# Silver- versus gold- or platinum catalyzed [4+2] cyclizations: synthesis of 2,3,3a,4-tetrahydro-1H-benzo[f]isoindol-1-one derivatives

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# General information

**Techniques:**

All reactions were carried out in oven dried glassware under an air atmosphere. An oil bath was used as heating source unless otherwise noted. Analytical thin layer chromatographies (TLC) were performed using precoated Merck silica gel 60 matrix, with fluorescent indicator 254 nm on Aluminum foils (200 µm silica layer). Visualization of the developed chromatograms were performed by UV absorbance (254 nm) or TLC stains ($KMnO_4$, *p*-anisaldehyde or phosphomolybdic acid). Flash column chromatography was performed using silica gel (230-400 mesh) with the indicated solvent system, using gradients of increasing polarity when necessary.

**Chemicals:**

All the chemicals were commercially purchased from Sigma-Aldrich, Fluorochem, Alfa-Aesar, Strem, and Acros. Unless otherwise stated, commercial reagents and solvents were used without further purification. Some solvents were freshly distilled, tetrahydrofuran (THF), dichloromethane (DCM), dichloroethane (DCE), toluene and nitromethane (MeNO2). Reagents were either used as received from commercial sources or prepared according to the protocols provided by literature.

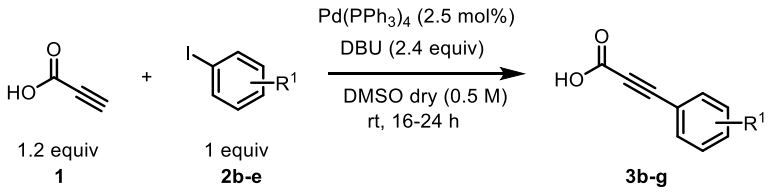
**Instrumentation:**

Nuclear magnetic resonance spectra were recorded on a Bruker Advance 400 (400 MHz), in deuterated chloroform (residual peaks $^{1}H$ δ 7.26 ppm, $^{13}C$ δ 77.16 ppm) unless otherwise noted. Chemical shifts (δ) are reported in ppm relative to TMS; coupling constants (J) are given in Hz. Multiplets are indicated by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, sept = septuplet and m = multiplet. $^{13}C$ and $^{19}F$ spectra were recorded in {1H}-decoupled manner and the values of the chemical shifts are rounded to one decimal point. $^{19}F$ NMR spectra were referenced to external $CFCl_3$.

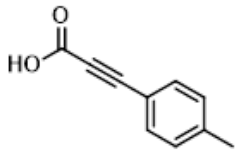
High-resolution mass spectra (HRMS) were obtained from the central analytic mass spectrometry department of Sorbonne University. High-resolution mass spectra were recorded on a micrOTOF (Bruker Daltonics) or a LTQ-XL/Orbitrap hybrid instrument (Thermo Fisher) using electrospray (ESI) or atmospheric pressure chemical ionization (APCI).

# General procedures

**General Procedure A: Synthesis of aryl propiolic acids 3.**



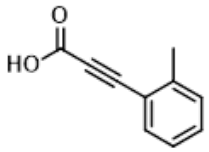

A dried round-bottom flask was charged with aryl iodide (10 mmol, 1 equiv.), 2,3,4,6,7,8,9,10-octahydropyrimidol[1,2-a]azepine DBU (24 mmol, 2.4 equiv.), tetrakis(triphenylphosphine)-palladium(0) $Pd(PPh_3)_4$ (2.5 mol%) and DMSO (10 mL) under $N_2$ atmosphere. The solution of propiolic acid (12 mmol, 1.2 equiv.) in DMSO (10 mL) was poured to the flask, and the mixture was stirred at room temperature for 16-24 h. Afterward, the reaction mixture was diluted with AcOEt (25.0 mL) and extracted with $NaHCO_3$ (sat. aq.). The aqueous layer was separated, acidified to pH=1 by adding cold HCl solution (1 M), and extracted with DCM. The combined organic layers were dried with anhydrous $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by silica gel column chromatography [ethyl acetate/hexane, with HOAc (1 %, v/v)].




Chemical Formula: $C_{10}H_8O_2$
Molecular Weight: 160.1720

**3-(p-tolyl)propiolic acid (3b)**

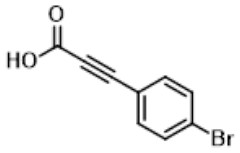
Prepared according to GP A using 10 mmol 1-iodo-4-methylbenzene.
(1.09 g, 6.8 mmol, 68%)
Spectral data were consistent with data reported in the literature[1].




Chemical Formula: $C_{10}H_8O_2$
Molecular Weight: 160.1720

**3-(o-tolyl)propiolic acid (3c)**

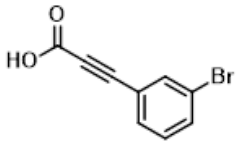
Prepared according to GP A using 10 mmol 1-iodo-2-methylbenzene.
(0.96 g, 6 mmol, 60%)
Spectral data were consistent with data reported in the literature[2].



Chemical Formula: $C_9H_5BrO_2$
Molecular Weight: 225.0410

**3-(4-bromophenyl)propiolic acid (3d)**

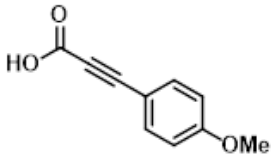
Prepared according to GP A using 10 mmol 1-bromo-4-iodobenzene.
(1.78 g, 7.9 mmol, 79%)
Spectral data were consistent with data reported in the literature[1].



Chemical Formula: $C_9H_5BrO_2$
Molecular Weight: 225.0410

**3-(3-bromophenyl)propiolic acid (3e)**

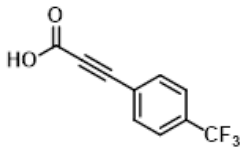
Prepared according to GP A using 10 mmol 1-bromo-3-iodobenzene.
(1.31 g, 5.8 mmol, 58%)
Spectral data were consistent with data reported in the literature[3].



Chemical Formula: $C_{10}H_8O_3$
Molecular Weight: 176.1710

**3-(4-methoxyphenyl)propiolic acid (3f)**

Prepared according to GP A using 10 mmol 1-iodo-4-methoxybenzene.
(1.37 g, 7.8 mmol, 78%)
Spectral data were consistent with data reported in the literature[1].



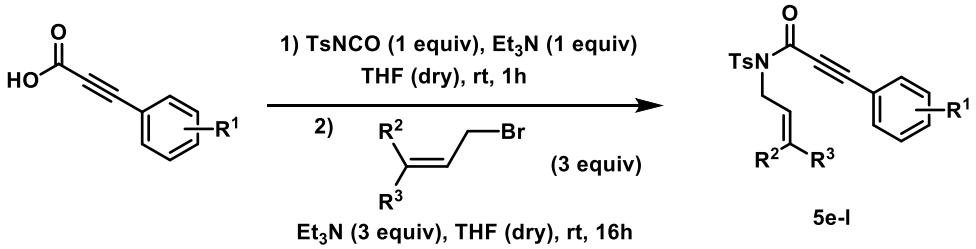
Chemical Formula: $C_{10}H_5F_3O_2$
Molecular Weight: 214.1432

**3-(4-(trifluoromethyl)phenyl)propiolic acid (3g)**

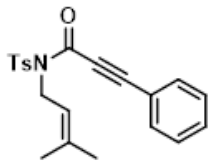
Prepared according to GP A using 10 mmol 1-iodo-4-(trifluoromethyl)benzene.
(1.82 g, 8.5 mmol, 85%)

Spectral data were consistent with data reported in the literature[1].

**General Procedure B: Preparation of substrates amide-1,6-enynes 5.**



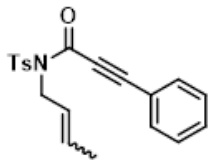

In 100 mL dried round-bottomed flask, the carboxylic acid (10 mmol, 1 equiv.) was dissolved in dry THF 20 mL under $N_2$ at room temperature, added tosyl isocyanate (1.59 mL, 10 mmol, 1 equiv.) and stirred for 10 minutes. Then $NEt_3$ (1.0 equiv.) was added drop wise to the open flask, released of the formed $CO_2$. After stirring 1 h, extra $NEt_3$ (3.0 equiv.) and 1-bromo-3-methylbut-2-ene (3.0 equiv.) were sequentially added and the mixture solution was stirred overnight. After complete consumption of the starting materials (monitored by TLC), the mixture was evaporated, the crude product was purified by silica-gel column chromatography (petroleum ether/ethyl acetate) to give the corresponding enyne product.



Chemical Formula: $C_{21}H_{21}NO_3S$
Molecular Weight: 367.4630

**N-(3-methylbut-2-en-1-yl)-3-phenyl-N-tosylpropiolamide (5a)**

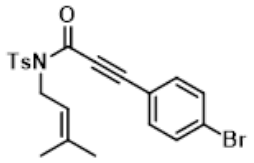
Prepared according to GP B using 5 mmol **3a** and 15 mmol 1-bromo-3-methyl-2-butene.
(1.07 g, 2.9 mmol, 58%)
Spectral data were consistent with data reported in the literature[4].



Chemical Formula: $C_{20}H_{19}NO_3S$
Molecular Weight: 353.4360

**N-(but-2-en-1-yl)-3-phenyl-N-tosylpropiolamide (5b)**

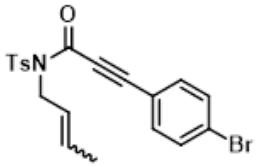
Prepared according to GP B using 5 mmol **3a** and 15 mmol crotylbromide.
(0.95 g, 2.7 mmol, 54%)
Spectral data were consistent with data reported in the literature[4].




Chemical Formula: $C_{21}H_{20}BrNO_3S$
Molecular Weight: 446.3590

**3-(4-bromophenyl)-N-(3-methylbut-2-en-1-yl)-N-tosylpropiolamide (5c)**

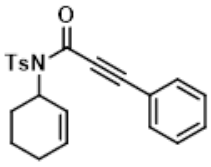
Prepared according to GP B using 5 mmol **3a** and 15 mmol crotylbromide.
(1.03 g, 2.3 mmol, 46%)
Spectral data were consistent with data reported in the literature[4].




Chemical Formula: $C_{20}H_{18}BrNO_3S$
Molecular Weight: 432.3320

**3-(4-bromophenyl)-N-(but-2-en-1-yl)-N-tosylpropiolamide (5d)**

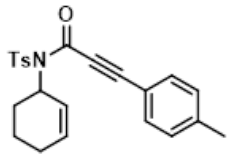
Prepared according to GP B using 5 mmol **3d** and 15 mmol crotylbromide.
(0.78 g, 1.8 mmol, 36%)
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.90 – 7.84 (m, 2H), 7.53 (dq, *J* = 8.9, 2.3 Hz, 2H), 7.38 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.91 – 5.79 (trans) (m, 1H), 5.73 (cis) (m, 0.30H), 5.65 – 5.54 (trans) (m, 1H), 5.55 – 5.47 (cis) (m, 0.28H), 4.72 (cis) (d, *J* = 6.5 Hz, 0.68H), 4.59 (trans) (d, *J* = 6.3 Hz, 2H), 2.43 (s, 4H), 1.80 (cis) (d, *J* = 6.9 Hz, 0.68H), 1.73 (trans) (dq, *J* = 6.5, 1.2 Hz, 3H), 1.53 (s, 1H).
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) 152.5, 145.2, 145.2, 136.2, 134.1, 132.3, 132.3, 131.4, 129.6, 129.6, 129.1, 128.8, 128.7, 125.9, 125.3, 125.0, 118.6, 92.0, 82.7, 49.1, 44.3, 21.8, 17.9, 13.3.




Chemical Formula: $C_{22}H_{21}NO_3S$
Molecular Weight: 379.4740

**N-(cyclohex-2-en-1-yl)-3-phenyl-N-tosylpropiolamide (5e)**

Prepared according to GP B using 5 mmol **3a** and 15 mmol 3-bromocyclohexene.
(0.76 g, 2 mmol, 40%)
**$^1$H NMR** (400 MHz, CDCl3): δ (ppm) 7.93 (dt, J = 8.3, 2.2 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.47 – 7.42 (m, 1H), 7.41 – 7.34 (m, 2H), 7.34 – 7.28 (m, 2H), 5.89 – 5.82 (m, 1H), 5.65 (d, J = 10.3 Hz, 1H), 5.39 – 5.25 (m, 1H), 2.52 – 2.44 (m, 1H), 2.43 (s, 3H), 2.18 – 1.88 (m, 4H), 1.83 – 1.73 (m, 1H).
**$^{13}$C NMR** (101 MHz, CDCl3): δ (ppm) 152.8, 145.0, 136.8, 132.6, 130.9, 129.6, 129.5, 128.8, 128.7, 128.0, 119.9, 93.2, 82.4, 57.5, 29.0, 24.2, 22.9, 21.8.
**HRMS** (ESI): Calculated for $C_{22}H_{21}NO_3SNa$ $[M+Na]^+$ : 402.1134, found 402.1133



Chemical Formula: $C_{23}H_{23}NO_3S$
Molecular Weight: 393.5010

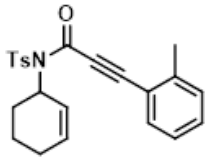
**N-(cyclohex-2-en-1-yl)-3-(p-tolyl)-N-tosylpropiolamide (5f)**

Prepared according to GP B using 5 mmol **3b** and 15 mmol 3-bromocyclohexene.
(0.59 g, 1.5 mmol, 30%)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.92 (dt, *J* = 8.5, 2.2 Hz, 2H), 7.38 (dt, *J* = 8.1, 1.9 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.20 – 7.14 (m, 2H), 5.89 – 5.82 (m, 1H), 5.65 (d, *J* = 10.3 Hz, 1H), 5.38 – 5.29 (m, 1H), 2.50 – 2.44 (m, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 2.16 – 2.04 (m, 3H), 2.04 – 1.92 (m, 1H), 1.83 – 1.70 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) 152.9, 144.9, 141.7, 136.9, 132.6, 129.6, 129.6, 129.4, 128.7, 128.1, 116.8, 93.8, 82.2, 57.5, 29.0, 24.3, 22.9, 21.9, 21.8.

**HRMS** (ESI): Calculated for $C_{23}H_{23}NO_3SNa$ $[M+Na]^+$ : 416.1291, found 416.1289



Chemical Formula: $C_{23}H_{23}NO_3S$
Molecular Weight: 393.5010

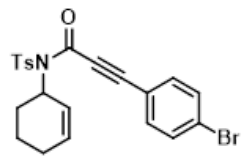
**N-(cyclohex-2-en-1-yl)-3-(o-tolyl)-N-tosylpropiolamide (5g)**

Prepared according to GP B using 5 mmol **3c** and 15 mmol 3-bromocyclohexene.
(0.65 g, 1.65 mmol, 33%)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.93 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.43 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.40 – 7.28 (m, 3H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 5.89 – 5.80 (m, 1H), 5.66 (d, *J* = 10.2 Hz, 1H), 5.40 – 5.29 (m, 1H), 2.54 – 2.45 (m, 1H), 2.44 (s, 6H), 2.19 – 2.08 (m, 2H), 2.08 – 1.92 (m, 2H), 1.80 – 1.67 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) 153.0, 144.9, 142.4, 136.9, 133.0, 130.9, 130.0, 129.6, 129.5, 128.7, 127.8, 126.0, 119.7, 92.8, 85.9, 58.0, 28.9, 24.2, 22.9, 21.8, 20.7.

**HRMS** (ESI): Calculated for $C_{23}H_{23}NO_3SNa$ $[M+Na]^+$ : 416.1291, found 416.1289



Chemical Formula: $C_{22}H_{20}BrNO_3S$
Molecular Weight: 458.3700

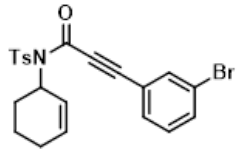
**3-(4-bromophenyl)-N-(cyclohex-2-en-1-yl)-N-tosylpropiolamide (5h)**

Prepared according to GP B using 5 mmol **3d** and 15 mmol 3-bromocyclohexene.
(0.85 g, 1.85 mmol, 37%)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.90 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.32 (dd, *J* = 11.8, 8.1 Hz, 4H), 5.84 (dq, *J* = 10.7, 3.4 Hz, 1H), 5.61 (d, *J* = 10.2 Hz, 1H), 5.29 (ddt, *J* = 12.5, 6.2, 3.1 Hz, 1H), 2.42 (s, 3H), 2.41 – 2.33 (m, 1H), 2.14 – 2.02 (m, 3H), 1.94 (t, *J* = 8.6 Hz, 1H), 1.82 – 1.67 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) 152.4, 145.0, 136.6, 133.8, 132.1, 129.5, 129.5, 128.5, 127.8, 125.7, 118.7, 91.8, 83.2, 57.3, 28.8, 24.1, 22.7, 21.7.

**HRMS** (ESI): Calculated for $C_{22}H_{20}BrNO_3SNa$ $[M+Na]^+$ : 480.0239, found 480.0237




Chemical Formula: $C_{22}H_{20}BrNO_3S$
Molecular Weight: 458.3700

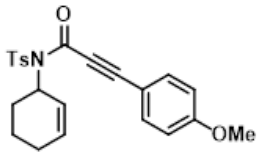
**3-(3-bromophenyl)-N-(cyclohex-2-en-1-yl)-N-tosylpropiolamide (5i)**

Prepared according to GP B using 5 mmol **3e** and 15 mmol 3-bromocyclohexene.
(0.85 g, 1.85 mmol, 37%)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (dt, *J* = 8.5, 2.2 Hz, 2H), 7.60 – 7.56 (m, 2H), 7.42 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 5.89 – 5.82 (m, 1H), 5.62 (dt, *J* = 10.4, 2.3 Hz, 1H), 5.34 – 5.25 (m, 1H), 2.44 (s, 3H), 2.42 – 2.34 (m, 1H), 2.16 – 2.05 (m, 3H), 2.00 – 1.92 (m, 1H), 1.82 – 1.73 (m, 1H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) 152.4, 145.1, 136.7, 135.1, 134.1, 131.1, 130.3, 129.7, 128.6, 127.8, 122.5, 121.9, 91.1, 83.2, 57.5, 28.9, 24.2, 22.8, 21.8.

**HRMS** (ESI): Calculated for $C_{22}H_{20}BrNO_3SNa$ $[M+Na]^+$ : 480.0239, found 480.0236




Chemical Formula: $C_{23}H_{23}NO_4S$
Molecular Weight: 409.5000

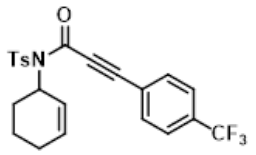
**N-(cyclohex-2-en-1-yl)-3-(4-methoxyphenyl)-N-tosylpropiolamide (5j)**

Prepared according to GP B using 5 mmol **3f** and 15 mmol 3-bromocyclohexene.
(1.62 g, 3.95 mmol, 79%)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.92 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.33 – 7.28 (m, 2H), 6.88 (dt, *J* = 9.0, 2.7 Hz, 2H), 5.89 – 5.81 (m, 1H), 5.66 (ddt, *J* = 10.1, 3.3, 1.6 Hz, 1H), 5.37 – 5.29 (m, 1H), 3.83 (s, 3H), 2.50 – 2.44 (m, 1H), 2.42 (s, 3H), 2.16 – 2.05 (m, 3H), 1.97 (ddt, *J* = 13.7, 3.7, 1.8 Hz, 1H), 1.78 (dddt, *J* = 13.6, 11.2, 5.4, 2.9 Hz, 1H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) 161.8, 153.0, 144.9, 136.9, 134.6, 129.5, 129.3, 128.7, 128.2, 114.5, 111.7, 94.2, 82.0, 57.4, 55.6, 28.9, 24.3, 22.9, 21.8.

**HRMS** (ESI): Calculated for $C_{23}H_{23}NO_4SNa$ $[M+Na]^+$ : 432.1240, found 432.1238



Chemical Formula: $C_{23}H_{20}F_3NO_3S$
Molecular Weight: 447.4722

**N-(cyclohex-2-en-1-yl)-N-tosyl-3-(4-(trifluoromethyl)phenyl)propiolamide (5k)**

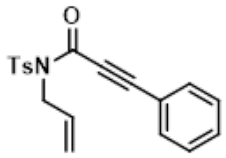
Prepared according to GP B using 5 mmol **3g** and 15 mmol 3-bromocyclohexene.
(0.65 g, 1.45 mmol, 29%)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (dt, *J* = 8.4, 2.3 Hz, 2H), 7.62 (q, *J* = 8.3 Hz, 4H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.89 – 5.81 (m, 1H), 5.61 (d, *J* = 10.3 Hz, 1H), 5.33 – 5.25 (m, 1H), 2.44 (s, 3H), 2.43 – 2.34 (m, 1H), 2.16 – 2.05 (m, 3H), 1.99 – 1.93 (m, 1H), 1.80 – 1.72 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) 152.2, 145.2, 136.6, 132.7, 132.4 (q, *J* = 32.9 Hz), 129.7, 129.6, 128.6, 127.7, 125.7 (q, *J* = 3.6 Hz), 123.7 (q, *J* = 1.5 Hz), 123.6 (q, *J* = 272.8 Hz), 90.8, 83.9, 57.4, 28.8, 24.2, 22.7, 21.7.

**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ (ppm) -63.2 (s).

**HRMS** (ESI): Calculated for $C_{23}H_{20}F_3NO_3SNa$ $[M+Na]^+$ : 470.1008, found 470.1005



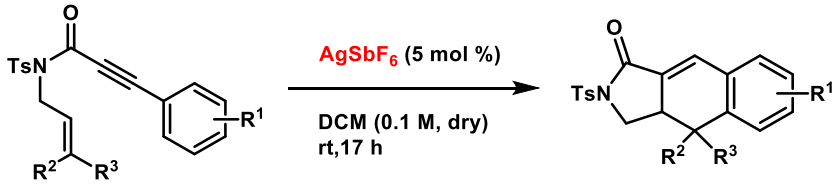
Chemical Formula: $C_{19}H_{17}NO_3S$
Molecular Weight: 329.4090

**N-allyl-3-phenyl-N-tosylpropiolamide (5l)**

Prepared according to GP B using 5 mmol **3a** and 15 mmol allylbromide.
(0.84 g, 2.6 mmol, 51%)

Spectral data were consistent with data reported in the literature[4].

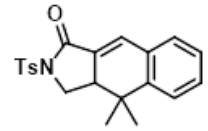
## General Procedure C: Silver-catalyzed intramolecular cycloaddition reactions of 1,6-enynes




5a-i 6a-i

In a dried screw-capped vial, the substrate (0.5 mol, 1 equiv.) was diluted with dry DCM (4 mL) and then the solution of $AgSbF_6$ previously prepared (5 mol %) in dry DCM (1 mL) was added. The mixture was stirred at room temperature. After 17 hours (reaction followed by TLC), the mixture was filtered through a short pad of silica gel with DCM and evaporated under reduced pressure. In the cases of tetracyclic compounds, the crude product was purified by

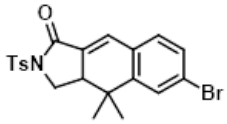
silica-gel column chromatography (mobile phase changed according to compound) to afford the corresponding product.




Chemical Formula: $C_{21}H_{21}NO_3S$
Molecular Weight: 367.4630

**4,4-dimethyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindol-1-one (6a)**

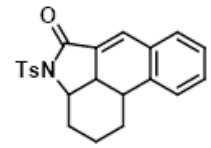
Prepared according to GP C using 0.5 mmol **5a**.
(163.52 mg, 0.45 mmol, 89%)
Spectral data were consistent with data reported in the literature[4].




Chemical Formula: $C_{21}H_{20}BrNO_3S$
Molecular Weight: 446.3590

**6-bromo-4,4-dimethyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindol-1-one (6c)**

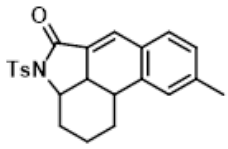
Prepared according to GP C using 0.5 mmol **5c**.
(209.79 mg, 0.47 mmol, 94%)
Spectral data were consistent with data reported in the literature[4].




Chemical Formula: $C_{22}H_{21}NO_3S$
Molecular Weight: 379.4740

**4-tosyl-2,3,3a,3a1,4,10b-hexahydronaphtho[3,2,1-cd]indol-5(1H)-one (6e)**

Prepared according to GP C using 0.5 mmol **5e**.
(164.89 mg, 0.43 mmol, 87%)
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.04 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.36 – 7.28 (m, 4H), 7.25 – 7.20 (m, 2H), 7.16 (d, *J* = 7.4 Hz, 1H), 4.64 (dt, *J* = 10.6, 6.9 Hz, 1H), 3.28 (td, *J* = 8.0, 3.4 Hz, 1H), 3.07 (ddd, *J* = 13.2, 8.3, 5.3 Hz, 1H), 2.56 – 2.46 (m, 1H), 2.43 (s, 3H), 1.78 – 1.69 (m, 1H), 1.62 – 1.57 (m, 1H), 1.35 (qt, *J* = 13.5, 2.6 Hz, 1H), 1.18 – 1.03 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) 165.3, 145.1, 139.7, 136.6, 131.8, 130.8, 130.6, 129.8, 129.7, 129.7, 128.7, 128.6, 127.6, 58.7, 38.8, 36.1, 32.0, 30.8, 22.9, 21.8.
**HRMS** (ESI): Calculated for $C_{22}H_{21}NO_3SNa$ $[M+Na]^+$ : 402.1134, found 402.1133




Chemical Formula: $C_{23}H_{23}NO_3S$
Molecular Weight: 393.5010

**9-methyl-4-tosyl-2,3,3a,3a1,4,10b-hexahydronaphtho[3,2,1-cd]indol-5(1H)-one (6f)**

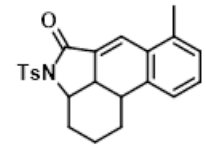
Prepared according to GP C using 0.5 mmol **5f**.

(121.99 g, 0.31 mmol, 62%)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.03 (d, *J* = 8.4 Hz, 2H), 7.31 (dd, *J* = 13.0, 5.9 Hz, 3H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.98 (s, 1H), 4.67 – 4.59 (m, 1H), 3.24 (t, *J* = 8.6 Hz, 1H), 3.06 – 2.97 (m, 1H), 2.50 (s, 1H), 2.43 (s, 3H), 2.34 (s, 3H), 1.73 (d, *J* = 13.4 Hz, 1H), 1.58 (s, 1H), 1.35 (q, *J* = 13.3 Hz, 1H), 1.16 – 1.03 (m, 2H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) 165.5, 145.0, 141.0, 139.8, 136.6, 131.8, 129.7, 129.6, 129.5, 128.7, 128.5, 128.2, 128.2, 58.8, 38.9, 36.1, 32.0, 30.9, 23.0, 21.8, 21.7.

**HRMS** (ESI): Calculated for $C_{23}H_{23}NO_3SNa$ $[M+Na]^+$ : 416.1291, found 416.1290




Chemical Formula: $C_{23}H_{23}NO_3S$
Molecular Weight: 393.5010

**7-methyl-4-tosyl-2,3,3a,3a1,4,10b-hexahydronaphtho[3,2,1-cd]indol-5(1H)-one (6g)**

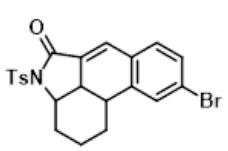
Prepared according to GP C using 0.5 mmol **5g**.

(131.82 g, 0.34 mmol, 67%)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.04 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.60 (d, *J* = 3.4 Hz, 1H), 7.33 (dd, *J* = 8.3, 2.0 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 4.64 (dt, *J* = 10.4, 6.9 Hz, 1H), 3.25 (td, *J* = 8.1, 3.5 Hz, 1H), 3.05 (ddd, *J* = 13.3, 8.4, 5.3 Hz, 1H), 2.56 – 2.47 (m, 1H), 2.43 (s, 3H), 2.37 (s, 3H), 1.72 (dt, *J* = 13.7, 3.5 Hz, 1H), 1.60 – 1.50 (m, 1H), 1.40 – 1.24 (m, 1H), 1.17 – 1.04 (m, 2H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) 165.6, 145.0, 139.9, 137.1, 136.6, 130.2, 129.6, 129.5, 129.4, 129.1, 128.7, 128.6, 126.5, 58.7, 39.2, 35.6, 32.1, 30.7, 22.9, 21.8, 19.3.

**HRMS** (ESI): Calculated for $C_{23}H_{23}NO_3SNa$ $[M+Na]^+$ : 416.1291, found 416.1289



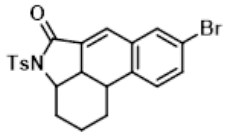

Chemical Formula: $C_{22}H_{20}BrNO_3S$
Molecular Weight: 458.3700

**9-bromo-4-tosyl-2,3,3a,3a1,4,10b-hexahydronaphtho[3,2,1-cd]indol-5(1H)-one (6h)**

Prepared according to GP C using 0.5 mmol **5h**.

(87.09 g, 0.19 mmol, 38%)

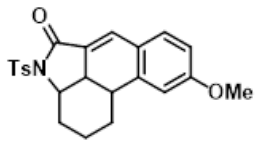
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.08 – 7.98 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 (dd, *J* = 2.4, 1.3 Hz, 2H), 7.25 (s, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 4.63 (dt, *J* = 10.6, 6.9 Hz, 1H), 3.24 (td, *J* = 8.0, 3.3 Hz, 1H), 3.05 (ddd, *J* = 13.3, 8.3, 5.3 Hz, 1H), 2.57 – 2.48 (m, 1H), 2.43 (s, 3H), 1.75 (dp, *J* = 13.2, 3.1 Hz, 1H), 1.62 – 1.55 (m, 1H), 1.41 – 1.28 (m, 1H), 1.10 (m, 2H).
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) 165.0, 145.2, 141.5, 136.4, 131.7, 130.9, 130.7, 130.6, 130.3, 129.7, 129.7, 128.7, 124.3, 58.5, 38.6, 35.9, 32.0, 30.7, 22.8, 21.8.
**HRMS** (ESI): Calculated for $C_{22}H_{20}BrNO_3SNa$ $[M+Na]^+$ : 480.0239, found 480.0237



Chemical Formula: $C_{22}H_{20}BrNO_3S$
Molecular Weight: 458.3700

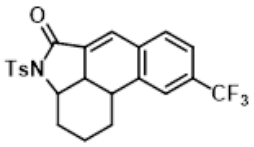
**8-bromo-4-tosyl-2,3,3a,3a1,4,10b-hexahydronaphtho[3,2,1-cd]indol-5(1H)-one (6i)**
Prepared according to GP C using 0.5 mmol **5i**.
(174.18 g, 0.38 mmol, 76%). In this case, rotamers were observed in NMR analysis.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.05 – 8.01 (m, 2H), 7.43 – 7.36 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.23 (dd, *J* = 6.5, 3.5 Hz, 1H), 7.12 – 7.02 (m, 1H), 4.70 – 4.59 (m, 1H), 3.50 (ddd, *J* = 12.8, 8.4, 5.1 Hz, 1H), 3.31 – 3.21 (m, 1H), 3.05 (ddd, *J* = 13.6, 8.4, 5.4 Hz, 1H), 2.53 (s, 1H), 2.43 (s, 3H), 1.88 – 1.68 (m, 2H), 1.42 – 1.30 (m, 1H), 1.17 – 1.02 (m, 2H), 0.94 (qd, *J* = 13.0, 2.8 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) 164.9, 145.2, 138.4, 136.3, 134.8, 133.2, 132.7, 132.2, 131.3, 130.9, 130.2, 130.1, 129.7, 129.1, 128.7, 128.7, 121.0, 58.6, 38.3, 38.0, 36.1, 36.0, 32.2, 32.0, 30.7, 26.5, 22.8, 22.7, 21.8.
**HRMS** (ESI): Calculated for $C_{22}H_{20}BrNO_3SNa$ $[M+Na]^+$ : 480.0239, found 480.0237



Chemical Formula: $C_{23}H_{23}NO_4S$
Molecular Weight: 409.5000

**9-methoxy-4-tosyl-2,3,3a,3a1,4,10b-hexahydronaphtho[3,2,1-cd]indol-5(1H)-one (6j)**
Prepared according to GP C using 0.5 mmol **5j**.
(102.38 g, 0.25 mmol, 50%)
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.06 – 8.00 (m, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 3.3 Hz, 1H), 7.17 (d, J = 8.3 Hz, 1H), 6.76 – 6.70 (m, 2H), 4.62 (dt, J = 10.5, 6.7 Hz, 1H), 3.81 (s, 3H), 3.24 (td, J = 7.9, 3.5 Hz, 1H), 3.02 (ddd, J = 13.2, 8.3, 5.3 Hz, 1H), 2.52 – 2.44 (m, 1H), 2.42 (s, 3H), 1.72 (dq, J = 13.6, 3.4 Hz, 1H), 1.64 – 1.52 (m, 1H), 1.39 – 1.27 (m, 1H), 1.16 – 1.03 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) 165.5, 161.5, 144.9, 141.9, 136.7, 131.6, 131.2, 129.6, 128.6, 126.8, 123.9, 115.0, 112.1, 58.7, 55.5, 39.3, 35.8, 31.8, 30.8, 22.9, 21.8.
**HRMS** (ESI): Calculated for $C_{23}H_{23}NO_4SNa$ $[M+Na]^+$ : 432.1240, found 432.1237



Chemical Formula: $C_{23}H_{20}F_3NO_3S$
Molecular Weight: 447.4722

**4-tosyl-9-(trifluoromethyl)-2,3,3a,3a1,4,10b-hexahydronaphtho[3,2,1-cd]indol-5(1H)-one (6k)**

Prepared according to GP C using 0.5 mmol **5k**.

(76.07 g, 0.17 mmol, 34%)

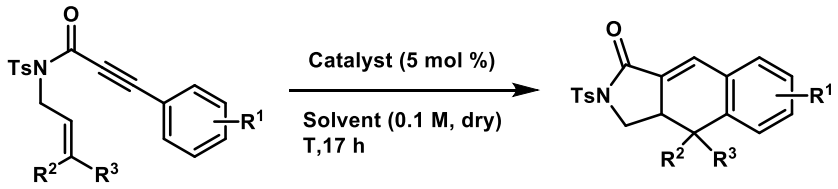
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.06 – 8.01 (m, 2H), 7.48 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.36 – 7.30 (m, 4H), 4.66 (dt, *J* = 10.6, 6.6 Hz, 1H), 3.31 (td, *J* = 8.0, 3.5 Hz, 1H), 3.16 (ddd, *J* = 13.6, 8.4, 5.4 Hz, 1H), 2.59 – 2.51 (m, 1H), 2.43 (s, 3H), 1.76 (dp, *J* = 13.7, 3.5 Hz, 1H), 1.65 – 1.57 (m, 1H), 1.37 (qt, *J* = 13.6, 2.6 Hz, 1H), 1.18 – 1.04 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) 164.7, 145.3, 140.2, 136.3, 134.0, 132.6, 131.9 (q, *J* = 32.5 Hz), 130.0, 129.7 (d, *J* = 1.8 Hz), 128.7, 125.3 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 3.8 Hz), 123.9 (d, *J* = 272.1 Hz), 58.5, 38.6, 36.0, 32.1, 30.6, 22.7, 21.8.

**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ (ppm) -62.8 (s).

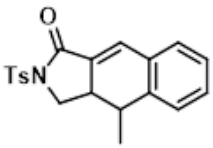
**HRMS** (ESI): Calculated for $C_{23}H_{20}F_3NO_3SNa$ $[M+Na]^+$ : 470.1008, found 470.1004

## General Procedure D: Transition metal catalyzed intramolecular cycloaddition reactions of 1,6-enynes




**5b, d, l, k** **6b, d, l, k**

In a dried screw-capped vial, the substrate (0.5 mol, 1 equiv.) and catalysts (5 mol%) was diluted with dry solvent (5 mL). The mixture was stirred at different temperature. After 17 hours (reaction followed by TLC), the mixture was evaporated under reduced pressure and the crude product was purified by silica-gel column chromatography (mobile phase changed according to compound) to afford the corresponding product.



Chemical Formula: $C_{20}H_{19}NO_3S$
Molecular Weight: 353.4360

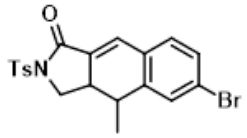
**4-methyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindol-1-one (6b)**

Prepared according to GP D using 0.5 mmol **5b** and 5 mol% of $IPrAuNTf_2$ in DCE at 80 ℃.
(132.54 g, 0.375 mmol, 75%)

**$^1$H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.99 (dt, *J* = 8.4, 2.3 Hz, 2H), 7.38 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 7.17 (q, *J* = 7.0 Hz, 1H), 7.08 – 7.04 (m, 2H), 6.36 (t, *J* = 2.7 Hz, 1H), 4.31 (dt, *J* = 2.3, 0.9 Hz, 2H), 2.44 (s, 3H), 1.58 (d, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$): δ(ppm) 167.5, 145.2, 138.7, 138.0, 136.7, 135.5, 133.4, 130.0, 129.9, 129.4, 128.7, 128.4, 127.5, 49.2, 21.8, 15.4.

**HRMS** (ESI): Calculated for $C_{20}H_{19}NO_3SNa$ $[M+Na]^+$ : 376.0978, found 376.0977




Chemical Formula: $C_{20}H_{18}BrNO_3S$
Molecular Weight: 432.3320

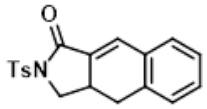
**6-bromo-4-methyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindol-1-one (6d)**

Prepared according to GP C using 0.5 mmol **5d** and 5 mol% of $PPh_3AuNTf_2$ in DCE at 80 ℃.
(136.19 g, 0.32 mmol, 63%)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.98 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.50 (dt, *J* = 8.8, 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.17 (q, *J* = 7.1 Hz, 1H), 6.95 (dt, *J* = 8.5, 2.4 Hz, 2H), 6.36 (t, *J* = 2.6 Hz, 1H), 4.34 – 4.30 (m, 2H), 2.44 (s, 3H), 1.58 (d, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ(ppm) 167.3, 145.3, 138.7, 136.8, 136.4, 135.5, 132.3, 132.0, 131.2, 130.7, 129.9, 128.4, 121.6, 49.2, 21.8, 15.4.

**HRMS** (ESI): Calculated for $C_{20}H_{18}BrNO_3SNa$ $[M+Na]^+$ : 454.0083, found 454.0081




Chemical Formula: $C_{19}H_{17}NO_3S$
Molecular Weight: 339.4090

**2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindol-1-one (6l)**

Prepared according to GP C using 0.5 mmol **5l** and 5 mol% of $PtCl_2$ in toluene at 100 ℃.
(44.12 g, 0.13 mmol, 26%)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.03 – 7.97 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.24 – 7.20 (m, 2H), 6.86 (t, *J* = 2.5 Hz, 1H), 6.36 (s, 1H), 5.48 (s, 1H), 4.41 (d, *J* = 2.6 Hz, 2H), 2.44 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) 167.2, 145.4, 141.3, 140.3, 139.4, 135.9, 135.4, 129.9, 128.6, 128.3, 128.1, 128.1, 120.0, 49.4, 21.8.

**HRMS** (ESI): Calculated for $C_{19}H_{17}NO_3SNa$ $[M+Na]^+$ : 362.0371, found 362.0369

# Reference

[1] Pradhan, R., Gutman, K. L., Mas Ud, A., Hulley, E. B., Waynant, K. V. *Organometallics,* **2023**, *42*, 362-371.

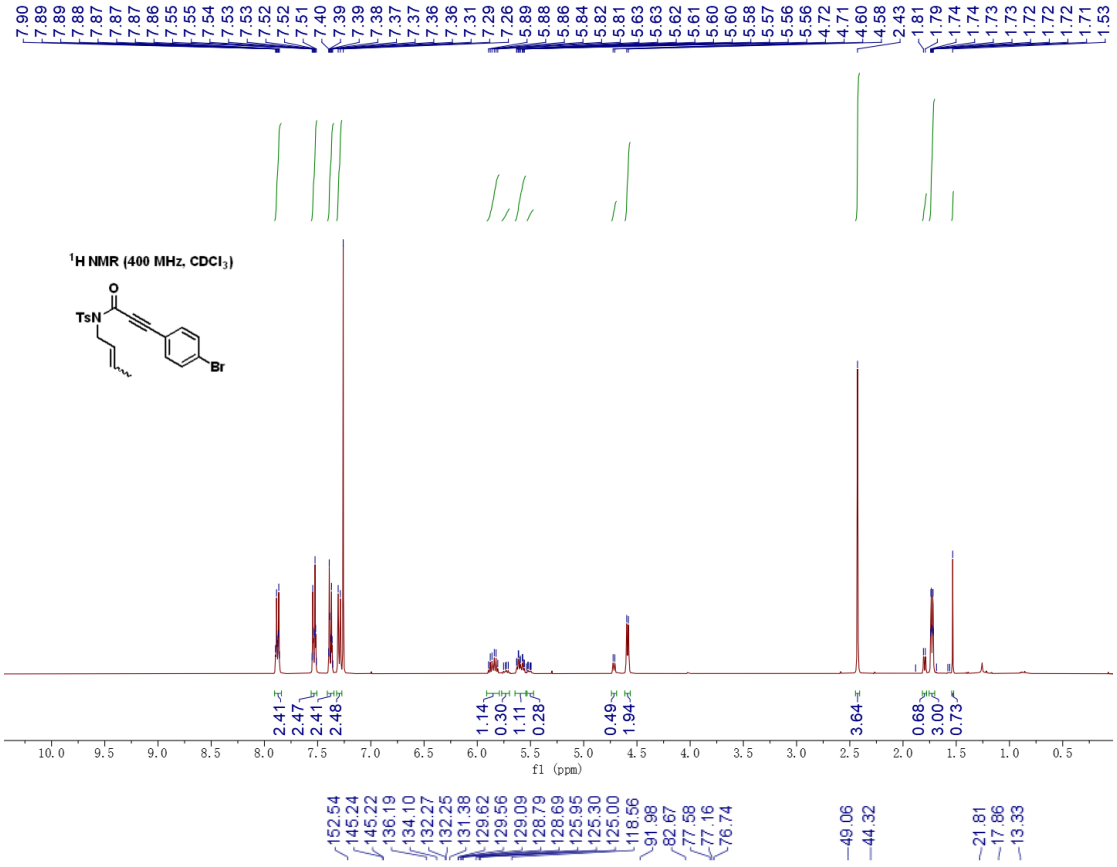
[2] Nelli, M. R., Cantrell, R. L., Looper, R. E. *J. Org. Chem*., **2023**, *88*, 15975-15982.

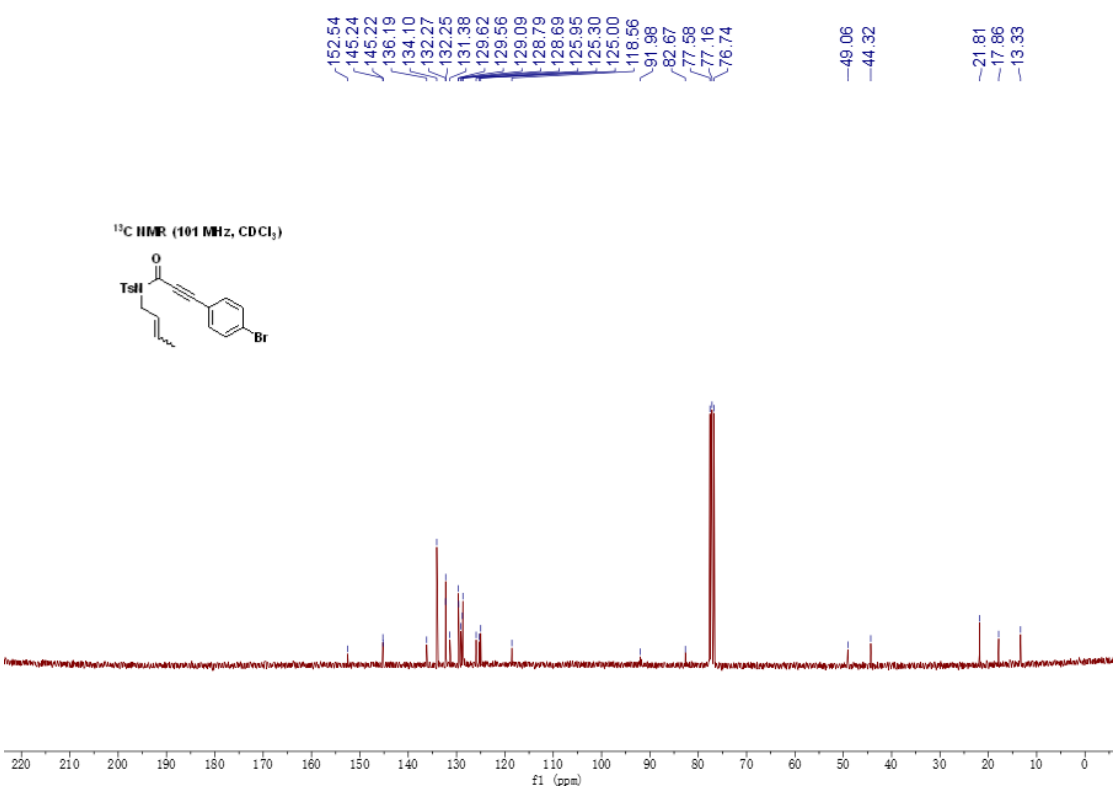
[3] Cheng, H., Zhao, B., Yao, Y., Lu, C. *Green Chem*, **2015**, *17*, 1675-1682.

[4] Chen, X., Fontaine-Vive, F., Poulain-Martini, S., Michelet, V. *Catal Commun*, **2020**, *147*, 106117.

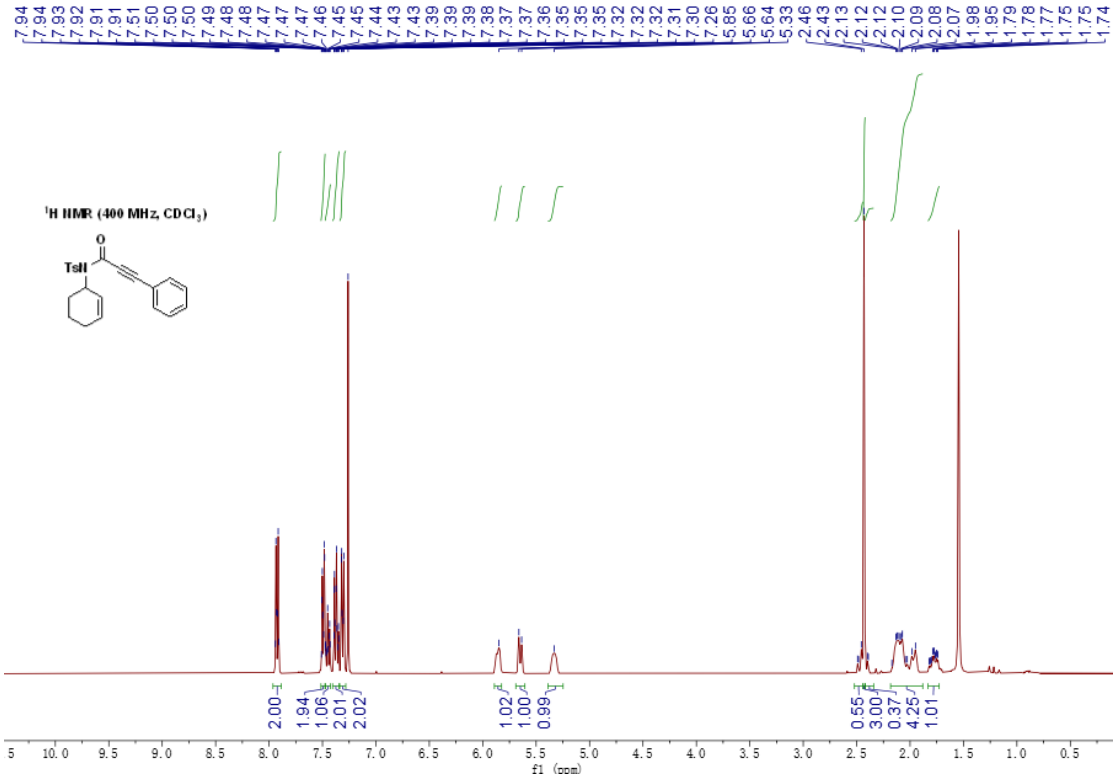
# NMR Spectra

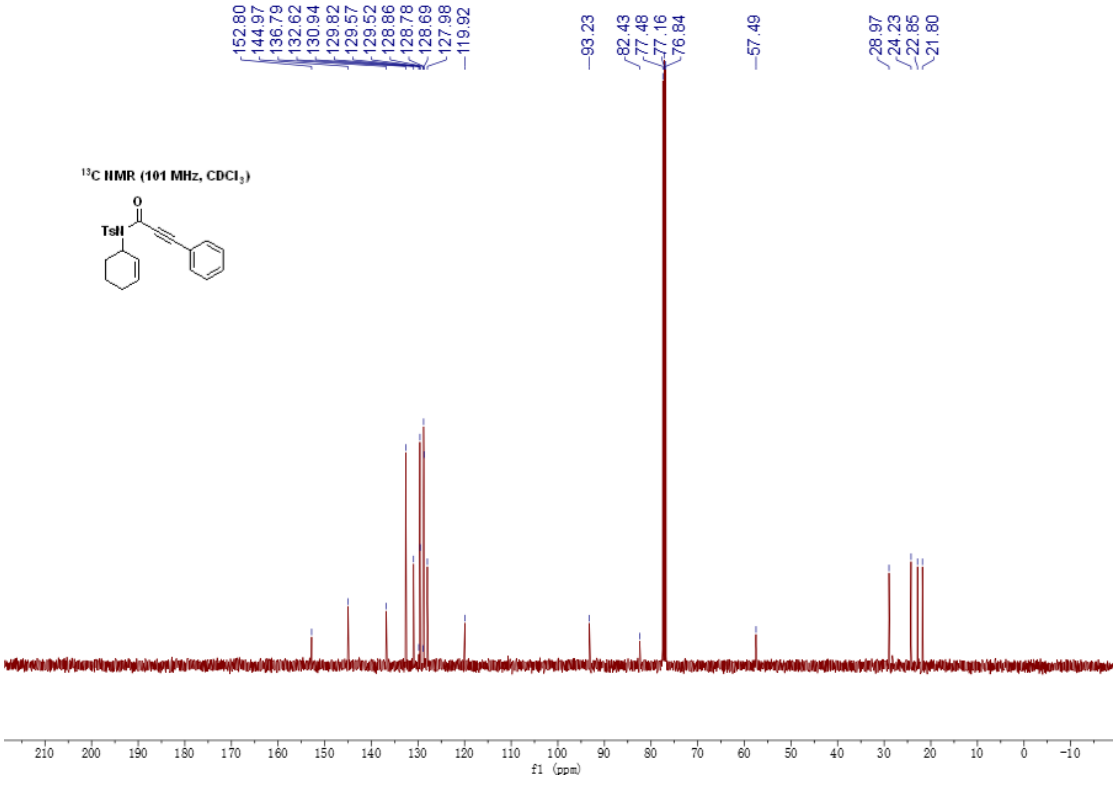
**5d**



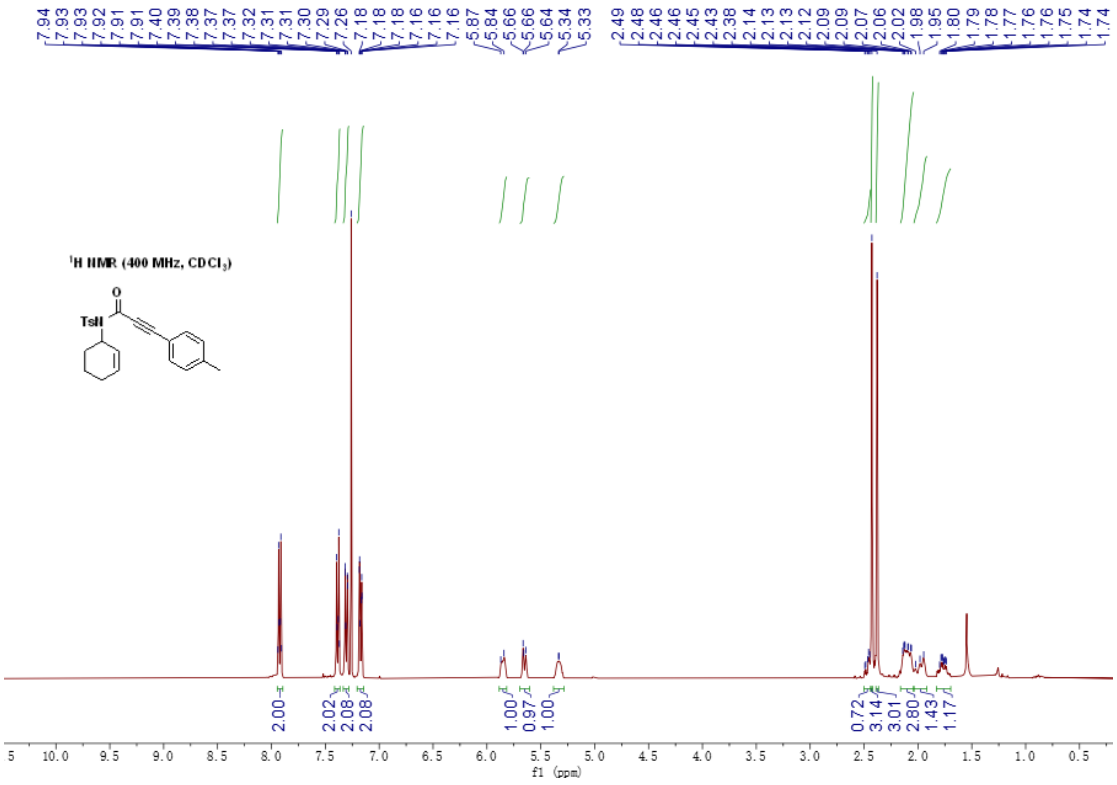



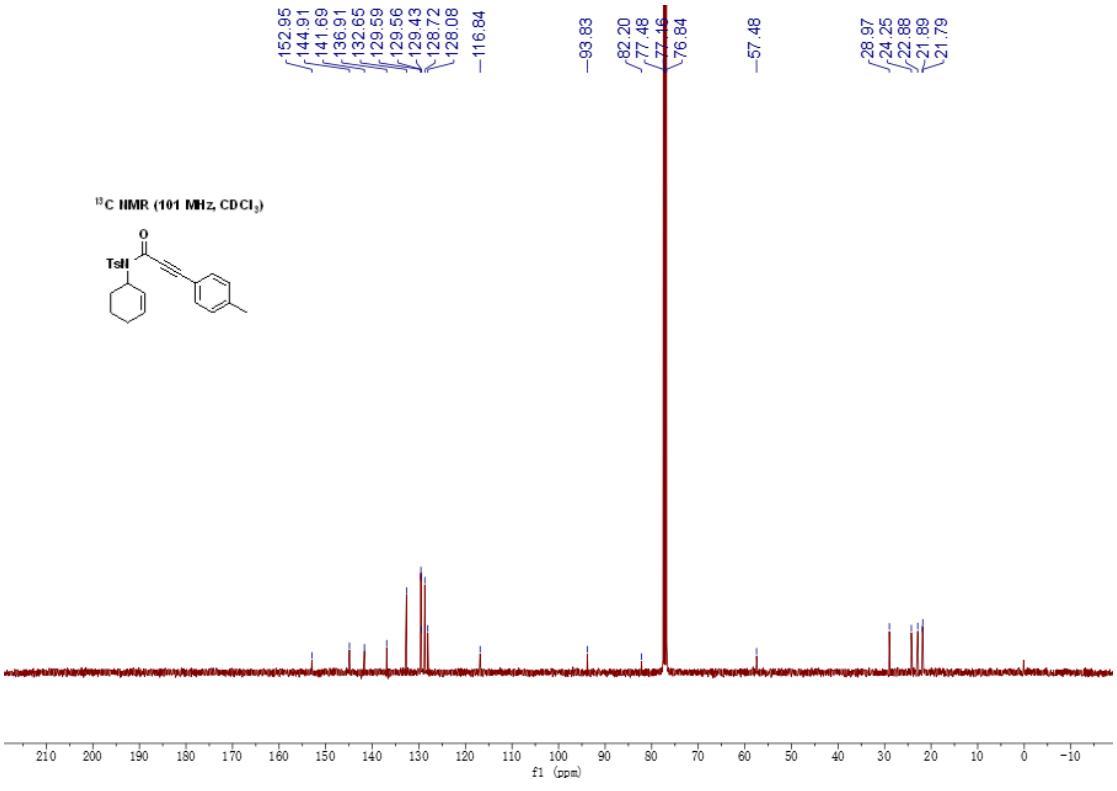
**5e**


7.94 7.94 7.93 7.92 7.91 7.91 7.51 7.50 7.50 7.50 7.49 7.48 7.48 7.47 7.47 7.47 7.46 7.45 7.45 7.44 7.43 7.43 7.39 7.39 7.39 7.38 7.37 7.37 7.36 7.35 7.35 7.35 7.32 7.32 7.32 7.31 7.30 7.26 5.85 5.66 5.64 5.33 2.46 2.43 2.13 2.12 2.12 2.10 2.09 2.08 2.07 1.98 1.95 1.79 1.78 1.77 1.75 1.75 1.74
$^1$H NMR (400 MHz, CDCl$_3$)
TsN
2.00 1.94 1.06 2.01 2.02 1.02 1.00 0.99 0.55 3.00 0.37 4.25 1.01
f1 (ppm)

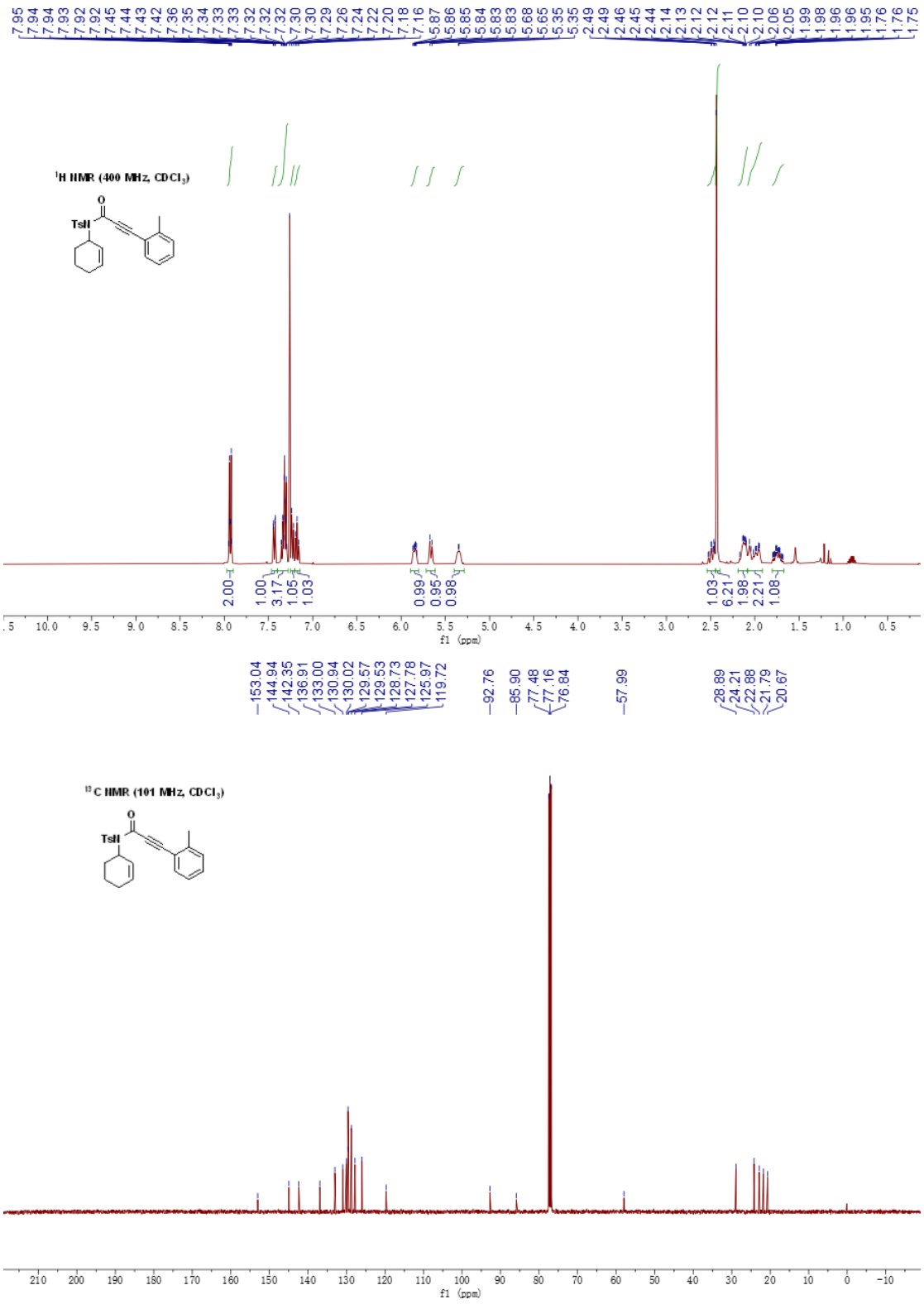

152.80 144.97 136.79 132.62 130.94 129.82 129.57 129.52 128.86 128.78 128.69 127.98 119.92 93.23 82.43 77.48 77.16 76.84 57.49 28.97 24.23 22.85 21.80
$^{13}$C NMR (101 MHz, CDCl$_3$)
TsN
f1 (ppm)

**5f**

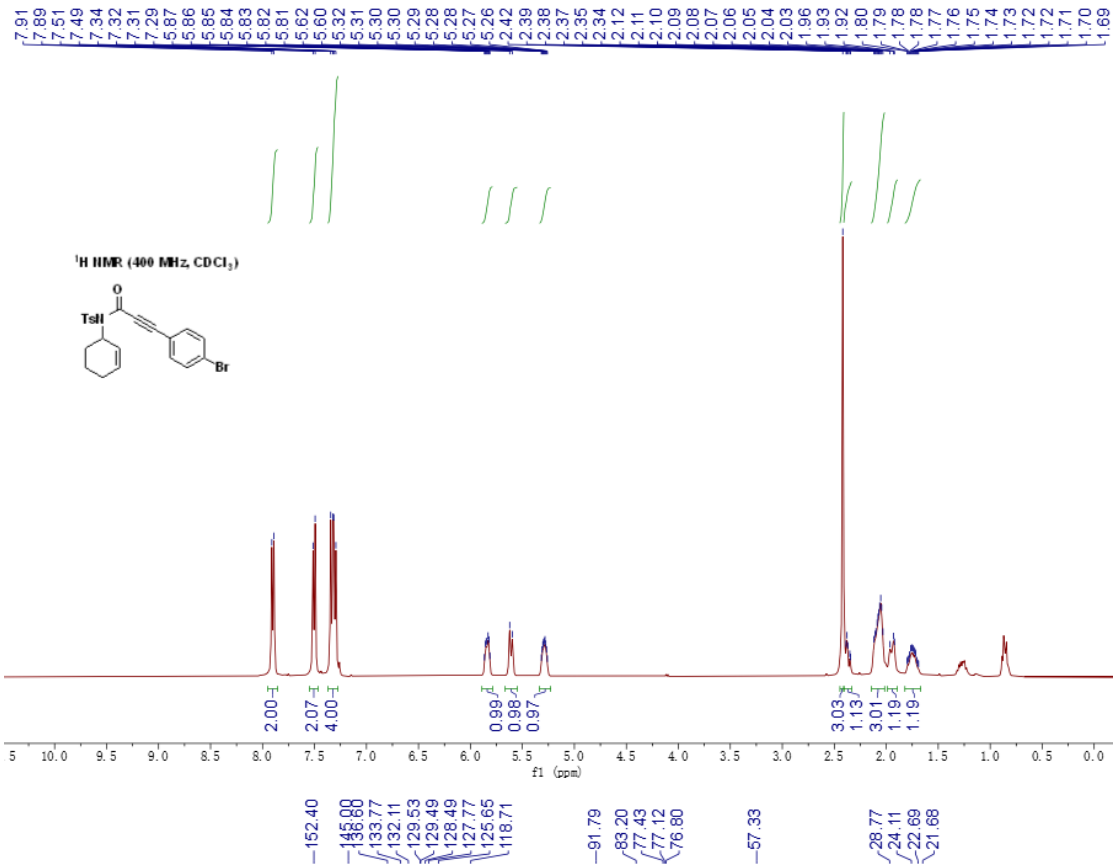

7.94 7.93 7.93 7.92 7.91 7.91 7.40 7.39 7.38 7.37 7.37 7.32 7.31 7.31 7.30 7.29 7.26 7.18 7.18 7.16 7.16 5.87 5.84 5.66 5.66 5.64 5.34 5.33 2.49 2.48 2.46 2.46 2.45 2.43 2.38 2.14 2.13 2.13 2.12 2.09 2.09 2.07 2.06 2.02 1.98 1.95 1.80 1.79 1.78 1.77 1.76 1.76 1.75 1.74 1.74
$^1$H NMR (400 MHz, CDCl$_3$)
TsN
2.00 2.02 2.08 2.08 1.00 0.97 1.00 0.72 3.14 3.01 2.80 1.43 1.17
f1 (ppm)

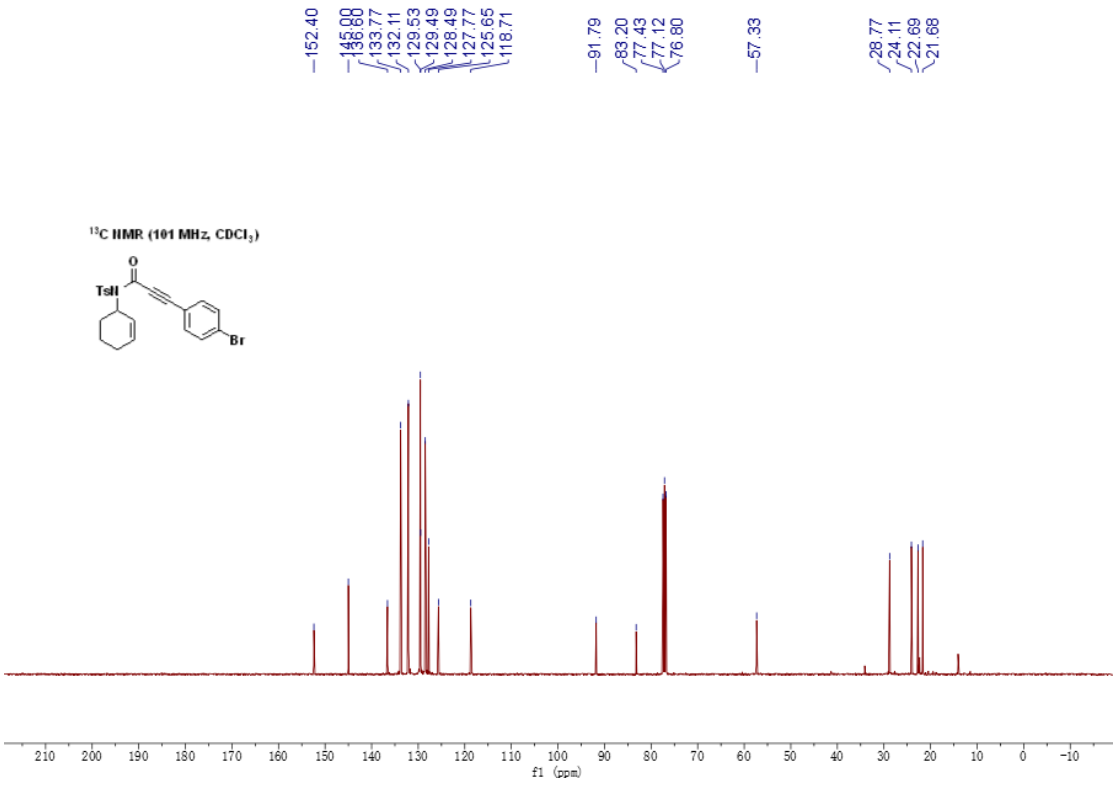

152.95 144.91 141.69 136.91 132.65 129.59 129.56 129.43 128.72 128.08 116.84 93.83 82.20 77.48 77.16 76.84 57.48 28.97 24.25 22.88 21.89 21.79
$^{13}$C NMR (101 MHz, CDCl$_3$)
TsN
f1 (ppm)

**5g**

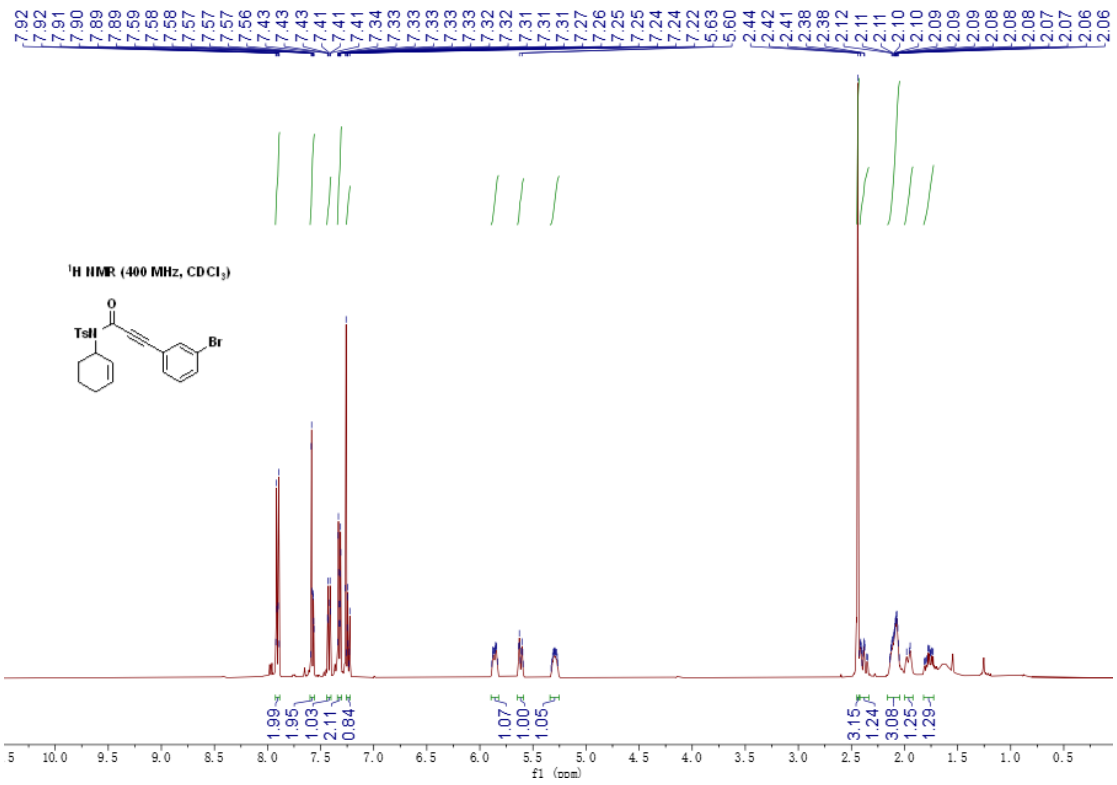

7.95 7.94 7.94 7.93 7.92 7.92 7.45 7.44 7.43 7.42 7.36 7.35 7.34 7.33 7.33 7.32 7.32 7.32 7.30 7.30 7.29 7.26 7.24 7.22 7.20 7.18 7.16 5.87 5.86 5.85 5.84 5.83 5.83 5.68 5.65 5.35 2.49 2.49 2.46 2.45 2.44 2.14 2.13 2.12 2.12 2.11 2.10 2.10 2.06 2.05 1.99 1.98 1.96 1.95 1.76 1.76 1.75
$^{1}$H NMR (400 MHz, CDCl$_3$)
TsN
2.00 1.00 3.17 1.05 1.03 0.99 0.95 0.98 1.03 6.21 1.98 2.21 1.08
f1 (ppm)
153.04 144.94 142.35 136.91 133.00 130.94 130.02 129.57 129.53 128.73 127.78 125.97 119.72 92.76 85.90 77.48 77.16 76.84 57.99 28.89 24.21 22.88 21.79 20.67
$^{13}$C NMR (101 MHz, CDCl$_3$)
TsN
f1 (ppm)

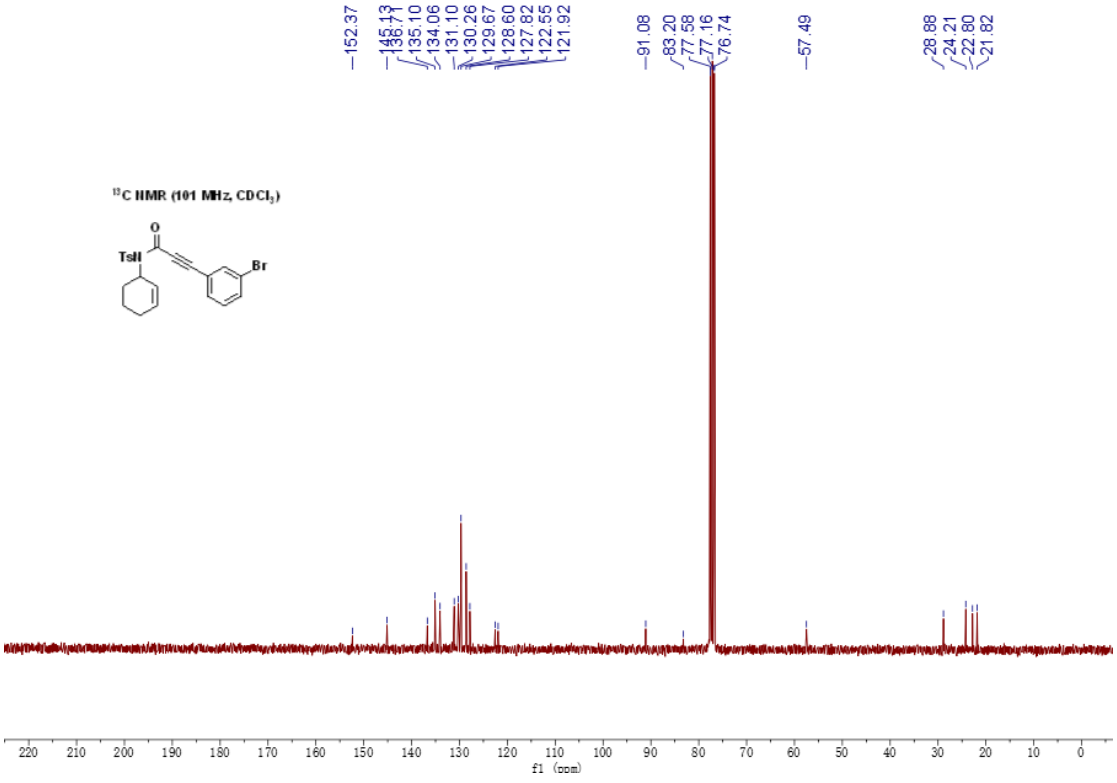
**5h**


7.91
7.89
7.51
7.49
7.34
7.32
7.31
7.29
5.87
5.86
5.85
5.84
5.83
5.82
5.81
5.62
5.60
5.32
5.31
5.30
5.30
5.29
5.28
5.28
5.27
5.26
2.42
2.39
2.38
2.37
2.35
2.34
2.12
2.11
2.10
2.09
2.08
2.07
2.06
2.05
2.04
2.03
1.96
1.93
1.92
1.80
1.79
1.78
1.78
1.77
1.76
1.75
1.74
1.73
1.72
1.72
1.71
1.70
1.69
$^{1}$H NMR (400 MHz, CDCl$_3$)
TsN
Br
2.00
2.07
4.00
0.99
0.98
0.97
3.03
1.13
3.01
1.19
1.19
f1 (ppm)

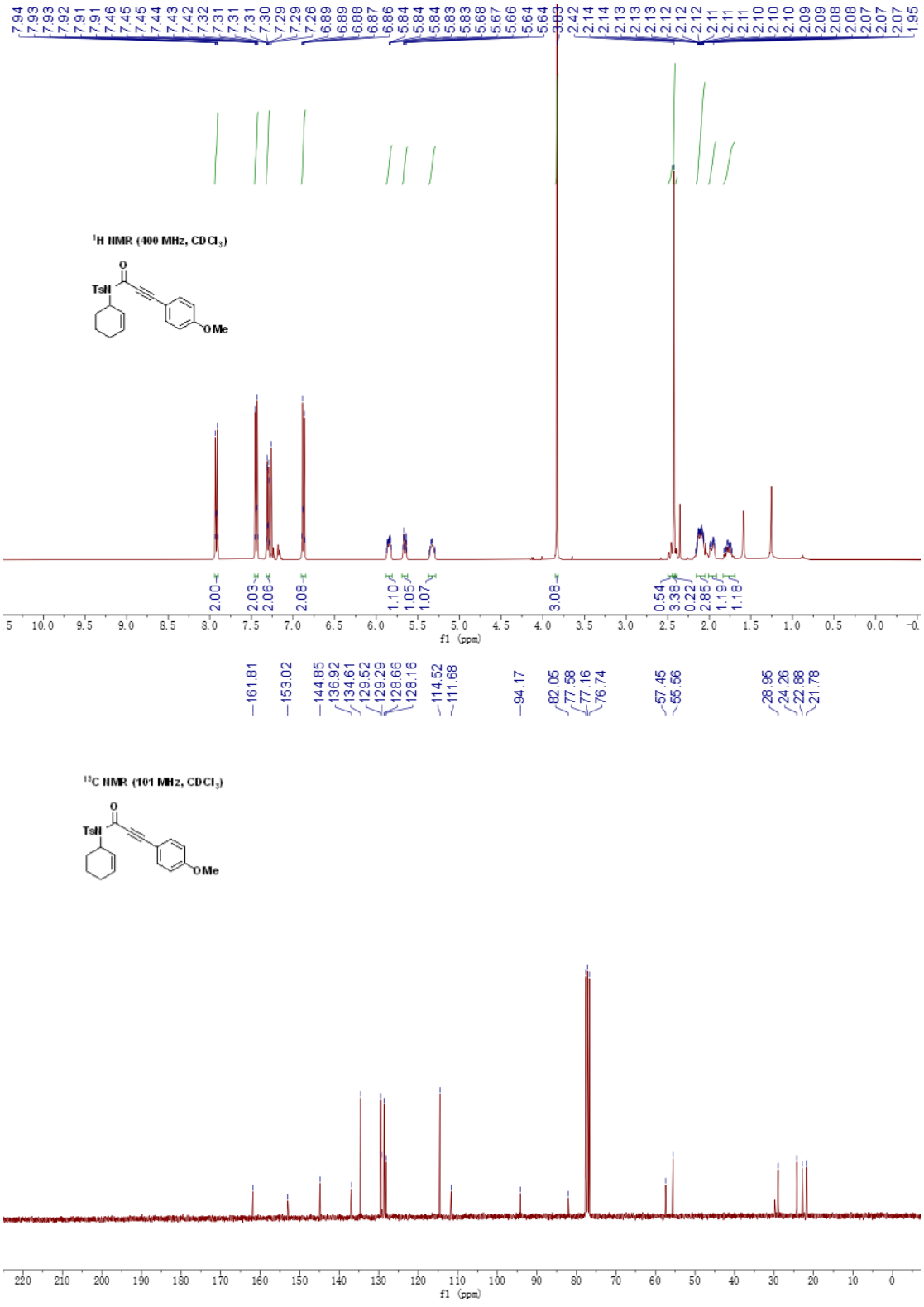

152.40
145.00
136.60
133.77
132.11
129.53
129.49
128.49
127.77
125.65
118.71
91.79
83.20
77.43
77.12
76.80
57.33
28.77
24.11
22.69
21.68
$^{13}$C NMR (101 MHz, CDCl$_3$)
TsN
Br
f1 (ppm)

**5i**

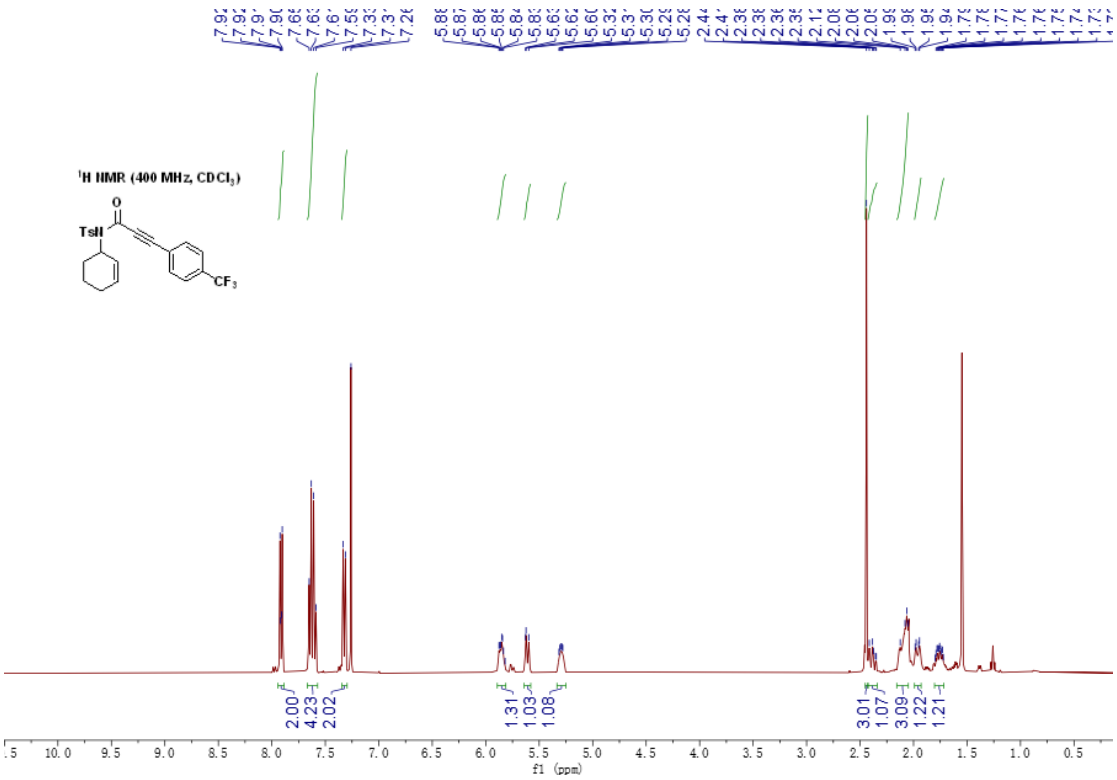

7.92 7.92 7.91 7.90 7.89 7.89 7.59 7.58 7.58 7.57 7.57 7.57 7.56 7.43 7.43 7.43 7.41 7.41 7.41 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.27 7.26 7.25 7.25 7.24 7.24 7.22 5.63 5.60 2.44 2.42 2.41 2.38 2.38 2.12 2.11 2.11 2.10 2.10 2.09 2.09 2.09 2.08 2.08 2.08 2.07 2.07 2.06 2.06
$^1$H NMR (400 MHz, CDCl$_3$)
TsN
O
Br
1.99 1.95 1.03 2.11 0.84 1.07 1.00 1.05 3.15 1.24 3.08 1.25 1.29
f1 (ppm)

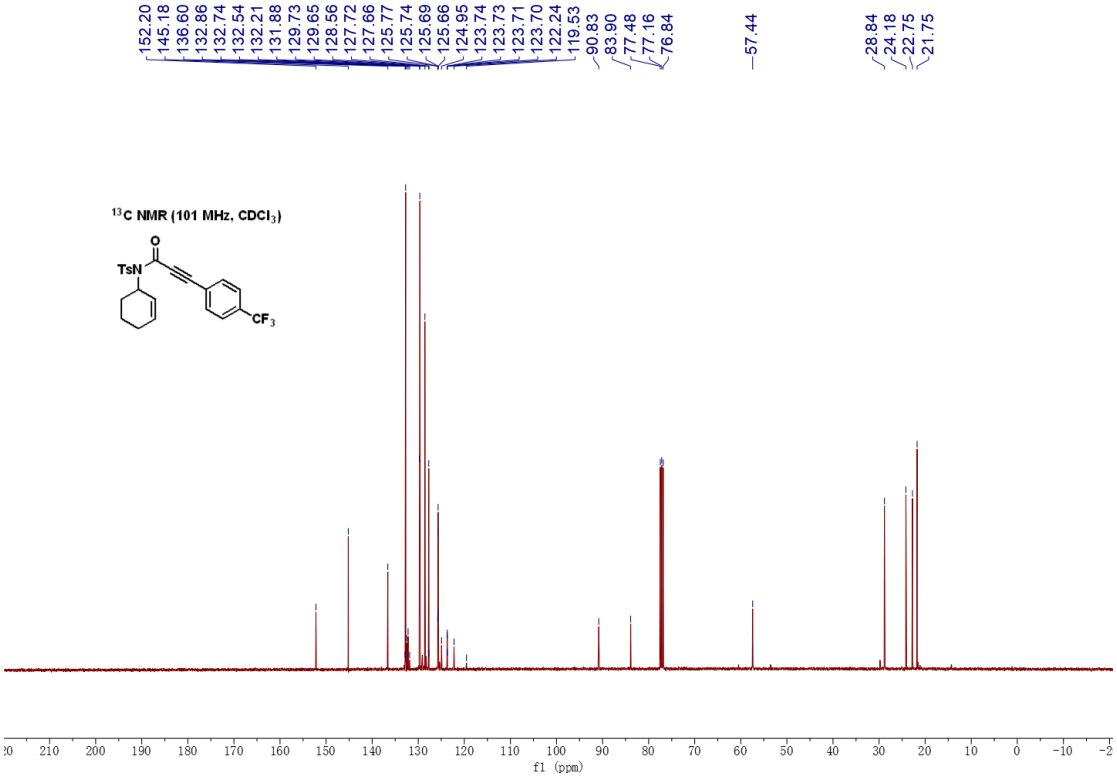

152.37 145.13 136.71 135.10 134.06 131.10 130.26 129.67 128.60 127.82 122.55 121.92 91.08 83.20 77.58 77.16 76.74 57.49 28.88 24.21 22.80 21.82
$^{13}$C NMR (101 MHz, CDCl$_3$)
TsN
O
Br
f1 (ppm)

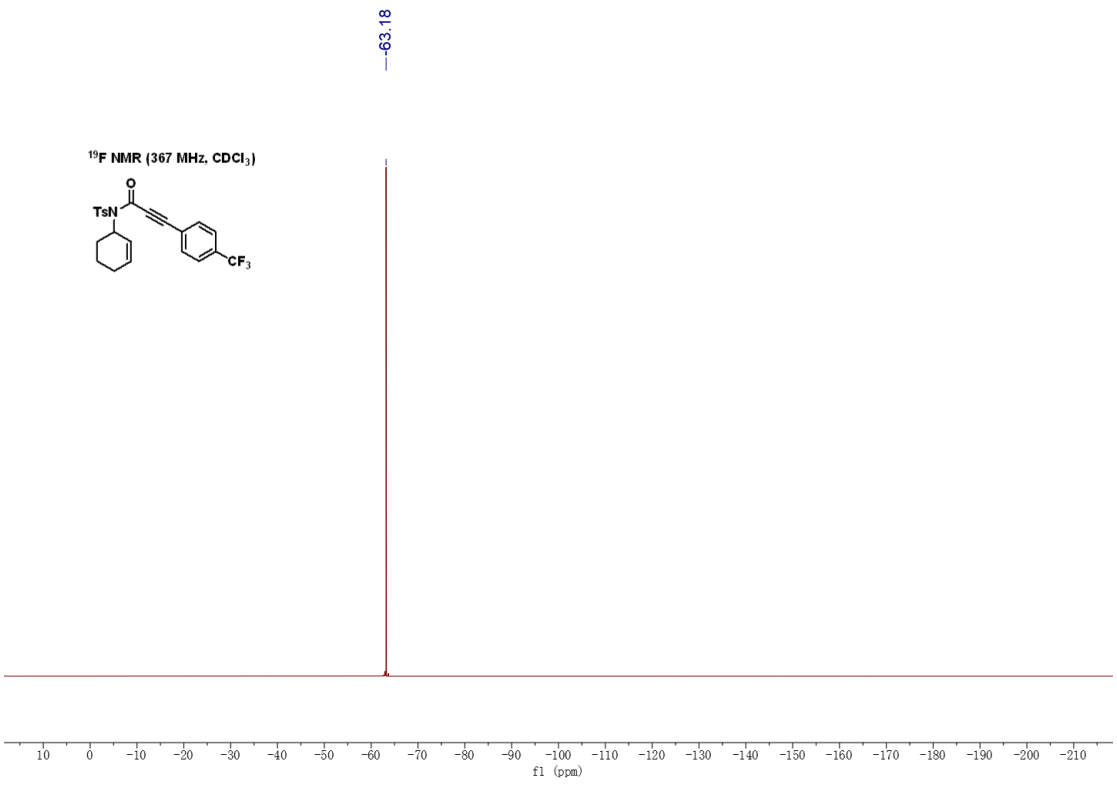
**5j**


7.94 7.93 7.93 7.92 7.91 7.91 7.46 7.45 7.45 7.44 7.43 7.42 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.26 6.89 6.89 6.88 6.87 6.86 5.84 5.84 5.84 5.83 5.83 5.68 5.67 5.66 5.64 5.64 3.83 2.42 2.14 2.14 2.13 2.13 2.12 2.12 2.12 2.11 2.11 2.11 2.10 2.10 2.10 2.09 2.09 2.08 2.08 2.07 2.07 2.07 1.95
$^{1}$H NMR (400 MHz, CDCl$_3$)
TsN
OMe
2.00 2.03 2.06 2.08 1.10 1.05 1.07 3.08 0.54 3.38 0.22 2.85 1.19 1.18
f1 (ppm)
161.81 153.02 144.85 136.92 134.61 129.52 129.29 128.66 128.16 114.52 111.68 94.17 82.05 77.58 77.16 76.74 57.45 55.56 28.95 24.26 22.88 21.78
$^{13}$C NMR (101 MHz, CDCl$_3$)
TsN
OMe
f1 (ppm)

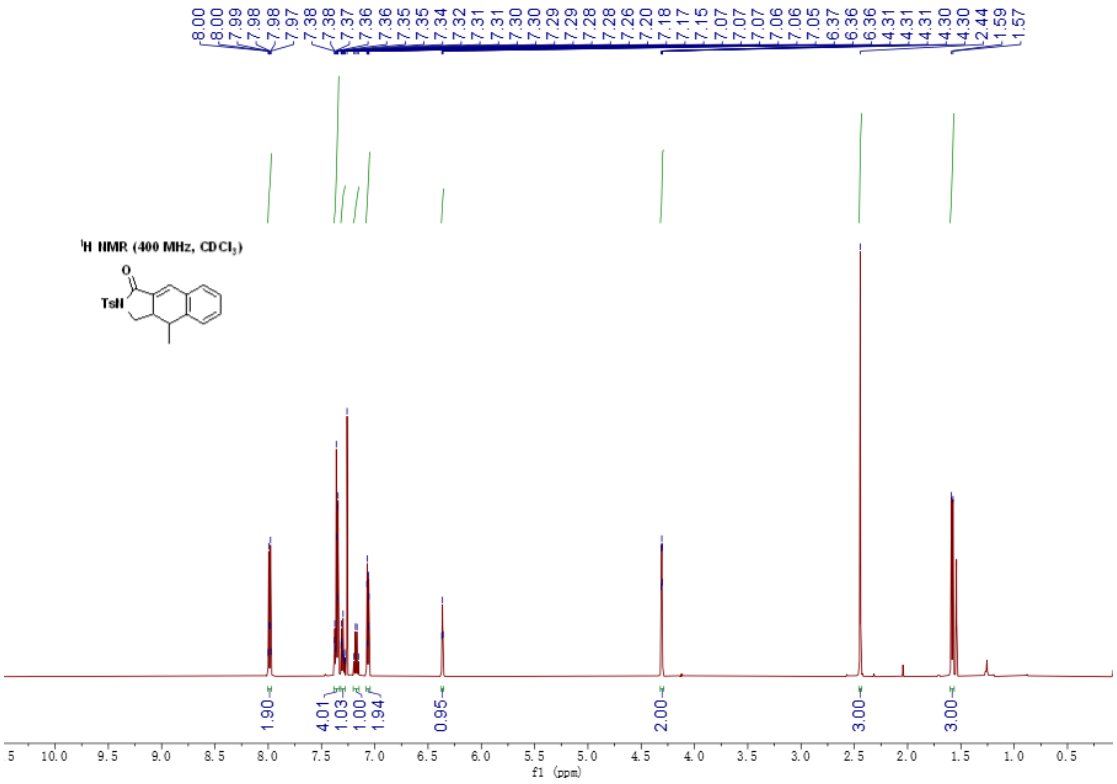
5k

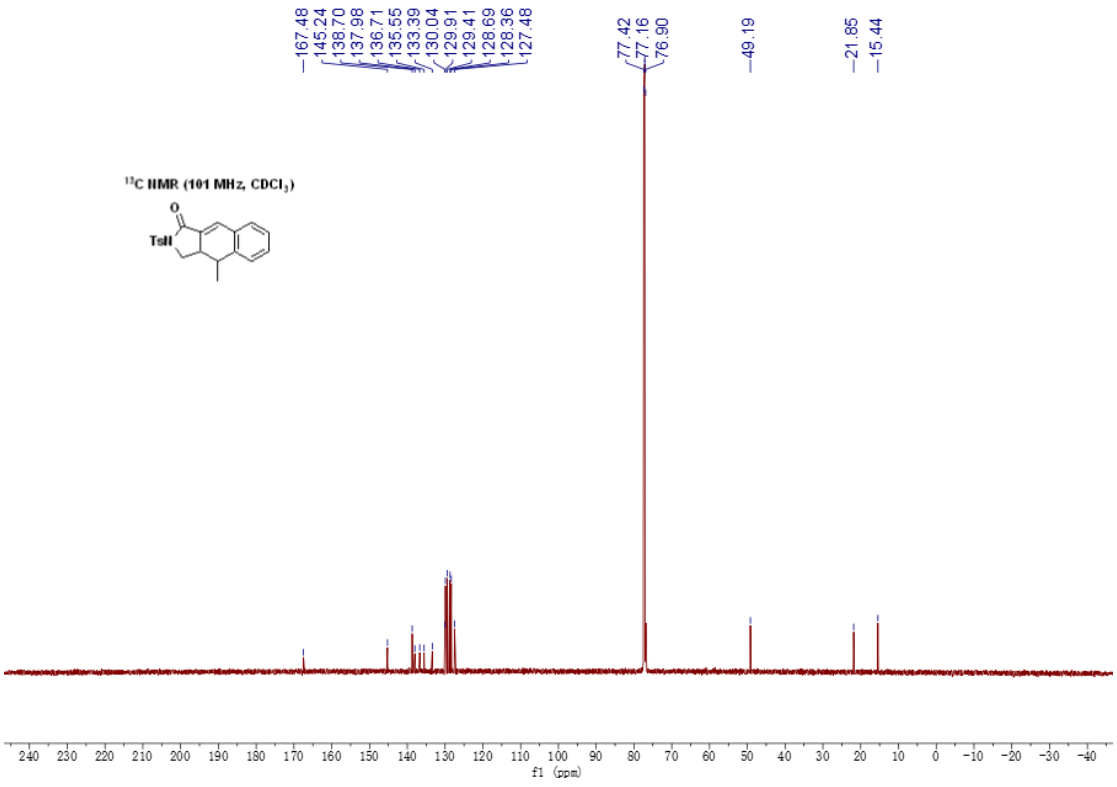

$^1$H NMR (400 MHz, $CDCl_3$)
TsN
O
$CF_3$
2.00
4.23
2.02
1.31
1.03
1.08
3.01
1.07
3.09
1.22
1.21
f1 (ppm)


$^{13}$C NMR (101 MHz, $CDCl_3$)
TsN
O
$CF_3$
152.20
145.18
136.60
132.86
132.74
132.54
132.21
131.88
129.73
129.65
128.56
127.72
127.66
125.77
125.74
125.69
125.66
124.95
123.74
123.73
123.71
123.70
122.24
119.53
90.83
83.90
77.48
77.16
76.84
57.44
28.84
24.18
22.75
21.75
f1 (ppm)

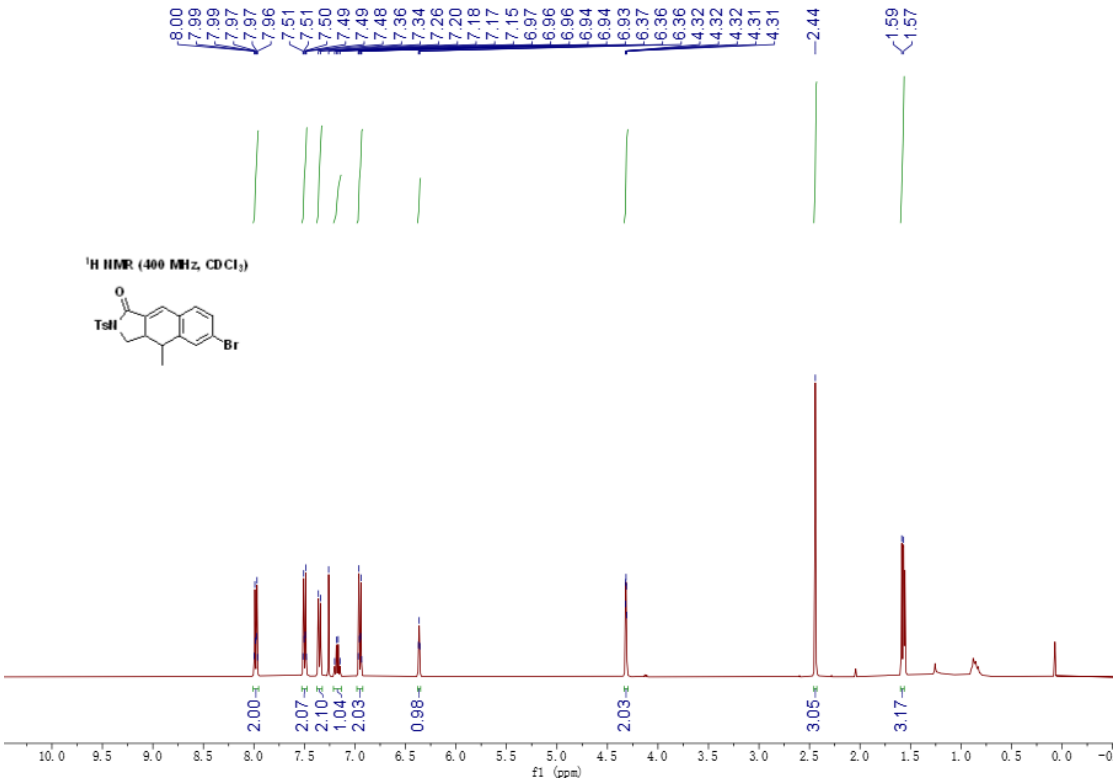

-63.18
$^{19}$F NMR (367 MHz, CDCl$_3$)
TsN
O
CF$_3$
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

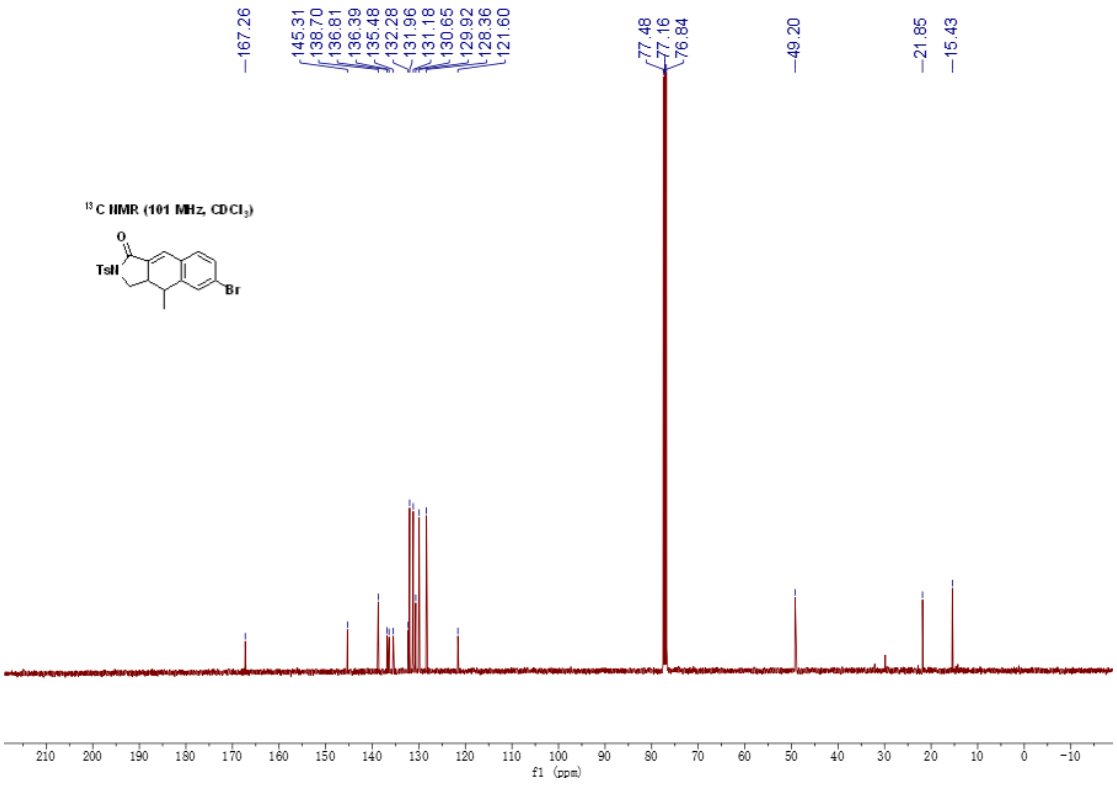
**6b**


8.00 8.00 7.99 7.98 7.98 7.97 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.34 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.26 7.20 7.18 7.17 7.15 7.07 7.07 7.07 7.06 7.05 6.37 6.36 6.36 4.31 4.31 4.31 4.30 4.30 2.44 1.59 1.57
$^1$H NMR (400 MHz, CDCl$_3$)
TsN
O
1.90 4.01 1.03 1.00 1.94 0.95 2.00 3.00 3.00
5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

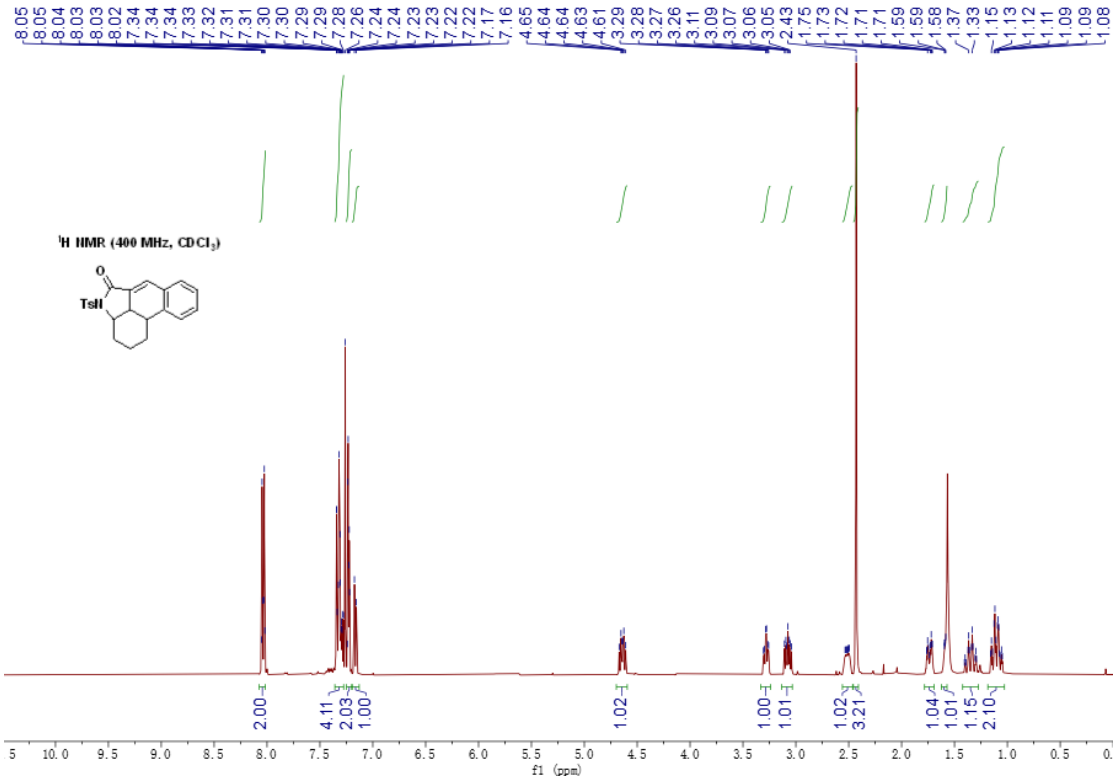

167.48
145.24
138.70
137.98
136.71
135.55
133.39
130.04
129.91
129.41
128.69
128.36
127.48
77.42
77.16
76.90
49.19
21.85
15.44
13C HMR (101 MHz, CDCl3)
TsN
O
f1 (ppm)

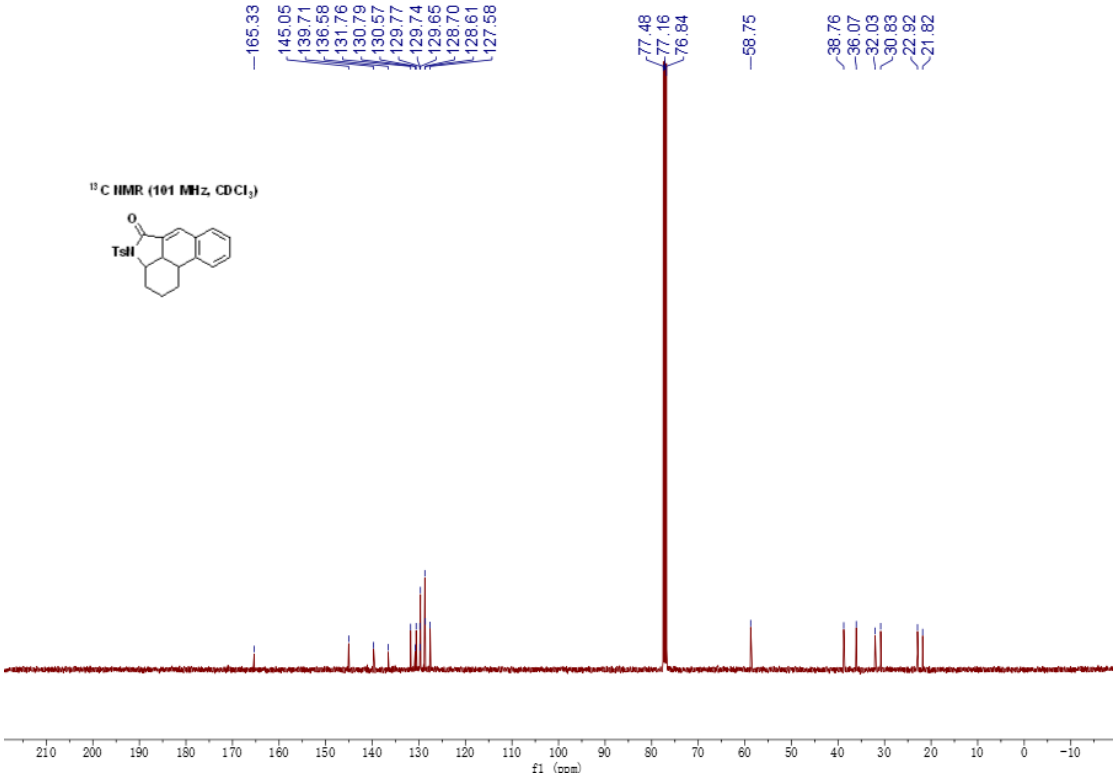
**6d**


8.00
7.99
7.99
7.97
7.97
7.96
7.51
7.51
7.50
7.49
7.49
7.48
7.36
7.34
7.26
7.20
7.18
7.17
7.15
6.97
6.96
6.96
6.94
6.94
6.93
6.37
6.36
6.36
4.32
4.32
4.31
4.31
2.44
1.59
1.57
1H HMR (400 MHz, CDCl3)
TsN
O
Br
2.00
2.07
2.10
1.04
2.03
0.98
2.03
3.05
3.17
f1 (ppm)

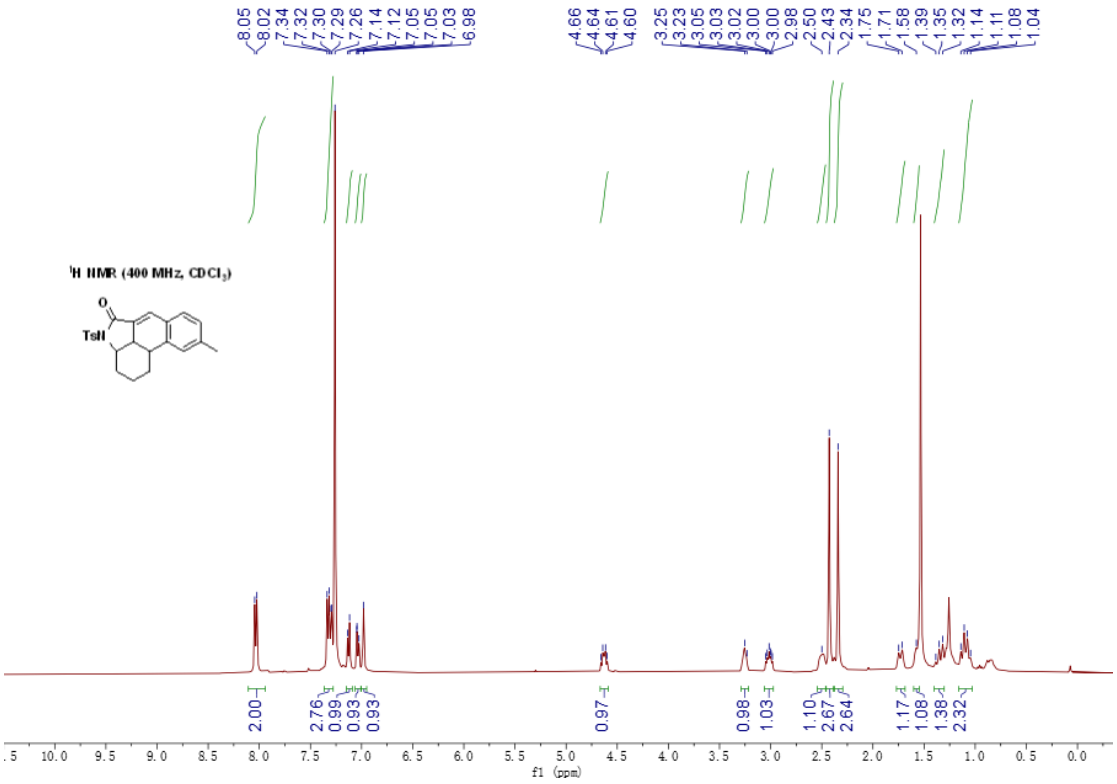

167.26
145.31
138.70
136.81
136.39
135.48
132.28
131.96
131.18
130.65
129.92
128.36
121.60
77.48
77.16
76.84
49.20
21.85
15.43
13C NMR (101 MHz, CDCl3)
O
TsN
Br
f1 (ppm)

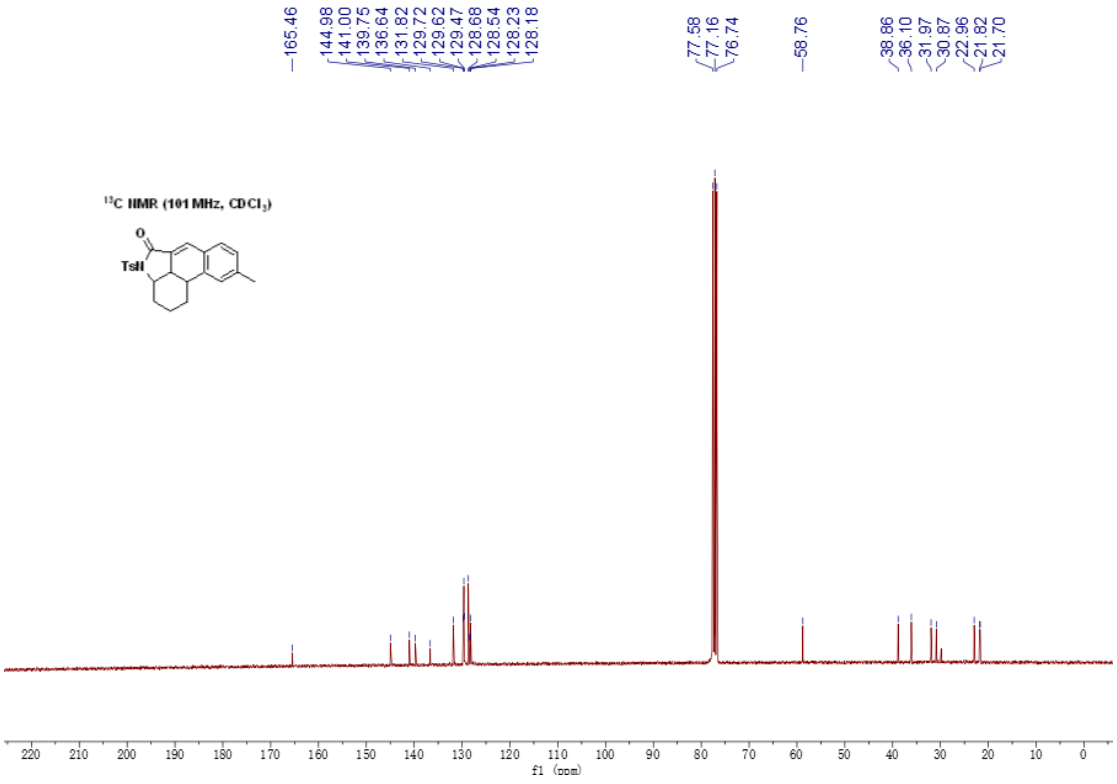
**6e**


8.05
8.04
8.03
8.02
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.26
7.24
7.23
7.22
7.17
7.16
4.65
4.64
4.63
4.61
3.29
3.28
3.27
3.26
3.11
3.09
3.07
3.06
3.05
2.43
1.75
1.73
1.72
1.71
1.59
1.58
1.37
1.33
1.15
1.13
1.12
1.11
1.09
1.08
1H NMR (400 MHz, CDCl3)
O
TsN
2.00
4.11
2.03
1.00
1.02
1.00
1.01
1.02
3.21
1.04
1.01
1.15
2.10
f1 (ppm)

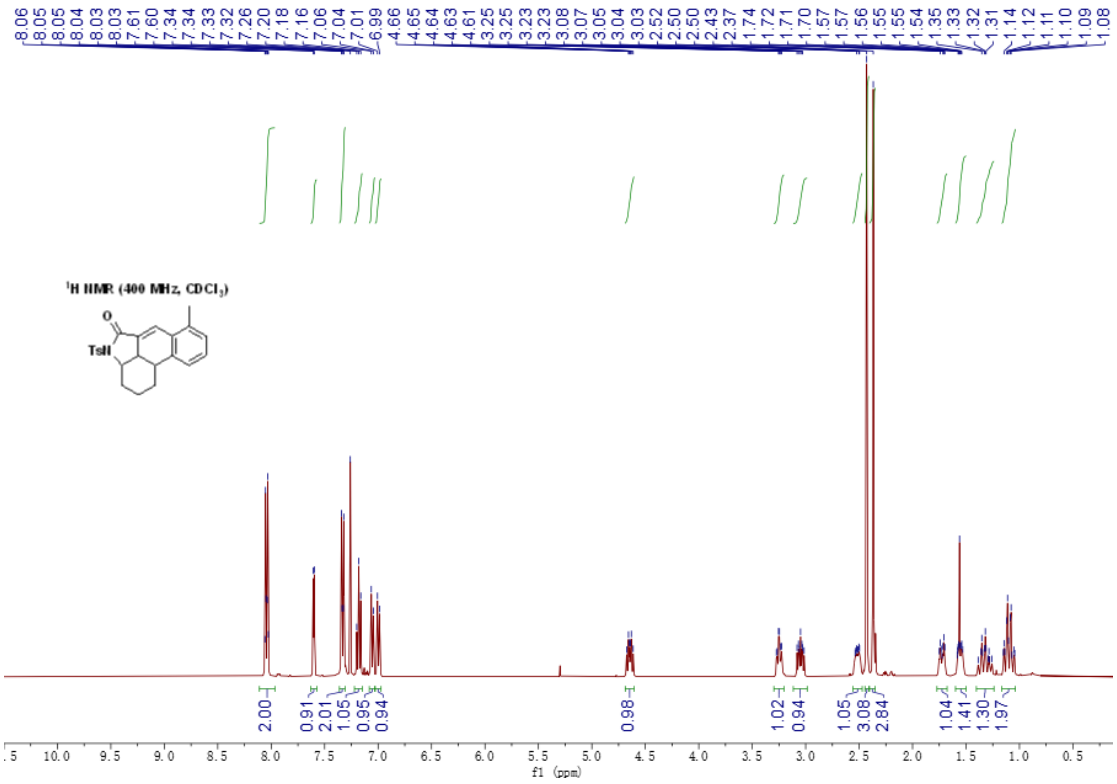

165.33
145.05
139.71
136.58
131.76
130.79
130.57
129.77
129.74
129.65
128.70
128.61
127.58
77.48
77.16
76.84
58.75
38.76
36.07
32.03
30.83
22.92
21.82
13C NMR (101 MHz, CDCl3)
O
TsN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

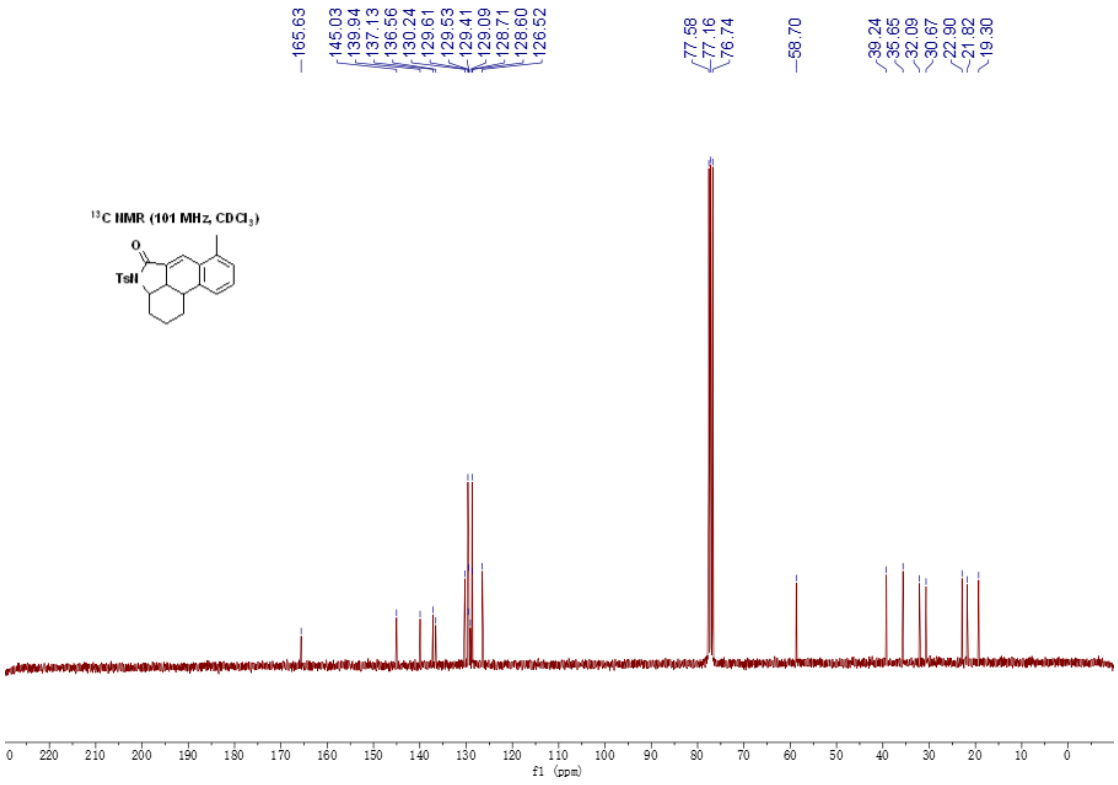
**6f**


8.05
8.02
7.34
7.32
7.30
7.29
7.26
7.14
7.12
7.05
7.05
7.03
6.98
4.66
4.64
4.61
4.60
3.25
3.23
3.05
3.03
3.02
3.00
3.00
2.98
2.50
2.43
2.34
1.75
1.71
1.58
1.39
1.35
1.32
1.14
1.11
1.08
1.04
1H NMR (400 MHz, CDCl3)
O
TsN
2.00
2.76
0.99
0.93
0.93
0.97
0.98
1.03
1.10
2.67
2.64
1.17
1.08
1.38
2.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

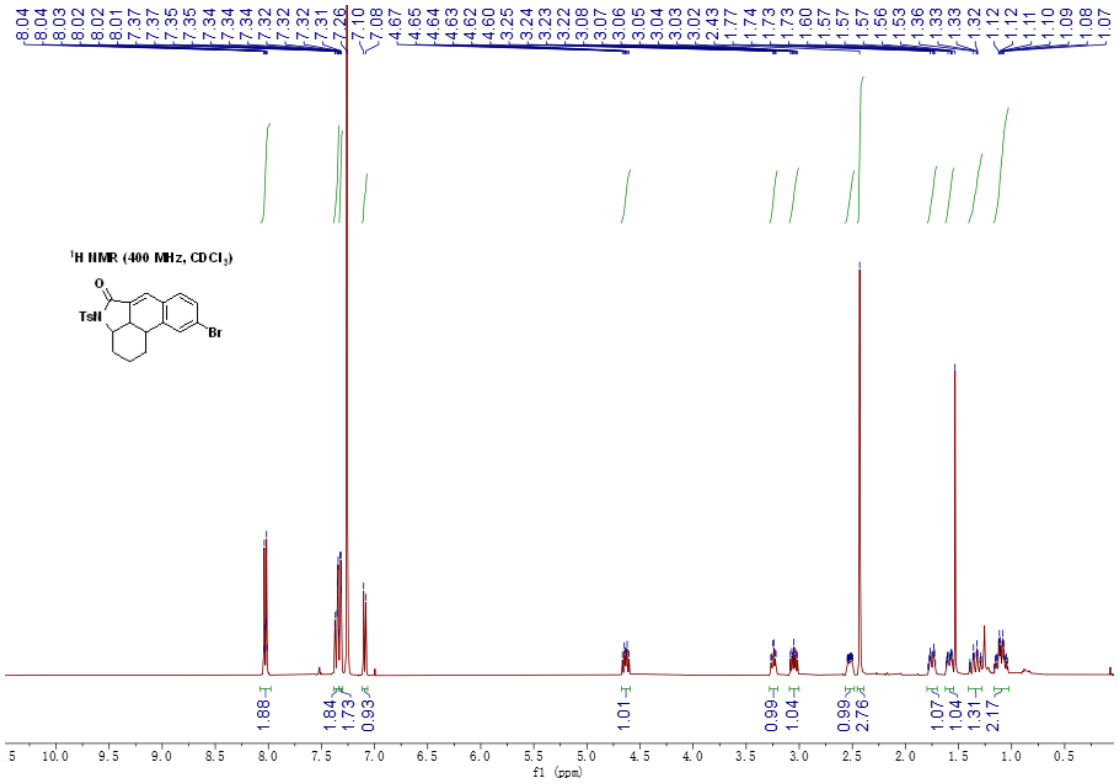

165.46
144.98
141.00
139.75
136.64
131.82
129.72
129.62
129.47
128.68
128.54
128.23
128.18
77.58
77.16
76.74
58.76
38.86
36.10
31.97
30.87
22.96
21.82
21.70
13C NMR (101 MHz, CDCl3)
TsN
f1 (ppm)

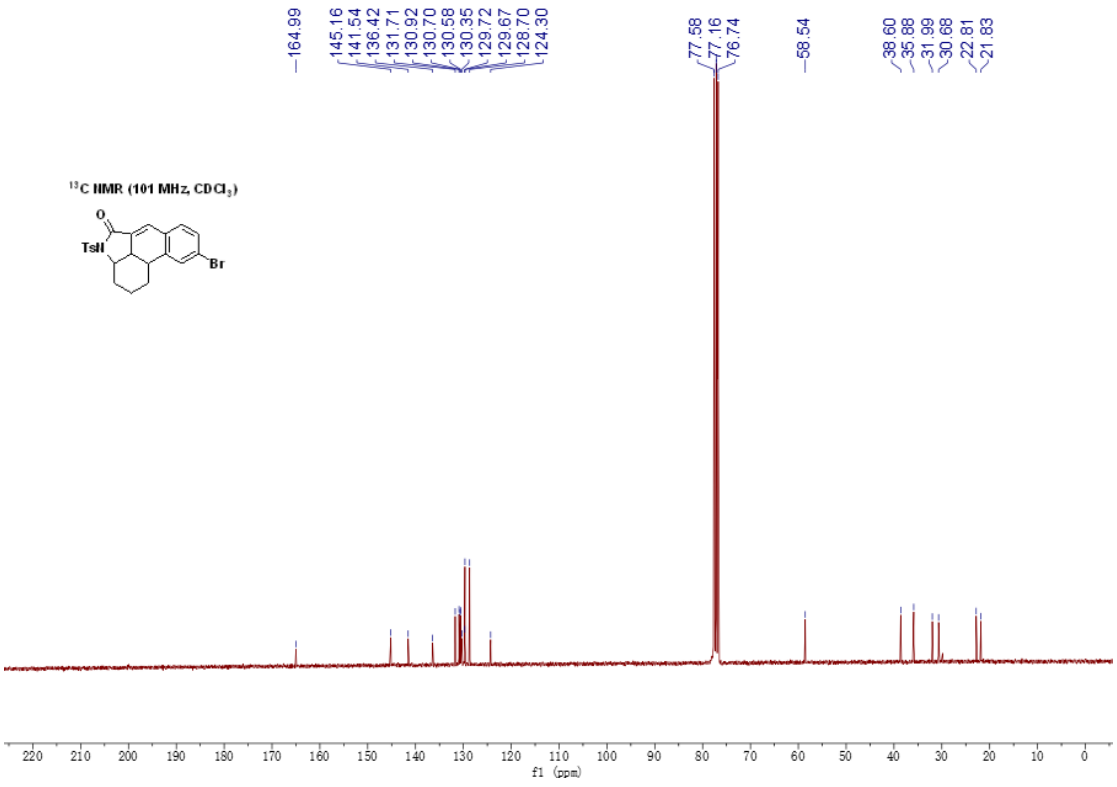
**6g**


8.06
8.05
8.05
8.04
8.03
8.03
7.61
7.60
7.34
7.34
7.33
7.32
7.26
7.20
7.18
7.16
7.06
7.04
7.01
6.99
4.66
4.65
4.64
4.63
4.61
3.25
3.25
3.23
3.23
3.08
3.07
3.05
3.04
3.03
2.52
2.50
2.50
2.43
2.37
1.74
1.72
1.71
1.70
1.57
1.57
1.56
1.55
1.55
1.54
1.35
1.33
1.32
1.31
1.14
1.12
1.11
1.10
1.09
1.08
1H NMR (400 MHz, CDCl3)
TsN
2.00
0.91
2.01
1.05
0.95
0.94
0.98
1.02
0.94
1.05
3.08
2.84
1.04
1.41
1.30
1.97
f1 (ppm)

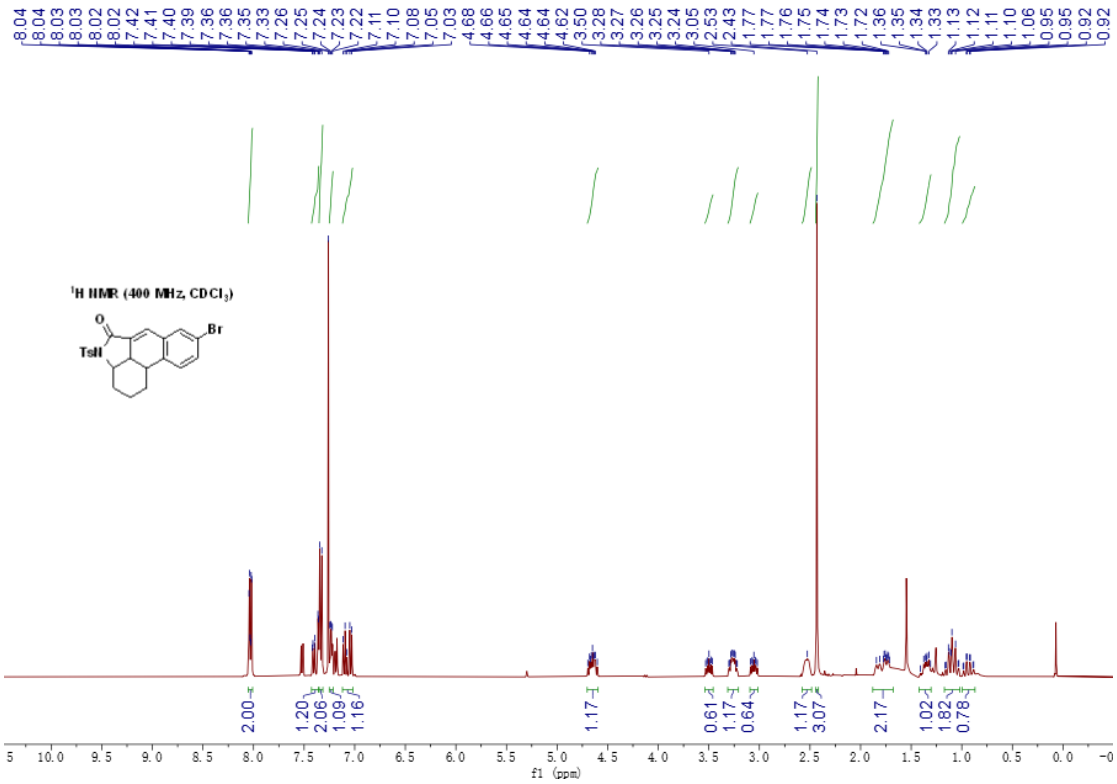

165.63
145.03
139.94
137.13
136.56
130.24
129.61
129.53
129.41
129.09
128.71
128.60
126.52
77.58
77.16
76.74
58.70
39.24
35.65
32.09
30.67
22.90
21.82
19.30
13C NMR (101 MHz, CDCl3)
TsN
f1 (ppm)

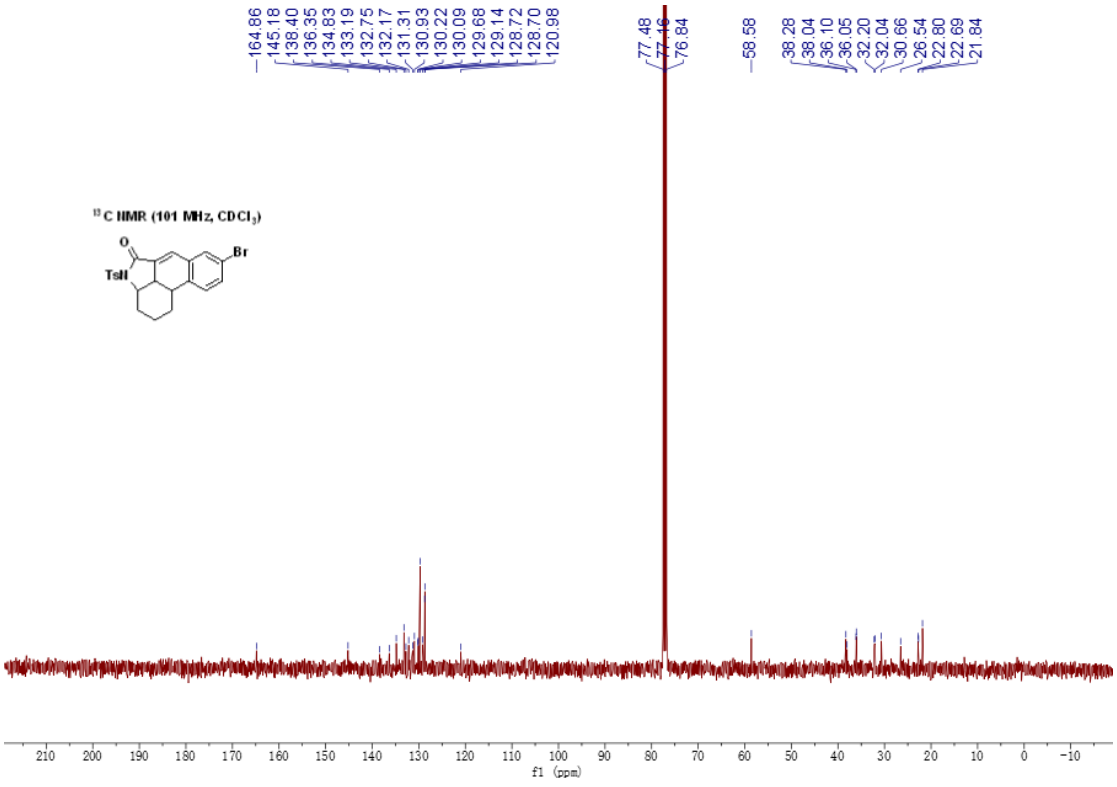
**6h**


8.04
8.03
8.02
8.01
7.37
7.35
7.34
7.32
7.31
7.26
7.10
7.08
4.67
4.65
4.63
4.62
4.60
3.25
3.24
3.23
3.22
3.08
3.07
3.06
3.05
3.04
3.03
3.02
2.43
1.77
1.74
1.73
1.60
1.57
1.56
1.53
1.36
1.33
1.32
1.12
1.11
1.10
1.09
1.08
1.07
1H NMR (400 MHz, CDCl3)
TsN
Br
1.88
1.84
1.73
0.93
1.01
0.99
1.04
0.99
2.76
1.07
1.04
1.31
2.17
f1 (ppm)

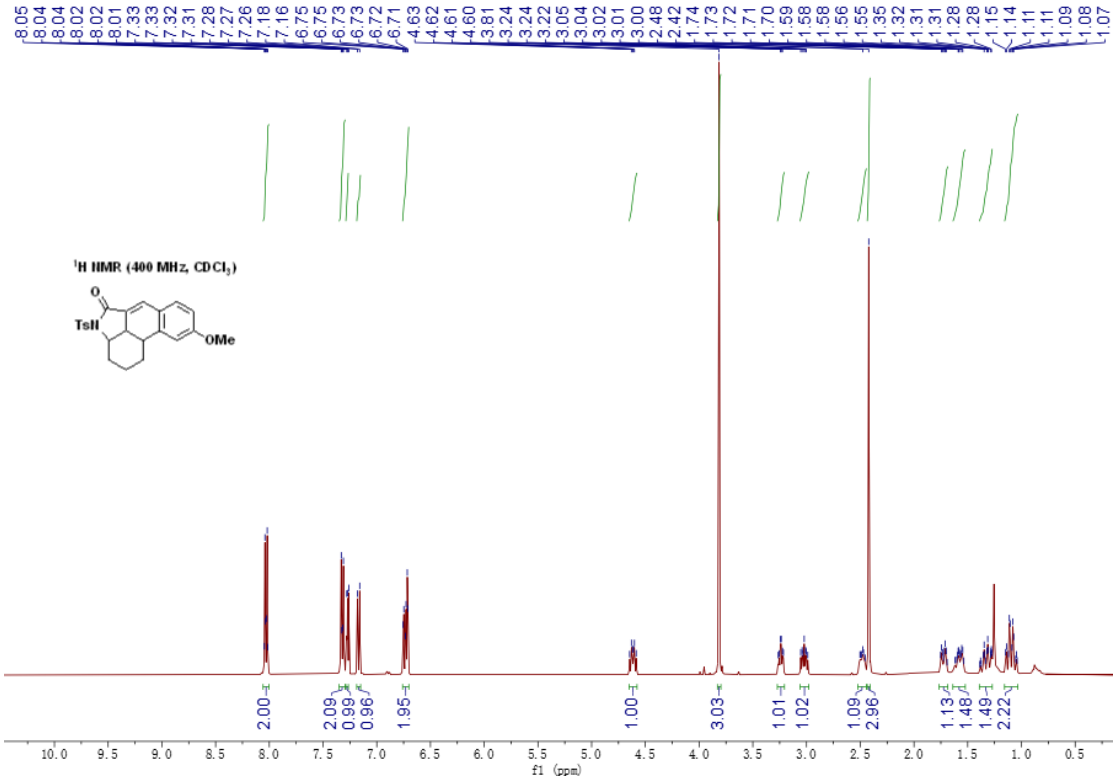

164.99
145.16
141.54
136.42
131.71
130.92
130.70
130.58
130.35
129.72
129.67
128.70
124.30
77.58
77.16
76.74
58.54
38.60
35.88
31.99
30.68
22.81
21.83
13C NMR (101 MHz, CDCl3)
Ts
Br
f1 (ppm)

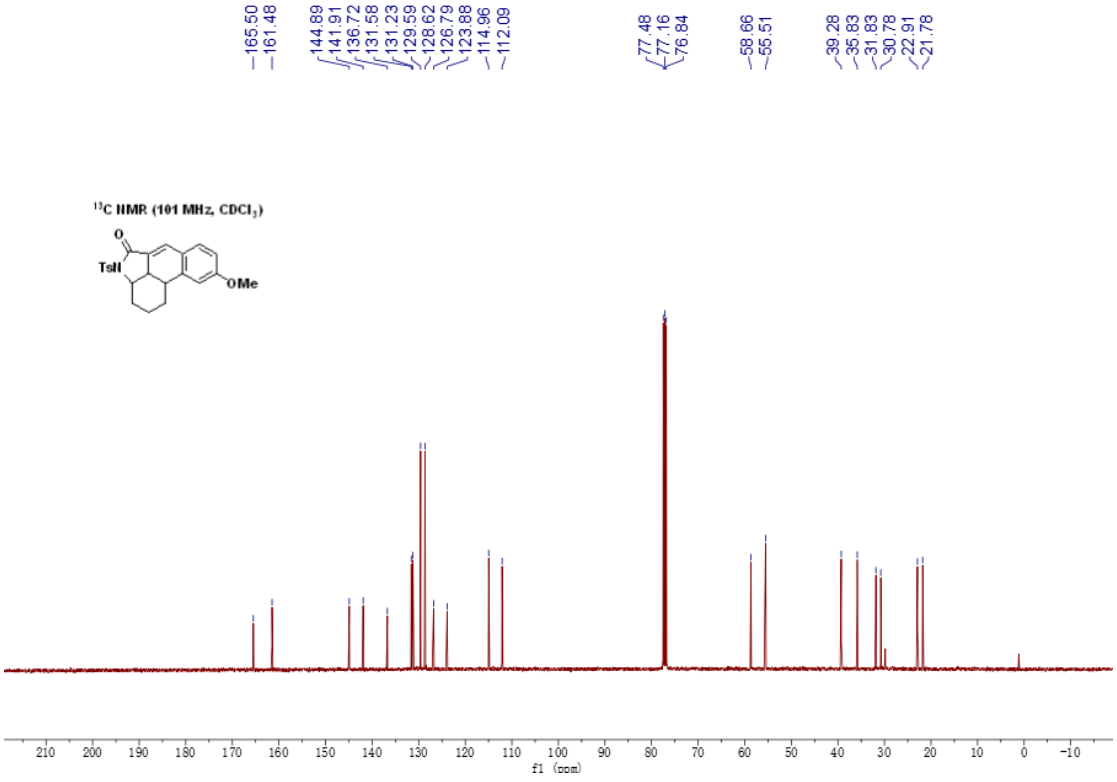
**6i**


8.04
8.03
8.02
7.42
7.41
7.40
7.39
7.36
7.35
7.33
7.26
7.25
7.24
7.23
7.22
7.11
7.10
7.08
7.05
7.03
4.68
4.66
4.65
4.64
4.62
3.50
3.28
3.27
3.26
3.25
3.24
3.05
2.53
2.43
1.77
1.76
1.75
1.74
1.73
1.72
1.36
1.35
1.34
1.33
1.13
1.12
1.11
1.10
1.06
0.95
0.92
1H NMR (400 MHz, CDCl3)
Ts
Br
2.00
1.20
2.06
1.09
1.16
1.17
0.61
1.17
0.64
1.17
3.07
2.17
1.02
1.82
0.78
f1 (ppm)

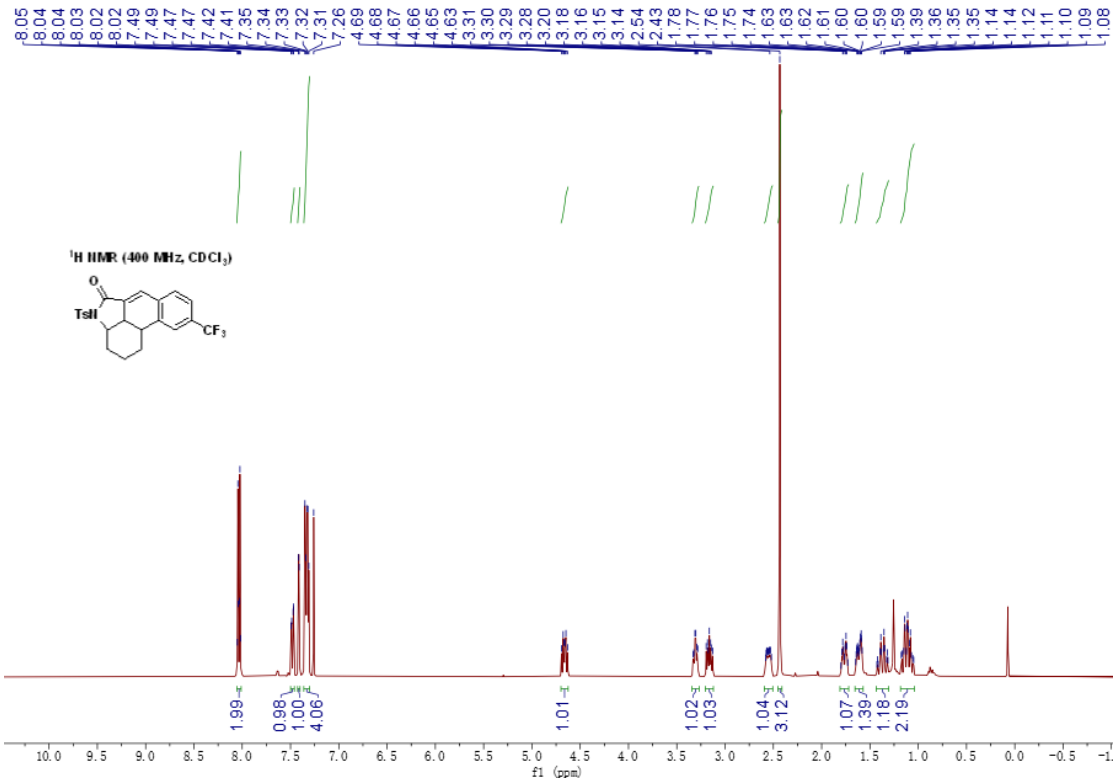

164.86
145.18
138.40
136.35
134.83
133.19
132.75
132.17
131.31
130.93
130.22
130.09
129.68
129.14
128.72
128.70
120.98
77.48
77.16
76.84
58.58
38.28
38.04
36.10
36.05
32.20
32.04
30.66
26.54
22.80
22.69
21.84
$^{13}$C NMR (101 MHz, CDCl$_3$)
O
TsN
Br
f1 (ppm)

**6j**

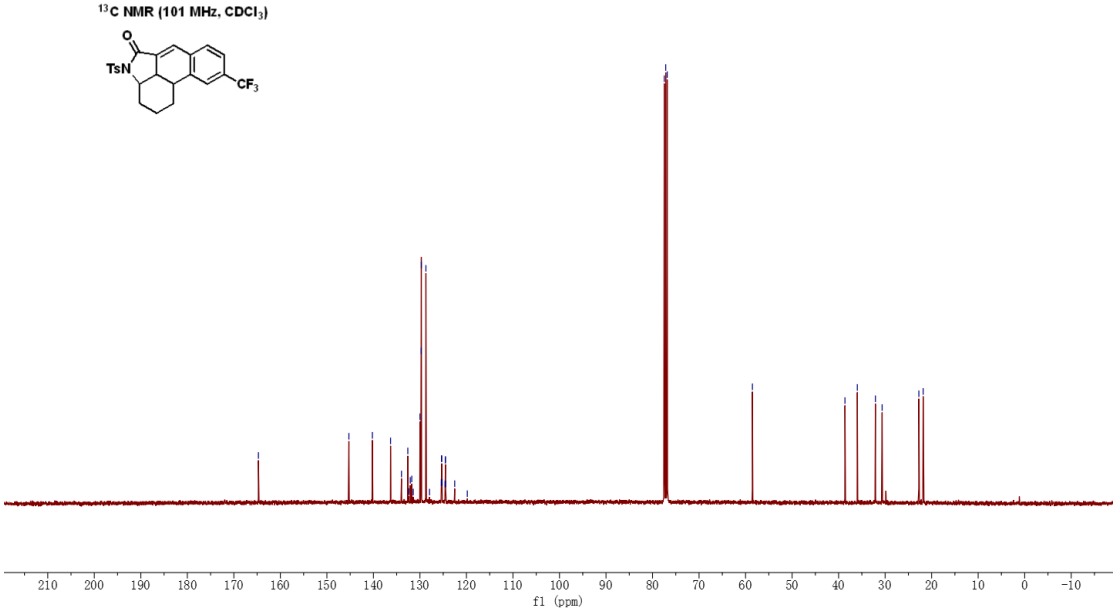

8.05
8.04
8.04
8.02
8.02
8.01
7.33
7.33
7.32
7.31
7.28
7.27
7.26
7.18
7.16
6.75
6.75
6.73
6.73
6.72
6.71
4.63
4.62
4.61
4.60
3.81
3.24
3.24
3.22
3.05
3.04
3.02
3.01
3.00
2.48
2.42
1.74
1.73
1.72
1.71
1.70
1.59
1.58
1.58
1.56
1.55
1.35
1.32
1.31
1.31
1.28
1.28
1.15
1.14
1.11
1.11
1.09
1.08
1.07
$^{1}$H NMR (400 MHz, CDCl$_3$)
O
TsN
OMe
2.00
2.09
0.99
0.96
1.95
1.00
3.03
1.01
1.02
1.09
2.96
1.13
1.48
1.49
2.22
f1 (ppm)

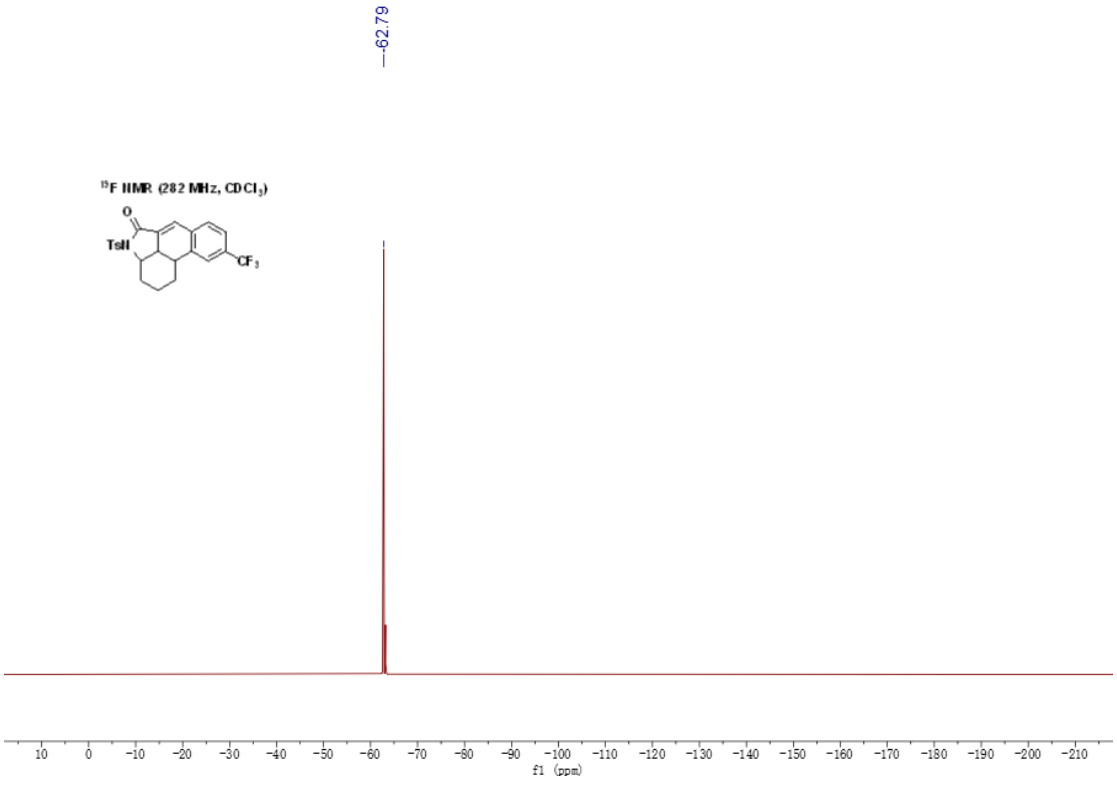

165.50
161.48
144.89
141.91
136.72
131.58
131.23
129.59
128.62
126.79
123.88
114.96
112.09
77.48
77.16
76.84
58.66
55.51
39.28
35.83
31.83
30.78
22.91
21.78
13C NMR (101 MHz, CDCl3)
TsN
OMe
f1 (ppm)

**6k**

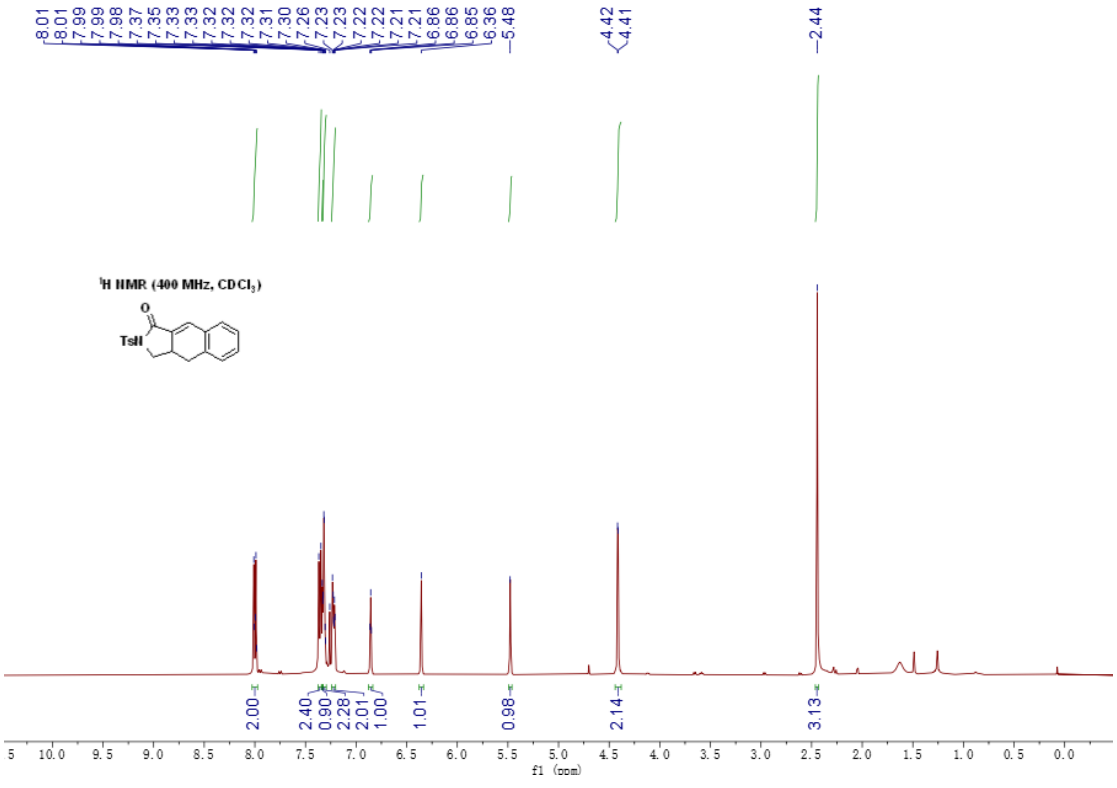

8.05
8.04
8.04
8.03
8.02
8.02
7.49
7.49
7.47
7.47
7.42
7.41
7.35
7.34
7.33
7.32
7.31
7.26
4.69
4.68
4.67
4.66
4.65
4.63
3.31
3.30
3.29
3.28
3.20
3.18
3.16
3.15
3.14
2.54
2.43
1.78
1.77
1.76
1.75
1.74
1.63
1.63
1.62
1.61
1.60
1.60
1.59
1.59
1.39
1.36
1.35
1.35
1.14
1.14
1.12
1.11
1.10
1.09
1.08
1H NMR (400 MHz, CDCl3)
TsN
CF3
1.99
0.98
1.00
4.06
1.01
1.02
1.03
1.04
3.12
1.07
1.39
1.18
2.19
f1 (ppm)

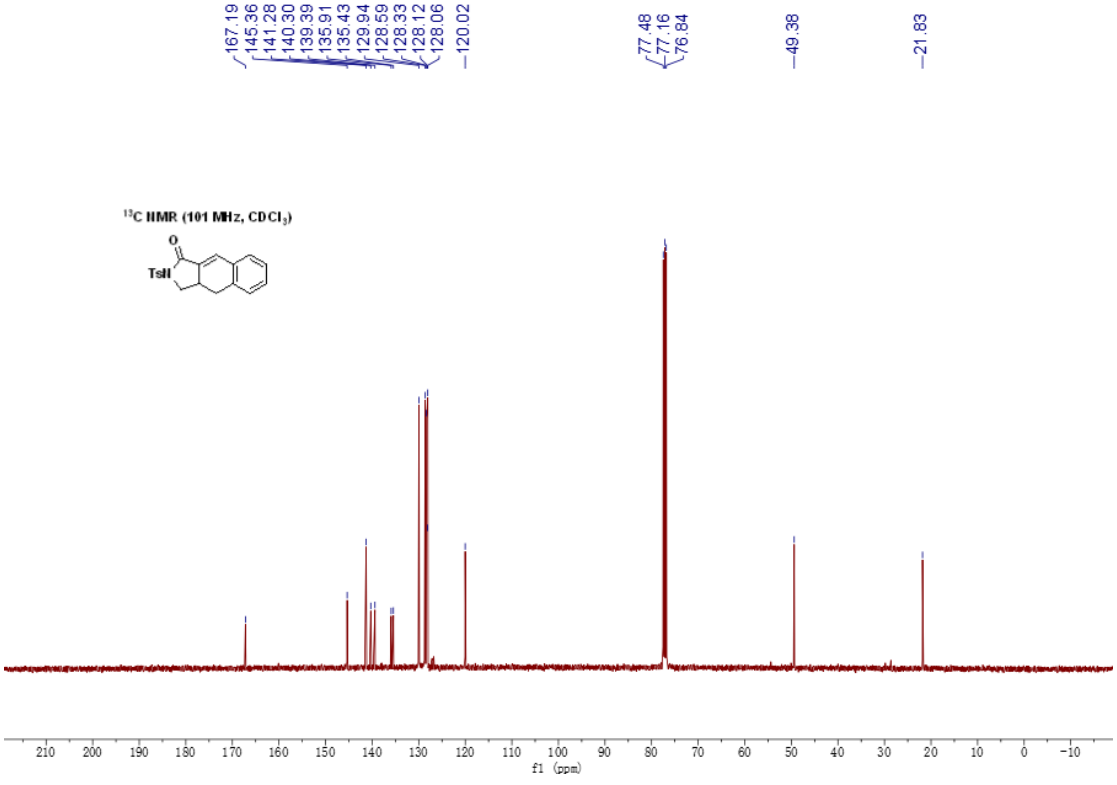

164.72
145.27
140.22
136.32
133.96
132.60
132.40
132.08
131.75
131.43
129.99
129.72
129.70
128.71
127.94
125.40
125.36
125.32
125.29
125.23
124.59
124.55
124.51
124.47
122.52
119.82
77.48
77.16
76.84
58.53
38.63
35.98
32.09
30.65
22.75
21.82


$^{13}$C NMR (101 MHz, CDCl$_3$)
O
TsN
CF$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


62.79
$^{19}$F NMR (282 MHz, CDCl$_3$)
O
TsN
CF$_3$
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

**6l**


8.01
8.01
7.99
7.99
7.98
7.37
7.35
7.33
7.33
7.32
7.32
7.32
7.31
7.30
7.26
7.23
7.23
7.22
7.22
7.21
7.21
6.86
6.86
6.85
6.36
5.48
4.42
4.41
2.44
$^1$H NMR (400 MHz, CDCl$_3$)
Ts
2.00
2.40
0.90
2.28
2.01
1.00
1.01
0.98
2.14
3.13
f1 (ppm)


167.19
145.36
141.28
140.30
139.39
135.91
135.43
129.94
128.59
128.33
128.12
128.06
120.02
77.48
77.16
76.84
49.38
21.83
$^{13}$C NMR (101 MHz, CDCl$_3$)
Ts
f1 (ppm)