Supporting Information

Rhodium(III)-Catalyzed Regioselective C2-Alkenylation of Indoles with CF^3-Imidoyl Sulfoxonium Ylides to Give Multi-Functionalized Enamines using Migratable Directing Group

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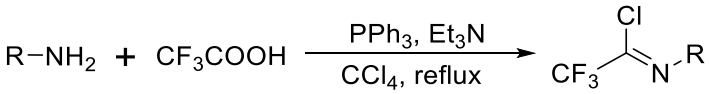
Contents

1. General Information

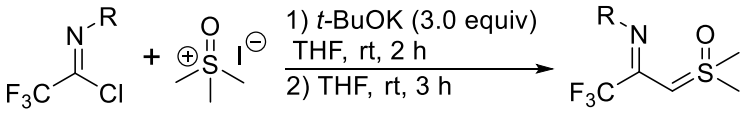
Unless otherwise noted, all reactions were carried out under N_2 atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. ^{1}NMR spectra were recorded on a Bruker Avance operating at for ^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and $CDCl_3$ (^{1}H NMR δ 7.26, ^{13}C NMR δ 77.16) or DMSO-D_6 (^{1}H NMR δ 2.50, ^{13}C NMR δ 39.5) as solvent. All coupling constants (*J*) are reported in Hz. 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. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or Waters TOFMS GCT Premier using EI or ESI ionization. Melting points were measured with WRR digital point apparatus and not corrected.

1.1 Preparation of Fluorinated Imidoyl Chlorides[1]



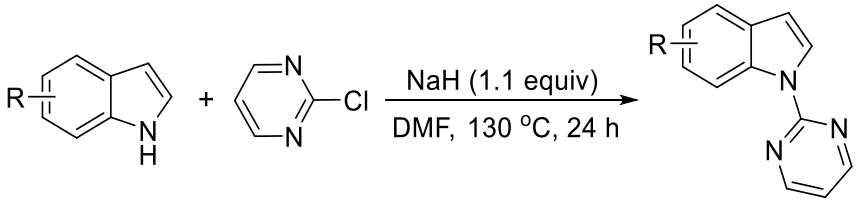
A 100 mL two-necked flask equipped with a septum cap, a condenser, and a Teflon-coated magnetic stir bar was charged with PPh_3 (9.84 g, 37.5 mmol), Et_3N (2.1 mL, 15 mmol), CCl_4 (20.0 mL), and TFA (1.2 mL, 15 mmol). After the solution was stirred for about 10 min (ice bath), amine (15 mmol) dissolved in CCl_4 (20.0 mL) was added. The mixture was then refluxed under stirring (3 h). After the reaction was completed, residual solid Ph_3PO, PPh_3 and Et_3N-HCl were washed with petroleum ether several times. Then the petroleum ether was filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel or neutral alumina to afford the corresponding product.

1.2 Preparation of CF_3-Imidoyl Sulfoxonium Ylides[2]



Trimethylsulfoxonium iodide (30 mmol, 3.0 equiv) was suspended in THF (150 mL) in a 250 mL round bottom flask, *t*-BuOK (30 mmol, 3.0 equiv) was added and the mixture was stirred at room temperature for 2 hours. Then, fluorinated imidoyl chloride (10 mmol, 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 (petroleum ether/EtOAc = 2 : 1) afforded products.

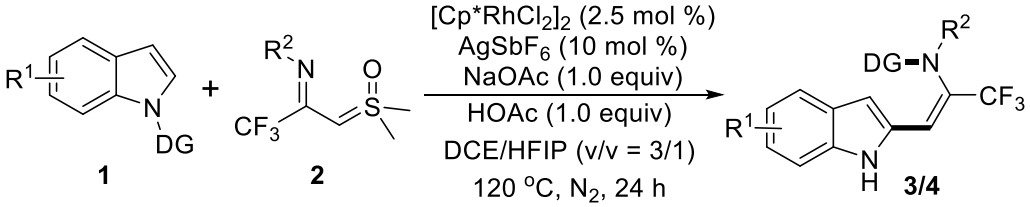
1.3 Preparation of *N*-(Pyrimidin-2-yl)-1H-indoles[3]



To an oven-dried Schlenk tube equipped with a magnetic stirring was added indole (1171 mg, 10 mmol) in DMF (25 mL). Then, NaH (60% dispersion in mineral oil, 440 mg, 11 mmol) was added in portions at 0 °C under stirring. After stirring for 30 min at 0 °C, 2-chloropyrimidine (1363 mg, 12 mmol) was added, and the mixture was stirred at 130 °C for 24 h. The mixture was then cooled to ambient temperature, poured into water (100 mL), and extracted with ethyl acetate (3 × 10 mL). The organic phase was combined and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the crude product was chromatographed on silica gel (petroleum ether/EtOAc: 5/1) to give the *N*-(pyrimidin-2-yl)-1H-indole products.

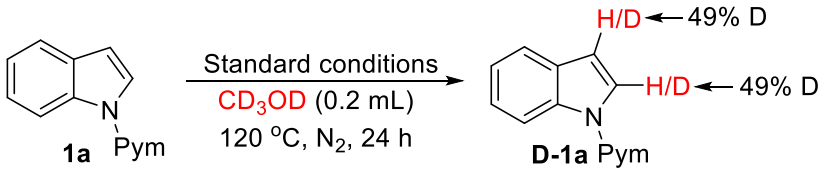
2. Experimental Procedures

2.1 General Procedure for the Synthesis of Products 3/4

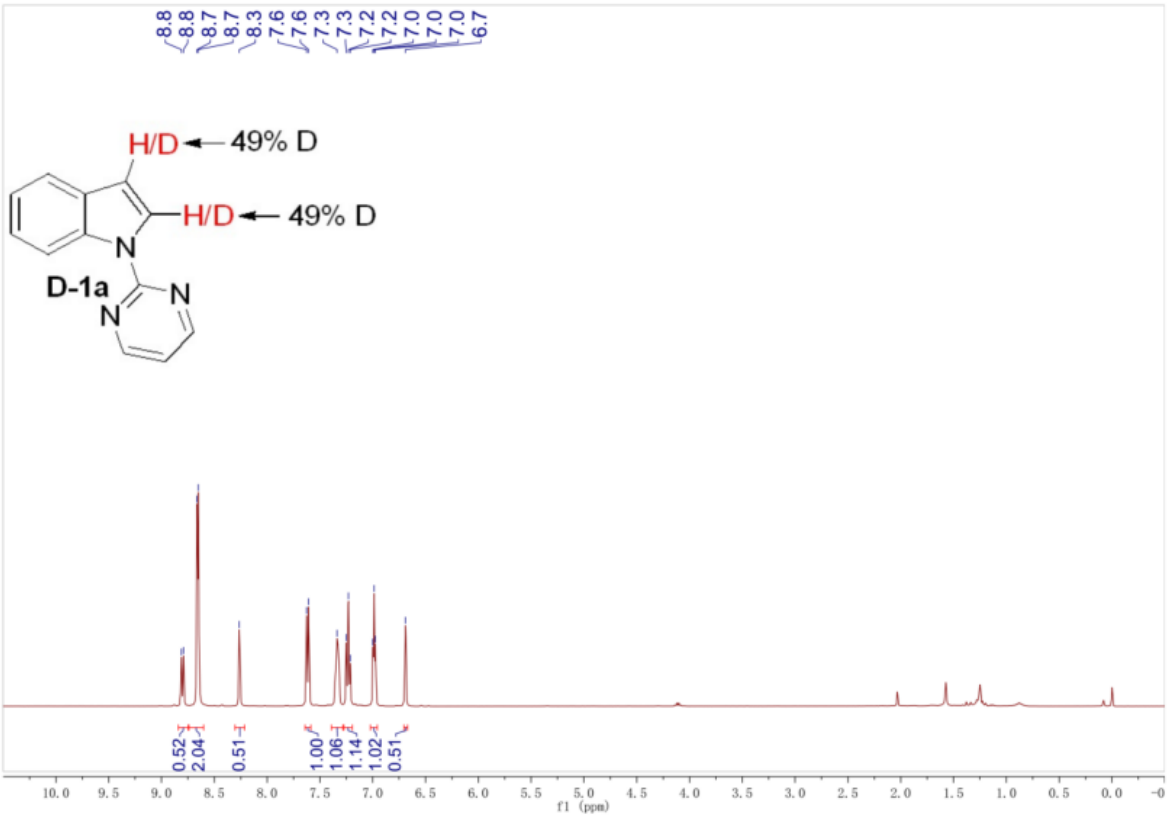


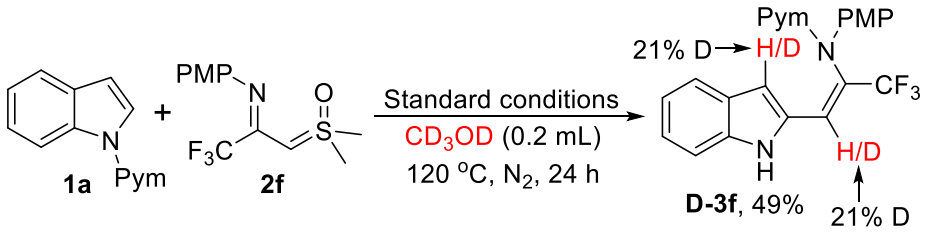
Under Nitrogen atmosphere, *N*-(pyrimidin-2-yl)-1*H*-indole **1** (0.2 mmol, 1.0 equiv), CF_3-imidoyl sulfoxonium ylides (TFISYs) **2** (0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 1.0 equiv), HOAc (12.0 mg, 1.0 equiv), DCE (1.5 mL) (extra dry) and HFIP (0.5 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 120 °C (oil bath) for 24 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the products **3/4**.

2.2 H/D Exchange Experiments

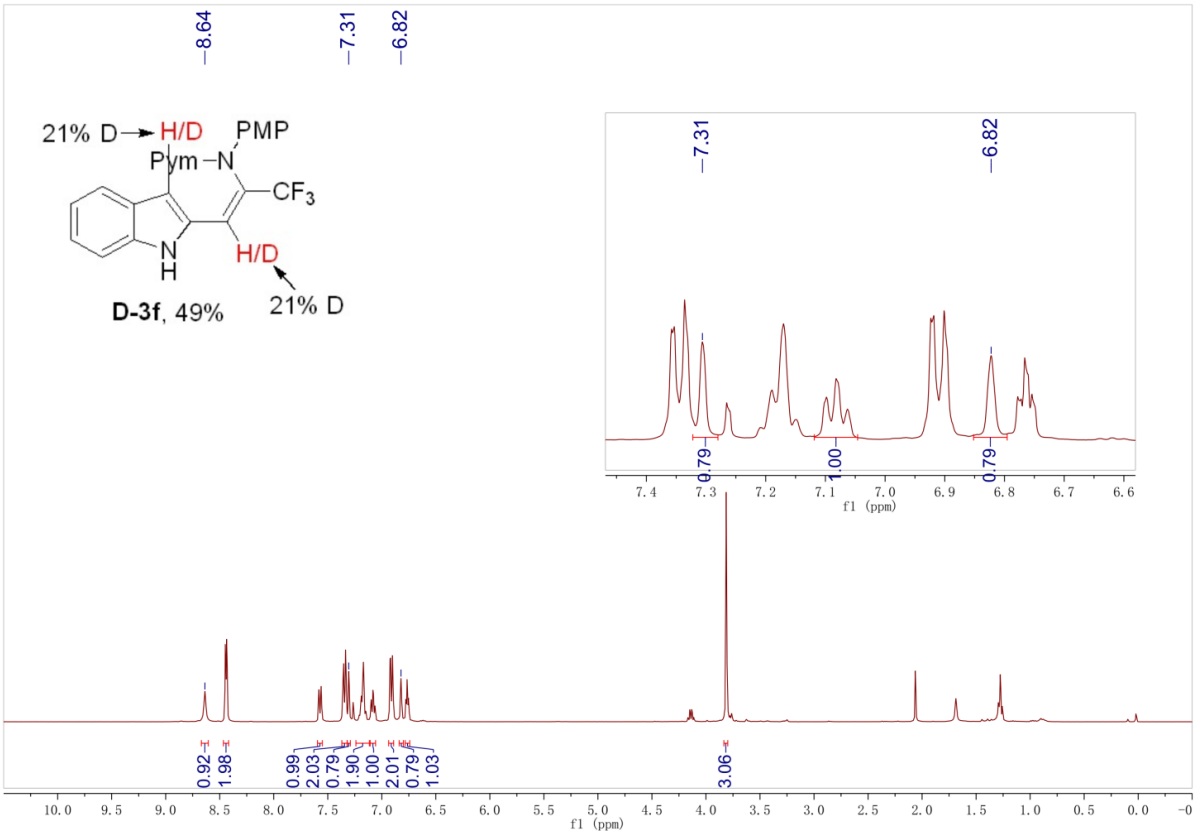


Under Nitrogen atmosphere, *N*-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 1.0 equiv), HOAc (12.0 mg, 1.0 equiv), DCE (1.5 mL) (extra dry), HFIP (0.5 mL) and CD_3OD (0.2 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 120 °C (oil bath) for 24 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the deuterated product **D-1a**. The D-incorporation in **D-1a** was determined by ^{1}H-NMR spectroscopy.

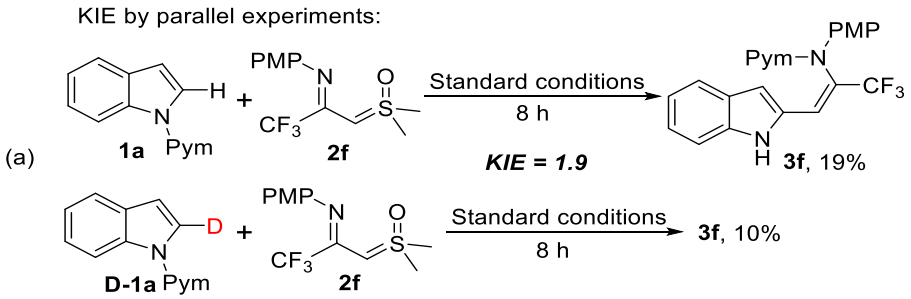




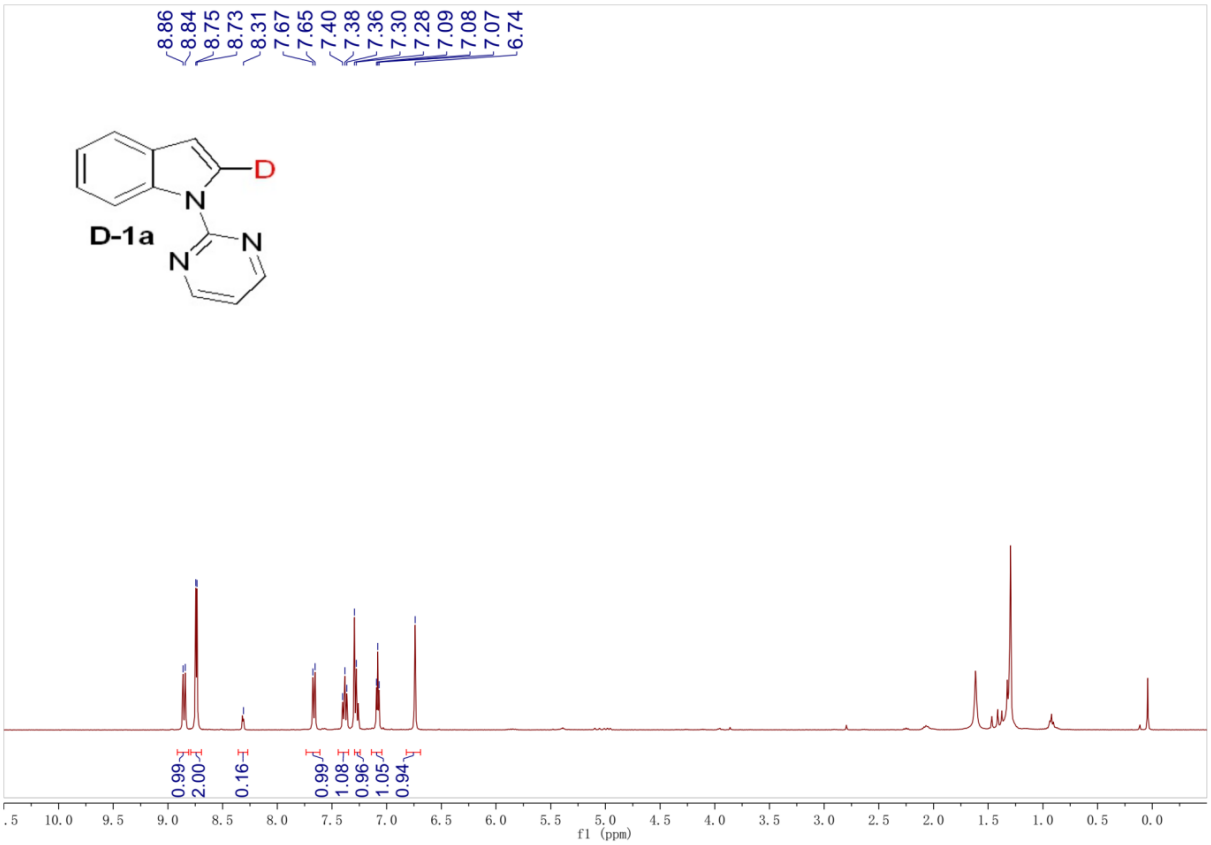
Under Nitrogen atmosphere, 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), and CF_3-imidoyl sulfoxonium ylides (TFISYs) **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 1.0 equiv), HOAc (12.0 mg, 1.0 equiv), DCE (1.5 mL) (extra dry), HFIP (0.5 mL) and CD_3OD (0.2 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 120 °C (oil bath) for 24 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the deuterated product **D-3f** (40.2 mg, 49%). The D-incorporation in **D-3f** was determined by ^{1}H-NMR spectroscopy.

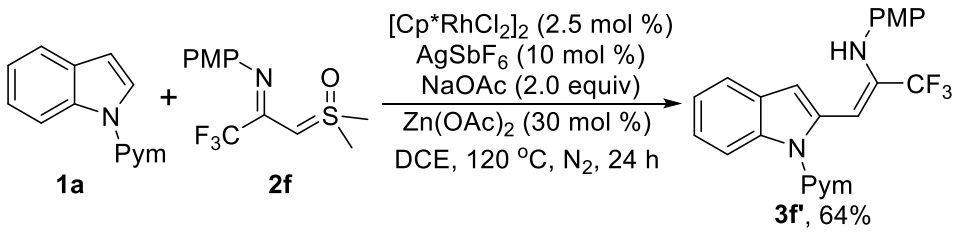


2.3 Control Experiments

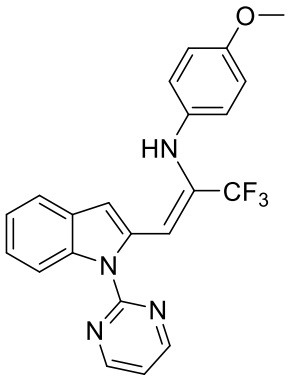


(a) Under Nitrogen atmosphere, **1a** or **D-1a** (39.4 mg, 0.2 mmol, 1.0 equiv), and CF_3-imidoyl sulfoxonium ylides (TFISYs) **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 1.0 equiv), HOAc (12.0 mg, 1.0 equiv), DCE (1.5 mL) (extra dry), HFIP (0.5 mL) were added to an oven-dried 15 mL *In-Ex* tube, respectively. Then the tube was sealed and the mixture was stirred at 120 °C (oil bath) for 8 h. The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **3f** as a white solid (15.6 mg, 19%) and (8.2 mg, 10%), respectively.





Under Nitrogen atmosphere, *N*-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), CF_3-imidoyl sulfoxonium ylide **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (32.8 mg, 0.4 mmol, 2.0 equiv), $Zn(OAc)_2$ (11.0 mg, 30 mol %) and DCE (2.0 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 120 °C (oil bath) for 24 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the product **3f'** (52.5 mg, 64%).



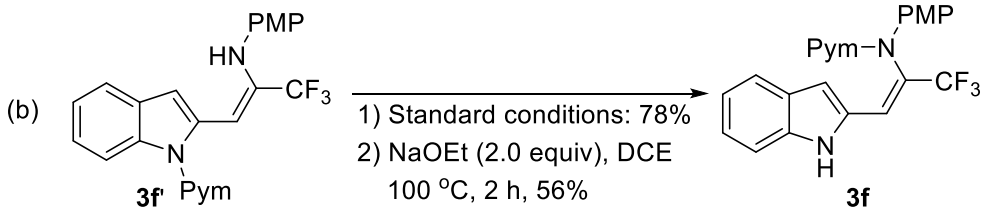
(*Z*)-4-methoxy-N-(3,3,3-trifluoro-1-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)prop-1-en-2-yl)aniline (**3f'**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.8 Hz, 2H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.28 (s, 1H), 7.25 (t, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 4.9 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.77 (s, 1H), 6.71 (d, *J* = 8.9 Hz, 2H), 5.28 (s, 1H), 3.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 158.0, 154.4, 136.9, 135.2, 132.1, 129.3, 125.9 (C-F, q, $^{2}J_{(C-F)}$ = 31.6 Hz), 124.5, 122.9 (C-F, q, $^{1}J_{(C-F)}$ = 274.8 Hz), 122.4, 121.1, 118.3, 117.6, 114.6, 113.9, 111.9 (C-F, q, $^{3}J_{(C-F)}$ = 4.3 Hz), 110.9, 55.6.

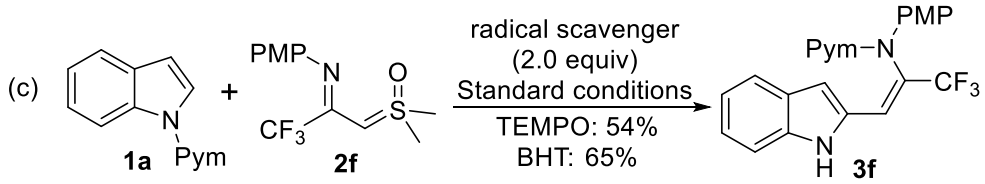
^{19}F NMR (377 MHz, $CDCl_3$) δ -68.9.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{18}F_3N_4O^+$ 411.1427, found 411.1431.

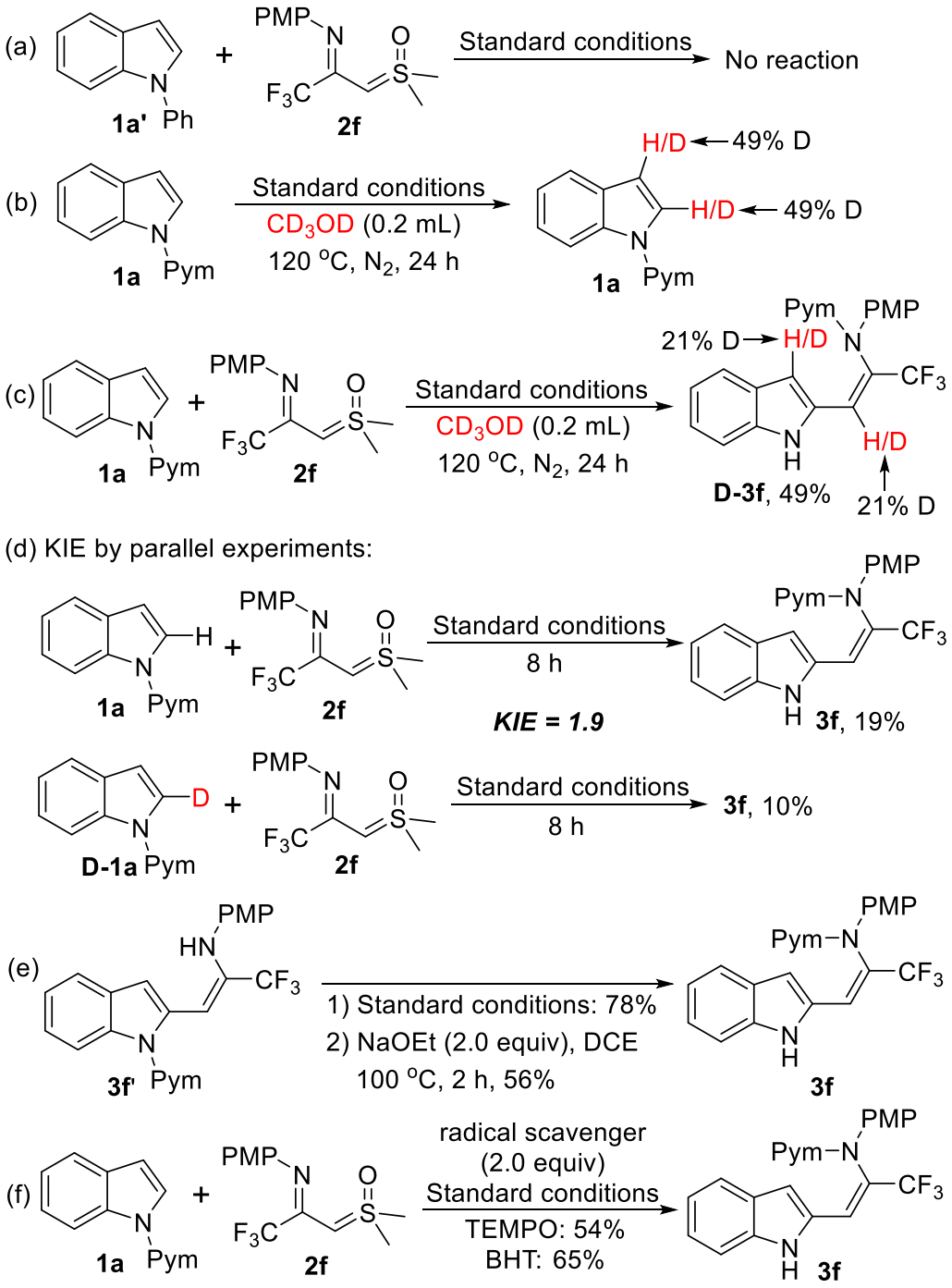


(b) 1) Under Nitrogen atmosphere, **3f'** (82.0 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 1.0 equiv), HOAc (12.0 mg, 1.0 equiv), DCE (1.5 mL) (extra dry), HFIP (0.5 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 120 °C (oil bath) for 24 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **3f** (64.0 mg, 78%).

(b) 2) Under Nitrogen atmosphere, **3f'** (82.0 mg, 0.2 mmol, 1.0 equiv), NaOEt (27.2 mg, 0.4 mmol, 2.0 equiv), DCE (2.0 mL) (extra dry), were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 2 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3× 10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **3f** (46.2 mg, 56%).

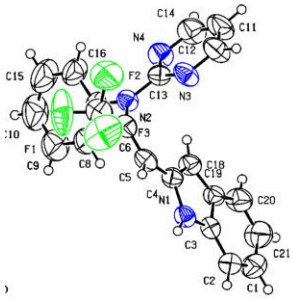


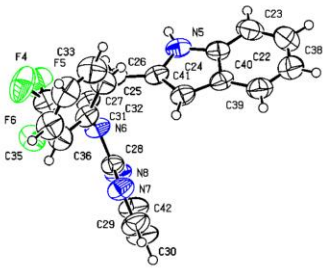
Under Nitrogen atmosphere, **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), and CF_3-imidoyl sulfoxonium ylides (TFISYs) **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol 1.0 equiv), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv) or BHT (88.0 mg, 0.4 mmol, 2.0 equiv), DCE (1.5 mL) (extra dry) and HFIP (0.5 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 120 °C (oil bath) for 24 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the products **3f** as a white solid (44.3 mg, 54% for TEMPO) and (53.3 mg, 65% for BHT), respectively.

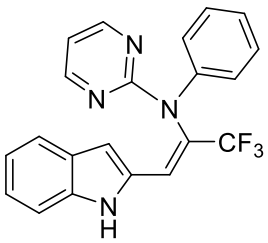


Scheme S1 Mechanistic investigations.

3 The Crystal Structure of Product 3a







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(a) Method for crystal growth of 3a

0.05 mmol of **3a** was dissolved in 2.0 mL of solvent (Petroleum ether/EtOAc/DCM = 3/1/1) in 3.0 mL sample bottle. After about 12 hours of natural volatilization at room temperature, single crystal could be obtained.

(b) Crystallographic structure analysis of 3a

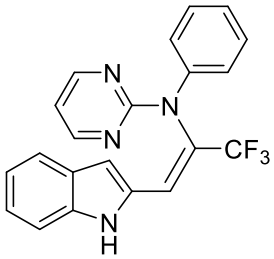
A suitable single crystal was mounted on a Xcalibur, Atlas, Gemini ultra at 296(2), 100.01(10), 296(2) and 296 K, using Mo Kα radiation (λ = 0.71073 Å). The intensity data were collected with CrysAlisPro program and reduced by CrysAlisPro program. The structure was solved by direct methods, expended by difference Fourier syntheses and refined by Full-matrix squares on F2 using SHELXL program packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms. Details of the X-Ray experiments and crystal data are summarized in **Table S1**.

Table S1. Crystal data and structure refinement for **3a**

Empirical formula	$C_{21}H_{15}F_3N_4$
Formula weight	380.37
Temperature/K	296(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	22.365(11)
b/Å	8.009(4)

c/Å	22.159(11)
α/°	90
β/°	108.930(7)
γ/°	90
Volume/Å^3	3754(3)
Z	8
ρ_{calc}g/cm^3	1.346
μ/mm^{-1}	0.103
F(000)	1568.0
Crystal size/mm^3	0.19 × 0.14 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.736 to 50.498
Index ranges	-26 ≤ h ≤ 26, -9 ≤ k ≤ 9, -25 ≤ l ≤ 26
Reflections collected	28948
Independent reflections	6812 [R_{int} = 0.1041, R_{sigma} = 0.1000]
Data/restraints/parameters	6812/0/505
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0616, wR_2 = 0.1273
Final R indexes [all data]	R_1 = 0.1603, wR_2 = 0.1663
Largest diff. peak/hole / e Å^{-3}	0.20/-0.33

4 Characterization Data of the Corresponding Products



(*Z*)-*N*-phenyl-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**3a**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2a** (105.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **3a** as a white solid (63.1 mg, 83%).

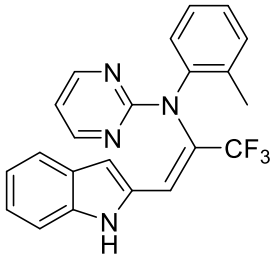
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.45 (d, *J* = 4.8 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.31 (m, 5H), 7.28 – 7.21 (m, 1H), 7.20 – 7.13 (m, 2H), 7.06 (ddd, *J* = 8.0, 6.0, 2.0 Hz, 1H), 6.82 (s, 1H), 6.79 (t, *J* = 4.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 158.6, 140.9, 137.6, 130.2, 129.3, 127.4, 126.3, 125.8 (C-F, q, $^2J_{(C\text{-}F)}$ = 33.7 Hz), 124.6, 124.5, 124.4 (C-F, q, $^3J_{(C\text{-}F)}$ = 3.7 Hz), 122.6 (C-F, q, $^1J_{(C\text{-}F)}$ = 276.6 Hz), 121.4, 120.6, 114.6, 111.2, 110.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.6.

M.p. 184.2-186.1 °C

HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{16}F_3N_4^+$ 381.1322, found 381.1320.



(*Z*)-*N*-(*o*-tolyl)-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**3b**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (110.9 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **3b** as a white solid (58.4 mg, 74%).

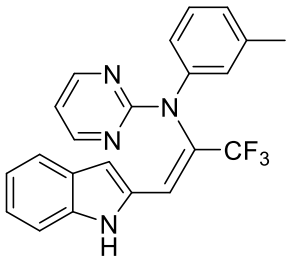
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.42 (d, *J* = 4.8 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.30 (s, 1H), 7.25 – 7.21 (m, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.16 – 7.10 (m, 2H), 7.04 (ddd, *J* = 7.9, 6.0, 1.9 Hz, 2H), 6.79 (s, 1H), 6.75 (t, *J* = 4.8 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 158.7, 141.1, 139.5, 137.8, 130.5, 129.3, 127.6, 127.5, 126.0 (C-F, q, $^2J_{(C-F)}$ = 33.5 Hz), 125.3, 124.6, 124.3 (C-F, q, $^3J_{(C-F)}$ = 3.6 Hz), 122.8 (C-F, q, ^1J = 278.1 Hz), 121.8, 121.5, 120.7, 114.6, 111.4, 110.5, 21.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.6.

M.p. 229.4-231.1 °C

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{18}F_3N_4^+$ 395.1478, found 395.1480.



(*Z*)-*N*-(*m*-tolyl)-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**3c**)

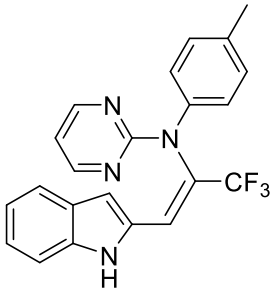
General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2c** (110.9 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **3c** as a white solid (63.1 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.42 (d, *J* = 4.1 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.30 (s, 1H), 7.30 – 7.13 (m, 5H), 7.04 (d, *J* = 5.9 Hz, 2H), 6.79 (s, 1H), 6,76 (t, *J* = 5.0 Hz, 1H) 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 158.7, 141.0, 139.5, 137.8, 130.5, 129.3, 127.5, 127.5, 126.0 (C-F, q, $^{2}J_{(C-F)}$ = 33.3 Hz), 125.3, 124.6, 124.3 (C-F, q, $^{3}J_{(C-F)}$ = 3.4 Hz), 122.8 (C-F, q, $^{1}J_{(C-F)}$ = 276.5 Hz), 121.8, 121.5, 120.7, 114.6, 111.4, 110.5, 21.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.6.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{18}F_3N_4^+$ 395.1478, found 395.1476.



(*Z*)-*N*-(*p*-tolyl)-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**3d**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2d** (110.9 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **3d** as a white solid (67.0 mg, 85%).

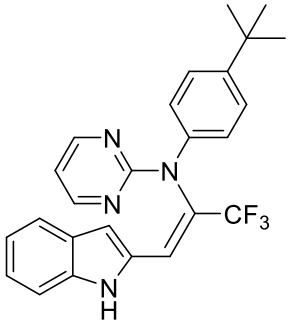
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.45 (d, *J* = 4.8 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 3H), 7.21 – 7.12 (m, 4H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.82 (s, 1H), 6.77 (t, *J* = 4.8 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 158.7, 138.4, 137.8, 136.5, 130.5, 130.2, 127.6, 126.1 (C-F, q, $^{2}J_{(C-F)}$ = 33.6 Hz), 124.8, 124.6, 124.2 (C-F, q, $^{3}J_{(C-F)}$ = 3.6 Hz), 121.5, 122.8 (C-F, q, $^{1}J_{(C-F)}$ = 277.4 Hz), 120.7, 114.5, 111.4, 110.4, 21.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.6.

M.p. 232.7-233.8 ºC

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{18}F_3N_4^+$ 395.1478, found 395.1480.



(*Z*)-*N*-(4-(tert-butyl)phenyl)-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**3e**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2e** (127.7 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **3e** as a white solid (63.7 mg, 73%).

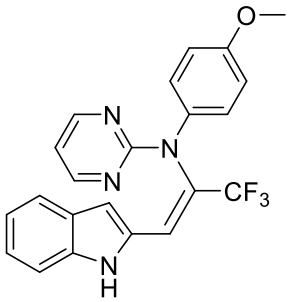
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.45 (d, *J* = 4.7 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.33 (m, 5H), 7.16 (s, 2H), 7.16 – 7.05 (m, 1H), 6.81 (s, 1H), 6.78 (t, *J* = 4.7 Hz, 1H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 158.7, 149.3, 138.3, 137.8, 130.5, 127.6, 126.4, 126.2 (C-F, q, $^2J_{(C\text{-}F)}$ = 33.8 Hz), 124.6, 124.4 (C-F, q, $^3J_{(C\text{-}F)}$ = 3.6 Hz), 124.1, 122.8 (C-F, q, $^1J_{(C\text{-}F)}$ = 278.0 Hz), 121.5, 120.7, 114.5, 111.4, 110.5, 34.7, 31.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.5.

M.p. 233.4-235.9 ºC

HRMS (ESI): $[M+H]^+$ calcd. for $C_{25}H_{24}F_3N_4^+$ 437.1948, found 437.1947.



(*Z*)-*N*-(4-methoxyphenyl)-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**3f**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.4) to give the titled product **3f** as a white solid (65.7 mg, 80%).

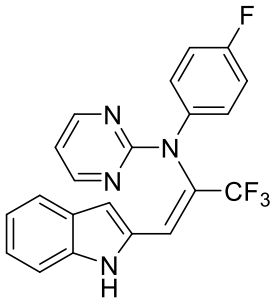
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.43 (d, *J* = 4.8 Hz, 2H),7.56 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.30 (s, 1H), 7.20 – 7.14 (m, 2H), 7.07 (ddd, *J* = 8.0, 6.0, 1.9 Hz, 1H), 6.92 – 6.88 (m, 2H), 6.81 (s, 1H), 6.76 (t, *J* = 4.8 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 158.8, 158.1, 137.7, 133.8, 130.5, 127.6, 126.6, 124.6, 126.2 (C-F, q, $^2J_{(C-F)}$ = 33.4 Hz), 124.0 (C-F, q, $^3J_{(C-F)}$ = 3.7 Hz), 122.8 (C-F, q, $^1J_{(C-F)}$ = 276.7 Hz), 121.5, 120.7, 114.8, 114.3, 111.4, 110.3, 55.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.7.

M.p. 222.3-224.1 °C

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{18}F_3N_4O^+$ 411.1427, found 411.1429.



(*Z*)-*N*-(4-fluorophenyl)-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**3g**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2g** (112.5 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **3g** as a white solid (63.7 mg, 80%).

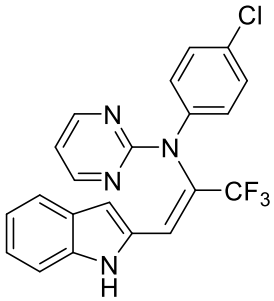
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.45 (d, *J* = 4.8 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.35 (m, 2H), 7.33 (s, 1H), 7.22 – 7.16 (m, 2H), 7.10 – 7.04 (m, 3H), 6.82 – 6.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (C-F, d, $^3J_{(C-F)}$ = 6.3 Hz), 159.7, 158.8, 137.7, 137.0 (C-F, d, $^4J_{(C-F)}$ = 2.8 Hz), 128.9 (C-F, d, $^1J_{(C-F)}$ = 255.4 Hz), 126.9, 126.8, 125.9 (C-F, q, $^2J_{(C-F)}$ = 34.1 Hz), 124.8, 124.5 (C-F, q, $^3J_{(C-F)}$ = 3.6 Hz), 122.7 (C-F, q, $^1J_{(C-F)}$ = 276.5 Hz), 121.6, 120.8, 116.4 (C-F, d, $^2J_{(C-F)}$ = 22.8 Hz), 114.7, 111.4, 110.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.7, -115.2.

M.p. 196.9-198.8 °C

HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{15}F_4N_4^+$ 399.1227, found 399.1230.



(*Z*)-*N*-(4-chlorophenyl)-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**3h**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2h** (119.1 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.4) to give the titled product **3h** as a white solid (53.9 mg, 65%).

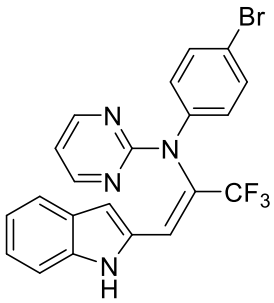
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.46 (d, *J* = 4.8 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.32 (s, 5H), 7.21 – 7.15 (m, 2H), 7.08 (dt, *J* = 7.8, 4.0 Hz, 1H), 6.84 – 6.81 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 158.8, 139.6, 137.8, 131.7, 130.1, 129.6, 127.6, 126.1, 125.6 (C-F, q, $^2J_{(C-F)}$ = 33.9 Hz), 124.9 (C-F, q, $^3J_{(C-F)}$ = 3.5 Hz), 124.8, 122.7 (C-F, q, $^1J_{(C-F)}$ = 276.5 Hz), 121.6, 120.9, 115.0, 111.4, 110.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.7.

M.p. 232.7-233.8 ºC

HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{15}ClF_3N_4^+$ 415.0932, found 415.0933.



(*Z*)-*N*-(4-bromophenyl)-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**3i**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2i** (136.9 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.4) to give the titled product **3i** as a white solid (68.9 mg, 75%).

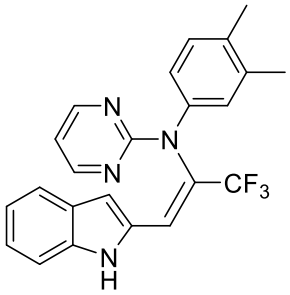
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.46 (d, *J* = 4.8 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.35 (s, 1H), 7.34 – 7.26 (m, 2H), 7.23 – 7.13 (m, 2H), 7.08 (ddd, *J* = 8.0, 6.2, 1.8 Hz, 1H), 6.84 – 6.81 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 158.8, 140.2, 137.8, 132.6, 130.1, 127.6, 126.3, 125.6 (C-F, q, $^2J_{(C\text{-}F)}$ = 33.2 Hz), 124.9 (C-F, q, $^3J_{(C\text{-}F)}$ = 3.7 Hz), 124.9, 122.7 (C-F, q, $^1J_{(C\text{-}F)}$ = 276.3 Hz), 121.6, 120.9, 119.6, 115.1, 111.4, 110.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.7.

M.p. 191.2-193.0 ºC

HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{15}BrF_3N_4^+$ 459.0427, found 459.0435.



(*Z*)-*N*-(3,4-dimethylphenyl)-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**3j**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2j** (116.5 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **3j** as a white solid (69.4 mg, 85%).

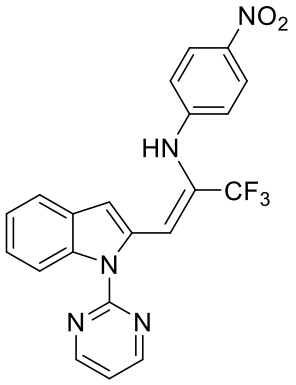
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.43 (d, *J* = 4.8 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.30 (s, 1H), 7.20 – 7.13 (m, 5H), 7.06 (ddd, *J* = 7.9, 6.6, 1.4 Hz, 1H), 6.81 (s, 1H), 6.75 (t, *J* = 4.8 Hz, 1H), 2.25 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 158.7, 138.7, 138.0, 137.8, 135.3, 130.7, 130.6, 127.5, 126.4 (C-F, q, $^2J_{(C-F)}$ = 32.9 Hz), 126.0, 124.6, 124.0 (C-F, q, $^3J_{(C-F)}$ = 3.7 Hz), 122.8 (C-F, q, $^1J_{(C-F)}$ = 276.7 Hz), 122.3, 121.5, 120.7, 114.4, 111.4, 110.5, 20.2, 19.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.6.

M.p. 152.4-153.9 °C

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{20}F_3N_4^+$ 409.1635, found 409.1633.



(*Z*)-4-nitro-*N*-(3,3,3-trifluoro-1-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)prop-1-en-2-yl)aniline (**3k'**)

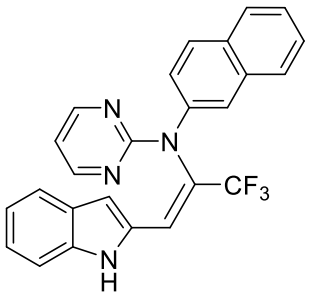
General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2k** (123.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.6) to give the titled product **3k'** as a yellow oil (62.1 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.8 Hz, 2H), 8.33 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 9.1 Hz, 2H), 7.60 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 4.8 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.90 – 6.71 (m, 3H), 5.86 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 157.7, 148.7, 140.5, 137.1, 130.5, 128.8, 126.0, 125.5, 122.5 (C-F, q, $^1J_{(C-F)}$ = 274.4 Hz), 122.8, 121.8 (C-F, q, $^2J_{(C-F)}$ = 33.0 Hz), 121.4, 120.8 (C-F, q, $^3J_{(C-F)}$ = 4.5 Hz), 117.8, 114.4, 114.2, 111.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -69.9.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{15}F_3N_5O_2^+$ 426.1172, found 426.1173.



(*Z*)-*N*-(naphthalen-2-yl)-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**3l**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2l** (125.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.6) to give the titled product **3l** as a yellow solid (56.0 mg, 65%).

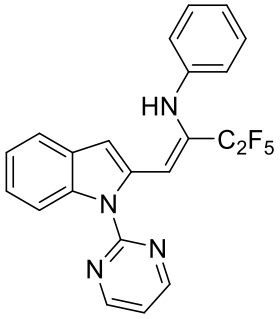
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.47 (d, *J* = 4.8 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.83 (dd, *J* = 5.9, 3.5 Hz, 2H), 7.72 – 7.69 (m, 1H), 7.59 – 7.55 (m, 2H), 7.46 – 7.41 (m, 2H), 7.41 (s, 1H), 7.18 – 7.14 (m, 2H), 7.08 (ddd, *J* = 8.0, 6.1, 1.9 Hz, 1H), 6.88 (s, 1H), 6.81 (t, *J* = 4.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 158.8, 138.7, 137.9, 134.0, 132.0, 130.4, 129.3, 127.9, 127.6, 126.7, 126.1, 125.6 (C-F, q, $^2J_{(C\text{-}F)}$ = 32.9 Hz), 124.7, 124.6 (C-F, q, $^3J_{(C\text{-}F)}$ = 3.5 Hz), 124.1, 122.8 (C-F, q, $^1J_{(C\text{-}F)}$ = 276.9 Hz), 121.9, 121.6, 120.8, 114.9, 111.5, 110.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.7.

M.p. 174.6-176.3 °C

HRMS (ESI): $[M+H]^+$ calcd. for $C_{25}H_{18}F_3N_4^+$ 431.1478, found 431.1486.



(*Z*)-*N*-(3,3,4,4,4-pentafluoro-1-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)but-1-en-2-yl)aniline (**3n'**)

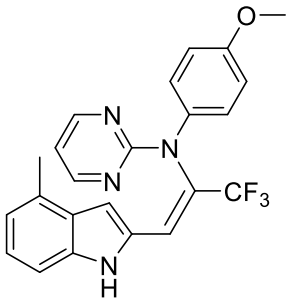
General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1a** (39.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2n** (125.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), $Zn(OAc)_2$ (11.0 mg, 0.006 mmol, 30 mol %), NaOAc (32.8 mg, 0.4 mmol, 2.0 equiv), DCE (1.5 mL), HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.6) to give the titled product **3n'** as a yellow oil (39.6 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.33 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 7.20 (t, *J* = 4.8 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.72 (s, 1H), 5.43 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 158.0, 141.5, 136.8, 132.1, 129.3, 129.1, 124.6, 123.0 (C-F, t, $^{2}J_{(C\text{-}F)}$ = 23.1 Hz), 122.4, 121.2, 120.6, 117.5, 116.4 (C-F, t, $^{3}J_{(C\text{-}F)}$ = 6.5 Hz), 116.1, 114.1, 111.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -83.3, -118.1.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{16}F_5N_4^+$ 431.1290, found 431.1292.



(*Z*)-*N*-(4-methoxyphenyl)-*N*-(3,3,3-trifluoro-1-(4-methyl-1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**4a**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1b** (41.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), and HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **4a** as a white solid (67.9 mg, 46%).

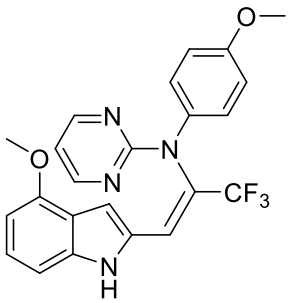
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.44 – 8.42 (m, 2H), 7.35 – 7.31 (m, 3H), 7.11 – 7.06 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.92 – 6.86 (m, 3H), 6.82 (s, 1H), 6.77 – 6.74 (m, 1H), 3.81 (s, 3H), 2.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 158.8, 158.1, 137.6, 133.9, 131.3, 130.0, 127.7, 126.6, 125.7 (C-F, q, $^{2}J_{(C\text{-}F)}$ = 33.3 Hz), 124.9, 124.0 (C-F, q, $^{3}J_{(C\text{-}F)}$ = 3.6 Hz), 122.8 (C-F, q, $^{1}J_{(C\text{-}F)}$ = 276.7 Hz), 120.7, 114.8, 114.2, 109.2, 108.9, 55.5, 18.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.6.

M.p. 200.8-203.4 ºC

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{20}F_3N_4O^+$ 425.1584, found 425.1585.



(*Z*)-*N*-(4-methoxyphenyl)-*N*-(3,3,3-trifluoro-1-(4-methoxy-1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**4b**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1c** (45.0 mg, 0.2 mmol, 1.0 equiv), TFISY **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), and HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **4b** as a white solid (72.2 mg, 82%).

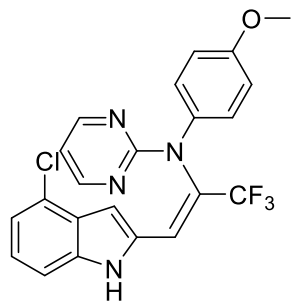
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.43 (d, *J* = 4.8 Hz, 2H), 7.32 (d, *J* = 9.0 Hz, 2H), 7.27 (s, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 9.1 Hz, 3H), 6.77 – 6.74 (m, 2H), 6.44 (d, J = 7.8 Hz, 1H), 3.91 (s, 3H), 3.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 158.8, 158.1, 154.0, 139.2, 133.9, 129.2, 126.5, 125.7, 125.4 (q, $^2J_{(C-F)}$ = 33.9 Hz), 124.0 (q, $^3J_{(C-F)}$ = 3.7 Hz), 122.9 (q, $^1J_{(C-F)}$ = 276.3 Hz), 118.9, 114.8, 114.3, 108.3, 104.4, 100.0, 55.6, 55.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.6.

M.p. 140.4-143.3 ºC

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{20}F_3N_4O_2^+$ 441.1533, found 441.1536.



(*Z*)-*N*-(1-(4-chloro-1*H*-indol-2-yl)-3,3,3-trifluoroprop-1-en-2-yl)-*N*-(4-methoxyphenyl)pyrimidin-2-amine (**4c**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1d** (45.9 mg, 0.2 mmol, 1.0 equiv), TFISY **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), and HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **4c** as a white solid (66.7 mg, 75%).

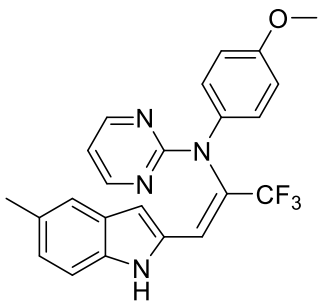
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.44 (d, *J* = 4.7 Hz, 2H), 7.31 (d, *J* = 8.9 Hz, 3H), 7.09 – 7.02 (m, 3H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.89 (s, 1H), 6.78 (t, *J* = 4.7 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 158.8, 158.2, 138.3, 133.7, 131.0, 126.9, 126.7, 126.5, 125.7 (C-F, q, $^2J_{(C\text{-}F)}$ = 34.4 Hz), 125.1, 123.5 (C-F, q, $^3J_{(C\text{-}F)}$ = 3.4 Hz), 122.6 (C-F, q, $^2J_{(C\text{-}F)}$ = 277.1 Hz), 120.4, 114.9, 114.5, 109.9, 108.7, 55.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.7.

M.p. 230.9-232.6 ºC

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{17}ClF_3N_4O^+$ 445.1037, found 445.1039.



(*Z*)-*N*-(4-methoxyphenyl)-*N*-(3,3,3-trifluoro-1-(5-methyl-1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**4d**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1e** (41.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), and HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **4d** as a white solid (67.9 mg, 80%).

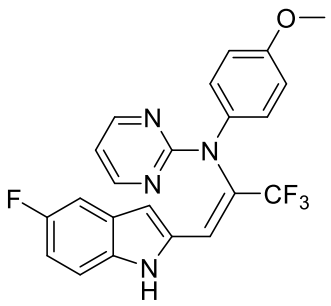
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.43 (d, *J* = 4.8 Hz, 2H), 7.32 (m, 3H), 7.27 (s, 1H), 7.03 (m, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.75 (t, *J* = 4.8 Hz, 1H), 6.73 (s, 1H), 3.80 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 158.7, 158.1, 136.2, 133.8, 130.5, 130.1, 127.9, 126.6, 126.3, 125.8 (q, $^2J_{(C\text{-}F)}$ = 33.6 Hz), 124.0 (q, $^3J_{(C\text{-}F)}$ = 3.2 Hz), 122.8 (q, $^1J_{(C\text{-}F)}$ = 276.5 Hz), 120.9, 114.8, 114.2, 111.0, 109.9, 55.6, 21.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.7.

M.p. 242.3-244.9 °C

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{20}F_3N_4O^+$ 425.1584, found 425.1588.



(*Z*)-*N*-(4-methoxyphenyl)-*N*-(3,3,3-trifluoro-1-(5-fluoro-1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**4e**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1f** (42.6 mg, 0.2 mmol, 1.0 equiv), TFISY **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), and HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **4e** as a white solid (67.9 mg, 70%).

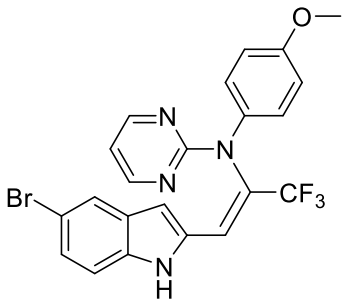
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.44 (d, *J* = 4.7 Hz, 2H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.26 (s, 1H), 7.18 (d, *J* = 9.2 Hz, 1H), 7.07 (dd, *J* = 8.7, 4.2 Hz, 1H), 6.98 – 6.88 (m, 3H), 6.82 – 6.72 (m, 2H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 159.4, 158.8, 158.0 (C-F, d, $^{1}J_{(C-F)}$ = 236.2 Hz), 134.1, 133.5, 131.9, 127.7 (C-F, d, $^{3}J_{(C-F)}$= 10.6 Hz), 126.7 (C-F, q, $^{2}J_{(C-F)}$ = 33.7 Hz), 126.4, 123.5 (C-F, q, $^{3}J_{(C-F)}$ = 3.5 Hz), 122.5 (C-F, q, $^{1}J_{(C-F)}$ = 277.0 Hz), 114.7, 114.2, 113.2 (C-F, d, $^{2}J_{(C-F)}$ = 26.8 Hz), 112.0 (C-F, d, $^{3}J_{(C-F)}$ = 9.6 Hz), 109.8 (C-F, d, $^{4}J_{(C-F)}$ = 4.8 Hz), 105.8 (C-F, d, $^{2}J_{(C-F)}$ = 23.5 Hz), 55.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.7, -123.2.

M.p. 247.8-250.2 ºC

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{17}F_4N_4O^+$ 429.1333, found 429.1334.



(*Z*)-*N*-(1-(5-bromo-1*H*-indol-2-yl)-3,3,3-trifluoroprop-1-en-2-yl)-*N*-(4-methoxyphenyl)pyrimidin-2-amine (**4f**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1g** (54.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), and HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **4f** as a white solid (70.4 mg, 72%).

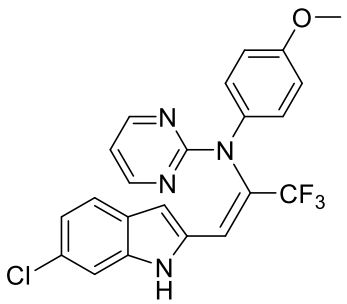
^{1}H NMR (400 MHz, DMSO) δ 11.64 (s, 1H), 8.45 (d, *J* = 4.8 Hz, 2H), 7.63 (s, 1H), 7.44 (s, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.9 Hz, 2H), 7.23 (dd, *J* = 8.7, 1.6 Hz, 1H), 6.91 (m, 3H), 6.57 (s, 1H), 3.73 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 160.9, 158.4, 157.3, 134.8, 133.1, 131.2, 129.7, 127.4 (C-F, q, $^2J_{(C-F)}$ = 32.5 Hz), 126.4, 125.8, 123.9 (C-F, q, $^3J_{(C-F)}$ = 3.0 Hz), 123.0, 122.7 (C-F, q, $^1J_{(C-F)}$= 276.8 Hz), 114.2, 114.0, 113.7, 112.4, 103.2, 55.2.

^{19}F NMR (377 MHz, DMSO) δ -63.6

M.p. 227.8-229.4 ºC

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{17}BrF_3N_4O^+$ 489.0532, found 489.0533.



(*Z*)-*N*-(1-(6-chloro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-3,3,3-trifluoroprop-1-en-2-yl)-4-methoxyanilin e (**4g**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1h** (45.9 mg, 0.2 mmol, 1.0 equiv), TFISY **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), and HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **4g** as a white solid (40.0 mg, 45%).

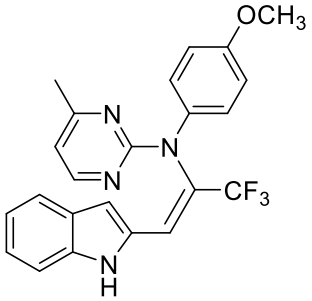
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.44 (d, *J* = 4.8 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 2H), 7.26 (s, 1H), 7.15 (s, 1H), 7.03 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.78 (t, *J* = 5.0 Hz, 1H), 6.77 (s, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 158.8, 158.2, 138.0, 133.7, 131.2, 130.5, 126.8 (q, $^2J_{(C-F)}$= 33.3 Hz), 126.5, 126.2, 123.6 (q, $^3J_{(C-F)}$= 3.6 Hz), 122.7 (q, $^1J_{(C-F)}$= 276.7 Hz), 122.4, 121.7, 114.8, 114.4, 111.2, 110.1, 55.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.7.

M.p. 180.6-183.0 °C

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{17}ClF_3N_4O^+$ 445.1037, found 445.1045.



(Z)-*N*-(4-methoxyphenyl)-4-methyl-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**4k**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1l** (41.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg,

0.2 mmol, 1.0 equiv), DCE (1.5 mL), and HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **4a** as a white solid (66.2 mg, 78%).

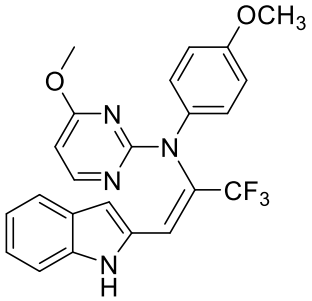
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.29 (d, *J* = 5.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.27 (m, 2H), 7.27 (s, 1H), 7.18 (d, *J* = 5.4 Hz, 2H), 7.07 (ddd, *J* = 8.0, 5.5, 2.5 Hz, 1H), 6.93 – 6.84 (m, 2H), 6.80 (s, 1H), 6.63 (d, *J* = 5.0 Hz, 1H), 3.80 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 162.2, 158.0, 157.8, 137.8, 134.2, 130.8, 127.6, 126.7 (C-F, q, $^2J_{(C\text{-}F)}$ = 33.1 Hz), 126.2, 124.5, 124.0 (C-F, q, $^3J_{(C\text{-}F)}$ = 3.7 Hz), 122.4 (C-F, q, $^1J_{(C\text{-}F)}$ = 276.7 Hz), 121.5, 120.6, 114.6, 114.1, 111.4, 110.2, 55.5, 24.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.4.

M.p. 191.1-193.4 °C

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{20}F_3N_4O^+$ 425.1584, found 425.1589.



(*Z*)-4-methoxy-*N*-(4-methoxyphenyl)-*N*-(3,3,3-trifluoro-1-(1*H*-indol-2-yl)prop-1-en-2-yl)pyrimidin-2-amine (**4l**)

General procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **1n** (45.0 mg, 0.2 mmol, 1.0 equiv), TFISY **2f** (117.3 mg, 0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv), DCE (1.5 mL), and HFIP (0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.5) to give the titled product **4l** as a white solid (67.9 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.19 (d, *J* = 5.7 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.28 (s, 1H), 7.19 (d, *J* = 5.8 Hz, 2H), 7.09 (t, *J* = 6.9 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.82 (s, 1H), 6.23 (d, *J* = 5.7 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 162.0, 158.3, 157.9, 137.9, 133.8, 130.7, 127.5, 126.4, 126.4 (C-F, q, $^{2}J_{(C-F)}$ = 33.6 Hz), 124.6, 124.1 (C-F, q, $^{3}J_{(C-F)}$ = 3.5 Hz), 122.9 (C-F, q, $^{1}J_{(C-F)}$ = 276.9 Hz), 121.5, 120.7, 114.6, 111.5, 110.4, 101.3, 55.5, 53.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -64.5.

M.p. 167.6-170.0 ºC

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{20}F_3N_4O_2^+$ 441.1533, found 441.1542.

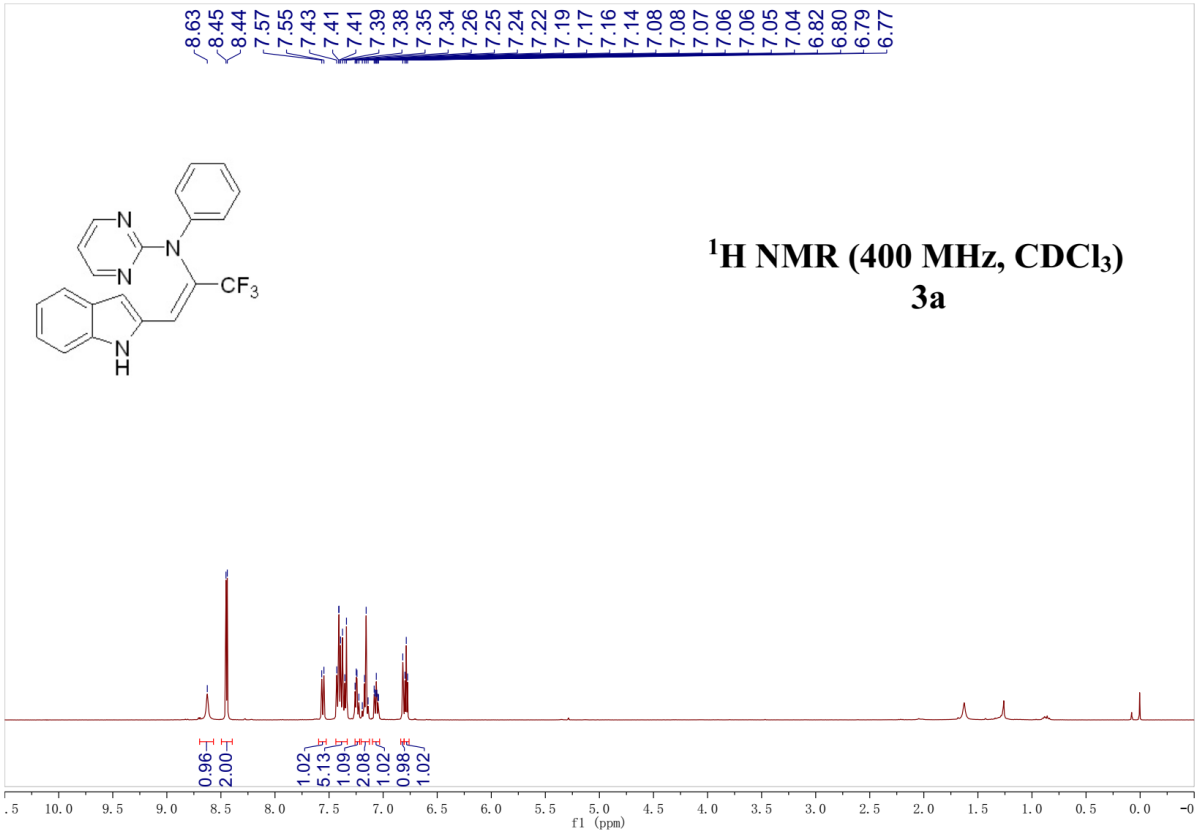
5 References

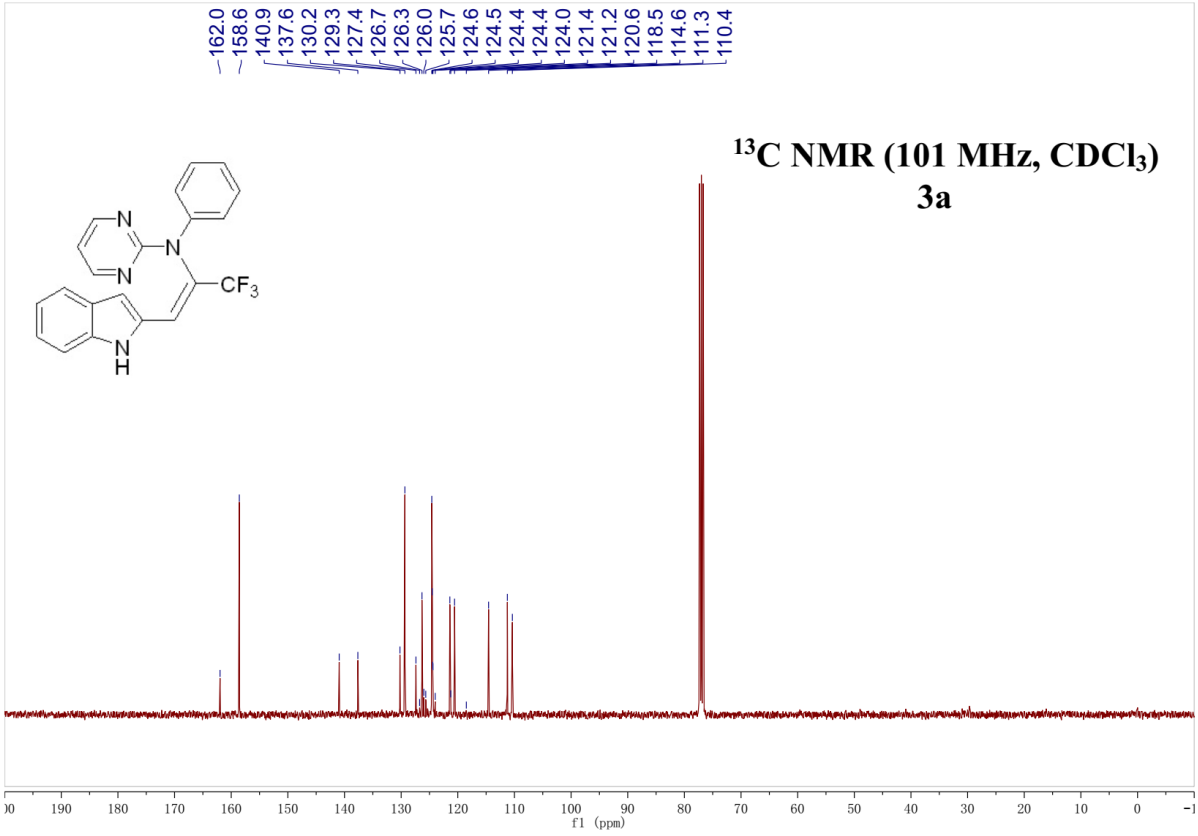
(1) K. Tamura, H. Mizukami, K. Maeda, H. Watanabe, K. Uneyama, *J. Org. Chem.* **1993**, *58*, 32.

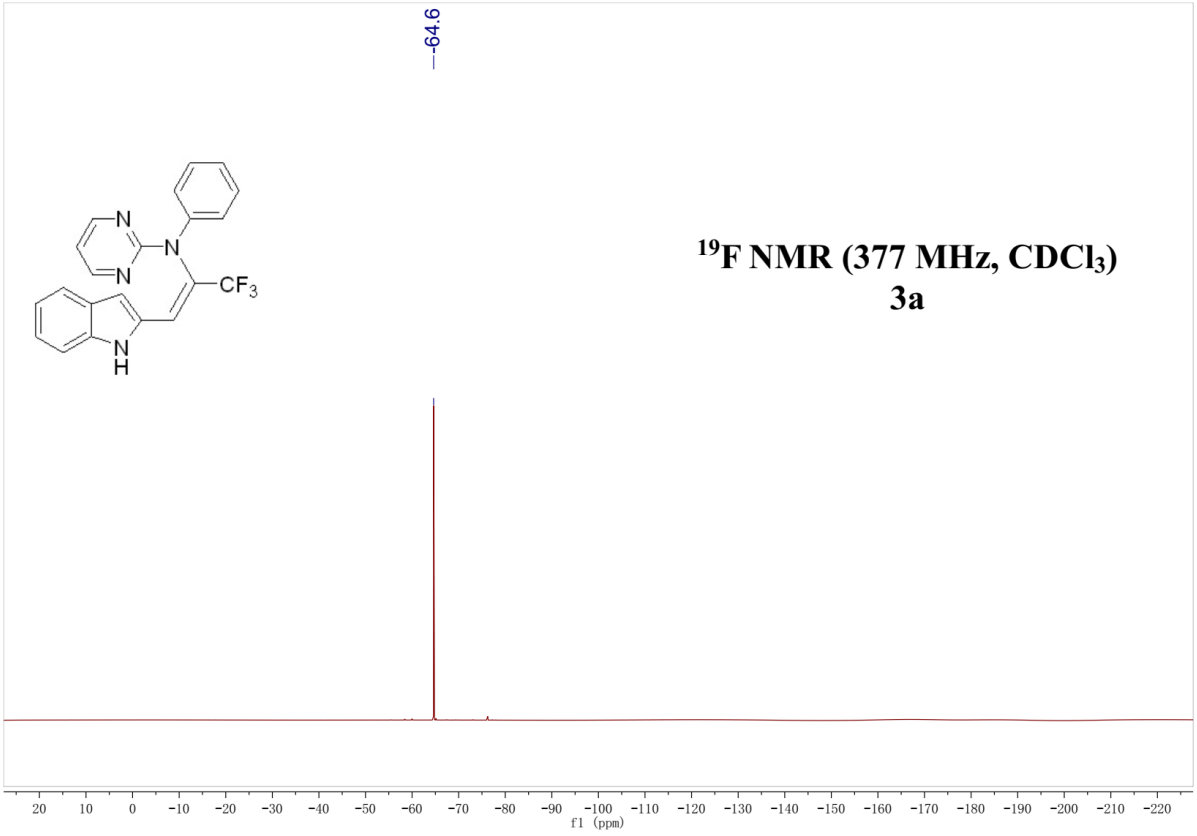
(2) S. Wen, Q. Tian, Y. Chen, Y. Zhang, G. Cheng, *Org. Lett.* **2021**, *23*, 7407.

(3) L. Qiao, K. Zhang, Z. Wang, H. Li, P. Lu, P. Wang, *J. Org. Chem.* **2021**, *86*, 7955.

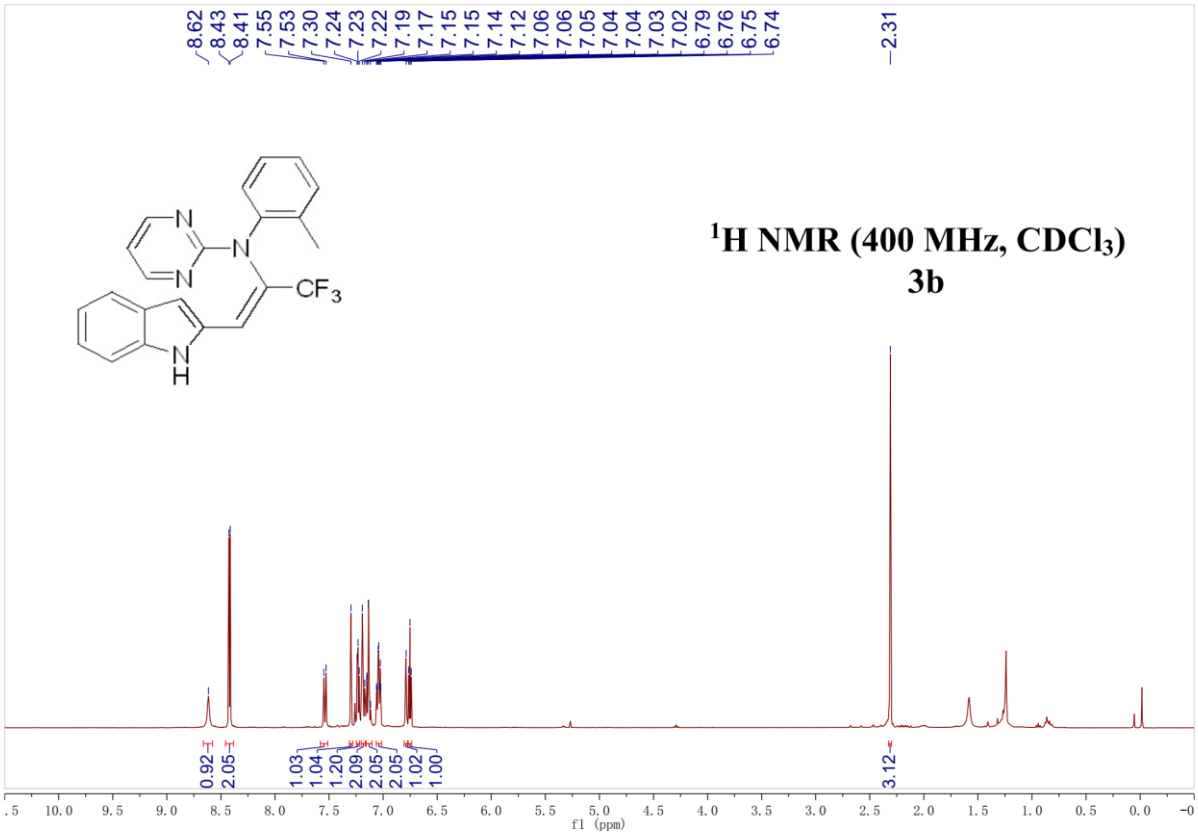
6 Copy of ^{1}H, ^{13}C and ^{19}F NMR Spectra of Products



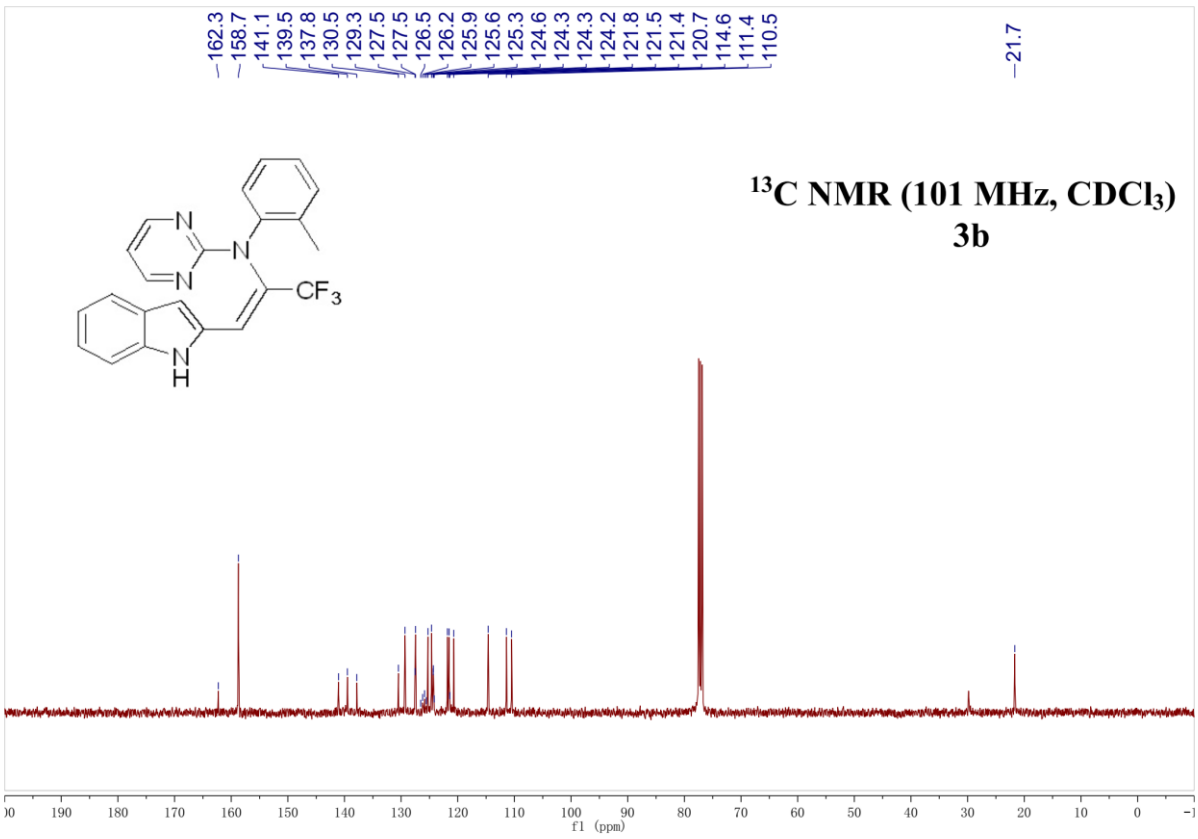




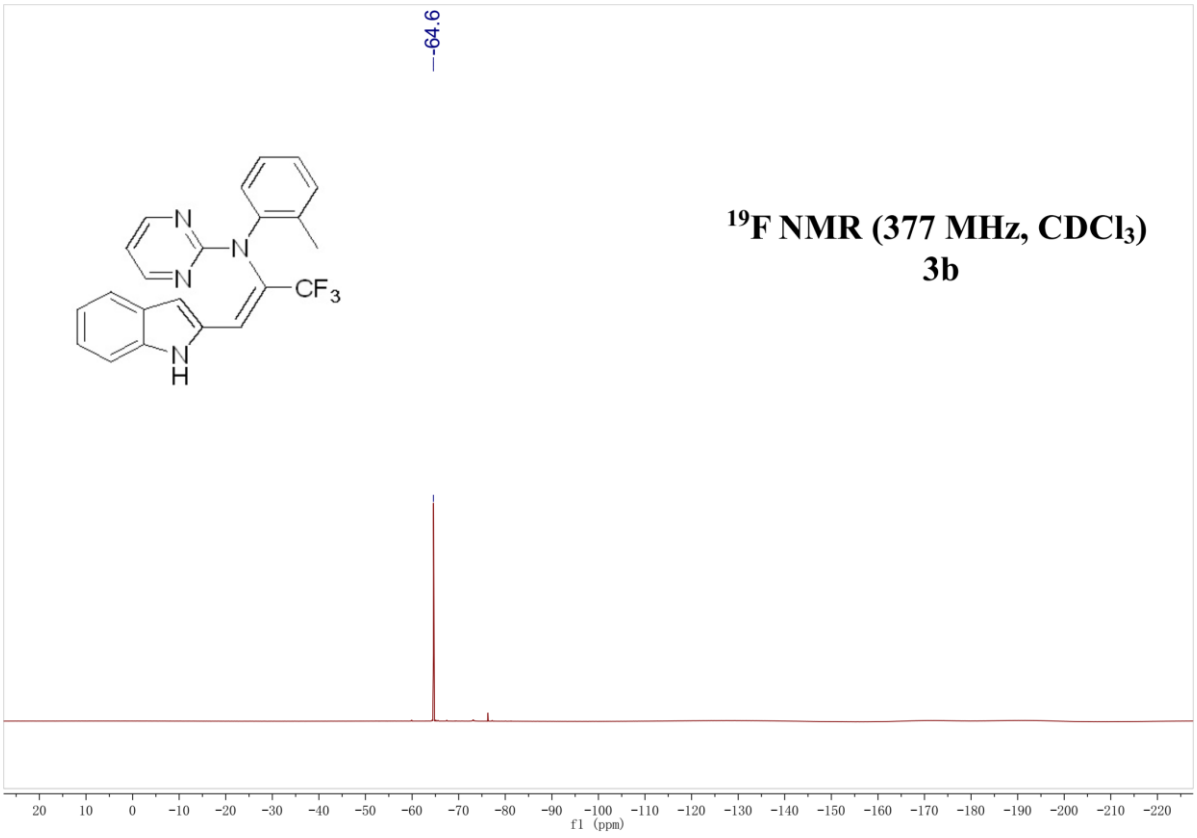
^{19}F NMR (377 MHz, $CDCl_3$)
3a



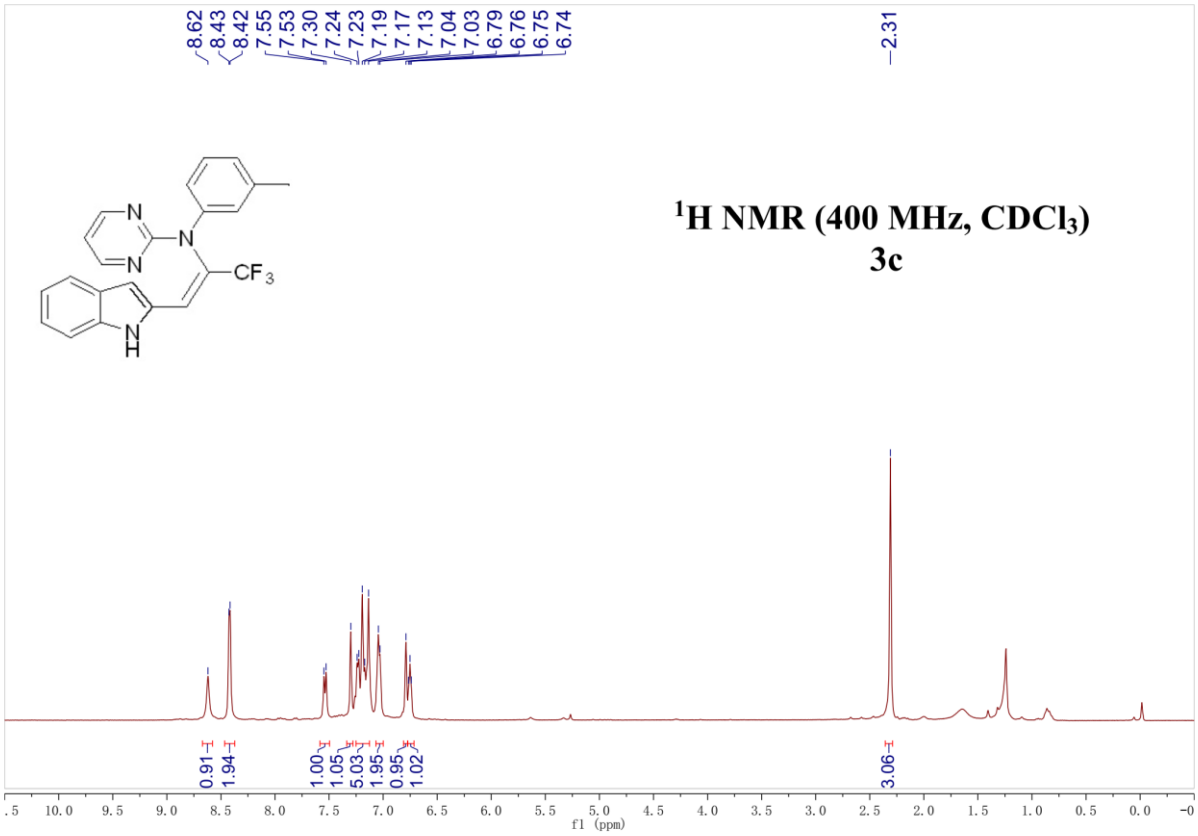
^{1}H NMR (400 MHz, $CDCl_3$)
3b



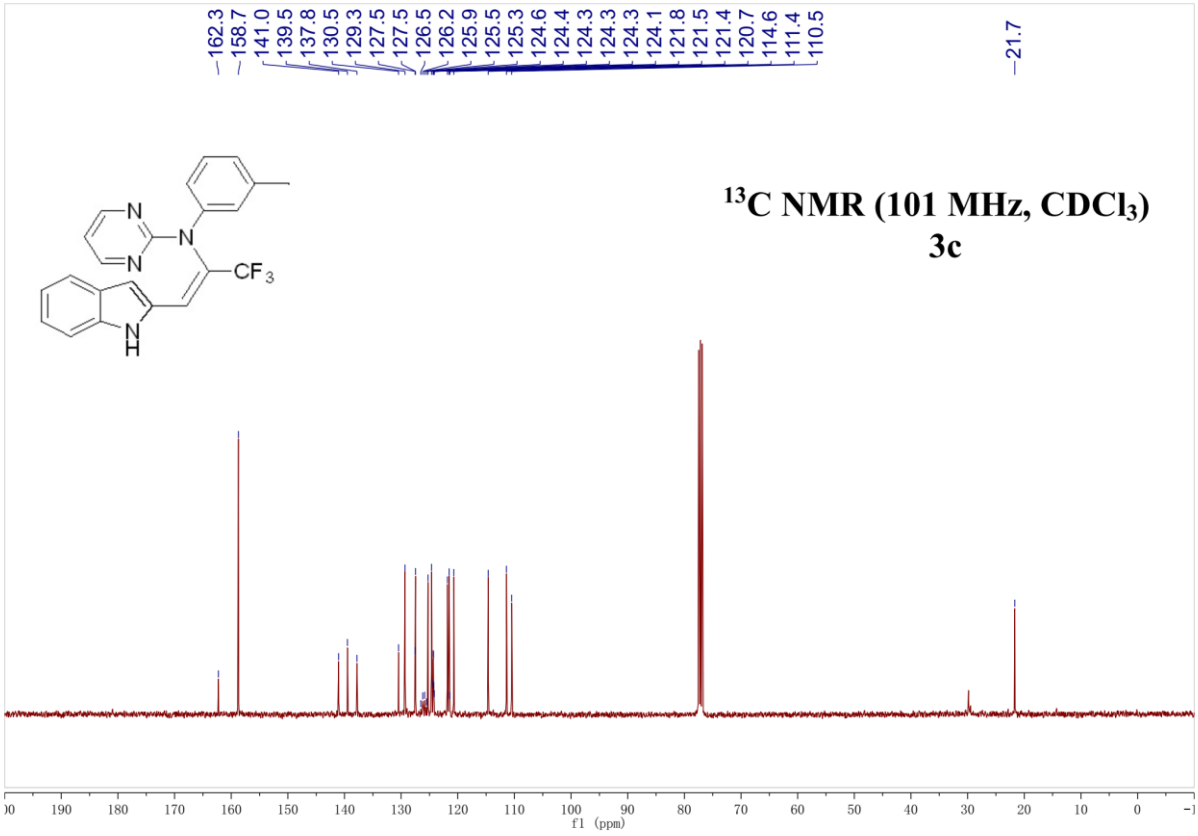
^{13}C NMR (101 MHz, $CDCl_3$)
3b



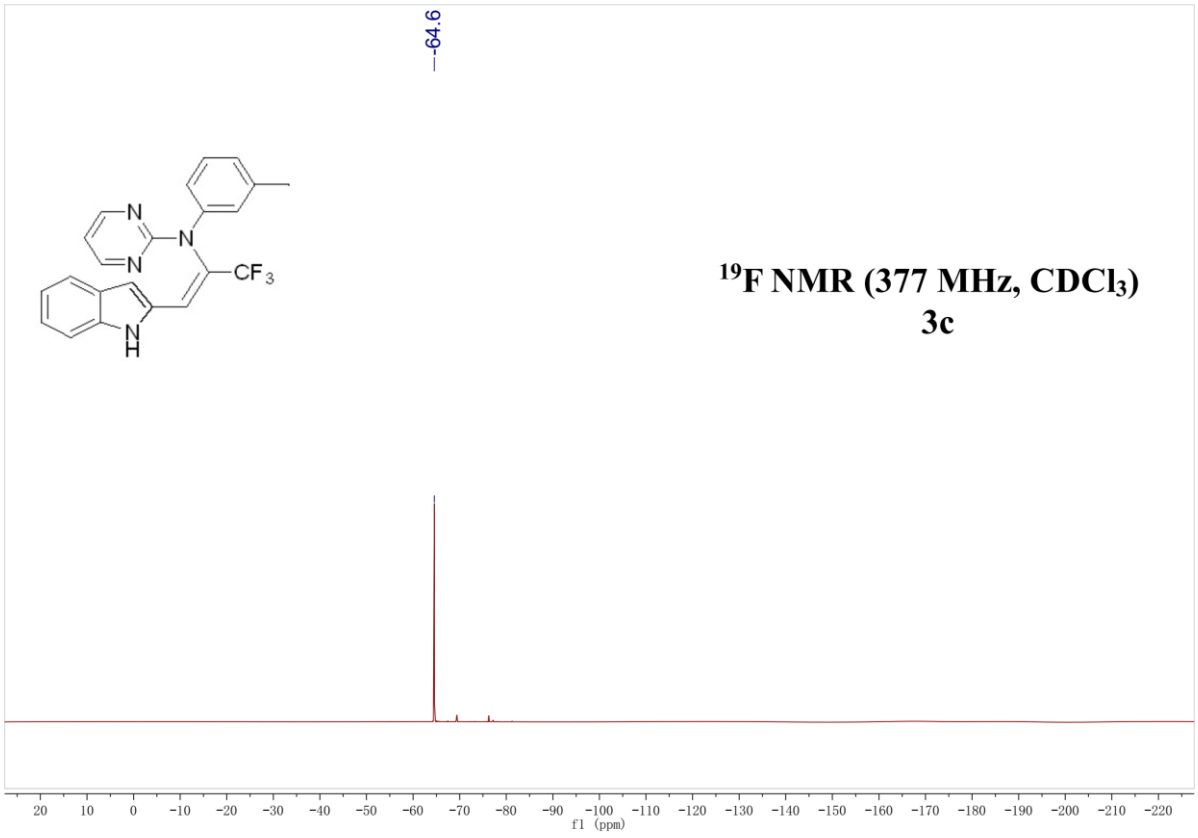
^{19}F NMR (377 MHz, $CDCl_3$)
3b



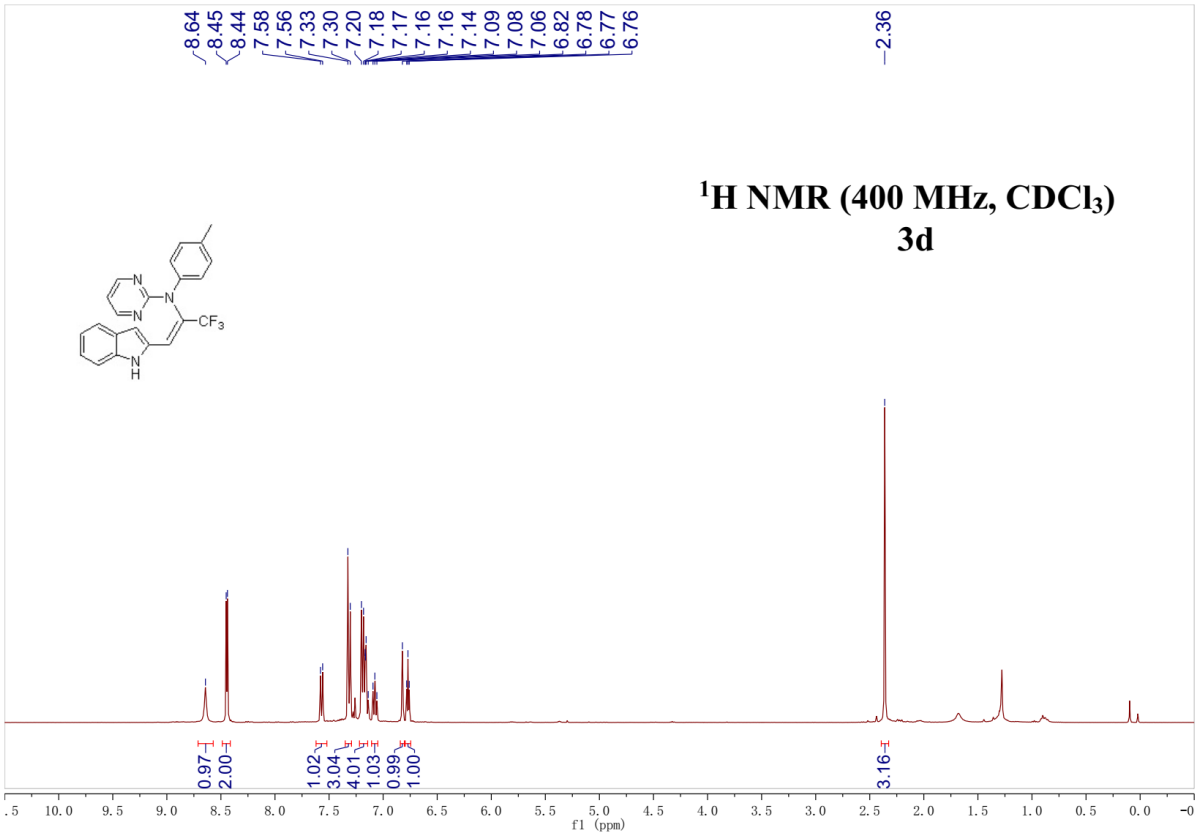
^{1}H NMR (400 MHz, $CDCl_3$)
3c



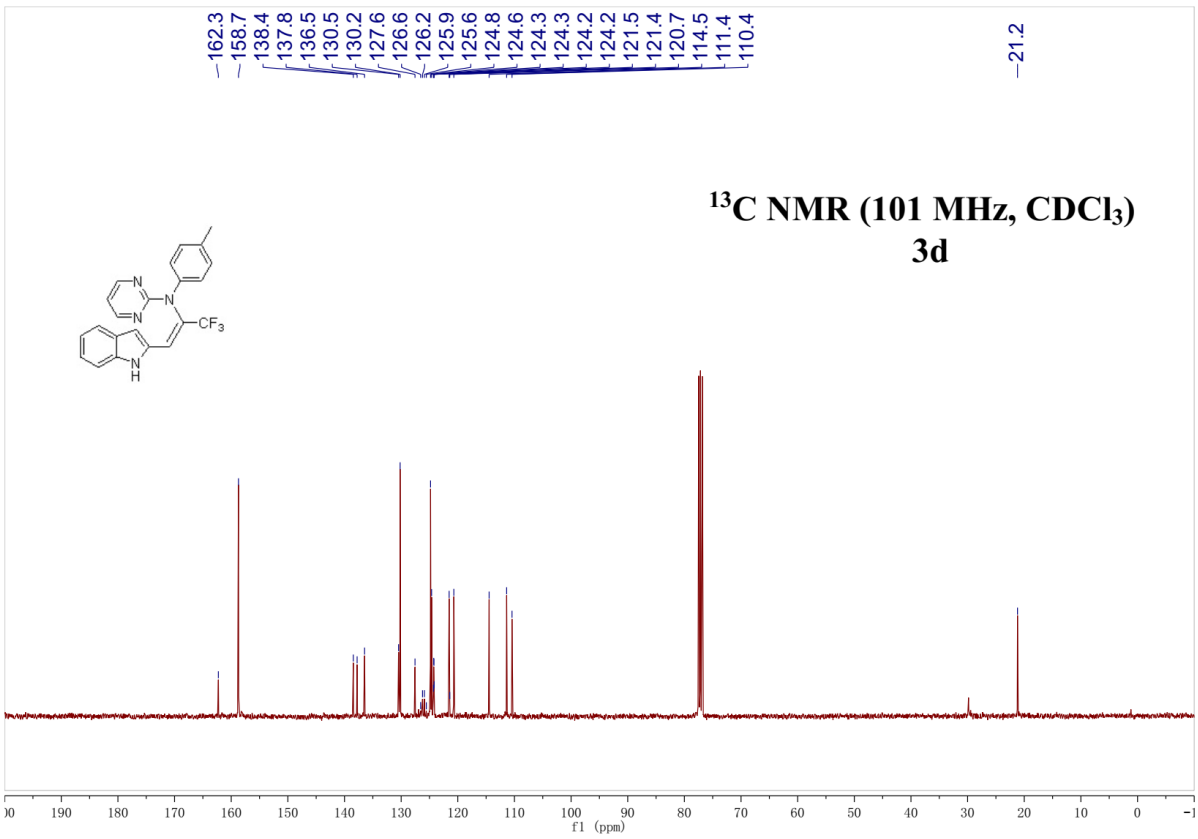
^{13}C NMR (101 MHz, $CDCl_3$)
3c



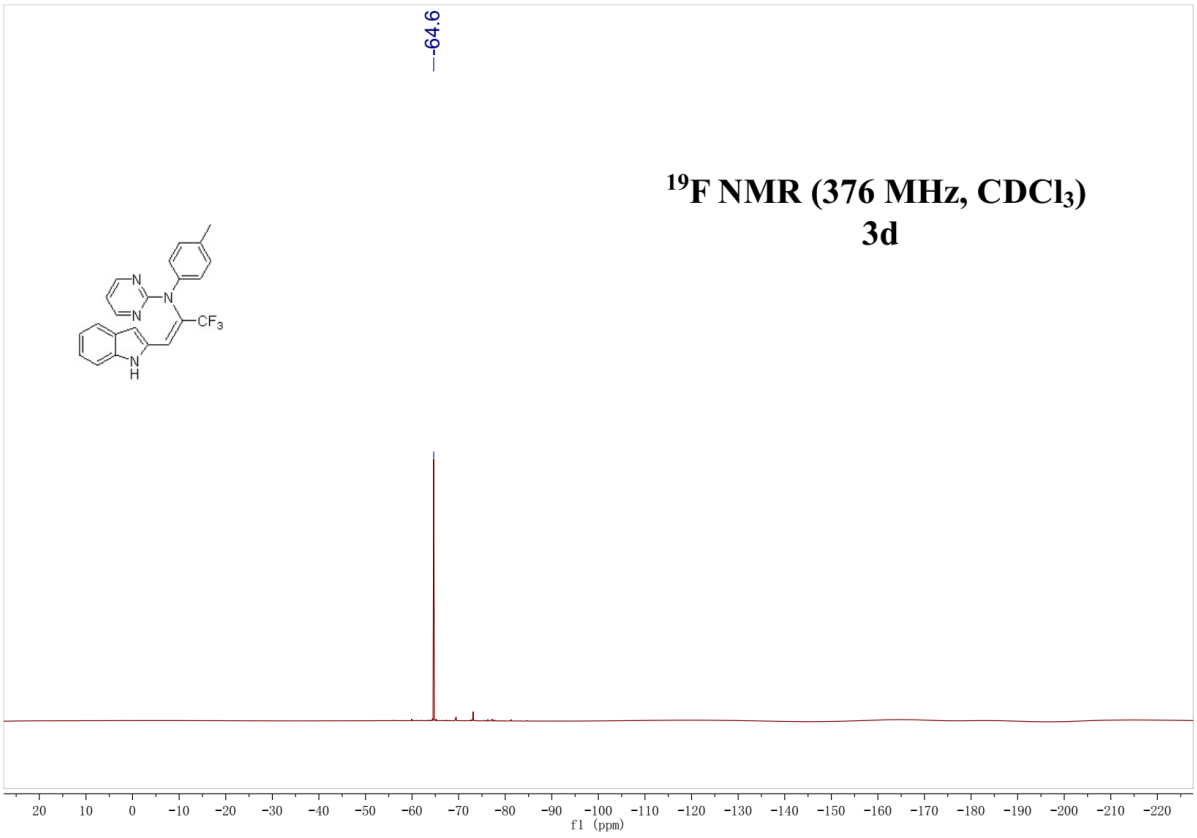
^{19}F NMR (377 MHz, $CDCl_3$)
3c

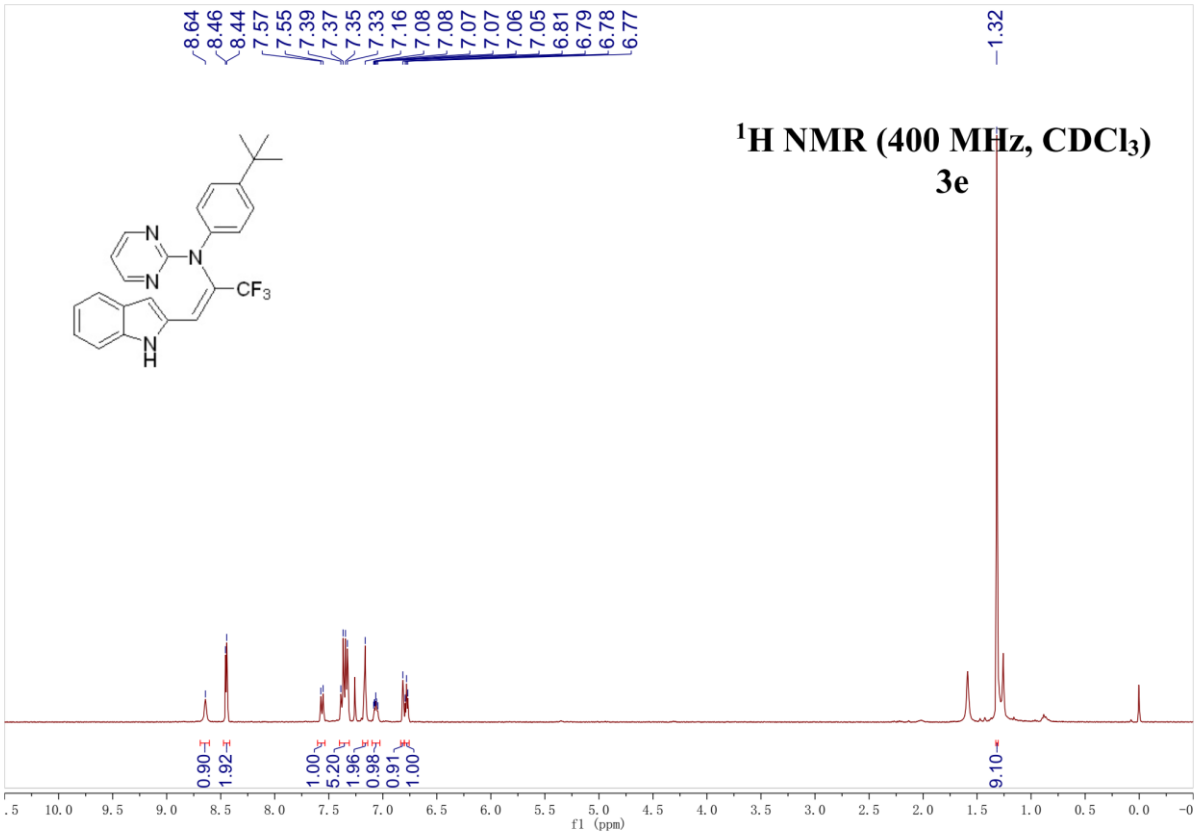


^{1}H NMR (400 MHz, $CDCl_3$)
3d



^{13}C NMR (101 MHz, $CDCl_3$)
3d


-64.6
19F NMR (376 MHz, CDCl3)
3d
CF3
N
H
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)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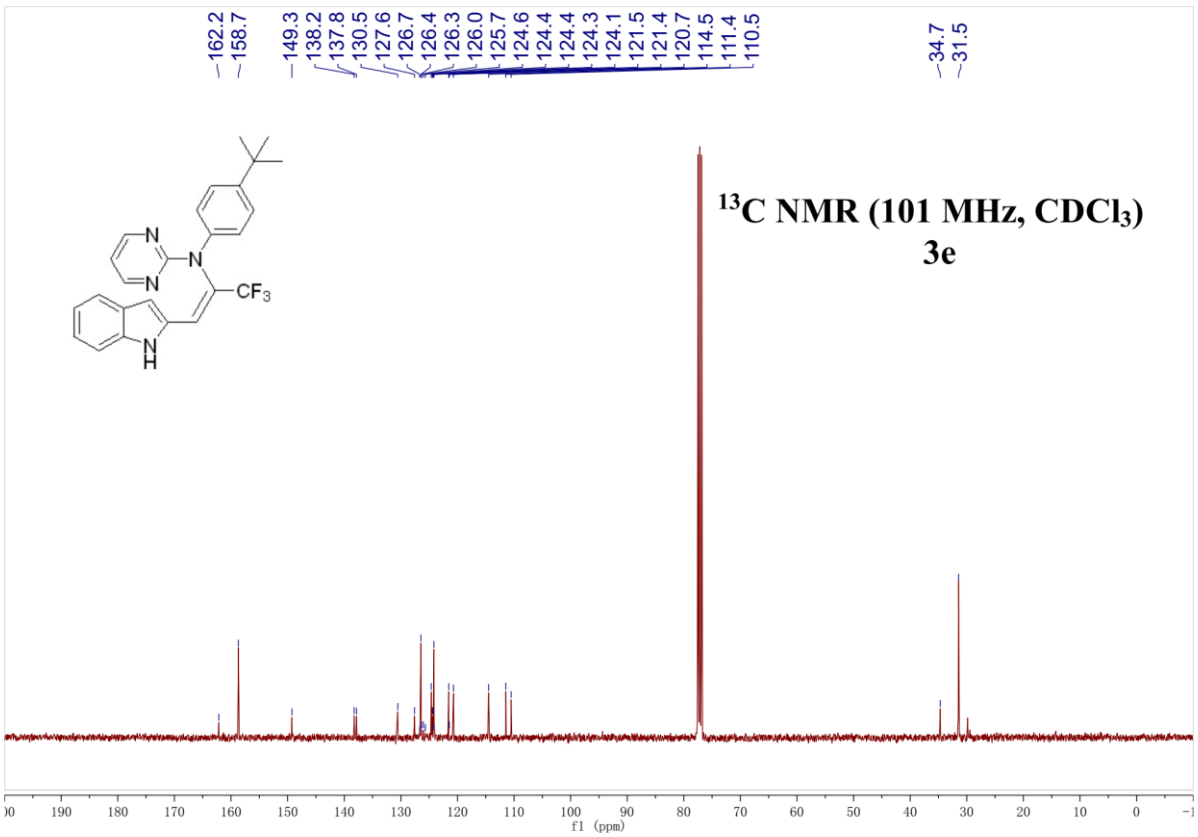
8.44
7.57
7.55
7.39
7.37
7.35
7.33
7.16
7.08
7.08
7.07
7.07
7.06
7.05
6.81
6.79
6.78
6.77
1.32
^{1}H NMR (400 MHz, CDCl$_3$)
3e
CF$_3$
0.90
1.92
1.00
5.20
1.96
0.98
0.91
1.00
9.10
f1 (ppm)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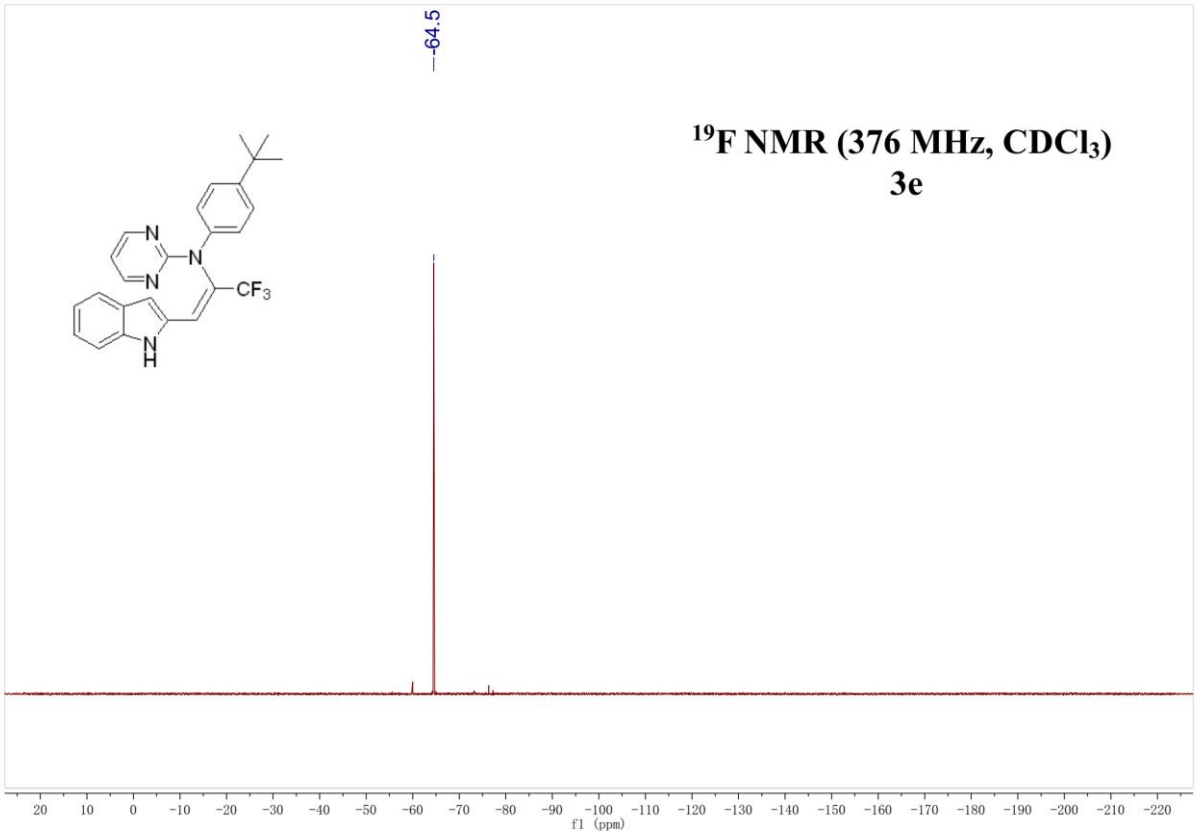
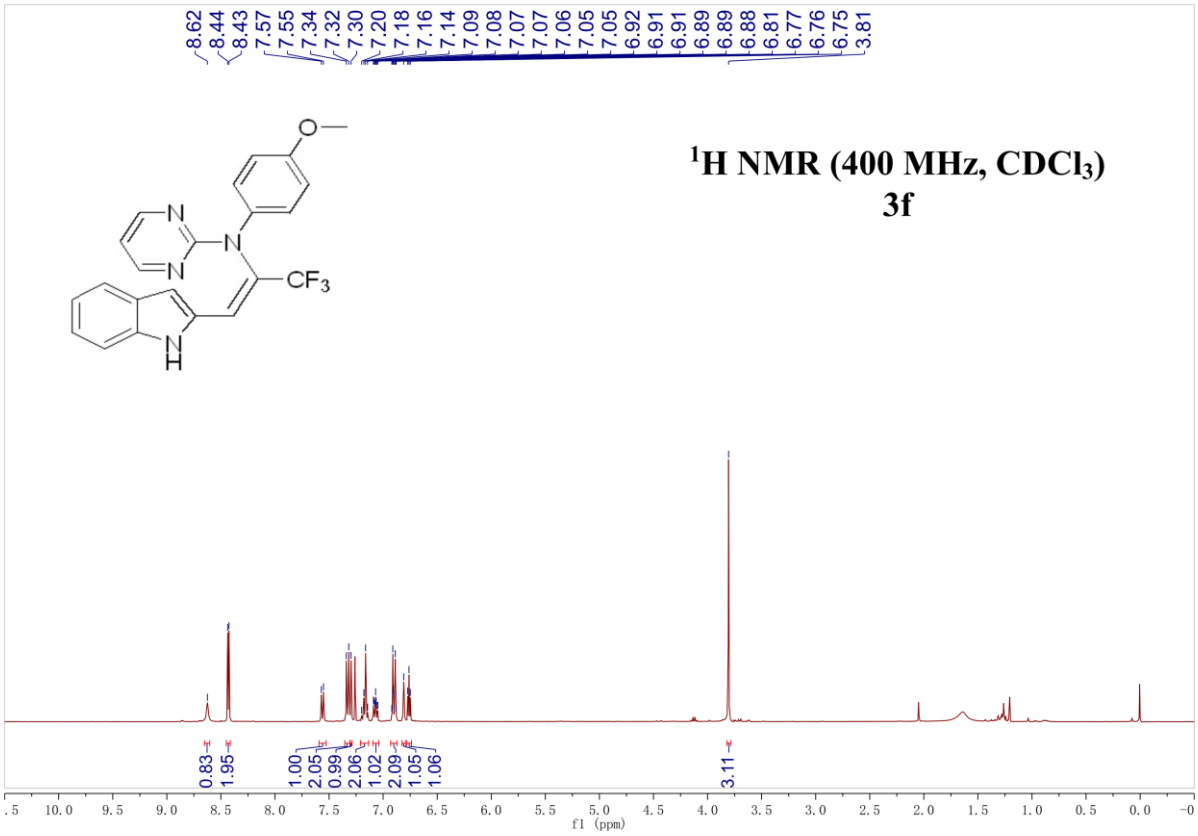
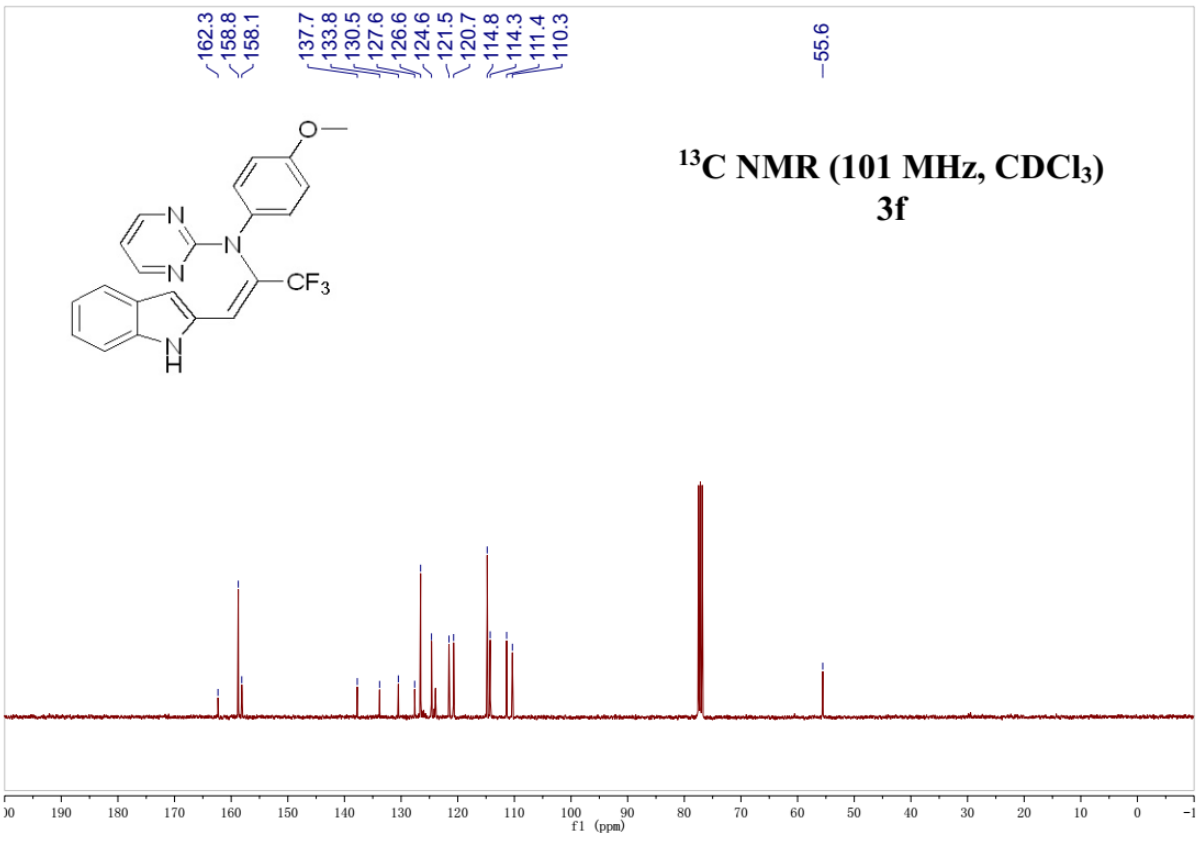
158.7
149.3
138.2
137.8
130.5
127.6
126.7
126.4
126.3
126.0
125.7
124.6
124.4
124.4
124.3
124.1
121.5
121.4
120.7
114.5
111.4
110.5
34.7
31.5
^{13}C NMR (101 MHz, CDCl$_3$)
3e
CF$_3$
f1 (ppm)

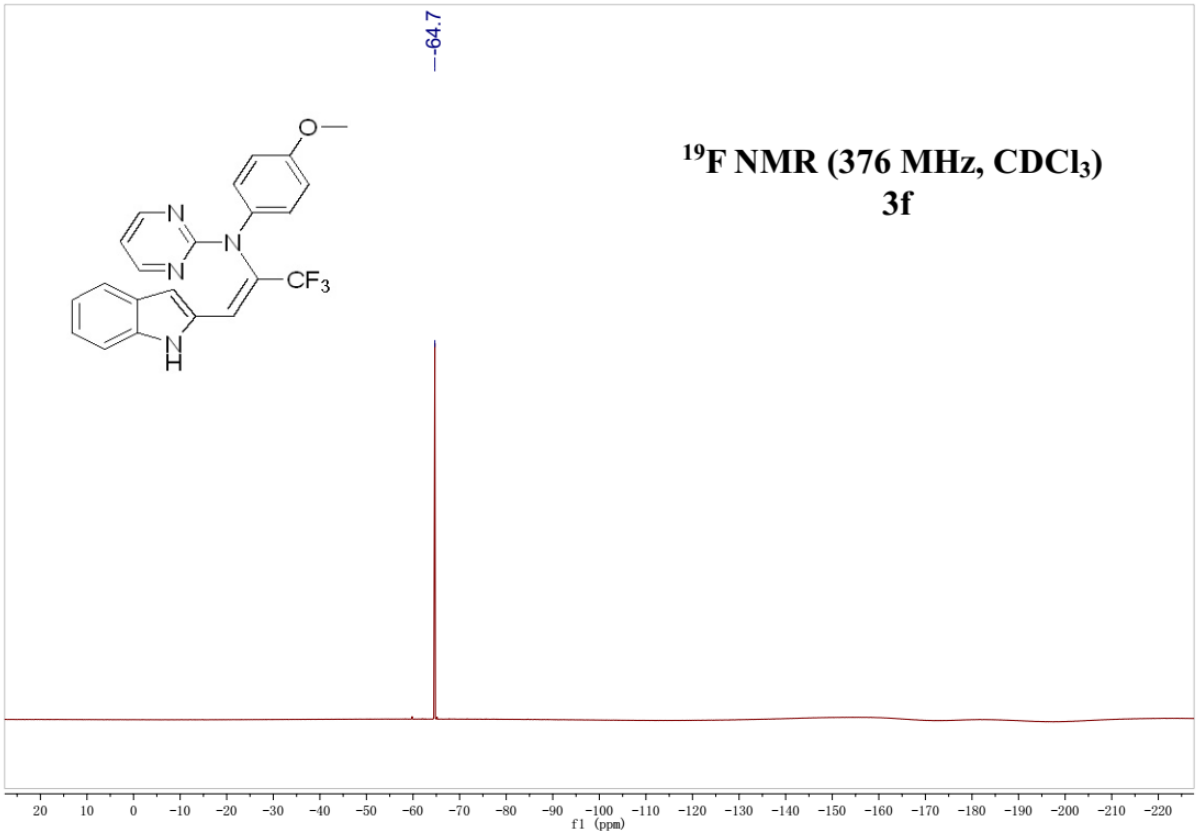

-64.5
19F NMR (376 MHz, CDCl3)
3e
N
N
N
CF3
H
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)
3f



^{13}C NMR (101 MHz, $CDCl_3$)
3f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O
N
N
N
CF3
N
H
19F NMR (376 MHz, CDCl3)
3f
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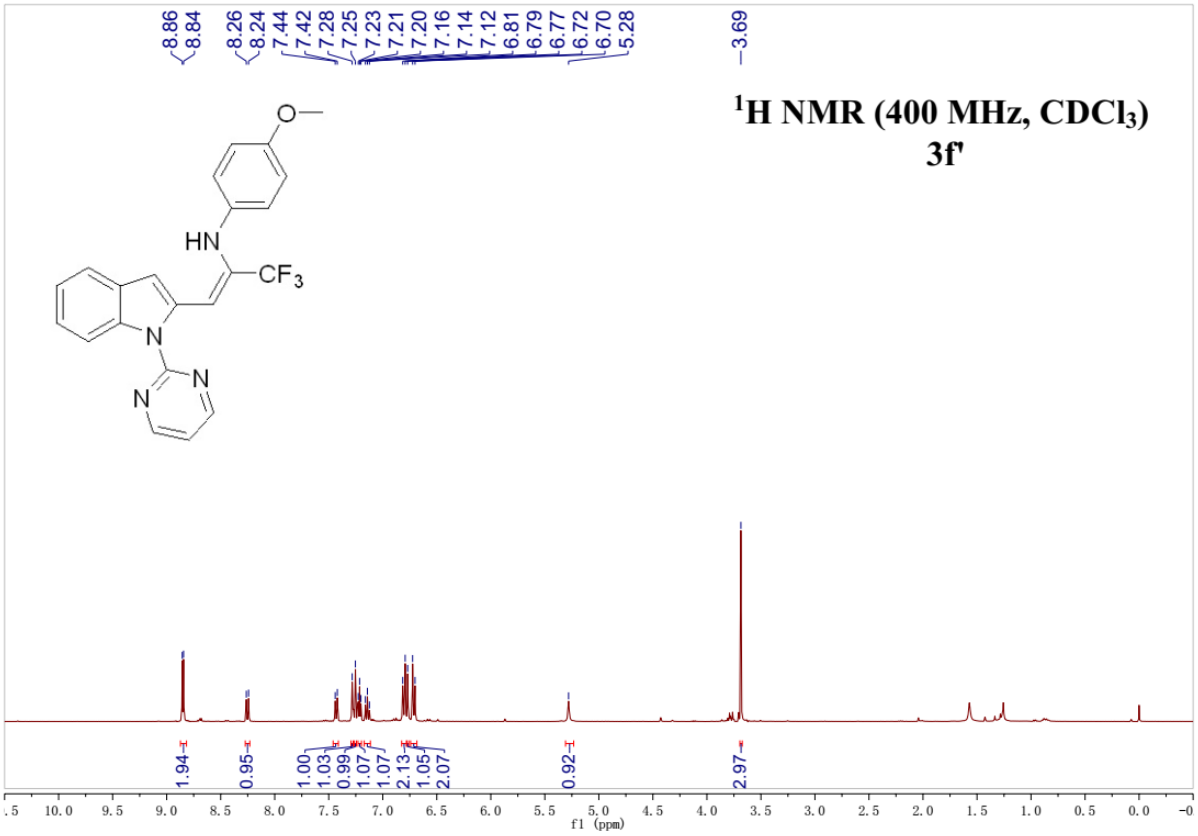
f1 (ppm)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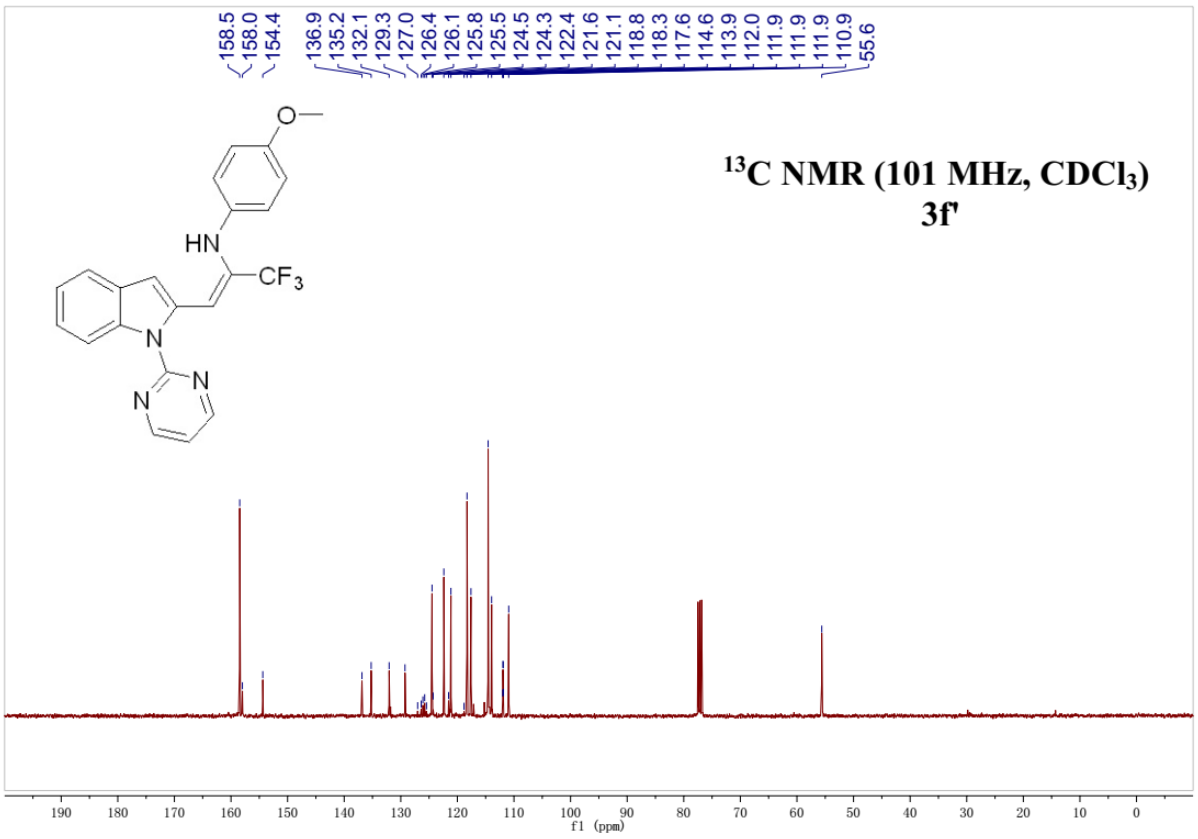
8.26
8.24
7.44
7.42
7.28
7.25
7.23
7.21
7.20
7.16
7.14
7.12
6.81
6.79
6.77
6.72
6.70
5.28
3.69
HN
CF3
N
N
N
O
1H NMR (400 MHz, CDCl3)
3f'
1.94
0.95
1.00
1.03
0.99
1.07
1.07
2.13
1.05
2.07
0.92
2.97
f1 (ppm)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158.0
154.4
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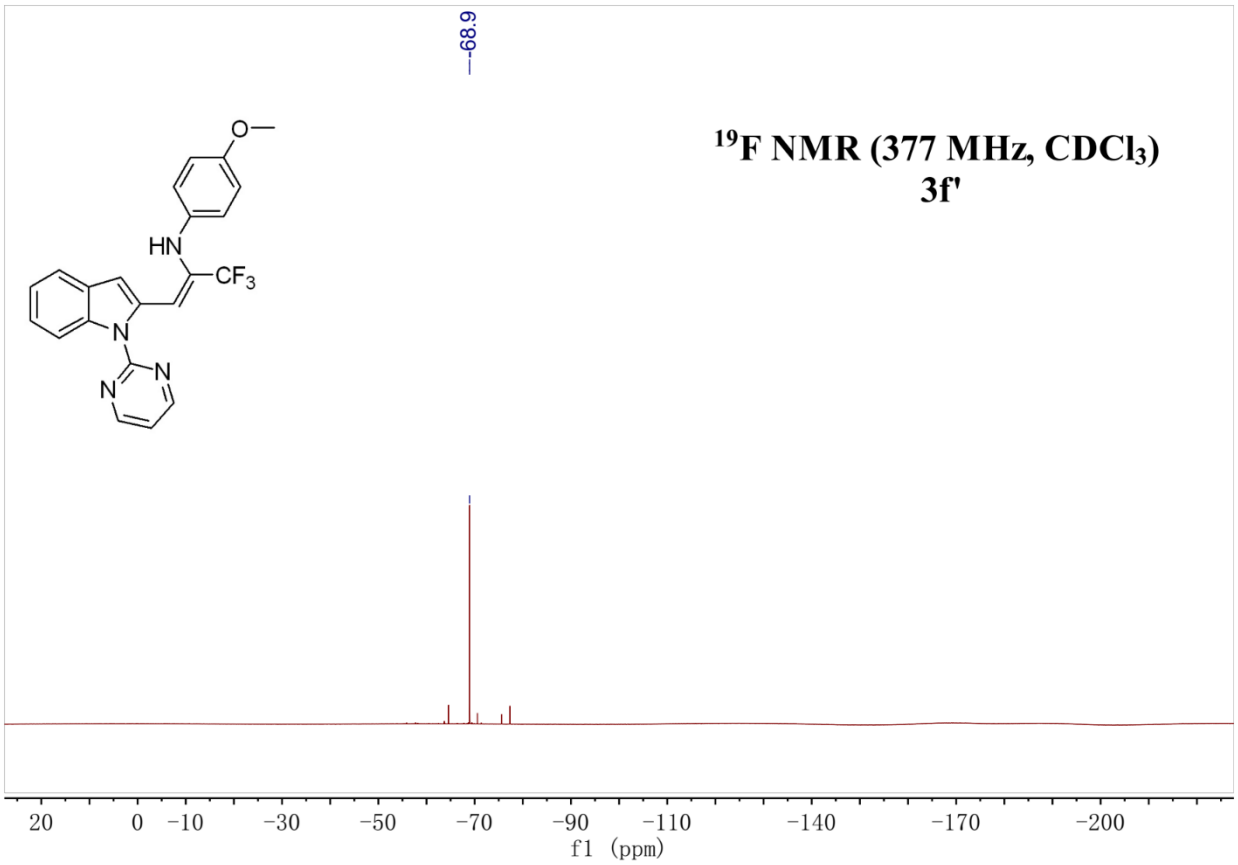
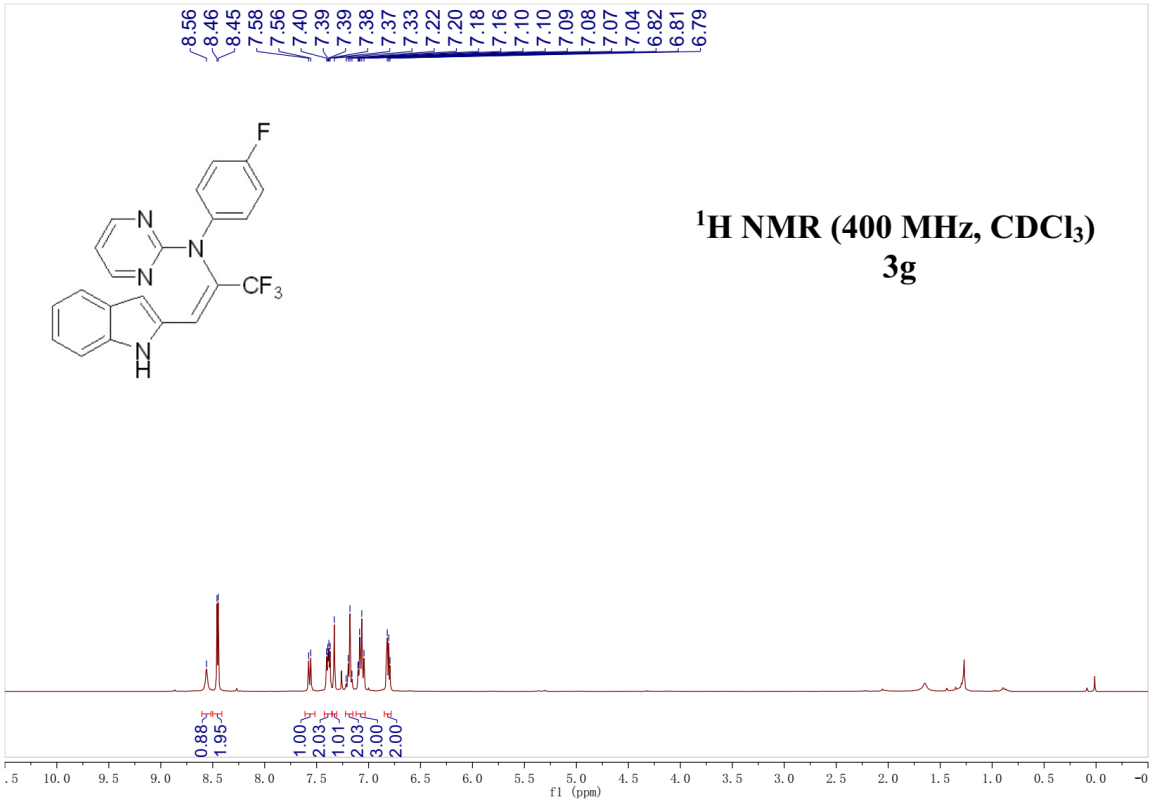
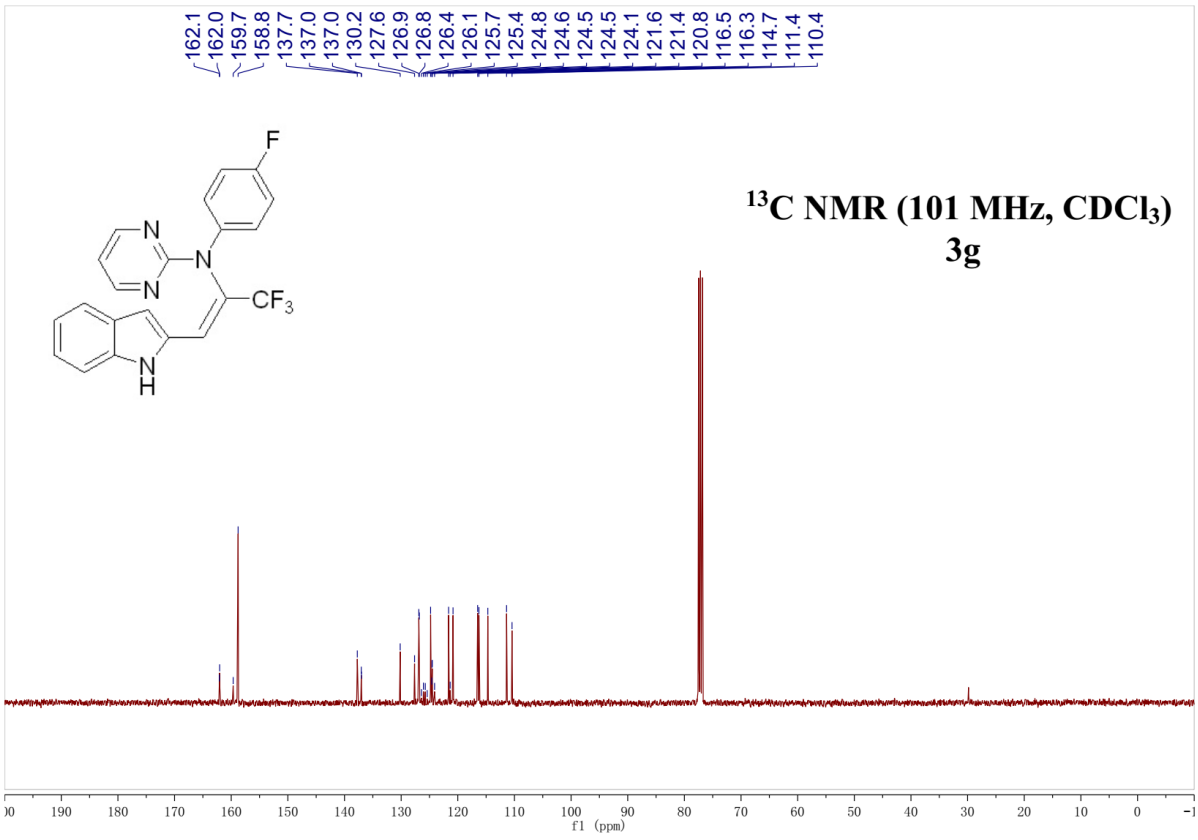
135.2
132.1
129.3
127.0
126.4
126.1
125.8
125.5
124.5
124.3
122.4
121.6
121.1
118.8
118.3
117.6
114.6
113.9
112.0
111.9
111.9
111.9
110.9
55.6
HN
CF3
N
N
N
O
13C NMR (101 MHz, CDCl3)
3f'
f1 (ppm)

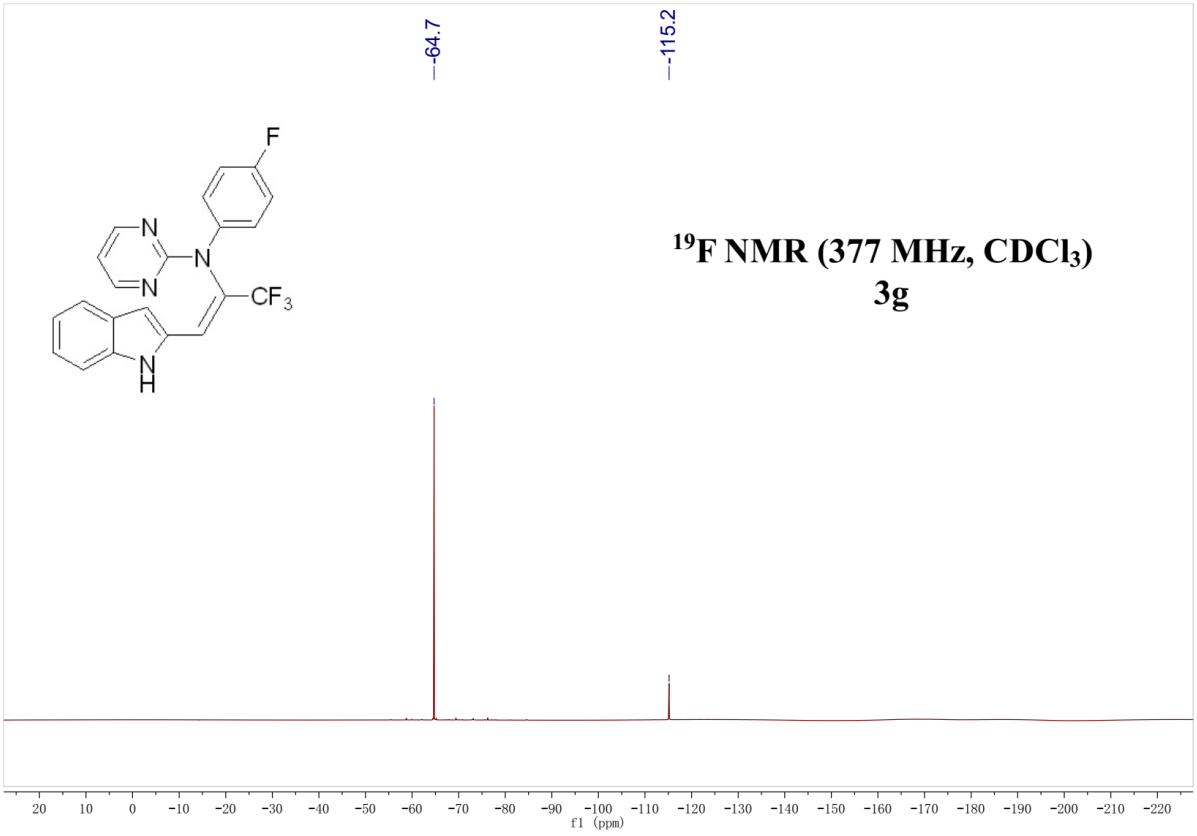

-68.9
O
HN
CF3
N
N
N
19F NMR (377 MHz, CDCl3)
3f'
20
0
-10
-30
-50
-70
-90
-110
-140
-170
-200
f1 (ppm)



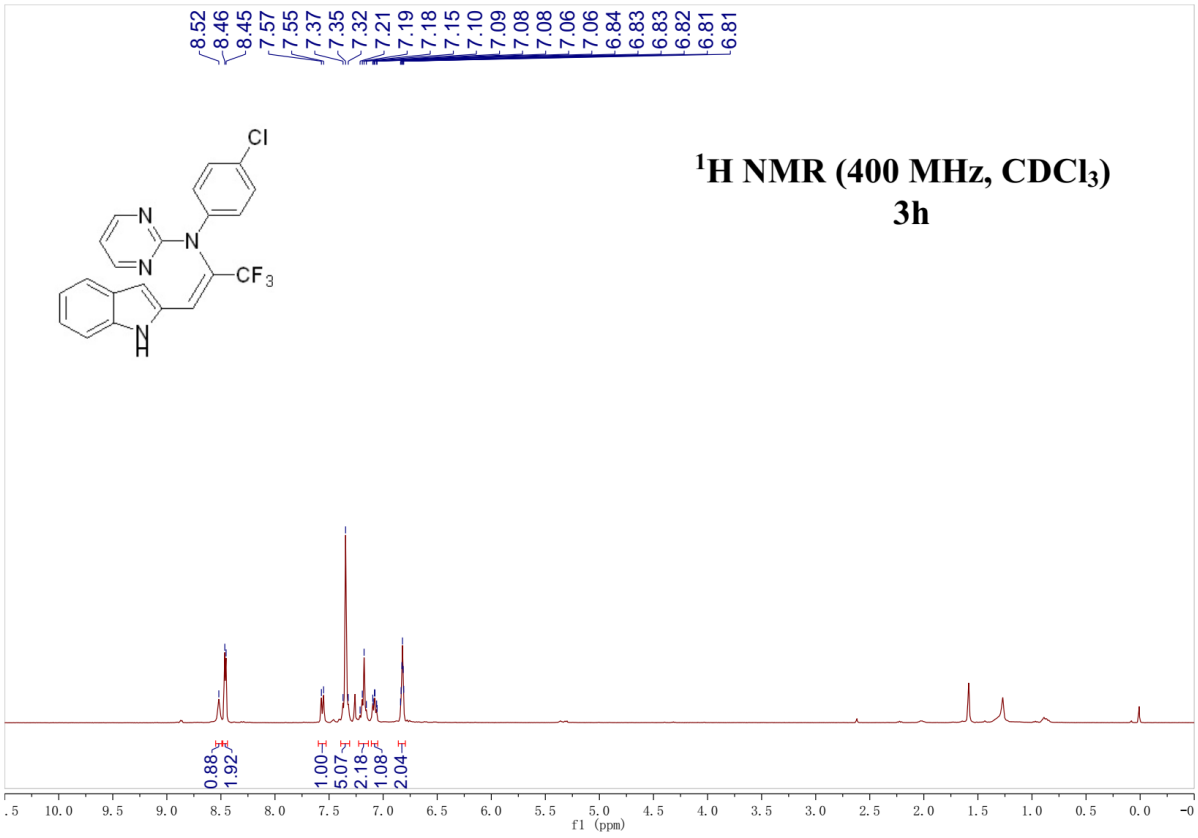
^{1}H NMR (400 MHz, $CDCl_3$)
3g



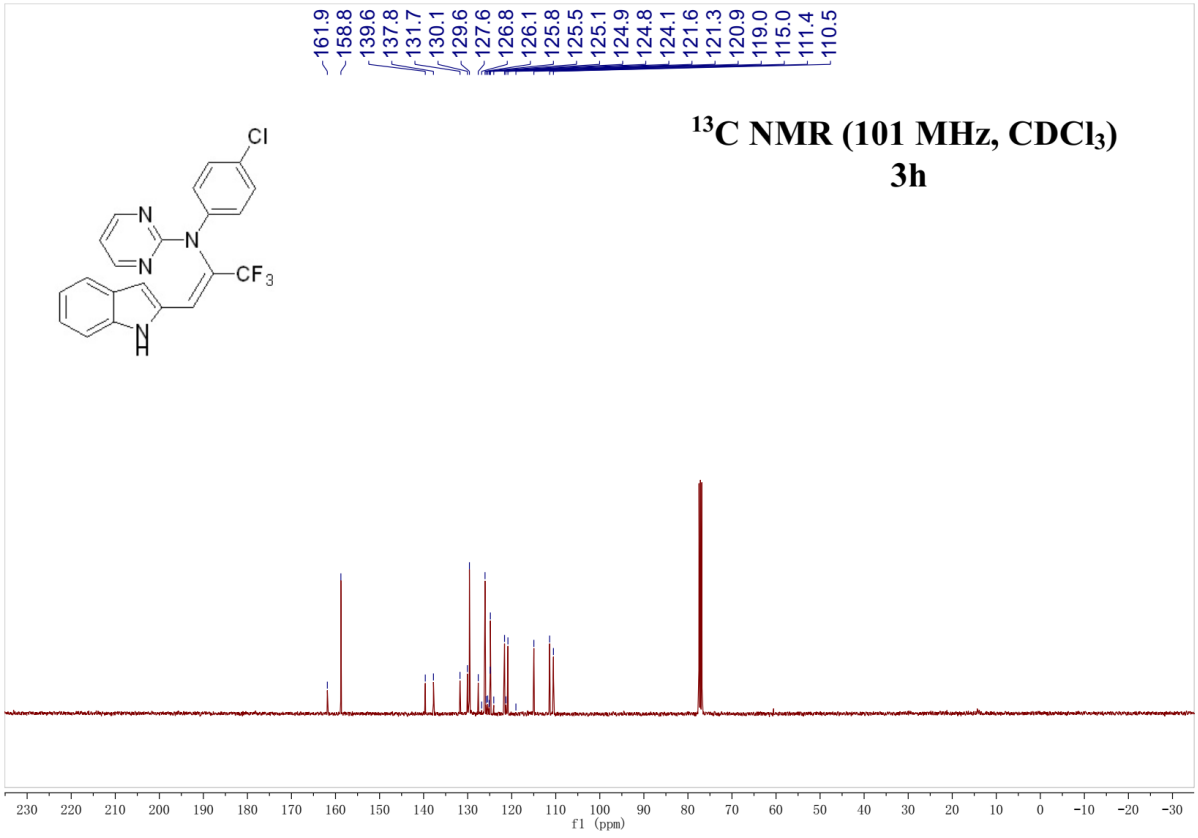
^{13}C NMR (101 MHz, $CDCl_3$)
3g



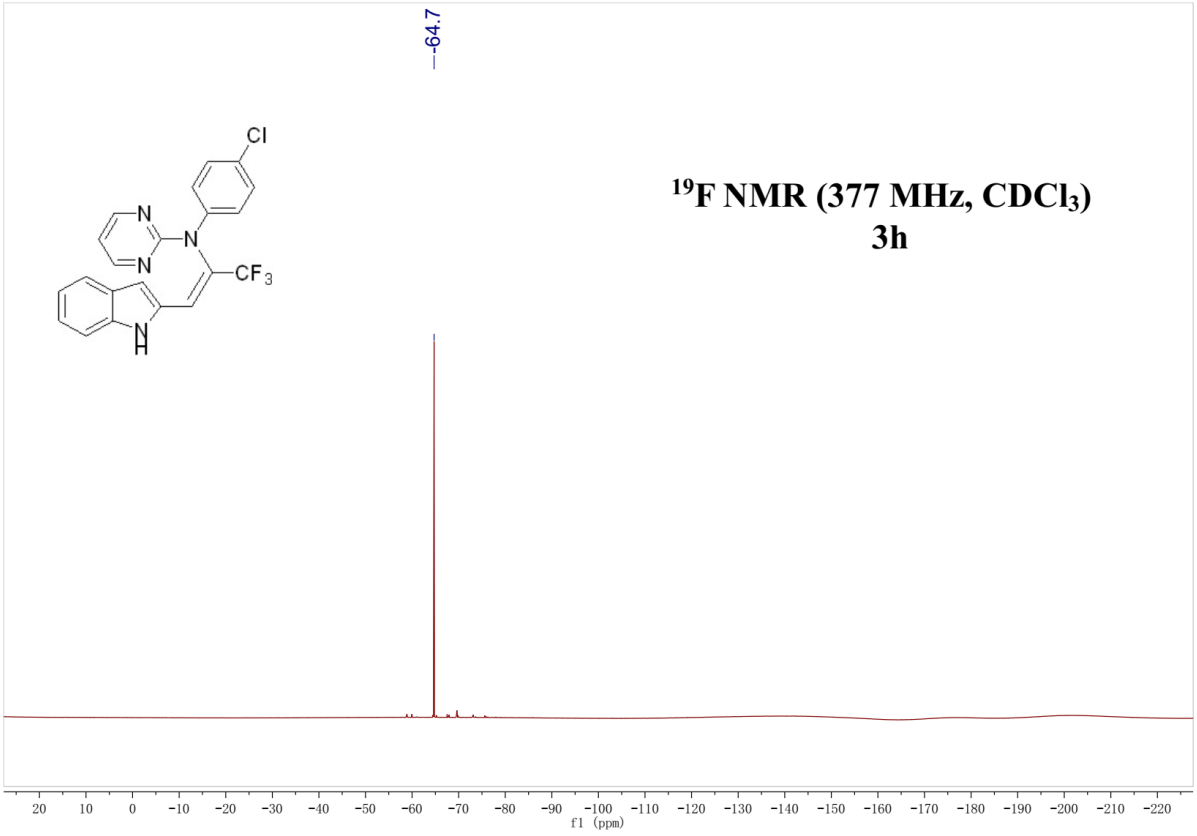
^{19}F NMR (377 MHz, $CDCl_3$)
3g



^{1}H NMR (400 MHz, $CDCl_3$)
3h



^{13}C NMR (101 MHz, $CDCl_3$)
3h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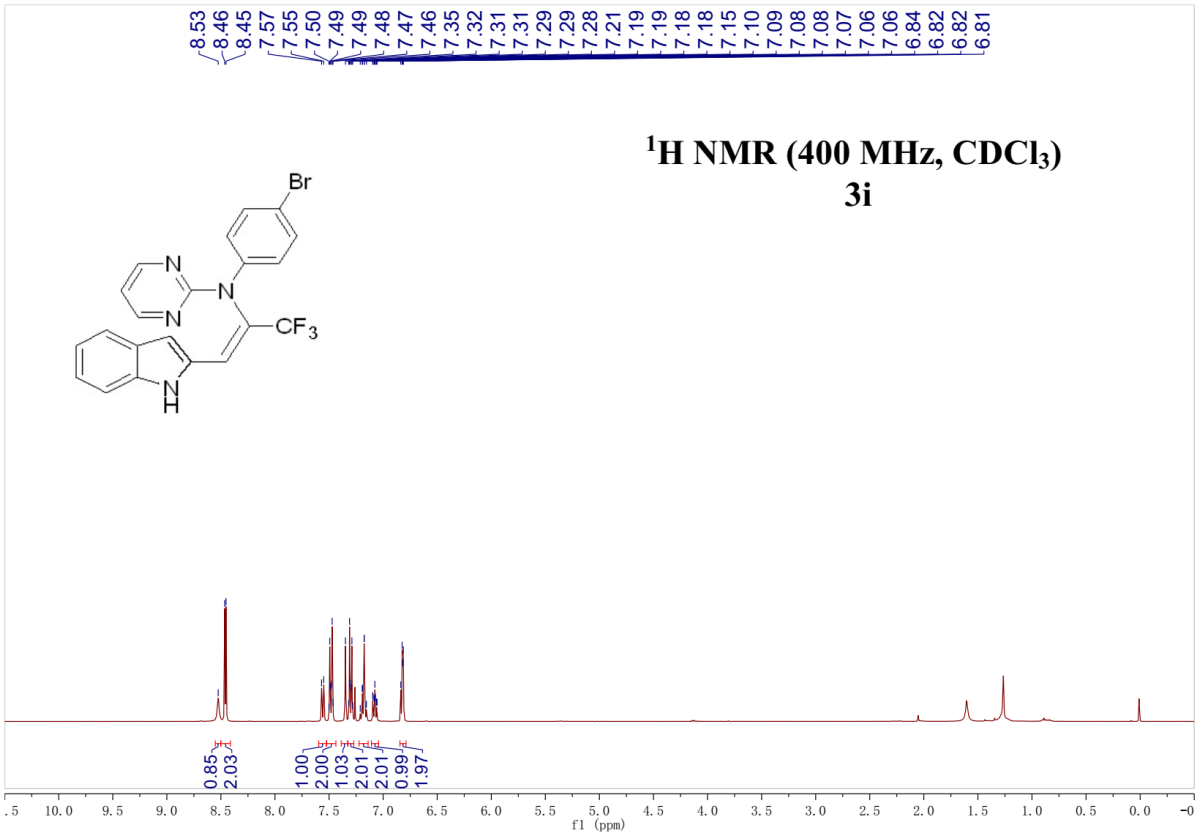
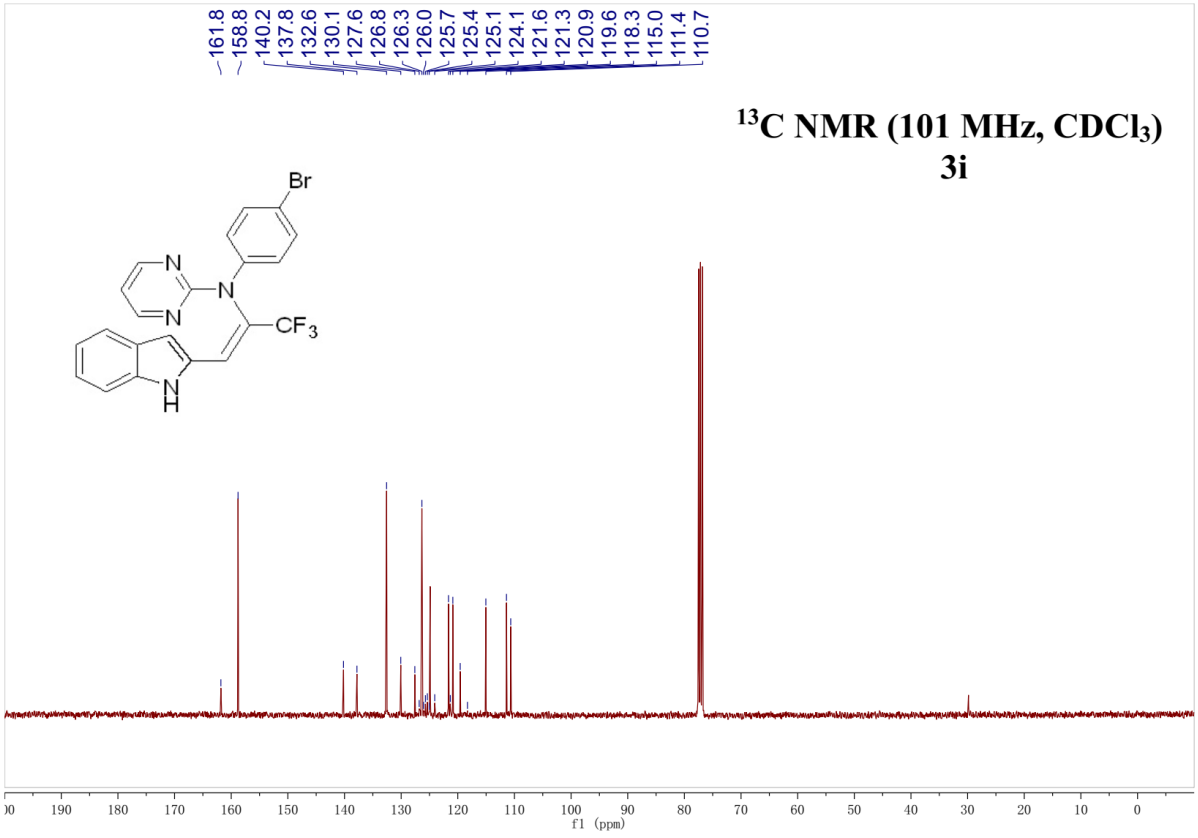
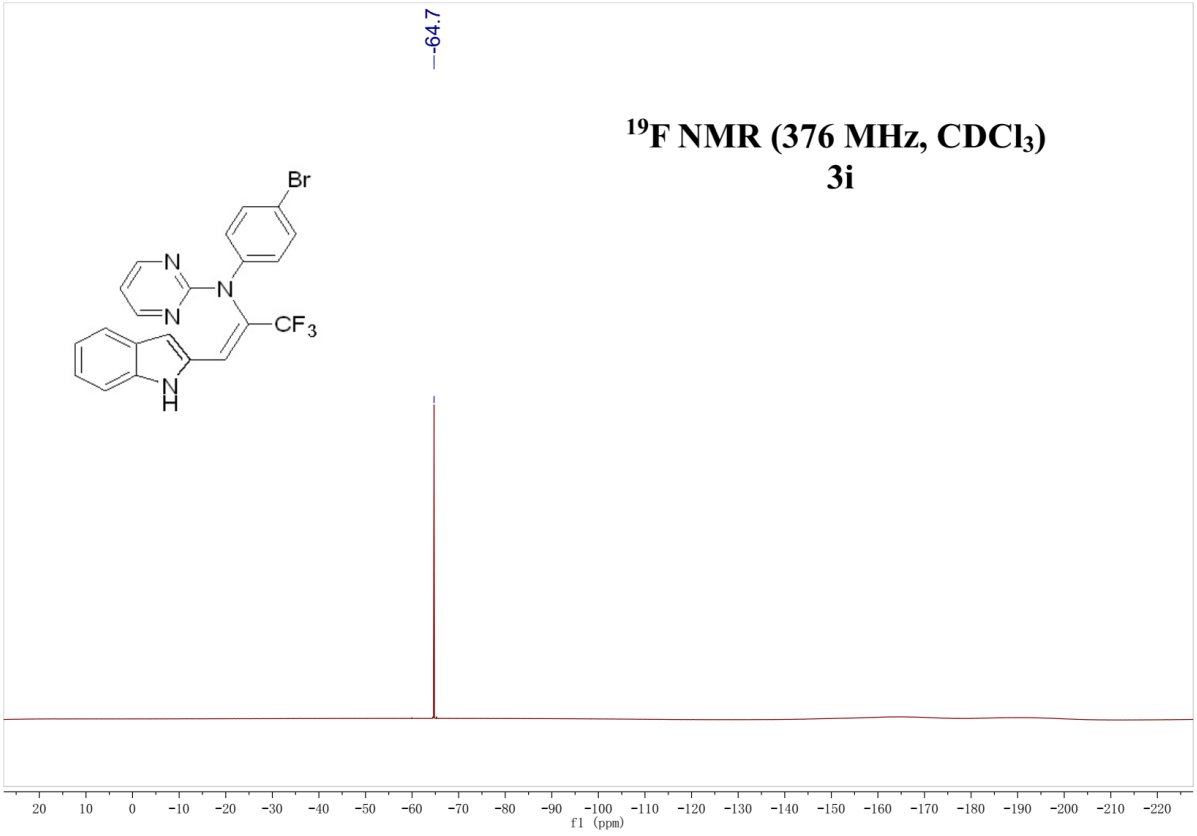
Cl
N
N
N
CF3
H
19F NMR (377 MHz, CDCl3)
3h
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



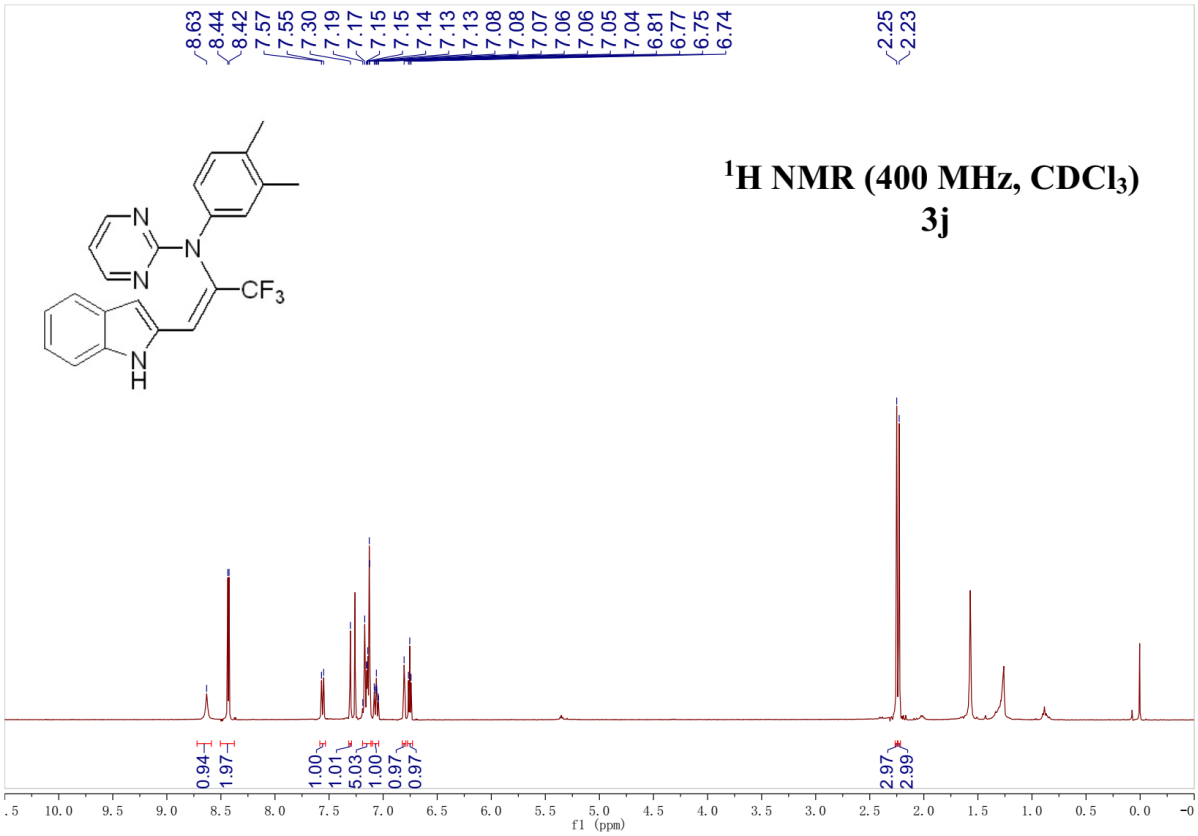
^{1}H NMR (400 MHz, $CDCl_3$)
3i



^{13}C NMR (101 MHz, $CDCl_3$)
3i



^{19}F NMR (376 MHz, $CDCl_3$)
3i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7.17
7.15
7.15
7.14
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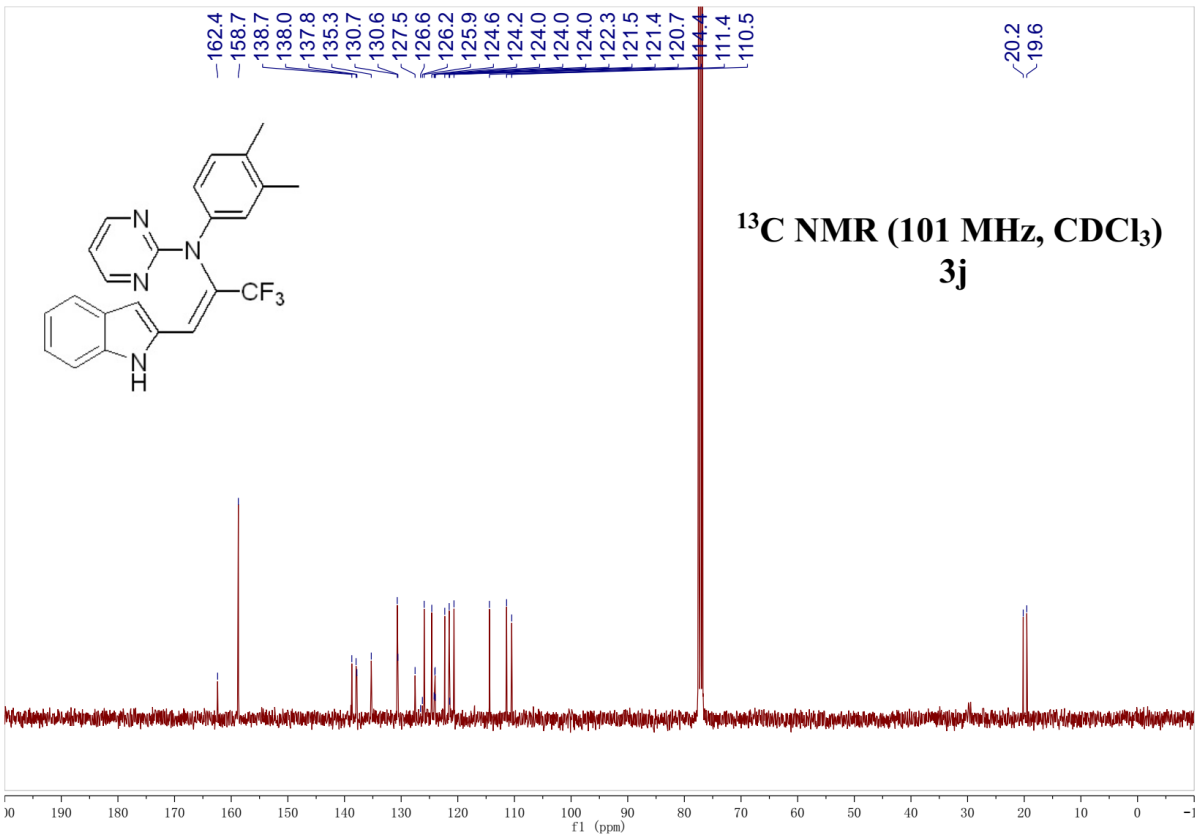
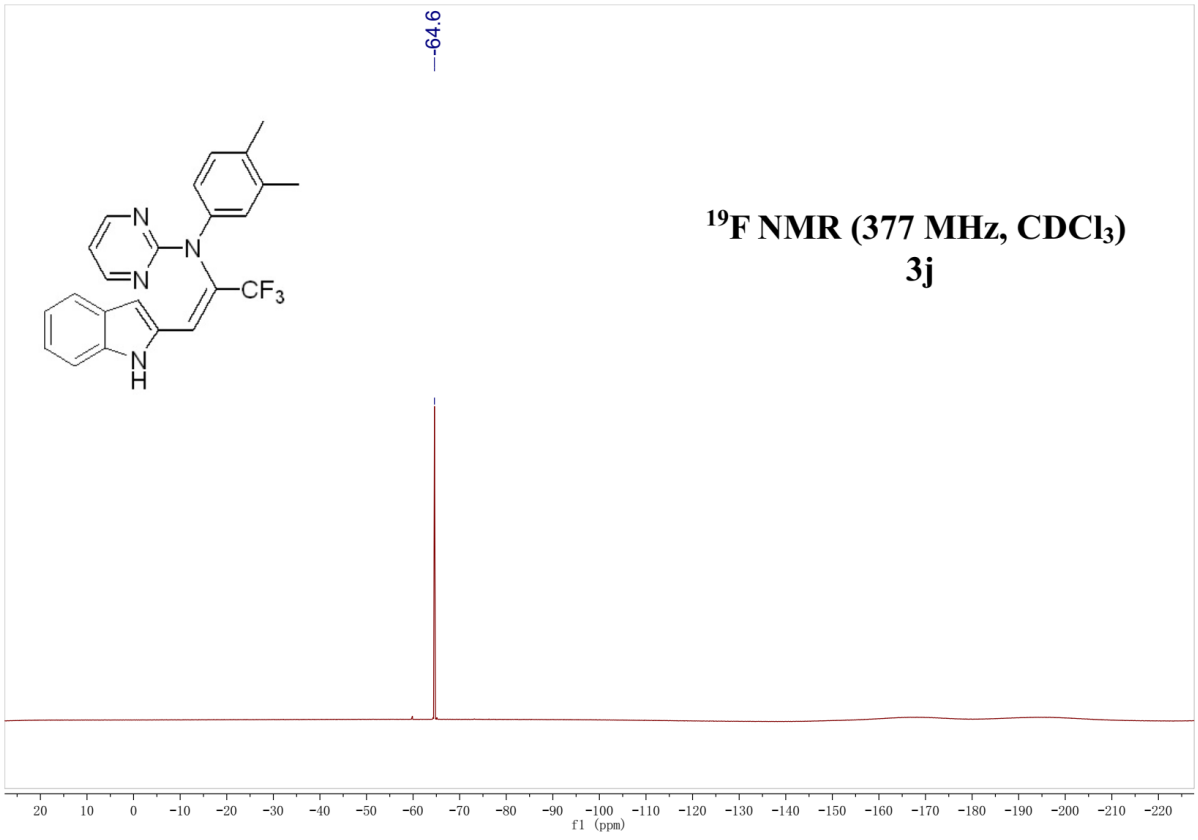
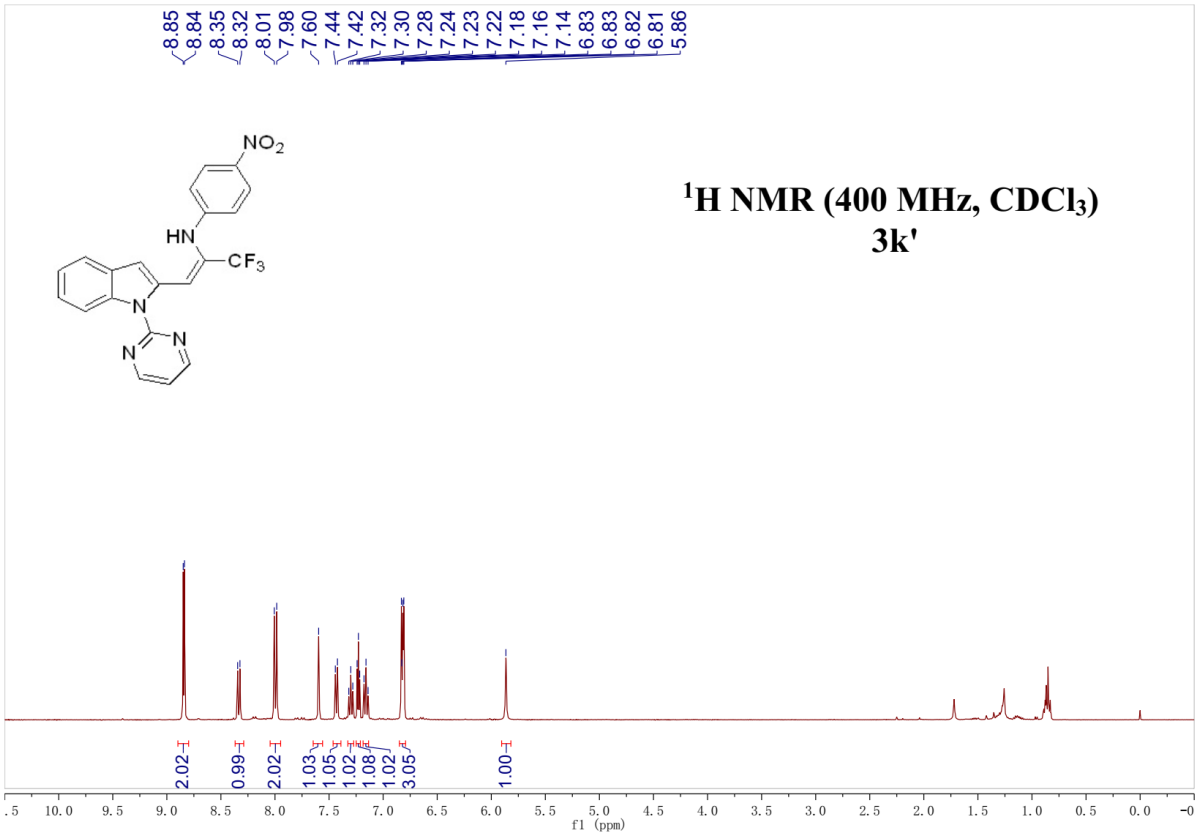
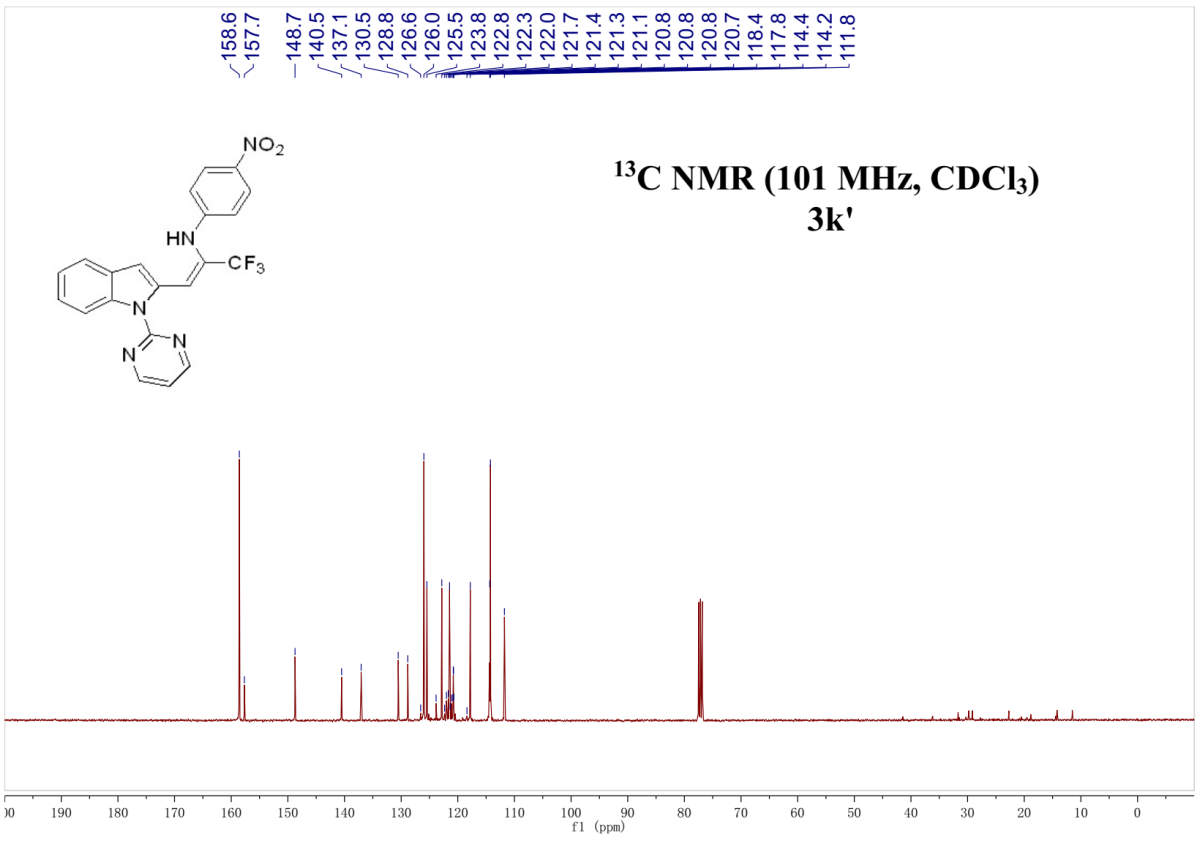
7.08
7.08
7.07
7.06
7.06
7.05
7.04
6.81
6.77
6.75
6.74
2.25
2.23
^{1}H NMR (400 MHz, CDCl$_3$)
3j
CF$_3$
N
N
N
H
0.94
1.97
1.00
1.01
5.03
1.00
0.97
0.97
2.97
2.99
f1 (ppm)


162.4
158.7
138.7
138.0
137.8
135.3
130.7
130.6
127.5
126.6
126.2
125.9
124.6
124.2
124.0
124.0
124.0
122.3
121.5
121.4
120.7
114.4
111.4
110.5
20.2
19.6
^{13}C NMR (101 MHz, CDCl$_3$)
3j
CF$_3$
N
N
N
H
f1 (ppm)

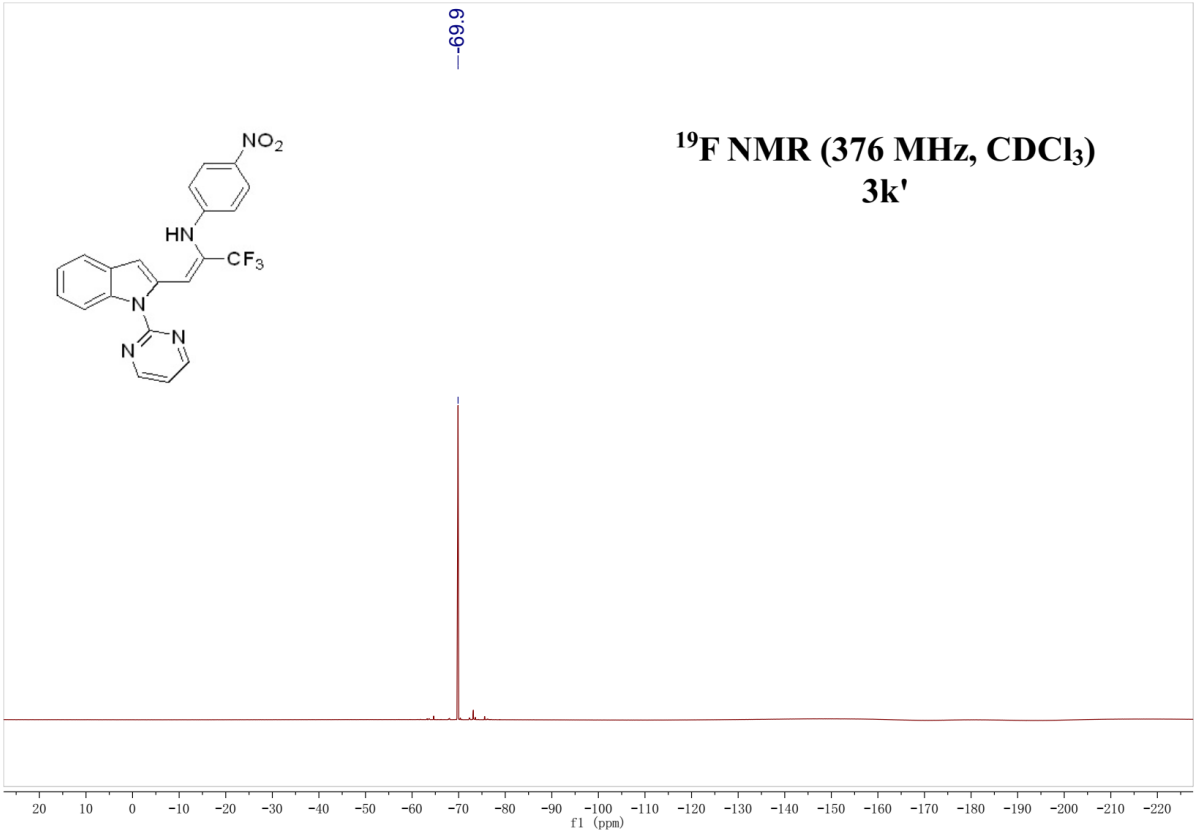

-64.6
N
N
N
CF3
N
H
19F NMR (377 MHz, CDCl3)
3j
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

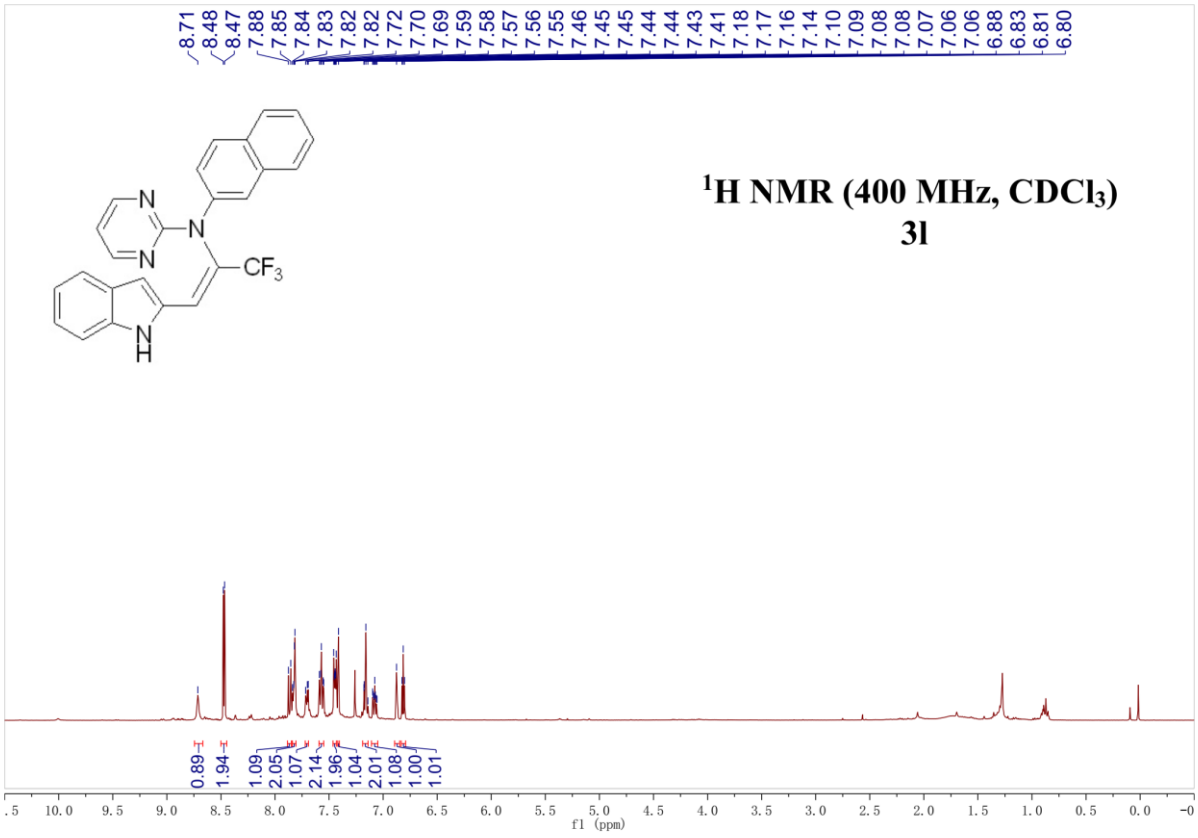


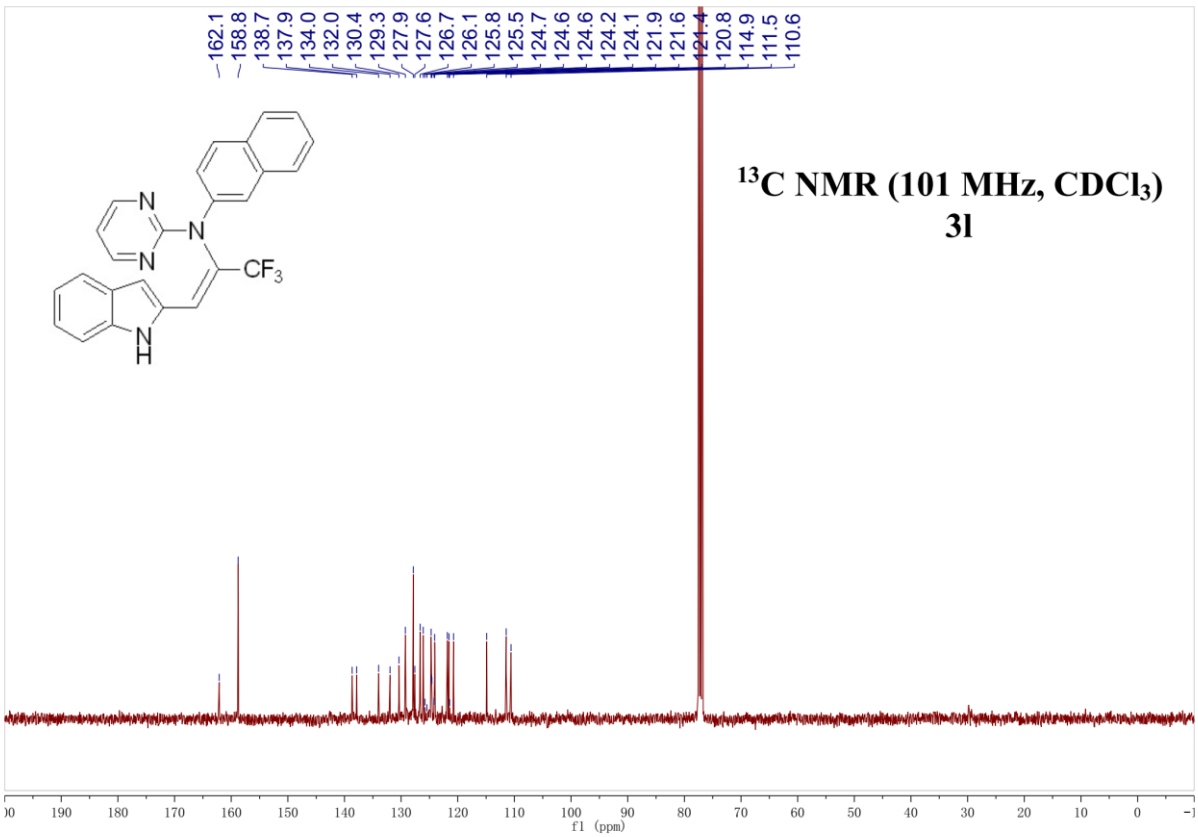
^{1}H NMR (400 MHz, $CDCl_3$)
3k'

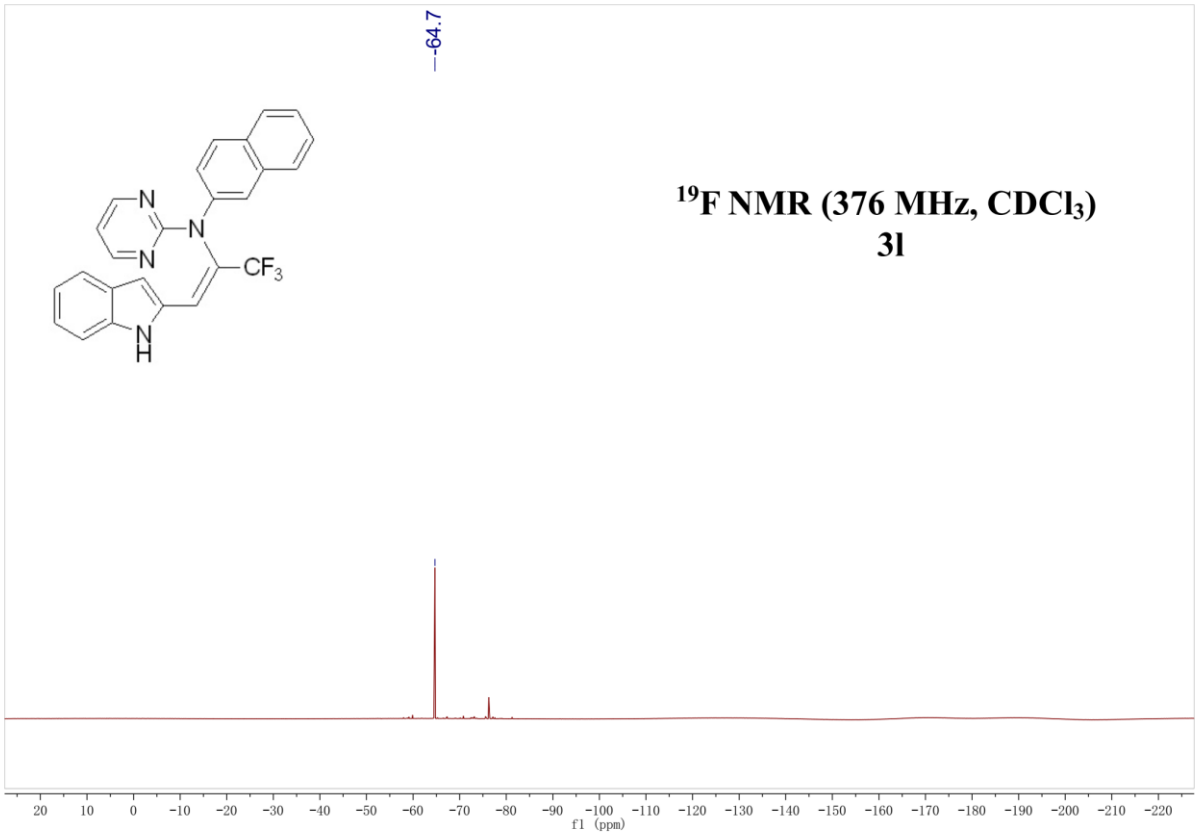


^{13}C NMR (101 MHz, $CDCl_3$)
3k'

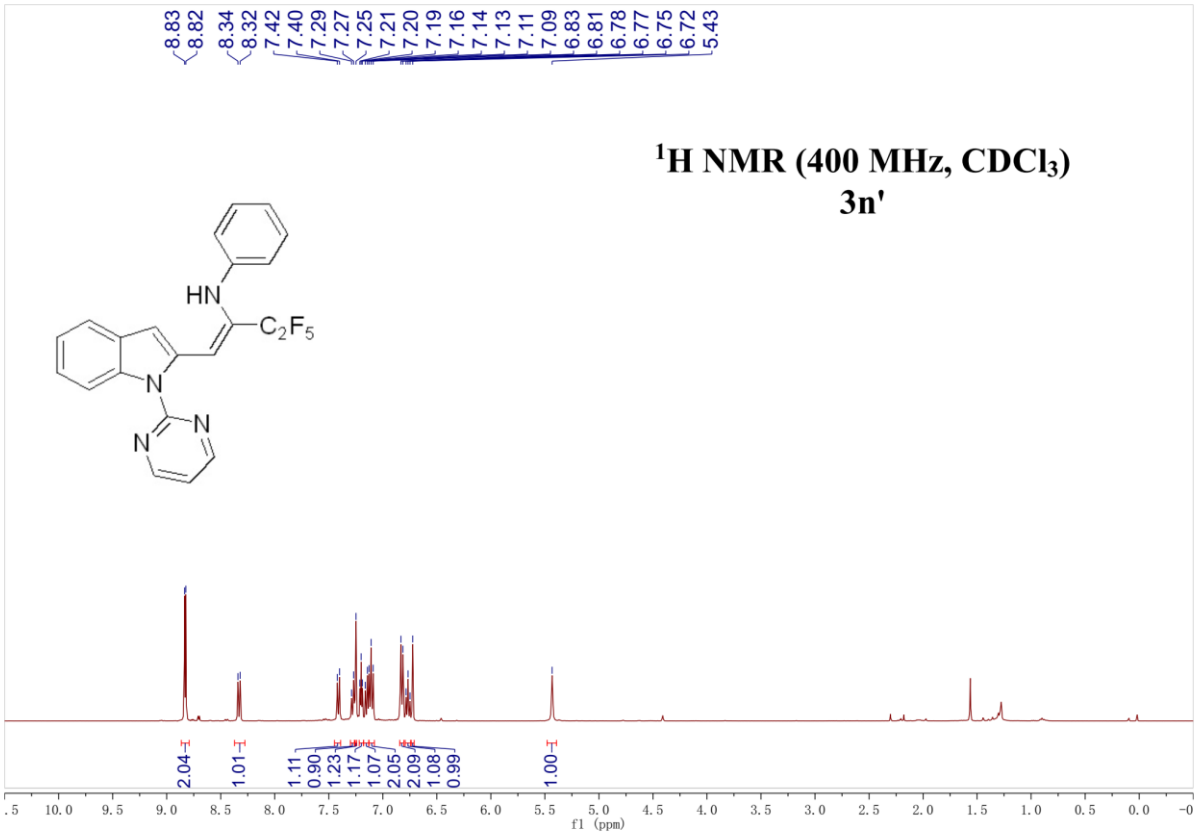

-69.9
NO2
HN
CF3
N
N
N
19F NMR (376 MHz, CDCl3)
3k'
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

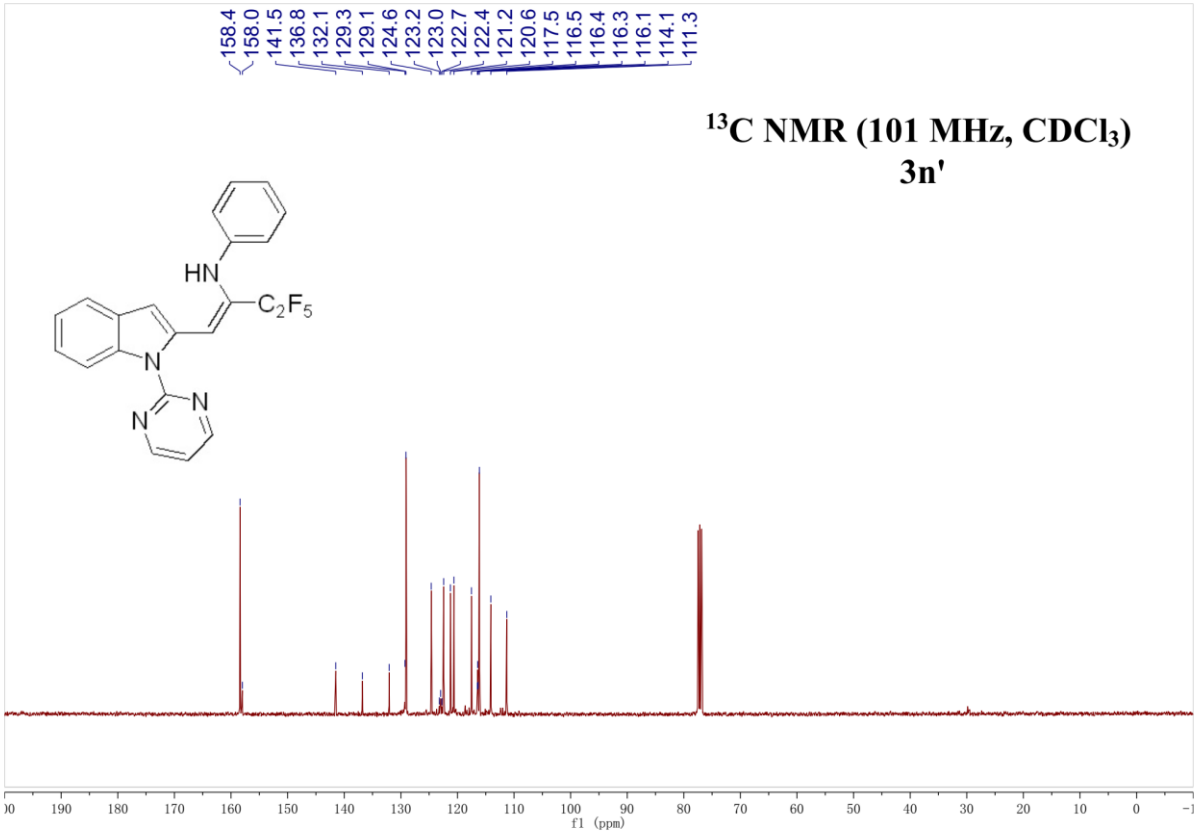

8.71
8.48
8.47
7.88
7.85
7.84
7.83
7.82
7.82
7.72
7.70
7.69
7.59
7.58
7.57
7.56
7.55
7.46
7.45
7.45
7.44
7.44
7.43
7.41
7.18
7.17
7.16
7.14
7.10
7.09
7.08
7.08
7.07
7.06
7.06
6.88
6.83
6.81
6.80
N
N
N
CF3
N
H
1H NMR (400 MHz, CDCl3)
3l
0.89
1.94
1.09
2.05
1.07
2.14
1.96
1.04
2.01
1.08
1.00
1.01
f1 (ppm)

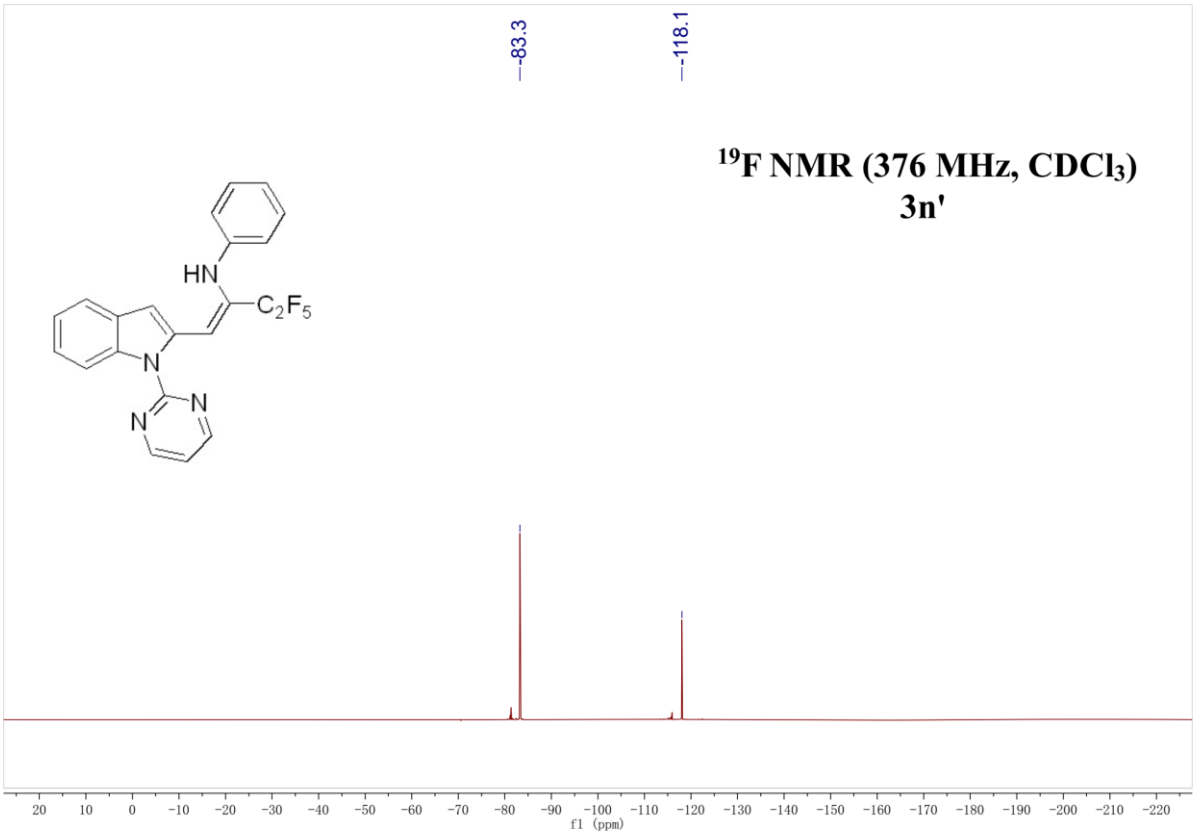

162.1
158.8
138.7
137.9
134.0
132.0
130.4
129.3
127.9
127.6
126.7
126.1
125.8
125.5
124.7
124.6
124.6
124.2
124.1
121.9
121.6
121.4
120.8
114.9
111.5
110.6
N
N
N
CF3
N
H
13C NMR (101 MHz, CDCl3)
3l
f1 (ppm)

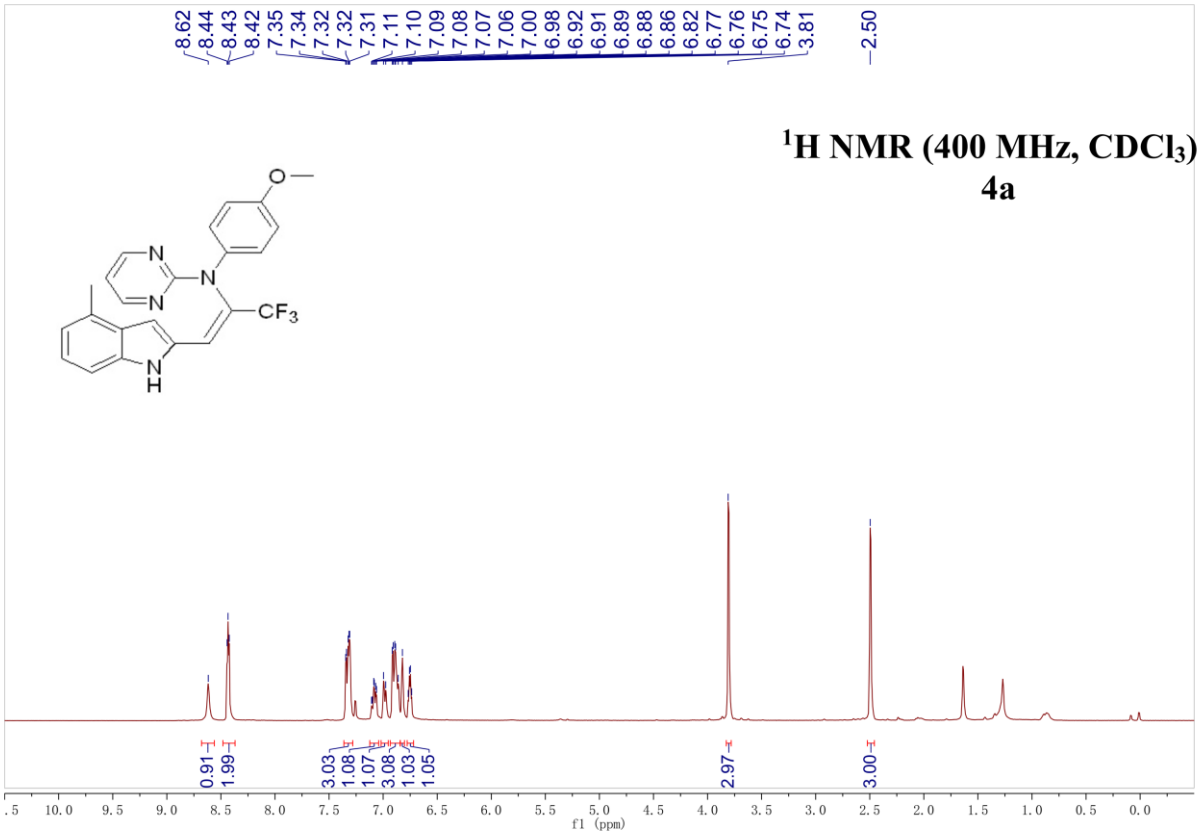


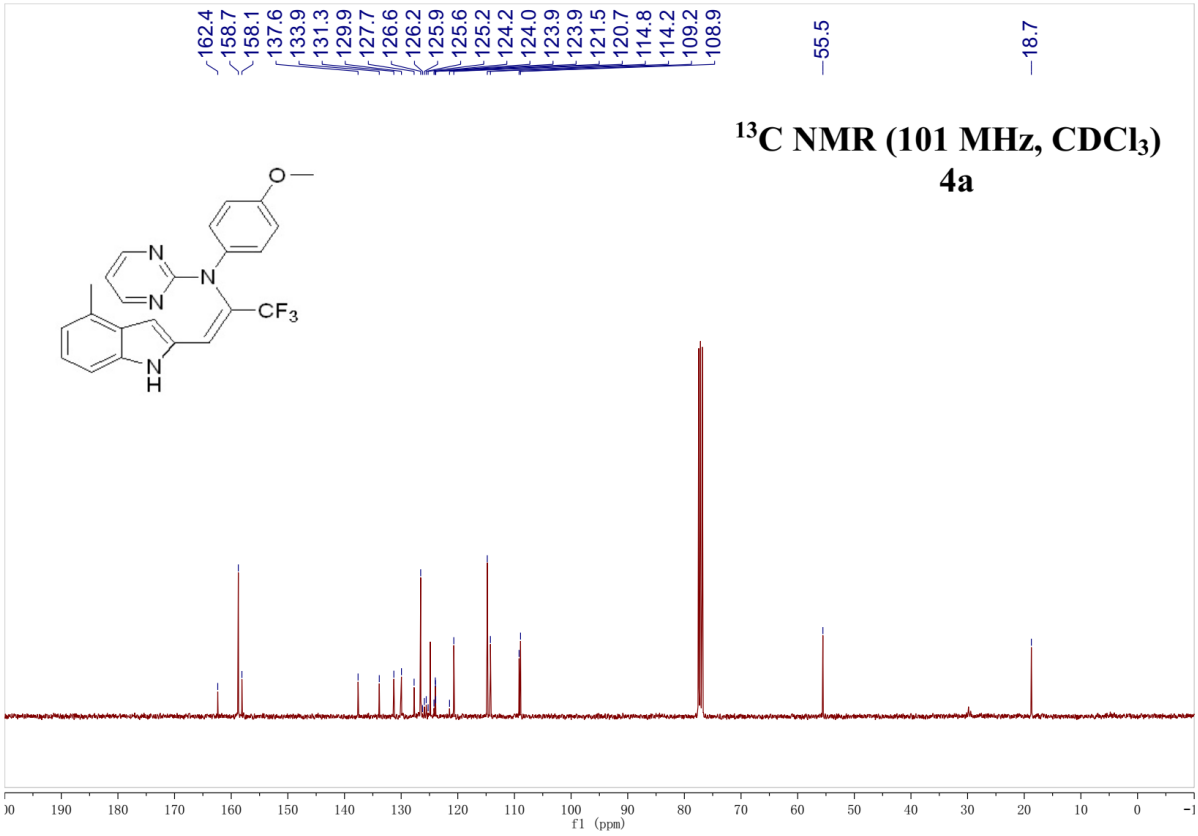
^{19}F NMR (376 MHz, $CDCl_3$)
3l

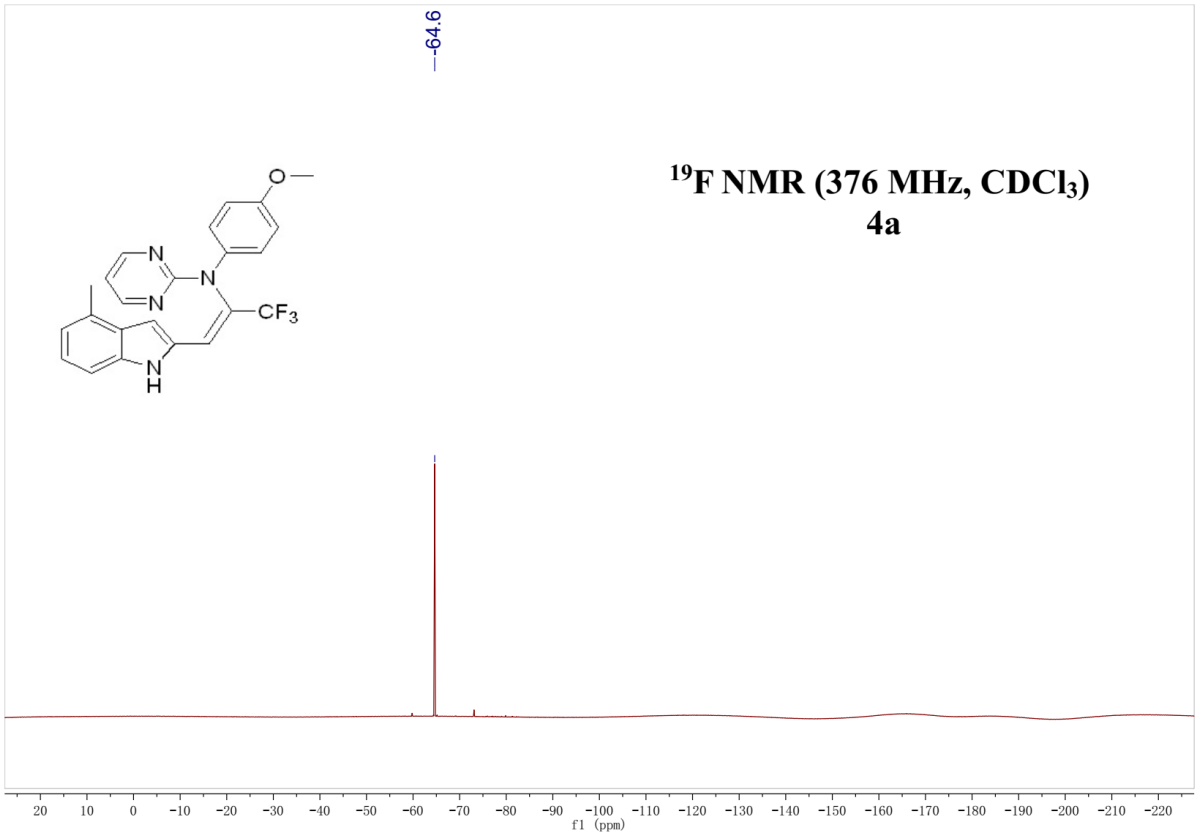

8.83
8.82
8.34
8.32
7.42
7.40
7.29
7.27
7.25
7.21
7.20
7.19
7.16
7.14
7.13
7.11
7.09
6.83
6.81
6.78
6.77
6.75
6.72
5.43
^{1}H NMR (400 MHz, CDCl$_3$)
3n'
HN
C_2F_5
N
N
N
2.04
1.01
1.11
0.90
1.23
1.17
1.07
2.05
2.09
1.08
0.99
1.00
f1 (ppm)


158.4
158.0
141.5
136.8
132.1
129.3
129.1
124.6
123.2
123.0
122.7
122.4
121.2
120.6
117.5
116.5
116.4
116.3
116.1
114.1
111.3
^{13}C NMR (101 MHz, CDCl$_3$)
3n'
HN
C_2F_5
N
N
N
f1 (ppm)

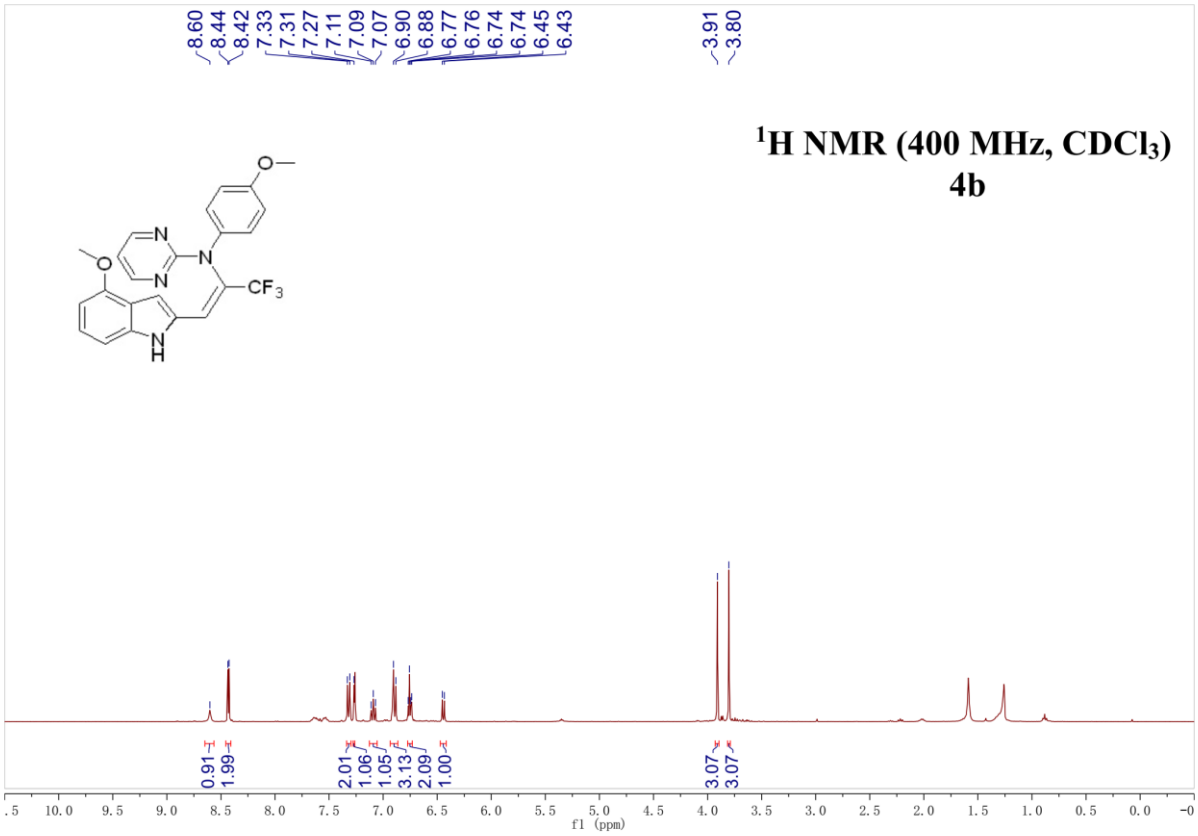

-83.3
-118.1
19F NMR (376 MHz, CDCl3)
3n'
HN
C2F5
N
N
N
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

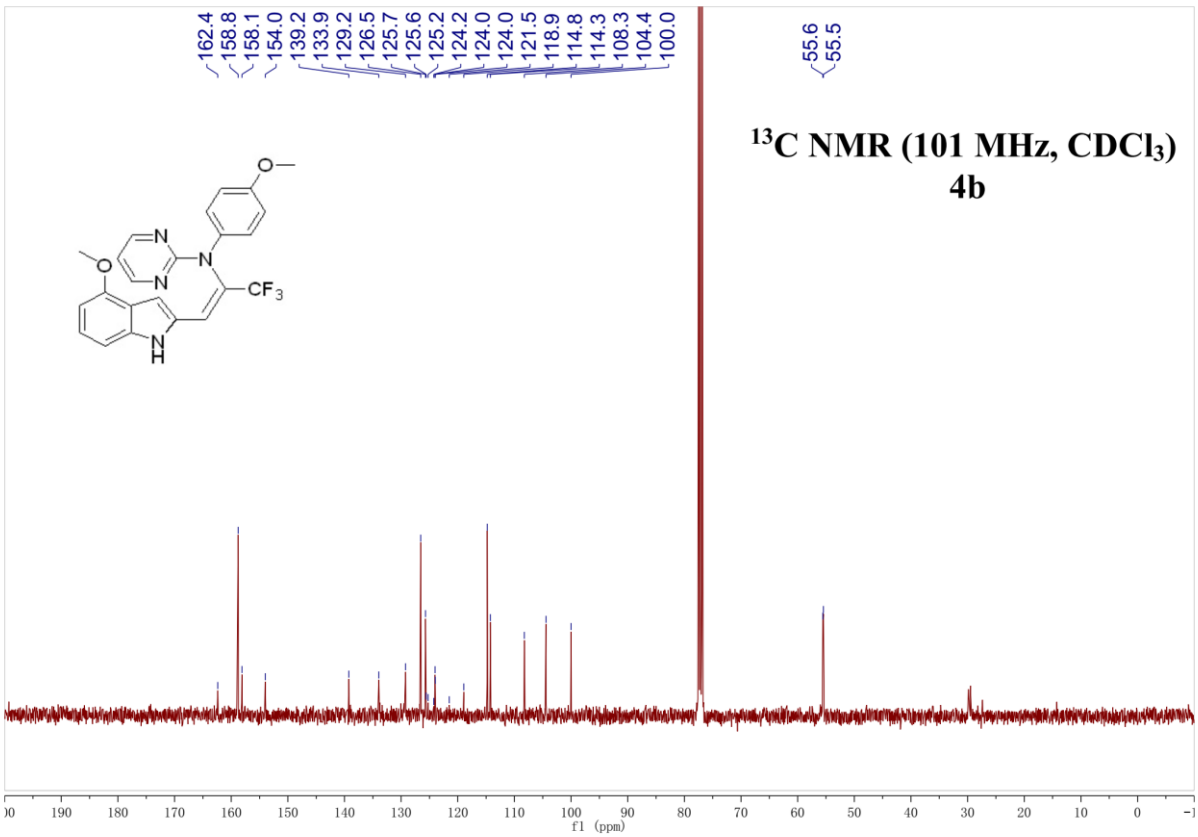

8.62
8.44
8.43
8.42
7.35
7.34
7.32
7.32
7.31
7.11
7.10
7.09
7.08
7.07
7.06
7.00
6.98
6.92
6.91
6.89
6.88
6.86
6.82
6.77
6.76
6.75
6.74
3.81
2.50
¹H NMR (400 MHz, CDCl₃)
4a
O
N
N
N
CF₃
N
H
0.91
1.99
3.03
1.08
1.07
3.08
1.03
1.05
2.97
3.00
f1 (ppm)

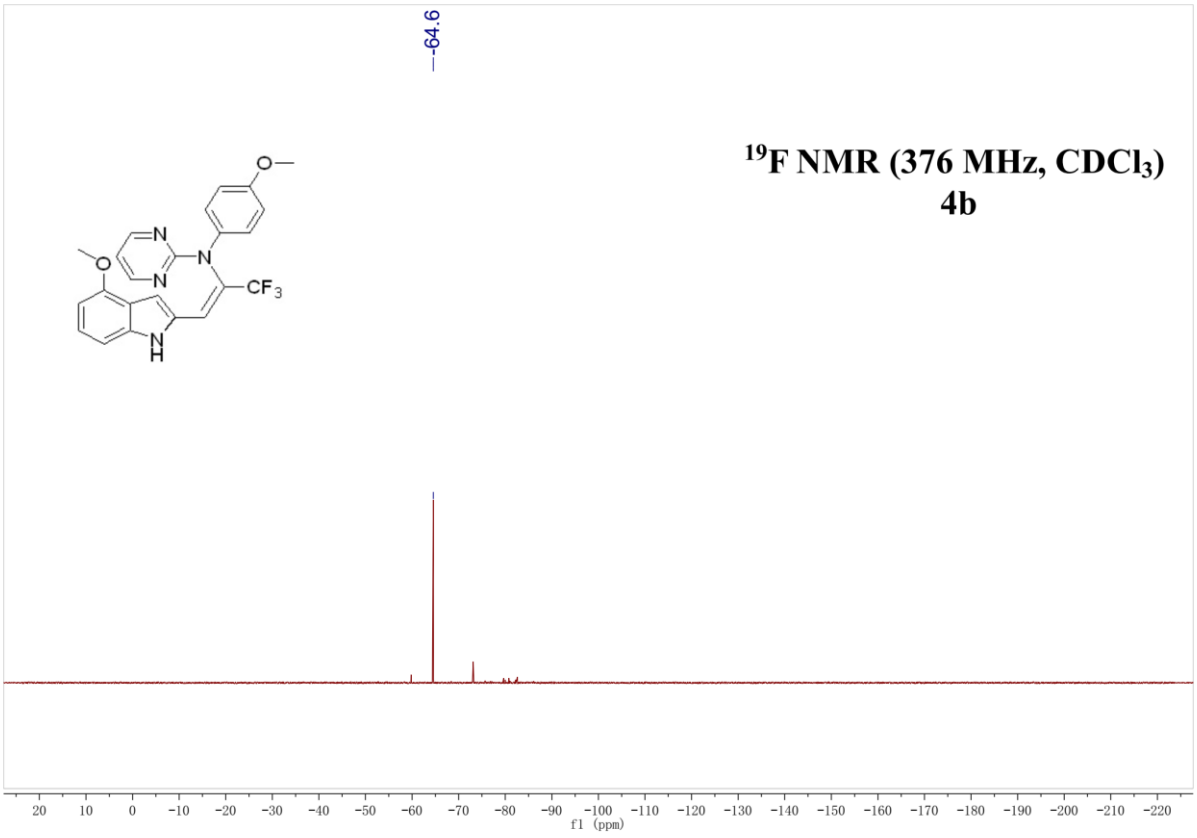

162.4
158.7
158.1
137.6
133.9
131.3
129.9
127.7
126.6
126.2
125.9
125.6
125.2
124.2
124.0
123.9
123.9
121.5
120.7
114.8
114.2
109.2
108.9
55.5
18.7
¹³C NMR (101 MHz, CDCl₃)
4a
O
N
N
N
CF₃
N
H
f1 (ppm)

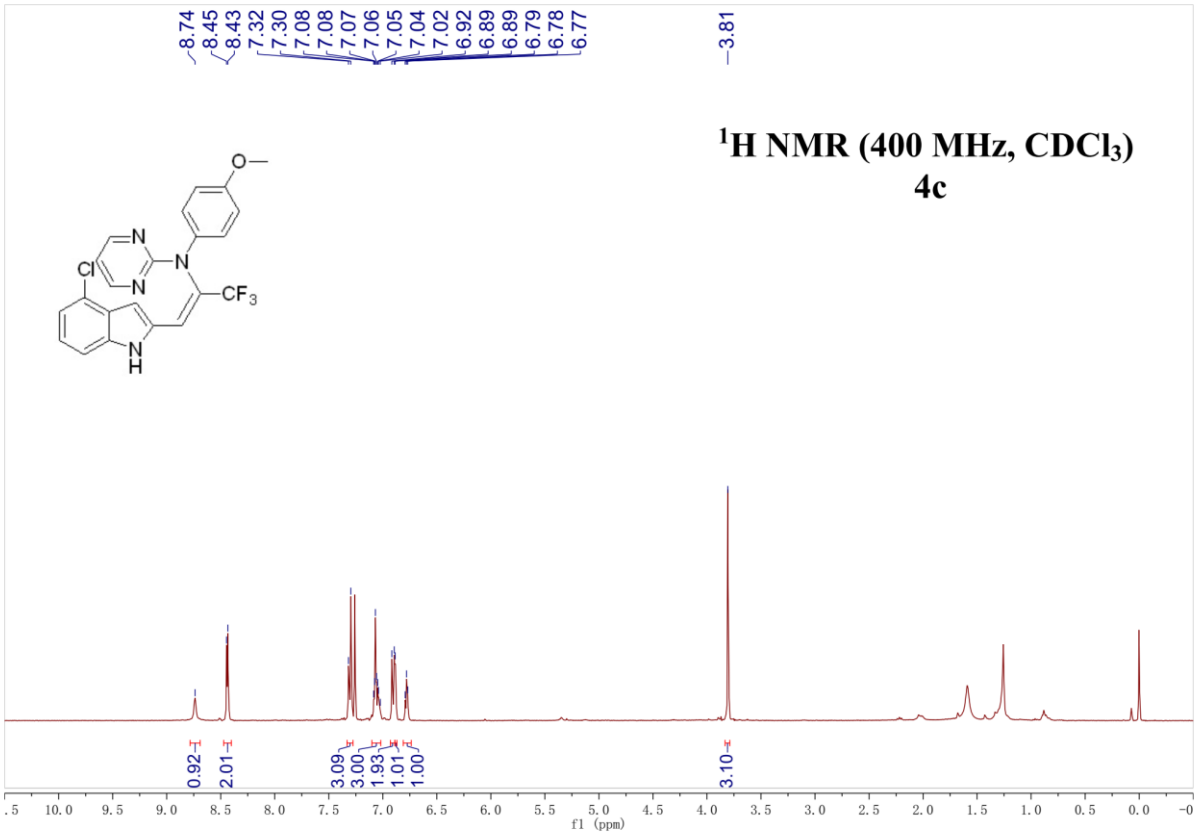


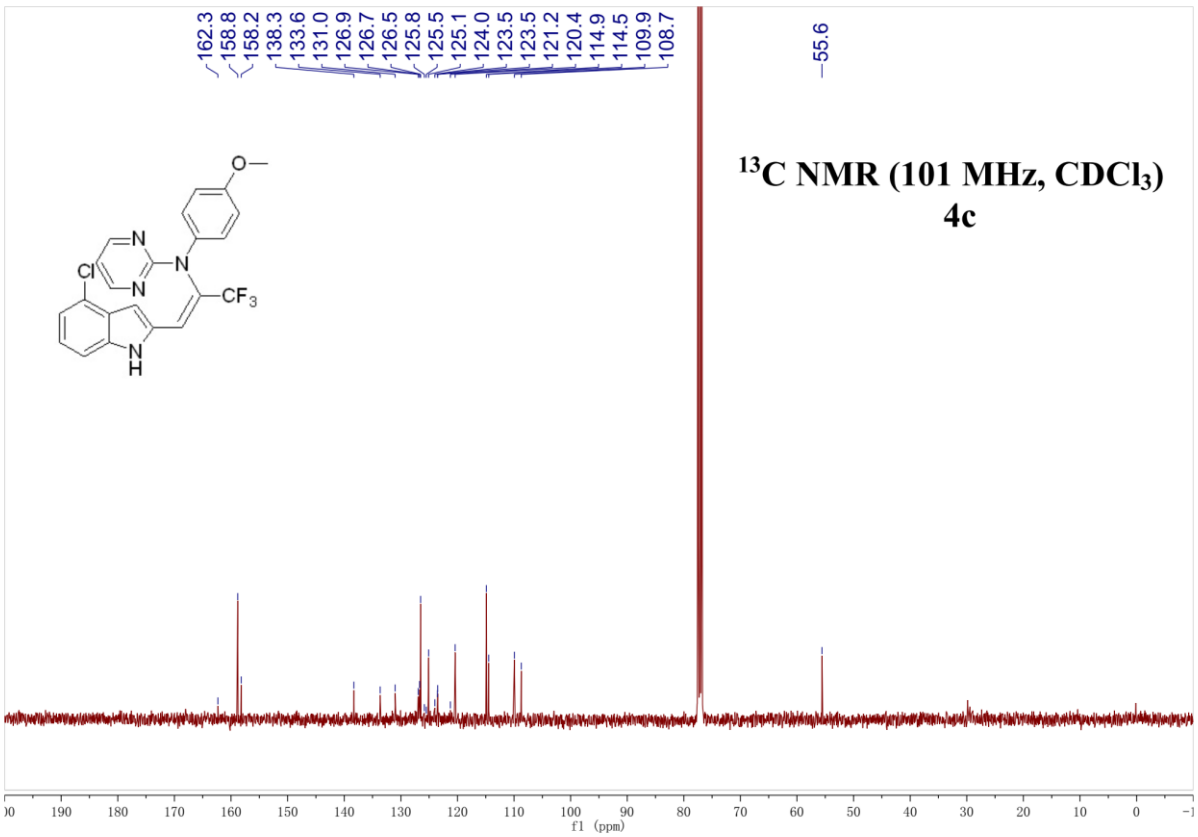
^{19}F NMR (376 MHz, $CDCl_3$)
4a

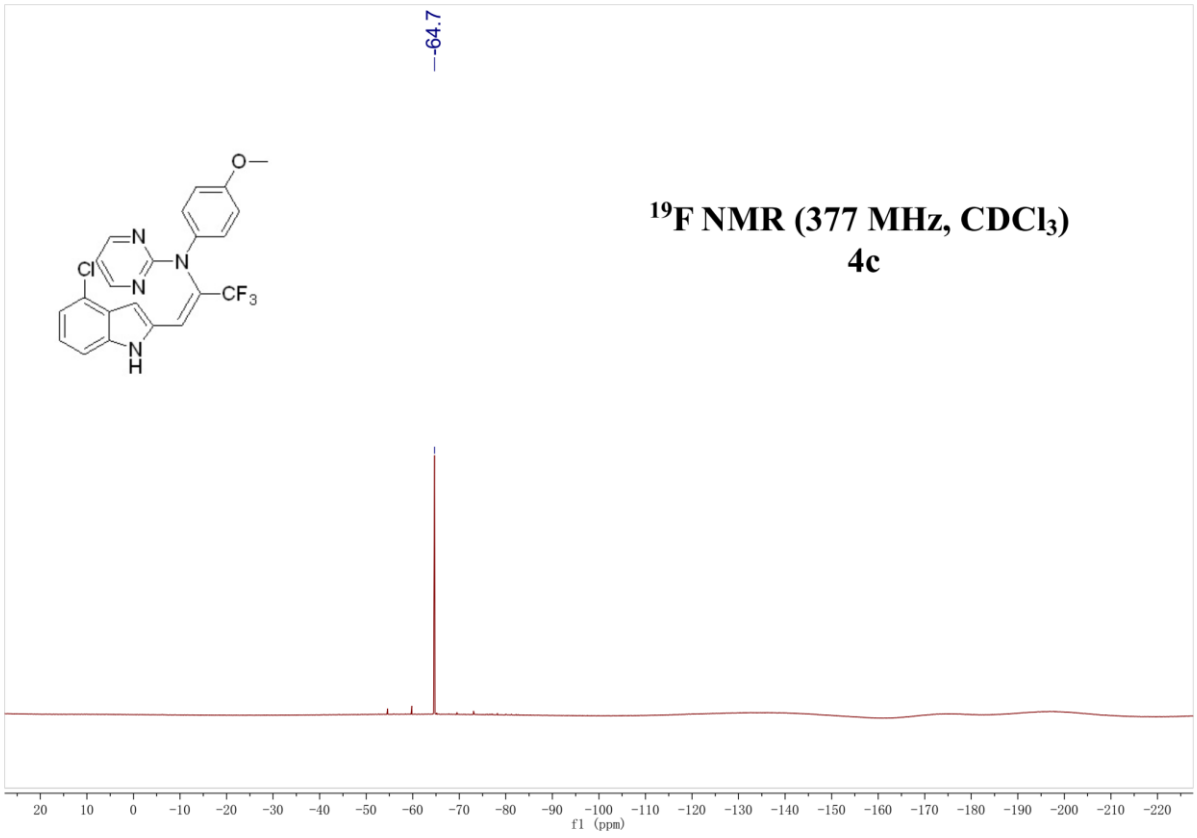

8.60
8.44
8.42
7.33
7.31
7.27
7.11
7.09
7.07
6.90
6.88
6.77
6.76
6.74
6.74
6.45
6.43
3.91
3.80
^{1}H NMR (400 MHz, CDCl$_3$)
4b
CF$_3$
0.91
1.99
2.01
1.06
1.05
3.13
2.09
1.00
3.07
3.07
f1 (ppm)

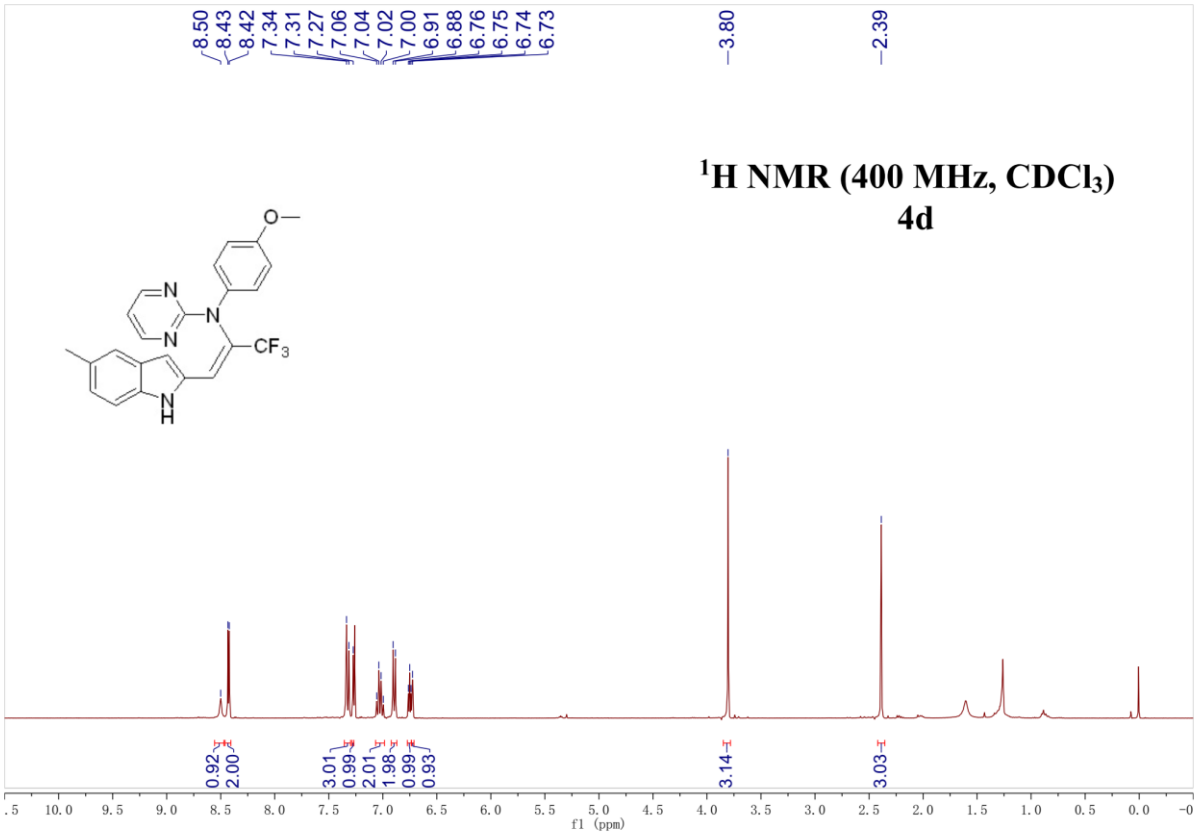

162.4
158.8
158.1
154.0
139.2
133.9
129.2
126.5
125.7
125.6
125.2
124.2
124.0
124.0
121.5
118.9
114.8
114.3
108.3
104.4
100.0
55.6
55.5
^{13}C NMR (101 MHz, CDCl$_3$)
4b
CF$_3$
f1 (ppm)

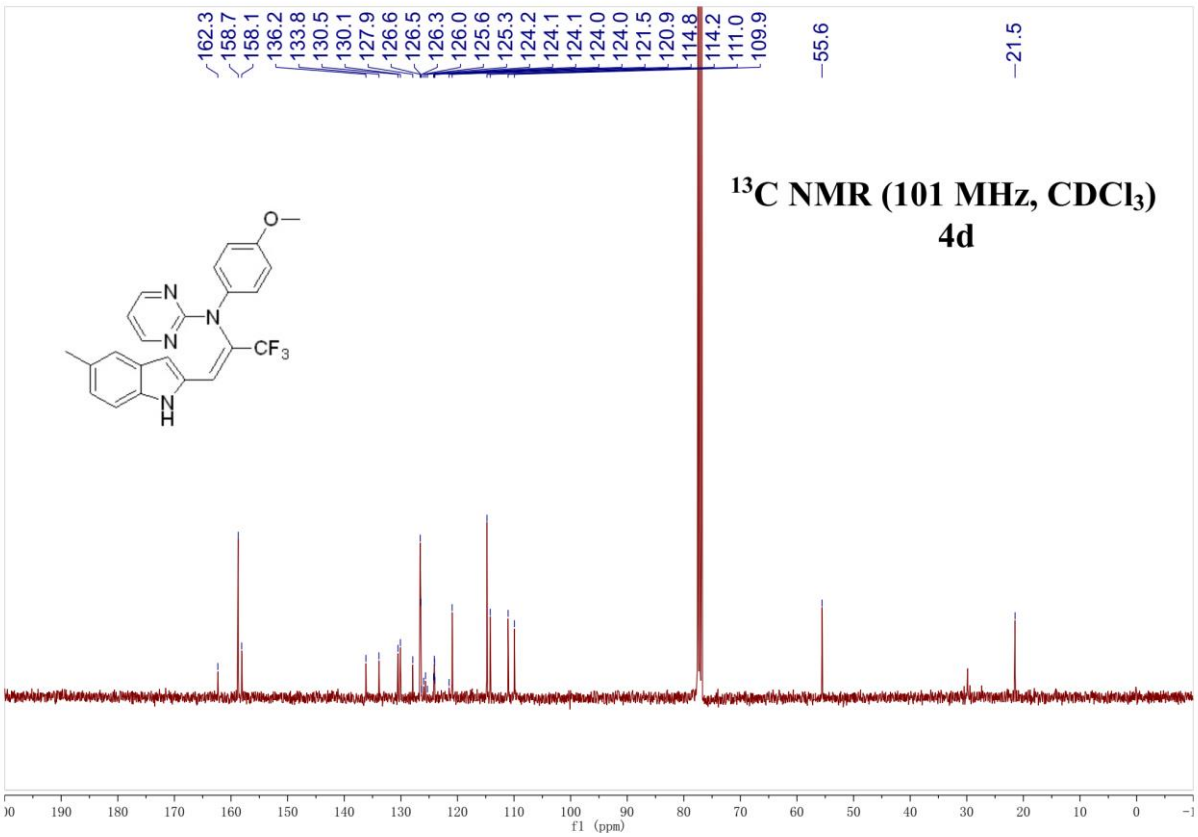

-64.6
19F NMR (376 MHz, CDCl3)
4b
O
N
N
N
O
CF3
N
H
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

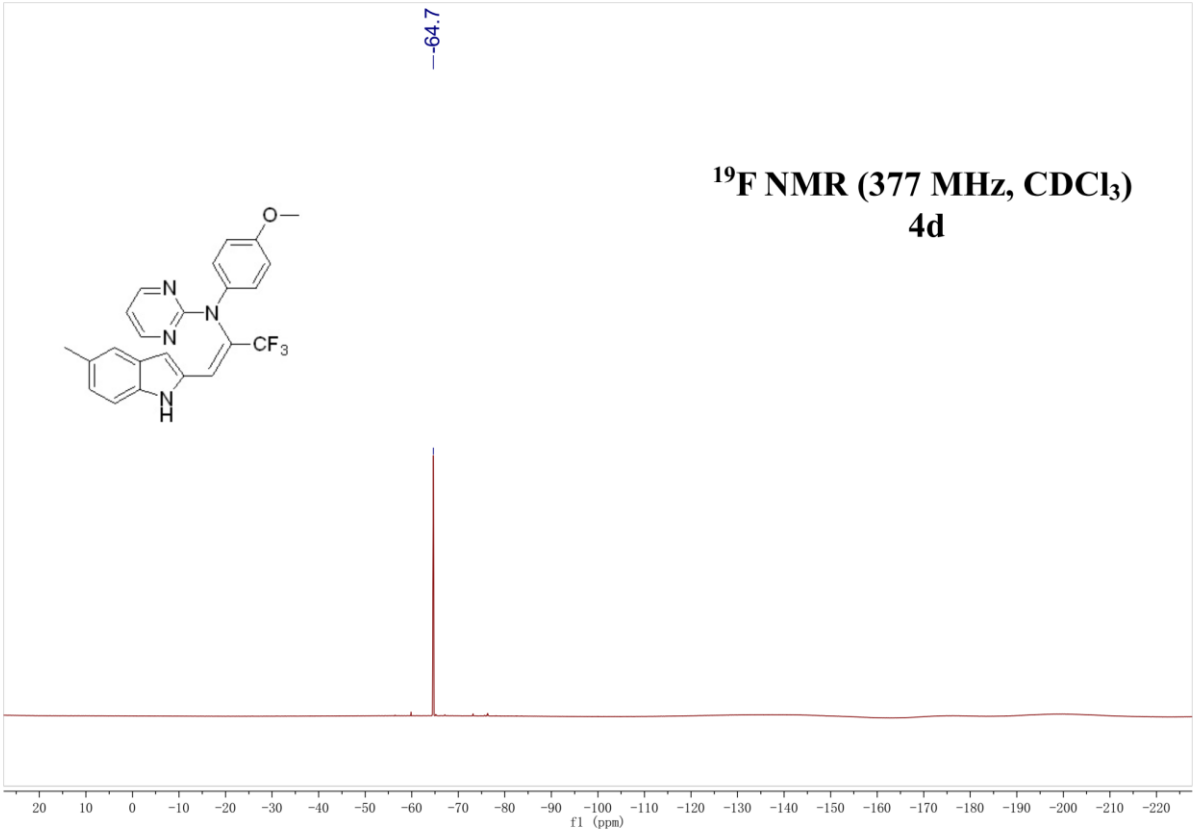

8.74
8.45
8.43
7.32
7.30
7.08
7.08
7.07
7.06
7.05
7.04
7.02
6.92
6.89
6.89
6.79
6.78
6.77
3.81
^{1}H NMR (400 MHz, CDCl$_3$)
4c
0.92
2.01
3.09
3.00
1.93
1.01
1.00
3.10
f1 (ppm)

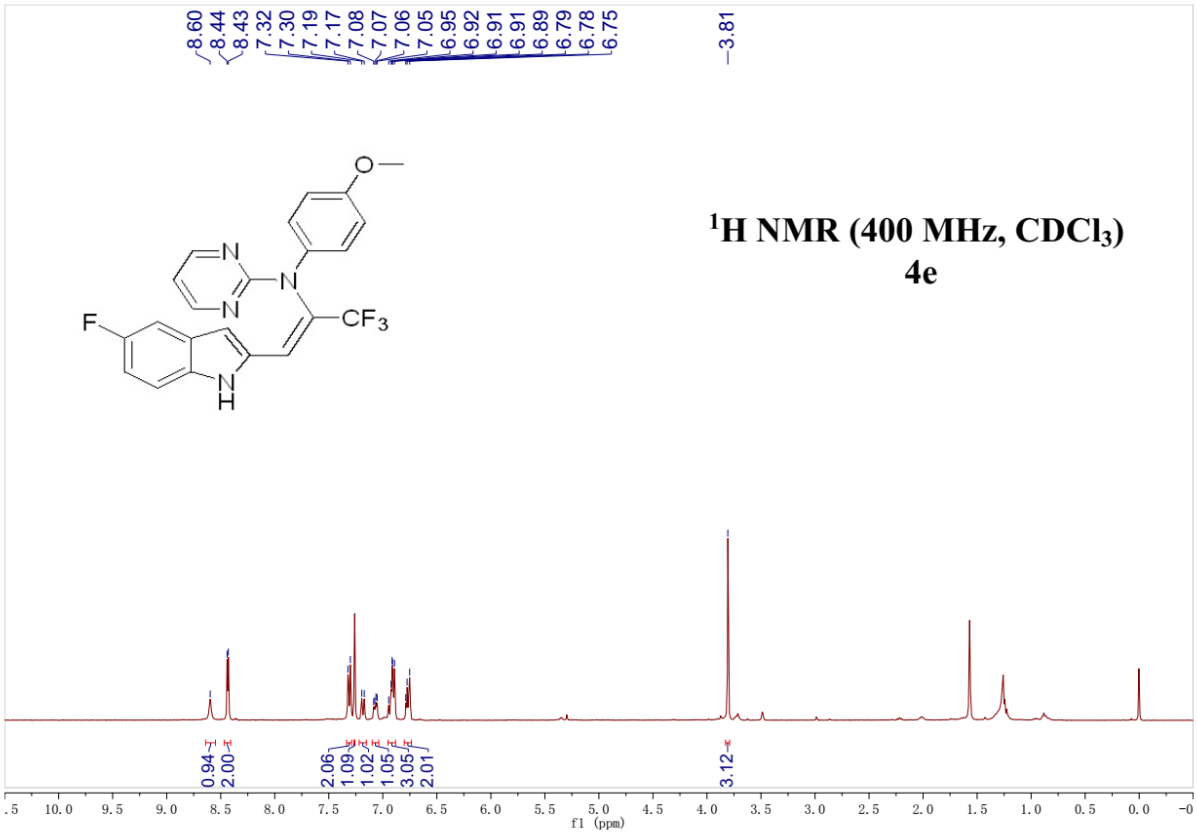

162.3
158.8
158.2
138.3
133.6
131.0
126.9
126.7
126.5
125.8
125.5
125.1
124.0
123.5
123.5
121.2
120.4
114.9
114.5
109.9
108.7
55.6
^{13}C NMR (101 MHz, CDCl$_3$)
4c
f1 (ppm)


-64.7
O
N
N
N
Cl
CF3
N
H
19F NMR (377 MHz, CDCl3)
4c
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

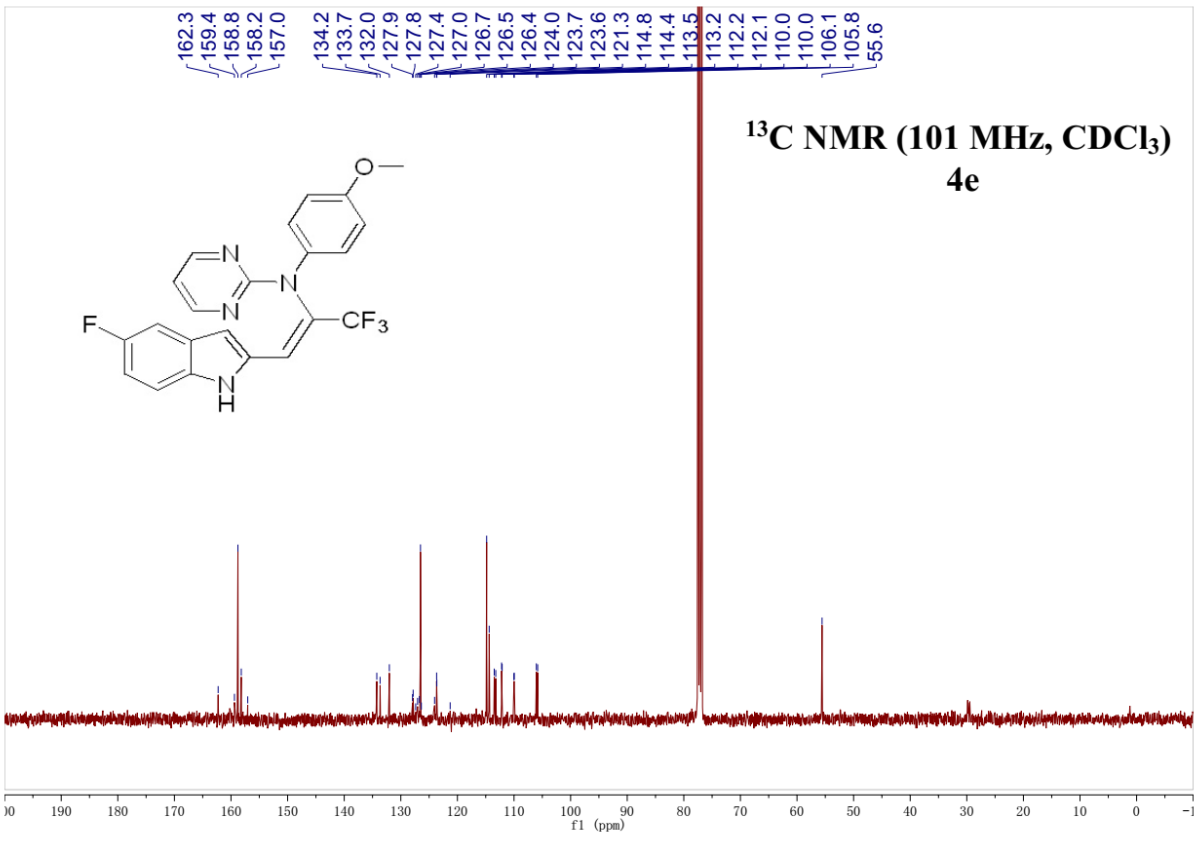

8.50
8.43
8.42
7.34
7.31
7.27
7.06
7.04
7.02
7.00
6.91
6.88
6.76
6.75
6.74
6.73
3.80
2.39
^{1}H NMR (400 MHz, CDCl$_3$)
4d
O
N
N
N
CF$_3$
N
H
0.92
2.00
3.01
0.99
2.01
1.98
0.99
0.93
3.14
3.03
f1 (ppm)


162.3
158.7
158.1
136.2
133.8
130.5
130.1
127.9
126.6
126.5
126.3
126.0
125.6
125.3
124.2
124.1
124.1
124.0
124.0
121.5
120.9
114.8
114.2
111.0
109.9
55.6
21.5
^{13}C NMR (101 MHz, CDCl$_3$)
4d
O
N
N
N
CF$_3$
N
H
f1 (ppm)

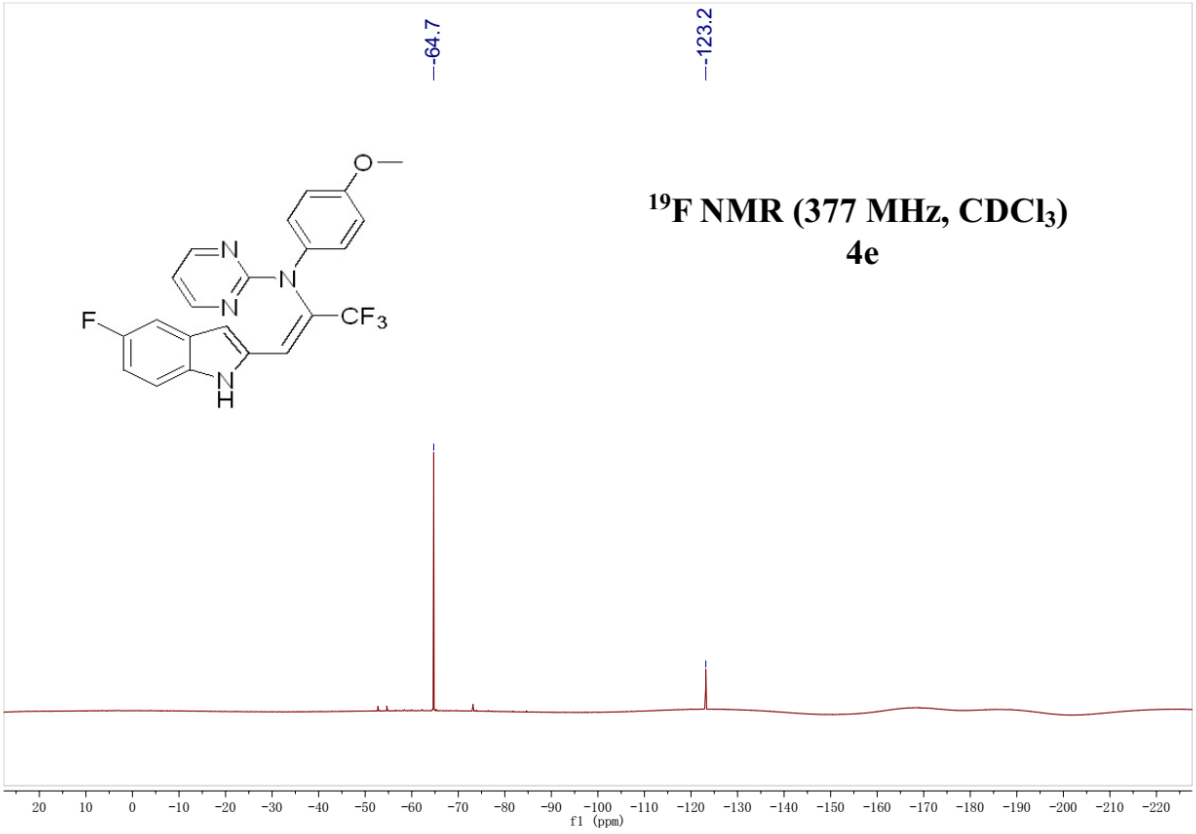

-64.7
19F NMR (377 MHz, CDCl3)
4d
O
N
N
N
CF3
N
H
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



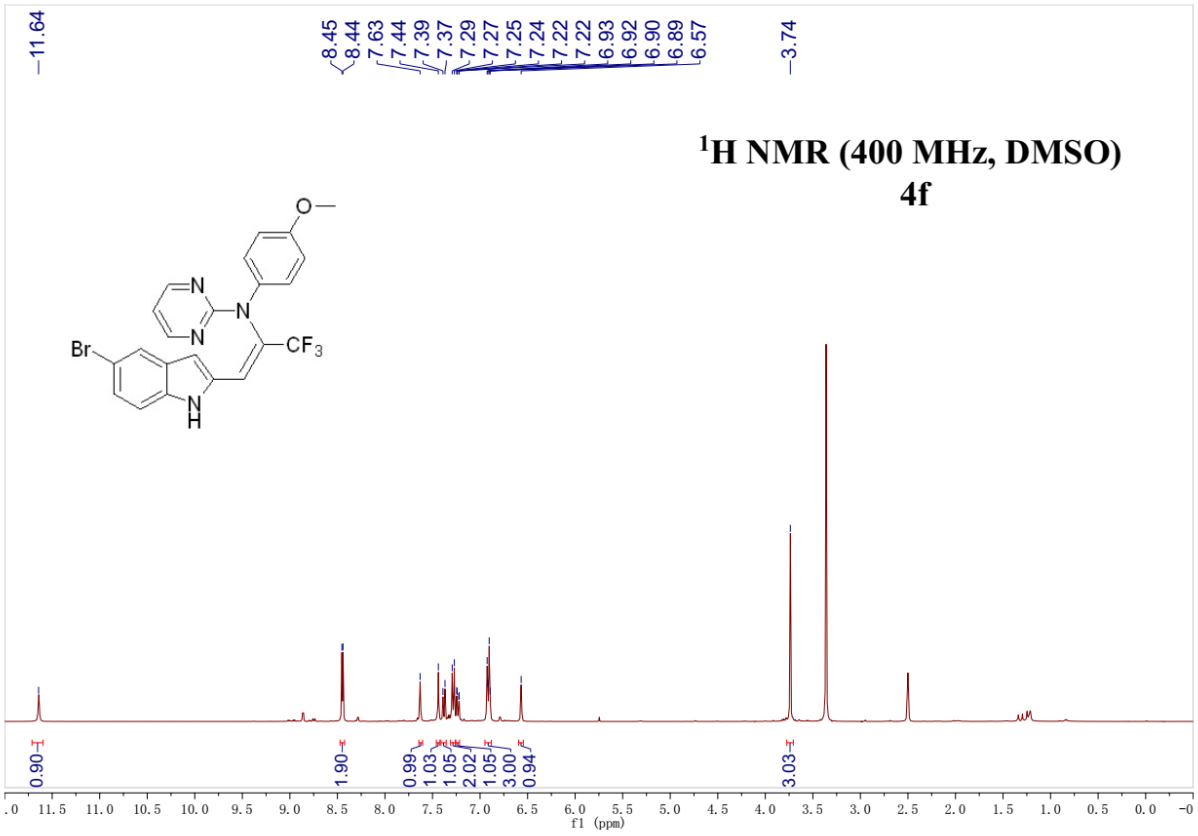
^{1}H NMR (400 MHz, $CDCl_3$)
4e

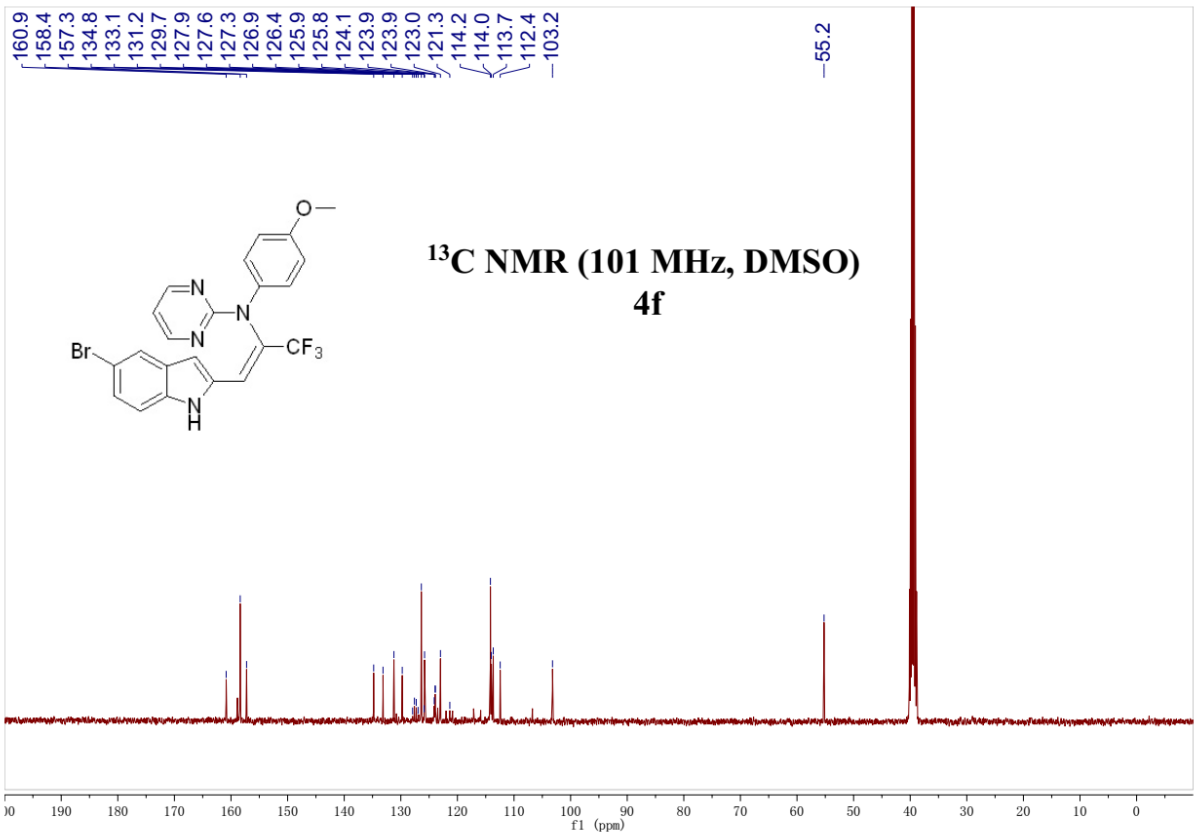


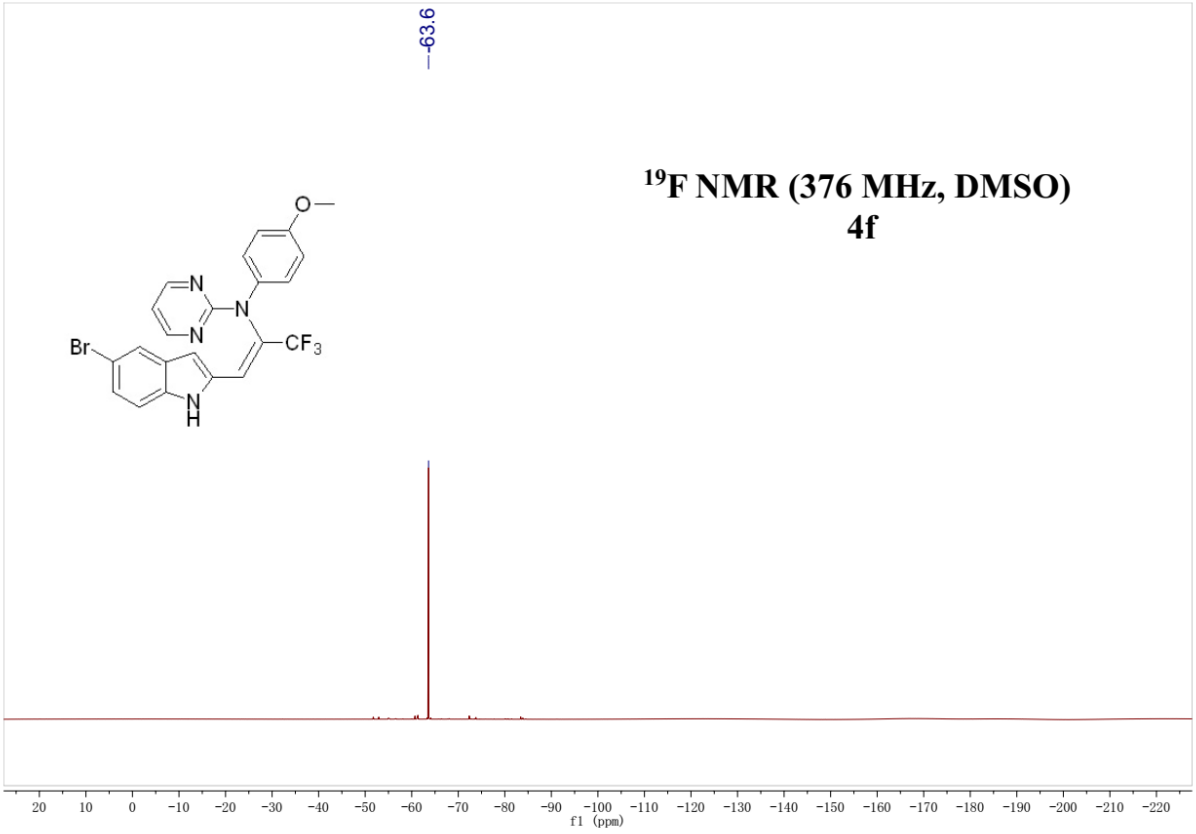
^{13}C NMR (101 MHz, $CDCl_3$)
4e



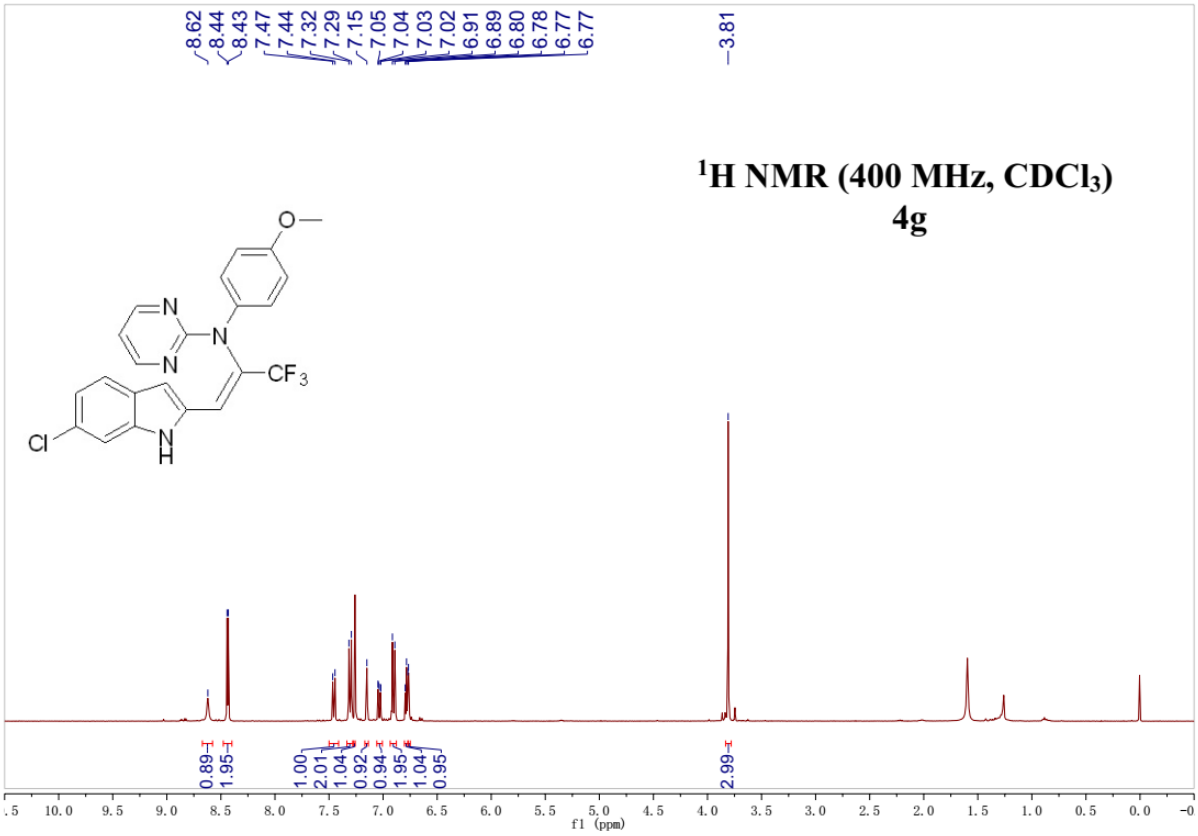
^{19}F NMR (377 MHz, $CDCl_3$)
4e


11.64
8.45
8.44
7.63
7.44
7.39
7.37
7.29
7.27
7.25
7.24
7.22
7.22
6.93
6.92
6.90
6.89
6.57
3.74
^{1}H NMR (400 MHz, DMSO)
4f
Br
CF3
0.90
1.90
0.99
1.03
1.05
2.02
1.05
3.00
0.94
3.03
f1 (ppm)

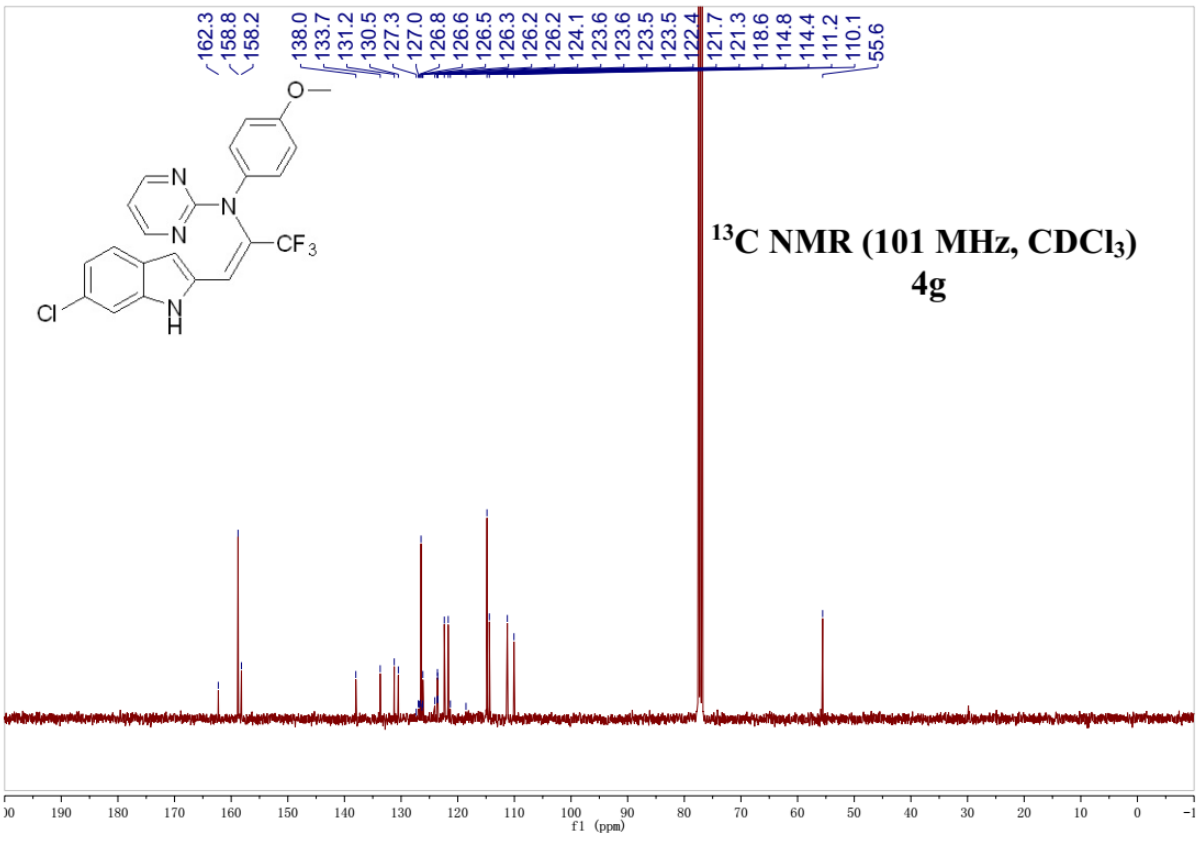

160.9
158.4
157.3
134.8
133.1
131.2
129.7
127.9
127.6
127.3
126.9
126.4
125.9
125.8
124.1
123.9
123.9
123.0
121.3
114.2
114.0
113.7
112.4
103.2
55.2
^{13}C NMR (101 MHz, DMSO)
4f
Br
CF3
f1 (ppm)



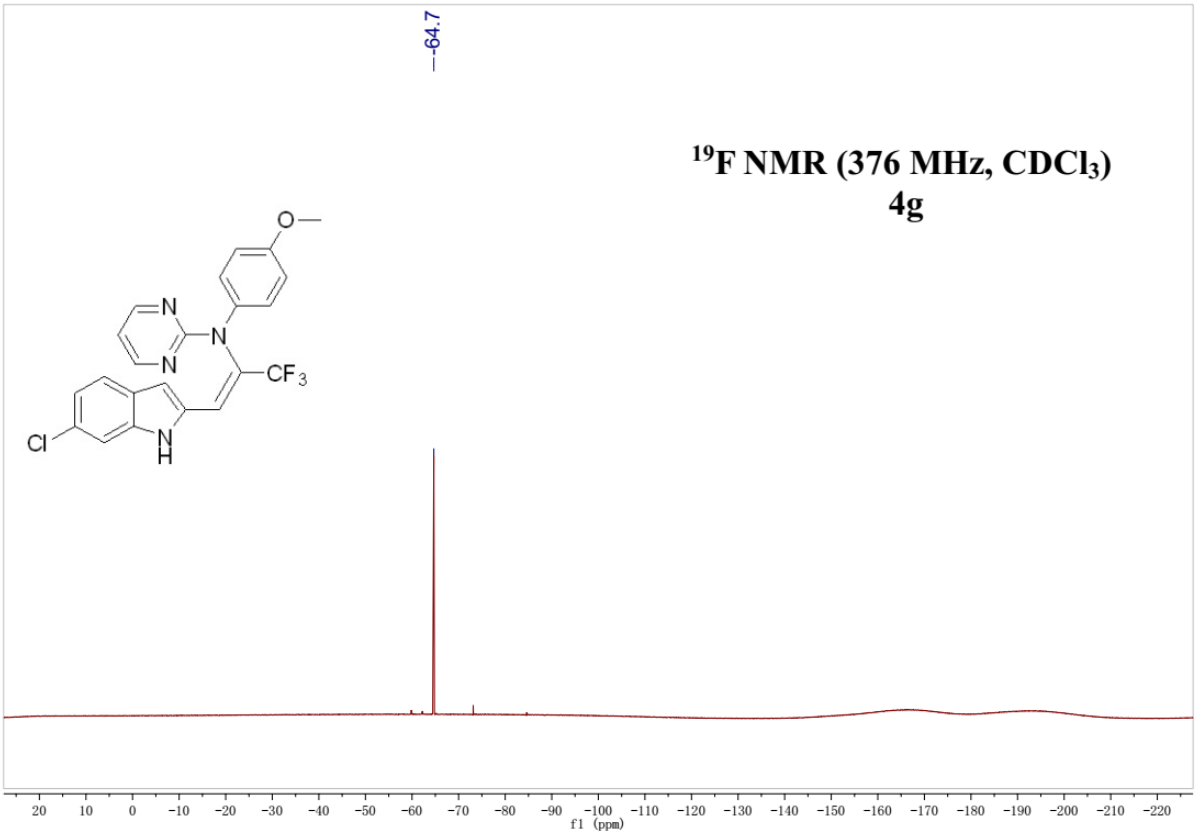
^{19}F NMR (376 MHz, DMSO)
4f

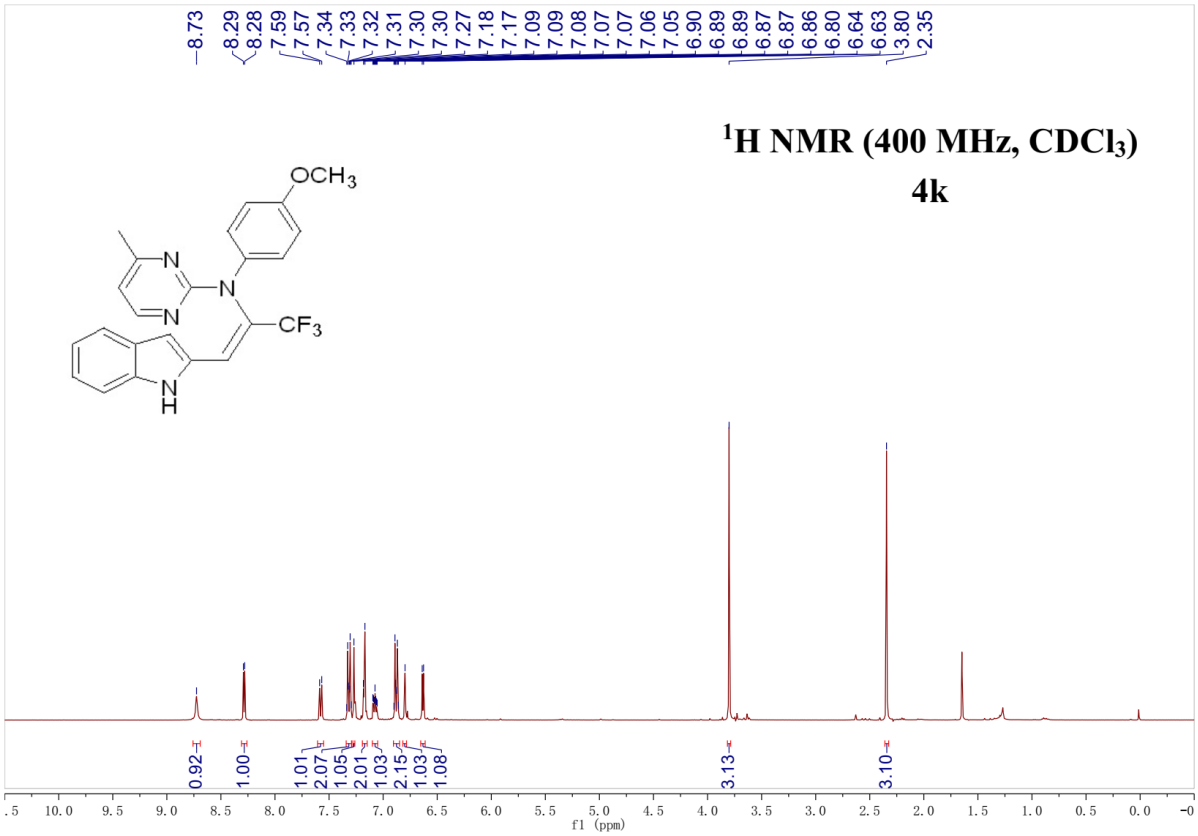


^{1}H NMR (400 MHz, $CDCl_3$)
4g



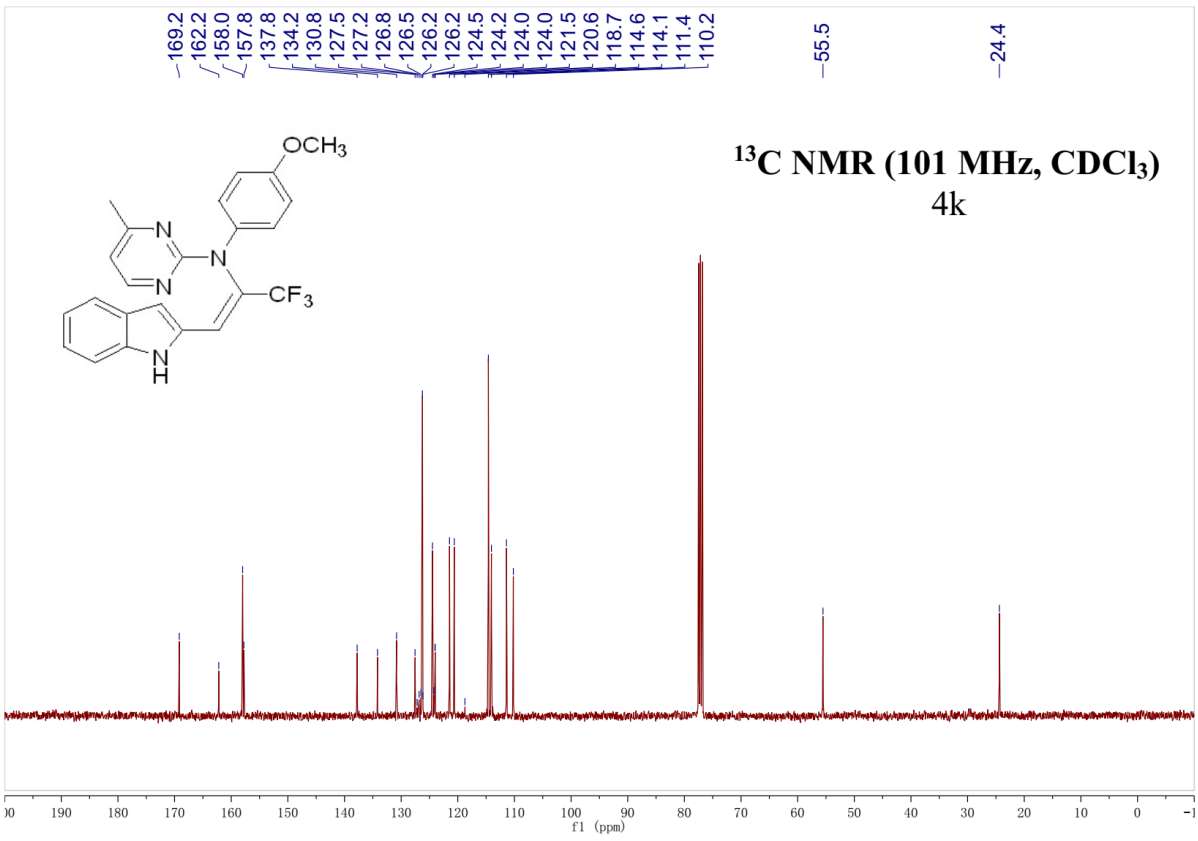
^{13}C NMR (101 MHz, $CDCl_3$)
4g


-64.7
19F NMR (376 MHz, CDCl3)
4g
O
N
N
N
CF3
Cl
N
H
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



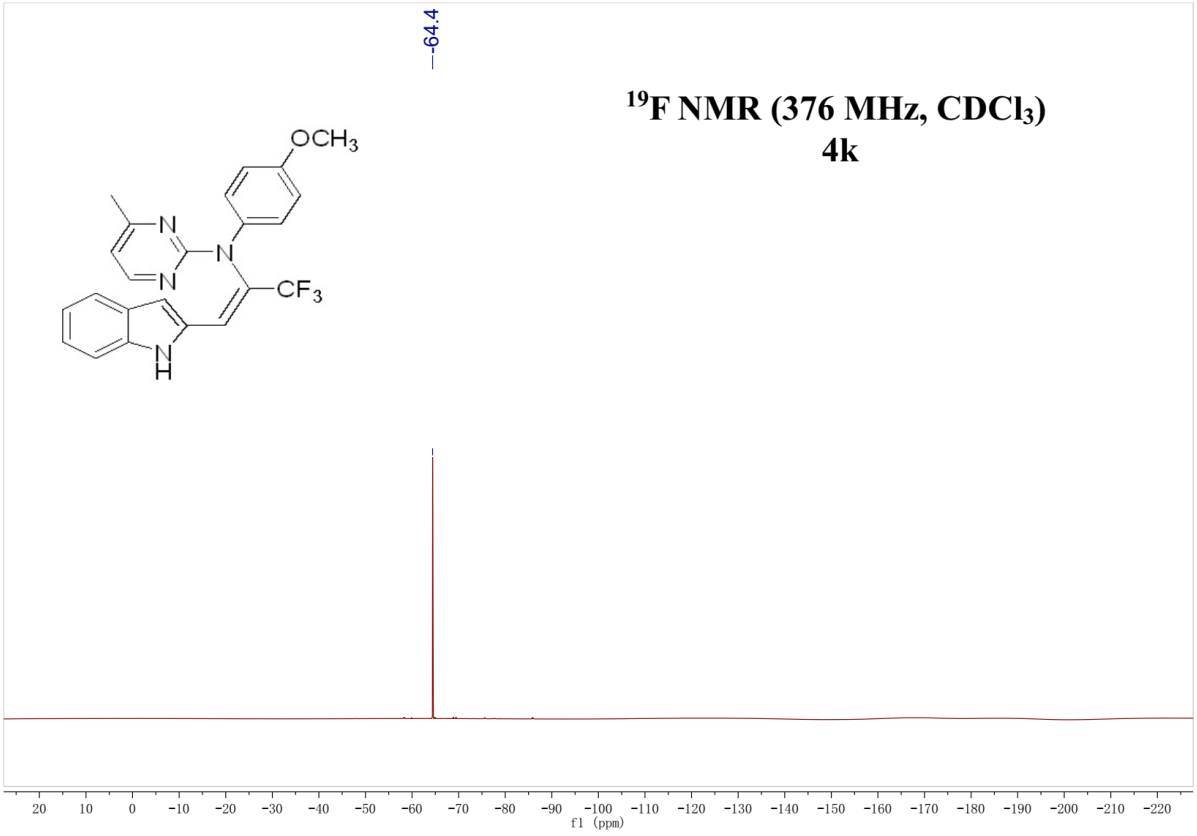
^{1}H NMR (400 MHz, $CDCl_3$)

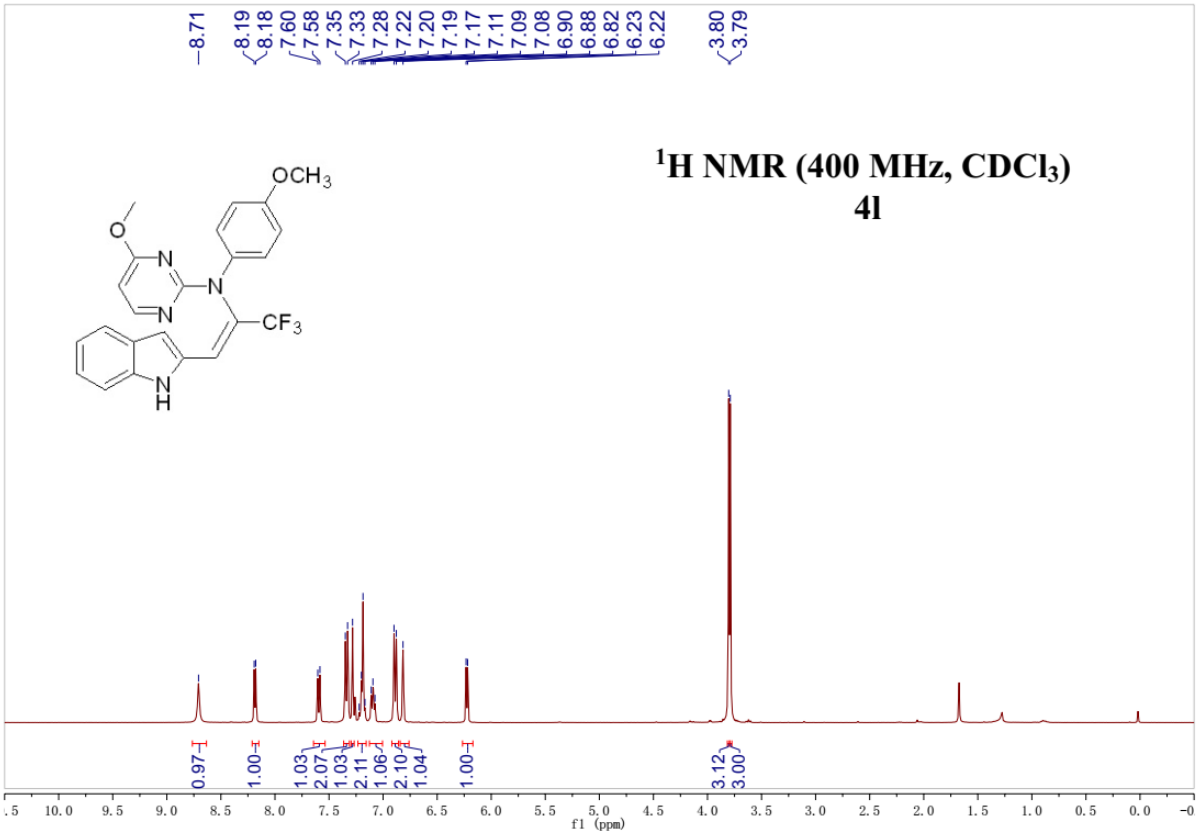
4k



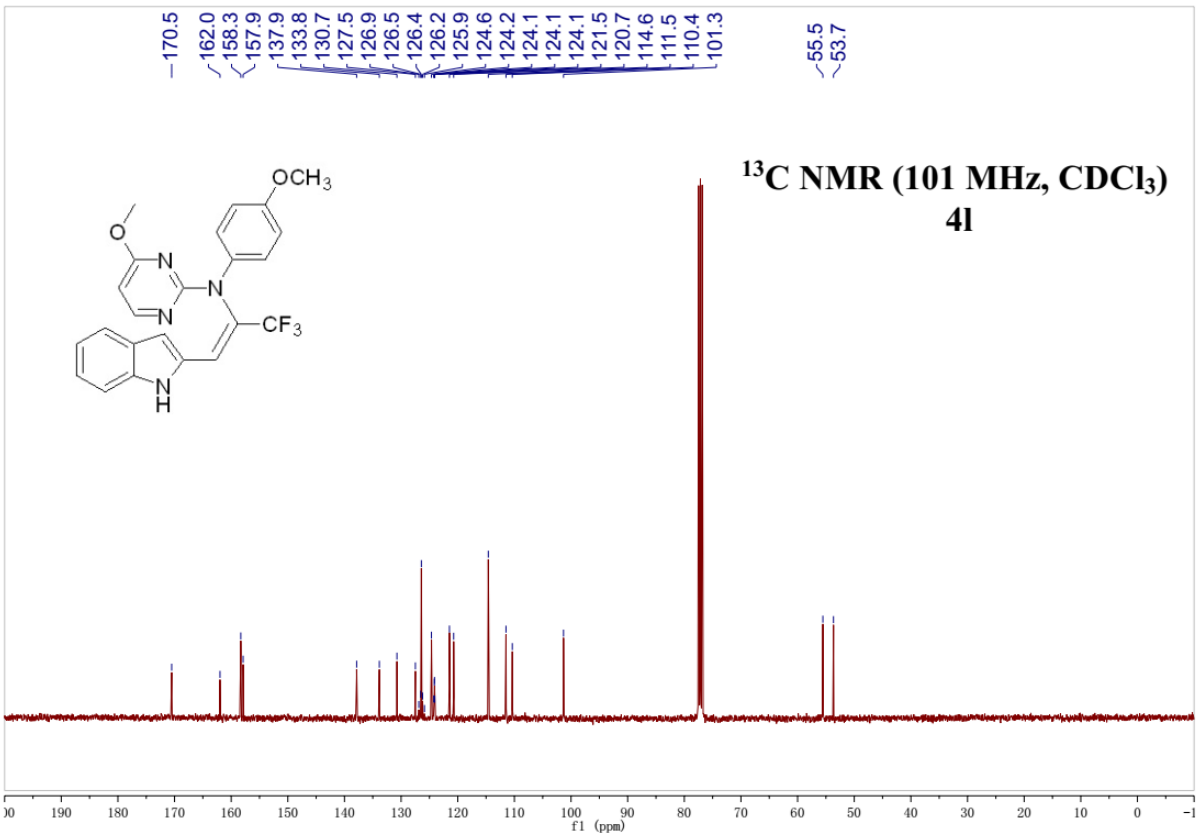
^{13}C NMR (101 MHz, $CDCl_3$)

4k

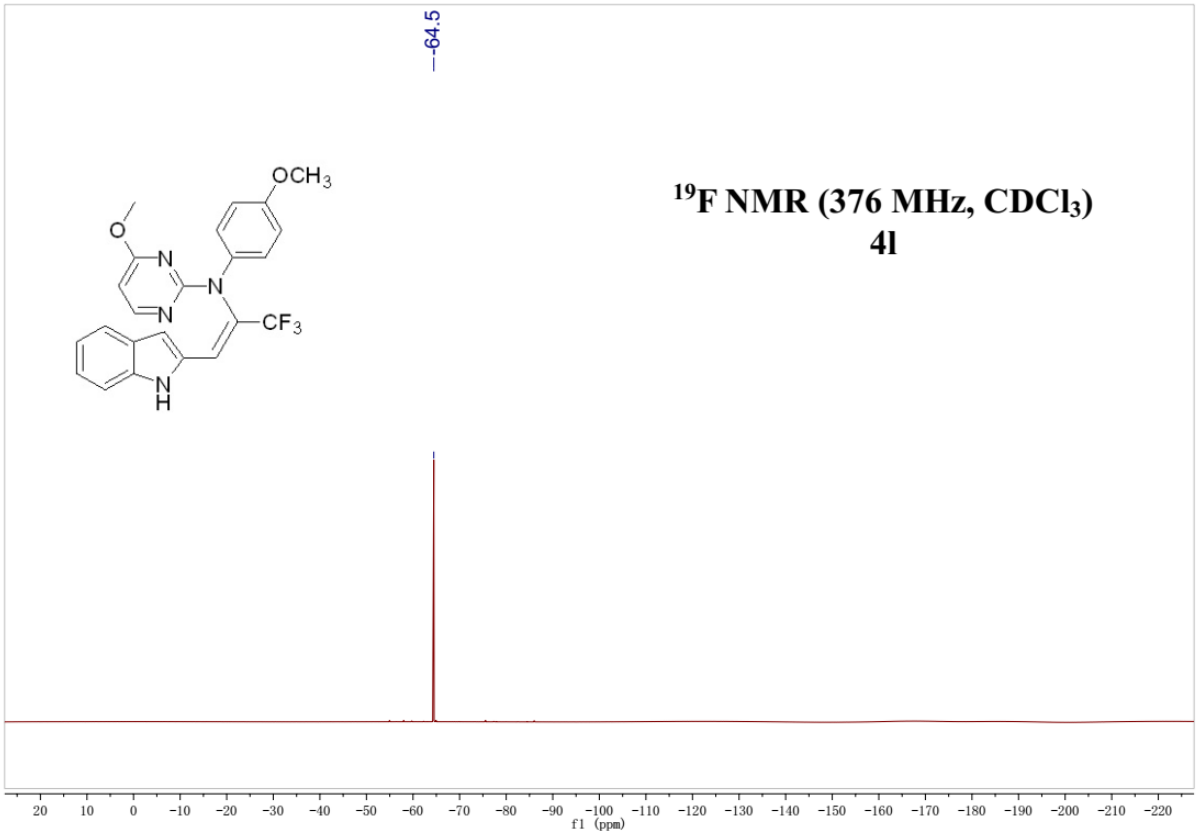

-64.4
19F NMR (376 MHz, CDCl3)
4k
OCH3
N
N
N
CF3
N
H
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)
4l



^{13}C NMR (101 MHz, $CDCl_3$)
4l


-64.5
OCH3
O
N
N
N
CF3
N
H
19F NMR (376 MHz, CDCl3)
4l
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)