Supporting Information

Rhodium-Catalyzed Synthesis of 1,2-Dihydropyridine by Tandem Reaction of 4-(1-Acetoxyallyl)-1-sulfonyl-1,2,3-triazole

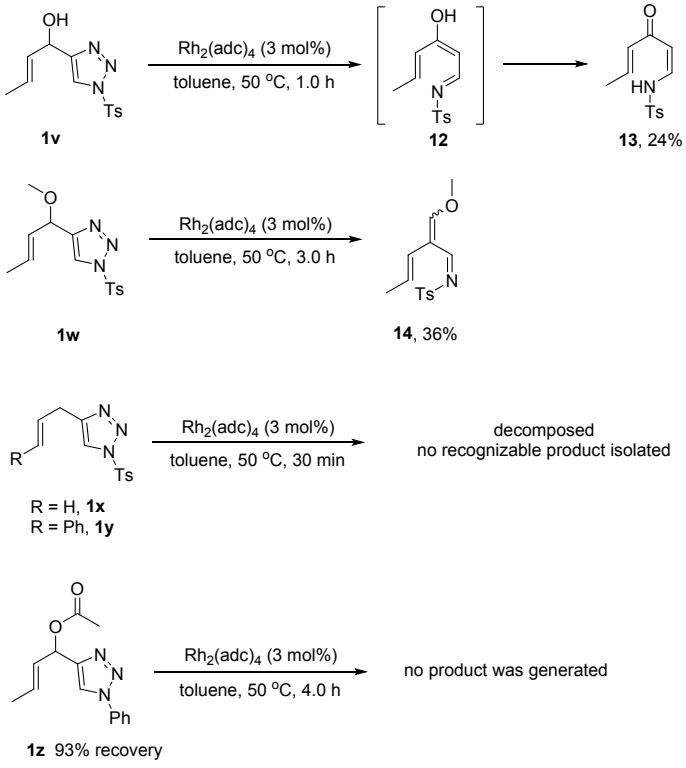
Haican Dai, SiSi Yu, Wanli Cheng, Ze-Feng Xu* and Chuan-Ying Li*

Department of Chemistry, Zhejiang Sci-Tech University, Xiasha West Higher Education District, Hangzhou, 310018, China

1. General Comments:

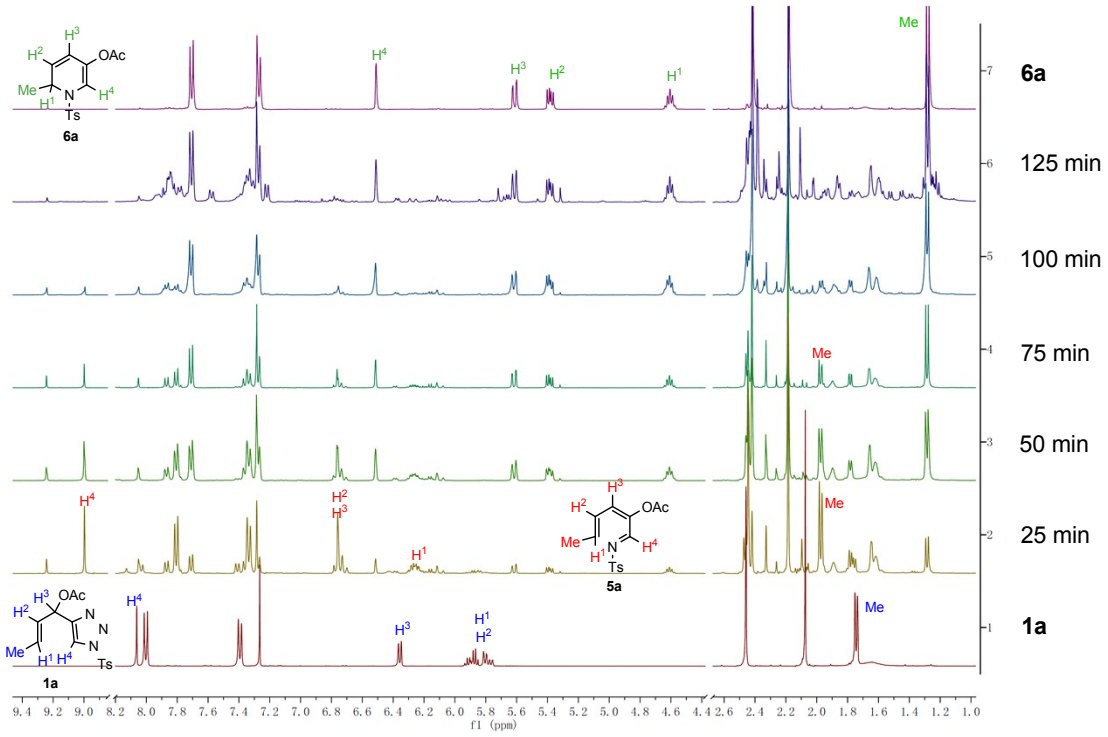
Analytical thin layer chromatography (TLC) was performed using Silica Gel HSGF254 pre-coated plates. Flash column chromatography was performed using 200 - 300 Mesh Silica Gel. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded using Brucker Avance IIDMX 400MHz spectrometers. Chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.00 ppm) or $CDCl_3$ (7.26 ppm). Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were recorded using a Brucker Avance II DMX 400 spectrometer at 100 MHz. Chemical shift is reported in ppm relative to the carbon resonance of $CDCl_3$ (77.00 ppm). High resolution mass spectra (HRMS) were obtained by Center for Instrumental Analysis of Zhejiang Sci-Tech University and a Waters TOFMS GCT Premier instrument for HRMS. The results are reported as m/e (relative ratio). Accurate masses are reported for the molecular ion (M+) or a suitable fragment ion.

2. Reactions of 1v-1z under the standard conditions



For free hydroxy substituted triazole **1v**, 1,2-hydrogen migration occurred and enol **12** was generated under the standard reaction conditions, tautomerization, rather than 6π-electron electrocyclic ring closure of **12** produced **13** eventually in 24% yield based on **1v**. For methoxy substituted triazole **1w**, 1,2-vinyl migration occurred and **14** was isolated in 36% yield. For **1x** and **1y**, the starting materials were consumed and no recognizable products were isolated. **1z** was inert under standard conditions and was recovered in 93% yield after 4.0 h.

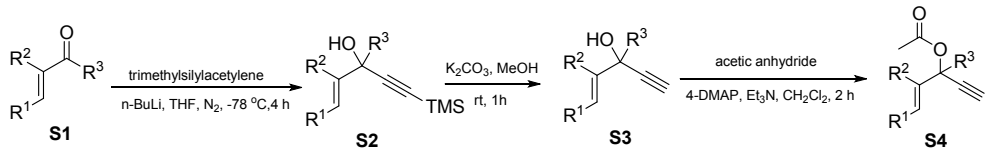
3. NMR monitoring of the reaction of 1a



The reaction of **1a** was carried out in $CDCl_3$ in order to monitor the reaction directly. Obviously, most of **1a** was converted to a compound and a little amount of desired product **6a** within 30 min. The formed compound was disappeared gradually along with the formation of **6a,** and was transformed to **6a** completely at last. Thus, it was safe enough to infer that this compound should be the key intermediate in the reaction. According to the experimental facts as well as some typical NMR signals as indicated in the monitoring spectra, this intermediate should be **5a**.

4. Synthetic procedures and spectra data of 1-sulfonyl-1,2,3-triazole

4.1 General procedures for preparation of S4



4.1.1 Synthesis of polysubstituted-5-(trimethylsilyl)pent-1-en-4-yn-3-ol (S2)[1]

General Procedure: In a dry flask, trimethylsilyl acetylene (11 mmol, 1.6 mL) was added into 10 mL of dry THF at -78 °C and then 7 mL of n-butyllithium (11 mmol, 2.4 M / THF) was slowly added. After 1 h of stirring, a solution of **S1** (10 mmol) in 5 mL THF was added by dropping funnel. The yellow solution was quenched after 2 h at -78 °C with saturated ammonium chloride aqueous solution. The aqueous phase was extracted twice with diethyl ether (2×10 mL), the combined organic layer was washed with water, brine, and then dried over Na_2SO_4, after filtration, the filtrate was concentrated to give crude **S2**.

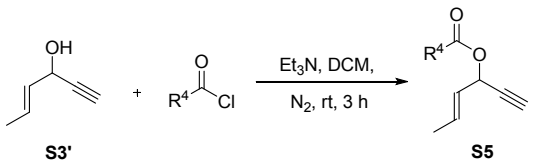
4.1.2 Synthesis of polysubstituted-pent-1-en-4-yn-3-ol (S3) [2]

General Procedure: To polysubstituted-5-(trimethylsilyl)pent-1-en-4-yn-3-ol (**S2**) a solution of K_2CO_3 (0.552 g, 4 mmol) in 30 mL MeOH was added and the mixture was stirred at room temperature, until TLC analysis showed that **S2** was completely consumed. The reaction mixture was filtered through a short plug of silica gel. The filtration was concentrated and then purified by flash chromatography to give the corresponding product **S3**.

4.1.3 Synthesis of polysubstituted-pent-1-en-4-yn-3-yl acetate (S4) [1]

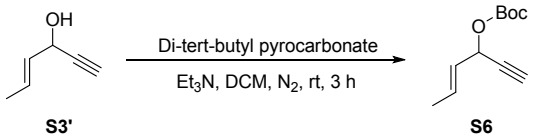
General Procedure: Acetic anhydride (20 mmol, 1.9 mL) was added to a mixture of polysubstituted-pent-1-en-4-yn-3-ol (**S3**) (10 mmol), 4-(dimethylamino) pyridine (2 mmol, 0.246 g) and triethylamine (20 mmol, 2.8 mL) in 10 mL of dry dichloromethane. The reaction mixture was stirred for 5 h and then poured into ethyl acetate. The solution was washed with 1 M HCl and saturated sodium bicarbonate aqueous solution. Each separate aqueous layer was extracted twice with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4, after filtration, the filtrate was concentrated. Purification by flash chromatography gave the corresponding product **S4**.

4.2 Synthesis of substituted hex-4-en-1-yn-3-yl ester (S5) [3]



General Procedure: To a 100 mL flask containing hex-4-en-1-yn-3-ol (**S3'**) (10 mmol, 1.38 g), DCM (15 mL) and Et_3N (1.7 mL, 12 mmol), acyl chloride (12 mmol) was added and the mixture was kept at 0 °C for 2 h. Then the solution was warmed to rt and kept for 1 h. The mixture was then poured into ethyl acetate. The organic layer was washed with 1 M HCl and then with saturated sodium bicarbonate aqueous solution. Each separate aqueous layer was extracted twice with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4, after filtration, the filtrate was concentrated and the residue was purified by flash chromatography to give the corresponding product **S5**.

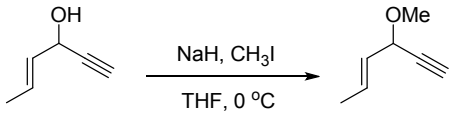
4.3 Synthesis of substituted tert-butyl hex-4-en-1-yn-3-yl carbonate (S6)



S3' **S6**

Di-*tert*-butyl pyrocarbonate (20 mmol, 4.6 mL) was added to a mixture of hex-4-en-1-yn-3-ol (**S3'**) (10 mmol，0.96 g), 4-(dimethylamino) pyridine (2 mmol, 0.246 g), and triethylamine (20 mmol, 2.8 mL) in 10 mL of dry dichloromethane. The reaction mixture was stirred for 5 h and then was then poured into ethyl acetate. The solution was washed with 1 M HCl and then with saturated sodium bicarbonate aqueous solution. Each separate aqueous layer was extracted twice with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4, after filtration, the filtrate was concentrated. The crude product was purified by flash chromatography with PE/EtOAc (100:1) as eluent to give the corresponding product **S6** (2.8 g, 94%) as a yellow oil.

4.4 Synthesis of 3-methoxyhex-4-en-1-yne (S7)

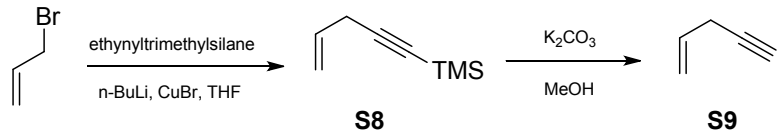


S3' **S7**

Under a nitrogen atmosphere, dry THF (10 mL) was added to a flask charged with NaH (0.32 g, 8 mmol) and S3' (0.576g 6 mmol). The reaction mixture was cooled in an ice-water bath. Subsequently, CH_3I (0.5 mL, 8 mmol) was added slowly and the reaction mixture was stirred

under 0 °C until TLC analysis showed that S3' was completely consumed. The reaction was quenched with brine. Each separate aqueous layer was extracted twice with ether. The combined organic layer was washed with brine, dried over Na_2SO_4, after filtration, the filtrate was concentrated giving crude **S7** without further purification.

4.5 Synthesis of pent-1-en-4-yne (S9)



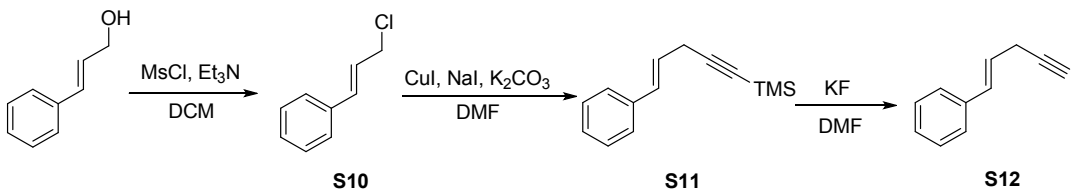
4.5.1 Synthesis of trimethyl(pent-4-en-1-yn-1-yl)silane (S8)[4]

n-BuLi in hexanes (2.4 M, 4.6 mL, 11mmol) was added into a solution of trimethylsilyl acetylene (1.4 mL, 10 mmol) in THF (20 mL) at -78 °C. After stirred at -78 °C for 30 min, CuBr (72 mg, 0.5 mmol) and allyl bromide (0.95 mL, 11 mmol) were added and the reaction temperature was increased to 50 °C. After stirred at 50 °C for 5 h, the reaction mixture was quenched with saturated NH_4Cl aqueous solution. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, dried over $MgSO_4$, after filtration, the filtrate was concentrated. The crude product was purified by flash column chromatography with PE/EtOAc (100:1) as eluent to give **S8** as a colorless oil (1.69 g, 82%).

4.5.2 Synthesis of pent-1-en-4-yne (S9)

To trimethyl(pent-4-en-1-yn-1-yl)silanea, the solution of K_2CO_3 (0.552 g, 4 mmol) in 30 mL MeOH was added and the mixture was stirred overnight at rt. The reaction was quenched by water, and then the mixture was poured into ether. After removal of MeOH by washing with water, the organic layer was dried over $MgSO_4$ and the ether was removed via distillation after filtration leaving crude **S9** without further purification.

4.6 Synthesis of pent-1-en-4-yn-1-ylbenzene (S12) [5]



4.6.1 Synthesis of (3-chloroprop-1-en-1-yl)benzene (S10)

MsCl (1.2 mL, 15 mmol) was added into a solution of 3-phenylprop-2-en-1-ol (1.34g 10 mmol) and trietylamine (3mL, 20 mmol) in DCM (10 mL) at 0 °C. After stirred for 1h at the same temperature, the mixture was poured into DCM (20 mL). The organic layer was washed with 1M HCl, saturated $NaHCO_3$ and brine, dried over $MgSO_4$. After filtration, the filtrate was evaporated to give crude **S10** (930 mg, 60% yield) which used directly in the next step.

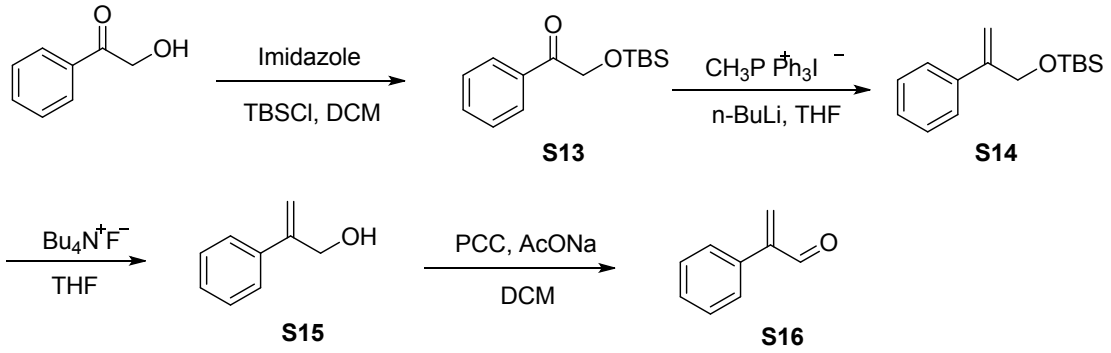
4.6.2 Synthesis of trimethyl(5-phenylpent-4-en-1-yn-1-yl)silane (S11)

Trimethylsilyl acetylene (0.8 mL, 6mmol) and (3-chloroprop-1-en-1-yl)benzene (930 mg, 6 mmol) were added to a suspension of copper (I) iodide (1.14 g, 6 mmol), sodium iodide (1.78 g, 12 mmol) and potassium carbonate (1.6g 12 mmol) in DMF (20 mL) at rt. The reaction was stirred overnight, and then quenched with saturated aqueous solution of NH_4Cl. The mixture was then extracted with ether (3×20 mL). The organic layer was washed with water (3×20 mL), then dried over $MgSO_4$. After filtration, the filtrate was concentrated. The crude product was purified by flash column chromatography with PE/EtOAc (100:1) as eluent to give the corresponding product (730 mg, 57 % yield) as a colorless oil.

4.6.3 Synthesis of pent-1-en-4-yn-1-ylbenzene (S12)

To a solution of trimethyl(5-phenylpent-4-en-1-yn-1-yl)silane (730 mg, 3 mmol) in DMF (10 mL), KF (340 mg, 6 mmol) was added at rt and stirred for 5 h. For workup, the mixture was diluted with ether and washed with brine. The combined organic phase was dried over $MgSO_4$, and after filtration, the filtrate was condensed under vacuum. The crude product was purified by flash column chromatography with PE as eluent to give the corresponding product (200 mg, 47 % yield) as a colorless oil.

4.7 Synthesis of 2-phenylacrylaldehyde (S16)



4.7.1 Synthesis of 2-((tert-butyldimethylsilyl)oxy)-1-phenylethanone (S13)

TBSCl (1.86 g, 12 mmol) was added into a solution of 2-hydroxy-1-phenylethanone (1.4g 10

mmol) and imidazole (1.02 g, 15 mmol) in DCM (15 mL) at 0 °C. After stirred for 0.5 h at the same temperature, the mixture was poured into saturated $NaHCO_3$ aqueous solution. The organic layer was dried over $MgSO_4$. After filtration, the filtrate was concentrated to give crude **S13** (2.4 g, 96% yield) which was used directly in the next step.

4.7.2 Synthesis of tert-butyldimethyl((2-phenylallyl)oxy)silane (S14)

In a dry flask, $CH_3P^+Ph_3I^-$(5.05 g, 12.5 mmol) was added into 20 mL of dry THF at 0 °C and then 7.5 mL of n-butyllithium (12 mmol, 2.4 M / THF) was slowly added. After 1 h of stirring, a solution of **S13** in 5 mL THF was added by dropping funnel. The yellow solution was quenched after 2 h at 0 °C with saturated ammonium chloride aqueous solution. The aqueous phase was extracted twice with petroleum ether (2×20 mL), the combined organic layer was washed with brine, and then dried over Na_2SO_4, after filtration with short silica gel, the filtrate was concentrated to give crude **S14** (2.2 g. 92%) which was used directly in the next step.

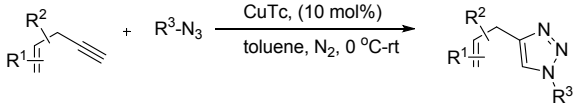
4.7.3 Synthesis of 2-phenylprop-2-en-1-ol (S15)

Tetrabutylammonium fluoride (15 mL, 15 mol, 1 M / THF) was added into a solution of S14 in THF (5 mL) at 0 °C. After stirred for 0.5 h at the same temperature, ice bath was removed. The mixture was stirred at room temperature for 1 h, then poured into ice water. The aqueous phase was extracted twice with EtOAc, the combined organic layer was washed with brine, and then dried over Na_2SO_4, after filtration, the filtrate was concentrated. Purification by flash chromatography gave the corresponding product **S15** (1.1 g, 91%).

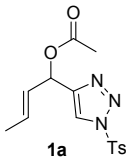
4.7.4 Synthesis of 2-phenylacrylaldehyde (S16)

S15 in DCM (10 mL) was added into a solution of PCC (4.3 g, 20 mmol) and AcONa (136 mg, 2 mmol) in DCM (10 mL) at 0 °C. After stirred for 10 min at the same temperature, ice bath was removed. The mixture was stirred at room temperature for 4 h. The reaction mixture was filtered through a short plug of silica gel. The filtration was concentrated and then purified by flash chromatography to give the **S16** (972 mg, 35%).

4.8 General procedures for synthesis of 1-sulfonyl-1,2,3-triazoles[6]

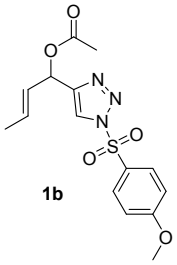


Under a nitrogen atmosphere, dry toluene (15 mL) was added to a flask charged with copper (I) thiophene-2-carboxylate (CuTC, 0.095 g, 0.5 mmol, 0.1 equiv in regards to alkyne) and the alkyne (5 mmol, 1 equiv). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (6 mmol, 1.2 equiv) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture was allowed to warm to room temperature and stirred until TLC analysis showed that alkyne was completely consumed. The reaction mixture filtered through a short plug of silica gel. The filtrate was concentrated and then purified by flash chromatography with PE/EtOAc (2:1) as eluent to give the corresponding product **1**.



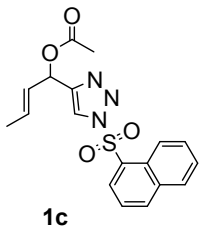
1a

1-(1-tosyl-1H-1,2,3-triazol-4-yl)but-2-en-1-yl acetate (1a): yellow oil, yield: 76.4%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 6.37 (d, *J* = 7.4 Hz, 1H), 5.92-5.75 (m, 2H), 2.46 (s, 3H), 2.07 (s, 3H), 1.74 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 147.5, 146.2, 132.8, 132.2, 130.5, 128.8, 126.3, 121.9, 68.5, 21.9, 21.1, 17.8. HRMS (ESI) calcd for $C_{15}H_{17}N_3NaO_4S^+$ 358.0837, found 358.0838.



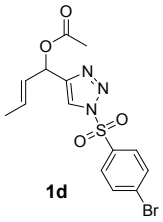
1b

1-(1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)but-2-en-1-yl acetate (1b): yellow oil, yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.04 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.36 (d, *J* = 7.3 Hz, 1H), 5.94 – 5.73 (m, 2H), 3.88 (s, 3H), 2.06 (s, 3H), 1.73 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 165.5, 146.1, 132.2, 131.3, 126.6, 126.3, 121.8, 115.1, 68.5, 56.0, 21.2, 17.8. HRMS (ESI) calcd for $C_{15}H_{17}N_3NaO_5S^+$ 374.0787, found 374.0787.



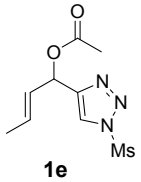
1c

1-(1-(naphthalen-1-ylsulfonyl)-1H-1,2,3-triazol-4-yl)but-2-en-1-yl acetate (1c): yellow oil, yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.19 (s, 1H), 8.03 – 7.97 (m, 3H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.61 (m, 2H), 6.38 (d, *J* = 7.3 Hz, 1H), 5.95 – 5.73 (m, 2H), 2.07 (s, 3H), 1.72 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 146.4, 136.0, 132.5, 132.3, 131.8, 131.4, 130.6, 130.4, 129.8, 128.4, 128.1, 126.2, 122.22, 122.16, 68.5, 21.5, 17.8. HRMS (ESI) calcd for $C_{18}H_{17}N_3NaO_4S^+$ 394.0837, found 394.0837.



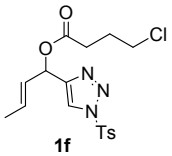
1d

1-(1-((4-bromophenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)but-2-en-1-yl acetate (1d): yellow oil, yield: 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 6.35 (d, *J* = 7.4 Hz, 1H), 5.91 – 5.75 (m, 2H), 2.06 (s, 3H), 1.72 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 146.5, 134.8, 133.3, 132.3, 131.6, 130.1, 126.2, 122.1, 68.4, 21.1, 17.8. HRMS (ESI) calcd for $C_{14}H_{14}BrN_3NaO_4S^+$ 421.9786, found 421.9786.



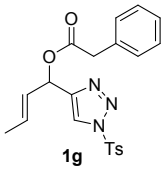
1e

1-(1-(methylsulfonyl)-1H-1,2,3-triazol-4-yl)but-2-en-1-yl acetate (1e): yellow oil, yield: 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 6.38 (d, *J* = 7.3 Hz, 1H), 5.95 – 5.76 (m, 2H), 3.53 (s, 3H), 2.07 (s, 3H), 1.73 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 146.4, 132.3, 126.2, 122.1, 68.4, 42.7, 21.1, 17.8. HRMS (ESI) calcd for $C_9H_{13}N_3NaO_4S^+$ 282.0524, found 282.0527.



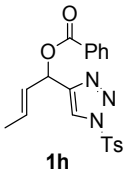
1f

1-(1-tosyl-1H-1,2,3-triazol-4-yl)but-2-en-1-yl 4-chlorobutanoate (1f): yellow oil, yield: 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.50 – 6.21 (d, *J* = 7.2 Hz, 1H), 5.93 – 5.70 (m, 2H), 3.54 (t, *J* = 6.3 Hz, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 2.08 – 2.01 (m, 2H), 1.70 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 147.6, 146.2, 132.7, 132.3, 130.5, 128.7, 126.2, 122.0, 68.6, 44.0, 31.3, 27.4, 21.9, 17.8. HRMS (ESI) calcd for $C_{17}H_{20}ClN_3NaO_4S^+$ 420.0761, found 420.0764.



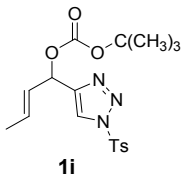
1g

1-(1-tosyl-1H-1,2,3-triazol-4-yl)but-2-en-1-yl 2-phenylacetate (1g): yellow oil, yield: 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.90 (s, 1H), 7.41 – 7.20 (m, 7H), 6.37 (d, *J* = 7.1 Hz, 1H), 5.90 – 5.69 (m, 2H), 3.64 (s, 2H), 2.44 (s, 3H), 1.71 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 147.5, 146.2, 133.6, 132.9, 132.4, 130.5, 129.3, 128.8, 128.6, 127.3, 126.2, 121.8, 69.0, 41.3, 21.9, 17.8. HRMS (ESI) calcd for $C_{21}H_{21}N_3NaO_4S^+$ 434.1150, found 4334.1149.



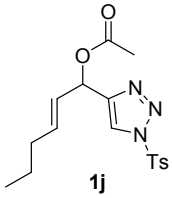
1h

1-(1-tosyl-1H-1,2,3-triazol-4-yl)but-2-en-1-yl benzoate (1h): yellow oil, yield: 49%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.06 – 7.97 (m, 4H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.32 (m, 4H), 6.65 (d, *J* = 6.6 Hz, 1H), 6.06 – 5.89 (m, 2H), 2.41 (s, 3H), 1.75 (d, *J* = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 147.5, 146.3, 133.3, 132.7, 132.2, 130.5, 129.7, 128.8, 128.4, 126.4, 122.1, 69.00, 21.8, 17.9. HRMS (ESI) calcd for $C_{20}H_{19}N_3NaO_4S^+$ 420.0994, found 420.0992.



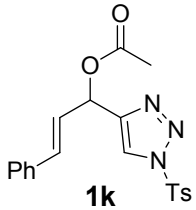
1i

tert-butyl (1-(1-tosyl-1H-1,2,3-triazol-4-yl)but-2-en-1-yl) carbonate (1i): white solid, m.p.: 110-112 °C, yield: 40%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.16 (d, *J* = 7.5 Hz, 1H), 5.95 – 5.70 (m, 2H), 2.41 (s, 3H), 1.71 (d, *J* = 6.3 Hz, 3H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 147.5, 146.2, 132.8, 132.4, 130.5, 128.7, 126.2, 122.0, 82.8, 71.4, 27.7, 21.8, 17.8. HRMS (ESI) calcd for $C_{18}H_{23}N_3NaO_4S^+$ 416.1256, found 416.1255.



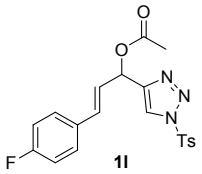
1j

1-(1-tosyl-1H-1,2,3-triazol-4-yl)hex-2-en-1-yl acetate (1j): yellow oil, yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 6.36 (d, *J* = 7.3 Hz, 1H), 5.89 – 5.67 (m, 2H), 2.41 (s, 3H), 2.07 – 1.97 (m, 5H), 1.41 – 1.32 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 147.5, 146.3, 137.1, 132.8, 130.5, 128.8, 125.1, 122.0, 68.5, 34.2, 21.83, 21.79, 21.1, 13.6. HRMS (ESI) calcd for $C_{17}H_{21}N_3NaO_4S^+$ 386.1150, found 386.1165.



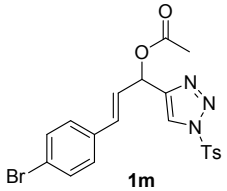
1k

3-phenyl-1-(1-tosyl-1H-1,2,3-triazol-4-yl)allyl acetate (1k): yellow oil, yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.30 (m, 3H), 6.74 (d, *J* = 15.7 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.47 (dd, *J* = 15.7, 7.6 Hz, 1H), 2.45 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 147.6, 145.9, 135.6, 134.8, 132.7, 130.5, 128.8, 128.6, 128.5, 126.9, 124.0, 122.2, 68.4, 21.9, 21.1. HRMS (ESI) calcd for $C_{20}H_{19}N_3NaO_4S^+$ 420.0994, found 420.0986.



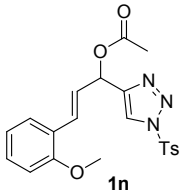
1l

3-(4-fluorophenyl)-1-(1-tosyl-1H-1,2,3-triazol-4-yl)allyl acetate (1l): yellow oil, yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.33 (m, 4H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 15.8 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.41 (dd, *J* = 15.8, 7.6 Hz, 1H), 2.45 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.80, 162.77 (d, *J* = 248.2 Hz), 147.62, 145.77, 133.66, 132.68, 131.75 (d, *J* = 3.3 Hz), 130.53, 128.83, 128.53 (d, *J* = 8.2 Hz), 123.73 (d, *J* = 2.1 Hz), 122.14, 115.60 (d, *J* = 21.7 Hz), 68.37, 21.87, 21.15. HRMS (ESI) calcd for $C_{20}H_{18}FN_3NaO_4S^+$ 438.0900, found 438.0901.



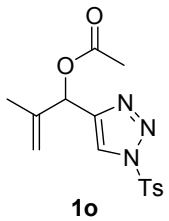
1m

3-(4-bromophenyl)-1-(1-tosyl-1H-1,2,3-triazol-4-yl)allyl acetate (1m): yellow solid, m.p.: 98-100 °C, yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.37 (m, 4H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 15.8 Hz, 1H), 6.58 (d, *J* = 7.4 Hz, 1H), 6.48 (dd, *J* = 15.8, 7.4 Hz, 1H), 2.44 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 147.6, 145.6, 134.5, 133.5, 132.7, 131.7, 130.5, 128.8, 128.4, 124.8, 122.4, 122.2, 68.2, 21.9, 21.1. HRMS (ESI) calcd for $C_{20}H_{18}BrN_3NaO_4S^+$ 498.0099, found 498.0098.



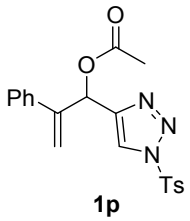
1n

3-(2-methoxyphenyl)-1-(1-tosyl-1H-1,2,3-triazol-4-yl)allyl acetate (1n): yellow oil, yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.34 (m, 3H), 7.30 – 7.25 (m, 1H), 7.09 (d, *J* = 14.9 Hz, 1H), 6.95 – 6.85 (m, 2H), 6.61 – 6.50 (m, 2H), 3.85 (s, 3H), 2.46 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 157.1, 147.5, 146.1, 132.8, 130.5, 130.0, 129.7, 128.8, 127.5, 124.41, 124.38, 122.2, 120.6, 110.9, 69.0, 55.4, 21.9, 21.2. HRMS (ESI) calcd for $C_{21}H_{21}N_3NaO_5S^+$ 450.1100, found 450.1103.



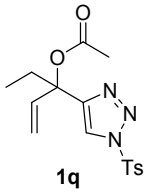
1o

2-methyl-1-(1-tosyl-1H-1,2,3-triazol-4-yl)allyl acetate (1o): yellow oil, yield: 30%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.28 (s, 1H), 5.05 (s, 1H), 4.92 (s, 1H), 2.30 (s, 3H), 1.99 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 147.6, 145.7, 140.7, 132.6, 130.5, 128.6, 122.3, 114.3, 70.7, 21.7, 20.8, 18.5. HRMS (ESI) calcd for $C_{15}H_{17}N_3NaO_4S^+$ 358.0837, found 358.0840.



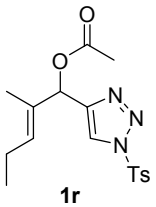
1p

2-phenyl-1-(1-tosyl-1H-1,2,3-triazol-4-yl)allyl acetate (1p): white solid, m.p.: 129-131 °C, yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.28 – 7.26 (m, 3H), 6.96 (s, 1H), 5.58 (s, 1H), 5.52 (s, 1H), 2.41 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 147.6, 145.7, 145.0, 137.9, 132.7, 130.5, 128.7, 128.5, 128.3, 126.7, 123.0 , 115.8, 68.7, 21.8, 21.0. HRMS (ESI) calcd for $C_{20}H_{19}N_3NaO_4S^+$ 420.0994, found 420.0986.



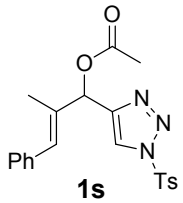
1q

3-(1-tosyl-1H-1,2,3-triazol-4-yl)pent-1-en-3-yl acetate (1q): yellow solid, m.p.: 69-71 °C, yield: 20%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.19 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.32 (d, *J* = 11.1 Hz, 1H), 5.22 (d, *J* = 17.5 Hz, 1H), 2.48 (s, 3H), 2.47 – 2.25 (m, 2H), 2.08 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 148.8, 147.4, 138.1, 132.8, 130.5, 128.6, 122.1, 115.9, 80.8, 30.9, 21.8, 21.7, 7.5. HRMS (ESI) calcd for $C_{16}H_{19}N_3NaO_4S^+$ 372.0994, found 372.0985.



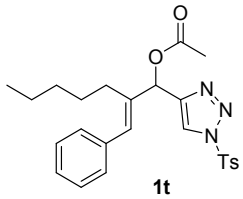
1r

2-methyl-1-(1-tosyl-1H-1,2,3-triazol-4-yl)pent-2-en-1-yl acetate (1r): yellow oil, yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.31 (s, 1H), 5.61 (t, *J* = 7.1 Hz, 1H), 2.42 (s, 3H), 2.08 (s, 3H), 2.05 – 1.99 (m, 2H), 1.58 (s, 3H), 0.94 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 147.5, 146.3, 132.7, 132.7, 130.5, 130.1, 128.7, 121.7, 73.0, 21.8, 21.1, 21.0, 13.6, 12.4. HRMS (ESI) calcd for $C_{17}H_{21}N_3NaO_4S^+$ 386.1150, found 380.1154.



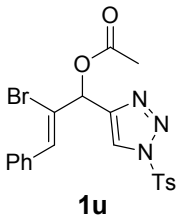
1s

2-methyl-3-phenyl-1-(1-tosyl-1H-1,2,3-triazol-4-yl)allyl acetate (1s): yellow oil, yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.24 (m, 7H), 6.73 (s, 1H), 6.52 (s, 1H), 2.47 (s, 3H), 2.17 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 147.6, 145.9, 136.4, 133.4, 132.7, 130.5, 129.5, 129.1, 128.8, 128.2, 127.1, 121.9, 73.0, 21.9, 21.1, 14.5. HRMS (ESI) calcd for $C_{21}H_{21}N_3NaO_4S^+$ 434.1150, found 434.1152.



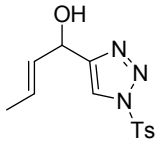
1t

2-benzylidene-1-(1-tosyl-1H-1,2,3-triazol-4-yl)heptyl acetate (1t): yellow oil, yield: 69%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.31 (m, 2H), 7.29 – 7.24 (m, 3H), 6.68 (s, 1H), 6.56 (s, 1H), 2.48 (s, 3H), 2.39 – 2.26 (m, 1H), 2.17 (s, 3H), 2.15 – 2.04 (m, 1H), 1.31 – 1.20 (m, 2H), 1.31 – 1.17 (m, 4H), 0.84 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 147.5, 146.3, 138.7, 136.6, 132.8, 130.5, 128.8, 128.7, 128.6, 128.3, 127.1, 122.1, 71.0, 31.9, 29.0, 28.2, 22.3, 21.9, 21.2, 14.0. HRMS (ESI) calcd for $C_{25}H_{29}N_3NaO_4S^+$ 490.1776, found 490.1776.



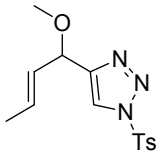
1u

2-bromo-3-phenyl-1-(1-tosyl-1H-1,2,3-triazol-4-yl)allyl acetate (1u): yellow oil, yield: 69%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.36 (s, 1H), 8.01 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.23 (m, 6H), 6.78 (s, 1H), 2.41 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 147.7, 144.7, 134.1, 132.8, 132.6, 130.6, 129.3, 128.9, 128.8, 128.2, 122.9, 120.4, 72.8, 21.9, 21.0. HRMS (ESI) calcd for $C_{20}H_{18}BrN_3NaO_4S^+$ 498.0099, found 498.0097.



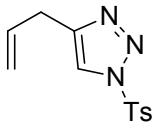
1v

1-(1-tosyl-1H-1,2,3-triazol-4-yl)but-2-en-1-ol (1v): yellow oil, yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 5.92 – 5.53 (m, 2H), 5.38 – 5.13 (m, 1H), 3.72 (s, 1H), 2.40 (s, 3H), 1.65 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 147.4, 132.8, 130.51, 130.48, 129.3, 128.6, 121.0, 67.4, 21.8, 17.7. HRMS (ESI) calcd for $C_{13}H_{16}N_3O_3S^+$ 294.0912, found 294.0919.



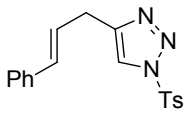
1w

4-(1-methoxybut-2-en-1-yl)-1-tosyl-1H-1,2,3-triazole (1w): yellow oil, yield: 69%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s,1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 5.91 – 5.81 (m, 1H), 5.59 – 5.50 (m, 1H), 4.81 (d, *J* = 8.0 Hz, 1H), 3.33 (s, 3H), 2.43 (s, 3H), 1.74 (d, *J* = 7.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 147.4, 132.9, 131.4, 130.4, 128.7, 128.4, 121.1, 76.7, 56.3, 21.8, 17.8. HRMS (ESI) calcd for $C_{14}H_{18}N_3O_3S^+$ 308.1069, found 308.1082.



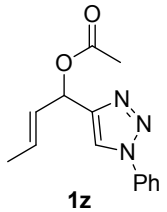
1x

4-allyl-1-tosyl-1H-1,2,3-triazole (1x): yellow oil, yield: 12%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.86 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 5.96 – 5.86 (m, 1H), 5.18 – 5.10 (m, 2H), 3.50 – 3.45 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 146.4, 133.6, 133.1, 130.4, 128.6, 120.9, 117.8, 29.9, 21.9. HRMS (ESI) calcd for $C_{12}H_{13}N_3O_2S^+$ 264.0807, found 264.0812.



1y

4-cinnamyl-1-tosyl-1H-1,2,3-triazole (1y): white solid, m.p.: 110-112 °C, yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.94 (s, 1H), 7.40 – 7.31 (m, 6H), 7.28 – 7.24 (m, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.36 – 6.29 (m , 1H), 3.71 – 3.63 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 146.6, 136.7, 133.1, 132.8, 130.5, 128.64, 128.61, 127.6, 126.3, 125.1, 123.0, 29.2, 21.9. HRMS (ESI) calcd for $C_{18}H_{18}N_3O_2S^+$ 340.1120, found 340.1134.

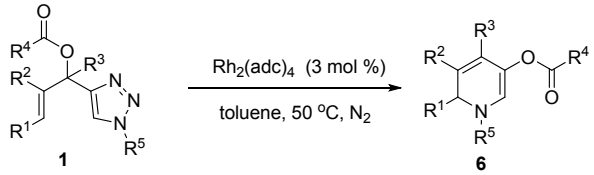


1z

1-(1-phenyl-1H-1,2,3-triazol-4-yl)but-2-en-1-yl acetate (1z): yellow oil, yield: 53%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 6.49 – 6.43 (m, 1H), 5.98 – 5.92 (m, 2H), 2.11 (s, 3H), 1.79 (d, *J* = 4.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 147.2, 136.9, 131.5, 129.7, 128.9, 126.9, 120.62, 120.57, 69.0, 21.3, 17.8. HRMS (ESI) calcd for $C_{14}H_{16}N_3O_2^+$ 258.1243, found 258.1247.

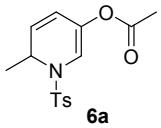
5. Reaction scope

Procedure for the preparation of 6



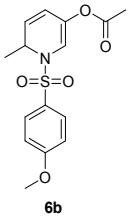
1 6

General procedure: Under a nitrogen atmosphere, dry toluene (2.0 mL) was added to reaction flask charged with $Rh_2(adc)_4$ (0.006 mmol) and 1-sulfonyl-1,2,3-triazoles **1** (0.2 mmol) at room temperature. Then the reaction mixture was stirred at 50 °C for the indicated time in the manuscript. The reaction mixture was cooled to room temperature and filtered through a short plug of silica gel. The filtrate was concentrated and the residue was purified by flash chromatography with PE/EtOAc (8:1) as eluent to give the corresponding product **6**.



6a

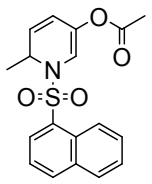
6-methyl-1-tosyl-1,6-dihydropyridin-3-yl acetate (6a): white solid, m.p.: 94-96 °C, 53 mg, yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.51 (s, 1H), 5.61 (d, *J* = 9.9 Hz, 1H), 5.38 (dd, *J* = 9.9, 6.1 Hz, 1H), 4.64 – 4.57 (m, 1H), 2.41 (s, 3H), 2.18 (s, 3H), 1.28 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 143.8, 137.7, 136.7, 129.7, 126.7, 124.5, 120.1, 114.7, 50.1, 21.6, 20.8, 20.2. HRMS (ESI) calcd for $C_{15}H_{17}NNaO_4S^+$ 330.0776, found 330.0772.



6b

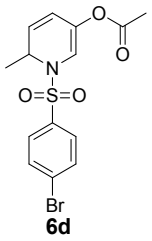
1-((4-methoxyphenyl)sulfonyl)-6-methyl-1,6-dihydropyridin-3-yl acetate (6b): yellow oil, 57 mg, yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.49 (s, 1H), 5.60 (d, *J* = 9.7 Hz, 1H), 5.37 (dd, *J* = 9.7, 6.1 Hz, 1H), 4.63 – 4.51 (m, 1H), 3.84 (s, 3H), 2.17 (s, 3H), 1.26 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 163.1, 137.8, 131.2, 128.8, 124.5, 120.1, 114.7, 114.2, 55.6, 50.0, 20.8, 20.1. HRMS (ESI) calcd for

$C_{15}H_{17}NNaO_5S^+$ 346.0725, found 346.0730.



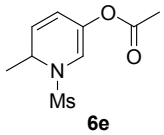
6c

6-methyl-1-(naphthalen-1-ylsulfonyl)-1,6-dihydropyridin-3-yl acetate (6c): yellow oil, 58.8 mg, yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.98 – 7.88 (m, 3H), 7.81 (d, *J* = 10.2 Hz, 1H), 7.63 (m, 2H), 6.63 (s, 1H), 5.58 (d, *J* = 9.9 Hz, 1H), 5.36 (dd, *J* = 9.9, 5.8 Hz, 1H), 4.83 – 4.49 (m, 1H), 2.18 (s, 3H), 1.32 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 137.9, 136.6, 134.9, 132.0, 129.5, 129.4, 128.9, 128.1, 127.9, 127.5, 124.6, 121.9, 120.2, 114.7, 50.2, 20.8, 20.2. HRMS (ESI) calcd for $C_{18}H_{17}NNaO_4S^+$ 366.0776, found 366.0780.



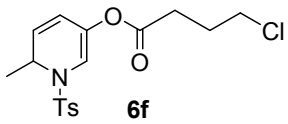
6d

1-((4-bromophenyl)sulfonyl)-6-methyl-1,6-dihydropyridin-3-yl acetate (6d): yellow oil, 52 mg, yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 6.49 (s, 1H), 5.62 (d, *J* = 9.9 Hz, 1H), 5.41 (dd, *J* = 9.9, 5.8 Hz, 1H), 4.63 – 4.56 (m, 1H), 2.19 (s, 3H), 1.30 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 138.5, 138.5, 132.3, 128.2, 128.0, 124.9, 120.2, 114.3, 50.3, 20.7, 20.1. HRMS (ESI) calcd for $C_{14}H_{14}BrNNaO_4S^+$ 393.9725, found 393.9728.



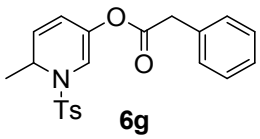
6e

6-methyl-1-(methylsulfonyl)-1,6-dihydropyridin-3-yl acetate (6e): yellow oil, 32.4 mg, yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (s, 1H), 5.90 (d, *J* = 9.9 Hz, 1H), 5.71 (dd, *J* = 9.6, 6.1 Hz, 1H), 4.68 – 4.62 (m, 1H), 2.92 (s, 3H), 2.20 (s, 3H), 1.29 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 138.1, 125.1, 120.6, 114.5, 50.2, 39.1 , 20.7, 20.1. HRMS (ESI) calcd for $C_9H_{13}NNaO_4S^+$ 254.0463, found 254.0461.



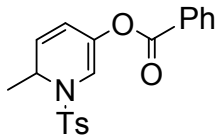
6f

6-methyl-1-tosyl-1,6-dihydropyridin-3-yl 4-chlorobutanoate (6f): yellow oil, 55.8mg, yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.52 (s, 1H), 5.61 (d, *J* = 10.3 Hz, 1H), 5.39 (dd, *J* = 10.3, 5.8 Hz, 1H), 4.67 – 4.45 (m, 1H), 3.64 (t, *J* = 6.2 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 2.28 – 2.04 (m, 2H), 1.28 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 143.9, 137.5, 136.7, 129.8, 126.6, 124.5, 120.0, 114.8, 50.1, 43.9, 30.9, 27.3, 21.6, 20.1. HRMS (ESI) calcd for $C_{17}H_{20}ClNNaO_4S^+$ 392.0699, found 392.0694.



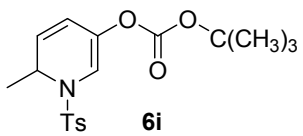
6g

6-methyl-1-tosyl-1,6-dihydropyridin-3-yl 2-phenylacetate (6g): yellow oil, 64.7 mg, yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.27 (m, 7H), 6.54 (s, 1H), 5.59 (d, *J* = 10.3 Hz, 1H), 5.38 (dd, *J* = 10.3, 5.8 Hz, 1H), 4.63 – 4.57 (m, 1H), 3.76 (s, 2H), 2.42 (s, 3H), 1.28 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 143.9, 137.7, 136.7, 133.1, 129.7, 129.3, 128.8, 127.5, 126.7, 124.5, 120.0, 114.8, 50.1, 40.9, 21.6, 20.1. HRMS (ESI) calcd for $C_{21}H_{21}NNaO_4S^+$ 406.1089, found 406.1079.



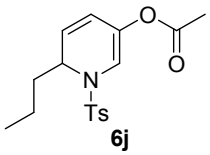
6h

6-methyl-1-tosyl-1,6-dihydropyridin-3-yl benzoate (6h): yellow oil, 60.6 mg, yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 8.1 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.67 (s, 1H), 5.75 (d, *J* = 9.8 Hz, 1H), 5.45 (dd, *J* = 9.8, 6.2 Hz, 1H), 4.70 – 4.63 (m, 1H), 2.44 (s, 3H), 1.35 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 143.9, 137.9, 136.8, 133.8, 130.1, 129.7, 128.6, 126.7, 124.5, 120.2, 114.9, 50.2, 21.6, 20.2. HRMS (ESI) calcd for $C_{20}H_{19}NNaO_4S^+$ 392.0932, found 392.0929.



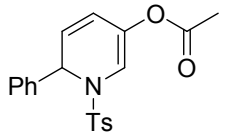
6i

tert-butyl (6-methyl-1-tosyl-1,6-dihydropyridin-3-yl) carbonate (6i): yellow oil, 66 mg, yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.25 (m, 2H), 6.57 (s, 1H), 5.68 (d, *J* = 9.9 Hz, 1H), 5.39 (dd, *J* = 9.9, 5.8 Hz, 1H), 4.65 – 4.59 (m, 1H), 2.41 (s, 3H), 1.52 (s, 9H), 1.29 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 143.8, 138.2, 136.7, 129.6, 126.7, 124.4, 119.9, 114.6, 83.9, 50.1, 27.6, 21.6, 20.2. HRMS (ESI) calcd for $C_{18}H_{23}NNaO_4S^+$ 388.1195, found 388.1188.



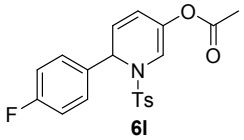
6j

6-propyl-1-tosyl-1,6-dihydropyridin-3-yl acetate (6j): yellow oil, 40.1 mg, yield: 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.20 (m, 2H), 6.46 (s, 1H), 5.57 (d, *J* = 9.8 Hz, 1H), 5.38 (dd, *J* = 9.8, 5.8 Hz, 1H), 4.53 – 4.49 (m, 1H), 2.41 (s, 3H), 2.17 (s, 3H), 1.76 – 1.37 (m, 4H), 0.94 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 143.7, 139.1, 136.6, 129.5, 126.8, 124.2, 120.3, 114.8, 54.0, 35.7, 21.6, 20.7, 17.7, 13.8. HRMS (ESI) calcd for $C_{17}H_{21}NNaO_4S^+$ 358.1089, found 358.1086.



6k

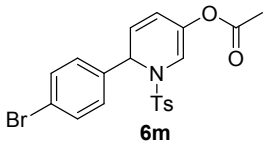
6-phenyl-1-tosyl-1,6-dihydropyridin-3-yl acetate (6k): yellow solid, m.p.: 120-122 °C, 39.2 mg, yield: 53%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.24 (m, 5H), 6.51 (s, 1H), 5.88 (d, *J* = 9.9 Hz, 1H), 5.70 (d, *J* = 6.1 Hz, 1H), 5.57 (dd, *J* = 9.9, 6.1 Hz, 1H), 2.42 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3,143.9, 138.5, 138.4, 136.5, 129.6, 128.6, 128.5, 127.5, 126.9, 122.2, 121.5, 115.2, 56.5, 21.6, 20.7. HRMS (ESI) calcd for $C_{20}H_{19}NNaO_4S^+$ 392.0932, found 392.0933.



6l

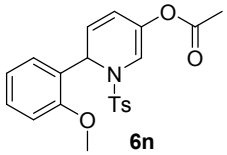
6-(4-fluorophenyl)-1-tosyl-1,6-dihydropyridin-3-yl acetate (6f): white solid, m.p.: 128-130 °C, 38.4 mg, yield: 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.54 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.47 (s, 1H), 5.89 (d, *J* = 9.9 Hz, 1H),

5.67 (d, J = 6.0 Hz, 1H), 5.53 (dd, J = 9.9, 6.0 Hz, 1H), 2.42 (s, 3H), 2.18 (s, 3H). ^{13}H NMR (100 MHz, $CDCl_3$) δ 169.39, 162.83 (d, J = 246.8 Hz), 144.05, 138.46, 136.38, 134.09 (d, J = 3.0 Hz), 129.68, 129.57 (d, J = 8.3 Hz), 126.82, 121.79 (d, J = 3.5 Hz), 115.41 (d, J = 21.5 Hz), 115.04, 55.67, 21.62, 20.70. HRMS (ESI) calcd for $C_{20}H_{18}FNNaO_4S^+$ 410.0838, found 410.0839.



6m

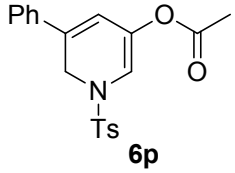
6-(4-bromophenyl)-1-tosyl-1,6-dihydropyridin-3-yl acetate (6m): white solid, m.p.: 147-149 °C, 51.6 mg, yield: 58%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.47 – 7.41(m, 4H), 7.27 (d, J = 8.0 Hz, 2H), 6.48 (s, 1H), 5.88 (d, J = 9.8 Hz, 1H), 5.64 (d, J = 6.1 Hz 1H), 5.52 (dd, J = 9.8, 6.1 Hz, 1H), 2.43 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 144.1, 138.4, 137.2, 136.3, 131.7, 129.7, 129.4, 126.8, 122.7, 122.0, 121.3, 115.2, 55.7, 21.7, 20.7. HRMS (ESI) calcd for $C_{20}H_{18}BrNNaO_4S^+$ 470.0038, found 470.0034.



6n

6-(2-methoxyphenyl)-1-tosyl-1,6-dihydropyridin-3-yl acetate (6n): yellow solid, m.p.: 123-125 °C, 35.2 mg, yield: 44%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 7.6 Hz, 1H), 7.29 – 7.20 (m, 3H), 6.91 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.77 (s, 1H), 6.05 (d, J = 5.2 Hz, 1H), 5.72 – 5.59 (m, 2H), 3.85 (s, 3H), 2.42 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 154.4, 143.8, 137.0, 136.3, 129.5, 129.1, 128.7, 127.6, 127.0, 123.4, 120.9, 119.4, 116.1, 110.4, 55.4, 52.3, 21.6, 20.8. HRMS (ESI) calcd for $C_{21}H_{21}NNaO_5S^+$ 422.1038, found 422.1045.

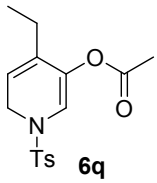
Compound **6o** is not stable upon silica gel column purification, we did a one pot reaction by treating the crude product with KOH to furnish compound **8o** (see below for more details).



6p

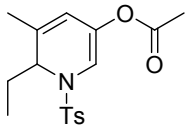
5-phenyl-1-tosyl-1,6-dihydropyridin-3-yl acetate (6p): yellow oil, 45 mg, yield: 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.23 (d, J = 7.9 Hz, 4H), 6.69 (s,

1H), 5.99 (s, 1H), 4.60 (s, 2H), 2.39 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 144.1, 139.4, 136.3, 134.9, 129.7, 129.4, 128.6, 128.4, 127.0, 125.2, 117.3, 116.1, 46.1, 21.6, 20.8. HRMS (ESI) calcd for $C_{20}H_{19}NNaO_4S^+$ 392.0932, found 392.0931.



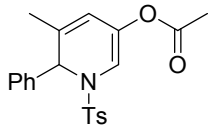
6q

4-ethyl-1-tosyl-1,6-dihydropyridin-3-yl acetate (6q): yellow oil, 27.1 mg, yield: 42%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.53 (s, 1H), 5.09 – 5.06 (m, 1H), 4.17 – 4.12 (m, 2H), 2.41 (s, 3H), 2.18 (s, 3H), 1.86 – 1.77 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 144.0, 138.9, 135.2, 135.1, 129.7, 127.2, 117.9, 112.9, 44.3, 22.3, 21.6, 20.5, 12.0. HRMS (ESI) calcd for $C_{16}H_{20}NO_4S^+$ 322.1113, found 322.1099.



6r

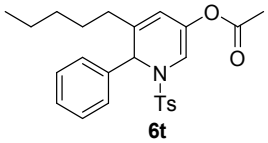
6-ethyl-5-methyl-1-tosyl-1,6-dihydropyridin-3-yl acetate (6r): white solid, m.p.: 116-118 °C, 28.8 mg, yield: 43%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.32 (s, 1H), 5.24 (s, 1H), 4.14 (dd, *J* = 9.6, 3.5 Hz, 1H), 2.41 (s, 3H), 2.16 (s, 3H), 1.75 – 1.45 (m, 2H), 1.54 (s, 3H), 1.03 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 143.6, 141.1, 136.1, 134.5, 129.4, 126.5, 115.7, 111.7, 59.8, 23.7, 21.6, 20.8, 20.7, 9.9. HRMS (ESI) calcd for $C_{17}H_{21}NNaO_4S^+$ 358.1089, found 358.1092.



6s

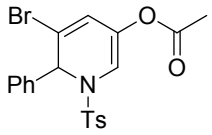
5-methyl-6-phenyl-1-tosyl-1,6-dihydropyridin-3-yl acetate (6s): yellow solid, m.p.: 124-126 °C, 26.2 mg, yield: 34%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.26 (m, 5H), 6.31 (s, 1H), 5.62 (s, 1H), 5.40 (s, 1H), 2.43 (s, 3H), 2.18 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 143.8, 140.0, 136.7, 135.9, 132.1, 129.5, 128.6, 127.9, 126.7, 117.6, 112.1, 60.7, 21.6, 20.8. HRMS (ESI) calcd for $C_{21}H_{21}NNaO_4S^+$ 406.1089,

found 406.1094.



6t

5-pentyl-6-phenyl-1-tosyl-1,6-dihydropyridin-3-yl acetate (6t): yellow solid, m.p.: 133-135 °C, 44.5 mg, yield: 51%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 6.3 Hz, 2H), 7.38 – 7.25 (m, 5H), 6.34 (s, 1H), 5.63 (s, 1H), 5.40 (s, 1H), 2.42 (s, 3H), 2.20 (s, 3H), 1.95 – 1.85 (m, 1H), 1.78 – 1.71(m, 1H), 1.23 – 0.99 (m, 6H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 143.8, 140.0, 137.1, 136.3, 129.5, 128.6, 128.5, 128.1, 126.8, 116.6, 112.4, 59.5, 34.0, 31.2, 26.5, 22.4, 21.6, 20.8, 13.9. HRMS (ESI) calcd for $C_{25}H_{29}NNaO_4S^+$ 462.1715, found 462.1714.

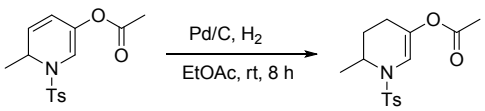


6u

5-bromo-6-phenyl-1-tosyl-1,6-dihydropyridin-3-yl acetate (6u): white solid, m.p.: 161-163 °C, 51.2 mg, yield: 57%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.53 (m, 2H), 7.43 – 7.35 (m, 3H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.47 (s, 1H), 6.21 (s, 1H), 5.84 (s, 1H), 2.45 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 144.4, 138.8, 135.3, 135.0, 129.7, 129.0, 128.7, 127.8, 126.9, 124.1, 114.0, 113.8, 63.1, 21.7, 20.6. HRMS (ESI) calcd for $C_{20}H_{18}BrNNaO_4S^+$ 470.0038, found 470.0037.

6. Procedure for derivation of products

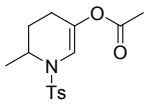
6.1 Synthesis of 6-methyl-1-tosyl-1,4,5,6-tetrahydropyridin-3-yl acetate[7]



6a **7a**

6-methyl-1-tosyl-1,6-dihydropyridin-3-yl acetate **6a** (0.2 mmol, 61.4 mg) was dissolved in MeOH (2.0 mL) and added to an oven-dried tube equipped with Pd/C (10 wt %) and a stir bar. The atmosphere was replaced by H_2 (H_2 balloon bubbling) and stirred for 8.0 h at rt until **6a** was completely consumed by TLC monitoring. Then the reaction mixture was filtered through a short

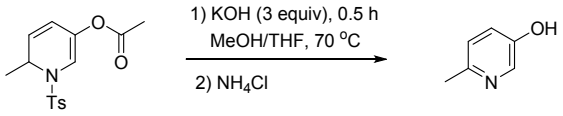
plug of silica gel. The filtrate was concentrated and the residue was purified by flash chromatography with PE/EtOAc (8:1) as eluent to give the corresponding product **7a** as a white solid**.**



7a

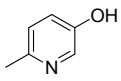
6-methyl-1-tosyl-1,4,5,6-tetrahydropyridin-3-yl acetate (7a): white solid, m.p.: 117°C~119°C, 55.5 mg, yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.63 (s, 1H), 4.11 – 3.98 (m, 1H), 2.43 (s, 3H), 2.35 – 2.26 (m, 1H), 2.15 (s, 3H), 1.95 – 1.87 (m, 1H), 1.46 (dd, *J* = 13.5, 6.7 Hz, 1H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.15 – 1.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 143.7, 135.9, 135.6, 129.8, 127.0, 115.5, 48.2, 24.5, 21.6, 20.8, 20.3, 17.9. HRMS (ESI) calcd for $C_{15}H_{20}NO_4S^+$ 310.1113, found 310.1112.

6.2 Synthesis of 6-methylpyridin-3-ol[8]



6a **8a**

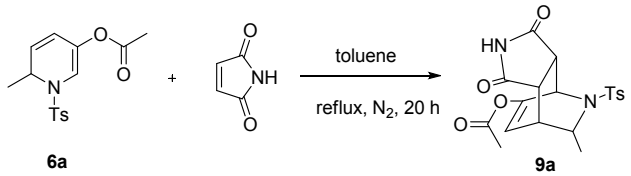
In a 10 mL round-bottom flask equipped with a stir bar, 6-methyl-1-tosyl-1,6-dihydropyridin-3-yl acetate **6a** (0.2 mmol, 61.4 mg) and KOH (0.6 mmol, 33.6 mg) were added. Subsequently, 2 mL of THF and methanol (v/v = 1/1) was added, and the mixture was kept at 70 °C for 0.5 h. Then the mixture was cooled to room temperature and 1 mL saturated NH_4Cl acqueous solution was added. The reaction mixture filtered through a short plug of silica gel. The filtrate was concentrated and the residue was purified by flash chromatography with EtOAc as eluent to give the corresponding product **8a** (18.4 mg, 84%) as a white solid.



8a

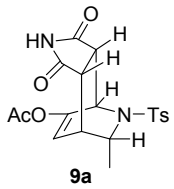
6-methylpyridin-3-ol (8a)[9]: white solid, 18.4 mg, yield: 84%; ^{1}H NMR (400 MHz, DMSO-d6) δ 9.69 (s, 1H), 8.04 (s, 1H), 7.12 – 7.05 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 151.4, 147.8, 136.7, 123.2, 122.6, 22.8.

6.3 Synthesis of 8-methyl-1,3-dioxo-9-tosyl-2,3,3a,4,7,7a-hexahydro-1H-4,7-(epiminomethano)isoindol-5-yl acetate[10]



6a 9a

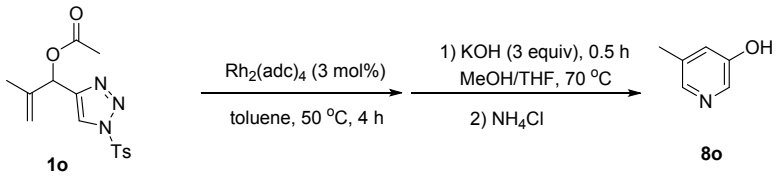
In a nitrogen-protected round-bottom flask with a stir bar, 6-methyl-1-tosyl-1,6-dihydropyridin-3-yl acetate **6a** (0.2 mmol, 61.4 mg), 1H-pyrrole-2,5-dione (0.6 mmol, 58.3 mg), and dry toluene (2 mL) were added. The reaction mixture was refluxed at 120 °C for 20 h. The resulting mixture was cooled to room temperature, and filtered through a short plug of silica gel. The filtrate was concentrated and the residue was purified by flash chromatography with PE/EtOAc (1:1) as eluent to give the corresponding product **9a** (76 mg, 94%) as a colourless oil**.**



9a

8-methyl-1,3-dioxo-9-tosyl-2,3,3a,4,7,7a-hexahydro-1H-4,7-(epiminomethano)isoindol-5-yl acetate (9a): yellow oil, 76 mg, yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.86 (dd, *J* = 7.1, 1.8 Hz, 1H), 4.68 (dd, *J* = 4.1, 2.0 Hz, 1H), 3.81 – 3.73 (m, 1H), 3.33 (dd, *J* = 8.0, 4.2 Hz, 1H), 3.27 (dt, *J* = 7.1, 2.6 Hz, 1H), 2.86 (dd, *J* = 8.0, 3.0 Hz, 1H), 2.44 (s, 3H), 2.12 (s, 3H), 1.16 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 175.6, 167.7, 148.4, 144.1, 137.0, 129.9, 127.4, 112.2, 53.9, 52.2, 45.3, 42.9, 39.5, 21.6, 21.0, 20.9. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_6S^+$ 405.1120, found 405.1117.

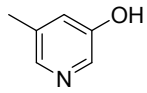
6.4 Synthesis of 6-methylpyridin-3-ol



1o 8o

Under a nitrogen atmosphere, dry toluene (2.0 mL) was added to a reaction flask charged with $Rh_2(adc)_4$ (0.006 mmol), 2-methyl-1-(1-tosyl-1H-1,2,3-triazol-4-yl)allyl acetate **1o** (0.2 mmol, 67 mg) and a stir bar at room temperature. Then the mixture was stirred at 50 °C for 4 h. The reaction mixture was cooled to room temperature and then evaporated in vacuo; KOH (0.6 mmol, 33.6 mg)

was added to the flask. Subsequently, 2 mL of THF and methanol (v/v = 1/1) was added, and the mixture was kept at 70 °C for 0.5 h. Then the mixture was cooled to room temperature and 1 mL saturated NH_4Cl aqueous solution was added. The reaction mixture was filtered through a short plug of silica gel. The filtrate was concentrated and purified by flash chromatography with EtOAc as eluent to give the corresponding product **8o** (11 mg, 51%) as a white solid.

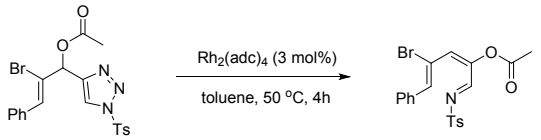


8o

5-methylpyridin-3-ol (8o)[11]: white solid, 11 mg, yield: 51%; ^{1}H NMR (400 MHz, DMSO-d6) δ 9.78 (s, 1H), 7.94 – 7.87 (m, 2H), 6.97 (s, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 153.8, 141.2, 135.6, 134.1, 122.9, 18.2.

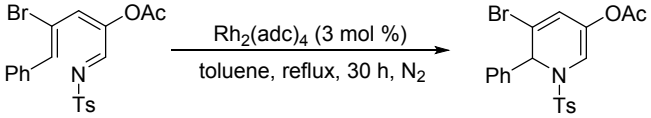
7. Isolation and transformation of the intermediates

Synthesis of 4-bromo-5-phenyl-1-(tosylimino)penta-2,4-dien-2-yl acetate 5u



1u **5u**

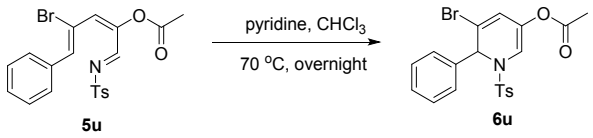
Under a nitrogen atmosphere, dry toluene (2.0 mL) was added to a reaction flask charged with $Rh_2(adc)_4$ (0.006 mmol), 2-bromo-3-phenyl-1-(1-tosyl-1H-1,2,3-triazol-4-yl)allyl acetate **1t** (0.2 mmol, 95 mg) and a stir bar was at room temperature. Then the mixture was stirred at 50 °C. After 4 h, the reaction mixture was cooled to room temperature and filtered through a short plug of silica gel. The filtrate was concentrated and purified by flash chromatography with PE/EtOAc (6:1) as eluent to give the corresponding product **5u** (18 mg, 20%) as a yellow solid and **6u** as a white solid (51.2 mg, 57%).



5u, 28% conversion **6u**, 25% yield

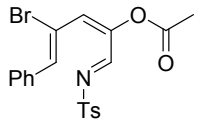
4-Bromo-5-phenyl-1-(tosylimino)penta-2,4-dien-2-yl acetate **5u** (45.0 mg, 0.1 mmol) was added to a sealed tube charged with $Rh_2(adc)_4$ (0.003 mmol) and a stir bar. Subsequently, 3 mL

dry toluene was added, and the mixture was kept at 120 °C for 30 h. The reaction mixture was cooled to room temperature and filtered through a short plug of silica gel. The solution of mixture was concentrated and purified by flash chromatography with PE/EtOAc (8:1) as eluent to give the corresponding product **6u** (11.3 mg, 25%) as a white solid and **5u**was recovered in 72% yield (32.4 mg).



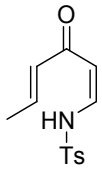
5u **6u**

5u (30 mg) was added to a sealed tube charged with a stir bar. Subsequently, 2 mL dry $CHCl_3$ and pyridine (48 mg, 3 equiv) were added, and the mixture was kept at 70 °C overnight. The reaction mixture was cooled to room temperature and filtered through a short plug of silica gel. The filtrate was concentrated and purified by flash column chromatography with PE/EtOAc (8:1) as eluent to give the corresponding product **6u** (20.9 mg, 70%) as a white solid.



5u

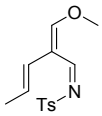
4-bromo-5-phenyl-1-(tosylimino)penta-2,4-dien-2-yl acetate (5u): yellow solid, m.p.: 139-141 °C, 18.0 mg, yield: 20%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.79 – 7.74 (m, 2H), 7.48 – 7.40 (m, 4H), 7.36 (d, *J* = 8.1 Hz, 2H), 6.93 (s, 1H), 2.46 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 165.0, 144.9, 142.8, 140.7, 138.7, 134.6, 134.3, 130.1, 130.0, 129.9, 128.5, 128.0, 112.8, 21.8, 20.7. HRMS (ESI) calcd for $C_{20}H_{19}BrNO_4S^+$ 448.0218, found 448.0213.



13

4-methyl-N-(3-oxohexa-1,4-dien-1-yl)benzenesulfonamide (13): yellow oil, yield: 24%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.84 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.11 (s, 1H), 6.87 (dq, *J* = 13.8, 6.8 Hz, 1H), 6.10 (d, *J* = 15.5 Hz, 1H), 5.59 (d, *J* = 8.4 Hz, 1H), 2.43 (s,

3H), 1.91 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 144.5, 143.1, 141.4, 137.0, 131.7, 130.0, 126.7, 101.8, 21.6, 18.4. HRMS (ESI) calcd for $C_{13}H_{16}NO_3S^+$ 266.0851, found 266.0857.



14

N-(2-(methoxymethylene)pent-3-en-1-ylidene)-4-methylbenzenesulfonamide (14): yellow oil, yield: 45%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.94 (s, 1H), 6.68 – 6.51 (m, 1H), 6.23 (d, J = 14.6 Hz, 1H), 4.05 (s, 3H), 2.44 (s, 3H), 1.81 (d, J = 8.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 168.1, 143.8, 136.5, 132.0, 129.6, 127.5, 118.6, 115.7, 63.3, 21.6, 19.5. HRMS (ESI) calcd for $C_{14}H_{18}NO_3S^+$ 280.1007, found 280.1013.

8. References

[1] C. Spino, C. Thibault and S. Gingras, *J. Org. Chem.*, 1998, **63**, 5283.

[2] J. He, Y. Shi, W. Cheng, Z. Man, D. Yang and C.-Y. Li, *Angew. Chem., Int. Ed.*, 2016, **55**, 4557.

[3] J. Zheng, T. Qi and S. Cui, *Org. Lett.*, 2016, **18**, 128.

[4] G. Zhu and Ei-ichi Negishi, *Chem. - Eur. J.*, 2008, **14**, 311.

[5] B. M. Trost and A. B. Pinkerton, *J. Org. Chem.*, 2001, **66**, 7714.

[6] J. Raushel and V. V. Fokin, *Org. Lett.*, 2010, **12**, 4952.

[7] B. Seo, W. H. JEOU, J. Kim, S. Kim and P. H. Lee, *J. Org. Chem.*, 2015, **80**, 722.

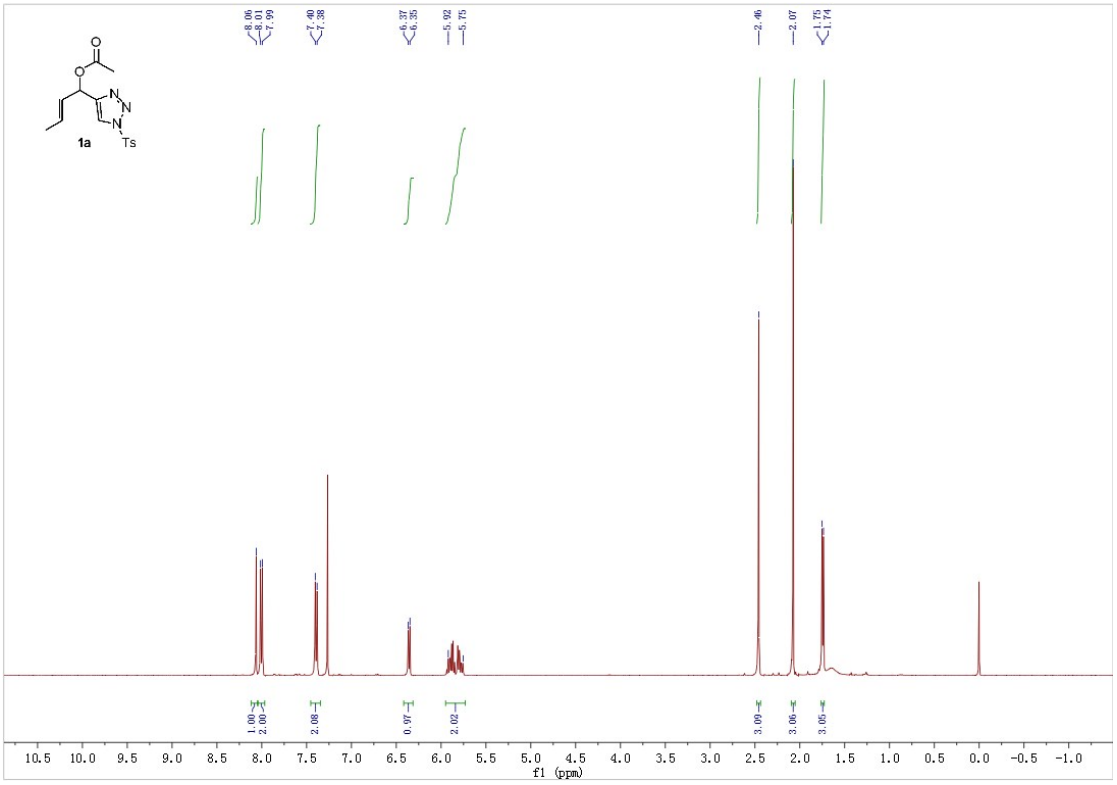
[8] S. Rajasekar and P. Anbarasan, *J. Org. Chem.*, 2014, **79**, 8428.

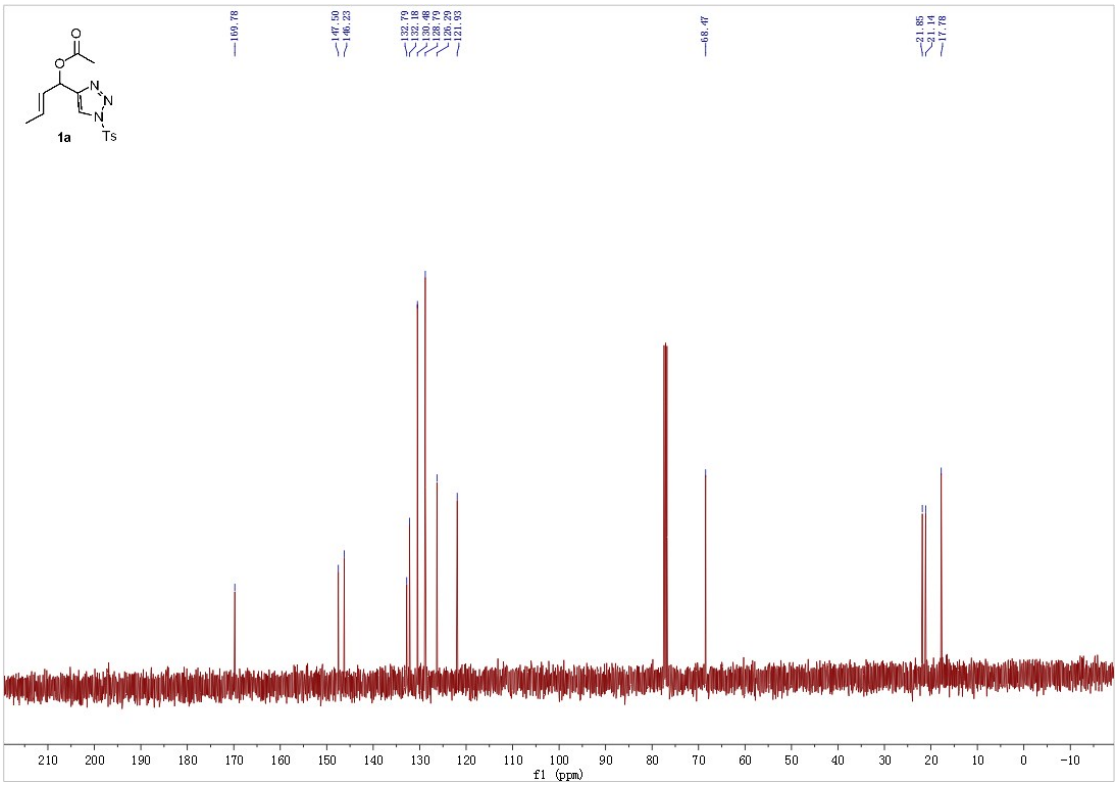
[9] D. Wang, D. Kuang, F. Zhang, S. Tang and W. Jiang, *Eur. J. Org. Chem.*, 2014, 315.

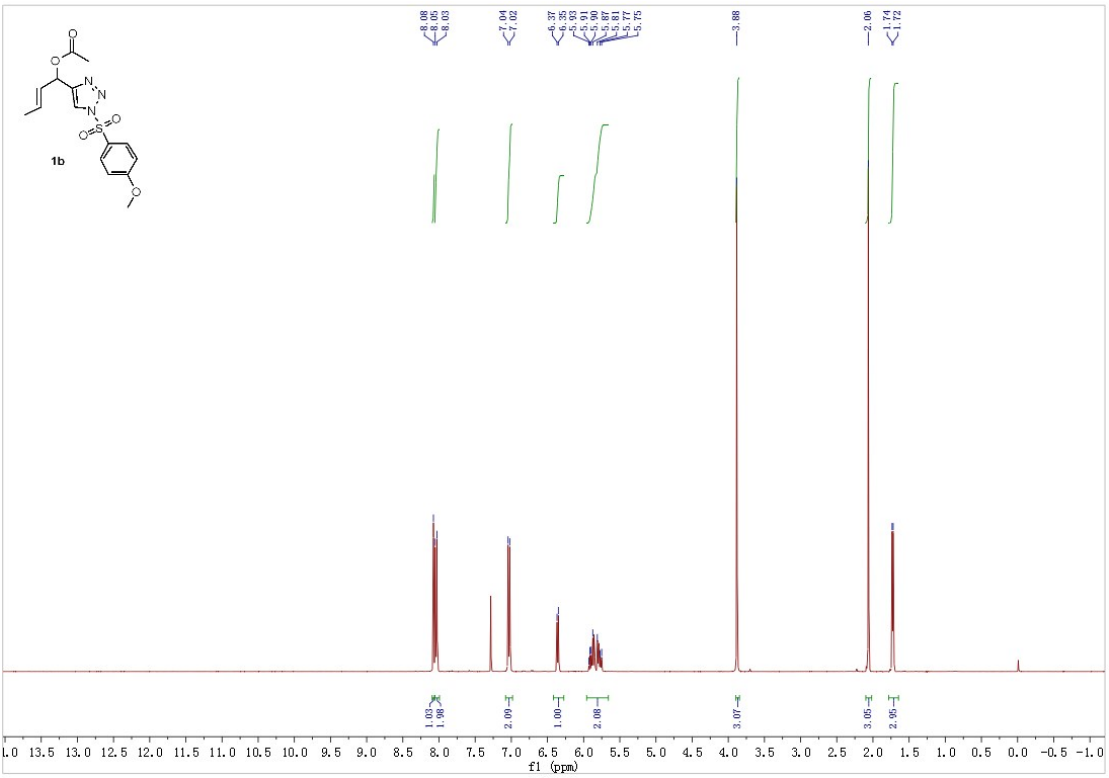
[10] Y. Funakoshi, T. Miura and M. Murakami, *Org. Lett.*, 2016, **18**, 6284.

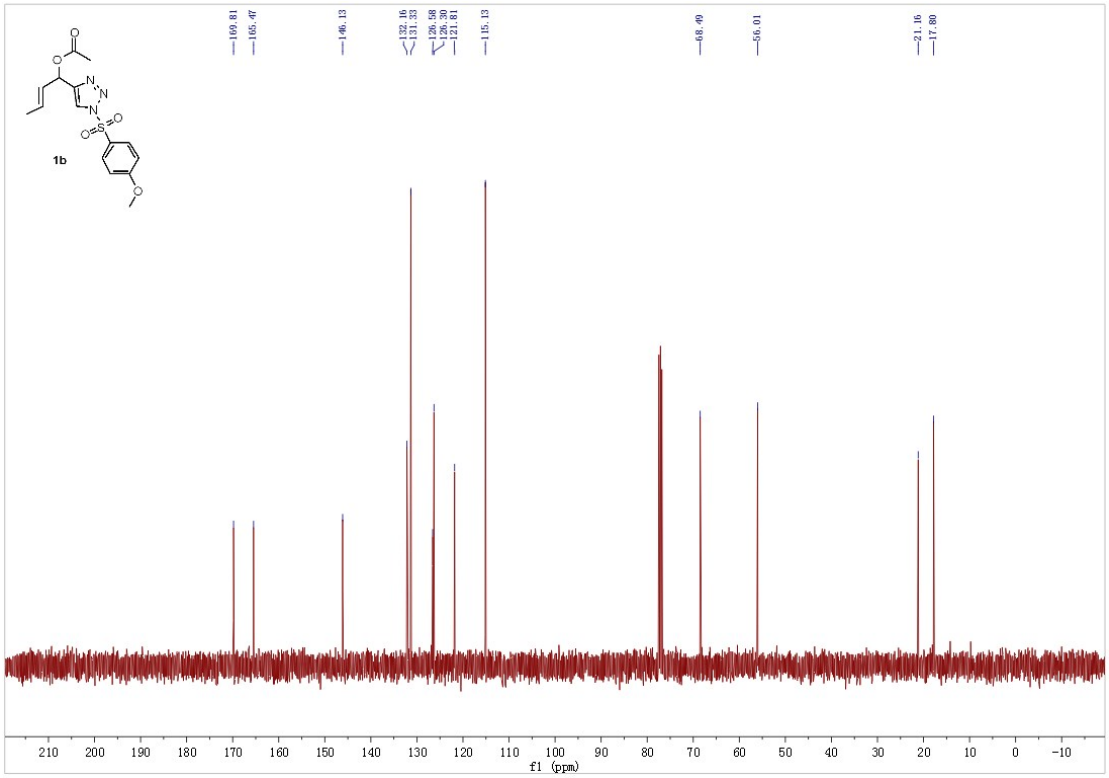
[11] L. Tian, J. Li and K. Wu, *J. Chem. Pharm. Res.*, 2014, **6**, 982.

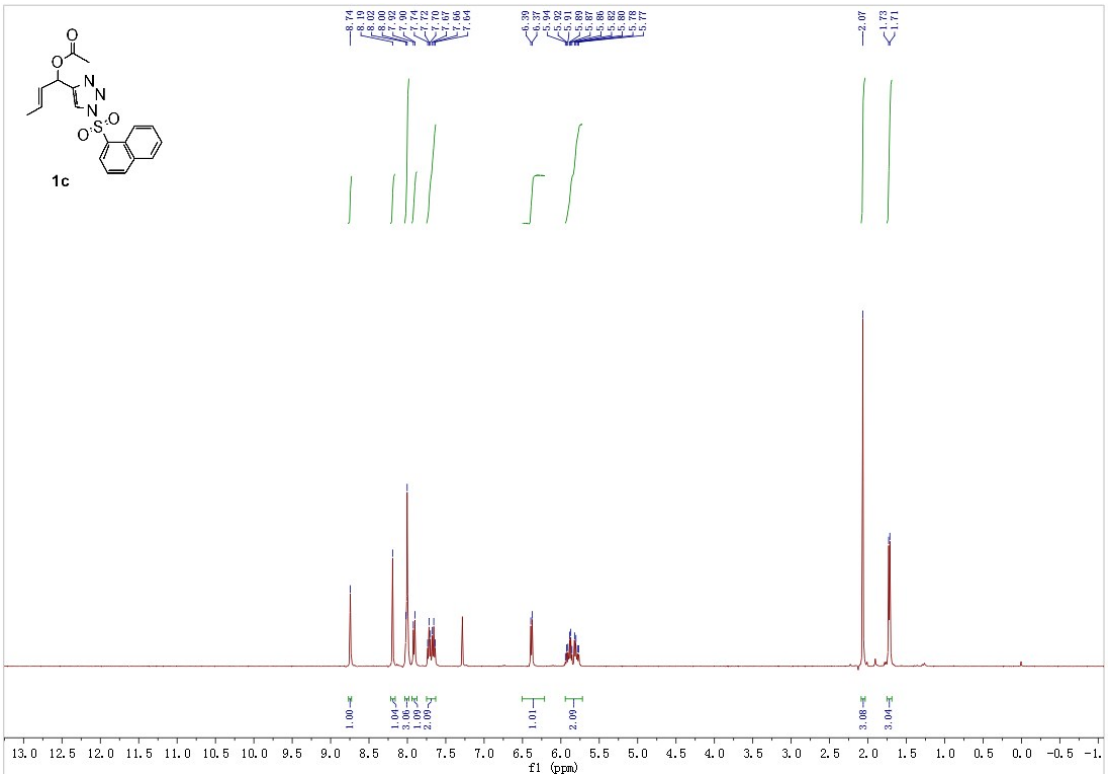
9. ^{1}H and ^{13}C NMR spectra for new compounds

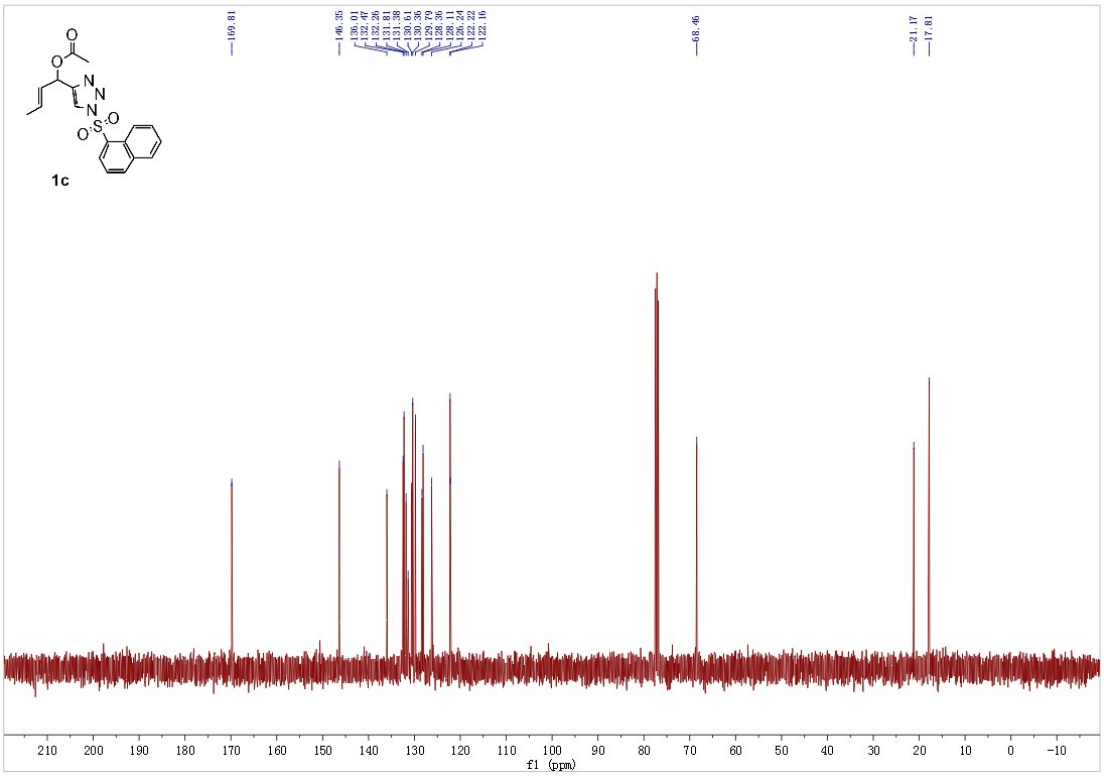


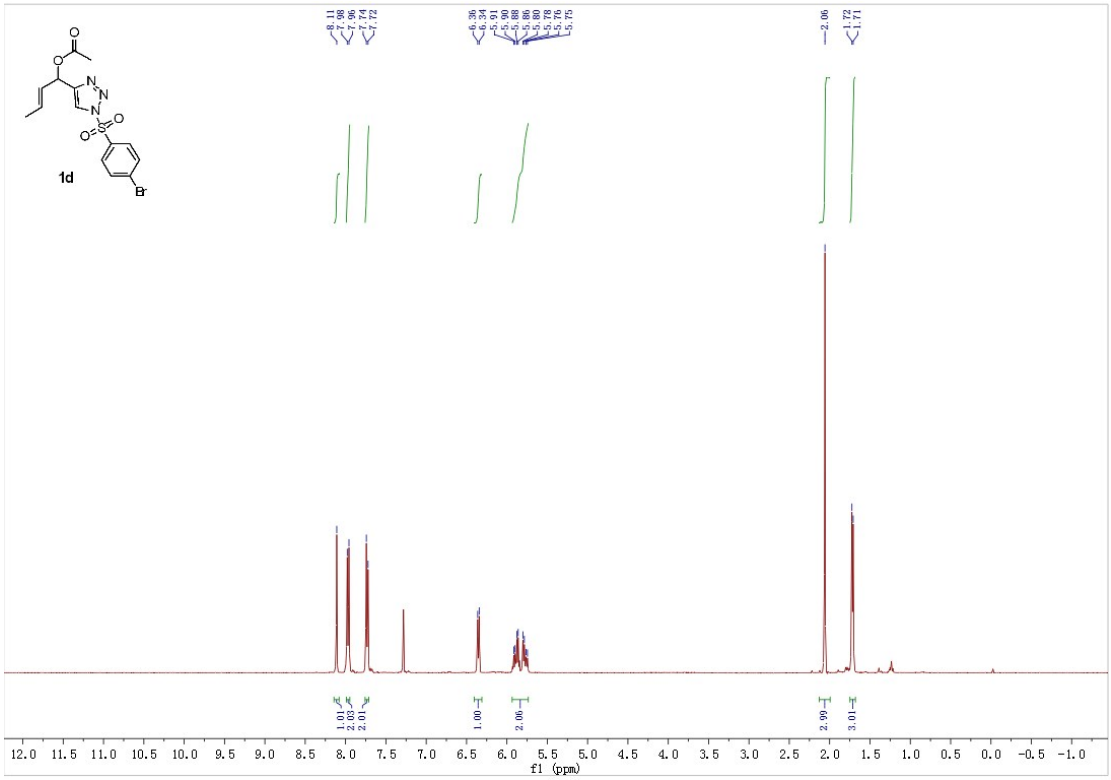


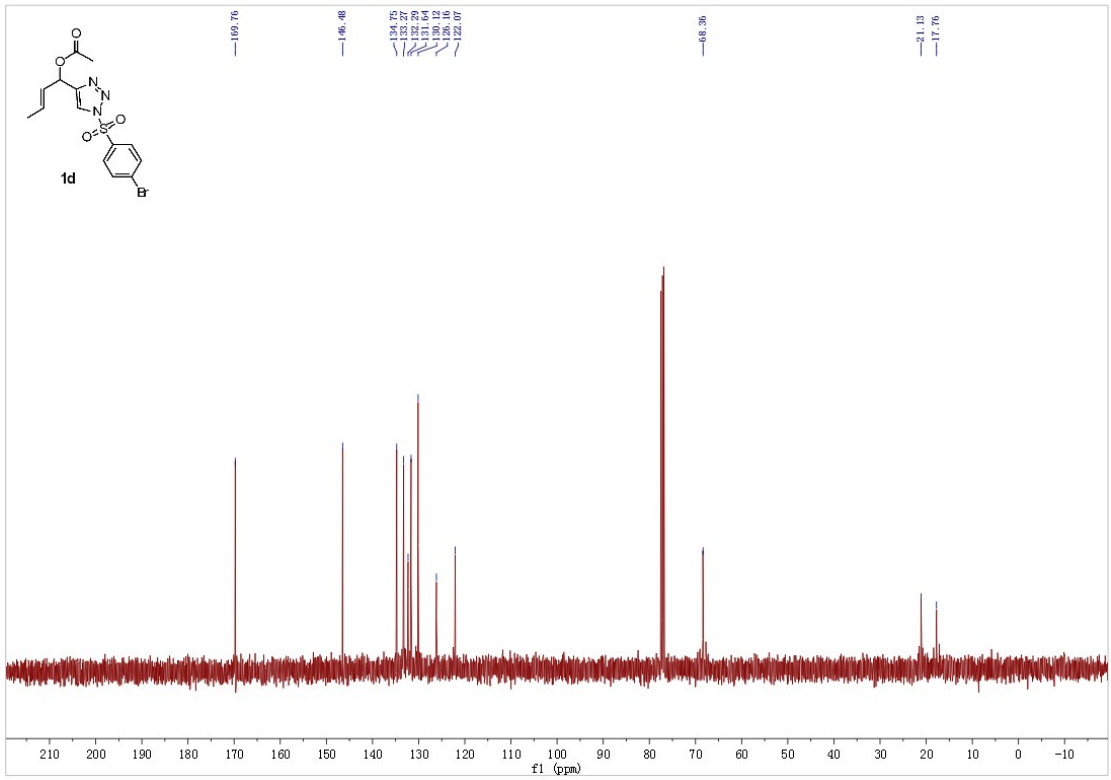

1b
8.08
8.05
8.03
7.04
7.02
6.37
6.35
5.91
5.90
5.87
5.81
5.77
5.75
3.88
2.06
1.74
1.72
1.03
1.98
2.09
1.00
2.08
3.07
3.05
2.96
f1 (ppm)

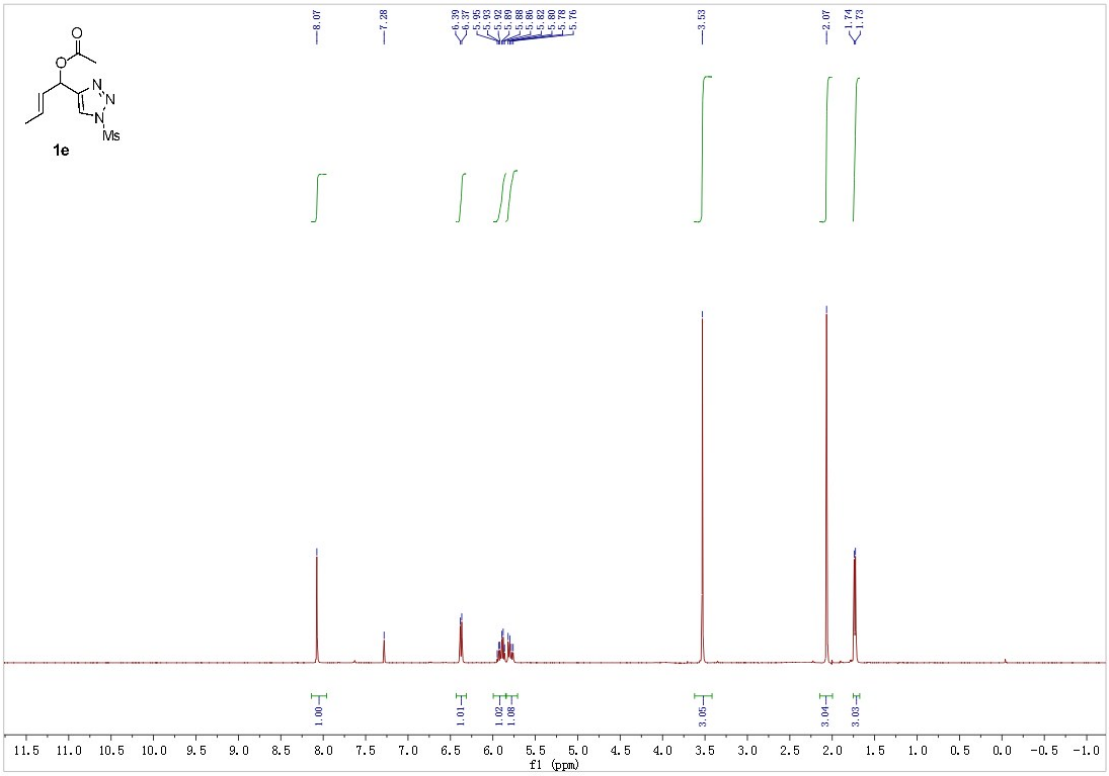

1b
169.81
165.47
146.13
132.16
131.33
126.58
126.30
121.81
115.13
68.49
56.01
21.16
17.80
f1 (ppm)

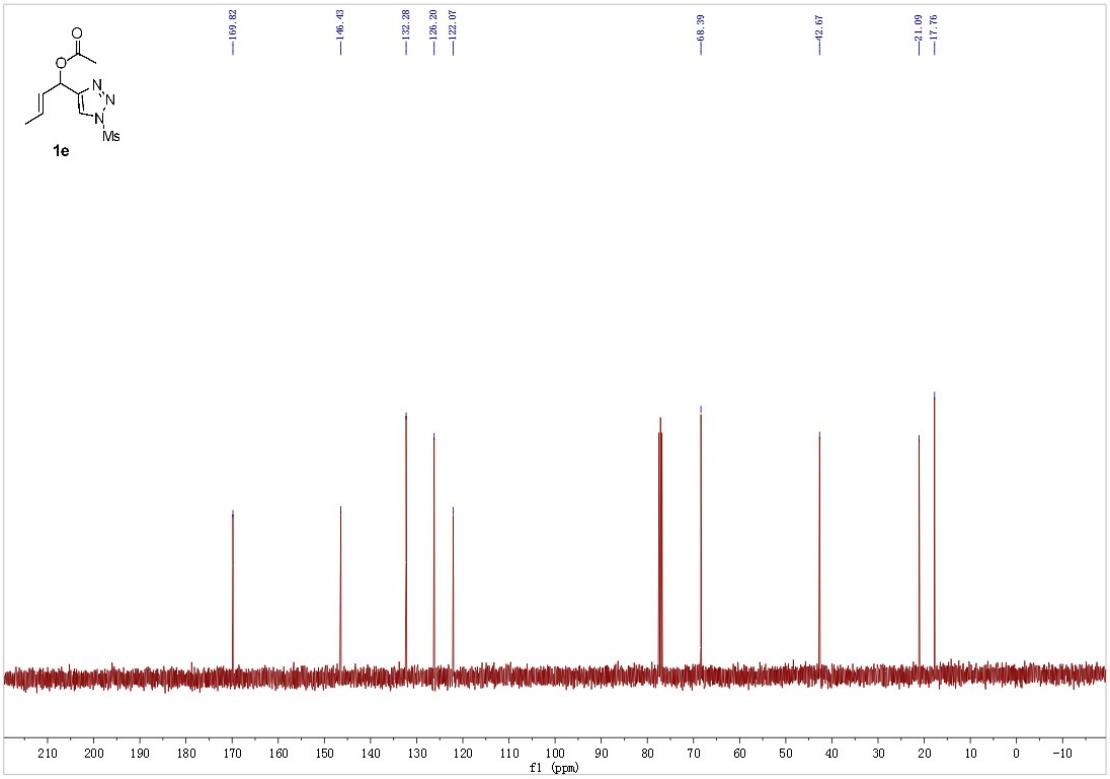

1c
f1 (ppm)

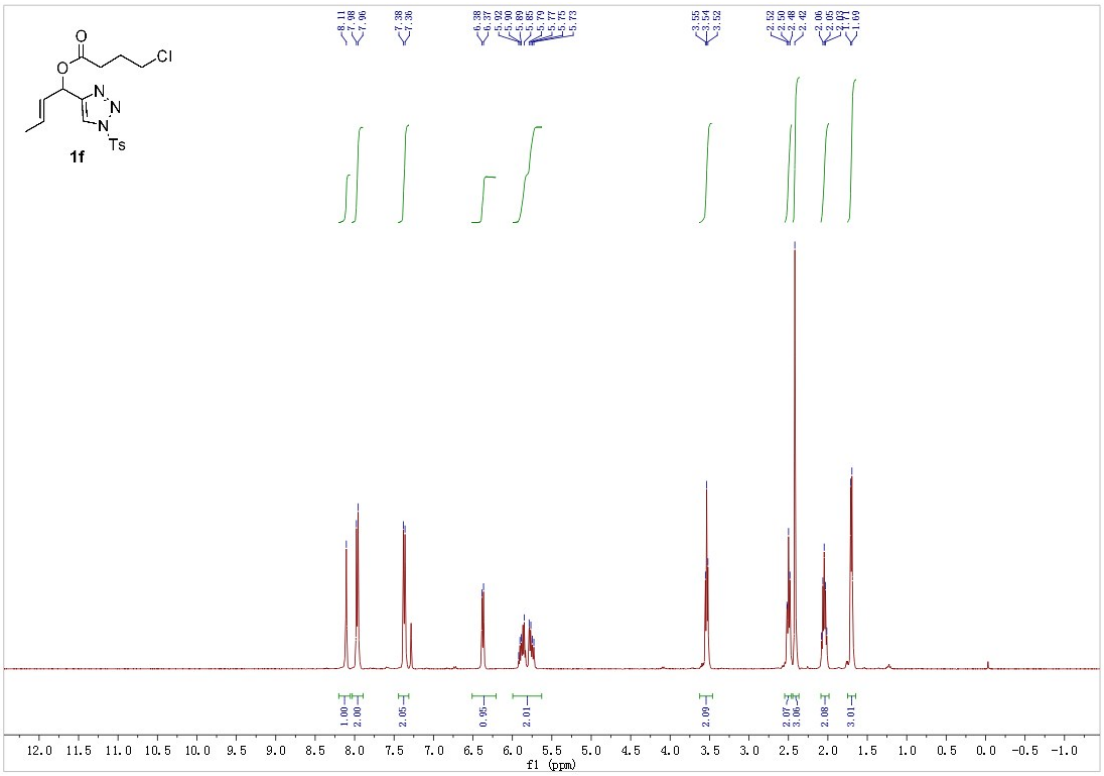

1c
f1 (ppm)

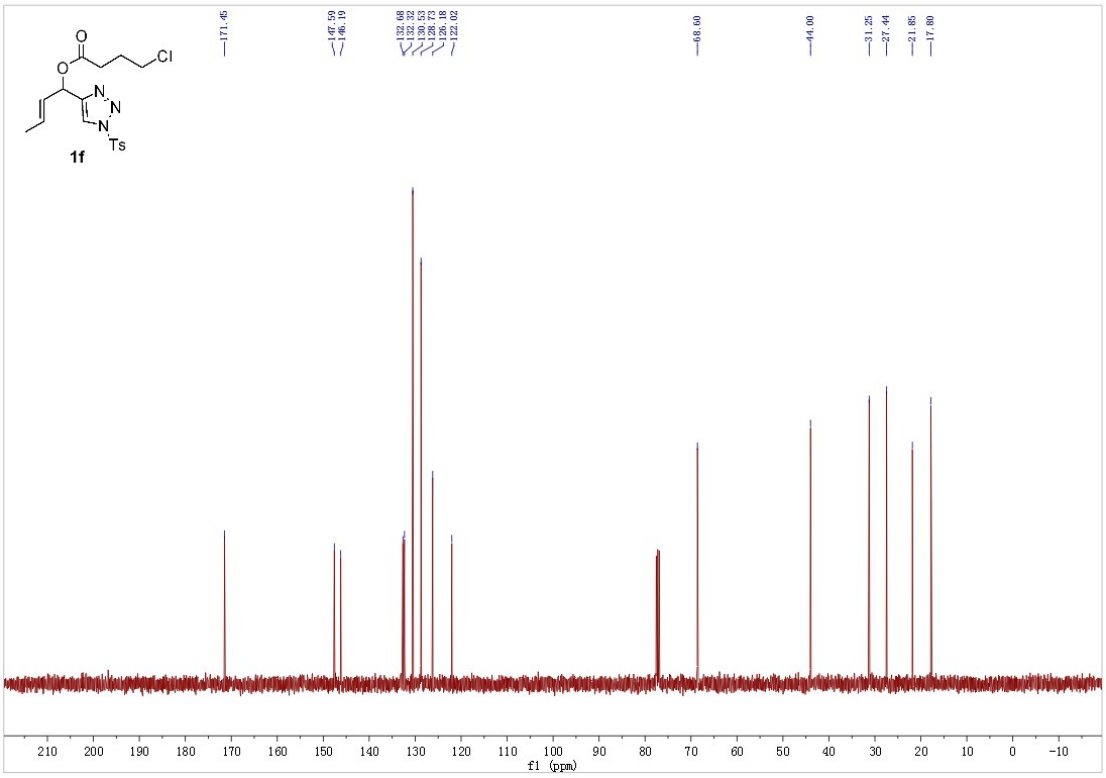

1d
8.11
7.98
7.96
7.74
7.72
6.36
6.34
5.91
5.90
5.88
5.86
5.80
5.78
5.76
5.75
2.06
1.72
1.71
1.01
1.01
2.01
1.00
2.06
2.99
3.01
f1 (ppm)

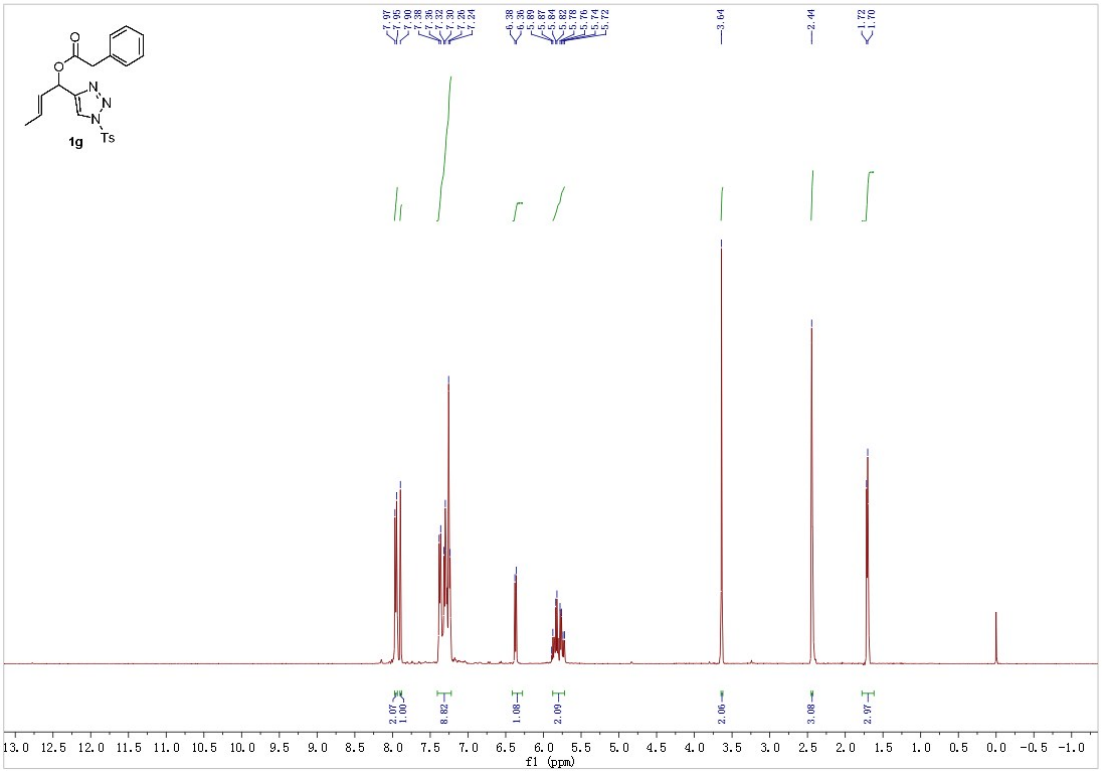

1d
169.76
146.48
134.75
133.27
132.29
131.64
130.12
126.16
122.07
68.36
21.13
17.76
f1 (ppm)

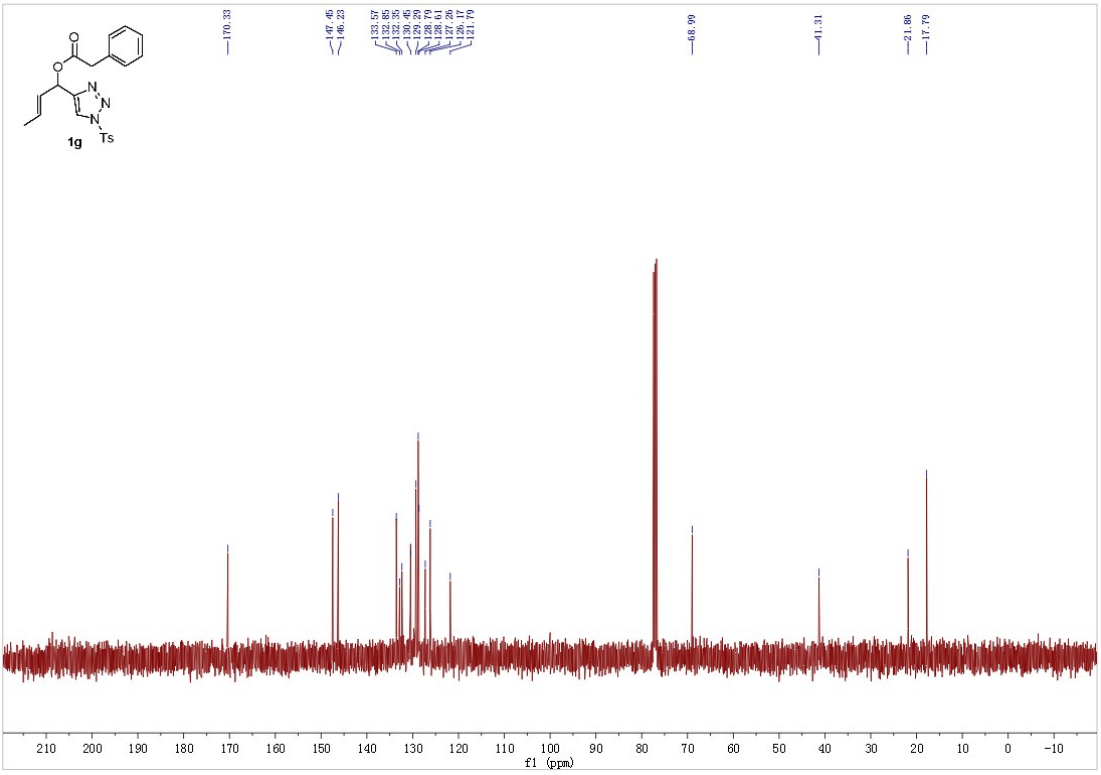

1e
Ms
8.07
7.28
6.39
6.37
5.95
5.93
5.92
5.89
5.88
5.86
5.82
5.80
5.78
5.76
3.53
2.07
1.74
1.73
1.00
1.01
1.02
1.08
3.06
3.04
3.03
f1 (ppm)

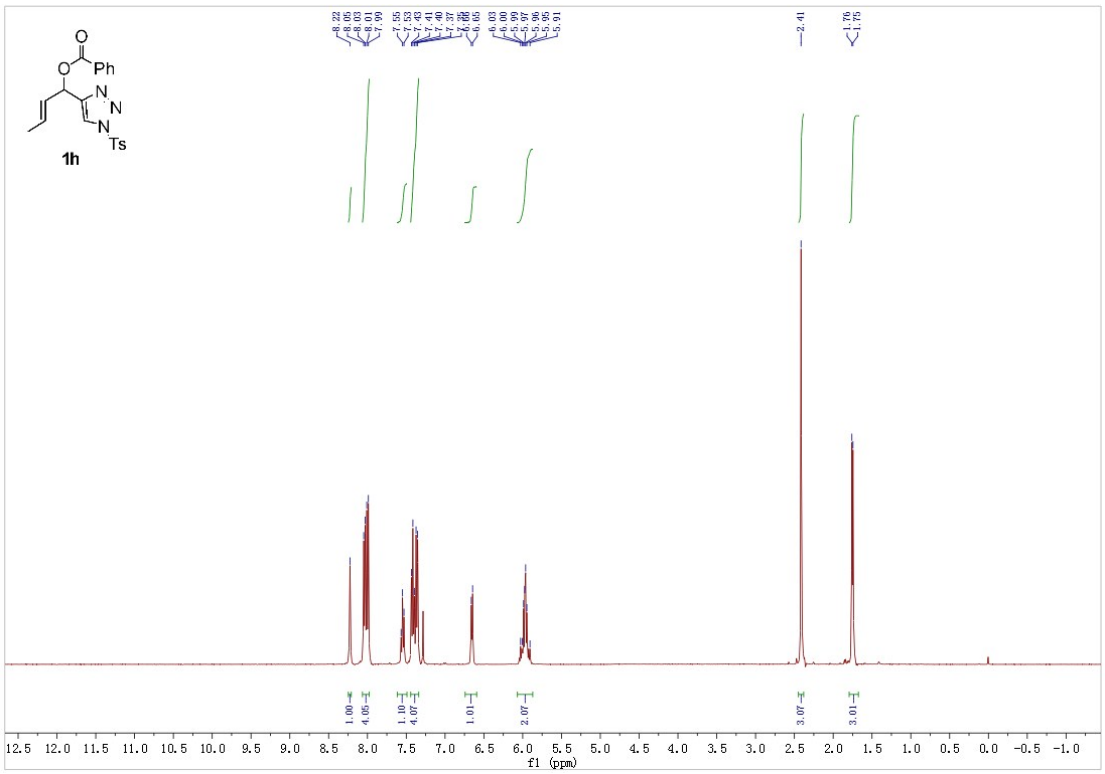

1e
Ms
169.82
146.43
132.28
126.20
122.07
68.39
42.67
21.09
17.76
f1 (ppm)

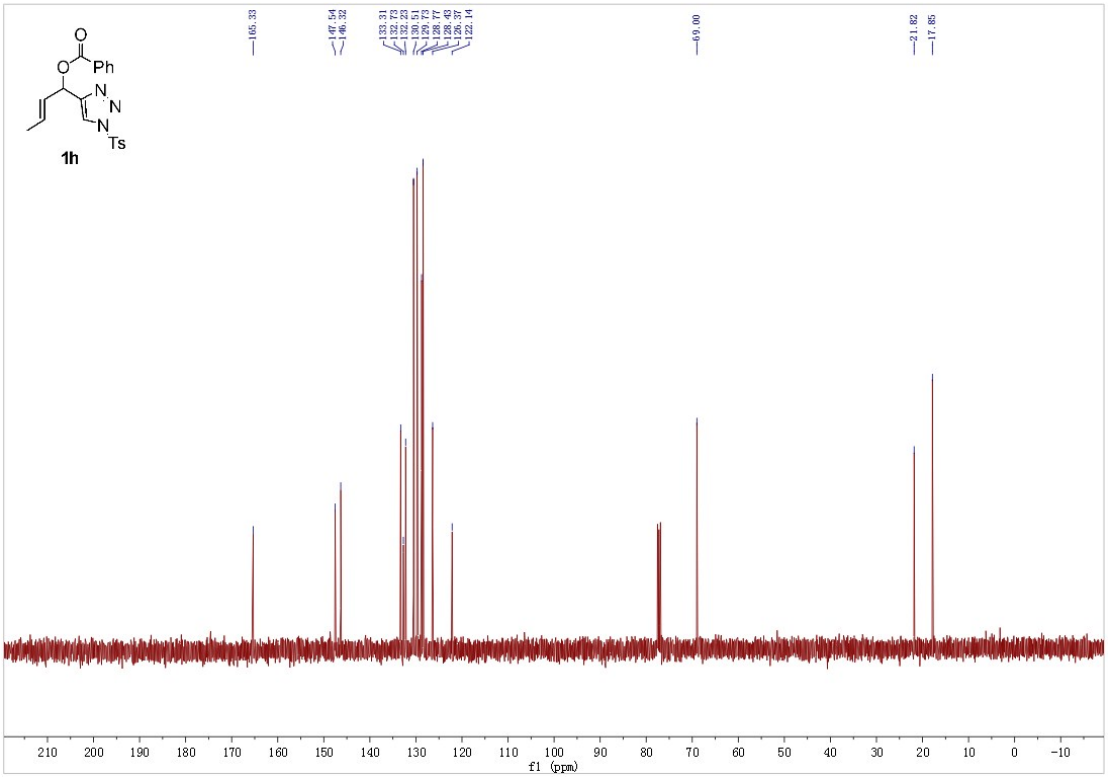

1f
8.11
7.98
7.96
7.38
7.36
6.38
6.37
5.92
5.90
5.89
5.85
5.77
5.75
5.73
3.55
3.54
3.52
2.52
2.50
2.48
2.42
2.06
2.05
1.69
1.00
2.00
2.05
0.96
2.01
2.09
2.07
3.06
2.08
3.01
f1 (ppm)

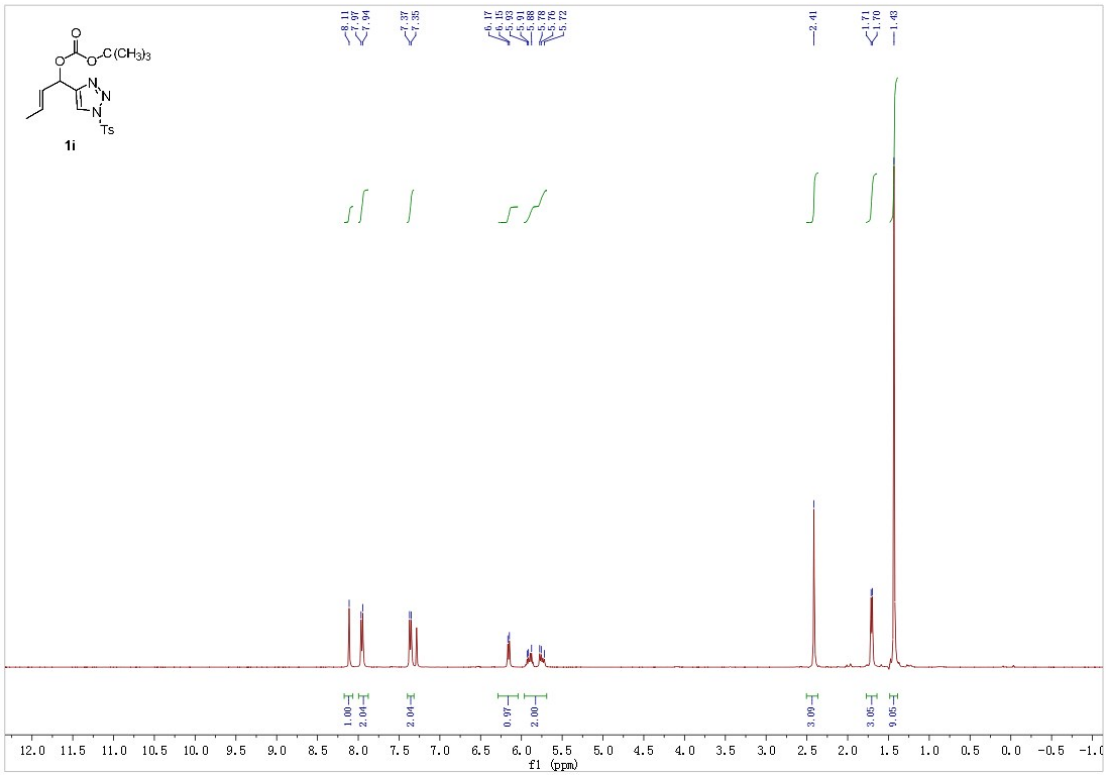

1f
171.45
147.59
146.19
132.68
132.32
130.53
128.18
125.18
122.02
68.60
44.00
31.25
27.44
21.85
17.80
f1 (ppm)

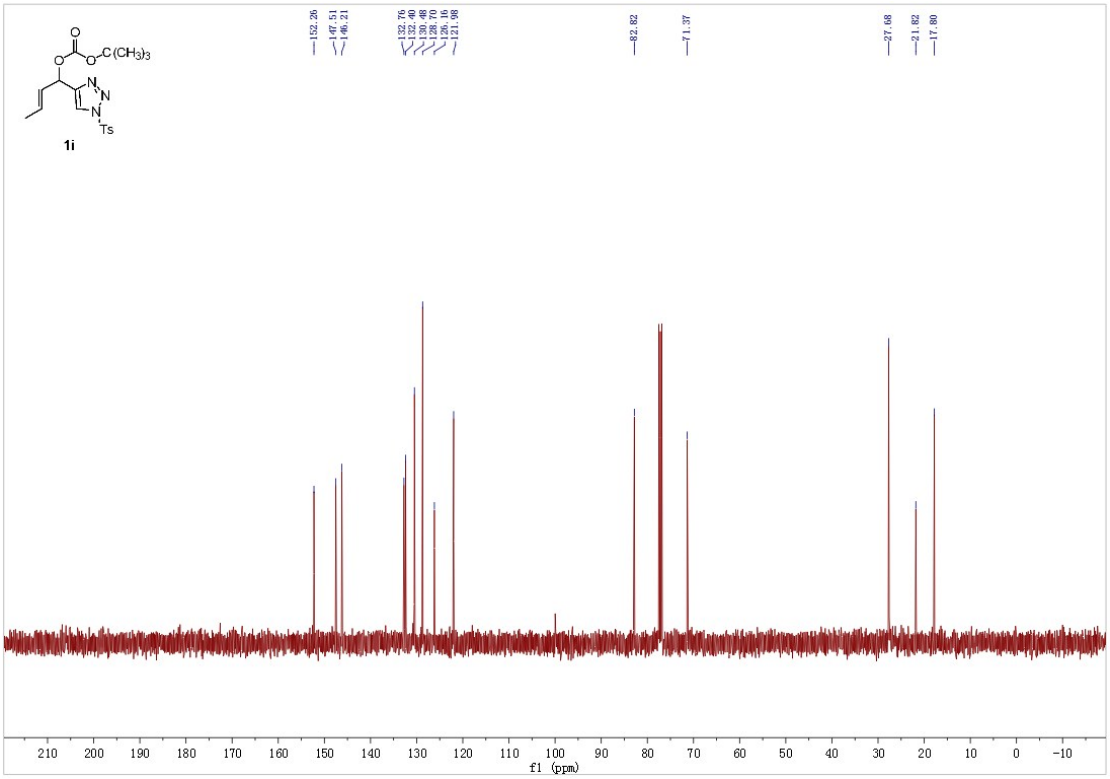

1g
Ts
7.97
7.95
7.90
7.38
7.36
7.32
7.30
7.26
7.24
6.38
6.36
5.89
5.87
5.84
5.82
5.78
5.76
5.74
5.72
3.64
2.44
1.72
1.70
2.05
1.00
8.82
1.08
2.09
2.06
3.08
2.97
f1 (ppm)

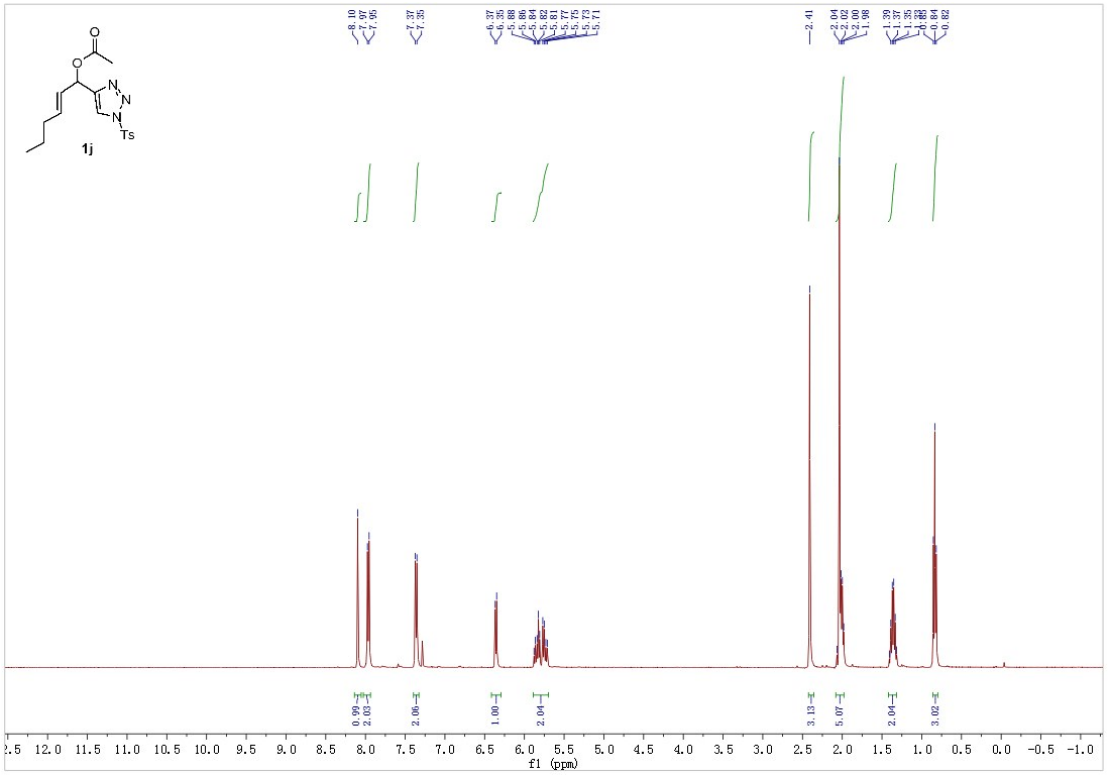

1g
Ts
170.33
147.45
146.23
133.57
132.85
132.35
130.45
129.29
128.79
128.41
127.26
126.17
121.79
68.99
41.31
21.86
17.79
f1 (ppm)

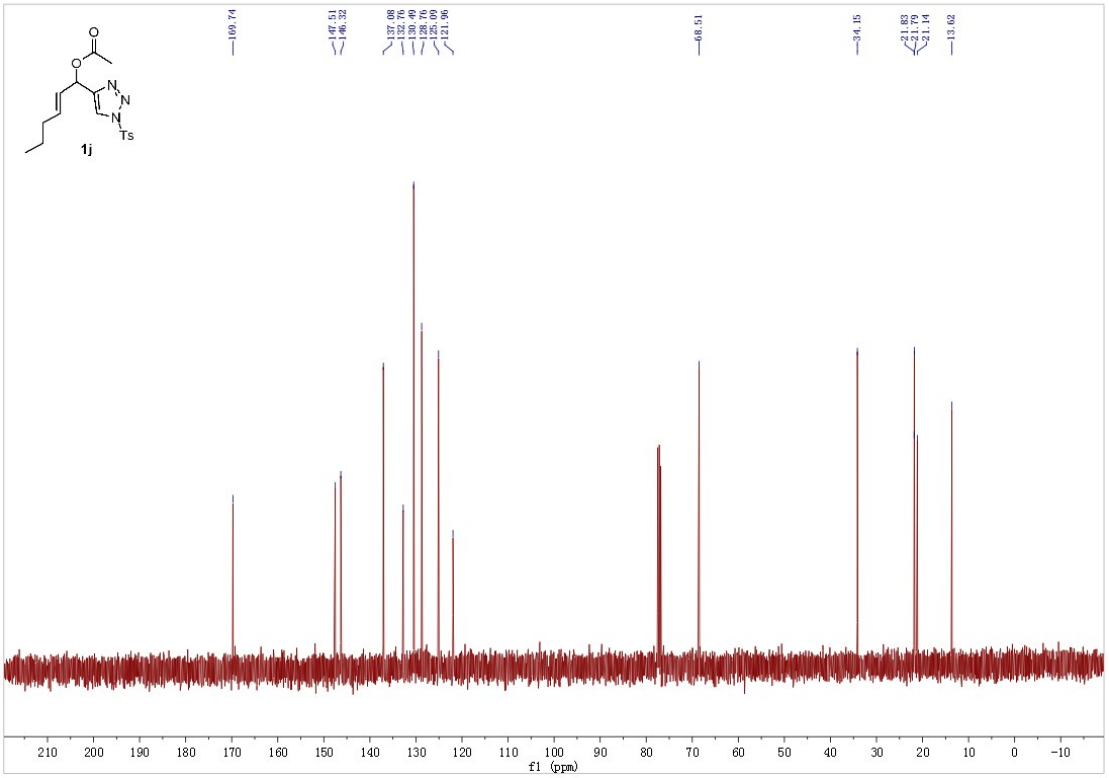

1h
8.22
8.05
8.03
8.01
7.99
7.55
7.53
7.43
7.41
7.40
7.37
6.65
6.03
6.00
5.99
5.97
5.96
5.95
5.91
2.41
1.76
1.75
1.00
4.05
1.10
4.07
1.01
2.07
3.07
3.01
f1 (ppm)

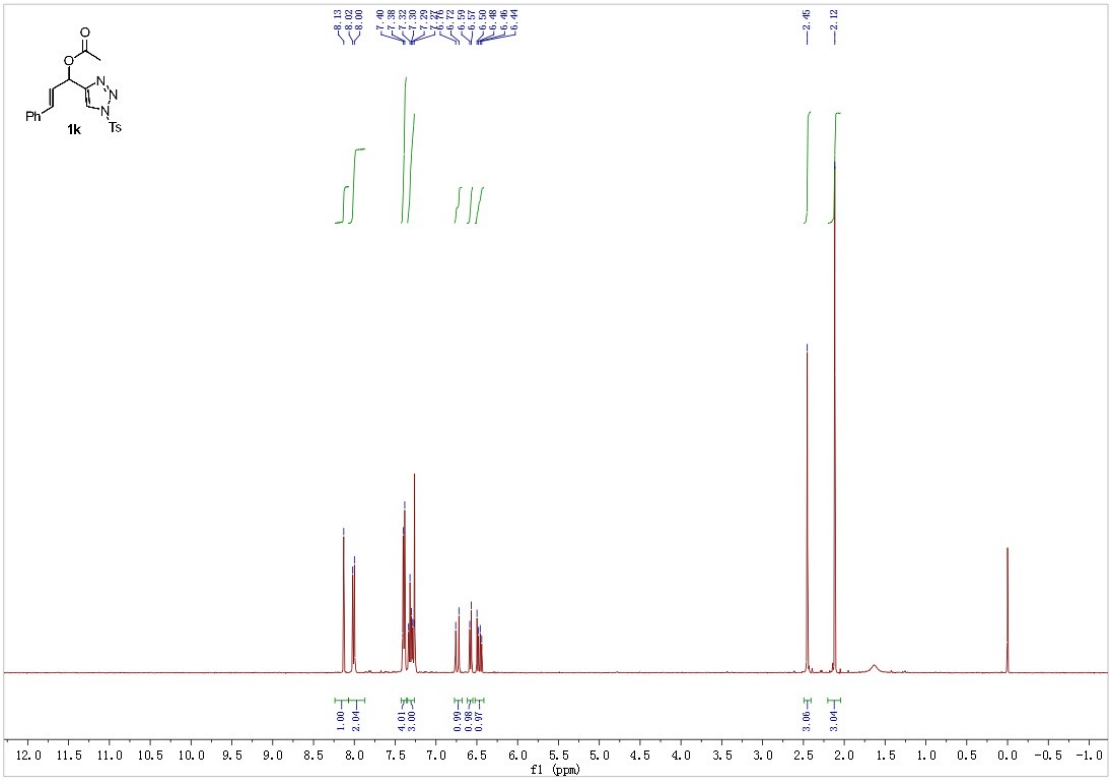

1h
165.33
147.54
146.32
133.31
132.73
132.23
130.51
129.73
128.77
128.45
126.37
122.14
69.00
21.82
17.85
f1 (ppm)

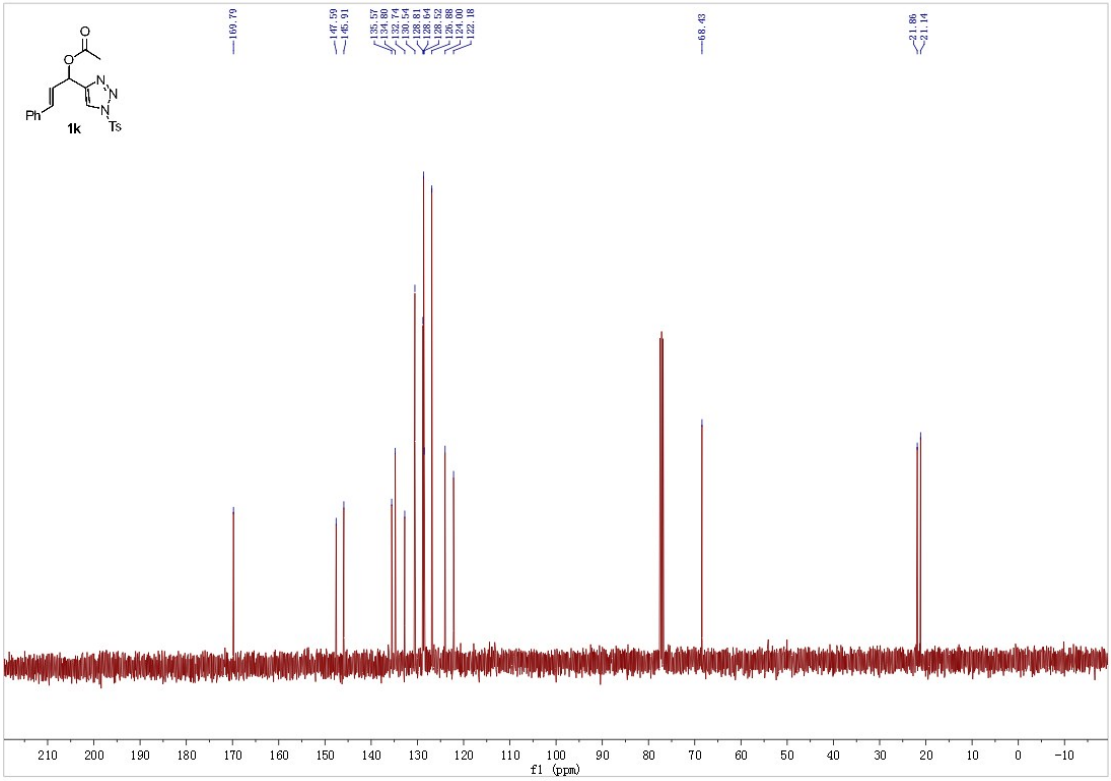

1i
8.11
7.97
7.94
7.37
7.35
6.17
6.15
5.93
5.91
5.88
5.78
5.76
5.72
2.41
1.71
1.70
1.43
1.00
2.04
2.04
0.97
2.00
3.09
3.05
9.05
f1 (ppm)

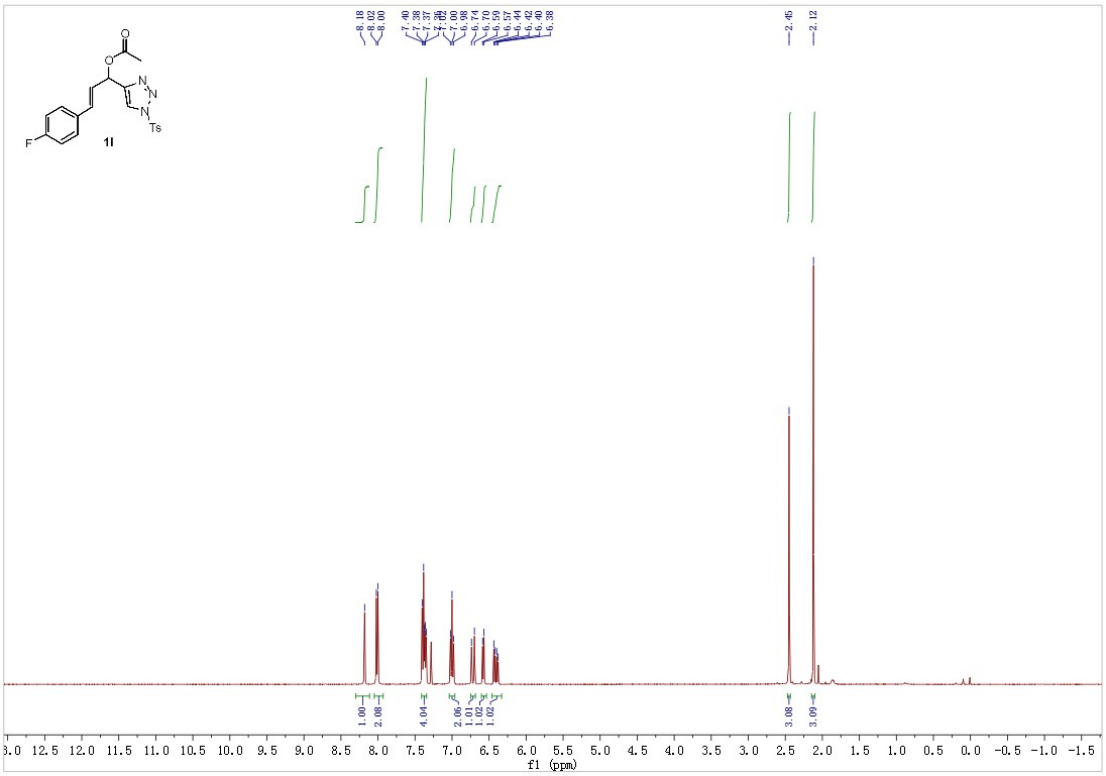

1i
152.26
147.51
146.21
132.76
132.40
130.48
128.70
126.16
121.98
82.82
71.37
27.68
21.82
17.80
f1 (ppm)

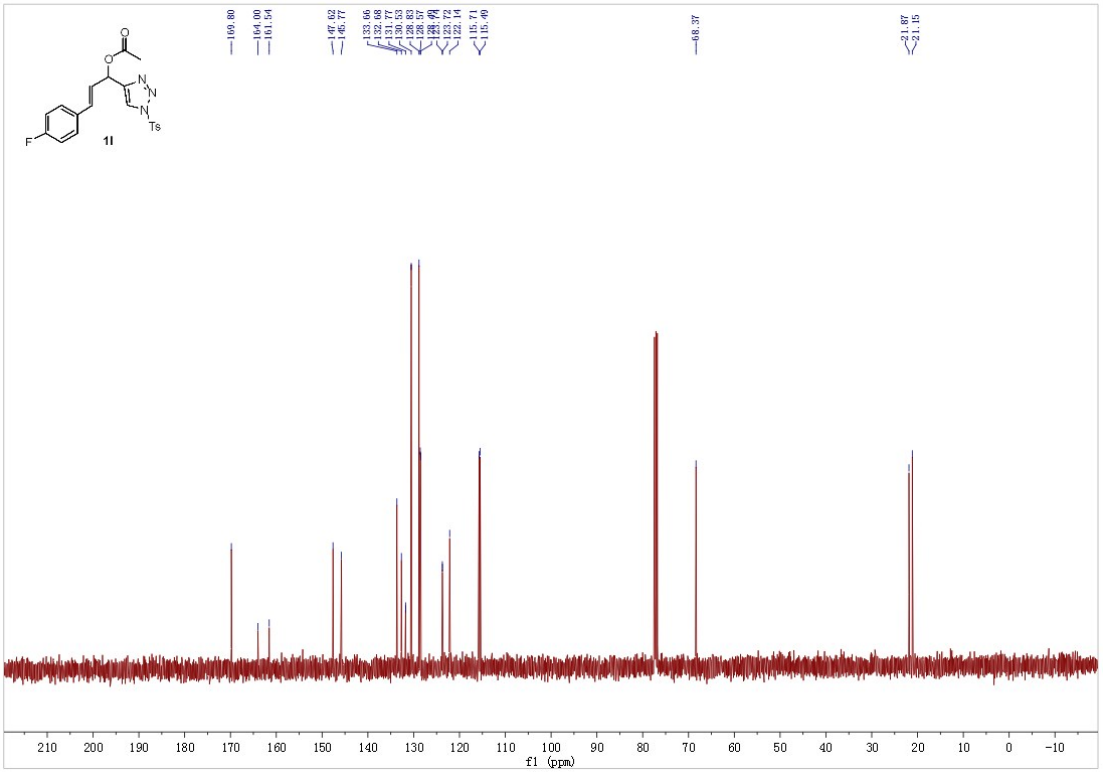

1j
f1 (ppm)

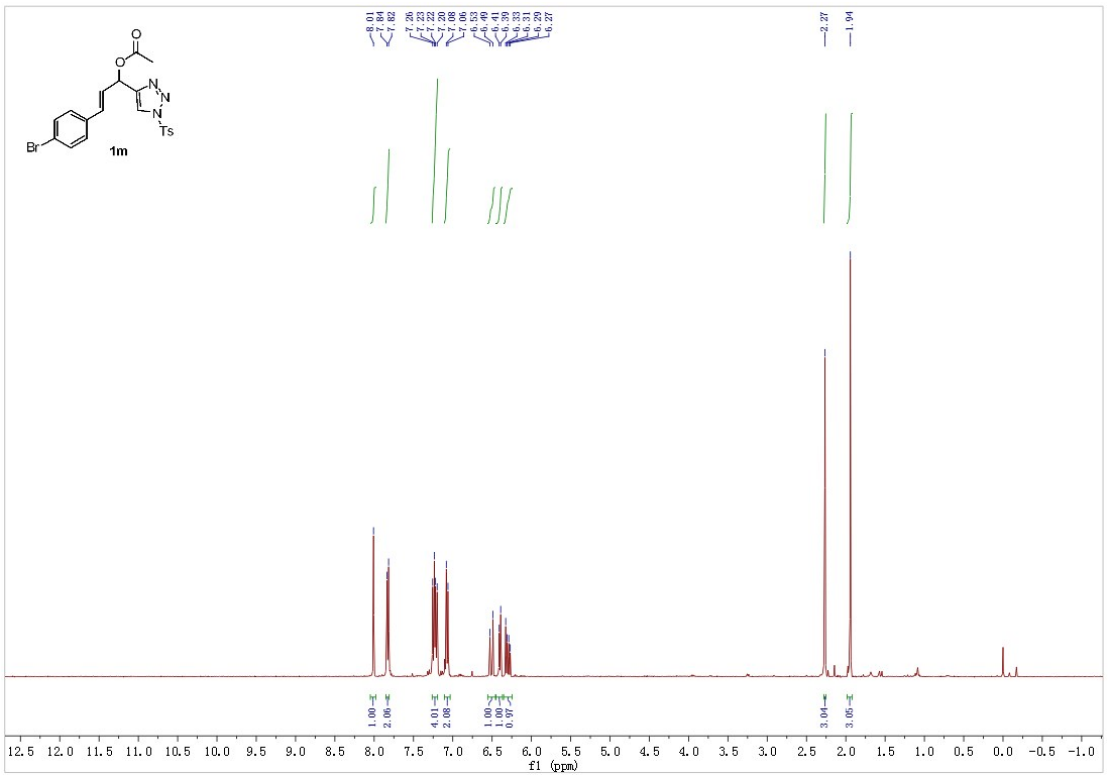

1j
f1 (ppm)

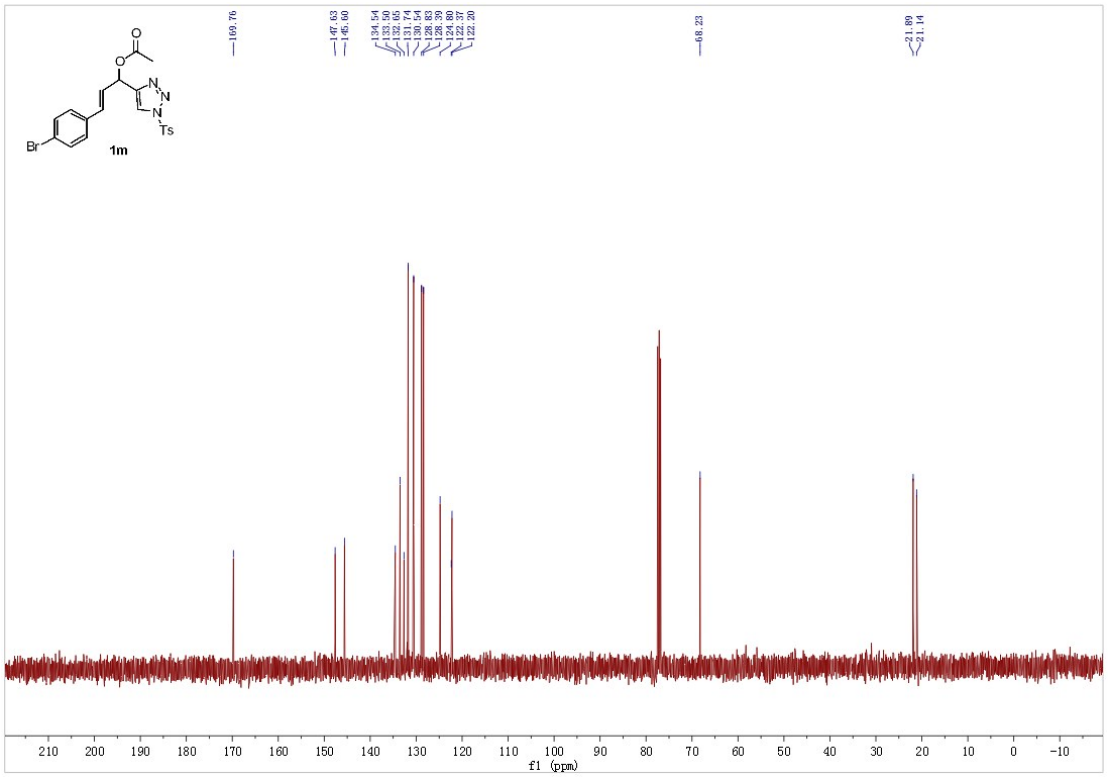

1k
Ph
Ts
8.13
8.03
8.00
7.40
7.38
7.33
7.30
7.29
6.72
6.57
6.50
6.48
6.46
6.44
2.46
2.12
1.00
2.04
4.01
3.00
0.99
0.98
0.97
3.00
3.04
f1 (ppm)

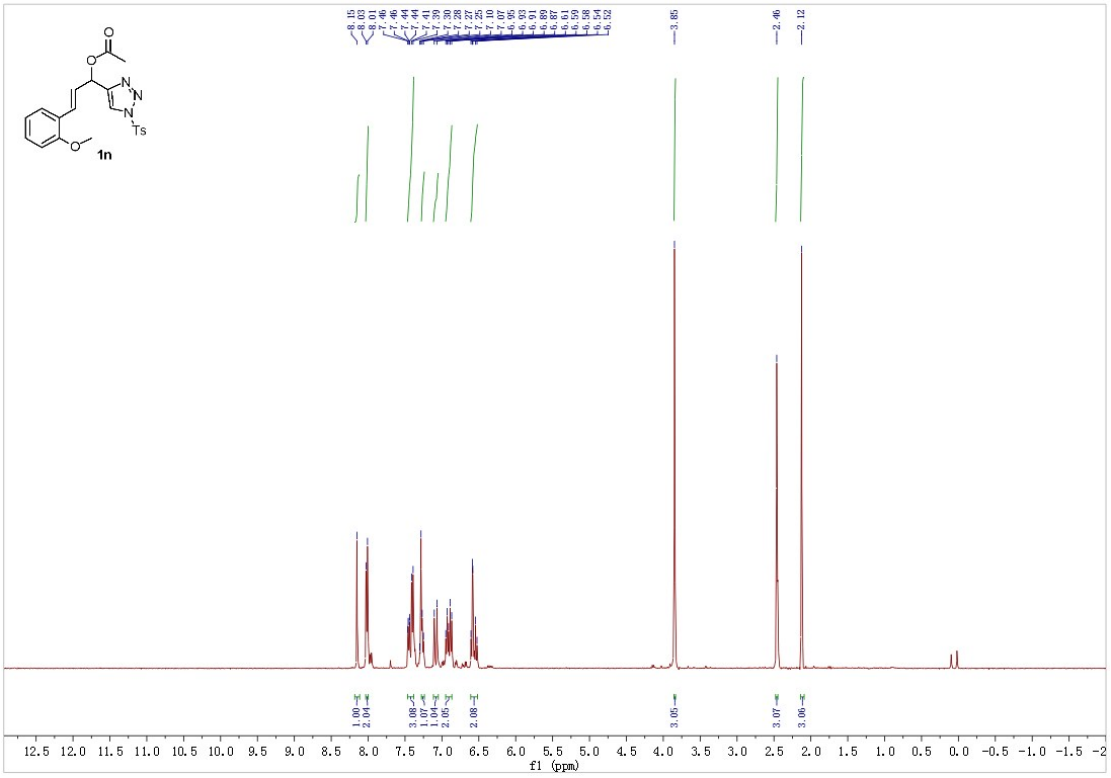

1k
Ph
Ts
169.79
147.59
145.91
135.57
134.80
132.74
130.54
128.81
128.64
128.52
126.88
124.00
122.18
68.43
21.86
21.14
f1 (ppm)

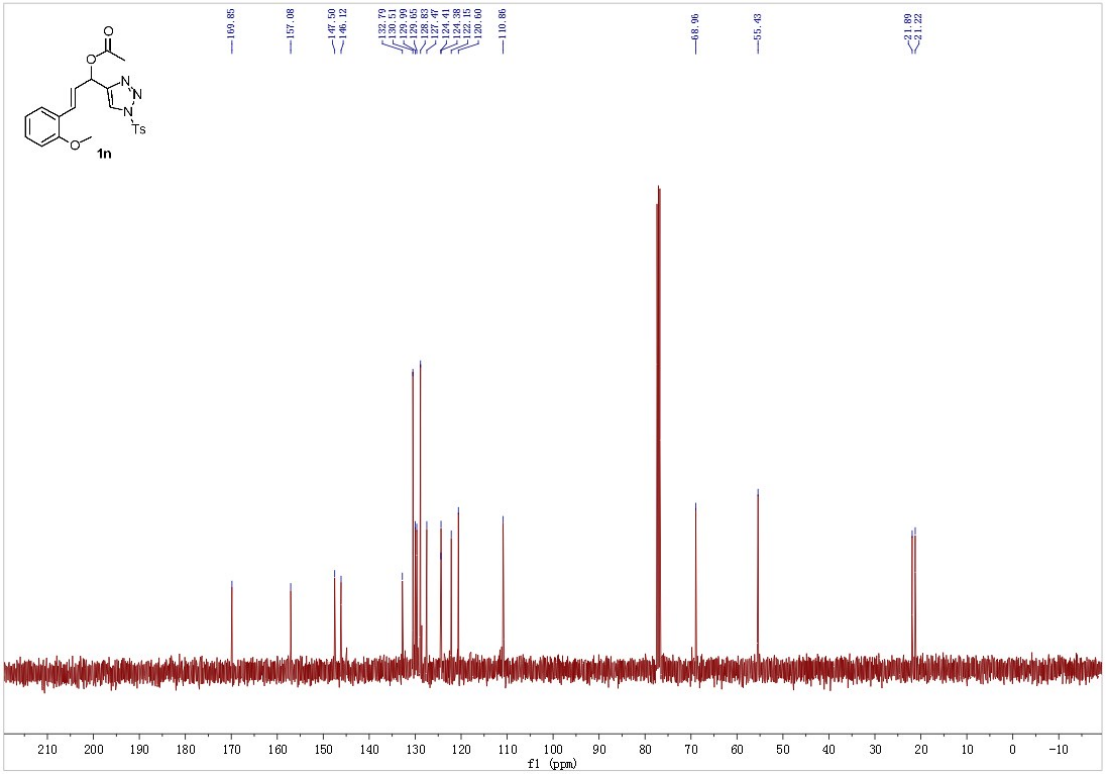

1l
Ts
F
8.18
8.02
8.00
7.40
7.38
7.37
7.28
7.00
6.98
6.74
6.70
6.59
6.57
6.44
6.42
6.40
6.38
2.45
2.12
1.00
2.08
4.04
2.06
1.01
1.02
1.02
3.08
3.09
f1 (ppm)

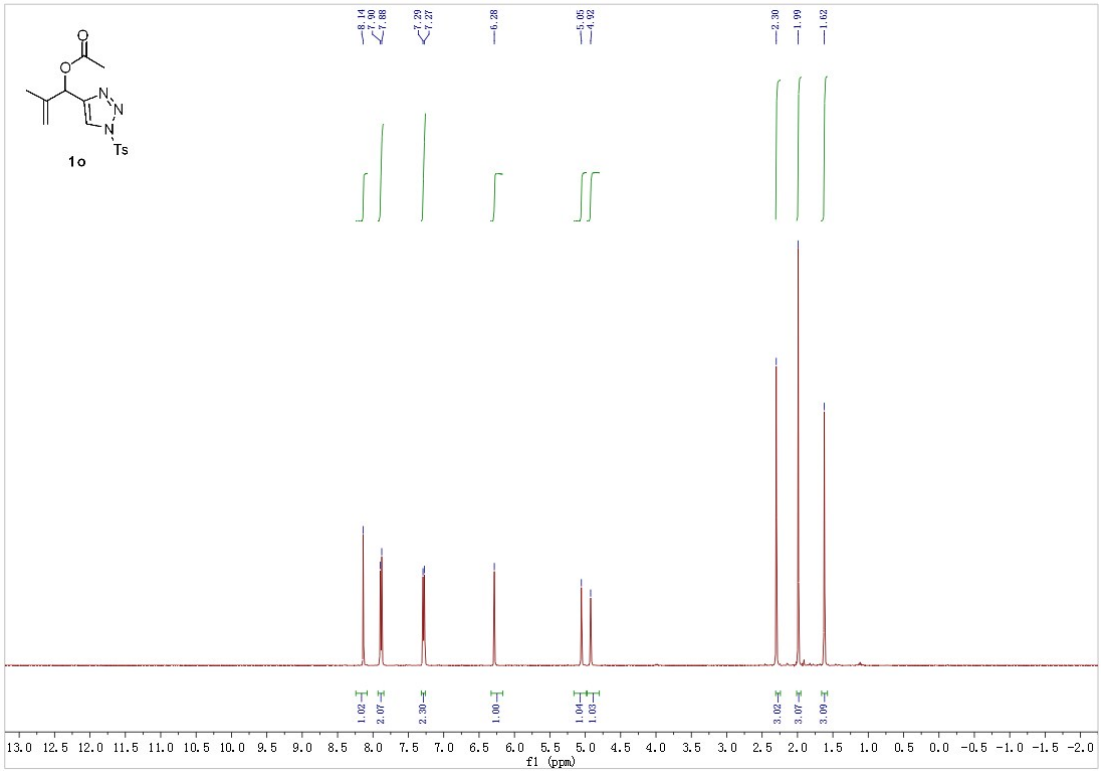

1l
Ts
F
169.80
164.00
161.54
147.62
146.77
133.66
132.68
131.77
131.55
128.83
128.57
123.72
122.14
115.71
115.49
68.37
21.87
21.15
f1 (ppm)

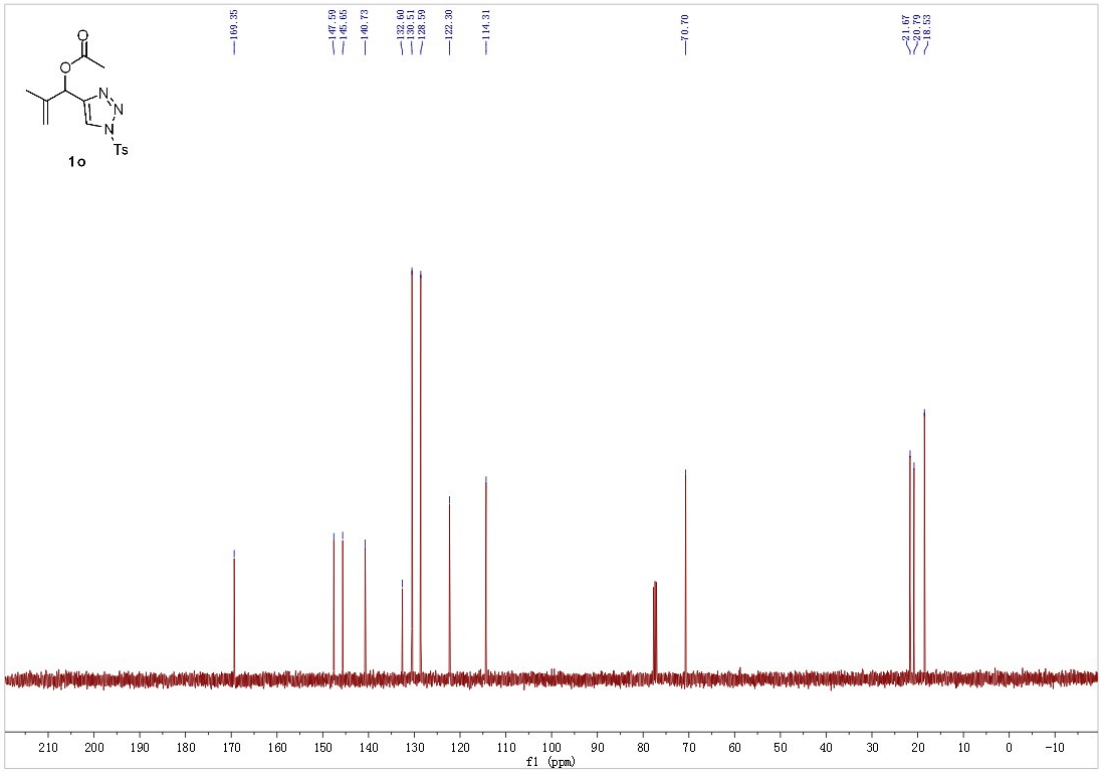

1m
Br
Ts
f1 (ppm)

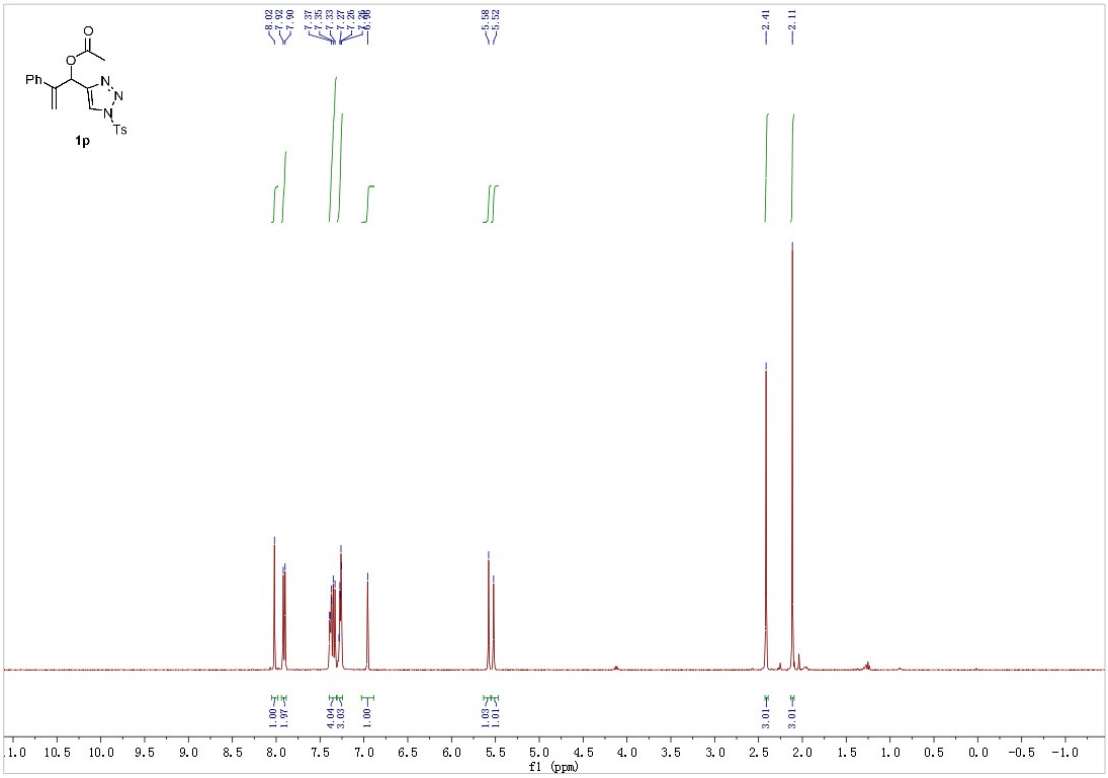

1m
Br
Ts
f1 (ppm)

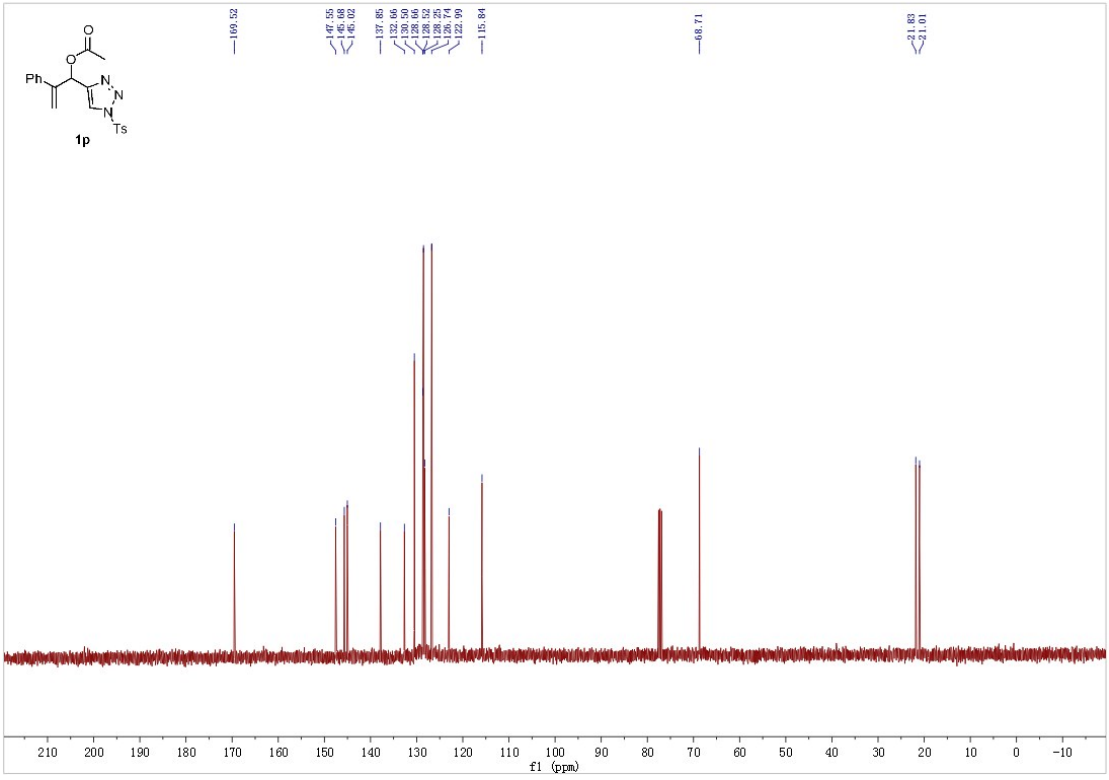

1n
f1 (ppm)

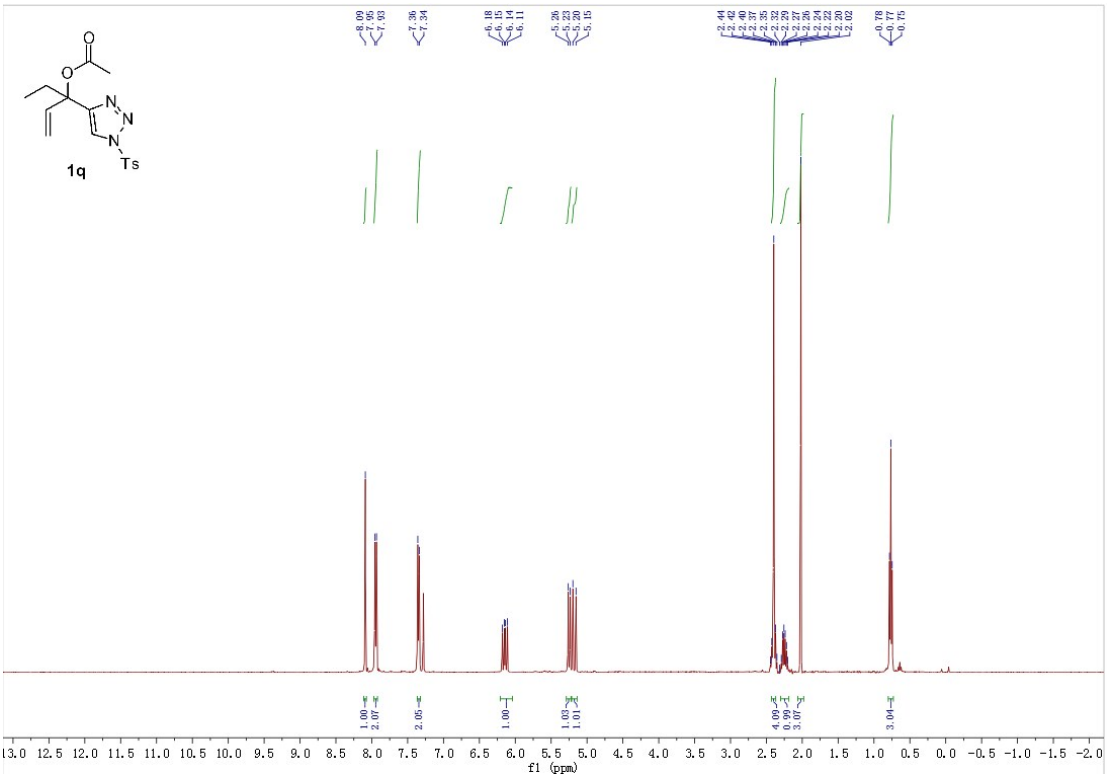

1n
f1 (ppm)

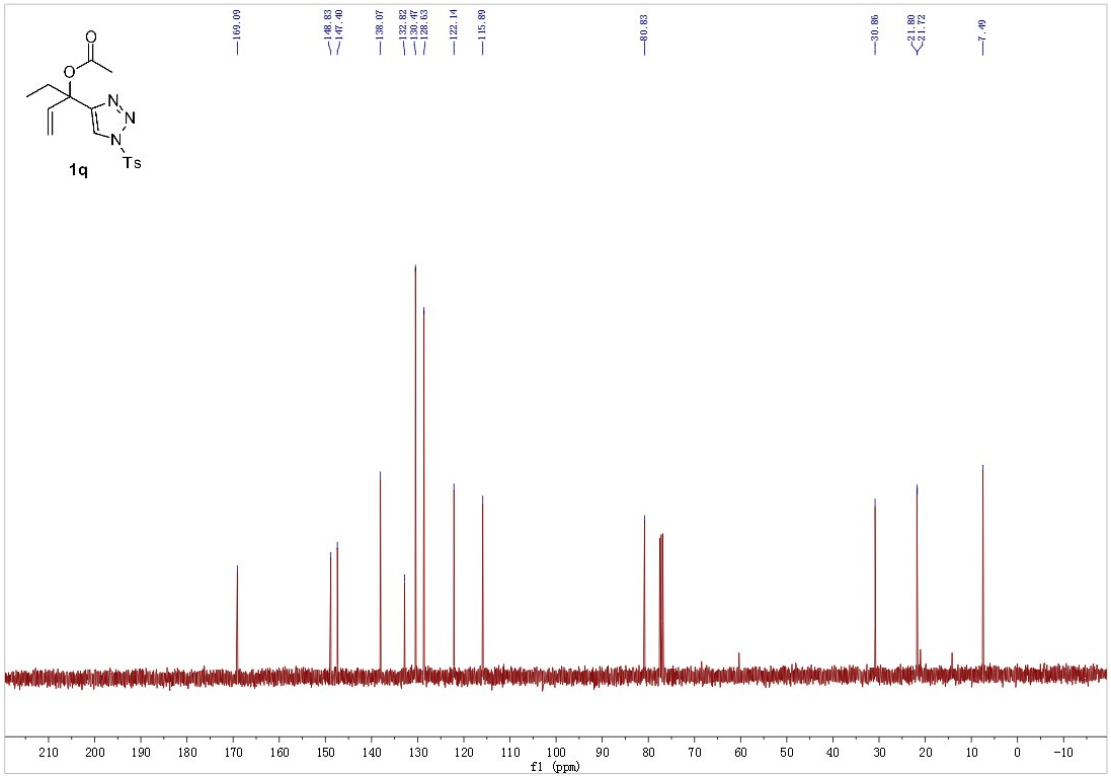

1o
Ts
8.14
7.90
7.88
7.29
7.27
6.28
5.05
4.92
2.30
1.99
1.62
1.02
2.07
2.30
1.00
1.04
1.03
3.02
3.07
3.09
f1 (ppm)

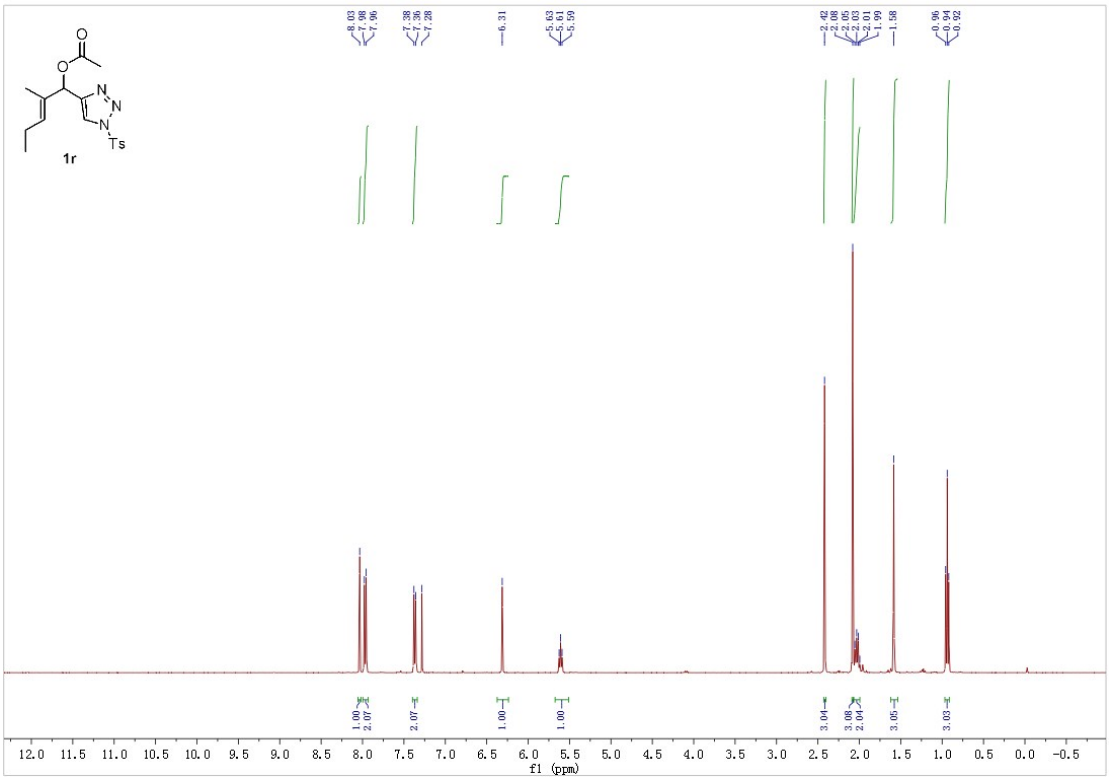

1o
Ts
169.35
147.59
146.05
140.73
132.60
130.51
128.59
122.30
114.31
76.70
21.67
20.79
18.53
f1 (ppm)

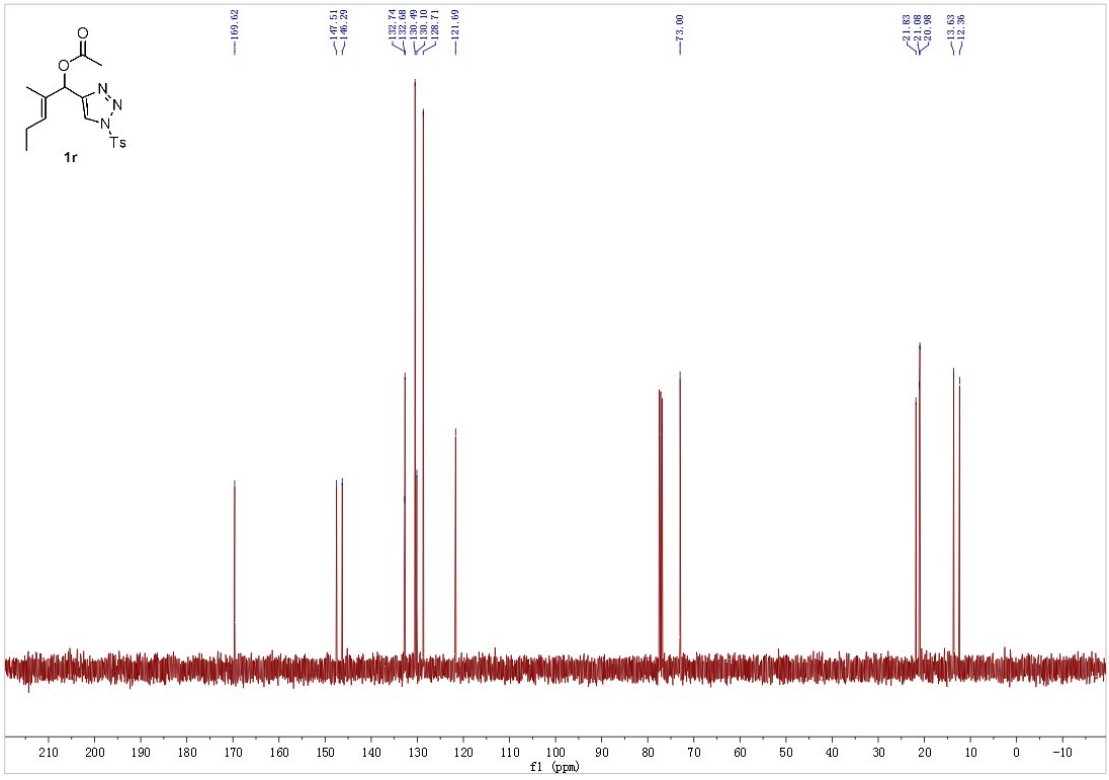

1p
8.02
7.92
7.90
7.37
7.35
7.33
7.27
7.26
5.58
5.52
2.41
2.11
1.00
1.97
4.04
3.03
1.00
1.03
1.01
3.01
3.01
f1 (ppm)

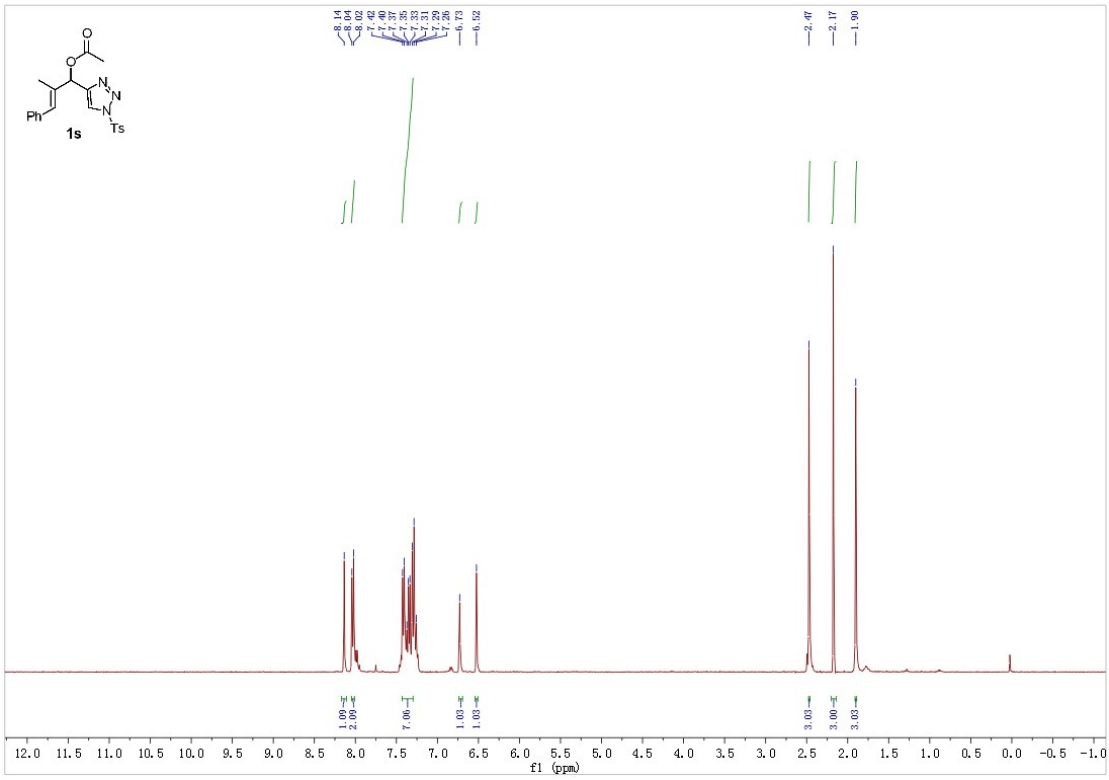

1p
169.52
147.55
145.68
145.02
137.85
132.66
130.50
128.86
128.52
128.25
126.74
122.99
115.84
68.71
21.83
21.01
f1 (ppm)

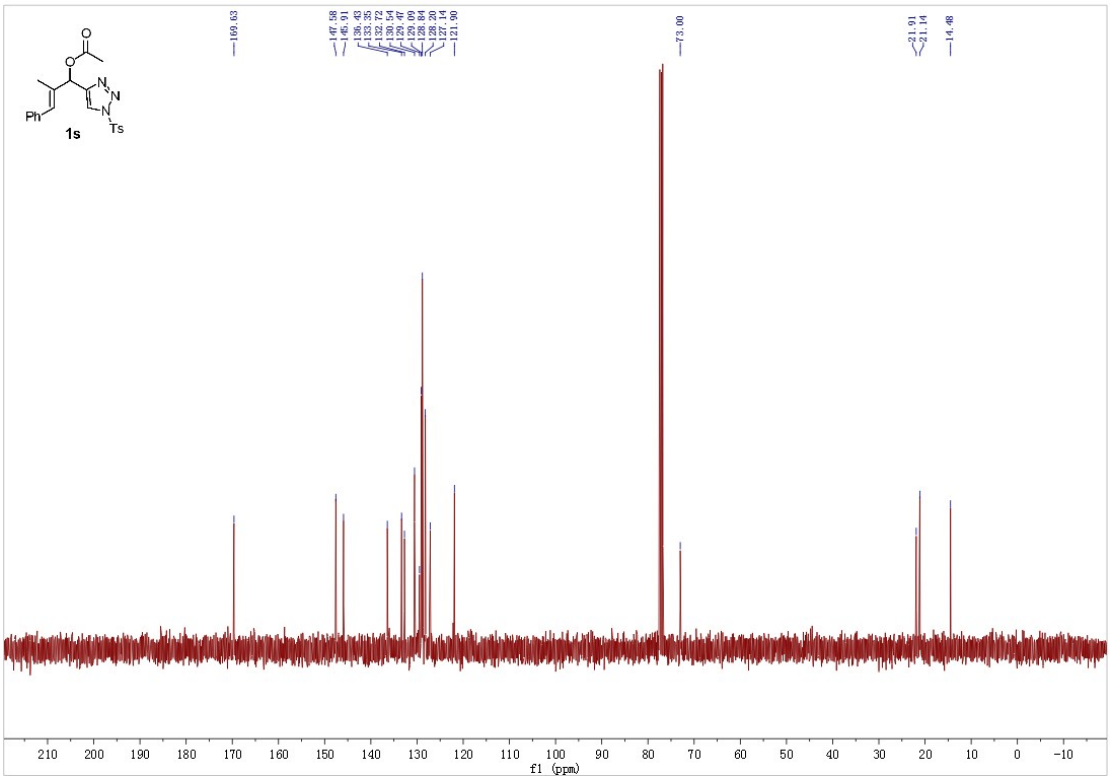

1q
Ts
f1 (ppm)

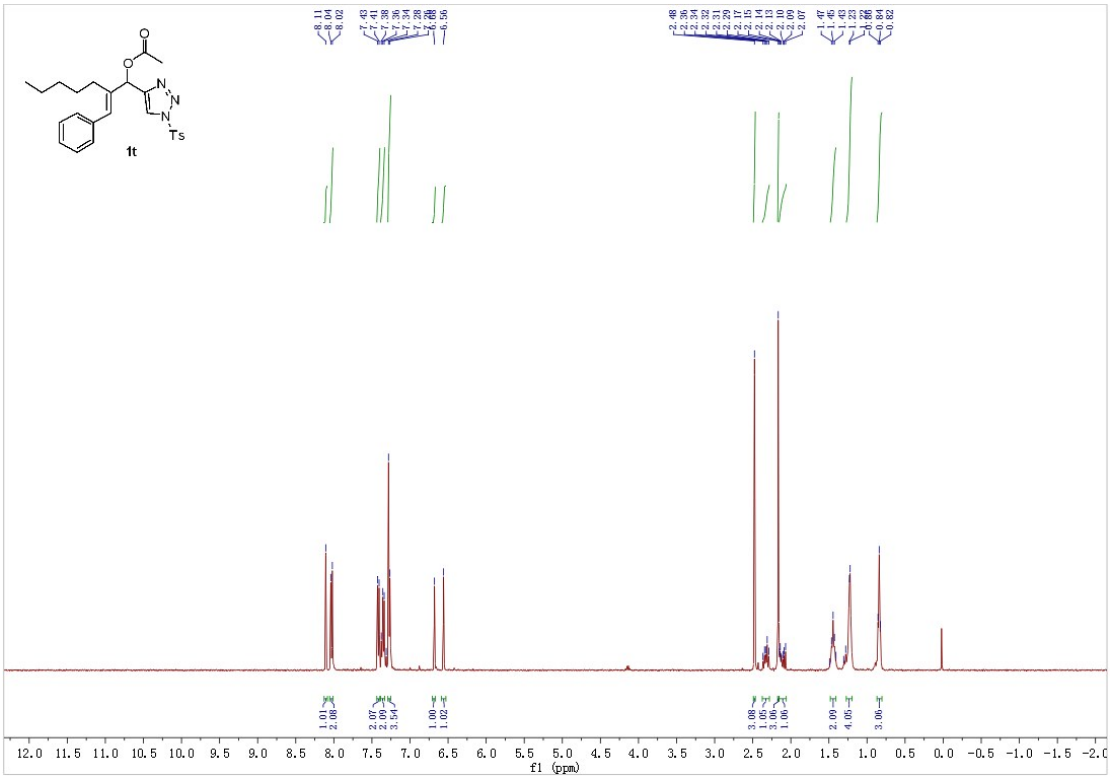

1q
Ts
f1 (ppm)

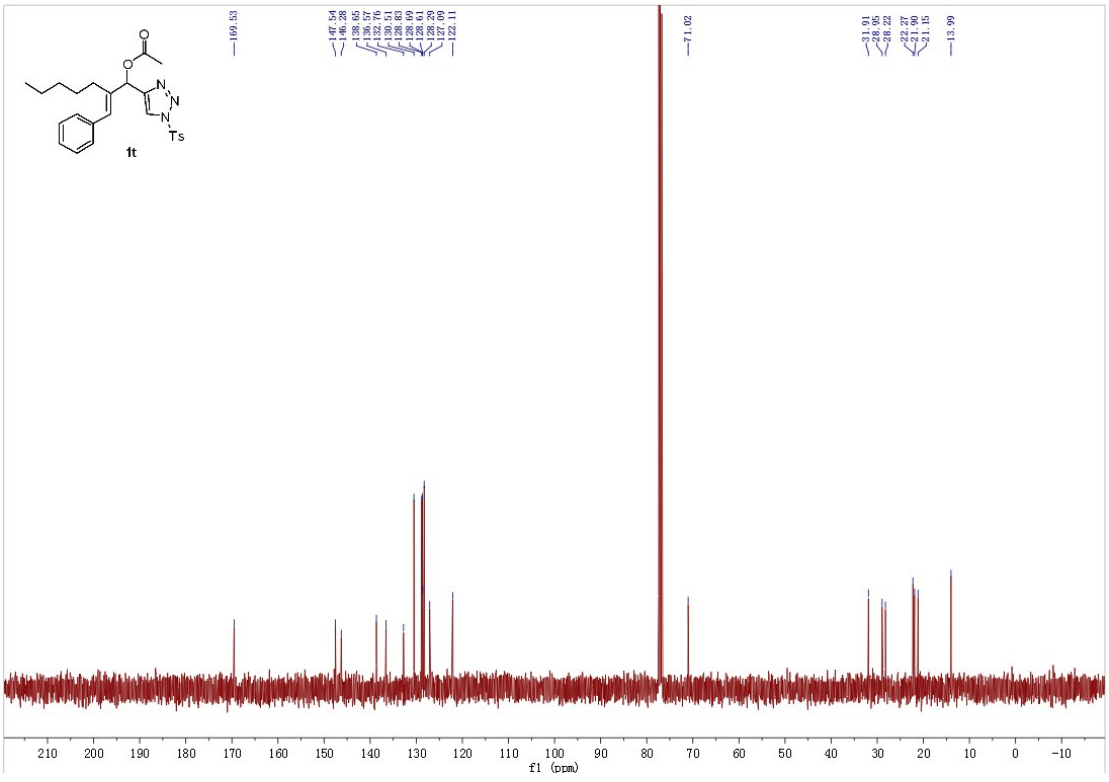

1r
Ts
8.03
7.98
7.96
7.38
7.36
7.28
6.31
5.63
5.61
5.59
2.42
2.06
2.05
2.03
2.01
1.99
1.98
0.96
0.94
0.92
1.00
2.07
2.07
1.00
1.00
3.04
3.08
2.04
3.05
3.03
f1 (ppm)

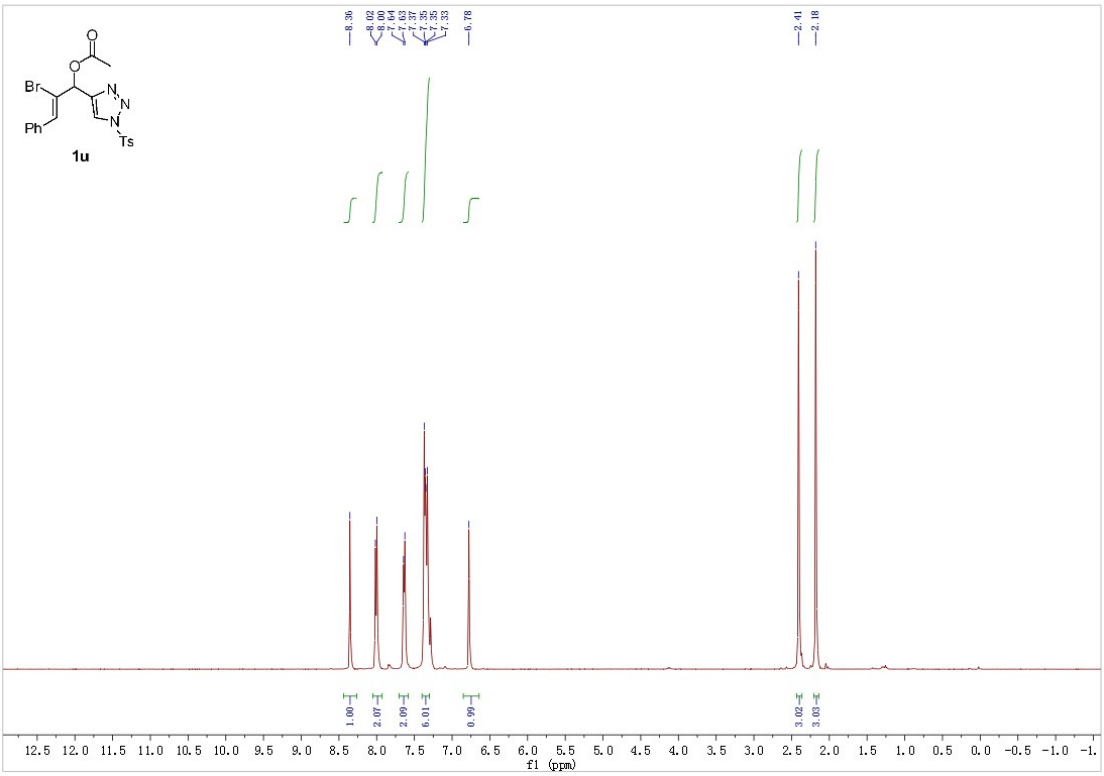

1r
Ts
169.62
147.51
146.20
132.74
132.48
130.40
130.10
128.71
121.69
73.00
21.83
21.08
20.98
13.63
12.36
f1 (ppm)

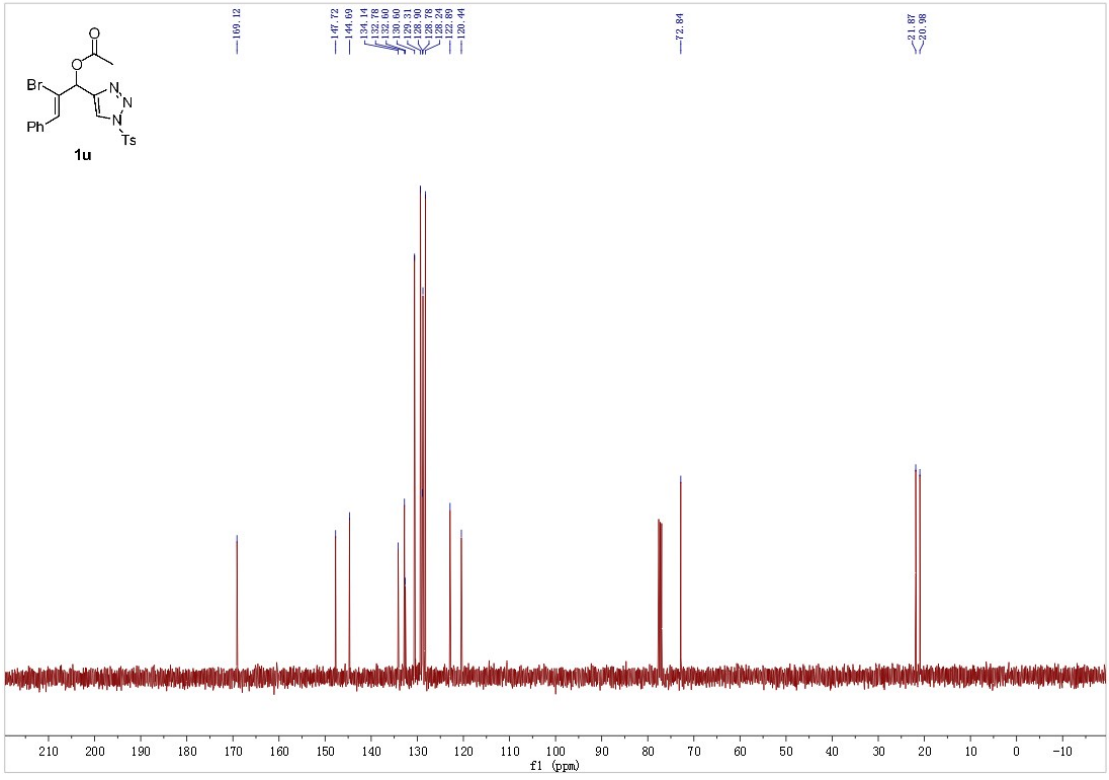

1s
Ph
Ts
8.14
8.04
8.02
7.42
7.40
7.37
7.35
7.33
7.31
7.29
7.26
6.73
6.52
2.47
2.17
1.90
1.09
2.09
7.06
1.03
1.03
3.03
3.00
3.03
f1 (ppm)

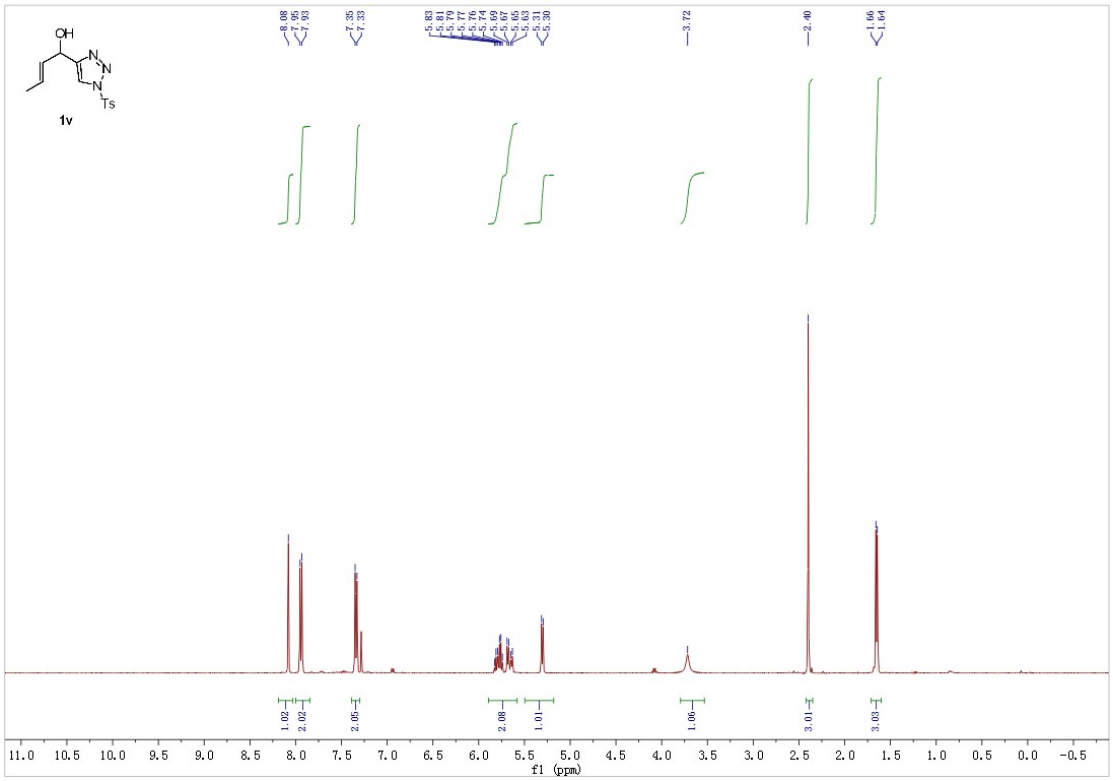

1s
Ph
Ts
169.63
147.58
145.91
136.43
133.35
132.72
130.54
130.47
129.09
128.84
128.20
127.15
121.90
73.00
21.91
21.14
14.48
f1 (ppm)

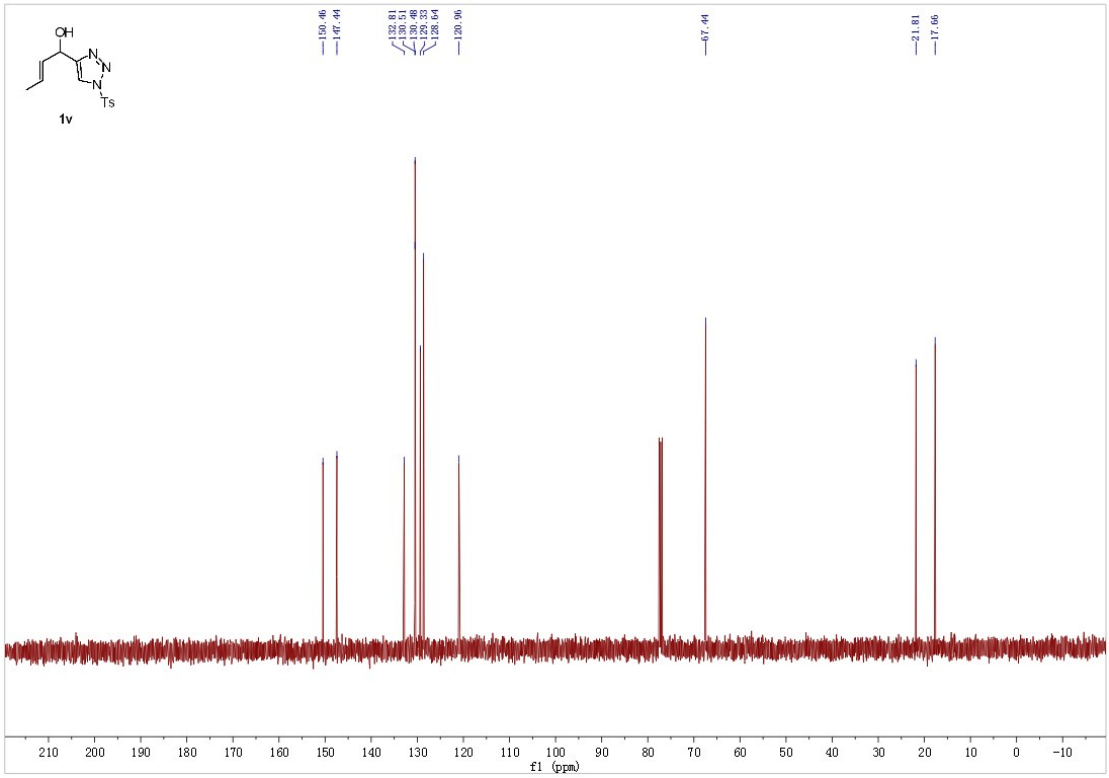

1t
Ts
f1 (ppm)

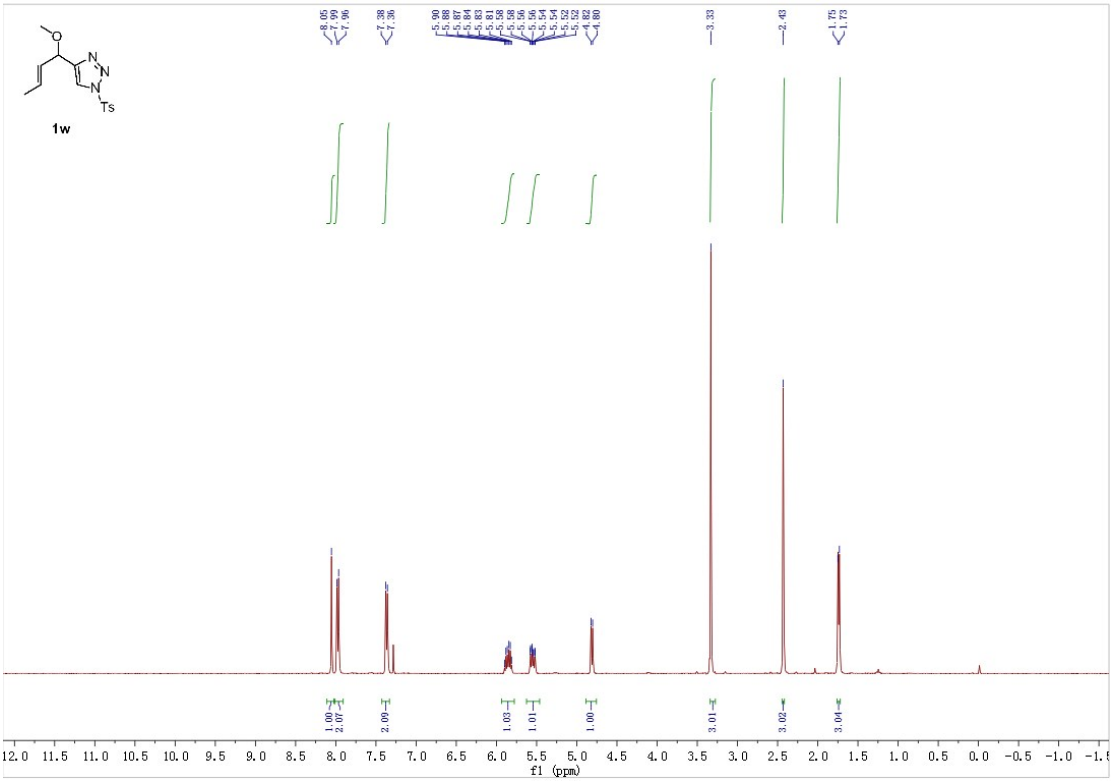

1t
Ts
f1 (ppm)

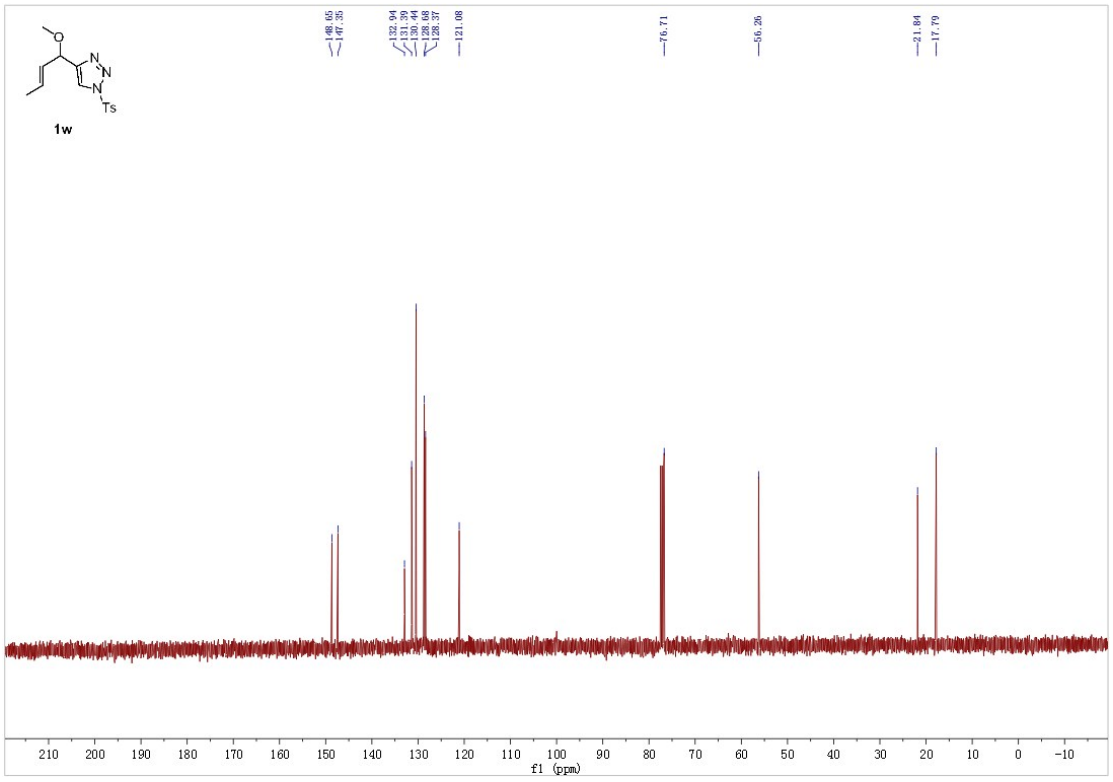

1u
8.36
8.02
8.00
7.64
7.63
7.37
7.35
7.33
6.78
2.41
2.18
1.00
2.07
2.09
6.01
0.99
3.02
3.03
f1 (ppm)

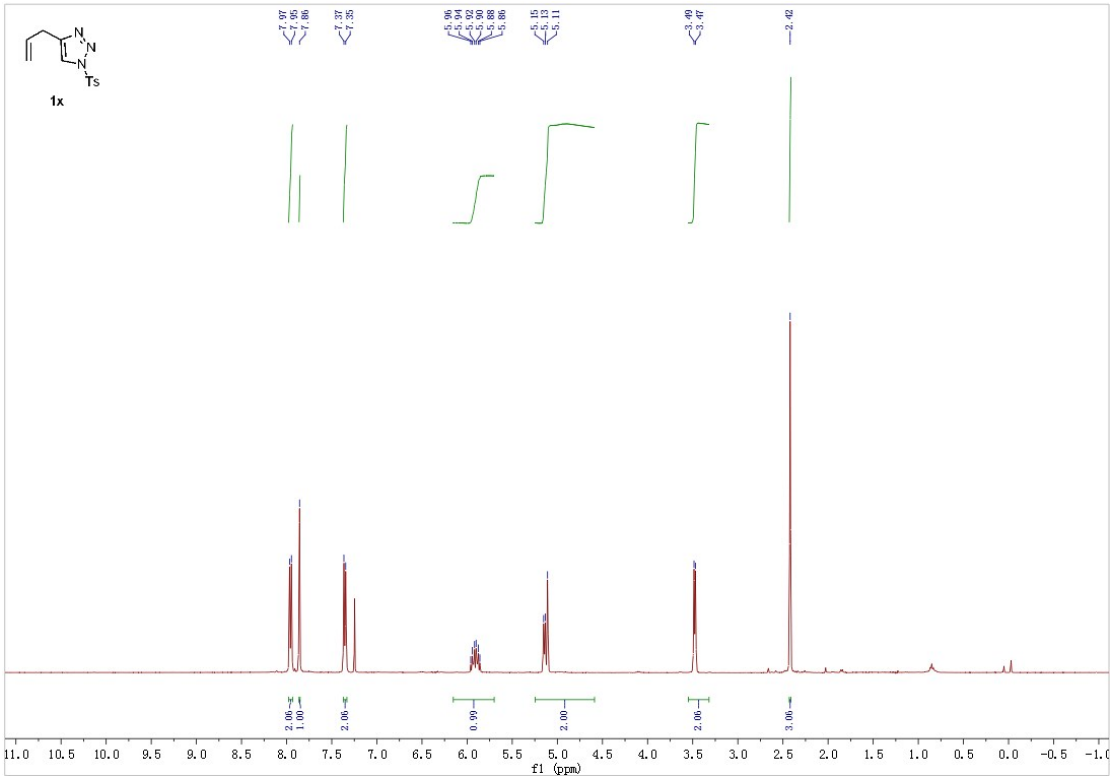

1u
169.12
147.72
144.69
134.14
132.18
132.03
130.60
129.31
128.90
128.83
128.24
122.89
120.44
72.84
21.87
20.98
f1 (ppm)

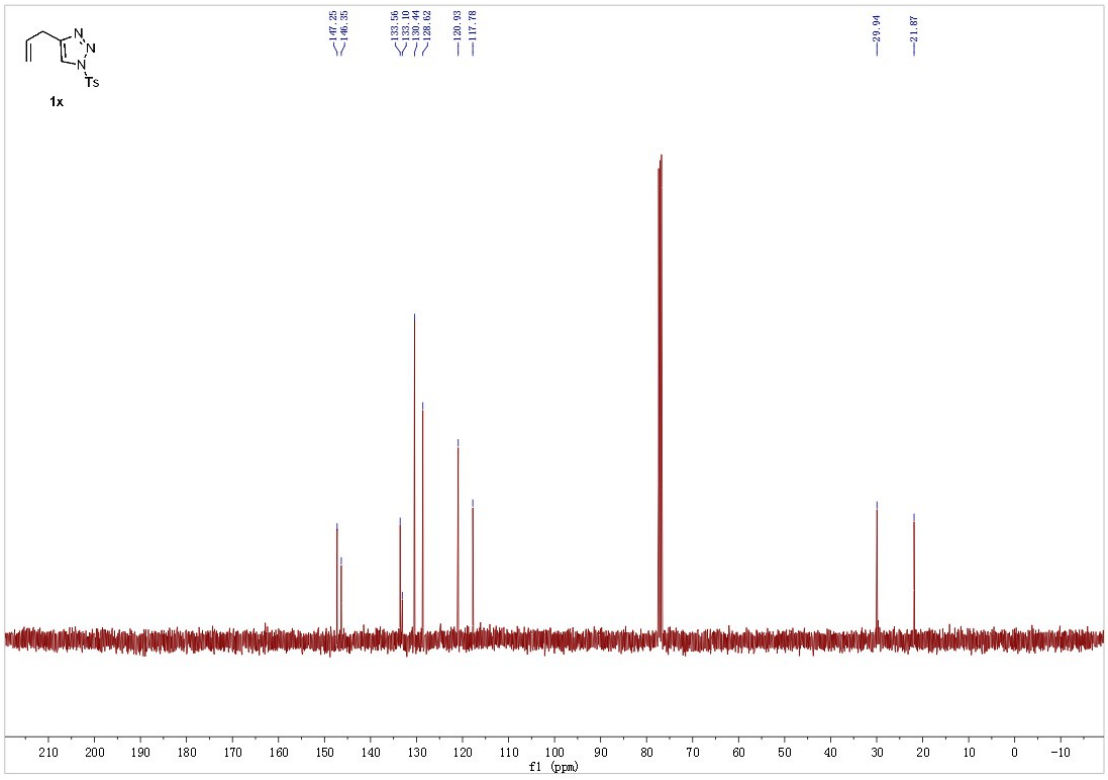

1v
8.08
7.95
7.93
7.35
7.33
5.83
5.81
5.70
5.77
5.76
5.74
5.69
5.67
5.65
5.66
5.31
5.30
3.72
2.40
1.66
1.64
1.02
2.02
2.05
2.08
1.01
1.06
3.01
3.03
f1 (ppm)

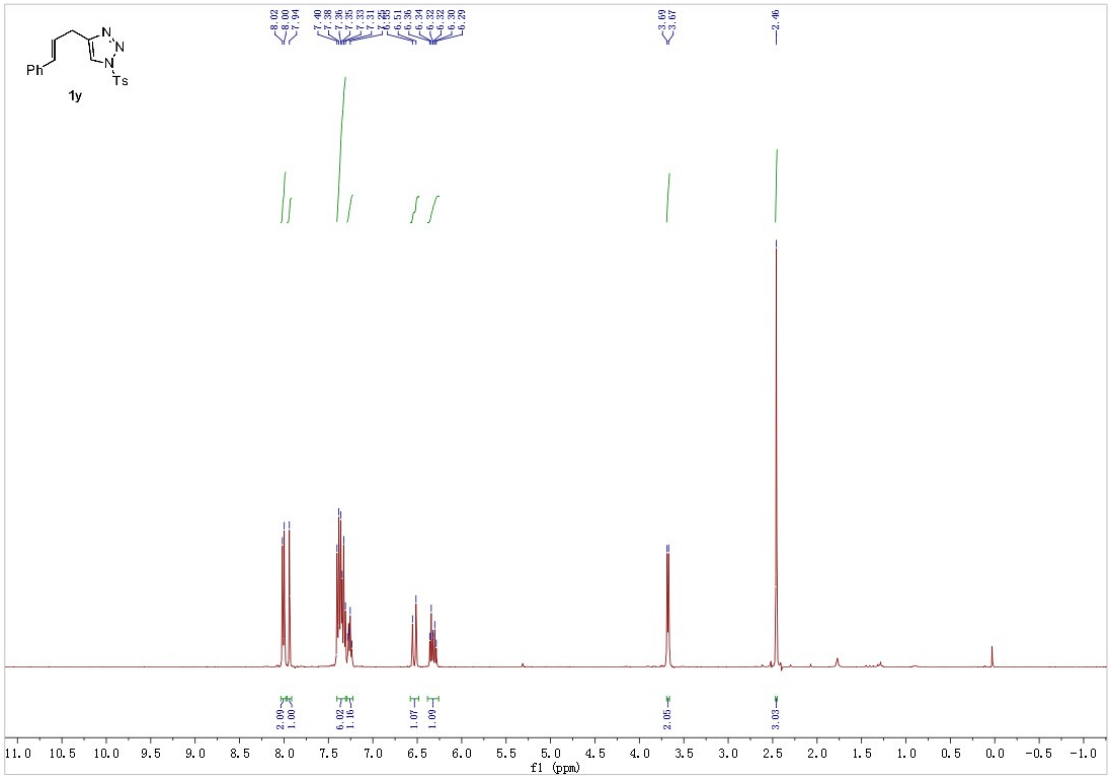

1v
150.46
147.44
132.81
130.71
130.48
129.33
128.64
120.96
67.44
21.81
17.66
f1 (ppm)

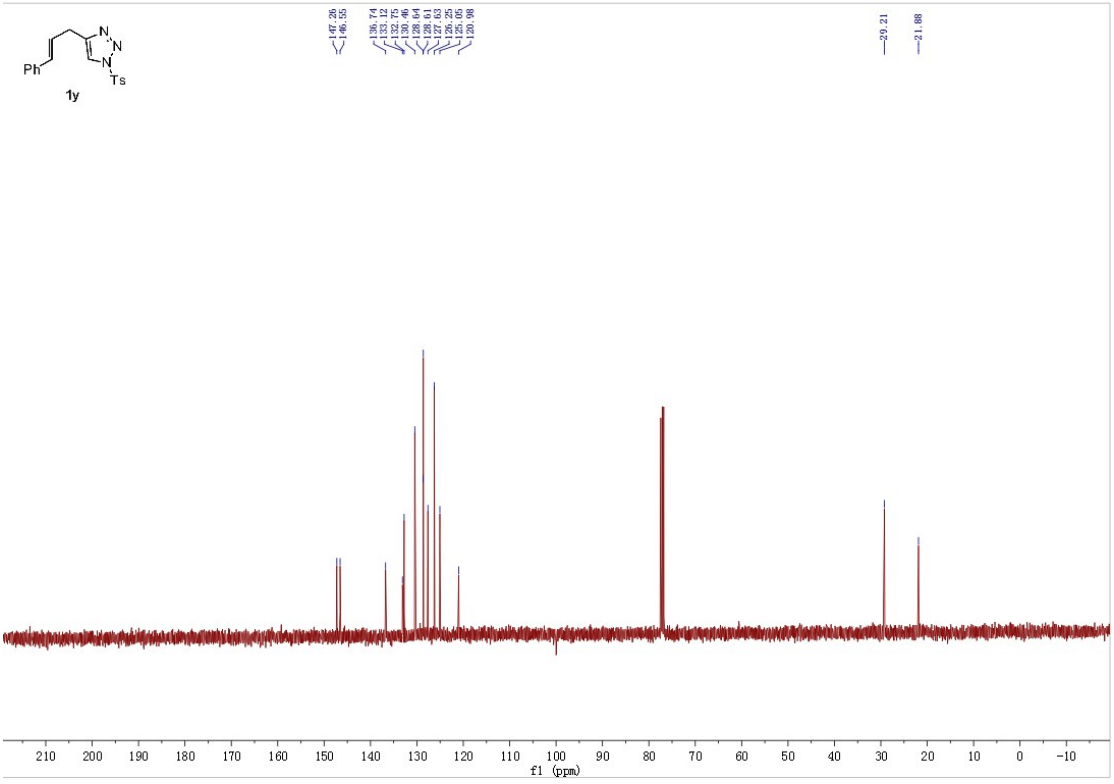

1w
Ts
8.05
7.99
7.96
7.38
7.36
5.90
5.88
5.87
5.84
5.83
5.81
5.58
5.56
5.54
5.52
4.82
4.80
3.33
2.43
1.75
1.73
1.00
2.07
2.09
1.03
1.01
1.00
3.01
3.02
3.04
f1 (ppm)

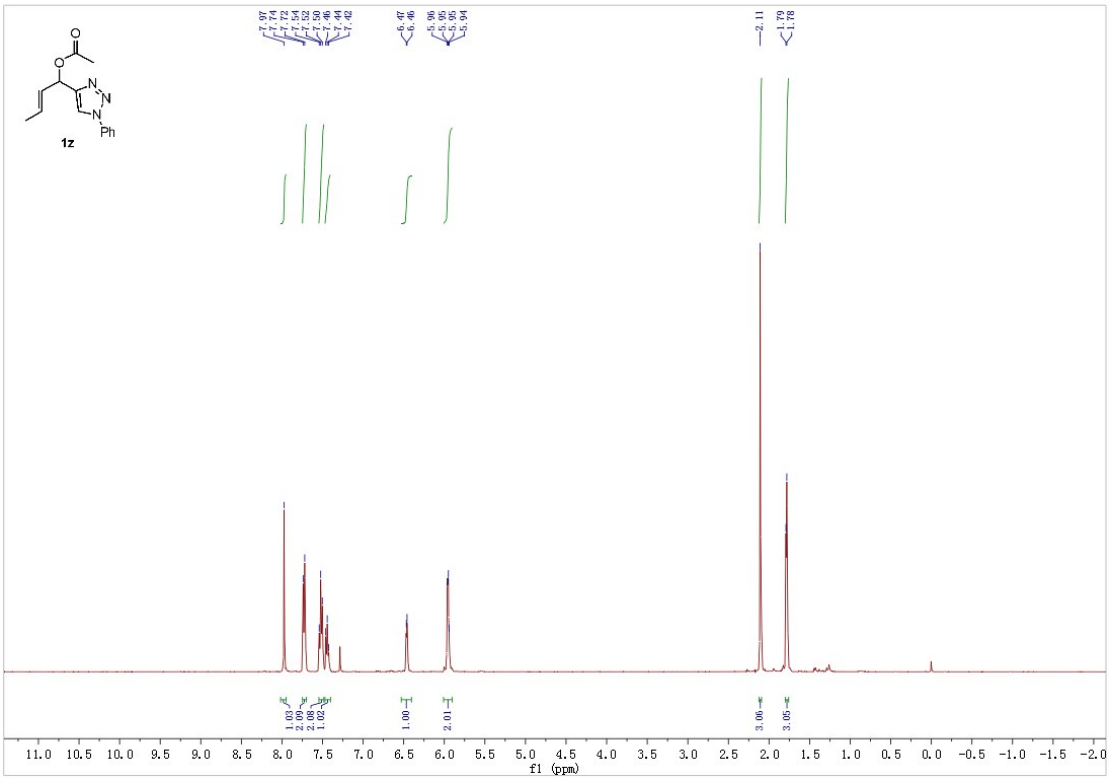

1w
Ts
148.65
147.35
132.94
131.39
130.44
128.68
128.37
121.08
76.71
56.26
21.84
17.79
f1 (ppm)

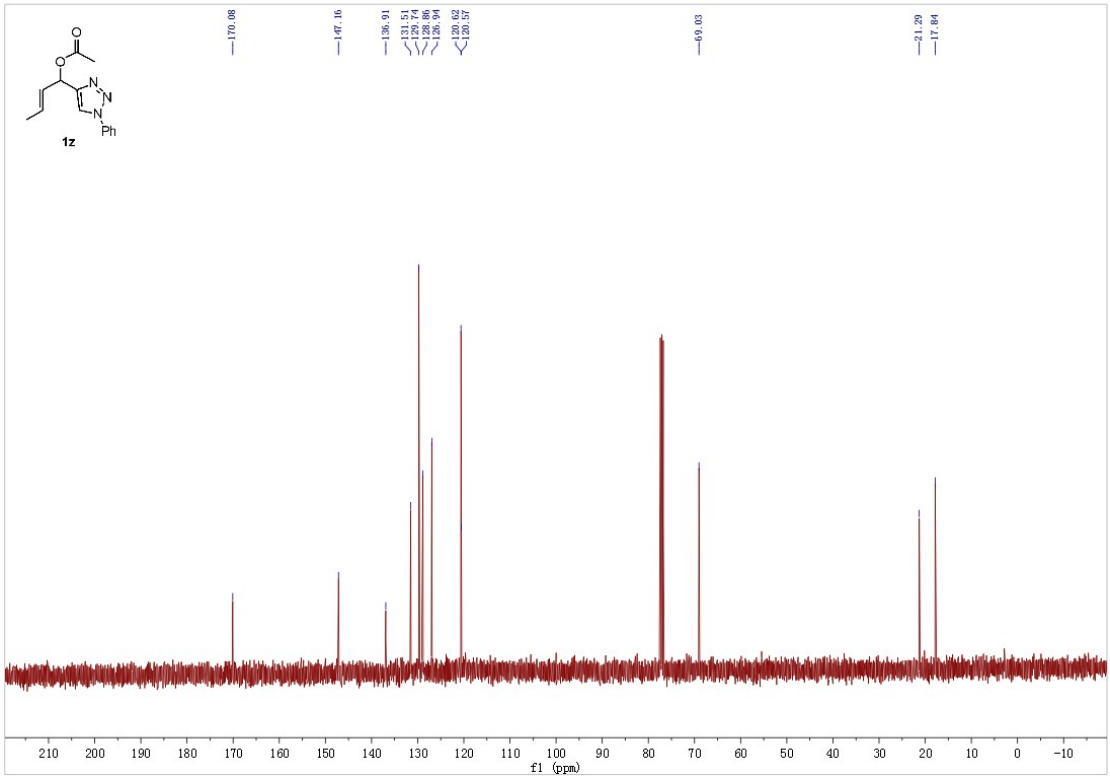

1x
Ts
7.97
7.95
7.86
7.37
7.35
5.96
5.94
5.92
5.90
5.88
5.86
5.15
5.13
5.11
3.49
3.47
2.42
2.06
1.00
2.06
0.99
2.00
2.06
3.06
f1 (ppm)

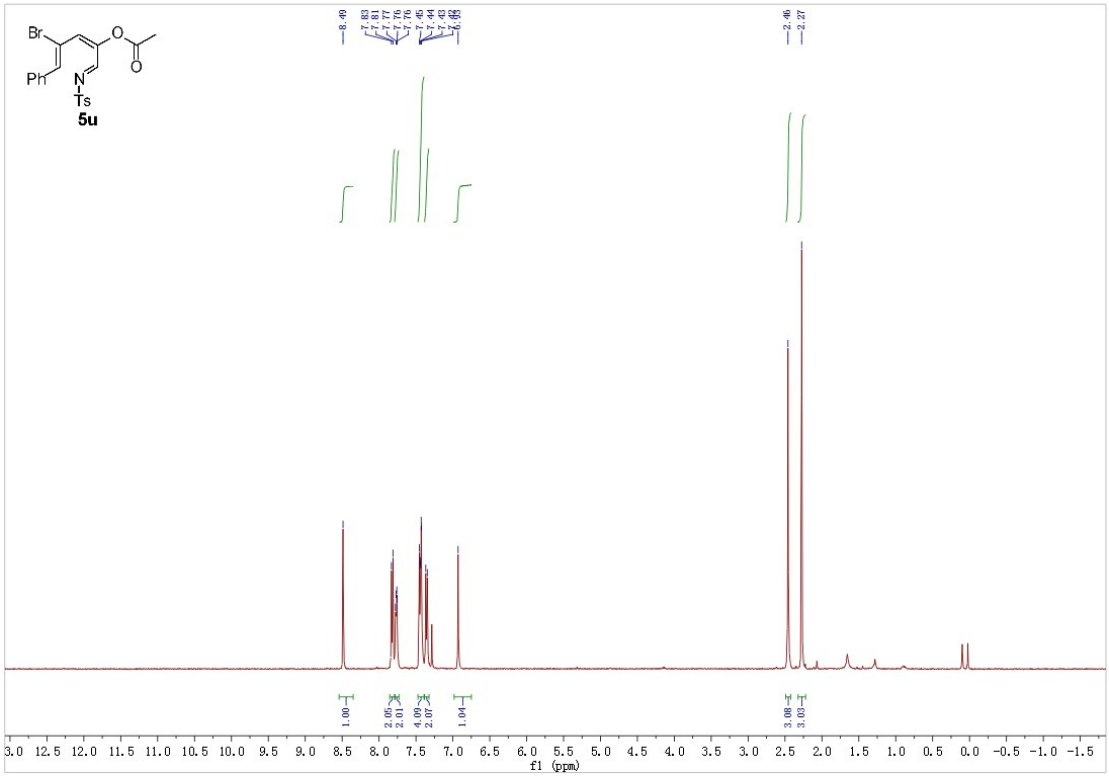

1x
Ts
147.25
146.35
133.56
133.10
130.44
128.62
120.93
117.78
29.94
21.87
f1 (ppm)

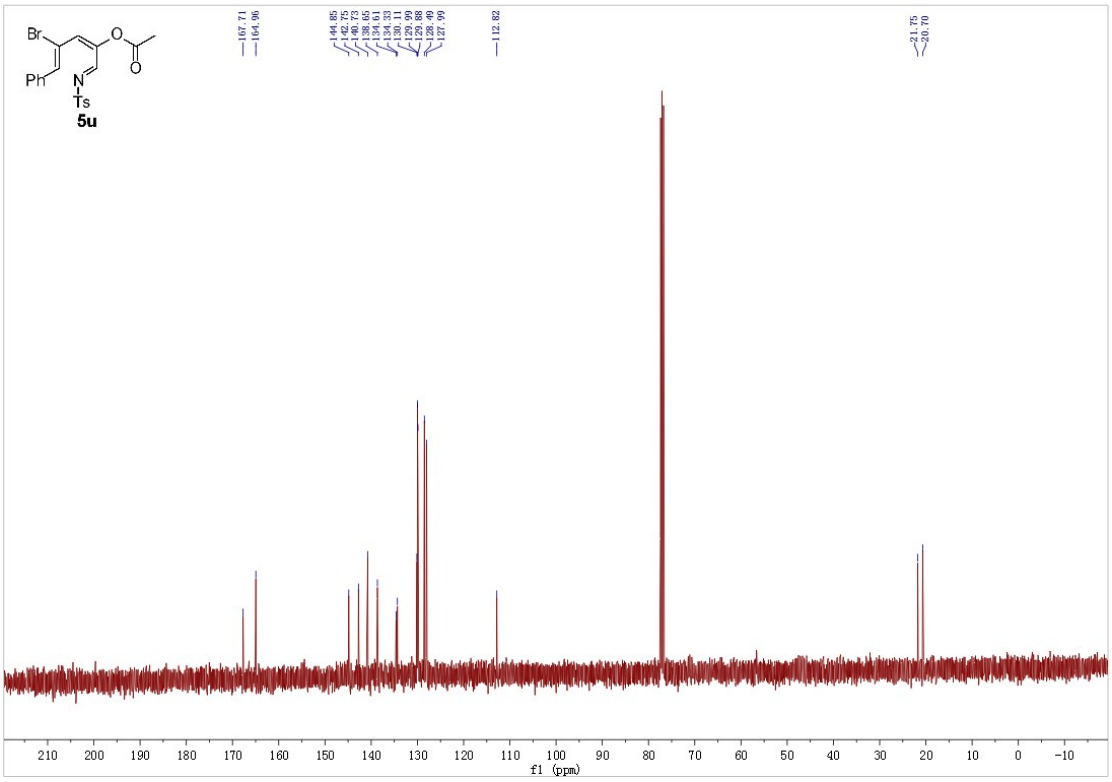

Ph
N
N
N
Ts
1y
8.02
8.00
7.94
7.40
7.38
7.36
7.35
7.33
7.31
6.51
6.36
6.34
6.32
6.30
6.29
3.69
3.67
2.46
2.09
1.00
6.02
1.16
1.07
1.00
2.05
3.03
f1 (ppm)

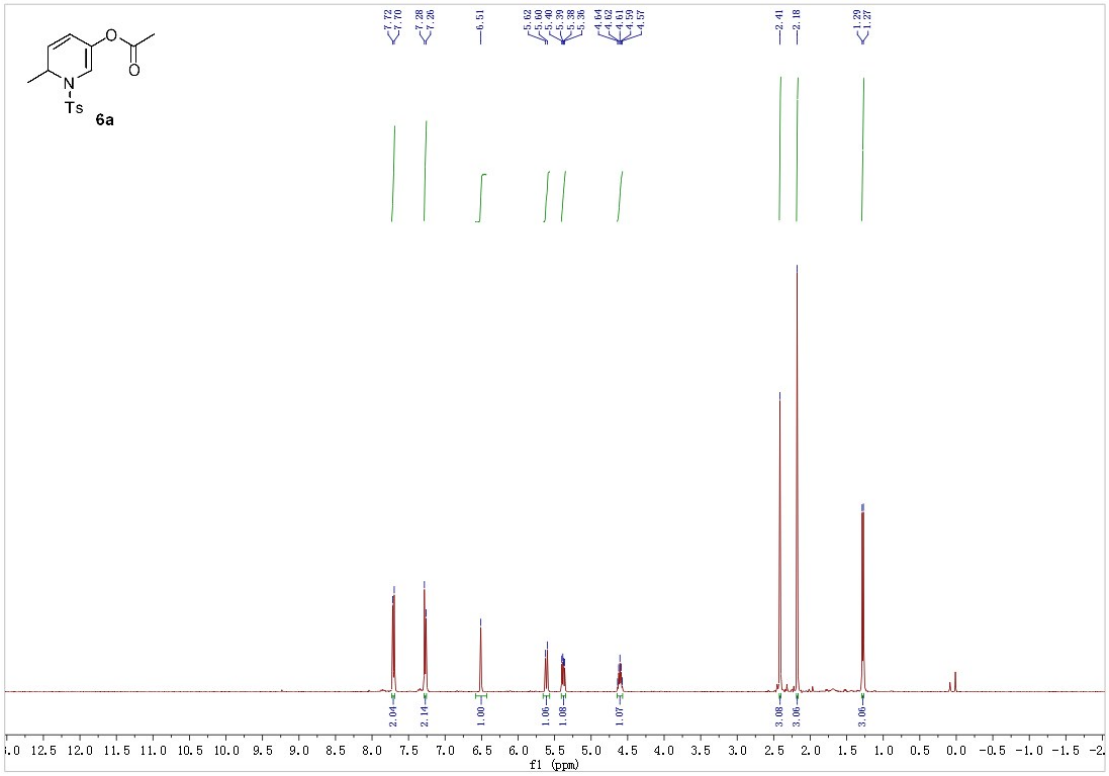

Ph
N
N
N
Ts
1y
147.26
146.55
136.74
133.12
132.75
130.46
128.64
128.61
127.63
126.25
125.95
120.98
29.21
21.88
f1 (ppm)

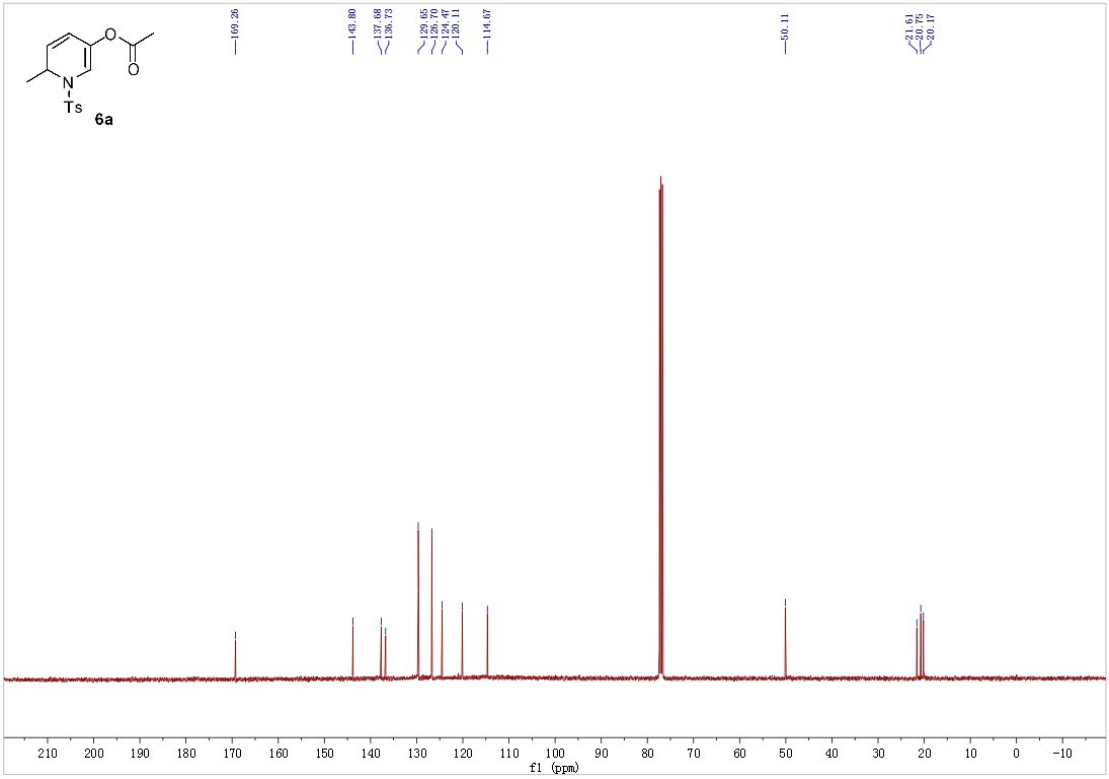

1z
7.97
7.74
7.72
7.54
7.52
7.50
7.46
7.44
7.42
6.47
6.46
5.96
5.95
5.95
5.94
2.11
1.79
1.78
1.03
2.09
2.08
1.02
1.00
2.01
3.00
3.05
f1 (ppm)

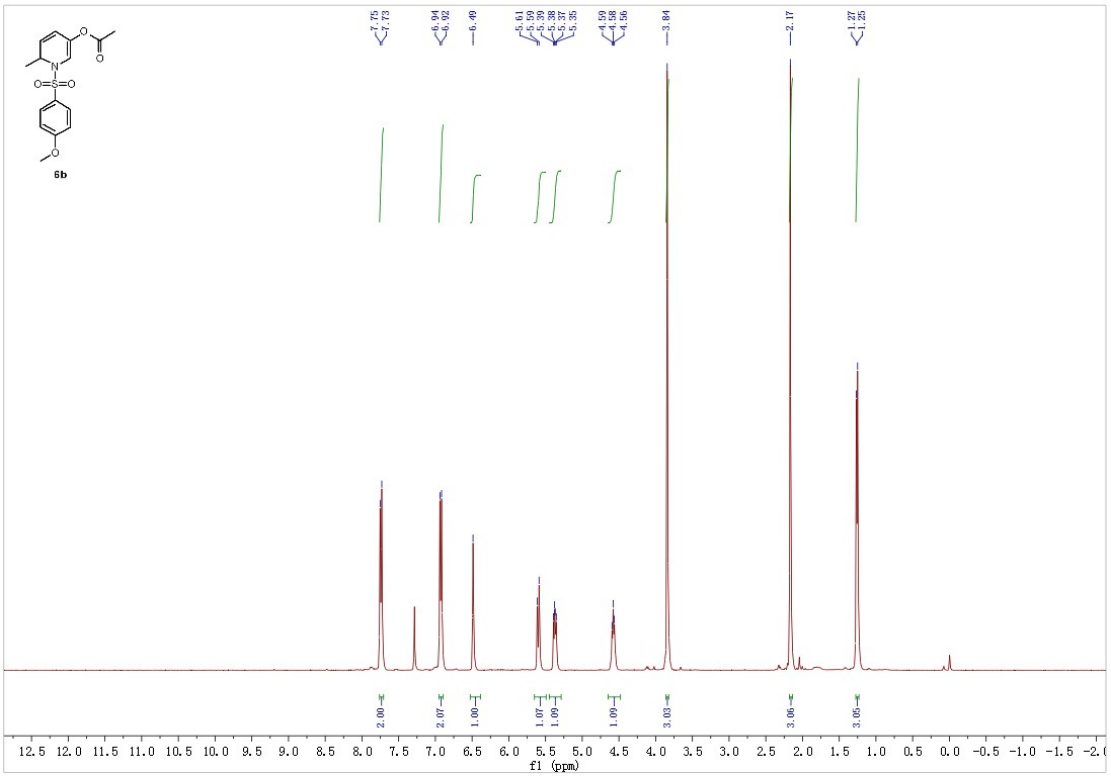

1z
170.08
147.16
136.91
131.51
129.74
128.86
126.94
120.62
120.57
69.03
21.29
17.84
f1 (ppm)

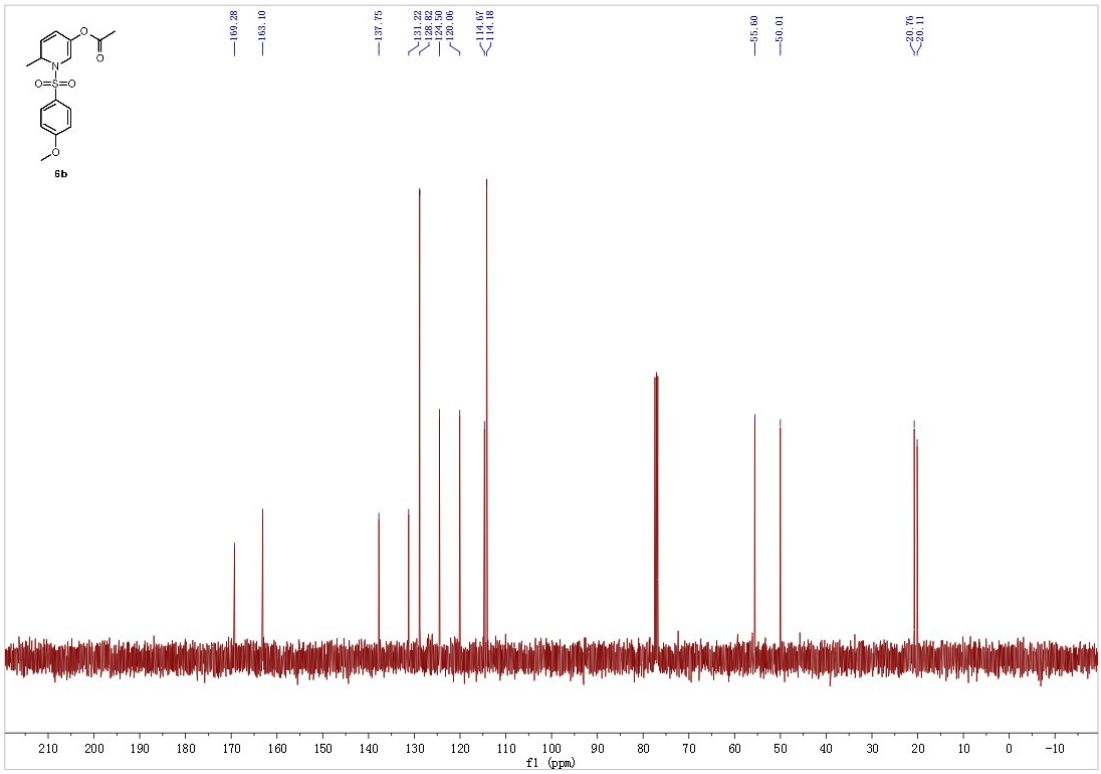

Br
O
O
Ph
N
Ts
5u
8.49
7.83
7.81
7.77
7.76
7.45
7.44
7.43
7.42
2.46
2.27
1.00
2.05
2.01
4.09
2.07
1.04
3.08
3.03
f1 (ppm)

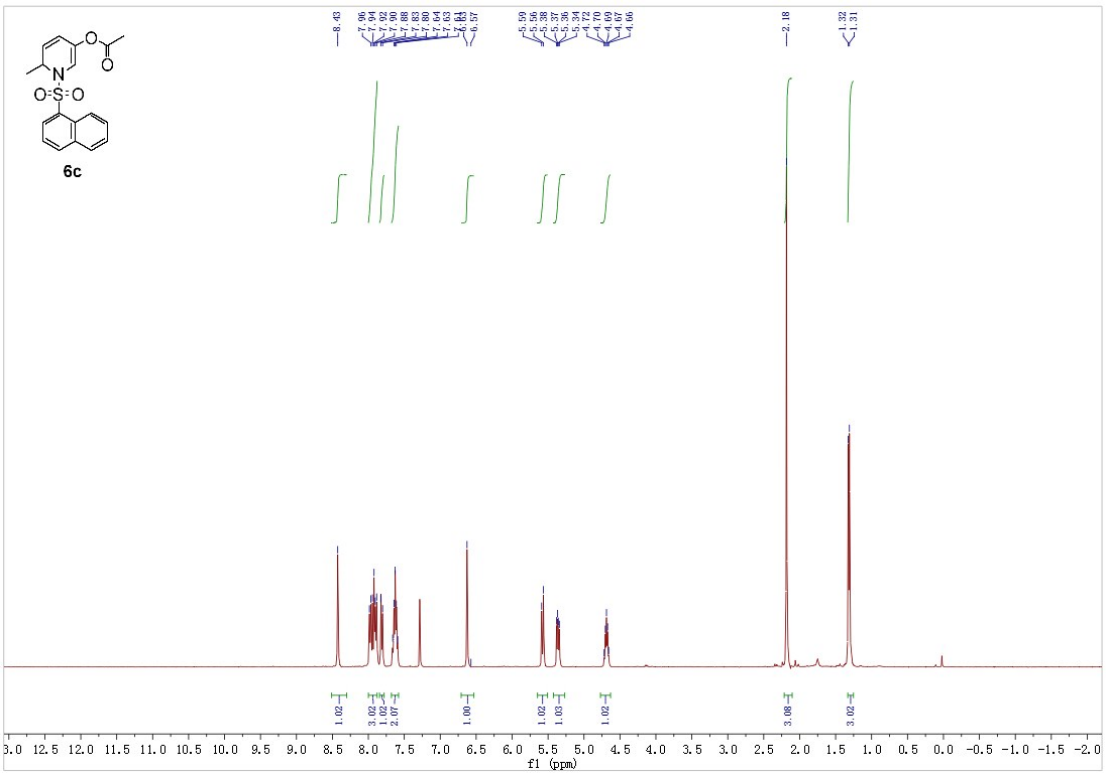

Br
O
O
Ph
N
Ts
5u
167.71
164.96
144.85
142.75
140.73
138.65
134.61
134.33
130.11
129.99
129.88
128.40
127.99
112.82
21.75
20.70
f1 (ppm)

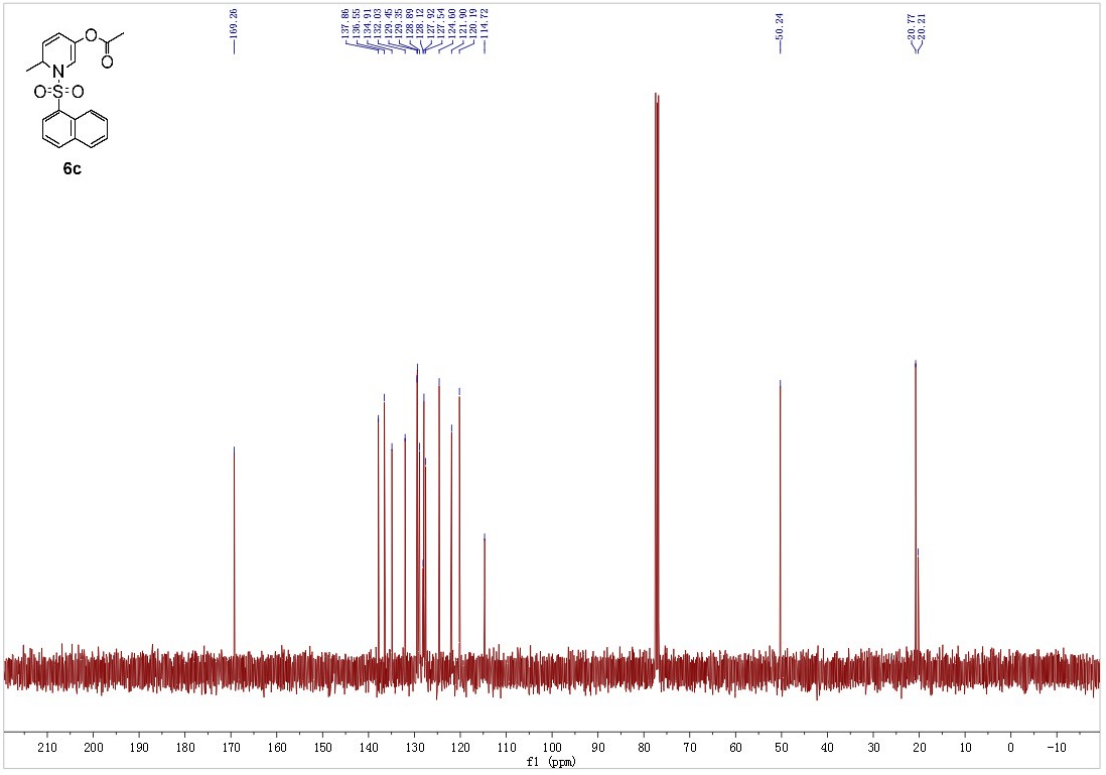

6a
f1 (ppm)

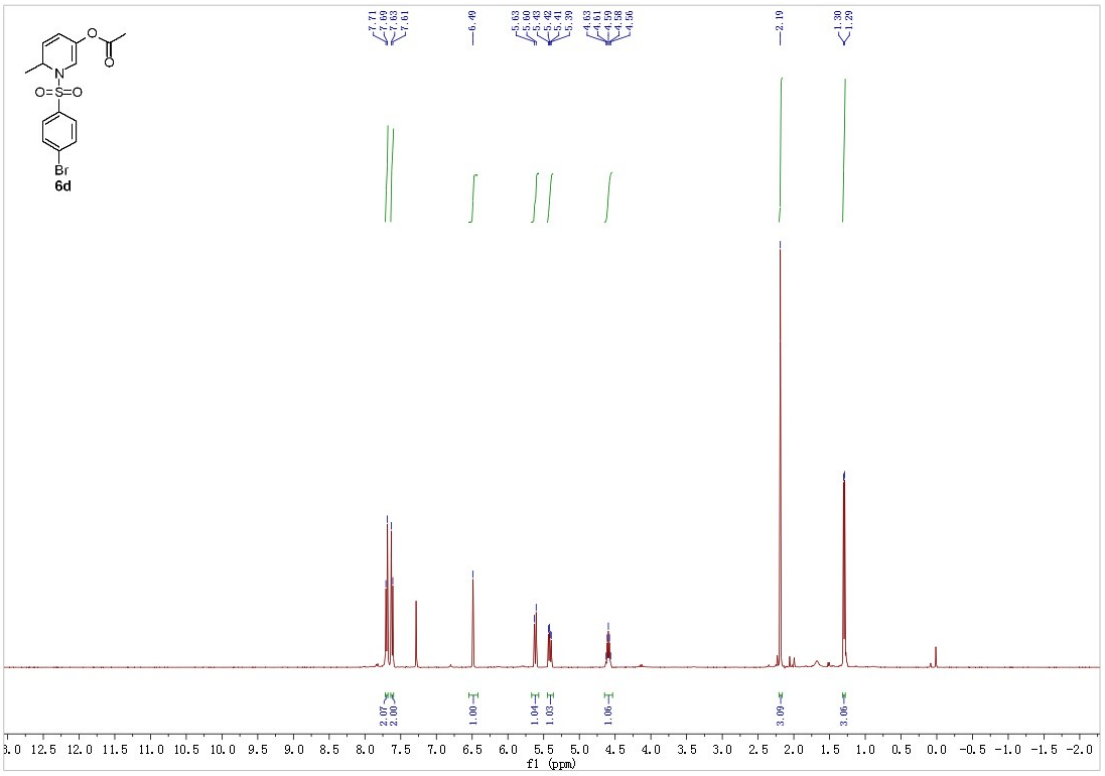

6a
f1 (ppm)

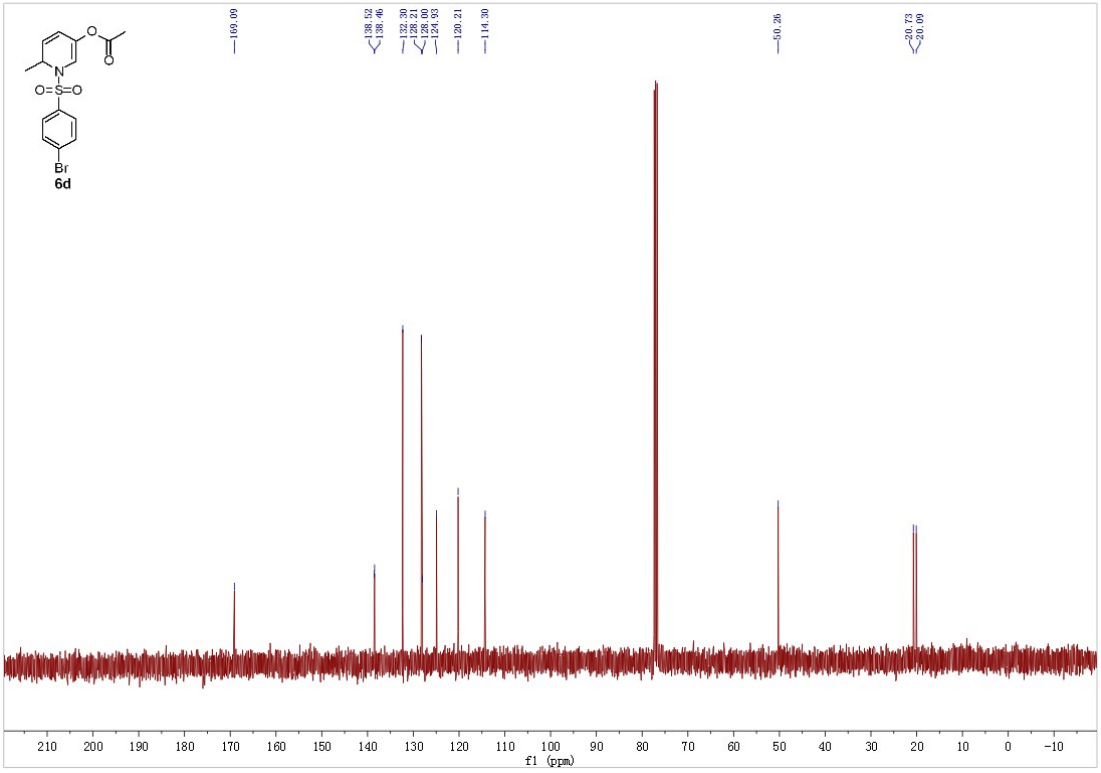

6b
7.75
7.73
6.94
6.92
6.49
5.61
5.59
5.39
5.38
5.37
5.35
4.59
4.58
4.56
3.84
2.17
1.27
1.25
2.00
2.07
1.00
1.07
1.09
1.09
3.03
3.06
3.05
f1 (ppm)

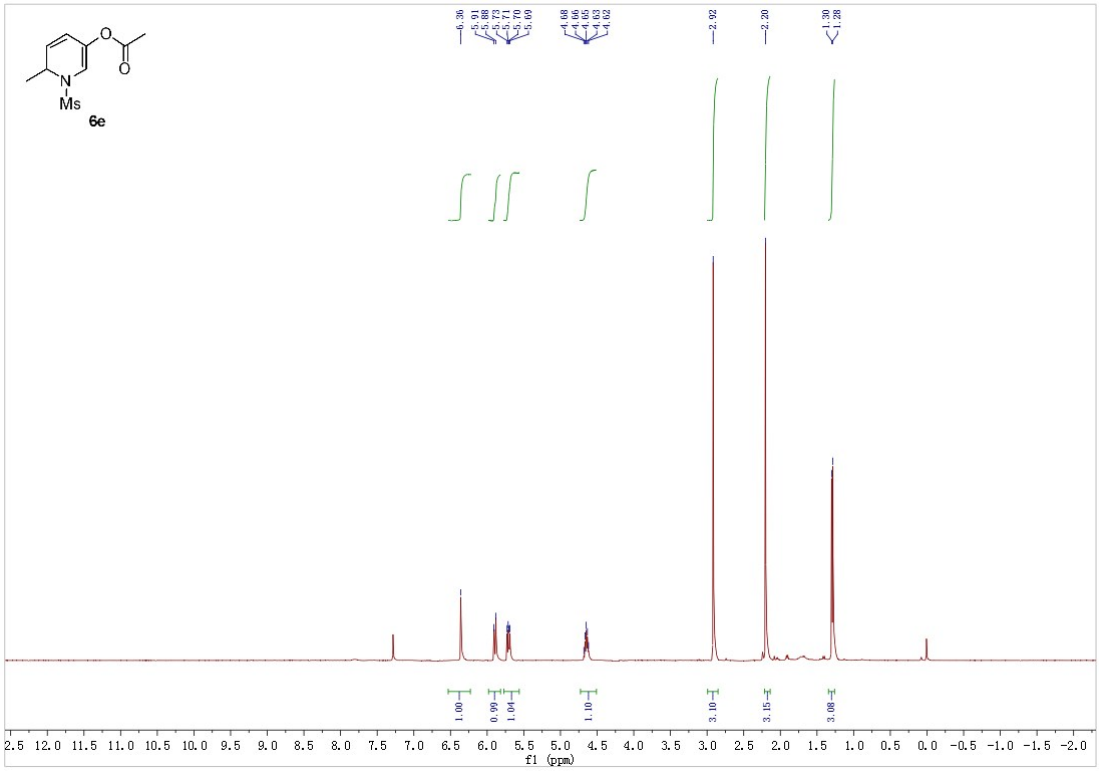

6b
169.28
163.10
137.75
131.22
128.52
124.50
120.06
114.67
114.18
55.60
50.01
20.75
20.11
f1 (ppm)

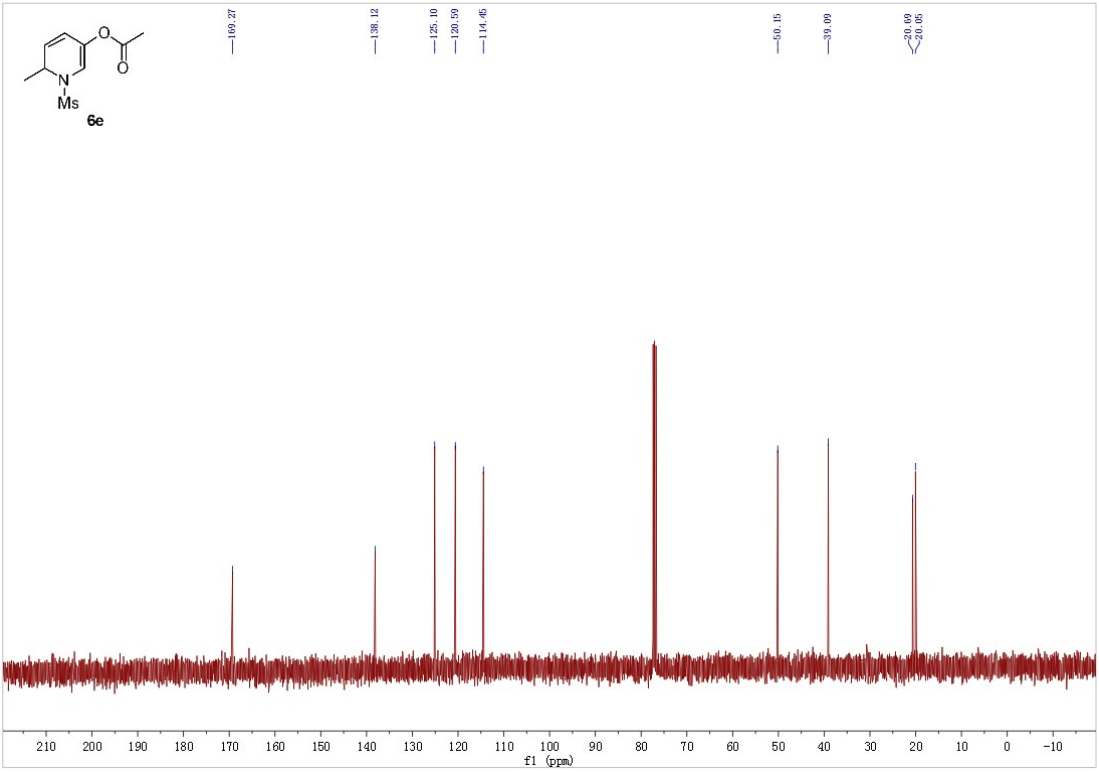

6c
f1 (ppm)

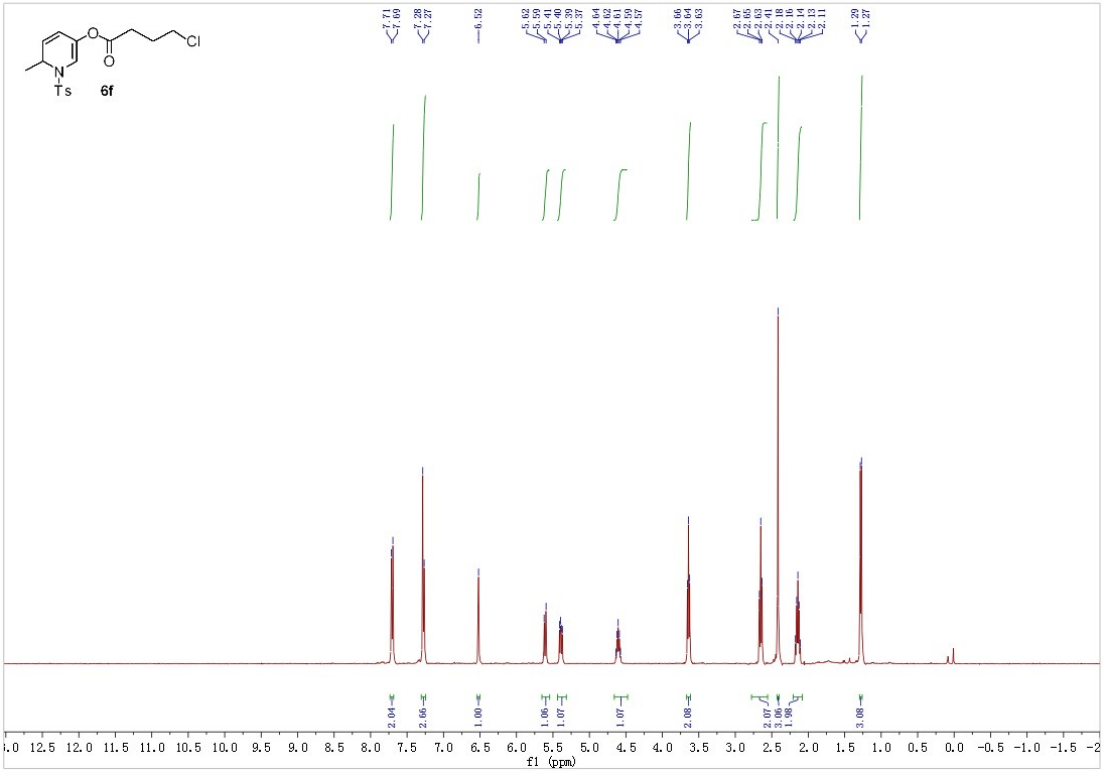

6c
f1 (ppm)

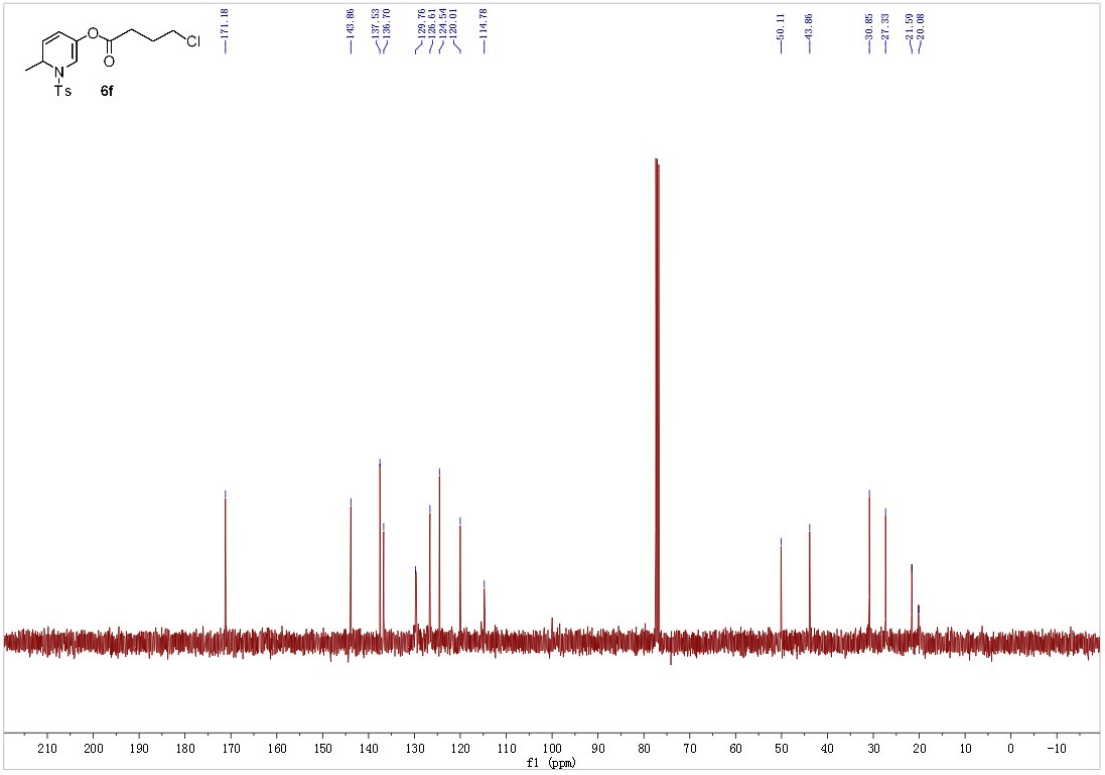

6d
7.71
7.69
7.63
7.61
6.49
5.63
5.60
5.43
5.42
5.41
5.39
4.63
4.61
4.59
4.58
4.56
2.19
1.30
1.29
2.07
2.00
1.00
1.04
1.03
1.06
3.09
3.06
f1 (ppm)

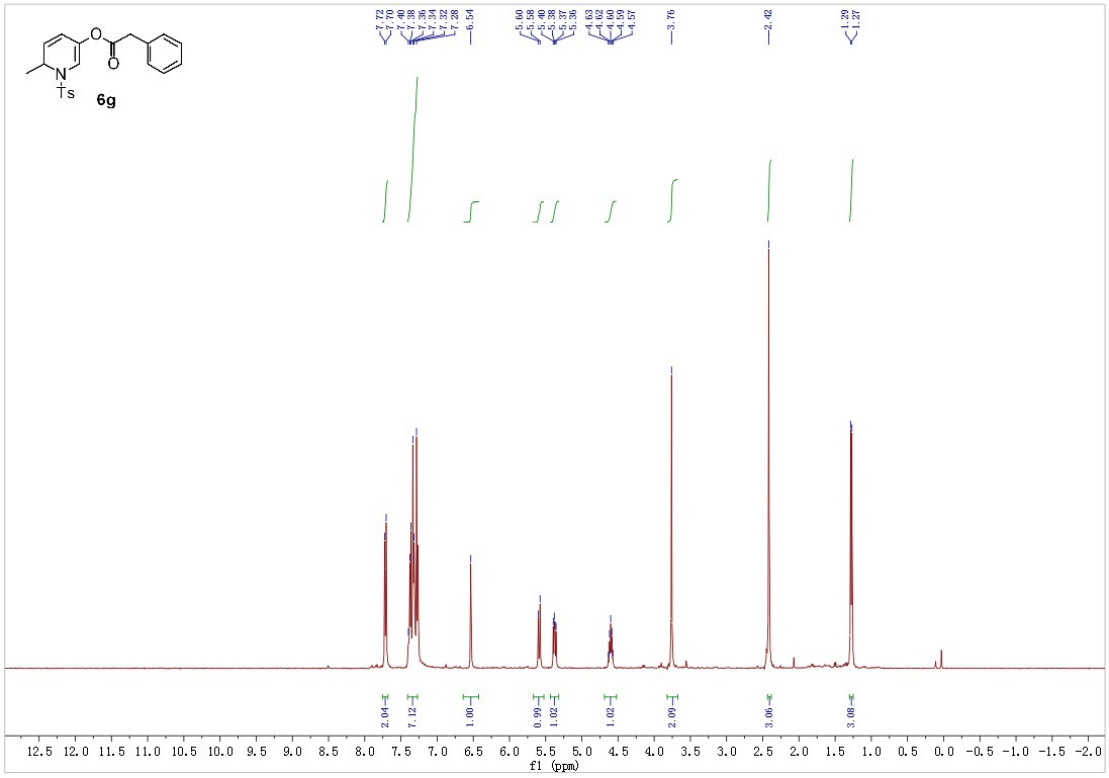

6d
169.09
138.52
138.46
132.30
128.27
128.00
124.93
120.21
114.30
50.26
20.73
20.09
f1 (ppm)

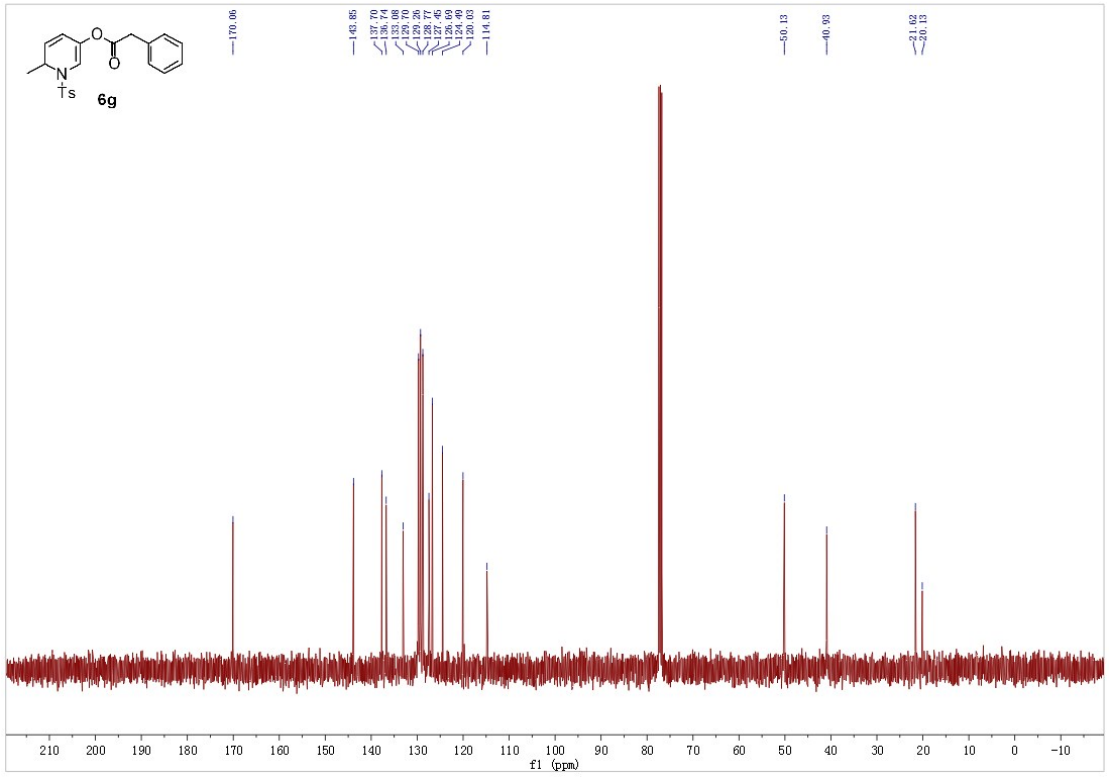

6e
6.36
5.91
5.88
5.73
5.71
5.70
5.69
4.68
4.66
4.65
4.63
4.62
2.92
2.20
1.30
1.28
1.00
0.99
1.04
1.10
3.10
3.15
3.08
f1 (ppm)

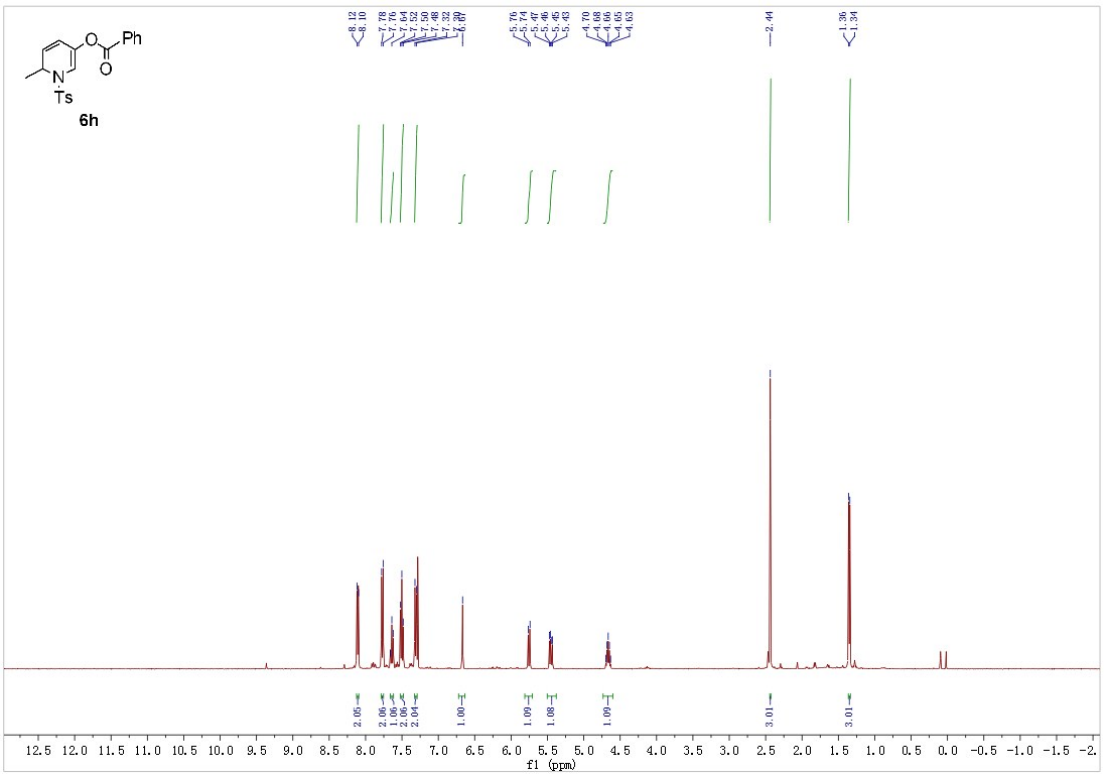

6e
169.27
138.12
125.10
120.59
114.45
50.15
39.09
20.69
20.05
f1 (ppm)

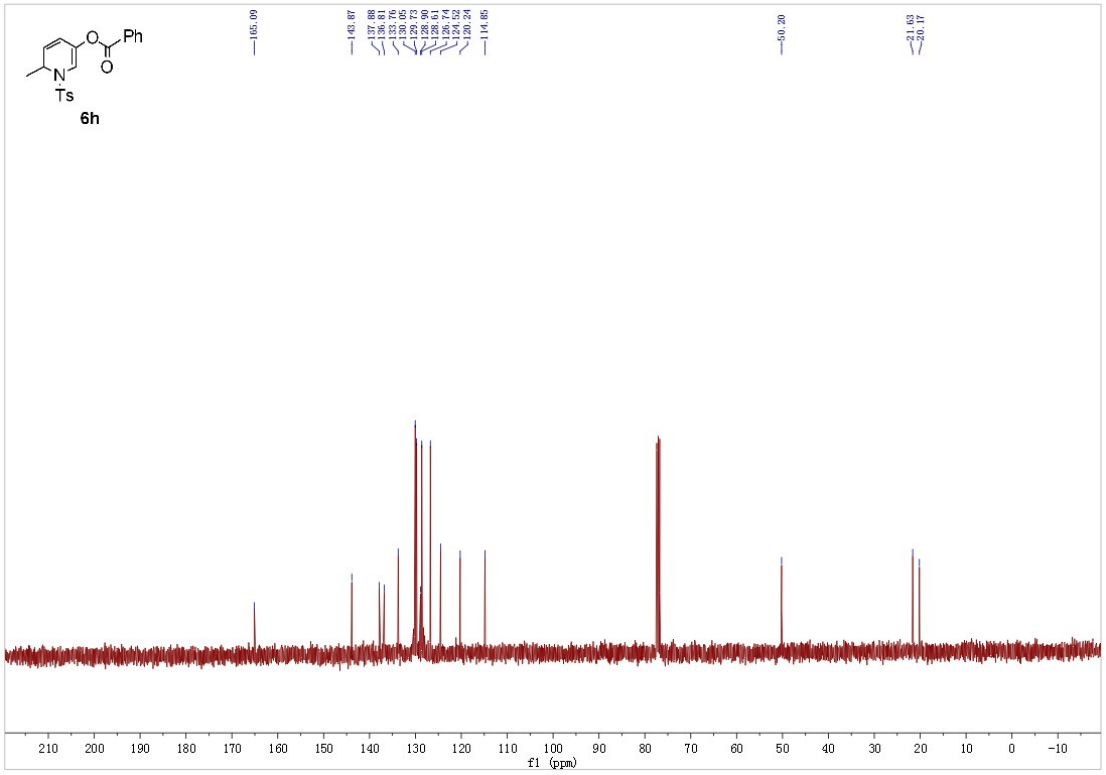

Ts
6f
Cl
f1 (ppm)

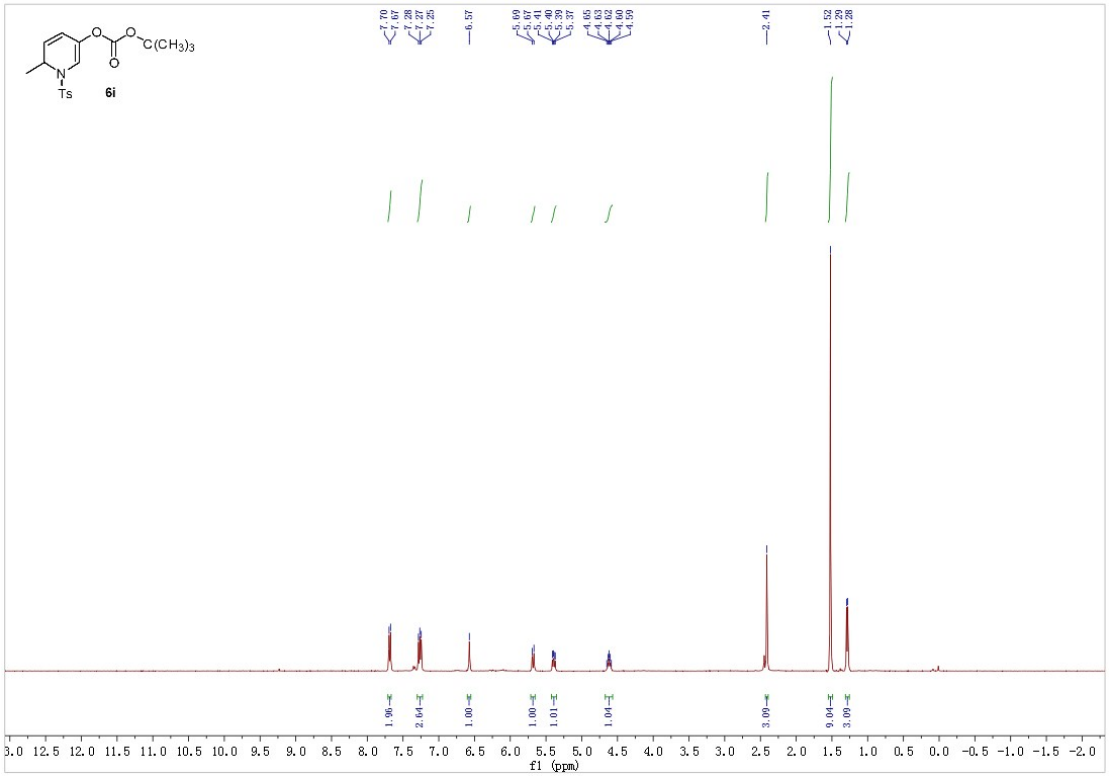

Ts
6f
Cl
f1 (ppm)

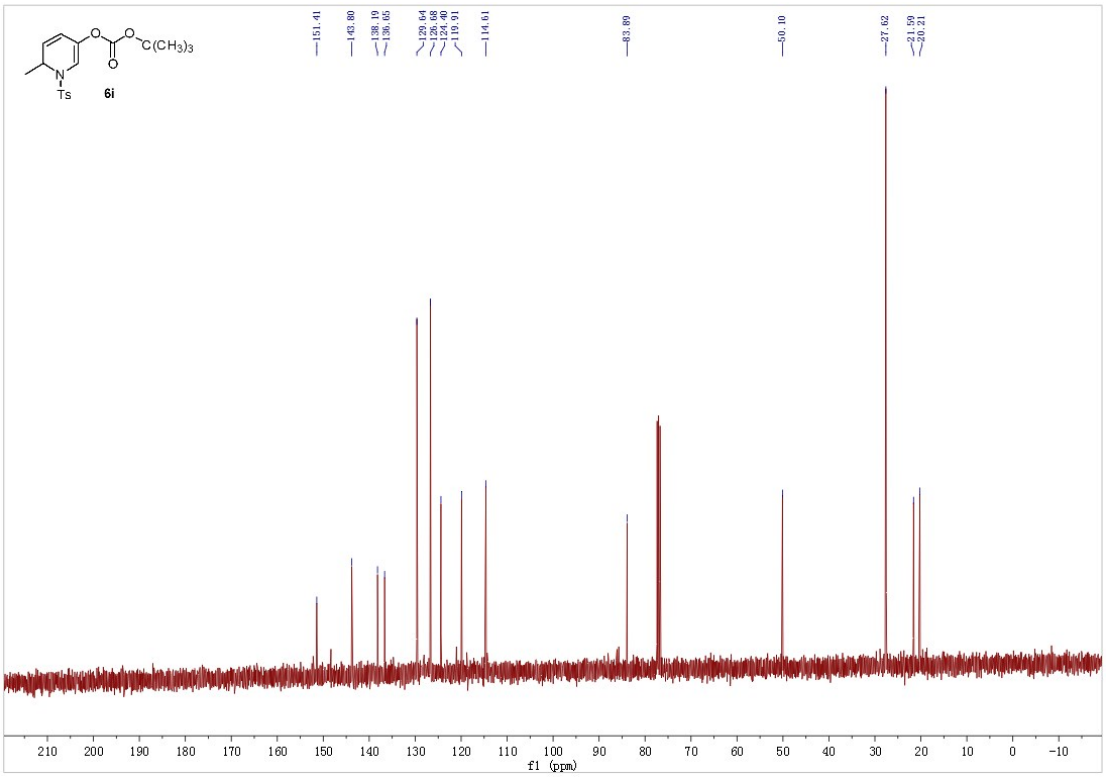

6g
7.72
7.70
7.40
7.38
7.36
7.34
7.32
7.28
6.54
5.60
5.58
5.40
5.38
5.37
5.36
4.63
4.62
4.60
4.59
4.57
3.76
2.42
1.29
1.27
2.04
7.12
1.00
0.99
1.02
1.02
2.09
3.06
3.08
f1 (ppm)

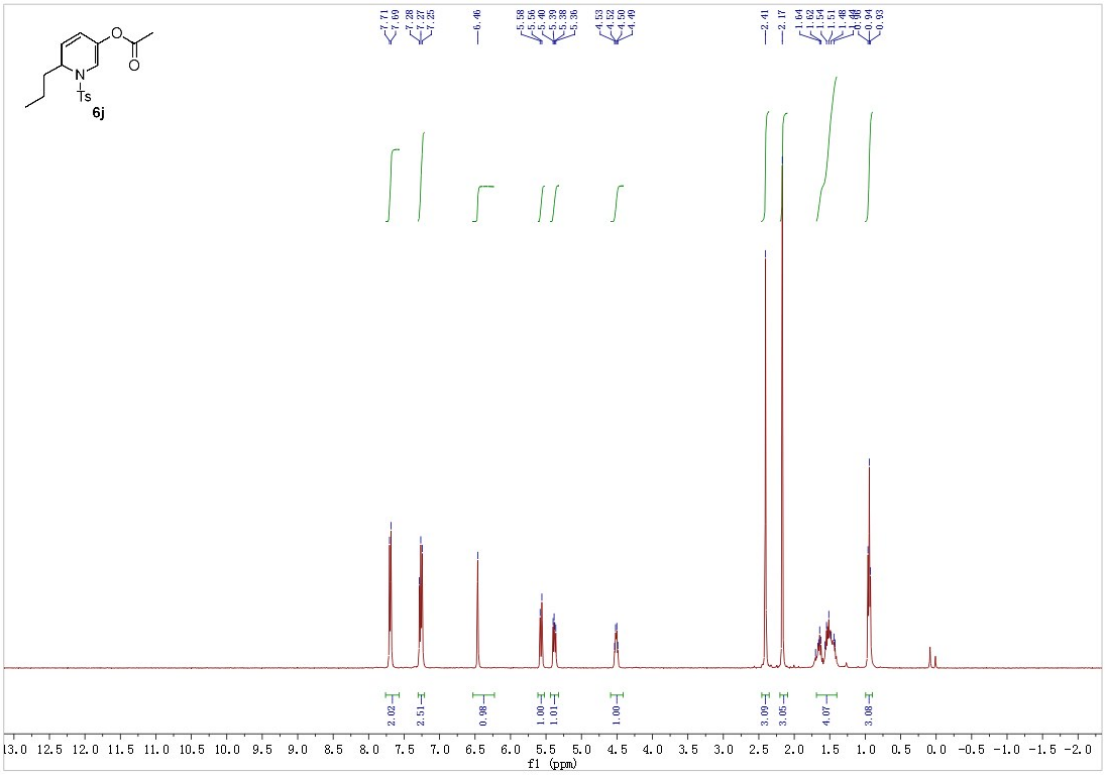

6g
170.06
143.85
137.70
136.74
133.08
129.70
129.26
128.77
127.45
126.69
126.40
120.03
114.81
50.13
40.93
21.02
20.13
f1 (ppm)

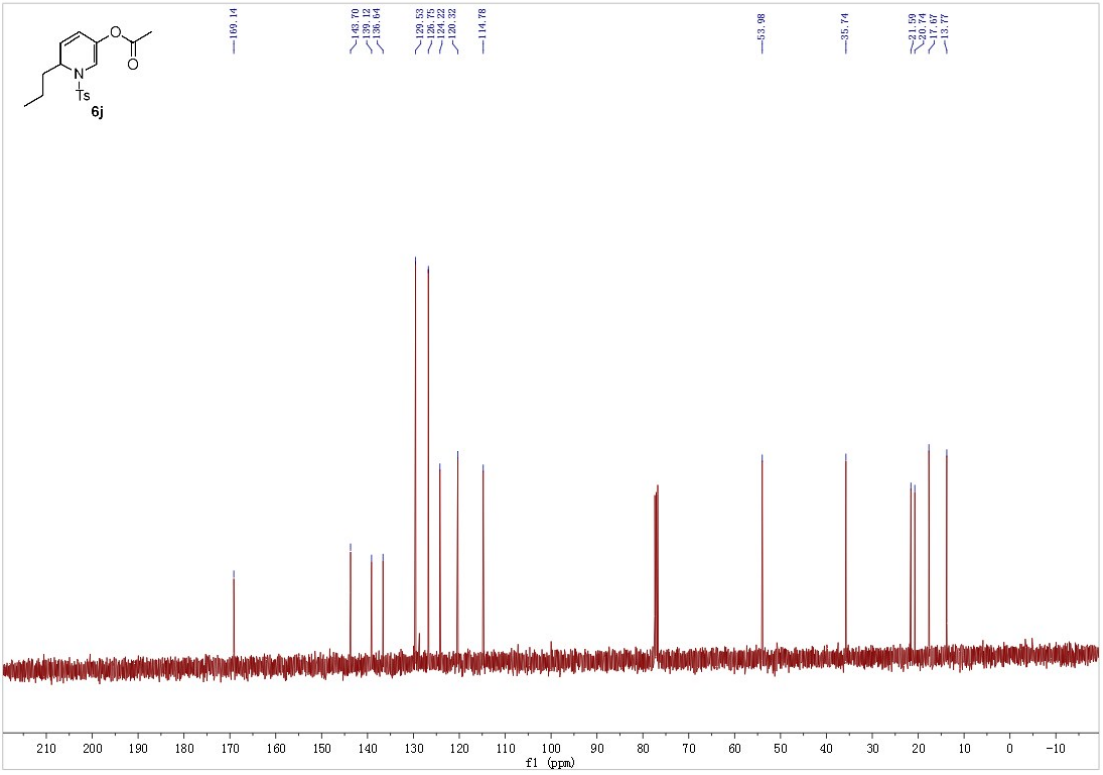

Ph
O
O
N
Ts
6h
8.12
8.10
7.78
7.76
7.64
7.52
7.50
7.48
7.32
7.30
6.87
5.76
5.74
5.47
5.46
5.45
5.43
4.70
4.68
4.66
4.65
4.63
2.44
1.36
1.34
2.05
2.06
1.06
1.06
2.04
1.00
1.09
1.08
1.09
3.01
3.01
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.
f1 (ppm)

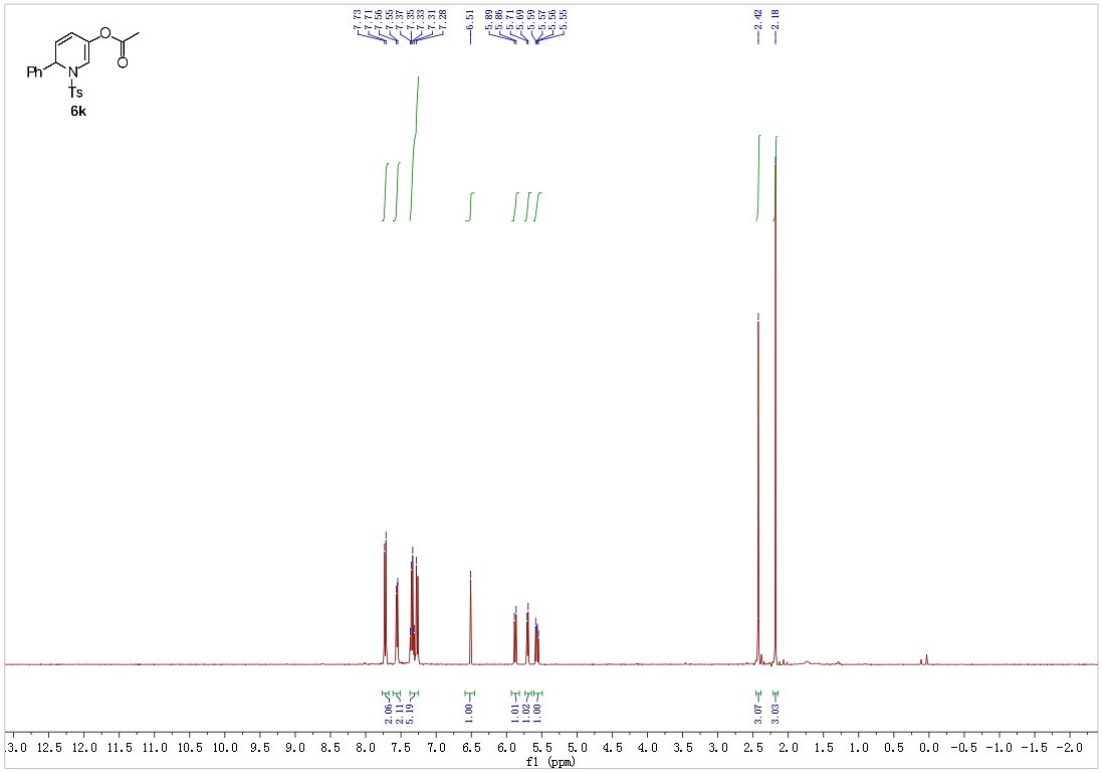

Ph
O
O
N
Ts
6h
165.09
143.87
137.88
136.81
133.76
130.05
129.73
128.90
128.61
126.74
126.52
120.24
114.85
50.20
21.63
20.17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

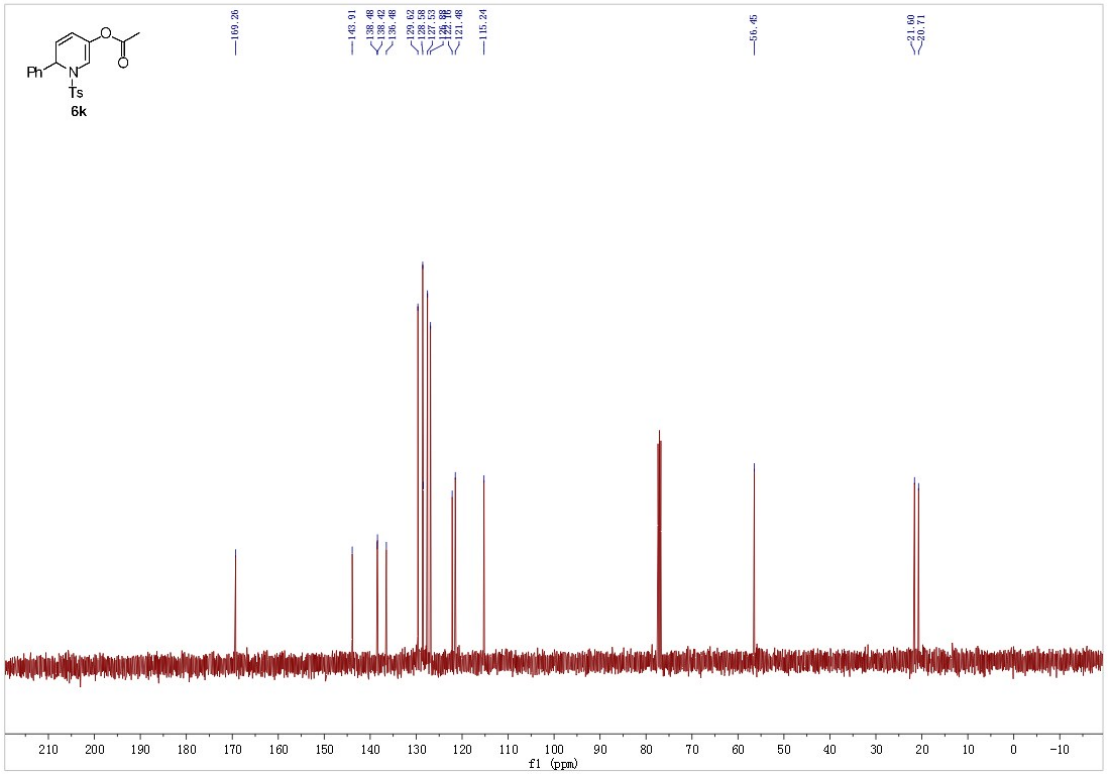

7.70
7.67
7.28
7.27
7.25
6.57
5.69
5.67
5.41
5.40
5.39
5.37
4.65
4.63
4.62
4.60
4.59
2.41
1.52
1.29
1.28
1.96
2.64
1.00
1.00
1.01
1.04
3.09
9.04
3.09
f1 (ppm)
Ts
6i

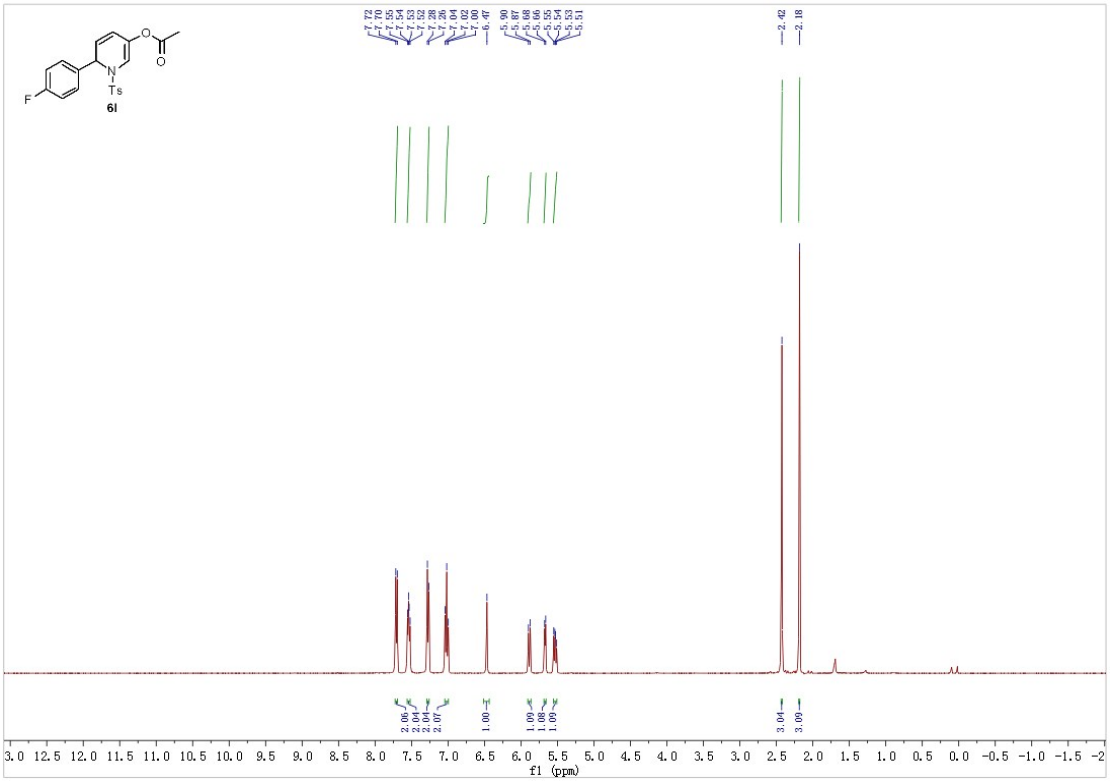

151.41
143.80
138.19
136.65
129.64
126.68
124.60
119.91
114.61
83.89
50.10
27.62
21.59
20.21
f1 (ppm)
Ts
6i

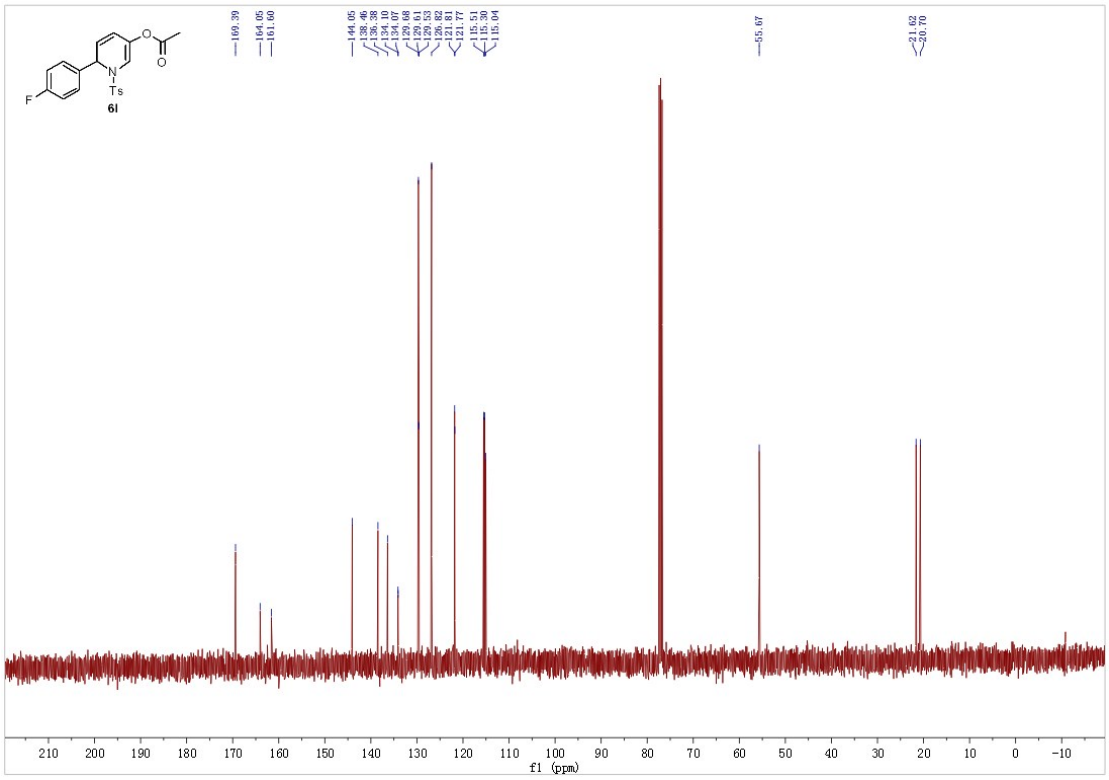

6j
7.71
7.69
7.28
7.27
7.25
6.46
5.58
5.56
5.40
5.39
5.38
5.36
4.53
4.52
4.50
4.49
2.41
2.17
1.64
1.62
1.51
1.48
0.94
0.93
2.02
2.51
0.98
1.00
1.01
1.00
3.09
3.05
4.07
3.08
f1 (ppm)

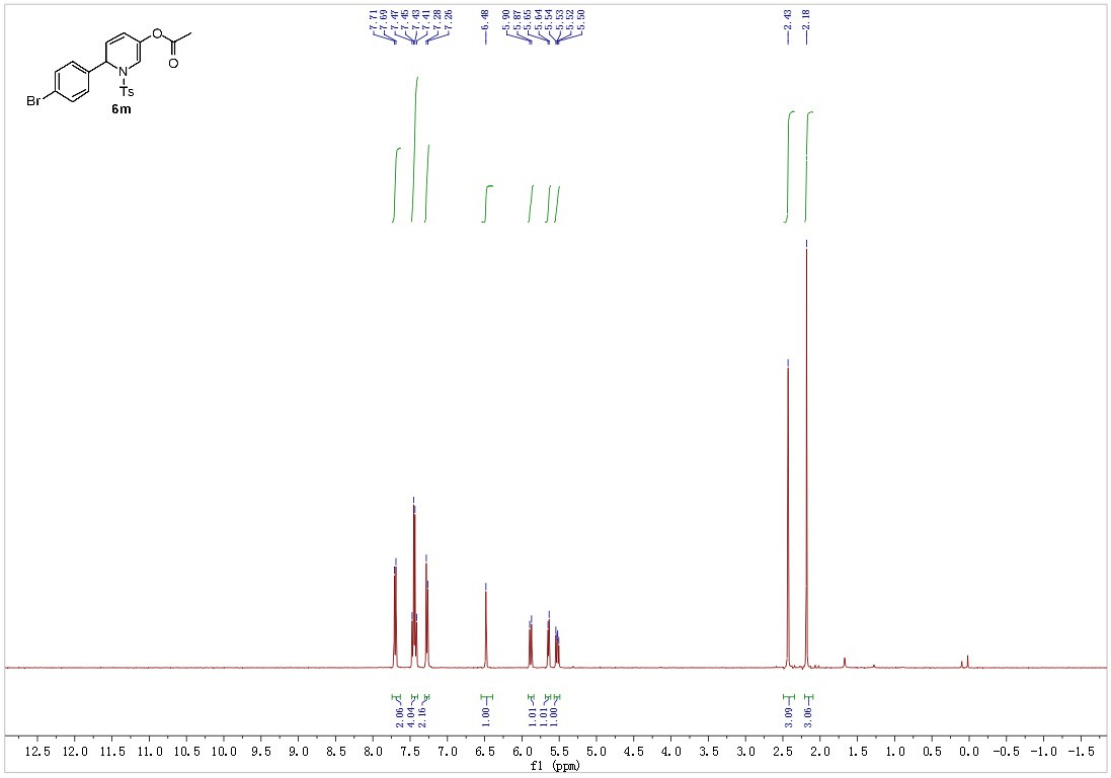

6j
169.14
143.70
139.12
136.64
129.53
128.75
128.22
126.32
114.78
53.98
35.74
21.59
20.74
17.67
13.77
f1 (ppm)

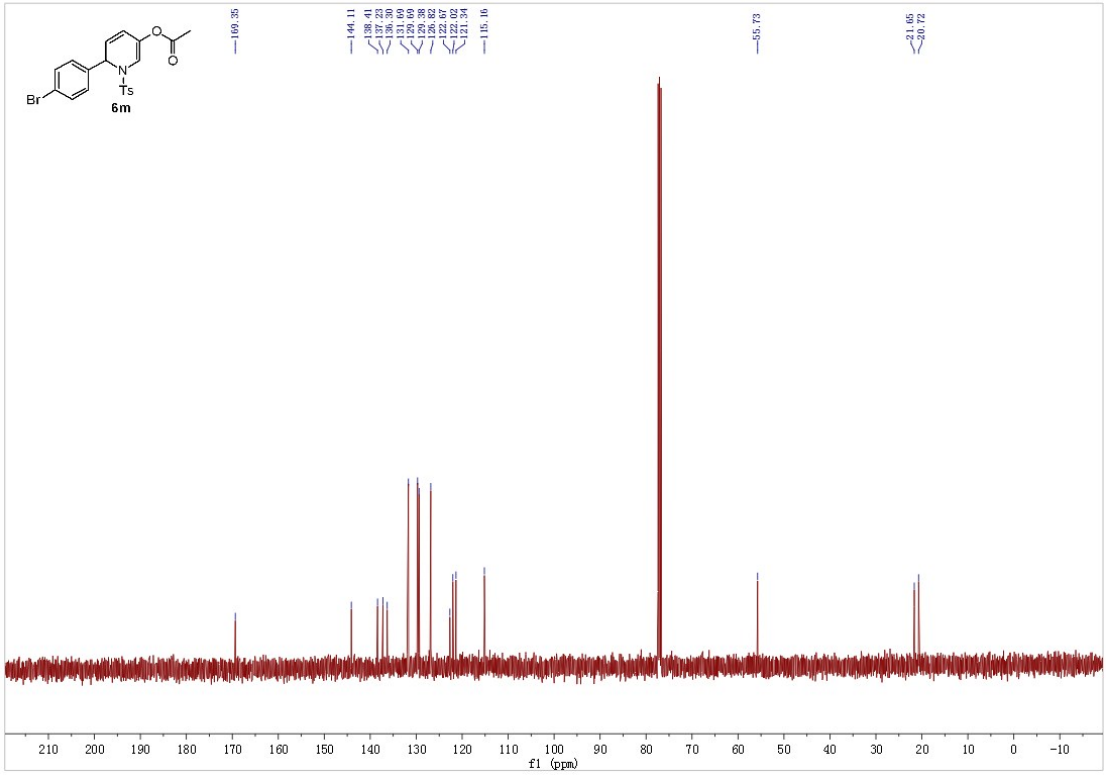

Ph
N
Ts
O
O
6k
7.73
7.71
7.56
7.55
7.37
7.35
7.33
7.31
7.28
6.51
5.89
5.86
5.71
5.69
5.59
5.57
5.56
5.55
2.42
2.18
2.06
2.11
5.19
1.00
1.01
1.02
1.00
3.07
3.03
f1 (ppm)

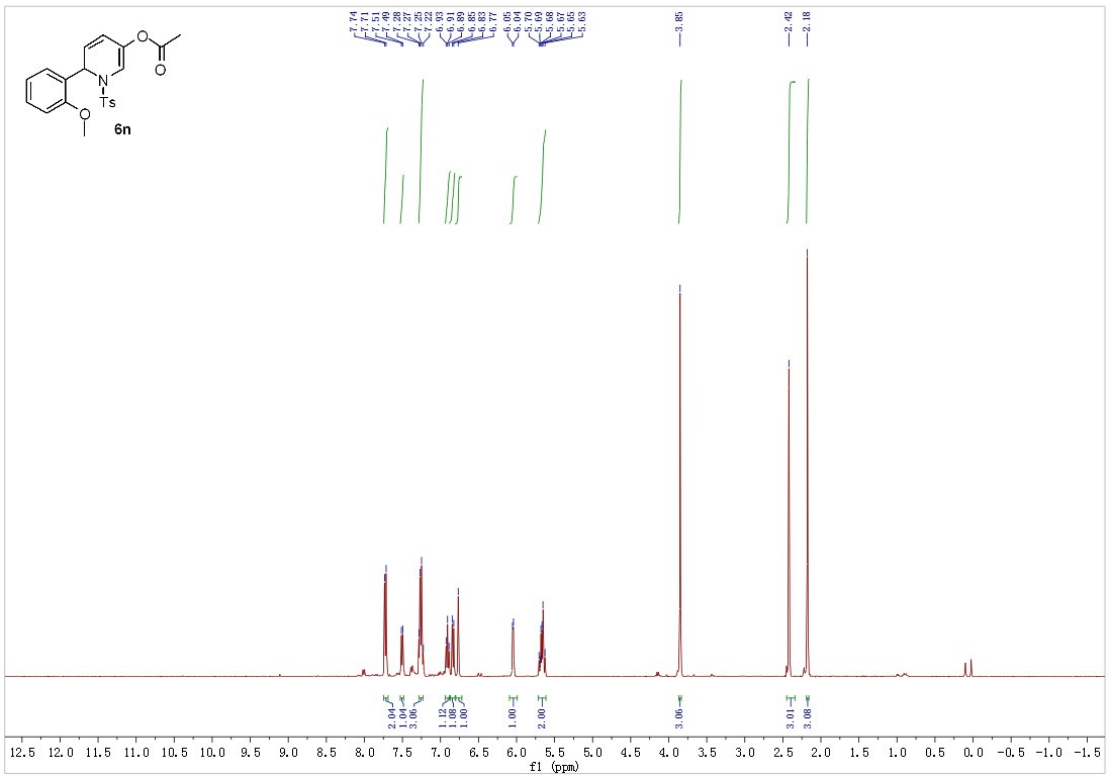

Ph
N
Ts
O
O
6k
169.26
143.91
138.48
138.42
136.48
129.02
128.58
128.53
127.55
124.88
124.68
121.48
115.24
56.45
21.60
20.71
f1 (ppm)

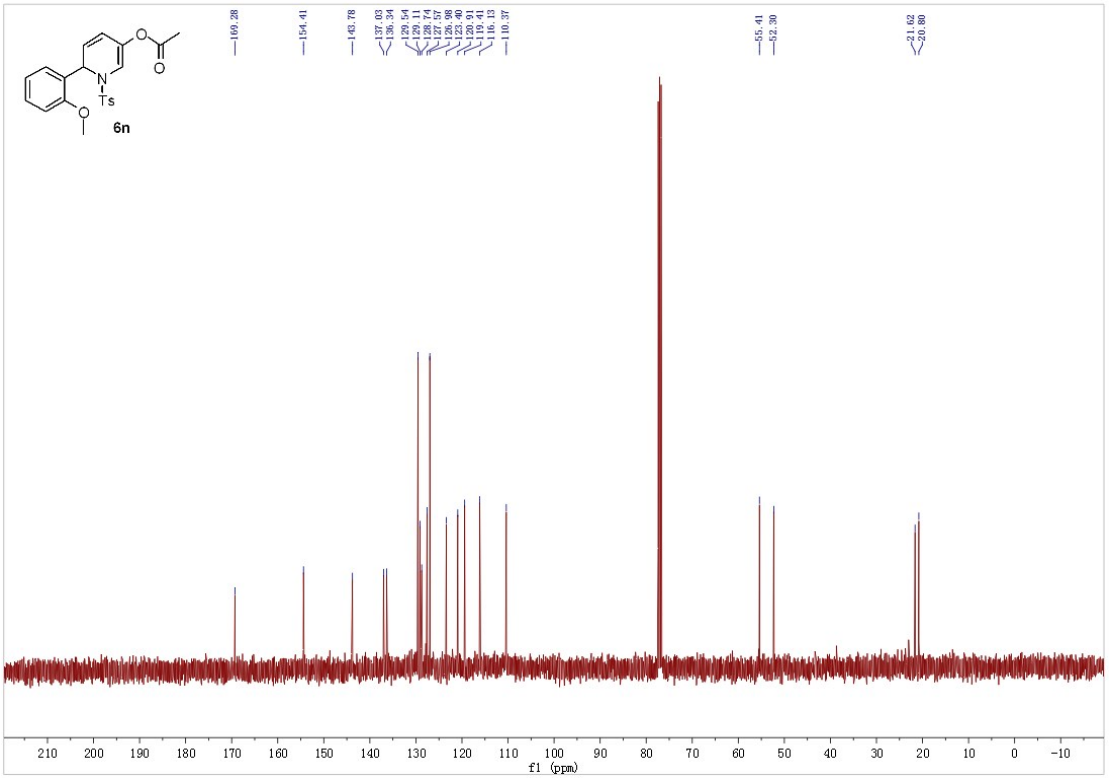

6l
F
Ts
7.72
7.70
7.55
7.54
7.53
7.52
7.28
7.26
7.04
7.02
7.00
6.47
5.90
5.87
5.68
5.66
5.55
5.54
5.53
5.51
2.42
2.18
2.06
2.04
2.04
2.07
1.00
1.09
1.08
1.09
3.04
3.09
f1 (ppm)

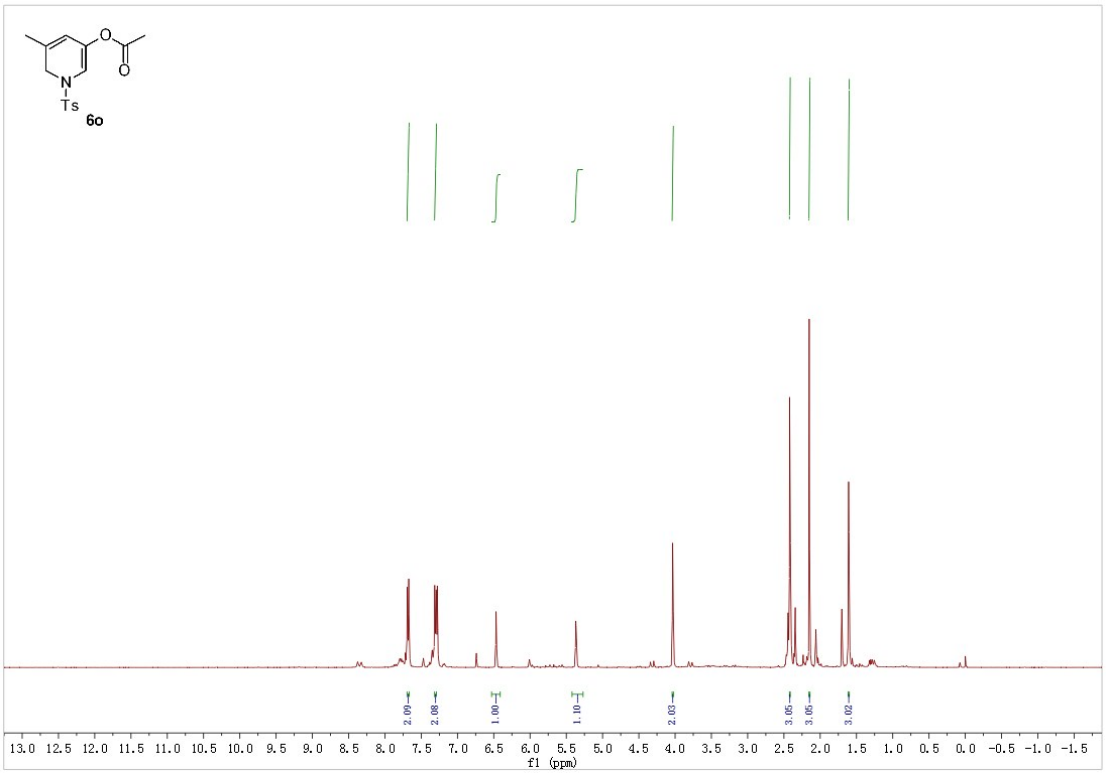

6l
F
Ts
169.39
164.05
161.60
144.05
138.46
138.38
134.10
134.07
129.68
129.61
129.53
126.82
121.84
121.77
115.51
115.30
115.04
55.67
21.62
20.70
f1 (ppm)

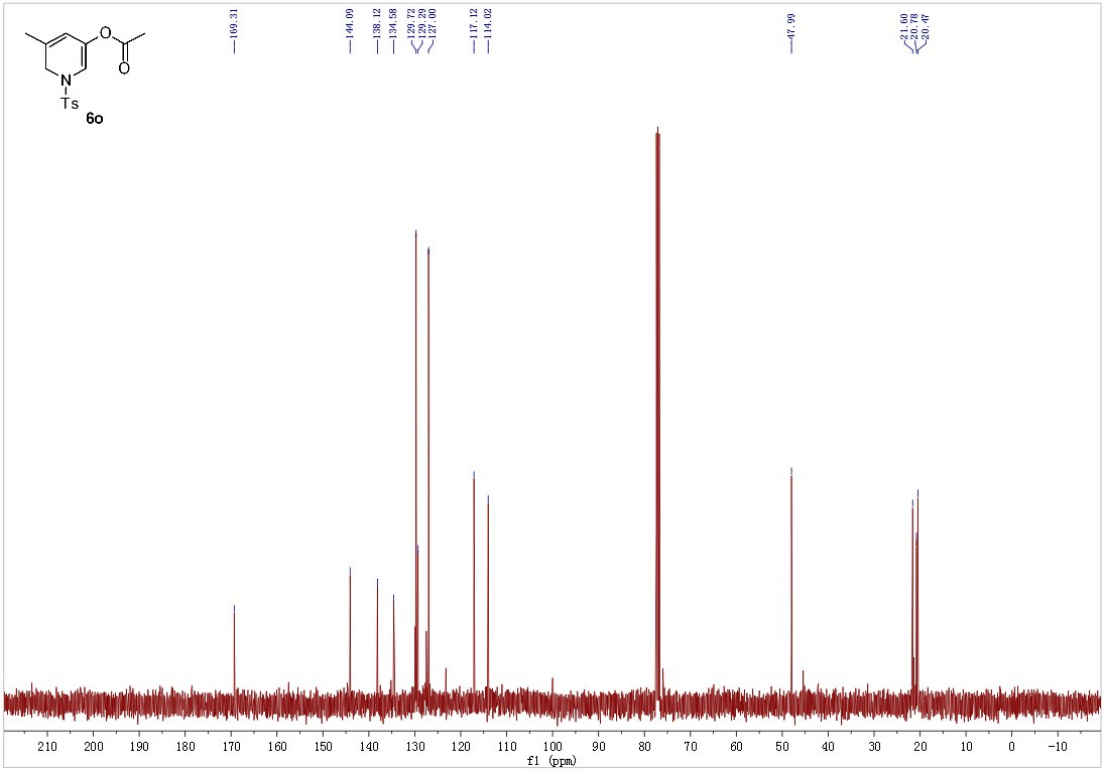

6m
7.71
7.69
7.47
7.45
7.43
7.41
7.28
7.26
6.48
5.90
5.87
5.65
5.64
5.54
5.53
5.52
5.50
2.43
2.18
2.06
4.04
2.16
1.00
1.01
1.01
1.00
3.09
3.06
f1 (ppm)

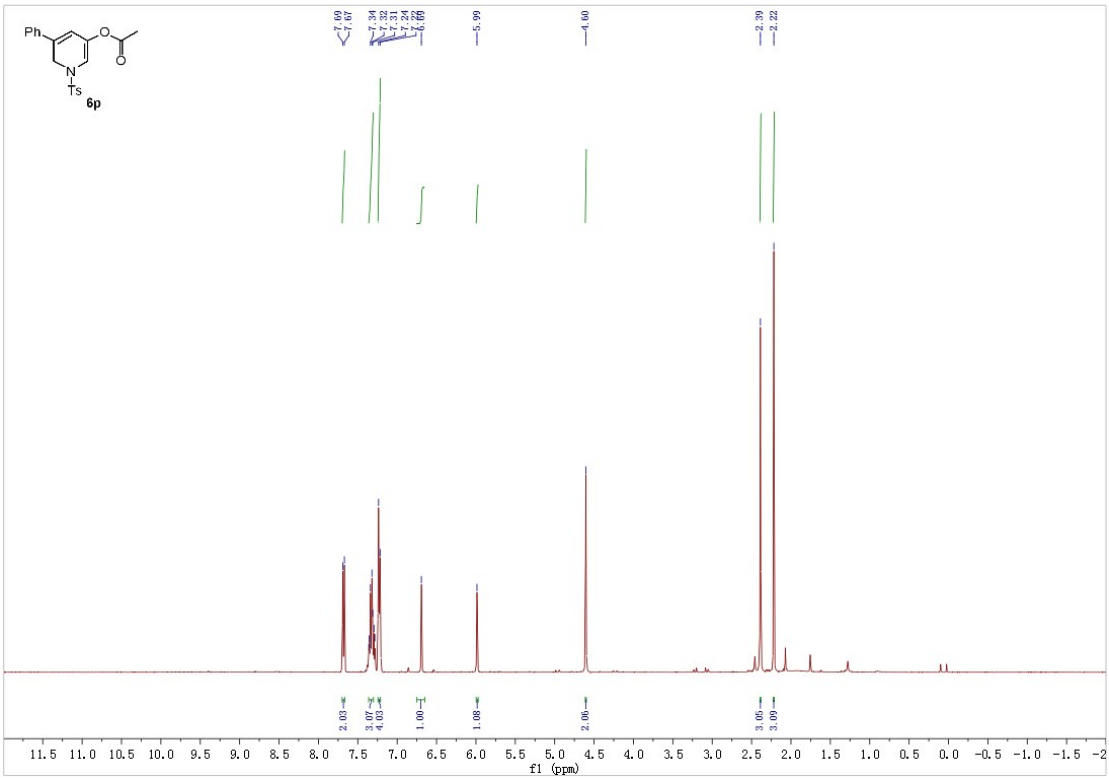

6m
169.35
144.11
138.41
137.23
136.30
131.69
129.69
129.38
126.82
122.67
122.02
121.34
115.16
55.73
21.65
20.72
f1 (ppm)

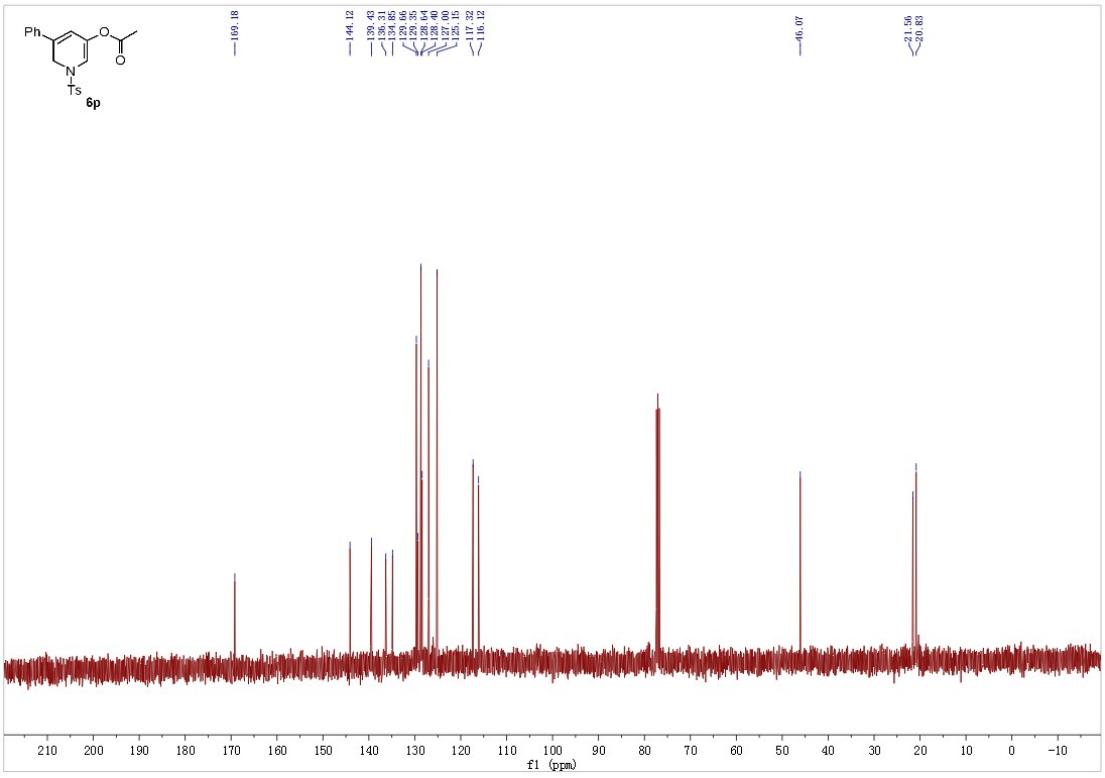

6n
7.74
7.71
7.51
7.49
7.28
7.27
7.25
7.22
6.93
6.91
6.89
6.85
6.83
6.77
6.05
6.04
5.70
5.69
5.68
5.67
5.66
5.63
3.85
2.42
2.18
2.04
2.04
3.06
1.12
1.08
1.00
1.00
2.00
3.06
3.01
3.08
f1 (ppm)

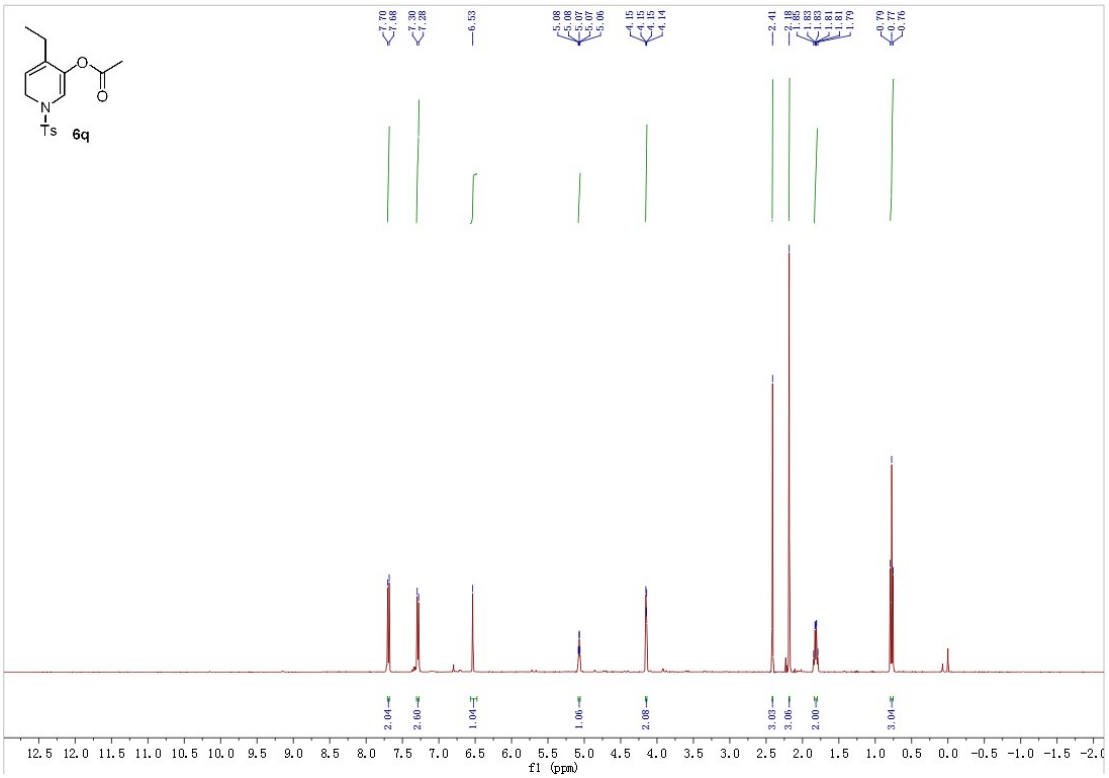

6n
169.28
154.41
143.78
137.03
136.34
129.54
129.11
128.74
127.57
125.98
125.40
120.91
119.41
116.13
110.37
55.41
52.30
21.62
20.80
f1 (ppm)

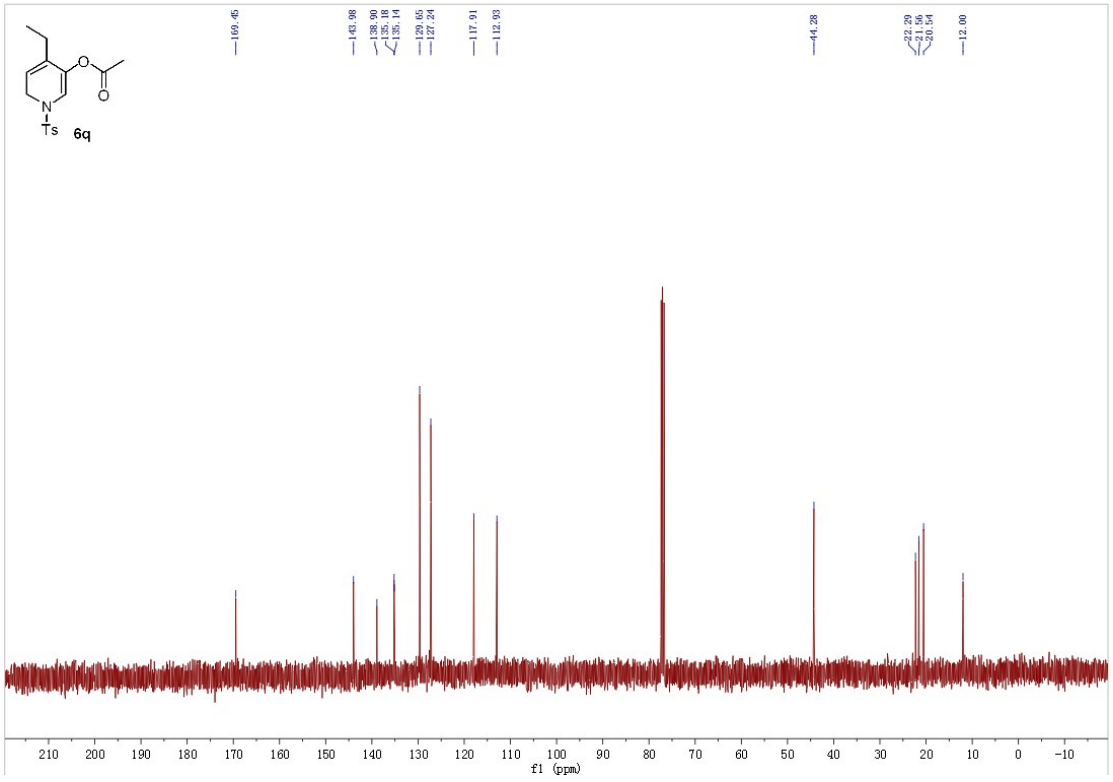

6o
2.09
2.08
1.00
1.10
2.03
3.05
3.05
3.02
f1 (ppm)

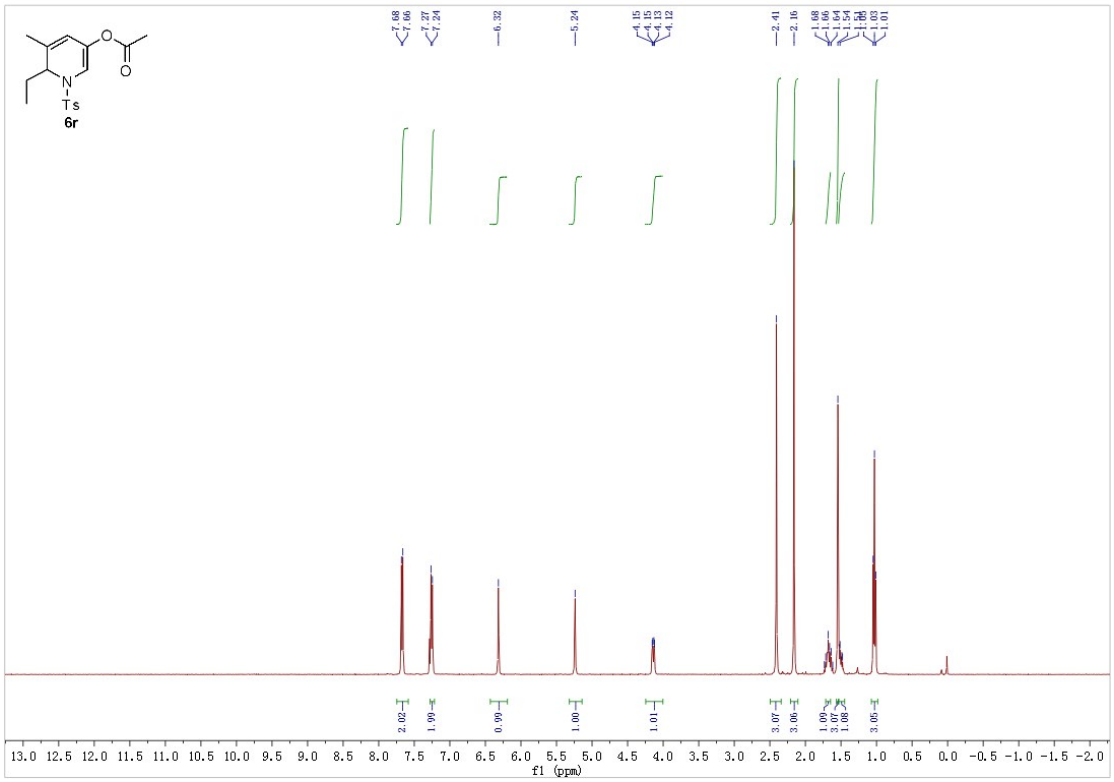

6o
169.31
144.09
138.12
134.58
129.72
129.20
127.60
117.12
114.02
47.99
21.60
20.78
20.47
f1 (ppm)

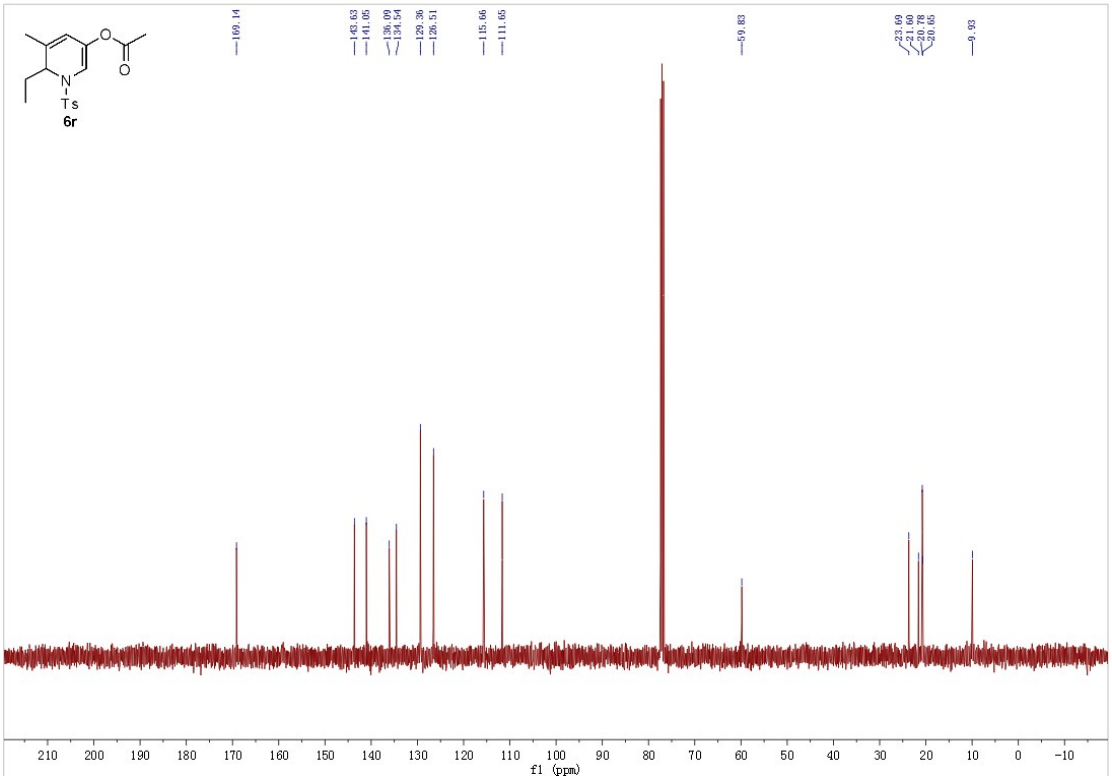

Ph
O
O
N
Ts
6p
7.69
7.67
7.34
7.32
7.31
7.24
7.23
6.00
5.99
4.60
2.39
2.22
2.03
3.07
4.03
1.00
1.08
2.00
3.05
3.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
f1 (ppm)

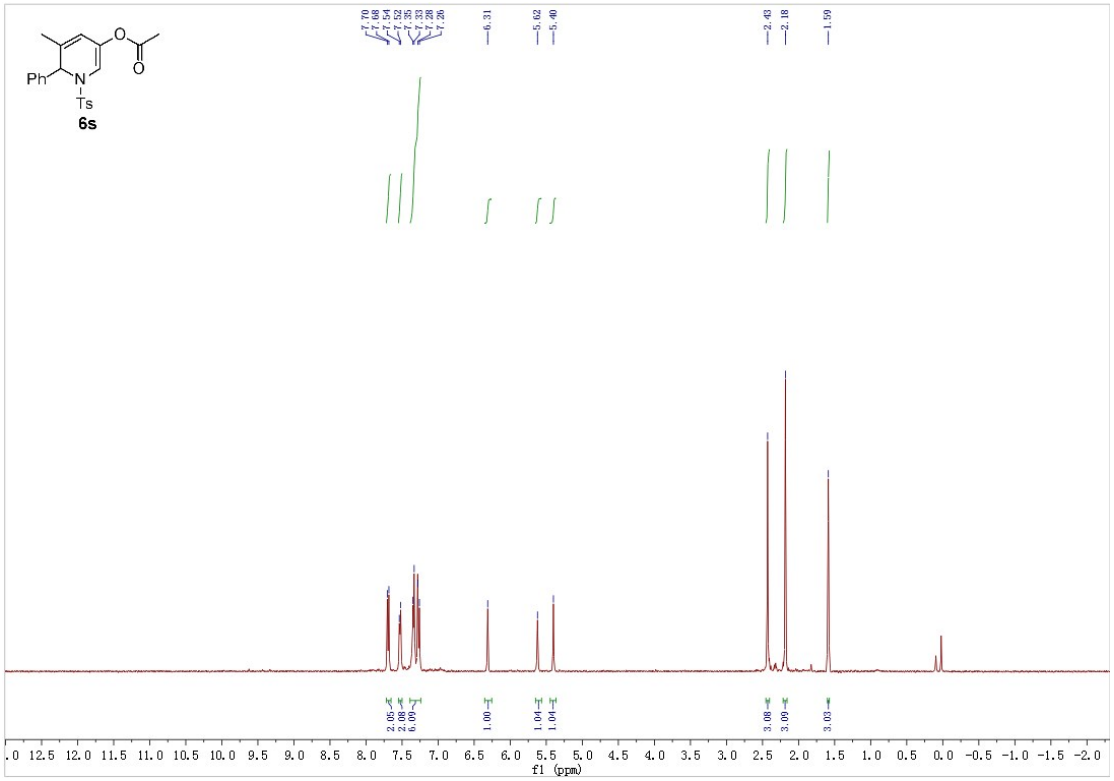

Ph
O
O
N
Ts
6p
169.18
144.12
139.43
136.31
134.85
129.66
129.35
128.64
128.40
127.00
125.15
117.32
116.12
46.07
21.56
20.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

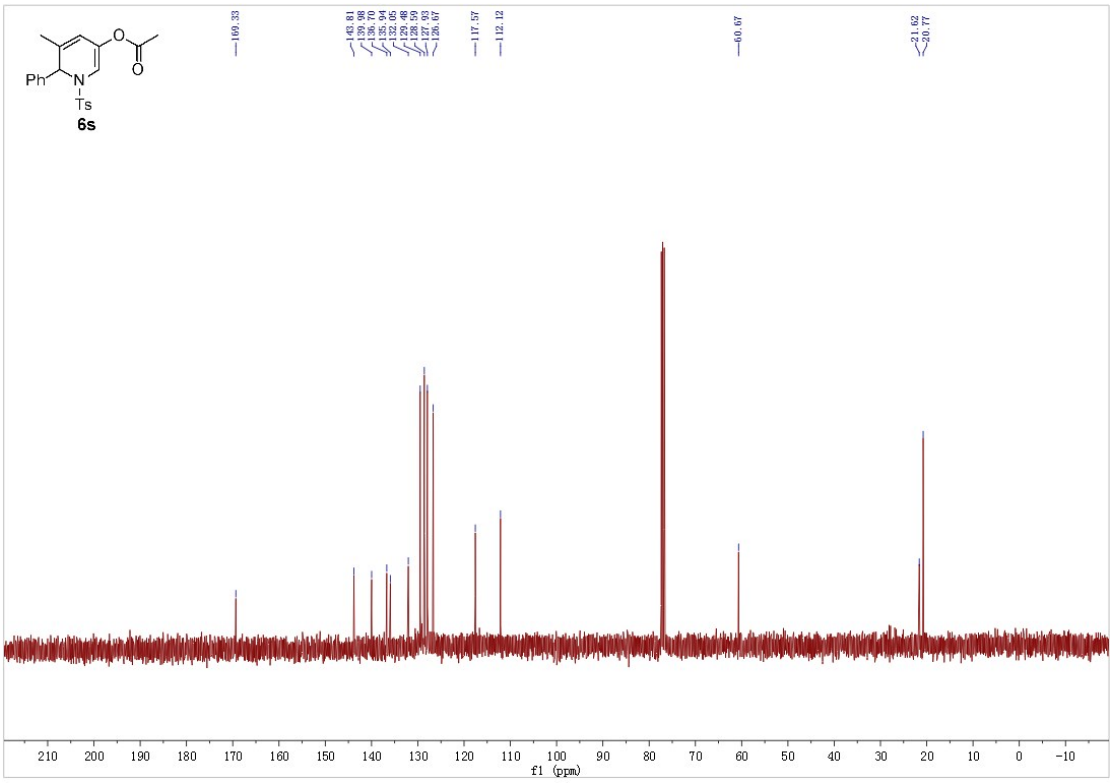

6q
7.70
7.68
7.30
7.28
6.53
5.08
5.08
5.07
5.07
5.06
4.15
4.15
4.15
4.14
2.41
2.18
1.85
1.83
1.83
1.81
1.81
1.79
0.79
0.77
0.76
2.04
2.60
1.04
1.06
2.08
3.03
3.06
2.00
3.04
f1 (ppm)

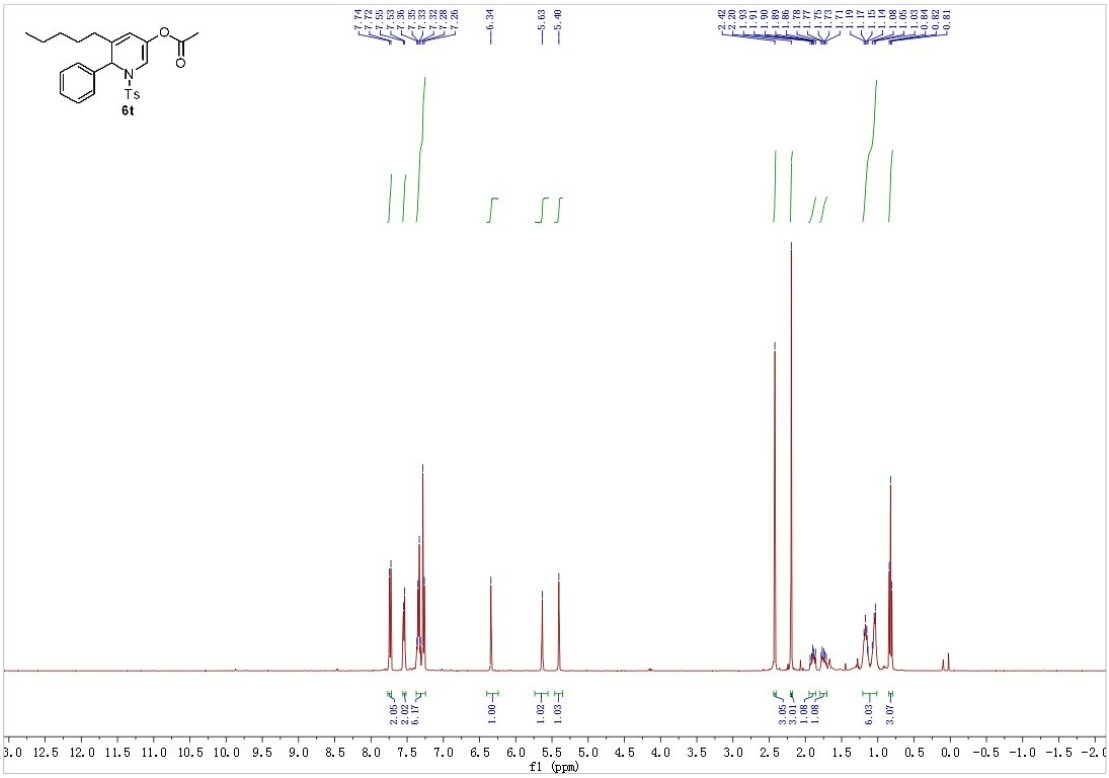

6q
169.45
143.98
138.90
135.18
135.14
129.65
127.24
117.91
112.93
44.28
22.29
21.56
20.54
12.00
f1 (ppm)

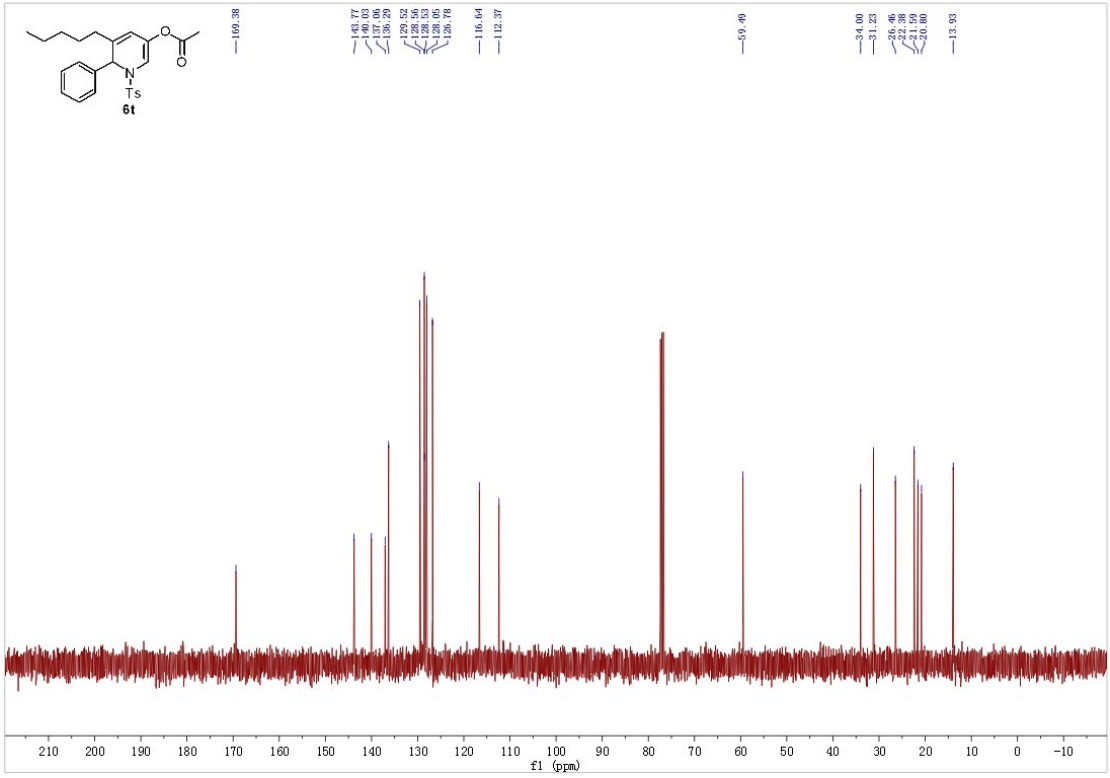

Ts
6r
7.68
7.66
7.27
7.24
6.32
5.24
4.15
4.15
4.13
4.12
2.41
2.16
1.68
1.66
1.64
1.54
1.03
1.01
2.02
1.99
0.99
1.00
1.01
3.07
3.06
1.09
3.07
1.08
3.05
f1 (ppm)

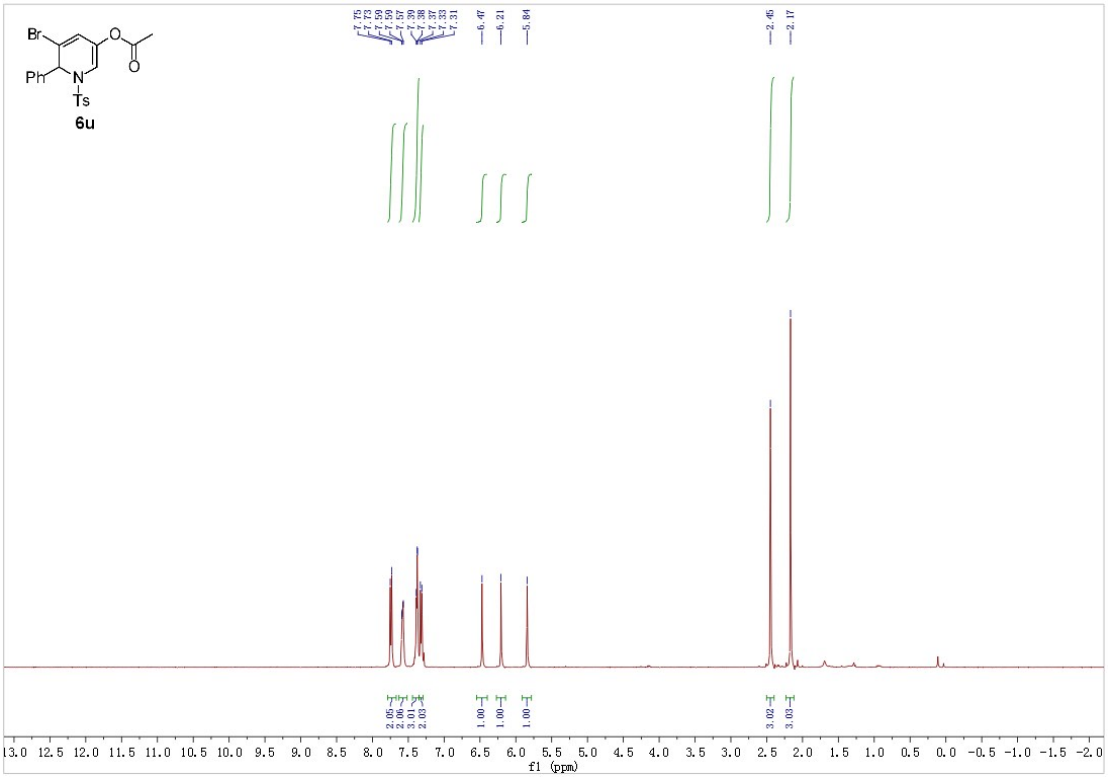

Ts
6r
169.14
143.63
141.05
136.09
134.54
129.36
126.51
115.66
111.65
59.83
23.69
21.60
20.78
20.65
9.93
f1 (ppm)

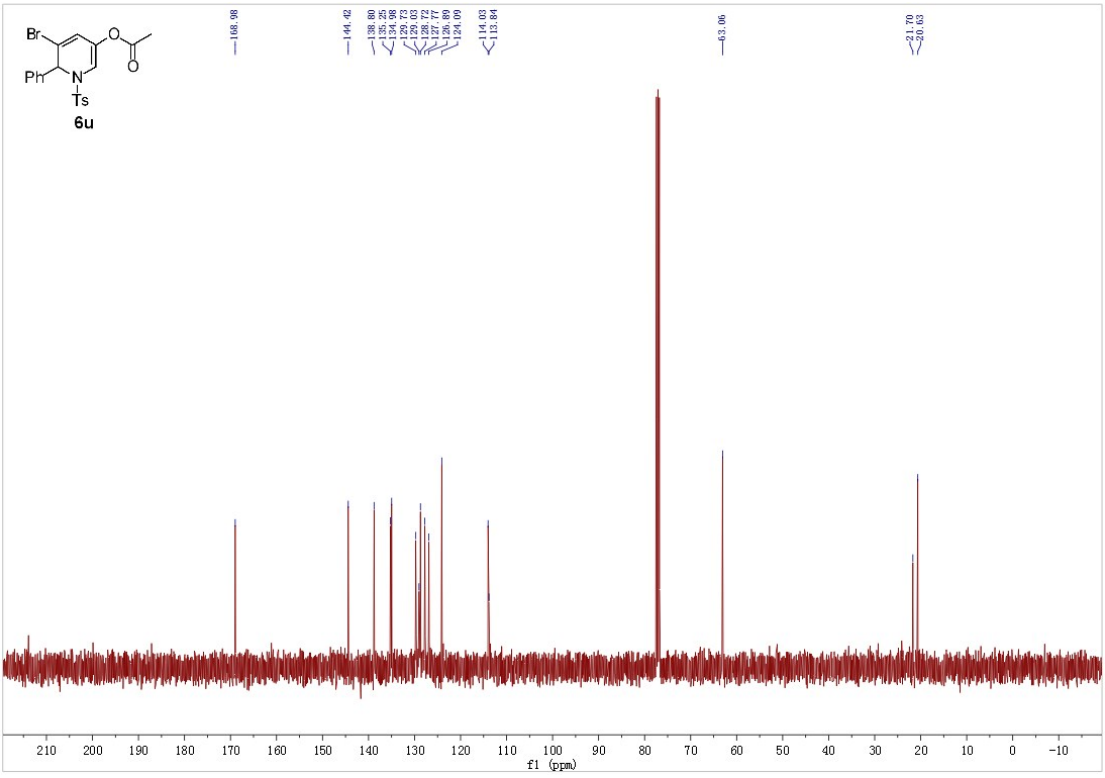

Ph
N
Ts
O
O
6s
7.70
7.68
7.54
7.52
7.35
7.33
7.28
7.26
6.31
5.62
5.40
2.43
2.18
1.59
2.05
2.04
6.09
1.00
1.04
1.04
3.08
3.09
3.03
f1 (ppm)

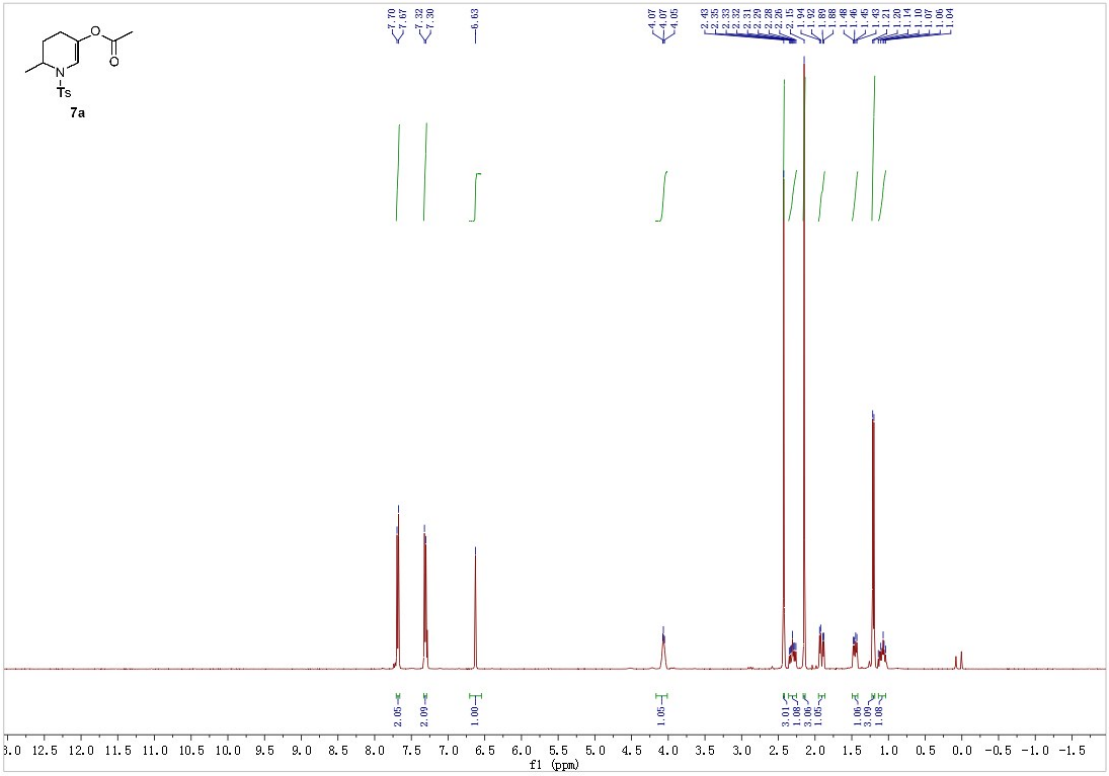

Ph
N
Ts
O
O
6s
169.33
143.81
139.98
139.70
135.94
132.05
129.46
128.59
127.93
126.67
117.57
112.12
60.67
21.62
20.77
f1 (ppm)

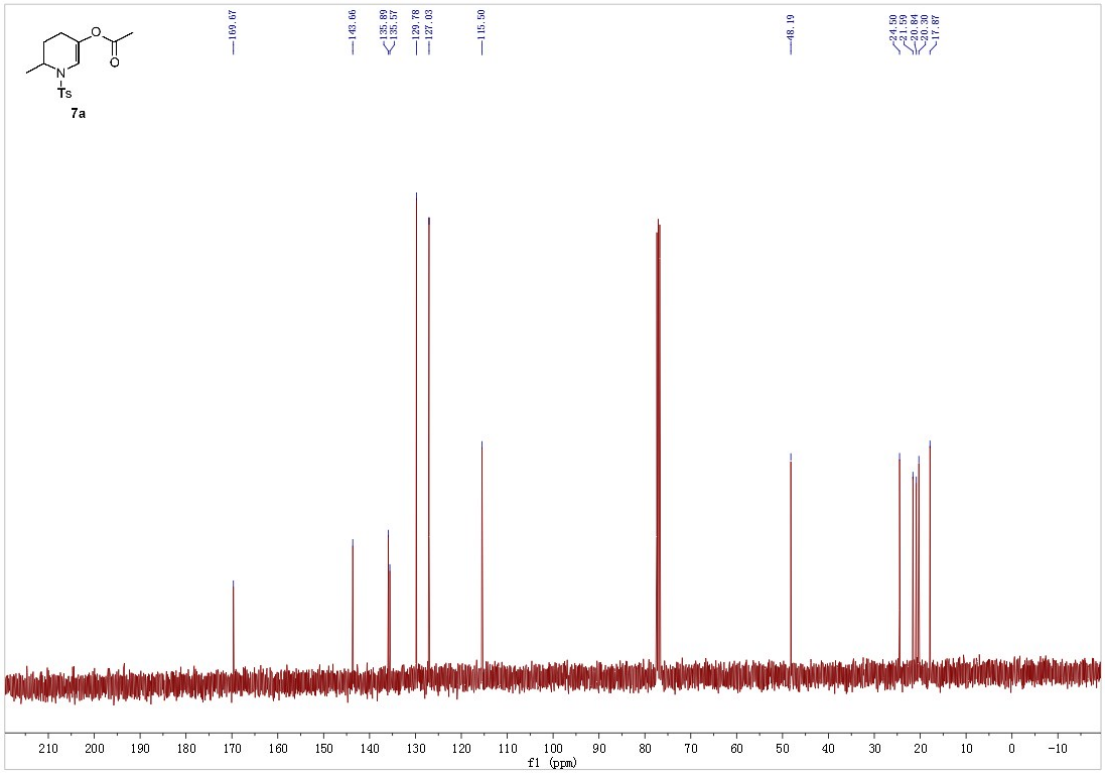

Ts
6t
f1 (ppm)

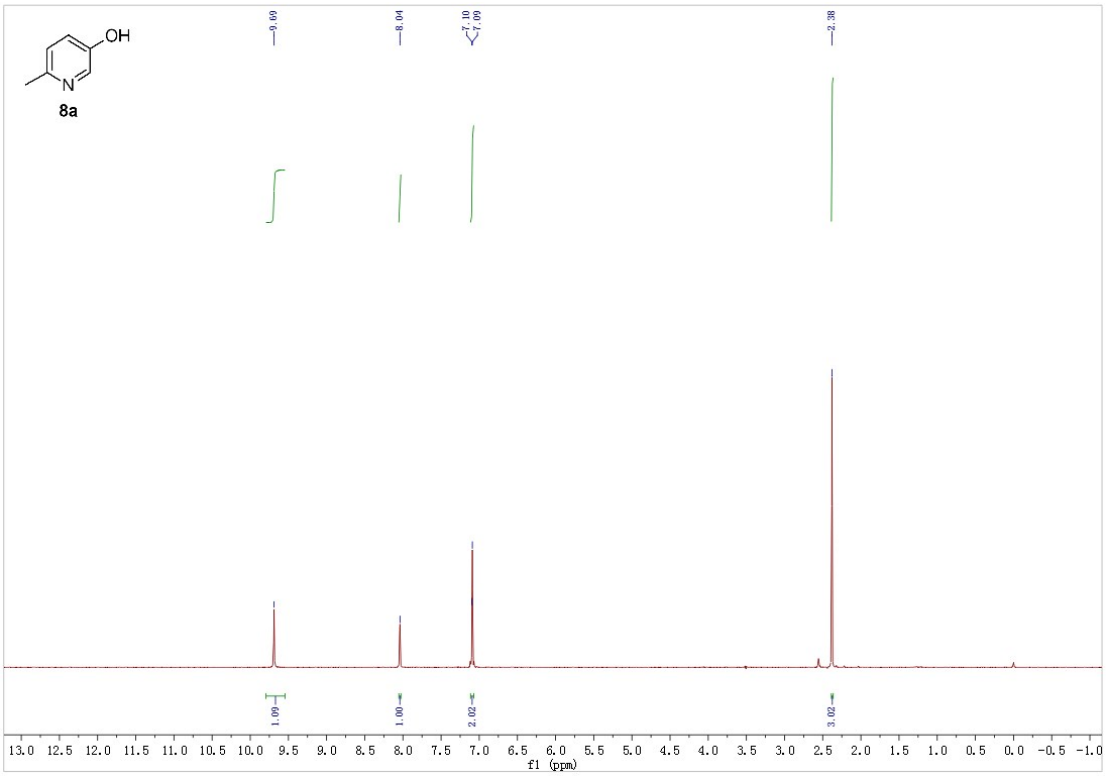

Ts
6t
f1 (ppm)

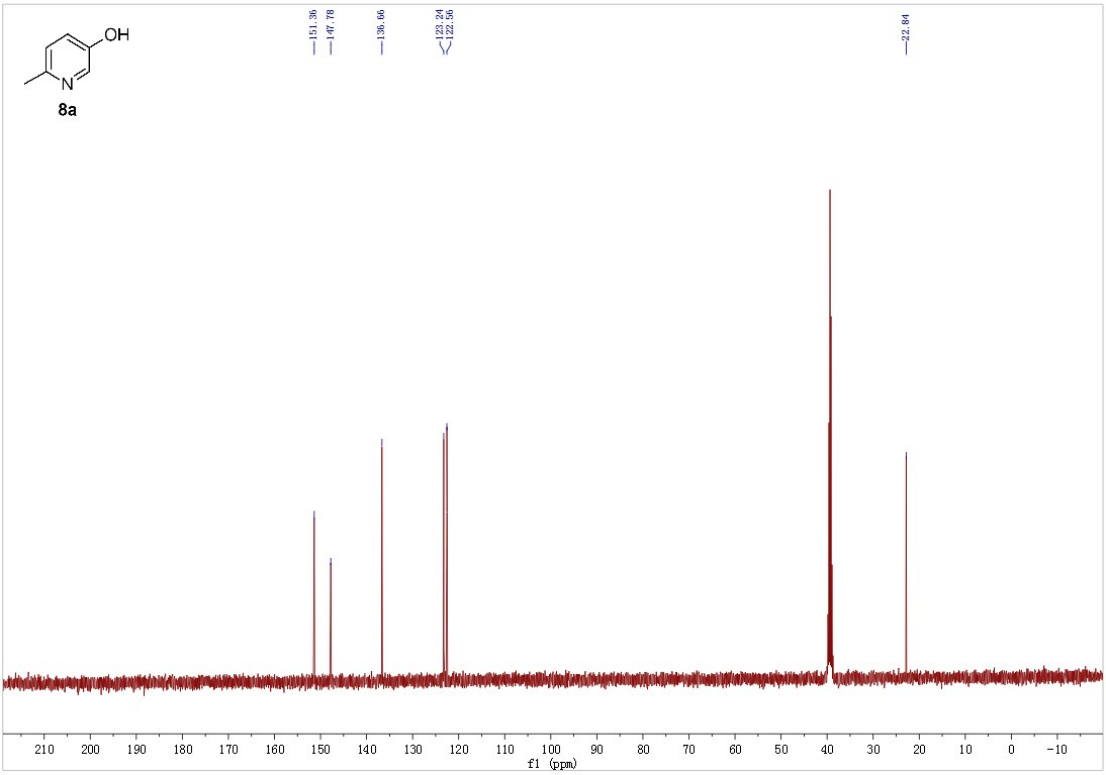

Br
O
O
Ph
N
Ts
6u
7.75
7.73
7.59
7.57
7.39
7.38
7.37
7.33
7.31
6.47
6.21
5.84
2.45
2.17
2.05
2.05
3.01
2.03
1.00
1.00
1.00
3.02
3.03
f1 (ppm)

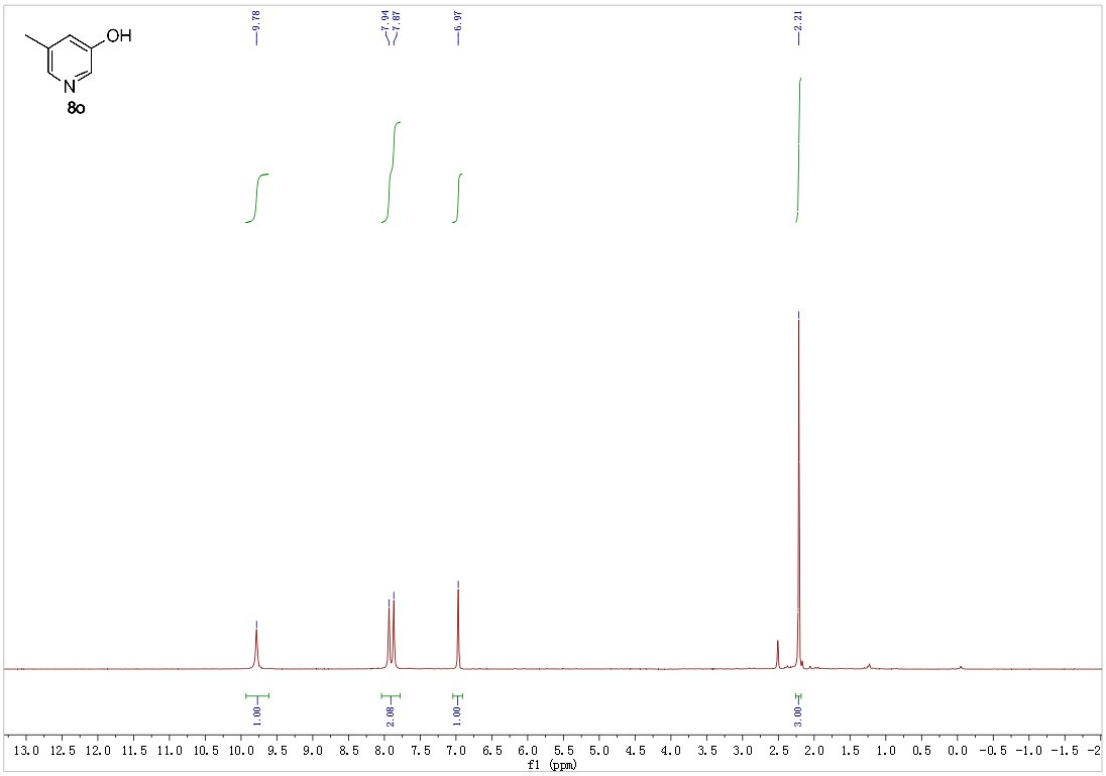

Br
O
O
Ph
N
Ts
6u
168.98
144.42
138.80
135.25
134.98
129.73
129.03
128.72
127.77
126.89
124.09
114.03
113.84
63.06
21.70
20.63
f1 (ppm)

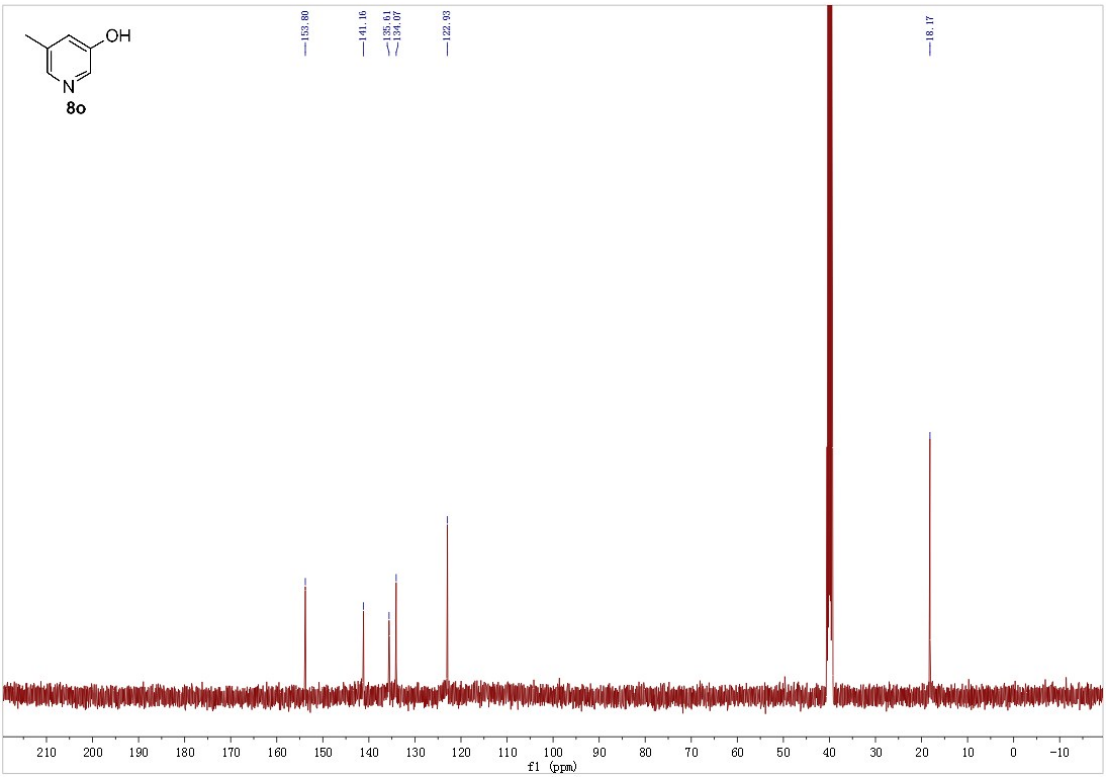

7a
f1 (ppm)

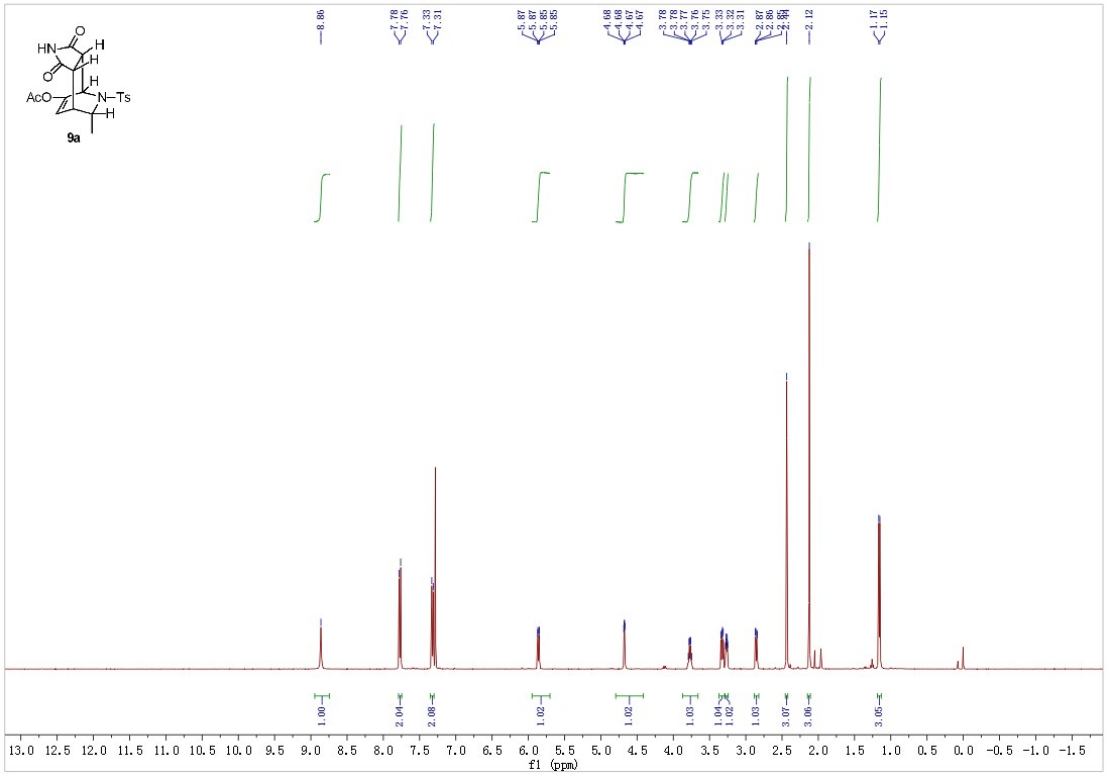

7a
f1 (ppm)

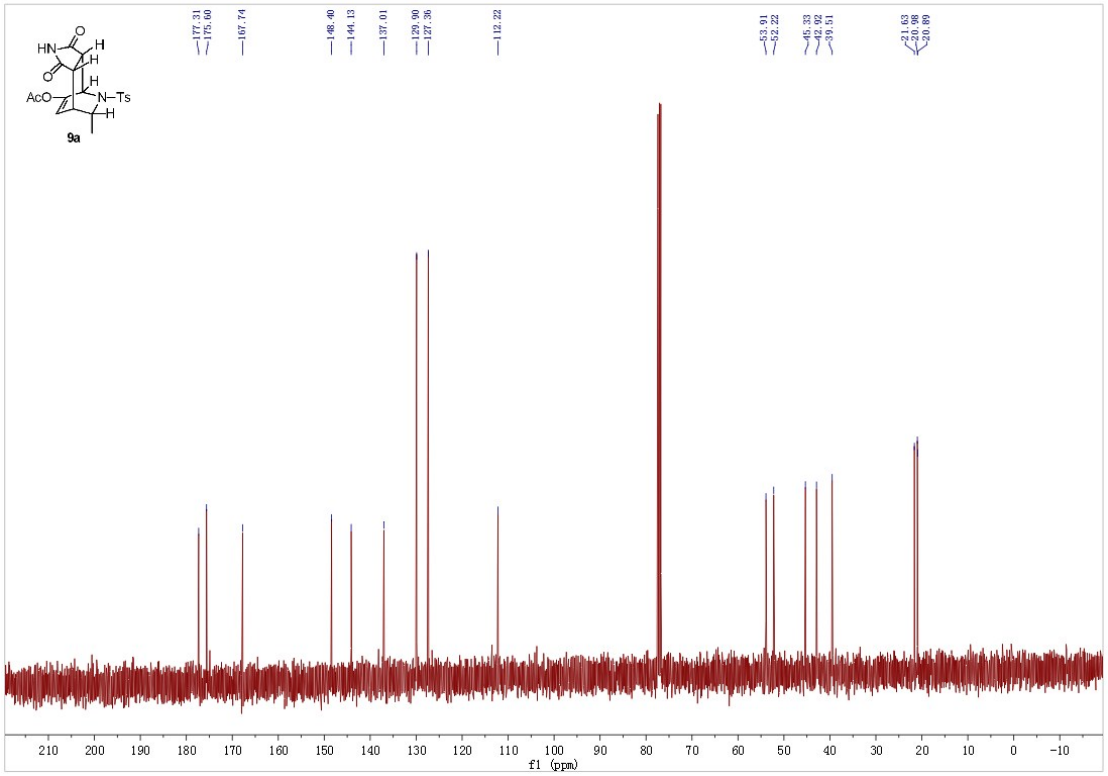

OH
N
8a
9.69
8.04
7.10
7.09
2.38
1.09
1.00
2.02
3.02
f1 (ppm)

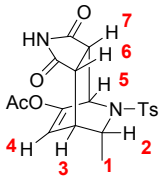

OH
N
8a
151.36
147.78
136.66
123.24
122.56
22.84
f1 (ppm)


OH
N
8o
9.78
7.94
7.87
6.97
2.21
1.00
2.08
1.00
3.00
f1 (ppm)

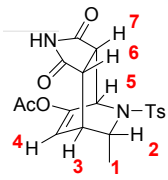

OH
N
8o
153.80
141.16
135.61
134.07
122.93
18.17
f1 (ppm)


HN
O
O
H
H
AcO
N–Ts
H
9a
8.86
7.78
7.76
7.33
7.31
5.87
5.87
5.86
5.85
4.68
4.68
4.67
4.67
3.78
3.77
3.77
3.76
3.75
3.33
3.32
3.31
2.87
2.86
2.84
2.12
1.17
1.15
1.00
2.04
2.08
1.02
1.02
1.03
1.04
1.02
1.03
3.07
3.06
3.05
13.0 12.5 12.0 11.5 11.0 10.5 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 0.0 -0.5 -1.0 -1.5
f1 (ppm)

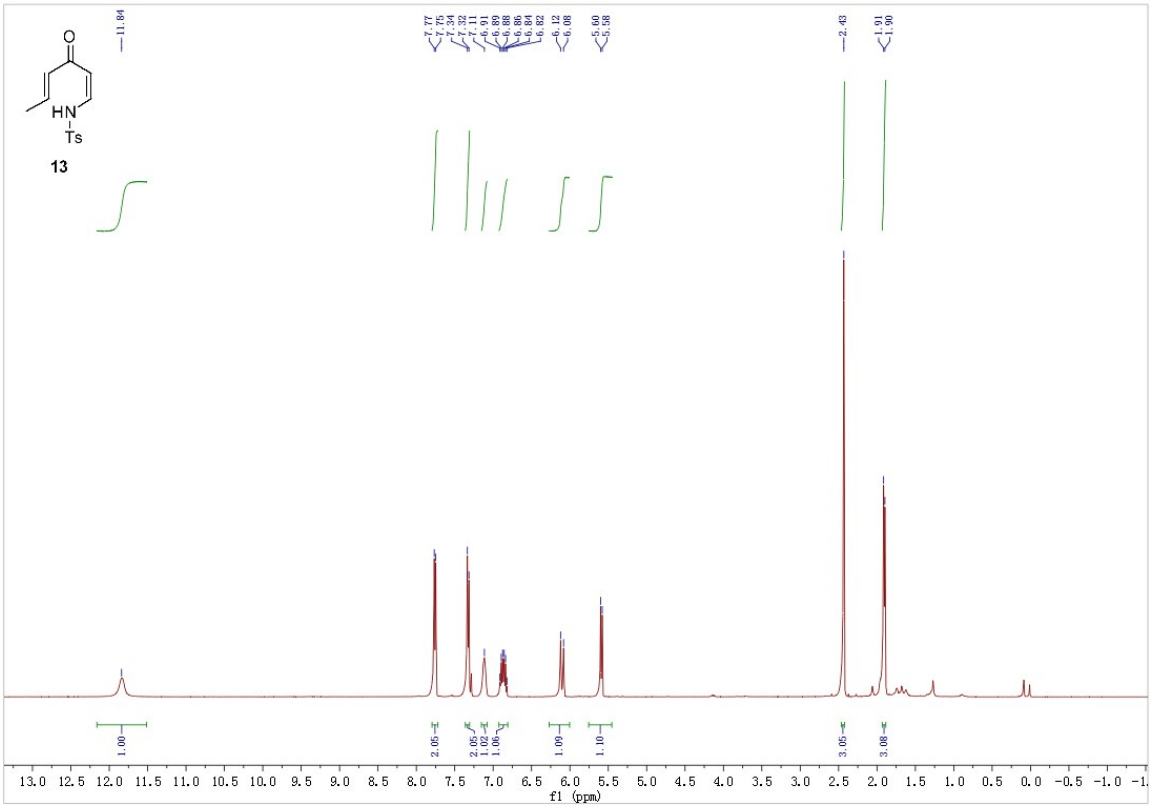

HN
O
O
H
H
AcO
N–Ts
H
9a
177.31
175.60
167.74
148.40
144.13
137.01
129.90
127.36
112.22
53.91
52.22
45.33
42.92
39.51
21.63
20.98
20.89
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

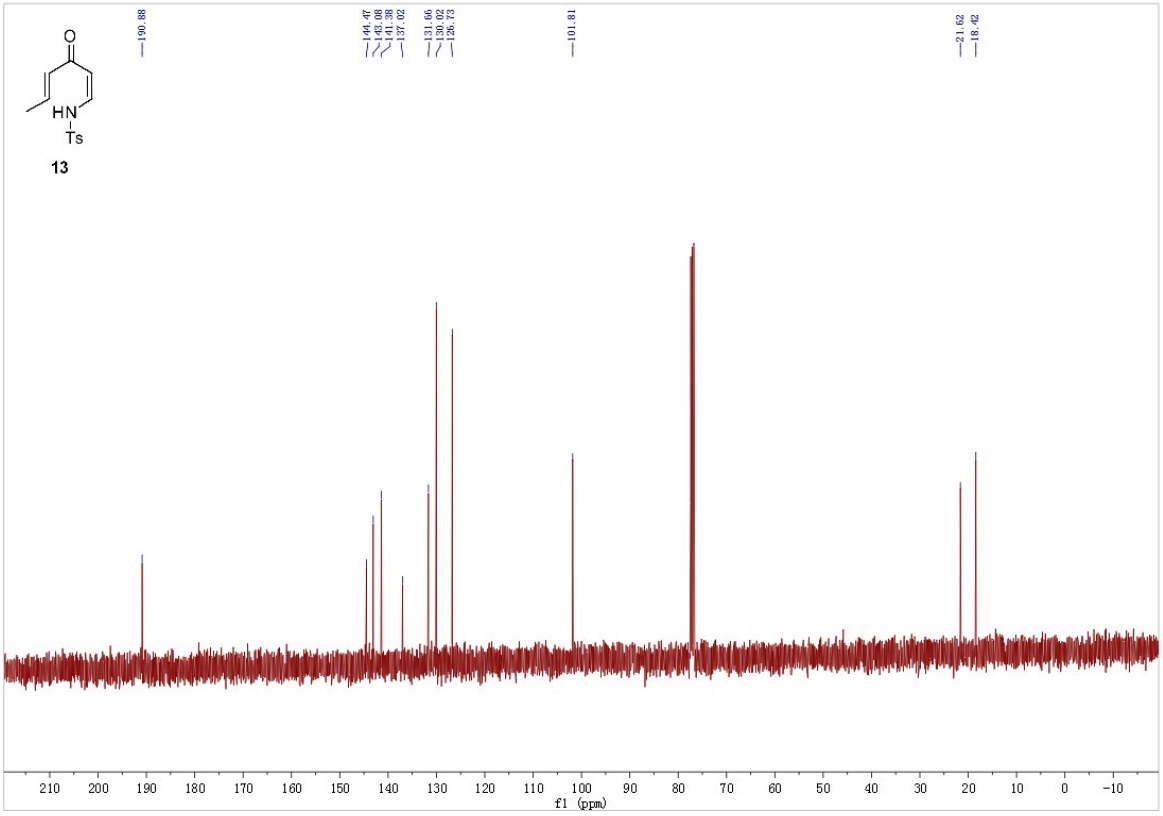


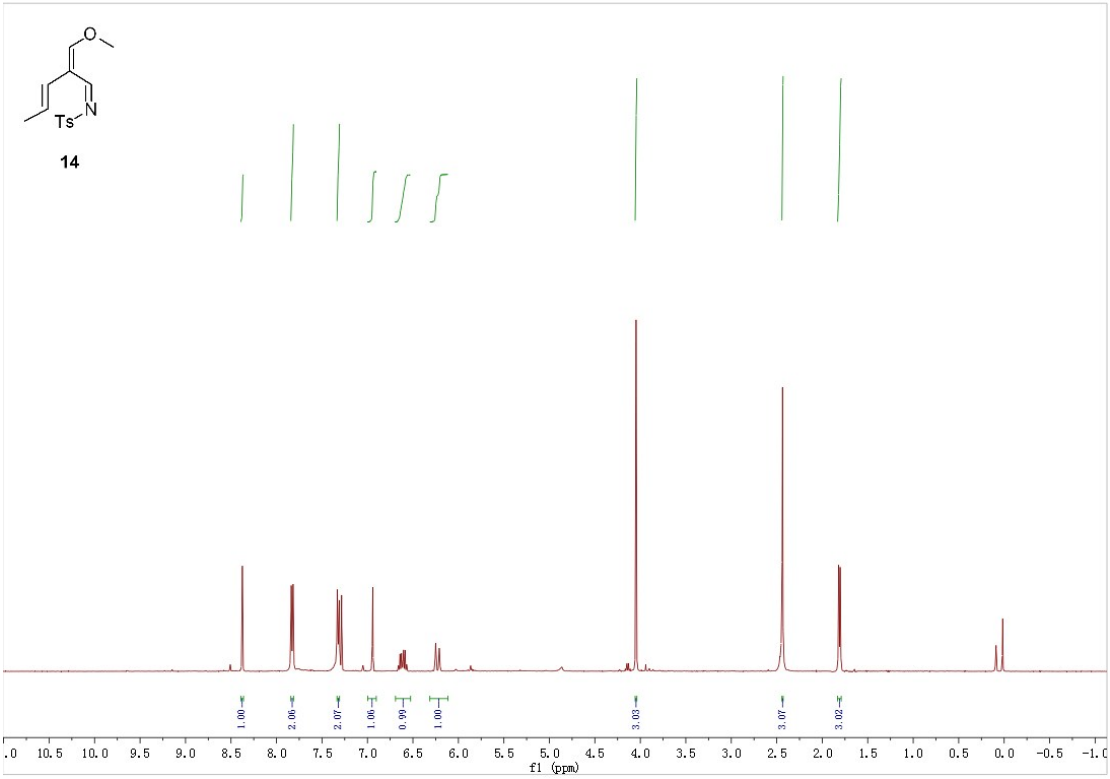
H-H COSY

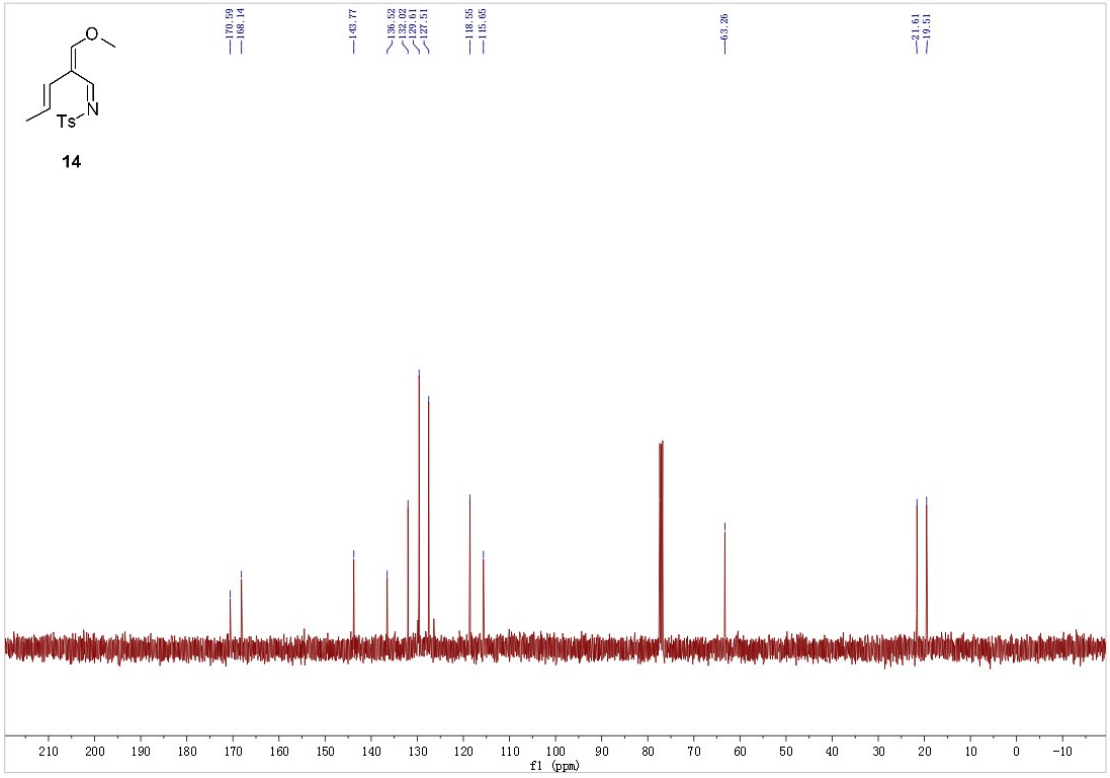


H-H noesy


13
11.84
7.77
7.75
7.34
7.32
7.11
7.09
6.89
6.88
6.86
6.84
6.82
6.12
6.08
5.60
5.58
2.43
1.91
1.90
1.00
2.05
2.05
1.02
1.06
1.09
1.10
3.05
3.08
f1 (ppm)


13
190.88
144.47
143.08
141.38
137.02
131.66
130.02
126.73
101.81
21.62
18.42
f1 (ppm)


Ts
N
O
14
1.00
2.06
2.07
1.06
0.99
1.00
3.03
3.07
3.02
f1 (ppm)


Ts
N
O
14
170.59
168.14
143.77
136.52
132.02
129.61
127.51
118.55
115.65
63.26
21.61
19.51
f1 (ppm)