

Supporting Information for

Syntheses of 4-Allyl-/4-allenyl-4-(arythio)-1,4-dihydroisoquinolin-3-ones via Photochemical Doyle-Kirmse reaction

*Jianwei Xie, Muhammad Suleman, Zaibin Wang, Xifei Mao, Beibei Mao, Jiale Fan,
Ping Lu* and Yanguang Wang**

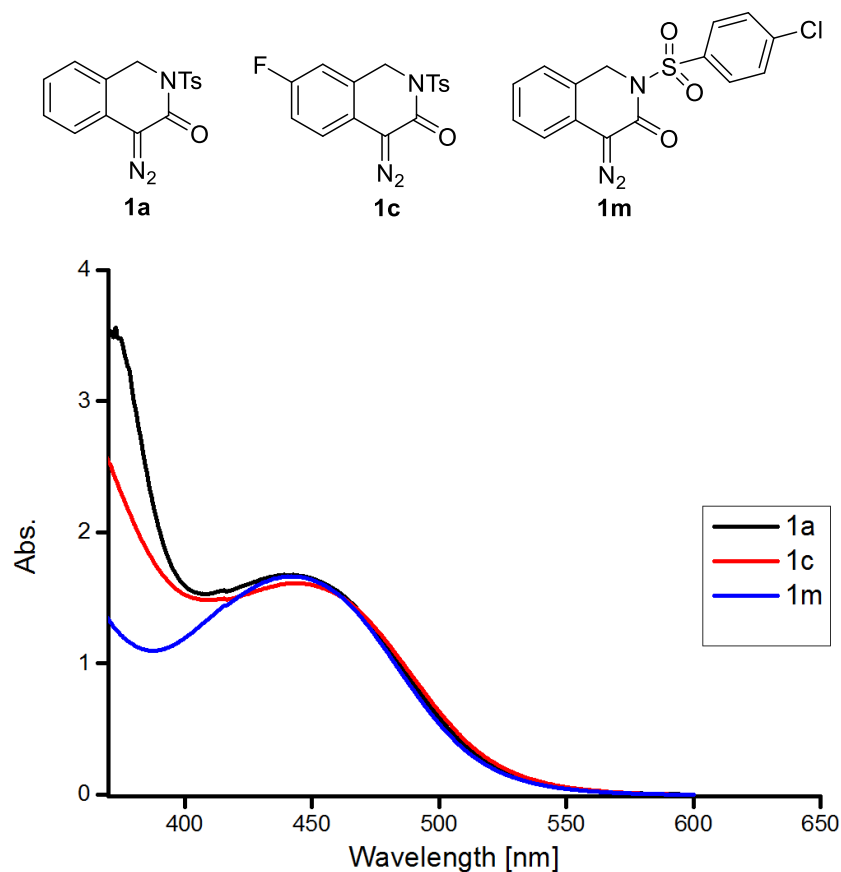
Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

E-mail: pinglu@zju.edu.cn; orgwyg@zju.edu.cn

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Figure S1. UV-Vis Absorbance Spectra of Diazo Compounds 1a, 1c and 1m in DCE (0.05 M)



General Information

Unless otherwise mentioned, solvent and reagent were purchased from commercial sources and used as received. ^1H NMR spectra were obtained on 400 or 600 MHz in CDCl_3 . The chemical shifts were quoted in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on 100 or 150 MHz in CDCl_3 . The chemical shifts were reported in ppm referenced to the internal solvent signals (77.0 ppm for CDCl_3). $^{13}\text{C}\{^1\text{H}\}$ for proton-decoupled carbon data was recorded. The following abbreviations were used to describe peak

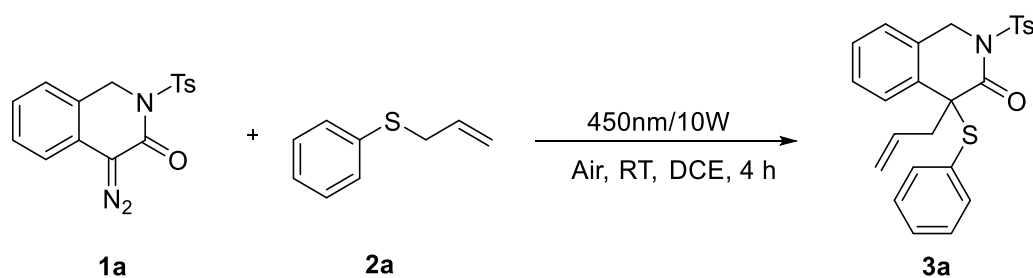
patterns where appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants J were reported in hertz unit (Hz). Infrared spectra were obtained on an FTIR spectrometer. High-resolution mass spectra (HRMS) data were obtained by using ESI or EI ionization. Melting points were measured with SGW X-4 micro melting point apparatus. Flash column chromatography was performed employing 300-400 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel HSGF254. The photocatalytic reactions were carried out in a temperature controlled WATTCAS Parallel Light Reactor.

Substrates **1**, **2** and **4** were prepared according to the published procedures.^{1,2}

References:

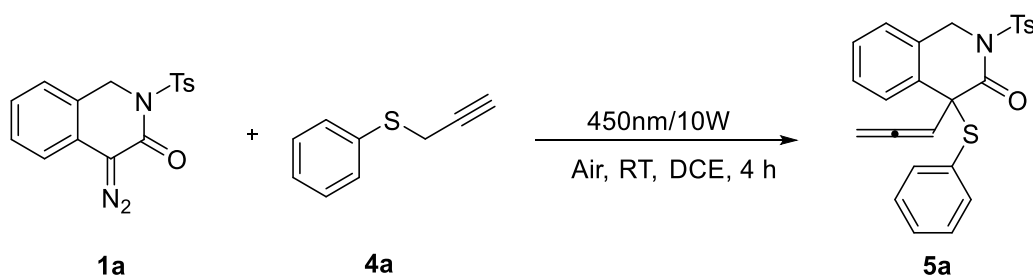
1. Z. M. Li, J. R. Chen, L. Wu, A. N. Ren, P. Lu and Y. G. Wang, *Org. Lett.*, 2019, **22**, 26.
2. V. Pace, L. Castoldi and W. Holzer, *Tetrahedron Lett.*, 2012, **8**, 53, 967.

General Procedure for the Synthesis of 3



To a quartz test tube equipped with a magnetic stirring bar was added sequentially **1a** (0.1 mmol), **2a** (1.0 mmol) and DCE (0.5 mL). The reaction was irradiated with blue light (450 nm/10 W) from the photocatalytic reactor. The temperature was set to ambient and cooling was realized with a fan. Upon completion, the solvent was evaporated in vacuum. The residue was purified by column chromatography on silica (petroleum ether/ethyl acetate/ dichloromethane = 25:1:2, v/v) to give the product **3a**.

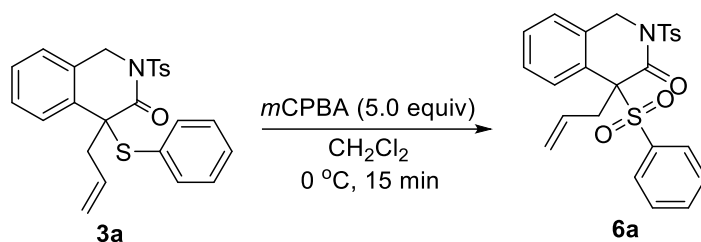
Typical Procedure for the Synthesis of 5a



To a quartz test tube equipped with a magnetic stirring bar was added sequentially **1a** (0.1 mmol), **4a** (1.0 mmol) and DCE (0.5 mL). The reaction was irradiated with blue light (450 nm/10 W) from the photocatalytic reactor. The temperature was set to ambient and cooling was realized with a fan. Upon completion, the solvent was evaporated in vacuum. The

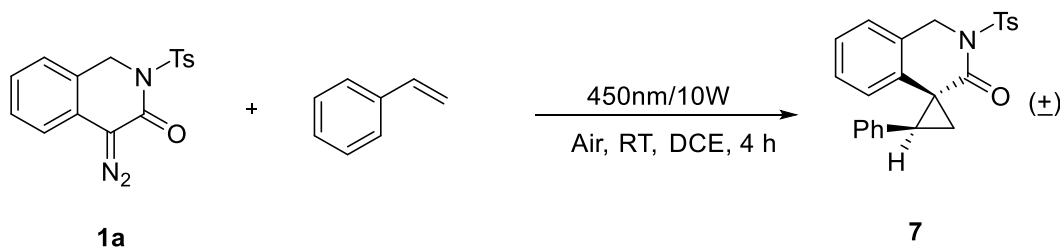
residue was purified by column chromatography on silica (petroleum ether/ethyl acetate = 15 : 1, v/v) to give the product **5a**.

Typical Procedure for the Synthesis of **6a**



To an oven-dried flask equipped with a magnetic stirring bar were added **3a** (0.1 mmol), *m*CPBA (0.5 mmol), and dry CH_2Cl_2 (2 mL) under an air atmosphere. The reaction mixture was stirred at $0\text{ }^\circ\text{C}$ for 15 minutes, and then quenched with saturated NaHCO_3 (aq.) solution and extracted with EA. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA/DCM = 25 : 1 : 2 to 15 : 1 : 2, v/v) to give compound **6a**.

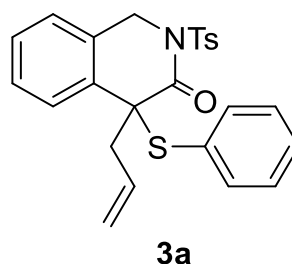
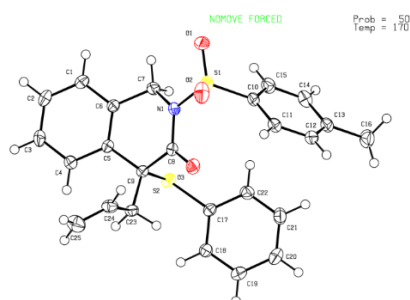
Procedure for the Synthesis of **7**



To a quartz test tube equipped with a magnetic stirring bar was added sequentially **1a** (0.1 mmol), styrene (1.0 mmol) and DCE (0.5 mL). The

reaction was irradiated with blue light (450 nm/10 W) from the photocatalytic reactor. The temperature was set to ambient and cooling was realized with a fan. Upon completion, the solvent was evaporated in vacuum. The residue was purified by column chromatography on silica (petroleum ether/ ethyl acetate/ dichloromethane = 15:1:2, v/v) to give the product **7**.

The ORTEP and Crystal Parameters of 3a wherein thermal ellipsoids are drawn at 30% probability level



Bond precision: C-C = 0.0018 Å

Wavelength=0.71073

Cell: a=9.009 (2) b=9.253 (3) c=13.987 (4)
 alpha=106.407 (11) beta=94.581 (11) gamma=91.510 (13)
 Temperature: 170 K

	Calculated	Reported
Volume	1113.5 (5)	1113.5 (5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C ₂₅ H ₂₃ N O ₃ S ₂	C ₂₅ H ₂₃ N O ₃ S ₂
Sum formula	C ₂₅ H ₂₃ N O ₃ S ₂	C ₂₅ H ₂₃ N O ₃ S ₂
Mr	449.56	449.56
Dx, g cm ⁻³	1.341	1.341
Z	2	2
Mu (mm ⁻¹)	0.266	0.266
F000	472.0	472.0
F000'	472.68	
h, k, lmax	11, 11, 17	11, 11, 17
Nref	4905	4900
Tmin, Tmax	0.920, 0.948	0.697, 0.746
Tmin'	0.901	

Correction method= # Reported T Limits: Tmin=0.697 Tmax=0.746
 AbsCorr = MULTI-SCAN

Data completeness= 0.999

Theta (max)= 27.093

R(reflections)= 0.0310 (4663)

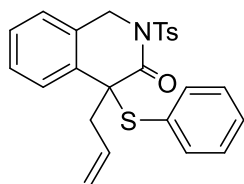
wR2(reflections)= 0.0827 (4900)

S = 1.058

Npar= 281

Characterization Data for Products

4-allyl-4-(phenylthio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3a)



White solid; Yield 62% (28 mg); M.p. 193-194 °C.

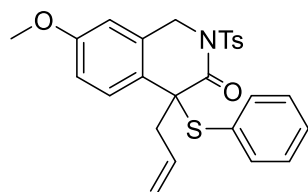
¹H NMR (400 MHz, Chloroform-d) δ 7.99 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.38 – 7.30 (m, 5H), 7.21 (d, J = 7.6 Hz, 1H), 7.10 – 7.05 (m, 2H), 6.87 (d, J = 6.8 Hz, 2H), 5.36 – 5.28 (m, 1H), 5.23 (d, J = 15.6 Hz, 1H), 4.97 (d, J = 16.8 Hz, 1H), 4.88 (d, J = 10.4 Hz, 1H), 4.65 (d, J = 15.2 Hz, 1H), 3.08 (dd, J = 14.8, 5.2 Hz, 1H), 2.96 (dd, J = 15.2, 8.0 Hz, 1H), 2.49 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 167.2, 144.9, 137.4, 135.7, 132.6, 132.3, 130.0, 129.3, 129.2, 129.1, 128.6, 128.3, 128.1, 127.6, 126.0, 119.2, 57.6, 47.5, 38.8, 21.7.

HRMS (ESI-TOF) calcd for C₂₅H₂₃NNaO₃S₂⁺ ([M+Na]⁺): 472.1012; found: 472.1015.

IR (film); 2924, 2847, 1687, 1592, 1449, 1437, 1357, 1260, 1188, 1173, 1116, 1046, 983, 925, 817 cm⁻¹.

4-allyl-7-methoxy-4-(phenylthio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3b)



White solid; Yield 26% (13 mg); M.p. 189-190 °C.

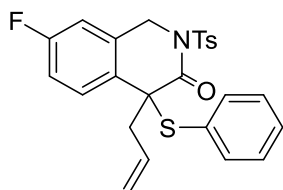
¹H NMR (400 MHz, Chloroform-d) δ 7.80 (d, J = 8.4 Hz, 2H), 7.28 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 7.16 – 7.14 (m, 2H), 7.03 (d, J = 8.4 Hz, 1H), 6.90 – 6.87 (m, 2H), 6.81 – 6.79 (m, 2H), 5.90 – 5.80 (m, 1H), 5.17 – 5.14 (m, 1H), 5.12 – 5.07 (m, 2H), 4.72 (s, 1H), 4.59 (d, J = 15.6 Hz, 1H), 3.85 (s, 3H), 3.51 (dt, J = 6.8, 1.2 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.6, 159.3, 144.9, 135.8, 135.4, 133.3, 133.0, 132.7, 129.54, 129.51, 129.3, 128.4, 127.9, 125.9, 117.9, 114.3, 111.7, 55.5, 54.2, 48.3, 36.8, 21.7.

HRMS (ESI-TOF) calcd for $\text{C}_{26}\text{H}_{25}\text{NNaO}_4\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 502.1117; found: 502.1118.

IR (film): 2923, 2843, 1687, 1611, 1505, 1353, 1171, 1142, 1034, 940, 815 cm^{-1} .

4-allyl-7-fluoro-4-(phenylthio)-2-tosyl-1,4-dihydroisoquinolin-3(2*H*)-one (3c)



White solid; Yield 67% (31 mg); M.p. 169-170 $^{\circ}\text{C}$.

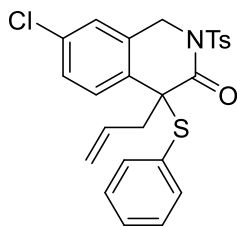
^1H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, $J = 8.4$, 2H), 7.44 – 7.40 (m, 1H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.32 – 7.31 (m, 1H), 7.10 – 7.06 (m, 3H), 6.93 – 6.90 (m, 1H), 6.87 (d, $J = 6.8$, 2H), 5.33 – 5.23 (m, 1H), 5.18 (d, $J = 15.6$ Hz, 1H), 4.95 (d, $J = 17.2$ Hz, 1H), 4.88 (d, $J = 10.4$ Hz, 1H), 4.59 (d, $J = 15.6$ Hz, 1H), 3.12 – 3.07 (m, 1H), 2.91 (dd, $J = 14.8$ Hz, 8.0 Hz, 1H), 2.49 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.9, 161.9 (d, $J = 248.0$ Hz), 145.1, 137.4, 135.5, 134.5 (d, $J = 8.1$ Hz), 132.4, 130.1, 129.9 (d, $J = 8.5$ Hz), 129.4, 129.2, 128.9, 128.7, 128.5 (d, $J = 3.1$ Hz), 119.4, 115.6 (d, $J = 21.6$ Hz), 112.8 (d, $J = 22.4$ Hz), 57.3, 47.1 (d, $J = 2.2$ Hz), 39.1, 21.7.

HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{22}\text{FNNaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 490.0917; found: 490.0919.

IR (film): 3075, 2920, 1695, 1597, 1500, 1360, 1280, 1171, 1119, 1088, 958, 810 cm^{-1} .

4-allyl-7-chloro-4-(phenylthio)-2-tosyl-1,4-dihydroisoquinolin-3(2*H*)-one (3d)



White solid; Yield 52% (25 mg); M.p. 191-192 °C.

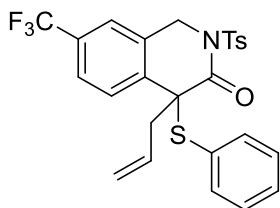
¹H NMR (400 MHz, Chloroform-d) δ 7.98 (d, J = 8.4 Hz, 2H), 7.39 – 7.30 (m, 5H), 7.21 (s, 1H), 7.11 – 7.07 (m, 2H), 6.88 (d, J = 6.4 Hz, 2H), 5.32 – 5.23 (m, 1H), 5.18 (d, J = 15.6 Hz, 1H), 4.95 (d, J = 17.2 Hz, 1H), 4.88 (d, J = 10.4 Hz, 1H), 4.58 (d, J = 15.6 Hz, 1H), 3.11 – 3.06 (m, 1H), 2.93 – 2.87 (m, 1H), 2.49 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 166.7, 145.1, 126.0, 119.5, 137.4, 135.4, 134.1, 134.0, 132.2, 131.3, 130.2, 129.4, 129.2, 128.77, 128.76, 128.66, 128.5, 57.2, 46.9, 38.9, 21.8.

HRMS (ESI-TOF) calcd for C₂₅H₂₂ClNNaO₃S₂⁺ ([M+Na]⁺): 506.0622; found: 506.0625.

IR (film): 3075, 2924, 1694, 1596, 1438, 1362, 1255, 1088, 971, 806 cm⁻¹.

4-allyl-4-(phenylthio)-2-tosyl-7-(trifluoromethyl)-1,4-dihydroisoquinolin-3(2H)-one (3e)



White solid; Yield 40% (21 mg); M.p. 142-143 °C.

¹H NMR (400 MHz, Chloroform-d) δ 7.99 (d, J = 8.4 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.47 (s, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.11 – 7.07 (m, 2H), 6.89 – 6.87 (m, 2H), 5.31 – 5.21 (m, 2H), 4.96 (dd, J = 17.2, 1.6 Hz, 1H), 4.89 (d, J = 10.0 Hz, 1H), 4.62 (d, J = 15.6 Hz, 1H), 3.14 (ddt, J = 14.4, 5.2, 1.6 Hz, 1H), 2.94 (dd, J = 14.8, 8.0 Hz, 1H), 2.49 (s, 3H).

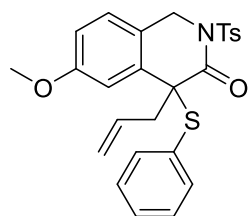
¹³C NMR (100 MHz, Chloroform-d) δ 166.5, 145.2, 137.4, 136.9, 135.4, 133.03, 132.02, 130.27 (q, $J = 32.6$ Hz), 130.33, 129.4, 129.2, 128.8, 128.43, 128.41, 125.0 (q, $J = 3.4$ Hz), 123.1 (q, $J = 2.9$ Hz), 123.6 (q, $J = 270.8$ Hz), 119.7, 57.4, 47.1, 38.9, 21.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.745.

HRMS (ESI-TOF) calcd for C₂₆H₂₂F₃NNaO₃S₂⁺ ([M+Na]⁺): 540.0885; found: 540.0886.

IR (film): 3075, 2922, 1694, 1596, 1438, 1362, 1255, 1088, 971, 806 cm⁻¹.

4-allyl-6-methoxy-4-(phenylthio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3f)



White solid; Yield 43% (21 mg); M.p. 196-197 °C.

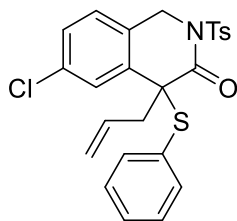
¹H NMR (400 MHz, Chloroform-d) δ 7.91 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.27 – 7.22 (m, 1H), 7.06 (d, $J = 8.8$ Hz, 1H), 7.03 – 6.99 (m, 2H), 6.88 (d, $J = 2.4$ Hz, 1H), 6.82 – 6.78 (m, 3H), 5.30 – 5.22 (m, 1H), 5.12 (d, $J = 14.8$ Hz, 1H), 4.91 (dd, $J = 17.2, 1.6$ Hz, 1H), 4.83 (d, $J = 10.4$ Hz, 1H), 4.56 (d, $J = 15.2$ Hz, 1H), 3.74 (s, 3H), 2.98 (ddt, $J = 14.8, 5.6, 1.6$ Hz, 1H), 2.83 (dd, $J = 14.8, 8.0$ Hz, 1H), 2.42 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 167.0, 159.4, 144.9, 137.4, 135.7, 133.9, 132.7, 130.0, 129.3, 129.2, 129.0, 128.6, 127.2, 124.6, 119.1, 114.1, 112.8, 57.7, 55.4, 47.0, 38.8, 21.7.

HRMS (ESI-TOF) calcd for C₂₆H₂₅NNaO₄S₂⁺ ([M+Na]⁺): 502.1117; found: 502.1120.

IR (film): 3445, 2963, 1693, 1616, 1507, 1471, 1357, 1260, 1187, 1088, 924, 817 cm⁻¹.

4-allyl-6-chloro-4-(phenylthio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3g)



White solid; Yield 59% (29 mg); M.p. 152-153 °C.

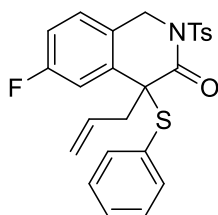
¹H NMR (400 MHz, Chloroform-d) δ 7.90 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 2.0 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.21 (dd, J = 8.0, 2.0 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 7.04 – 7.00 (m, 2H), 6.84 – 6.76 (dd, J = 8.0, 1.2 Hz, 2H), 5.26 – 5.16 (m, 1H), 5.12 (d, J = 15.6 Hz, 1H), 4.90 (dd, J = 17.2, 1.6 Hz, 1H), 4.83 (dd, J = 10.4, 1.2 Hz, 1H), 4.48 (d, J = 15.6 Hz, 1H), 3.01 (ddt, J = 14.8, 5.6, 1.6 Hz, 1H), 2.80 (dd, J = 14.8, 7.6 Hz, 1H), 2.42 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 166.6, 145.1, 137.4, 135.4, 134.7, 134.2, 132.0, 130.7, 130.2, 129.4, 129.2, 128.8, 128.6, 128.3, 127.8, 127.4, 119.7, 57.3, 47.0, 38.8, 21.8.

HRMS (ESI-TOF) calcd for C₂₅H₂₂ClNNaO₃S₂⁺ ([M+Na]⁺): 506.0622; found: 506.0625.

IR (film): 3419, 2924, 1749, 1688, 1595, 1454, 1357, 1260, 1171, 1088, 935, 808 cm⁻¹.

4-allyl-6-fluoro-4-(phenylthio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3h)



White solid; Yield 60% (28 mg); M.p. 175-176 °C.

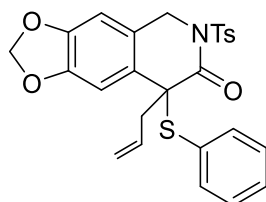
¹H NMR (400 MHz, Chloroform-d) δ 7.98 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.19 – 7.12 (m, 2H), 7.10 – 7.06 (m, 2H), 7.04 – 6.99 (m, 1H), 6.89 – 6.86 (m, 2H), 5.35 – 5.24 (m, 1H), 5.20 (d, J = 15.2 Hz, 1H), 5.00 – 4.95 (m, 1H), 4.90 (d, J = 10.0 Hz, 1H), 4.56 (d, J = 15.2, 1H), 3.11 – 3.06 (m, 1H), 2.85 (dd, J = 14.8, 8.0 Hz, 1H), 2.49 (s, 3H).

^{13}C NMR (100 MHz, Chloroform- d) δ 166.6, 162.4 (d, $J = 245.3$ Hz), 145.0, 137.4, 135.5, 135.2 (d, $J = 7.8$ Hz), 132.1, 130.2, 129.4, 129.2, 128.7, 128.6, 128.1 (d, $J = 2.9$ Hz), 127.8 (d, $J = 8.3$ Hz), 119.6, 115.5 (d, $J = 22.0$ Hz), 114.5 (d, $J = 23.5$ Hz), 57.5 (d, $J = 1.8$ Hz), 46.9, 38.9, 21.7.

HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{22}\text{FNNaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 490.0917; found: 490.0919.

IR (film): 3079, 2963, 1704, 1689, 1613, 1596, 1506, 1438, 1260, 1173, 1113, 931, 818 cm^{-1} .

8-allyl-8-(phenylthio)-6-tosyl-5,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-7(6H)-one (3i)



White solid; Yield 33% (16 mg); M.p. 187-188 $^{\circ}\text{C}$.

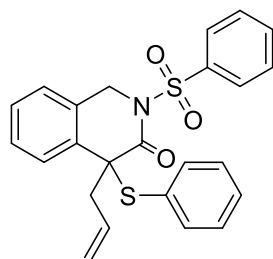
^1H NMR (400 MHz, Chloroform- d) δ 7.98 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.34 – 7.29 (m, 1H), 7.10 – 7.06 (m, 2H), 6.91 (s, 1H), 6.88 – 6.86 (m, 2H), 6.63 (s, 1H), 6.02 – 6.00 (m, 2H), 5.37 – 5.26 (m, 1H), 5.08 (d, $J = 15.2$ Hz, 1H), 4.97 (dd, $J = 17.2, 1.2$ Hz, 1H), 4.90 (dd, $J = 10.4, 1.6$ Hz, 1H), 4.51 (d, $J = 15.2$ Hz, 1H), 3.06 – 3.00 (m, 1H), 2.82 (dd, $J = 14.8, 8.0$ Hz, 1H), 2.49 (s, 3H).

^{13}C NMR (100 MHz, Chloroform- d) δ 166.9, 148.0, 147.6, 144.9, 137.3, 135.6, 132.5, 129.9, 129.3, 129.19, 129.17, 128.6, 126.5, 125.9, 119.2, 107.3, 105.9, 101.6, 57.7, 47.3, 39.1, 21.7.

HRMS (ESI-TOF) calcd for $\text{C}_{26}\text{H}_{23}\text{NNaO}_5\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 516.0910; found: 516.0910.

IR (film): 3059, 2963, 2922, 1694, 1596, 1505, 1488, 1359, 1261, 1171, 1089, 1035, 934, 800 cm^{-1} .

4-allyl-2-(phenylsulfonyl)-4-(phenylthio)-1,4-dihydroisoquinolin-3(2H)-one (3j)



White solid; Yield 60% (26 mg); M.p. 157-158 °C.

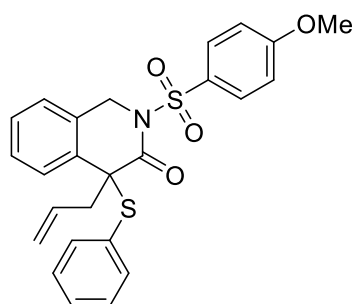
¹H NMR (400 MHz, Chloroform-d) δ 8.12 – 8.10 (m, 2H), 7.73 – 7.68 (m, 1H), 7.60 – 7.56 (m, 2H), 7.48 – 7.46 (m, 1H), 7.39 – 7.29 (m, 3H), 7.21 (d, $J = 7.2$ Hz, 1H), 7.10 – 7.06 (m, 2H), 6.88 – 6.86 (m, 2H), 5.35 – 5.23 (m, 2H), 4.96 (dd, $J = 1.6, 17.2$ Hz, 1H), 4.86 (dd, $J = 10.4, 1.2$ Hz, 1H), 4.65 (d, $J = 15.6$ Hz, 1H), 3.08 (ddt, $J = 14.8, 6.0, 1.6$ Hz, 1H), 2.97 (dd, $J = 14.4, 7.6$ Hz, 1H).

¹³C NMR (100 MHz, Chloroform-d) δ 167.2, 138.6, 137.4, 133.8, 132.5, 132.4, 132.2, 130.0, 129.1, 128.9, 128.7, 128.3, 128.2, 127.6, 126.0, 119.3, 57.6, 47.5, 38.7.

HRMS (ESI-TOF) calcd for $C_{24}H_{21}NNaO_3S_2^+$ ($[M+Na]^+$): 458.0855; found: 458.0853.

IR (film): 3073, 2920, 1694, 1639, 1471, 1449, 1360, 1438, 1259, 1182, 1115, 1087, 917, 854 cm^{-1} .

4-allyl-2-((4-methoxyphenyl)sulfonyl)-4-(phenylthio)-1,4-dihydroisoquinolin-3(2H)-one (3k)



White solid; Yield 59% (27 mg); M.p. 205-206 °C.

¹H NMR (400 MHz, Chloroform-d) δ 8.05 (d, $J = 8.8$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.38 – 7.29 (m, 3H), 7.20 (d, $J = 7.6$ Hz, 1H), 7.11 – 7.07 (m, 2H), 7.03 (d, $J = 8.8$ Hz, 2H), 6.90 – 6.88 (m, 2H), 5.36 – 5.27 (m, 1H), 5.22 (d, $J = 15.2$ Hz, 1H), 4.98 (dd, $J = 17.2, 1.6$ Hz,

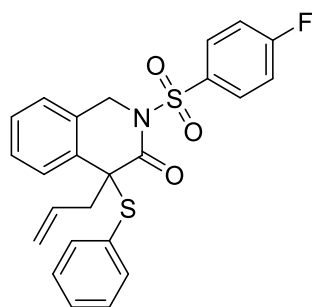
1H), 4.88 (dd, $J = 10.4, 1.2$ Hz, 1H), 4.61 (d, $J = 15.2$ Hz, 1H), 3.91 (s, 3H), 3.14 – 3.08 (m, 1H), 2.97 (dd, $J = 14.8, 8.0$ Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-d) δ 167.2, 163.9, 137.4, 132.59, 132.57, 132.4, 131.6, 130.0, 129.9, 129.0, 128.7, 128.2, 128.1, 127.6, 126.0, 119.2, 113.8, 57.6, 55.8, 47.4, 38.8.

HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{23}\text{NNaO}_4\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 488.0961; found: 488.0963.

IR (film): 3076, 2976, 1682, 1591, 1497, 1448, 1355, 1262, 1216, 1160, 1115, 1088, 932, 837 cm^{-1} .

4-allyl-2-((4-fluorophenyl)sulfonyl)-4-(phenylthio)-1,4-dihydroisoquinolin-3(2H)-one (3l)



White solid; Yield 58% (26 mg); M.p. 182-183 °C.

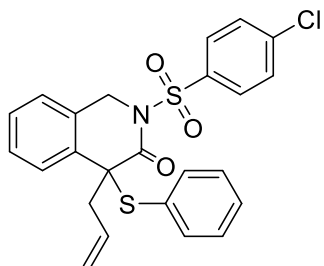
^1H NMR (400 MHz, Chloroform-d) δ 8.14 – 8.11 (m, 2H), 7.48 – 7.46 (m, 1H), 7.39 – 7.31 (m, 3H), 7.26 – 7.20 (m, 3H), 7.14 – 7.11 (m, 2H), 6.95 – 6.93 (m, 2H), 5.34 – 5.24 (m, 1H), 5.21 (d, $J = 15.6$ Hz, 1H), 4.95 (dd, $J = 17.2, 1.6$ Hz, 1H), 4.87 (dd, $J = 10.4, 1.6$ Hz, 1H), 4.63 (d, $J = 15.2$ Hz, 1H), 3.13 – 3.07 (m, 1H), 2.99 (dd, $J = 14.8, 7.6$ Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-d) δ 167.3, 165.8 (d, $J = 255.1$ Hz), 137.3, 134.5 (d, $J = 3.2$ Hz), 132.4, 132.3 (d, $J = 33.7$ Hz), 132.2, 132.1, 130.1, 129.0, 128.7, 128.4, 128.2, 127.6, 126.0, 119.3, 115.9 (d, $J = 22.7$ Hz), 57.7, 47.5, 38.8.

HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{20}\text{FNNaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 476.0761; found: 476.0763.

IR (film): 3070, 2925, 1687, 1587, 1492, 1362, 1261, 1179, 1159, 1086, 1046, 932, 848 cm^{-1} .

4-allyl-2-((4-chlorophenyl)sulfonyl)-4-(phenylthio)-1,4-dihydroisoquinolin-3(2H)-one (3m)



White solid; Yield 53% (25 mg); M.p. 184-185 °C.

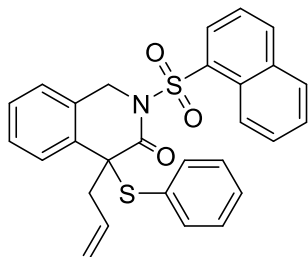
¹H NMR (400 MHz, Chloroform-d) δ 8.04 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 7.6 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.22 (d, J = 7.2 Hz, 1H), 7.14 – 7.10 (m, 2H), 6.91 (d, J = 6.8 Hz, 2H), 5.35 – 5.27 (m, 1H), 5.22 (d, J = 15.2 Hz, 1H), 4.97 (d, J = 17.2 Hz, 1H), 4.89 (d, J = 10.4 Hz, 1H), 4.67 (d, J = 15.2 Hz, 1H), 3.11 – 3.06 (m, 1H), 3.02 – 2.97 (m, 1H).

¹³C NMR (100 MHz, Chloroform-d) δ 167.2, 140.5, 137.3, 137.0, 132.4, 132.1, 130.7, 130.1, 129.0, 128.9, 128.7, 128.4, 128.2, 127.6, 126.1, 119.3, 57.6, 47.5, 38.7.

HRMS (ESI-TOF) calcd for $C_{24}H_{20}ClNNaO_3S_2^+$ ($[M+Na]^+$): 492.0465; found: 492.0467.

IR (film): 3067, 3006, 1686, 1438, 1361, 1182, 1115, 1085, 972, 824 cm^{-1} .

4-allyl-2-(naphthalen-1-ylsulfonyl)-4-(phenylthio)-1,4-dihydroisoquinolin-3(2H)-one (3n)



White solid; Yield 38% (18 mg); M.p. 184-185 °C.

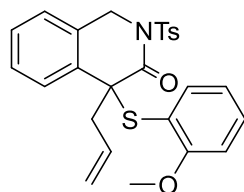
¹H NMR (400 MHz, Chloroform-d) δ 8.74 (s, 1H), 8.07 – 8.02 (m, 3H), 8.00 – 7.96 (m, 1H), 7.74 – 7.70 (m, 1H), 7.69 – 7.65 (m, 1H), 7.47 (dd, $J = 7.2, 1.6$ Hz, 1H), 7.40 – 7.32 (m, 2H), 7.273 – 7.269 (m, 1H), 7.15 – 7.10 (m, 1H), 6.68 – 6.63 (m, 4H), 5.38 – 5.27 (m, 2H), 4.95 (dd, $J = 17.2, 1.6$ Hz, 1H), 4.84 (dd, $J = 10.4, 1.6$ Hz, 1H), 4.80 (d, $J = 15.2$ Hz, 1H), 3.06 – 2.92 (m, 2H).

¹³C NMR (100 MHz, Chloroform-d) δ 167.1, 137.3, 135.4, 135.2, 132.55, 132.52, 132.3, 131.8, 131.6, 129.9, 129.8, 129.5, 128.9, 128.8, 128.44, 128.35, 128.2, 127.9, 127.6, 126.1, 123.3, 119.2, 57.4, 47.7, 38.6.

HRMS (ESI-TOF) calcd for $C_{28}H_{23}NNaO_3S_2^+$ ($[M+Na]^+$): 508.1012; found: 508.1011.

IR (film): 3060, 2920, 1692, 1590, 1453, 1354, 1261, 1172, 1114, 1088, 1071, 971, 859 cm^{-1} .

4-allyl-4-((2-methoxyphenyl)thio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3o)



White solid; Yield 58% (28 mg); M.p. 169-170 °C.

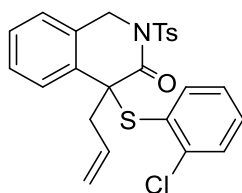
¹H NMR (400 MHz, Chloroform-d) δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.43 – 7.40 (m, 1H), 7.33 – 7.27 (m, 5H), 7.22 – 7.20 (m, 1H), 6.82 (dd, $J = 7.6, 1.6$ Hz, 1H), 6.77 (dd, $J = 8.4, 1.2$ Hz, 1H), 6.64 (td, $J = 7.6, 1.2$ Hz, 1H), 5.27 (d, $J = 15.2$ Hz, 1H), 5.23 – 5.14 (m, 1H), 4.91 – 4.83 (m, 2H), 4.78 (d, $J = 10.0$ Hz, 1H), 3.71 (s, 3H), 3.17 – 3.12 (m, 1H), 3.10 – 3.04 (m, 1H), 2.44 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 167.1, 161.3, 144.7, 140.0, 135.8, 133.0, 132.7, 132.6, 132.3, 129.2, 128.9, 127.92, 127.87, 127.8, 125.8, 120.5, 118.9, 117.0, 110.8, 58.3, 55.6, 47.4, 38.6, 21.7.

HRMS (ESI-TOF) calcd for $C_{26}H_{25}NNaO_4S_2^+$ ($[M+Na]^+$): 502.1117; found: 502.1118.

IR (film): 3069, 2916, 1694, 1582, 1475, 1357, 1275, 1171, 1115, 1088, 913, 813 cm^{-1} .

4-allyl-4-((2-chlorophenyl)thio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3p)



White solid; Yield 39% (18 mg); M.p. 179-180 °C.

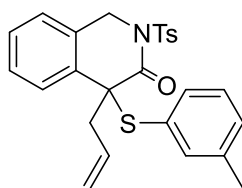
¹H NMR (400 MHz, Chloroform-d) δ 7.97 (d, J = 8.4 Hz, 2H), 7.49 – 7.47 (m, 1H), 7.36 – 7.33 (m, 5H), 7.29 – 7.27 (m, 1H), 7.25 – 7.22 (m, 1H), 6.96 – 6.91 (m, 1H), 6.81 (dd, J = 7.6, 1.6 Hz, 1H), 5.34 (d, J = 15.2 Hz, 1H), 5.29 – 5.20 (m, 1H), 4.98 – 4.93 (m, 2H), 4.86 (d, J = 10.0 Hz, 1H), 3.17 (dd, J = 14.8, 7.6 Hz, 1H), 3.06 – 3.04 (m, 1H), 2.47 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 166.6, 144.9, 141.0, 139.8, 135.6, 132.51, 132.48, 132.1, 131.3, 129.9, 129.3, 129.1, 128.5, 128.40, 128.38, 127.8, 126.9, 126.2, 119.4, 58.8, 47.4, 38.1, 21.7.

HRMS (ESI-TOF) calcd for $C_{25}H_{22}ClNNaO_3S_2^+$ ($[M+Na]^+$): 506.0622; found: 506.0626.

IR (film): 3071, 2921, 1694, 1449, 1360, 1261, 1187, 1172, 1115, 1088, 1036, 971, 853 cm^{-1} .

4-allyl-4-(*m*-tolylthio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3q)



White solid; Yield 61% (28 mg); M.p. 183-184 °C.

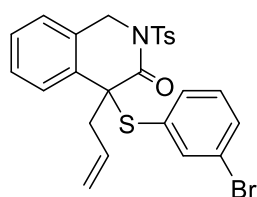
¹H NMR (400 MHz, Chloroform-d) δ 7.96 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.38 – 7.29 (m, 4H), 7.19 (d, J = 7.2 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 6.97 – 6.92 (m, 2H), 6.63 (d, J = 7.6 Hz, 1H), 5.34 – 5.17 (m, 1H), 5.19 (d, J = 15.2 Hz, 1H), 4.97 – 4.92 (m, 1H), 4.85 (d, J = 10.4 Hz, 1H), 4.59 (d, J = 15.6 Hz, 1H), 3.13 – 3.07 (m, 1H), 2.95 (dd, J = 14.8, 7.6 Hz, 1H), 2.46 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, Chloroform- d) δ 167.3, 144.8, 138.5, 138.1, 135.8, 134.3, 132.6, 132.4, 130.8, 129.3, 129.0, 128.7, 128.4, 128.2, 128.0, 127.6, 125.9, 119.1, 57.6, 47.5, 38.7, 21.7, 21.0.

HRMS (ESI-TOF) calcd for $\text{C}_{26}\text{H}_{25}\text{NNaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 486.1168; found: 486.1170.

IR (film): 3075, 2922, 1694, 1594, 1453, 1359, 1259, 1187, 1172, 1116, 1089, 913, 813 cm^{-1} .

4-allyl-4-((3-bromophenyl)thio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3r)



White solid; Yield 47% (25 mg); m.p. 165-166 $^{\circ}\text{C}$.

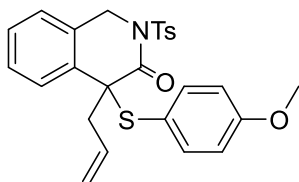
^1H NMR (400 MHz, Chloroform- d) δ 7.97 (d, J = 8.4 Hz, 2H), 7.45 – 7.43 (m, 2H), 7.37 – 7.32 (m, 4H), 7.24 (d, J = 7.2 Hz, 1H), 7.20 – 7.19 (m, 1H), 6.98 – 6.94 (m, 1H), 6.82 – 6.80 (m, 1H), 5.34 – 5.22 (m, 2H), 4.99 – 4.94 (m, 1H), 4.88 (d, J = 10.4 Hz, 1H), 4.71 (d, J = 15.2 Hz, 1H), 3.11 – 2.92 (m, 1H), 2.95 (dd, J = 14.4, 7.6 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, Chloroform- d) δ 167.0, 145.0, 139.5, 135.8, 135.5, 133.1, 132.22, 132.18, 132.1, 131.2, 129.9, 129.4, 129.0, 128.4, 128.36, 127.7, 126.1, 122.0, 119.5, 57.8, 47.5, 38.7, 21.8.

HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{22}\text{BrNNaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 550.0117; found: 550.0119.

IR (film): 3073, 2921, 1693, 1556, 1457, 1359, 1187, 1172, 1116, 972, 813 cm^{-1} .

4-allyl-4-((4-methoxyphenyl)thio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3s)



White solid; Yield 52% (25 mg); M.p. 194-195 °C.

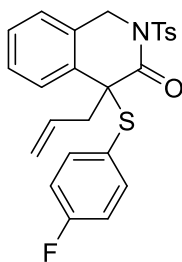
¹H NMR (400 MHz, Chloroform-d) δ 7.99 (d, J = 8.4 Hz, 2H), 7.44 (dd, J = 7.7, 1.6 Hz, 1H), 7.38 – 7.29 (m, 4H), 7.22 (dd, J = 7.6, 1.6 Hz, 1H), 6.82 – 6.78 (m, 2H), 6.61 – 6.57 (m, 2H), 5.36 – 5.23 (m, 2H), 4.97 (dd, J = 17.2, 1.6 Hz, 1H), 4.87 (dd, J = 10.4, 1.2 Hz, 1H), 4.71 (d, J = 15.2 Hz, 1H), 3.78 (s, 3H), 3.06 (ddt, J = 14.8, 5.6, 2.0 Hz, 1H), 2.94 (dd, J = 14.4, 7.6 Hz, 1H), 2.49 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 167.2, 161.1, 144.8, 139.0, 135.8, 132.7, 132.6, 132.3, 129.3, 129.2, 128.2, 128.0, 127.5, 126.1, 119.8, 119.0, 114.2, 57.6, 55.2, 47.5, 38.4, 21.7.

HRMS (ESI-TOF) calcd for C₂₆H₂₅NNaO₄S₂⁺ ([M+Na]⁺): 502.1117; found: 502.1121.

IR (film): 3011, 2925, 1693, 1590, 1492, 1359, 1289, 1251, 1172, 1140, 1088, 923, 827 cm⁻¹.

4-allyl-4-((4-fluorophenyl)thio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3t)



White solid; Yield 49% (23 mg); M.p. 163-164 °C.

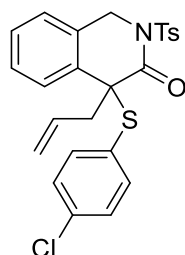
¹H NMR (400 MHz, Chloroform-d) δ 7.98 (d, J = 8.4 Hz, 2H), 7.46 (dd, J = 7.6, 1.6 Hz, 1H), 7.39 – 7.31 (m, 4H), 7.25 – 7.23 (m, 1H), 6.90 – 6.86 (m, 2H), 6.79 – 6.75 (m, 2H), 5.35 – 5.24 (m, 2H), 4.96 (d, J = 17.2 Hz, 1H), 4.88 (d, J = 10.4 Hz, 1H), 4.74 (d, J = 15.6 Hz, 1H), 3.08 – 3.02 (m, 1H), 2.97 – 2.92 (m, 1H), 2.49 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 166.9, 163.9 (d, *J* = 250.0 Hz), 145.0, 139.4 (*J* = 8.6 Hz), 135.7, 132.3 (d, *J* = 16.7 Hz), 129.3, 129.2, 128.34, 128.28, 127.6, 126.1, 124.5 (d, *J* = 3.5 Hz), 119.3, 116.0, 115.8, 57.6, 47.5, 38.6, 21.7.

HRMS (ESI-TOF) calcd for C₂₅H₂₂FNNaO₃S₂⁺ ([M+Na]⁺): 490.0917; found: 490.0920.

IR (film): 3073, 2916, 1694, 1588, 1489, 1360, 1260, 1224, 1187, 1172, 1089, 914, 834 cm⁻¹.

4-allyl-4-((4-chlorophenyl)thio)-2-tosyl-1,4-dihydroisoquinolin-3(2*H*)-one (3u)



White solid; Yield 54% (26 mg); M.p. 174-175 °C.

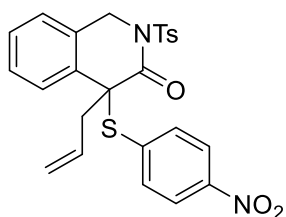
¹H NMR (400 MHz, Chloroform-d) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.46 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.06 – 7.03 (m, 2H), 6.86 – 6.82 (m, 2H), 5.35 – 5.25 (m, 2H), 4.97 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.88 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.78 (d, *J* = 15.6 Hz, 1H), 3.05 (ddt, *J* = 14.8, 5.6, 1.6 Hz, 1H), 2.95 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.50 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 166.8, 145.0, 138.5, 136.6, 135.6, 132.34, 132.25, 132.2, 129.3, 129.2, 128.9, 128.4, 128.3, 127.62, 127.58, 126.2, 119.4, 57.7, 47.5, 38.7, 21.7.

HRMS (ESI-TOF) calcd for C₂₅H₂₂ClNNaO₃S₂⁺ ([M+Na]⁺): 506.0622; found: 506.0622.

IR (film): 2923, 1694, 1571, 1492, 1474, 1359, 1262, 1188, 1172, 1091, 1014, 929, 816 cm⁻¹.

4-allyl-4-((4-nitrophenyl)thio)-2-tosyl-1,4-dihydroisoquinolin-3(2*H*)-one (3v)



White solid; Yield 27% (13 mg); M.p.149-150 °C.

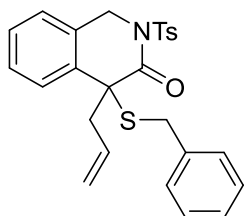
¹H NMR (400 MHz, Chloroform-d) δ 7.98 – 7.95 (m, 2H), 7.91 – 7.86 (m, 2H), 7.53 – 7.51 (m, 1H), 7.42 – 7.35 (m, 4H), 7.30 – 7.28 (m, 1H), 7.12 – 7.09 (m, 2H), 5.36 – 5.25 (m, 2H), 5.00 – 4.90 (m, 3H), 3.08 – 3.00 (m, 2H), 2.51 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 166.5, 148.2, 145.4, 138.0, 137.1, 135.4, 132.1, 131.8, 131.7, 129.4, 129.2, 128.7, 128.6, 127.7, 126.4, 123.4, 119.8, 58.6, 47.5, 39.3, 21.7.

HRMS (ESI-TOF) calcd for C₂₅H₂₂N₂NaO₅S₂⁺ ([M+Na]⁺): 517.0962; found: 517.0864.

IR (film): 3088, 2963, 1692, 1597, 1521, 1344, 1261, 1172, 1088, 854, 800 cm⁻¹.

4-allyl-4-(benzylthio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3w)



White solid; Yield 50% (23 mg); M.p.105-106 °C.

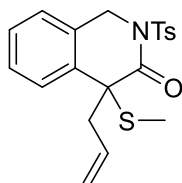
¹H NMR (400 MHz, Chloroform-d) δ 8.03 (d, J = 8.4 Hz, 2H), 7.45 – 7.42 (m, 1H), 7.37 – 7.31 (m, 4H), 7.29 – 7.27 (m, 1H), 7.23 – 7.16 (m, 3H), 6.98 – 6.95 (m, 2H), 5.49 – 5.41 (m, 1H), 5.31 (d, J = 14.8 Hz, 1H), 5.09 – 4.95 (m, 2H), 4.96 (d, J = 10.4 Hz, 1H), 3.57 (d, J = 11.6 Hz, 1H), 3.44 – 3.38 (m, 1H), 3.10 (d, J = 11.6 Hz, 1H), 3.01 (dd, J = 15.2, 7.6 Hz, 1H), 2.41 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 166.6, 145.1, 135.55, 135.46, 132.8, 132.3, 131.8, 129.4, 129.1, 128.9, 128.4, 128.32, 128.28, 127.28, 127.25, 126.4, 119.1, 55.2, 47.7, 38.0, 34.8, 21.7.

HRMS (ESI-TOF) calcd for C₂₆H₂₅NNaO₃S₂⁺ ([M+Na]⁺): 486.1168; found: 486.1169.

IR (film): 3029, 2923, 1686, 1596, 1494, 1453, 1361, 1187, 1172, 1116, 1088, 972, 813 cm^{-1} .

4-allyl-4-(methylthio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3x)



White solid; Yield 59% (23 mg); M.p. 125-126 °C.

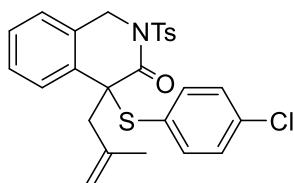
^1H NMR (400 MHz, Chloroform- d) δ 7.87 (d, J = 8.4 Hz, 2H), 7.37 – 7.34 (m, 1H), 7.28 – 7.38 (m, 1H), 7.26 – 7.19 (m, 4H), 5.41 – 5.31 (m, 1H), 5.21 (d, J = 15.2 Hz, 1H), 4.97 (d, J = 15.6 Hz, 2H), 4.89 – 4.86 (m, 1H), 3.25 – 3.20 (m, 1H), 2.83 (dd, J = 14.8, 7.6 Hz, 1H), 2.36 (s, 3H), 1.59 (s, 3H).

^{13}C NMR (100 MHz, Chloroform- d) δ 166.3, 144.9, 135.5, 132.83, 132.76, 131.9, 129.2, 128.6, 128.3, 128.2, 127.2, 126.4, 119.0, 53.4, 47.8, 36.9, 21.7, 12.9.

HRMS (ESI-TOF) calcd for $\text{C}_{20}\text{H}_{21}\text{NNaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 410.0855; found: 410.0857.

IR (film): 2921, 1689, 1596, 1493, 1452, 1358, 1260, 1187, 1172, 1117, 1089, 919, 813 cm^{-1} .

4-((4-chlorophenyl)thio)-4-(2-methylallyl)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3y)



White solid; Yield 37% (19 mg); M.p. 167-168 °C.

^1H NMR (400 MHz, Chloroform- d) δ 7.97 (d, J = 8.4 Hz, 2H), 7.42 – 7.40 (m, 1H), 7.37 – 7.30 (m, 4H), 7.22 – 7.20 (m, 1H), 7.04 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H),

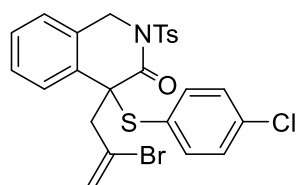
5.27 (d, $J = 15.2$ Hz, 1H), 4.69 (d, $J = 15.2$ Hz, 1H), 4.54 (d, $J = 1.6$ Hz, 1H), 4.11 (s, 1H), 3.11 (d, $J = 16.0$ Hz, 1H), 2.93 (d, $J = 16.0$ Hz, 1H), 2.49 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, Chloroform- d) δ 167.1, 145.0, 139.9, 138.5, 136.6, 135.5, 132.5, 131.1, 129.24, 129.22, 128.8, 128.3, 128.2, 127.6, 127.5, 125.8, 114.5, 57.5, 47.5, 42.1, 23.5, 21.7.

HRMS (ESI-TOF) calcd for $\text{C}_{26}\text{H}_{24}\text{ClNNaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 520.0778; found: 520.0782.

IR (film): 2922, 1694, 1596, 1572, 1474, 1453, 1360, 1261, 1187, 1171, 1144, 1124, 1092, 1014, 910, 814 cm^{-1} .

4-(2-bromoallyl)-4-((4-chlorophenyl)thio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3z)



White solid; Yield 26% (15 mg); M.p. 183-184 °C.

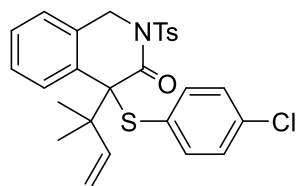
^1H NMR (400 MHz, Chloroform- d) δ 7.97 (d, $J = 8.4$ Hz, 2H), 7.41 – 7.34 (m, 5H), 7.25 – 7.24 (m, 1H), 7.08 (d, $J = 8.4$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 2H), 5.30 (d, $J = 15.6$ Hz, 1H), 5.19 (dd, $J = 3.2, 1.6$ Hz, 1H), 4.85 – 4.81 (m, 2H), 3.55 (dt, $J = 16.8, 2.0$ Hz, 1H), 3.36 (d, $J = 16.8$ Hz, 1H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, Chloroform- d) δ 166.2, 145.2, 138.6, 137.0, 135.2, 131.3, 131.2, 129.28, 129.25, 129.0, 128.6, 128.4, 127.3, 126.9, 126.6, 126.1, 120.2, 57.7, 47.5, 45.3, 21.7.

HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{21}\text{BrClNNaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 583.9727; found: 583.9730.

IR (film): 2923, 1694, 1596, 1572, 1474, 1454, 1389, 1361, 1262, 1187, 1172, 1123, 1091, 1014, 909, 817 cm^{-1} .

4-((4-chlorophenyl)thio)-4-(2-methylbut-3-en-2-yl)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (3A)



White solid; Yield 41% (21 mg); M.p. 160-161 °C.

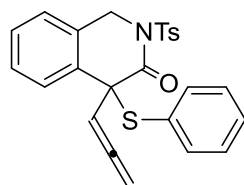
¹H NMR (400 MHz, Chloroform-d) δ 7.95 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 2H), 7.32 – 7.28 (m, 3H), 7.26 – 7.23 (m, 1H), 7.11 (dd, $J = 7.2, 1.2$ Hz, 1H), 6.74 – 6.69 (m, 4H), 5.76 (dd, $J = 17.2, 10.4$ Hz, 1H), 5.06 (d, $J = 16.4$ Hz, 1H), 5.00 (dd, $J = 10.4, 0.8$ Hz, 1H), 4.85 – 4.78 (m, 2H), 2.48 (s, 3H), 1.21 (s, 3H), 1.16 (s, 3H).

¹³C NMR (100 MHz, Chloroform-d) δ 167.5, 145.0, 141.8, 135.6, 135.0, 133.8, 132.6, 132.2, 130.8, 130.3, 129.12, 129.06, 128.3, 127.7, 126.6, 125.4, 115.1, 71.5, 48.9, 47.6, 24.4, 23.6, 21.7.

HRMS (ESI-TOF) calcd for $C_{27}H_{26}ClNNaO_3S_2^+$ ($[M+Na]^+$): 534.0935; found: 534.0938.

IR (film): 2926, 1693, 1475, 1385, 1359, 1259, 1281, 1188, 1171, 1120, 1091, 1013, 916, 825 cm^{-1} .

4-(phenylthio)-4-(propa-1,2-dien-1-yl)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (5a)



Yellow solid; Yield 38% (17 mg); M.p. 140-141 °C

¹H NMR (600 MHz, Chloroform-d) δ 7.95 (d, $J = 8.4$ Hz, 2H), 7.58 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.35 – 7.30 (m, 4H), 7.26 – 7.25 (m, 1H), 7.17 (d, $J = 7.2$ Hz, 1H), 7.06 – 7.04 (m,

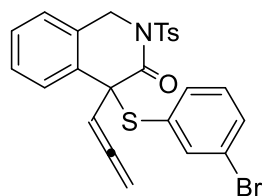
2H), 6.99 – 6.97 (m, 2H), 5.59 (t, $J = 6.6$ Hz, 1H), 5.16 (d, $J = 15.6$ Hz, 1H), 5.07 (dd, $J = 6.6$, 2.4 Hz, 2H), 4.56 (d, $J = 15.6$ Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (150 MHz, Chloroform- d) δ 209.9, 167.4, 145.0, 136.3, 135.4, 133.8, 131.7, 130.2, 129.4, 129.3, 129.2, 128.5, 128.45, 128.42, 128.2, 125.8, 91.9, 80.4, 58.9, 47.9, 21.7.

HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{21}\text{NNaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 470.0855; found: 470.0855.

IR (film): 2988, 2922, 1957, 1697, 1596, 1452, 1384, 1359, 1259, 1187, 1171, 1121, 1088, 938, 855 cm^{-1} .

4-((3-bromophenyl)thio)-4-(propa-1,2-dien-1-yl)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (5b)



Yellow solid; Yield 32% (17 mg); M.p. 146-147 $^{\circ}\text{C}$

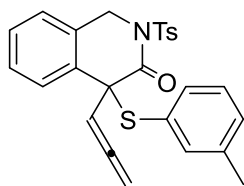
^1H NMR (400 MHz, Chloroform- d) δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.56 – 7.54 (m, 1H), 7.39 – 7.34 (m, 3H), 7.29 – 7.27 (m, 3H), 7.25 – 7.24 (m, 1H), 6.97 – 6.90 (m, 2H), 5.59 (t, $J = 6.8$ Hz, 1H), 5.22 (d, $J = 15.6$ Hz, 1H), 5.13 – 5.04 (m, 2H), 4.76 (d, $J = 16.0$ Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, Chloroform- d) δ 210.0, 166.9, 145.1, 137.8, 135.2, 133.8, 133.3, 132.7, 132.1, 131.7, 129.8, 129.4, 129.0, 128.8, 128.4, 128.3, 126.0, 121.9, 91.5, 80.5, 59.2, 47.9, 21.7.

HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{20}\text{BrNNaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 547.9960; found: 547.9963.

IR (film): 2988, 1957, 1697, 1596, 1557, 1457, 1384, 1360, 1259, 1187, 1172, 1121, 1087, 909, 814 cm^{-1} .

4-(propa-1,2-dien-1-yl)-4-(m-tolylthio)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (5c)



Yellow solid; Yield 34% (16 mg); M.p. 80-81 °C

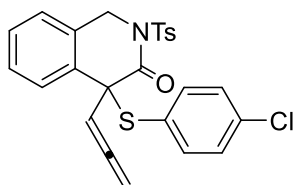
¹H NMR (600 MHz, Chloroform-d) δ 7.93 (d, J = 8.4 Hz, 2H), 7.57 (dd, J = 7.8, 1.2 Hz, 1H), 7.36 – 7.28 (m, 4H), 7.15 (d, J = 7.8 Hz, 1H), 7.09 (d, J = 7.2 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.78 – 6.76 (m, 1H), 5.58 (t, J = 6.6 Hz, 1H), 5.11 – 5.07 (m, 3H), 4.46 (d, J = 15.6 Hz, 1H), 2.43 (s, 3H), 2.20 (s, 3H).

¹³C NMR (150 MHz, Chloroform-d) δ 209.8, 167.5, 144.9, 138.3, 137.2, 135.5, 133.8, 133.3, 131.7, 130.3, 129.7, 129.3, 129.1, 128.5, 128.33, 128.26, 128.1, 125.6, 91.9, 80.3, 58.7, 47.9, 21.7, 21.0.

HRMS (ESI-TOF) calcd for C₂₆H₂₃NNaO₃S₂⁺ ([M+Na]⁺):484.1012; found: 484.1015.

IR (film): 2922, 1957, 1698, 1594, 1453, 1359, 1281, 1259, 1187, 1172, 1122, 1088, 1019, 939, 852 cm⁻¹.

4-((4-chlorophenyl)thio)-4-(propa-1,2-dien-1-yl)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (5d)



Yellow solid; Yield 36% (17 mg); M.p. 131-132 °C

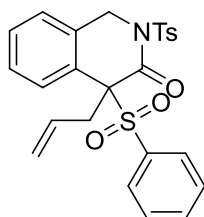
¹H NMR (400 MHz, Chloroform-d) δ 7.93 (d, J = 8.4 Hz, 2H), 7.58 – 7.56 (m, 1H), 7.37 – 7.35 (m, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.25 – 7.24 (m, 1H), 7.01 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 5.59 (t, J = 6.8 Hz, 1H), 5.26 (d, J = 15.6 Hz, 1H), 5.13 – 5.03 (m, 2H), 4.81 (d, J = 15.6 Hz, 1H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, Chloroform- d) δ 210.0, 166.9, 145.3, 136.9, 135.7, 135.2, 133.5, 131.7, 129.3, 129.2, 128.8, 128.72, 128.69, 128.4, 128.3, 126.0, 91.6, 80.5, 59.2, 47.8, 21.8.

HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{20}\text{ClNNaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 504.0465; found: 504.0468.

IR (film): 2924, 1958, 1696, 1596, 1572, 1475, 1360, 1261, 1187, 1171, 1121, 1091, 1013, 938, 816 cm^{-1} .

4-allyl-4-(phenylsulfonyl)-2-tosyl-1,4-dihydroisoquinolin-3(2H)-one (6a)



White solid; Yield 52% (25 mg); M.p. 236-237 $^{\circ}\text{C}$.

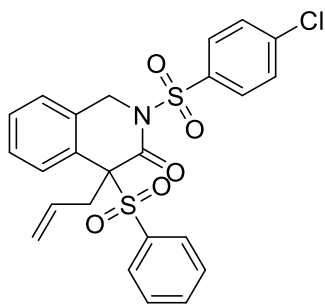
^1H NMR (600 MHz, Chloroform- d) δ 8.00 (d, $J = 8.4$ Hz, 2H), 7.61 (t, $J = 7.8$ Hz, 1H), 7.48 – 7.45 (m, 2H), 7.43 – 7.41 (m, 3H), 7.32 – 7.29 (m, 3H), 7.16 (d, $J = 7.8$ Hz, 2H), 5.29 (d, $J = 15.0$ Hz, 1H), 5.18 – 5.11 (m, 1H), 4.97 (dd, $J = 16.8, 1.2$ Hz, 1H), 4.91 (d, $J = 15.0$ Hz, 1H), 4.87 (dd, $J = 10.2, 1.2$ Hz, 1H), 3.10 (d, $J = 6.6$ Hz, 2H), 2.52 (s, 3H).

^{13}C NMR (150 MHz, Chloroform- d) δ 163.2, 145.3, 135.2, 134.7, 134.4, 133.8, 130.8, 130.5, 129.8, 129.7, 129.5, 129.3, 128.5, 127.8, 126.4, 124.4, 120.8, 76.6, 48.9, 35.0, 21.8.

HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{23}\text{NNaO}_5\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 504.0910; found: 504.0910.

IR (film): 2923, 2856, 1688, 1397, 1362, 1306, 1189, 1174, 1146, 1080, 931 cm^{-1} .

4-allyl-2-((4-chlorophenyl)sulfonyl)-4-(phenylsulfonyl)-1,4-dihydroisoquinolin-3(2H)-one (6b)



White solid; Yield 58% (29 mg); M.p. 209-210 °C.

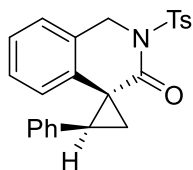
¹H NMR (600 MHz, Chloroform-d) δ 8.06 (d, J = 8.4 Hz, 2H), 7.65 – 7.63 (m, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.38 – 7.32 (m, 3H), 7.19 (d, J = 7.8 Hz, 2H), 5.28 (d, J = 15.0 Hz, 1H), 5.18 – 5.11 (m, 1H), 4.98 – 4.94 (m, 2H), 4.89 (d, J = 10.2 Hz, 1H), 3.13 – 3.07 (m, 2H).

¹³C NMR (150 MHz, Chloroform-d) δ 163.5, 140.9, 136.4, 134.62, 134.61, 133.5, 131.0, 130.8, 130.4, 129.8, 129.6, 129.0, 128.7, 128.0, 126.4, 124.3, 121.0, 76.7, 49.0, 35.0.

HRMS (ESI-TOF) calcd for C₂₄H₂₀CINNaO₅S₂⁺ ([M+Na]⁺): 524.0364; found: 524.0367.

IR (film): 3094, 2927, 1688, 1583, 1476, 1447, 1397, 1371, 1308, 1183, 1145, 1115, 1082, 1047, 1014, 932, 826 cm⁻¹.

(1R,2S)-2-phenyl-2'-tosyl-1',2'-dihydro-3'H-spiro[cyclopropane-1,4'-isoquinolin]-3'-one (7)



White solid; Yield 45% (18 mg); M.p. 157-158 °C.

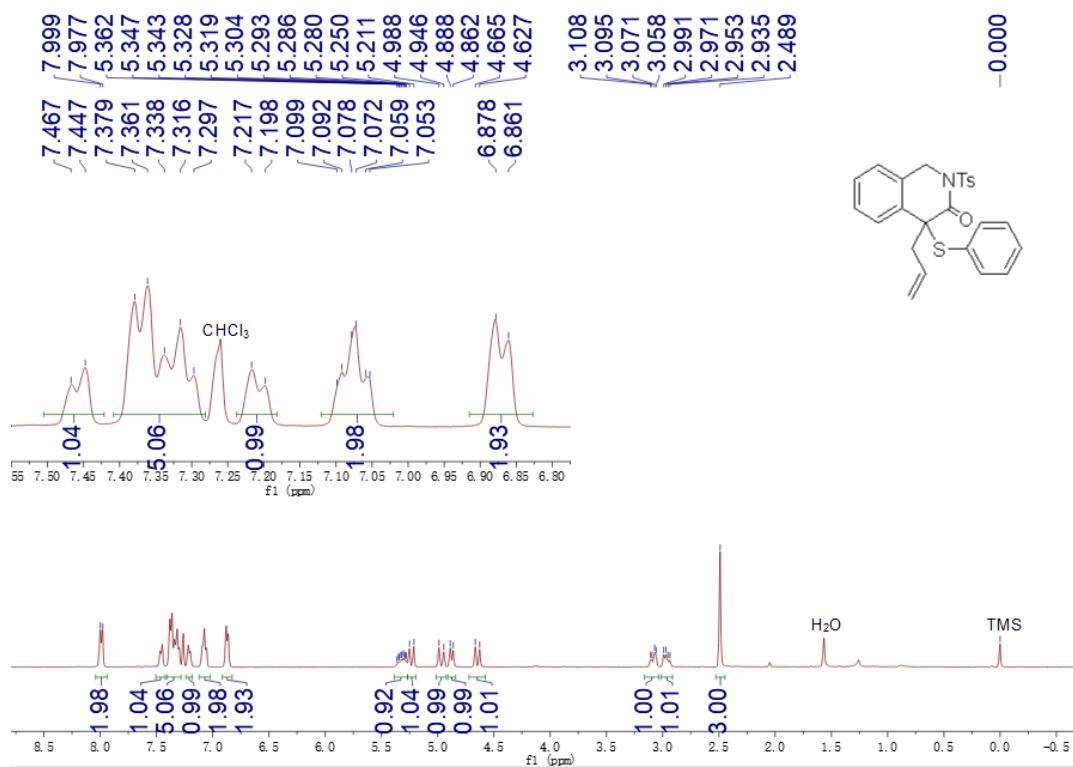
¹H NMR (400 MHz, Chloroform-d) δ 7.92 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.6 Hz, 1H), 7.10 – 7.00 (m, 5H), 6.93 – 6.90 (m, 2H), 6.66 (d, J = 8.0 Hz, 1H), 5.41 (d, J = 14.8 Hz, 1H), 4.71 (d, J = 14.4 Hz, 1H), 2.85 (dd, J = 9.2, 7.2 Hz, 1H), 2.41 (s, 3H), 2.39 – 2.37 (m, 1H), 2.08 (dd, J = 7.2, 5.6 Hz, 1H).

¹³C NMR (100 MHz, Chloroform-d) δ 171.0, 144.8, 135.7, 134.3, 132.9, 130.9, 129.4, 129.0, 128.4, 128.0, 127.4, 127.0, 126.7, 125.6, 125.1, 47.8, 37.7, 36.2, 21.6, 14.0.

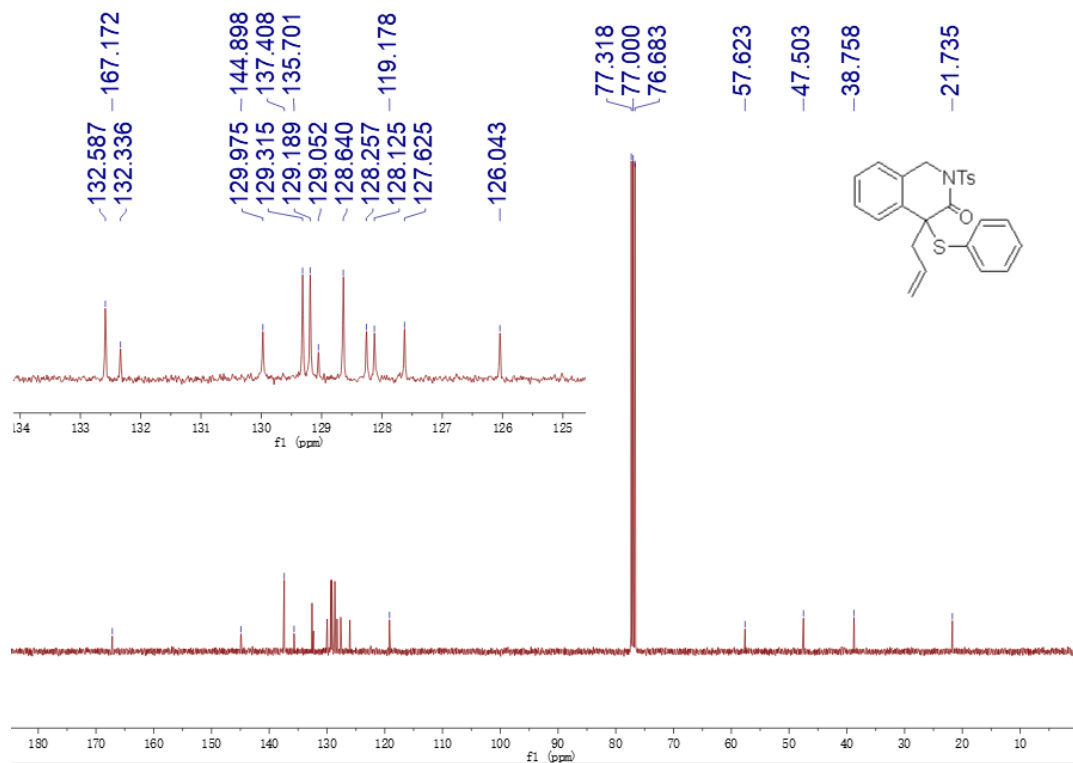
HRMS (ESI-TOF) calcd for C₂₄H₂₁NNaO₃S⁺ ([M+Na]⁺): 426.1134; found: 426.1136.

IR (film): 2955, 2924, 2851, 1689, 1459, 1379, 1260, 1172, 1117, 1087, 817 cm⁻¹.

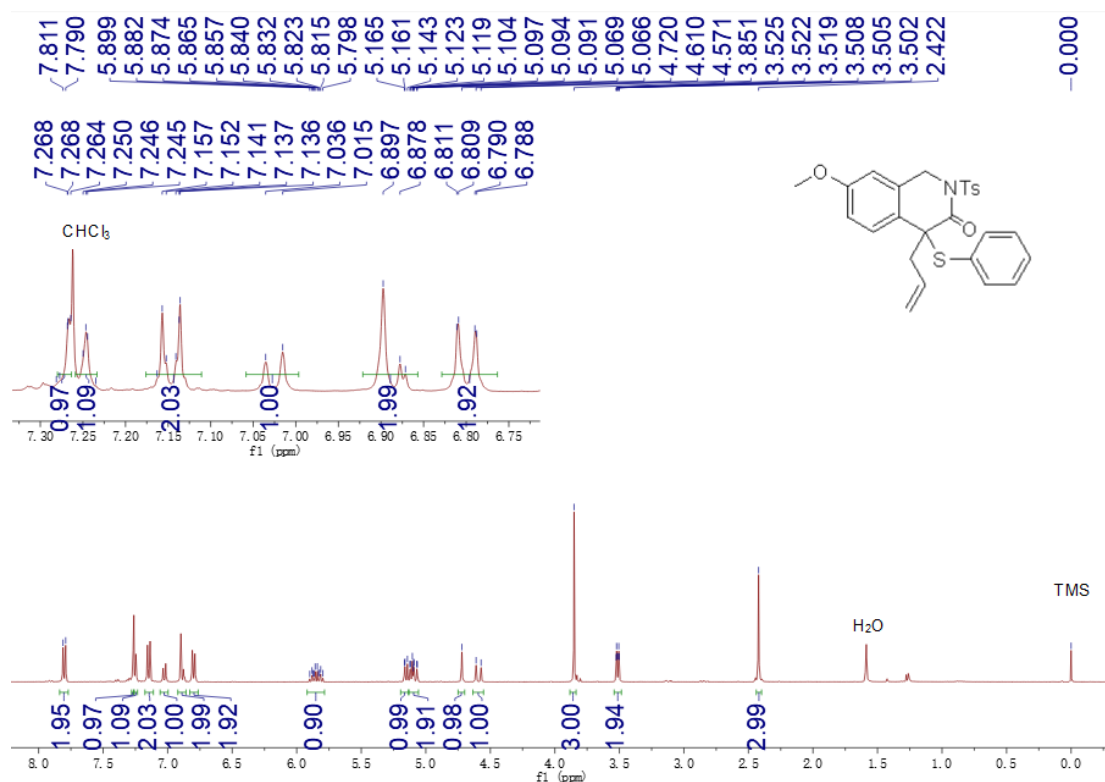
Copies of NMR Spectra



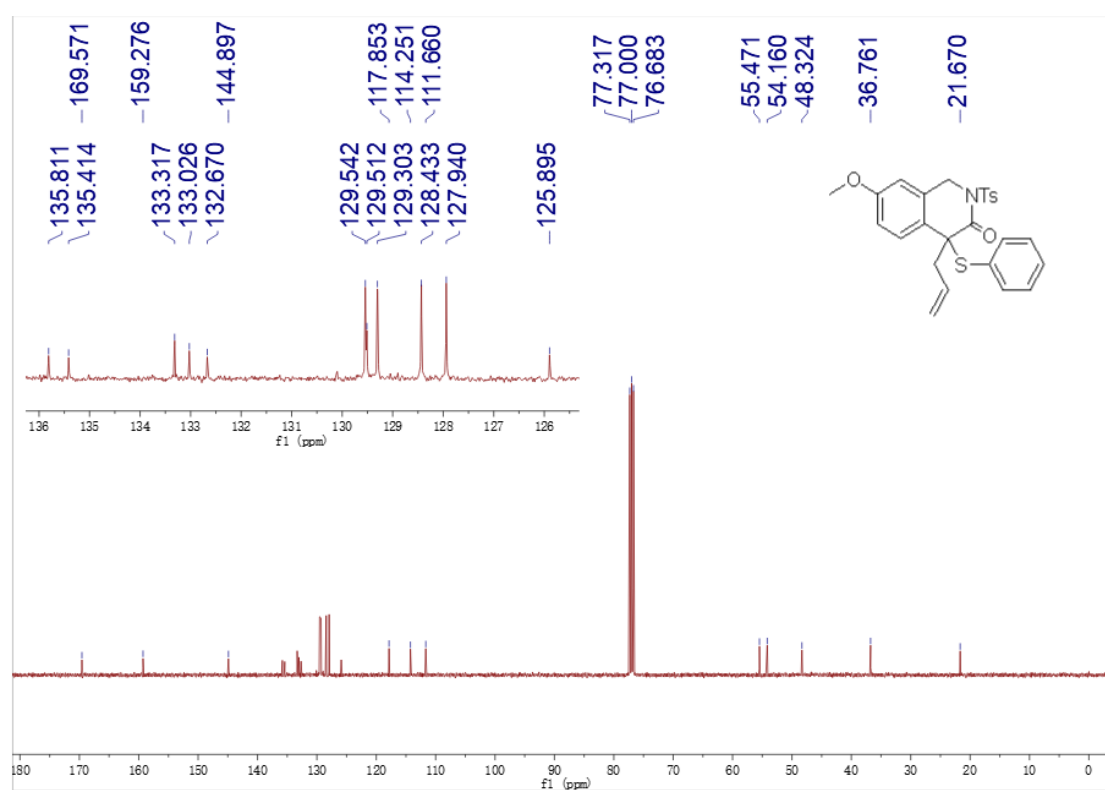
¹H NMR of 3a (CDCl₃, 400 MHz)



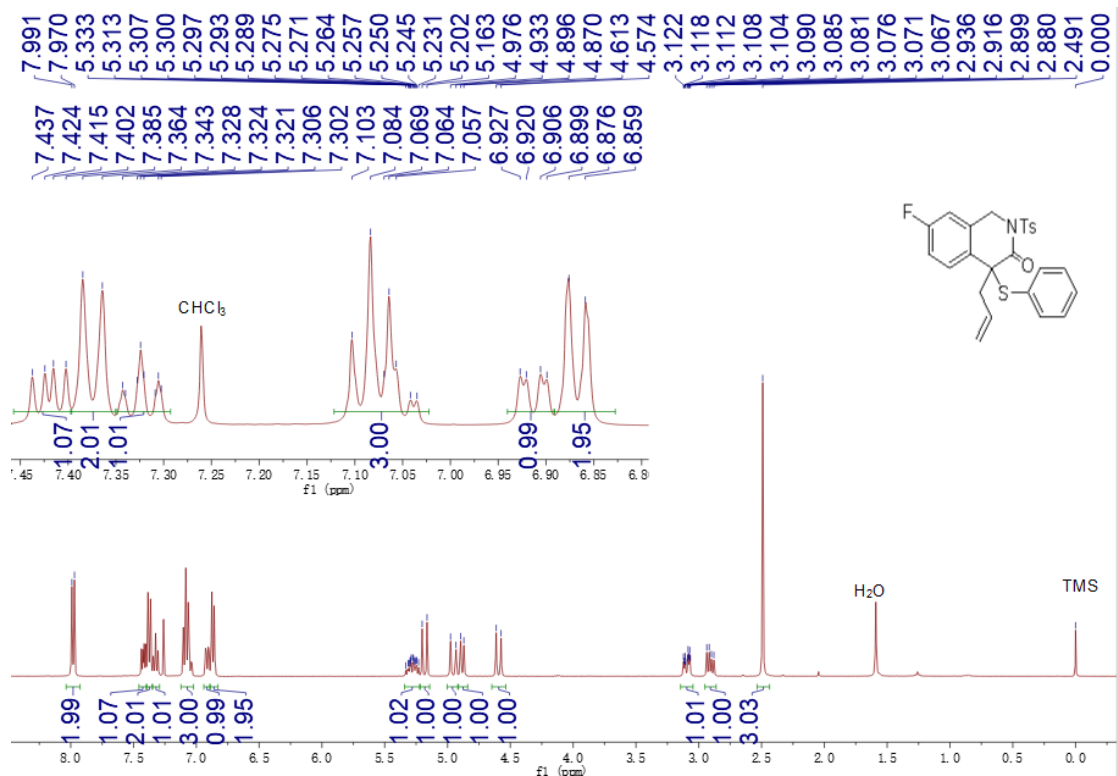
¹³C{¹H} NMR of 3a (CDCl₃, 100 MHz)



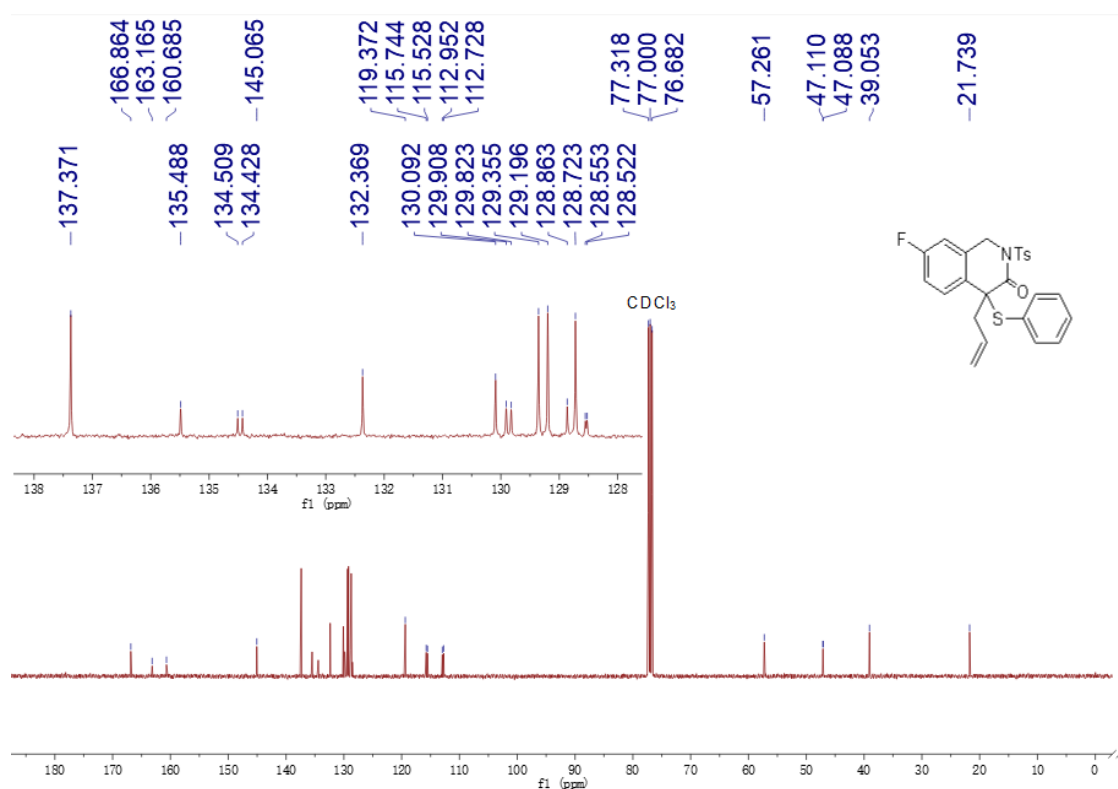
¹H NMR of **3b** (CDCl₃, 400 MHz)



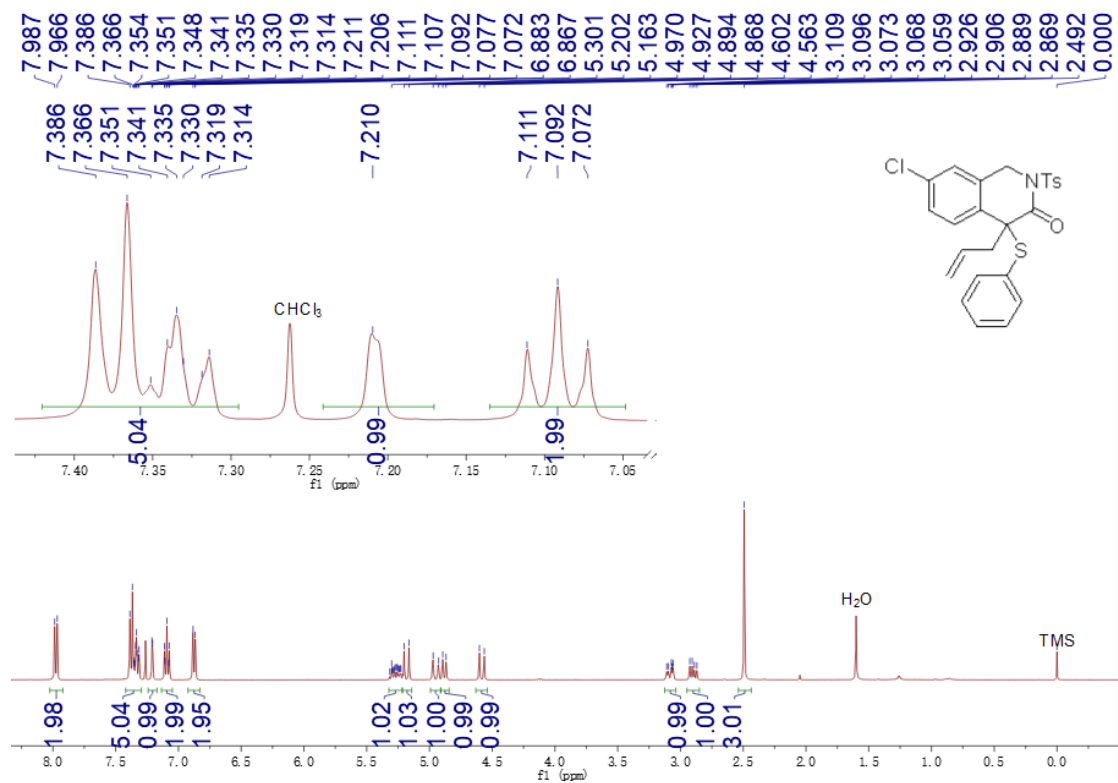
¹³C{¹H} NMR of **3b** (CDCl₃, 100 MHz)



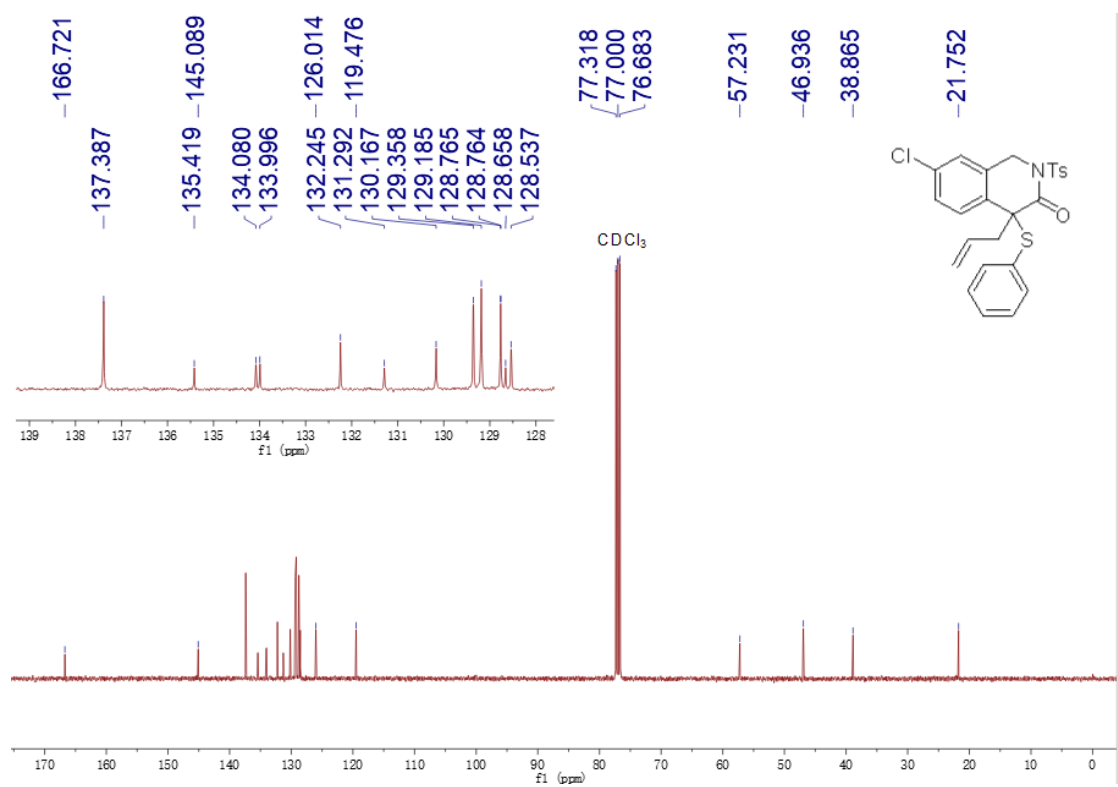
¹H NMR of **3c** (CDCl₃, 400 MHz)



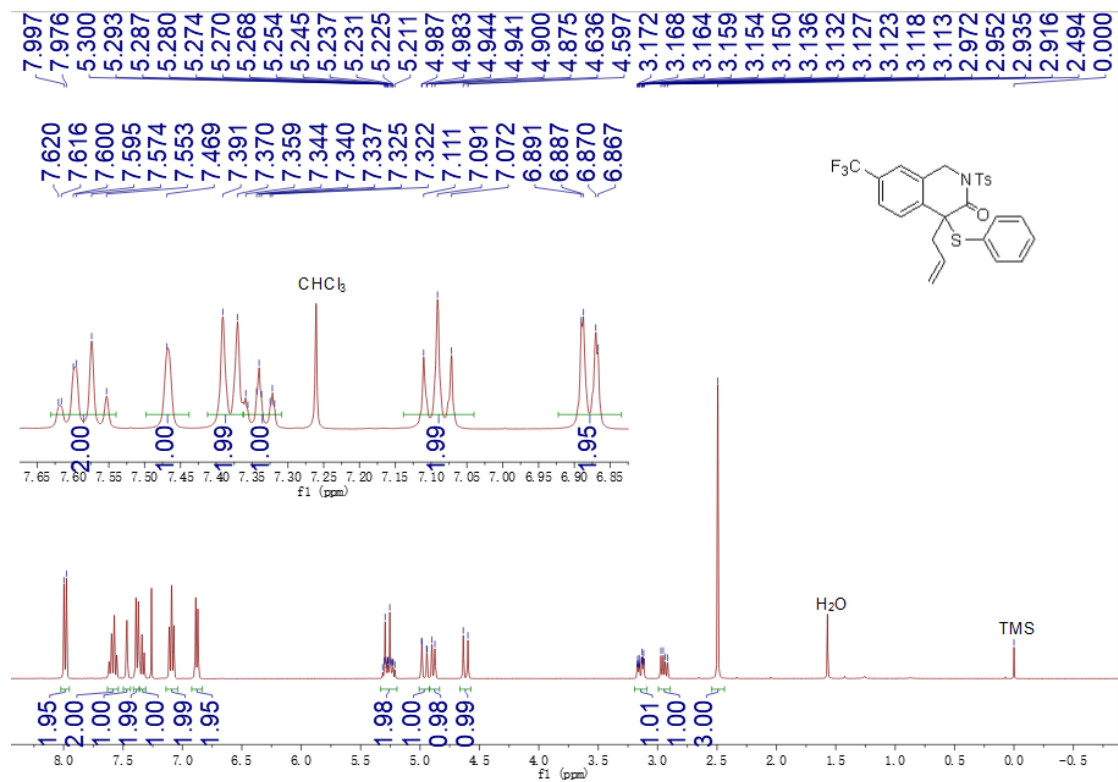
¹³C{¹H} NMR of **3c** (CDCl₃, 100 MHz)



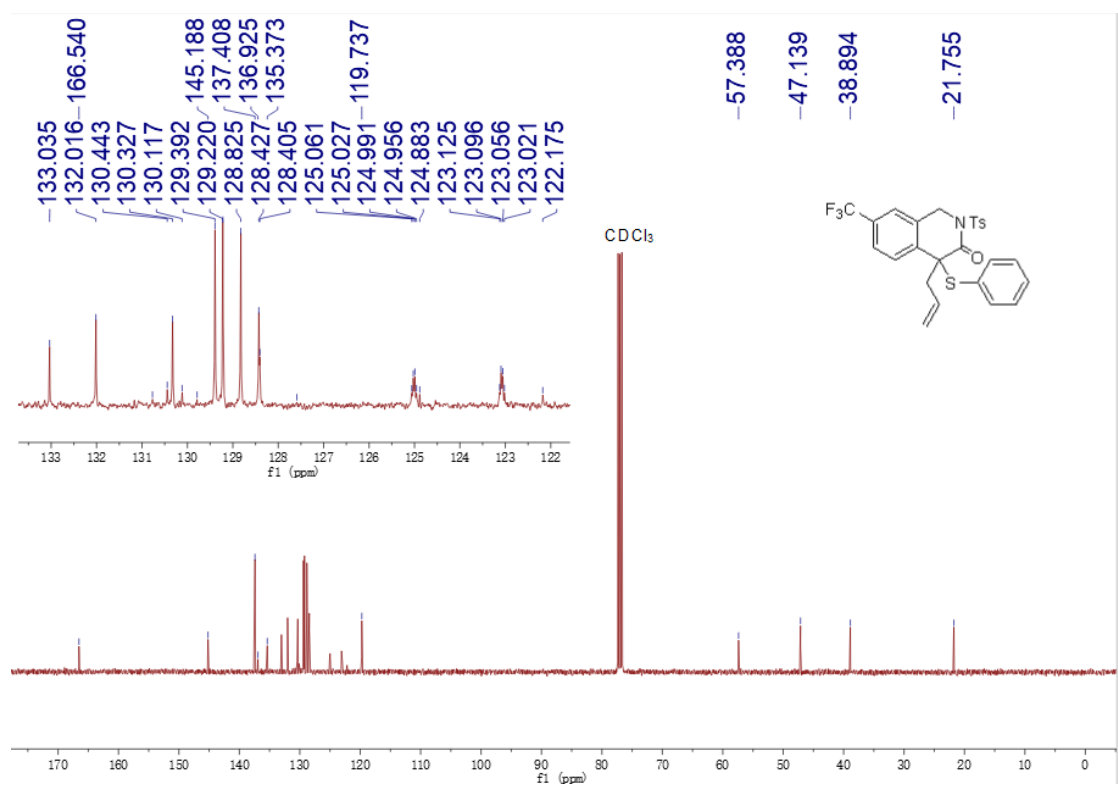
$^1\text{H NMR}$ of **3d** (CDCl_3 , 400 MHz)



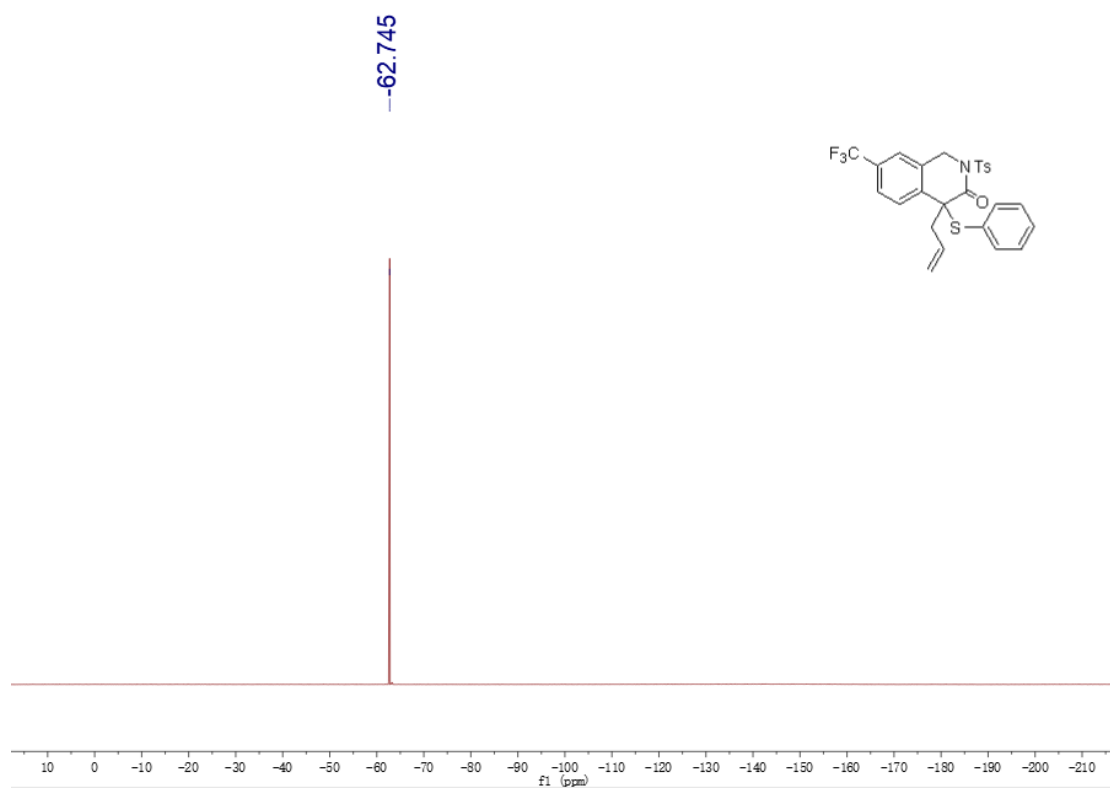
$^{13}\text{C}\{^1\text{H}\}$ NMR of **3d** (CDCl_3 , 100 MHz)



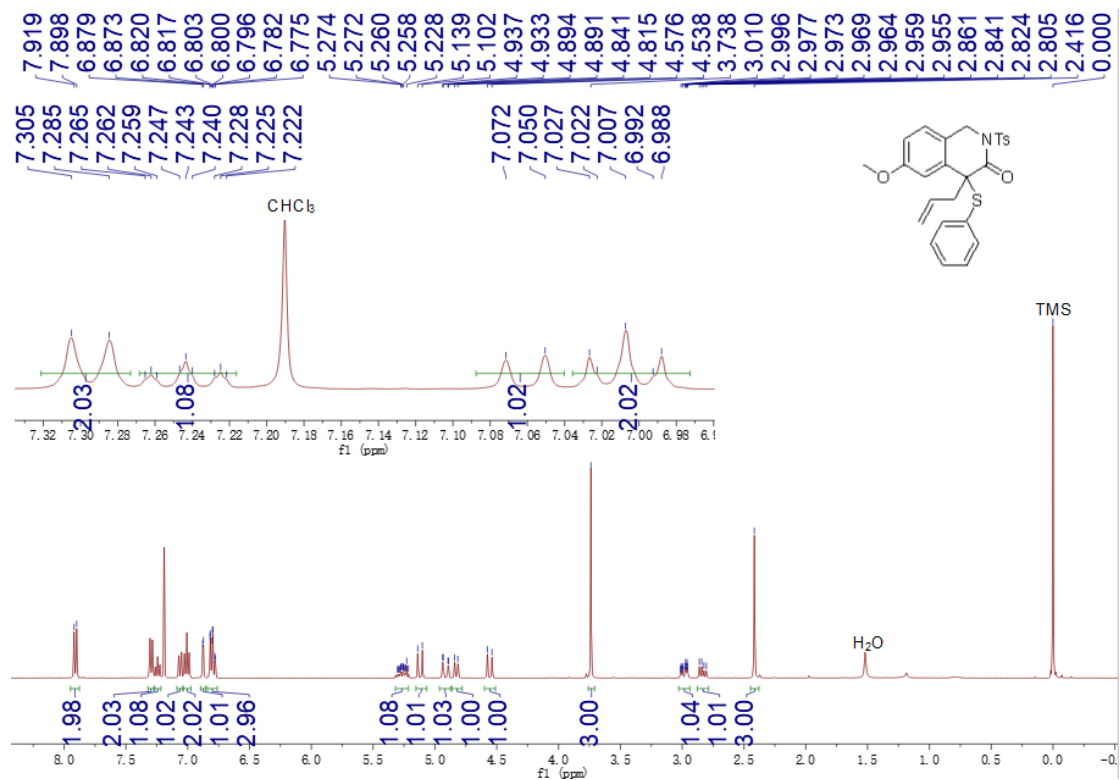
¹H NMR of **3e** (CDCl₃, 400 MHz)



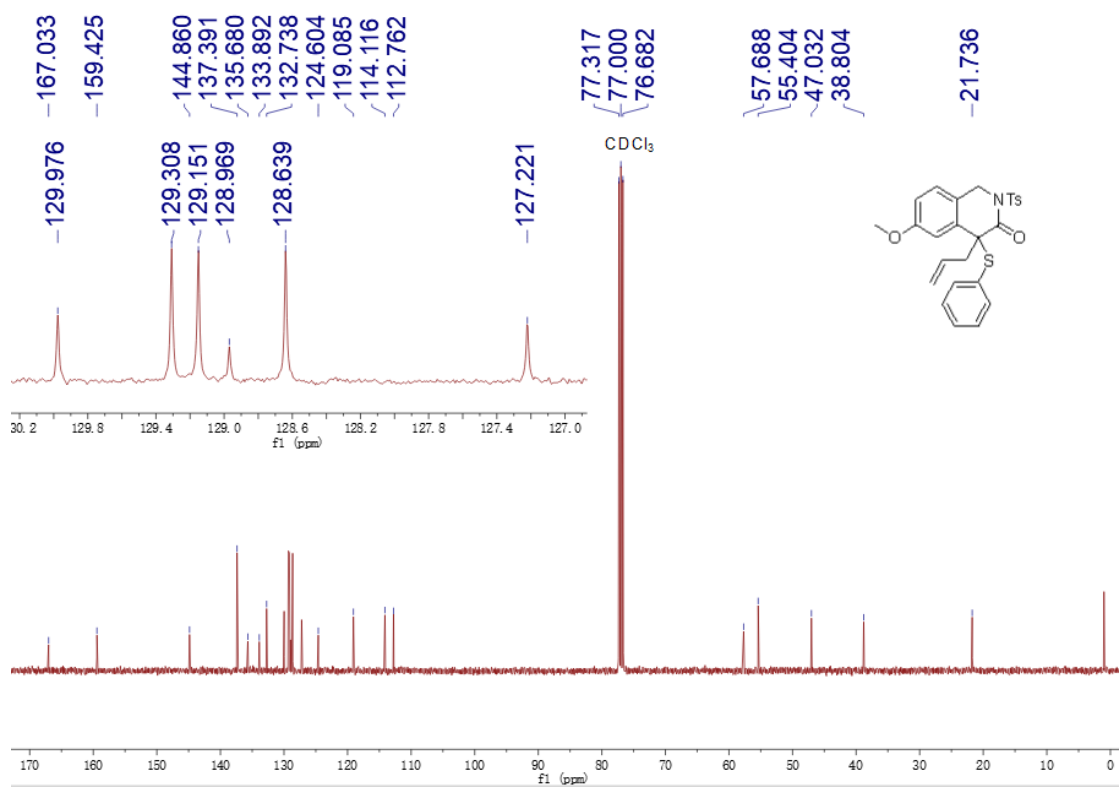
¹³C{¹H} NMR of **3e** (CDCl₃, 100 MHz)



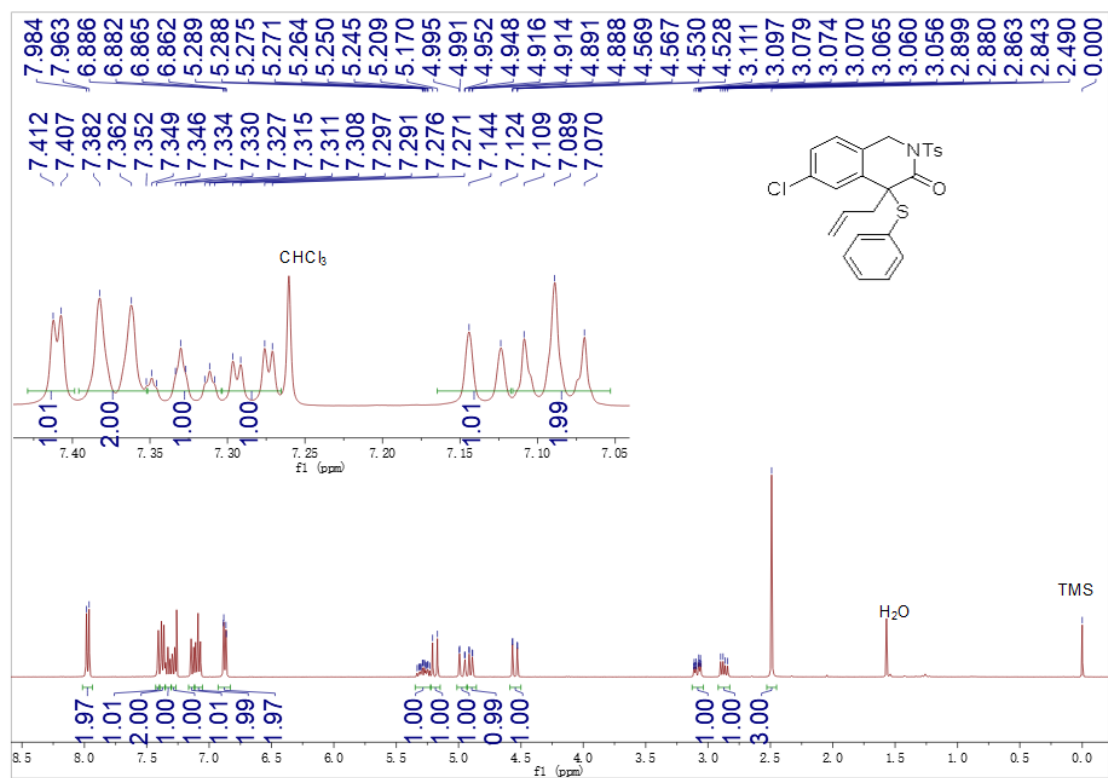
^{19}F NMR of **3e** (CDCl_3 , 376 MHz)



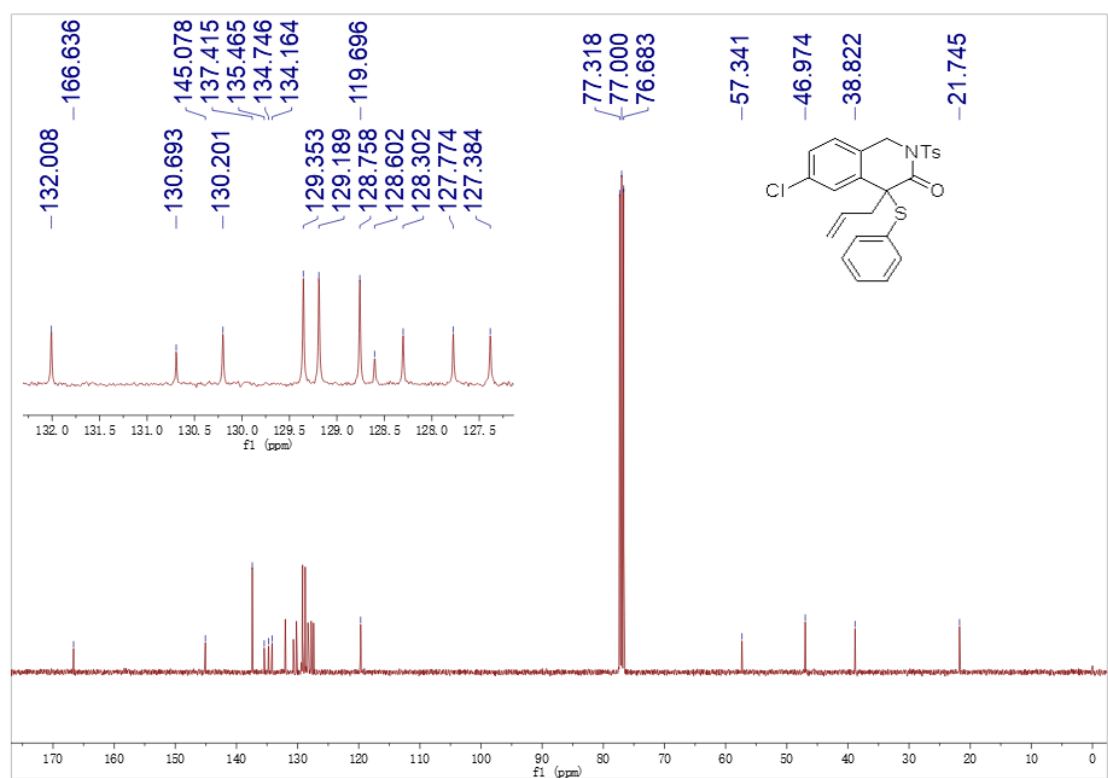
¹H NMR of **3f** (CDCl₃, 400 MHz)



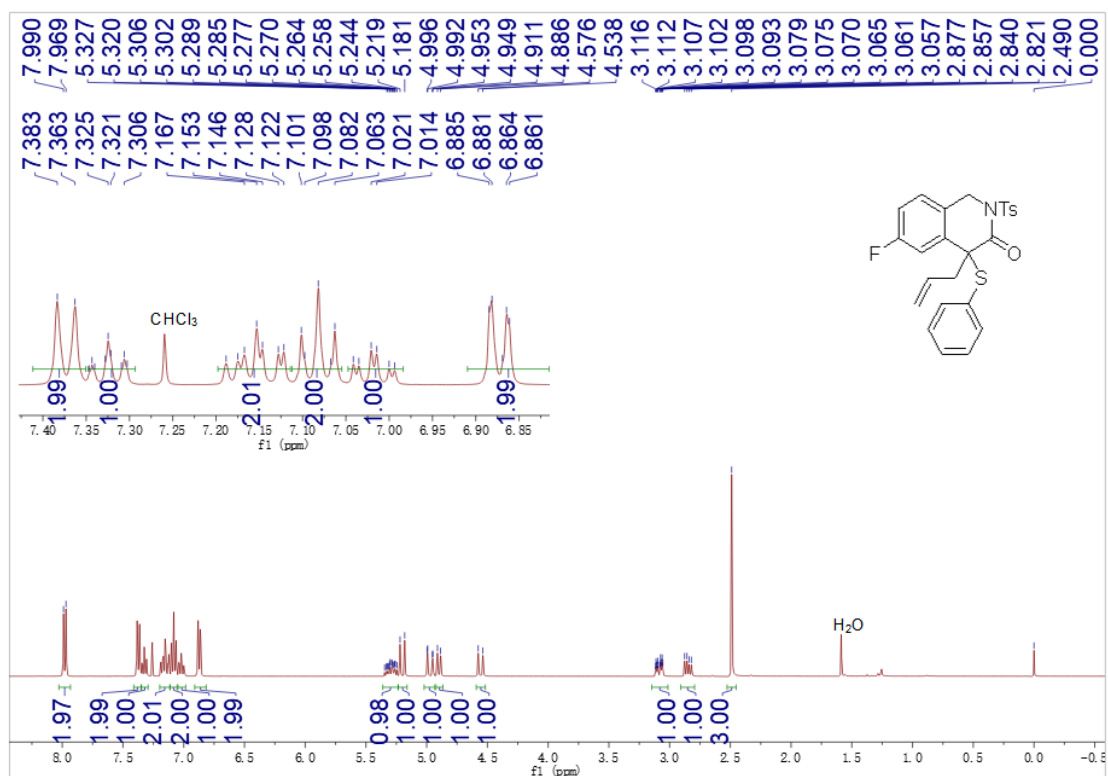
¹³C{¹H} NMR of **3f** (CDCl₃, 100 MHz)



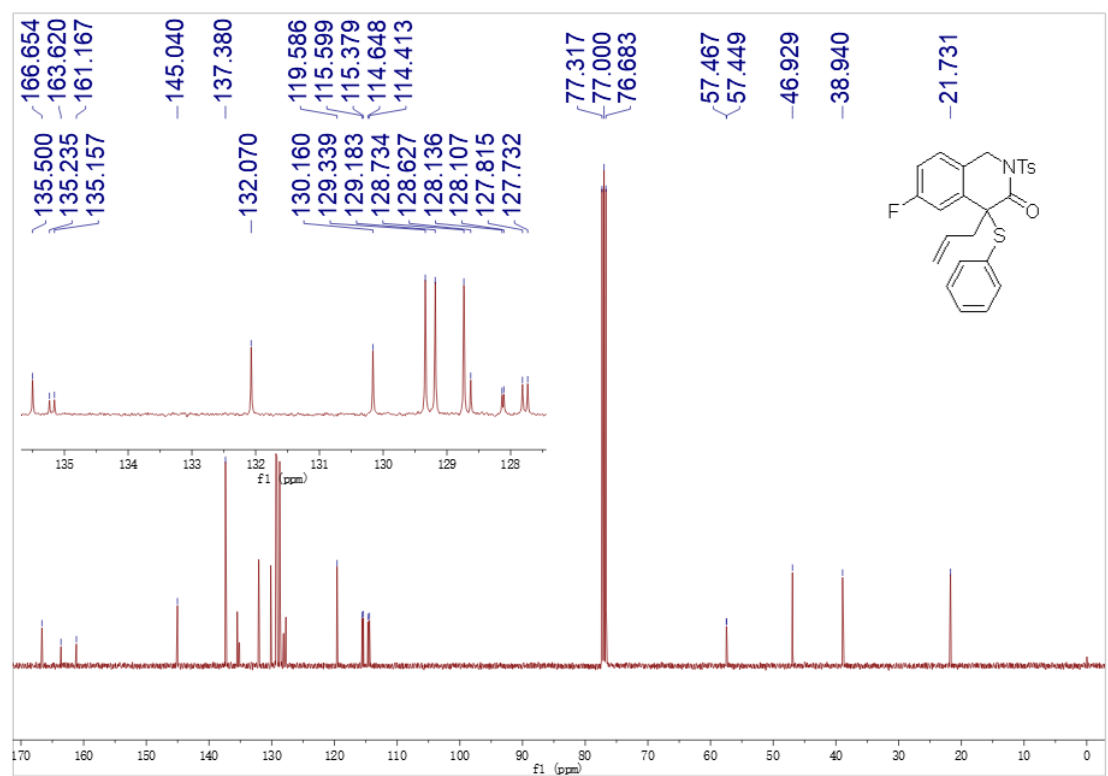
¹H NMR of **3g** (CDCl₃, 400 MHz)



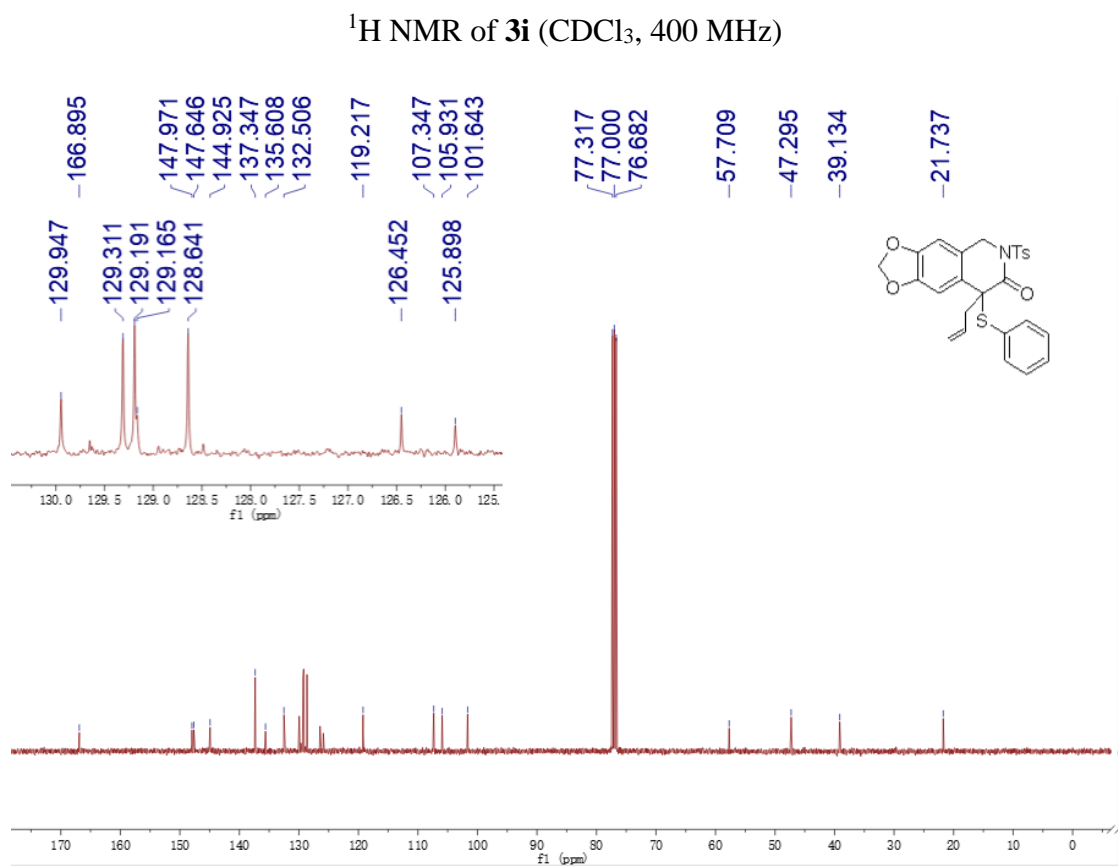
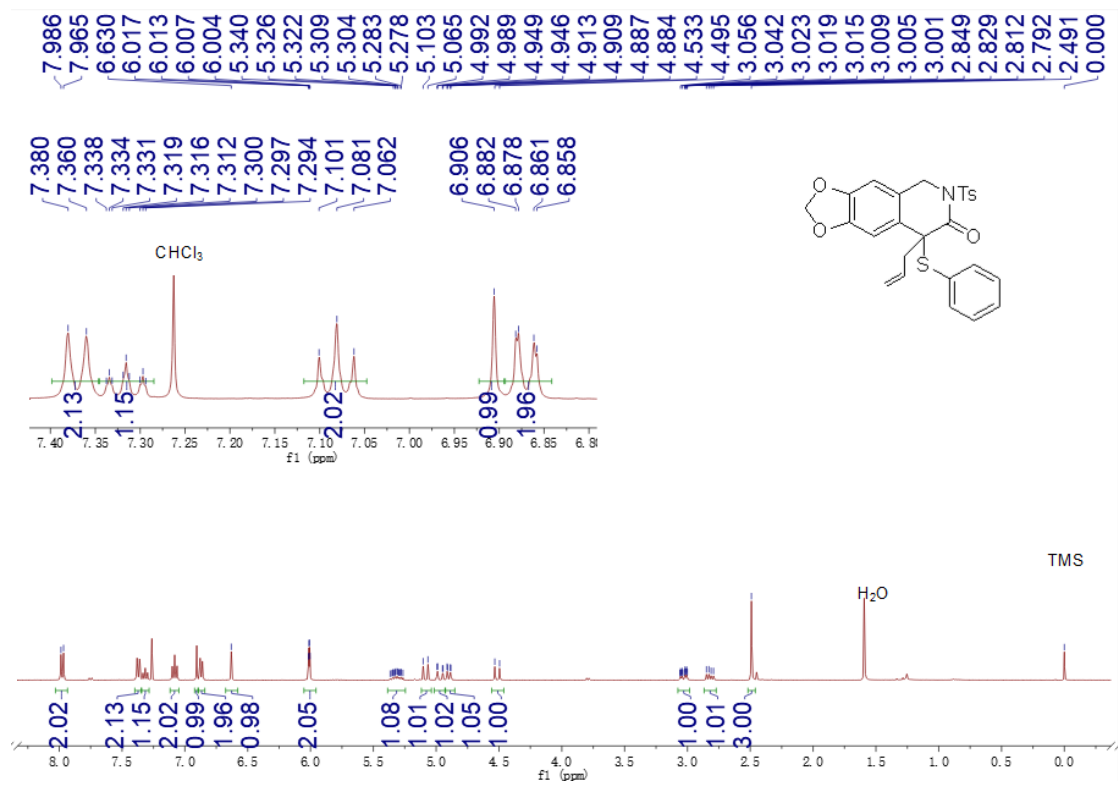
¹³C{¹H} NMR of **3g** (CDCl₃, 100 MHz)

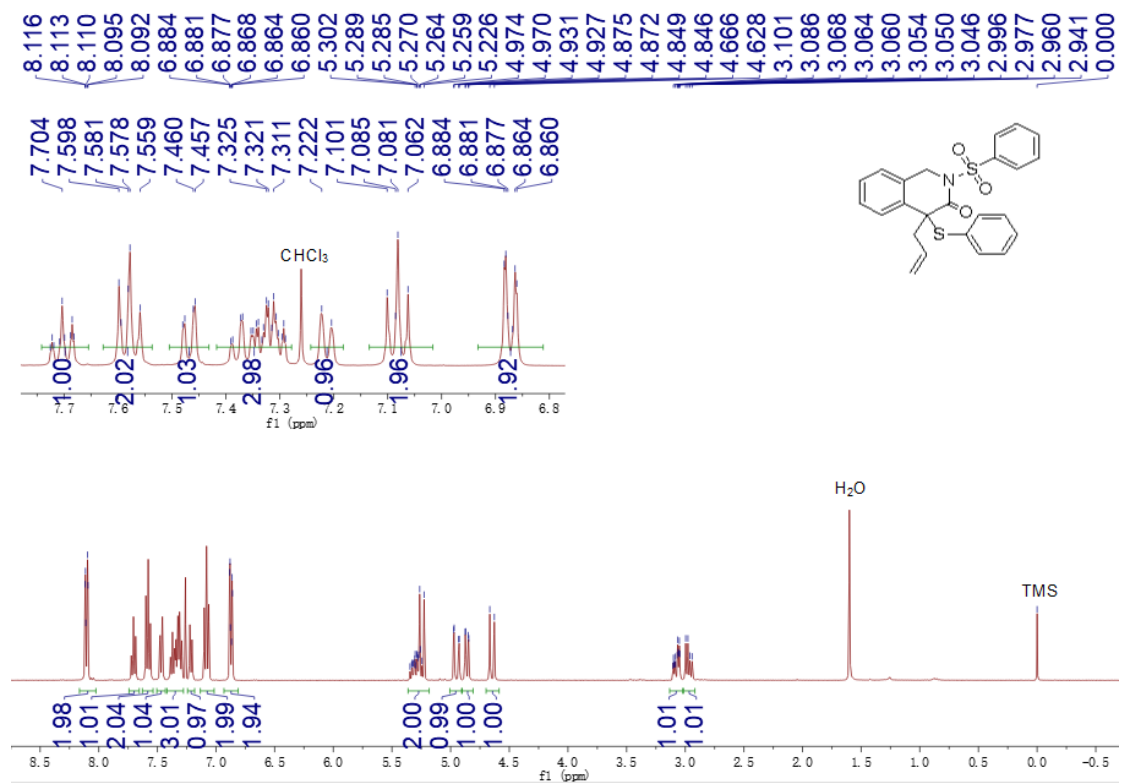


¹H NMR of **3h** (CDCl₃, 400 MHz)

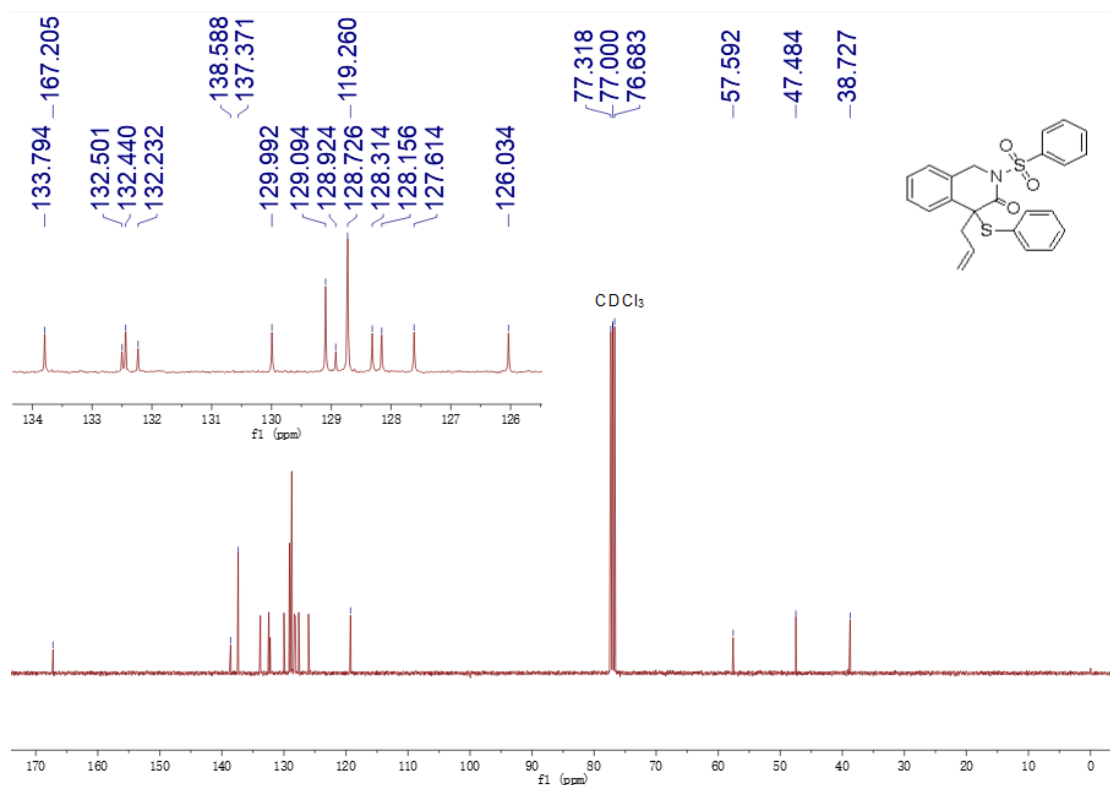


¹³C{¹H} NMR of **3h** (CDCl₃, 100 MHz)

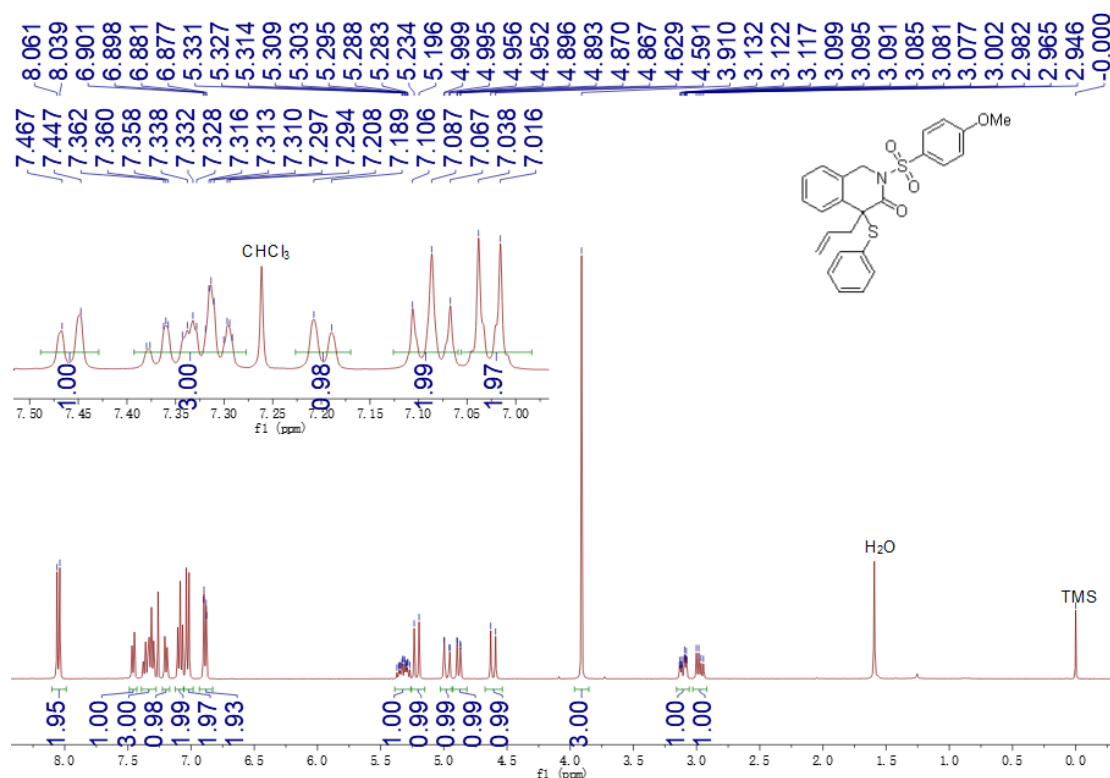




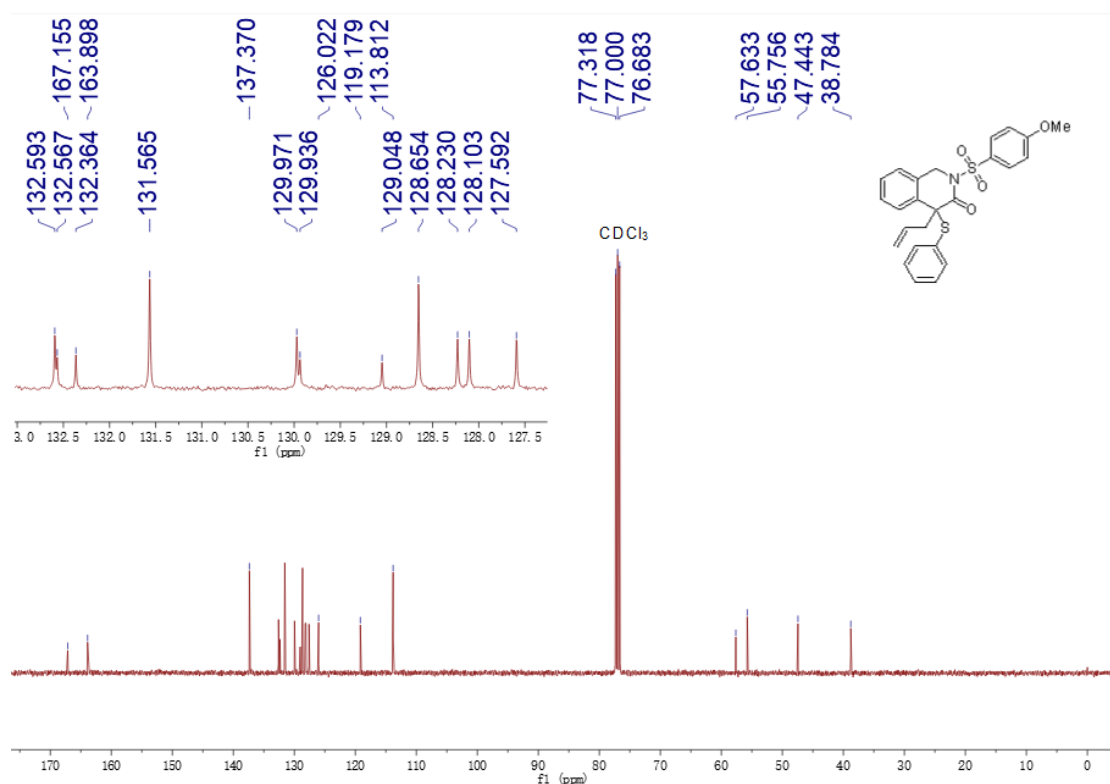
¹H NMR of **3j** (CDCl₃, 400 MHz)



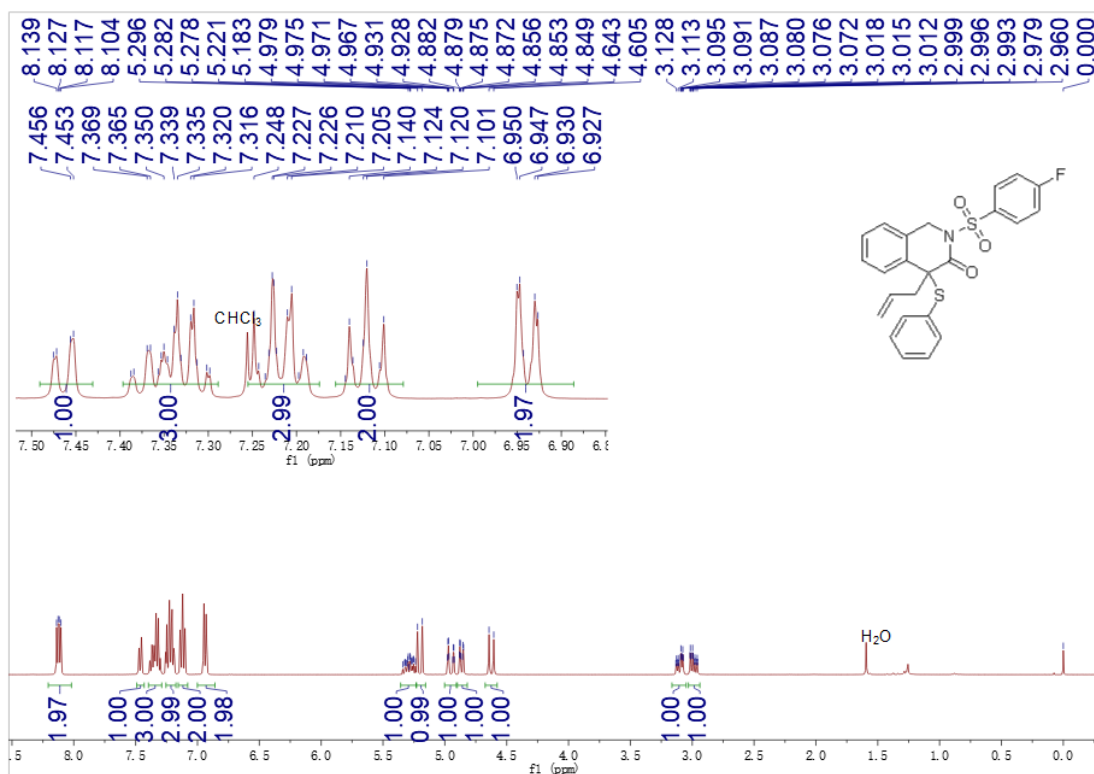
¹³C{¹H} NMR of **3j** (CDCl₃, 100 MHz)



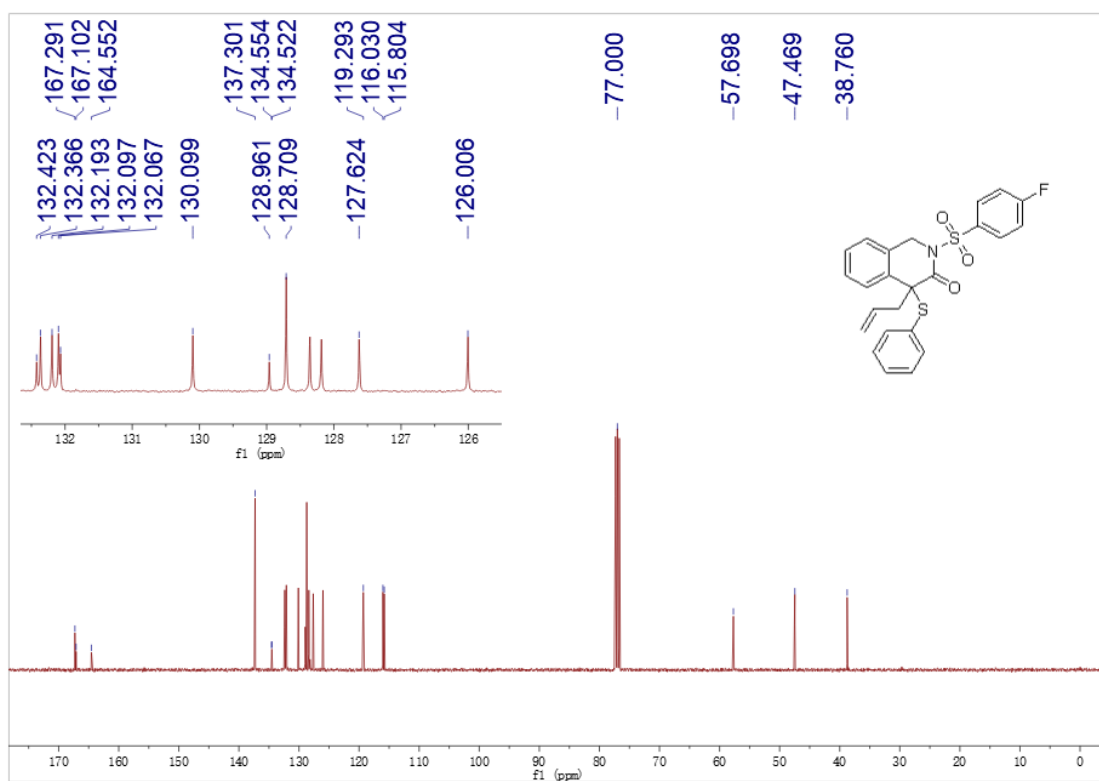
¹H NMR of **3k** (CDCl₃, 400 MHz)



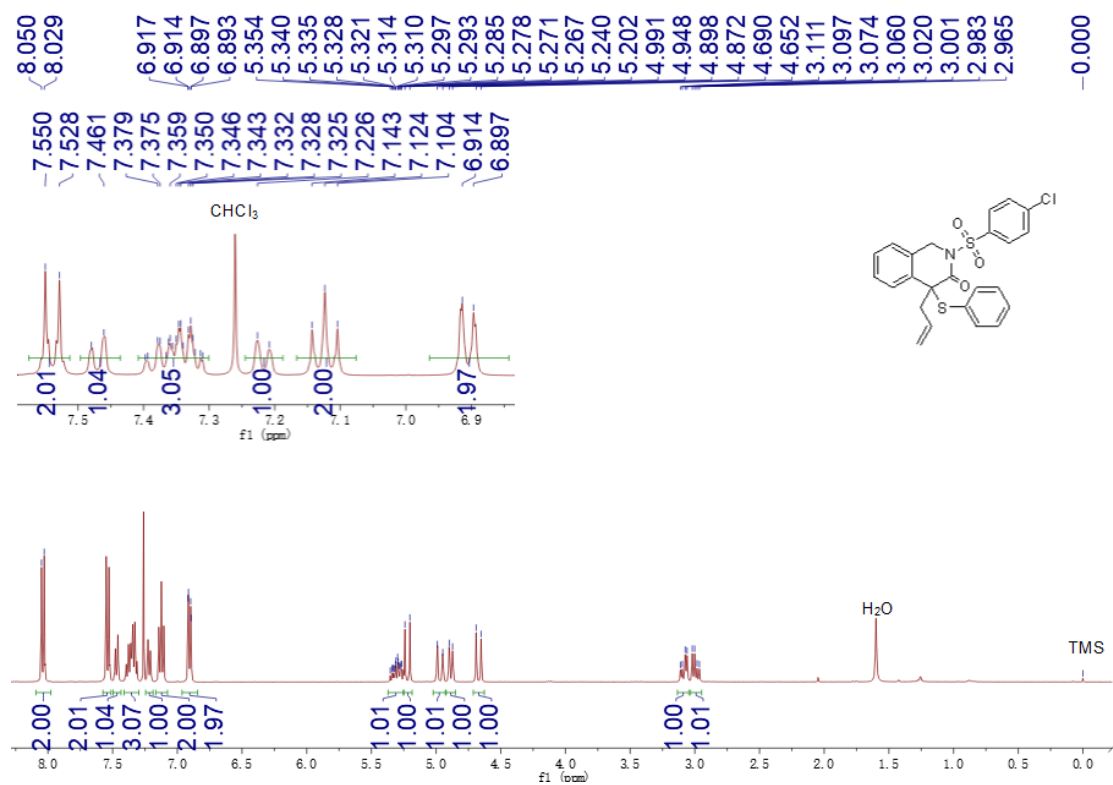
¹³C{¹H} NMR of **3k** (CDCl₃, 100 MHz)



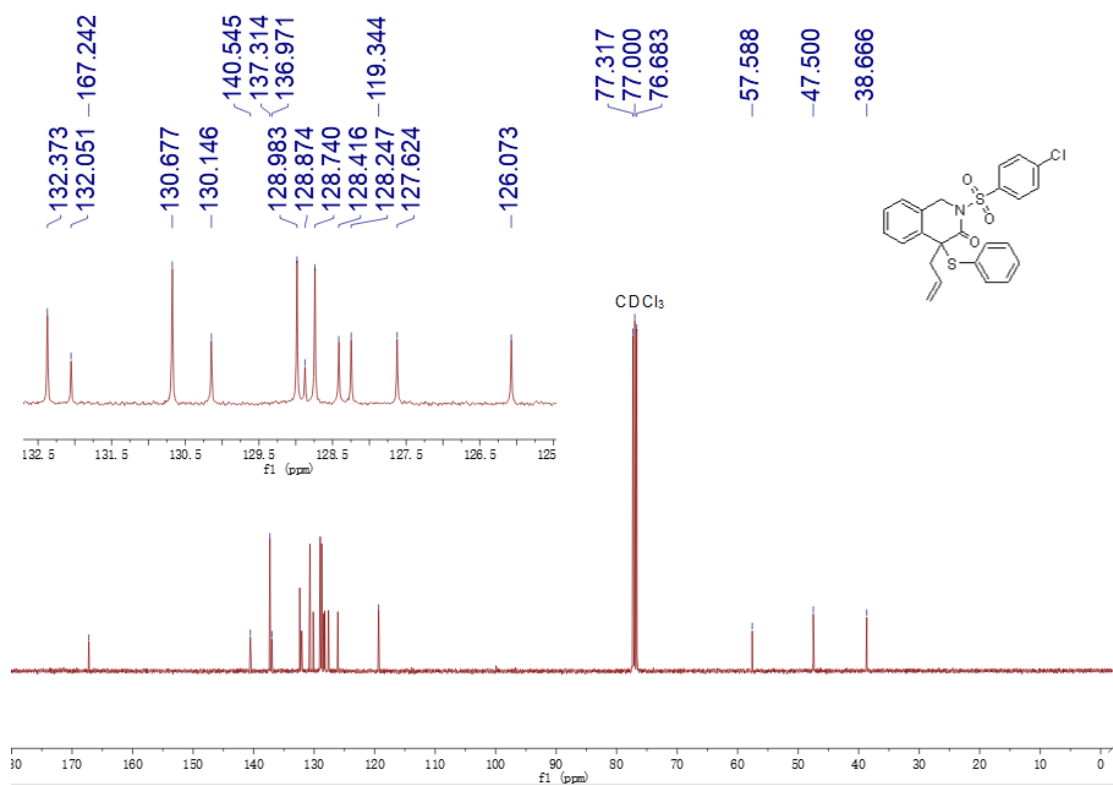
¹H NMR of **3l** (CDCl₃, 400 MHz)



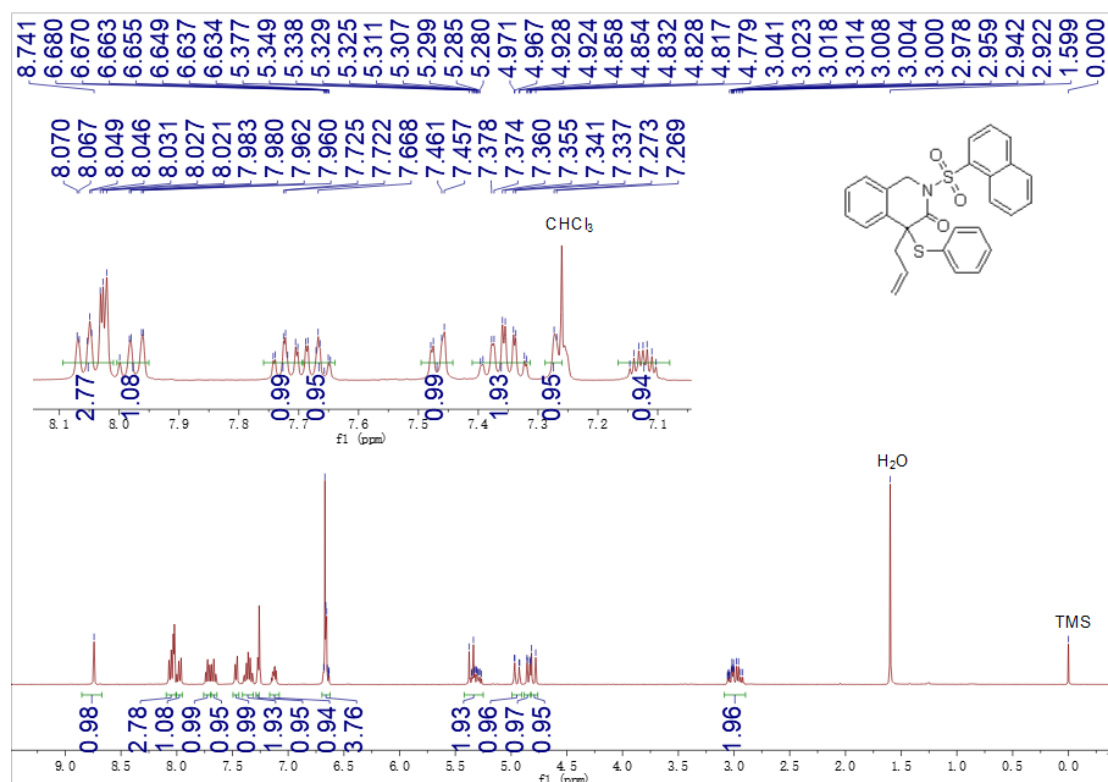
¹³C{¹H} NMR of **3l** (CDCl₃, 100 MHz)



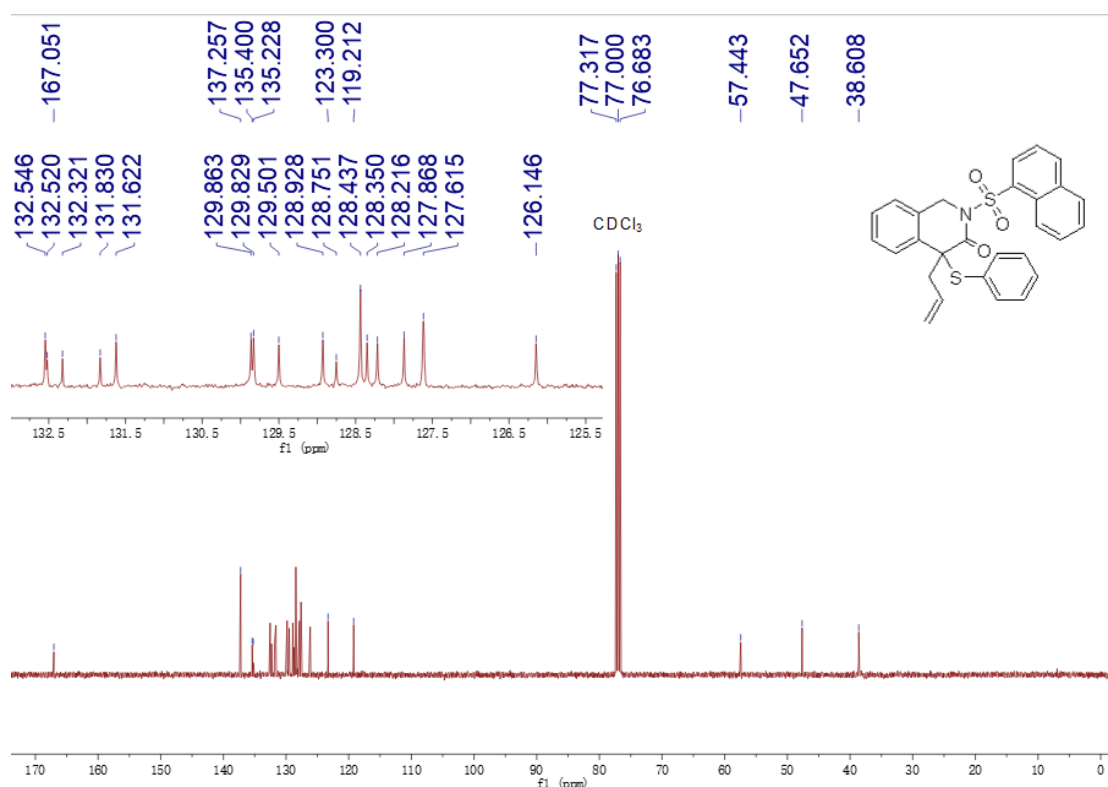
¹H NMR of **3m** (CDCl₃, 400 MHz)



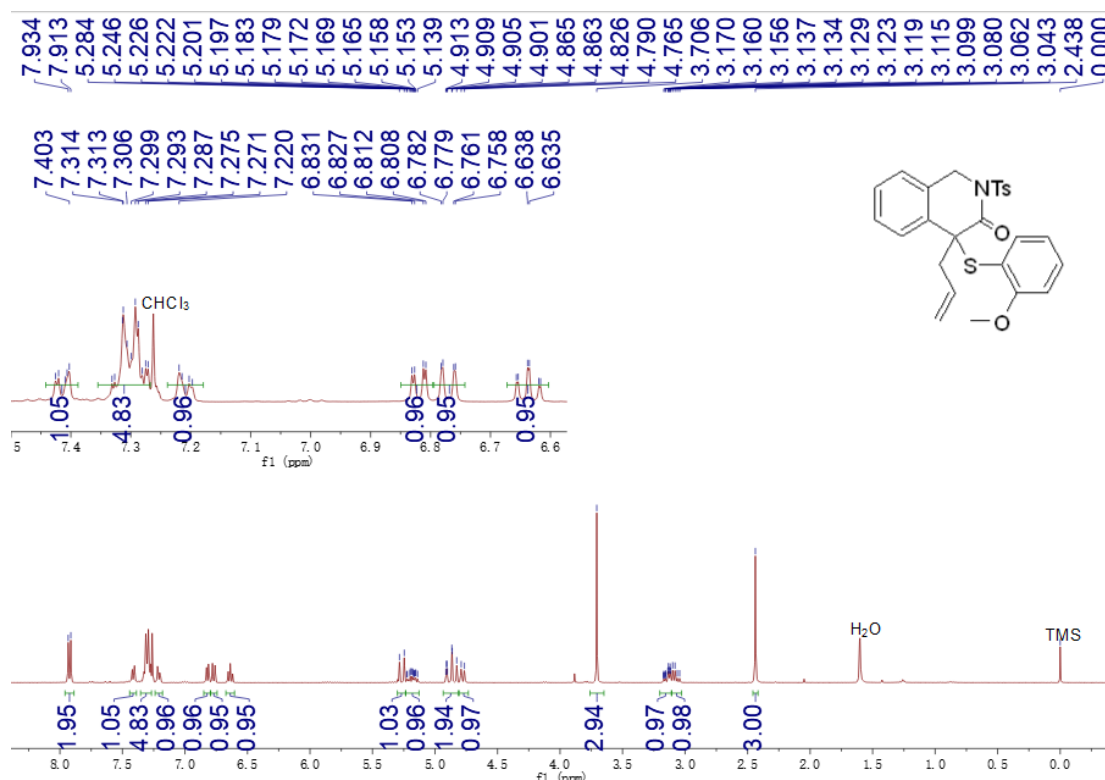
¹³C{¹H} NMR of **3m** (CDCl₃, 100 MHz)



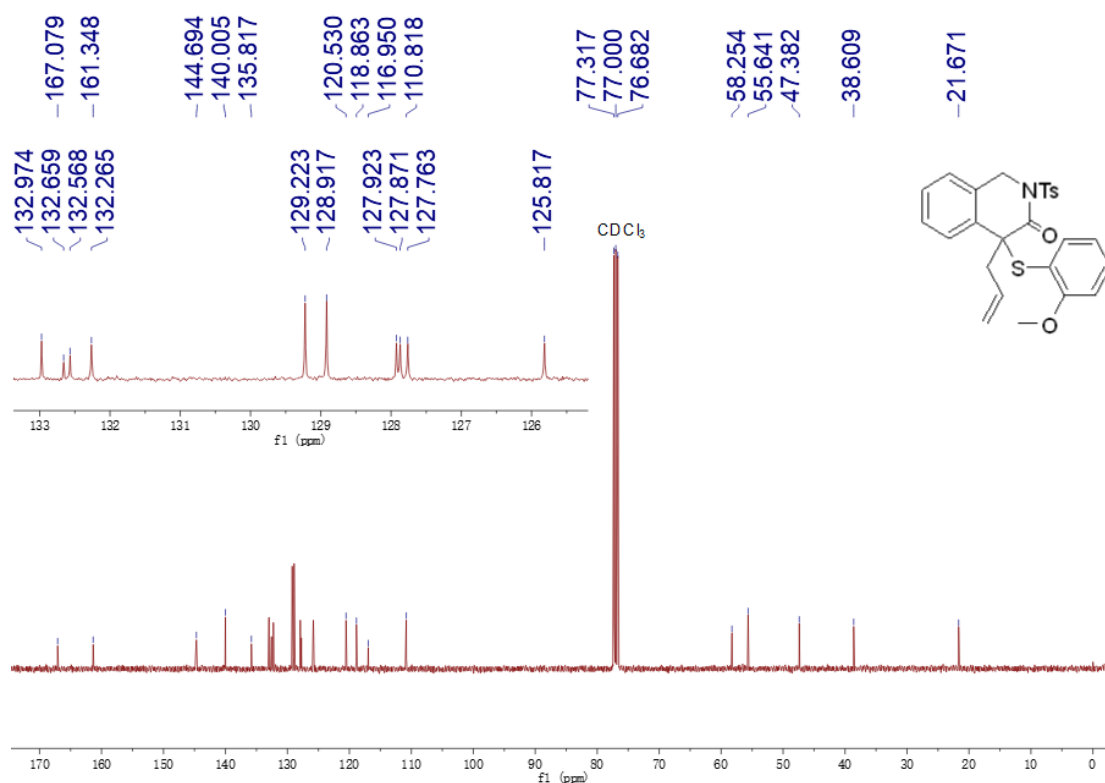
¹H NMR of **3n** (CDCl₃, 400 MHz)



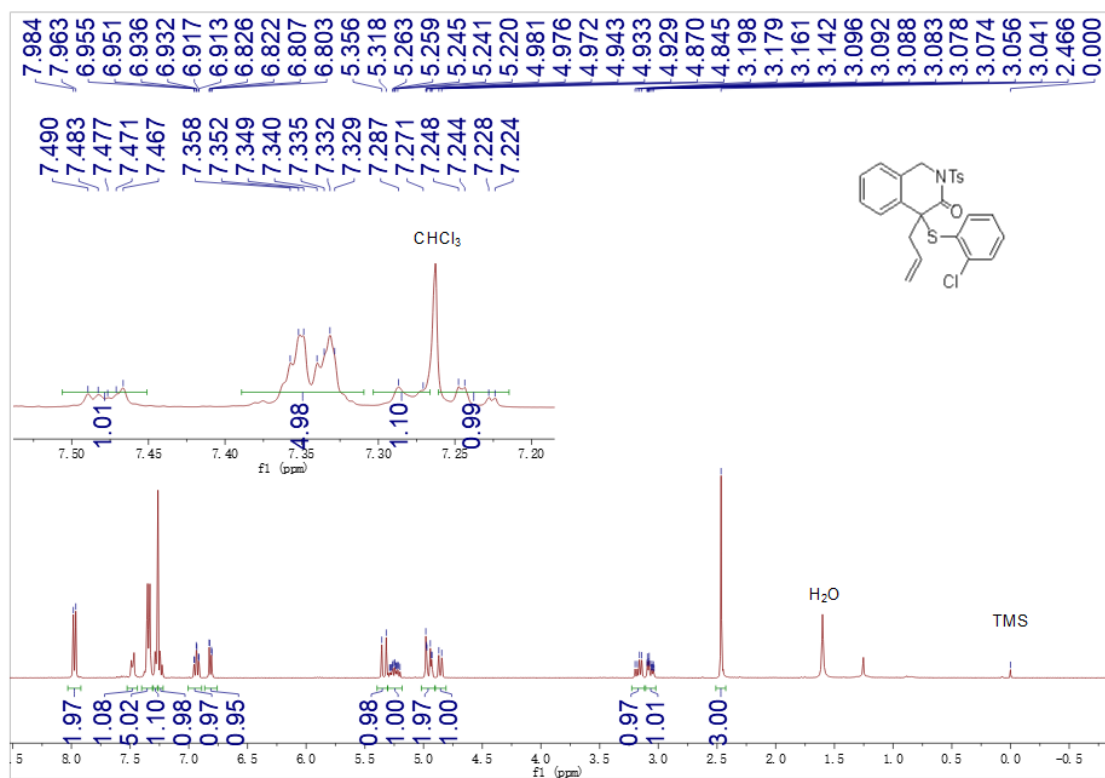
¹³C{¹H} NMR of **3n** (CDCl₃, 100 MHz)



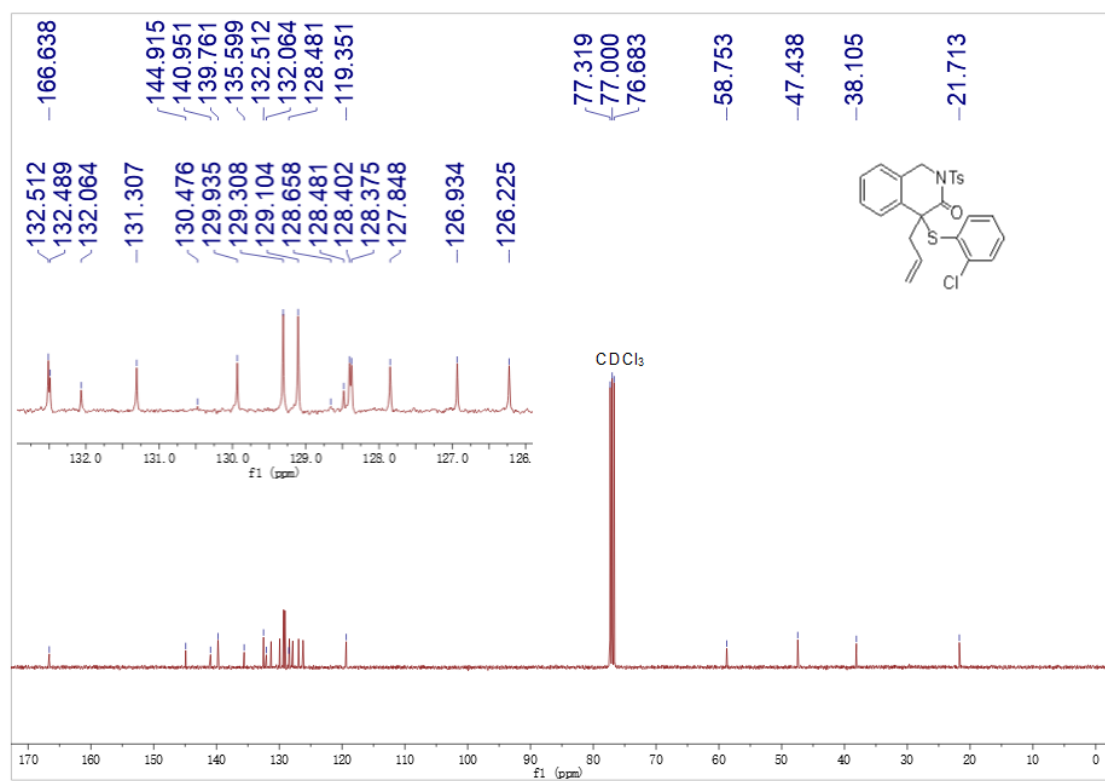
¹H NMR of **3o** (CDCl₃, 400 MHz)



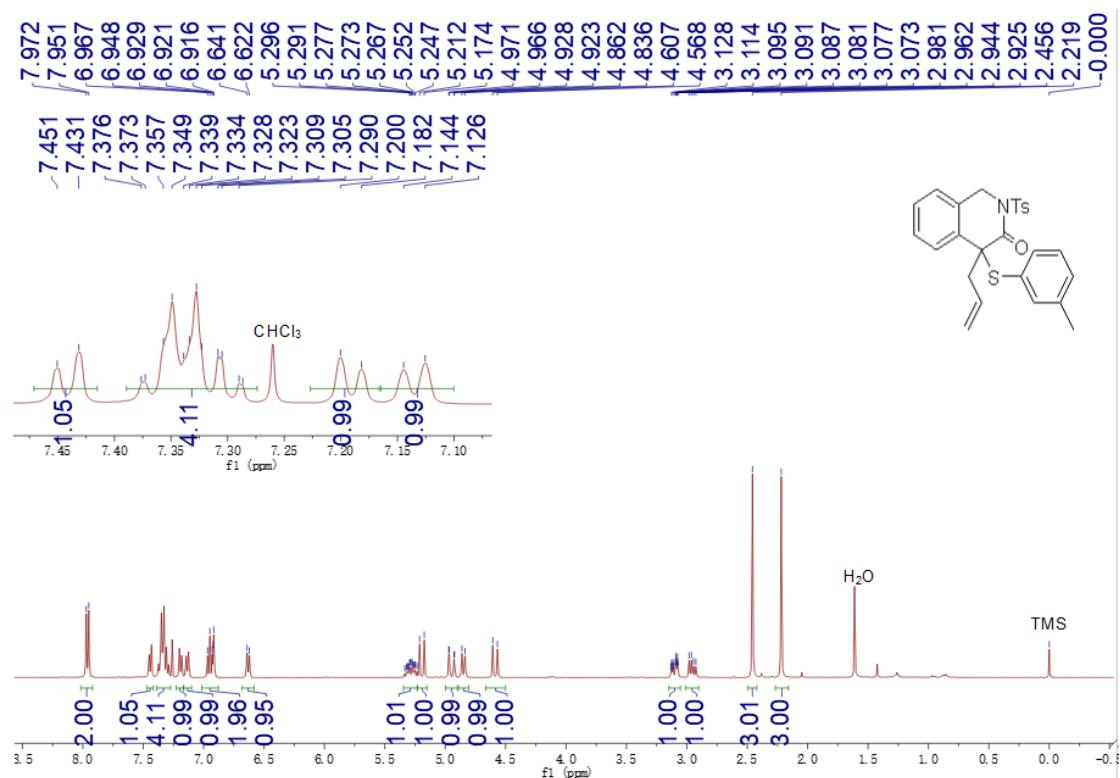
¹³C{¹H} NMR of **3o** (CDCl₃, 100 MHz)



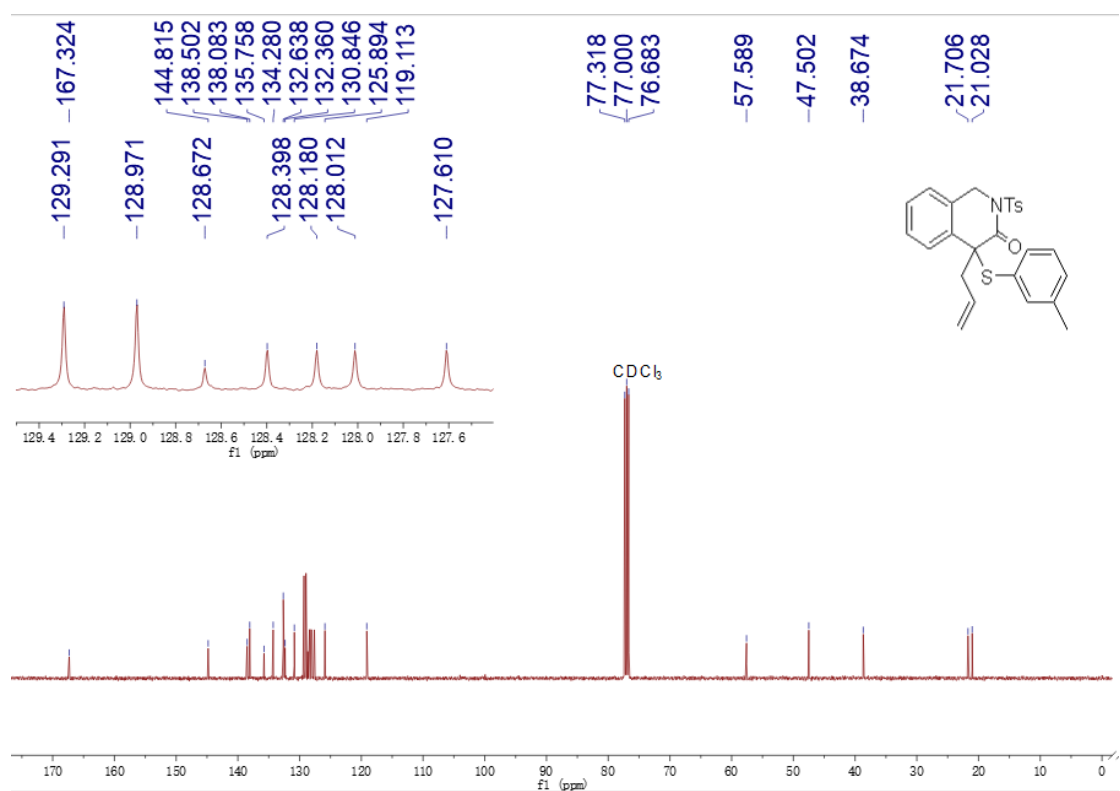
¹H NMR of **3p** (CDCl₃, 400 MHz)



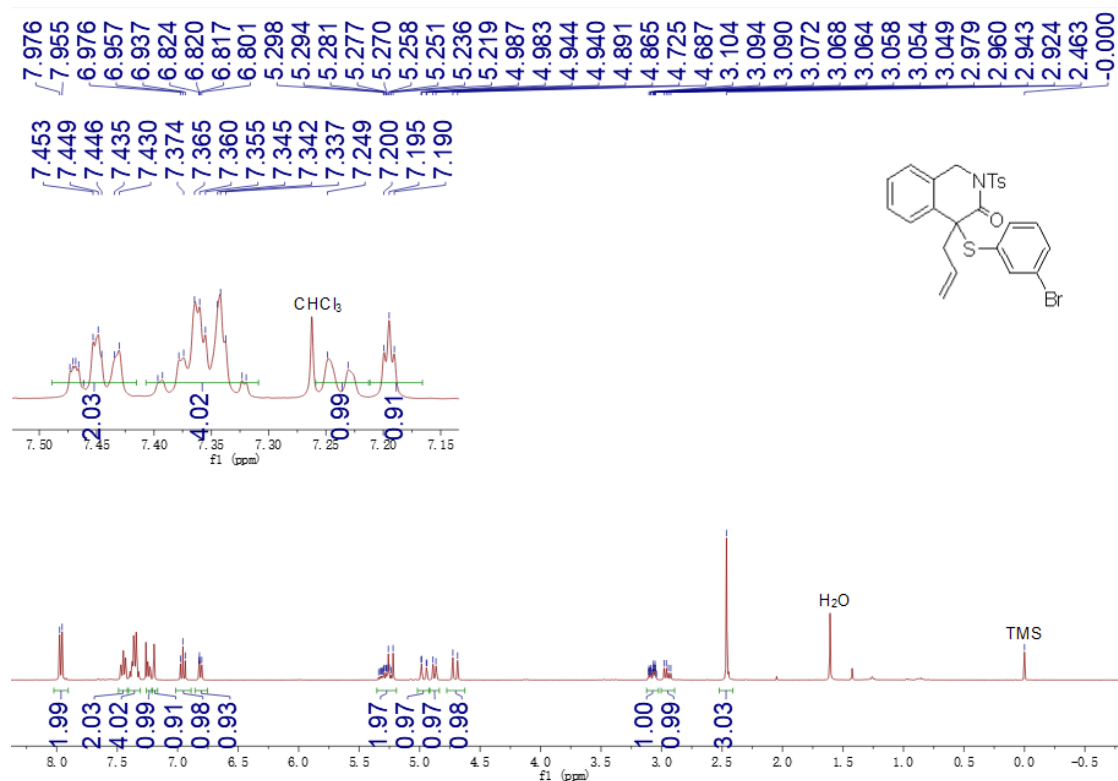
¹³C{¹H} NMR of **3p** (CDCl₃, 100 MHz)



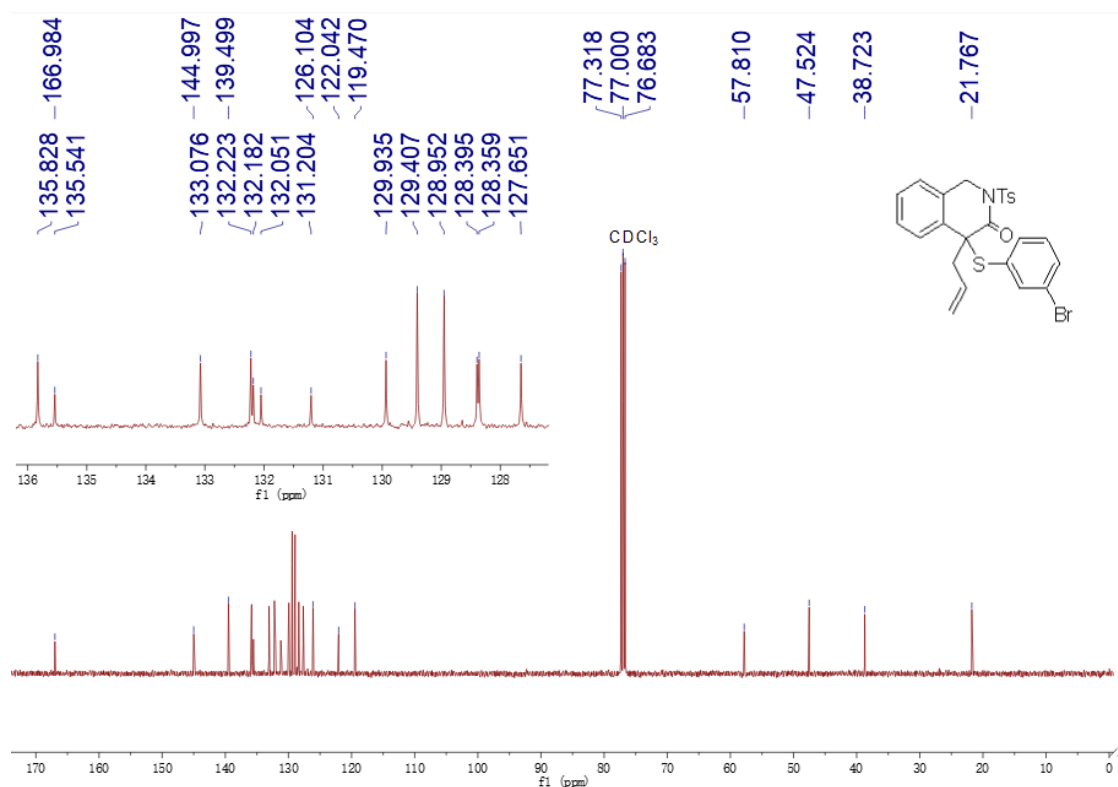
¹H NMR of **3q** (CDCl₃, 400 MHz)



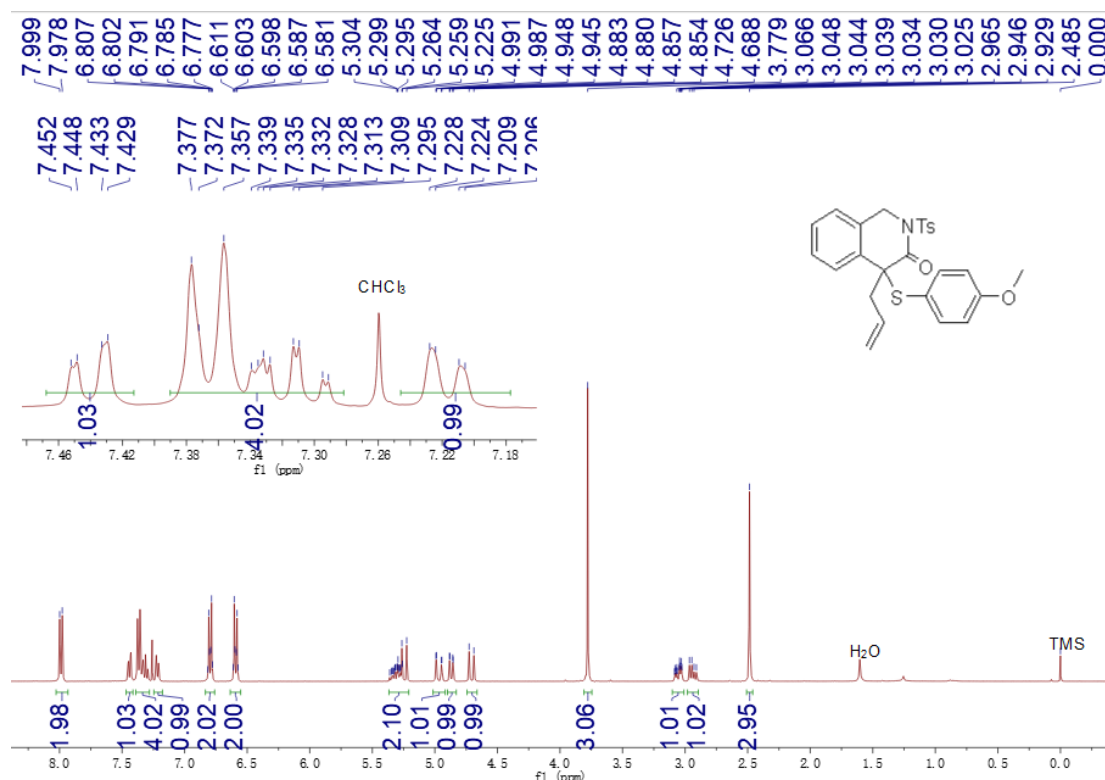
¹³C{¹H} NMR of **3q** (CDCl₃, 100 MHz)



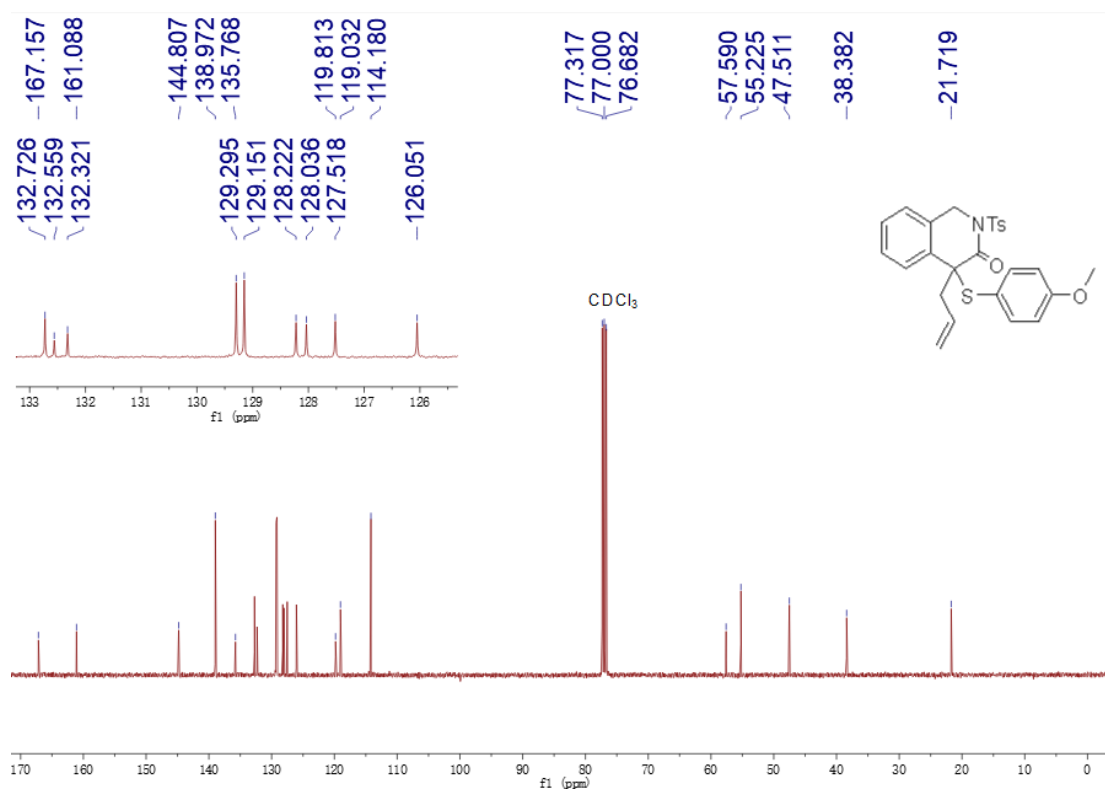
¹H NMR of **3r** (CDCl₃, 400 MHz)



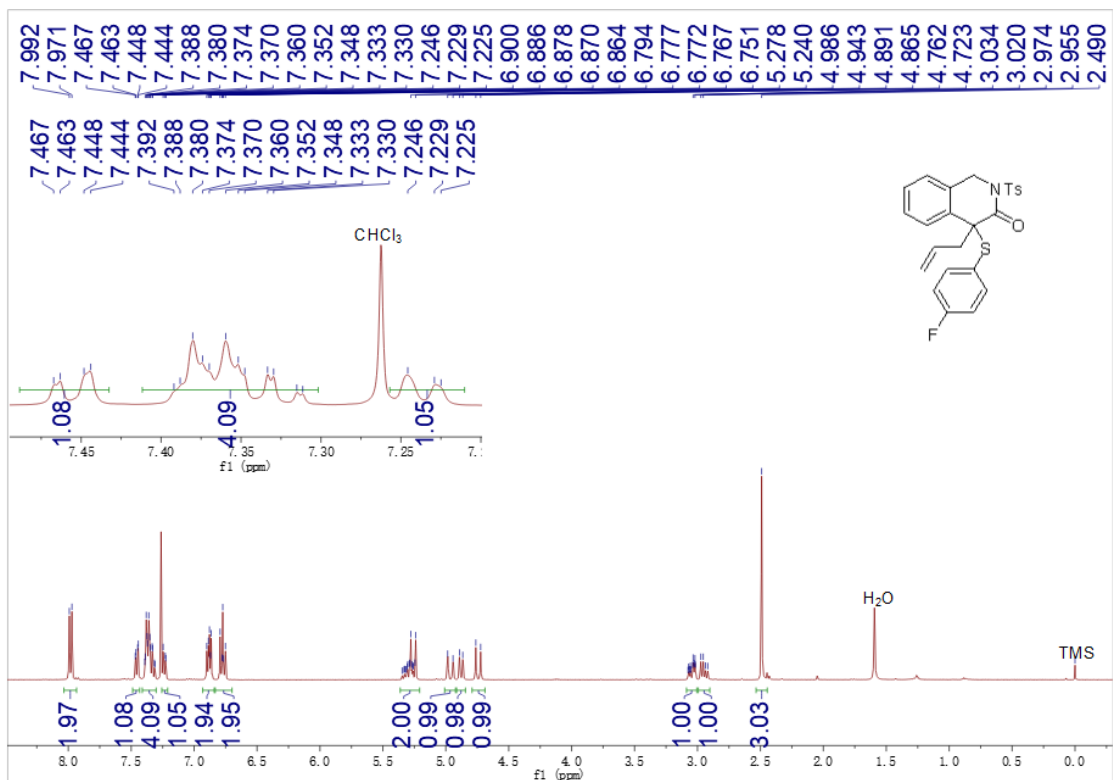
¹³C{¹H} NMR of **3r** (CDCl₃, 100 MHz)



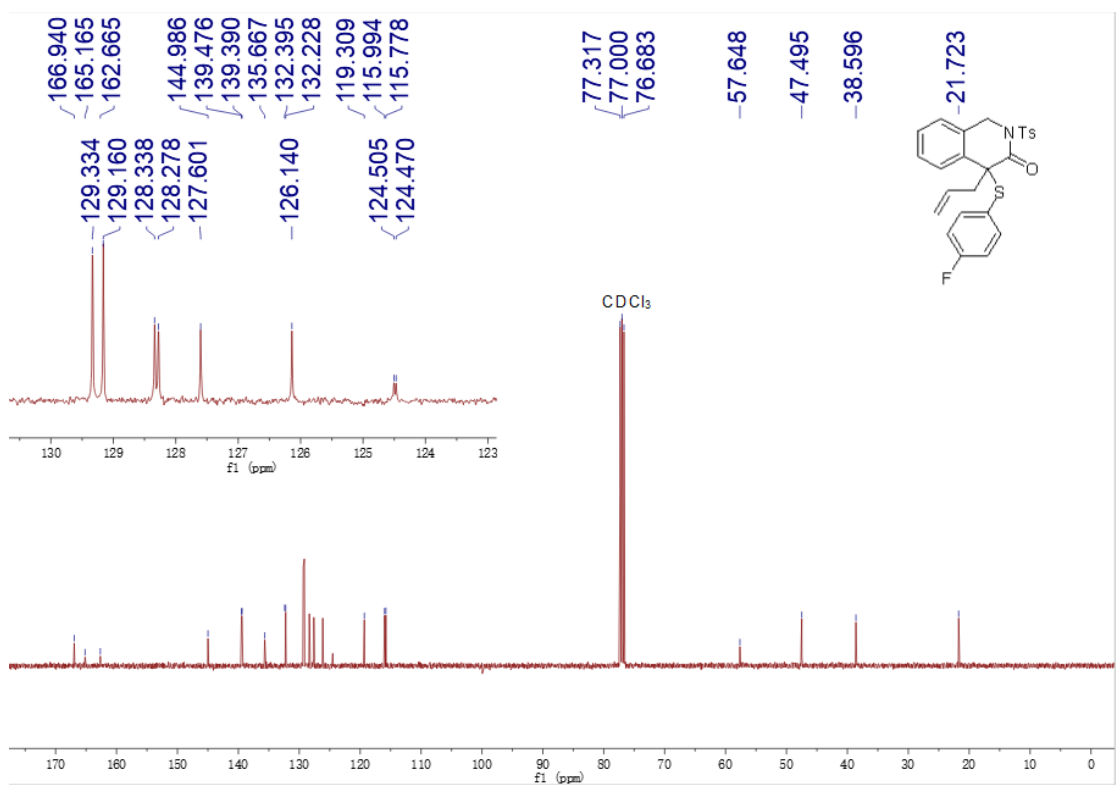
¹H NMR of 3s (CDCl₃, 400 MHz)



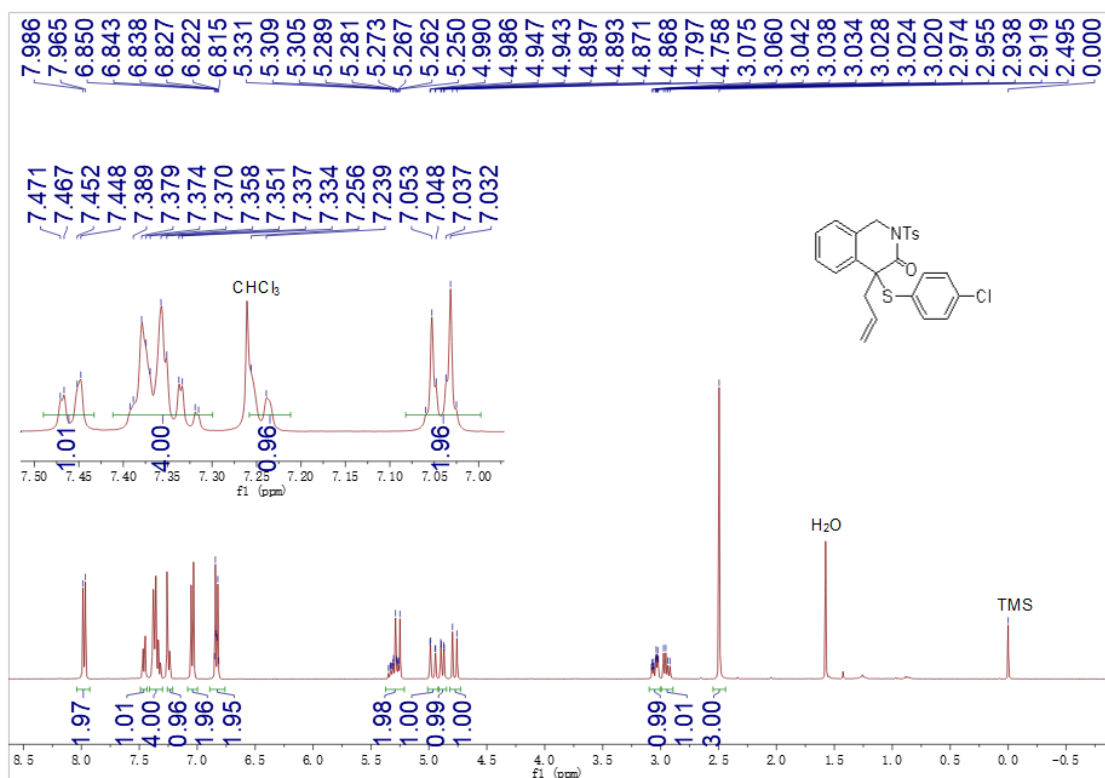
¹³C{¹H} NMR of 3s (CDCl₃, 100 MHz)



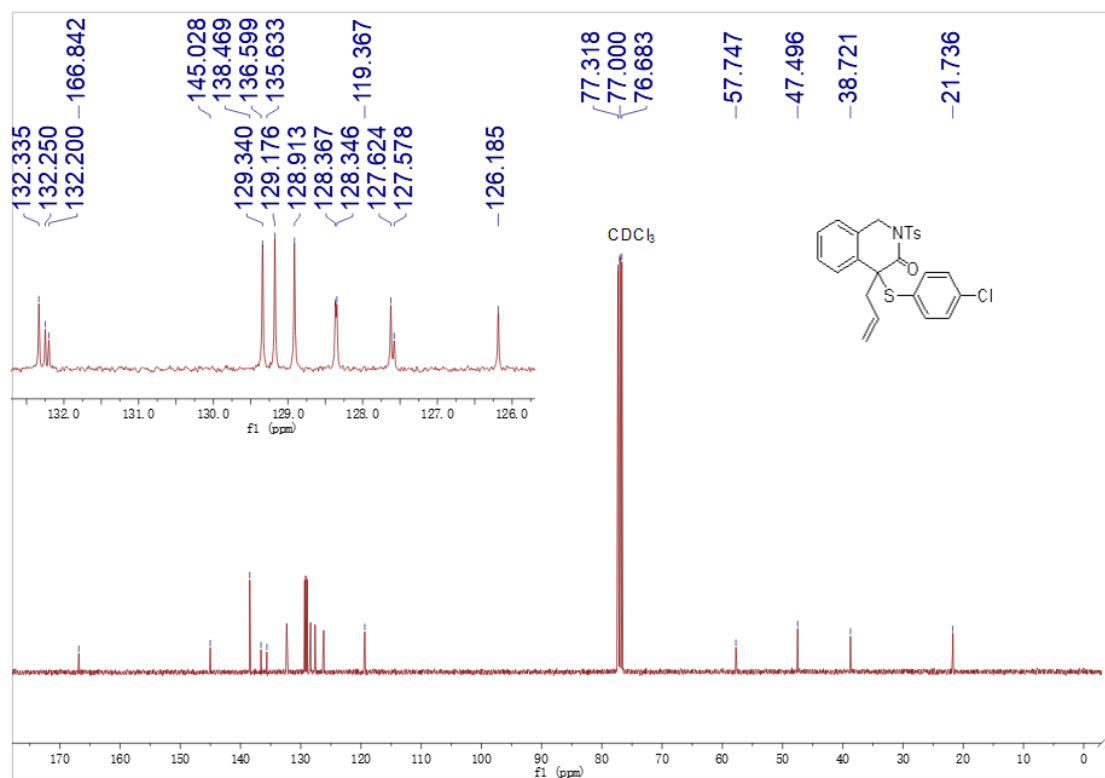
¹H NMR of **3t** (CDCl₃, 400 MHz)



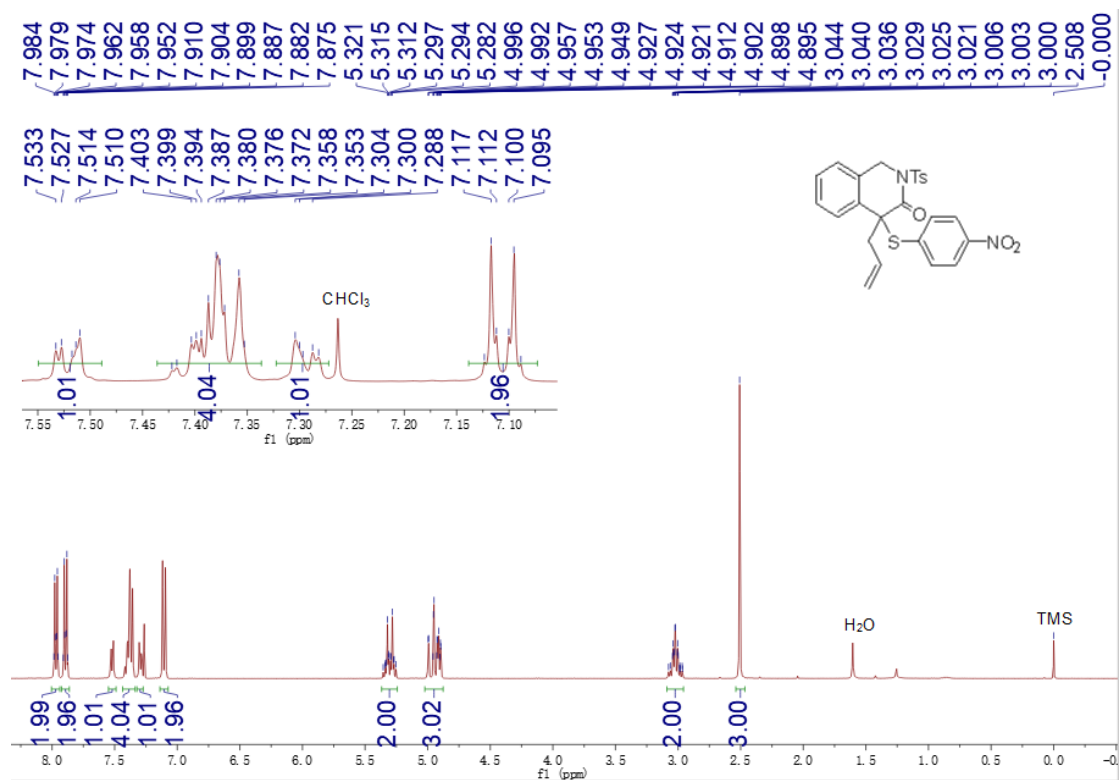
¹³C{¹H} NMR of **3t** (CDCl₃, 100 MHz)



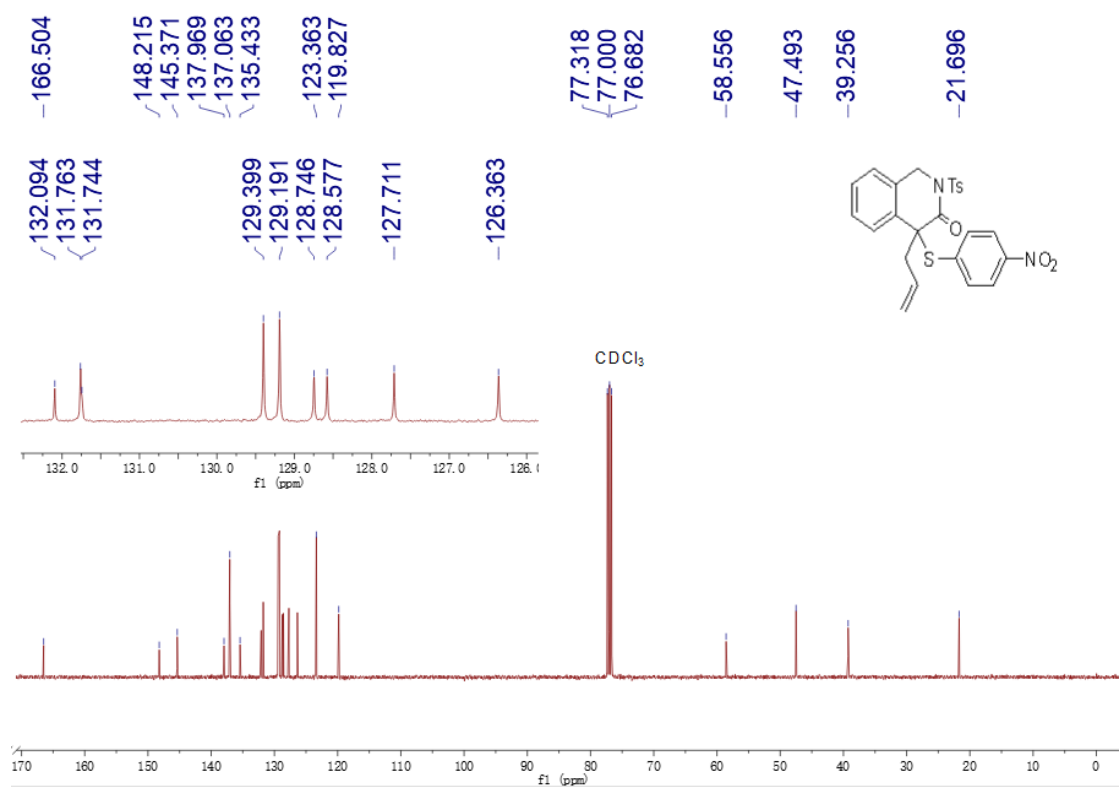
¹H NMR of **3u** (CDCl₃, 400 MHz)



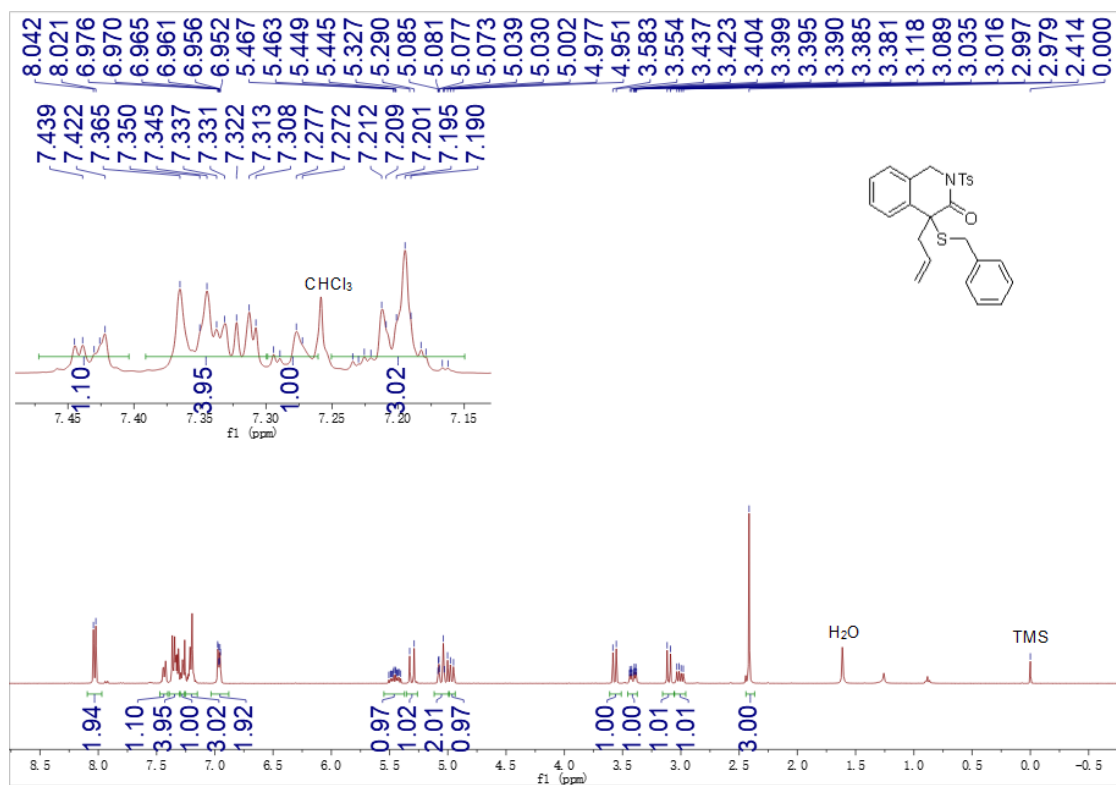
¹³C{¹H} NMR of **3u** (CDCl₃, 100 MHz)



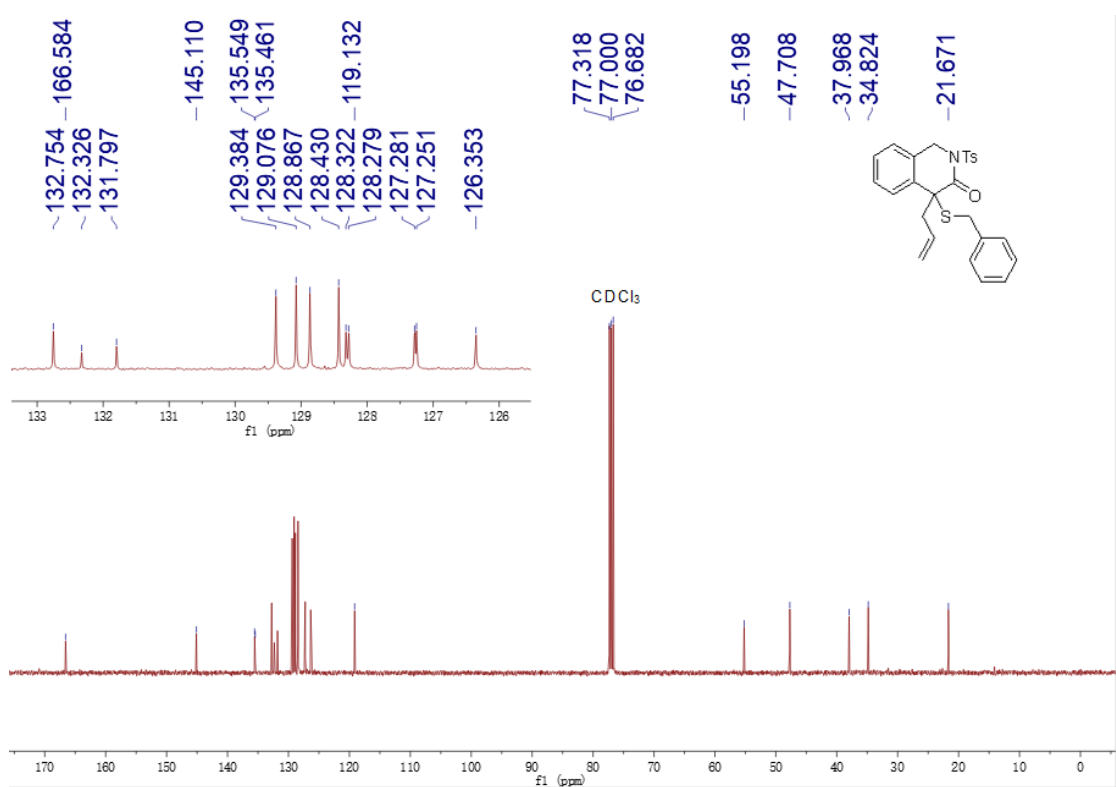
¹H NMR of 3v (CDCl₃, 400 MHz)



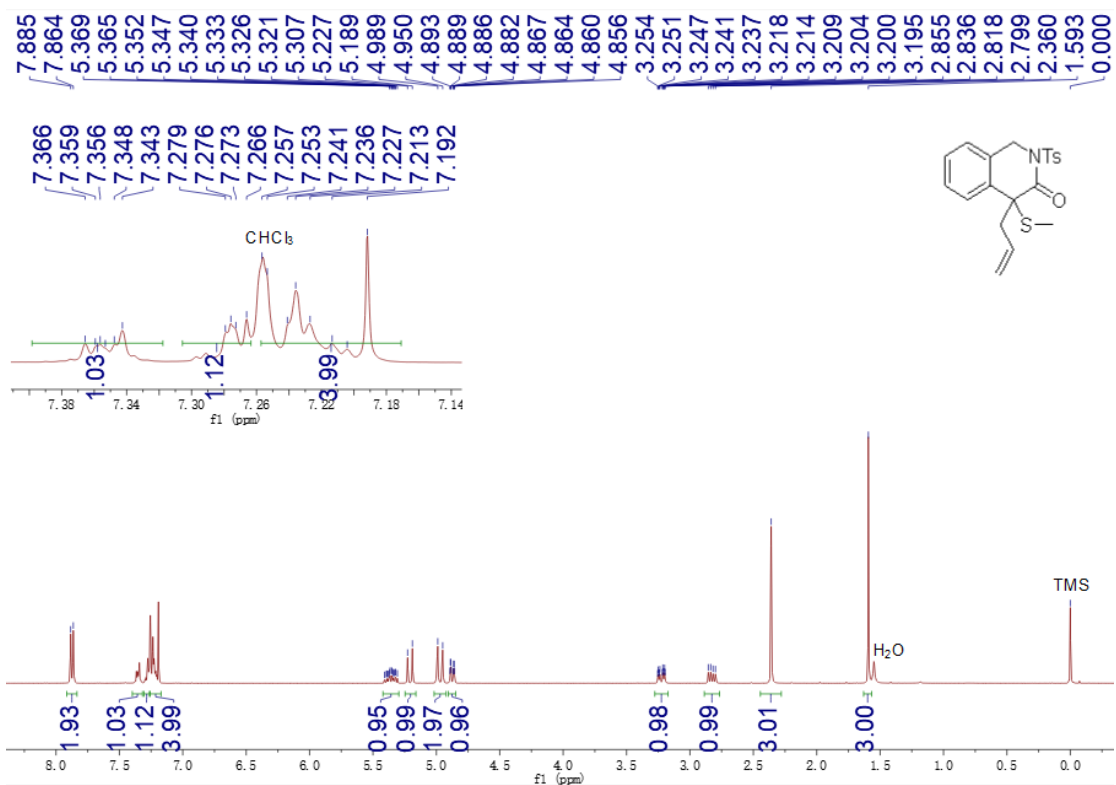
¹³C{¹H} NMR of 3v (CDCl₃, 100 MHz)



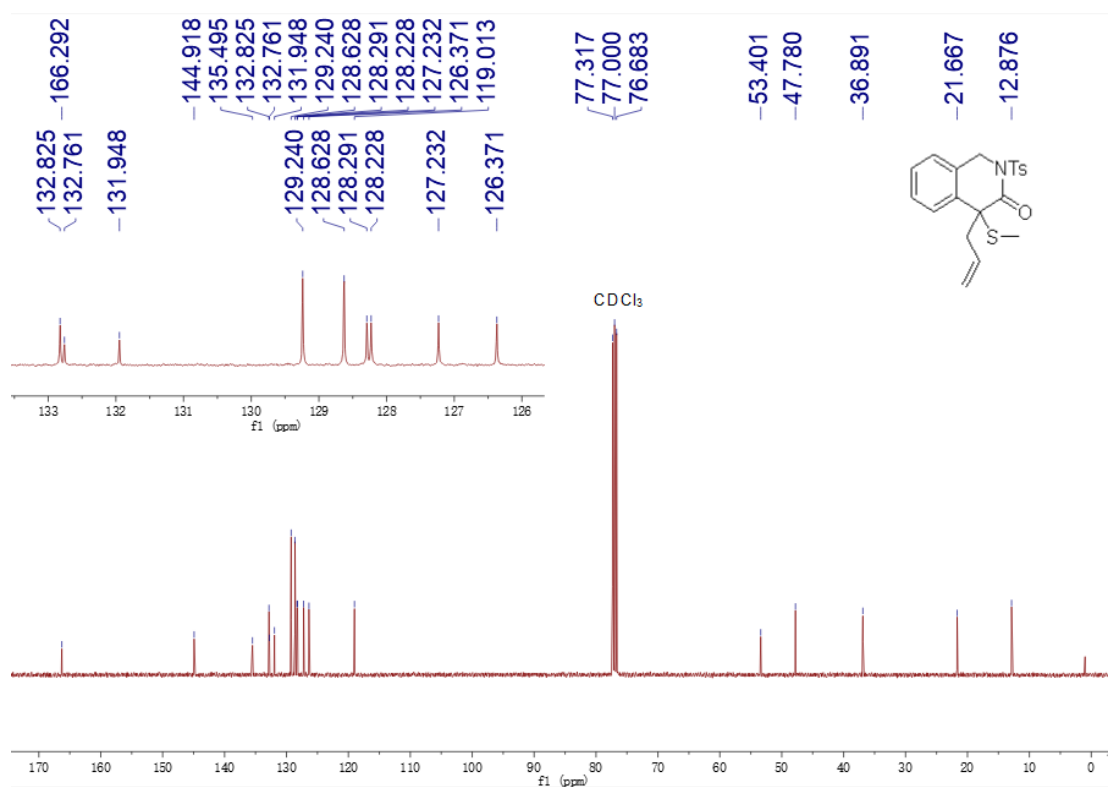
¹H NMR of **3w** (CDCl₃, 400 MHz)



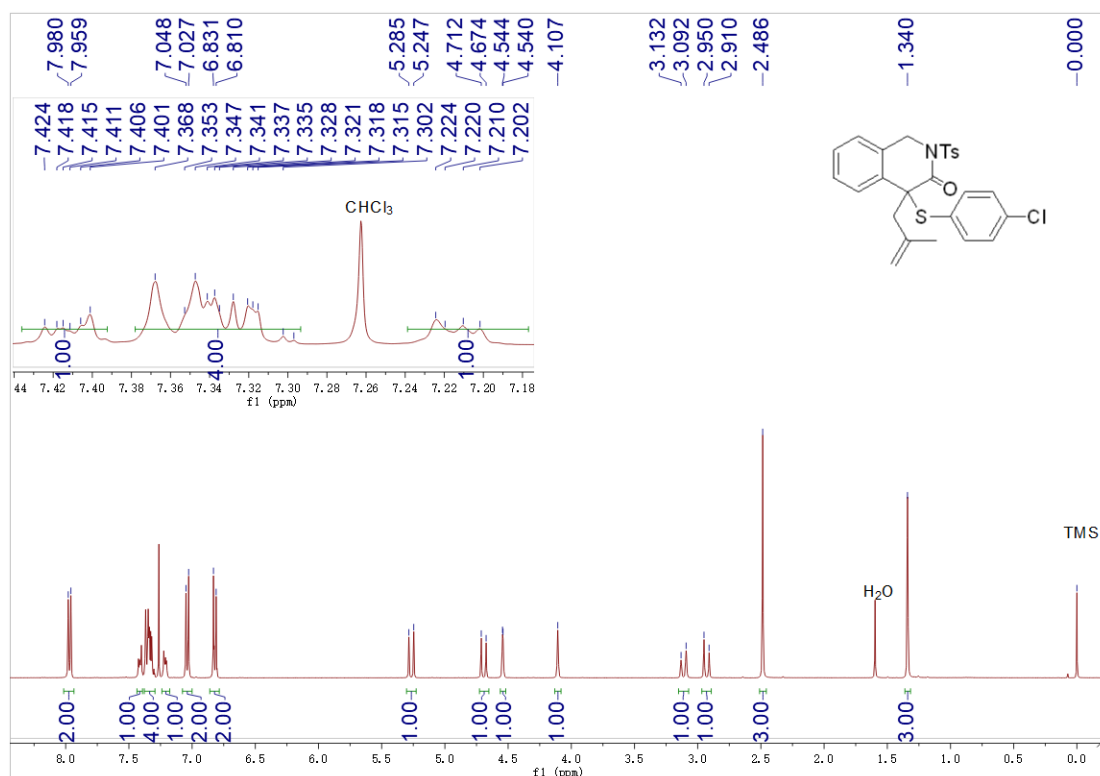
¹³C{¹H} NMR of **3w** (CDCl₃, 100 MHz)



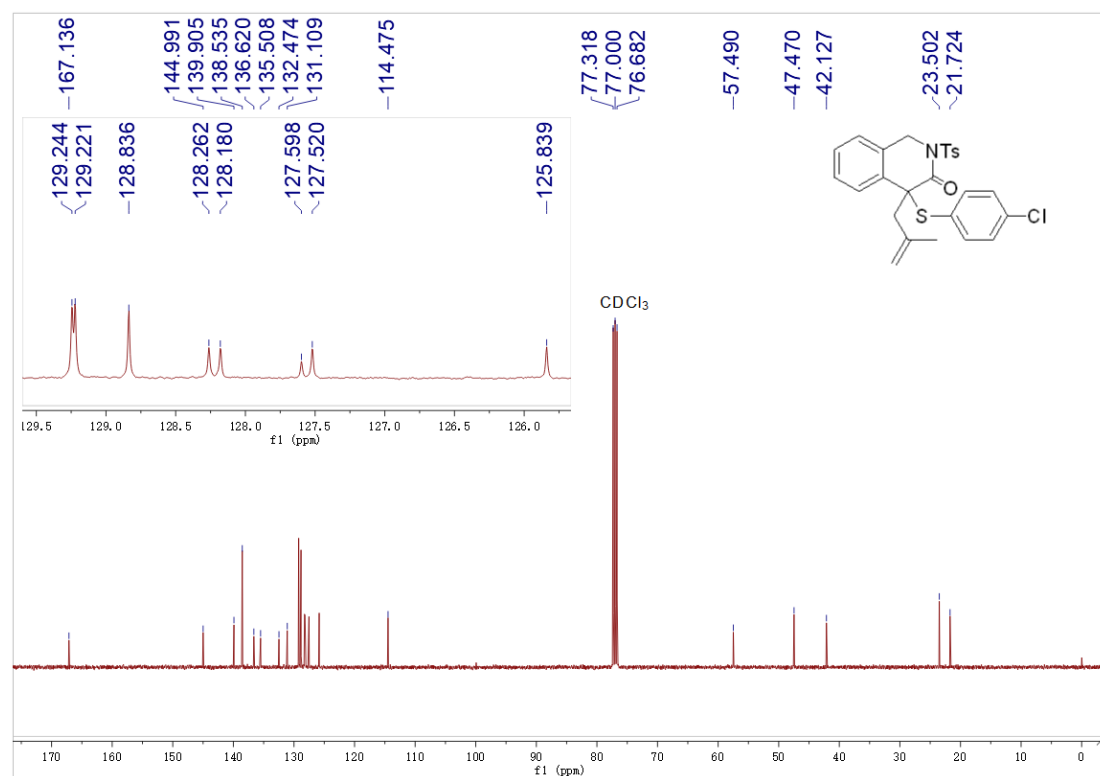
¹H NMR of **3x** (CDCl₃, 400 MHz)



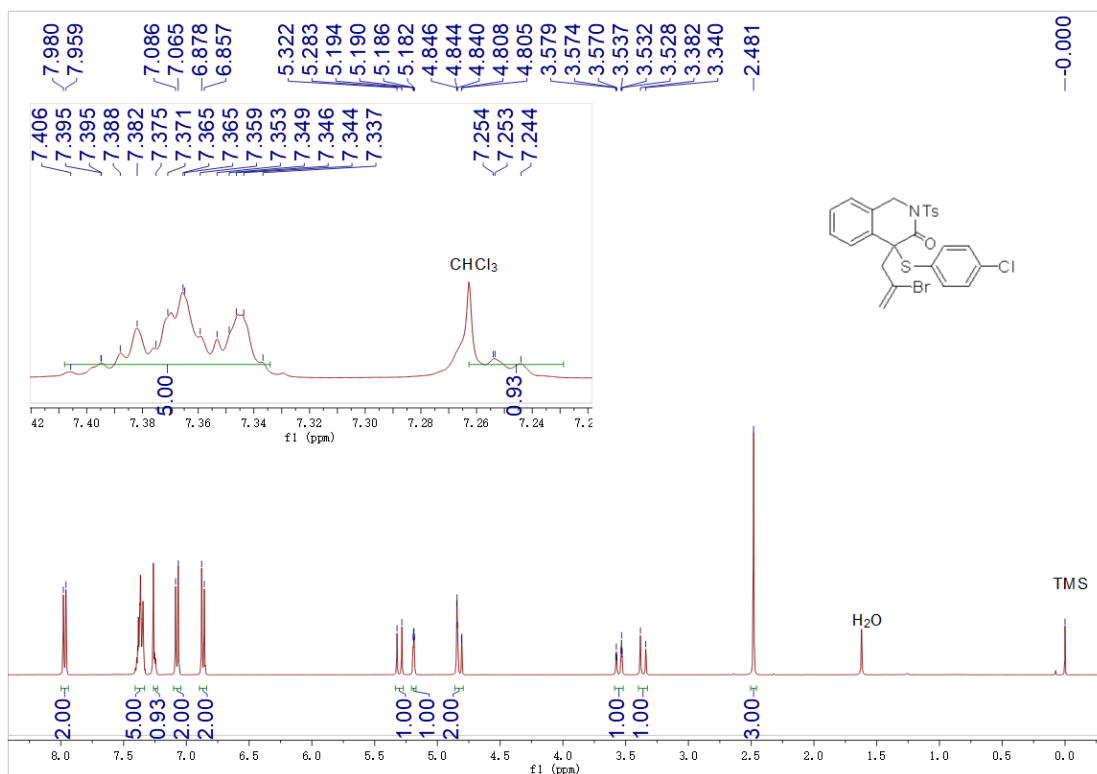
¹³C{¹H} NMR of **3x** (CDCl₃, 100 MHz)



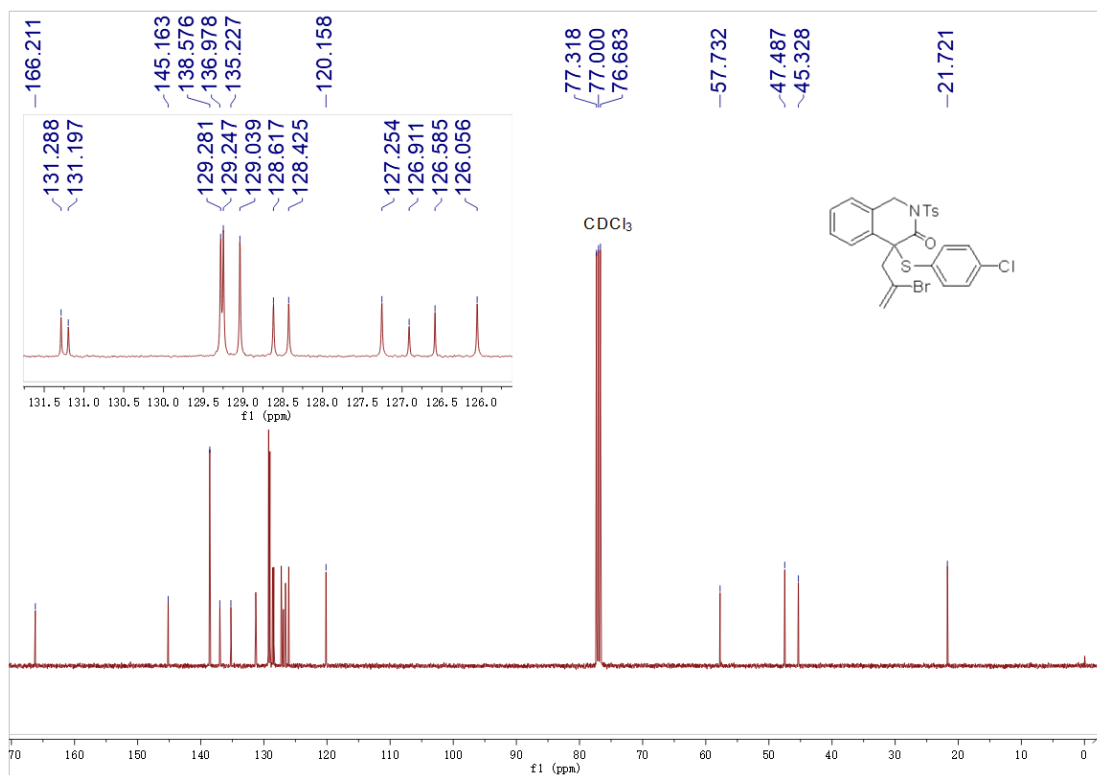
¹H NMR of **3y** (CDCl₃, 400 MHz)



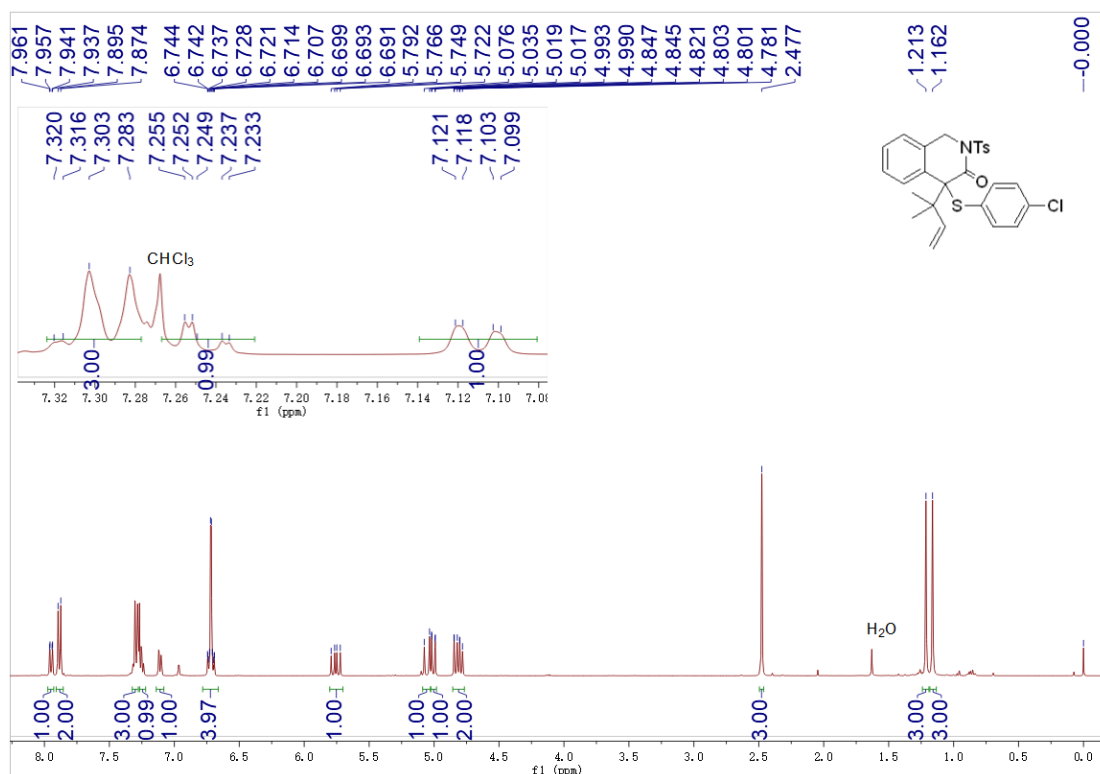
¹³C{¹H} NMR of **3y** (CDCl₃, 100 MHz)



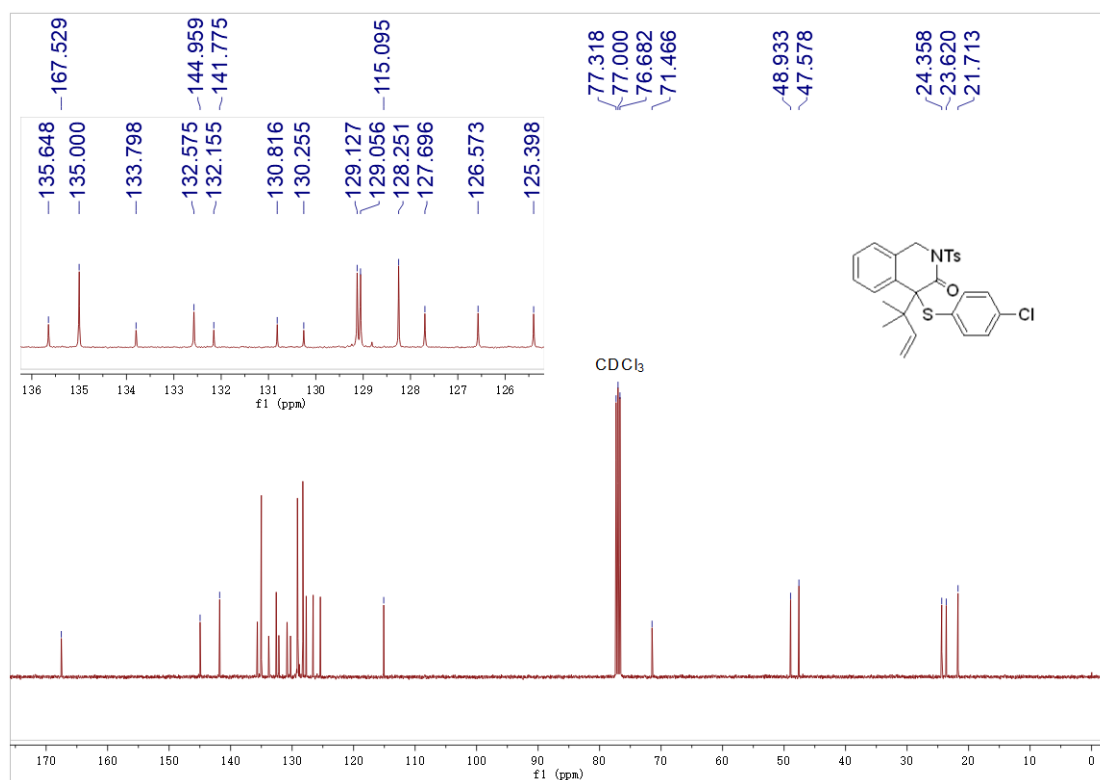
¹H NMR of **3z (CDCl₃, 400 MHz)**



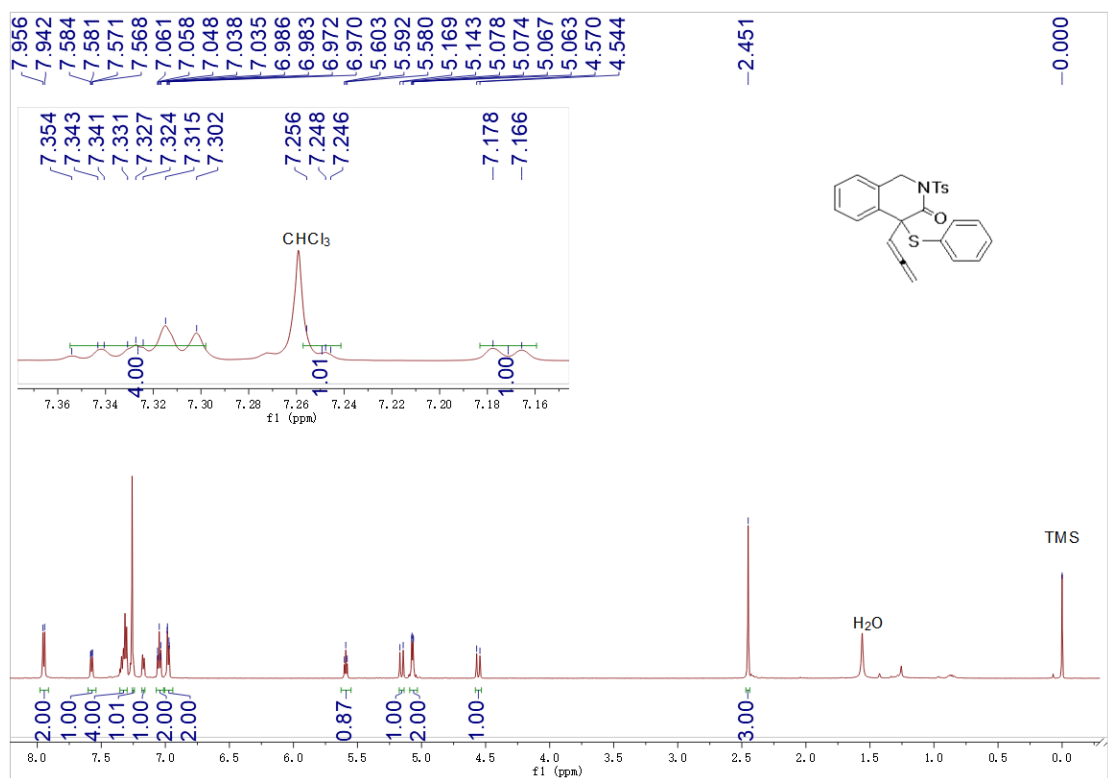
¹³C{¹H} NMR of **3z (CDCl₃, 100 MHz)**



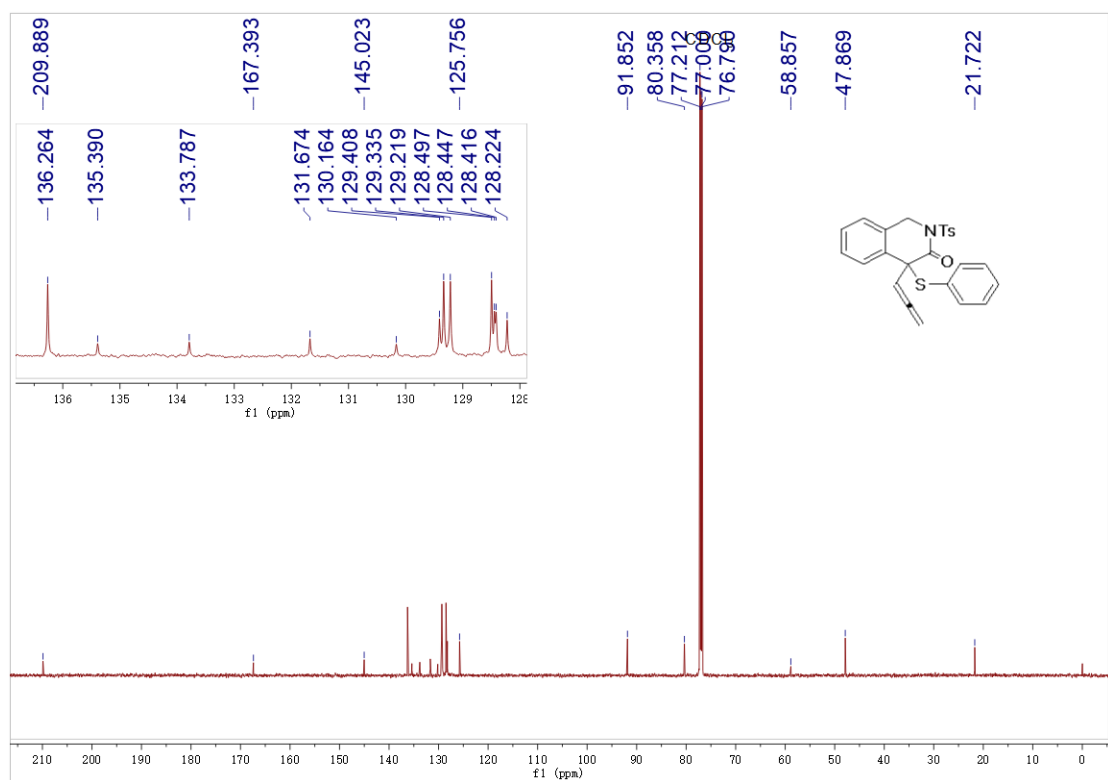
¹H NMR of 3A (CDCl₃, 400 MHz)



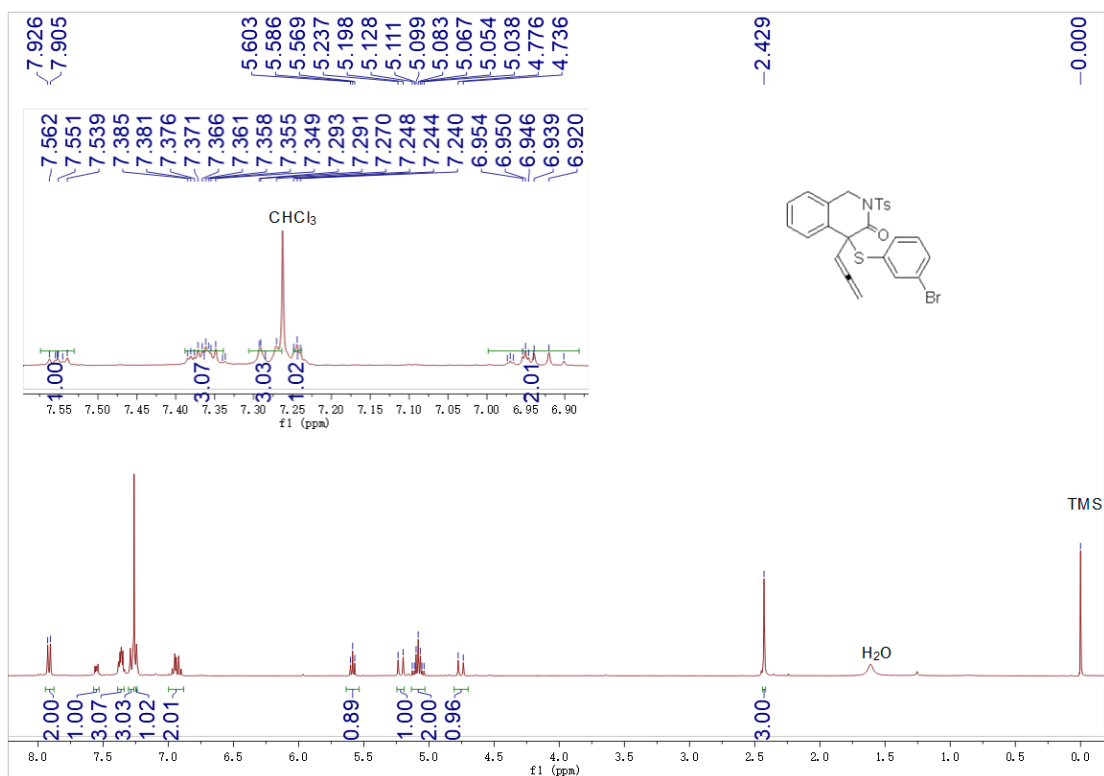
¹³C {¹H} NMR of 3A (CDCl₃, 100 MHz)



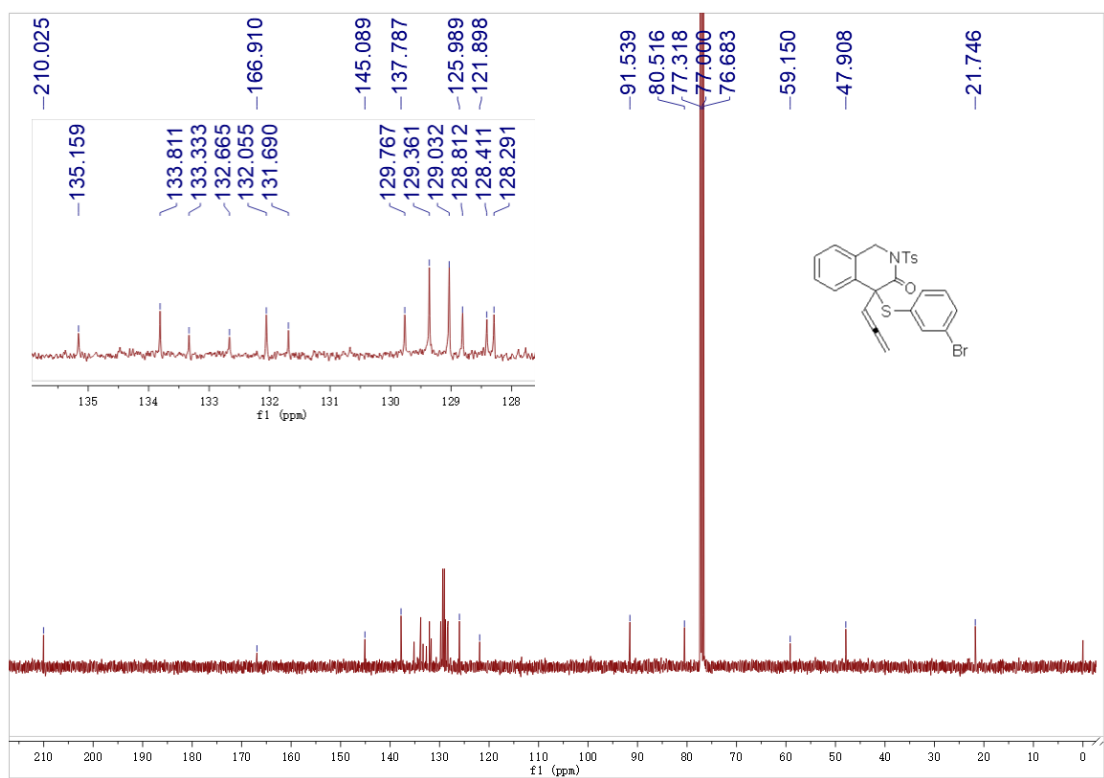
¹H NMR of **5a** (CDCl₃, 600 MHz)



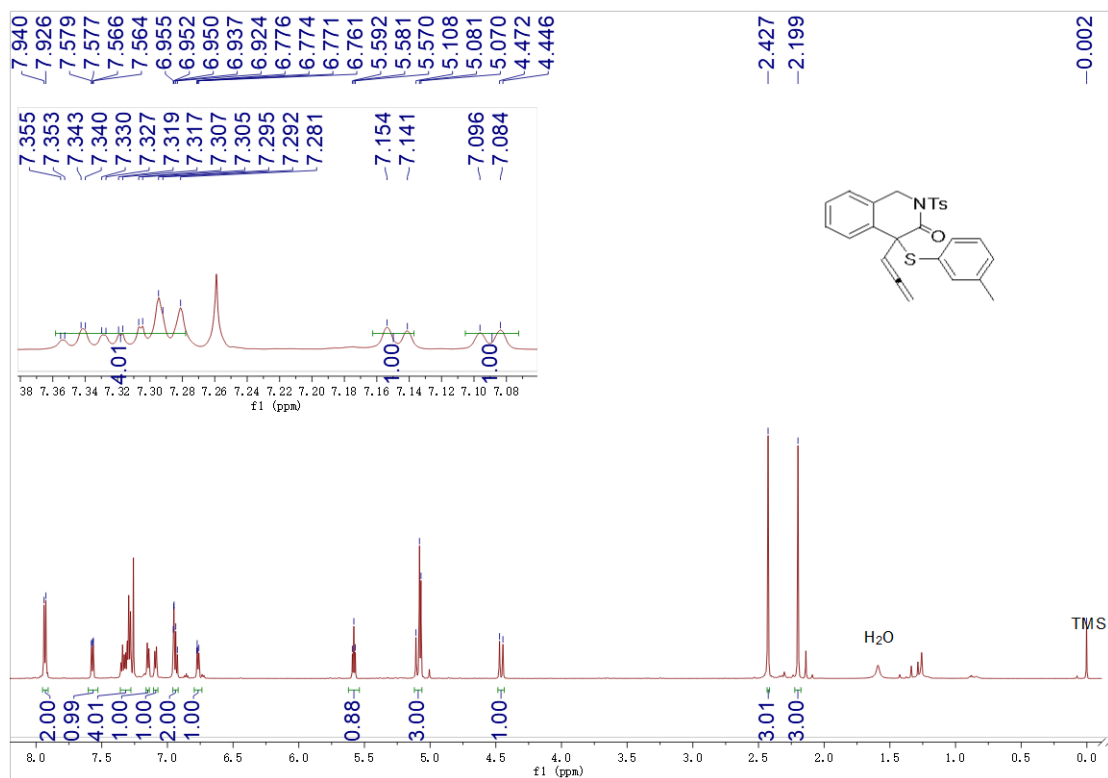
¹³C{¹H} NMR of **5a** (CDCl₃, 150 MHz)



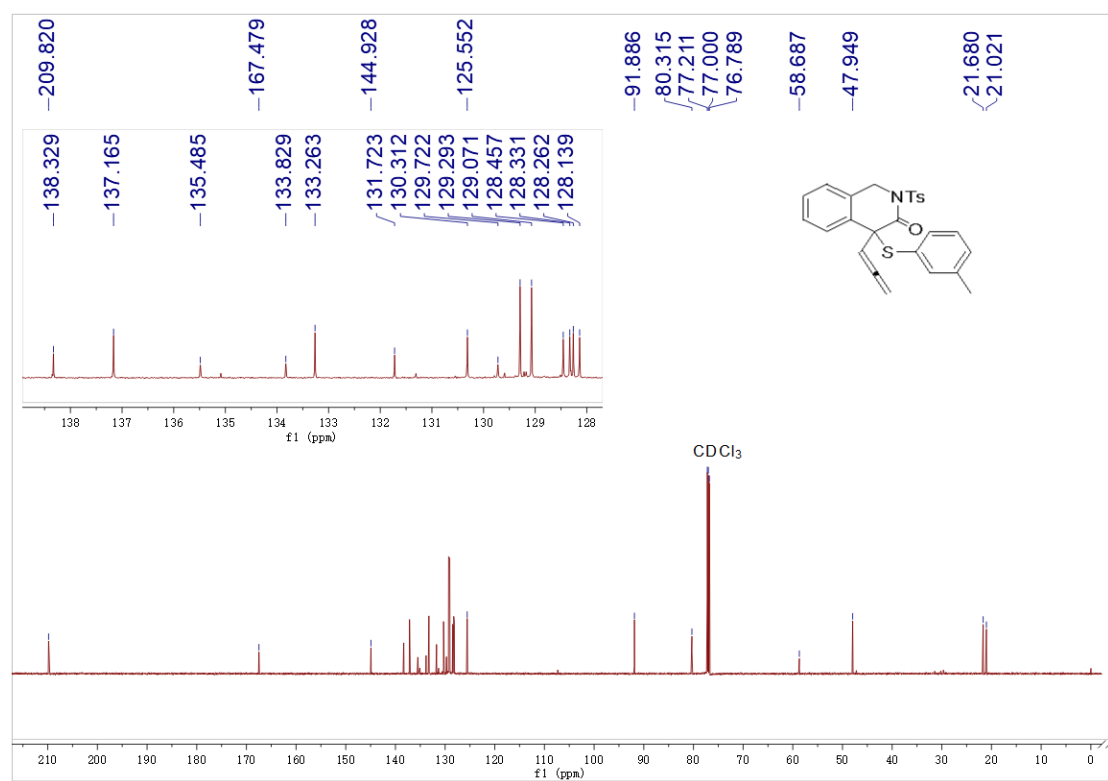
¹H NMR of **5b** (CDCl₃, 400 MHz)



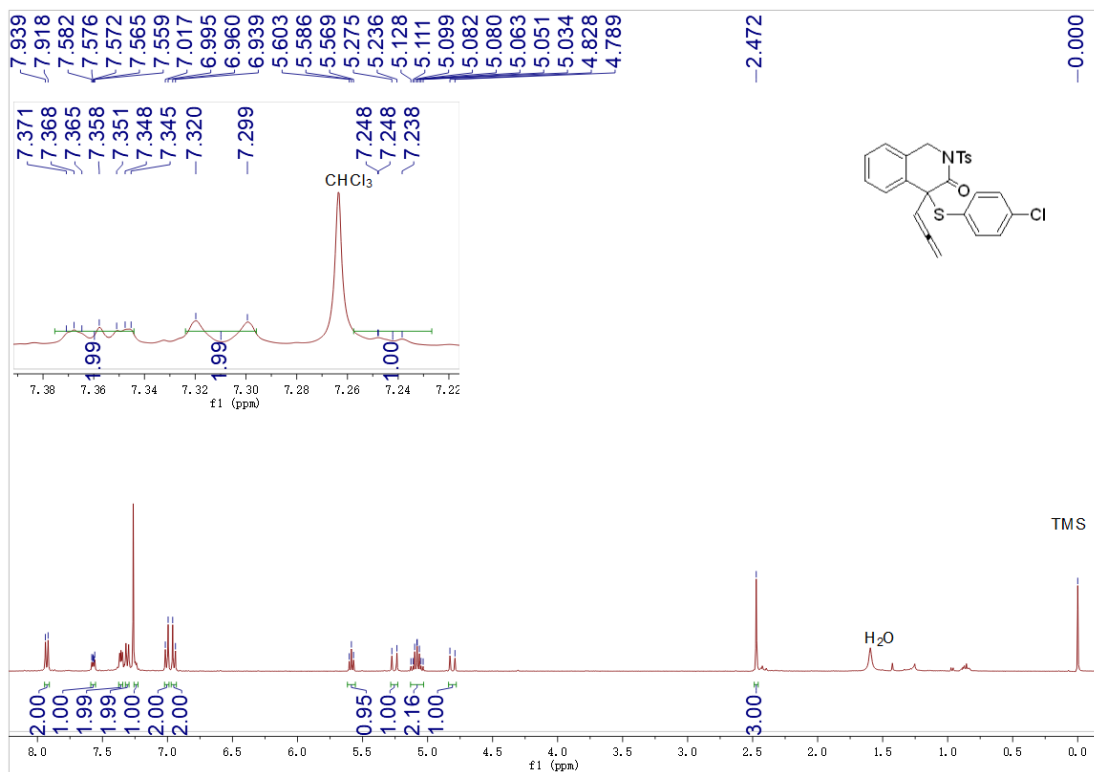
¹³C{¹H} NMR of **5b** (CDCl₃, 100 MHz)



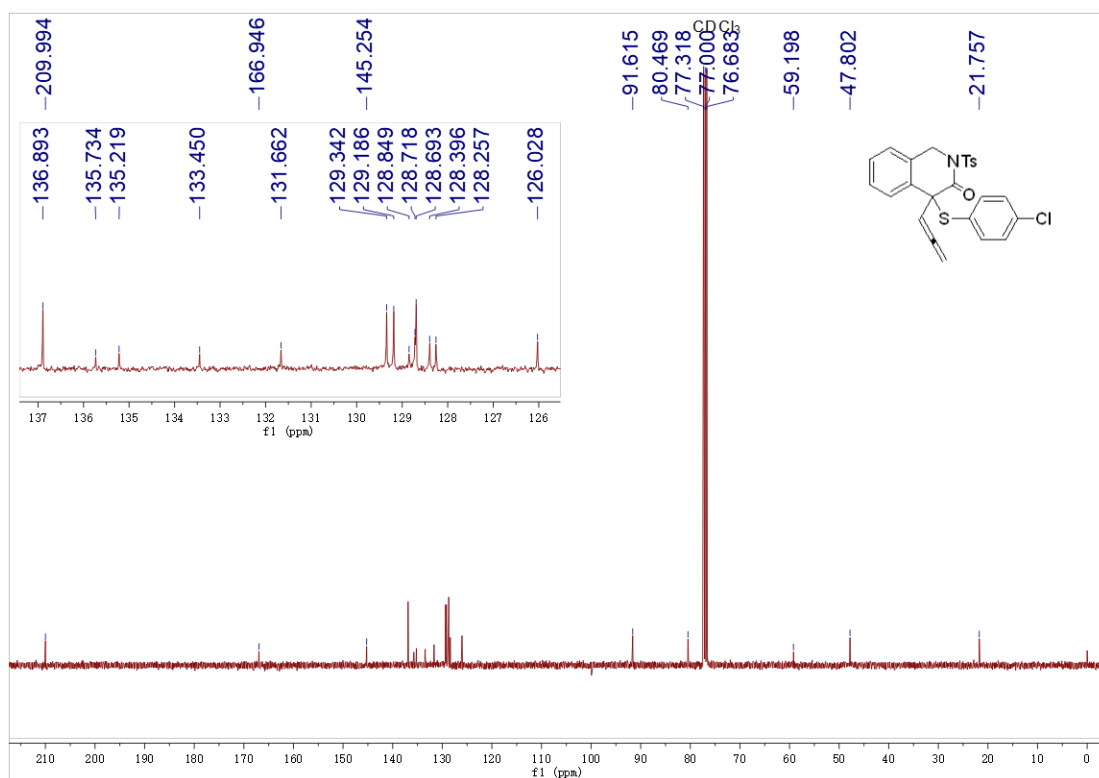
¹H NMR of 5c (CDCl₃, 600 MHz)



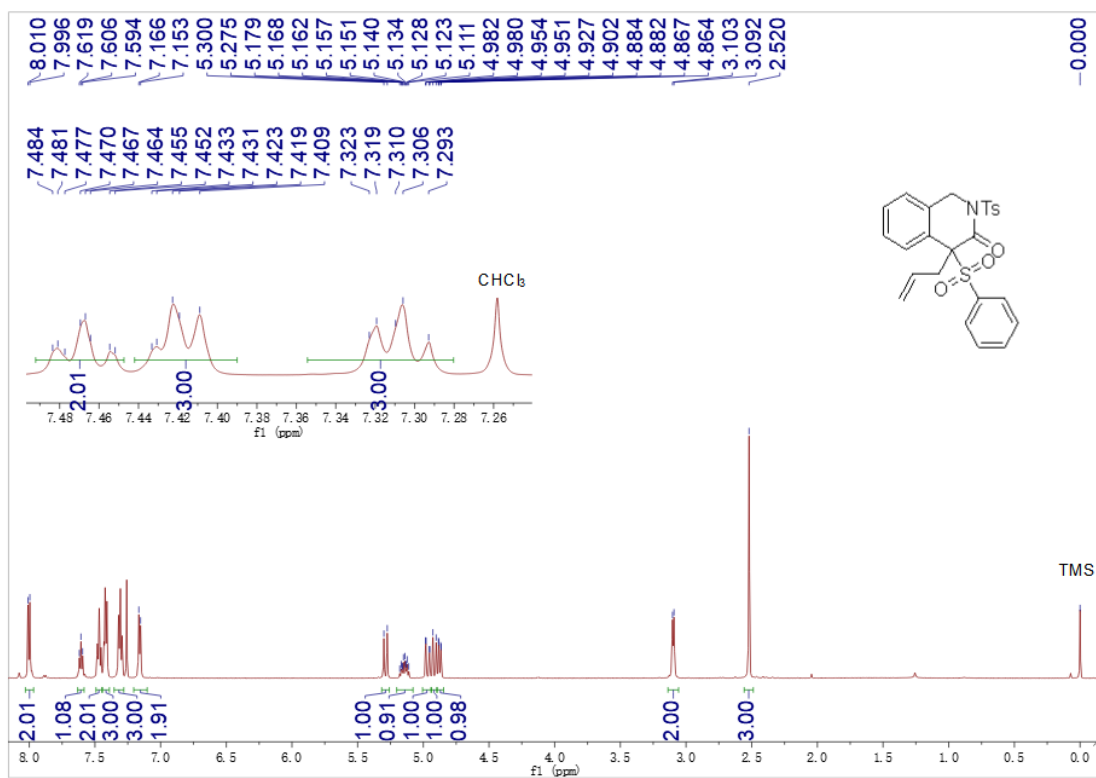
¹³C NMR of 5c (CDCl₃, 150 MHz)



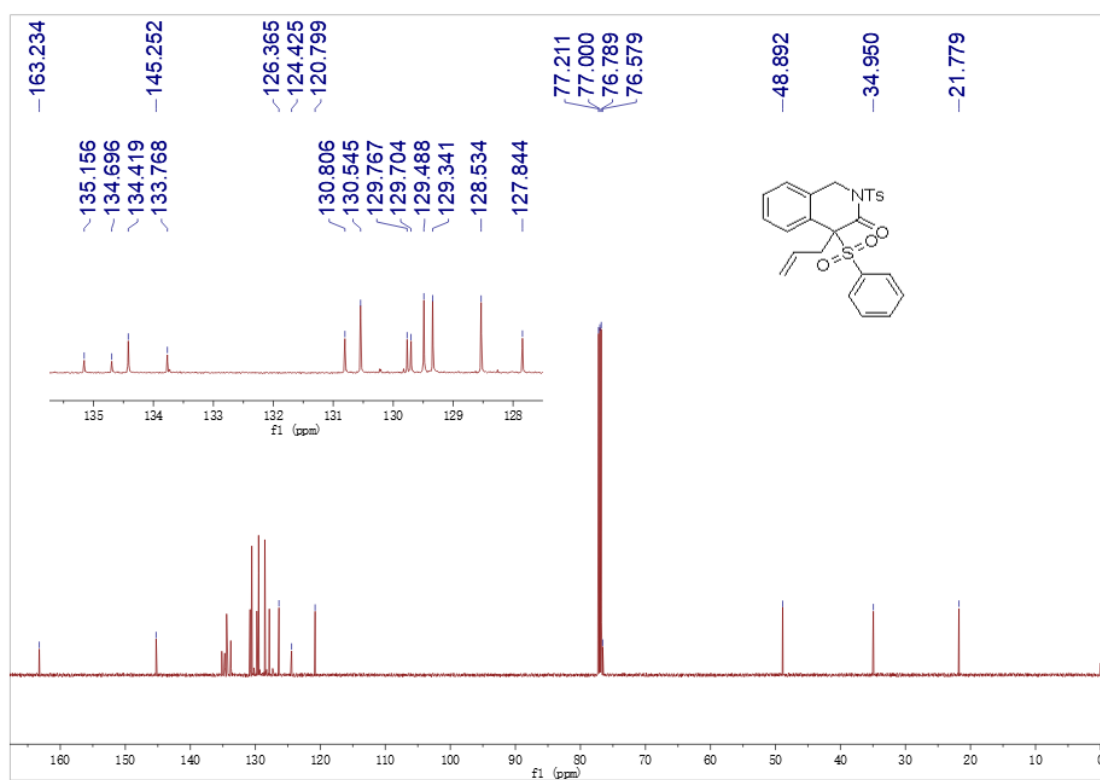
¹H NMR of **5d** (CDCl₃, 400 MHz)



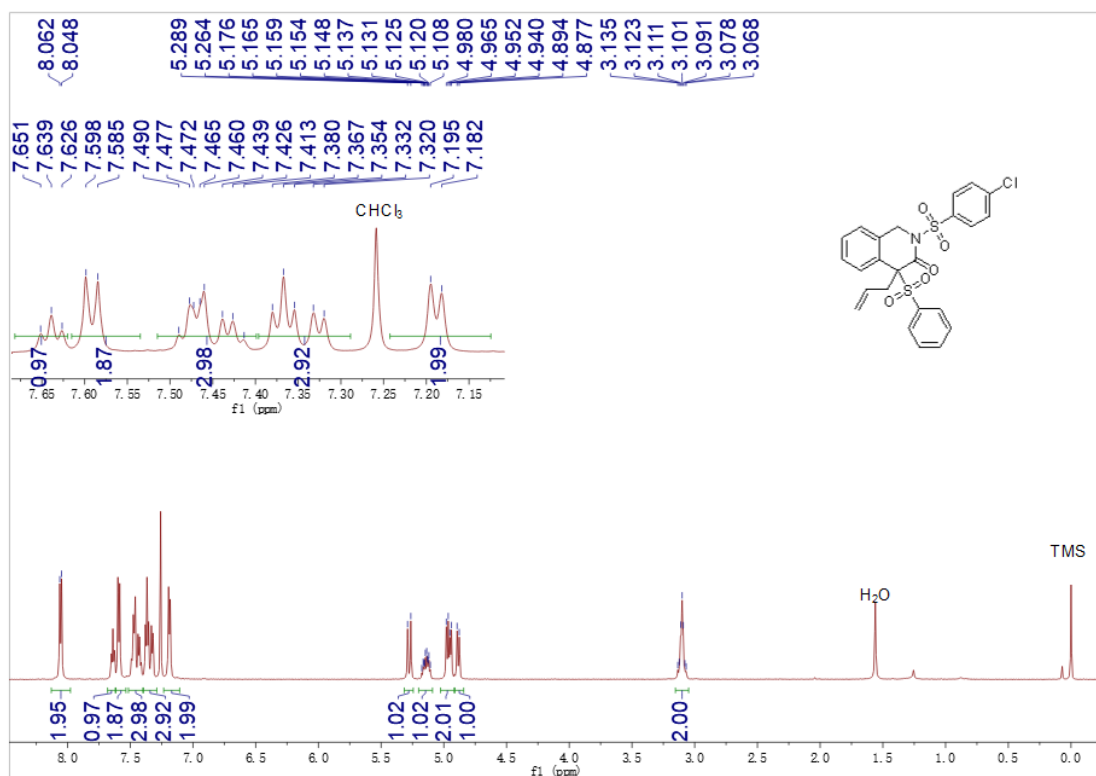
¹³C{¹H} NMR of **5d** (CDCl₃, 100 MHz)



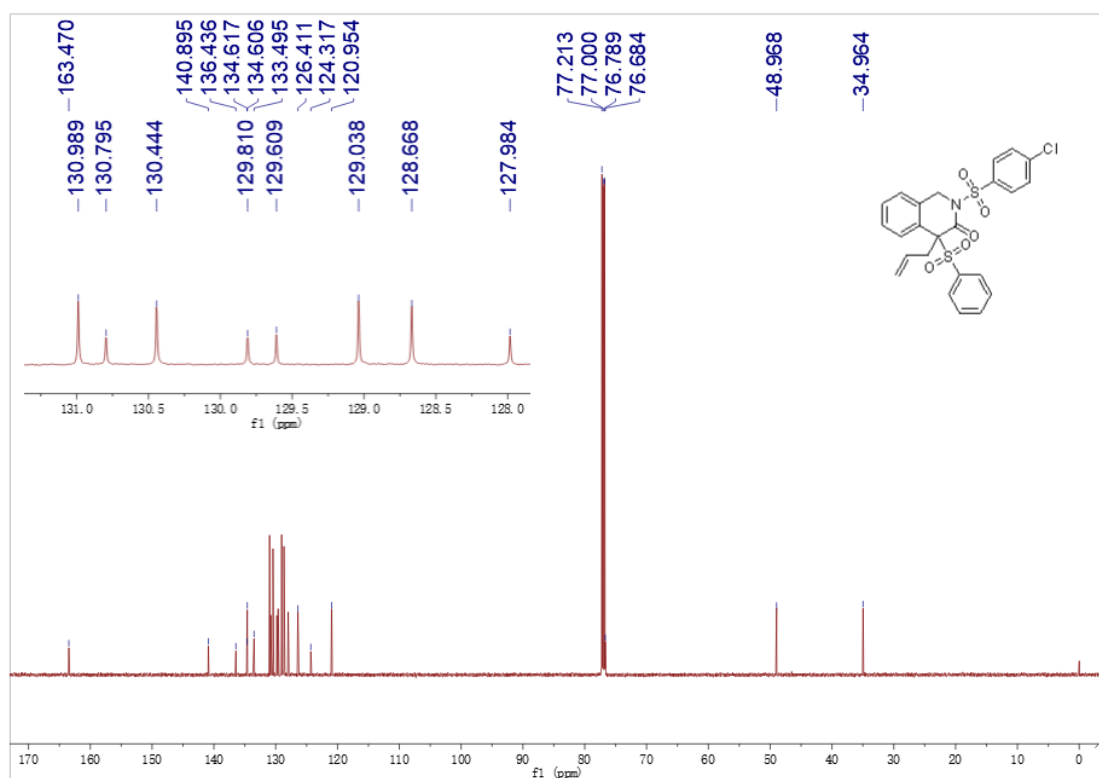
¹H NMR of **6a** (CDCl₃, 600 MHz)



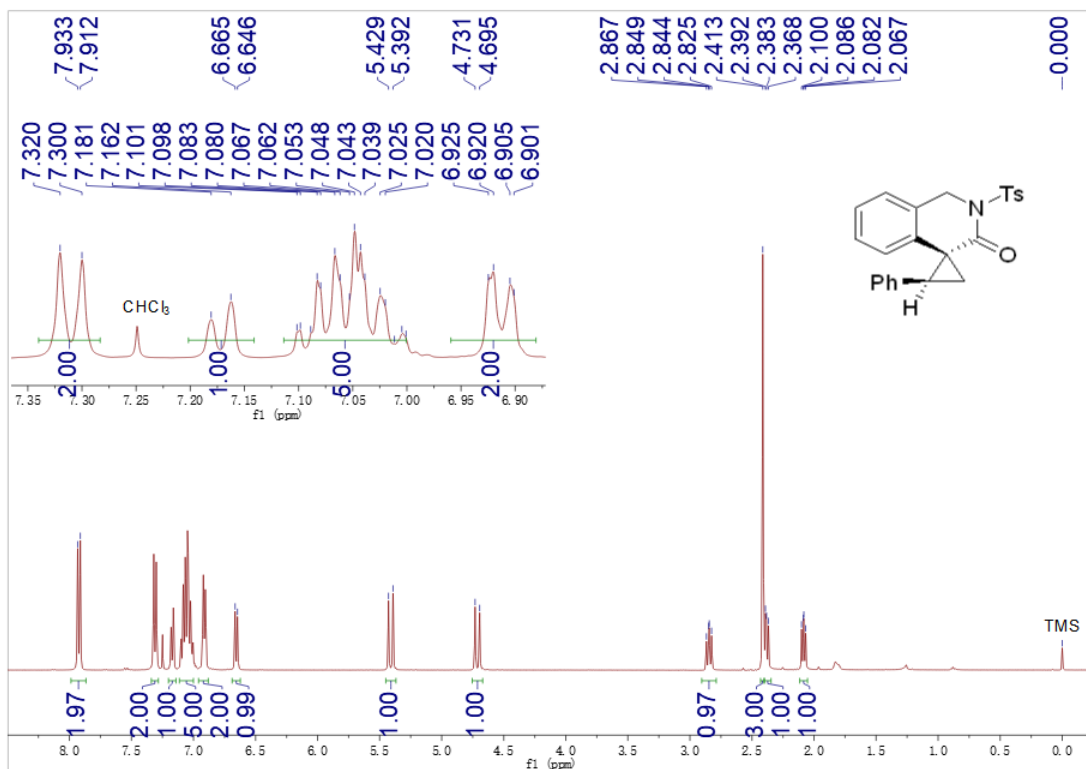
¹³C{¹H} NMR of **6a** (CDCl₃, 150 MHz)



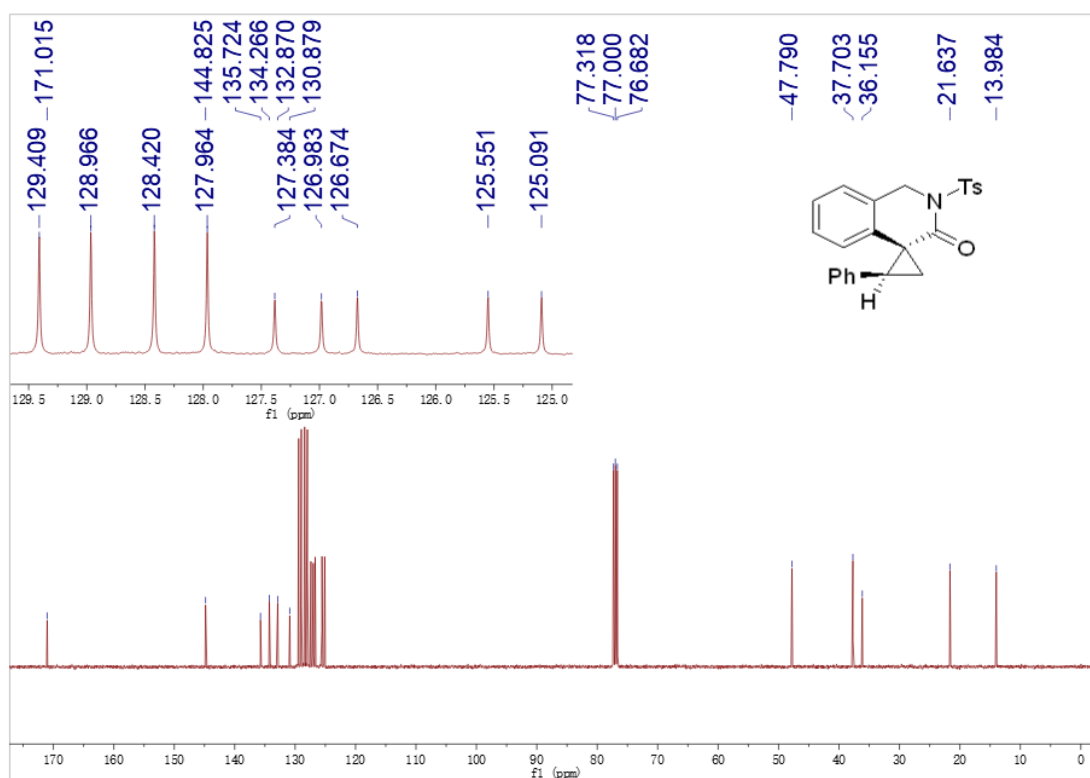
¹H NMR of **6b** (CDCl₃, 600 MHz)



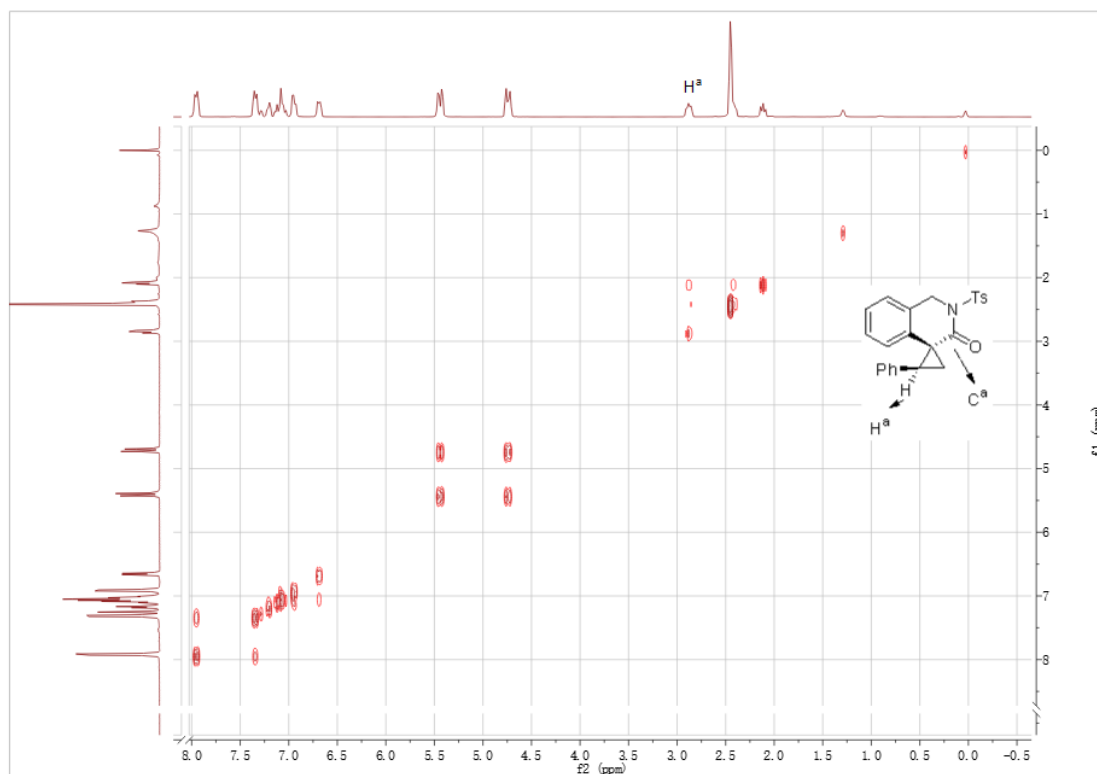
¹³C{¹H} NMR of **6b** (CDCl₃, 150 MHz)



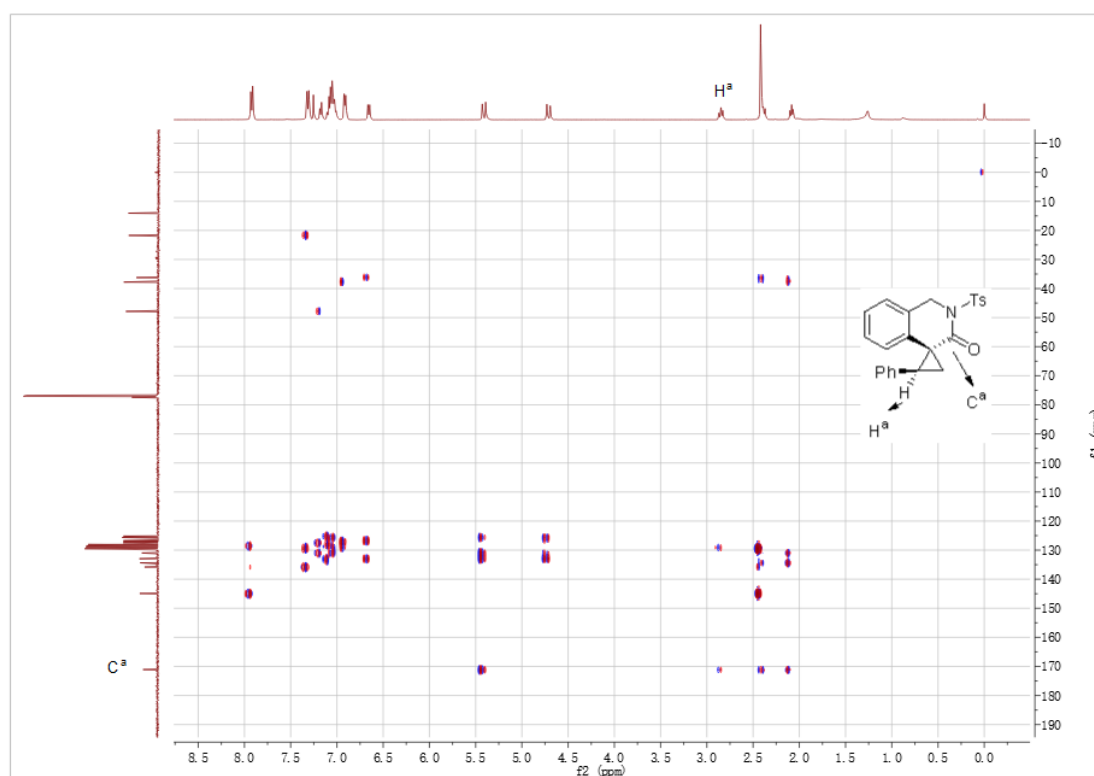
¹H NMR of 7 (CDCl₃, 400 MHz)



¹³C{¹H} NMR of 7 (CDCl₃, 100 MHz)



$^1\text{H} - ^1\text{H}$ COSY NMR of **7** (CDCl_3 , 400 MHz)



$^1\text{H} - ^{13}\text{C}$ HMBC NMR of **7** (CDCl_3 , 100 MHz)