# Supporting Information

## Rhodium(I)-Catalyzed Vinylation/[2+1] Carbocyclization of 1,6-Enynes with *alpha*-Diazocarbonyl Compounds

Junmin Huang, Xinwei Hu, Fengjuan Chen, Jiao Gui, and Wei Zeng *

Key Laboratory of Functional Molecular Engineering of Guangdong Province, Guangdong Engineering Research Center for Green Fine Chemicals, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, China

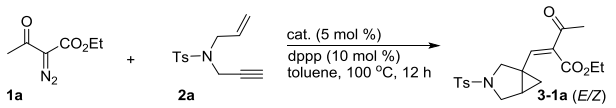
## Supporting Information

**Table of Contents**

**1. General Experimental Information**

All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using silica gel (400 – 630 mesh). Infrared spectra were recorded by preparing a KBr pellet containing the title compounds. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). α-diazo-β-ketoesters **1a-1v**[1] and 1,6-enynes **2a-2k**[2,3,4] and were prepared according to the previous literature.

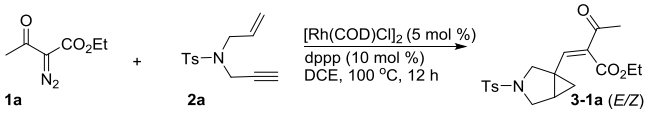
**1.1 Table S-1**. Catalyst screening for the coupling-cyclization of α-diazo-β-ketoester **1a** with terminal alkene-substituted 1,6-enynes **2a** [a]




| entry | catalyst | ligand(10 mol%) | solvent | yield (%) [b] *(E/Z)* [c] |
|---|---|---|---|---|
| 1 | $Pd(PPh_3)_4$ | dppp | toluene | 0 |
| 2 | $Ni(COD)_2$ | dppp | toluene | 0 |
| 3 | $Ru_3(CO)_{12}$ | dppp | toluene | 0 |
| 4 | $[Rh(C_2H_4)_2Cl]_2$ | dppp | toluene | 41(*E*/*Z*=17/34) |
| 5 | $[Rh(COD)(OH)]_2$ | dppp | toluene | 18(*E*/*Z*=5/13) |
| 8 | $CoBr_2$ | dppp | toluene | 0 |
| 9 | $Pd_2(dba)_3$ | dppp | toluene | 0 |
| 10 | $[Rh(COD)Cl]_2$ | dppp | toluene | 84(*E*/*Z*=41/43) |

[a]Unless otherwise noted, all the reactions were performed using α-diazo-β-ketoester **1a** (0.4 mmol) and enyne **2a** (0.4 mmol) in the presence of catalysts (5 mol %) with dppp (10 mol %) in toluene (2.0 mL) at 100 °C for 12 h under Ar in a sealed reaction tube. Followed by flash chromatography on $SiO_2$. [b]Isolated yield. [c]The *E*/*Z* ratios were calculated based on the isolated yields.

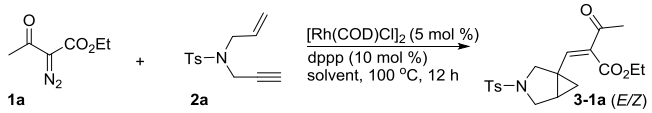
**1.2 Table S-2**. The effect of additives on the coupling-cyclization of α-diazo-β-ketoester 1a with terminal alkene-substituted 1,6-enynes **2a** [a]




| entry | additives(20 mol%) | yield (%)[b] *(E/Z)* [c] |
|---|---|---|
| 1 | $AgSbF_6$ | 78(*E*/*Z*=38/40) |
| 2 | $AgBF_4$ | 61(*E*/*Z*=29/32) |
| 3 | $AgNTf_2$ | 66(*E*/*Z*=35/31) |
| 4 | $AgClO_4$ | 27(*E*/*Z*=15/12) |

[a]Unless otherwise noted, all the reactions were performed using α-diazo-β-ketoester **1a** (0.4 mmol) and enyne **2a** (0.4 mmol) in the presence of $[Rh(COD)Cl]_2$ (5 mol %) with dppp (10 mol %) in DCE (2.0 mL) at 100 °C for 12 h under Ar in a sealed reaction tube. Followed by flash chromatography on $SiO_2$. [b] Isolated yield. [c]The *E*/*Z* ratios were calculated based on the isolated yields.

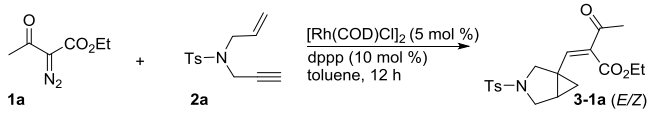
**1.3 Table S-3**. The effect of solvents on the coupling-cyclization of α-diazo-β-ketoester 1a with terminal alkene-substituted 1,6-enynes **2a** [a]




| entry | solvent | yield (%)[b] (*E*/*Z*)[c] |
|---|---|---|
| 1 | DCE | 76(*E*/*Z*=34/42) |
| 2 | $CH_3CN$ | 15(*E*/*Z*=0/15) |
| 3 | $PhCF_3$ | 75(*E*/*Z*=36/39) |
| 4 | THF | 69(*E*/*Z*=32/37) |
| 5 | 1,4-Dioxane | 58(*E*/*Z*=27/31) |
| 6 | DMF | 0 |
| 7 | DMSO | 12(*E*/*Z*=0/12) |

[a]Unless otherwise noted, all the reactions were performed using $\alpha$-diazo-$\beta$-ketoester **1a** (0.4 mmol) and enyne **2a** (0.4 mmol) in the presence of $[Rh(COD)Cl]_2$ (5 mol %) with dppp (10 mol %) in solvents (2.0 mL) at 100 °C for 12 h under Ar in a sealed reaction tube. Followed by flash chromatography on $SiO_2$. [b]Isolated yield. [c]The *E*/*Z* ratios were calculated based on the isolated yields.

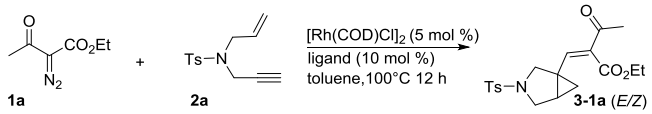
**1.4 Table S-4**. The effect of temperature on the coupling-cyclization of α-diazo-β-ketoester **1a** with terminal alkene-substituted 1,6-enynes **2a** [a]




| entry | T (°C) | yield (%)[b] (*E*/*Z*)[c] |
|---|---|---|
| 1 | 80 | 78(*E*/*Z*=37/41） |
| 2 | 100 | 84(*E*/*Z*=41/43) |
| 3 | 120 | 70(*E*/*Z*=35/45) |

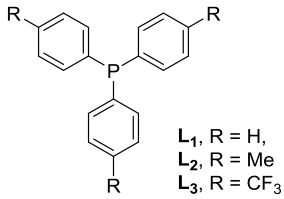
[a]Unless otherwise noted, all the reactions were performed using α-diazo-β-ketoester **1a** (0.4 mmol) and enyne **2a** (0.4 mmol) in the presence of $[Rh(COD)Cl]_2$ (5 mol %) with dppp (10 mol %) in toluene (2.0 mL) for 12 h under Ar in a sealed reaction tube. Followed by flash chromatography on $SiO_2$. [b]Isolated yield. [c]The *E*/*Z* ratios were calculated based on the isolated yields.

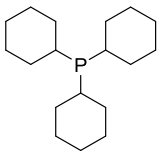
**1.5 Table S-5**. The effect of ligands on the coupling-cyclization of α-diazo-β-ketoester 1a with terminal alkene-substituted 1,6-enynes **2a** [a]

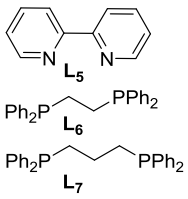



| entry | ligand | yield (%)[b] (*E*/*Z*)[c] |
|---|---|---|
| 1 | **$L_1$** | 38(*E*/*Z*=16/22) |
| 2 | **$L_2$** | 22(*E*/*Z*=8/14) |
| 3 | **$L_3$** | 0 |
| 4 | **$L_4$** | 0 |
| 5 | **$L_5$** | 0 |
| 6 | **$L_6$** | 0 |
| 7 | **$L_7$** | 84(*E*/*Z*=41/43) |

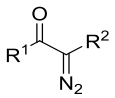
[a]Unless otherwise noted, all the reactions were performed using α-diazo-β-ketoester **1a** (0.4 mmol) and enyne **2a** (0.4 mmol) in the presence of $[Rh(COD)Cl]_2$ (5 mol %) with ligand (10 mol %) in toluene (2.0 mL) for 12 h under Ar in a sealed reaction tube. Followed by flash chromatography on $SiO_2$. [b] Isolated yield. [c] The *E*/*Z* ratios were calculated based on the isolated yields.



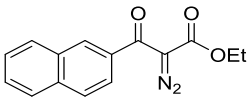



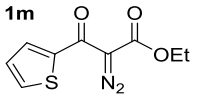

## 2. General Procedure for the Synthesis of Diazo Compounds (1a~1v) [1]



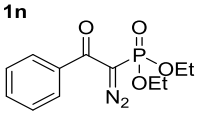

**1a**, $R^1$ = H, $R^2$=$CO_2Et$
**1b**, $R^1$ = Et, $R^2$=$CO_2Et$
**1c**, $R^1$ = Ph, $R^2$=$CO_2Et$
**1d**, $R^1$ = 4-F-$C_6H_4$, $R^2$=$CO_2Et$
**1e**, $R^1$ = 4-Cl-$C_6H_4$, $R^2$=$CO_2Et$
**1f**, $R^1$ = 4-Br-$C_6H_4$, $R^2$=$CO_2Et$
**1g**, $R^1$ = 4-Me-$C_6H_4$, $R^2$=$CO_2Et$
**1h**, $R^1$ = 3-Me-$C_6H_4$, $R^2$=$CO_2Et$
**1i**, $R^1$ = 2-Me-$C_6H_4$, $R^2$=$CO_2Et$
**1j**, $R^1$ = 4-MeO-$C_6H_4$, $R^2$=$CO_2Et$
**1k**, $R^1$ = 4-MeO-$C_6H_4$, $R^2$=$CO_2Et$
**1l**, $R^1$ = 4-$CF_3$-$C_6H_4$, $R^2$=$CO_2Et$



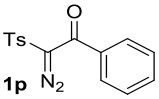

**1m**



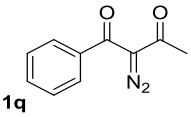

**1n**



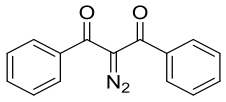

**1o**



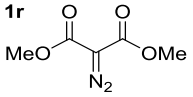

**1p**



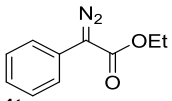

**1q**



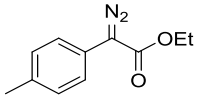

**1r**



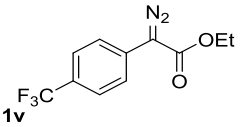

**1s**




**1t**




**1u**

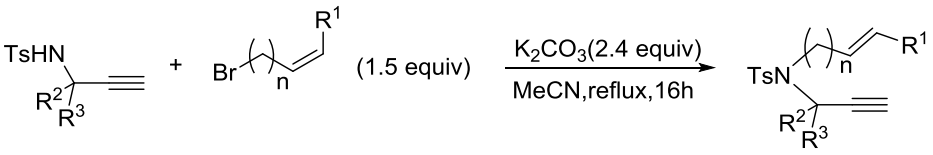



**1v**

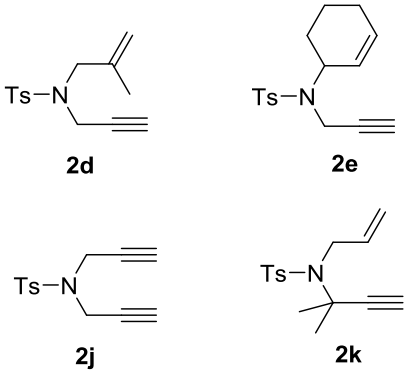
**General Method**: To a solution of β-ketoester or β-diketone (15 mmol, 1.0 equiv) and 4-methylbenzenesulfonyl azide (18 mmol, 1.2 equiv) in $CH_3CN$ (20 mL) at 0 $^oC$ was added DBU (1,8-diazabicyclo[5.4.0]undec-7-ene 21 mmol, 1.4 equiv). The resulting solution was stirred at 0 $^oC$ for 3 h and slowly cooled down to room temperature. Upon completion as indicated by thin layer chromatography (TLC), the reaction was quenched with water, extracted with ethyl acetate, and dried over anhydrous $Na_2SO_4$. The reaction mixture was concentrated under reduced pressure, and the crude products were purified by column chromatography using petroleum ether/ethyl acetate = 20:1 as eluent.

## 3. General Procedure for the Synthesis of 1,6-Enynes (2a~2k) [2]

### 3.1 The synthesis of 1,6-enynes (2a~2f, 2j and 2k) starting from propargylamines and allyl bromides[2]

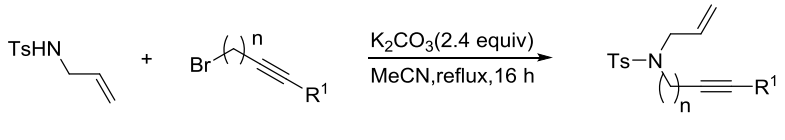


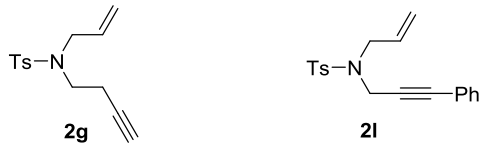

**2a**, $R^1$ = H, n=1, $R^2$=H, $R^3$=H
**2b**, $R^1$ = Ph, n=1, $R^2$=H, $R^3$=H
**2c**, $R^1$ = Me, n=1, $R^2$=H, $R^3$=H
**2f**, $R^1$ = H, n=2, $R^2$=H, $R^3$=H




**General Method**: 4-Methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1 equiv, 28.7 mmol), $K_2CO_3$ (2.4 equiv, 60.1 mmol) and acetonitrile (0.4 M) were added to a sealed tube. The corresponding allyl bromide (1.5 equiv, 43.1 mmol) was added and the reaction mixture was heated under reflux overnight. Then, the mixture was cooled to room temperature, the salts were filtered and the solvent was evaporated. The enyne was purified by column chromatography using cyclohexane/ ethyl acetate = 95 : 5 as eluent.

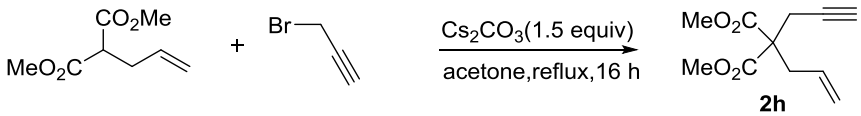
### 3.2 The synthesis of 1,6-enynes (2g and 2l) starting from propargyl bromides and allyl amines [2]




**General Method**: *N*-Allyl-4-methylbenzenesulfonamide (1 equiv, 3.3 mmol), $K_2CO_3$ (2.4 equiv, 8.0 mmol) and acetonitrile (0.4 M) were added to a sealed tube. The corresponding propargyl bromide (1.5 equiv, 5.0 mmol) was added and the reaction mixture was heated under reflux overnight. Then, the mixture was cooled to room temperature, the salts were filtered and the solvent was evaporated. The product was purified by column chromatography using cyclohexane/ ethyl acetate = 95:5 as eluent.

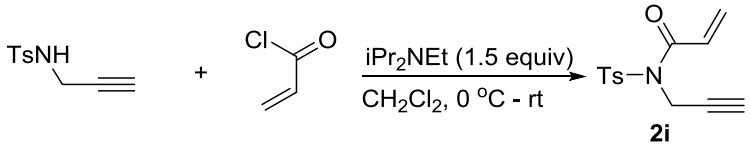
### 3.3 The synthesis of dimethyl 2-allyl-2-(prop-2-yn-1-yl)malonate (2h) [3]




**General Method**: Dimethyl 2-allylmalonate (1 equiv, 29.0 mmol), $Cs_2CO_3$ (1.5 equiv, 43.5 mmol)

and acetone (0.4 M) were added to a sealed tube. The propargyl bromide (1.5 equiv, 43.5 mmol) was added and the reaction mixture was heated under reflux overnight. Then, the mixture was cooled to room temperature, the salts were filtered and the solvent was evaporated. The compound was purified by column chromatography using cyclohexane/ ethyl acetate = 95:5 as eluent.

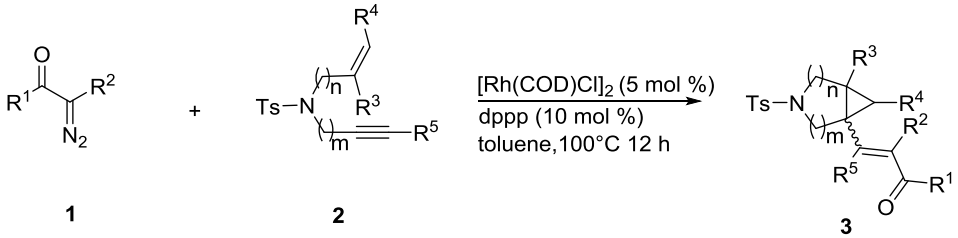
### 3.4 The synthesis of *N*-(prop-2-yn-1-yl)-*N*-tosylacrylamide (2i) [4]




**2i**

**General Method**: To a solution of 4-methyl-N-(prop-2-ynyl)benzenesulfonamide (1.0 mmol) in $CH_2Cl_2$ (5 mL) was added $iPr_2NEt$ (1.5 mmol), which was then cooled to 0 °C in the ice−water bath. Acryloyl chloride (1.2 mmol) was slowly added to the solution at 0 ℃, and then the mixture was stirred at room temperature for 1 h. The reaction was quenched by water, and the aqueous layer was extracted with $CH_2Cl_2$ (10 mL × 3). The combined organic layers were washed with brine, dried over $Na_2SO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography using petroleum ether / ethyl acetate = 4:1 as eluent.

### 4. General Procedure for the Synthesis of Azabicyclo[3.1.0]hexanes Derivatives (3-1a~3-1u) and (3-2a~3-2i)

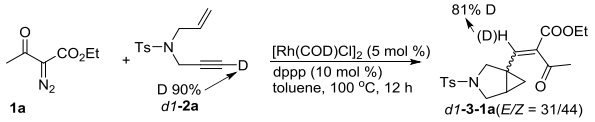



**1** **2** **3**

To an oven-dried sealed tube charged with $[Rh(COD)Cl]_2$ (5 mol %), dppp (10 mol %), *alpha*-diazo-*beta*-ketoester(0.4 mmol) and 1,6-enynes (0.4 mmol), toluene (2.0 mL) were added under Argon atmosphere. The reaction mixture was then allowed to stir at 100 °C for 12 h. Followed by flash chromatography on $SiO_2$. The compounds was purified by column chromatography using petroleum ether /ethyl acetate = 5:1 as eluent.

### 5. Control Experiments for the Mechanism Studies

### 5.1 Cycloadditions of 1a with *d1*-2a for the mechanism studies




**1a** *d1*-**3-1a**(*E*/*Z* = 31/44)

*d*1-**2a** was produced according to previous literature.[5] *d*1-**2a**: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.73 (m, 1H), 4.09 (s, 2H), 3.83 (d, *J* = 6.5 Hz, 2H), 2.42 (s, 3H).

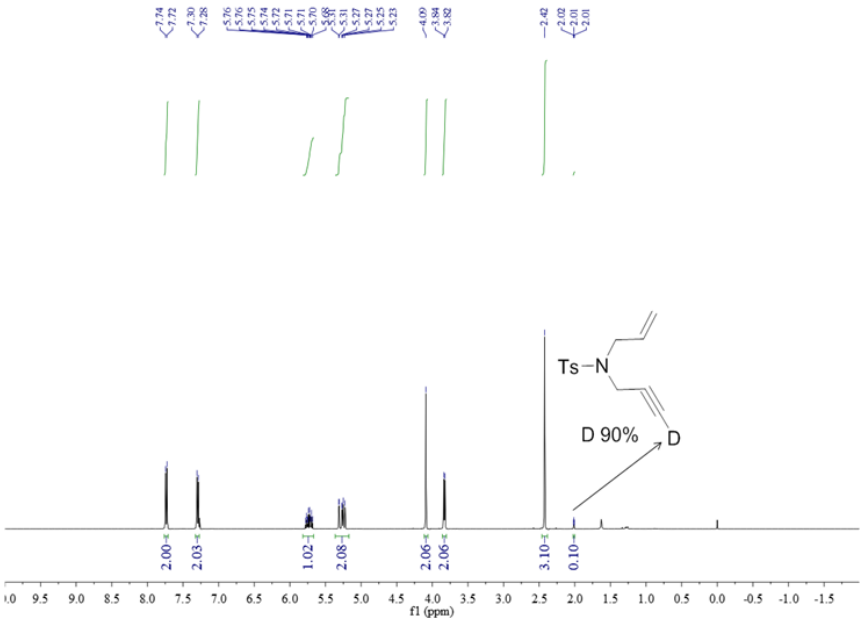



**Figure S-1.** $^{1}$H NMR spectrum for *d*1-**2a**

A Schlenk tube (20 mL) with a stirring bar was loaded with the **1a** (62.4 mg, 0.4 mmol), *d*1-**2a** (100.4 mg, 0.4 mmol), $[Rh(COD)Cl]_2$ (9.9 mg, 5 mol %) and dppp (16.5 mg, 10 mol %). Under an Ar atmosphere (1 atm), dry tol (2.0 mL), was added, and the reaction mixture was allowed to stir at 100 ℃ for 12 h. After cooling to room temperature, the compound was purified by column chromatography using petroleum ether/AcOEt 10:1($R_f$ = 0.3) as eluent to give the product *d*1-**3-1a** (*E*/*Z*=31/44, overall yield: 75 %).

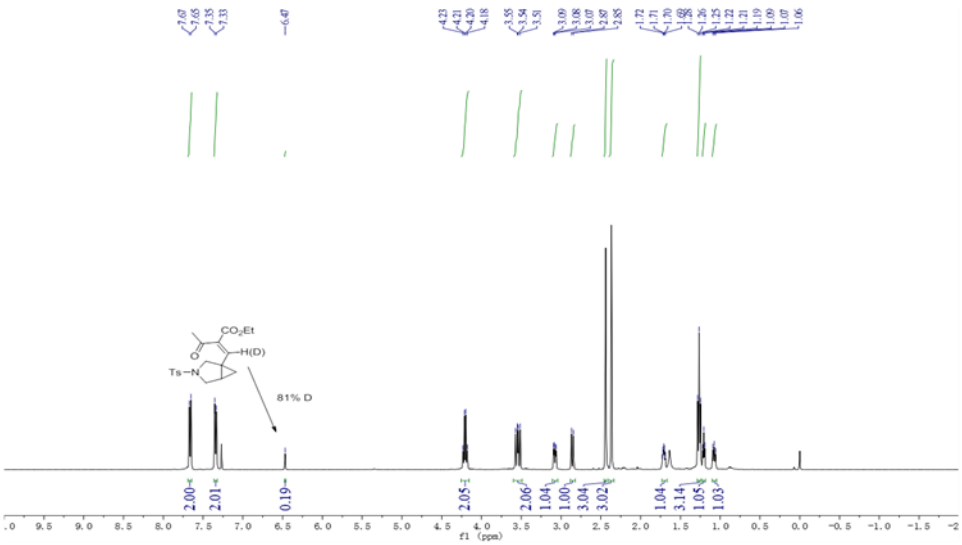



**Figure S-2.** $^{1}$H NMR spectrum for **(*E*)**-*d*1-**3-1a**

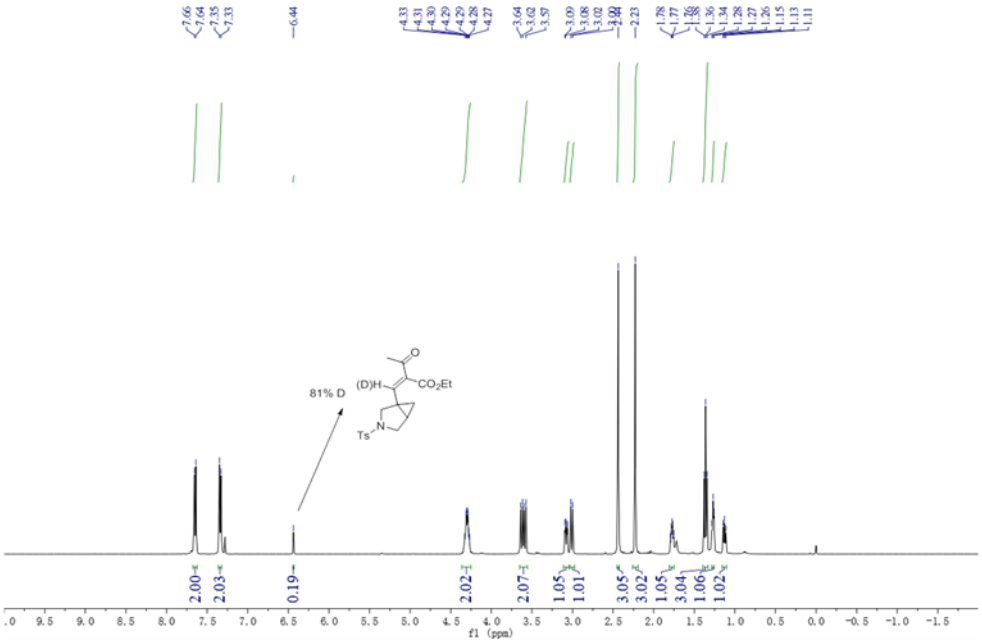
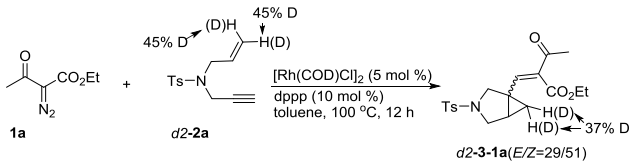



**Figure S-3.** $^1$H NMR spectrum for **(*E*)-*d*1-3-1a**

## 5.2 Cycloadditions of 1a with *d2*-2a for the mechanism studies




*d2*-**2a** was produced according to previous literature.[6] *d*2-**2a**：$^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.75 (m, 1H), 5.35 – 5.22 (m, 1H), 4.11 (d, *J* = 2.3 Hz, 2H), 3.85 (d, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 2.03 (t, *J* = 2.3 Hz, 1H).

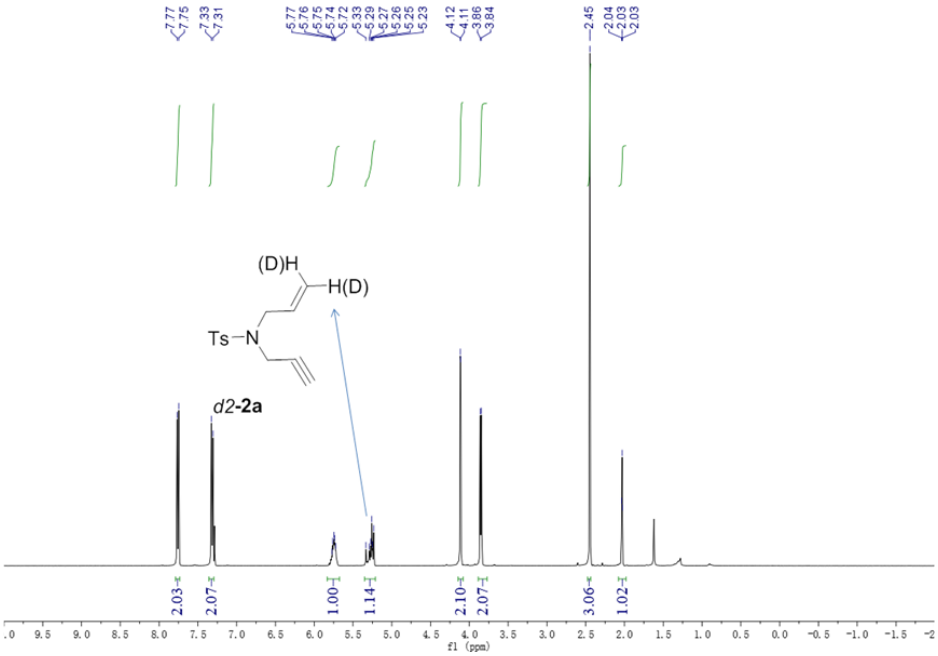



**Figure S-4.** $^1$H NMR spectrum for *d*2-**2a**

A Schlenk tube (20 mL) with a stirring bar was loaded with the **1a** (62.4 mg, 0.4 mmol), *d*2-**2a** (100.4 mg, 0.4 mmol), $[Rh(COD)Cl]_2$ (9.9 mg, 5 mol %) and dppp (16.5 mg, 10 mol %). Under an Ar atmosphere (1 atm), dry tol (2.0 mL), was added, and the reaction mixture was allowed to stir at 100 ℃ for 12 h. After cooling to room temperature, the compound was purified by column chromatography using petroleum ether /AcOEt = 10:1 as eluent to give the product *d2*-**3a** (*E*/*Z* = 29/51, overall yield: 80 %).

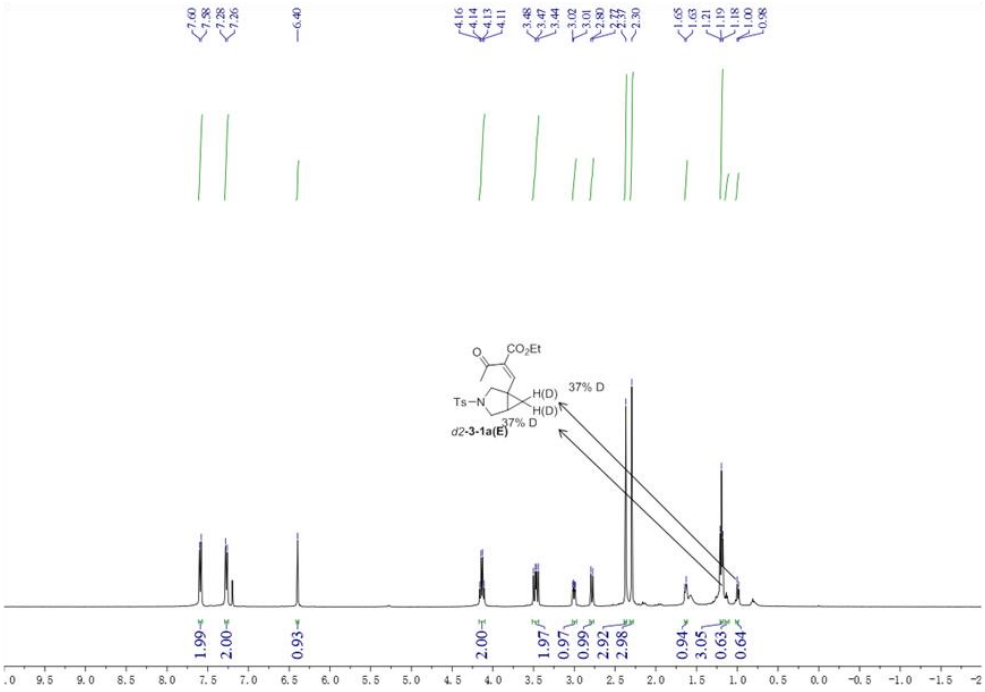



**Figure S-5.** $^1$H NMR spectrum for **(*E*)**-*d*2-**3-1a**

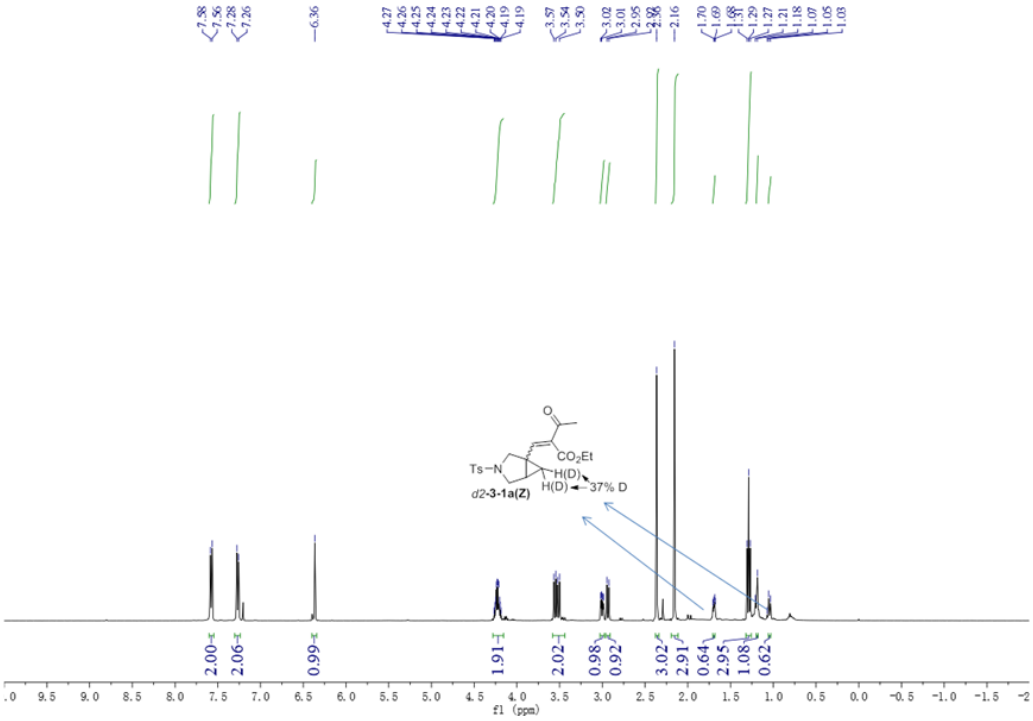
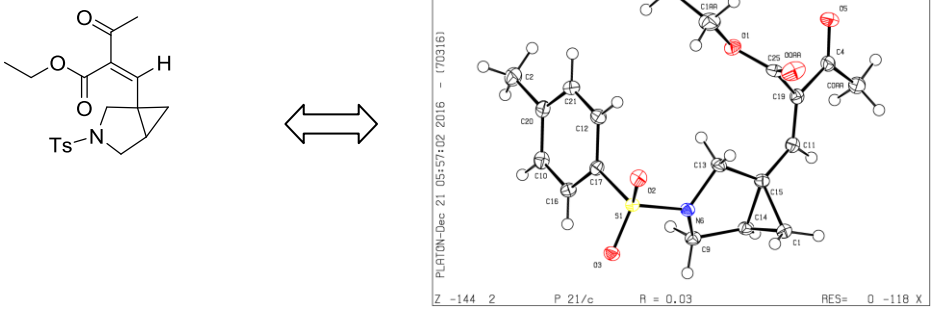



**Figure S-6.** $^1$H NMR spectrum for **(*E*)**-*d*2-**3-1a**

## 6. Single Crystal Data for (*E*)-3-1a




**Fingure S-7.** The single crystal structure of **3-1a(*Z*)** (the ellipsoid contour probability level is 30%)

**6.1 Table S-6**. Crystal data and structure refinement for **3-1a(*Z*)**.

| | |
|---|---|
| Empirical formula | $C_{19}$ $H_{23}$ N $O_5$ S |
| Formula weight | 377.14 |
| Temperature/K | 293(2) |
| Crystal system | monoclinic |
| Space group | P21/c |
| a/Å | 12.417(3) |
| b/Å | 6.0979(12) |
| c/Å | 25.184(5) |
| α/° | 90 |
| β/ ° | 101.93(3) |
| γ/° | 90 |
| Volume/Å3 | 1865.8(7) |
| Z | 24 |
| ρcalcg/cm3 | 1.344 |
| μ/mm-1 | 0.203 |
| F(000) | 800.0 |
| Crystal size/mm3 | 0.300 ×0.200 ×0.200 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.172 to 50.052 |
| Index ranges | -14 ≤ h ≤ 10, -5 ≤ k ≤ 7, -21 ≤ l ≤ 29 |
| Reflections collected | 6139 |
| Independent reflections | 3292 [Rint = 0.0165, Rsigma = 0.0211] |
| Data/restraints/parameters | 3292/0/250 |
| Goodness-of-fit on F2 | 1.017 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0330, wR2 = 0.0877 |
| Final R indexes [all data] | R1 = 0.0350, wR2 = 0.0895 |

**6.2 Table S-7**. Atomic coordinates and equivalent isotropic displacement parameters for shelxl.

U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| S1 | 1960.4(3) | 3960.9(5) | 2591.0(2) | 12.98(12) |
| O2 | 2069.0(8) | 6304.1(16) | 2598.8(4) | 18.3(2) |
| O3 | 1495.5(8) | 2831.5(16) | 2097.5(4) | 18.1(2) |
| O5 | 2446.4(9) | 5379(2) | 5706.9(4) | 27.1(3) |
| N6 | 1183.3(9) | 3370.5(19) | 3020.2(4) | 14.4(3) |
| C9 | 878.0(11) | 1043(2) | 3076.1(6) | 16.6(3) |
| C10 | 4558.8(12) | -126(2) | 2912.3(6) | 19.5(3) |
| C11 | 942.2(11) | 3134(2) | 4466.3(6) | 15.9(3) |
| C12 | 4039.8(12) | 4051(2) | 3219.6(6) | 18.8(3) |
| C13 | 1433.9(12) | 4431(2) | 3560.3(6) | 16.5(3) |
| C14 | 317.1(11) | 1123(2) | 3551.9(6) | 16.5(3) |
| C15 | 700.3(11) | 3215(2) | 3872.1(6) | 15.5(3) |
| C16 | 3529.9(12) | 746(2) | 2694.1(6) | 17.5(3) |
| C17 | 3274.5(11) | 2844(2) | 2850.0(6) | 15.7(3) |
| C19 | 1605.6(11) | 4440(2) | 4818.0(6) | 15.7(3) |
| C20 | 5332.5(12) | 1043(2) | 3284.9(6) | 19.4(3) |
| C21 | 5059.2(12) | 3149(3) | 3433.5(6) | 20.7(3) |
| C25 | 2129.3(12) | 6476(2) | 4650.0(6) | 18.2(3) |
| C2 | 6454.9(12) | 107(3) | 3515.8(7) | 25.7(3) |
| C4 | 1818.8(11) | 4120(2) | 5416.8(6) | 18.9(3) |
| C0AA | 1252.6(12) | 2285(3) | 5647.2(6) | 22.1(3) |
| O1 | 3178.6(8) | 6192.2(17) | 4616.9(4) | 21.5(2) |
| O0AA | 1644.8(9) | 8188.6(18) | 4558.5(5) | 29.8(3) |
| C1AA | 3720.5(14) | 8130(3) | 4454.1(7) | 31.2(4) |
| C2AA | 4929.2(14) | 7640(3) | 4549.5(8) | 39.7(5) |
| C1 | -493.3(11) | 2899(3) | 3568.8(6) | 19.1(3) |

**6.3 Table S-8** Bond Lengths for **3-1a(*Z*)**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| S1 | O2 | 1.4350(11) | C13 | C15 | 1.5136(19) |
| S1 | O3 | 1.4336(11) | C14 | C15 | 1.5317(19) |
| S1 | N6 | 1.6311(12) | C14 | C1 | 1.485(2) |
| S1 | C17 | 1.7641(14) | C15 | C1 | 1.5329(19) |
| O5 | C4 | 1.2228(18) | C16 | C17 | 1.394(2) |
| N6 | C9 | 1.4830(17) | C19 | C25 | 1.502(2) |
| N6 | C13 | 1.4798(17) | C19 | C4 | 1.489(2) |
| C9 | C14 | 1.506(2) | C20 | C21 | 1.399(2) |
| C10 | C16 | 1.388(2) | C20 | C2 | 1.507(2) |

| | | | | | |
|---|---|---|---|---|---|
| C10 | C20 | 1.393(2) | C25 | O1 | 1.3341(18) |
| C11 | C15 | 1.4651(19) | C25 | O0AA | 1.2036(19) |
| C11 | C19 | 1.340(2) | C4 | C0AA | 1.500(2) |
| C12 | C17 | 1.395(2) | O1 | C1AA | 1.4597(19) |
| C12 | C21 | 1.383(2) | C1AA | C2AA | 1.500(3) |

**6.4 Table S-9** Bond Angles for **3-1a(*Z*)**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O2 | S1 | N6 | 106.10(6) | C14 | C15 | C1 | 57.96(9) |
| O2 | S1 | C17 | 107.59(6) | C10 | C16 | C17 | 118.97(13) |
| O3 | S1 | O2 | 120.67(6) | C12 | C17 | S1 | 119.58(11) |
| O3 | S1 | N6 | 106.33(6) | C12 | C17 | C16 | 120.60(13) |
| O3 | S1 | C17 | 108.13(7) | C16 | C17 | S1 | 119.80(11) |
| N6 | S1 | C17 | 107.36(6) | C11 | C19 | C25 | 123.21(13) |
| C9 | N6 | S1 | 118.15(9) | C11 | C19 | C4 | 123.20(13) |
| C9 | N6 | C13 | 109.89(11) | C4 | C19 | C25 | 113.39(12) |
| C13 | N6 | S1 | 118.16(9) | C10 | C20 | C21 | 118.60(13) |
| N6 | C9 | C14 | 102.35(11) | C10 | C20 | C2 | 121.35(14) |
| C16 | C10 | C20 | 121.40(14) | C21 | C20 | C2 | 120.04(13) |
| C19 | C11 | C15 | 128.55(13) | C12 | C21 | C20 | 120.93(13) |
| C21 | C12 | C17 | 119.50(13) | O1 | C25 | C19 | 113.31(12) |
| N6 | C13 | C15 | 103.19(11) | O0AA | C25 | C19 | 122.88(13) |
| C9 | C14 | C15 | 107.53(11) | O0AA | C25 | O1 | 123.81(14) |
| C1 | C14 | C9 | 118.28(12) | O5 | C4 | C19 | 118.73(14) |
| C1 | C14 | C15 | 61.06(9) | O5 | C4 | C0AA | 121.93(13) |
| C11 | C15 | C13 | 121.88(12) | C19 | C4 | C0AA | 119.35(13) |
| C11 | C15 | C14 | 119.03(12) | C25 | O1 | C1AA | 115.18(12) |
| C11 | C15 | C1 | 118.54(12) | O1 | C1AA | C2AA | 107.32(15) |
| C13 | C15 | C14 | 106.84(11) | C14 | C1 | C15 | 60.98(9) |

**6.5 Table S-10** Hydrogen Atom Coordinates ($Å \times 10^{4)}$ and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3-1a(*Z*)**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H9A | 1524 | 109 | 3151 | 20 |
| H9B | 381 | 524 | 2751 | 20 |
| H10 | 4735 | -1521 | 2807 | 23 |
| H11 | 589 | 2030 | 4620 | 19 |
| H12 | 3866 | 5452 | 3321 | 23 |
| H13A | 1256 | 5981 | 3534 | 20 |
| H13B | 2204 | 4257 | 3731 | 20 |

| | | | | |
|---|---|---|---|---|
| H16 | 3019 | -58 | 2448 | 21 |
| H21 | 5570 | 3953 | 3680 | 25 |
| H2A | 6432 | -1460 | 3479 | 39 |
| H2B | 6668 | 489 | 3893 | 39 |
| H2C | 6980 | 696 | 3323 | 39 |
| H0AA | 1468 | 908 | 5516 | 33 |
| H0AB | 470 | 2457 | 5536 | 33 |
| H0AC | 1458 | 2316 | 6036 | 33 |
| H1AA | 3589 | 9390 | 4667 | 37 |
| H1AB | 3436 | 8451 | 4074 | 37 |
| H2AA | 5047 | 6373 | 4342 | 60 |
| H2AB | 5204 | 7358 | 4928 | 60 |
| H2AC | 5310 | 8874 | 4439 | 60 |
| H14 | 266(14) | -200(30) | 3737(7) | 26(5) |
| H1A | -714(14) | 3830(30) | 3252(7) | 25(4) |
| H1B | -1026(14) | 2680(30) | 3800(7) | 24(4) |

## 7. References


[1] Hu, X.; Chen, X.; Shao, Y.; Xie, H.; Deng, Y.; Ke, Z.; Jiang, H.; Zeng, W. *ACS Catal.* 2018, **8**, 1308.

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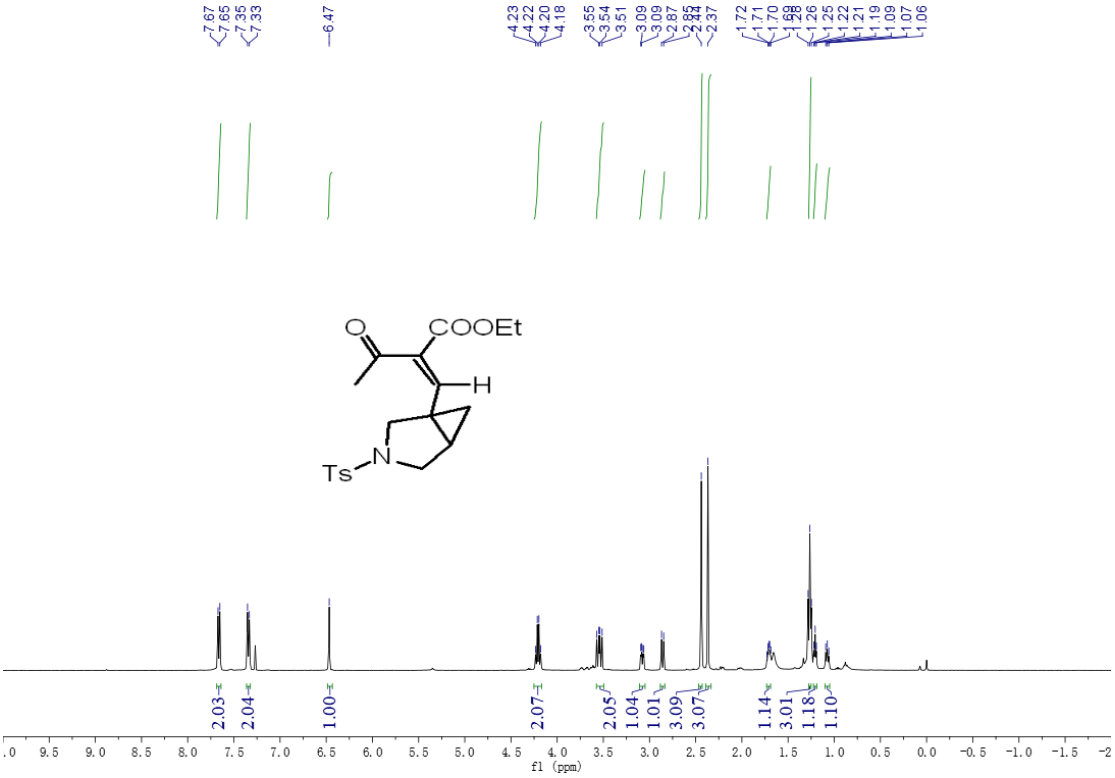
[4] Zheng, L.; Liang, Y. *J. Org. Chem.* 2017, **82,** 13, 7000.

[5] Liu, R; Ni, Z.; Giordano, L.; Tenaglia, A. *Org. Lett.* 2016, **18**, 4040.

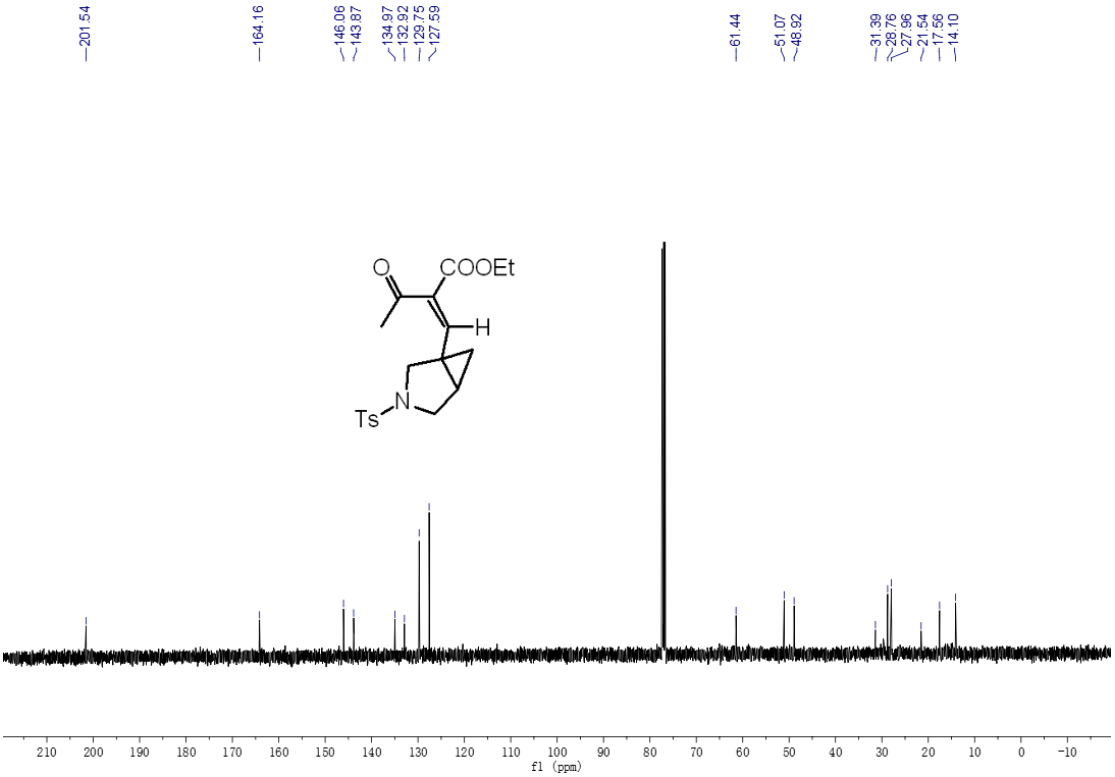
[6] Zhu, H; Chen, P.;and Liu, G. *J. Am. Chem. Soc.* 2014, **136**, 1766.

## 8. $^{1}$H NMR and $^{13}$C NMR Spectrum for All Isolated Products

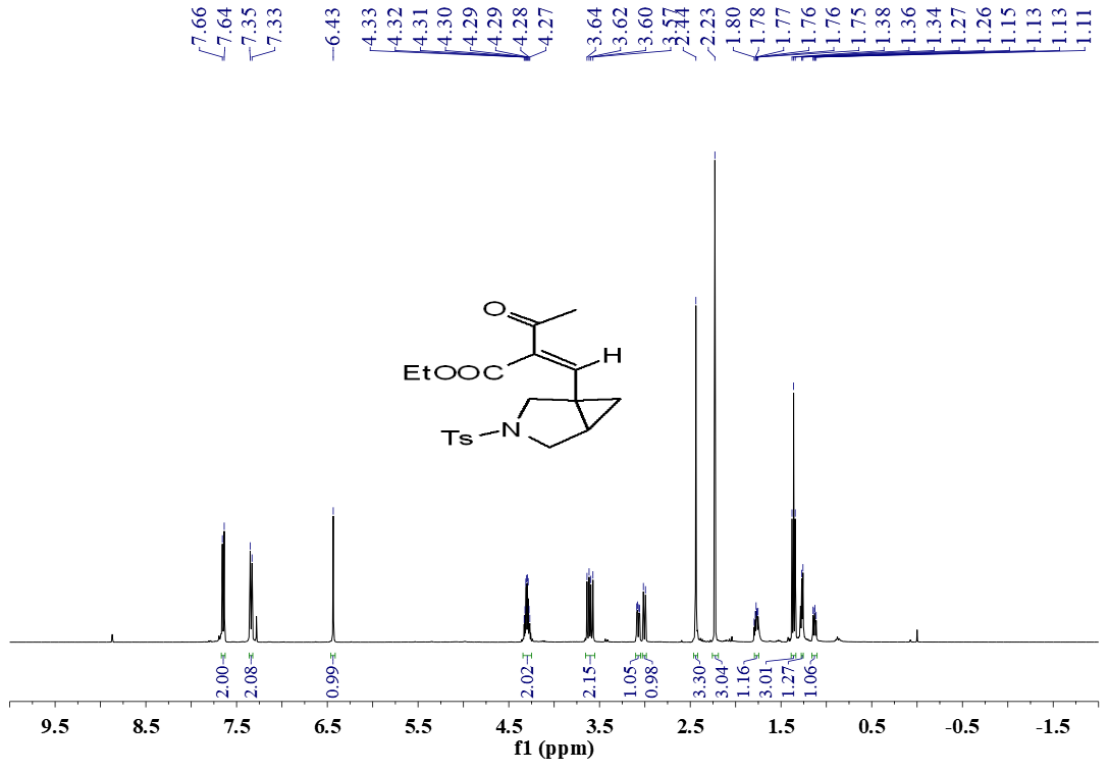
1) $^{1}$H NMR of ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butanoate **(*E*)-3-1a** (400 MHz, $CDCl_3$)



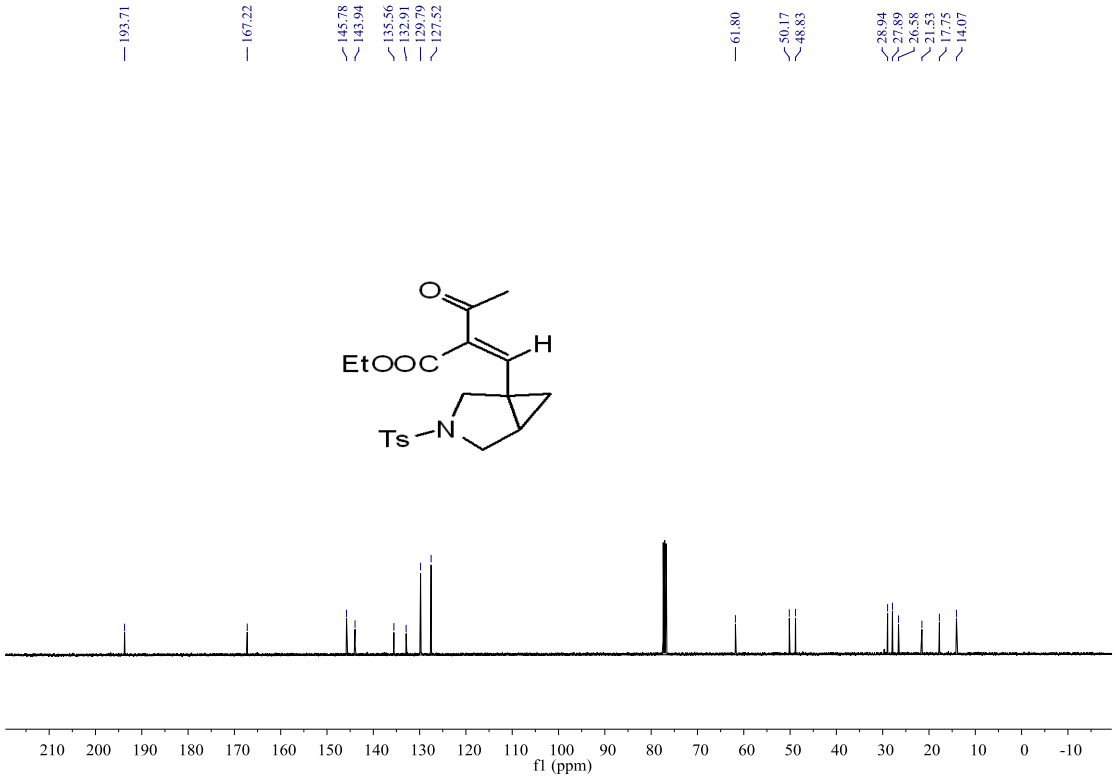

$^{13}$C NMR of ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butanoate **(*E*)-3-1a** (101 MHz, $CDCl_3$)



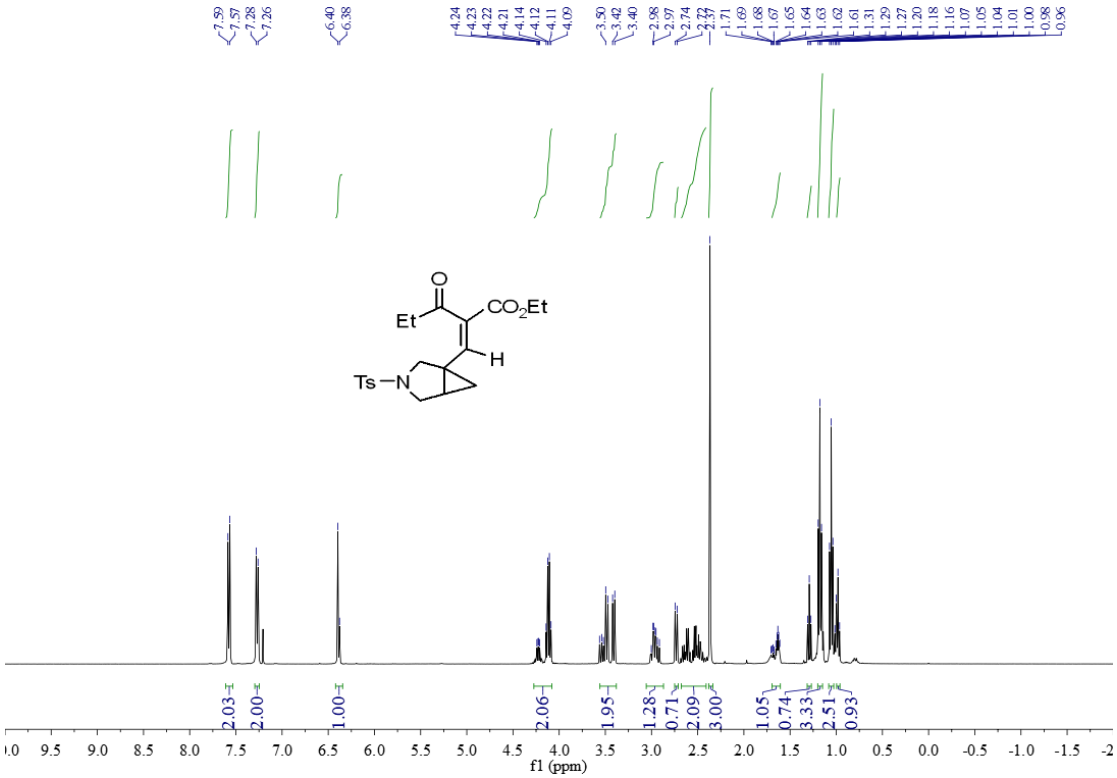
2) $^{1}$H NMR of ethyl (Z)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butanoate **(*Z*)-3-1a** (400 MHz, $CDCl_3$)



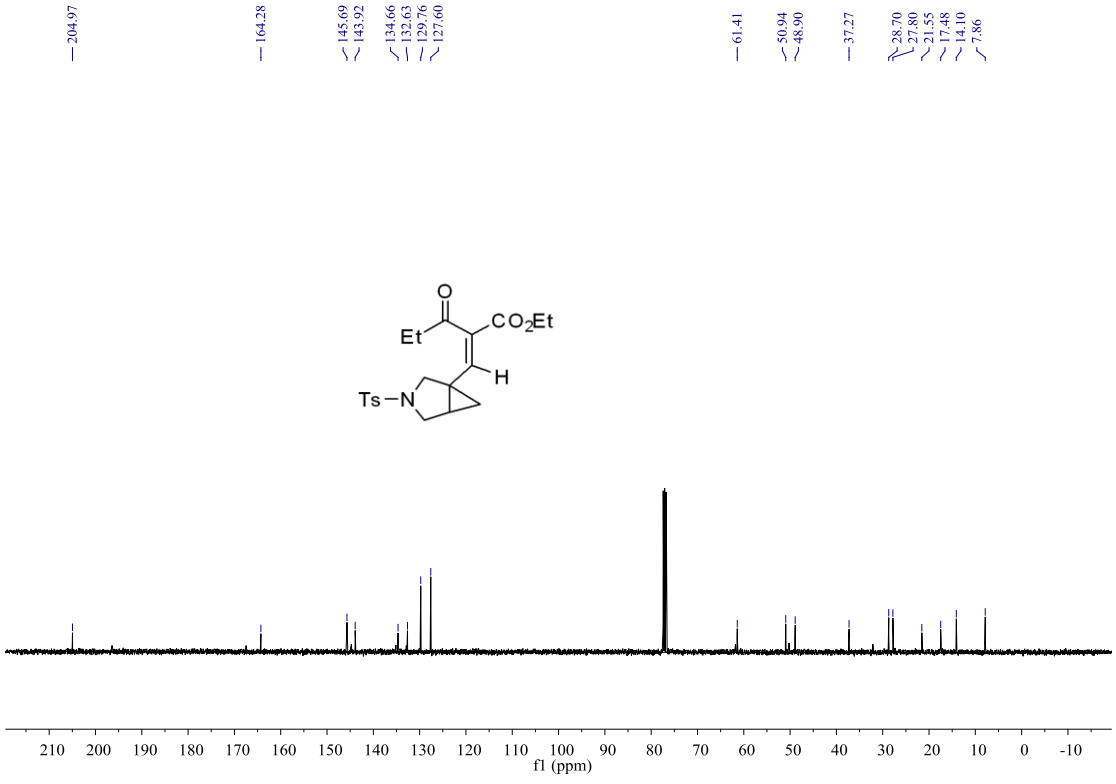

$^{13}$C NMR of ethyl (*Z*)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butanoate **(*Z*)-3-1a** (101 MHz, $CDCl_3$)



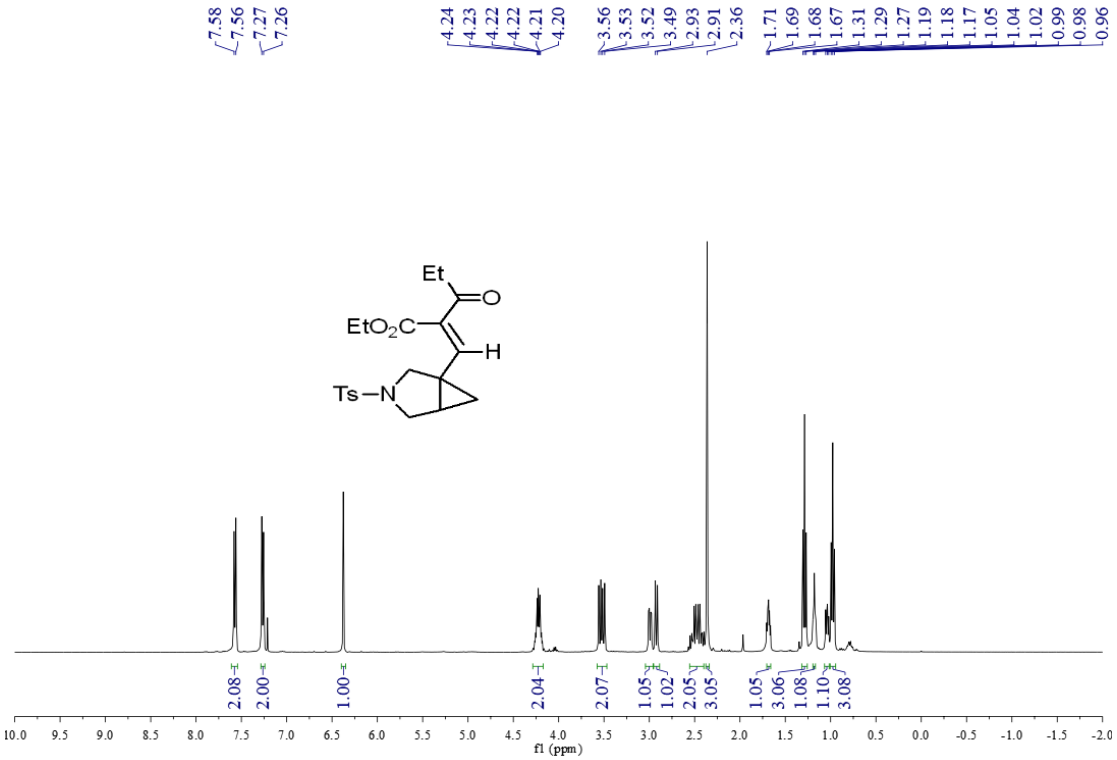
3) $^{1}$H NMR of ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)pentanoate **(*E*)-3-1b** (400 MHz, $CDCl_3$)



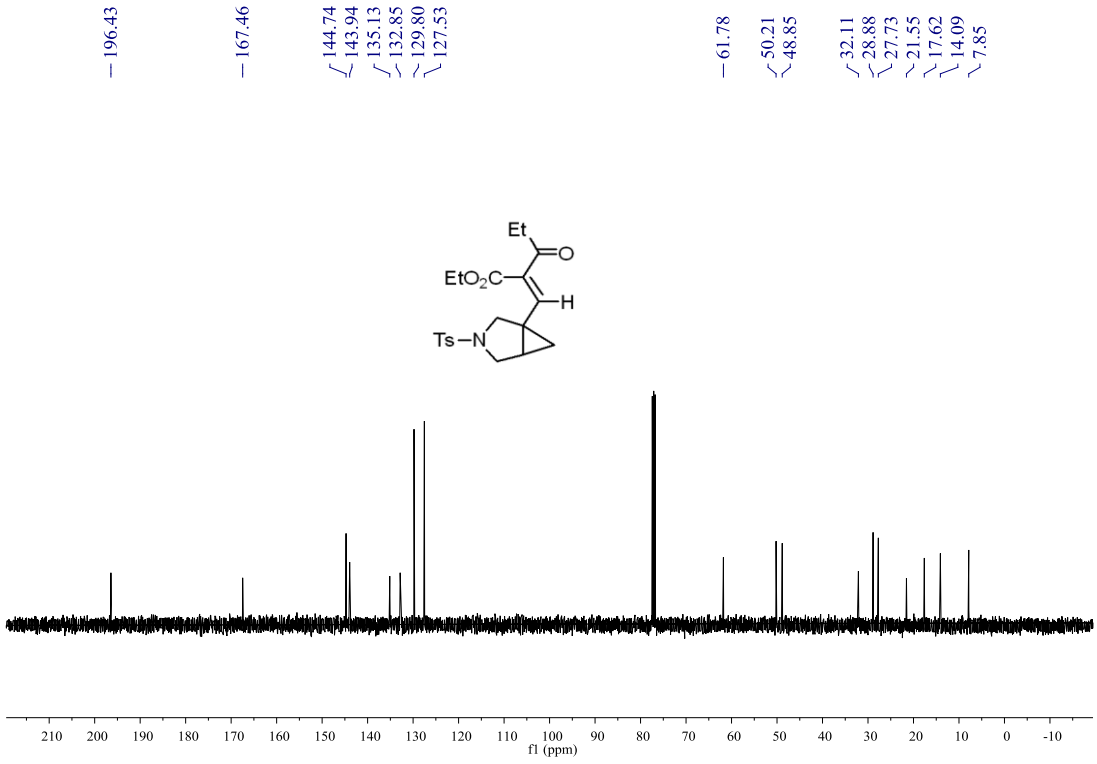

$^{13}$C NMR of ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)pentanoate **(*E*)-3-1b** (400 MHz, $CDCl_3$)



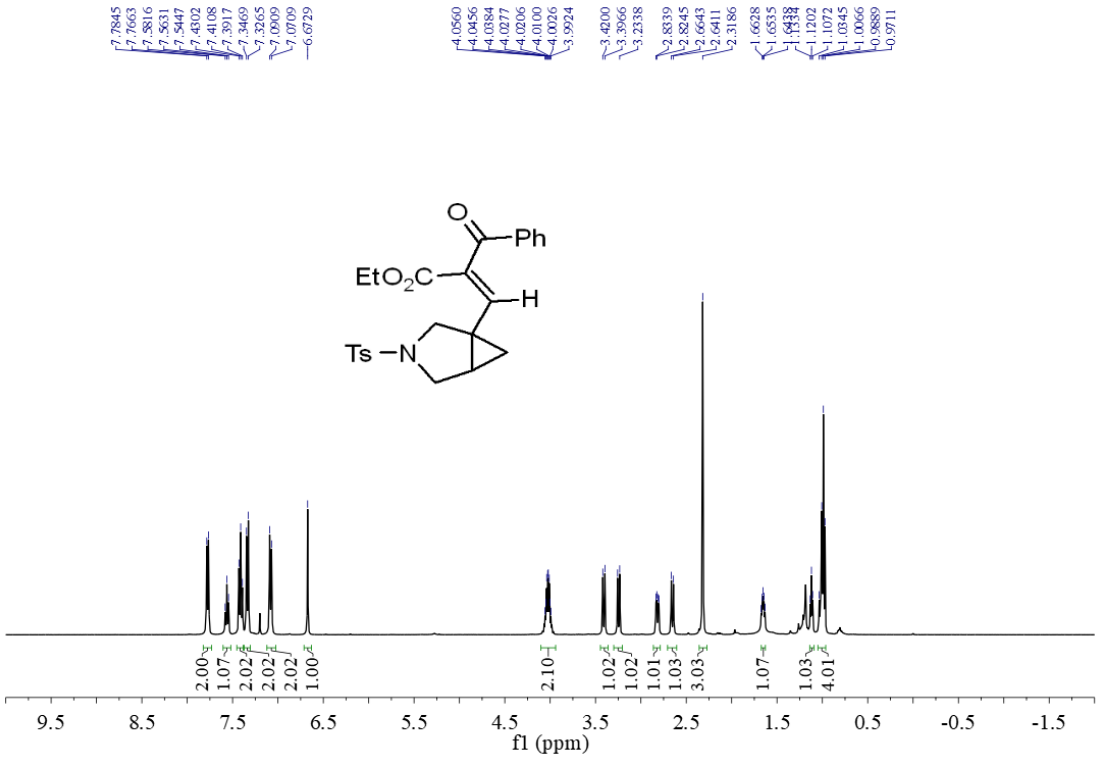
4) $^{1}$H NMR of ethyl (*Z*)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)pentanoate **(*Z*)-3-1b** (400 MHz, $CDCl_3$)



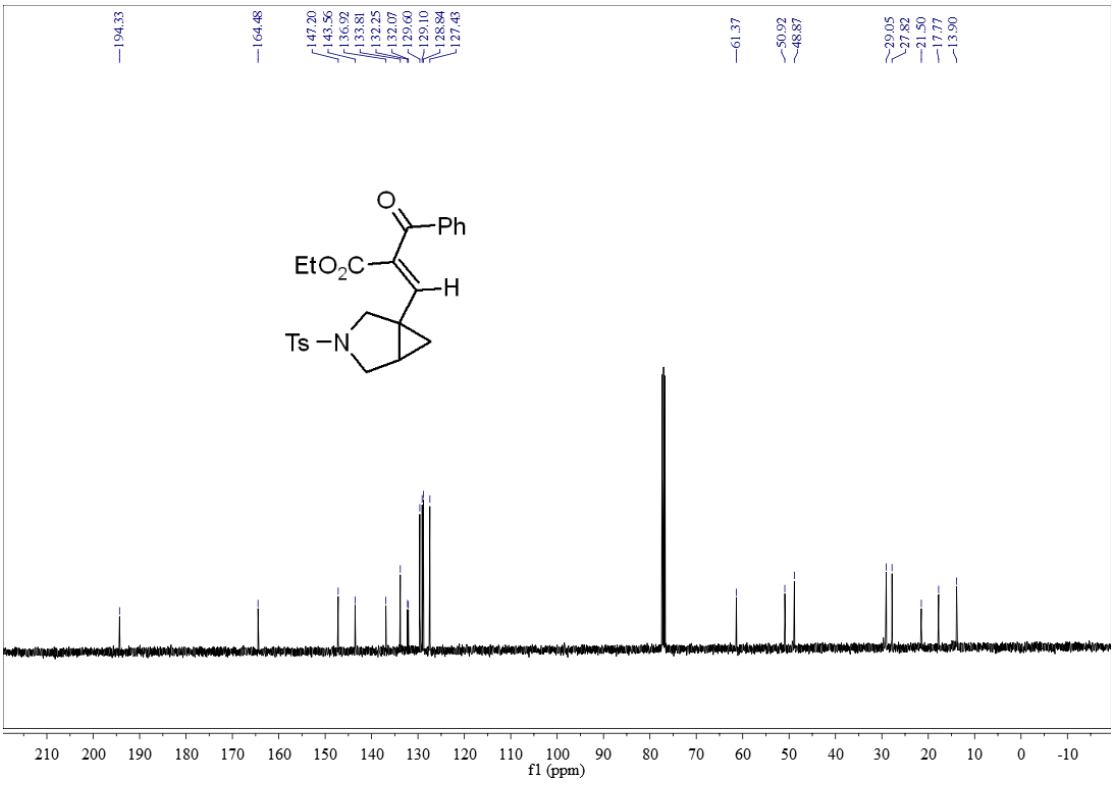

$^{13}$C NMR of ethyl (*Z*)-3-oxo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)pentanoate **(*Z*)-3-1b** (400 MHz, $CDCl_3$)



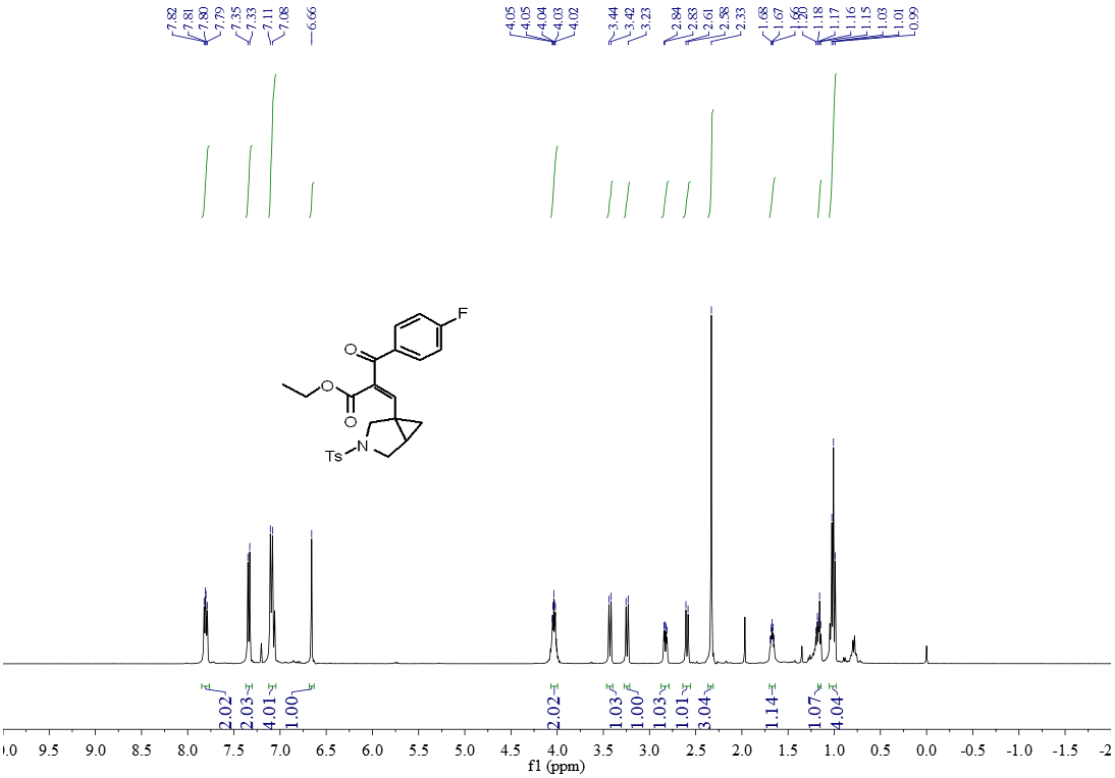
5) $^{1}$H NMR of ethyl (*Z*)-2-benzoyl-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1c** (400 MHz, $CDCl_3$)



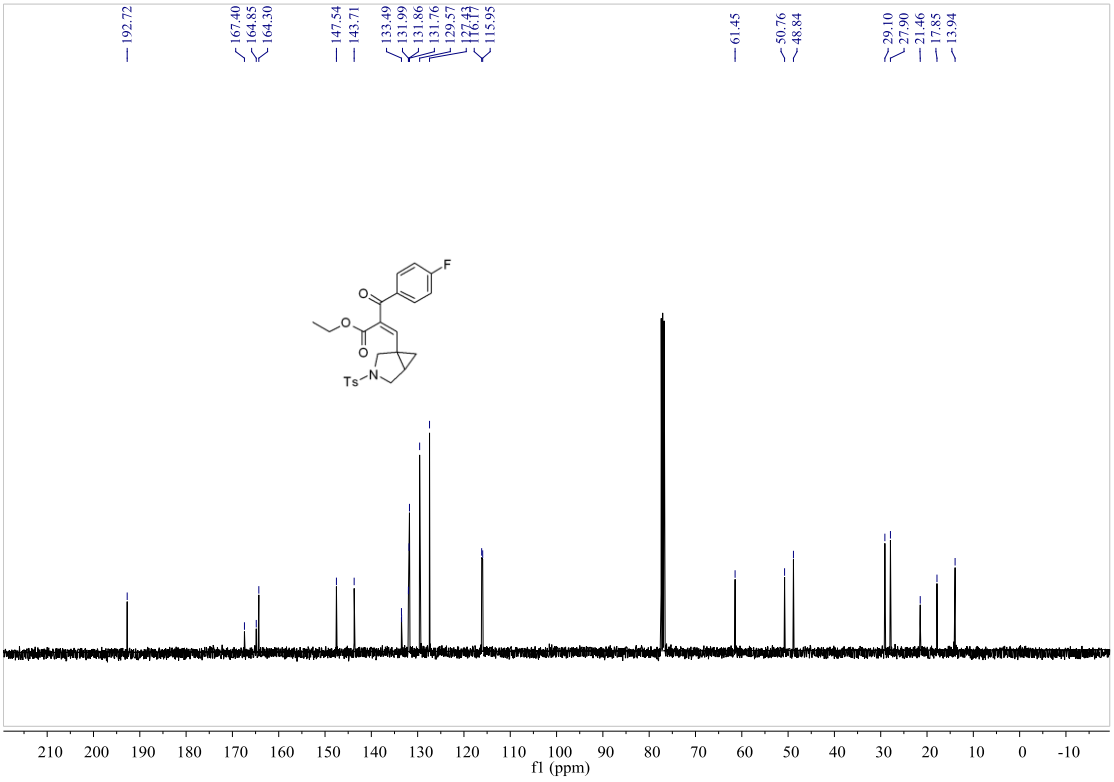

$^{13}$C NMR of ethyl (*Z*)-2-benzoyl-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1c** (101 MHz, $CDCl_3$)



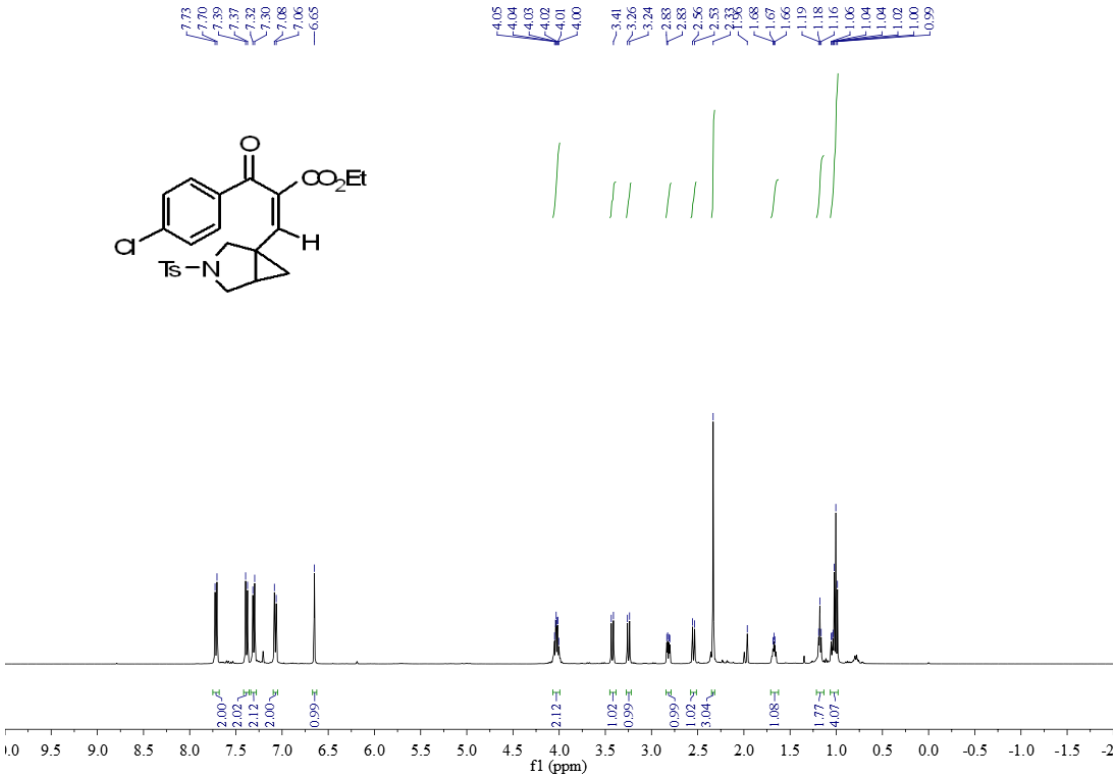
6) $^{1}$H NMR of ethyl (*Z*)-2-(4-fluorobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate (400 MHz, $CDCl_3$) **(*Z*)-3-1d**



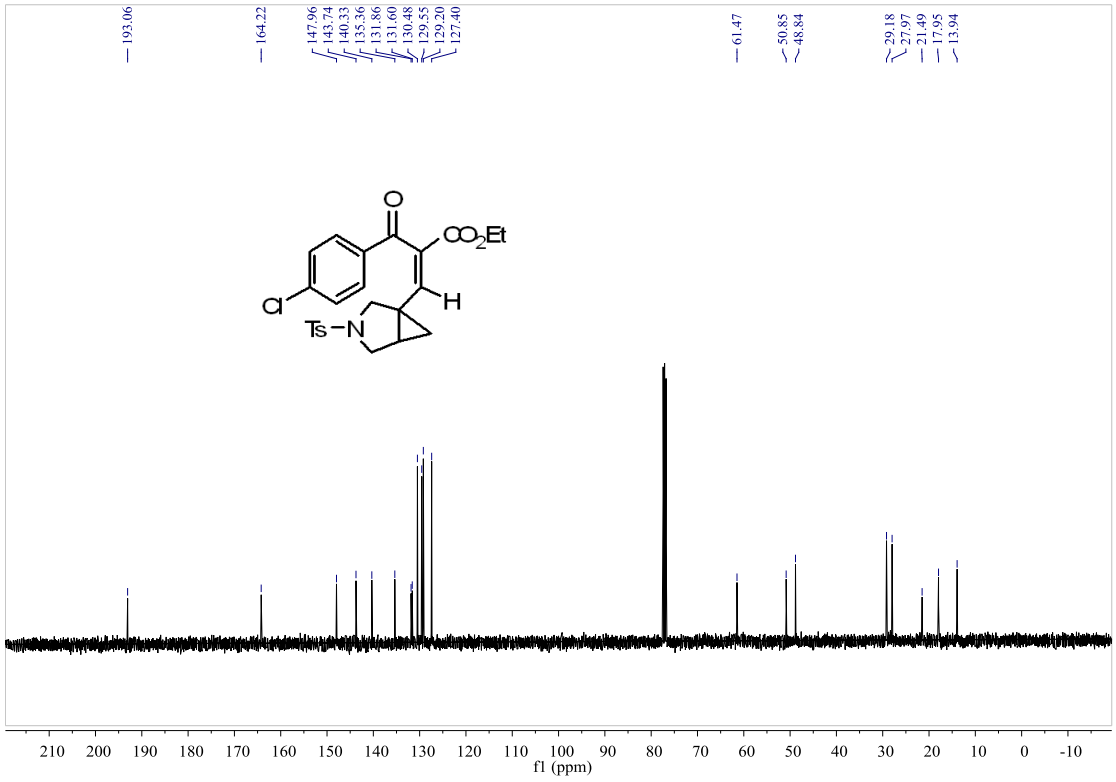

$^{13}$C NMR of ethyl (*Z*)-2-(4-fluorobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1d** (101 MHz, $CDCl_3$)



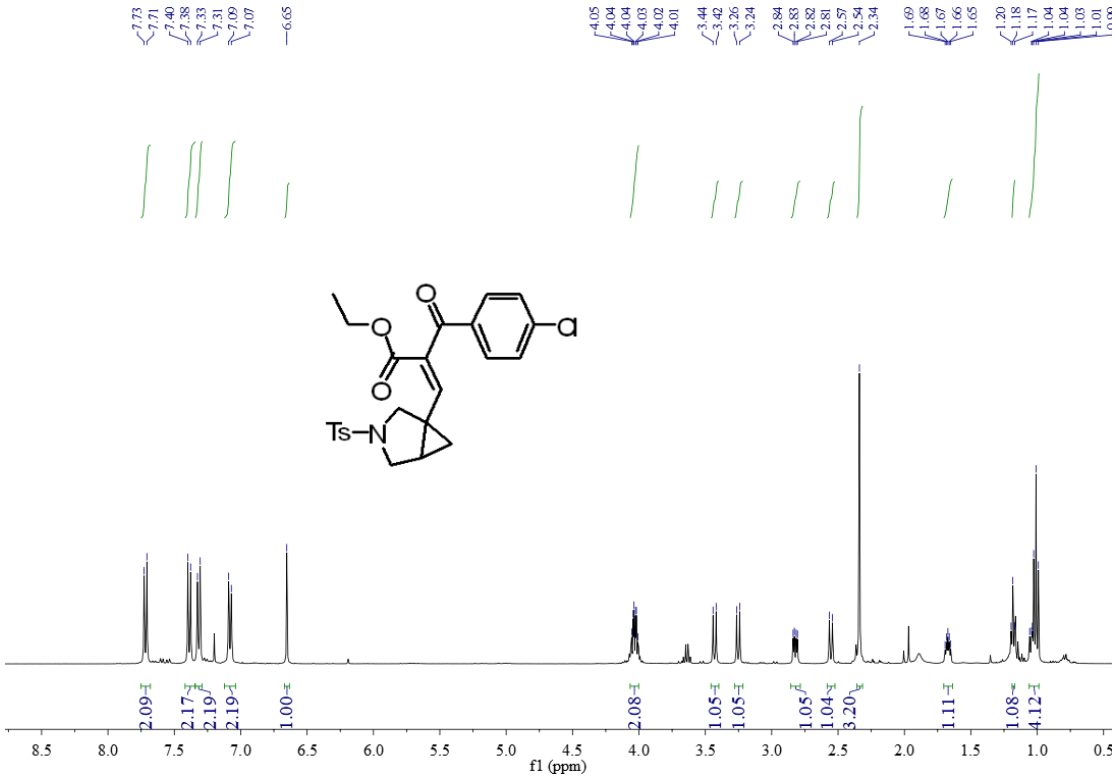
7) $^{1}$H NMR of ethyl (*E*)-2-(4-chlorobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1e** (400 MHz, $CDCl_3$)



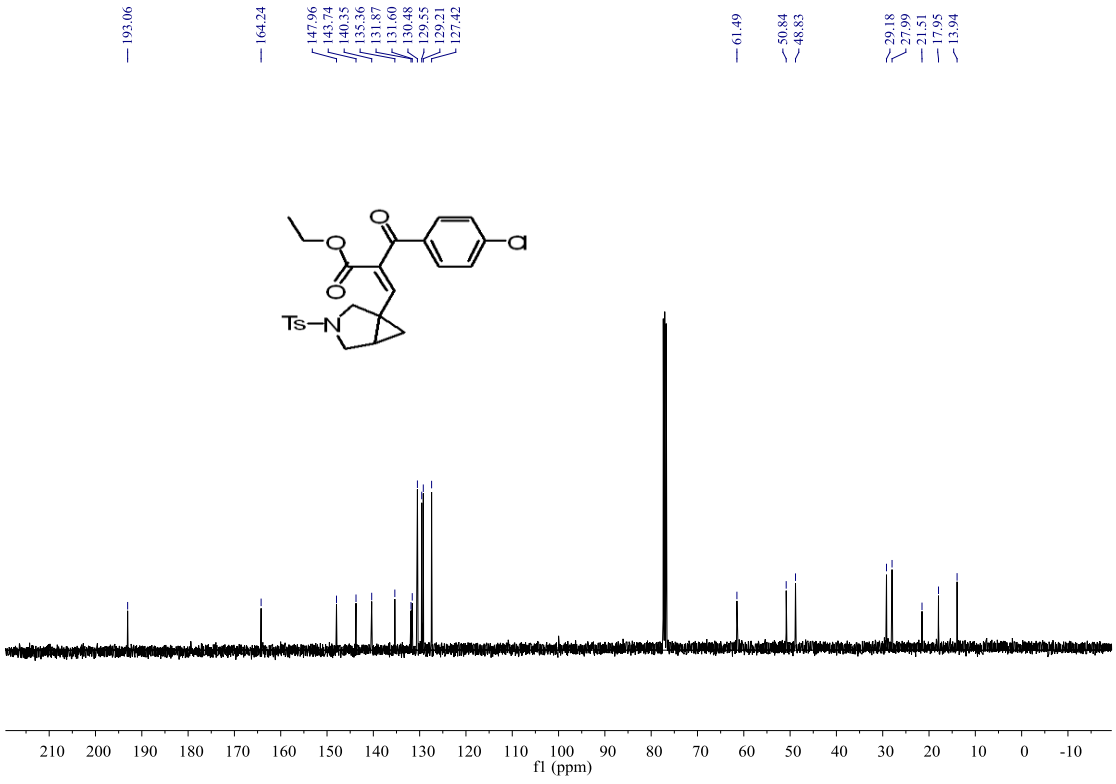

$^{13}$C NMR of ethyl (*E*)-2-(4-chlorobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1e** (101 MHz, $CDCl_3$)



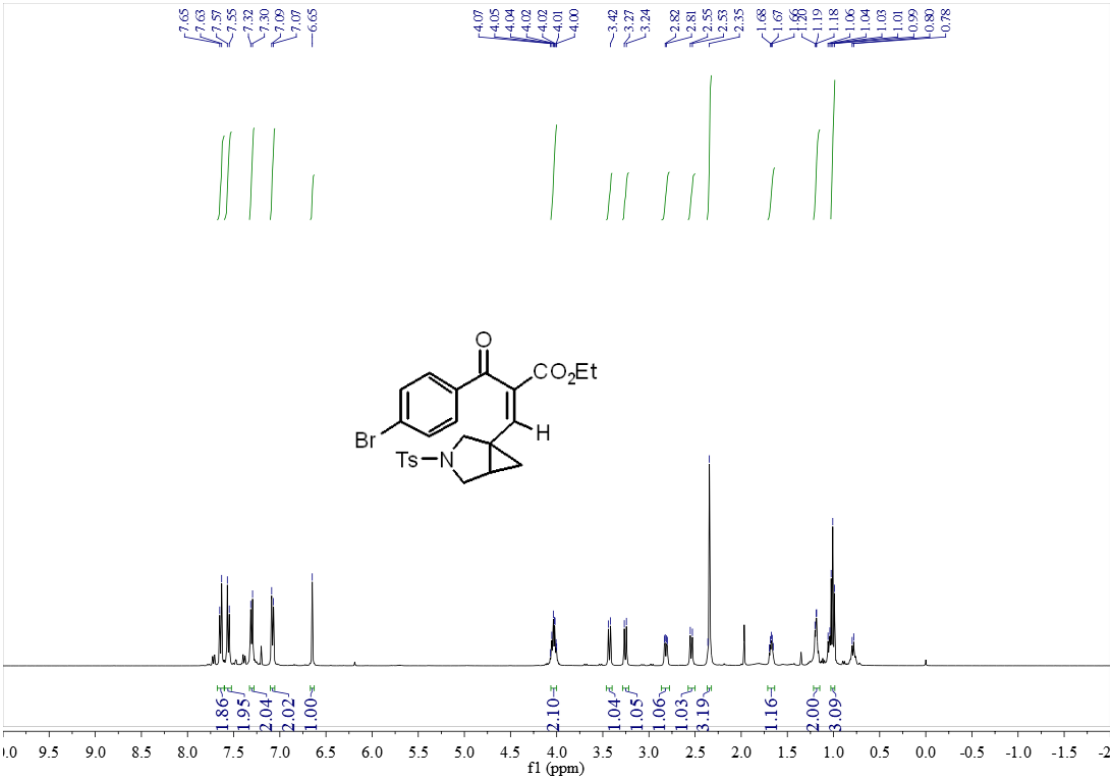
8) $^{1}$H NMR of ethyl (*Z*)-2-(4-chlorobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1e** (400 MHz, $CDCl_3$)



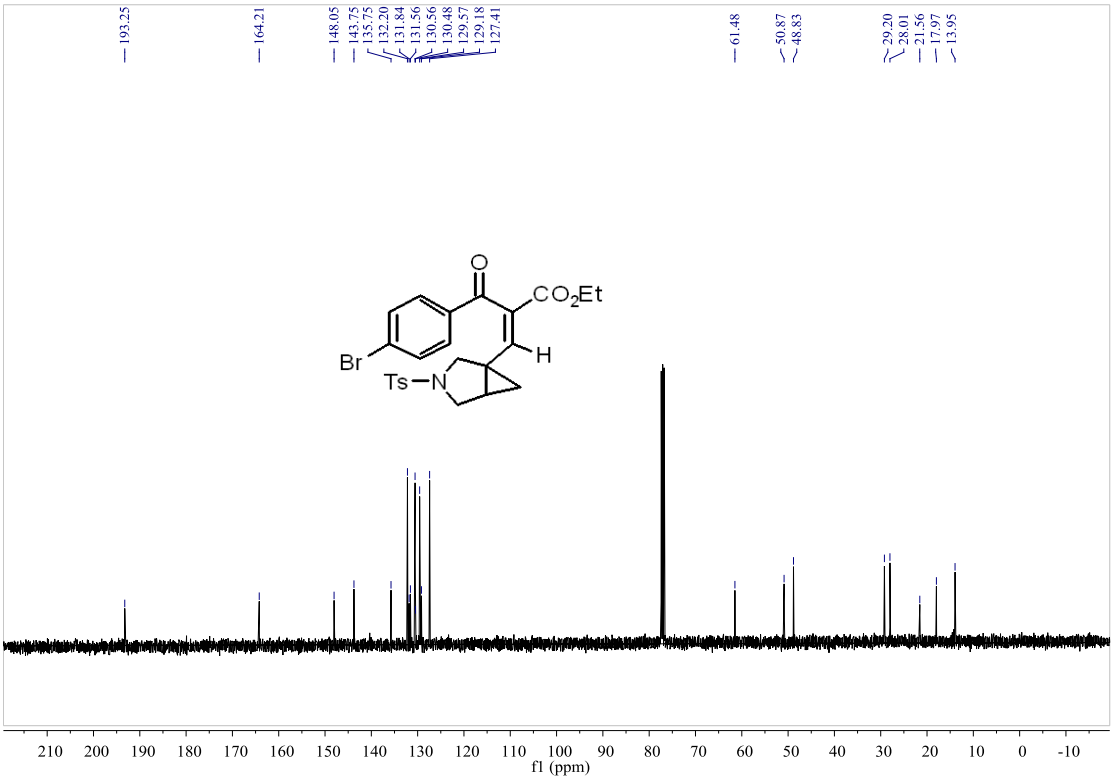

$^{13}$C NMR of ethyl (*Z*)-2-(4-chlorobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1e** (101 MHz, $CDCl_3$)



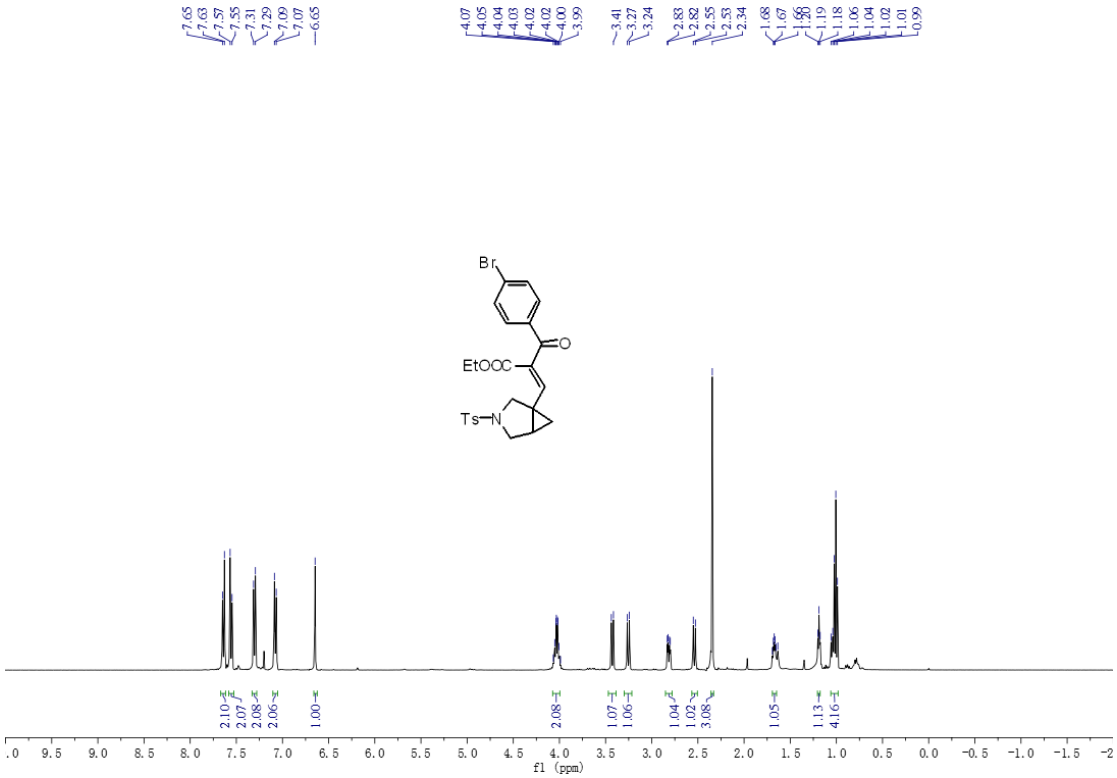
9) $^{1}$H NMR of ethyl (*E*)-2-(4-bromobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1f** (400 MHz, $CDCl_3$)



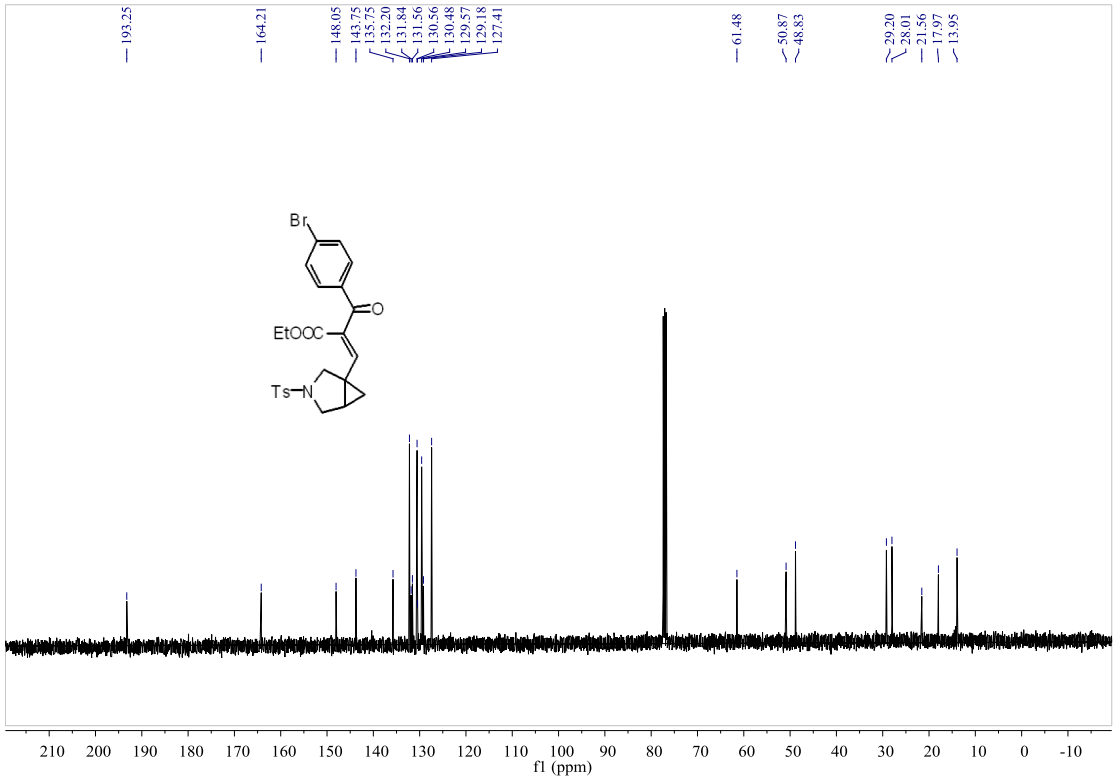

$^{13}$C NMR of ethyl (*E*)-2-(4-bromobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1f** (400 MHz, $CDCl_3$)



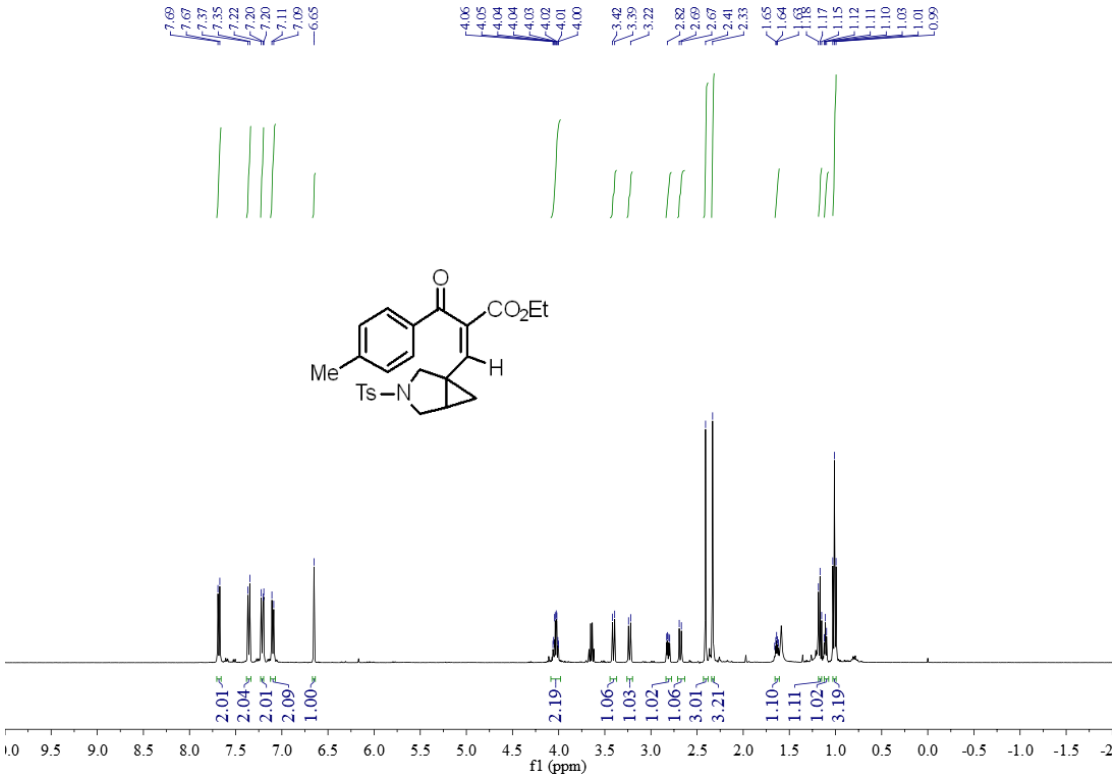
10) $^{1}$H NMR of ethyl (*Z*)-2-(4-bromobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1f** (400 MHz, $CDCl_3$)



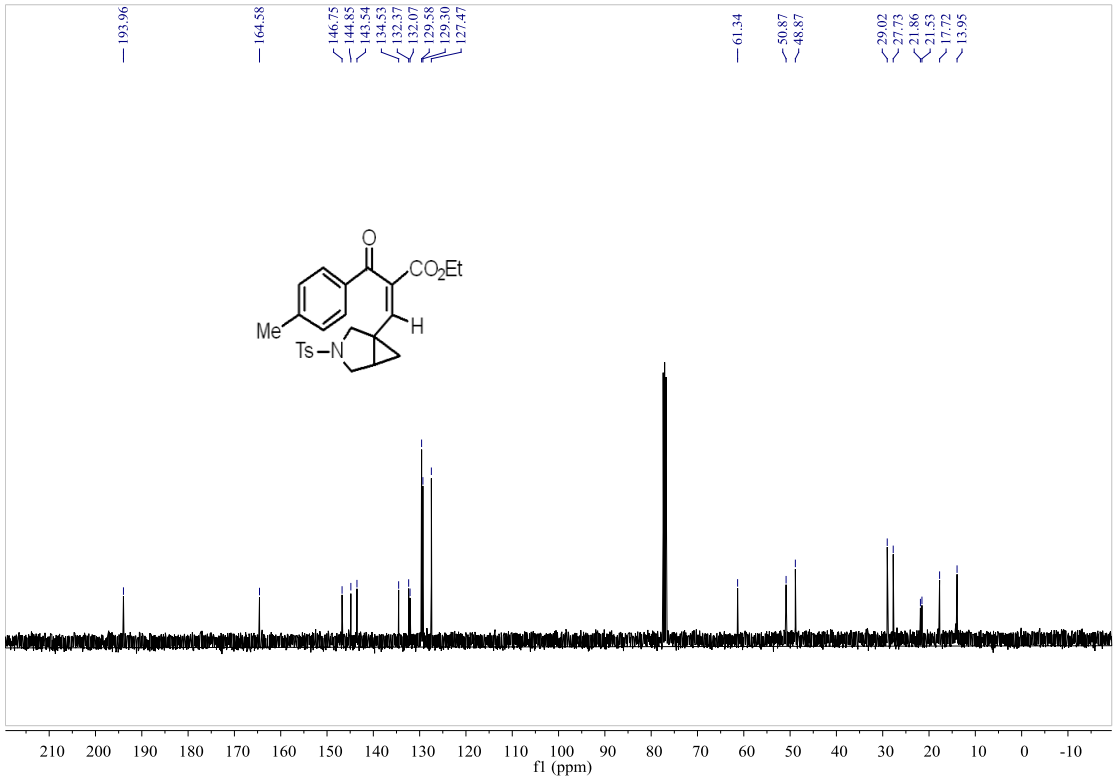

$^{13}$C NMR of ethyl (*Z*)-2-(4-bromobenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1f** (400 MHz, $CDCl_3$)



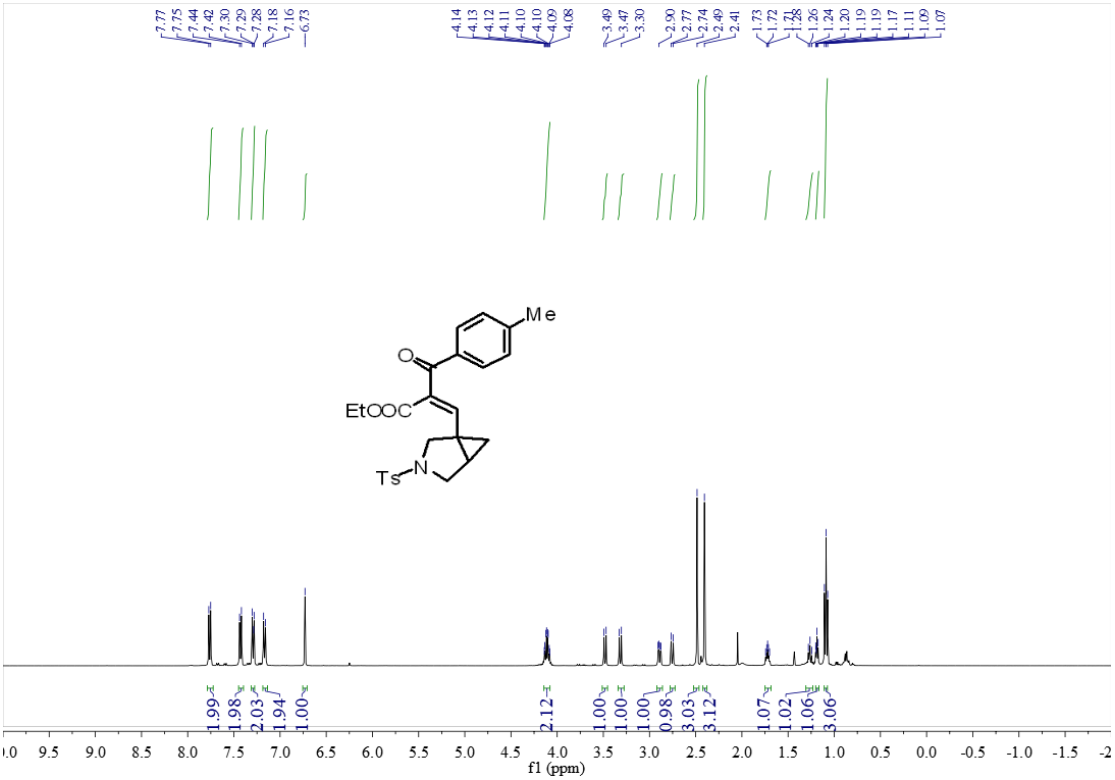
11) $^{1}$H NMR of ethyl (*E*)-2-(4-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1g** (400 MHz, $CDCl_3$)



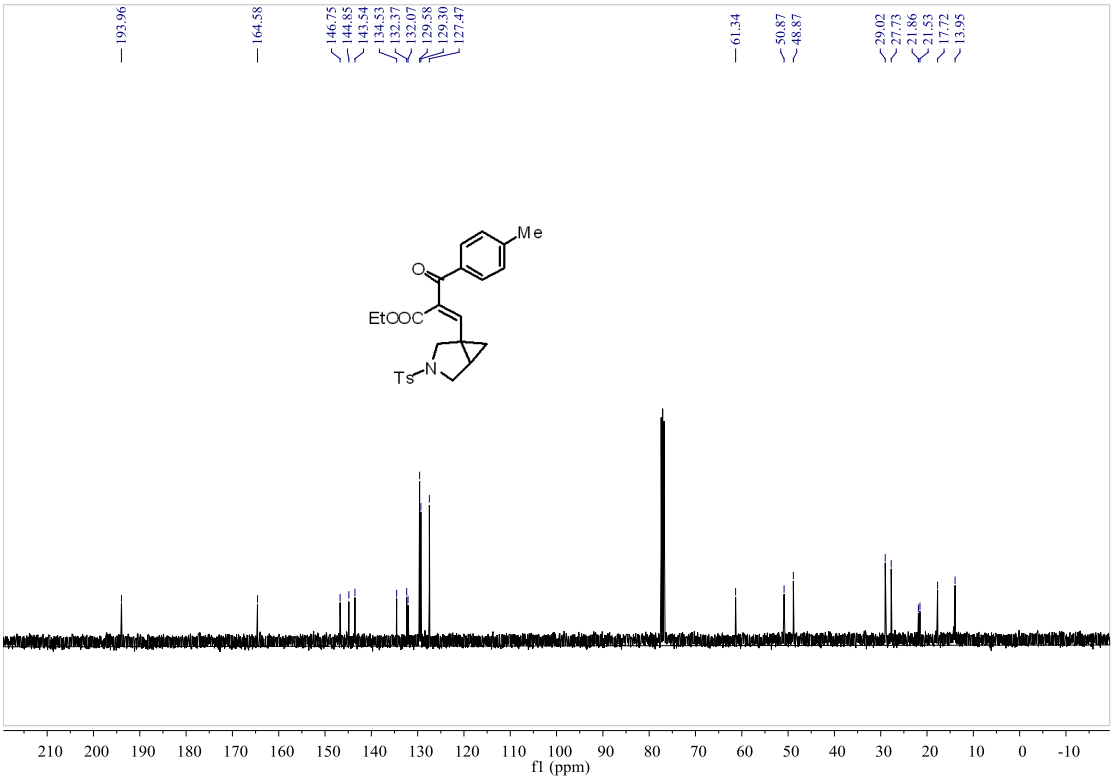

$^{13}$C NMR of ethyl (*E*)-2-(4-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1g** (400 MHz, $CDCl_3$)



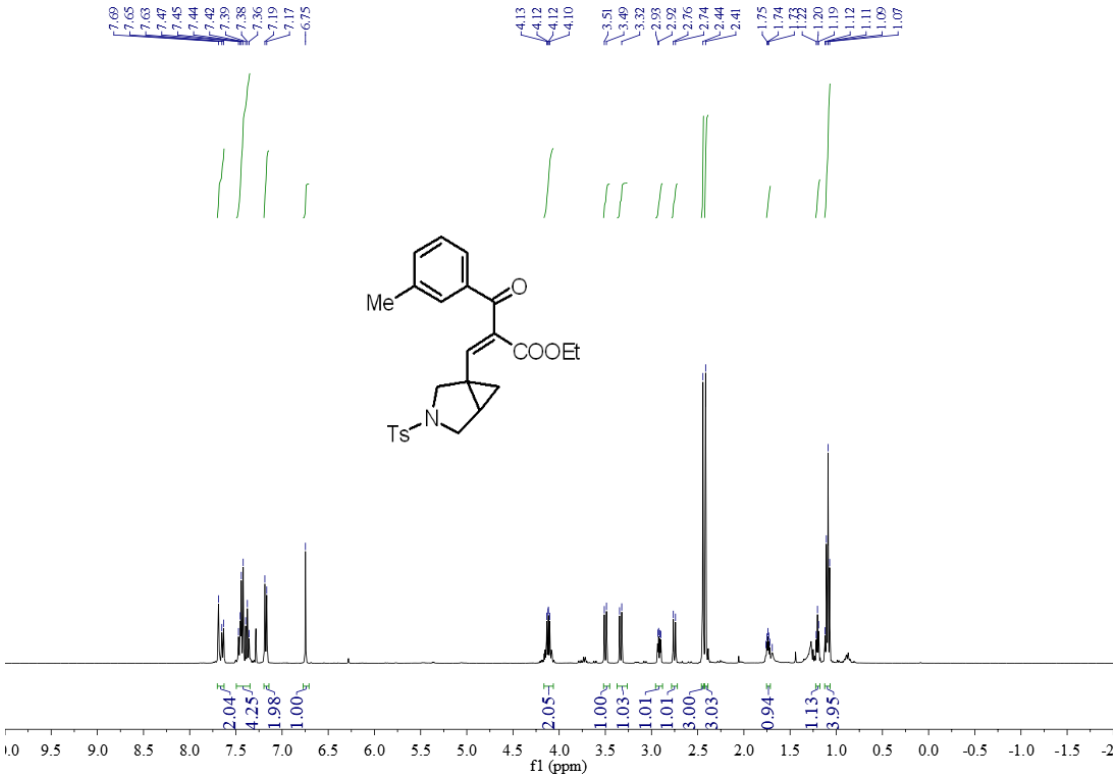
12) $^{1}$H NMR of ethyl (*Z*)-2-(4-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1g** (400 MHz, $CDCl_3$)



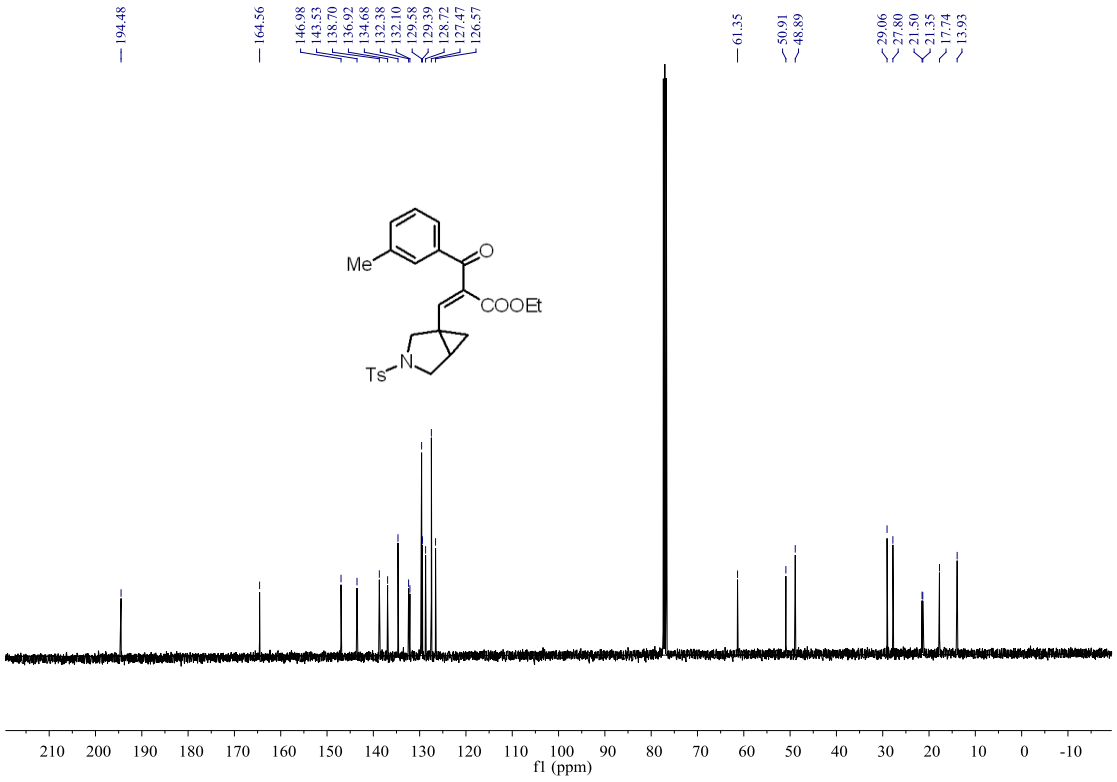

$^{13}$C NMR of ethyl (*Z*)-2-(4-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1g** (101 MHz, $CDCl_3$)



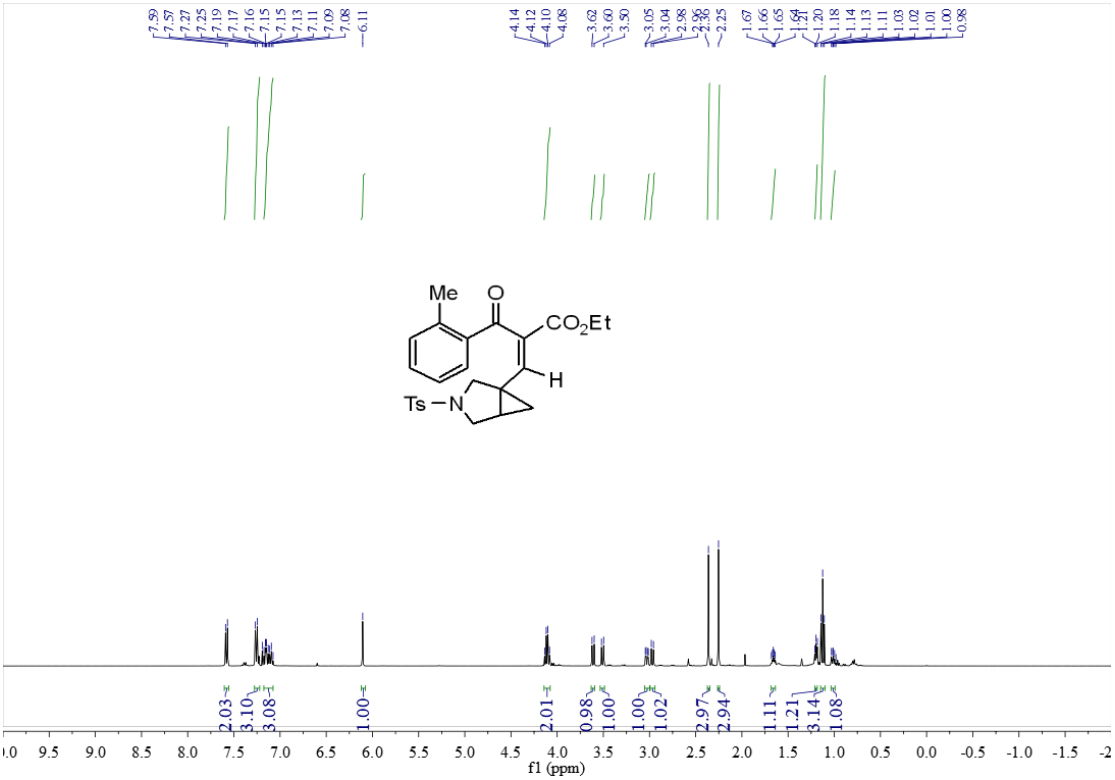
13) $^{1}$H NMR of ethyl (*Z*)-2-(3-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1h** (400 MHz, $CDCl_3$)



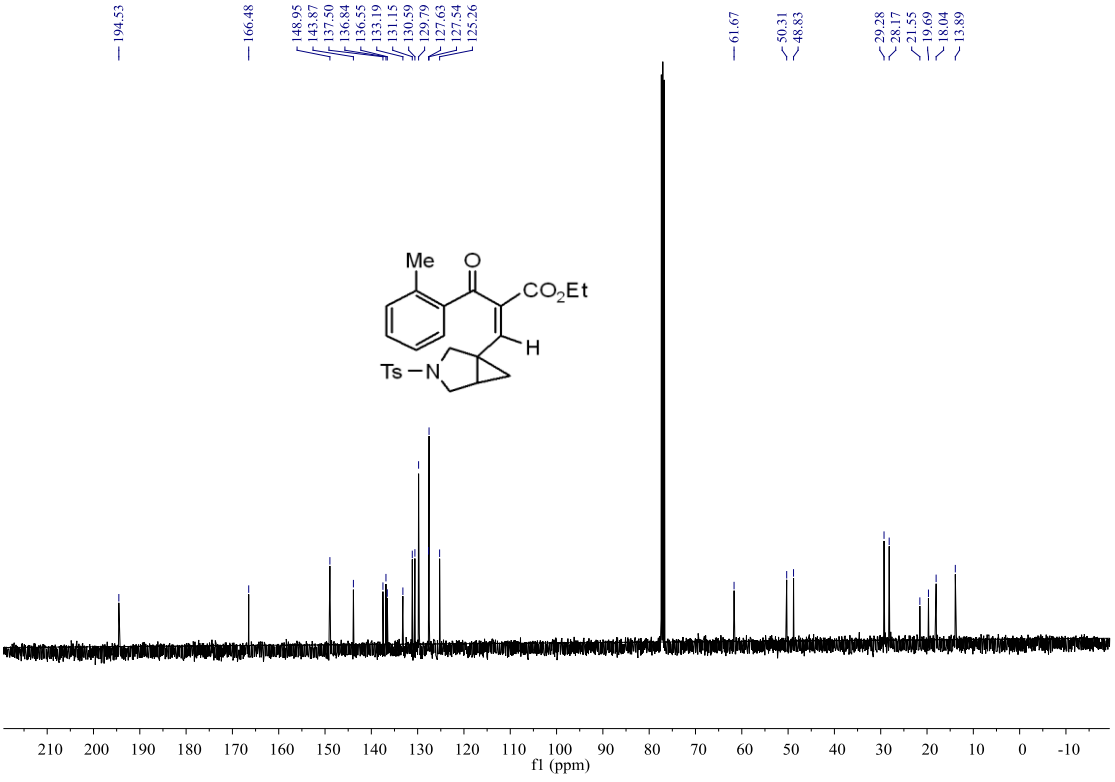

$^{13}$C NMR of ethyl (*Z*)-2-(3-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1h** (101 MHz, $CDCl_3$)



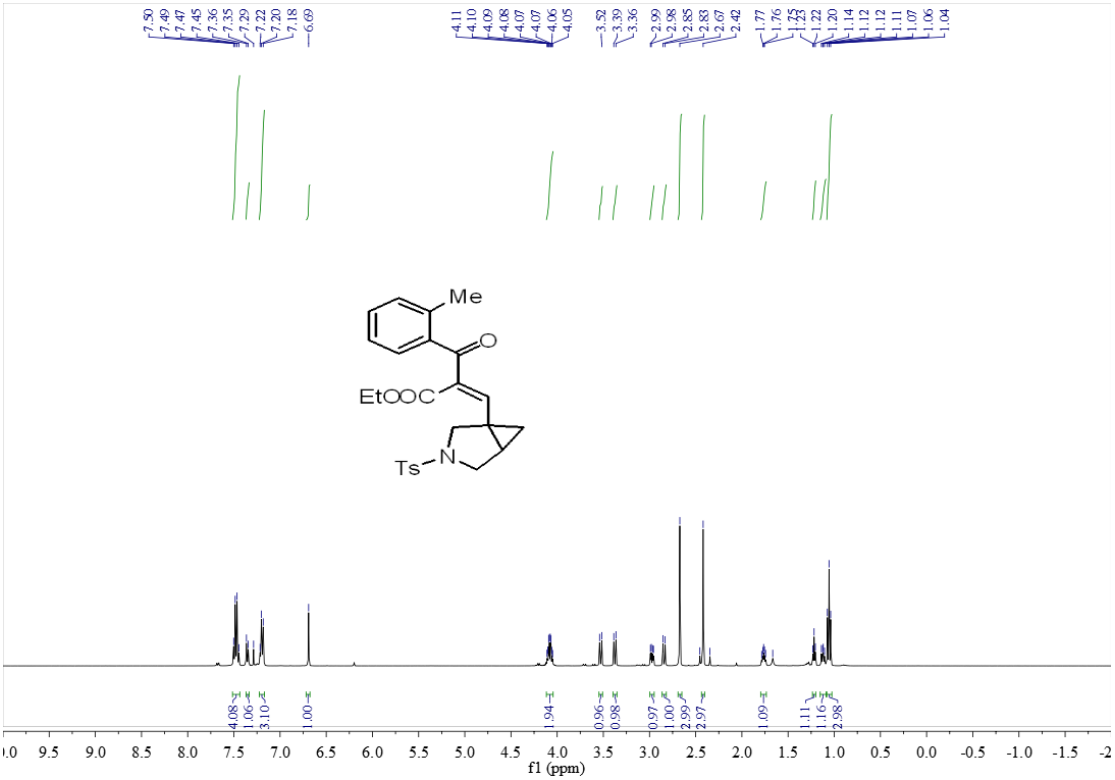
14) $^{1}$H NMR of ethyl (*E*)-2-(2-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1i** (400 MHz, $CDCl_3$)



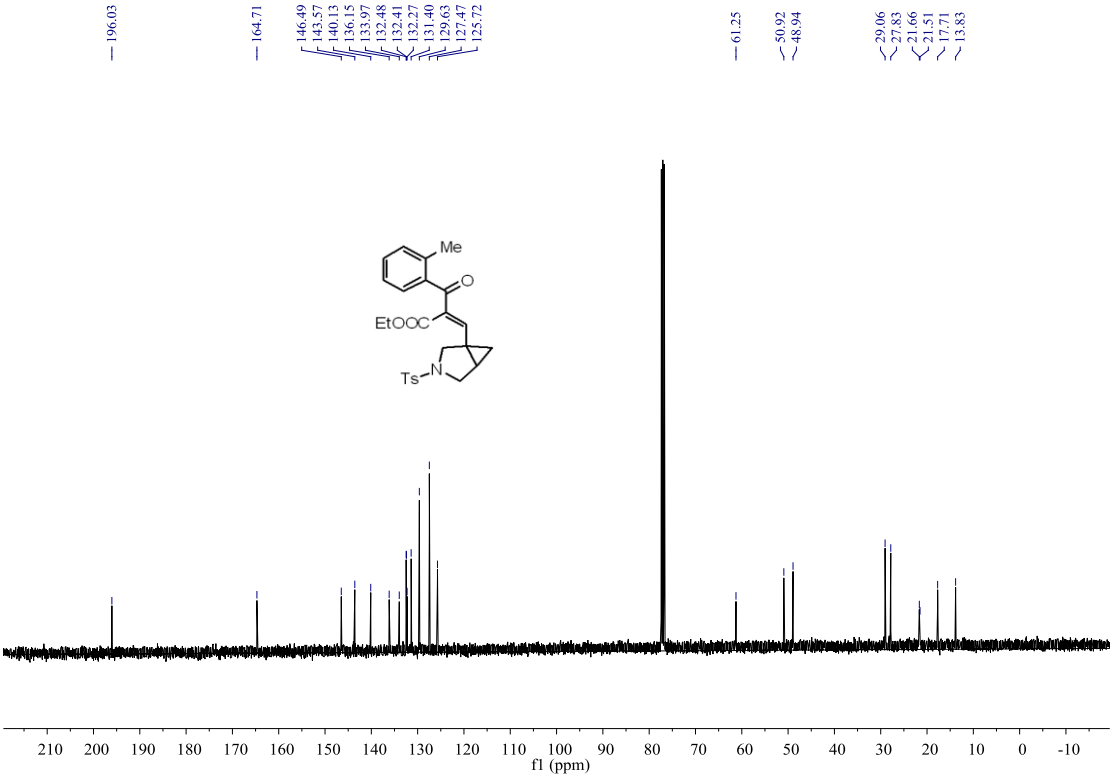

$^{13}$C NMR of ethyl (*E*)-2-(2-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1i** (101 MHz, $CDCl_3$)



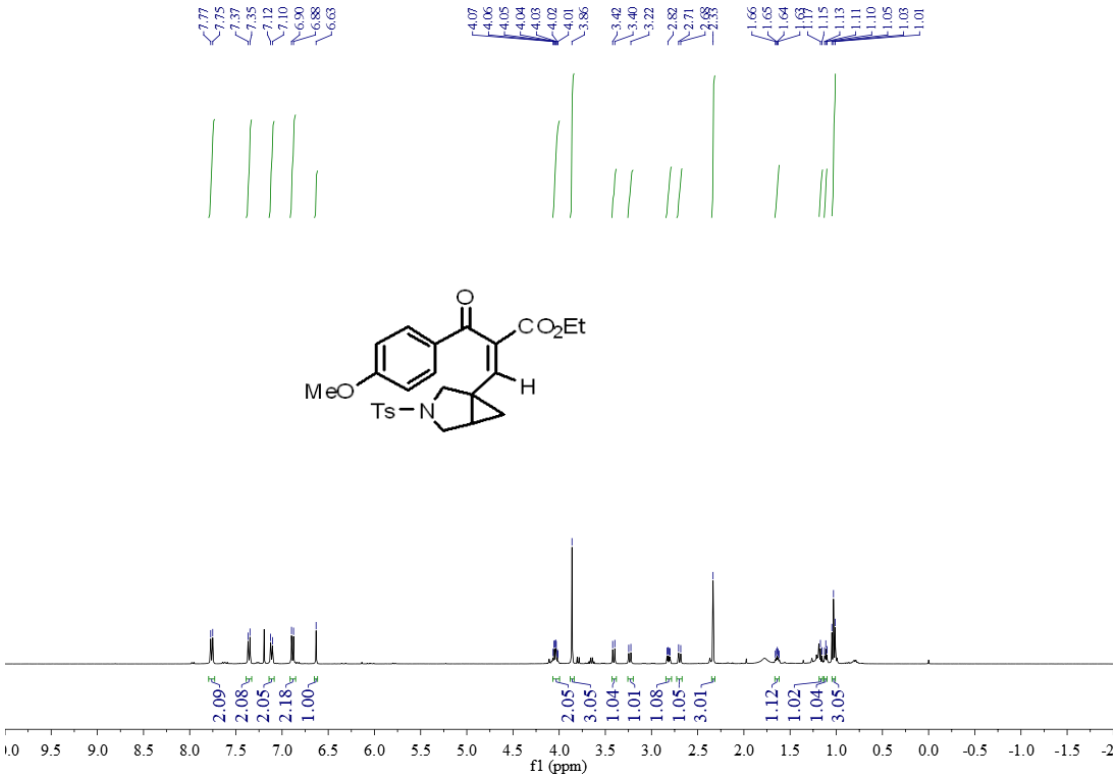
15) $^{1}$H NMR of ethyl (*Z*)-2-(2-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1i** (400 MHz, $CDCl_3$)



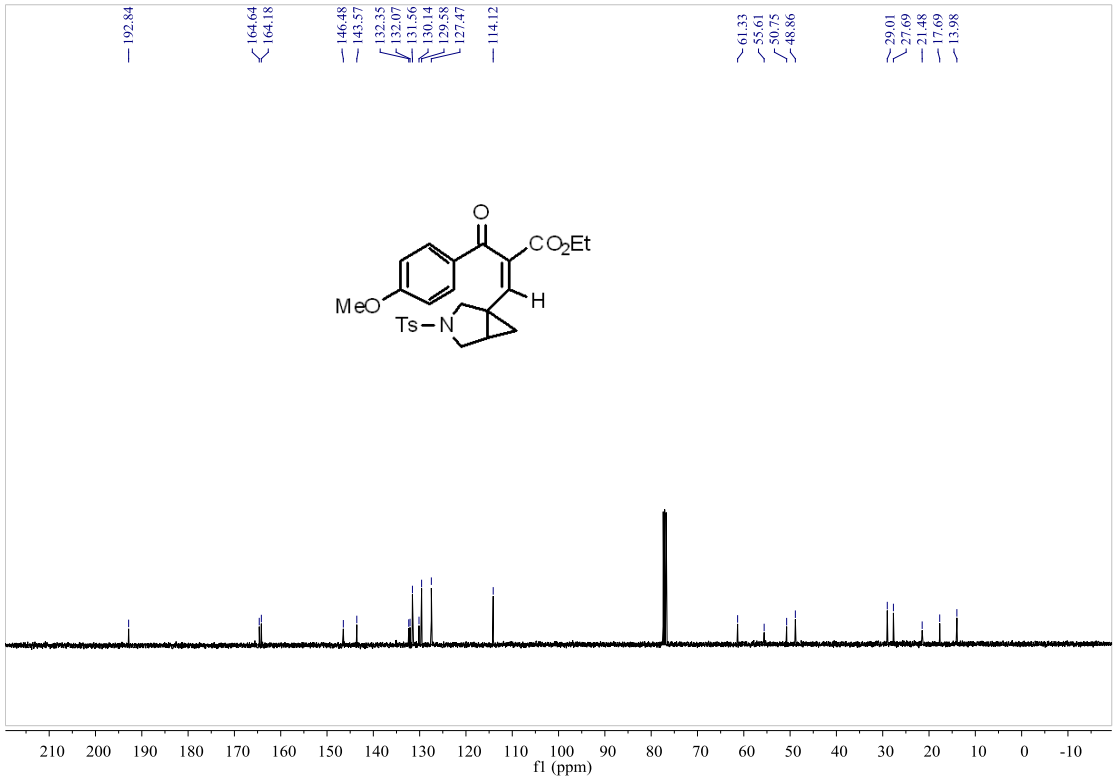

$^{13}$C NMR of ethyl (*Z*)-2-(2-methylbenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1i** (101 MHz, $CDCl_3$)



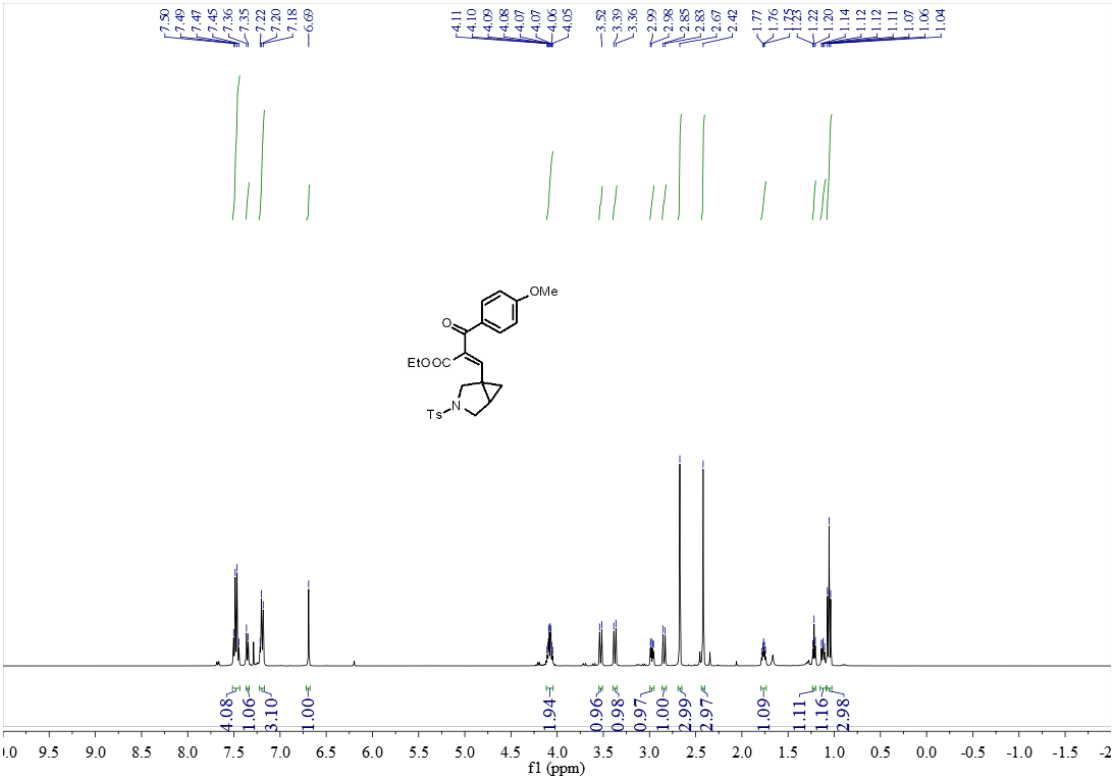
16) $^{1}$H NMR of ethyl(*E*)-2-(4-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1j** (400 MHz, $CDCl_3$)



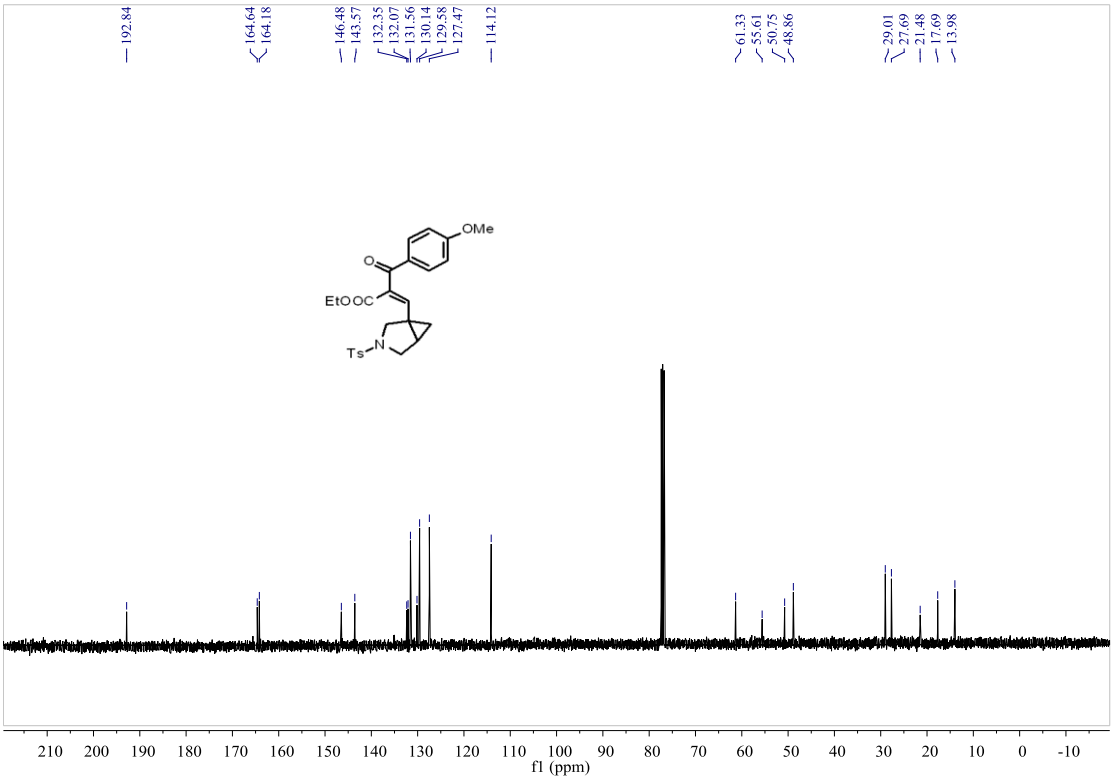

$^{13}$C NMR of ethyl (*E*)-2-(4-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1j** (101 MHz, $CDCl_3$)



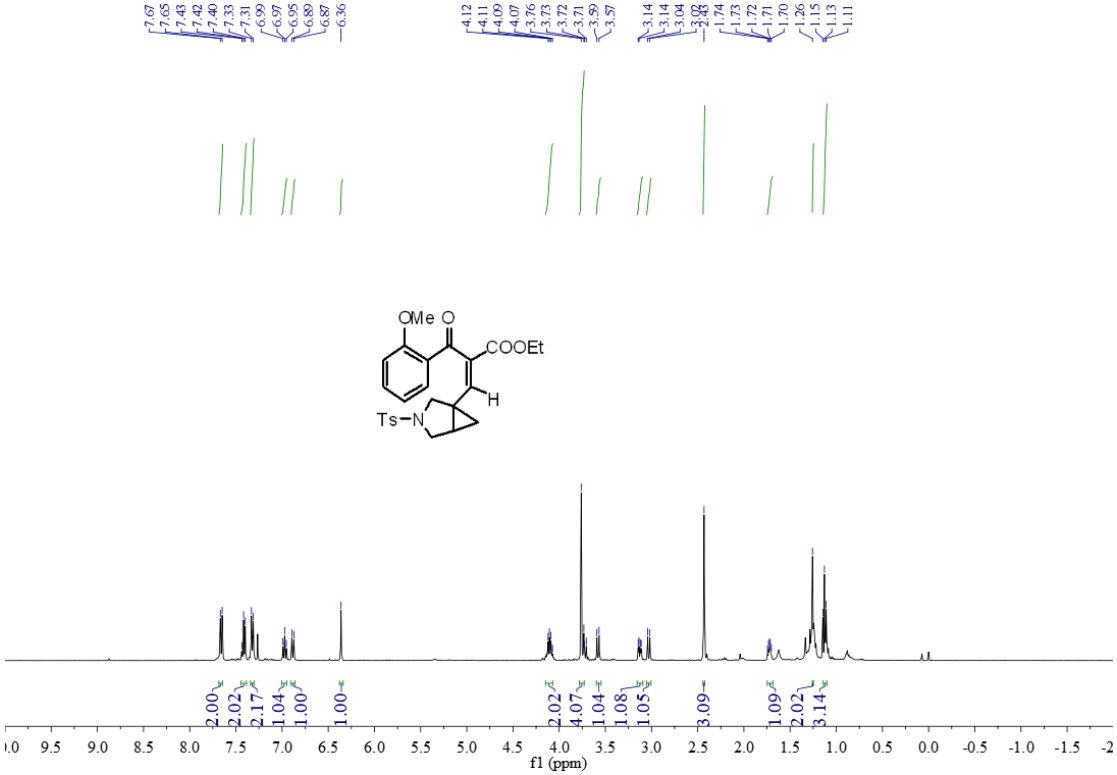
17) $^{1}$H NMR of ethyl (*Z*)-2-(4-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1j** (400 MHz, $CDCl_3$)



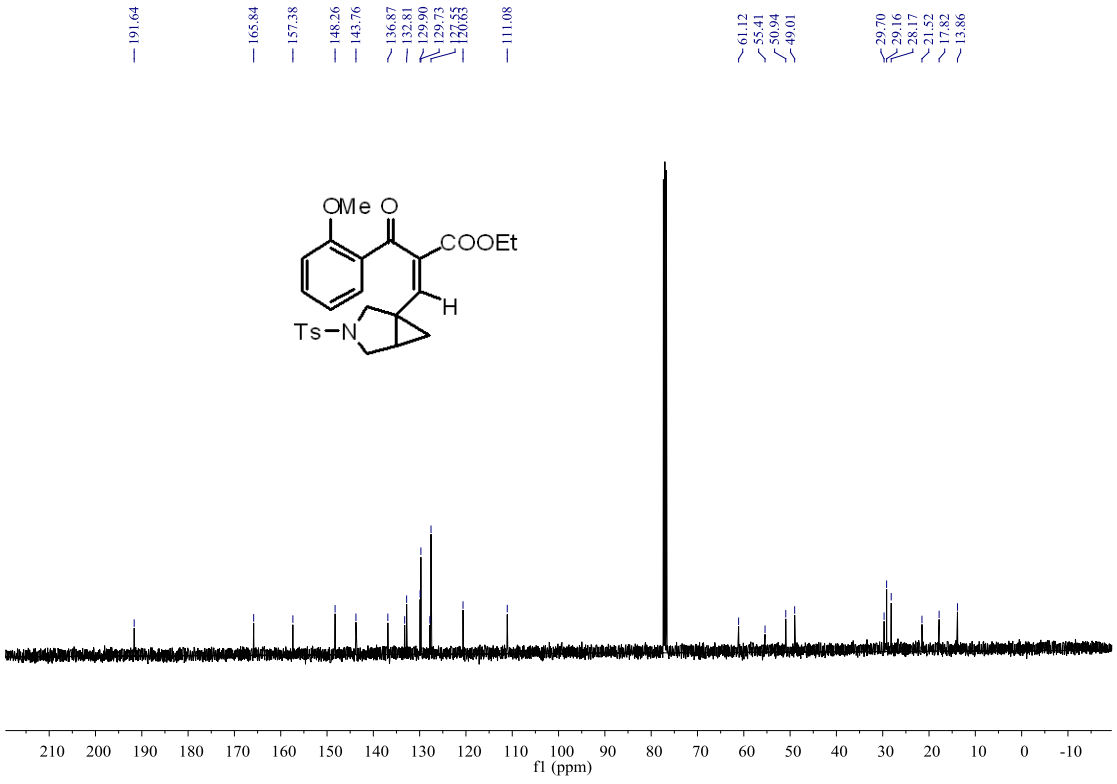

$^{13}$C NMR of ethyl (*Z*)-2-(4-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1j** (101 MHz, $CDCl_3$)



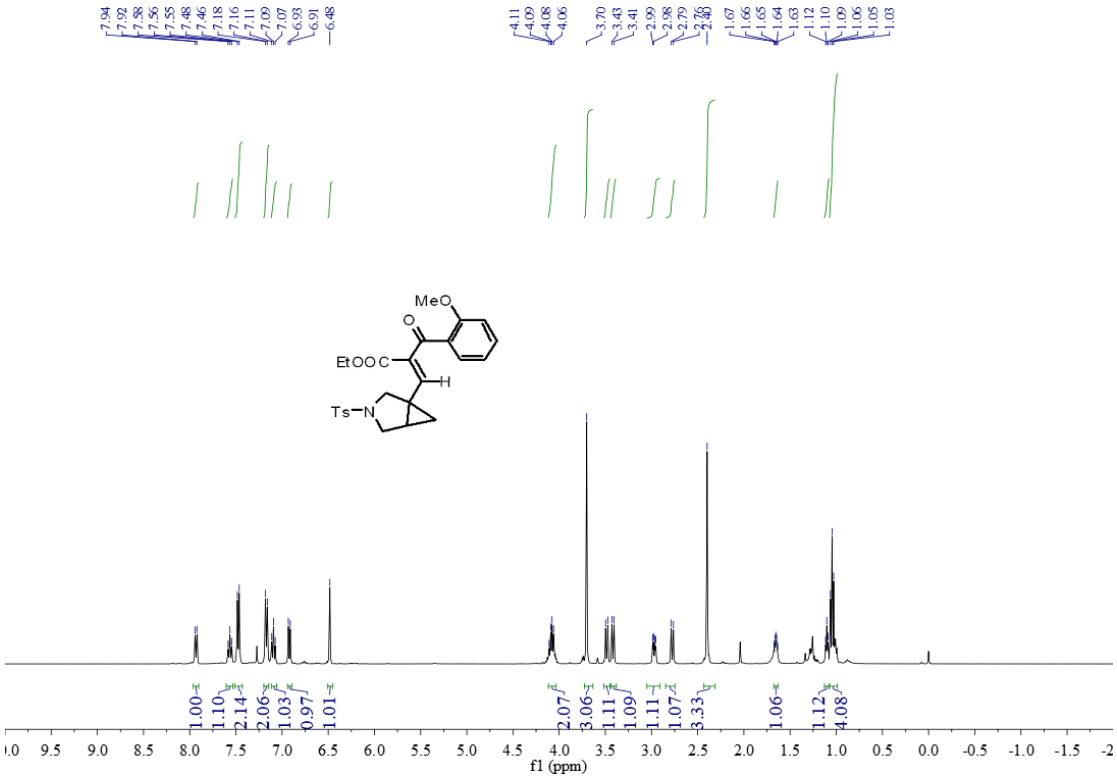
18) $^{1}$H NMR of ethyl(*E*)-2-(2-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1k** (400 MHz, $CDCl_3$)



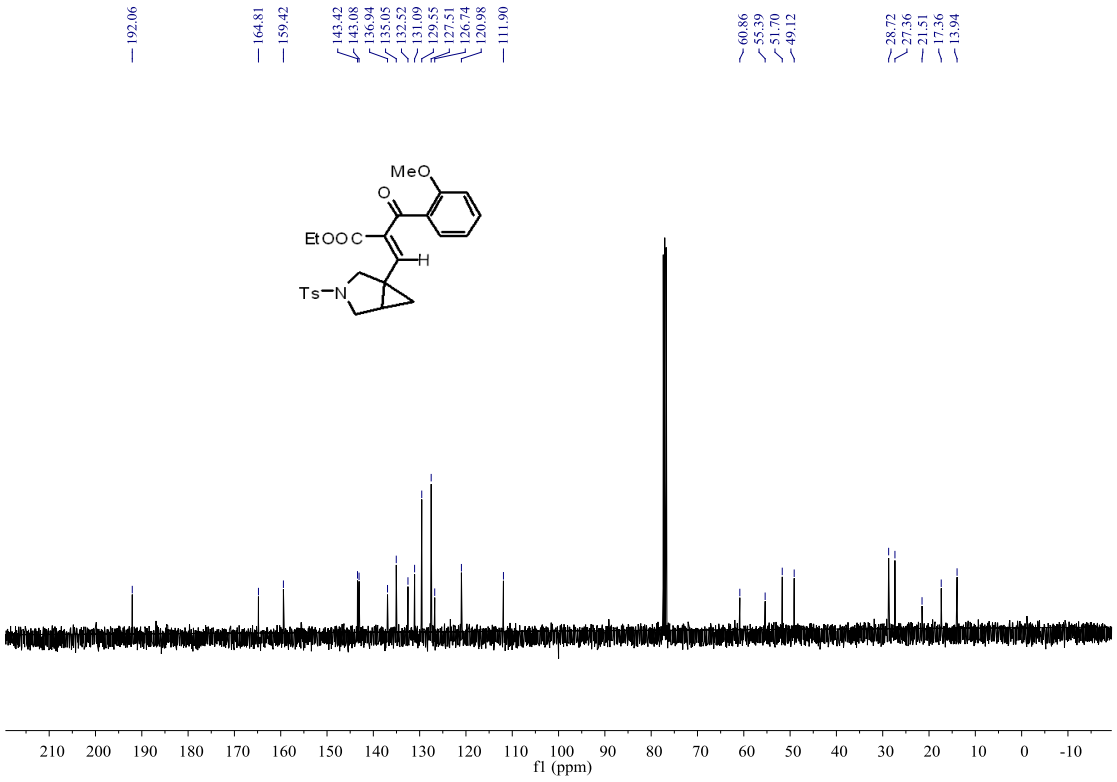

$^{13}$C NMR of ethyl (*E*)-2-(2-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*E*)-3-1k** (101 MHz, $CDCl_3$)



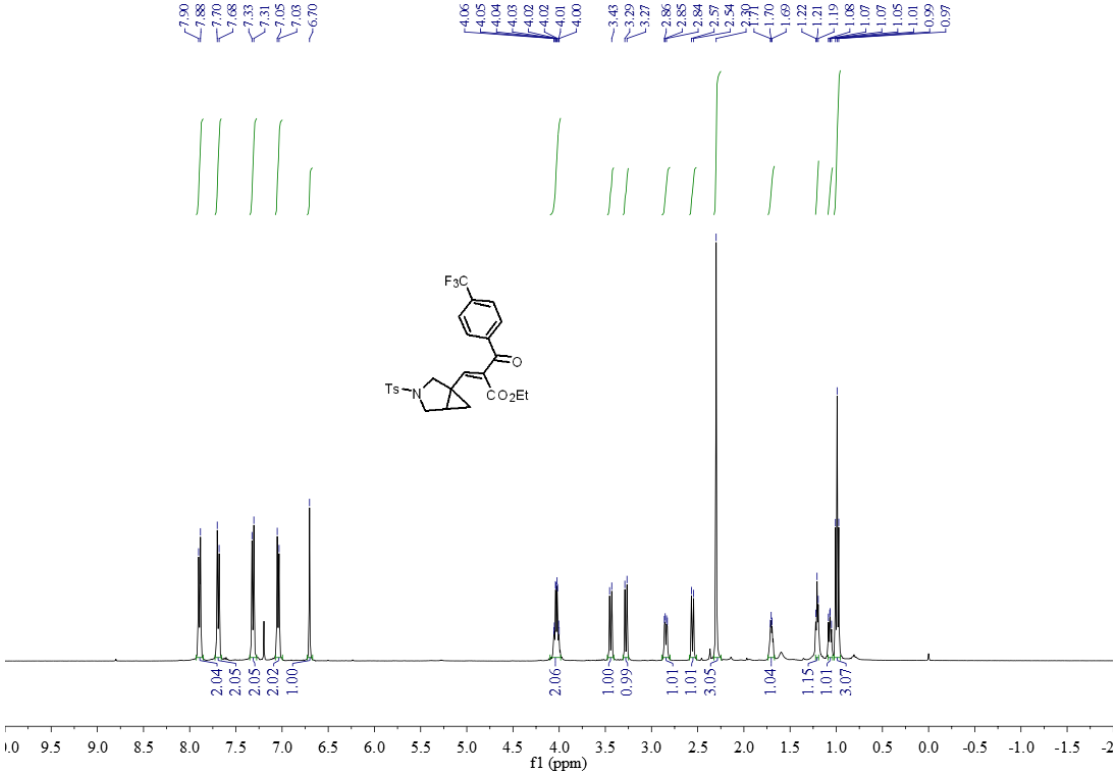
19) $^{1}$H NMR of ethyl (*Z*)-2-(2-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1k** (400 MHz, $CDCl_3$)



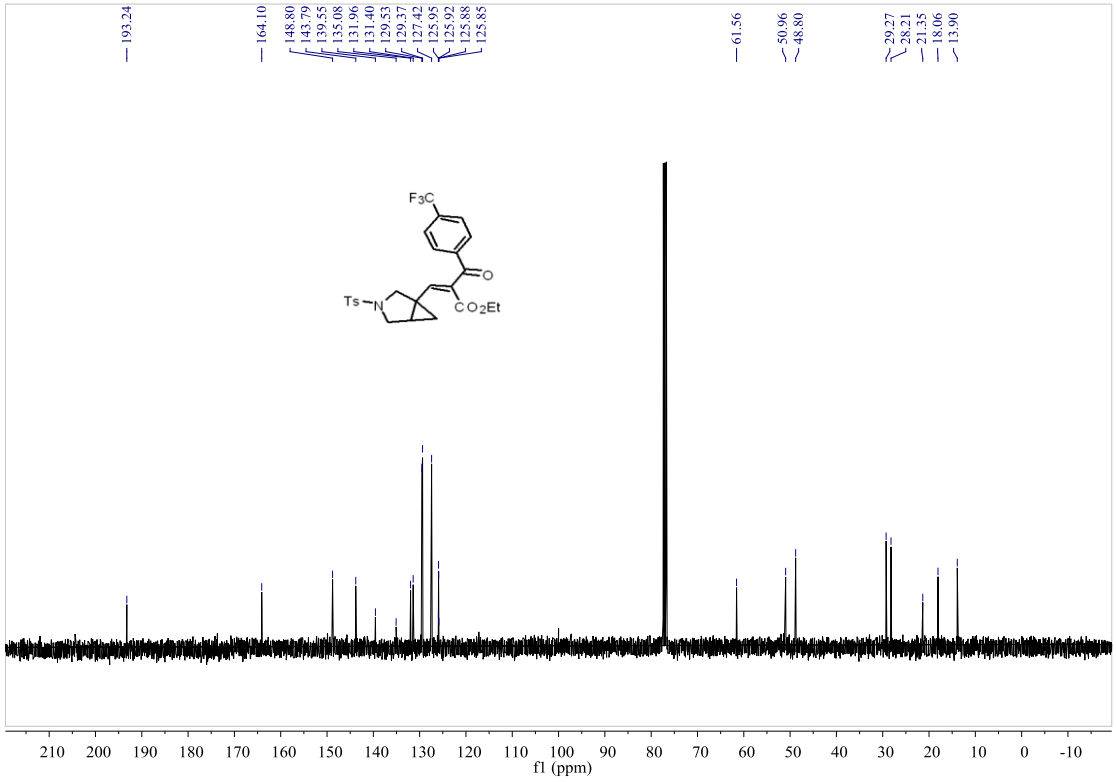

$^{13}$C NMR of ethyl (*Z*)-2-(2-methoxybenzoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1k** (101 MHz, $CDCl_3$)



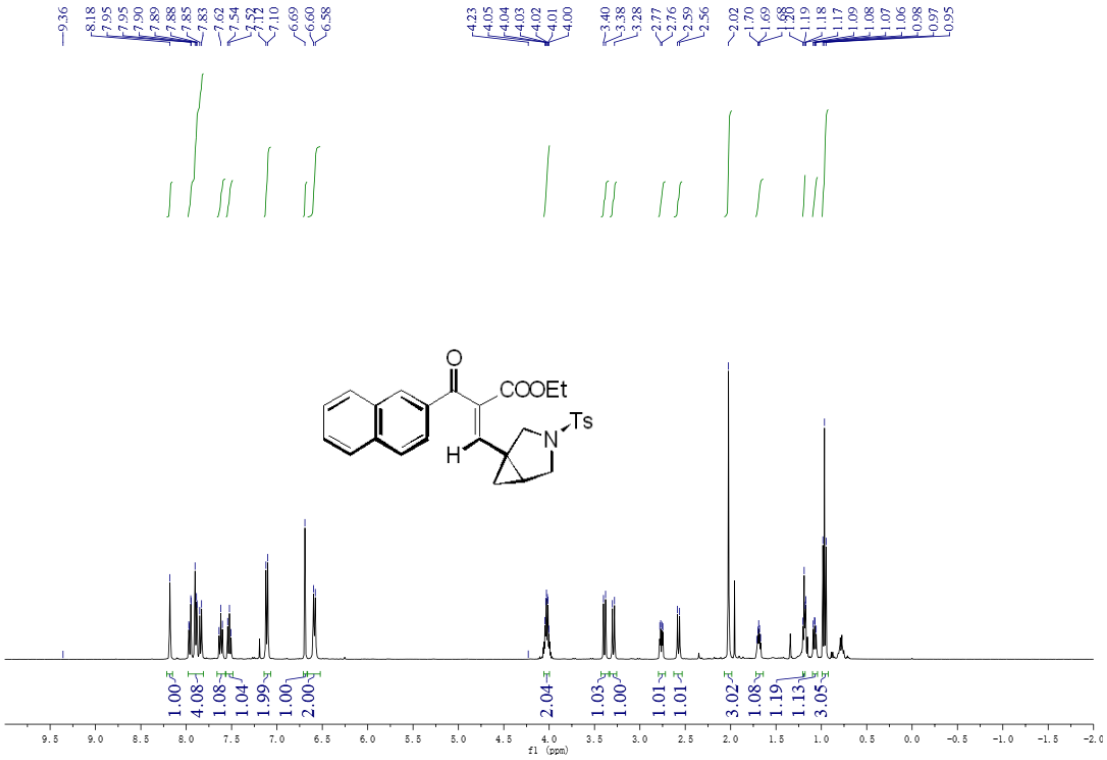
20) $^{1}$H NMR of ethyl (*Z*)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)-2-(4-(trifluoromethyl) benzoyl)acrylate **(*Z*)-3-1l** (400 MHz, $CDCl_3$)



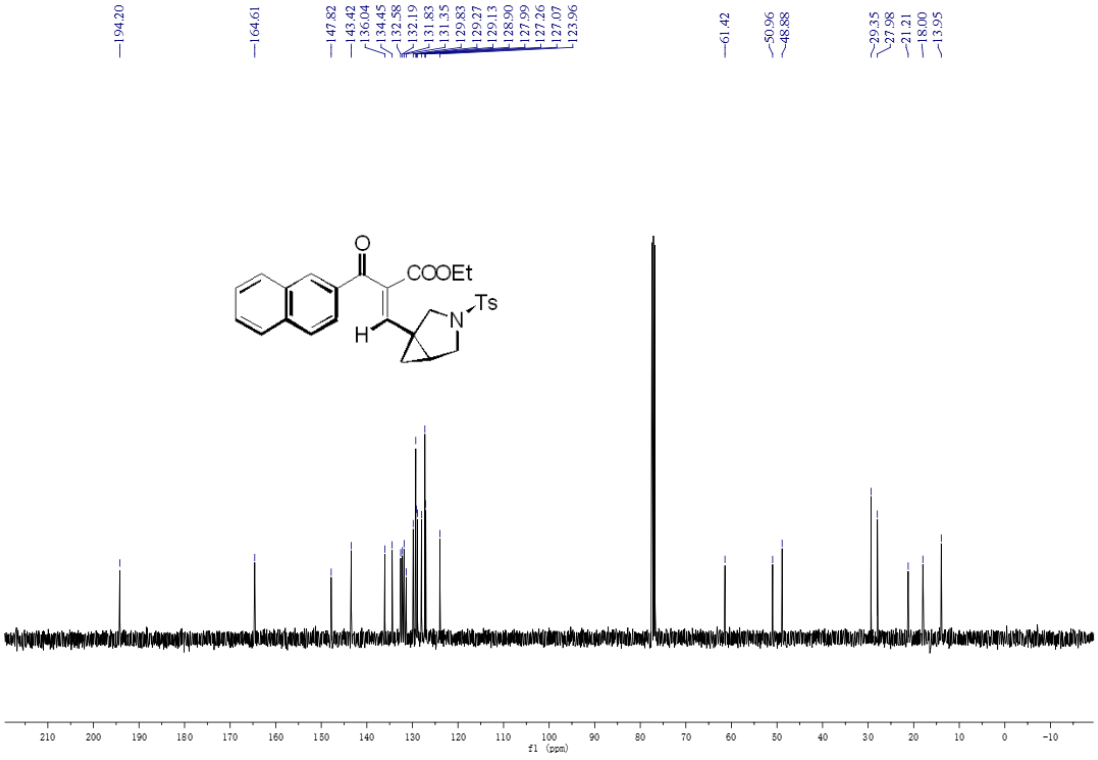

$^{13}$C NMR of ethyl (*Z*)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)-2-(4-(trifluoromethyl)benzoyl) acrylate **(*Z*)-3-1l** (101 MHz, $CDCl_3$)



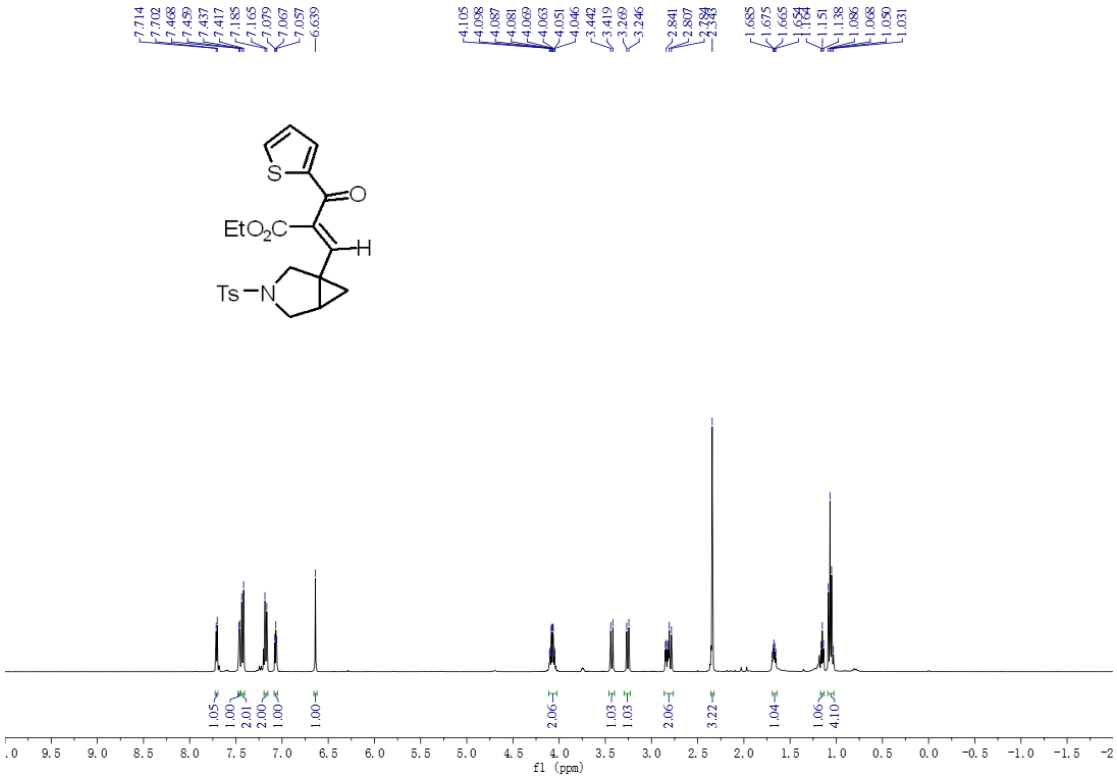
21) $^{1}$H NMR of ethyl (*Z*)-2-(2-naphthoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1m** (400 MHz, $CDCl_3$)



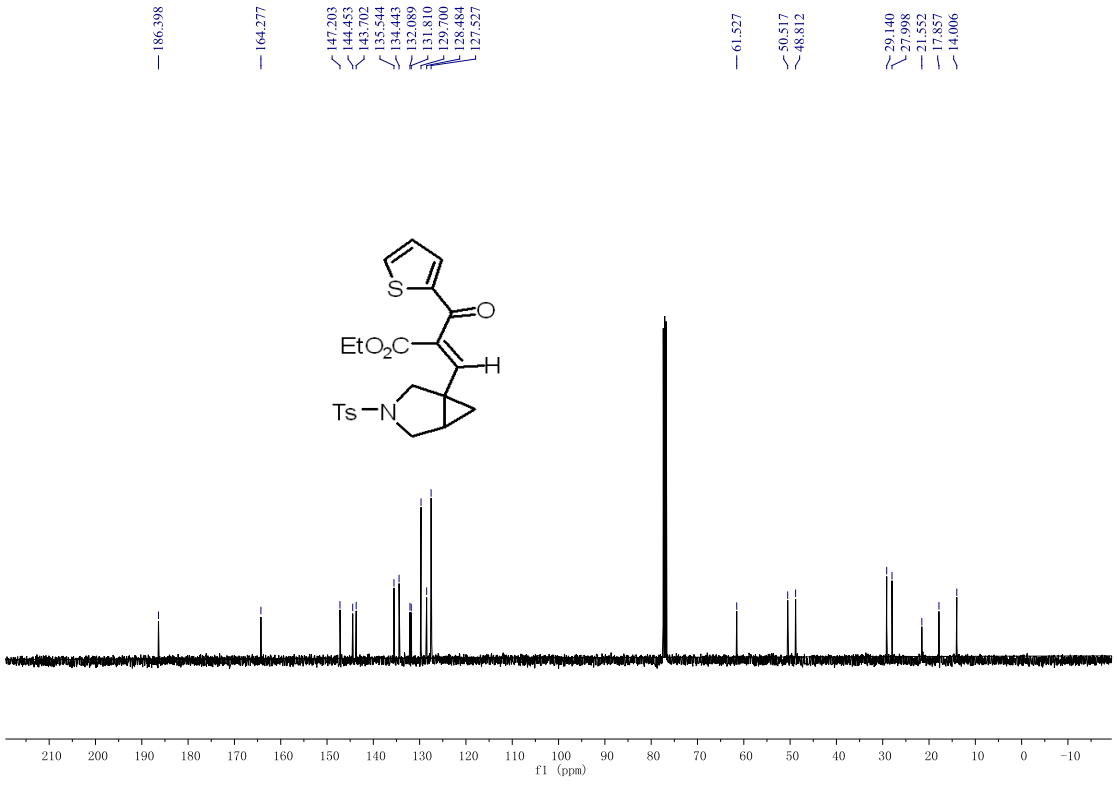

$^{13}$C NMR of ethyl (*Z*)-2-(2-naphthoyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1m** (101 MHz, $CDCl_3$)



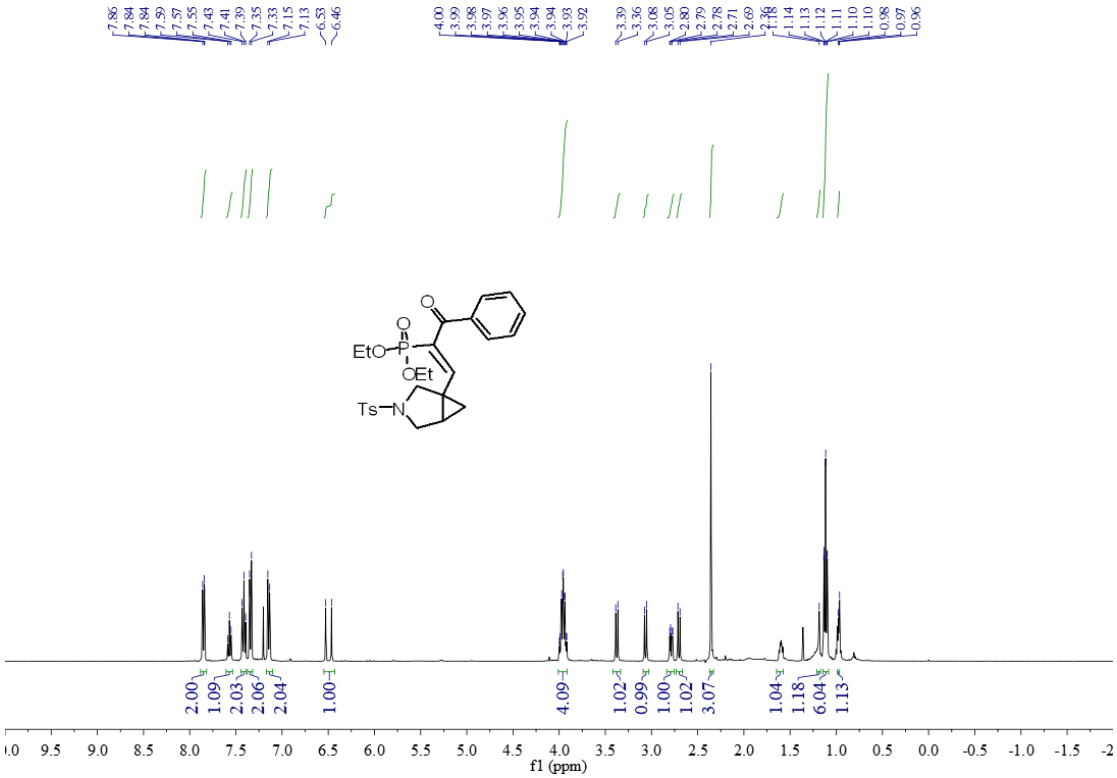
22) $^{1}$H NMR of ethyl (*Z*)-2-(thiophene-2-carbonyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl) acrylate **(*Z*)-3-1n** (400 MHz, $CDCl_3$)



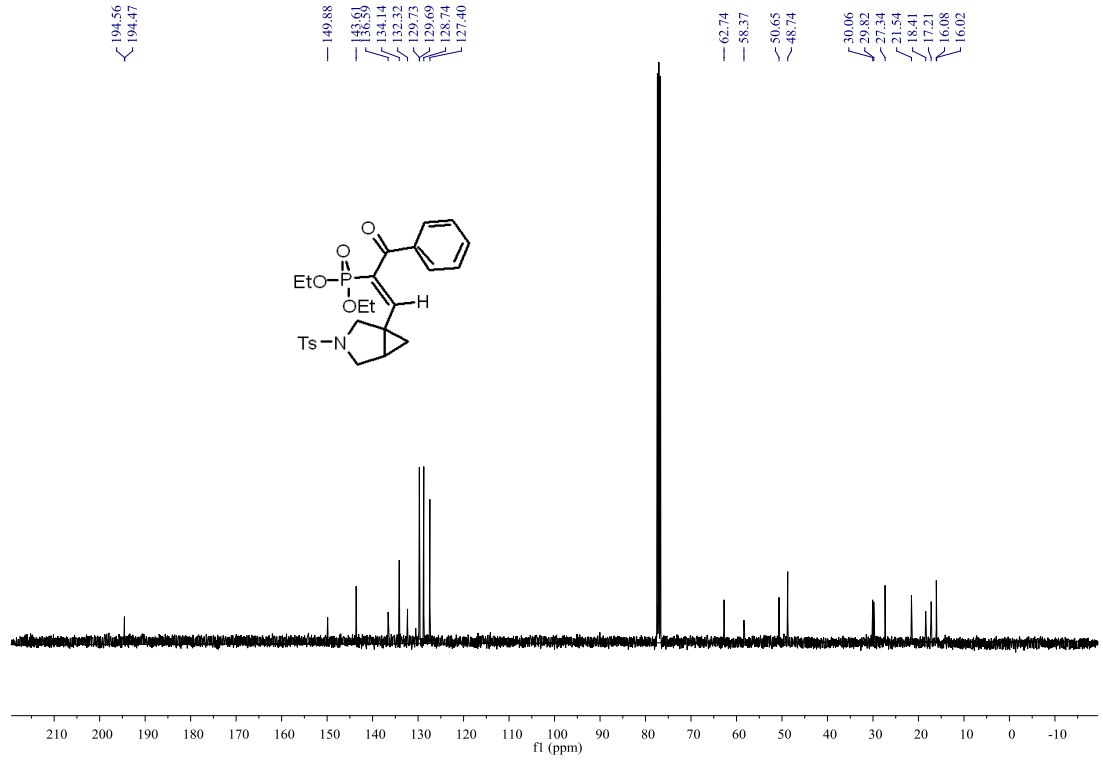

$^{13}$C NMR of ethyl (*Z*)-2-(thiophene-2-carbonyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl) acrylate **(*Z*)-3-1n** (101 MHz, $CDCl_3$)



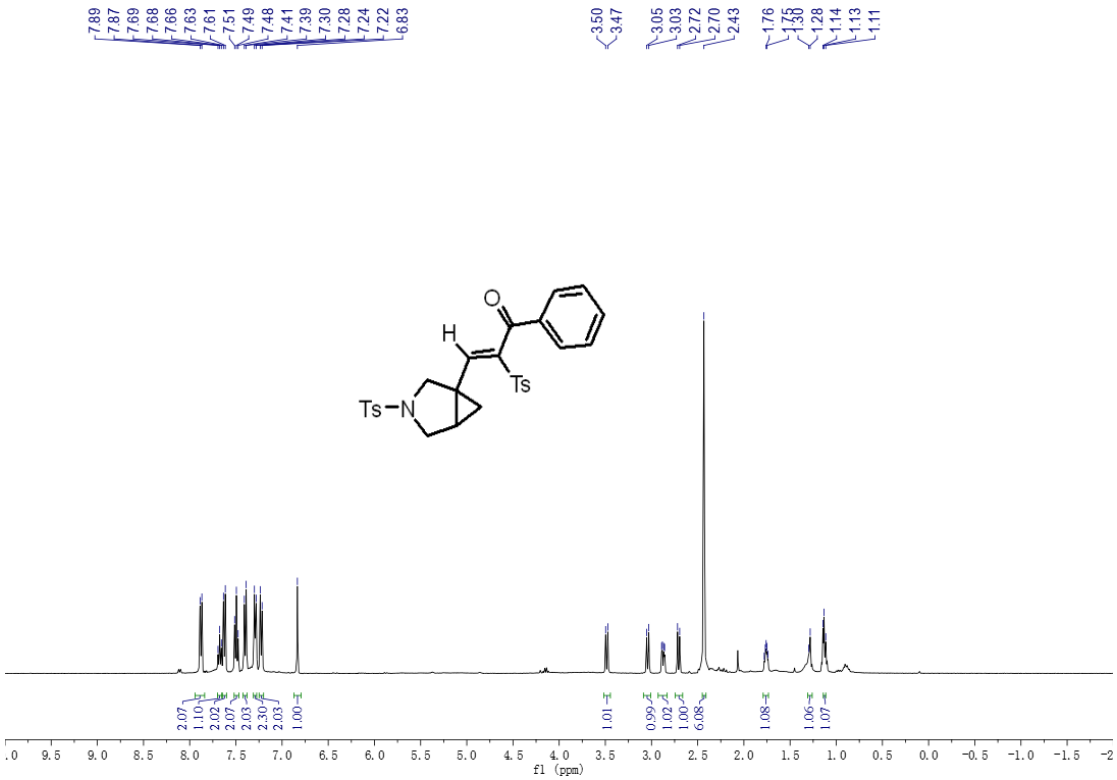
23) $^{1}$H NMR of diethyl (*Z*)-(3-oxo-3-phenyl-1-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)prop-1-en-2-yl)phosphonate **(*Z*)-3-1o** (400 MHz, $CDCl_3$)



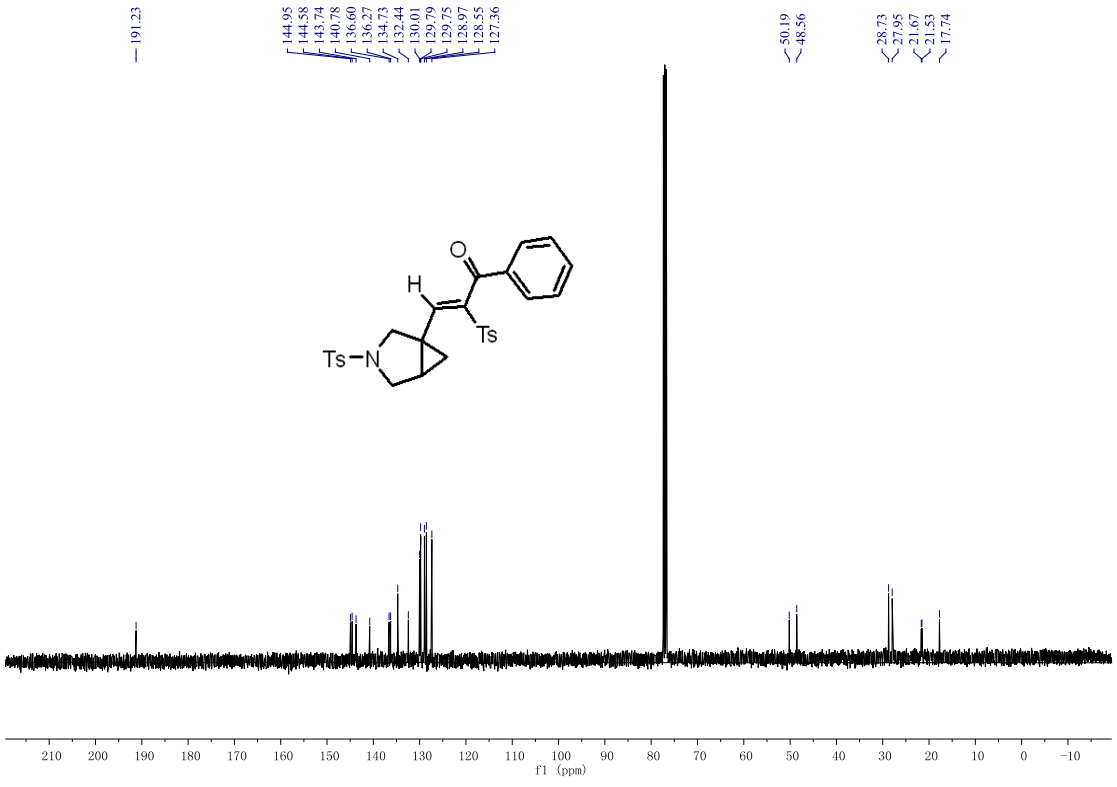

$^{13}$C NMR of diethyl (*Z*)-(3-oxo-3-phenyl-1-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)prop-1-en-2-yl)phosphonate **(*Z*)-3-1o** (101 MHz, $CDCl_3$)



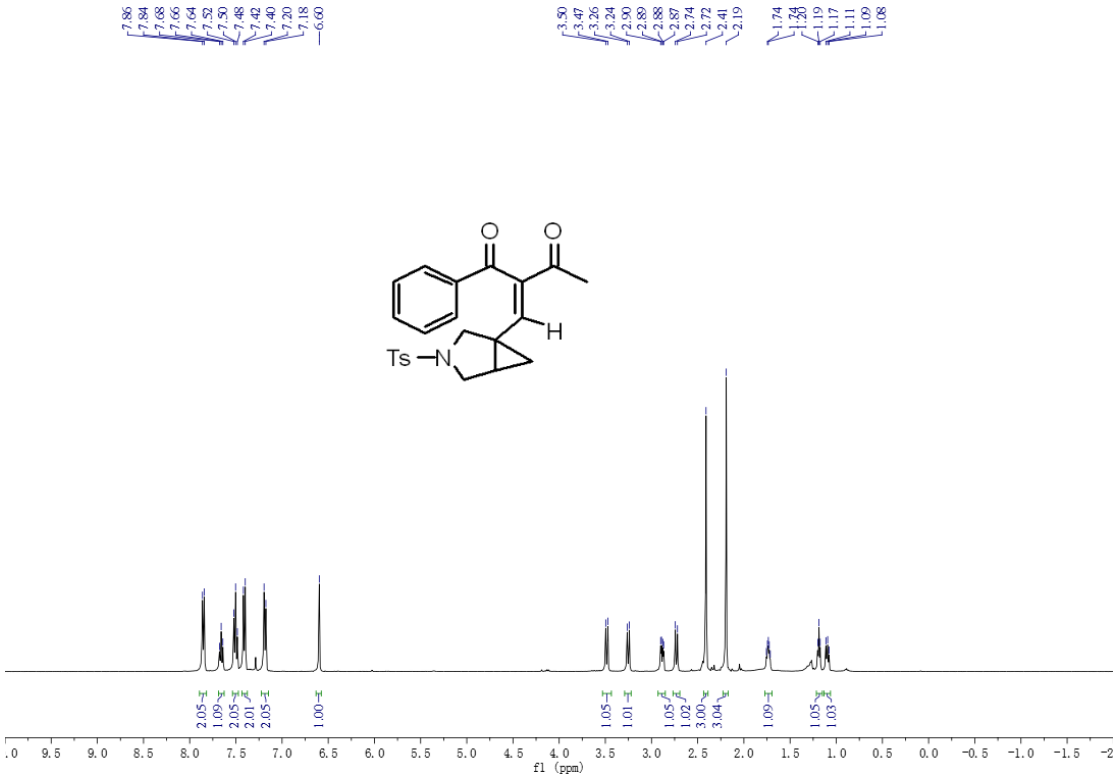
24) $^{1}$H NMR of (*Z*)-1-phenyl-2-tosyl-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)prop-2-en-1-one **(*Z*)-3-1p** (400 MHz, $CDCl_3$)



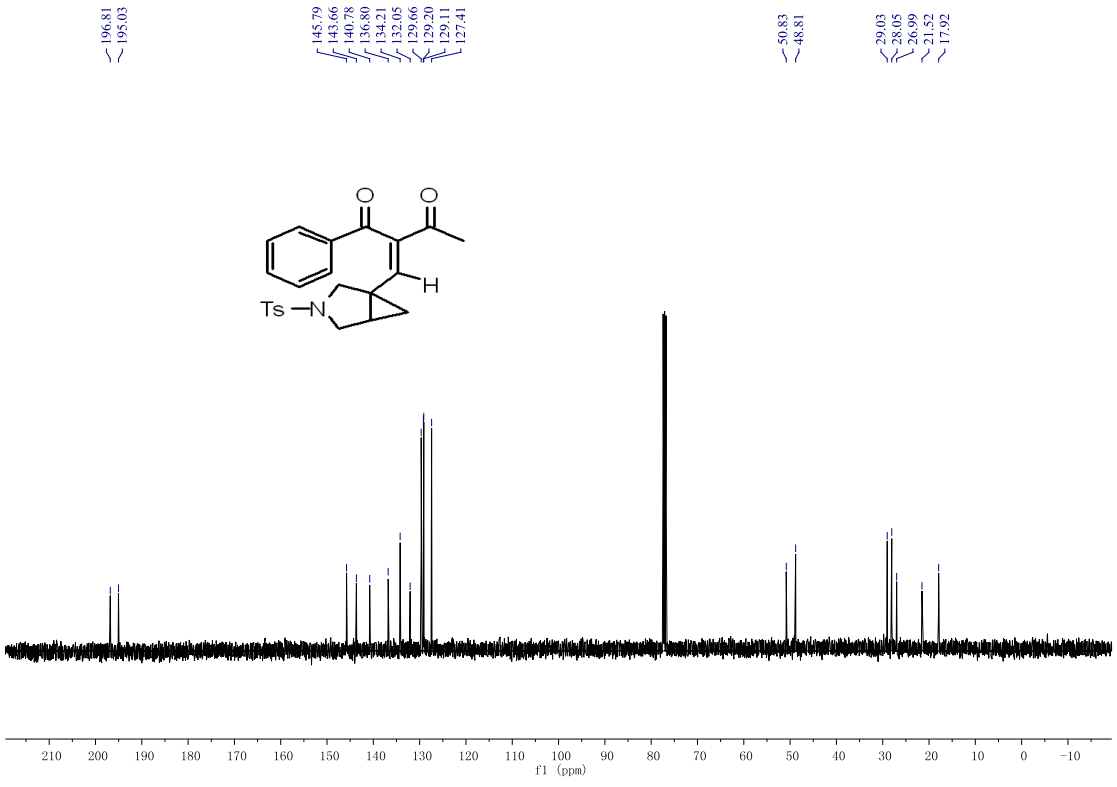

$^{13}$C NMR of (*Z*)-1-phenyl-2-tosyl-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)prop-2-en-1-one **(*Z*)-3-1p** (101 MHz, $CDCl_3$)



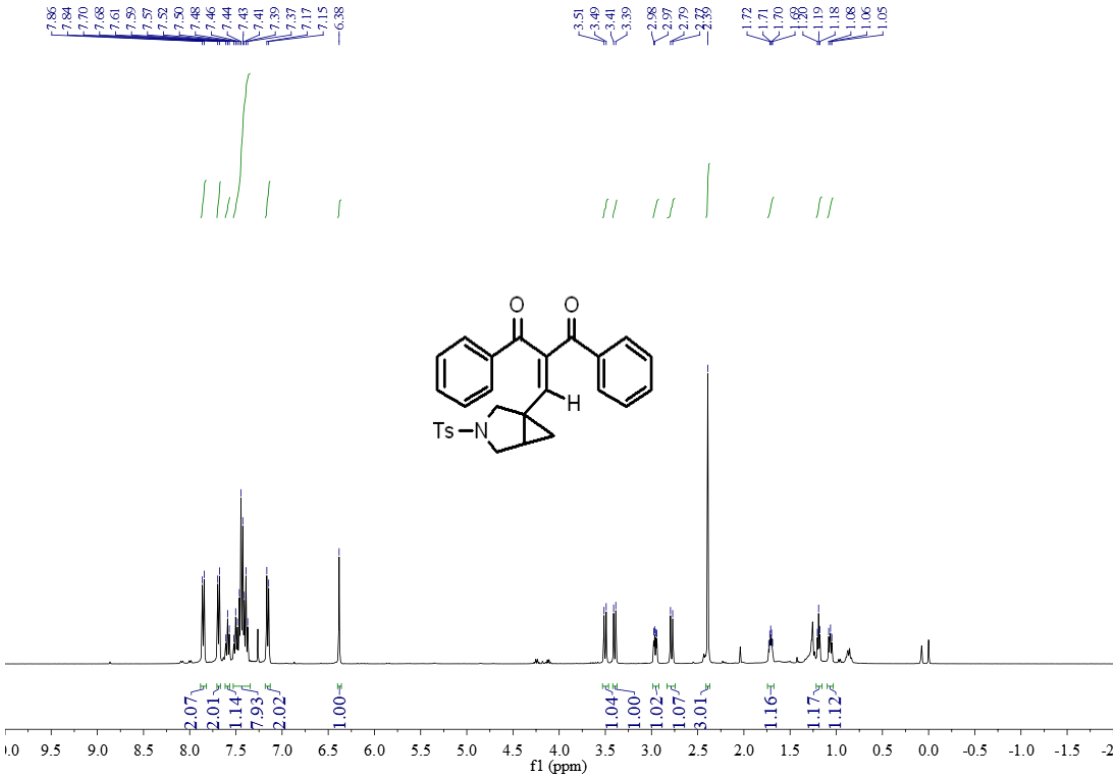
25) $^{1}$H NMR of (*Z*)-1-phenyl-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butane-1,3-dione **(*Z*)-3-1q** (400 MHz, $CDCl_3$)



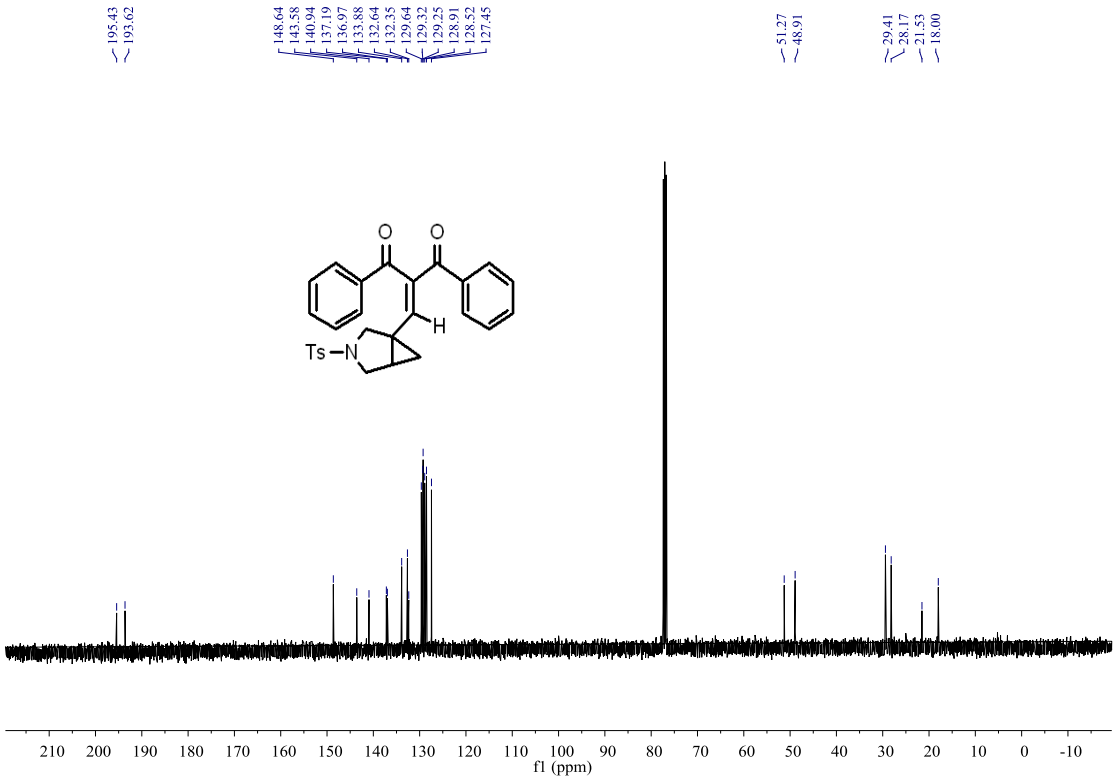

$^{13}$C NMR of (*Z*)-1-phenyl-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)butane-1,3-dione **(*Z*)-3-1q** (101 MHz, $CDCl_3$)



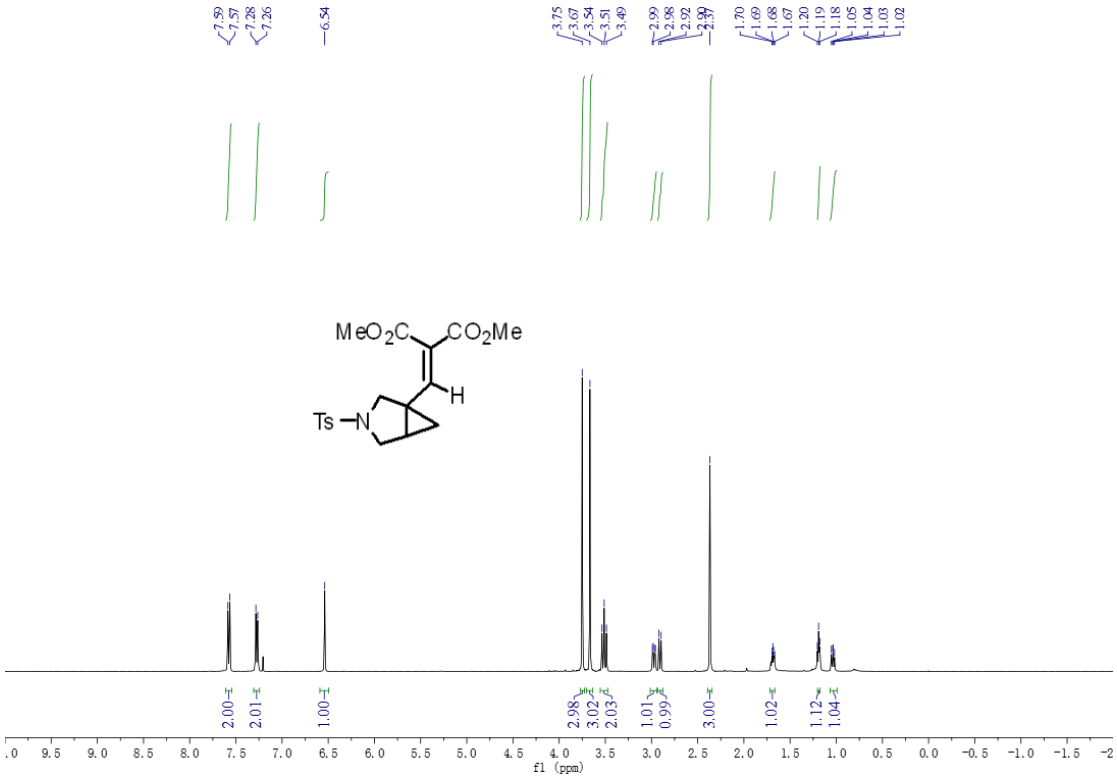
26) $^{1}$H NMR of 1,3-diphenyl-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)propane-1,3-dione **(3-1r)** (400 MHz, $CDCl_3$)



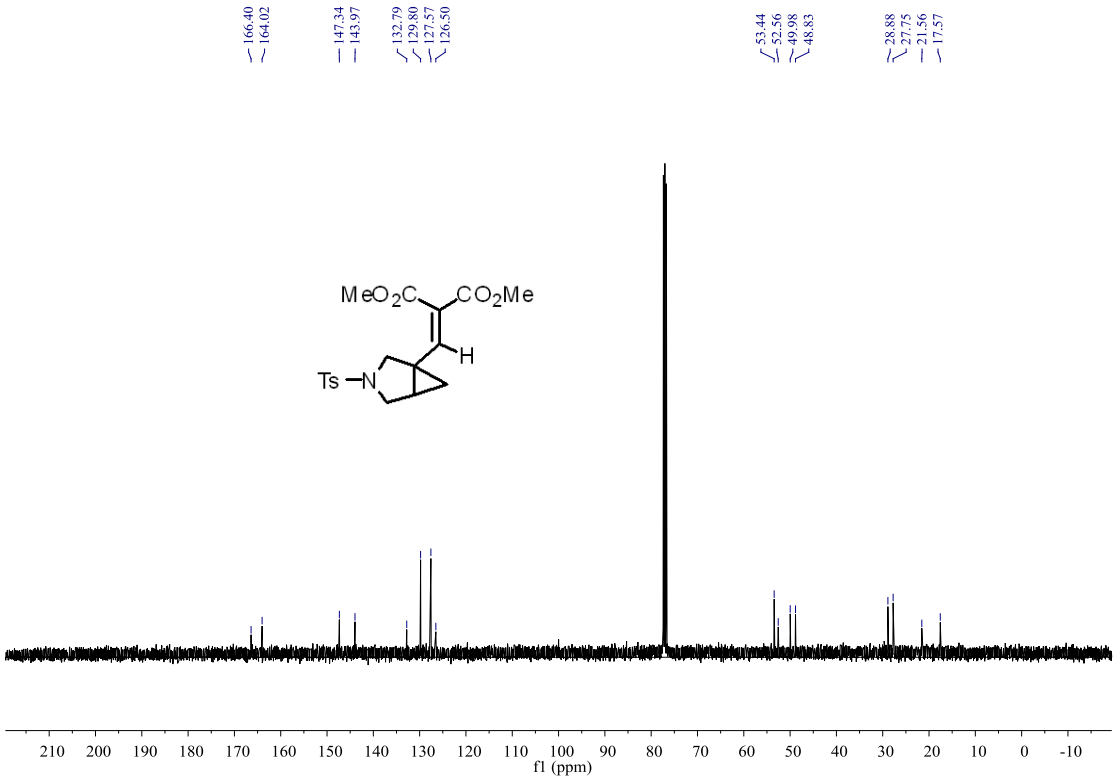

$^{13}$C NMR of 1,3-diphenyl-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)propane-1,3-dione **(3-1r)** (101 MHz, $CDCl_3$)



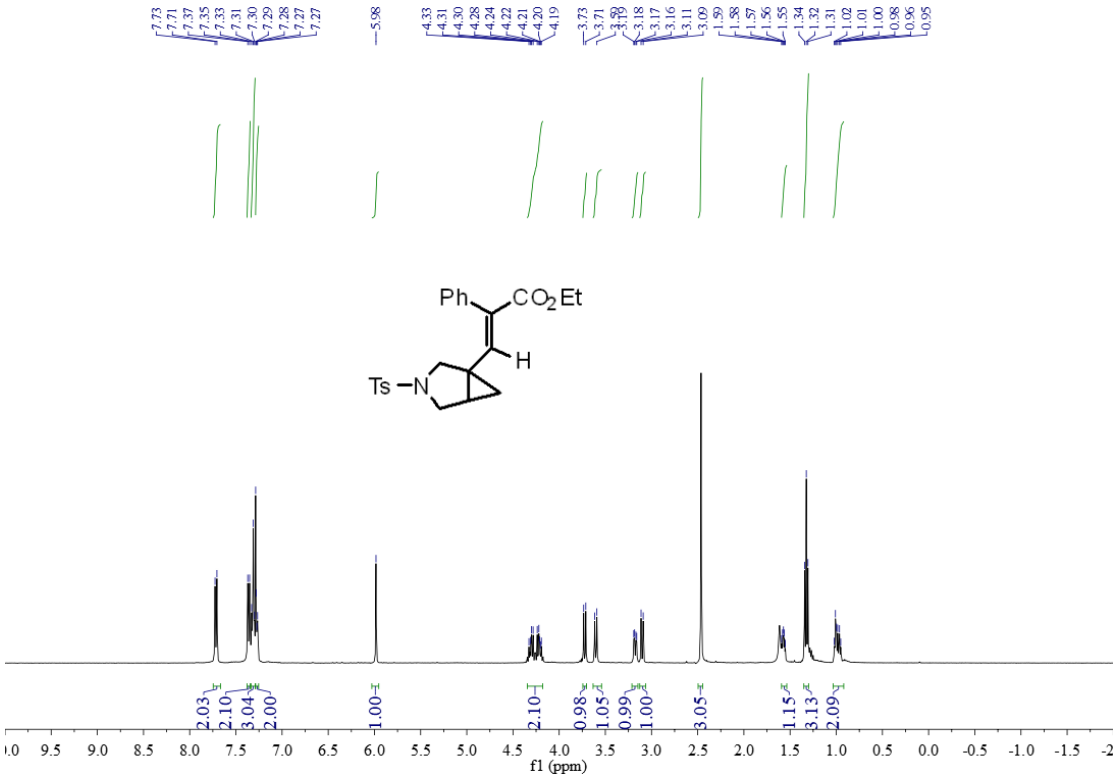
27) $^{1}$H NMR of dimethyl 2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)malonate **(3-1s)** (400 MHz, $CDCl_3$)



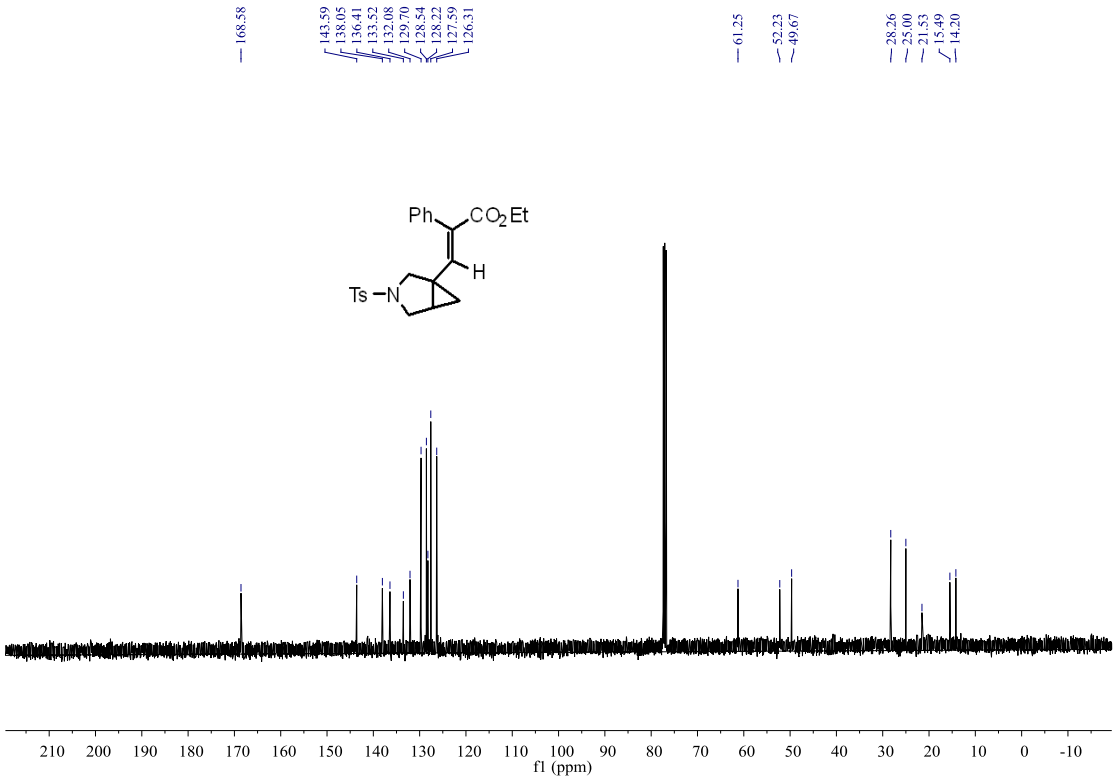

$^{13}$C NMR of dimethyl 2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)malonate **(3-1s)** (101 MHz, $CDCl_3$)



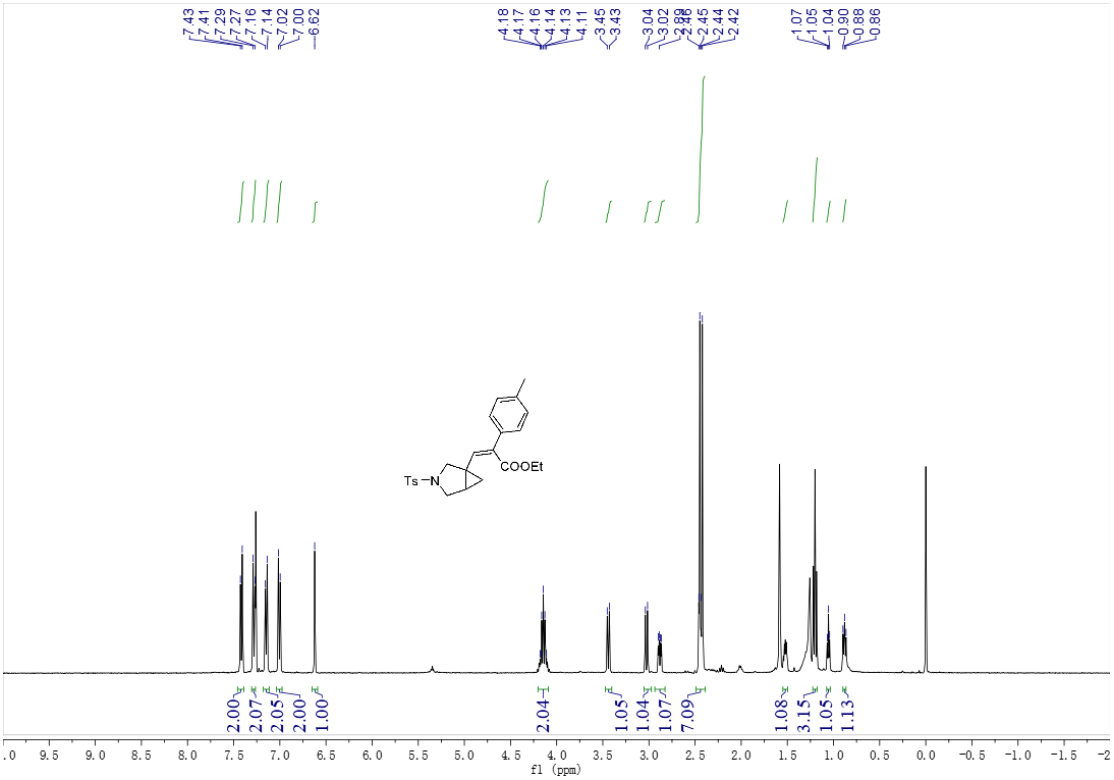
28) $^{1}$H NMR of ethyl (*Z*)-2-phenyl-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1t** (400 MHz, $CDCl_3$)



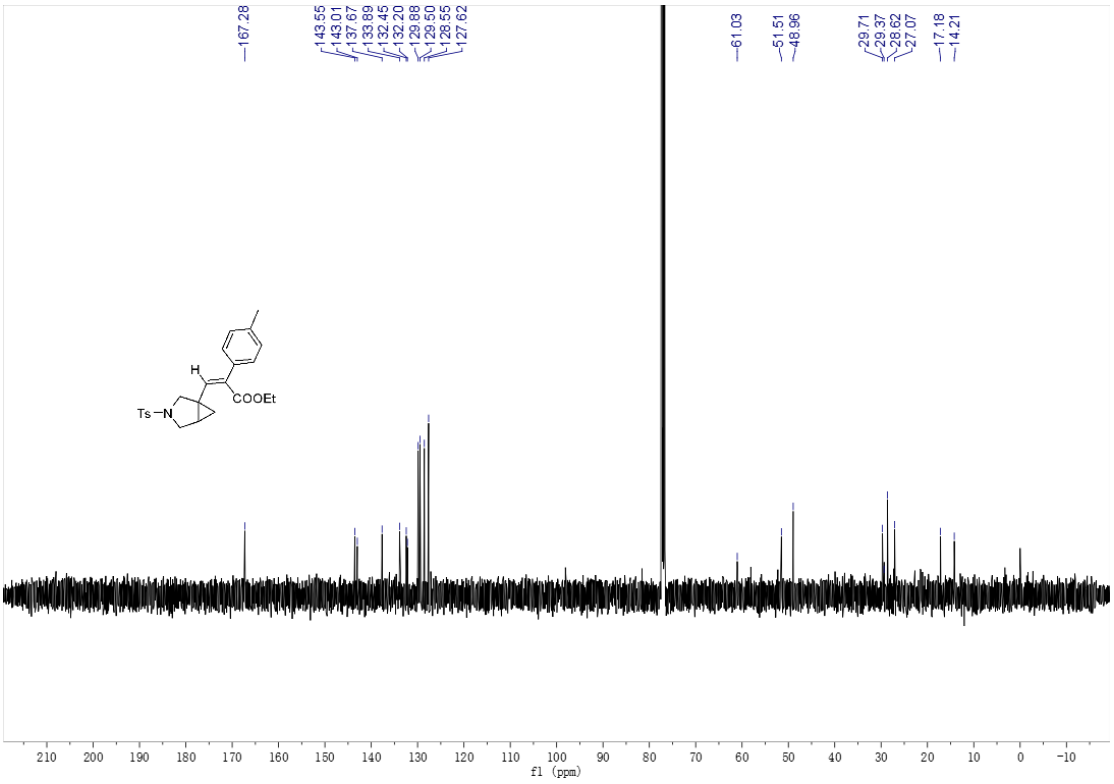

$^{13}$C NMR of ethyl (*Z*)-2-phenyl-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(*Z*)-3-1t** (101 MHz, $CDCl_3$)



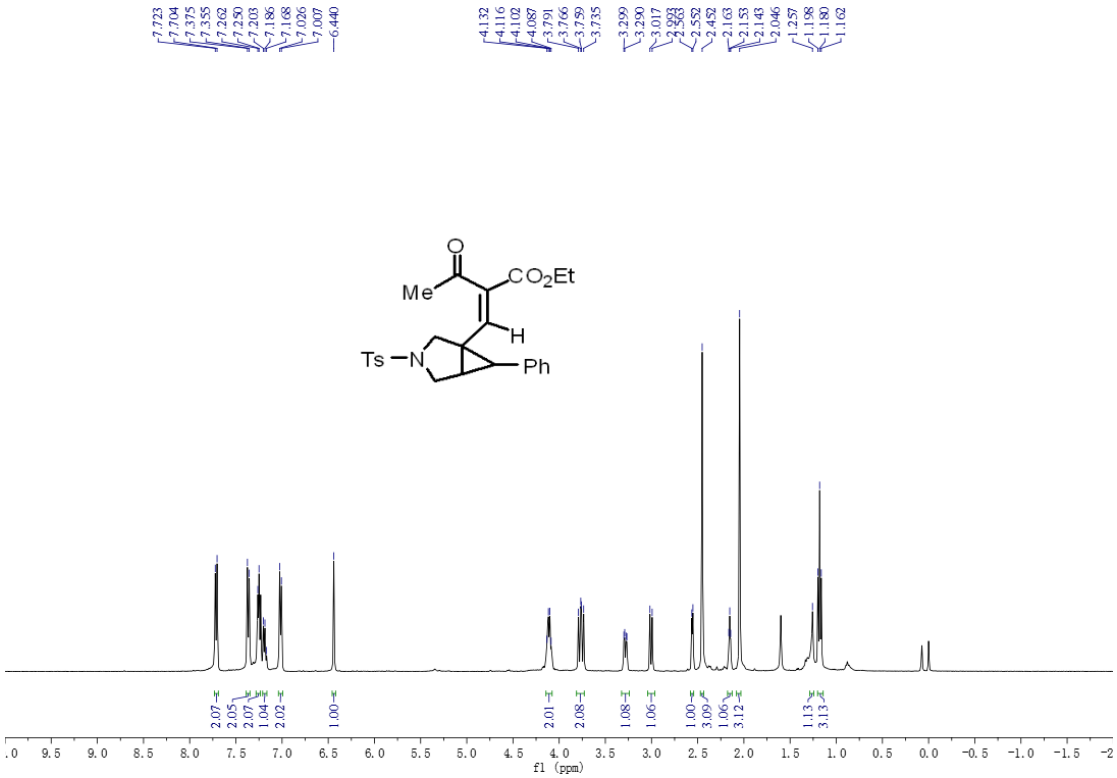
29) $^{1}$H NMR of ethyl (Z)-2-(p-tolyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(Z)-3-1u** (400 MHz, $CDCl_3$)



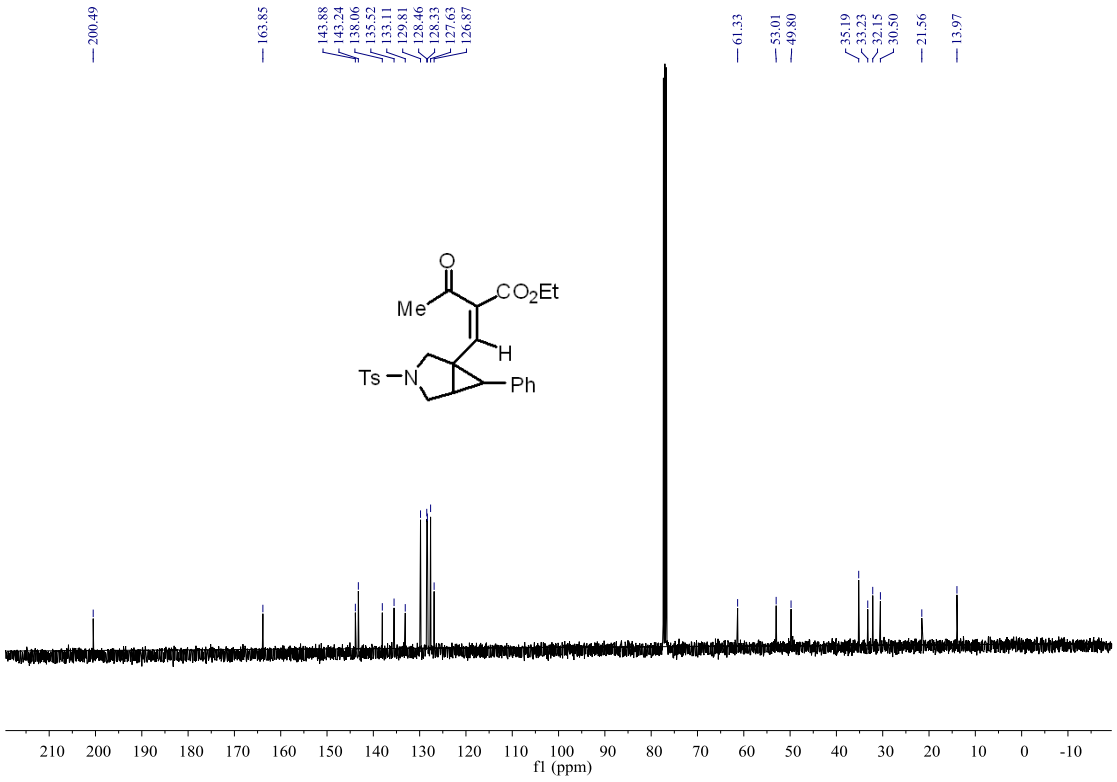

$^{13}$C NMR of ethyl (Z)-2-(p-tolyl)-3-(3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate **(Z)-3-1u** (400 MHz, $CDCl_3$)



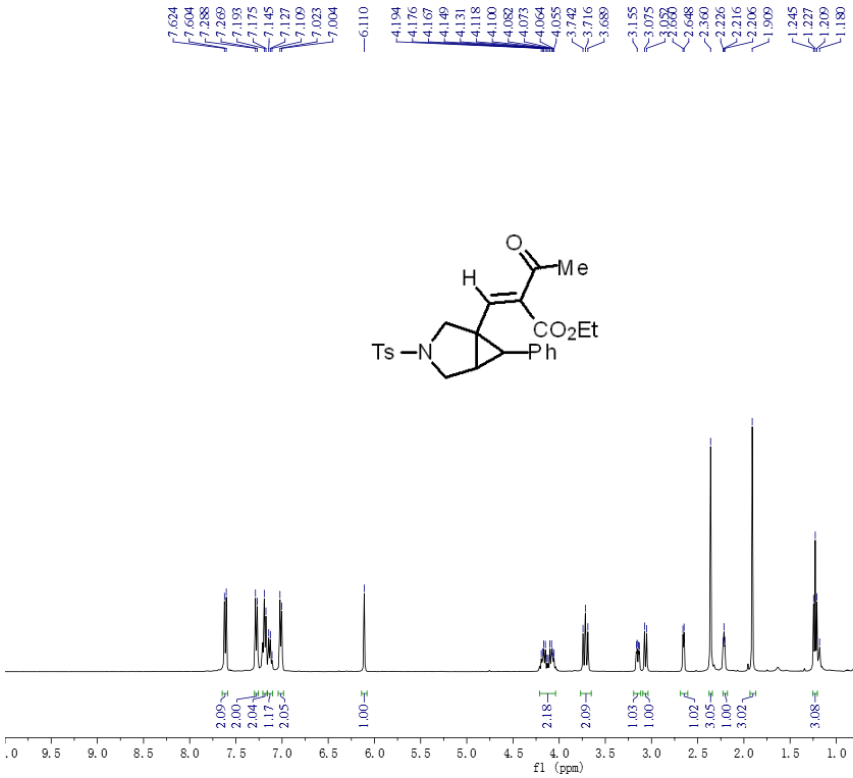
30) $^{1}$H NMR of ethyl (*E*)-3-oxo-2-((6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene) butanoate **(*E*)-3-2a** (400 MHz, $CDCl_3$)



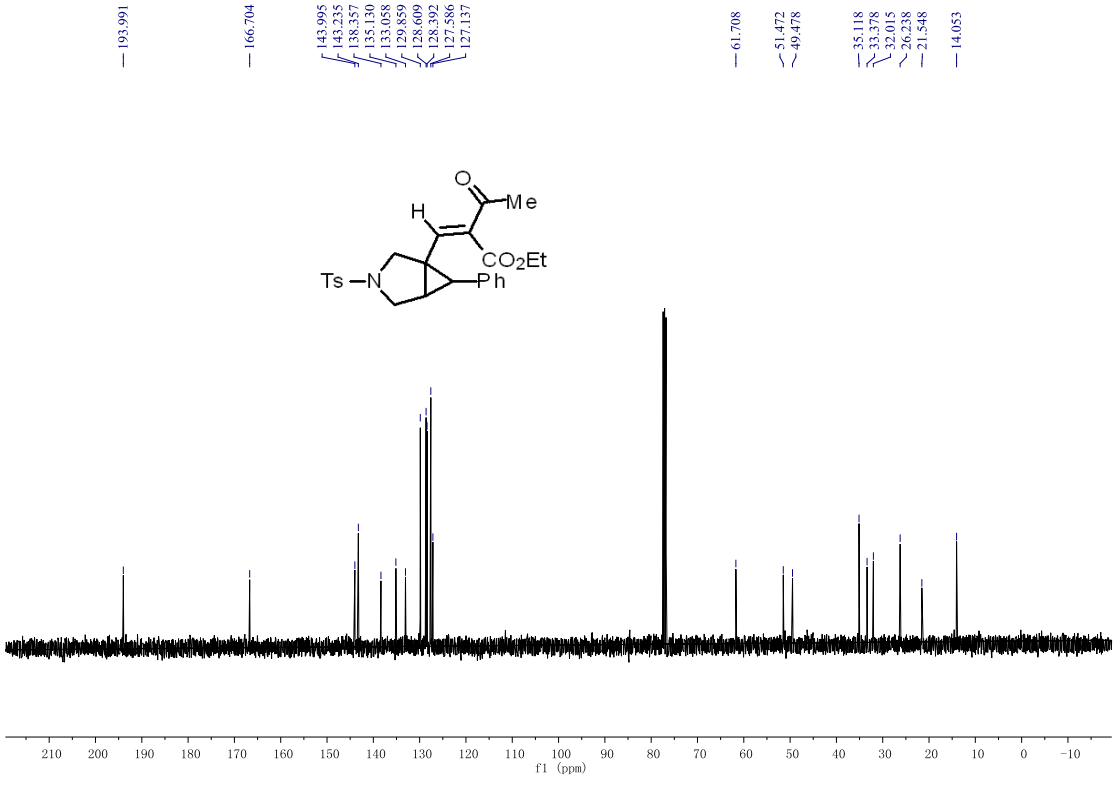

$^{13}$C NMR of ethyl (*E*)-3-oxo-2-((6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene) butanoate **(*E*)-3-2a** (101 MHz, $CDCl_3$)



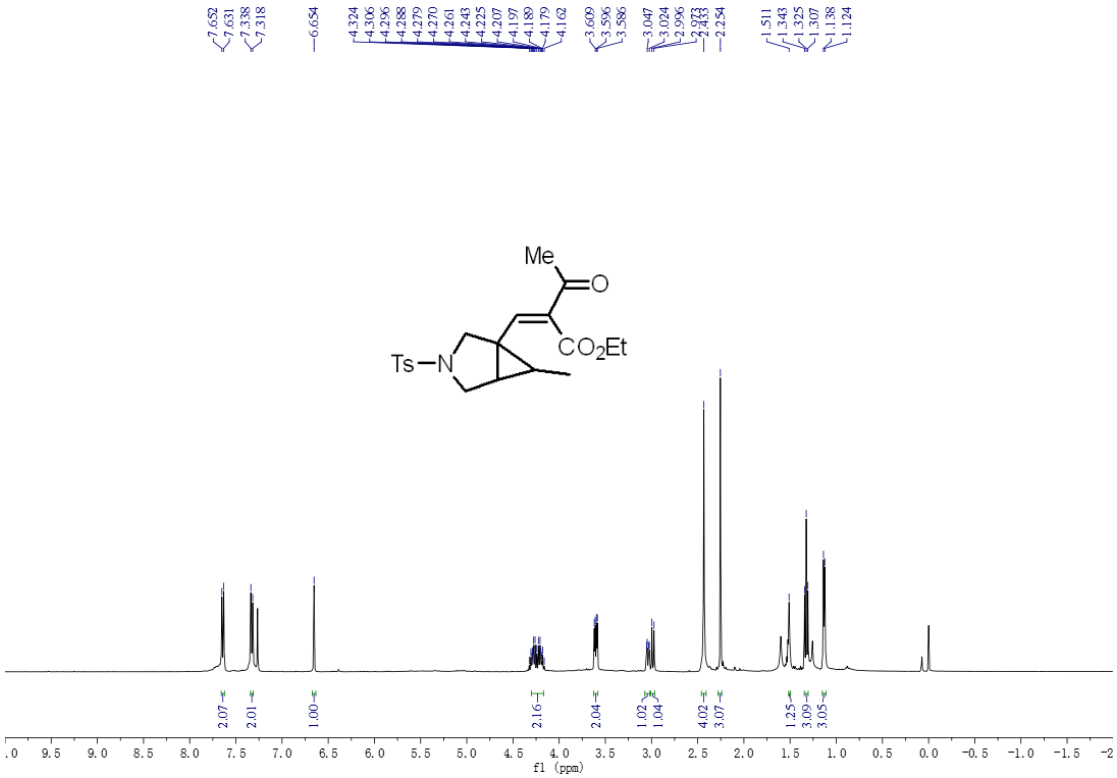
31) $^{1}$H NMR of ethyl (*Z*)-3-oxo-2-((6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene) butanoate **(*Z*)-3-2a** (400 MHz, $CDCl_3$)



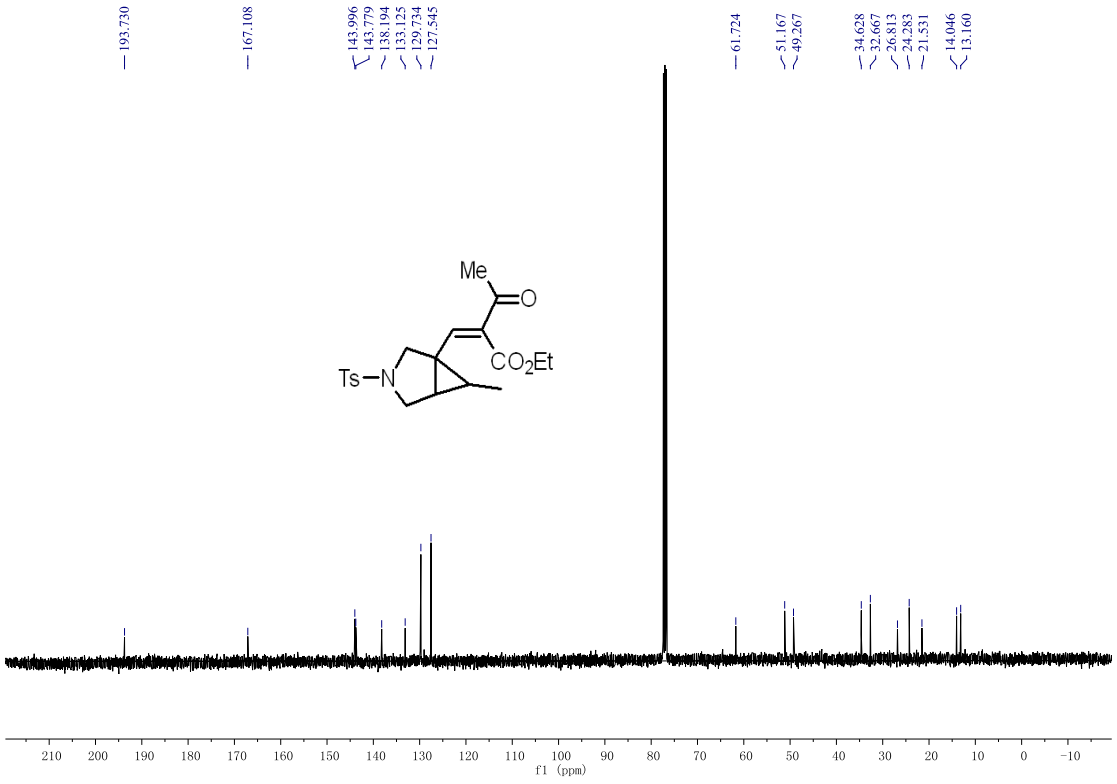

$^{13}$C NMR of ethyl (*Z*)-3-oxo-2-((6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene) butanoate **(*Z*)-3-2a** (101 MHz, $CDCl_3$)



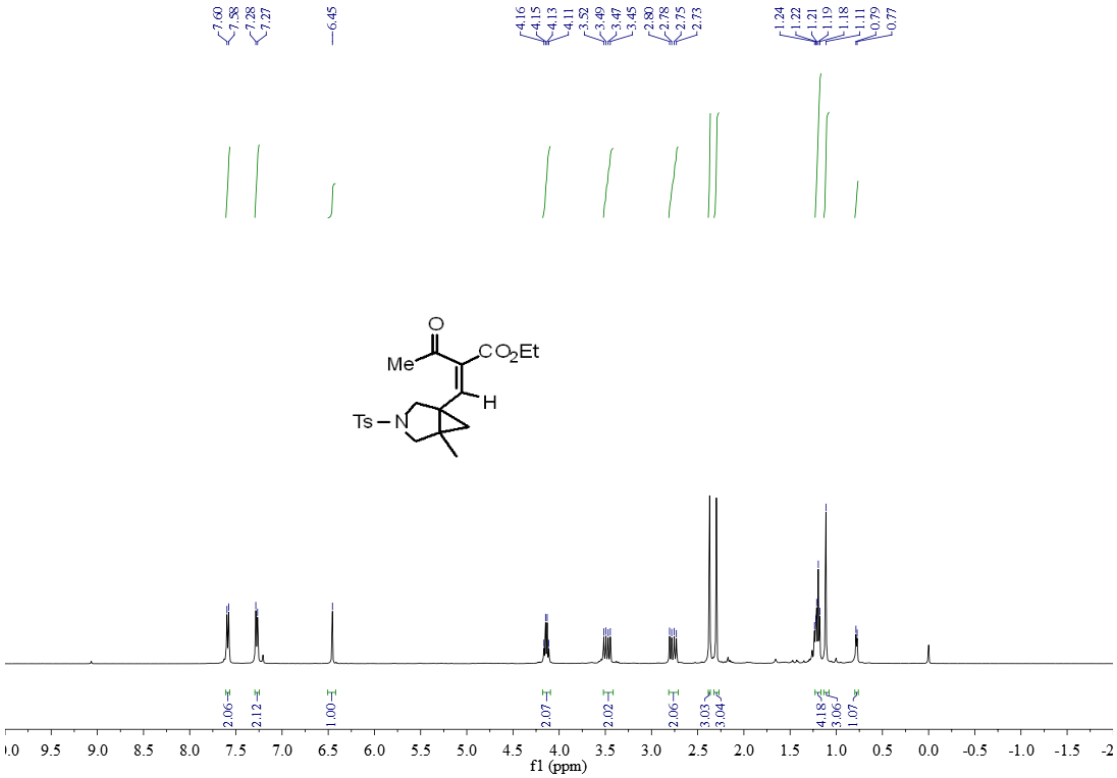
32) $^{1}$H NMR of ethyl (*Z*)-2-((6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)-3-oxobutanoate **(*Z*)-3-2b** (400 MHz, $CDCl_3$)



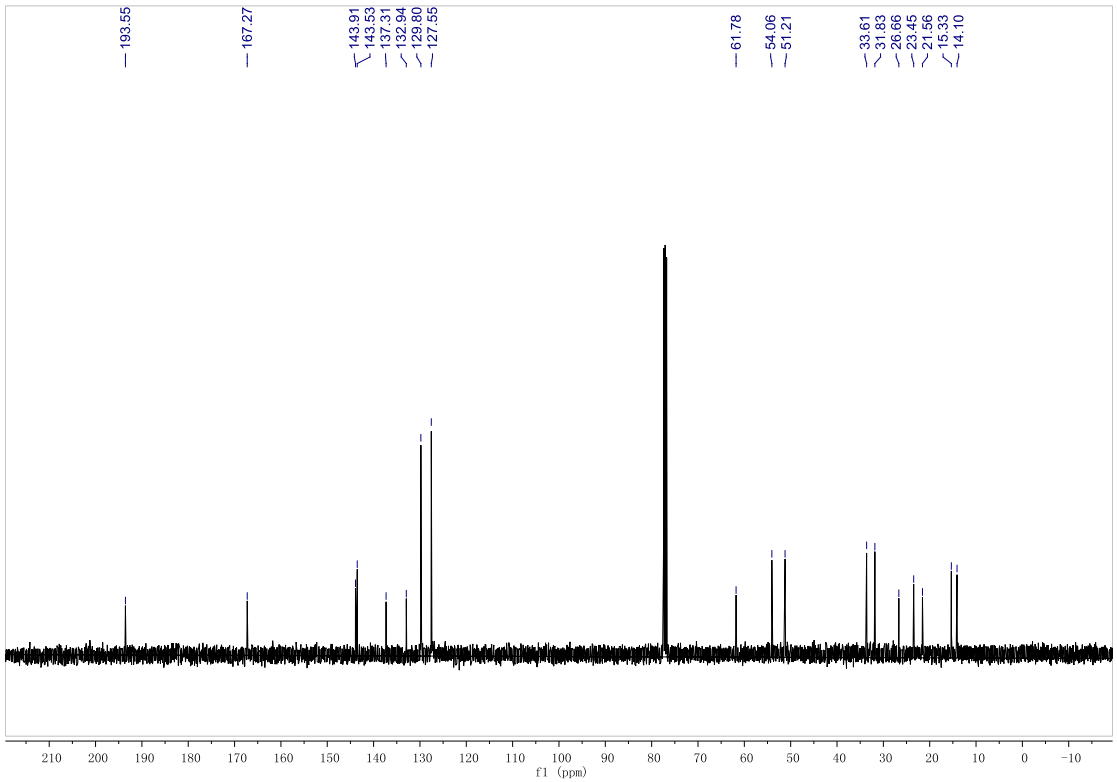

$^{13}$C NMR of ethyl (*Z*)-2-((6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)-3-oxobutanoate **(*Z*)-3-2b** (101 MHz, $CDCl_3$)



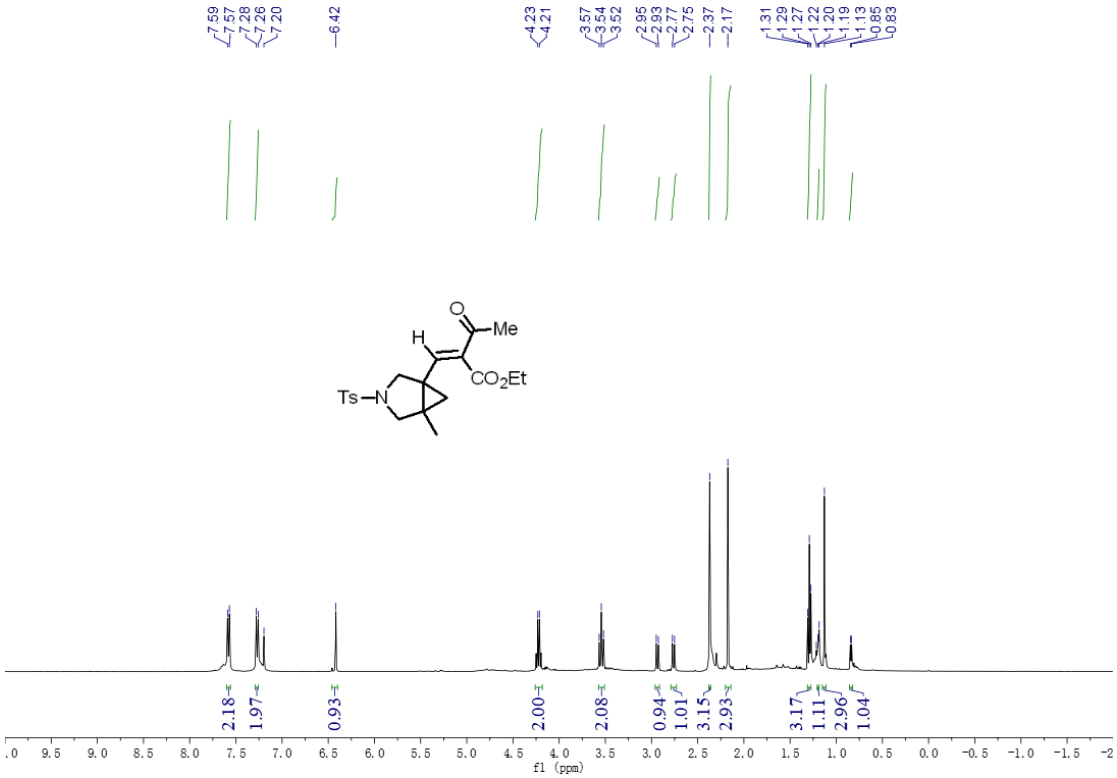
33) $^{1}$H NMR of ethyl (*E*)-2-((5-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)-3-oxobutanoate **(*E*)-3-2c** (400 MHz, $CDCl_3$)



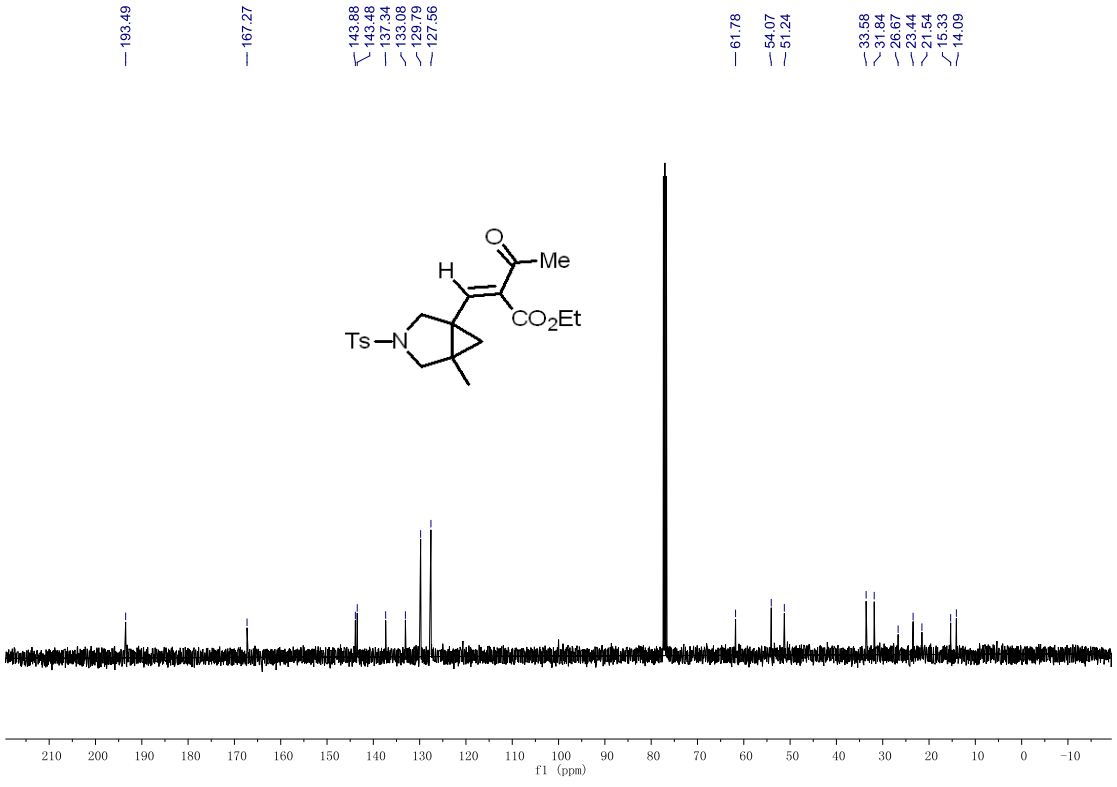

$^{13}$C NMR of ethyl (*E*)-2-((5-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)-3-oxobutanoate **(*E*)-3-2c** (101 MHz, $CDCl_3$)



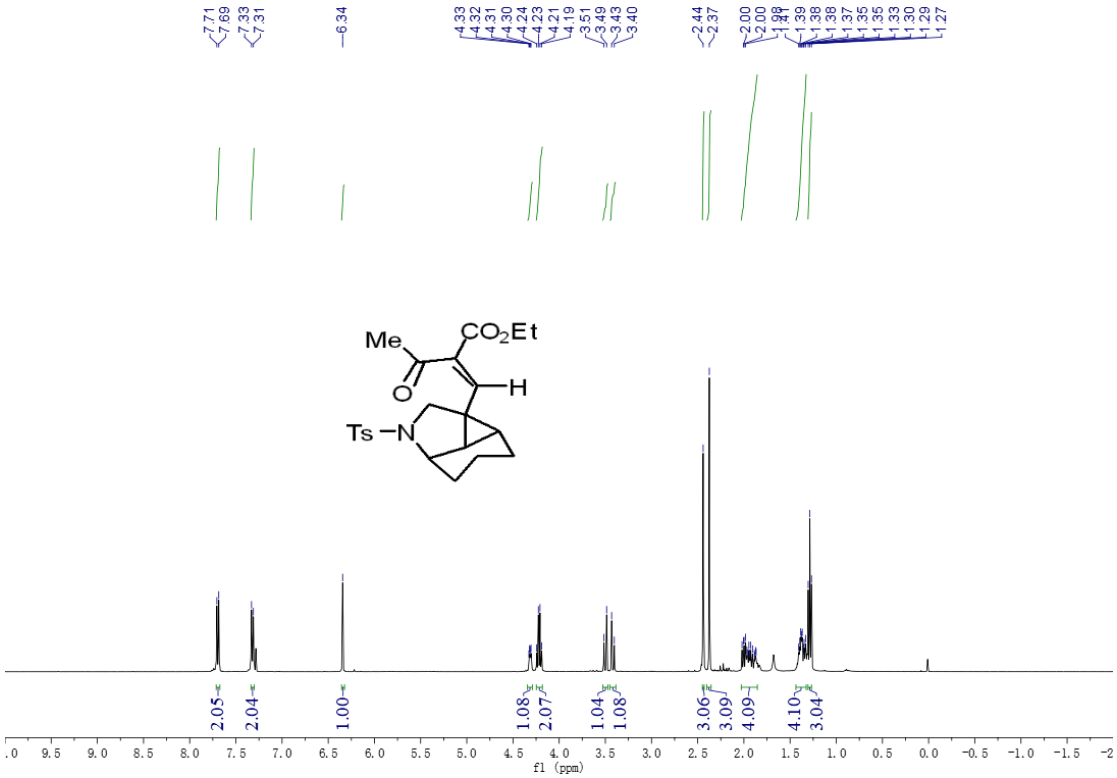
34) $^{1}$H NMR of ethyl (*Z*)-2-((5-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)-3-Oxobutanoate **(3-2c)**(400 MHz, $CDCl_3$)



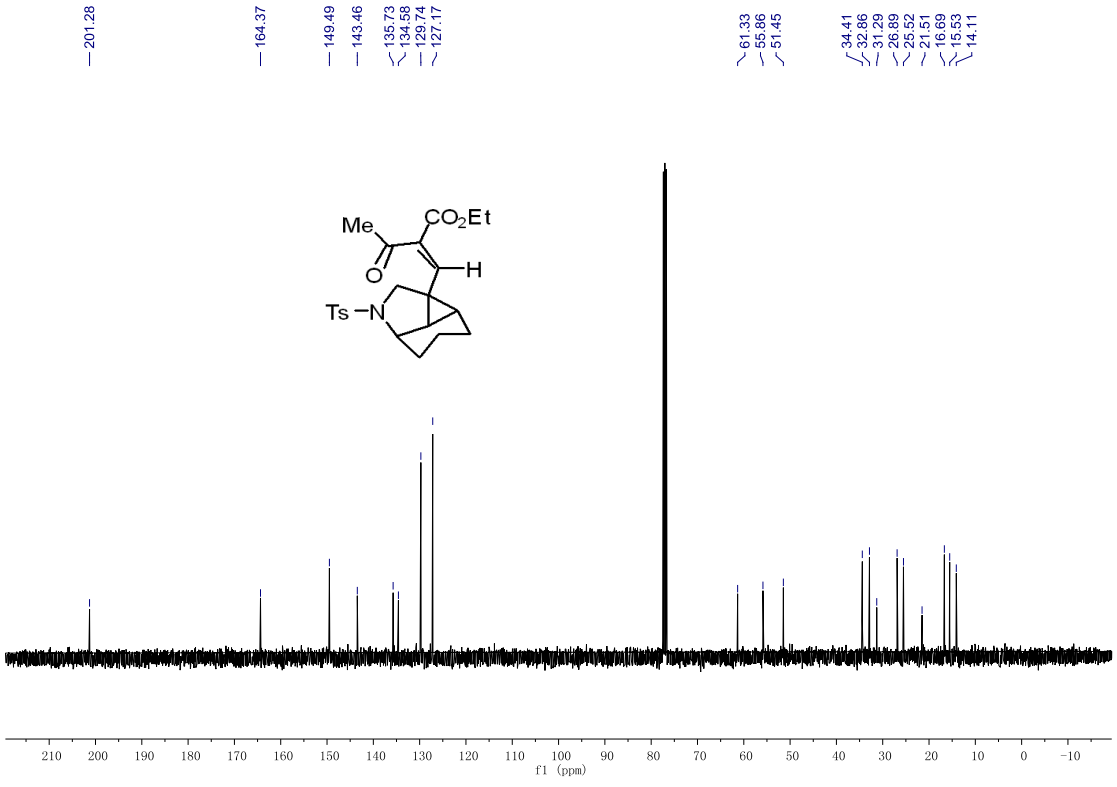

$^{13}$C NMR of ethyl (*Z*)-2-((5-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene)-3-Oxobutanoate **(3-2c)** (101 MHz, $CDCl_3$)



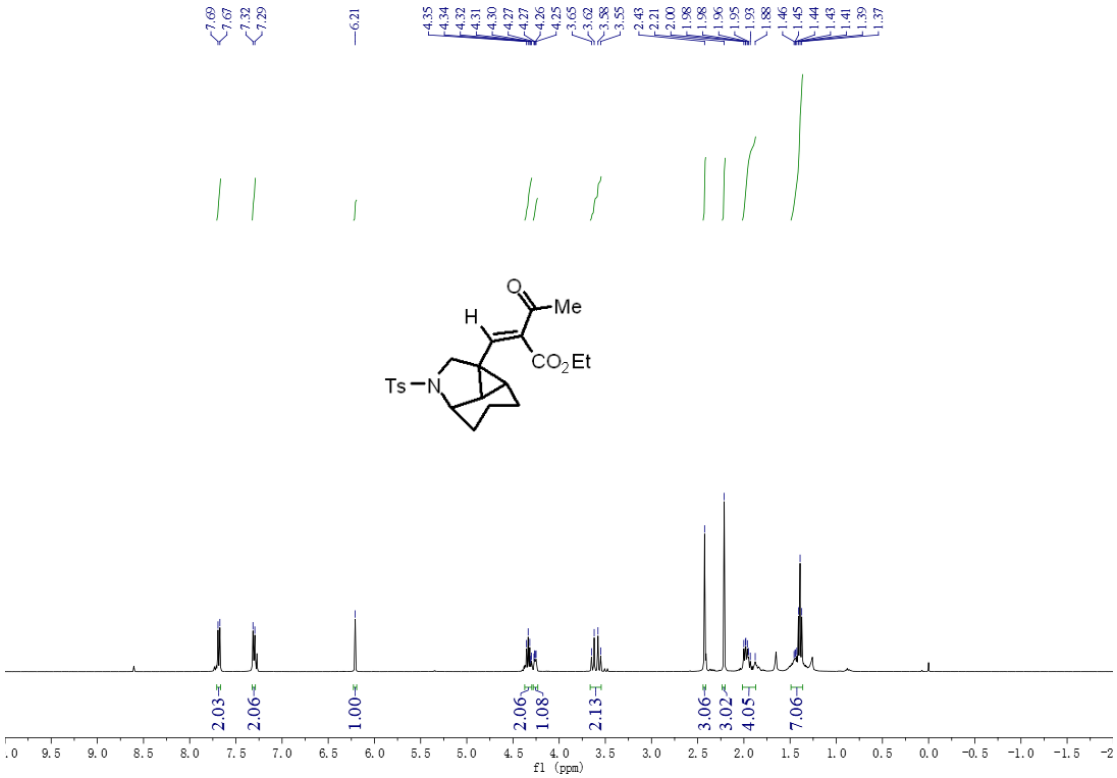
35) $^{1}$H NMR of ethyl (*E*)-3-oxo-2-{(1-tosyloctahydro-2aH-cyclopropa[cd]indol-2a-yl) methylene} butanoate **(*E*)-3-2d** (400 MHz, $CDCl_3$)



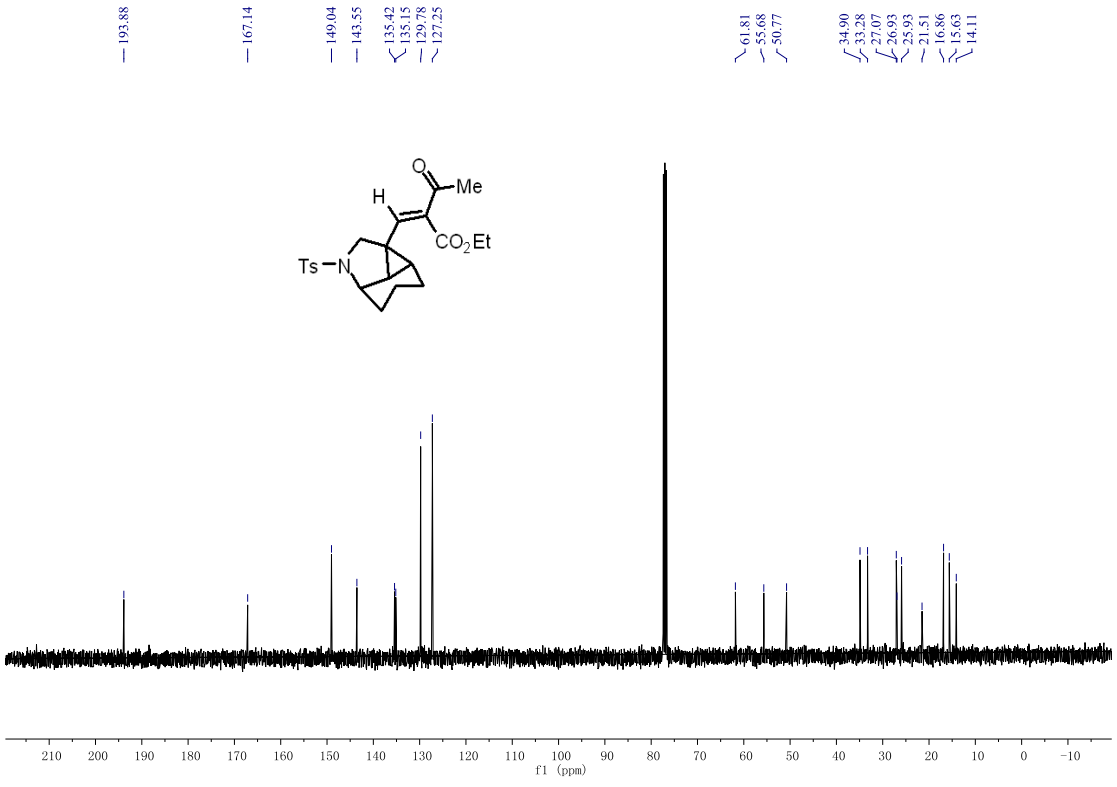

$^{13}$C NMR of ethyl (*E*)-3-oxo-2-{(1-tosyloctahydro-2aH-cyclopropa[cd]indol-2a-yl) methylene} butanoate **(*E*)-3-2d** (101 MHz, $CDCl_3$)



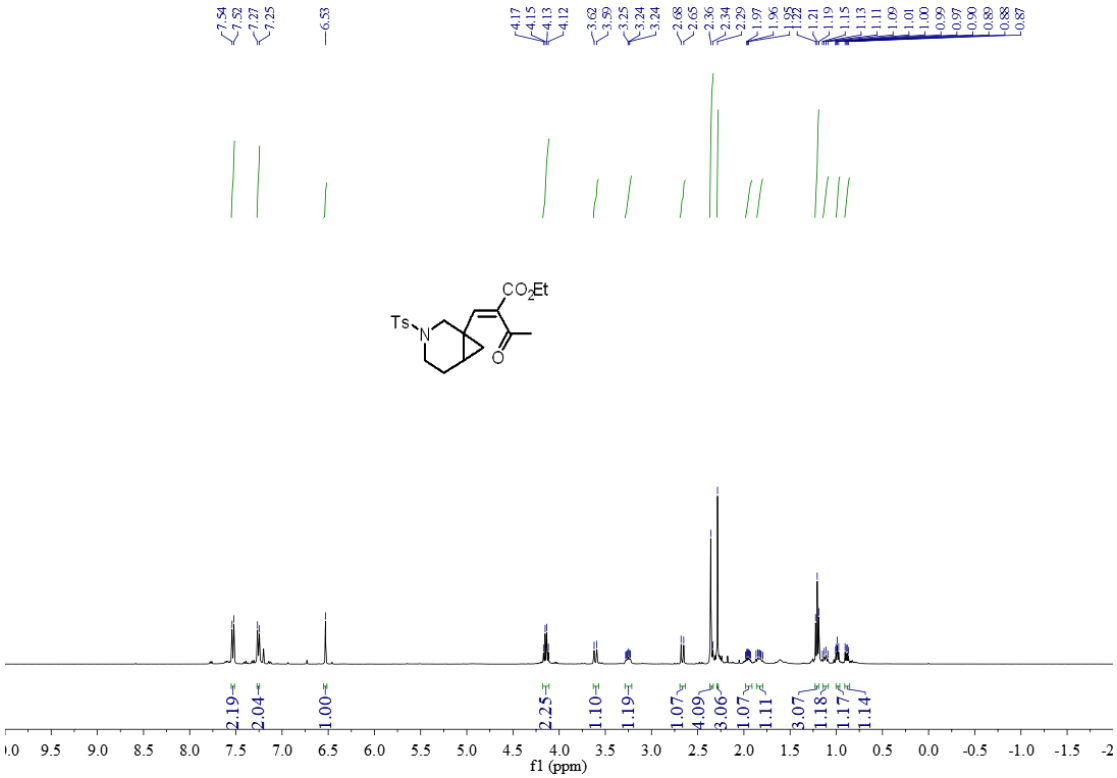
36) $^{1}$H NMR of ethyl (*Z*)-3-oxo-2-{(1-tosyloctahydro-2aH-cyclopropa[cd]indol-2a-yl) methylene} butanoate **(*Z*)-3-2d** (400 MHz, $CDCl_3$)



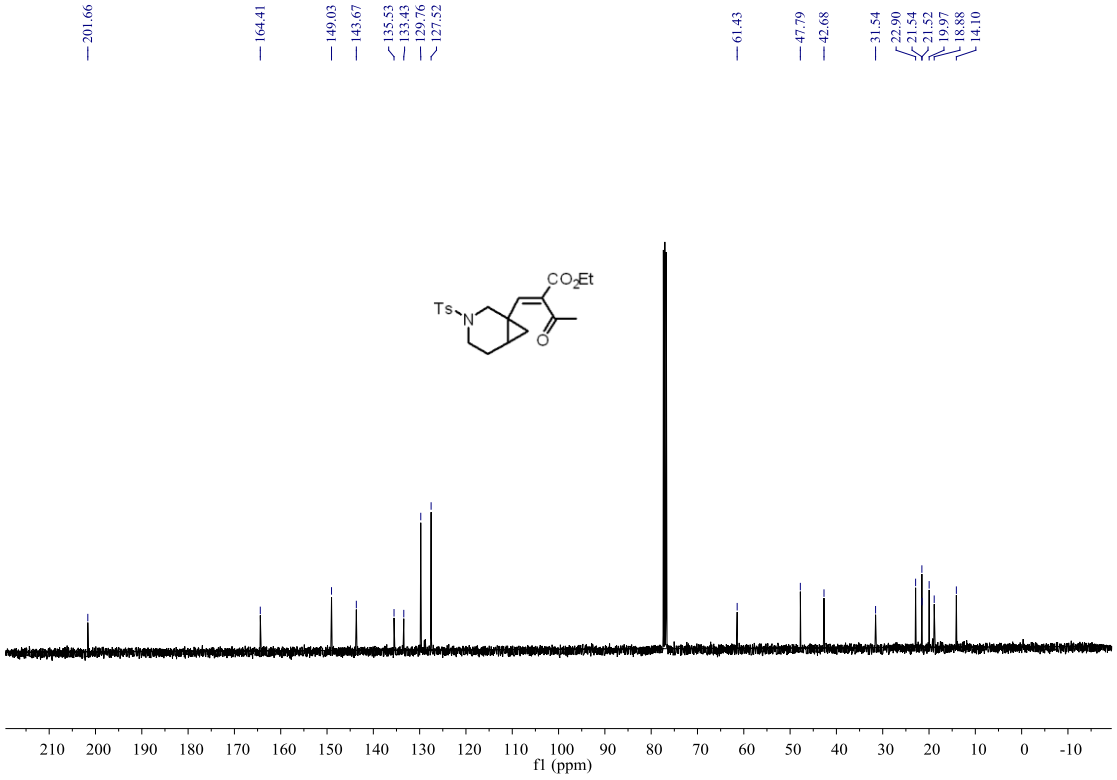

$^{13}$C NMR of ethyl (*Z*)-3-oxo-2-{(1-tosyloctahydro-2aH-cyclopropa[cd]indol-2a-yl) methylene} butanoate **(*Z*)-3-2d** (101 MHz, $CDCl_3$)



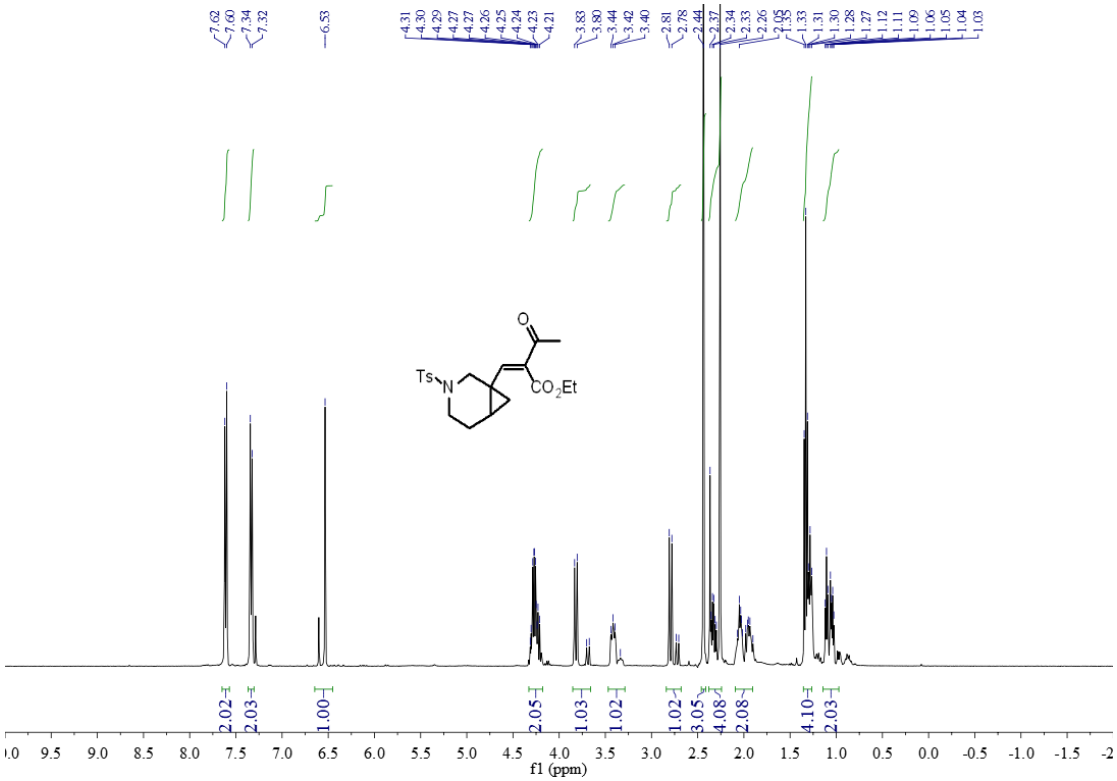
37) $^{1}$H NMR of ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-5-yl)methylene)butanoate **(*E*)-3-2e** (400 MHz, $CDCl_3$)



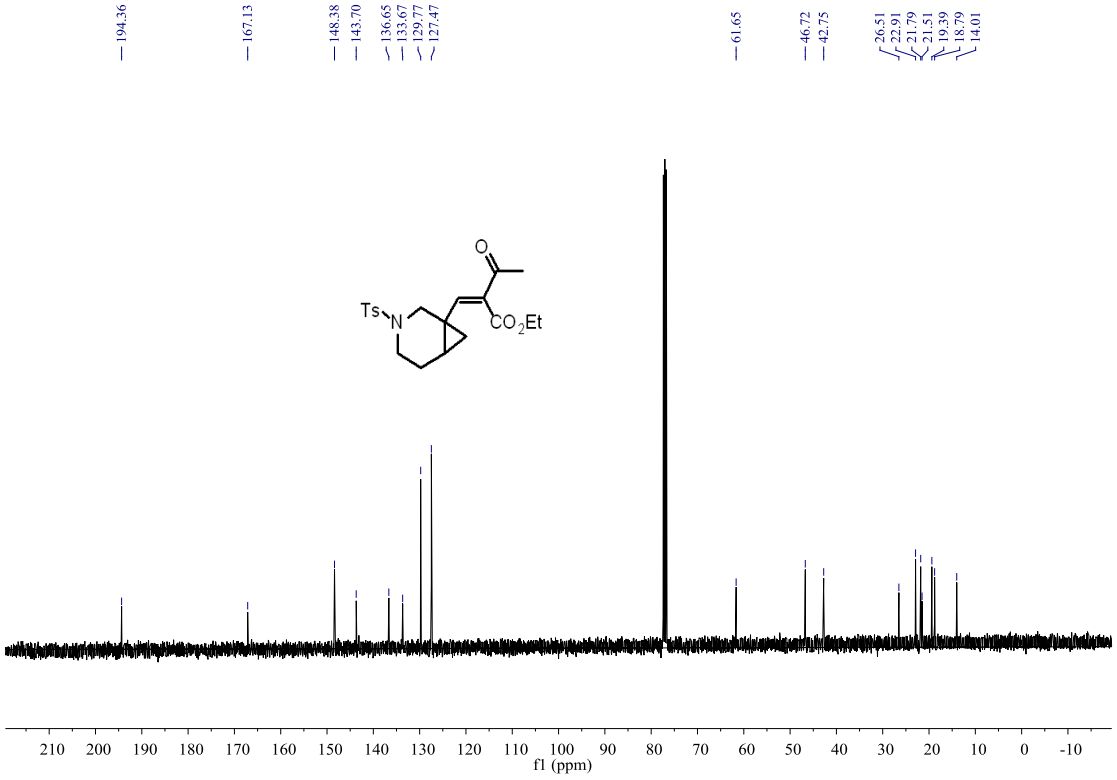

$^{13}$C NMR of ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-5-yl)methylene)butanoate **(*E*)-3-2e** (101 MHz, $CDCl_3$)



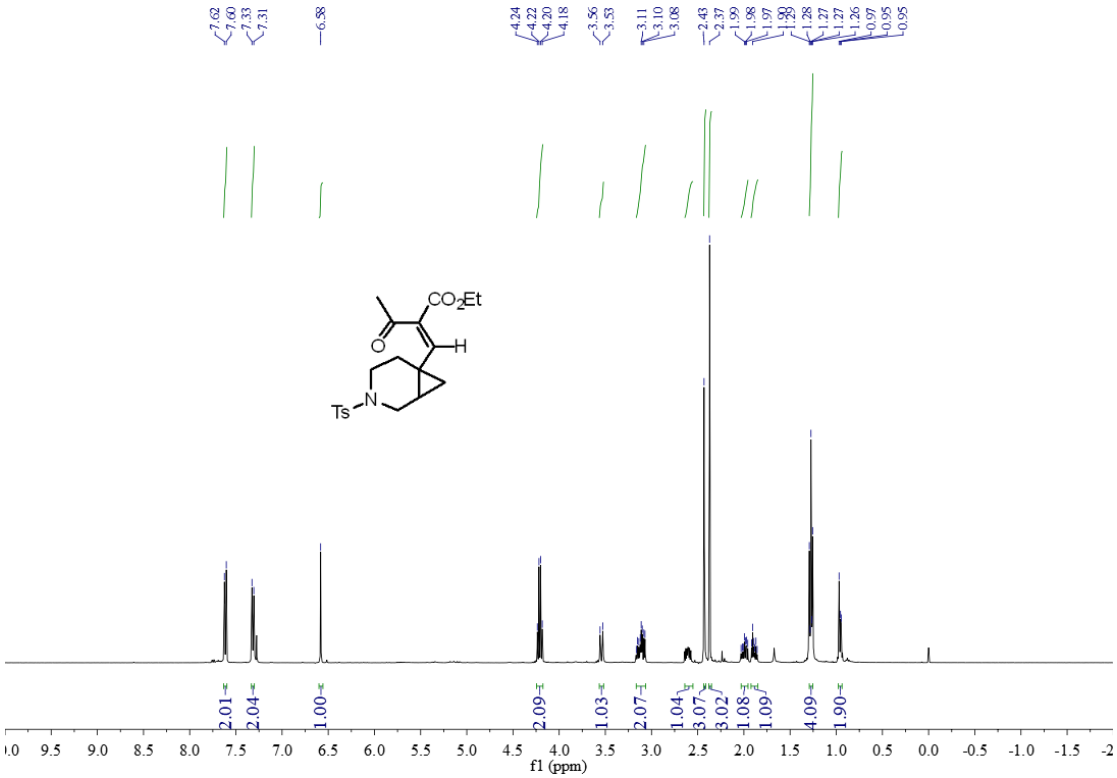
38) $^{1}$H NMR of ethyl (*Z*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-5-yl)methylene)butanoate **(*Z*)-3-2e** (400 MHz, $CDCl_3$)



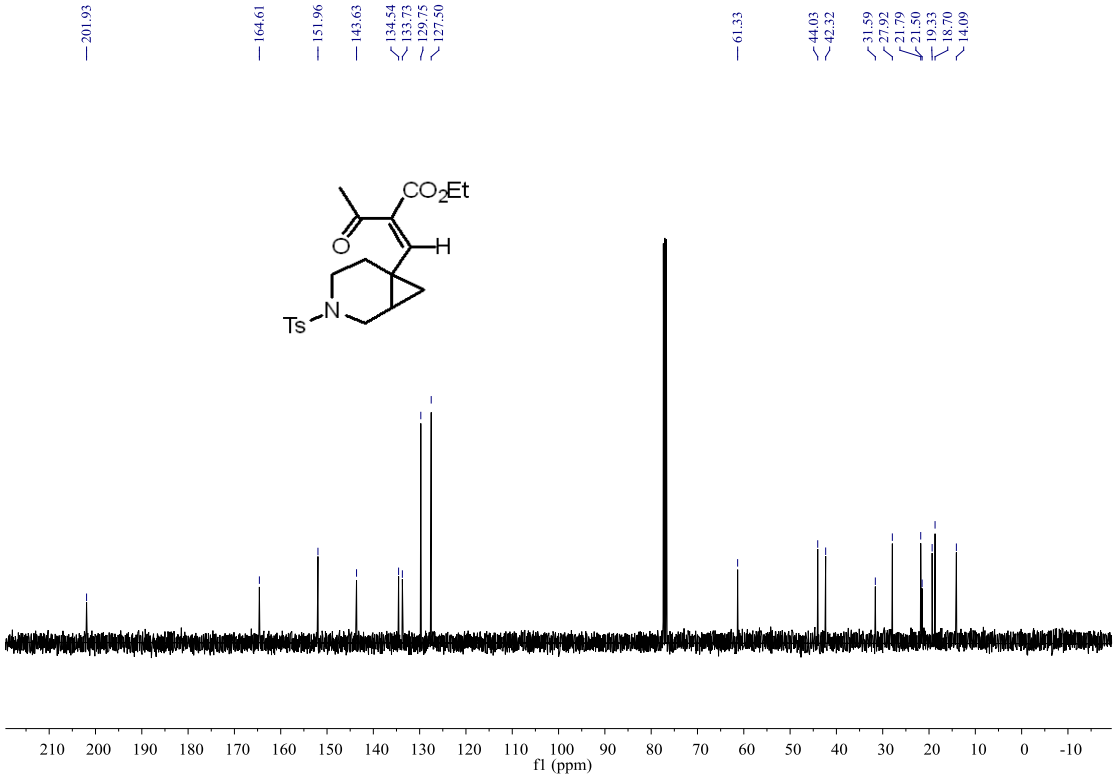

$^{13}$C NMR of ethyl (*Z*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-5-yl)methylene)butanoate **(*Z*)-3-2e** (101 MHz, $CDCl_3$)



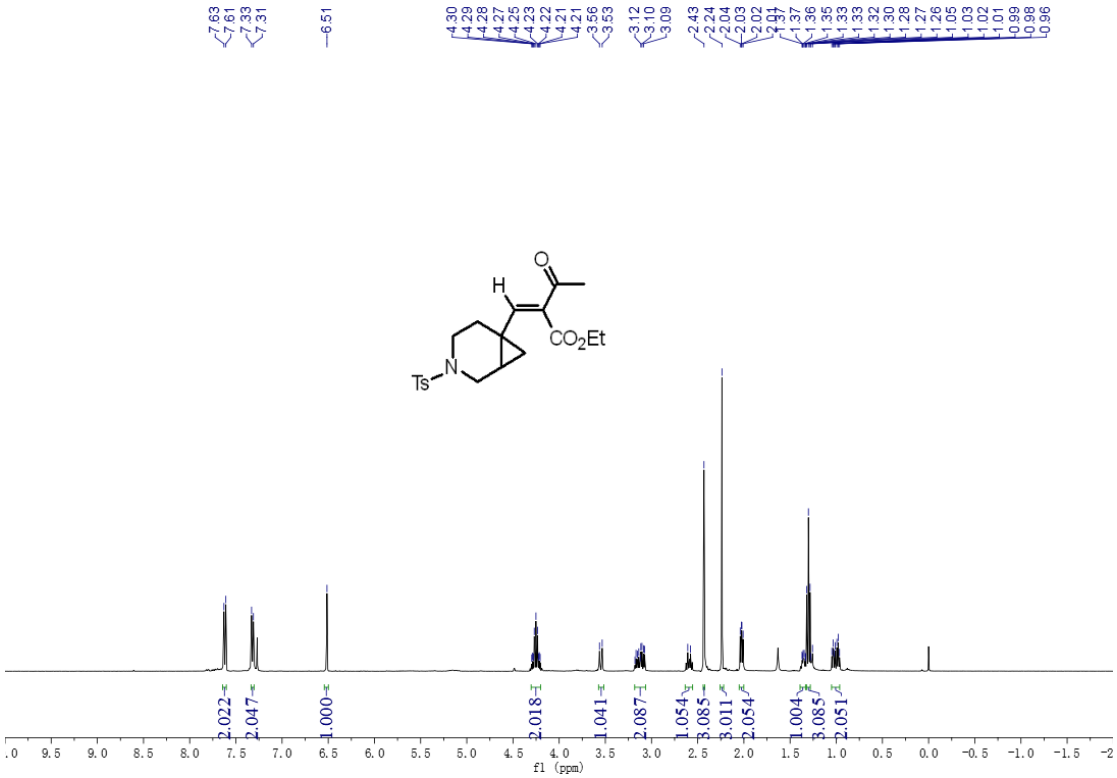
39) $^{1}$H NMR of ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)methylene)butanoate **(*E*)-3-2f** (400 MHz, $CDCl_3$)



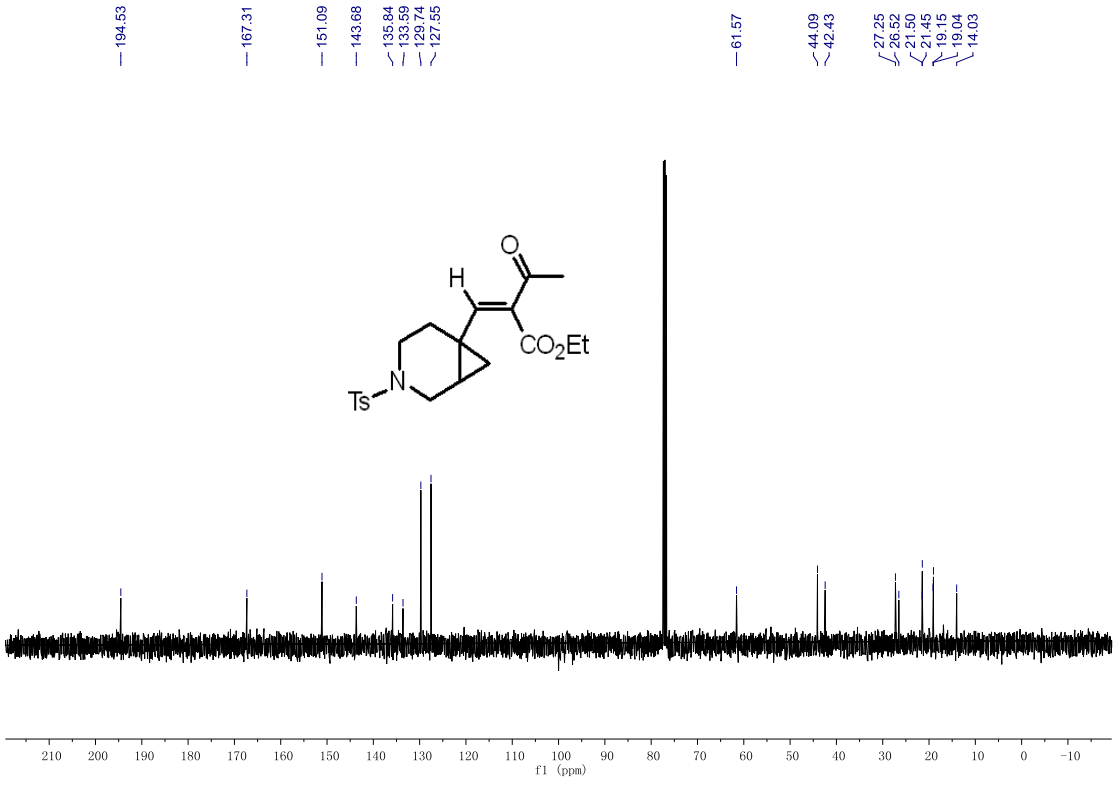

$^{13}$C NMR of ethyl (*E*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)methylene)butanoate **(*E*)-3-2f** (101 MHz, $CDCl_3$)



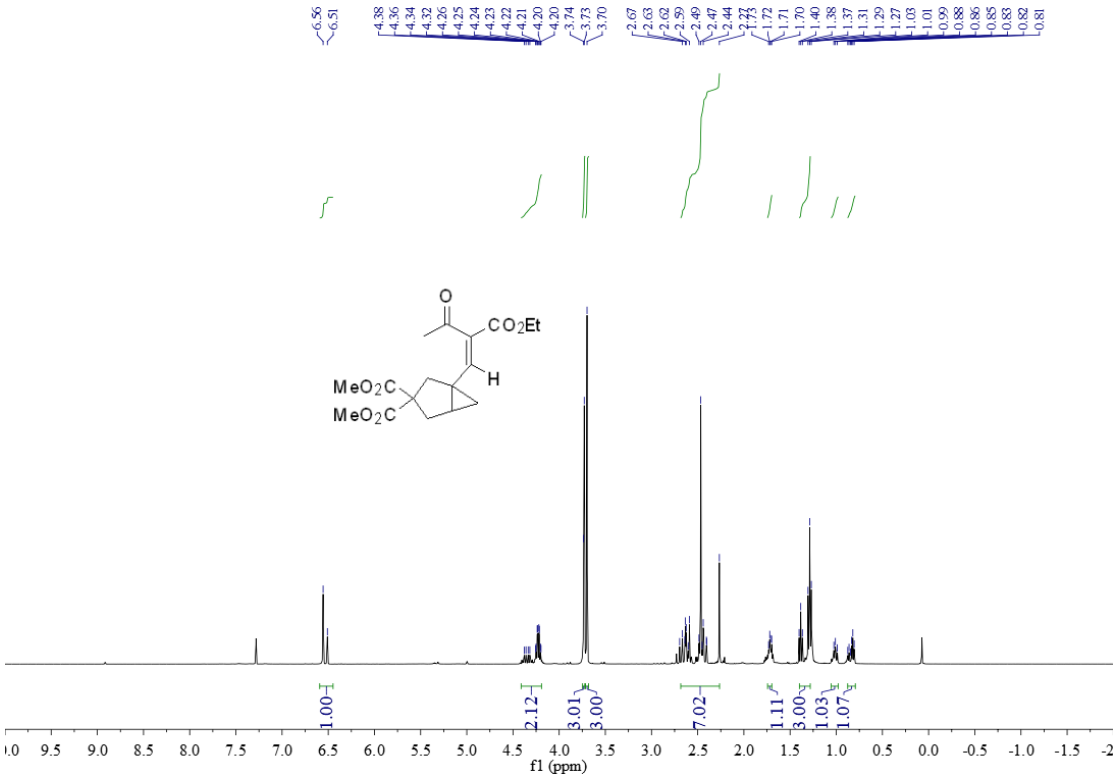
40) $^{1}$H NMR of ethyl (*Z*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)methylene)butanoate **(*Z*)-3-2f** (400 MHz, $CDCl_3$)



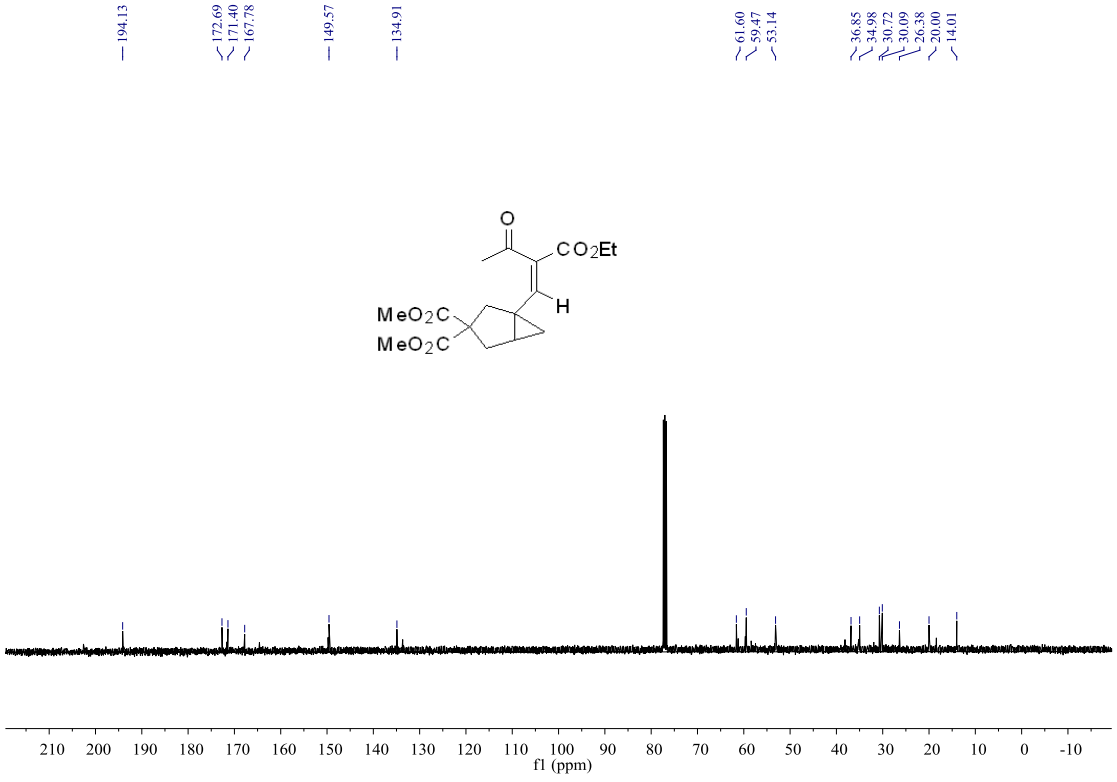

$^{13}$C NMR of ethyl (*Z*)-3-oxo-2-((3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)methylene)butanoate **(*Z*)-3-2f** (101 MHz, $CDCl_3$)



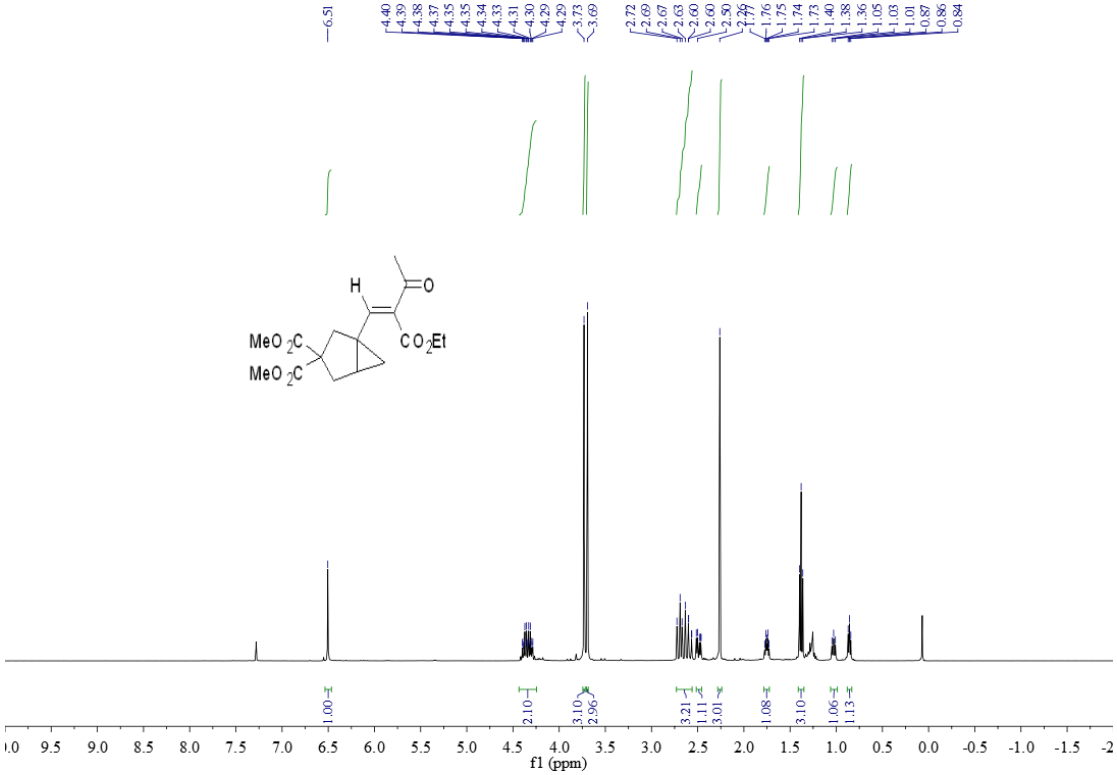
41) $^{1}$H NMR of dimethyl (*E*)-1-(2-(ethoxycarbonyl)-3-oxobut-1-en-1-yl)bicyclo[3.1.0] hexane-3,3-dicarboxylate **(*E*)-3-2g** (400 MHz, $CDCl_3$)



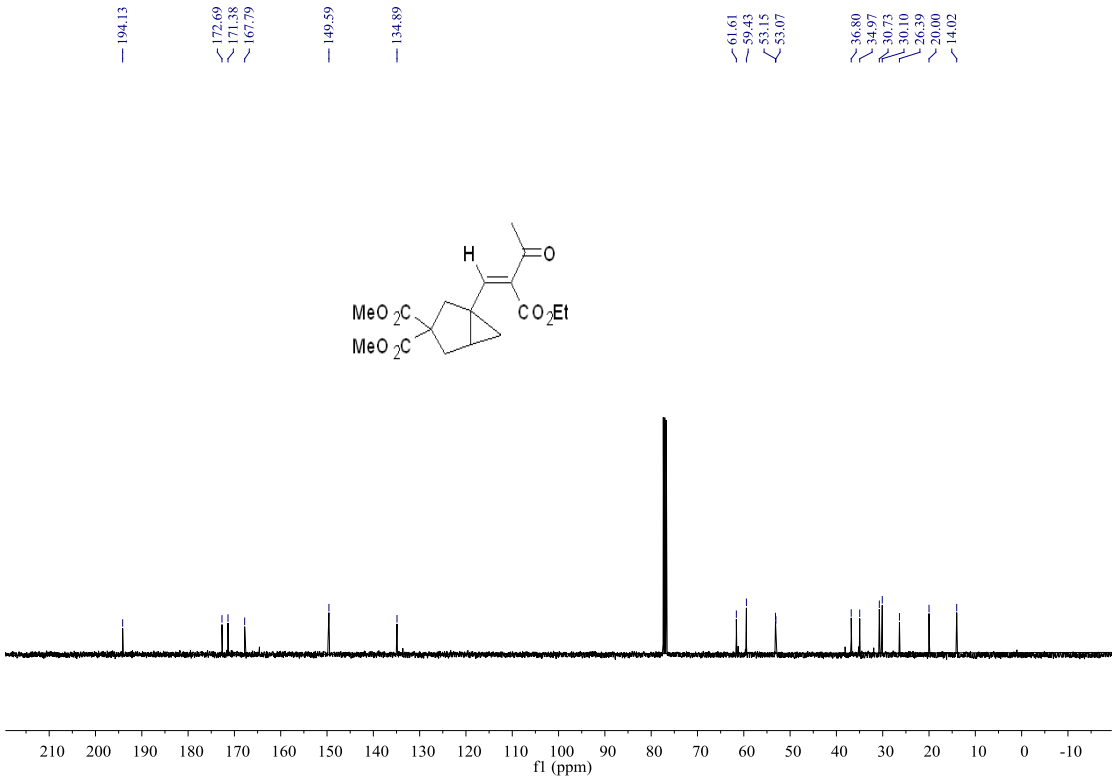

$^{13}$C NMR of dimethyl (*E*)-1-(2-(ethoxycarbonyl)-3-oxobut-1-en-1-yl)bicyclo[3.1.0] hexane-3,3-dicarboxylate **(*E*)-3-2g** (101 MHz, $CDCl_3$)



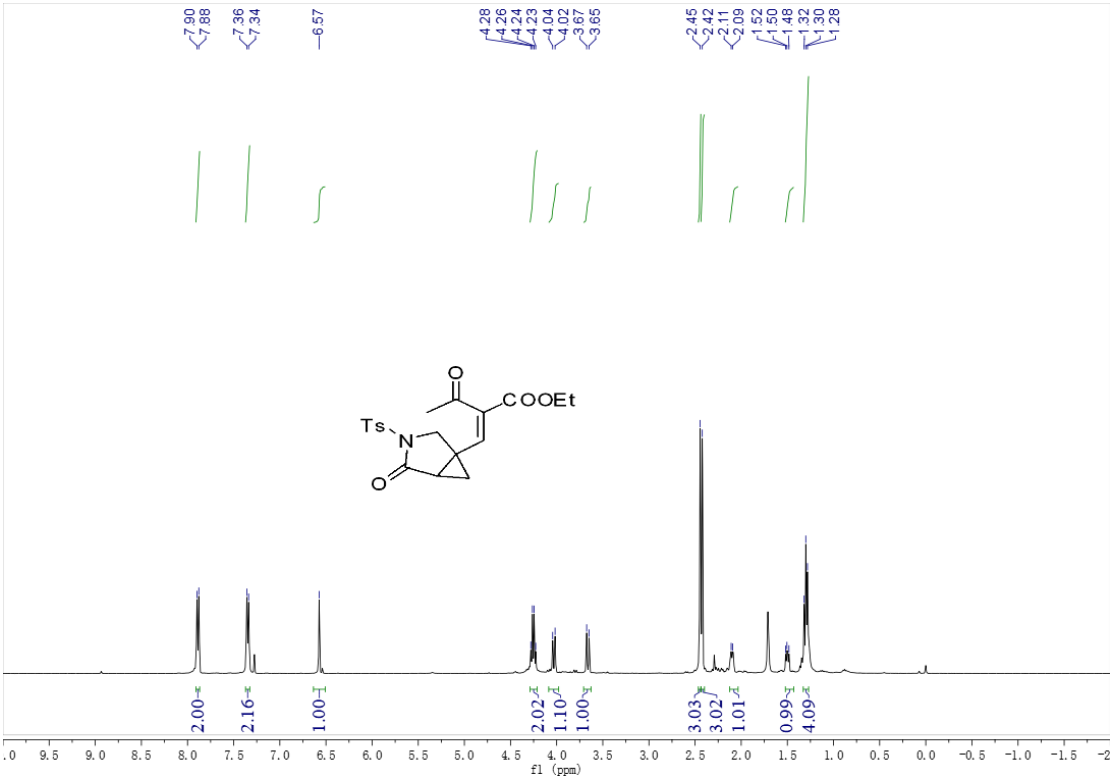
42) $^{1}$H NMR of dimethyl (*Z*)-1-(2-(ethoxycarbonyl)-3-oxobut-1-en-1-yl)bicyclo[3.1.0] hexane-3,3-dicarboxylate **(*Z*)-3-2g** (400 MHz, $CDCl_3$)



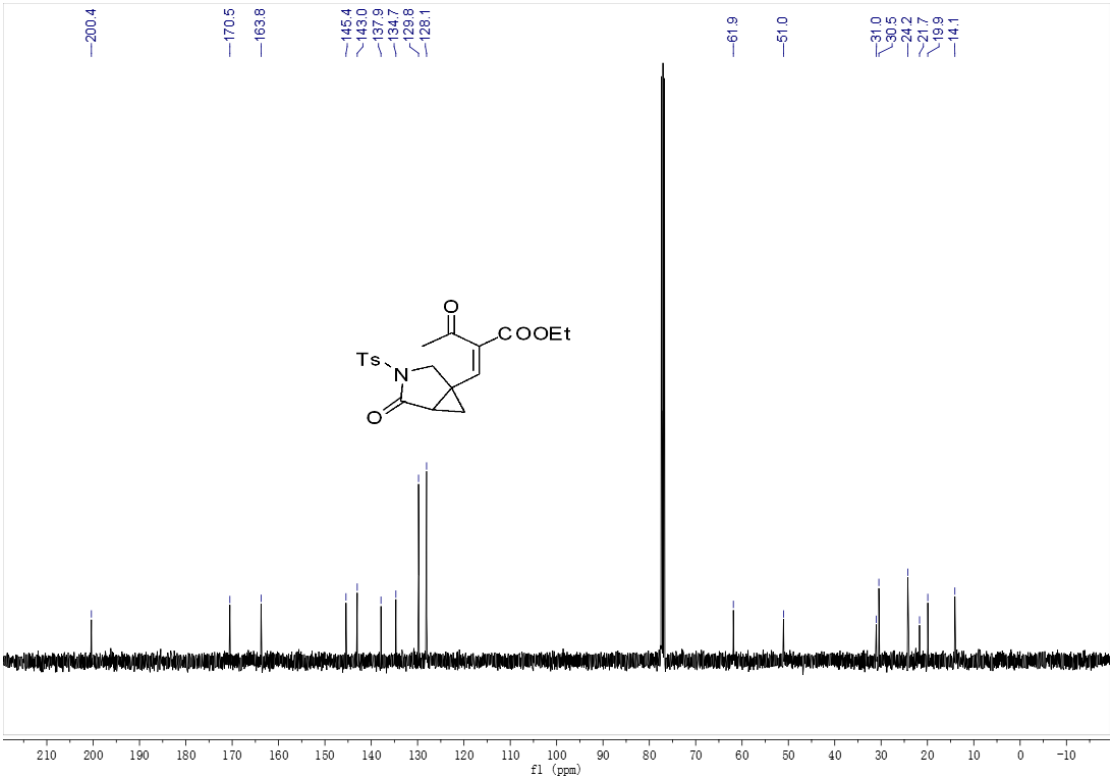

$^{13}$C NMR of dimethyl (*Z*)-1-(2-(ethoxycarbonyl)-3-oxobut-1-en-1-yl)bicyclo[3.1.0] hexane-3,3-dicarboxylate **(*Z*)-3-2g** (101 MHz, $CDCl_3$)



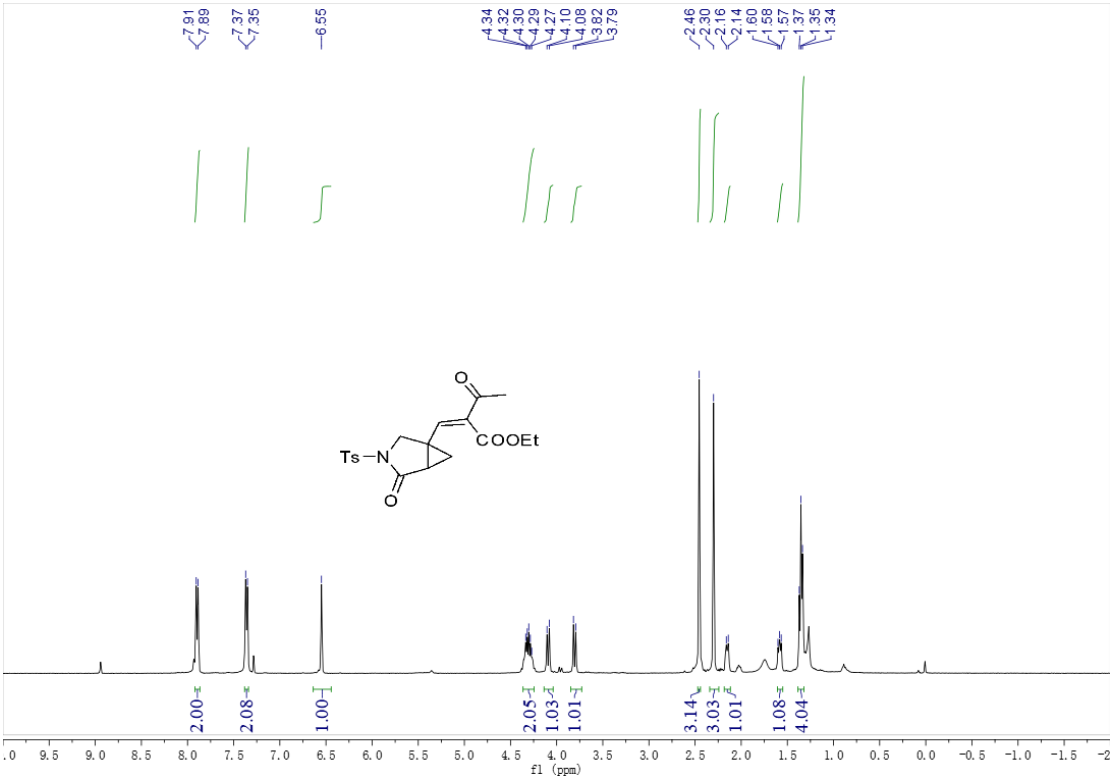
43) $^{1}$H NMR of ethyl (*E*)-3-oxo-2-((4-oxo-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene) butanoate **(3-2h)** (400 MHz, $CDCl_3$)



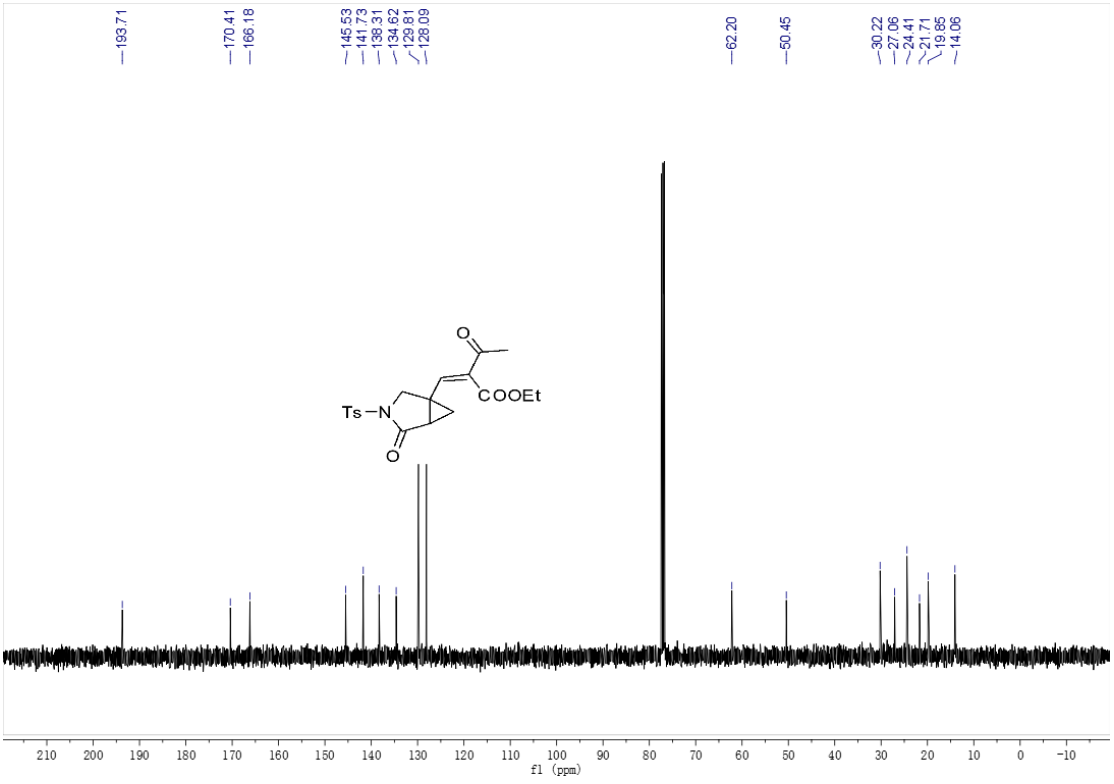

$^{13}$C NMR of ethyl (*E*)-3-oxo-2-((4-oxo-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene) butanoate **(3-2h)** (101 MHz, $CDCl_3$)



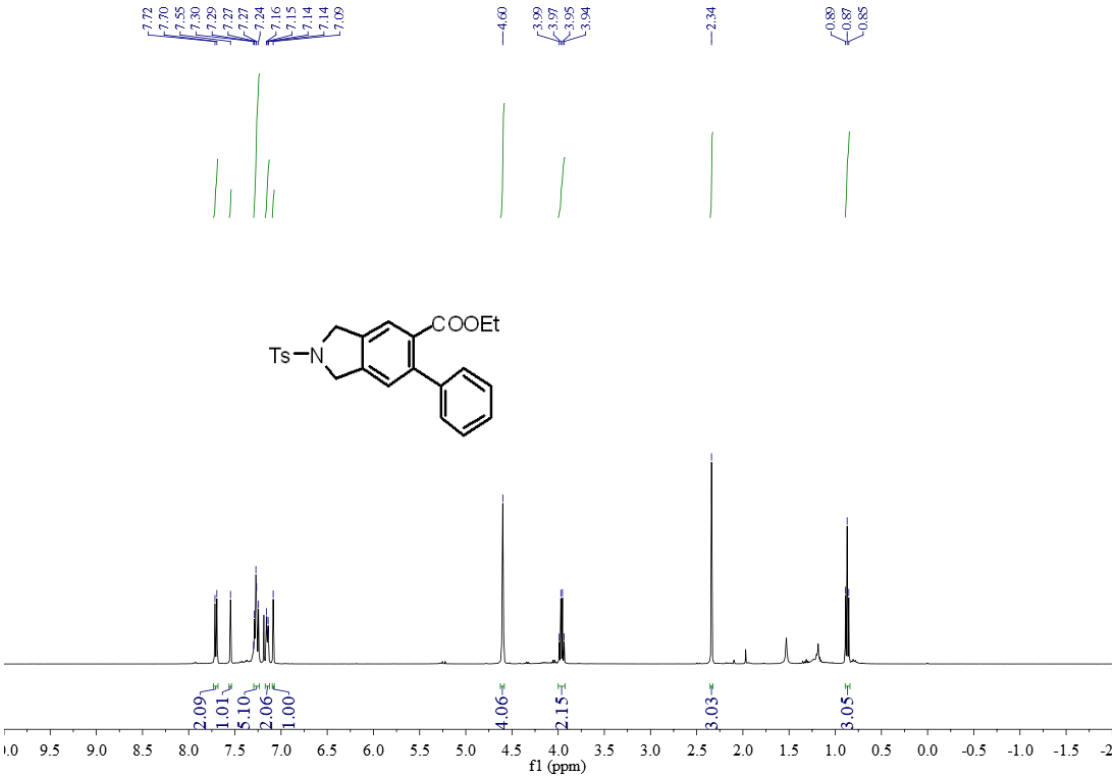
44) $^{1}$H NMR of ethyl (*Z*)-3-oxo-2-((4-oxo-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene) butanoate **(3-2h)** (400 MHz, $CDCl_3$)



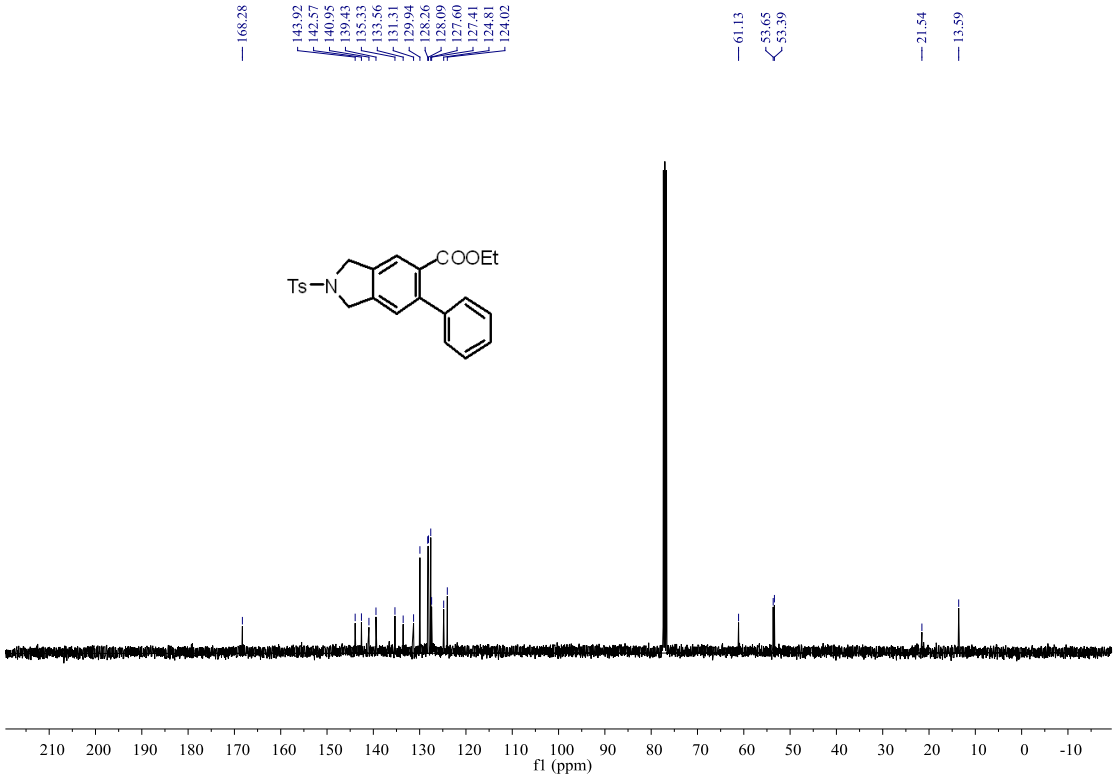

$^{13}$C NMR of ethyl (*Z*)-3-oxo-2-((4-oxo-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene) butanoate **(3-2h)** (101 MHz, $CDCl_3$)



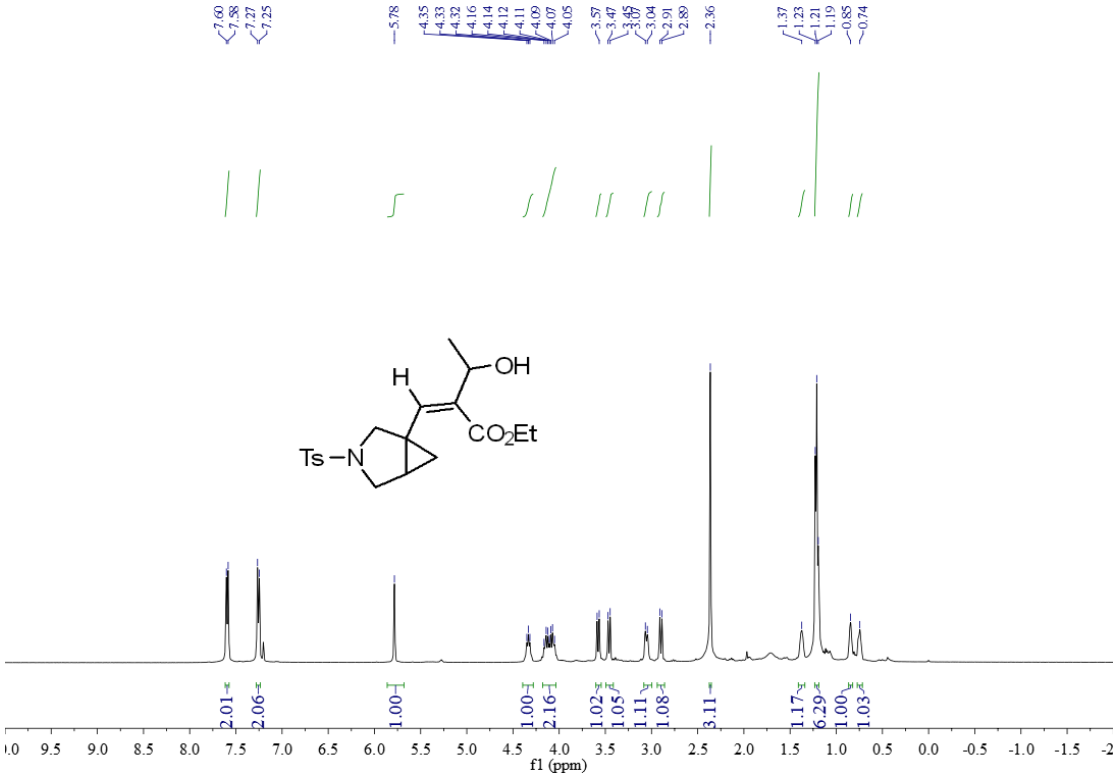
45) $^{1}$H NMR of ethyl 6-phenyl-2-tosylisoindoline-5-carboxylate **(3-2i)** (400 MHz, $CDCl_3$)



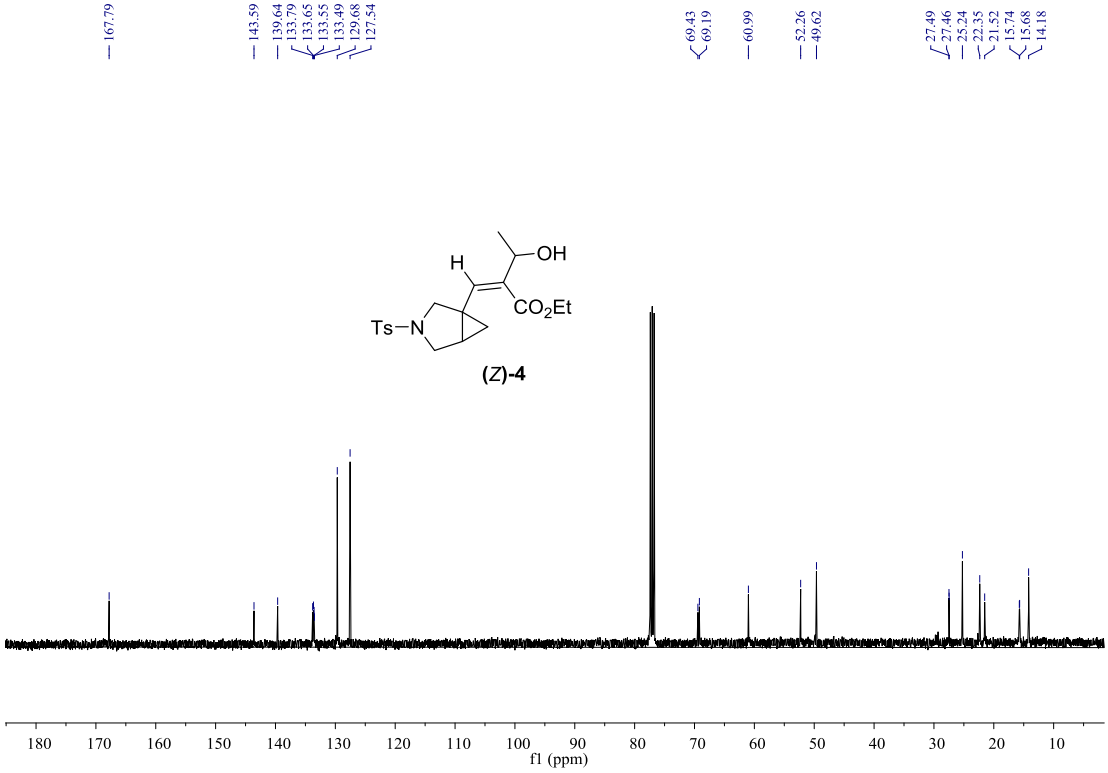

$^{13}$C NMR of ethyl 6-phenyl-2-tosylisoindoline-5-carboxylate **(3-2i)** (101 MHz, $CDCl_3$)



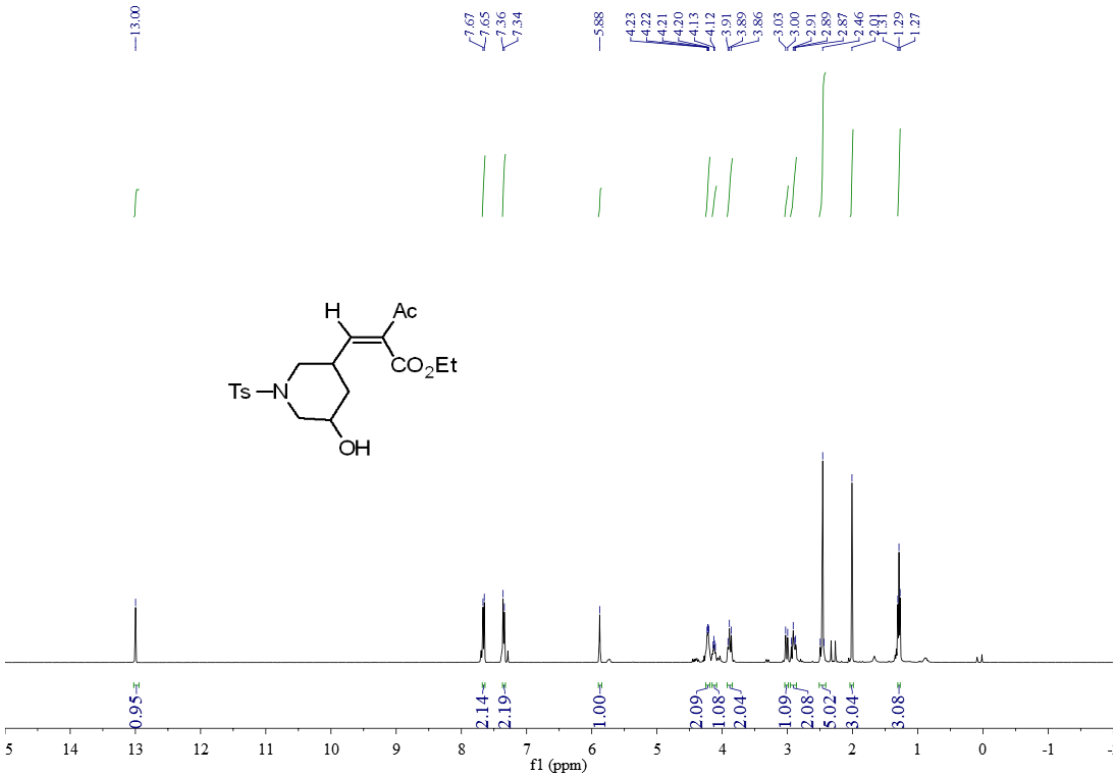
46) $^{1}$H NMR of ethyl(*Z*)-3-hydroxy-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene) Butanoate **(*Z*)-4** (400 MHz, $CDCl_3$)




$^{13}$C NMR of ethyl(*Z*)-3-hydroxy-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methylene) Butanoate **(*Z*)-4** (101 MHz, $CDCl_3$)



47) $^{1}$H NMR of Ethyl (*Z*)-2-((5-hydroxy-1-tosylpiperidin-3-yl)methylene)-3-oxobutanoate **(*Z*)-5** (400 MHz, $CDCl_3$)




$^{13}$C NMR of Ethyl (*Z*)-2-((5-hydroxy-1-tosylpiperidin-3-yl)methylene)-3-oxobutanoate **(*Z*)-5** (101 MHz, $CDCl_3$)