Supporting Information

Visible light-induced cascade annulation of sulfoxonium ylides with azides for the synthesis of 2-trifluoromethyl indoles

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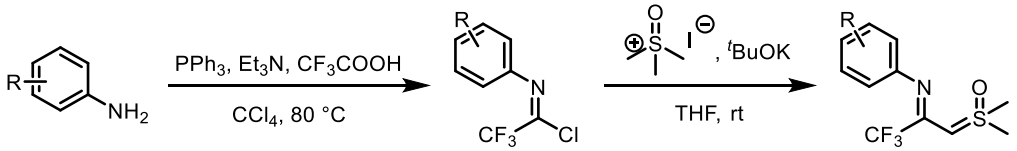
1. General information

All reactions were prepared under nitrogen atmosphere using standard Schlenk techniques, unless otherwise noted below. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. ^{1}H, ^{13}C, ^{19}F NMR spectra were collected on a Bruker AV 400 MHz NMR spectrometer using residue solvent peaks as an internal standard (^{1}H NMR: $CDCl_3$, δ 7.26 ppm, acetone-d_6 at 2.05 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm, acetone-d_6 at 29.84 ppm). All coupling constants (*J*) are reported in Hz. Blue light reactor (8 wells, 72 W, maximum emission around 450-465 nm) was purchased from Wuhan Geochemical Technology Co., Ltd. (China). The magnetic stirrer (IKA RCT Basic) was used to stir the mixed solution at high speed. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. HRMS all data were obtained using ESI-TOF (Electrospray ionization-time of flight) or Waters GCT Premier mass spectrometerusing EI-TOF (electronionizationtime of flight). The X-ray diffraction patterns was recorded on a Bruker D8 Venture (Ga) Single Crystal XRD system. All melting points were measured with the samples after column chromatography and uncorrected.

2. Synthesis of the substrates and products

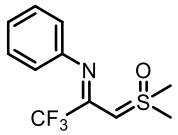
The sulfoxonium ylides **1a-n**,[1] **1o**,[2] **1p**,[3] **1q**,[2] and **1r**[4] were synthesized according to the published procedures, the azides **2a**,[5] **2b-e**,[6] **2f**,[7] **2g-h**,[6] **2i-k**,[8] **2l-m**,[7] **2o**,[5] and **2p**[9] were synthesized according to the published procedures.

General procedure A: the preparation of Sulfoxonium Ylides 1a-q



To a solution of triphenylphosphine (60 mmol, 3.0 equiv) in CCl_4 (100 mL), triethylamine (24 mmol, 1.2 equiv) and fluorinated carboxylic acid (20 mmol, 1.0 equiv) were added dropwise at 0 ℃. After stirring for 10 min at 0 ℃, aniline (20 mmol, 1.0 equiv) was added. The mixture was refluxed on an oil bath for 4 h and then cooled at room temperature, and then filtered under reduced pressure. The filtrate was concentrated under vacuum, and the resulting residue was purified by flash chromatography on silica gel with petroleum ether.

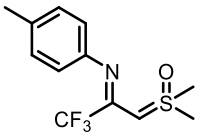
Trimethylsulfoxonium iodide (3.0 equiv) was suspended in THF (150 mL) in a 250 mL round bottom flask. *t*-BuOK (3.0 equiv) was added and the mixture was stirred at room temperature for 2 hours. After, fluorinated acetimidoyl chloride (1.0 equiv) was added. The mixture was stirred at room temperature for 3 h and then filtered through a plug of celite before all volatiles were removed under vacuum. Purification by flash chromatography afforded products.



1a

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine (1a) was prepared from aniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 65% yield (3.4 g, 2 steps).

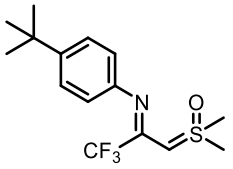
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.0 Hz, 2H), 6.99 (t, *J* = 7.1 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 2H), 4.13 (s, 1H), 3.48 (s, 6H).



1b

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(*p*-tolyl)propan-2-imine (1b) was prepared from *p*-toluidine and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 63% yield (3.5 g, 2 steps).

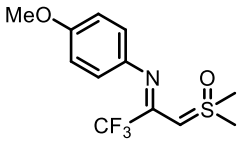
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.05 (d, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 7.5 Hz, 2H), 4.10 (s, 1H), 3.47 (s, 6H), 2.30 (s, 3H).



1c

(*E*)-*N*-(4-(*tert*-butyl)phenyl)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoropropan-2-imine (1c) was prepared from 4-(*tert*-butyl)aniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 25% yield (1.57 g, 2 steps).

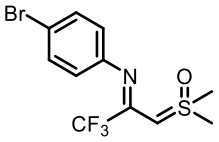
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 (d, *J* = 6.8 Hz, 2H), 6.73 (d, *J* = 7.1 Hz, 2H), 4.08 (s, 1H), 3.47 (s, 6H), 1.30 (s, 9H).



1d

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(4-methoxyphenyl)propan-2-imine (1d) was prepared from 4-methoxyaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 49% yield (2.86 g, 2 steps).

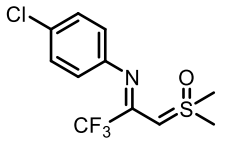
^{1}H NMR (400 MHz, CDCl$_3$) δ 6.91-6.63 (m, 4H), 4.11 (s, 1H), 3.78 (s, 3H), 3.47 (s, 6H).



1e

(*E*)-*N*-(4-bromophenyl)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoropropan-2-imine (1e) was prepared from 4-bromoaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 50% yield (3.41 g, 2 steps).

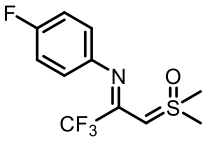
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 8.1 Hz, 2H), 4.17 (s, 1H), 3.45 (s, 6H).



1f

(*E*)-*N*-(4-chlorophenyl)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoropropan-2-imine (1f) was prepared from 4-chloroaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 37% yield (2.19 g, 2 steps).

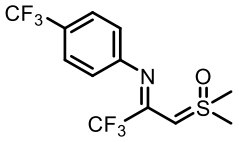
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.0 Hz, 2H), 6.72 (d, *J* = 8.1 Hz, 2H), 4.17 (s, 1H), 3.47 (s, 6H).



1g

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(4-fluorophenyl)propan-2-imine (1g) was prepared from 4-fluoroaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 55% yield (3.1 g, 2 steps).

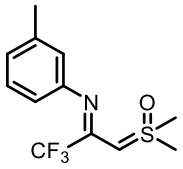
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 2H), 6.73 (s, 2H), 4.15 (s, 1H), 3.48 (s, 6H).



1h

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(4-(trifluoromethyl)phenyl)propan-2-imine (1h) was prepared from 4-(trifluoromethyl)aniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 51% yield (3.4 g, 2 steps).

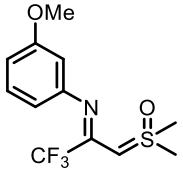
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 6.85 (d, J = 8.2 Hz, 2H), 4.18 (s, 1H), 3.45 (s, 6H).



1i

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(*m*-tolyl)propan-2-imine (1i) was prepared from *m*-toluidine and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 63% yield (3.5 g, 2 steps).

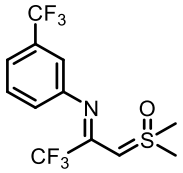
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.0 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.69-6.53 (m, 2H), 4.11 (s, 1H), 3.47 (s, 6H), 2.31 (s, 3H).



1j

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(3-methoxyphenyl)propan-2-imine (1j) was prepared from 3-methoxyaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 50% yield (2.9 g, 2 steps).

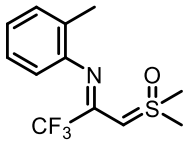
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H), 6.54 (s, 1H), 6.36 (s, 2H), 4.16 (s, 1H), 3.80-3.71 (m, 3H), 3.41 (s, 6H).



1k

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(3-(trifluoromethyl)phenyl)propan-2-imine (1k) was prepared from 3-(trifluoromethyl)aniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 53% yield (3.5 g, 2 steps).

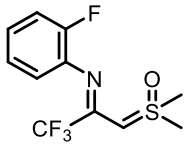
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 4.20 (s, 1H), 3.47 (s, 6H).



1l

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(*o*-tolyl)propan-2-imine (1l) was prepared from *o*-toluidine and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 59% yield (3.3 g, 2 steps).

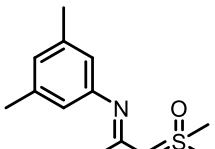
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.04 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.66 (s, 1H), 4.13 (s, 1H), 3.48 (s, 6H).



1m

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(2-fluorophenyl)propan-2-imine (1m) was prepared from 2-fluoroaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 41% yield (2.3 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05-6.97 (m, 2H), 6.97-6.91 (m, 1H), 6.86 (t, *J* = 8.2 Hz, 1H), 4.19 (s, 1H), 3.50 (s, 6H).



1n

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-*N*-(3,5-dimethylphenyl)-1,1,1-trifluoropropan-2-imine (1n) was prepared from 3,5-dimethylaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 53% yield (3.1 g, 2 steps).

Physical state: white solid.

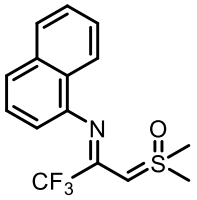
M.p.: 89.9-90.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 1H), 6.44 (s, 2H), 4.09 (s, 1H), 3.42 (s, 6H), 2.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 148.9, 138.1, 124.2, 118.3, 59.1, 41.4, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.65.

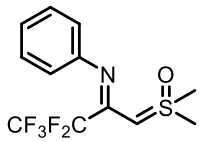
HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}F_3NOS$ 292.0978, found: 292.0984.



1o

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(naphthalen-1-yl)propan-2-imine (1o) was prepared from naphthalen-1-amine and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 22% yield (1.4 g, 2 steps).

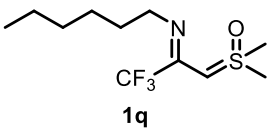
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.76 (m, 2H), 7.55-7.33 (m, 4H), 6.79 (s, 1H), 4.26 (s, 1H), 3.45 (s, 6H).



1p

(*E*)-1-(dimethyl(oxo)-λ^6-sulfaneylidene)-3,3,4,4,4-pentafluoro-*N*-phenylbutan-2-imine (1p) was prepared from aniline and 2,2,3,3,3-pentafluoropropanoic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 24% yield (1.5 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.7 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.80 (s, 2H), 3.98 (s, 1H), 3.19 (s, 6H).

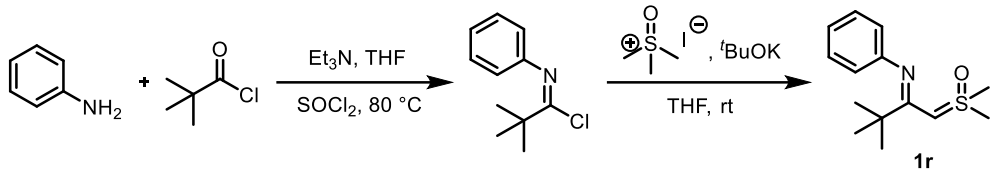


1q

(*E*)-1-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylbutan-2-imine (1q) was prepared from hexan-1-amine and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) in 31% yield (1.7 g, 2 steps).

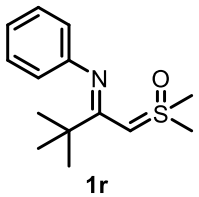
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (s, 1H), 3.42 (s, 6H), 1.58 (t, *J* = 5.64 Hz, 2H), 1.38-1.18 (m, 6H), 0.83 (t, *J* = 6.4 Hz, 3H).

General procedure B: the preparation of Sulfoxonium Ylides 1r



To a dry round-bottom flask containing aniline solution (20 mmol, 1 equiv) in THF (100 mL) and triethylamine (26 mmol, 1.3 equiv) at 0 ℃ was added pivaloyl chloride (22 mmol, 1.1 equiv) dropwise. The reaction mixture was increased to room temperature, and stirred for 12 h. The resulting mixture was filtered to remove NH_4Cl salt, and the solvent was evaporated. The resulting solid was washed with hexane to obtain the *N*-phenylbenzamide or *N*-phenylpivalamide in quantitative yield. *N*-phenylbenzamide or *N*-phenylpivalamide (1.0 equiv) was then added to a flask coupled to a reflux system. This substrate was dissolved in thionyl chloride (10 mL) and heated in a preheated oil bath at 80 ℃ for 4 h. At the end of the reaction, the thionyl chloride was evaporated and the resulting mixture was washed with hexane, filtered, and concentrated on a rotary evaporator. The *N*-phenylbenzimidoyl chloride or *N*-phenylpivalimidoyl chloride obtained was then used directly in the next step without further purification.

Trimethylsulfoxonium iodide (3.0 equiv) was suspended in THF (100 mL) in a 250 mL round bottom flask, *t*-BuOK (3.0 equiv) was added and the mixture was stirred at room temperature for 2 hours. After, fluorinated acetimidoyl chloride (1.0 equiv) was added. The mixture was stirred at room temperature for 3 hours and then filtered through a plug of celite before all volatiles were removed under vacuum. Purification by flash chromatography afforded the product.

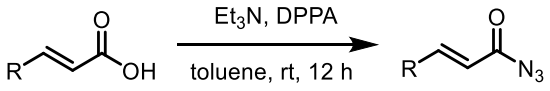


1r

(*E*)-1-(dimethyl(oxo)-λ^6-sulfaneylidene)-3,3-dimethyl-*N*-phenylbutan-2-imine (1r) was prepared from aniline and 2,2,2-trifluoroacetic acid according to the General Procedure B (eluent: PE/EA = 3:1) in 38% yield (1.9 g, 2 steps).

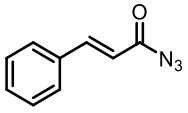
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.8 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 7.3 Hz, 2H), 3.73 (s, 1H), 3.21 (s, 6H), 1.11 (s, 9H).

General procedure C: the preparation of azides 2a, 2n-p



2a, 2n-p

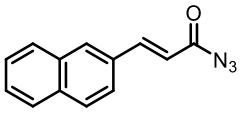
Under ambient atmosphere, cinnamic acid (15 mmol, 1.0 equiv) was added to a 100 mL round-bottom flask with a magnetic bar. toluene (25 mL) was charged. Then Et_3N (2.5 mL, 18 mmol, 1.2 equiv) and diphenyl azidophosphate (3.56 mL, 16.5 mmol, 1.1 equiv) were charged sequentially. The reaction was stirred at room temperature for 12 h which was washed with H_2O (32 mL). The aqueous phase was washed with toluene (2 × 30 mL). The organic layer was dried over anhydrous sodium sulphate (Na_2SO_4), concentrated and subjected for silica gel to obtain the desired products.



2a

cinnamoyl azide (2a) was prepared from cinnamic acid according to the General Procedure C (eluent: PE/EA = 100:1) in 75% yield (1.9 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 15.9 Hz, 1H), 7.55-7.53 (m, 2H), 7.45-7.38 (m, 3H), 6.43 (d, *J* = 15.8 Hz, 1H).



2n

(*E*)-3-(naphthalen-2-yl)acryloyl azide (2n) was prepared from cinnamic acid according to the General Procedure C (eluent: PE/EA = 100:1) in 70% yield (2.3 g).

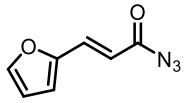
Physical state: white solid.

M.p.: 110.1-110.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.81 (m, 5H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.58-7.48 (m, 2H), 6.52 (d, *J* = 15.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 146.9, 134.7, 133.3, 131.4, 131.1, 129.0, 128.9, 127.9, 127.8, 127.0, 123.5, 119.2.

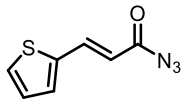
HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{13}H_9N_3O$ 223.0746, found: 223.0748.



2o

(*E*)-3-(furan-2-yl)acryloyl azide (2o) was prepared from cinnamic acid according to the General Procedure C (eluent: PE/EA = 100:1) in 83% yield (2.0 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.48 (d, *J* = 15.6 Hz, 1H), 6.71 (d, *J* = 3.4 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.30 (d, *J* = 15.5 Hz, 1H).

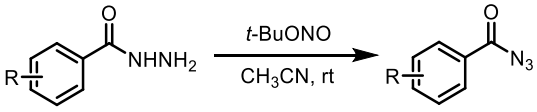


2p

(*E*)-3-(thiophen-2-yl)acryloyl azide (2p) was prepared from cinnamic acid according to the General Procedure C (eluent: PE/EA = 100:1) in 76% yield (2.0 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 15.5 Hz, 1H), 7.45 (d, *J* = 5.1 Hz, 1H), 7.31 (d, *J* = 3.7 Hz, 1H), 7.08 (t, *J* = 4.5 Hz, 1H), 6.21 (d, *J* = 15.6 Hz, 1H).

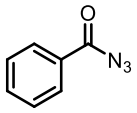
General procedure D: the preparation of azides 2b-m



2b-m

The substituted carbonyl hydrazines (8 mmol) was stirred in acetonitrile (20 mL) at room temperature to which 3 equiv. of tert-butyl nitrite (TBN) was added. The progress of the reaction was monitored by TLC. After completion, acetonitrile was evaporated and then, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried

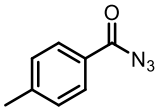
over anhydrous sodium sulphate (Na_2SO_4), concentrated and subjected for silica gel to obtain the desired products.



2b

benzoyl azide (2b) was prepared from carbonyl hydrazine according to the General Procedure D (eluent: PE/EA = 100:1) in 36% yield (420 mg).

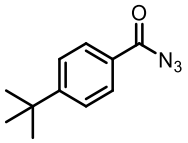
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-7.99 (m, 2H), 7.65-7.57 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H).



2c

4-methylbenzoyl azide (2c) was prepared from 4-methylbenzohydrazide according to the General Procedure D (eluent: PE/EA = 100:1) in 40% yield (516 mg).

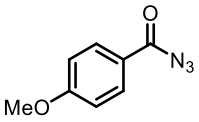
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 9.1 Hz, 2H), 2.42 (s, 3H).



2d

4-(*tert*-butyl)benzoyl azide (2d) was prepared from 4-(*tert*-butyl)benzohydrazide according to the General Procedure D (eluent: PE/EA = 100:1) in 37% yield (601 mg).

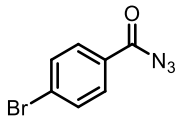
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.92 (m, 2H), 7.50-7.44 (m, 2H), 1.34 (s, 9H).



2e

4-methoxybenzoyl azide (2e) was prepared from 4-methoxybenzohydrazide according to the General Procedure D (eluent: PE/EA = 100:1) in 30% yield (425 mg).

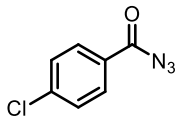
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.93 (m, 2H), 6.95-6.89 (m, 2H), 3.87 (s, 3H).



2f

4-bromobenzoyl azide (2f) was prepared from 4-bromobenzohydrazide according to the General Procedure D (eluent: PE/EA = 100:1) in 13% yield (234 mg).

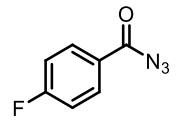
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.84 (m, 2H), 7.63-7.56 (m, 2H).



2g

4-chlorobenzoyl azide (2g) was prepared from 4-chlorobenzohydrazide according to the General Procedure D (eluent: PE/EA = 100:1) in 36% yield (521 mg).

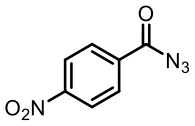
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H).



2h

4-fluorobenzoyl azide (2h) was prepared from 4-fluorobenzohydrazide according to the General Procedure D (eluent: PE/EA = 100:1) in 31% yield (410 mg).

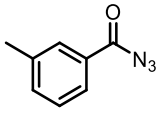
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.99 (m, 2H), 7.15-7.07 (m, 2H).



2i

4-nitrobenzoyl azide (2i) was prepared from 4-nitrobenzohydrazide according to the General Procedure D (eluent: PE/EA = 100:1) in 14% yield (215 mg).

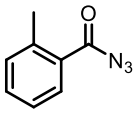
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.26 (m, 2H), 8.24-8.17 (m, 2H).



2j

3-methylbenzoyl azide (2j) was prepared from 3-methylbenzohydrazide according to the General Procedure D (eluent: PE/EA = 100:1) in 42% yield (540 mg).

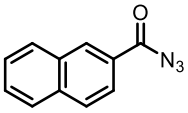
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 10.9 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 2.40 (s, 3H).



2k

2-methylbenzoyl azide (2k) was prepared from 2-methylbenzohydrazide according to the General Procedure D (eluent: PE/EA = 100:1) in 12% yield (155 mg).

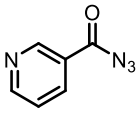
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.18 (m, 1H), 7.16 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.14-7.05 (m, 2H), 2.35 (s, 3H).



2l

2-naphthoyl azide (2l) was prepared from 2-naphthohydrazide according to the General Procedure D (eluent: PE/EA = 100:1) in 23% yield (363 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.04 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.89 (dd, *J* = 8.4, 2.7 Hz, 2H), 7.67-7.52 (m, 2H).

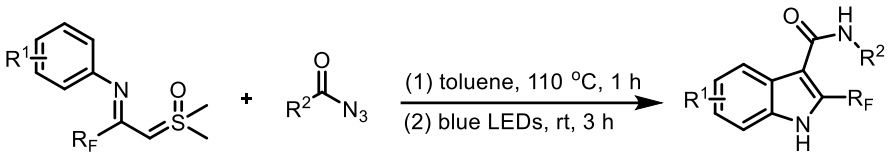


2m

nicotinoyl azide (2m) was prepared from 2-naphthohydrazide according to the General Procedure D (eluent: PE/EA = 5:1) in 60% yield (710 mg).

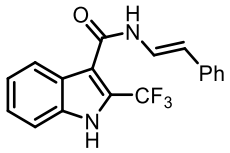
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 1.7 Hz, 1H), 8.81 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.27 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.41 (ddd, *J* = 8.0, 4.9, 0.9 Hz, 1H).

General procedure E: the preparation of product 3aa-3pa, 3ab-3ap



1a-p **2a-p** **3**

A dried 10 mL Schlenk tube was charged with azides **2a-p** (0.36 mmol, 1.2 equiv) and toluene (3.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in a preheated oil bath at 110 ℃ for 1 h. Then cooled at room temperature, **1a-p** (0.3 mmol) was added. The reaction mixture was irradiation by blue LEDs at room temperature for 3 h under nitrogen atmosphere. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the pure product **3**.



3aa

(*E*)-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3aa) was prepared from cinnamoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 91% yield (90 mg).

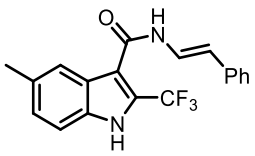
Physical state: yellow oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.73 (s, 1H), 9.61 (d, *J* = 10.3 Hz, 1H), 7.93-7.77 (m, 2H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.46-7.37 (m, 3H), 7.35-7.26 (m, 3H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 14.7 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 161.2, 137.8, 136.1, 129.5, 127.2, 126.3, 126.1, 126.0, 125.9 (q, $J_{C\text{-}F}$ = 38.4 Hz), 124.4, 122.8, 121.8 (q, $J_{C\text{-}F}$ = 270.7 Hz), 122.0, 114.1, 113.7, 113.5.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.82.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{13}F_3N_2O$ 331.1053, found: 331.1047.



3ba

(*E*)-5-methyl-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ba) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(p-tolyl)propan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 90% yield (93 mg).

Physical state: yellow solid.

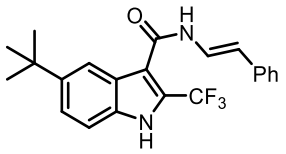
M.p.: 137.9-138.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ δ 9.67 (s, 1H), 7.88 (d, *J* = 10.8 Hz, 1H), 7.81-7.68 (m, 2H), 7.39-7.27 (m, 5H), 7.24-7.15 (m, 2H), 6.25 (d, *J* = 14.5 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 136.0, 133.0, 132.6, 128.8, 127.5, 127.0, 125.8, 125.7, 125.5 (q, $J_{C\text{-}F}$ = 38.4 Hz), 122.5, 120.9 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.3, 113.9, 112.4, 111.1, 21.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.76.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{15}F_3N_2O$ 345.1209, found: 345.1209.



3ca

(*E*)-5-(tert-butyl)-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ca) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-*N*-(4-(*tert*-butyl)phenyl)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoropropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 95% yield (110 mg).

Physical state: yellow solid.

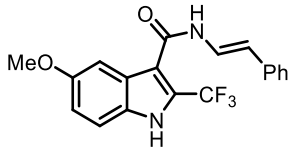
M.p.: 246.6-247.3 °C.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.57 (s, 1H), 9.62 (d, *J* = 10.0 Hz, 1H), 7.86-7.80 (m, 2H), 7.52 (d, *J* = 1.3 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 14.8 Hz, 1H), 1.38 (s, 9H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 161.4, 145.6, 137.8, 134.3, 129.5, 127.1, 126.2, 125.8, 125.5 (q, $J_{C\text{-}F}$ = 38.7 Hz), 124.7, 124.4, 122.1 (q, $J_{C\text{-}F}$ = 269.8 Hz), 117.3, 114.1, 113.5, 113.1, 35.3, 31.9.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.60.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}F_3N_2O$ 387.1679, found: 387.1675.



3da

(*E*)-5-methoxy-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3da) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(4-methoxyphenyl)propan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 93% yield (100 mg).

Physical state: yellow solid.

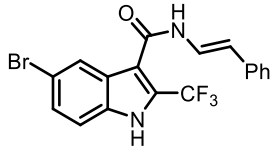
M.p.: 212.7-213.5 °C.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.60 (s, 1H), 9.52 (d, *J* = 10.3 Hz, 1H), 7.81 (dd, *J* = 14.8, 10.3 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.36-7.28 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.04 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.51 (d, *J* = 14.8 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 161.4, 156.6, 137.8, 131.0, 129.5, 127.1, 126.5, 126.2, 125.9 (q, $J_{C\text{-}F}$ = 39.4 Hz), 124.4, 122.0 (q, $J_{C\text{-}F}$ = 269.7 Hz), 117.3, 114.5, 113.7, 113.5, 102.4, 55.9.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.63.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{15}F_3N_2O_2$ 361.1159, found: 361.1154.



3ea

(*E*)-5-bromo-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ea) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-*N*-(4-bromophenyl)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoropropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 89% yield (109 mg).

Physical state: yellow solid.

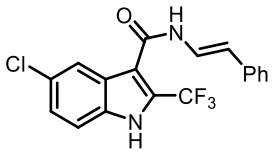
M.p.: 223.7-224.6 °C.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.90 (s, 1H), 9.68 (d, *J* = 10.3 Hz, 1H), 8.04 (s, 1H), 7.80 (dd, *J* = 14.7, 10.1 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.50 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 14.8 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 160.6, 137.7, 134.7, 129.5, 128.9, 127.4, 127.3, 127.1 (q, $J_{C\text{-}F}$ = 41.4 Hz), 126.3, 124.5, 124.2, 121.7 (q, $J_{C\text{-}F}$ = 270.7 Hz), 115.6, 115.5, 114.1, 113.6.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -59.06.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{12}BrF_3N_2O$ 409.0158, found: 409.0157.



3fa

(*E*)-5-chloro-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3fa) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-*N*-(4-chlorophenyl)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoropropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 84% yield (92 mg).

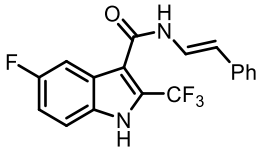
Physical state: yellow oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.88 (s, 1H), 9.67 (d, *J* = 10.0 Hz, 1H), 7.88 (s, 1H), 7.80 (dd, *J* = 14.7, 10.2 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.38 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 14.8 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 160.6, 137.7, 134.4, 129.5, 128.1, 127.3, 127.2 (q, $J_{C\text{-}F}$ = 39.4 Hz), 126.8, 126.4, 126.3, 124.2, 121.7 (q, $J_{C\text{-}F}$ = 270.7 Hz), 121.3, 115.2, 114.1, 113.6.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -59.07.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{12}ClF_3N_2O$ 365.0663, found: 365.0659.



3ga

(*E*)-5-fluoro-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ga) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-

trifluoro-*N*-(4-fluorophenyl)propan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 95% yield (99 mg).

Physical state: yellow solid.

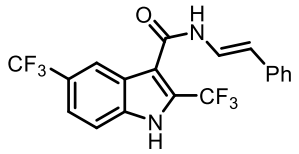
M.p.: 162.7-163.5 ºC.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.89 (s, 1H), 9.61 (s, 1H), 7.80 (dd, *J* = 14.7, 10.1 Hz, 1H), 7.65-7.56 (m, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.24-7.16 (m, 2H), 6.52 (d, *J* = 14.8 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 160.8, 158.4, 137.7, 132.6, 129.5, 127.5 (q, $J_{C\text{-}F}$ = 39.4 Hz), 127.2, 126.3, 126.2, 124.2, 124.1, 121.8 (q, $J_{C\text{-}F}$ = 269.7 Hz), 115.1, 115.0 (d, $J_{C\text{-}F}$ = 35.4 Hz), 114.0, 106.7 (d, $J_{C\text{-}F}$ = 25.3 Hz).

^{19}F NMR (376 MHz, Acetone-*d*6) δ -59.07, -121.96.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{12}F_4N_2O$ 349.0959, found: 349.0948.



3ha

(*E*)-*N*-styryl-2,5-bis(trifluoromethyl)-1*H*-indole-3-carboxamide (3ha) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(4-(trifluoromethyl)phenyl))propan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 83% yield (99 mg, 12 h).

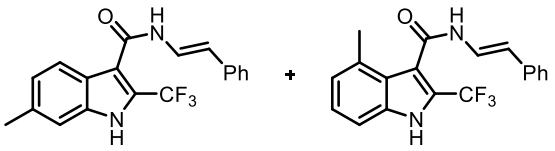
Physical state: yellow oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 12.13 (s, 1H), 9.82 (d, *J* = 9.2 Hz, 1H), 8.25 (s, 1H), 7.87-7.77 (m, 2H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 14.8 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 160.5, 137.6, 137.5, 129.6, 127.7 (q, $J_{C\text{-}F}$ = 38.0 Hz), 127.3, 126.4, 125.9 (q, $J_{C\text{-}F}$ = 269.0 Hz), 125.3, 124.5 (q, $J_{C\text{-}F}$ = 32.0 Hz), 124.2, 122.4 (q, $J_{C\text{-}F}$ = 3.0 Hz), 121.7 (q, $J_{C\text{-}F}$ = 268.0 Hz), 120.1 (q, $J_{C\text{-}F}$ = 5.0 Hz), 115.1, 114.7, 114.3.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -53.96, -56.13.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{12}F_6N_2O$ 421.0746, found: 421.0753.



3ia

(*E*)-6-methyl-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide and (*E*)-4-methyl-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ia) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(*m*-tolyl)propan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 95% yield (98 mg).

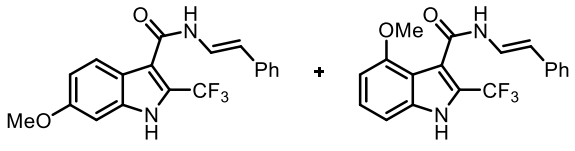
Physical state: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.63 (s, 1H), 8.10 (d, *J* = 9.9 Hz, 1H), 8.00 (d, *J* = 10.2 Hz, 1H), 7.74-7.65 (m, 3H), 7.29-7.22 (m, 7H), 7.21-7.15 (m, 2H), 7.14-7.11 (m, 2H), 7.08 (s, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.91-6.85 (m, 1H), 6.21 (dd, *J* = 14.6, 3.6 Hz, 2H), 2.46 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.7, 160.8, 136.0, 136.0, 135.8, 135.1, 135.0, 132.0, 129.0, 128.8, 128.7, 128.6, 127.1, 126.9, 125.9, 125.8, 125.7 (q, $J_{C\text{-}F}$ = 43.8 Hz), 125.2, 125.0, 124.9, 123.4, 123.3 (q, $J_{C\text{-}F}$ = 253.7 Hz), 123.2 (q, $J_{C\text{-}F}$ = 37.8 Hz), 122.3, 120.9 (q, $J_{C\text{-}F}$ = 270.3 Hz), 120.6, 114.5, 113.8, 113.4, 112.3, 111.6, 110.0, 21.8, 19.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.72, -58.36.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{15}F_3N_2O$ 345.1209, found: 345.1201.



3ja

(*E*)-6-methoxy-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide and (*E*)-4-methoxy-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ja) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-

trifluoro-*N*-(3-methoxyphenyl)propan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 84% yield (91 mg).

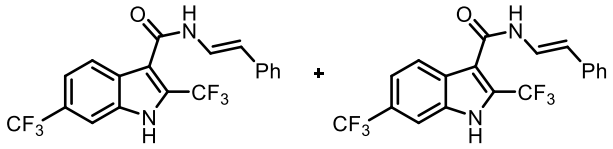
Physical state: yellow oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 10.69 (s, 1H), 10.49 (s, 1H), 10.17 (d, *J* = 10.2 Hz, 1H), 9.56 (d, *J* = 10.2 Hz, 1H), 7.86-7.73 (m, 3H), 7.43 (t, *J* = 7.2 Hz, 4H), 7.31 (t, *J* = 7.9 Hz, 4H), 7.24-7.15 (m, 4H), 7.03 (d, *J* = 2.2 Hz, 1H), 6.93 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.51 (d, *J* = 14.8 Hz, 1H), 6.41 (d, *J* = 14.8 Hz, 1H), 4.05 (s, 3H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 161.3, 161.1, 159.5, 154.3, 138.0, 137.8, 137.6, 137.1, 129.5, 129.5, 127.4, 127.2, 127.0, 126.4 (q, $J_{C\text{-}F}$ = 49.0 Hz), 126.3, 126.2, 124.5, 124.4 (q, $J_{C\text{-}F}$ = 39.0 Hz), 124.3, 122.71, 122.2 (q, $J_{C\text{-}F}$ = 267.0 Hz), 122.1 (q, $J_{C\text{-}F}$ = 267.0 Hz), 120.1, 115.5, 114.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 114.0, 113.7, 113.5 (q, $J_{C\text{-}F}$ = 3.0 Hz), 112.9, 106.8, 103.0, 95.2, 56.4, 55.8.

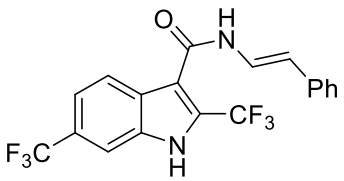
^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.42, -59.05.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{15}F_3N_2O_2$ 383.0978, found: 383.0984.



3ka

(*E*)-*N*-styryl-2,6-bis(trifluoromethyl)-1*H*-indole-3-carboxamide and (*E*)-*N*-styryl-2,4-bis(trifluoromethyl)-1*H*-indole-3-carboxamide (3ka) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(3-(trifluoromethyl)phenyl)propan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 89% yield (106 mg, 24 h).



3ka-A

(*E*)-*N*-styryl-2,6-bis(trifluoromethyl)-1*H*-indole-3-carboxamide (3ka-A) (46%, 55 mg)

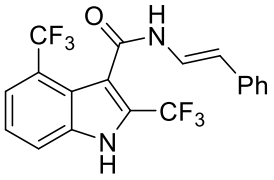
Physical state: yellow oil.

^{1}H NMR (400 MHz, $CHCl_3$) δ 10.49 (s, 1H), 8.06 (d, *J* = 10.4 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.70-7.61 (m, 2H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.30-7.24 (m, 4H), 7.18 (t, *J* = 6.7 Hz, 1H), 6.28 (d, *J* = 14.6 Hz, 1H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 160.4, 135.6, 133.5, 128.9, 127.8 (q, $J_{C\text{-}F}$ = 32.0 Hz), 127.7, 127.7 (q, $J_{C\text{-}F}$ = 39.0 Hz), 127.3, 125.9, 124.4 (q, $J_{C\text{-}F}$ = 270.0 Hz), 122.0, 121.9, 120.4 (q, $J_{C\text{-}F}$ = 268.0 Hz), 119.2 (d, $J_{C\text{-}F}$ = 4.0 Hz), 115.1, 111.8 (d, $J_{C\text{-}F}$ = 2.0 Hz), 110.5 (q, $J_{C\text{-}F}$ = 4.0 Hz).

^{19}F NMR (376 MHz, $CHCl_3$) δ -58.23, -61.59.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{12}F_6N_2O$ 421.0746, found: 421.0751.



3ka-B

(*E*)-*N*-styryl-2,4-bis(trifluoromethyl)-1*H*-indole-3-carboxamide (3ka-B) (43%, 51 mg)

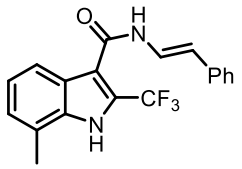
Physical state: yellow oil.

^{1}H NMR (400 MHz, $CHCl_3$) δ 11.20 (s, 1H), 7.83 (d, *J* = 10.8 Hz, 1H), 7.71 (dd, *J* = 14.4, 10.8 Hz, 1H), 7.57-7.52 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 3H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.22 (d, *J* = 14.5 Hz, 1H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 162.6, 136.0, 135.7, 128.8, 127.2, 126.0 (q, $J_{C\text{-}F}$ = 63.0 Hz), 126.0, 124.2, 123.0, 122.2 (q, $J_{C\text{-}F}$ = 33.0 Hz), 122.1, 120.7 (q, $J_{C\text{-}F}$ = 6.0 Hz), 120.2 (q, $J_{C\text{-}F}$ = 268.0 Hz), 119.3 (d, $J_{C\text{-}F}$ = 1.0 Hz), 117.2, 115.2, 111.6 (q, $J_{C\text{-}F}$ = 2.0 Hz).

^{19}F NMR (376 MHz, $CHCl_3$) δ -59.58, -59.88.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{12}F_6N_2O$ 421.0746, found: 421.0751.



3la

(*E*)-7-methyl-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3la) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-

trifluoro-*N*-(*o*-tolyl)propan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 98% yield (101 mg).

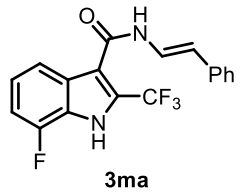
Physical state: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.91 (d, *J* = 10.9 Hz, 1H), 7.81-7.68 (m, 2H), 7.37-7.26 (m, 4H), 7.25-7.16 (m, 3H), 6.24 (d, *J* = 14.6 Hz, 1H), 2.54 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 136.0, 134.3, 128.8, 126.9, 126.1, 125.7, 125.4 (q, J_{C-F} = 38.4 Hz), 125.2, 123.2, 122.6, 122.2, 120.9 (q, J_{C-F} = 270.7 Hz), 118.6, 113.8, 112.5, 16.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.78.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{15}F_3N_2O$ 345.1209, found: 345.1200.



3ma

(*E*)-7-fluoro-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ma) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(2-fluorophenyl)propan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 72% yield (75 mg, 12 h).

Physical state: yellow solid.

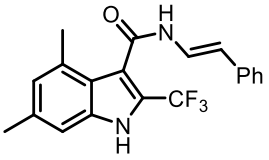
M.p.: 170.3-171.9 °C.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 12.11 (s, 1H), 9.68 (s, 1H), 7.80 (dd, *J* = 14.7, 10.5 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.28-7.22 (m, 1H), 7.21-7.11 (m, 2H), 6.51 (d, *J* = 14.8 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 160.7, 150.5 (d, J_{C-F} = 247.5 Hz), 137.7, 129.6, 129.4 (d, J_{C-F} = 4.0 Hz), 127.3, 126.7 (q, J_{C-F} = 40.5 Hz), 126.3, 124.2, 124.1, 123.2 (d, J_{C-F} = 6.1 Hz), 121.7 (q, J_{C-F} = 269.7 Hz), 118.0 (d, J_{C-F} = 4.0 Hz), 115.1, 114.1, 110.4 (d, J_{C-F} = 16.2 Hz).

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.94, -133.42.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{12}F_4N_2O$ 349.0959, found: 349.0948.



3na

(*E*)-4,6-dimethyl-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3na) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-*N*-(3,5-dimethylphenyl)-1,1,1-trifluoropropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 86% yield (92 mg).

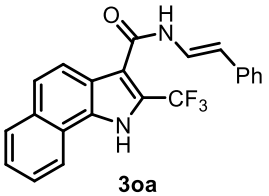
Physical state: yellow oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.32 (s, 1H), 9.81 (s, 1H), 7.85-7.74 (m, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.22-7.15 (m, 2H), 6.83 (s, 1H), 6.43 (d, *J* = 14.8 Hz, 1H), 2.48 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 163.4, 137.6, 137.0, 136.1, 132.0, 129.5, 127.3, 126.3, 125.5, 124.0, 123.0, 122.4 (q, $J_{C\text{-}F}$ = 268.7 Hz), 122.3 (q, $J_{C\text{-}F}$ = 38.4 Hz), 115.3, 113.9, 110.4, 21.7, 19.2.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.95.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}F_3N_2O$ 359.1366, found: 359.1357.



3oa

(*E*)-*N*-styryl-2-(trifluoromethyl)-1*H*-benzo[g]indole-3-carboxamide (3oa) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(naphthalen-1-yl)propan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 97% yield (110 mg).

Physical state: yellow solid.

M.p.: 246.1-246.9 °C.

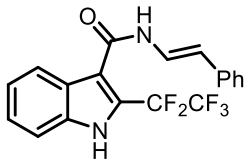
^{1}H NMR (400 MHz, Acetone-*d*6) δ 12.34 (s, 1H), 9.74 (d, *J* = 9.9 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.91-7.79 (m, 2H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.66-7.56 (m,

2H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 14.8 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 161.3, 137.8, 132.6, 131.7, 129.6, 129.6, 127.4, 127.2, 126.7, 126.3, 124.4, 124.2, 124.0, 122.8, 122.5, 122.2 (q, $J_{C\text{-}F}$ = 269.7 Hz), 122.0, 120.4, 116.1, 113.8.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -57.74.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{15}F_3N_2O$ 381.1209, found: 381.1202.



3pa

(*E*)-2-(perfluoroethyl)-*N*-styryl-1*H*-indole-3-carboxamide (3pa) was prepared from (*E*)-4-Phenyl-*N*-styrylbutanamide and (*E*)-1-(dimethyl(oxo)-λ^6-sulfaneylidene)-3,3,4,4,4-pentafluoro-*N*-phenylbutan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 96% yield (109 mg).

Physical state: yellow solid.

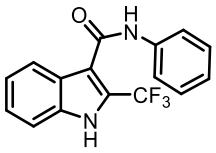
M.p.: 88.7-89.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.82-7.70 (m, 2H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.43-7.38 (m, 1H), 7.37-7.28 (m, 5H), 7.23-7.18 (m, 1H), 6.25-6.16 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.4, 135.9, 135.3, 128.9, 127.0, 126.2, 126.1, 125.8, 122.9, 122.5, 122.1 (t, $J_{C\text{-}F}$ = 28.7 Hz), 121.3, 119.8 (t, $J_{C\text{-}F}$ = 39.3 Hz), 117.9 (t, $J_{C\text{-}F}$ = 39.3 Hz), 115.0, 113.9, 112.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -84.02, -110.21.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{13}F_5N_2O$ 381.1021, found: 381.1023.



3ab

***N*-phenyl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ab)** was prepared from benzoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 97% yield (88 mg).

Physical state: white solid.

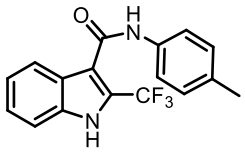
M.p.: 177.4-178.3 °C.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.69 (s, 1H), 9.45 (s, 1H), 7.92-7.85 (m, 3H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.42-7.36 (m, 3H), 7.31-7.25 (m, 1H), 7.17-7.12 (m, 1H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 162.3, 140.2, 136.1, 129.6, 126.0, 125.9, 125.2 (q, $J_{C\text{-}F}$ = 38.4 Hz), 124.6, 122.6, 122.2 (q, $J_{C\text{-}F}$ = 269.7 Hz), 121.9, 120.7, 115.5 (q, $J_{C\text{-}F}$ = 3.0 Hz), 113.4.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.75.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{11}F_3N_2O$ 305.0896, found: 305.0895.



3ac

***N*-(*p*-tolyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ac)** was prepared from 4-methylbenzoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 96% yield (92 mg).

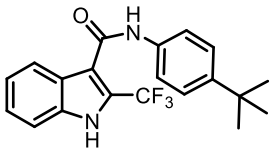
Physical state: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.83 (s, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.28-7.24 (m, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 135.0, 134.8, 134.7, 129.7, 125.4, 125.3 (q, $J_{C\text{-}F}$ = 38.4 Hz), 125.3, 122.5, 120.9 (q, $J_{C\text{-}F}$ = 270.7 Hz), 120.7, 120.7, 112.8, 112.6 (d, $J_{C\text{-}F}$ = 2.4 Hz), 20.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.82.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{13}F_3N_2O$ 319.1053, found: 319.1058.



3ad

***N*-(4-(*tert*-butyl)phenyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ad)** was prepared from 4-(*ter*t-butyl)Benzoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 96% yield (104 mg).

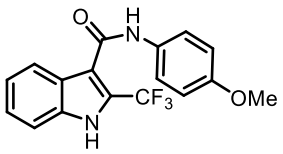
Physical state: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.80 (s, 1H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.43-7.36 (m, 3H), 7.33-7.21 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 148.1, 135.0, 134.7, 126.1, 125.5, 125.4 (q, $J_{C\text{-}F}$ = 38.4 Hz), 125.3, 122.5, 120.9 (q, $J_{C\text{-}F}$ = 270.7 Hz), 120.7, 120.5, 112.9, 112.7 (d, $J_{C\text{-}F}$ = 2.0 Hz), 34.5, 31.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.77.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{19}F_3N_2O$ 361.1522, found: 361.1524.



3ae

***N*-(4-methoxyphenyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ae)** was prepared from 4-methoxybenzoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro- *N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 94% yield (94 mg).

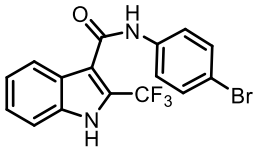
Physical state: yellow oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.64 (s, 1H), 9.32 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 6.98-6.92 (m, 2H), 3.80 (s, 3H).

^{13}C NMR (150 MHz, Acetone-*d*6) δ 162.0, 157.2, 136.1, 133.3, 126.0, 125.9, 125.0 (q, $J_{C\text{-}F}$ = 39.3 Hz), 122.6, 122.4, 122.2 (q, $J_{C\text{-}F}$ = 270.3 Hz), 121.9, 115.6, 114.7, 113.4, 55.7.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.70.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{13}F_3N_2O_2$ 335.1002, found: 335.0996.



3af

***N*-(4-bromophenyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3af)** was prepared from 4-bromobenzoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 96% yield (110 mg).

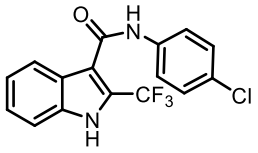
Physical state: yellow oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.69 (s, 1H), 9.56 (s, 1H), 7.87 (dd, *J* = 8.5, 3.1 Hz, 3H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 162.3, 139.6, 136.0, 132.5, 126.0, 125.9, 125.4 (q, $J_{C\text{-}F}$ = 39.4 Hz), 122.7, 122.5, 122.1 (q, $J_{C\text{-}F}$ = 269.7 Hz), 121.9, 116.6, 115.1 (d, $J_{C\text{-}F}$ = 2.6 Hz), 113.5.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.84.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{10}BrF_3N_2O$ 383.0002, found: 382.9995.



3ag

***N*-(4-chlorophenyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ag)** was prepared from 4-chlorobenzoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 89% yield (90 mg).

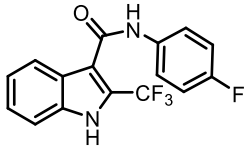
Physical state: colorless oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.71 (s, 1H), 9.58 (s, 1H), 7.95-7.84 (m, 3H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.45-7.36 (m, 3H), 7.31-7.24 (m, 1H), .

^{13}C NMR (100 MHz, Acetone-*d*6) δ 162.3, 139.6, 136.0, 132.5, 126.0, 125.9, 125.4 (q, J_{C-F} = 39.4 Hz), 122.7, 122.5, 121.9, 122.1 (q, J_{C-F} = 269.7 Hz), 116.6, 115.1 (d, J_{C-F} = 3.0 Hz), 113.5.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.81.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{10}ClF_3N_2O$ 339.0507, found: 339.0501.



3ah

***N*-(4-fluorophenyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ah)** was prepared from 4-fluorobenzoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 97% yield (94 mg).

Physical state: yellow solid.

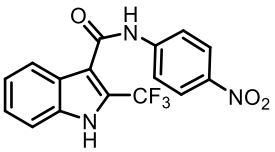
M.p.: 146.2-147.1 ºC.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.73 (s, 1H), 9.53 (s, 1H), 7.95-7.83 (m, 3H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.20-7.12 (m, 2H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 162.2, 159.9 (d, J_{C-F} = 241.4 Hz), 136.4 (d, J_{C-F} = 3.0 Hz), 135.9, 125.9, 125.9, 125.1 (q, J_{C-F} = 39.4 Hz), 122.7, 122.5 (d, J_{C-F} = 8.1 Hz), 122.1 (q, J_{C-F} = 270.7 Hz), 121.9, 116.0 (d, J_{C-F} = 22.2 Hz), 115.1 (q, J_{C-F} = 3.0 Hz), 113.4.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.76, -120.18.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{10}F_4N_2O$ 323.0802, found: 323.0799.



3ai

***N*-(4-nitrophenyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ai)** was prepared from 4-nitrobenzoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-

phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 97% yield (101 mg).

Physical state: white solid.

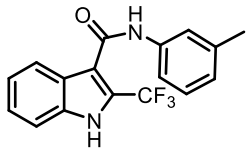
M.p.: 201.5-202.4 °C.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.82 (s, 1H), 10.02 (s, 1H), 8.30 (d, *J* = 9.3 Hz, 2H), 8.19-8.11 (m, 2H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.34-7.27 (m, 1H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 162.8, 146.1, 144.1, 136.0, 126.1, 126.0 (q, $J_{C\text{-}F}$ = 38.4 Hz), 125.7, 125.6, 123.0, 122.0 (q, $J_{C\text{-}F}$ = 269.7 Hz), 121.9, 120.3, 114.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 113.6.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.81.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{10}F_3N_3O_3$ 350.0747, found: 350.0744.



3aj

***N*-(*m*-tolyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3aj)** was prepared from 3-methylbenzoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 98% yield (93 mg).

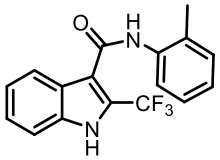
Physical state: colorless oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.74 (s, 1H), 9.41 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.76 (s, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.31-7.23 (m, 2H), 6.97 (d, *J* = 7.5 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 162.4, 140.1, 139.2, 136.1, 129.5, 126.0, 125.9, 125.4, 125.1 (q, $J_{C\text{-}F}$ = 38.4 Hz), 122.6, 122.2 (q, $J_{C\text{-}F}$ = 269.7 Hz), 121.8, 121.3, 117.9, 115.4 (q, $J_{C\text{-}F}$ = 2.0 Hz), 113.4, 21.6.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.64.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{13}F_3N_2O$ 319.1053, found: 319.1056.



3ak

***N*-(*o*-tolyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ak)** was prepared from 2-methylbenzoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 69% yield (66 mg).

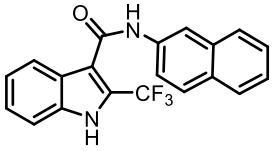
Physical state: colorless oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.64 (s, 1H), 8.83 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.33-7.22 (m, 3H), 7.14 (t, *J* = 7.4 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 162.4, 137.6, 136.1, 132.5, 131.3, 127.1, 126.3, 126.3, 125.9, 125.4, 125.1 (q, $J_{C\text{-}F}$ = 38.4 Hz), 122.7, 122.2 (q, $J_{C\text{-}F}$ = 269.7 Hz), 121.9, 115.3, 113.5, 18.4.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.47.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{13}F_3N_2O$ 319.1053, found: 319.1052.



3al

***N*-(naphthalen-2-yl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3al)** was prepared from 2-naphthoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 95% yield (101 mg).

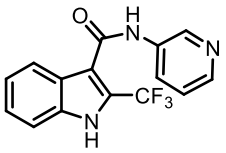
Physical state: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.33 (d, *J* = 2.1 Hz, 1H), 8.04-7.94 (m, 2H), 7.83-7.72 (m, 3H), 7.75 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.49-7.36 (m, 3H), 7.33-7.24 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 135.1, 134.6, 133.8, 131.0, 129.0, 127.8, 127.7, 126.7, 125.5, 125.4 (q, $J_{C\text{-}F}$ = 38.4 Hz), 125.3, 122.7, 120.8 (q, $J_{C\text{-}F}$ = 270.7 Hz), 120.7, 120.3, 117.5, 112.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.66.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{13}F_3N_2O$ 355.1053, found: 355.1060.



3am

***N*-(pyridin-3-yl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3am)** was prepared from nicotinoyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*- phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 76% yield (70 mg).

Physical state: white solid.

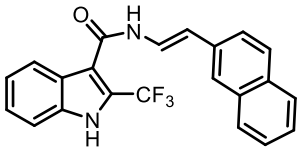
M.p.: 252.1-252.9 °C.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.83 (s, 1H), 9.65 (s, 1H), 9.00 (s, 1H), 8.36 (d, *J* = 5.3 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.40 (t, *J* = 6.7 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (150 MHz, Acetone-*d*6) δ 162.6, 145.7, 142.5, 136.9, 136.1, 127.5, 126.1, 125.9, 125.6 (q, $J_{C\text{-}F}$ = 39.3 Hz), 124.3, 122.8, 122.1 (q, $J_{C\text{-}F}$ = 270.3 Hz), 122.0, 114.8, 113.5.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.91.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{10}F_3N_3O$ 306.0849, found: 306.0843.



3an

(*E*)-*N*-(2-(naphthalen-2-yl)vinyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3an) was prepared from (*E*)-3-(naphthalen-2-yl)acryloyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 81% yield (92 mg).

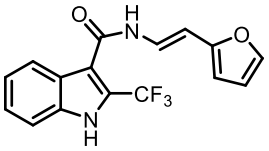
Physical state: yellow oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.84 (s, 1H), 9.75 (d, *J* = 10.4 Hz, 1H), 7.99 (dd, *J* = 14.7, 10.2 Hz, 1H), 7.94-7.76 (m, 5H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.51-7.36 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 14.7 Hz, 1H).

^{13}C NMR (150 MHz, Acetone-*d*6) δ 161.2, 136.1, 135.4, 134.9, 133.4, 129.2, 128.5, 128.4, 127.1, 126.2, 126.0, 125.9 (q, $J_{C\text{-}F}$ = 40.8 Hz), 125.9, 125.4, 124.9, 124.0, 122.8, 122.1 (q, $J_{C\text{-}F}$ = 270.3 Hz), 122.0, 114.0, 113.8, 113.6.

^{19}F NMR (376 MHz, Acetone-*d*6) δ 118.74.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{15}F_3N_2O$ 381.1209, found: 381.1200.



3ao

(*E*)-*N*-(2-(furan-2-yl)vinyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ao) was prepared from (*E*)-3-(furan-2-yl)acryloyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 85% yield (82 mg).

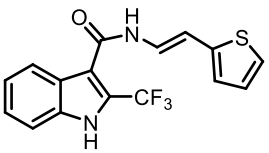
Physical state: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.98 (d, *J* = 10.8 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.61 (dd, *J* = 14.5, 10.8 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.27-7.15 (m, 3H), 6.31 (s, 1H), 6.12 (dd, *J* = 8.9, 5.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 151.4, 141.6, 134.6, 125.7 (q, $J_{C\text{-}F}$ = 38.4 Hz), 125.5, 125.4, 122.8, 121.8, 120.8, 120.7 (q, $J_{C\text{-}F}$ = 270.7 Hz), 112.8, 111.5, 106.7, 103.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.90.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{11}F_3N_2O_2$ 321.0846, found: 321.0839.



3ap

(*E*)-*N*-(2-(thiophen-2-yl)vinyl)-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (3ap) was prepared from (*E*)-3-(thiophen-2-yl)acryloyl azide and (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine according to the General Procedure E (eluent: PE/EA = 3:1) in 88% yield (89 mg).

Physical state: yellow oil.

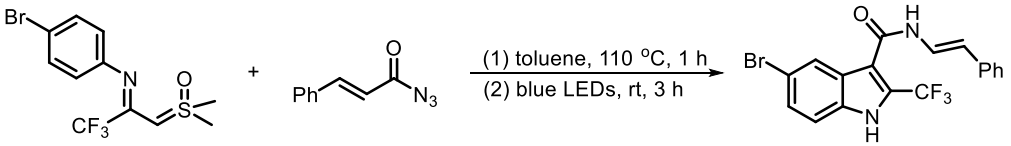
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.04 (d, *J* = 10.6 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 14.3, 10.7 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.32-7.22 (m, 2H), 7.10 (d, *J* = 5.0 Hz, 1H), 6.96-6.87 (m, 2H), 6.46 (d, *J* = 14.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.8, 140.3, 134.6, 127.5, 125.7 (q, $J_{C\text{-}F}$ = 39.3 Hz), 125.6, 125.4, 124.7, 123.4, 122.8, 122.1, 120.8, 120.7 (q, $J_{C\text{-}F}$ = 270.3 Hz), 112.8, 111.5, 108.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.82.

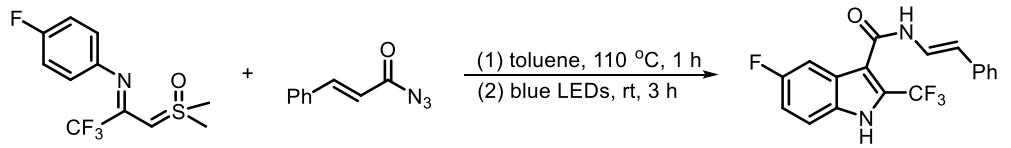
HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{11}F_3N_2OS$ 337.0617, found: 337.0610.

3. Scale-up reactions



1e, 2 mmol **2a**, 2.4 mmol **3ea**, 720 mg, 88%

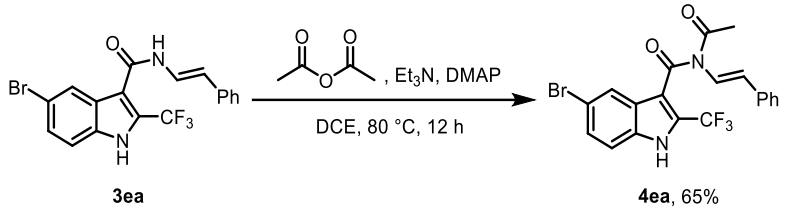
A dried 50 mL Schlenk tube was charged with azide **2a** (2.4 mmol, 1.2 equiv) in Toluene (20.0 mL). The reaction mixture was stirred in a preheated oil bath at 110 ℃ for 1 h. Then cooled at room temperature, **1e** (2.0 mmol) was added. The reaction mixture was irradiation by blue LEDs at room temperature for 3 h under nitrogen atmosphere. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the pure product **3ea** (720 mg, 88%)**.**



1g, 2 mmol **2a**, 2.4 mmol **3ga**, 660 mg, 95%

A dried 50 mL Schlenk tube was charged with azide **2a** (2.4 mmol, 1.2 equiv) in toluene (20.0 mL). The reaction mixture was stirred in a preheated oil bath at 110 ℃ for 1 h. Then cooled at room temperature, **1g** (2.0 mmol) was added. The reaction mixture was irradiation by blue LEDs at room temperature for 3 h under nitrogen atmosphere. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the pure product **3ga** (660 mg, 95%)**.**

4. Synthetic transformations



3ea **4ea**, 65%

(*E*)-*N*-acetyl-5-bromo-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (4ea). In a dried 10 mL Schlenk tube, add acetic anhydride (5 equiv), Et_3N (5 equiv) and DMAP (0.5 equiv) to a solution of **3ea** (0.1 mmol) in DCE (1 mL). Stir the reaction mixture was stirred in a preheated oil bath at 80 ℃ for 12 h under nitrogen atmosphere. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the pure product **4ea** (29 mg, 65%).

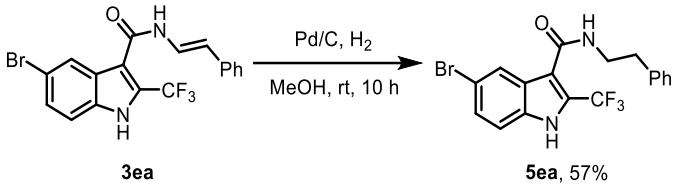
Physical state: colorless oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 12.17 (s, 1H), 8.03 (d, *J* = 1.3 Hz, 1H), 7.57-7.48 (m, 2H), 7.36 (d, *J* = 14.6 Hz, 1H), 7.23 (d, *J* = 4.4 Hz, 4H), 7.21-7.14 (m, 1H), 6.24 (d, *J* = 14.7 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (150 MHz, Acetone-*d*6) δ 171.3, 166.2, 136.1, 134.6, 132.3 (q, $J_{C\text{-}F}$ = 187.2 Hz), 129.5, 129.4, 128.6, 127.2, 127.0, 126.2, 125.1, 124.2, 121.5 (q, $J_{C\text{-}F}$ = 268.8 Hz), 117.0, 116.0, 115.9, 24.5.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -59.95.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{14}BrF_3N_2O_2$ 451.0264, found: 451.0259.



5-bromo-*N*-phenethyl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (5ea). In a dried 10 mL Schlenk tube, a stirred suspension of compound **3ea** (0.2 mmol, 1.0 equiv) in MeOH (2.0 mL) and palladium on activated carbon (10 mol%) was added. The reaction mixture was stirred under H_2 atmosphere at room temperature for 10 h. The mixture was filtered over SiO_2 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (eluent: PE/EA = 3:1) to afford **5ea** (46 mg, 57% yield).

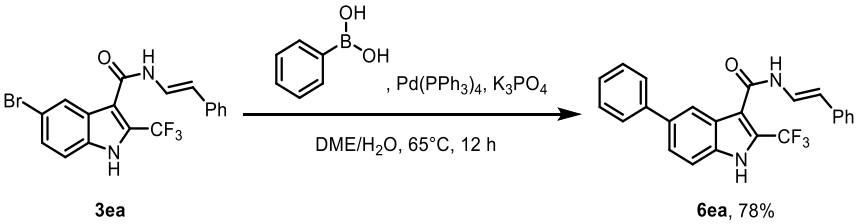
Physical state: yellow oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.60 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.43 (s, 1H), 7.34-7.31 (m, 4H), 7.26-7.20 (m, 1H), 7.20-7.15 (m, 1H), 3.74 (q, *J* = 6.7 Hz, 2H), 3.01 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (150 MHz, Acetone-*d*6) δ 163.6, 140.5, 136.0, 129.7, 129.3, 127.0, 126.0, 125.7, 125.0 (q, $J_{C\text{-}F}$ = 37.8 Hz), 122.3, 122.2 (q, $J_{C\text{-}F}$ = 270.3 Hz), 122.0, 115.3 (q, $J_{C\text{-}F}$ = 3.0 Hz), 113.3, 41.9, 36.3.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.60.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{14}BrF_3N_2O$ 411.0315, found: 411.0323.



(*E*)-5-phenyl-*N*-styryl-2-(trifluoromethyl)-1*H*-indole-3-carboxamide (6ea). In a dried 10 mL Schlenk tube, add phenylboronic acid (1.2 equiv), $Pd(PPh_3)_4$ (3 mol%) and K_3PO_4 (2.0 equiv) to a solution of **3ea** (0.1 mmol) in DME/H_2O (1 mL). Stir the reaction mixture was stirred in a preheated oil bath at 65 ℃ for 12 h under nitrogen atmosphere. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the pure product **6ea** (32 mg, 78%).

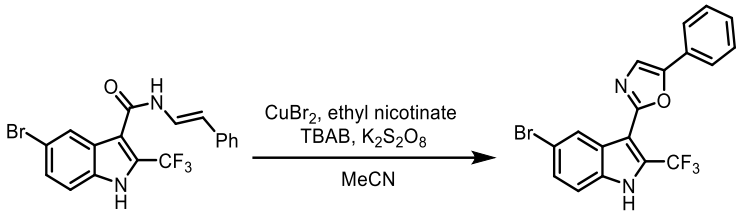
Physical state: yellow oil.

^{1}H NMR (400 MHz, Acetone-*d*6) δ 11.79 (s, 1H), 9.74 (s, 1H), 8.09 (s, 1H), 7.90-7.79 (m, 1H), 7.74-7.67 (m, 4H), 7.50-7.40 (m, 4H), 7.39-7.28 (m, 3H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 14.8 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-*d*6) δ 161.1, 142.3, 137.8, 136.1, 135.5, 129.7, 129.5, 128.1, 127.8, 127.2, 126.7 (q, $J_{C\text{-}F}$ = 39.4 Hz), 126.3, 125.7, 124.4, 122.0 (q, $J_{C\text{-}F}$ = 269.7 Hz), 121.1, 120.1, 114.3, 114.0, 113.8.

^{19}F NMR (376 MHz, Acetone-*d*6) δ -58.84.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{17}F_3N_2O$ 407.1366, found: 407.1368.



3ea **7ea**, 78%

2-(5-bromo-2-(trifluoromethyl)-1*H*-indol-3-yl)-5-phenyloxazole (7ea). In a dried 10 mL Schlenk tube, add tetrabutylammonium bromide (TBAB, 1.2 equiv), $K_2S_2O_8$ (1.3 equiv), $CuBr_2$ (0.075 equiv), ethyl nicotinate (1.5 equiv) to a solution of **3ea** (0.1 mmol) in MeCN (2 mL) under argon atmosphere. Stir the reaction mixture was stirred in a preheated oil bath at 80 ℃ for 12 h under nitrogen atmosphere. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the pure product **7ea** (32 mg, 78%).

Physical state: yellow oil.

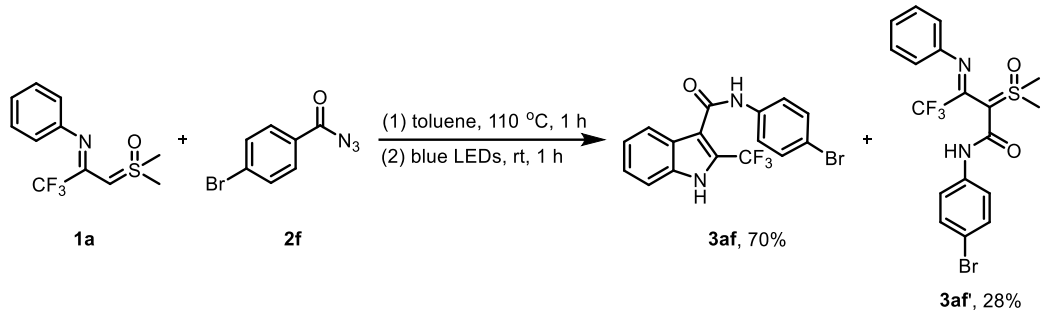
^{1}H NMR (600 MHz, Acetone-*d*6) δ 12.12 (s, 1H), 8.71 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.79 (s, 1H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.56-7.49 (m, 3H), 7.39 (t, *J* = 7.4 Hz, 1H).

^{13}C NMR (150 MHz, Acetone-*d*6) δ 156.6, 151.5, 134.9, 130.0, 129.4, 129.3, 128.8, 127.8, 125.7 (q, $J_{C\text{-}F}$ = 40.8 Hz), 125.7, 124.8, 124.5, 122.1 (q, $J_{C\text{-}F}$ = 268.8 Hz), 116.2, 115.6, 104.7.

^{19}F NMR (376 MHz, Acetone-*d*6) δ 117.42.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{10}BrF_3N_2O$ 407.0002, found: 406.9996.

5. Control experiments



A dried 10 mL Schlenk tube was charged with azide **2f** (0.36 mmol, 1.2 equiv) and toluene (3.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in a preheated oil bath at 110 ℃ for 1 h. Then cooled at room temperature, **1a** (0.3 mmol) was added. The reaction mixture was irradiation by blue LEDs at room temperature for 1 h under nitrogen atmosphere. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the product **3af** (81 mg, 70%) and **3af'** (39 mg, 28%).

(*E*)-*N*-(4-bromophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-4,4,4-trifluoro-3-(phenylimino)butanamide (3af').

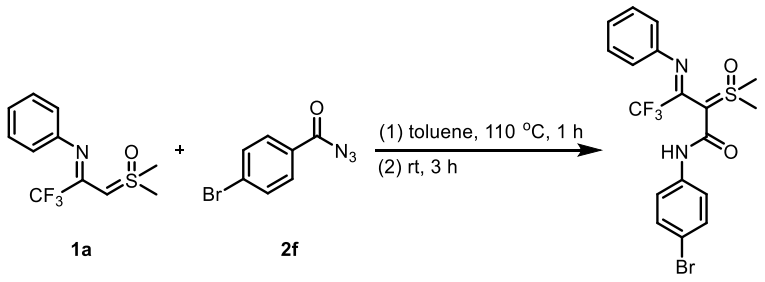
Physical state: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.41-7.34 (m, 4H), 7.20-7.12 (m, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 3.22 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7, 151.0 (q, J_{C-F} = 34.7 Hz), 150.5, 140.4, 132.0, 129.5, 126.1, 122.3, 122.2, 121.3 (q, J_{C-F} = 279.4 Hz), 120.6, 114.8, 60.7, 43.4.

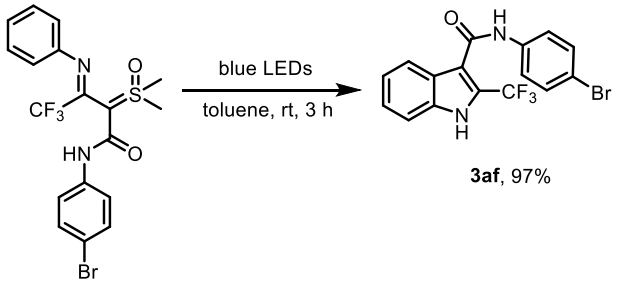
^{19}F NMR (376 MHz, $CDCl_3$) δ -71.69.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}BrF_3N_2O_2S$ 461.0141, found: 461.0137.



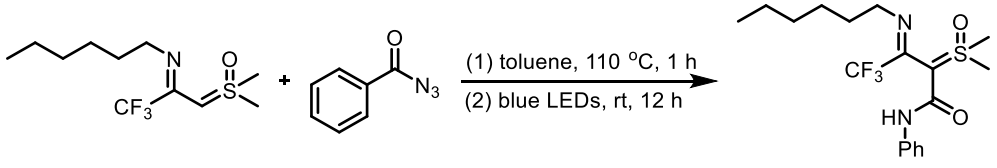
1a **2f** **3af'**, 94%

A dried 10 mL Schlenk tube was charged with azide **2f** (0.36 mmol, 1.2 equiv) and toluene (3.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in a preheated oil bath at 110 ℃ for 1 h. Then cooled at room temperature, **1a** (0.3 mmol) was added. The reaction mixture was stirred at room temperature for 3 h under nitrogen atmosphere. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the product **3af'** (130 mg, 94%).



3af' **3af**, 97%

A dried 10 mL Schlenk tube was charged with **3af'** (0.1 mmol) and toluene (1.0 mL) under nitrogen atmosphere. The reaction mixture was irradiation by blue LEDs at room temperature for 3 h. After the reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the product **3af** (37 mg, 97%).



1q **2b** **3qb'**, 74%

A dried 10 mL Schlenk tube was charged with azide **2b** (0.36 mmol, 1.2 equiv) and toluene (3.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in a preheated oil bath at 110 ℃ for 1 h. Then cooled at room temperature, **1q** (0.3 mmol) was added. The reaction mixture was irradiation by blue LEDs at room temperature for 12 h under nitrogen atmosphere.

After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the product **3qb'** (87 mg, 74%).

(*E*)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-4,4,4-trifluoro-3-(hexylimino)-*N*-phenylbutanamide (3qb').

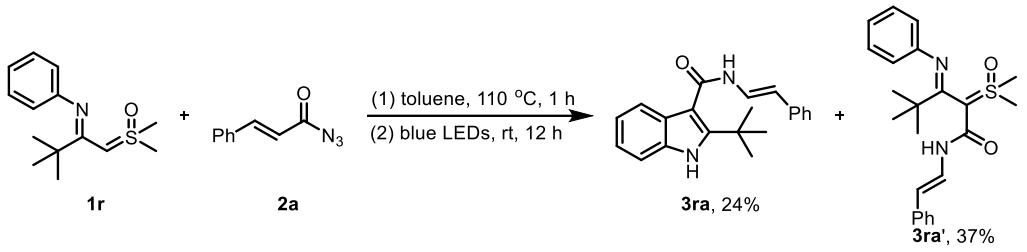
Physical state: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.19 (m, 4H), 7.07-6.95 (m, 1H), 6.15 (s, 1H), 3.70 (q, *J* = 6.4 Hz, 2H), 3.59-3.31 (m, 6H), 1.79-1.63 (m, 2H), 1.41-1.22 (m, 6H), 0.92-0.79 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.6, 150.5 (q, J_{C-F} = 34.7 Hz), 138.4, 129.0, 123.5, 120.1, 56.3, 55.2, 45.0, 43.4, 31.6, 30.0, 27.4, 22.6, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -70.15.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{25}F_3N_2O_2S$ 391.1662, found: 391.1654.



A dried 10 mL Schlenk tube was charged with azide **2a** (0.36 mmol, 1.2 equiv) and toluene (3.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in a preheated oil bath at 110 ℃ for 1 h. Then cooled at room temperature, **1r** (0.3 mmol) was added. The reaction mixture was irradiation by blue LEDs at room temperature for 12 h under nitrogen atmosphere. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the product **3ra** (23 mg, 24%) and **3ra'** (44 mg, 37%).

(*E*)-2-(*tert*-butyl)-*N*-styryl-1*H*-indole-3-carboxamide (3ra).

Physical state: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.90-7.72 (m, 2H), 7.71-7.62 (m, 1H), 7.43-7.40 (m, 1H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24-7.17 (m, 3H), 6.16 (d, *J* = 14.1 Hz, 1H), 1.57 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.9, 150.5, 136.5, 133.4, 128.8, 127.1, 126.6, 125.6, 123.5, 122.4, 121.5, 118.5, 111.9, 111.5, 107.1, 33.6, 29.7.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{22}N_2O$ 319.1805, found: 319.1800.

(*E*)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-4,4-dimethyl-3-(phenylimino)-*N*-((*E*)-styryl)pentanamide (3ra').

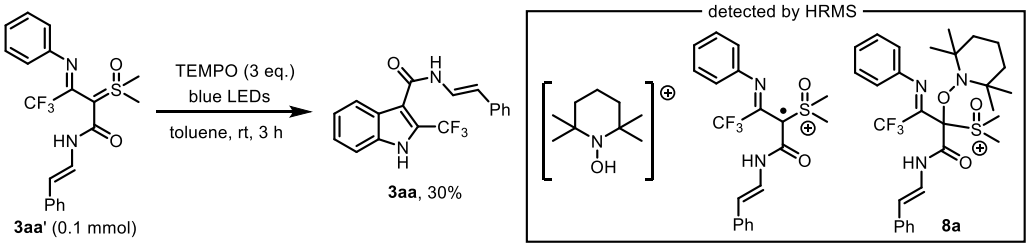
Physical state: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 14.5, 11.1 Hz, 1H), 7.31-7.23 (m, 6H), 7.14-7.09 (m, 1H), 7.05-7.01 (m, 1H), 6.73 (dd, *J* = 8.4, 1.0 Hz, 2H), 6.38 (d, *J* = 11.1 Hz, 1H), 5.92 (d, *J* = 14.5 Hz, 1H), 3.40 (s, 3H), 2.48 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3, 161.3, 152.6, 137.0, 128.6, 128.6, 125.7, 125.0, 123.6, 123.4, 119.2, 108.1, 44.8, 42.5, 41.4, 29.6.

HRMS (ESI, TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{28}N_2O_2S$ 397.1944, found: 397.1947.

6. Radical-trapping experiments.



3aa' (0.1 mmol) was suspended in toluene (1.0 mL) in a 5 mL round bottom flask. Then TEMPO (3.0 equiv) was added and the reaction mixture was irradiation by blue LEDs at room temperature for 3 h under nitrogen atmosphere. After completion of the reaction, the radical trapping adduct **8a** was observed through HRMS analysis of the reaction solution, shown in Figure S1.

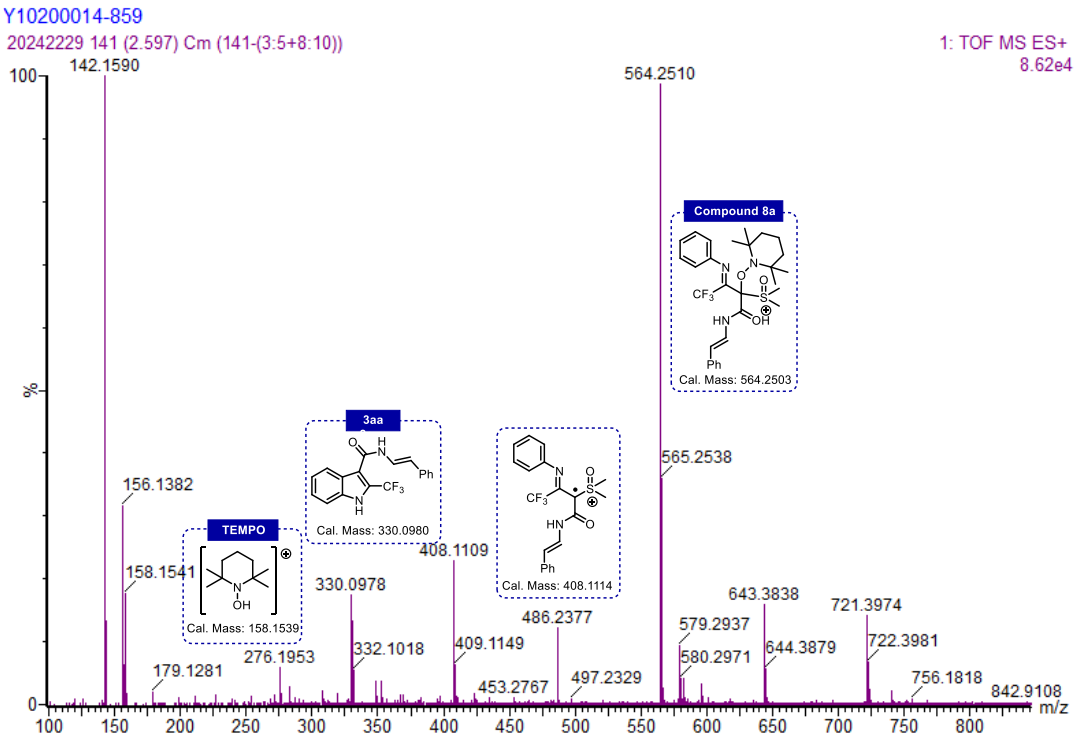
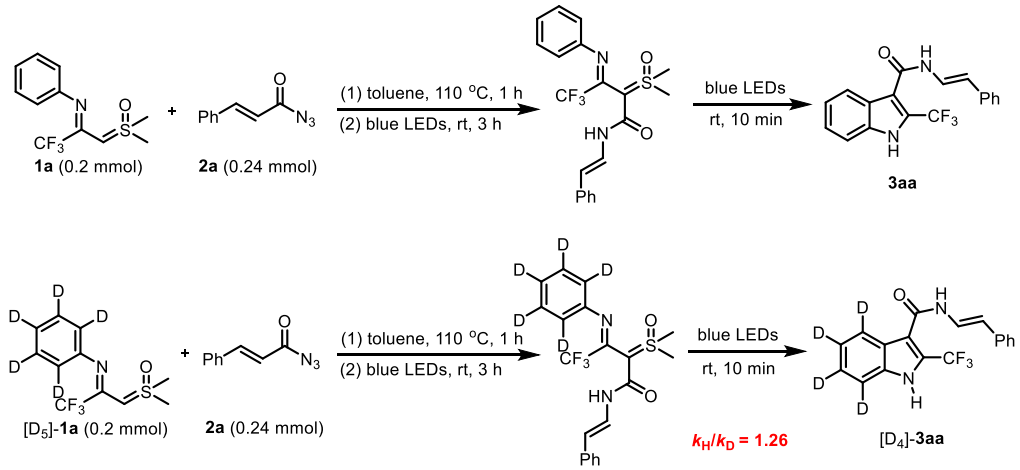


Figure S1. HRMS spectra.

7. Kinetic isotope experiments

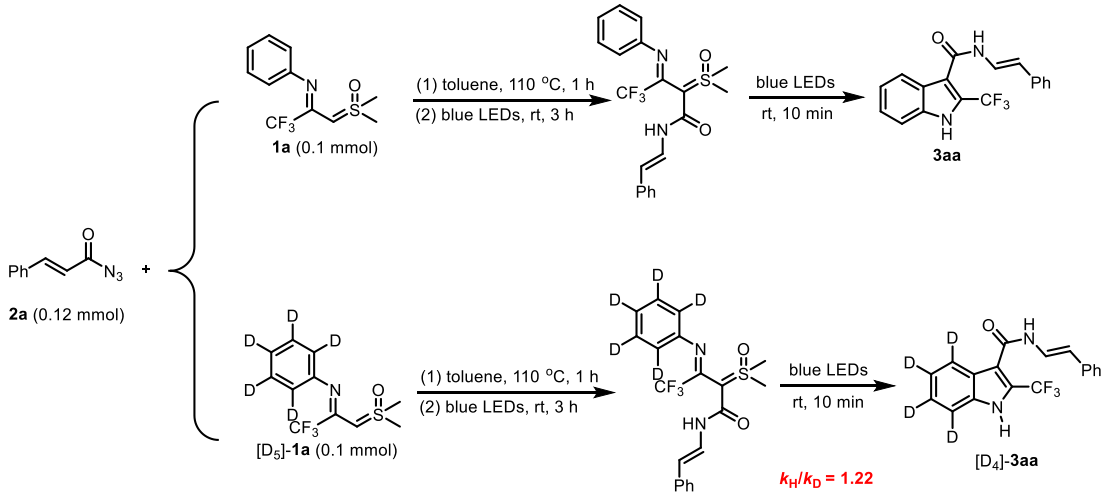
7.1. Parallel reaction



A dried 10 mL Schlenk tube was charged with azide **2a** (0.24 mmol, 1.2 equiv) and toluene (3.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in a preheated oil bath at 110 ℃ for 1 h. Then cooled at room temperature, **1a** or **[D$_5$]-1a** (0.2 mmol) was added. The

reaction mixture was stirred at room temperature for 3 h under nitrogen atmosphere. Then the reaction solution was irradiation by blue LEDs at room temperature for 10 min under nitrogen atmosphere. The reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the product **3aa** (15.3 mg, 23%) or **[D$_4$]-3aa** (12.1 mg, 18%).

7.2. Competitive reaction



A dried 10 mL Schlenk tube was charged with azide **2a** (0.24 mmol, 1.2 equiv) and toluene (3.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in a preheated oil bath at 110 ℃ for 1 h. Then cooled at room temperature, **1a** and **[D$_5$]-1a** (0.2 mmol) was added. The reaction mixture was stirred at room temperature for 3 h under nitrogen atmosphere. Then the reaction solution was irradiation by blue LEDs at room temperature for 10 min under nitrogen atmosphere. The reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the product **3aa** and **[D$_4$]-3aa** (12.7 mg, 20%).

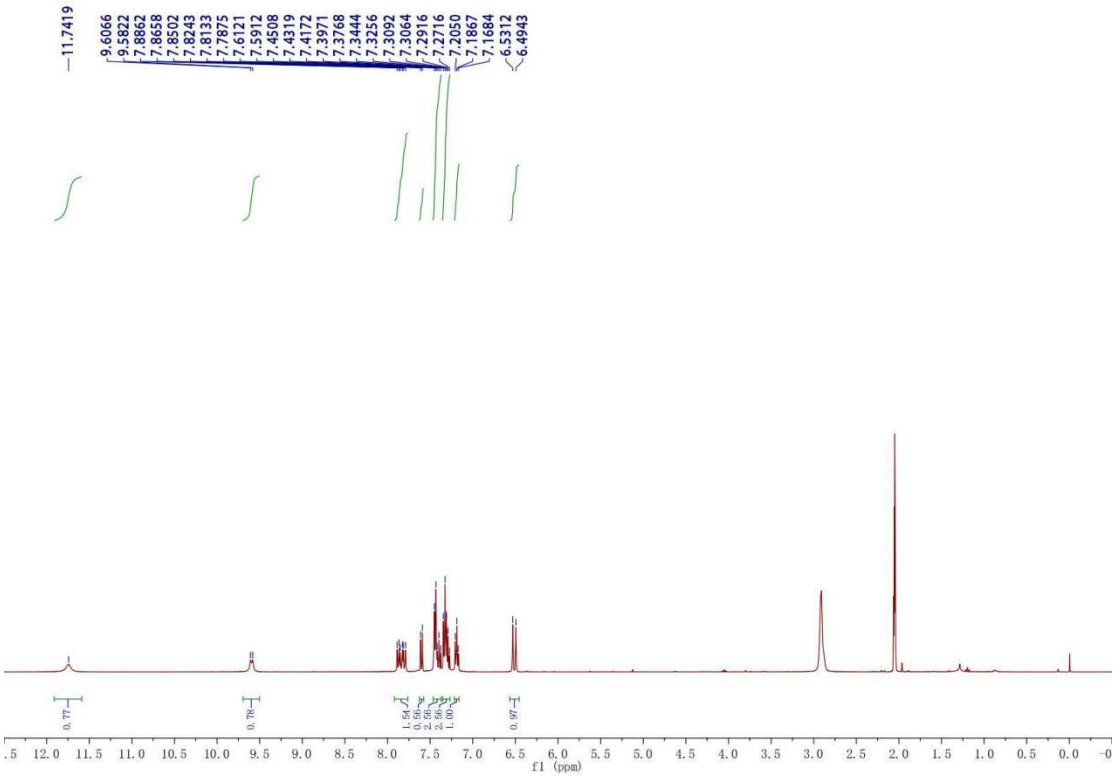


Figure S2. ^{1}H NMR of **3aa** and **[D$_4$]-3aa**

8. Crystal data and structural refinement of compounds 3aa and 3af'

Single crystal of compound **3aa** was obtained by slow evaporation from $CHCl_3$ solution.

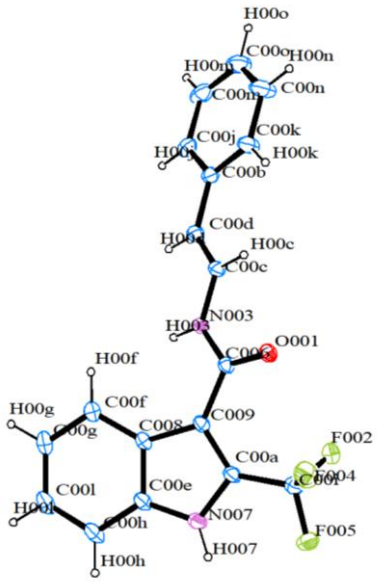


Figure S1. Crystal data and structure refinement of product **3aa** (with thermal ellipsoils shown at the 50% probability level)

Table 1. Crystal data and structure refinement for **3aa**.

Identification code	**3aa**	
Empirical formula	$C_{18}\ H_{13}\ F_3\ N_2\ O$	
Formula weight	330.30	
Temperature	294.00 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Fdd2	
Unit cell dimensions	a = 16.2399(12) Å	a= 90 °
	b = 47.800(4) Å	b= 90 °
	c = 8.1006(7) Å	g = 90 °
Volume	6288.2(9) $Å^3$	
Z	16	
Density (calculated)	1.396 Mg/m^3	

Absorption coefficient	0.959 mm^{-1}
F(000)	2720
Crystal size	0.27 x 0.19 x 0.18 mm^3
Theta range for data collection	3.699 to 68.742 °
Index ranges	-19<=h<=19, -57<=k<=57, -9<=l<=9
Reflections collected	27508
Independent reflections	2873 [R(int) = 0.0582]
Completeness to theta = 67.679?	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.6448
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2873 / 1 / 217
Goodness-of-fit on F^2	1.167
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.1019
R indices (all data)	R1 = 0.0454, wR2 = 0.1033
Absolute structure parameter	0.06(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.151 and -0.226 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3aa**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(001)	5204(1)	3957(1)	3810(3)	51(1)
F(002)	4962(1)	4494(1)	5358(3)	79(1)

N(003)	4261(1)	3639(1)	4659(3)	48(1)
F(004)	5072(1)	4569(1)	2782(4)	95(1)
F(005)	4254(1)	4820(1)	4238(5)	112(1)
C(006)	4481(2)	3890(1)	4031(3)	44(1)
N(007)	3081(2)	4478(1)	3341(4)	62(1)
C(008)	2955(2)	4011(1)	3187(3)	46(1)
C(009)	3790(2)	4079(1)	3649(4)	45(1)
C(00A)	3834(2)	4366(1)	3691(4)	52(1)
C(00B)	5169(2)	2968(1)	6282(4)	52(1)
C(00C)	4828(2)	3430(1)	5045(4)	48(1)
C(00D)	4616(2)	3195(1)	5798(4)	52(1)
C(00E)	2531(2)	4265(1)	3024(4)	54(1)
C(00F)	2535(2)	3763(1)	2825(4)	55(1)
C(00G)	1721(2)	3779(1)	2381(5)	67(1)
C(00H)	1698(2)	4281(1)	2599(5)	67(1)
C(00I)	4532(2)	4559(1)	4018(6)	68(1)
C(00J)	4850(2)	2742(1)	7159(5)	64(1)
C(00K)	6007(2)	2967(1)	5935(5)	70(1)
C(00L)	1305(2)	4036(1)	2289(5)	70(1)
C(00M)	5355(3)	2528(1)	7705(5)	82(1)
C(00N)	6509(3)	2751(1)	6479(7)	98(2)
C(00O)	6184(3)	2533(1)	7357(6)	95(1)

Table 3. Bond lengths [Å] and angles [°] for **3aa**.

O(001)-C(006)	1.229(3)
F(002)-C(00I)	1.328(5)
N(003)-H(003)	0.8600
N(003)-C(006)	1.355(4)

N(003)-C(00C)	1.391(3)
F(004)-C(00I)	1.331(5)
F(005)-C(00I)	1.336(4)
C(006)-C(009)	1.472(4)
N(007)-H(007)	0.8600
N(007)-C(00A)	1.366(4)
N(007)-C(00E)	1.380(4)
C(008)-C(009)	1.445(4)
C(008)-C(00E)	1.401(4)
C(008)-C(00F)	1.399(4)
C(009)-C(00A)	1.375(4)
C(00A)-C(00I)	1.485(4)
C(00B)-C(00D)	1.461(4)
C(00B)-C(00J)	1.395(4)
C(00B)-C(00K)	1.389(4)
C(00C)-H(00C)	0.9300
C(00C)-C(00D)	1.327(4)
C(00D)-H(00D)	0.9300
C(00E)-C(00H)	1.397(4)
C(00F)-H(00F)	0.9300
C(00F)-C(00G)	1.373(4)
C(00G)-H(00G)	0.9300
C(00G)-C(00L)	1.400(5)
C(00H)-H(00H)	0.9300
C(00H)-C(00L)	1.361(5)
C(00J)-H(00J)	0.9300
C(00J)-C(00M)	1.381(5)
C(00K)-H(00K)	0.9300

C(00K)-C(00N)	1.389(5)
C(00L)-H(00L)	0.9300
C(00M)-H(00M)	0.9300
C(00M)-C(00O)	1.376(7)
C(00N)-H(00N)	0.9300
C(00N)-C(00O)	1.367(7)
C(00O)-H(00O)	0.9300
C(006)-N(003)-H(003)	118.5
C(006)-N(003)-C(00C)	123.1(2)
C(00C)-N(003)-H(003)	118.5
O(001)-C(006)-N(003)	122.4(2)
O(001)-C(006)-C(009)	122.6(2)
N(003)-C(006)-C(009)	115.0(2)
C(00A)-N(007)-H(007)	125.4
C(00A)-N(007)-C(00E)	109.1(2)
C(00E)-N(007)-H(007)	125.4
C(00E)-C(008)-C(009)	106.9(2)
C(00F)-C(008)-C(009)	134.6(3)
C(00F)-C(008)-C(00E)	118.3(3)
C(008)-C(009)-C(006)	129.2(3)
C(00A)-C(009)-C(006)	124.5(2)
C(00A)-C(009)-C(008)	106.2(2)
N(007)-C(00A)-C(009)	109.9(2)
N(007)-C(00A)-C(00I)	118.5(3)
C(009)-C(00A)-C(00I)	131.6(3)
C(00J)-C(00B)-C(00D)	118.9(3)
C(00K)-C(00B)-C(00D)	123.5(3)
C(00K)-C(00B)-C(00J)	117.6(3)

N(003)-C(00C)-H(00C)	118.7
C(00D)-C(00C)-N(003)	122.6(2)
C(00D)-C(00C)-H(00C)	118.7
C(00B)-C(00D)-H(00D)	116.8
C(00C)-C(00D)-C(00B)	126.3(3)
C(00C)-C(00D)-H(00D)	116.8
N(007)-C(00E)-C(008)	107.8(2)
N(007)-C(00E)-C(00H)	129.1(3)
C(00H)-C(00E)-C(008)	123.2(3)
C(008)-C(00F)-H(00F)	120.8
C(00G)-C(00F)-C(008)	118.4(3)
C(00G)-C(00F)-H(00F)	120.8
C(00F)-C(00G)-H(00G)	119.0
C(00F)-C(00G)-C(00L)	122.0(3)
C(00L)-C(00G)-H(00G)	119.0
C(00E)-C(00H)-H(00H)	121.6
C(00L)-C(00H)-C(00E)	116.8(3)
C(00L)-C(00H)-H(00H)	121.6
F(002)-C(00I)-F(004)	106.1(3)
F(002)-C(00I)-F(005)	106.7(3)
F(002)-C(00I)-C(00A)	113.6(3)
F(004)-C(00I)-F(005)	106.9(3)
F(004)-C(00I)-C(00A)	112.9(3)
F(005)-C(00I)-C(00A)	110.2(3)
C(00B)-C(00J)-H(00J)	119.5
C(00M)-C(00J)-C(00B)	121.1(3)
C(00M)-C(00J)-H(00J)	119.5
C(00B)-C(00K)-H(00K)	119.5

C(00N)-C(00K)-C(00B)	120.9(4)
C(00N)-C(00K)-H(00K)	119.5
C(00G)-C(00L)-H(00L)	119.4
C(00H)-C(00L)-C(00G)	121.2(3)
C(00H)-C(00L)-H(00L)	119.4
C(00J)-C(00M)-H(00M)	119.9
C(00O)-C(00M)-C(00J)	120.2(4)
C(00O)-C(00M)-H(00M)	119.9
C(00K)-C(00N)-H(00N)	119.8
C(00O)-C(00N)-C(00K)	120.4(4)
C(00O)-C(00N)-H(00N)	119.8
C(00M)-C(00O)-H(00O)	120.1
C(00N)-C(00O)-C(00M)	119.8(4)
C(00N)-C(00O)-H(00O)	120.1

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3aa**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(001)	33(1)	57(1)	64(1)	-1(1)	4(1)	0(1)
F(002)	61(1)	72(1)	104(2)	-11(1)	-22(1)	-2(1)
N(003)	32(1)	50(1)	64(2)	6(1)	3(1)	4(1)
F(004)	64(1)	102(2)	121(2)	33(2)	11(1)	-22(1)
F(005)	70(1)	47(1)	221(4)	-1(2)	-21(2)	2(1)
C(006)	36(1)	49(1)	47(2)	-2(1)	2(1)	2(1)
N(007)	46(1)	52(1)	86(2)	12(1)	-7(1)	8(1)

C(008)	36(1)	59(2)	44(1)	4(1)	-1(1)	0(1)
C(009)	34(1)	52(1)	50(1)	4(1)	0(1)	2(1)
C(00A)	37(1)	52(2)	68(2)	9(1)	-3(1)	3(1)
C(00B)	57(2)	44(1)	54(2)	-3(1)	0(1)	4(1)
C(00C)	38(1)	48(1)	57(2)	0(1)	1(1)	6(1)
C(00D)	42(1)	51(2)	64(2)	1(1)	4(1)	2(1)
C(00E)	41(1)	63(2)	58(2)	14(1)	-4(1)	3(1)
C(00F)	50(2)	65(2)	50(2)	0(1)	-5(1)	-4(1)
C(00G)	52(2)	89(2)	60(2)	3(2)	-11(2)	-20(2)
C(00H)	42(2)	88(2)	70(2)	22(2)	-7(2)	8(2)
C(00I)	49(2)	51(2)	105(3)	8(2)	-7(2)	2(1)
C(00J)	81(2)	51(2)	61(2)	1(1)	-1(2)	-7(2)
C(00K)	58(2)	61(2)	92(3)	15(2)	4(2)	14(2)
C(00L)	44(2)	102(3)	66(2)	20(2)	-13(2)	-6(2)
C(00M)	128(4)	47(2)	72(2)	7(2)	-10(2)	1(2)
C(00N)	83(3)	81(3)	130(4)	22(3)	1(3)	34(2)
C(00O)	114(4)	68(2)	103(3)	11(2)	-17(3)	31(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x $10^{3)}$ for **3aa**.

	x	y	z	U(eq)
H(003)	3748	3606	4828	58
H(007)	2967	4654	3321	74
H(00C)	5378	3458	4765	57
H(00D)	4060	3171	6040	62
H(00F)	2802	3591	2883	66

H(00G)	1437	3616	2135	80
H(00H)	1426	4452	2533	80
H(00J)	4289	2734	7380	77
H(00K)	6235	3113	5330	84
H(00L)	749	4038	2010	85
H(00M)	5133	2381	8310	99
H(00N)	7069	2754	6245	118
H(00O)	6522	2388	7719	114

Table 6. Torsion angles [°] for **3aa**.

O(001)-C(006)-C(009)-C(008)	152.1(3)
O(001)-C(006)-C(009)-C(00A)	-28.6(4)
N(003)-C(006)-C(009)-C(008)	-28.5(4)
N(003)-C(006)-C(009)-C(00A)	150.8(3)
N(003)-C(00C)-C(00D)-C(00B)	-178.5(3)
C(006)-N(003)-C(00C)-C(00D)	173.7(3)
C(006)-C(009)-C(00A)-N(007)	-177.5(3)
C(006)-C(009)-C(00A)-C(00I)	3.3(6)
N(007)-C(00A)-C(00I)-F(002)	132.3(3)
N(007)-C(00A)-C(00I)-F(004)	-106.8(4)
N(007)-C(00A)-C(00I)-F(005)	12.6(5)
N(007)-C(00E)-C(00H)-C(00L)	177.5(4)
C(008)-C(009)-C(00A)-N(007)	1.9(4)
C(008)-C(009)-C(00A)-C(00I)	-177.3(4)
C(008)-C(00E)-C(00H)-C(00L)	-2.1(5)
C(008)-C(00F)-C(00G)-C(00L)	-0.2(5)
C(009)-C(008)-C(00E)-N(007)	1.0(3)
C(009)-C(008)-C(00E)-C(00H)	-179.4(3)

C(009)-C(008)-C(00F)-C(00G)	-178.4(3)
C(009)-C(00A)-C(00I)-F(002)	-48.5(5)
C(009)-C(00A)-C(00I)-F(004)	72.4(5)
C(009)-C(00A)-C(00I)-F(005)	-168.2(4)
C(00A)-N(007)-C(00E)-C(008)	0.2(4)
C(00A)-N(007)-C(00E)-C(00H)	-179.4(3)
C(00B)-C(00J)-C(00M)-C(00O)	-1.4(6)
C(00B)-C(00K)-C(00N)-C(00O)	0.6(7)
C(00C)-N(003)-C(006)-O(001)	-2.6(4)
C(00C)-N(003)-C(006)-C(009)	177.9(3)
C(00D)-C(00B)-C(00J)-C(00M)	-177.2(3)
C(00D)-C(00B)-C(00K)-C(00N)	177.6(4)
C(00E)-N(007)-C(00A)-C(009)	-1.4(4)
C(00E)-N(007)-C(00A)-C(00I)	178.0(3)
C(00E)-C(008)-C(009)-C(006)	177.6(3)
C(00E)-C(008)-C(009)-C(00A)	-1.8(3)
C(00E)-C(008)-C(00F)-C(00G)	-2.2(4)
C(00E)-C(00H)-C(00L)-C(00G)	-0.4(5)
C(00F)-C(008)-C(009)-C(006)	-5.9(5)
C(00F)-C(008)-C(009)-C(00A)	174.7(3)
C(00F)-C(008)-C(00E)-N(007)	-176.2(3)
C(00F)-C(008)-C(00E)-C(00H)	3.4(5)
C(00F)-C(00G)-C(00L)-C(00H)	1.6(6)
C(00J)-C(00B)-C(00D)-C(00C)	176.0(3)
C(00J)-C(00B)-C(00K)-C(00N)	-1.5(6)
C(00J)-C(00M)-C(00O)-C(00N)	0.5(7)
C(00K)-C(00B)-C(00D)-C(00C)	-3.1(5)
C(00K)-C(00B)-C(00J)-C(00M)	1.9(5)

C(00K)-C(00N)-C(00O)-C(00M) -0.1(8)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3aa**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Single crystal of compound **3af'** was obtained by slow evaporation from CH_2Cl_2 solution.

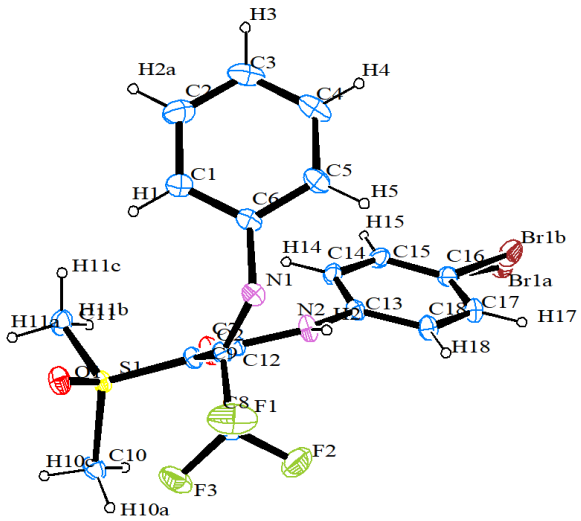


Figure S2. Crystal data and structure refinement of product **3af'** (with thermal ellipsoils shown at the 50% probability level)

Table 1. Crystal data and structure refinement for **3af'**.

Identification code	**3af'**	
Empirical formula	$C_{18}\ H_{16}\ Br\ F_3\ N_2\ O_2\ S$	
Formula weight	461.30	
Temperature	295.00 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 16.5134(7) Å	a= 90 °
	b = 8.0265(4) Å	b= 117.207 °
	c = 16.5356(7) Å	c= 90 °
Volume	1949.22(16) $Å^3$	
Z	4	
Density (calculated)	1.572 Mg/m^3	
Absorption coefficient	4.278 mm^{-1}	

F(000)	928
Crystal size	0.25 x 0.21 x 0.2 mm^3
Theta range for data collection	6.026 to 68.272 °
Index ranges	-19<=h<=19, -9<=k<=9, -19<=l<=19
Reflections collected	30846
Independent reflections	3476 [R(int) = 0.0515]
Completeness to theta = 67.679?	97.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.4239
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3476 / 1 / 256
Goodness-of-fit on F^2	1.130
Final R indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.1274
R indices (all data)	R1 = 0.0518, wR2 = 0.1292
Extinction coefficient	n/a
Largest diff. peak and hole	0.513 and -0.571 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3af'**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1A)	8481(4)	5723(7)	6045(4)	58(1)
S(1)	3554(1)	4490(1)	7509(1)	37(1)
O(2)	4957(2)	4014(2)	6919(2)	56(1)
O(1)	2877(2)	5263(3)	7714(2)	54(1)

F(3)	4355(2)	6375(3)	9304(2)	89(1)
N(1)	4233(2)	8960(3)	7593(2)	43(1)
N(2)	5614(2)	6563(3)	7321(2)	46(1)
F(1)	4295(3)	8955(4)	9206(2)	114(1)
F(2)	5496(2)	7719(6)	9440(2)	126(1)
C(12)	4964(2)	5406(3)	7238(2)	40(1)
C(13)	6256(2)	6399(3)	6985(2)	39(1)
C(7)	4323(2)	7537(3)	7961(2)	37(1)
C(6)	3937(2)	9140(3)	6646(2)	44(1)
C(14)	6075(2)	5515(4)	6197(2)	47(1)
C(9)	4337(2)	5905(3)	7567(2)	38(1)
C(8)	4609(2)	7635(4)	8974(2)	48(1)
C(17)	7743(2)	7085(4)	7152(2)	50(1)
C(16)	7554(2)	6183(4)	6379(2)	47(1)
C(5)	4465(3)	10109(4)	6373(3)	58(1)
C(15)	6723(2)	5412(5)	5894(2)	50(1)
C(18)	7094(2)	7184(4)	7454(2)	49(1)
C(10)	4059(3)	2777(4)	8228(3)	55(1)
C(1)	3110(3)	8531(5)	6010(2)	59(1)
C(11)	3022(2)	3562(5)	6426(2)	59(1)
C(4)	4174(4)	10413(5)	5461(3)	78(1)
C(2)	2815(4)	8870(6)	5096(3)	82(1)
C(3)	3354(4)	9802(6)	4826(3)	86(1)
Br(1B)	8460(3)	6130(20)	5961(5)	80(2)

Table 3. Bond lengths [Å] and angles [°] for **3af'**.

Br(1A)-C(16)	1.886(6)
S(1)-O(1)	1.448(2)

S(1)-C(9)	1.691(3)
S(1)-C(10)	1.759(3)
S(1)-C(11)	1.759(3)
O(2)-C(12)	1.234(3)
F(3)-C(8)	1.306(4)
N(1)-C(7)	1.270(4)
N(1)-C(6)	1.420(4)
N(2)-H(2)	0.8600
N(2)-C(12)	1.378(4)
N(2)-C(13)	1.411(4)
F(1)-C(8)	1.312(4)
F(2)-C(8)	1.308(4)
C(12)-C(9)	1.430(4)
C(13)-C(14)	1.391(4)
C(13)-C(18)	1.391(4)
C(7)-C(9)	1.468(4)
C(7)-C(8)	1.520(4)
C(6)-C(5)	1.388(5)
C(6)-C(1)	1.378(5)
C(14)-H(14)	0.9300
C(14)-C(15)	1.375(5)
C(17)-H(17)	0.9300
C(17)-C(16)	1.375(5)
C(17)-C(18)	1.375(4)
C(16)-C(15)	1.380(5)
C(16)-Br(1B)	1.915(6)
C(5)-H(5)	0.9300
C(5)-C(4)	1.379(6)

C(15)-H(15)	0.9300
C(18)-H(18)	0.9300
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(1)-H(1)	0.9300
C(1)-C(2)	1.386(6)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(4)-H(4)	0.9300
C(4)-C(3)	1.369(7)
C(2)-H(2A)	0.9300
C(2)-C(3)	1.384(7)
C(3)-H(3)	0.9300
O(1)-S(1)-C(9)	110.56(14)
O(1)-S(1)-C(10)	110.82(16)
O(1)-S(1)-C(11)	109.91(17)
C(9)-S(1)-C(10)	111.88(16)
C(9)-S(1)-C(11)	110.77(17)
C(10)-S(1)-C(11)	102.65(19)
C(7)-N(1)-C(6)	121.8(2)
C(12)-N(2)-H(2)	117.0
C(12)-N(2)-C(13)	126.1(2)
C(13)-N(2)-H(2)	117.0
O(2)-C(12)-N(2)	120.6(3)
O(2)-C(12)-C(9)	123.3(3)
N(2)-C(12)-C(9)	116.1(2)

C(14)-C(13)-N(2)	122.6(3)
C(18)-C(13)-N(2)	118.3(3)
C(18)-C(13)-C(14)	119.1(3)
N(1)-C(7)-C(9)	127.7(3)
N(1)-C(7)-C(8)	113.0(2)
C(9)-C(7)-C(8)	118.4(2)
C(5)-C(6)-N(1)	117.8(3)
C(1)-C(6)-N(1)	121.8(3)
C(1)-C(6)-C(5)	120.1(3)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-C(13)	120.1(3)
C(15)-C(14)-H(14)	119.9
C(12)-C(9)-S(1)	117.3(2)
C(12)-C(9)-C(7)	125.5(2)
C(7)-C(9)-S(1)	117.2(2)
F(3)-C(8)-F(1)	104.9(3)
F(3)-C(8)-F(2)	106.3(3)
F(3)-C(8)-C(7)	115.0(3)
F(1)-C(8)-C(7)	113.5(3)
F(2)-C(8)-F(1)	105.7(3)
F(2)-C(8)-C(7)	110.7(3)
C(16)-C(17)-H(17)	120.5
C(18)-C(17)-H(17)	120.5
C(18)-C(17)-C(16)	119.0(3)
C(17)-C(16)-Br(1A)	120.4(3)
C(17)-C(16)-C(15)	121.2(3)
C(17)-C(16)-Br(1B)	117.7(4)
C(15)-C(16)-Br(1A)	117.9(3)

C(15)-C(16)-Br(1B)	121.0(3)
C(6)-C(5)-H(5)	120.1
C(4)-C(5)-C(6)	119.8(4)
C(4)-C(5)-H(5)	120.1
C(14)-C(15)-C(16)	119.7(3)
C(14)-C(15)-H(15)	120.2
C(16)-C(15)-H(15)	120.2
C(13)-C(18)-H(18)	119.6
C(17)-C(18)-C(13)	120.9(3)
C(17)-C(18)-H(18)	119.6
S(1)-C(10)-H(10A)	109.5
S(1)-C(10)-H(10B)	109.5
S(1)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(6)-C(1)-H(1)	120.2
C(6)-C(1)-C(2)	119.6(4)
C(2)-C(1)-H(1)	120.2
S(1)-C(11)-H(11A)	109.5
S(1)-C(11)-H(11B)	109.5
S(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(5)-C(4)-H(4)	119.9
C(3)-C(4)-C(5)	120.3(4)
C(3)-C(4)-H(4)	119.9

C(1)-C(2)-H(2A)	120.0
C(3)-C(2)-C(1)	120.1(5)
C(3)-C(2)-H(2A)	120.0
C(4)-C(3)-C(2)	120.1(4)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3af'**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Br(1A)	46(1)	79(2)	62(1)	4(1)	35(1)	9(1)
S(1)	40(1)	30(1)	48(1)	-1(1)	24(1)	0(1)
O(2)	68(2)	32(1)	88(2)	-14(1)	53(1)	-7(1)
O(1)	50(1)	46(1)	79(2)	-2(1)	42(1)	3(1)
F(3)	145(2)	78(2)	54(1)	-7(1)	53(2)	-40(2)
N(1)	52(2)	33(1)	49(1)	-4(1)	28(1)	2(1)
N(2)	49(2)	34(1)	70(2)	-11(1)	40(1)	-6(1)
F(1)	197(4)	86(2)	63(2)	-11(1)	63(2)	40(2)
F(2)	62(2)	248(4)	54(1)	13(2)	15(1)	-32(2)
C(12)	45(2)	31(1)	50(2)	2(1)	27(1)	3(1)
C(13)	43(2)	28(1)	54(2)	3(1)	28(1)	3(1)
C(7)	40(2)	31(1)	44(2)	-3(1)	23(1)	-3(1)
C(6)	65(2)	27(1)	50(2)	1(1)	34(2)	9(1)
C(14)	38(2)	59(2)	44(2)	-2(1)	18(1)	-5(1)

C(9)	41(2)	29(1)	49(2)	0(1)	26(1)	-1(1)
C(8)	53(2)	47(2)	46(2)	-5(1)	25(2)	-7(1)
C(17)	43(2)	50(2)	60(2)	-5(2)	26(2)	-8(1)
C(16)	41(2)	57(2)	48(2)	8(1)	25(1)	7(1)
C(5)	78(2)	40(2)	66(2)	3(2)	44(2)	1(2)
C(15)	45(2)	70(2)	35(2)	-2(1)	18(1)	0(2)
C(18)	53(2)	40(2)	60(2)	-12(1)	32(2)	-8(1)
C(10)	66(2)	36(2)	69(2)	9(2)	35(2)	0(2)
C(1)	67(2)	55(2)	55(2)	4(2)	27(2)	5(2)
C(11)	53(2)	64(2)	56(2)	-13(2)	21(2)	-12(2)
C(4)	126(4)	51(2)	86(3)	16(2)	74(3)	8(2)
C(2)	92(3)	83(3)	54(2)	5(2)	18(2)	8(2)
C(3)	134(4)	72(3)	53(2)	16(2)	44(3)	18(3)
Br(1B)	48(1)	144(4)	57(1)	-10(2)	32(1)	-9(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3af'**.

	x	y	z	U(eq)
H(2)	5630	7471	7605	55
H(14)	5515	4993	5874	57
H(17)	8300	7620	7466	60
H(5)	5014	10552	6804	69
H(15)	6601	4825	5366	60
H(18)	7218	7785	7979	58
H(10A)	4308	3128	8851	83

H(10B)	4537	2336	8113	83
H(10C)	3608	1931	8113	83
H(1)	2751	7896	6192	71
H(11A)	2593	2742	6413	88
H(11B)	3474	3038	6299	88
H(11C)	2710	4401	5976	88
H(4)	4535	11036	5277	93
H(2A)	2254	8472	4664	99
H(3)	3160	10013	4212	103

Table 6. Torsion angles [º] for **3af'**.

Br(1A)-C(16)-C(15)-C(14)	170.4(3)
O(2)-C(12)-C(9)-S(1)	0.1(4)
O(2)-C(12)-C(9)-C(7)	179.3(3)
O(1)-S(1)-C(9)-C(12)	-169.9(2)
O(1)-S(1)-C(9)-C(7)	10.7(3)
N(1)-C(7)-C(9)-S(1)	-122.5(3)
N(1)-C(7)-C(9)-C(12)	58.2(5)
N(1)-C(7)-C(8)-F(3)	152.7(3)
N(1)-C(7)-C(8)-F(1)	31.8(4)
N(1)-C(7)-C(8)-F(2)	-86.8(4)
N(1)-C(6)-C(5)-C(4)	-175.6(3)
N(1)-C(6)-C(1)-C(2)	174.1(3)
N(2)-C(12)-C(9)-S(1)	-177.9(2)
N(2)-C(12)-C(9)-C(7)	1.4(4)
N(2)-C(13)-C(14)-C(15)	179.2(3)
N(2)-C(13)-C(18)-C(17)	-179.2(3)
C(12)-N(2)-C(13)-C(14)	31.8(5)

C(12)-N(2)-C(13)-C(18)	-149.6(3)
C(13)-N(2)-C(12)-O(2)	7.0(5)
C(13)-N(2)-C(12)-C(9)	-174.9(3)
C(13)-C(14)-C(15)-C(16)	0.3(5)
C(7)-N(1)-C(6)-C(5)	-127.7(3)
C(7)-N(1)-C(6)-C(1)	59.0(4)
C(6)-N(1)-C(7)-C(9)	13.7(5)
C(6)-N(1)-C(7)-C(8)	-177.7(3)
C(6)-C(5)-C(4)-C(3)	1.8(6)
C(6)-C(1)-C(2)-C(3)	0.6(7)
C(14)-C(13)-C(18)-C(17)	-0.5(5)
C(9)-C(7)-C(8)-F(3)	-37.5(4)
C(9)-C(7)-C(8)-F(1)	-158.4(3)
C(9)-C(7)-C(8)-F(2)	83.0(4)
C(8)-C(7)-C(9)-S(1)	69.4(3)
C(8)-C(7)-C(9)-C(12)	-109.9(3)
C(17)-C(16)-C(15)-C(14)	-1.3(5)
C(16)-C(17)-C(18)-C(13)	-0.5(5)
C(5)-C(6)-C(1)-C(2)	1.0(5)
C(5)-C(4)-C(3)-C(2)	-0.2(7)
C(18)-C(13)-C(14)-C(15)	0.6(5)
C(18)-C(17)-C(16)-Br(1A)	-170.1(3)
C(18)-C(17)-C(16)-C(15)	1.4(5)
C(18)-C(17)-C(16)-Br(1B)	178.2(7)
C(10)-S(1)-C(9)-C(12)	66.0(3)
C(10)-S(1)-C(9)-C(7)	-113.3(3)
C(1)-C(6)-C(5)-C(4)	-2.2(5)
C(1)-C(2)-C(3)-C(4)	-1.1(7)

C(11)-S(1)-C(9)-C(12)	-47.8(3)
C(11)-S(1)-C(9)-C(7)	132.8(2)
Br(1B)-C(16)-C(15)-C(14)	-178.0(7)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3af'** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

9. References

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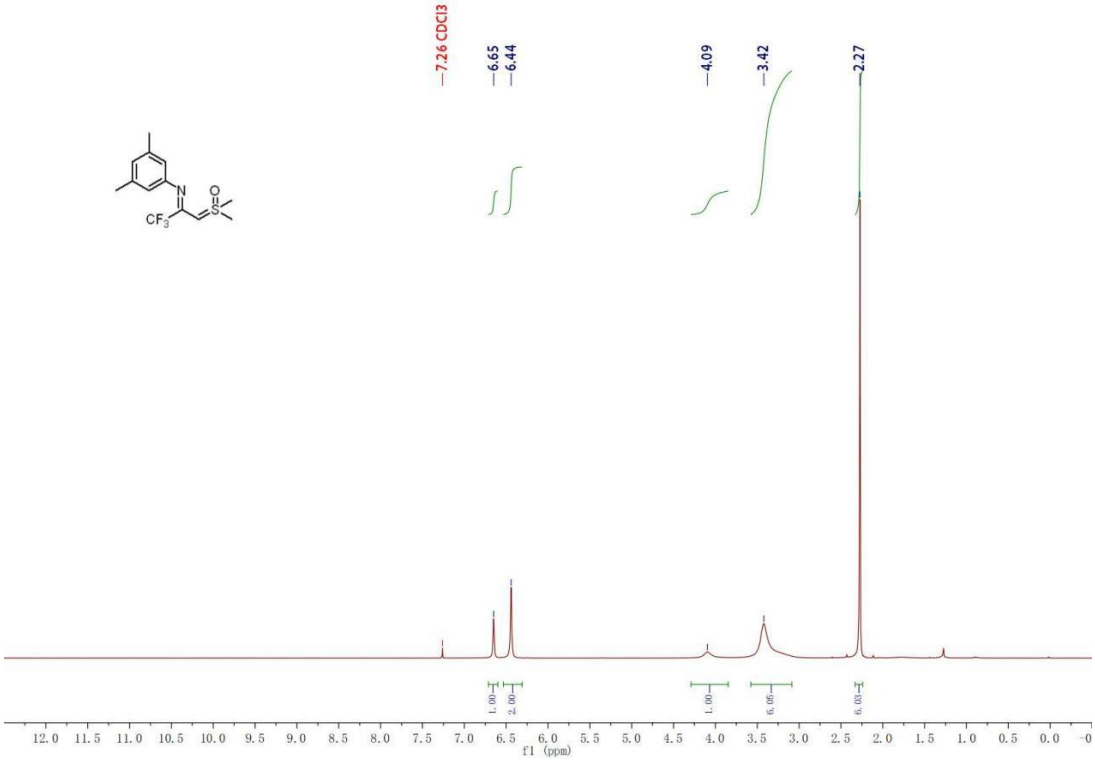
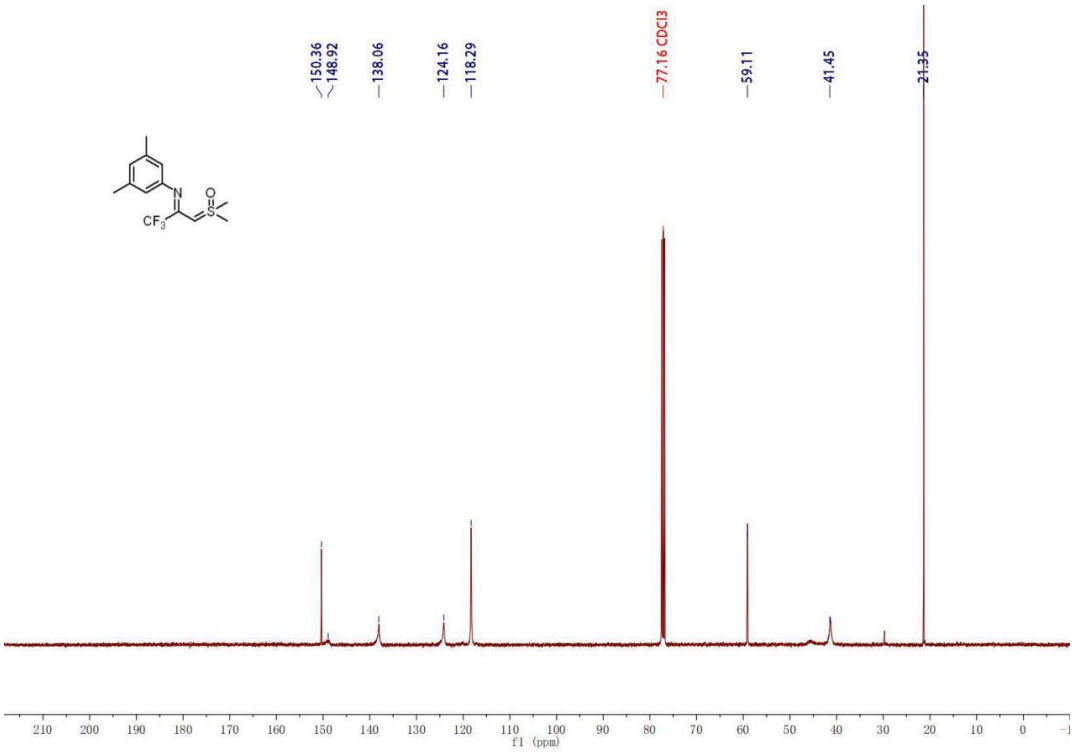
10. Copies of the NMR spectra

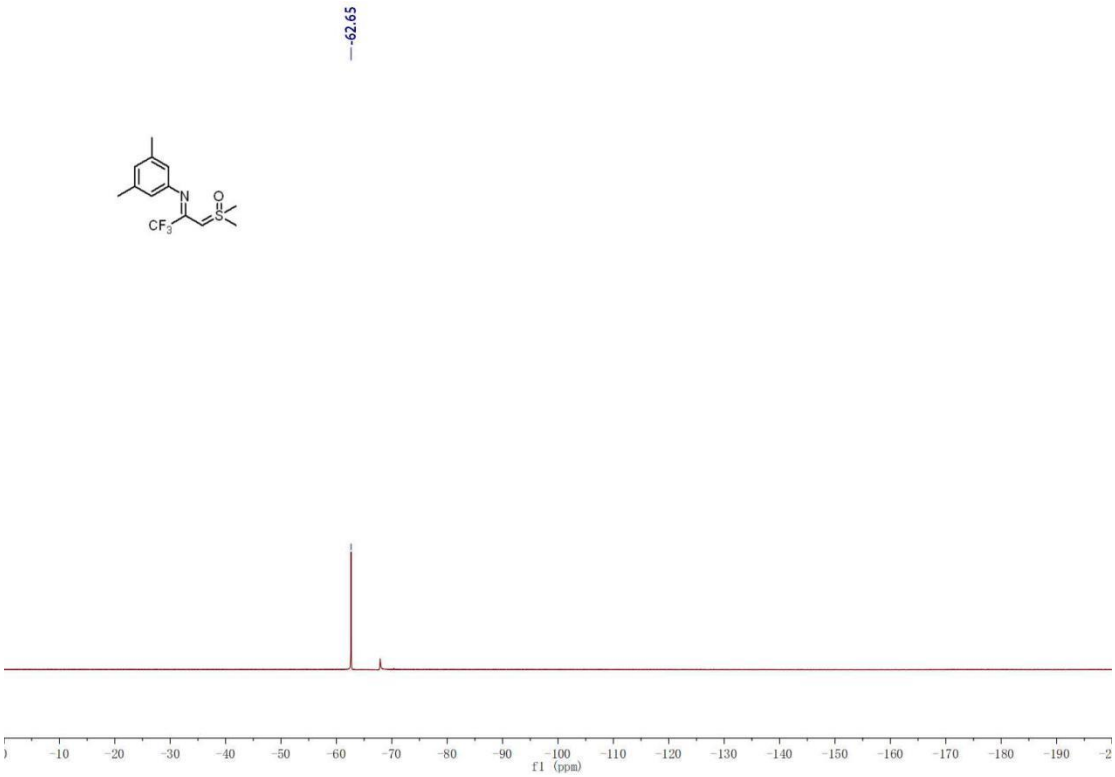
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1n



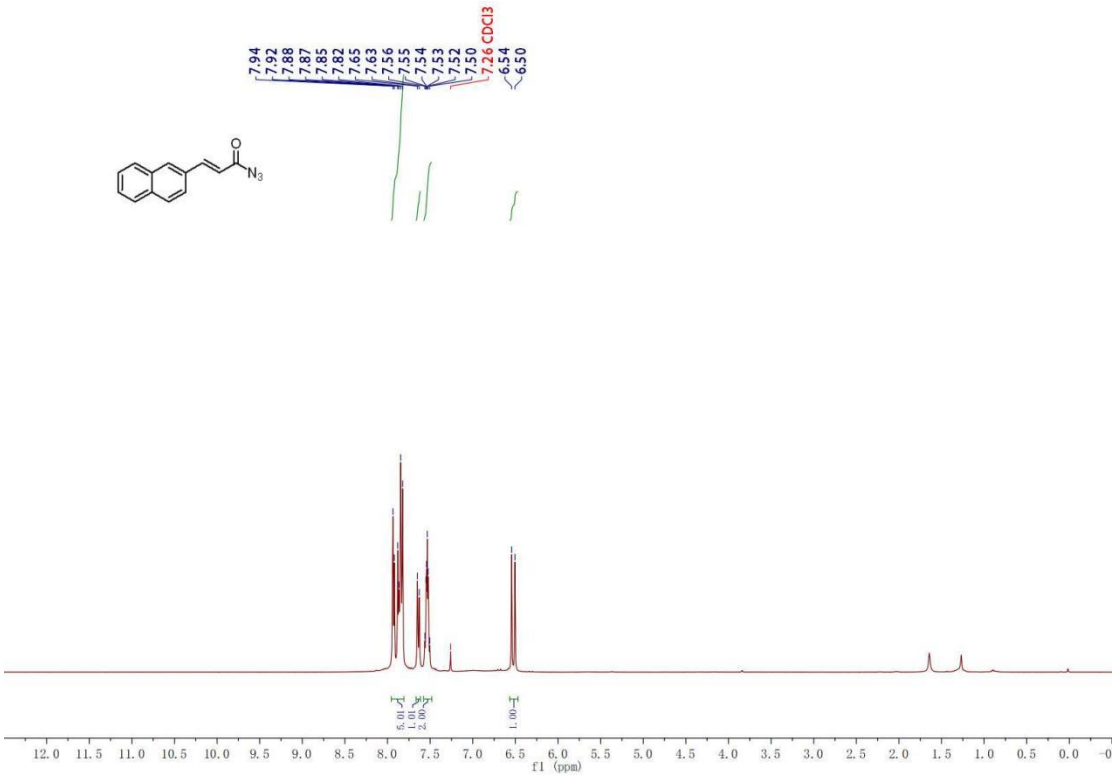
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1n



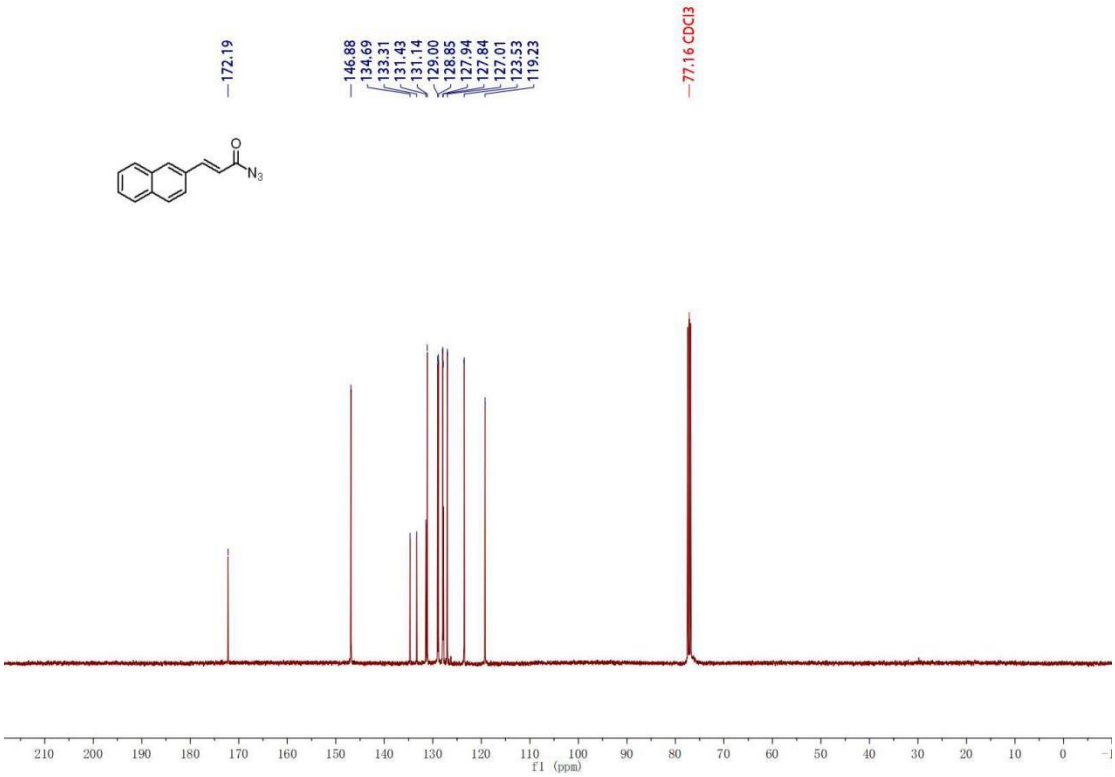
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1n



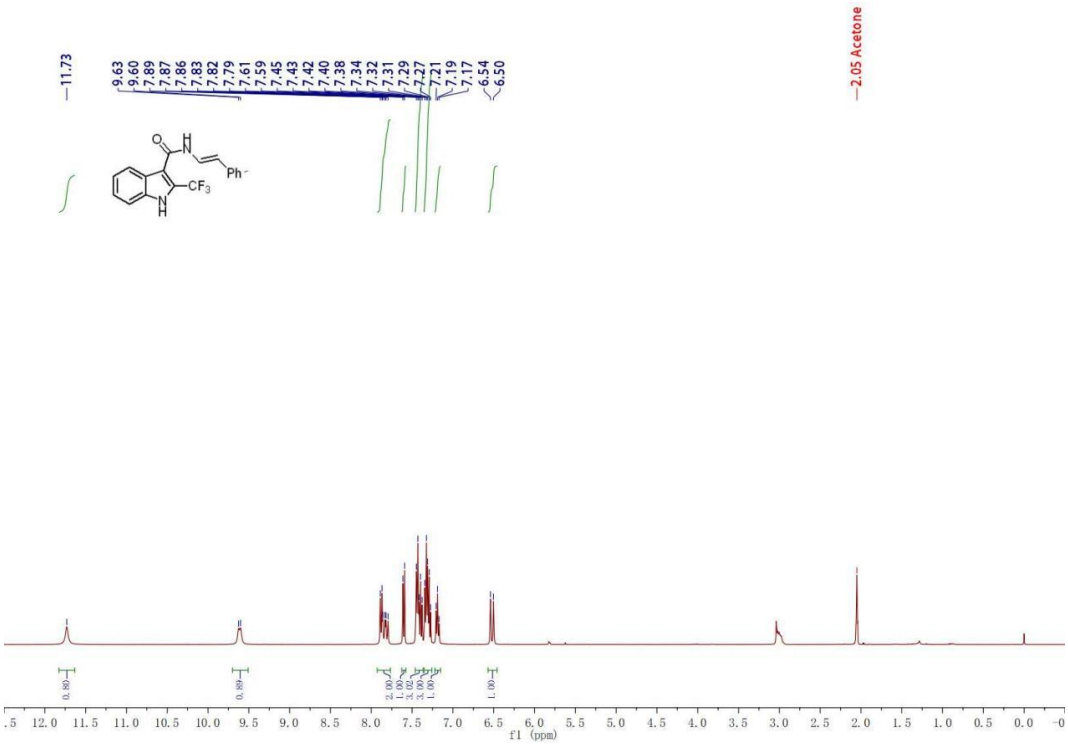
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2n



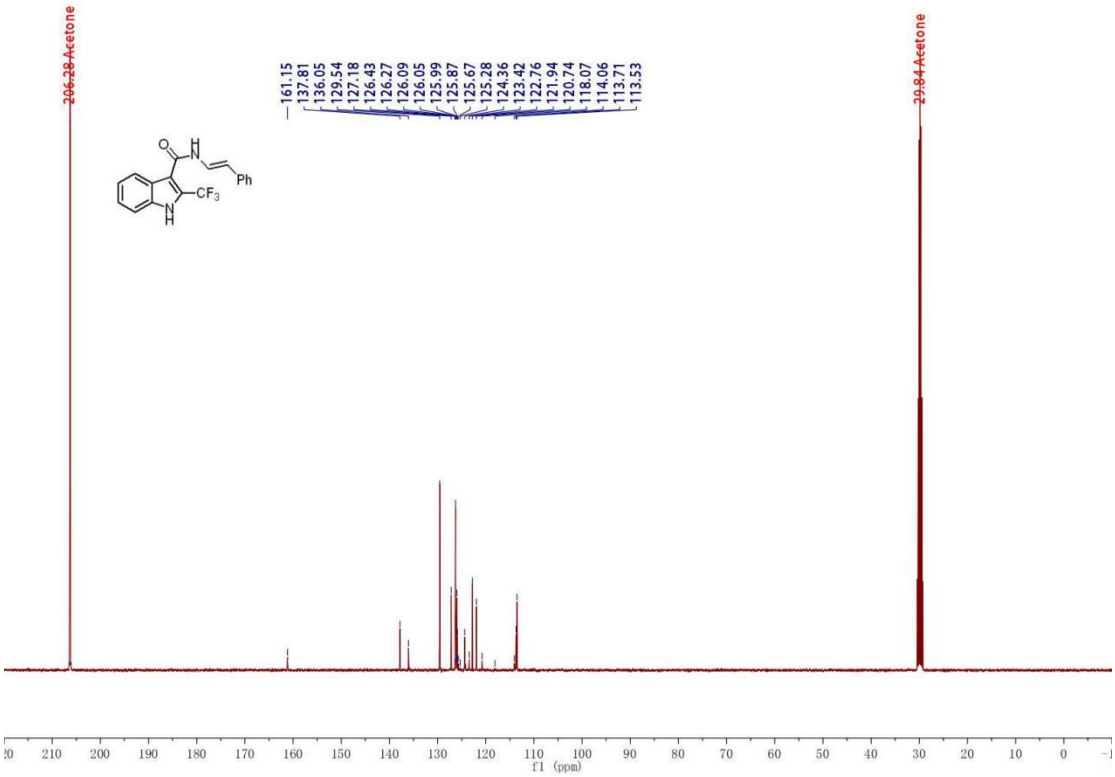
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2n



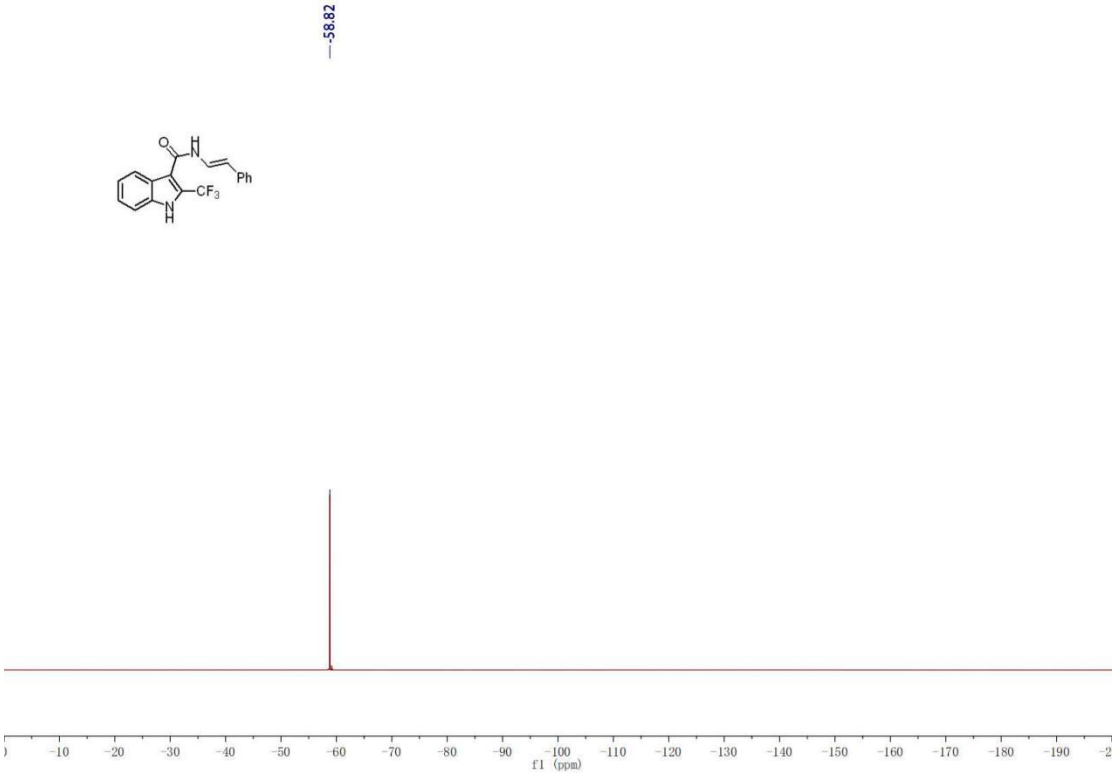
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3aa



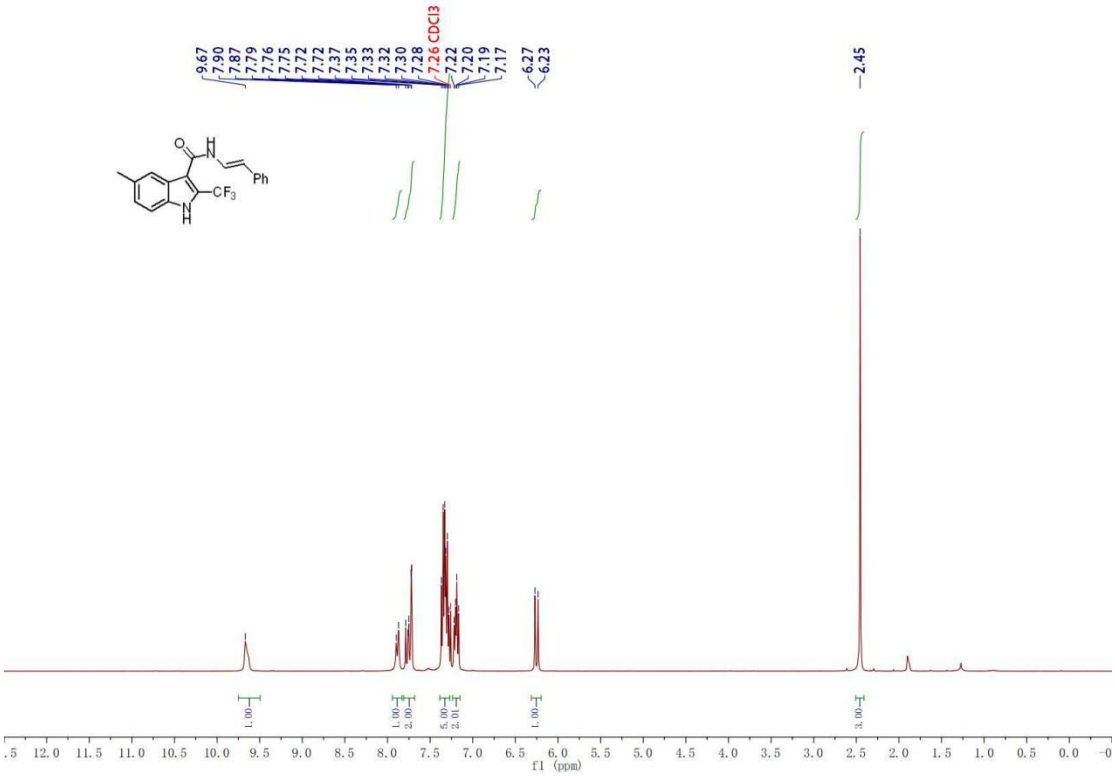
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3aa



^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3aa



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ba



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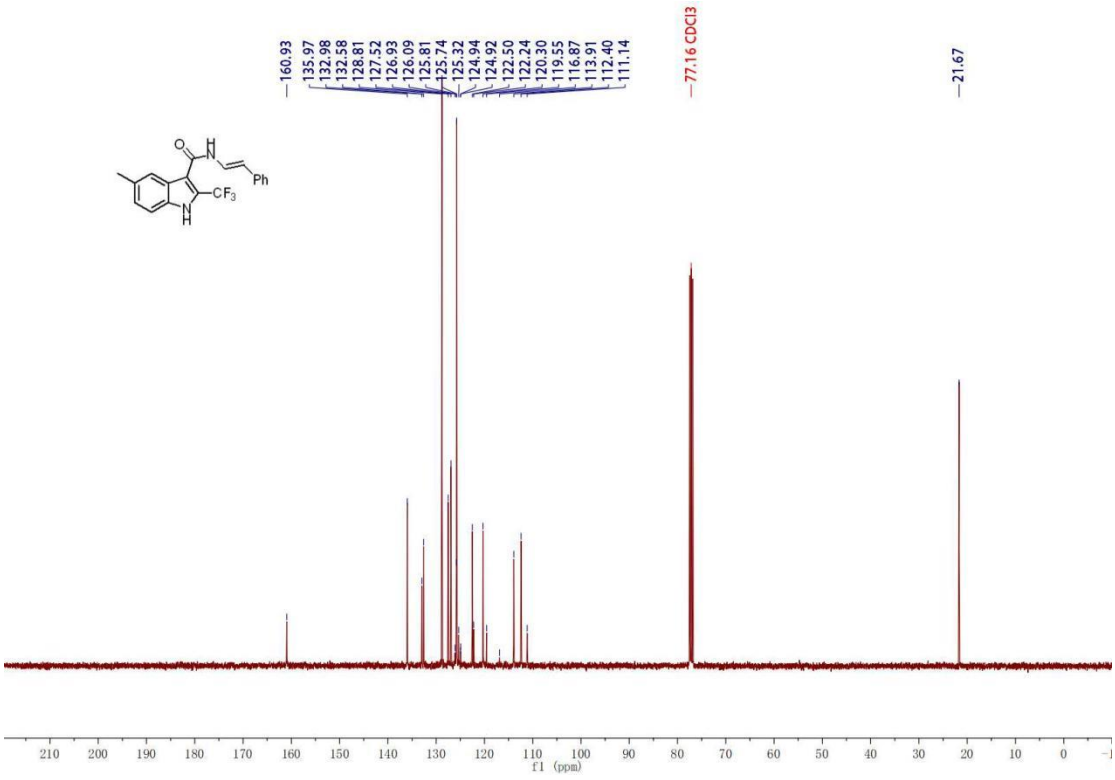
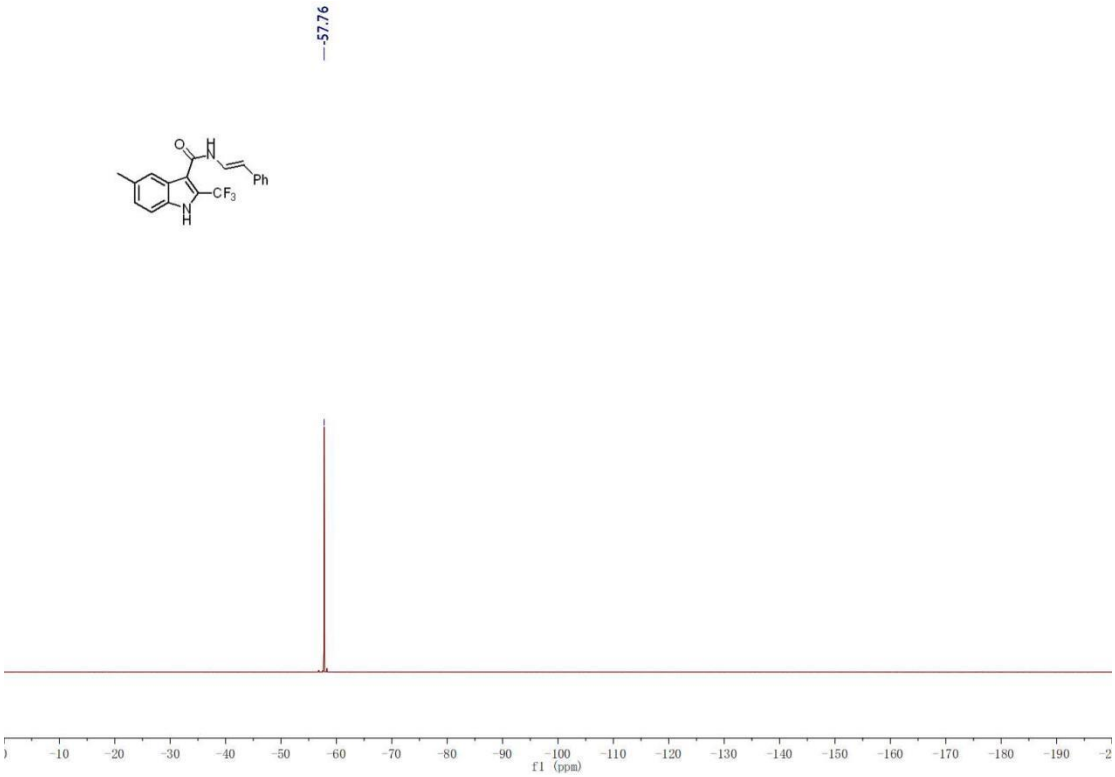
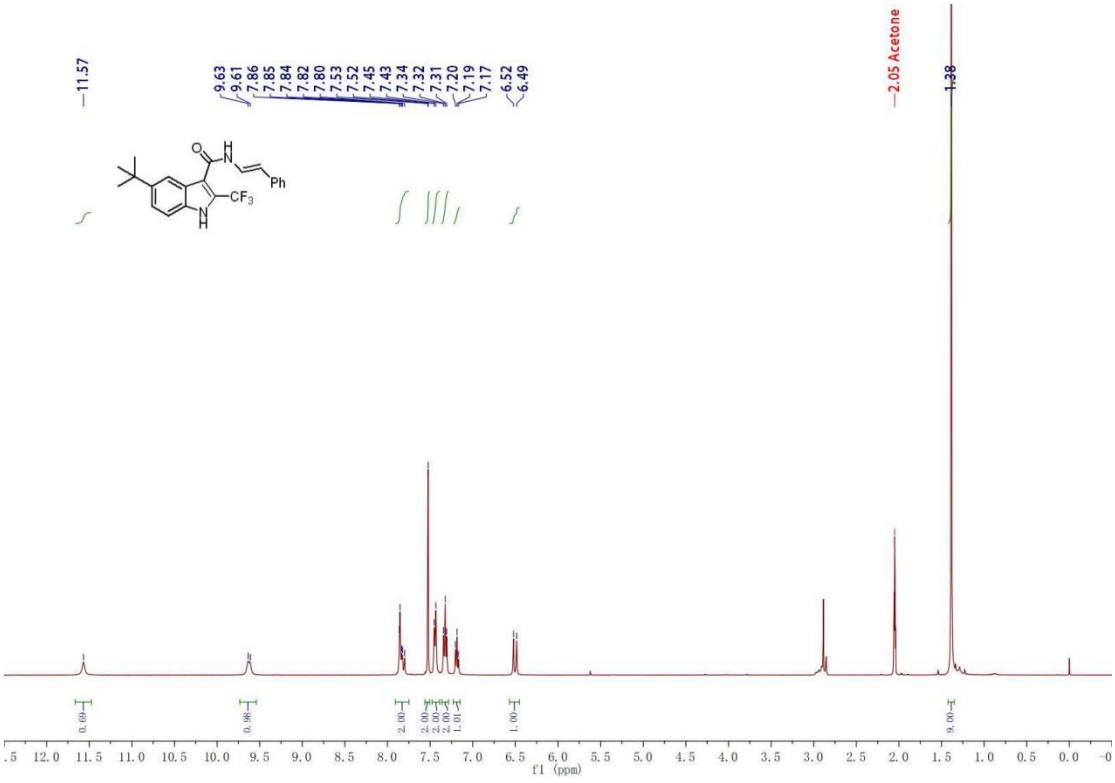


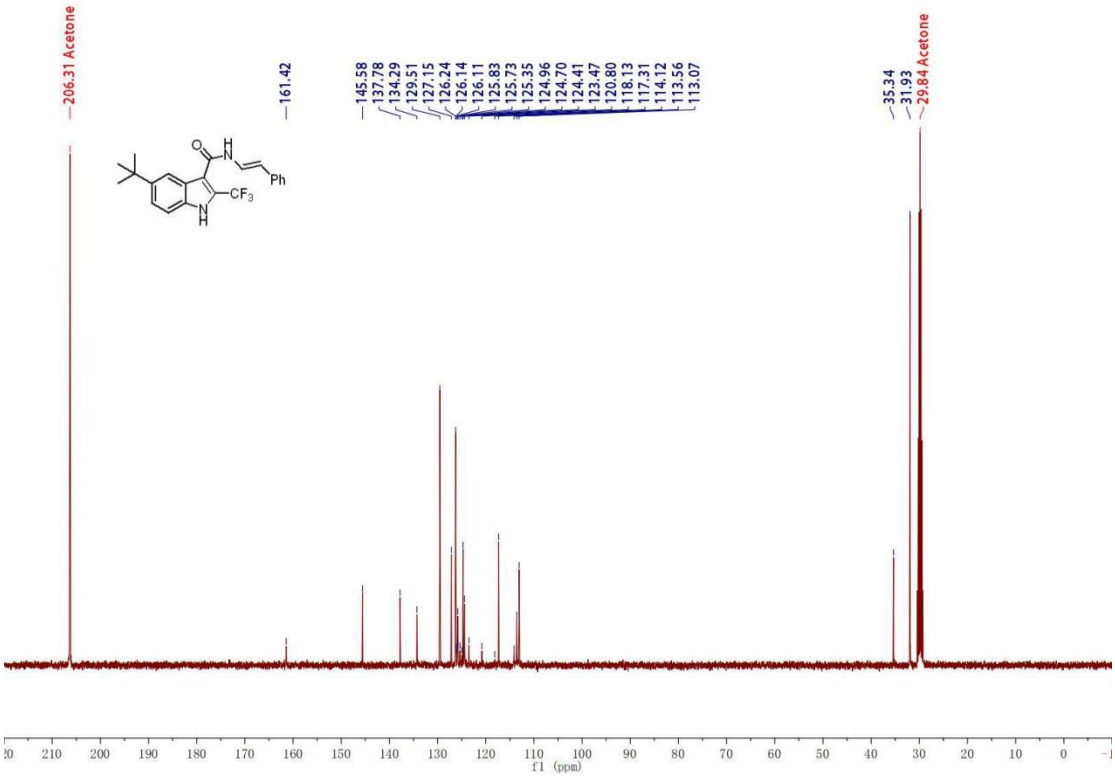
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ba



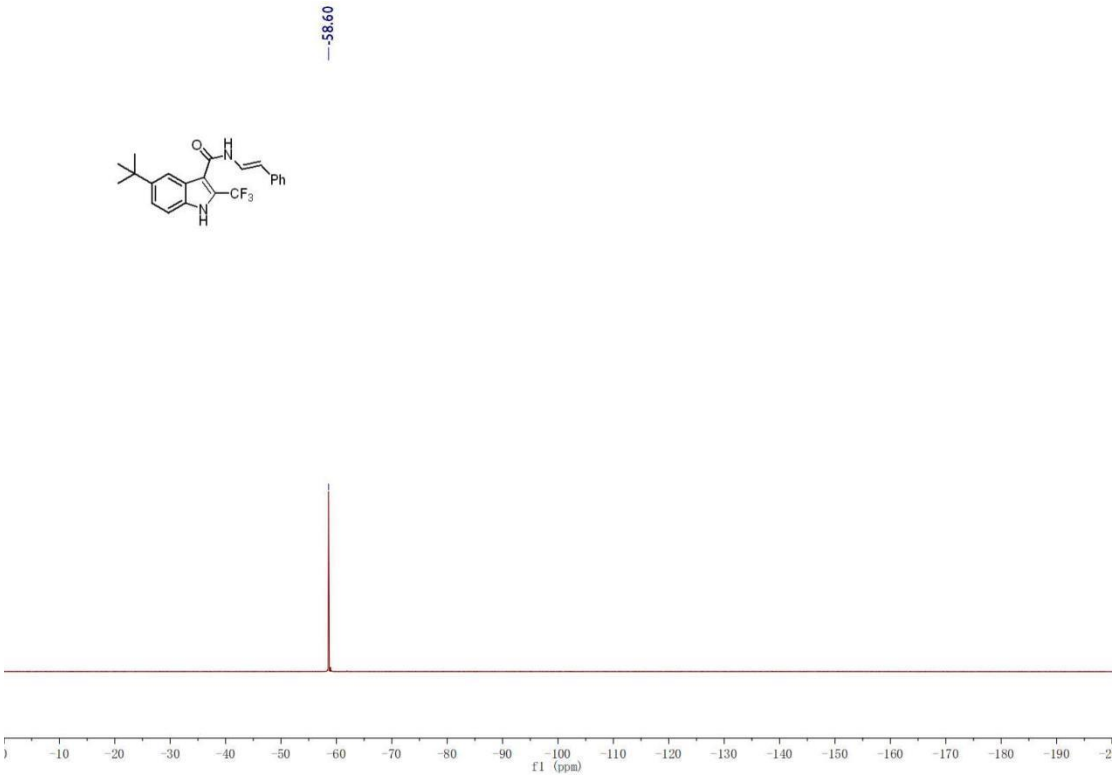
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ca



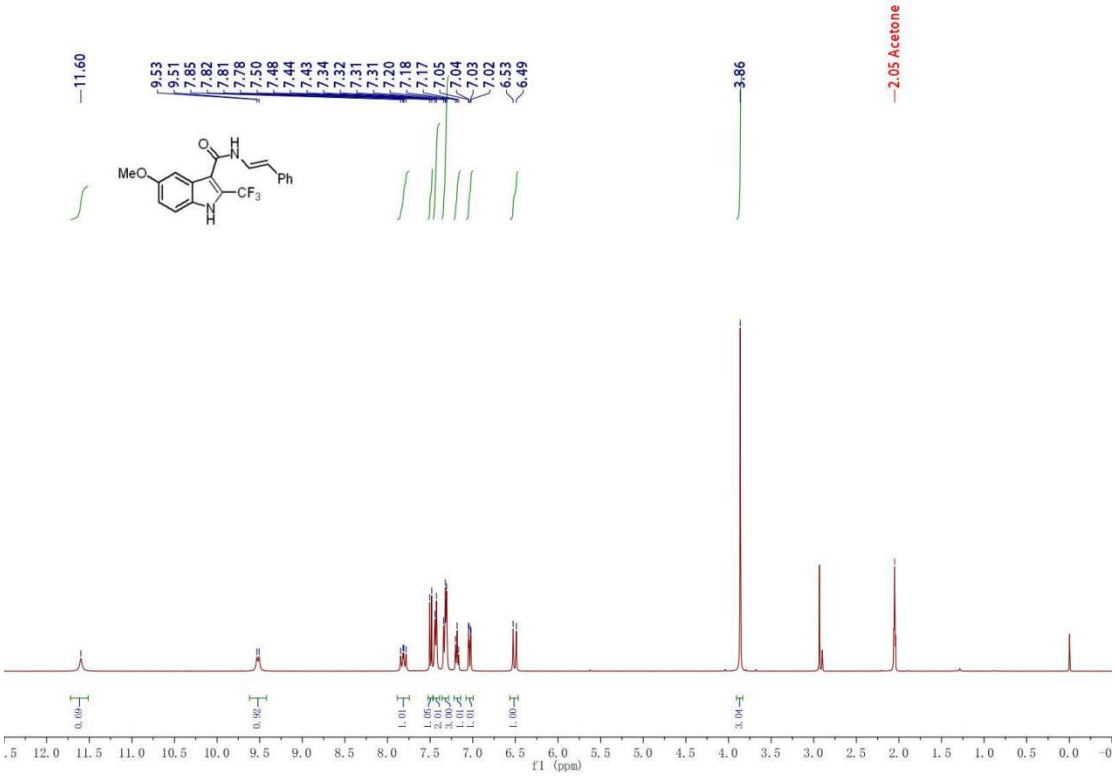
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ca



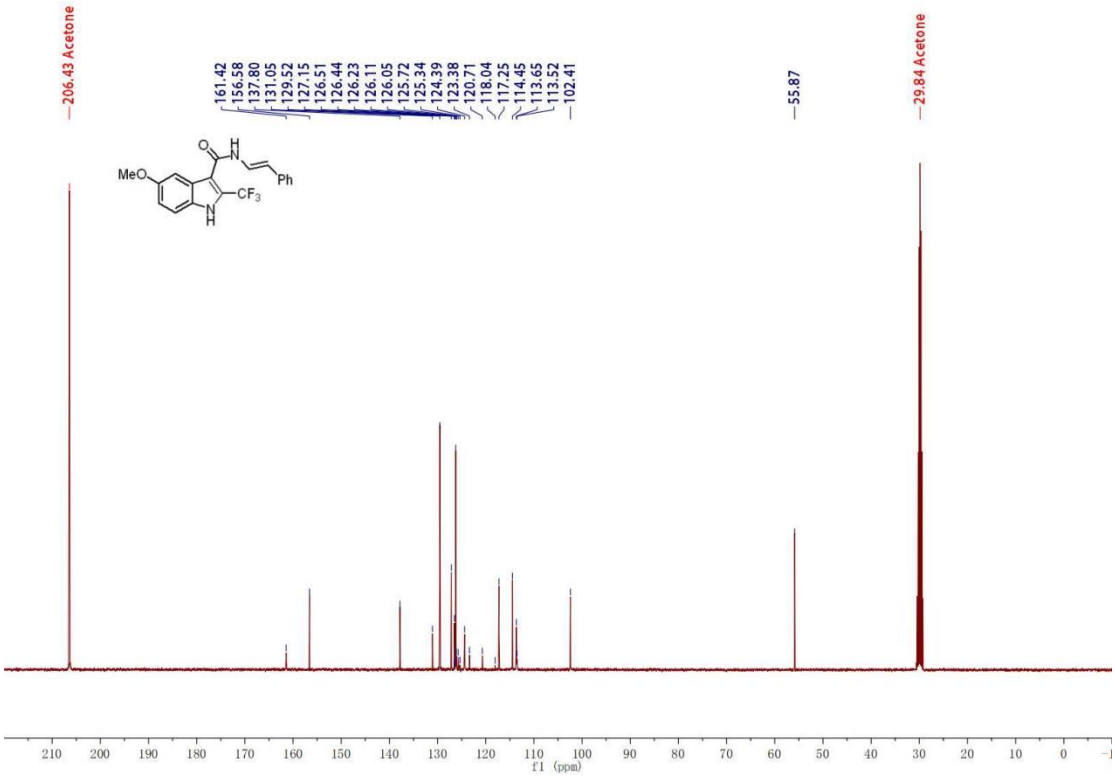
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ca



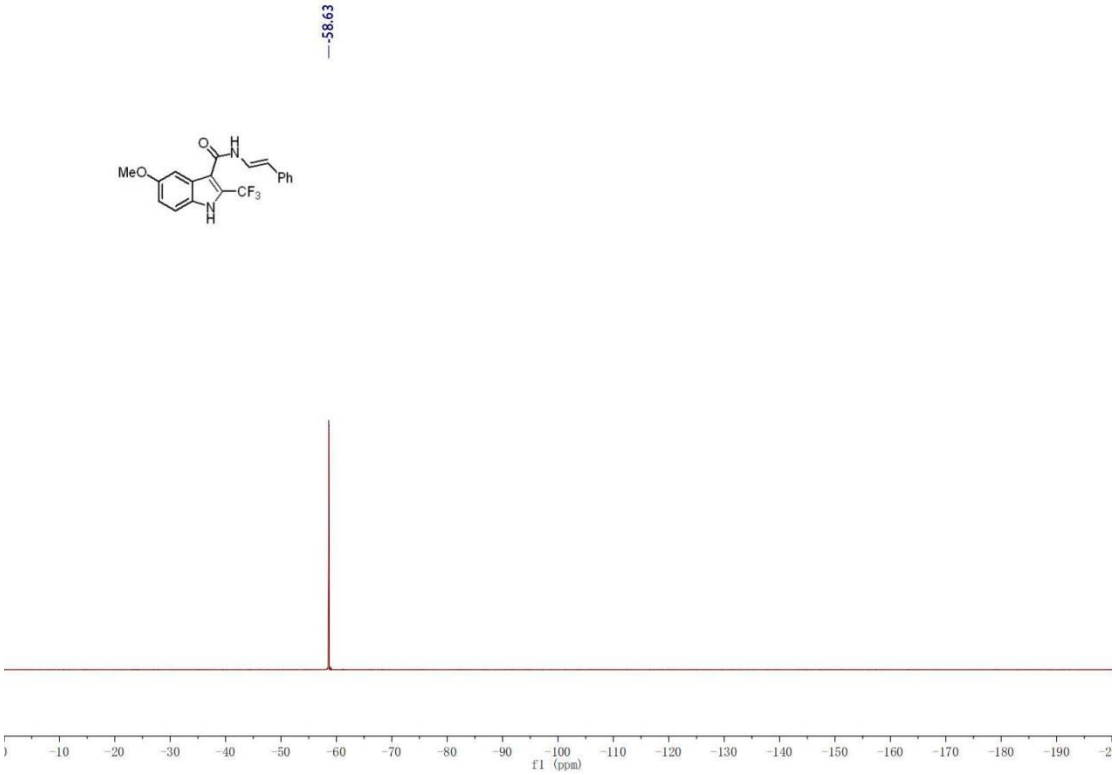
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3da



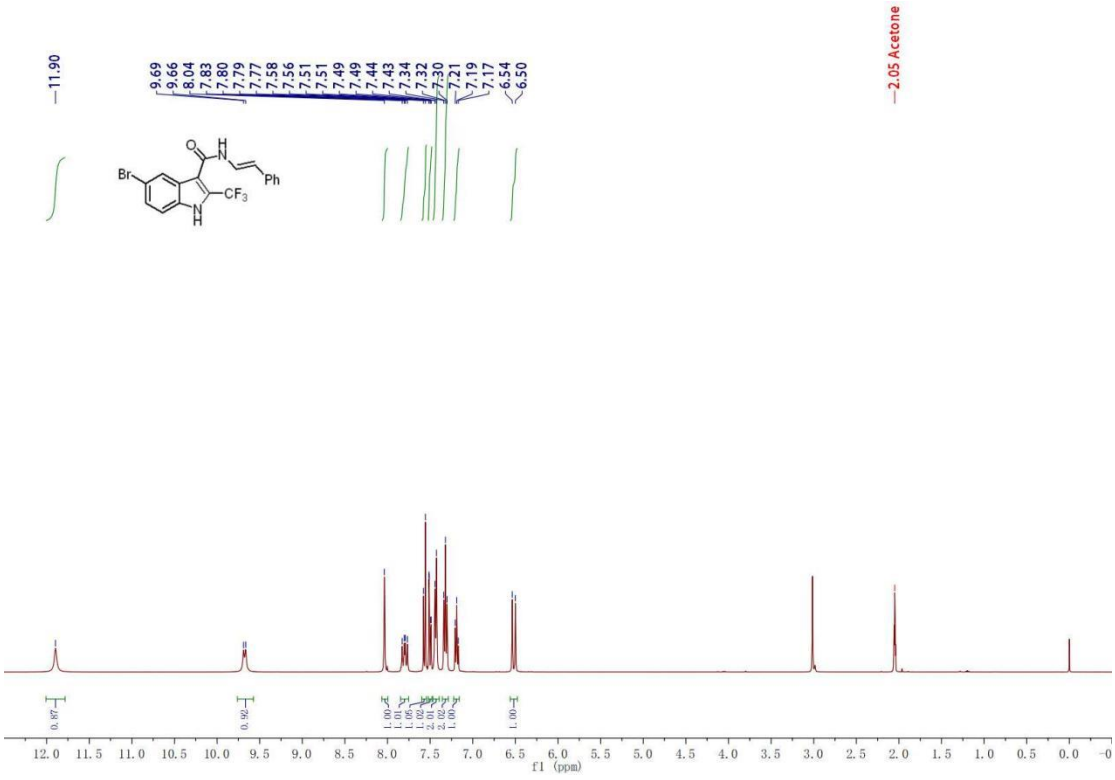
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3da



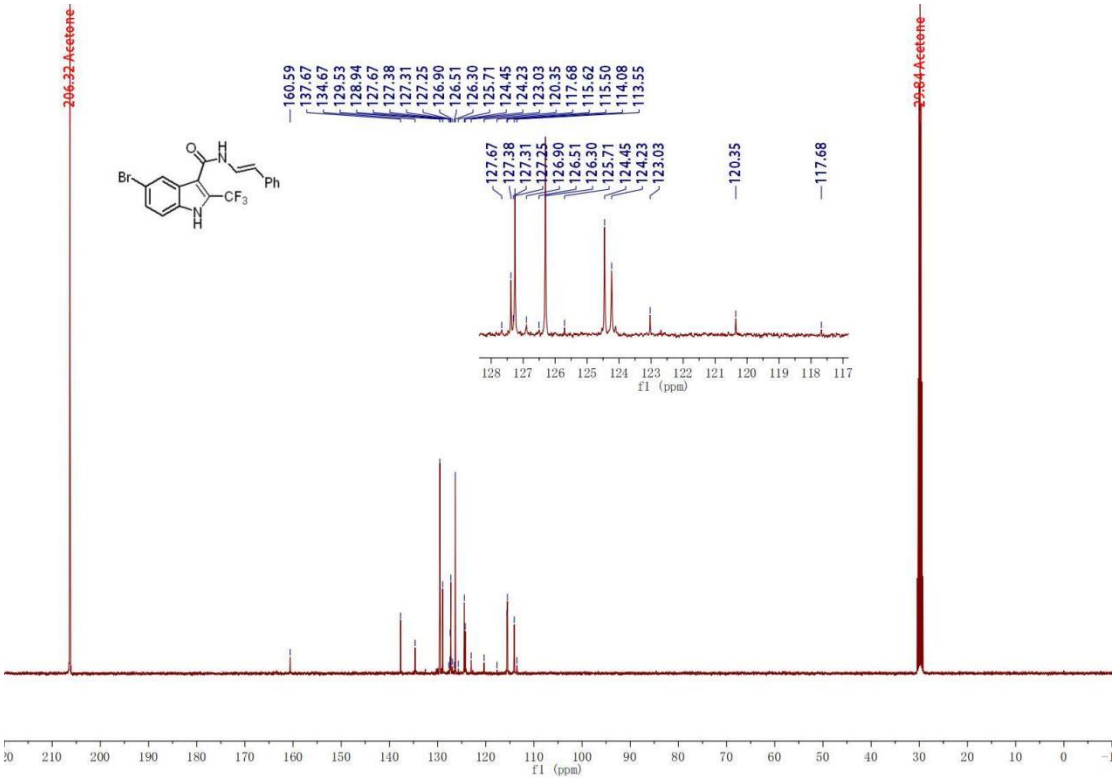
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3da



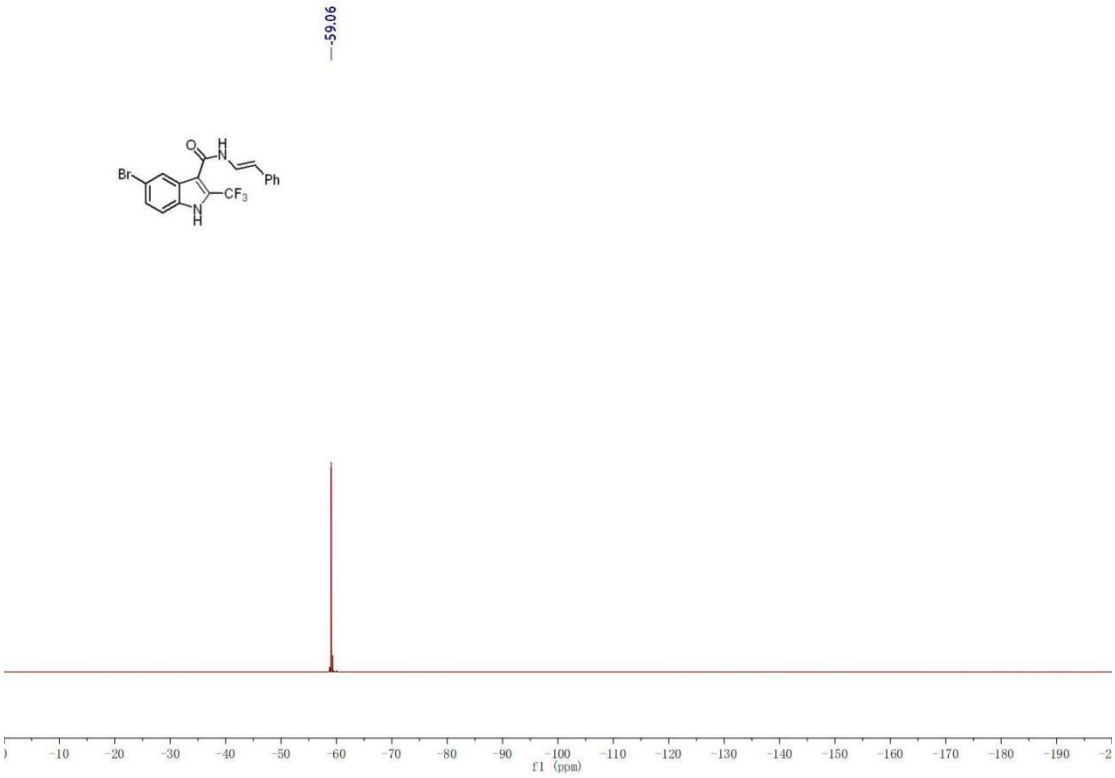
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ea



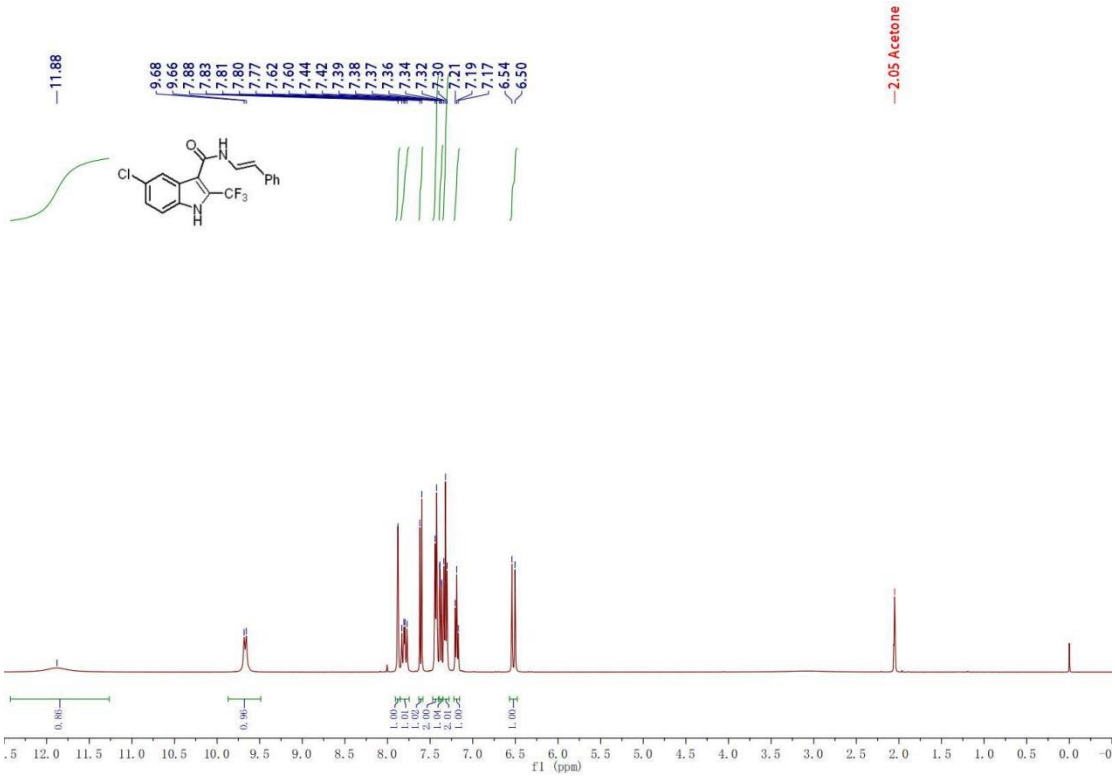
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ea



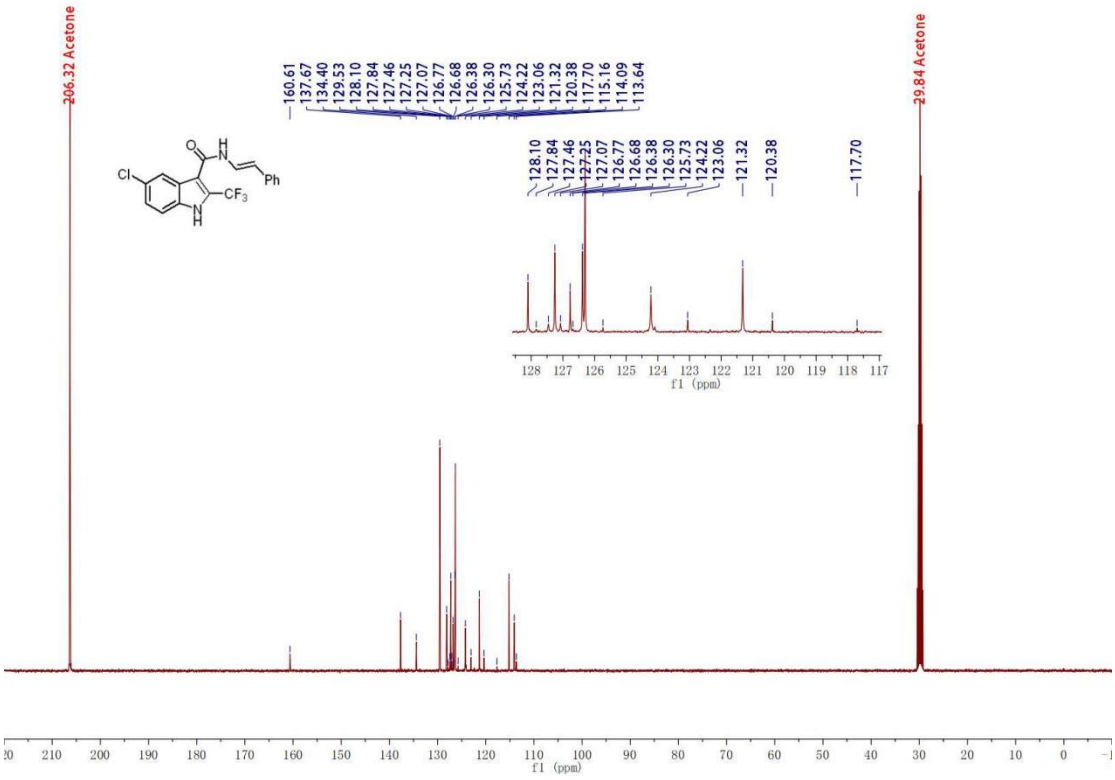
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ea



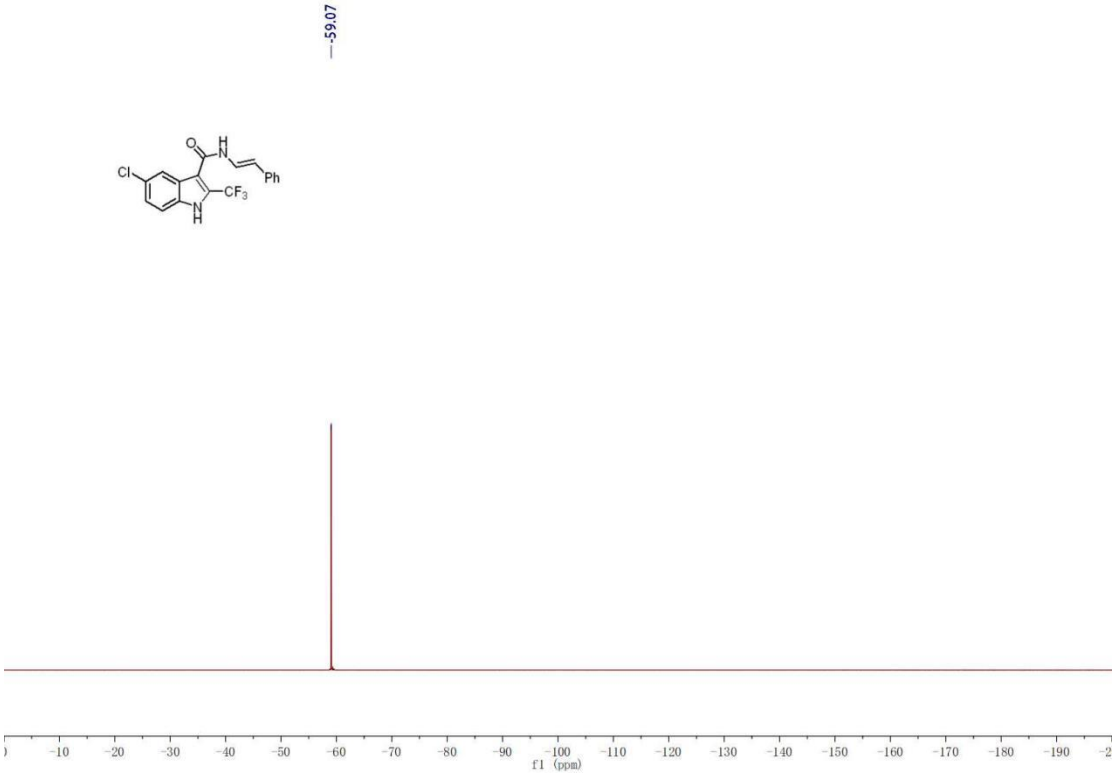
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3fa



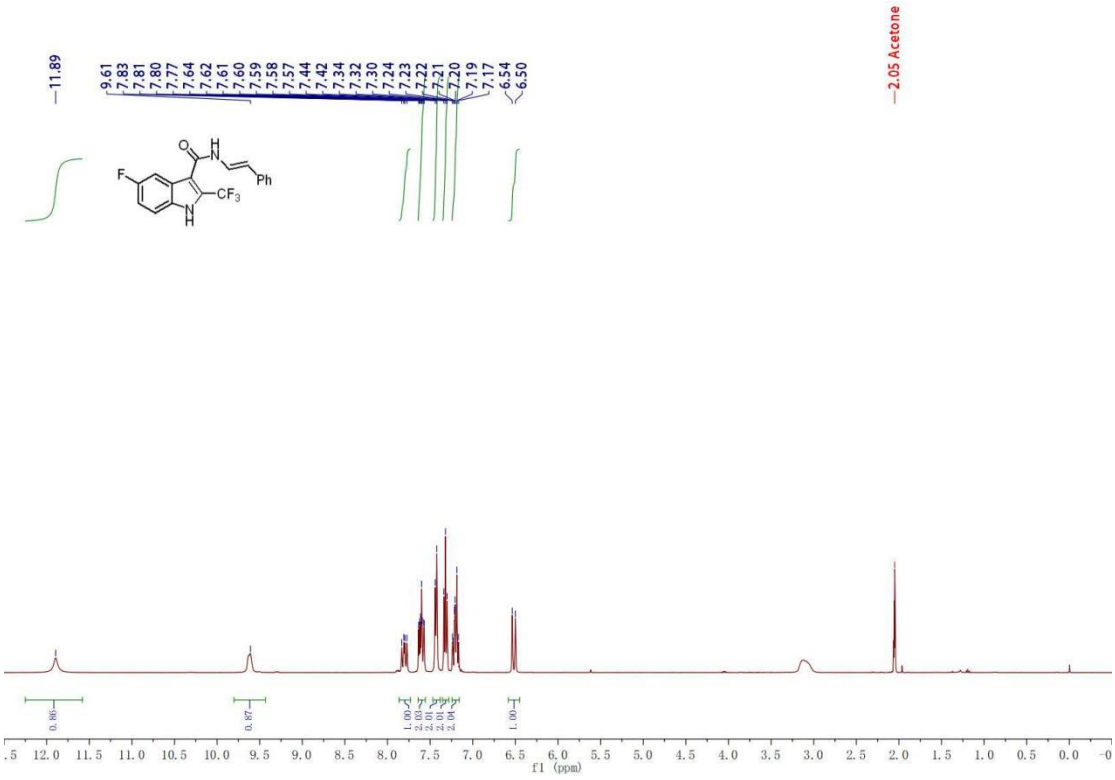
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3fa



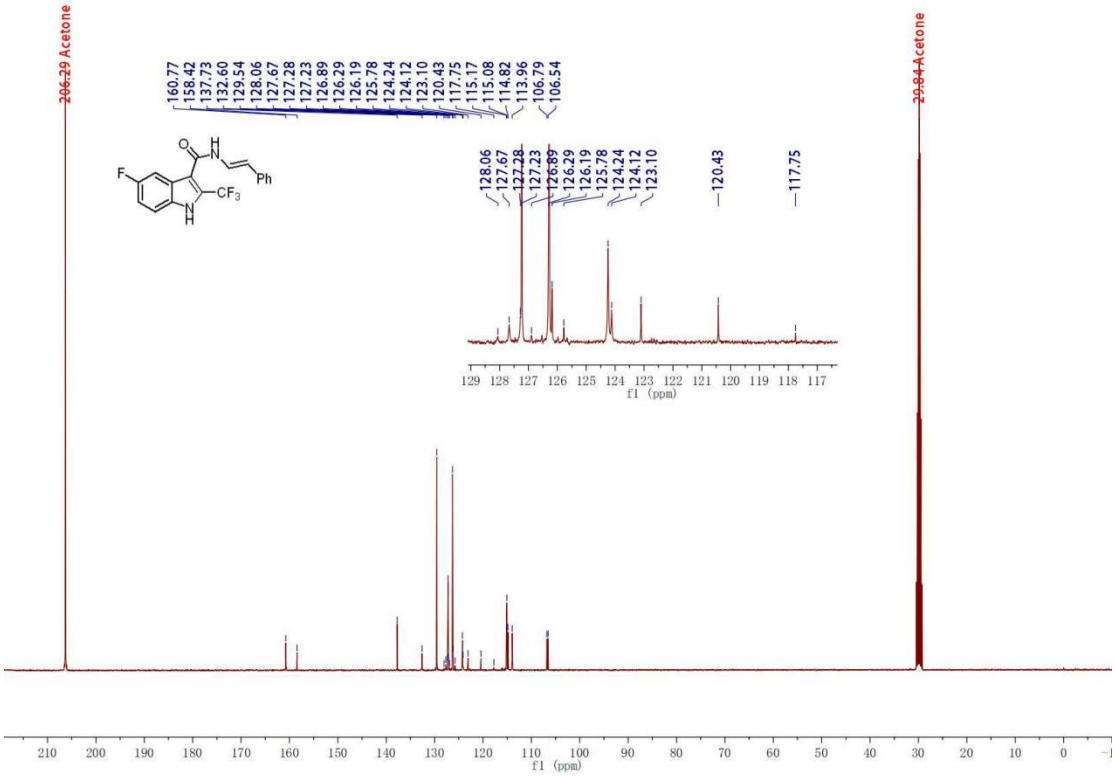
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3fa



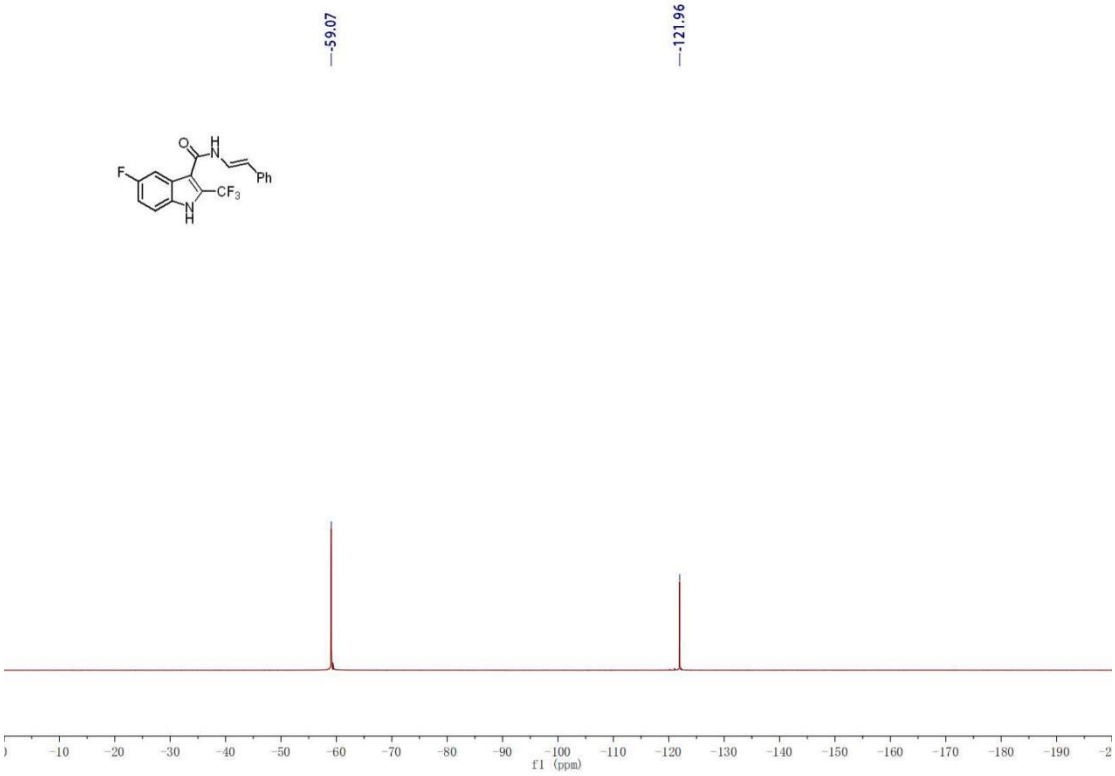
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ga



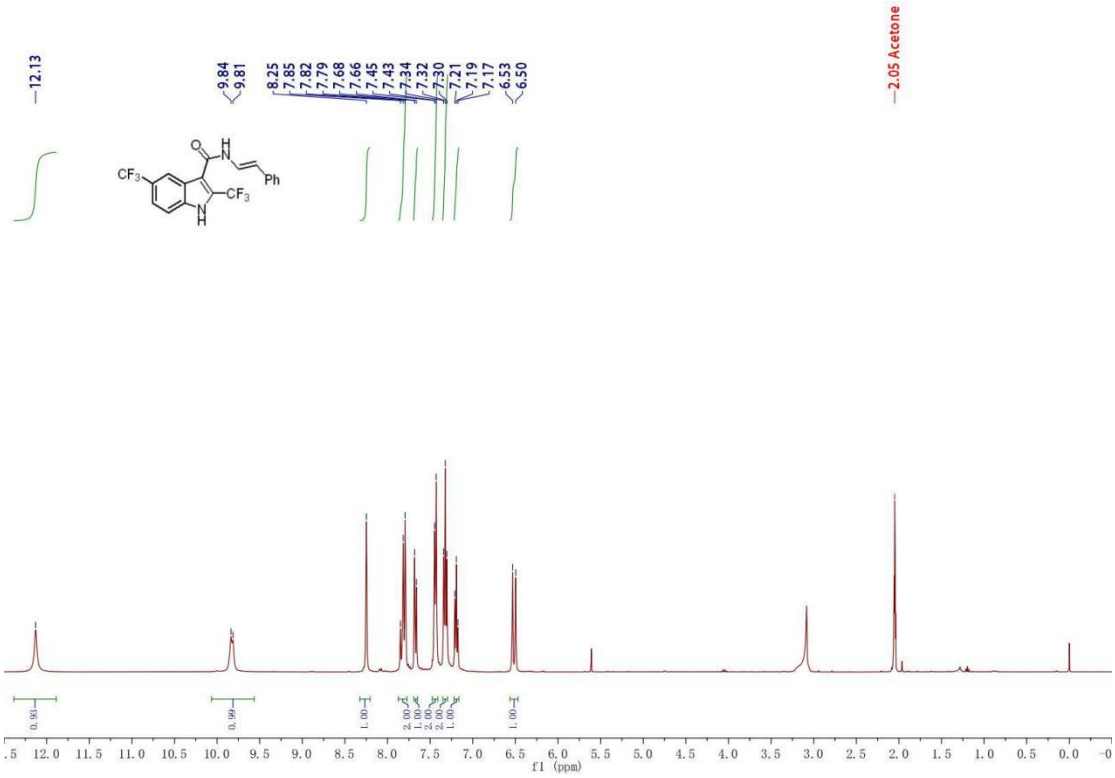
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ga



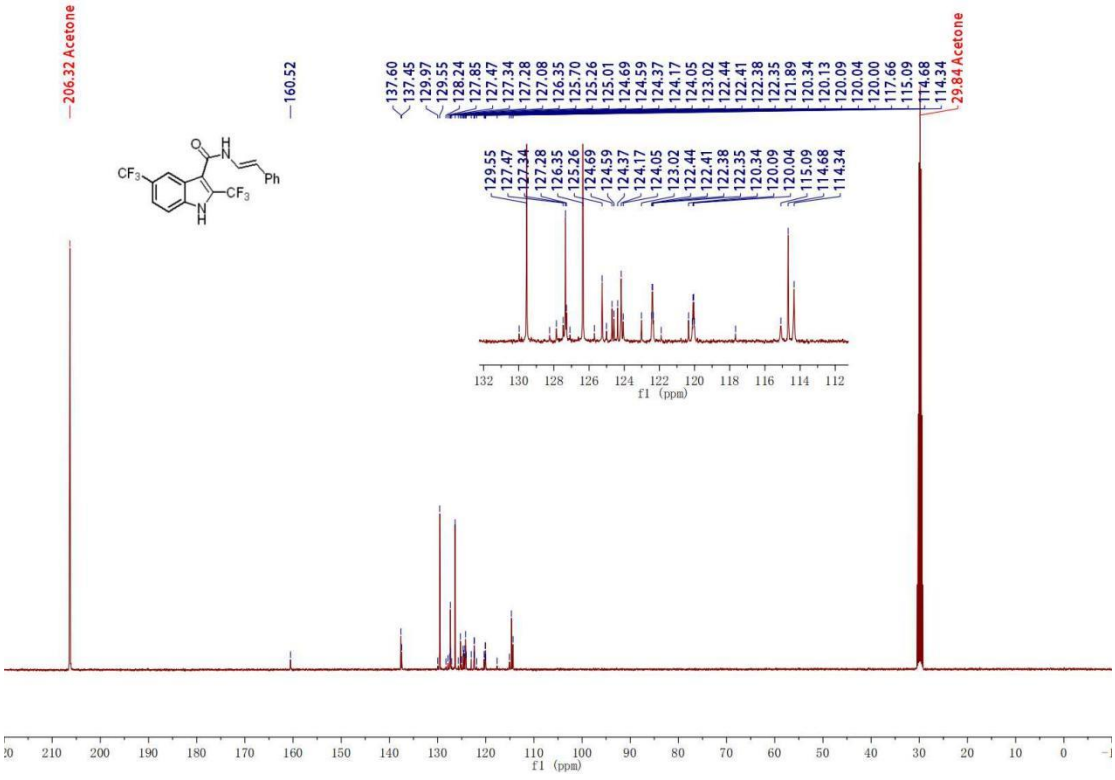
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ga



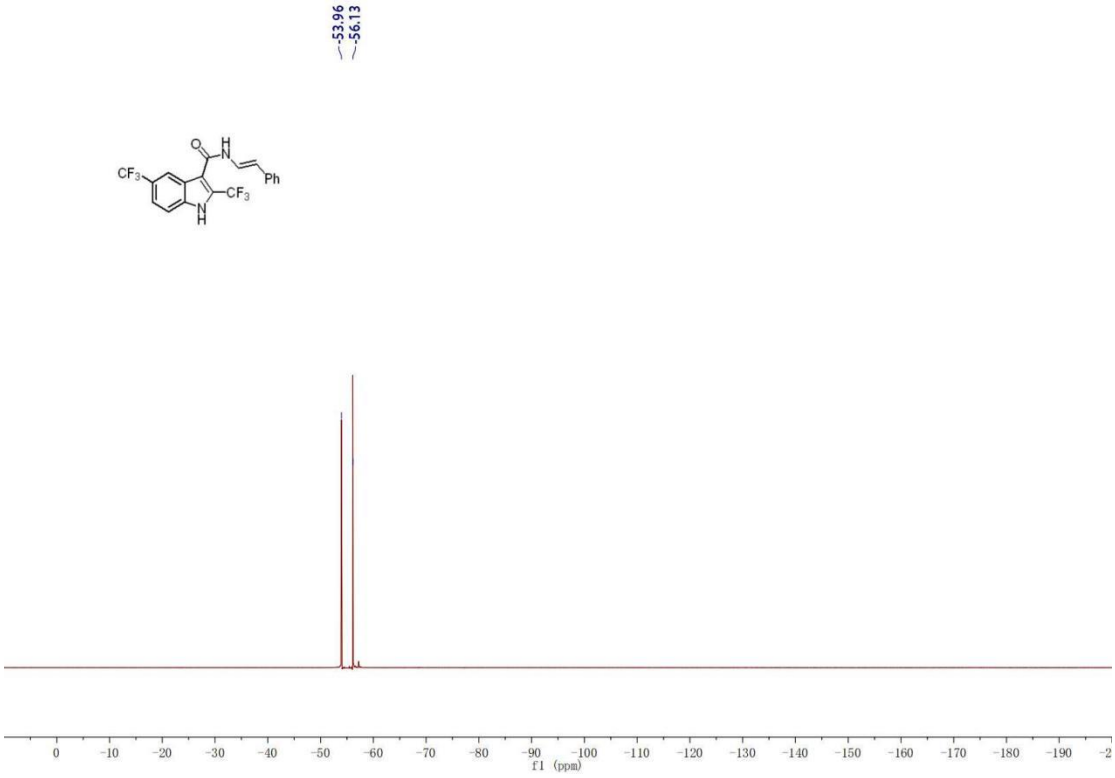
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ha



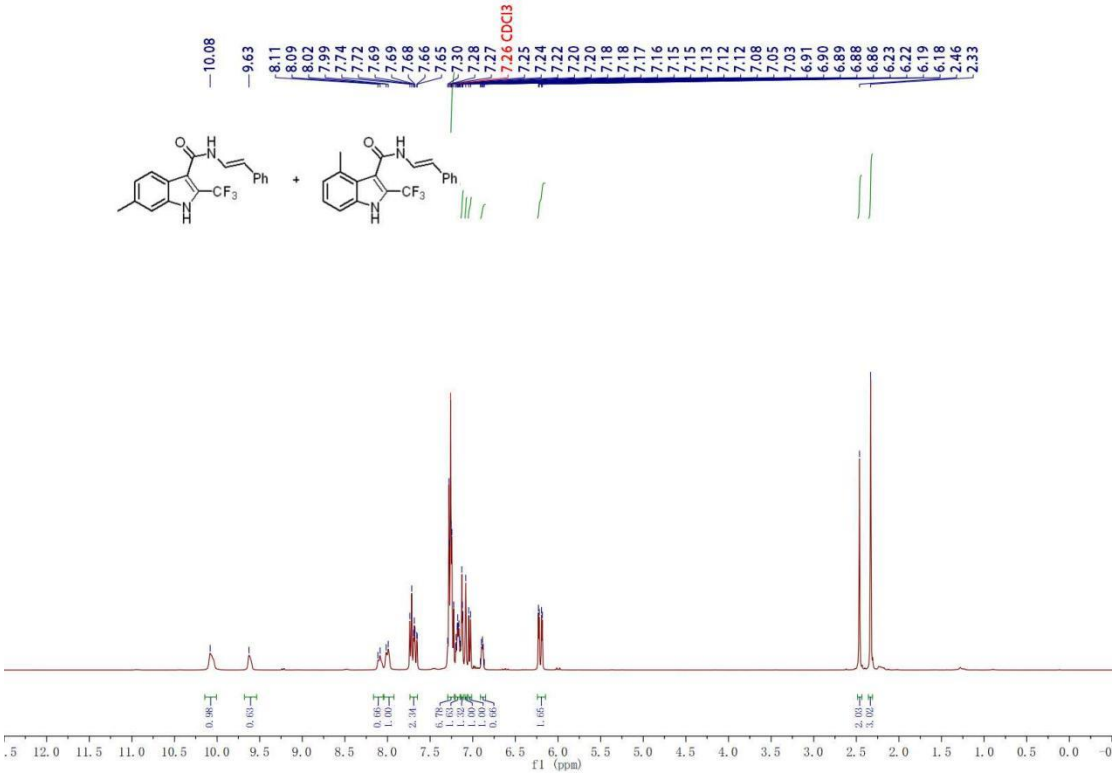
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ha



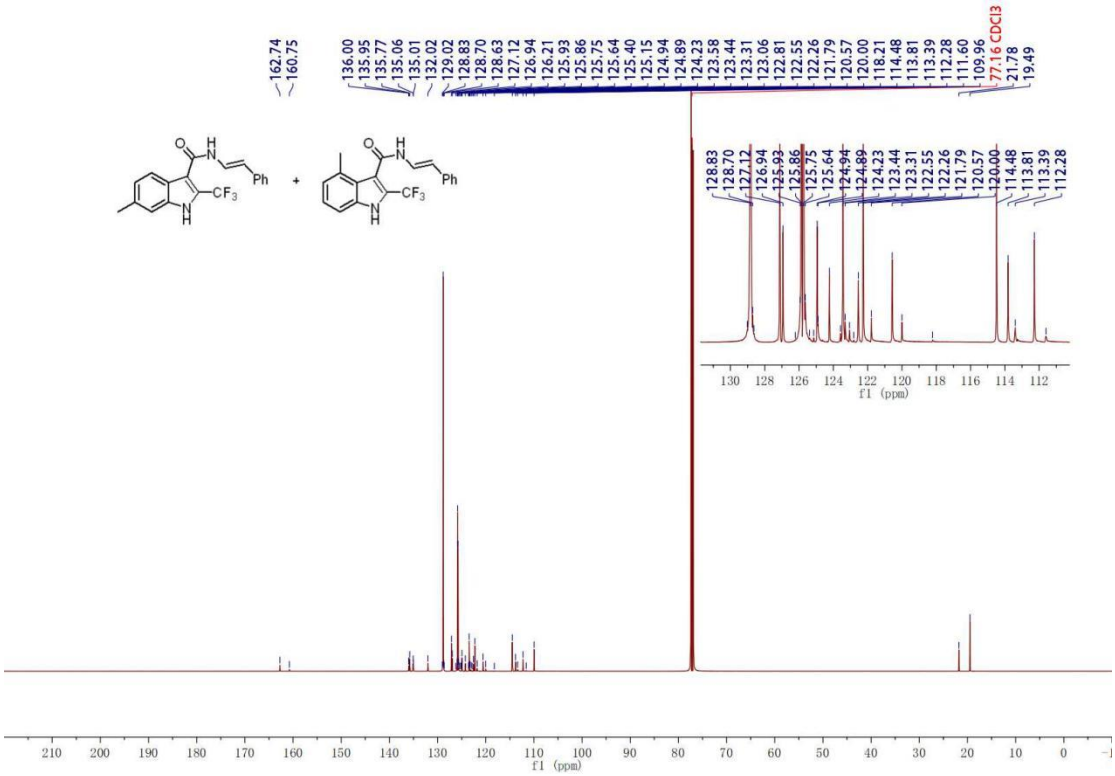
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ha



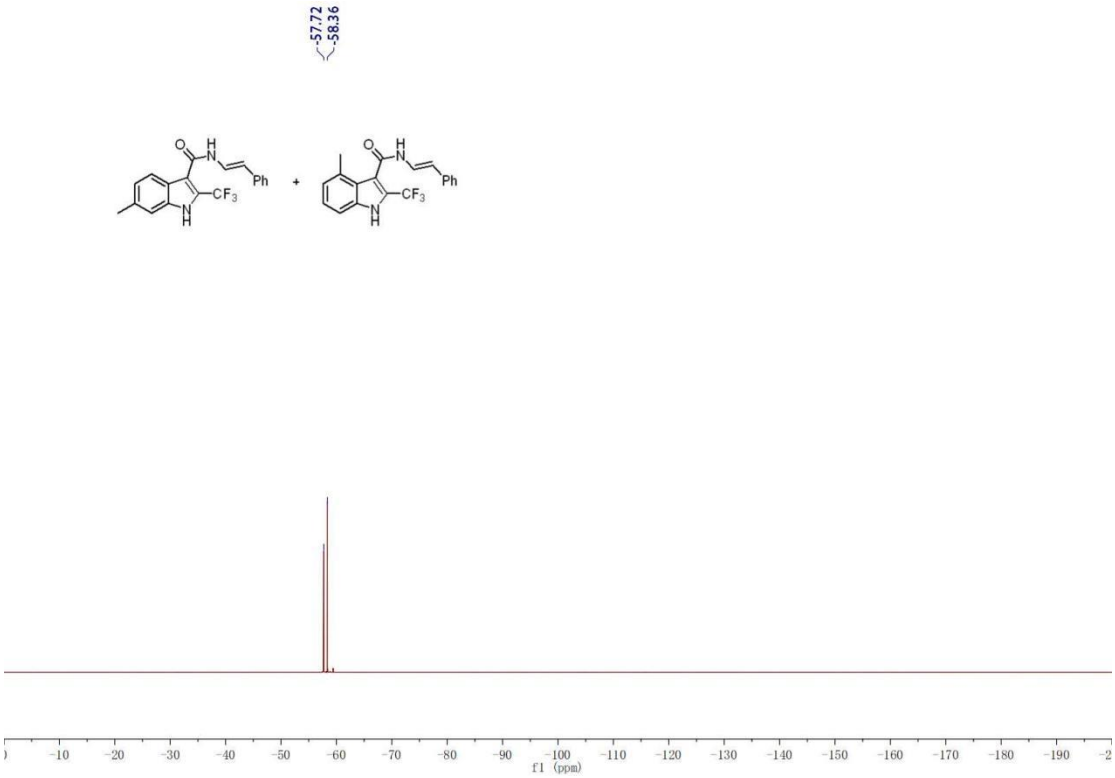
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ia



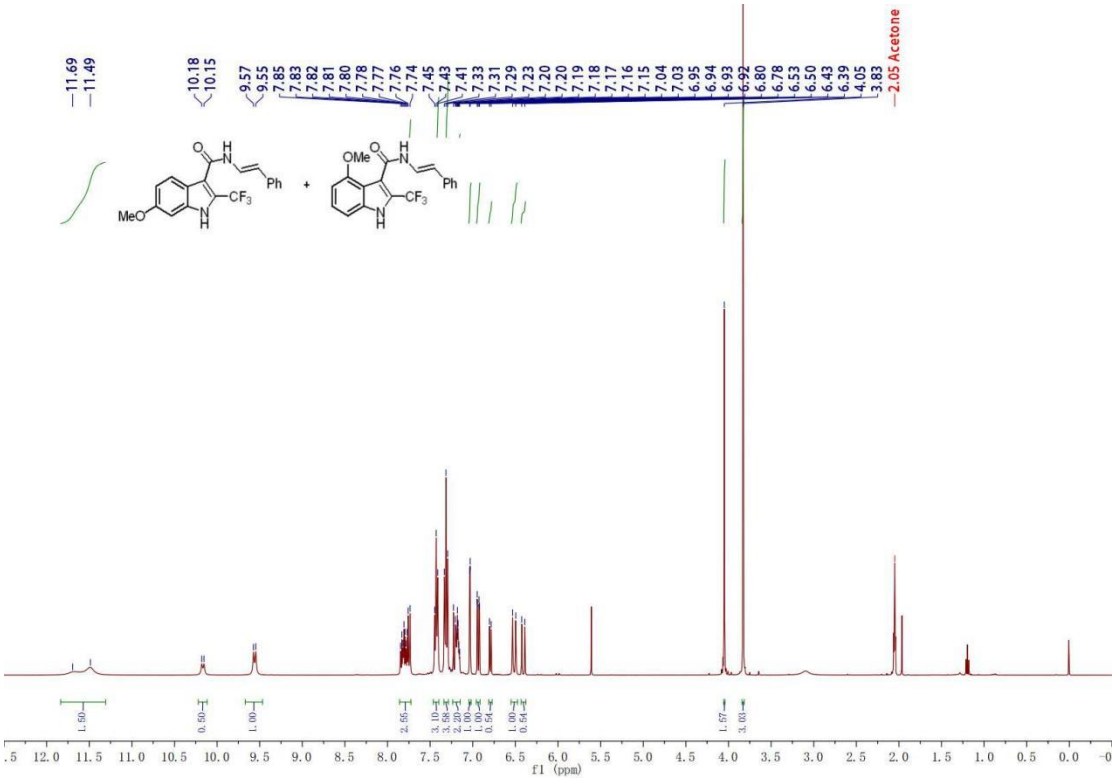
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ia



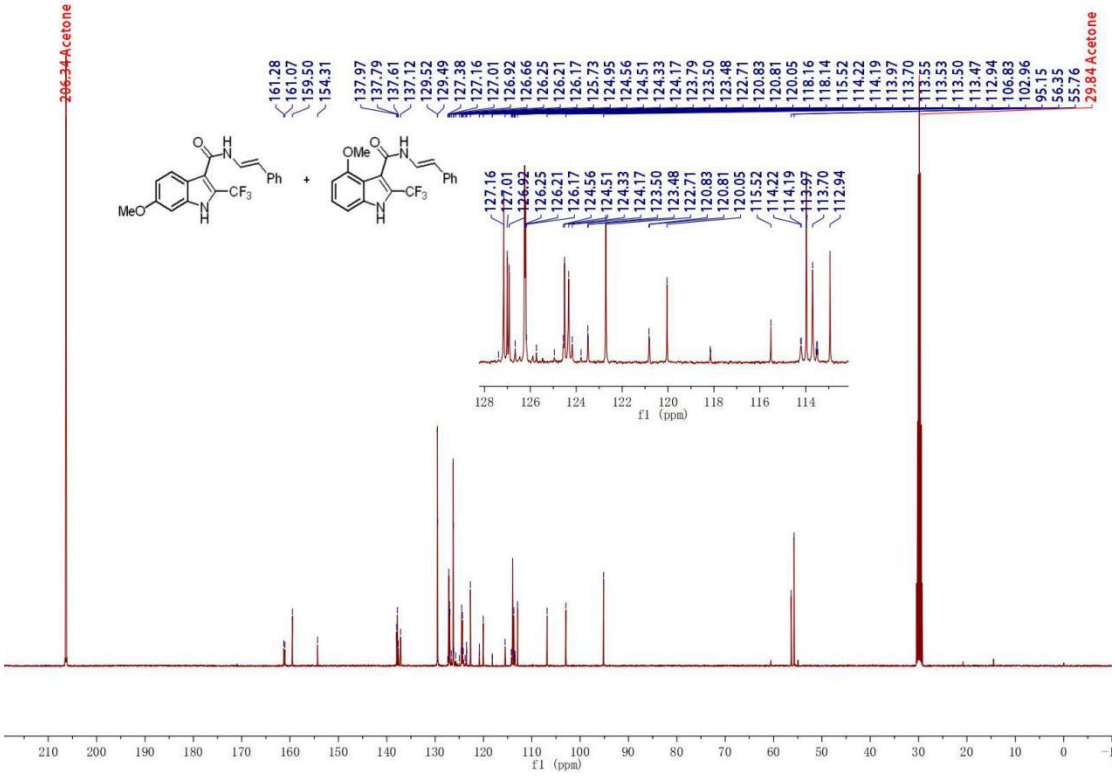
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ia



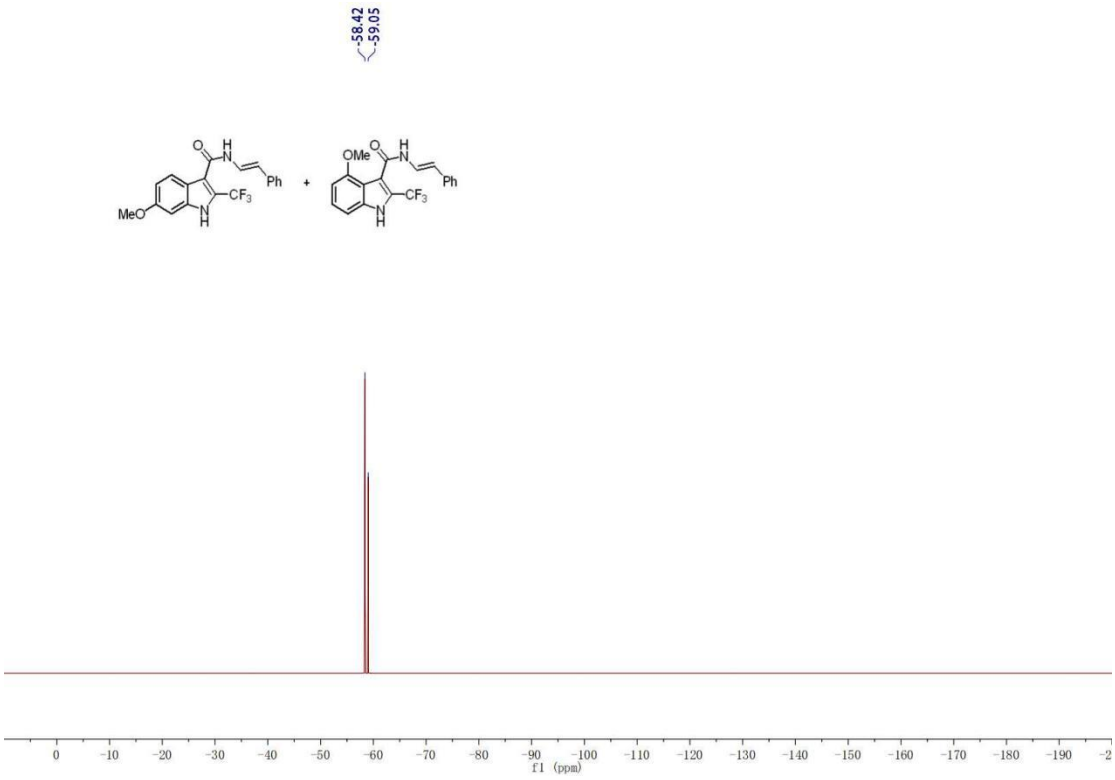
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ja



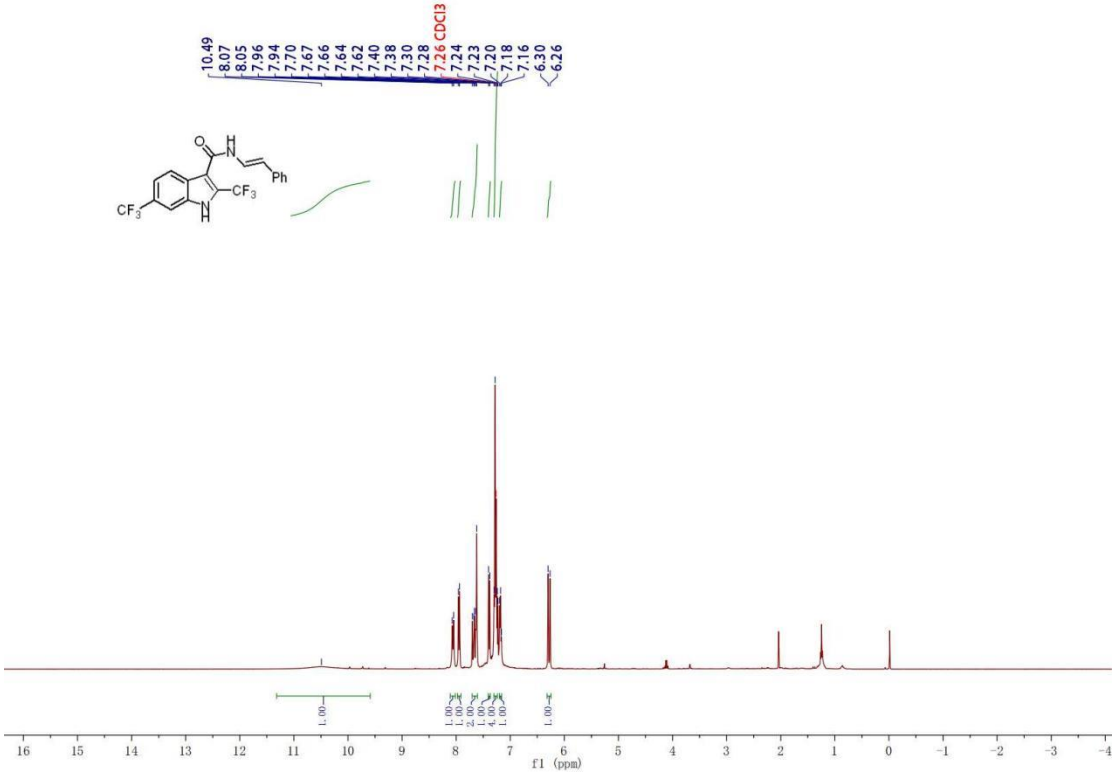
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ja



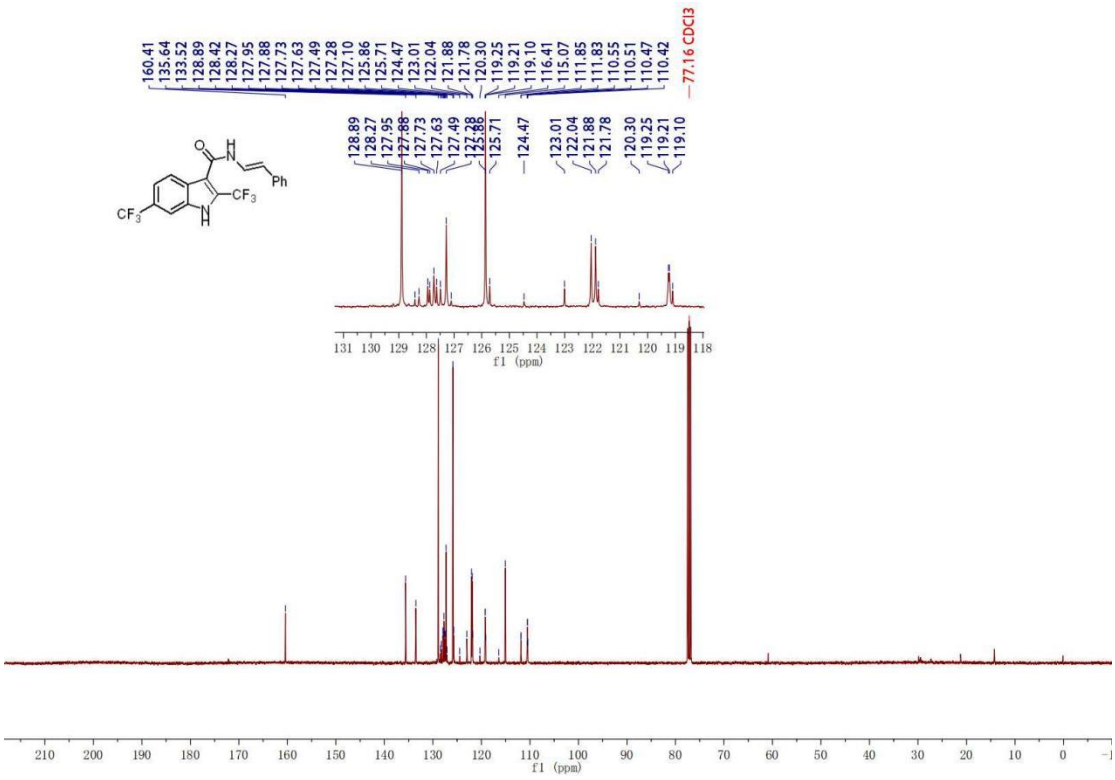
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ja



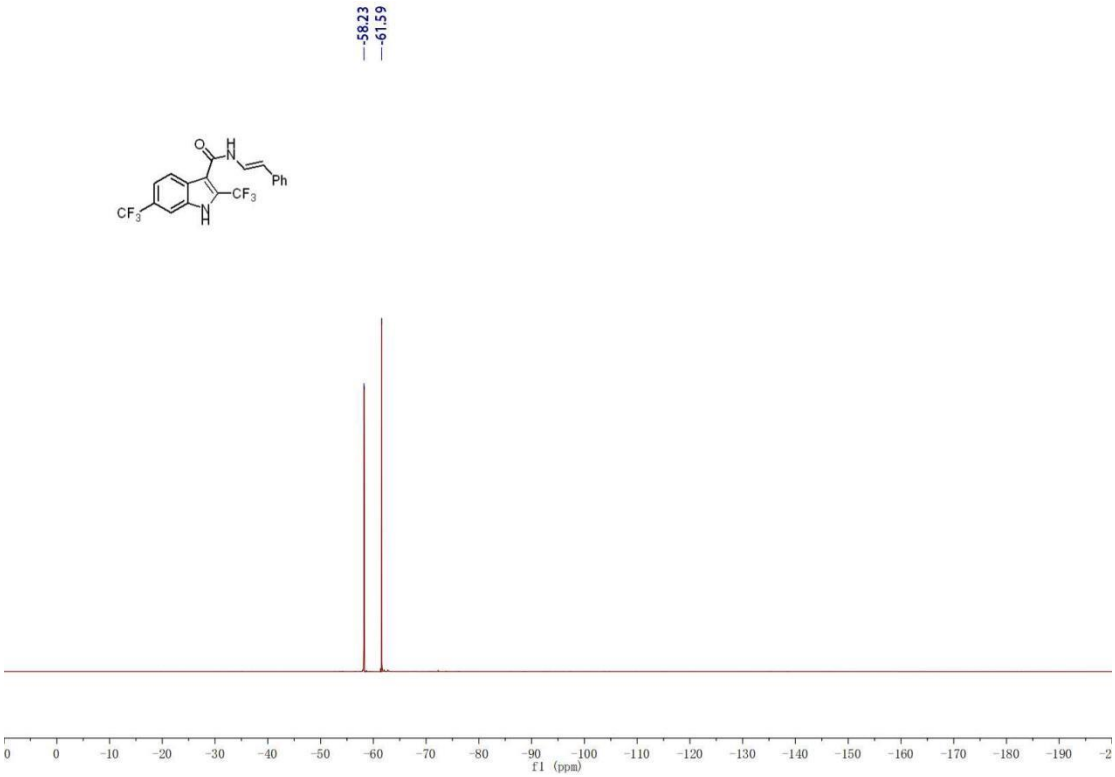
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ka



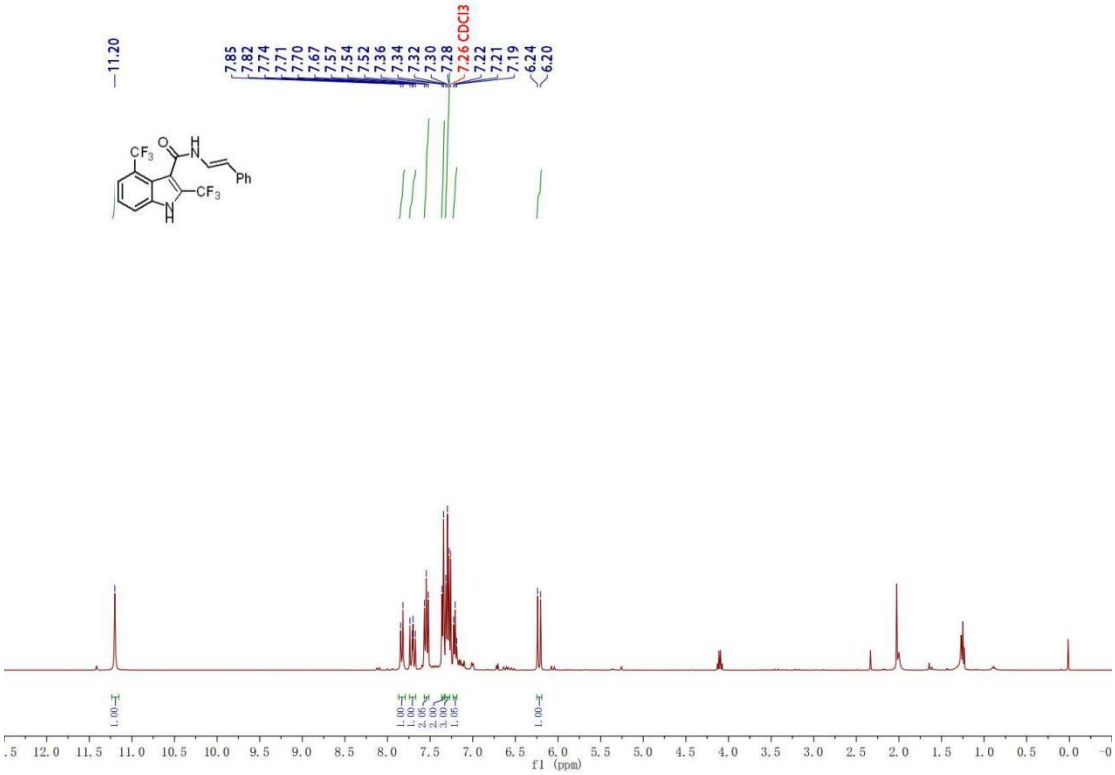
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ka



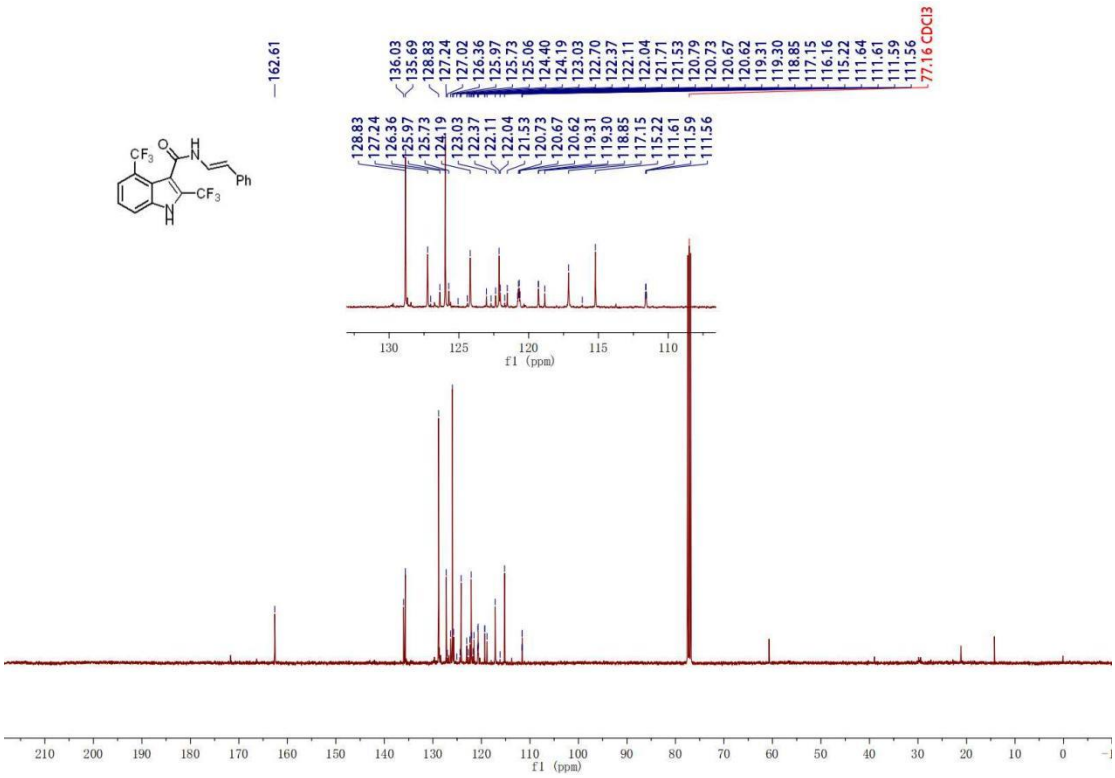
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ka



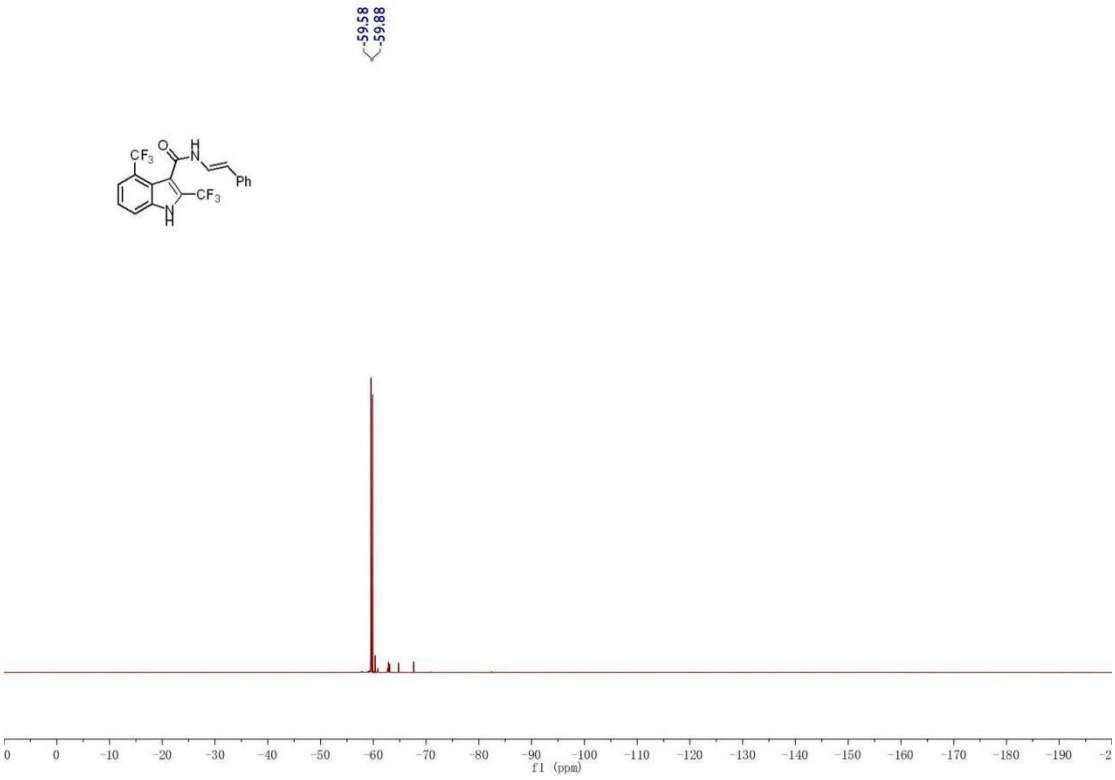
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ka'



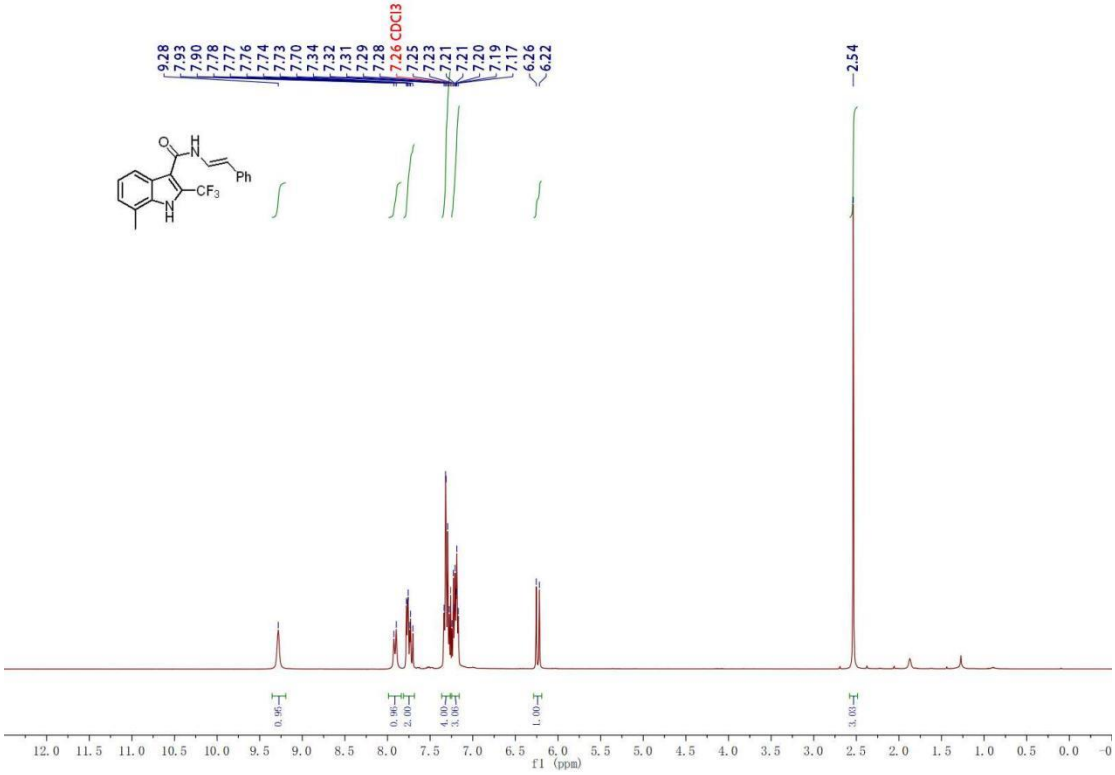
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ka'



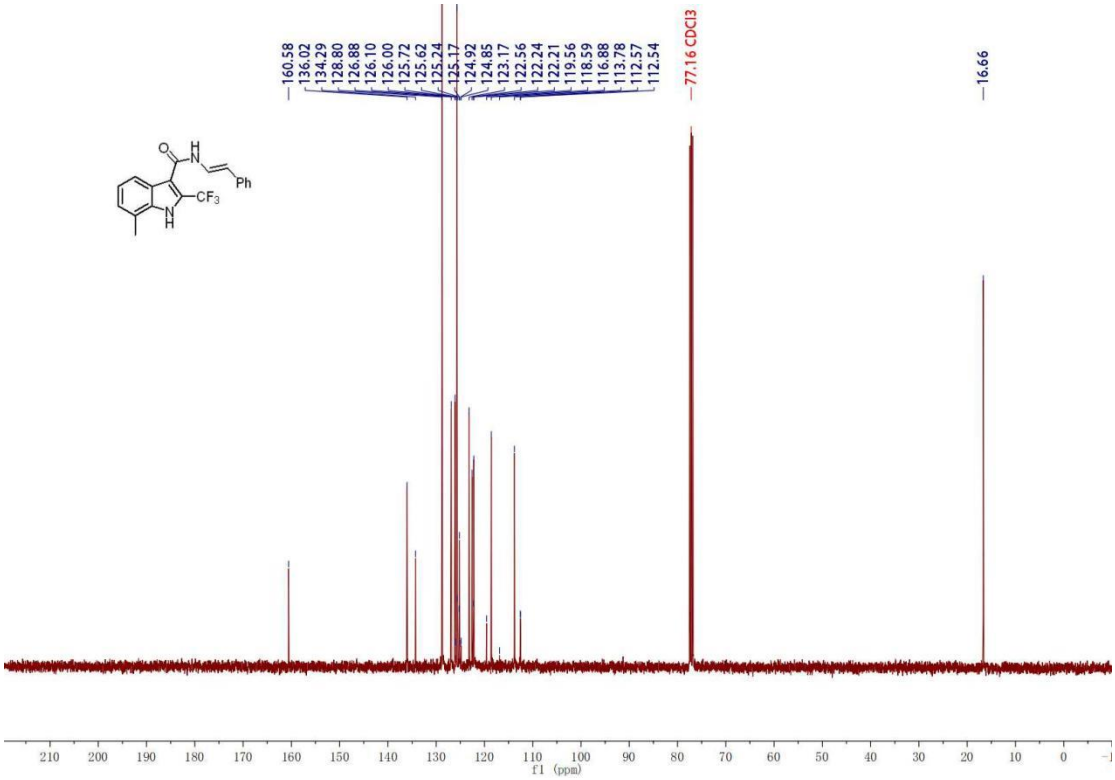
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ka'



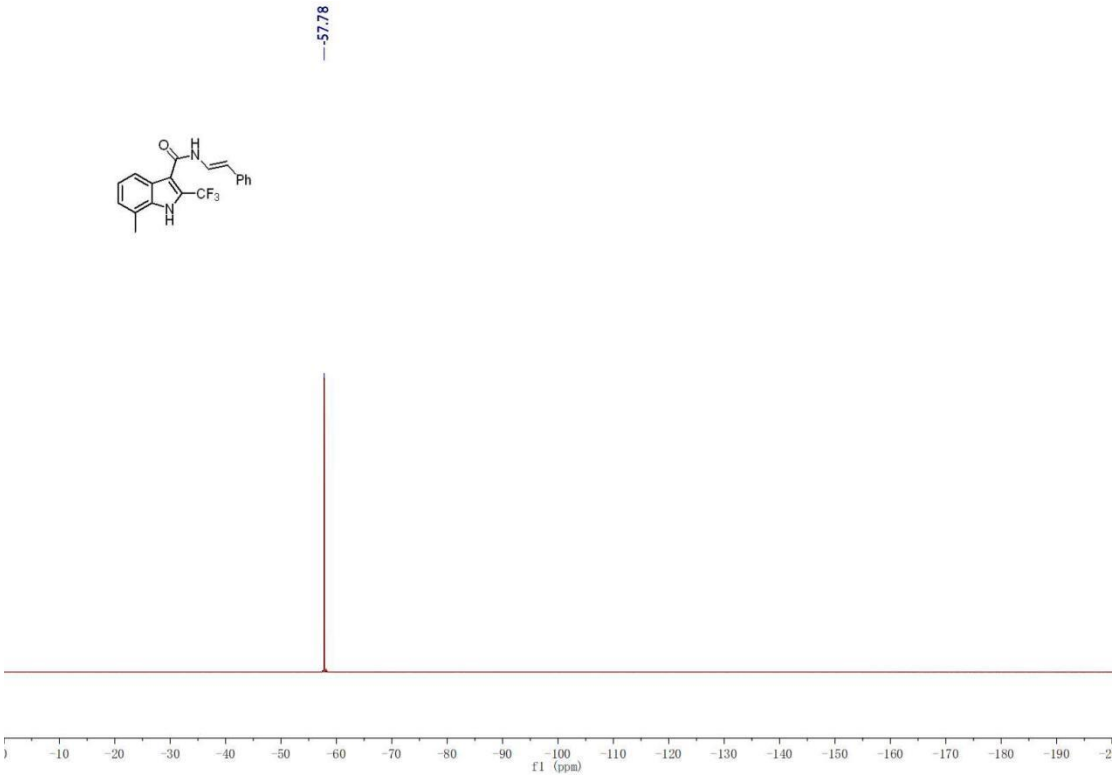
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3la



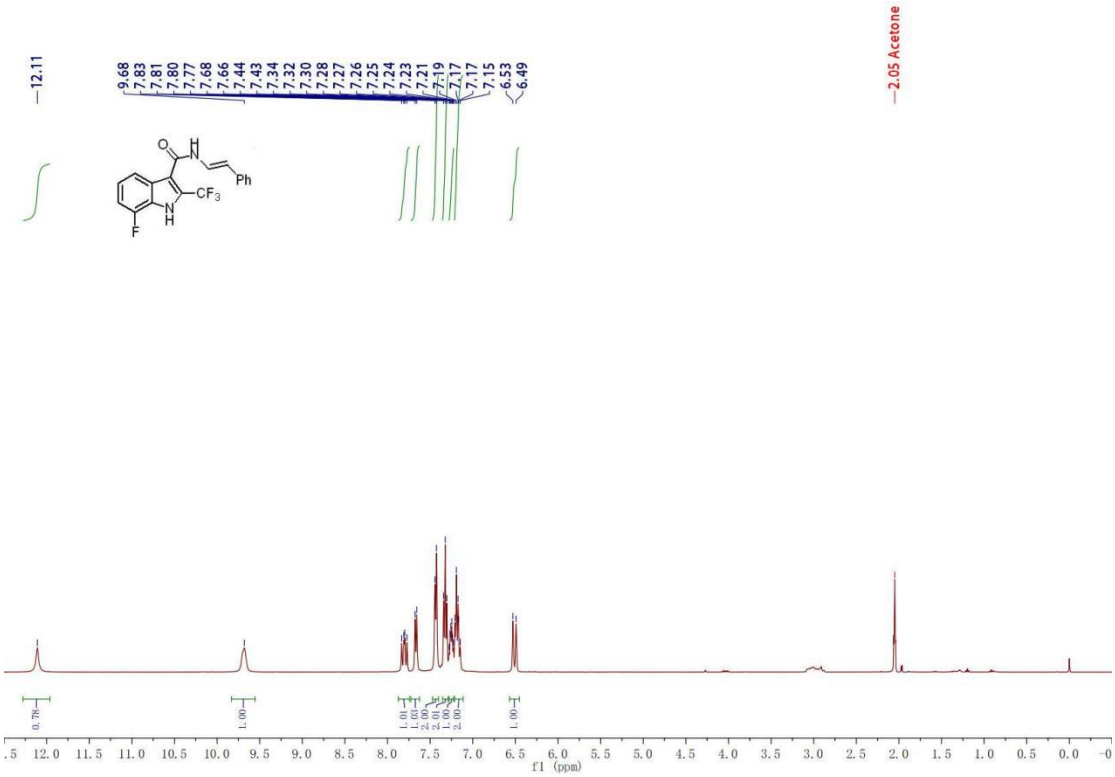
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3la



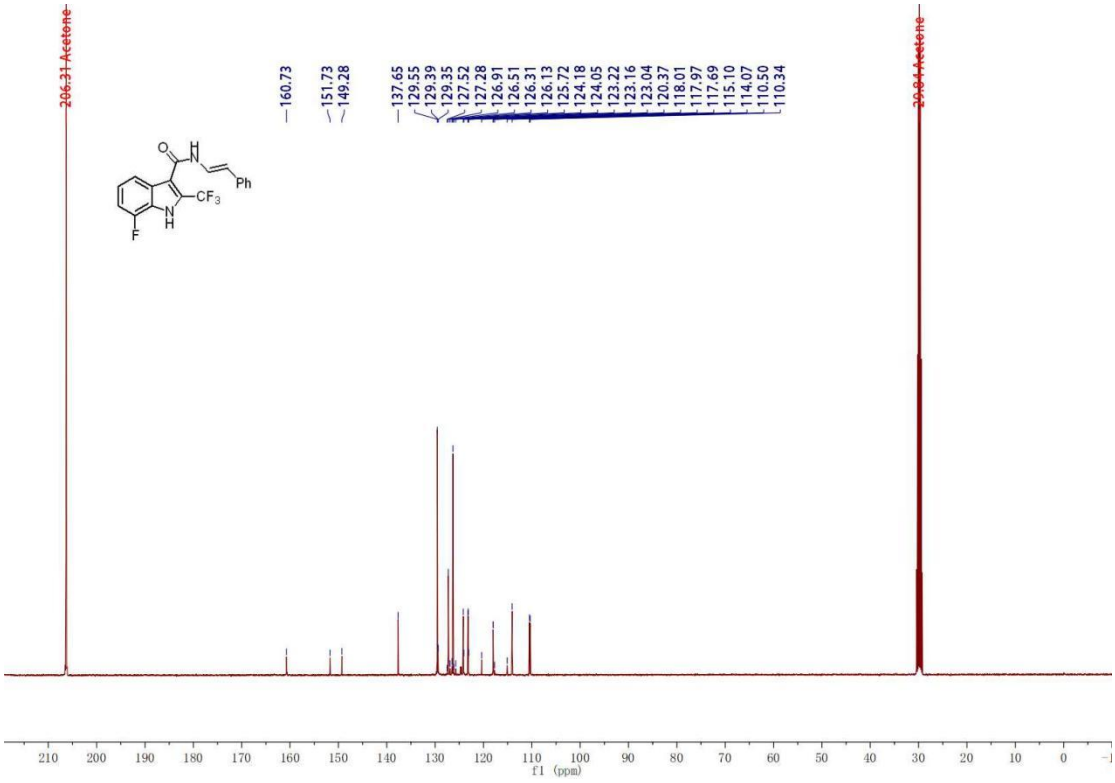
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3la



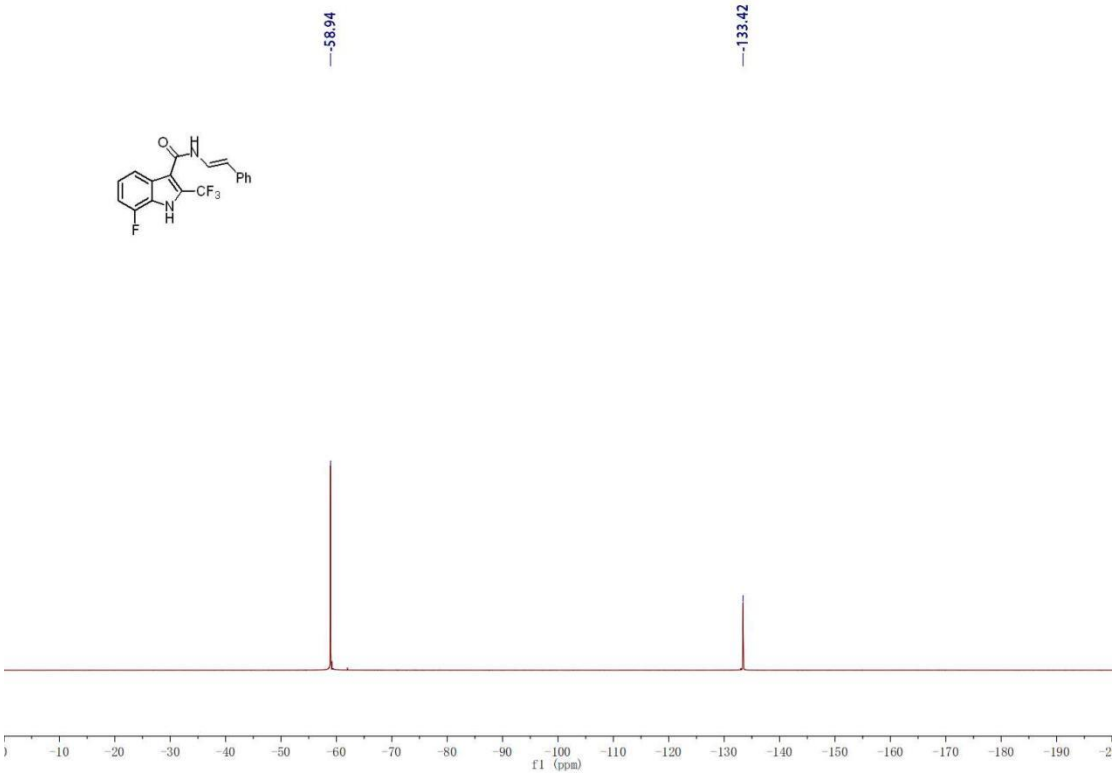
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ma



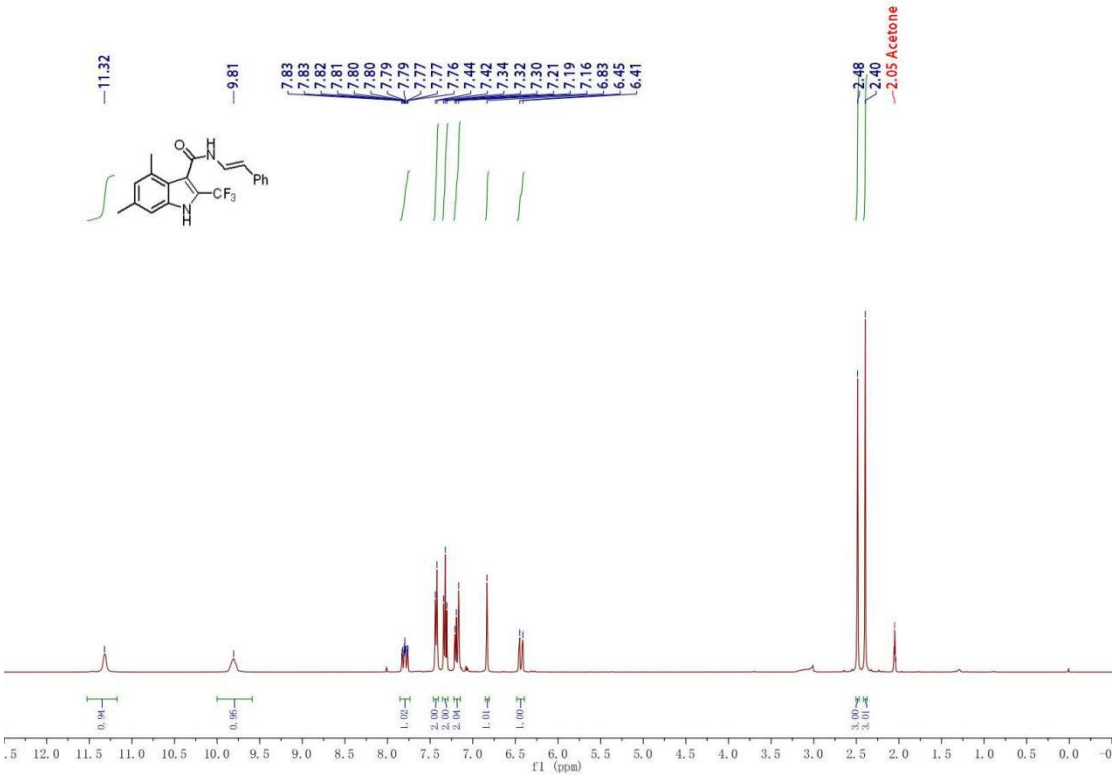
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ma



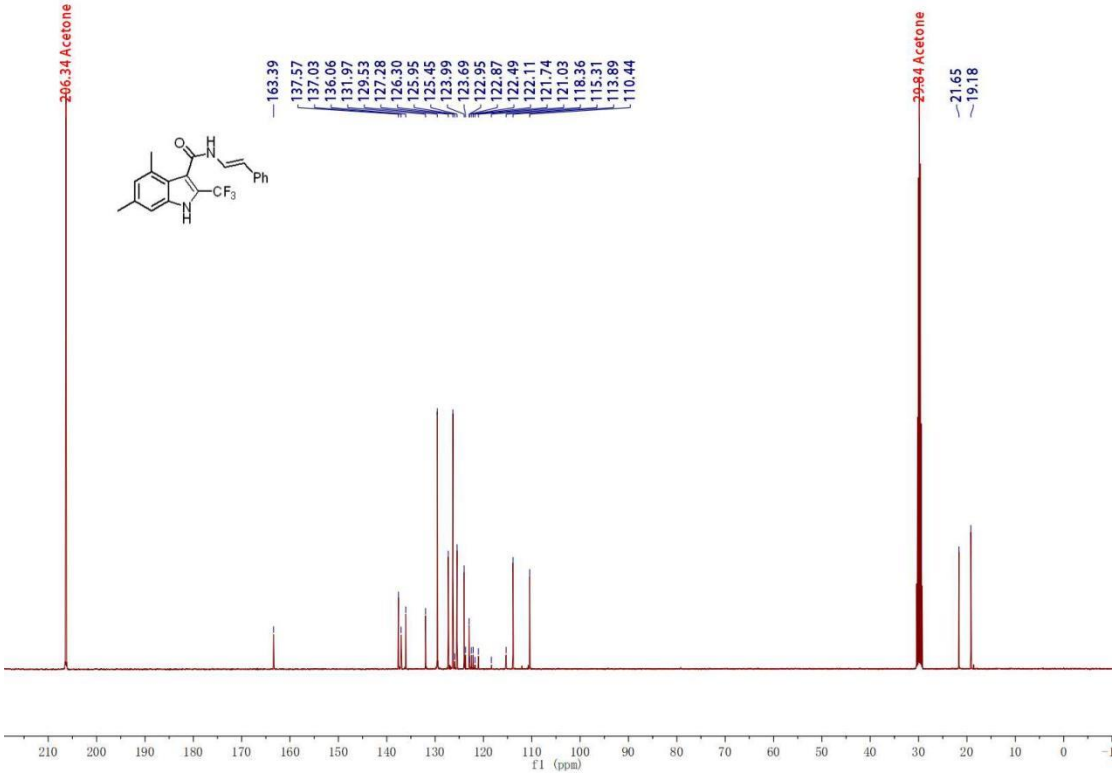
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ma



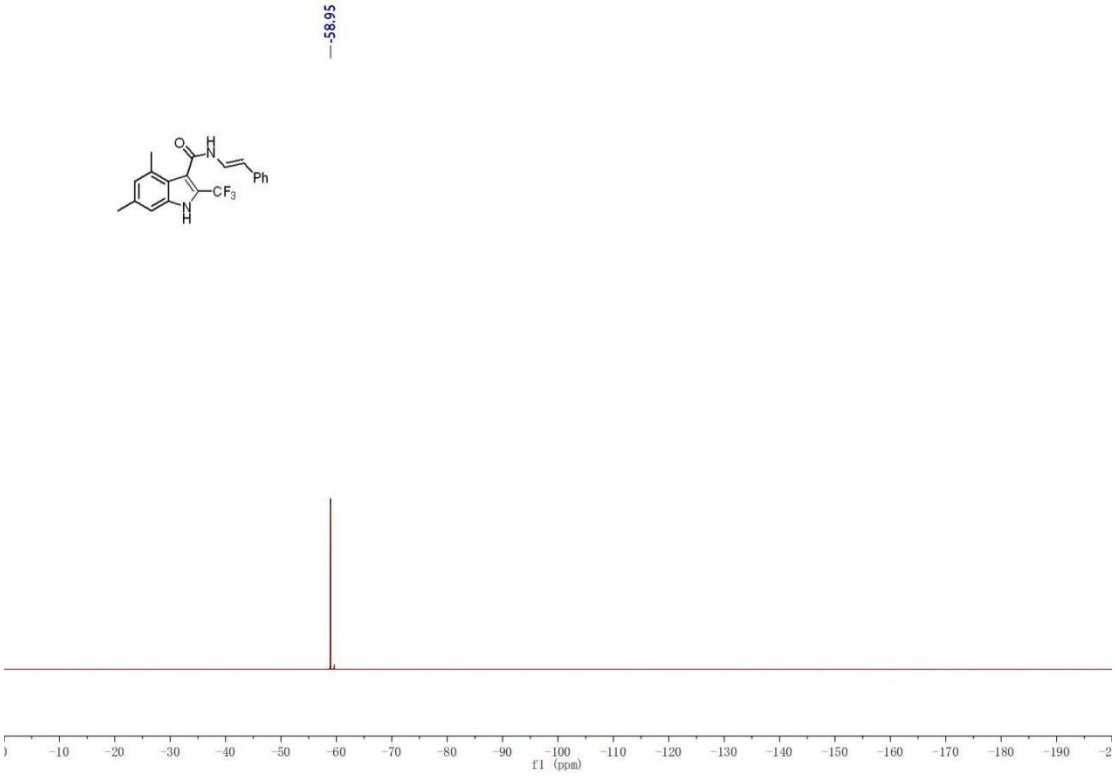
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3na



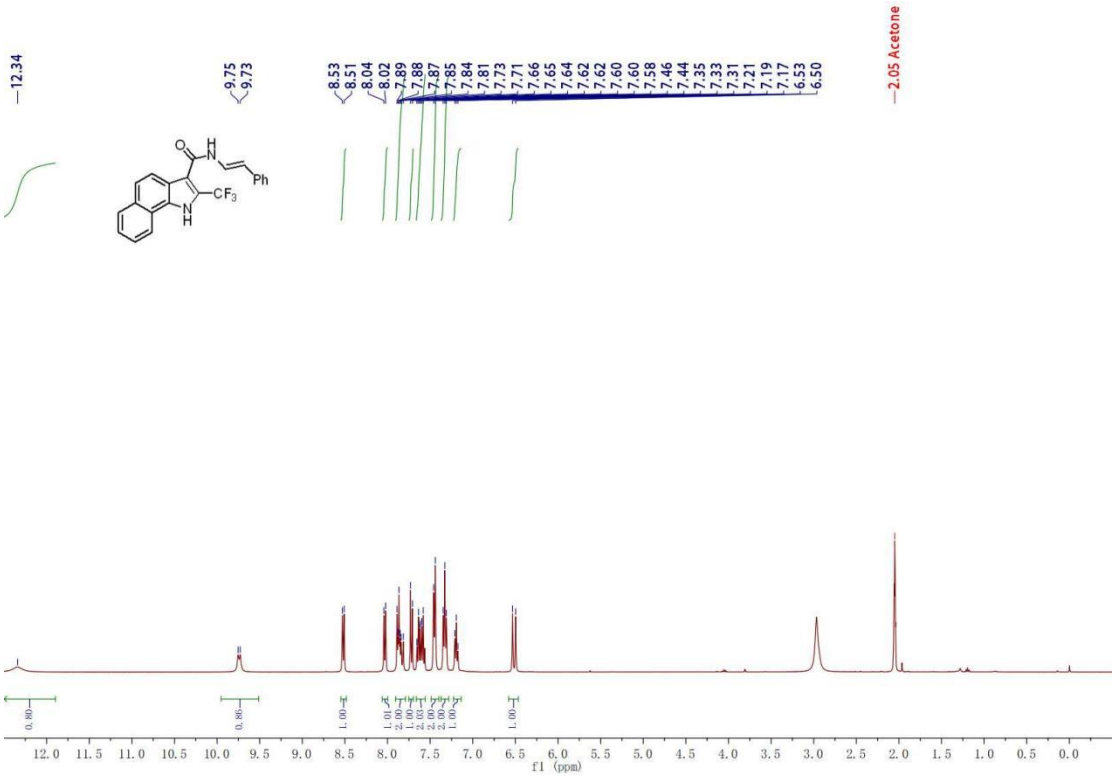
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3na



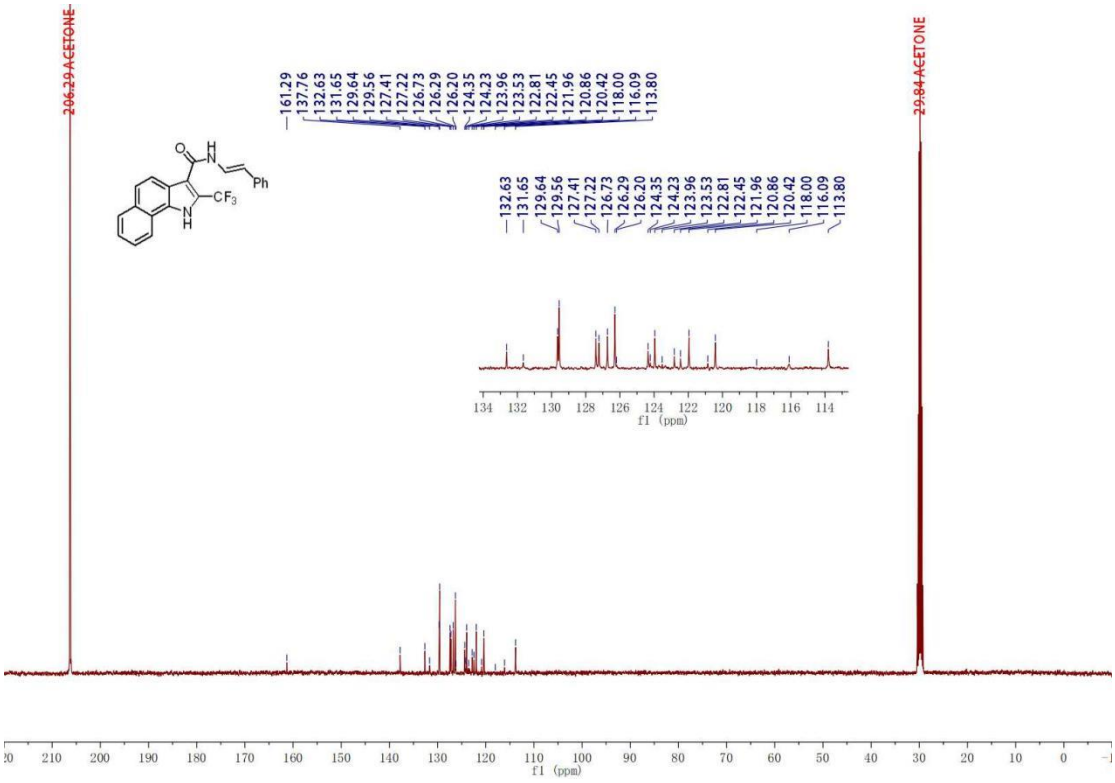
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3na



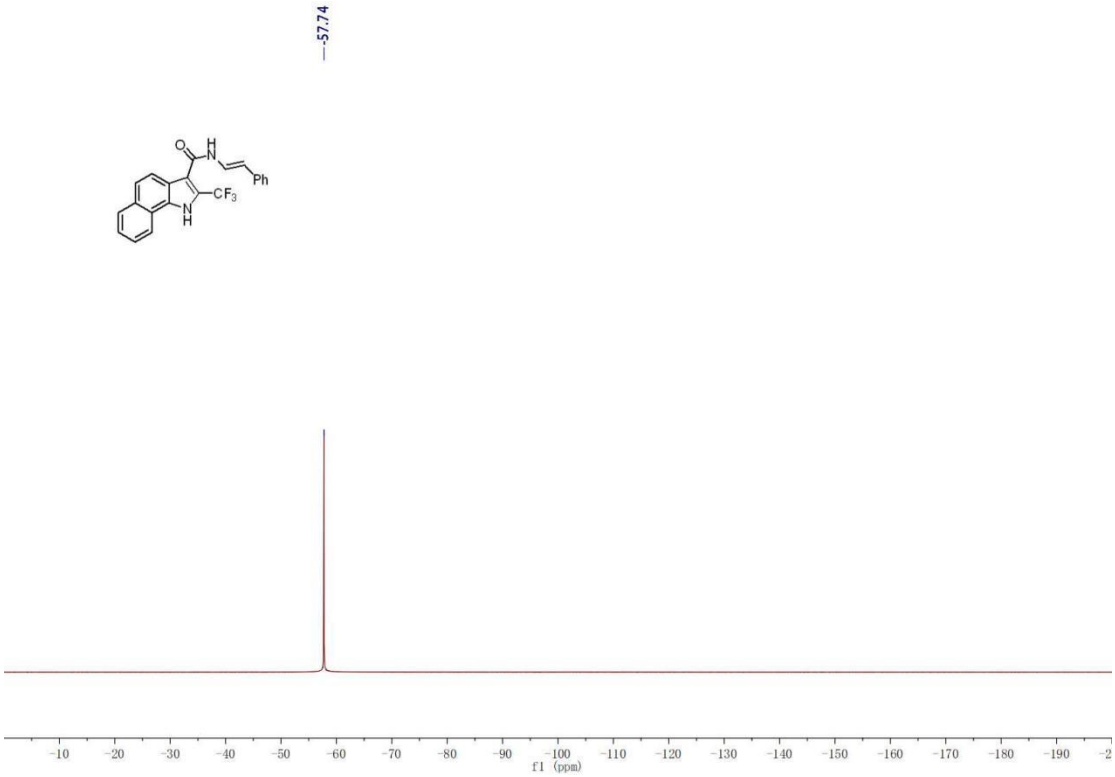
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3oa



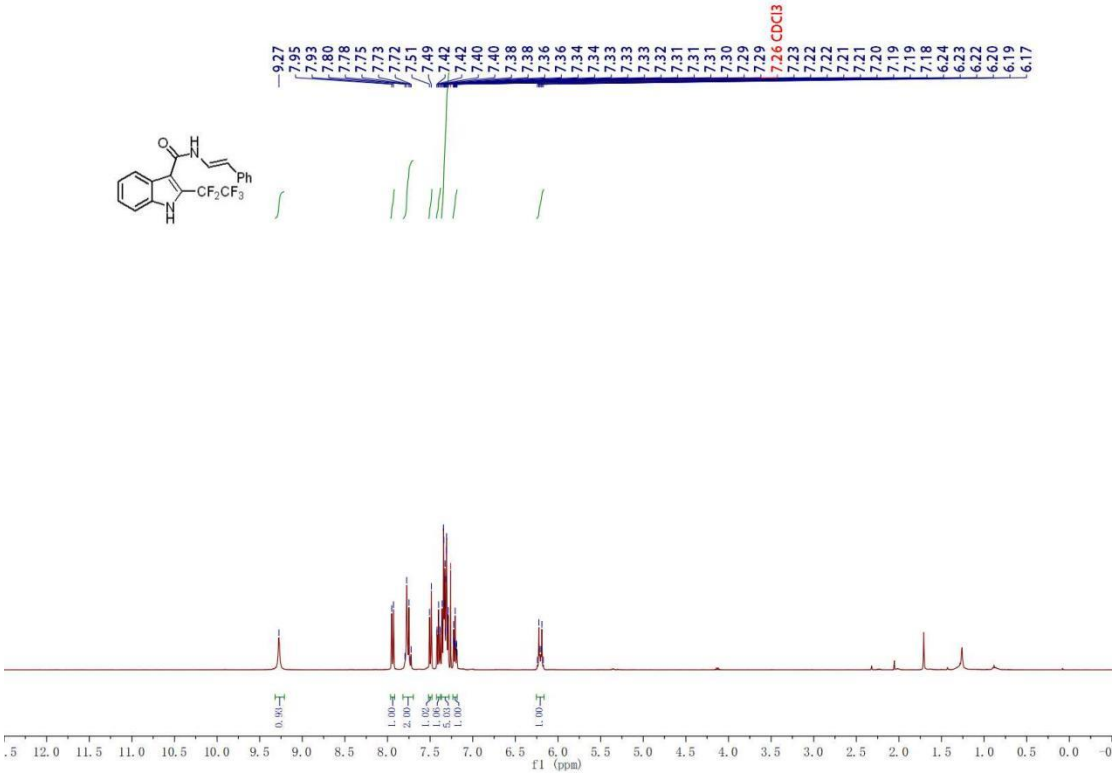
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3oa



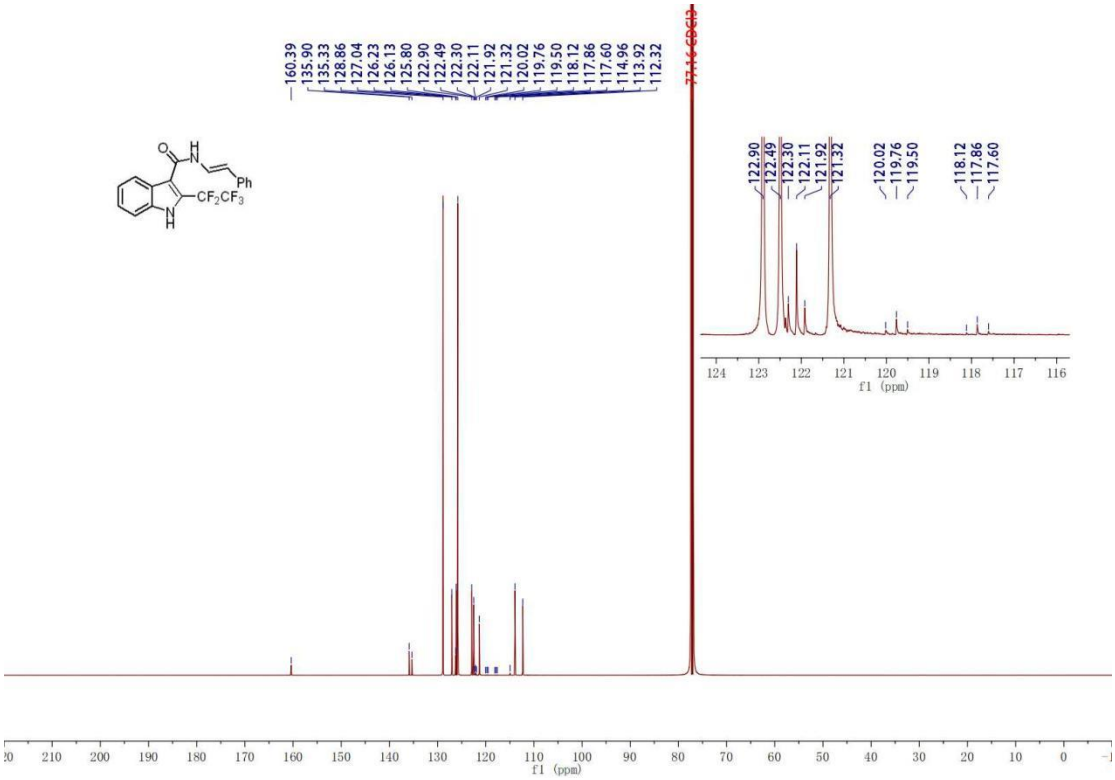
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3oa



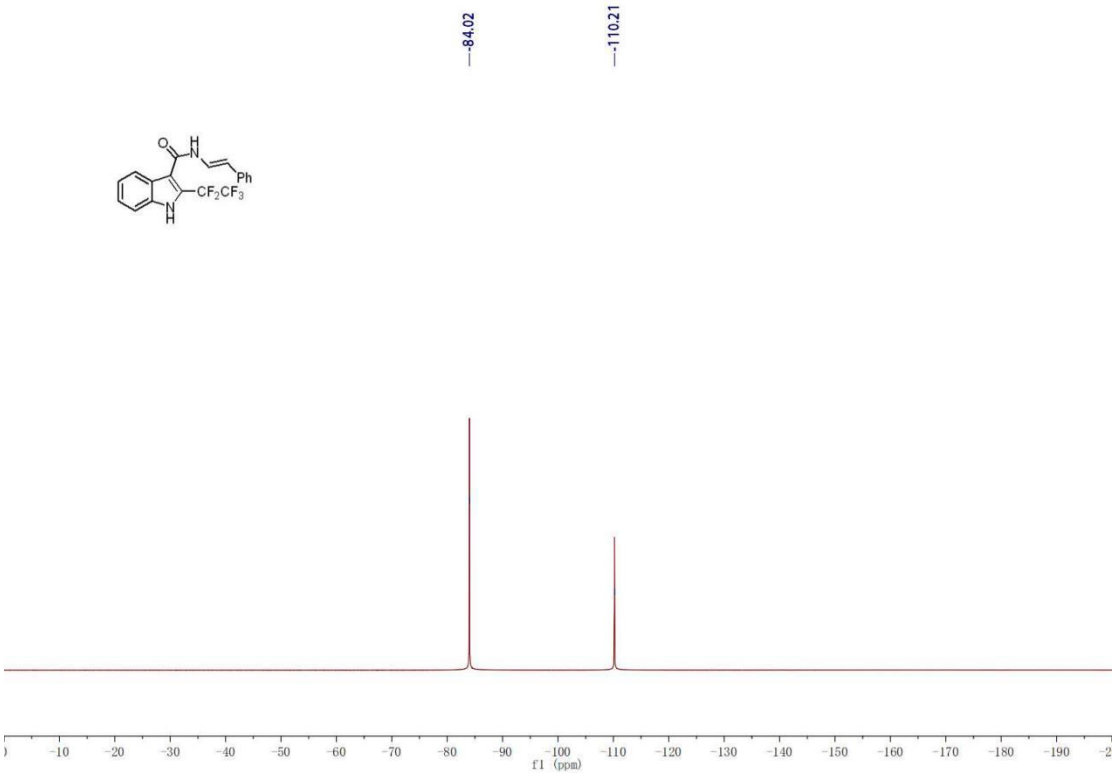
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3pa



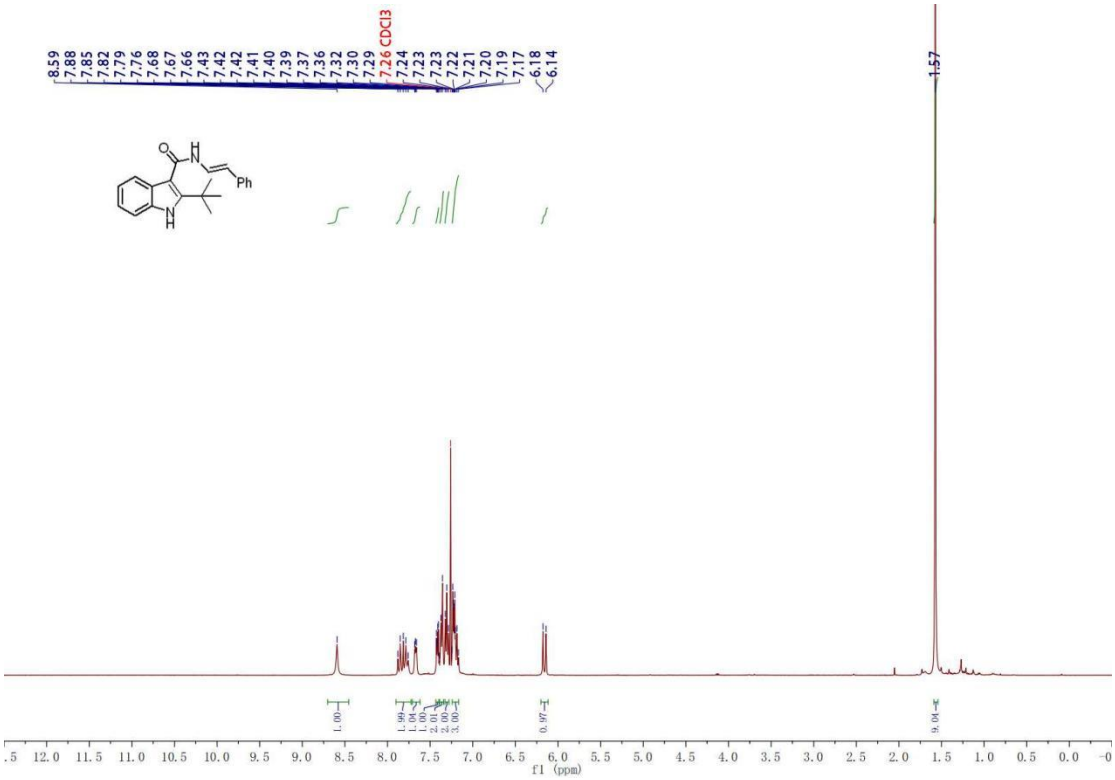
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3pa



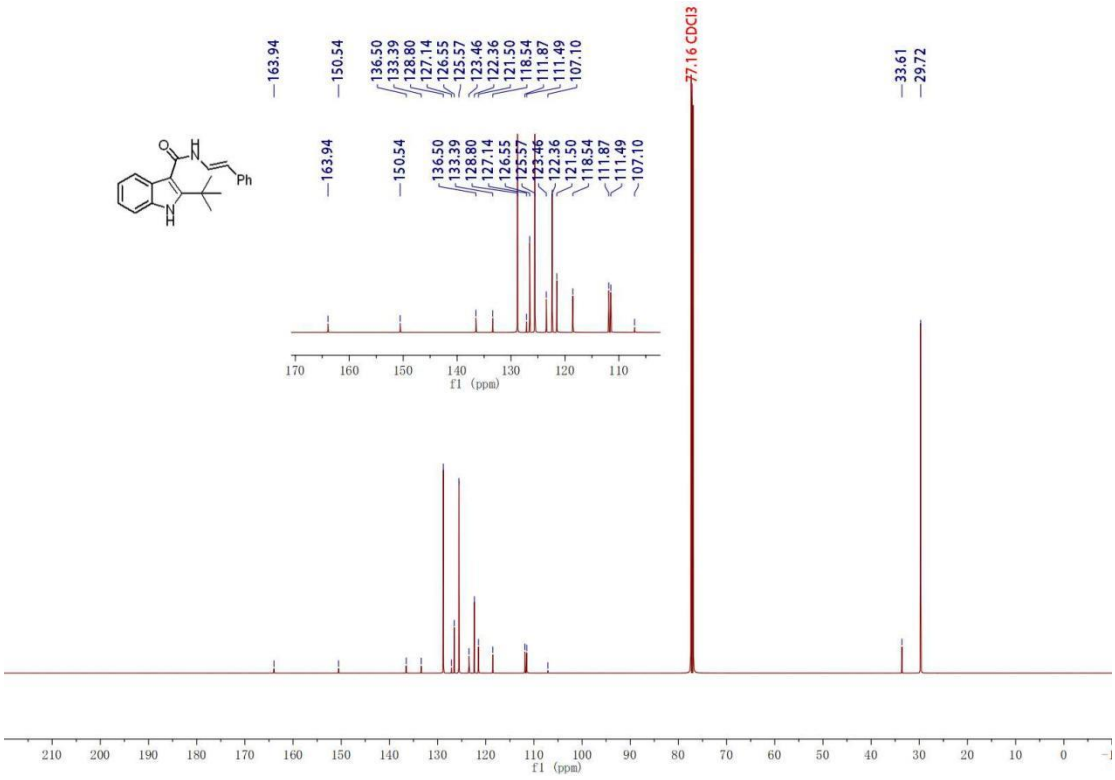
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3pa



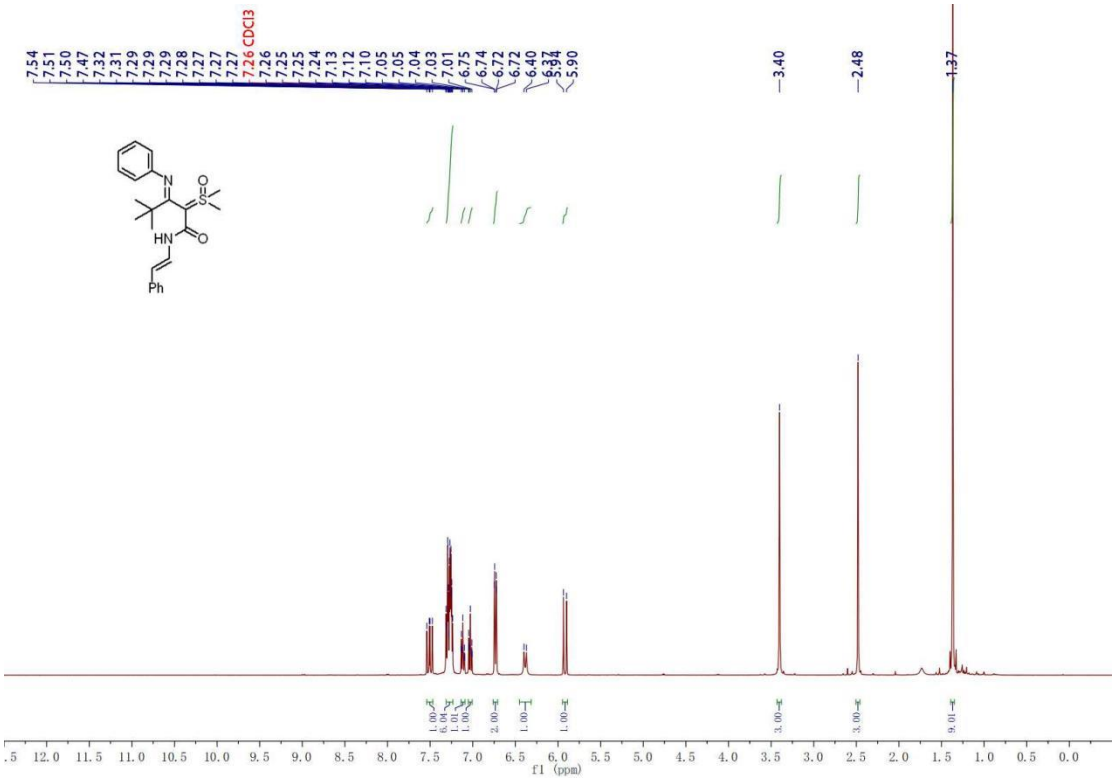
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ra



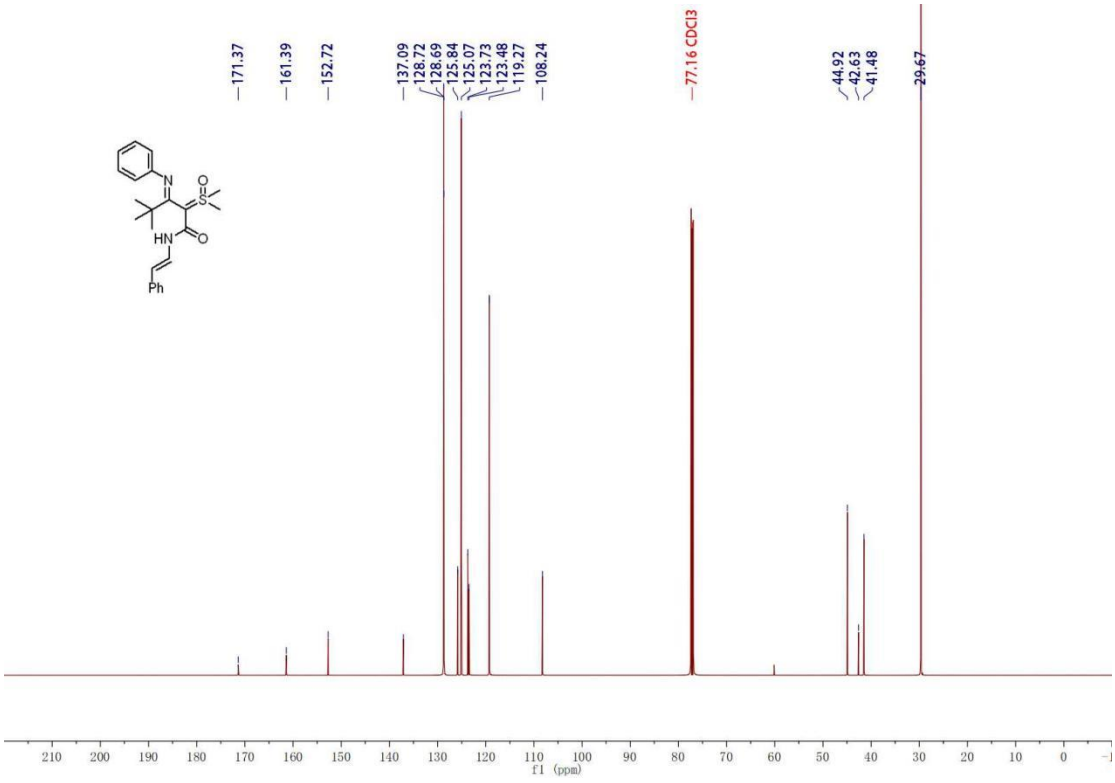
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ra



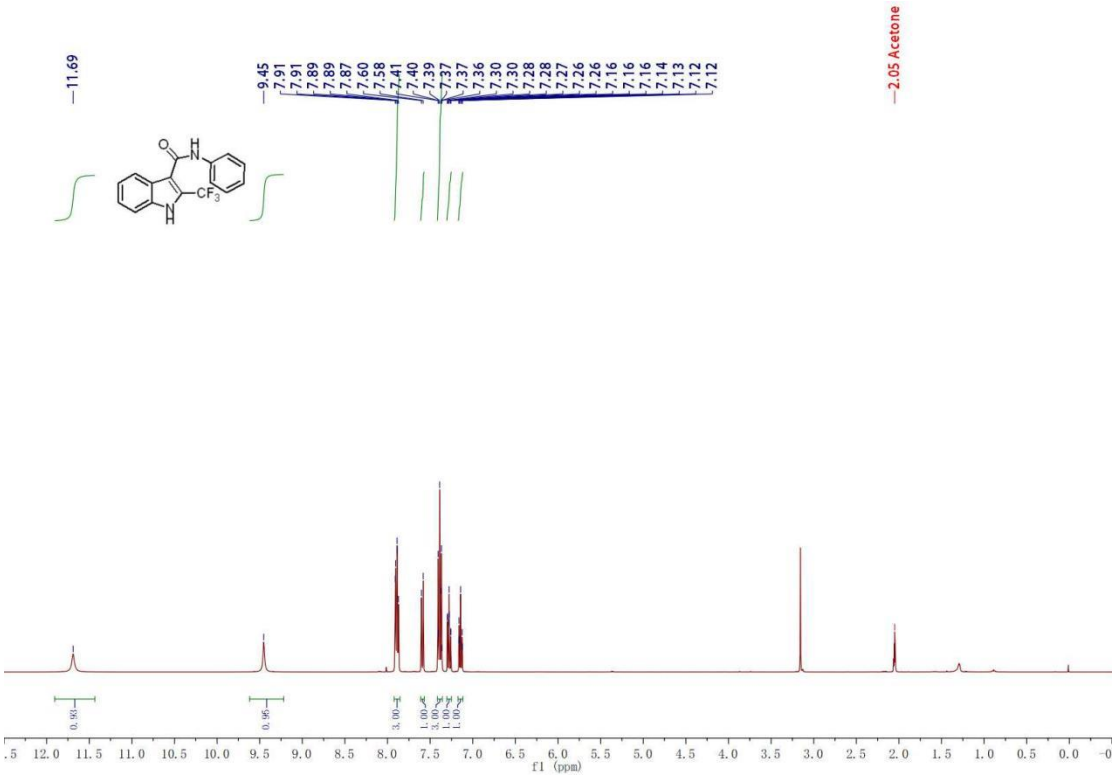
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ra'



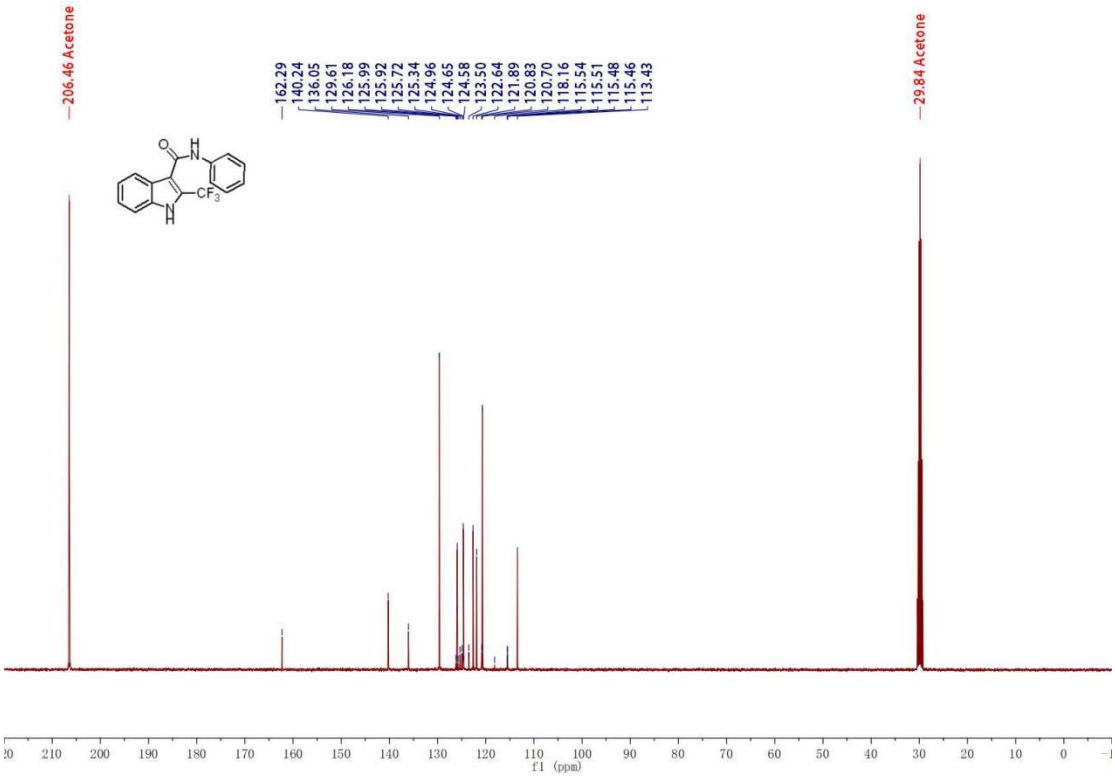
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ra'



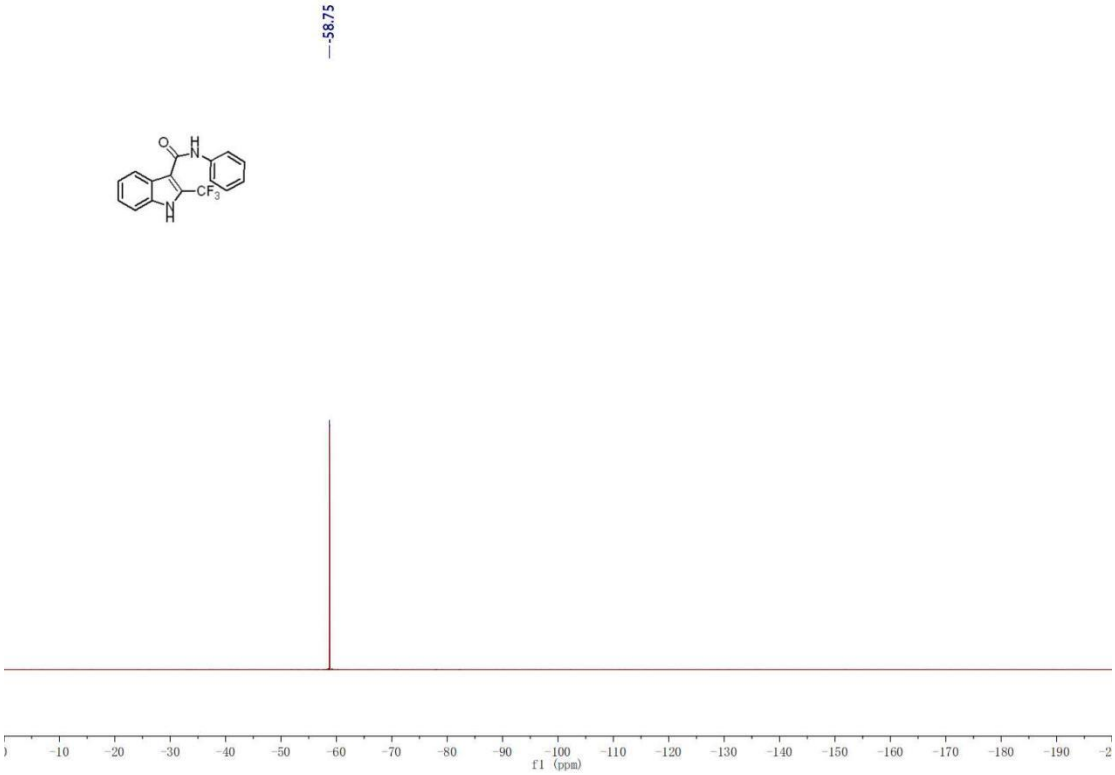
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ab



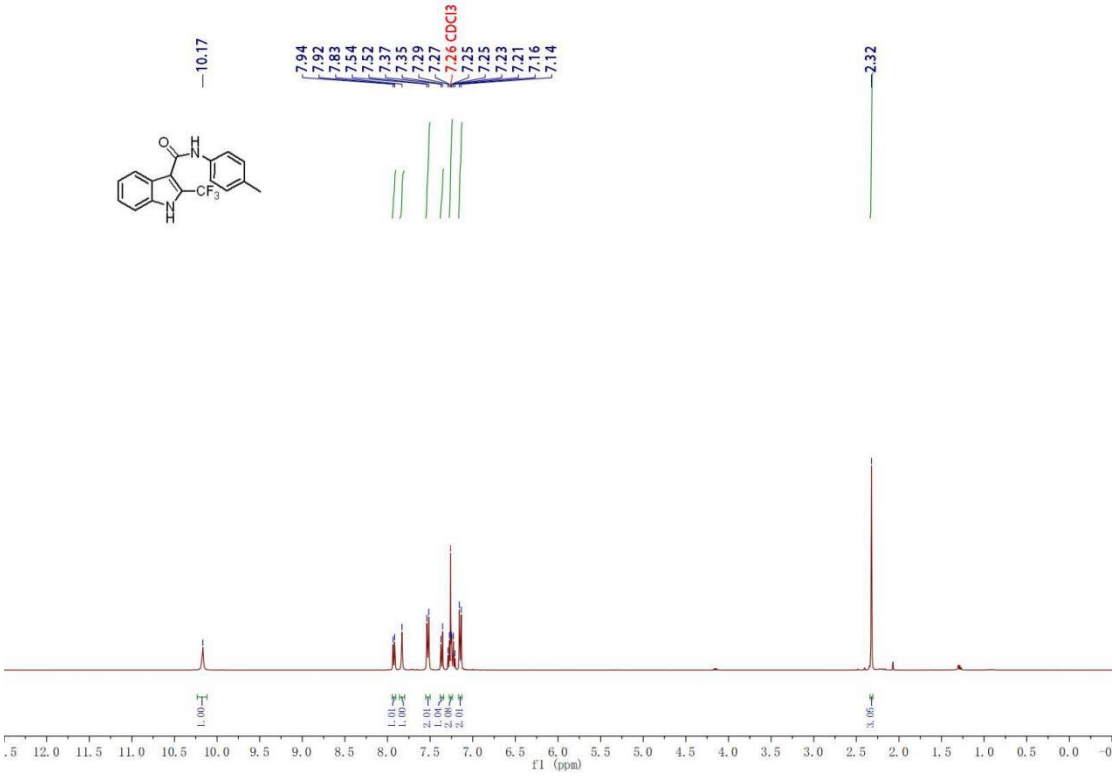
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ab



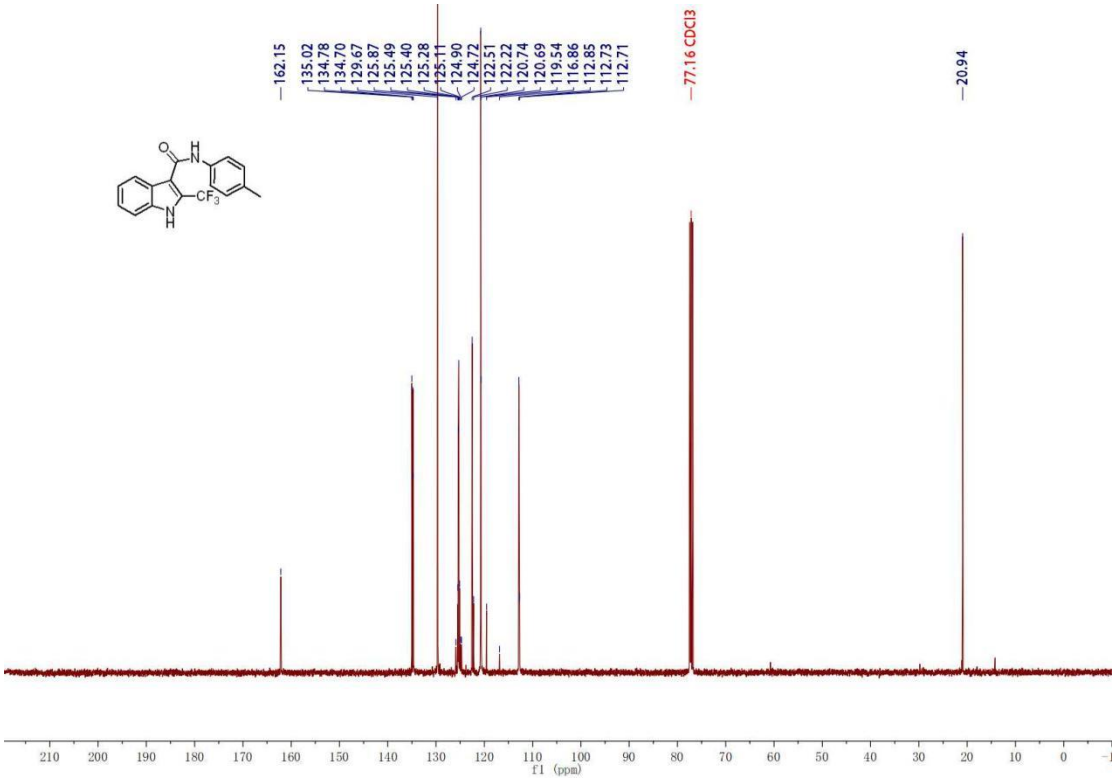
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ab



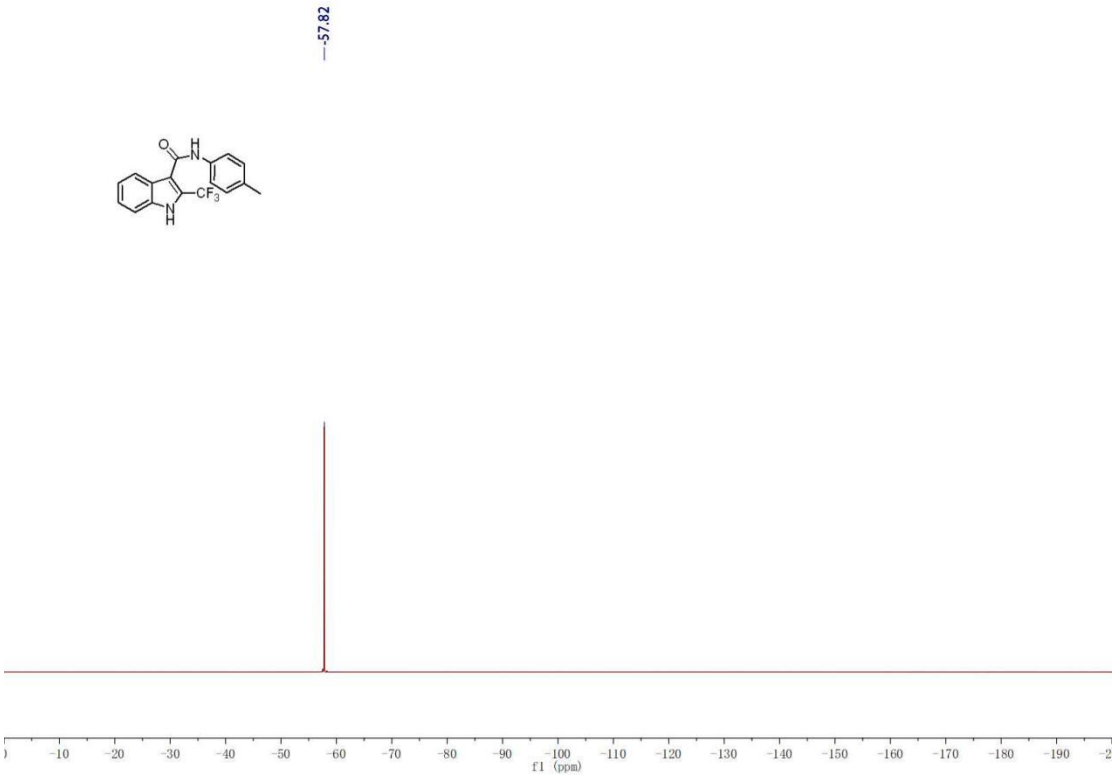
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ac



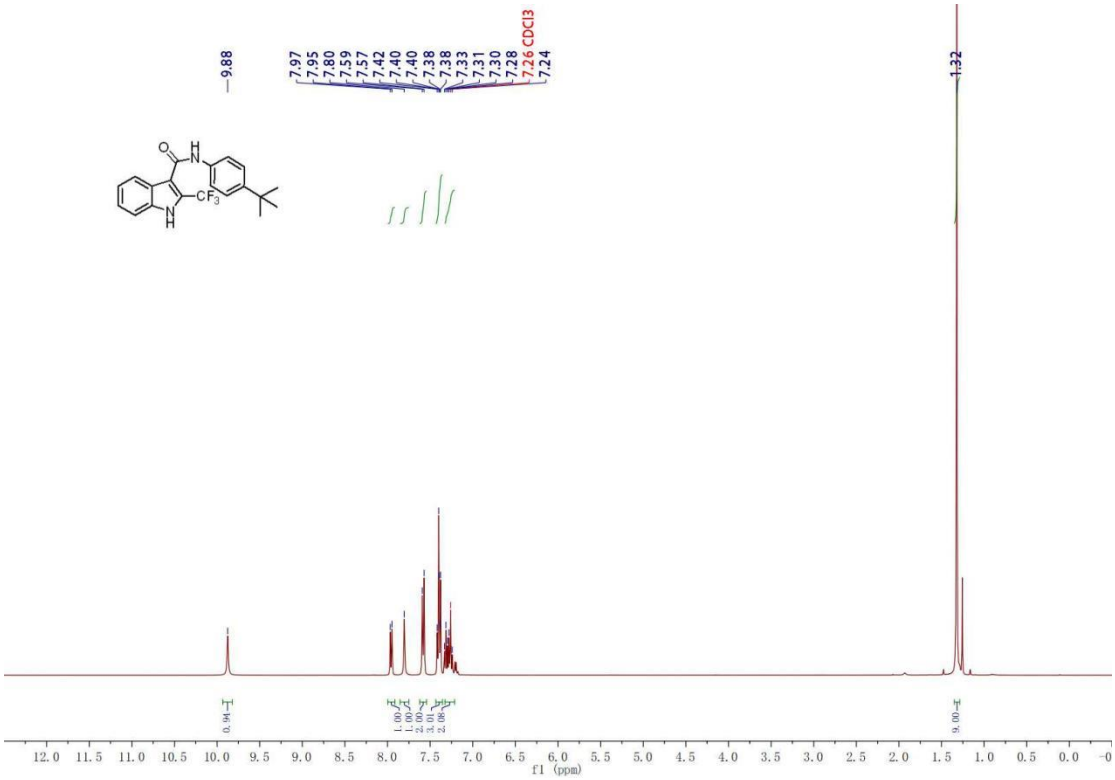
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ac



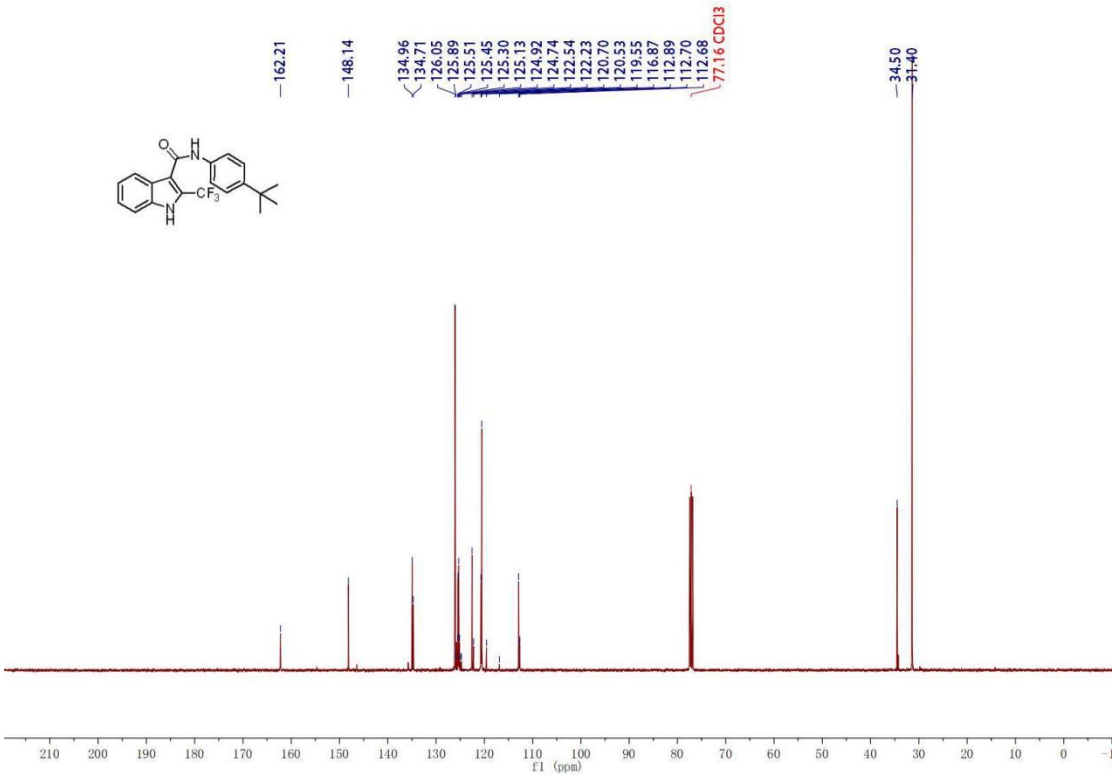
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ac



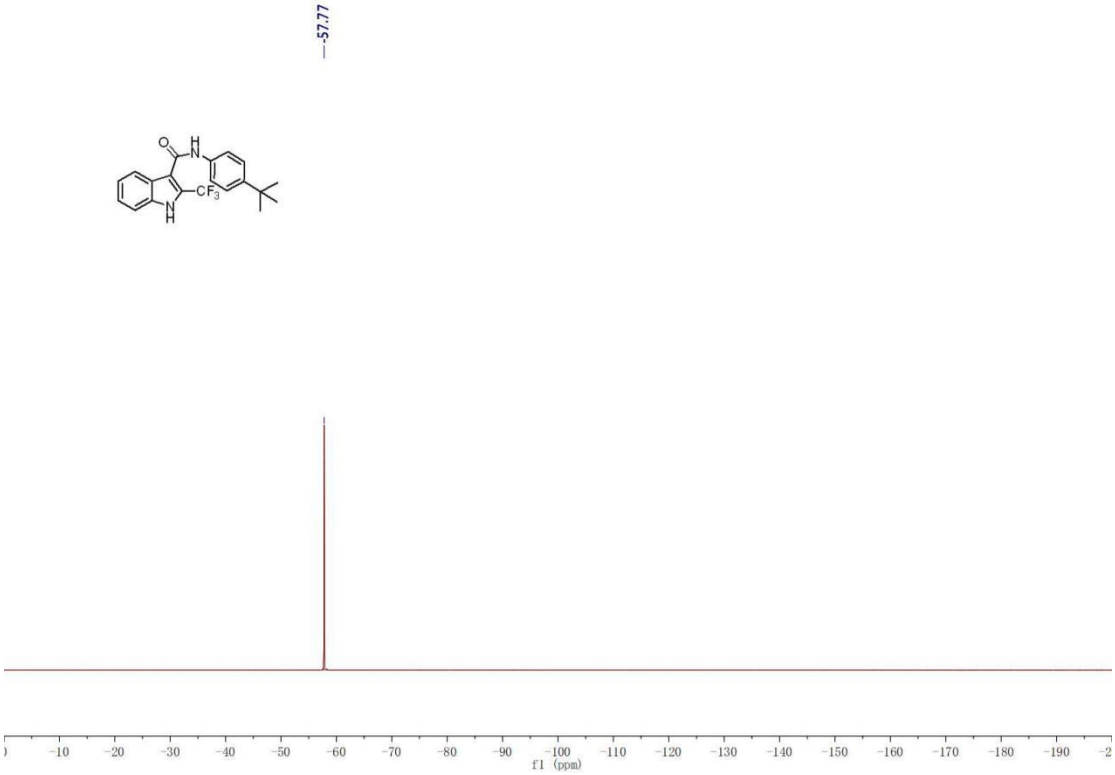
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ad



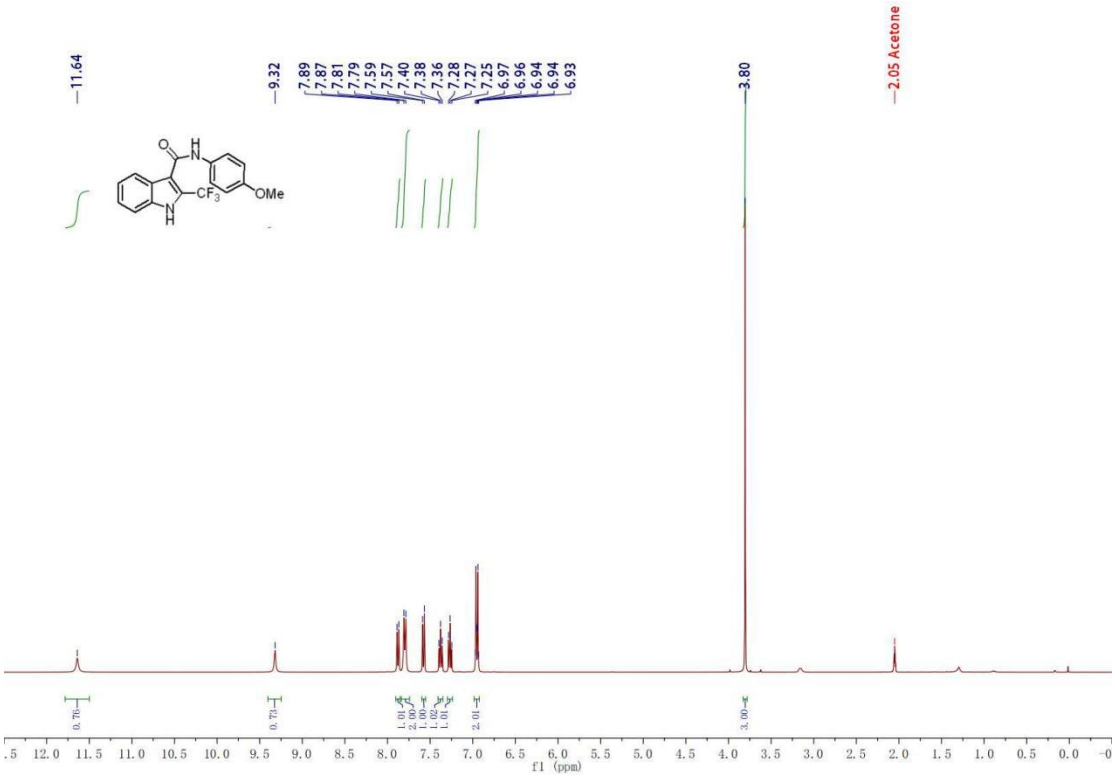
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ad



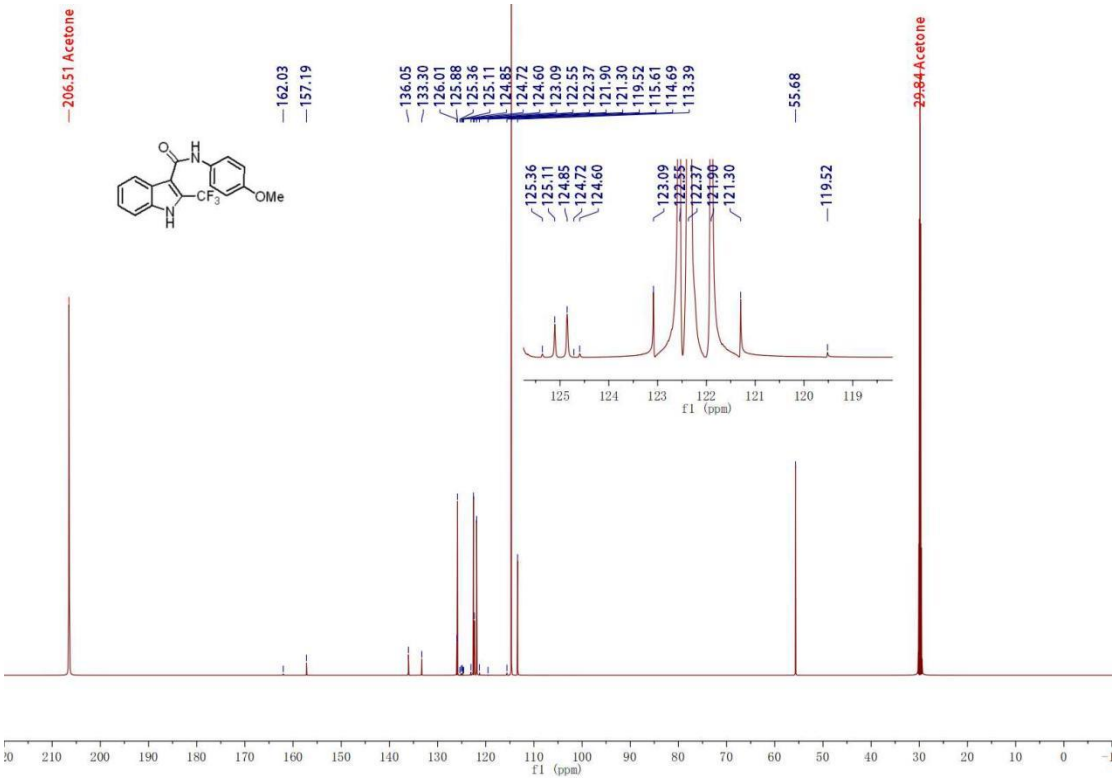
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ad



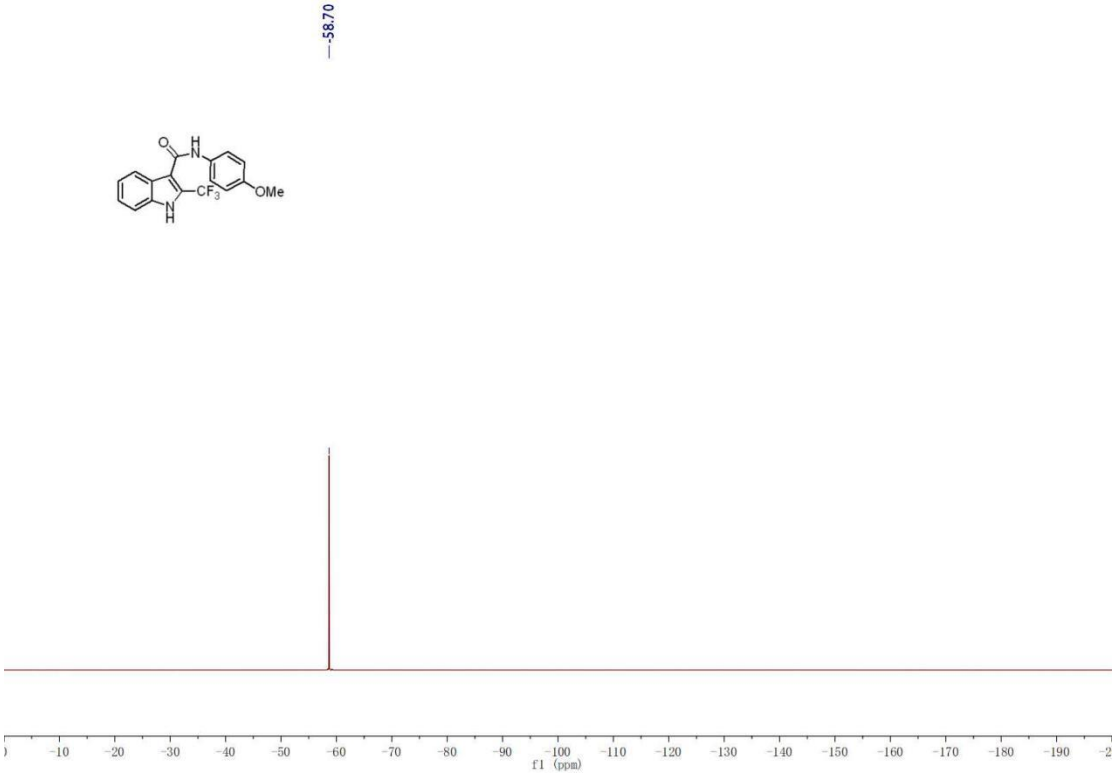
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ae



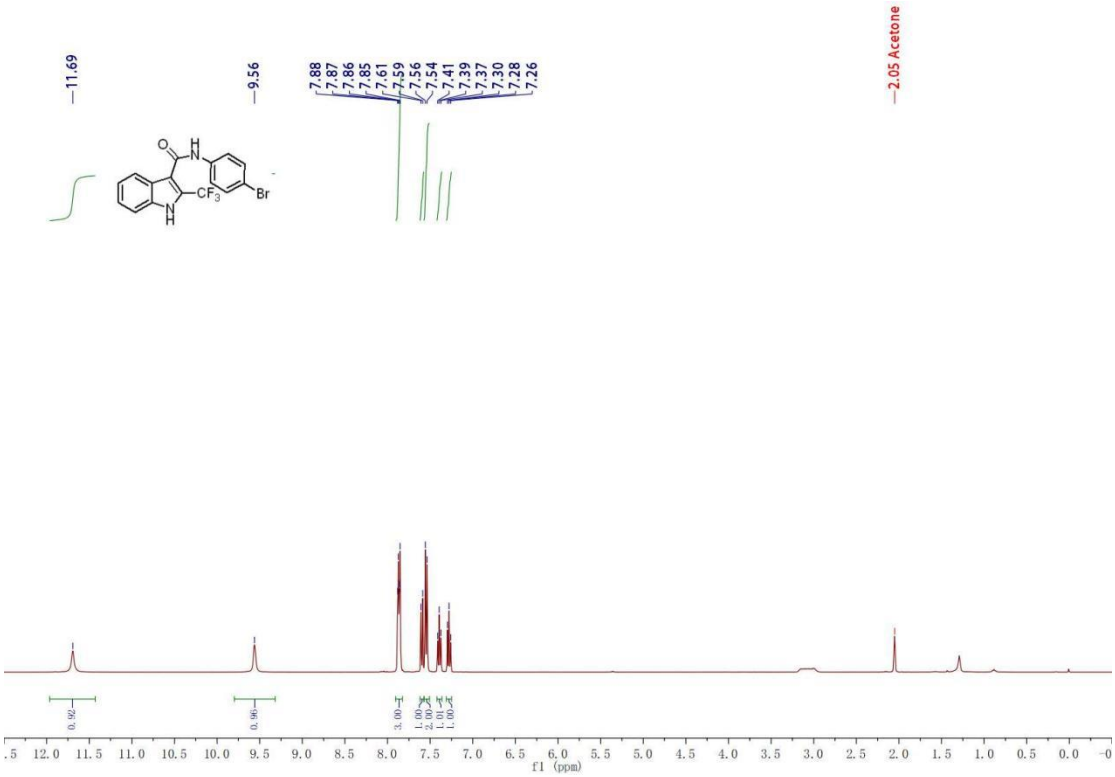
^{13}C NMR (150 MHz, Acetone-*d*6) spectrum of 3ae



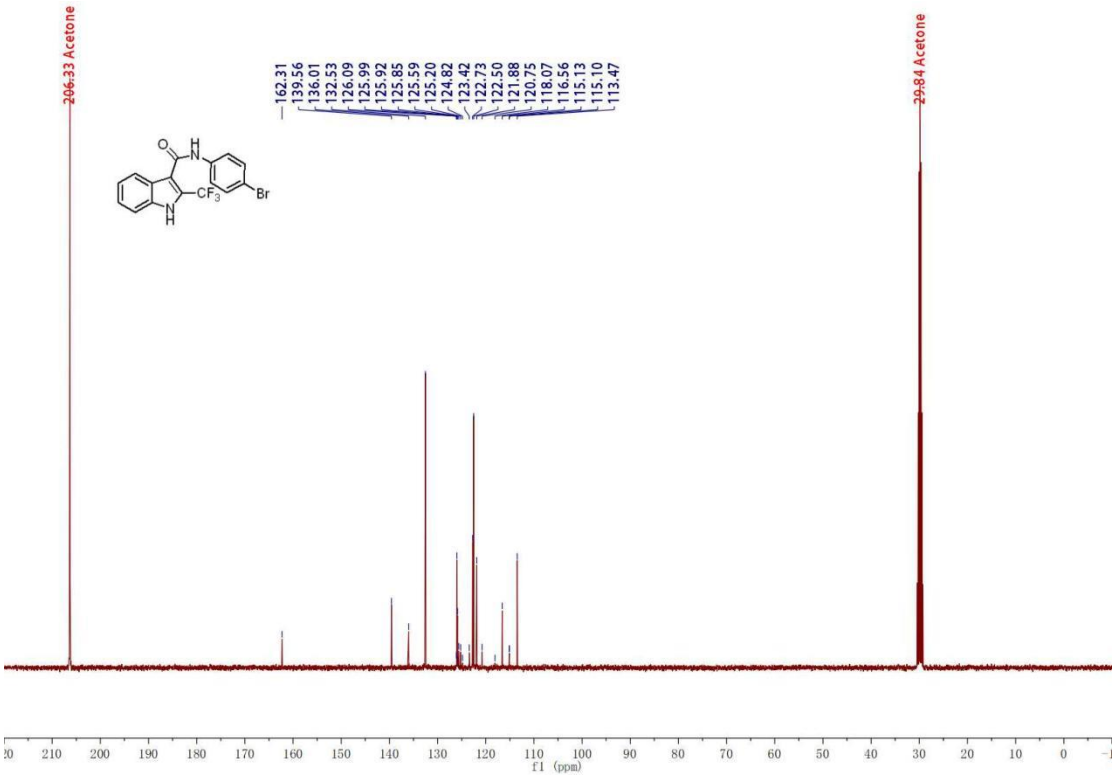
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ae



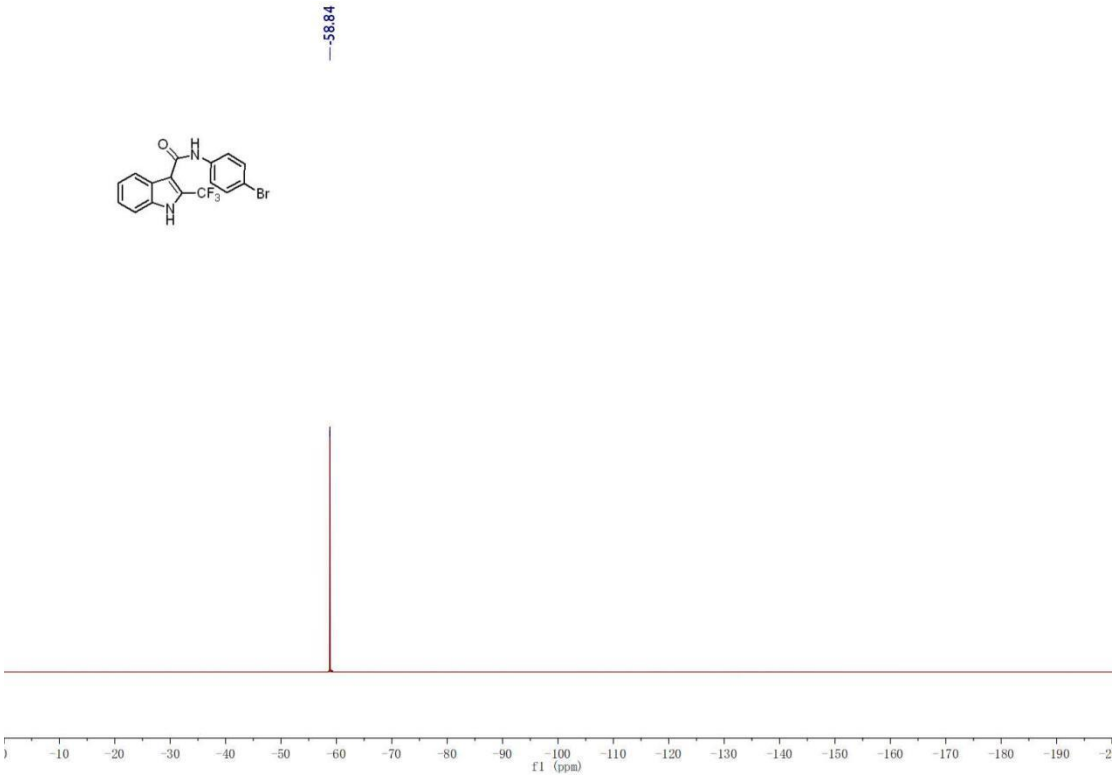
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3af



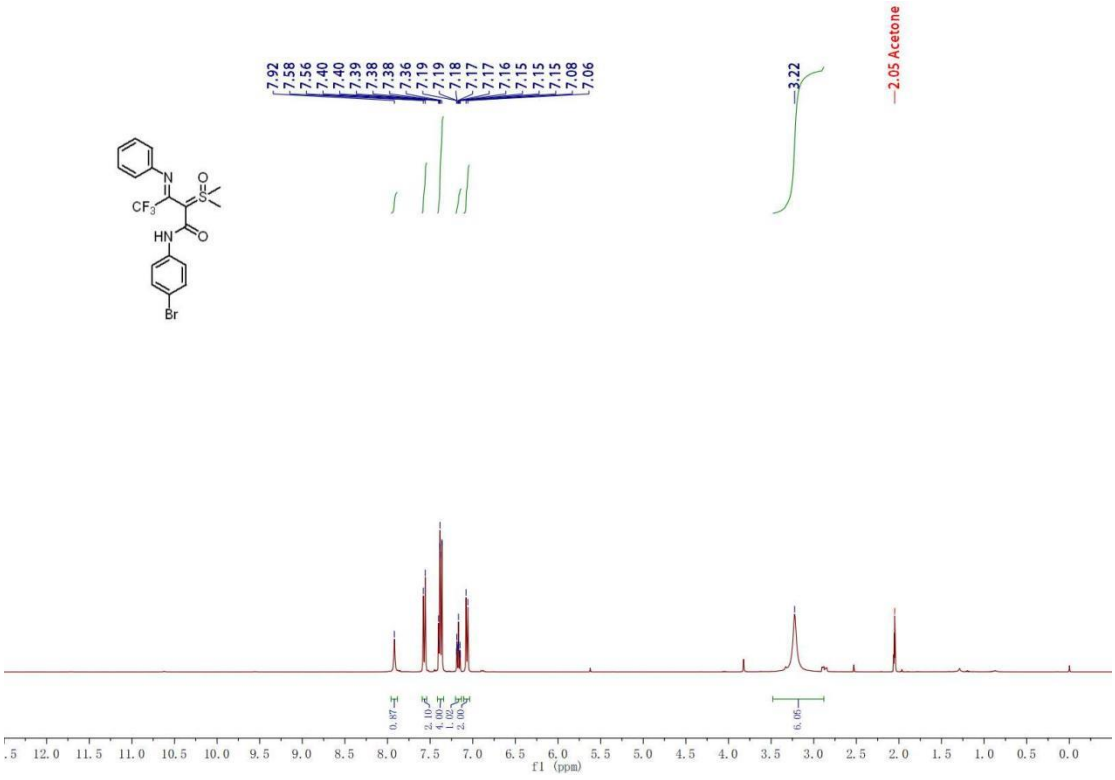
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3af



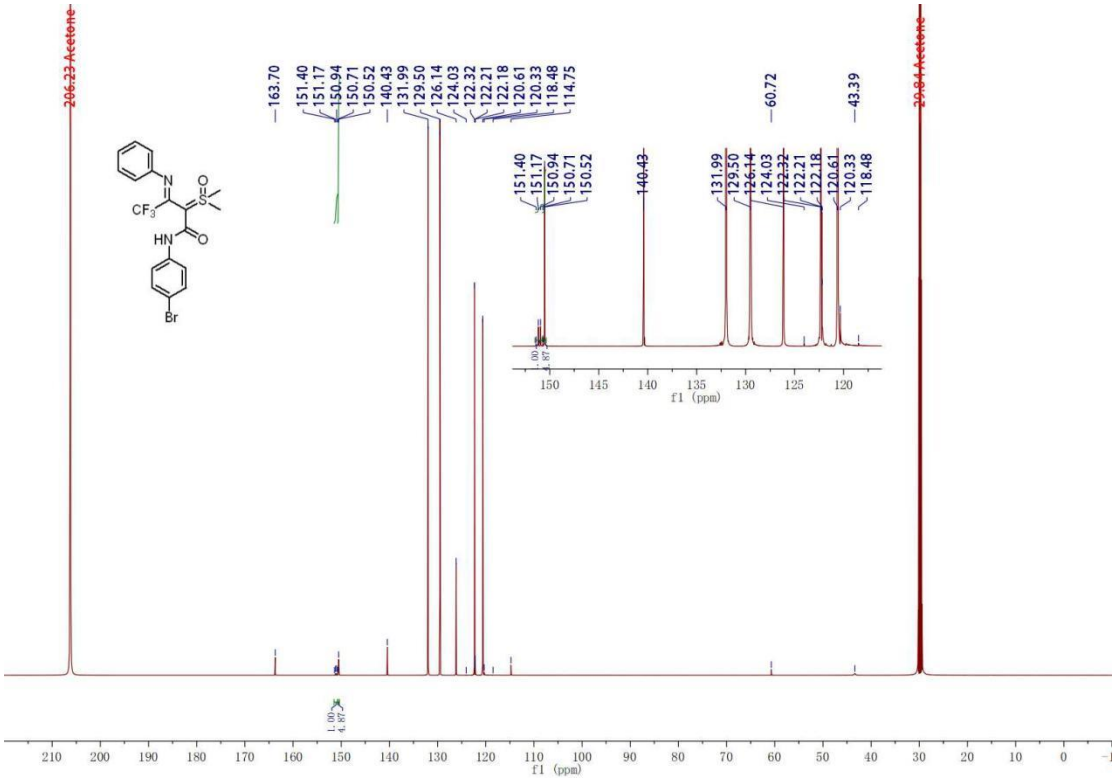
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3af



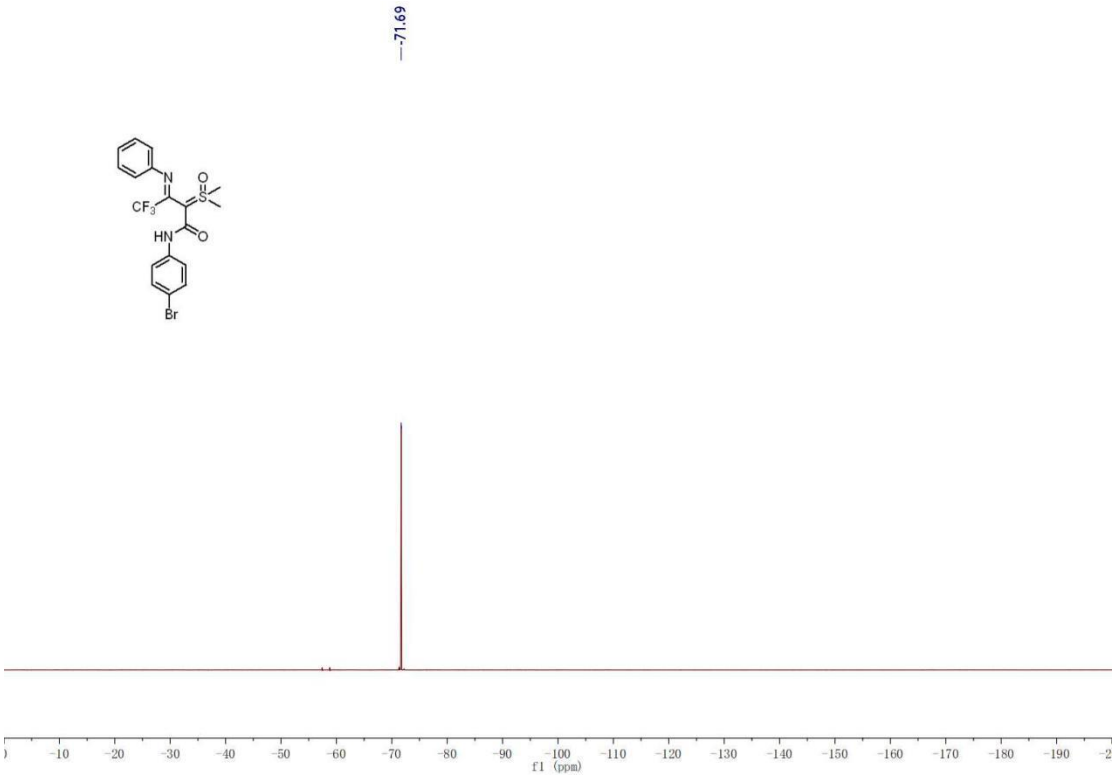
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3af'



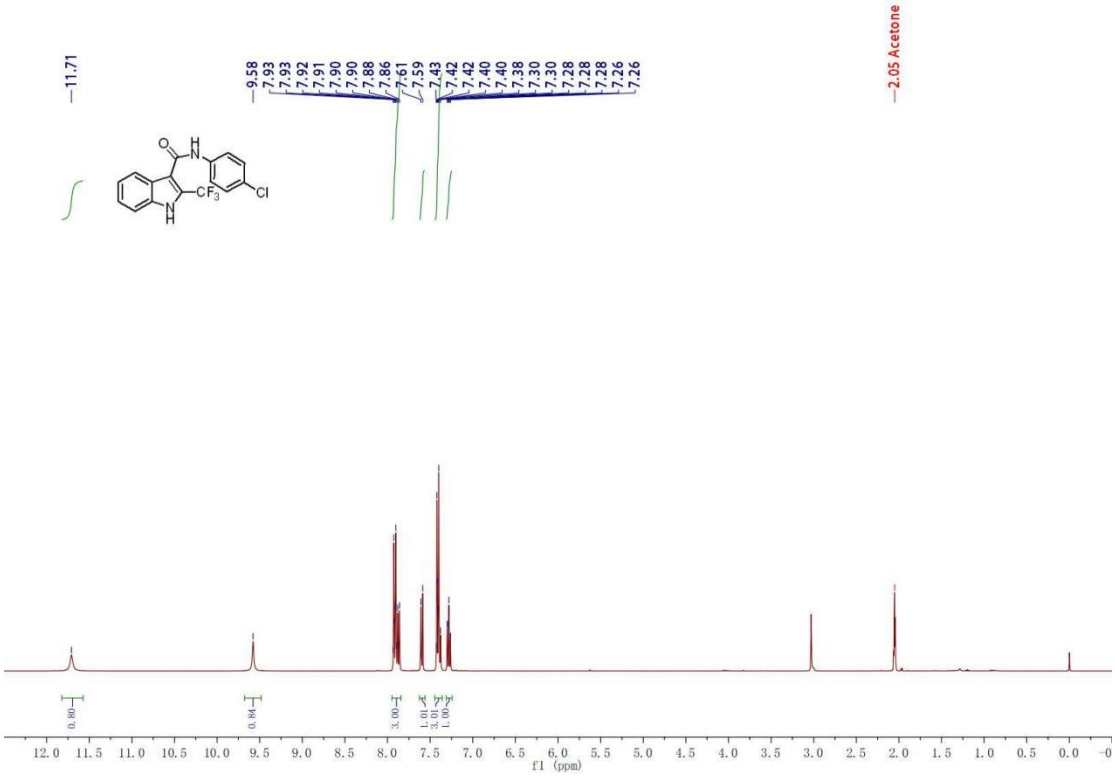
^{13}C NMR (150 MHz, Acetone-*d*6) spectrum of 3af'



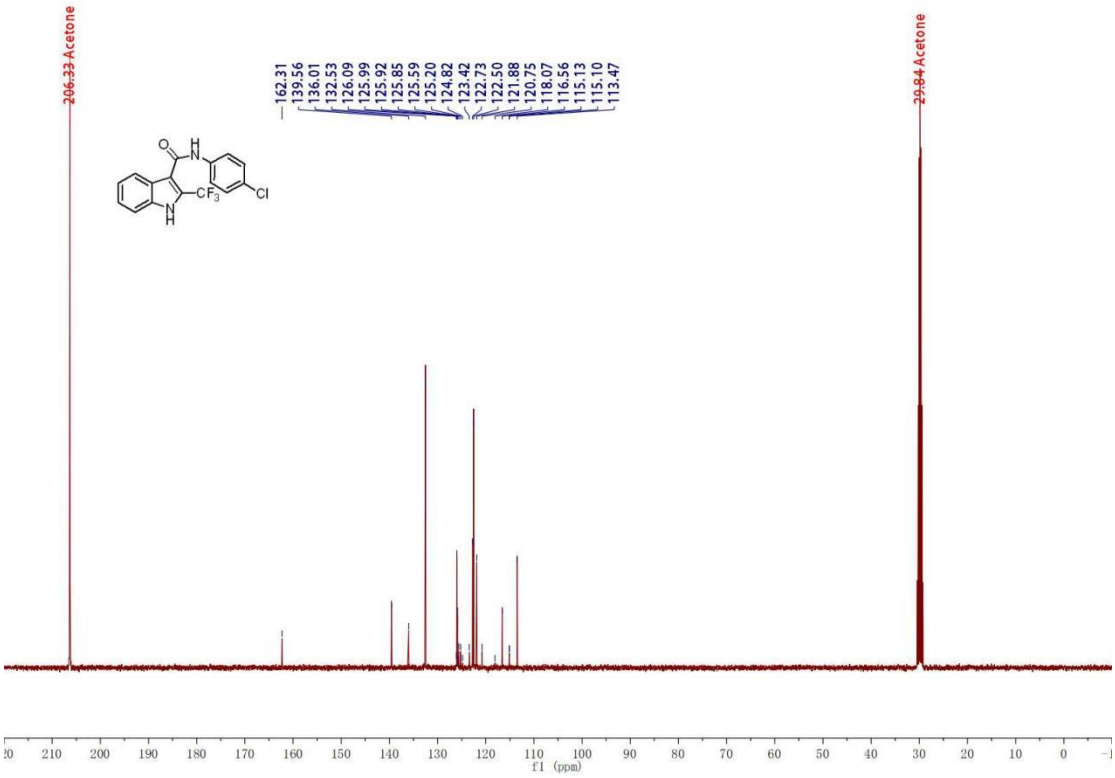
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3af'



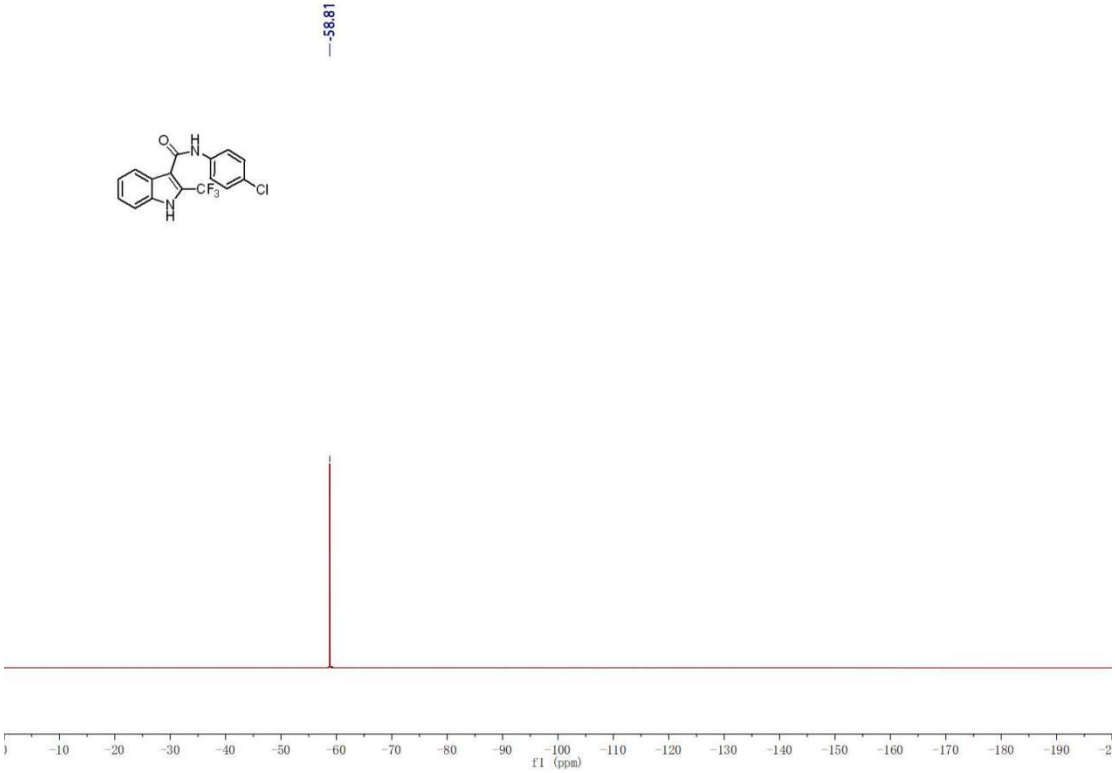
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ag



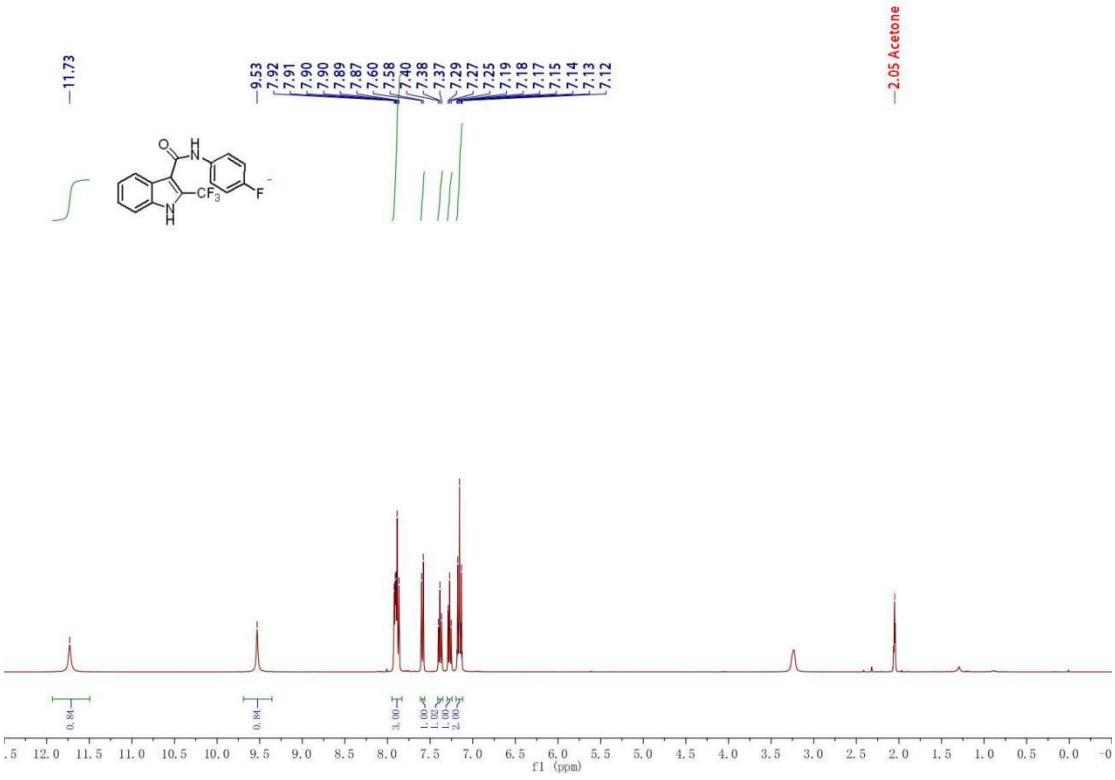
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ag



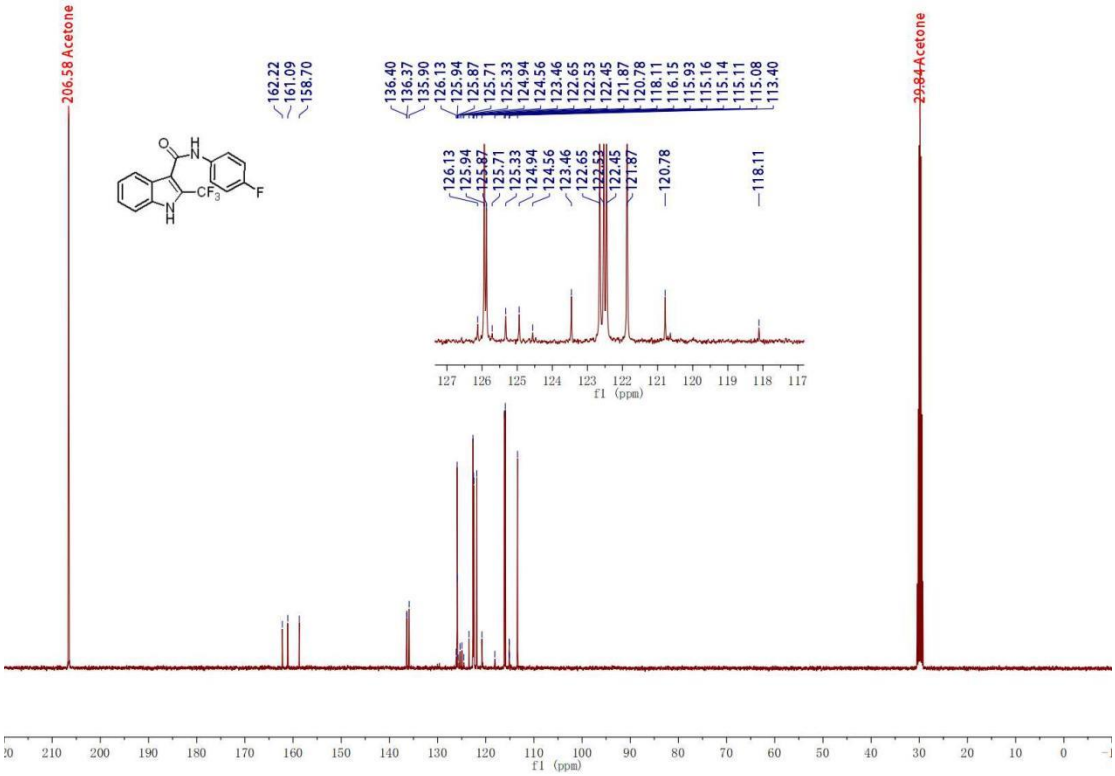
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ag



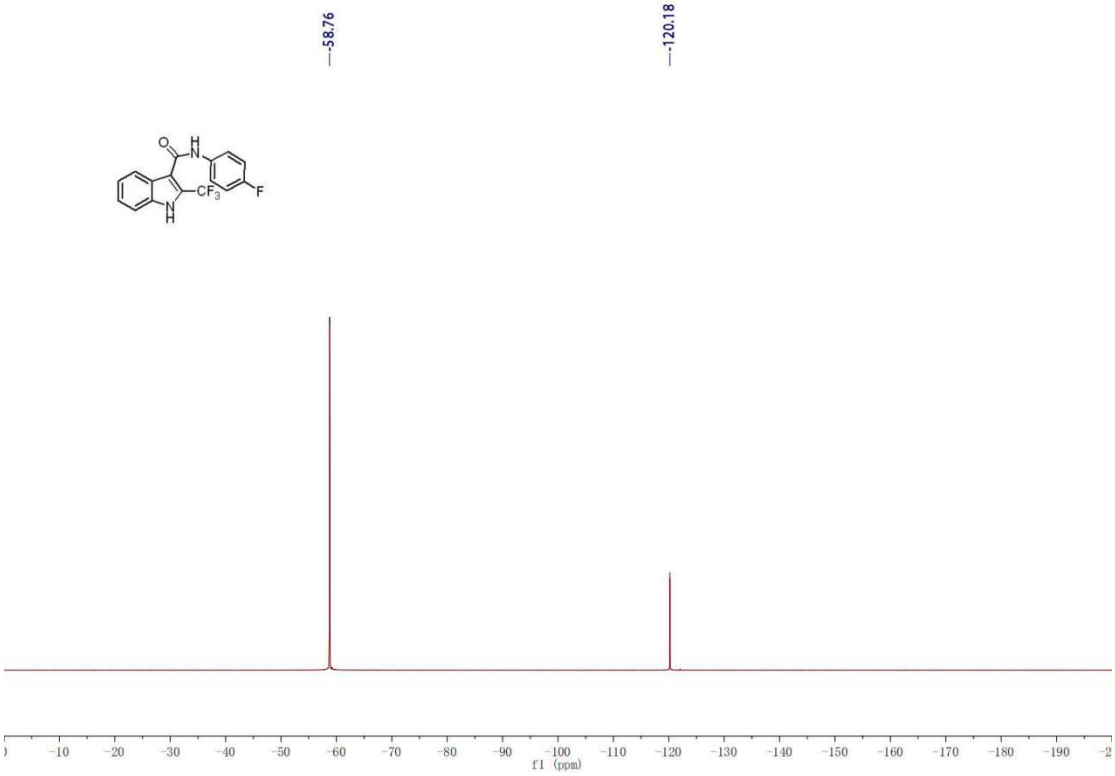
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ah



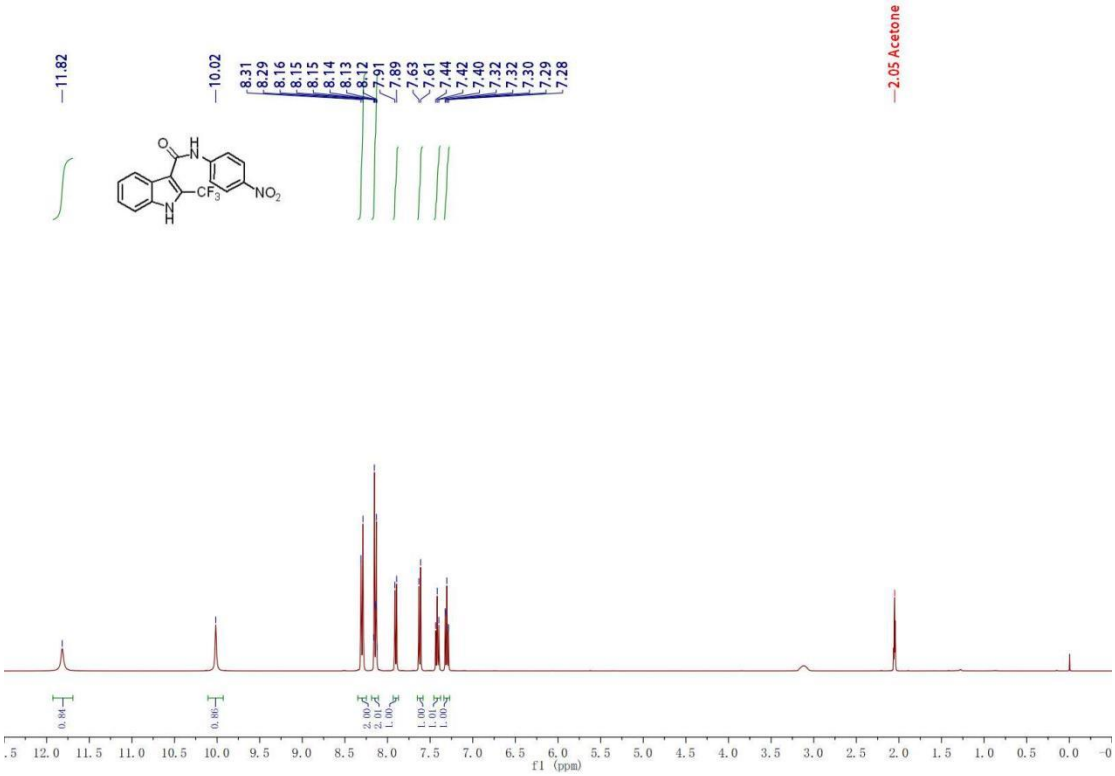
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ah



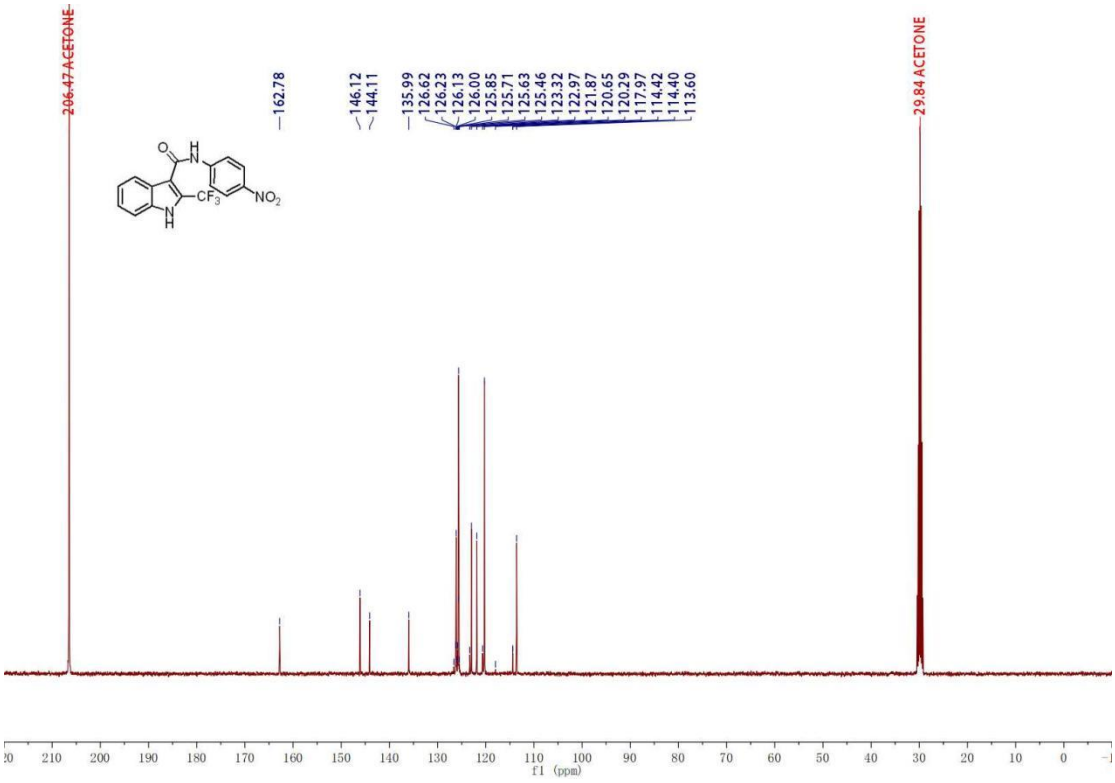
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ah



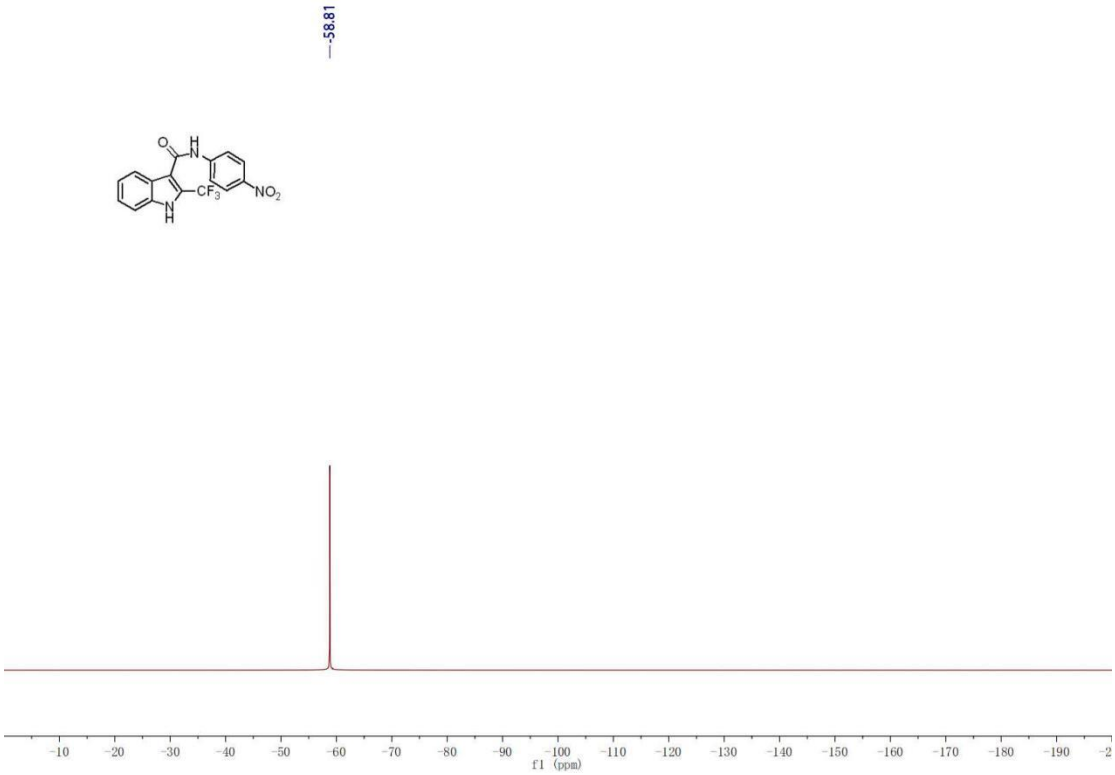
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ai



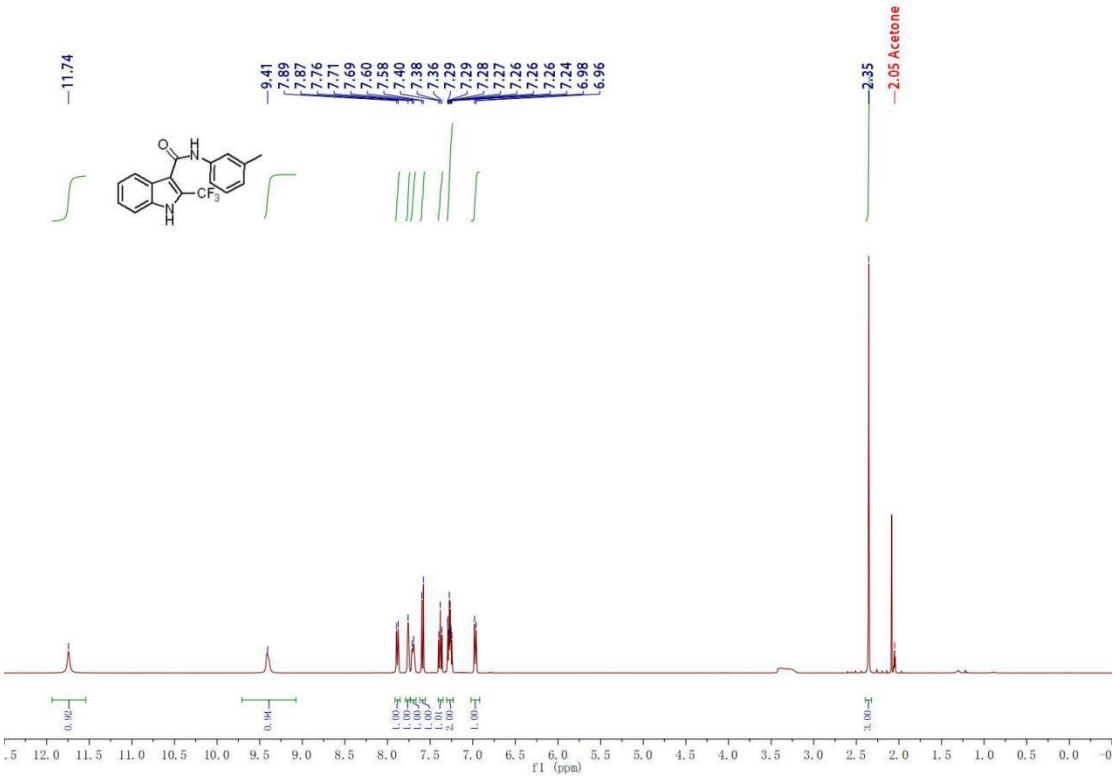
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ai



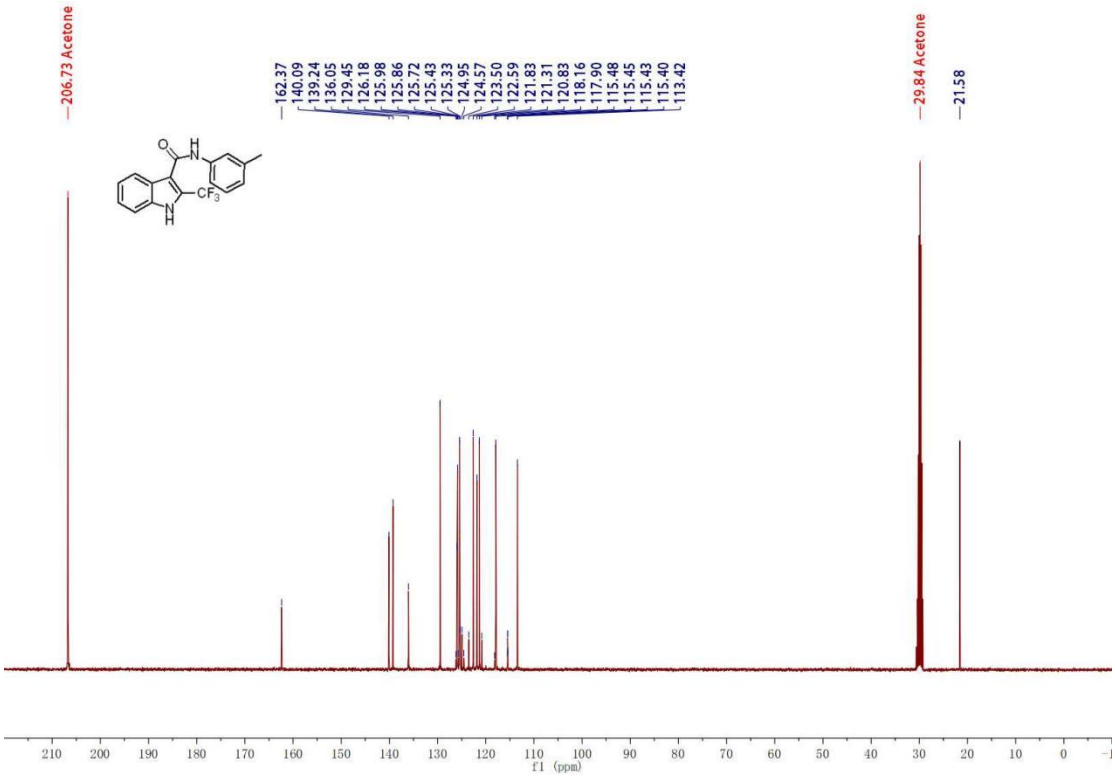
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ai



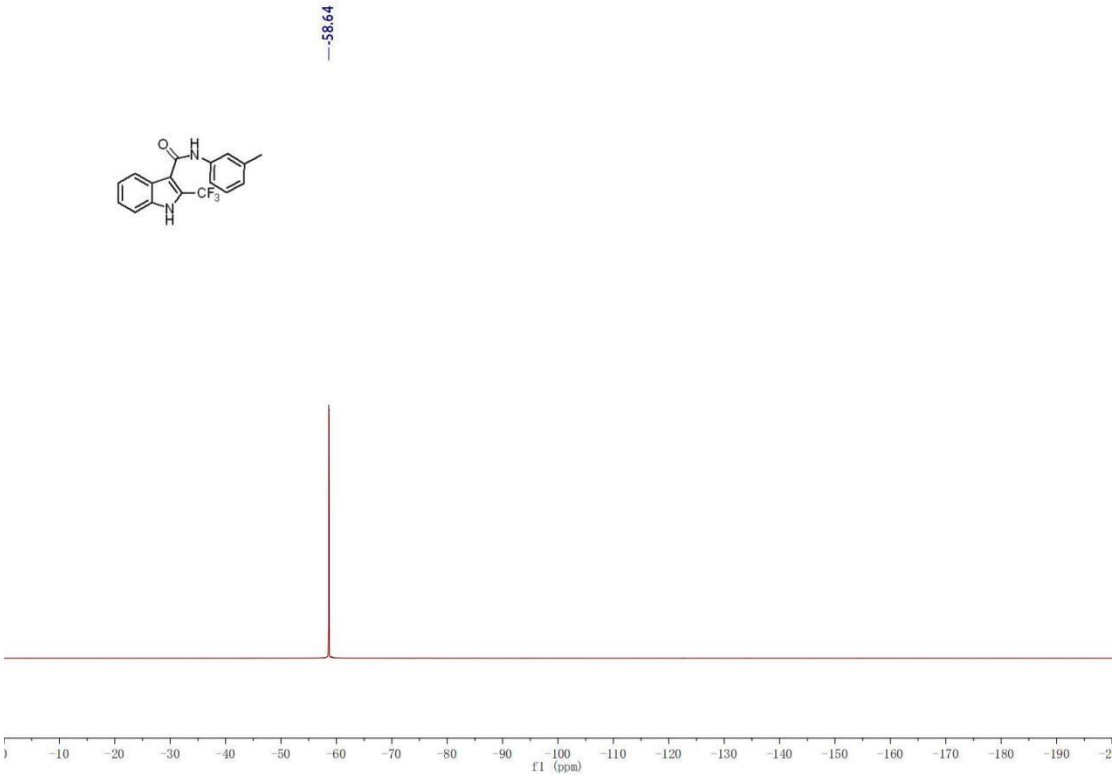
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3aj



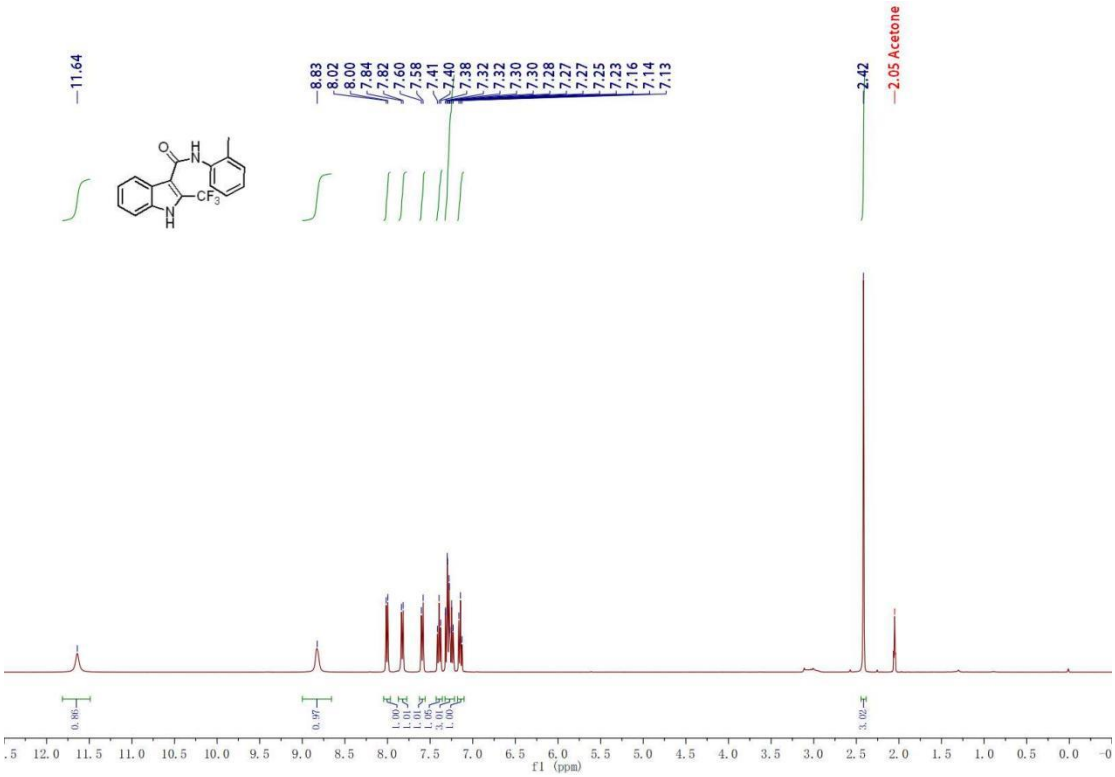
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3aj



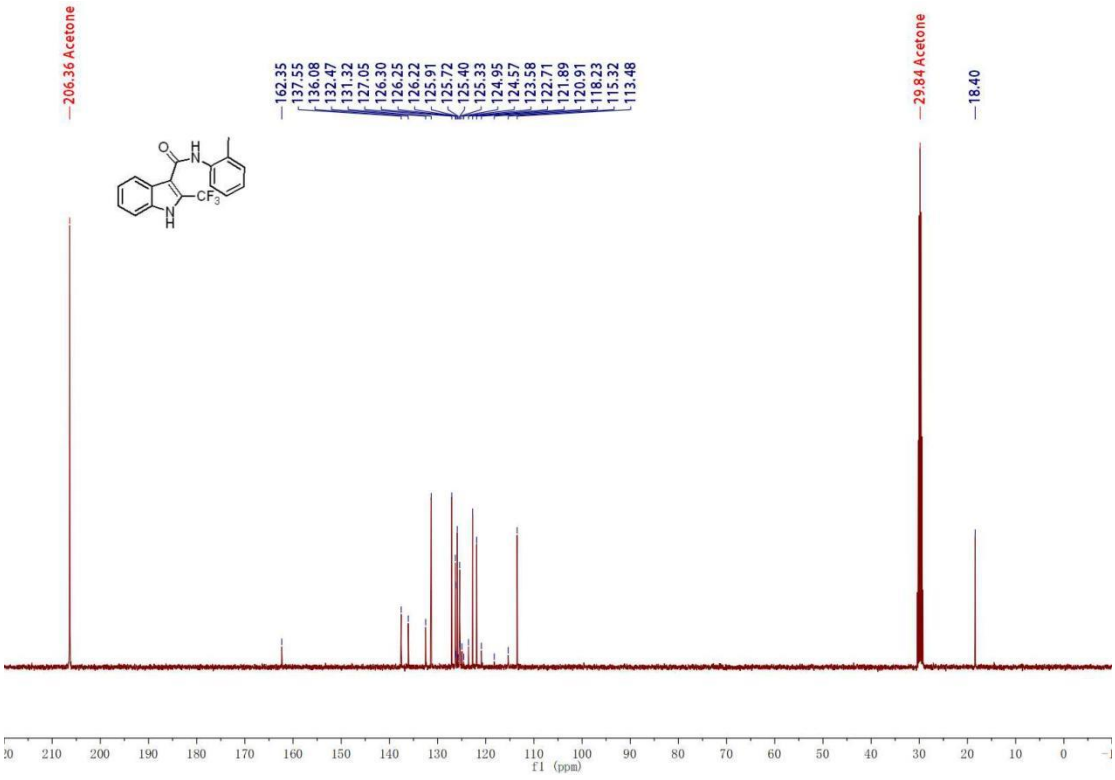
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3aj



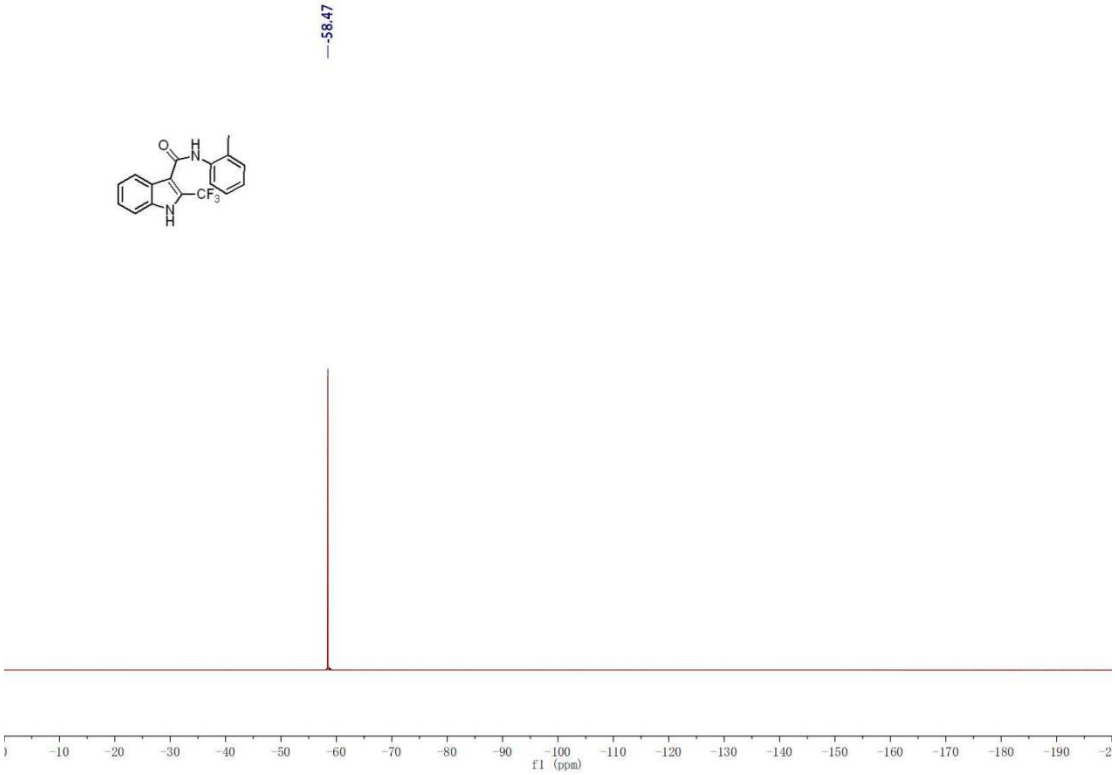
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3ak



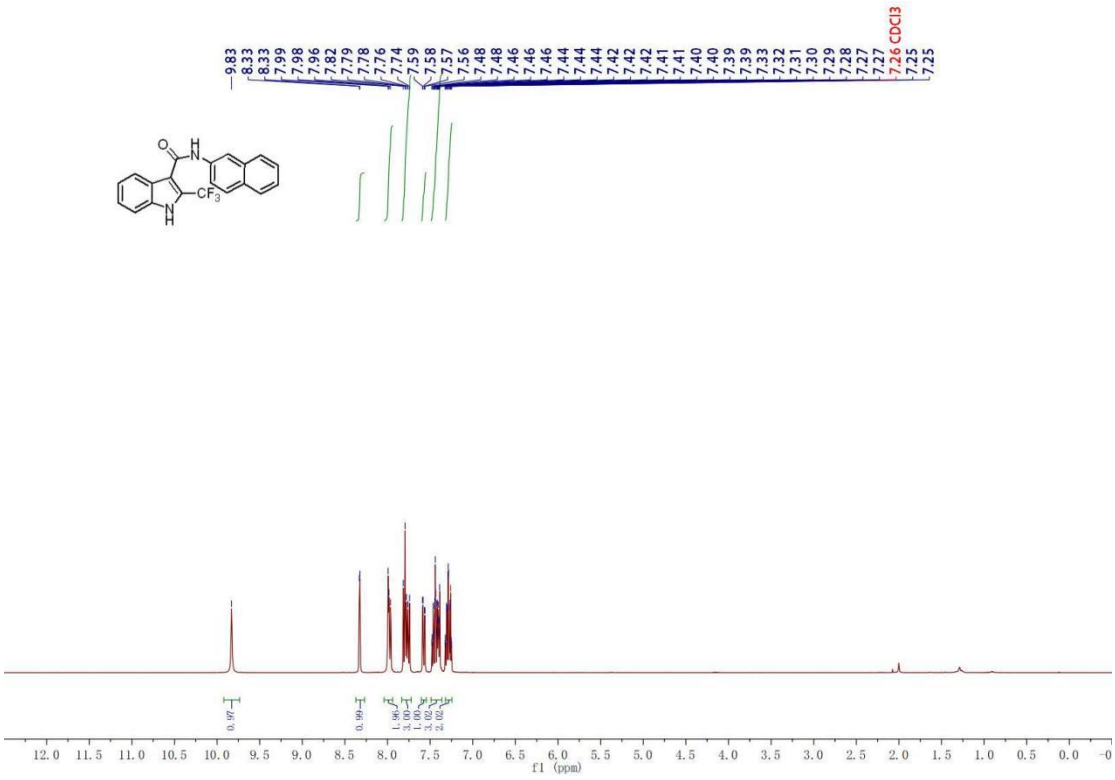
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 3ak



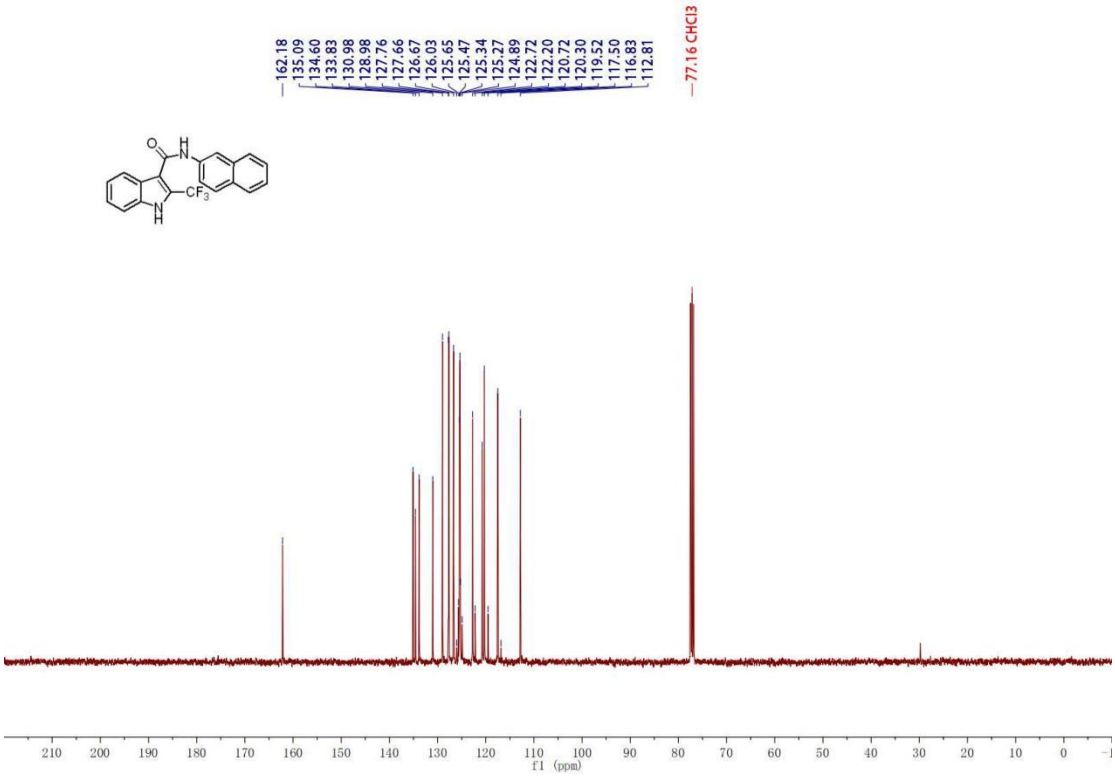
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3ak



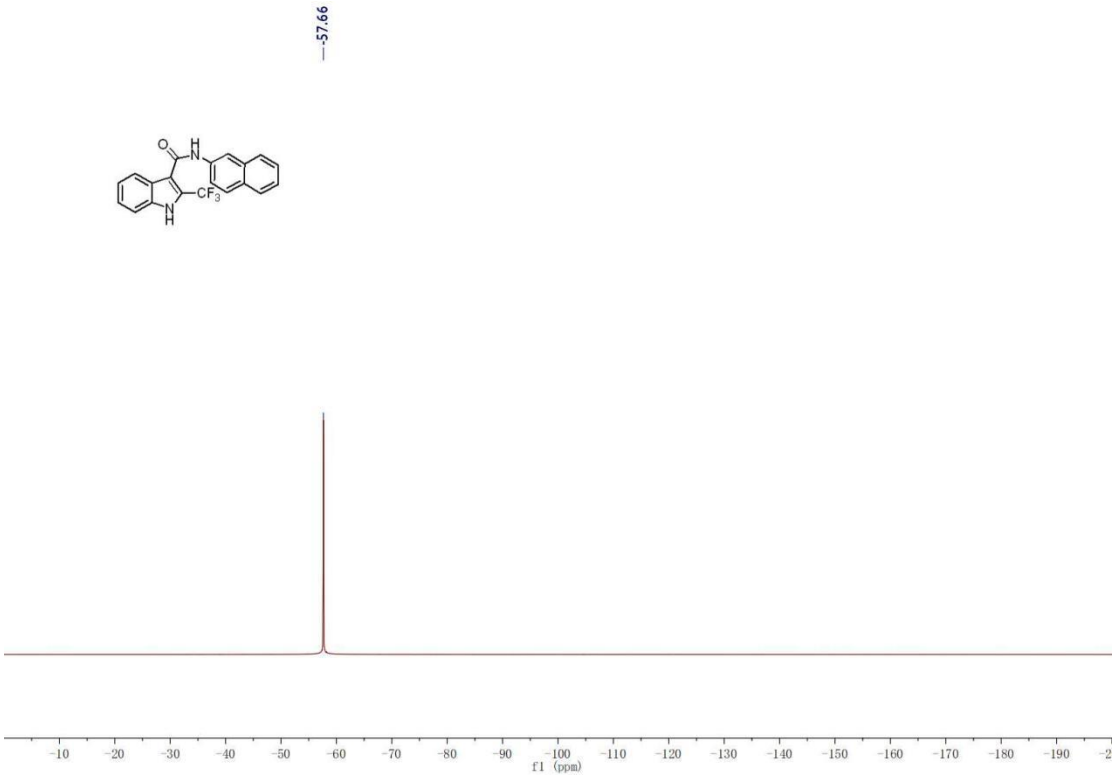
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3al



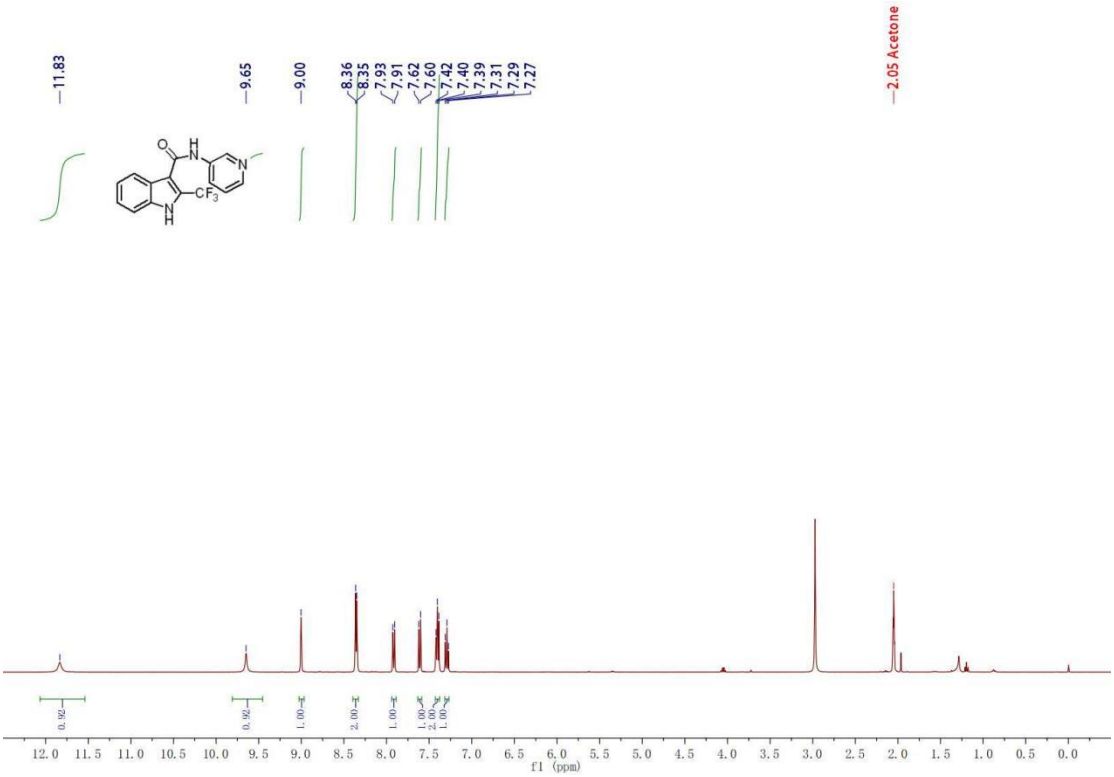
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3al



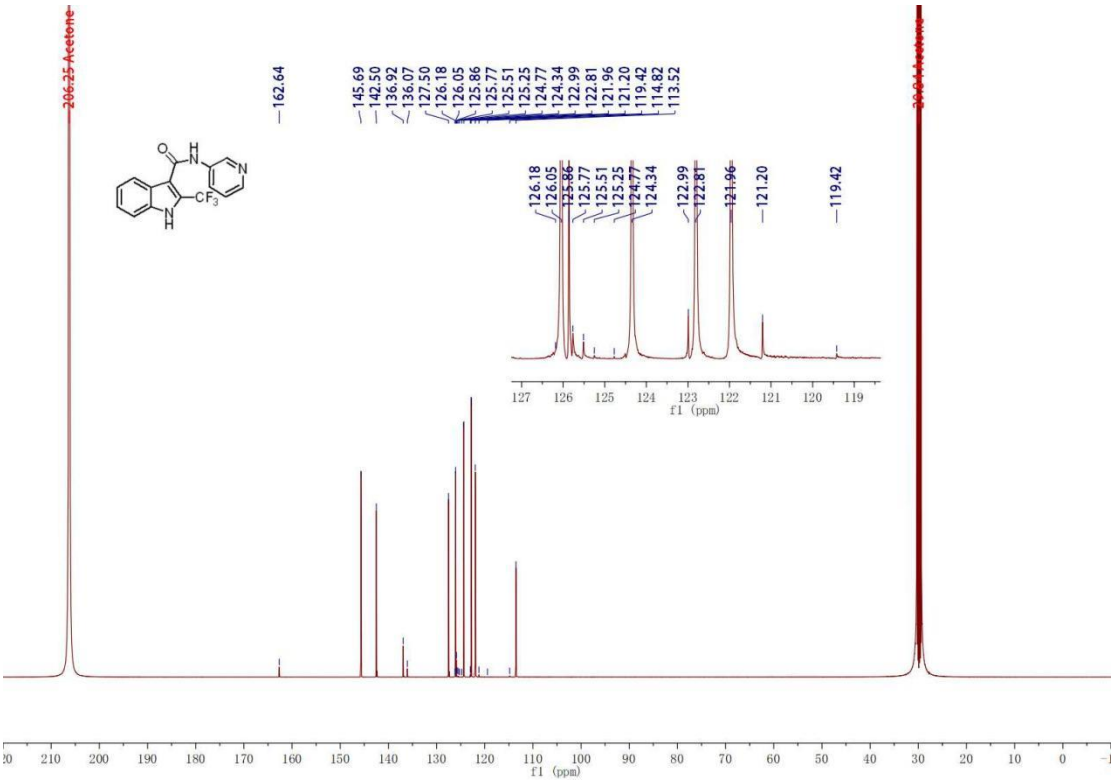
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3al



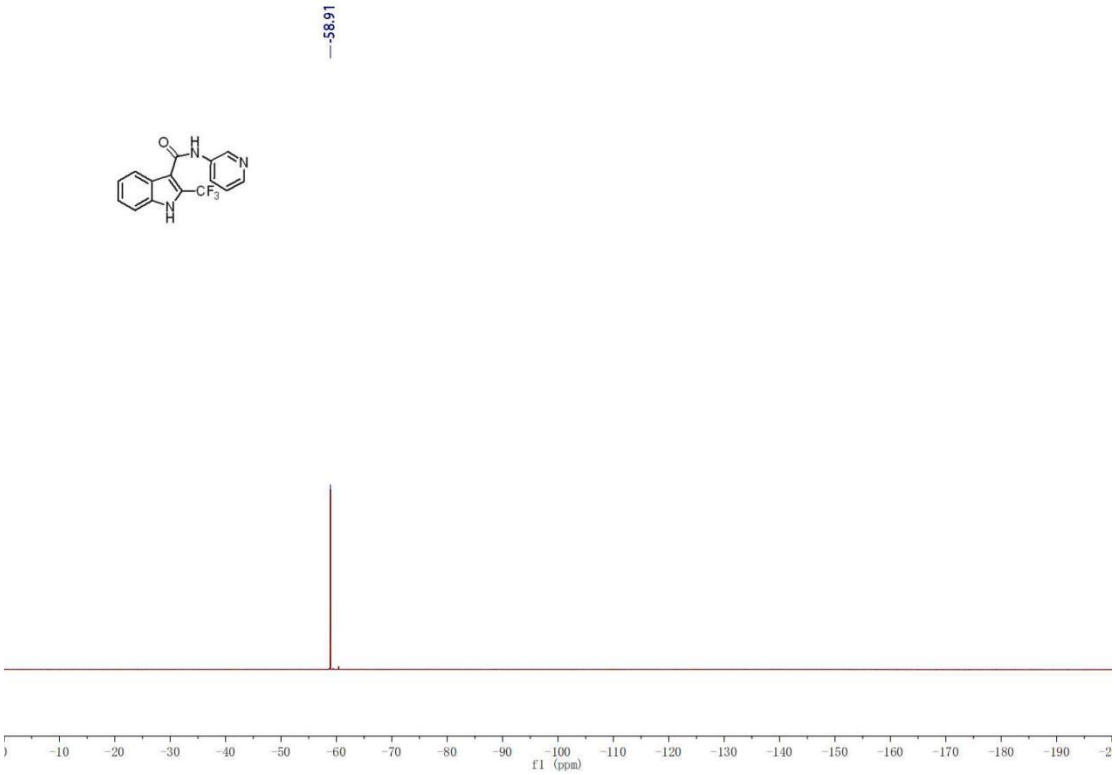
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3am



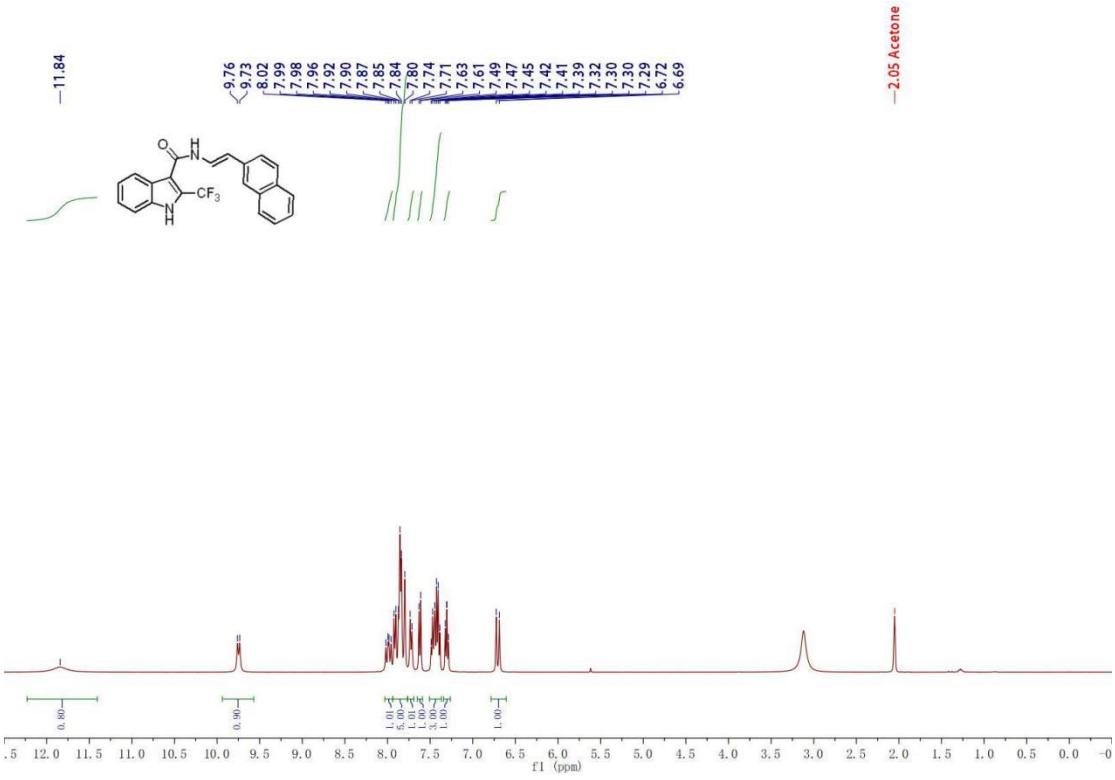
^{13}C NMR (150 MHz, Acetone-*d*6) spectrum of 3am



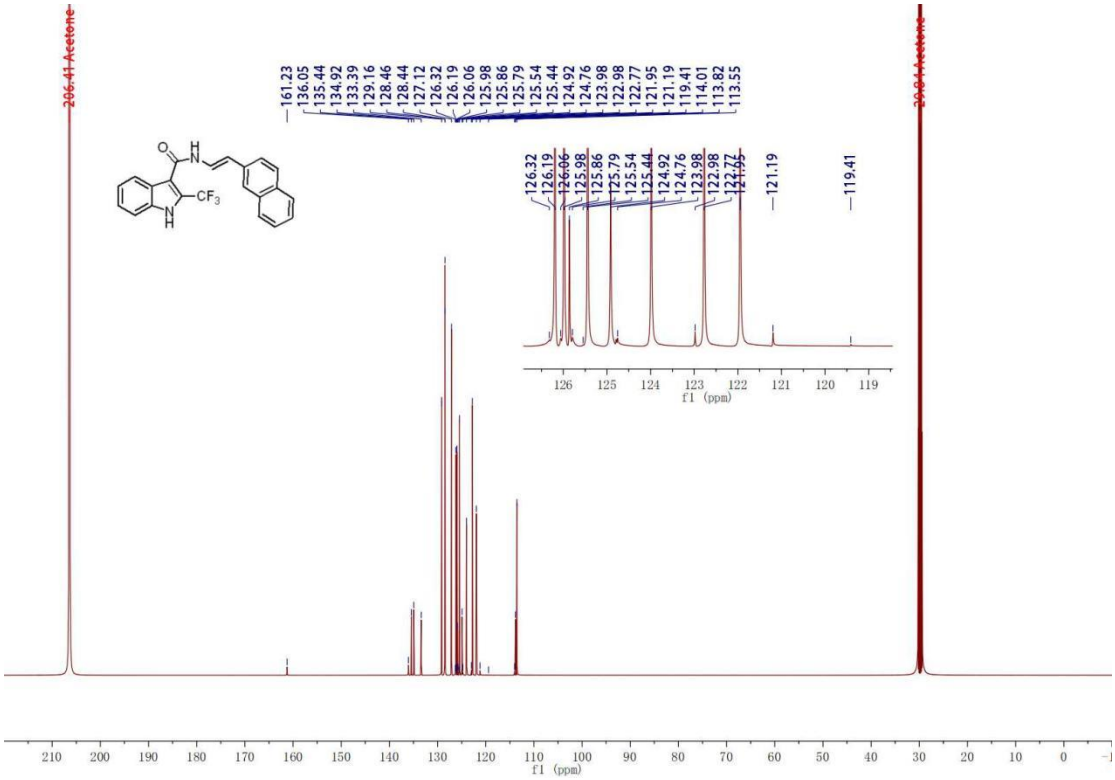
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3am



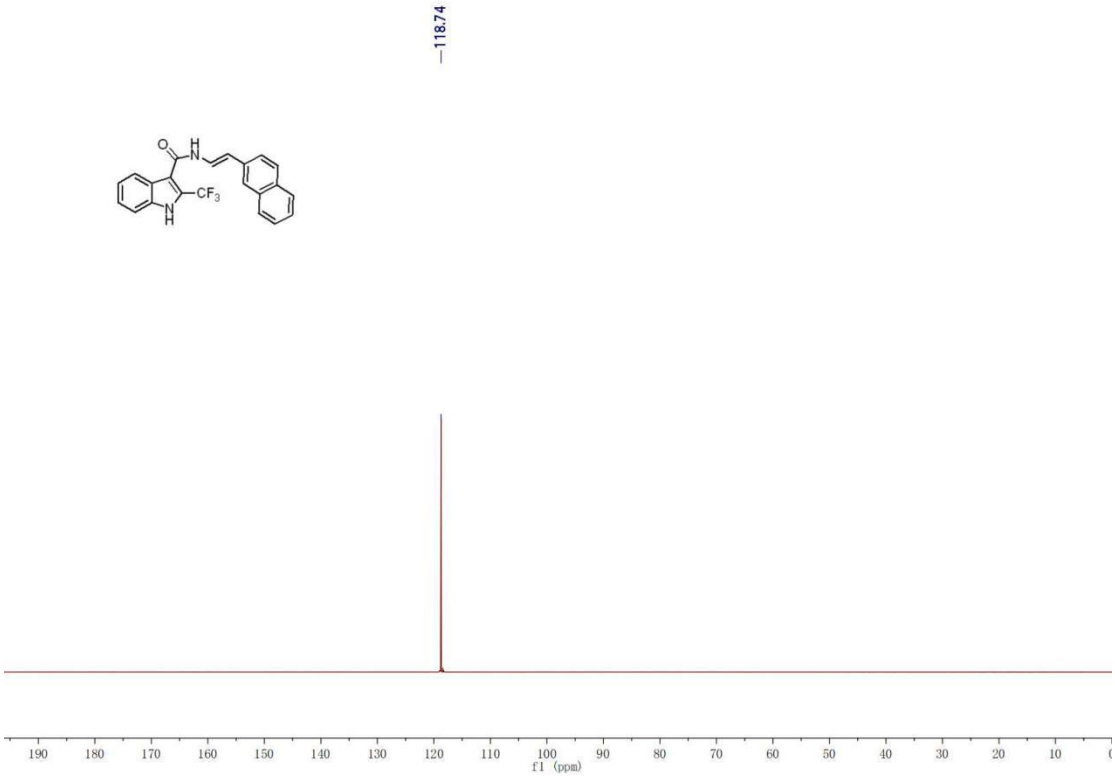
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 3an



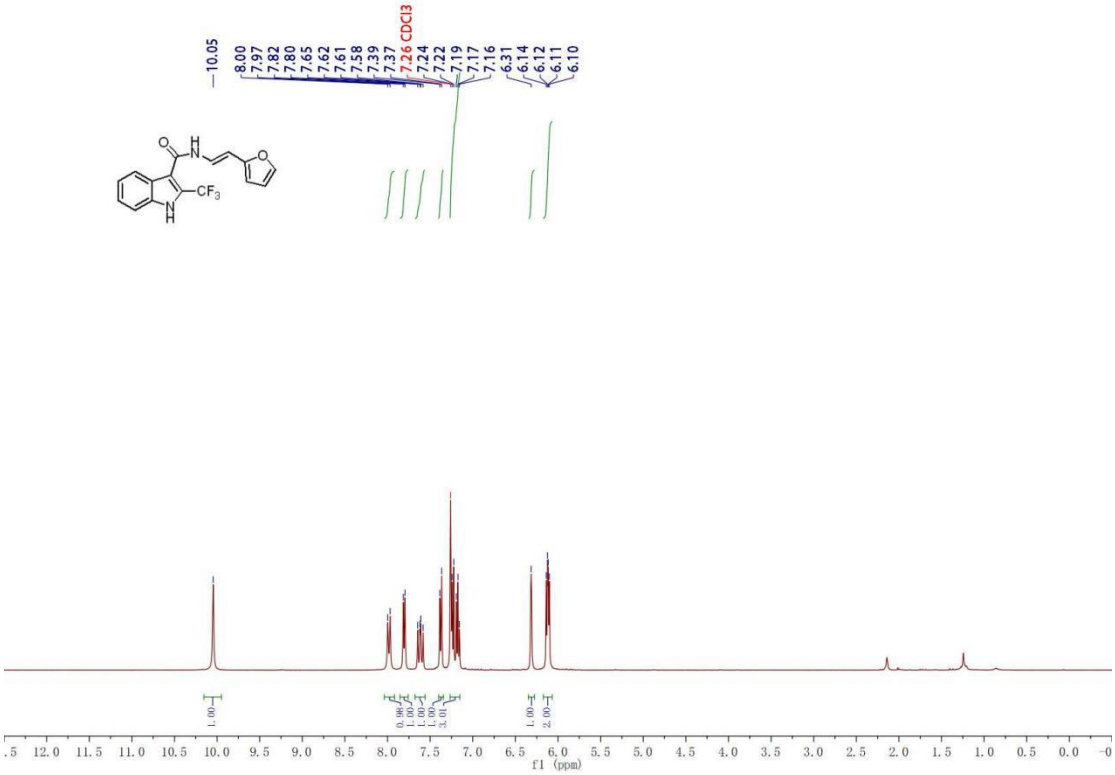
^{13}C NMR (150 MHz, Acetone-*d*6) spectrum of 3an



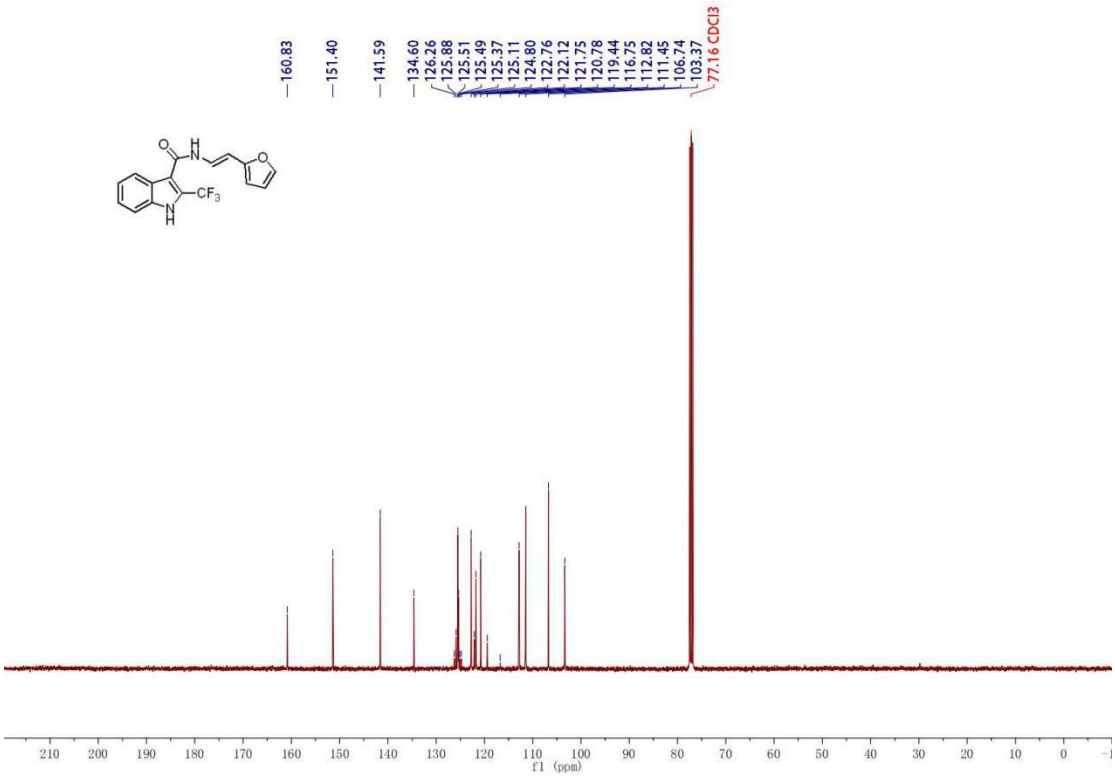
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 3an



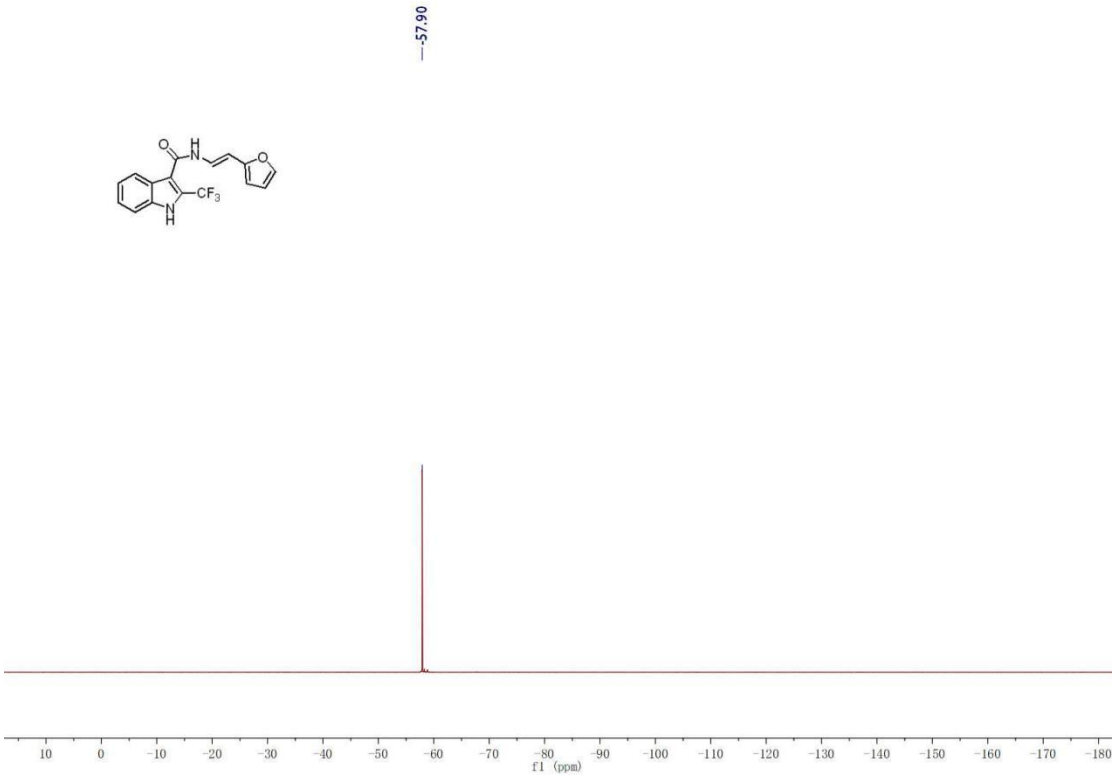
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ao



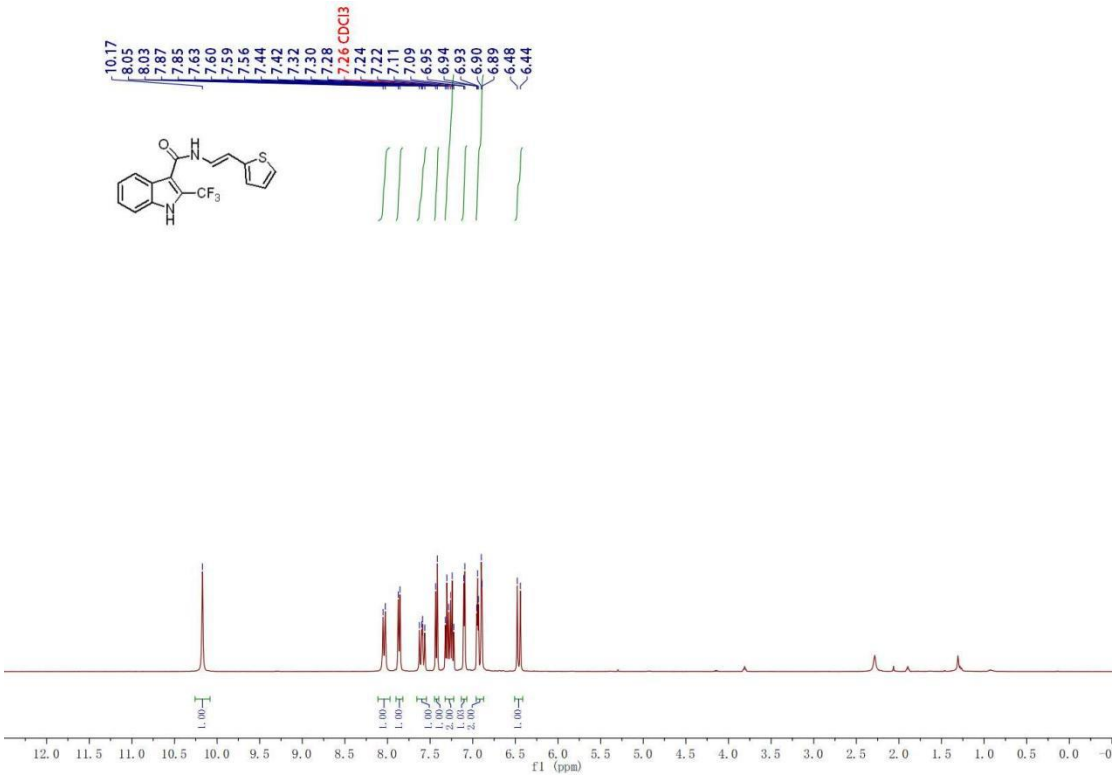
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ao



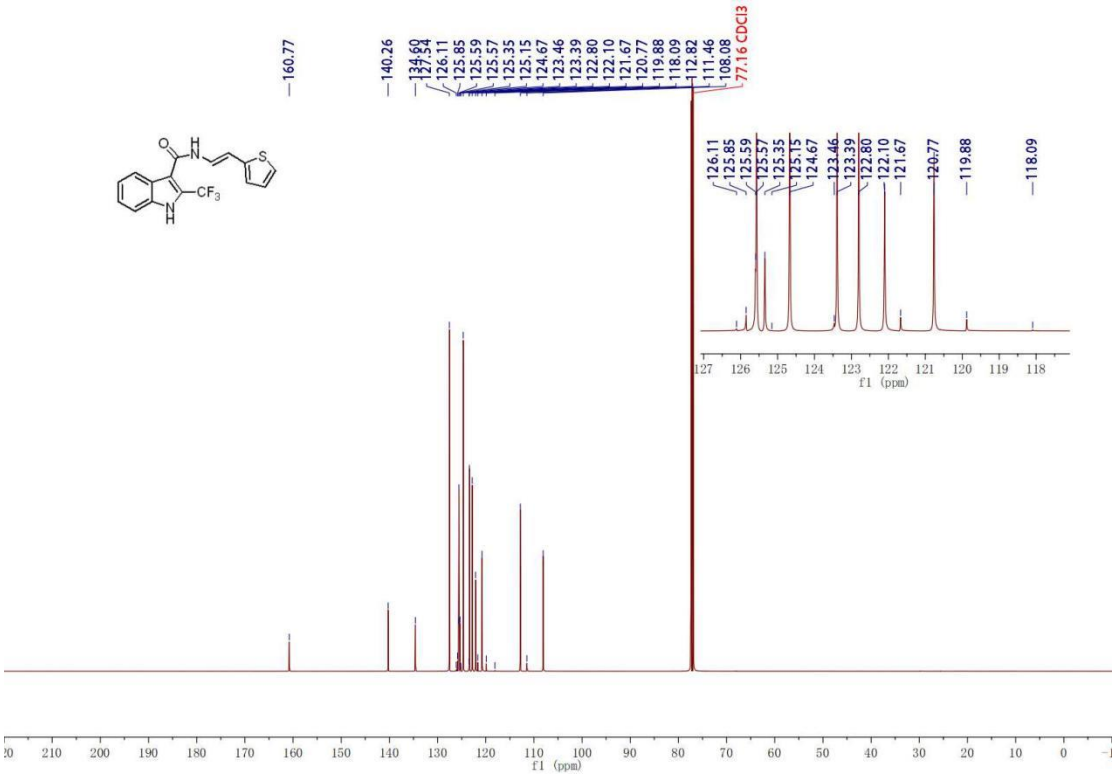
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ao



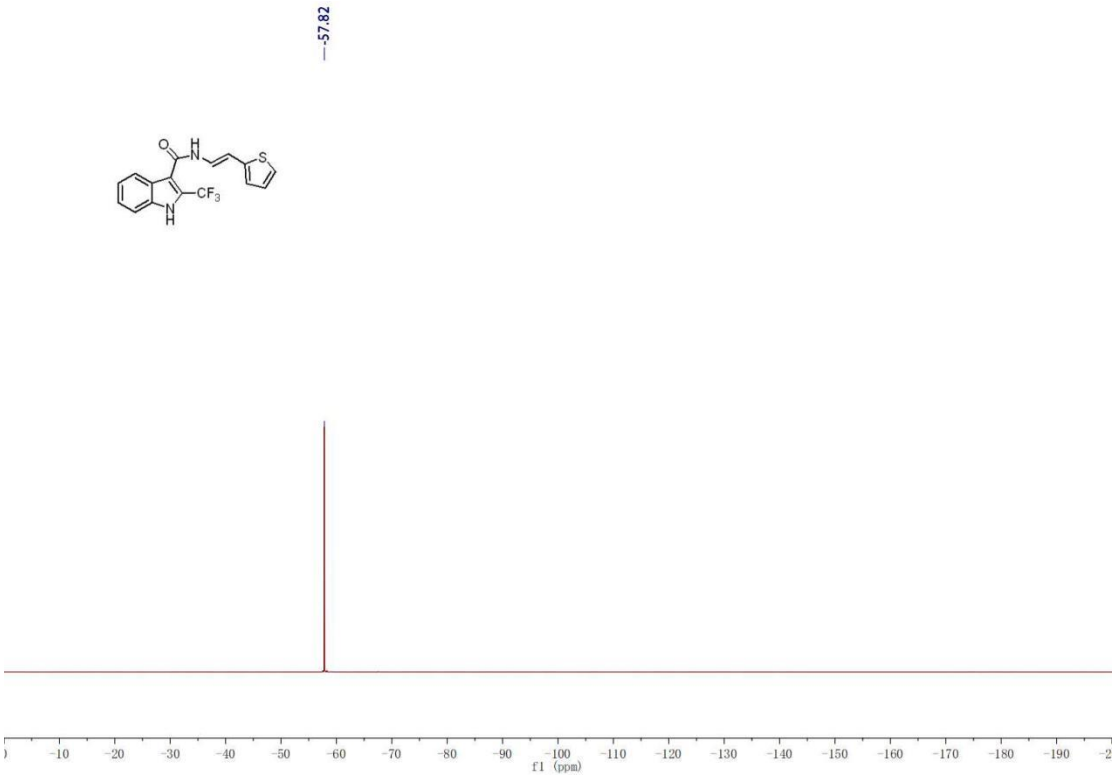
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ap



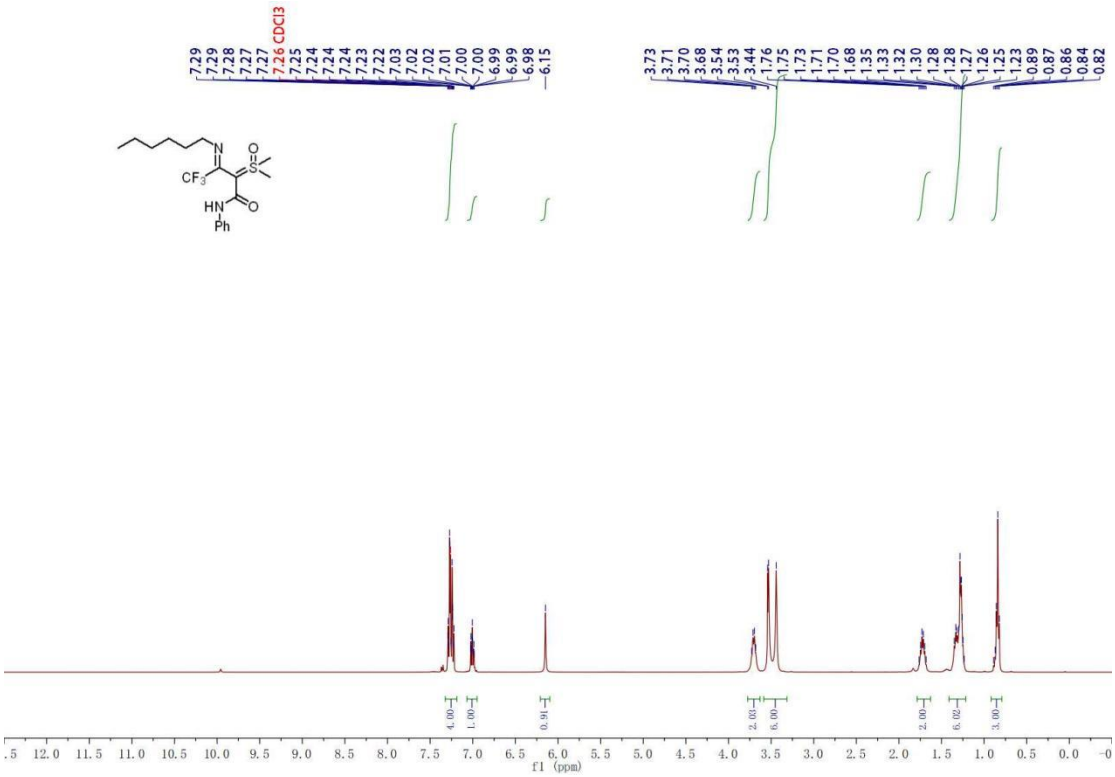
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ap



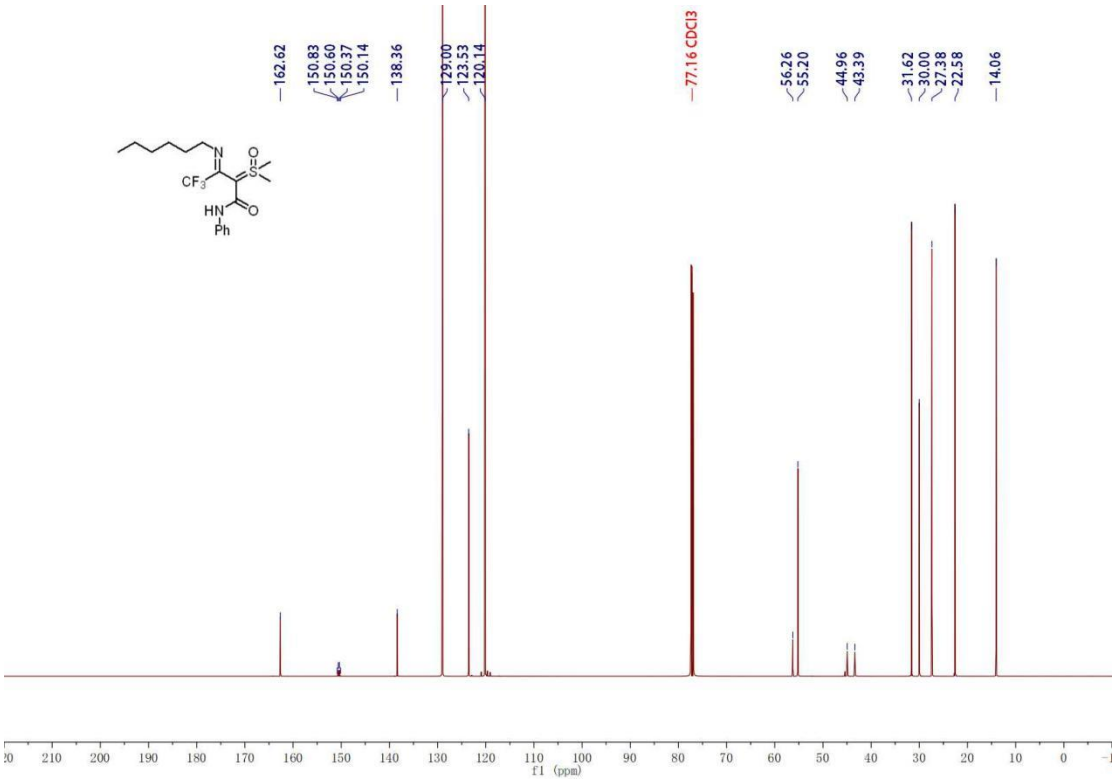
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ap



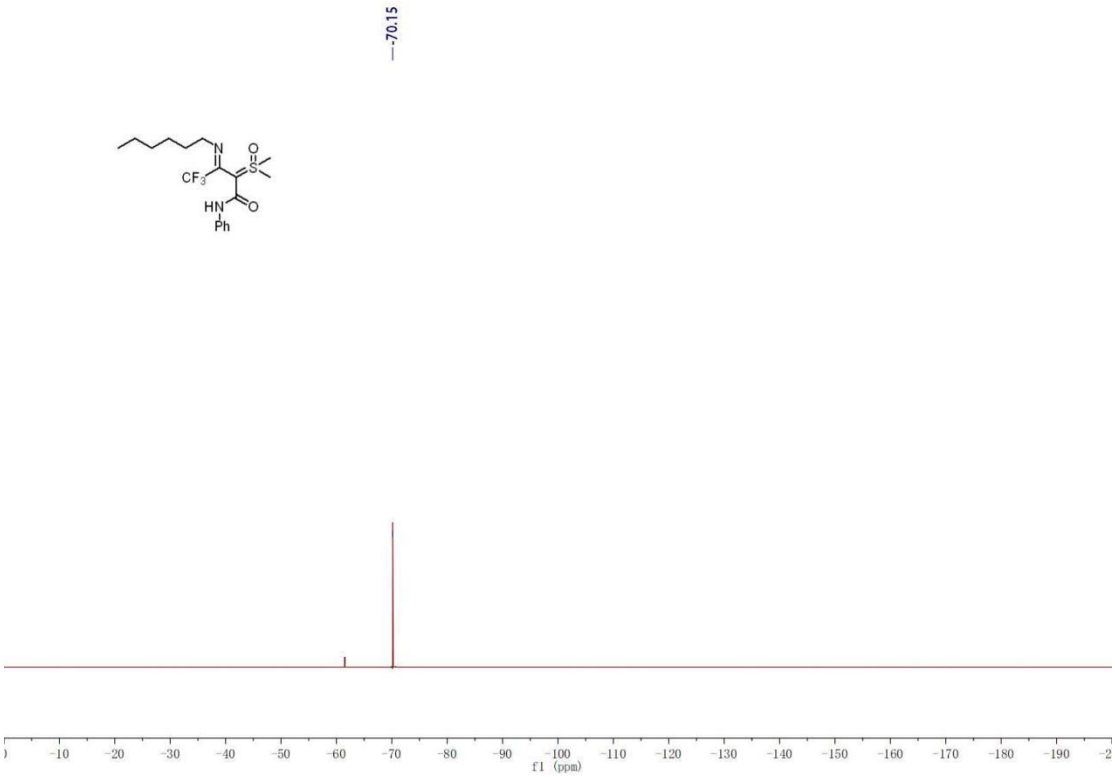
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3qb'



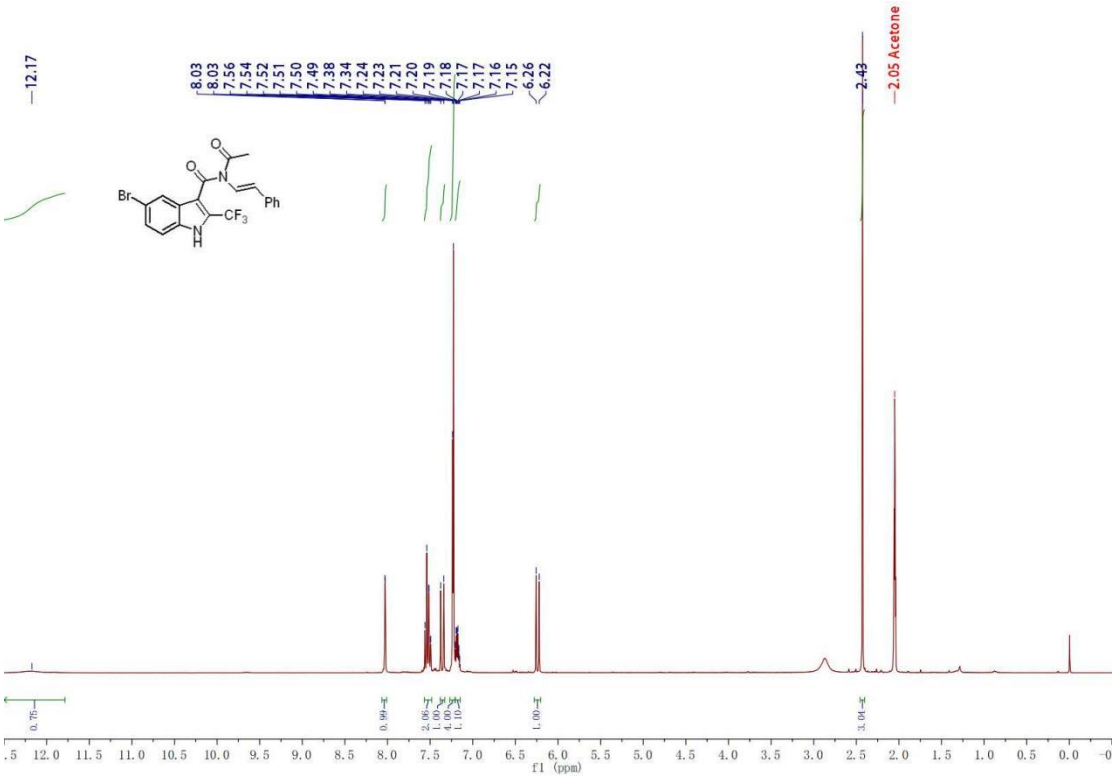
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3qb'



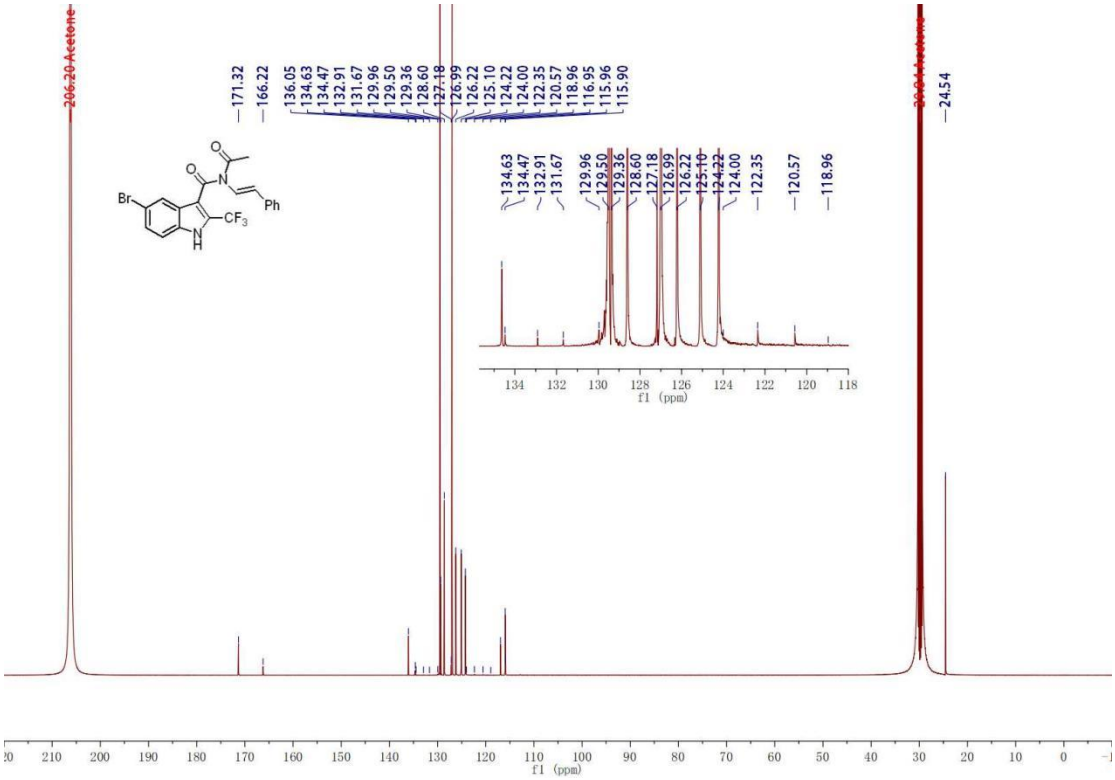
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3qb'



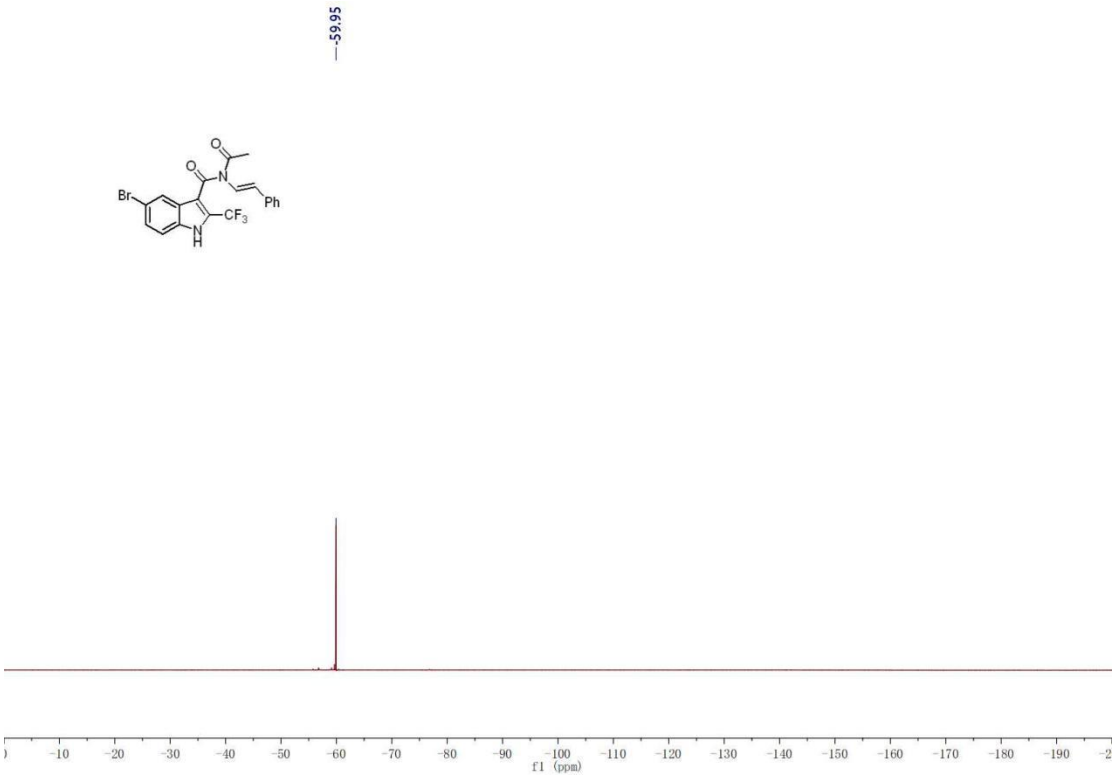
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 4ea



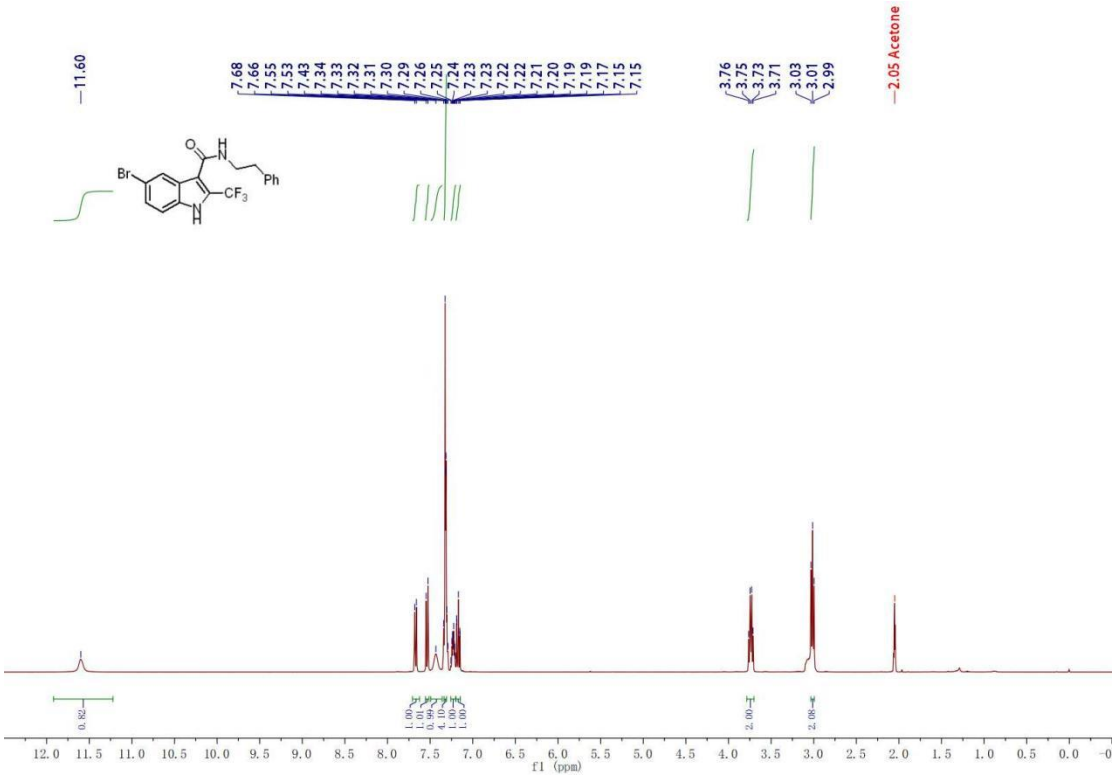
^{13}C NMR (150 MHz, Acetone-*d*6) spectrum of 4ea



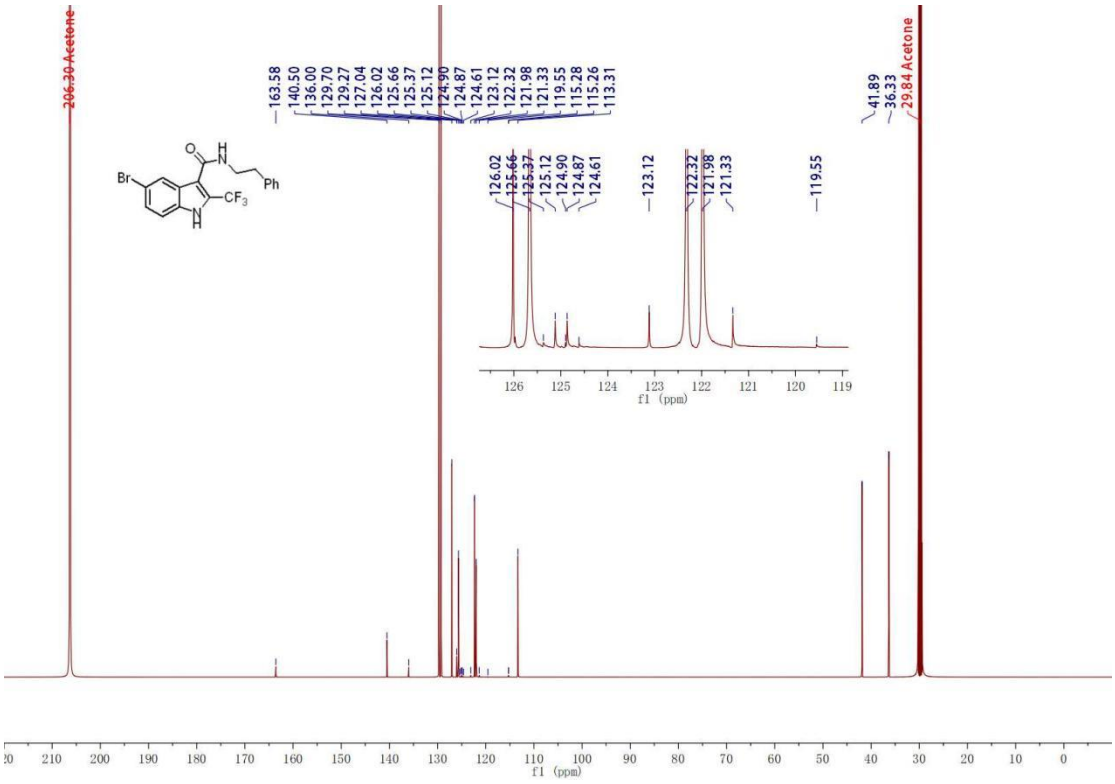
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 4ea



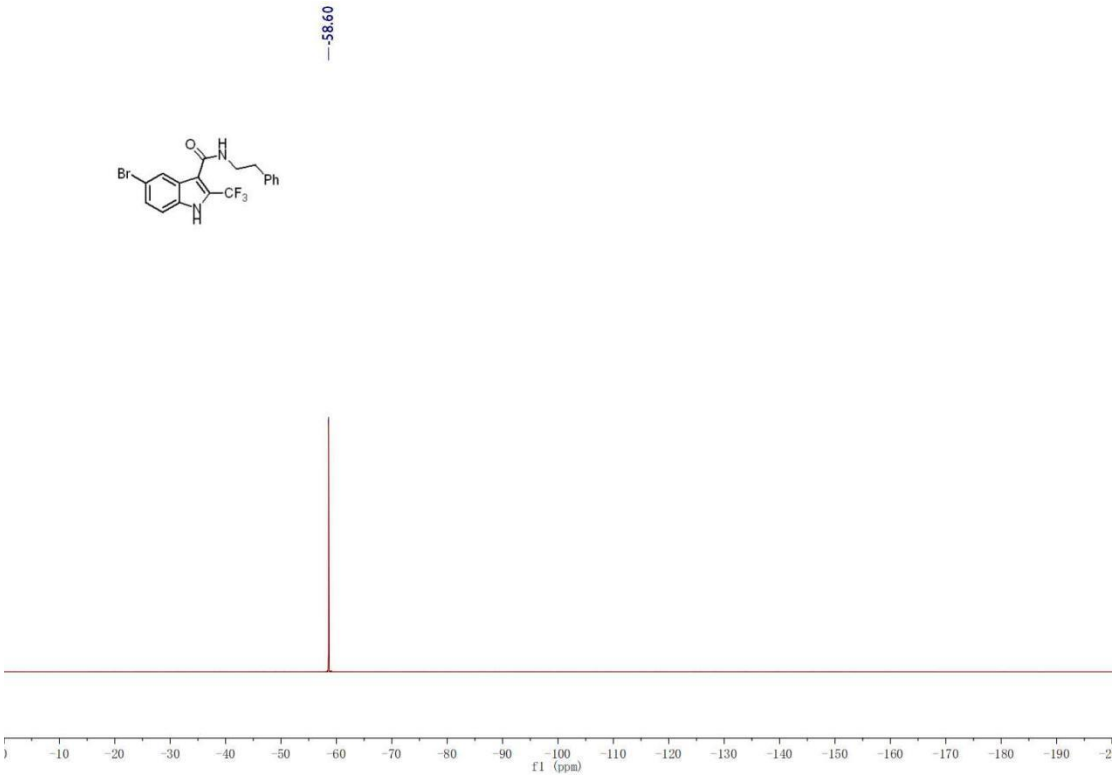
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 5ea



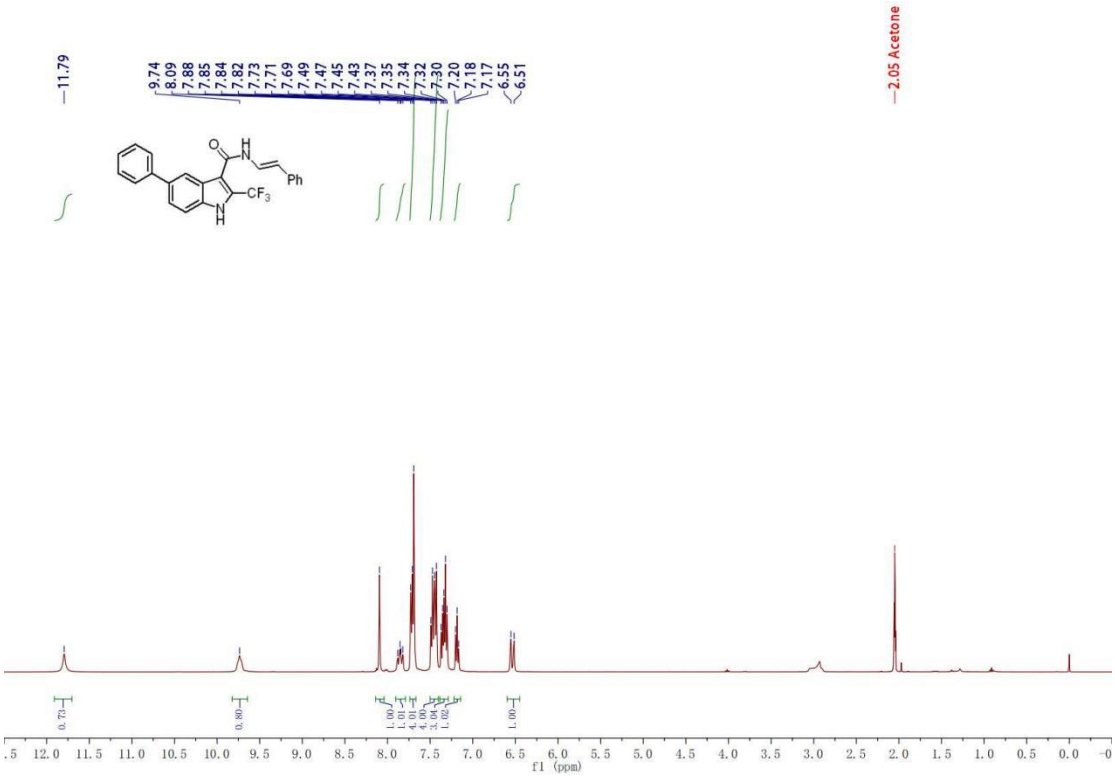
^{13}C NMR (150 MHz, Acetone-*d*6) spectrum of 5ea



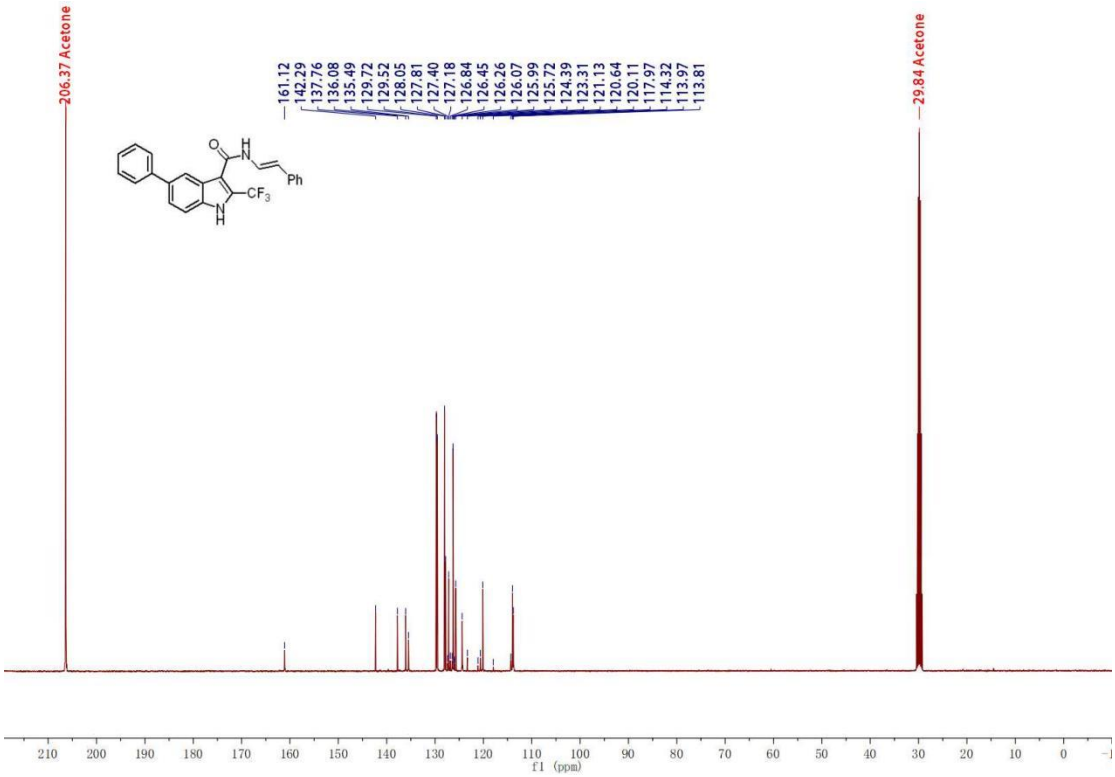
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 5ea



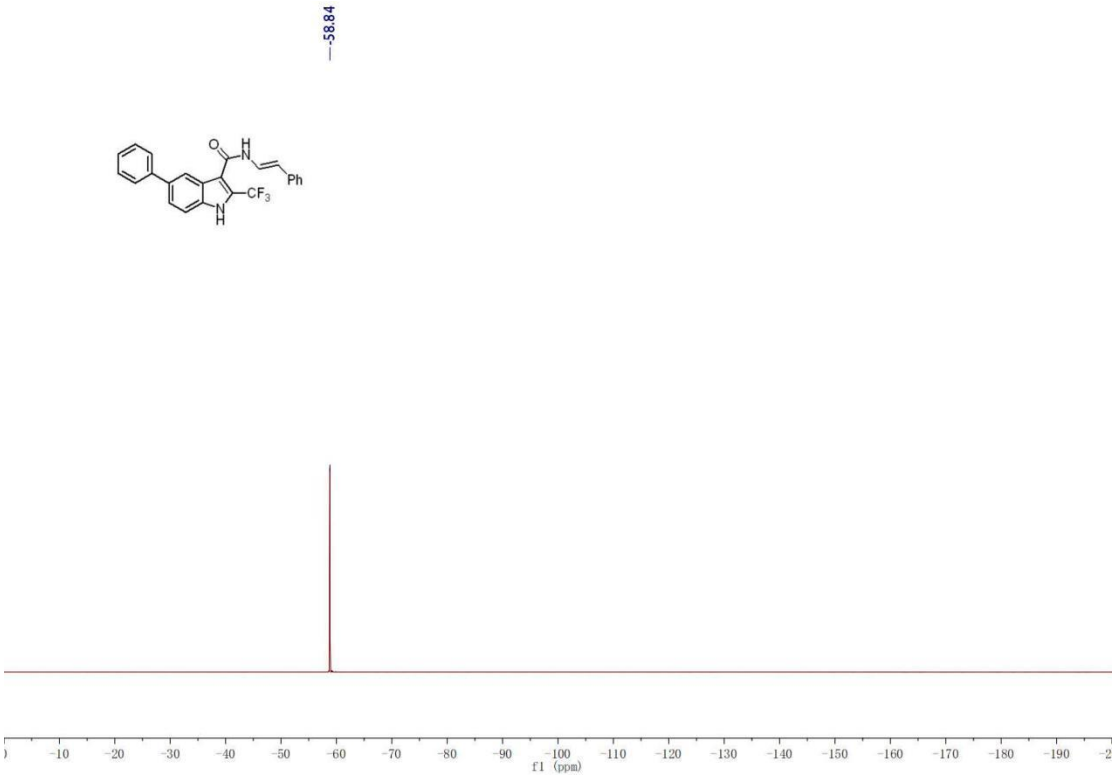
^{1}H NMR (400 MHz, Acetone-*d*6) spectrum of 6ea



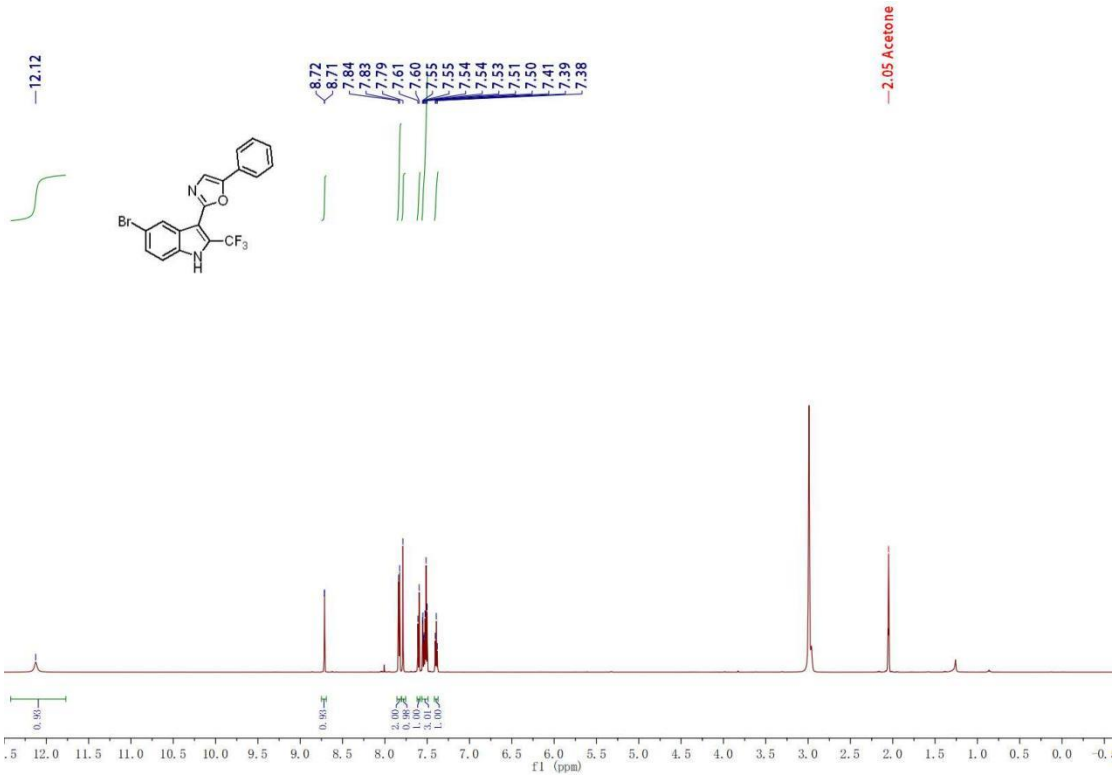
^{13}C NMR (100 MHz, Acetone-*d*6) spectrum of 6ea



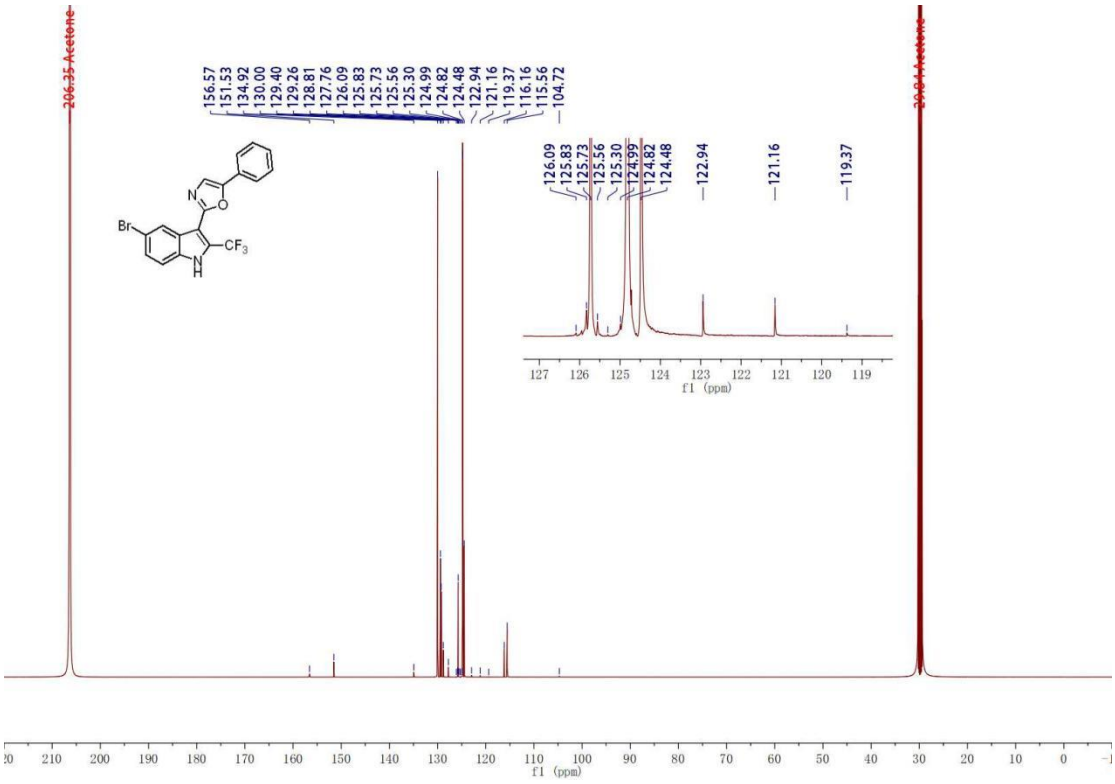
^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 6ea



^{1}H NMR (600 MHz, Acetone-*d*6) spectrum of 7ea



^{13}C NMR (150 MHz, Acetone-*d*6) spectrum of 7ea



^{19}F NMR (376 MHz, Acetone-*d*6) spectrum of 7ea