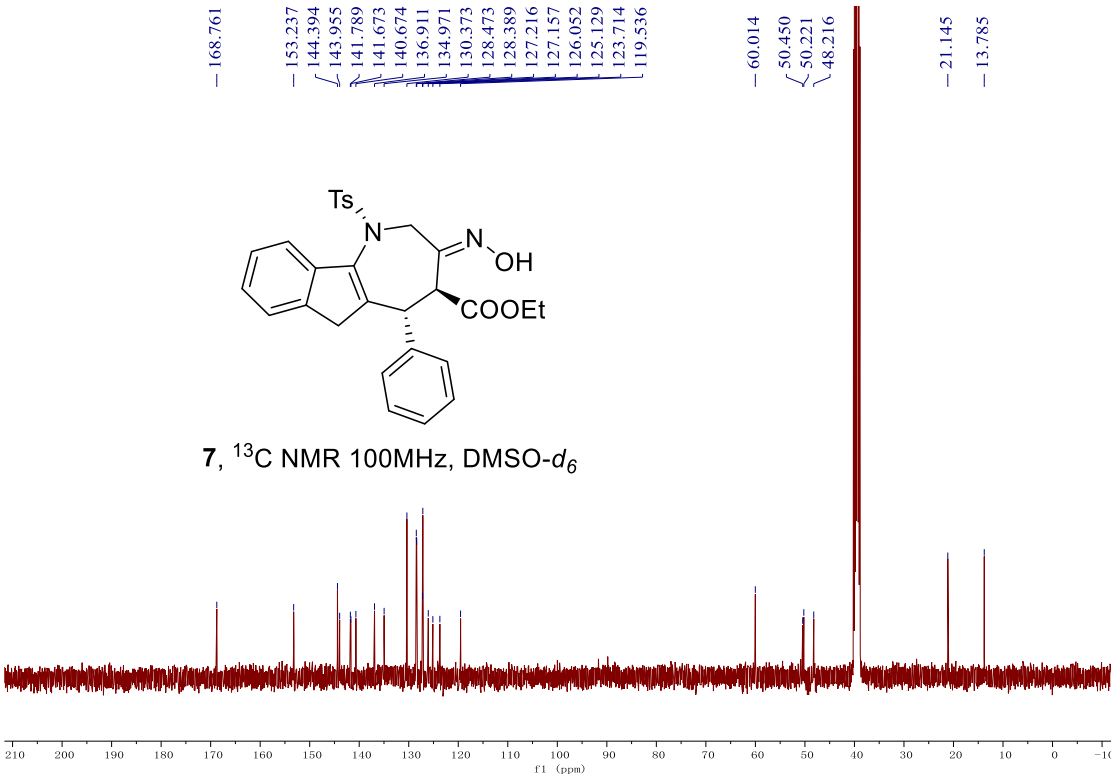

174.837
143.996
142.053
141.079
138.229
137.632
129.944
128.686
128.578
128.337
127.521
127.232
126.521
126.196
125.190
123.480
121.591
120.551
68.782
60.864
50.497
44.348
39.930
21.631
13.646
Ts
N
OH
CO2Et
5, 13C NMR 100MHz, CDCl3
f1 (ppm)


7.941
7.765
7.746
7.608
7.589
7.398
7.379
7.323
7.278
7.242
7.223
7.207
7.190
7.171
7.154
7.135
7.030
4.533
4.496
4.225
4.102
4.067
4.022
3.993
3.775
3.676
3.669
3.143
3.084
2.985
2.954
2.911
2.882
2.668
2.627
2.605
2.575
2.519
2.447
0.812
0.795
0.777
Ts
N
OH
CO2Et
6, 1H NMR 400MHz, CDCl3
2.06
3.01
2.08
4.99
0.83
1.98
2.71
2.89
5.07
3.00
f1 (ppm)


172.678
145.246
144.123
142.023
140.497
139.014
138.001
137.546
129.933
128.844
128.338
127.661
127.376
126.525
125.348
123.299
120.992
71.207
60.559
55.270
53.684
43.452
40.193
21.676
13.627
Ts
N
OH
CO2Et
6, 13C NMR 100MHz, CDCl3
f1 (ppm)

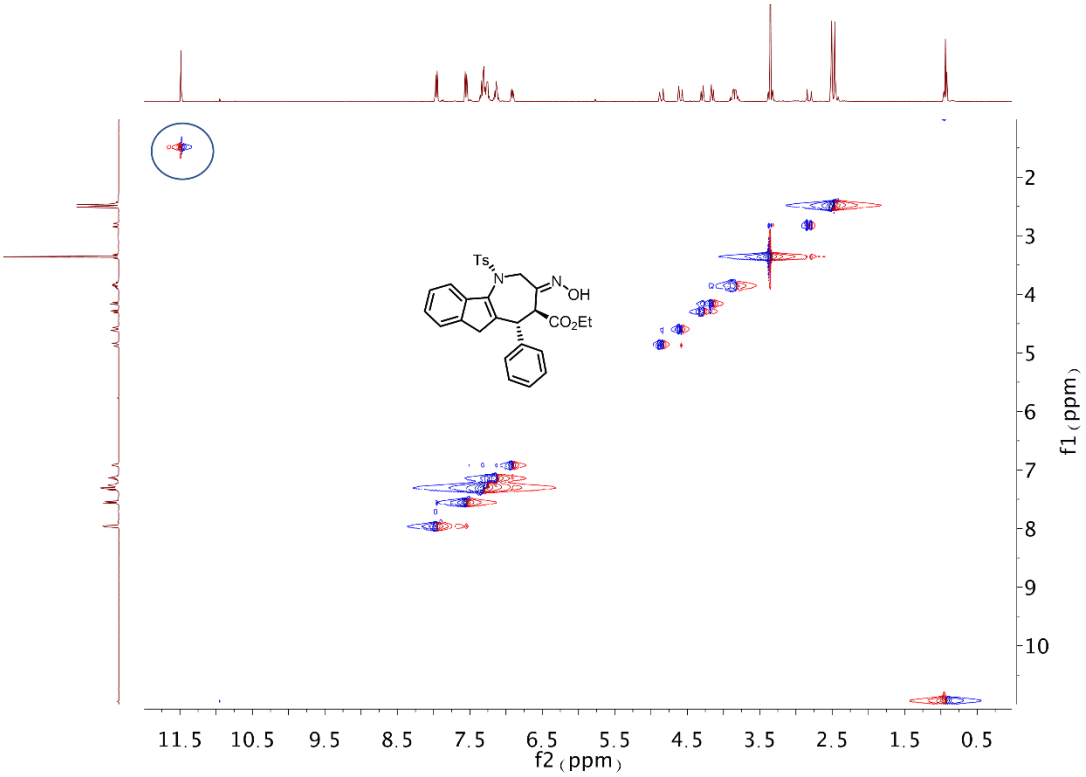


7, ^{1}H NMR 400MHz, DMSO-d_6



7, ^{13}C NMR 100MHz, DMSO-d_6

8. NOESY spectra of 7

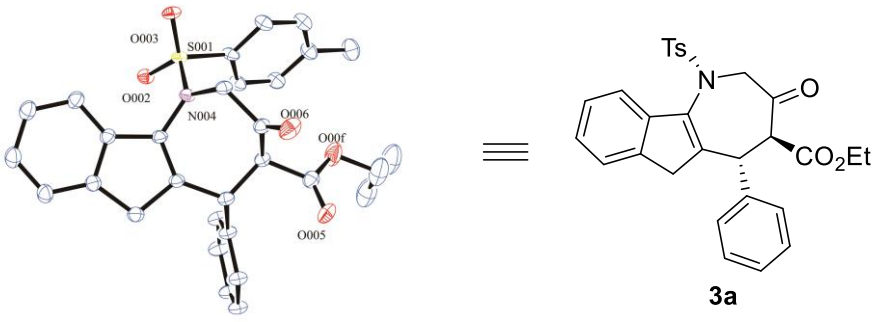


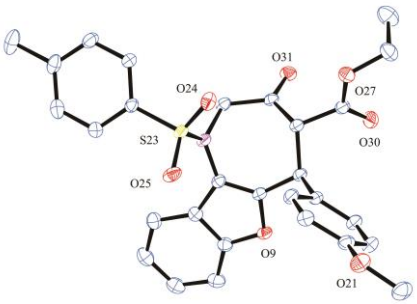
9. References

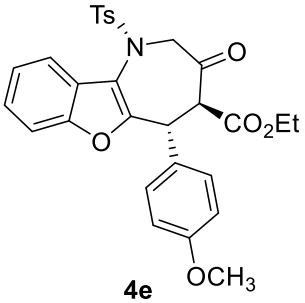
(1) K. Verma and P. Banerjee, Synthesis of Indenopyridine Derivatives *via* MgI_2-Promoted [2+4] Cycloaddition Reaction of *In-situ* Generated 2-Styrylmalonate from Donor-Acceptor Cyclopropanes and Chalconimines, *Adv. Synth. Catal.,* 2018, **360**, 3687-3692.

(2) S. P. Midya, E. Gopi, N. Satam and I. N. N. Namboothiri, Synthesis of fused cyanopyrroles and spirocyclopropanes *via* addition of *N*-ylides to chalconimines, *Org. Biomol. Chem.,* 2017, **15**, 3616-3627.

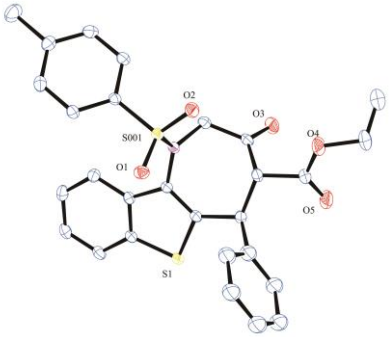
10. X-ray crystal structures

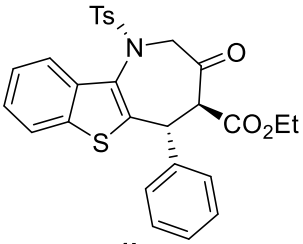



O31
O24
O27
S23
O30
O25
O9
O21

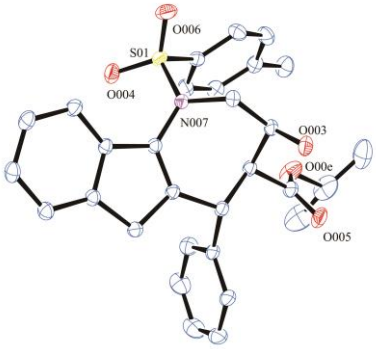

Ts
N
O
O
CO2Et
OCH3

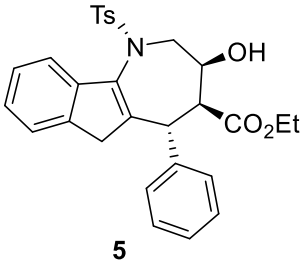
4e


O2
S001
O3
O4
O1
O5
S1

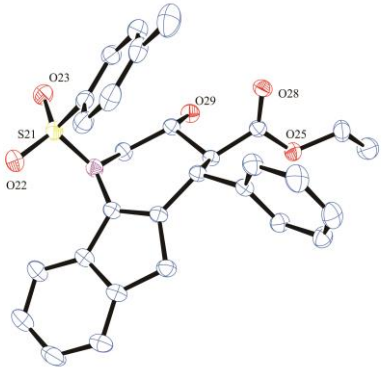

Ts
N
O
CO2Et
S

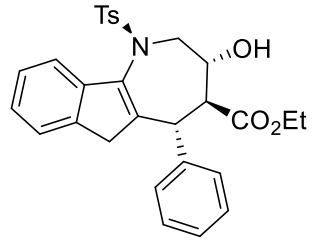
4h


O006
S01
O004
N007
O003
O00e
O005


Ts
N
OH
CO2Et

5


O23
O29
O28
S21
O25
O22


Ts
N
OH
CO2Et

6