Supplementary information

The Cascade Coupling/Iodoaminocyclization Reaction of Trifluoroacetimidoyl Chlorides and Allylamines: Metal-free Access to 2-Trifluoromethyl-imidazolines

Yufei Song,[a] Le-Cheng Wang,[a] Shiying Du,[a] Zhengkai Chen,[a,*] Xiao-Feng Wu[b,c,*]

[a] Department of Chemistry, Key Laboratory of Surface & Interface Science of Polymer Materials of Zhejiang Province, Zhejiang Sci-Tech University, Hangzhou 310018, China.

[b] Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023, Dalian, Liaoning, China.

[c] Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Straβe 29a, 18059 Rostock, Germany.

E-mail: zkchen@zstu.edu.cn

xiao-feng.wu@catalysis.de

Contents

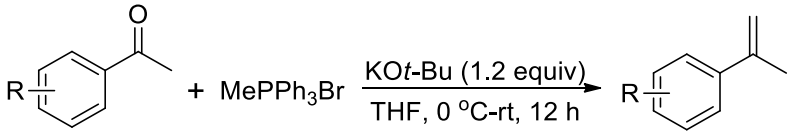
1. General Information

Unless otherwise noted, all reactions were carried out under air 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 ^{19}F NMR at 377 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) 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. Gas chromatography (GC) analyses were performed on a Shimadzu GC-2014C chromatograph equipped with a FID detector. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV. 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]

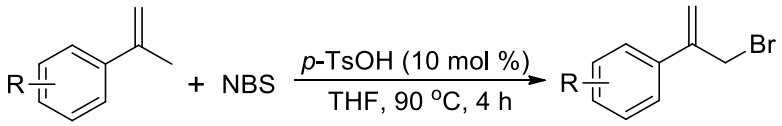
A 200 mL two-necked flask equipped with a septum cap, a condenser, and a Tefloncoated magnetic stir bar was charged with PPh_3 (34.5 g, 132 mmol), Et_3N (7.3 mL, 53 mmol), CCl_4 (21.1 mL, 220 mmol), and TFA (3.4 mL, 44 mmol). After the solution was stirred for about 10 min (ice bath), amine (53 mmol) dissolved in CCl_4 (21.1 mL, 220 mmol) 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 hexane several times. Then the hexane 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 General Procedure for the Synthesis of 2-Phenylprop-2-en-1-amine

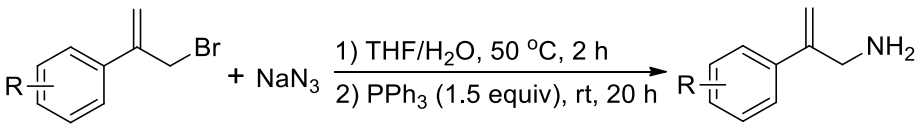


Synthesis of prop-1-en-2-ylbenzene[2]: Under nitrogen atmosphere, a solution of methyl

triphenylphosphonium bromide (21.4 g, 60.0 mmol) in anhydrous THF (80 mL) was cooled to 0 °C, followed by addition of KO*t*-Bu (6.72 g, 60.0 mmol). The reaction mixture was stirred at 0 °C for 1 h, and then a solution of acetophenone (5.80 mL, 50.0 mmol) in anhydrous THF (20 mL) was added dropwise. The resulting mixture was warmed gradually to room temperature and kept stirring for 12 h. The resultant reaction solution was filtered over Celite®, and the filtrate was concentrated under vacuum to yield a residue, which was further purified over silica gel flash column chromatography (petroleum ether) to afford the product as colorless oil (5.72 g, 97%).



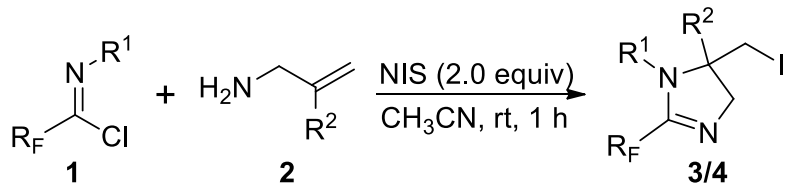
Synthesis of (3-bromoprop-1-en-2-yl)benzene[3]: To a solution of α-methylstyrene (13.0 mL, 100 mmol) in anhydrous THF (100 mL) was added *N*-bromosuccinimide (19.6 g, 110 mmol) and *p*-TsOH (1.72 g, 10 mmol). The reaction mixture was heated to 90 °C and kept stirring for 4 h. Then the reaction solution was cooled to room temperature, concentrated under vacuum, and purified by silica gel flash column chromatography (petroleum ether) to afford the product as pale yellow oil (17.1 g, 87%).



Synthesis of 2-phenylprop-2-en-1-amine 2c[4]: The above obtained product (3.35 g, 17.0 mmol) was dissolved in THF (65 ml) and H_2O (15 mL), followed by addition of NaN_3 (1.17 g, 18.0 mmol). The turbid mixture was stirred at 50 °C for 2 h. The solution was cooled to ambient temperature, then PPh_3 (6.69 g, 25.5 mmol) was added and the mixture was stirred for 20 h. Most of the THF was removed under vacuum and the residue was dissolved with aqueous HCl (60 mL, 1 M). The aqueous layer was extracted with diethyl ether (3 × 75 mL), then was basified with solid NaOH (3.2 g, 80 mmol) and again extracted with diethyl ether (3 × 75 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The product **2c** was obtained as yellow oil (2.12 g, 16.0 mmol, 94%), which was directly used without further purification.

Note: The substrates 2-arylprop-2-en-1-amine **2c-f** is prepared using the above general procedures.

2. General Procedure for the Synthesis of 2-Trifluoromethyl-imidazolines

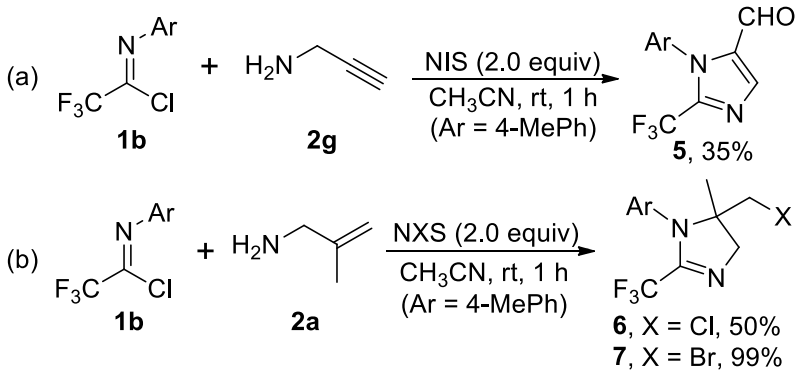


1 2 3/4

Under air atmosphere, NIS (0.135 g, 0.6 mmol, 2.0 equiv.) and 4 Å MS (60 mg) were added to a solution of trifluoroacetimidoyl chloride **1** (0.3 mmol, 1.0 equiv.) and allylamine **2** (0.75 mmol, 2.5 equiv.) in MeCN (2.0 mL). The mixture was stirred at room temperature for 1 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the product **3** or **4**.

Scale-up Reaction: Under air atmosphere, NIS (2.25 g, 10 mmol, 2.0 equiv.) and 4 Å MS (1000 mg) were added to a solution of *(E)*-2,2,2-trifluoro-*N*-(p-tolyl)acetimidoyl chloride **1b** (1.1 g, 5.0 mmol, 1.0 equiv.) and 2-methylprop-2-en-1-amine **2a** (0.889 g, 12.5 mmol, 2.5 equiv.) in MeCN (20 mL). The mixture was stirred at room temperature for 1 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the product **3b** as a yellow solid (1.725 g, 90%).

3. Cascade Reactions with Different Coupling Partner or Halogen Sources



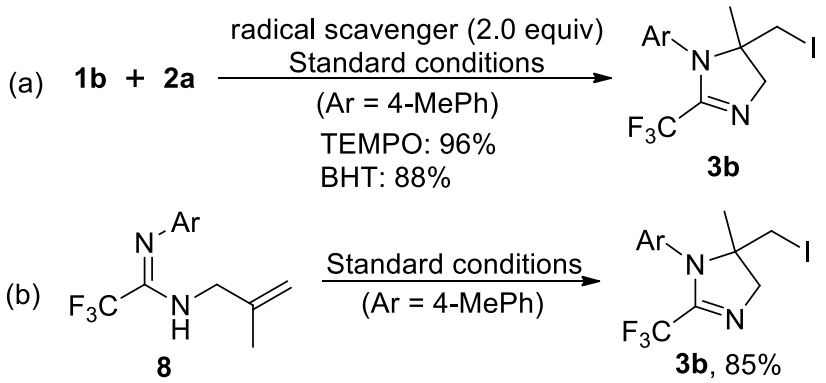
1b 2g 1b 2a

Eq a: Under air atmosphere, NIS (135 mg, 0.6 mmol, 2.0 equiv.) and 4 Å MS (100 mg) were added to a solution of *(E)*-2,2,2-trifluoro-*N*-(*p*-tolyl)acetimidoyl chloride **1b** (66.3 mg, 0.3 mmol, 1.0 equiv.) and prop-2-yn-1-amine **2g** (41.3 mg, 0.75 mmol, 2.5 equiv) in MeCN (2 mL). The mixture was

stirred at room temperature for 1 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the product **5** as yellow oily liquid (26.7 mg, 35%).

Eq b: Under air atmosphere, NCS (80 mg, 0.6 mmol, 2.0 equiv.) or NBS (106.8 mg, 0.6 mmol, 2.0 equiv.) and 4 Å MS (100 mg) were added to a solution of *(E)*-2,2,2-trifluoro-*N*-(*p*-tolyl)acetimidoyl chloride **1b** (66.3 mg, 0.3 mmol, 1.0 equiv.) and 2-methylprop-2-en-1-amine **2a** (53.3 mg, 0.75 mmol, 2.5 equiv) in MeCN (2 mL). The mixture was stirred at room temperature for 1 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the product **6** as yellow oily liquid (43.5 mg, 50%) or the product **7** as yellow oily liquid (100.0 mg, 99%), respectively.

4. Control Experiments



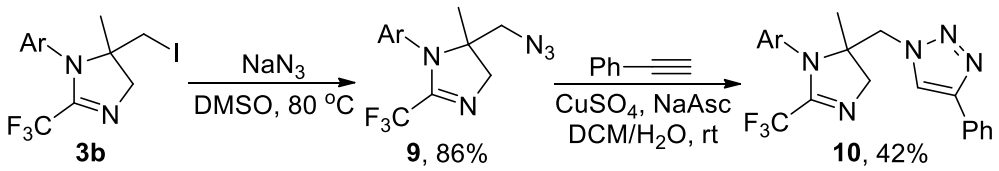
Eq a: Under air atmosphere, NIS (135 mg, 0.6 mmol, 2.0 equiv.) and 4 Å MS (60 mg) were added to a solution of *(E)*-2,2,2-trifluoro-*N*-(*p*-tolyl)acetimidoyl chloride **1b** (66.3 mg, 0.3 mmol, 1.0 equiv.), 2-methylprop-2-en-1-amine **2a** (53.3 mg, 0.75 mmol, 2.5 equiv) and TEMPO (93.8 mg, 0.6 mmol, 2.0 equiv) or BHT (132.2 mg, 0.6 mmol, 2.0 equiv) in MeCN (2 mL). The mixture was stirred at room temperature for 1 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the product **3b** as a yellow solid (110 mg, 96% or 100.1 mg, 88%).

Preparation of the Coupling Product 8: Under air atmosphere, *(E)*-2,2,2-trifluoro-*N*-(*p*-tolyl)acetimidoyl chloride **1a** (66 mg, 0.3 mmol, 1.0 equiv.), 2-methylprop-2-en-1-amine **2a** (53.3 mg, 0.75 mmol, 2.5 equiv.) and MeCN (2.0 mL) were added to

an oven-dried 15 mL *In-Ex* tube. The mixture was stirred at room temperature for 1 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the coupling product **8** as a yellow oily liquid in 90% yield (69.4 mg).

Eq b: Under air atmosphere, NIS (135 mg, 0.6 mmol, 2.0 equiv.) and 4 Å MS (100 mg) were added to a solution of the coupling product **8** (121.3 mg, 0.3 mmol, 1.0 equiv.) in MeCN (2 mL). The mixture was stirred at room temperature for 1 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the product **3b** as a yellow solid (97.4 mg, 85%).

5. Synthetic Transformation



Synthesis of Compound 9: To a stirred solution of NaN_3 (71.5 mg, 1.1 mmol) in DMSO (2 mL) was added compound **3b** (382 mg, 1.0 mmol). The reaction mixture was stirred at 80°C for overnight. Then the reaction mixture was cooled to room temperature and diluted with water (5 mL). The mixture was extracted with ether (3×5 mL) and washed by brine, dried over Na_2SO_4 and concentrated under vacuum to give the product **9** as a white solid in 86% yield (255.3 mg).

Synthesis of Compound 10: Under air atmosphere, azide **9** (89 mg, 0.3 mmol, 1.0 equiv.), ethynylbenzene (76.8 mg, 0.75 mmol, 2.5 equiv.), $CuSO_4$ (5 mg, 0.03 mmol, 0.1 equiv.), NaAsc (118.8 mg, 0.6 mmol, 2.0 equiv.) and DCM/H_2O (1 mL/1 mL) were added to an oven-dried 15 mL *In-Ex* tube. The mixture was stirred at room temperature for 6 h. After the reaction was completed, the mixture was concentrated by vacuum, and then purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **10** as a yellow solid in 42% yield (50.3 mg).

6. Characterization Data of the Corresponding Products

5-(iodomethyl)-5-methyl-1-phenyl-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3a)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **3a** as a yellow solid (101.9 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.25 (m, 5H), 4.17 (d, J = 17.6 Hz, 1H), 3.91 (d, J = 17.6 Hz, 1H), 3.30 (d, J = 10.6 Hz, 1H), 3.21 (d, J = 10.6 Hz, 1H), 1.44 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.5 (C-F, q, $^{2}J_{C\text{-}F}$ = 35.3 Hz), 134.8, 130.8, 129.5, 129.3, 117.8 (C-F, q, $^{1}J_{C\text{-}F}$ = 275.7 Hz), 67.8, 67.0, 24.8, 16.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ – 65.7.

M.p. 106.4 – 107.2 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{12}H_{12}F_3IN_2$ 369.0070; Found 369.0074.

5-(iodomethyl)-5-methyl-1-(p-tolyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3b)

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 **3b** as a yellow solid (113.7 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 4H), 4.15 (d, J = 17.1 Hz, 1H), 3.96 (d, J = 17.1 Hz, 1H), 3.28 (d, J = 10.7 Hz, 1H), 3.21 (d, J = 10.7 Hz, 1H), 2.40 (s, 3H), 1.47 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.6 (C-F, q, $^{2}J_{C\text{-}F}$ = 35.7 Hz), 139.5, 131.0, 130.1, 129.9, 117.2 (C-F, q, $^{1}J_{C\text{-}F}$ = 276.5 Hz), 67.8, 65.4, 24.6, 21.1, 15.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ - 65.8.

M.p. 112.4 - 113.5 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{13}H_{14}F_3IN_2$ 383.0227; Found 383.0236.

5-(iodomethyl)-5-methyl-1-(m-tolyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3c)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.4) to give the titled product **3c** as a yellow solid (113.1 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 6.96 (m, 4H), 4.13 (d, J = 17.5 Hz, 1H), 3.87 (d, J = 17.5 Hz, 1H), 3.28 (d, J = 10.5 Hz, 1H), 3.18 (d, J = 10.5 Hz, 1H), 2.38 (s, 3H), 1.41 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.8 (C-F, q, $^2J_{C-F}$ = 35.4 Hz), 139.7, 134.8, 131.4, 130.4, 129.4, 127.9, 118.0 (C-F, q, $^1J_{C-F}$ = 275.9 Hz), 68.0, 67.0, 25.1, 21.8, 16.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ - 65.6.

M.p. 105.3 - 106.2 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{13}H_{14}F_3IN_2$ 383.0227; Found 383.0235.

5-(iodomethyl)-5-methyl-1-(o-tolyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3d)

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 **3d** as a yellow solid (42.6 mg, 37%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 2H), 7.26 (d, J = 5.3 Hz, 2H), 4.21 (d, J = 15.9 Hz, 1H), 3.83 (d, J = 17.6 Hz, 1H), 3.37 (d, J = 10.3 Hz, 1H), 3.24 (d, J = 10.3 Hz, 1H), 2.29 (s, 3H), 1.37 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.4 (C-F, q, $^2J_{C-F}$ = 35.3 Hz), 139.2, 133.1, 131.5, 129.3, 126.7, 117.4 (C-F, q, $^1J_{C-F}$ = 275.7 Hz), 68.6, 66.3, 23.1, 18.4, 15.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ - 67.4.

M.p. 117.2 - 119.7 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{13}H_{14}F_3IN_2$ 383.0227; Found 383.0238.

1-(4-(tert-butyl)phenyl)-5-(iodomethyl)-5-methyl-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3e)

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 **3e** as a yellow solid (119.2 mg, 94%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.6 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 4.12 (dd, J = 15.8, 1.6 Hz, 1H), 3.86 (dd, J = 15.8, 1.5 Hz, 1H), 3.27 (d, J = 10.5 Hz, 1H), 3.17 (d, J = 10.5 Hz, 1H), 1.41 (s, 4H), 1.32 (s, 9H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.6 (C-F, q, $^2J_{C-F}$ = 35.2 Hz), 131.8, 130.2, 126.3, 117.8 (C-F, q, $^1J_{C-F}$ = 275.7 Hz), 67.7, 66.8, 35.0, 31.5, 24.8, 16.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ - 65.8.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{16}H_{20}F_3IN_2$ 425.0696; Found 425.0702.

5-(iodomethyl)-1-(4-methoxyphenyl)-5-methyl-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3f)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **3f** as a yellow solid (118.2 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 24.4 Hz, 2H), 6.91 (d, J = 9.1 Hz, 2H), 4.12 (dd, J = 15.8, 1.7 Hz, 1H), 3.93 – 3.75 (m, 4H), 3.25 (d, J = 10.5 Hz, 1H), 3.17 (d, J = 10.5 Hz, 1H), 1.41 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.8, 153.0, 152.6, 152.3 (C-F, q, $^2J_{C\text{-}F}$ = 35.3 Hz), 131.8, 126.7, 121.6, 118.9, 116.2, 114.3, 113.4 (C-F, q, $^1J_{C\text{-}F}$ = 275.7 Hz), 67.3, 66.4, 55.5, 24.5, 16.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ - 66.0.

M.p. 126.3 - 127.6 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{13}H_{14}F_3IN_2O$ 399.0176; Found 399.0177.

5-(iodomethyl)-5-methyl-1-(4-(methylthio)phenyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3g)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.2) to give the titled product **3g** as a yellow oily liquid (112.7 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.9 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 4.13 (dd, *J* = 15.9, 1.7 Hz, 1H), 3.87 (dd, *J* = 15.9, 1.7 Hz, 1H), 3.24 (d, *J* = 10.6 Hz, 1H), 3.17 (d, *J* = 10.6 Hz, 1H), 2.51 (s, 2H), 1.41 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.2 (C-F, q, $^2J_{C\text{-}F}$ = 35.3 Hz), 140.3, 118.9, 117.5 (C-F, q, $^1J_{C\text{-}F}$ = 275.6 Hz), 116.1, 113.4, 67.5, 66.6, 24.6, 16.0, 15.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ – 65.8.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{13}H_{15}F_3IN_2S$ 414.9947; Found 414.9951.

1-(4-fluorophenyl)-5-(iodomethyl)-5-methyl-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3h)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **3h** as a yellow oily liquid (110.2 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.07 (m, 4H), 4.14 (dd, J = 15.9, 1.7 Hz, 1H), 3.89 (dd, J = 15.9, 1.7 Hz, 1H), 3.24 (q, J = 10.7 Hz, 1H), 1.45 (s, 2H)

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.7 (C-F, d, $^1J_{C-F}$ = 250.1 Hz), 152.1 (C-F, q, $^2J_{C-F}$ = 35.5 Hz), 152.2, 151.9, 132.4 (C-F, d, $^3J_{C-F}$ = 8.8 Hz), 130.4, 117.4 (C-F, q, $^1J_{C-F}$ = 286.2 Hz), 117.2, 116.2 (C-F, q, $^2J_{C-F}$ = 22.7 Hz), 67.4, 66.7, 24.6, 15.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ - 111.3, - 65.8.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{12}H_{11}F_4IN_2$ 386.9976; Found 386.9984.

1-(4-chlorophenyl)-5-(iodomethyl)-5-methyl-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3i)

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 yellow oily liquid (98.5 mg, 82%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.9 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 4.14 (dd, J = 16.0, 1.8 Hz, 1H), 3.89 (dd, J = 16.0, 1.7 Hz, 1H), 3.20 (q, J = 10.7 Hz, 2H), 1.42 (s, 5H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 151.2 (C-F, q, $^2J_{C-F}$ = 35.4 Hz), 135.2, 133.2, 131.8, 129.6, 117.4 (C-F, q, $^1J_{C-F}$ = 275.7 Hz), 67.6, 66.8, 24.6, 15.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ - 65.6.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{12}H_{11}ClF_3IN_2$ 402.9680; Found 402.9684.

1-(4-bromophenyl)-5-(iodomethyl)-5-methyl-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3j)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **3j** as a yellow solid (132.5 mg, 99%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 4.17 (d, J = 17.6 Hz, 1H), 3.92 (d, J = 17.5 Hz, 1H), 3.23 (q, J = 10.7 Hz, 1H), 1.45 (s, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.1 (C-F, q, $^2J_{C-F}$ = 35.5 Hz), 133.9, 132.8, 132.3, 123.5, 117.7 (C-F, q, $^1J_{C-F}$ = 275.7 Hz), 67.8, 67.0, 24.8, 16.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ - 65.6.

M.p. 119.3 - 121.6 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{12}H_{11}BrF_3IN_2$ 446.9175; Found 446.9180.

5-(iodomethyl)-5-methyl-2-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-imidazole (3k)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **3k** as a yellow solid (109.6 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 4.18 (dd, J = 16.0, 1.7 Hz, 1H), 3.93 (dd, J = 16.0, 1.7 Hz, 1H), 3.23 (q, J = 10.8 Hz, 2H), 1.45 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.7 (C-F, q, $^2J_{C\text{-}F}$ = 35.7 Hz), 138.2, 131.1 (C-F, q, $^2J_{C\text{-}F}$ = 33.0 Hz), 130.7, 126.4, 123.6 (C-F, q, $^1J_{C\text{-}F}$ = 272.3 Hz), 117.4 (C-F, q, $^1J_{C\text{-}F}$ = 275.7 Hz), 67.8, 66.9, 24.6, 15.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ - 62.7, - 65.5.

M.p. 102.4 – 104.3 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{13}H_{11}F_6IN_2$ 436.9944; Found 436.9950.

1-(2-chlorophenyl)-5-(iodomethyl)-5-methyl-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3l)

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 **3l** as a yellow solid (120.4 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.31 (m, 4H), 4.17 (d, J = 17.5 Hz, 1H), 3.92 (d, J = 17.9 Hz, 1H), 3.32 (d, J = 10.5 Hz, 1H), 3.24 (d, J = 10.5 Hz, 1H), 1.42 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.1 (C-F, q, $^2J_{C\text{-}F}$ = 36.0 Hz), 136.2, 133.0, 132.8, 132.5, 130.8, 130.5, 127.8, 127.4, 117.3 (C-F, q, $^1J_{C\text{-}F}$ = 275.9 Hz), 68.7, 66.6, 22.6, 16.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ - 67.5.

M.p. 104.8 - 105.3 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{12}H_{11}ClF_3IN_2$ 402.9680; Found 402.9683.

1-(3,4-dimethylphenyl)-5-(iodomethyl)-5-methyl-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3m)

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 **3m** as a yellow oily liquid (118.3 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 5.9 Hz, 1H), 7.03 (s, 2H), 4.13 (d, J = 15.3 Hz, 1H), 3.86 (d, J = 15.8 Hz, 1H), 3.28 (d, J = 13.1 Hz, 1H), 3.18 (d, J = 13.2 Hz, 1H), 2.28 (s, 6H), 1.41 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.6 (C-F, q, $^2J_{C-F}$ = 35.3 Hz), 138.0, 137.8, 132.2, 131.5, 130.4, 128.0, 117.8 (C-F, q, $^1J_{C-F}$ = 275.8 Hz), 67.6, 66.8, 24.8, 20.1, 19.7, 16.5

^{19}F NMR (377 MHz, $CDCl_3$) δ - 65.7.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{14}H_{16}F_3IN_2$ 397.0383; Found 397.0391.

5-(iodomethyl)-5-methyl-1-(naphthalen-1-yl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3n)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.2) to give the titled product **3n** as a yellow solid (56.4 mg, 45%).

^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.1 Hz, 1H), 7.92 (t, J = 8.0 Hz, 2H), 7.62 – 7.52 (m, 2H), 7.49 (t, J = 7.8 Hz, 1H), 7.34 (d, J = 7.3 Hz, 1H), 4.20 (d, J = 17.7 Hz, 1H), 4.04 (d, J = 15.8 Hz, 1H), 3.58 (d, J = 9.8 Hz, 1H), 2.97 (d, J = 9.8 Hz, 1H), 1.52 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.4 (C-F, q, $^2J_{C-F}$ = 35.2 Hz), 134.5, 133.3, 131.4, 129.9, 129.3, 128.5, 127.2, 126.6, 125.0, 123.4, 117.6 (C-F, q, $^1J_{C-F}$ = 276.1 Hz), 69.3, 67.6, 25.0, 15.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ – 66.3.

M.p. 96.3 – 97.8 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{16}H_{14}F_3IN_2$ 419.0227; Found 419.0211.

5-(iodomethyl)-5-methyl-1-(1-phenylethyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (3o)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **3o** as a yellow solid (69.7 mg, 59%). dr = 1.3: 1.

^1H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.25 (m, 5H), 5.06 (q, J = 7.2 Hz, 1H), 3.98 – 3.87 (m, 1H), 3.62 – 3.55 (m, 1H), 3.44 – 3.27 (m, 1H), 2.64 (s, 1H), 1.83 – 1.74 (m, 3H), 1.58 (s, 1.84H), 1.06 (s, 1.39H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.0 (C-F, q, $^2J_{C-F}$ = 34.9 Hz), 140.8, 139.2, 128.5, 128.5, 128.2, 127.7, 127.6, 126.8, 118.1 (C-F, t, $^1J_{C-F}$ = 275.6 Hz), 67.7, 67.4, 52.8, 52.2, 29.6, 25.5, 24.6, 20.2, 19.7, 17.2, 16.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ – 65.3, – 65.5.

M.p. 121.2 - 123.1 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{14}H_{16}F_3IN_2$ 397.0383; Found 397.0384.

2-(difluoromethyl)-5-(iodomethyl)-5-methyl-1-phenyl-4,5-dihydro-1H-imidazole (3p)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.2) to give the titled product **3p** as a yellow solid (103.9 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.48 – 7.20 (m, 5H), 6.05 (t, J = 52.9 Hz, 1H), 4.10 (d, J = 15.6 Hz, 1H), 3.84 (d, J = 15.6 Hz, 1H), 3.29 (d, J = 10.5 Hz, 1H), 3.20 (d, J = 10.5 Hz, 1H), 1.42 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.1 (C-F, t, $^2J_{C\text{-}F}$ = 25.1 Hz), 135.0, 130.3, 129.3, 128.8, 109.0 (C-F, t, $^1J_{C\text{-}F}$ = 242.3 Hz), 67.0, 24.5, 16.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.6 (qd, J = 338.1 Hz, 52.8 Hz, 2F).

M.p. 105.8 - 106.3 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{12}H_{13}F_2IN_2$ 351.0164; Found 351.0170.

2-(chlorodifluoromethyl)-5-(iodomethyl)-5-methyl-1-phenyl-4,5-dihydro-1H-imidazole (3q)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3q** as a yellow solid (108.3 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.36 (m, 5H), 4.14 (d, J = 15.9 Hz, 1H), 3.87 (d, J = 15.9 Hz, 1H), 3.27 (d, J = 10.6 Hz, 1H), 3.17 (d, J = 10.6 Hz, 1H), 1.40 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.4 (C-F, t, $^2J_{C\text{-}F}$ = 28.7 Hz), 135.0, 131.4, 129.3, 122.0 (C-F, t, $^1J_{C\text{-}F}$ = 291.7 Hz), 68.0, 66.6, 24.9, 16.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -53.4 (q, J = 115.1 Hz, 2F).

M.p. 123.6 – 124.2 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{12}H_{12}ClF_2IN_2$ 384.9775; Found 384.9780.

5-(iodomethyl)-5-methyl-2-(perfluoroethyl)-1-phenyl-4,5-dihydro-1H-imidazole (3r)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **3r** as a yellow solid (124.1 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.15 (m, 5H), 4.17 (d, J = 16.1 Hz, 1H), 3.91 (d, J = 16.1 Hz, 1H), 3.28 (d, J = 10.6 Hz, 1H), 3.19 (d, J = 10.6 Hz, 1H), 1.39 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.5 (C-F, t, $^2J_{C\text{-}F}$ = 26.0 Hz), 130.4, 129.1, 128.9, 118.0 (C-F, qt, $J_{C\text{-}F}$ = 286.4 Hz, 34.5 Hz), 109.7 (C-F, tq, $^1J_{C\text{-}F}$ = 256.9 Hz, 38.0 Hz), 67.3, 66.8, 24.5, 16.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -82.0, -113.5 (q, J = 301.6 Hz, 2F).

M.p. 106.4 – 107.2 °C

HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{13}H_{12}F_5IN_2$ 440.9858; Found 440.9841.

5-(iodomethyl)-5-methyl-2-(perfluoropropyl)-1-phenyl-4,5-dihydro-1H-imidazole (3s)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.2) to give the titled product **3s** as a yellow solid (133.4 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.04 (m, 5H), 4.18 (d, J = 16.1 Hz, 1H), 3.92 (d, J = 16.1 Hz, 1H), 3.26 (d, J = 10.6 Hz, 1H), 3.19 (d, J = 10.6 Hz, 1H), 1.38 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.5 (C-F, t, $^2J_{C\text{-}F}$ = 26.0 Hz), 135.3, 130.3, 129.0, 128.9, 117.6 (C-F, qt, $^1J_{C\text{-}F}$ = 288.9 Hz, 34.0 Hz), 110.4, 106.6 (C-F, tt, $^1J_{C\text{-}F}$ = 259.3 Hz, 37.8Hz), 67.2, 67.1, 24.5, 16.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -79.9, -109.8 – -111.9 (m, 2F), -124.9.

M.p. 127.5 – 128.7 °C

HRMS (ESI): $[M+ Na]^+$ Calcd. for $C_{14}H_{12}F_7IN_2$ 490.9826; Found 490.9832.

5-(iodomethyl)-1-phenyl-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (4a)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **4a** as a yellow oily liquid (50.1 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 24.9 Hz, 2H), 6.91 (d, J =8.9 Hz, 2H), 4.12 (dd, J = 15.8, 1.4 Hz, 1H), 3.94 - 3.76 (m, 2H), 3.25 (d, J = 10.6 Hz, 1H), 3.17 (d, J = 10.5 Hz, 1H), 1.41 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.8 (C-F, q, $^2J_{C\text{-}F}$ = 37.3 Hz), 130.2, 130.1, 129.1, 115.7 (C-F, q, $^1J_{C\text{-}F}$ = 287.7 Hz), 114.9, 113.4, 53.1, 44.2, 20.5, 9.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -75.6.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{11}H_{10}F_3IN_2$ 369.0070; Found 369.0068.

5-(iodomethyl)-5-phenyl-1-(p-tolyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (4b)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **4b** as a yellow solid (115.2 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.17 (m, 5H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 7.9 Hz, 2H), 4.62 (d, *J* = 17.9 Hz, 1H), 4.46 (d, *J* = 18.3 Hz, 1H), 3.72 (q, *J* = 10.6 Hz, 2H), 2.27 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.4 (C-F, q, $^2J_{C-F}$ = 35.3 Hz), 140.4, 138.8, 131.6, 129.8, 129.4, 128.7, 128.5, 127.0, 117.6 (C-F, q, $^1J_{C-F}$ = 275.7 Hz), 71.9, 69.6, 21.1, 13.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ - 65.5.

M.p. 118.3 – 119.2 °C.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{18}H_{16}F_3IN_2$ 445.0383; Found 445.0390.

5-(3-chlorophenyl)-5-(iodomethyl)-1-(p-tolyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (4c)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **4c** as a yellow oily liquid (128.2 mg, 90%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.23 (m, 3H), 7.18 (d, *J* = 6.8 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 4.57 (d, *J* = 16.6 Hz, 1H), 4.45 (d, *J* = 16.6 Hz, 1H), 3.67 (d, *J* = 3.3 Hz, 2H), 2.29 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.4 (C-F, q, $^2J_{C-F}$ = 35.7 Hz), 142.4, 139.1, 134.7, 131.4, 129.9, 129.8, 129.5, 128.7, 127.2, 125.3, 117.5 (C-F, q, $^1J_{C-F}$ = 275.9 Hz), 71.6, 69.5, 21.1, 12.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -65.5.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{18}H_{15}ClF_3IN_2$ 478.9993; Found 479.0000.

5-(iodomethyl)-5-(naphthalen-1-yl)-1-(p-tolyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (4d)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.2) to give the titled product **4d** as a yellow solid (37.1 mg, 25%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.6, 4.2 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.65 (t, *J* = 8.5 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 1H), 7.37 -7.27 (m, 2H), 6.66 (d, *J* = 7.5 Hz, 2H), 4.69 (d, *J* = 18.5 Hz, 1H), 4.44 (d, *J* = 18.2 Hz, 1H), 3.94 (dd, *J* = 43.1, 10.5 Hz, 2H), 2.19 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.4 (C-F, q, $^2J_{C-F}$ = 35.5 Hz), 139.1, 134.8, 131.4, 131.1, 130.6, 130.2, 129.9, 129.4, 129.3, 128.5, 127.4, 125.9, 123.9, 123.5, 120.5, 117.6 (C-F, q, $^1J_{C-F}$ = 275.9 Hz), 76.1, 66.7, 26.7, 21.1, 21.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ -65.8.

M.p. 135.6 – 137.2 °C

HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{22}H_{18}F_3IN_2$ 517.0359; Found 517.0362.

1-(p-tolyl)-2-(trifluoromethyl)-1H-imidazole-5-carbaldehyde (5)

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 **5** as a yellow oily liquid (26.7 mg, 35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.92 (s, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 2.47 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 178.9, 153.2 (C-F, q, $^{2}J_{C\text{-}F}$ = 36.2 Hz), 140.9, 137.5, 134.7, 130.8, 130.1, 126.8, 118.1 (C-F, q, $^{1}J_{C\text{-}F}$ = 271.7 Hz), 29.7, 21.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -60.4.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{12}H_9F_3N_2O$ 255.0740; Found 255.0746.

5-(chloromethyl)-5-methyl-1-(p-tolyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (6)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **6** as a yellow oily liquid (43.5 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 4.27 (d, *J* = 15.6 Hz, 1H), 3.83 (d, *J* = 15.6 Hz, 1H), 3.46 (d, *J* = 11.7 Hz, 1H), 3.34 (d, *J* = 11.7 Hz, 1H), 2.39 (s, 2H), 1.29 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.6 (C-F, q, $^{2}J_{C\text{-}F}$ = 35.3 Hz), 139.2, 131.6, 130.4, 129.8, 117.5 (C-F, q, $^{1}J_{C\text{-}F}$ = 275.6 Hz), 68.4, 63.6, 49.7, 23.9, 21.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -66.0.

HRMS (ESI): $[M+H]^+$ Calcd. For $C_{13}H_{14}ClF_3N_2$ 291.0870; Found 291.0883.

5-(bromomethyl)-5-methyl-1-(p-tolyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (7)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **7** as a yellow oily liquid (100.0 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.25 (dd, *J* = 15.8, 1.7 Hz, 1H), 3.85 (dd, *J* = 15.8, 1.7 Hz, 1H), 3.38 (d, *J* = 10.9 Hz, 1H), 3.27 (d, *J* = 10.9 Hz, 1H), 2.39 (s, 1H), 1.35 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.5 (C-F, q, $^{2}J_{C\text{-}F}$ = 35.3 Hz), 139.2, 131.6, 130.4, 129.8, 117.5 (C-F, q, $^{1}J_{C\text{-}F}$ = 275.7 Hz), 67.8, 64.7, 39.6, 24.3, 21.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -65.9.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{13}H_{14}BrF_3N_2$ 335.0365; Found 335.0384.

2,2,2-trifluoro-N-(2-methylallyl)-N'-(p-tolyl)acetimidamide (8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 6.57 (m, 4H), 4.96 – 4.71 (m, 2H), 3.93 (s, 1H), 3.55 (s, 1H), 2.30 (s, 3H), 1.87 – 1.51 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.0 (C-F, q, $^2J_{C\text{-}F}$ = 43.1 Hz), 141.4, 133.1, 131.9, 129.9, 129.0, 120.4, 118.6 (C-F, q, $^1J_{C\text{-}F}$ = 299.9 Hz), 111.3, 48.7, 46.5, 20.8.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{13}H_{16}F_3N_2$ 257.1260; Found 257.1265.

5-(azidomethyl)-5-methyl-1-(p-tolyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole (9)

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 **9** as a white solid (255.3 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 4.14 (d, *J* = 17.4 Hz, 1H), 3.80 (d, *J* = 17.4 Hz, 1H), 3.38 (d, *J* = 12.6 Hz, 1H), 3.20 (d, *J* = 12.6 Hz, 1H), 2.40 (s, 3H), 1.22 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.7 (C-F, q, $^2J_{C\text{-}F}$ = 35.4 Hz), 139.0, 132.0, 130.2, 129.8, 127.6, 117.5 (C-F, q, $^1J_{C\text{-}F}$ = 275.6 Hz), 67.7, 63.6, 57.2, 23.5, 21.2, 21.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -65.9.

M.p. 148.4 - 149.5 °C.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{13}H_{14}F_3N_5$ 298.1274; Found 298.1284.

1-((5-methyl-1-(p-tolyl)-2-(trifluoromethyl)-4,5-dihydro-1H-imidazol-5-yl)methyl)-4-phenyl-1H-1,2,3-triazole (10)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.2) to give the titled product **10** as a yellow solid (50.3 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.1 Hz, 2H), 7.72 (s, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 4.57 (d, *J* = 14.1 Hz, 1H), 4.31 (d, *J* = 14.1 Hz, 2H), 4.29 (dd, *J* = 16.0, 1.6 Hz, 2H), 3.81 (dd, *J* = 16.0, 1.7 Hz, 1H), 2.41 (s, 3H), 1.25 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.8 (C-F, q, $^2J_{C-F}$ = 35.3 Hz), 147.9, 139.4, 132.1, 130.2, 117.4 (C-F, q, $^1J_{C-F}$ = 275.8 Hz), 118.8, 116.0, 113.3, 67.8, 64.7, 56.4, 29.7, 23.4, 21.2, 21.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -65.8.

M.p. 145.3 - 146.7 °C

HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{21}H_{20}F_3N_5$ 422.1563; Found 422.1567.

7. References

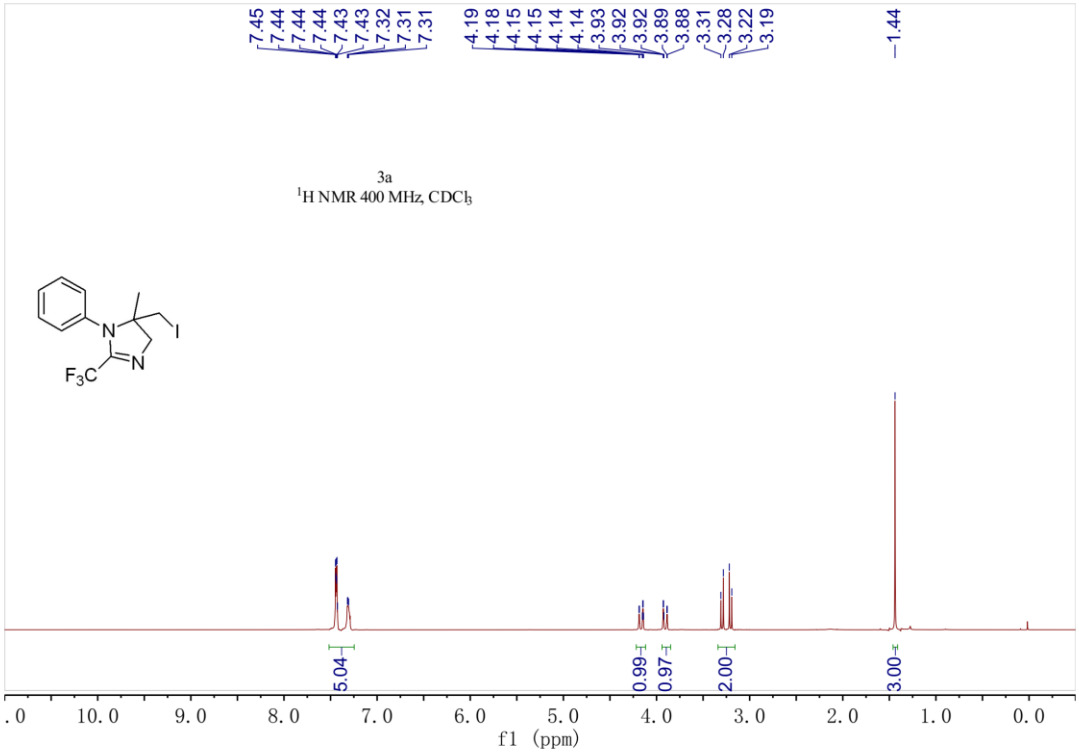
(1) Tamura, K.; Mizukami, H.; Maeda, K.; Watanabe, H.; Uneyama, K., One-pot synthesis of trifluoroacetimidoyl halides. *J. Org. Chem.* **1993**, *58*, 32-35.

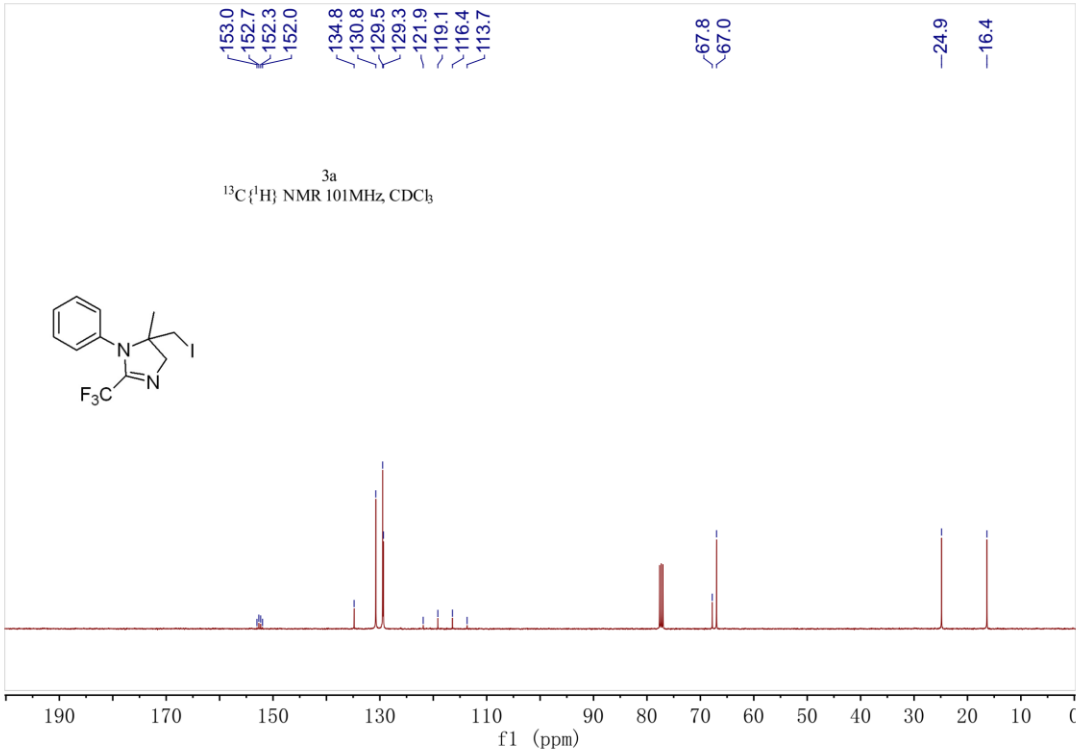
(2) Li, X.-T.; Gu, Q.-S.; Dong, X.-Y.; Meng, X.; Liu, X.-Y., A Copper Catalyst with a Cinchona-Alkaloid-Based Sulfonamide Ligand for Asymmetric Radical Oxytrifluoromethylation of Alkenyl Oximes. *Angew. Chem. Int. Ed.* **2018,** *57*, 7668-7672.

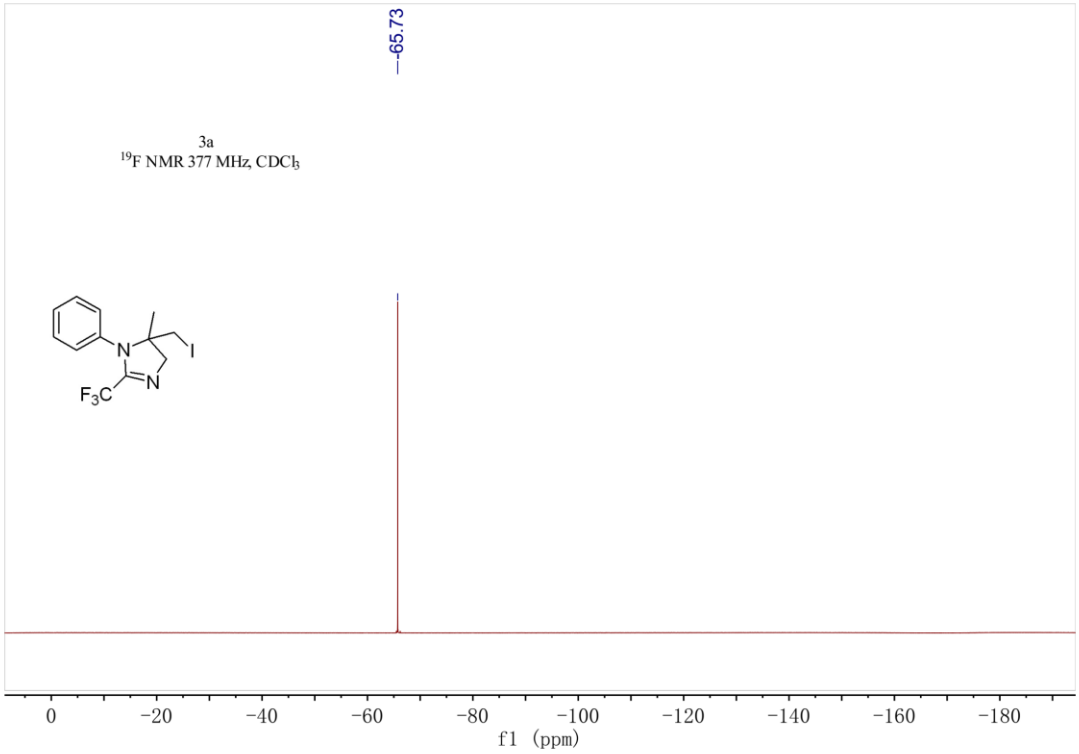
(3) Atkinson, S. J.; Demont, E. H.; Harrison, L. A.; Lucas, S. C. C.; Preston, A. G.; Seal, J. T.; Wall, I. D.; Watson, R. J.; Woolven, J. M. Preparation of 2,3-dihydrobenzofurans as bromodomain inhibitors useful in treatment of diseases. *PCT Int. Appl.*, **2019**, 2019068782.

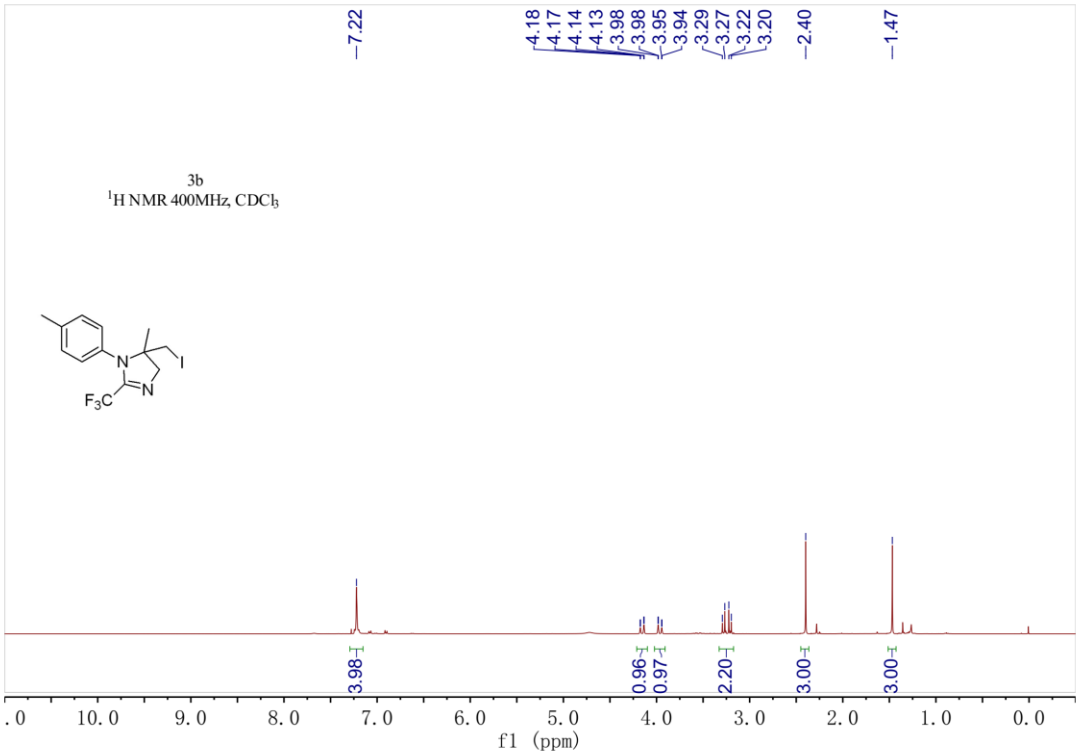
(4) (a) Scheidt, F.; Neufeld, J.; Schäfer, M.; Thiehoff, C.; Gilmour, R., Catalytic Geminal Difluorination of Styrenes for the Construction of Fluorine-rich Bioisosteres. *Org. Lett.* **2018,** *20*, 8073-8076; (b) Kawato, Y.; Kubota, A.; Ono, H.; Egami, H.; Hamashima, Y., Enantioselective Bromocyclization of Allylic Amides Catalyzed by BINAP Derivatives. *Org. Lett.* **2015,** *17*, 1244-1247.

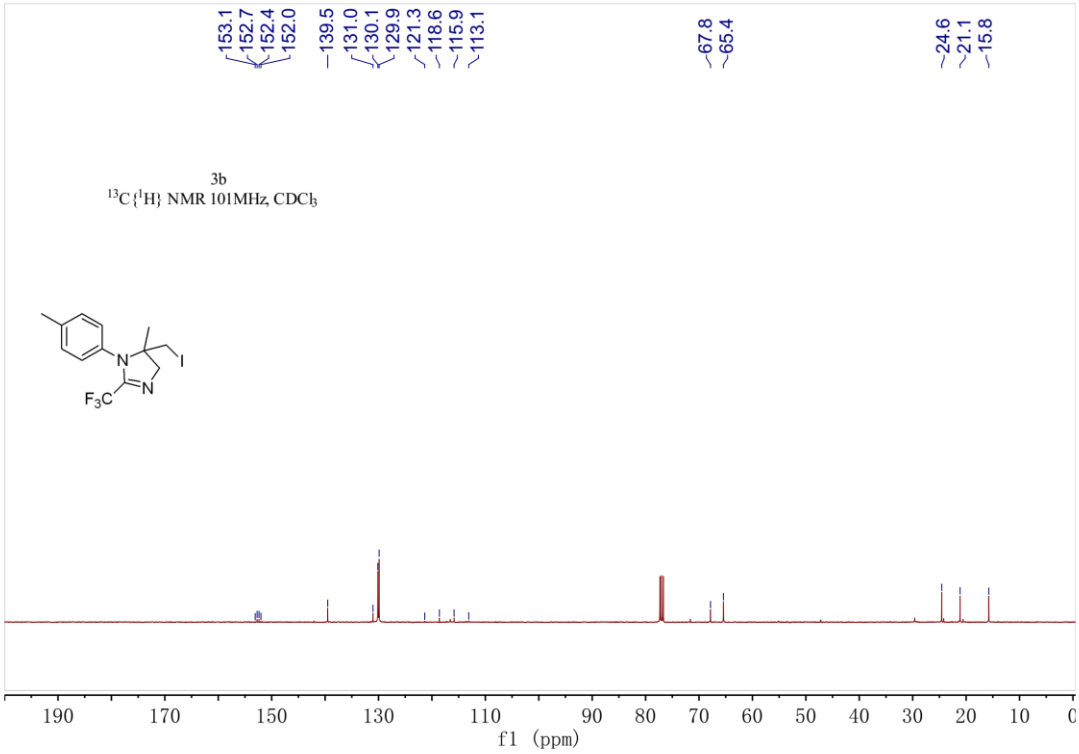
8. Copy of ^{1}H, ^{13}C and ^{19}F-NMR Spectra of Products

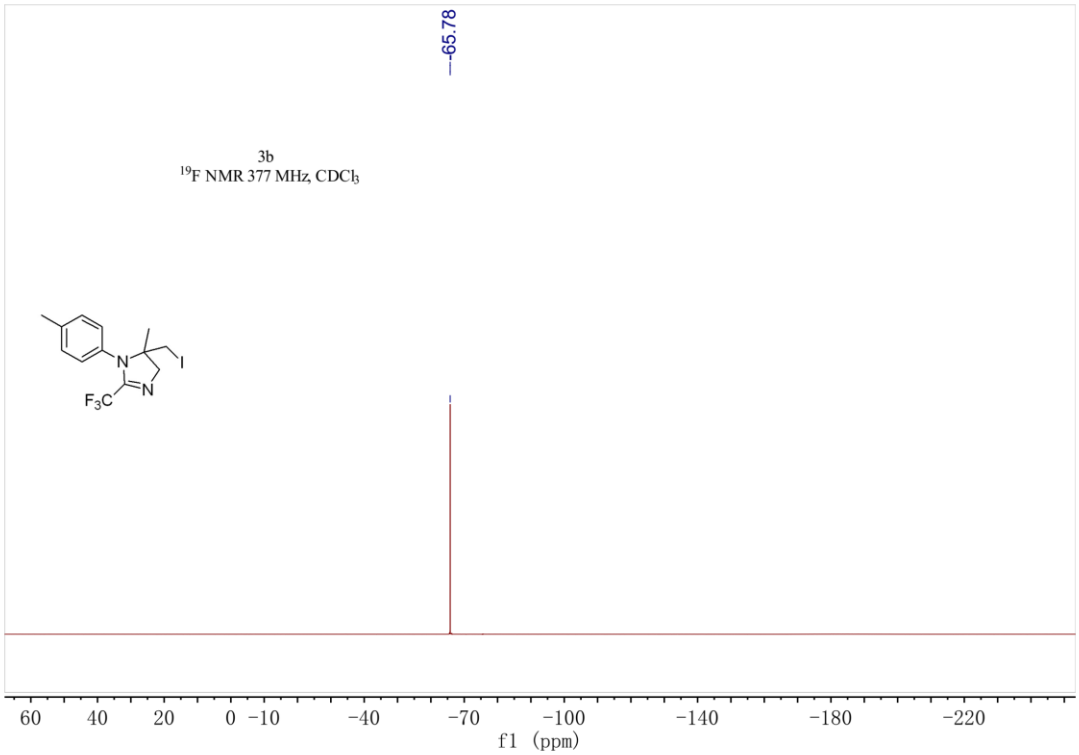


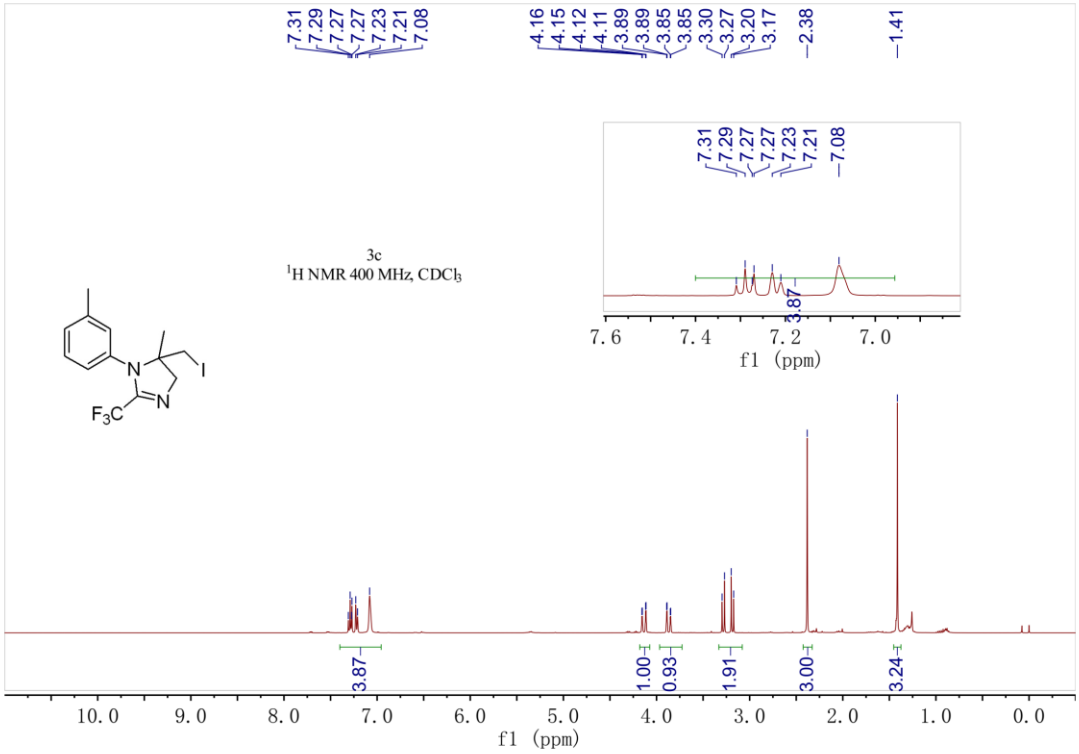


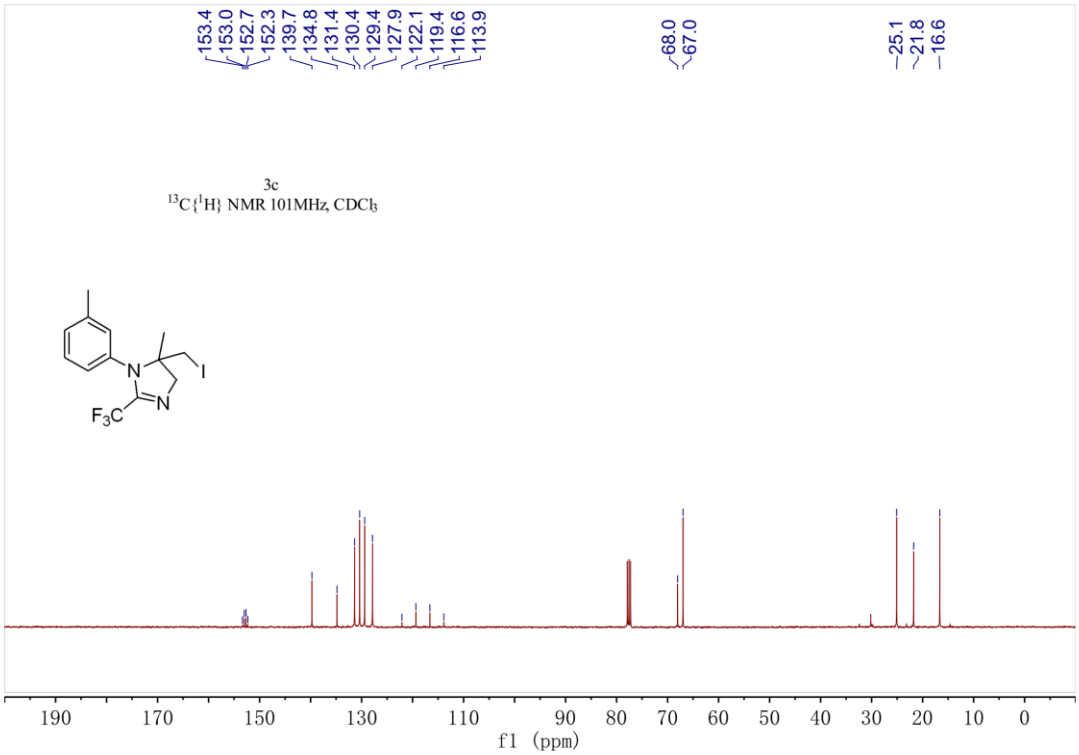

-65.73
3a
19F NMR 377 MHz, CDCl3
N
I
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

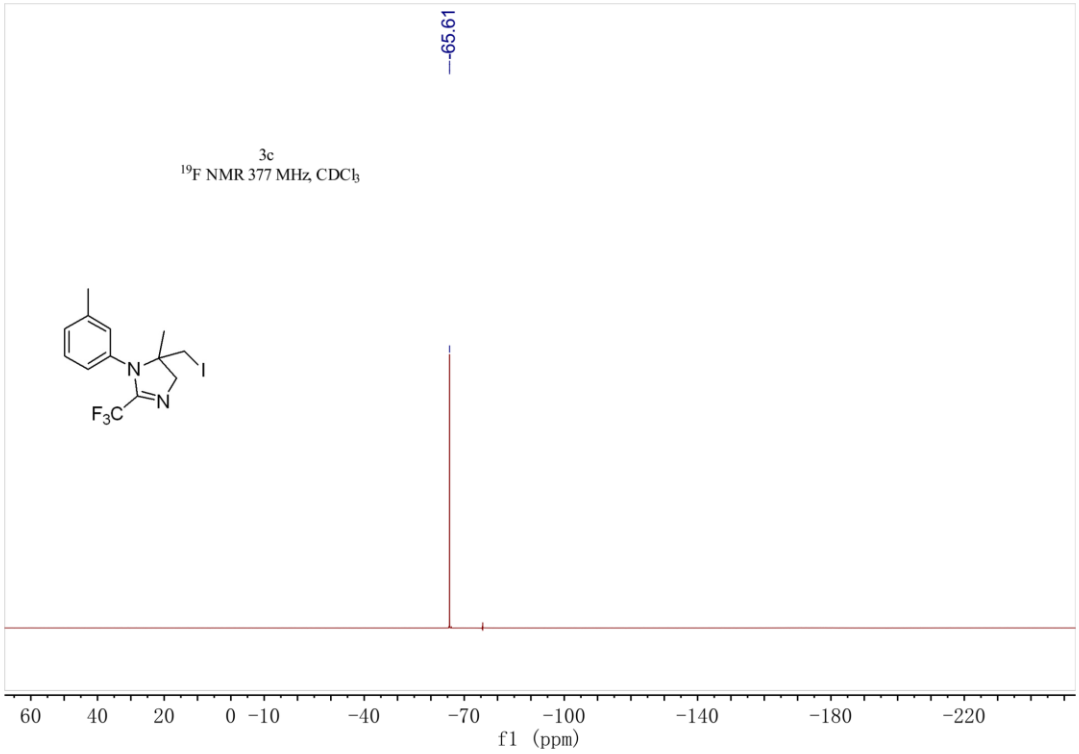

7.22
4.18
4.17
4.14
4.13
3.98
3.98
3.95
3.94
3.29
3.27
3.22
3.20
2.40
1.47
3b
1H NMR 400MHz, CDCl3
N
I
N
F3C
3.98
0.96
0.97
2.20
3.00
3.00
.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

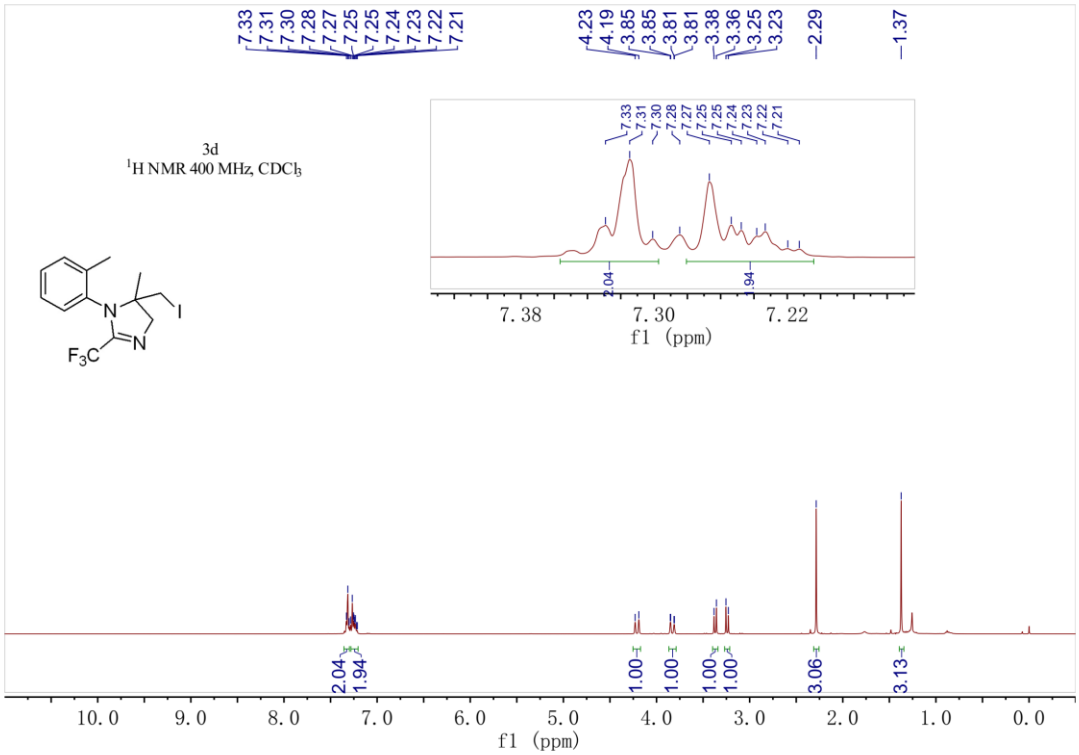

153.1
152.7
152.4
152.0
139.5
131.0
130.1
129.9
121.3
118.6
115.9
113.1
67.8
65.4
24.6
21.1
15.8
3b
13C{1H} NMR 101MHz, CDCl3
N
I
F3C
N
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

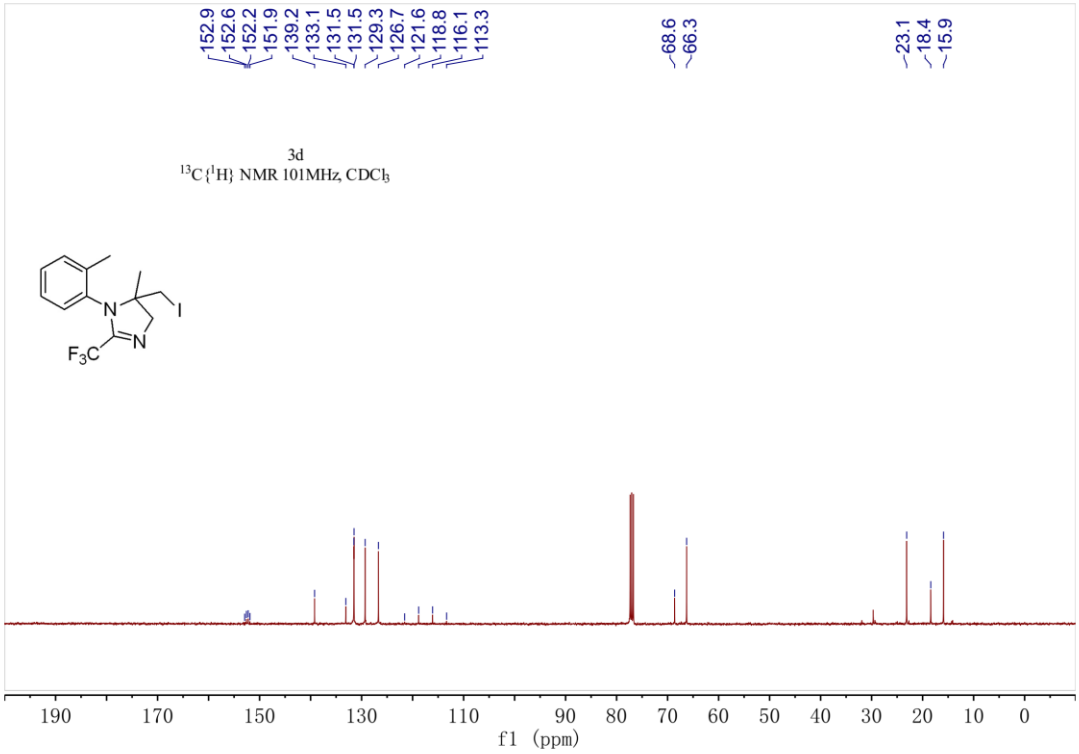

-65.78
3b
19F NMR 377 MHz, CDCl3
N
I
F3C
N
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
f1 (ppm)

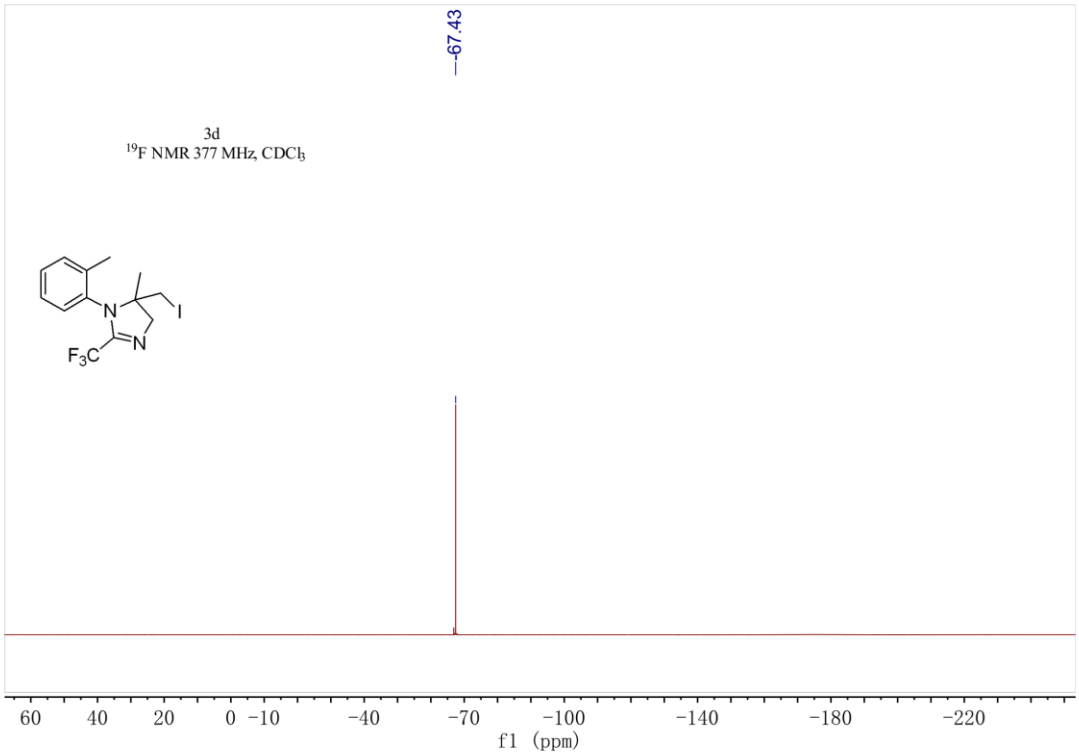

7.31
7.29
7.27
7.27
7.23
7.21
7.08
4.16
4.15
4.12
4.11
3.89
3.89
3.85
3.85
3.30
3.27
3.20
3.17
2.38
1.41
3c
^{1}H NMR 400 MHz, CDCl$_3$
I
N
N
F$_3$C
3.87
1.00
0.93
1.91
3.00
3.24
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
7.6
7.4
7.2
7.0
f1 (ppm)

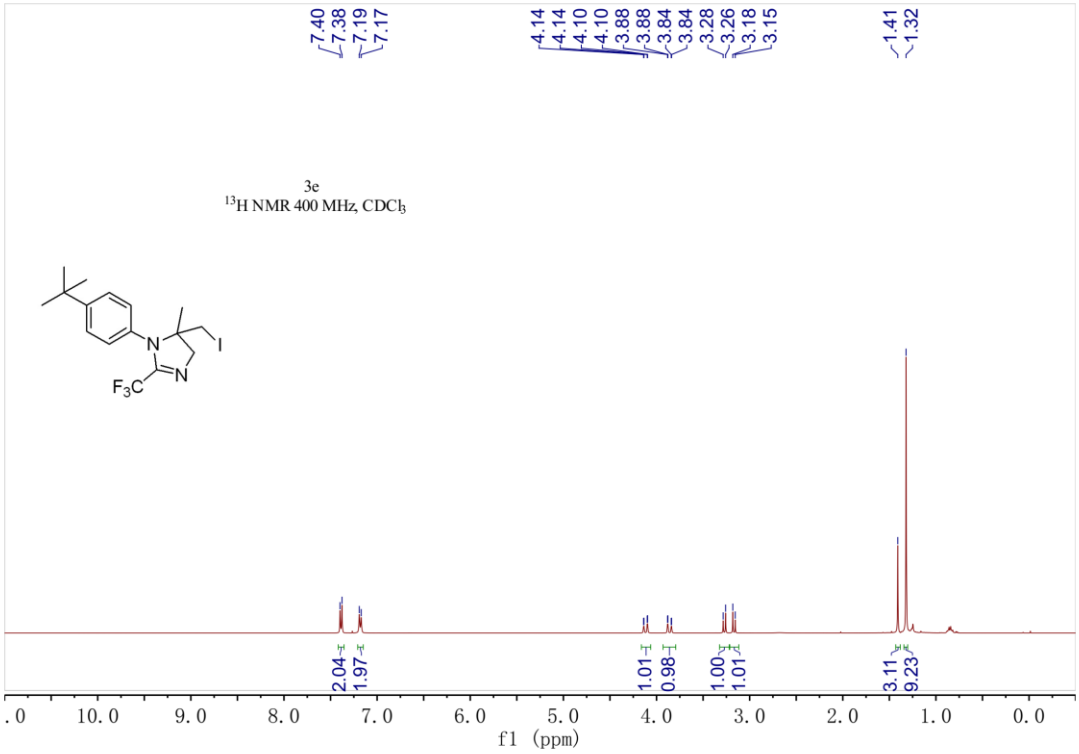

153.4
153.0
152.7
152.3
139.7
134.8
131.4
130.4
129.4
127.9
122.1
119.4
116.6
113.9
68.0
67.0
25.1
21.8
16.6
3c
^{13}C{^{1}H} NMR 101MHz, CDCl$_3$
I
N
N
F$_3$C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

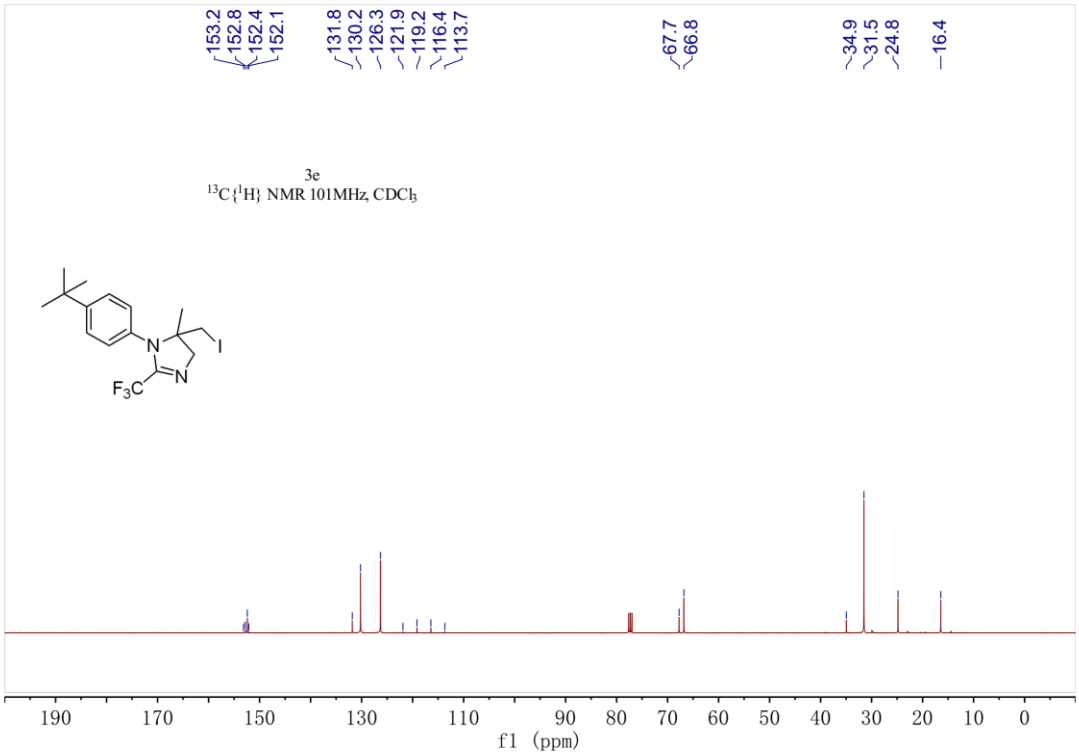

-65.61
3c
19F NMR 377 MHz, CDCl3
N
I
F3C
N
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
f1 (ppm)

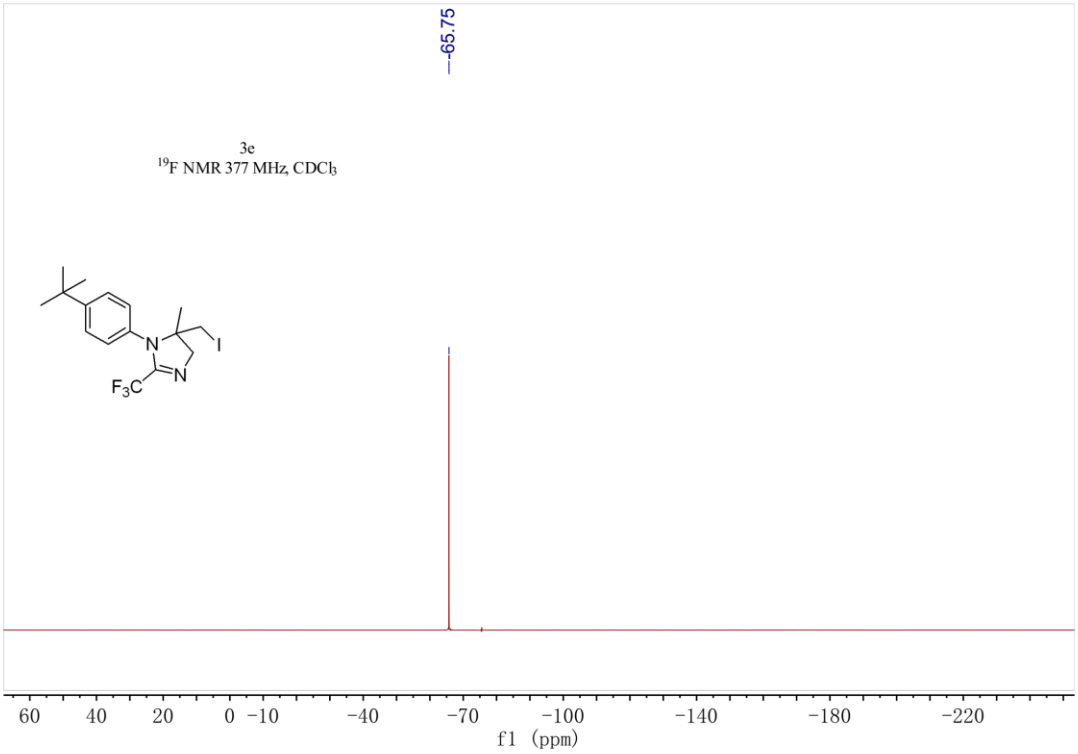

7.33
7.31
7.30
7.28
7.27
7.25
7.25
7.24
7.23
7.22
7.21
4.23
4.19
3.85
3.85
3.81
3.81
3.38
3.36
3.25
3.23
2.29
1.37
3d
1H NMR 400 MHz, CDCl3
N
I
F3C
N
2.04
1.94
7.38
7.30
7.22
f1 (ppm)
2.04
1.94
1.00
1.00
1.00
1.00
3.06
3.13
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

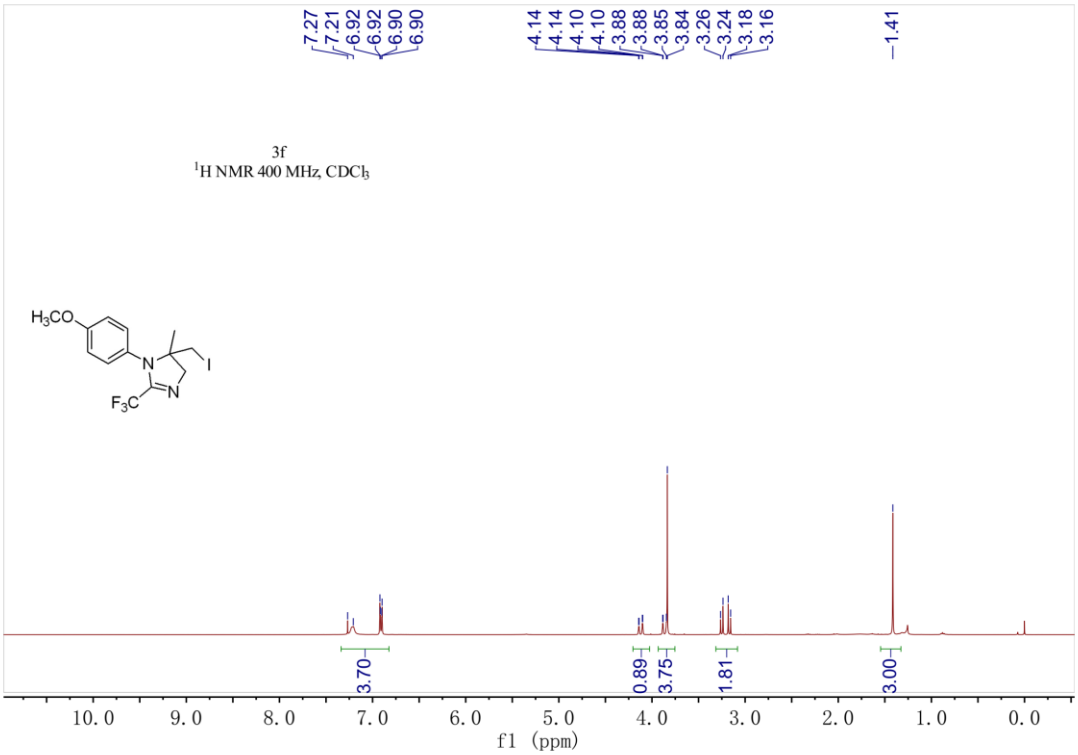

152.9
152.6
152.2
151.9
139.2
133.1
131.5
131.5
129.3
126.7
121.6
118.8
116.1
113.3
68.6
66.3
23.1
18.4
15.9
3d
13C {1H} NMR 101MHz, CDCl3
N
I
N
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

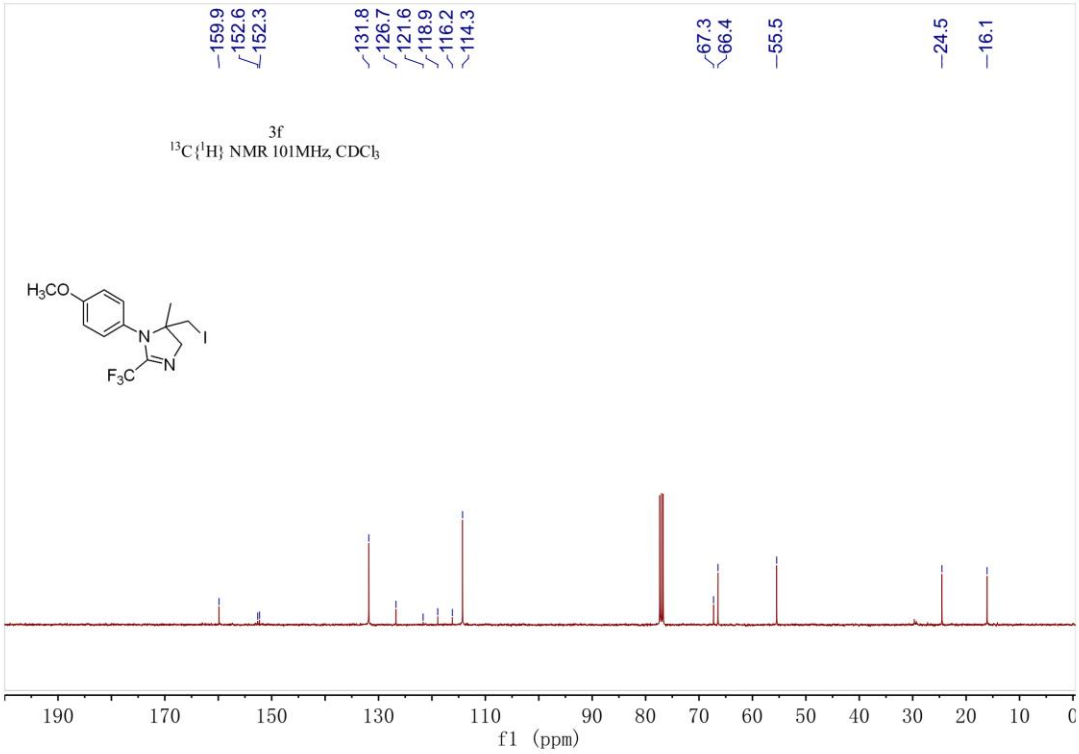

67.43
3d
19F NMR 377 MHz, CDCl3
N
I
N
F3C
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
f1 (ppm)

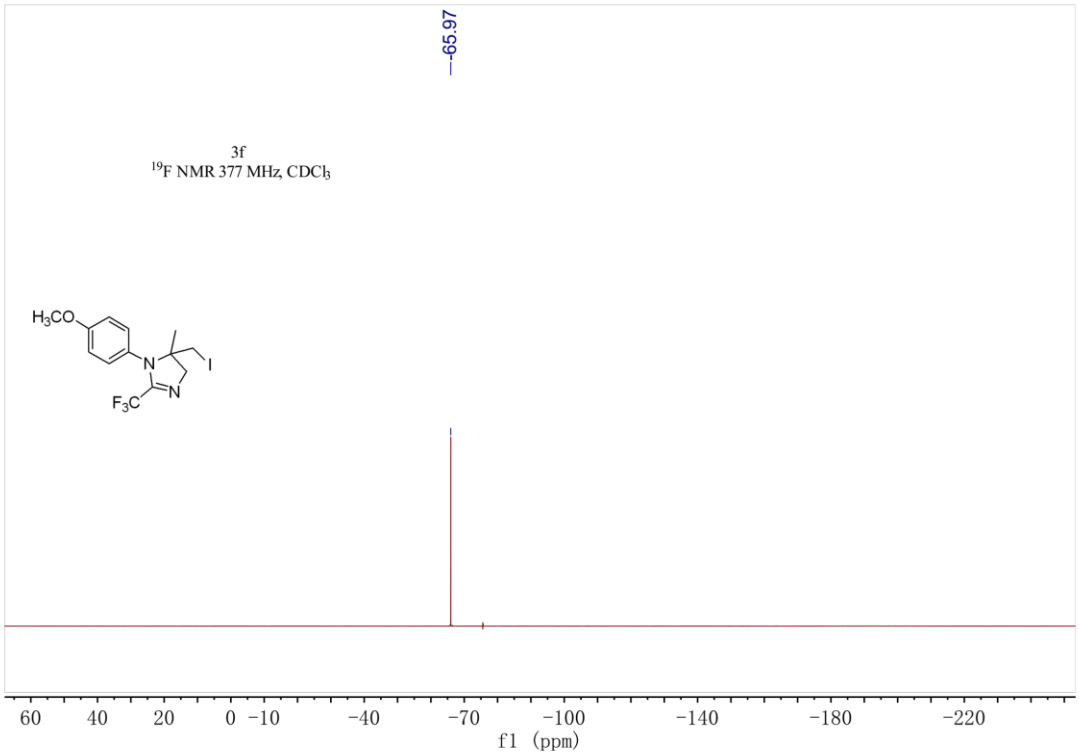

7.40
7.38
7.19
7.17
4.14
4.14
4.10
4.10
3.88
3.88
3.84
3.84
3.28
3.26
3.18
3.15
1.41
1.32
3e
13H NMR 400 MHz, CDCl3
N
I
F3C
N
2.04
1.97
1.01
0.98
1.00
1.01
3.11
9.23
.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

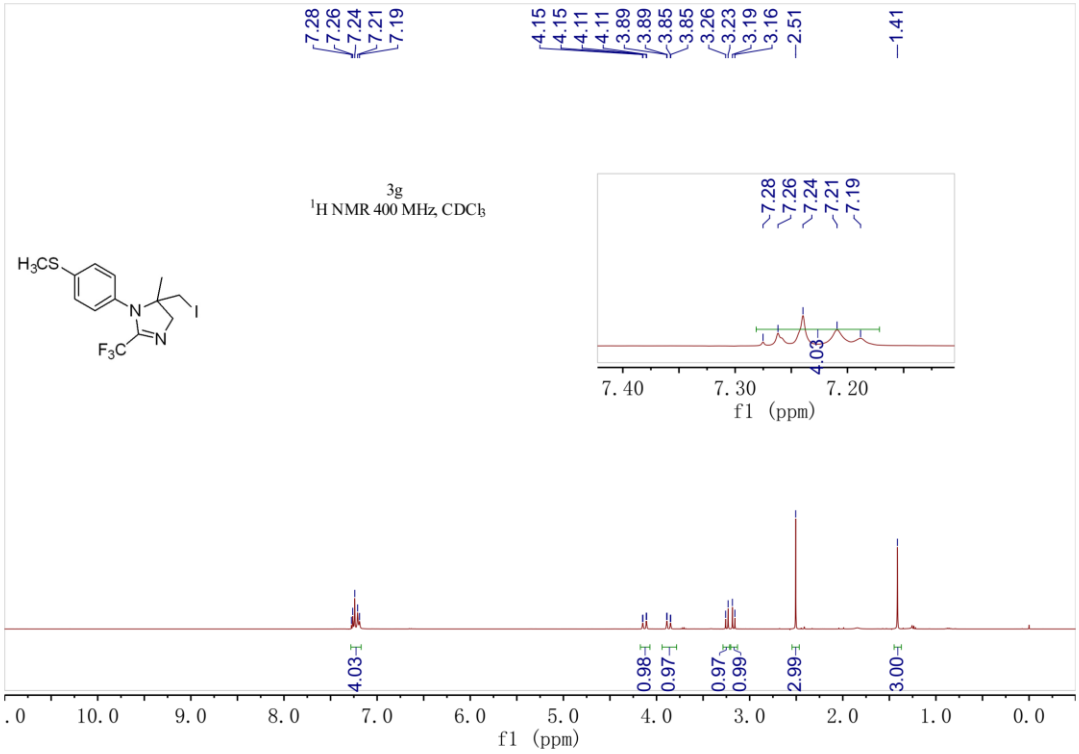

153.2
152.8
152.4
152.1
131.8
130.2
126.3
121.9
119.2
116.4
113.7
67.7
66.8
34.9
31.5
24.8
16.4
3e
13C{1H} NMR 101MHz, CDCl3
N
I
F3C
N
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

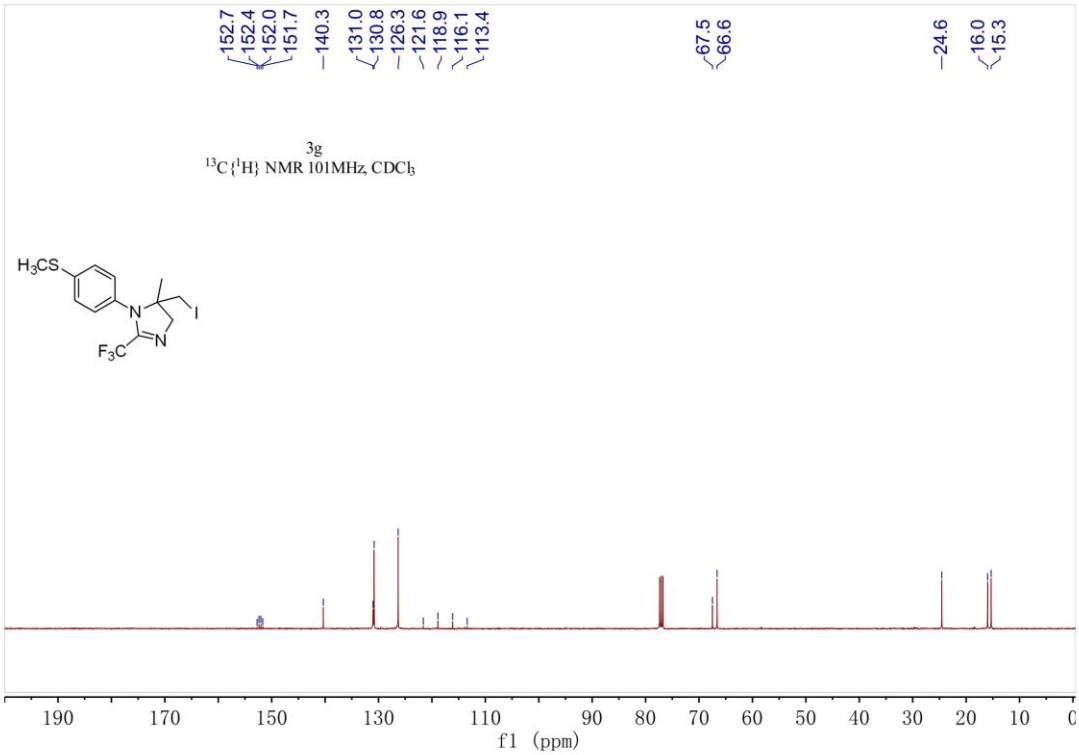

-65.75
3e
19F NMR 377 MHz, CDCl3
N
I
F3C
N
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
f1 (ppm)

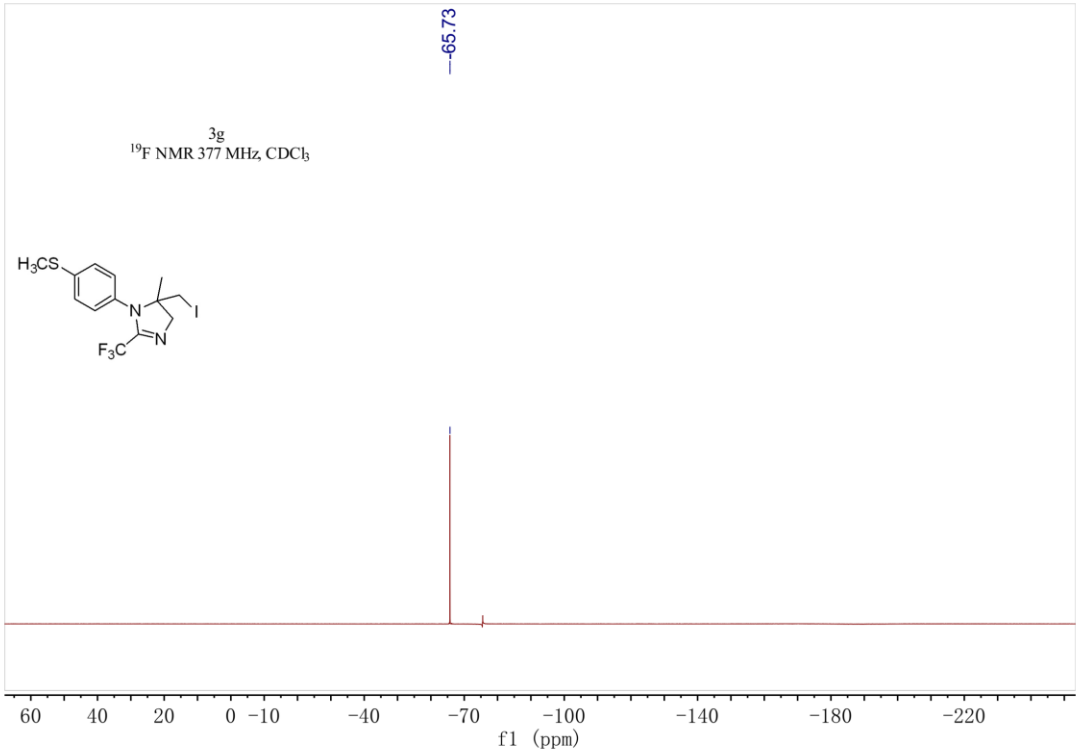

7.27
7.21
6.92
6.92
6.90
6.90
4.14
4.14
4.10
4.10
3.88
3.88
3.85
3.84
3.26
3.24
3.18
3.16
1.41
3f
1H NMR 400 MHz, CDCl3
H3CO
N
I
F3C
N
3.70
0.89
3.75
1.81
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

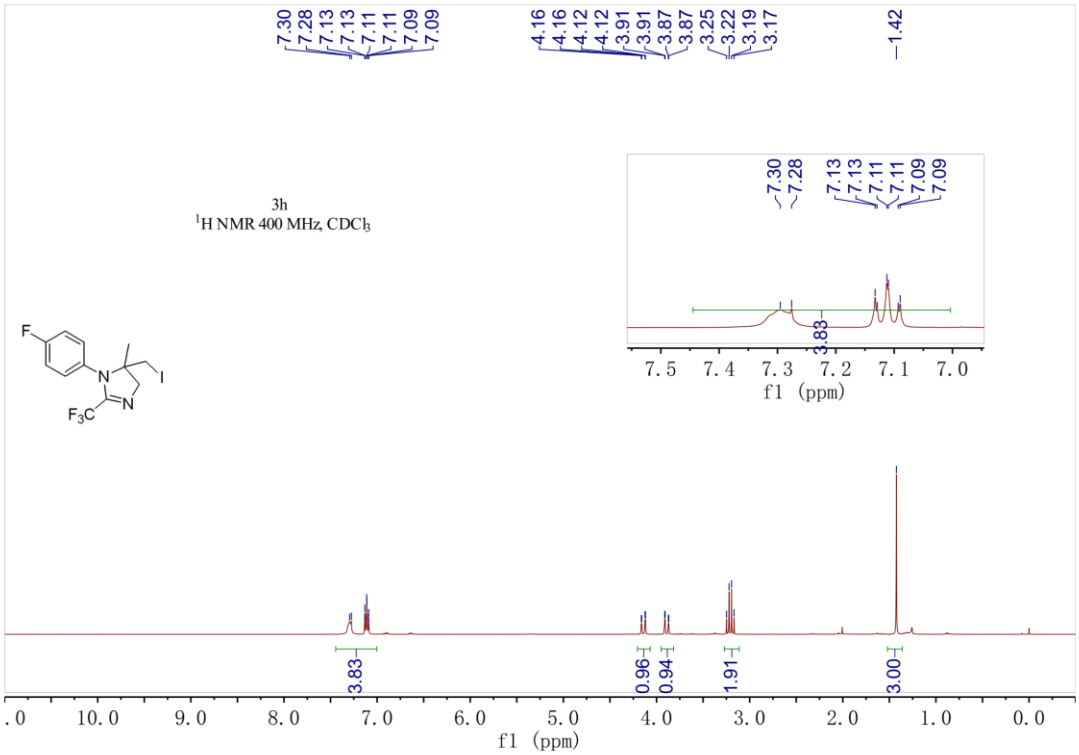

159.9
152.6
152.3
131.8
126.7
121.6
118.9
116.2
114.3
67.3
66.4
55.5
24.5
16.1
3f
$^{13}C\{^{1}H\}$ NMR 101MHz, $CDCl_3$
H_3CO
N
I
N
F_3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

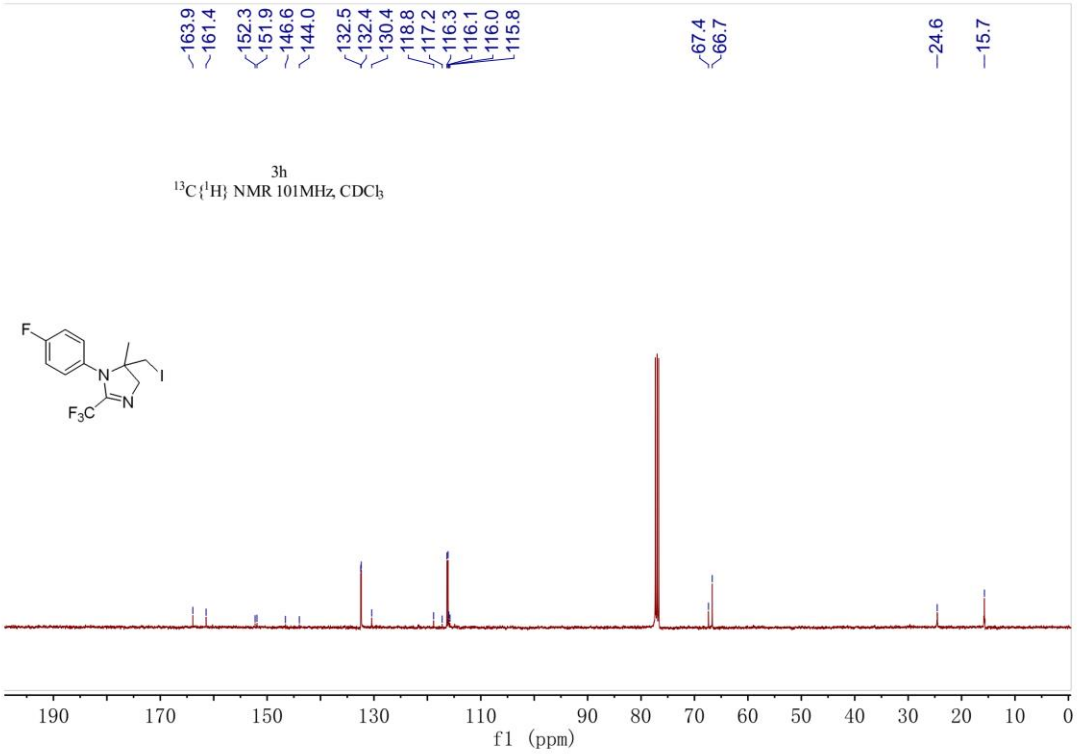

-65.97
3f
^{19}F NMR 377 MHz, $CDCl_3$
H_3CO
N
I
N
F_3C
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
f1 (ppm)

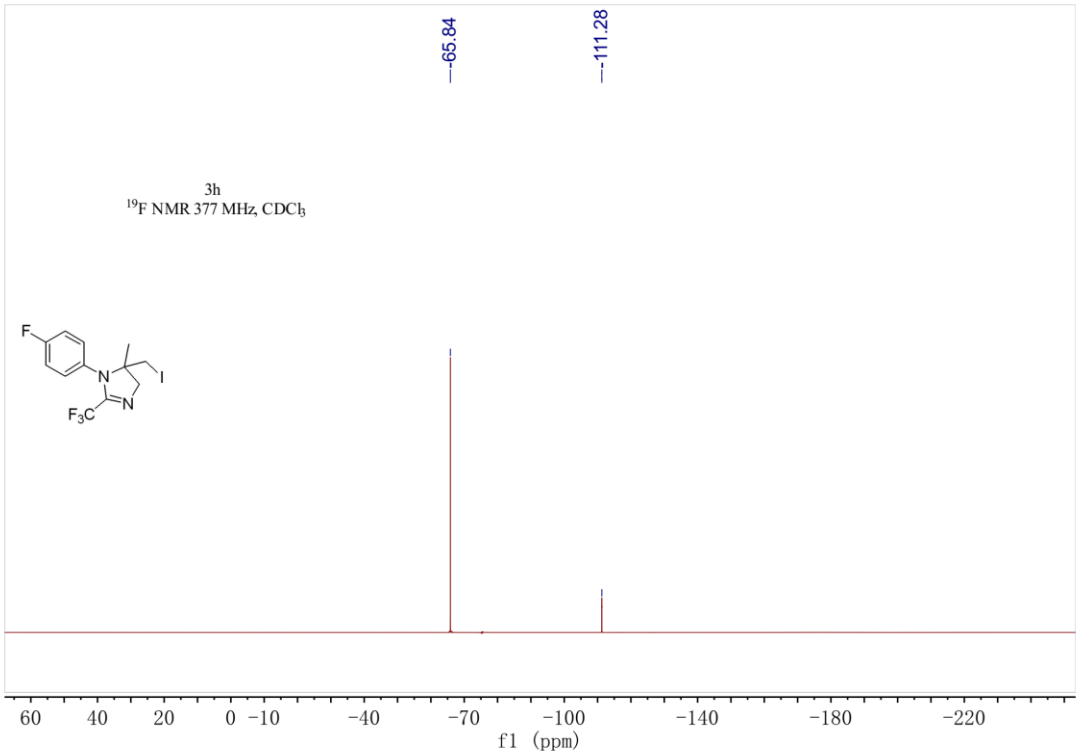

7.28
7.26
7.24
7.21
7.19
4.15
4.11
3.89
3.85
3.26
3.23
3.19
3.16
2.51
1.41
3g
1H NMR 400 MHz, CDCl3
H3CS
N
I
F3C
4.03
7.40
7.30
7.20
f1 (ppm)
4.03
0.98
0.97
0.97
0.99
2.99
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

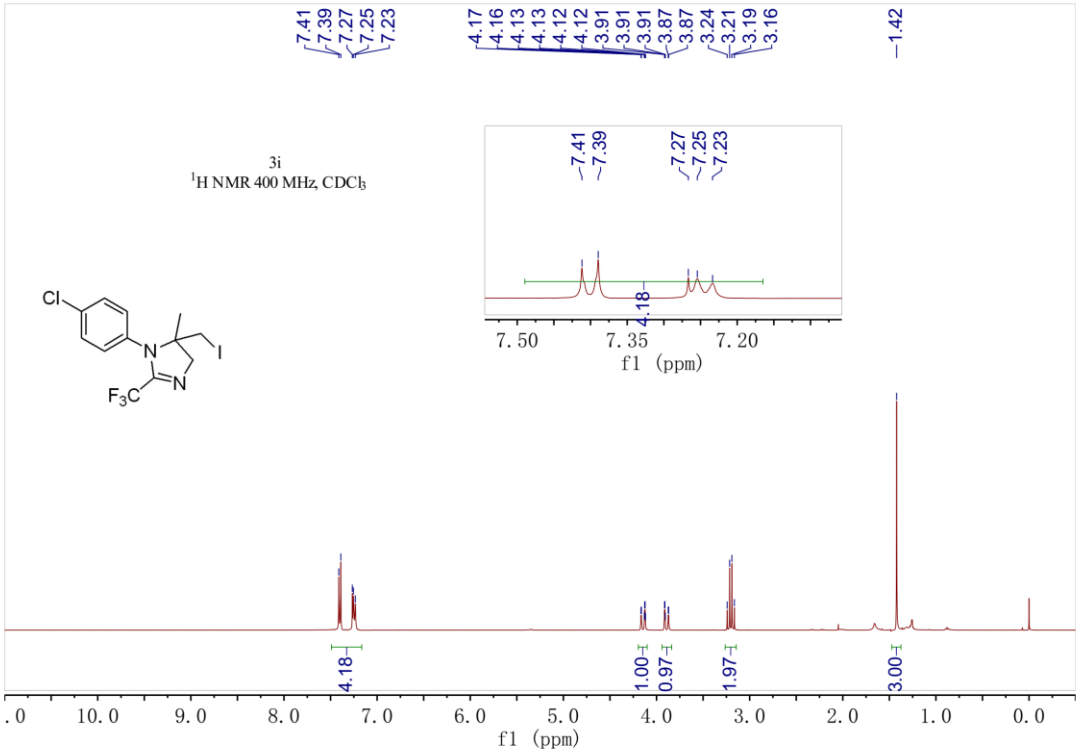

152.7
152.4
152.0
151.7
140.3
131.0
130.8
126.3
121.6
118.9
116.1
113.4
67.5
66.6
24.6
16.0
15.3
3g
13C{1H} NMR 101MHz, CDCl3
H3CS
N
I
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

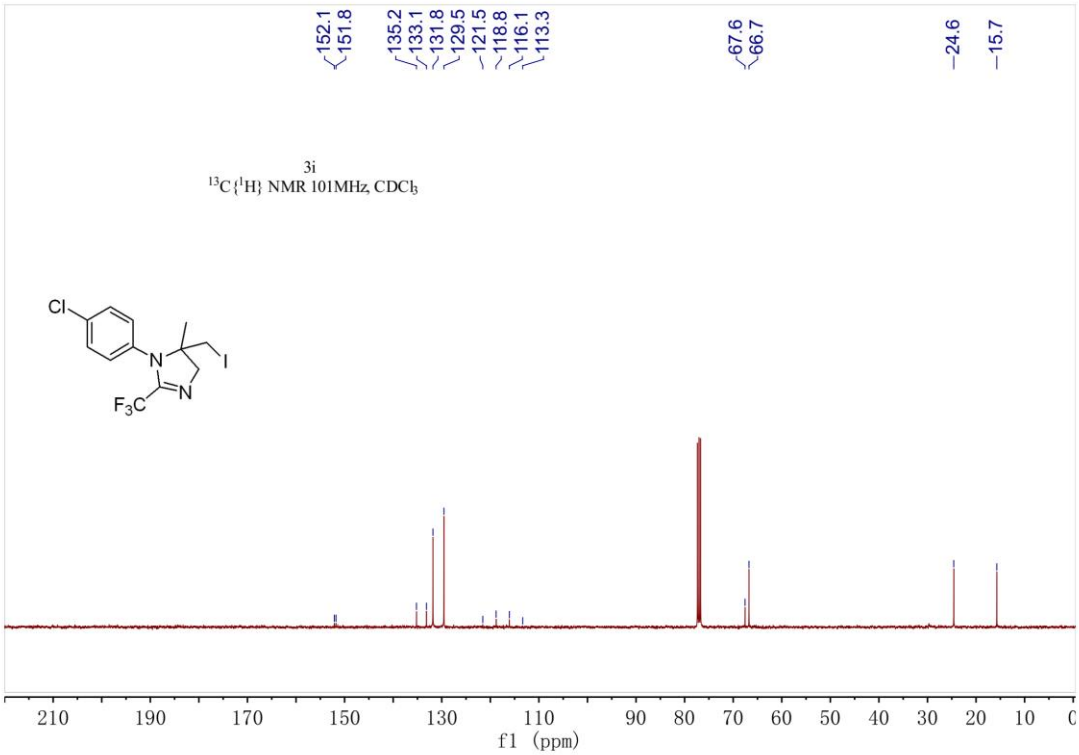

-65.73
3g
19F NMR 377 MHz, CDCl3
H3CS
N
I
F3C
N
60 40 20 0 -10 -40 -70 -100 -140 -180 -220
f1 (ppm)

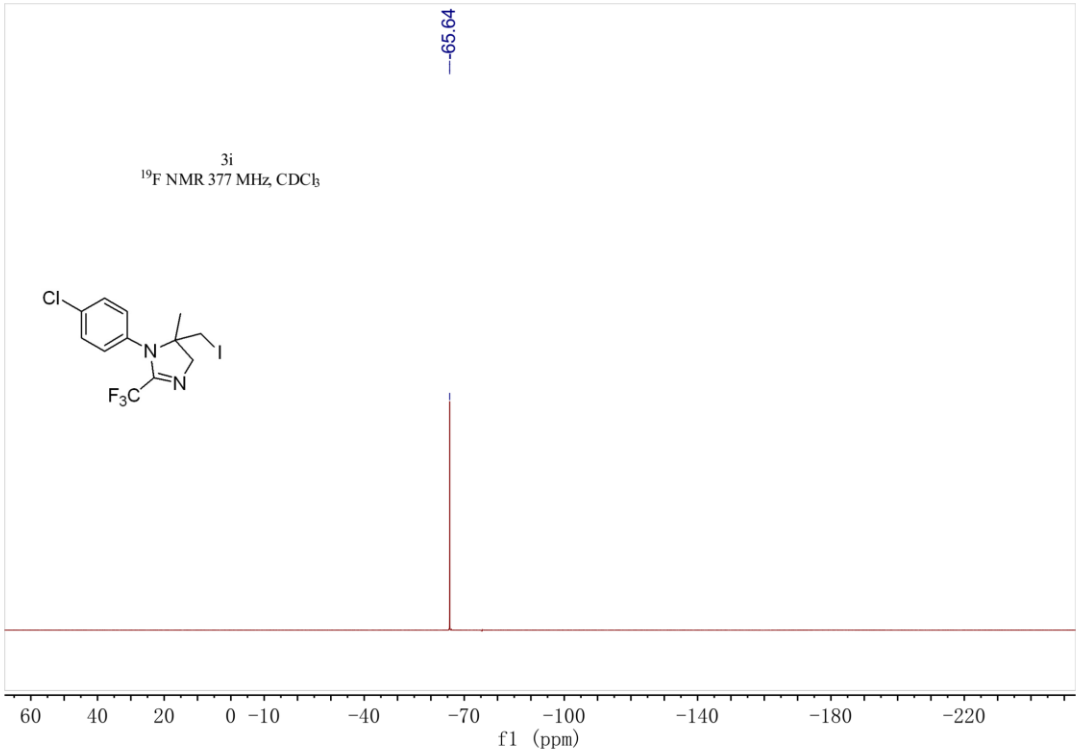

7.30
7.28
7.13
7.13
7.11
7.11
7.09
7.09
4.16
4.16
4.12
4.12
3.91
3.91
3.87
3.87
3.25
3.22
3.19
3.17
1.42
3h
1H NMR 400 MHz, CDCl3
F
N
I
F3C
N
7.30
7.28
7.13
7.13
7.11
7.11
7.09
7.09
3.83
7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
3.83
0.96
0.94
1.91
3.00
.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

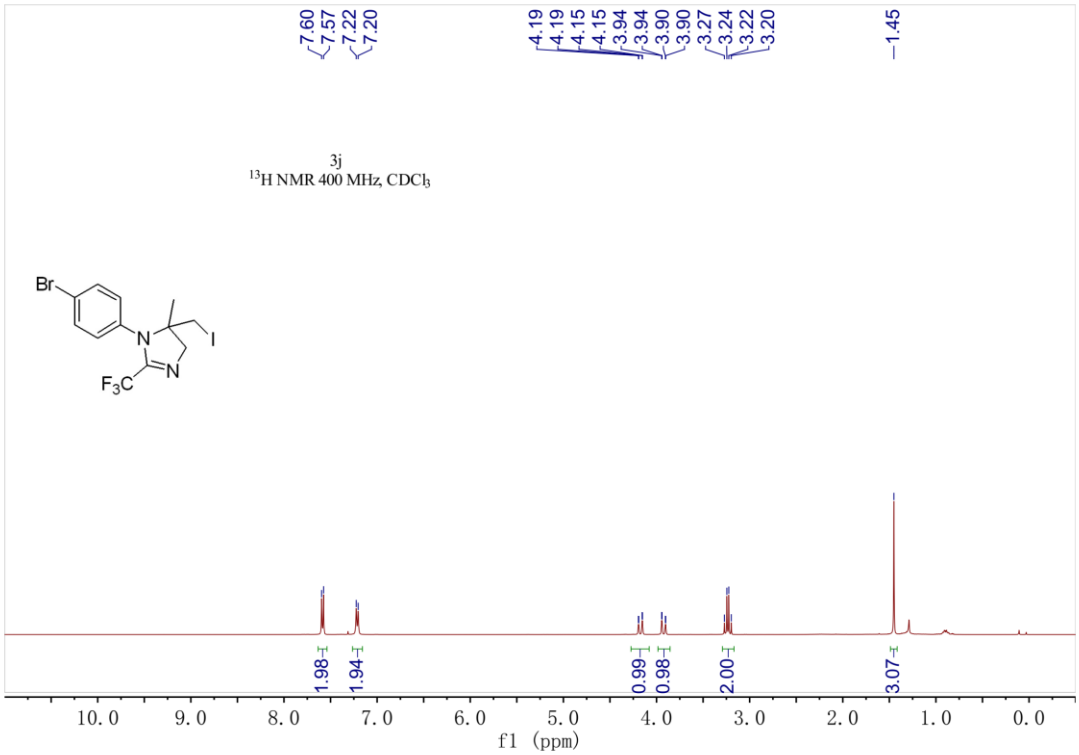

163.9
161.4
152.3
151.9
146.6
144.0
132.5
132.4
130.4
118.8
117.2
116.3
116.1
116.0
115.8
67.4
66.7
24.6
15.7
3h
13C{1H} NMR 101MHz, CDCl3
F
N
I
F3C
N
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

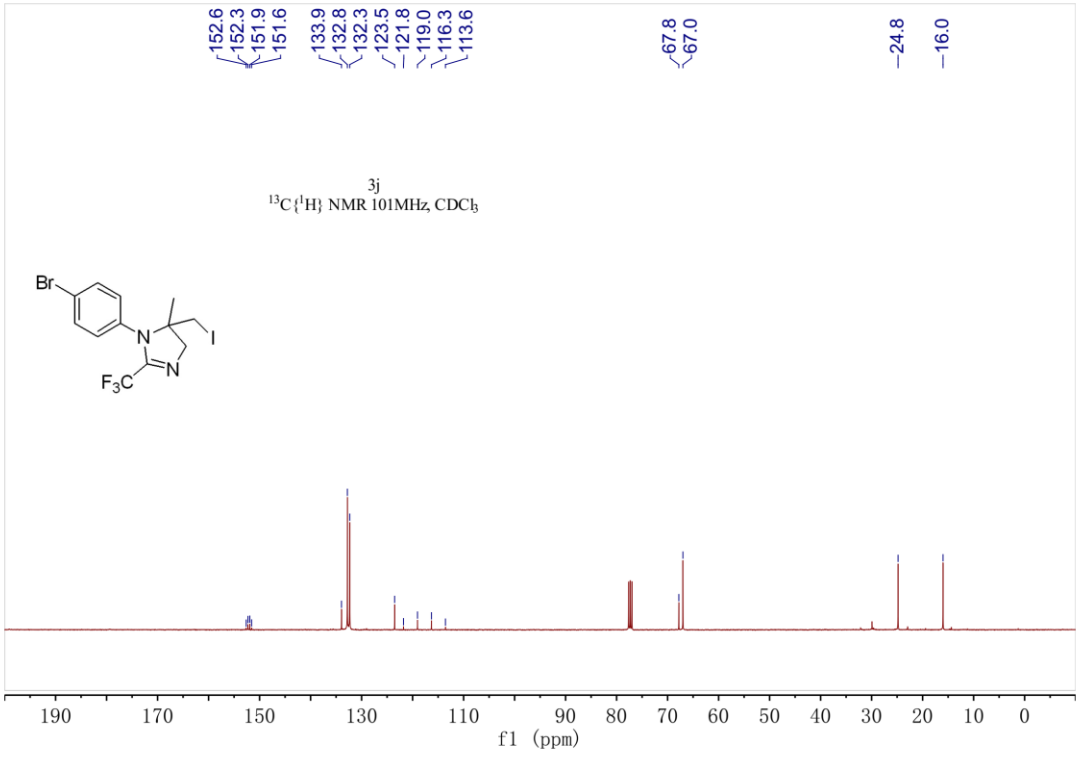

-65.84
-111.28
3h
19F NMR 377 MHz, CDCl3
F
N
I
F3C
N
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
f1 (ppm)

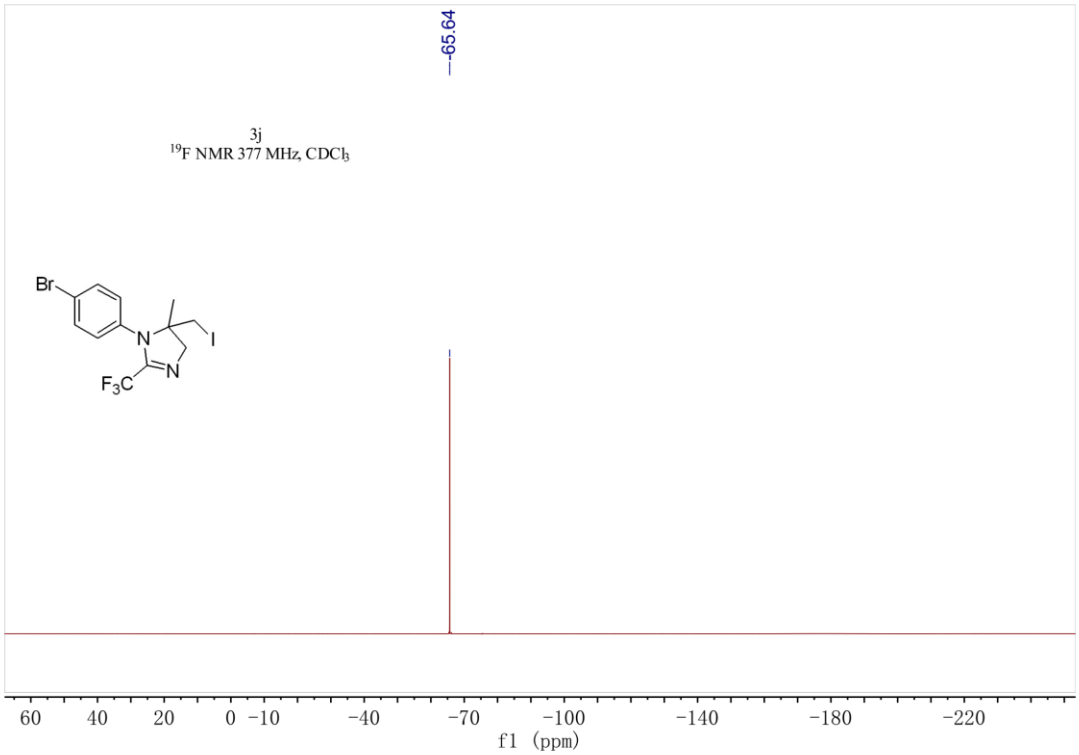

7.41
7.39
7.27
7.25
7.23
4.17
4.16
4.13
4.13
4.12
4.12
3.91
3.91
3.91
3.87
3.87
3.24
3.21
3.19
3.16
1.42
3i
^{1}H NMR 400 MHz, CDCl$_3$
Cl
N
I
F$_3$C
N
4.18
1.00
0.97
1.97
3.00
f1 (ppm)

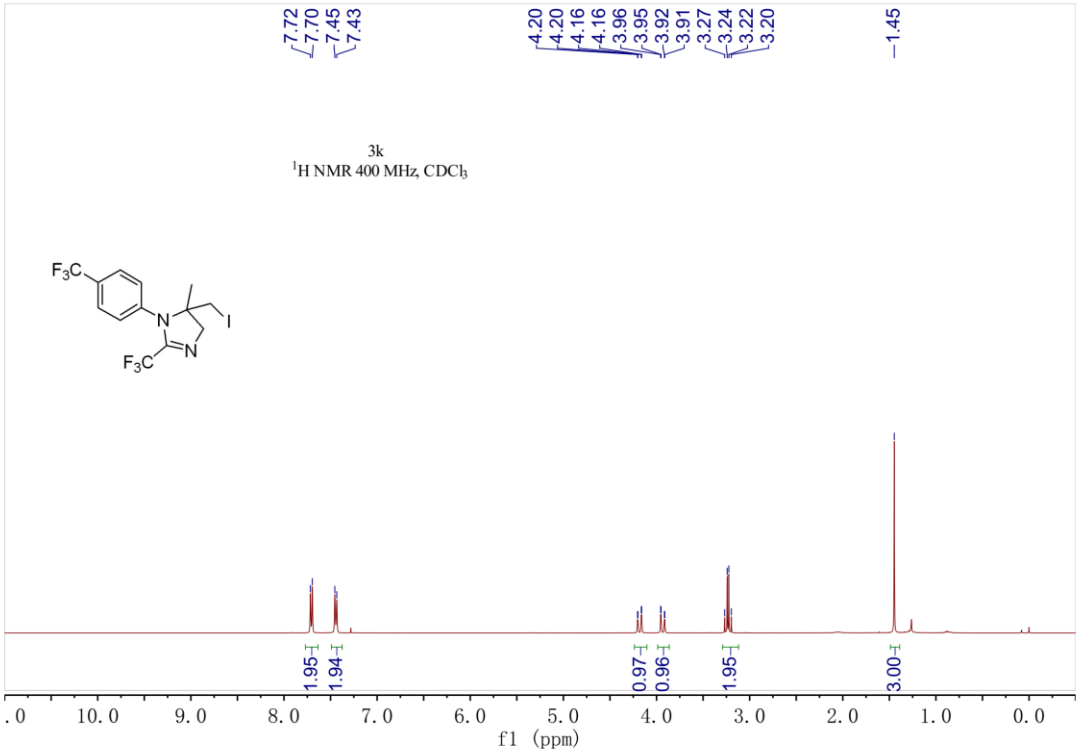

152.1
151.8
135.2
133.1
131.8
129.5
121.5
118.8
116.1
113.3
67.6
66.7
24.6
15.7
3i
^{13}C{^{1}H} NMR 101MHz, CDCl$_3$
Cl
N
I
F$_3$C
N
f1 (ppm)

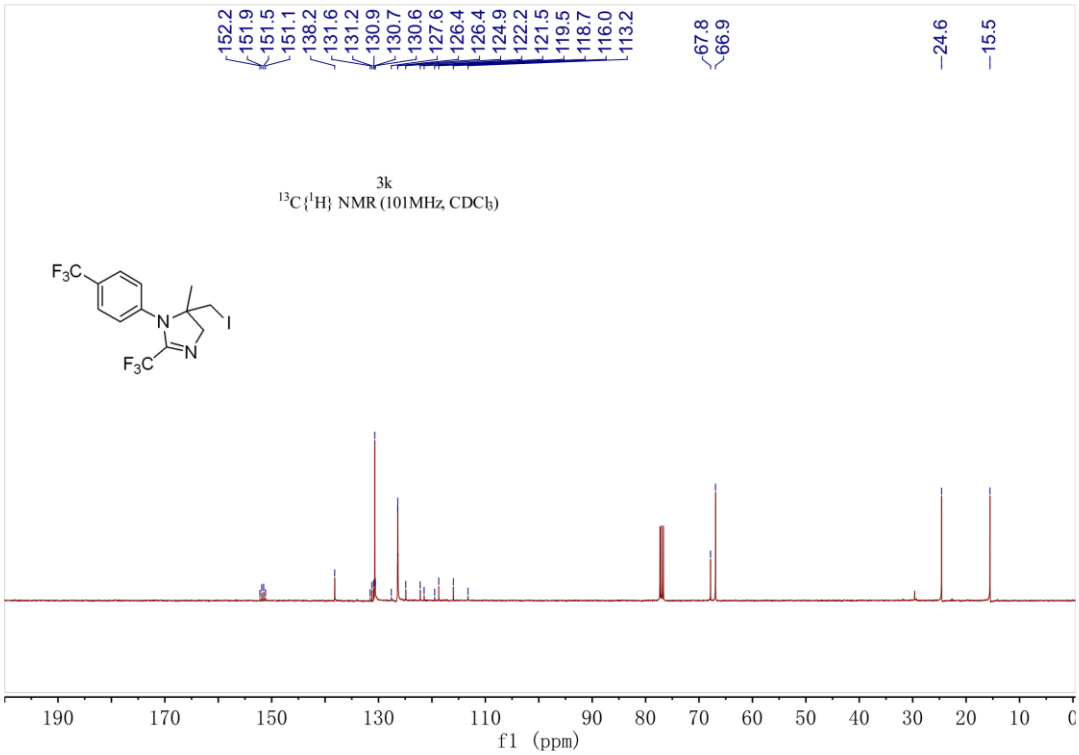

-65.64
3i
19F NMR 377 MHz, CDCl3
Cl
N
I
F3C
N
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
f1 (ppm)

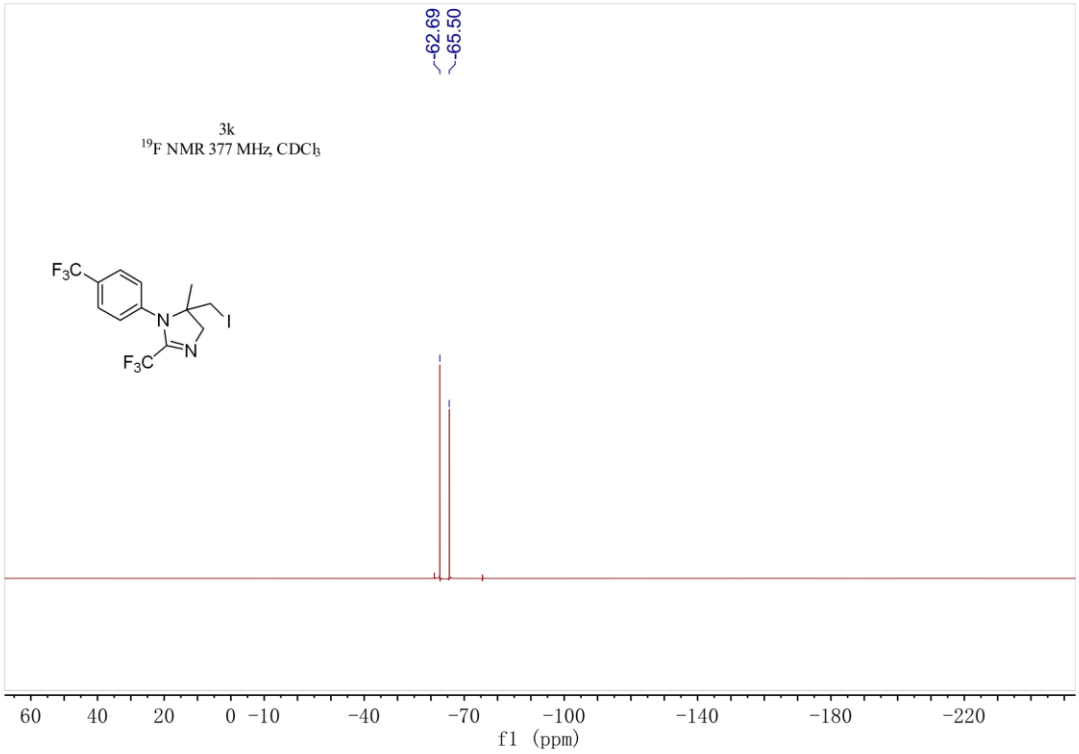

7.60
7.57
7.22
7.20
4.19
4.19
4.15
4.15
3.94
3.94
3.90
3.90
3.27
3.24
3.22
3.20
1.45
3j
13H NMR 400 MHz, CDCl3
Br
N
I
F3C
N
1.98
1.94
0.99
0.98
2.00
3.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

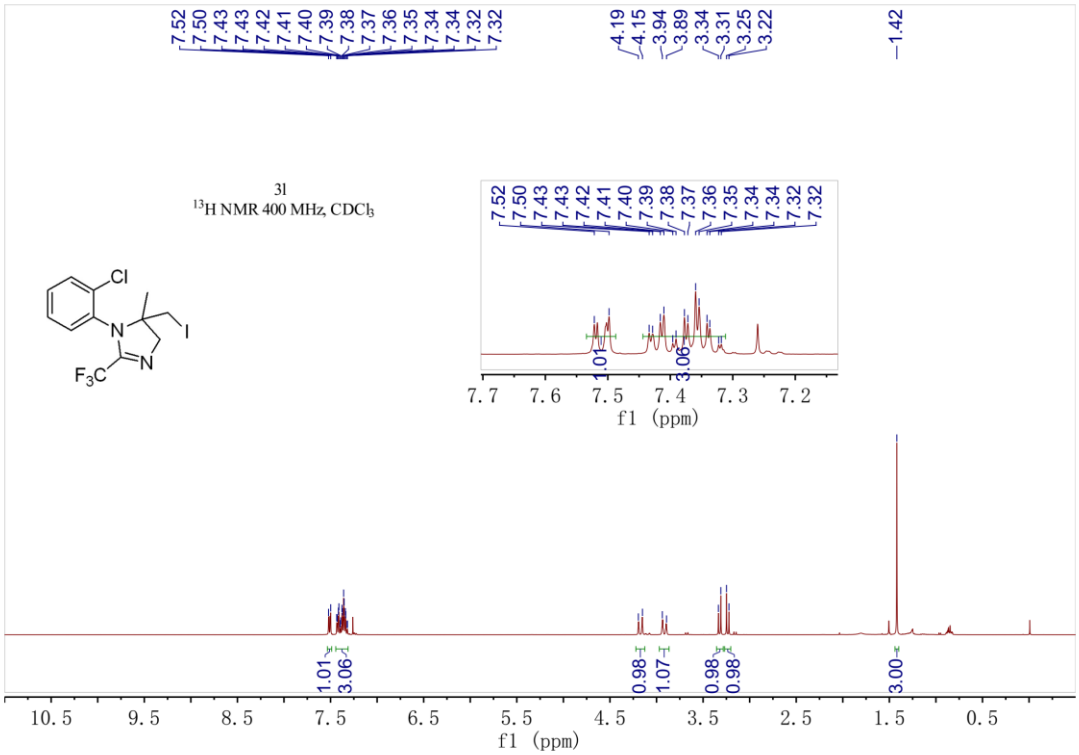

152.6
152.3
151.9
151.6
133.9
132.8
132.3
123.5
121.8
119.0
116.3
113.6
67.8
67.0
24.8
16.0
3j
13C {1H} NMR 101MHz, CDCl3
Br
N
I
N
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

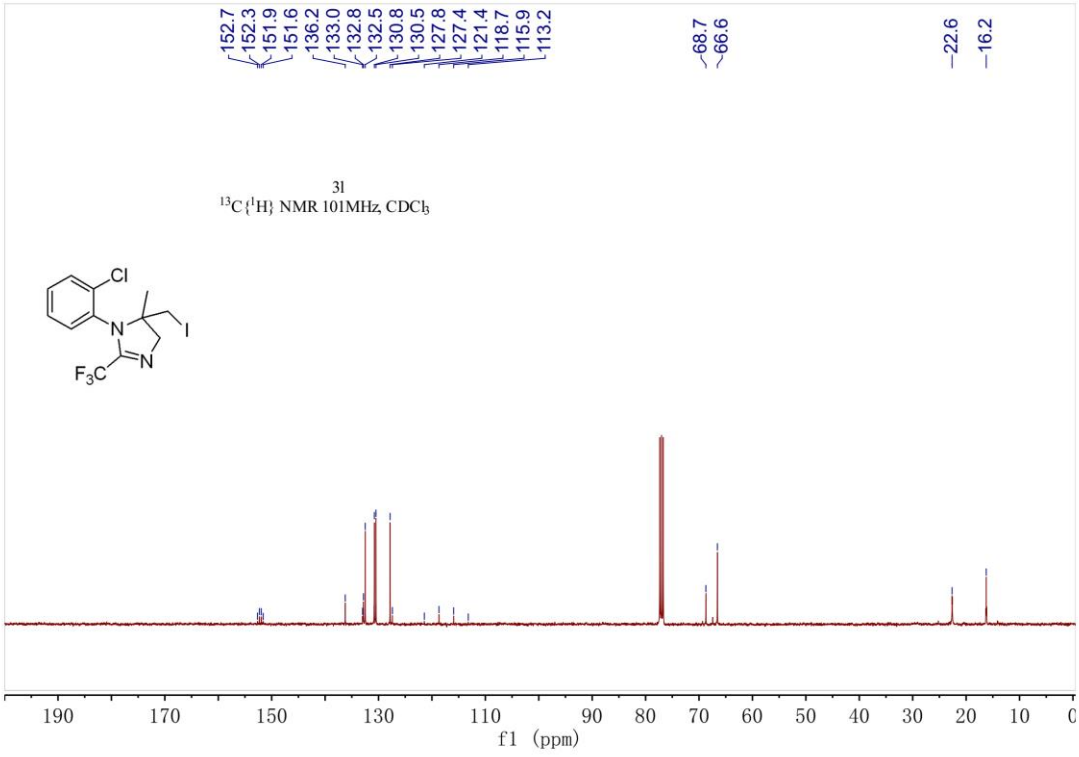

-65.64
3j
19F NMR 377 MHz, CDCl3
Br
N
I
N
F3C
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
f1 (ppm)

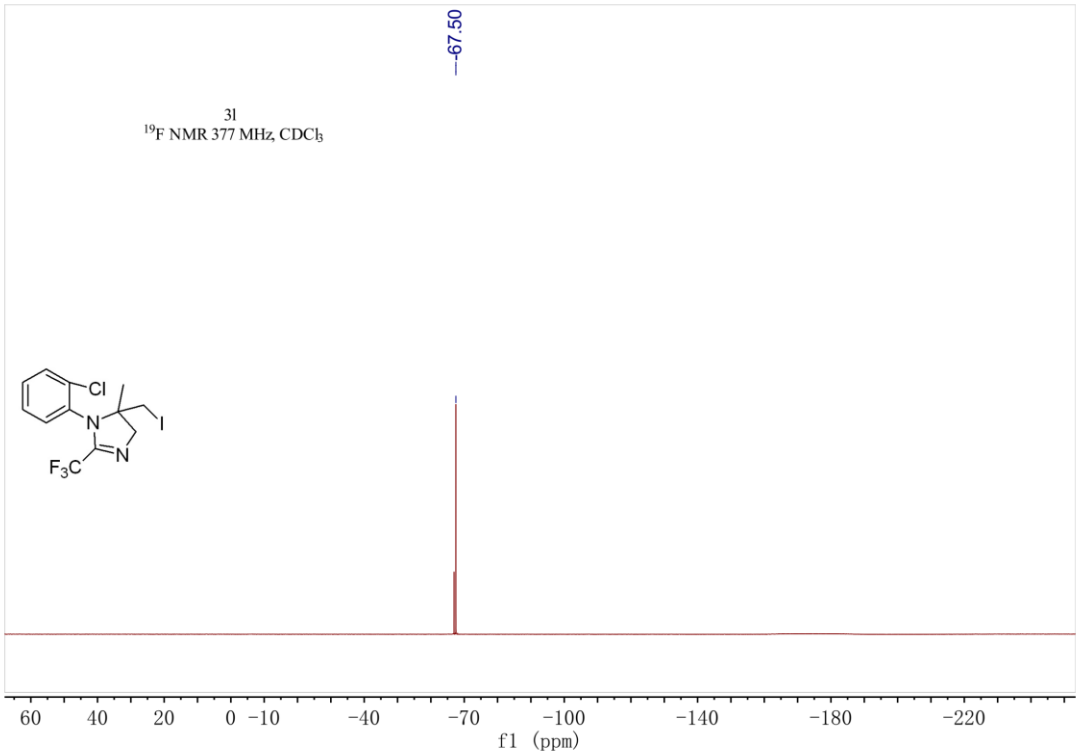

7.72
7.70
7.45
7.43
4.20
4.20
4.16
4.16
3.96
3.95
3.92
3.91
3.27
3.24
3.22
3.20
1.45
3k
1H NMR 400 MHz, CDCl3
F3C
N
I
F3C
N
1.95
1.94
0.97
0.96
1.95
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

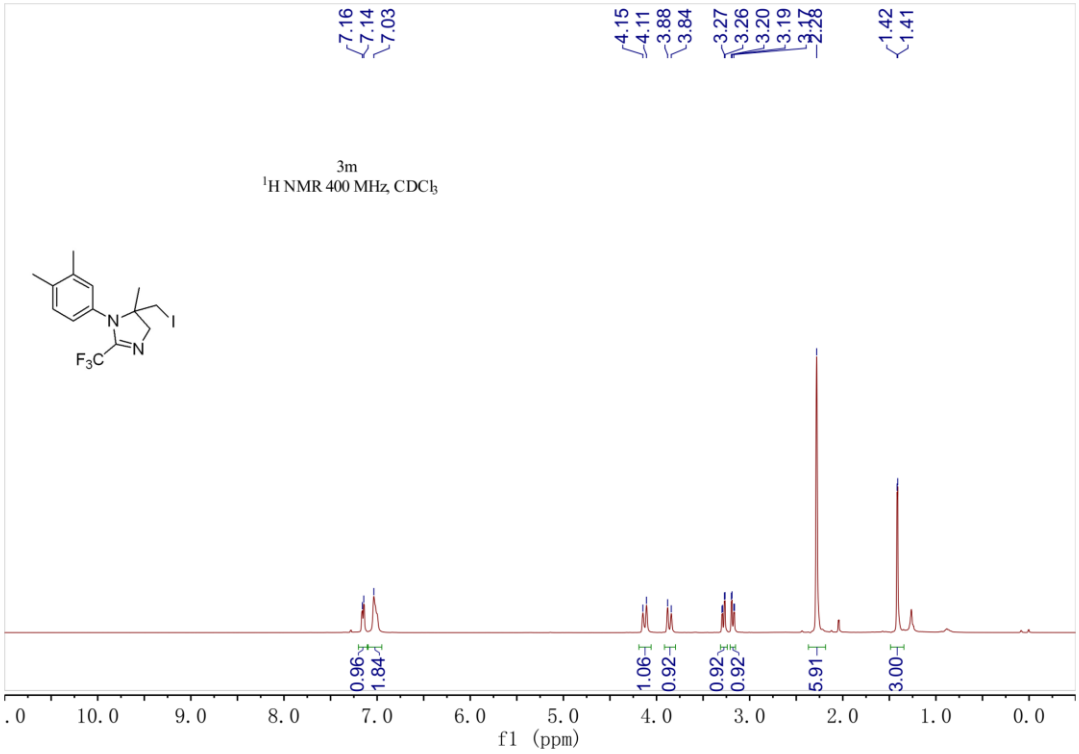

152.2
151.9
151.5
151.1
138.2
131.6
131.2
130.9
130.7
130.6
127.6
126.4
126.4
124.9
122.2
121.5
119.5
118.7
116.0
113.2
67.8
66.9
24.6
15.5
3k
13C{1H} NMR (101MHz, CDCl3)
F3C
N
I
F3C
N
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

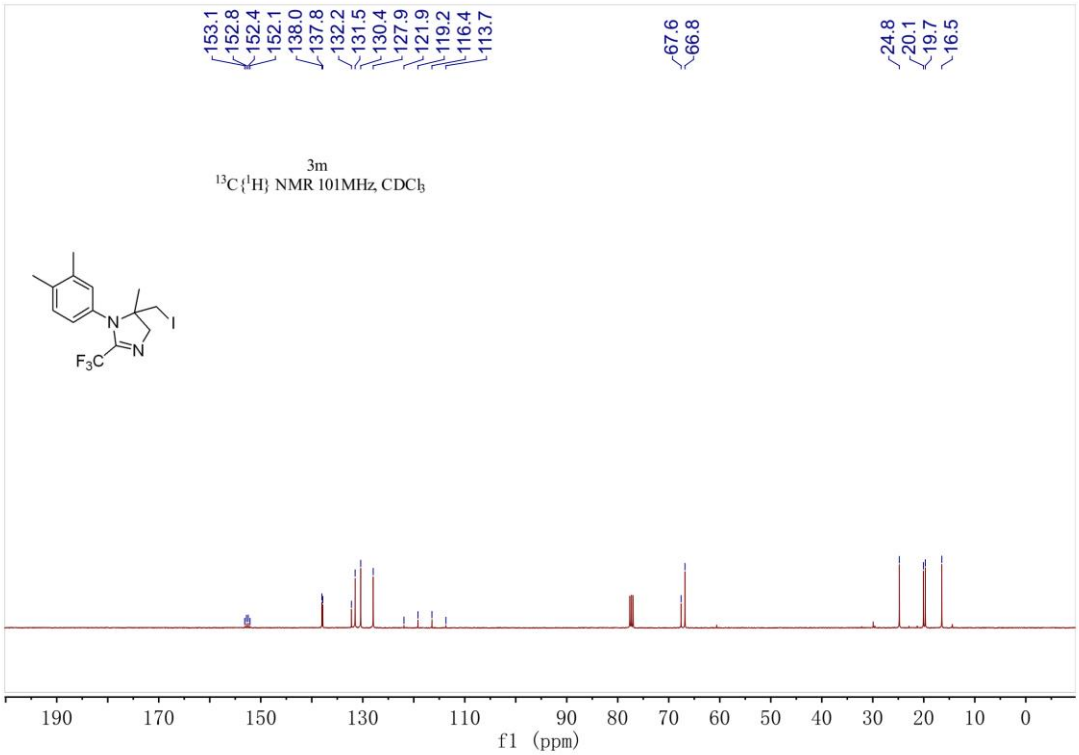

-62.69
-65.50
3k
19F NMR 377 MHz, CDCl3
F3C
N
I
F3C
N
60 40 20 0 -10 -40 -70 -100 -140 -180 -220
f1 (ppm)

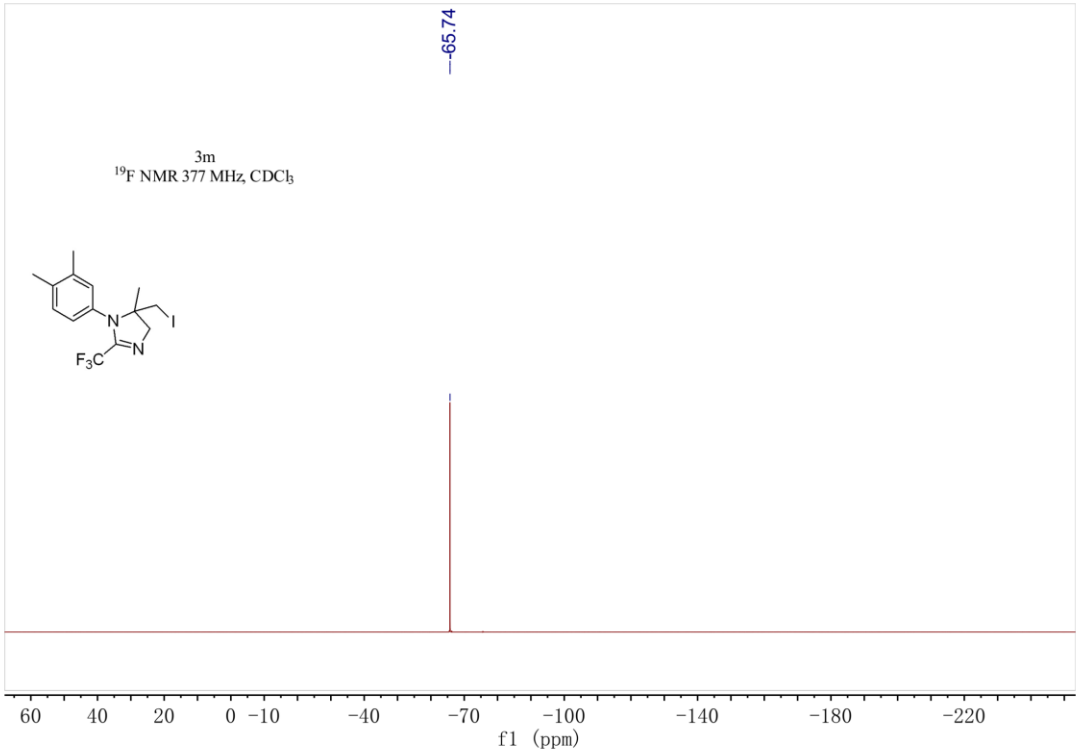

7.52 7.50 7.43 7.43 7.42 7.41 7.40 7.39 7.38 7.37 7.36 7.35 7.34 7.34 7.32 7.32
4.19 4.15 3.94 3.89 3.34 3.31 3.25 3.22
1.42
3l
13H NMR 400 MHz, CDCl3
Cl
N
I
F3C
N
1.01
3.06
7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
1.01 3.06 0.98 1.07 0.98 0.98 3.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

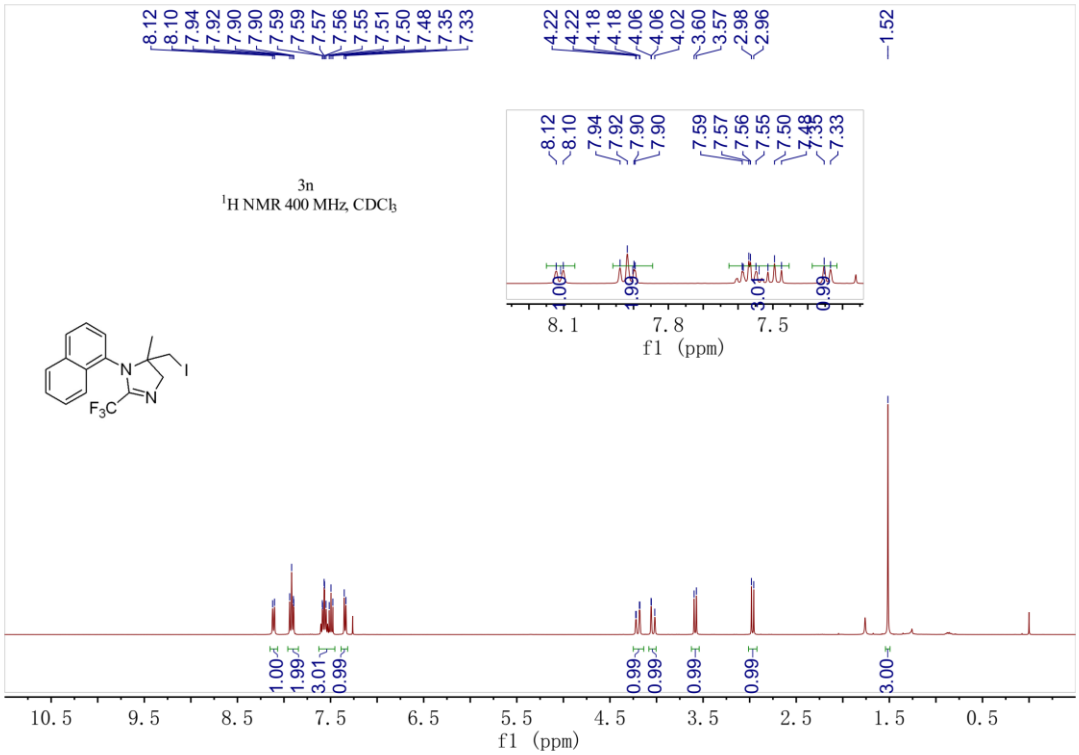

152.7
152.3
151.9
151.6
136.2
133.0
132.8
132.5
130.8
130.5
127.8
127.4
121.4
118.7
115.9
113.2
68.7
66.6
22.6
16.2
3l
$^{13}C\{^{1}H\}$ NMR 101MHz, $CDCl_3$
Cl
N
I
N
F_3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

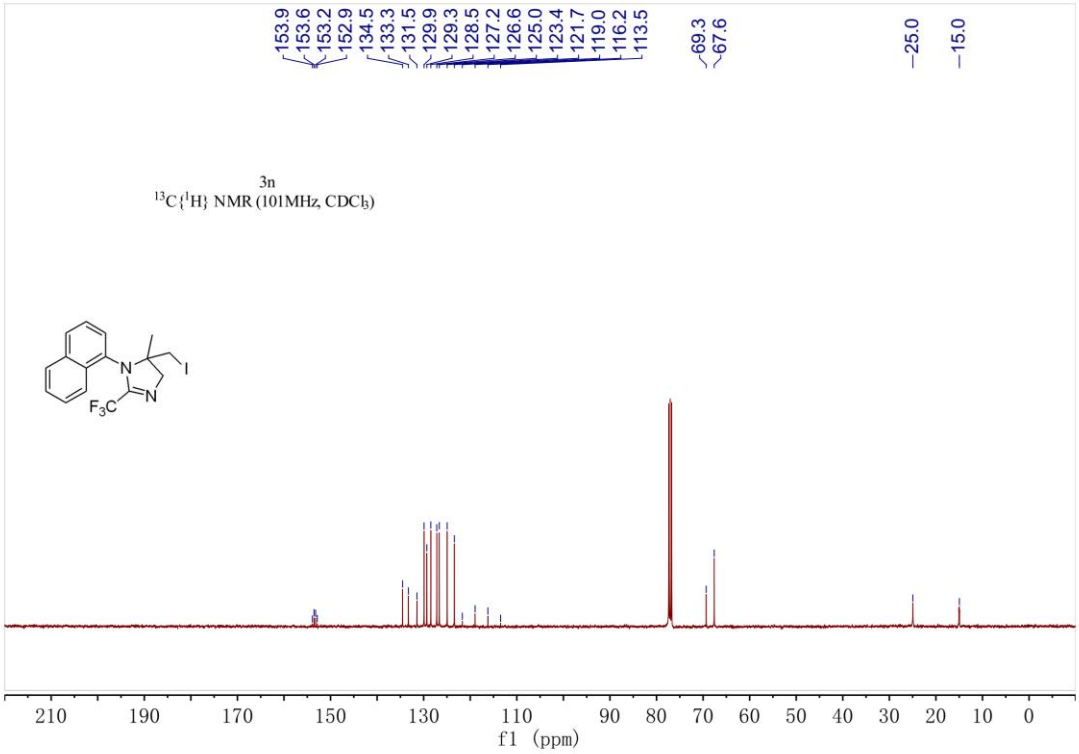

-67.50
3l
^{19}F NMR 377 MHz, $CDCl_3$
Cl
N
I
N
F_3C
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
f1 (ppm)

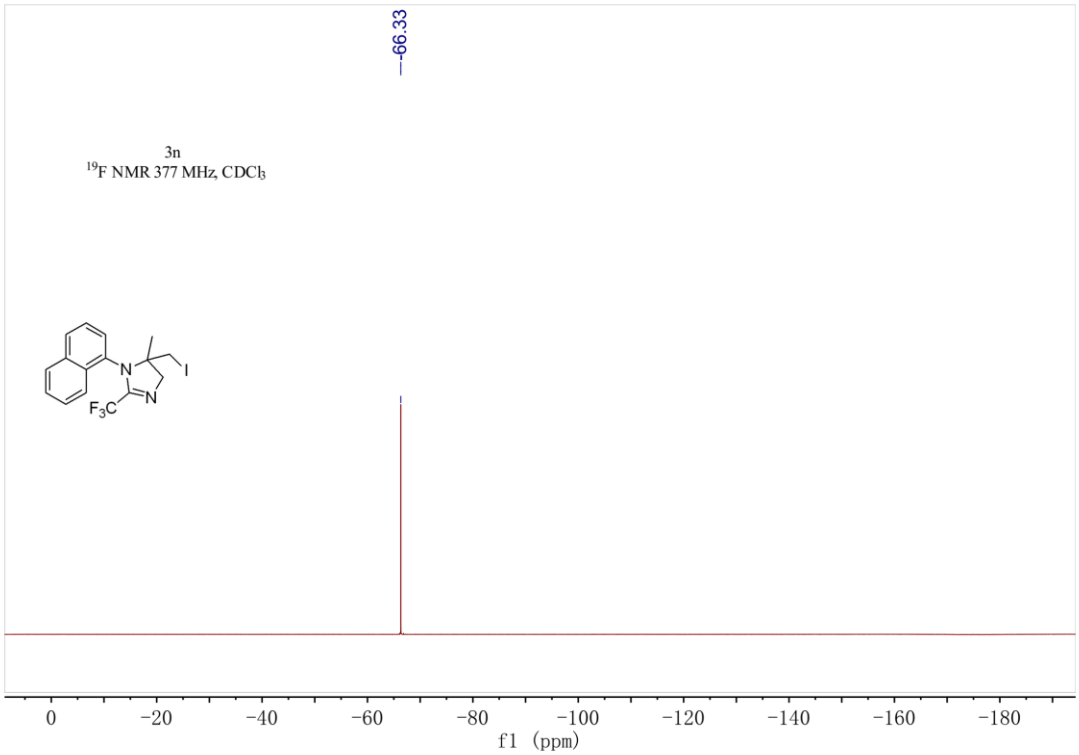

7.16
7.14
7.03
4.15
4.11
3.88
3.84
3.27
3.26
3.20
3.19
2.28
1.42
1.41
3m
1H NMR 400 MHz, CDCl3
0.96
1.84
1.06
0.92
0.92
0.92
5.91
3.00
f1 (ppm)

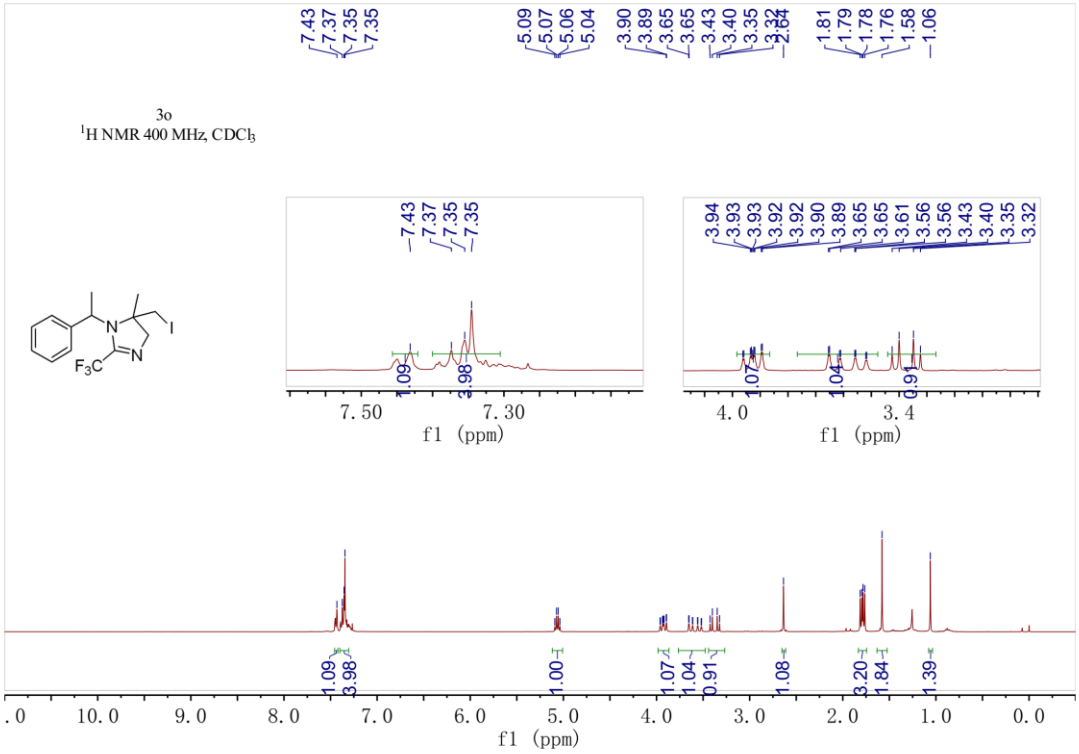

153.1
152.8
152.4
152.1
138.0
137.8
132.2
131.5
130.4
127.9
121.9
119.2
116.4
113.7
67.6
66.8
24.8
20.1
19.7
16.5
3m
13C{1H} NMR 101MHz, CDCl3
f1 (ppm)

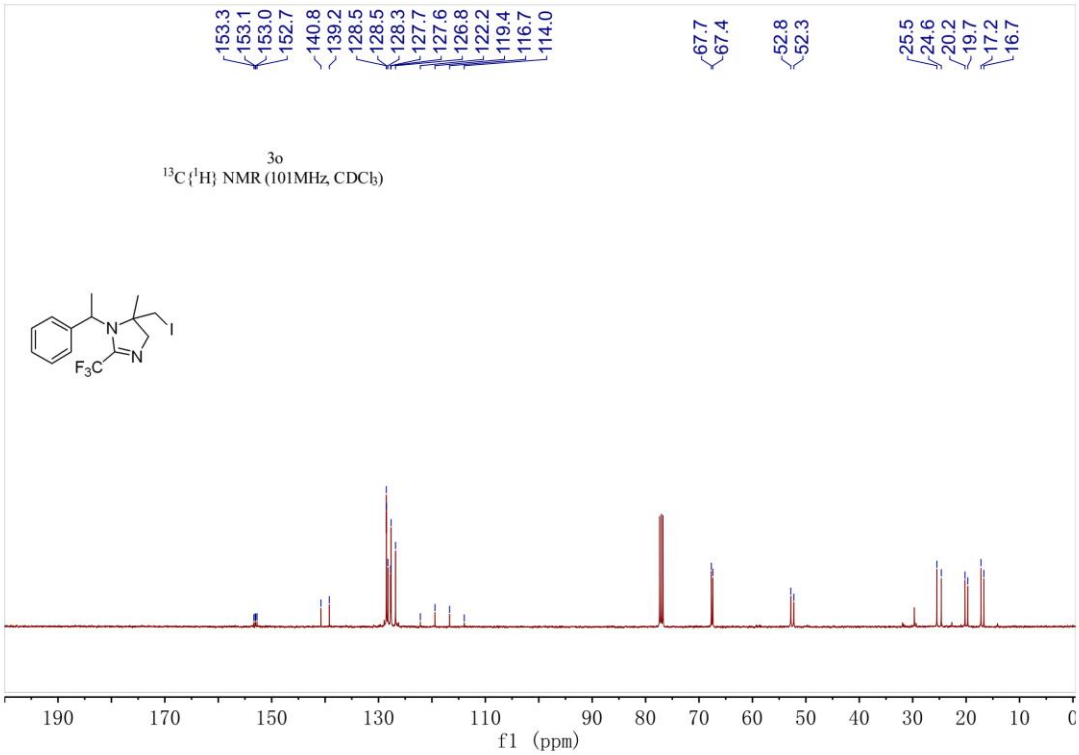

-65.74
3m
19F NMR 377 MHz, CDCl3
F3C
N
I
60 40 20 0 -10 -40 -70 -100 -140 -180 -220
f1 (ppm)

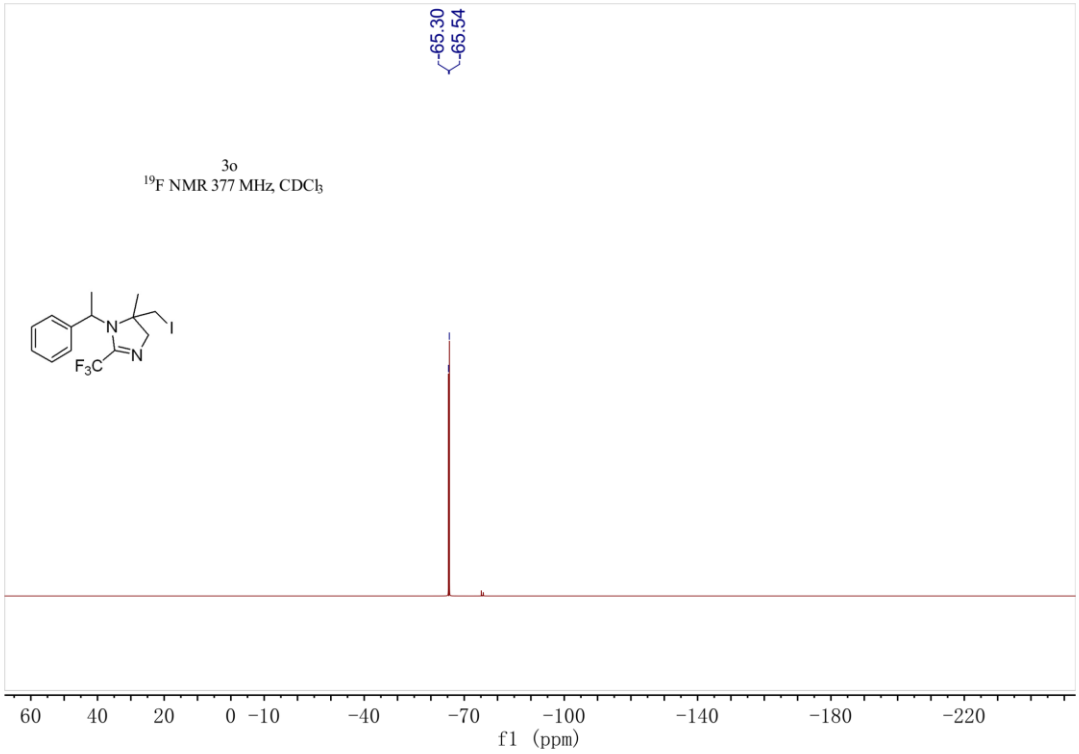

8.12 8.10 7.94 7.92 7.90 7.90 7.59 7.59 7.57 7.56 7.55 7.51 7.50 7.48 7.35 7.33
4.22 4.22 4.18 4.18 4.06 4.06 4.02 3.60 3.57 2.98 2.96
1.52
3n
1H NMR 400 MHz, CDCl3
F3C
N
I
1.00 1.99 3.01 0.99 0.99 0.99 0.99 0.99 3.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)
8.1 7.8 7.5
f1 (ppm)

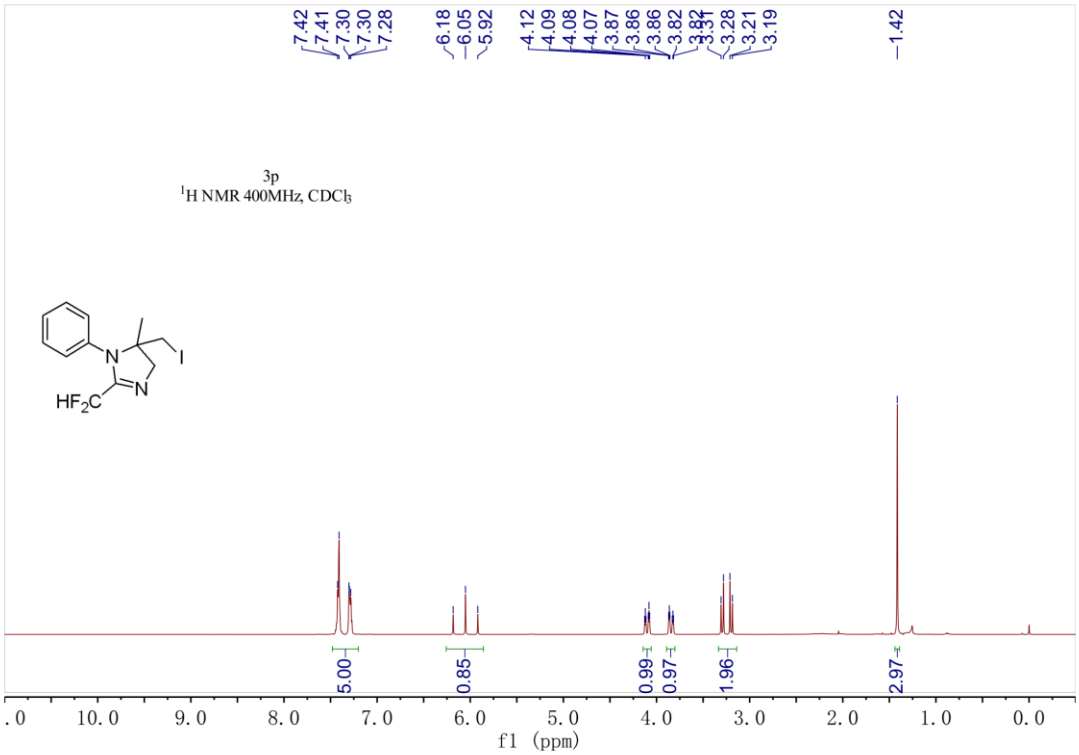

153.9
153.6
153.2
152.9
134.5
133.3
131.5
129.9
129.3
128.5
127.2
126.6
125.0
123.4
121.7
119.0
116.2
113.5
69.3
67.6
25.0
15.0
3n
13C{1H} NMR (101MHz, CDCl3)
N
I
F3C
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

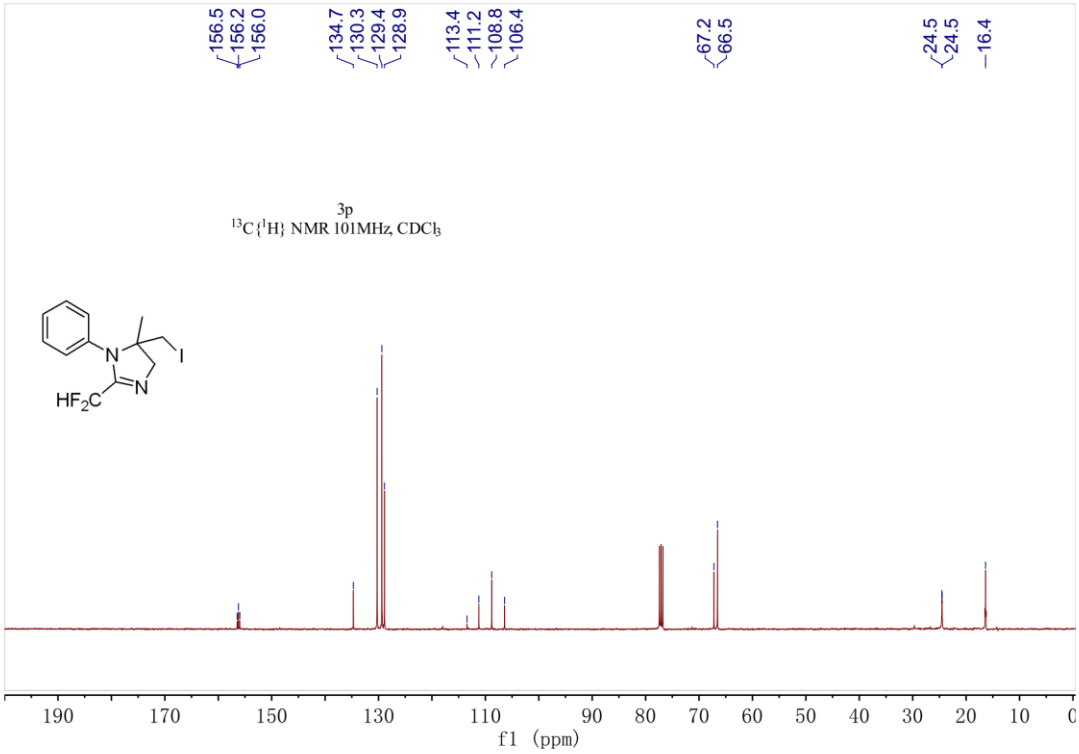

66.33
3n
19F NMR 377 MHz, CDCl3
N
I
F3C
N
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

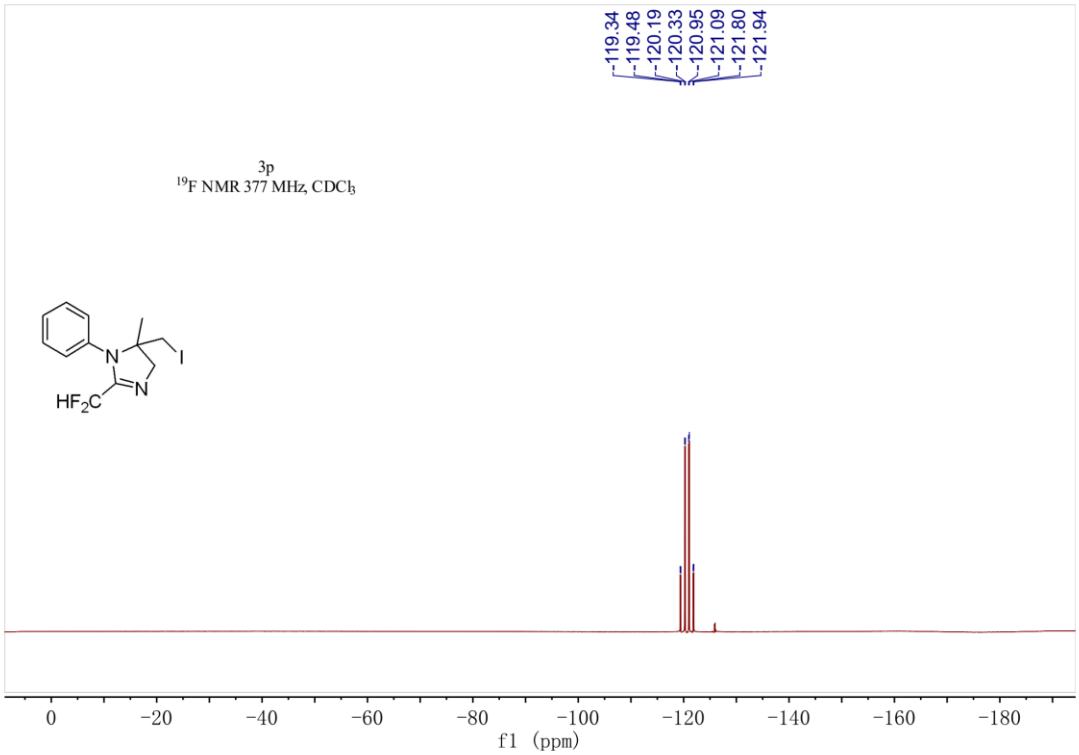

7.43
7.37
7.35
7.35
5.09
5.07
5.06
5.04
3.90
3.89
3.65
3.65
3.43
3.40
3.35
1.81
1.79
1.78
1.76
1.58
1.06
3o
1H NMR 400 MHz, CDCl3
F3C
N
I
1.09
3.98
1.07
1.04
0.91
7.50
7.30
f1 (ppm)
4.0
3.4
f1 (ppm)
1.09
3.98
1.00
1.07
1.04
0.91
1.08
3.20
1.84
1.39
f1 (ppm)

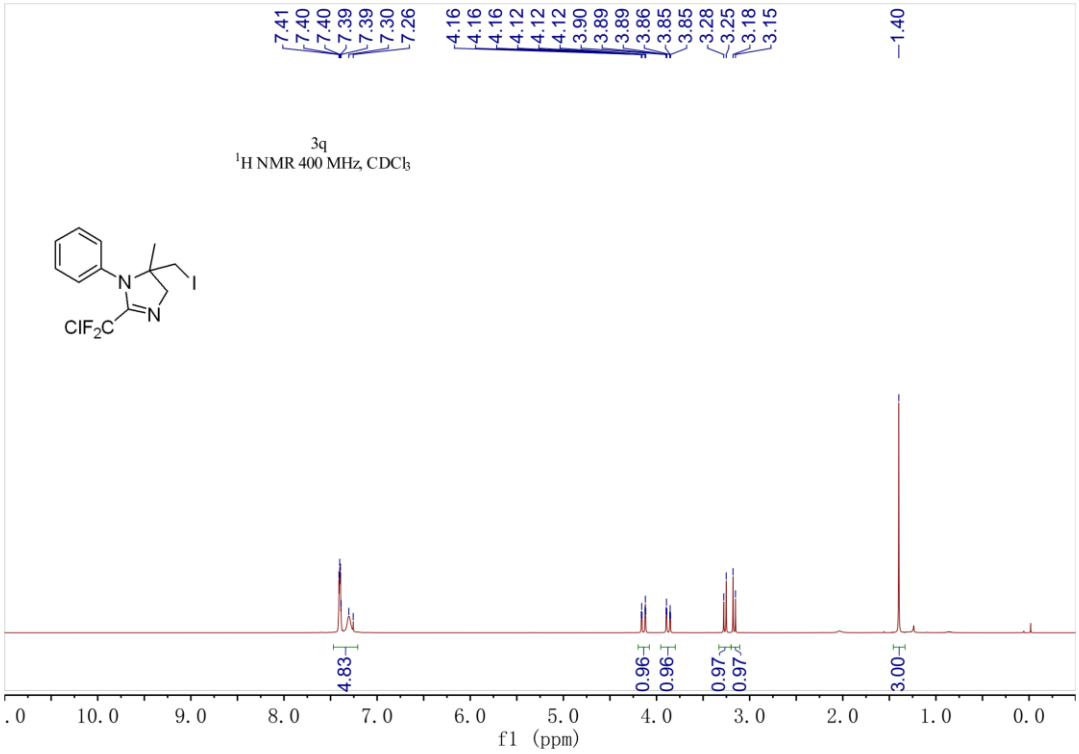

153.3
153.1
153.0
152.7
140.8
139.2
128.5
128.5
128.3
127.7
127.6
126.8
122.2
119.4
116.7
114.0
67.7
67.4
52.8
52.3
25.5
24.6
20.2
19.7
17.2
16.7
3o
13C{1H} NMR (101MHz, CDCl3)
F3C
N
I
f1 (ppm)

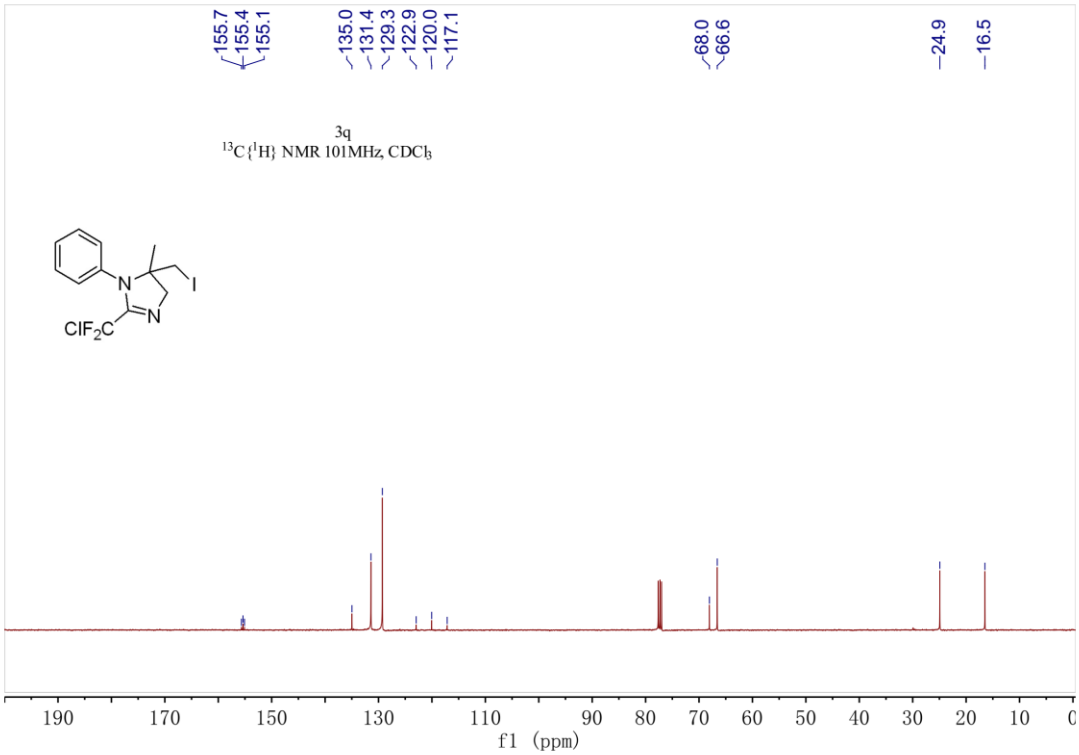

-65.30
-65.54
3o
19F NMR 377 MHz, CDCl3
F3C
N
N
I
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
f1 (ppm)

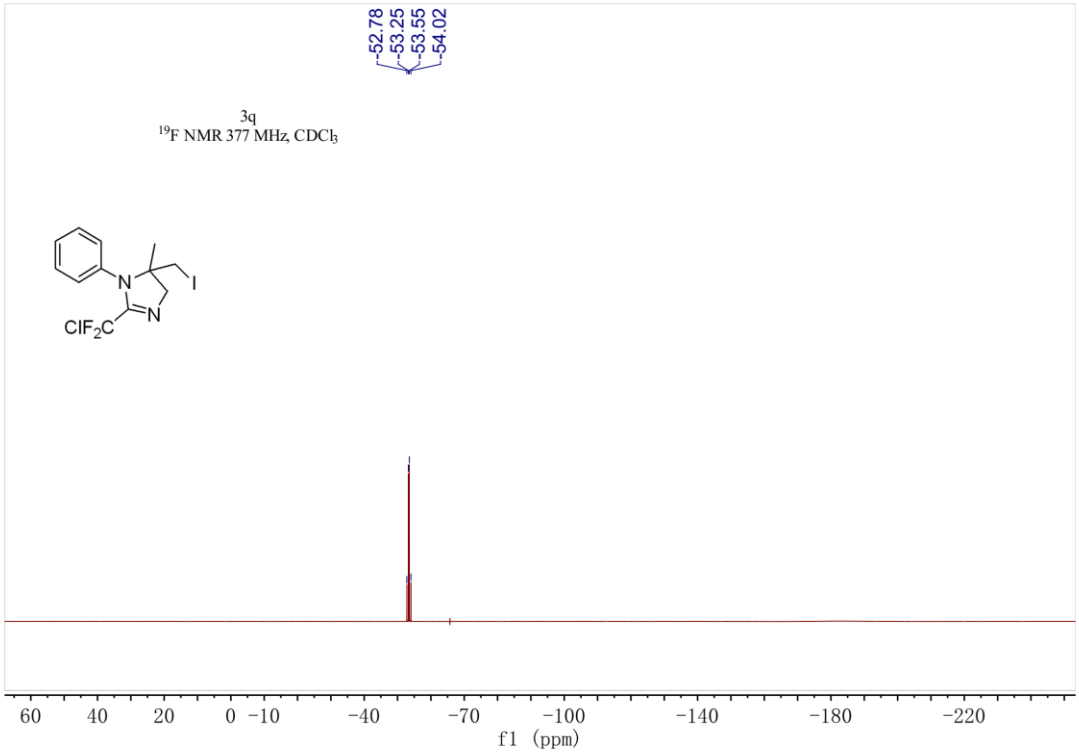

7.42
7.41
7.30
7.30
7.28
6.18
6.05
5.92
4.12
4.09
4.08
4.07
3.87
3.86
3.86
3.82
3.28
3.21
3.19
1.42
3p
1H NMR 400MHz, CDCl3
HF2C
N
N
I
5.00
0.85
0.99
0.97
1.96
2.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

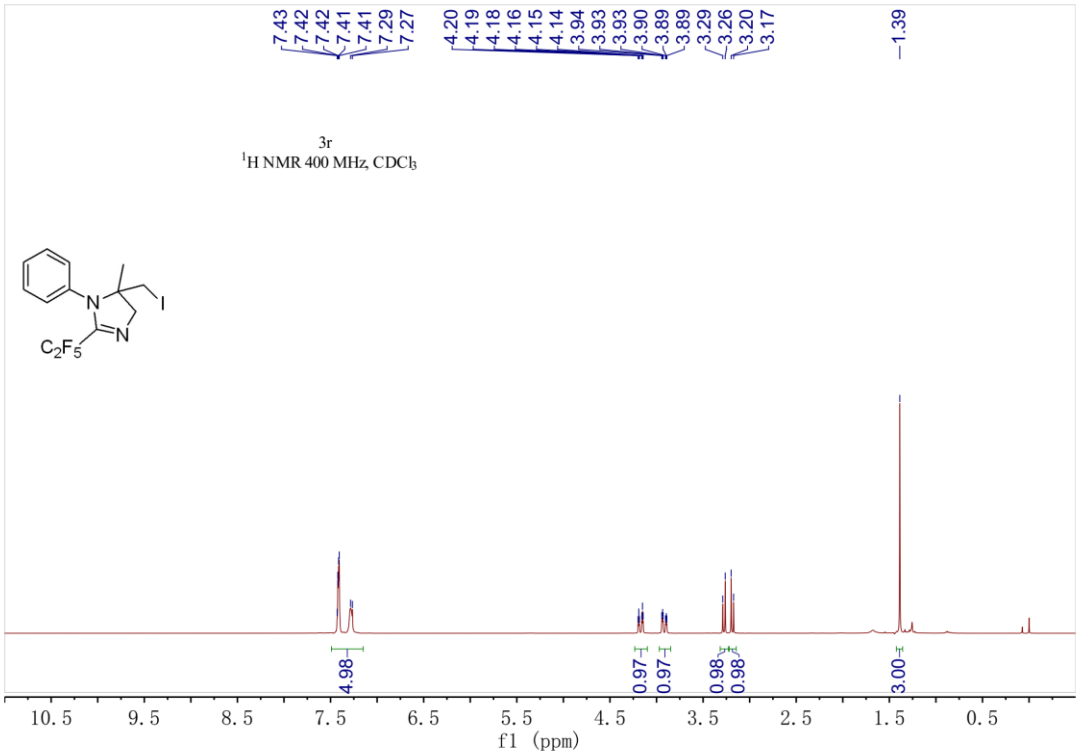

156.5
156.2
156.0
134.7
130.3
129.4
128.9
113.4
111.2
108.8
106.4
67.2
66.5
24.5
24.5
16.4
3p
13C{1H} NMR 101MHz, CDCl3
N
I
N
HF2C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

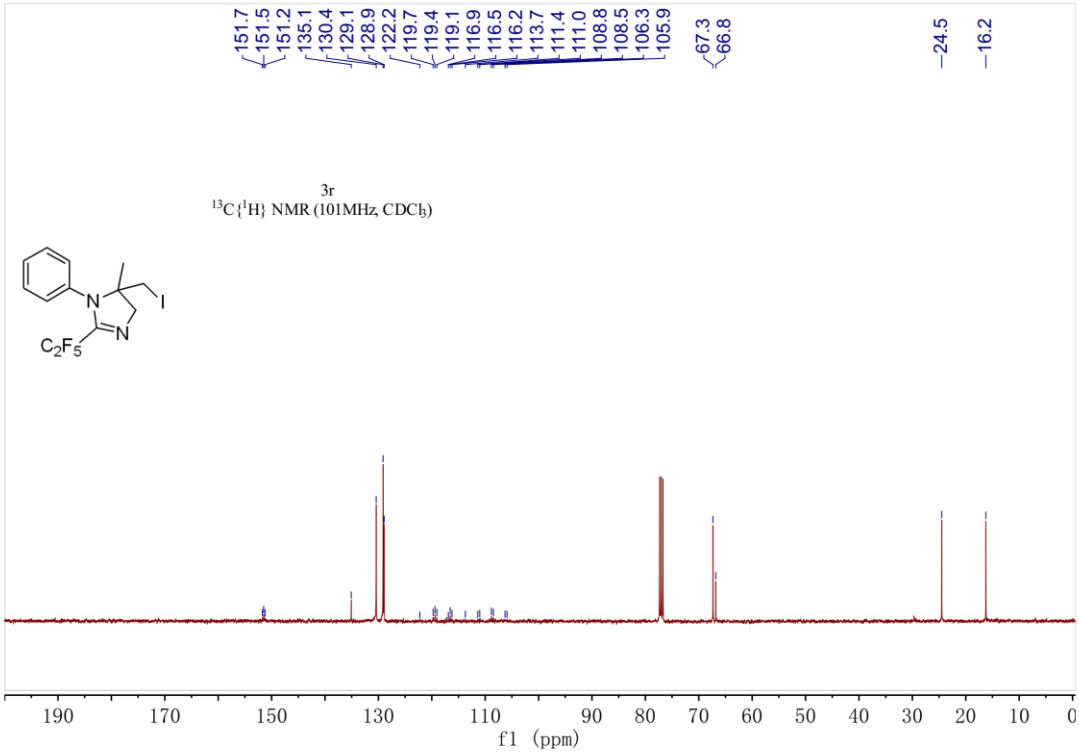

119.34
119.48
120.19
120.33
120.95
121.09
121.80
121.94
3p
19F NMR 377 MHz, CDCl3
N
I
N
HF2C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

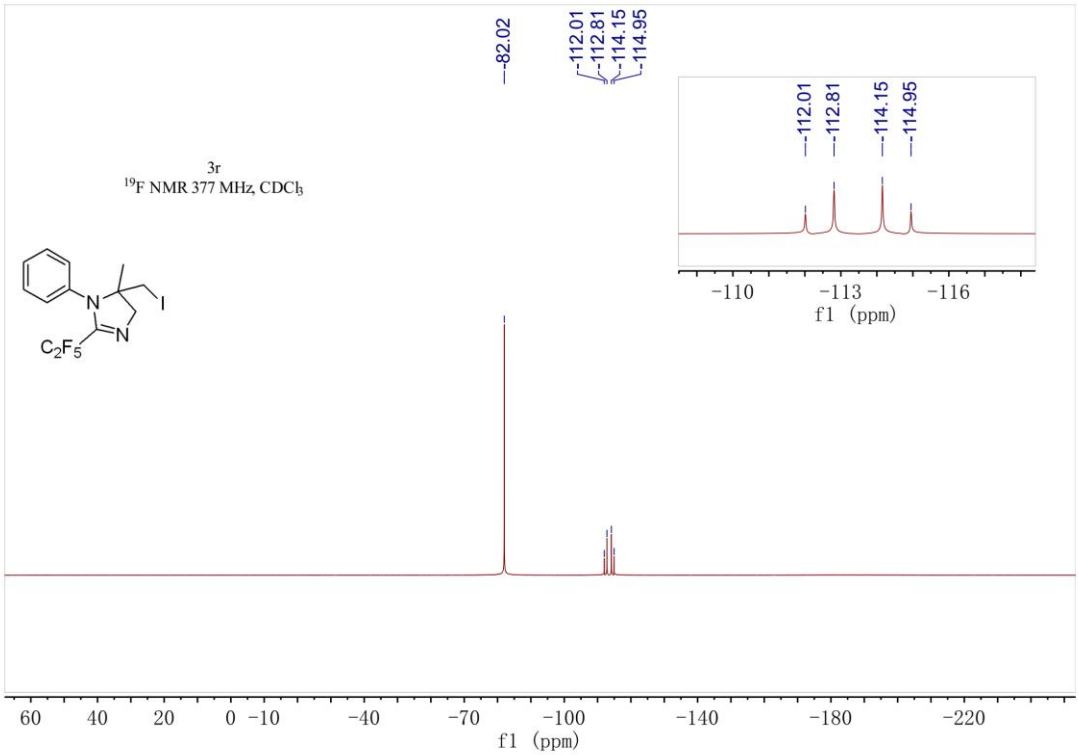

7.41
7.40
7.40
7.39
7.39
7.30
7.26
4.16
4.16
4.16
4.12
4.12
4.12
3.90
3.89
3.89
3.89
3.86
3.85
3.85
3.85
3.28
3.25
3.18
3.15
1.40
3q
1H NMR 400 MHz, CDCl3
ClF2C
I
4.83
0.96
0.96
0.97
0.97
3.00
f1 (ppm)

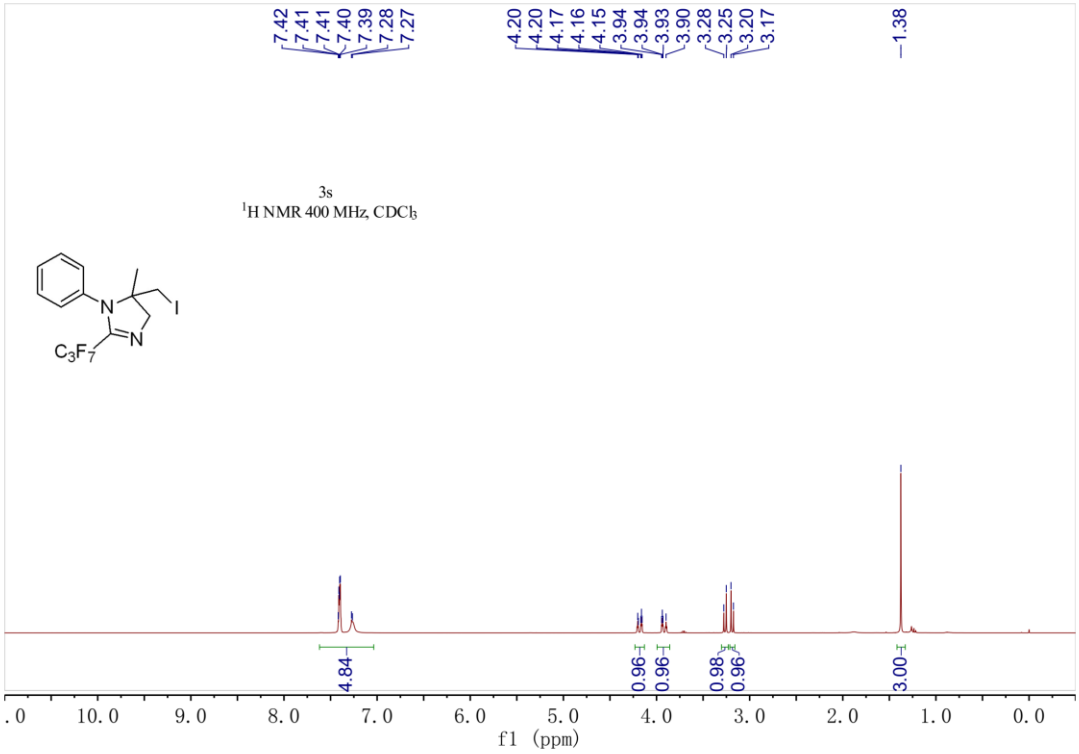

155.7
155.4
155.1
135.0
131.4
129.3
122.9
120.0
117.1
68.0
66.6
24.9
16.5
3q
13C{1H} NMR 101MHz, CDCl3
ClF2C
I
f1 (ppm)

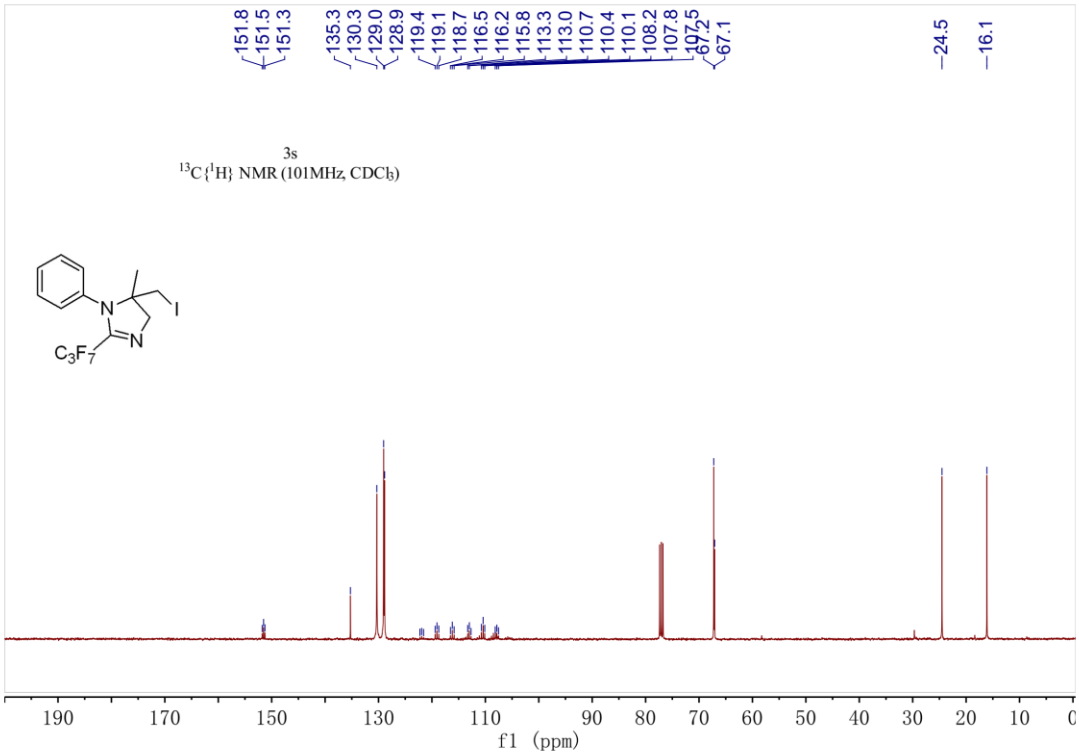

-52.78
-53.25
-53.55
-54.02
3q
19F NMR 377 MHz, CDCl3
N
I
N
ClF2C
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
f1 (ppm)

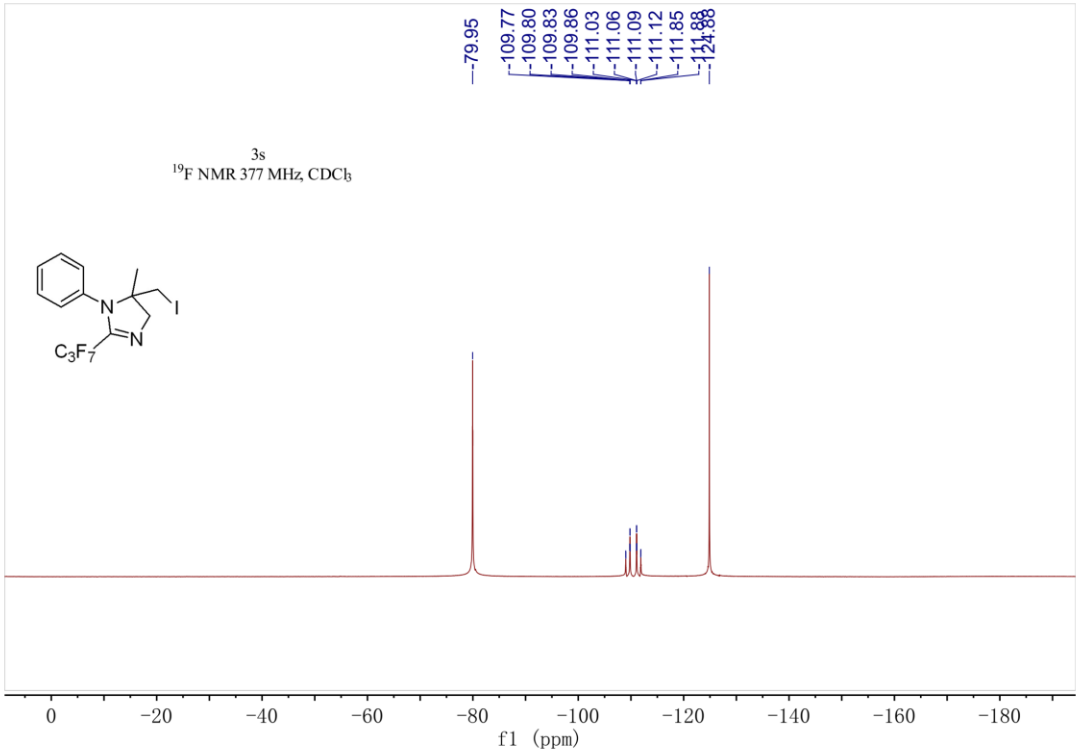

7.43
7.42
7.42
7.41
7.41
7.29
7.27
4.20
4.19
4.18
4.16
4.15
4.14
3.94
3.93
3.93
3.90
3.89
3.89
3.29
3.26
3.20
3.17
1.39
3r
1H NMR 400 MHz, CDCl3
N
I
N
C2F5
4.98
0.97
0.97
0.98
0.98
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

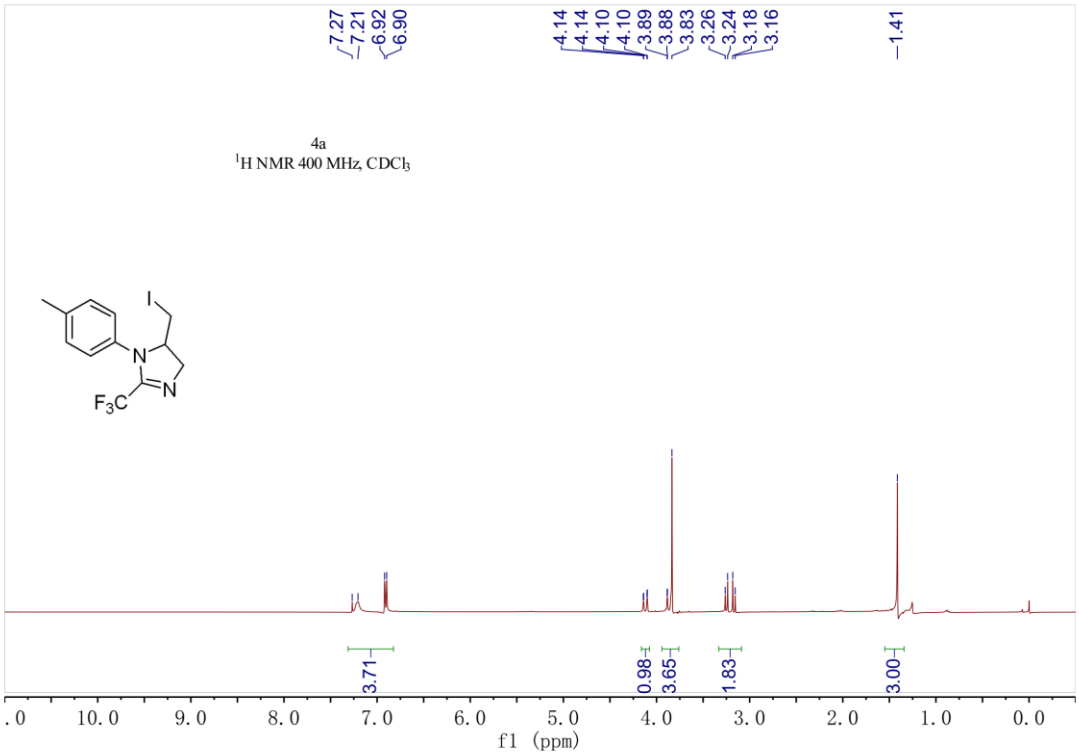

151.7
151.5
151.2
135.1
130.4
129.1
128.9
122.2
119.7
119.4
119.1
116.9
116.5
116.2
113.7
111.4
111.0
108.8
108.5
106.3
105.9
67.3
66.8
24.5
16.2
3r
13C{1H} NMR (101MHz, CDCl3)
I
N
N
C2F5
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

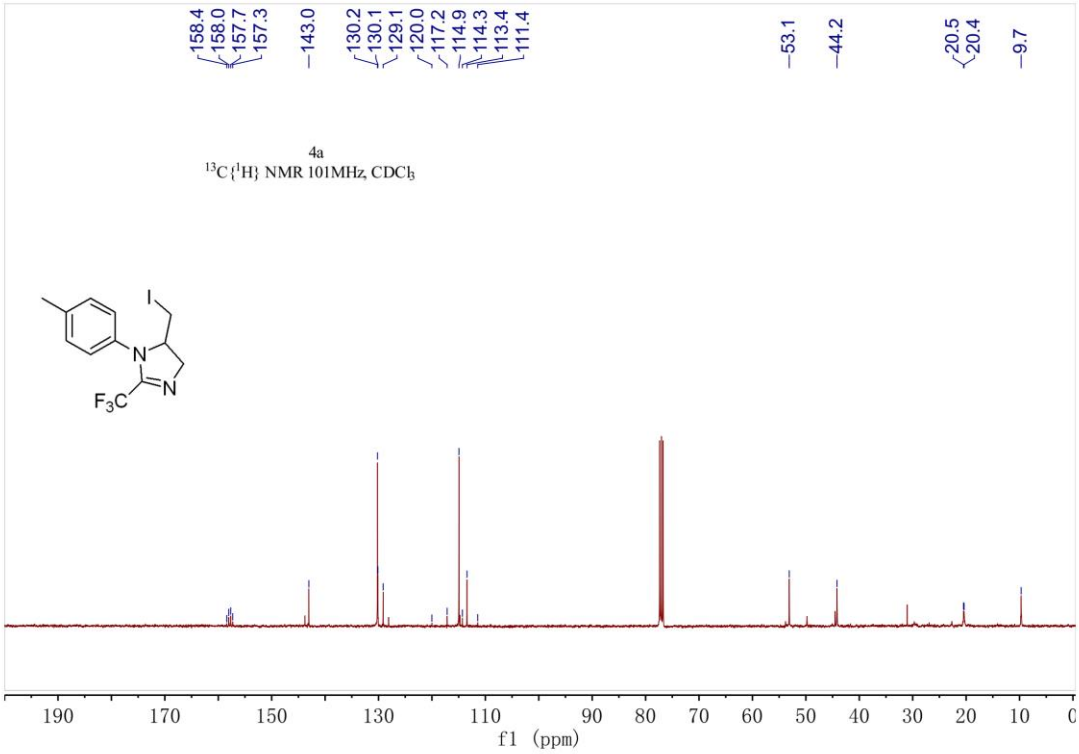

82.02
112.01
112.81
114.15
114.95
3r
19F NMR 377 MHz, CDCl3
I
N
N
C2F5
112.01
112.81
114.15
114.95
−110
−113
−116
f1 (ppm)
60
40
20
0
−10
−40
−70
−100
−140
−180
−220
f1 (ppm)

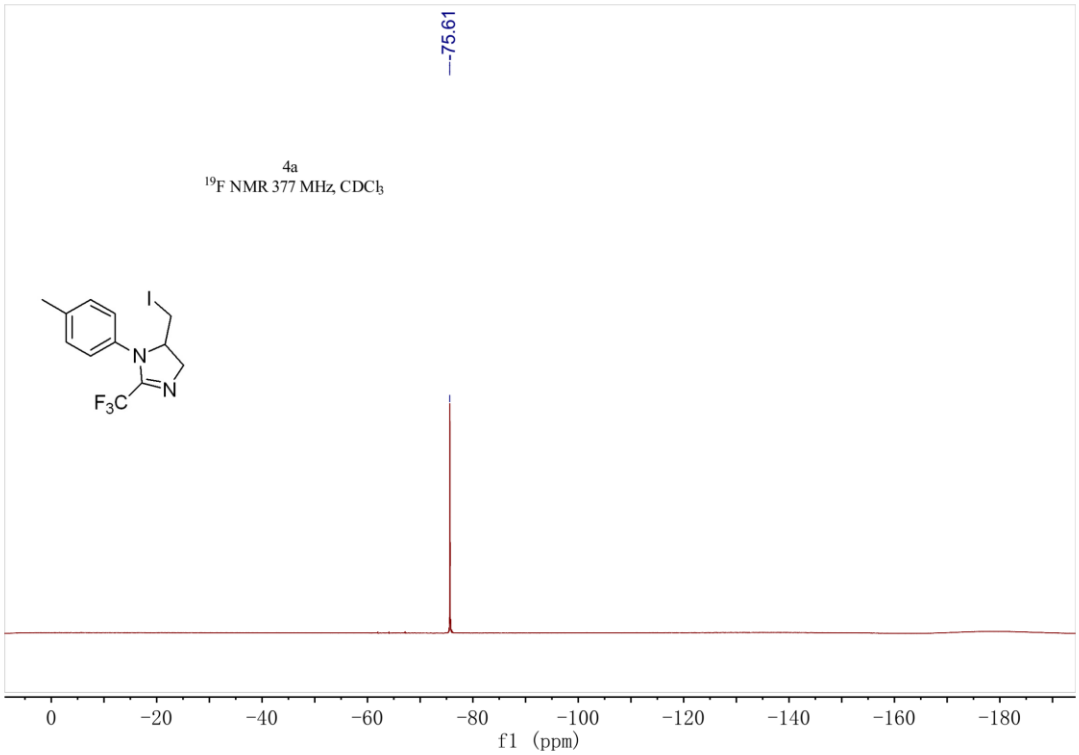

7.42
7.41
7.41
7.40
7.39
7.28
7.27
4.20
4.20
4.17
4.16
4.15
3.94
3.94
3.93
3.90
3.28
3.25
3.20
3.17
1.38
3s
1H NMR 400 MHz, CDCl3
N
I
N
C3F7
4.84
0.96
0.96
0.98
0.96
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

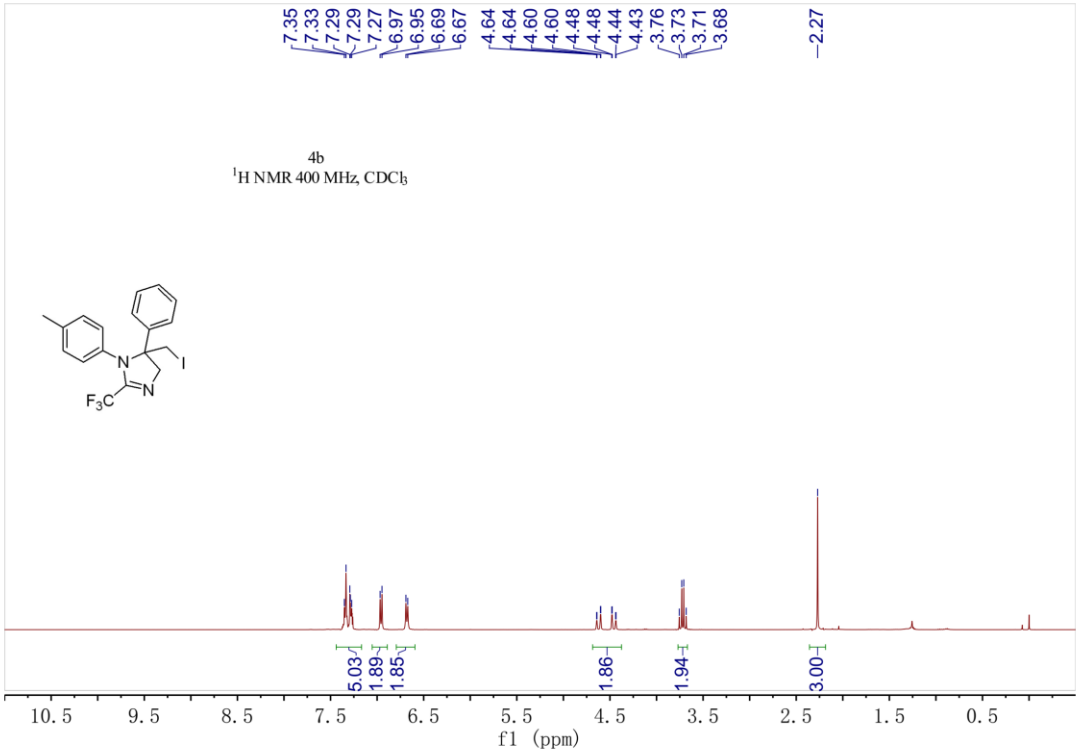

151.8
151.5
151.3
135.3
130.3
129.0
128.9
119.4
119.1
118.7
116.5
116.2
115.8
113.3
113.0
110.7
110.4
110.1
108.2
107.8
107.5
67.2
67.1
24.5
16.1
3s
13C{1H} NMR (101MHz, CDCl3)
N
I
N
C3F7
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

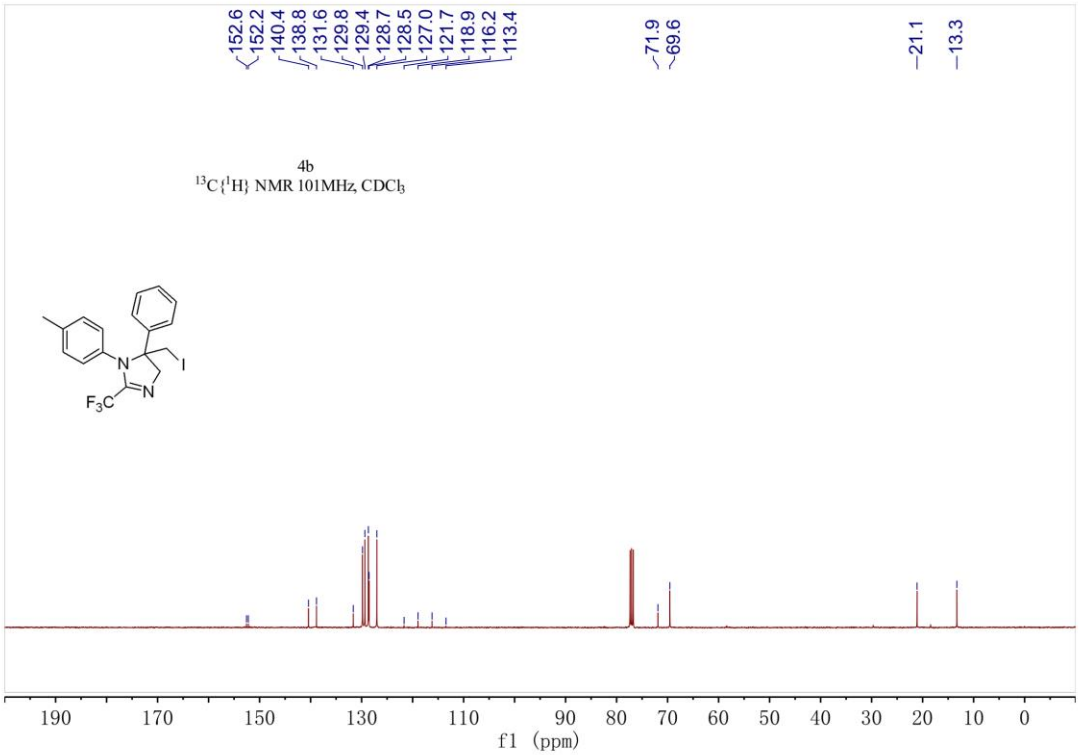

-79.95
-109.77
-109.80
-109.83
-109.86
-111.03
-111.06
-111.09
-111.12
-111.85
-111.88
-124.86
3s
19F NMR 377 MHz, CDCl3
N
I
N
C3F7
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

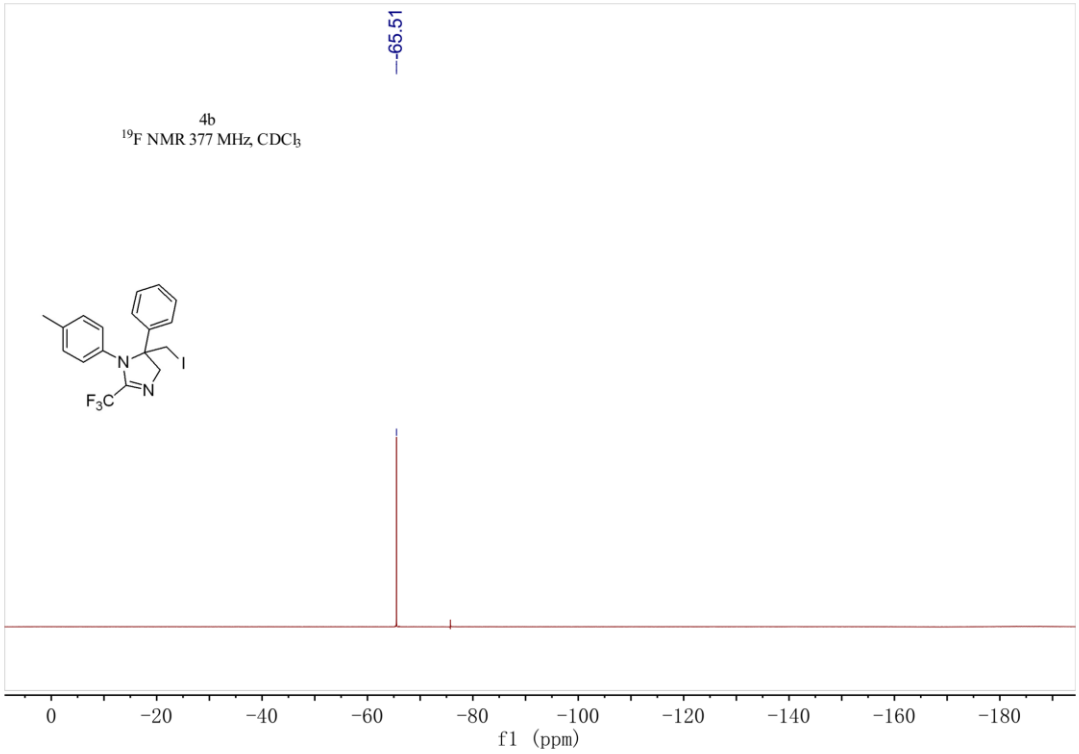

7.27
7.21
6.92
6.90
4.14
4.14
4.10
4.10
3.89
3.88
3.83
3.26
3.24
3.18
3.16
1.41
4a
1H NMR 400 MHz, CDCl3
I
N
N
F3C
3.71
0.98
3.65
1.83
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

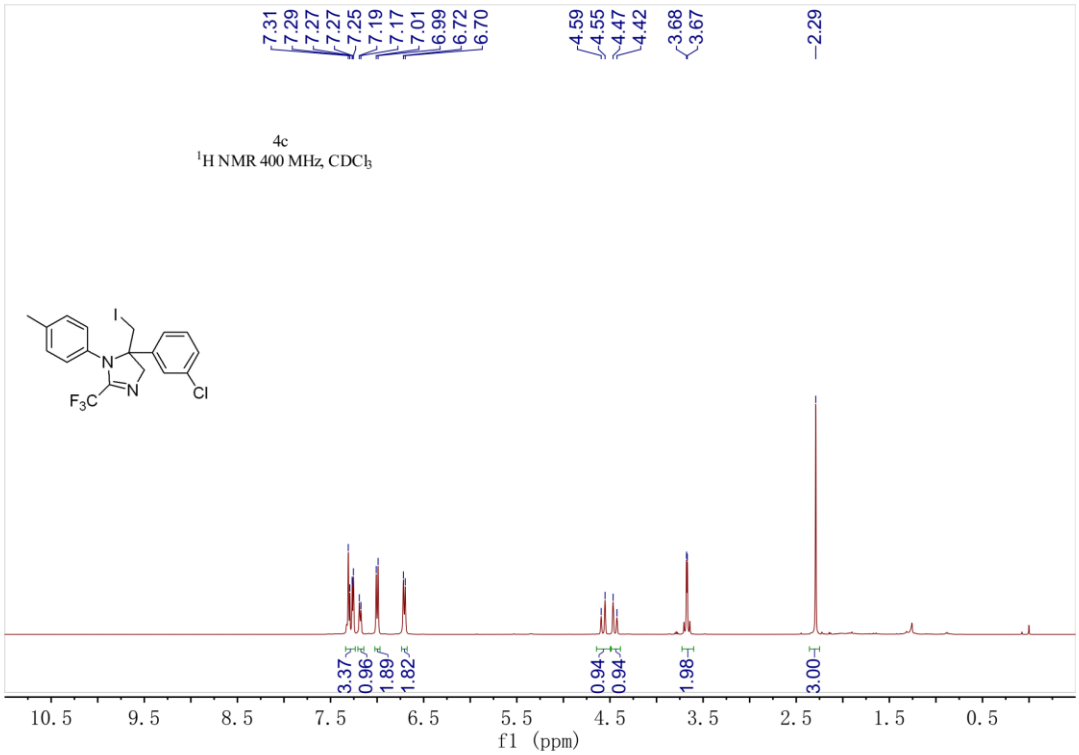

158.4
158.0
157.7
157.3
143.0
130.2
130.1
129.1
120.0
117.2
114.9
114.3
113.4
111.4
53.1
44.2
20.5
20.4
9.7
4a
13C{1H} NMR 101MHz, CDCl3
I
N
N
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

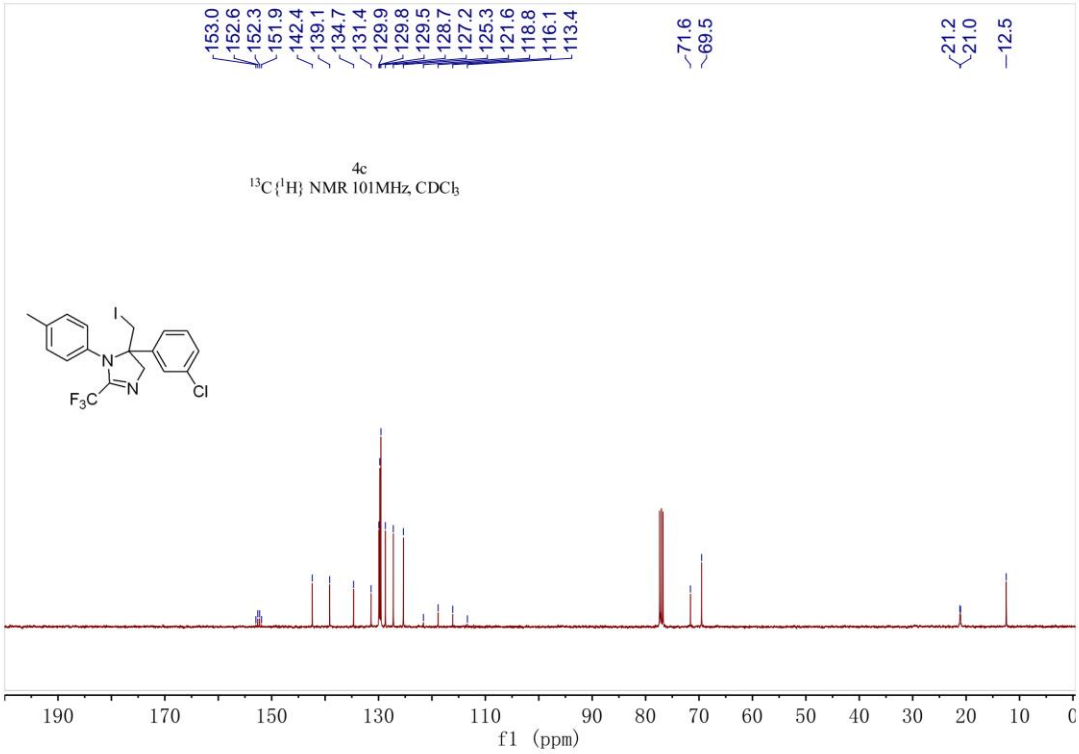

-75.61
4a
19F NMR 377 MHz, CDCl3
I
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

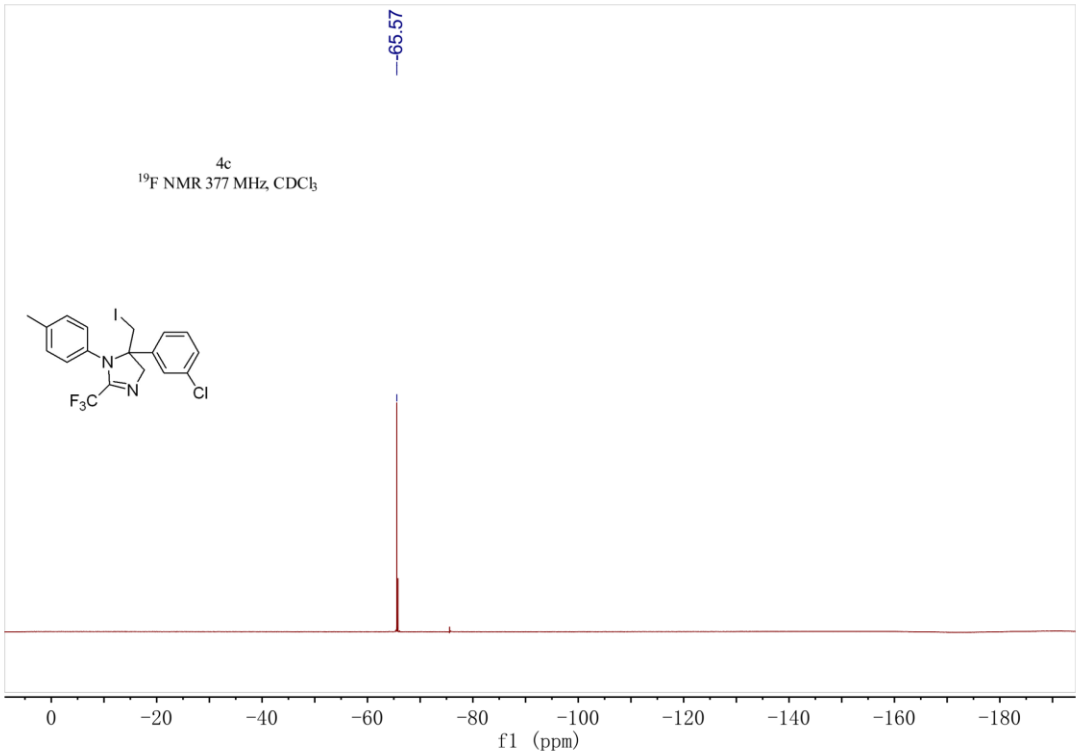

7.35
7.33
7.29
7.29
7.27
6.97
6.95
6.69
6.67
4.64
4.64
4.60
4.60
4.48
4.48
4.44
4.43
3.76
3.73
3.71
3.68
2.27
4b
1H NMR 400 MHz, CDCl3
5.03
1.89
1.85
1.86
1.94
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

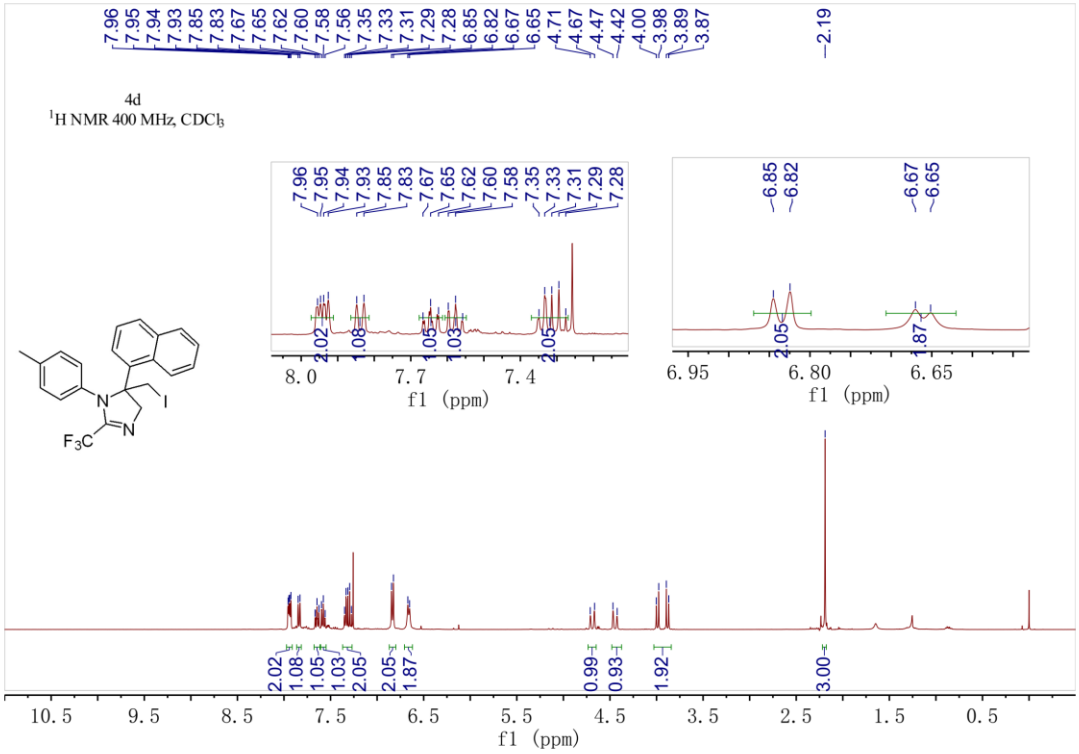

152.6
152.2
140.4
138.8
131.6
129.8
129.4
128.7
128.5
127.0
121.7
118.9
116.2
113.4
71.9
69.6
21.1
13.3
4b
13C{1H} NMR 101MHz, CDCl3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

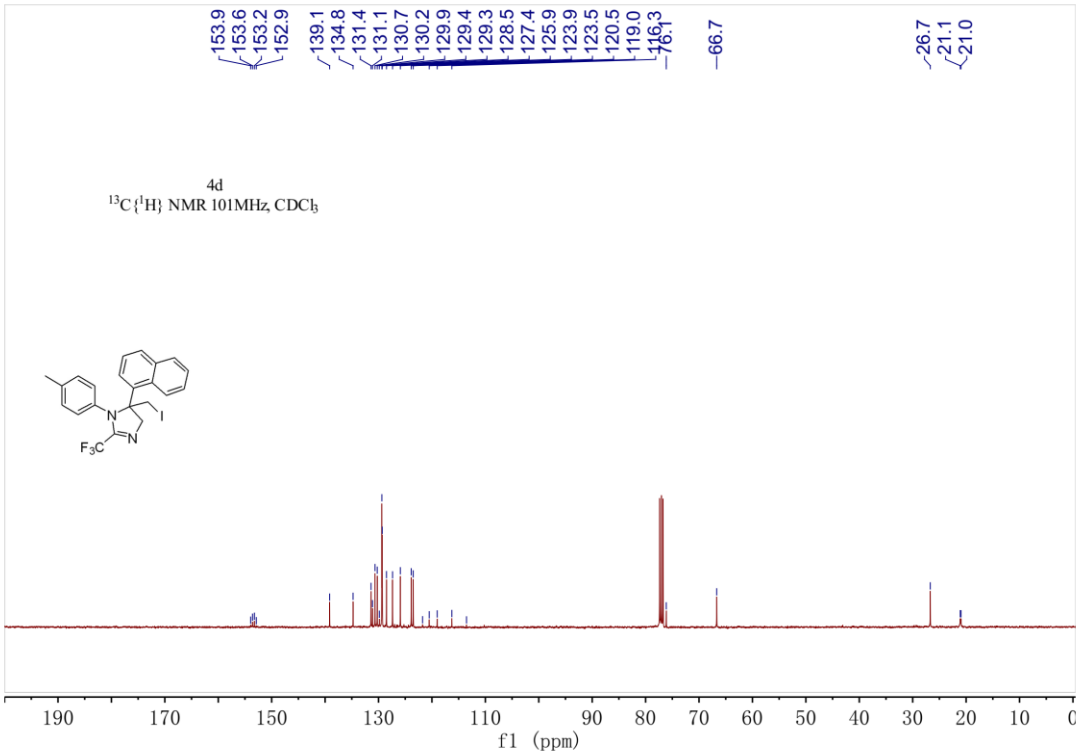

-65.51
4b
19F NMR 377 MHz, CDCl3
N
I
F3C
N
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

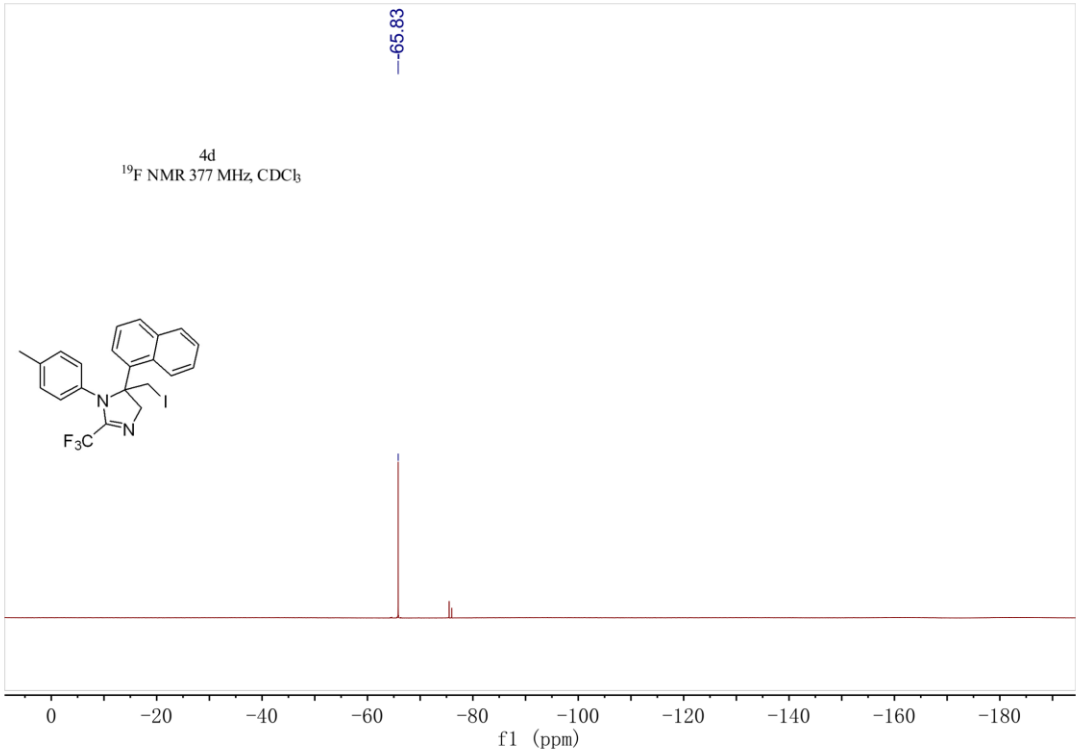

7.31
7.29
7.27
7.27
7.25
7.19
7.17
7.01
6.99
6.72
6.70
4.59
4.55
4.47
4.42
3.68
3.67
2.29
4c
1H NMR 400 MHz, CDCl3
I
N
F3C
N
Cl
3.37
0.96
1.89
1.82
0.94
0.94
1.98
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

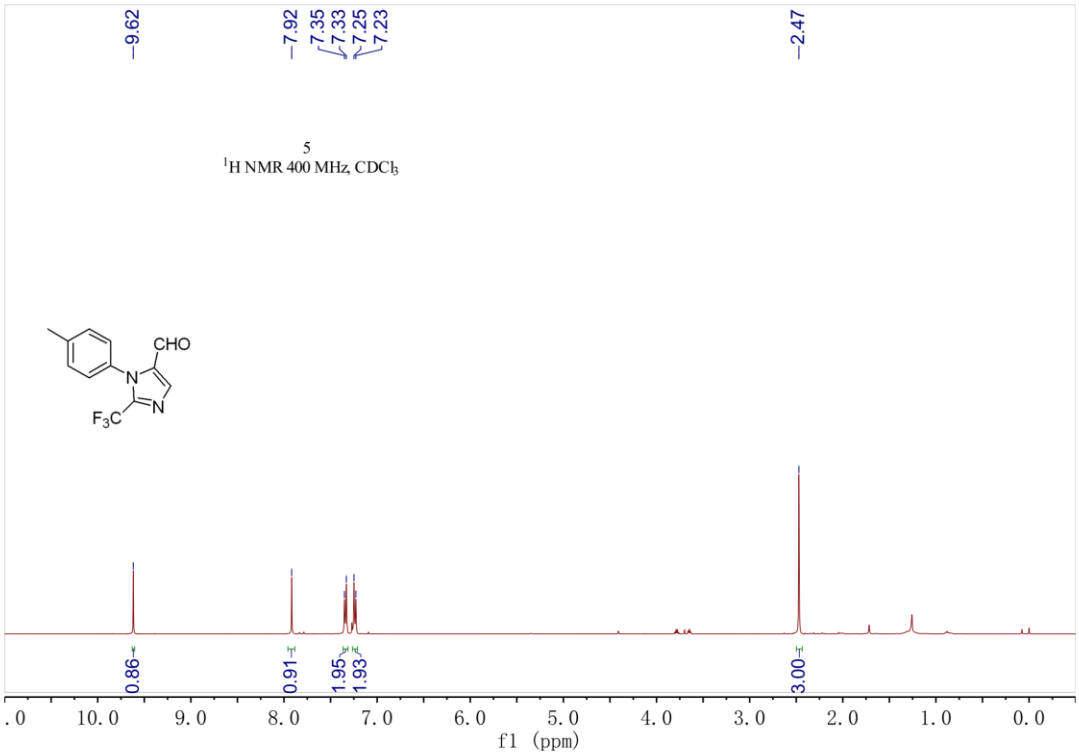

153.0
152.6
152.3
151.9
142.4
139.1
134.7
131.4
129.9
129.8
129.5
128.7
127.2
125.3
121.6
118.8
116.1
113.4
71.6
69.5
21.2
21.0
12.5
4c
$^{13}C\{^{1}H\}$ NMR 101MHz, $CDCl_3$
I
N
N
F_3C
Cl
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

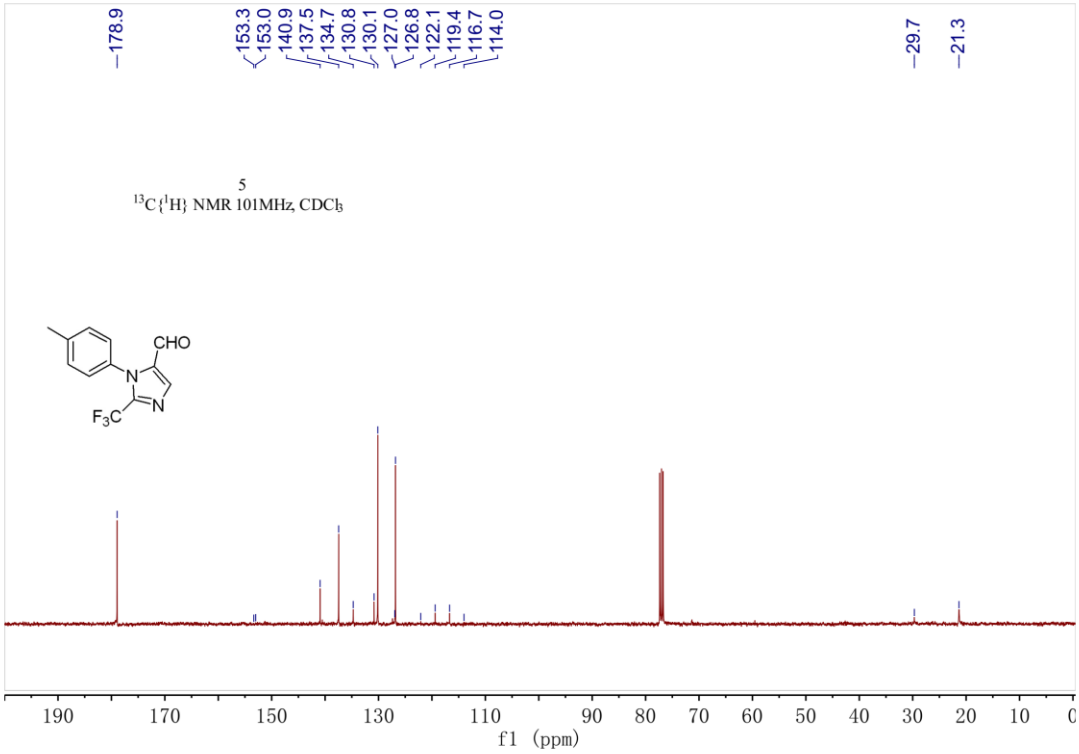

-65.57
4c
^{19}F NMR 377 MHz, $CDCl_3$
I
N
N
F_3C
Cl
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

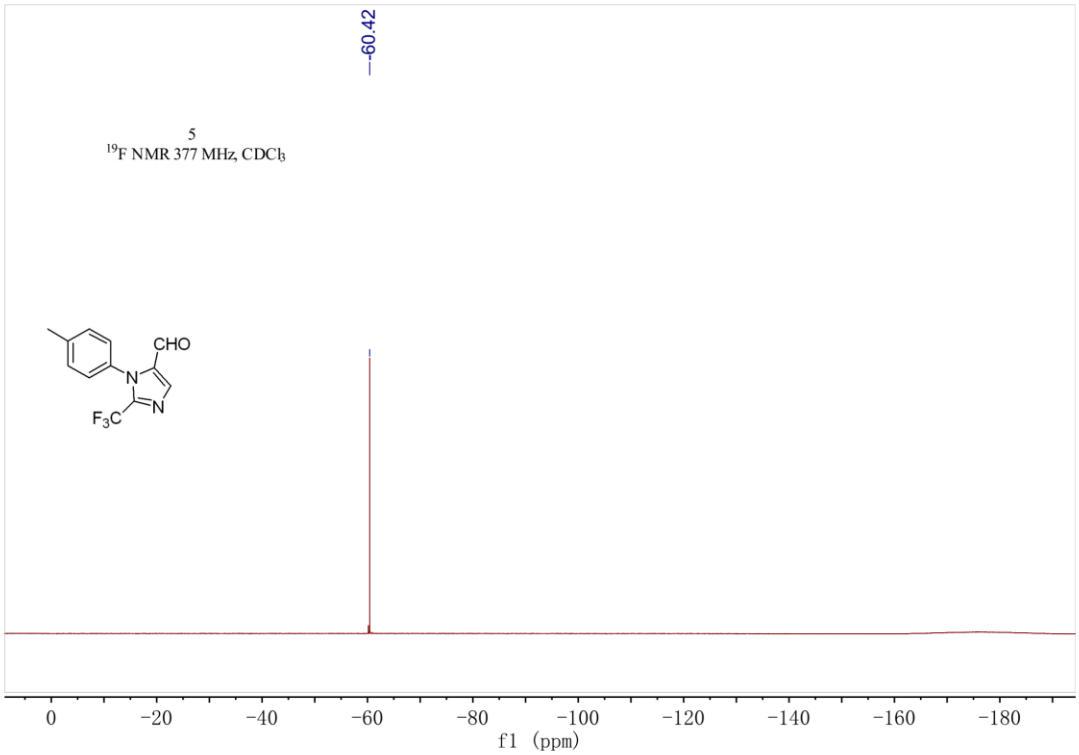

4d
1H NMR 400 MHz, CDCl3
f1 (ppm)

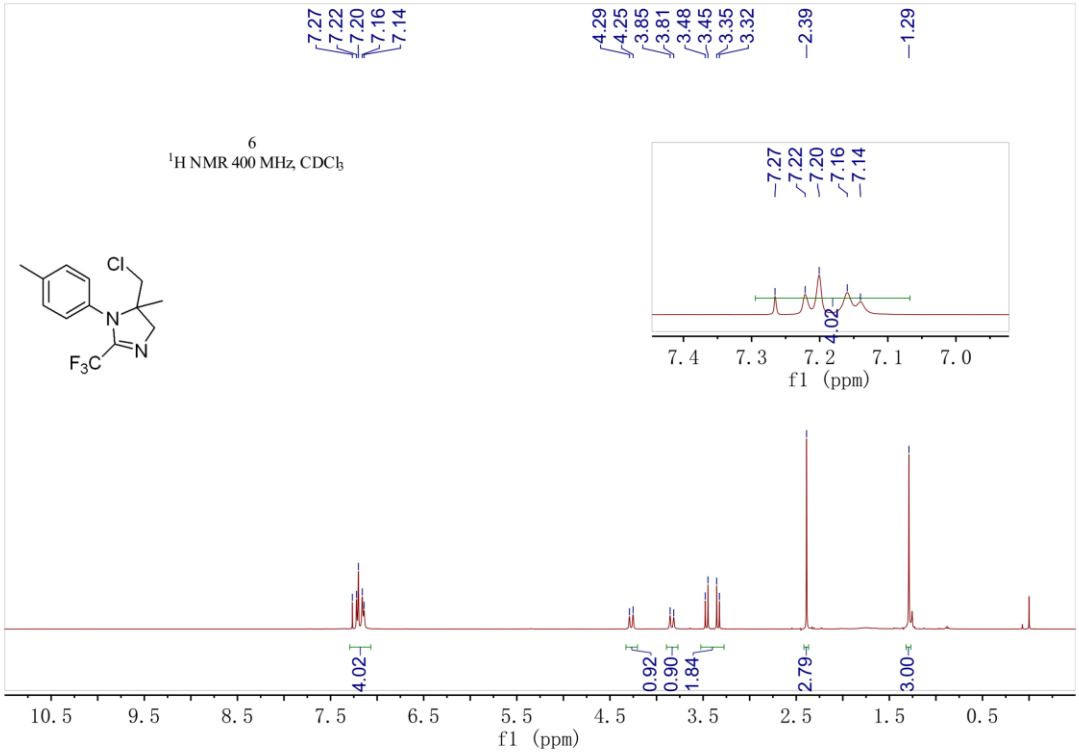

4d
13C{1H} NMR 101MHz, CDCl3
f1 (ppm)

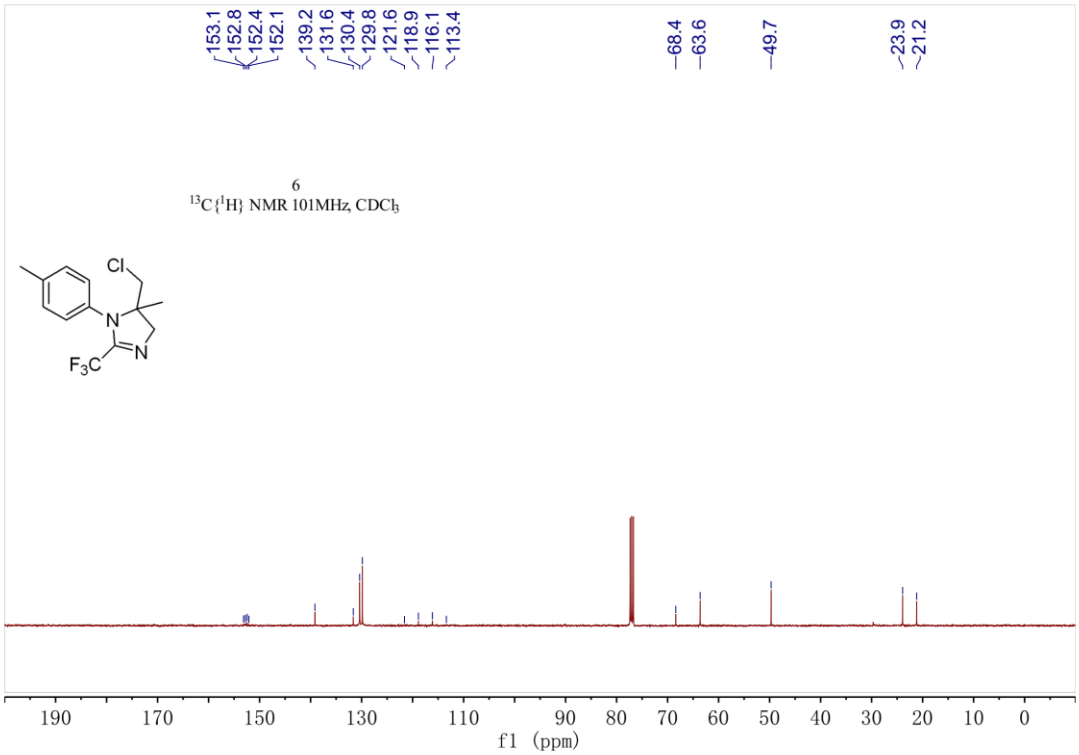

-65.83
4d
19F NMR 377 MHz, CDCl3
N
I
F3C
N
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

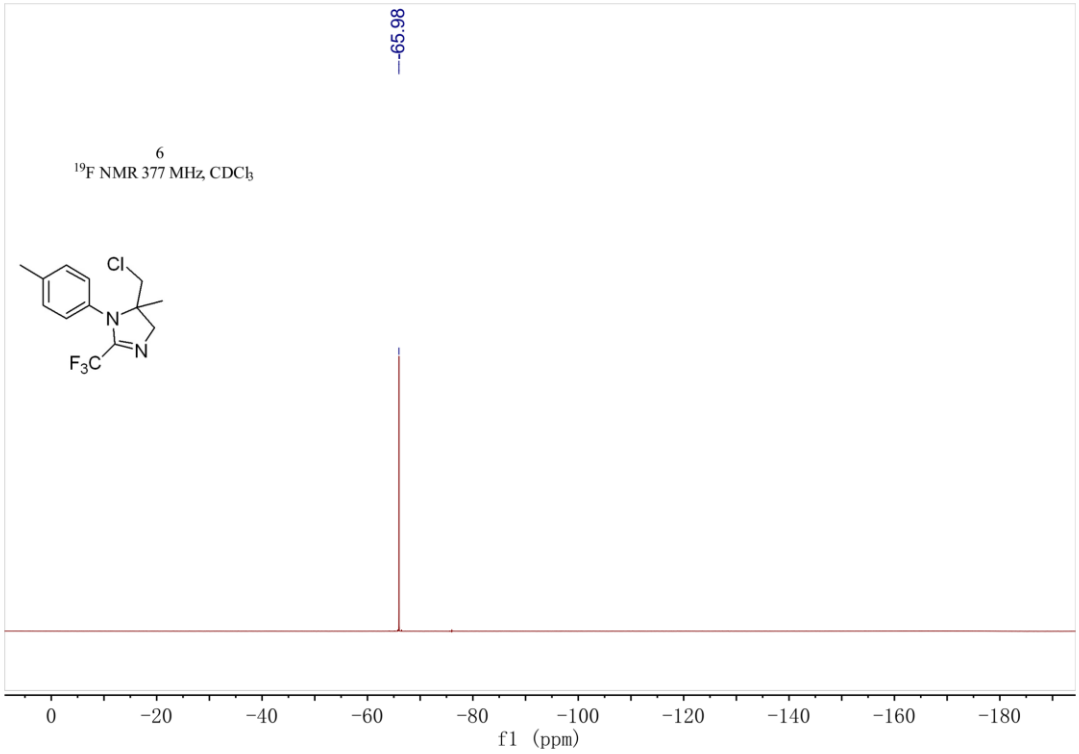

-9.62
-7.92
7.35
7.33
7.25
7.23
-2.47
5
1H NMR 400 MHz, CDCl3
CHO
N
F3C
N
0.86
0.91
1.95
1.93
3.00
.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

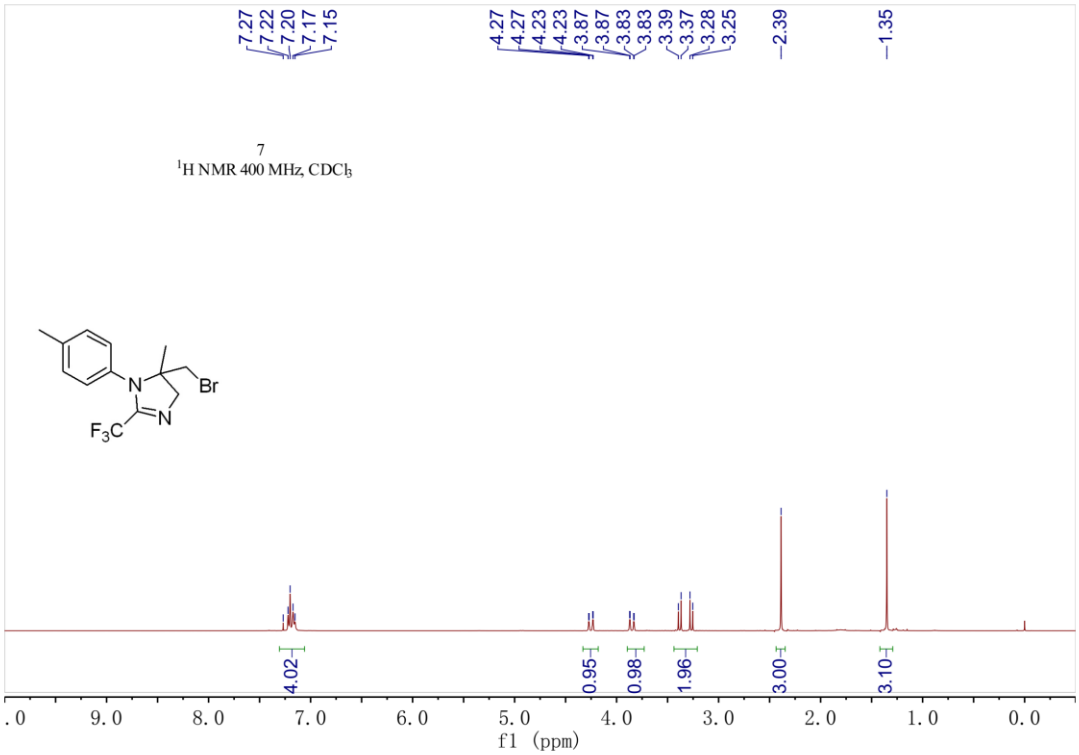

178.9
153.3
153.0
140.9
137.5
134.7
130.8
130.1
127.0
126.8
122.1
119.4
116.7
114.0
29.7
21.3
5
13C{1H} NMR 101MHz, CDCl3
CHO
N
N
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

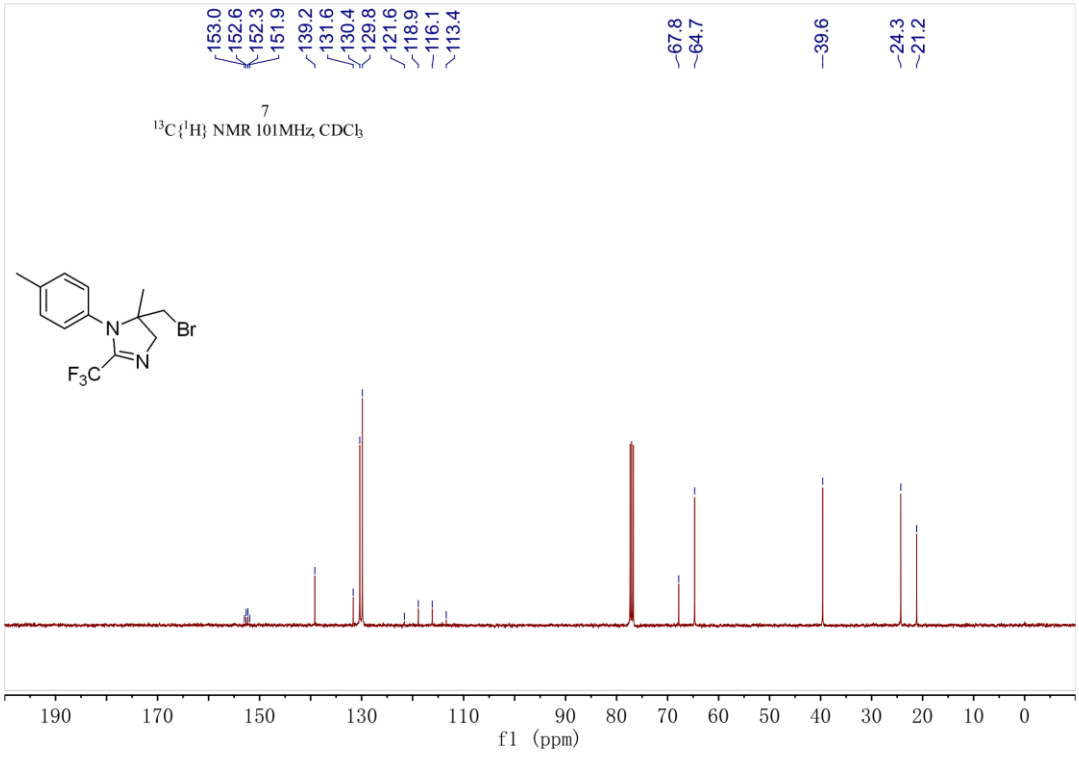

60.42
5
19F NMR 377 MHz, CDCl3
CHO
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

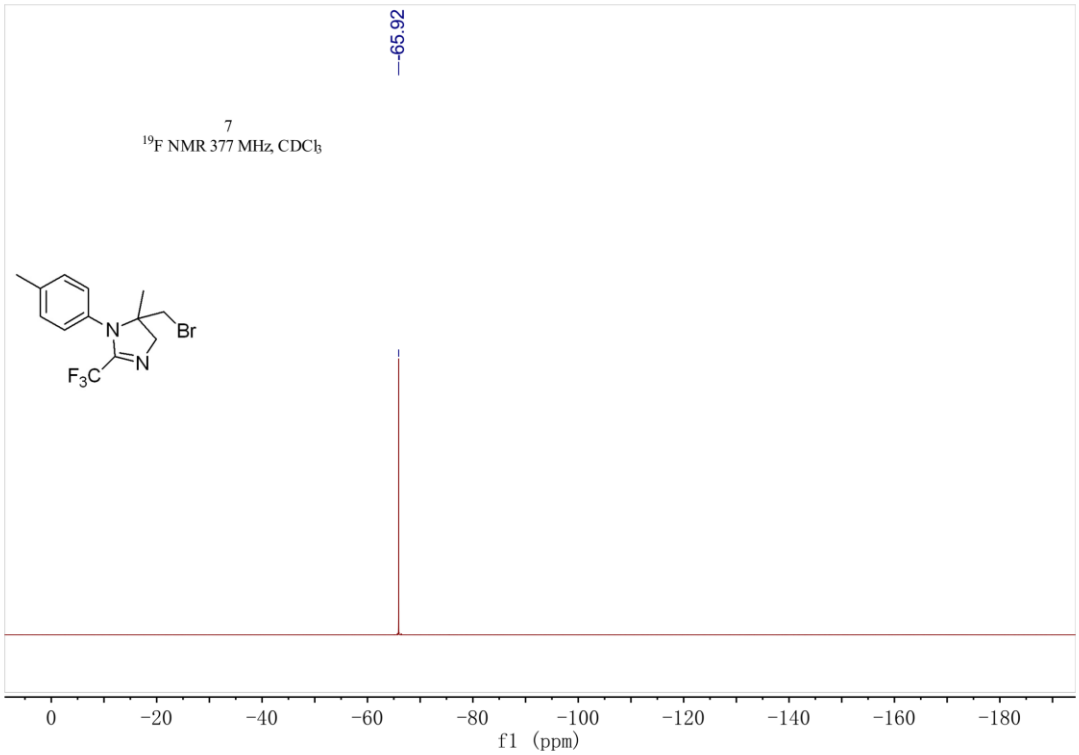

7.27
7.22
7.20
7.16
7.14
4.29
4.25
3.85
3.81
3.48
3.45
3.35
3.32
2.39
1.29
6
1H NMR 400 MHz, CDCl3
Cl
N
F3C
N
4.02
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
4.02
0.92
0.90
1.84
2.79
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

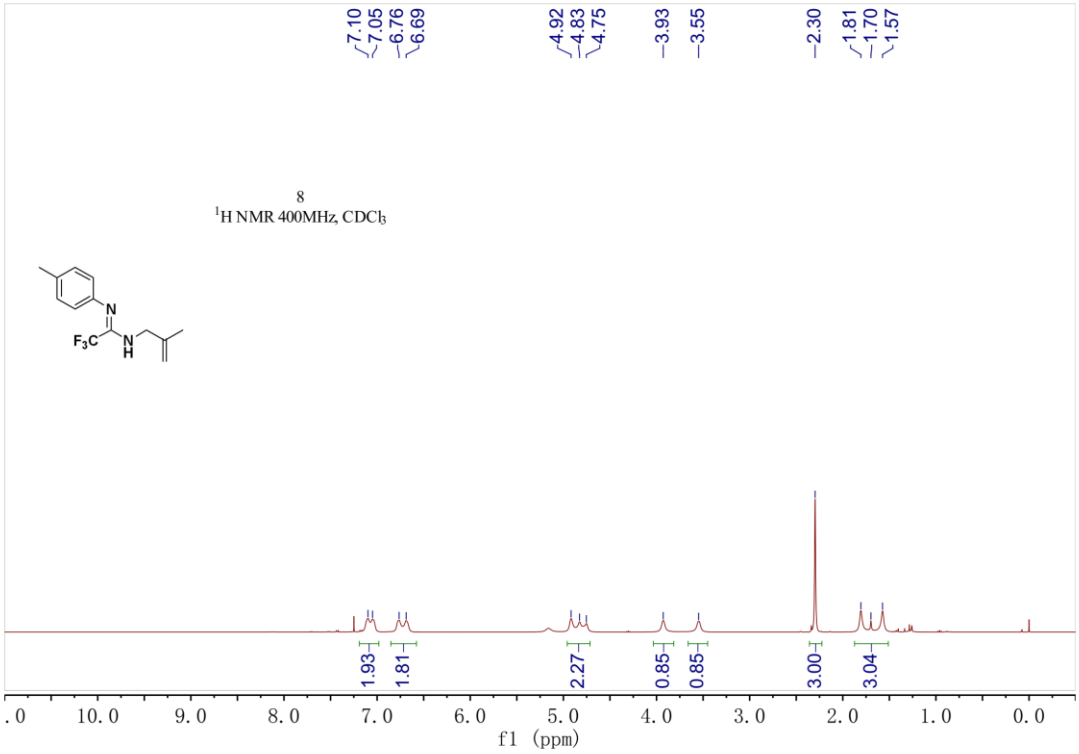

153.1
152.8
152.4
152.1
139.2
131.6
130.4
129.8
121.6
118.9
116.1
113.4
68.4
63.6
49.7
23.9
21.2
6
13C{1H} NMR 101MHz, CDCl3
Cl
N
F3C
N
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

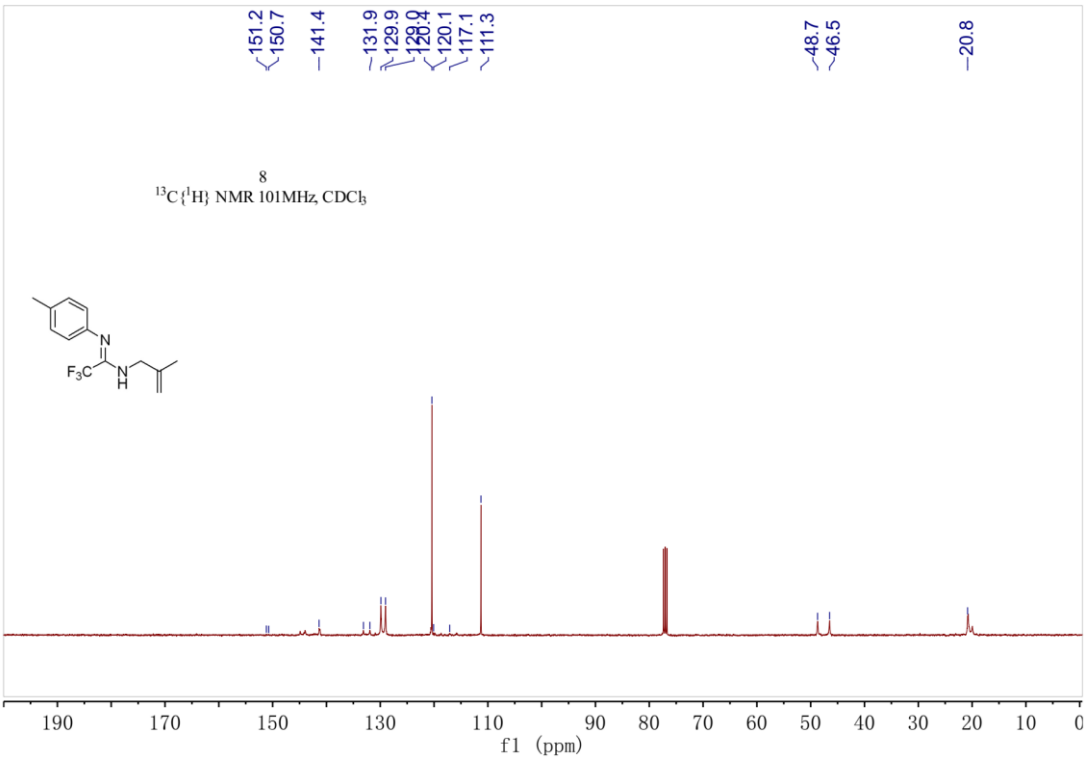

-65.98
6
19F NMR 377 MHz, CDCl3
Cl
N
F3C
N
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

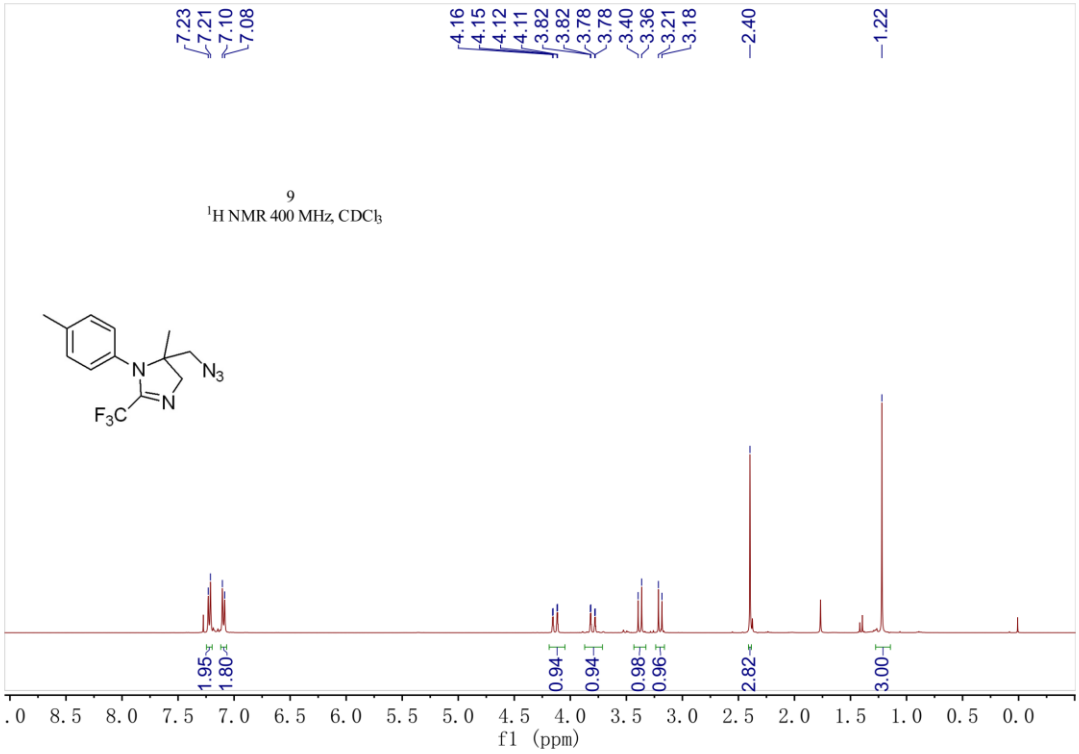

7.27
7.22
7.20
7.17
7.15
4.27
4.27
4.23
4.23
3.87
3.87
3.83
3.83
3.39
3.37
3.28
3.25
2.39
1.35
7
1H NMR 400 MHz, CDCl3
N
Br
F3C
N
4.02
0.95
0.98
1.96
3.00
3.10
.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

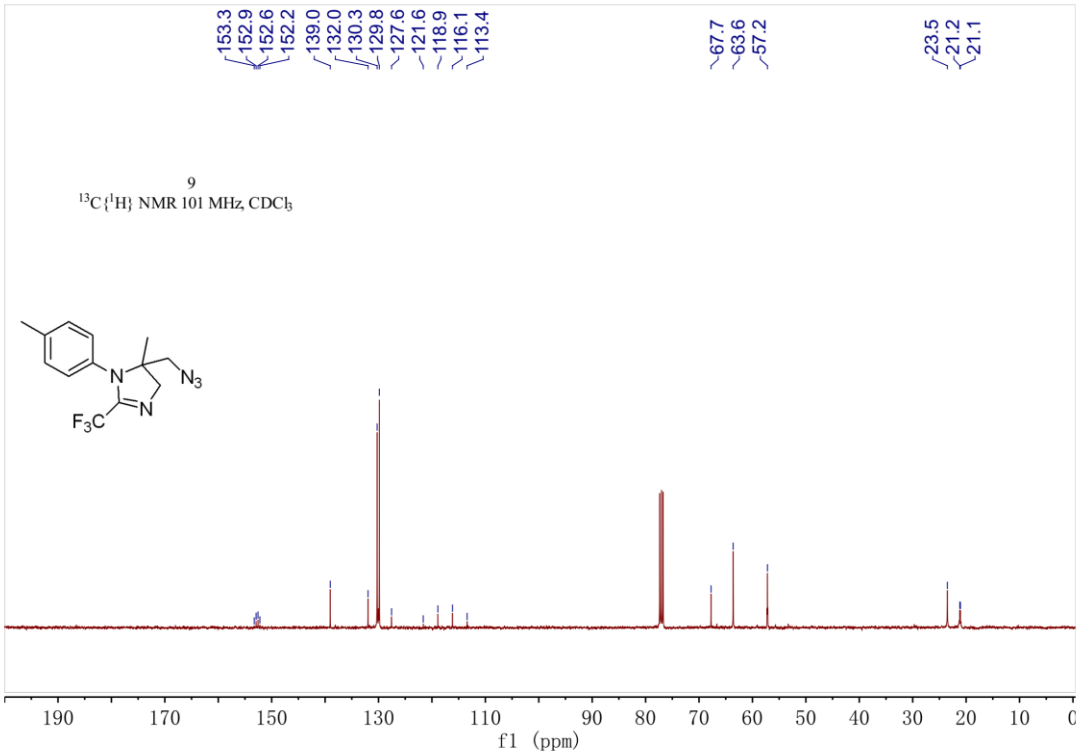

153.0
152.6
152.3
151.9
139.2
131.6
130.4
129.8
121.6
118.9
116.1
113.4
67.8
64.7
39.6
24.3
21.2
7
13C{1H} NMR 101MHz, CDCl3
Br
N
N
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

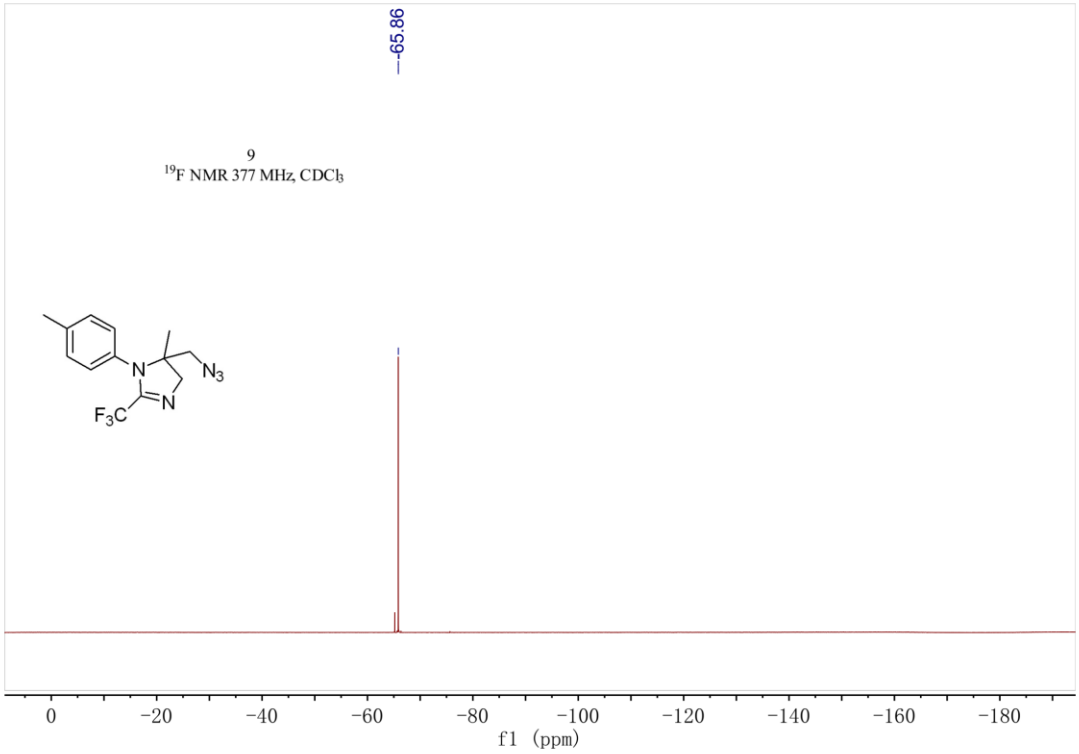

65.92
7
19F NMR 377 MHz, CDCl3
Br
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

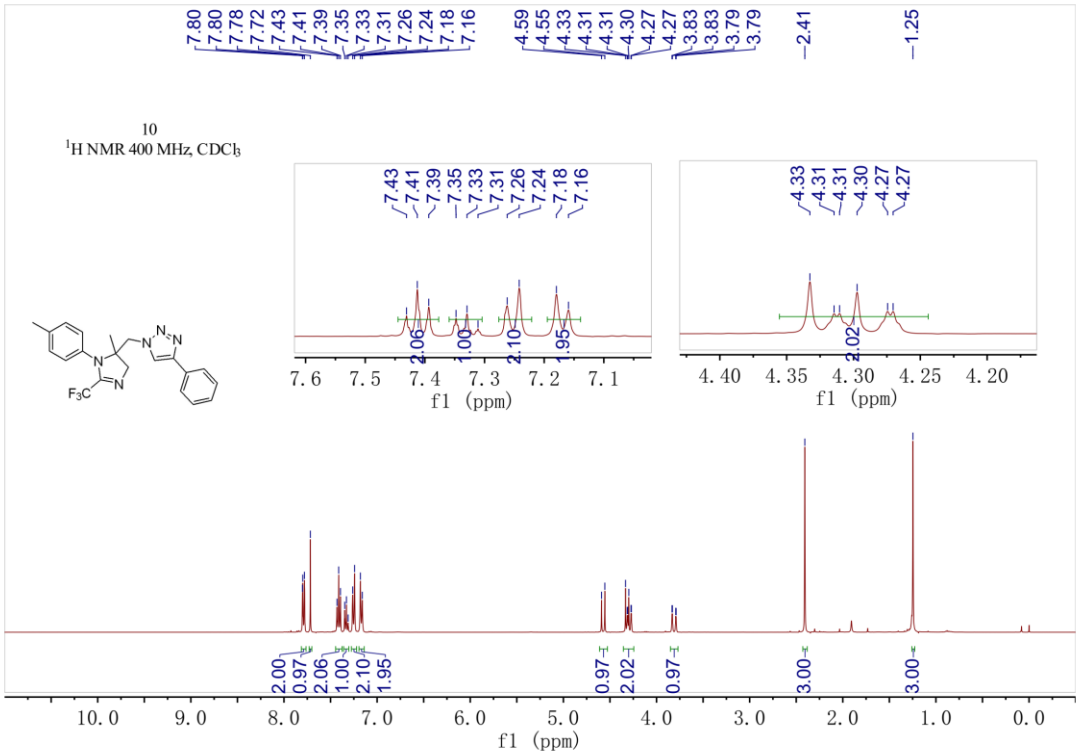

7.10
7.05
6.76
6.69
4.92
4.83
4.75
3.93
3.55
2.30
1.81
1.70
1.57
8
1H NMR 400MHz, CDCl3
1.93
1.81
2.27
0.85
0.85
3.00
3.04
f1 (ppm)

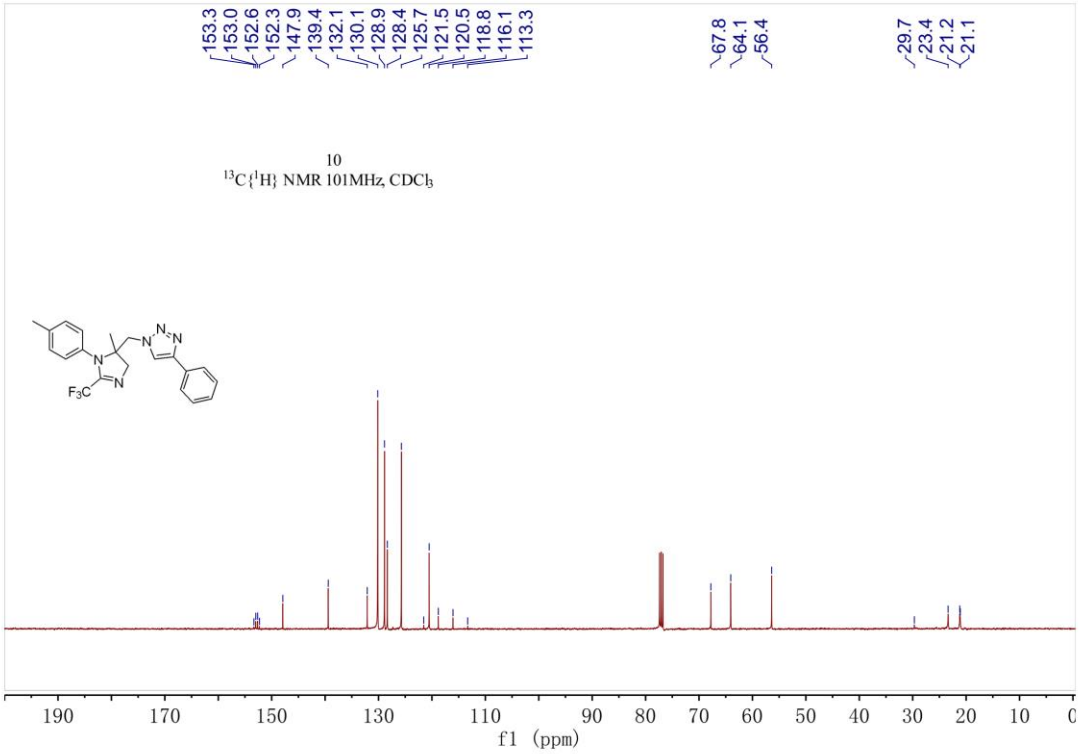

151.2
150.7
141.4
131.9
129.9
120.1
117.1
111.3
48.7
46.5
20.8
8
13C{1H} NMR 101MHz, CDCl3
f1 (ppm)

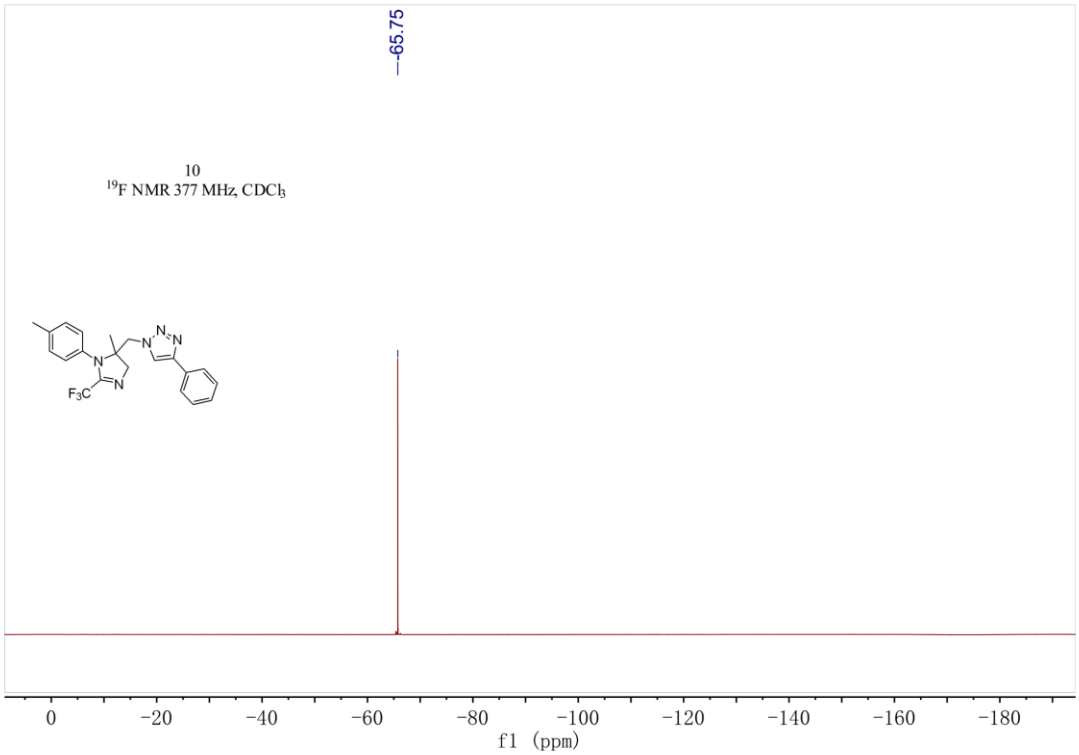

7.23
7.21
7.10
7.08
4.16
4.15
4.12
4.11
3.82
3.82
3.78
3.78
3.40
3.36
3.21
3.18
2.40
1.22
9
1H NMR 400 MHz, CDCl3
N
N3
F3C
N
1.95
1.80
0.94
0.94
0.98
0.96
2.82
3.00
f1 (ppm)


153.3
152.9
152.6
152.2
139.0
132.0
130.3
129.8
127.6
121.6
118.9
116.1
113.4
67.7
63.6
57.2
23.5
21.2
21.1
9
13C{1H} NMR 101 MHz, CDCl3
N
N3
F3C
N
f1 (ppm)


-65.86
9
19F NMR 377 MHz, CDCl3
N3
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)


7.80
7.80
7.78
7.72
7.43
7.41
7.39
7.35
7.33
7.31
7.26
7.24
7.18
7.16
4.59
4.55
4.33
4.31
4.31
4.30
4.27
3.83
3.83
3.79
3.79
2.41
1.25
10
1H NMR 400 MHz, CDCl3
2.06
1.00
2.10
1.95
2.02
7.6
7.5
7.4
7.3
7.2
7.1
4.40
4.35
4.30
4.25
4.20
f1 (ppm)
2.00
0.97
2.06
1.00
2.10
1.95
0.97
2.02
0.97
3.00
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


153.3
153.0
152.6
152.3
147.9
139.4
132.1
130.1
128.9
128.4
125.7
121.5
120.5
118.8
116.1
113.3
67.8
64.1
56.4
29.7
23.4
21.2
21.1
10
$^{13}C\{^{1}H\}$ NMR 101MHz, $CDCl_3$
F_3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)


-65.75
10
^{19}F NMR 377 MHz, $CDCl_3$
F_3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)