# Supporting Information

## Radical cascade silylation/cyclization of 1,7-dienes to access silylsubstituted benzo[b]azepin-2-ones

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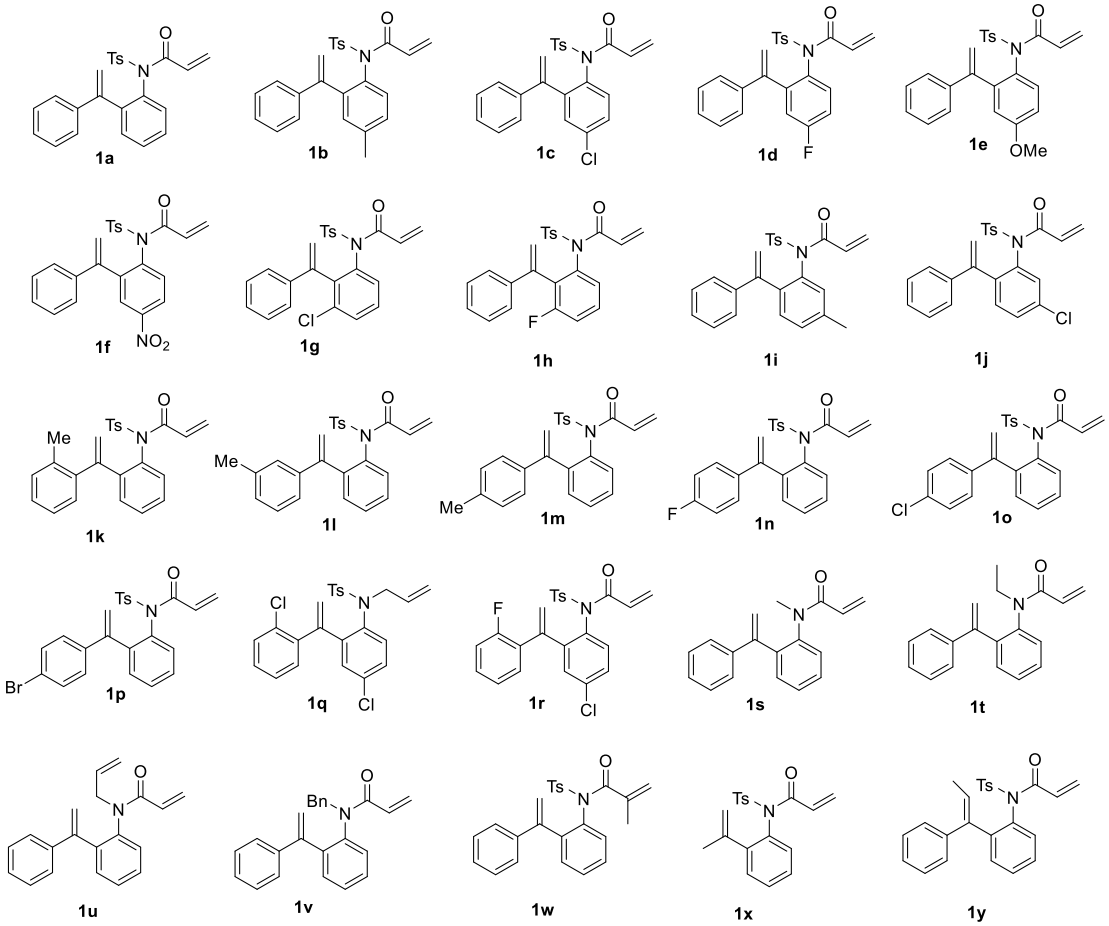
## 1. General

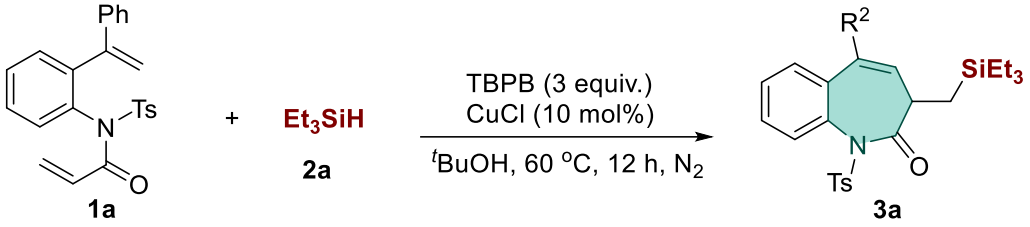
All reactions were performed in a glass vial under atmosphere. The boiling point of petroleum ether is between 60 °C and 90 °C. For chromatography, mesh silica gel (Qingdao, China) was employed. $^{1}H$, and $^{13}C$ NMR spectra were recorded on Ascend 400, Bruker Biospin GmbH 500 or 600 spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ ($^{1}H$, TMS δ 0; $^{13}C$, δ 77.16), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, h = heptet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad). HMRS were obtained on a Waters Xevo G2-XS-QTOF mass spectrometer. The X-ray diffraction data were collected at 100K on a Rigaku diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) for product 6m. All reagents and solvents were obtained from commercial sources and used as supplied unless otherwise noted.

## 2. Preparation of material 1



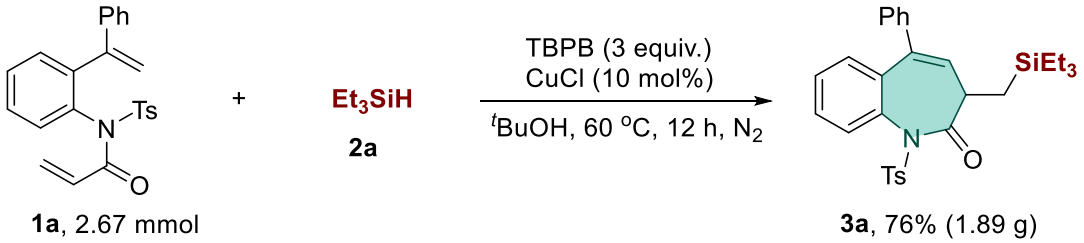

All substrates **1** were synthesized following reported procedure.[1]

## 3. General produce for the synthesis of 3



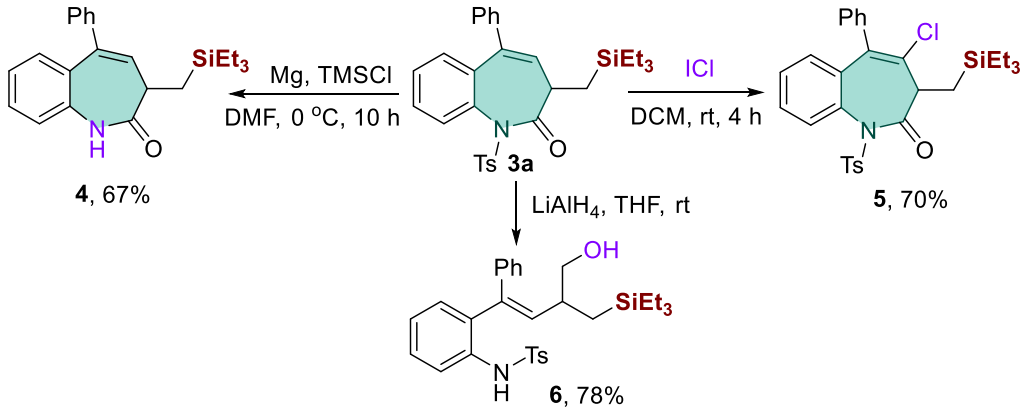

To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **1a** (0.3 mmol, 121.1 mg) and $^{t}$BuOH (3 mL). Then, $Et_3SiH$ (2.40 mmol, 382.5 uL), CuCl (0.03 mmol, 3.0 mg) and TBPB (0.9 mmol, 177.0 uL) were added. The reaction mixture was stirred at 60 °C for 12 h under $N_2$. Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate =15:1-10:1) to afford **3a** in 78 % yield (120.9 mg).

## 4. The gram-scale synthesis of compound 3a




To a 100 mL dry thick walled tube equipped with a magnetic stir bar, was added **1a** (2.67 mmol, 1.076 g) and $^{t}$BuOH (27 mL). Then, the $Et_3SiH$ (21.36 mmol, 3.40 ml), CuCl (0.267 mmol, 26.4 mg) and TBPB (8.01 mmol, 1.575 ml) were added. The reaction mixture was stirred at 60 °C for 12 h under $N_2$. Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate =15:1-10:1) to afford **3a** (1.89 g, 76%).

## 5. Produces for further transformations of compound 3a.



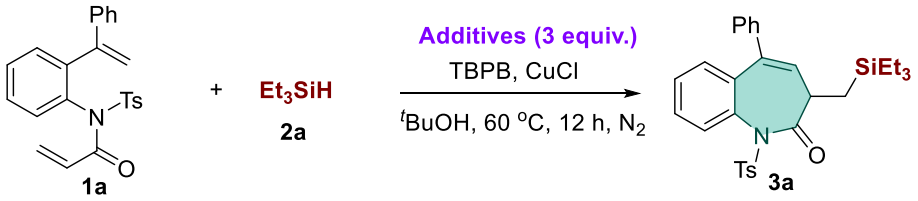

To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **3a** (0.3 mmol, 121.1 mg) and DMF (3 mL). Then, the Mg (0.9 mmol, 21.9 mg), TMSCl (1.5 mmol, 191.4 uL) was added.

The tube was sealed and the reaction mixture was stirred at 0 °C for 10 h. Upon the reaction completed, $H_2O$ was added to mixture and extracted with ethyl acetate (3×20 mL). The combined organic layer was dried (anhydrous $Na_2SO_4$), filtered, and evaporated followed by a silica gel column chromatography (petroleum ether/ethyl acetate = 10:1-5:1) to afford desired product **4** (108.9 mg, 67%).

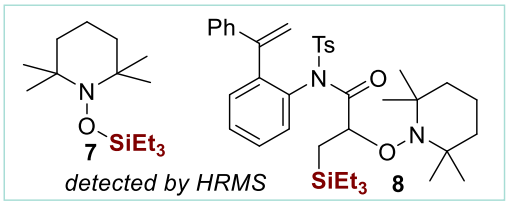
To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **3a** (0.3 mmol, 121.1 mg) and DCM (3 mL). Then, the ICl (0.45 mmol, 22.5 uL) were added. The tube was sealed and the reaction mixture was stirred at room temperature for 4 h. Upon the reaction completed, $H_2O$ was added to mixture and extracted with DCM (3×20 mL). The combined organic layer was dried (anhydrous $Na_2SO_4$), filtered, and evaporated followed by a silica gel column chromatography (petroleum ether/ethyl acetate = 10:1-5:1) to afford desired product **5** (115.9 mg, 70%).

To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **3a** (0.3 mmol, 121.1 mg) and THF (3 mL). Then, the $LiAlH_4$ (0.9 mmol, 34.2 mg) were added. The tube was sealed and the reaction mixture was stirred at room temperature for 12 h. Upon the reaction completed, $H_2O$ was added to mixture and extracted with ethyl acetate (3×20 mL). The combined organic layer was dried (anhydrous $Na_2SO_4$), filtered, and evaporated followed by a silica gel column chromatography (petroleum ether/ethyl acetate = 7:1-4:1) to afford desired product **6** (122.0 mg, 78%).

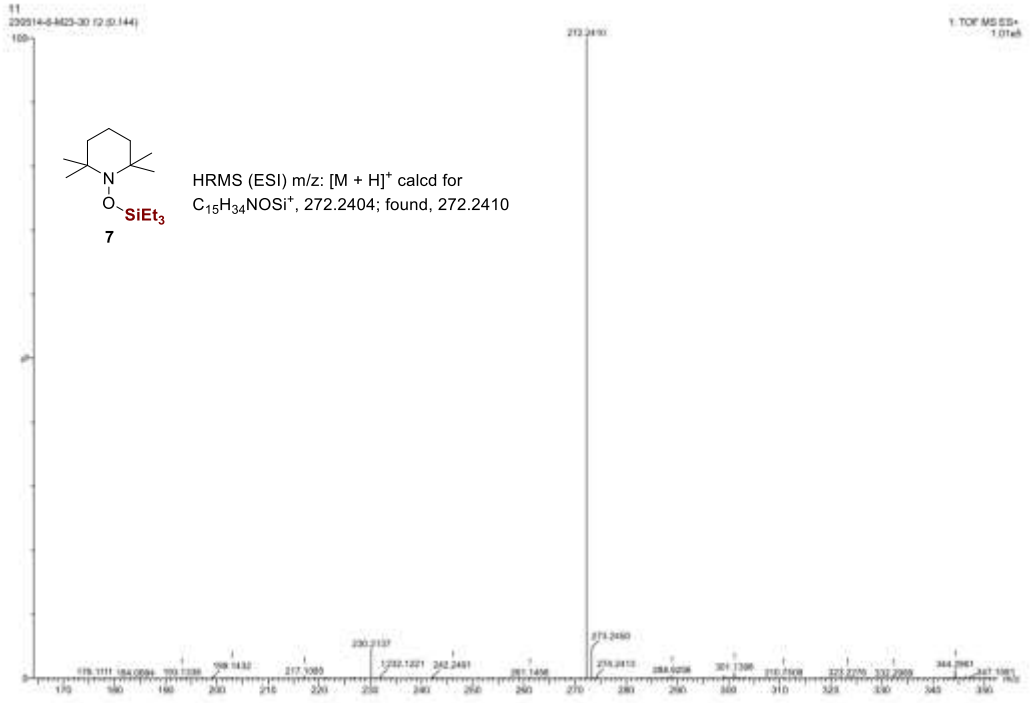
## 6. Radical trapping experiments




| Additives | Yield of **3a** |
|---|---|
| TEMPO | 0% |
| BHT | 0% |
| DPE | 44% |



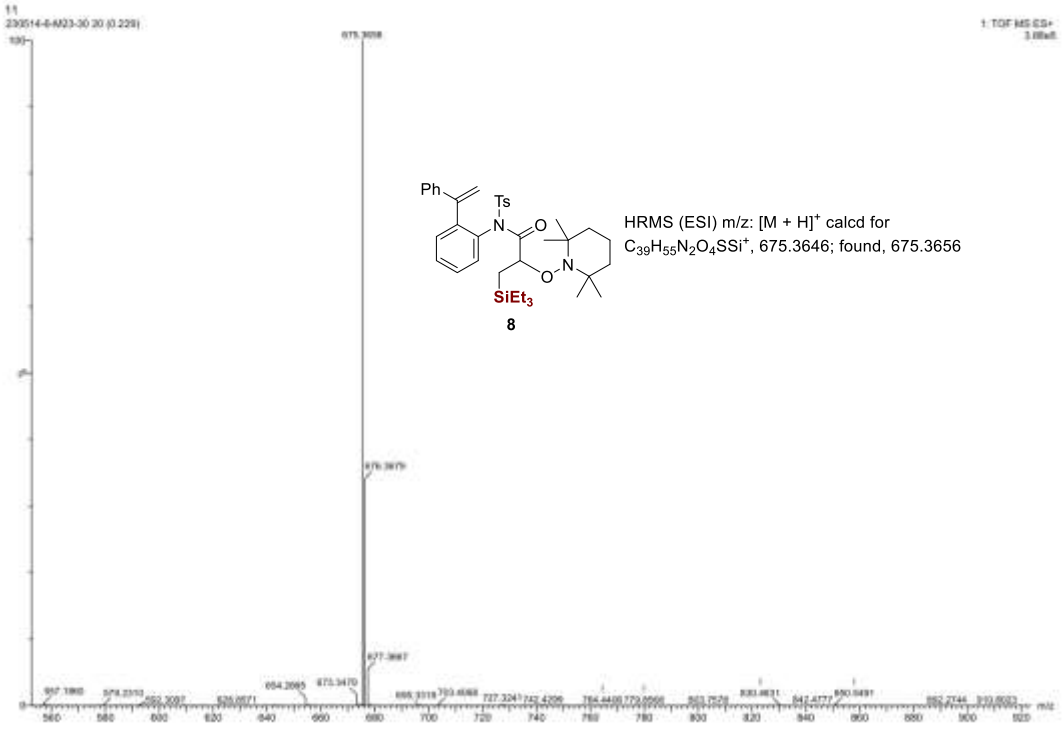

To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **1a** (0.3 mmol, 121.1 mg) and $^t$BuOH (3 mL). Then, $Et_3SiH$ (2.40 mmol, 382.5 uL), CuCl (0.03 mmol, 3.0 mg) and TBPB (0.9 mmol, 177.0 uL), Additives (0.9 mmol) were added. The reaction mixture was stirred at oil bath 60 °C for 12 h under $N_2$. Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate =15:1-10:1) to afford **3a**.





**7**

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{34}NOSi^+$, 272.2404; found, 272.2410



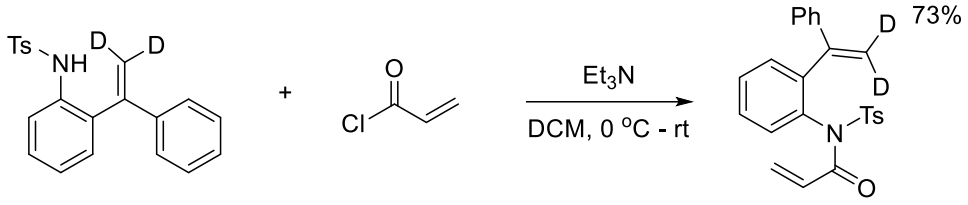


**8**

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{39}H_{55}N_2O_4SSi^+$, 675.3646; found, 675.3656

## 7. Deuterium-labelling experiment

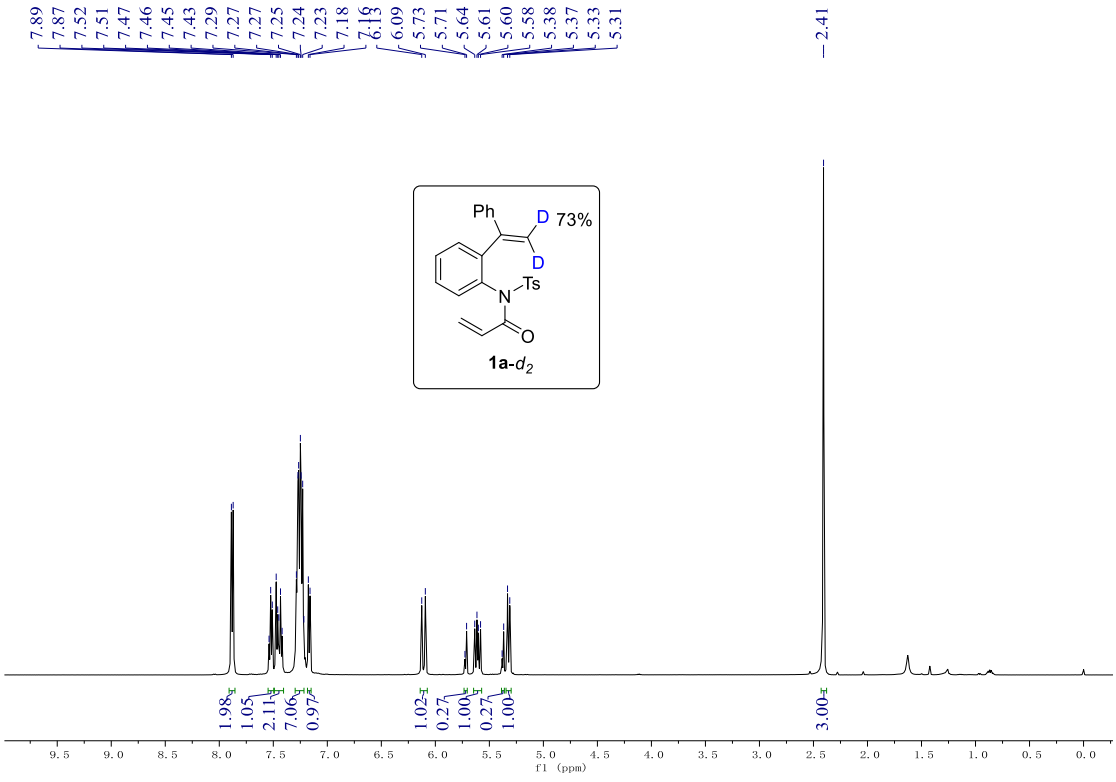
**Preparation of the deuterated 1a-$d_2$:**



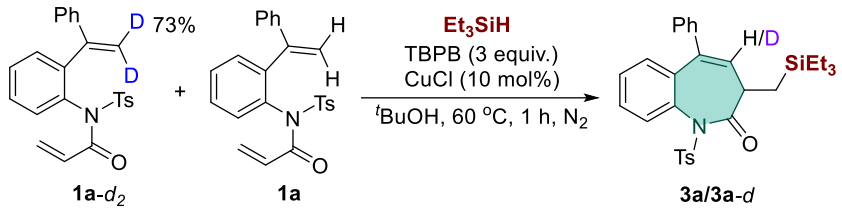

**Sub-$d_2$** **1a-$d_2$**

**Sub**-$d_2$ was synthesized following reported procedure.[2]

To a round-bottomed flask of dichloromethane (20 mL) solution dissolved with acryloyl chloride (1.84 mmol, 1.1 equiv.), **Sub**-$d_2$ (1.68 mmol, 1.0 equiv.) was added and then triethylamine (2.02 mmol, 1.2 equiv.) was dropped at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. Upon the reaction completed, the reaction mixture was extracted with dichloromethane (3 x 20 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 = 20:1-15:1) to afford product **1a**-$d_2$ (65% yield, 73% deuteration).



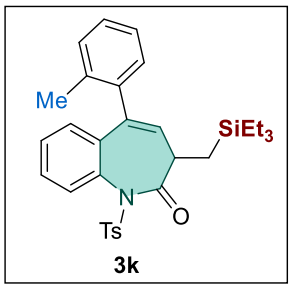
*Deuterium-labelling experiment*



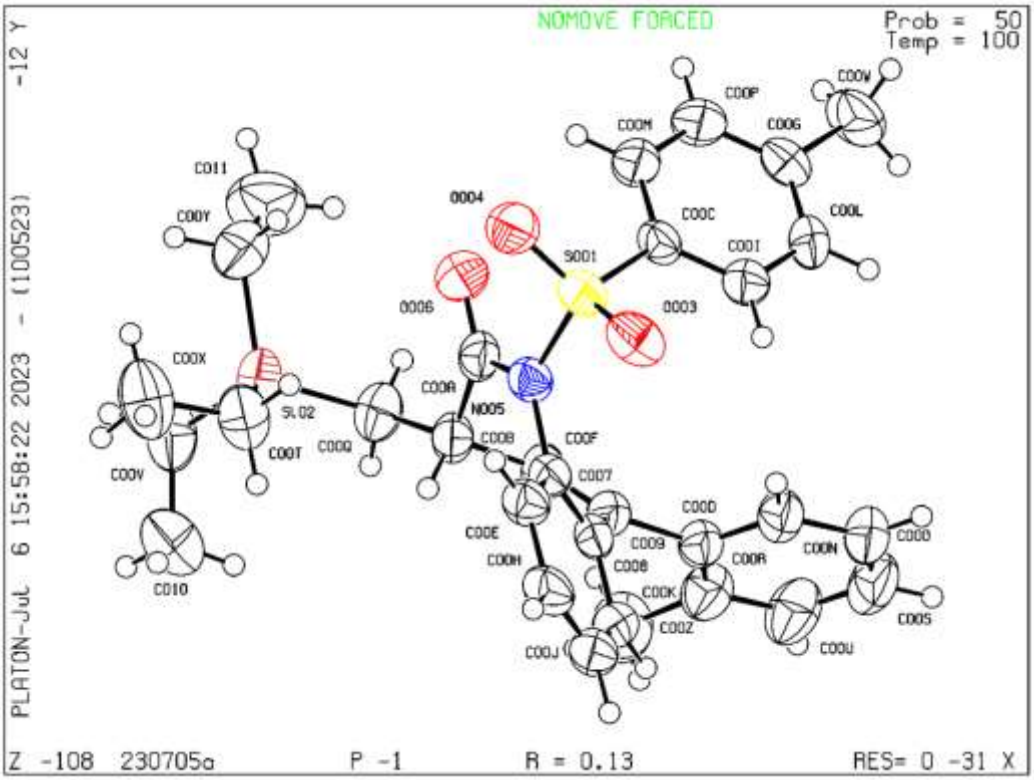

The KIE value was calculated according to previous documents.[2,3] To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **1a** (0.19 mmol, 76.4 mg), **1a**-$d_2$ (0.41 mmol, 166.2 mg), and $^t$BuOH (3 mL). Then, $Et_3SiH$ (1.5 mmol, 238.0 uL), CuCl (0.03 mmol, 3.0 mg) and TBPB (0.9 mmol, 177.0 uL) were added. The reaction mixture was stirred at 60 °C under $N_2$. This reaction was conducted five times in parallel and reacted for 15, 25, 35, 45, and 60 minutes. The mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate =15:1-10:1) to afford **3a**/**3a**-*d*. The KIE value was calculated by detecting the ratio of two products, then averaged the results.

| Entry | 1 | 2 | 3 | 4 | 5 | Average value |
|---|---|---|---|---|---|---|
| Reaction time | 15mins | 25mins | 35mins | 45mins | 60mins | |
| Ratio of **3a**/**3a**-*d* | 1.38 | 1.32 | 1.5 | 1.32 | 1.27 | 1.36 |

## 8. Crystal data and structure refinement for 3k




**Method for crystal growth of 3k**: Single crystals of product **3k** was obtained through slow evaporation at room temperature of a solution in acetone (0.4 M) for 5 days. The crystal data of **3k** has already been deposited at Cambridge Crystallographic Data Center, UK, and the CCDC reference number is 2311768.




**3k** (ellipsoid contour at 50% probability level)

## Datablock: 230705a

Bond precision: C-C = 0.0081 A Wavelength=0.71073

Cell: a=9.4620(9) b=9.6433(9) c=17.6776(19)
alpha=75.612(2) beta=75.789(2) gamma=87.111(3)
Temperature: 100 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1514.5(3) | 1514.5(3) |
| Space group | P -1 | P -1 |
| Hall group | -P 1 | -P 1 |
| Moiety formula | C31 H37 N O3 S Si | C31 H37 N O3 S Si |
| Sum formula | C31 H37 N O3 S Si | C31 H37 N O3 S Si |
| Mr | 531.77 | 531.76 |
| Dx,g cm-3 | 1.166 | 1.166 |
| Z | 2 | 2 |
| Mu (mm-1) | 0.177 | 0.177 |
| F000 | 568.0 | 568.0 |
| F000' | 568.62 | |
| h,k,lmax | 12,13,23 | 12,12,23 |
| Nref | 7824 | 7198 |
| Tmin,Tmax | 0.965,0.965 | |
| Tmin' | 0.965 | |

Correction method= Not given

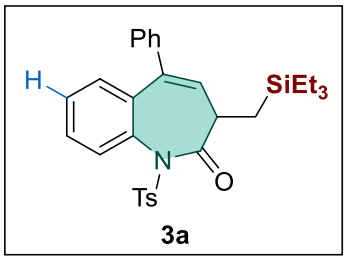
Data completeness= 0.920 Theta(max)= 28.706

R(reflections)= 0.1280( 3786) wR2(reflections)= 0.3530( 7198)

S = 1.176 Npar= 315

## 9. Characteristic Data

### 5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3a)



3a

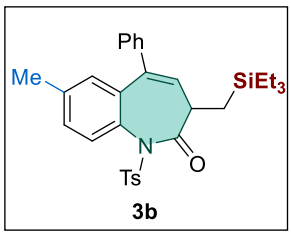
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 78 % (120.9 mg); mp 123-125 °C;

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 3H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 6.3 Hz, 4H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 3.3 Hz, 1H), 7.04 (s, 2H), 5.58 (d, *J* = 6.2 Hz, 1H), 2.87 – 2.73 (m, 1H), 2.28 (s, 3H), 1.14 (dd, *J* = 15.0, 4.1 Hz, 1H), 1.01 – 0.94 (m, 1H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.45 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.9, 144.8, 140.5, 139.3, 136.0, 135.3, 134.8, 130.3, 129.8, 129.5, 129.1, 128.9, 128.7, 128.33, 128.31, 128.27, 128.1, 42.4, 21.7, 11.1, 7.4, 3.8.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{35}NO_3SSiNa^+$, 540.2000; found, 540.2006

### 7-methyl-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3b)



3b

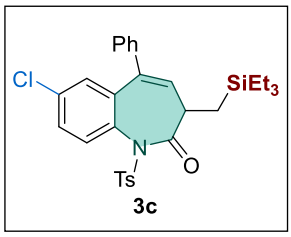
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 70 % (111.5 mg); mp 117-120 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.39 (q, *J* = 7.0, 6.6 Hz, 3H), 7.35 – 7.31 (m, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.05 – 6.99 (m, 3H), 5.54 (d, *J* = 6.1 Hz, 1H), 2.85 – 2.80 (m, 1H), 2.35 (s, 3H), 2.27 (s, 3H), 1.14 (dd, *J* = 15.1, 4.1 Hz, 1H), 0.96 (dd, *J* = 15.1, 10.4 Hz, 1H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.45 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.9, 144.7, 140.5, 139.4, 138.2, 136.1, 135.0, 132.4, 130.2, 129.9, 129.3, 129.2, 129.1, 128.8, 128.7, 128.3, 128.2, 42.3, 21.7, 21.3, 11.1, 7.4, 3.8.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{31}H_{37}NO_3SSiNa^+$, 554.2156; found, 554.2168

**7-chloro-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3c)**



**3c**

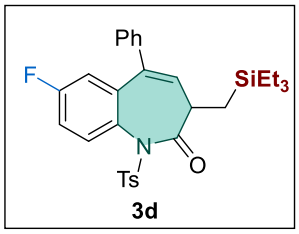
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 57 % (94.4 mg); mp 150-151 °C;

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.45 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.41 (q, *J* = 5.6 Hz, 3H), 7.33 – 7.28 (m, 2H), 7.24 (s, 1H), 7.04 (d, *J* = 8.2 Hz, 2H), 5.60 (d, *J* = 6.2 Hz, 1H), 2.78 (ddd, *J* = 10.3, 6.1, 4.3 Hz, 1H), 2.28 (s, 3H), 1.15 (dd, *J* = 15.1, 4.2 Hz, 1H), 0.97 (dd, *J* = 15.1, 10.4 Hz, 1H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.46 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.4, 145.1, 139.6, 138.6, 136.8, 135.7, 134.0, 133.2, 131.4, 130.8, 129.4, 129.2, 128.94, 128.87, 128.64, 128.56, 128.2, 42.4, 21.7, 11.1, 7.4, 3.7.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{34}ClNO_3SSiNa^+$, 574.1609; found, 574.1619

**7-fluoro-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3d)**



**3d**

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 64 % (102.7 mg); mp 167-169 °C;

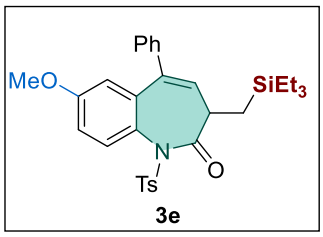
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 3H), 7.41 (q, *J* = 5.6 Hz, 3H), 7.33 – 7.29 (m, 2H), 7.19 (ddd, *J* = 10.4, 8.4, 2.9 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.95 (dd, *J* = 9.1, 2.9 Hz, 1H), 5.60 (d, *J* = 6.1 Hz, 1H), 2.81 (ddd, *J* = 10.3, 6.0, 4.2 Hz, 1H), 2.28 (s, 3H), 1.15 (dd, *J* = 15.1, 4.0 Hz, 1H), 0.97 (dd, *J* = 15.1, 10.4 Hz, 1H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.46 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.6, 162.4, 160.4, 145.0, 139.9, 138.6, 137.33, 137.26, 135.7, 131.44, 131.37, 131.1, 130.90, 130.88, 129.2, 128.89, 128.86, 128.6, 128.2, 116.0, 115.94, 115.86, 115.8, 42.4, 21.7, 11.1, 7.4, 3.7.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -111.9.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{34}FNO_3SSiNa^+$, 558.1905; found, 558.1917

**7-methoxy-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3e)**



**3e**

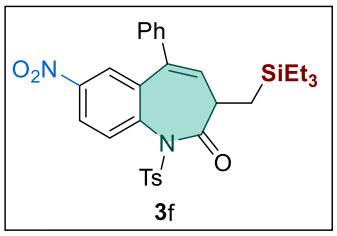
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 66 % (96.5 mg); mp 128-130 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.34 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.04 – 7.00 (m, 3H), 6.72 (d, *J* = 2.9 Hz, 1H), 5.54 (d, *J* = 6.2 Hz, 1H), 3.77 (s, 3H), 2.87 (ddd, *J* = 10.3, 6.1, 4.1 Hz, 1H), 2.27 (s, 3H), 1.14 (dd, *J* = 15.1, 4.1 Hz, 1H), 0.98 – 0.95 (m, 1H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.46 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.9, 158.8, 144.7, 140.4, 139.1, 136.5, 135.9, 130.7, 130.4, 129.1, 128.8, 128.7, 128.3, 128.2, 128.0, 114.3, 114.2, 55.7, 42.3, 21.7, 11.1, 7.4, 3.8.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{31}H_{37}NO_4SSiNa^+$, 570.2105; found, 570.2116

**7-nitro-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3f)**



**3f**

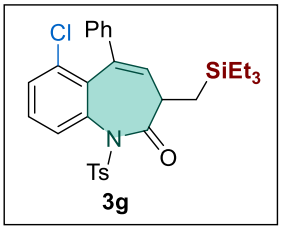
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 47 % (79.2 mg); mp 193-195 °C;

$^1$H NMR (600 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.9, 2.6 Hz, 1H), 8.15 (d, *J* = 2.6 Hz, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.44 (dd, *J* = 5.0, 1.5 Hz, 3H), 7.29 (dd, *J* = 6.6, 2.8 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 5.71 (d, *J* = 6.2 Hz, 1H), 2.69 (ddd, *J* = 10.3, 6.0, 4.3 Hz, 1H), 2.31 (s, 3H), 1.19 – 1.16 (m, 1H), 1.00 (dd, *J* = 15.1, 10.3 Hz, 1H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.46 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 171.9, 146.8, 145.6, 139.5, 139.4, 138.1, 136.5, 135.4, 132.3, 130.7, 129.4, 129.2, 129.1, 129.0, 128.2, 125.1, 42.6, 21.8, 11.1, 7.4, 3.7.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{34}N_2O_5SSiNa^+$, 585.1850; found, 585.1860

**6-chloro-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3g)**



3g

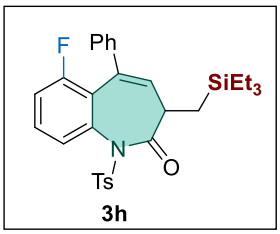
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 66 % (109.3 mg); mp 150-152 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 3H), 7.45 (q, *J* = 8.0, 7.1 Hz, 2H), 7.36 (dt, *J* = 12.7, 6.8 Hz, 3H), 7.25 (d, *J* = 6.6 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 5.71 (d, *J* = 6.9 Hz, 1H), 2.87 (ddd, *J* = 10.7, 6.9, 3.8 Hz, 1H), 2.27 (s, 3H), 1.07 (dd, *J* = 15.1, 3.8 Hz, 1H), 0.99 – 0.95 (m, 1H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.46 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 173.1, 145.0, 138.9, 138.8, 136.7, 135.5, 134.2, 133.4, 133.3, 130.8, 129.09, 129.06, 128.9, 128.8, 128.0, 127.8, 126.4, 42.7, 21.7, 10.7, 7.4, 3.8.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{34}ClNO_3SSiNa^+$, 574.1610; found, 574.1622

**6-fluoro-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3h)**



3h

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 68 % (109.1 mg); mp 142-144 °C;

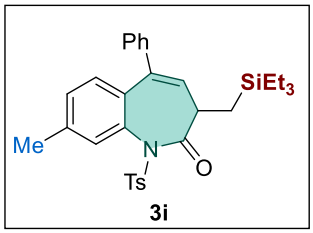
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.49 (td, *J* = 8.1, 5.7 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.33 – 7.29 (m, 2H), 7.17 – 7.13 (m, 1H), 6.98 (d, *J* = 8.1 Hz, 2H), 5.68 (d, *J* = 6.6 Hz, 1H), 2.87 (ddd, *J* = 10.6, 6.5, 4.2 Hz, 1H), 2.27 (s, 3H), 1.12 (dd, *J* = 15.1, 4.2 Hz, 1H), 1.00 – 0.96 (m, 1H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.46 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.7, 160.7, 158.7, 145.0, 138.7, 136.2, 136.1, 135.9, 135.6, 132.6, 129.2, 129.1, 128.9, 128.7, 128.2, 126.3, 125.34, 125.31, 123.4, 123.3, 116.1, 115.9, 42.6, 21.7, 10.9, 7.3, 3.7.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.4.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{34}FNO_3SSiNa^+$, 558.1905; found, 558.1904

**8-methyl-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3i)**



3i

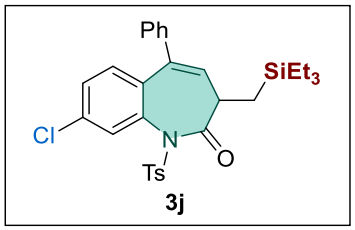
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 63 % (100.4 mg); mp 132-134 °C;

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.50 (s, 1H), 7.40 – 7.32 (m, 5H), 7.18 – 7.12 (m, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 5.50 (d, *J* = 6.1 Hz, 1H), 2.81 (ddd, *J* = 10.3, 6.0, 4.0 Hz, 1H), 2.48 (s, 3H), 2.27 (s, 3H), 1.12 (dd, *J* = 15.1, 3.9 Hz, 1H), 0.97 – 0.91 (m, 1H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.45 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 172.9, 144.7, 140.4, 139.4, 138.6, 136.1, 134.6, 132.4, 129.9, 129.49, 129.45, 129.2, 129.1, 128.8, 128.7, 128.3, 42.3, 21.7, 21.4, 11.0, 7.4, 3.8.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{31}H_{37}NO_3SSiNa^+$, 554.2156; found, 554.2161

**8-chloro-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3j)**



3j

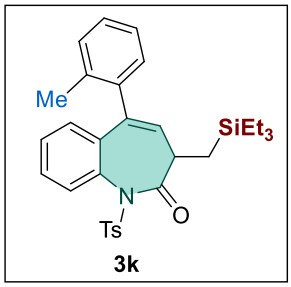
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 59 % (97.7 mg); mp 170-172 °C;

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.73 – 7.68 (m, 3H), 7.41 (d, *J* = 6.7 Hz, 3H), 7.35 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 5.59 (d, *J* = 6.2 Hz, 1H), 2.78 (ddd, *J* = 10.3, 6.0, 4.2 Hz, 1H), 2.30 (s, 3H), 1.15 (dd, *J* = 15.1, 4.0 Hz, 1H), 1.02 – 0.98 (m, 1H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.47 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.4, 145.1, 139.8, 138.9, 135.7, 135.5, 133.9, 133.8, 130.7, 130.5, 129.4, 129.2, 128.90, 128.86, 128.6, 128.5, 128.2, 42.4, 21.7, 11.1, 7.4, 3.8.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{34}ClNO_3SSiNa^+$, 574.1610; found, 574.1614

**5-(o-tolyl)-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3k)**



3k

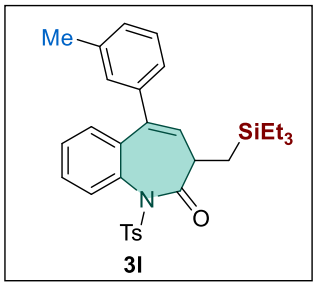
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 66 % (105.1 mg); mp 101-103 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.65 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.42 (td, *J* = 7.8, 1.6 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.28 (dtd, *J* = 7.4, 4.4, 3.9, 1.7 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.05 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.59 (d, *J* = 5.7 Hz, 1H), 2.80 (ddd, *J* = 10.1, 5.6, 4.4 Hz, 1H), 2.43 (s, 3H), 2.11 (s, 3H), 1.19 – 1.14 (m, 1H), 1.00 (dd, *J* = 15.2, 10.2 Hz, 1H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.45 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 174.4, 145.0, 141.4, 139.2, 136.9, 136.8, 136.6, 133.7, 133.0, 130.8, 130.4, 129.43, 129.39, 128.4, 128.3, 128.0, 127.9, 126.0, 42.1, 21.8, 21.0, 11.1, 7.4, 3.8.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{31}H_{37}NO_3SSiNa^+$, 554.2156; found, 554.2160

**5-(m-tolyl)-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3l)**



3l

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 67 % (106.7 mg); mp 119-121 °C;

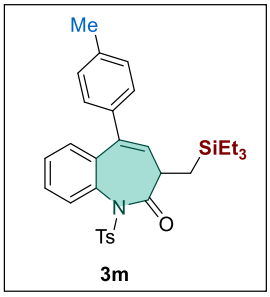
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.4, 2.6 Hz, 3H), 7.49 – 7.45 (m, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 5.9 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 5.55 (d, *J* = 6.1 Hz, 1H), 2.82 – 2.78 (m, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 1.14 (dd, *J* = 15.1, 4.1 Hz, 1H), 0.97 (dd, *J* = 15.1, 10.4 Hz, 1H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.45 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.9, 144.7, 140.5, 139.3, 138.3, 136.0, 135.4, 134.7, 130.1, 129.8, 129.5, 129.09, 129.06, 129.0, 128.9, 128.6, 128.2, 128.1, 125.5, 42.3, 21.7, 21.6, 11.1, 7.4, 3.7.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{31}H_{37}NO_3SSiNa^+$, 554.2156; found, 554.2152

**5-(p-tolyl)-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one**

**(3m)**



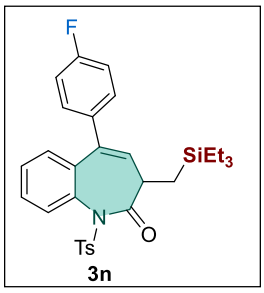

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 71 % (113.1 mg); mp 167-170 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 3H), 7.50 – 7.44 (m, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.26 (dd, *J* = 5.6, 2.1 Hz, 1H), 7.24 – 7.18 (m, 4H), 7.04 (d, *J* = 8.2 Hz, 2H), 5.53 (d, *J* = 6.1 Hz, 1H), 2.79 (ddd, *J* = 10.3, 6.0, 4.1 Hz, 1H), 2.41 (s, 3H), 2.28 (s, 3H), 1.13 (dd, *J* = 15.1, 4.1 Hz, 1H), 1.01 – 0.94 (m, 1H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.44 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 173.0, 144.7, 140.3, 138.2, 136.5, 136.0, 135.5, 134.8, 129.8, 129.5, 129.4, 129.1, 128.8, 128.19, 128.17, 128.1, 42.3, 21.7, 21.3, 11.0, 7.4, 3.7.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{31}H_{37}NO_3SSiNa^+$, 554.2156; found, 554.2164

**5-(4-fluorophenyl)-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3n)**



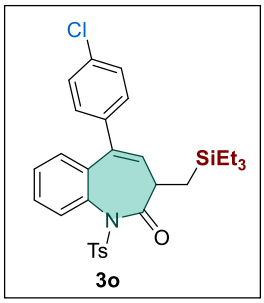

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 73 % (117.2 mg); mp 134-136 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 3H), 7.51 – 7.46 (m, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.24 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.08 (dd, *J* = 18.8, 8.4 Hz, 4H), 5.54 (d, *J* = 6.2 Hz, 1H), 2.80 (ddd, *J* = 10.4, 6.1, 4.2 Hz, 1H), 2.31 (s, 3H), 1.14 (dd, *J* = 15.1, 4.1 Hz, 1H), 0.97 (dd, *J* = 15.1, 10.4 Hz, 1H), 0.84 (d, *J* = 15.9 Hz, 9H), 0.44 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.9, 163.8, 161.9, 144.9, 139.4, 136.0, 135.41, 135.38, 135.2, 134.8, 130.2, 129.9, 129.8, 129.6, 129.5, 129.1, 128.8, 128.5, 128.2, 42.3, 21.7, 11.0, 7.4, 3.7.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{34}FNO_3SSiNa^+$, 558.1905; found, 558.1906

**5-(4-chlorophenyl)-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3o)**



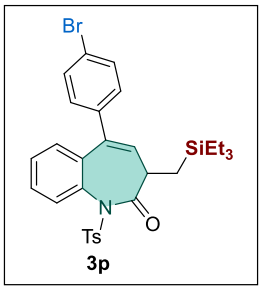

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 64 % (105.9 mg); mp 142-144 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.7, 5.6 Hz, 3H), 7.51 – 7.47 (m, 1H), 7.39 – 7.35 (m, 3H), 7.28 – 7.25 (m, 2H), 7.24 – 7.21 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 5.58 (d, *J* = 6.2 Hz, 1H), 2.80 (ddd, *J* = 10.3, 6.0, 4.4 Hz, 1H), 2.31 (s, 3H), 1.15 (dd, *J* = 15.1, 4.2 Hz, 1H), 0.96 (dd, *J* = 15.1, 10.3 Hz, 1H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.44 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.7, 144.9, 139.3, 137.7, 136.0, 134.9, 134.8, 134.3, 130.7, 129.6, 129.53, 129.46, 129.1, 129.0, 128.8, 128.6, 128.3, 42.4, 21.7, 11.0, 7.4, 3.7.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{34}ClNO_3SSiNa^+$, 574.1609; found, 574.1613

**5-(4-bromophenyl)-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3p)**



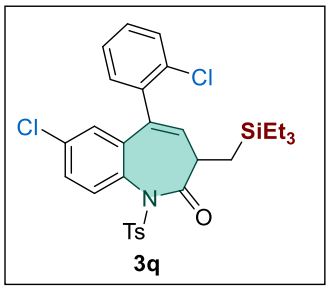

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 48 % (85.9 mg); mp 132-135 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 3H), 7.56 – 7.48 (m, 3H), 7.41 – 7.34 (m, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 5.59 (d, *J* = 6.1 Hz, 1H), 2.82 – 2.77 (m, 1H), 2.31 (s, 3H), 1.15 (dd, *J* = 15.1, 4.2 Hz, 1H), 0.97 – 0.93 (m, 1H), 0.86 – 0.82 (m, 9H), 0.44 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.7, 144.9, 139.4, 138.2, 136.0, 134.81, 134.84, 132.0, 130.8, 129.8, 129.6, 129.5, 129.2, 128.8, 128.6, 128.3, 122.5, 42.4, 21.7, 11.0, 7.4, 3.7.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{34}BrNO_3SSiNa^+$, 618.1105; found, 618.1111

**7-chloro-5-(2-chlorophenyl)-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3q)**



3q

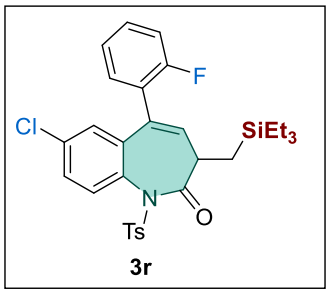
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 48 % (84.3 mg); mp 126-129 °C;

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.44 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.41 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.29 – 7.27 (m, 2H), 7.27 (s, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 5.67 (d, *J* = 5.7 Hz, 1H), 2.78 (dt, *J* = 10.1, 4.9 Hz, 1H), 2.40 (s, 3H), 1.18 (dd, *J* = 15.1, 4.2 Hz, 1H), 0.96 (dd, *J* = 15.2, 10.3 Hz, 1H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.46 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.4, 145.1, 138.3, 137.6, 137.0, 136.3, 135.4, 133.8, 133.6, 132.2, 131.9, 130.6, 130.1, 129.9, 129.5, 129.4, 128.3, 127.7, 127.3, 42.2, 21.8, 11.0, 7.4, 3.8.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{33}Cl_2NO_3SSiNa^+$, 608.1220; found, 608.1230

**7-chloro-5-(2-fluorophenyl)-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3r)**



3r

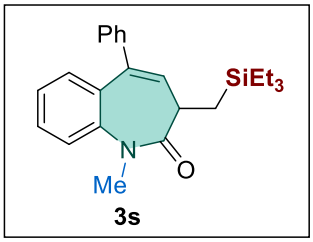
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 63 % (107.7 mg); mp 154-156 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.43 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.24 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.15 (d, *J* = 8.1 Hz, 3H), 7.13 (d, *J* = 2.3 Hz, 1H), 5.68 (d, *J* = 6.0 Hz, 1H), 2.80 (ddd, *J* = 10.2, 5.9, 4.2 Hz, 1H), 2.33 (s, 3H), 1.16 (dd, *J* = 15.1, 4.1 Hz, 1H), 0.97 (dd, *J* = 15.2, 10.4 Hz, 1H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.46 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.4, 161.1, 159.1, 145.0, 136.7, 135.8, 135.01, 134.99, 134.4, 134.0, 132.2, 131.4, 131.3, 130.6, 130.5, 129.2, 128.4, 128.1, 126.5, 126.4, 124.68, 124.65, 116.6, 116.4, 42.3, 21.8, 11.0, 7.4, 3.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -105.1.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{33}ClFNO_3SSiNa^+$, 592.1516; found, 592.1506

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



**3s**

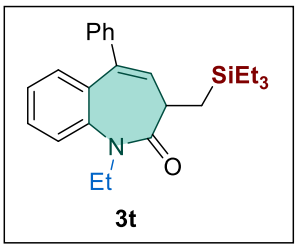
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White liquid; yield 62 % (70.1 mg);

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 4H), 7.24 – 7.19 (m, 2H), 7.13 – 7.09 (m, 1H), 5.85 (d, *J* = 6.3 Hz, 1H), 3.44 (s, 3H), 2.60 (dt, *J* = 10.5, 5.8 Hz, 1H), 1.32 (d, *J* = 4.8 Hz, 1H), 1.22 – 1.17 (m, 1H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.53 (q, *J* = 8.0 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 174.0, 142.9, 140.6, 139.3, 133.24, 133.18, 130.1, 128.7, 128.6, 128.5, 127.7, 124.2, 122.5, 40.1, 36.9, 11.9, 7.5, 3.9.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{31}NOSiNa^+$, 400.2067; found, 400.2072

**1-ethyl-5-phenyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3t)**



**3t**

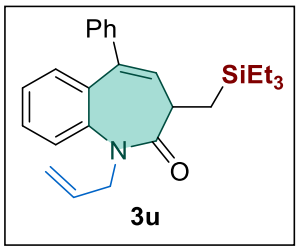
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White liquid; yield 58 % (68.1 mg);

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.34 – 7.29 (m, 3H), 7.24 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.20 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.14 – 7.09 (m, 1H), 5.85 (d, *J* = 6.3 Hz, 1H), 4.42 (dd, *J* = 13.7, 7.1 Hz, 1H), 3.66 (dd, *J* = 13.7, 6.9 Hz, 1H), 2.61 (dt, *J* = 9.5, 5.8 Hz, 1H), 1.35 (dd, *J* = 15.0, 5.4 Hz, 1H), 1.19 (dd, *J* = 15.0, 9.4 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.53 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.4, 141.2, 140.7, 139.1, 134.8, 133.7, 129.8, 128.6, 128.5, 128.4, 127.6, 124.6, 123.4, 44.0, 40.2, 13.2, 11.7, 7.4, 3.8.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{25}H_{33}NOSiNa^+$, 414.2224; found, 414.2228

**1-allyl-5-phenyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3u)**



3u

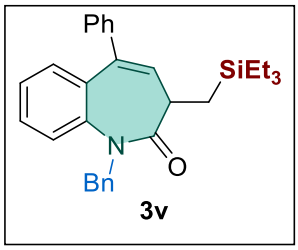
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); Colourless liquid; yield 58 % (70.1 mg);

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.29 (m, 4H), 7.25 – 7.22 (m, 2H), 7.19 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.13 – 7.09 (m, 1H), 5.86 (d, *J* = 6.3 Hz, 1H), 5.82 – 5.73 (m, 1H), 5.11 – 5.03 (m, 2H), 4.75 (dd, *J* = 15.8, 5.1 Hz, 1H), 4.38 (dd, *J* = 15.8, 5.8 Hz, 1H), 2.66 (dt, *J* = 9.6, 5.6 Hz, 1H), 1.38 – 1.33 (m, 1H), 1.20 (dd, *J* = 15.0, 9.5 Hz, 1H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.53 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.9, 141.6, 140.6, 139.5, 134.3, 133.7, 133.5, 129.9, 128.64, 128.58, 128.5, 127.7, 124.6, 123.2, 116.6, 51.7, 40.2, 11.8, 7.5, 3.9.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{26}H_{33}NOSiNa^+$, 426.2224; found, 426.2227

**1-benzyl-5-phenyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3v)**



3v

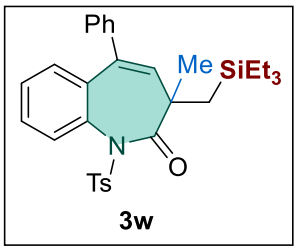
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 68 % (92.5 mg); mp 106-108 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.25 (m, 3H), 7.12 (s, 2H), 7.10 – 7.06 (m, 2H), 7.05 (d, *J* = 7.0 Hz, 1H), 7.01 (d, *J* = 6.6 Hz, 2H), 6.99 – 6.95 (m, 2H), 5.86 (d, *J* = 6.3 Hz, 1H), 5.76 (d, *J* = 15.2 Hz, 1H), 4.72 (d, *J* = 15.2 Hz, 1H), 2.71 (dt, *J* = 11.0, 5.7 Hz, 1H), 1.38 (dd, *J* = 15.0, 5.1 Hz, 1H), 1.27 – 1.22 (m, 1H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.54 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 173.2, 140.8, 140.4, 139.7, 137.5, 135.0, 133.2, 129.9, 128.7, 128.5, 128.3, 127.70, 127.69, 127.1, 124.7, 123.5, 51.6, 40.1, 11.9, 7.5, 3.9.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{35}NOSiNa^+$, 476.2381; found, 476.2383

**3-methyl-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3w)**



**3w**

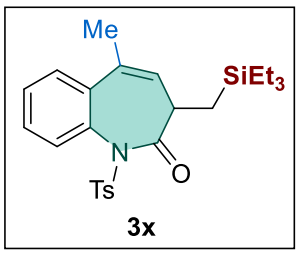
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 74 % (117.9 mg); mp 129-131 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.41 – 7.34 (m, 5H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 5.74 (s, 1H), 2.32 (s, 3H), 1.36 (s, 3H), 0.71 (t, *J* = 7.9 Hz, 9H), 0.55 (d, *J* = 14.9 Hz, 1H), 0.48 (d, *J* = 15.0 Hz, 1H), 0.45 – 0.30 (m, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.9, 144.6, 140.8, 140.2, 136.6, 135.7, 135.1, 134.8, 129.9, 129.2, 128.9, 128.8, 128.7, 128.4, 128.3, 128.2, 127.8, 47.0, 27.6, 21.7, 15.9, 7.4, 4.6.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{31}H_{37}NO_3SSiNa^+$, 554.2156; found, 554.2155

**5-methyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3x)**



**3x**

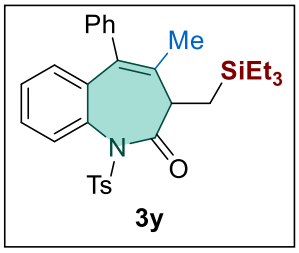
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 30 % (41 mg); mp 125-127 °C;

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.51 – 7.48 (m, 1H), 7.43 (q, *J* = 4.8, 3.6 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.14 (d, *J* = 5.7 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.41 (s, 3H), 2.12 (s, 3H), 1.06 (dd, *J* = 15.1, 4.6 Hz, 1H), 0.85 – 0.81 (m, 1H), 0.79 (t, *J* = 7.9 Hz, 9H), 0.37 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.0, 144.8, 136.4, 136.2, 134.4, 133.2, 130.2, 129.8, 129.1, 128.9, 128.4, 127.7, 126.5, 41.7, 21.8, 20.7, 10.9, 7.3, 3.7.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{33}NO_3SSiNa^+$, 478.1843; found, 478.1853

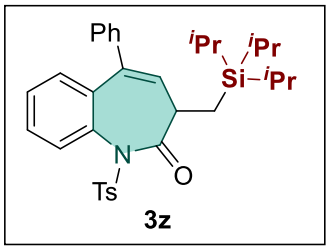
**4-methyl-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3y)**



**3y**

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 47 % (74.9 mg); mp 126-129 °C;
$^1$H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.67 – 7.65 (m, 1H), 7.41 – 7.37 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.15 (dd, *J* = 13.8, 7.6 Hz, 4H), 7.01 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.03 (dd, *J* = 8.4, 5.9 Hz, 1H), 2.33 (s, 3H), 1.55 (s, 3H), 1.20 (dd, *J* = 14.8, 8.6 Hz, 1H), 0.80 (t, *J* = 7.9 Hz, 10H), 0.42 – 0.37 (m, 6H).
$^{13}$C NMR (151 MHz, $CDCl_3$) δ 170.9, 144.6, 140.2, 137.3, 136.3, 136.2, 135.4, 134.6, 130.8, 130.4, 129.1, 128.7, 128.6, 128.4, 127.9, 127.57, 127.56, 45.1, 21.7, 16.8, 8.5, 7.4, 3.6.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{31}H_{37}NO_3SSiNa^+$, 554.2156; found, 554.2161

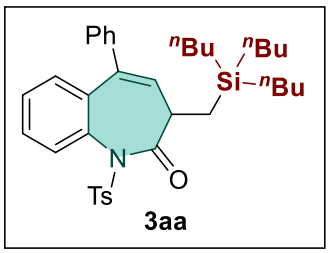
**5-phenyl-1-tosyl-3-((triisopropylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3z)**



**3z**

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 65 % (109.2 mg); mp 143-144 °C;
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 5.8 Hz, 2H), 7.67 (s, 1H), 7.48 (td, *J* = 8.1, 1.4 Hz, 1H), 7.42 – 7.35 (m, 4H), 7.35 – 7.32 (m, 2H), 7.26 – 7.22 (m, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 5.64 (d, *J* = 6.3 Hz, 1H), 2.92 (ddd, *J* = 10.0, 6.3, 3.5 Hz, 1H), 2.28 (s, 3H), 1.30 (dd, *J* = 15.4, 3.6 Hz, 1H), 1.01 (d, *J* = 10.1 Hz, 1H), 0.97 – 0.92 (m, 12H), 0.92 – 0.87 (m, 9H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.9, 144.8, 140.4, 139.1, 135.9, 135.3, 134.9, 130.5, 129.7, 129.4, 129.1, 128.82, 128.77, 128.4, 128.3, 128.20, 128.15, 42.3, 21.7, 18.7, 18.7, 11.2, 8.4.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{33}H_{41}NO_3SSiNa^+$, 582.2469; found, 582.2480

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



**3aa**

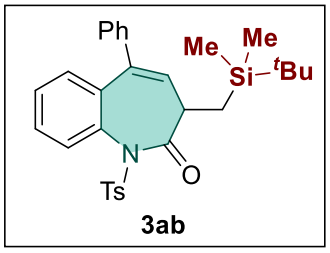
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 90 % (149.4 mg); mp 199-201 °C;
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 2.6 Hz, 1H), 7.69 (t, *J* = 3.6 Hz, 2H), 7.50 –

7.45 (m, 1H), 7.41 – 7.33 (m, 6H), 7.28 – 7.26 (m, 1H), 7.03 (d, *J* = 8.2 Hz, 2H), 5.58 (d, *J* = 6.2 Hz, 1H), 2.82 (ddd, *J* = 10.3, 6.2, 3.8 Hz, 1H), 2.28 (s, 3H), 1.27 – 1.19 (m, 6H), 1.16 (s, 1H), 1.15 – 1.09 (m, 6H), 0.97 (dd, *J* = 15.1, 10.7 Hz, 1H), 0.79 (t, *J* = 7.2 Hz, 9H), 0.48 – 0.38 (m, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 173.0, 144.8, 140.4, 139.2, 136.0, 135.4, 134.9, 130.3, 129.7, 129.5, 129.1, 128.9, 128.7, 128.32, 128.27, 128.1, 42.5, 26.9, 26.1, 21.7, 13.8, 12.7, 11.9.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{36}H_{47}NO_3SSiNa^+$, 624.2938; found, 624.2941

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



**3ab**

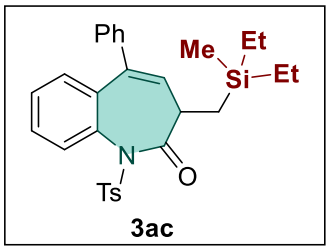
Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 75 % (116.3 mg); mp 114-117 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 3H), 7.48 (td, *J* = 7.8, 1.6 Hz, 1H), 7.40 – 7.33 (m, 6H), 7.29 – 7.26 (m, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 5.58 (d, *J* = 6.2 Hz, 1H), 2.80 (ddd, *J* = 10.4, 6.1, 4.2 Hz, 1H), 2.28 (s, 3H), 1.18 (dd, *J* = 15.1, 4.2 Hz, 1H), 0.99 – 0.94 (m, 1H), 0.81 (s, 9H), -0.05 (s, 3H), -0.20 (s, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.8, 144.8, 140.4, 139.2, 136.0, 135.3, 134.8, 130.3, 129.8, 129.5, 129.1, 128.8, 128.7, 128.35, 128.31, 128.27, 128.2, 42.6, 26.4, 21.7, 16.5, 11.6, -4.8, -5.9.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{35}NO_3SSiNa^+$, 540.2000; found, 540.2007

**3-((diethyl(methyl)silyl)methyl)-5-phenyl-1-tosyl-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3ac)**



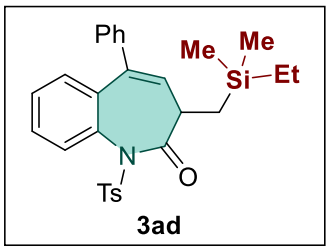
**3ac**

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 64 % (96.6 mg); mp 128-130 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 3H), 7.48 (td, *J* = 7.9, 1.5 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.33 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.28 – 7.26 (m, 1H), 7.04 (s, 1H), 7.02 (s, 1H), 5.57 (d, *J* = 6.2 Hz, 1H), 2.81 (ddd, *J* = 10.4, 6.1, 4.4 Hz, 1H), 2.28 (s, 3H), 1.13 (dd, *J* = 15.1, 4.3 Hz, 1H), 0.99 – 0.94 (m, 1H), 0.85 (q, *J* = 8.0 Hz, 6H), 0.43 (dtd,

*J* = 11.6, 7.8, 5.0 Hz, 4H), -0.11 (s, 3H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.8, 144.8, 140.4, 139.3, 136.0, 135.3, 134.8, 130.2, 129.8, 129.5, 129.1, 128.8, 128.7, 128.33, 128.30, 128.27, 128.1, 42.4, 21.7, 12.6, 7.4, 7.3, 5.6, 5.3, -5.4.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{29}H_{33}NO_3SSiNa^+$, 526.1843; found, 526.1853

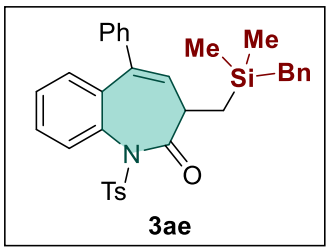
**3-((ethyldimethylsilyl)methyl)-5-phenyl-1-tosyl-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3ad)**



**3ad**

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 57 % (83.7 mg); mp 134-136 °C;
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.7, 5.5 Hz, 3H), 7.50 – 7.46 (m, 1H), 7.38 (t, *J* = 6.6 Hz, 4H), 7.35 – 7.32 (m, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 2H), 5.57 (d, *J* = 6.1 Hz, 1H), 2.80 (dt, *J* = 10.3, 5.1 Hz, 1H), 2.28 (s, 3H), 1.13 (dd, *J* = 15.0, 4.4 Hz, 1H), 0.97 (dd, *J* = 15.0, 10.2 Hz, 1H), 0.85 (t, *J* = 7.9 Hz, 3H), 0.42 (q, *J* = 8.0 Hz, 2H), -0.07 (s, 3H), -0.09 (s, 3H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.8, 144.8, 140.4, 139.3, 136.0, 135.3, 134.8, 130.2, 129.8, 129.5, 129.1, 128.9, 128.7, 128.33, 128.30, 128.28, 128.2, 42.5, 21.7, 14.2, 7.4, 7.3, -3.0, -3.3.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{31}NO_3SSiNa^+$, 512.1686; found, 512.1684

**3-((benzyldimethylsilyl)methyl)-5-phenyl-1-tosyl-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3ae)**

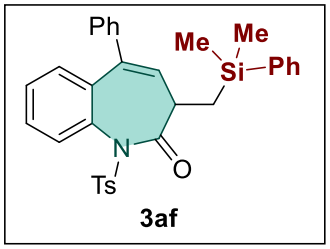


**3ae**

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 53 % (87.7 mg); mp 114-117 °C;
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.3, 1.6 Hz, 3H), 7.48 (td, *J* = 7.7, 1.6 Hz, 1H), 7.37 (qd, *J* = 4.0, 3.5, 1.2 Hz, 4H), 7.32 – 7.28 (m, 2H), 7.25 (d, *J* = 0.8 Hz, 1H), 7.10 – 7.05 (m, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.88 – 6.84 (m, 2H), 5.51 (d, *J* = 6.1 Hz, 1H), 2.67 (ddd, *J* = 9.7, 6.1, 5.0 Hz, 1H), 2.27 (s, 3H), 2.02 (s, 2H), 1.17 (dd, *J* = 15.0, 5.0 Hz, 1H), 0.97 (dd, *J* = 15.1, 9.7 Hz, 1H), -0.03 (s, 3H), -0.07 (s, 3H).

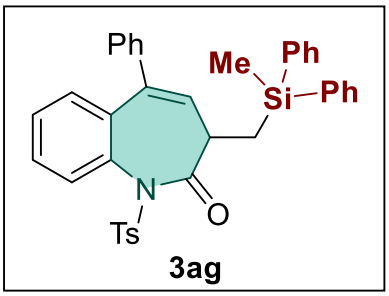
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.6, 144.8, 140.5, 139.5, 139.2, 136.0, 135.2, 134.7, 130.0, 129.8, 129.6, 129.1, 128.8, 128.7, 128.35, 128.30, 128.27, 128.1, 128.0, 124.3, 42.3, 26.1, 21.7, 14.3, -2.3, -2.7.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{33}H_{33}NO_3SSiNa^+$, 574.1843; found, 574.1841

**3-((dimethyl(phenyl)silyl)methyl)-5-phenyl-1-tosyl-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3af)**




Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 53 % (85.5 mg); mp 161-163 °C;
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 6.6 Hz, 2H), 7.29 (dt, *J* = 27.9, 7.5 Hz, 7H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.12 – 7.05 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.42 (d, *J* = 6.1 Hz, 1H), 2.77 (dt, *J* = 10.3, 5.3 Hz, 1H), 2.26 (s, 3H), 1.31 (dd, *J* = 15.0, 4.4 Hz, 1H), 1.22 (dd, *J* = 14.9, 10.3 Hz, 1H), 0.24 (d, *J* = 7.6 Hz, 6H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.7, 144.7, 140.3, 139.1, 138.3, 136.0, 135.2, 134.7, 133.7, 129.8, 129.7, 129.5, 129.2, 129.1, 128.8, 128.5, 128.21, 128.17, 128.04, 128.01, 42.6, 21.7, 15.3, -1.9, -3.0.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{32}H_{31}NO_3SSiNa^+$, 560.1686; found, 560.1686

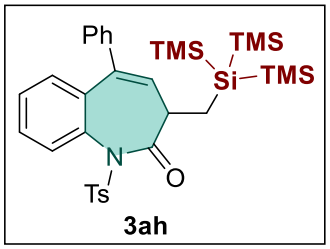
**3-((methyldiphenylsilyl)methyl)-5-phenyl-1-tosyl-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3ag)**




Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 71 % (127.8 mg); mp 192-194 °C;
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.37 (m, 6H), 7.36 – 7.32 (m, 3H), 7.30 – 7.26 (m, 6H), 7.19 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 2H), 5.40 (d, *J* = 6.2 Hz, 1H), 2.83 (q, *J* = 7.0 Hz, 1H), 2.27 (s, 3H), 1.59 (s, 1H), 1.27 (d, *J* = 3.8 Hz, 1H), 0.91 – 0.82 (m, 1H), 0.48 (s, 3H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.7, 144.8, 140.3, 139.0, 136.5, 136.0, 135.8, 135.2,

134.74, 134.71, 134.5, 129.64, 129.62, 129.56, 129.50, 129.48, 129.1, 128.8, 128.5, 128.23, 128.18, 128.14, 128.07, 128.0, 42.6, 21.7, 13.7, -3.5.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{37}H_{33}NO_3SSiNa^+$, 622.1843; found, 622.1842

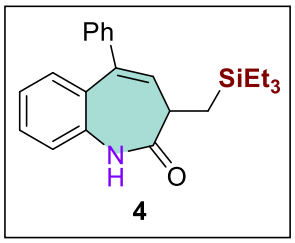
**3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-5-phenyl-1-tosyl-1,3-dihydro-2H-benzo[*b*]azepin-2-one (3ah)**



**3ah**

Purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1); White solid; yield 66 % (128.7 mg); mp 184-185 °C;
$^1$H NMR (600 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.8, 3.8 Hz, 3H), 7.49 – 7.46 (m, 1H), 7.39 – 7.34 (m, 6H), 7.27 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 5.64 (d, *J* = 6.3 Hz, 1H), 2.87 – 2.84 (m, 1H), 2.27 (s, 3H), 1.66 (dd, *J* = 15.0, 4.8 Hz, 1H), 1.02 (dd, *J* = 15.0, 7.8 Hz, 1H), 0.03 (s, 27H).
$^{13}$C NMR (151 MHz, $CDCl_3$) δ 172.4, 144.8, 140.6, 138.7, 135.9, 135.4, 135.0, 130.8, 129.9, 129.6, 129.1, 128.9, 128.7, 128.4, 128.15, 128.11, 45.9, 21.7, 6.7, 1.1.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{33}H_{47}NO_3SSi_4Na^+$, 672.2246; found, 672.2247

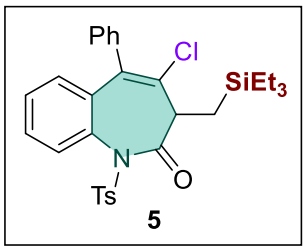
**5-phenyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (4)**



**4**

Purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1); White solid; yield 67 % (73.1 mg); mp 152-153 °C;
$^1$H NMR (500 MHz, $CDCl_3$) δ 9.17 (s, 1H), 7.36 – 7.30 (m, 4H), 7.22 – 7.19 (m, 4H), 7.08 (t, *J* = 7.5 Hz, 1H), 5.78 (d, *J* = 6.1 Hz, 1H), 2.64 (s, 1H), 1.36 (d, *J* = 13.6 Hz, 1H), 1.15 (dd, *J* = 14.7, 10.4 Hz, 1H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.9 Hz, 6H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.5, 141.4, 140.5, 137.1, 131.35, 131.25, 130.7, 128.9, 128.8, 128.4, 127.7, 123.7, 121.8, 39.8, 11.1, 7.5, 3.9.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{29}NOSiNa^+$, 386.1911; found, 386.1914

**4-chloro-5-phenyl-1-tosyl-3-((triethylsilyl)methyl)-1,3-dihydro-2H-benzo[*b*]azepin-2-one (5)**



**5**

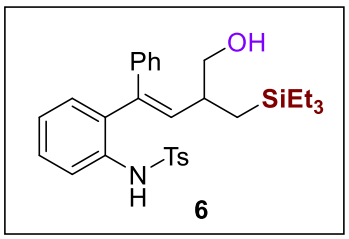
Purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1); White solid; yield 70 % (116.0 mg); mp 117-121 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.38 (m, 4H), 7.33 – 7.30 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.06 (dd, *J* = 7.9, 1.6 Hz, 1H), 3.25 (t, *J* = 7.2 Hz, 1H), 2.34 (s, 3H), 1.20 (dd, *J* = 15.1, 7.0 Hz, 1H), 1.11 (dd, *J* = 15.1, 7.5 Hz, 1H), 0.82 (t, *J* = 7.9 Hz, 9H), 0.43 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.5, 145.1, 138.5, 136.9, 136.0, 135.7, 134.5, 130.6, 130.4, 130.3, 129.4, 128.9, 128.7, 128.6, 128.4, 128.3, 45.7, 21.8, 9.6, 7.4, 3.6.

HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{30}H_{35}ClNO_3SSi$, 552.1790; found, 552.1793

**(E)-N-(2-(4-hydroxy-1-phenyl-3-((triethylsilyl)methyl)but-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (6)**



**6**

Purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1); White solid; yield 78 % (122.1 mg); mp 123-125 °C;

$^1$H NMR (500 MHz, $CDCl_3$) δ 9.12 (s, 1H), 7.79 – 7.69 (m, 1H), 7.58 – 7.51 (m, 2H), 7.27 – 7.24 (m, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 6.9 Hz, 1H), 7.00 (t, *J* = 7.7 Hz, 2H), 6.96 (s, 2H), 6.92 – 6.89 (m, 1H), 6.77 – 6.73 (m, 2H), 6.07 (d, *J* = 10.5 Hz, 1H), 3.74 (dt, *J* = 9.7, 3.8 Hz, 1H), 3.46 (td, *J* = 10.2, 2.8 Hz, 1H), 2.99 (d, *J* = 3.6 Hz, 1H), 2.33 – 2.28 (m, 4H), 0.76 (t, *J* = 7.9 Hz, 9H), 0.44 (d, *J* = 6.8 Hz, 2H), 0.31 (q, *J* = 7.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 143.1, 141.0, 137.5, 136.6, 136.2, 134.7, 131.6, 131.4, 129.5, 128.4, 128.1, 127.2, 126.7, 126.5, 124.5, 122.0, 68.2, 38.1, 21.6, 13.7, 7.4, 3.7.

HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{30}H_{40}NO_3SSi$, 522.2493; found, 522.2489

## Reference

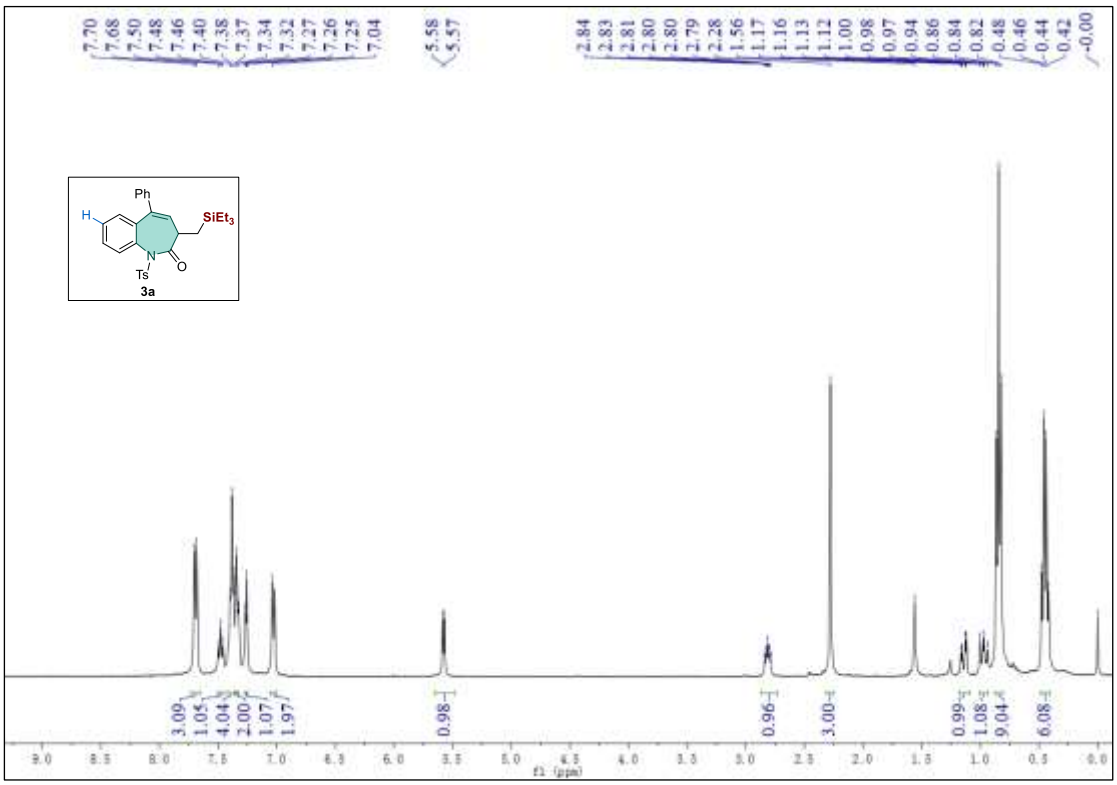
(1) Zhang, Z.; Tan, P.; Wang, S.; Wang, H.; Xie, L.; Chen, Y.; Han, L.; Yang, S.; Sun, K. Visible-Light-Promoted Selective Sulfonylation and Selenylation of Dienes to Access Sulfonyl-/Seleno-Benzazepine Derivatives. *Org. Lett.* **2023**, *25*, 4208-4213.

(2) Wu, L.; Meng, Y.; Ferguson, J.; Wang, L.; Zeng, F. Palladium-Catalyzed Oxidative Annulation of Ortho-Alkenylanilines and Allenes: An Access to Benzo[B]Azepines. *J. Org. Chem.* **2017**, *82*, 4121-4128.

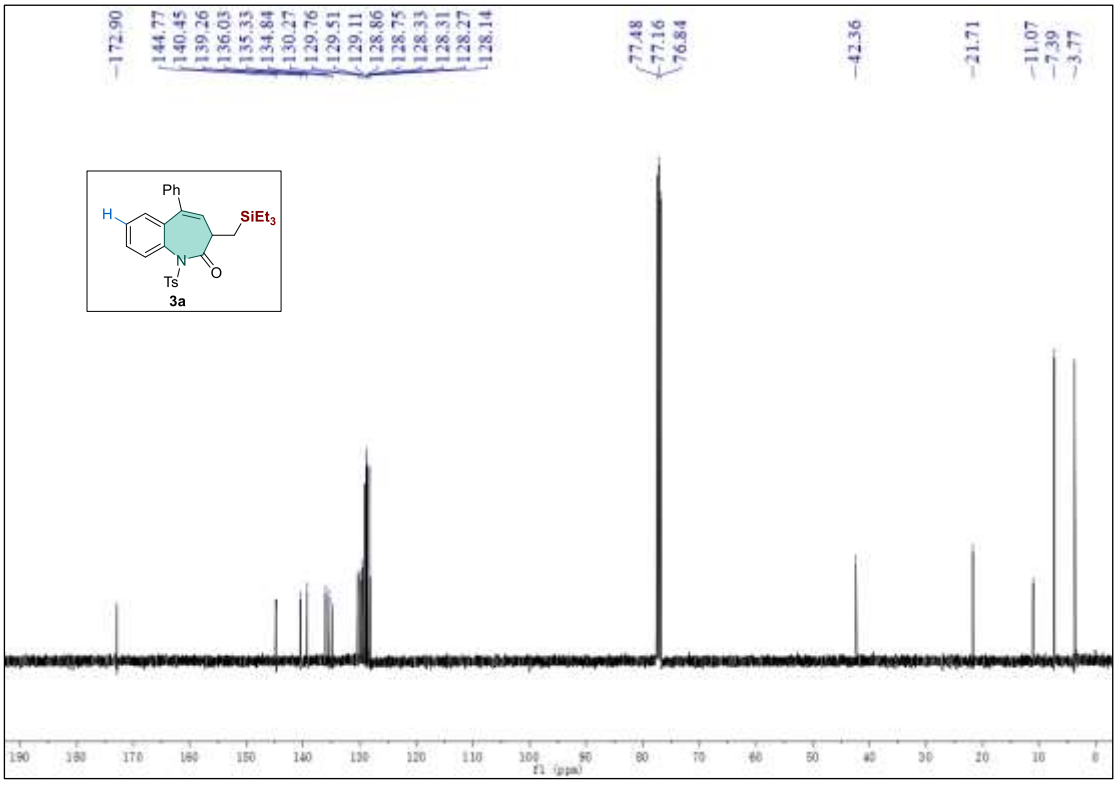
(3) Casanova, N.; Del Rio, K. P.; Garcia-Fandino, R.; Mascarenas, J. L.; Gulias, M. Palladium(Ii)-Catalyzed Annulation between Ortho-Alkenylphenols and Allenes. Key Role of the Metal Geometry in Determining the Reaction Outcome. *ACS Catal* **2016**, *6*, 3349-3353.

## 10. Copy of $^{1}H$ , $^{19}F$ and $^{13}C$ NMR

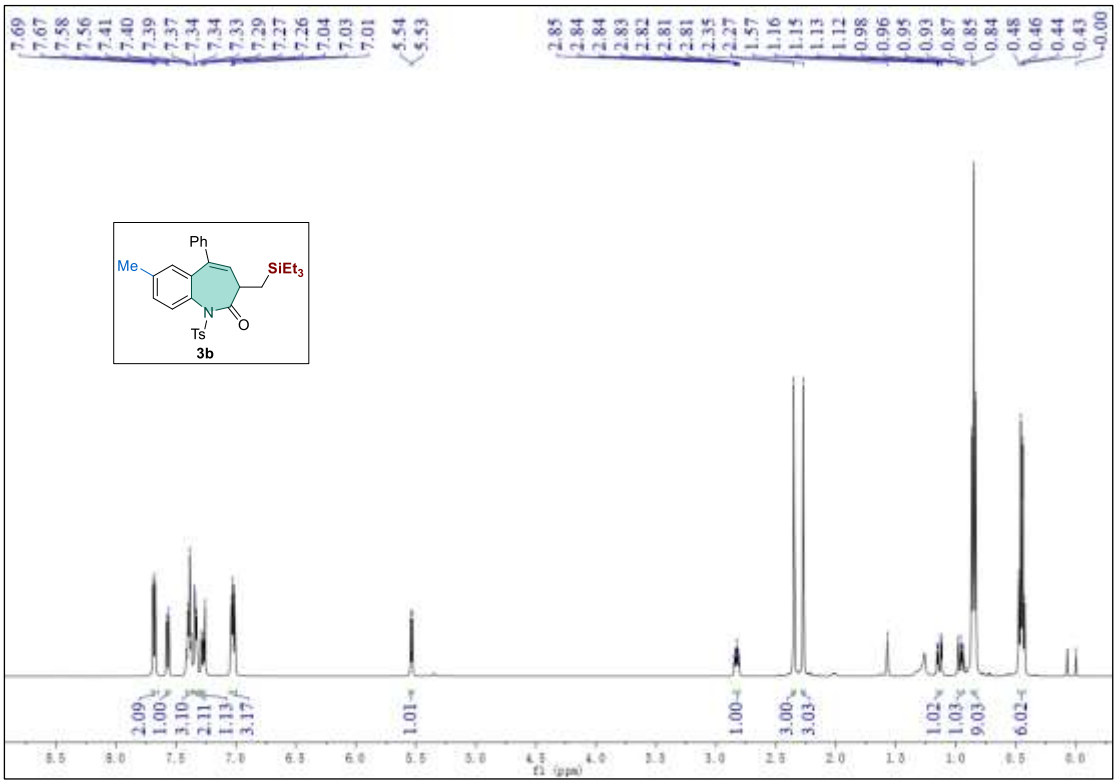
$^{1}H$ NMR (400 MHz, $CDCl_3$)



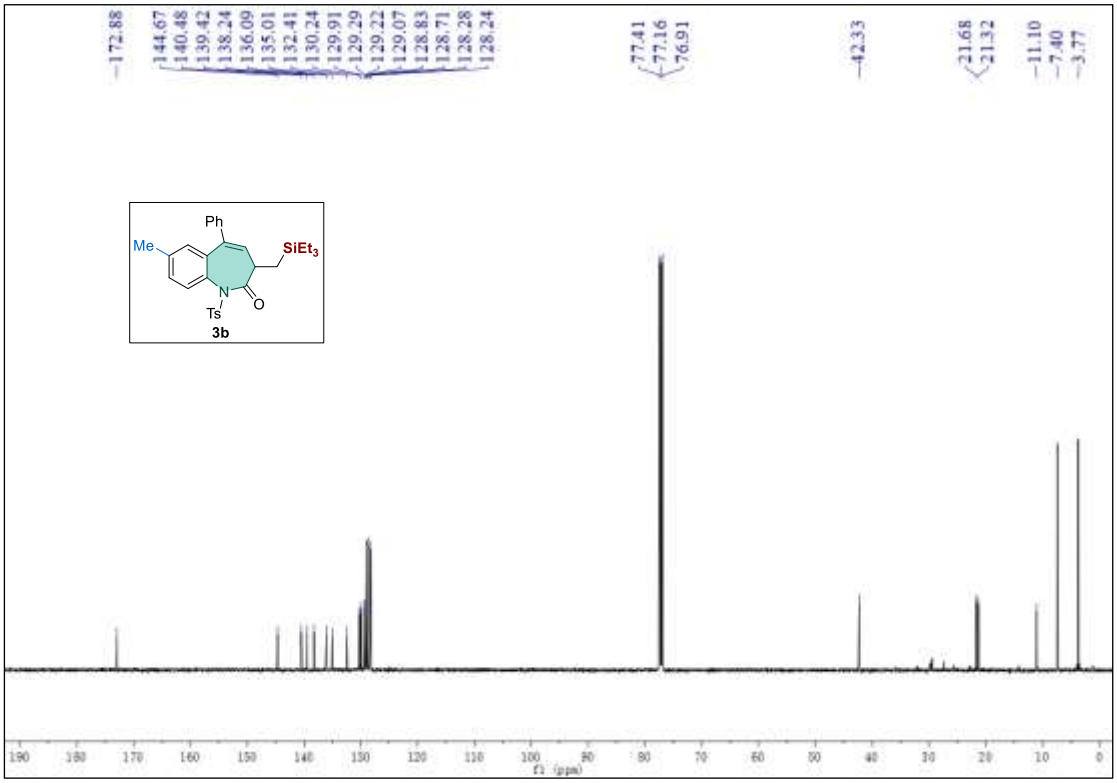

$^{13}C$ NMR (101 MHz, $CDCl_3$)



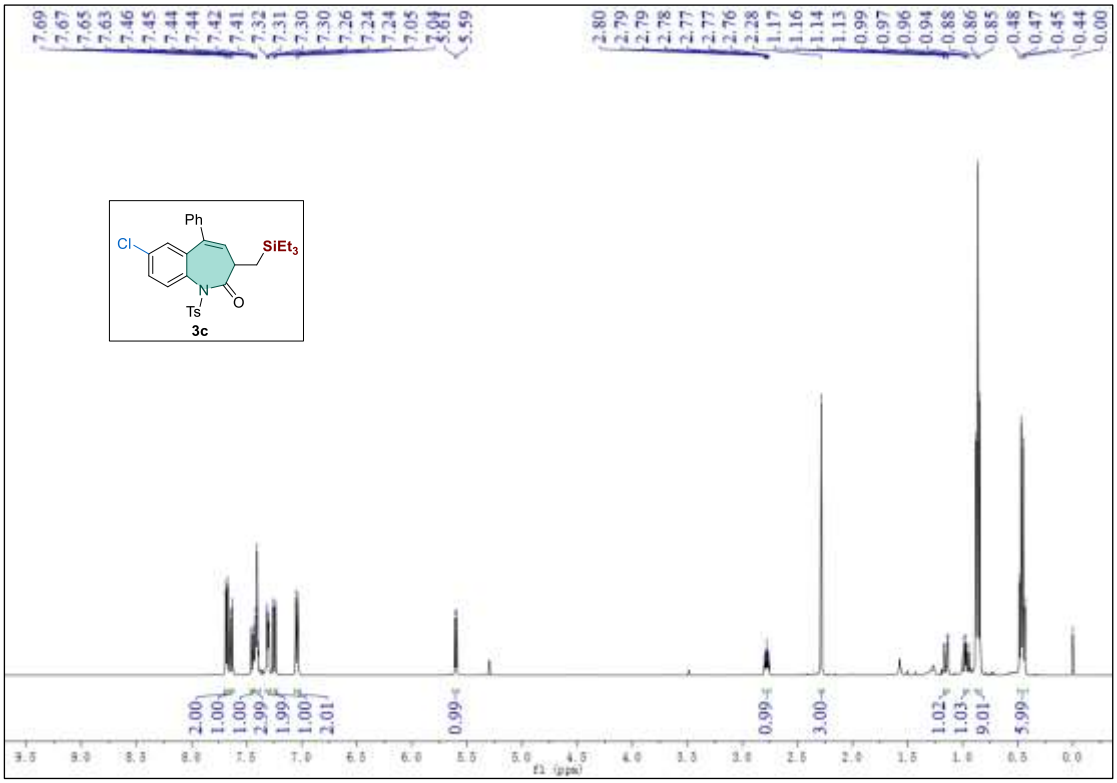
$^{1}$H NMR (500 MHz, $CDCl_3$)



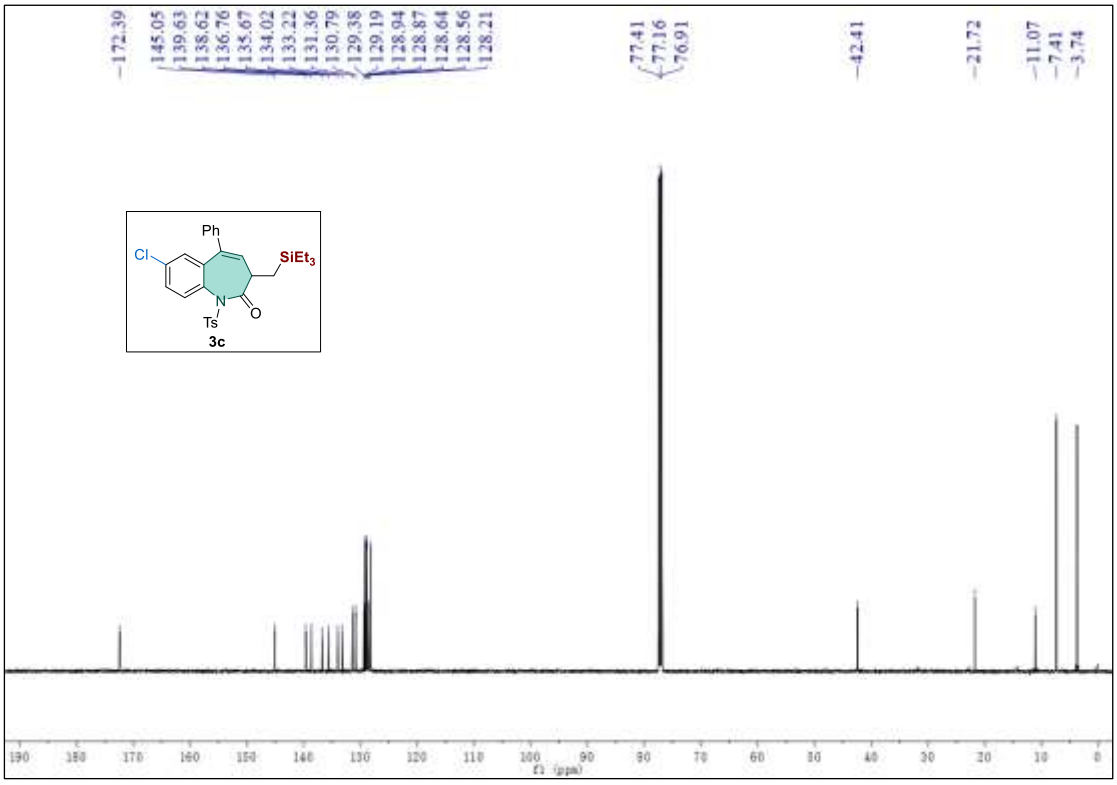

$^{13}$C NMR (126 MHz, $CDCl_3$)



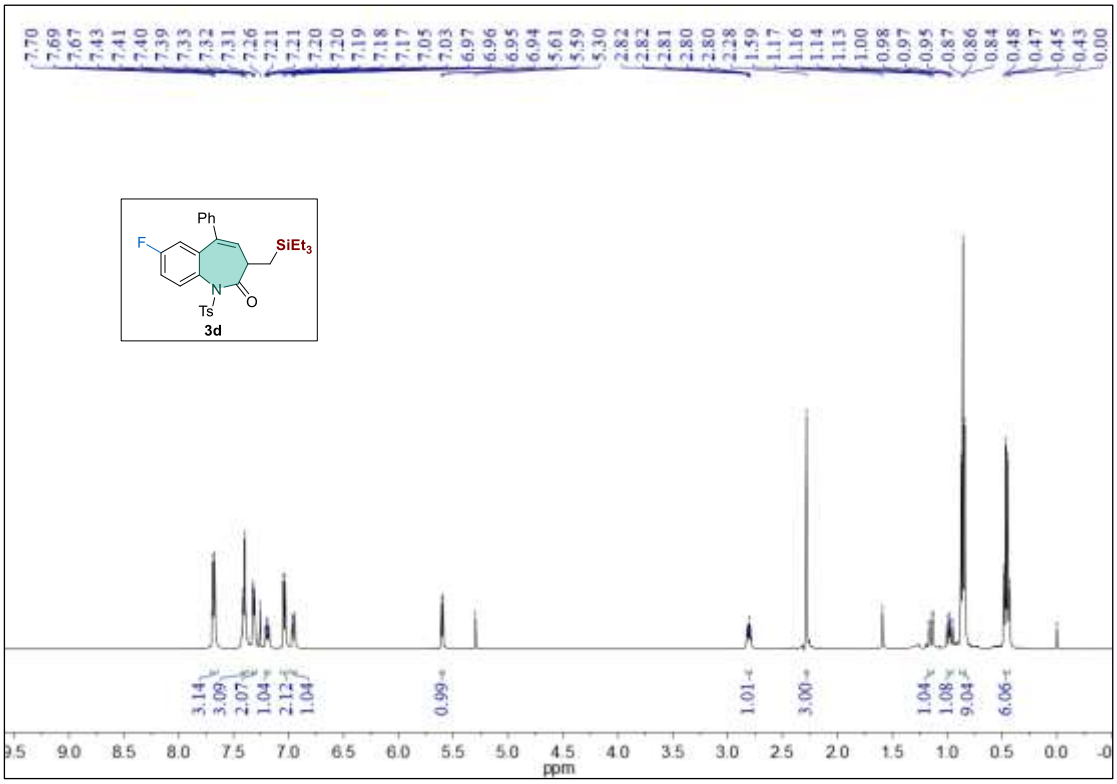
$^{1}$H NMR (500 MHz, $CDCl_3$)



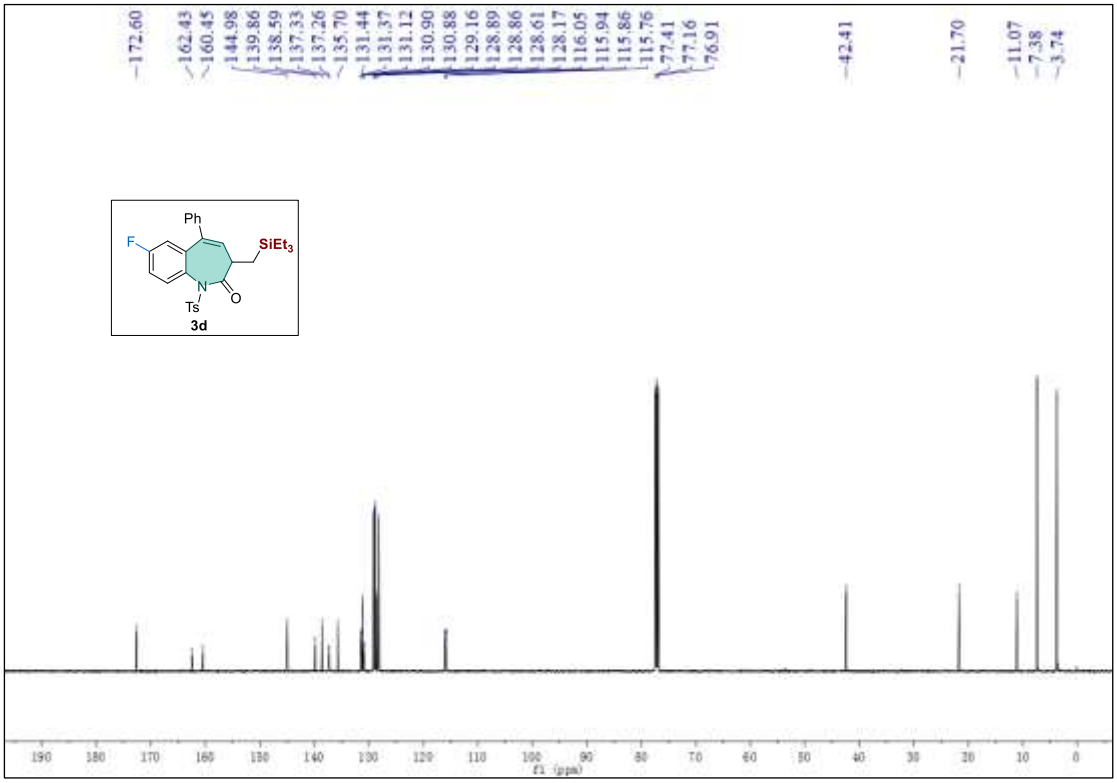

$^{13}$C NMR (126 MHz, $CDCl_3$)



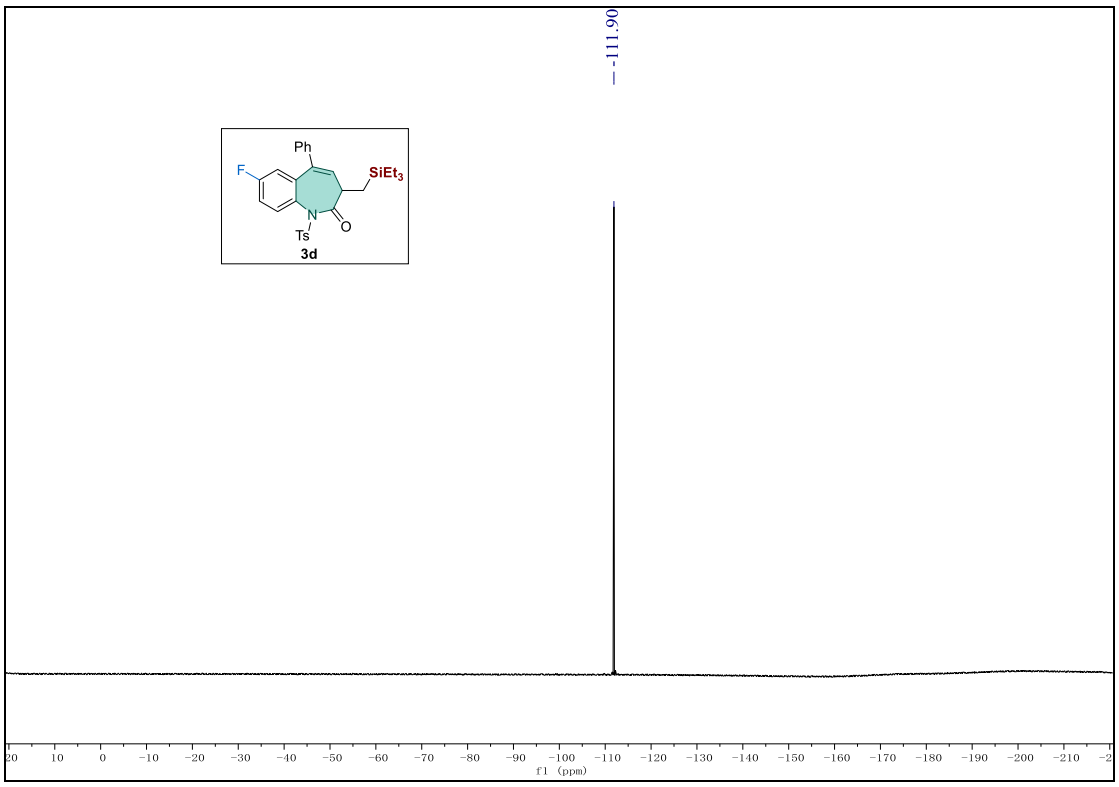
$^{1}$H NMR (500 MHz, $CDCl_3$)



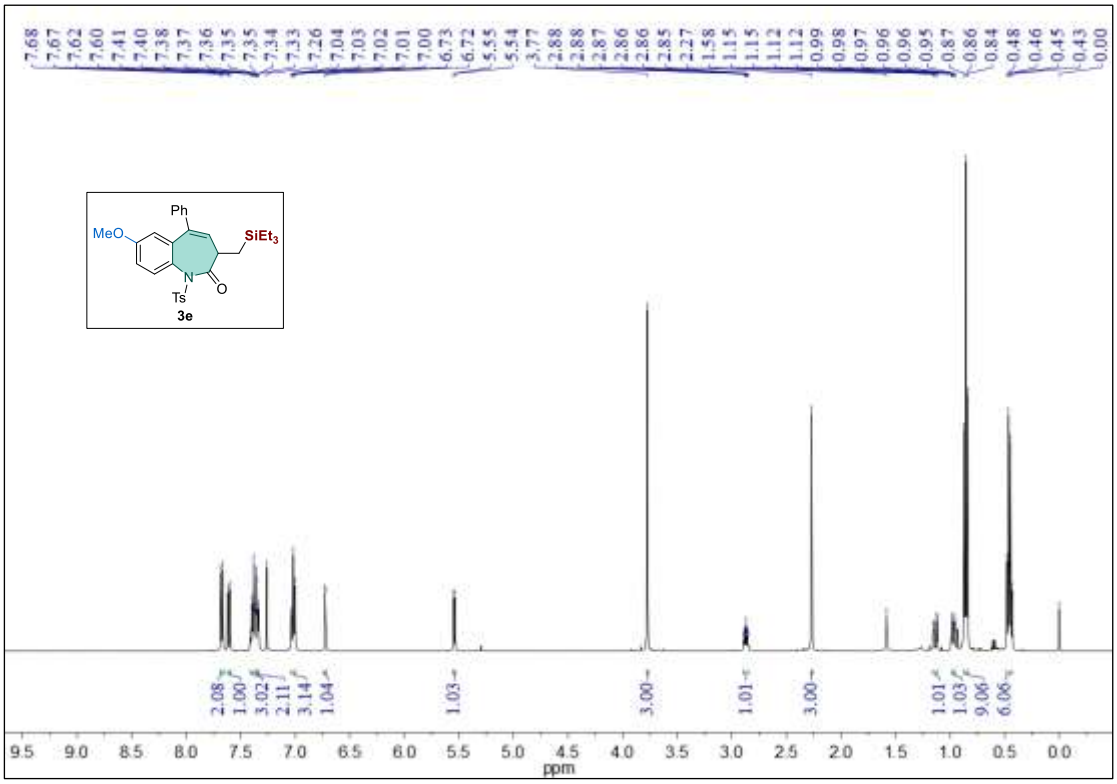

$^{13}$C NMR (126 MHz, $CDCl_3$)



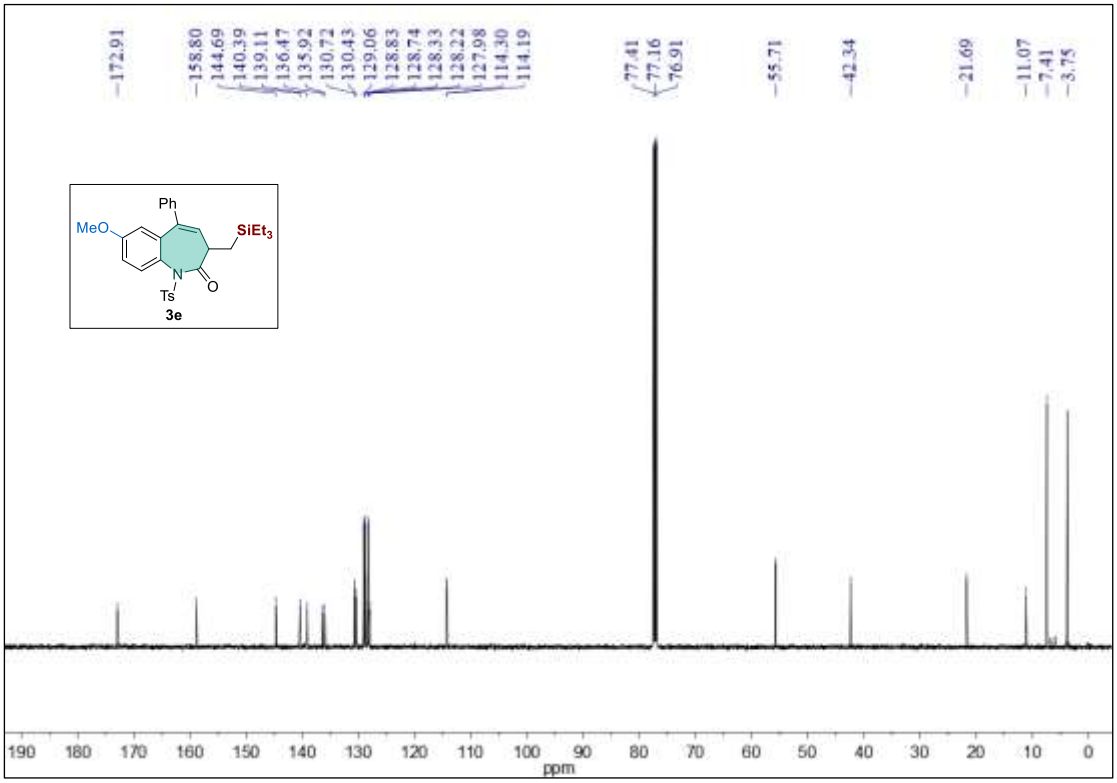
$^{19}F$ NMR (376 MHz, $CDCl_3$)



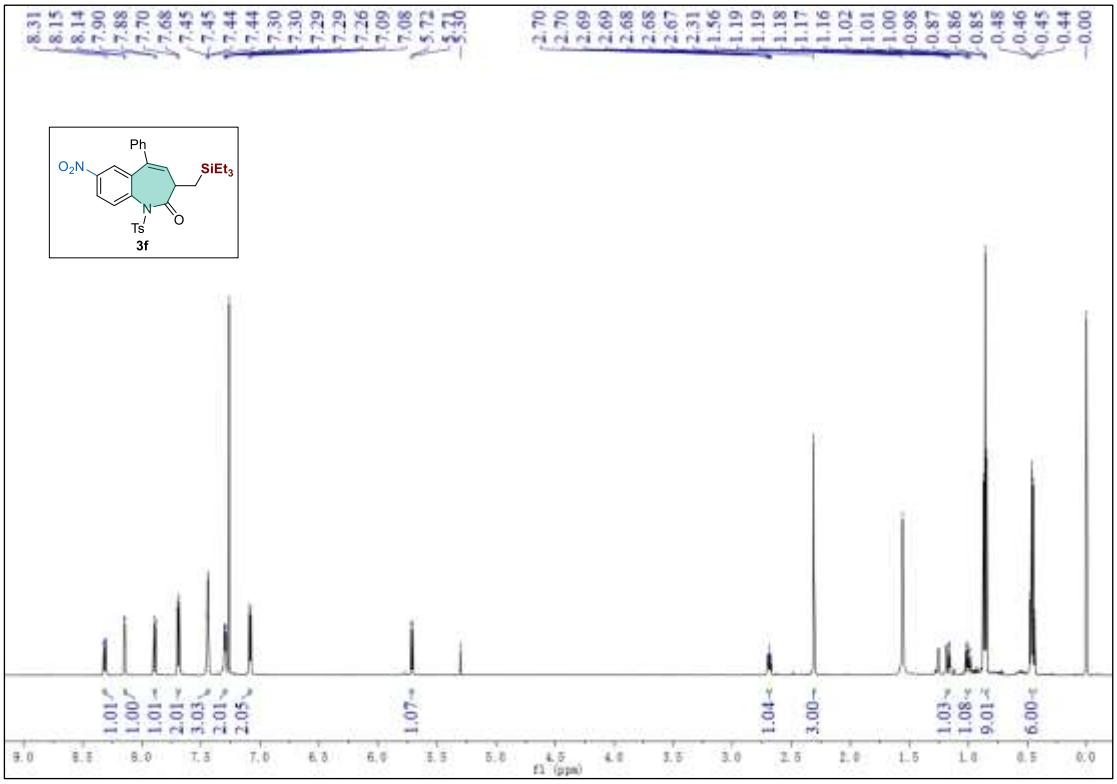
$^{1}$H NMR (500 MHz, $CDCl_3$)



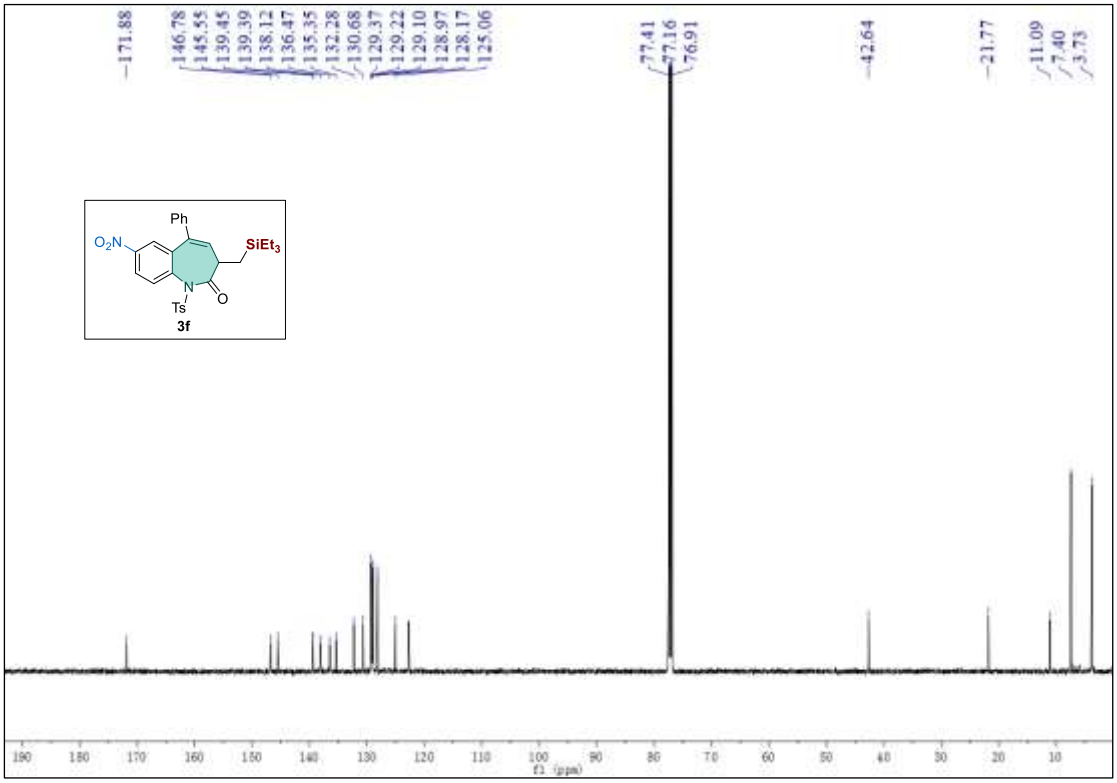

$^{13}$C NMR (126 MHz, $CDCl_3$)



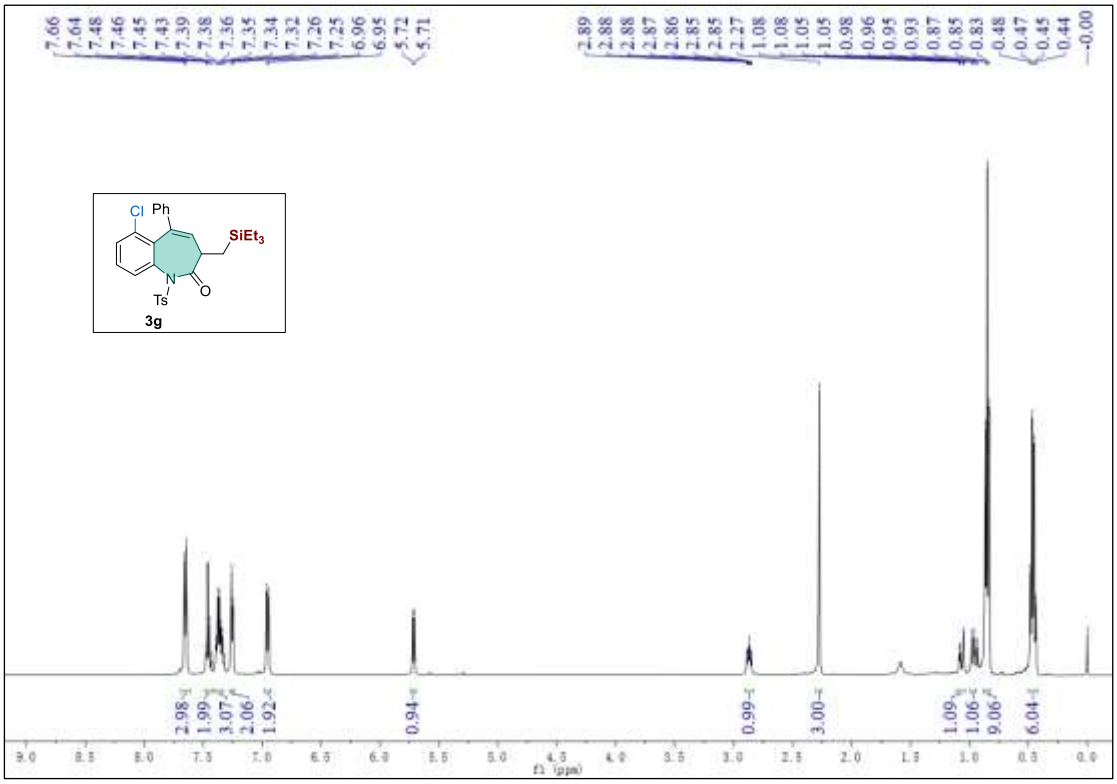
$^{1}$H NMR (600 MHz, $CDCl_3$)



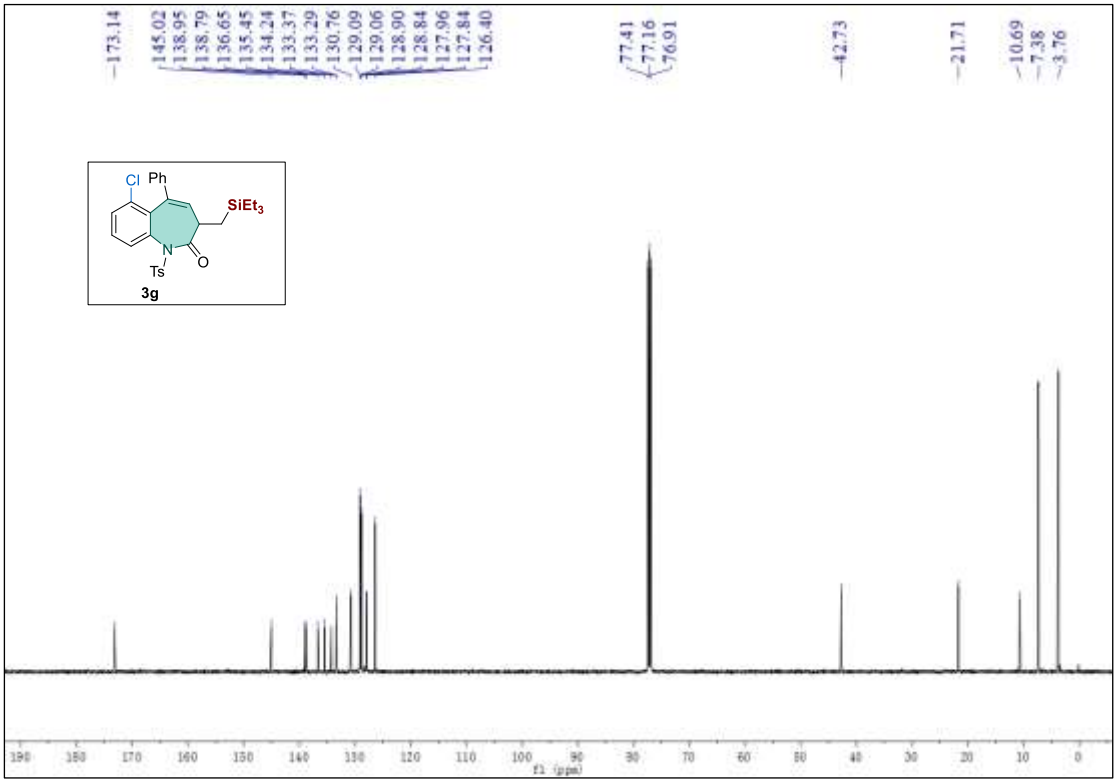

$^{13}$C NMR (126 MHz, $CDCl_3$)



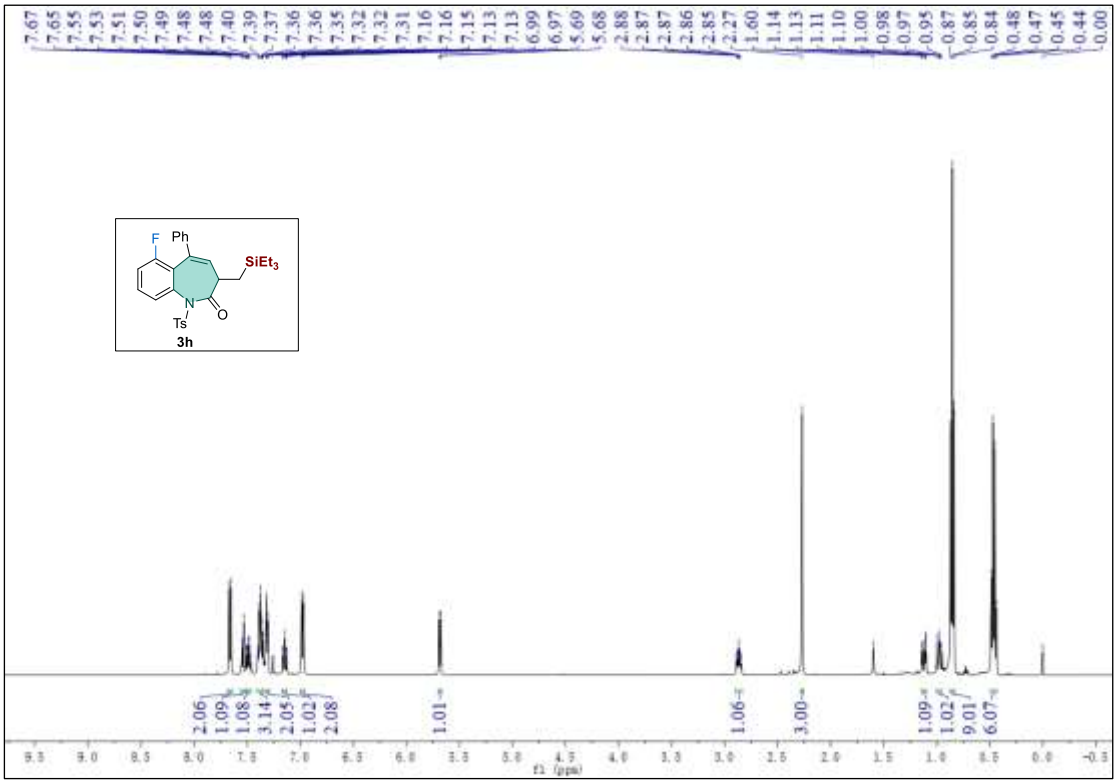
$^{1}$H NMR (500 MHz, $CDCl_3$)



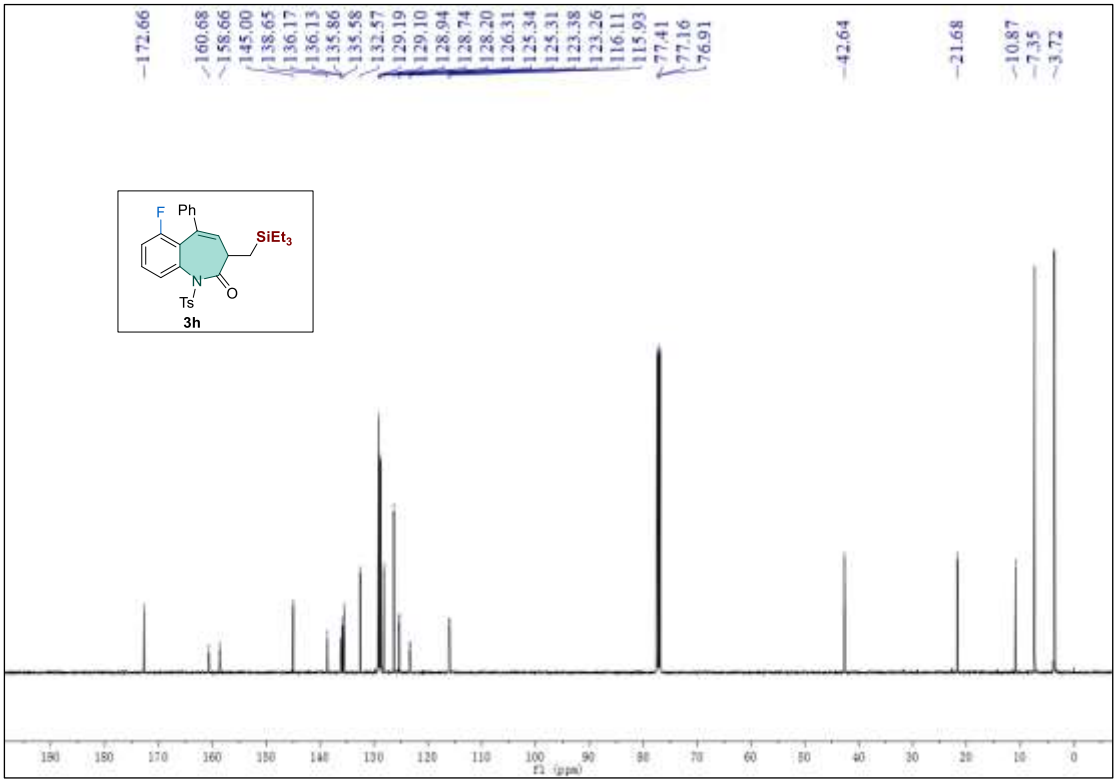

$^{13}$C NMR (126 MHz, $CDCl_3$)



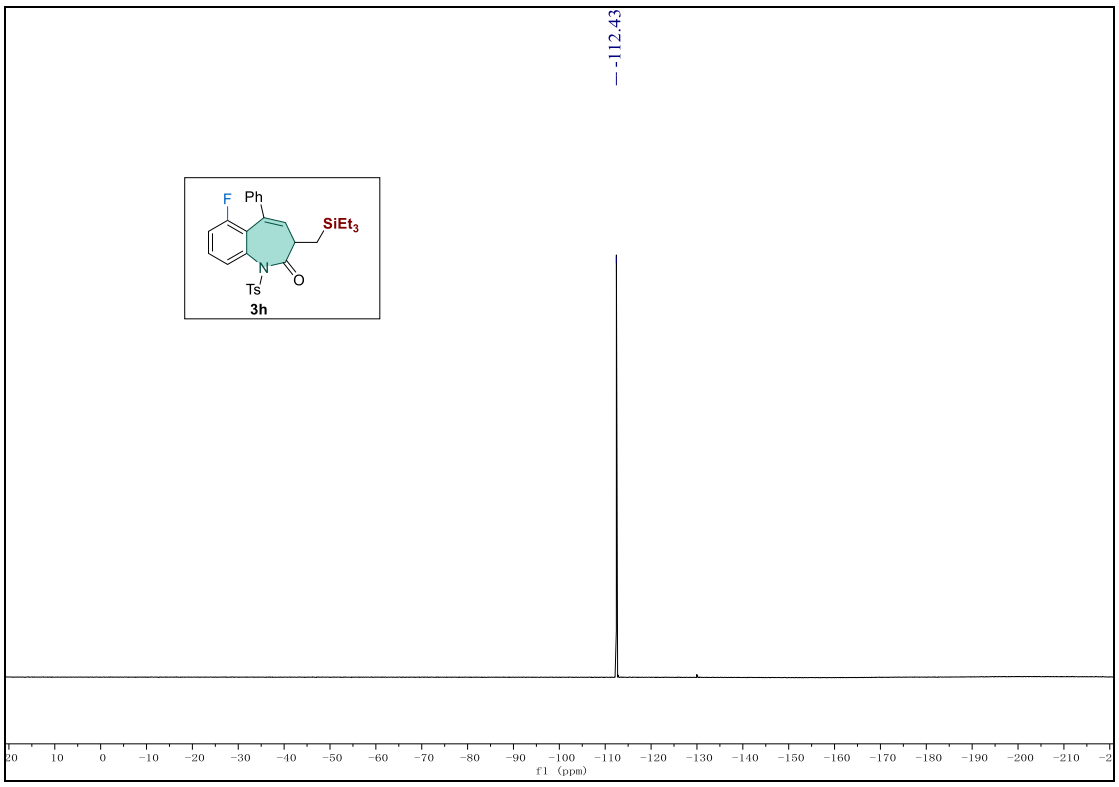
$^{1}$H NMR (500 MHz, $CDCl_3$)



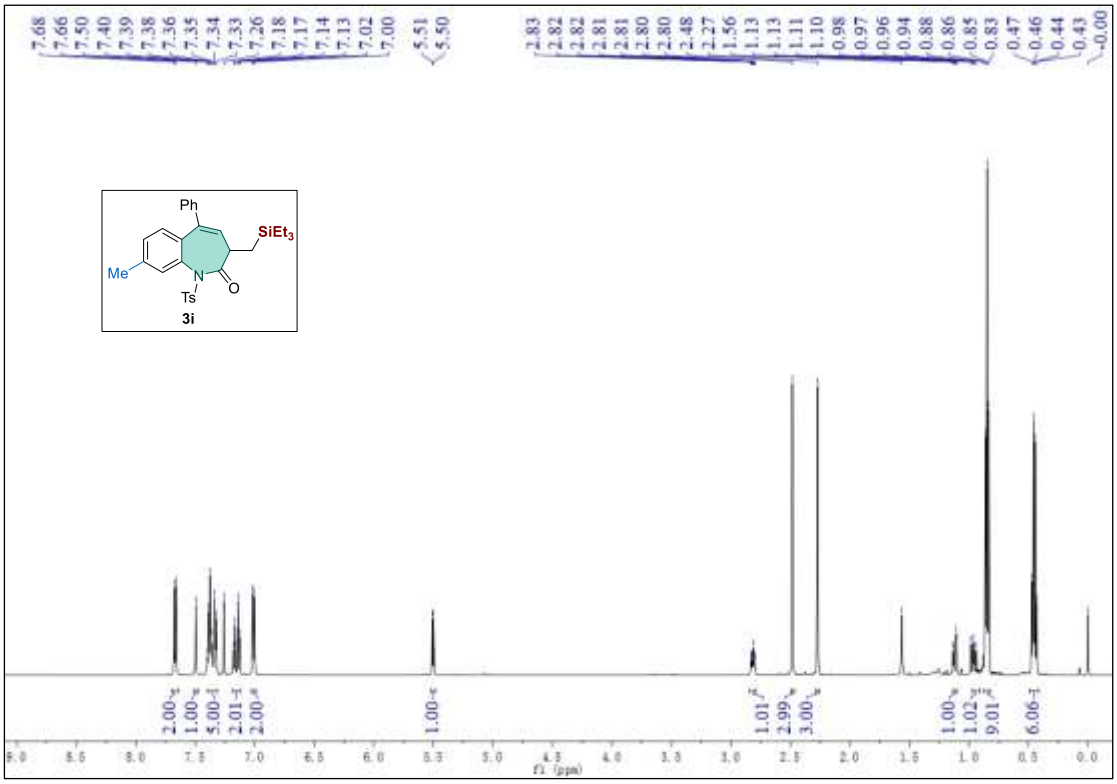

$^{13}$C NMR (126 MHz, $CDCl_3$)



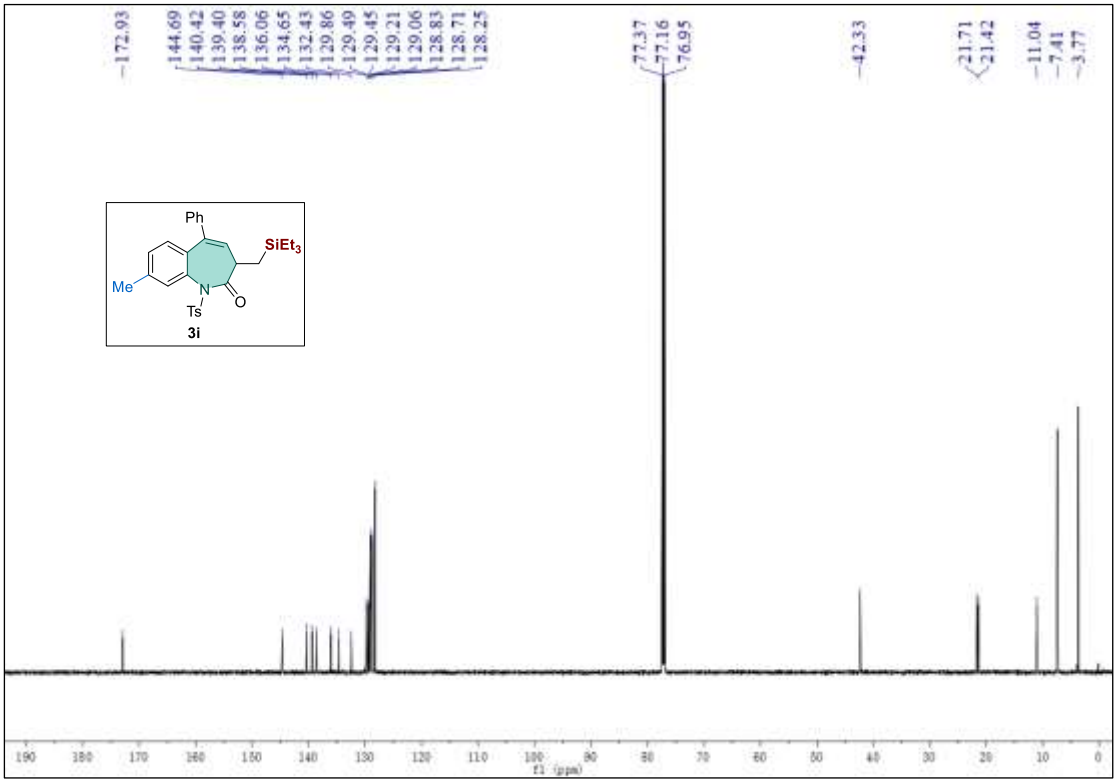
$^{19}F$ NMR (376 MHz, $CDCl_3$)



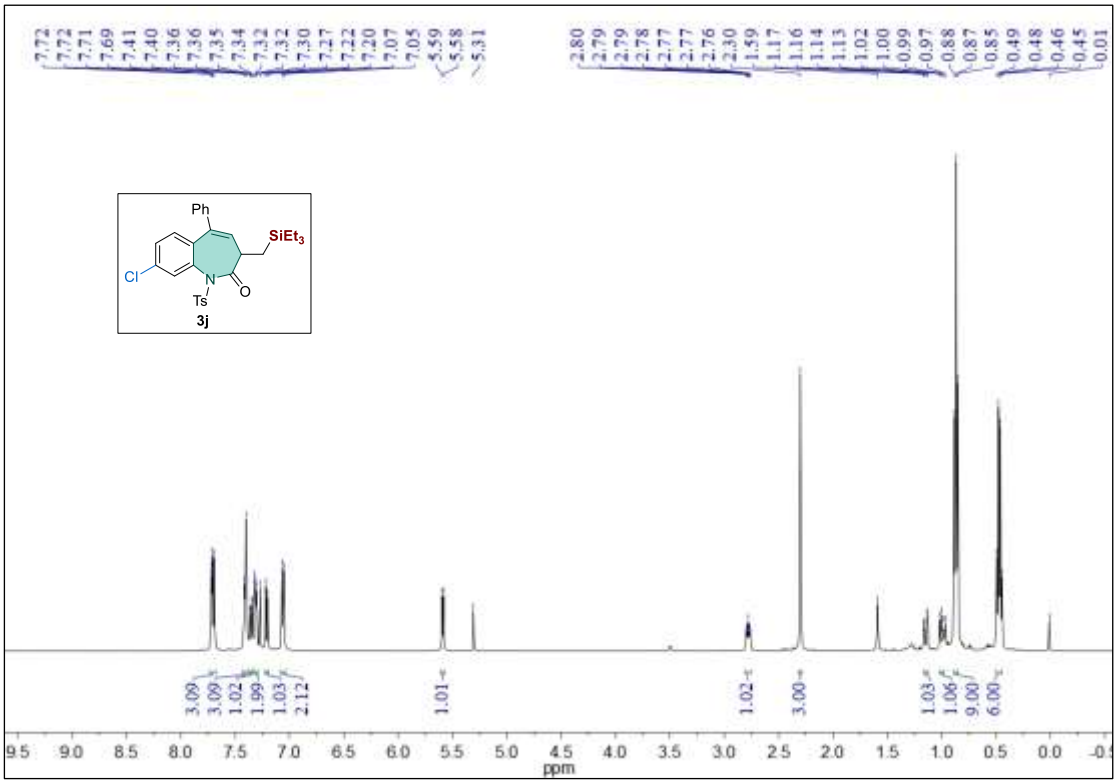
$^{1}$H NMR (600 MHz, $CDCl_3$)



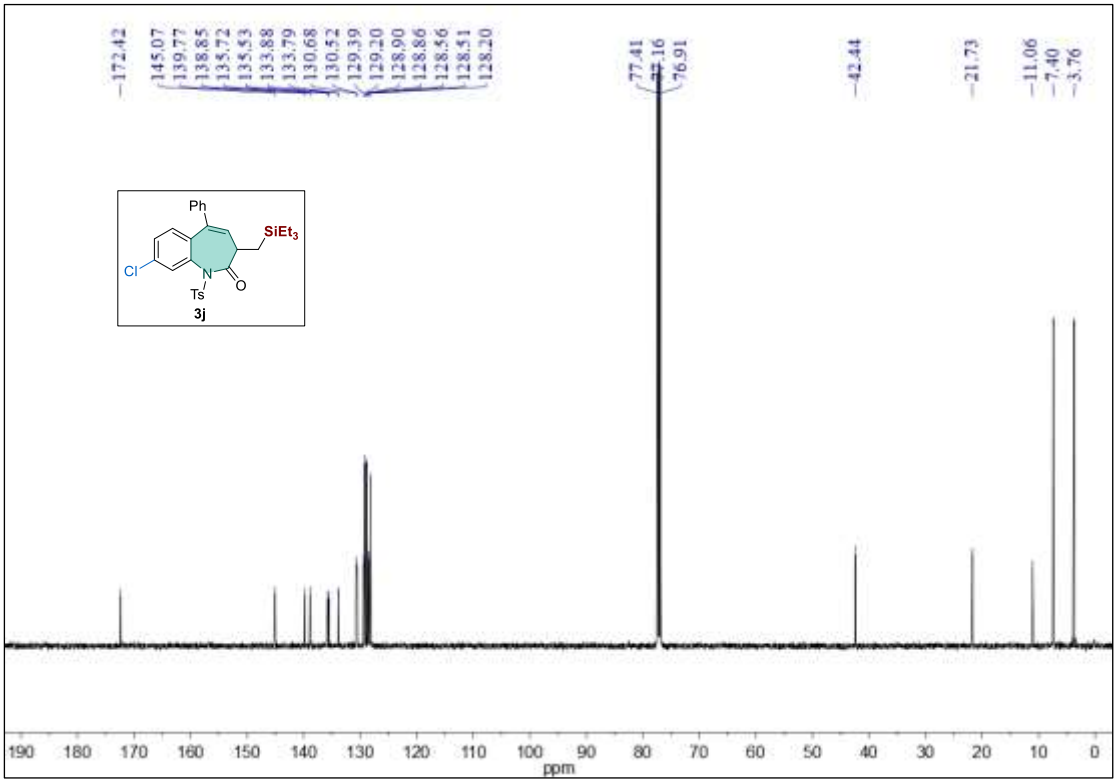

$^{13}$C NMR (151 MHz, $CDCl_3$)



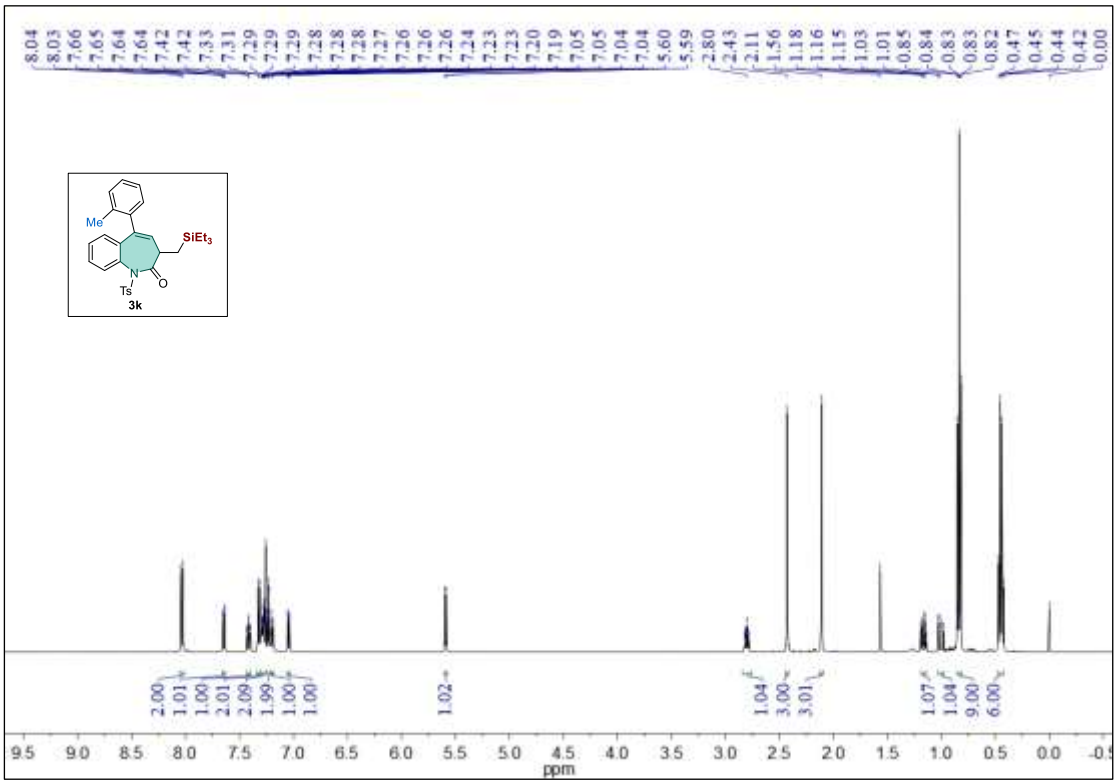
$^{1}$H NMR (500 MHz, $CDCl_3$)



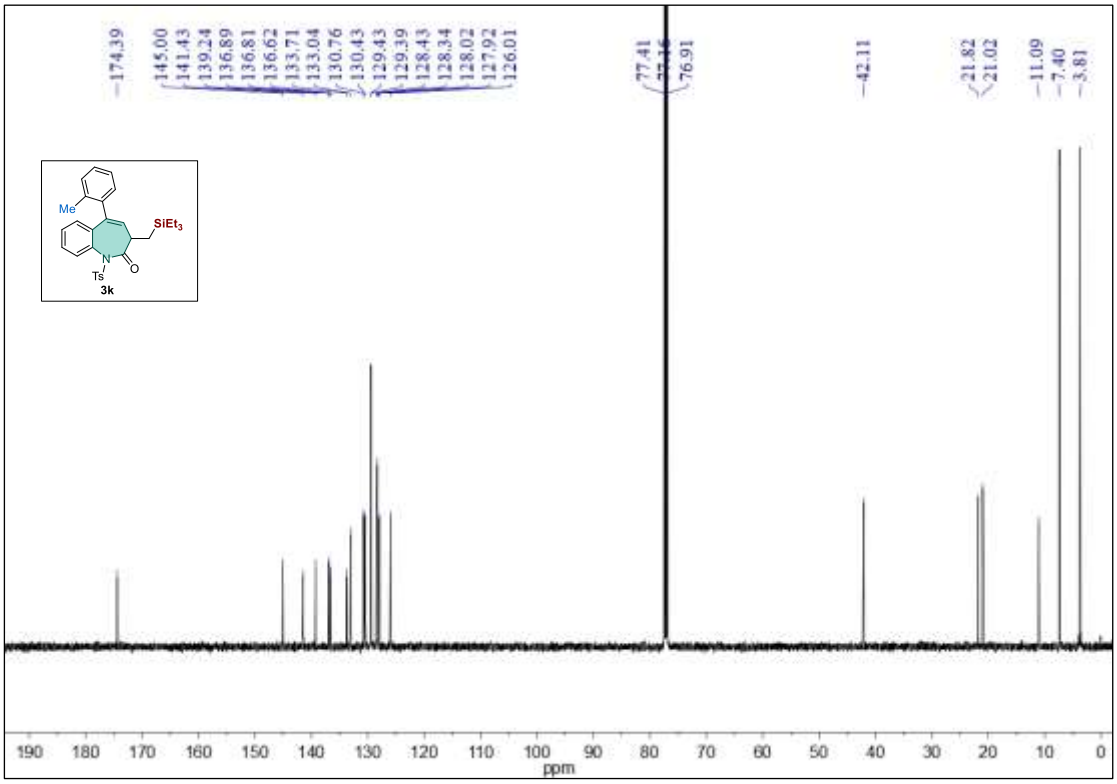

$^{13}$C NMR (126 MHz, $CDCl_3$)



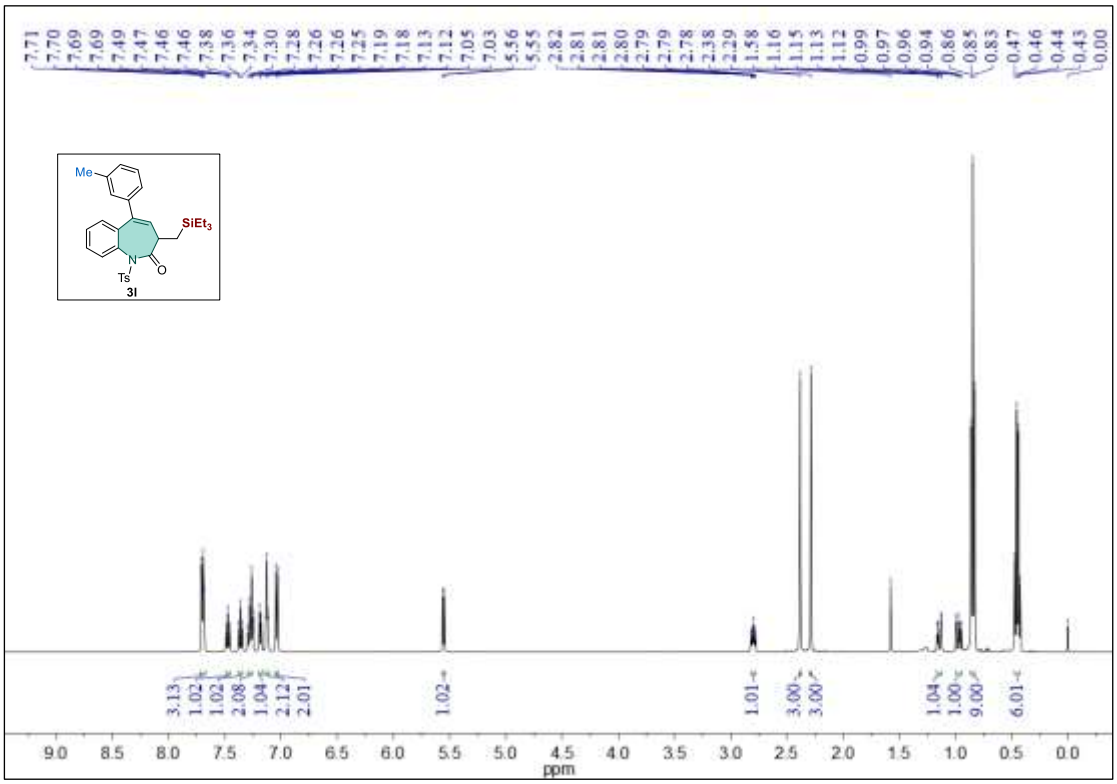
$^{1}$H NMR (500 MHz, $CDCl_3$)




$^{13}$C NMR (126 MHz, $CDCl_3$)



$^{1}$H NMR (500 MHz, $CDCl_3$)

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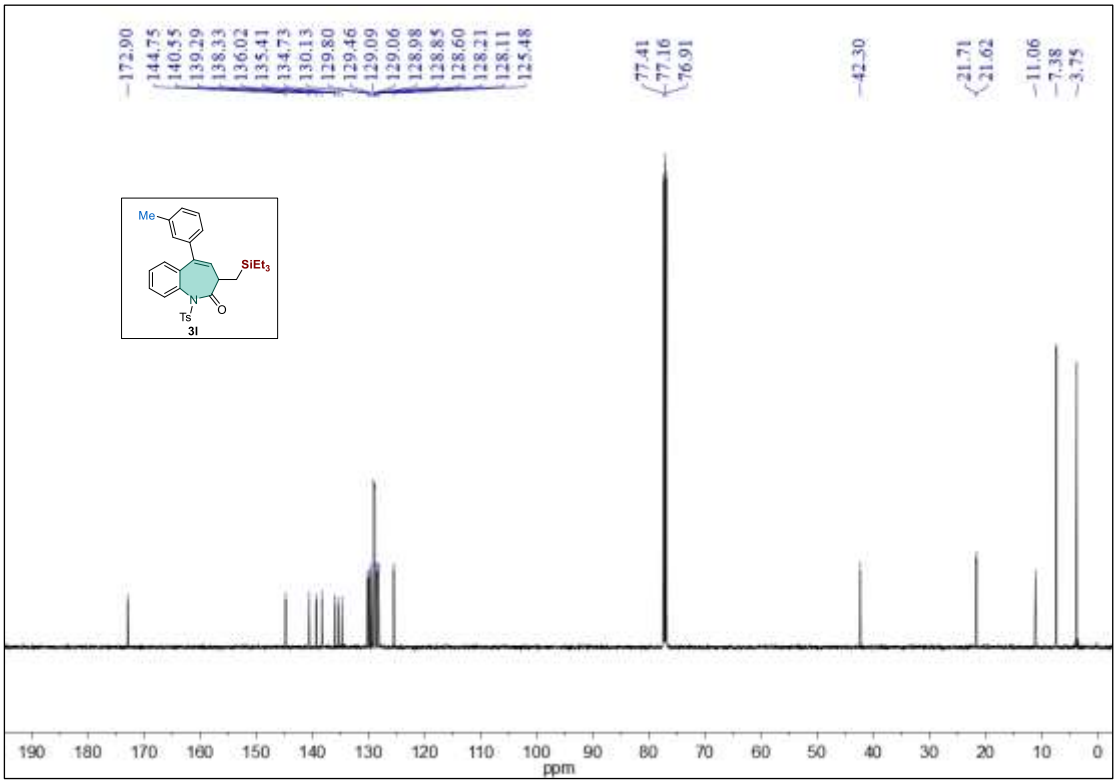

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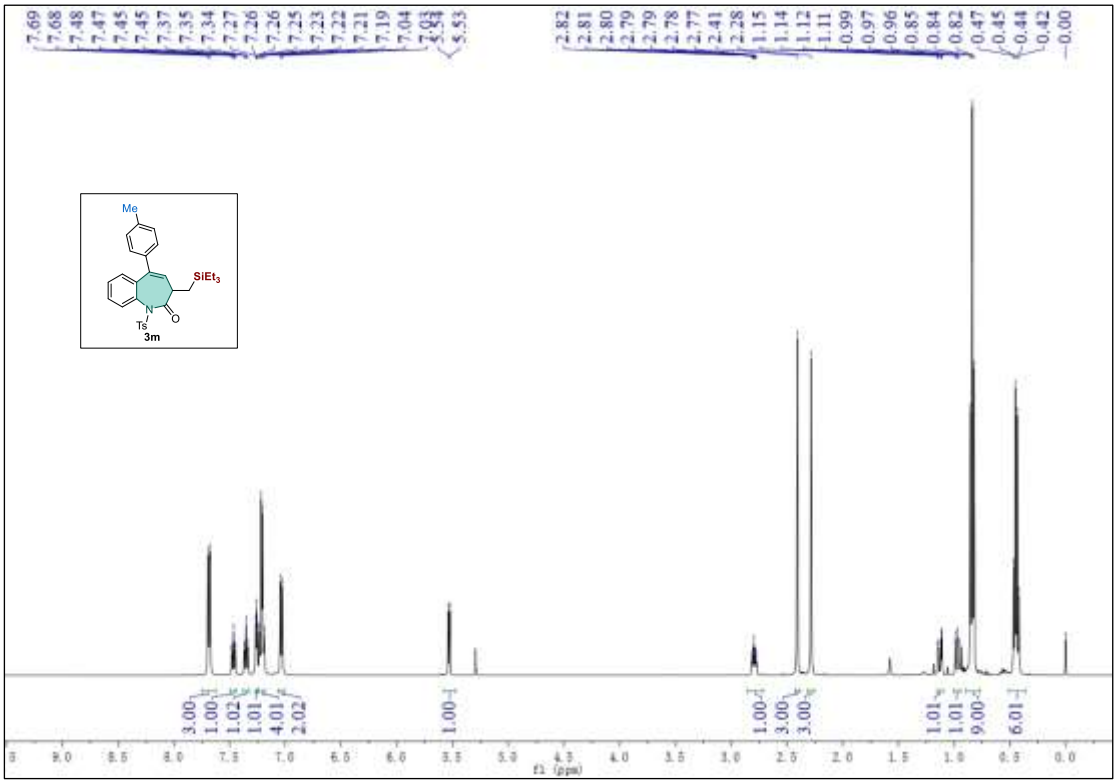


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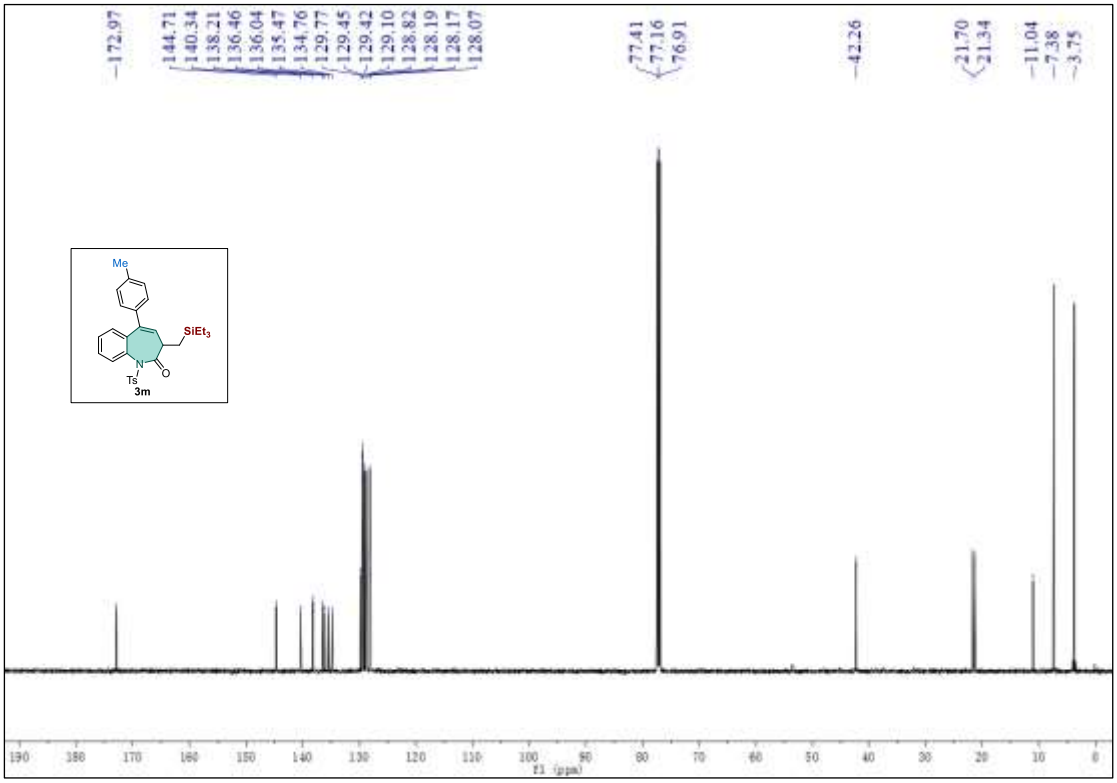

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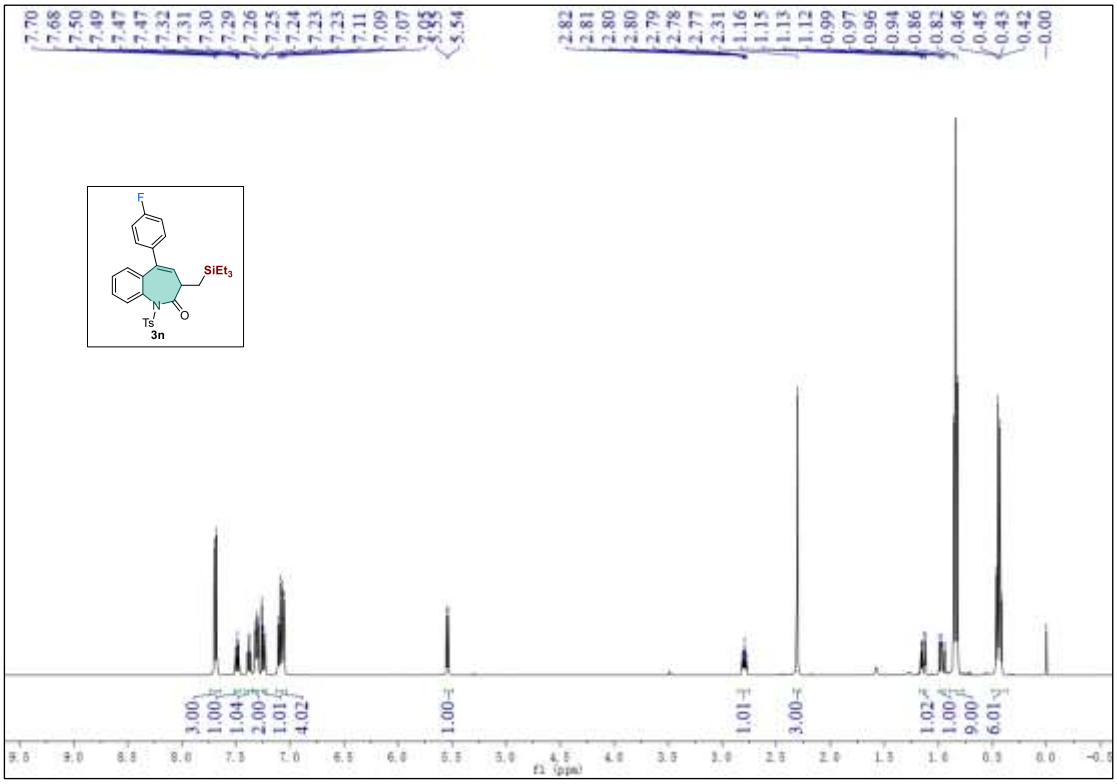


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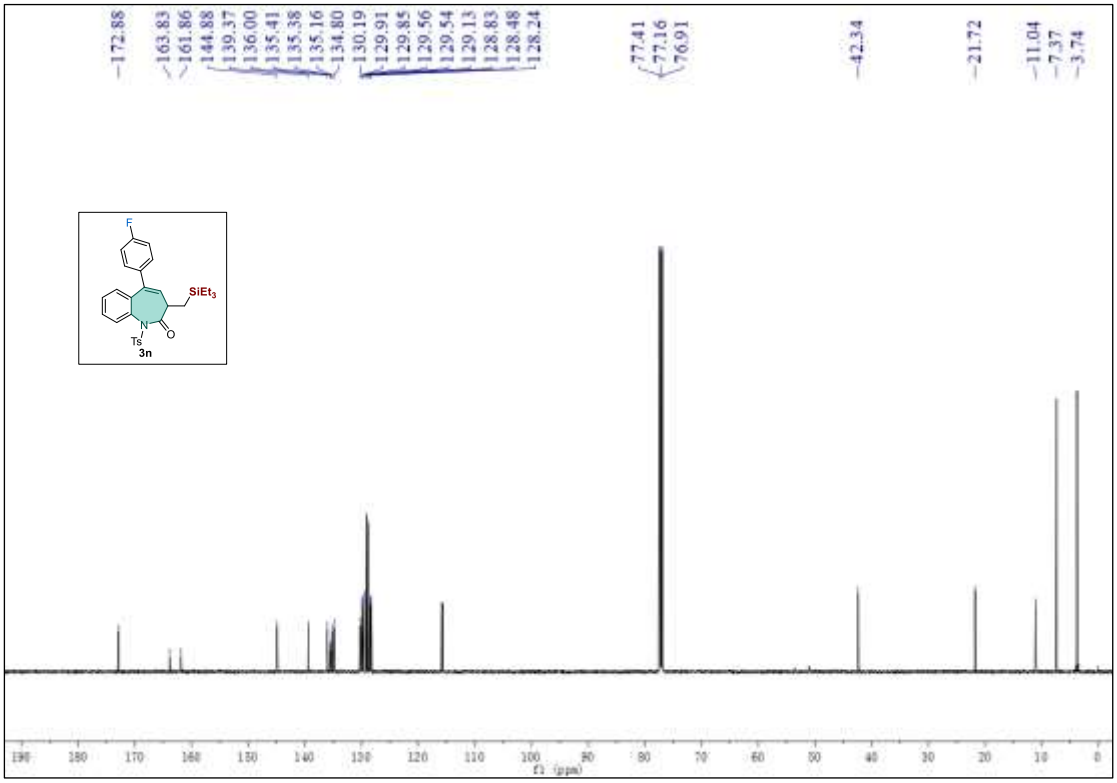
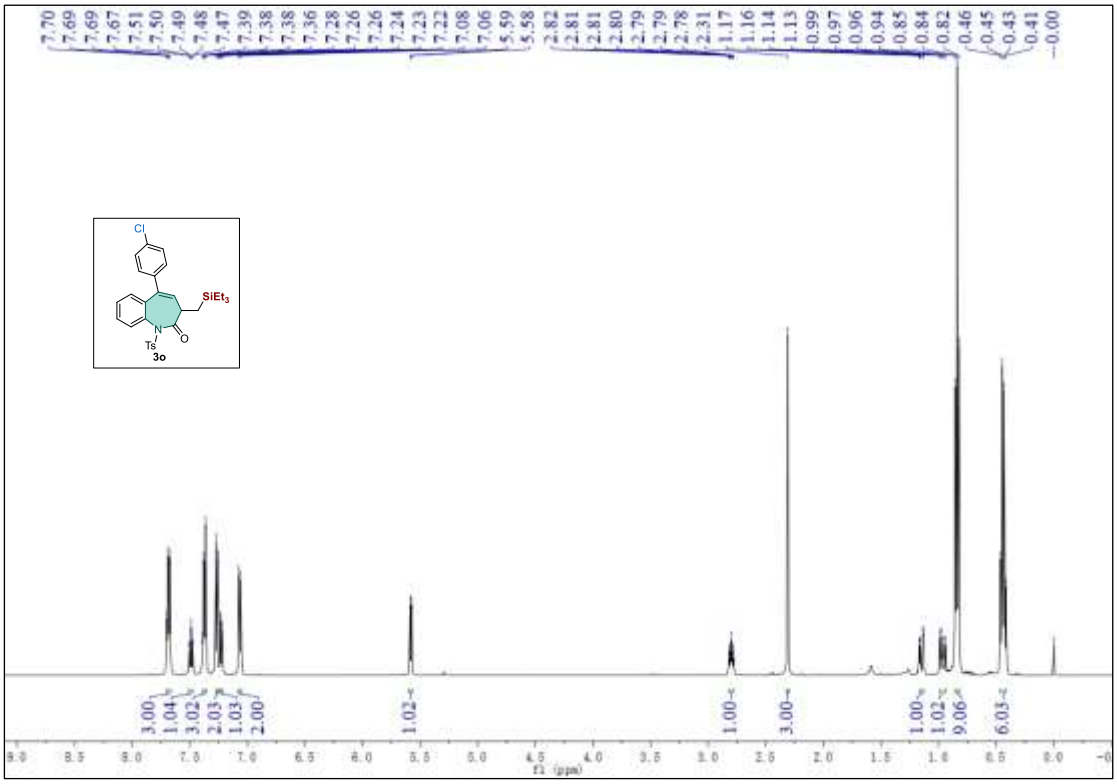
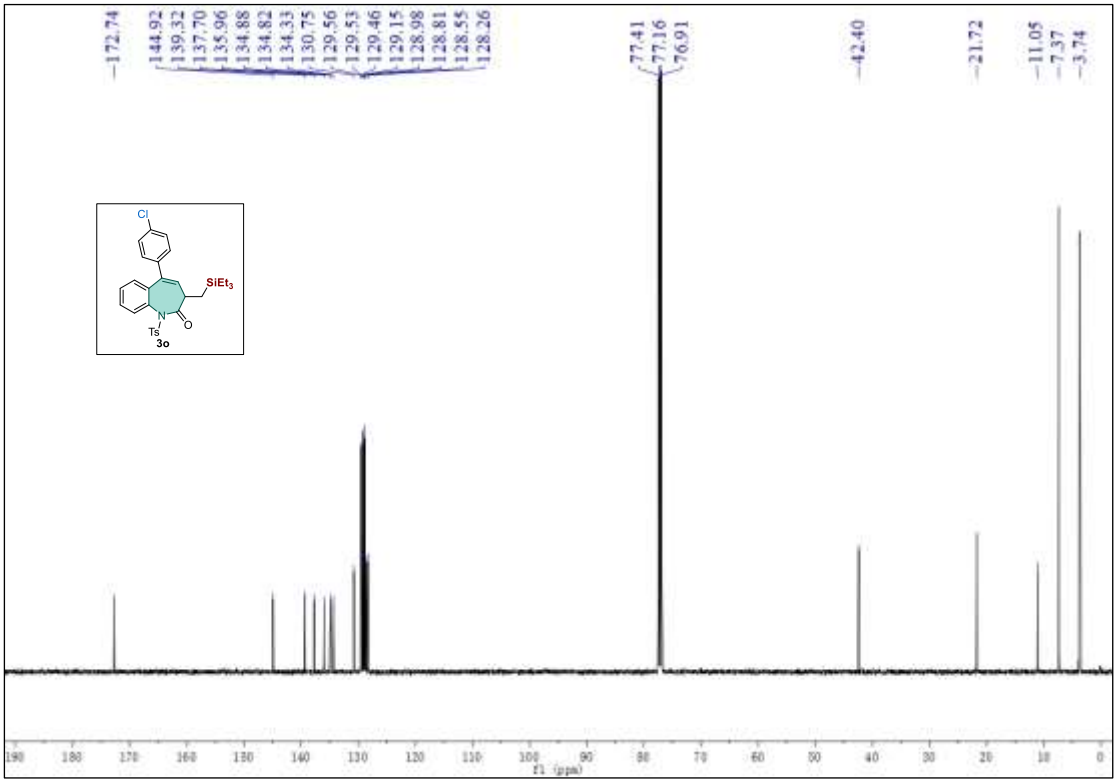


$^{1}$H NMR (500 MHz, $CDCl_3$)




$^{13}$C NMR (126 MHz, $CDCl_3$)



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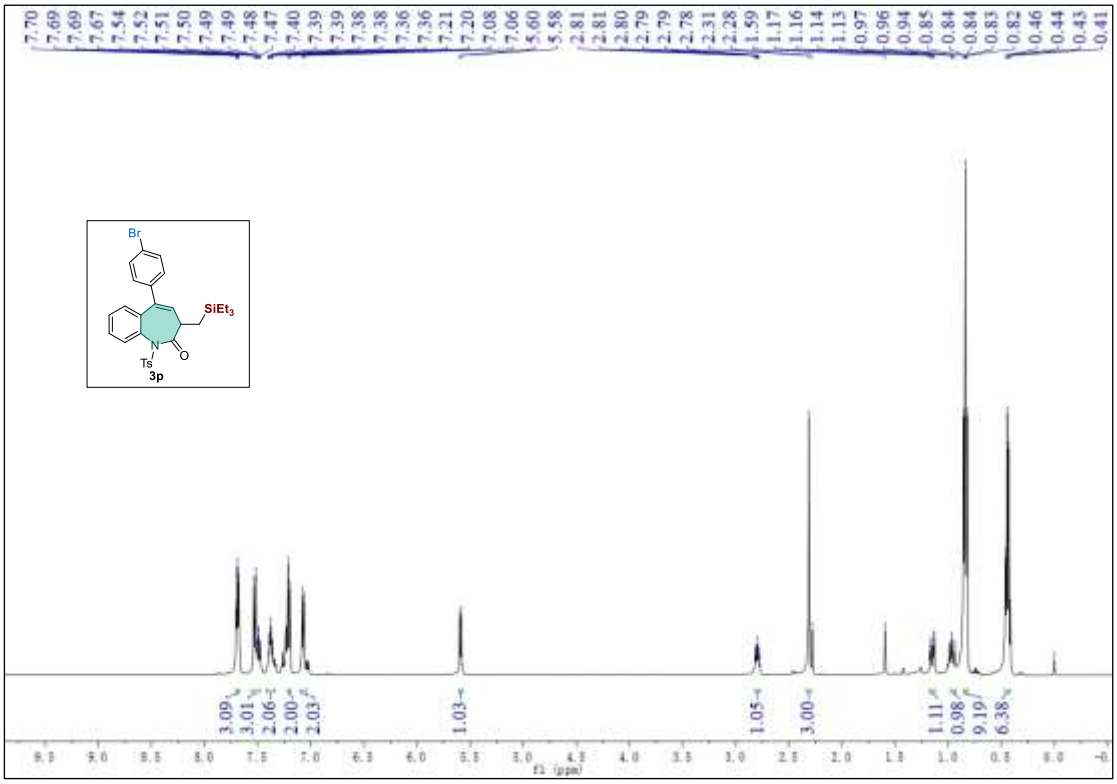
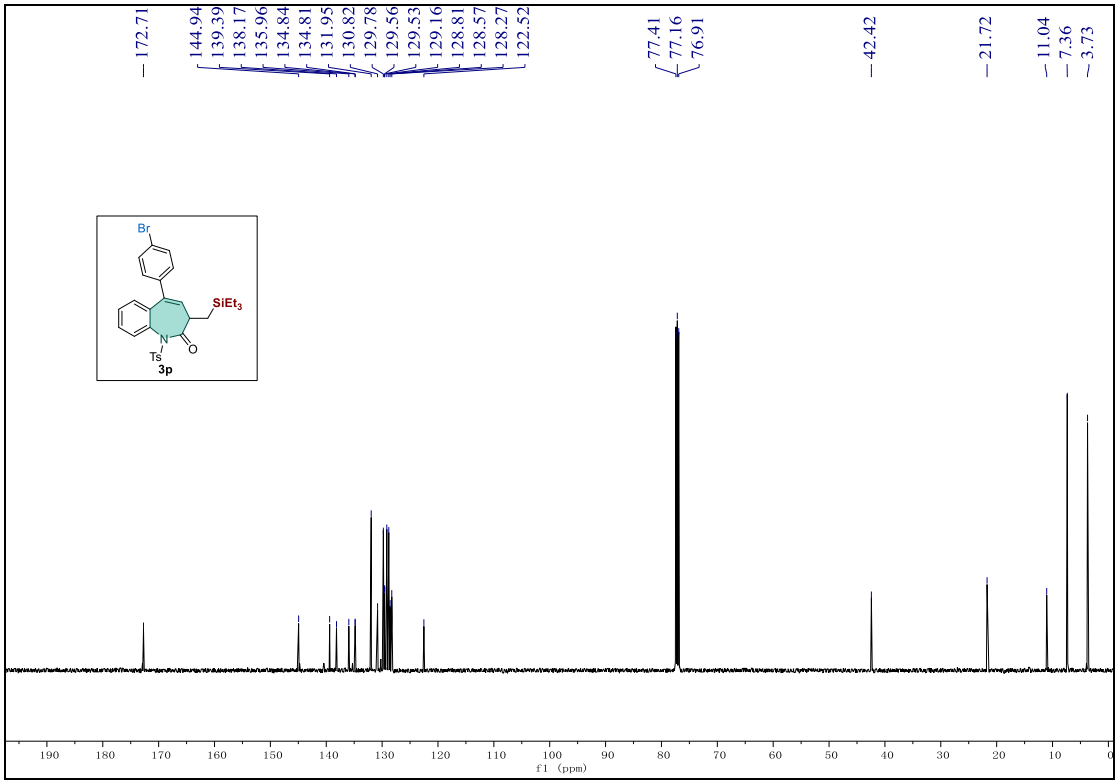
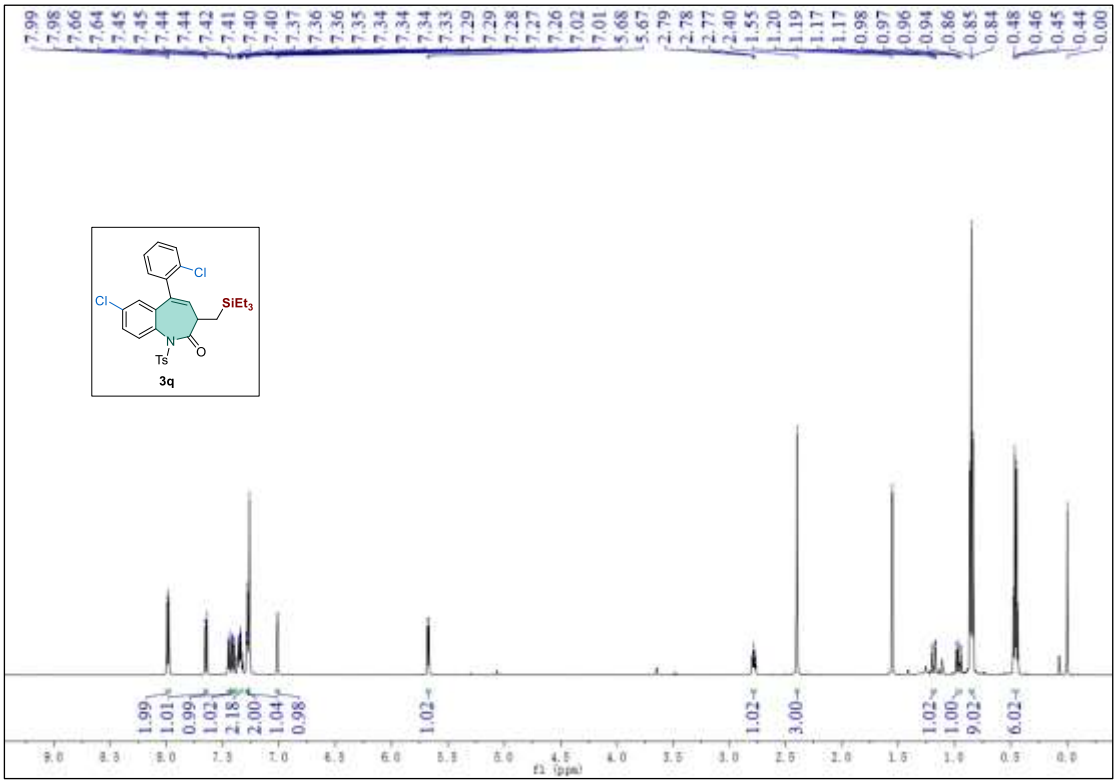


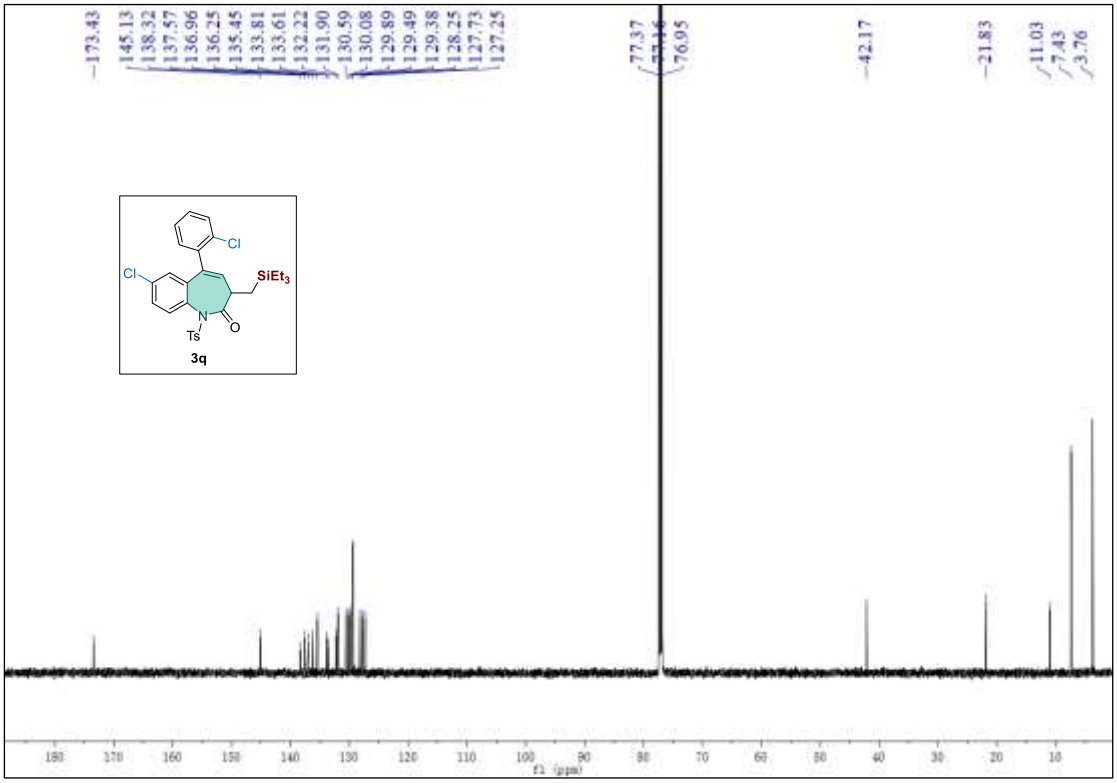

$^{13}$C NMR (126 MHz, $CDCl_3$)



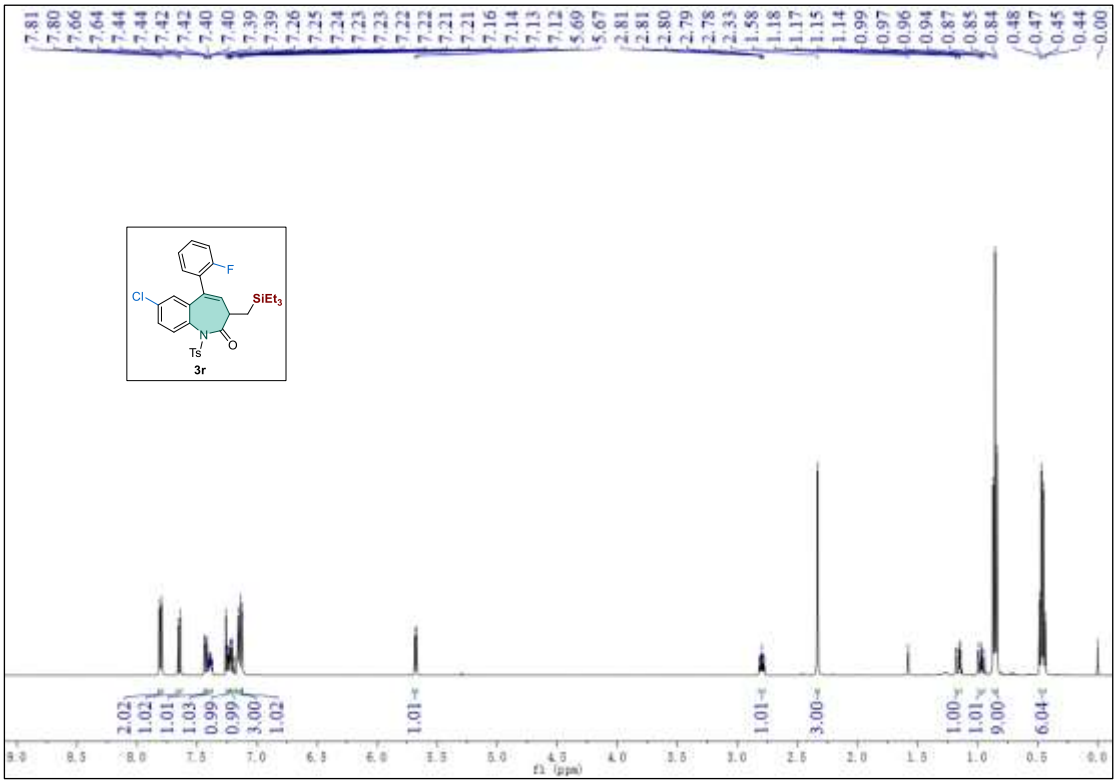
$^{1}$H NMR (600 MHz, $CDCl_3$)



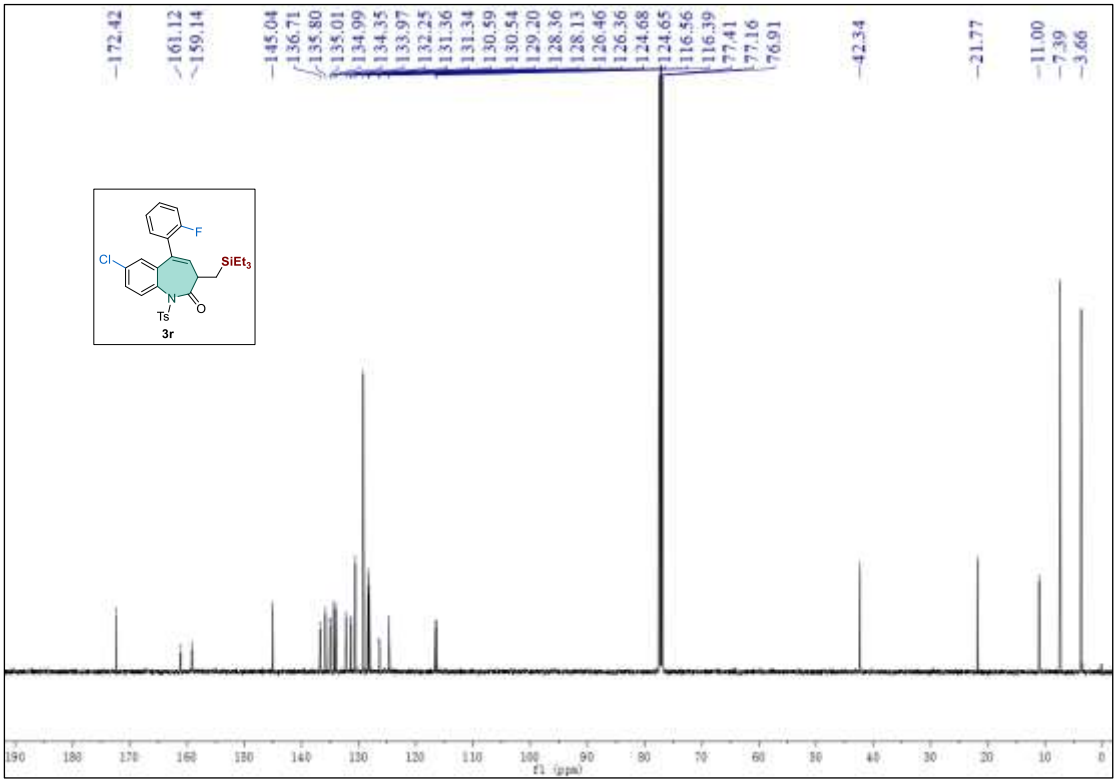

$^{13}$C NMR (151 MHz, $CDCl_3$)



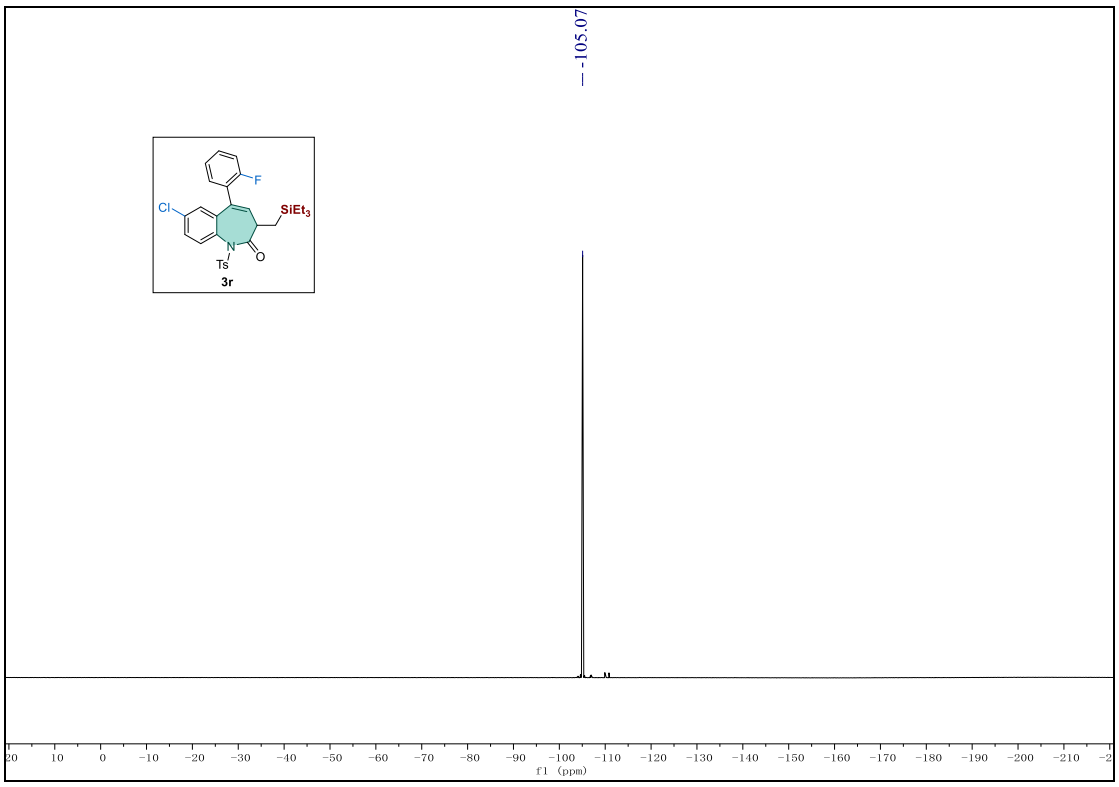
$^{1}$H NMR (500 MHz, $CDCl_3$)



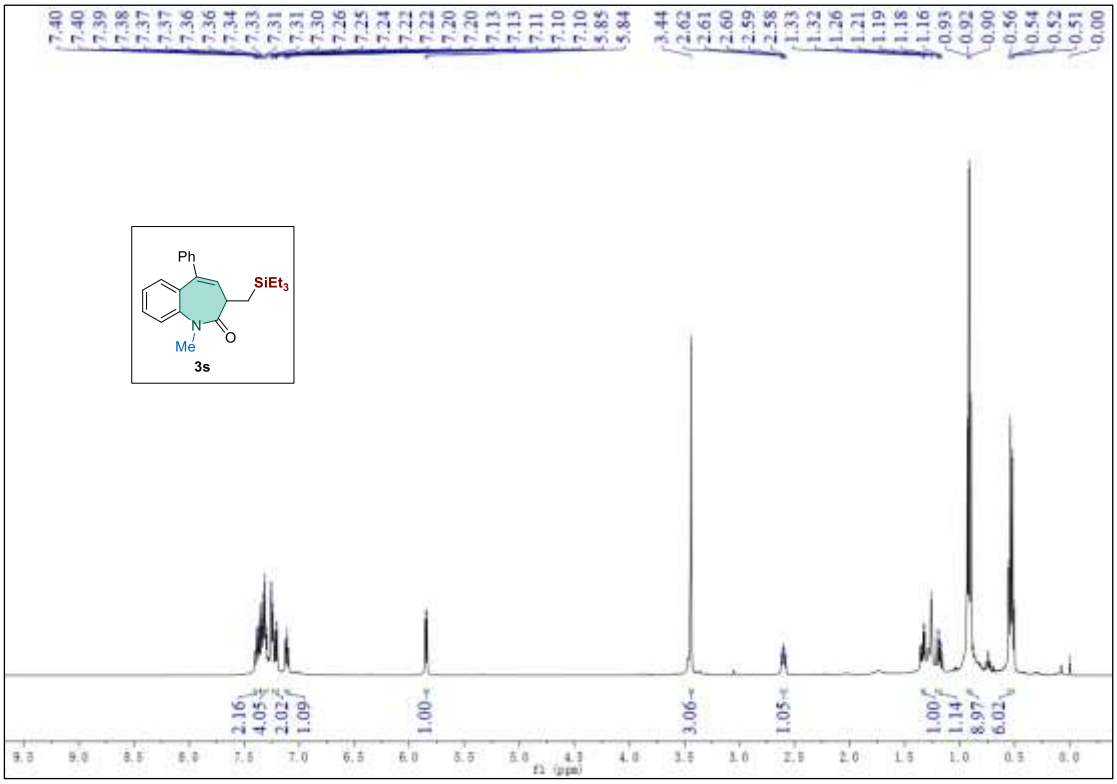

$^{13}$C NMR (126 MHz, $CDCl_3$)



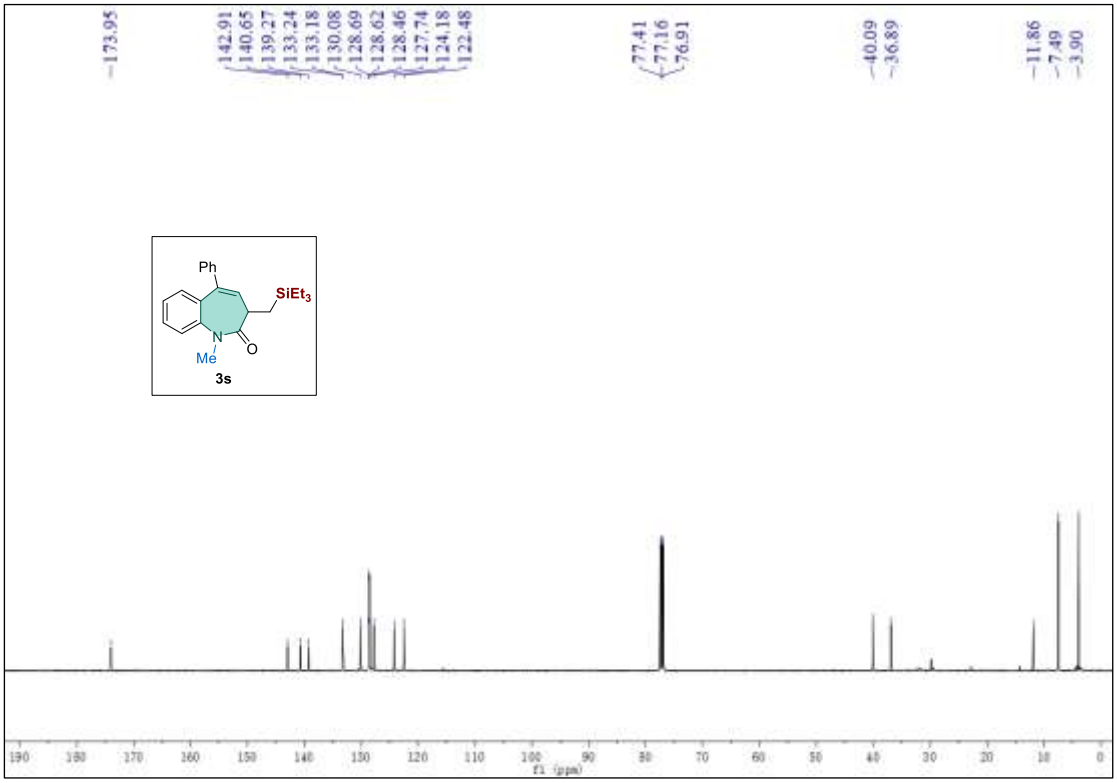
$^{19}F$ NMR (376 MHz, $CDCl_3$)



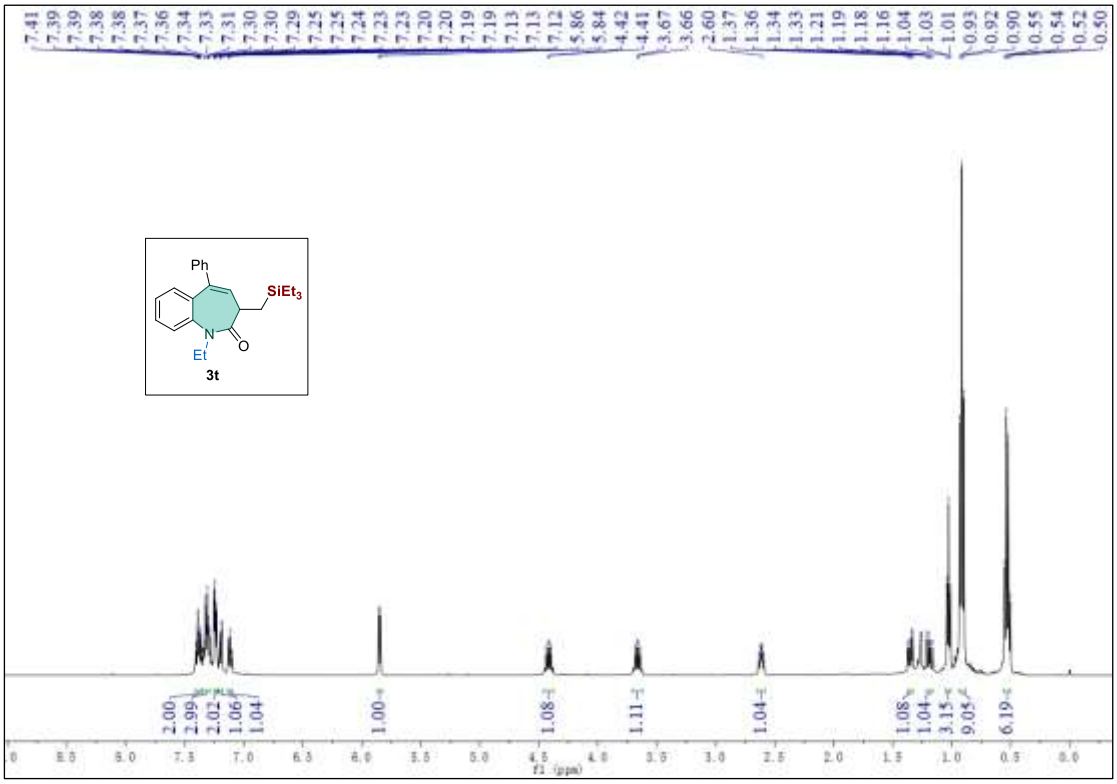
$^{1}$H NMR (500 MHz, $CDCl_3$)




$^{13}$C NMR (126 MHz, $CDCl_3$)



$^{1}$H NMR (500 MHz, $CDCl_3$)

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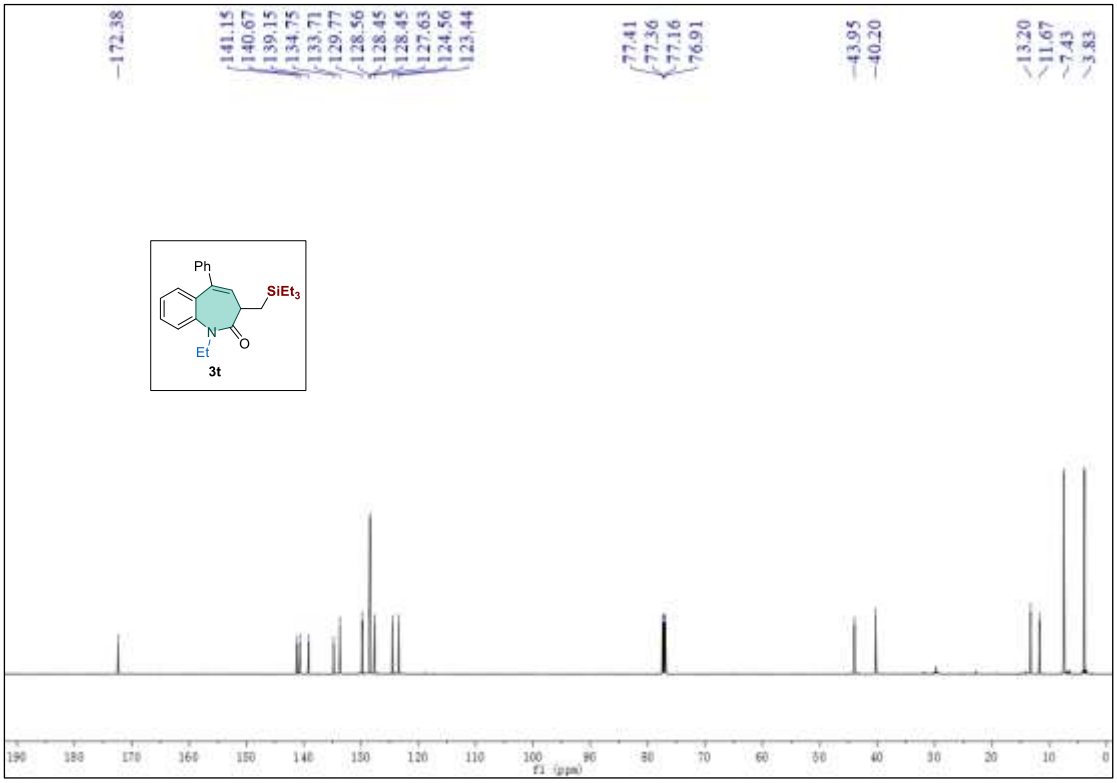

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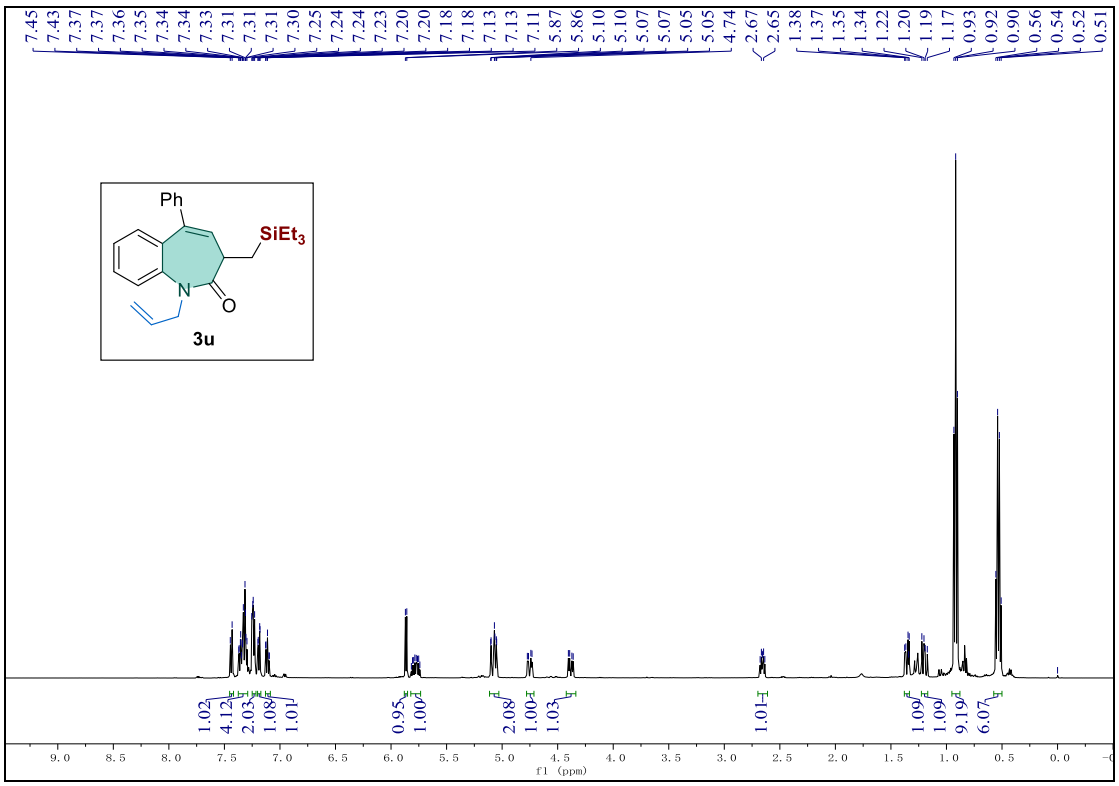


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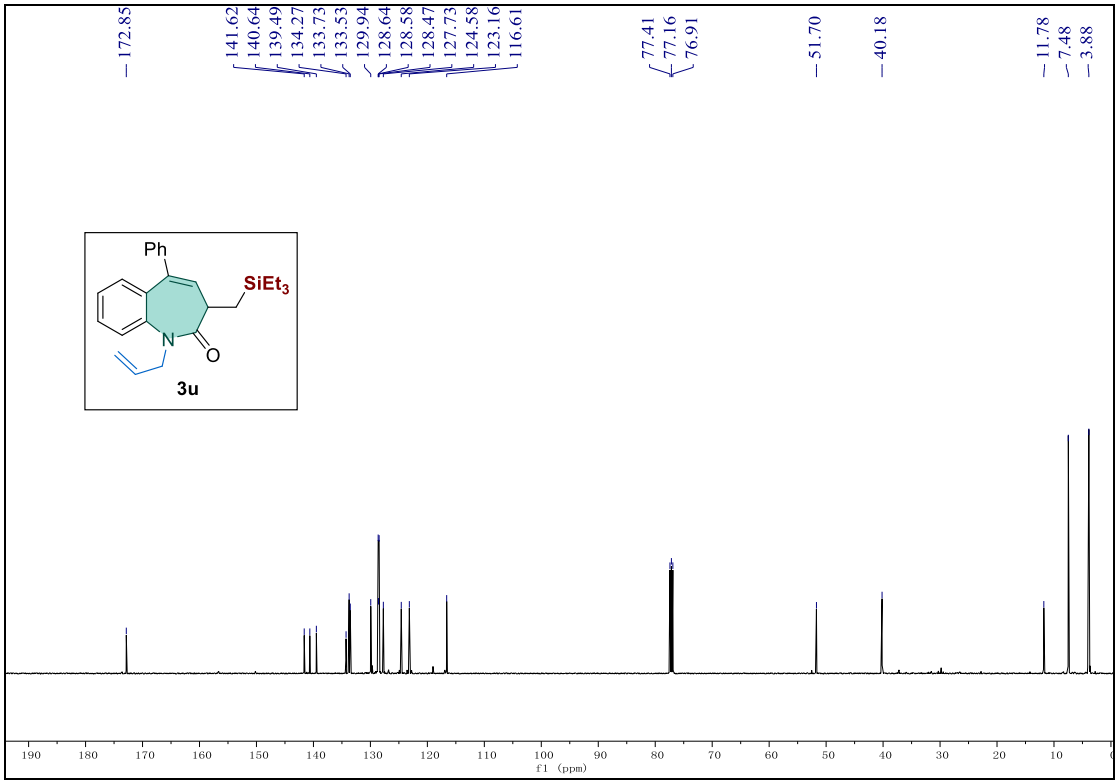

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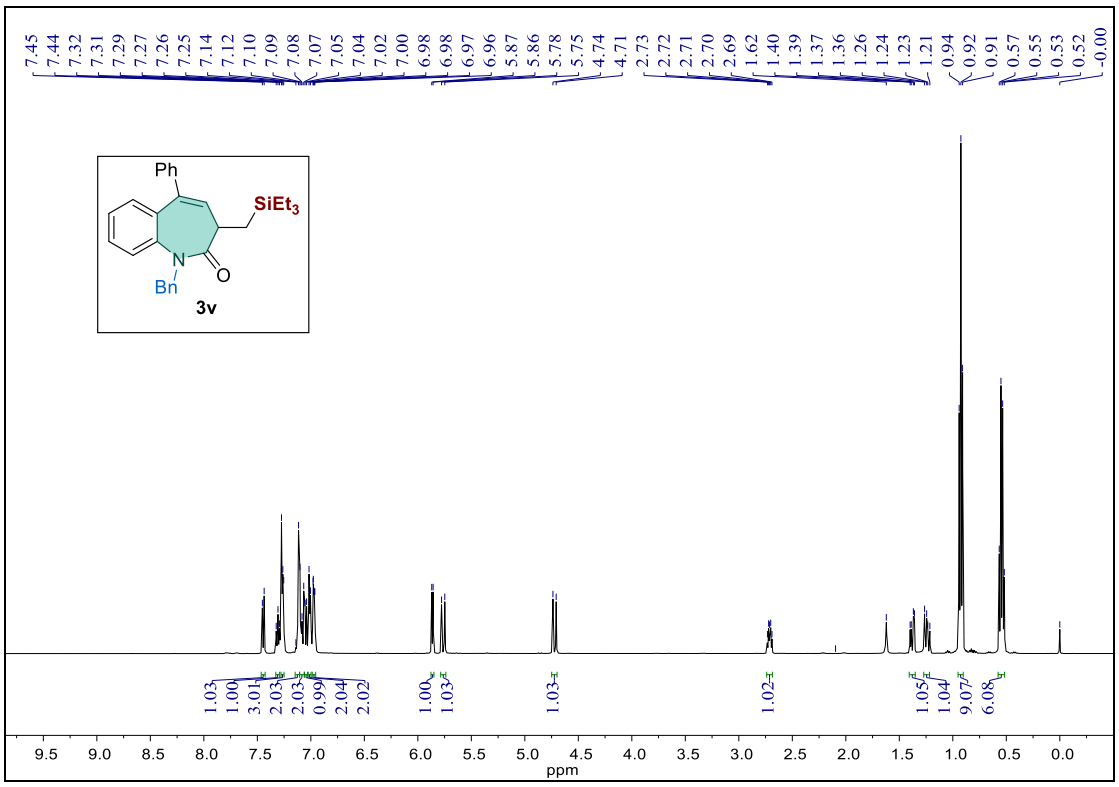
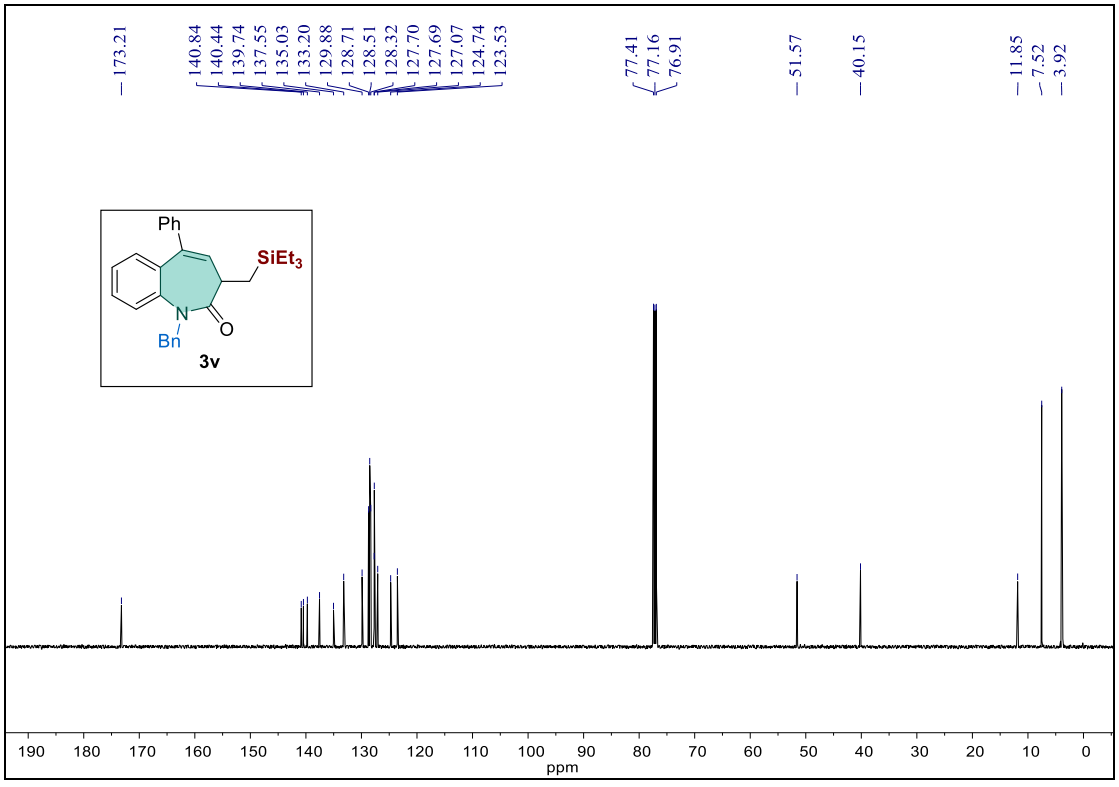
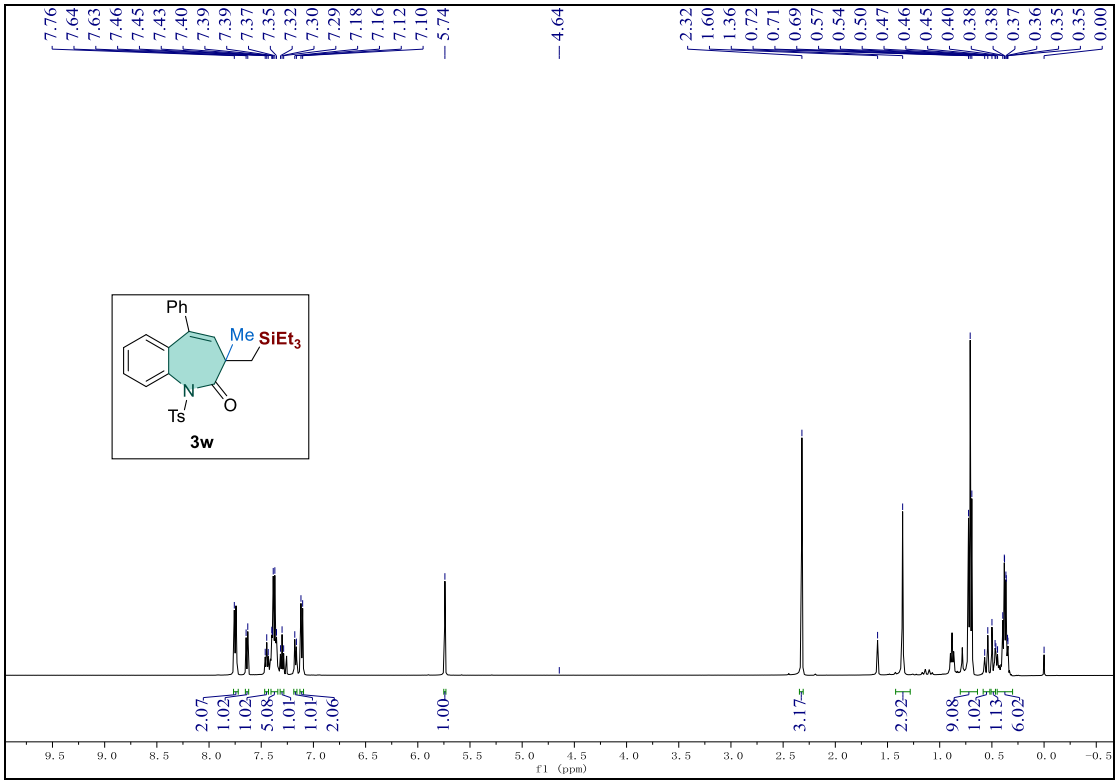


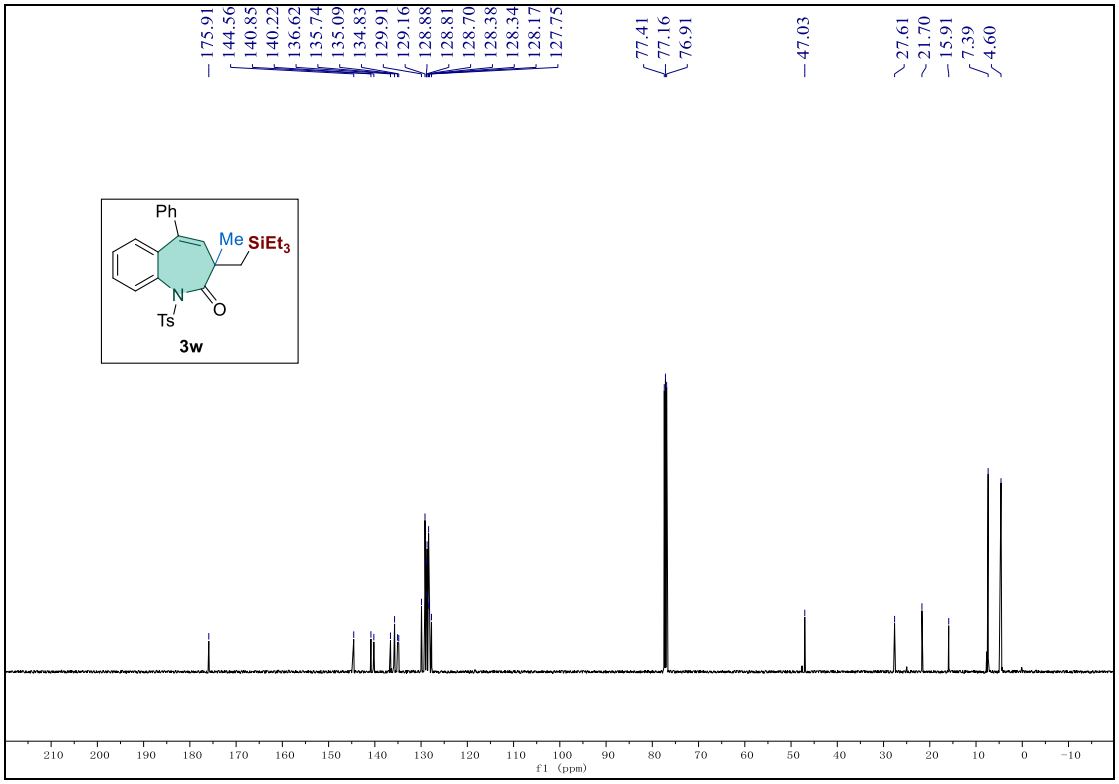

$^{13}$C NMR (126 MHz, $CDCl_3$)



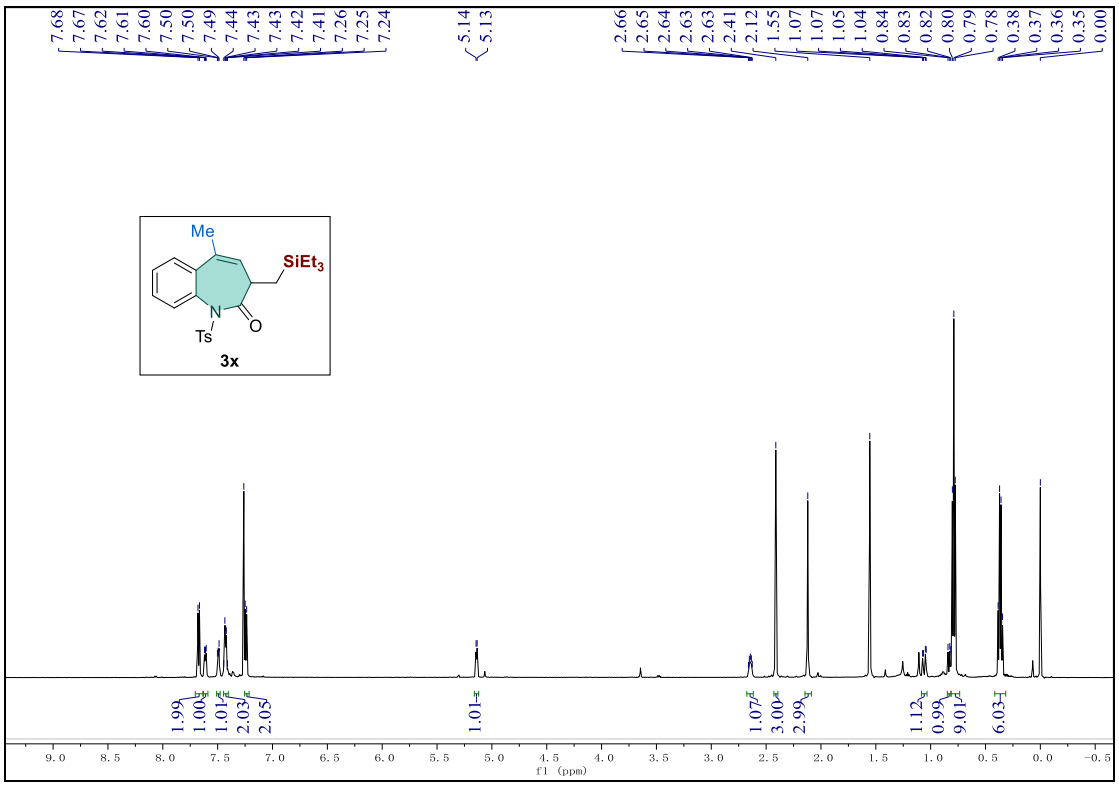
$^{1}$H NMR (500 MHz, $CDCl_3$)



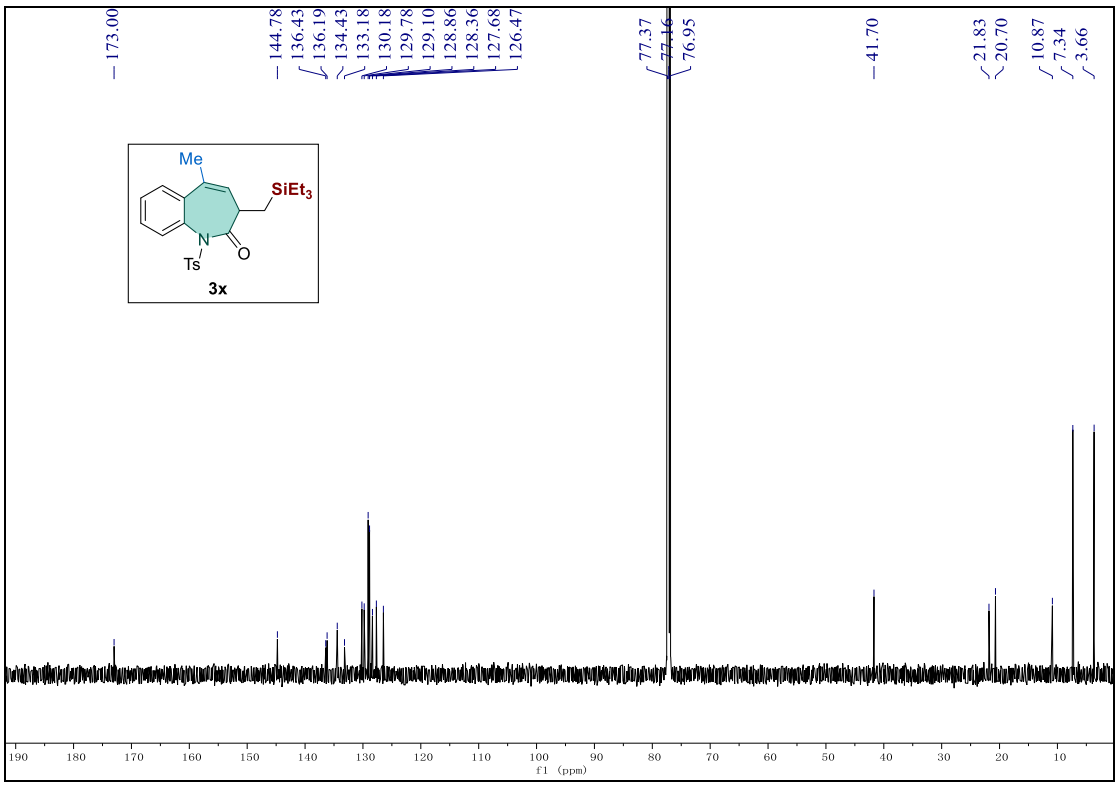

$^{13}$C NMR (126 MHz, $CDCl_3$)



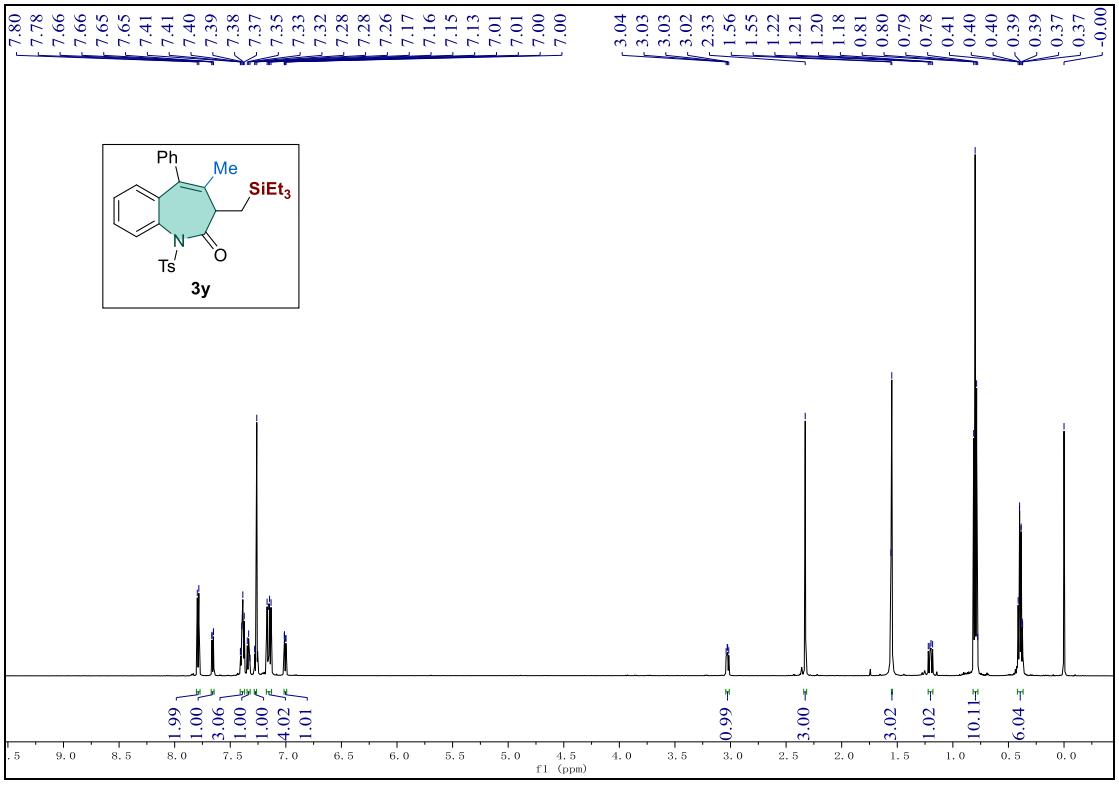
$^{1}$H NMR (600 MHz, $CDCl_3$)



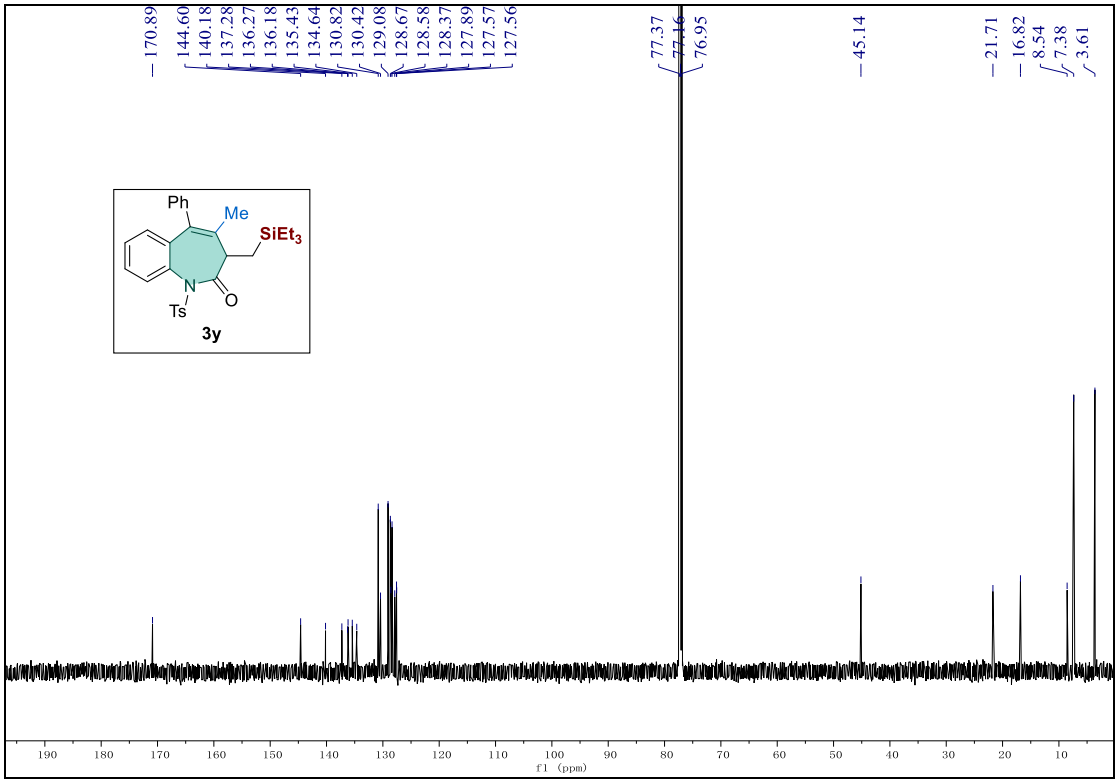

$^{13}$C NMR (151 MHz, $CDCl_3$)



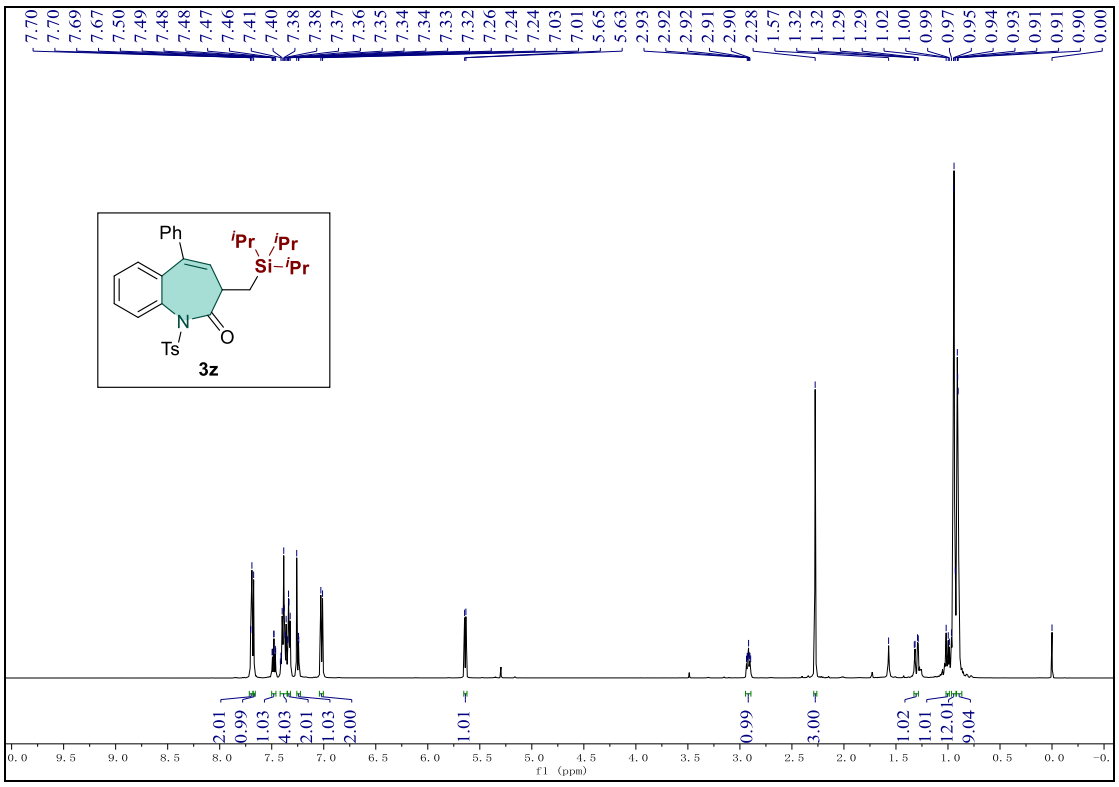
$^{1}$H NMR (600 MHz, $CDCl_3$)




$^{13}$C NMR (151 MHz, $CDCl_3$)



$^{1}$H NMR (500 MHz, $CDCl_3$)

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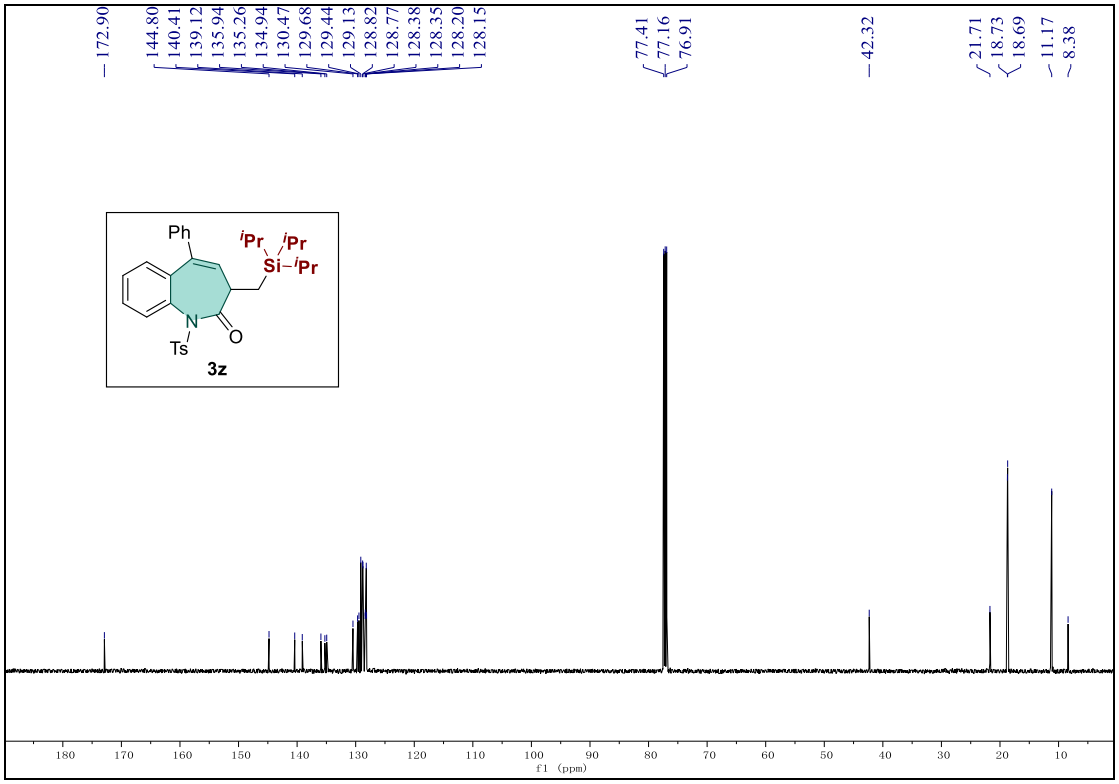

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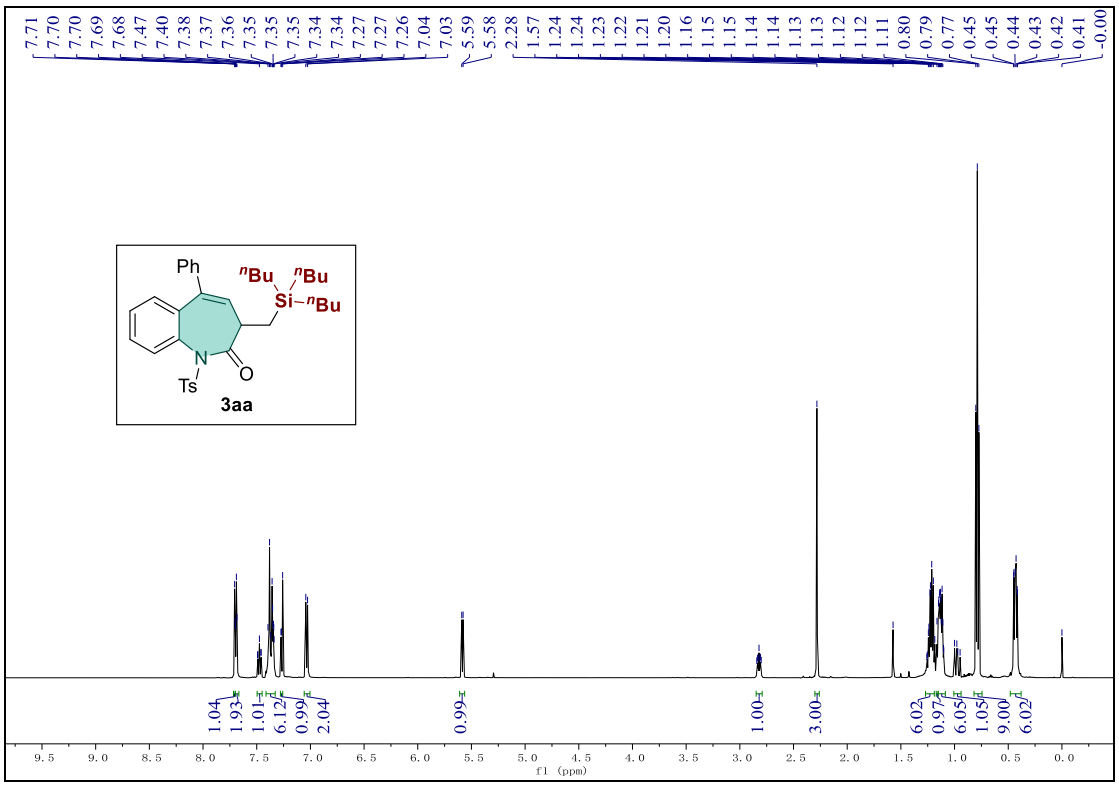


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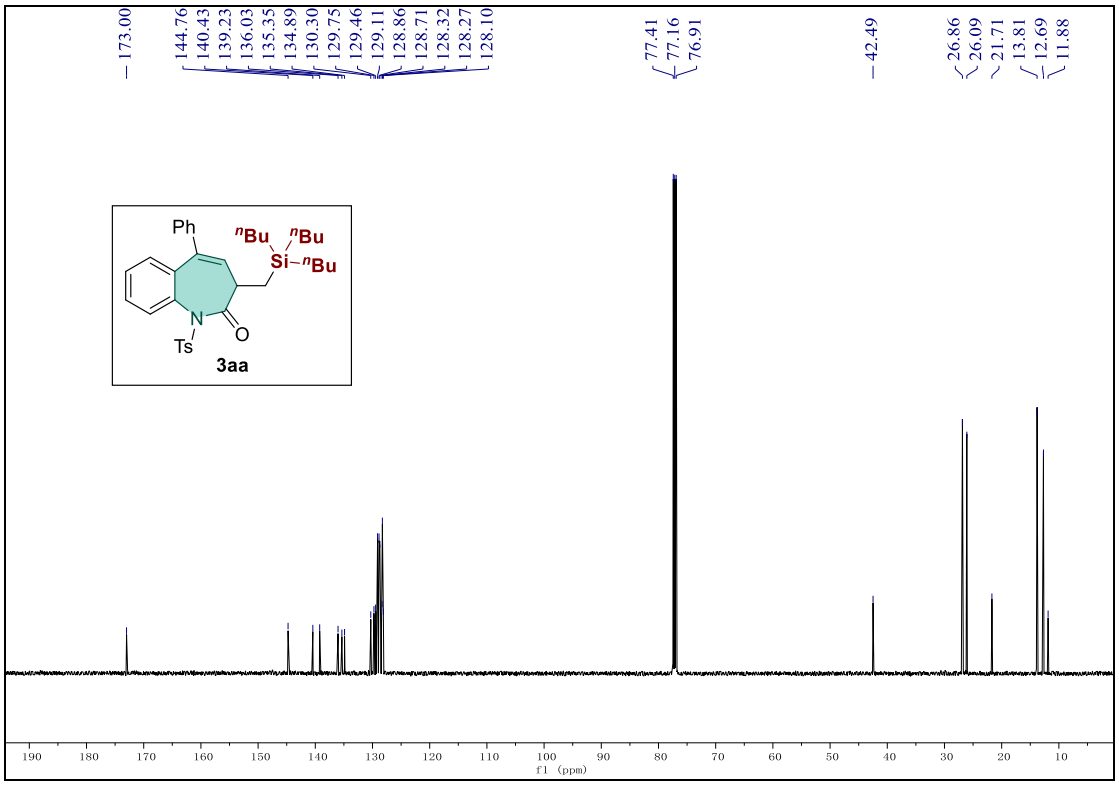
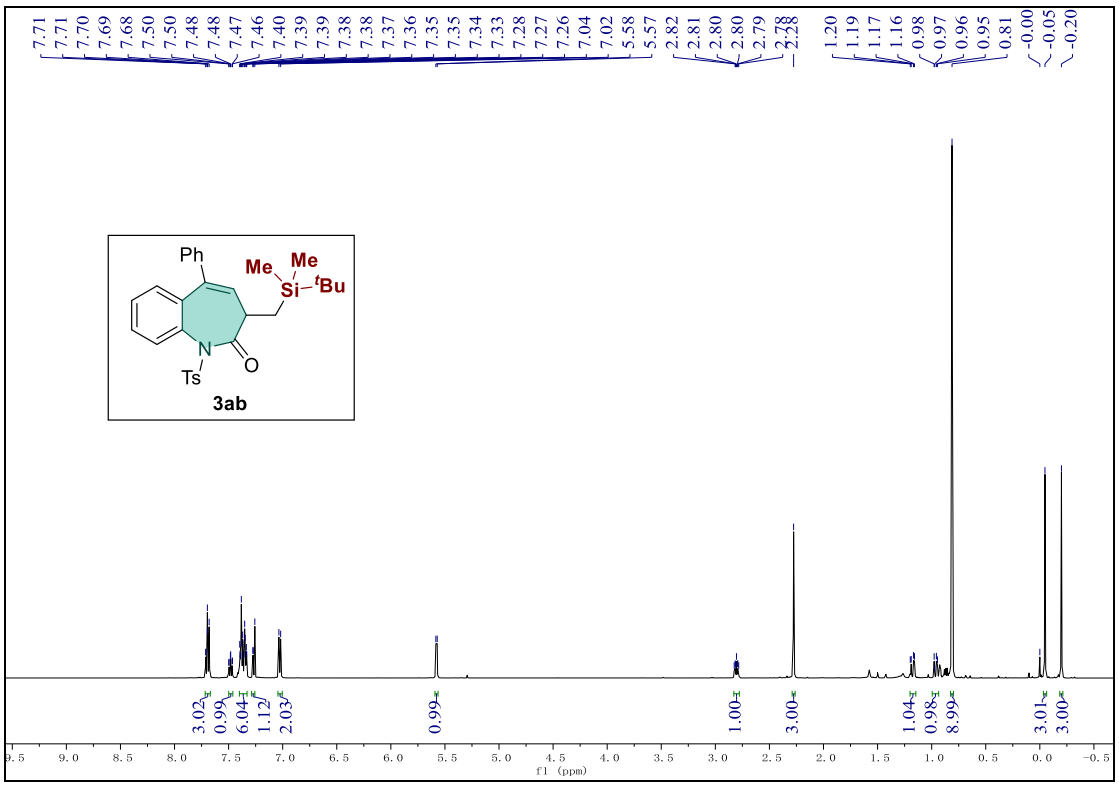


$^{1}$H NMR (500 MHz, $CDCl_3$)

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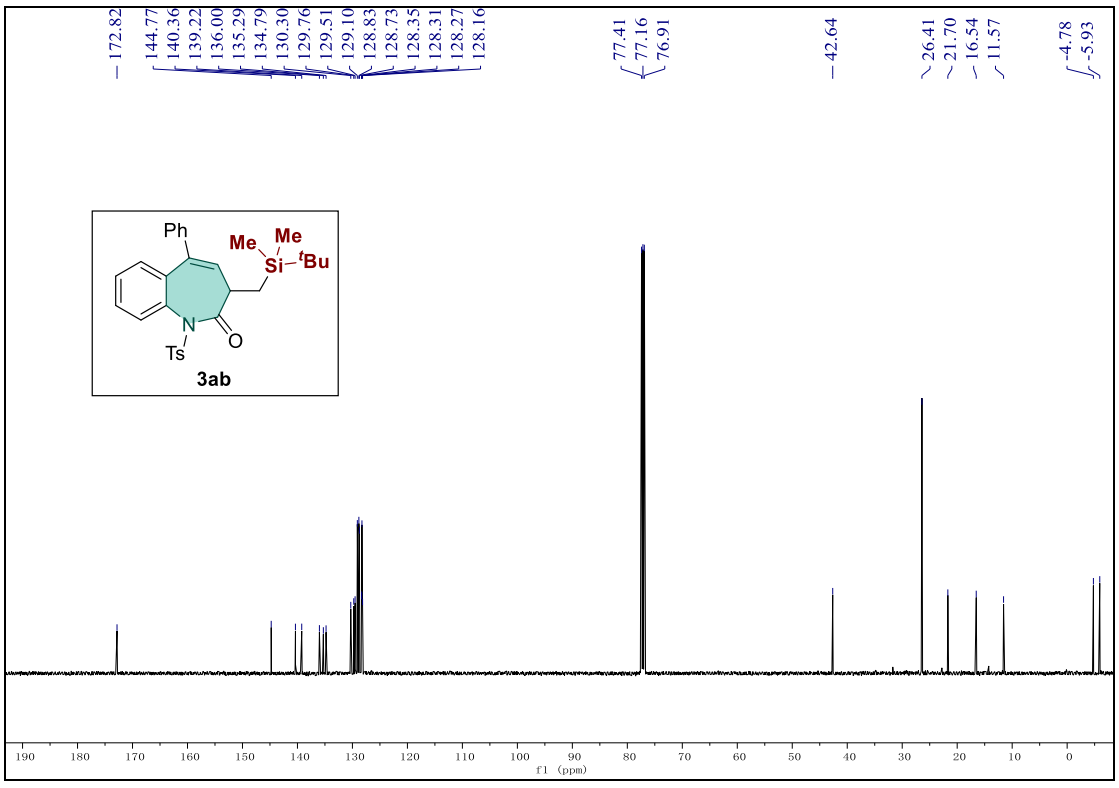

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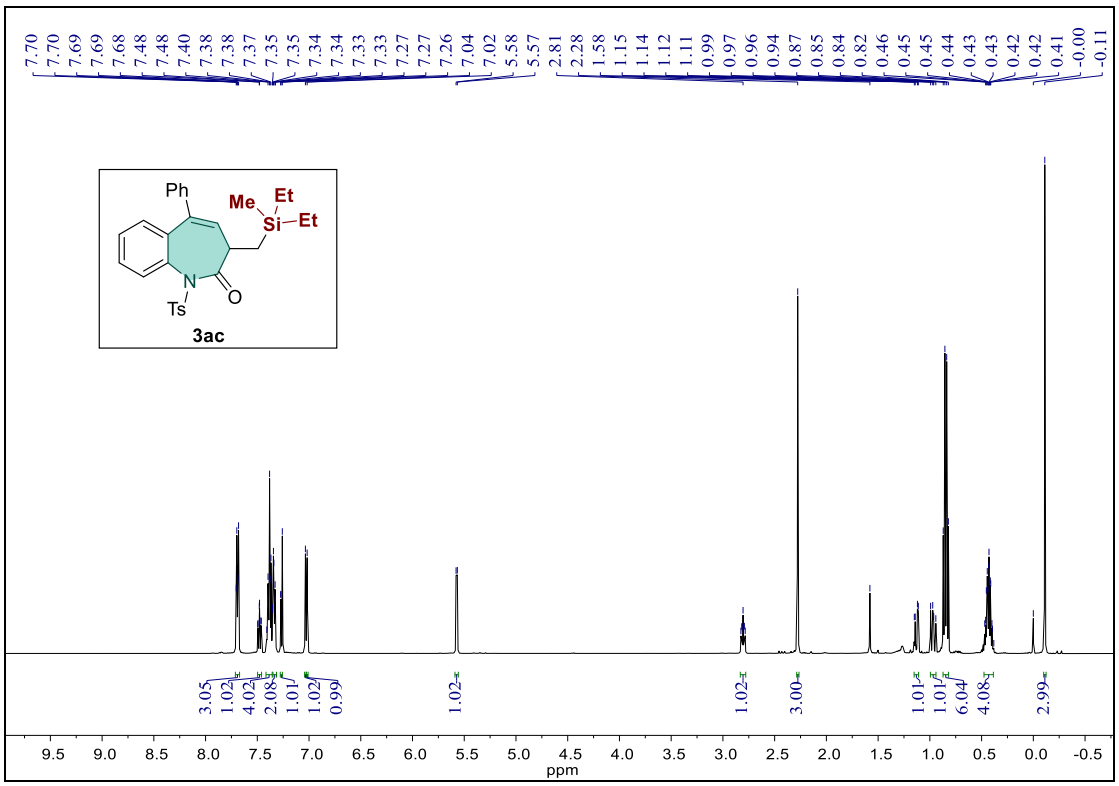


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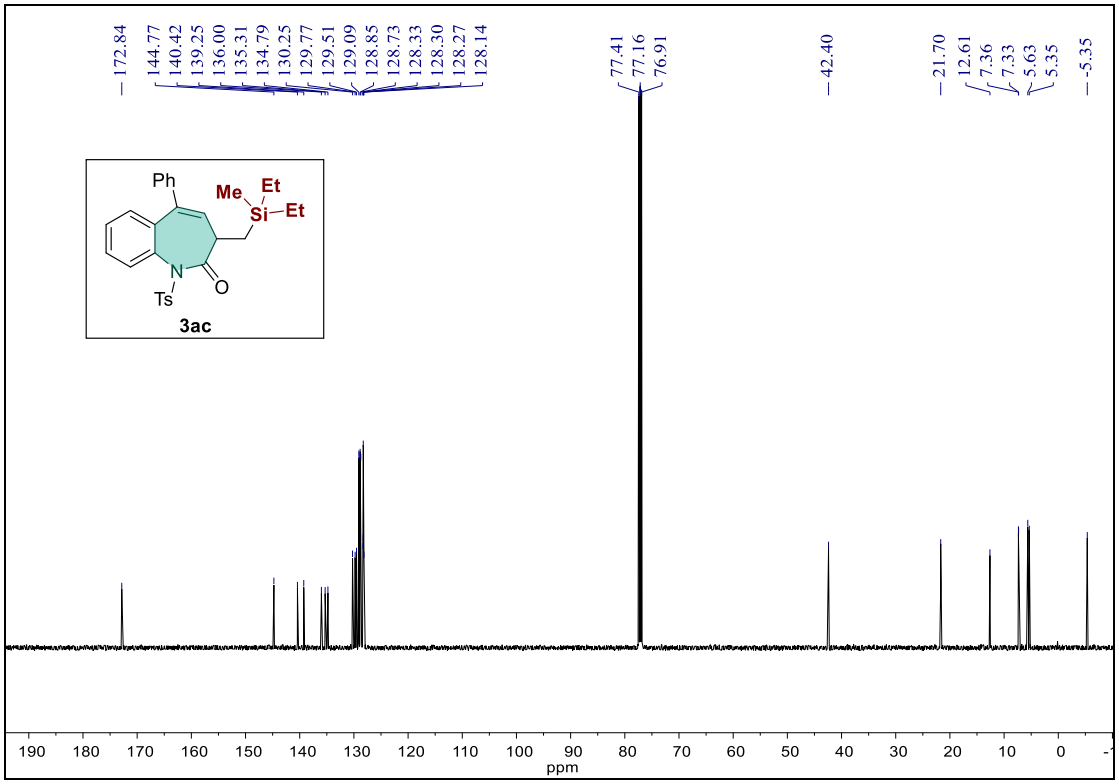
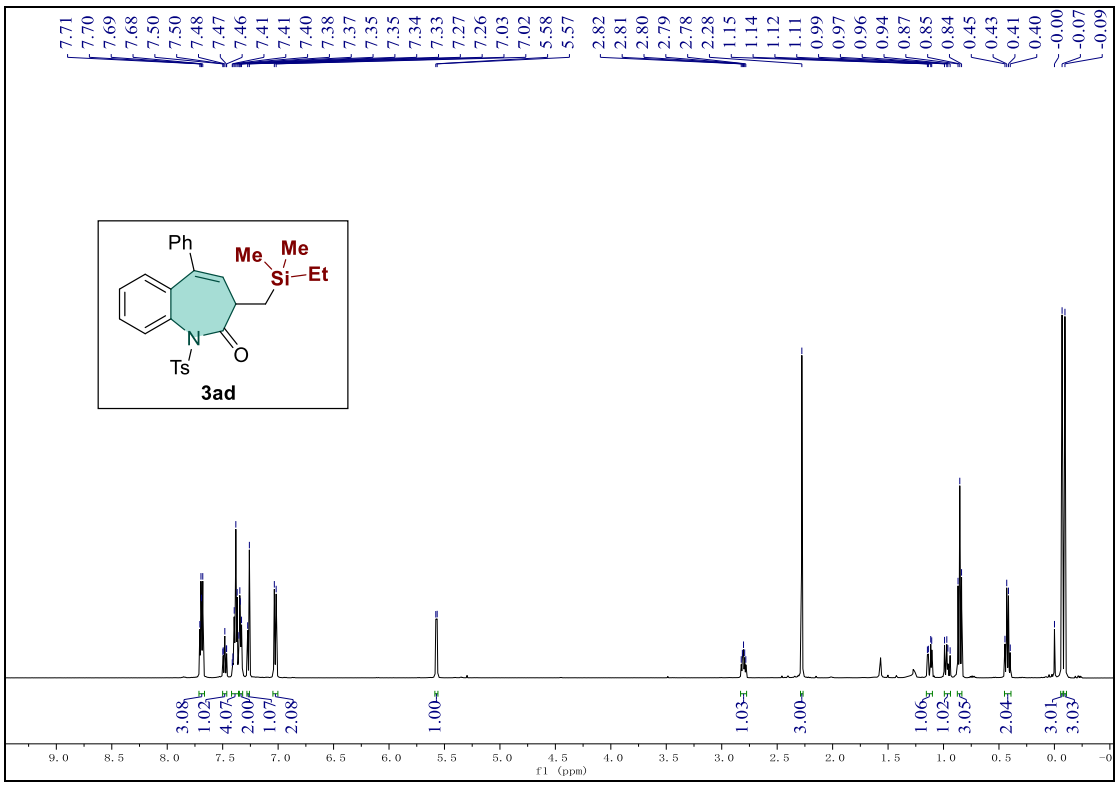
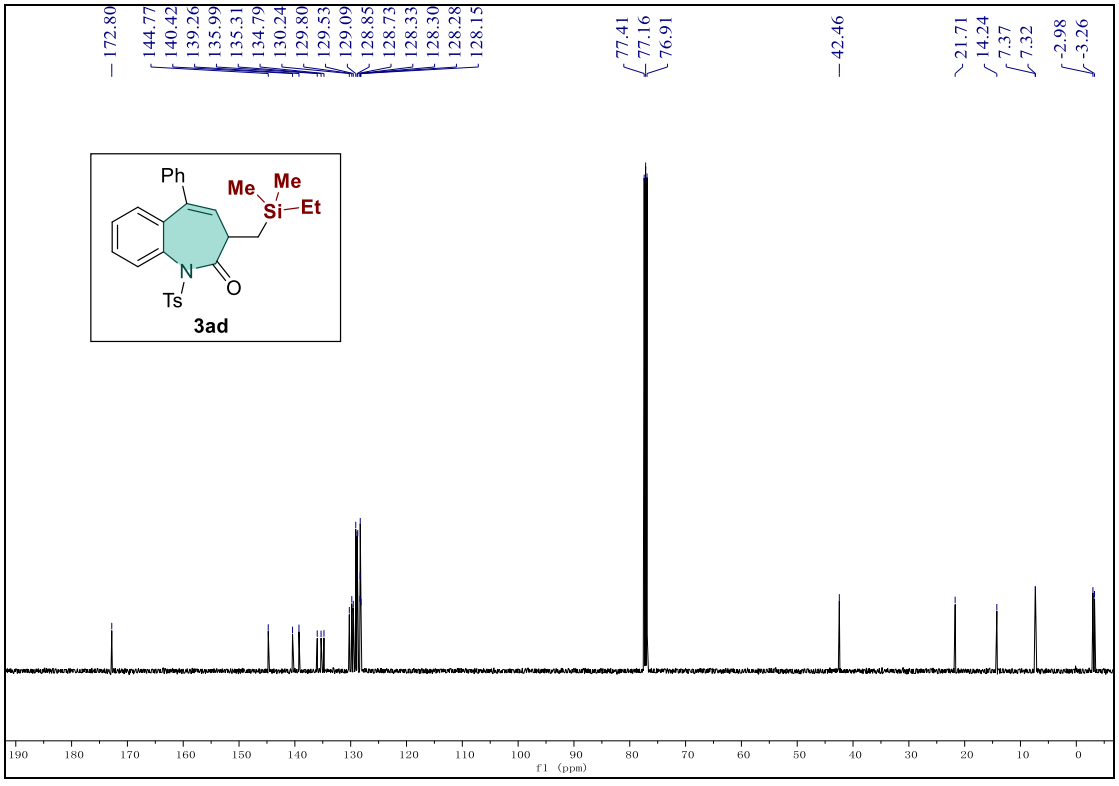


$^{1}$H NMR (500 MHz, $CDCl_3$)




$^{13}$C NMR (126 MHz, $CDCl_3$)



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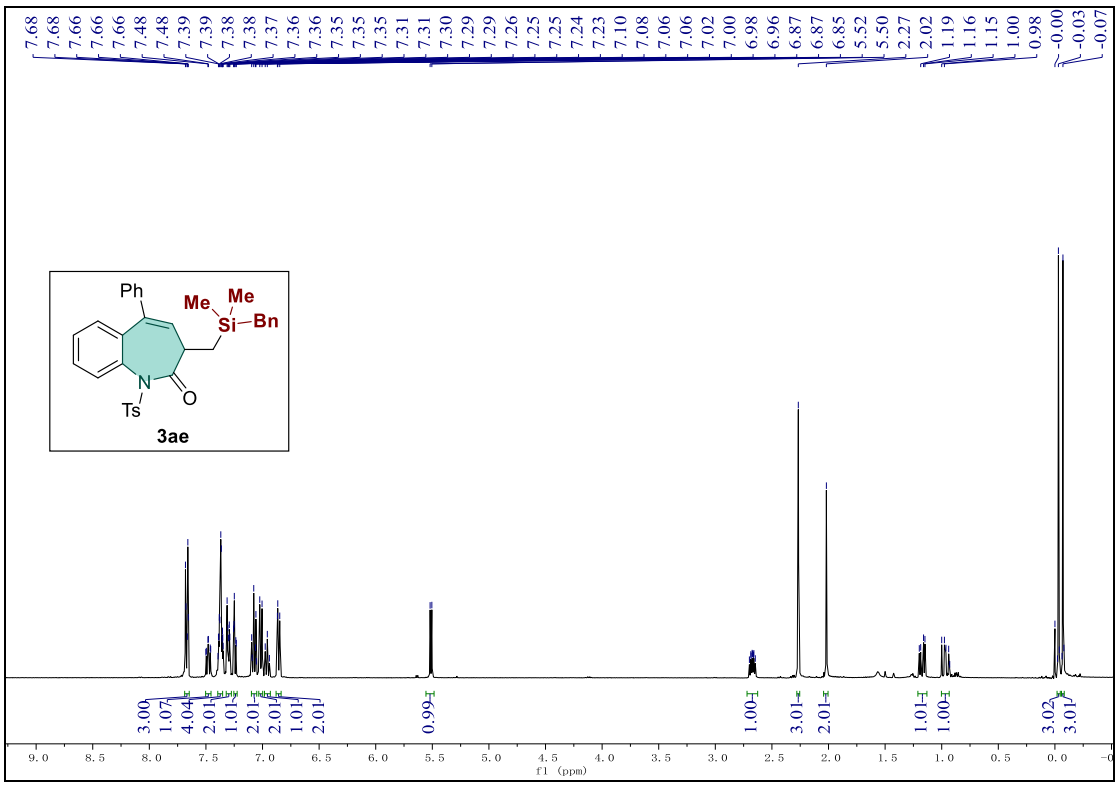


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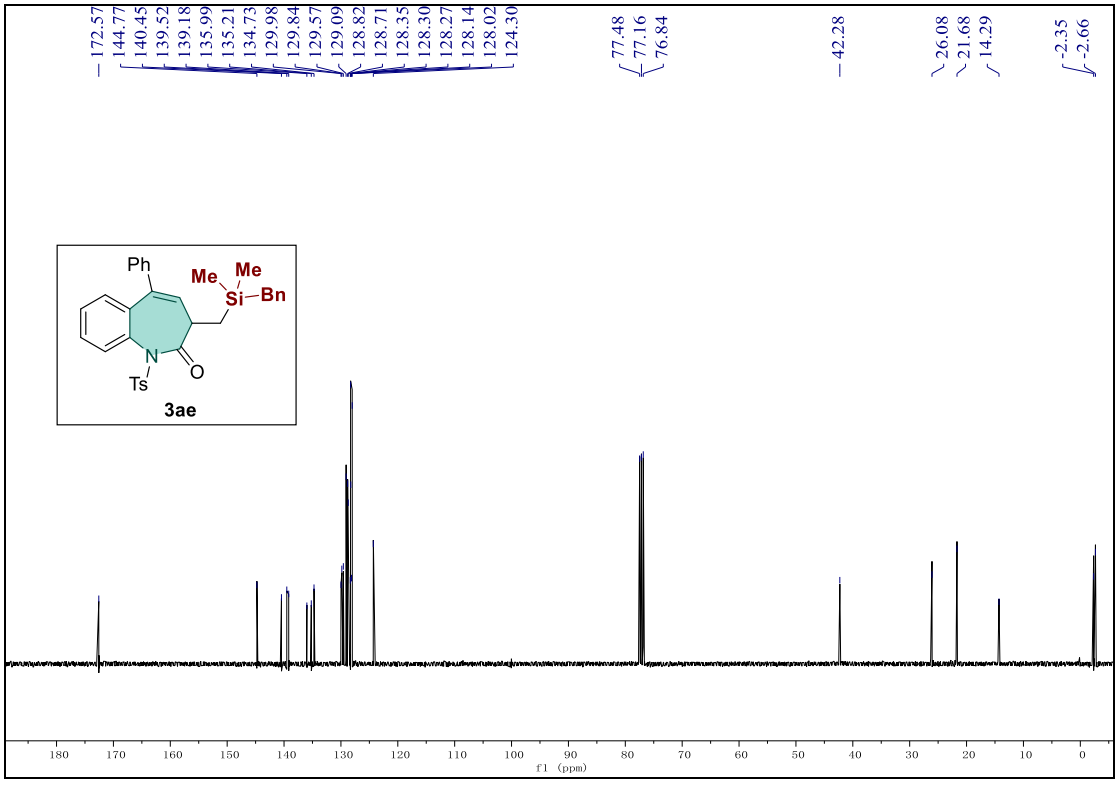
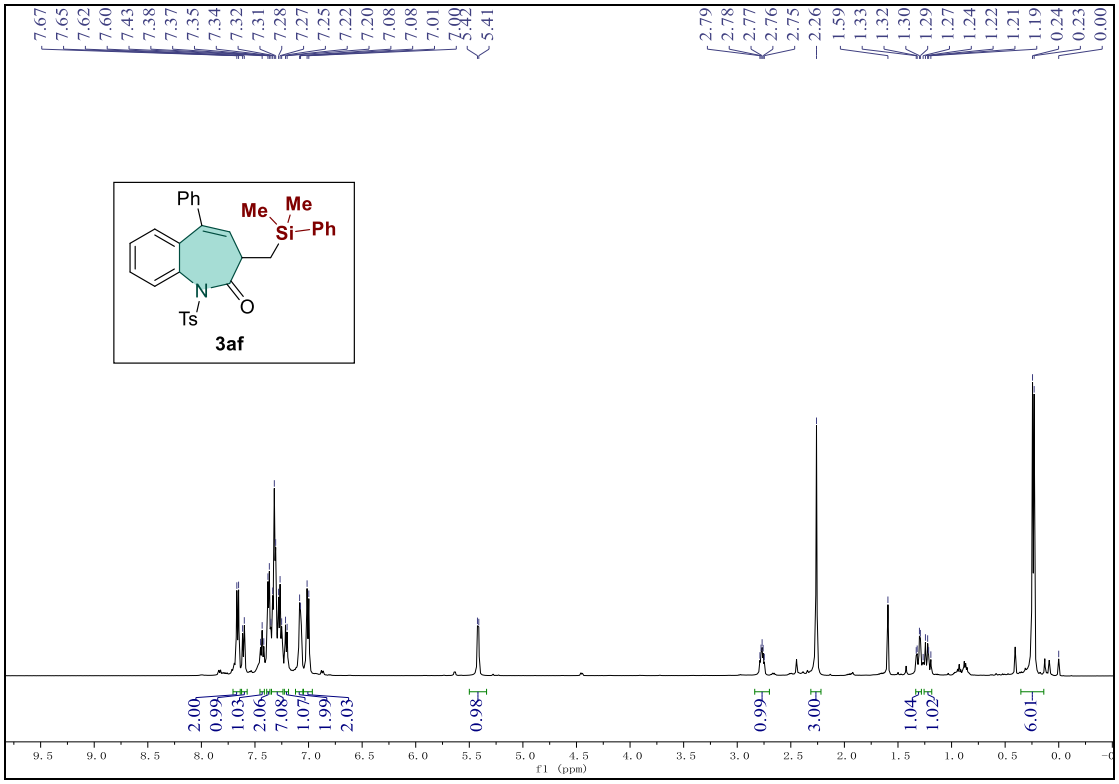
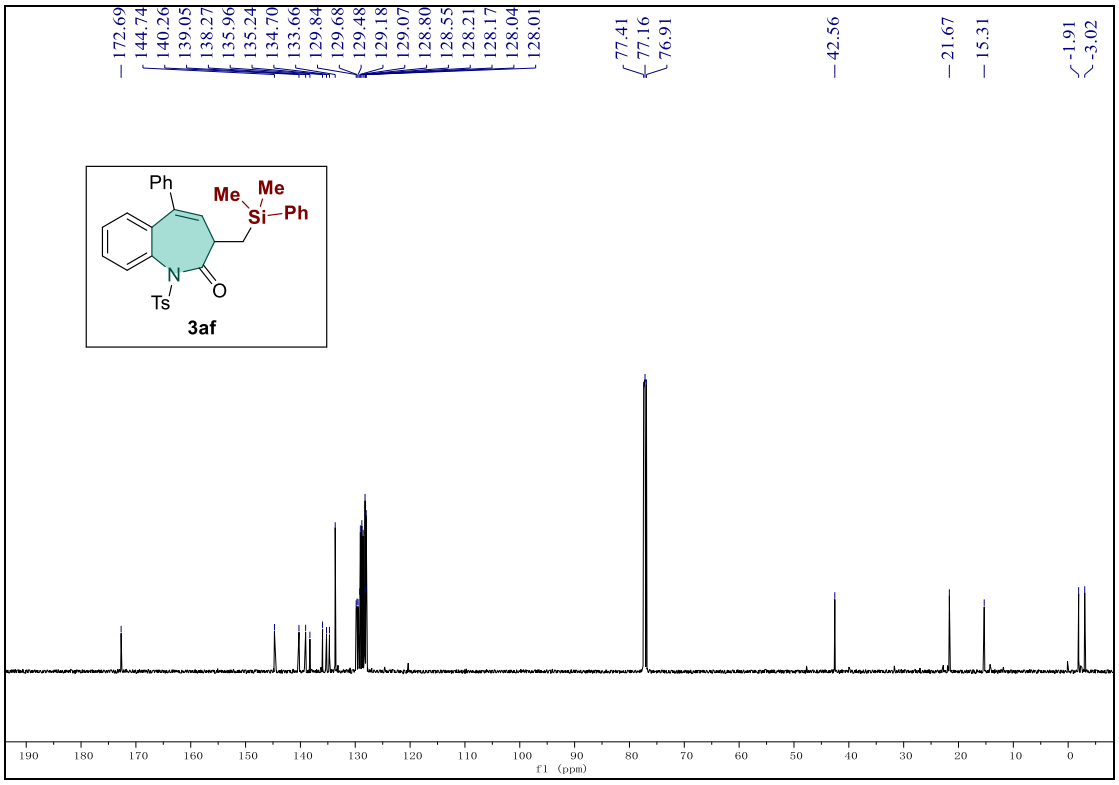


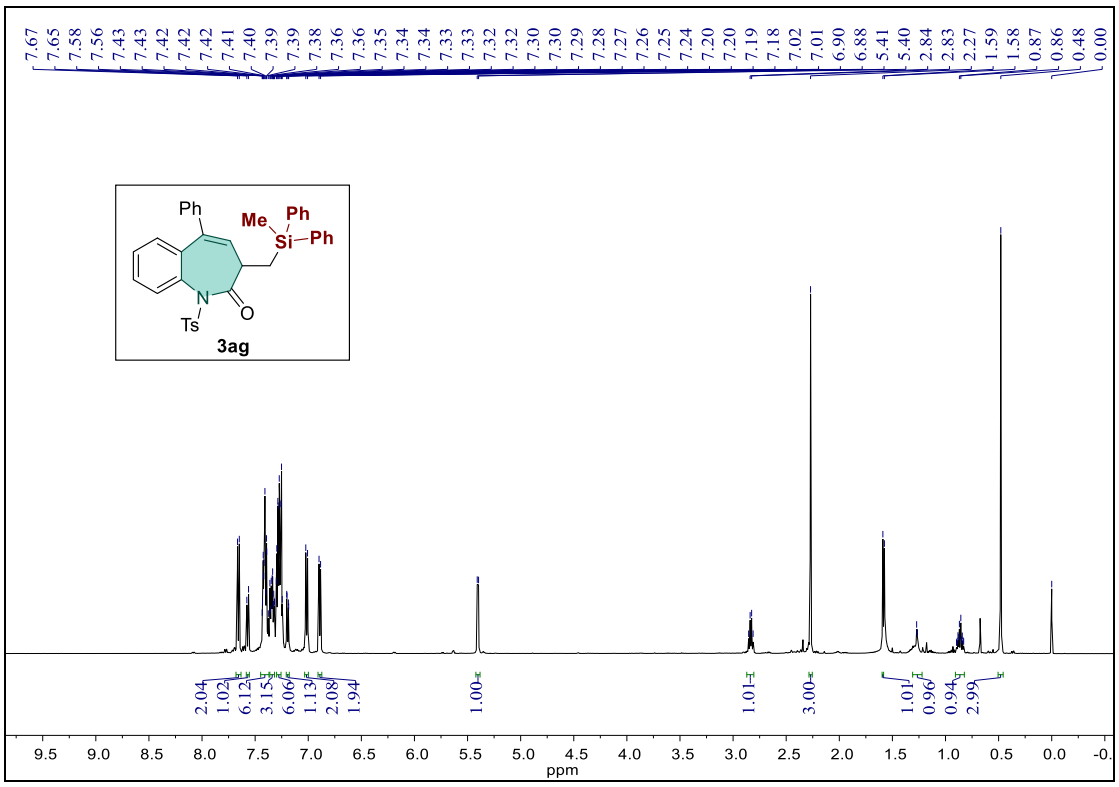
$^{1}$H NMR (500 MHz, $CDCl_3$)




$^{13}$C NMR (126 MHz, $CDCl_3$)



$^{1}$H NMR (500 MHz, $CDCl_3$)

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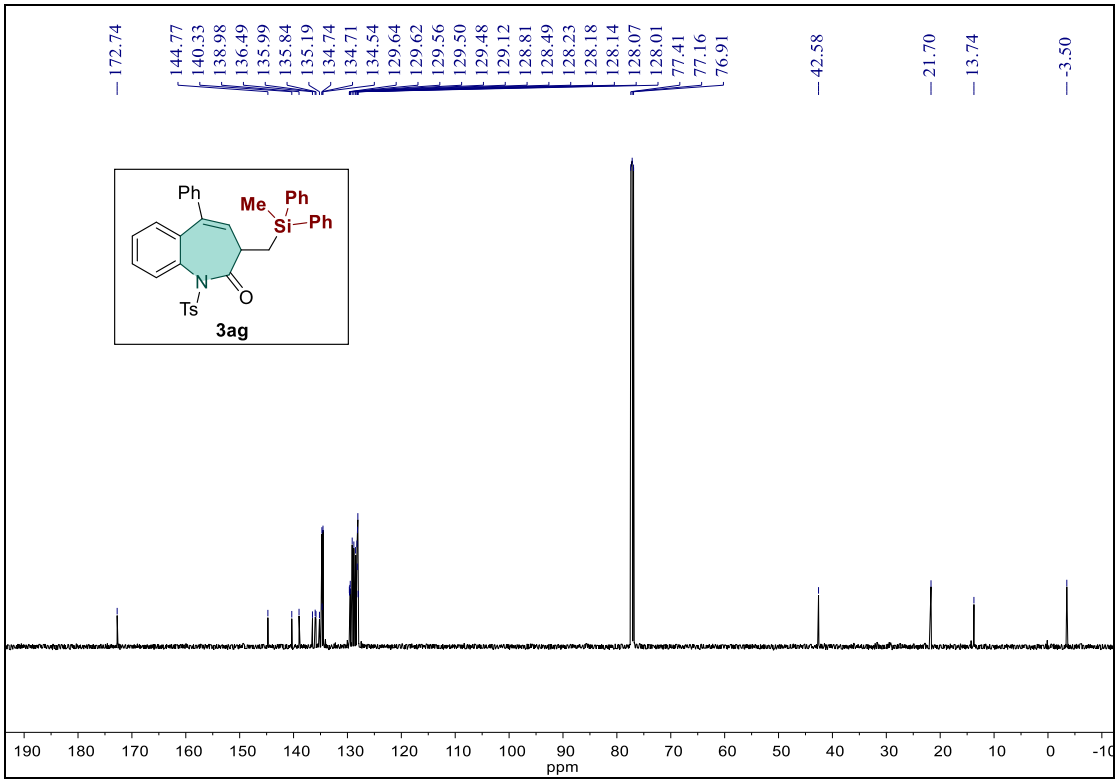
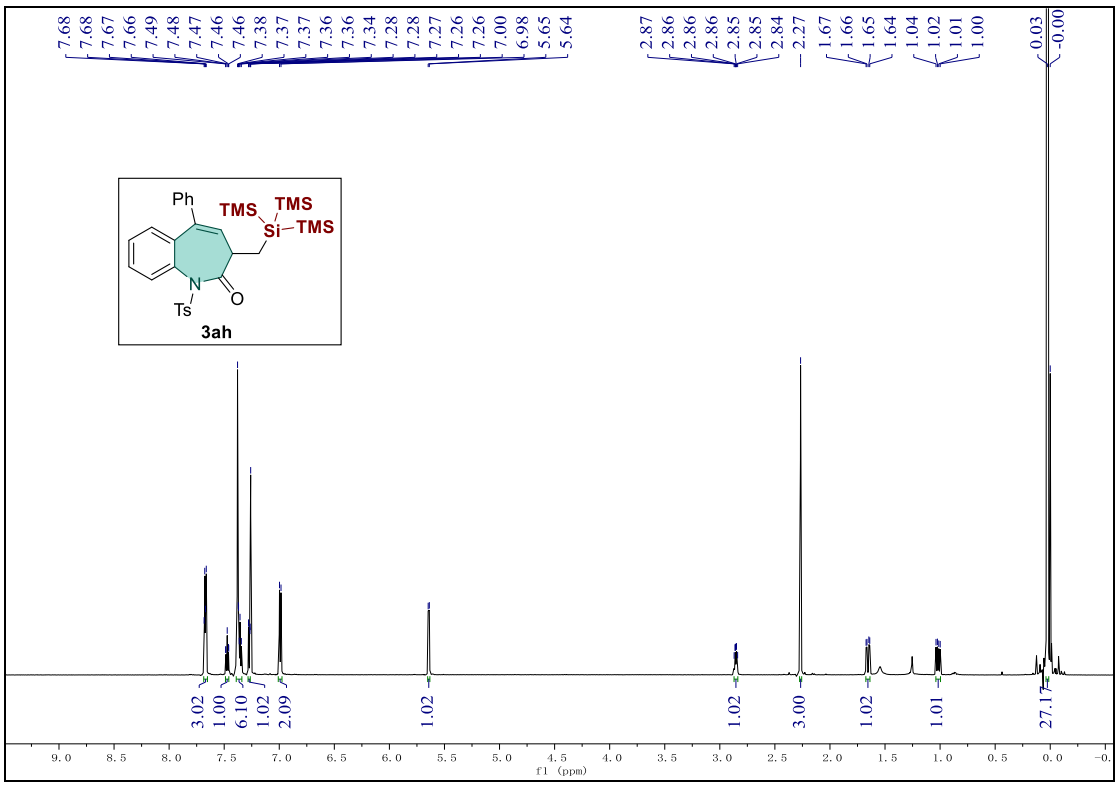
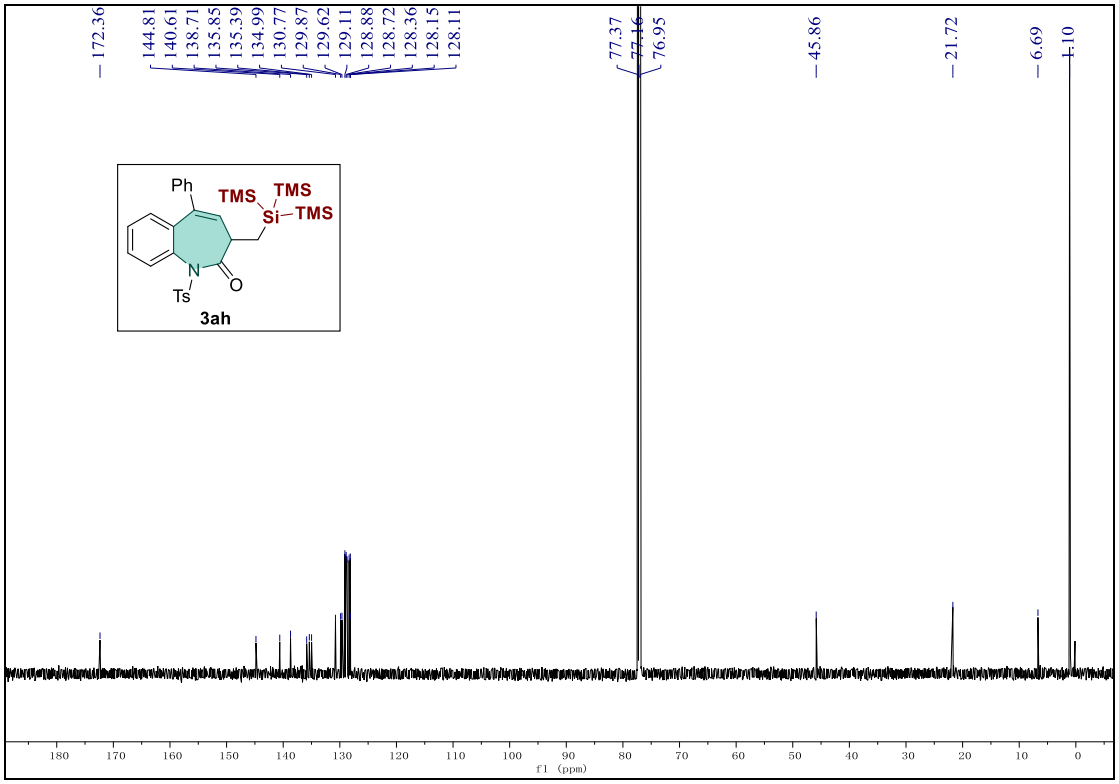


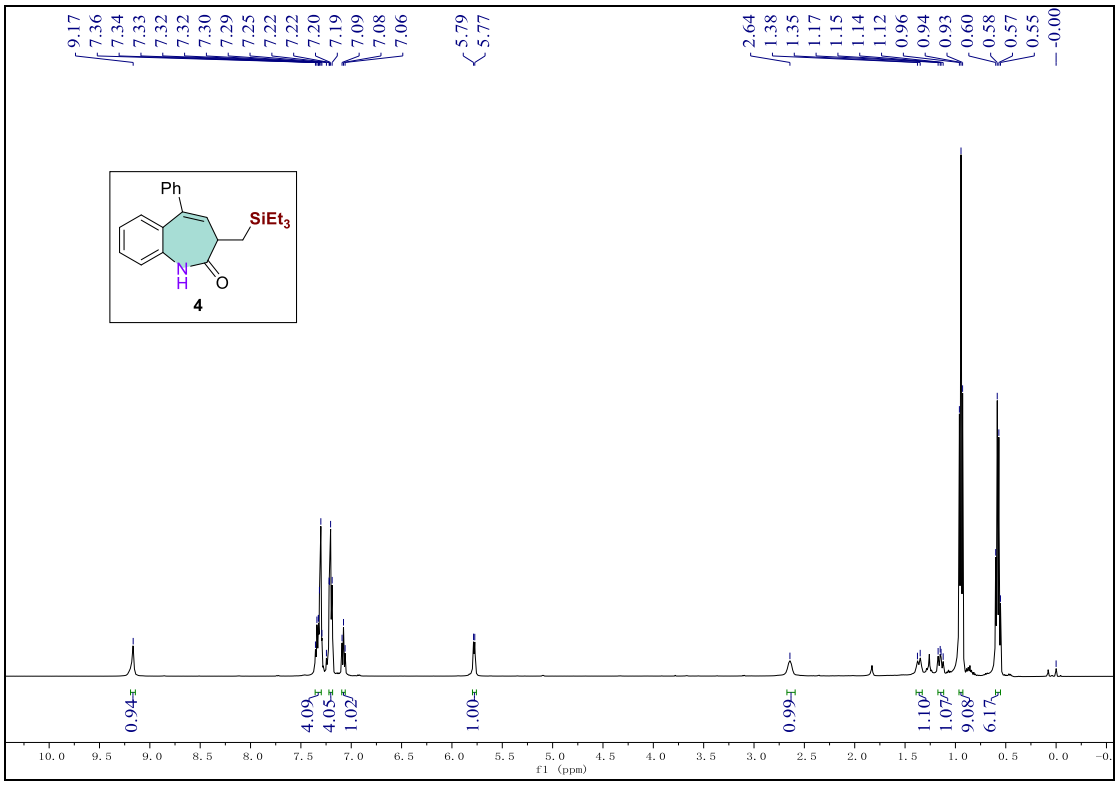
$^{1}$H NMR (600 MHz, $CDCl_3$)



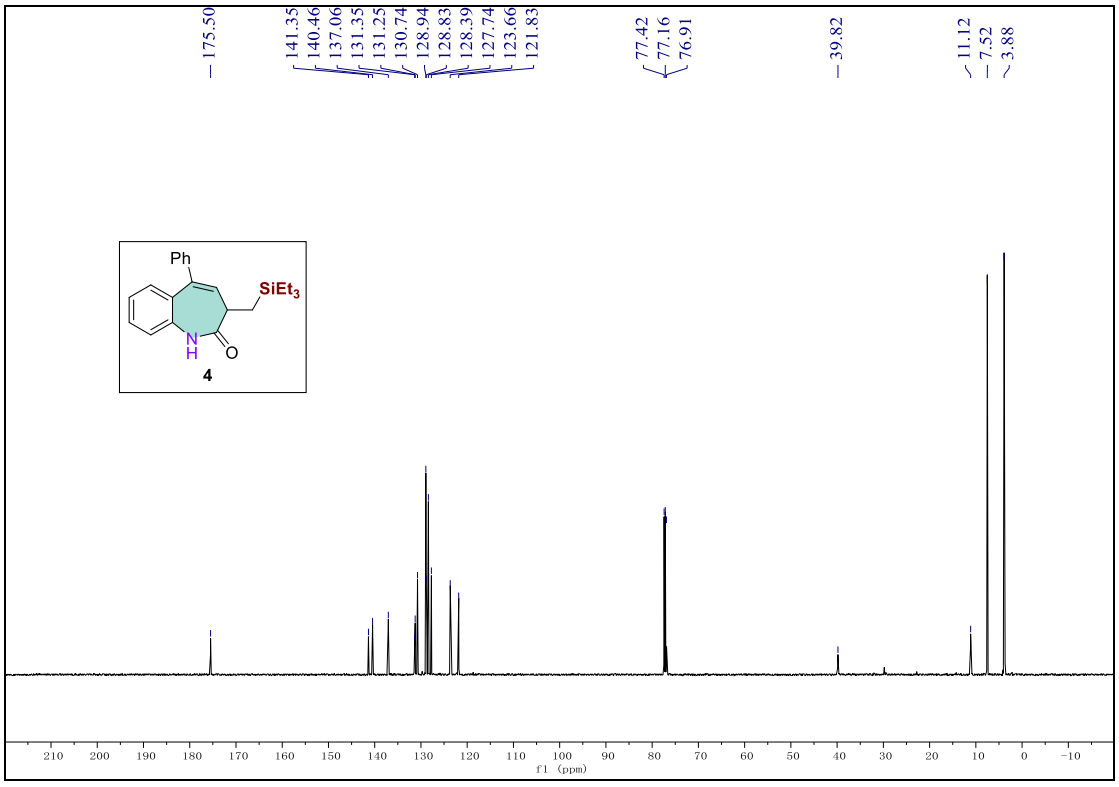

$^{13}$C NMR (151 MHz, $CDCl_3$)



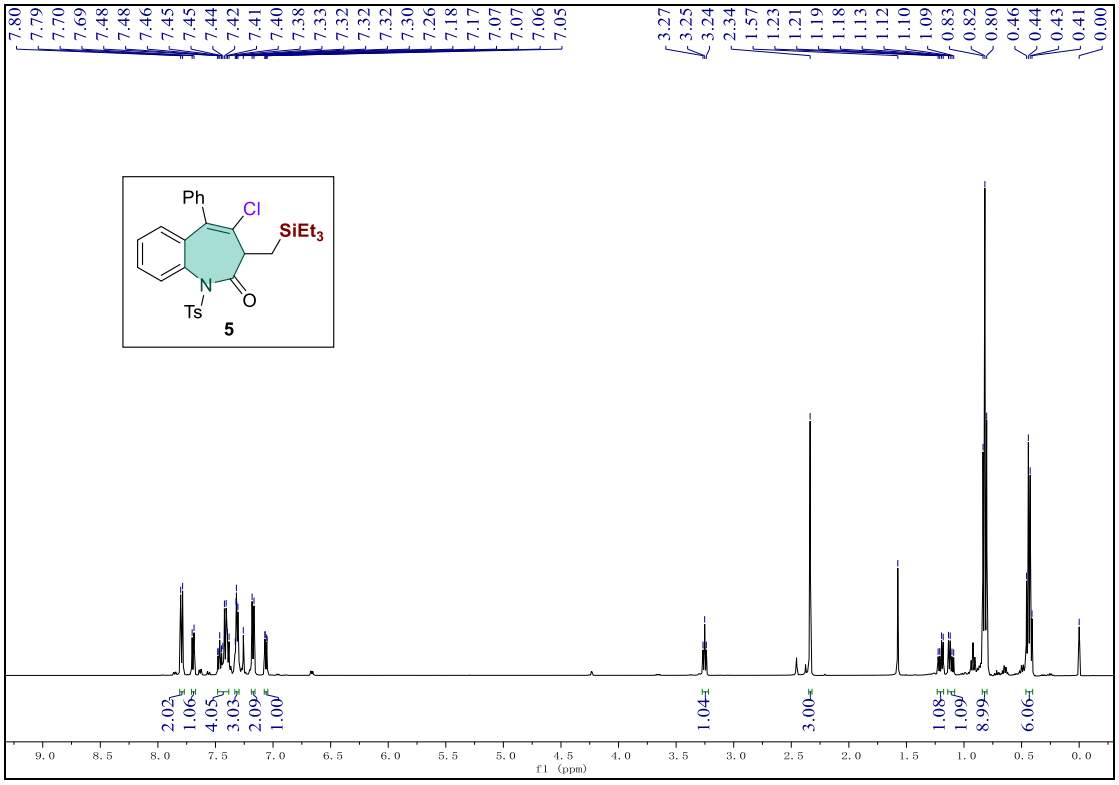
$^{1}$H NMR (500 MHz, $CDCl_3$)



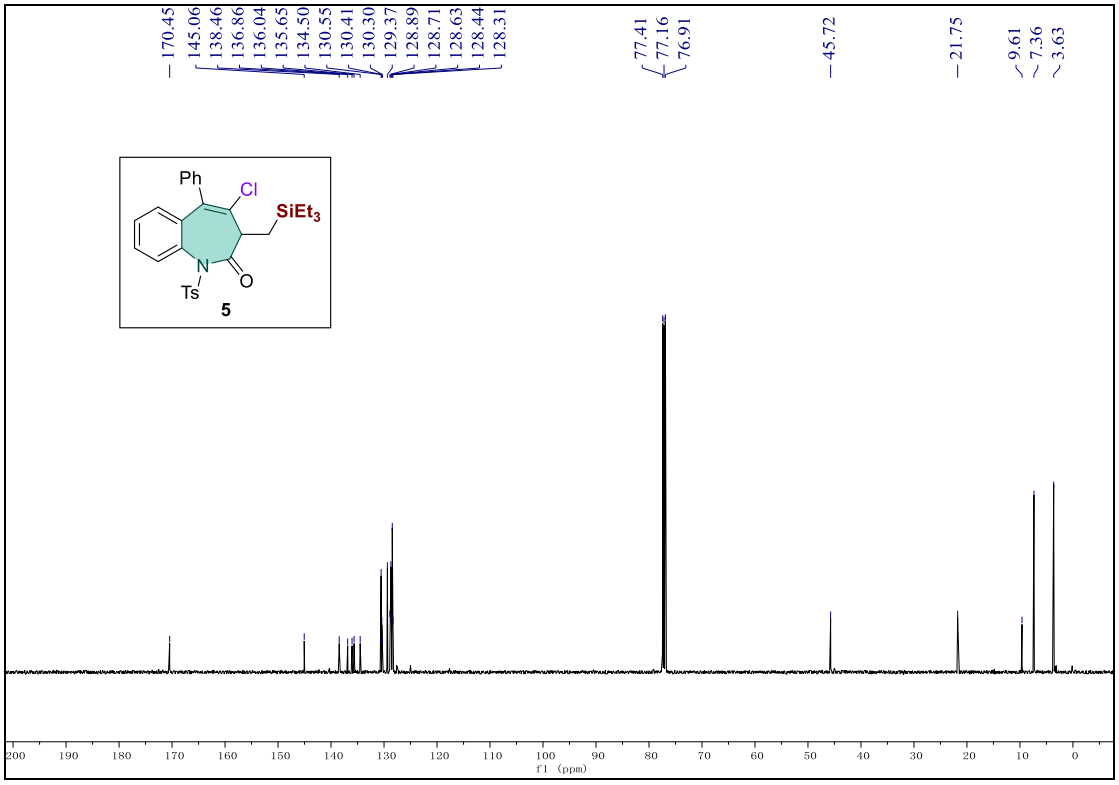

$^{13}$C NMR (126 MHz, $CDCl_3$)



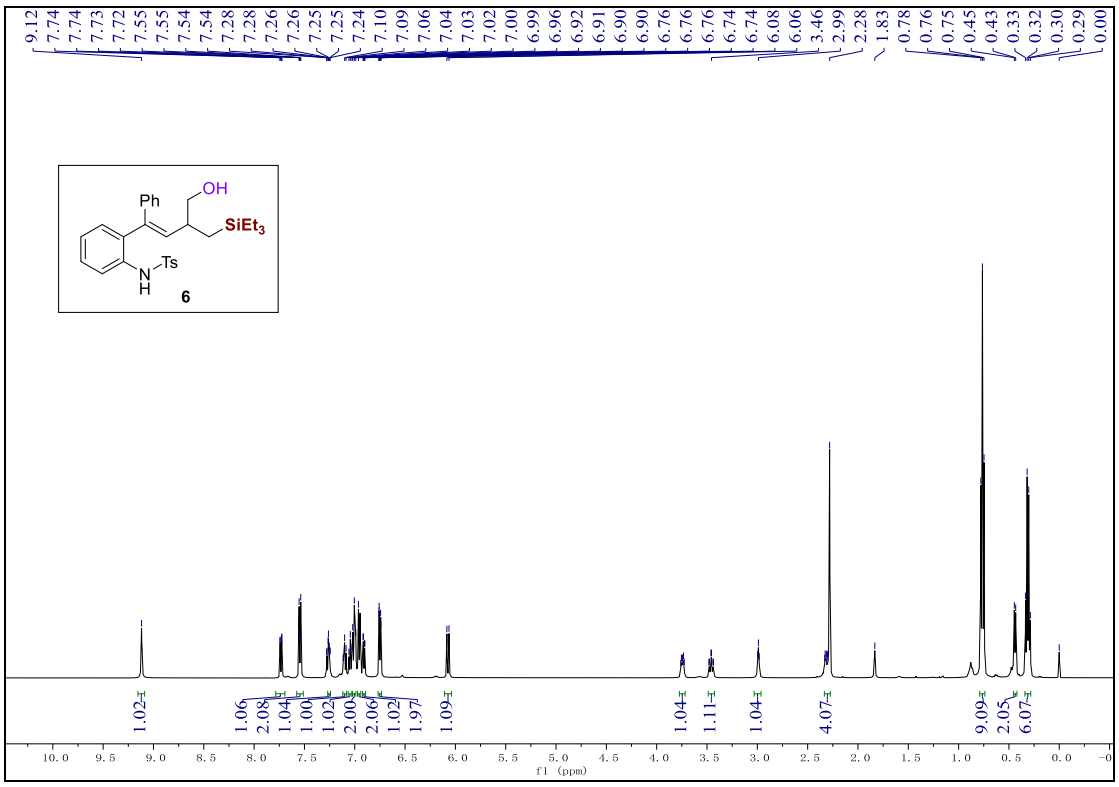
$^{1}$H NMR (500 MHz, $CDCl_3$)




$^{13}$C NMR (126 MHz, $CDCl_3$)



$^{1}$H NMR (500 MHz, Chloroform-*d*)




$^{13}$C NMR (126 MHz, Chloroform-*d*)