Radical Annulation of Designed Diene System: Access to Nitro-Benzo[*b*]azepines

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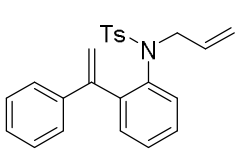
Contents

1. General conditions

All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. All reactions were run under air with no precautions taken to exclude moisture. ^{1}H、^{13}C and ^{19}F NMR spectra were recorded on a Bruker Ascend 400 or Bruker Ascend 500 spectrometer in deuterated solvents containing TMS as an internal reference standard, Chemical shifts are reported in ppm relative to $CDCl_3$ (^{1}H, TMS δ 0; ^{13}C, δ 77.16). Melting points were obtained with Micro melting point tester and are uncorrected. High resolution mass spectra were recorded on Bruck microtof. NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and brs = broad singlet), coupling constant in Hz and integration. All reactions were monitored by TLC with Yantai GF254 silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure.

2. Preparation of material 1



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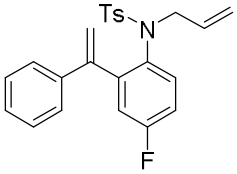

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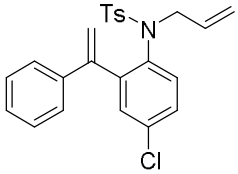

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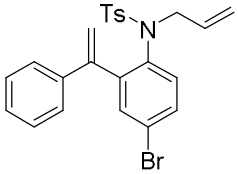

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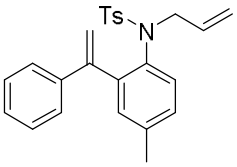

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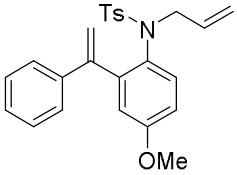

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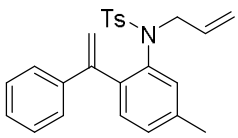

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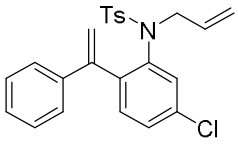

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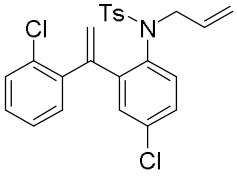

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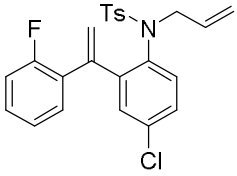

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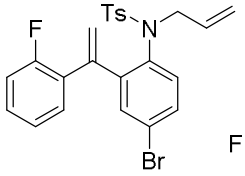

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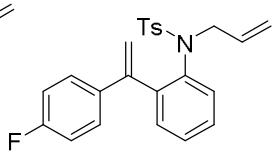

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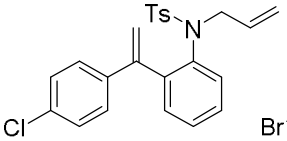

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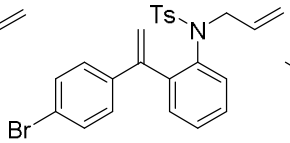

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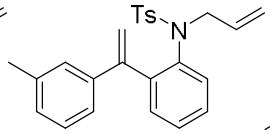

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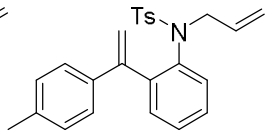

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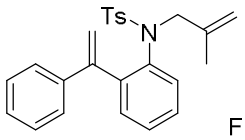

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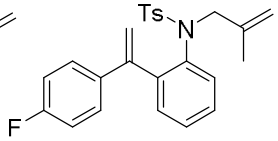

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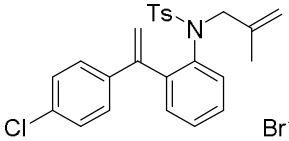

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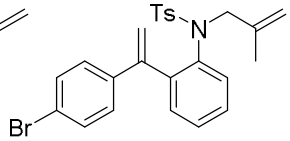

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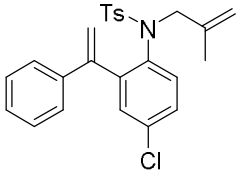

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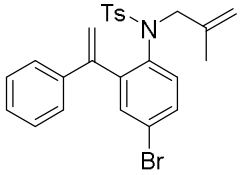

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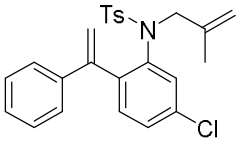

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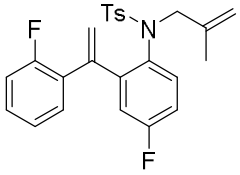

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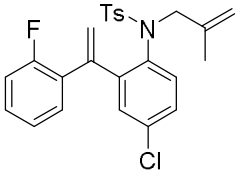

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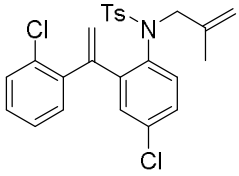
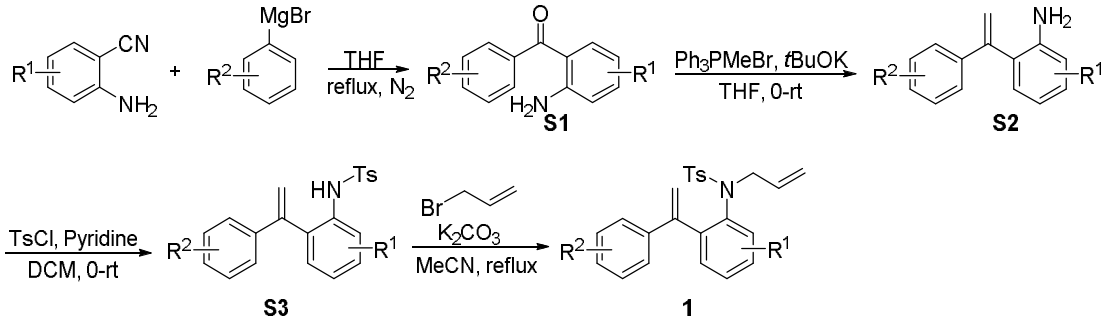
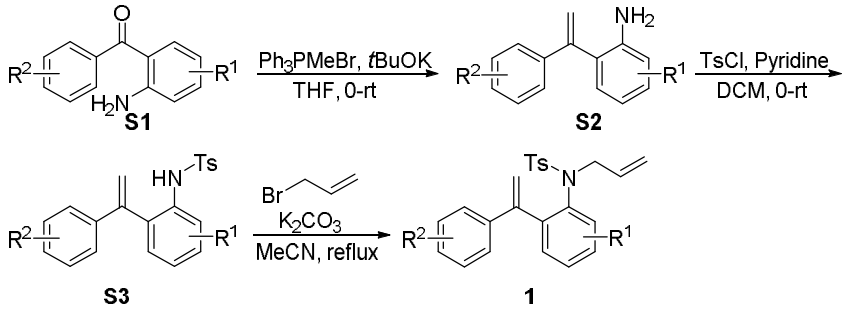


1ab

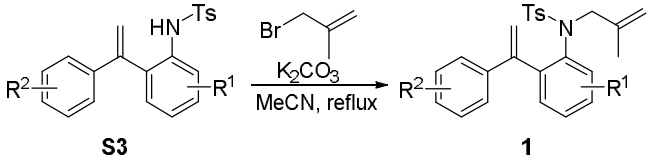
1e, **1f**, **1g**, **1o**, **1p** were prepared from 2-aminobenzonitrile.



1a, **1b**, **1c**, **1d**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1o**, **1p** were prepared from (2-aminophenyl)(phenyl)methanone **S1**.



1s, **1t**, **1u**, **1v**, **1w**, **1x**, **1y**, **1z**, **1aa**, **1ab**, were prepared from (2-aminophenyl)(phenyl)methanone **S3**.



General Procedure for the synthesis of S1

To a round-bottomed flask charged with the 2-aminobenzonitrile (10 mmol, 1.0 equiv) in dry THF (20 mL), arylmagnesium bromide (30 mmol, 3.0 equiv, 2.8 M in THF) was added dropwise via syringe at 0 °C in a nitrogen atmosphere. The reaction mixture was heated to 65 °C in oil bath for 4 hours. Upon the reaction completed, the suspension was cooled to 0 °C, the reaction mixture was quenched by 3 M HCl, extracted with EtOAc (3 × 40 mL). The separated organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 15:1) to afford **S1**.

General Procedure for the synthesis of S2

To a round-bottom flask of tetrahydrofuran (20 mL) solution containing Ph_3PMeBr (10.0 mmol, 1.5 equiv), potassium *tert*-butanol (7.5 mmol, 1.5 equiv) was added in batches at 0 °C under air atmosphere. Half an hour later, **S1** (5.0 mmol, 1.0 equiv) was added dropwise at 0 °C. The reaction mixture was warmed to room temperature and stirred for 4 hours. Upon the

reaction completed, the desired product **S2** was purified on silica gel column by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1).

General Procedure for the synthesis of S3

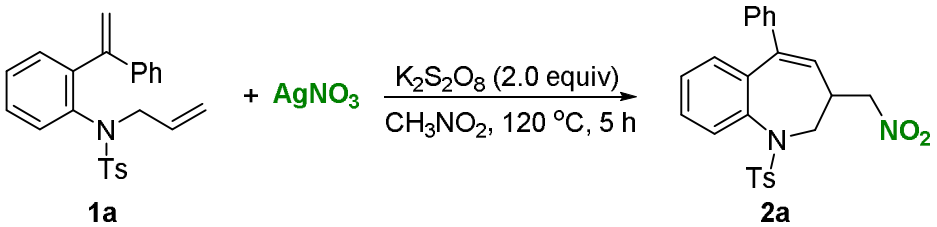
To a round-bottomed flask of dichloromethane (15 mL) solution dissolved with TsCl (2.4 mmol, 1.2 equiv), **S2** (2.0 mmol, 1.0 equiv) was added and then pyridine (3.0 mmol, 1.5 equiv) was dropped at 0 ^{o}C. The reaction mixture was warmed to room temperature and stirred for 12 h. Upon the reaction completed, the reaction mixture was extracted with EtOAc (3 × 15 mL). The separated organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 15:1) to afford **S3**.

General Procedure for the synthesis of 1

To a round bottom flask containing potassium carbonate (1.4 mmol, 1.2 equiv) and product **S3** (1.2 mmol, 1.0 equiv), the acetonitrile (10 mL) and propylene bromide (2.4 mmol, 2.0 equiv) were added. The reaction mixture was stirred at 80 ^{o}C in oil bath for 4 h. Upon the reaction completed, the reaction mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford **1**.

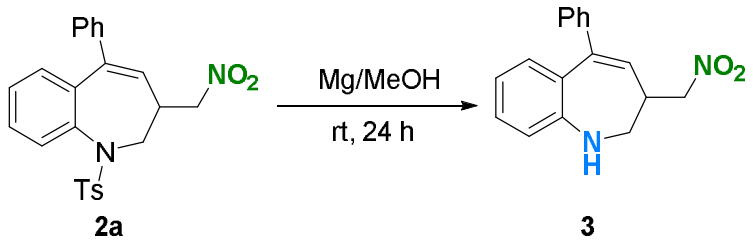
3. General procedure for the synthesis of 2a

To a solution of **1a** (0.3 mmol, 162.2 mg) in $MeNO_2$ (3 mL) were added, $AgNO_3$ (0.3 mmol, 51.0 mg) and $K_2S_2O_8$ (0.6 mmol, 243.3 mg) were added. The reaction mixture was stirred at 120 ^{o}C for 5 h under an air atmosphere. After the reaction finished, the reaction mixture was cooled to room temperature and quenched by water. The mixture was extracted with EtOAc (10 mL × 3), the combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The residue was purified by column chromatography to give the corresponding product **2a**.



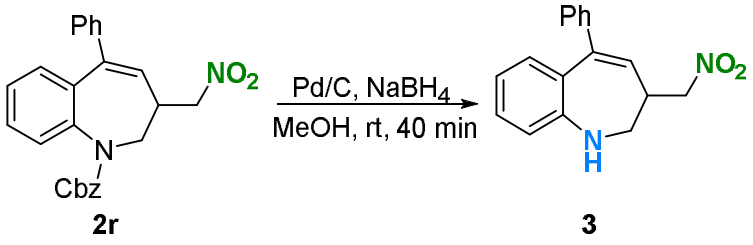
1a **2a**

4. General procedure for the synthesis of 5-phenyl-3-((phenylselanyl)methyl)-2,3-dihydro-1*H*-benzo[*b*]azepine (3)



2a **3**

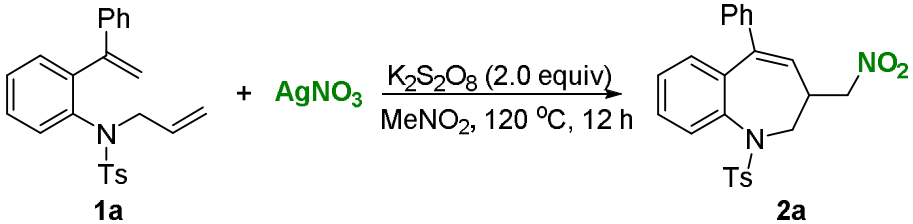
To a 10 mL dry thick walled tube equipped with a magnetic stir bar, **2a** (0.3 mmol, 130.4 mg), Mg (3.5 mmol, 78.3 mg) and MeOH (3 mL) were added. The tube was sealed and the reaction mixture was stirred at room temperature for 24 h. Upon the reaction completed, H_2O was added to mixture and extracted with ethyl acetate. The combined organic layer was dried (anhydrous Na_2SO_4), filtered, and evaporated followed by a silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 30:1) to afford desired product **3** (59.7 mg, 71%).



2r **3**

To a 10 mL thick-walled tube equipped with a magnetic stir bar was added a molar excess of $NaBH_4$ (10.0 equiv) to a solution of *N*-Cbz aniline **2r** (0.3 mmol, 124.3 mg) and 10% Pd-C (2.0 equiv) in MeOH. The reaction was carried out for 40 min. After the reaction was completed, H_2O was added to the mixture and extracted with ethyl acetate. The combined organic layers were dried (anhydrous Na_2SO_4), filtered and evaporated, followed by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 30:1) to give the desired product **3** (59.7 mg, 87%).

5. The gram-scale synthesis of compound 2a



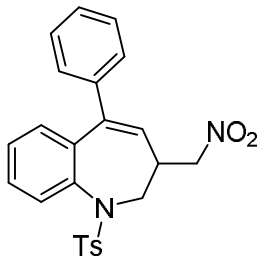
1a **2a**

To a 100 mL dry thick walled tube equipped with a magnetic stir bar, was added **1a** (2.6 mmol, 1.0 g) and $MeNO_2$ (25 mL). Then, the $AgNO_3$ (2.6 mmol, 411.7 mg) and $K_2S_2O_8$ (5.2

mmol, 1.4 g) were added. The reaction mixture was stirred at 120 °C for 12 h. After the reaction finished, the reaction mixture was cooled to room temperature and quenched by water. The mixture was extracted with EtOAc (50 mL × 3), the combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the desired product **2a** (689.1 mg, 61%).

6. Product characterization

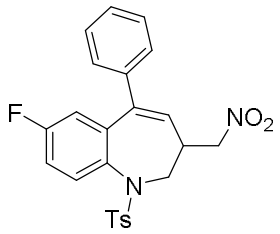
3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2a)



N-allyl-4-methyl-*N*-(2-(1-phenylvinyl)phenyl)benzenesulfonamide (194.7 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 138-139 °C) in 81% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.23; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58-7.47 (m, 3H), 7.35 (t, J = 7.1 Hz, 1H), 7.31-7.24 (m, 2H), 7.20 (t, J = 7.4 Hz, 2H), 7.03-6.84 (m, 5H), 6.00 (s, 1H), 4.49 (dd, J = 23.3, 6.2 Hz, 3H), 4.11 (s, 1H), 3.24 (s, 1H), 2.24 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.97, 143.35, 139.34, 137.48, 131.04, 130.86, 129.85, 129.67, 129.47, 129.02, 128.56, 128.08, 127.99, 127.35, 127.28, 76.51, 53.49, 36.88, 21.42; **HRMS** (ESI) calcd for $C_{24}H_{23}N_2O_4S$ $[M+H]^+$: 435.1373, found: 435.1369.

7-fluoro-3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2b)

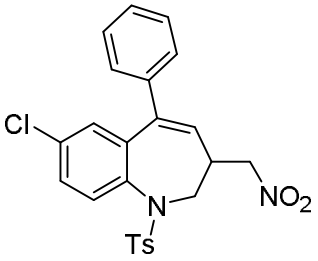


N-allyl-*N*-(4-fluoro-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (203.7 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 126-127 °C) in 69% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.17; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34-7.23 (m, 3H), 7.05-7.03 (m, 1H), 6.98 (t, J = 7.5 Hz, 2H), 6.82-6.79 (m, 1H), 6.76 (d, J = 6.9 Hz, 2H), 6.66 (d, J = 7.4 Hz, 2H), 6.43 (d, J = 7.4 Hz, 1H), 5.85 (s, 1H), 4.52-4.11 (m, 3H), 3.86 (d, J =

25.1 Hz, 1H), 2.96 (s, 1H), 2.00 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.13 (d, J = 249.2 Hz), 143.55, 143.12, 141.85, 138.40, 137.25, 132.99, 129.57, 128.22, 128.13, 128.10 (d, J = 28.7 Hz), 126.02, 117.43, 116.02 (d, J = 22.5 Hz). 76.26, 60.67, 36.71, 21.39; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -111.49; **HRMS** (ESI) calcd for $C_{24}H_{22}FN_2O_4S$ $[M+H]^+$: 453.1279, found: 453.1267.

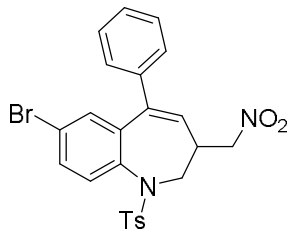
3-chloro-3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2c)



N-allyl-*N*-(4-chloro-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (211.9 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 152-153 ^oC) in 74% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.23; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49-7.42 (m, 3H), 7.28-7.27 (m, 1H), 7.25-7.22 (m, 1H), 7.18 (t, J = 7.5 Hz, 2H), 6.96 (d, J = 7.8 Hz, 2H), 6.90 (s, 1H), 6.83 (d, J = 7.4 Hz, 2H), 6.00 (s, 1H), 4.62-4.29 (m, 3H), 4.07 (s, 1H), 3.19 (s, 1H), 2.20 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.63, 143.05, 137.15, 135.91, 134.62, 132.41, 130.62, 129.95, 129.81, 129.60, 129.14, 128.27, 128.18, 128.00, 127.34, 127.22, 76.27, 60.32, 36.72, 21.43; **HRMS** (ESI) calcd for $C_{24}H_{22}ClN_2O_4S$ $[M+H]^+$: 469.0983, found: 469.0975.

7-bromo-3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2d)

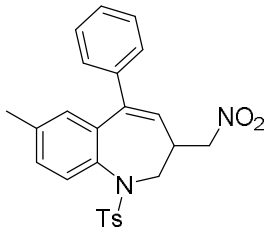


N-allyl-*N*-(4-bromo-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (234.2 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 178-179 ^oC) in 65% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.29; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68-7.44 (m, 3H), 7.39 (d, J = 8.5 Hz, 1H), 7.26-7.21 (m, 1H), 7.18 (t, J = 7.5 Hz, 2H), 7.04 (s, 1H), 6.96 (d, J = 7.8 Hz, 2H), 6.83 (d, J = 7.5 Hz, 2H), 5.99 (s, 1H), 4.60-4.30 (m, 3H), 4.05 (s, 1H), 3.18 (s, 1H), 2.20 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.64, 142.96, 137.13, 136.53,

133.55, 132.64, 132.13, 129.60, 128.29, 128.20, 127.99, 127.34, 126.22, 122.73, 76.27, 60.26, 36.51, 21.44; **HRMS** (ESI) calcd for $C_{24}H_{22}BrN_2O_4S$ $[M+H]^+$: 513.0478, found: 513.0472.

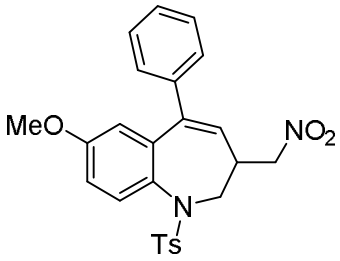
7-methyl-3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2e)



N-allyl-4-methyl-*N*-(4-methyl-2-(1-phenylvinyl)phenyl)benzenesulfonamide (201.8 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 90-91 ^oC) in 55% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.31; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 7.1 Hz, 1H), 7.19 (t, J = 7.5 Hz, 2H), 7.14 (d, J = 7.9 Hz, 1H), 6.96 (d, J = 7.7 Hz, 2H), 6.90 (d, J = 7.5 Hz, 2H), 6.74 (s, 1H), 5.97 (d, J = 2.9 Hz, 1H), 4.47 (d, J = 33.6 Hz, 3H), 4.04 (s, 1H), 3.19 (s, 1H), 2.24 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.07, 143.24, 139.18, 138.67, 137.59, 134.70, 131.19, 130.84, 129.84, 129.45, 128.07, 127.97, 127.91, 127.35, 124.86, 76.52, 60.28, 36.88, 21.41, 21.14; **HRMS** (ESI) calcd for $C_{25}H_{25}N_2O_4S$ $[M+H]^+$: 449.1530, found: 449.1523.

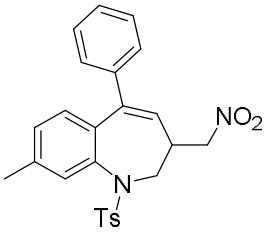
7-methoxy-3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2f)



N-allyl-*N*-(4-methoxy-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (209.8 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a white solid (m. p. 90-91 ^oC) in 61% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.31; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (t, J = 7.7 Hz, 3H), 7.27-7.16 (m, 4H), 7.05-6.83 (m, 5H), 6.45 (s, 1H), 6.00 (s, 1H), 4.71-3.91 (m, 4H), 3.69 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.38, 143.97, 143.22, 140.76, 138.84, 137.49, 132.35, 129.64, 129.44, 127.97, 127.35, 125.04, 115.64, 114.46, 76.47, 60.12, 55.50, 36.84, 21.39; **HRMS** (ESI) calcd for $C_{25}H_{25}N_2O_5S$ $[M+H]^+$: 465.1479, found: 465.1474.

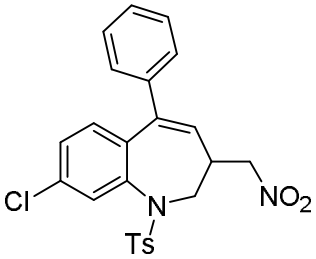
8-methyl-3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2g)



N-allyl-4-methyl-*N*-(5-methyl-2-(1-phenylvinyl)phenyl)benzenesulfonamide (201.8 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 110-111 ^oC) in 46% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.26; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.1 Hz, 2H), 7.38 (s, 1H), 7.25 (dd, J = 9.8, 4.5 Hz, 1H), 7.19 (t, J = 7.5 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 6.96 (d, J = 7.6 Hz, 2H), 6.89 (d, J = 7.4 Hz, 2H), 6.82 (d, J = 7.7 Hz, 1H), 5.92 (s, 1H), 4.47 (dd, J = 21.6, 6.3 Hz, 3H), 4.10 (s, 1H), 3.24 (s, 1H), 2.38 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.89, 143.27, 139.30, 137.49, 137.27, 136.08, 131.68, 130.58, 129.41, 128.06, 127.93, 127.89, 127.37, 124.26, 76.57, 59.89, 36.98, 21.40, 21.19; **HRMS** (ESI) calcd for $C_{25}H_{25}N_2O_4S$ $[M+H]^+$: 449.1530, found: 449.1523.

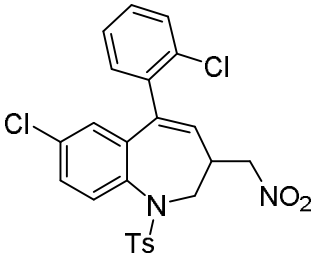
8-chloro-3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2h)



N-allyl-*N*-(5-chloro-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (211.9 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 137-138 ^oC) in 67% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.29; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 1.9 Hz, 1H), 7.51 (d, J = 8.1 Hz, 2H), 7.24-7.03 (m, 4H), 7.02 (d, J = 7.9 Hz, 2H), 6.87 (t, J = 8.1 Hz, 3H), 5.99 (d, J = 4.7 Hz, 1H), 4.54-4.46 (m, 3H), 4.21 (s, 1H), 3.25 (s, 1H), 2.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.71, 143.08, 138.62, 137.09, 134.20, 131.77, 131.04, 130.42, 129.61, 128.86, 128.40, 128.18, 128.11, 128.01, 127.36, 127.07, 77.34, 59.94, 37.11, 21.44; **HRMS** (ESI) calcd for $C_{24}H_{22}ClN_2O_4S$ $[M+H]^+$: 469.0983, found: 469.0979.

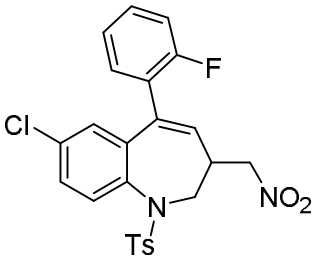
5-chloro-5-(2-chlorophenyl)-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2i)



N-allyl-*N*-(4-chloro-2-(1-(2-chlorophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (229.2 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 147-148 ^oC) in 72% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.25; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.17-7.03 (m, 5H), 6.67 (s, 1H), 6.59 (s, 1H), 5.78 (s, 1H), 4.46-4.38 (m, 2H), 4.19 (s, 1H), 3.52 (s, 1H), 2.29 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.10, 140.25, 138.49, 137.41, 137.28, 133.76, 133.15, 131.79, 131.59, 130.43, 129.95, 129.90, 129.72, 129.35, 128.64, 127.48, 126.89, 76.25, 60.68, 38.76, 21.57; **HRMS** (ESI) calcd for $C_{24}H_{21}Cl_2N_2O_4S$ $[M+H]^+$: 503.0594, found: 503.0588.

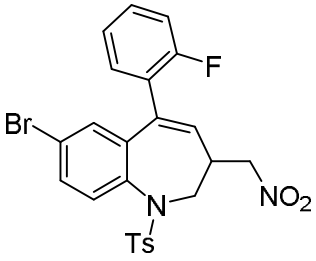
4-chloro-5-(2-fluorophenyl)-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2j)



N-allyl-*N*-(4-chloro-2-(1-(2-fluorophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (220.9 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 141-142 ^oC) in 71% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.19; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.5 Hz, 1H), 7.24-7.10 (m, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.02-6.96 (m, 2H), 6.82 (s, 1H), 6.69 (t, J = 7.4 Hz, 1H), 6.03 (s, 1H), 4.47-4.44 (m, 3H), 4.14 (s, 1H), 3.36 (s, 1H), 2.27 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.02, 159.03, 143.77, 137.38, 136.35, 134.37, 131.40 (d, J = 2.2 Hz), 130.53, 130.15, 129.90, 129.84, 129.67, 128.98, 127.37, 127.13, 124.03 (d, J = 3.3 Hz), 116.10, 115.92, 76.21, 58.12, 37.52, 21.47; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.89; **HRMS** (ESI) calcd for $C_{24}H_{21}ClFN_2O_4S$ $[M+H]^+$: 487.0889, found: 487.0880.

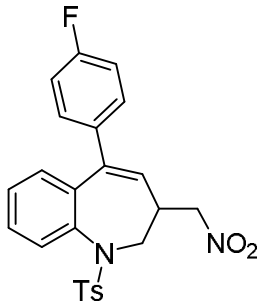
6-bromo-5-(2-fluorophenyl)-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2k)



N-allyl-*N*-(4-bromo-2-(1-(2-fluorophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (243.2 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 128-129 ^oC) in 76% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.32; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.58 (s, 1H), 7.43-7.39 (m, 1H), 7.38 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 5.5 Hz, 1H), 7.13 (s, 1H), 7.12 (s, 1H), 7.03-6.74 (m, 3H), 6.73 (d, J = 7.4 Hz, 1H), 6.06 (s, 1H), 4.61-4.37 (m, 3H), 4.16 (s, 1H), 3.38 (s, 1H), 2.31 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.02, 158.95, 143.77, 137.37, 133.09, 131.97, 131.59, 131.46 (t, J = 13.2 Hz), 129.88 (d, J = 8.3 Hz), 129.67, 127.37, 124.04 (d, J = 3.4 Hz), 122.45, 116.12, 115.94, 76.21, 60.28, 37.75, 21.49; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.80; **HRMS** (ESI) calcd for $C_{24}H_{21}BrFN_2O_4S$ $[M+H]^+$: 531.0384, found: 531.0378.

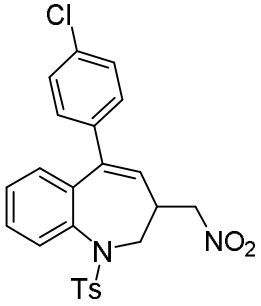
5-(4-fluorophenyl)-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2l)



N-allyl-*N*-(2-(1-(4-fluorophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (203.8 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 161-162 ^oC) in 65% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.27; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.20 (m, 3H), 7.26 (t, J = 7.5 Hz, 1H), 7.20-7.17 (m, 1H), 6.92 (d, J = 7.9 Hz, 2H), 6.81-6.79 (m, 5H), 5.89 (s, 1H), 4.57-4.21 (m, 3H), 4.00 (s, 1H), 3.12 (s, 1H), 2.17 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.59, 161.62, 143.41, 142.90, 137.60, 131.10, 130.66, 129.79, 129.76 (d, J = 7.7 Hz), 129.17, 128.71, 127.33, 114.97, 114.80, 76.41, 60.37, 36.99, 21.40; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.96; **HRMS** (ESI) calcd for $C_{24}H_{22}FN_2O_4S$ $[M+H]^+$: 453.1279, found: 453.1268.

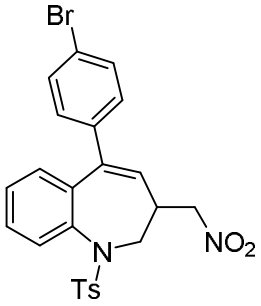
5-(4-chlorophenyl)-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2m)



N-allyl-*N*-(2-(1-(4-chlorophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (212.0 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 92-93 ^oC) in 71% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.29; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.28 (m, 3H), 7.26 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.3 Hz, 1H), 7.06 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 7.7 Hz, 2H), 6.82 (d, J = 7.3 Hz, 1H), 6.74 (d, J = 8.3 Hz, 2H), 5.94 (s, 1H), 4.38-4.45 (m, 3H), 4.02 (s, 1H), 3.11 (s, 1H), 2.15 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.47, 142.73, 137.56, 133.86, 131.23, 130.60, 129.47, 129.27, 128.76, 128.17, 127.33, 125.58, 76.33, 60.41, 36.92, 21.41; **HRMS** (ESI) calcd for $C_{24}H_{22}ClN_2O_4S$ $[M+H]^+$: 469.0984, found: 469.0972.

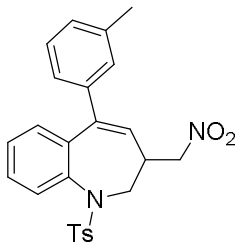
5-(4-bromophenyl)-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2n)



N-allyl-*N*-(2-(1-(4-bromophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (234.2 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 136-137 ^oC) in 71% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.32; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.38 (m, 3H), 7.30-7.20 (m, 4H), 6.91 (d, J = 7.7 Hz, 2H), 6.83 (d, J = 7.3 Hz, 1H), 6.69 (d, J = 8.4 Hz, 2H), 5.96 (s, 1H), 4.58-4.26 (m, 3H), 3.83 (s, 1H), 3.11 (s, 1H), 2.17 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.50, 142.79, 137.55, 131.14, 130.61, 129.55, 129.47, 129.30, 128.77, 128.37, 127.33, 123.81, 122.09, 76.31, 60.11, 36.97, 21.44; **HRMS** (ESI) calcd for $C_{24}H_{22}BrN_2O_4S$ $[M+H]^+$: 513.0479, found: 513.0480.

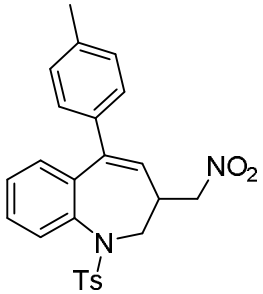
3-(nitromethyl)-5-(*m*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2o)



N-allyl-4-methyl-*N*-(2-(1-(m-tolyl)vinyl)phenyl)benzenesulfonamide (201.8 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 156-157 ^oC) in 58% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.23; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, J = 7.9 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 7.20-7.15 (m, 1H), 6.98 (d, J = 6.2 Hz, 2H), 6.87 (dd, J = 18.5, 7.6 Hz, 3H), 6.64 (s, 1H), 6.59 (d, J = 6.2 Hz, 1H), 5.90 (s, 1H), 4.55 -4.27 (m, 3H), 4.01 (s, 1H), 3.12 (s, 1H), 2.18 (s, 3H), 2.12 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.92, 143.27, 139.43, 137.54, 137.48, 130.89, 129.42, 128.94, 128.74, 128.67, 128.52, 127.88, 127.39, 125.32, 124.84, 76.50, 60.34, 36.74, 21.42, 21.41; **HRMS** (ESI) calcd for $C_{25}H_{25}N_2O_4S$ $[M+H]^+$: 449.1530, found: 449.1523.

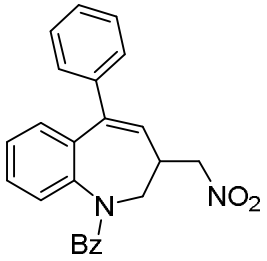
3-(nitromethyl)-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2p)



N-allyl-4-methyl-*N*-(2-(1-(p-tolyl)vinyl)phenyl)benzenesulfonamide (201.8 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 70-71 ^oC) in 51% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.31; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 7.8 Hz, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.20 (td, J = 7.6, 1.2 Hz, 2H), 7.14 (d, J = 7.3 Hz, 1H), 7.09 (dd, J = 13.6, 6.8 Hz, 2H), 6.72 (d, J = 7.6 Hz, 2H), 5.73 (s, 1H), 4.51 (d, J = 6.3 Hz, 2H), 4.28 (s, 1H), 3.65 (s, 1H), 2.40 (s, 3H), 1.98 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.86, 138.76, 137.97, 136.17, 131.02, 130.33, 130.17, 129.89, 128.72, 128.45, 127.99, 127.88, 127.70, 127.40, 125.73, 76.74, 54.64, 39.28, 21.58, 19.95; **HRMS** (ESI) calcd for $C_{25}H_{25}N_2O_4S$ $[M+H]^+$: 449.1530, found: 449.1523.

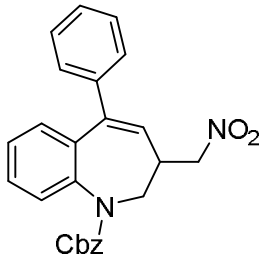
3-(nitrosomethyl)-5-phenyl-2,3-dihydro-1*H*-benzo[*b*]azepin-1-yl)(phenyl)methanone(2q)



N-allyl-*N*-(2-(1-phenylvinyl)phenyl)benzamide (169.7 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 90-91 ^oC) in 24% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.43; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 7H), 7.27-7.06 (m, 7H), 6.34 (d, J = 5.3 Hz, 1H), 4.64-4.50 (m, 3H), 3.89-3.84 (m, 1H), 3.41-3.38 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.75, 143.82, 140.43, 139.60, 138.28, 136.42, 130.34, 129.04, 128.82, 128.59, 128.48, 128.37, 128.09, 127.87, 127.31, 125.59, 118.10, 67.38, 57.35, 36.91; **HRMS** (ESI) calcd for $C_{24}H_{21}N_2O_2$ $[M+H]^+$: 385.1547, found: 385.1536.

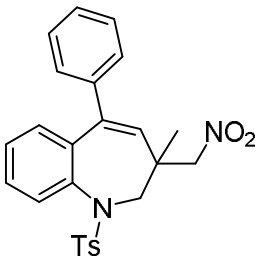
Benzyl 3-(nitromethyl)-5-phenyl-2,3-dihydro-1*H*-benzo[*b*]azepine-1-carboxylate(2r)



Benzyl allyl(2-(1-phenylvinyl)phenyl)carbamate (184.7 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 90-91 ^oC) in 51% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.31; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.31 (m, 8H), 7.30-7.26 (m, 2H), 7.24-7.17 (m, 3H), 7.15-7.04 (m, 1H), 6.09 (dd, J = 10 Hz, 1H), 5.10-5.04 (m, 2H), 4.56-4.49 (m, 3H), 3.79-3.76 (m, 1H), 3.24 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.74, 143.85, 140.41, 139.59, 138.26, 136.39, 130.34, 129.02, 128.81, 128.58, 128.46, 128.35, 128.07, 127.86, 127.30, 127.00, 125.52, 67.38, 57.34, 53.48, 36.91; **HRMS** (ESI) calcd for $C_{25}H_{23}N_2O_4$ $[M+H]^+$: 415.1653, found: 415.1644.

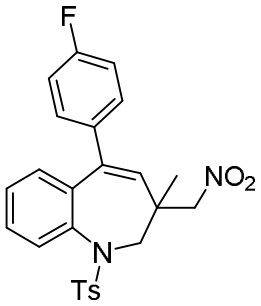
3-methyl-3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2s)



4-methyl-*N*-(2-methylallyl)-*N*-(2-(1-phenylvinyl)phenyl)benzenesulfonamide (201.8 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 122-123 ^oC) in 89% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.25; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 7.9 Hz, 1H), 7.32-7.17 (m, 5H), 7.09 (d, J = 8.1 Hz, 2H), 6.96 (d, J = 7.0 Hz, 2H), 6.91-6.85 (m, 1H), 5.89 (s, 1H), 4.25 (s, 4H), 2.28 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.55, 142.19, 142.09, 138.95, 138.44, 137.78, 132.47, 131.38, 129.62, 129.10, 128.79, 128.54, 128.40, 128.06, 127.89, 127.45, 82.41, 62.93, 41.68, 26.07, 21.49; **HRMS** (ESI) calcd for $C_{25}H_{25}N_2O_4S$ $[M+H]^+$: 449.5445, found: 449.5439.

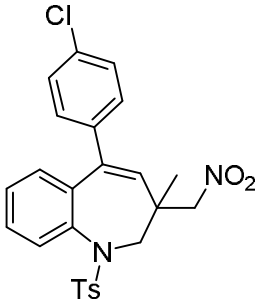
5-(4-fluorophenyl)-3-methyl-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2t)



N-(2-(1-(4-fluorophenyl)vinyl)phenyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (210.8mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 129-130 ^oC) in 76% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.26; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 7.9 Hz, 1H), 7.33-7.22 (m, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.00-6.90 (m, 4H), 6.87 (d, J = 7.7 Hz, 1H), 5.88 (s, 1H), 4.23 (d, J = 15.1 Hz, 4H), 2.33 (s, 3H), 1.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.3.57, 161.60, 143.55, 141.25, 138.78, 138.60, 138.17, 137.86, 132.39, 131.16, 130.19 (d, J = 7.9 Hz), 129.58, 129.25, 128.90, 128.57, 127.42, 114.93 (d, J = 21.6 Hz), 82.38, 63.26, 41.56, 26.07, 21.47; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.16; **HRMS** (ESI) calcd for $C_{25}H_{24}FN_2O_4S$ $[M+H]^+$: 467.1436, found: 467.1438.

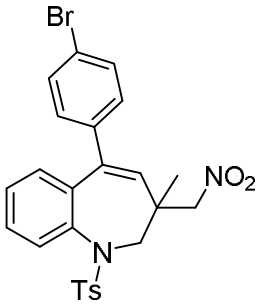
5-(4-chlorophenyl)-3-methyl-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2u)



N-(2-(1-(4-chlorophenyl)vinyl)phenyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (219.0 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 72-73 ^oC) in 67% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.15; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 7.8 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.17 (m, 3H), 7.06 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 7.7 Hz, 1H), 5.85 (s, 1H), 4.46-3.82 (m, 4H), 2.27 (s, 3H), 1.30 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.61, 141.10, 140.51, 138.82, 138.29, 137.81, 133.84, 132.84, 131.12, 129.79, 129.59, 129.34, 128.96, 128.61, 128.23, 127.41, 82.35, 63.22, 41.62, 26.01, 21.47; **HRMS** (ESI) calcd for $C_{25}H_{24}ClN_2O_4S$ $[M+H]^+$: 483.1140, found: 483.1130.

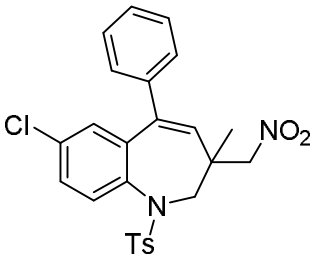
5-(4-bromophenyl)-3-methyl-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2v)



N-(2-(1-(4-bromophenyl)vinyl)phenyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (241.2 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 126-127 ^oC) in 52% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.31; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 7.9 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.24 (td, J = 7.7, 1.4 Hz, 1H), 7.20-7.16 (m, 1H), 7.06 (d, J = 8.1 Hz, 2H), 6.80 (dd, J = 11.6, 4.8 Hz, 3H), 5.85 (s, 1H), 4.25-4.16 (m, 4H), 2.27 (s, 3H), 1.29 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.62, 141.18, 140.96, 138.84, 138.19, 137.79, 132.84, 131.20, 131.13, 130.09, 129.58, 129.36, 128.94, 128.60, 127.42, 122.07, 82.33, 63.19, 41.65, 26.02, 21.49; **HRMS** (ESI) calcd for $C_{25}H_{24}BrN_2O_4S$ $[M+H]^+$: 527.0635, found: 527.0618.

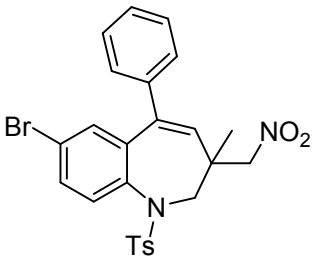
7-chloro-3-methyl-3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2w)



N-(4-chloro-2-(1-phenylvinyl)phenyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (219.0 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 147-148 ^oC) in 76% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.43; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 7.8 Hz, 1H), 7.26-7.20 (m, 1H), 7.21-7.11 (m, 1H), 7.09 (d, J = 8.1 Hz, 2H), 6.97-6.85 (m, 4H), 6.85-6.80 (m, 1H), 5.84 (s, 1H), 4.20 (d, J = 14.6 Hz, 4H), 2.29 (s, 3H), 1.32 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.84, 141.63, 141.02, 139.99, 137.59, 137.37, 134.25, 133.85, 131.09, 129.96, 129.72, 129.13, 128.49, 128.26, 128.17, 127.45, 82.39, 62.57, 41.80, 26.05, 21.50; **HRMS** (ESI) calcd for $C_{25}H_{24}ClN_2O_4S$ $[M+H]^+$: 483.1140, found: 483.1142.

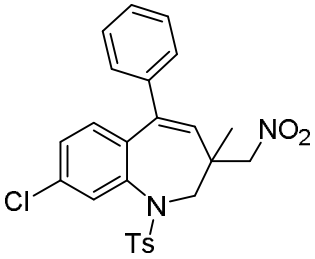
7-bromo-3-methyl-3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2x)



N-(4-bromo-2-(1-phenylvinyl)phenyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (241.2 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 159-160 ^oC) in 66% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.31; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.34 (s, 2H), 7.25-7.18 (m, 3H), 7.06 (d, J = 8.1 Hz, 2H), 6.95 (s, 1H), 6.90-6.86 (m, 2H), 5.87 (s, 1H), 4.24 (d, J = 7.3 Hz, 4H), 2.25 (s, 3H), 1.30 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.85, 141.65, 140.94, 140.21, 138.15, 137.33, 134.03, 133.88, 132.11, 130.15, 129.72, 128.47, 128.27, 128.18, 127.46, 122.32, 82.40, 62.51, 41.81, 26.05, 21.51; **HRMS** (ESI) calcd for $C_{25}H_{24}BrN_2O_4S$ $[M+H]^+$: 527.0635, found: 527.0629.

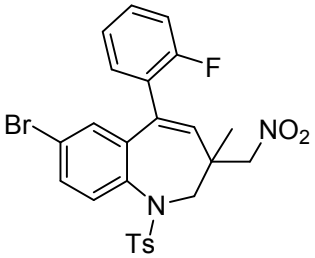
8-chloro-3-methyl-3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2y)



N-(5-chloro-2-(1-phenylvinyl)phenyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (219.0 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 113-114 ^oC) in 66% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.31; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 2.1 Hz, 1H), 7.25-7.20 (m, 3H), 7.16-7.09 (m, 3H), 6.90-6.81 (m, 2H), 6.77 (d, J = 8.5 Hz, 1H), 5.85 (s, 1H), 4.30-4.25 (m, 4H), 2.30 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.92, 142.20, 140.96, 140.33, 137.25, 136.32, 134.27, 133.13, 132.45, 129.71, 128.50, 128.47, 128.28, 128.17, 128.02, 127.51, 82.42, 76.71, 62.16, 42.05, 26.05, 21.49; **HRMS** (ESI) calcd for $C_{25}H_{24}ClN_2O_4S$ $[M+H]^+$: 483.1140, found: 483.1149.

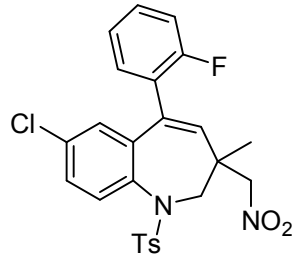
7-bromo-5-(2-fluorophenyl)-3-methyl-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2*z*)



N-(4-bromo-2-(1-(2-fluorophenyl)vinyl)phenyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (250.2 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 133-134 ^oC) in 64% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.37; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.6 Hz, 1H), 7.20-7.15 (m, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.99 (t, J = 7.4 Hz, 1H), 6.91-6.85 (m, 2H), 6.82 (d, J = 1.7 Hz, 1H), 5.81 (s, 1H), 4.35 (s, 2H), 4.12-4.01 (m, 2H), 2.25 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.73, 158.75, 144.12, 139.11, 137.44 (d, J = 3.8 Hz), 136.99, 133.71, 133.34, 131.76, 131.57 (d, J = 2.5 Hz), 130.04 (d, J = 8.2 Hz), 129.99 (d, J = 3.8 Hz), 129.83, 128.09, 127.56, 124.34 (d, J = 3.5 Hz), 121.50, 115.97 (d, J = 21.9 Hz), 82.48, 59.84, 43.33, 27.03, 25.51, 21.57; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.89; **HRMS** (ESI) calcd for $C_{25}H_{23}FBrN_2O_4S$ $[M+H]^+$: 545.0541, found: 545.0537.

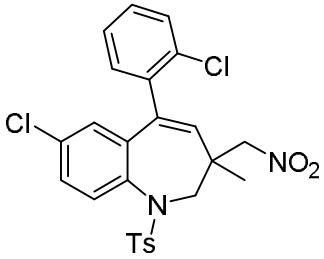
7-chloro-5-(2-fluorophenyl)-3-methyl-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2aa)



N-(4-chloro-2-(1-(2-fluorophenyl)vinyl)phenyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (228.0 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 90-91 ^oC) in 71% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.25; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.7 Hz, 1H), 7.33-7.26 (m, 1H), 7.21 (d, J = 8.2 Hz, 2H), 7.15 (dd, J = 8.6, 2.4 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.06-6.98 (m, 2H), 6.79 (d, J = 2.3 Hz, 1H), 5.93 (s, 1H), 4.68-3.94 (m, 4H), 2.33 (s, 3H), 1.38 (s, 3H); **^{13}C NMR** (125 MHz, CDCl3) δ 160.74, 158.76, 144.13, 138.60, 137.36 (d, J = 19.8 Hz), 137.10, 133.62 (d, J = 45.7 Hz), 131.62 (d, J = 2.3 Hz), 130.37, 130.06 (d, J = 8.8 Hz), 129.85, 128.76, 127.92, 127.55, 124.37 (d, J = 3.4 Hz), 115.95 (d, J = 21.9 Hz), 82.42, 77.56, 77.30, 77.05, 59.91, 43.32, 25.52, 21.53; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.14; **HRMS** (ESI) calcd for $C_{25}H_{23}FClN_2O_4S$ $[M+H]^+$: 501.1046, found: 501.1032.

7-chloro-5-(2-chlorophenyl)-3-methyl-3-(nitromethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine(2ab)

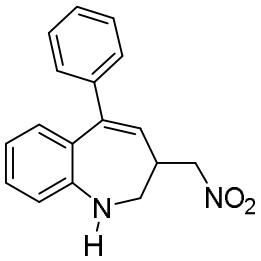


N-(4-chloro-2-(1-(2-chlorophenyl)vinyl)phenyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (236.2 mg, 0.5 mmol) was reacted with $AgNO_3$ according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 138-139 ^oC) in 72% yield.

Rf (petroleum ether/ethyl acetate = 5:1): 0.26; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.7 Hz, 1H), 7.43-7.25 (m, 1.4 Hz, 1H), 7.20-7.12 (m, 4H), 7.10-7.03 (m, 1H), 6.97 (d, J = 6.7 Hz, 1H), 6.54 (d, J = 2.4 Hz, 1H), 5.70 (s, 1H), 4.48 (t, J = 13.7 Hz, 2H), 4.16 (d, J = 14.5 Hz, 1H), 3.95 (d, J = 13.7 Hz, 1H), 2.30 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.37, 141.59, 139.35, 137.41, 136.69, 136.24, 135.69, 133.18, 132.92,

131.62, 130.53, 129.88, 129.40, 128.47, 127.93, 127.12, 126.33, 82.56, 58.42, 44.10, 25.40, 21.60; **HRMS** (ESI) calcd for $C_{25}H_{23}Cl_2N_2O_4S$ $[M+H]^+$: 517.0751, found: 517.0751.

3-(nitromethyl)-5-phenyl-2,3-dihydro-1*H*-benzo[*b*]azepine(3)

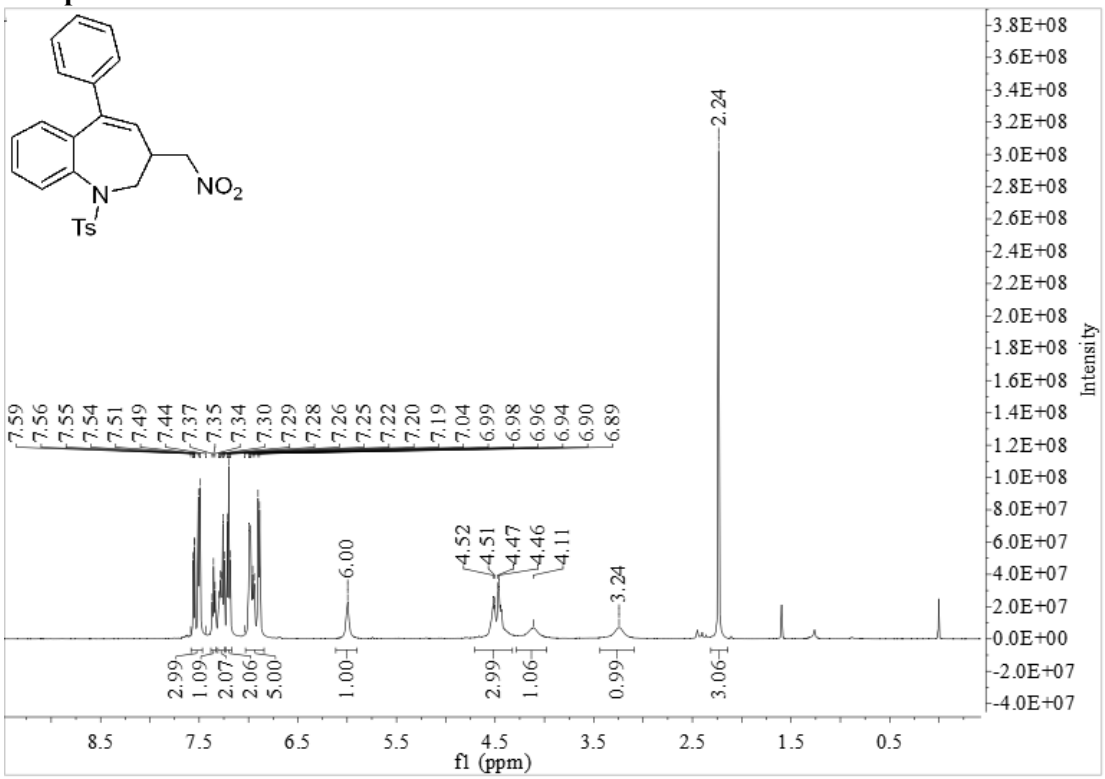


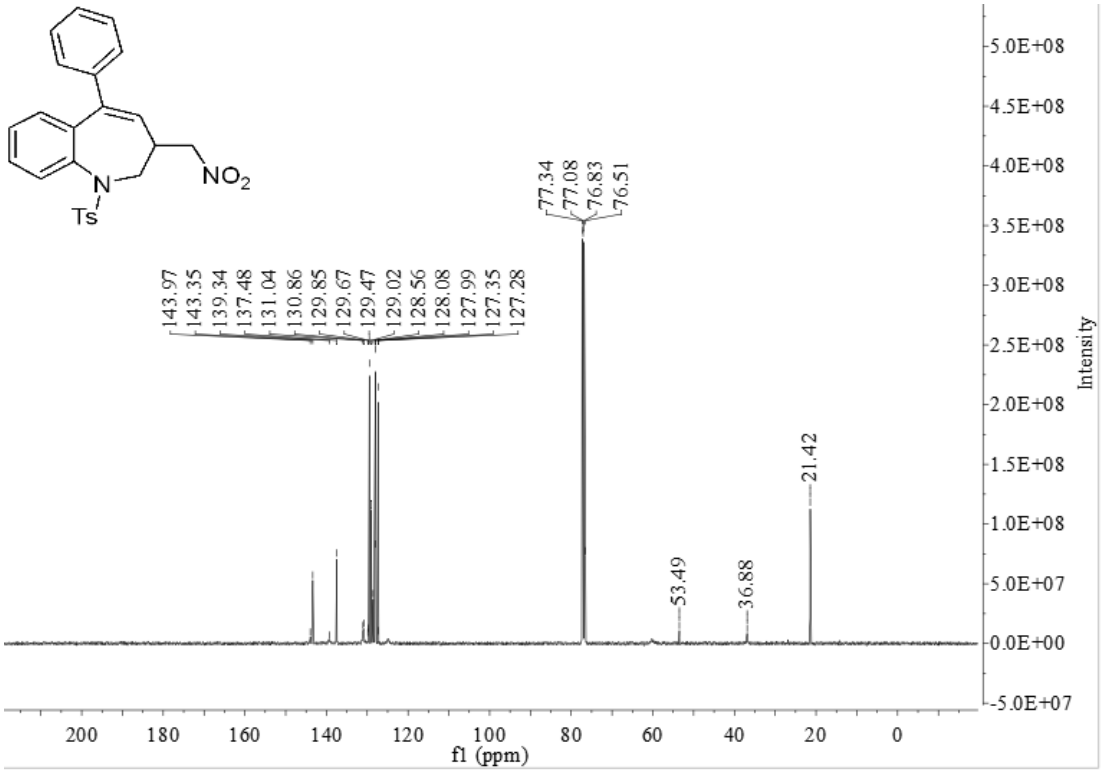
3-(nitromethyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (217.3 mg, 0.5 mmol) was reacted with Mg according to General Procedure. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid (m. p. 91-92 ^{o}C) in 71% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, J = 7.5 Hz, 3H), 7.20 (m, 2H), 7.10-7.05 (m, 1H), 6.86 (m, 1H), 6.76 (m, 1H), 6.74-6.69 (m, 1H), 5.79 (d, J = 6.5 Hz, 1H), 4.70 (m, 1H), 4.49 (m, 1H), 3.45 (m, 2H), 3.36 (d, J = 10.4 Hz, 1H), 1.26 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.71, 145.14, 143.52, 133.37, 129.22, 128.34, 128.12, 127.67, 127.05, 125.39, 119.83, 118.76, 76.82, 48.69, 42.06; **HRMS** (ESI) calcd for $C_{17}H_{17}N_2O_2$ $[M+H]^+$: 281.1285, found: 281.1278.

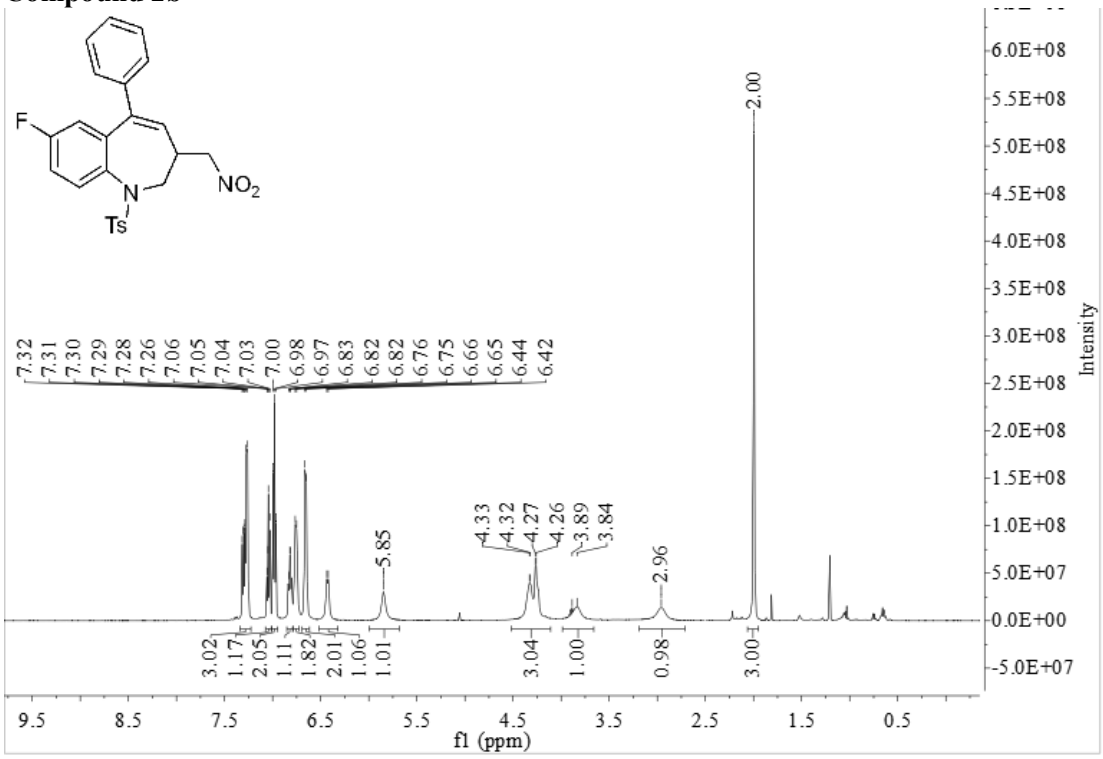
7. ^{1}H、 ^{13}C NMR and ^{19}F Spectra

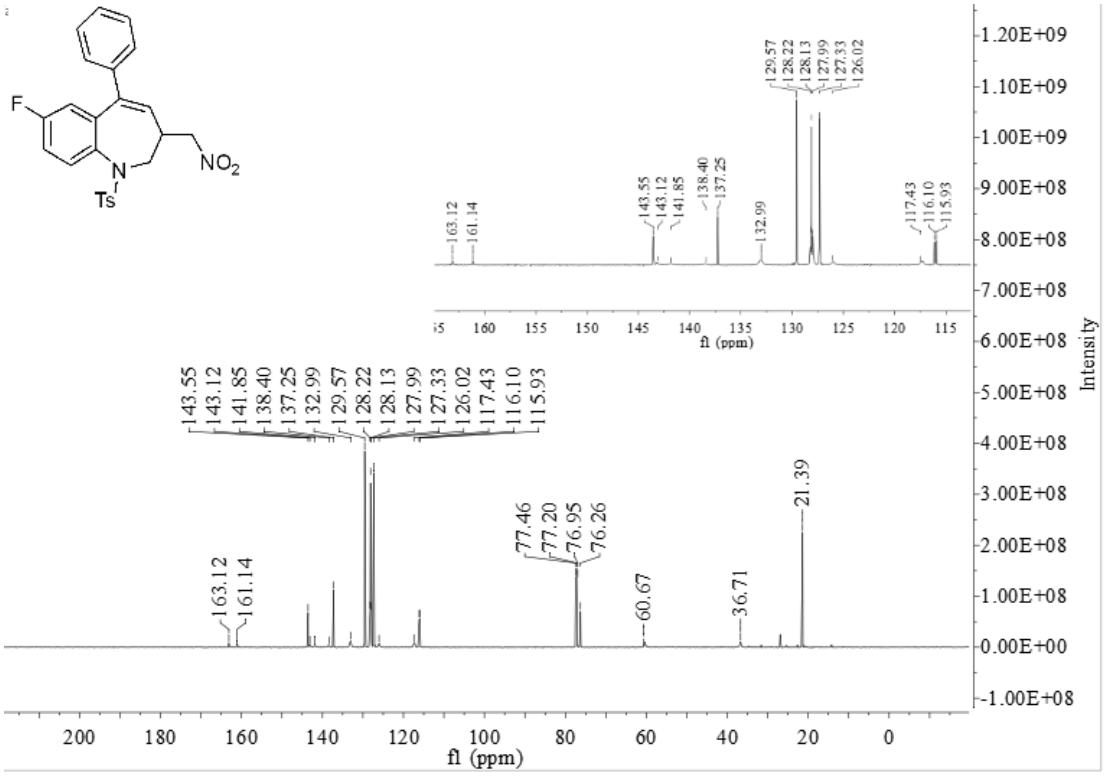
Compound 2a

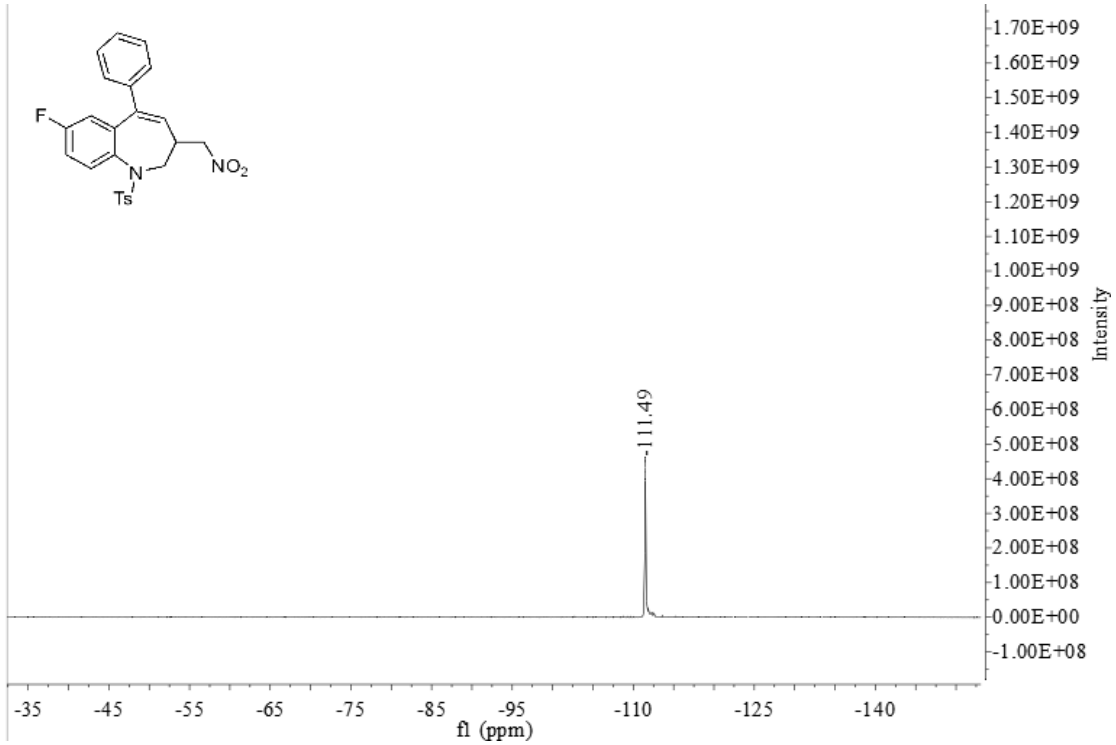




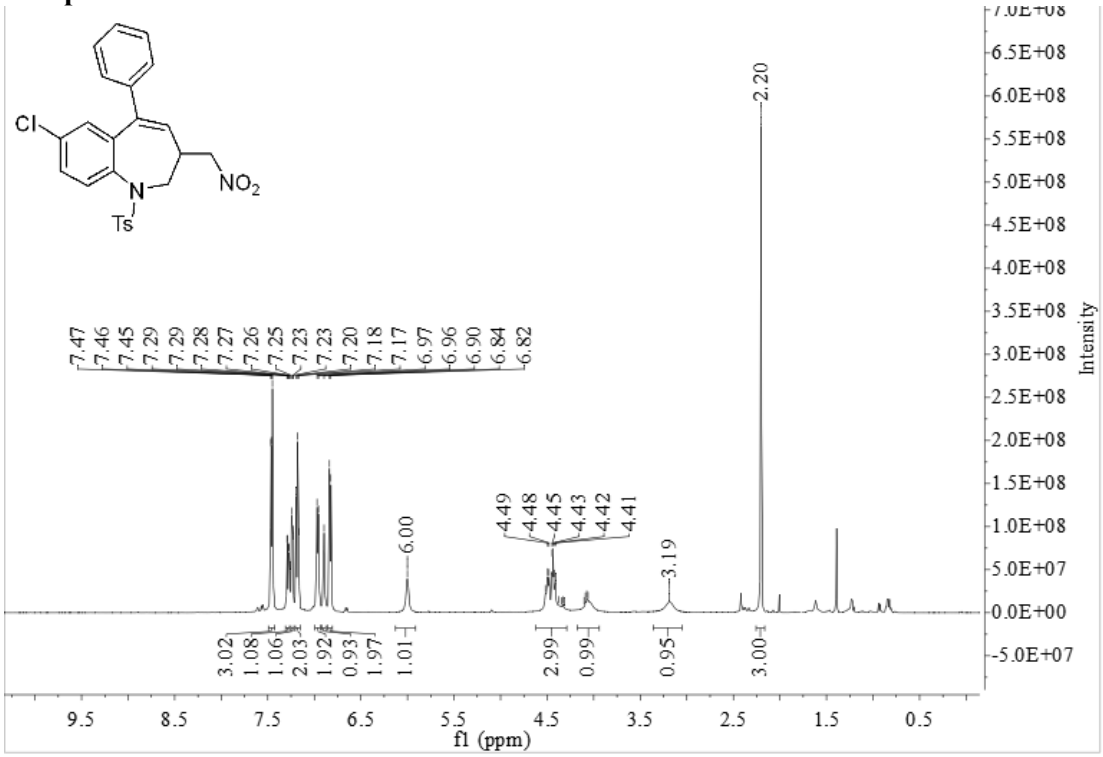
Compound 2b

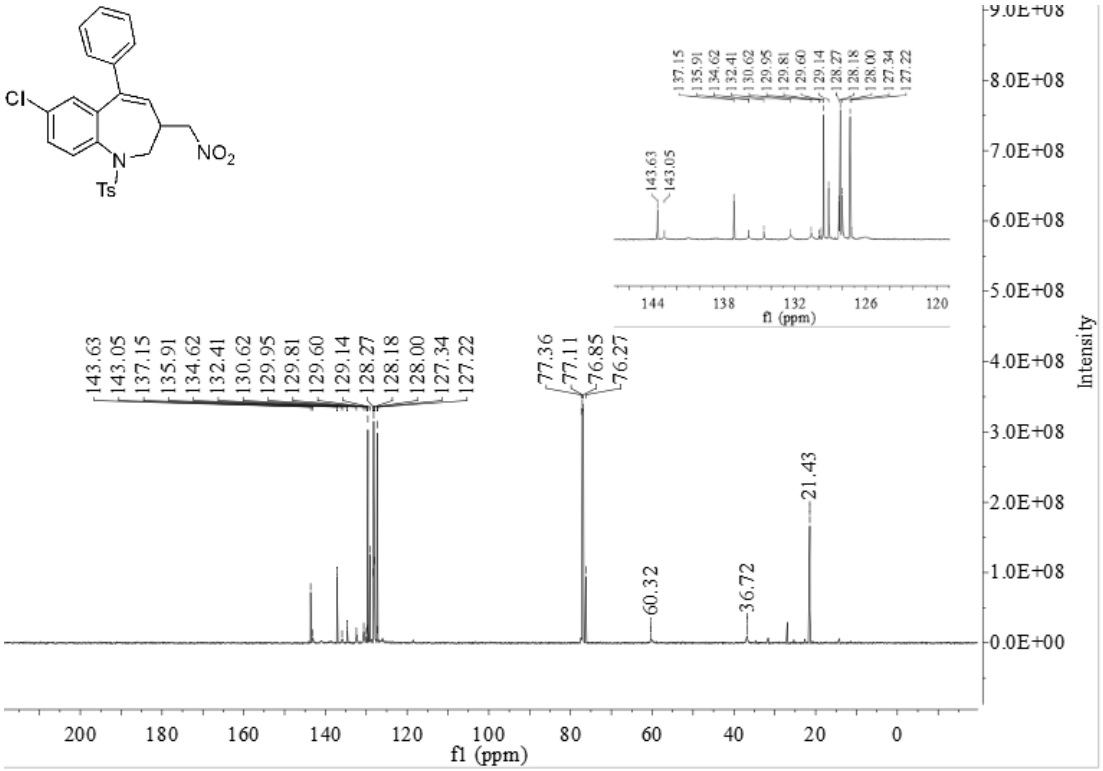

F
N
Ts
NO2
7.32
7.31
7.30
7.29
7.28
7.26
7.06
7.05
7.04
7.03
7.00
6.98
6.97
6.83
6.82
6.82
6.76
6.75
6.66
6.65
6.44
6.42
5.85
4.33
4.32
4.27
4.26
3.89
3.84
2.96
2.00
3.02
1.17
2.05
1.11
1.82
2.01
1.06
1.01
3.04
1.00
0.98
3.00
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
Intensity
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


F
N
Ts
NO2
163.12
161.14
143.55
143.12
141.85
138.40
137.25
132.99
129.57
128.22
128.13
127.99
127.33
126.02
117.43
116.10
115.93
77.46
77.20
76.95
76.26
60.67
36.71
21.39
Intensity
fl (ppm)

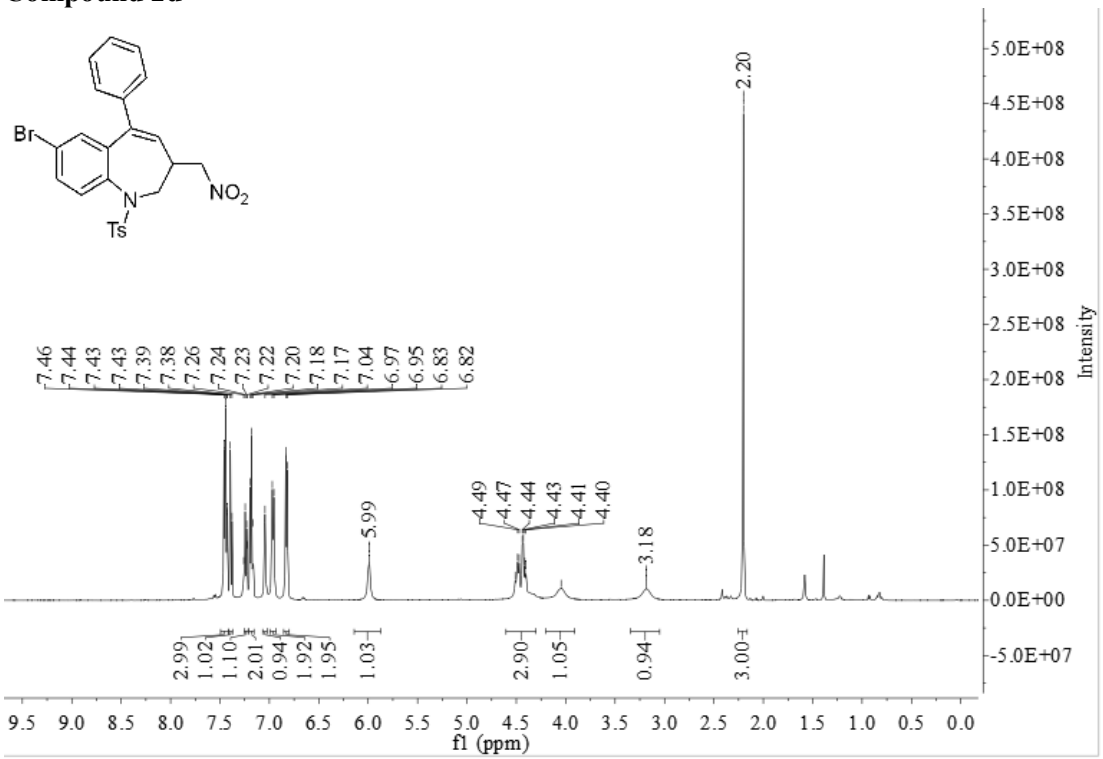

F
N
Ts
NO2
-111.49
Intensity
fl (ppm)

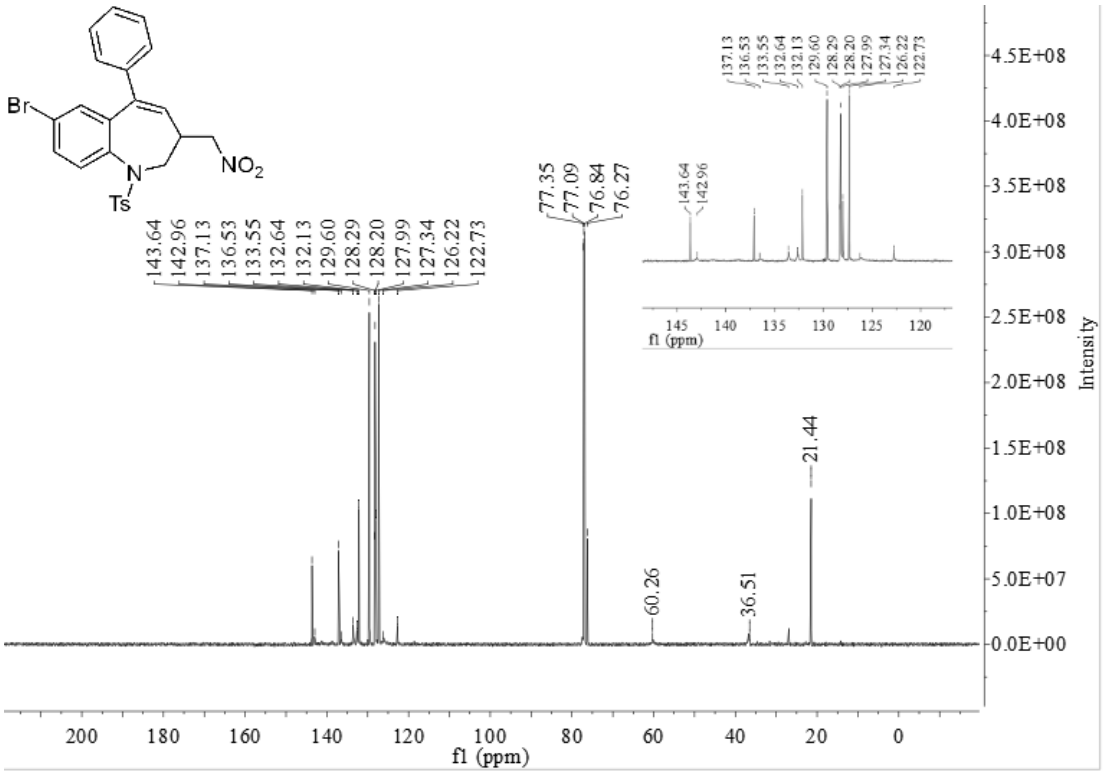
Compound 2c


Cl
NO2
N
Ts
7.47
7.46
7.45
7.29
7.29
7.28
7.27
7.26
7.25
7.23
7.23
7.20
7.18
7.17
6.97
6.96
6.90
6.84
6.82
6.00
4.49
4.48
4.45
4.43
4.42
4.41
3.19
2.20
3.02
1.08
1.06
2.03
1.92
0.93
1.97
1.01
2.99
0.99
0.95
3.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
Intensity

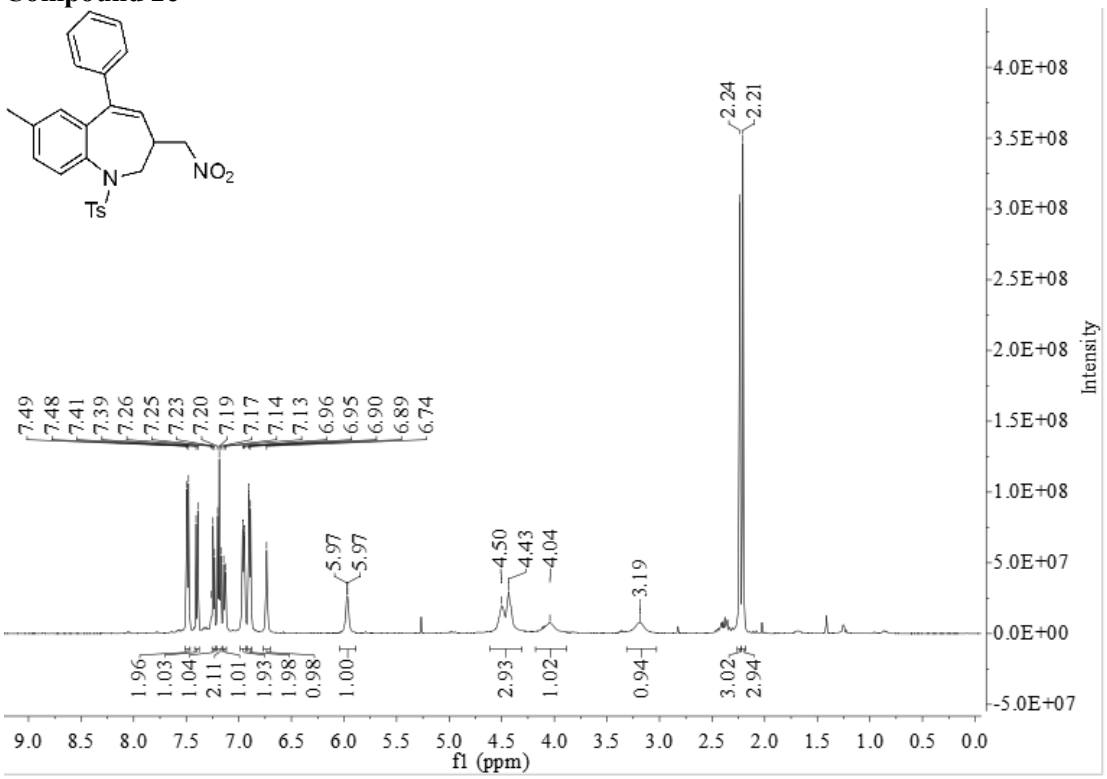

Cl
NO2
N
Ts
143.63
143.05
137.15
135.91
134.62
132.41
130.62
129.95
129.81
129.60
129.14
128.27
128.18
128.00
127.34
127.22
77.36
77.11
76.85
76.27
60.32
36.72
21.43
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)
Intensity

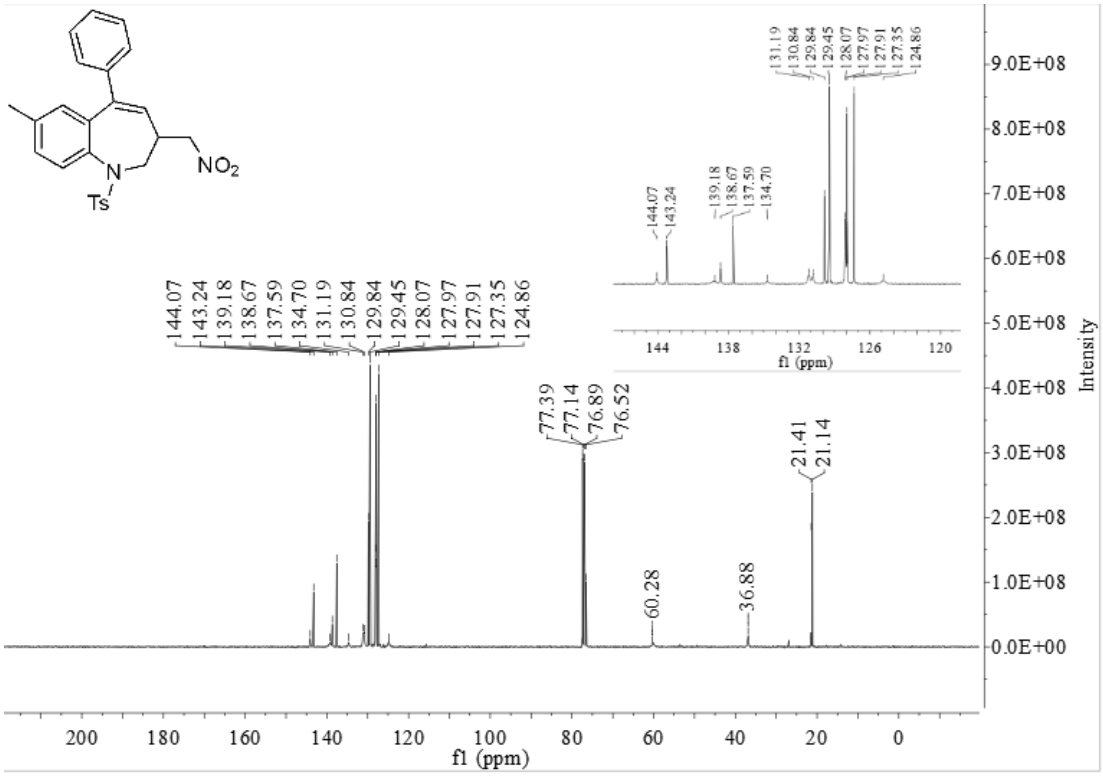
Compound 2d


Br
NO2
N
Ts
7.46
7.44
7.43
7.43
7.39
7.38
7.26
7.24
7.23
7.22
7.20
7.18
7.17
7.04
6.97
6.95
6.83
6.82
5.99
4.49
4.47
4.44
4.43
4.41
4.40
3.18
2.20
2.99
1.02
1.10
2.01
0.94
1.92
1.95
1.03
2.90
1.05
0.94
3.00
Intensity
fl (ppm)

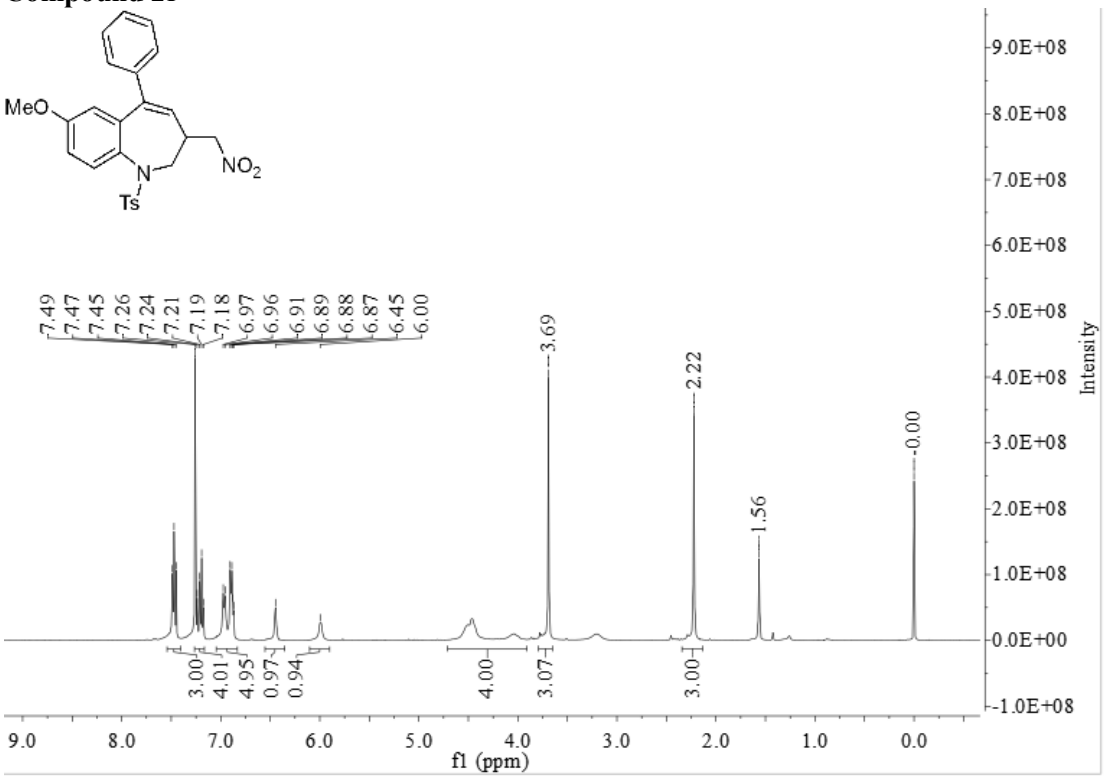

Br
NO2
N
Ts
143.64
142.96
137.13
136.53
133.55
132.64
132.13
129.60
128.29
128.20
127.99
127.34
126.22
122.73
77.35
77.09
76.84
76.27
60.26
36.51
21.44
Intensity
fl (ppm)

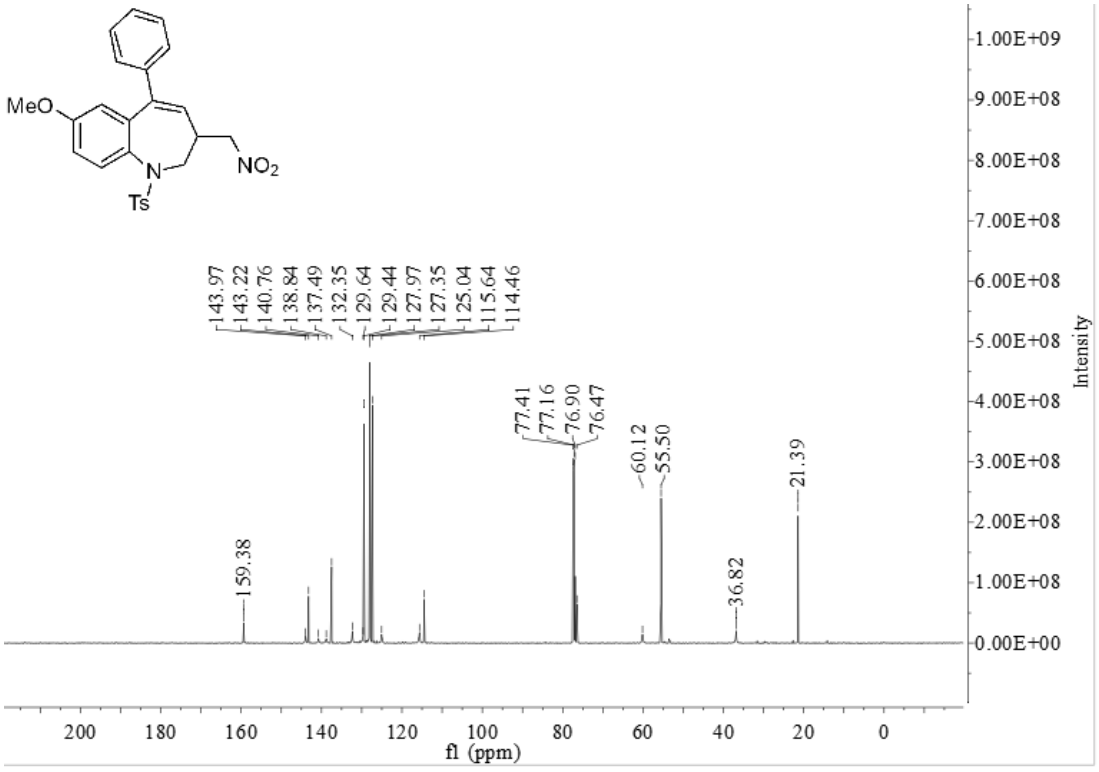
Compound 2e


NO2
N
Ts
7.49
7.48
7.41
7.39
7.26
7.25
7.23
7.20
7.19
7.17
7.14
7.13
6.96
6.95
6.90
6.89
6.74
5.97
5.97
4.50
4.43
4.04
3.19
2.24
2.21
1.96
1.03
1.04
2.11
1.01
1.93
1.98
0.98
1.00
2.93
1.02
0.94
3.02
2.94
Intensity
fl (ppm)

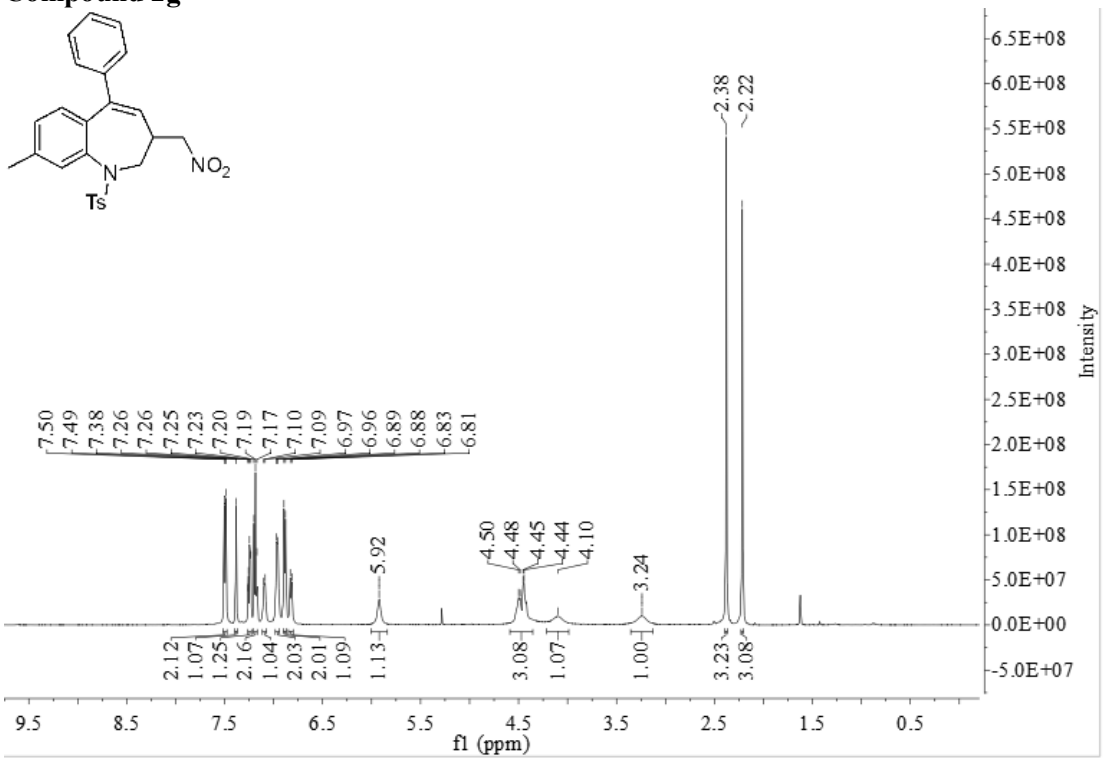

NO2
N
Ts
144.07
143.24
139.18
138.67
137.59
134.70
131.19
130.84
129.84
129.45
128.07
127.97
127.91
127.35
124.86
77.39
77.14
76.89
76.52
60.28
36.88
21.41
21.14
Intensity
fl (ppm)

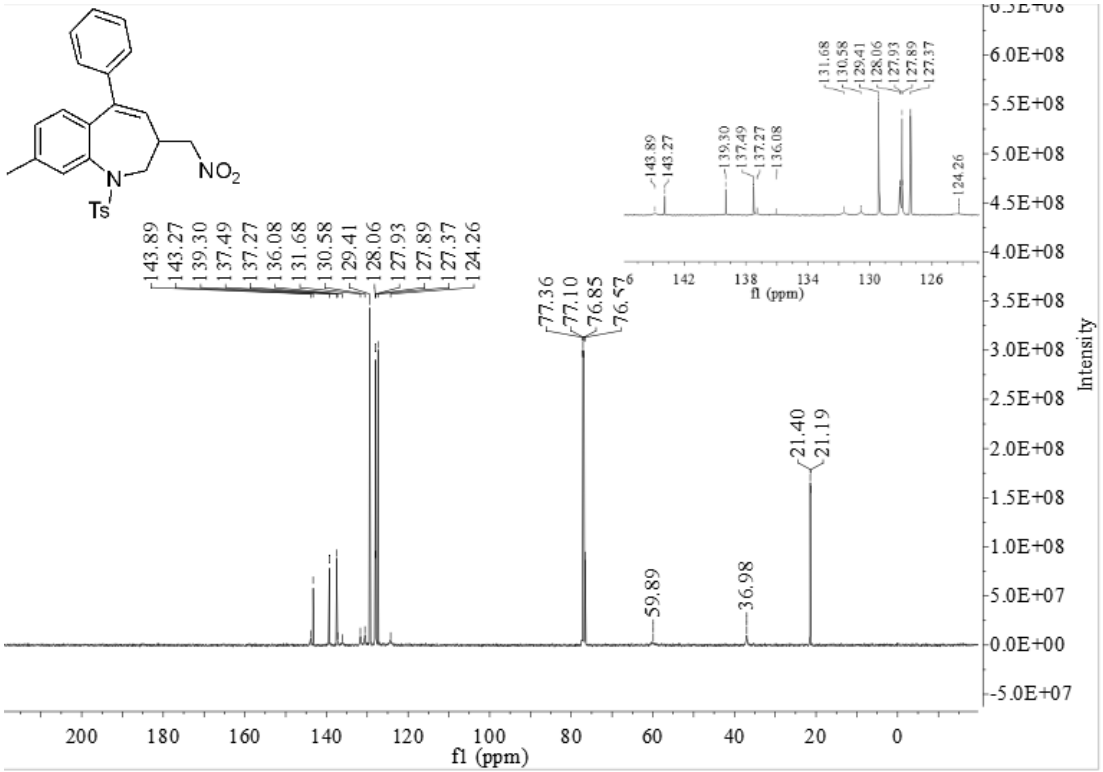
Compound 2f


MeO
NO2
N
Ts
7.49
7.47
7.45
7.26
7.24
7.21
7.19
7.18
6.97
6.96
6.91
6.89
6.88
6.87
6.45
6.00
3.69
2.22
1.56
0.00
3.00
4.01
4.95
0.97
0.94
4.00
3.07
3.00
Intensity
fl (ppm)

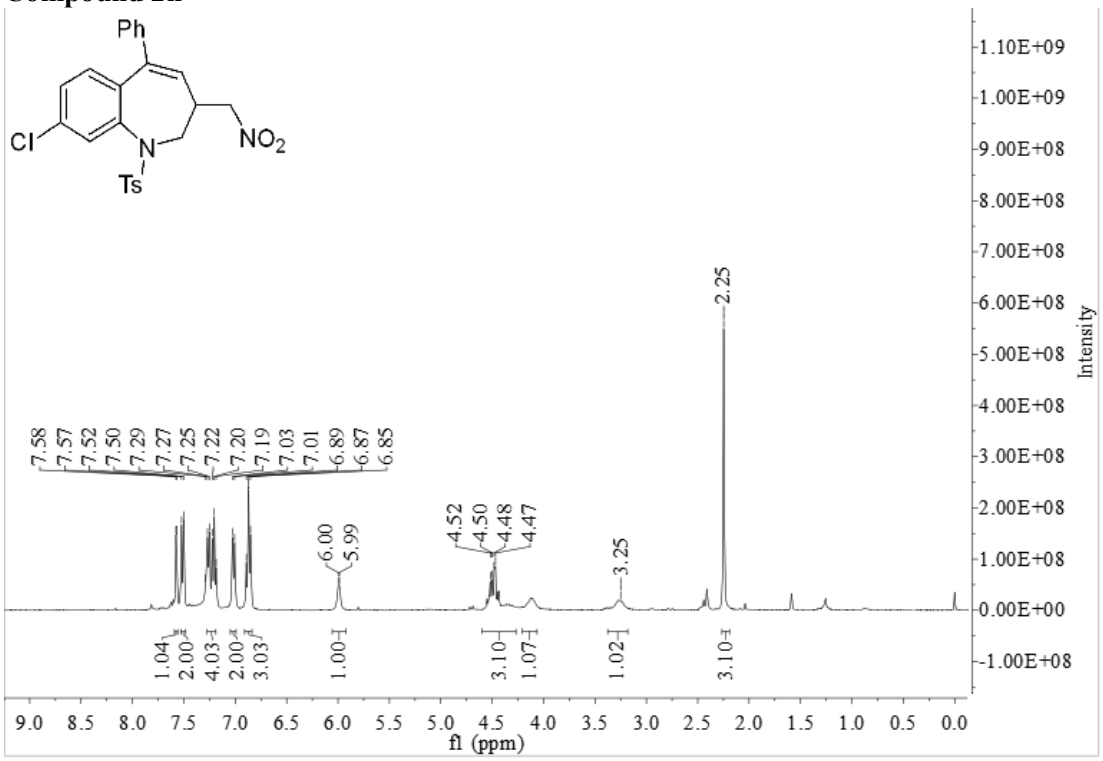

MeO
NO2
N
Ts
143.97
143.22
140.76
138.84
137.49
132.35
129.64
129.44
127.97
127.35
125.04
115.64
114.46
77.41
77.16
76.90
76.47
60.12
55.50
21.39
159.38
36.82
Intensity
fl (ppm)

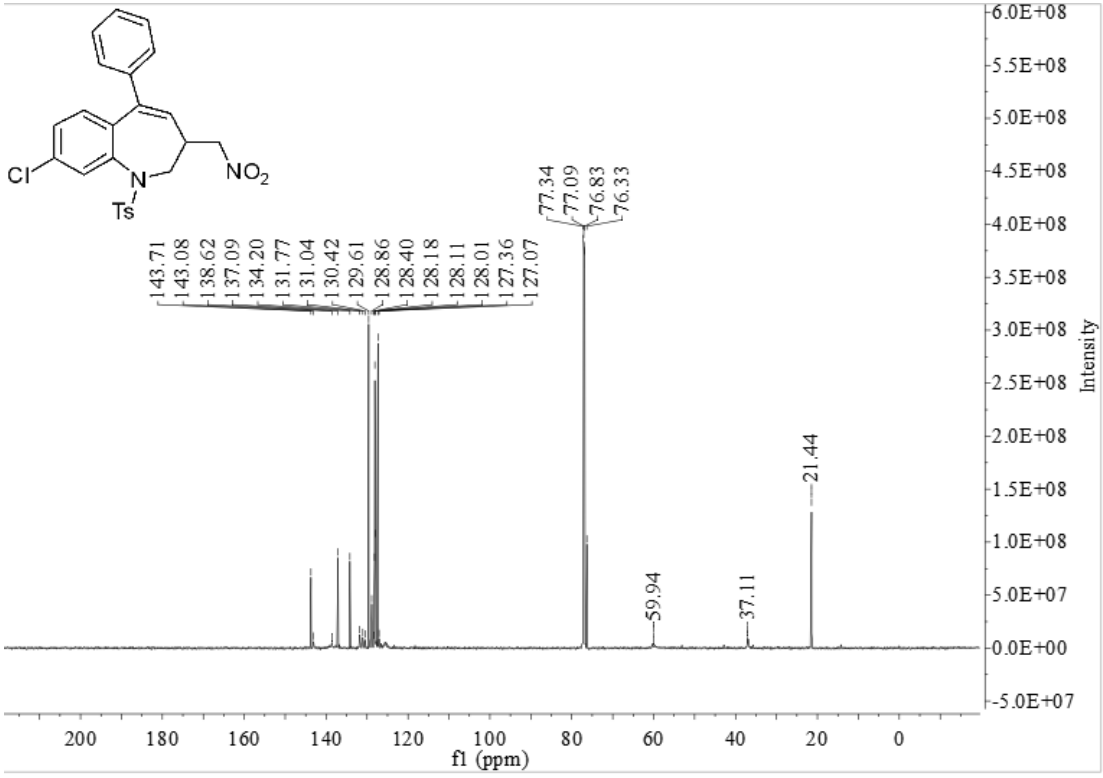
Compound 2g


NO2
Ts
7.50
7.49
7.38
7.26
7.26
7.25
7.23
7.20
7.19
7.17
7.10
7.09
6.97
6.96
6.89
6.88
6.83
6.81
5.92
4.50
4.48
4.45
4.44
4.10
3.24
2.38
2.22
2.12
1.07
1.25
2.16
1.04
2.03
2.01
1.09
1.13
3.08
1.07
1.00
3.23
3.08
Intensity
fl (ppm)

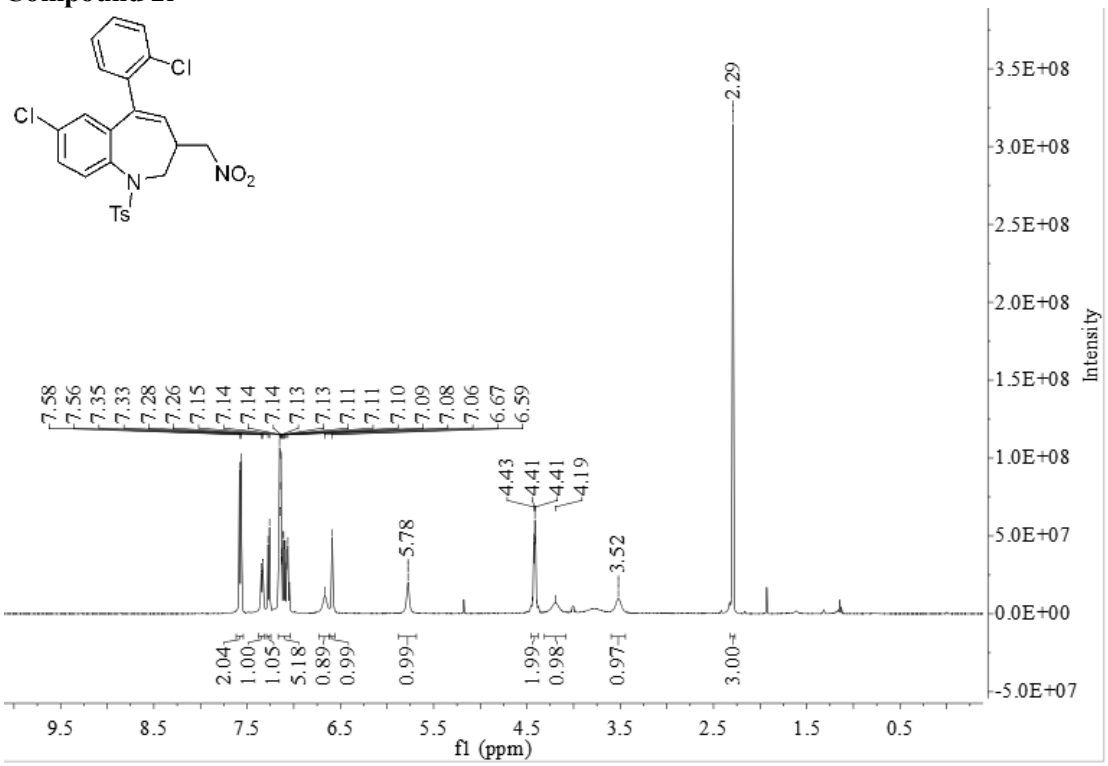

NO2
Ts
143.89
143.27
139.30
137.49
137.27
136.08
131.68
130.58
129.41
128.06
127.93
127.89
127.37
124.26
77.36
77.10
76.85
59.89
36.98
21.40
21.19
Intensity
fl (ppm)

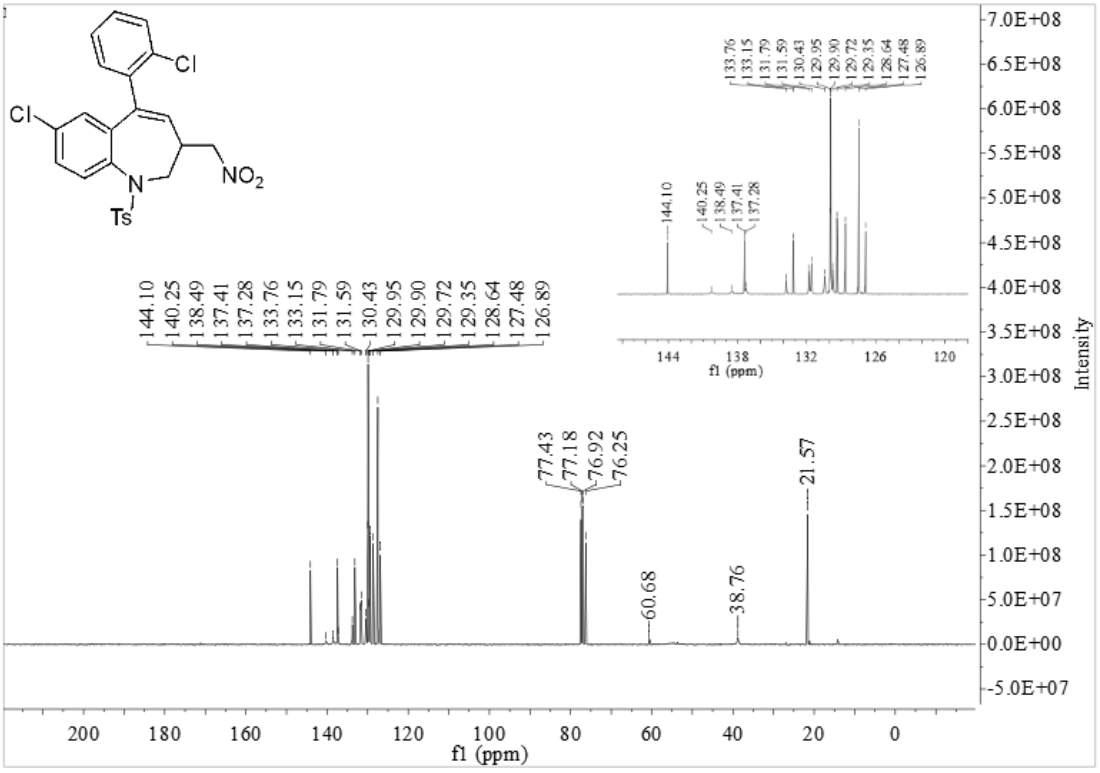
Compound 2h


Ph
Cl
N
Ts
NO2
7.58
7.57
7.52
7.50
7.29
7.27
7.25
7.22
7.20
7.19
7.03
7.01
6.89
6.87
6.85
6.00
5.99
4.52
4.50
4.48
4.47
3.25
2.25
1.04
2.00
4.03
2.00
3.03
1.00
3.10
1.07
1.02
3.10
Intensity
fl (ppm)

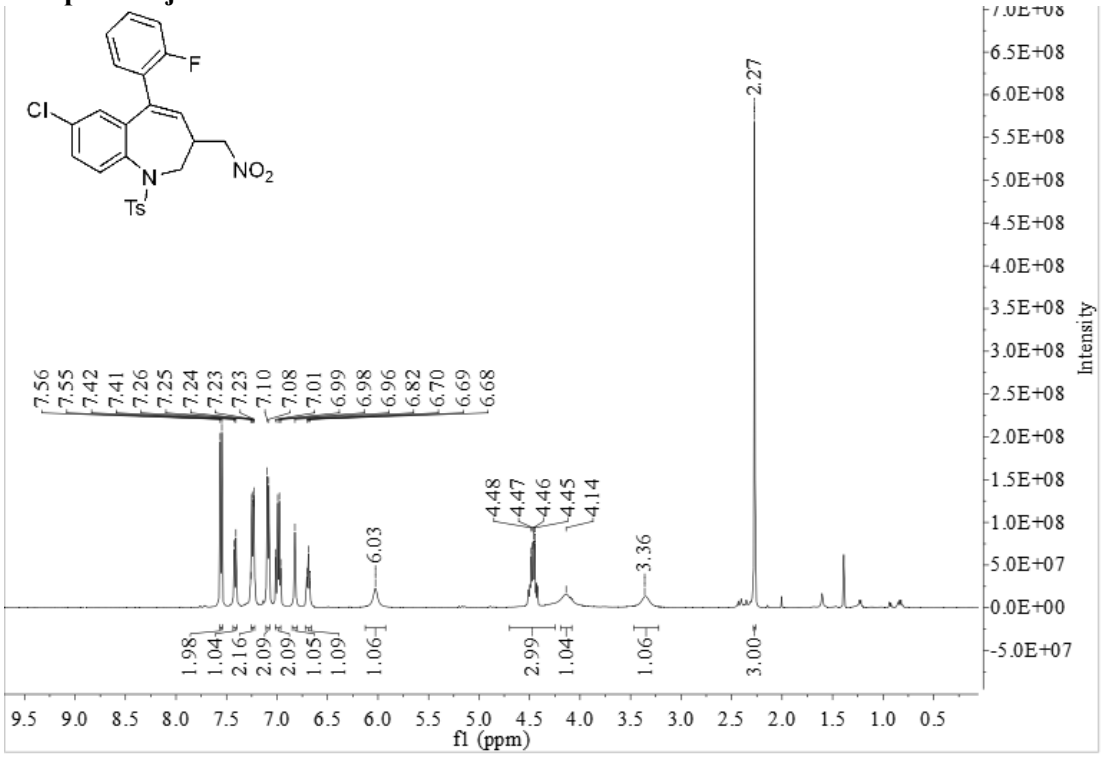

Cl
N
Ts
NO2
143.71
143.08
138.62
137.09
134.20
131.77
131.04
130.42
129.61
128.86
128.40
128.18
128.11
128.01
127.36
127.07
77.34
77.09
76.83
76.33
59.94
37.11
21.44
Intensity
fl (ppm)

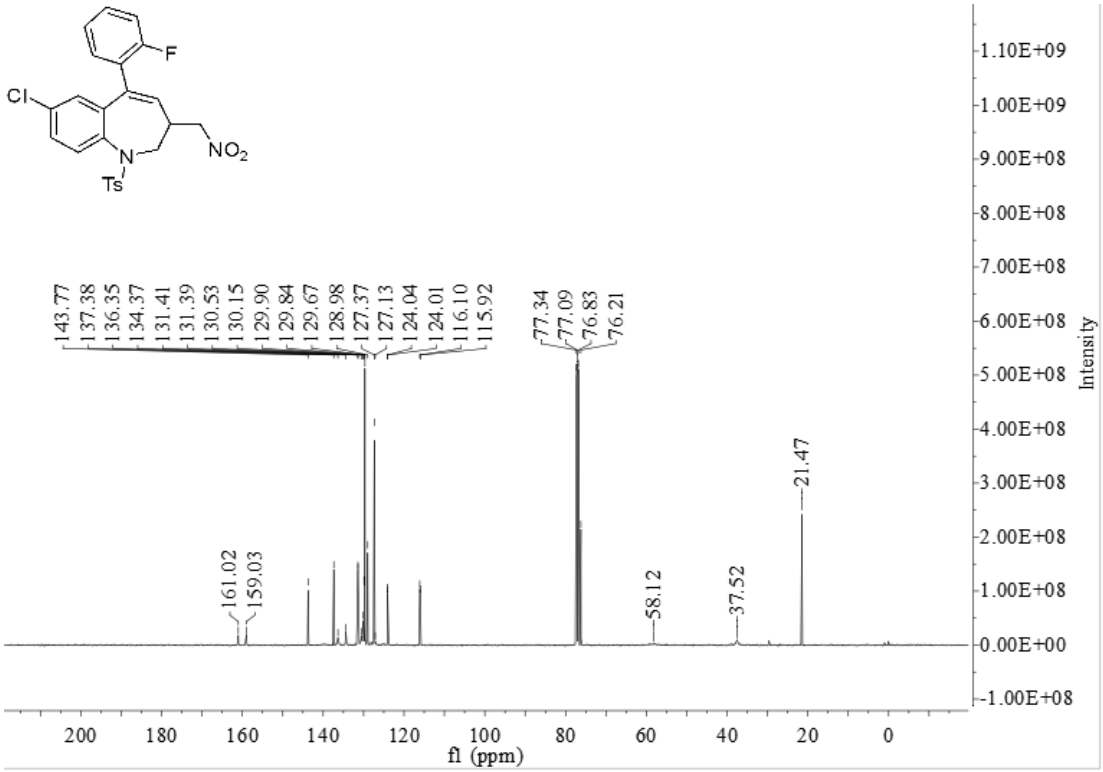
Compound 2i

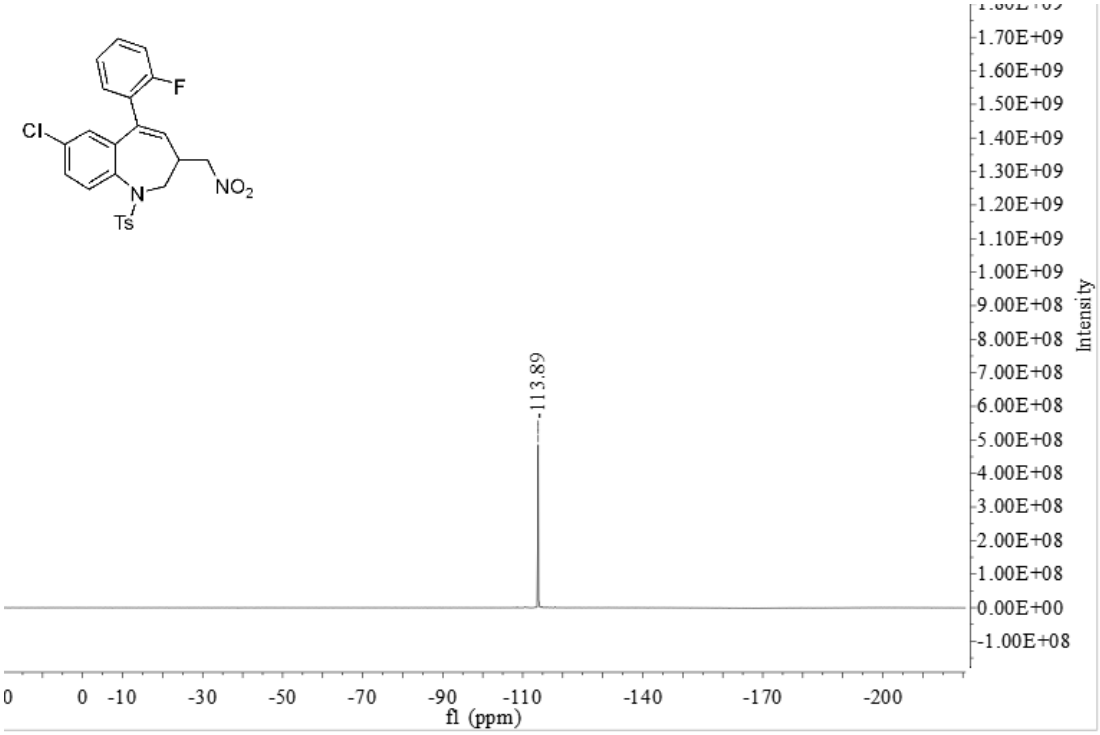

Cl
Cl
N
Ts
NO2
7.58
7.56
7.35
7.33
7.28
7.26
7.15
7.14
7.14
7.14
7.13
7.13
7.11
7.11
7.10
7.09
7.08
7.06
6.67
6.59
4.43
4.41
4.41
4.19
5.78
3.52
2.29
2.04
1.00
1.05
5.18
0.89
0.99
0.99
1.99
0.98
0.97
3.00
Intensity
fl (ppm)


Cl
Cl
N
Ts
NO2
144.10
140.25
138.49
137.41
137.28
133.76
133.15
131.79
131.59
130.43
129.95
129.90
129.72
129.35
128.64
127.48
126.89
77.43
77.18
76.92
76.25
60.68
38.76
21.57
Intensity
fl (ppm)

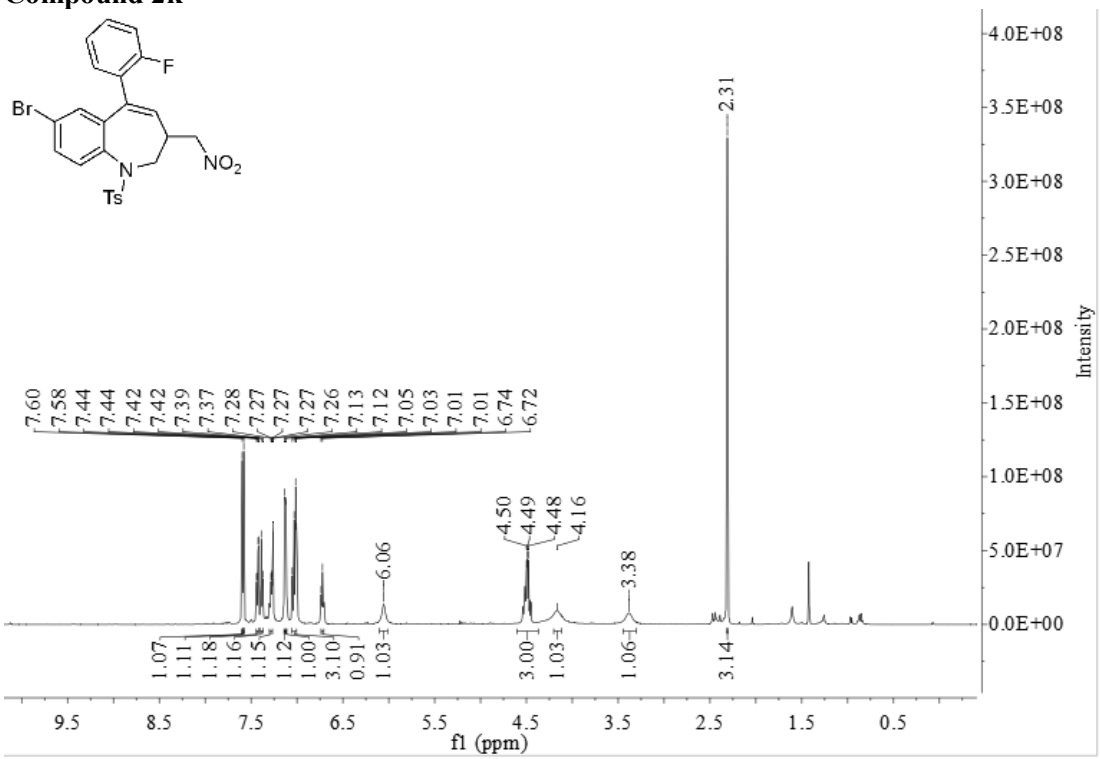
Compound 2j

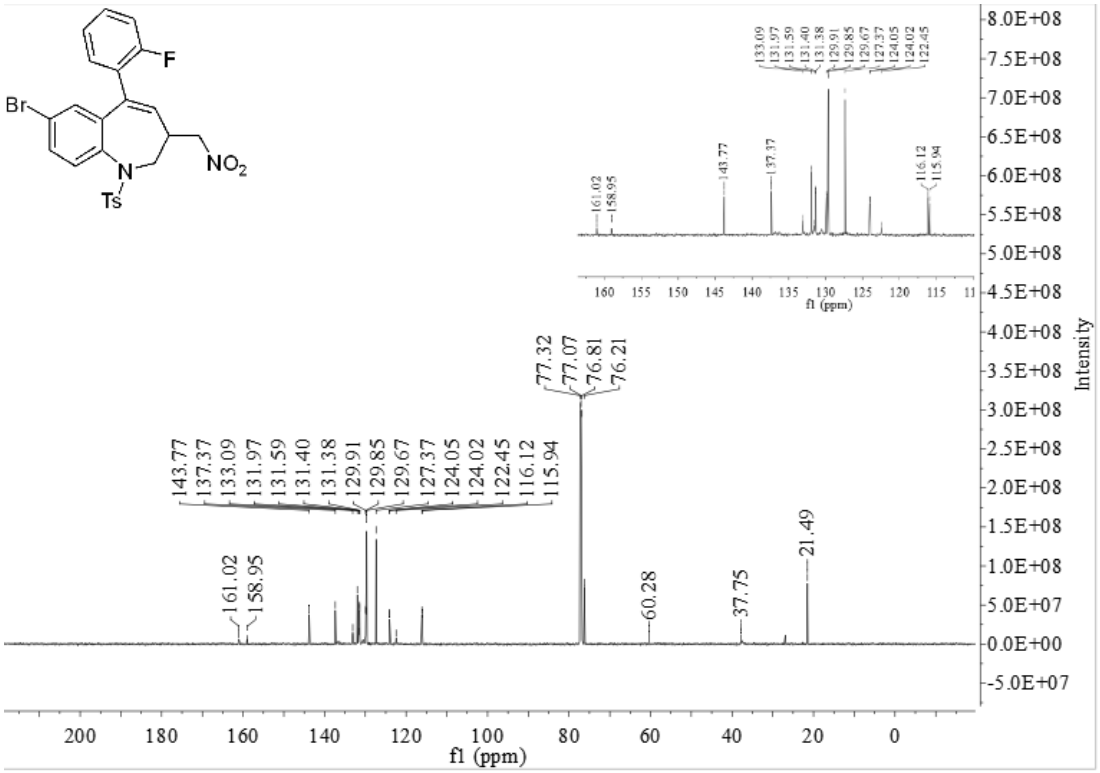

F
Cl
N
Ts
NO2
7.56
7.55
7.42
7.41
7.26
7.25
7.24
7.23
7.23
7.10
7.08
7.01
6.99
6.98
6.96
6.82
6.70
6.69
6.68
4.48
4.47
4.46
4.45
4.14
6.03
3.36
2.27
1.98
1.04
2.16
2.09
2.09
1.05
1.09
1.06
2.99
1.04
1.06
3.00
Intensity
fl (ppm)

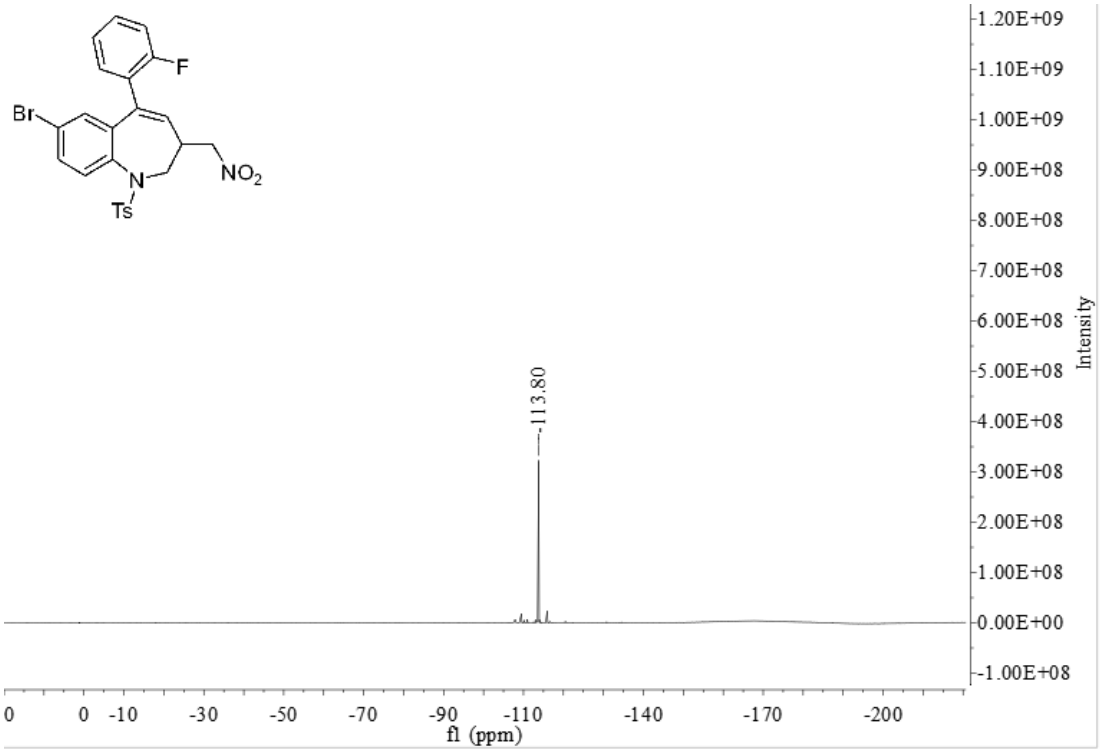

F
Cl
N
Ts
NO2
143.77
137.38
136.35
134.37
131.41
131.39
130.53
130.15
129.90
129.84
129.67
128.98
127.37
127.13
124.04
124.01
116.10
115.92
77.34
77.09
76.83
76.21
161.02
159.03
58.12
37.52
21.47
Intensity
fl (ppm)


F
Cl
N
Ts
NO2
-113.89
Intensity
f1 (ppm)

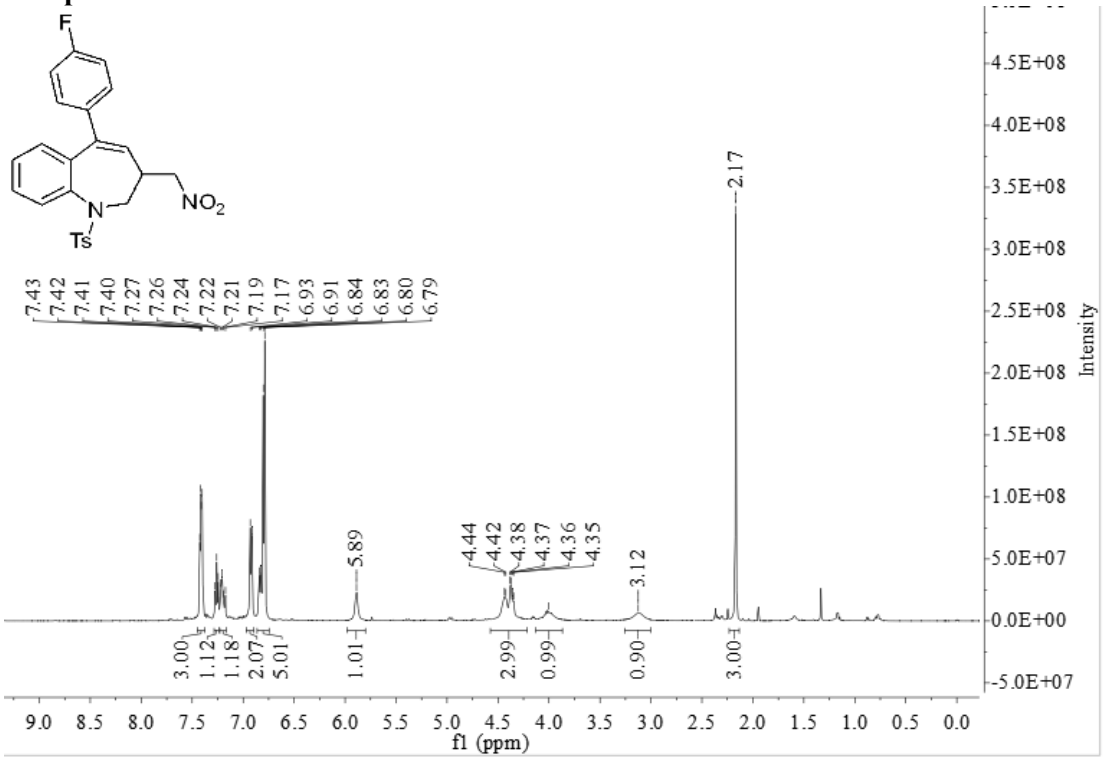
Compound 2k

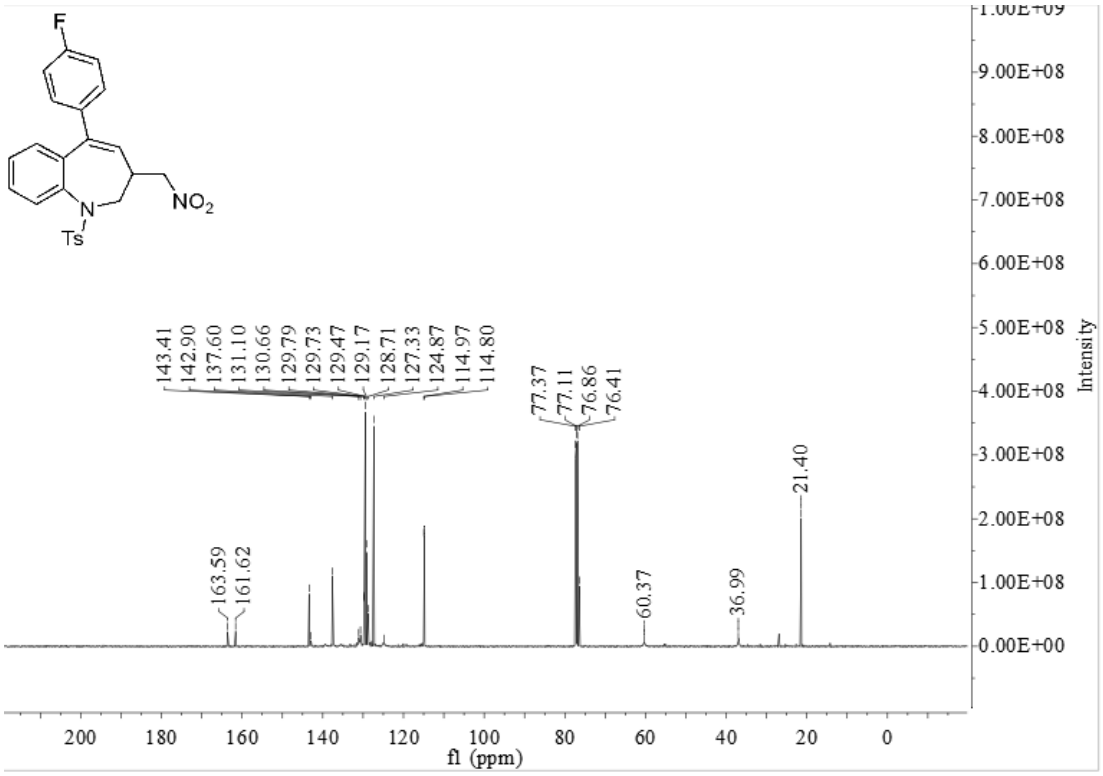

F
Br
N
Ts
NO2
2.31
7.60
7.58
7.44
7.44
7.42
7.42
7.39
7.37
7.28
7.27
7.27
7.27
7.26
7.13
7.12
7.05
7.03
7.01
7.01
6.74
6.72
4.50
4.49
4.48
4.16
6.06
3.38
1.07
1.11
1.18
1.16
1.15
1.12
1.00
3.10
0.91
1.03
3.00
1.03
1.06
3.14
Intensity
f1 (ppm)


F
Br
N
Ts
NO2
161.02
158.95
143.77
137.37
133.09
131.97
131.59
131.40
131.38
129.91
129.85
129.67
127.37
124.05
124.02
122.45
116.12
115.94
77.32
77.07
76.81
76.21
60.28
37.75
21.49
f1 (ppm)
Intensity

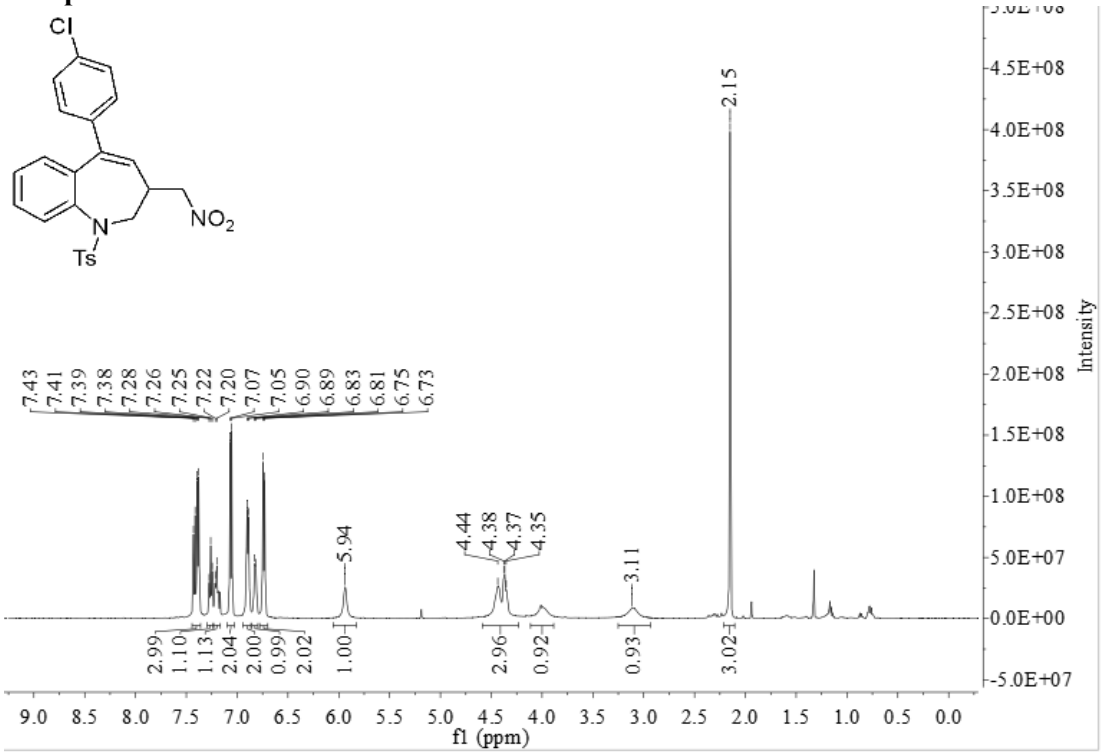

F
Br
N
Ts
NO2
113.80
f1 (ppm)
Intensity

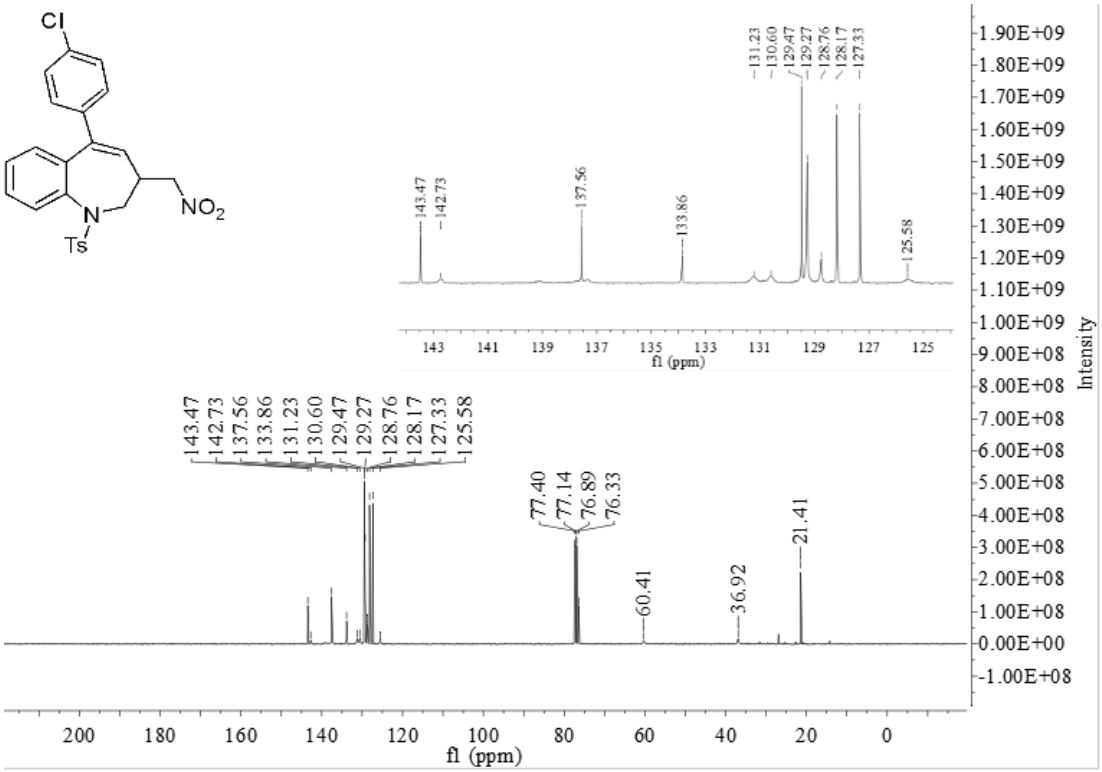
Compound 2l


F
NO2
N
Ts
7.43
7.42
7.41
7.40
7.27
7.26
7.24
7.22
7.21
7.19
7.17
6.93
6.91
6.84
6.83
6.80
6.79
5.89
4.44
4.42
4.38
4.37
4.36
4.35
3.12
2.17
3.00
1.12
1.18
2.07
5.01
1.01
2.99
0.99
0.90
3.00
Intensity
fl (ppm)

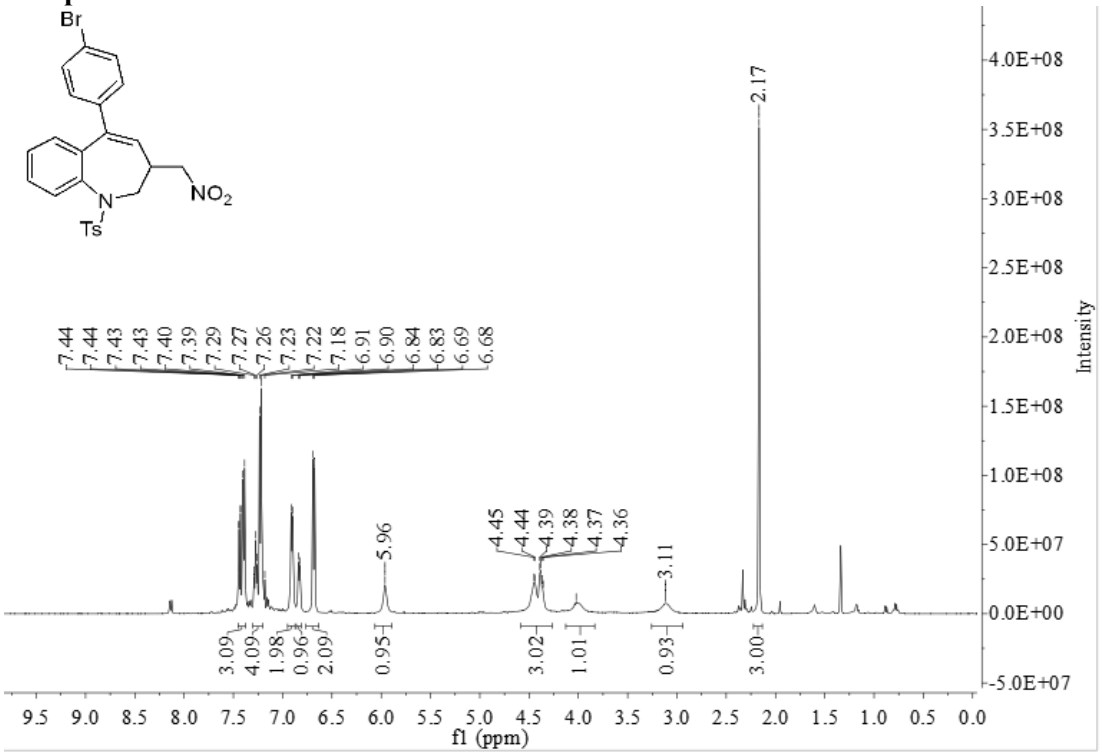

F
NO2
N
Ts
143.41
142.90
137.60
131.10
130.66
129.79
129.73
129.47
129.17
128.71
127.33
124.87
114.97
114.80
77.37
77.11
76.86
76.41
163.59
161.62
60.37
36.99
21.40
Intensity
fl (ppm)

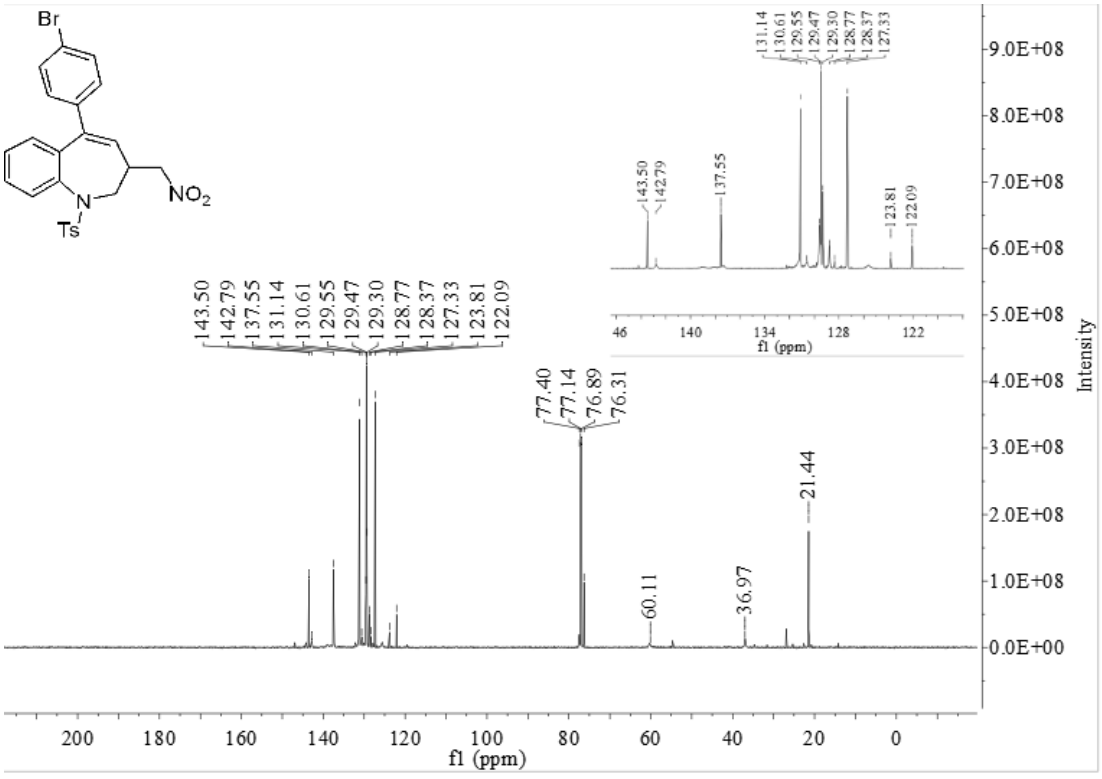
Compound 2m


Cl
NO2
N
Ts
7.43
7.41
7.39
7.38
7.28
7.26
7.25
7.22
7.20
7.07
7.05
6.90
6.89
6.83
6.81
6.75
6.73
5.94
4.44
4.38
4.37
4.35
3.11
2.15
2.99
1.10
1.13
2.04
2.00
0.99
2.02
1.00
2.96
0.92
0.93
3.02
Intensity
f1 (ppm)

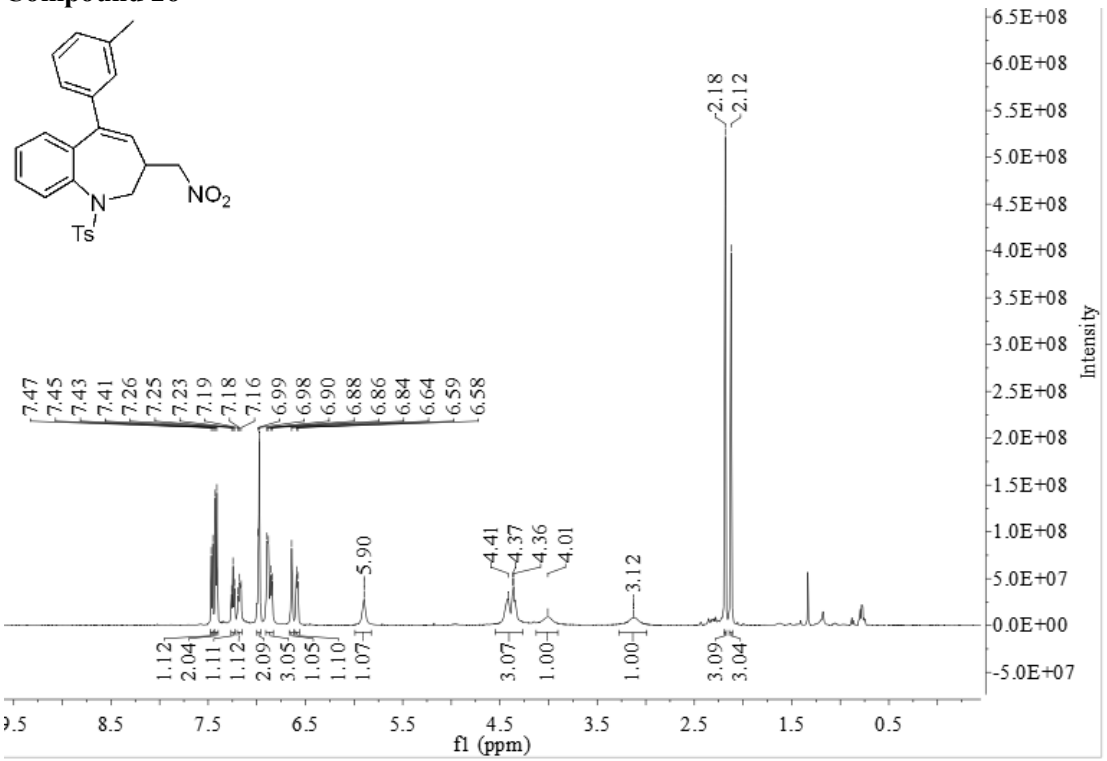

Cl
NO2
N
Ts
143.47
142.73
137.56
133.86
131.23
130.60
129.47
129.27
128.76
128.17
127.33
125.58
77.40
77.14
76.89
76.33
60.41
36.92
21.41
Intensity
f1 (ppm)

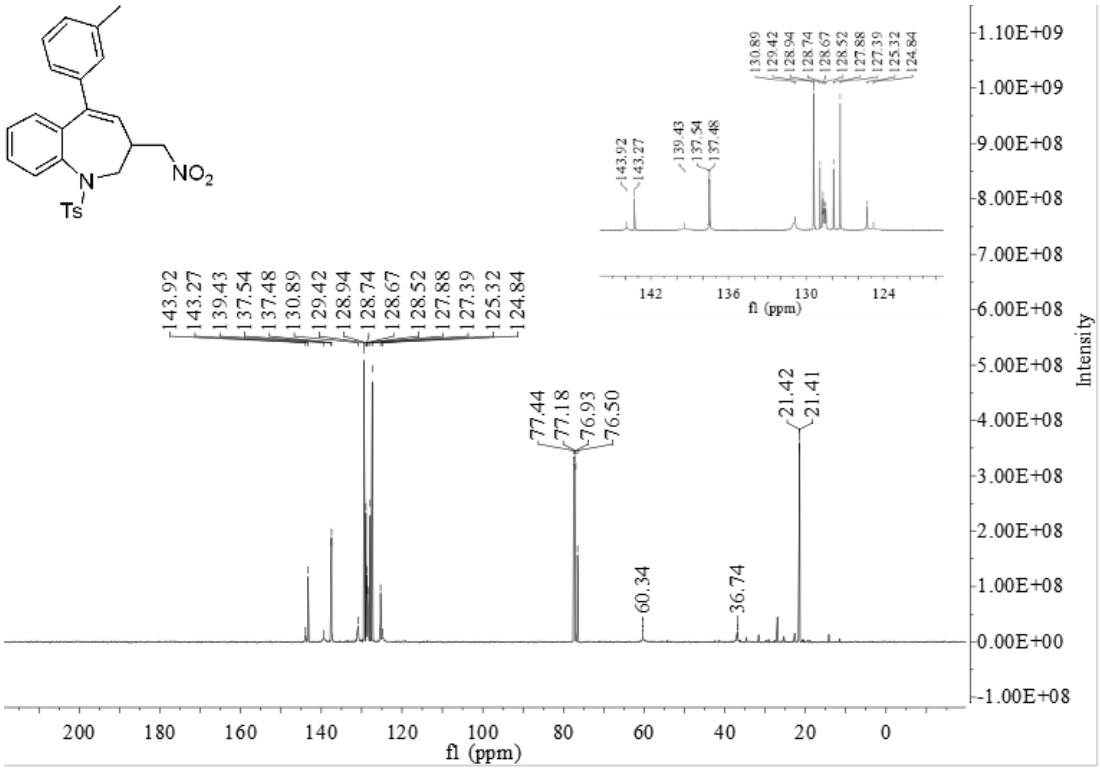
Compound 2n


Br
NO2
N
Ts
7.44
7.44
7.43
7.43
7.40
7.39
7.29
7.27
7.26
7.23
7.22
7.18
6.91
6.90
6.84
6.83
6.69
6.68
5.96
4.45
4.44
4.39
4.38
4.37
4.36
3.11
2.17
3.09
4.09
1.98
0.96
2.09
0.95
3.02
1.01
0.93
3.00
Intensity
f1 (ppm)

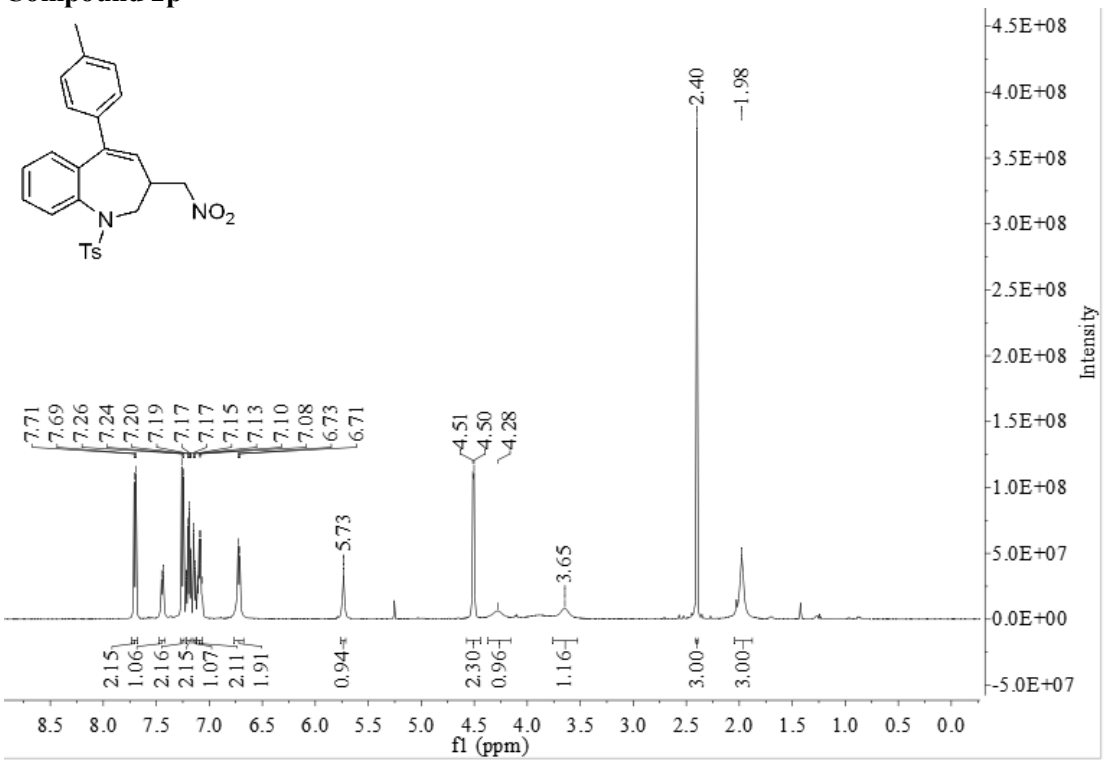

Br
NO2
N
Ts
131.14
130.61
129.55
129.47
129.30
128.77
128.37
127.33
143.50
142.79
137.55
123.81
122.09
77.40
77.14
76.89
76.31
60.11
36.97
21.44
Intensity
f1 (ppm)

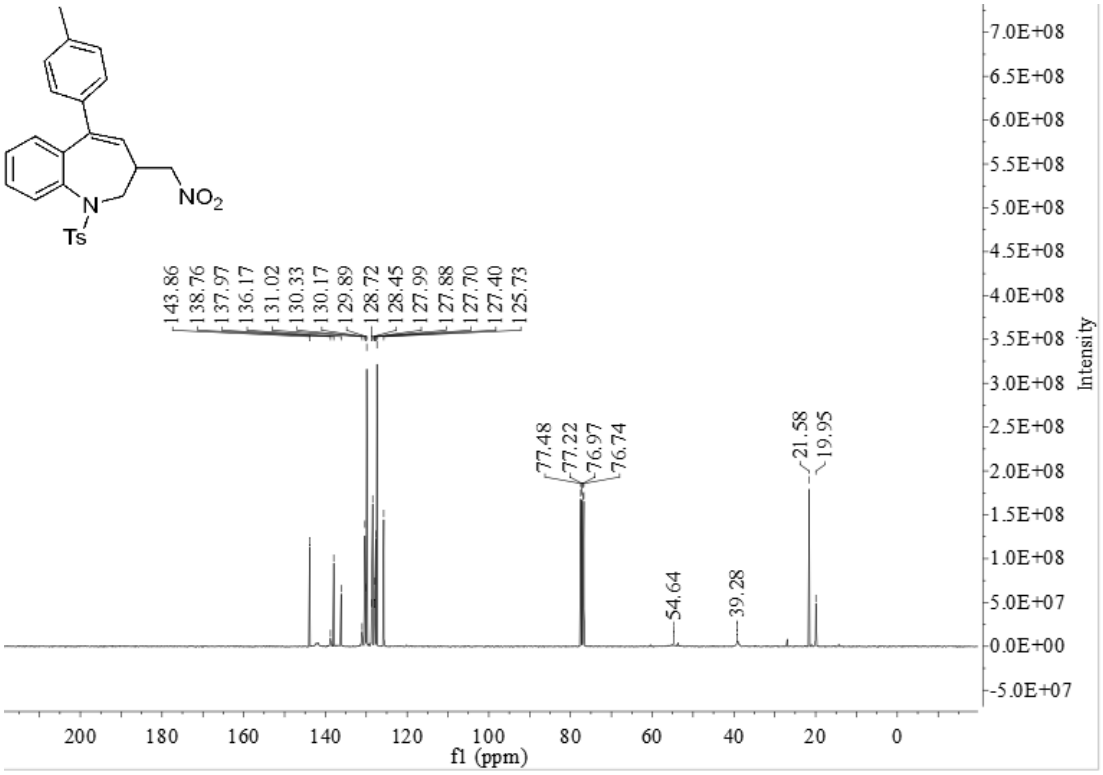
Compound 2o


NO2
N
Ts
7.47
7.45
7.43
7.41
7.26
7.25
7.23
7.19
7.18
7.16
6.99
6.98
6.90
6.88
6.86
6.84
6.64
6.59
6.58
5.90
4.41
4.37
4.36
4.01
3.12
2.18
2.12
1.12
2.04
1.11
1.12
2.09
3.05
1.05
1.10
1.07
3.07
1.00
1.00
3.09
3.04
Intensity
fl (ppm)

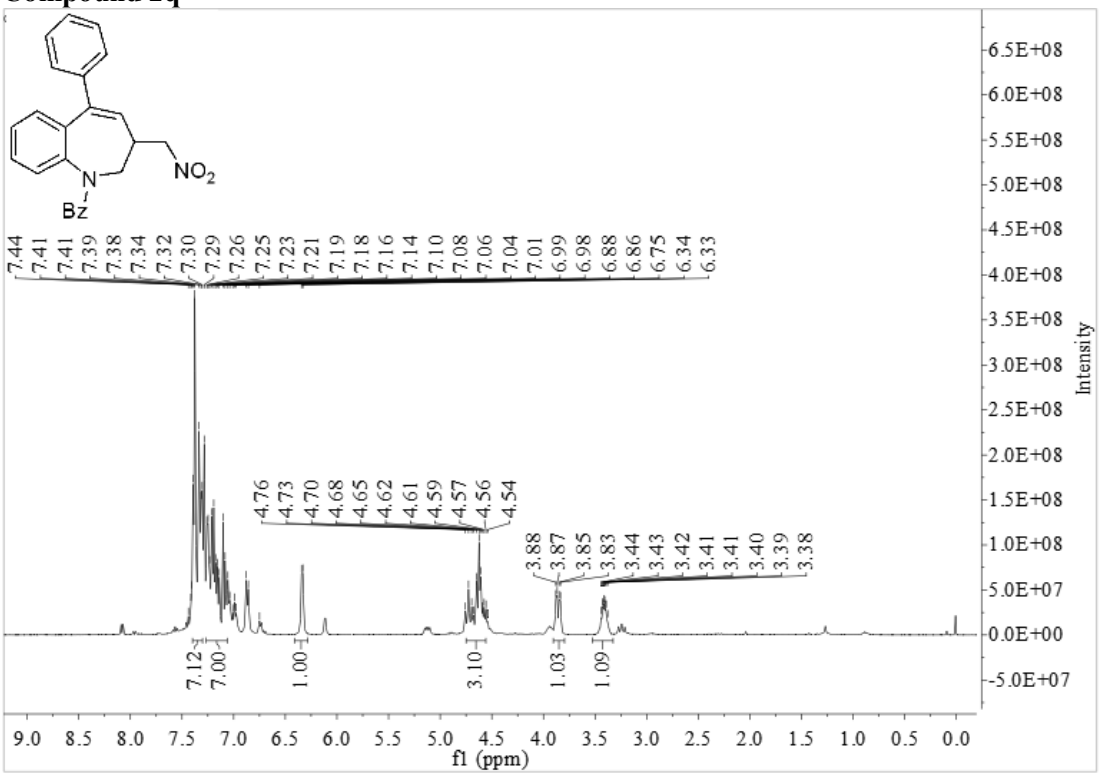

NO2
N
Ts
143.92
143.27
139.43
137.54
137.48
130.89
129.42
128.94
128.74
128.67
128.52
127.88
127.39
125.32
124.84
77.44
77.18
76.93
76.50
60.34
36.74
21.42
21.41
Intensity
fl (ppm)

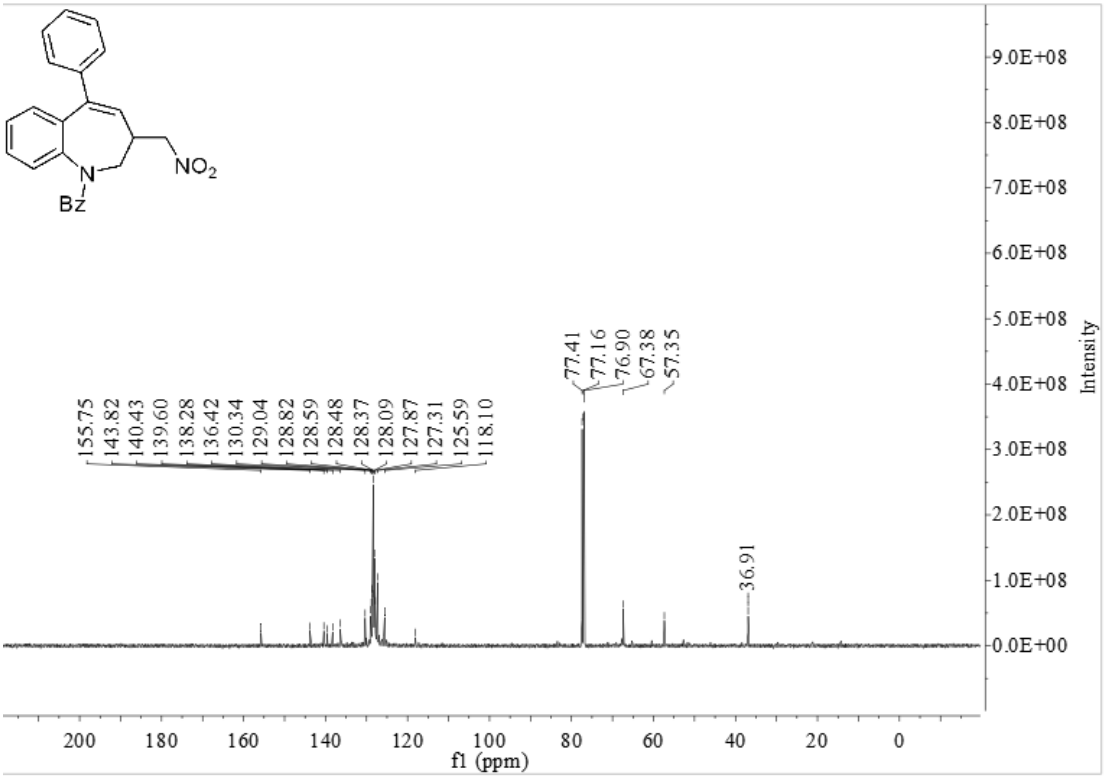
Compound 2p


NO2
Ts
7.71
7.69
7.26
7.24
7.20
7.19
7.17
7.17
7.15
7.13
7.10
7.08
6.73
6.71
4.51
4.50
4.28
5.73
3.65
2.40
1.98
2.15
1.06
2.16
2.15
1.07
2.11
1.91
0.94
2.30
0.96
1.16
3.00
3.00
Intensity
f1 (ppm)

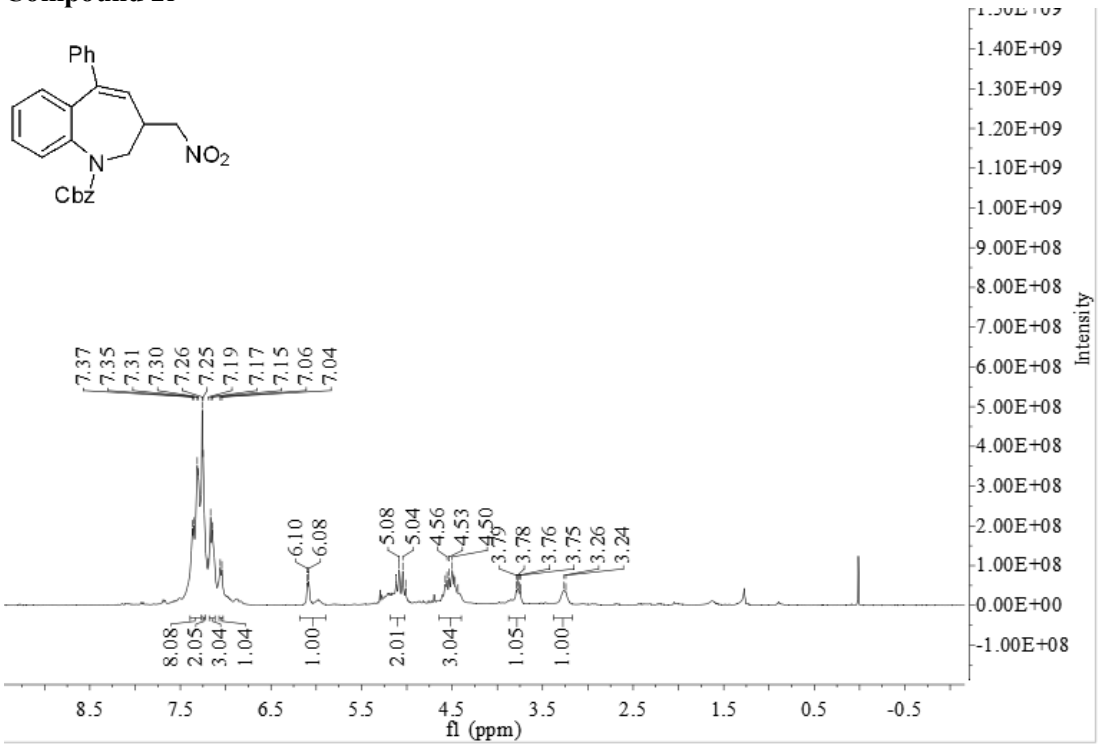

NO2
Ts
143.86
138.76
137.97
136.17
131.02
130.33
130.17
129.89
128.72
128.45
127.99
127.88
127.70
127.40
125.73
77.48
77.22
76.97
76.74
54.64
39.28
21.58
19.95
Intensity
f1 (ppm)

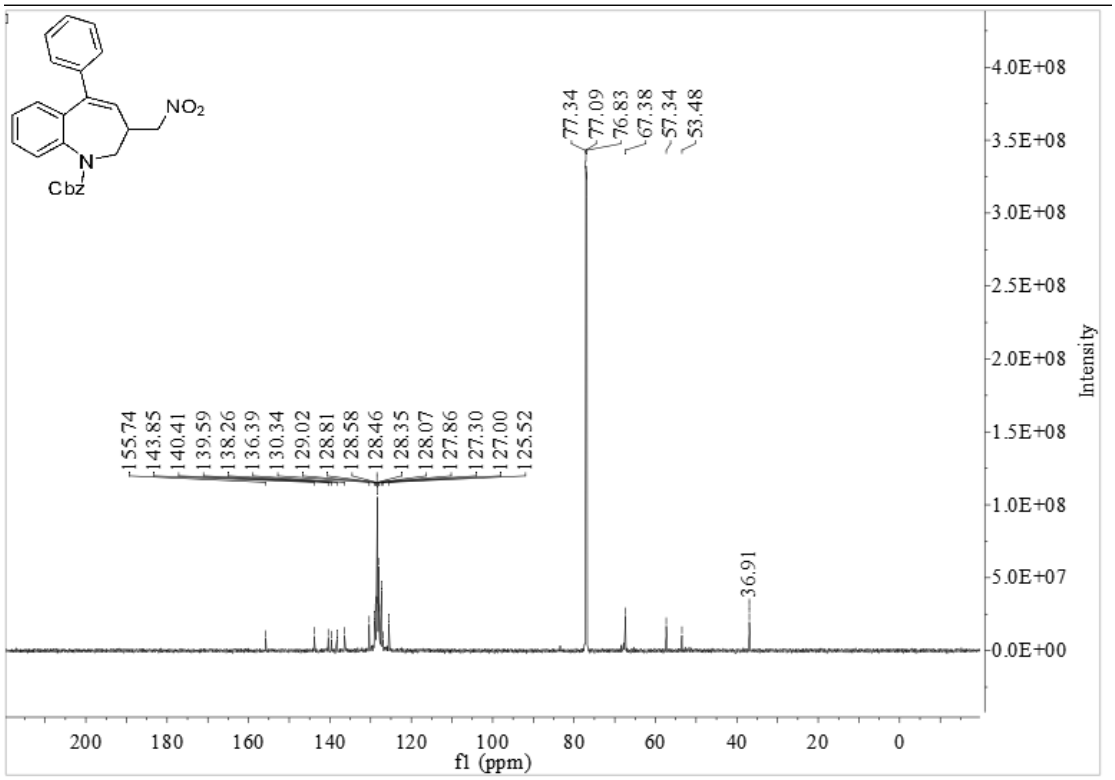
Compound 2q


NO2
N
Bz
7.44
7.41
7.41
7.39
7.38
7.34
7.32
7.30
7.29
7.26
7.25
7.23
7.21
7.19
7.18
7.16
7.14
7.10
7.08
7.06
7.04
7.01
6.99
6.98
6.88
6.86
6.75
6.34
6.33
4.76
4.73
4.70
4.68
4.65
4.62
4.61
4.59
4.57
4.56
4.54
3.88
3.87
3.85
3.83
3.44
3.43
3.42
3.41
3.41
3.40
3.39
3.38
7.12
7.00
1.00
3.10
1.03
1.09
Intensity
f1 (ppm)

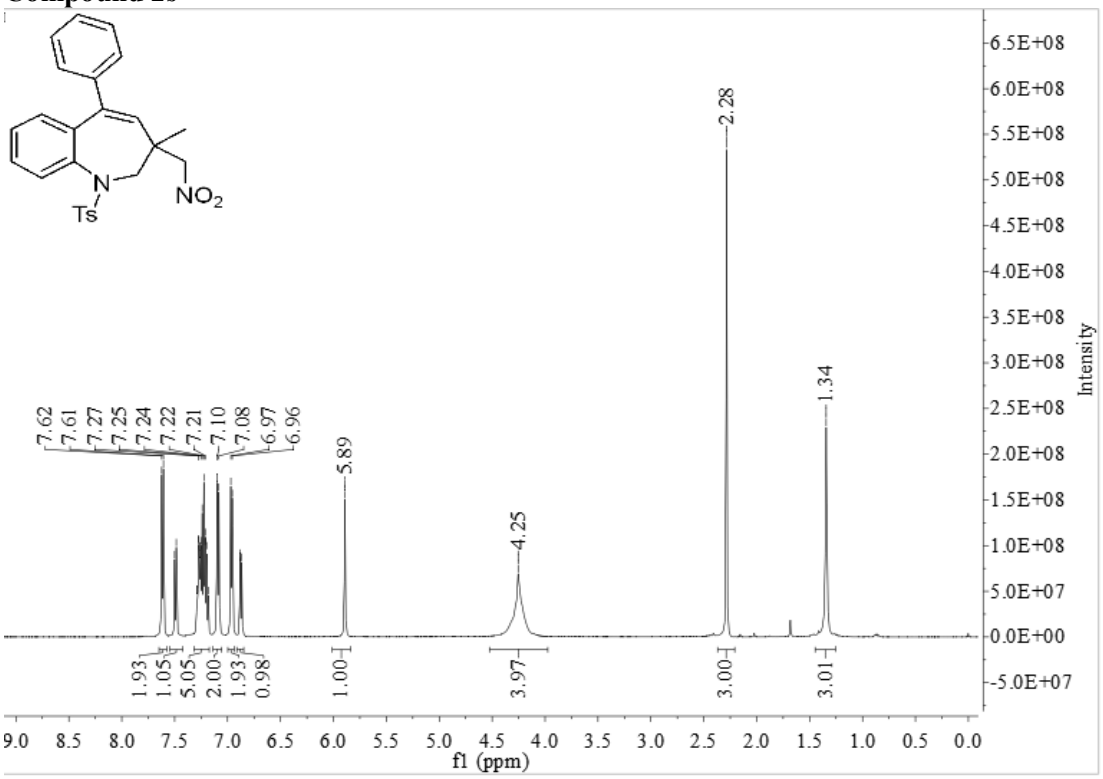

NO2
N
Bz
155.75
143.82
140.43
139.60
138.28
136.42
130.34
129.04
128.82
128.59
128.48
128.37
128.09
127.87
127.31
125.59
118.10
77.41
77.16
76.90
67.38
57.35
36.91
Intensity
f1 (ppm)

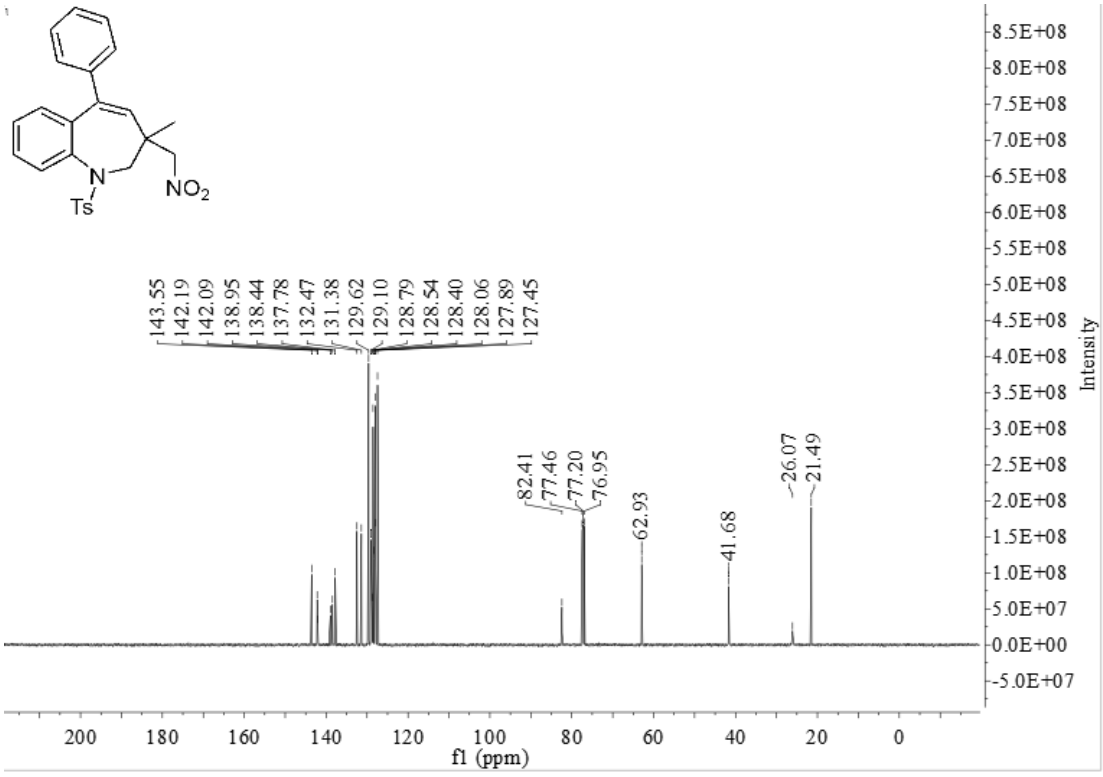
Compound 2r


Ph
NO2
N
Cbz
7.37
7.35
7.31
7.30
7.26
7.25
7.19
7.17
7.15
7.06
7.04
6.10
6.08
5.08
5.04
4.56
4.53
4.50
3.79
3.78
3.76
3.75
3.26
3.24
8.08
2.05
3.04
1.04
1.00
2.01
3.04
1.05
1.00
fl (ppm)
Intensity

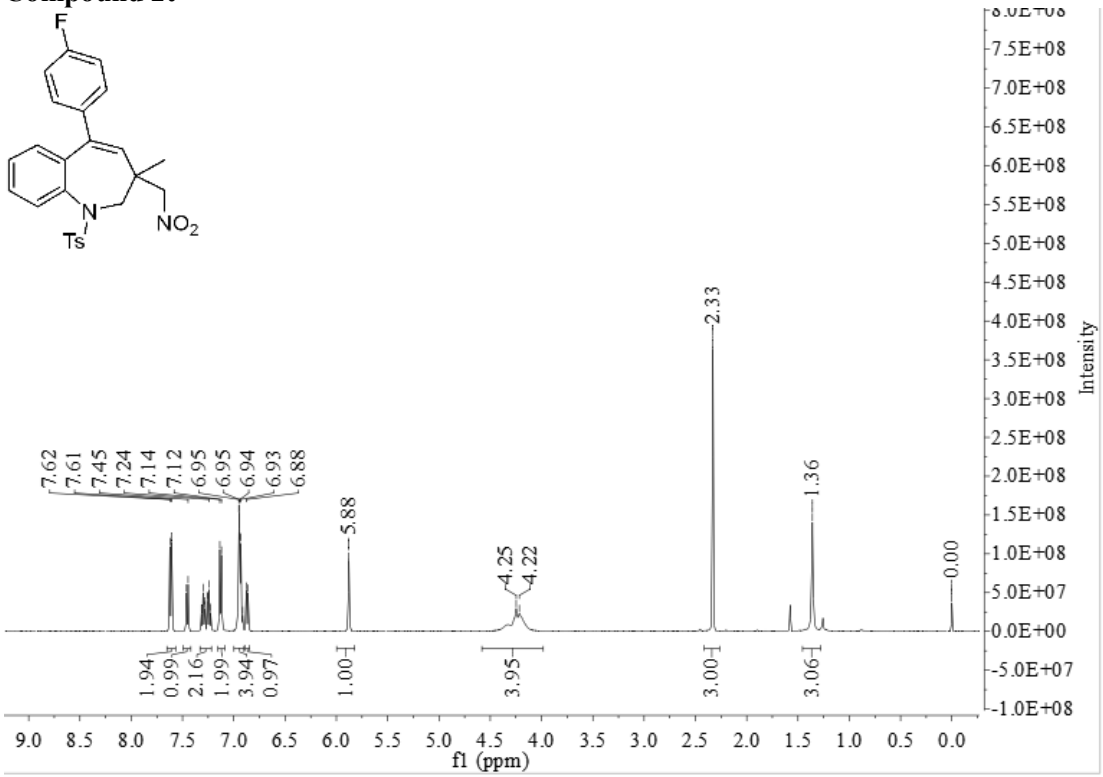

NO2
N
Cbz
77.34
77.09
76.83
67.38
57.34
53.48
155.74
143.85
140.41
139.59
138.26
136.39
130.34
129.02
128.81
128.58
128.46
128.35
128.07
127.86
127.30
127.00
125.52
36.91
fl (ppm)
Intensity

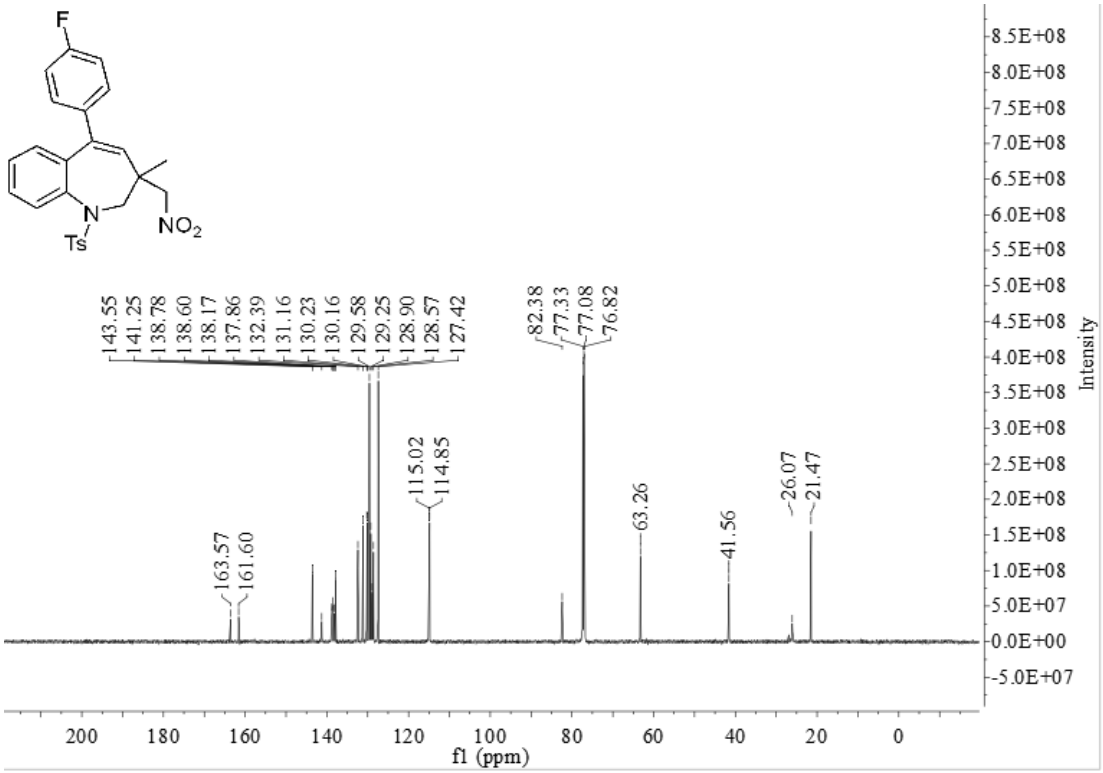
Compound 2s

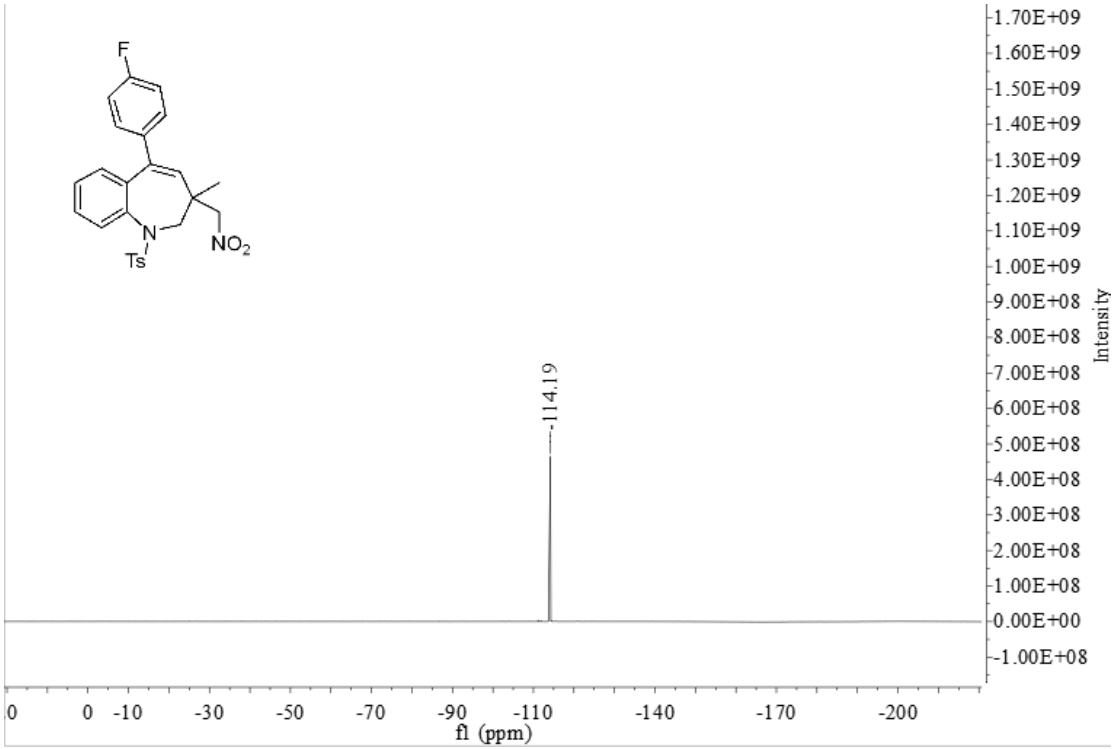

Ts
N
NO2
7.62
7.61
7.27
7.25
7.24
7.22
7.21
7.10
7.08
6.97
6.96
5.89
4.25
2.28
1.34
1.93
1.05
5.05
2.00
1.93
0.98
1.00
3.97
3.00
3.01
Intensity
f1 (ppm)


Ts
N
NO2
143.55
142.19
142.09
138.95
138.44
137.78
132.47
131.38
129.62
129.10
128.79
128.54
128.40
128.06
127.89
127.45
82.41
77.46
77.20
76.95
62.93
41.68
26.07
21.49
Intensity
f1 (ppm)

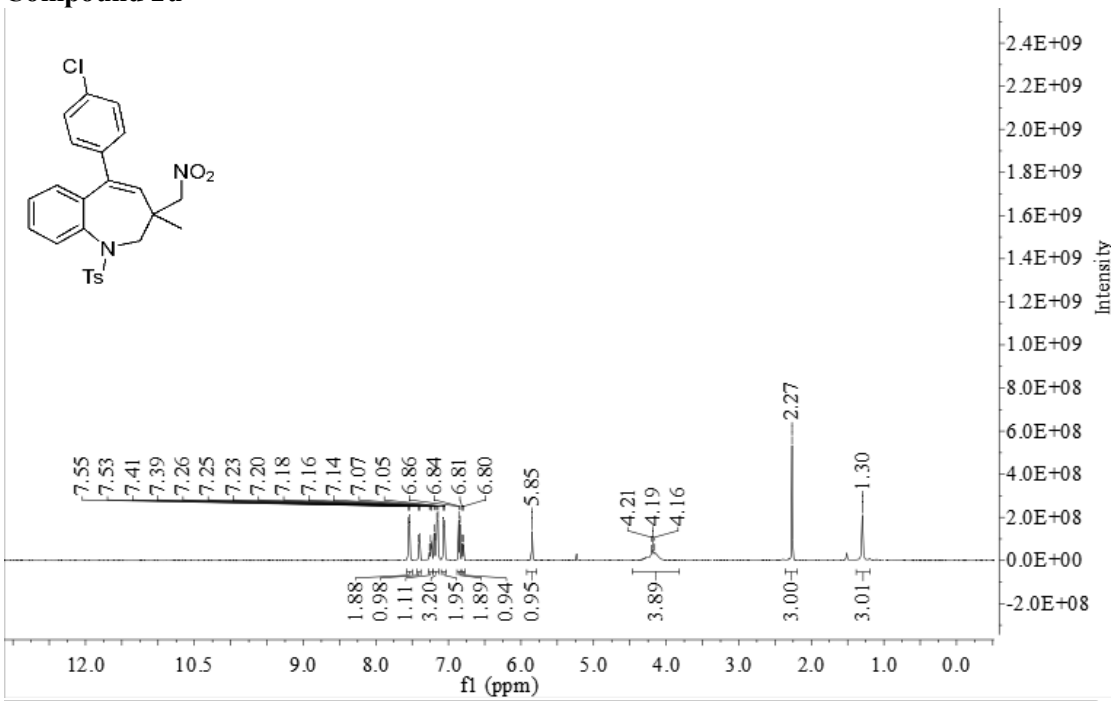
Compound 2t

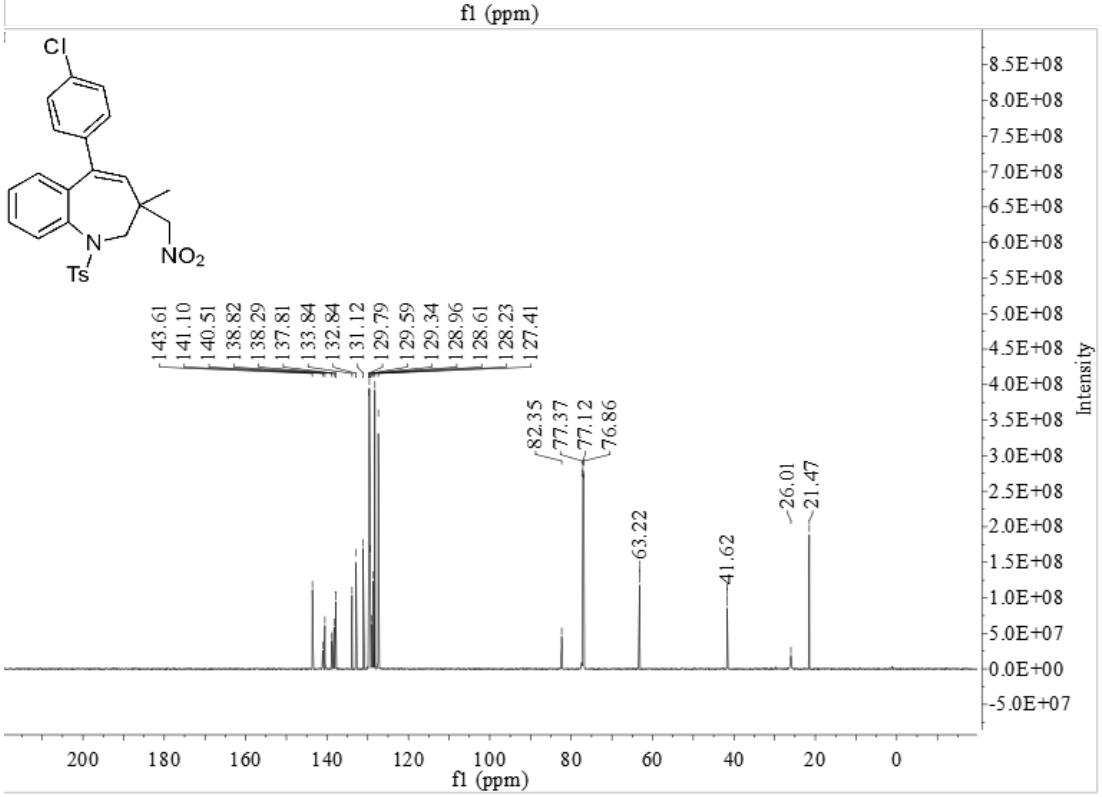

F
N
Ts
NO2
7.62
7.61
7.45
7.24
7.14
7.12
6.95
6.95
6.94
6.93
6.88
5.88
4.25
4.22
2.33
1.36
0.00
1.94
0.99
2.16
1.99
3.94
0.97
1.00
3.95
3.00
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Intensity
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
-1.0E+08


F
N
Ts
NO2
143.55
141.25
138.78
138.60
138.17
137.86
132.39
131.16
130.23
130.16
129.58
129.25
128.90
128.57
127.42
82.38
77.33
77.08
76.82
115.02
114.85
63.26
41.56
26.07
21.47
163.57
161.60
Intensity
fl (ppm)

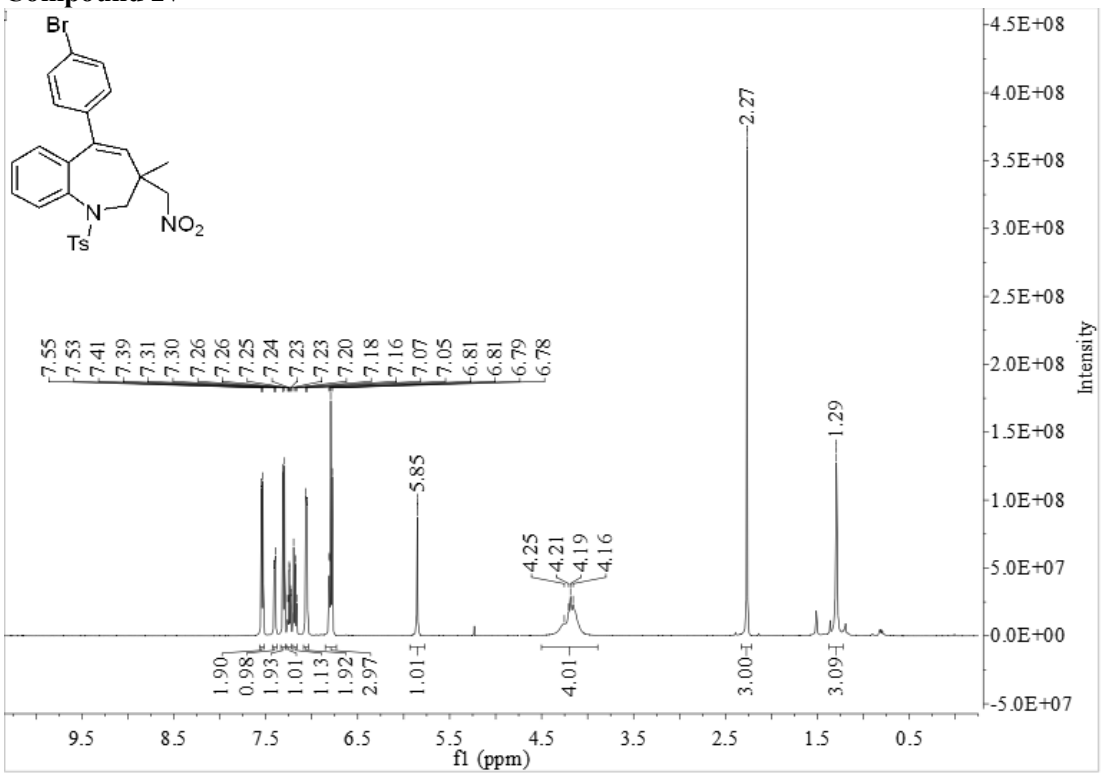

F
N
Ts
NO2
-114.19
Intensity
fl (ppm)

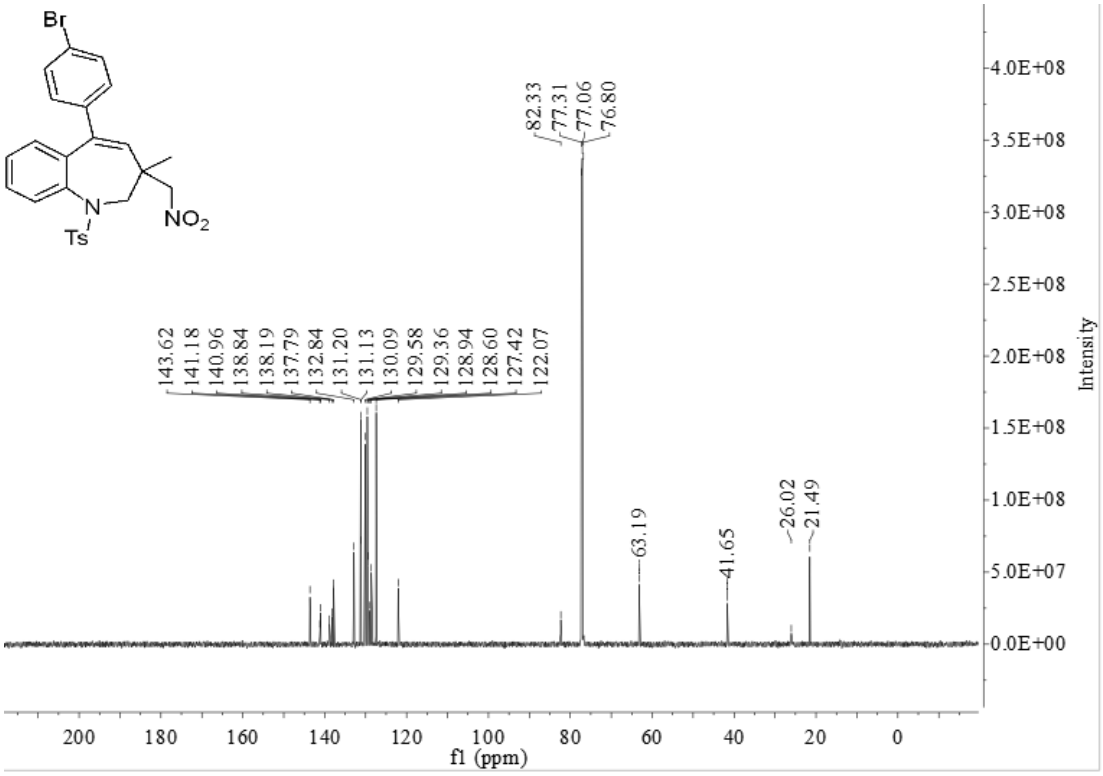
Compound 2u


Cl
NO2
N
Ts
7.55
7.53
7.41
7.39
7.26
7.25
7.23
7.20
7.18
7.16
7.14
7.07
7.05
6.86
6.84
6.81
6.80
5.85
4.21
4.19
4.16
2.27
1.30
1.88
0.98
1.11
3.20
1.95
1.89
0.94
0.95
3.89
3.00
3.01
Intensity
fl (ppm)

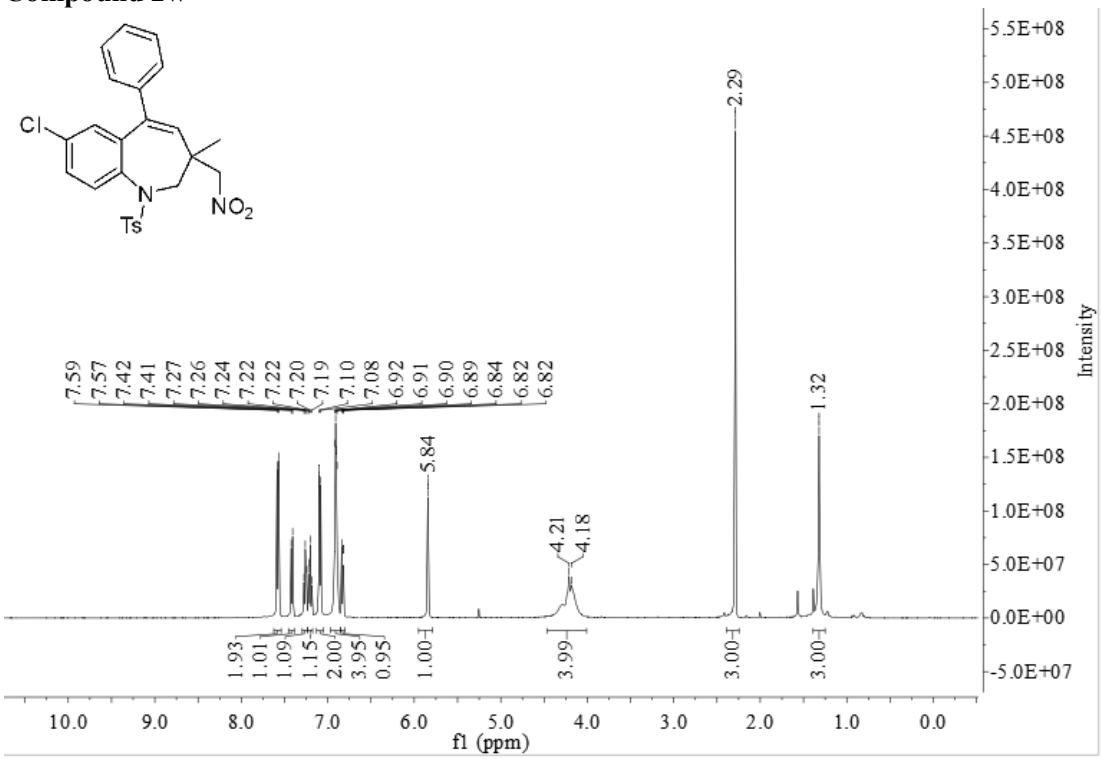

Cl
N
Ts
NO2
143.61
141.10
140.51
138.82
138.29
137.81
133.84
132.84
131.12
129.79
129.59
129.34
128.96
128.61
128.23
127.41
82.35
77.37
77.12
76.86
63.22
41.62
26.01
21.47
Intensity
fl (ppm)

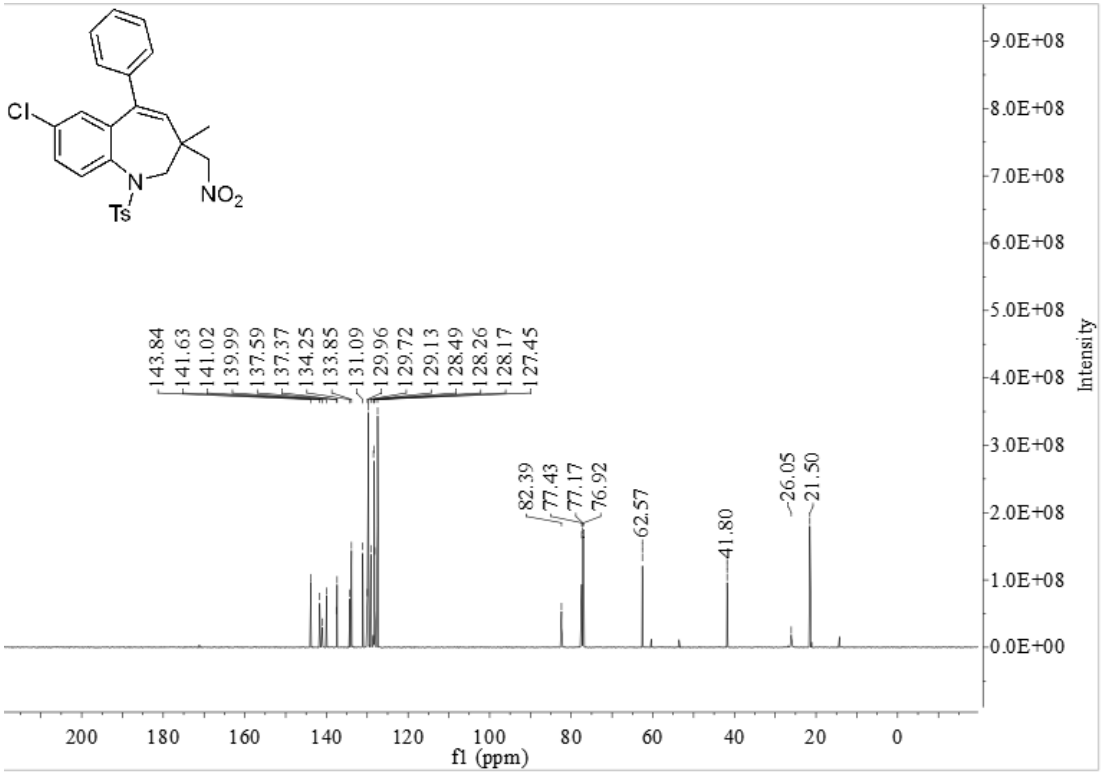
Compound 2v


Br
N
Ts
NO2
7.55
7.53
7.41
7.39
7.31
7.30
7.26
7.26
7.25
7.24
7.23
7.23
7.20
7.18
7.16
7.07
7.05
6.81
6.81
6.79
6.78
5.85
4.25
4.21
4.19
4.16
2.27
1.29
1.90
0.98
1.93
1.01
1.13
1.92
2.97
1.01
4.01
3.00
3.09
Intensity
fl (ppm)

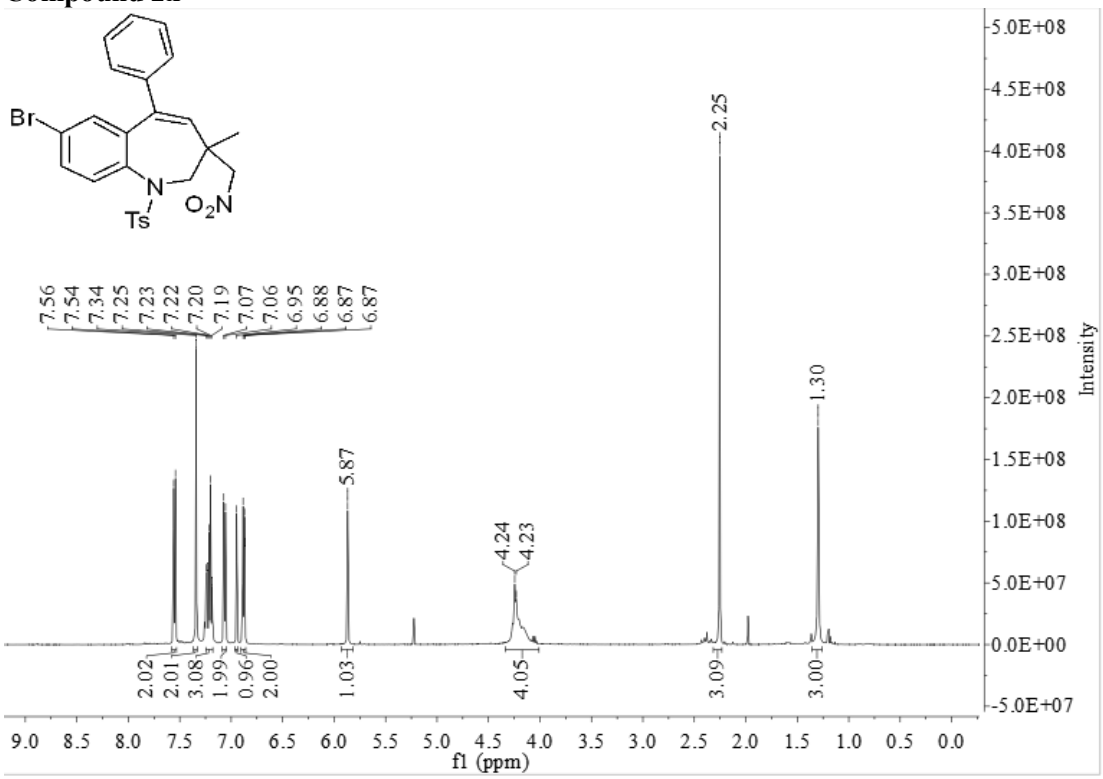

Br
N
Ts
NO2
82.33
77.31
77.06
76.80
143.62
141.18
140.96
138.84
138.19
137.79
132.84
131.20
131.13
130.09
129.58
129.36
128.94
128.60
127.42
122.07
63.19
41.65
26.02
21.49
Intensity
fl (ppm)

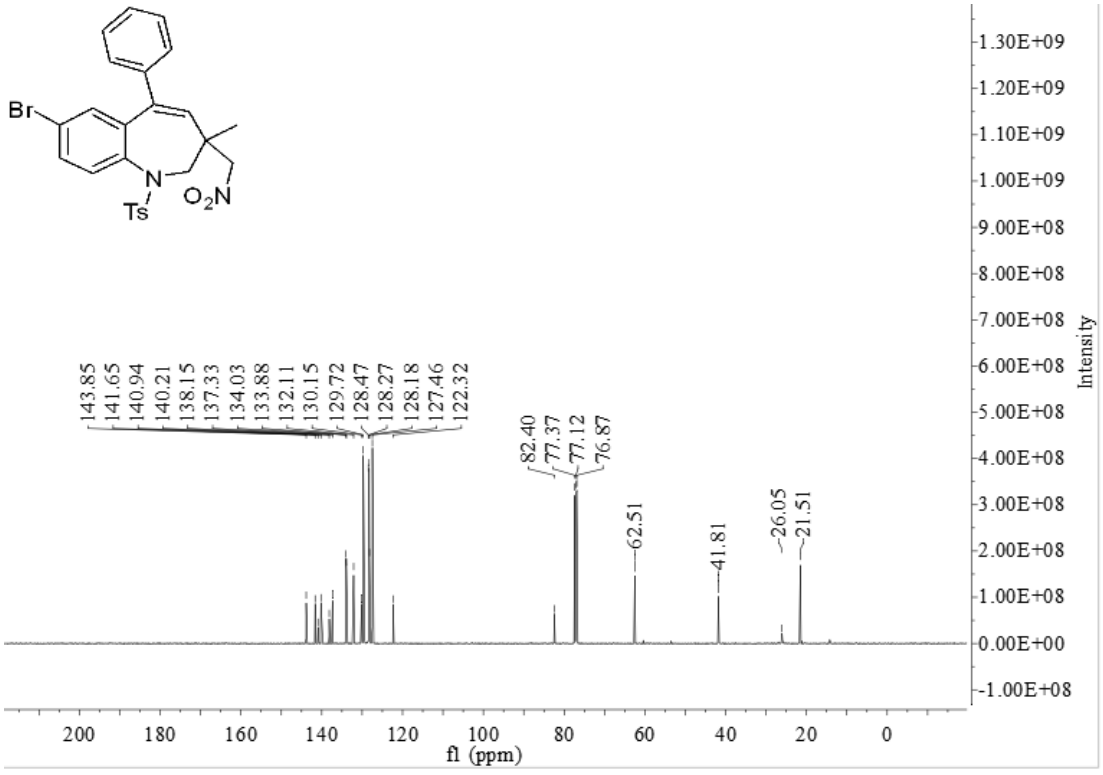
Compound 2w


Cl
N
Ts
NO2
7.59
7.57
7.42
7.41
7.27
7.26
7.24
7.22
7.22
7.20
7.19
7.10
7.08
6.92
6.91
6.90
6.89
6.84
6.82
6.82
5.84
4.21
4.18
2.29
1.32
1.93
1.01
1.09
1.15
2.00
3.95
0.95
1.00
3.99
3.00
3.00
Intensity
fl (ppm)

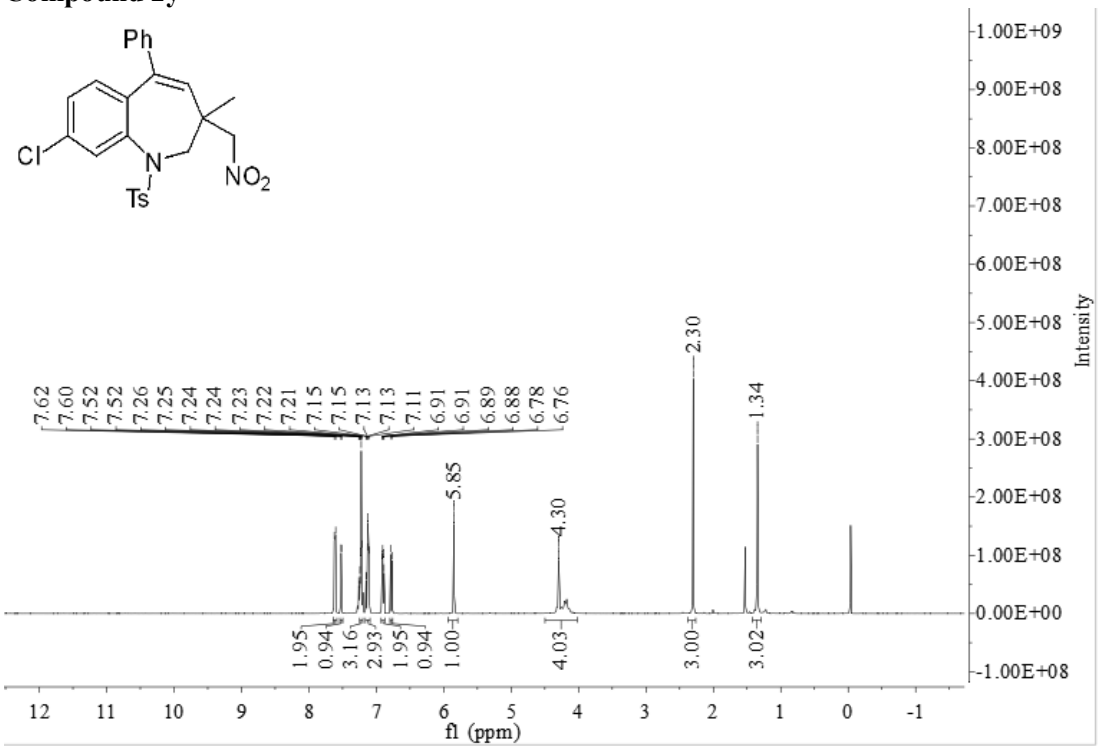

Cl
N
Ts
NO2
143.84
141.63
141.02
139.99
137.59
137.37
134.25
133.85
131.09
129.96
129.72
129.13
128.49
128.26
128.17
127.45
82.39
77.43
77.17
76.92
62.57
41.80
26.05
21.50
Intensity
fl (ppm)

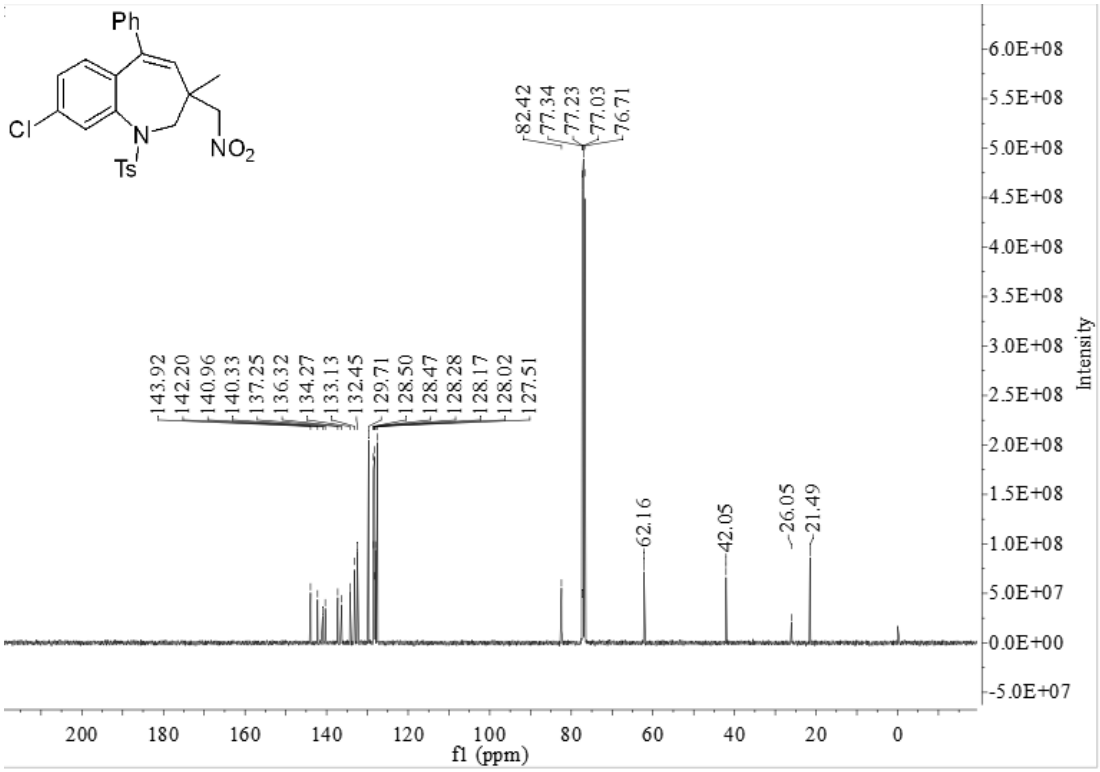
Compound 2x


Br
N
Ts
O2N
7.56
7.54
7.34
7.25
7.23
7.22
7.20
7.19
7.07
7.06
6.95
6.88
6.87
6.87
5.87
4.24
4.23
2.25
1.30
2.02
2.01
3.08
1.99
0.96
2.00
1.03
4.05
3.09
3.00
Intensity
fl (ppm)

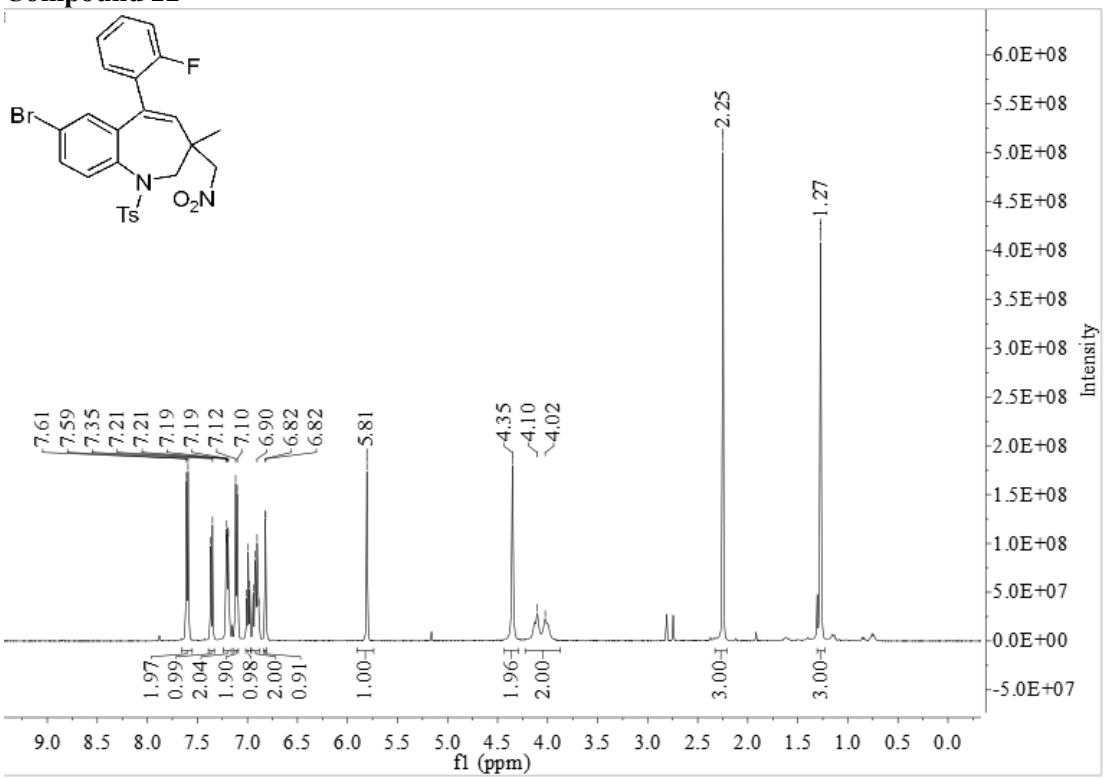

Br
N
Ts
O2N
143.85
141.65
140.94
140.21
138.15
137.33
134.03
133.88
132.11
130.15
129.72
128.47
128.27
128.18
127.46
122.32
82.40
77.37
77.12
76.87
62.51
41.81
26.05
21.51
Intensity
fl (ppm)

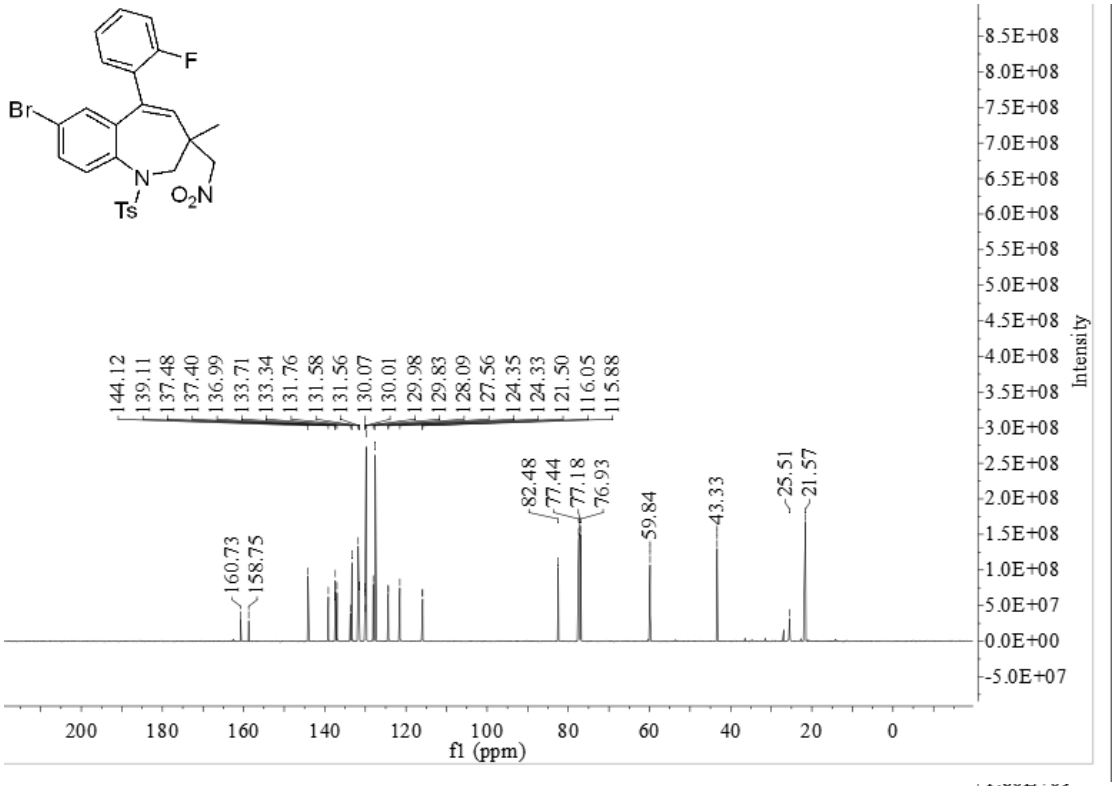
Compound 2y

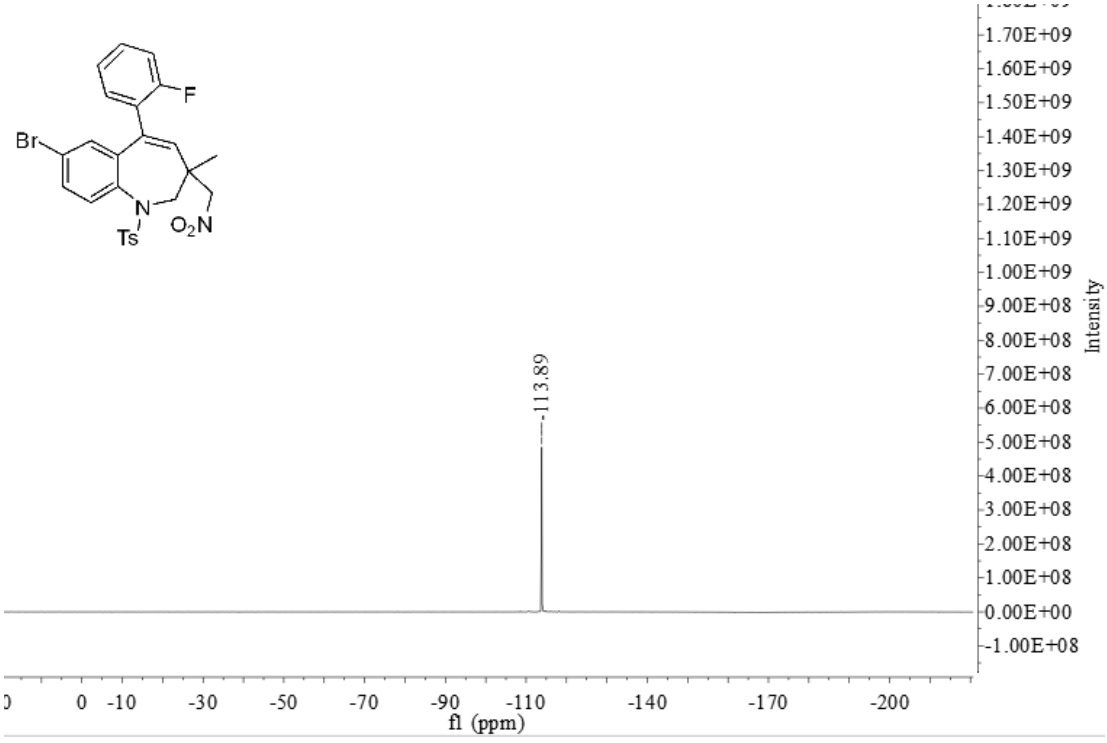

Ph
Cl
N
Ts
NO2
7.62
7.60
7.52
7.52
7.26
7.25
7.24
7.24
7.23
7.22
7.21
7.15
7.15
7.13
7.13
7.11
6.91
6.91
6.89
6.88
6.78
6.76
5.85
4.30
2.30
1.34
1.95
0.94
3.16
2.93
1.95
0.94
1.00
4.03
3.00
3.02
Intensity
fl (ppm)


Ph
Cl
N
Ts
NO2
82.42
77.34
77.23
77.03
76.71
143.92
142.20
140.96
140.33
137.25
136.32
134.27
133.13
132.45
129.71
128.50
128.47
128.28
128.17
128.02
127.51
62.16
42.05
26.05
21.49
Intensity
fl (ppm)

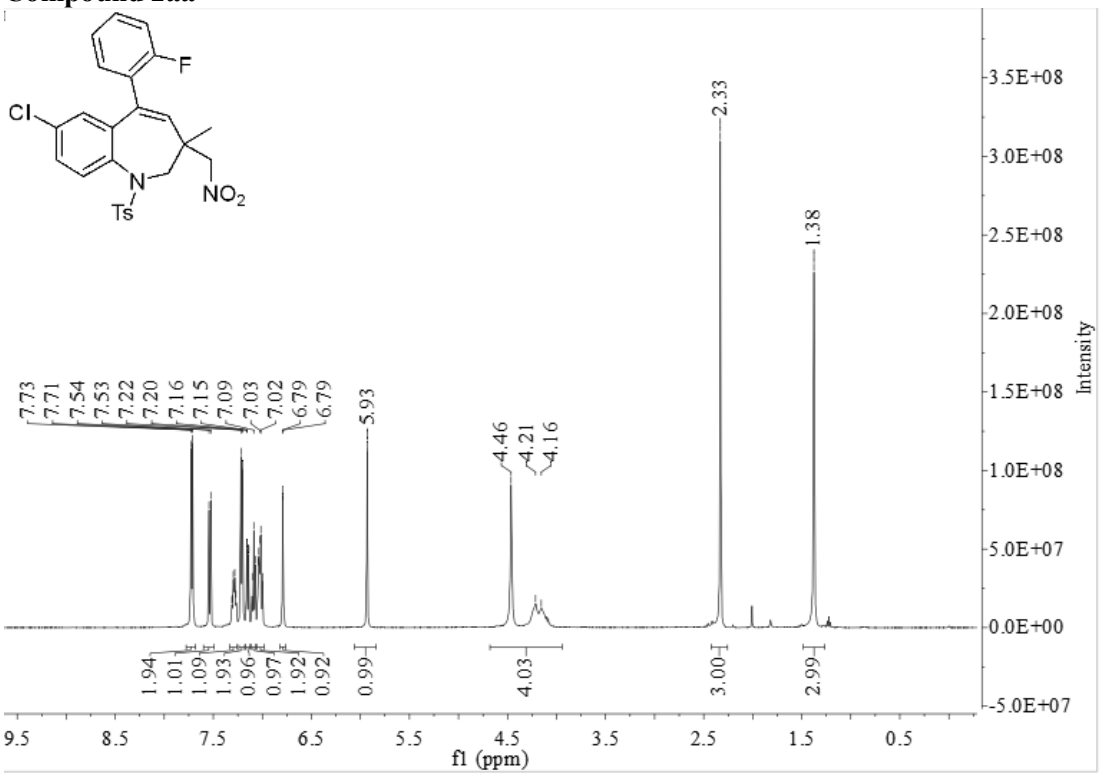
Compound 2z

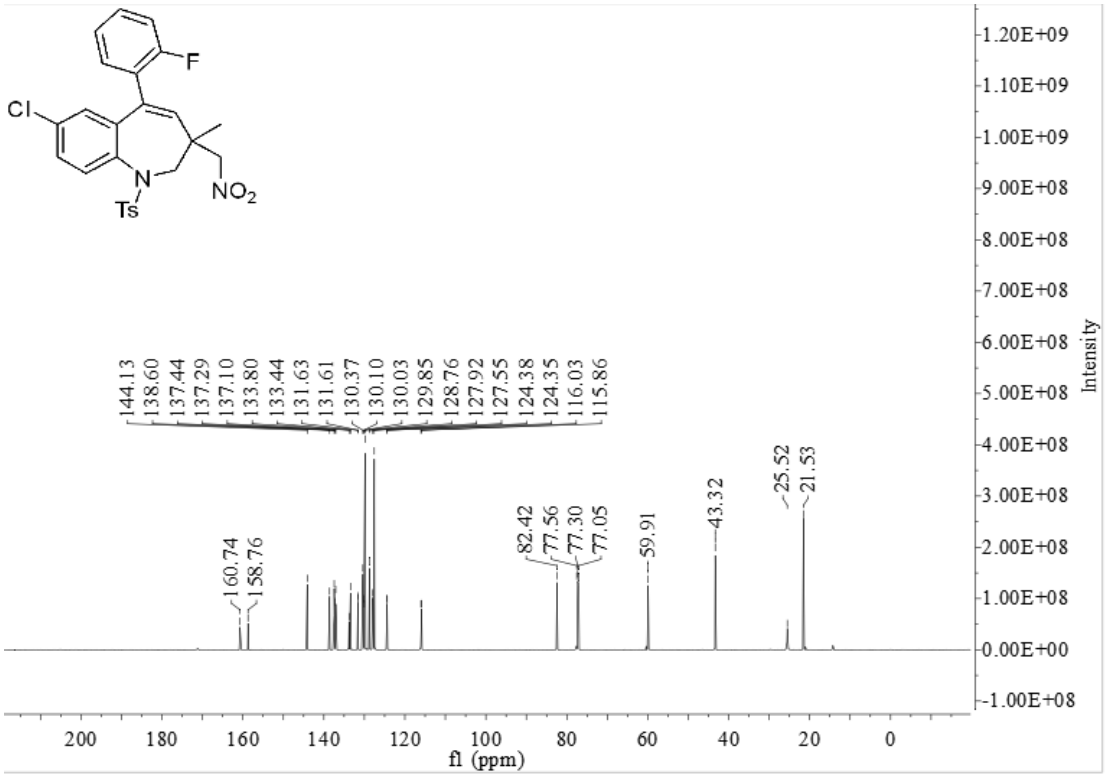

F
Br
N
Ts
O2N
7.61
7.59
7.35
7.21
7.21
7.19
7.19
7.12
7.10
6.90
6.82
6.82
5.81
4.35
4.10
4.02
2.25
1.27
1.97
0.99
2.04
1.90
0.98
2.00
0.91
1.00
1.96
2.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
Intensity

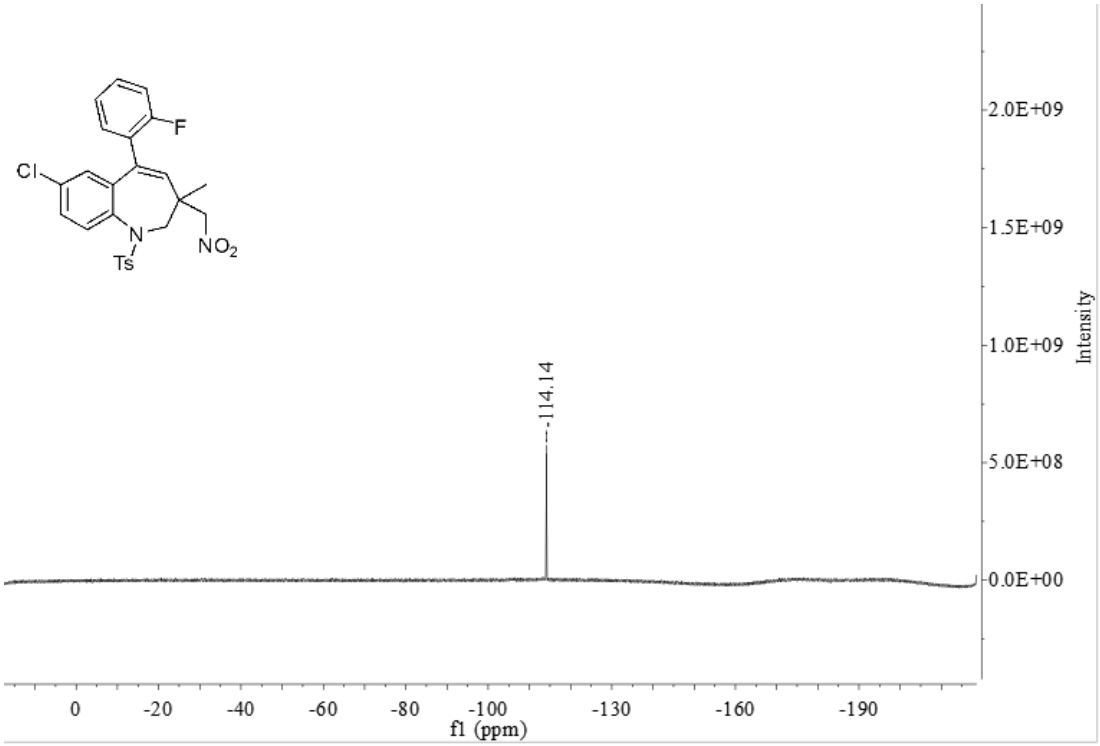

F
Br
N
Ts
O2N
144.12
139.11
137.48
137.40
136.99
133.71
133.34
131.76
131.58
131.56
130.07
130.01
129.98
129.83
128.09
127.56
124.35
124.33
121.50
116.05
115.88
82.48
77.44
77.18
76.93
59.84
43.33
25.51
21.57
160.73
158.75
Intensity
f1 (ppm)


F
Br
N
Ts
O2N
-113.89
Intensity
f1 (ppm)

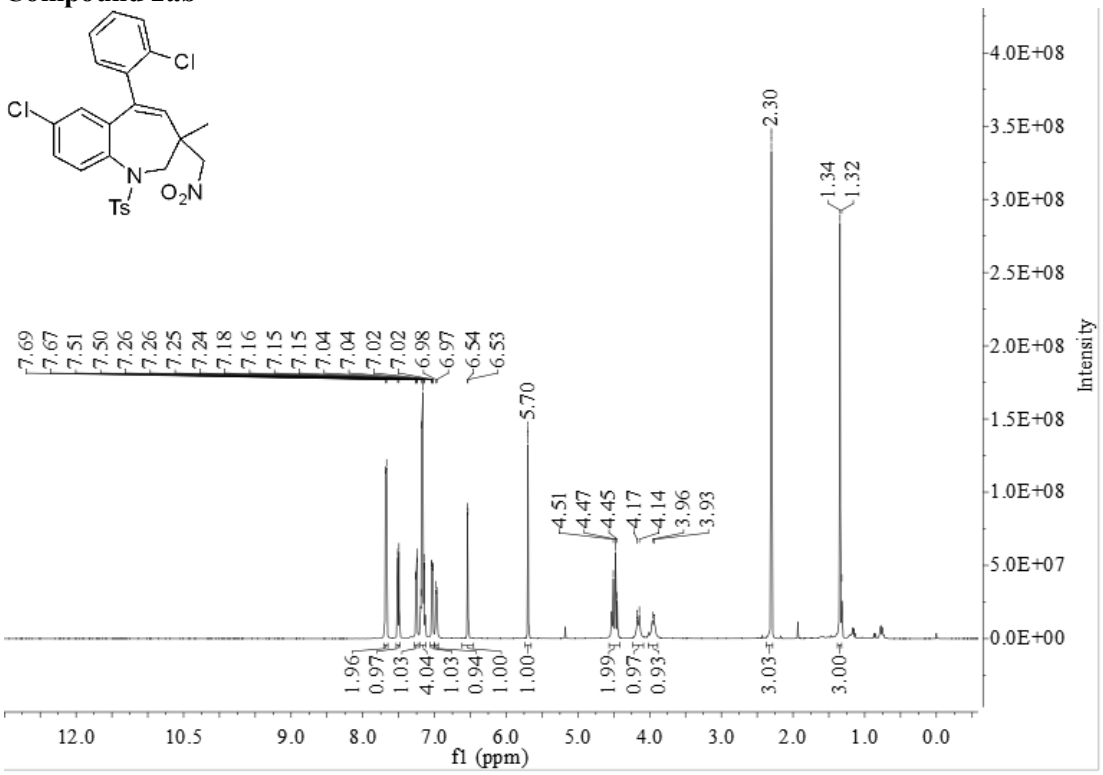
Compound 2aa

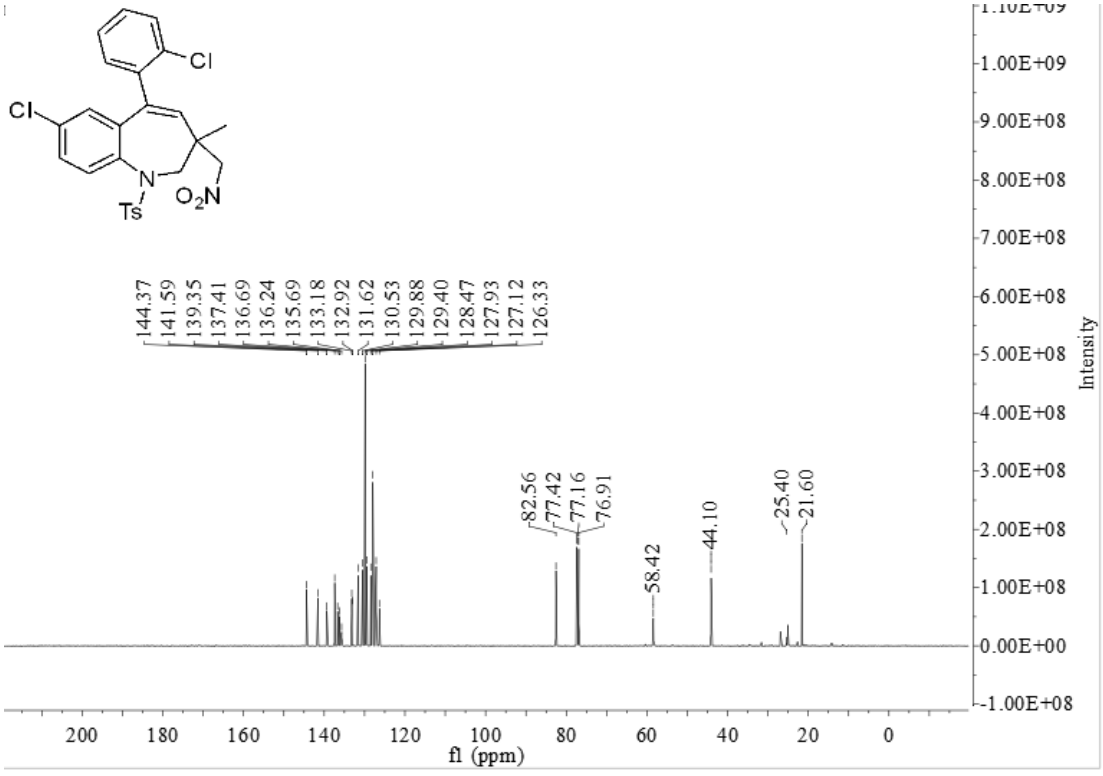



F
Cl
N
Ts
NO2
144.13
138.60
137.44
137.29
137.10
133.80
133.44
131.63
131.61
130.37
130.10
130.03
129.85
128.76
127.92
127.55
124.38
124.35
116.03
115.86
160.74
158.76
82.42
77.56
77.30
77.05
59.91
43.32
25.52
21.53
Intensity
fl (ppm)

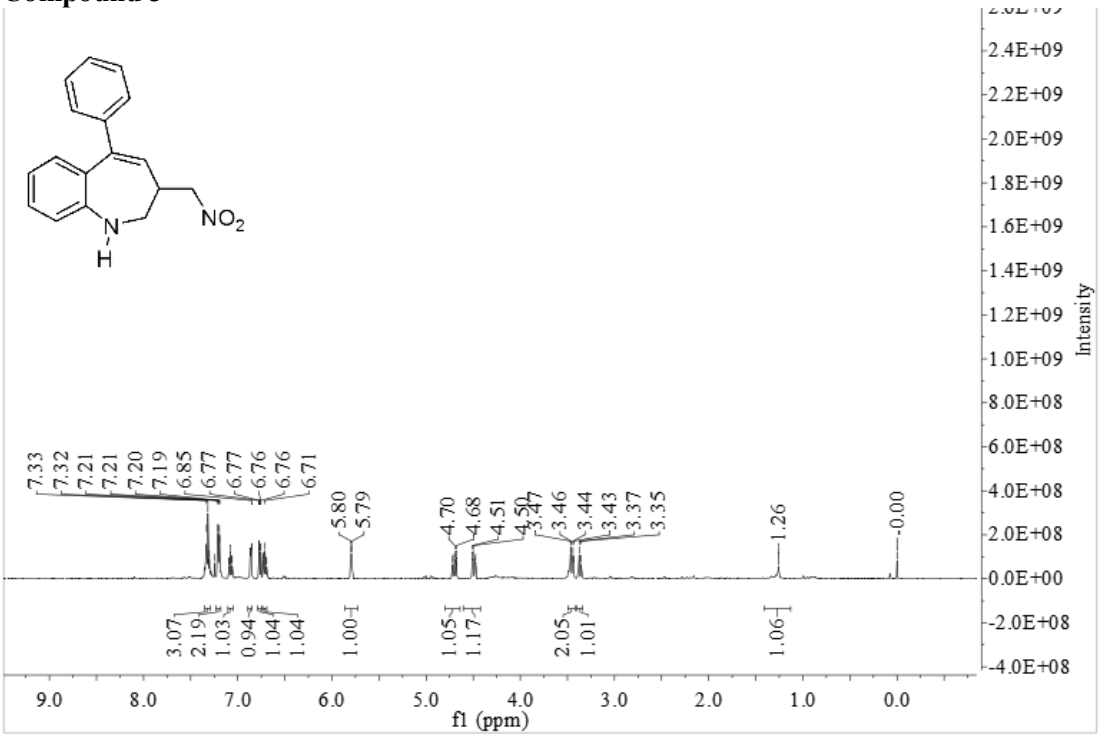

F
Cl
N
Ts
NO2
-114.14
Intensity
fl (ppm)

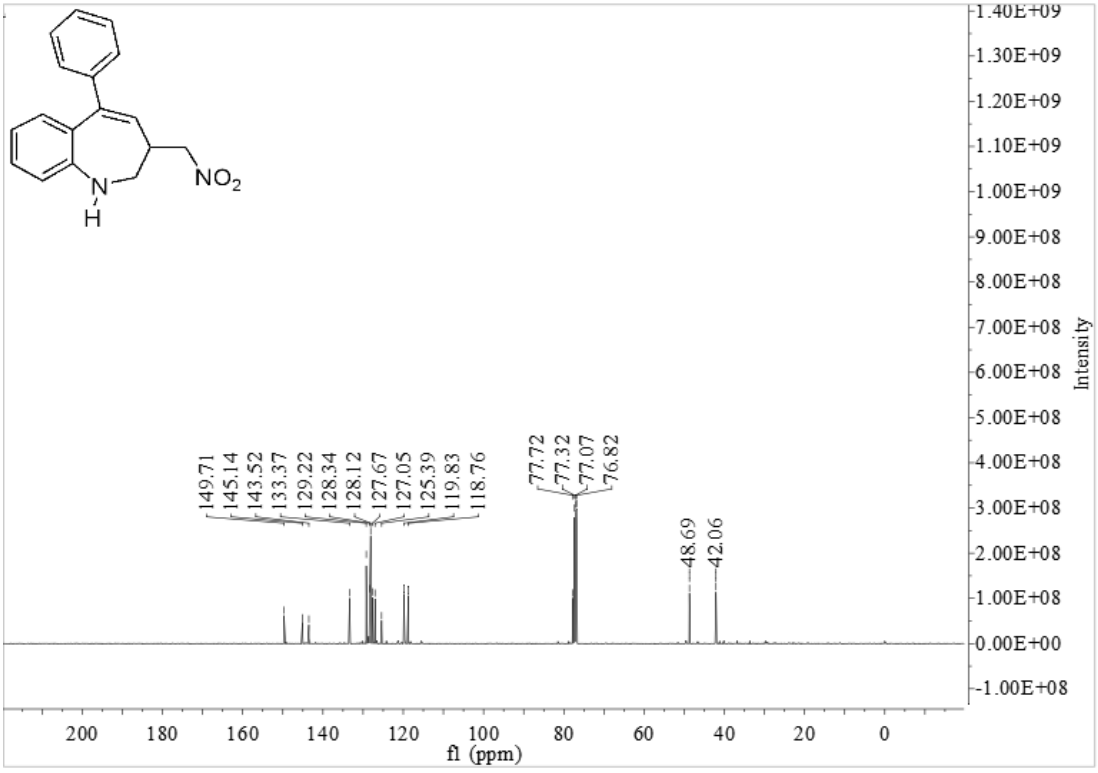
Compound 2ab





Compound 3


NO2
N
H
7.33
7.32
7.21
7.21
7.20
7.19
6.85
6.77
6.77
6.76
6.76
6.71
5.80
5.79
4.70
4.68
4.51
4.50
4.47
3.46
3.44
3.43
3.37
3.35
1.26
0.00
3.07
2.19
1.03
0.94
1.04
1.04
1.00
1.05
1.17
2.05
1.01
1.06
Intensity
fl (ppm)


NO2
N
H
149.71
145.14
143.52
133.37
129.22
128.34
128.12
127.67
127.05
125.39
119.83
118.76
77.72
77.32
77.07
76.82
48.69
42.06
Intensity
fl (ppm)