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Supporting Information

Electrochemical trifluoroalkylation/annulation for the synthesis of CF_3-functionalized tetrahydroquinolines and dihydroquinolinones

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Contents

1. General Information

Commercial reagents were purchased from J&K Scientific, Aladdin, Energy-chemical, Macklin companies and used without further purification. The reactions were detected by thin layer chromatography (TLC) on Yinlong silica gel HSGF254 plates (0.2 ± 0.03 mm), appeared by ultraviolet light or by appropriate staining with a phosphomolybdic acid solutions or alkaline potassium permanganate solutions. ^{1}H NMR spectra were obtained on Bruker Avance 400MR or Bruker Avance 600MR spectrometer at ambient temperature. The data marking mode as follows: chemical shift on the δ scale using residual proton solvent as internal standard [δ 7.26 ($CDCl_3$) ppm; TMS: 0.00 ppm], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), integration, and coupling constant (*J*) in hertz (Hz). ^{13}C NMR spectra were obtained with proton decoupling on Bruker Avance 400MR (101 MHz) or Bruker Avance 600MR (151 MHz) spectrometer and were reported in ppm with residual solvent for internal standard [δ 77.0 ($CDCl_3$) ppm]. High resolution mass spectra were obtained on a Bruker impact II spectrometer. Mettler toledo electronic balance is used for reaction feeding, which model is ME204E/02 produced by Shanghai Mettler-Toledo Instrument Co., Ltd. Its maximum weighing is 220g, and the actual scale is 0.1 mg. The potentiometer is ITECH IT6720 model (60V / 5A / 100W).

2. General Procedures for The Electrolysis

A 10 mL three-necked round-bottomed flask (Figure S1) was equipped with a graphite rod (Ø = 6.0 mm) anode and a Platinum (2 cm x 1 cm x 1mm) cathode, then remove water and oxygen with Schlenk line. Then the the flask was charged with **1a** (0.2 mmol, 1.0 eq.), $LiClO_4$ (0.8 mmol, 4.0 eq.), $NaSO_2CF_3$ (0.8 mmol, 4.0 eq.) CuOTf (0.01mmol, 0.05 eq.), 2,2'-bipyridine (0.02 mmol, 0.1 eq.), then Superdry CH_3CN (5 mL) was added respectively. The electrolysis reaction was carried out at room temperature using a constant current of 10 mA until complete consumption of the substrate (monitored by TLC). The reaction mixture was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/hexane to give the desired products.

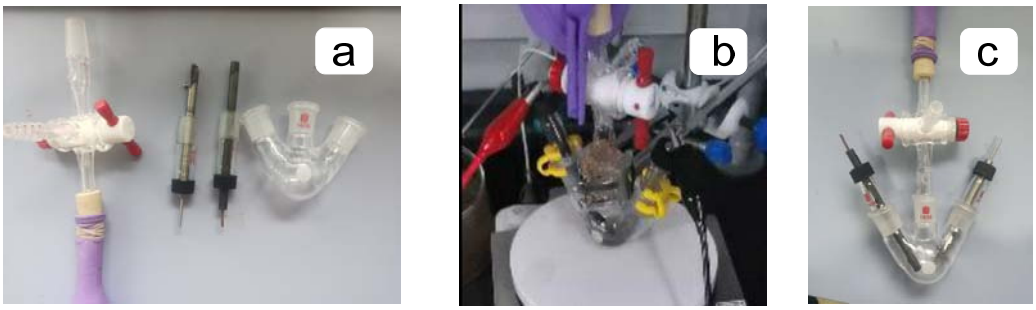
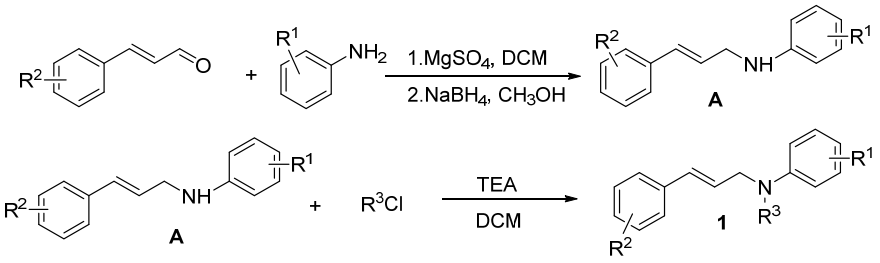


Figure S1. The electrolytic cell for small scale reactions.

3. Synthesis of Starting Materials

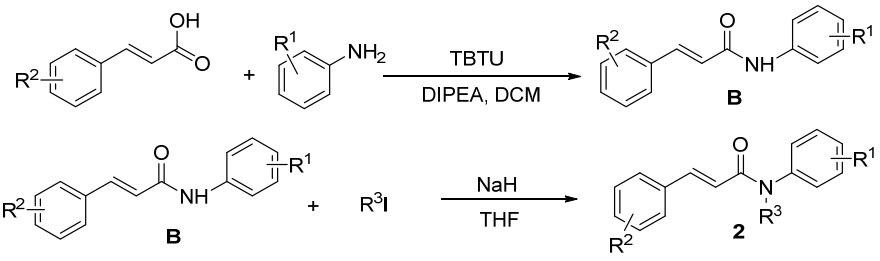
3.1 General procedures for the synthesis of 1a-1k



Procedure A[1]: The primary amine (1.0 eq.), aldehyde (1.0 eq.) and $MgSO_4$ (3.0 eq.) were added to a round bottom flask with DCM solution for 12 hours in an ice bath and filtered. The liquid phase was concentrated under reduced pressure, dissolved with MeOH. Then add $NaBH_4$ in batches in ice bath for 1 hour, quench the reaction with water, separation of liquid by extraction. The corresponding products (**A**) were obtained by eluted the silica gel column with ethyl acetate to petroleum ether from 1:30 to 1:10.

The **A** (1.0 eq.), Et_3N (3.0 eq.), acyl chloride (1.5 eq.) and DCM were added to a round bottom flask, ice bathed for 12 hours. After the reaction is completed, it was diluted with water and extracted with DCM. The combined organic phases were washed with saturated NaCl solution and dried over anhydrous Na_2SO_4. Finally, the dried organic phase is concentrated in vacuo. The concentrated crude products were respectively loaded onto a silica gel column and the corresponding products were afforded by eluted the silica gel column with ethyl acetate to petroleum ether from 1:10 to 1:2. These products **1** are mainly white solids.

3.2 General procedures for the synthesis of 2a – 2i

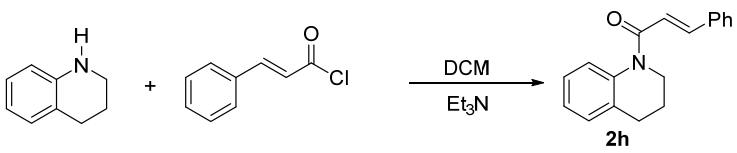


Procedure B[2]: The carboxylic acid (1.0 eq.), amine (1.0 eq.), TBTU (1.1 eq.), DIPEA (3.0 eq.) and DCM were added to a round bottom flask for 12 hours. After the reaction is completed, it was diluted with water and extracted with DCM. The organic phase was dried by $MgSO_4$. The corresponding products (**B**) were obtained by eluted the silica gel column with ethyl acetate to petroleum ether from 1:10 to 1:4.

Put **B** (1.0 eq.) and THF into a round bottom flask, ice bath and add NaH in batches. After 1 hour of stirring,

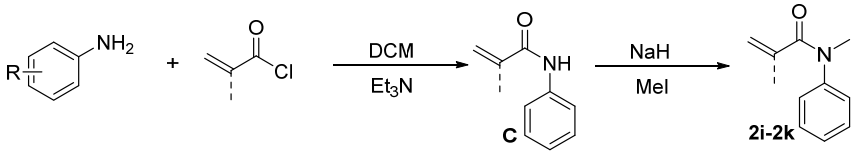
halogenated hydrocarbon (3.0 eq.) was added into flask and the mixture keep stirred for 5 hours. Separation of liquid by extraction. The corresponding products were afforded by eluted the silica gel column with ethyl acetate to petroleum ether from 1:20 to 1:5. Products **2** are white solid.

3.3 General procedure for the synthesis of 2h



The 1,2,3,4-tetrahydroquinoline (0.27 g,1.0 eq.), Et_3N (0.61 g, 3.0 eq.), cinnamoyl chloride (0.33g ,1.0 eq.) and DCM were added to a round bottom flask, ice bathed for 12 hours. After the reaction is completed, it was diluted with water and extracted with DCM. After evaporation of the solvent under reduced pressure, the crude product was purified by flash chromatography on silica gel with ethyl acetate to petroleum ether from 1:20 to 1:2. The product **2h** is white solid.

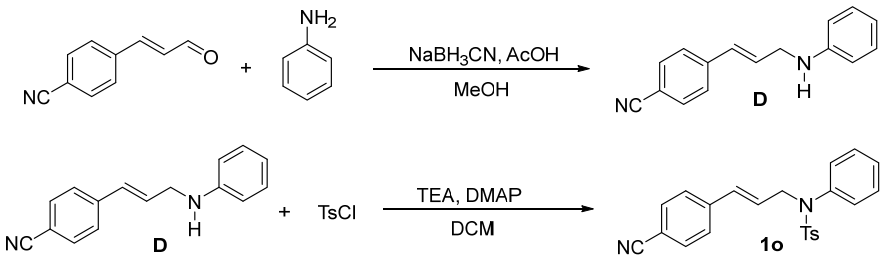
3.4 General procedure for the synthesis of 2i-2k[3]



The aniline (1.0 eq.), methacryloyl chloride (1.5 eq.), Et_3N (3.0 eq.) and DCM were added to a round bottom flask for 12 hours. After the reaction is completed, it was diluted with water and extracted with DCM. The organic phase was dried by $MgSO_4$. The corresponding product **C** was obtained by eluted the silica gel column with ethyl acetate to petroleum ether from 1:10.

Put *N*-phenylmethacrylamide **C** (1.0 eq.) and THF into a round bottom flask, ice bath and add NaH in batches. After 1 hour of stirring, iodomethane (3.0 eq.) was added into flask and the mixture keep stirred for 5 hours. Separation of liquid by extraction. The corresponding products were afforded by eluted the silica gel column with ethyl acetate to petroleum ether from 1:5. The products **2i-2k** were obtained.

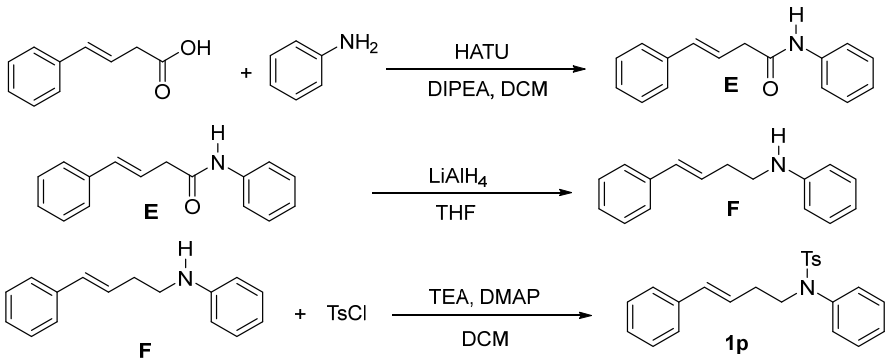
3.5 General procedure for the synthesis of 1o[1]



Put (*E*)-4-(3-oxoprop-1-en-1-yl) benzonitrile (726 mg, 1.0 eq.), MeOH, $NaBH_3CN$ (471 mg, 1.1 eq.), aniline (466 mg, 1.1 eq.) and AcOH (0.5 mL) into a round bottom flask in ice bath and stirred at room temperature for overnight. The reaction was diluted with water, quenched with 10 % NaOH and filtered. The aqueous phase extracted with ethyl acetate. The combined organic extracts were dried by anhydrous Na_2SO_4. The corresponding product **D** was obtained by eluted the silica gel column with ethyl acetate to petroleum ether 1:20.

The (*E*)-4-(3-(phenylamino)prop-1-en-1-yl) benzonitrile **D** (749 mg, 1.0 eq.), DCM, Et_3N (1.3 mL, 2.0 eq.), DMAP (61 mg. 0.1 eq.) and 4-methylbenzene-sulfonyl chloride (677 mg, 1.2 eq.) were added into flask and the mixture was stirred at room temperature for 5 hours. The reaction mixture was concentrated under reduced pressure. The crude mixture was purified on silica gel with ethyl acetate to petroleum ether 1:10 as eluent to give the corresponding product (*E*)-*N*-(3-(4-cyanophenyl) allyl)-4-methyl-*N*-phenylbenzenesulfonamide **1o**.

3.6 General procedure for the synthesis of 1p[1]



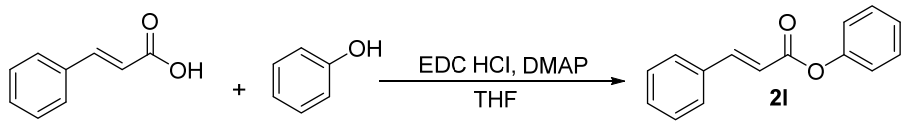
The (*E*)-4-phenylbut-3-enoic acid (500.0 mg, 1.0 eq.), amine (286.8 mg, 1.0 eq.), HATU (1.5 g, 1.25 eq.), DIPEA (1.2 g, 3.0 eq.) and DCM were added to a round bottom flask for 12 hours. After the reaction is completed, it was diluted with water and extracted with DCM. The organic phase was dried by anhydrous Na_2SO_4. The corresponding product (*E*)-*N*,4-diphenylbut-3-enamide **E** was obtained by eluted the silica gel column with ethyl acetate to petroleum ether from 1:10 to 1:5.

Put (E)-N,4-diphenylbut-3-enamide **E** (700 mg, 1.0 eq.) and THF into a round bottom flask, and add $LiAlH_4$

(335.8 mg, 3.0 eq.) in batches for 2 hours. The reaction was diluted with water, quenched with 10 % NaOH and filtered. The aqueous phase extracted with ethyl acetate. The combined organic extracts were dried by anhydrous Na_2SO_4. The corresponding product **F** was obtained by eluted the silica gel column with ethyl acetate to petroleum ether 1:10.

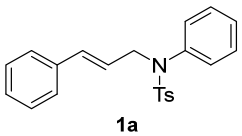
The (*E*)-*N*-(4-phenylbut-3-en-1-yl) aniline **F** (71.6 mg, 1.0 eq.), DCM, Et_3N (64.8 mg, 2.0 eq.), DMAP (3.59 mg, 0.1 eq.) and 4-methylbenzene-sulfonyl chloride (73.2 mg, 1.2 eq.) were added into flask and the mixture was stirred at room temperature for 5 hours. The reaction mixture was concentrated under reduced pressure. The crude mixture was purified on silica gel with ethyl acetate to petroleum ether 1:10 as eluent to give the corresponding product **1p**.

3.7 General procedure for the synthesis of 2l[7]



The cinnamic acid (865.8 mg, 1.1 eq.), phenol (500.0 mg, 1.0 eq.), THF, EDC·HCl (1.12 g, 1.1 eq.) and DMAP (33.0 mg, 0.05 eq.) were added to a round bottom flask for overnight. After the reaction is completed, it was diluted with water and extracted with DCM. The organic phase was dried by anhydrous Na_2SO_4. The corresponding product phenyl cinnamate **2l** was obtained by eluted the silica gel column with ethyl acetate to petroleum ether from 1:10 to 1:5.

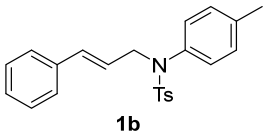
***N*-cinnamyl-4-methyl-*N*-phenylbenzenesulfonamide(1a) [1]:**



1a

According to procedure **A**, aniline (0.93 g, 1.0 eq.), 3-phenylpropanal (1.32 g, 22.0 mmol, 1.1 equiv) and 4-methylbenzenesulfonyl chloride (2.01 g, 1.05 eq.) gave **1a** (2.61 g, 72 %) as white solid; R_f = 0.62 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 7.9 Hz, 2H), 7.30 – 7.11 (m, 8H), 7.20 (dd, J = 13.0, 5.9 Hz, 2H), 7.10 – 7.06 (m, 2H), 6.37 (d, J = 15.8 Hz, 1H), 6.10 (dt, J = 15.7, 6.6 Hz, 1H), 4.33 (d, J = 6.6 Hz, 2H), 2.42 (s, 3H).

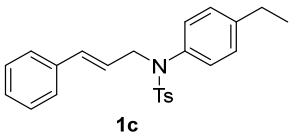
***N*-cinnamyl-4-methyl-*N*-(p-tolyl)benzenesulfonamide (1b) [1]:**



1b

According to procedure **A**, p-toluidine (1.13 g, 1.05 eq.), 3-phenylpropanal (1.32 g, 1.0 eq.) and 4-methylbenzenesulfonyl chloride (2.01 g, 1.05 eq.) gave **1b** (1.83 g, 69 %) as white solid; R_f = 0.56 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, J = 7.9 Hz, 2H), 7.31 – 7.17 (m, 7H), 7.07 (d, J = 7.9 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.36 (d, J = 15.8 Hz, 1H), 6.09 (dt, J = 15.8, 6.6 Hz, 1H), 4.30 (d, J = 6.5 Hz, 2H), 2.43 (s, 3H), 2.30 (s, 3H).

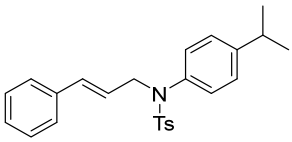
***N*-cinnamyl-*N*-(4-ethylphenyl)-4-methylbenzenesulfonamide (1c):**



1c

According to procedure **A**, 4-ethylaniline (0.61 g, 1.0 eq.), 3-phenylpropanal (0.66 g, 1.0 eq.) and 4-methylbenzenesulfonyl chloride (2.01 g, 1.05 eq.) gave **1c** (1.83 g, 69 %) as white solid; mp 117-121 ˚C; R_f = 0.56 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, J = 7.8 Hz, 2H), 7.28 – 7.17 (m, 6H), 7.20 – 7.18 (m, 1H),7.09 (d, J = 7.8 Hz, 2H), 6.98 (d, J = 7.8 Hz, 2H), 6.37 (d, J = 15.9 Hz, 1H), 6.10 (dt, J = 15.8, 6.6 Hz, 1H), 4.31 (d, J = 6.5 Hz, 2H), 2.61 (q, J = 7.6 Hz, 2H), 2.42 (s, 3H), 1.20 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.0, 143.3, 136.9, 136.5, 136.2, 133.6, 129.4, 128.8, 128.5, 128.4, 127.8, 127.7, 126.5, 124.4, 53.5, 28.4, 21.5, 15.1 MS (ESI) m/z calcd for $C_{24}H_{25}NNaO_2S^+$ $[M+Na]^+$ 414.1498, found 414.1498.

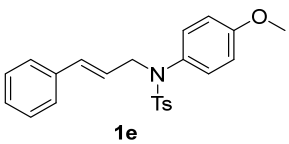
***N*-cinnamyl-*N*-(4-isopropylphenyl)-4-methylbenzenesulfonamide (1d):**



1d

According to procedure **A**, 4-isopropylaniline (0.68 g, 1.0 eq.), 3-phenylpropanal (0.66 g, 1.0 eq.) and 4-methylbenzenesulfonyl chloride (2.01 g, 1.05 eq.) gave **1d** (1.36 g, 67 %) as white solid; mp 123-124˚C; R_f = 0.56 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 2H), 7.23 (dt, *J* = 23.7, 7.6 Hz, 7H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.7, 6.6 Hz, 1H), 4.30 (d, *J* = 6.6 Hz, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.6, 143.2, 136.9, 136.5, 133.5, 129.4, 128.7, 128.5, 127.8, 127.7, 127.0, 126.4, 124.5, 53.5, 33.7, 23.8, 21.5. MS (ESI) m/z calcd for $C_{25}H_{28}NO_2S^+$ $[M+H]^+$ 406.1835, found 406.1835.

***N*-cinnamyl-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (1e) [1]:**

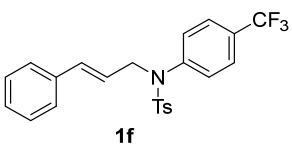


1e

According to procedure **A**, 4-methoxyaniline (1.29 g, 1.05 eq.), 3-phenylpropanal (1.32 g, 1.0 eq.) and 4-methylbenzenesulfonyl chloride (4.02 g, 1.05 eq.) gave **1e** (1.96 g, 50 %) as white solid; R_f = 0.60 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 2H), 7.27 – 7.18 (m, 7H), 6.98 – 6.94 (m, 2H), 6.80 – 6.75 (m, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.7, 6.7 Hz, 1H), 4.31 – 4.27 (m, 2H), 3.77 (s, 3H), 2.43 (s, 3H).

***N*-cinnamyl-4-methyl-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (1f) [1]:**

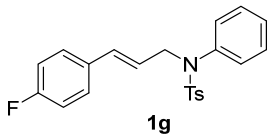
According to procedure **A**, 4-(trifluoromethyl)aniline (1.13 g, 1.05 eq.), 3-phenylpropanal (1.32 g, 1.0 eq.) and 4-methylbenzenesulfonyl chloride (1.65 g, 1.05 eq.) gave **1f** (1.76 g, 66 %) as white solid; R_f = 0.57 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 24.2, 8.1 Hz, 4H), 7.27 – 7.19 (m, 9H), 6.39 (d, *J* = 15.8 Hz,



1f

1H), 6.07 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.36 (d, *J* = 6.5 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.9, 142.7, 136.1, 135.5, 134.3, 129.7, 129.6(q, J_{C-F}= 31.5 Hz), 128.7, 128.6, 128.0, 127.7, 126.5, 126.1, 126.0, 123.8(q, J_{C-F}= 270 Hz), 123.5, 53.0, 21.5. MS (ESI) m/z calcd for $C_{23}H_{20}F_3NNaO_2S^+$ $[M+Na]^+$ 454.1059, found 454.1059.

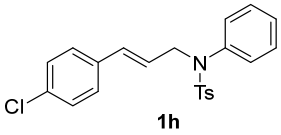
***N*-(3-(4-fluorophenyl)allyl)-4-methyl-*N*-phenylbenzenesulfonamide (1g) [1]:**



1g

According to procedure **A**, aniline (0.65 g, 1.05 eq.), 3-(4-fluorophenyl)acrylaldehyde (1 g, 1.0 eq.) and 4-methylbenzenesulfonyl chloride (1.22 g, 1.05 eq.) gave **1g** (1.78 g, 63 %) as white solid; R_f = 0.57 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.31 – 7.22 (m, 5H), 7.19 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.09 – 7.05 (m, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.02 (dt, J = 15.7, 6.6 Hz, 1H), 4.32 (d, *J* = 6.3 Hz, 2H), 2.43 (s, 3H).

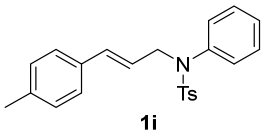
***N*-(3-(4-chlorophenyl)allyl)-4-methyl-*N*-phenylbenzenesulfonamide (1h) [1]:**



1h

According to procedure **A**, aniline (0.51 g, 1.1 eq.), 3-(4-chlorophenyl)acrylaldehyde (0.83 g, 1.0 eq.) and 4-methylbenzenesulfonyl chloride (1.93 g, 1.1 eq.) gave **1h** (1.08 g, 55 %) as white solid; R_f = 0.59 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.19 (m, 7H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.09 – 7.05 (m, 2H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.08 (dt, *J* = 15.8, 6.5 Hz, 1H), 4.32 (dd, *J* = 6.5, 1.4 Hz, 2H), 2.42 (s, 3H).

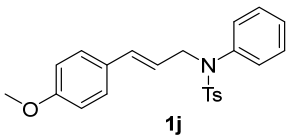
4-Methyl-*N*-phenyl-*N*-(3-(p-tolyl)allyl)benzenesulfonamide (1i) [1]:



1i

According to procedure **A**, aniline (0.67 g, 1.05 eq.), 3-(p-tolyl)acrylaldehyde (1 g, 1.0 eq.) and 4-methylbenzenesulfonyl chloride (0.88 g, 1.05 eq.) gave **1i** (1.88 g, 71 %) as white solid; R_f = 0.62 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.31 – 7.15 (m, 9H), 7.06 – 7.01 (m, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.27 (d, *J* = 15.8 Hz, 1H), 6.11 (dt, *J* = 15.7, 7.0 Hz, 1H), 4.46 (dd, *J* = 14.3, 6.2 Hz, 1H), 4.05 (dd, *J* = 14.3, 7.8 Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H).

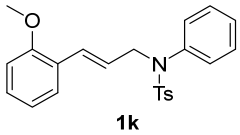
***N*-(3-(4-methoxyphenyl)allyl)-4-methyl-*N*-phenylbenzenesulfonamide (1j) [1]:**



1j

According to procedure **A**, aniline (0.61 g, 1.05 eq.), 3-(4-methoxyphenyl) acrylaldehyde (1 g, 1.0 eq.) and 4-methylbenzenesulfonyl chloride (1.23 g, 1.05 eq.) gave **1j** (2.18 g, 89 %) as white solid; R_f = 0.65 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.31 – 7.21 (m, 5H), 7.18 – 7.14 (m, 2H), 7.07 (dt, *J* = 5.9, 1.6 Hz, 2H), 6.81 – 6.76 (m, 2H), 6.30 (d, *J* = 15.8 Hz, 1H), 5.95 (dt, *J* = 15.7, 6.7 Hz, 1H), 4.33 – 4.30 (m, 2H), 3.77 (s, 3H), 2.42 (s, 3H).

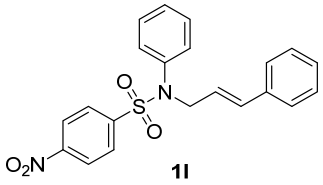
***N*-cinnamyl-4-methyl-N-(o-tolyl)benzenesulfonamide (1k):**



1k

According to procedure **A**, aniline (0.61 g, 1.0 eq.), 3-(2-methoxyphenyl) acrylaldehyde (0.66 g, 1.0 eq.) and 4-methylbenzenesulfonyl chloride (1.05 g, 1.05 eq.) gave **1k** (1.33 g, 53 %) as white solid; mp 115-120 ˚C; R_f = 0.65 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.28 – 7.21 (m, 6H), 7.19 – 7.14 (m, 1H), 7.08 (dt, *J* = 7.5, 2.3 Hz, 2H), 6.86 – 6.81 (m, 1H), 6.79 (dd, *J* = 8.3, 3.0 Hz, 1H), 6.68 (dd, *J* = 16.1, 3.3 Hz, 1H), 6.09 (dddd, *J* = 15.8, 8.8, 4.3, 2.1 Hz, 1H), 4.37 – 4.32 (m, 2H), 3.75 – 3.72 (m, 3H), 2.42 – 2.39 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 143.3, 139.4, 136.0, 129.4, 129.0, 128.9, 128.8, 127.8, 127.7, 127.0, 125.6, 124.7, 120.6, 111.0, 55.5, 53.7, 21.5.MS (ESI) m/z calcd for $C_{23}H_{23}NNaO_3S^+$ $[M+Na]^+$ 416.1291, found 416.1283.

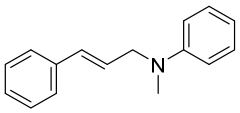
***N*-cinnamyl-4-nitro-*N*-phenylbenzenesulfonamide (1l):**



1l

According to procedure **A**, aniline (0.52 g, 1.0 eq.), 3-phenylpropanal (0.66 g, 1.0 eq.) and 4-nitrobenzenesulfonyl chloride (1.05 g, 1.25 eq.) gave **1l** (1.18 g, 59 %) as pink solid; mp 127-130 ˚C; R_f = 0.55 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 – 8.25 (m, 2H), 7.82 – 7.78 (m, 2H), 7.33 – 7.29 (m, 3H), 7.28 – 7.19 (m, 5H), 7.07 (dd, *J* = 7.1, 2.7 Hz, 2H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.7, 6.7 Hz, 1H), 4.39 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 144.8, 138.5, 136.0, 134.7, 129.4, 128.9, 128.9, 128.6, 128.5, 128.5, 128.1, 126.5, 124.1, 123.2, 54.0. MS (ESI) m/z calcd for $C_{21}H_{18}N_2NaO_4S^+$ $[M+Na]^+$ 417.0879, found 417.0881.

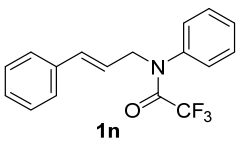
***N*-cinnamyl-*N*-methylaniline (1m) [1]:**



1m

According to procedure **A**, aniline (0.52 g, 1.0 eq.), 3-phenylpropanal (0.66 g, 1.0 eq.) and iodomethane (2.128 g, 3.0 eq.) gave 1**m** (0.94 g, 84 %) as white solid; R_f = 0.55 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.14 (m, 7H), 6.79 (dd, *J* = 8.3, 4.0 Hz, 2H), 6.72 (dt, *J* = 11.4, 5.6 Hz, 1H), 6.55 – 6.49 (m, 1H), 6.24 (dtd, *J* = 15.8, 5.5, 3.0 Hz, 1H), 4.08 (dd, *J* = 5.2, 2.9 Hz, 2H), 2.98 (dd, *J* = 5.0, 2.7 Hz, 3H).

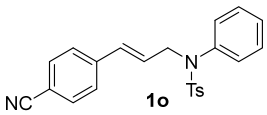
***N*-cinnamyl-2,2,2-trifluoro-*N*-phenylacetamide (1n) [1]:**



1n

According to procedure **A**, aniline (0.93 g, 1.0 eq.), 3-phenylpropanal (1.32 g, 1.0 eq.) and 2,2,2-trifluoroacetyl chloride (2.62 g, 2 eq.) gave **1n** (2.74 g, 92 %) as white solid; R_f = 0.42 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 4.9, 2.0 Hz, 3H), 7.35 – 7.29 (m, 4H), 7.28 – 7.19 (m, 3H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.46 (d, *J* = 7.0 Hz, 2H).

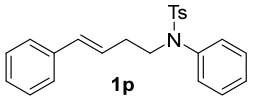
(*E*)-*N*-(3-(4-cyanophenyl) allyl)-4-methyl-*N*-phenylbenzenesulfonamide (1o):



1o

Aniline (466 mg, 1.1 eq.), (*E*)-4-(3-oxoprop-1-en-1-yl) benzonitrile (726 mg, 1.0 eq.) and 4-methylbenzene-sulfonyl chloride (677 mg, 1.2 eq.) gave **1o** (427 mg, 34 %) as white solid; R_f = 0.30 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.43 (m, 4H), 7.37 – 7.21 (m, 8H), 7.13 – 7.02 (m, 2H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.25 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.36 (dd, *J* = 6.3, 1.4 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.66, 140.81, 132.35, 131.79, 129.51, 129.10, 128.78, 128.51, 128.03, 127.75, 126.93, 118.78, 111.09, 53.04, 21.55. MS (ESI) m/z calcd for $C_{23}H_{21}N_2O_2S^+$ $[M+H]^+$ 389.1318, found 389.1319.

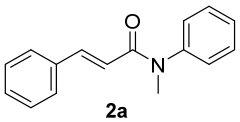
(*E*)-4-methyl-*N*-phenyl-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (1p) [1]:



1p

Aniline (286.8 mg, 1.0 eq.), (*E*)-4-phenylbut-3-enoic acid (500.0 mg, 1.0 eq.) and 4-methylbenzene-sulfonyl chloride (73.2 mg, 1.2 eq.) gave **1p** (70.4 mg, 61 %) as white solid; Rf = 0.30 (silica gel, PE: EA = 5:1). 1H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 2H), 7.29 (dd, J = 21.1, 5.8 Hz, 7H), 7.25 – 7.18 (m, 3H), 7.07 (dd, J = 7.4, 2.0 Hz, 2H), 6.33 (d, J = 15.8 Hz, 1H), 6.08 (dt, J = 15.8, 7.0 Hz, 1H), 3.67 (t, J = 7.3 Hz, 2H), 2.41 (s, 4H), 2.35 (q, J = 7.2 Hz, 2H).

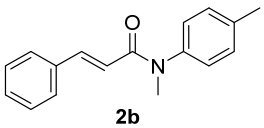
***N*-methyl-*N*-phenylcinnamamide (2a) [2]:**



2a

According to procedure **B**, aniline (1 g, 1.0 eq.), cinnamoyl chloride (1.97 g, 1.1 eq.) and iodomethane (1.68 g, 3 eq.) gave **2a** (0.6 g, 24 %) as white solid; R_f = 0.48 (silica gel, PE: EA = 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 15.5 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.33 – 7.26 (m, 5H), 7.25 – 7.22 (m, 2H), 6.37 (d, *J* = 15.5 Hz, 1H), 3.41 (s, 3H).

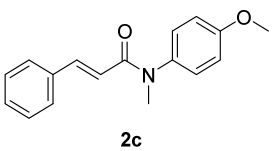
***N*-methyl-*N*-(p-tolyl)cinnamamide (2b) [2]:**



2b

According to procedure **B**, p-toluidine (0.54 g, 1.0 eq.), cinnamoyl chloride (0.92 g, 1.1 eq.) and iodomethane (2.13 g, 3 eq.) gave **2b** (0.82 g, 65 %) as white solid; R_f = 0.47 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 15.5 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.27 (dd, J = 8.3, 5.6 Hz, 3H), 7.22 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 6.38 (d, J = 15.5 Hz, 1H), 3.38 (s, 3H), 2.41 (s, 3H).

***N*-(4-methoxyphenyl)-*N*-methylcinnamamide (2c) [2]:**

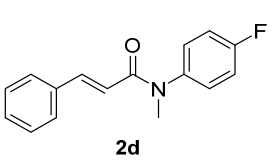


2c

According to procedure **B**, 4-methoxyaniline (0.62 g, 1.0 eq.), cinnamoyl chloride (0.92 g, 1.1 eq.) and iodomethane (2.13 g, 3 eq.) gave **2c** (0.3 g, 23 %) as white solid; R_f = 0.51 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 15.6 Hz, 1H), 7.33 – 7.25 (m, 5H), 7.16 – 7.12 (m, 2H), 6.96 – 6.88 (m, 2H), 6.37 (d, *J* = 15.5 Hz, 1H), 3.85 (s, 3H), 3.37

(s, 3H).

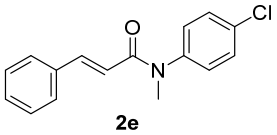
***N*-(4-fluorophenyl)-*N*-methylcinnamamide (2d) [2]:**



2d

According to procedure **B**, 4-fluoroaniline (0.56 g, 1.0 eq.), cinnamoyl chloride (0.92 g, 1.1 eq.) and iodomethane (2.13 g, 3 eq.) gave **2d** (0.5 g, 30 %) as white solid; R_f = 0.42 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 15.5 Hz, 1H), 7.34 – 7.26 (m, 5H), 7.21 (dd, *J* = 8.6, 4.9 Hz, 2H), 7.13 (t, *J* = 8.3 Hz, 2H), 6.32 (d, *J* = 15.5 Hz, 1H), 3.38 (s, 3H).

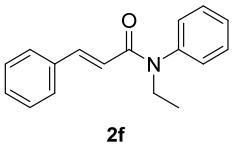
***N*-(4-chlorophenyl)-*N*-methylcinnamamide (2e) [2]:**



2e

According to procedure **B**, 4-chloroaniline (0.64 g, 1.0 eq.), cinnamoyl chloride (0.92 g, 1.1 eq.) and iodomethane (2.13 g, 3 eq.) gave **2e** (0.82 g, 61 %) as white solid; R_f = 0.5 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 15.5 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.35 – 7.27 (m, 5H), 7.20 – 7.15 (m, 2H), 6.35 (d, *J* = 15.5 Hz, 1H), 3.38 (s, 3H).

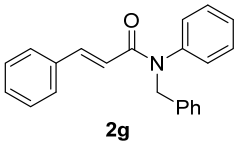
***N*-ethyl-*N*-phenylcinnamamide (2f) [2]:**



2f

According to procedure **B**, aniline (0.21 g, 1.0 eq.), cinnamoyl chloride (0.31 g, 1.1 eq.) and iodomethane (0.78 g, 3 eq.) gave **2f** (0.36 g, 86 %) as white solid; R_f = 0.61 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 15.6 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.38 (dd, *J* = 8.4, 6.5 Hz, 1H), 7.30 – 7.26 (m, 5H), 7.21 (dd, *J* = 7.3, 1.8 Hz, 2H), 6.27 (d, *J* = 15.6 Hz, 1H), 3.89 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H).

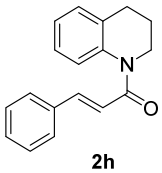
***N*-benzyl-*N*-phenylcinnamamide (2g) [2]:**



2g

According to procedure **B**, aniline (0.19 g, 1.0 eq.), cinnamoyl chloride (0.28 g, 1.1 eq.) and iodomethane (0.26 g, 1.5 eq.) gave **2g** (0.20 g, 63 %) as white solid; R_f = 0.64 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 15.5 Hz, 1H), 7.34 (dt, *J* = 11.0, 6.6 Hz, 3H), 7.27 (qd, *J* = 8.9, 8.1, 5.4 Hz, 10H), 7.06 (d, *J* = 7.3 Hz, 2H), 6.33 (d, *J* = 15.5 Hz, 1H), 5.03 (s, 2H).

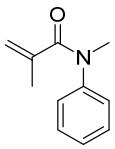
1-(3,4-dihydroquinolin-1(2H)-yl)-3-phenylprop-2-en-1-one (2h) [4]:



2h

According to 3.3 procedure, gave **2h** (0.20 g, 63 %) as white solid; R_f = 0.64 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 15.6 Hz, 1H), 7.44 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.22 – 7.11 (m, 4H), 6.85 (d, *J* = 15.5 Hz, 1H), 3.92 (t, *J* = 6.7 Hz, 2H), 2.76 (t, *J* = 6.6 Hz, 2H), 2.01 (p, *J* = 6.6 Hz, 2H).

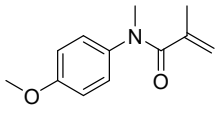
***N*-benzyl-*N*-phenylcinnamamide (2i) [3]:**



2i

According to 3.4 procedure, aniline (0.93 g, 1.0 eq.), cinnamoyl chloride (1.15 g, 1.1 eq.) and iodomethane (2.11 g, 1.5 eq.) gave **2i** (1.42 g, 72 %) as white solid; R_f = 0.52 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.8 Hz, 2H), 7.26 (s, 1H), 7.16 – 7.12 (m, 2H), 5.03 (t, *J* = 1.6 Hz, 1H), 4.99 (s, 1H), 3.35 (s, 3H), 1.76 (s, 3H).

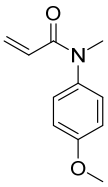
***N*-(4-methoxyphenyl)-*N*-methylmethacrylamide (2j) [3]:**



2j

According to 3.4 procedure, aniline (1.0 g, 1.0 eq.), cinnamoyl chloride (1.15 g, 1.1 eq.) and iodomethane (2.11 g, 1.5 eq.) gave **2j** (1.08 g, 64 %) as white solid; R_f = 0.5 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 – 7.00 (m, 2H), 6.95 – 6.78 (m, 2H), 5.02 (s, 1H), 4.99 (s, 1H), 3.81 (s, 3H), 3.30 (s, 3H), 1.74 (s, 3H).

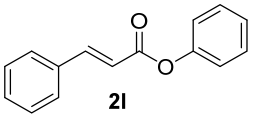
***N*-methyl-*N*-(*p*-tolyl)acrylamide (2k) [3]:**



2k

According to 3.4 procedure, aniline (0.5 g, 1.0 eq.), cinnamoyl chloride (1.15 g, 1.1 eq.) and iodomethane (2.11 g, 1.5 eq.) gave **2k** (0.56 g, 71 %) as white solid; R_f = 0.5 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.05 (m, 2H), 6.99 – 6.89 (m, 2H), 6.34 (dd, *J* = 16.8, 2.1 Hz, 1H), 6.07 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.49 (dd, *J* = 10.3, 2.1 Hz, 1H), 3.83 (s, 3H), 3.32 (s, 3H).

Phenyl cinnamate (2l) [7]:



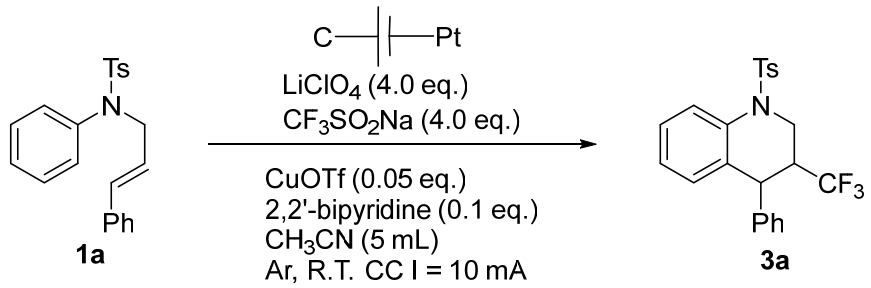
2l

According to 3.7 procedure, cinnamic acid (865.8 mg, 1.1 eq.) and phenol (500.0 mg, 1.0 eq.) gave **2l** (0.45 g, 38 %) as white solid; Rf = 0.70 (silica gel, PE: EA = 5:1). 1H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 15.9 Hz, 1H), 7.56 (dd, J = 6.6, 3.0 Hz, 2H), 7.39 (dd, J = 8.9, 5.6 Hz, 6H), 7.23 (t, J = 7.5 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 6.62 (d, J = 16.0 Hz, 1H).

4. Reaction Conditions Exploration and Products Data

4.1 Other optimization of the reaction conditions

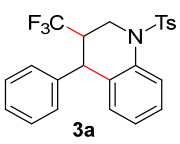
Table S1. Condition exploration



Entry	Deviation from above conditions	Yield(%)
1	None	60
2	No $LiClO_4$	trace
3	HCF_2SO_2Na instead of CF_3SO_2Na	0
4	CF_3SO_2Li instead of CF_3SO_2Na	0
5	$TMSCF_3$ instead of CF_3SO_2Na	0
6	80 ℃	40
7	DPPE instead of 2,2'-bipyridine	39
8	Pt(+) | Pt(-)	0
9	Pt(+) | C(-)	0
10	C(+) | C(-)	0
11	DMF	0
12	DMA	0
13	CF_3CH_2OH / MeCN (1:9)	0
14	Ackermann's conditions[6]	trace

4.2 Products 3 and 4 data

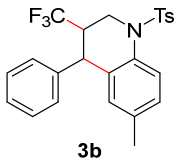
4-phenyl-1-tosyl-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (3a):



3a

According to general procedure, **1a** (72 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **3a** (52 mg, 60 %) as white solid; mp 129-132 ˚C; R_f = 0.75 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.18 (dt, *J* = 25.8, 7.9 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 2H), 7.03 – 6.98 (m, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 7.2 Hz, 2H), 4.65 (dd, *J* = 14.3, 3.8 Hz, 1H), 4.08 (d, *J* = 10.5 Hz, 1H), 3.49 (dd, *J* = 14.3, 11.7 Hz, 1H), 2.64 (dtp, *J* = 15.1, 7.7, 4.7, 3.8 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.5, 143.0, 136.6, 135.8, 131.8, 130.9, 130.2, 128.5, 128.5, 127.6, 127.2, 127.0, 126.6 (q, J_{C-F}= 279 Hz), 126.0, 124.8, 77.3, 77.0, 76.8, 45.0 (q, J_{C-F}= 3 Hz), 43.7 (q, J_{C-F}= 25.5 Hz), 43.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.62. MS (ESI) m/z calcd for $C_{23}H_{21}F_3NO_2S^+$ $[M+H]^+$ 432.1240, found 432.1238

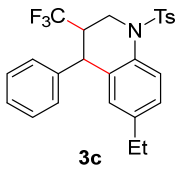
6-methyl-4-phenyl-1-tosyl-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (3b):



3b

According to general procedure, **1b** (76 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **3b** (40 mg, 45 %) as shapeless jelly; R_f = 0.75 (silica gel, PE: EA = 5:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.13 (m, 1H), 7.10 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.01 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.53 – 6.50 (m, 1H), 6.47 – 6.43 (m, 2H), 4.62 (dd, *J* = 14.3, 3.8 Hz, 1H), 4.03 (d, *J* = 10.4 Hz, 1H), 3.45 (dd, *J* = 14.3, 11.7 Hz, 1H), 2.61 (dtt, *J* = 15.0, 7.3, 3.6 Hz, 1H), 2.47 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3, 143.1, 136.7, 135.8, 133.3, 131.5, 131.1, 130.2, 128.5, 128.4, 128.1, 127.6, 126.9, 126.0 (q, J_{C-F}= 279 Hz), 124.8, 45.0 (q, J_{C-F}= 3 Hz), 43.8 (q, J_{C-F}= 24 Hz), 43.5, 21.6, 20.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.63. MS (ESI) m/z calcd for $C_{24}H_{22}F_3NNaO_2S^+$ $[M+Na]^+$ 468.1216, found 468.1214.

6-ethyl-4-phenyl-1-tosyl-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (3c):

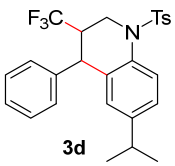


3c

According to general procedure, **1c** (79 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **3c** (42 mg, 45 %) as shapeless jelly; R_f = 0.80 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.13 (dt, *J* = 32.1, 7.5 Hz, 3H), 7.05 – 7.01 (m, 1H), 6.53 (s, 1H), 6.49 (d, *J* = 7.5 Hz, 2H), 4.61 (dd, *J* = 14.3, 3.8 Hz, 1H), 4.05 (d, *J* = 10.4 Hz, 1H), 3.47 (dd, *J* = 14.3, 11.7 Hz, 1H), 2.63 (dtd, *J* = 14.5, 7.5, 3.4 Hz, 1H), 2.47 (s, 3H), 2.41 (dp, *J* = 14.7, 7.2 Hz, 2H), 1.06 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3, 143.2, 142.0, 136.8, 133.5, 131.5, 130.1, 129.9, 128.5, 128.4, 127.6, 126.9, 126.8, 126.1 (q, J_{C-F}= 279 Hz), 124.7, 45.0 (q,

J_{C-F}= 4.5 Hz), 44.0 (q, J_{C-F}= 25.5 Hz), 43.5, 28.1, 21.5, 15.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.60. MS (ESI) m/z calcd for $C_{25}H_{25}F_3NO_2S^+$ $[M+H]^+$ 460.1553, found 460.1550.

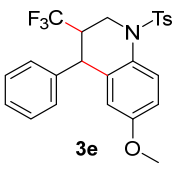
6-isopropyl-4-phenyl-1-tosyl-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (3d):



3d

According to general procedure, **1d** (81 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **3d** (32 mg, 34 %) as colorless liquid; R_f = 0.80 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.04 (m, 4H), 6.53 (dd, *J* = 16.6, 4.8 Hz, 3H), 4.59 (dd, *J* = 14.3, 3.9 Hz, 1H), 4.06 (d, *J* = 10.3 Hz, 1H), 3.47 (dd, *J* = 14.2, 11.6 Hz, 1H), 2.71 – 2.60 (m, 2H), 2.46 (s, 3H), 1.06 (dd, *J* = 23.7, 6.9 Hz, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 146.5, 144.3, 143.2, 136.3, 133.9, 131.4, 130.1, 128.7, 128.5, 128.4, 127.6, 126.9, 126.7(q, J_{C-F}= 265.5 Hz) 125.1, 124.6, 45.0, 45.0, 44.1(q, J_{C-F}= 24 Hz), 43.6, 33.3, 23.7, 23.6, 21.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.58. MS (ESI) m/z calcd for $C_{26}H_{26}F_3NNaO_2S^+$ $[M+Na]^+$ 496.1529, found 496.1526**.**

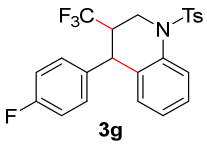
methoxy-4-phenyl-1-tosyl-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (3e):



3e

According to general procedure, **1e** (79 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **3e** (32 mg, 35 %) as shapeless jelly; R_f = 0.70 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.0 Hz, 1H), 7.69 – 7.57 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.12 (m, 1H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.77 (dd, *J* = 9.1, 2.9 Hz, 1H), 6.41 (d, *J* = 7.2 Hz, 2H), 6.20 (d, *J* = 2.9 Hz, 1H), 4.64 (dd, *J* = 14.4, 3.8 Hz, 1H), 3.99 (d, *J* = 10.7 Hz, 1H), 3.61 (d, *J* = 1.3 Hz, 3H), 3.45 (dd, *J* = 14.4, 11.9 Hz, 1H), 2.59 (ddp, *J* = 15.2, 7.8, 3.8 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 144.3, 142.7, 136.2, 134.4, 130.2, 129.8, 128.5, 128.5, 127.7, 126.9, 126.5, 126.0 (q, J_{C-F}= 279 Hz), 115.4, 113.1, 55.2, 45.2 (q, J_{C-F}= 4.5 Hz), 43.8, 43.4 (q, J_{C-F}= 25.5 Hz), 21.1. MS (ESI) m/z calcd for $C_{24}H_{22}F_3NNaO_2S^+$ $[M+Na]^+$ 484.1165, found 484.1163.

4-(4-fluorophenyl)-1-tosyl-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (3g):

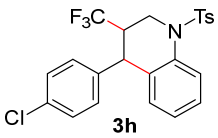


3g

According to general procedure, **1g** (77 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **3g** (41 mg, 46 %, *dr* 6/1) as brown oil; R_f = 0.67 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (dd, J = 8.3, 1.3 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.02 (td, J = 7.5, 1.3 Hz, 1H), 6.80 (t, J = 8.6 Hz, 2H), 6.71 (d, J = 7.9 Hz, 1H), 6.45 (dd, J = 8.5, 5.4 Hz, 2H), 4.63 (dd, J = 14.3, 3.8 Hz, 1H), 4.09 (d, J = 10.5 Hz, 1H), 3.47 (dd, J = 14.3, 11.7 Hz, 1H), 2.61 (tqd, J = 11.5, 7.6, 4.5 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 160.9, 144.5, 138.8, 138.8, 136.6, 135.8, 131.6, 130.7, 130.2, 130.1, 130.0, 127.7 (q, J_{C-F}= 279 Hz), 127.6, 127.3, 126.1, 125.0, 124.9, 115.5, 115.3, 45.0 (q,

J_{C-F}= 4.5 Hz), 44.2, 43.9 (q, J_{C-F}= 24 Hz), 43.7, 42.8, 29.7, 21.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.61, -115.26. MS (ESI) m/z calcd for $C_{23}H_{19}F_4NNaO_2S^+$ $[M+Na]^+$ 472.0965, found 472.0965.

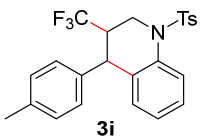
4-(4-chlorophenyl)-1-tosyl-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (3h):



3h

According to general procedure, **1h** (80 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **3h** (46 mg, 50 %, *dr* 2/1) as colorless oil; R_f = 0.72 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.22 (td, *J* = 8.3, 7.9, 1.6 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.02 (td, *J* = 7.6, 1.3 Hz, 1H), 6.70 (dt, *J* = 7.9, 1.3 Hz, 1H), 6.44 – 6.40 (m, 2H), 4.64 (dd, *J* = 14.3, 3.8 Hz, 1H), 4.08 (d, *J* = 10.5 Hz, 1H), 3.46 (dd, *J* = 14.3, 11.8 Hz, 1H), 2.60 (dtt, *J* = 15.2, 7.7, 3.8 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.6, 141.6, 136.6, 135.9, 132.9, 131.2, 130.7, 130.2, 129.9, 128.7, 127.6, 127.4, 126.1, 125.9 (q, J_{C-F}= 279 Hz), 125.0, 44.9 (q, J_{C-F}= 4.5 Hz), 44.9, 43.8 (q, J_{C-F}= 24 Hz), 42.9, 21.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.62. MS (ESI) m/z calcd for $C_{23}H_{20}ClF_3NO_2S^+$ $[M+H]^+$ 466.0850, found 466.0849.

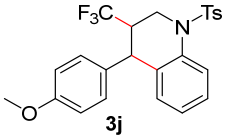
4-(p-tolyl)-1-tosyl-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (3i):



3i

According to general procedure, **1i** (73 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **3i** (51 mg, 57 %) as colorless oil; R_f = 0.75 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.03 (q, *J* = 8.4, 7.5 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 2H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.39 (d, *J* = 7.7 Hz, 2H), 4.65 (dt, *J* = 14.5, 5.4 Hz, 1H), 4.07 (d, *J* = 10.4 Hz, 1H), 3.51 (td, *J* = 12.8, 11.6, 2.3 Hz, 1H), 2.64 (tq, *J* = 7.7, 3.8 Hz, 1H), 2.50 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.4, 140.0, 136.7, 136.6, 135.8, 131.9, 130.8, 130.1, 129.2, 128.4, 127.6, 127.4, 127.1, 125.9, 124.7, 45.0 (q, J_{C-F}= 3 Hz), 43.7 (q, J_{C-F}= 24 Hz), 43.2, 21.6, 21.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.62. MS (ESI) m/z calcd for $C_{24}H_{22}F_3NNaO_2S^+$ $[M+Na]^+$ 468.1216, found 468.1214.

4-(4-methoxyphenyl)-1-tosyl-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (3j):

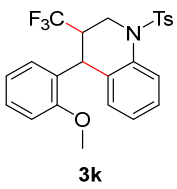


3j

According to general procedure, **1j** (79 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **3f** (52 mg, 56 %) as shapeless jelly; R_f = 0.70 (silica gel, PE: EA = 5:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.77 – 6.73 (m, 1H), 6.63 (d, *J* = 8.5 Hz, 2H), 6.38 (d, *J* = 8.5 Hz, 2H), 4.63 (dd, *J* = 14.3, 3.8 Hz, 1H), 4.03 (d, *J* = 10.4 Hz, 1H), 3.75 (s, 3H), 3.48 (dd, *J* = 14.3, 11.8 Hz, 1H), 2.59 (dtd,

J = 14.7, 7.7, 3.5 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 160.9, 144.5, 138.8, 138.8, 136.6, 135.8, 131.6, 130.7, 130.2, 130.1, 130.0, 127.8 (q, J_{C-F}= 279 Hz), 127.6, 127.3, 126.1, 125.0, 124.9, 115.5, 115.3, 45.0, 45.0 (q, J_{C-F}= 4.5 Hz), 44.2, 43.9 (q, J_{C-F}= 24 Hz), 43.7, 42.8, 21.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -70.46. MS (ESI) m/z calcd for $C_{24}H_{22}F_3NNaO_2S^+$ $[M+Na]^+$ 484.1165, found 484.1163.

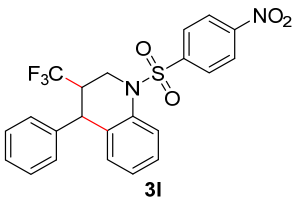
4-(2-methoxyphenyl)-1-tosyl-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (3k):



3k

According to general procedure, **1k** (76 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **3k** (45 mg, 49 %) as colorless liquid; R_f = 0.80 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 1H), 7.75 – 7.68 (m, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.18 – 7.13 (m, 2H), 6.97 (td, J = 7.6, 1.3 Hz, 1H), 6.86 – 6.82 (m, 1H), 6.74 (d, J = 7.7 Hz, 1H), 6.66 – 6.61 (m, 1H), 6.04 (s, 1H), 4.64 (d, J = 10.0 Hz, 1H), 4.49 (dd, J = 14.0, 3.8 Hz, 1H), 3.75 (s, 3H), 3.55 (dd, J = 14.0, 10.8 Hz, 1H), 2.86 (d, J = 10.2 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.2, 144.1, 137.1, 136.2, 131.7, 131.5, 130.2, 130.0, 129.4, 128.2, 127.4, 126.7, 126.1(q, J_{C-F}= 279 Hz), 125.4, 123.7, 120.6, 111.1, 55.6, 44.9 (q, J_{C-F}= 4.5 Hz), 42.7 (q, J_{C-F}= 25.5 Hz), 36.5, 21.5. MS (ESI) m/z calcd for $C_{24}H_{23}F_3NO_2S^+$ $[M+H]^+$ 462.1345, found 462.1344.

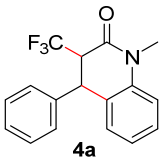
1-((4-nitrophenyl)sulfonyl)-4-phenyl-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (3l):



3l

According to general procedure, **1l** (76 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **3l** (21 mg, 23 %, *dr* 19/1) as colorless oil; R_f = 0.59 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 – 8.34 (m, 2H), 8.02 – 7.96 (m, 2H), 7.80 – 7.73 (m, 1H), 7.27 – 7.04 (m, 5H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.58 – 6.54 (m, 2H), 4.57 (dd, *J* = 14.2, 4.1 Hz, 1H), 4.14 (d, *J* = 9.7 Hz, 1H), 3.64 (dd, *J* = 14.1, 11.0 Hz, 1H), 2.75 – 2.66 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.6, 145.3, 142.6, 135.3, 131.5, 131.2, 128.7, 128.7, 128.2, 127.6, 127.4, 126.5, 125.8 (q, J_{C-F}= 279 Hz) ,124.7, 123.8, 45.1 (q, J_{C-F}= 24 Hz), 45.0 (q, J_{C-F}= 4.5 Hz), 43.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.62. MS (ESI) m/z calcd for $C_{22}H_{17}F_3N_2NaO_4S^+$ $[M+Na]^+$ 485.0753, found 485.0751.

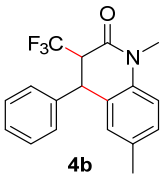
1-methyl-4-phenyl-3-(trifluoromethyl)-3,4-dihydroquinolin-2(1H)-one (4a) [4]:



4a

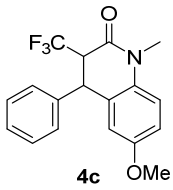
According to general procedure, **2a** (48 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **4a** (27 mg, 44 %) as white solid; R_f = 0.81 (silica gel, PE: EA = 10:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 1H), 7.29 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 7.11 (dd, *J* = 10.1, 7.9 Hz, 2H), 7.02 – 6.98 (m, 2H), 4.50 (s, 1H), 3.69 – 3.62 (m, 1H), 3.46 (d, *J* = 2.3 Hz, 3H).

1,6-dimethyl-4-phenyl-3-(trifluoromethyl)-3,4-dihydroquinolin-2(1H)-one (4b) [5]:



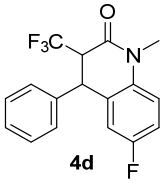
According to general procedure, **2b** (52 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **4b** (33.5 mg, 52 %) as colorless liquid; R_f = 0.76 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 6.8 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.02 – 6.98 (m, 4H), 4.44 (s, 1H), 3.62 (q, *J* = 9.5 Hz, 1H), 3.43 (s, 3H), 2.30 (s, 3H).

6-methoxy-1-methyl-4-phenyl-3-(trifluoromethyl)-3,4-dihydroquinolin-2(1H)-one (4c) [4]:



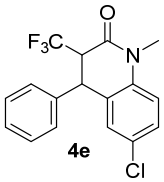
According to general procedure, **2c** (54 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **4c** (33 mg, 49 %) as colorless liquid; R_f = 0.56 (silica gel, PE: EA = 5:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 6.7 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 7.03 – 6.98 (m, 4H), 4.44 (s, 1H), 3.62 (q, *J* = 9.5 Hz, 1H), 3.44 (s, 3H), 2.30 (s, 3H).

6-fluoro-1-methyl-4-phenyl-3-(trifluoromethyl)-3,4-dihydroquinolin-2(1H)-one (4d) [5]:



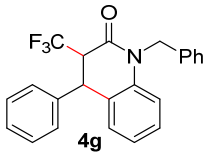
According to general procedure, **2d** (51 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **4d** (27 mg, 42%) as colorless liquid; R_f = 0.68 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 5H), 7.05 (d, *J* = 8.7 Hz, 1H), 6.99 (dd, *J* = 7.2, 1.8 Hz, 2H), 4.46 (s, 1H), 3.71 – 3.61 (m, 1H), 3.45 (s, 3H).

6-chloro-1-methyl-4-phenyl-3-(trifluoromethyl)-3,4-dihydroquinolin-2(1H)-one(4e) [6]:



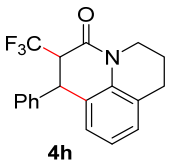
According to general procedure, **2e** (55 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **4e** (17 mg, 25 %) as colorless liquid; R_f = 0.70 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 3H), 7.11 – 7.03 (m, 2H), 7.02 – 6.93 (m, 3H), 4.46 (s, 1H), 3.65 (q, *J* = 9.3 Hz, 1H), 3.45 (d, *J* = 1.4 Hz, 3H).

1-benzyl-4-phenyl-3-(trifluoromethyl)-3,4-dihydroquinolin-2(1H)-one (4g) [5]:



According to general procedure, **2g** (79 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **4g** (25 mg, 33%) as colorless liquid; R_f = 0.76 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.17 (m, 10H), 7.06 (q, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 5.41 (d, *J* = 16.0 Hz, 1H), 5.06 (d, *J* = 16.1 Hz, 1H), 4.55 (s, 1H), 3.78 (q, *J* = 9.4 Hz, 1H).

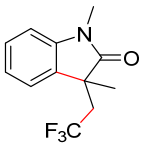
7-phenyl-6-(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-5-one (4h) [4]:



4h

According to general procedure, **2h** (53 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **4h** (17 mg, 26%) as colorless liquid; R_f = 0.66 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 3H), 7.24 – 7.19 (m, 1H), 7.10 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.05 – 6.96 (m, 3H), 4.47 (s, 1H), 4.35 (dt, *J* = 12.4, 5.7 Hz, 1H), 3.62 (qd, *J* = 9.5, 1.5 Hz, 1H), 3.53 (dt, *J* = 12.8, 6.3 Hz, 1H), 2.88 (dtd, *J* = 22.0, 16.1, 6.4 Hz, 2H), 2.06 – 1.97 (m, 2H).

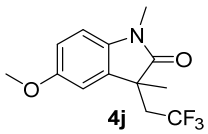
1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (4i)[6]:



4i

According to general procedure, **2i** (36 mg, 0.2 mmol, 1.0 eq.) reacted for 2 h to produce **4i** (13 mg, 26%) as colorless liquid; R_f = 0.46 (silica gel, PE: EA = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 6.0 Hz,1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 3.24 (d, *J* = 2.1 Hz, 3H), 2.87 – 2.73 (m, 1H), 2.71 – 2.59 (m, 1H), 1.41 (s, 3H).

5-methoxy-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (4j) [6]:

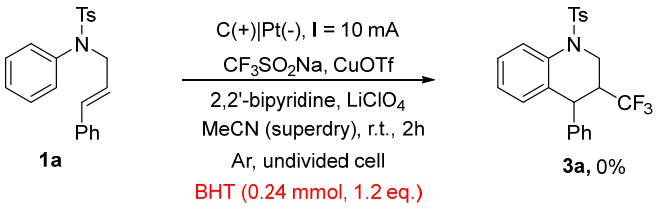


4j

According to general procedure, **2j** (0.2 mmol, 1.0 eq.) reacted for 2 h to produce **4j** (24.8 mg, 45 %) as oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.88 (d, *J* = 2.5 Hz, 1H), 6.84 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.23 – 3.20 (m, 3H), 2.81 (dq, *J* = 15.2, 10.8 Hz, 1H), 2.62 (dq, *J* = 15.2, 10.5 Hz, 1H), 1.40 (s, 3H).

5. Mechanistic Studies

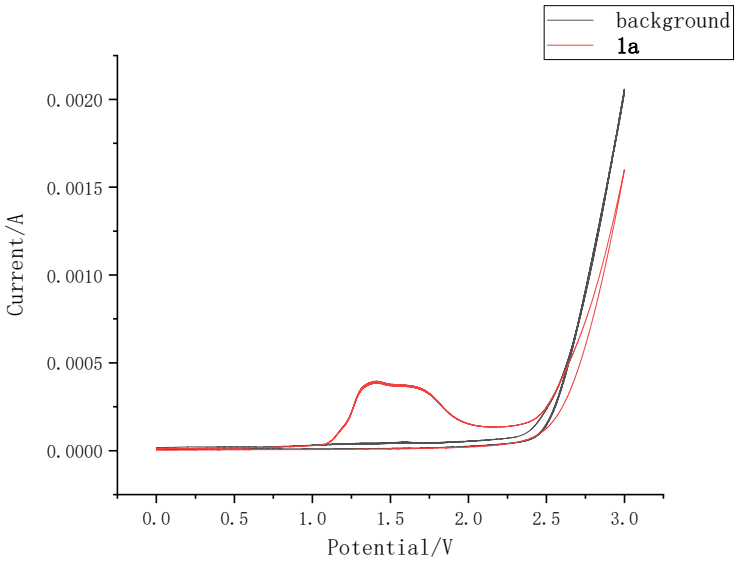
5.1 Free radical capture experiment



A 10 mL three-necked round-bottomed flask (Figure S1) was equipped with a graphite rod (Ø = 6.0 mm) anode and a Platinum (2 cm x 1 cm x 1mm) cathode, and remove water and oxygen with Schlenk line. Then the the flask was charged with **1a** (0.2 mmol, 1.0 eq.), $LiClO_4$ (0.8 mmol, 4.0 eq.), $Na_2SO_2CF_3$ (0.8 mmol, 4.0 eq.) CuOTf (0.01 mmol, 0.05 eq.), 2,2'-bipyridine (0.02 mmol, 0.1 eq.) and BHT (0.24 mmol, 1.2 eq.) Then Superdry CH_3CN (5 mL) was added. The electrolysis reaction was carried out at room temperature using a constant current of 10 mA for 2h.

5.2 Cyclic voltammetry

The cyclic voltammetry was carried out with a Shang Hai Hua Chen electrochemical workstation (CHI660E B18733) and following analysis was performed with Origin 2019 software. A glassy-carbon electrode (3 mm-diameter, disc-electrode) was used as the working electrode, a Pt wire as auxiliary electrode and a SCE electrode was used as the reference. The measurements were carried out at a scan rate of 100 mVs^{-1}.



Conditions: a glassy carbon working clectrode, a saturated calomel clectrode(SCE)reference electrode,and a platinum wire counter electrode, $LiClO_4$(0.16M in CH_3CN), 0.1 V/s with (a) background ;(b) **1a** (0.04 M). The cyclic voltammetry was carried out with a Shanghai Chenhua electrochemical workstation (CHI660E B18733) and following analysis was performed with Origin2019 software. A glassy-carbon electrode electrode (Ø= 6.0 mm) was used as the working electrode, a Pt wire as auxiliaryelectrode and a SCE electrode was used as the reference. The measurements were carried outat a scan rate of 100 mVs^{-1}.

6. X-ray Crystallographic Data of Compound 3a:

The crystals **3a** were prepared from the solution of **3a** in DCM/ hexane at ambient temperature.

6.1 X-ray crystallographic Data of Compound **3a**:

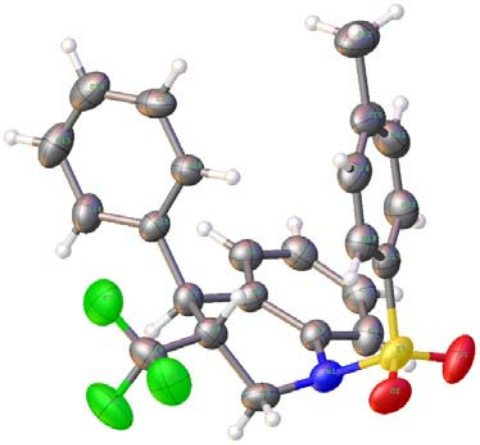


Figure 1. X-ray derived ORTEP representation of **3a**.

Crystal data and structure refinement for 3a (CCDC:2261873)

Empirical formula	C23H20F3NO2S
Formula weight	431.46
Temperature/K	291.5(4)
Crystal system	monoclinic
Space group	P21/n
a/Å	13.6163(17)
b/Å	9.1345(7)
c/Å	17.600(5)
α /°	90
β /°	108.01(2)
γ /°	90
Volume/Å3	2081.8(7)
Z	4
ρ calcg/cm3	1.377
μ /mm-1	1.792
F(000)	896.0
Crystal size/mm3	? × ? × ?
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.226 to 170.394
Index ranges	-16 ⩽ h ⩽ 16, -11 ⩽ k ⩽ 10, -21 ⩽ l ⩽ 22
Reflections collected	18425

Independent reflections	4052 [Rint = 0.1285, Rsigma = 0.0707]
Data/restraints/parameters	4052/0/273
Goodness-of-fit on F2	1.635
Final R indexes [I>=2σ (I)]	R1 = 0.1724, wR2 = 0.4238
Final R indexes [all data]	R1 = 0.1919, wR2 = 0.4494
Largest diff. peak/hole / e Å-3	1.28/-0.43

7. References

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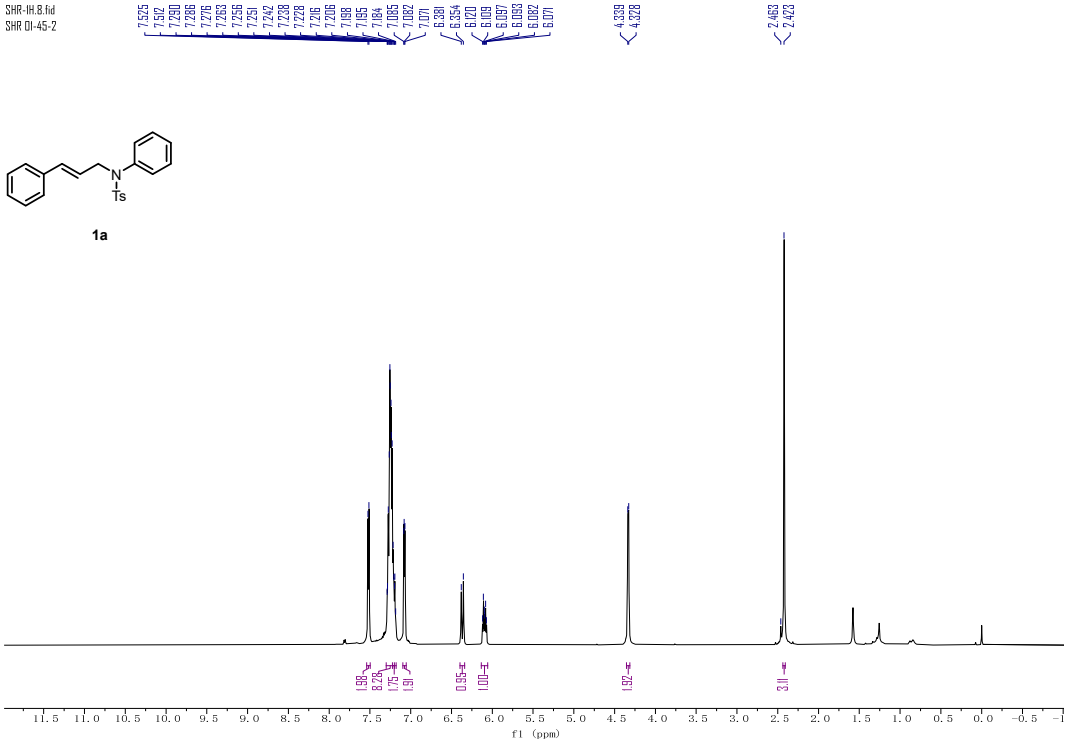
2. Gao, F.; Yang, C.; Gao, G.-L.; Zheng, L.; Xia, W., Visible-Light Induced Trifluoromethylation of N-Arylcinnamamides for the Synthesis of CF_3-Containing 3,4-Disubstituted Dihydroquinolinones and 1-Azaspiro[4.5]decanes. *Org. Lett.,* **2015,** *17*, 3478.
3. Ruan, Z.; Huang, Z.; Xu, Z.; Mo, G.; Tian, X.; Yu, X.-Y.; Ackermann, L., Catalyst-Free, Direct Electrochemical Tri- and Difluoroalkylation/Cyclization: Access to Functionalized Oxindoles and Quinolinones. *Org. Lett.,* **2019,** *21*, 1237.
4. Mai, W.-P.; Wang, J.-T.; Yang, L.-R.; Yuan, J.-W.; Xiao, Y.-M.; Mao, P.; Qu, L.-B., Silver-Catalyzed Radical Tandem Cyclization for the Synthesis of 3,4-Disubstituted Dihydroquinolin-2(1H)-ones. *Org. Lett.,* **2014,** *16*, 204.
5. Gao, F.; Yang, C.; Gao, G.-L.; Zheng, L.; Xia, W., Visible-Light Induced Trifluoromethylation of N-Arylcinnamamides for the Synthesis of CF_3-Containing 3,4-Disubstituted Dihydroquinolinones and 1-Azaspiro[4.5]decanes. *Org. Lett.,* **2015,** *17*, 3478.
6. Ruan, Z.; Huang, Z.; Xu, Z.; Mo, G.; Tian, X.; Yu, X.-Y.; Ackermann, L., Catalyst-Free, Direct Electrochemical Tri- and Difluoroalkylation/Cyclization: Access to Functionalized Oxindoles and Quinolinones. *Org. Lett.,* **2019,** *21*, 1237.
7. He, X. X.; Chang, H. -H.; Zhao, Y. -X.; Li, X. -J.; Liu, S. -A.; Zang, Z. -L.; Zhou, C. -H.; Cai, G. -X., $CuCl_2$-Catalyzed α-Chloroketonation of Aromatic Alkenes via Visible-light-induced LMCT. *Chem. Asian J.,* **2023**, *18*, e202200954.

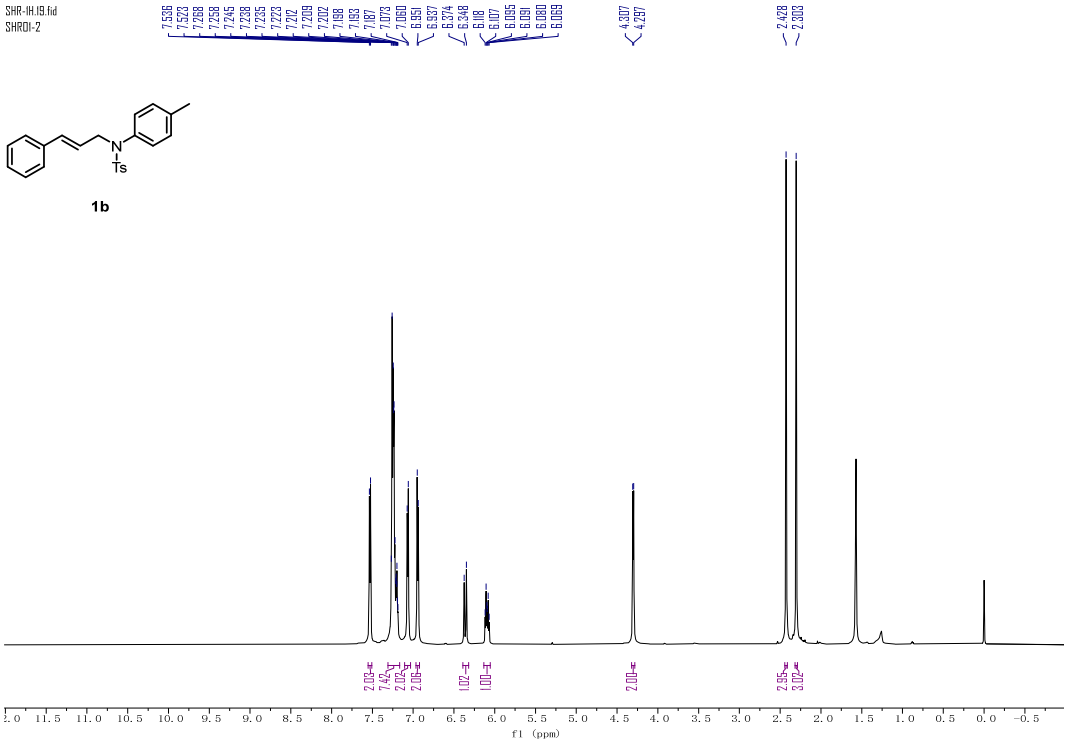
8. Experimental Spectra

8.1 Experimental spectra of starting materials 1

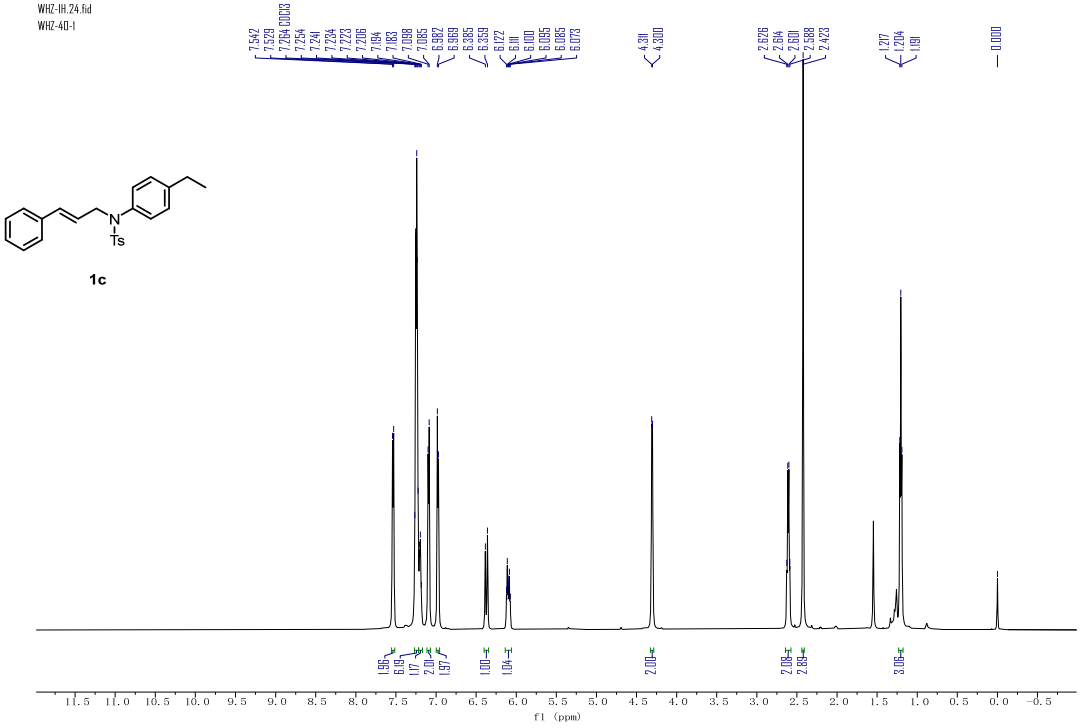
^{1}H NMR spectrum of **1a** (600 MHz, $CDCl_3$)



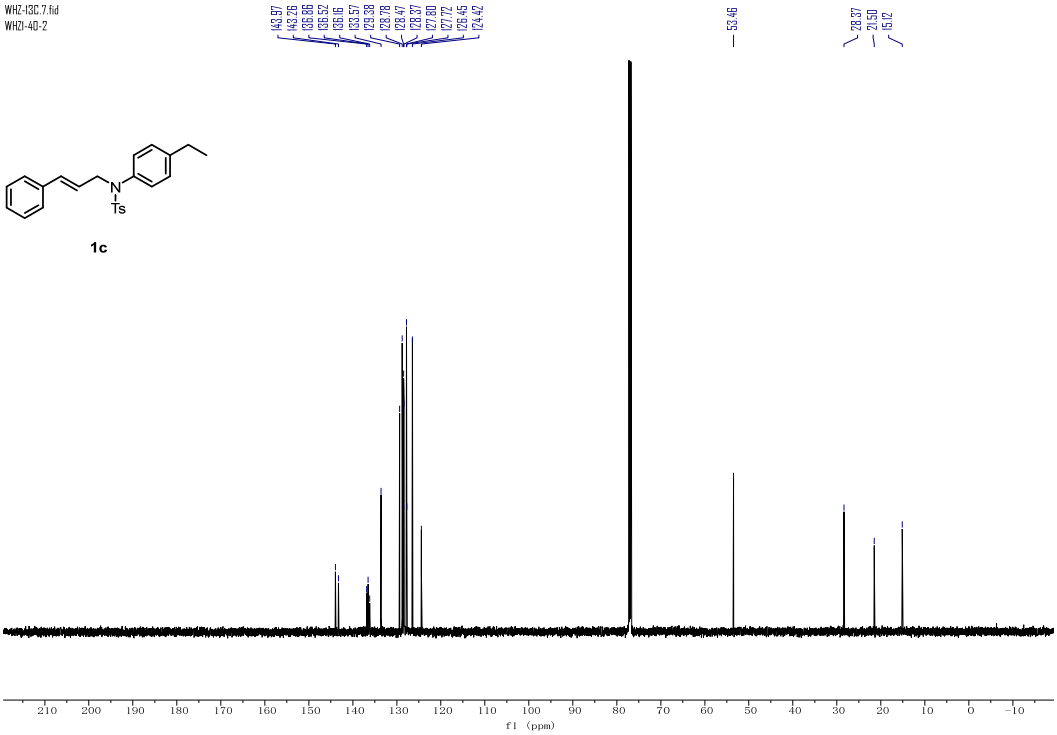
^{1}H NMR spectrum of **1b** (600 MHz, $CDCl_3$)



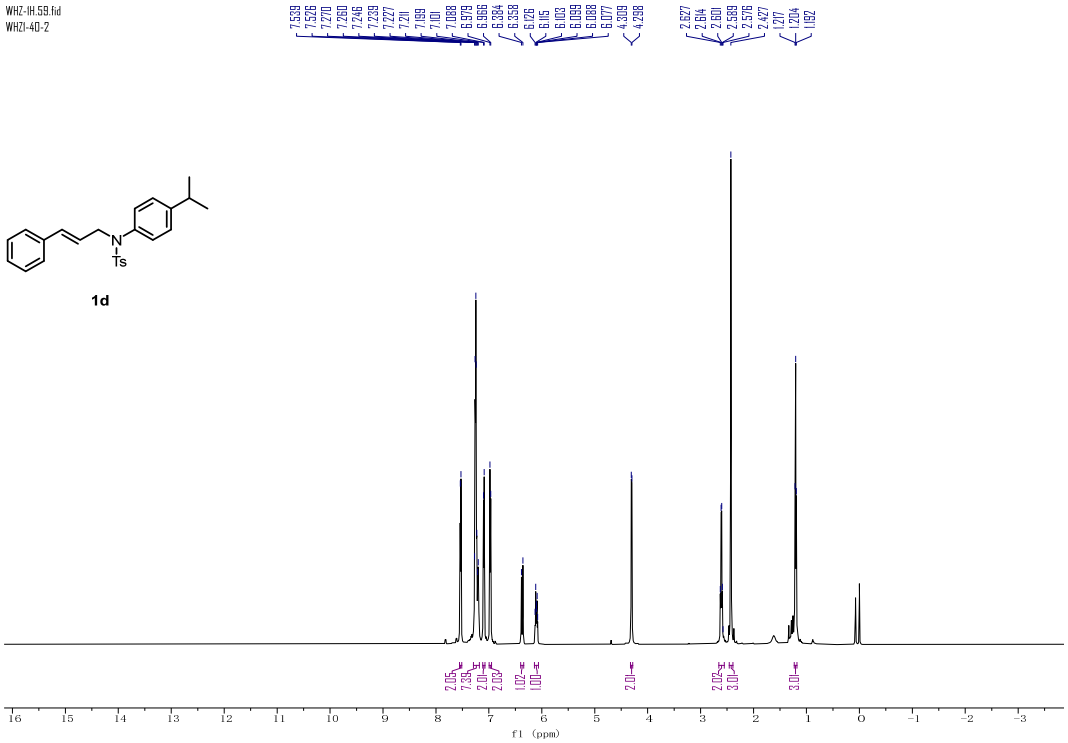
^{1}H NMR spectrum of **1c** (600 MHz, $CDCl_3$)



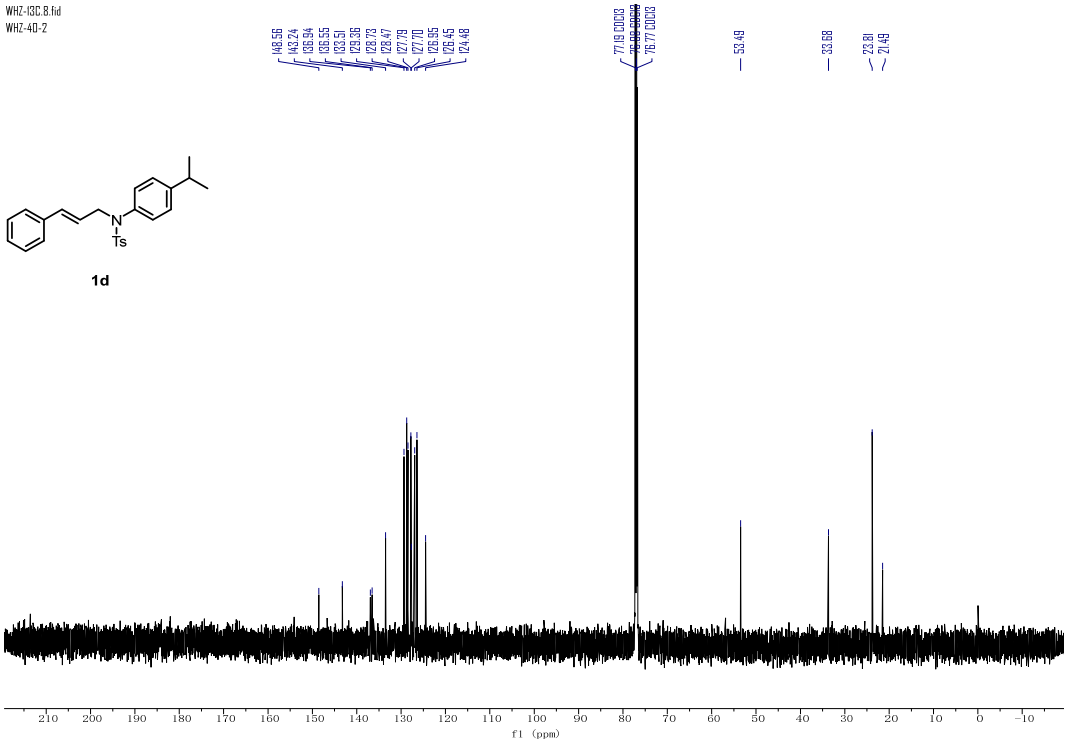
^{13}C NMR spectrum of **1c** (151 MHz, $CDCl_3$)



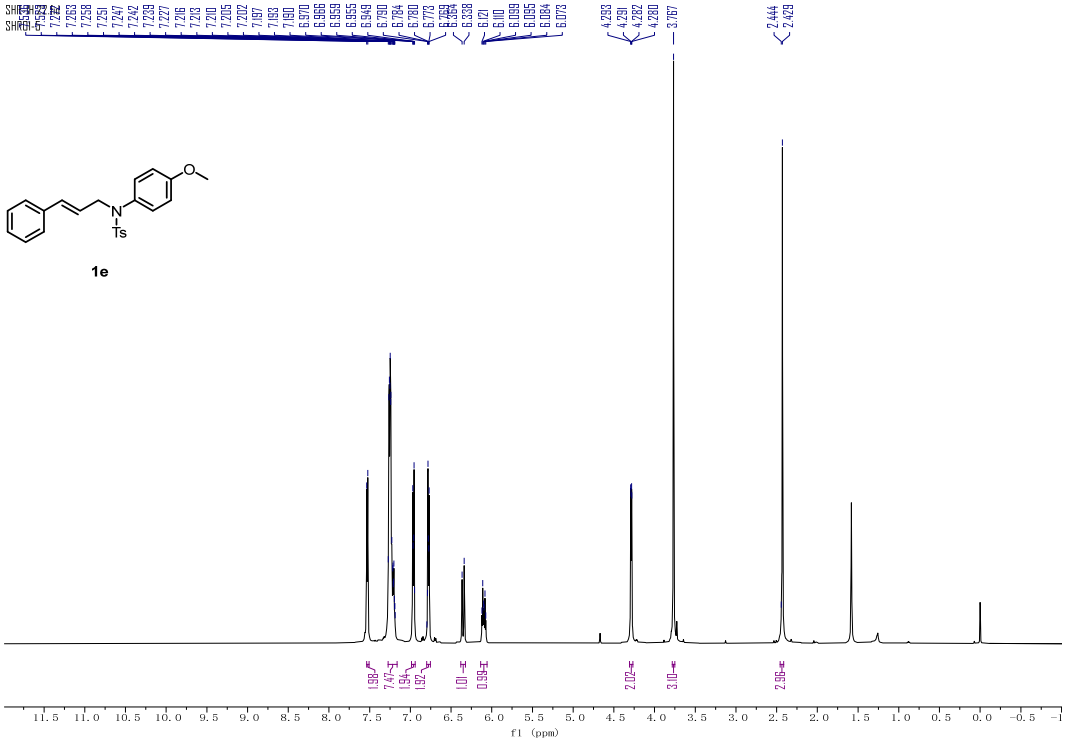
^{1}H NMR spectrum of **1d** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of **1d** (151 MHz, $CDCl_3$)

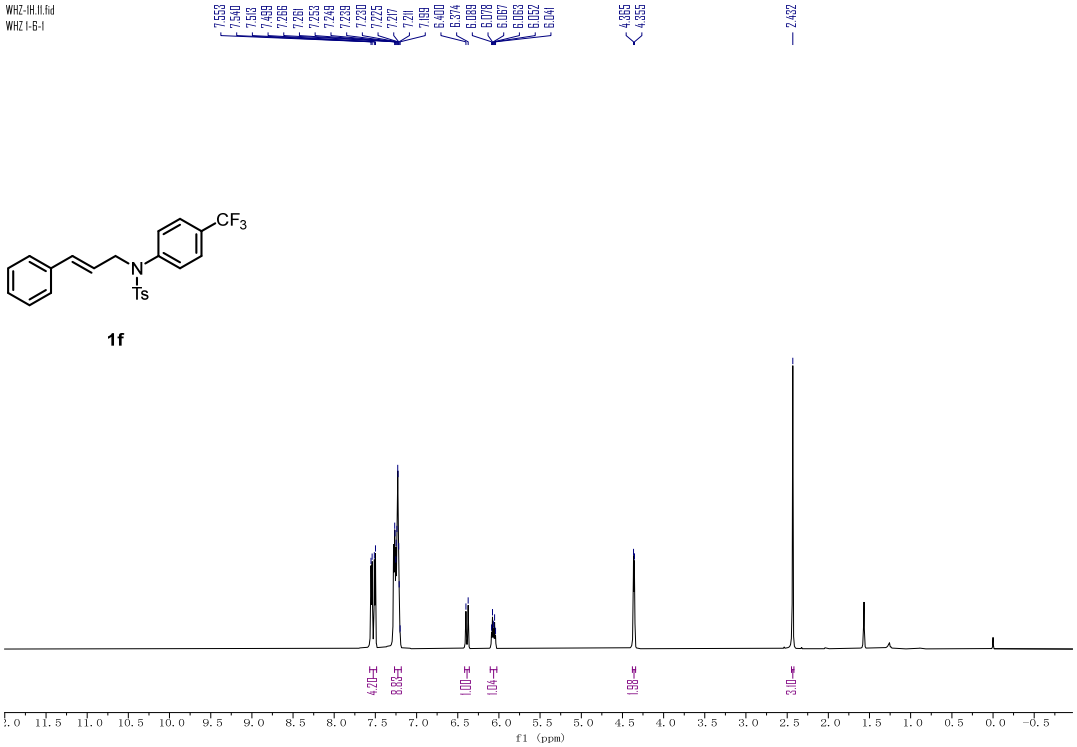


^{1}H NMR spectrum of **1e** (600 MHz, $CDCl_3$)



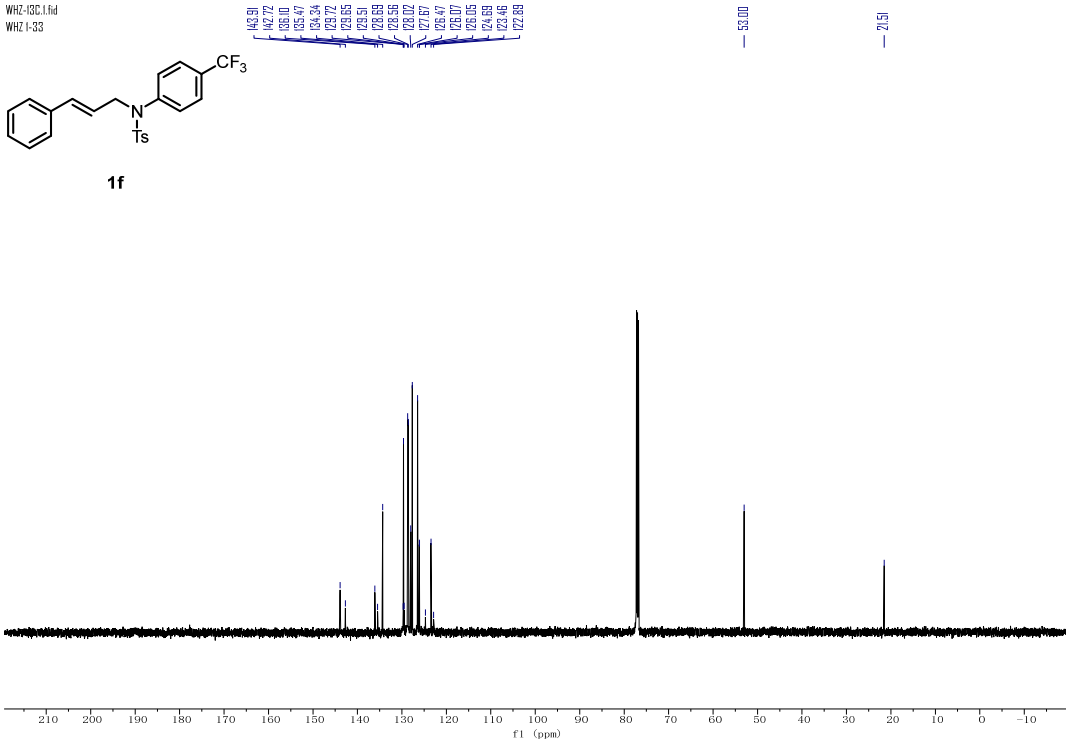
1e

^{1}H NMR spectrum of **1f** (600 MHz, $CDCl_3$)

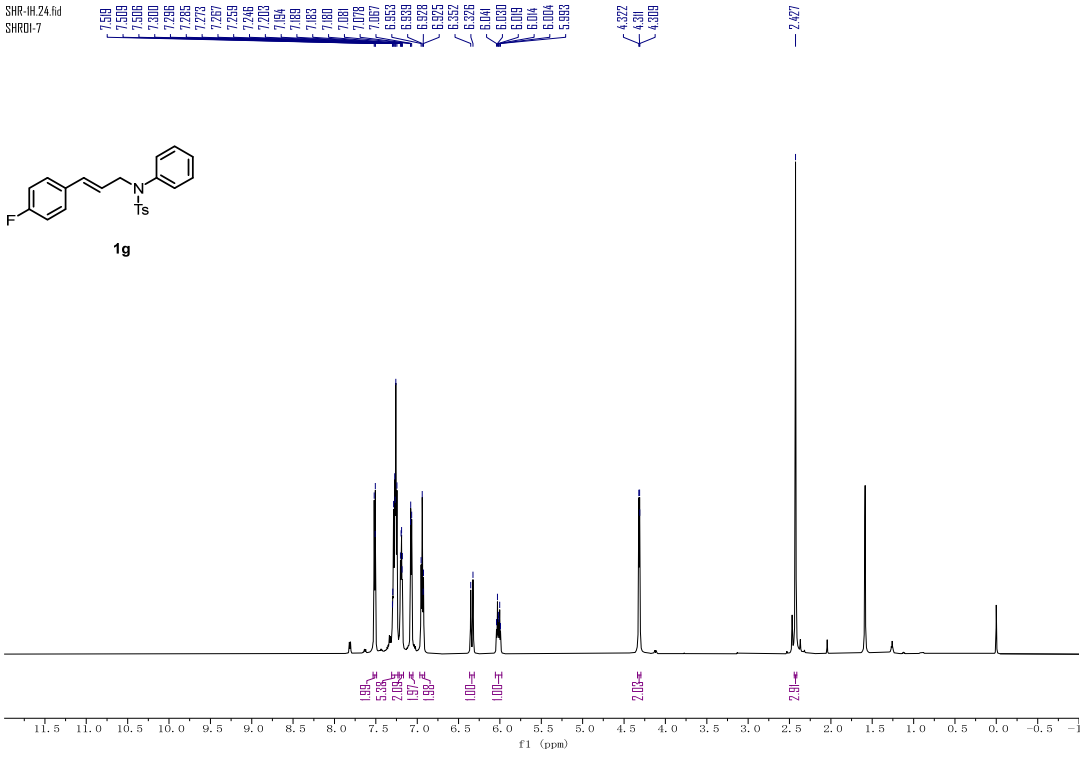


1f

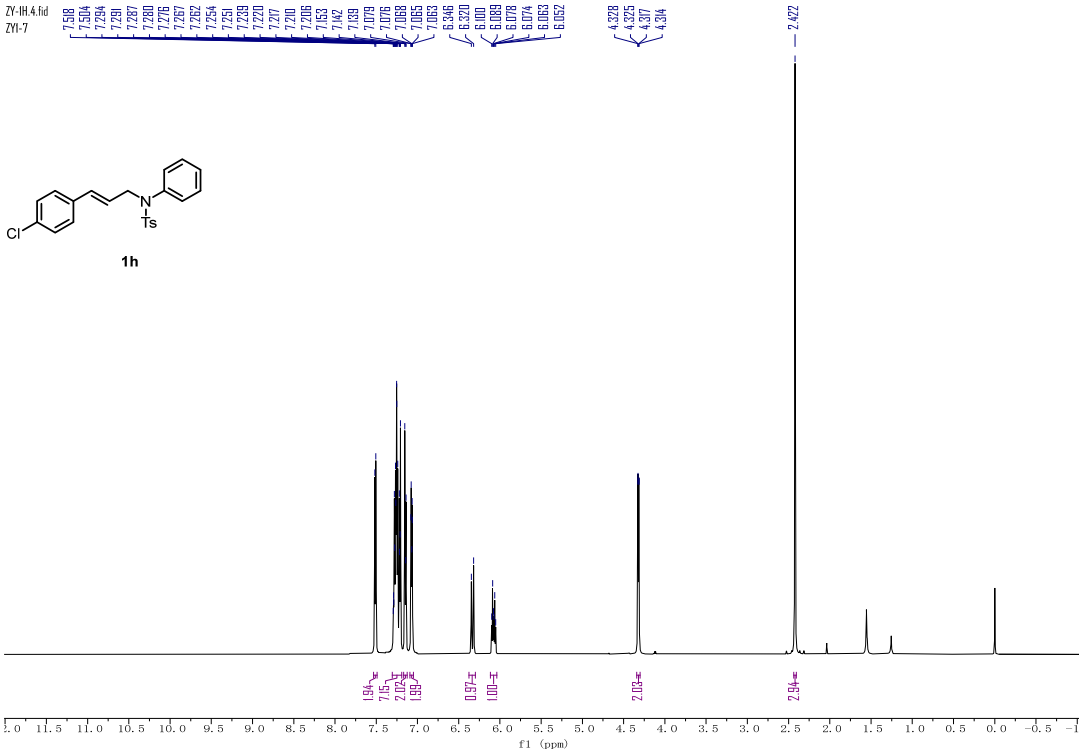
^{13}C NMR spectrum of **1f** (151 MHz, $CDCl_3$)



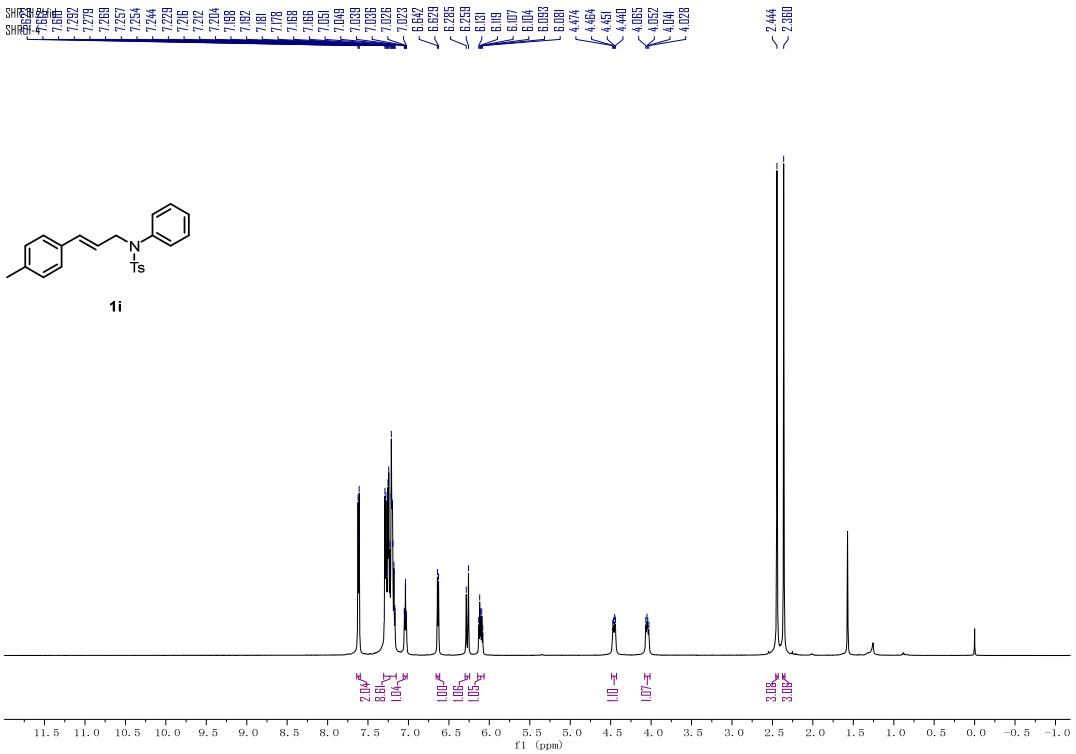
^{1}H NMR spectrum of **1g** (600 MHz, $CDCl_3$)



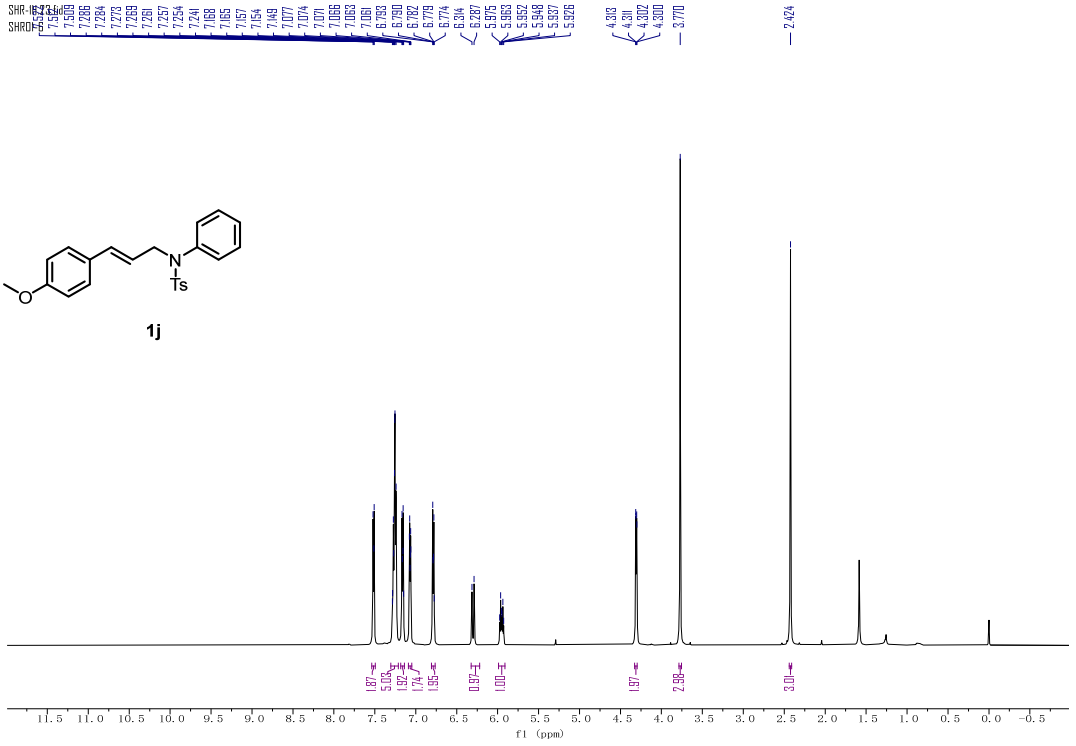
^{1}H NMR spectrum of **1h** (600 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1i** (600 MHz, $CDCl_3$)

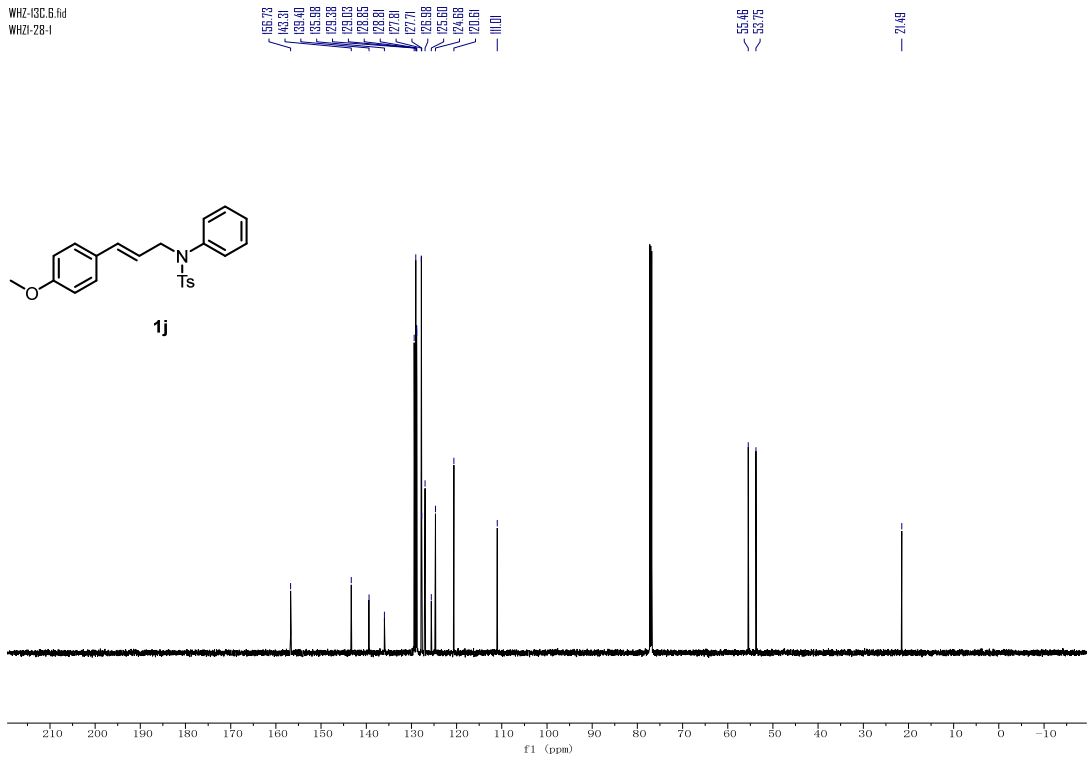


^{1}H NMR spectrum of **1j** (600 MHz, $CDCl_3$)



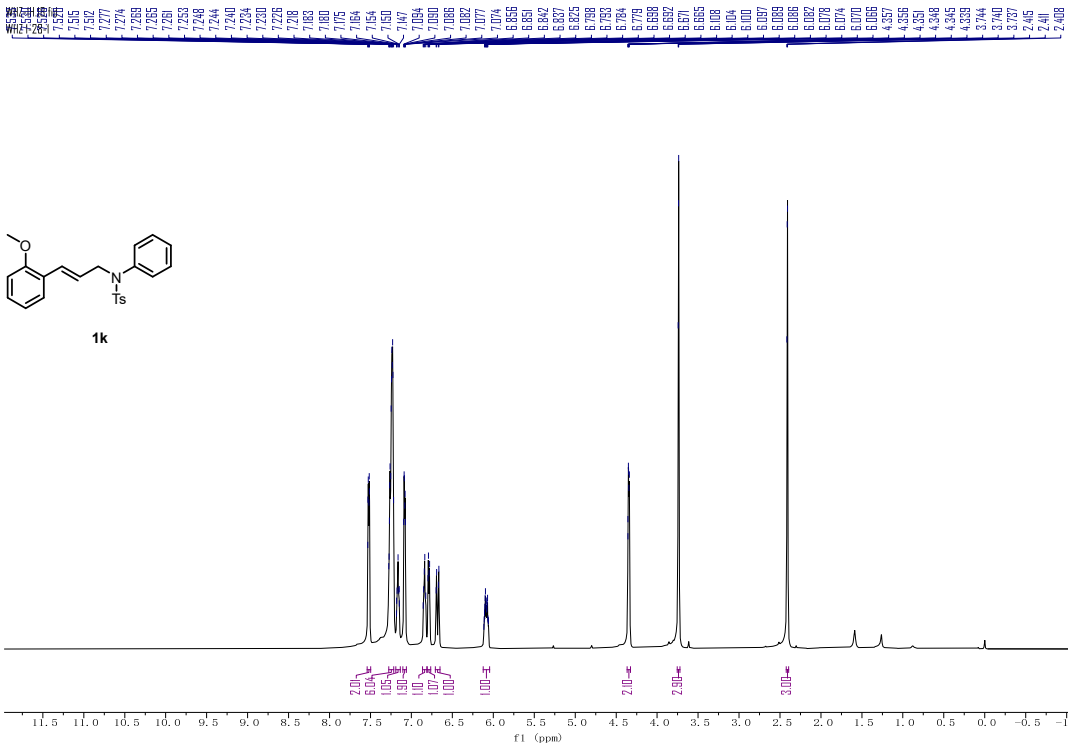
1j

^{13}C NMR spectrum of **1j** (151 MHz, $CDCl_3$)

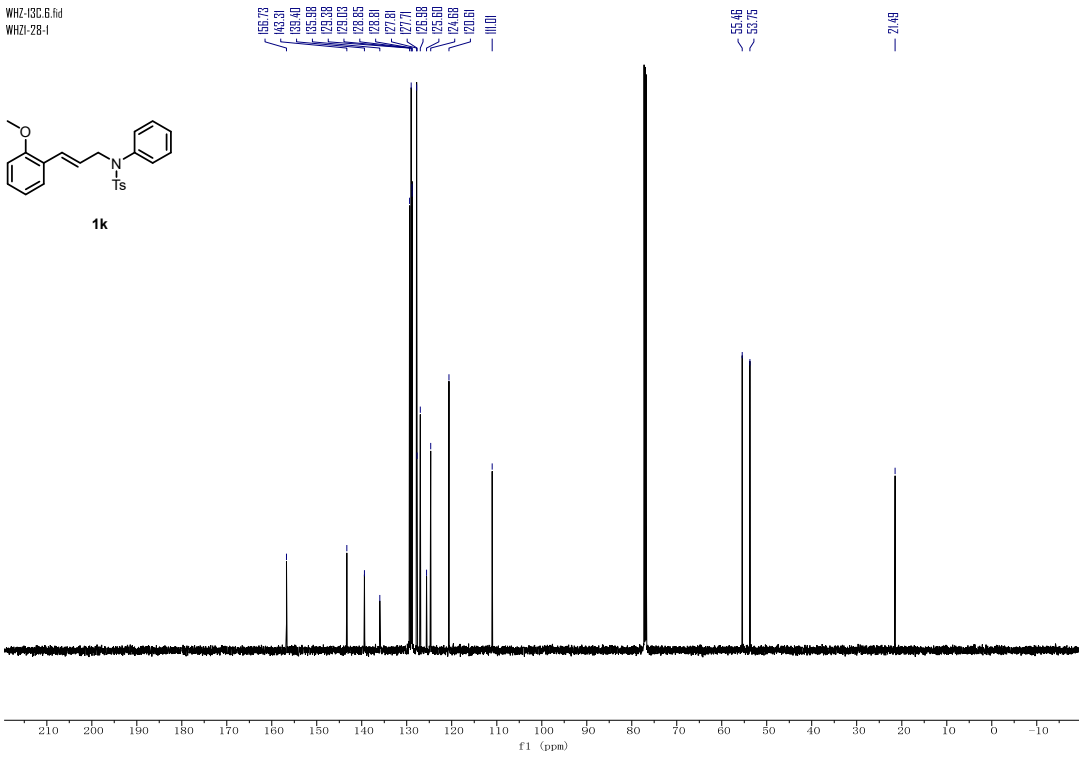


1j

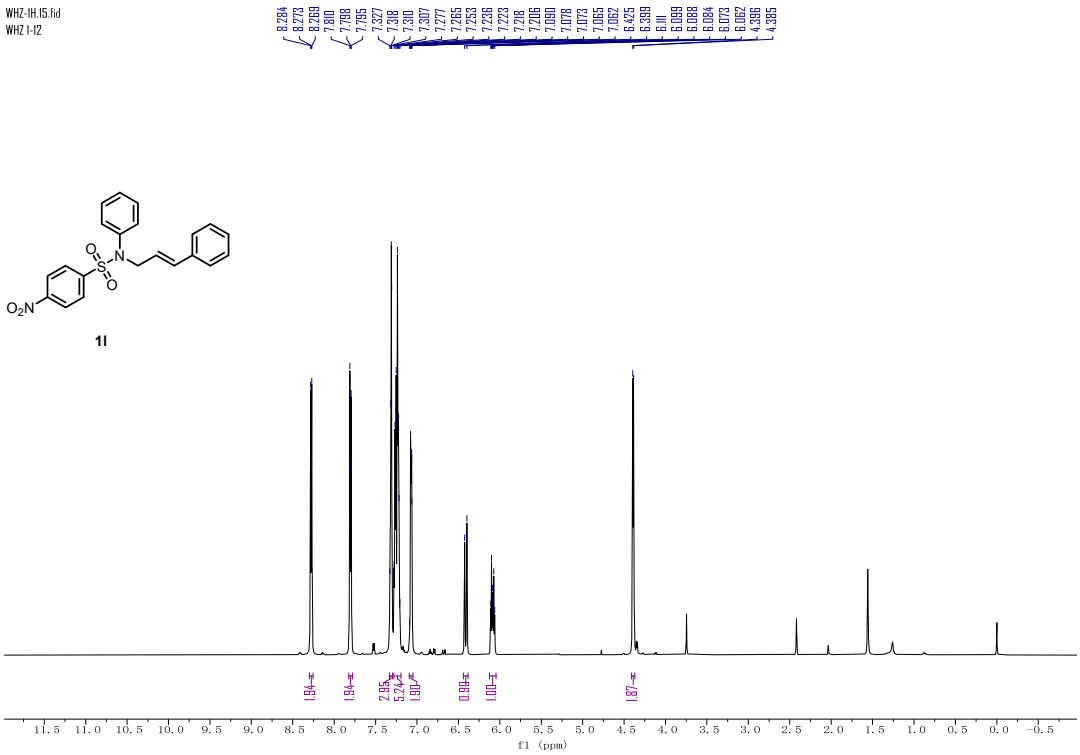
^{1}H NMR spectrum of **1k** (600 MHz, $CDCl_3$)



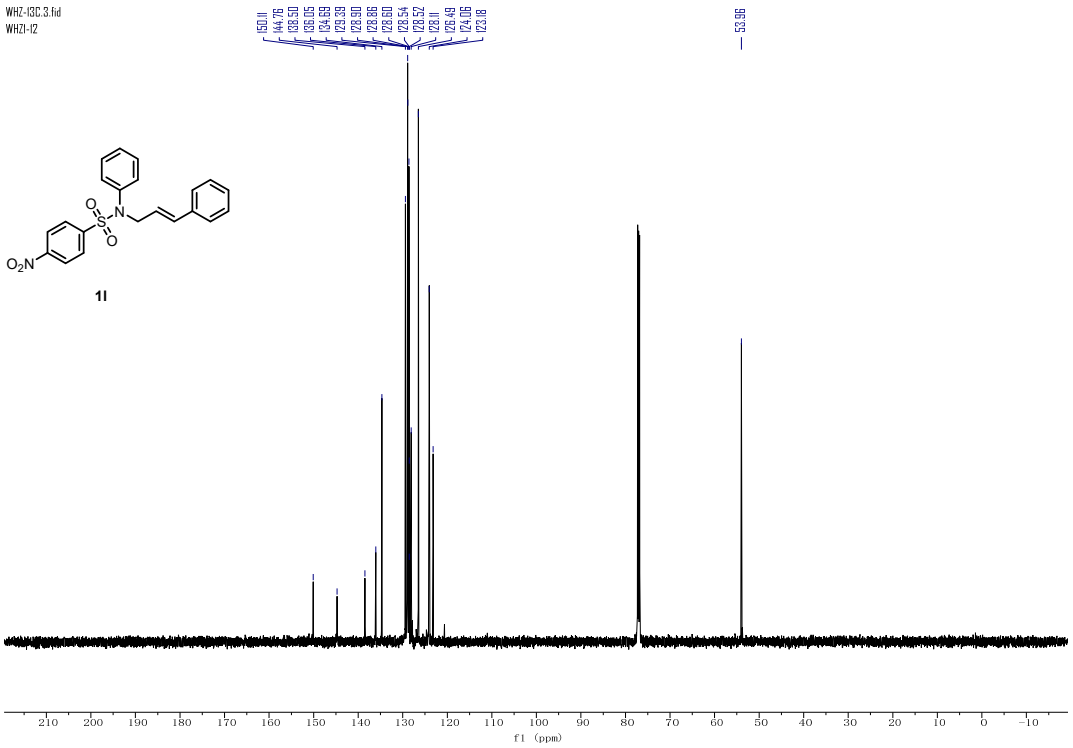
^{13}C NMR spectrum of **1k** (151 MHz, $CDCl_3$)



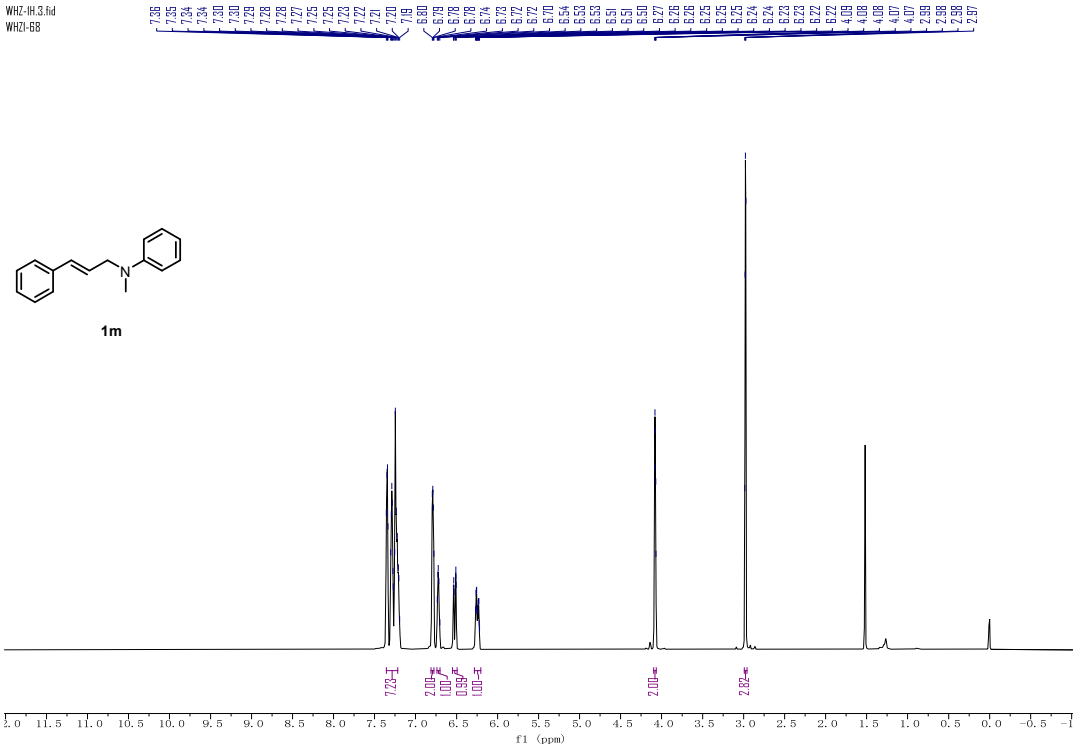
^{1}H NMR spectrum of **1l** (600 MHz, $CDCl_3$)



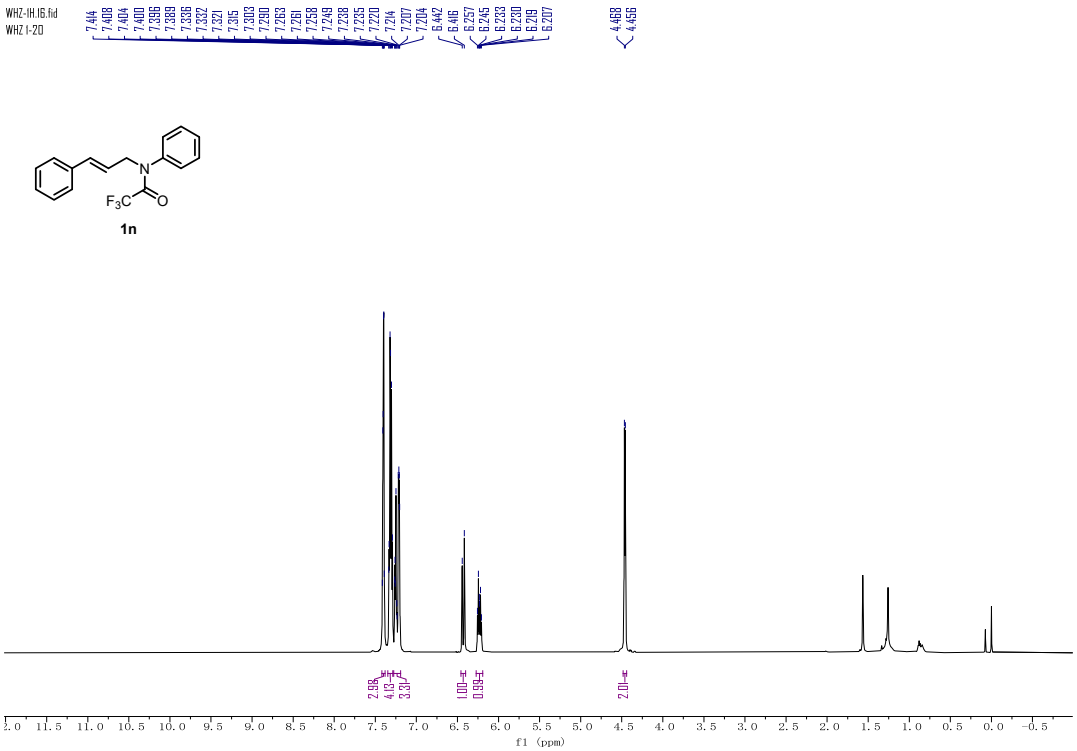
^{13}C NMR spectrum of **1l** (151 MHz, $CDCl_3$)



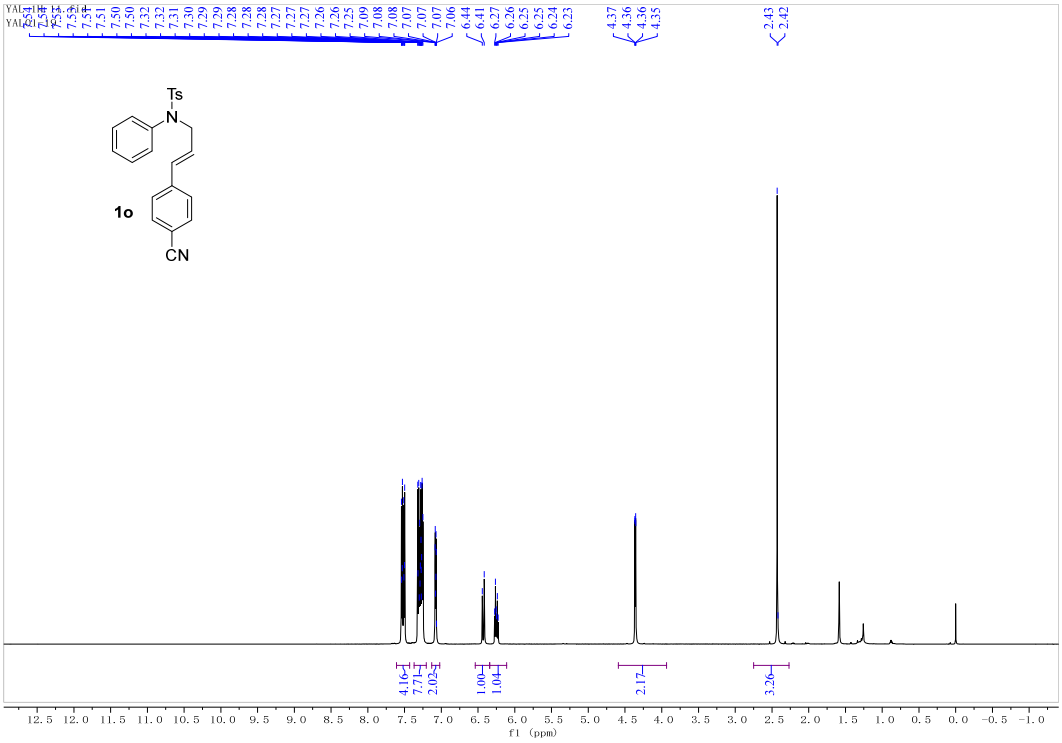
^{1}H NMR spectrum of **1m** (600 MHz, $CDCl_3$)



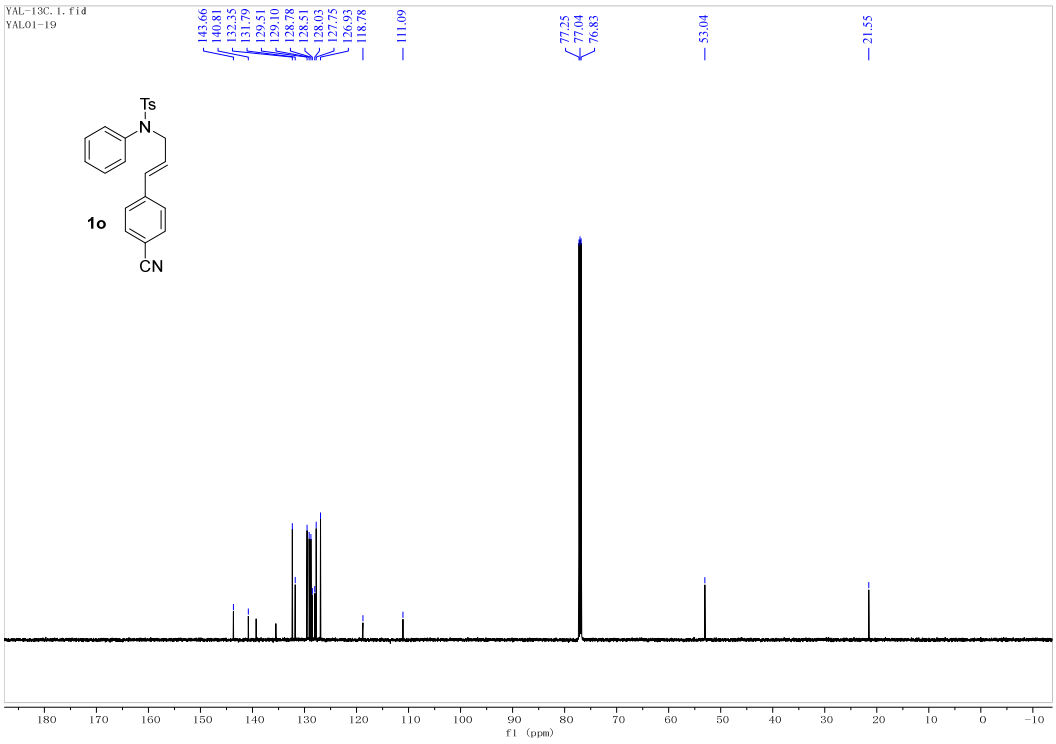
^{1}H NMR spectrum of **1n** (600 MHz, $CDCl_3$)



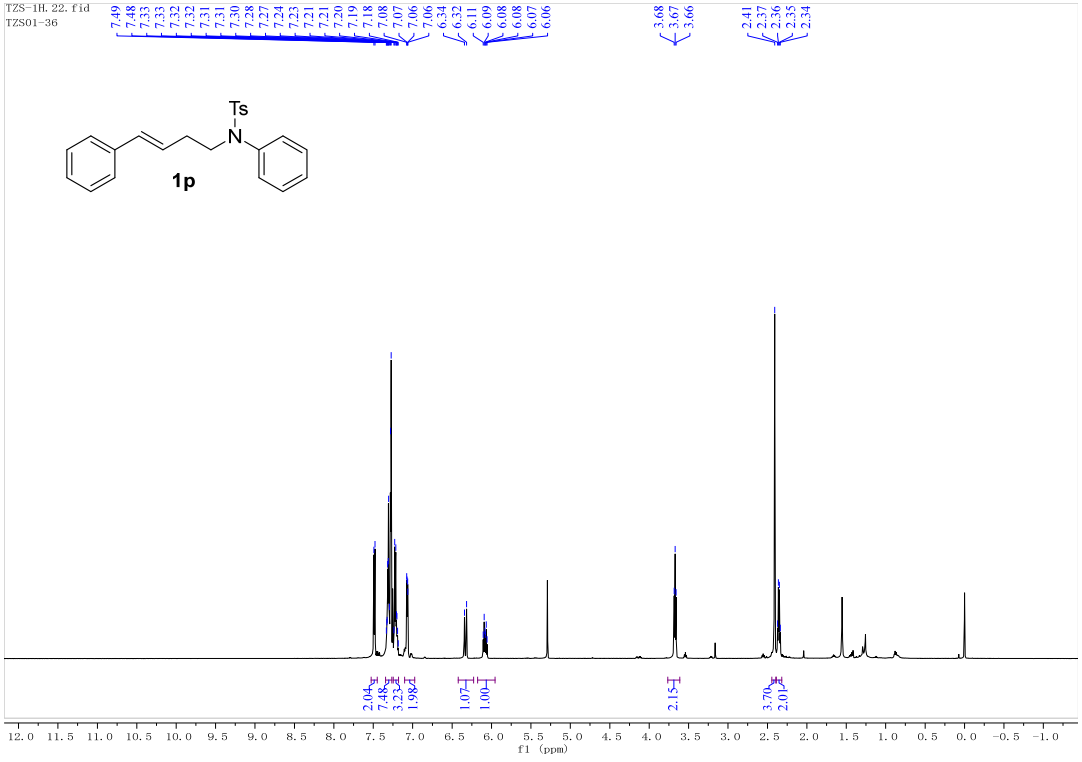
^{1}H NMR spectrum of **1o** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of **1o** (151 MHz, $CDCl_3$)

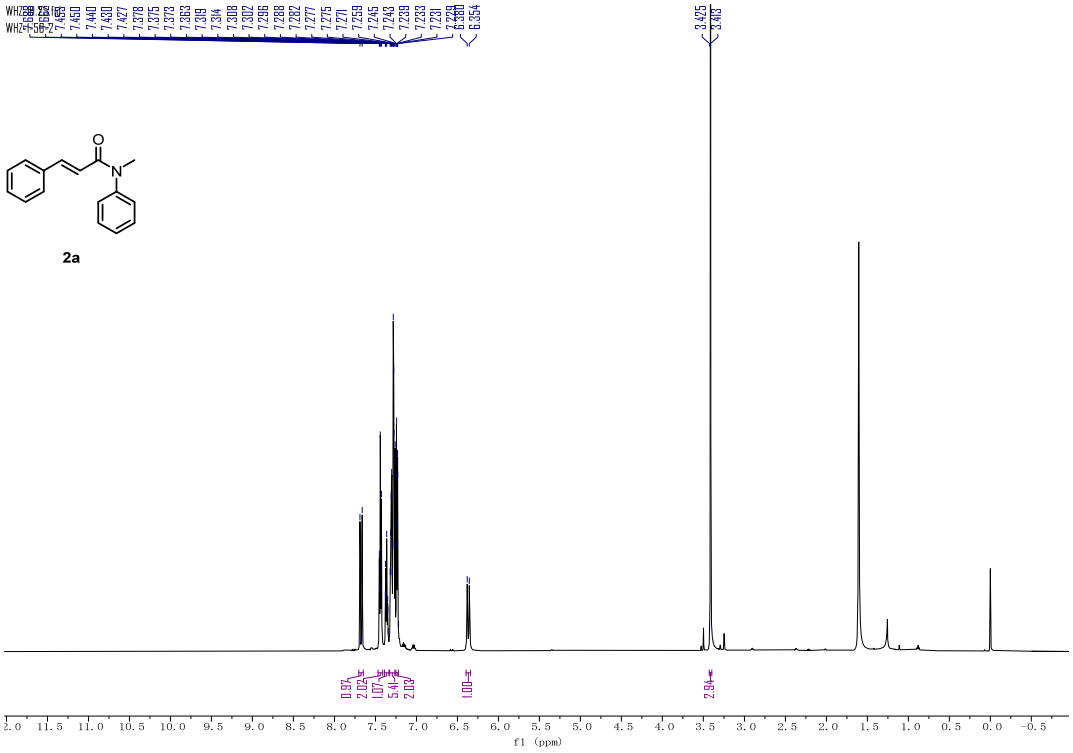


^{1}H NMR spectrum of **1p** (600 MHz, $CDCl_3$)

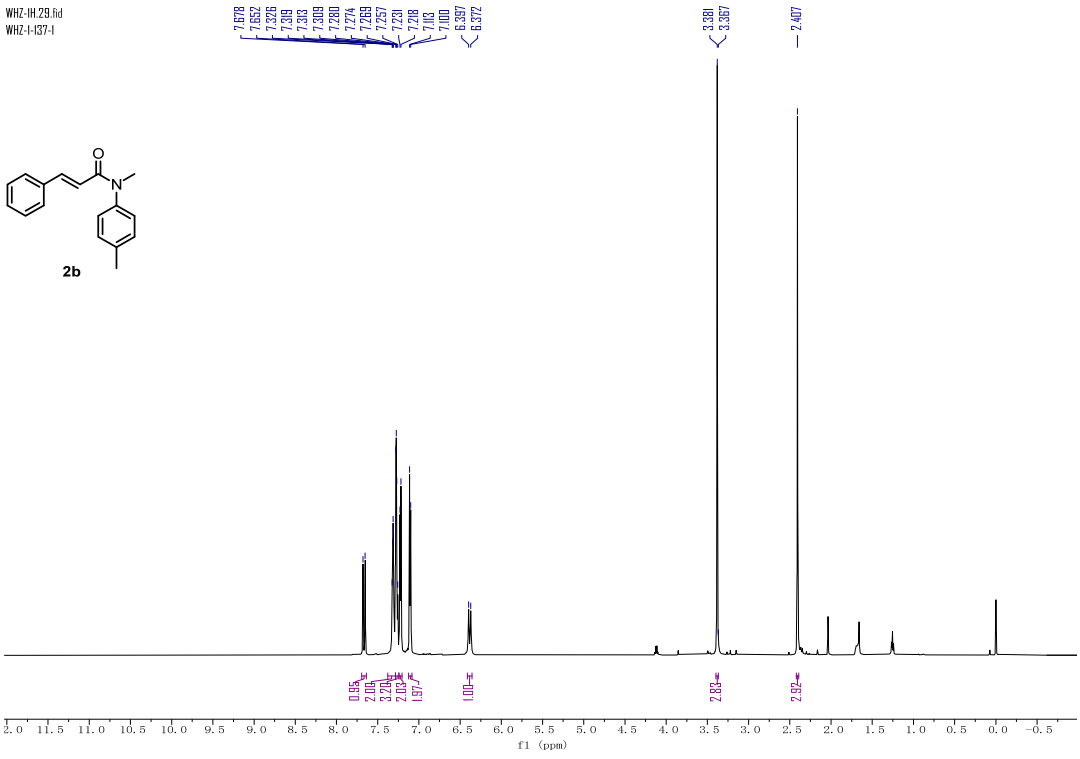


8.2 Experimental spectra of starting materials 2

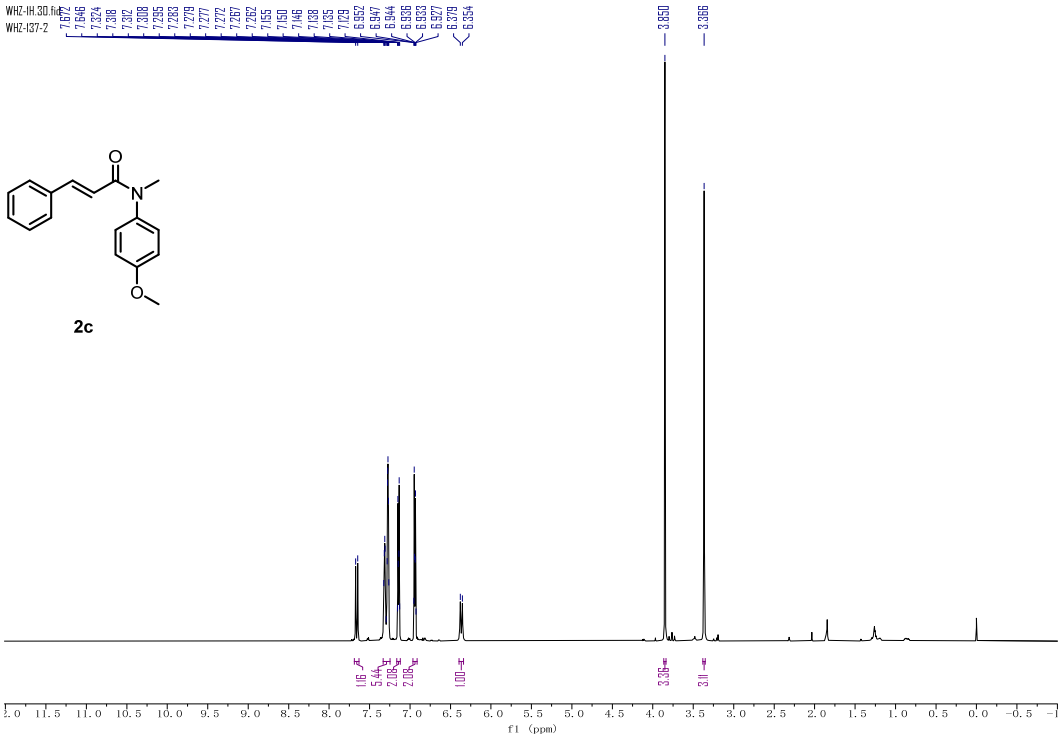
^{1}H NMR spectrum of **2a** (600 MHz, $CDCl_3$)



^{1}H NMR spectrum of **2b** (600 MHz, $CDCl_3$)

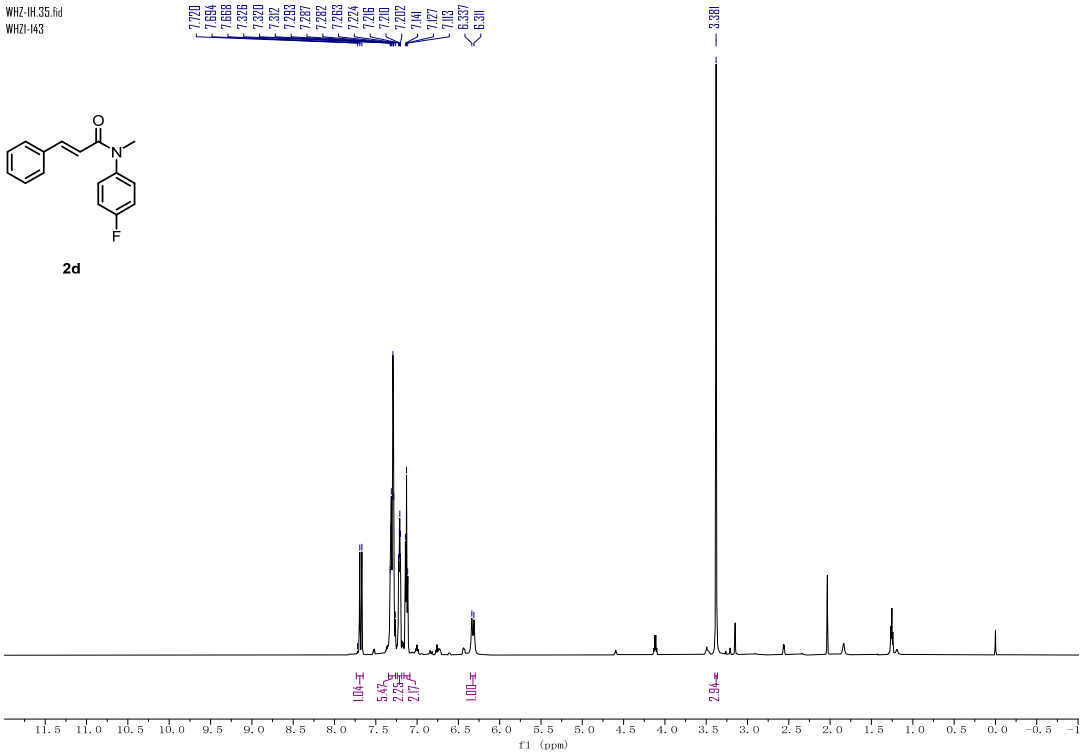


^{1}H NMR spectrum of **2c** (600 MHz, $CDCl_3$)



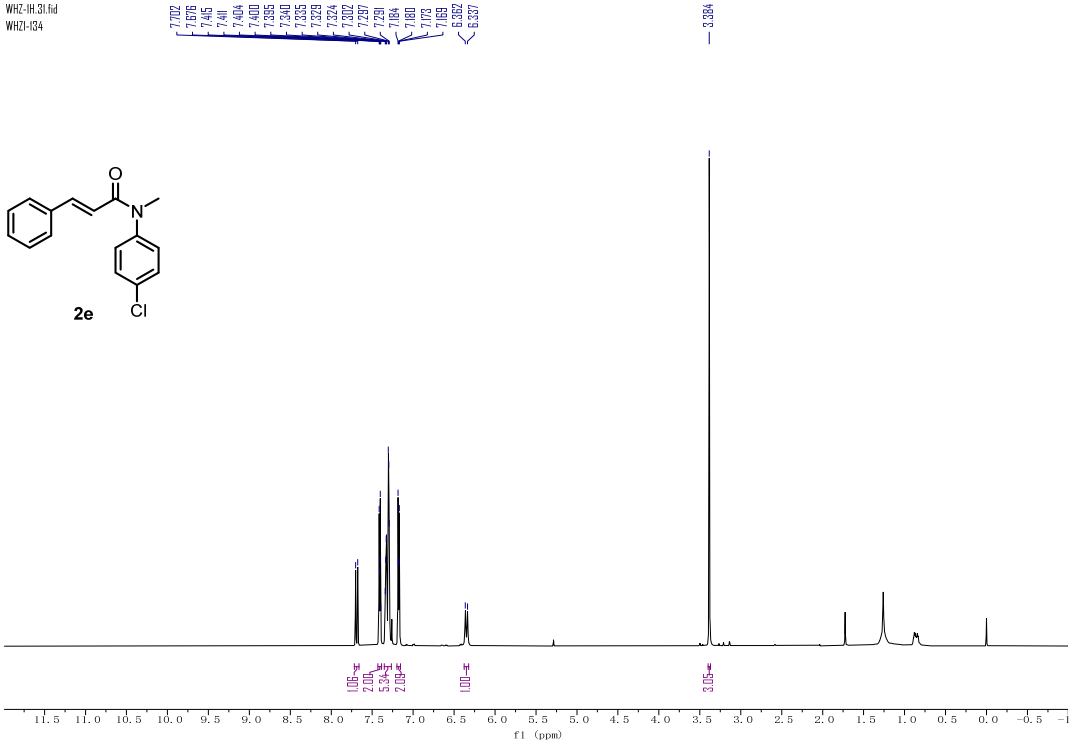
2c

^{1}H NMR spectrum of **2d** (600 MHz, $CDCl_3$)

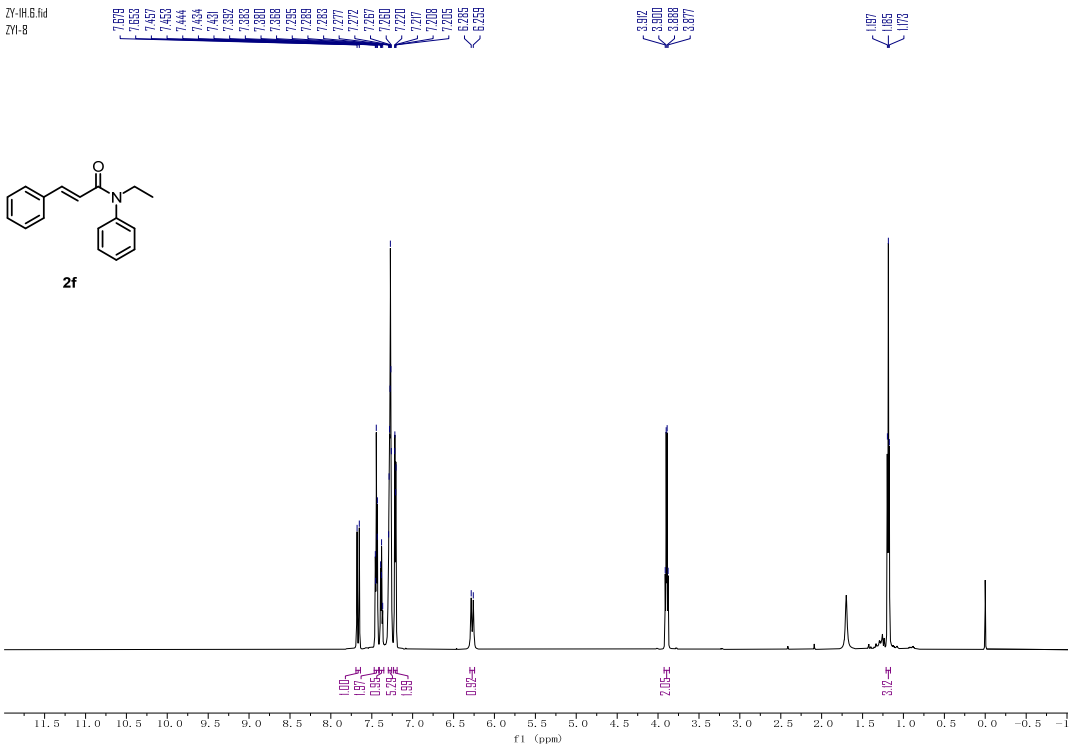


2d

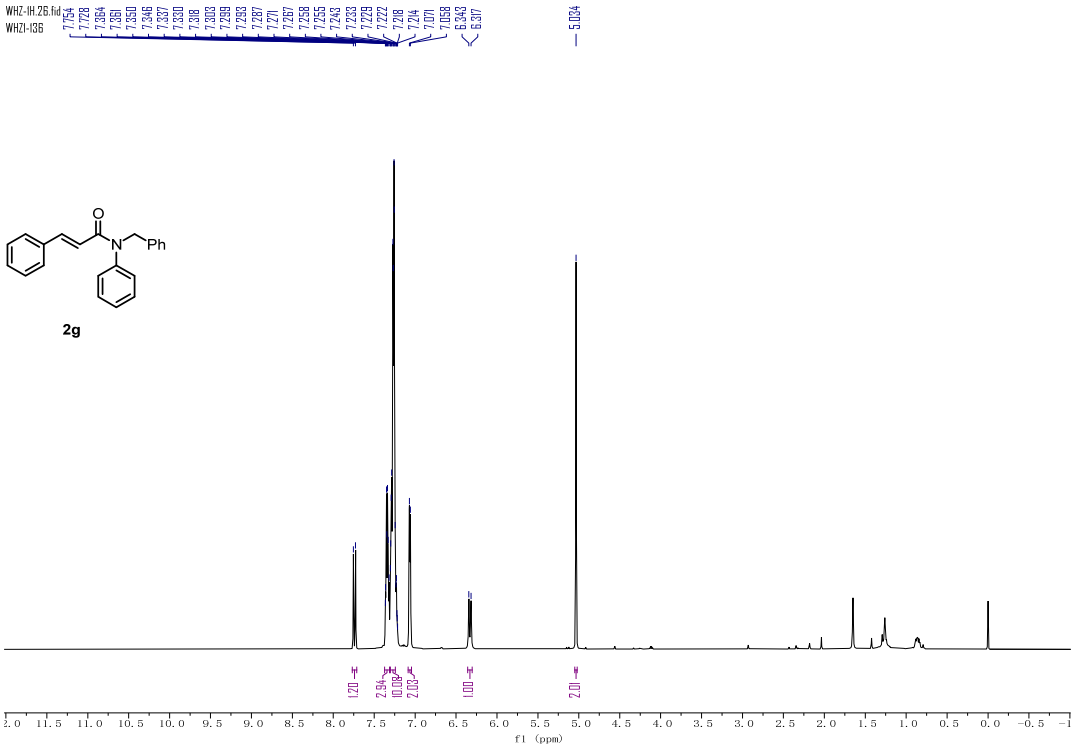
^{1}H NMR spectrum of **2e** (600 MHz, $CDCl_3$)



^{1}H NMR spectrum of **2f** (600 MHz, $CDCl_3$)

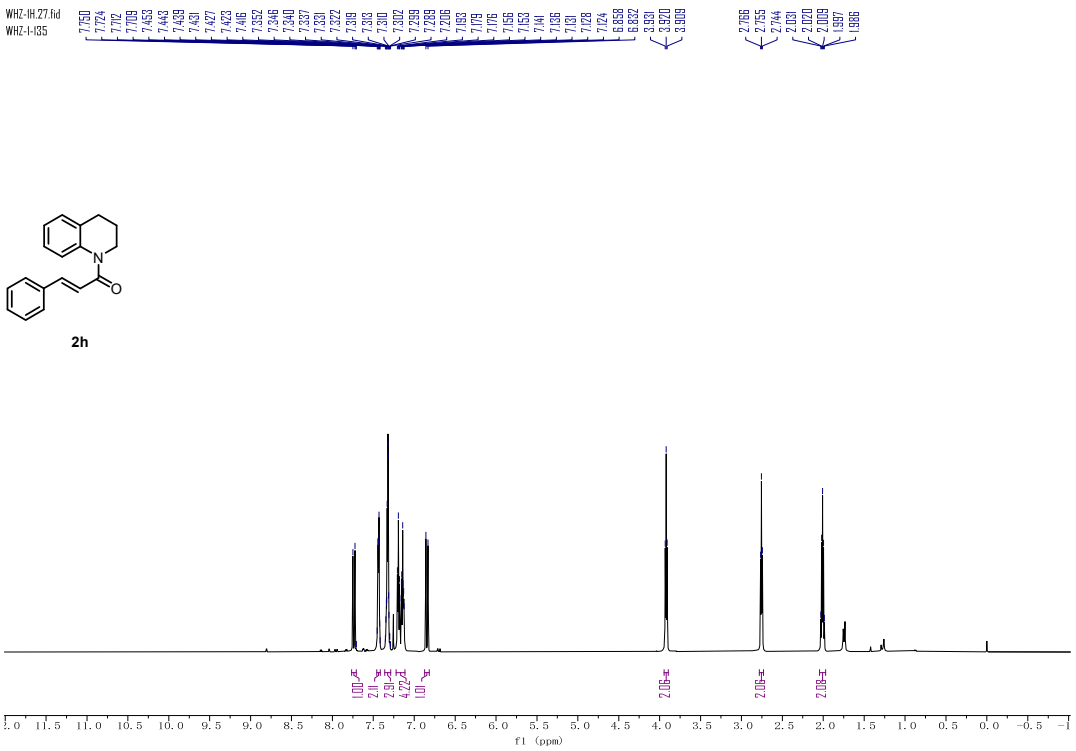


^{1}H NMR spectrum of **2g** (600 MHz, $CDCl_3$)



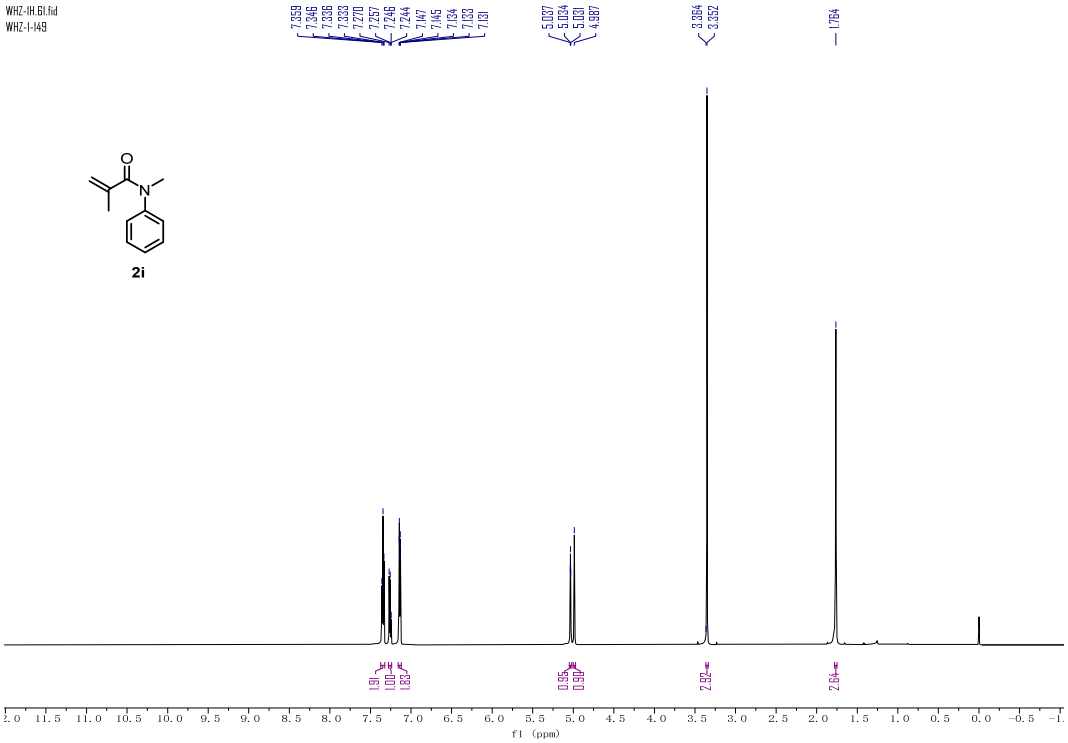
2g

^{1}H NMR spectrum of **2h** (600 MHz, $CDCl_3$)



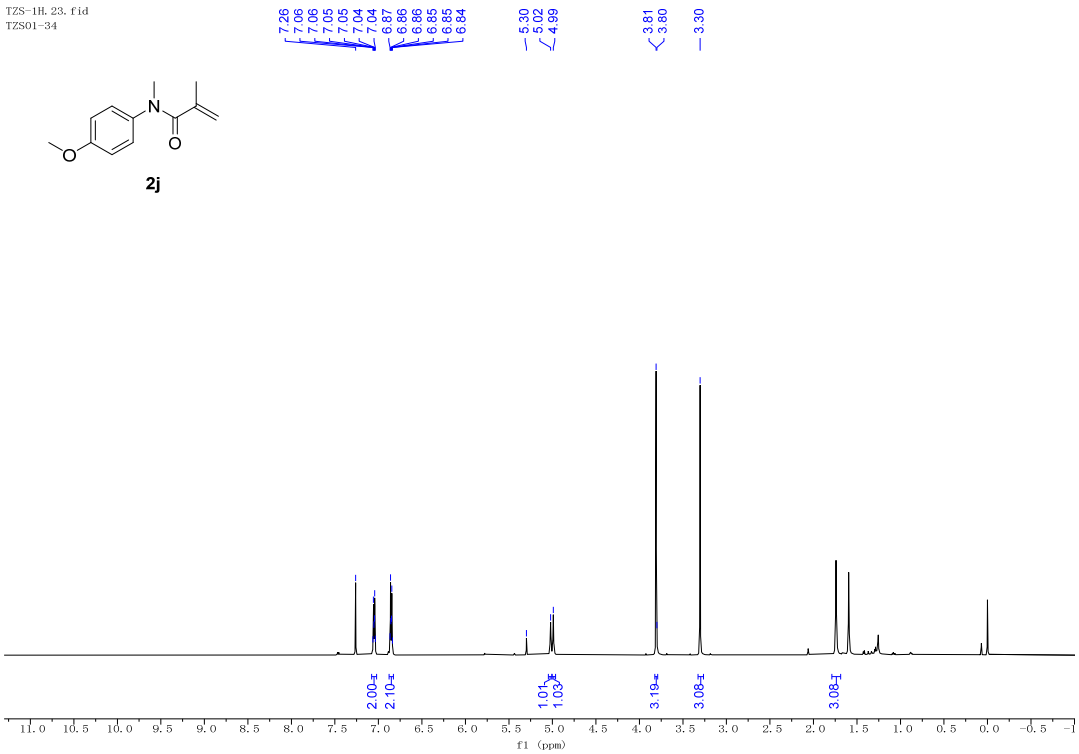
2h

^{1}H NMR spectrum of **2i** (600 MHz, $CDCl_3$)



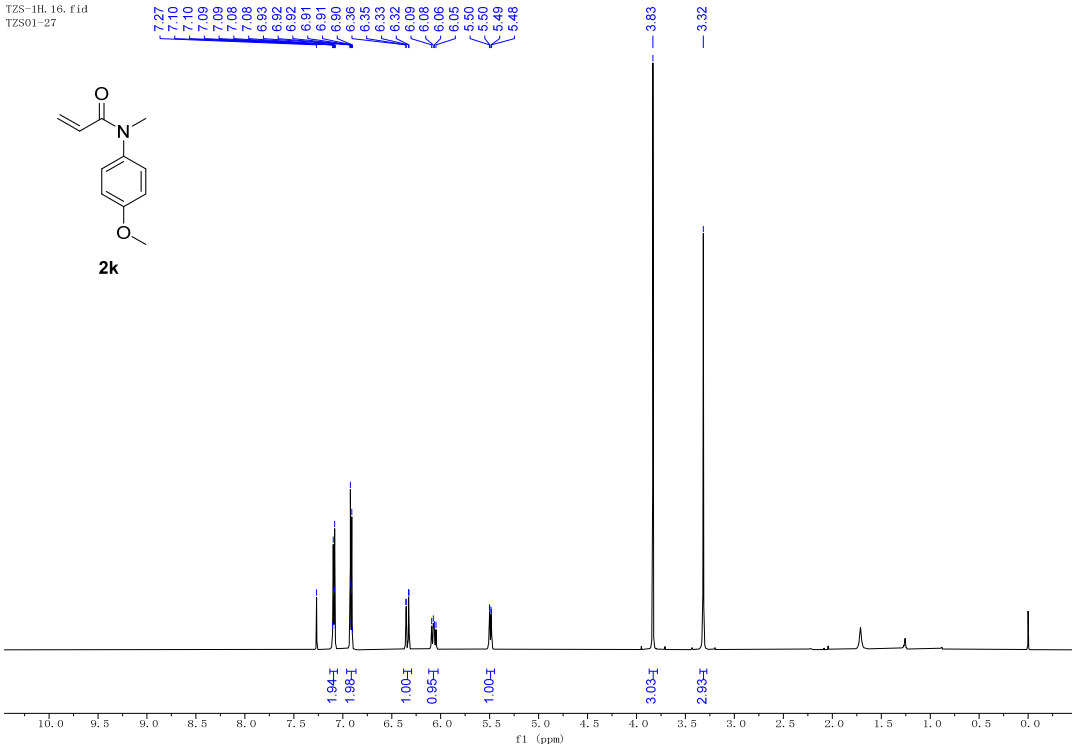
2i

^{1}H NMR spectrum of **2j** (600 MHz, $CDCl_3$)

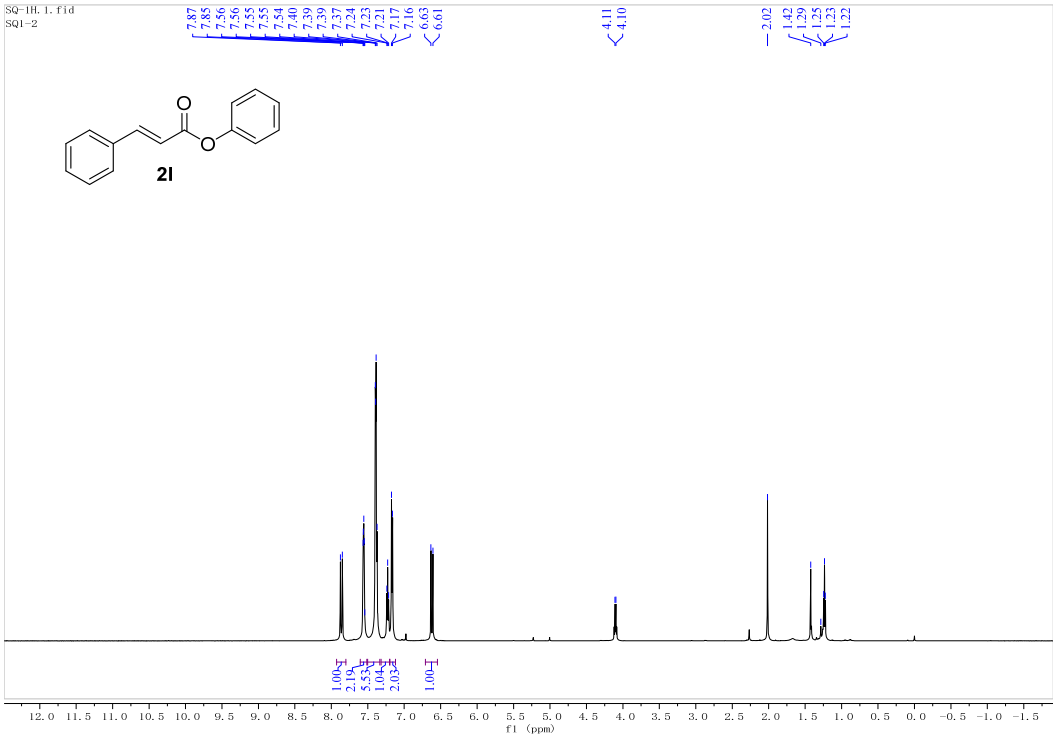


2j

^{1}H NMR spectrum of **2k** (600 MHz, $CDCl_3$)

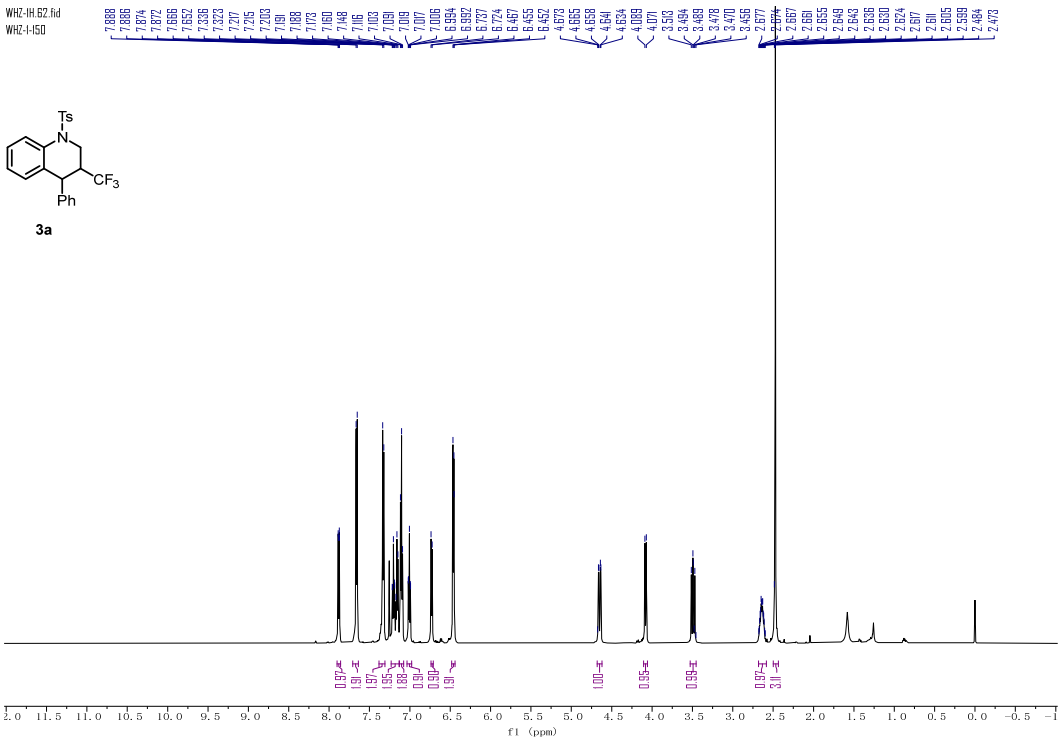


^{1}H NMR spectrum of **2l** (600 MHz, $CDCl_3$)

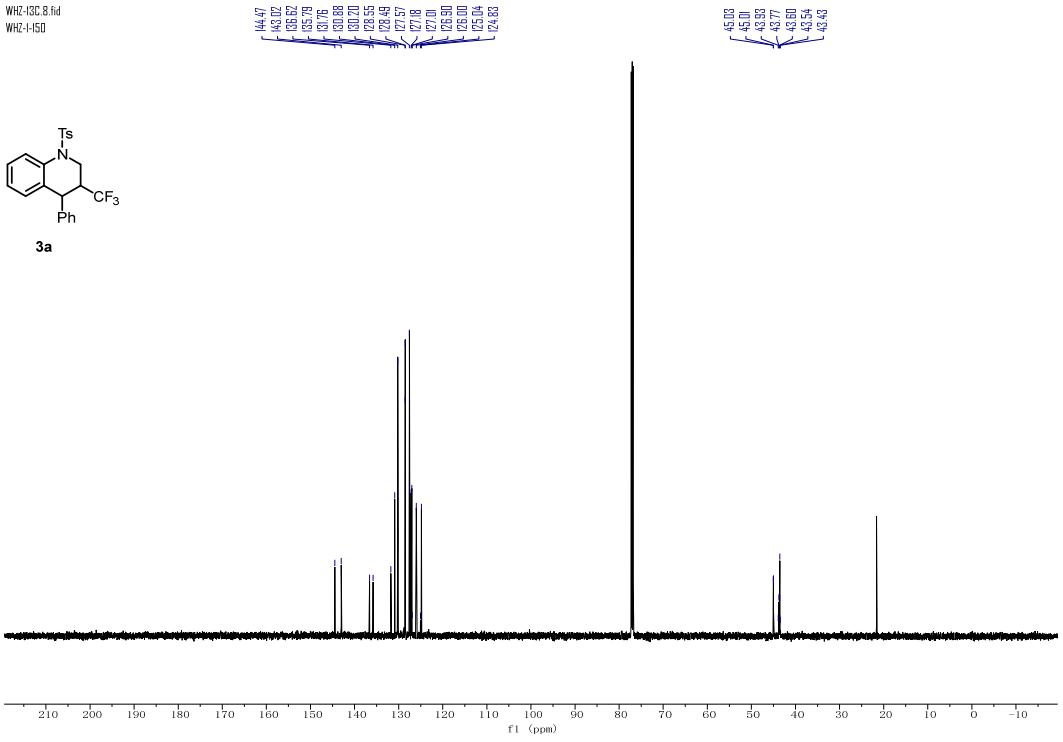


8.3 Experimental spectra of products 3

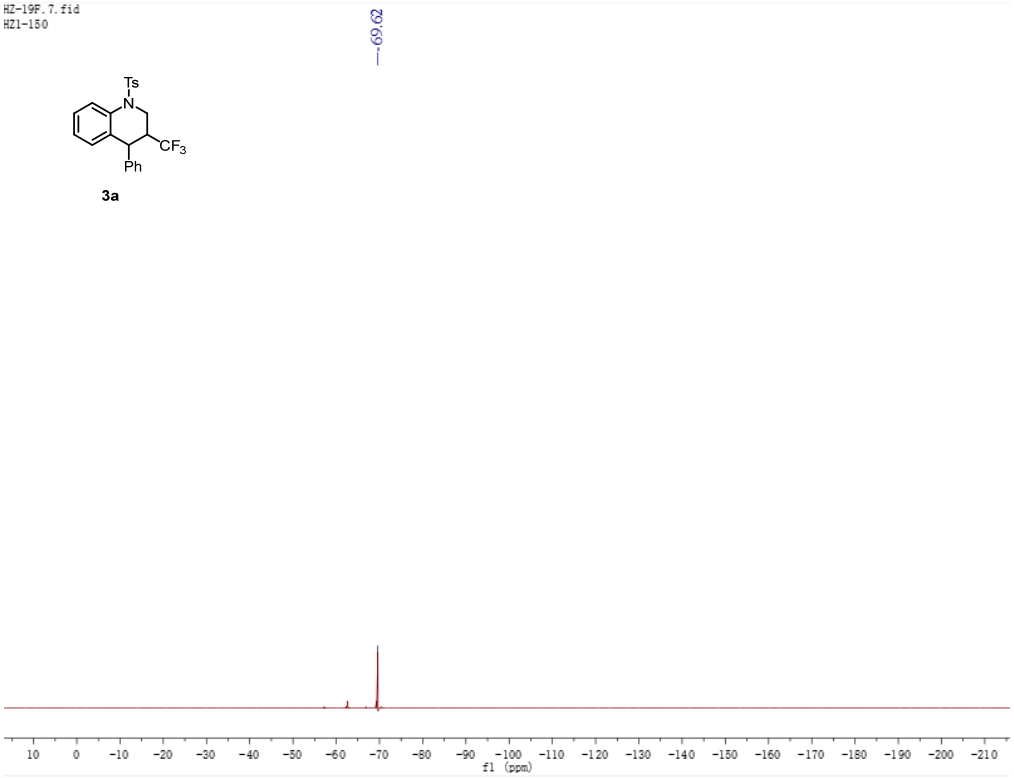
^{1}H NMR spectrum of **3a** (600 MHz, $CDCl_3$)



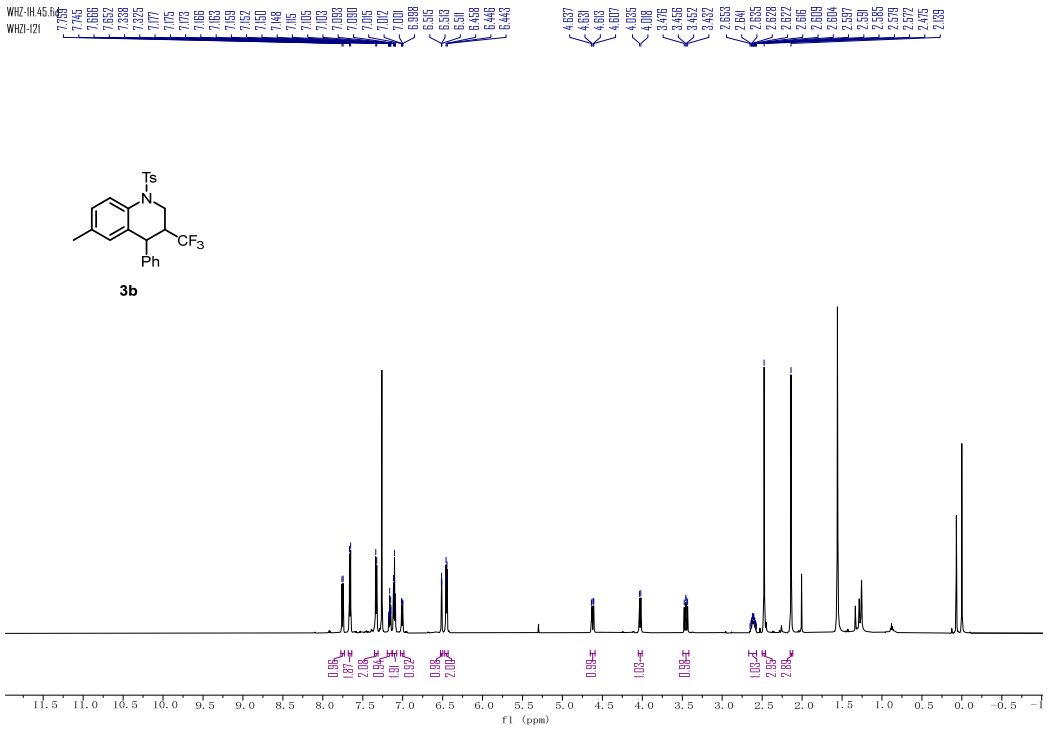
^{13}C NMR spectrum of **3a** (151 MHz, $CDCl_3$)



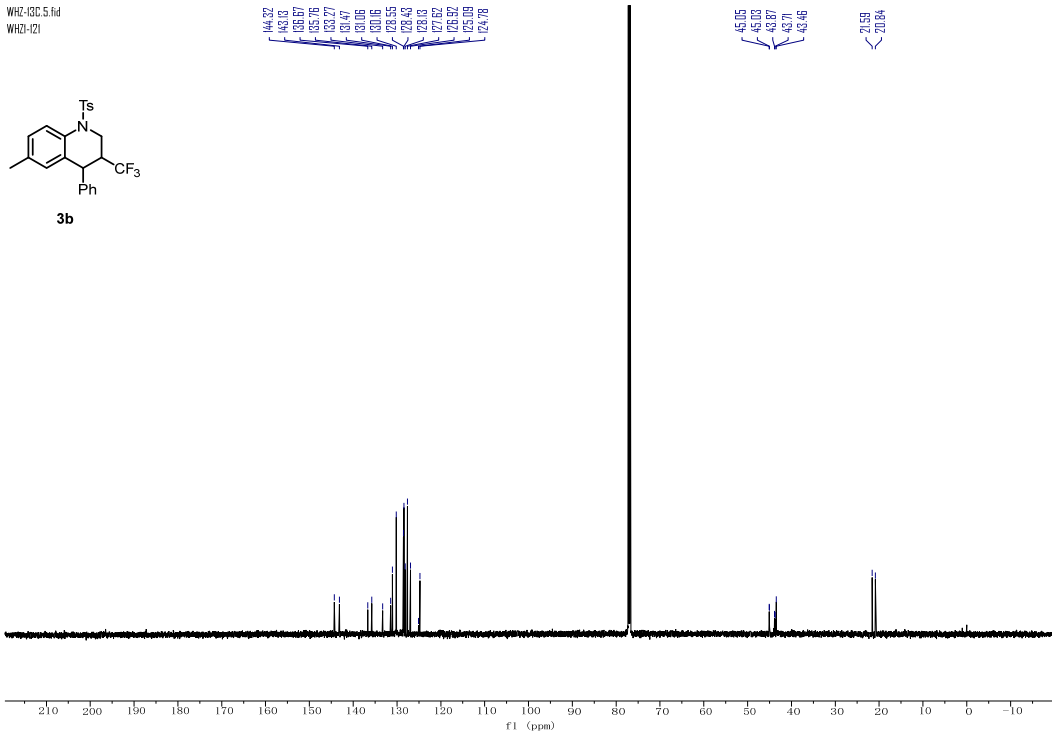
^{19}F NMR spectrum of **3a** (565 MHz, $CDCl_3$)



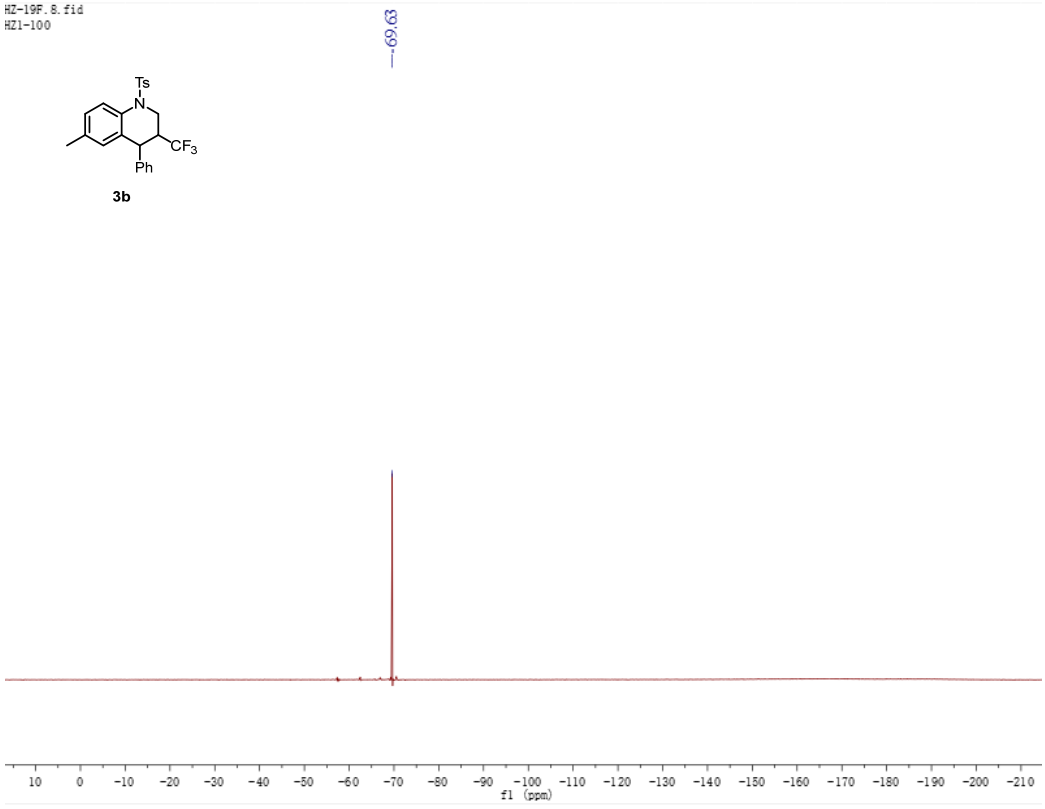
^{1}H NMR spectrum of **3b** (600 MHz, $CDCl_3$)



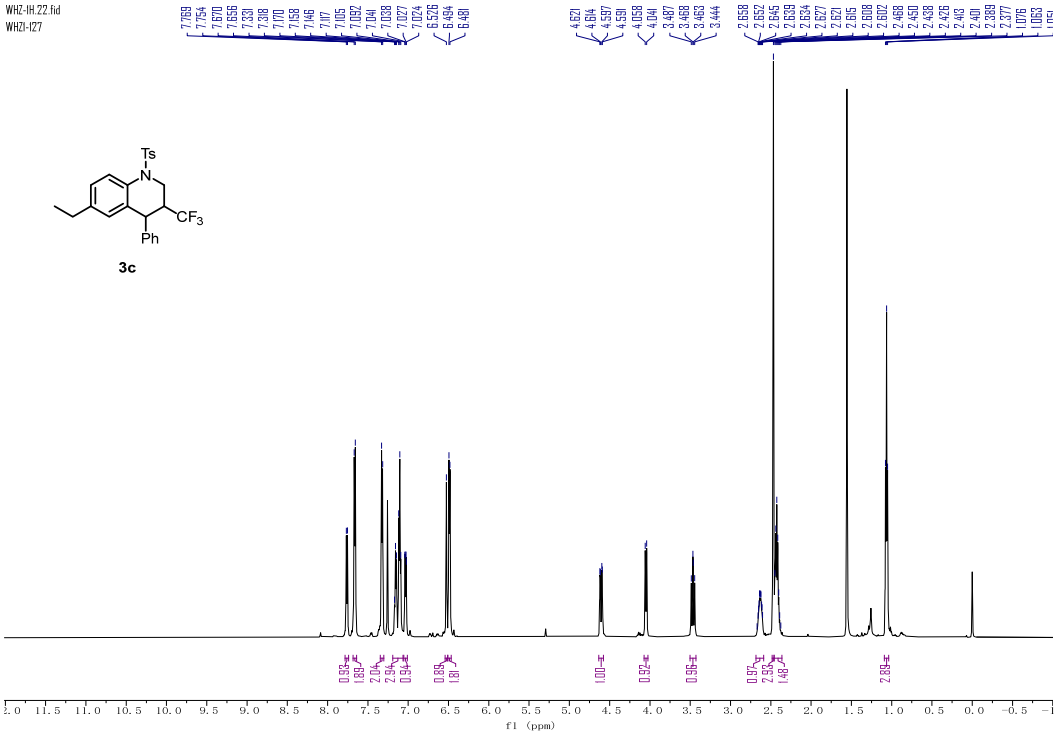
^{13}C NMR spectrum of **3b** (151 MHz, $CDCl_3$)



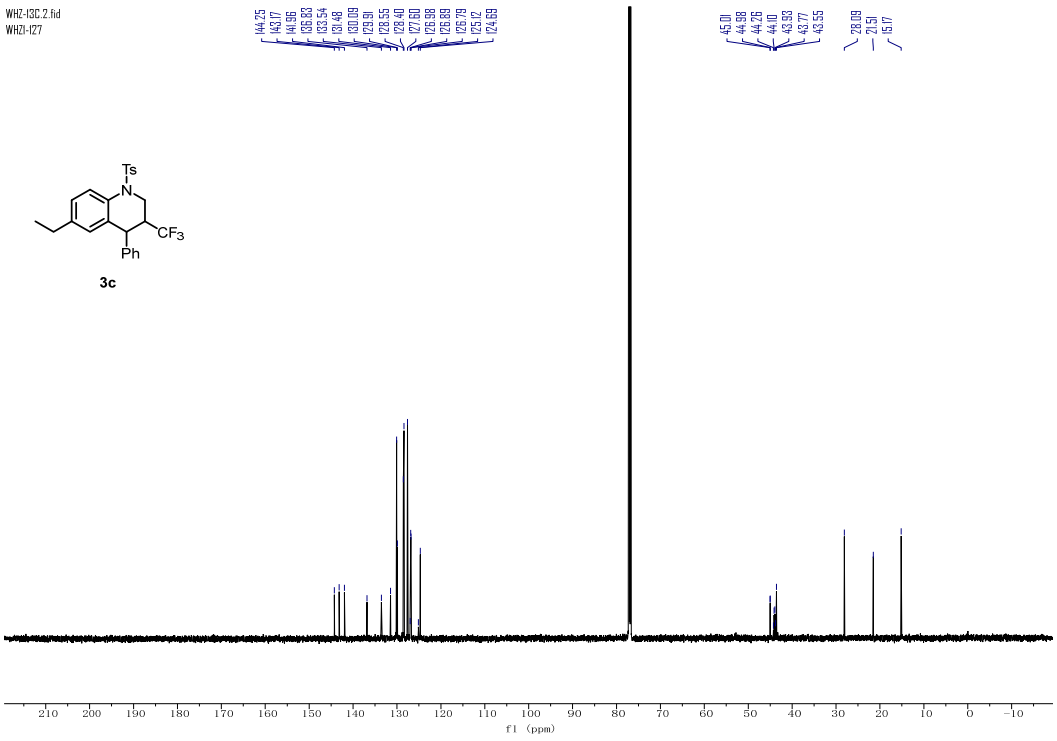
^{19}F NMR spectrum of **3b** (565 MHz, $CDCl_3$)



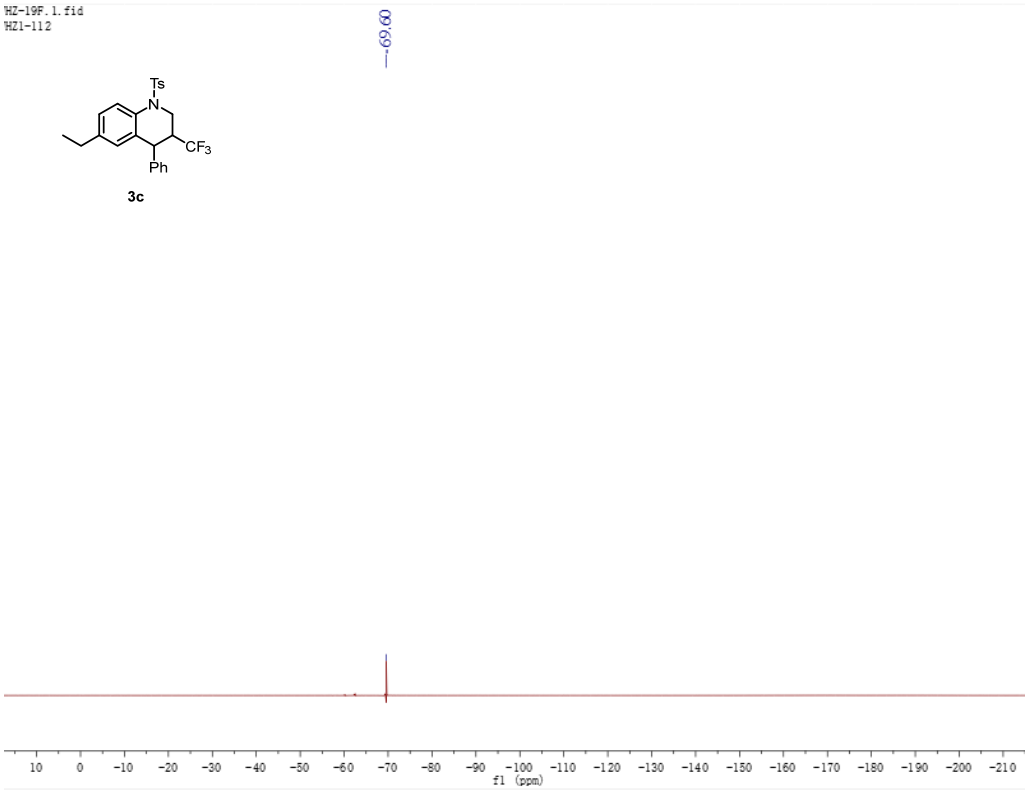
^{1}H NMR spectrum of **3c** (600 MHz, $CDCl_3$)



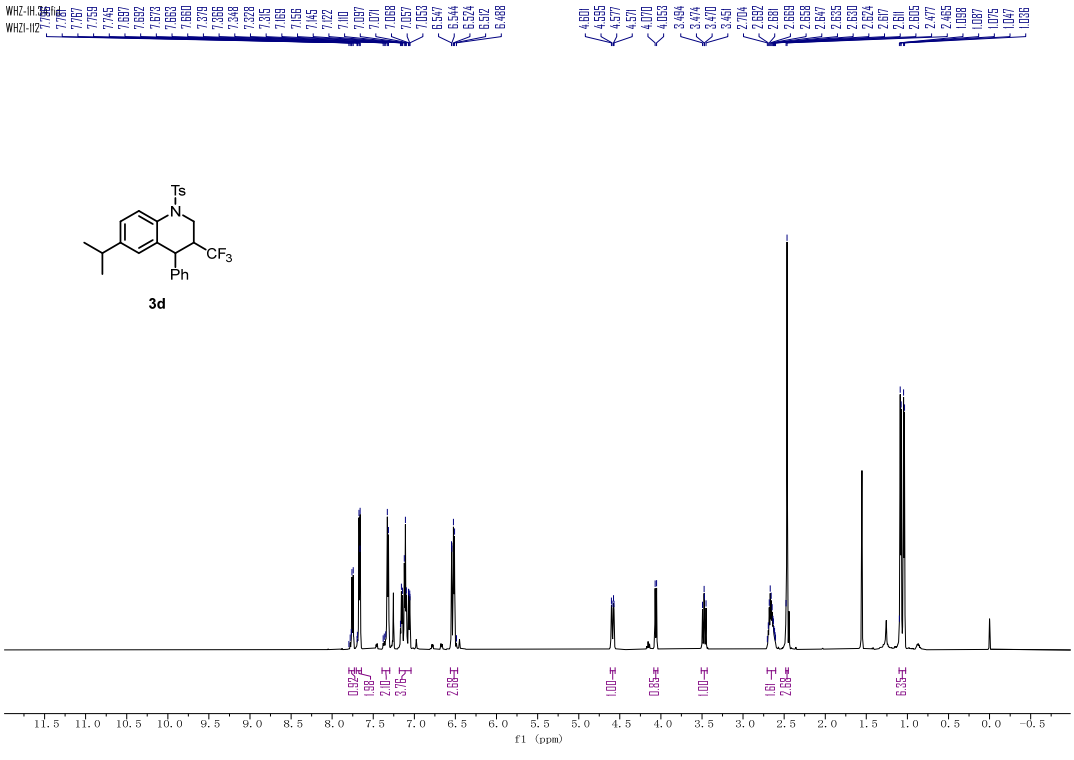
^{13}C NMR spectrum of **3c** (151 MHz, $CDCl_3$)



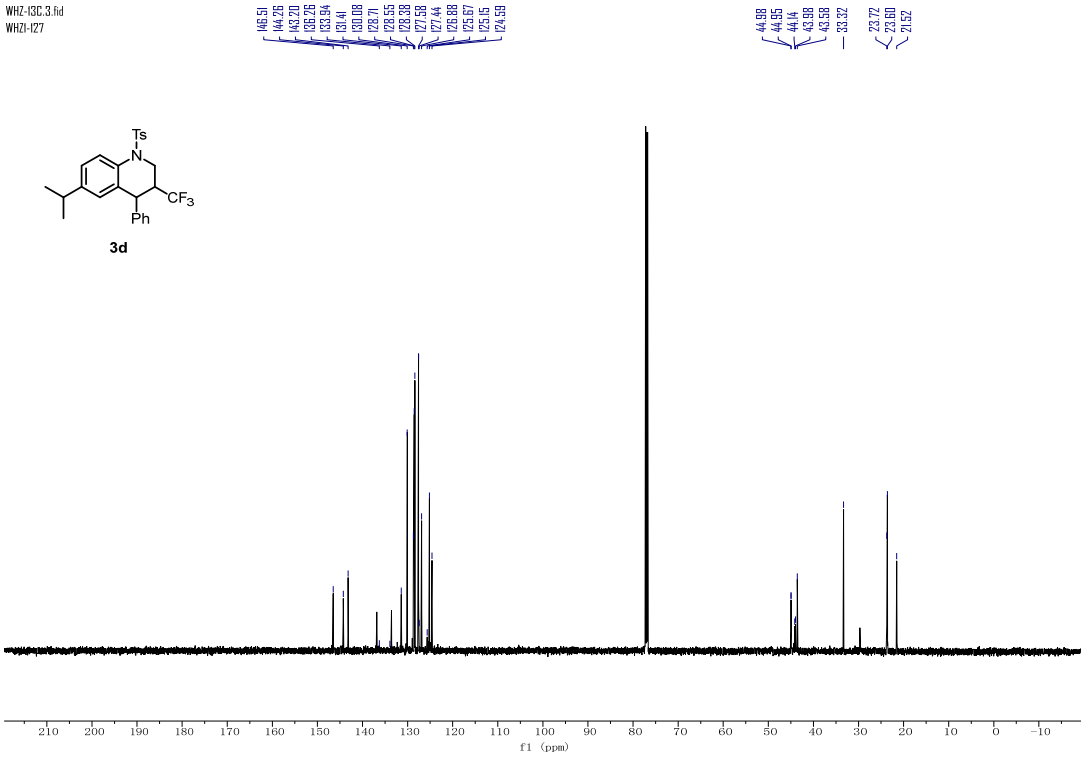
^{19}F NMR spectrum of **3c** (565 MHz, $CDCl_3$)



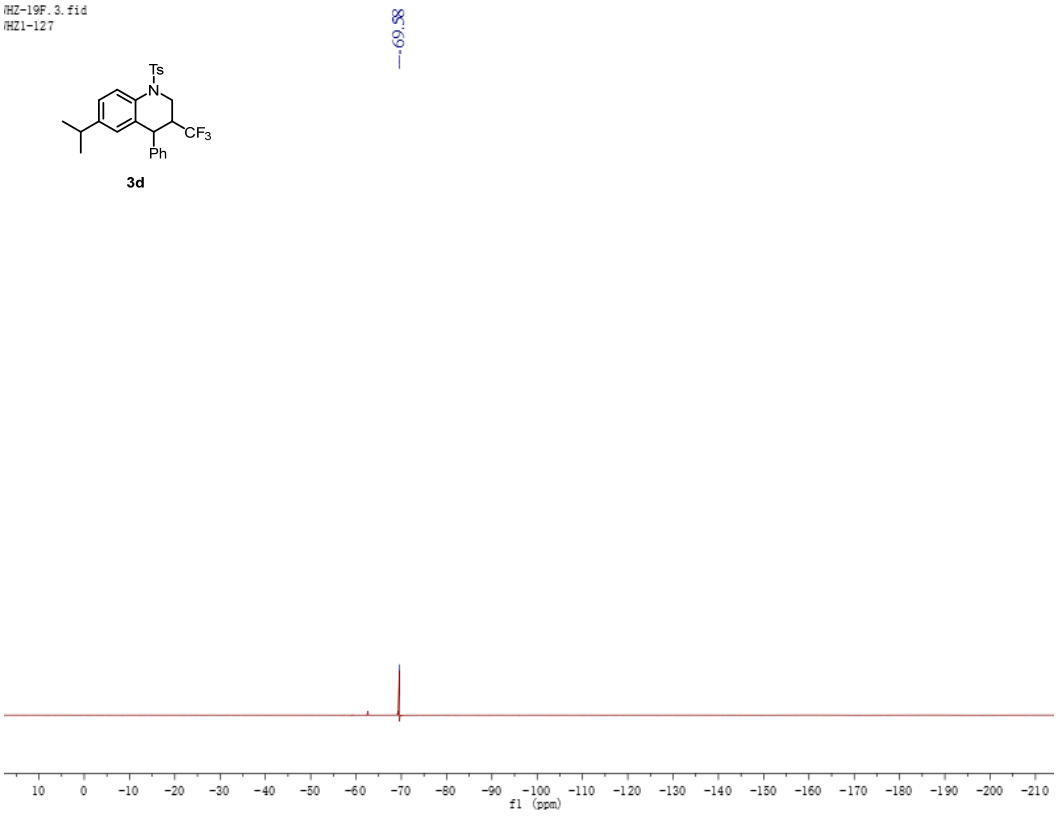
^{1}H NMR spectrum of **3d** (600 MHz, $CDCl_3$)



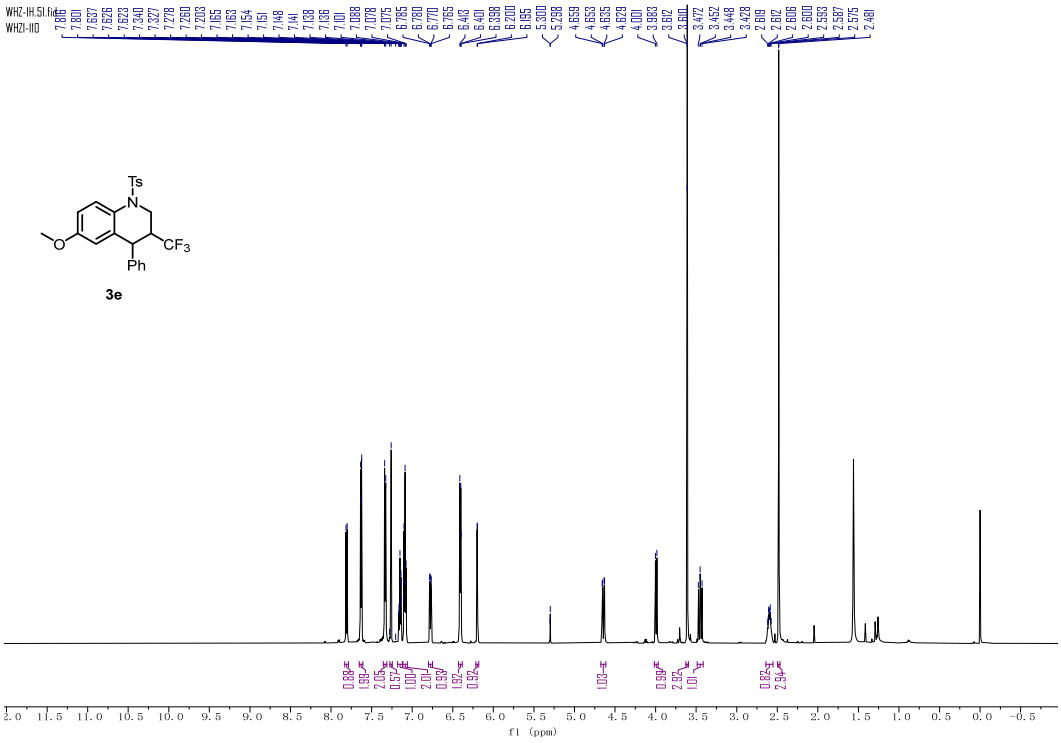
^{13}C NMR spectrum of **3d** (151 MHz, $CDCl_3$)



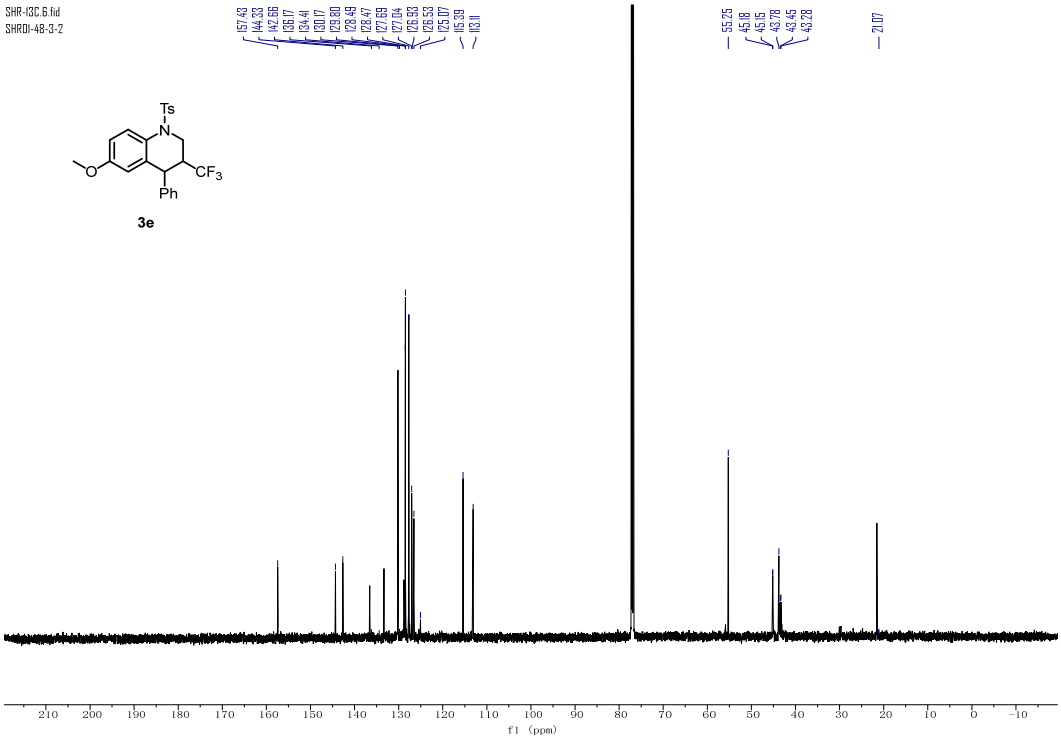
^{19}F NMR spectrum of **3d** (565 MHz, $CDCl_3$)



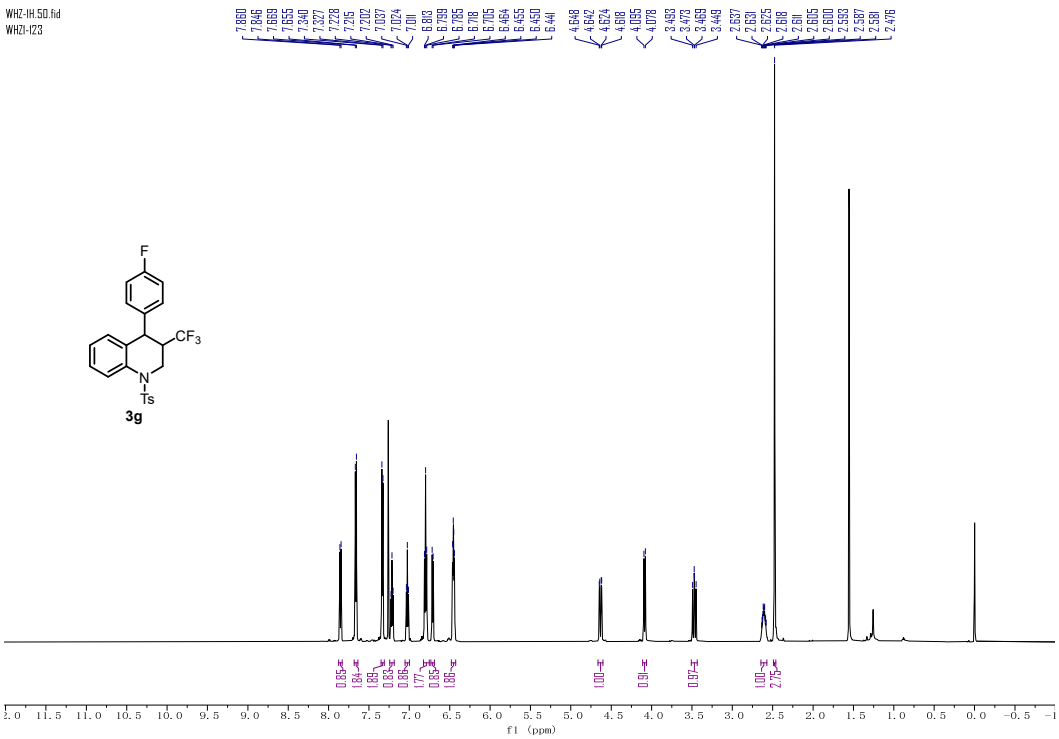
^{1}H NMR spectrum of **3e** (600 MHz, $CDCl_3$)



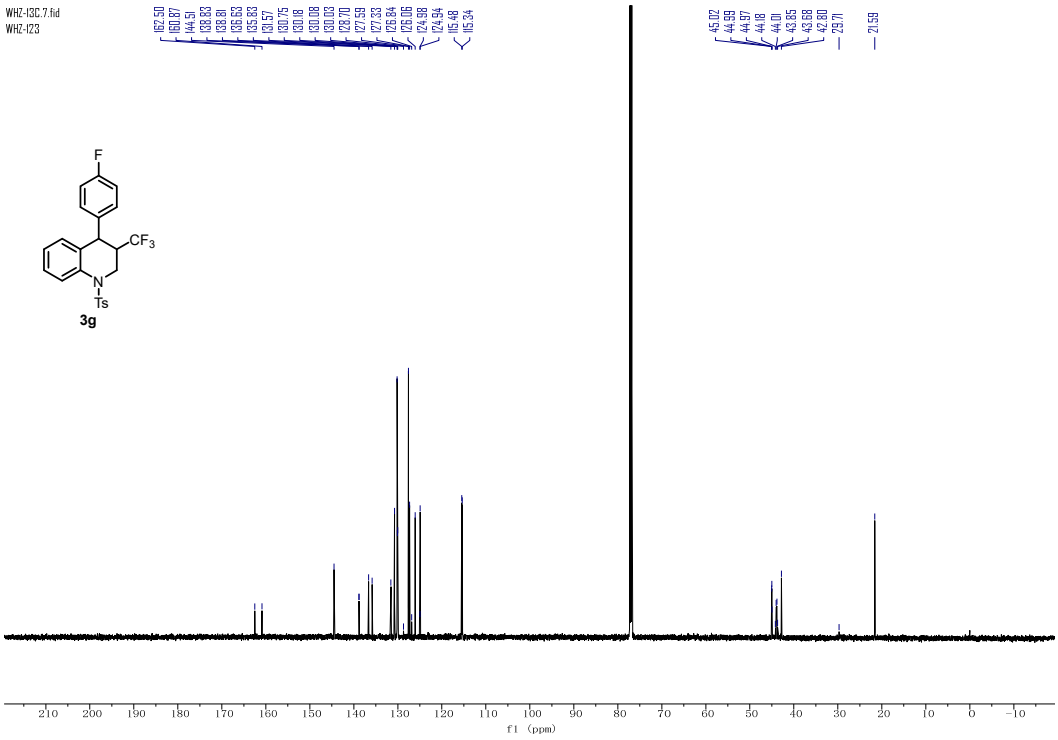
^{13}C NMR spectrum of **3e** (151 MHz, $CDCl_3$)



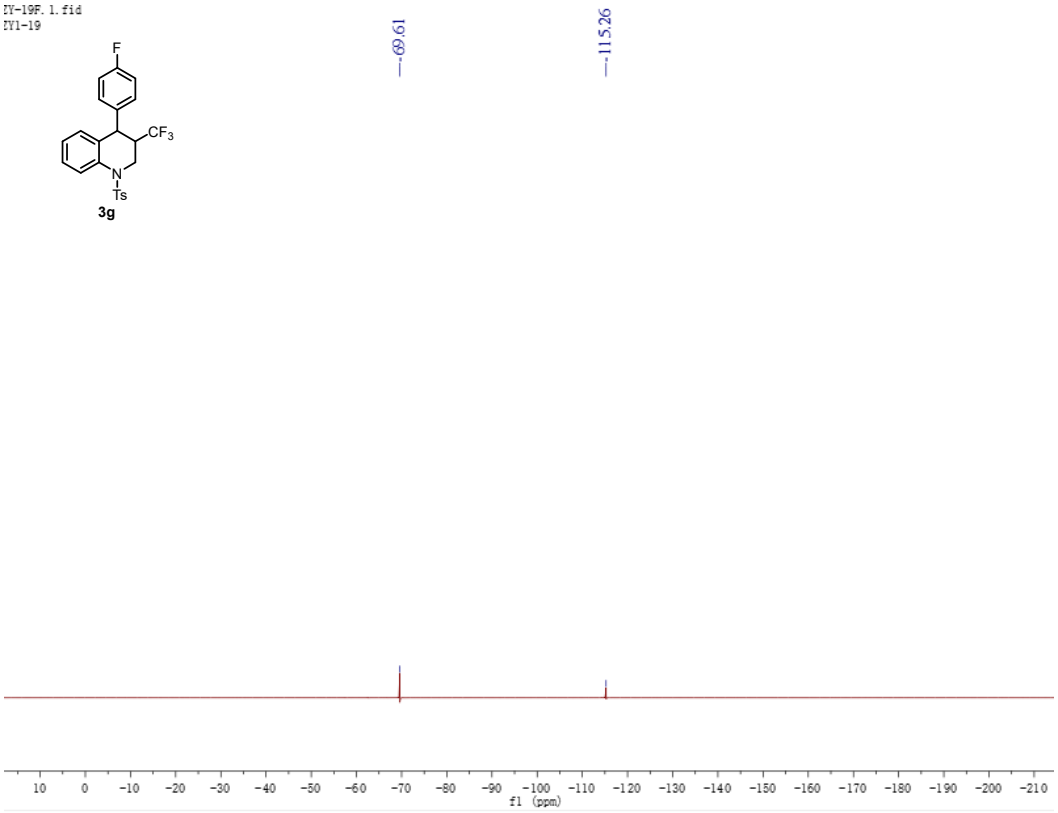
^{1}H NMR spectrum of **3g** (600 MHz, $CDCl_3$)



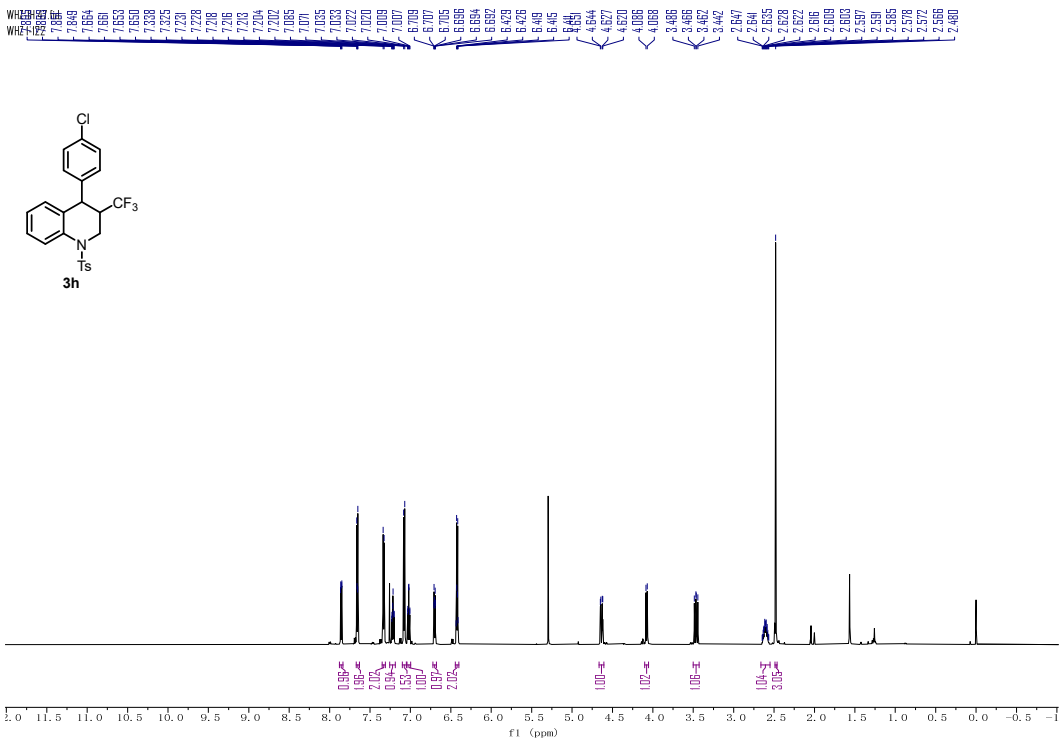
^{13}C NMR spectrum of **3g** (151 MHz, $CDCl_3$)



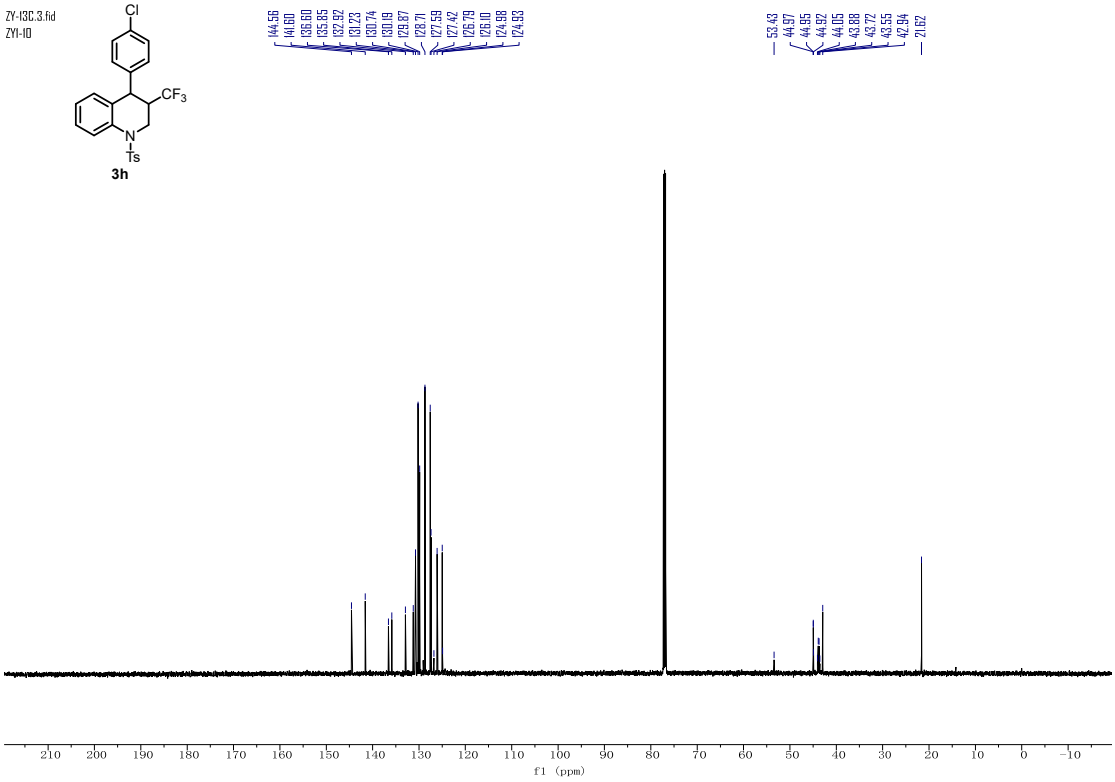
^{19}F NMR spectrum of **3g** (565 MHz, $CDCl_3$)



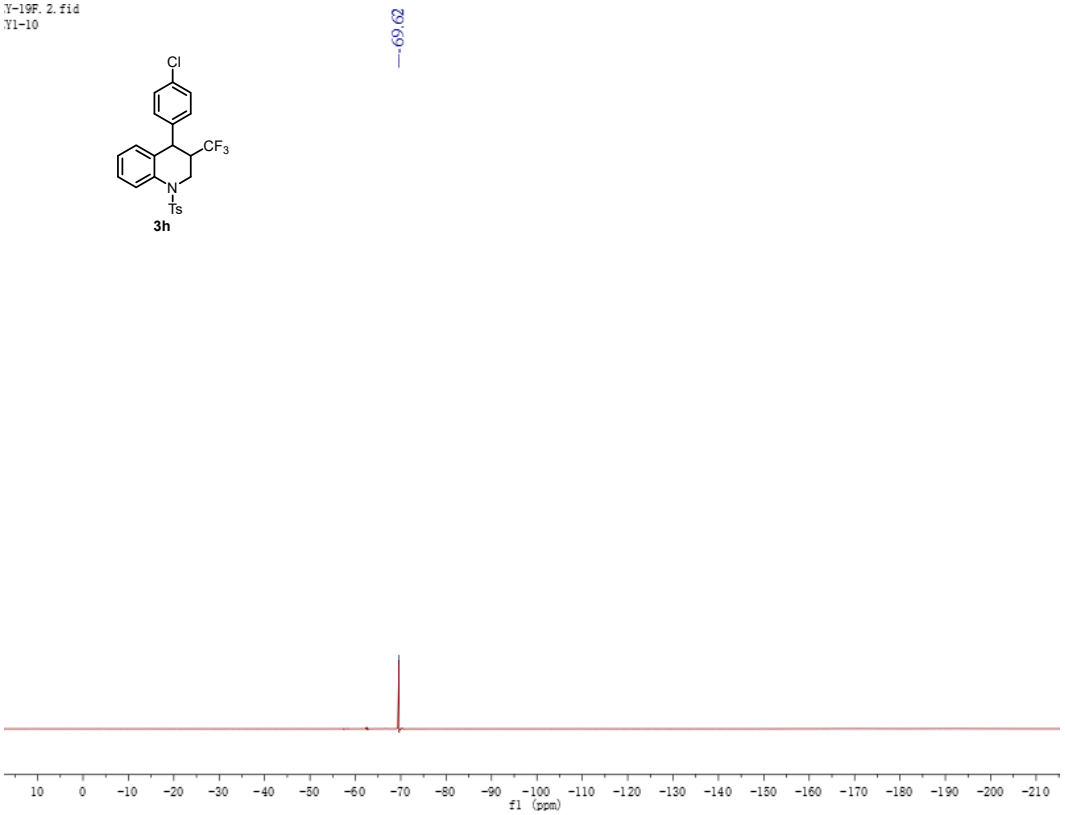
^{1}H NMR spectrum of **3h** (600 MHz, $CDCl_3$)



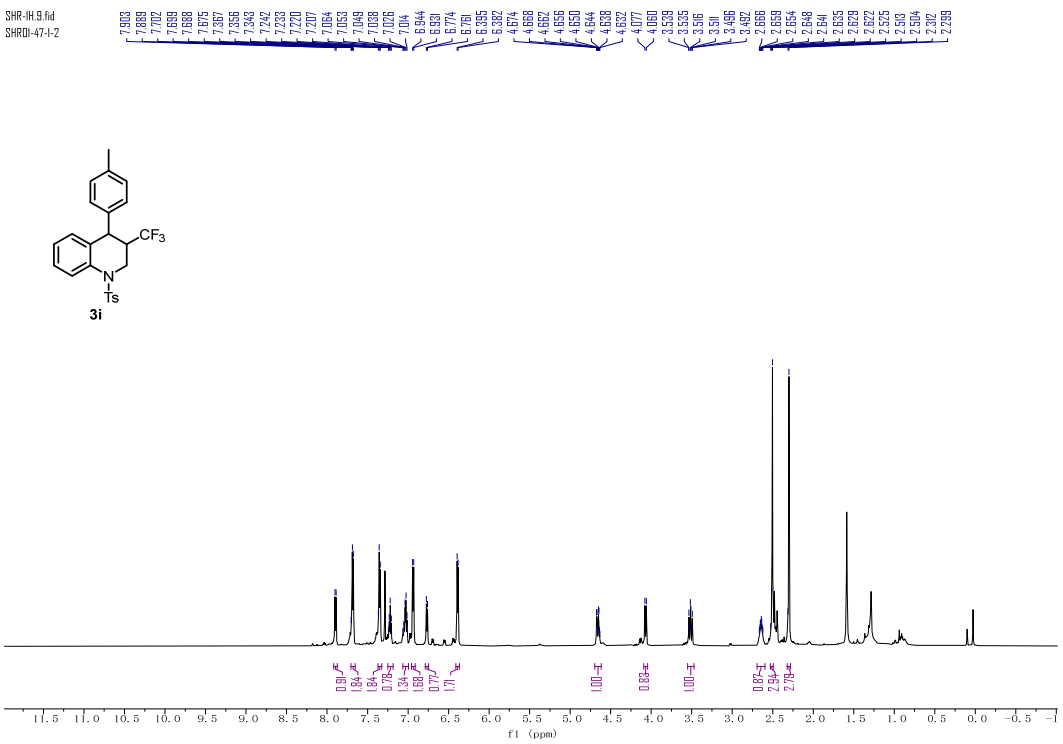
^{13}C NMR spectrum of **3h** (151 MHz, $CDCl_3$)



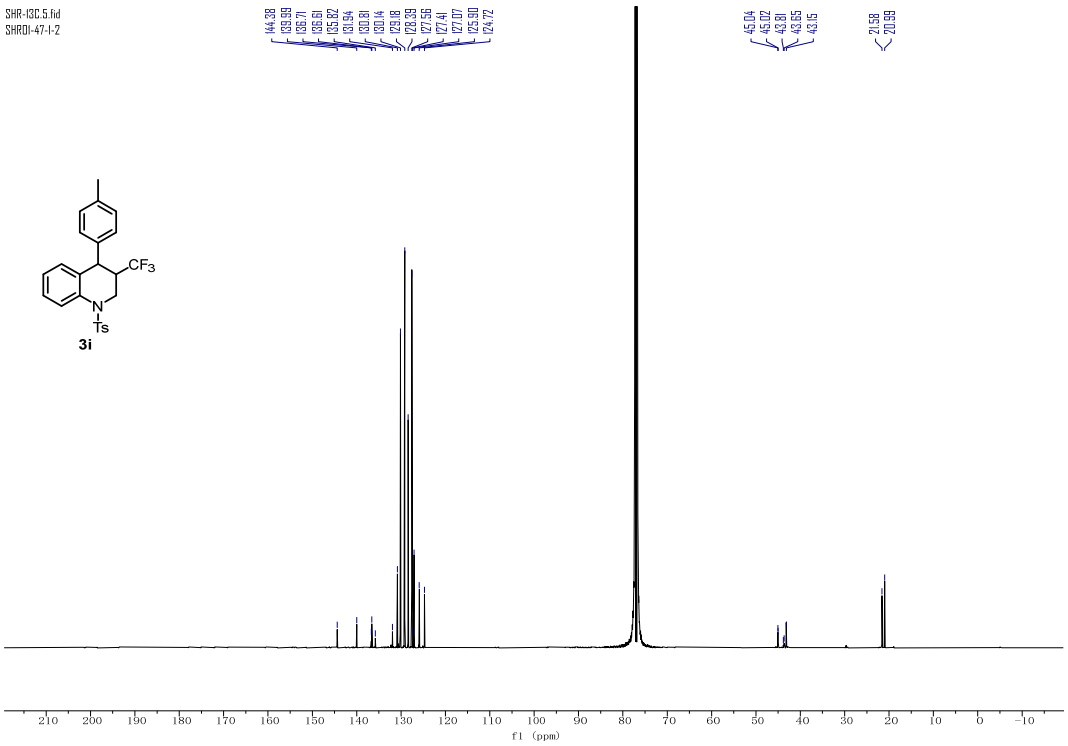
^{19}F NMR spectrum of **3h** (565 MHz, $CDCl_3$)



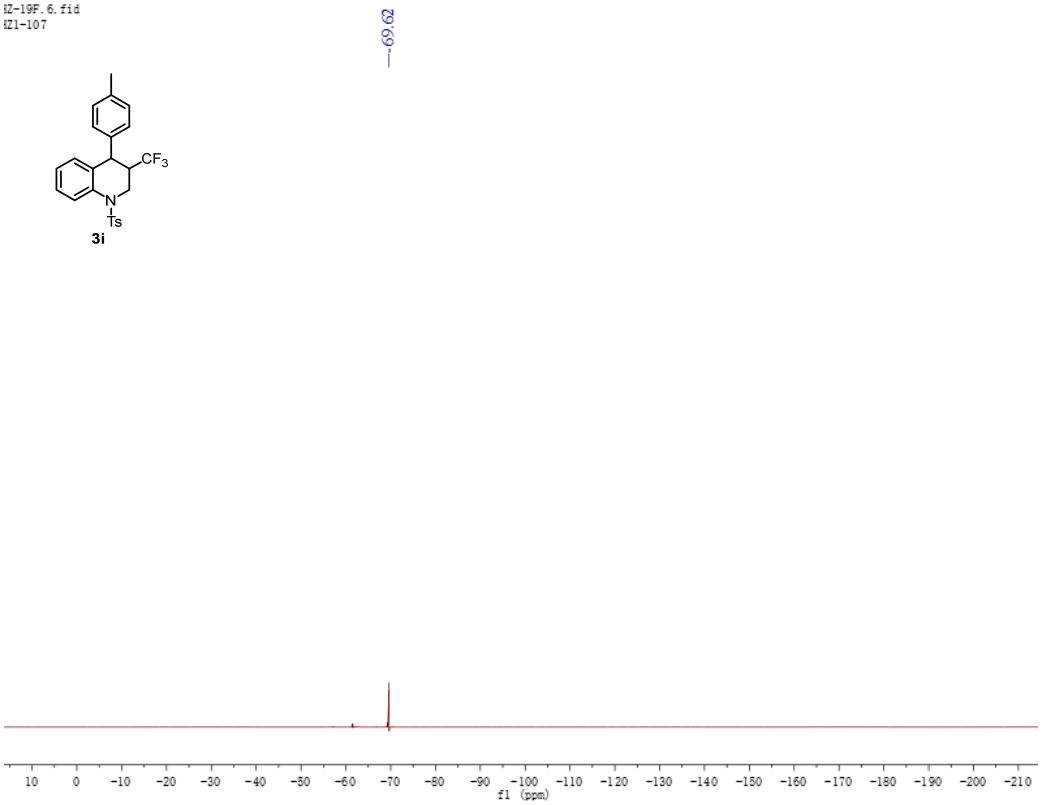
^{1}H NMR spectrum of **3i** (600 MHz, $CDCl_3$)



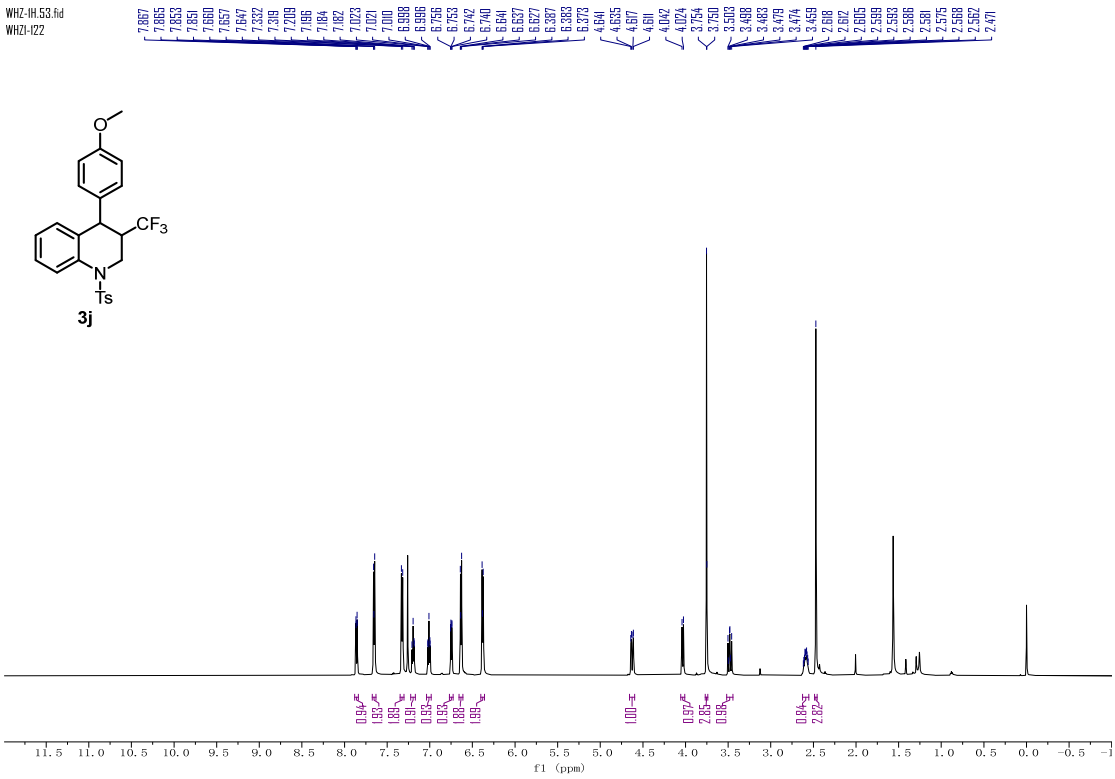
^{13}C NMR spectrum of **3i** (151 MHz, $CDCl_3$)



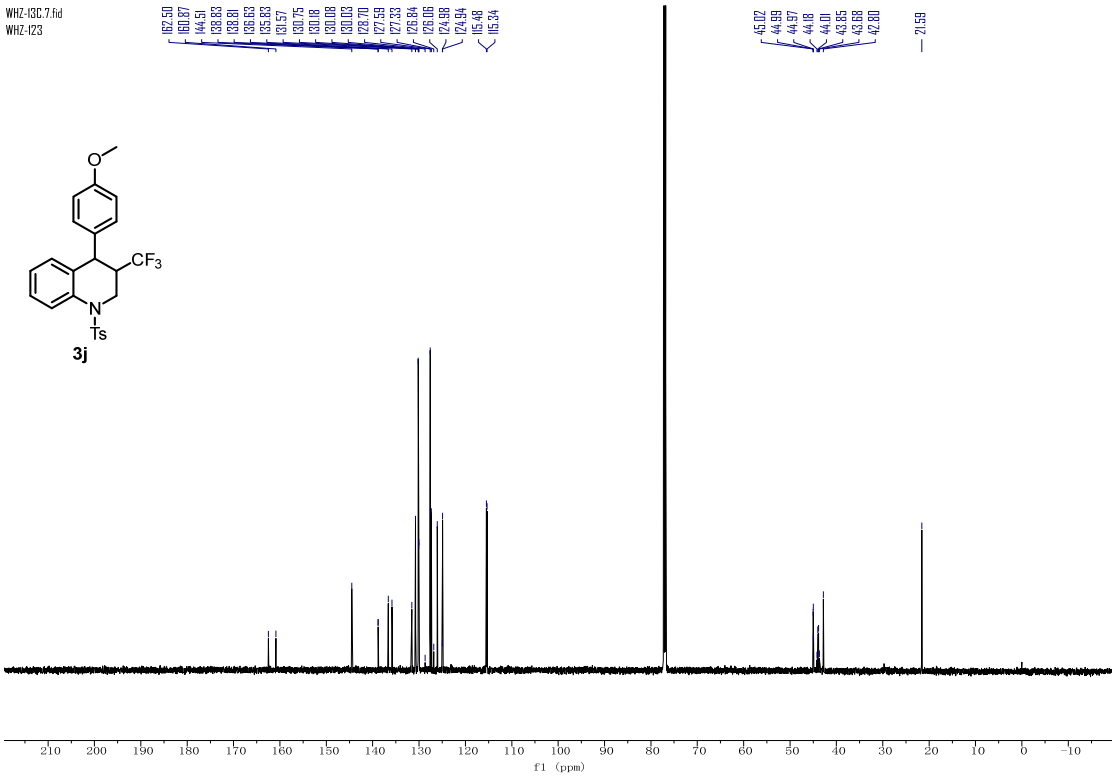
^{19}F NMR spectrum of **3i** (565 MHz, $CDCl_3$)



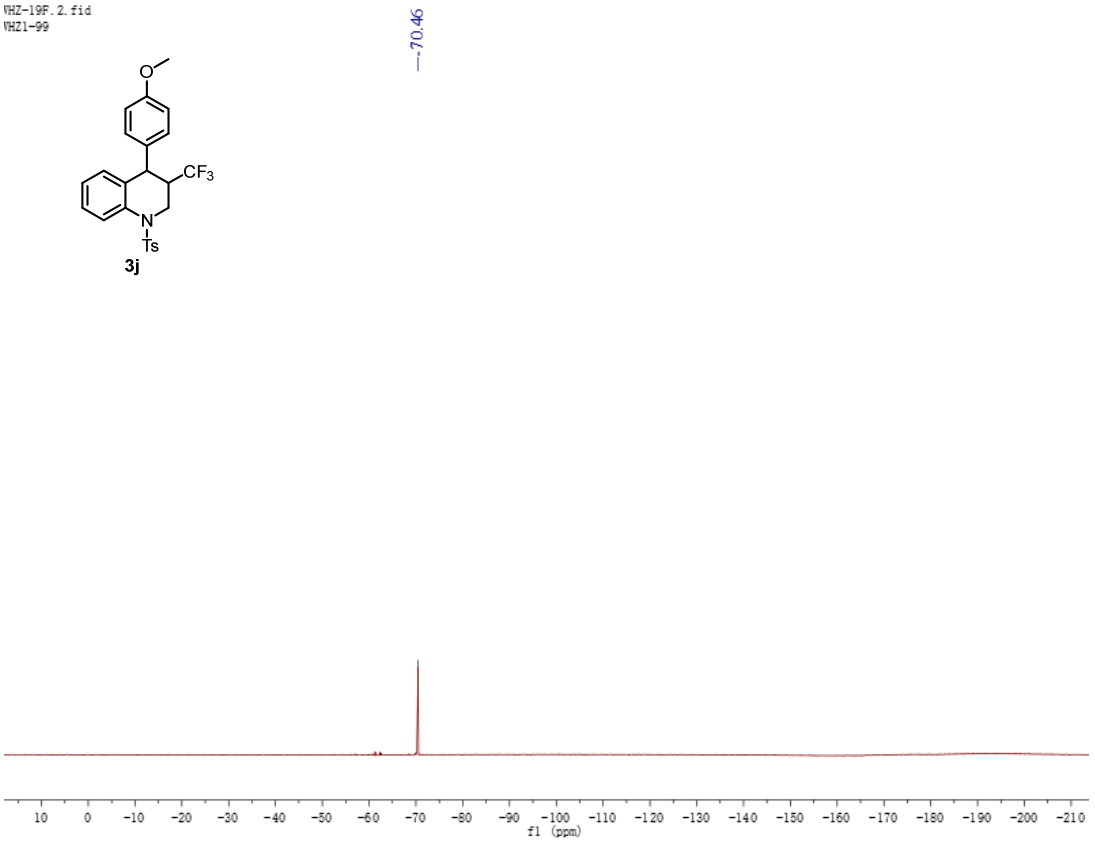
^{1}H NMR spectrum of **3j** (600 MHz, $CDCl_3$)



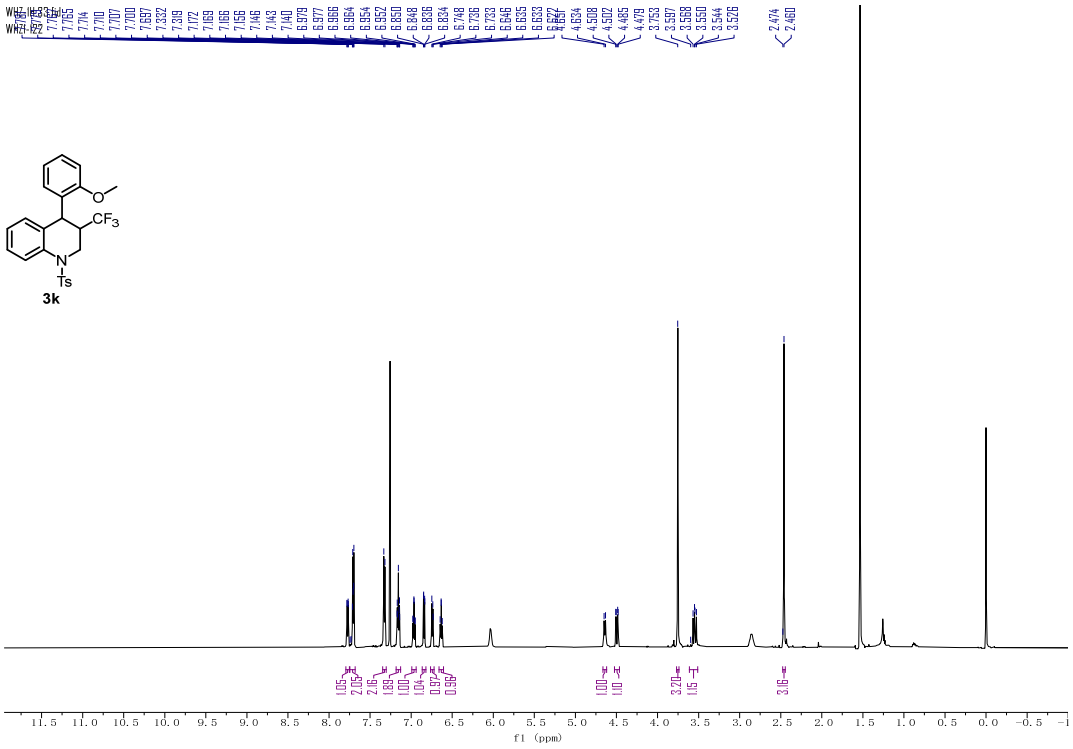
^{13}C NMR spectrum of **3j** (151 MHz, $CDCl_3$)



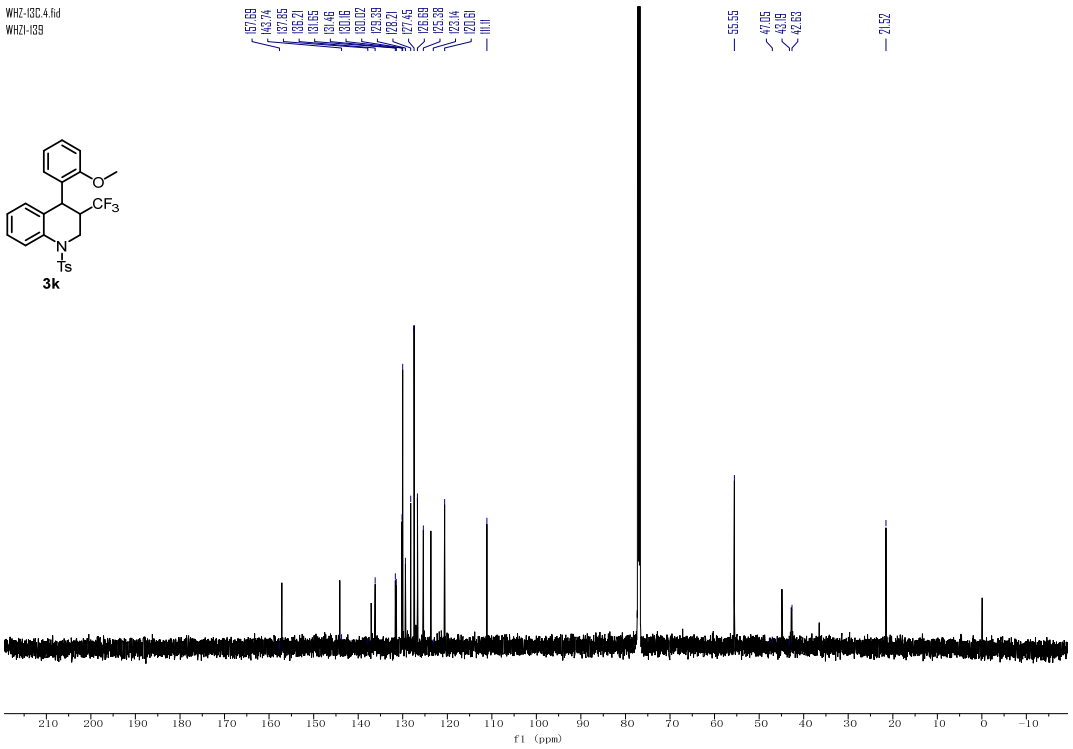
^{19}F NMR spectrum of **3j** (565 MHz, $CDCl_3$)



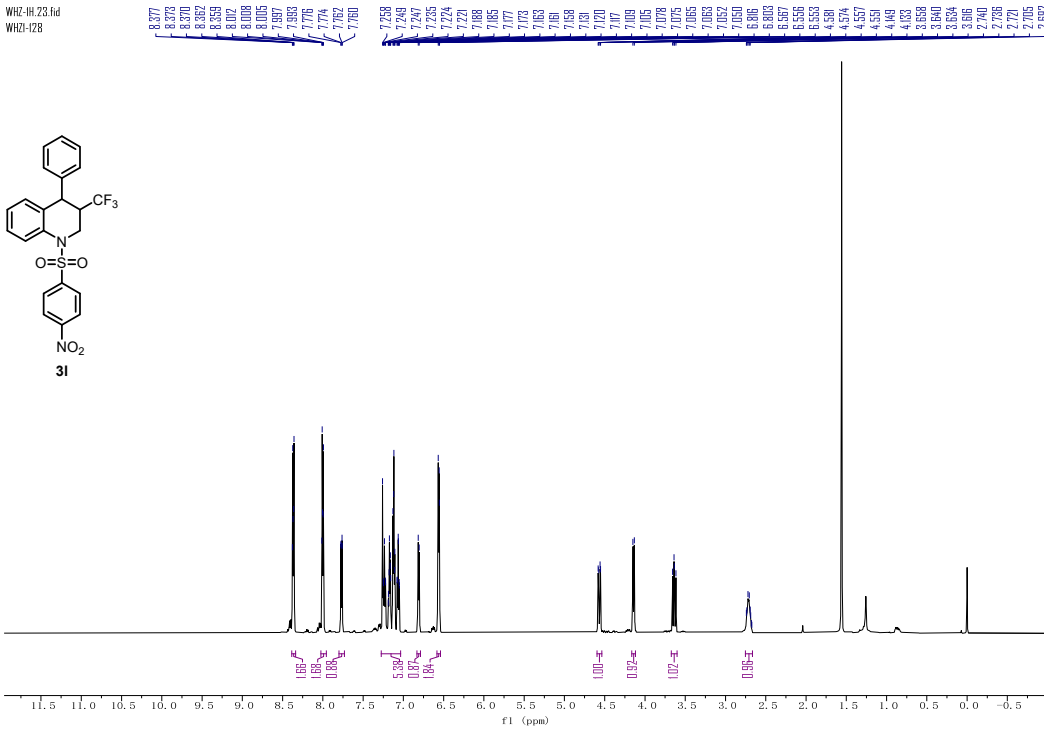
^{1}H NMR spectrum of **3k** (600 MHz, $CDCl_3$)



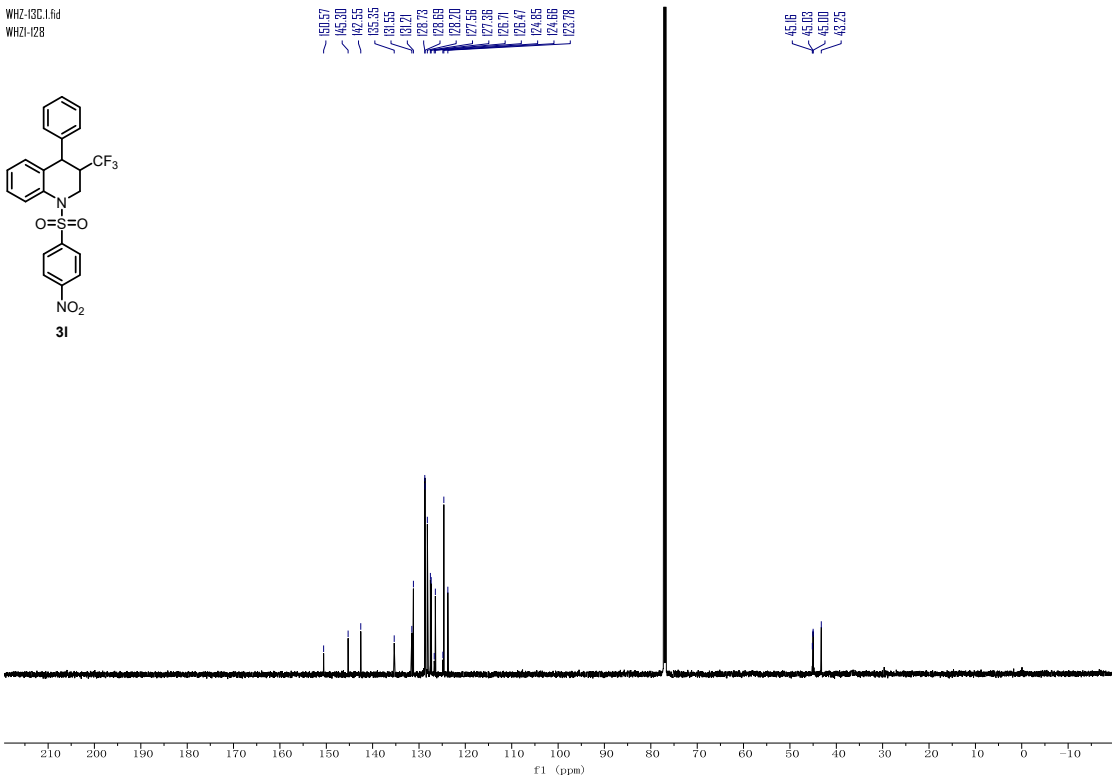
^{13}C NMR spectrum of **3k** (151 MHz, $CDCl_3$)



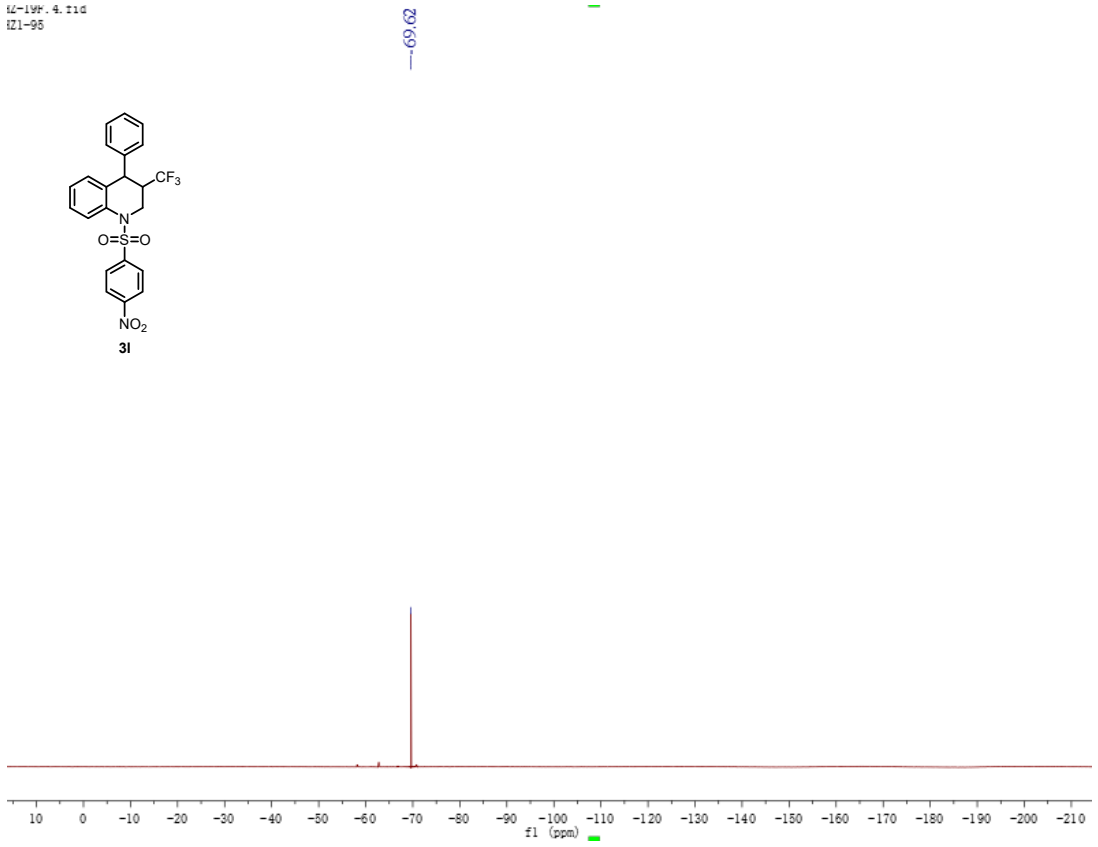
^{1}H NMR spectrum of **3l** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3l** (151 MHz, $CDCl_3$)

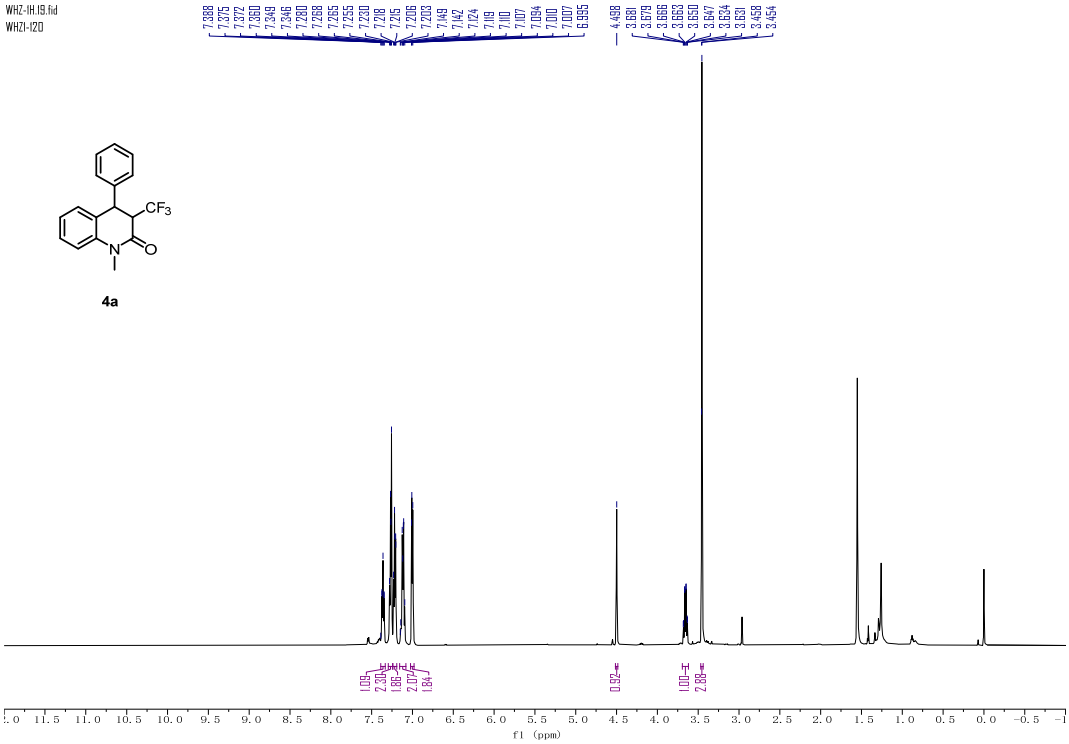


^{19}F NMR spectrum of **3l** (565 MHz, $CDCl_3$)

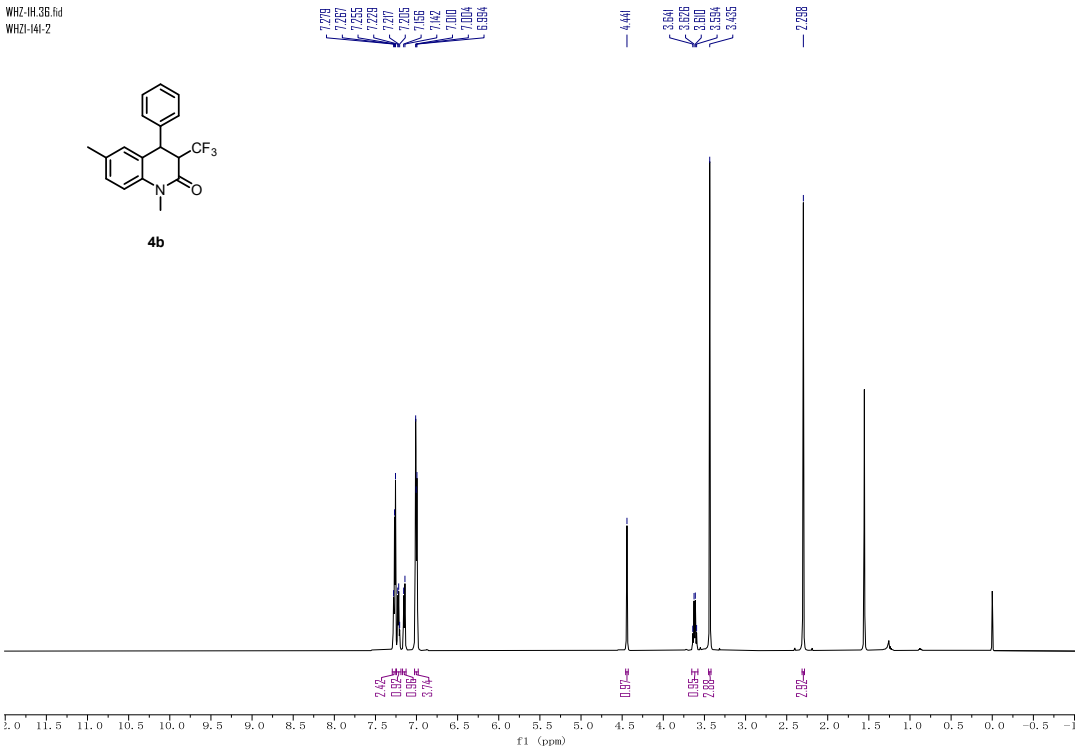


8.4 Experimental spectra of products 4

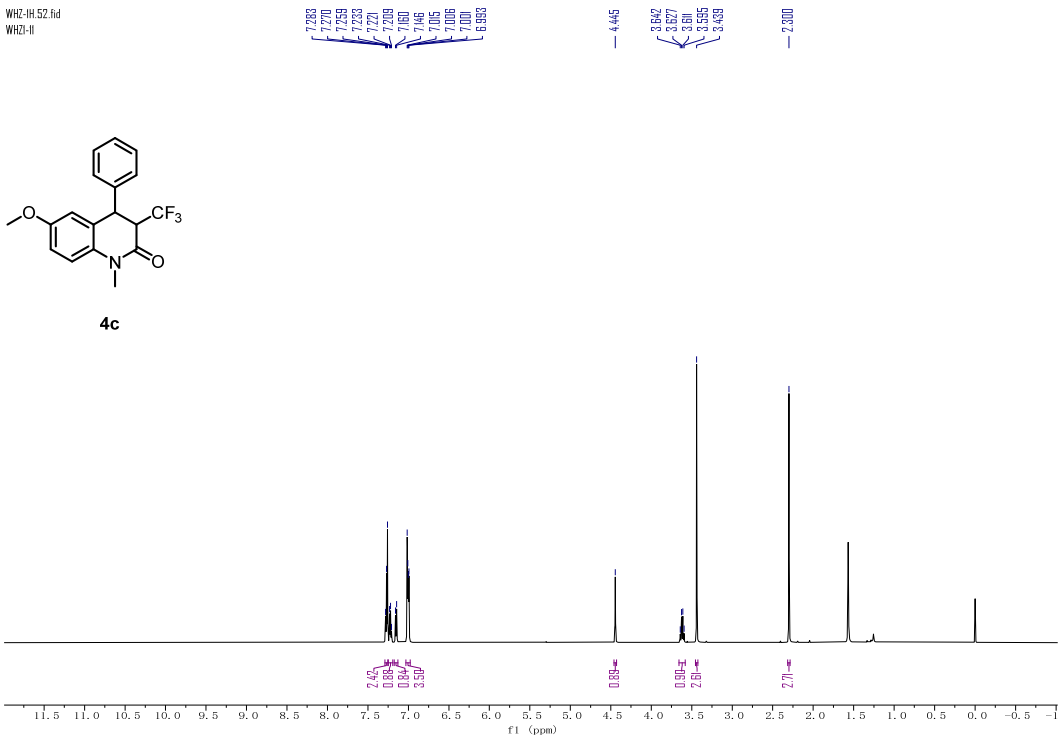
^{1}H NMR spectrum of **4a** (600 MHz, $CDCl_3$)



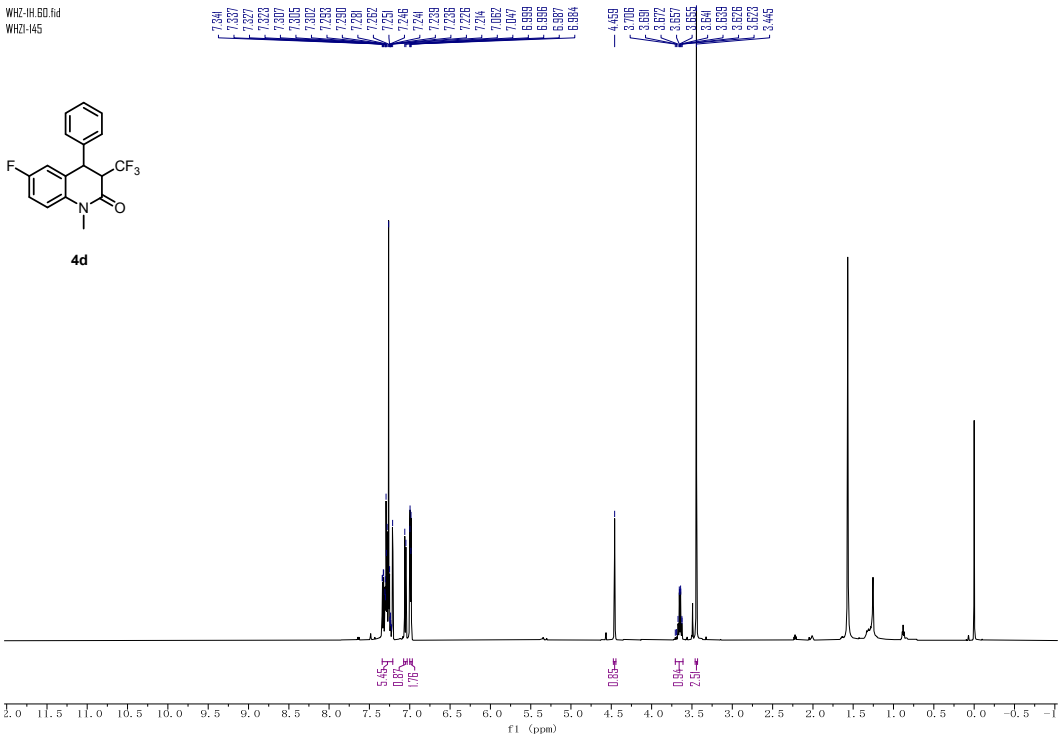
^{1}H NMR spectrum of **4b** (600 MHz, $CDCl_3$)



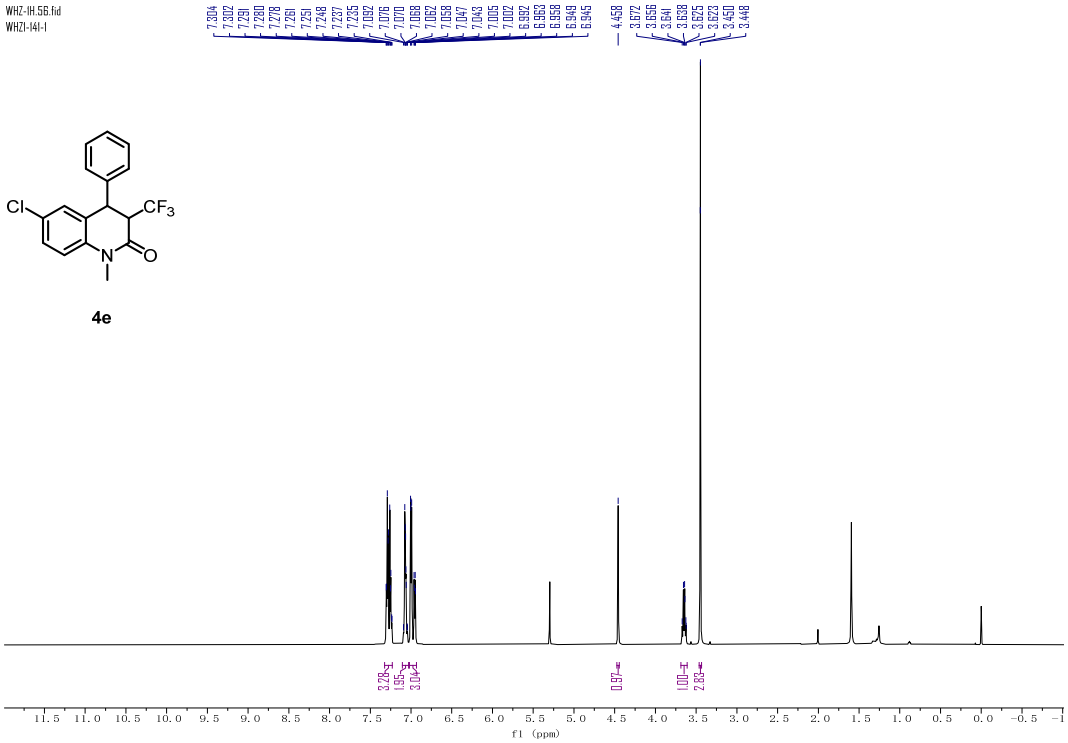
^{1}H NMR spectrum of **4c** (600 MHz, $CDCl_3$)



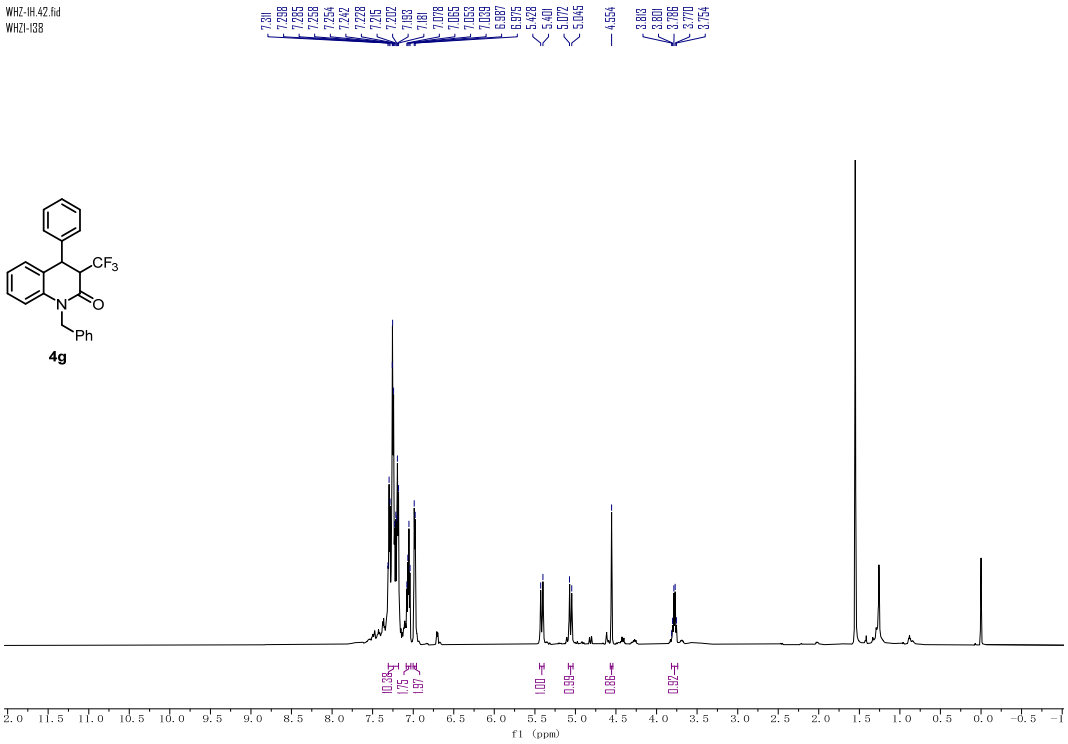
^{1}H NMR spectrum of **4d** (600 MHz, $CDCl_3$)



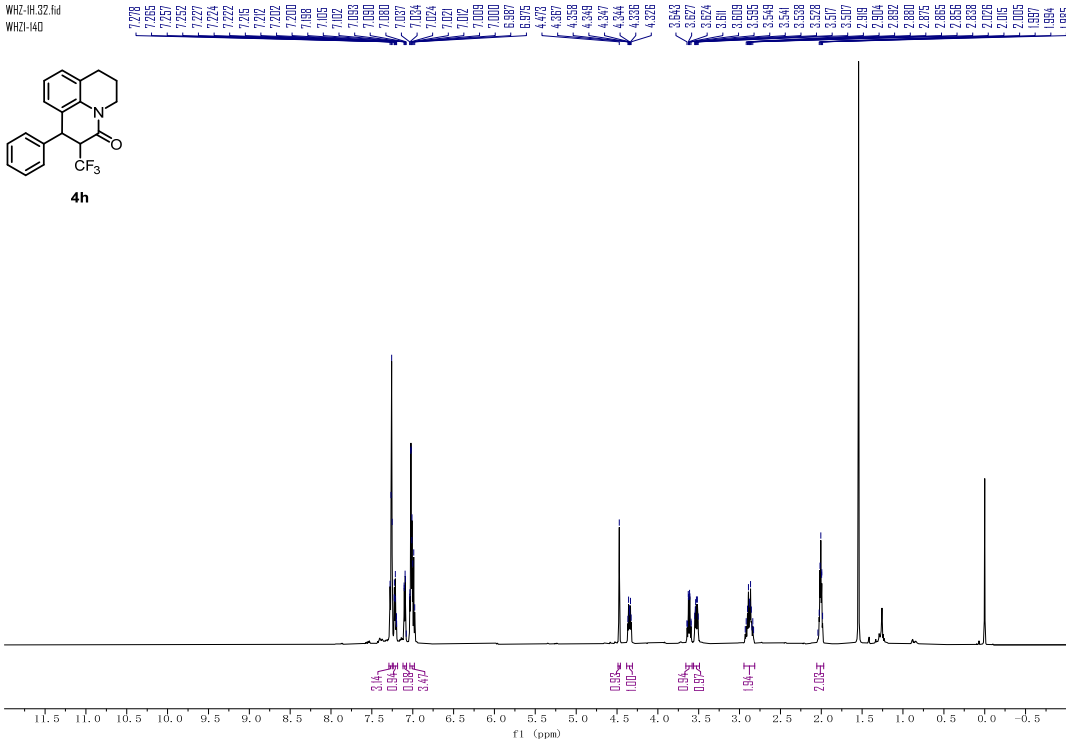
^{1}H NMR spectrum of **4e** (600 MHz, $CDCl_3$)



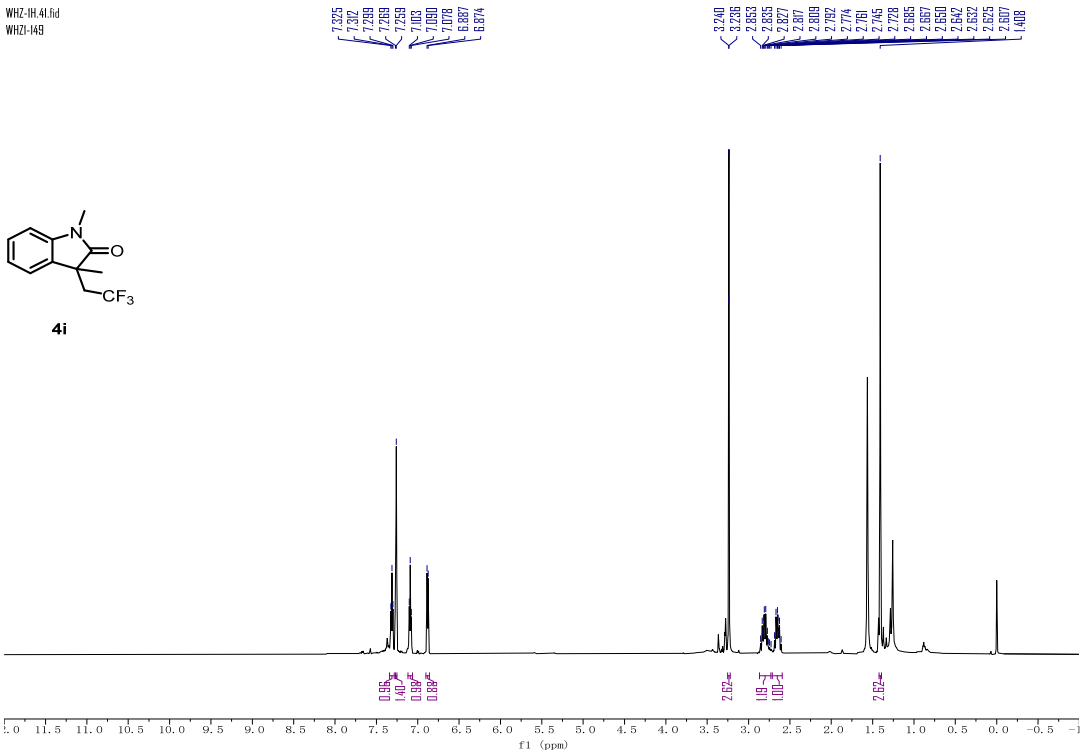
^{1}H NMR spectrum of **4g** (600 MHz, $CDCl_3$)



^{1}H NMR spectrum of **4h** (600 MHz, $CDCl_3$)



^{1}H NMR spectrum of **4i** (600 MHz, $CDCl_3$)



^{1}H NMR spectrum of **4j** (600 MHz, $CDCl_3$)