Electronic Supplementary Information

Photocatalytic stereoselective synthesis of amido-substituted (*E*)-α-trifluoromethyl allylamines via Heck-type alkylation

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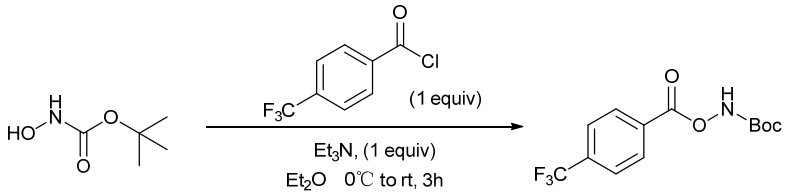
1. General Considerations

General Information: Unless otherwise noted, all chemicals were purchased from Energy Chemical or Bidepharmatech and used without further purification. All reactions were monitored by Thin Layer Chromatography (TLC) using silica gel F254 plates. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker-Avance 400 MHz NMR spectrometer (101 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0) as the internal standard. The coupling constants J are given in Hz. High-resolution mass spectra (HRMS) were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive ion mode. Emission intensities were recorded using a FS5 spectrophotometer.

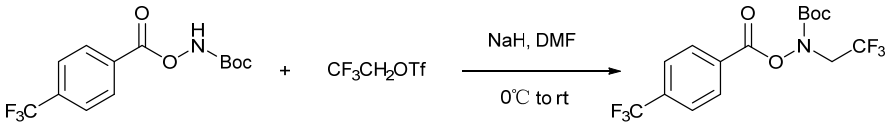
2. General Synthetic Procedures

2.1 All Enamides **(1a-1w)** were prepared according to the previous reports.[1]

2.2 General procedure for the synthesis of Compounds 2b and 2c[2]



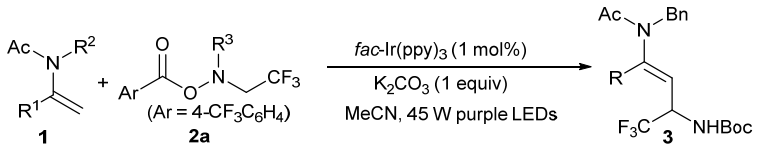
To a stirred suspension of *N*-hydroxycarbamate (1.0 equiv.) in diethyl ether (0.15 M) at 0 °C, triethylamine (1.0 equiv.) was added dropwise over 10 min. 4-(Trifluoromethyl)benzoyl chloride (1.0 equiv.) was added dropwise at the same temperature and subsequently warmed to room temperature and stirred for a further 3 h before quenching by 1.0 M aq. HCl. The phases were separated, and the organic phase was washed sequentially with H_2O, sat. aq. $NaHCO_3$, brine, dried ($MgSO_4$), filtered and concentrated in vacuo to afford the crude product.



To a solution of *tert*-butyl (benzoyloxy)carbamate (10 mmol, 1.0 equiv.) in dry DMF (80 mL) was added NaH (15 mmol, 1.6 equiv, 60% dispersion in mineral oil) portion wise at 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes and 2,2,2-trifluoroethyl trifluoromethanesulfonate (12 mmol, 1.5 equiv.) was added drop wise at 0 °C. The reaction mixture was allowed to warm to room temperature and

stirred for 30 minutes. After completion of the reaction (monitored by TLC), the reaction mixture was quenched by H_2O, extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silicagel eluting with a mixture of pentane and EtOAc to give the desired product **2a**.

2.3 General procedure for the synthesis of Compounds (3a-3cc)



Under N_2, the mixture of enamides **1** (0.2 mmol), **2a** (0.4 mmol), *fac*-Ir(ppy)$_3$ (1 mol%, 1.3 mg), K_2CO_3 (0.2 mmol, 27.6 mg) and CH_3CN (2 mL) were added to a Schlenk tube and sealed. The mixture was stirred at room temperature under 380-390 nm purple LEDs for 36 hours. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography to obtain the product **3**.

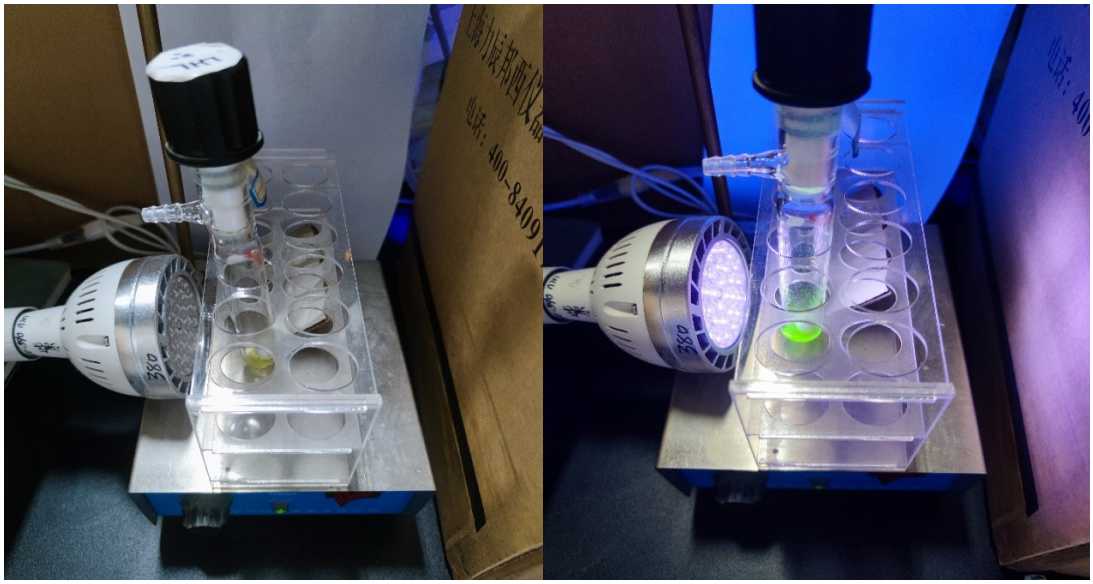


Figure S1. Photoreactor used in this work (45 W purple LEDs, λmax = 395 nm).

The Light Source and the Material of the Irradiation Vessel:

The photochemical reaction was carried out under visible light irradiation by a purple LED at room temperature. This 45 W 380-390 nm purple LED was purchased from taobao (link: https://item.taobao.com/item.htm?id=613485925423&ft=t). The purple LED's energy peak wavelength is 388 nm, the peak width at half-height is 12.5 nm, and irradiance@45 W is 61.54 mW/cm^2. The reaction vessel is a borosilicate

glass tube. The distance between the tube and lamp is about 1cm, and no filter is applied.

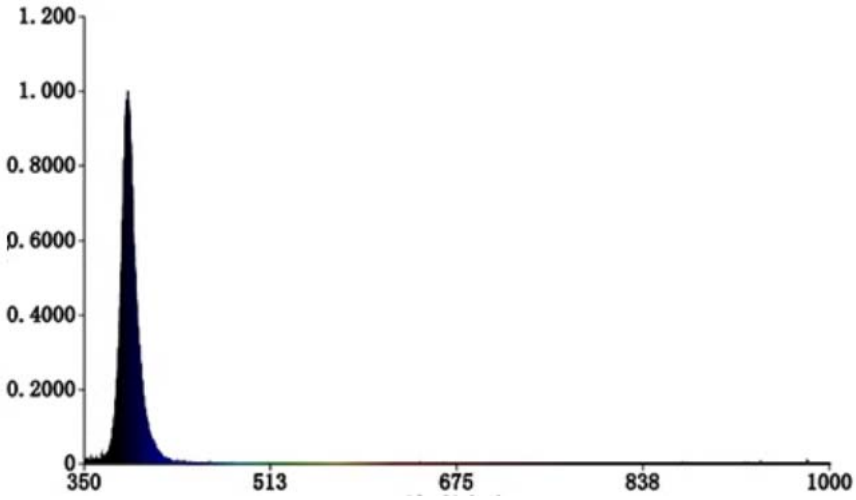
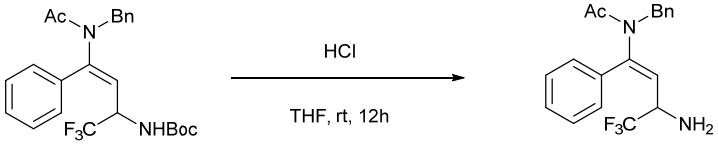


Figure S2. The spectral distribution of 45 W 380-390 nm purple LED

2.4 Synthetic applications:

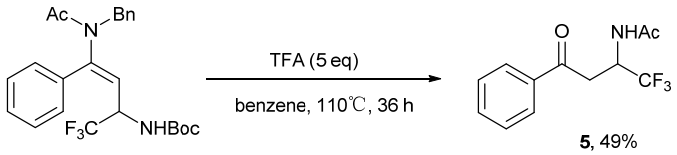
(1) Cleavage of N-Boc Protecting Group



3a **4**, 81%

3a (44.8 mg, 0.1 mmol) was dissolved in THF (1.0 mL) and concentrated hydrochloric acid (1 mL) was added sequentially. The mixture was stirred at rt for 12 h. Upon completion, the solution was concentrated in vacuum and the product was isolated through flash column chromatography to give **4** as colorless oil (28.2 mg, 81% yield).

(2) Hydrolysis of 3a

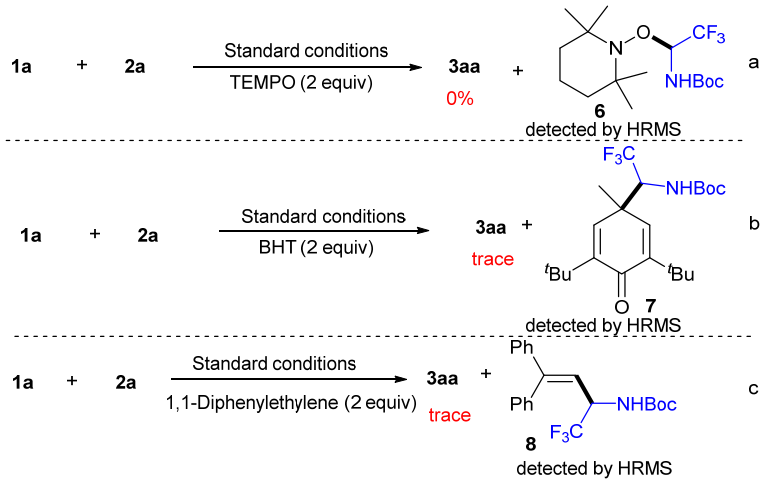


3a **5**, 49%

A mixture of **3a** (44.8 mg, 0.1 mmol), trifluoroacetic acid (57.0 mg, 0.5 mmol) in dry benzene (2.0 mL) were stirred at 110 °C for 36 h. Upon completion, the solution was concentrated in vacuum and the product was isolated through flash column chromatography to furnish **5** as colorless oil (12.7 mg, 49% yield).

3. Mechanism Studies

3.1 Radical inhibiting experiments



Under standard conditions, radical inhibitor TEMPO (0.4 mmol, 62.5 mg, 2 equiv), BHT (0.4 mmol, 88.1 mg, 2 equiv) or 1,1-diphenylethylene (0.4 mmol, 36.1 mg, 2 equiv) was added, the mixture was stirred at room temperature under 380-390 nm purple LEDs for 36 hours. Then, the mixture was detected by HRMS.

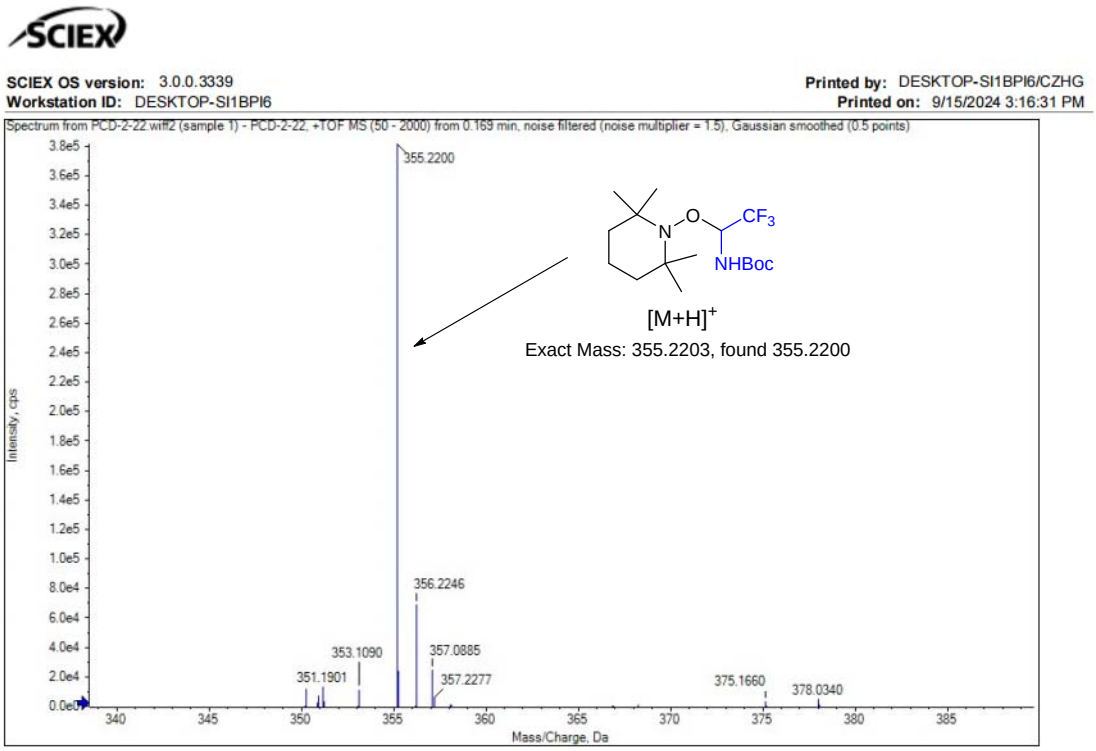


Figure S3. The HRMS spectrum for the radical-trapping experiment with TEMPO.

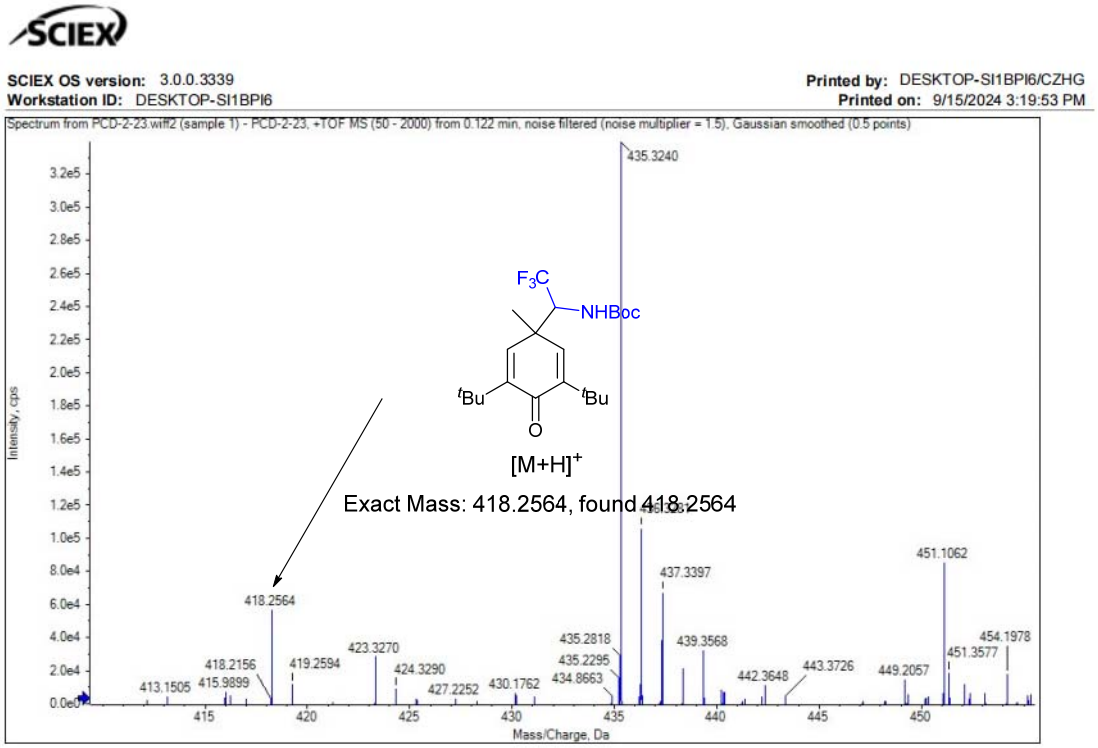


Figure S4. The HRMS spectrum for the radical-trapping experiment with BHT.

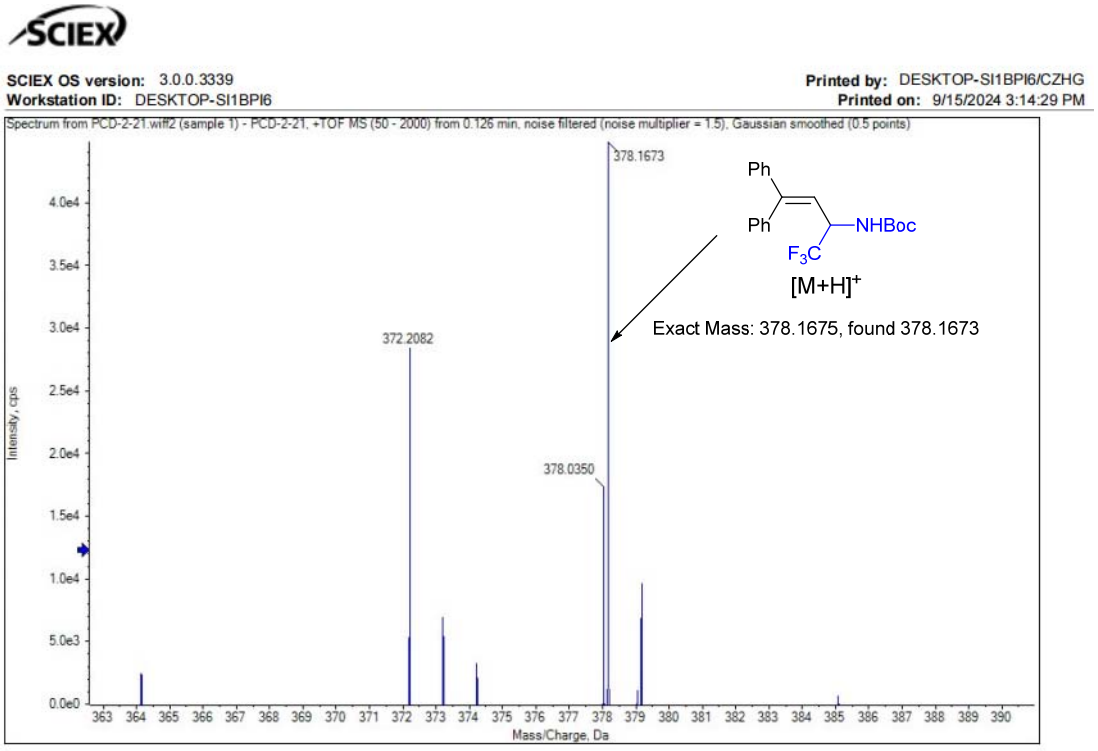


Figure S5. The HRMS spectrum for the radical-trapping experiment with 1,1-diphenylethylene.

3.2 Fluorescence quenching experiments

Fluorescence quenching experiments were measured on an FS5

spectrophotometer with a 4 mL quartz cuvette (d = 1 cm) with a cap. CH_3CN was degassed by N_2 bubbling for 30 minutes before using. fac-Ir(ppy)$_3$ was excited at 360 nm and the emission spectrum λmax = 520 nm was recorded. In a typical experiment, the emission spectrum of a 5×10^{-3} M solution of fac-Ir(ppy)$_3$ with different concentrations of quencher in degassed CH_3CN in 10 mm path length quartz cuvette was collected after degassing with a stream of N_2 for 5 minutes. The concentrations of the quencher stock solution were 0 M, 2.5 x 10^{-3} M, 4.90 x 10^{-3} M, 7.4 x 10^{-3} M, 9.8 x 10^{-3} M, 1.21 x 10^{-2} M in MeCN, respectively. Linear regression of I_0/I against concentration is done in Origin 2018 (Figure S6).

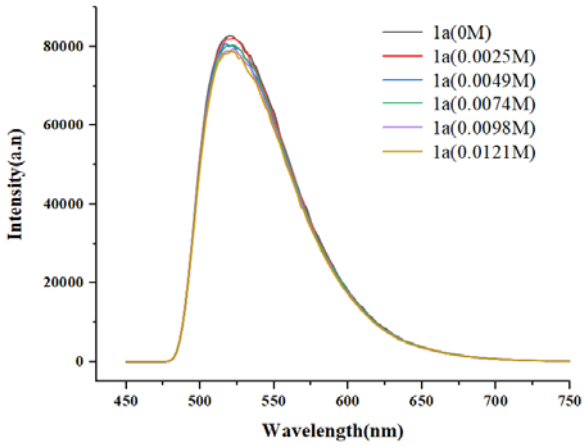


Figure S6. Fluorescence quenching of the excited *fac*-Ir(ppy)$_3$ with different concentrations of **1a**.

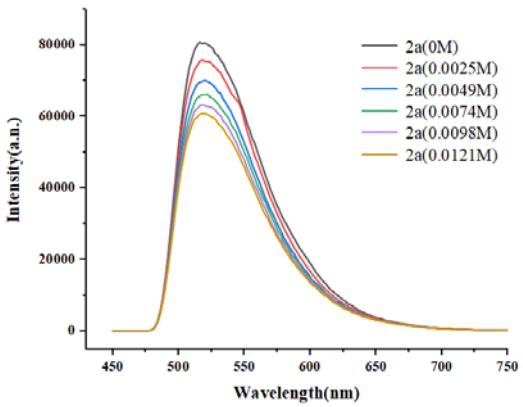


Figure S7. Fluorescence quenching of the excited *fac*-Ir(ppy)$_3$ with different concentrations of **2a**.

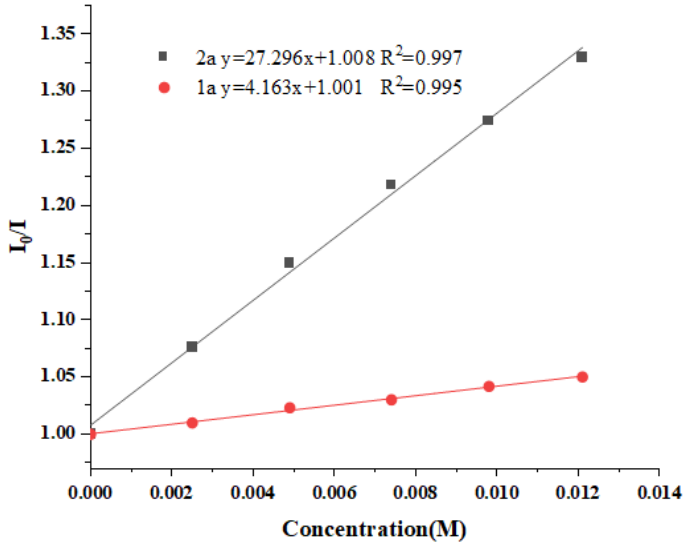
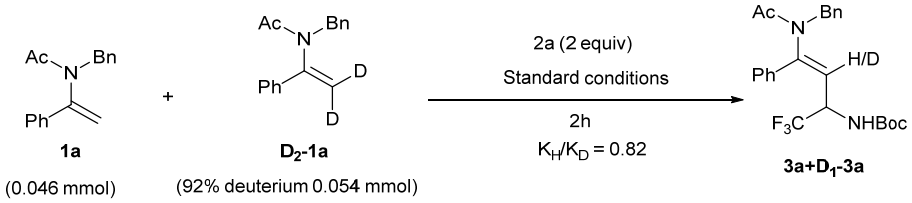
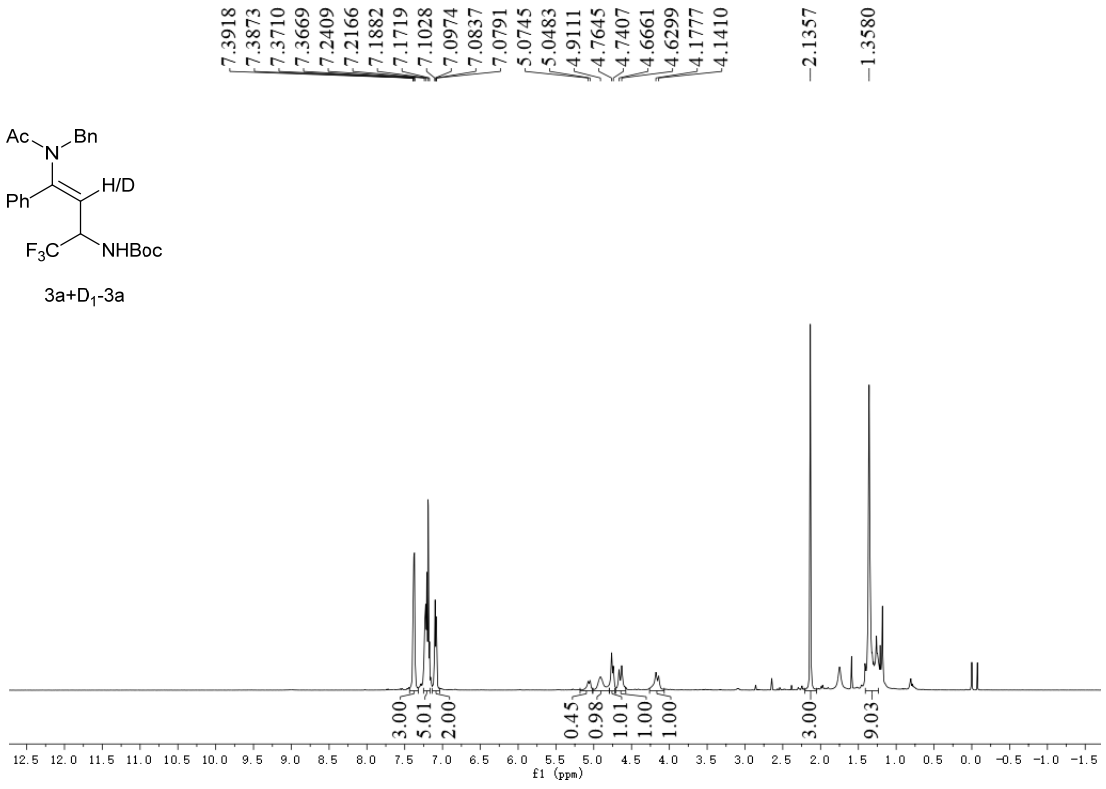


Figure S8. Stern-Volmer quenching studies of the excited *fac*-Ir(ppy)$_3$ with **1a** and **2a**

3.3 Intermolecular Kinetic Isotopic Effect (KIE) Study



Enamide **D_2-1a** was prepared according to the literatures,[3] as a light yellow oil with 92% deuterium. Under N_2, the mixture of enamides **1a** (0.046 mmol), enamides **D_2-1a** (0.054 mmol), **2a** (2 equiv), K_2CO_3 (1 equiv), *fac*-Ir(ppy)$_3$ (1 mol%) and MeCN (1 mL) were added to a Schlenk tube and sealed. The mixture was stirred at room temperature under 380-390nm purple LEDs for 2 hours. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography to obtain product **3a+D_1-3a** as colorless oil. A KIE value of 0.82 was observed.


7.3918
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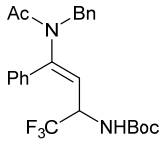
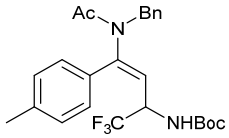
7.3710
7.3669
7.2409
7.2166
7.1882
7.1719
7.1028
7.0974
7.0837
7.0791
5.0745
5.0483
4.9111
4.7645
4.7407
4.6661
4.6299
4.1777
4.1410
2.1357
1.3580
Ac
N
Bn
Ph
H/D
F3C
NHBoc
3a+D1-3a
3.00
5.01
2.00
0.45
0.98
1.01
1.00
1.00
3.00
9.03
f1 (ppm)

4. Characterization Data for the Products



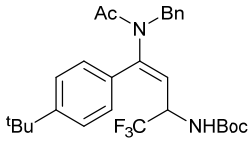
Tert-butyl

(*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)carbamate (3a, 71.8 mg, 80%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 6.5 Hz, 3H), 7.24-7.15 (m, 5H), 7.08 (d, J = 7.9 Hz, 2H), 5.08 (d, J = 9.8 Hz, 1H), 4.98-4.91 (m, 2H), 4.62 (d, J = 14.6 Hz, 1H), 4.21 (d, J = 43.3 Hz, 1H), 2.12 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 154.0, 146.0, 136.9, 133.2, 130.1, 129.1, 129.0, 128.7, 128.4, 127.5, 124.5 (q, $J_{C\text{-}F}$ = 281.8 Hz), 120.7, 80.8, 51.1 (q, $J_{C\text{-}F}$ = 33.3 Hz), 49.1, 28.2, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.41. HRMS (ESI) m/z calcd for $C_{24}H_{28}F_3N_2O_3$ [M+H$^+$]: 449.2047, found 449.2038.



Tert-butyl

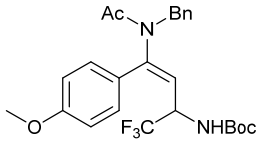
(*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(p-tolyl)but-3-en-2-yl)carbamate (**3b,** 65.7 mg, 71%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.14 (m, 5H), 7.11 -7.07 (m, 4H), 5.18-4.78 (m, 3H), 4.61 (d, J = 14.5 Hz, 1H), 4.16 (d, 1H), 2.31 (s, 3H), 2.10 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 154.1, 146.0, 140.2, 137.0, 130.1, 129.8, 129.0, 128.5, 128.3, 127.4, 124.5 (q, $J_{C\text{-}F}$ = 283.5 Hz), 120.1, 80.7, 51.1 (q, $J_{C\text{-}F}$ = 31.9 Hz), 49.0 (q, $J_{C\text{-}F}$ = 11.3 Hz), 28.1, 22.3, 21.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.47. HRMS (ESI) m/z calcd for $C_{25}H_{30}F_3N_2O_3$ [M+H$^+$]: 463.2203, found 463.2200.



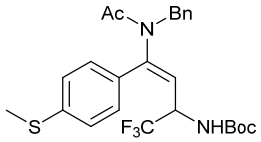
Tert-butyl

(*E*)-(4-(N-benzylacetamido)-4-(4-(tert-butyl)phenyl)-1,1,1-trifluorobut-3-en-2-yl) carbamate (3c, 91.8 mg, 91%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.2 Hz, 4H), 7.09 (d, J = 7.8 Hz, 2H), 4.99 (s, 3H), 4.62 (d, J = 14.4 Hz, 1H), 4.15 (d, J = 14.4 Hz, 1H), 2.10 (s, 3H), 1.36 (s, 9H), 1.27 (s, 9H);

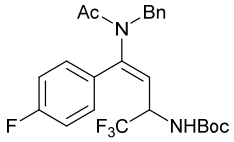
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 154.1, 153.2, 145.8, 137.0, 129.1, 128.4, 128.3, 127.4, 126.1, 124.5 (q, $J_{C\text{-}F}$ = 281.5 Hz), 120.3, 80.8, 51.1 (q, $J_{C\text{-}F}$ = 31.9 Hz), 49.1, 34.8, 31.2, 28.2, 28.17, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.43. HRMS (ESI) m/z calcd for $C_{28}H_{36}F_3N_2O_3$ [M+H$^+$]: 505.2673, found 505.2664.



Tert-butyl (*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-yl)carbamate (3d, 83.3 mg, 87%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, J = 7.3 Hz, 5H), 7.08 (d, J = 7.0 Hz, 2H), 6.87 (d, J = 8.3 Hz, 2H), 5.12-4.76 (m, 3H), 4.60 (d, J = 14.4 Hz, 1H), 4.19 (d, J = 14.6 Hz, 1H), 3.76 (s, 3H), 2.09 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 160.8, 154.2, 145.7, 137.0, 130.1, 129.0, 128.3, 127.4, 124.5 (q, $J_{C\text{-}F}$ = 280.6 Hz), 125.2, 119.5, 114.5, 80.7, 55.4, 51.2 (q, $J_{C\text{-}F}$ = 31.9 Hz), 49.0, 28.2, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.44. HRMS (ESI) m/z calcd for $C_{25}H_{30}F_3N_2O_4$ [M+H$^+$]: 479.2152, found 479.2153.

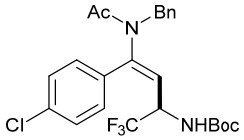


Tert-butyl (*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(4-(methylthio)phenyl)but-3-en-2-yl)carbamate (**3e,** 81.1 mg, 82%), colorless oil; ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.21-7.12 (m, 7H), 7.08 (d, J = 7.6 Hz, 2H), 5.15-4.76 (m, 3H), 4.61 (d, J = 14.4 Hz, 1H), 4.19 (d, J = 14.6 Hz, 1H), 2.43 (s, 3H), 2.10 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 154.1, 145.5, 141.6, 136.8, 129.0, 128.4, 127.5, 126.2, 124.5 (q, $J_{C\text{-}F}$ = 283.8 Hz), 120.4, 80.8, 51.1 (q, $J_{C\text{-}F}$ = 32.6 Hz), 49.1, 28.1, 22.3, 15.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.40. HRMS (ESI) m/z calcd for $C_{25}H_{30}F_3N_2O_3S$ [M+H$^+$]: 495.1924, found 495.1914.

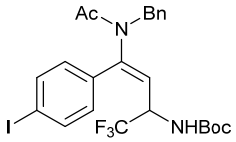


Tert-butyl (*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(4-fluorophenyl)but-3-en-2-yl)carbamate (**3f**, 71.8 mg, 77%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.14 (m,

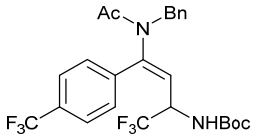
5H), 7.04 (t, J = 8.1 Hz, 4H), 5.45-5.09 (m, 2H), 4.90-4.84 (m, 1H), 4.57 (d, J = 14.7 Hz, 1H), 4.20 (d, J = 14.5 Hz, 1H), 2.10 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 163.5 (d, $J_{C\text{-}F}$ = 252.1 Hz), 154.2, 144.9, 136.7, 130.7 (d, $J_{C\text{-}F}$ = 8.5 Hz), 129.2, 128.9, 128.4, 127.6, 124.4 (q, $J_{C\text{-}F}$ = 282.9 Hz), 120.9, 116.3 (d, $J_{C\text{-}F}$ = 21.9 Hz), 80.9, 51.1 (q, $J_{C\text{-}F}$ = 32.1 Hz), 49.1, 28.1, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.31, -110.05. HRMS (ESI) m/z calcd for $C_{24}H_{27}F_4N_2O_3$ [M+H$^+$]: 467.1952, found 467.1949.



Tert-butyl (*E*)-(4-(N-benzylacetamido)-4-(4-chlorophenyl)-1,1,1-trifluorobut-3-en-2-yl)carbamate (**3g,** 68.6 mg, 71%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.2 Hz, 2H), 7.18 (m, 5H), 7.08-7.05 (m, 2H), 5.08 (d, J = 9.4 Hz, 1H), 4.87 (d, J = 7.7 Hz, 2H), 4.61 (d, J = 14.5 Hz, 1H), 4.18 (d, J = 14.6 Hz, 1H), 2.11 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 154.0, 144.9, 136.6, 136.2, 131.6, 130.0, 129.5, 128.9, 128.4, 127.6, 124.3 (q, $J_{C\text{-}F}$ = 283.2 Hz), 121.2, 81.0, 51.1 (q, $J_{C\text{-}F}$ = 32.1 Hz), 49.0, 28.1, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.29. HRMS (ESI) m/z calcd for $C_{24}H_{27}ClF_3N_2O_3$ [M+H$^+$]: 483.1657, found 483.1658.

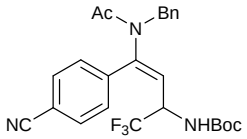


Tert-butyl (*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(4-iodophenyl)but-3-en-2-yl)carbamate (3h, 44.8 mg, 39%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 5.3 Hz, 2H), 6.97-6.95 (m, 2H), 6.85 (d, J = 8.1 Hz, 2H), 4.96 (d, J = 10.0 Hz, 1H), 4.76-4.65 (m, 2H), 4.52 (d, J = 14.5 Hz, 1H), 4.07 (d, J = 14.4 Hz, 1H), 2.00 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 154.0, 145.1, 138.4, 136.7, 132.7, 130.3, 128.9, 128.4, 127.6, 124.3 (q, $J_{C\text{-}F}$ = 283.8 Hz), 121.3, 96.5, 81.1, 51.1 (q, $J_{C\text{-}F}$ = 33.9 Hz), 49.1, 28.1, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.33. HRMS (ESI) m/z calcd for $C_{24}H_{27}IF_3N_2O_3$ [M+H$^+$]: 575.1013, found 575.0987.



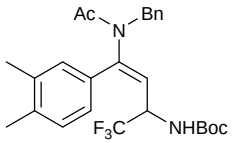
Tert-butyl

(*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)carbamate (**3i**, 73.3 mg, 71%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.9 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 7.21-7.18 (m, 3H), 7.09-7.03 (m, 2H), 5.16 (d, J = 8.4 Hz, 1H), 4.87 (d, J = 11.8 Hz, 2H), 4.62 (d, J = 14.6 Hz, 1H), 4.18 (d, J = 14.6 Hz, 1H), 2.13 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 154.1, 144.6, 136.9, 136.5, 131.9 (q, $J_{C\text{-}F}$ = 33.2 Hz), 129.2, 128.9, 128.5, 127.7, 126.2 (q, $J_{C\text{-}F}$ = 1.3 Hz), 124.2 (q, JC-F = 282.7 Hz), 125.0, 122.4 (q, JC-F = 3.4 Hz), 81.2, 51.4 (q, $J_{C\text{-}F}$ = 33.3 Hz), 49.2, 28.1, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.90, -75.28. HRMS (ESI) m/z calcd for $C_{25}H_{26}F_6N_2O_3$ [M+H$^+$]: 517.1920, found 517.1903.



Tert-butyl

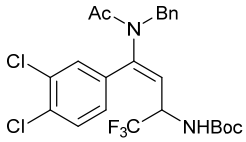
(*E*)-(4-(N-benzylacetamido)-4-(4-cyanophenyl)-1,1,1-trifluorobut-3-en-2-yl)carbamate (**3j**, 68.2 mg, 72%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.9 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 5.1 Hz, 3H), 7.13-7.11 (m, 2H), 5.28 (d, J = 10.2 Hz, 1H), 4.98-4.86 (m, 2H), 4.68 (d, J = 14.5 Hz, 1H), 4.37-4.26 (m, 1H), 2.20 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 154.0, 144.3 136.3, 132.8, 132.1, 129.4, 128.8, 128.7, 128.5, 127.7, 126.6, 124.1 (q, $J_{C\text{-}F}$ = 283.3 Hz), 118.0, 113.7, 81.2, 51.1 (q, $J_{C\text{-}F}$ = 31.7 Hz), 49.9, 28.1, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.13. HRMS (ESI) m/z calcd for $C_{25}H_{26}F_3N_3NaO_3$ [M+Na$^+$]: 496.1818, found 496.1796.



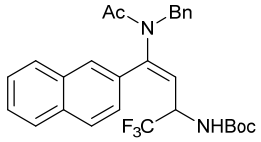
Tert-butyl

(*E*)-(4-(N-benzylacetamido)-4-(3,4-dimethylphenyl)-1,1,1-trifluorobut-3-en-2-yl)carbamate (**3k**, 91.5 mg, 96%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.14 (m, 3H), 7.09 (t, J = 7.3 Hz, 3H), 6.94 (d, J = 8.6 Hz, 2H), 5.04-4.94 (m, 3H), 4.68 (d,

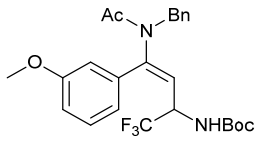
J = 14.4 Hz, 1H), 4.11 (d, *J* = 14.5 Hz, 1H), 2.20 (d, *J* = 6.8 Hz, 6H), 2.09 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 154.1, 146.3, 139.0, 137.5, 137.0, 130.3, 129.8, 129.0, 128.3, 127.4, 126.0, 124.6 (q, $J_{C\text{-}F}$ = 285.2 Hz), 119.76, 80.7, 51.1 (q, $J_{C\text{-}F}$ = 31.5 Hz), 28.2, 22.3, 19.8, 19.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.60. HRMS (ESI) m/z calcd for $C_{26}H_{32}F_3N_2O_3$ [M+H$^+$]: 477.2360, found 477.2359.



Tert-butyl (*E*)-(4-(N-benzylacetamido)-4-(3,4-dichlorophenyl)-1,1,1-trifluorobut-3-en-2-yl)carbamate (3l, 95.2 mg, 92%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 1H), 7.24-7.17 (m, 4H), 7.09-6.98 (m, 3H), 5.50-5.11 (m, 2H), 4.88-4.81 (m, 1H), 4.60 (d, *J* = 14.6 Hz, 1H), 4.21 (d, *J* = 14.7 Hz, 1H), 2.09 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 154.1, 143.8, 136.4, 134.5, 133.6, 133.2, 131.2, 130.5, 128.9, 128.5, 128.0, 127.7, 124.3 (q, $J_{C\text{-}F}$ = 282.8 Hz), 122.1, 81.1, 51.1 (q, $J_{C\text{-}F}$ = 32.0 Hz), 49.3, 28.1, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.23. HRMS (ESI) m/z calcd for $C_{24}H_{26}Cl_2F_3N_2O_3$ [M+H$^+$]: 517.1267, found 517.1281.

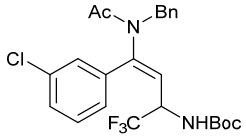


Tert-butyl (*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(naphthalen-2-yl)but-3-en-2-yl)carbamate (**3m**, 90.7 mg, 91%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 1H), 7.89-7.85 (m, 2H), 7.81 (s, 1H), 7.57-7.55 (m, 2H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.31-7.24 (m, 4H), 7.20-7.18 (m, 2H), 5.29-5.1 (m, 2H), 4.88-4.80 (m, 2H), 4.26-4.21 (m, 1H), 2.26 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 154.0, 146.2, 136.9, 133.8, 133.0, 130.3, 129.2, 129.0, 128.6, 128.4, 127.8, 127.5, 127.4, 126.9, 126.4, 124.5 (q, $J_{C\text{-}F}$ = 283.6 Hz), 125.0, 120.8, 80.9, 51.2 (q, $J_{C\text{-}F}$ = 33.8 Hz), 49.2, 28.2, 22.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.45. HRMS (ESI) m/z calcd for $C_{28}H_{30}F_3N_2O_3$ [M+H$^+$]: 499.2203, found 499.2200.



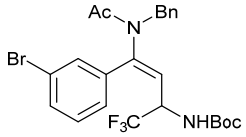
Tert-butyl

(*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(3-methoxyphenyl)but-3-en-2-yl)carbamate (3n, 74.6 mg, 78%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, J = 8.0 Hz, 1H), 7.21-7.09 (m, 5H), 6.89 (d, J = 8.4, 2.4 Hz, 1H), 6.81 (d, J = 7.7 Hz, 1H), 6.73 (s, 1H), 5.08-4.81 (m, 3H), 4.66 (d, J = 14.6 Hz, 1H), 4.16 (d, J = 14.5 Hz, 1H), 3.72 (s, 3H), 2.11 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 160.0, 154.1, 145.9, 136.9, 134.5, 130.2, 129.0, 128.3, 127.5, 124.5 (q, $J_{C\text{-}F}$ = 283.5 Hz), 120.9, 120.6, 115.9, 113.9, 80.8, 55.3,51.1 (q, $J_{C\text{-}F}$ = 28.4 Hz), 49.2, 28.1, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.42. HRMS (ESI) m/z calcd for $C_{25}H_{30}F_3N_2O_4$ [M+Na^+]: 501.1972, found 501.1961.



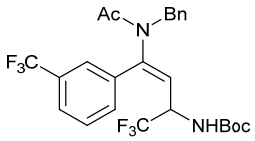
Tert-butyl

(*E*)-(4-(N-benzylacetamido)-4-(3-chlorophenyl)-1,1,1-trifluorobut-3-en-2-yl)carbamate (3o, 79.2 mg, 83%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 2H), 7.22-7.12 (m, 5H), 7.07 (d, J = 7.0 Hz, 2H), 5.13 (d, J = 10.2 Hz, 2H), 4.98-4.83 (m, 2H), 4.62 (d, J = 14.6 Hz, 1H), 4.18 (d, J = 14.9 Hz, 1H), 2.11 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 154.0, 144.7, 136.6, 135.2, 130.4, 130.2, 128.9, 128.6, 128.4, 127.6, 127.0, 124.3 (q, $J_{C\text{-}F}$ = 283.4 Hz), 121.7, 81.0, 51.1 (q, $J_{C\text{-}F}$ = 31.5 Hz), 49.2, 28.2, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.34. HRMS (ESI) m/z calcd for $C_{24}H_{27}ClF_3N_2O_3$ [M+H^+]: 483.1657, found 483.1666.



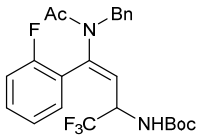
Tert-butyl

(*E*)-(4-(N-benzylacetamido)-4-(3-bromophenyl)-1,1,1-trifluorobut-3-en-2-yl)carbamate (3p, 67.5 mg, 64%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.29 (m, 2H), 7.25-7.16 (m, 5H), 7.08-7.06 (m, 2H), 5.12 (d, J = 8.3 Hz, 1H), 4.86 (s, 2H), 4.65 (d, J = 14.6 Hz, 1H), 4.16 (d, J = 14.8 Hz, 1H), 2.12 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 154.0, 144.7, 136.6, 135.2, 133.2, 131.5, 130.6, 128.9, 128.4, 127.6, 127.4, 124.3(q, $J_{C\text{-}F}$ = 282.9 Hz), 123.3, 121.7, 81.1, 51.0 (q, $J_{C\text{-}F}$ = 32.7 Hz), 49.2, 28.2, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.37. HRMS (ESI) m/z calcd for $C_{24}H_{27}BrF_3N_2O_3$ [M+H^+]: 527.1152, found 527.1145.



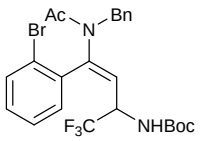
Tert-butyl

(*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(3-(trifluoromethyl)phenyl)but-3-en-2-yl)carbamate (3q, 72.3 mg, 70%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.7 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.43-7.39 (m, 2H), 7.18 (d, J = 6.1 Hz, 3H), 7.05 (d, J = 6.6 Hz, 2H), 5.21 (d, J = 10.3 Hz, 1H), 4.96 (d, J = 9.4 Hz, 1H), 4.84-4.77 (m, 1H), 4.64 (d, J = 14.7 Hz, 1H), 4.19 (d, J = 14.7 Hz, 1H), 2.13 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 154.0, 144.8, 136.5, 134.3, 132.1, 131.7 (q, $J_{C\text{-}F}$ = 33.1 Hz), 129.7, 128.9, 128.5, 127.7, 126.8 (q, $J_{C\text{-}F}$ = 2.6 Hz), 124.3 (q, $J_{C\text{-}F}$ = 282.9 Hz), 125.5 (q, $J_{C\text{-}F}$ = 3.2 Hz), 123.6 (q, $J_{C\text{-}F}$ = 273.7 Hz), 122.0, 81.10, 51.4 (q, $J_{C\text{-}F}$ = 31.9 Hz), 49.3, 28.1, 22.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.79, -75.34. HRMS (ESI) m/z calcd for $C_{25}H_{26}F_6N_2O_3$ [M+H$^+$]: 517.1920, found 517.1911.



Tert-butyl

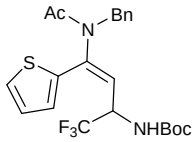
(*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(2-fluorophenyl)but-3-en-2-yl)carbamate (3r, 53.2 mg, 57%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 1H), 7.20-7.02 (m, 8H), 5.27 (d, J = 10.0 Hz, 1H), 5.06-5.00 (m, 1H), 4.74-4.65 (m, 1H),4.57 (d, J = 14.8 Hz, 1H), 4.23 (d, J = 15.1 Hz, 1H), 2.17 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 160.3 (d, $J_{C\text{-}F}$ = 251.1 Hz), 154.1, 141.4, 136.9, 132.0 (d, $J_{C\text{-}F}$ = 8.5 Hz), 131.5, 128.6, 128.3, 127.4, 124.3 (q, $J_{C\text{-}F}$ = 285.0 Hz), 124.6 (d, $J_{C\text{-}F}$ = 3.6 Hz), 121.0, 116.5 (d, $J_{C\text{-}F}$ = 21.7 Hz), 80.7, 51.3 (q, $J_{C\text{-}F}$ = 33.3 Hz), 48.7, 28.1, 22.3, 22.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.54, -112.52. HRMS (ESI) m/z calcd for $C_{24}H_{27}F_4N_2O_3$ [M+H$^+$]: 467.1952, found 467.1949.



Tert-butyl

(*E*)-(4-(N-benzylacetamido)-4-(2-bromophenyl)-1,1,1-trifluorobut-3-en-2-yl)carbamate (3s, 78.0 mg, 74%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J =

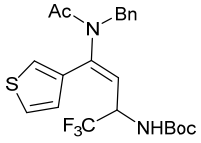
7.9 Hz, 1H), 7.38-7.24 (m, 6H), 7.16-7.14 (m, 2H), 5.18 (d, J = 10.5 Hz, 1H), 4.97-4.80 (m, 2H), 4.74 (d, J = 14.6 Hz, 1H), 4.23 (d, J = 14.8 Hz, 1H), 2.20 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 153.9, 144.7, 136.6, 135.2, 133.2, 131.4, 130.6, 128.9, 128.4, 127.6, 127.4, 124.3 (q, $J_{C\text{-}F}$ = 283.5 Hz), 123.3, 121.6, 81.13, 51.0 (q, $J_{C\text{-}F}$ = 32.5 Hz), 49.1, 28.2, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.38. HRMS (ESI) m/z calcd for $C_{24}H_{27}BrF_3N_2O_3$ [M+H$^+$]: 527.1152, found 527.1152.



Tert-butyl

(*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(thiophen-2-yl)but-3-en-2-yl)carba

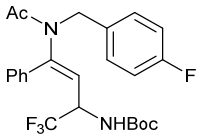
mate (**3t**, 70.0 mg, 77%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 5.0 Hz, 1H), 7.26-7.18 (m, 4H), 7.14-7.11 (m, 2H), 7.04 (t, J = 4.4 Hz, 1H), 5.24-5.18 (m, 1H), 5.01-4.89 (m, 2H), 4.59 (d, J= 15.0 Hz, 1H), 4.47-4.42 (m, 1H), 2.04 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 154.3, 139.1, 136.7, 136.5, 129.6, 129.4, 128.7, 128.4, 128.2, 127.7, 127.1, 124.4 (q, $J_{C\text{-}F}$ = 280.1 Hz), 121.4, 81.0, 51.2 (q, $J_{C\text{-}F}$ = 34.3 Hz), 49.6, 28.7, 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.36. HRMS (ESI) m/z calcd for $C_{22}H_{26}F_3N_2O_3S$ [M+H$^+$]: 455.1611, found 455.1606.



Tert-butyl

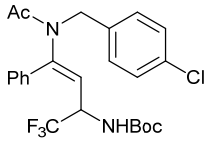
(*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-(thiophen-3-yl)but-3-en-2-yl)carba

mate (**3u**, 79.0 mg, 87%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.34-7.32 (m, 1H), 7.20-7.15 (m, 3H), 7.11-7.09 (m, 2H), 6.98 (d, J = 5.0 Hz, 1H), 5.13-4.96 (m, 3H), 4.64 (d, J = 14.2 Hz, 1H), 4.27 (d, J = 14.2 Hz, 1H), 2.03 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 154.3, 140.9, 136.8, 134.5, 129.2, 128.3, 127.6, 127.3, 127.0, 124.4 (q, $J_{C\text{-}F}$ = 283.1 Hz), 120.8, 80.9, 51.0 (q, $J_{C\text{-}F}$ = 32.0 Hz), 49.4, 28.2, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.39. HRMS (ESI) m/z calcd for $C_{22}H_{26}F_3N_2O_3S$ [M+H$^+$]: 455.1611, found 455.1609.



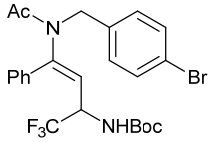
Tert-butyl

(*E*)-(1,1,1-trifluoro-4-(N-(4-fluorobenzyl)acetamido)-4-phenylbut-3-en-2-yl)carba mate (**3v**, 68.1 ,68.1 mg, 73%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 3H), 7.25-7.23 (m, 2H), 7.08-7.04 (m, 2H), 6.87 (t, J = 8.5 Hz, 2H), 5.06-4.92 (m, 3H), 4.57 (d, J = 14.5 Hz, 1H), 4.13 (d, J = 14.4 Hz, 1H), 2.13 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 162.1 (d, $J_{C\text{-}F}$ = 246.7 Hz), 154.0, 145.9, 133.0, 132.7, 130.7 (d, $J_{C\text{-}F}$ = 8.1 Hz), 130.1, 129.2, 128.6, 124.4 (q, JC-F = 282.9 Hz), 120.8, 115.2 (d, $J_{C\text{-}F}$ = 21.4 Hz), 80.9, 51.1 (q, $J_{C\text{-}F}$ = 31.5 Hz), 48.2, 28.1, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.33, -114.85. HRMS (ESI) m/z calcd for $C_{24}H_{27}F_4N_2O_3$ [M+H$^+$]: 467.1952, found 467.19491.



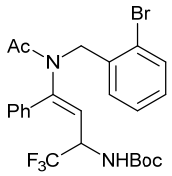
Tert-butyl

(*E*)-(4-(N-(4-chlorobenzyl)acetamido)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)carb amate (3w, 76.3 mg, 79%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.44 (m, 3H), 7.32-7.30 (m, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.16-4.86 (m, 3H), 4.66 (d, J = 14.6 Hz, 1H), 4.17 (d, J = 14.6 Hz, 1H), 2.20 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 154.1, 145.9, 135.4, 133.3, 132.9, 130.4, 130.2, 129.2, 128.6, 128.5, 124.4 (q, $J_{C\text{-}F}$ = 283.8 Hz), 120.8, 80.9, 51.2 (q, $J_{C\text{-}F}$ = 31.1 Hz), 48.3, 28.1, 22.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.31. HRMS (ESI) m/z calcd for $C_{24}H_{27}ClF_3N_2O_3$ [M+H$^+$]: 483.1657, found 483.1656.

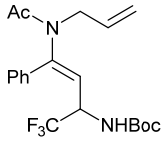


Tert-butyl

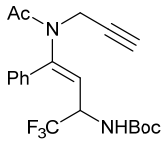
(*E*)-(4-(N-(4-bromobenzyl)acetamido)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)carb amate (3x, 71.7 mg, 68%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 3H), 7.40-7.37 (m, 2H), 7.32-7.30 (m, 2H), 7.04 (d, J = 8.4Hz, 2H), 5.15-5.13 (m, 1H), 5.00 (s, 2H), 4.66 (d, J = 14.5 Hz, 1H), 4.13 (d, J = 14.6 Hz, 1H), 2.20 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 154.0, 145.9, 135.9, 132.9, 131.5, 130.7, 130.2, 129.2, 128.6, 124.4 (q, $J_{C\text{-}F}$ = 282.7 Hz), 121.5, 120.8, 81.0, 51.2 (q, $J_{C\text{-}F}$ = 29.9 Hz), 48.4, 28.2, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.33. HRMS (ESI) m/z calcd for $C_{24}H_{27}BrF_3N_2O_3$ [M+H$^+$]: 527.1152, found 527.1152.



Tert-butyl (*E*)-(4-(N-(2-bromobenzyl)acetamido)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)carbamate (3y, 73.8 mg, 70%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 1H), 7.36-7.32 (m, 3H), 7.17-7.14 (m, 2H), 7.11 (d, J = 7.5 Hz, 1H), 7.06-6.99 (m, 2H), 5.33 (d, J = 10.2 Hz, 1H), 5.02 (d, J = 9.4 Hz, 1H), 4.95-4.89 (m, 1H), 4.74 (d, J = 15.4 Hz, 1H), 4.41 (d, J = 15.2 Hz, 1H), 2.18 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 154.0, 146.0, 135.8, 132.8, 130.9, 130.1, 129.0, 128.6, 127.3, 124.5 (q, $J_{C\text{-}F}$ = 283.7 Hz), 123.8, 120.7, 80.8, 51.0 (q, $J_{C\text{-}F}$ = 31.4 Hz), 49.2, 28.1, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.47. HRMS (ESI) m/z calcd for $C_{24}H_{27}BrF_3N_2O_3$ [M+H$^+$]: 527.1152, found 527.1155.

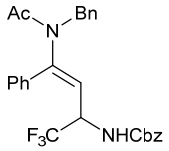


Tert-butyl (*E*)-(4-(N-allylacetamido)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)carbamate (3z, 45.4 mg, 57%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 3H), 7.25-7.21 (m, 2H), 5.72-5.62 (m, 1H), 5.40 (d, J = 10.2 Hz, 1H), 5.22 (d, J = 9.5 Hz, 1H), 5.04-4.85 (m, 3H), 4.02-3.97 (m, 1H), 3.73-3.67 (m, 1H), 2.10 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 154.1, 146.5, 133.4, 132.5, 130.0, 129.1, 128.6, 124.6 (q, $J_{C\text{-}F}$ = 281.7 Hz), 119.7, 118.3, 80.9, 51.2 (q, $J_{C\text{-}F}$ = 31.6 Hz), 48.8, 28.1, 22.3; ^{9}F NMR (282 MHz, $CDCl_3$) δ -75.52. HRMS (ESI) m/z calcd for $C_{20}H_{26}F_3N_2O_3$ [M+H$^+$]: 399.1890, found 399.1892.



Tert-butyl (E)-(1,1,1-trifluoro-4-phenyl-4-(N-(prop-2-yn-1-yl)acetamido)but-3-en-2-yl)carbamate (3aa, 69.0 mg, 87%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.43 (m, 3H), 7.36-7.34 (m, 2H), 5.62 (d, J = 10.2 Hz, 1H), 5.33-4.89 (m, 2H), 4.30 (d, J = 19.8 Hz, 1H), 3.97 (d, J = 17.5 Hz, 1H), 2.20-2.19 (d, J = 2.3 Hz, 1H), 2.16 (s, 3H),

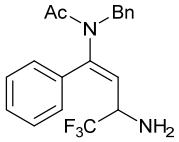
1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 154.1, 145.9, 132.8, 130.2, 129.1, 128.7, 124.6 (q, $J_{C\text{-}F}$ = 283.3 Hz), 120.2, 81.0, 78.3, 72.2, 51.2 (q, $J_{C\text{-}F}$ = 32.0 Hz), 35.6, 28.2, 22.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.47. HRMS (ESI) m/z calcd for $C_{20}H_{24}F_3N_2O_3$ [M+H$^+$]: 397.1734, found 397.1731.



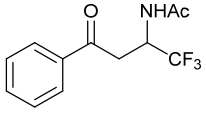
Benzyl

(*E*)-(4-(N-benzylacetamido)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)carbamate

(3bb, 69.5 mg, 72%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 5.3 Hz, 2H), 7.39-7.28 (m, 8H), 7.25 (d, J = 6.6 Hz, 3H), 7.16-7.14 (m, 2H), 5.36 (d, J = 9.0 Hz, 1H), 5.17-5.07 (m, 4H), 4.72 (d, J = 14.5 Hz, 1H), 4.23 (d, J = 14.5 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 154.9, 146.4, 136.8, 135.8, 135.5, 133.0, 130.2, 129.2, 128.9, 128.6, 128.5, 128.4, 128.2, 128.1, 127.5, 124.3 (q, $J_{C\text{-}F}$ = 283.4 Hz), 120.1, 67.6, 51.7 (q, $J_{C\text{-}F}$ = 32.9 Hz), 49.1, 22.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.35. HRMS (ESI) m/z calcd for $C_{27}H_{26}F_3N_2O_3$ [M+Na$^+$]: 505.1709, found 505.1673.



(*E*)-N-(3-amino-4,4,4-trifluoro-1-phenylbut-1-en-1-yl)-N-benzylacetamide (**4,** 56.4 mg, 81%) colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.44 (m, 3H), 7.40-7.36 (m, 2H), 7.31-7.24 (m, 3H), 7.19-7.17 (m, 2H), 5.20 (d, J = 10.2 Hz, 1H), 4.84 (d, J = 14.4 Hz, 1H), 4.14 (d, J = 14.2 Hz, 1H), 3.99-3.91 (m, 1H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 145.0, 136.9, 133.7, 129.8, 129.1, 129.0, 128.6, 128.4, 127.5, 125.6 (q, $J_{C\text{-}F}$ = 283.1 Hz), 123.5, 52.4 (q, $J_{C\text{-}F}$ = 30.5 Hz), 49.0, 22.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -77.38. HRMS (ESI) m/z calcd for $C_{19}H_{19}F_3N_2O$ [M+H$^+$]: 349.1522, found 349.1523.



N-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)acetamide (**5,** 25.4 mg, 49%) colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.64-7.60 (m, 1H), 7.52-7.48 (m, 2H), 6.59 (d, J = 9.5 Hz, 1H), 5.30-5.18 (m, 1H), 3.50-3.43 (m, 1H), 3.32-3.27 (m, 1H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 169.9, 136.0, 134.0, 129.2,

128.9, 128.1, 125.0 ($J_{C\text{-}F}$ = 283.0 Hz), 47.3 ($J_{C\text{-}F}$ = 32.0 Hz), 36.1, 23.1, 21.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.97. HRMS (ESI) m/z calcd for $C_{12}H_{12}F_3NO$ [$M+H^+$]: 260.0893, found 260.0897.

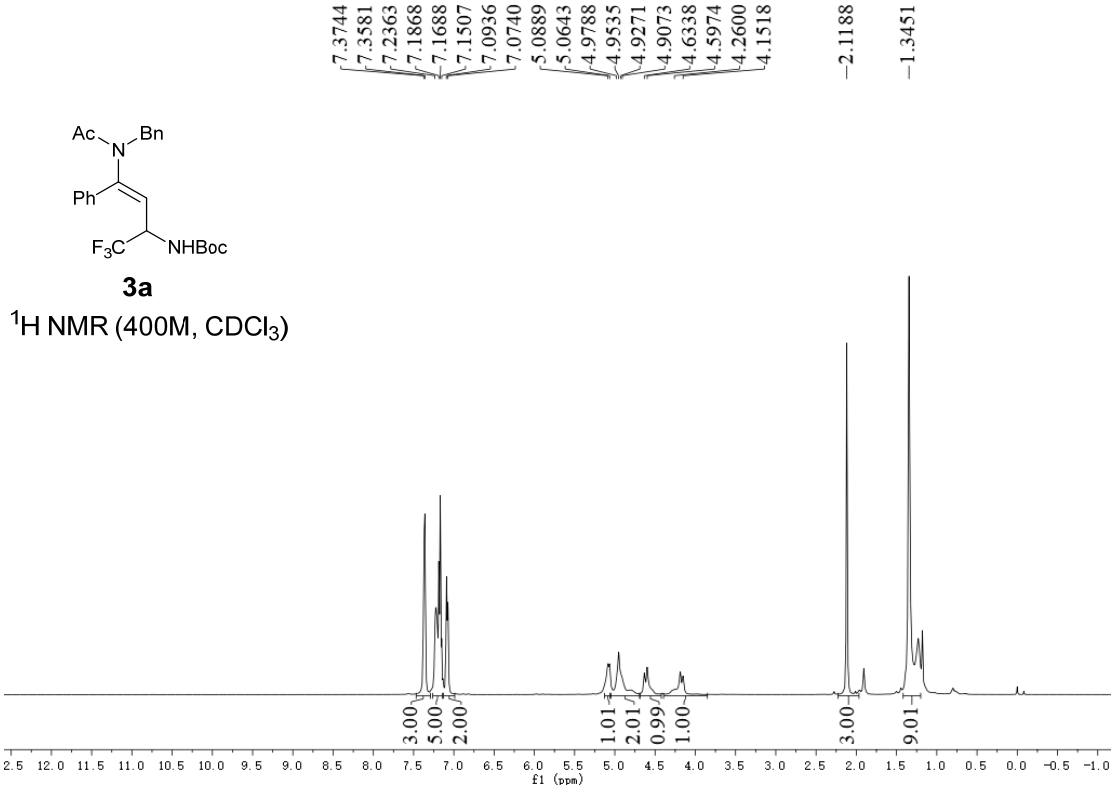
5. References

[1] K. Tang, Y. Chen, J. Guan, Z. Wang, K. Chen, H. Xiang and H. Yang, *Org. Biomol. Chem.,* 2021, **19**, 7475.

[2] J. Wang, S. Liu, Y. Huang, X.-H. Xu and F.-L. Qing, *Chem. Commun.,* 2022, **58**, 1346.

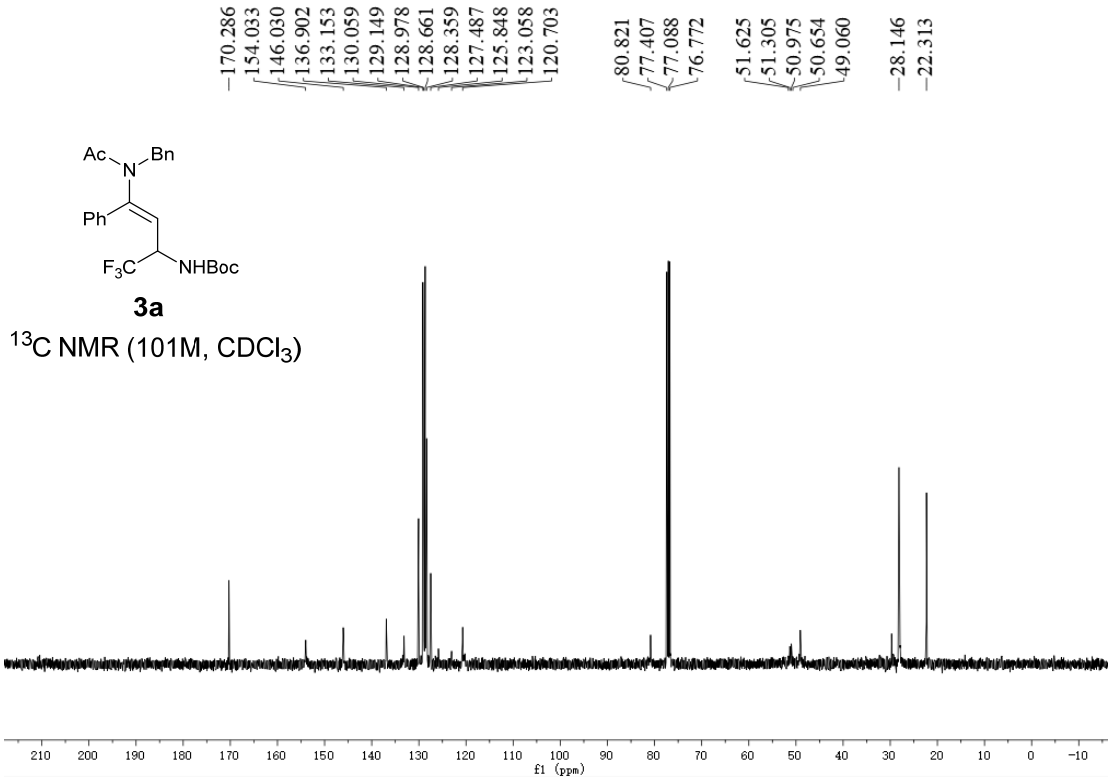
[3] W. Yu, J. Chen, K. Gao, Z. Liu and Y. Zhang, *Org. Lett.,* 2014, **16**, 4870.

6. Copies of the ^{1}H NMR and ^{13}C NMR Spectra



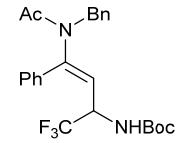
3a

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



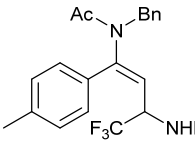
3a

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



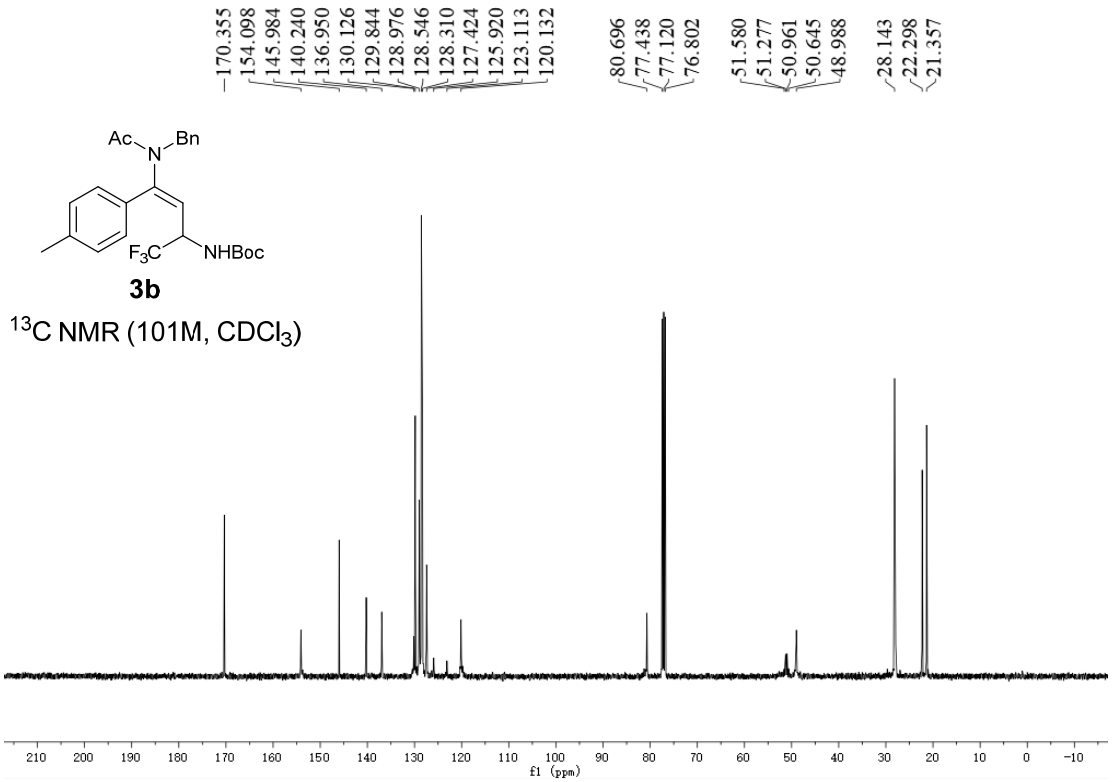
3a

^{19}F NMR (282M, $CDCl_3$)



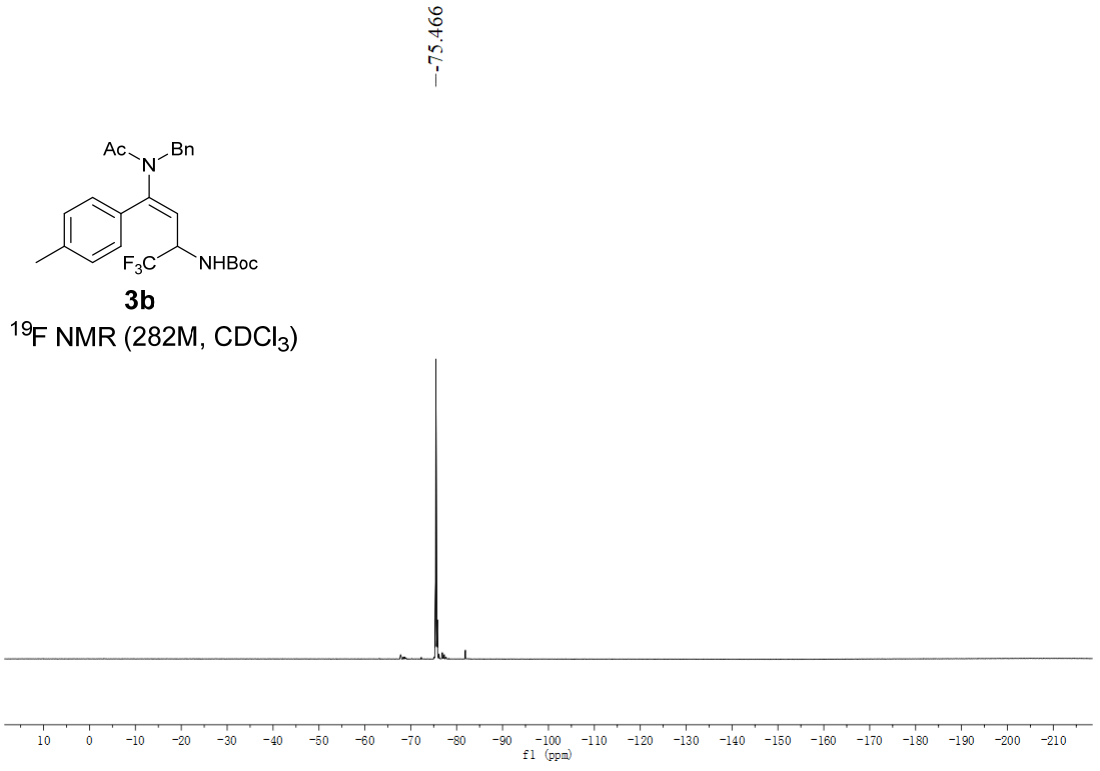
3b

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



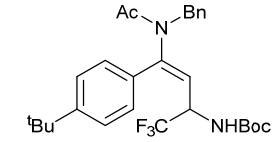
3b

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



3b

^{19}F NMR (282M, $CDCl_3$)

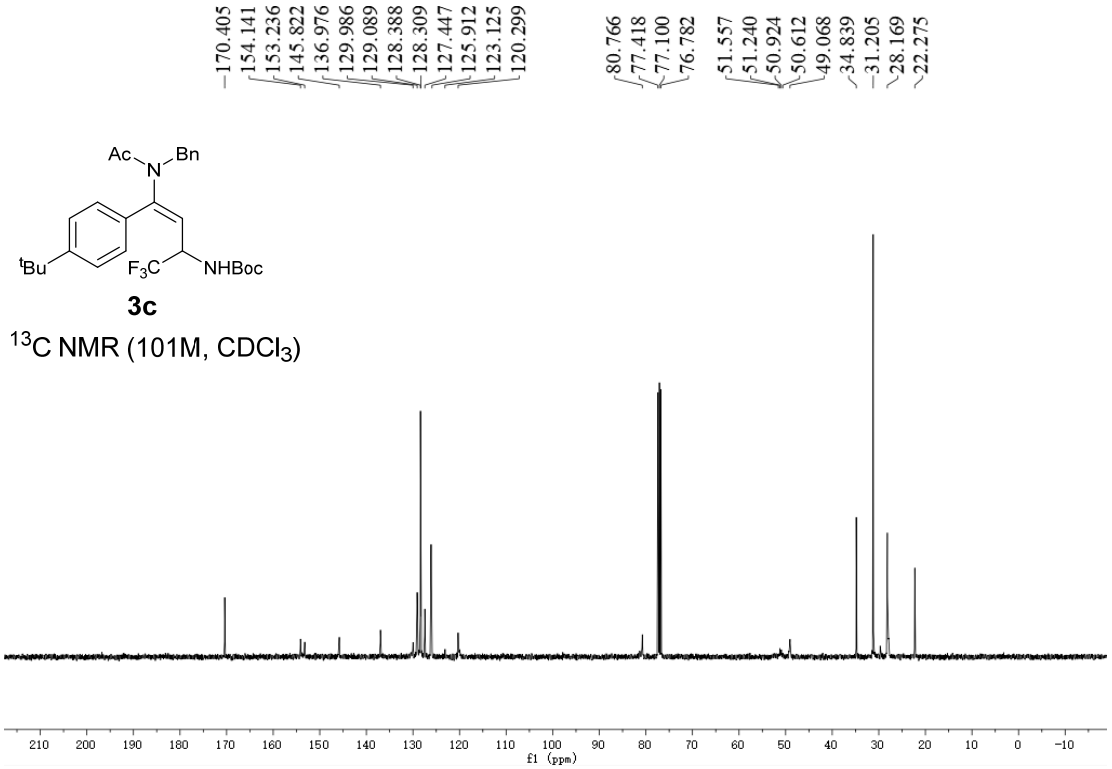


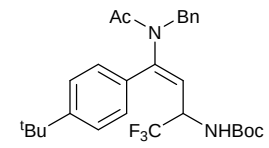
3c

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

3c

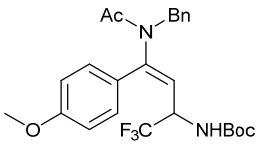
^{13}C NMR (101M, $CDCl_3$)





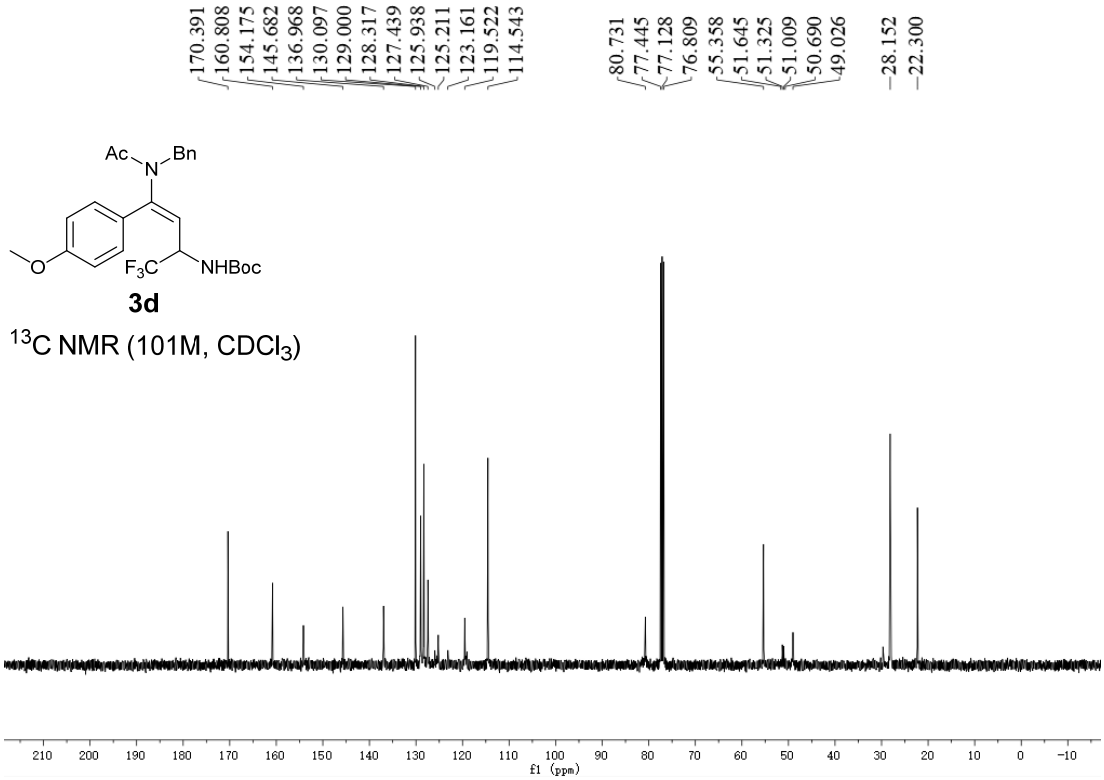
3c

^{19}F NMR (282M, $CDCl_3$)



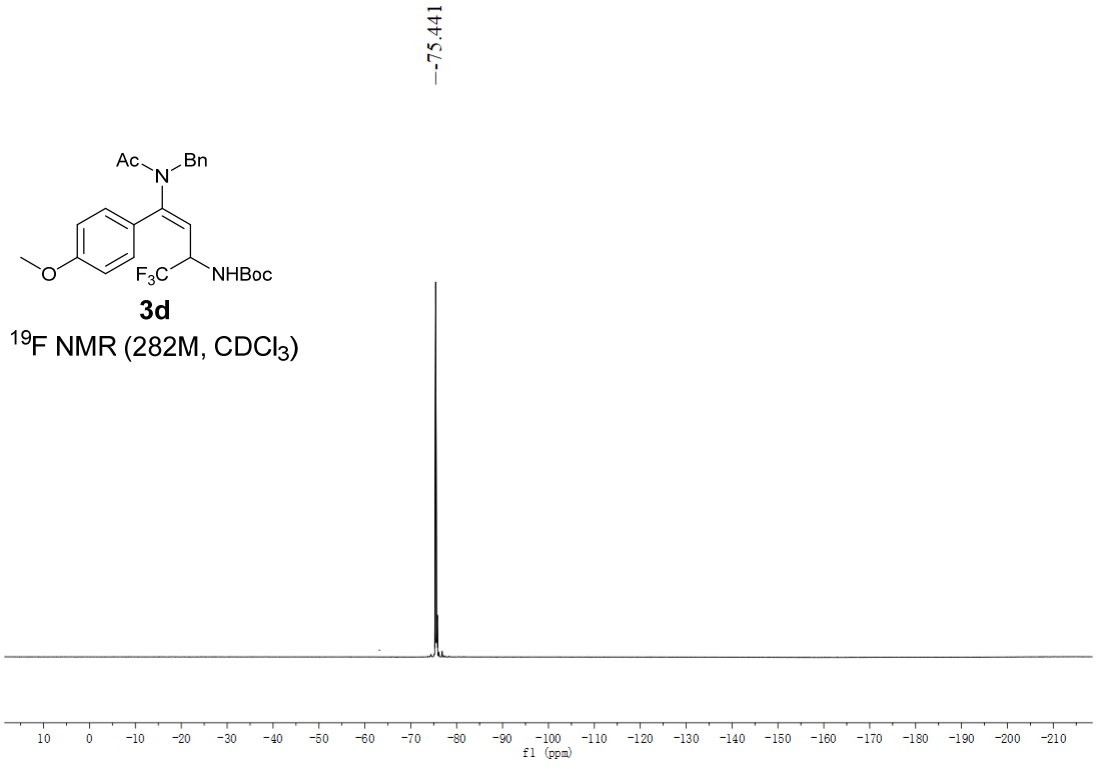
3d

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



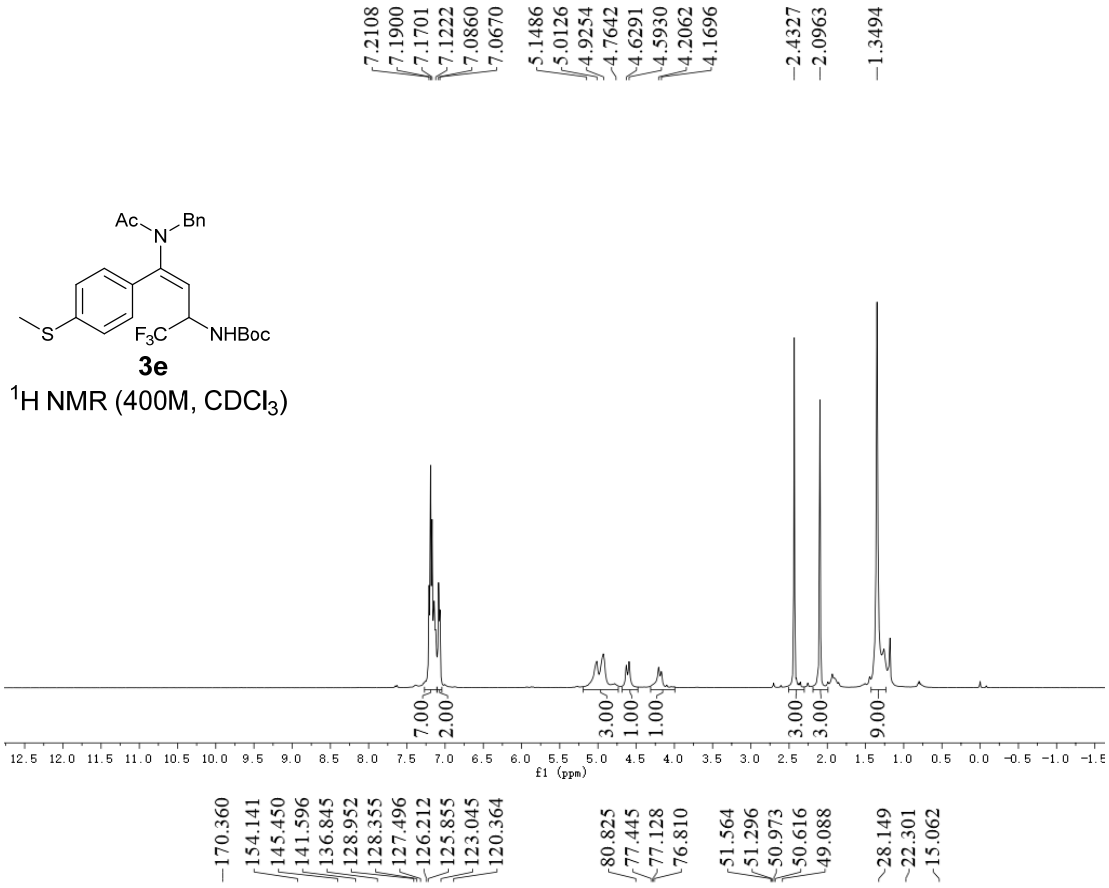
3d

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



3d

^{19}F NMR (282M, $CDCl_3$)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4.2062
4.1696
2.4327
2.0963
1.3494
Ac
N
Bn
S
F3C
NHBoc
3e
1H NMR (400M, CDCl3)
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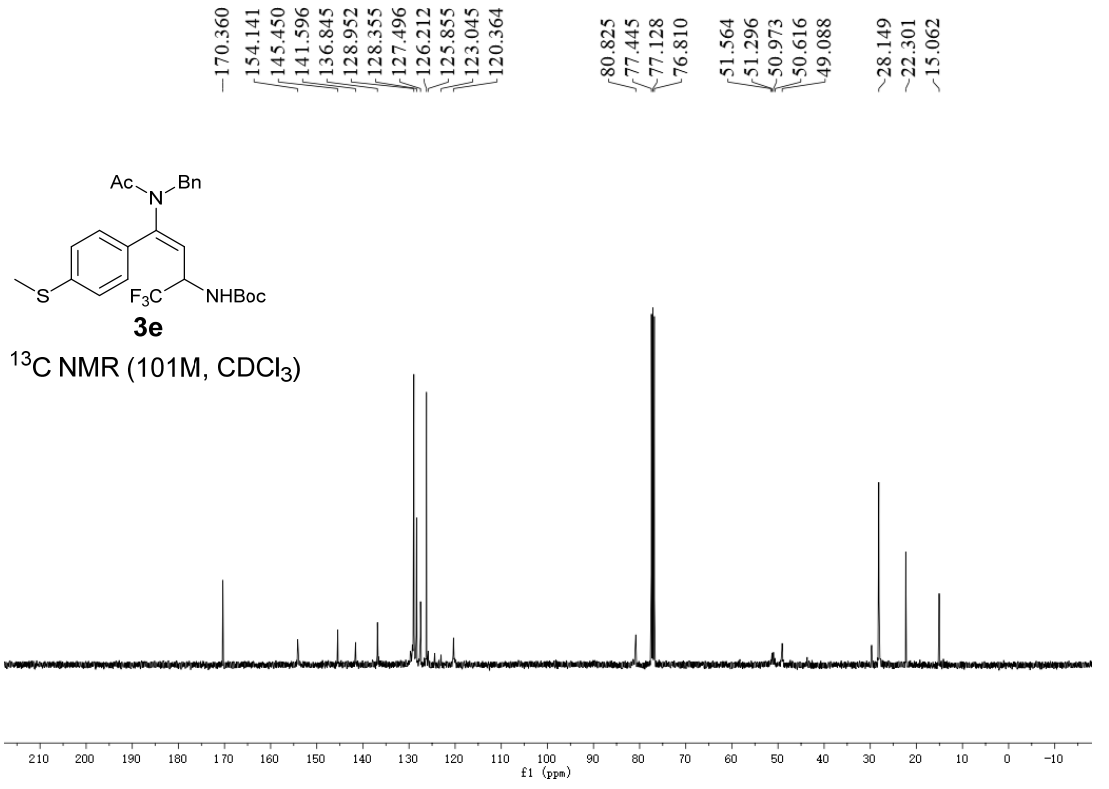
3.00
1.00
1.00
3.00
3.00
9.00
f1 (ppm)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76.810
51.564
51.296
50.973
50.616
49.088
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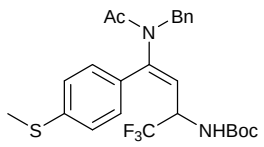
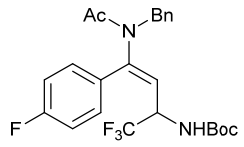
Ac
N
Bn
S
F3C
NHBoc
3e
13C NMR (101M, CDCl3)
f1 (ppm)



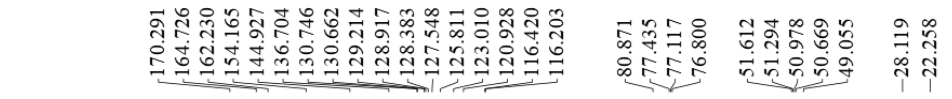
3e

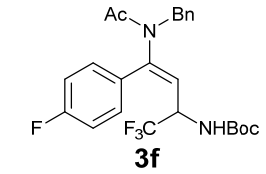
^{19}F NMR (282M, $CDCl_3$)



3f

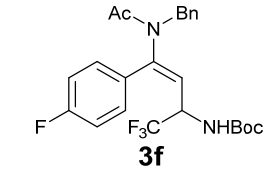
^{1}H NMR (400M, $CDCl_3$)





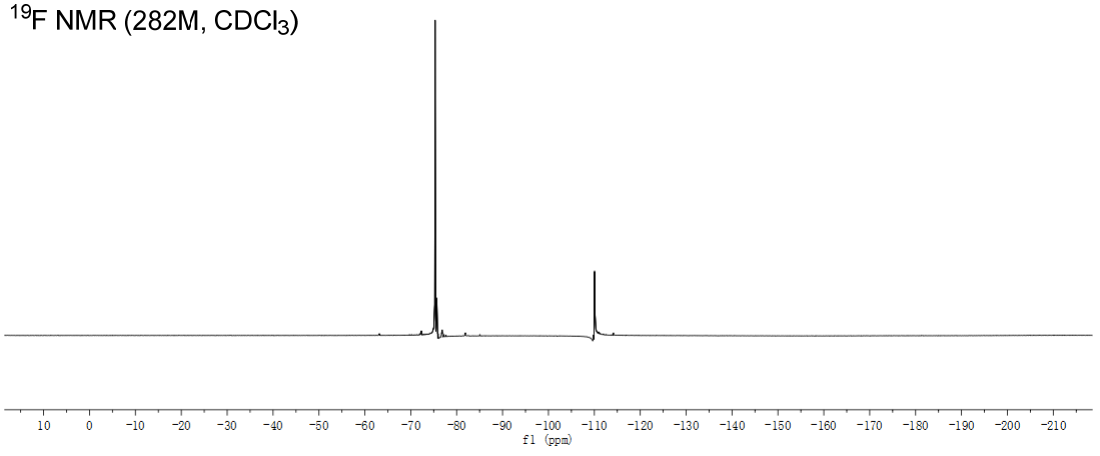
3f

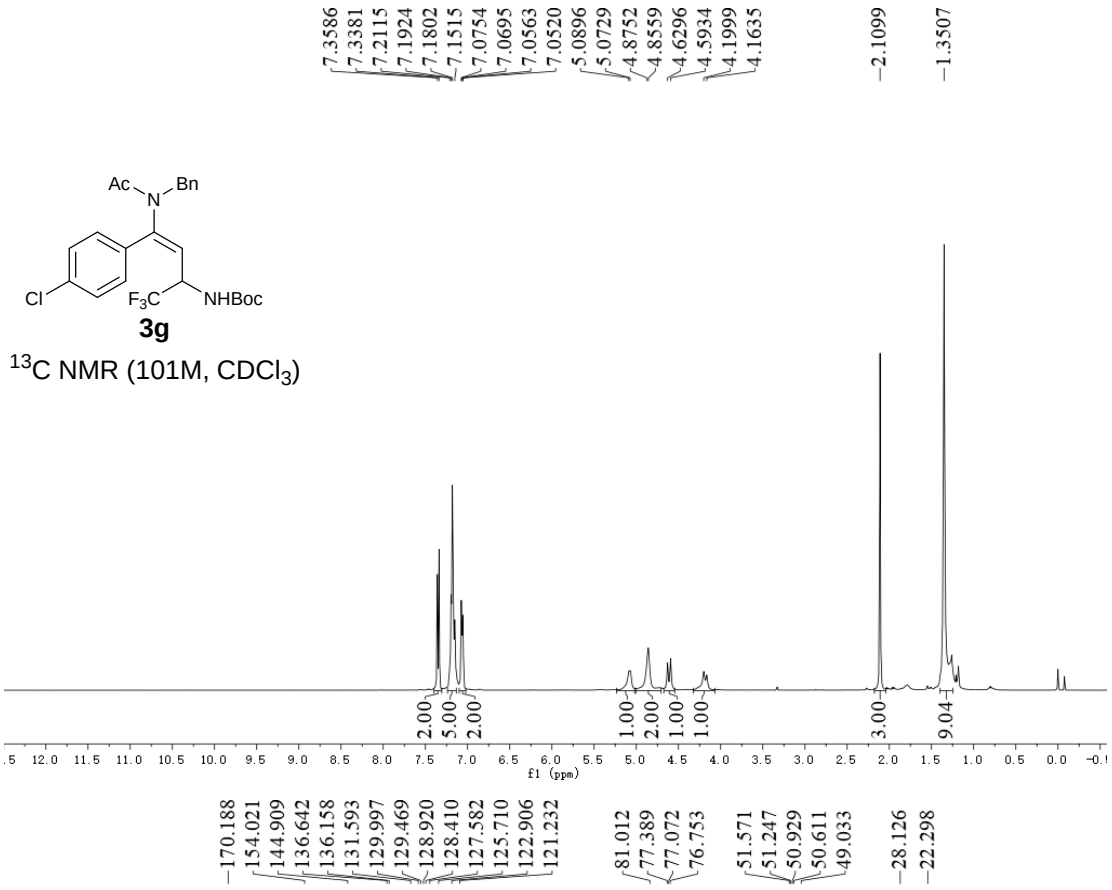
^{13}C NMR (101M, $CDCl_3$)



3f

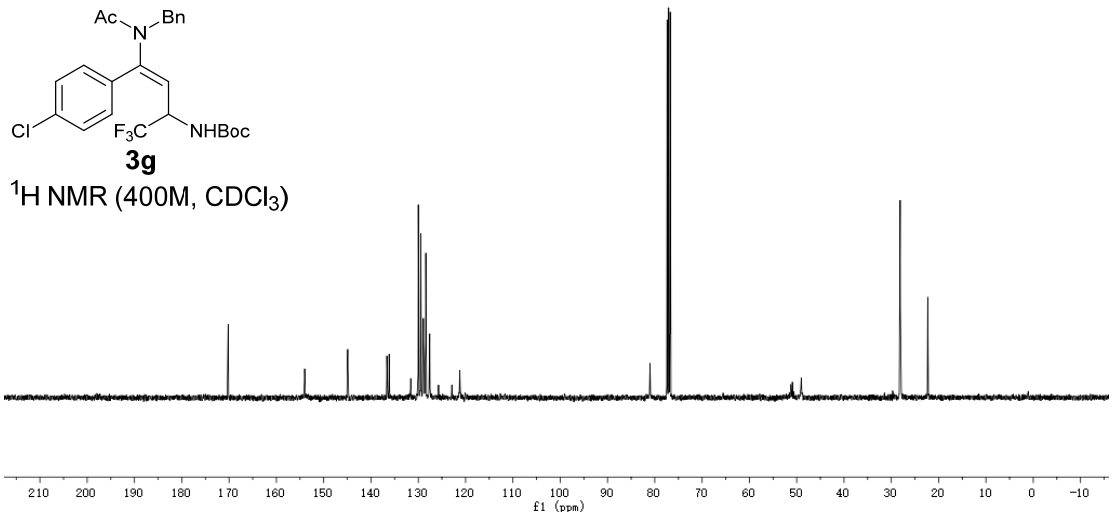
^{19}F NMR (282M, $CDCl_3$)





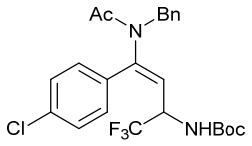
3g

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



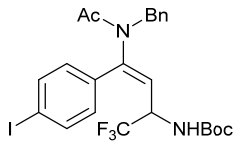
3g

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



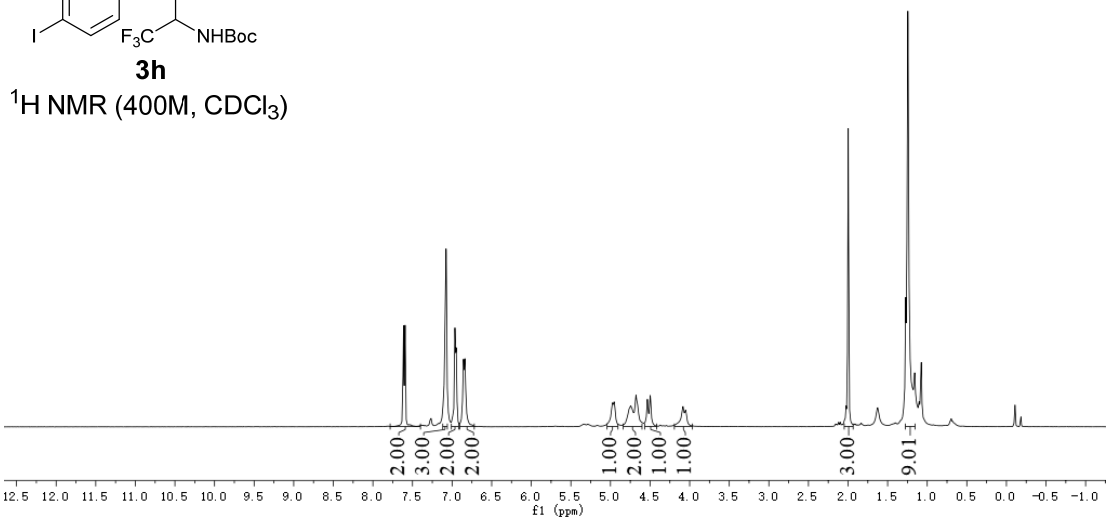
3g

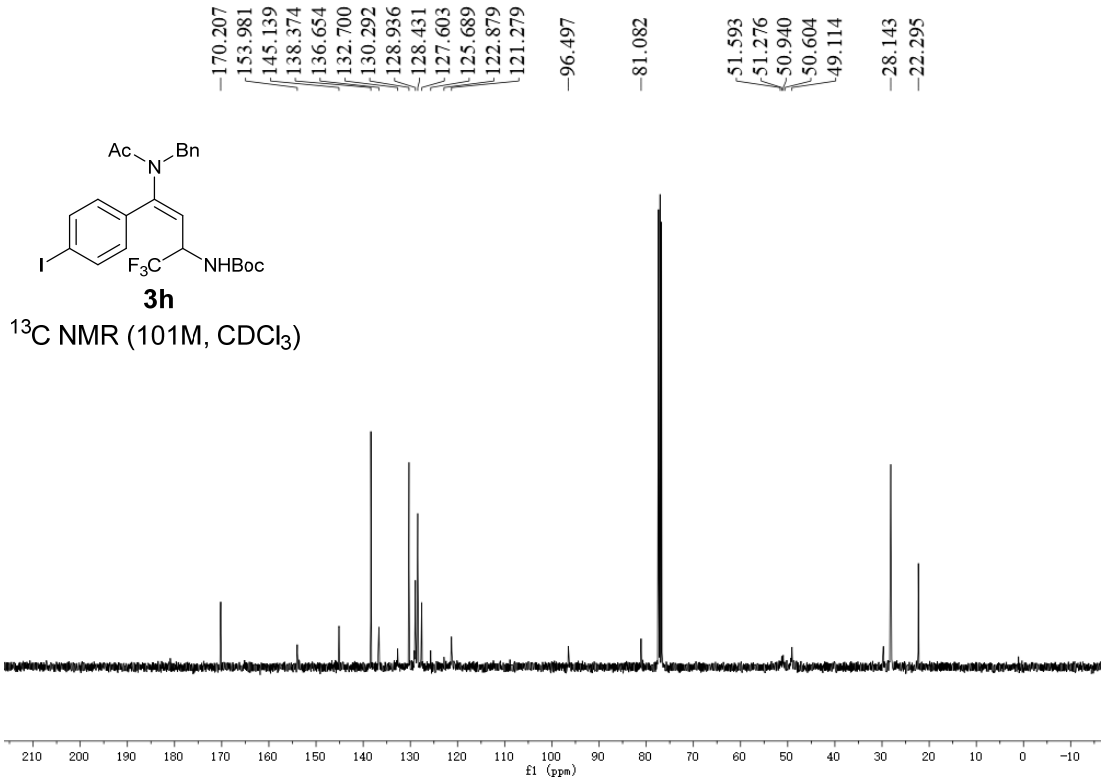
^{19}F NMR (376M, $CDCl_3$)



3h

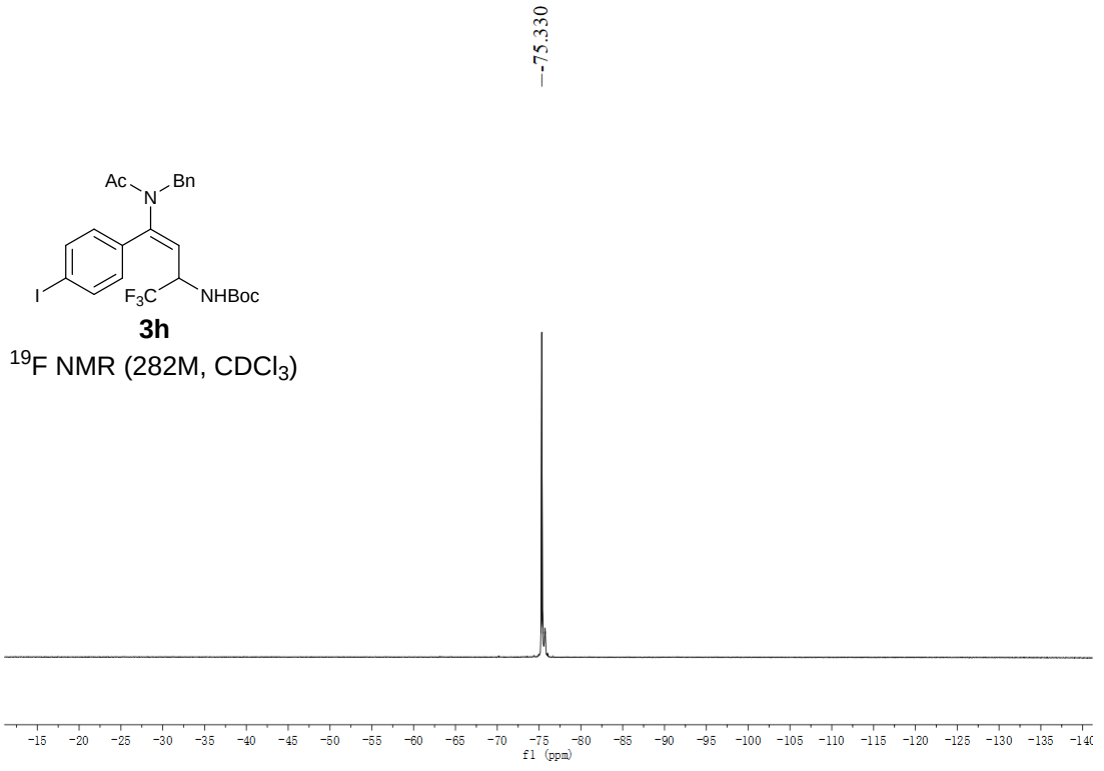
^{1}H NMR (400M, $CDCl_3$)





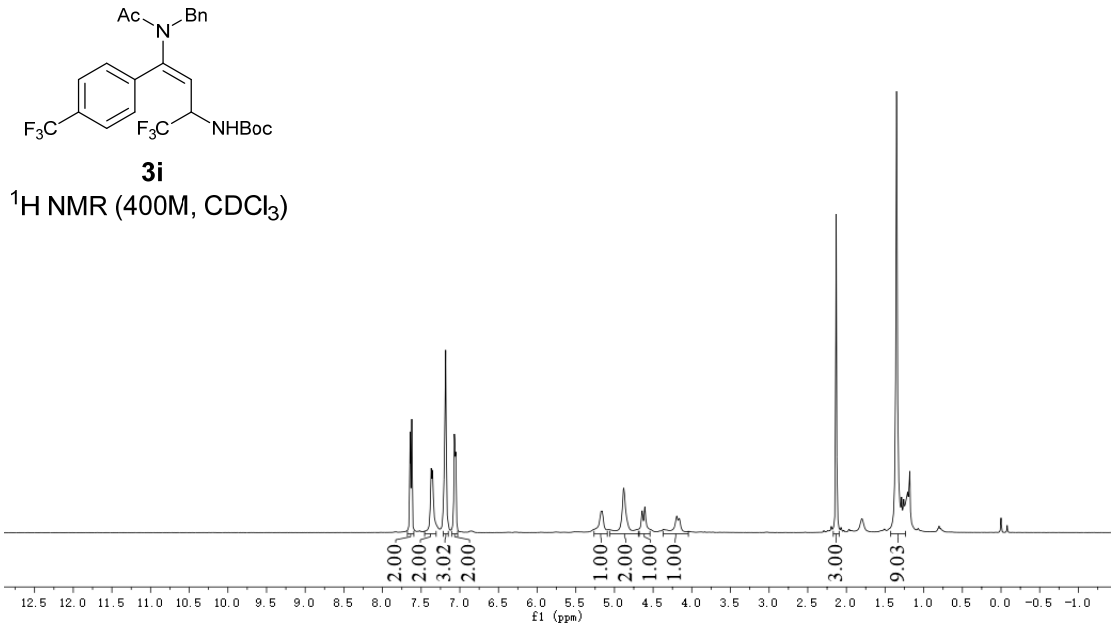
3h

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



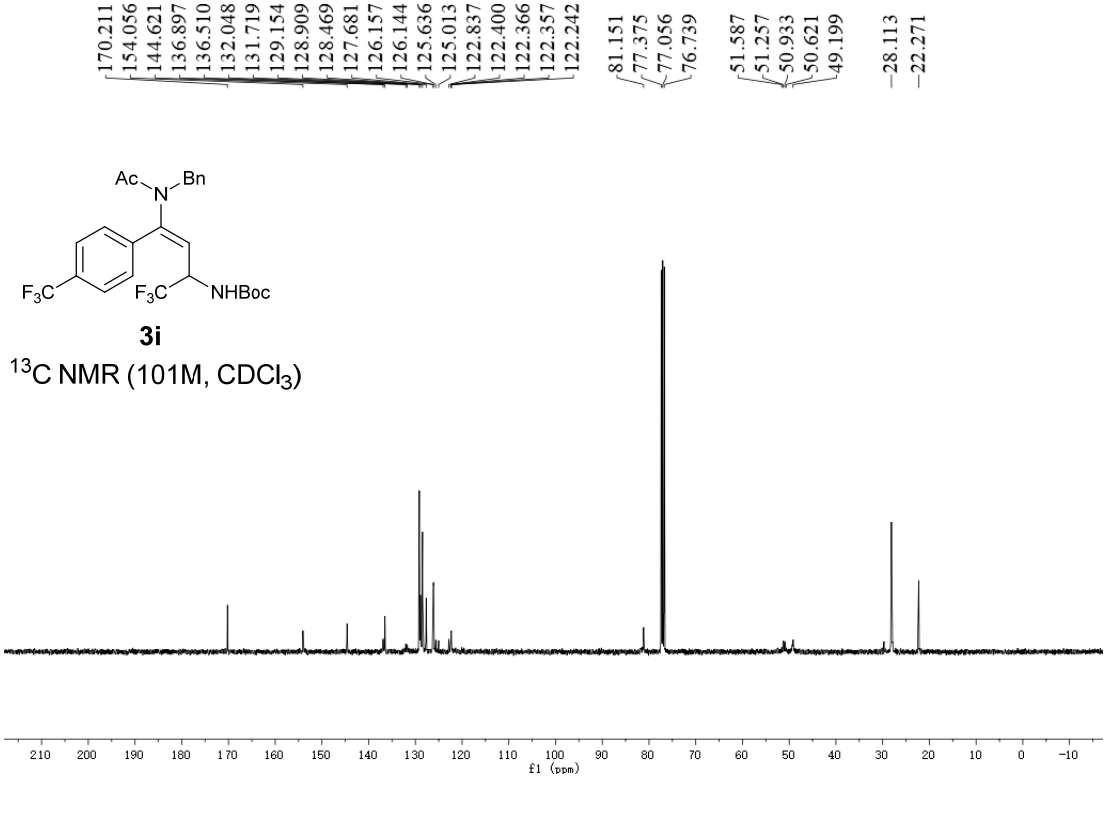
3h

^{19}F NMR (282M, $CDCl_3$)



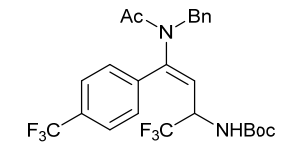
3i

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



3i

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

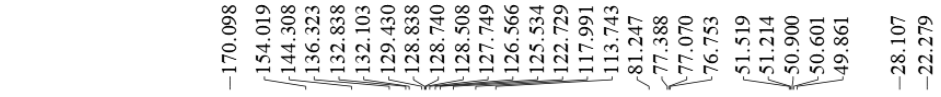


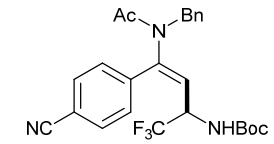
3i

^{19}F NMR (282M, $CDCl_3$)

3j

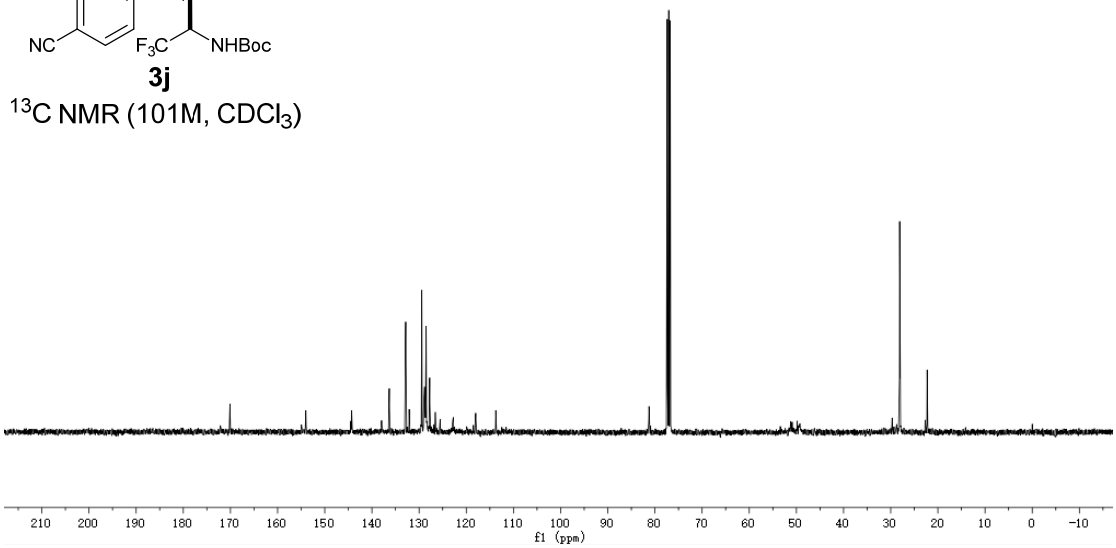
^{1}H NMR (400M, $CDCl_3$)

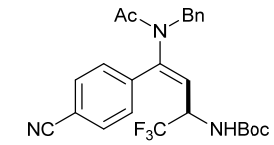




3j

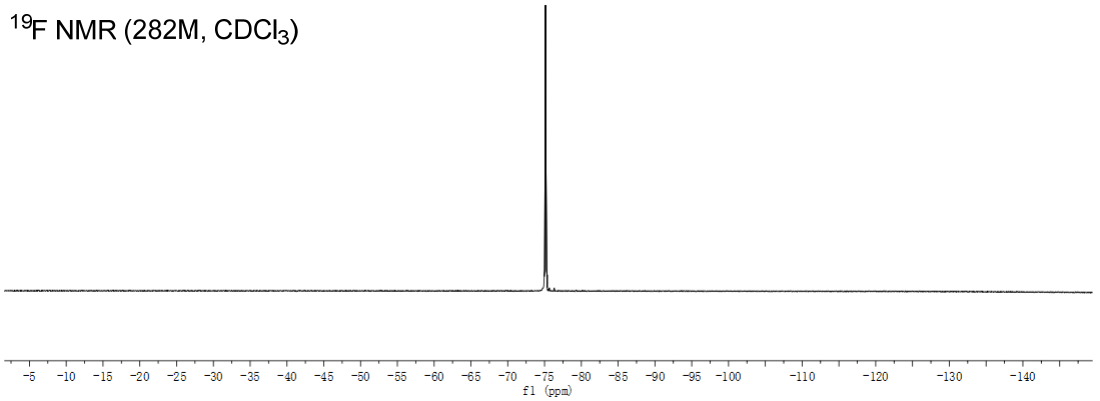
^{13}C NMR (101M, $CDCl_3$)

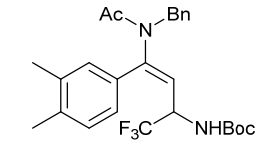




3j

^{19}F NMR (282M, $CDCl_3$)



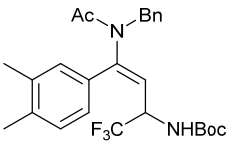


3k

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

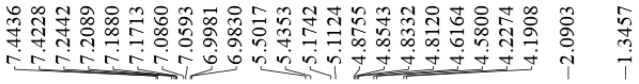
3k

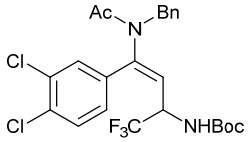
^{13}C NMR (101M, $CDCl_3$)



3k

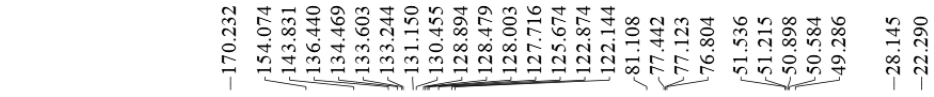
^{19}F NMR (282M, $CDCl_3$)

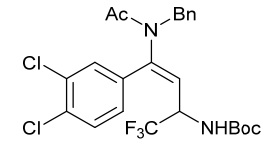




3l

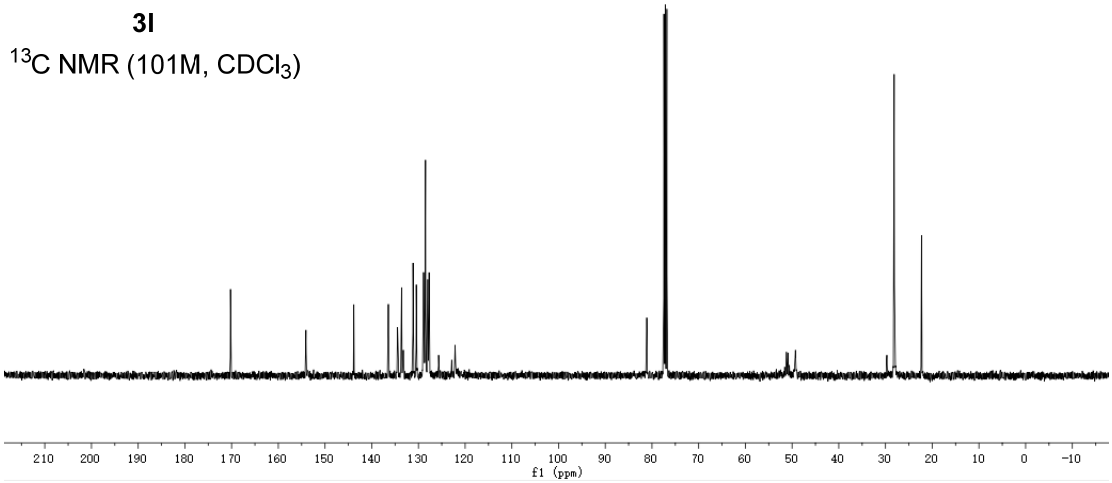
^{1}H NMR (400M, $CDCl_3$)

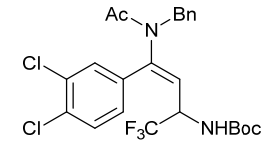




3l

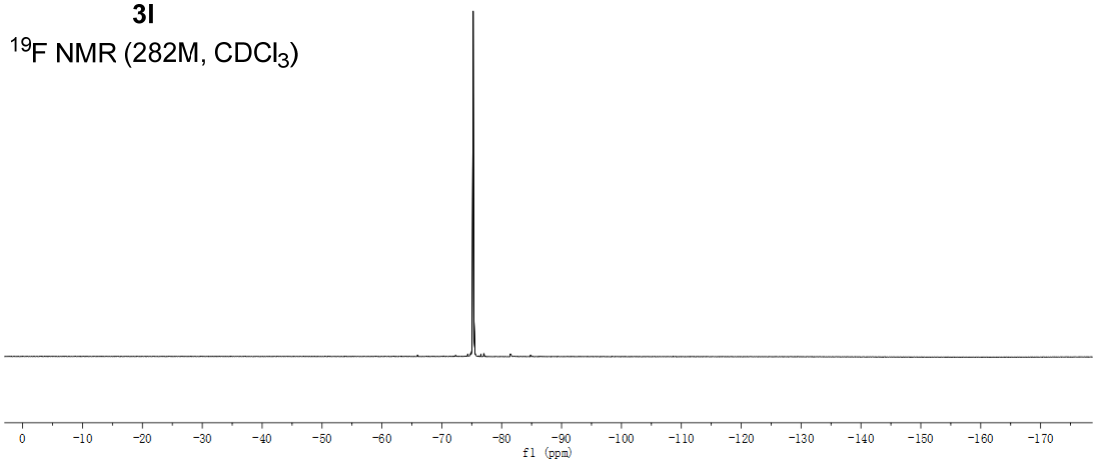
^{13}C NMR (101M, $CDCl_3$)

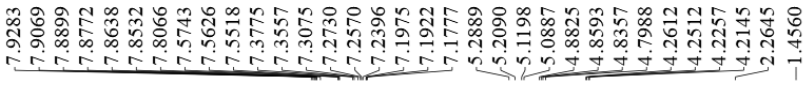


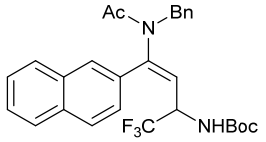


3l

^{19}F NMR (282M, $CDCl_3$)

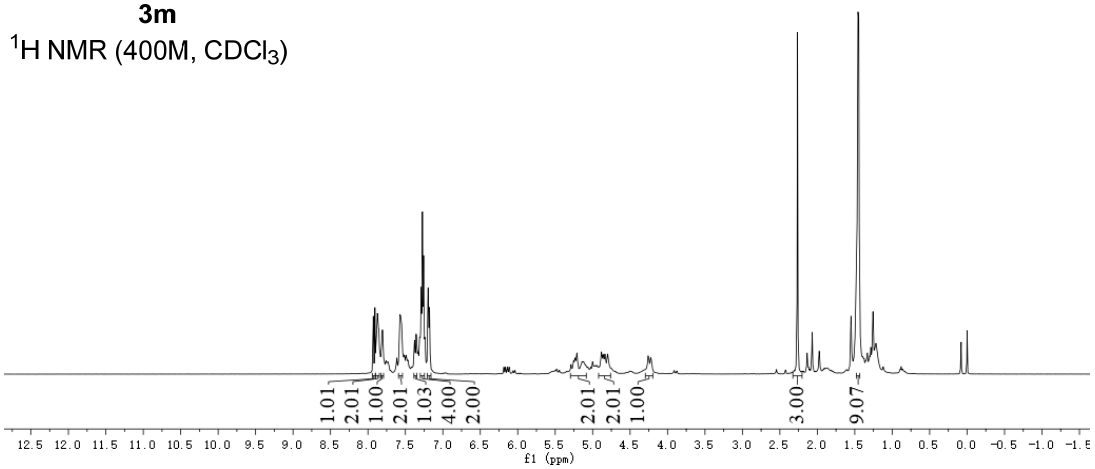


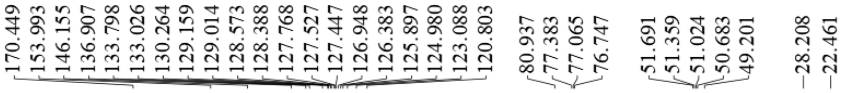


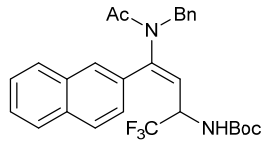


3m

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

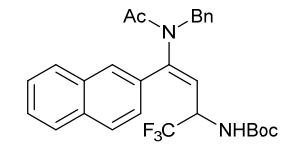






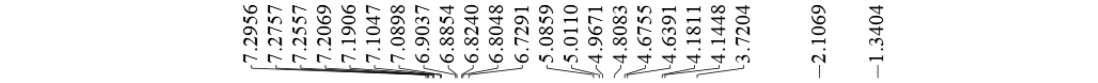
3m

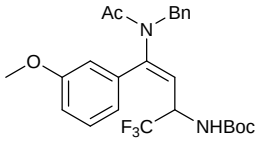
^{13}C NMR (101M, $CDCl_3$)



3m

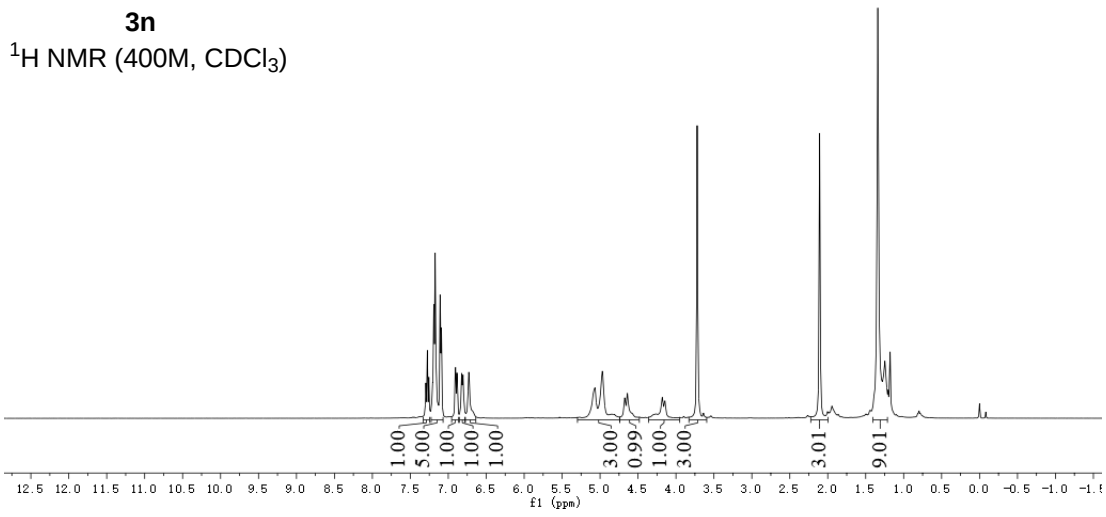
^{19}F NMR (282M, $CDCl_3$)

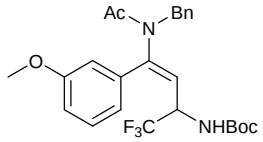




3n

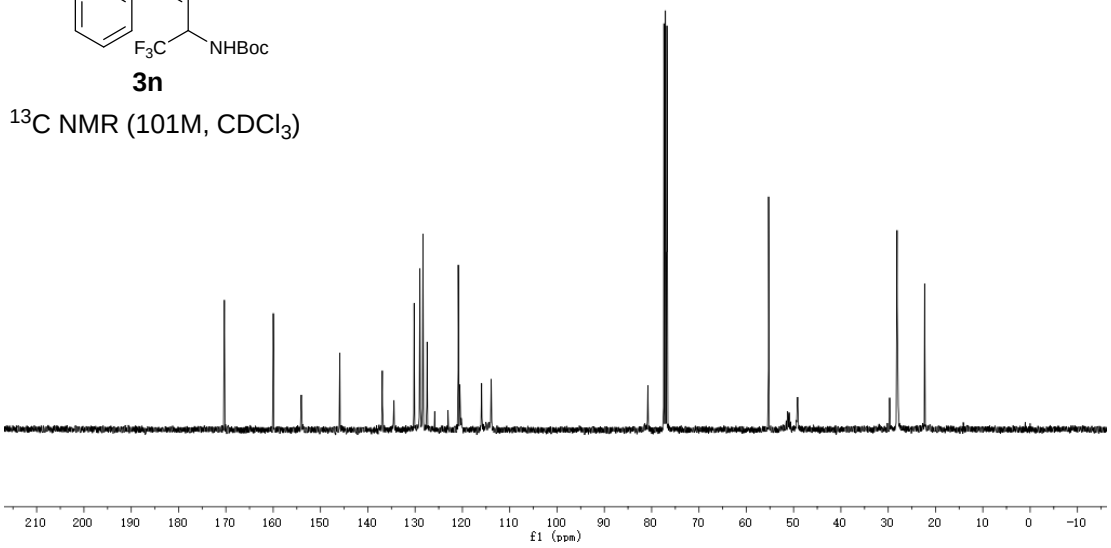
^{1}H NMR (400M, $CDCl_3$)

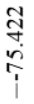


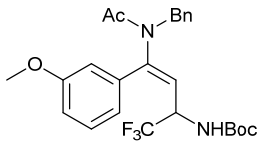


3n

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

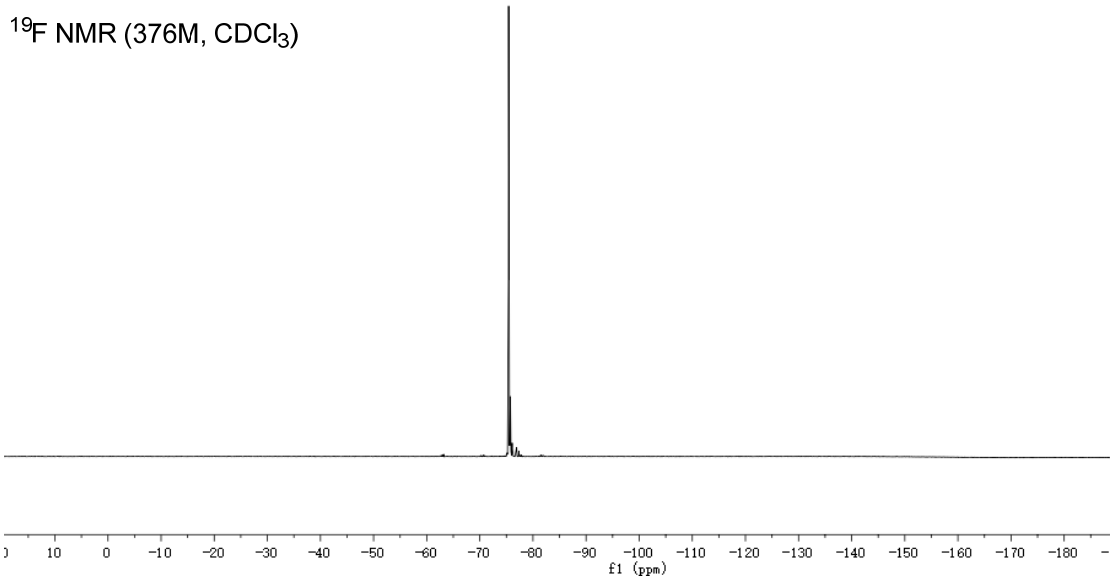


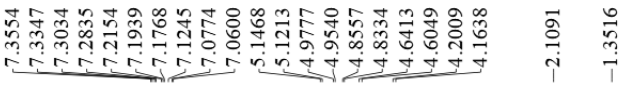


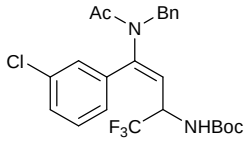


3n

^{19}F NMR (376M, $CDCl_3$)

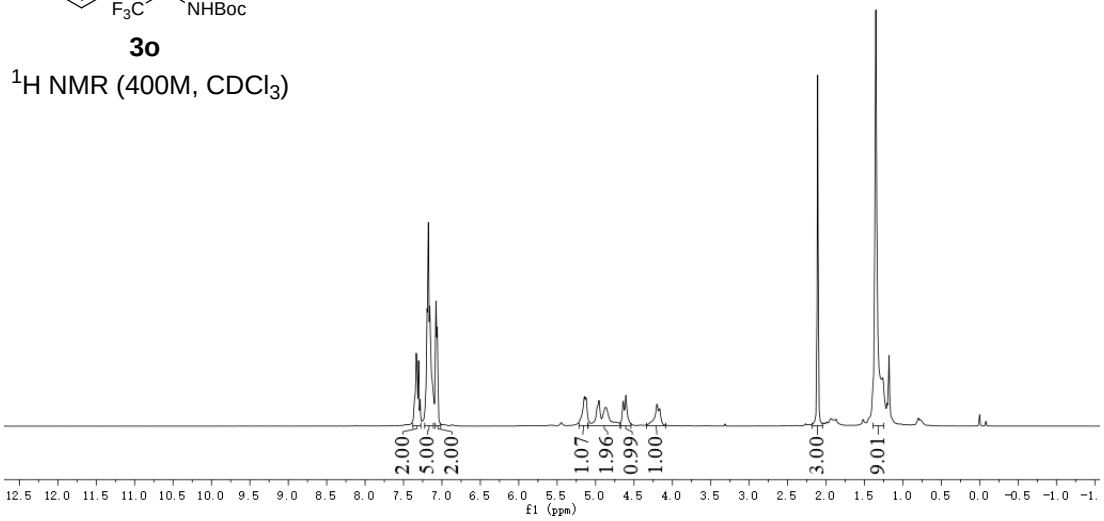


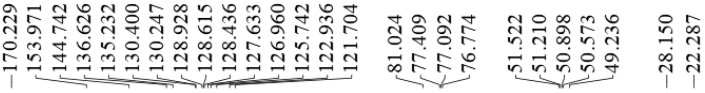


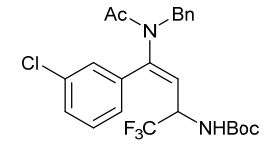


3o

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

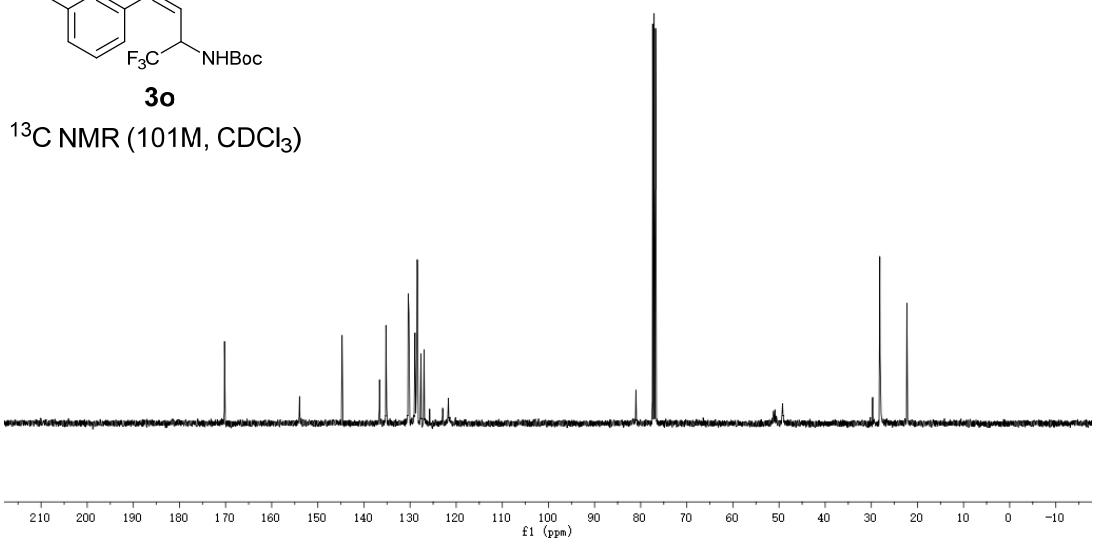


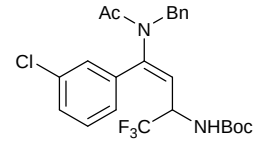




3o

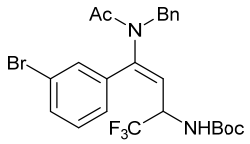
^{13}C NMR (101M, $CDCl_3$)





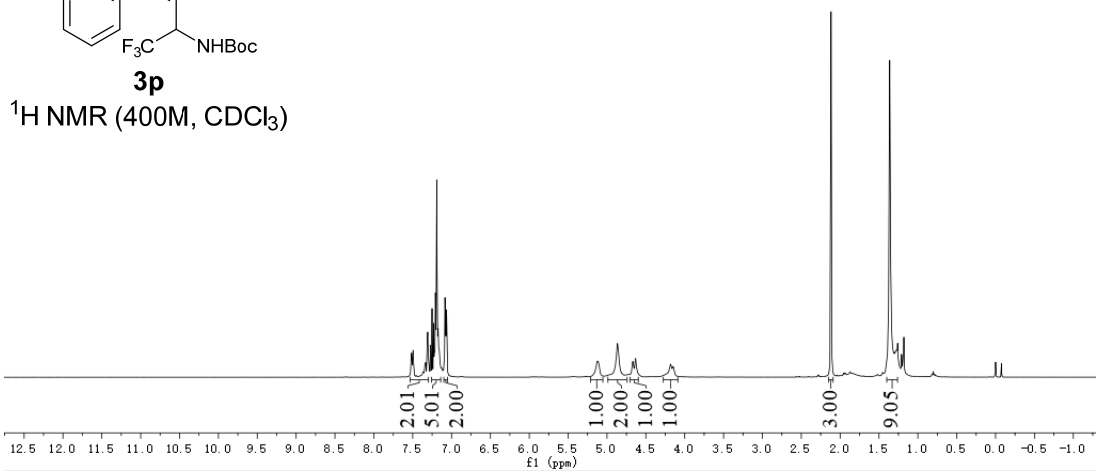
3o

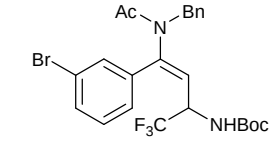
^{19}F NMR (282M, $CDCl_3$)



3p

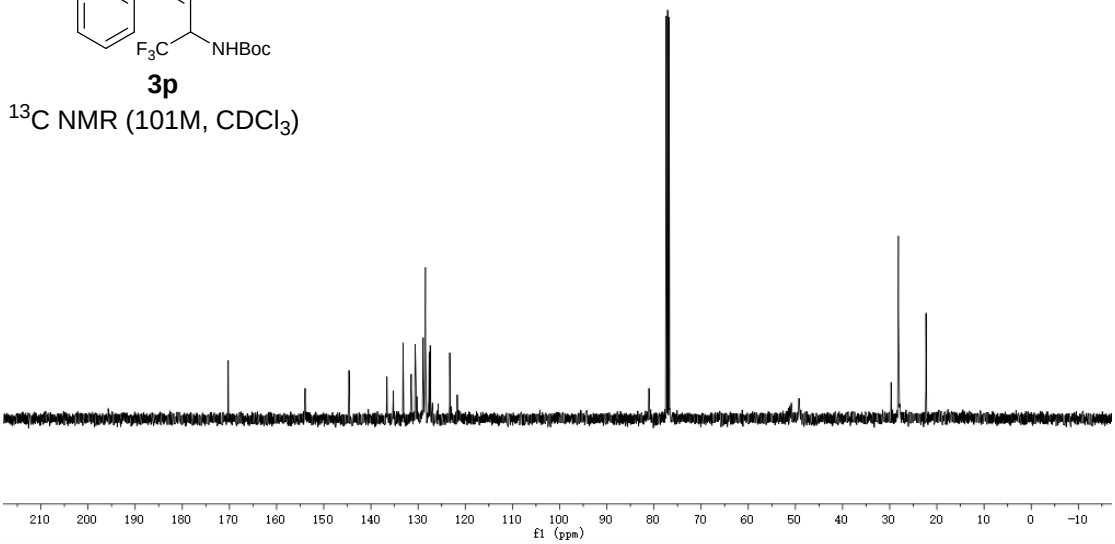
^{1}H NMR (400M, $CDCl_3$)

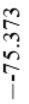


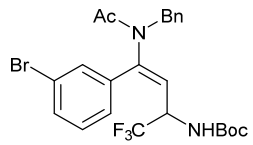


3p

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

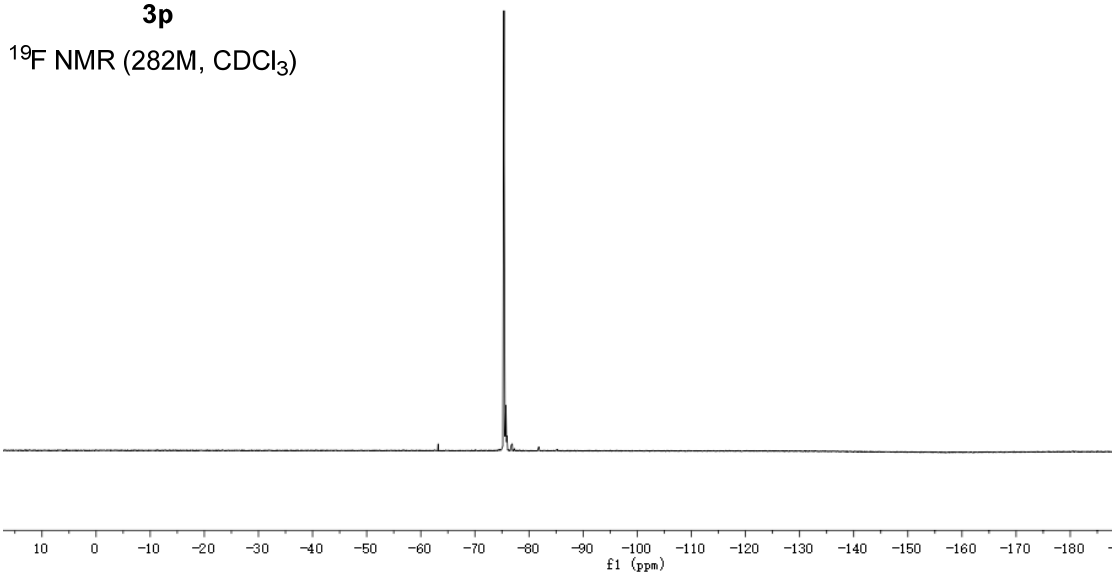


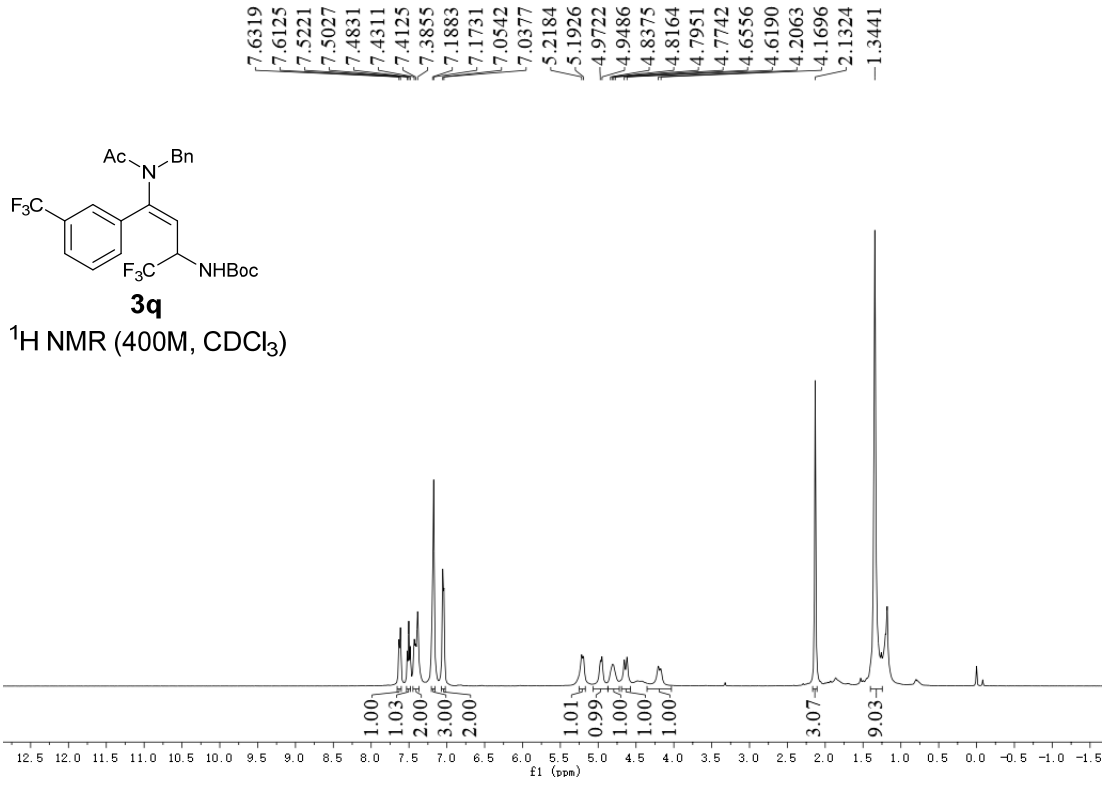




3p

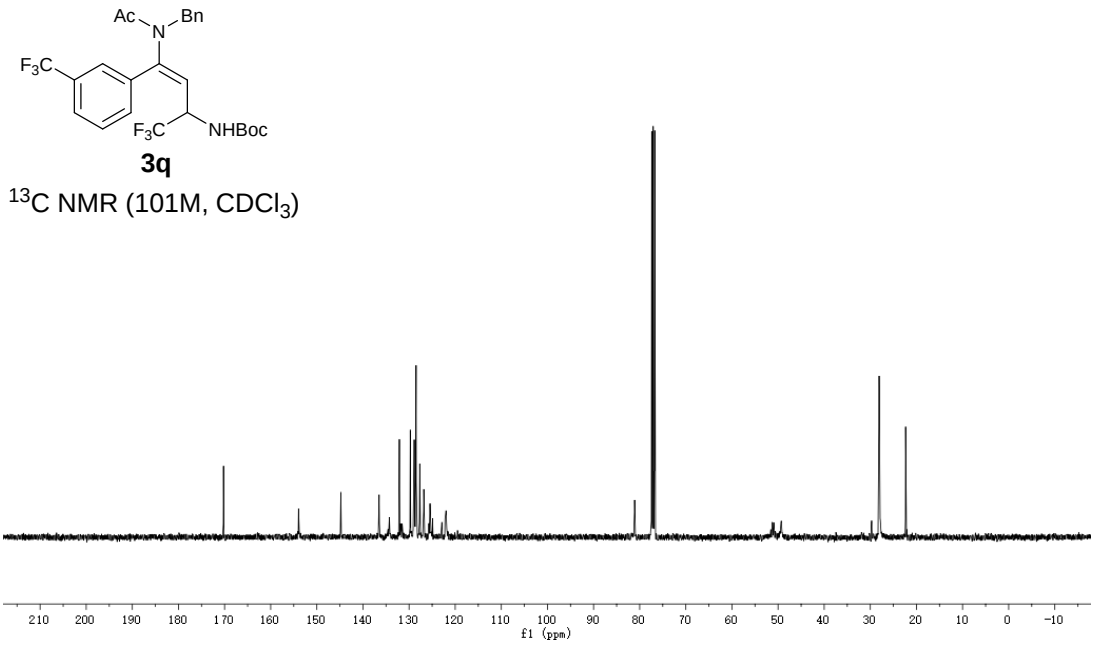
^{19}F NMR (282M, $CDCl_3$)





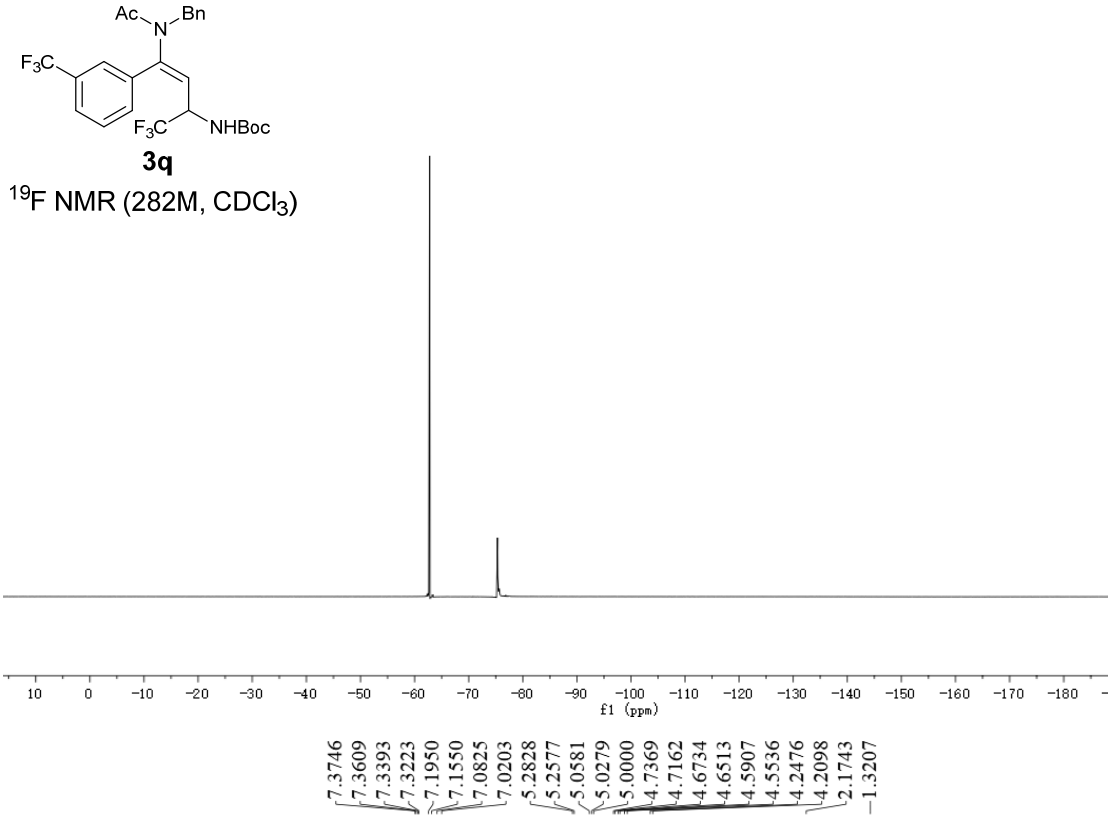
3q

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



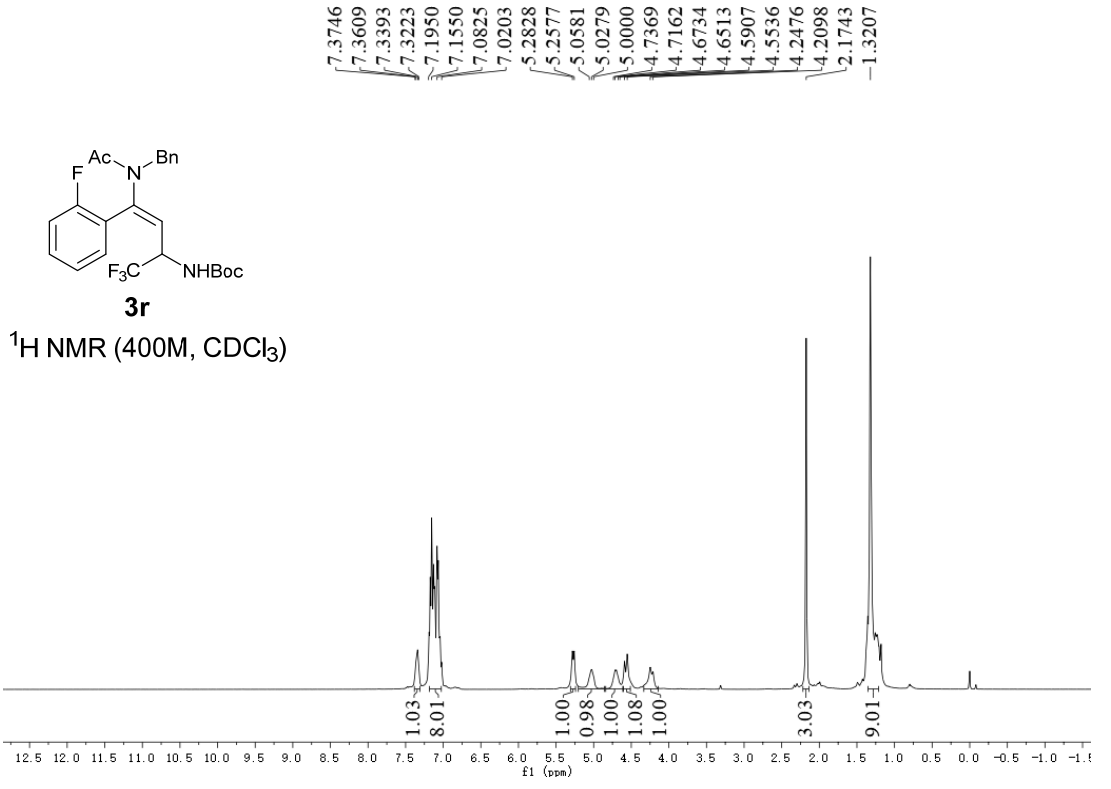
3q

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



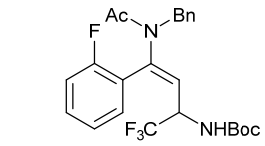
3q

^{19}F NMR (282M, $CDCl_3$)



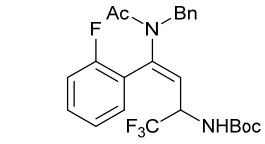
3r

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



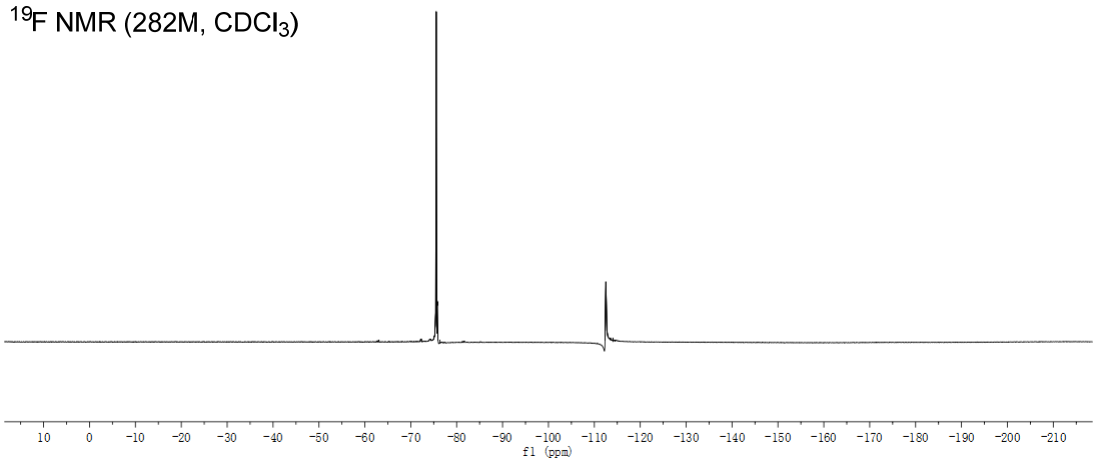
3r

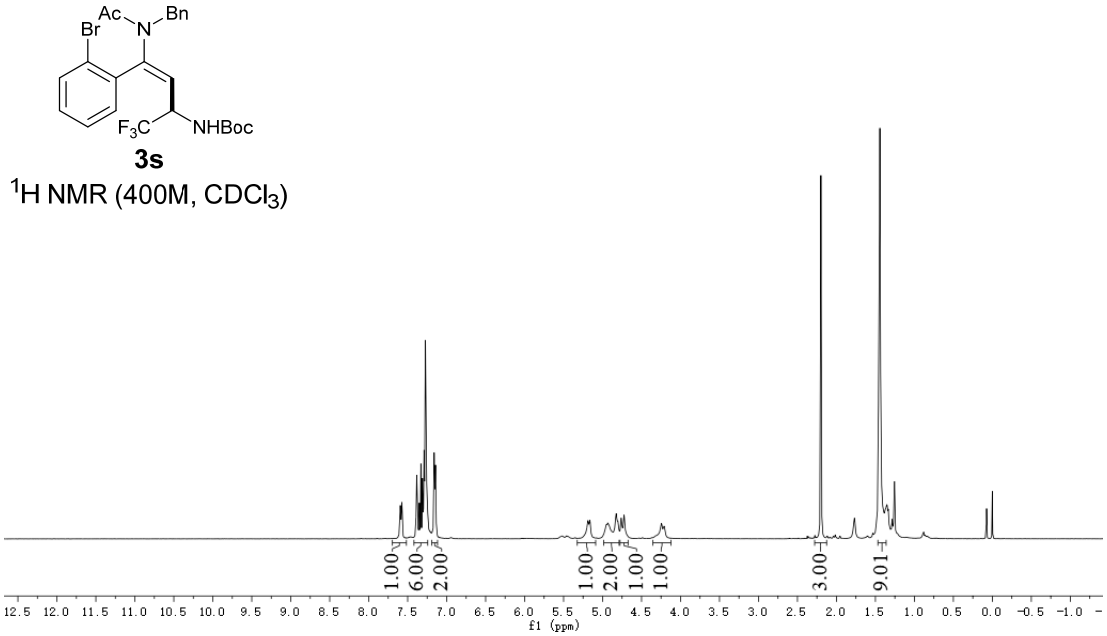
^{13}C NMR (101M, $CDCl_3$)



3r

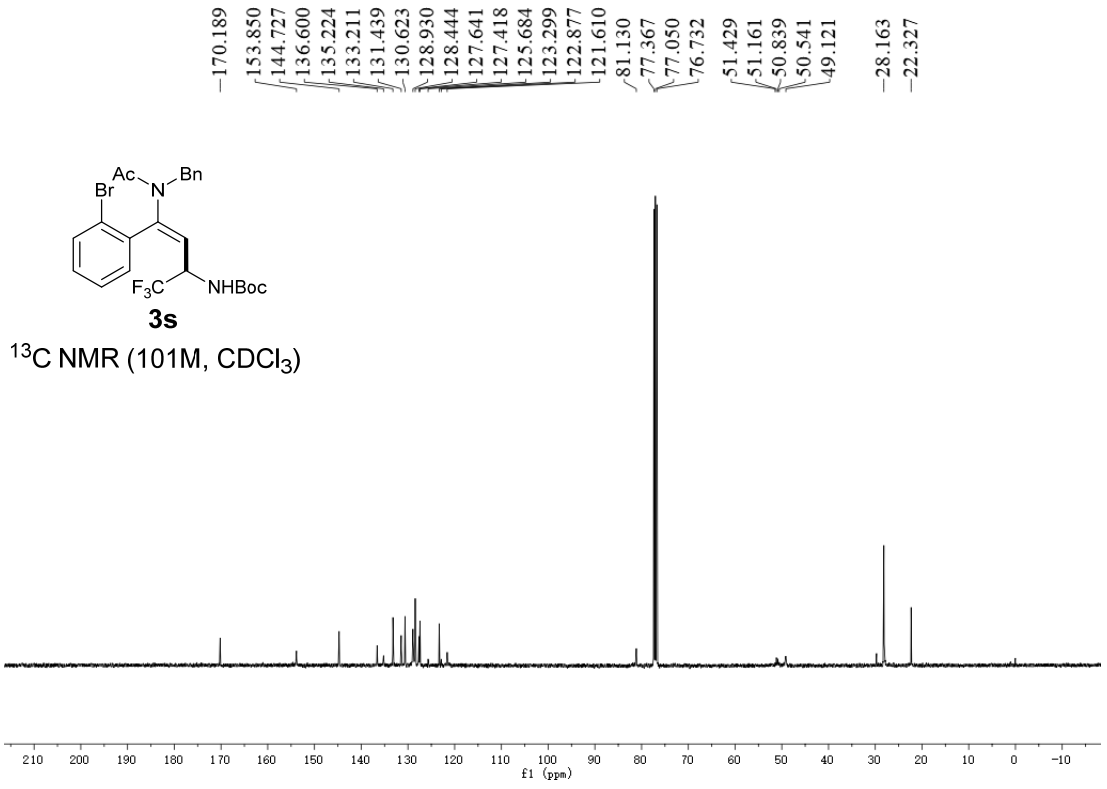
^{19}F NMR (282M, $CDCl_3$)





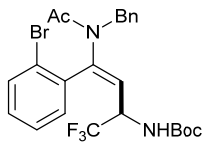
3s

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



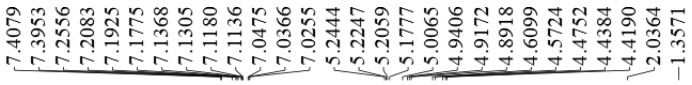
3s

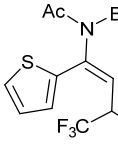
^{13}C NMR (101M, $CDCl_3$)



3s

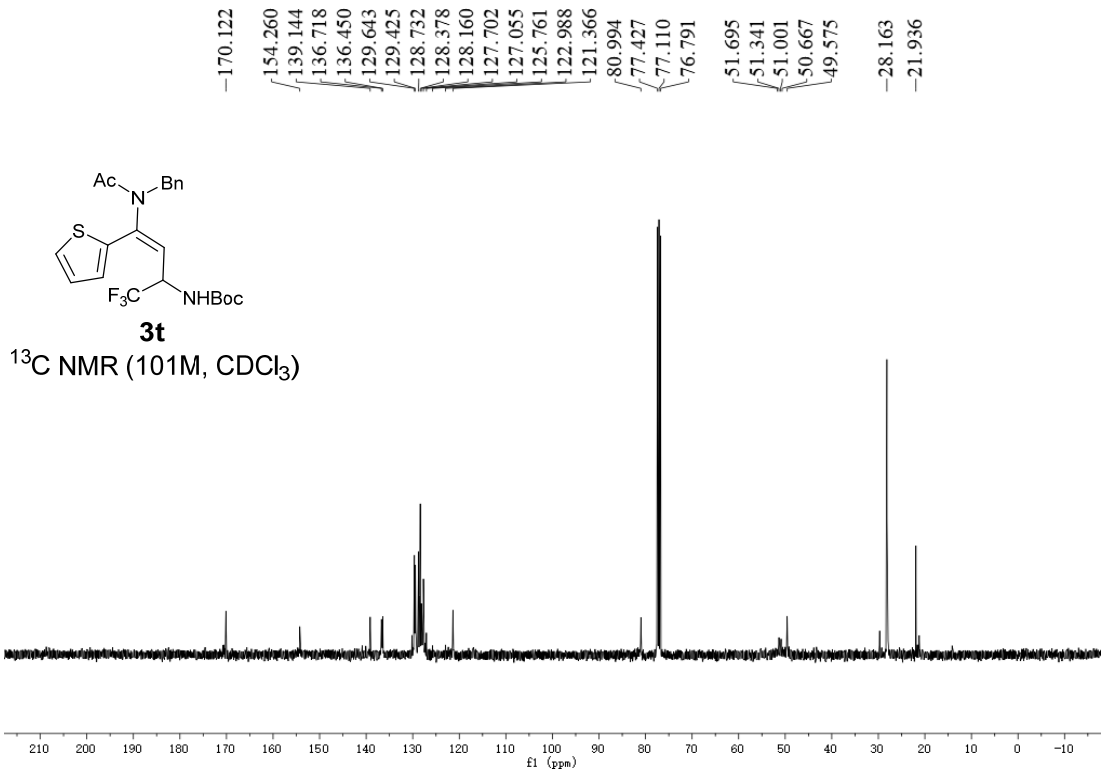
^{19}F NMR (282M, $CDCl_3$)





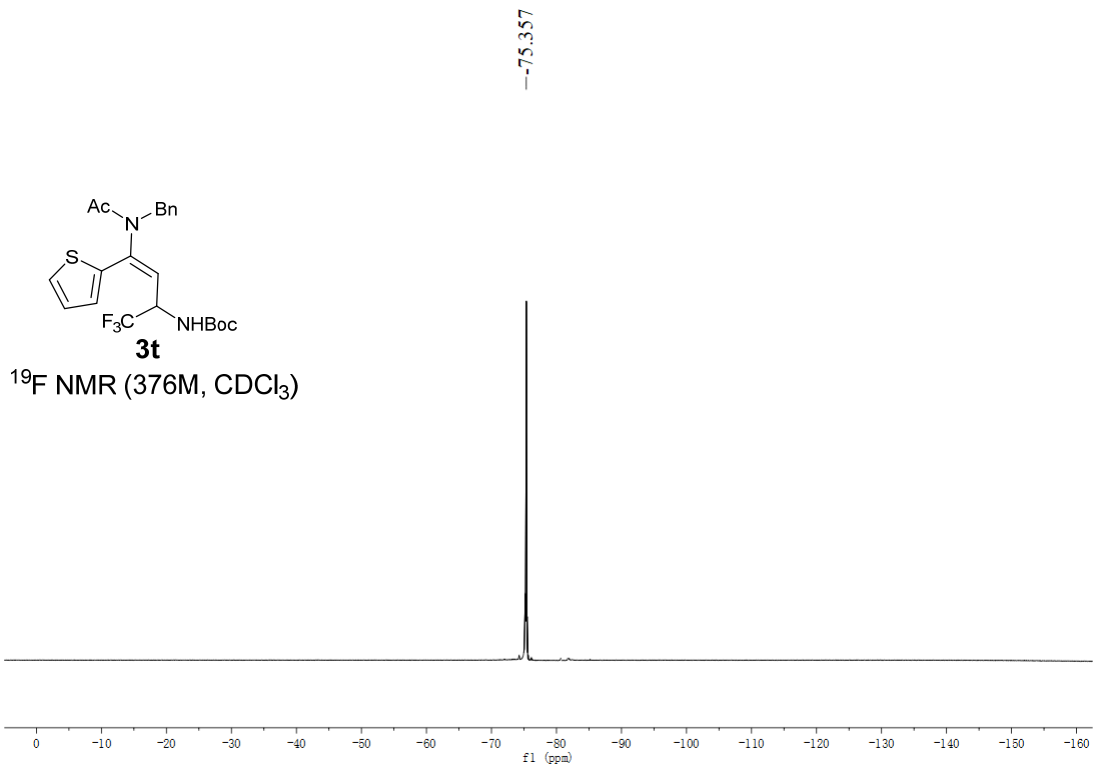
3t

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



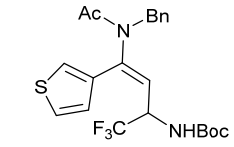
3t

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



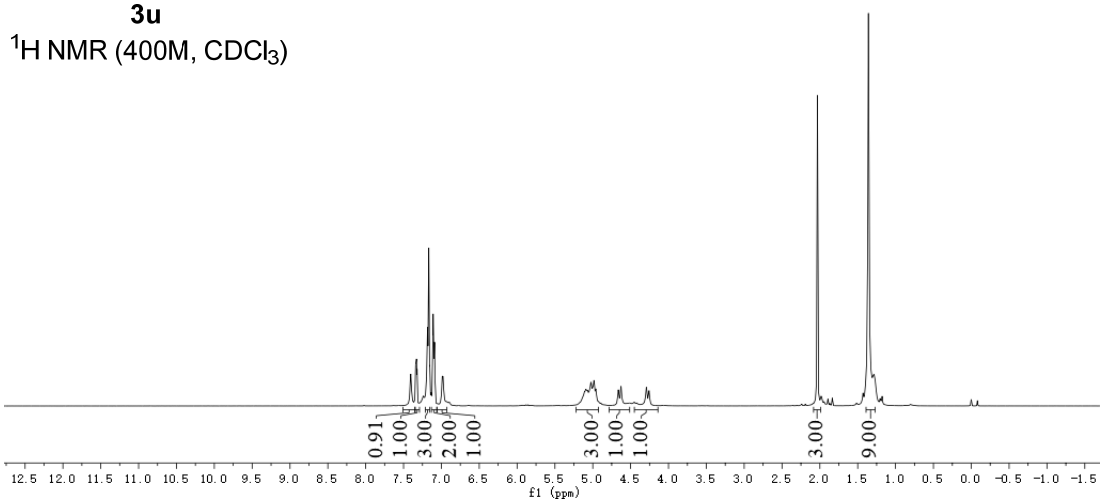
3t

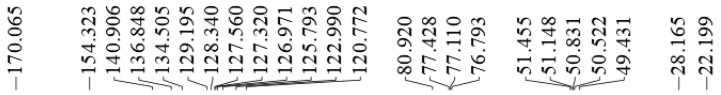
^{19}F NMR (376M, $CDCl_3$)

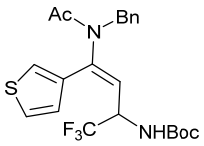


3u

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

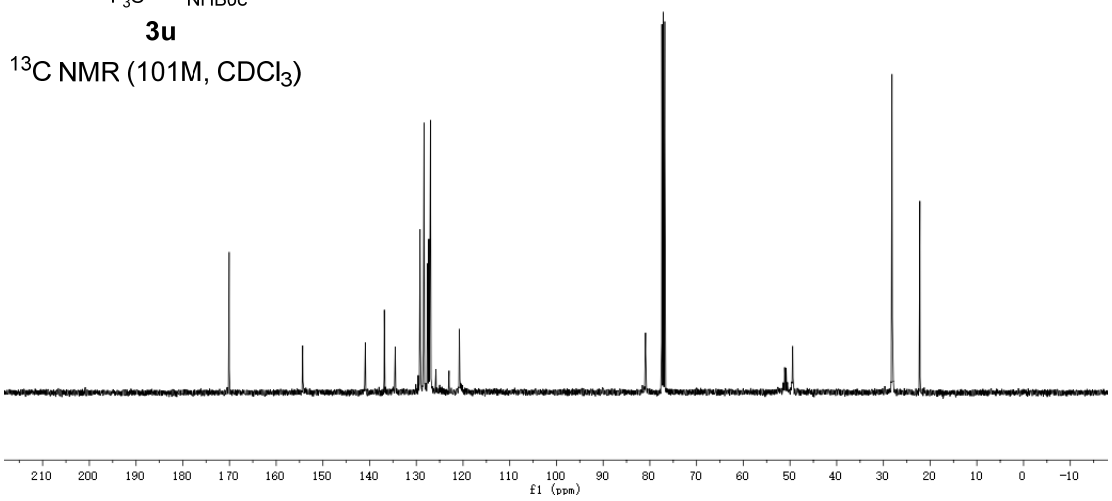


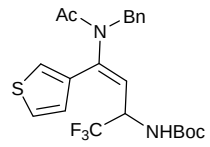




3u

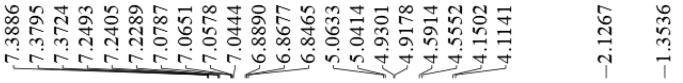
^{13}C NMR (101M, $CDCl_3$)

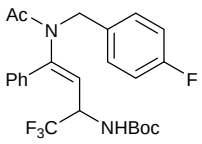




3u

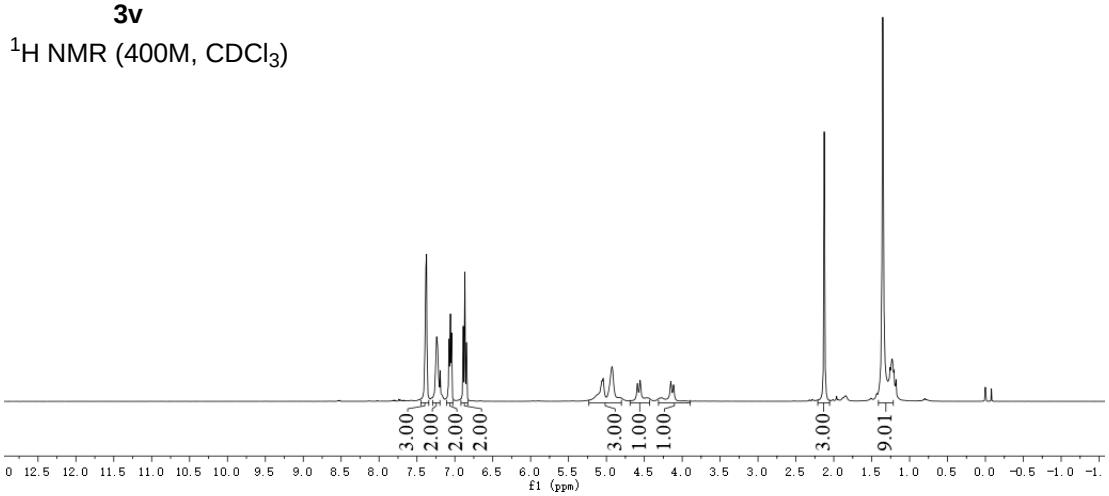
^{19}F NMR (376M, $CDCl_3$)

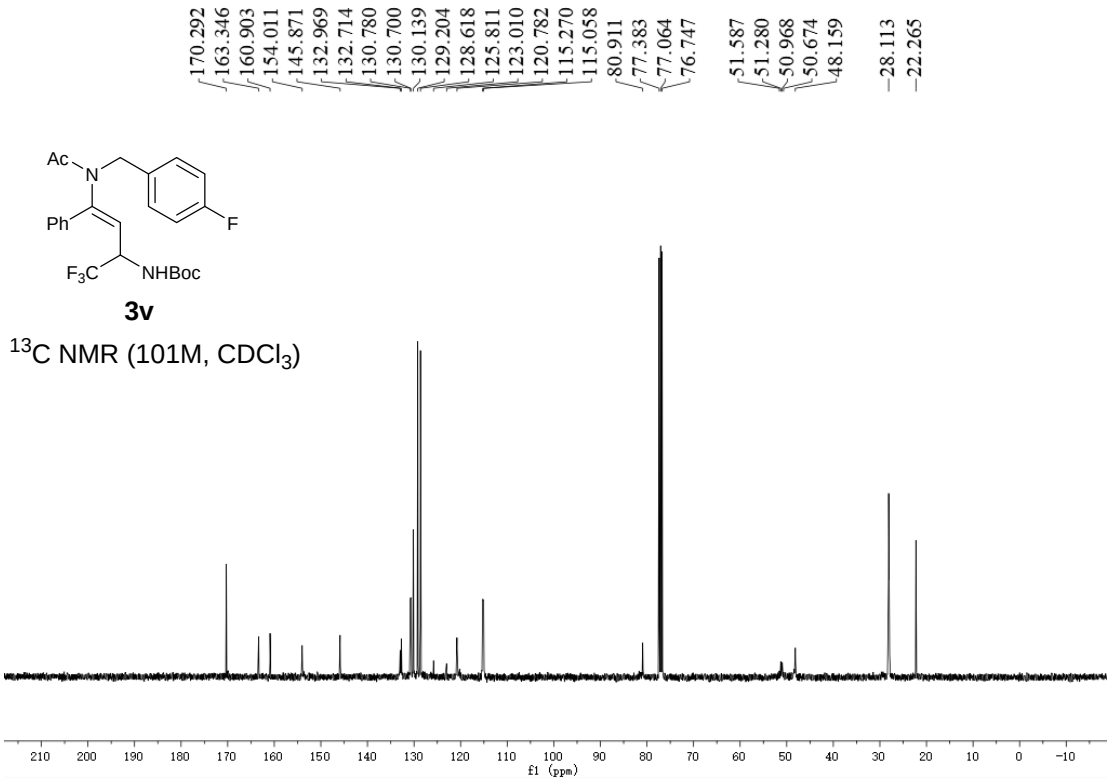




3v

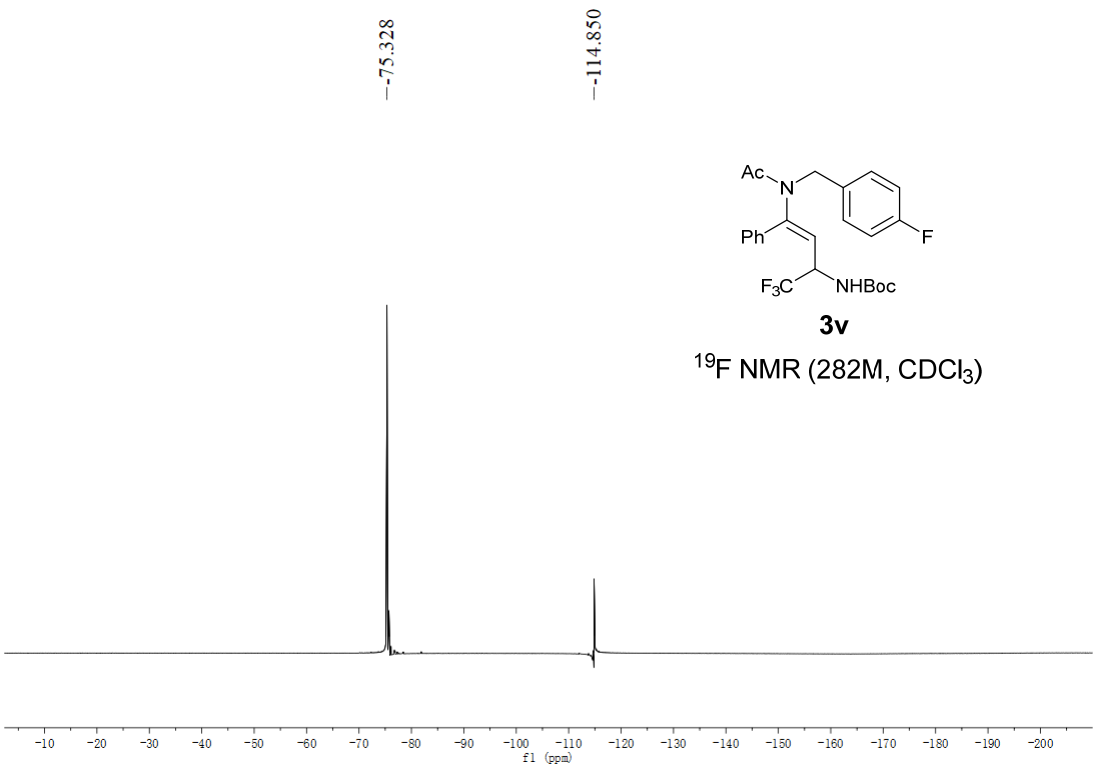
^{1}H NMR (400M, $CDCl_3$)





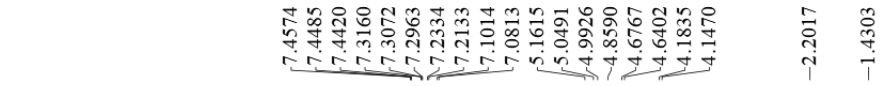
3v

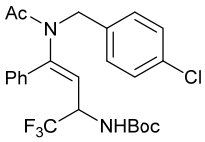
^{13}C NMR (101M, $CDCl_3$)



3v

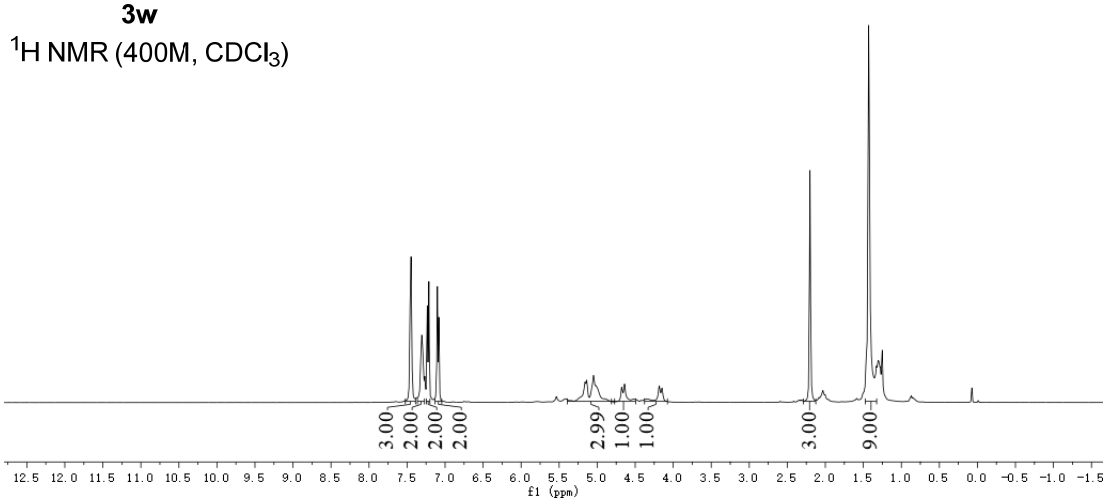
^{19}F NMR (282M, $CDCl_3$)

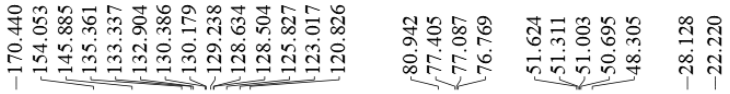


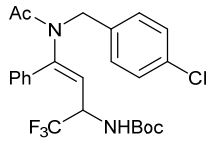


3w

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

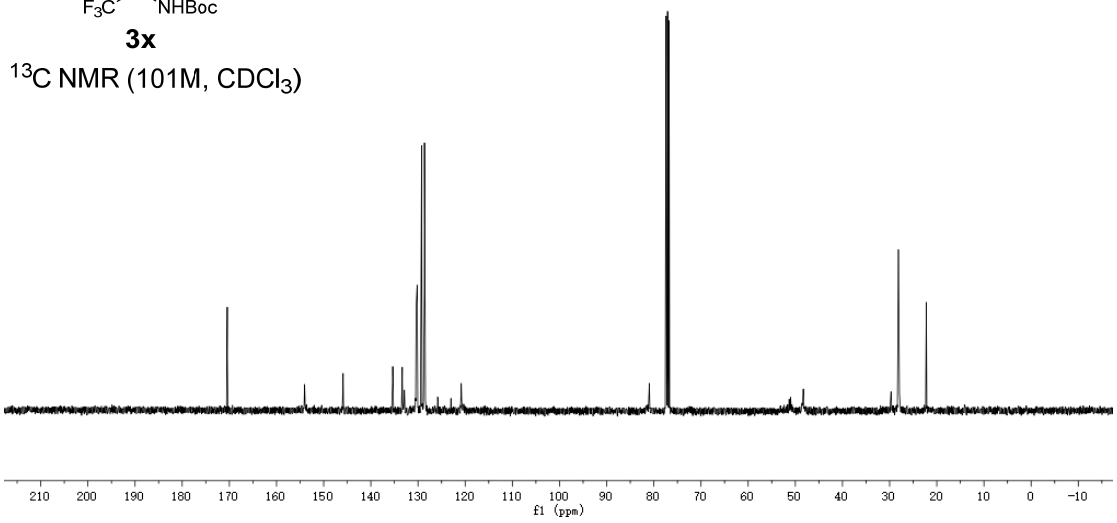


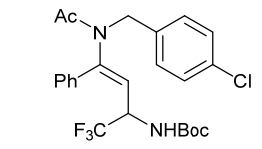




3x

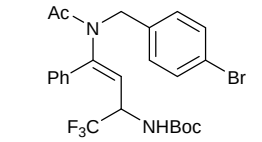
^{13}C NMR (101M, $CDCl_3$)





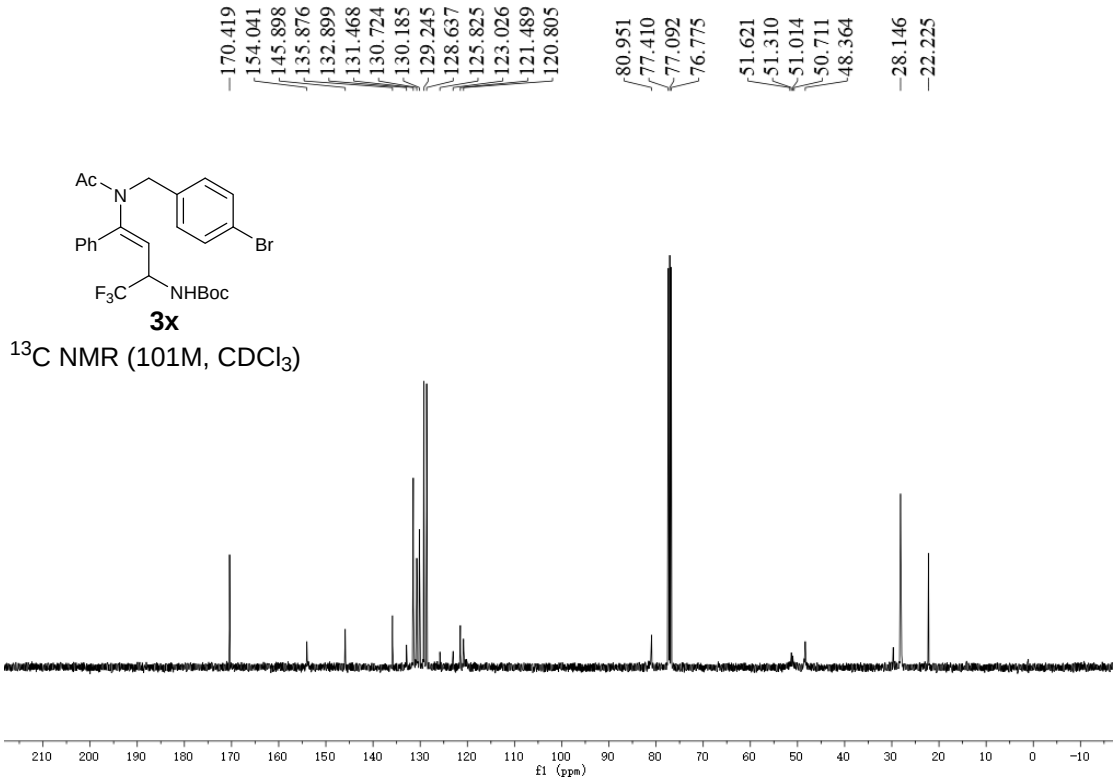
3w

^{19}F NMR (282M, $CDCl_3$)



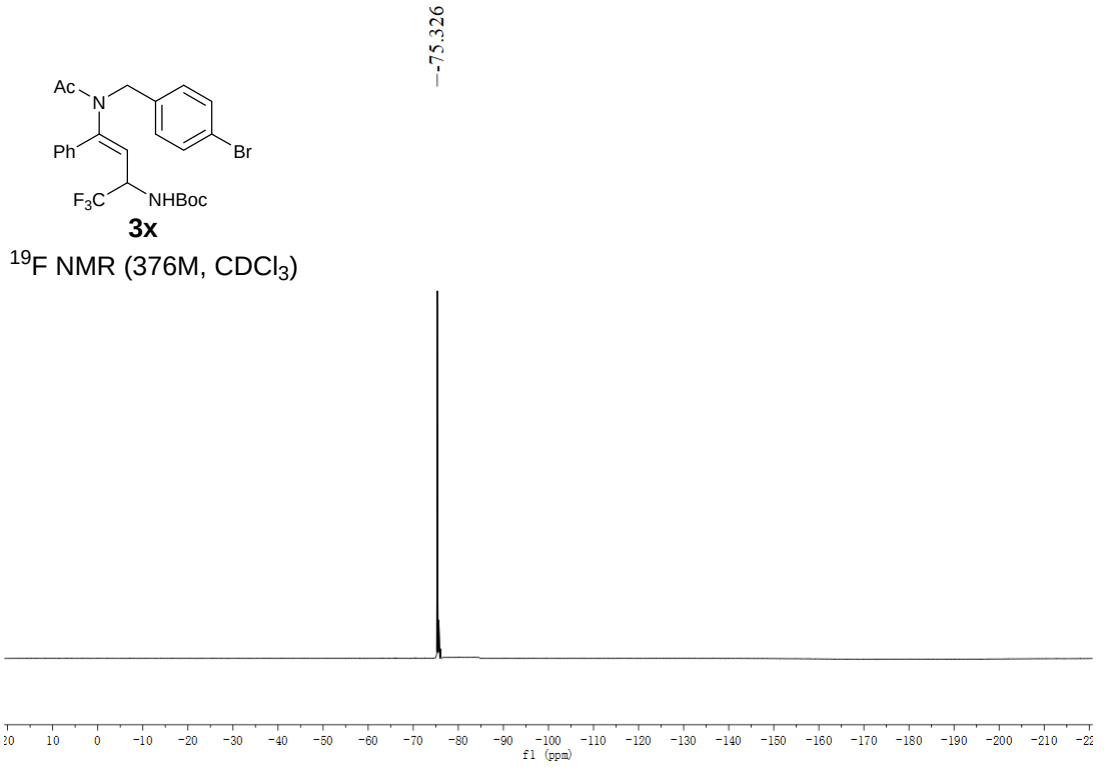
3x

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



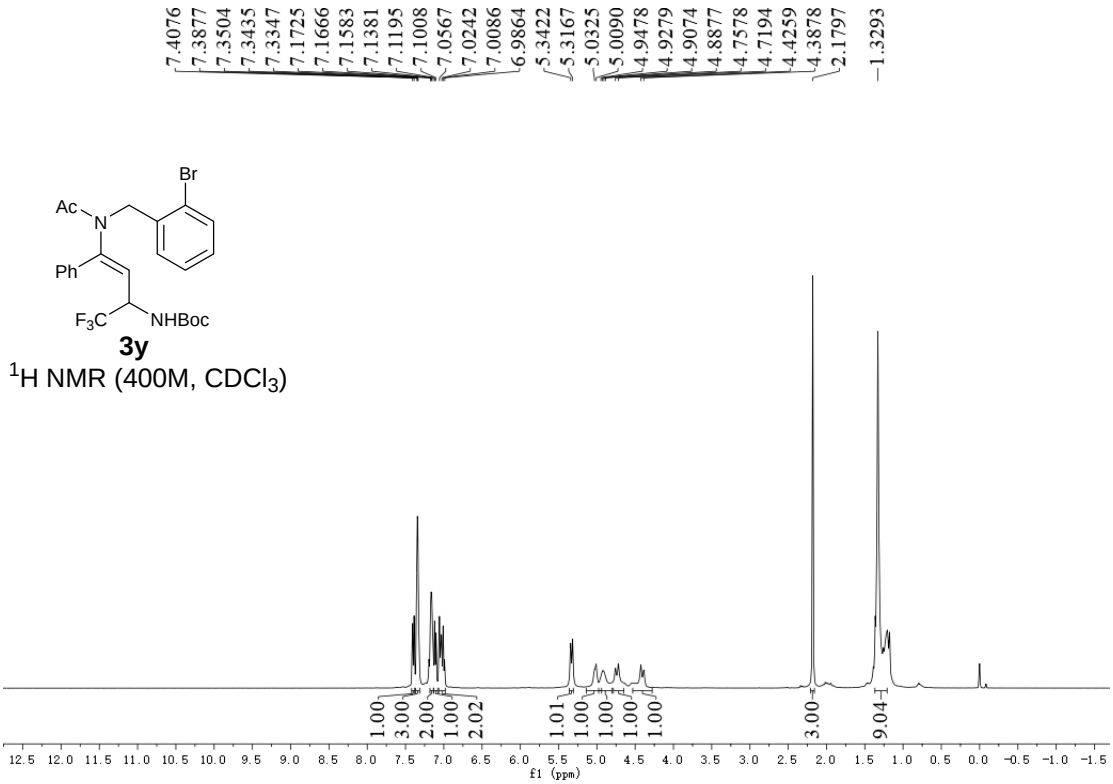
3x

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



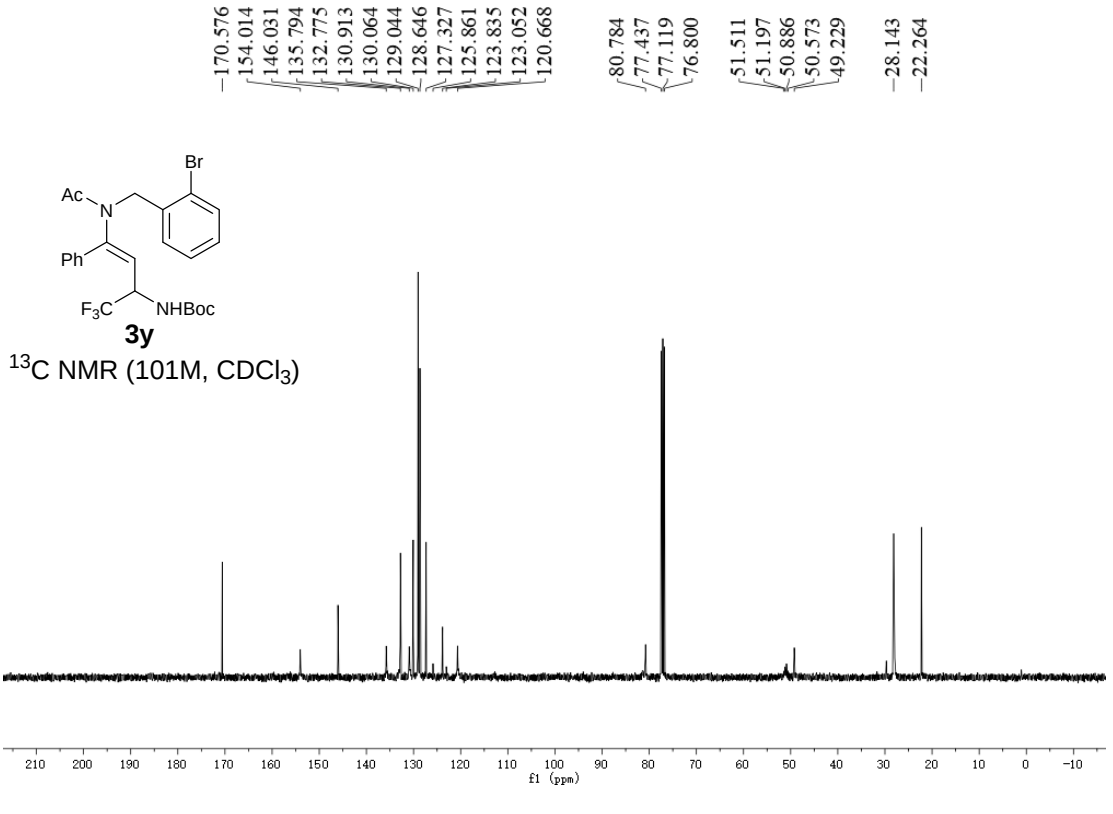
3x

^{19}F NMR (376M, $CDCl_3$)



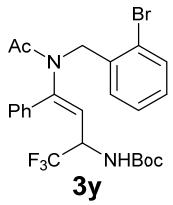
3y

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



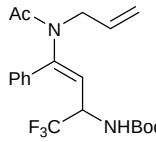
3y

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



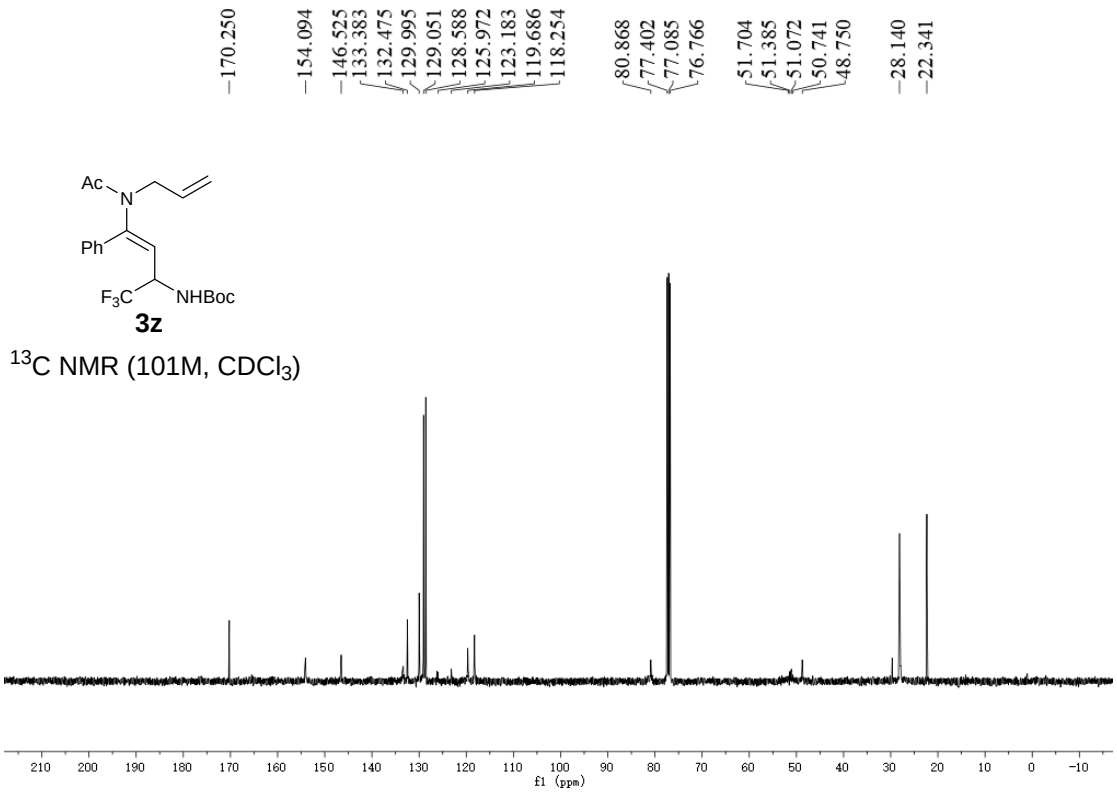
3y

^{19}F NMR (282M, $CDCl_3$)



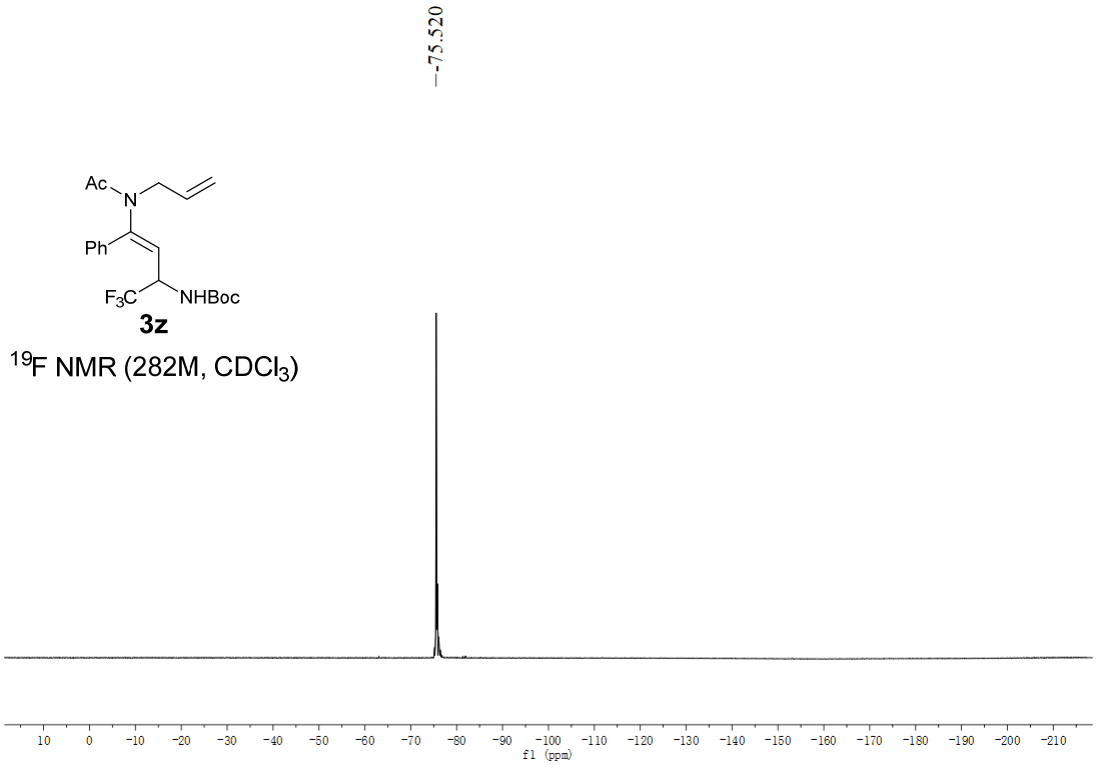
3z

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



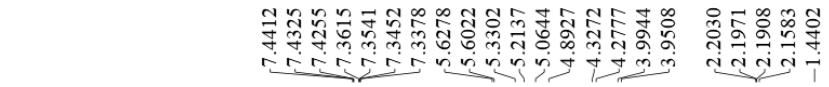
3z

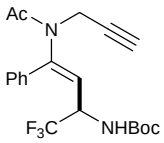
^{13}C NMR (101M, $CDCl_3$)



3z

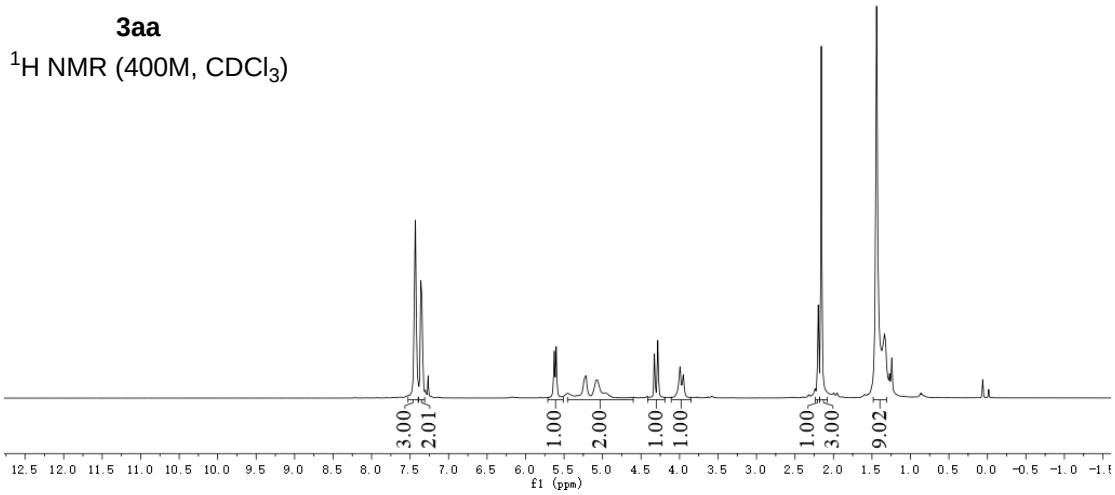
^{19}F NMR (282M, $CDCl_3$)

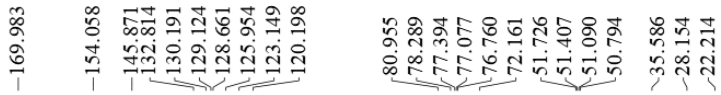


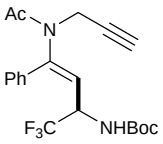


3aa

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

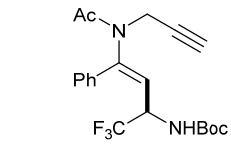






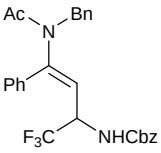
3aa

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



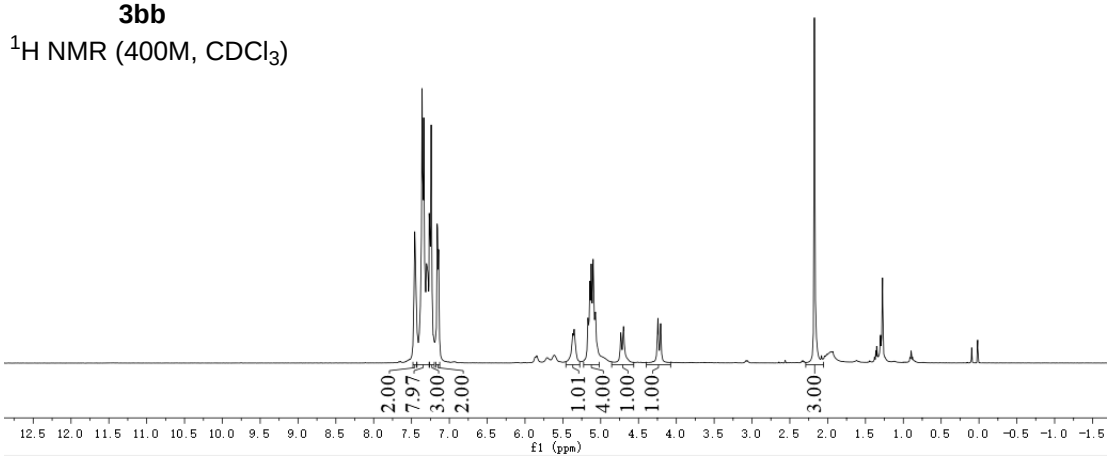
3aa

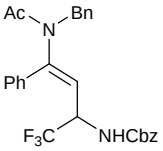
^{19}F NMR (282M, $CDCl_3$)



3bb

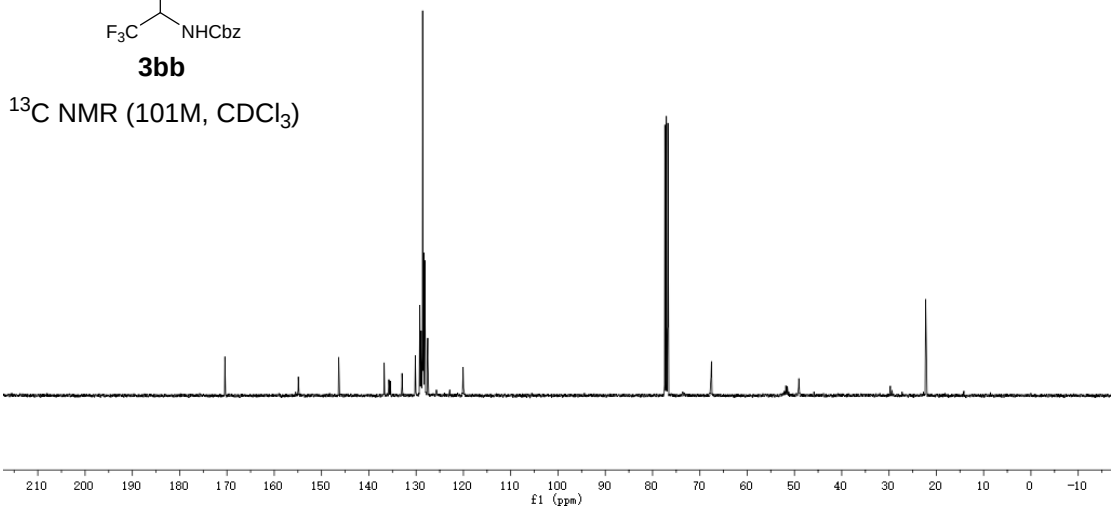
^{1}H NMR (400M, $CDCl_3$)

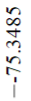


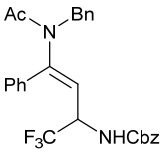


3bb

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

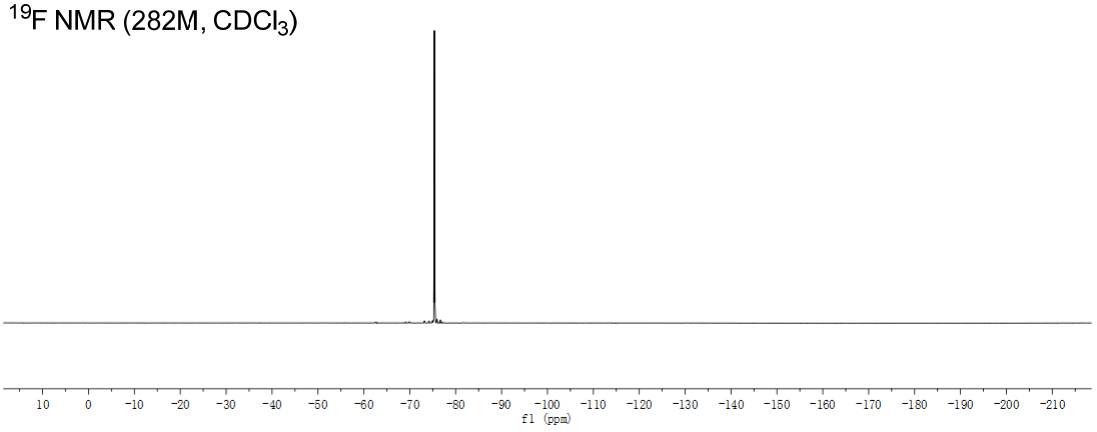


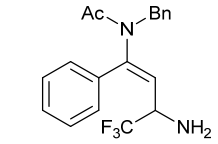




3bb

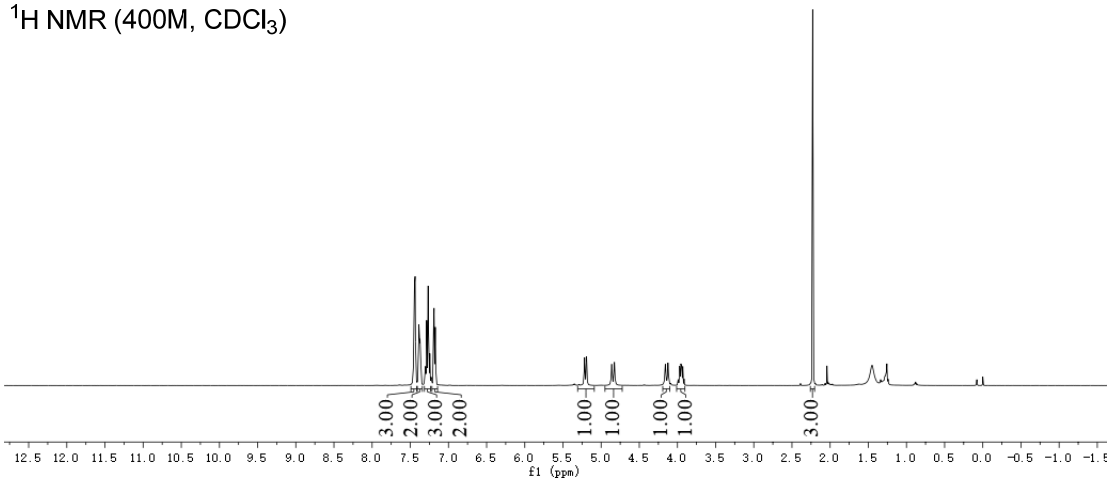
^{19}F NMR (282M, $CDCl_3$)

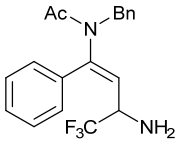




4

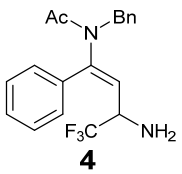
^{1}H NMR (400M, $CDCl_3$)





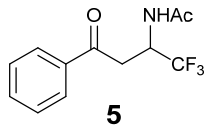
4

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



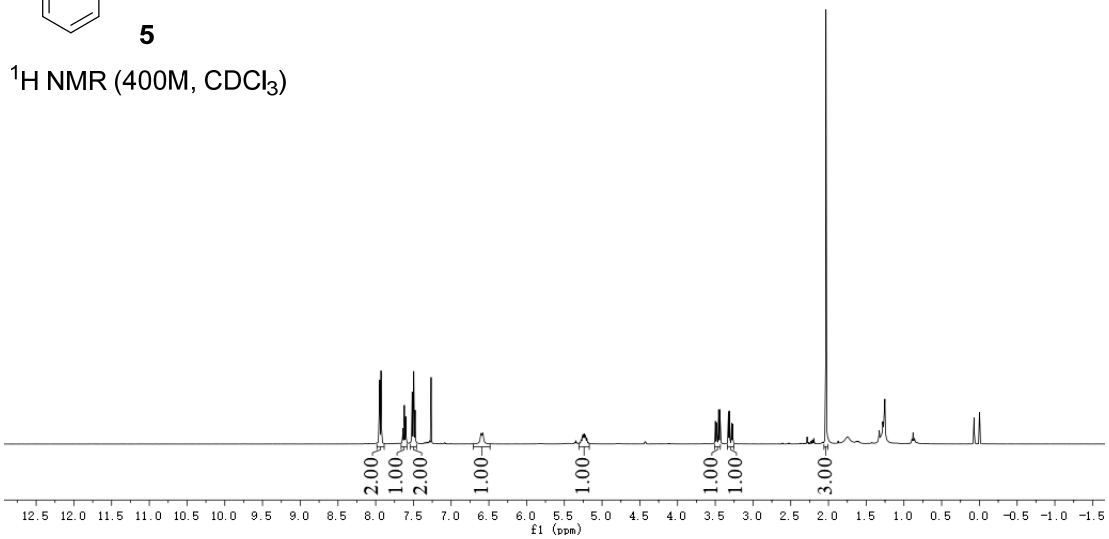
4

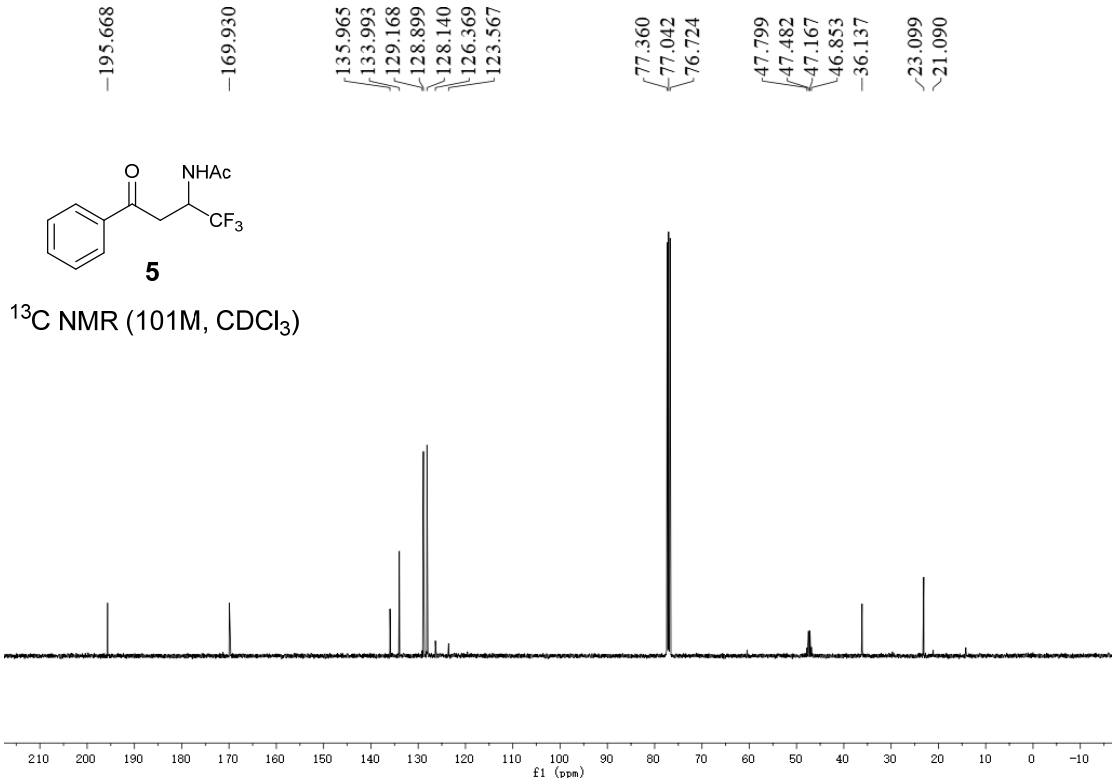
^{19}F NMR (282M, $CDCl_3$)



5

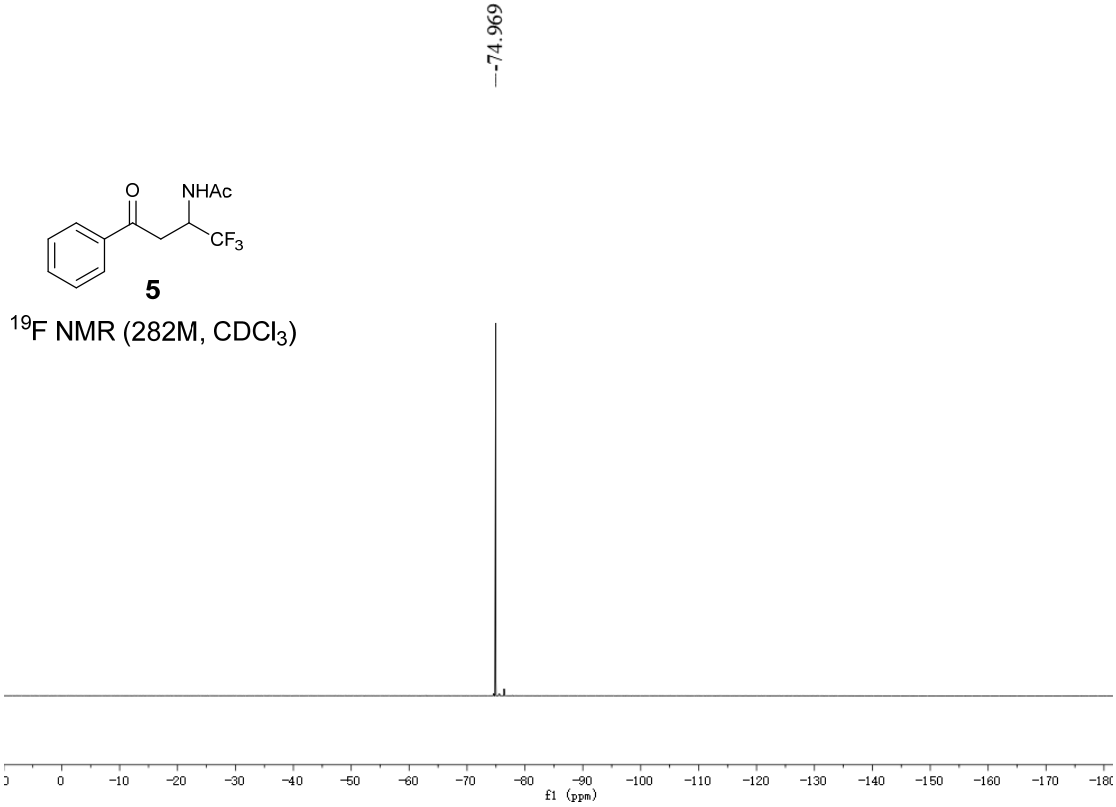
^{1}H NMR (400M, $CDCl_3$)





5

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



5

^{19}F NMR (282M, $CDCl_3$)