Supporting Information *for*

Copper-mediated three-component synthesis of 2-trifluoromethylbenzimidazoles

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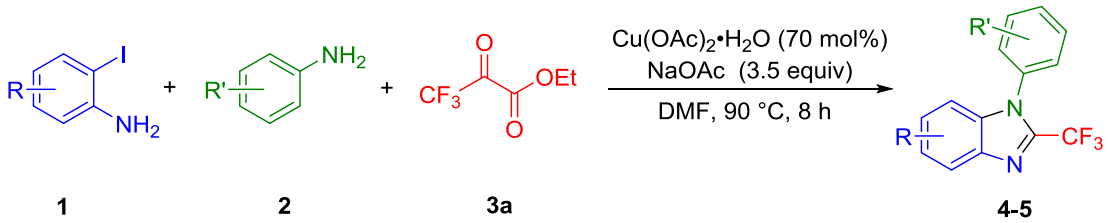
Table of Contents

General information

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR ($CDCl_3$ δ 7.26), ^{13}C NMR ($CDCl_3$ δ 77.0), ^{1}H NMR (DMSO-d_6 δ 2.50) and ^{13}C NMR (DMSO-d_6 δ 39.50). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. 2,2,2-Trifluoro-*N*-phenylacetamide **7**[1] and 2,2,2-trifluoro-*N*-(2-iodophenyl)acetamide **8**[2] were prepared according to the published procedures. Other reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published procedures prior to use. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60.

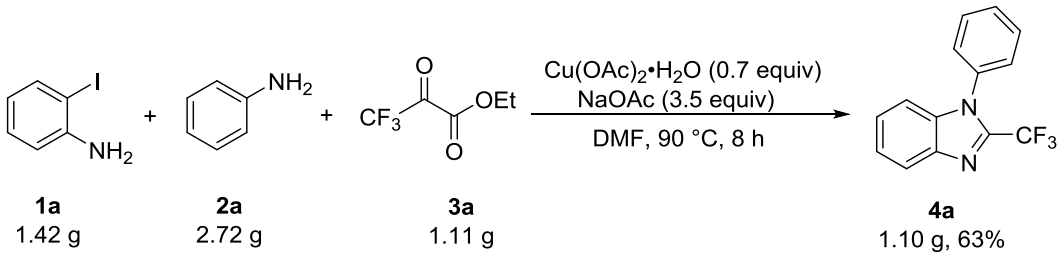
General procedure of the synthesis of 1-aryl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazoles 4 and 5



1 **2** **3a** **4-5**

In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar was added 2-iodoaniline **1** (0.80 mmol, 1.0 equiv), aniline **2** (3.60 mmol, 4.5 equiv), ethyl trifluoropyruvate **3a** (136.1 mg, 0.80 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (111.1 mg, 0.56 mmol, 0.70 equiv), NaOAc (229.7 mg, 2.80 mmol, 3.5 equiv) and *N*,*N*-dimethylformamide (5 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 90 °C for 8 h. After cooling to room temperature, the crude mixture was diluted with water (100 mL) and ethyl acetate (50 mL). The organic phase was extracted and dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting 2-trifluoromethylbenzimidazole product was purified by column chromatography on silica gel with *n*-pentane/ethyl acetate.

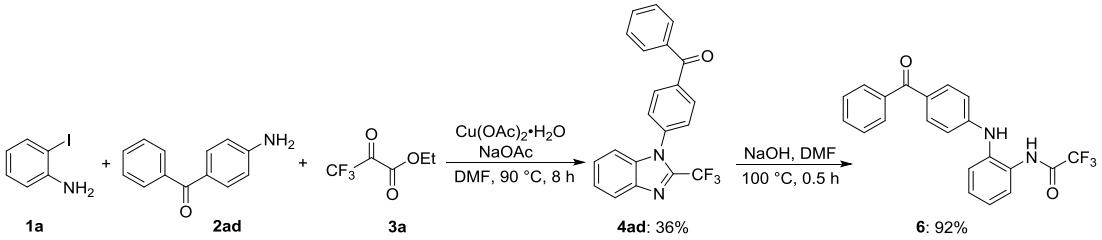
Procedure for gram scale reaction for synthesis of 1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4a)



1a 1.42 g | **2a** 2.72 g | **3a** 1.11 g | **4a** 1.10 g, 63%

In a glove box filled with nitrogen, to an oven-dried 100 mL pressure tube equipped with a stir bar was added 2-iodoaniline **1a** (1.42 g, 6.50 mmol, 1.0 equiv), aniline **2a** (2.72 g, 29.25 mmol, 4.5 equiv), ethyl trifluoropyruvate **3a** (1.11 g, 6.50 mmol, 1.0 equiv), $Cu(OAc)_2$ Ꮒ$_2O$ (0.91 g, 4.55 mmol, 0.7 equiv), NaOAc (1.86 g, 22.75 mmol, 3.5 equiv) and *N*,*N*-dimethylformamide (40 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 90 °C for 8 h. After cooling to room temperature, the crude mixture was diluted with water (300 mL) and ethyl acetate (150 mL). The organic phase was extracted and dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with *n*-pentane/ethyl acetate (10:1) to give 1.10 g of product **4a** (63% yield).

Synthetic utility for the preparation of aminobenzophenone 6

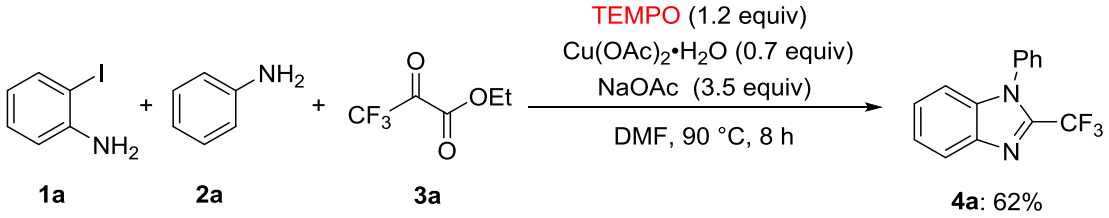


In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar was added 2-iodoaniline **1a** (175.2 mg, 0.80 mmol, 1.0 equiv), (4-aminophenyl)(phenyl)methanone **2ad** (709.5 mg, 3.60 mmol, 4.5 equiv), ethyl trifluoropyruvate **3a** (136.1 mg, 0.80 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (111.1 mg, 0.56 mmol, 0.70 equiv), NaOAc (229.7 mg, 2.80 mmol, 3.5 equiv) and *N*,*N*-dimethylformamide (5 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 90 °C for 8 h. After cooling to room temperature, the crude mixture was diluted with water (100 mL) and ethyl acetate (50 mL). The organic phase was extracted and dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with *n*-pentane/ethyl acetate (10:1) to give 105.4 mg of phenyl(4-(2-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-1-yl)phenyl)methanone **4ad** (36% yield).

To an oven-dried 25 mL pressure tube equipped with a stir bar was added **4ad** (105.4 mg, 0.29 mmol, 1.0 equiv), NaOH (23.2 mg, 0.58 mmol, 2.0 equiv) and *N*,*N*-dimethylformamide (5 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 0.5 h. After cooling to room temperature, the crude mixture was diluted with water (100 mL) and ethyl acetate (50 mL). The organic phase was extracted and dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with *n*-pentane/ethyl acetate (4:1) to give 102.5 mg of *N*-(2-((4-benzoylphenyl)amino)phenyl)-2,2,2-trifluoroacetamide **6** (92% yield).

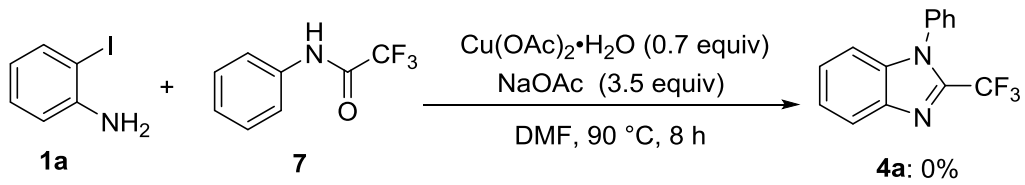
Experiments for Mechanistic Investigation

(a) Raction of 1a and 2a with 3a in the presence of TEMPO under standard conditions



In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar was added 2-iodoaniline **1a** (175.2 mg, 0.80 mmol, 1.0 equiv), aniline **2a** (335.3 mg, 3.60 mmol, 4.5 equiv), ethyl trifluoropyruvate **3a** (136.1 mg, 0.80 mmol, 1.0 equiv), TEMPO (150.0 mg, 0.96 mmol, 1.2 equiv), $Cu(OAc)_2$ H_2O (111.1 mg, 0.56 mmol, 0.7 equiv), NaOAc (229.7 mg, 2.80 mmol, 3.5 equiv) and *N*,*N*-dimethylformamide (5 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 90 °C for 8 h. After cooling to room temperature, the crude mixture was diluted with water (100 mL) and ethyl acetate (50 mL). The organic phase was extracted and dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with *n*-pentane/ethyl acetate (10:1) to give product **4a** in 62% yield.

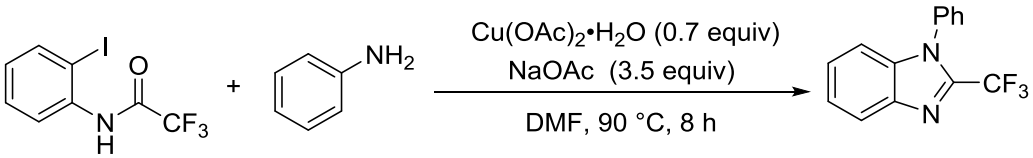
(b) Reaction of 2,2,2-trifluoro-*N*-phenylacetamide 7 with 1a under standard conditions



In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar was added 2-iodoaniline **1a** (175.2 mg, 0.80 mmol, 1.0 equiv),

2,2,2-trifluoro-*N*-phenylacetamide **7** (680.5 mg, 3.60 mmol, 4.5 equiv), $Cu(OAc)_2 \cdot H_2O$ (111.1 mg, 0.56 mmol, 0.7 equiv), NaOAc (229.7 mg, 2.80 mmol, 3.5 equiv) and *N*,*N*-dimethylformamide (5 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 90 °C for 8 h. The tube was removed from the oil bath and cooled to room temperature. A ^{19}F NMR spectrum was acquired, and no trace of 1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole **4a** was detected.

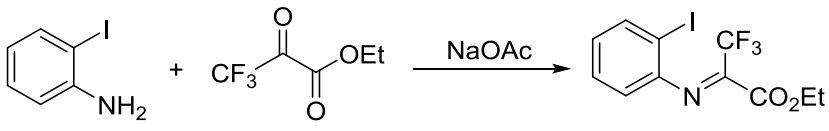
(c) Reaction of 2,2,2-trifluoro-*N*-(2-iodophenyl)acetamide 8 with 2a under standard conditions



8 **2a** **4a**: 66%

In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar was added 2,2,2-trifluoro-*N*-(2-iodophenyl)acetamide **8** (251.9 mg, 0.80 mmol, 1.0 equiv), aniline **2a** (335.0 mg, 3.60 mmol, 4.5 equiv), $Cu(OAc)_2 \cdot H_2O$ (111.1 mg, 0.56 mmol, 0.70 equiv), NaOAc (229.7 mg, 2.80 mmol, 3.5 equiv) and *N*,*N*-dimethylformamide (5 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 90 °C for 8 h. After cooling to room temperature, the crude mixture was diluted with water (100 mL × 3) and ethyl acetate (50 mL). The organic phase was extracted and dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with *n*-pentane/ethyl acetate (10:1) to afford product **4a** in 66% yield.

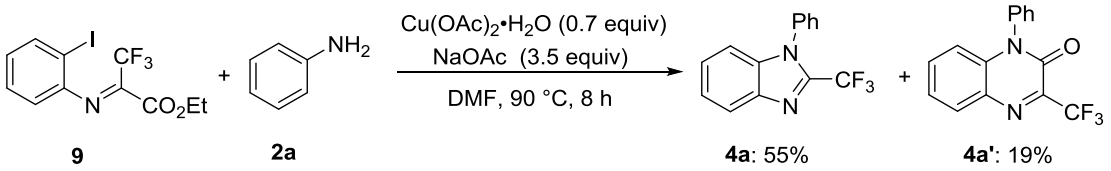
(d) Reaction of 1a with 3a



1a **3a** **9**: 81%

In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar was added 2-iodoaniline **1a** (175.2 mg, 0.80 mmol, 1.0 equiv), ethyl trifluoropyruvate **3a** (136.1 mg, 0.80 mmol, 1.0 equiv), NaOAc (229.7 mg, 2.80 mmol, 3.5 equiv) and *N*,*N*-dimethylformamide (5 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 90 °C for 8 h. After cooling to room temperature, the crude mixture was diluted with water (100 mL) and ethyl acetate (50 mL). The organic phase was extracted and dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with *n*-pentane/ethyl acetate (10:1) to give 240.4 mg of ethyl-3,3,3-trifluoro-2-((2-iodophenyl)imino)propanoate **9** (81% yield).

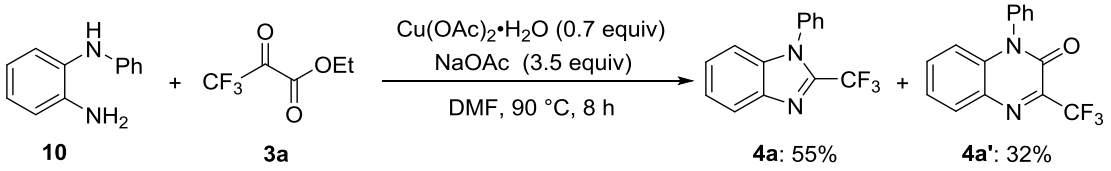
(e) Reaction of 9 with 2a under standard conditions



9 **2a** **4a**: 55% **4a'**: 19%

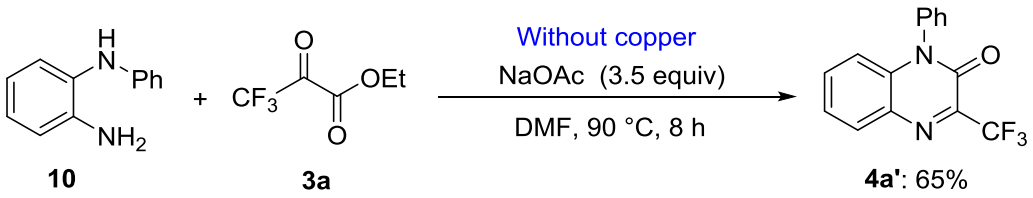
In a glove box filled with nitrogen, to an oven-dried 100 mL pressure tube equipped with a stir bar was added **9** (296.8 mg, 0.80 mmol, 1.0 equiv), aniline **2a** (335.0 mg, 3.60 mmol, 4.5 equiv), $Cu(OAc)_2 \cdot H_2O$ (111.1 mg, 0.56 mmol, 0.70 equiv), NaOAc (229.7 mg, 2.80 mmol, 3.5 equiv) and *N*,*N*-dimethylformamide (5 mL).The tube was sealed with Teflon screw cap and the solution was stirred at 90 °C for 8 h. After cooling to room temperature, the crude mixture was diluted with water (300 mL) and ethyl acetate (150 mL). The organic phase was extracted and dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with *n*-pentane/ethyl acetate (10:1) to afford product **4a** and **4a′** in 55% and 19% yield, respectively.

(f) Reaction of *N*-phenylbenzene-1,2-diamine 10 with 3a under standard conditions



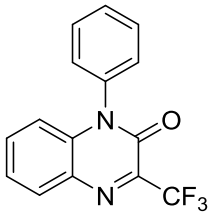
In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar was added *N*-phenylbenzene-1,2-diamine **10** (147.3 mg, 0.80 mmol, 1.0 equiv), ethyl trifluoropyruvate **3a** (136.1 mg, 0.80 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (111.1 mg, 0.56 mmol, 0.7 equiv), NaOAc (229.7 mg, 2.80 mmol, 3.5 equiv) and *N*,*N*-dimethylformamide (5 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 90 °C for 8 h. After cooling to room temperature, the crude mixture was diluted with water (100 mL × 3) and ethyl acetate (50 mL). The organic phase was extracted and dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with *n*-pentane/ethyl acetate (10:1) to afford products **4a** and **4a′** in 55% and 32% yield, respectively.

(g) Reaction of *N*-phenylbenzene-1,2-diamine 10 with 3a under conditions without copper



In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar was added *N*-phenylbenzene-1,2-diamine **10** (147.3 mg, 0.80 mmol, 1.0 equiv), ethyl trifluoropyruvate **3a** (136.1 mg, 0.80 mmol, 1.0 equiv), NaOAc (229.7 mg, 2.80 mmol, 3.5 equiv) and *N*,*N*-dimethylformamide (5 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 90 °C for 8 h. After cooling to room temperature, the crude mixture was diluted with water (100 mL × 3) and ethyl

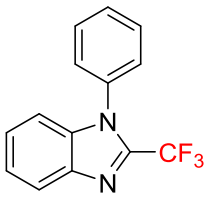
acetate (50 mL). The organic phase was extracted and dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with *n*-pentane/ethyl acetate (10:1) to afford product **4a′** in 65% yield.



1-phenyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**4a′**)[3]

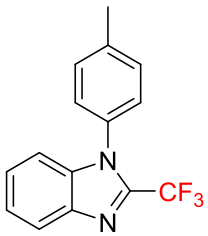
Obtained as a white solid. Mp: 178–181 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.70 – 7.55 (m, 3H), 7.57 – 7.46 (m, 1H), 7.47 – 7.35 (m, 1H), 7.35 – 7.27 (m, 2H), 6.78 (dd, *J* = 8.4, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4 (s), 144.8 (q, *J* = 34.0 Hz), 135.6 (s), 134.8 (s), 133.3 (s), 131.4 (s), 130.9 (s), 130.6 (s), 130.1 (s), 128.2 (s), 124.8 (s), 120.0 (q, *J* = 276.7 Hz), 115.9 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.80 (s, 3F). IR (ATR): ν 1677, 1603, 1561, 1465, 1360, 1312, 1189, 1145, 1057, 763, 696, 586 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{10}F_3N_2O$ $[M + H]^+$: 291.0740; found: 291.0737.

Data for compounds



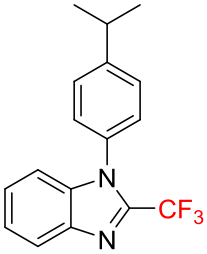
1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4a)

Obtained as a yellow liquid in 67% yield (140.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.65 – 7.54 (m, 3H), 7.49 – 7.34 (m, 4H), 7.16 (d, *J* = 7.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.51 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9 (q, *J* = 38.5 Hz), 140.8 (s), 137.4 (s), 134.6 (s), 130.1 (s), 129.9 (s), 127.6 (s), 125.9 (s), 124.2 (s), 121.5 (s), 118.9 (q, *J* = 271.9 Hz), 111.3 (s). IR (ATR): ν 3053, 1595, 1525, 1499, 1450, 1417, 1289, 1264, 1207, 1162, 1139, 763, 746, 695 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_{10}F_3N_2$ $[M + H]^+$: 263.0791; found: 263.0786.



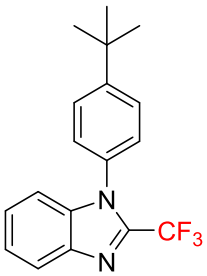
1-(*p*-tolyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4b)

Obtained as a white solid in 65% yield (143.0 mg). Mp: 56–58 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 6.8, 1.8 Hz, 1H), 7.46 – 7.33 (m, 4H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.16 (dd, *J* = 6.9, 1.8 Hz, 1H), 2.49 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.59 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1 (q, *J* = 38.3 Hz), 140.8 (s), 140.3 (s), 137.5 (s), 131.9 (s), 130.5 (s), 127.3 (s), 125.8 (s), 124.1 (s), 121.5 (s), 119.0 (q, *J* = 271.9 Hz), 111.4 (s), 21.4 (s). IR (ATR): ν 3031, 1524, 1515, 1452, 1420, 1264, 1208, 1179, 1163, 1139, 747, 737 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{15}H_{12}F_3N_2$ $[M + H]^+$: 277.0947; found: 277.0943.



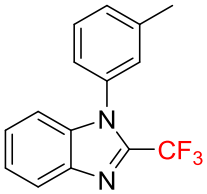
1-(4-isopropylphenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4c)

Obtained as a colorless liquid in 68% yield (165.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.30 (m, 6H), 7.18 (d, *J* = 7.3 Hz, 1H), 3.09 – 2.99 (m, 1H), 1.34 (d, *J* = 6.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.56 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0 (s), 141.1 (q, *J* = 38.4 Hz), 140.8 (s), 137.5 (s), 132.1 (s), 127.8 (s), 127.3 (s), 125.8 (s), 124.1 (s), 121.5 (s), 119.0 (q, *J* = 272.0 Hz), 111.5 (s), 34.1 (s), 24.0 (s). IR (ATR): ν 2962, 1621, 1583, 1524, 1515, 1452, 1418, 1265, 1207, 1179, 1163, 1139, 746 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{17}H_{16}F_3N_2$ $[M + H]^+$: 305.1260; found: 305.1257.



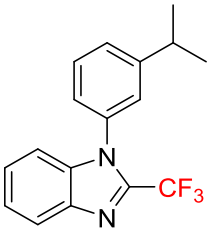
1-(4-(*tert*-butyl)phenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4d)

Obtained as a white solid in 56% yield (142.0 mg). Mp: 99–100 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.55 – 7.33 (m, 4H), 7.26 – 7.17 (m, 2H), 1.41 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.53 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3 (s), 141.1 (q, *J* = 38.3 Hz), 140.8 (s), 137.5 (s), 131.8 (s), 127.0 (s), 126.8 (s), 125.8 (s), 124.0 (s), 121.4 (s), 119.0 (q, *J* = 271.9 Hz), 111.5 (s), 35.0 (s), 31.4 (s). IR (ATR): ν 2964, 1606, 1580, 1519, 1453, 1423, 1265, 1203, 1182, 1164, 1144, 1130, 1106, 852, 748, 733, 629 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{18}H_{18}F_3N_2$ $[M + H]^+$: 319.1417; found: 319.1413.



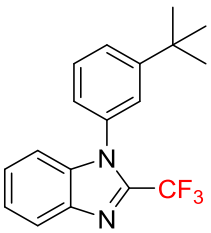
1-(*m*-tolyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4e)

Obtained as a yellow liquid in 64% yield (141.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.57. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.58 – 7.33 (m, 4H), 7.27 – 7.12 (m, 3H), 2.46 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.53 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0 (q, *J* = 38.5 Hz), 140.8 (s), 140.1 (s), 137.4 (s), 134.5 (s), 130.8 (s), 129.6 (s), 128.0 (s), 125.9 (s), 124.6 (s), 124.1 (s), 121.5 (s), 119.0 (q, *J* = 271.9 Hz), 111.4 (s), 21.4 (s). IR (ATR): ν 2926, 1608, 1590, 1524, 1492, 1454, 1414, 1265, 1198, 1178, 1130, 745, 737, 702, 692 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{15}H_{12}F_3N_2$ $[M + H]^+$: 277.0947; found: 277.0944.



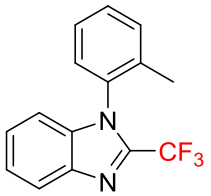
1-(3-isopropylphenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4f)

Obtained as a yellow liquid in 63% yield (153.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 6.4, 2.1 Hz, 1H), 7.53 – 7.32 (m, 4H), 7.39 – 7.17 (m, 3H), 3.07 – 2.94 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.52 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1 (s), 141.1 (q, *J* = 38.5 Hz), 140.8 (s), 137.3 (q, *J* = 1.4 Hz), 134.5 (s), 129.7 (s), 128.2 (s), 125.8 (s), 125.5 (s), 124.7 (s), 124.1 (s), 121.5 (s), 119.0 (q, *J* = 271.8 Hz), 111.4 (s), 34.0 (s), 23.9 (s). IR (ATR): ν 2963, 1605, 1589, 1524, 1492, 1454, 1414, 1264, 1201, 1179, 1160, 1128, 744, 736, 702 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{17}H_{16}F_3N_2$ $[M + H]^+$: 305.1260; found: 305.1256.



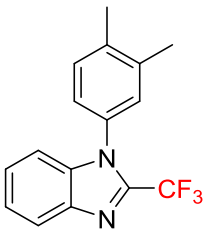
1-(3-(*tert*-butyl)phenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4g)

Obtained as a yellow liquid in 63% yield (188.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 6.7, 2.4 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.46 – 7.33 (m, 3H), 7.32 – 7.15 (m, 2H), 1.36 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.48 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6 (s), 141.0 (q, *J* = 38.5 Hz), 140.8 (s), 137.4 (s), 134.3 (s), 129.4 (s), 126.8 (s), 125.9 (s), 124.7 (s), 124.3 (s), 124.1 (s), 121.5 (s), 119.0 (q, *J* = 271.9 Hz), 111.4 (s), 35.0 (s), 31.3 (s). IR (ATR): ν 2964, 1604, 1586, 1524, 1412, 1256, 1205, 1178, 1162, 1131, 744, 735, 701 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{18}H_{18}F_3N_2$ $[M + H]^+$: 319.1417; found: 319.1413.



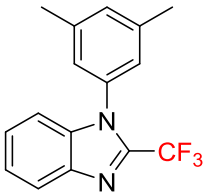
1-(*o*-tolyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4h)

Obtained as a yellow liquid in 63% yield (188.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.69. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.52 – 7.21 (m, 6H), 7.00 (d, *J* = 7.2 Hz, 1H), 1.96 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.95 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0 (q, *J* = 37.5 Hz), 140.9 (s), 136.8 (s), 136.6 (s), 133.3 (s), 131.4 (s), 130.5 (s), 128.7 (s), 127.3 (s), 126.0 (s), 124.1 (s), 121.7 (s), 118.9 (q, *J* = 272.0 Hz), 111.2 (s), 17.1 (s). IR (ATR): ν 2926, 1525, 1498, 1415, 1263, 1200, 1181, 1166, 1140, 1119, 747, 737, 712 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{15}H_{12}F_3N_2$ $[M + H]^+$: 277.0947; found: 277.0944.



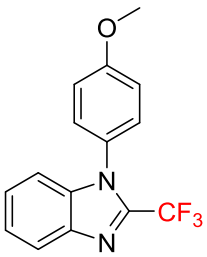
1-(3,4-dimethylphenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4i)

Obtained as a colorless liquid in 61% yield (141.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.30 (m, 3H), 7.17 – 7.13 (m, 3H), 2.38 (s, 3H), 2.34 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.58 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1 (q, *J* = 38.5 Hz), 140.8 (s), 138.9 (s), 138.5 (s), 137.5 (s), 132.1 (s), 130.8 (s), 128.3 (s), 125.8 (s), 124.8 (s), 124.0 (s), 121.5 (s), 119.1 (q, *J* = 271.9 Hz), 111.5 (s), 19.9 (s), 19.7 (s). IR (ATR): ν 2924, 1609, 1601, 1522, 1503, 1452, 1420, 1263, 1201, 1176, 1130, 746, 713, 643 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{16}H_{14}F_3N_2$ $[M + H]^+$: 291.1104; found: 291.1100.



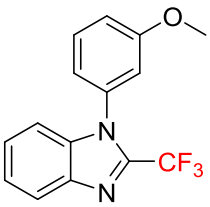
1-(3,5-dimethylphenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4j)

Obtained as a white solid in 65% yield (151.0 mg). Mp: 78–79 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 6.6, 2.0 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.22 – 7.13 (m, 2H), 7.02 (s, 2H), 2.41 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.56 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9 (q, *J* = 38.5 Hz), 140.7 (s), 139.7 (s), 137.3 (s), 134.3 (s), 131.5 (s), 125.6 (s), 125.0 (s), 123.9 (s), 121.3 (s), 118.9 (q, *J* = 271.8 Hz), 111.4 (s), 21.2 (s). IR (ATR): ν 2923, 1613, 1597, 1523, 1460, 1411, 1296, 1272, 1244, 1200, 1178, 1134, 1114, 859, 763, 746, 700 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{16}H_{14}F_3N_2$ $[M + H]^+$: 291.1104; found: 291.1100.



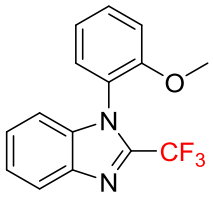
1-(4-methoxyphenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4k)

Obtained as a white solid in 60% yield (139.0 mg). Mp: 83–84 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.44 – 7.29 (m, 4H), 7.21 – 7.10 (m, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.72 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7 (s), 141.3 (q, *J* = 38.2 Hz), 140.7 (s), 137.7 (s), 128.8 (s), 127.0 (s), 125.8 (s), 124.1 (s), 121.5 (s), 119.0 (q, *J* = 271.8 Hz), 115.0 (s), 111.4 (s), 55.7 (s). IR (ATR): ν 2937, 1609, 1580, 1512, 1453, 1417, 1263, 1250, 1203, 1171, 1129, 1112, 1028, 982, 848, 746, 628 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{15}H_{12}F_3N_2O$ $[M + H]^+$: 293.0896; found: 293.0891.



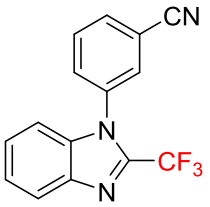
1-(3-methoxyphenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4l)

Obtained as a yellow liquid in 70% yield (163.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 1H), 7.48 (t, *J* = 8.1 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.24 – 7.17 (m, 1H), 7.11 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.96 (s, 1H), 3.85 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.57 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6 (s), 140.9 (q, *J* = 38.5 Hz), 140.8 (s), 137.3 (s), 135.5 (s), 130.6 (s), 125.9 (s), 124.2 (s), 121.5 (s), 119.6 (s), 119.0 (q, *J* = 271.9 Hz), 115.7 (s), 113.2 (s), 111.4 (s), 55.7 (s). IR (ATR): ν 2942, 1604, 1591, 1523, 1493, 1457, 1415, 1266, 1201, 1178, 1152, 1128, 1044, 744, 700, 689 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{15}H_{12}F_3N_2O$ $[M + H]^+$: 293.0896; found: 293.0893.



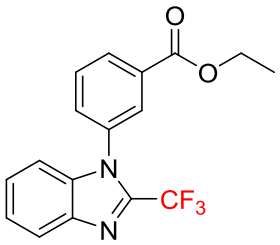
1-(2-methoxyphenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4m)

Obtained as a yellow liquid in 48% yield (112.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 6.8, 1.4 Hz, 1H), 7.58 – 7.46 (m, 1H), 7.40 – 7.32 (m, 3H), 7.15 – 7.01 (m, 3H), 3.70 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.27 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6 (s), 141.5 (q, *J* = 38.5 Hz), 140.9 (s), 137.2 (s), 131.7 (s), 129.4 (s), 125.6 (s), 123.8 (s), 123.0 (s), 121.3 (s), 120.9 (s), 119.0 (q, *J* = 272.0 Hz), 112.3 (s), 111.3 (s), 55.8 (s). IR (ATR): ν 2947, 1600, 1524, 1506, 1466, 1417, 1263, 1248, 1201, 1180, 1162, 1132, 1118, 1023, 742, 701 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{15}H_{12}F_3N_2O$ $[M + H]^+$: 293.0896; found: 293.0893.



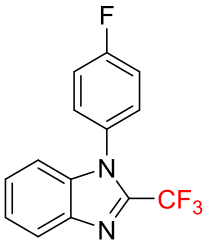
3-(2-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-1-yl)benzonitrile (4n)

Obtained as a white solid in 43% yield (99.0 mg). Mp: 136–137 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.88 (m, 2H), 7.81 – 7.69 (m, 3H), 7.50 – 7.40 (m, 2H), 7.16 – 7.09 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.26 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8 (s), 140.6 (q, *J* = 38.7 Hz), 136.9 (s), 135.6 (s), 133.7 (s), 132.2 (s), 131.2 (s), 131.1 (s), 126.6 (s), 124.8 (s), 121.9 (s), 118.8 (q, *J* = 271.9 Hz), 117.2 (s), 114.6 (s), 110.7 (s). IR (ATR): ν 3067, 1602, 1580, 1526, 1482, 1455, 1416, 1262, 1209, 1174, 1154, 1132, 1117, 803, 749, 734, 695 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{15}H_9F_3N_3$ $[M + H]^+$: 288.0743; found: 288.0740.



ethyl 3-(2-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-1-yl)benzoate (4o)

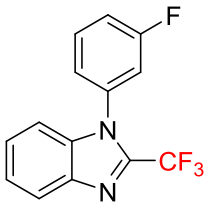
Obtained as a colorless liquid in 60% yield (160.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.7 Hz, 1H), 8.12 (s, 1H), 8.01 – 7.91 (m, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.64 – 7.62 (m, 1H), 7.53 – 7.36 (m, 2H), 7.21 – 7.10 (m, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.40 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2 (s), 140.9 (q, *J* = 38.5 Hz), 140.8 (s), 137.2 (s), 134.9 (s), 132.7 (s), 131.8 (s), 131.2 (s), 130.1 (s), 128.7 (s), 126.2 (s), 124.4 (s), 121.7 (s), 118.9 (q, *J* = 271.9 Hz), 111.1 (s), 61.8 (s), 14.4 (s). IR (ATR): ν 2982, 1719, 1589, 1526, 1491, 1454, 1414, 1292, 1251, 1205, 1181, 1162, 1132, 1115, 1024, 743, 730, 693 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{17}H_{14}F_3N_2O_2$ $[M + H]^+$: 335.1002; found: 335.0998.



1-(4-fluorophenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4p)

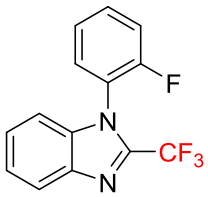
Obtained as a white solid in 56% yield (126.0 mg). Mp: 84–85 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 1H), 7.46 – 7.35 (m, 4H), 7.33 – 7.21 (m, 2H), 7.18 – 7.11 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.59 (s, 3F), -110.01 – -110.08 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (d, *J* = 250.9 Hz), 141.0 (q, *J* = 38.1 Hz), 140.7 (s), 137.4 (s), 130.4 (d, *J* = 3.1 Hz), 129.6 (d, *J* = 9.0 Hz), 126.1 (s), 124.3 (s), 121.6 (s), 118.9 (q, *J* = 271.9 Hz), 117.1 (d, *J* = 23.1 Hz), 111.1 (s). IR (ATR): ν 3071, 1603, 1589, 1525, 1506, 1263, 1201, 1166,

1136, 1090, 854, 767, 752, 736, 566 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_9F_4N_2$ $[M + H]^+$: 281.0696; found: 281.0692.



1-(3-fluorophenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4q)

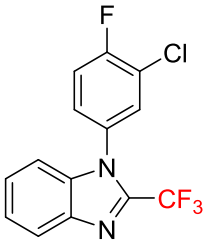
Obtained as a colorless liquid in 45% yield (101.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.61. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 1H), 7.63 – 7.53 (m, 1H), 7.47 – 7.35 (m, 2H), 7.31 (t, *J* = 8.3 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 6.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.52 (s, 3F), -109.67 – -109.77 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 250.3 Hz), 140.8 (s), 140.7 (q, *J* = 38.8 Hz), 137.1 (s), 135.9 (d, *J* = 9.7 Hz), 131.2 (d, *J* = 9.0 Hz), 126.2 (s), 124.4 (s), 123.5 (d, *J* = 3.1 Hz), 121.7 (s), 118.9 (q, *J* = 271.9 Hz), 117.4 (d, *J* = 20.9 Hz), 115.3 (d, *J* = 23.7 Hz), 111.1 (s). IR (ATR): ν 3070, 1598, 1526, 1492, 1459, 1413, 1265, 1198, 1177, 1126, 865, 744, 737, 688 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_9F_4N_2$ $[M + H]^+$: 281.0696; found: 281.0694.



1-(2-fluorophenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4r)

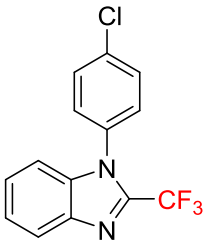
Obtained as a colorless liquid in 50% yield (112.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 6.7, 2.6 Hz, 1H), 7.64 – 7.53 (m, 1H), 7.51 – 7.29 (m, 5H), 7.14 – 7.06 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.94 (d, *J* = 3.4 Hz, 3F), -120.28 (s, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (d, *J* = 254.5 Hz), 141.2 (q, *J* = 38.7 Hz), 140.9 (s), 137.0 (s), 132.3 (d, *J* = 7.8 Hz), 129.9 (s), 126.2 (s), 125.2 (d, *J* = 4.2 Hz), 124.3 (s), 122.3 (d, *J* = 13.4 Hz), 121.7 (s), 117.2

(d, *J* = 19.3 Hz), 118.8 (q, *J* = 272.0 Hz), 111.0 (s). IR (ATR): ν 3058, 1616, 1594, 1528, 1506, 1463, 1450, 1415, 1263, 1202, 1165, 1136, 1115, 759, 745, 738 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_9F_4N_2$ $[M + H]^+$: 281.0696; found: 281.0692.



1-(3-chloro-4-fluorophenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4s)

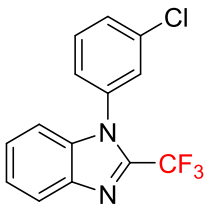
Obtained as a colorless liquid in 49% yield (123.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.56. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 1H), 7.64 (t, *J* = 8.1 Hz, 1H), 7.47 – 7.35 (m, 2H), 7.30 – 7.27 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.20 – 7.15 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.46 (s, 3F), -110.66 (t, *J* = 8.2 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2 (d, *J* = 253.3 Hz), 140.7 (s), 140.5 (q, *J* = 38.7 Hz), 136.8 (s), 133.9 (d, *J* = 8.6 Hz), 131.7 (s), 126.3 (s), 124.5 (s), 124.1 (s), 123.4 (d, *J* = 17.5 Hz), 121.7 (s), 118.7 (q, *J* = 272.0 Hz), 116.3 (d, *J* = 23.1 Hz), 110.8 (s). IR (ATR): ν 2924, 1587, 1529, 1494, 1454, 1411, 1266, 1206, 1179, 1155, 1135, 746, 737 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_8ClF_4N_2$ $[M + H]^+$: 315.0307; found: 315.0303.



1-(4-chlorophenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4t)

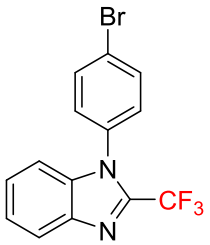
Obtained as a white solid in 54% yield (128.0 mg). Mp: 81–82 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.46 – 7.35 (m, 4H), 7.15 (d, *J* = 6.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.48 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9 (q, *J* = 38.3 Hz), 140.8

(s), 137.2 (s), 136.3 (s), 133.1 (s), 130.3 (s), 128.9 (s), 126.2 (s), 124.4 (s), 121.7 (s), 118.9 (q, J = 272.0 Hz), 111.1 (s). IR (ATR): ν 3057, 1618, 1583, 1526, 1494, 1451, 1414, 1263, 1205, 1173, 1160, 1128, 1089, 983, 743, 733, 623 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_9ClF_3N_2$ $[M + H]^+$: 296.0401; found: 296.0398.



1-(3-chlorophenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4u)

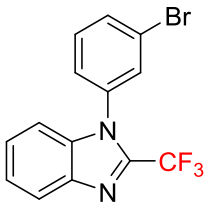
Obtained as a colorless liquid in 51% yield (120.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 1H), 7.69 – 7.49 (m, 2H), 7.48 – 7.37 (m, 3H), 7.35 (d, J = 7.7 Hz, 1H), 7.22 – 7.14 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.44 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8 (s), 140.7 (q, J = 38.7 Hz), 137.1 (s), 135.7 (s), 135.6 (s), 130.9 (s), 130.5 (s), 127.9 (s), 126.3 (s), 125.9 (s), 124.4 (s), 121.7 (s), 118.9 (q, J = 272.0 Hz), 110.1 (s). IR (ATR): ν 3068, 1590, 1527, 1480, 1451, 1411, 1264, 1208, 1163, 1129, 1114, 744, 735, 693 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_9ClF_3N_2$ $[M + H]^+$: 296.0401; found: 296.0398.



1-(4-bromophenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4v)

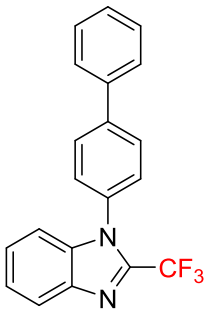
Obtained as a white solid in 53% yield (144.0 mg). Mp: 64–65 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 1H), 7.73 (d, J = 8.8 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.31 (d, J = 8.8 Hz, 2H), 7.17 – 7.13 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.44 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8 (s), 140.7 (q, J = 38.7 Hz), 137.1 (s), 133.6 (s), 133.3 (s), 129.2 (s), 126.2 (s), 124.4 (s),

124.3 (s), 121.7 (s), 118.9 (q, J = 271.9 Hz), 111.1 (s). IR (ATR): ν 3054, 1608, 1587, 1487, 1417, 1262, 1202, 1177, 1158, 1131, 1102, 1065, 1016, 981, 747, 711, 530 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_9BrF_3N_2$ $[M + H]^+$: 340.9896; found: 340.9893.



1-(3-bromophenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4w)

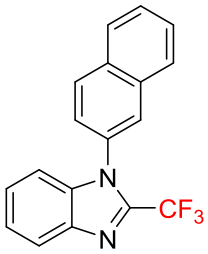
Obtained as a colorless liquid in 54% yield (147.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.62 (s, 1H), 7.50 – 7.39 (m, 4H), 7.18 – 7.16 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.41 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8 (s), 140.7 (q, J = 38.6 Hz), 137.1 (s), 135.7 (s), 133.4 (s), 131.2 (s), 130.7 (s), 126.4 (s), 126.3 (s), 124.5 (s), 123.2 (s), 121.7 (s), 118.9 (q, J = 271.9 Hz), 111.1 (s). IR (ATR): ν 3063, 1590, 1527, 1481, 1450, 1412, 1290, 1264, 1207, 1183, 1163, 1139, 760, 746, 692 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_9BrF_3N_2$ $[M + H]^+$: 340.9896; found: 340.9893.



1-([1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4x)

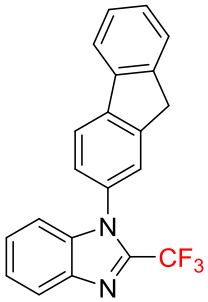
Obtained as a white solid in 52% yield (140.0 mg). Mp: 112–114 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.57. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 7.2 Hz, 2H), 7.52 – 7.38 (m, 7H), 7.25 – 7.22 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.42 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1 (s), 141.0 (q, J = 38.4 Hz), 140.9 (s), 139.7 (s), 137.4 (s), 133.6 (s),

129.2 (s), 128.5 (s), 128.3 (s), 127.9 (s), 127.4 (s), 126.0 (s), 124.2 (s), 121.6 (s), 119.1 (q, J = 271.9 Hz), 111.4 (s). IR (ATR): ν 3034, 1618, 1577, 1521, 1489, 1451, 1419, 1264, 1209, 1181, 1138, 762, 735, 696 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{20}H_{14}F_3N_2$ $[M + H]^+$: 339.1104; found: 339.1098.



1-(naphthalen-2-yl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4y)

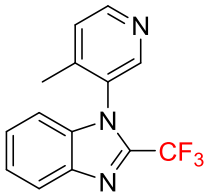
Obtained as a yellow liquid in 61% yield (152.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.61. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.93 – 7.90 (m, 2H), 7.65 – 7.59 (m, 2H), 7.47 – 7.35 (m, 3H), 7.17 (d, J = 7.9 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.43 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2 (q, J = 38.9 Hz), 140.9 (s), 137.6 (s), 133.5 (s), 133.3 (s), 131.9 (s), 130.1 (s), 128.4 (s), 128.1 (s), 127.8 (s), 127.5 (s), 126.8 (s), 126.0 (s), 124.7 (s), 124.2 (s), 121.6 (s), 119.1 (q, J = 271.9 Hz), 111.4 (s). IR (ATR): ν 3057, 1615, 1600, 1523, 1507, 1474, 1450, 1416, 1262, 1208, 1194, 1178, 1156, 1132, 1122, 813, 742, 476 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{18}H_{12}F_3N_2$ $[M + H]^+$: 313.0947; found: 313.0941.



1-(9*H*-fluoren-2-yl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4z)

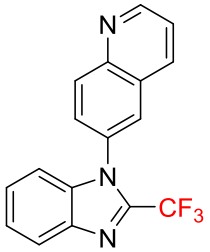
Obtained as a white solid in 55% yield (154.0 mg). Mp: 163–164 ℃. R_f

(*n*-pentane:ethyl acetate = 10:1) = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, *J* = 7.5 Hz, 2H), 7.86 (d, *J* = 7.4 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.45 – 7.36 (m, 5H), 7.20 (d, *J* = 7.4 Hz, 1H), 3.99 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.46 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8 (s), 143.7 (s), 143.6 (s), 141.2 (q, *J* = 38.3 Hz), 140.8 (s), 140.4 (s), 137.6 (s), 132.7 (s), 127.9 (s), 127.3 (s), 126.3 (s), 125.9 (s), 125.4 (s), 124.2 (s), 124.1 (s), 121.5 (s), 120.8 (s), 119.1 (q, *J* = 271.9 Hz), 120.6 (s), 111.4 (s), 37.1 (s). IR (ATR): ν 3056, 1615, 1589, 1523, 1489, 1460, 1416, 1263, 1206, 1171, 1127, 768, 731, 703 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{21}H_{14}F_3N_2$ $[M + H]^+$: 351.1104; found: 351.1100.



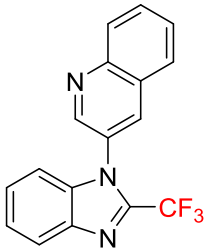
1-(4-methylpyridin-3-yl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (4aa)

Obtained as a yellow liquid in 48 % yield (106.0 mg). R_f (*n*-pentane:ethyl acetate = 3:1) = 0.58. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 7.68 (d, *J* = 5.7 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.15 (d, *J* = 6.3 Hz, 1H), 2.73 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.45 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8 (s), 147.6 (s), 141.0 (q, *J* = 38.7 Hz), 140.8 (s), 137.3 (s), 135.3 (s), 129.0 (s), 126.3 (s), 124.5 (s), 124.1 (s), 121.8 (s), 118.8 (q, *J* = 271.9 Hz), 110.9 (s), 24.5 (s). IR (ATR): ν 3057, 1615, 1570, 1537, 1492, 1451, 1417, 1262, 1206, 1182, 1163, 1126, 744, 738, 730 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_{11}F_3N_3$ $[M + H]^+$: 278.0900; found: 278.0897.



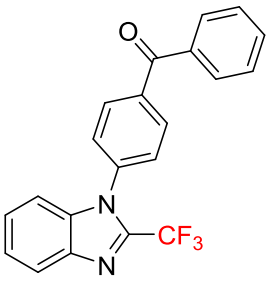
6-(2-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-1-yl)quinoline (4ab)

Obtained as a white solid in 54% yield (135.0 mg). Mp: 88–89 ℃. R_f (*n*-pentane:ethyl acetate=3:1) = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (br s, 1H), 8.36 (d, *J* = 8.9 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 7.98 (s, 2H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.59 (s, 1H), 7.49 – 7.37 (m, 2H), 7.18 (d, *J* = 7.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.36 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9 (s), 148.2 (s), 141.1 (s), 140.9 (q, *J* = 38.7 Hz), 140.7 (s), 137.3 (s), 136.4 (s), 132.4 (s), 131.8 (s), 128.3 (s), 126.7 (s), 126.1 (s), 124.3 (s), 122.7 (s), 121.6 (s), 118.9 (q, *J* = 271.9 Hz), 111.1 (s). IR (ATR): ν 3056, 3021, 1615, 1586, 1525, 1499, 1418, 1263, 1212, 1171, 1130, 1005, 914, 847, 800, 770, 744 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{17}H_{11}F_3N_3$ $[M + H]^+$: 314.0900; found: 314.0896.



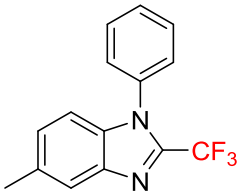
3-(2-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-1-yl)quinoline (4ac)

Obtained as a yellow liquid in 52 % yield (130.0 mg). R_f (*n*-pentane:ethyl acetate = 3:1) = 0.66. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.33 – 8.26 (m, 2H), 8.03 – 7.87 (m, 3H), 7.73 (t, *J* = 7.2 Hz, 1H), 7.51 – 7.38 (m, 2H), 7.17 (d, *J* = 9.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.29 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4 (s), 148.3 (s), 141.2 (q, *J* = 38.7 Hz), 141.0 (s), 137.6 (s), 134.6 (s), 131.6 (s), 129.9 (s), 128.5 (s), 128.4 (s), 128.2 (s), 127.6 (s), 126.6 (s), 124.7 (s), 122.0 (s), 118.9 (q, *J* = 272.0 Hz), 110.9 (s). IR (ATR): ν 3058, 1612, 1603, 1523, 1450, 1415, 1262, 1208, 1178, 1131, 1121, 812, 742, 660 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{17}H_{11}F_3N_3$ $[M + H]^+$: 314.0900; found: 314.0895.



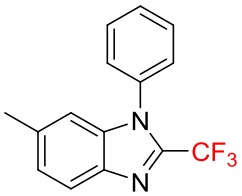
phenyl(4-(2-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-1-yl)phenyl)methanone (4ad)

Obtained as a white solid in 36% yield (105.4 mg). Mp: 102–105 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H), 8.00 – 7.93 (m, 1H), 7.88 (d, *J* = 7.1 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.61 – 7.51 (m, 4H), 7.49 – 7.39 (m, 2H), 7.28 – 7.19 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.22 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3 (s), 140.9 (s), 140.7 (q, *J* = 38.7 Hz), 139.0 (s), 137.9 (s), 137.0 (s), 136.9 (s), 133.2 (s), 131.6 (s), 130.2 (s), 128.7 (s), 127.5 (s), 126.3 (s), 124.5 (s), 121.8 (s), 118.9 (q, *J* = 272.2 Hz), 111.1 (s). IR (ATR): ν 1662, 1600, 1527, 1451, 1316, 1275, 1254, 1209, 1181, 1163, 1138, 936, 924, 746, 733, 700 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{21}H_{14}F_3N_2O$ $[M + H]^+$: 367.1053; found: 367.1057.



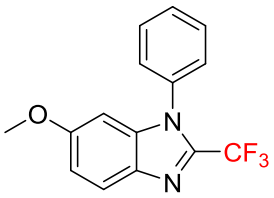
5-methyl-1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (5a)

Obtained as a white solid in 66% yield (146.0 mg). Mp: 74–75 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.63 – 7.54 (m, 3H), 7.46 – 7.37 (m, 2H), 7.21 (d, *J* = 6.9 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 2.51 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.43 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1 (s), 140.8 (q, *J* = 38.3 Hz), 135.6 (s), 134.8 (s), 134.1 (s), 130.0 (s), 129.9 (s), 127.7 (s), 127.5 (s), 121.0 (s), 119.0 (q, *J* = 271.7 Hz), 110.8 (s), 21.7 (s). IR (ATR): ν 2921, 1635, 1595, 1524, 1500, 1456, 1440, 1407, 1278, 1208, 1190, 1161, 1131, 797, 766, 699 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{12}F_3N_2$ $[M + H]^+$: 277.0947; found: 277.0942.



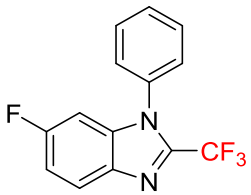
6-methyl-1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (5b)

Obtained as a white solid in 60% yield (133.0 mg). Mp: 99–100 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.57 (m, 3H), 7.42 – 7.40 (m, 2H), 7.22 (d, *J* = 6.8 Hz, 1H), 6.93 (s, 1H), 2.43 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.44 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4 (q, *J* = 38.4 Hz), 138.9 (s), 137.6 (s), 136.4 (s), 134.7 (s), 129.9 (s), 129.8 (s), 127.6 (s), 126.0 (s), 121.0 (s), 119.0 (q, *J* = 271.6 Hz), 110.9 (s), 21.9 (s). IR (ATR): ν 2925, 1601, 1596, 1524, 1499, 1437, 1415, 1308, 1285, 1268, 1194, 1166, 1123, 808, 762, 737, 703, 694 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{15}H_{12}F_3N_2$ $[M + H]^+$: 277.0947; found: 277.0944.



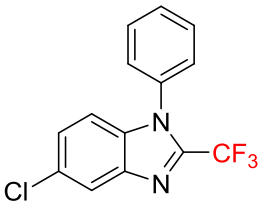
6-methoxy-1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (5c)

Obtained as a white solid in 72% yield (196.0 mg). Mp: 68–69 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.2 Hz, 1H), 7.60 (s, 3H), 7.44 (s, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.52 (s, 1H), 3.76 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.37 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 (s), 139.9 (q, *J* = 38.3 Hz), 138.2 (s), 135.1 (s), 134.6 (s), 130.1 (s), 130.0 (s), 127.6 (s), 122.2 (s), 119.0 (q, *J* = 271.3 Hz), 114.6 (s), 93.4 (s), 55.9 (s). IR (ATR): ν 2948, 1621, 1595, 1527, 1499, 1441, 1416, 1312, 1280, 1209, 1170, 1167, 1128, 819, 737, 702, 694 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{15}H_{12}F_3N_2O$ $[M + H]^+$: 293.0896; found: 293.0893.



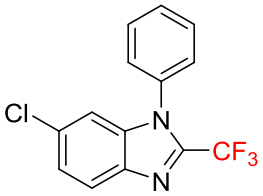
6-fluoro-1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (5e)

Obtained as a colorless liquid in 60% yield (134 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 9.0, 4.7 Hz, 1H), 7.68 – 7.54 (m, 3H), 7.47 – 7.37 (m, 2H), 7.16 (td, *J* = 9.2, 2.4 Hz, 1H), 6.83 (dd, *J* = 8.3, 2.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.70 (s, 3F), -113.84 – -113.90 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, *J* = 244.5 Hz), 141.7 (q, *J* = 38.9 Hz), 137.4 (d, *J* = 14.1 Hz), 137.3 (s), 134.2 (s), 130.3 (s), 130.1 (s), 127.4 (s), 122.8 (d, *J* = 10.3 Hz), 118.8 (q, *J* = 271.9 Hz), 113.3 (d, *J* = 25.7 Hz), 97.8 (d, *J* = 28.1 Hz). IR (ATR): ν 3059, 1624, 1598, 1530, 1500, 1486, 1445, 1417, 1204, 1192, 1172, 1138, 1106, 739, 703, 694 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_9F_4N_2$ $[M + H]^+$: 281.0696; found: 281.0893.



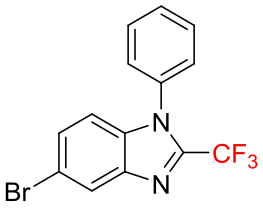
5-chloro-1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (5f)

Obtained as a white solid in 58% yield (137.0 mg). Mp: 67–68 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.9 Hz, 1H), 7.64 – 7.52 (m, 3H), 7.45 – 7.38 (m, 2H), 7.35 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.74 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1 (q, *J* = 38.8 Hz), 141.5 (s), 136.0 (s), 134.2 (s), 130.4 (s), 130.1 (s), 129.9 (s), 127.5 (s), 126.7 (s), 121.2 (s), 118.7 (q, *J* = 272.1 Hz), 112.3 (s). IR (ATR): ν 3069, 1595, 1523, 1498, 1455, 1437, 1407, 1270, 1205, 1184, 1172, 1125, 1055, 800, 764, 738, 694 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_9ClF_3N_2$ $[M + H]^+$: 297.0401; found: 297.0397.



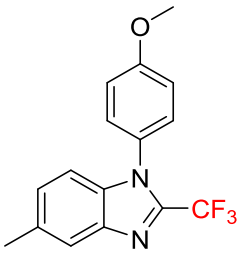
6-chloro-1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (5g)

Obtained as a white solid in 65% yield (154.0 mg). Mp: 76–78 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.60 (m, 3H), 7.43 – 7.35 (m, 3H), 7.15 (d, *J* = 1.9 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.72 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7 (q, *J* = 38.8 Hz), 139.4 (s), 137.8 (s), 134.0 (s), 131.9 (s), 130.4 (s), 130.1 (s), 127.4 (s), 125.1 (s), 122.5 (s), 118.7 (q, *J* = 272.1 Hz), 111.4 (s). IR (ATR): ν 3069, 1598, 1582, 1524, 1498, 1440, 1411, 1306, 1273, 1203, 1185, 1131, 1059, 811, 765, 727, 693 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_9ClF_3N_2$ $[M + H]^+$: 297.0401; found: 297.0397.



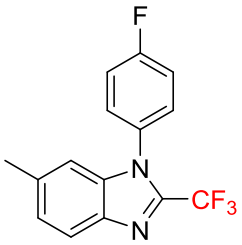
5-bromo-1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (5h)

Obtained as a white solid in 72% yield (196.0 mg). Mp: 68–69 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.8 Hz, 1H), 7.61 – 7.60 (m, 3H), 7.48 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.04 (d, *J* = 8.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.72 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0 (s), 141.9 (q, *J* = 38.9 Hz), 136.3 (s), 134.1 (s), 130.4 (s), 130.1 (s), 129.2 (s), 127.4 (s), 124.3 (s), 118.7 (q, *J* = 272.2 Hz), 117.2 (s), 112.7 (s). IR (ATR): ν 3067, 1596, 1580, 1522, 1497, 1452, 1435, 1405, 1270, 1203, 1185, 1174, 1126, 1044, 798, 764, 693 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{14}H_9BrF_3N_2$ $[M + H]^+$: 340.9896; found: 340.9891.



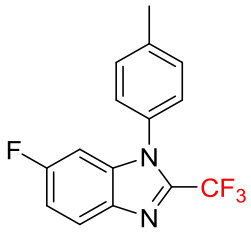
1-(4-methoxyphenyl)-5-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (5i)

Obtained as a yellow liquid in 52% yield (150.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.06 – 7.02 (m, 3H), 3.89 (s, 3H), 2.50 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.62 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (s), 140.9 (s), 140.8 (q, *J* = 38.1 Hz), 135.8 (s), 133.8 (s), 128.6 (s), 127.4 (s), 127.0 (s), 120.8 (s), 119.0 (q, *J* = 271.8 Hz), 114.8 (s), 110.7 (s), 55.6 (s), 21.5 (s). IR (ATR): ν 2936, 1609, 1587, 1512, 1445, 1409, 1277, 1251, 1208, 1172, 1157, 1127, 1031, 831, 797, 735 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{16}H_{14}F_3N_2O$ $[M + H]^+$: 307.1053; found: 307.1050.



1-(4-fluorophenyl)-6-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (5j)

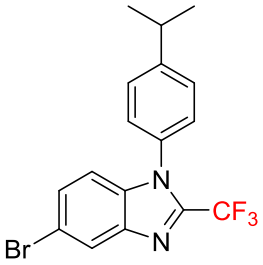
Obtained as a white solid in 62% yield (150.0 mg). Mp: 92–93 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.9 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.29 – 7.22 (m, 3H), 6.91 (s, 1H), 2.45 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.52 (s, 3F), -110.21 – -110.28 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (d, *J* = 250.7 Hz), 140.4 (q, *J* = 38.4 Hz), 138.8 (s), 137.6 (s), 136.6 (s), 130.5 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 9.0 Hz), 126.1 (s), 121.1 (s), 119.0 (q, *J* = 271.5 Hz), 117.0 (d, *J* = 23.1 Hz), 110.6 (s), 21.9 (s). IR (ATR): ν 2925, 1588, 1526, 1509, 1440, 1418, 1312, 1267, 1195, 1167, 1123, 983, 854, 835, 808 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{15}H_{11}F_4N_2$ $[M + H]^+$: 295.0853; found: 295.0850.



6-fluoro-1-(*p*-tolyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (5k)

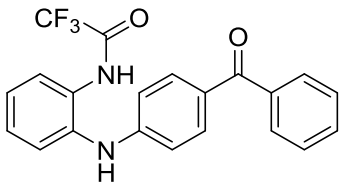
Obtained as a yellow liquid in 72% yield (132.0 mg). R_f (*n*-pentane:ethyl acetate = 10:1) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 9.2, 4.8 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 2H), 7.15 (t, *J* = 9.2 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 2.49 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.78 (s, 3F), -114.02 – -114.15 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, *J* = 244.3 Hz), 141.7 (q, *J* = 38.4 Hz), 140.6 (s), 137.8 (d, *J* = 13.1 Hz), 137.2 (s), 131.5 (s), 130.6 (s), 127.1 (s), 122.7 (d, *J* = 10.3 Hz), 118.7 (q, *J* = 272.7 Hz), 113.2 (d, *J* = 25.7 Hz), 97.9 (d, *J* = 28.1 Hz), 21.4 (s). IR (ATR): ν 2927, 1622, 1597, 1529, 1514, 1486, 1447, 1418, 1319, 1192, 1170,

1136, 1106, 838, 800 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{15}H_{11}F_4N_2$ $[M + H]^+$: 295.0853; found: 295.0848.



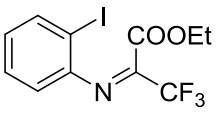
5-bromo-1-(4-isopropylphenyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (5l)

Obtained as a white solid in 60% yield (135.0 mg). Mp: 59–60 ℃. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.47 – 7.42 (m, 3H), 7.31 (d, *J* = 6.7 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 3.12 – 2.97 (m, 1H), 1.34 (d, *J* = 7.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.77 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3 (s), 142.0 (q, *J* = 38.7 Hz), 141.9 (s), 136.4 (s), 131.6 (s), 129.0 (s), 128.0 (s), 127.2 (s), 124.2 (s), 118.7 (q, *J* = 272.1 Hz), 117.1 (s), 112.8 (s), 34.1 (s), 23.9 (s). IR (ATR): ν 2963, 2930, 1516, 1439, 1406, 1271, 1206, 1180, 1155, 1139, 868, 799 cm^{-1}. HRMS (DART) m/z: calcd. for $C_{17}H_{15}BrF_3N_2$ $[M + H]^+$: 383.0365; found: 383.0362.



_N_-(2-((4-benzoylphenyl)amino)phenyl)-2,2,2-trifluoroacetamide (6)

Obtained as a red solid. Mp: 188–191 ℃. R_f (*n*-pentane:ethyl acetate = 4:1) = 0.53. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.83 (s, 1H), 8.49 (s, 1H), 7.73 – 7.64 (m, 4H), 7.64 – 7.57 (m, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.34 (td, *J* = 7.7, 1.6 Hz, 1H), 7.18 (td, *J* = 7.6, 1.4 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -73.86 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 193.8 (s), 155.4 (q, *J* = 36.8 Hz), 149.0 (s), 138.5 (s), 135.8 (s), 132.1 (s), 131.6 (s), 129.0 (s), 128.3 (s), 127.9 (s), 127.8 (s), 127.5 (s), 126.9 (s), 123.8 (s), 123.2 (s), 116.0 (q, *J* = 288.2 Hz), 113.9 (s). IR (ATR): ν 3393, 1724, 1643, 1589, 1522, 1317, 1282, 1150, 1049, 1024, 1003, 823, 760, 703, 624 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{21}H_{16}F_3N_2O_2$ $[M + H]^+$: 385.1158; found: 385.1161.



ethyl-3,3,3-trifluoro-2-((2-iodophenyl)imino)propanoate (9)

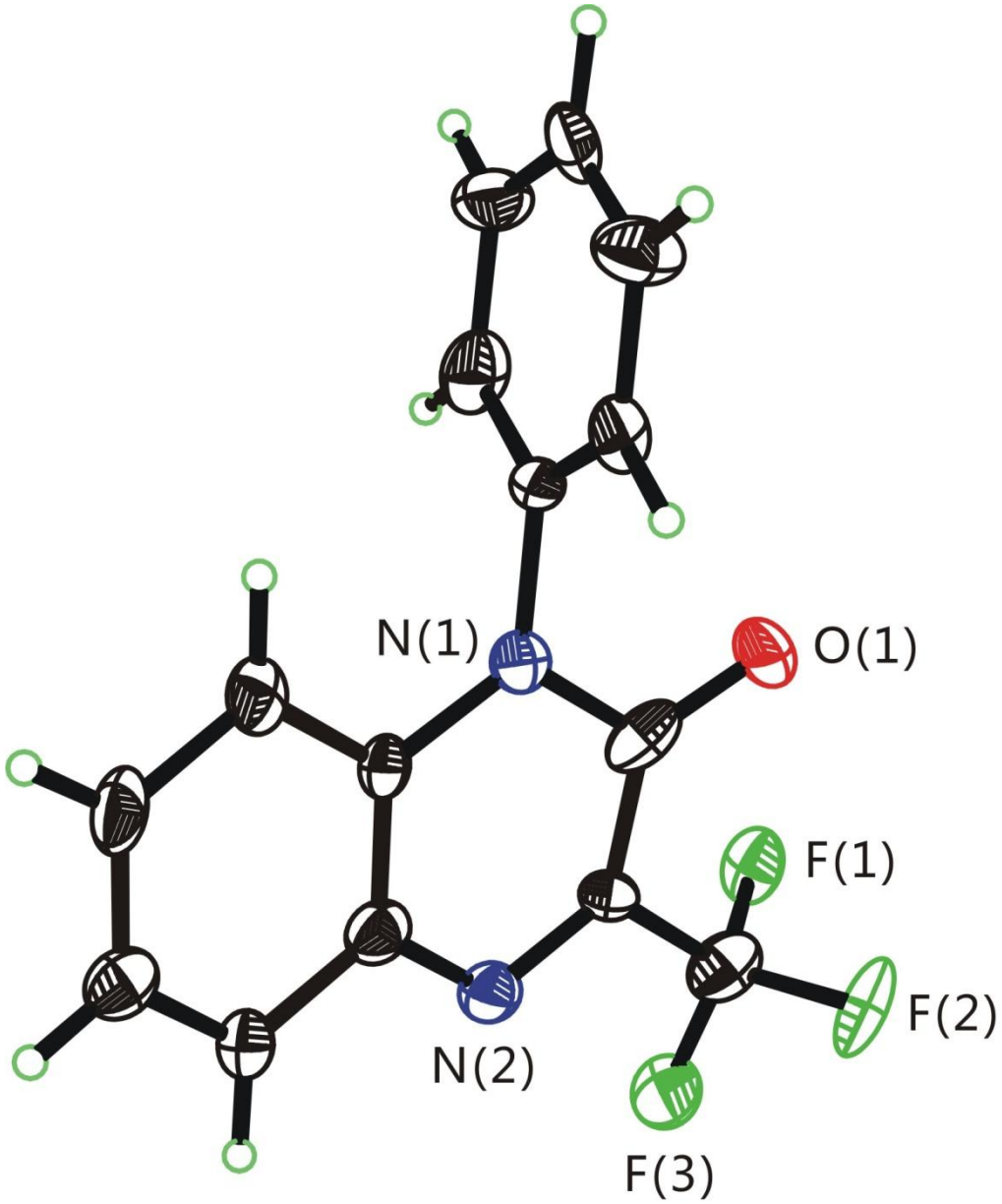
Obtained as a yellow liquid. R_f (*n*-pentane:ethyl acetate = 10:1) = 0.66. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.36 – 7.28 (m, 1H), 6.94 (td, *J* = 7.6, 1.5 Hz, 1H), 6.73 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.05 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.71 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (s), 149.9 (q, *J* = 37.2 Hz), 148.7 (s), 139.4 (s), 128.9 (s), 127.9 (s), 118.1 (q, *J* = 278.7 Hz), 117.5 (s), 88.2 (s), 63.1 (s), 13.7 (s). IR (ATR): ν 1744, 1585, 1499, 1461, 1434, 1369, 1325, 1252, 1224, 1189, 1155, 1047, 1032, 1018, 755 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{11}H_{10}F_3INO_2$ $[M + H]^+$: 371.9703; found: 371.9707.

Crystal structure analyses

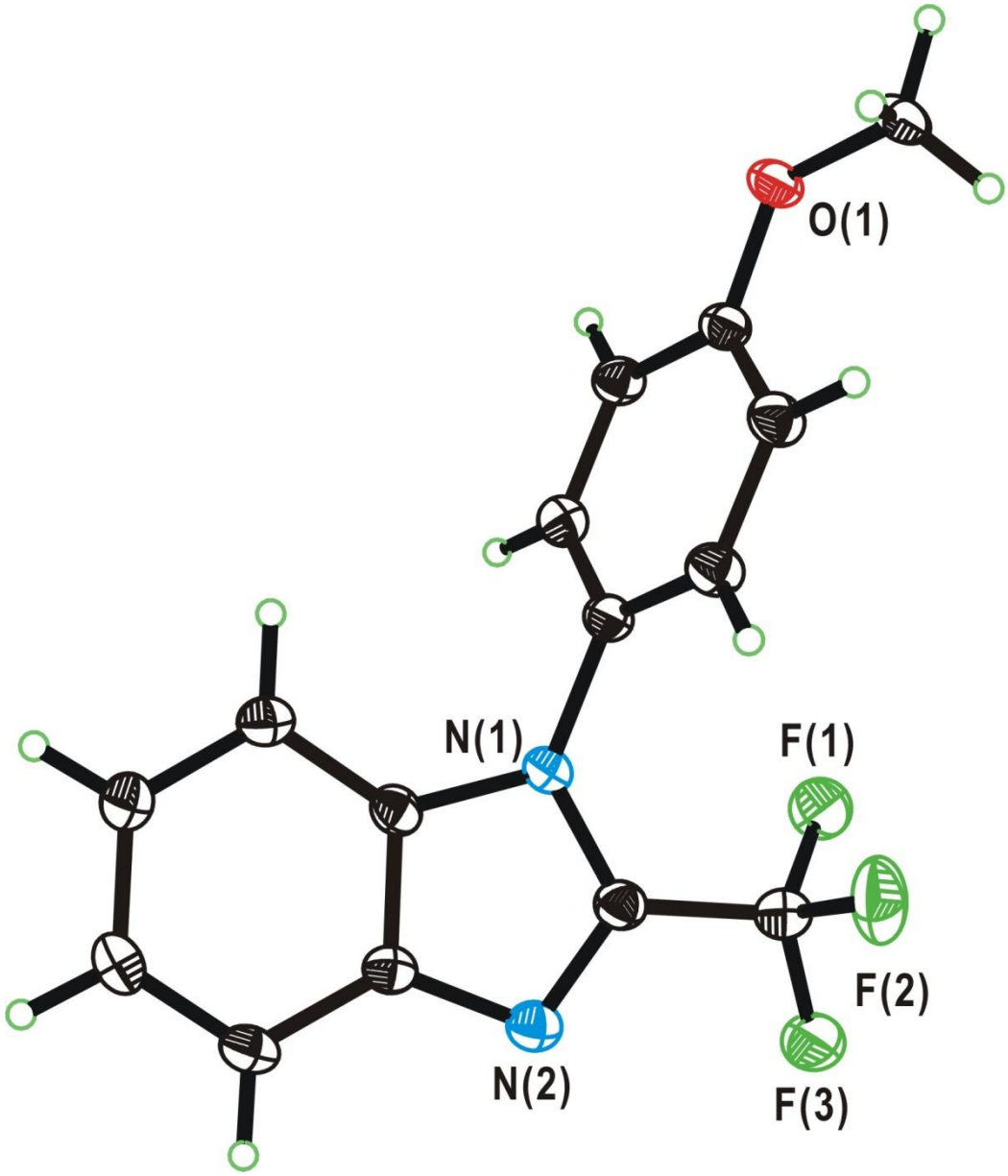
The crystal samples of **4a′**, **4k**, and **6** were prepared by slow volatilization in a $CH_2Cl_2/CDCl_3$ (3:1) solvent mixture. The suitable crystals of **4a′** (CCDC 2166079), **4k** (CCDC 2100010) and **6** (CCDC 2123484) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 ºC, using MoKα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the **SMART** suite of programs and for absorption effects with SADABS.[4] Structure solution and refinement were carried out with the SHELXTL suite of programs.[4] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

For crystal structure of **4a′** (CCDC 2166079), there are some Level A and B alerts in the CheckCIF report. We still did not solve the alert when we tried to give additional refinement cycles or use new space group. However, we have provided sufficient evidence to prove the accuracy of the structure by NMR and HRMS.

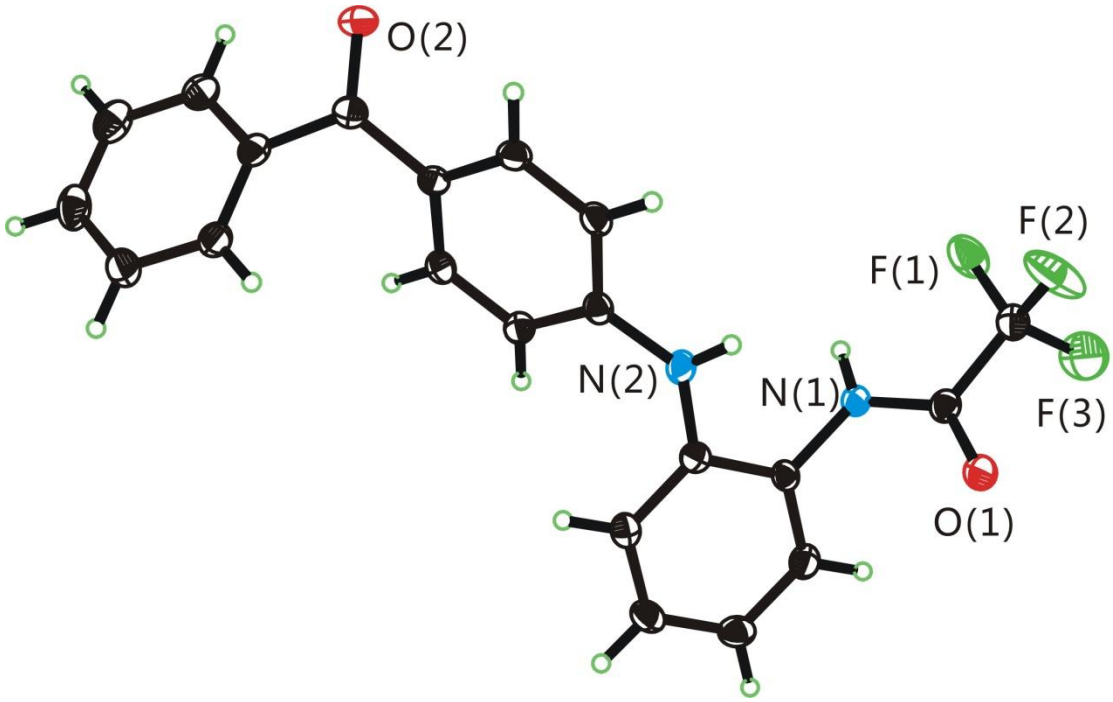
ORTEP diagrams



ORTEP diagram of compound 4a′. Thermal ellipsoids are drawn at 40% probability



ORTEP diagram of compound 4k. Thermal ellipsoids are drawn at 40% probability



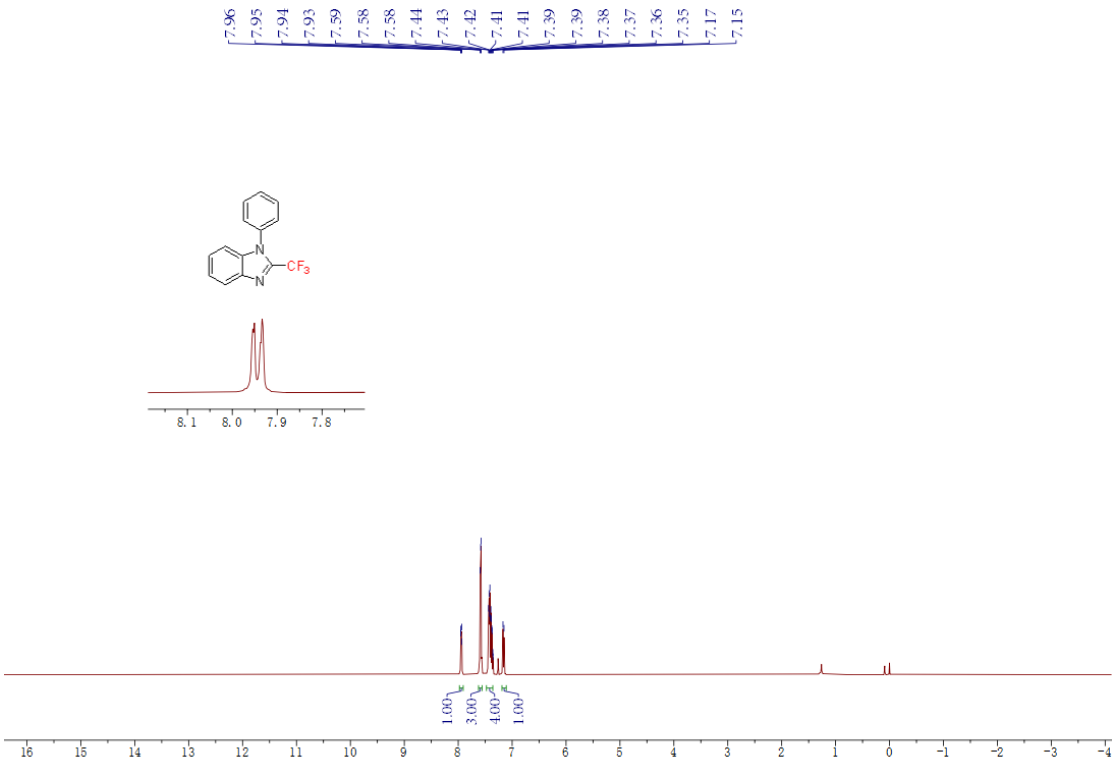
ORTEP diagram of compound 6. Thermal ellipsoids are drawn at 40% probability

References:

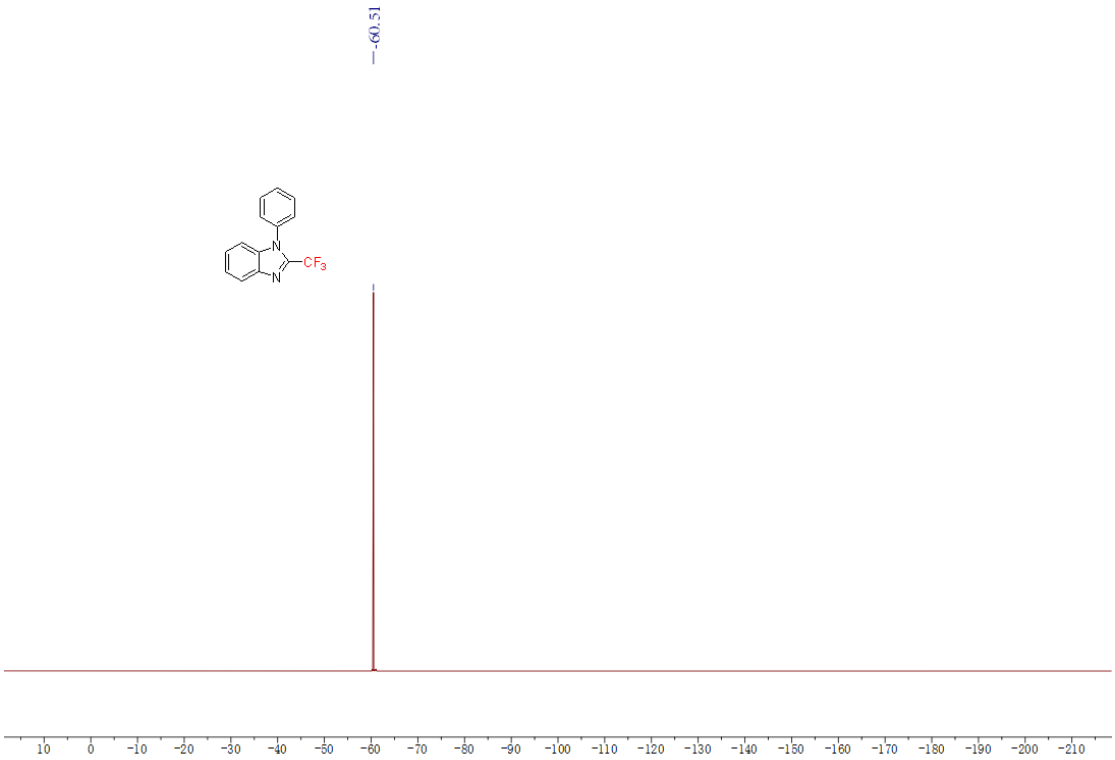
1. K. Song, K. Kim, D. Hong, J. Kim, C. E. Heo, H. I. Kim and S. H. Hong, Highly active ruthenium metathesis catalysts enabling ring-opening metathesis polymerization of cyclopentadiene at low temperatures, *Nat. Commun.*, 2019, **10**, 3860.
2. H. Song, Y. Liu, Y. Liu and Q. Wang, Self-Induced Stereoselective in Situ Trifluoromethylation: Preparation of Spiro[indoline-3,3′-quinoline] via Palladium-Catalyzed Cascade Reaction, *Org. Lett.*, 2014, **16**, 3240-3243.
3. W. Xue, Y. Su, K.-H. Wang, L. Cao, Y. Feng, W. Zhang, D. Huang and Y. Hu, Phenyliodonium Diacetate Mediated Carbotrifluoromethylation of Quinoxalin-2(1*H*)-ones, *Asian J. Org. Chem.*, 2019, **8**, 887-892.
4. SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra

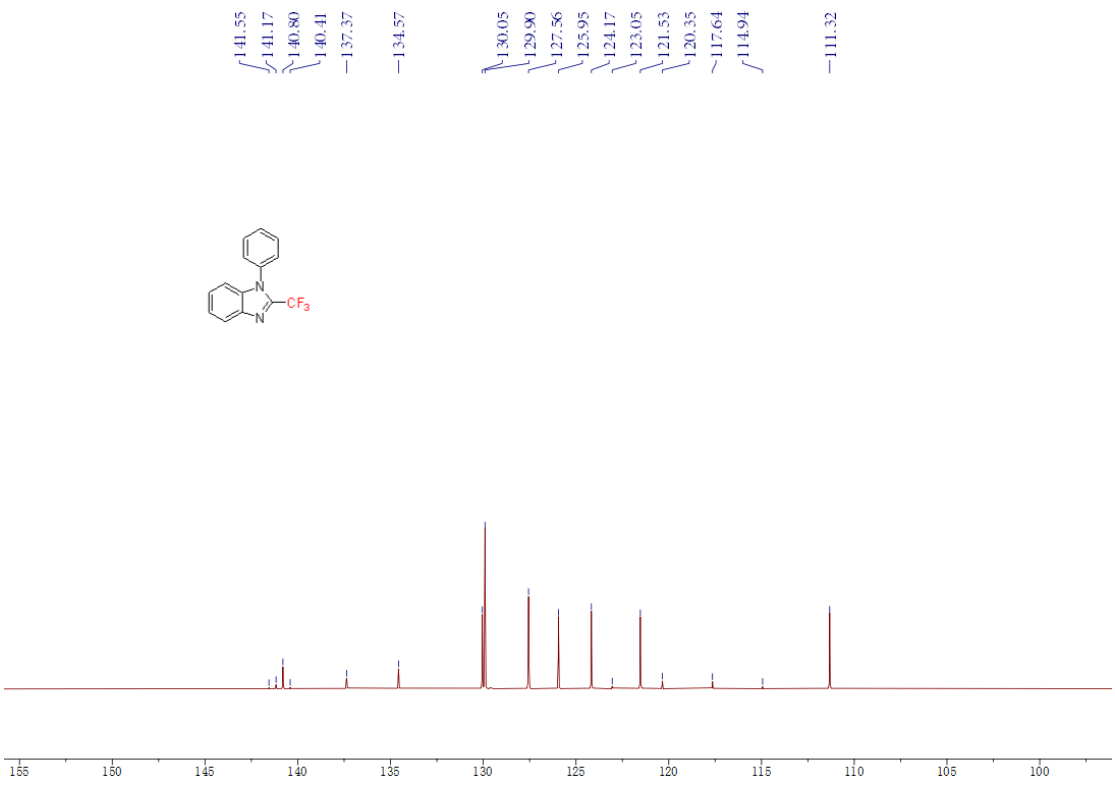
^{1}H NMR spectra of **4a** in $CDCl_3$



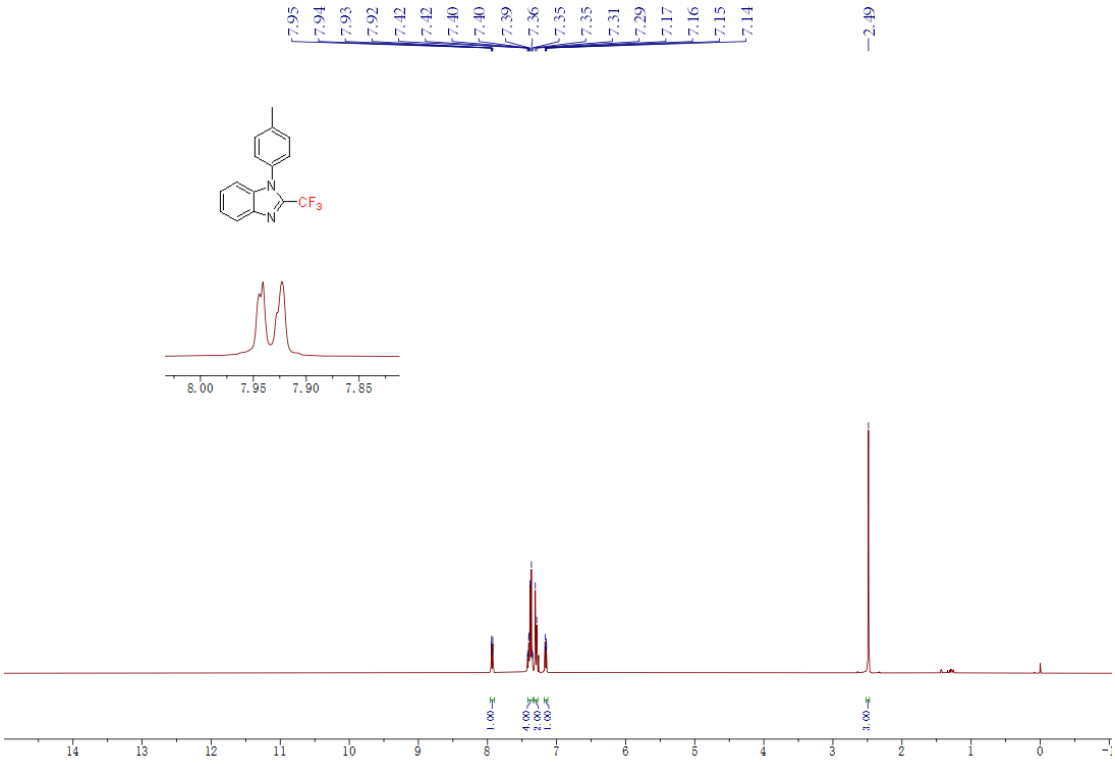
^{19}F NMR spectra of **4a** in $CDCl_3$



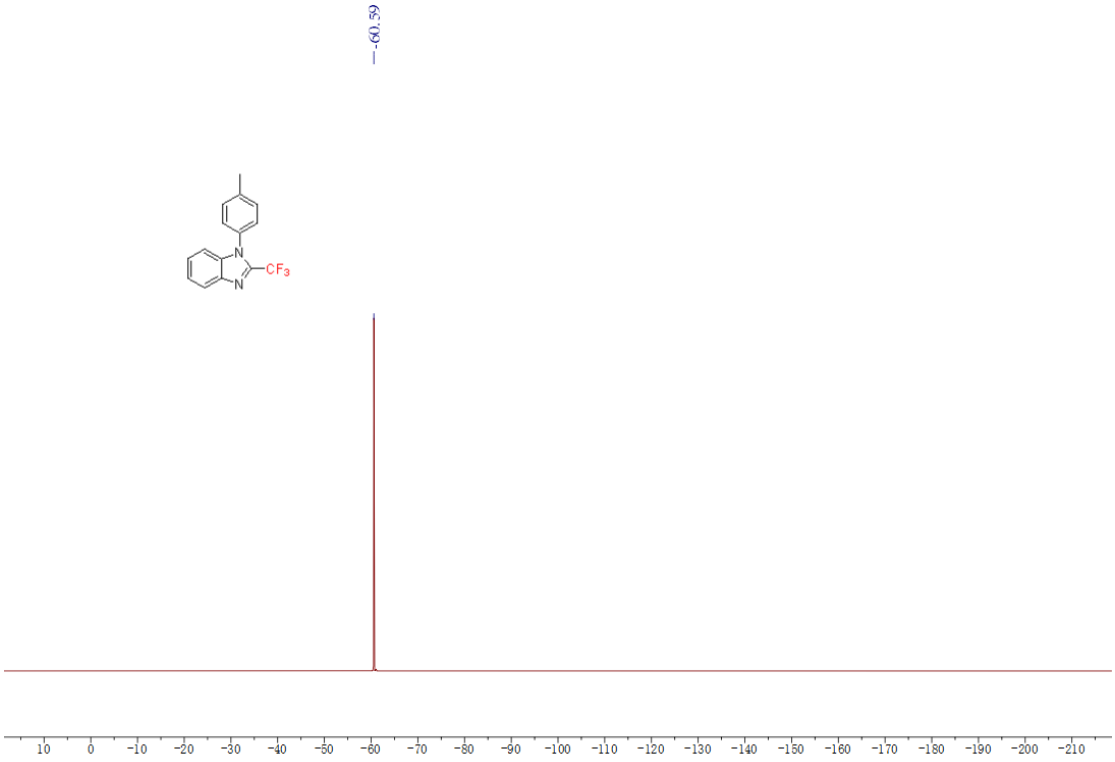
^{13}C NMR spectra of **4a** in $CDCl_3$



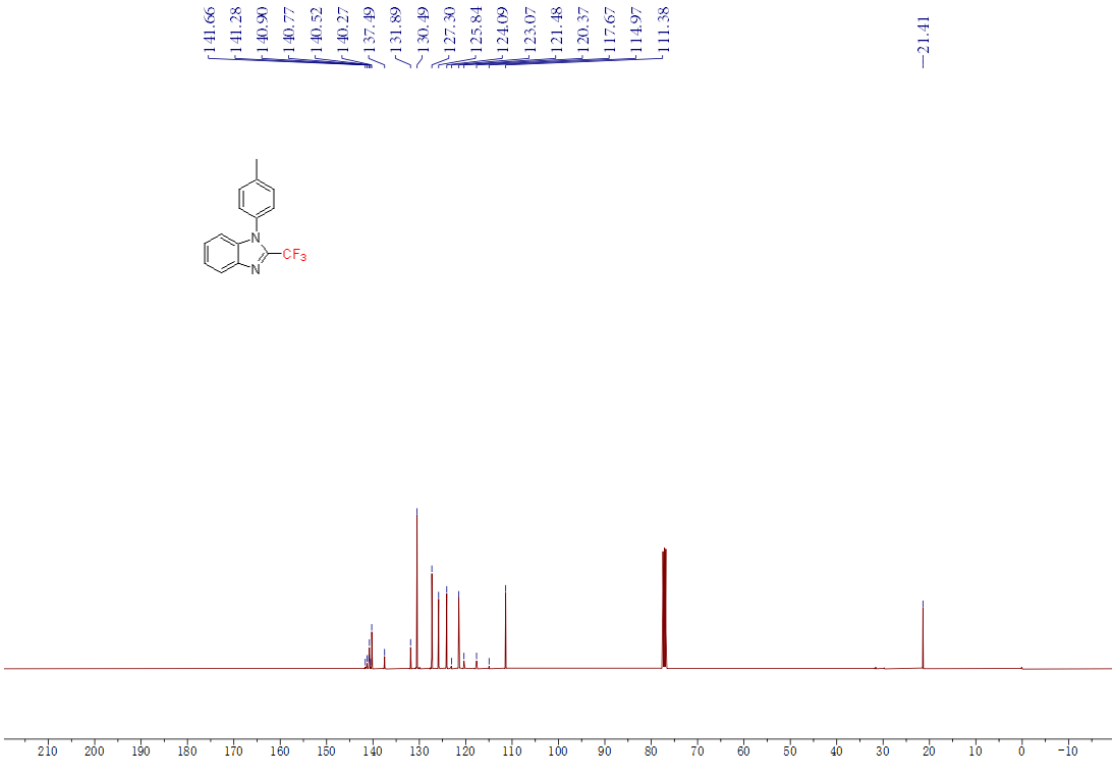
^{1}H NMR spectra of **4b** in $CDCl_3$



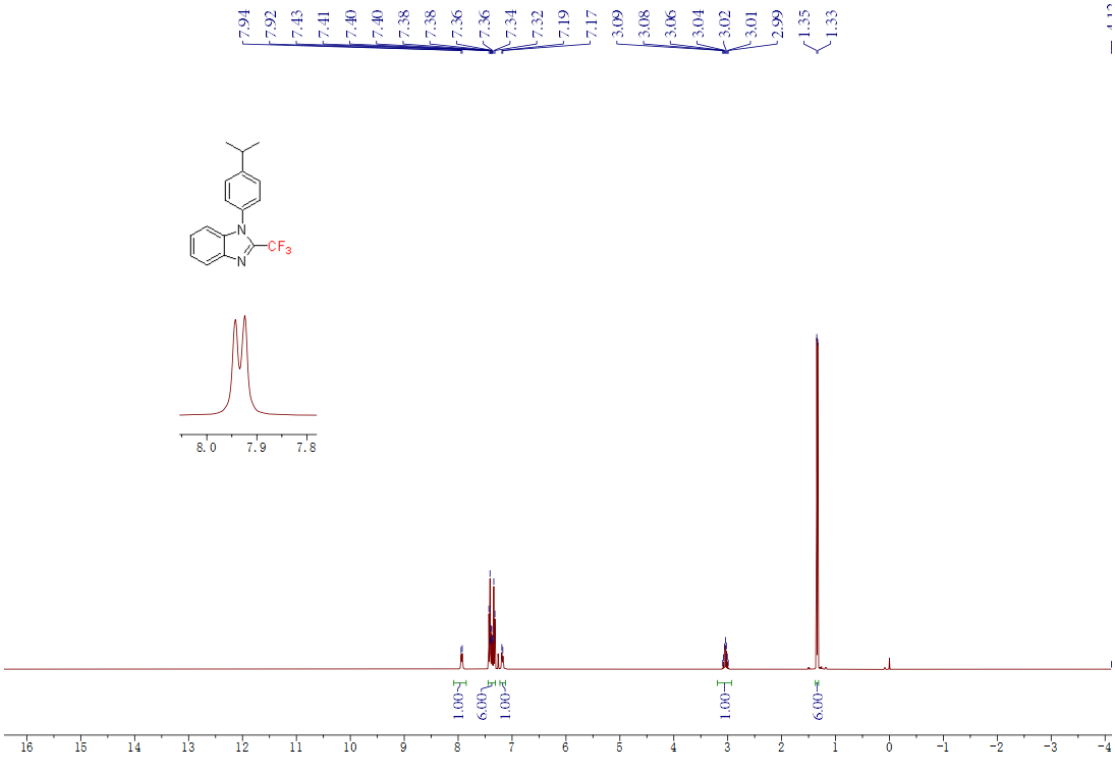
^{19}F NMR spectra of **4b** in $CDCl_3$



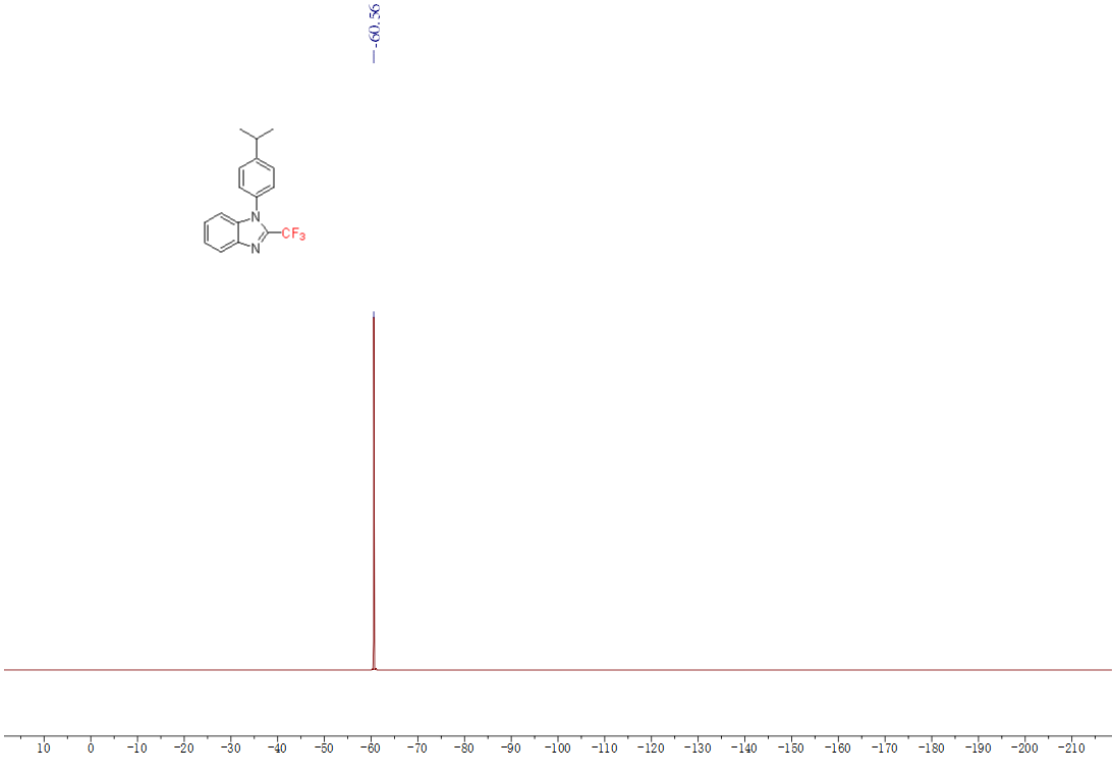
^{13}C NMR spectra of **4b** in $CDCl_3$



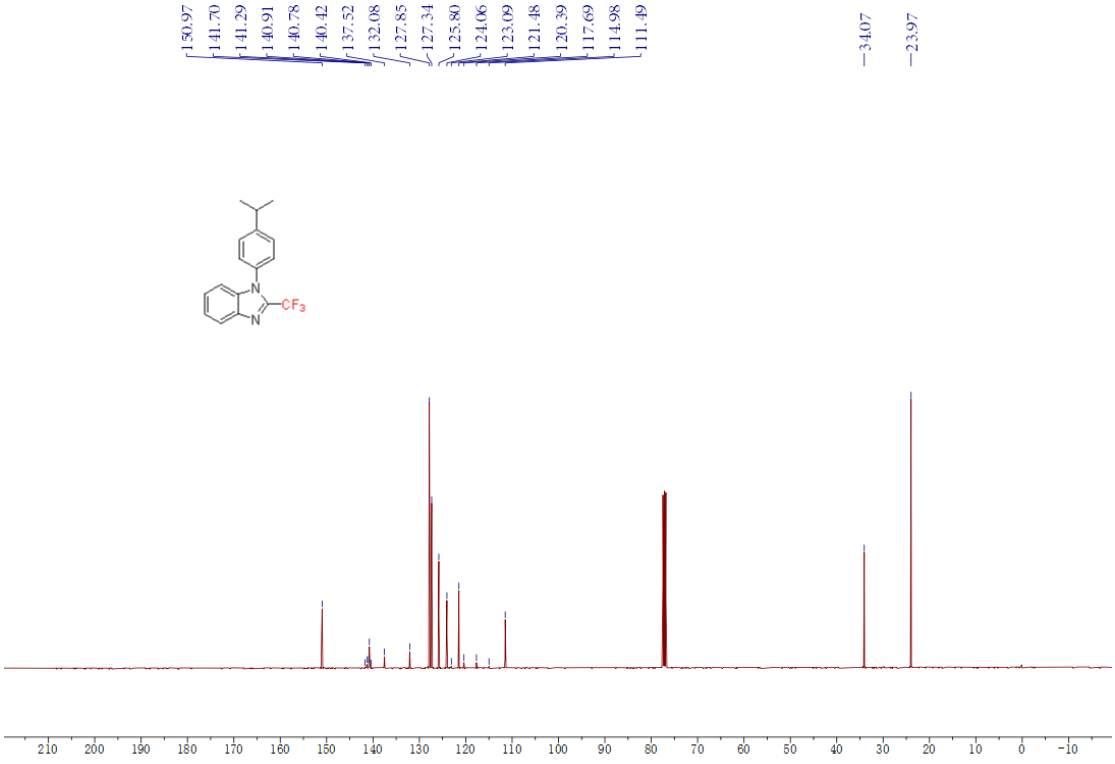
^{1}H NMR spectra of **4c** in $CDCl_3$



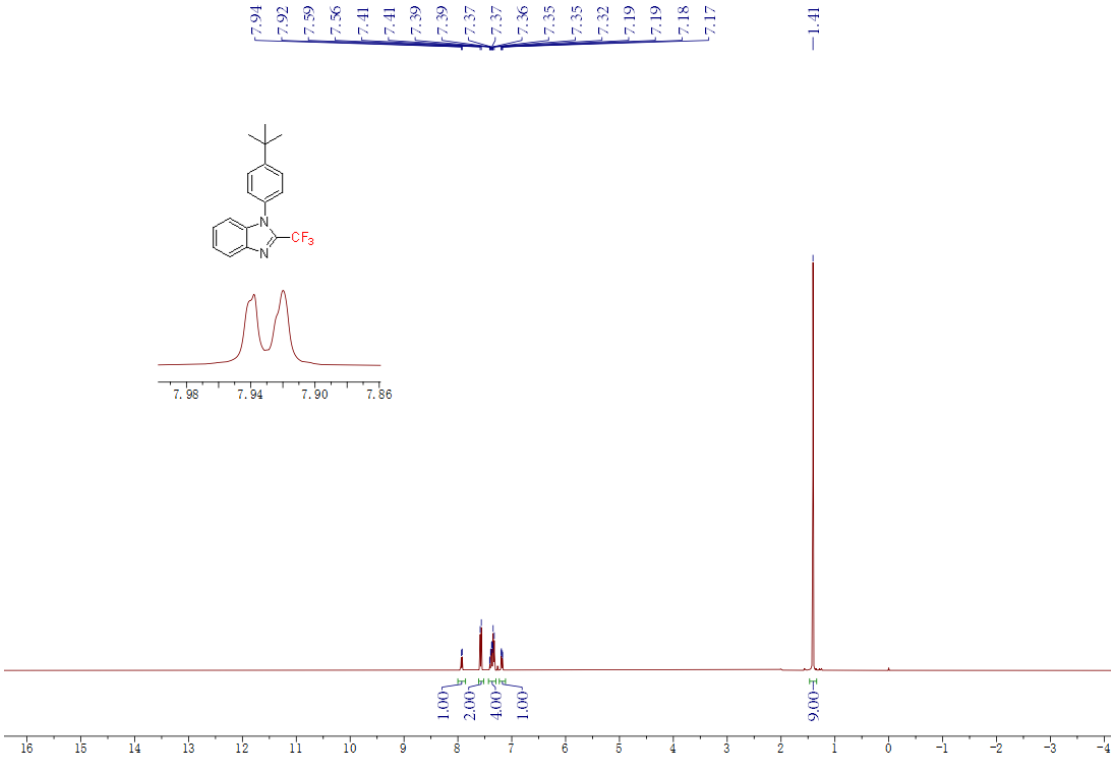
^{19}F NMR spectra of **4c** in $CDCl_3$



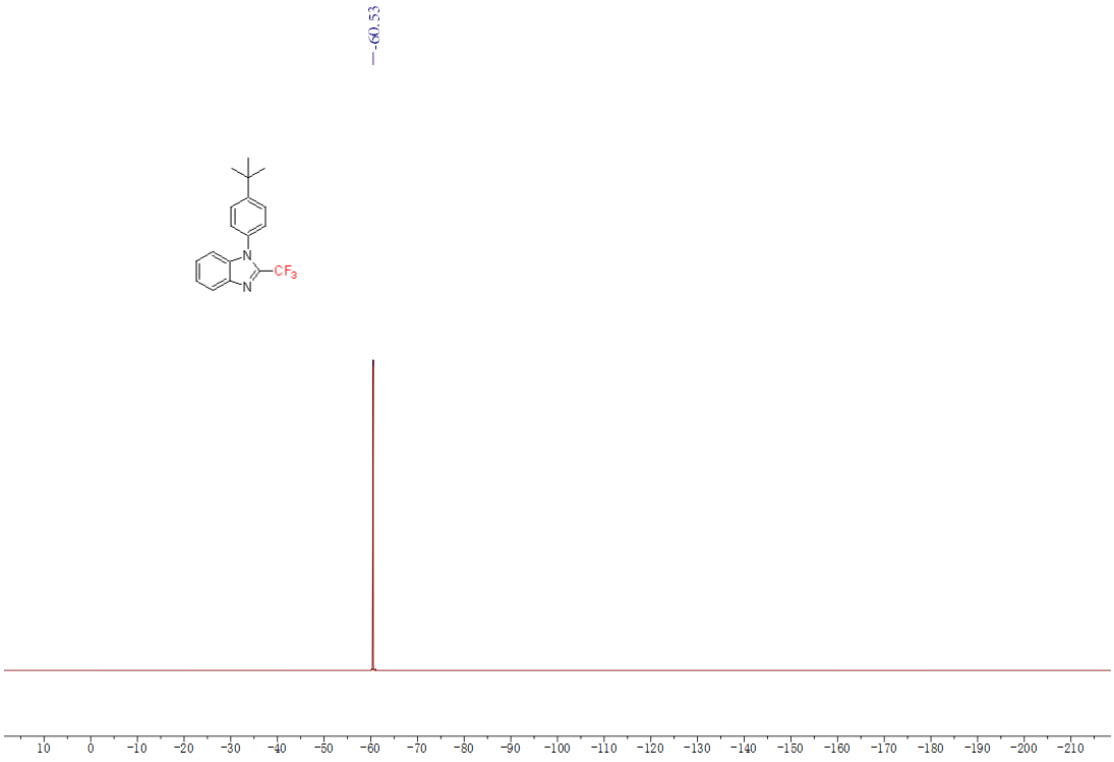
^{13}C NMR spectra of **4c** in $CDCl_3$



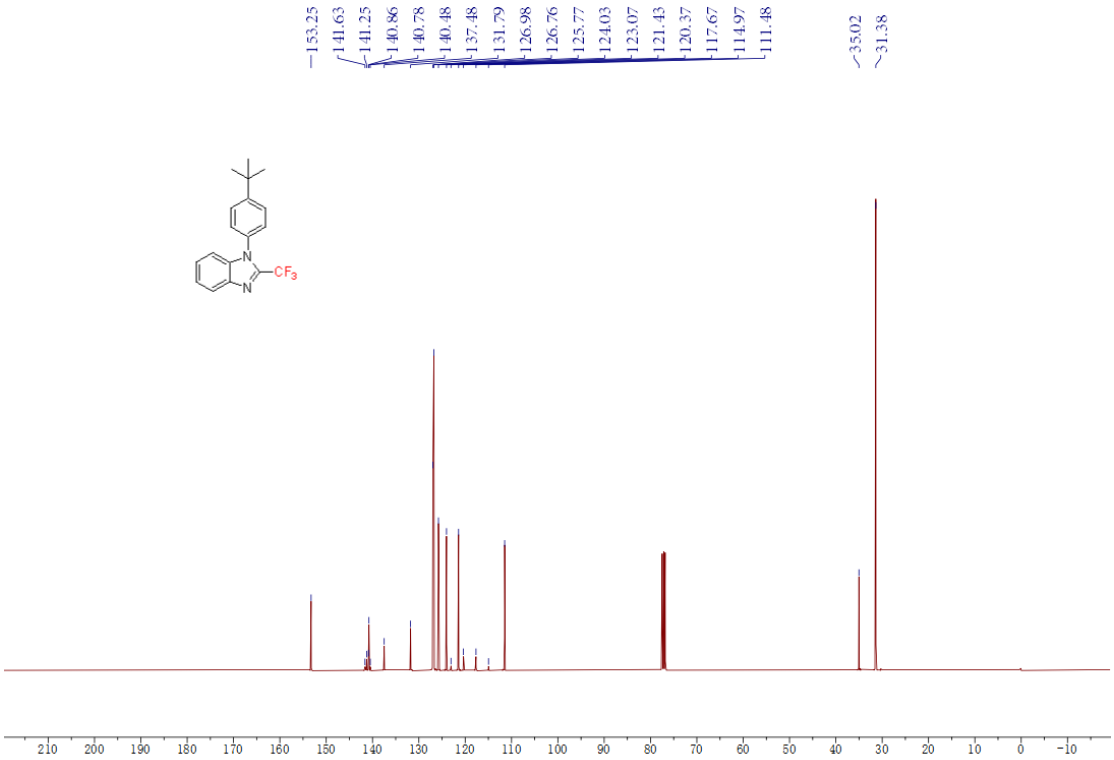
^{1}H NMR spectra of **4d** in $CDCl_3$



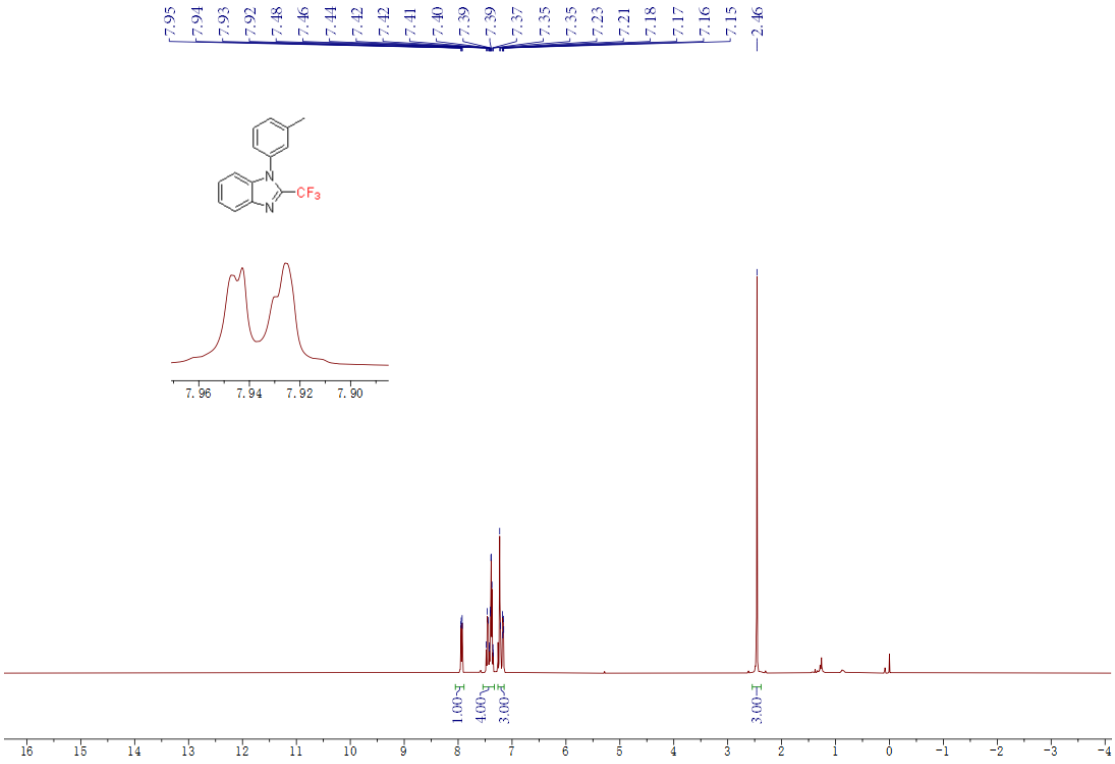
^{19}F NMR spectra of **4d** in $CDCl_3$



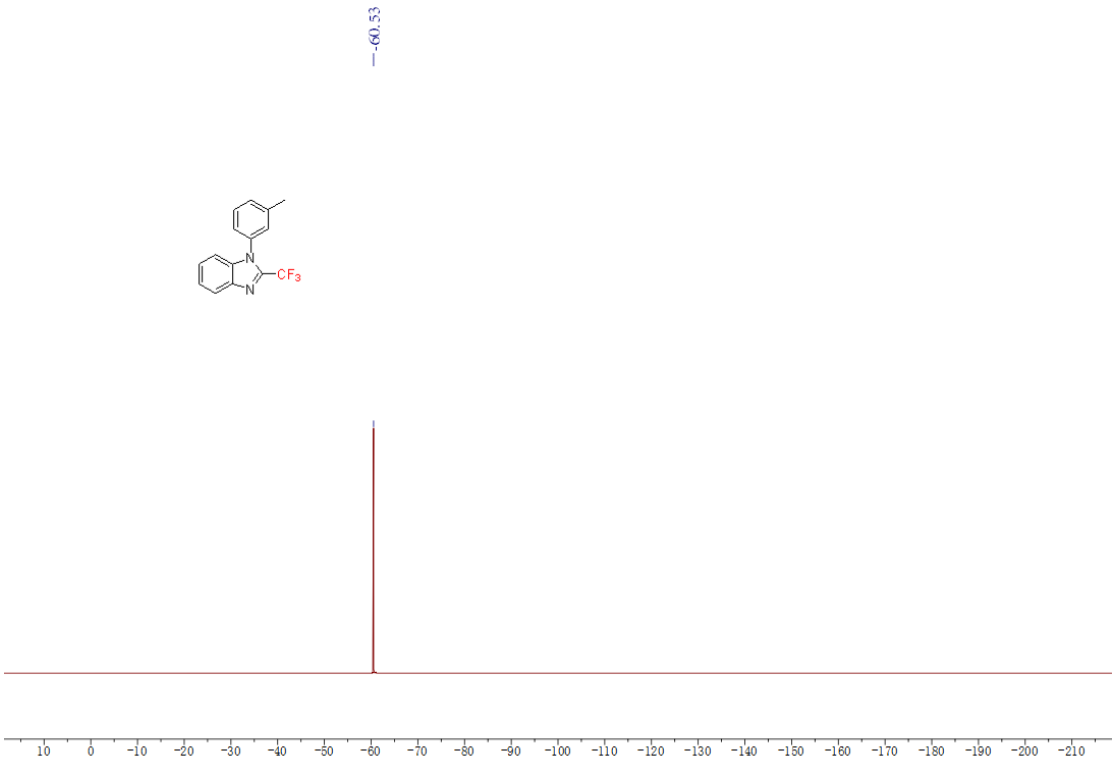
^{13}C NMR spectra of **4d** in $CDCl_3$



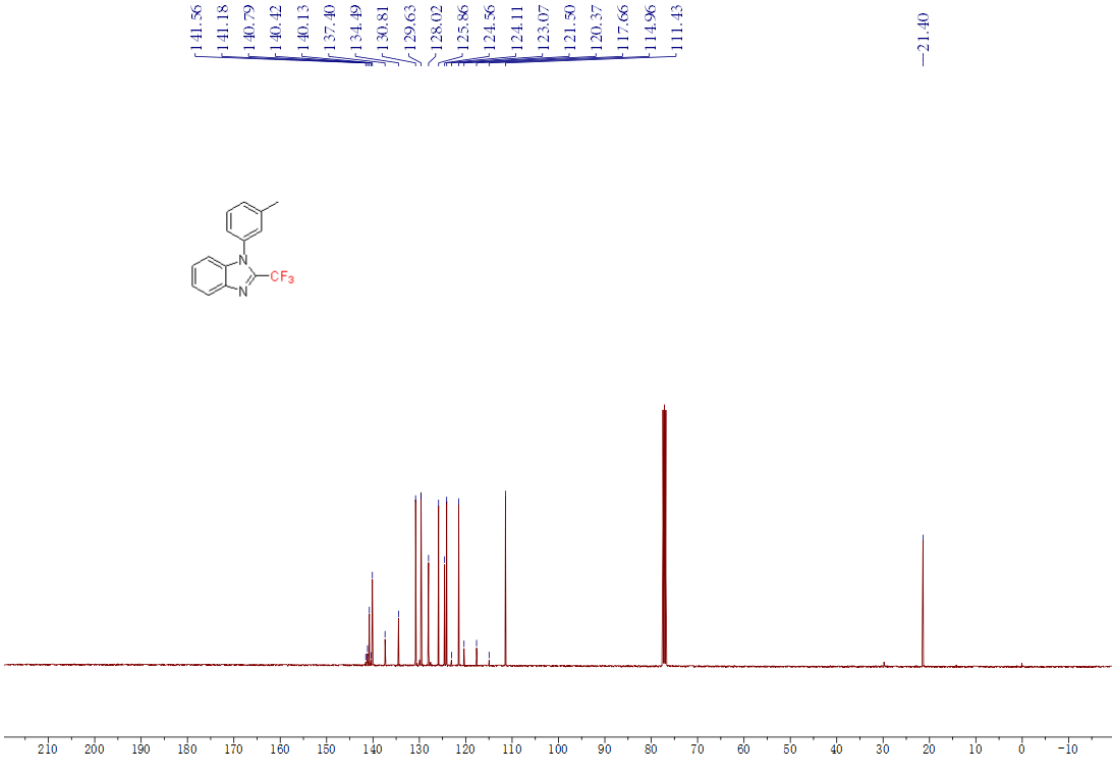
^{1}H NMR spectra of **4e** in $CDCl_3$



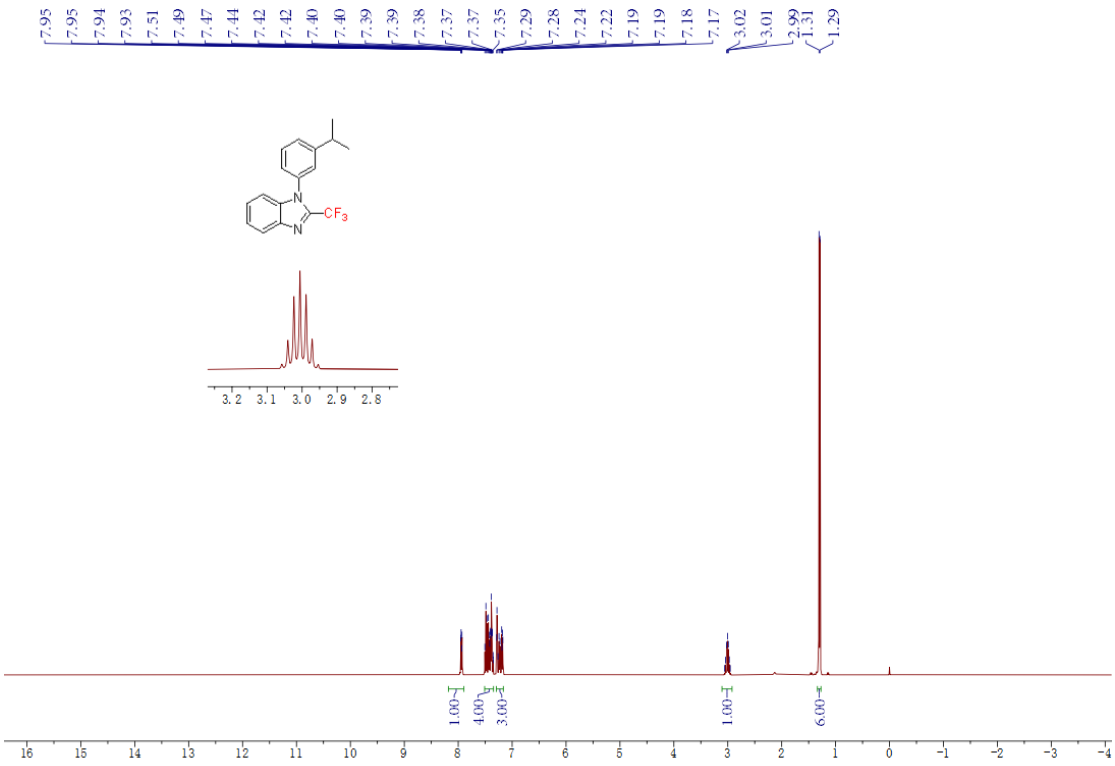
^{19}F NMR spectra of **4e** in $CDCl_3$



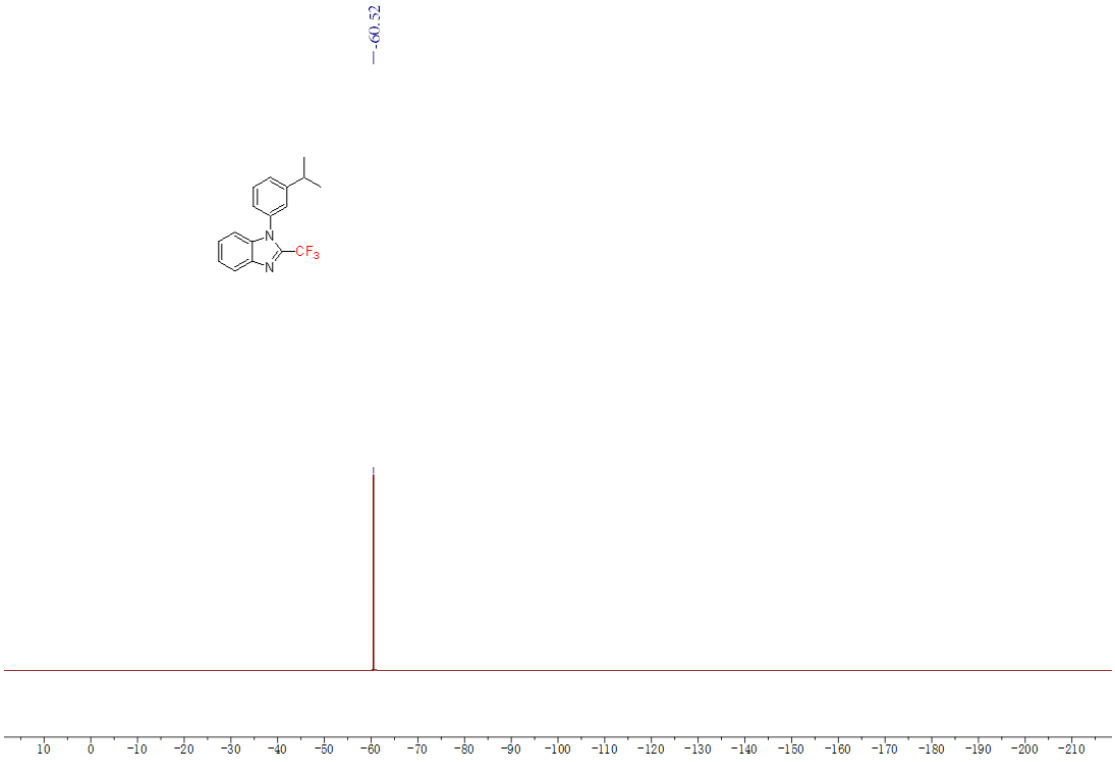
^{13}C NMR spectra of **4e** in $CDCl_3$



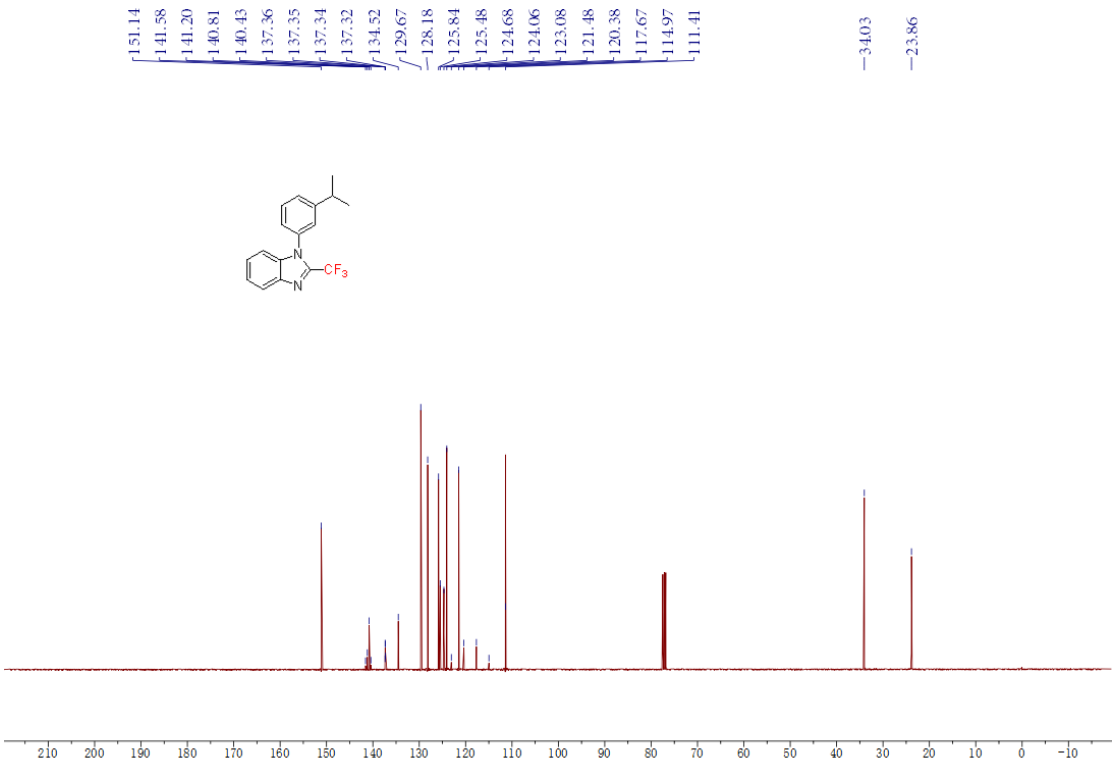
^{1}H NMR spectra of **4f** in $CDCl_3$



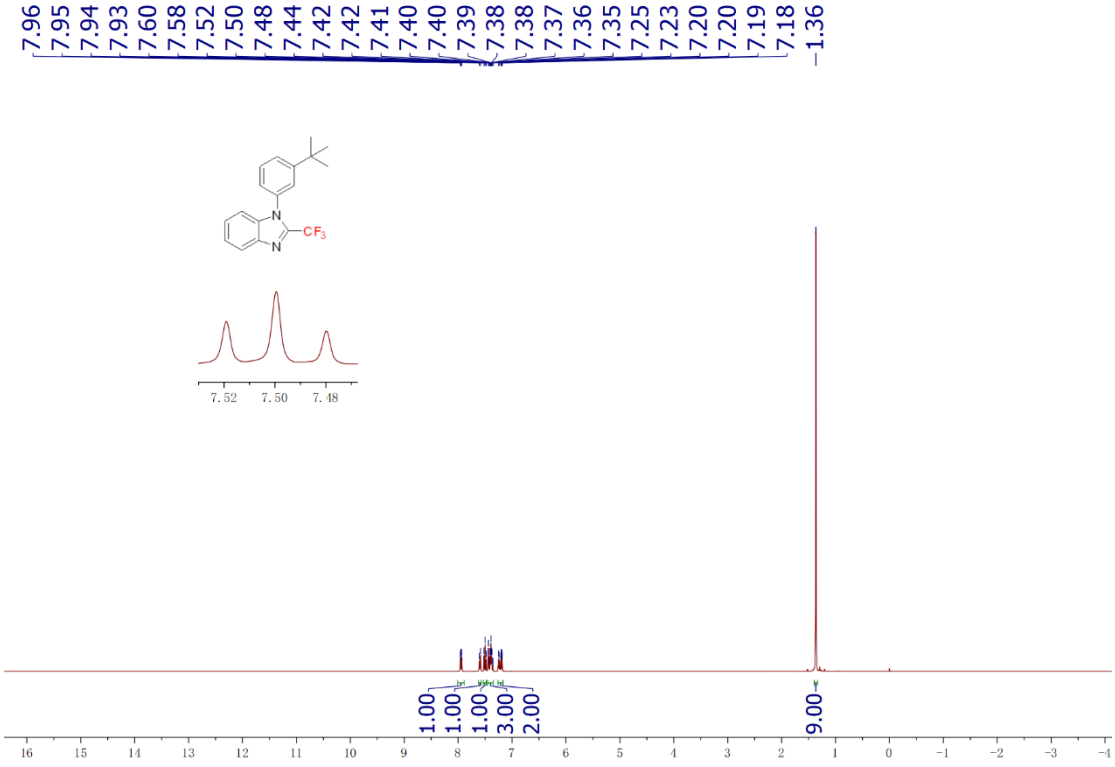
^{19}F NMR spectra of **4f** in $CDCl_3$



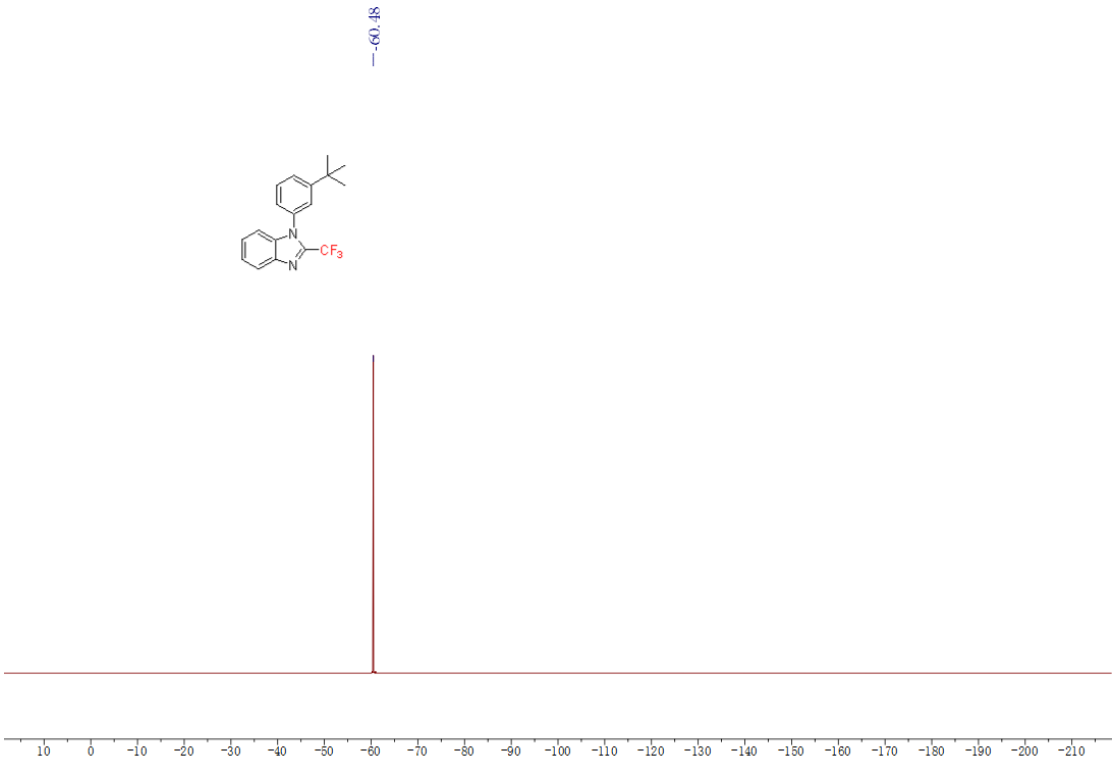
^{13}C NMR spectra of **4f** in $CDCl_3$



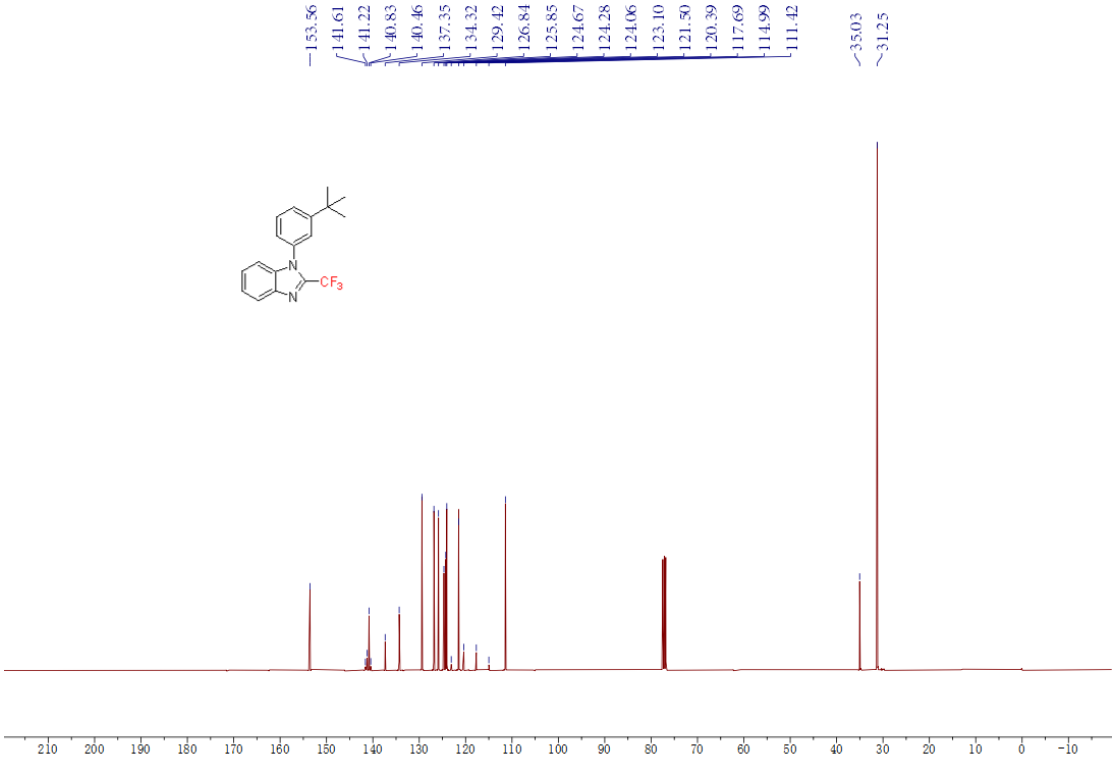
^{1}H NMR spectra of **4g** in $CDCl_3$



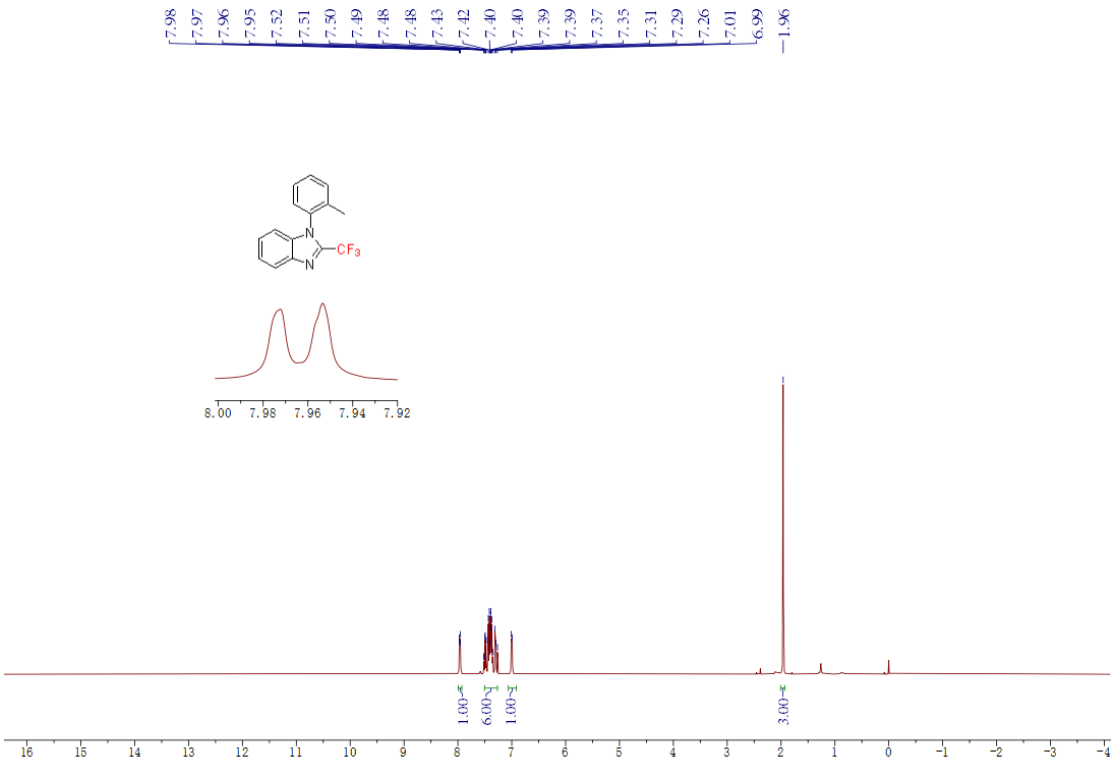
^{19}F NMR spectra of **4g** in $CDCl_3$



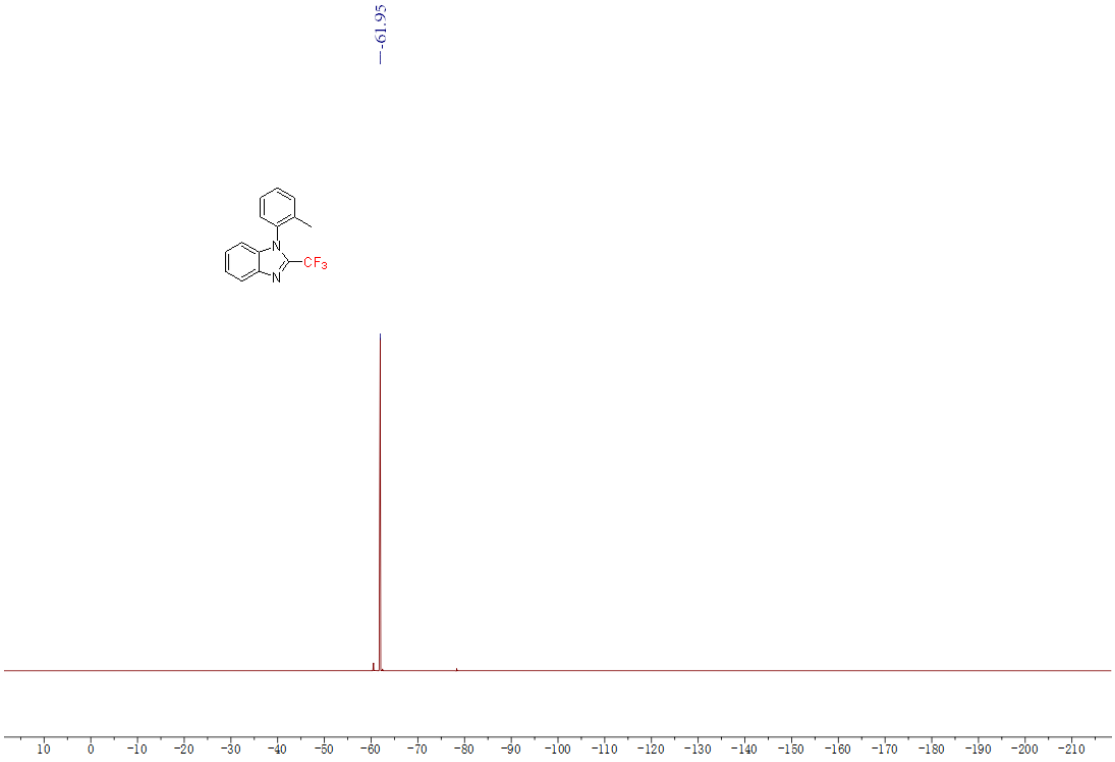
^{13}C NMR spectra of **4g** in $CDCl_3$



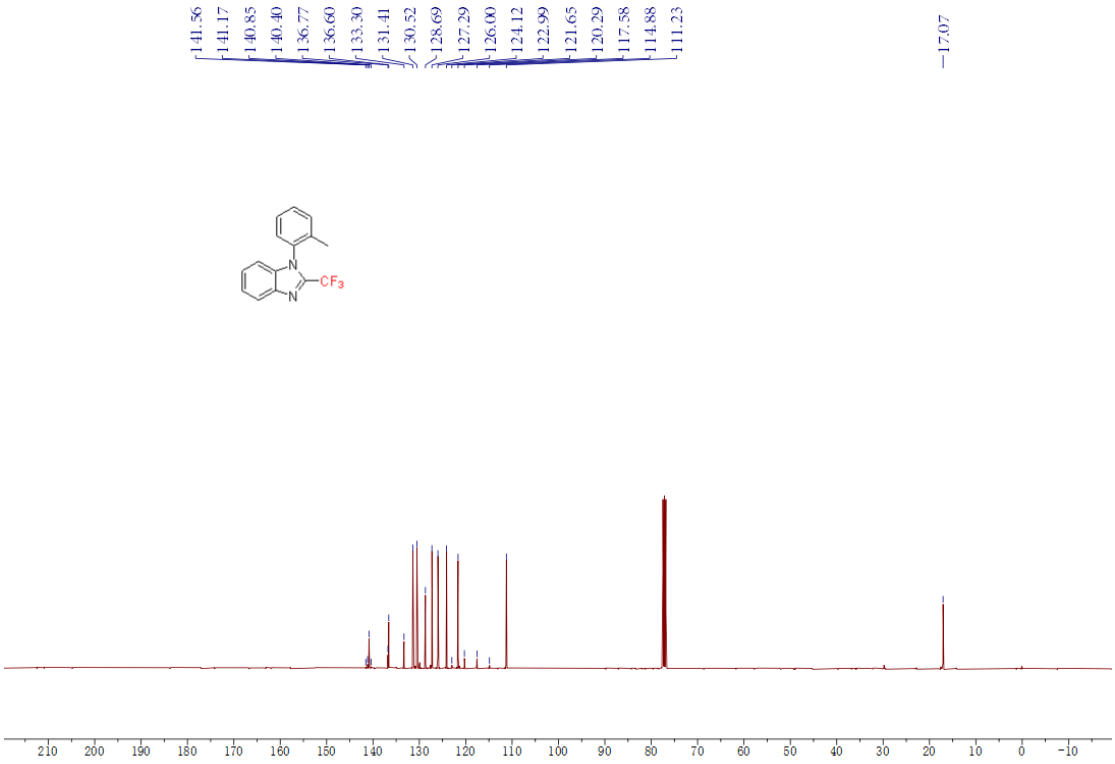
^{1}H NMR spectra of **4h** in $CDCl_3$



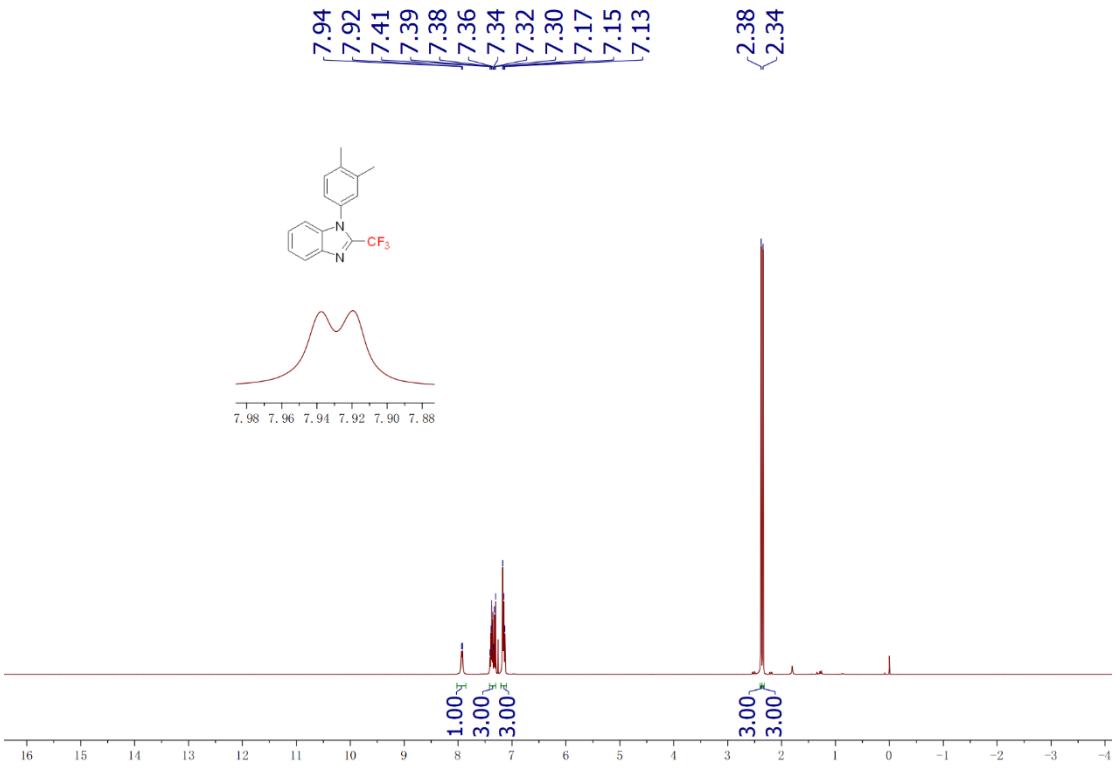
^{19}F NMR spectra of **4h** in $CDCl_3$



^{13}C NMR spectra of **4h** in $CDCl_3$

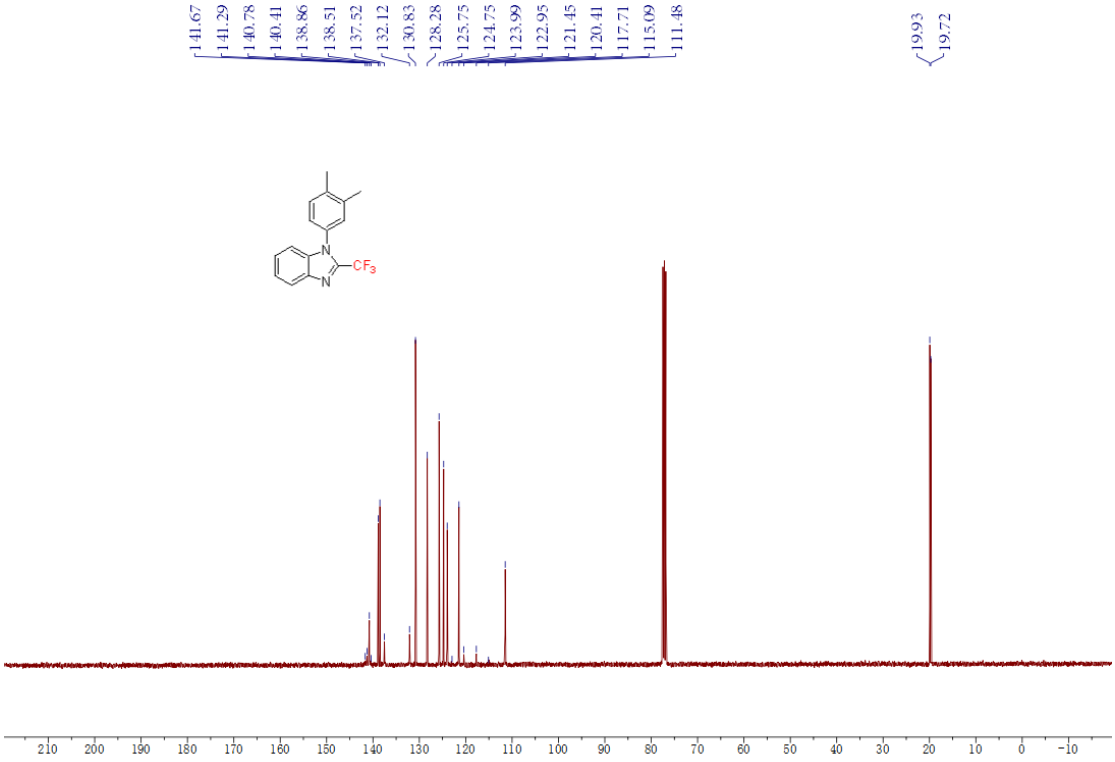


^{1}H NMR spectra of **4i** in $CDCl_3$

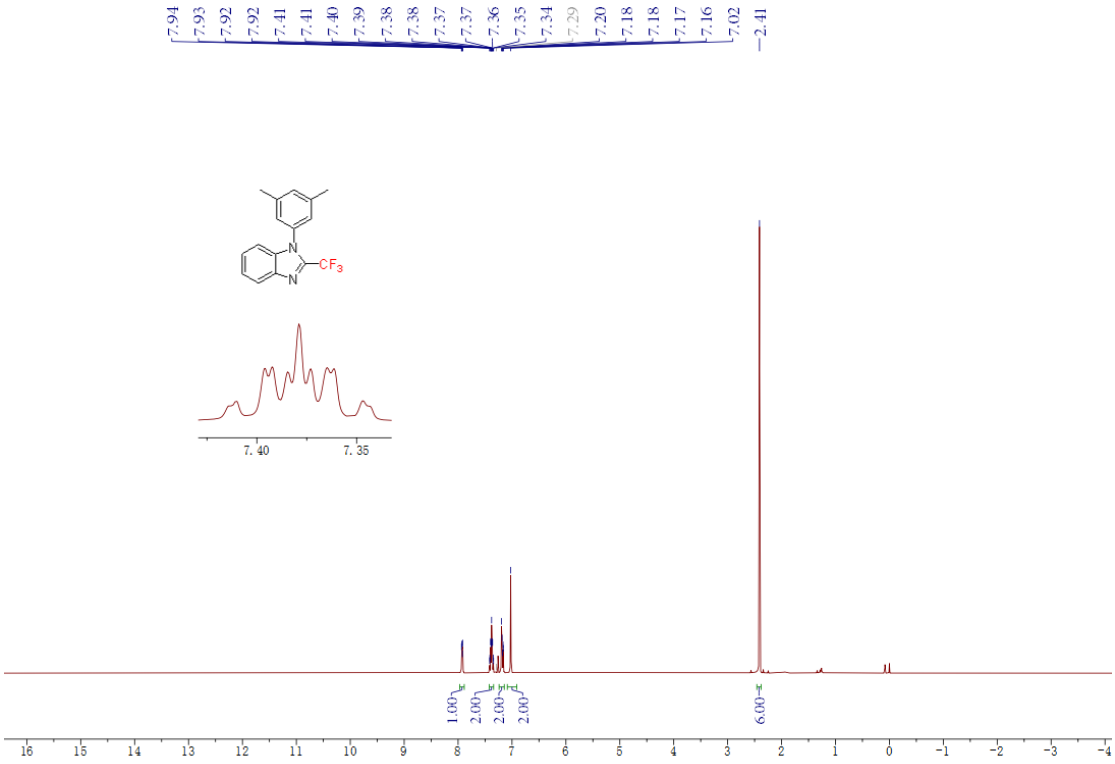


^{19}F NMR spectra of **4i** in $CDCl_3$

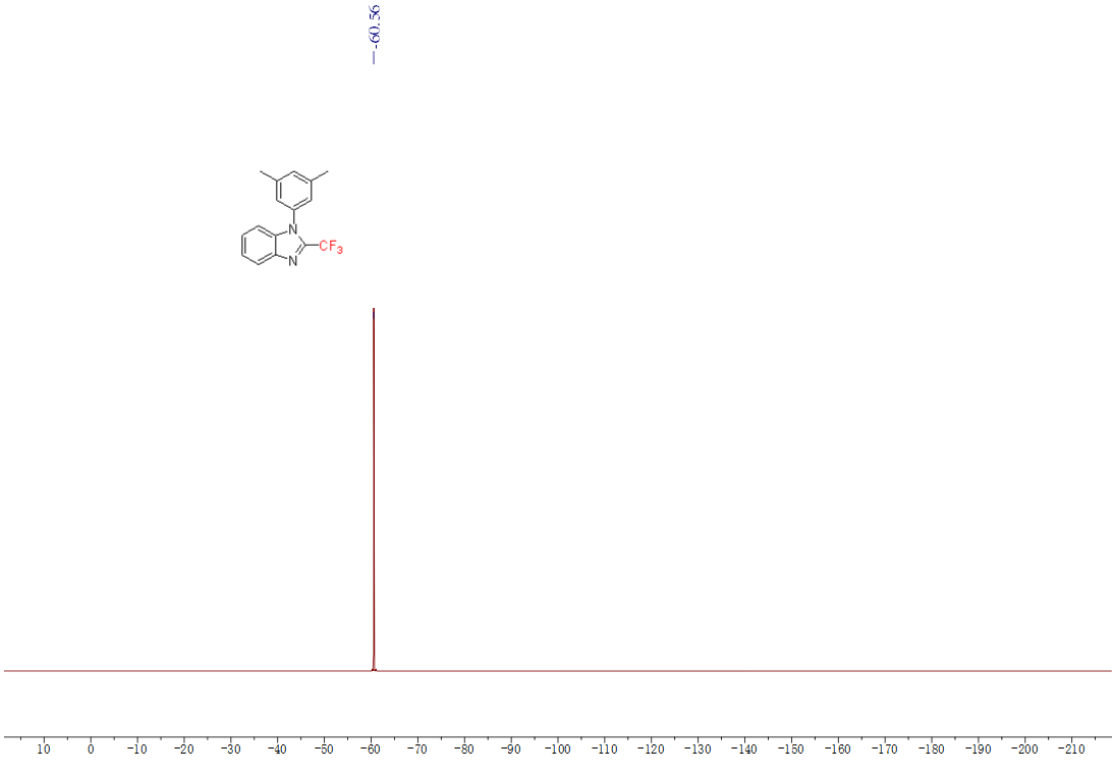
^{13}C NMR spectra of **4i** in $CDCl_3$



^{1}H NMR spectra of **4j** in $CDCl_3$



^{19}F NMR spectra of **4j** in $CDCl_3$



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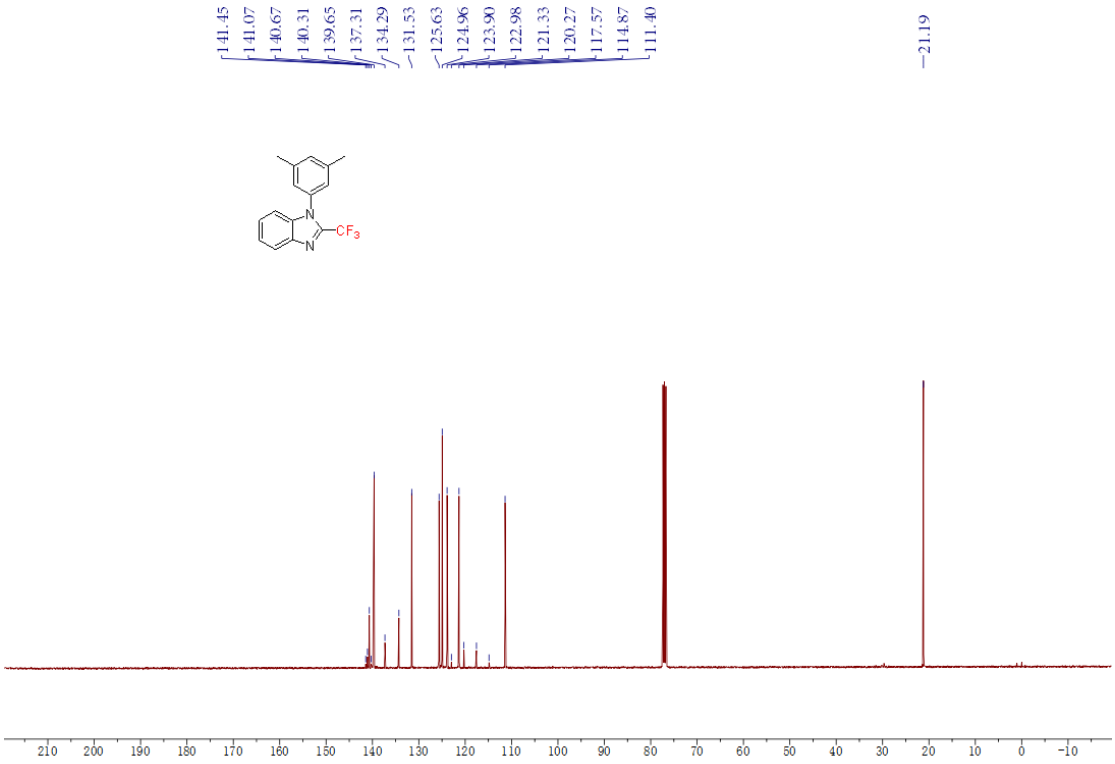
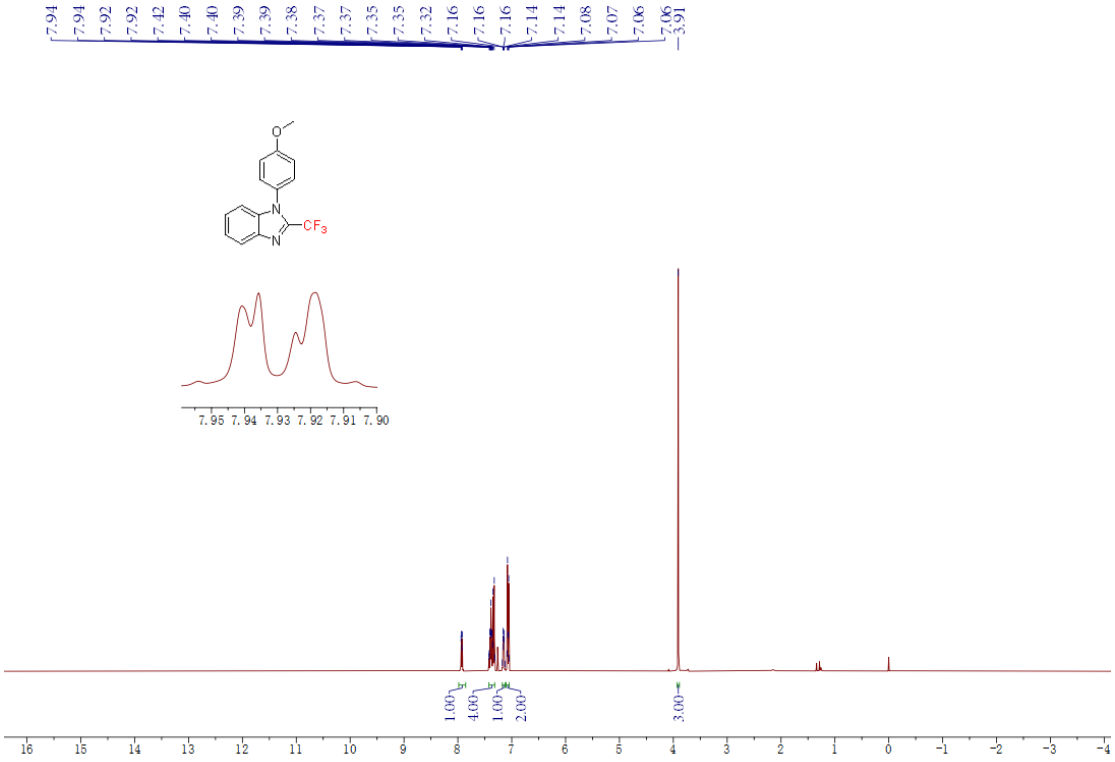
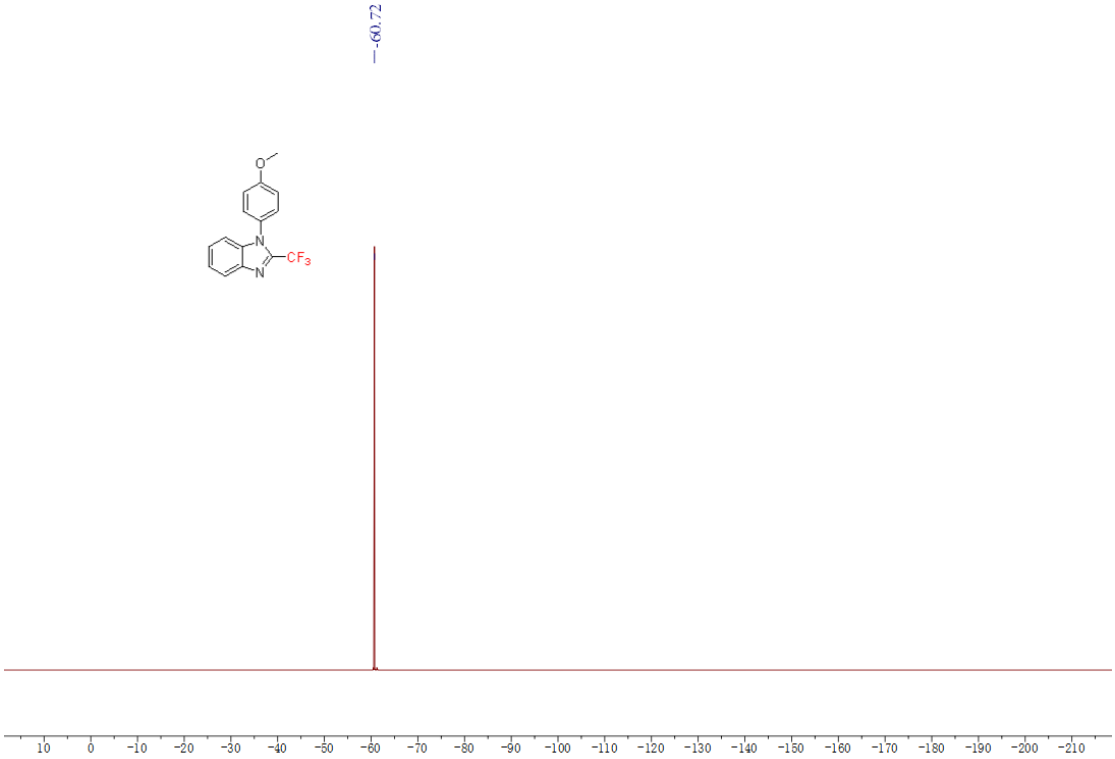


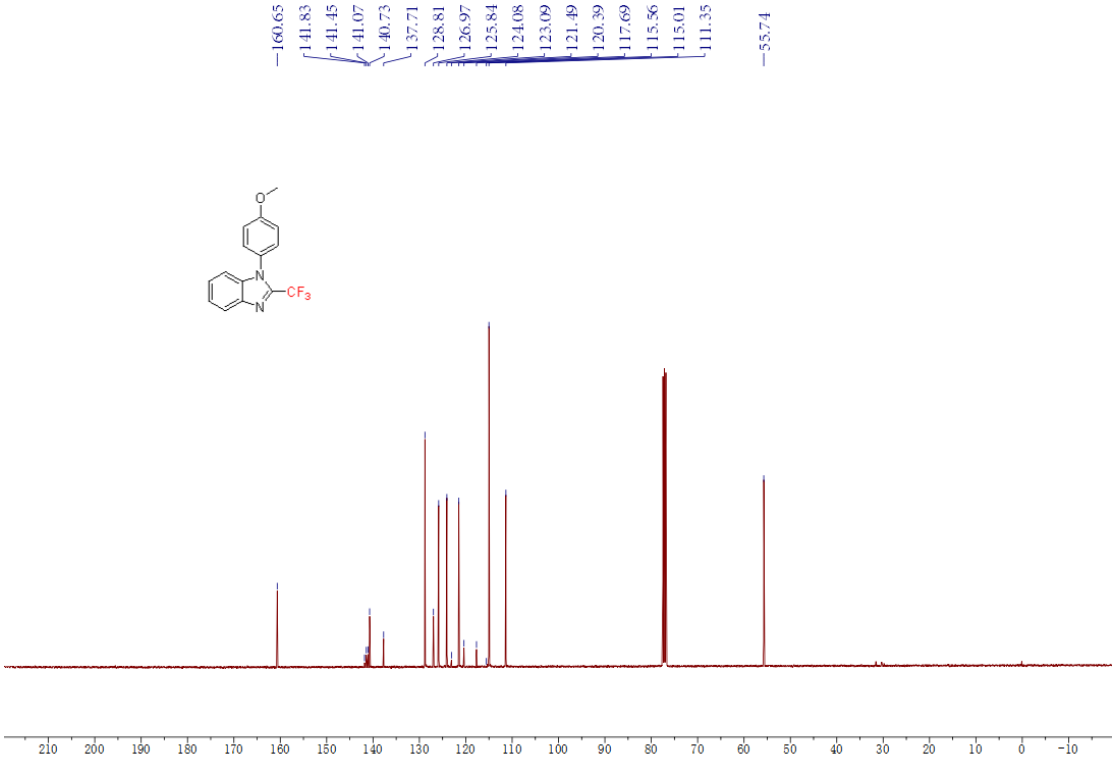
^{1}H NMR spectra of **4k** in $CDCl_3$



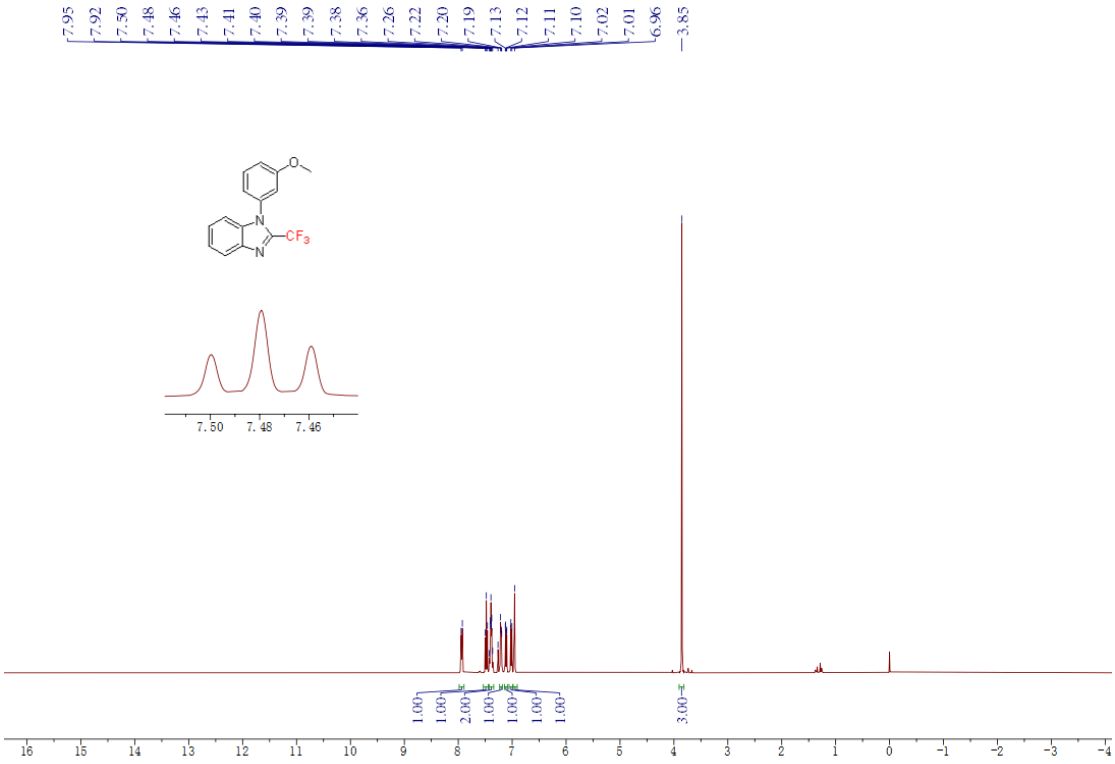
^{19}F NMR spectra of **4k** in $CDCl_3$



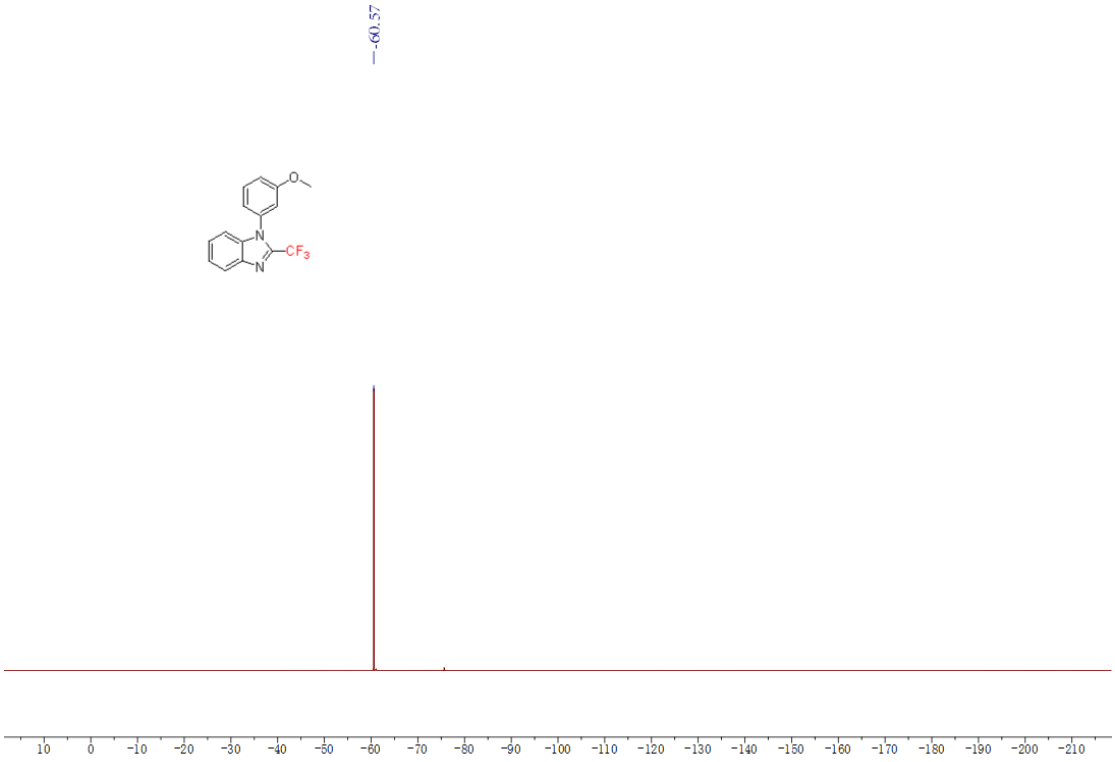
^{13}C NMR spectra of **4k** in $CDCl_3$



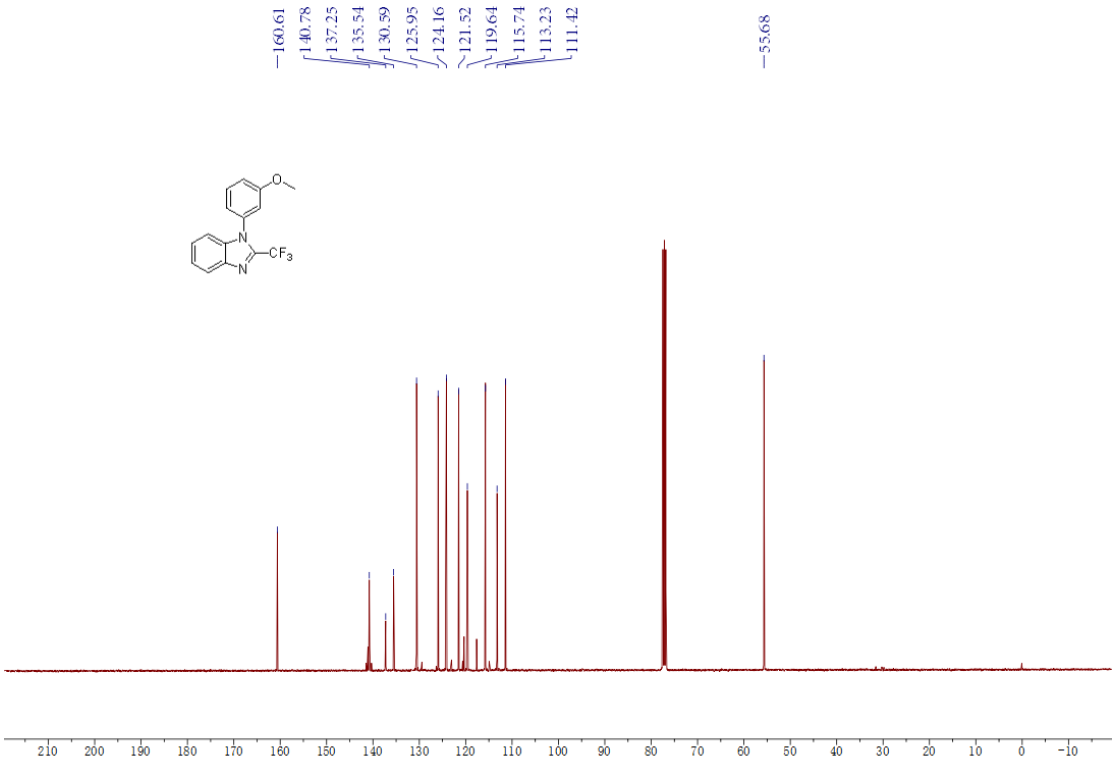
^{1}H NMR spectra of **4l** in $CDCl_3$



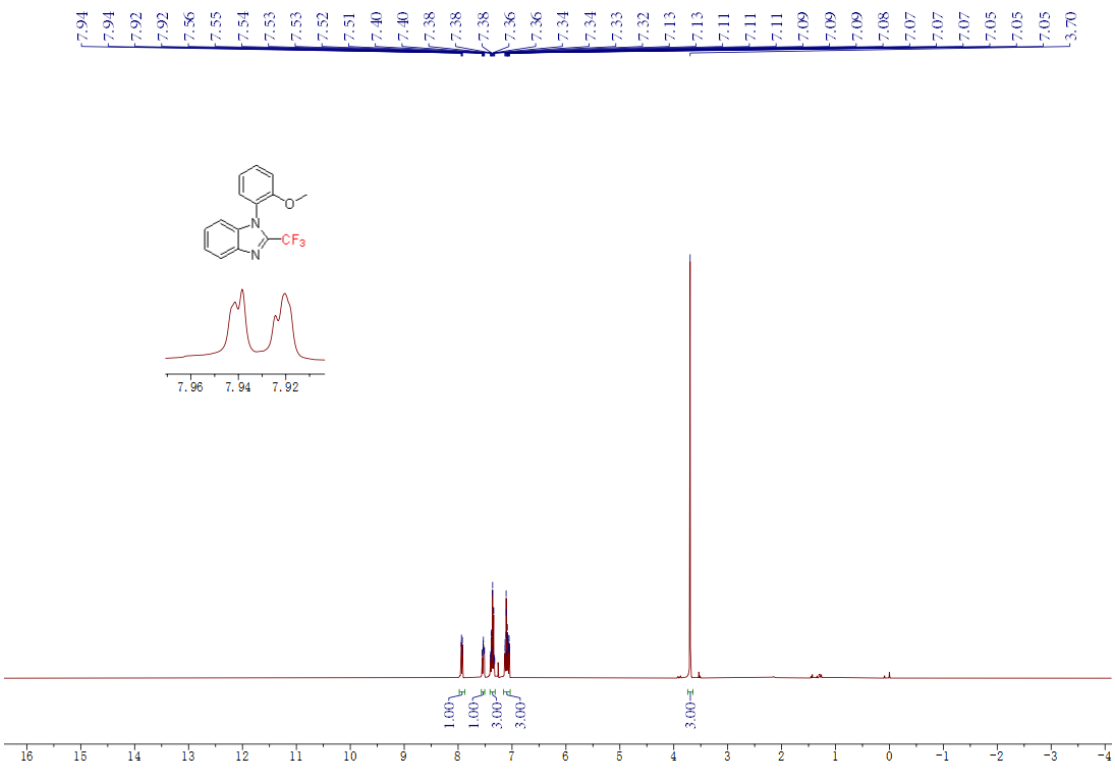
^{19}F NMR spectra of **4l** in $CDCl_3$



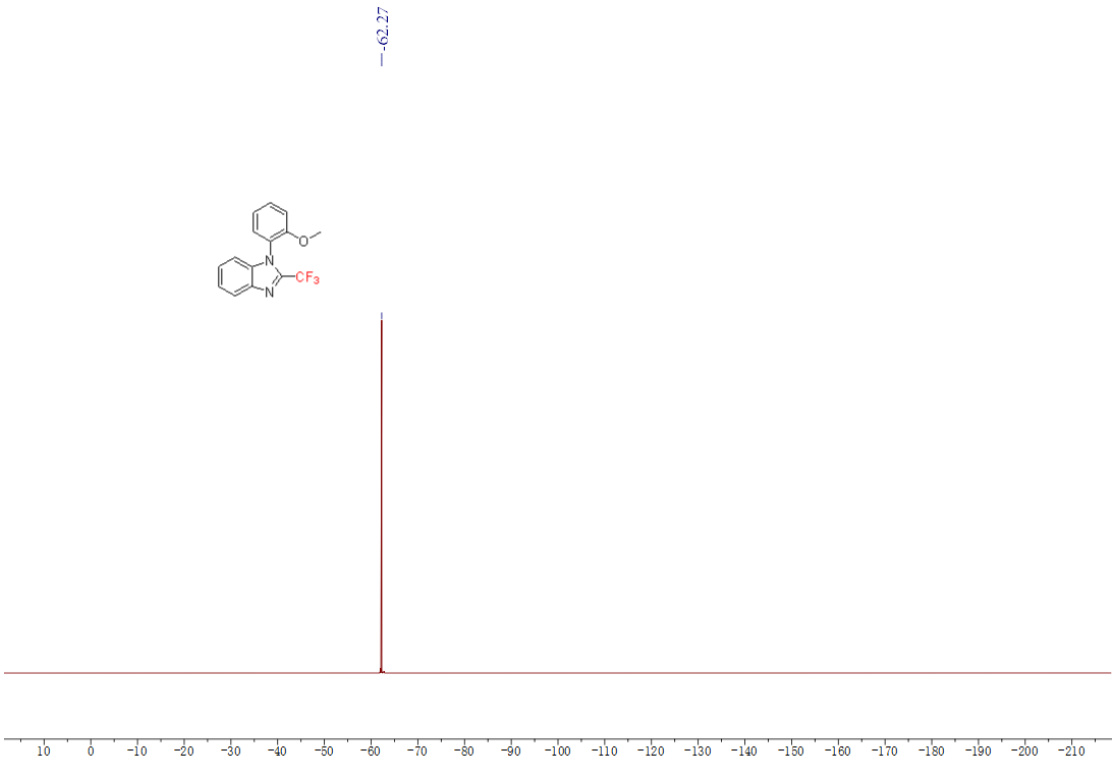
^{13}C NMR spectra of **4l** in $CDCl_3$



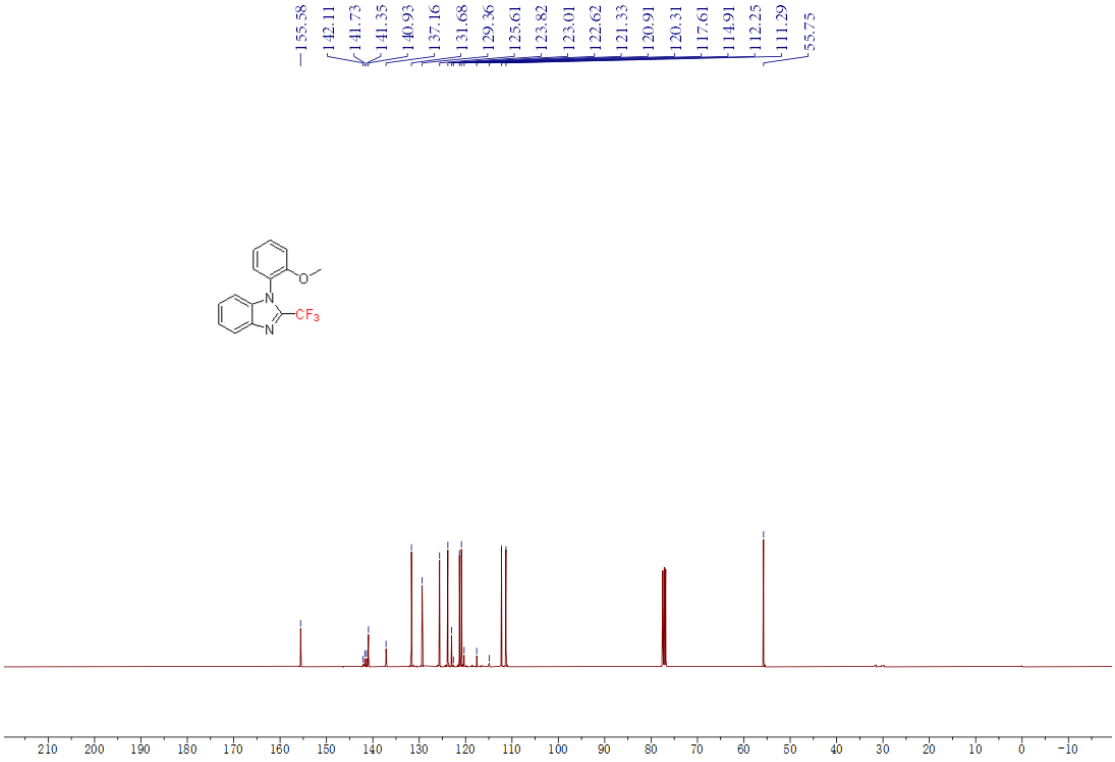
^{1}H NMR spectra of **4m** in $CDCl_3$



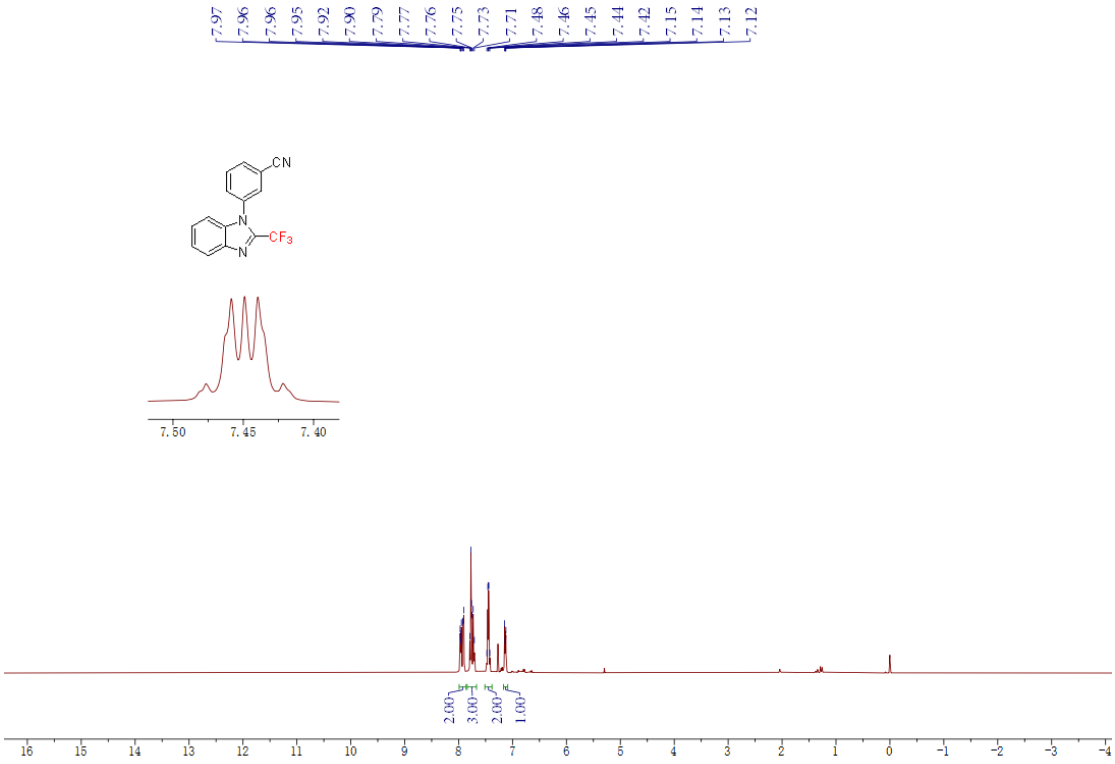
^{19}F NMR spectra of **4m** in $CDCl_3$



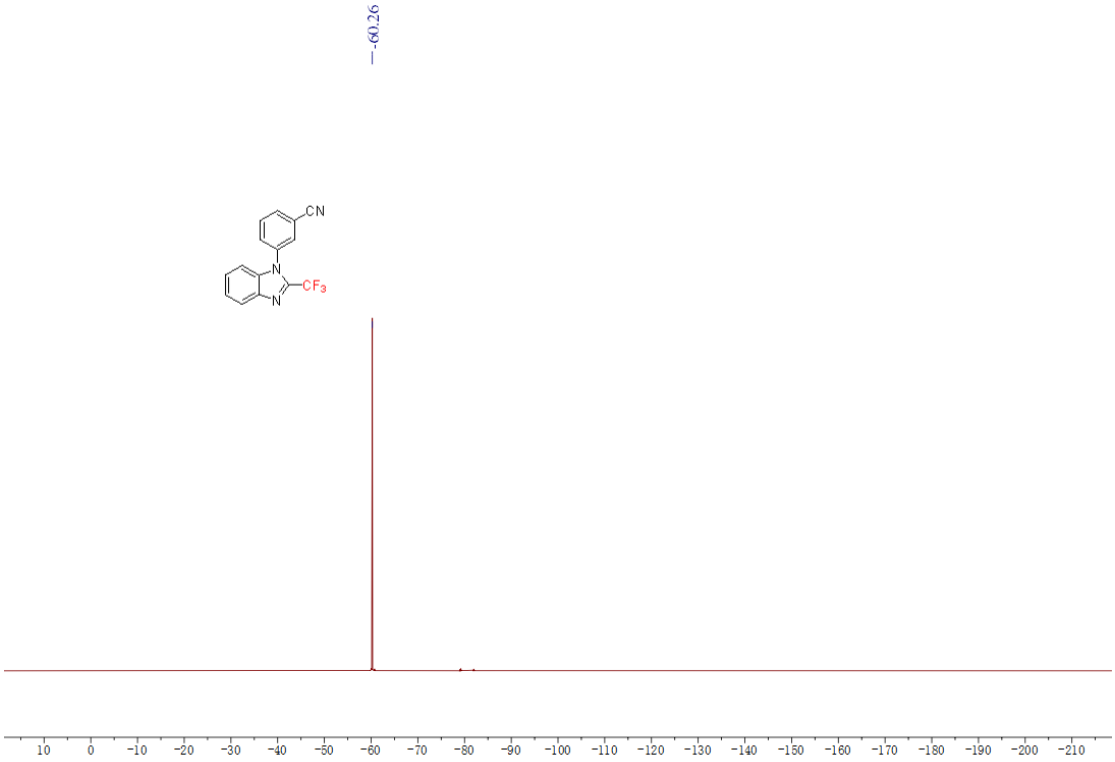
^{13}C NMR spectra of **4m** in $CDCl_3$



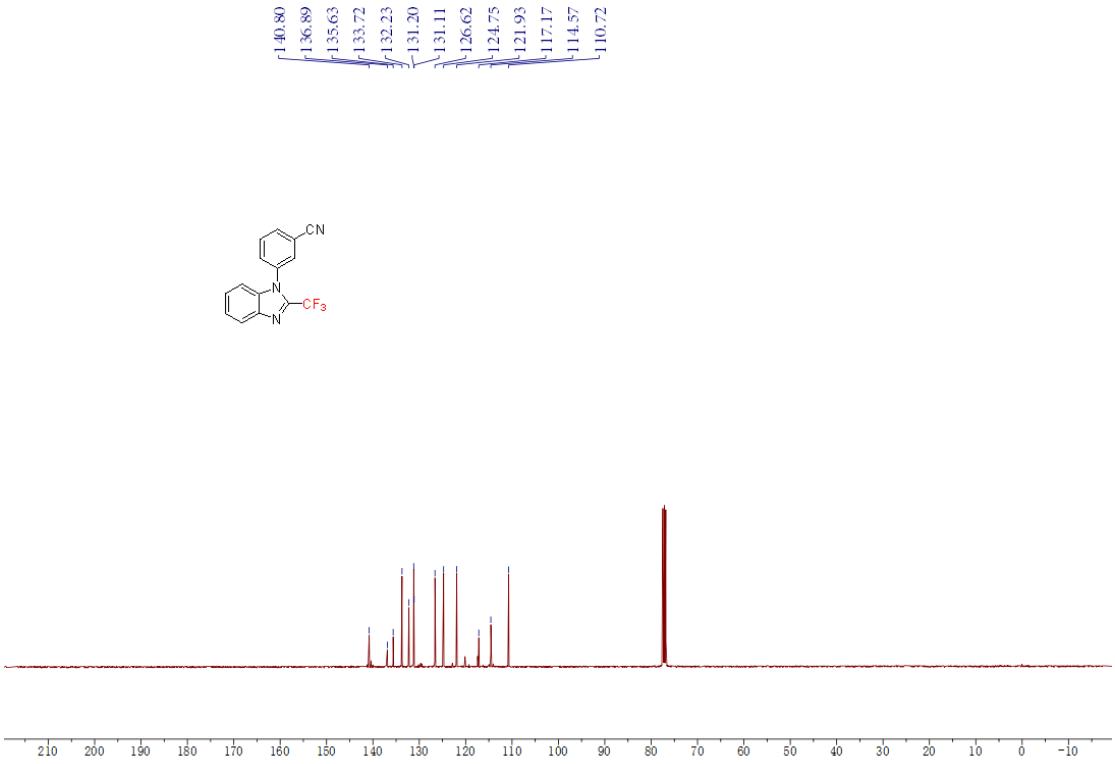
^{1}H NMR spectra of **4n** in $CDCl_3$



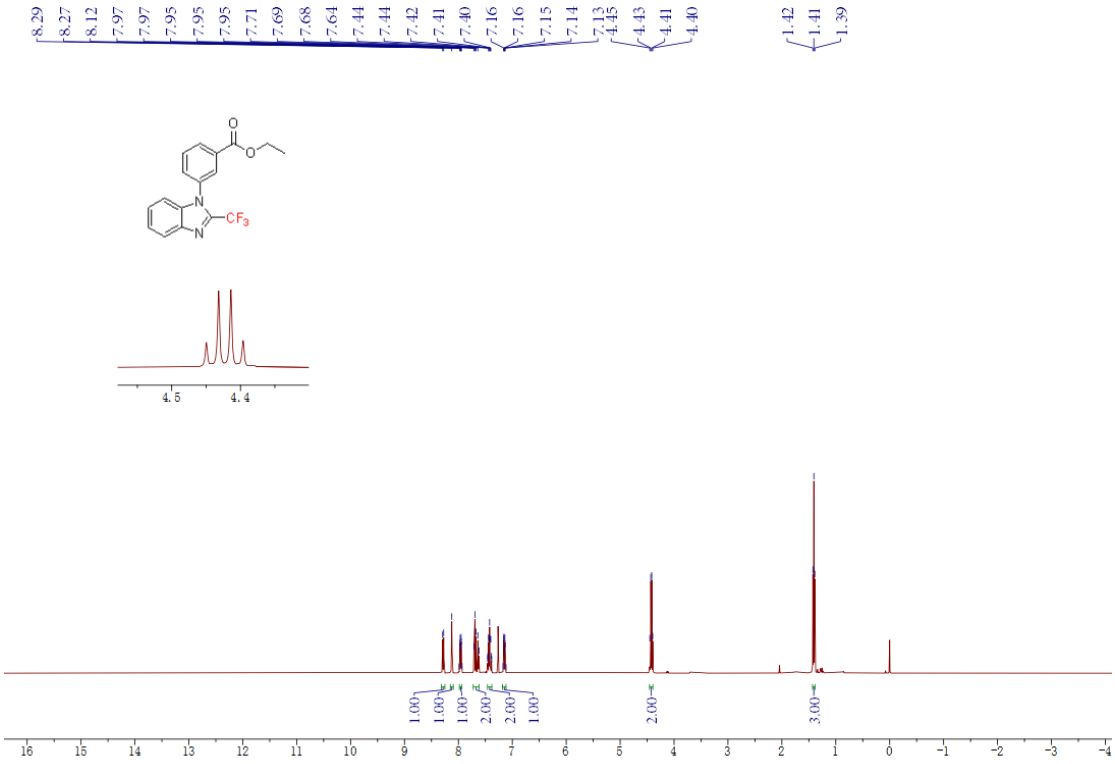
^{19}F NMR spectra of **4n** in $CDCl_3$



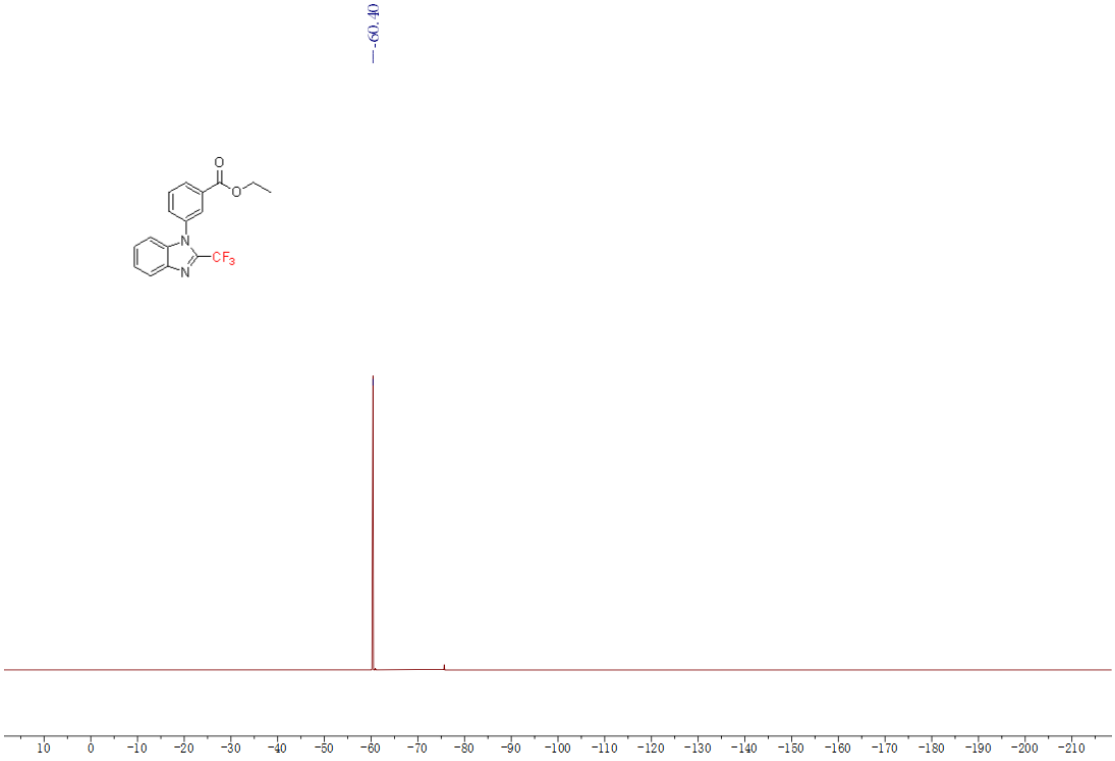
^{13}C NMR spectra of **4n** in $CDCl_3$



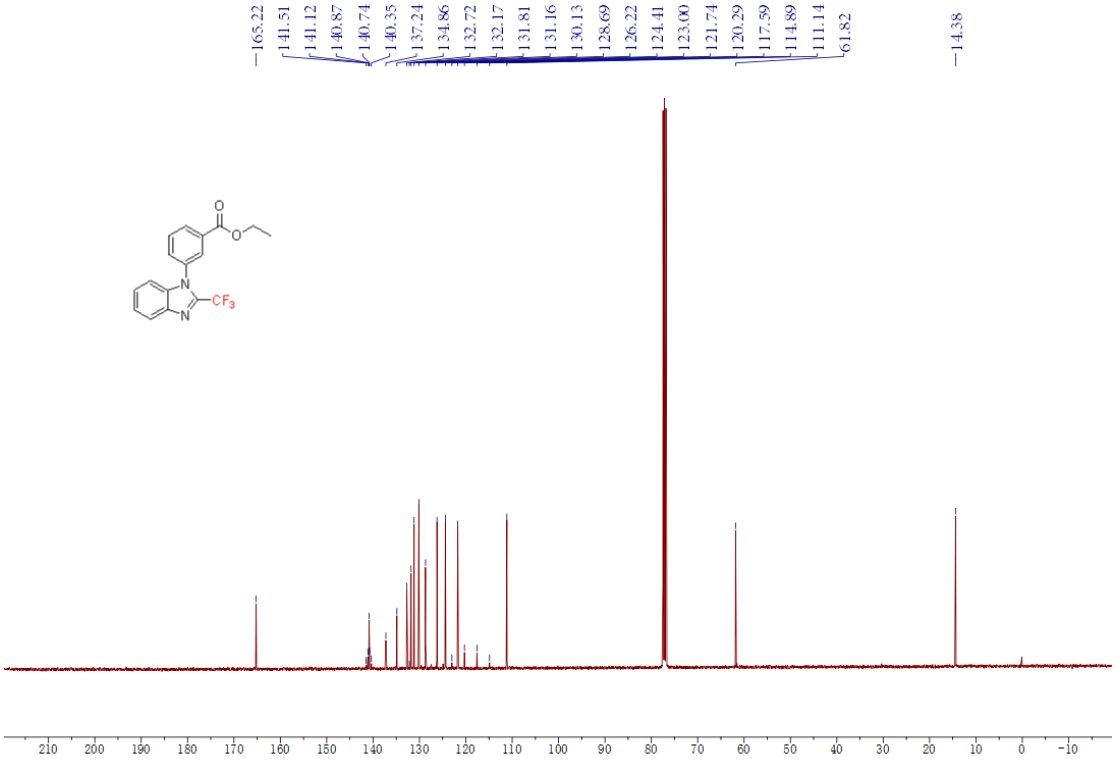
^{1}H NMR spectra of **4o** in $CDCl_3$



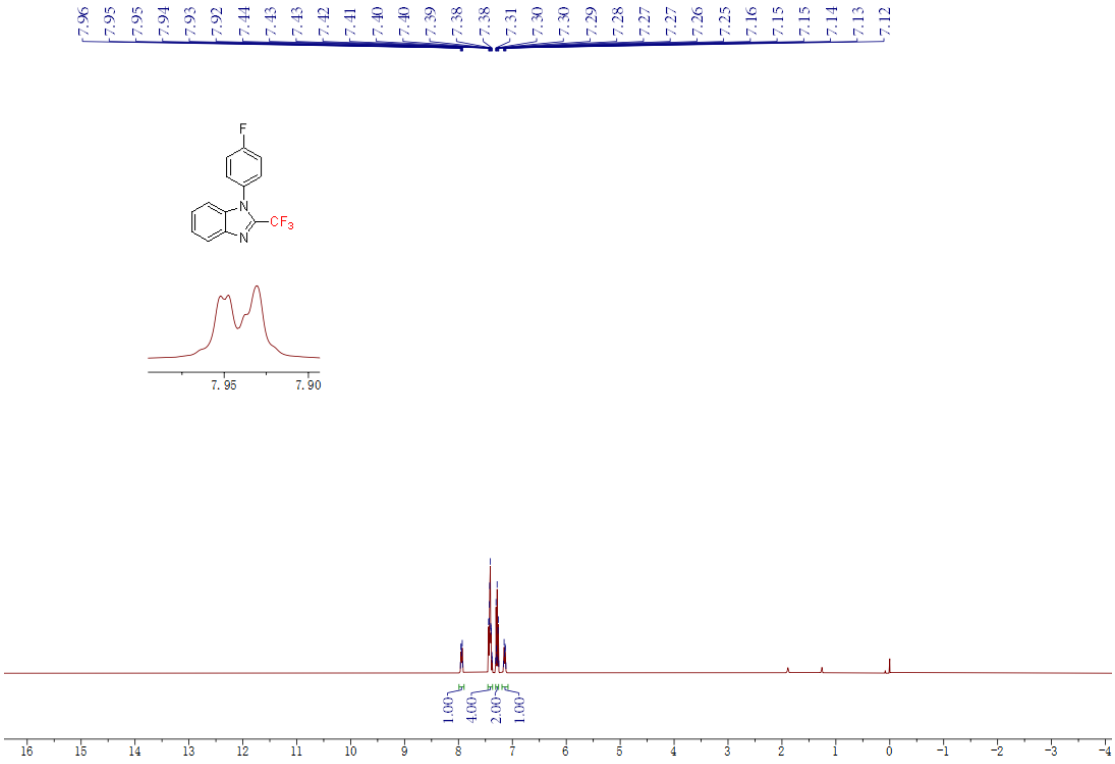
^{19}F NMR spectra of **4o** in $CDCl_3$



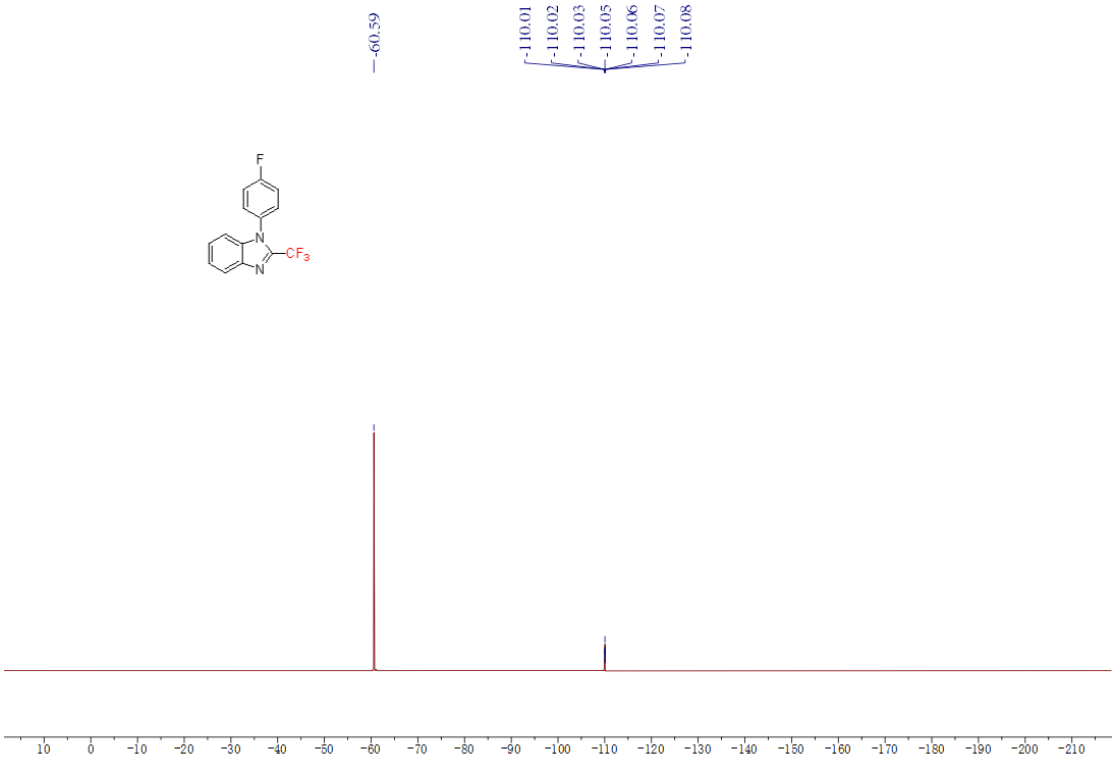
^{13}C NMR spectra of **4o** in $CDCl_3$



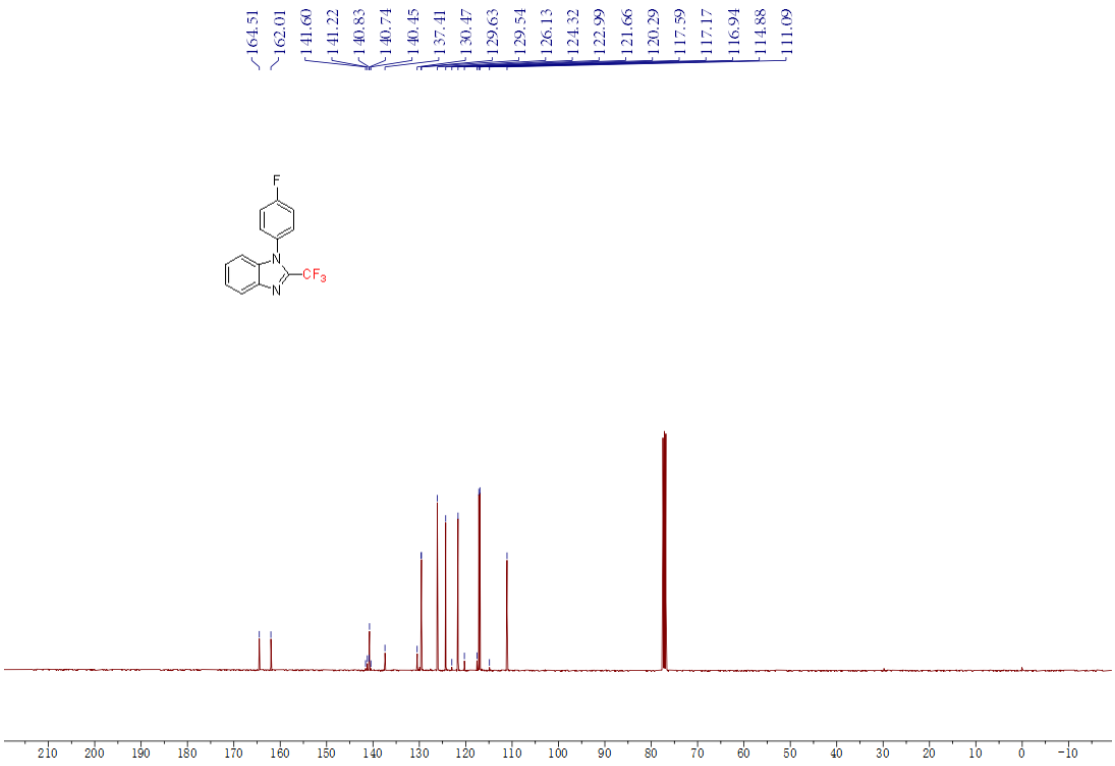
^{1}H NMR spectra of **4p** in $CDCl_3$



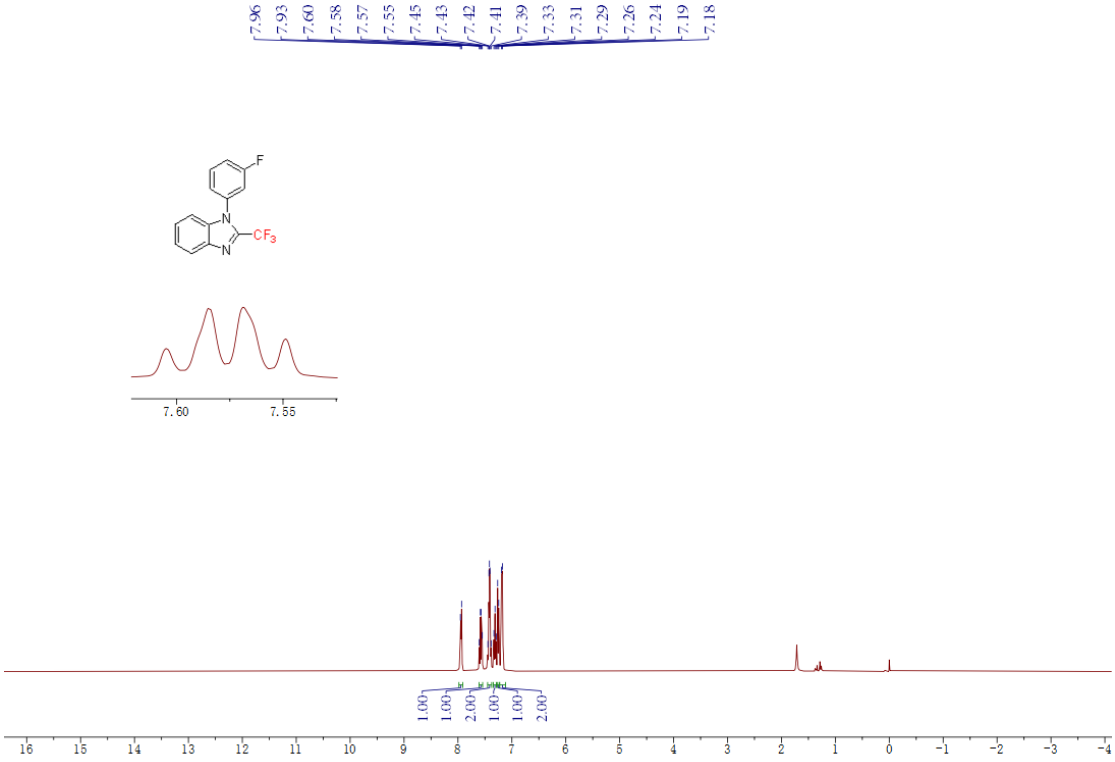
^{19}F NMR spectra of **4p** in $CDCl_3$



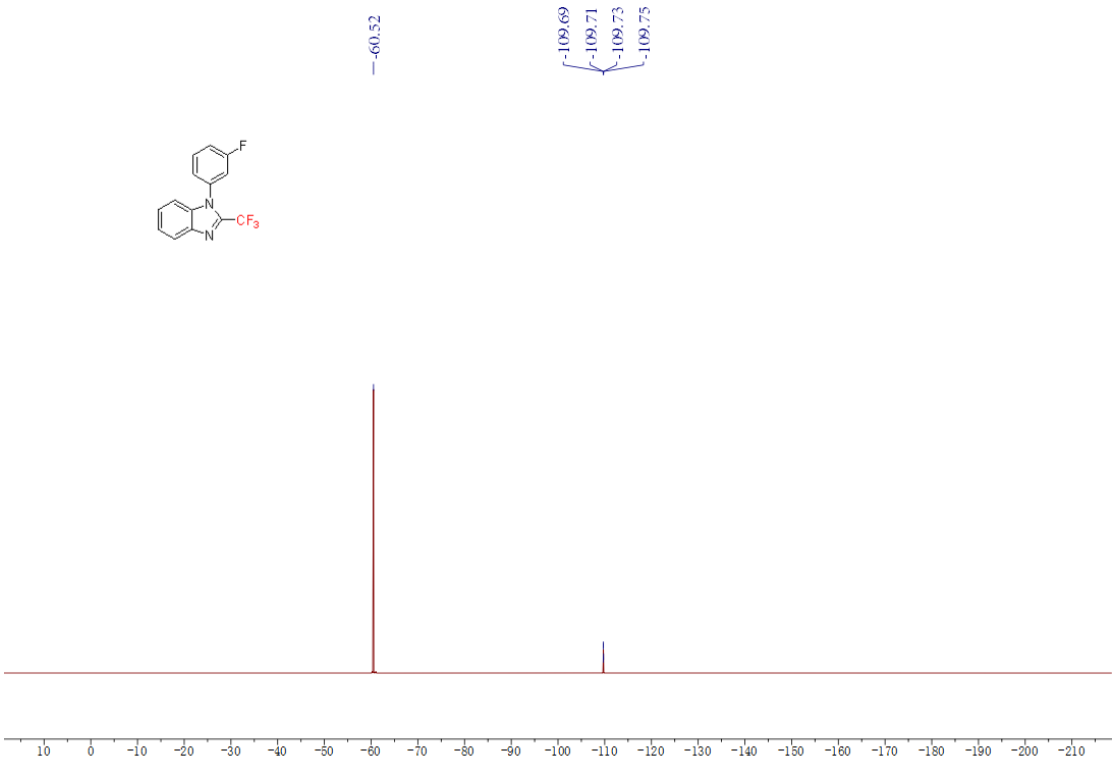
^{13}C NMR spectra of **4p** in $CDCl_3$



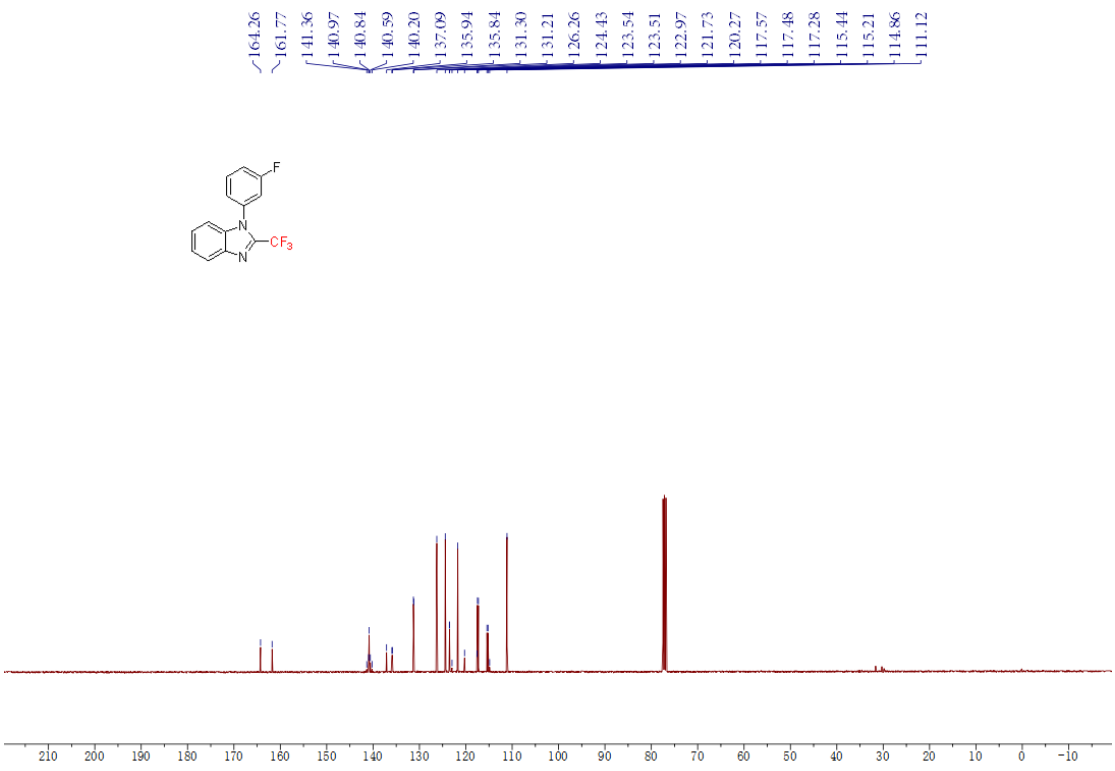
^{1}H NMR spectra of **4q** in $CDCl_3$



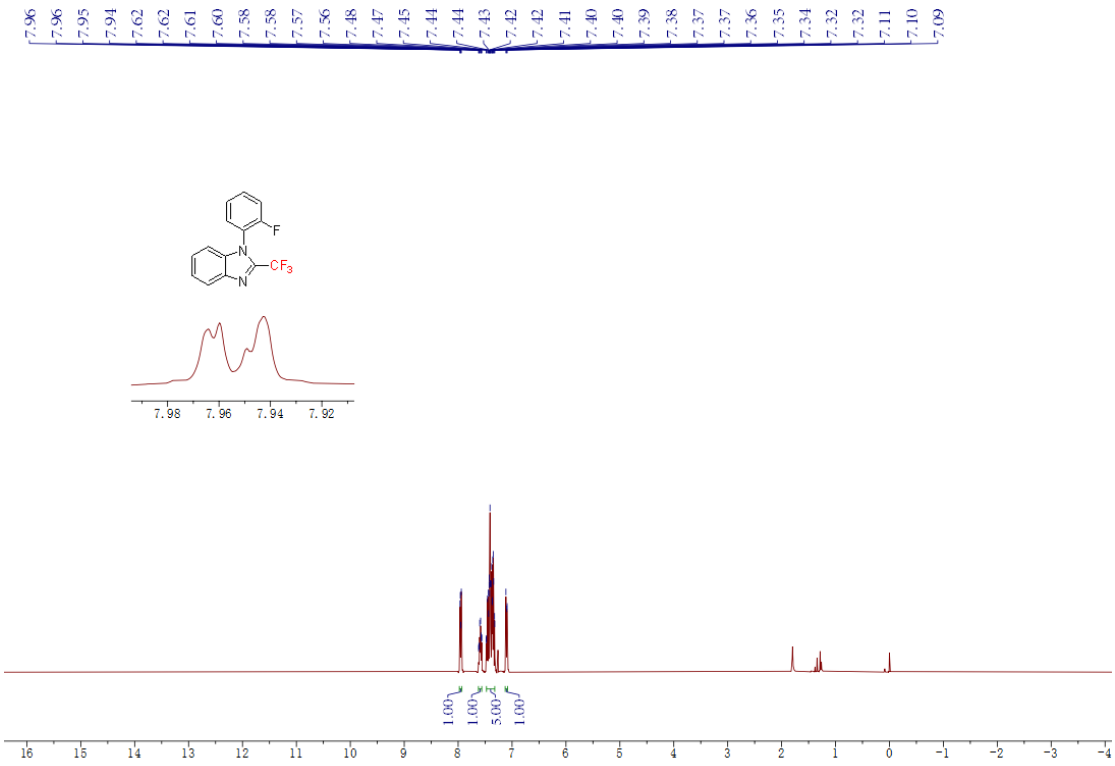
^{19}F NMR spectra of **4q** in $CDCl_3$



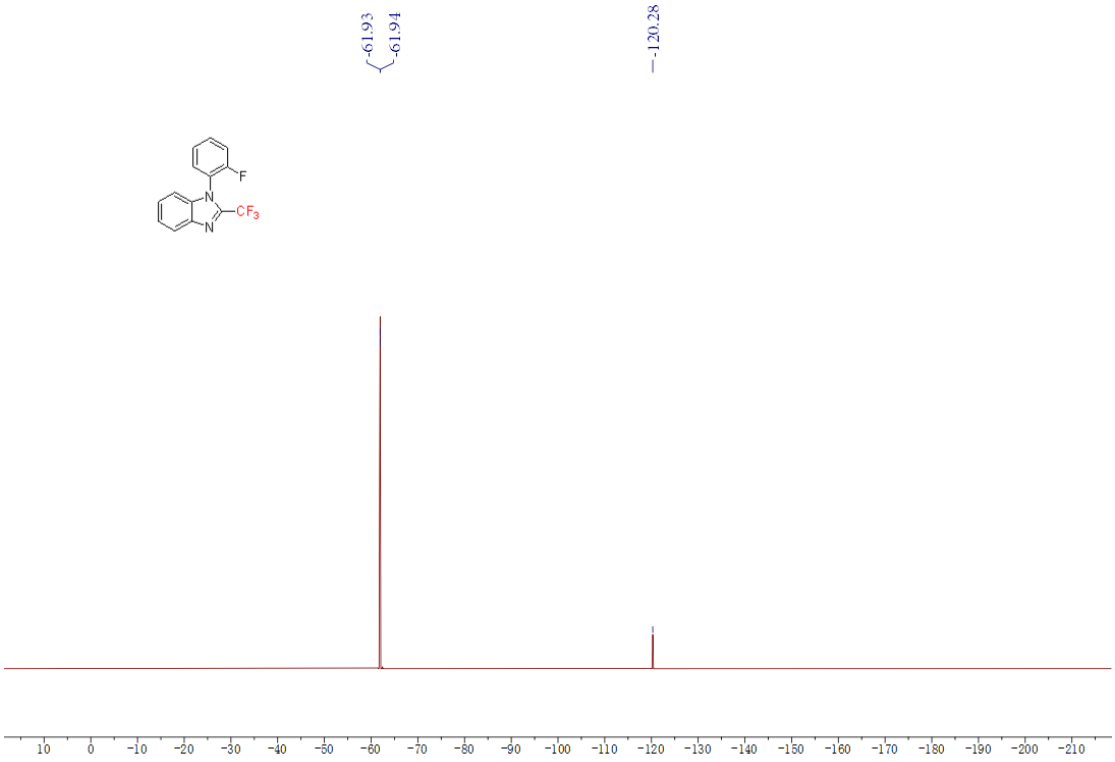
^{13}C NMR spectra of **4q** in $CDCl_3$



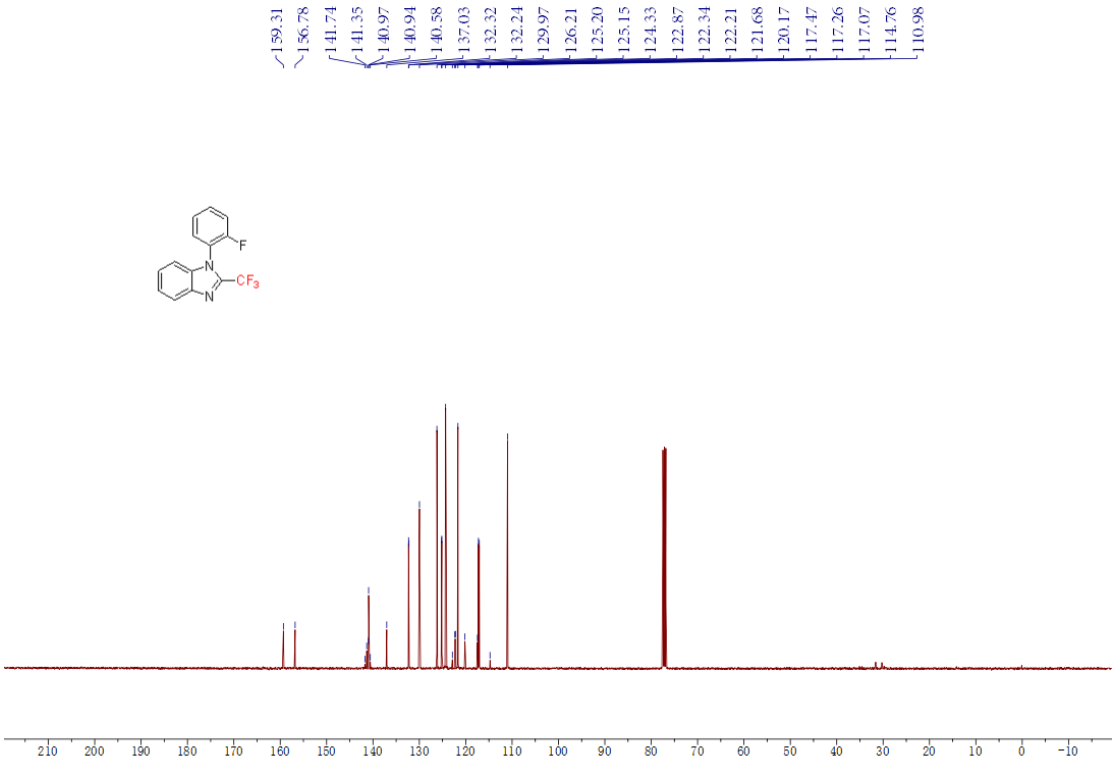
^{1}H NMR spectra of **4r** in $CDCl_3$



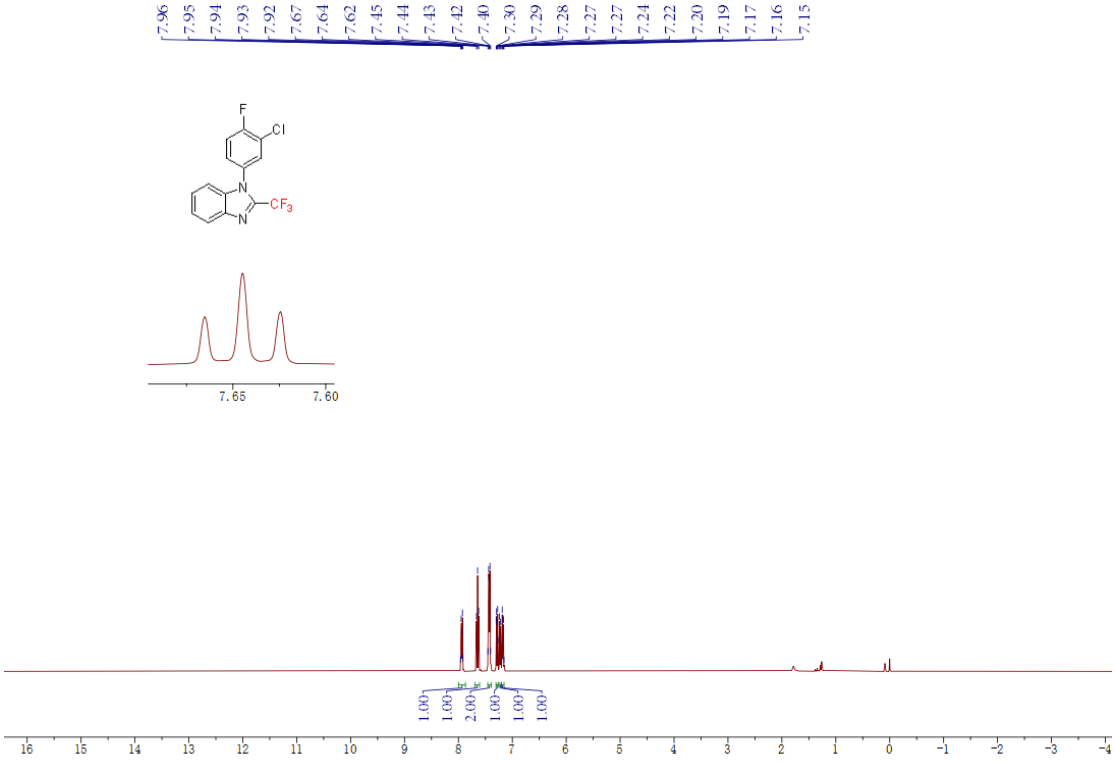
^{19}F NMR spectra of **4r** in $CDCl_3$



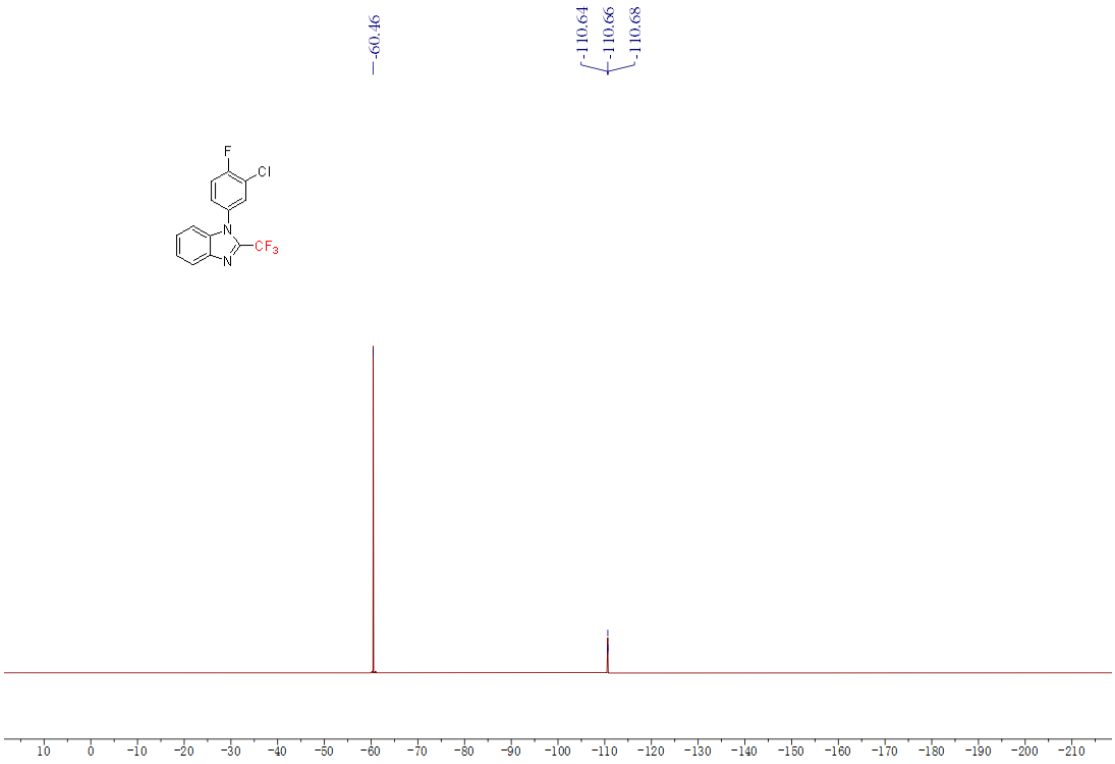
^{13}C NMR spectra of **4r** in $CDCl_3$



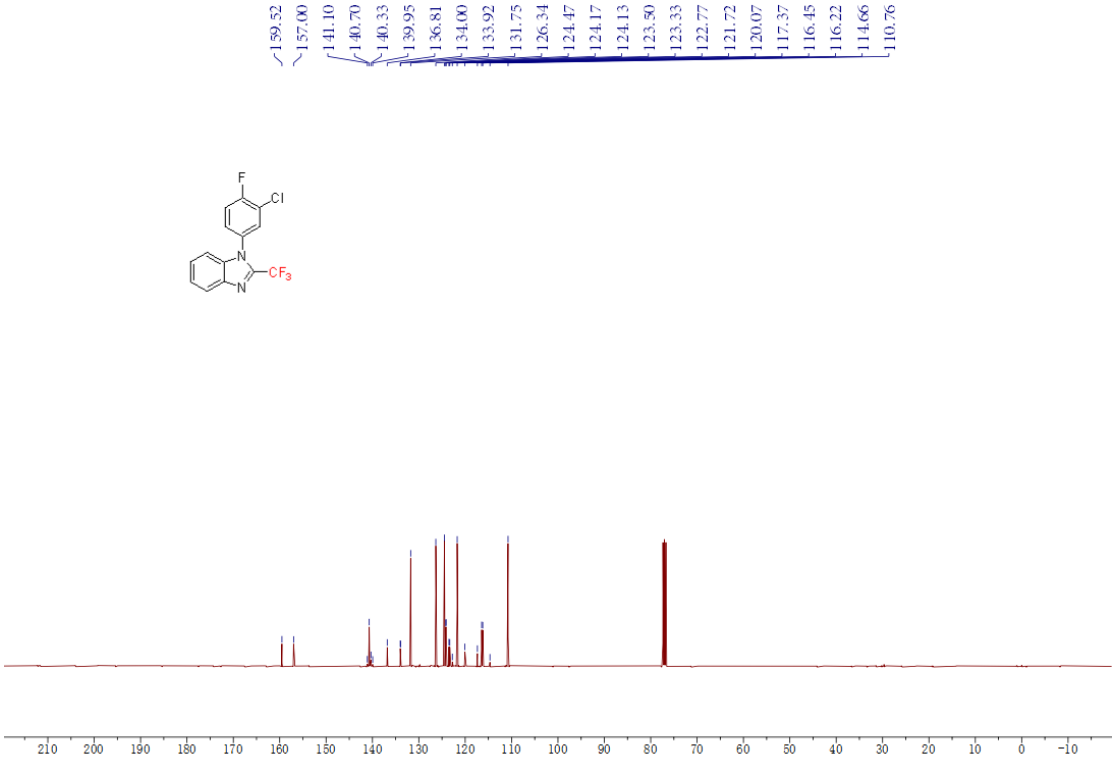
^{1}H NMR spectra of **4s** in $CDCl_3$



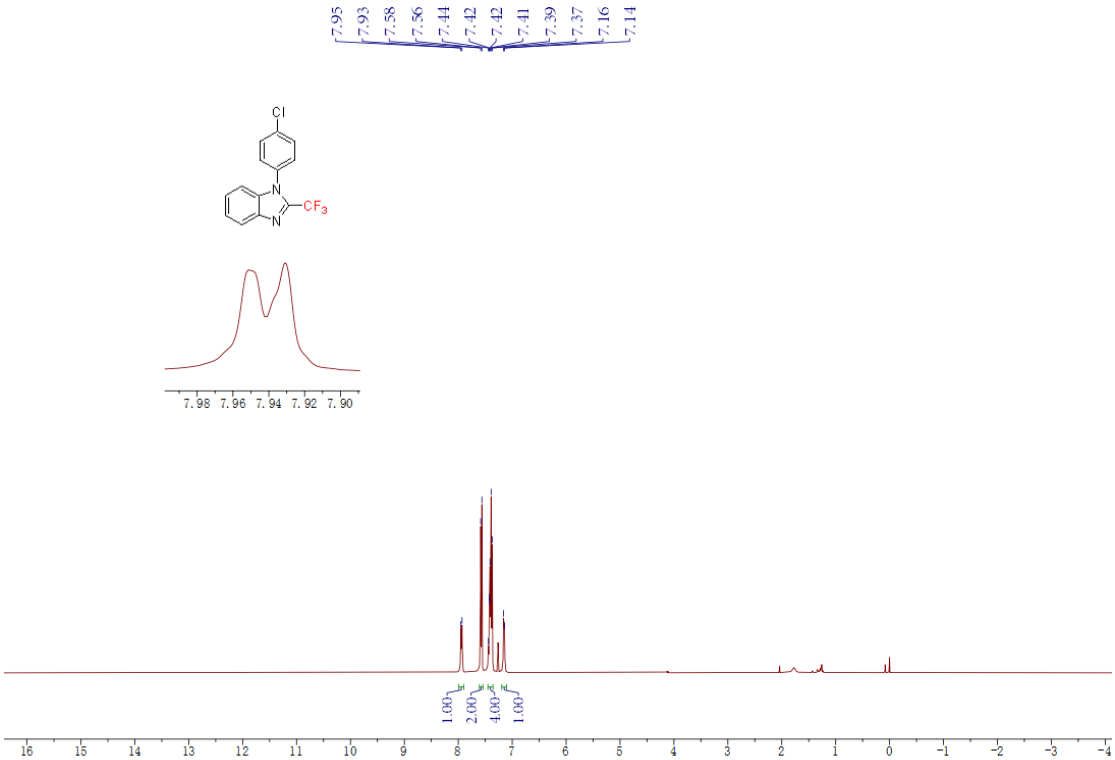
^{19}F NMR spectra of **4s** in $CDCl_3$



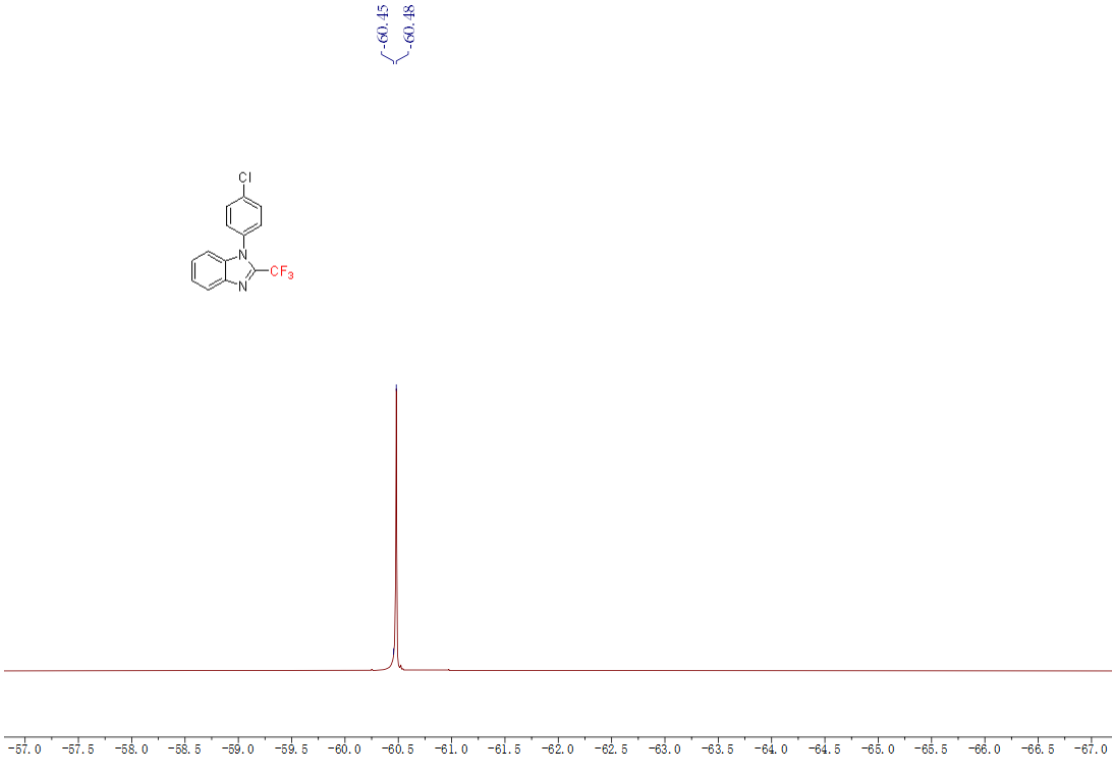
^{13}C NMR spectra of **4s** in $CDCl_3$



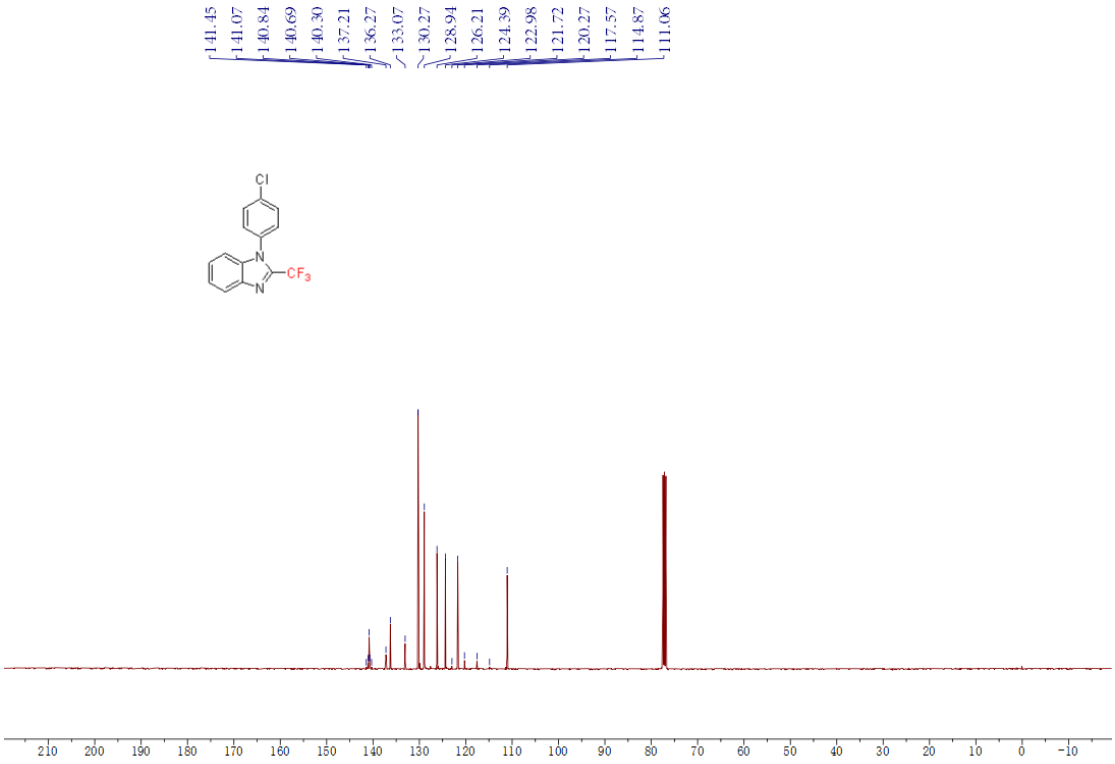
^{1}H NMR spectra of **4t** in $CDCl_3$



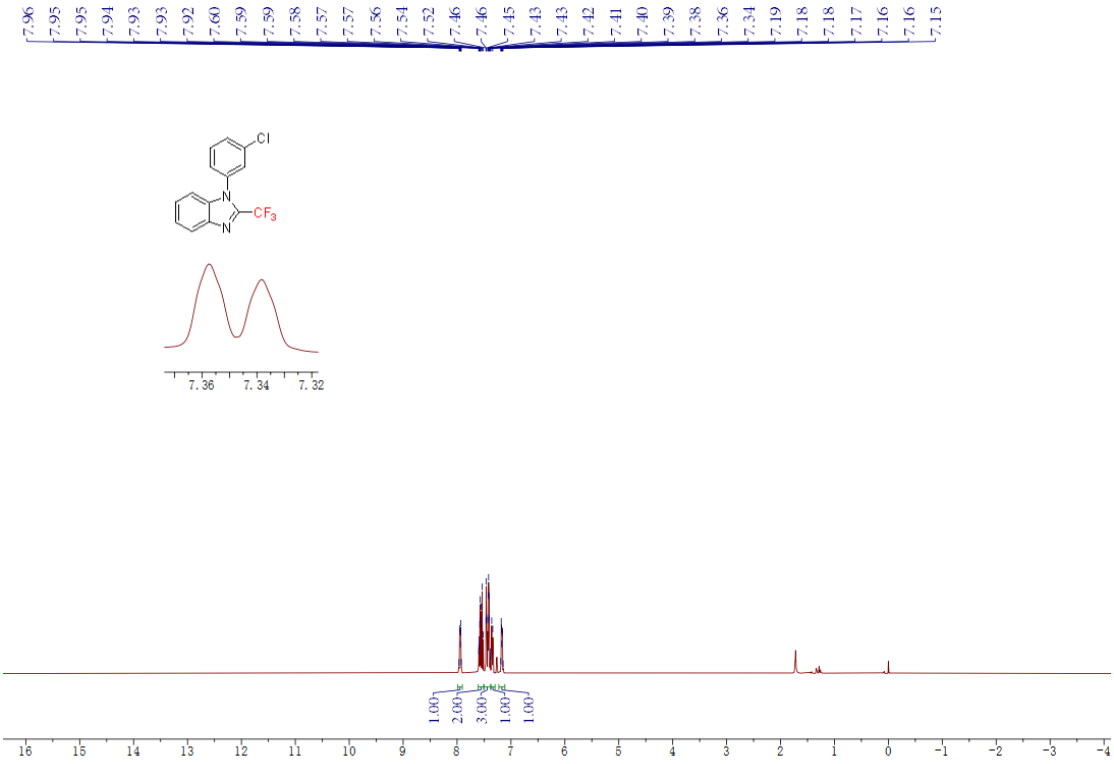
^{19}F NMR spectra of **4t** in $CDCl_3$



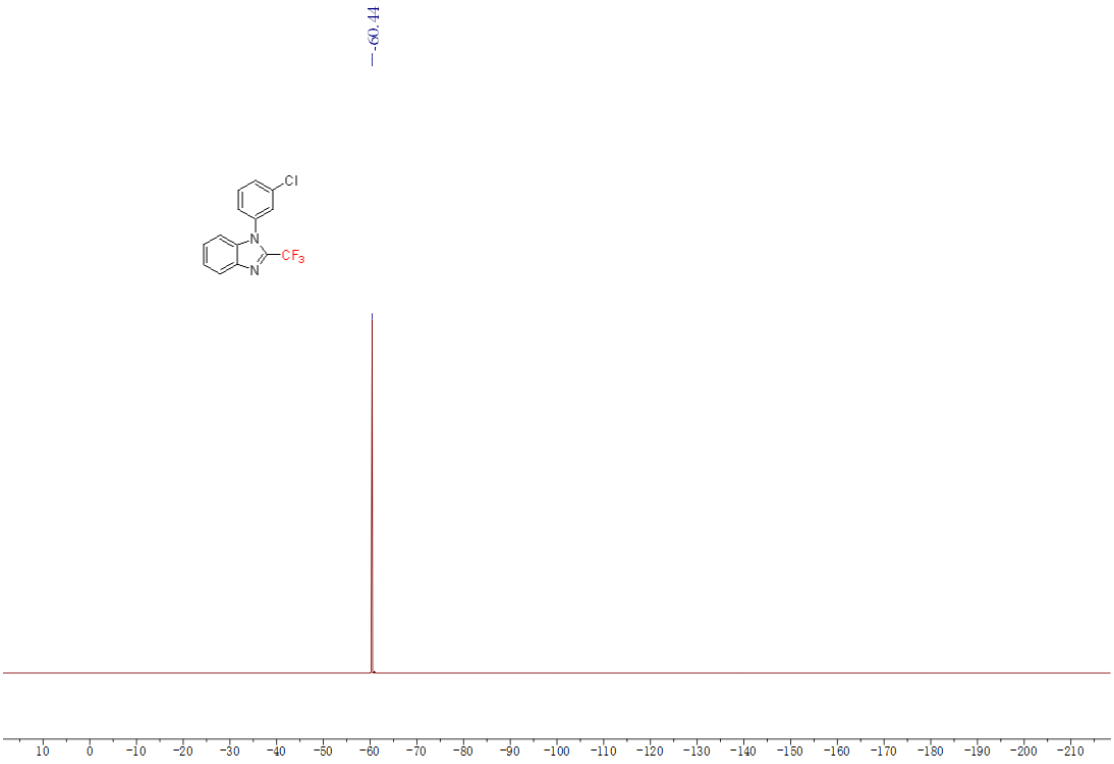
^{13}C NMR spectra of **4t** in $CDCl_3$



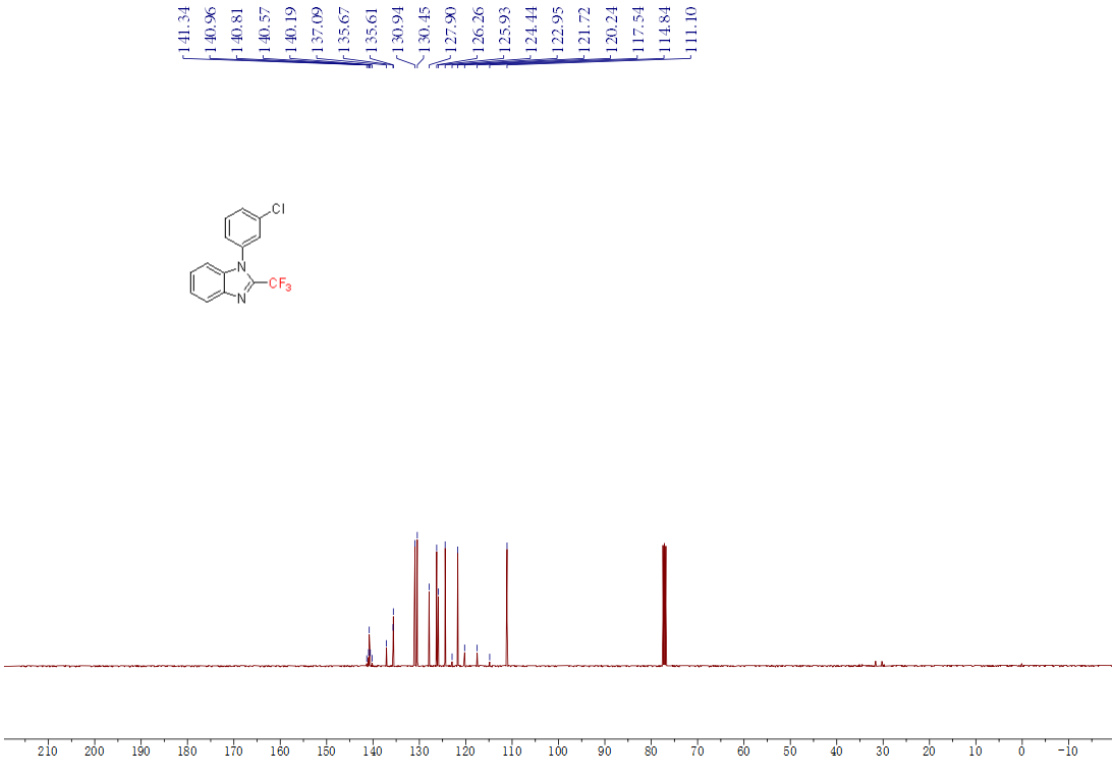
^{1}H NMR spectra of **4u** in $CDCl_3$



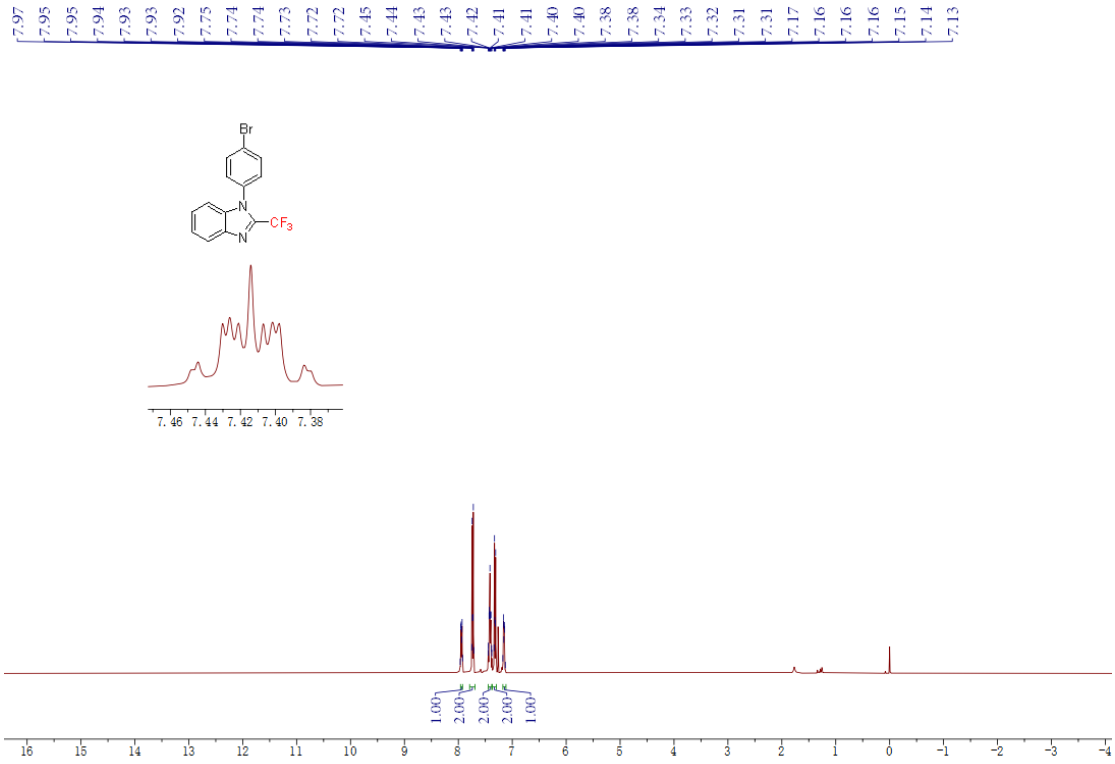
^{19}F NMR spectra of **4u** in $CDCl_3$



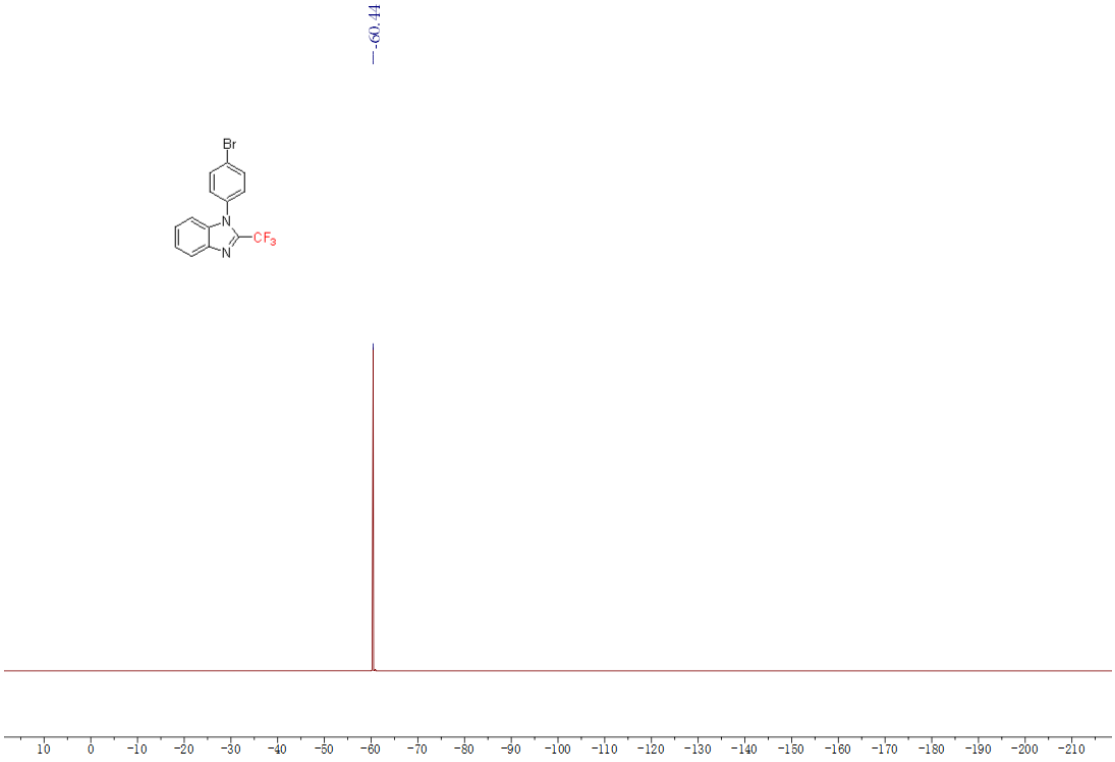
^{13}C NMR spectra of **4u** in $CDCl_3$



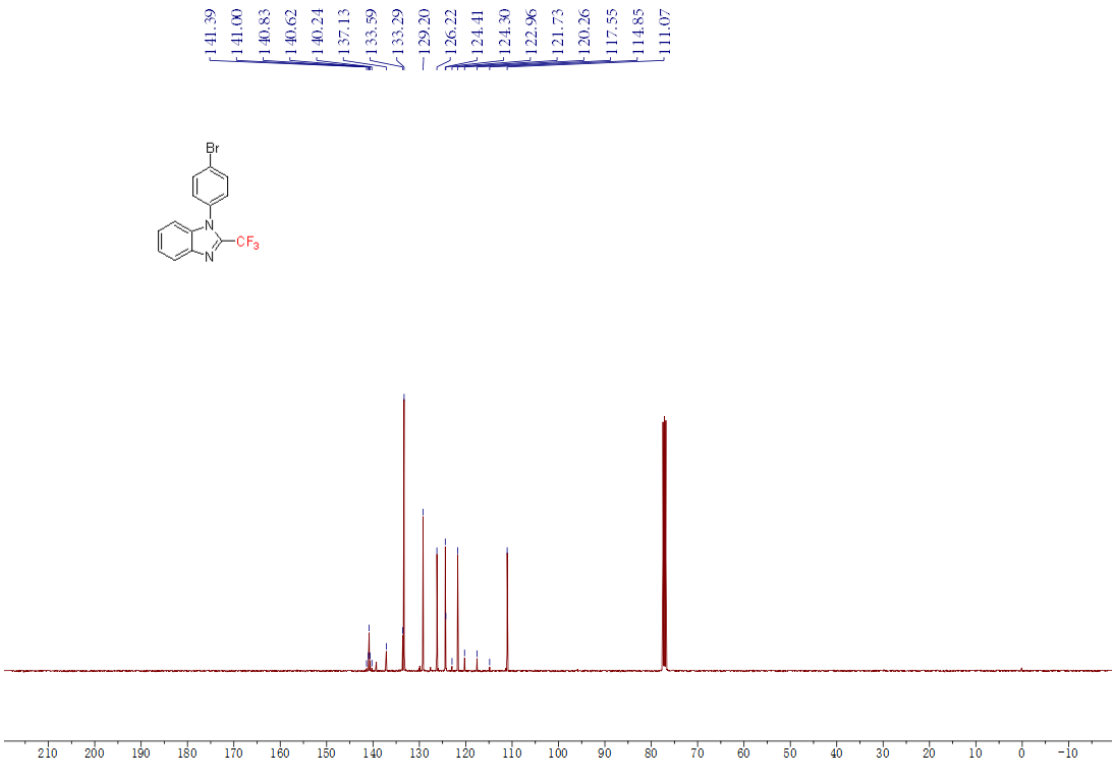
^{1}H NMR spectra of **4v** in $CDCl_3$



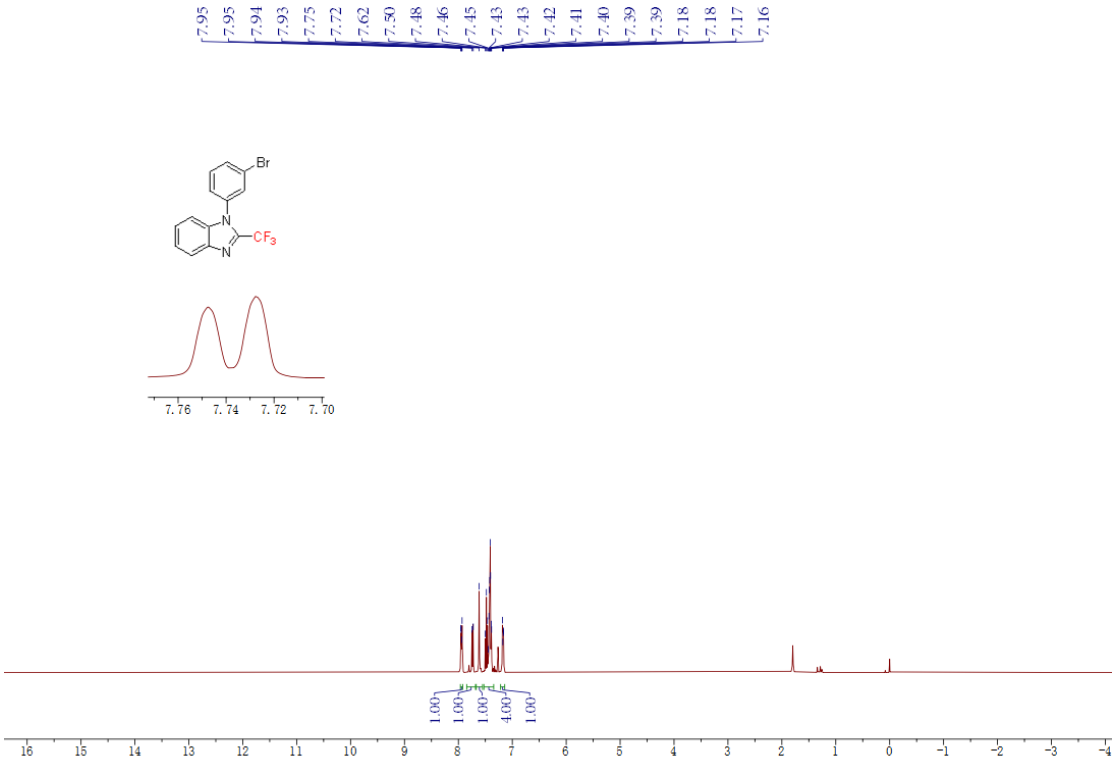
^{19}F NMR spectra of **4v** in $CDCl_3$



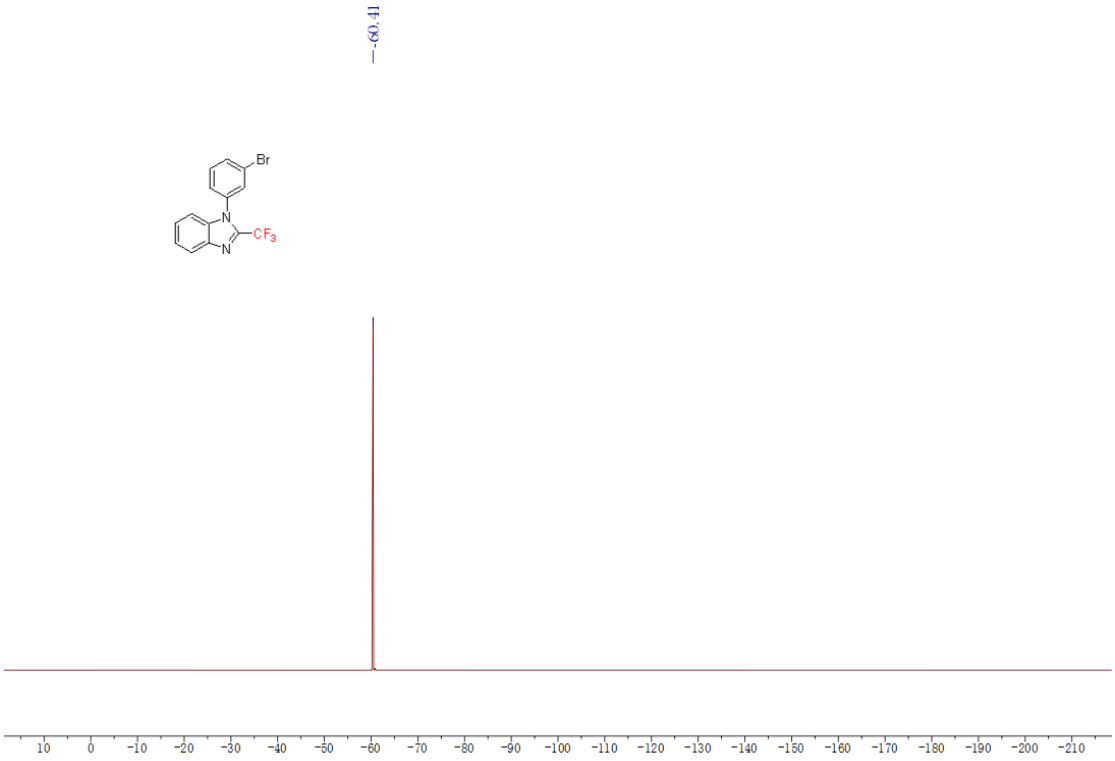
^{13}C NMR spectra of **4v** in $CDCl_3$



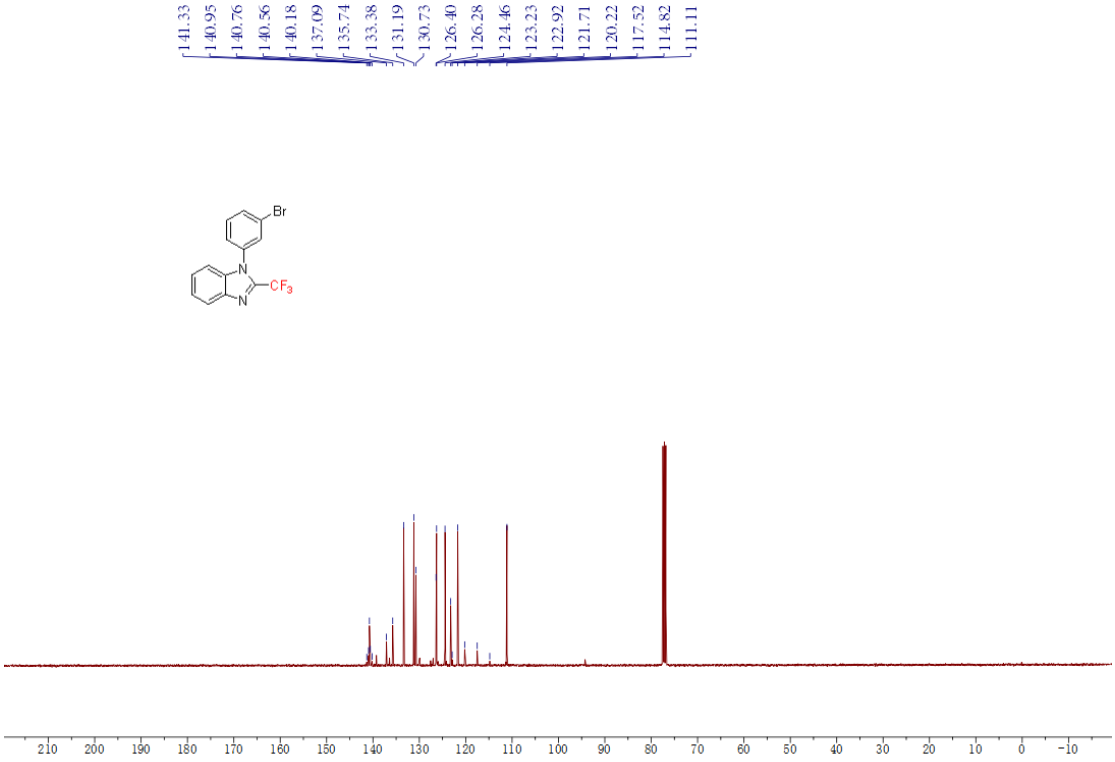
^{1}H NMR spectra of **4w** in $CDCl_3$



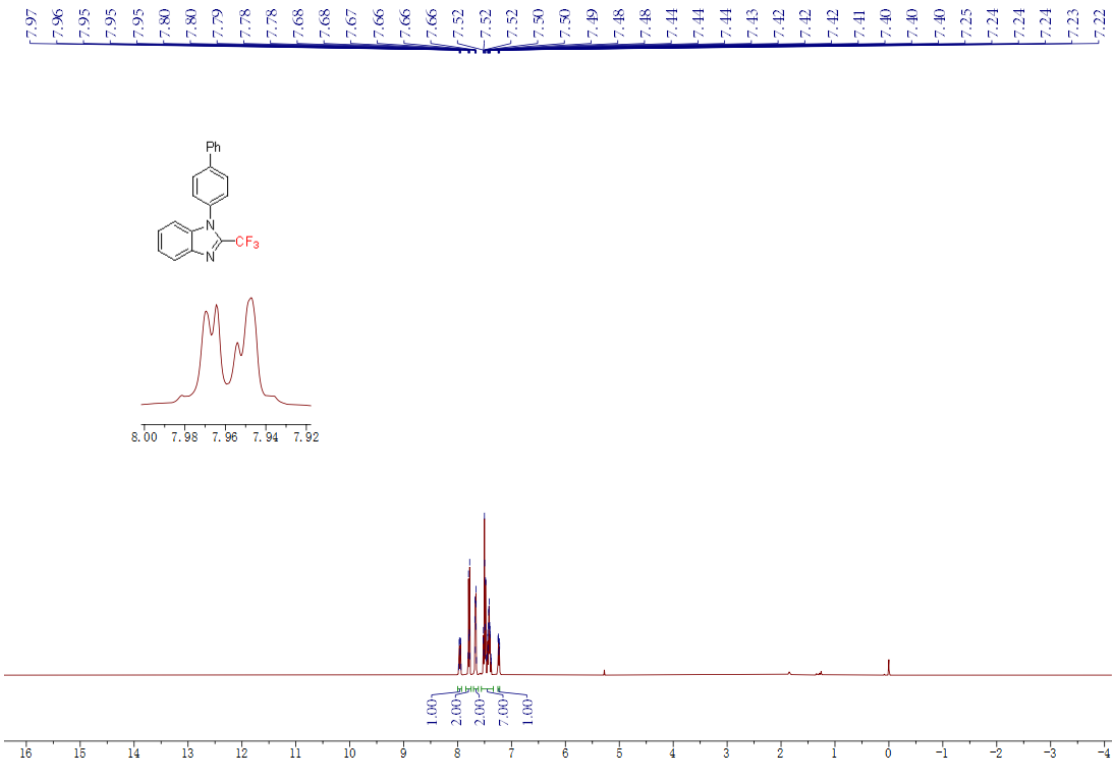
^{19}F NMR spectra of **4w** in $CDCl_3$



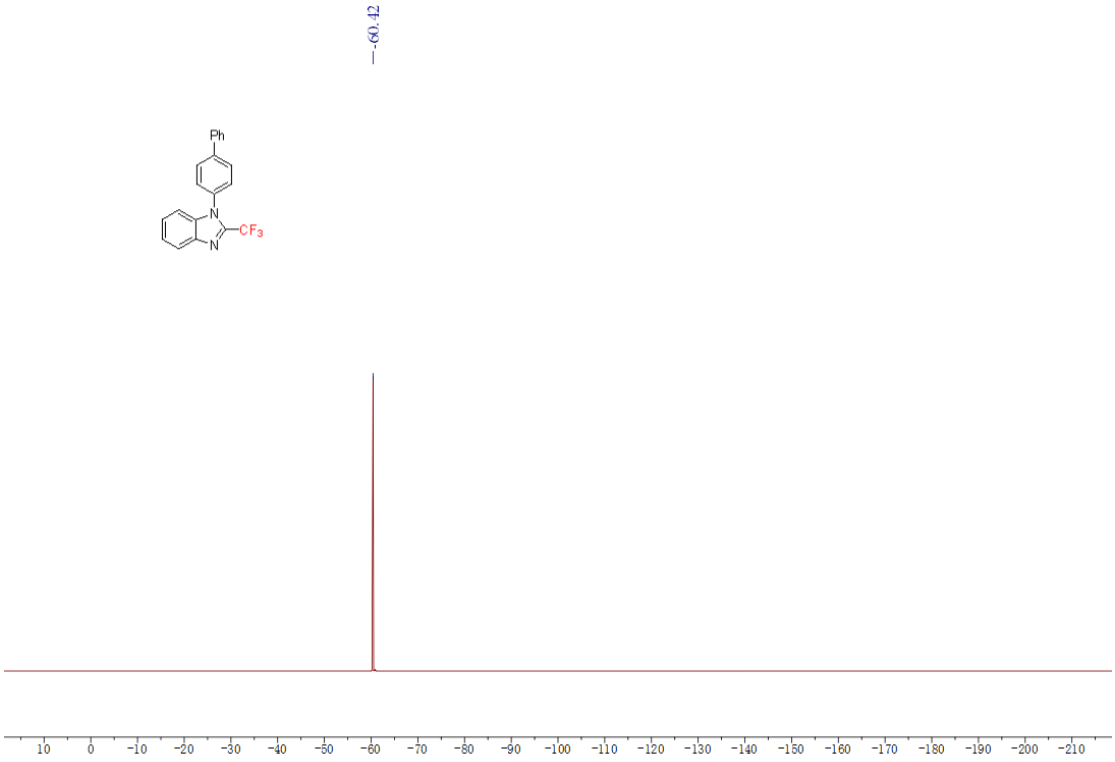
^{13}C NMR spectra of **4w** in $CDCl_3$



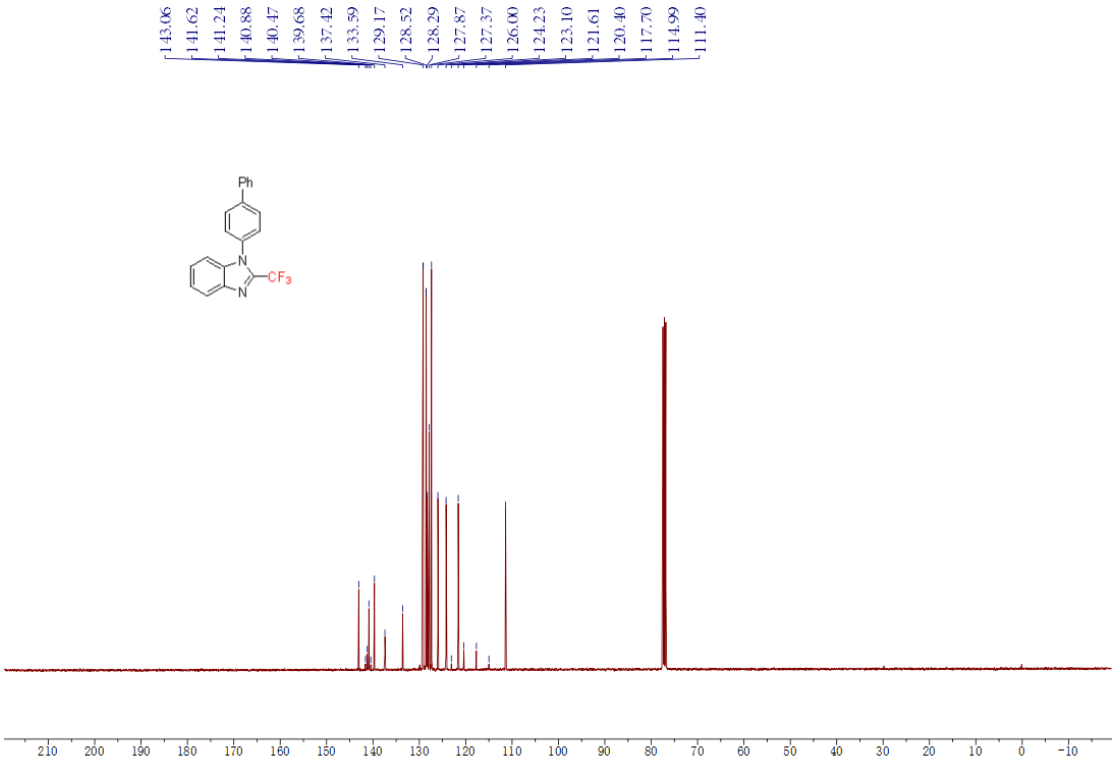
^{1}H NMR spectra of **4x** in $CDCl_3$



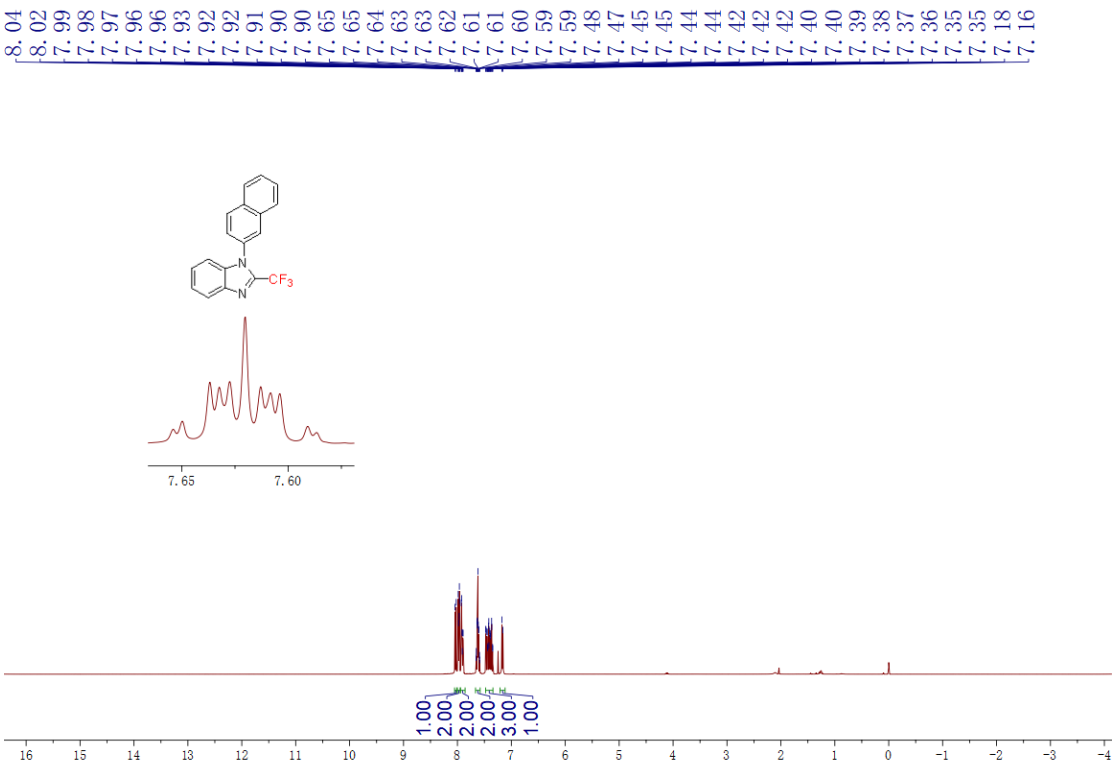
^{19}F NMR spectra of **4x** in $CDCl_3$



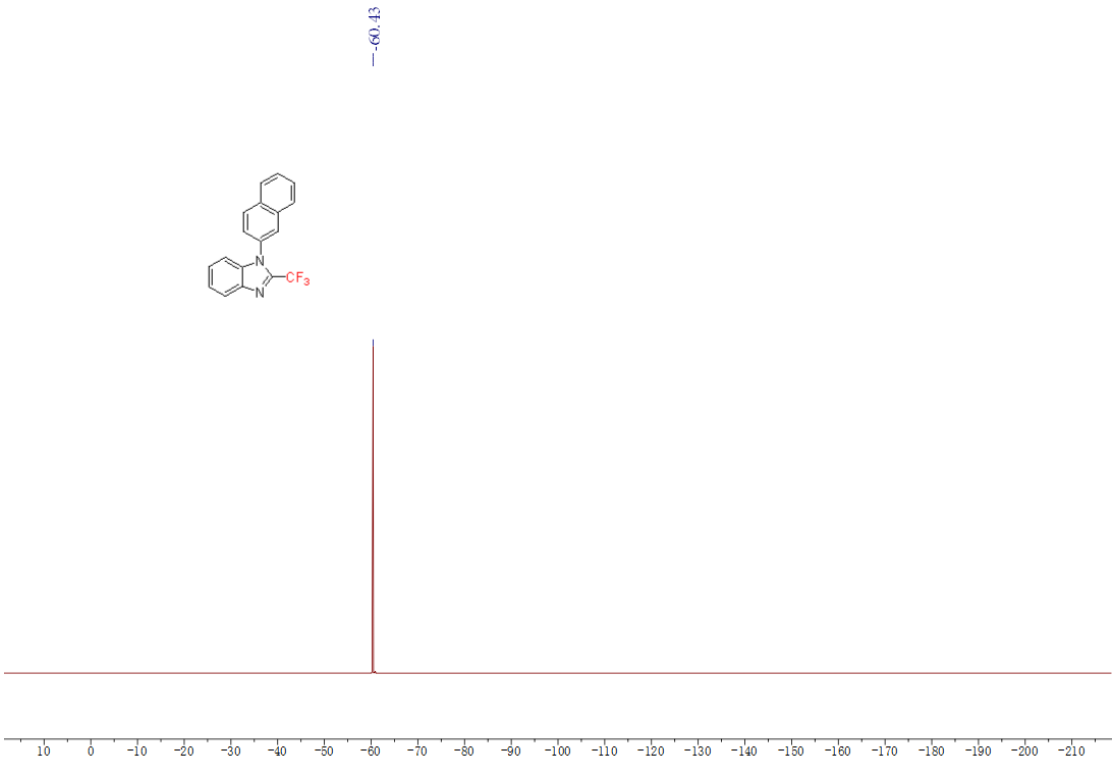
^{13}C NMR spectra of **4x** in $CDCl_3$



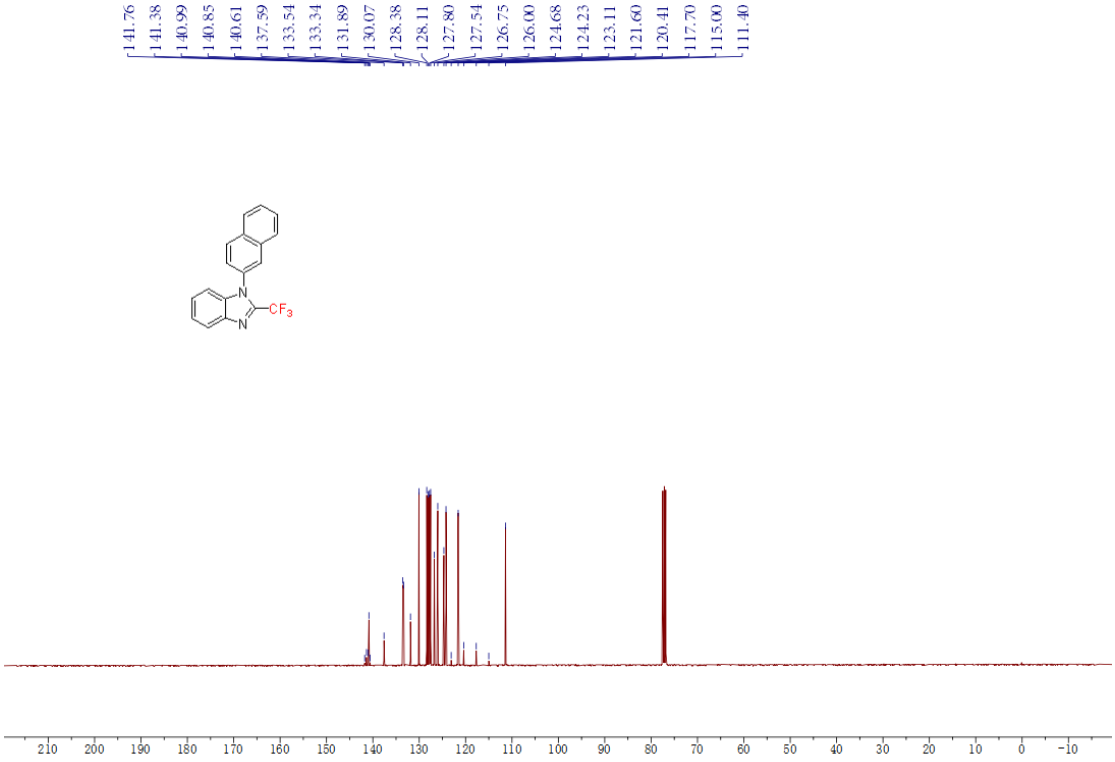
^{1}H NMR spectra of **4y** in $CDCl_3$



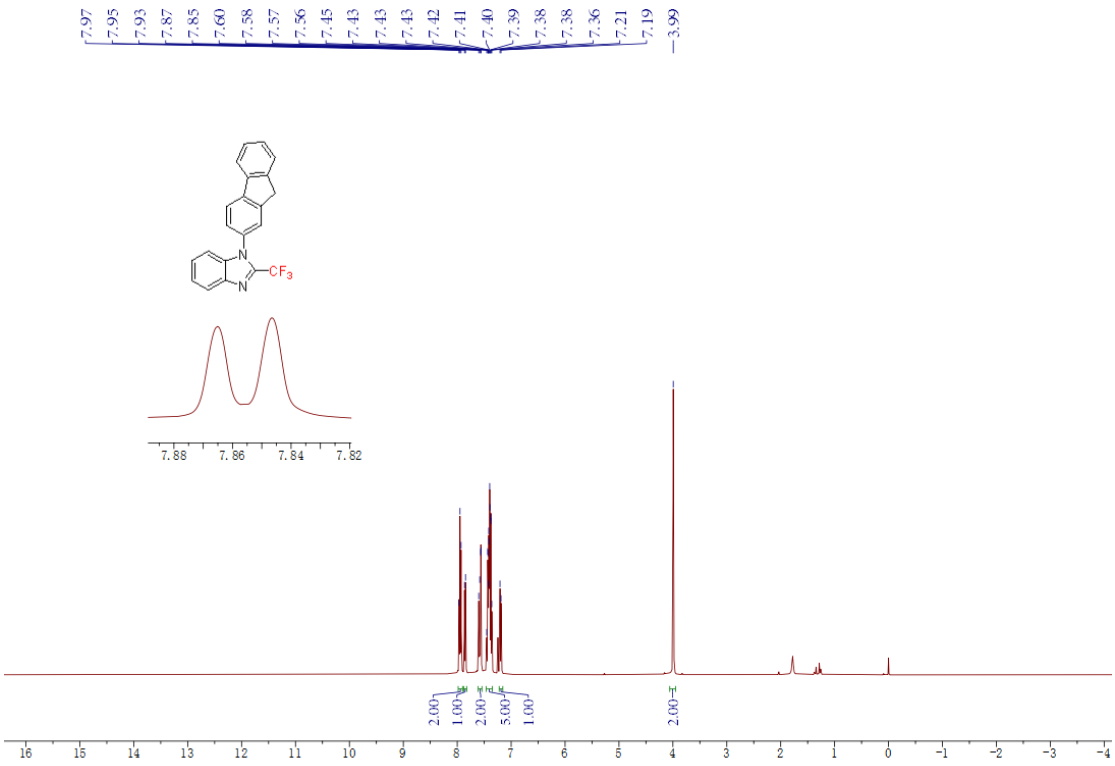
^{19}F NMR spectra of **4y** in $CDCl_3$



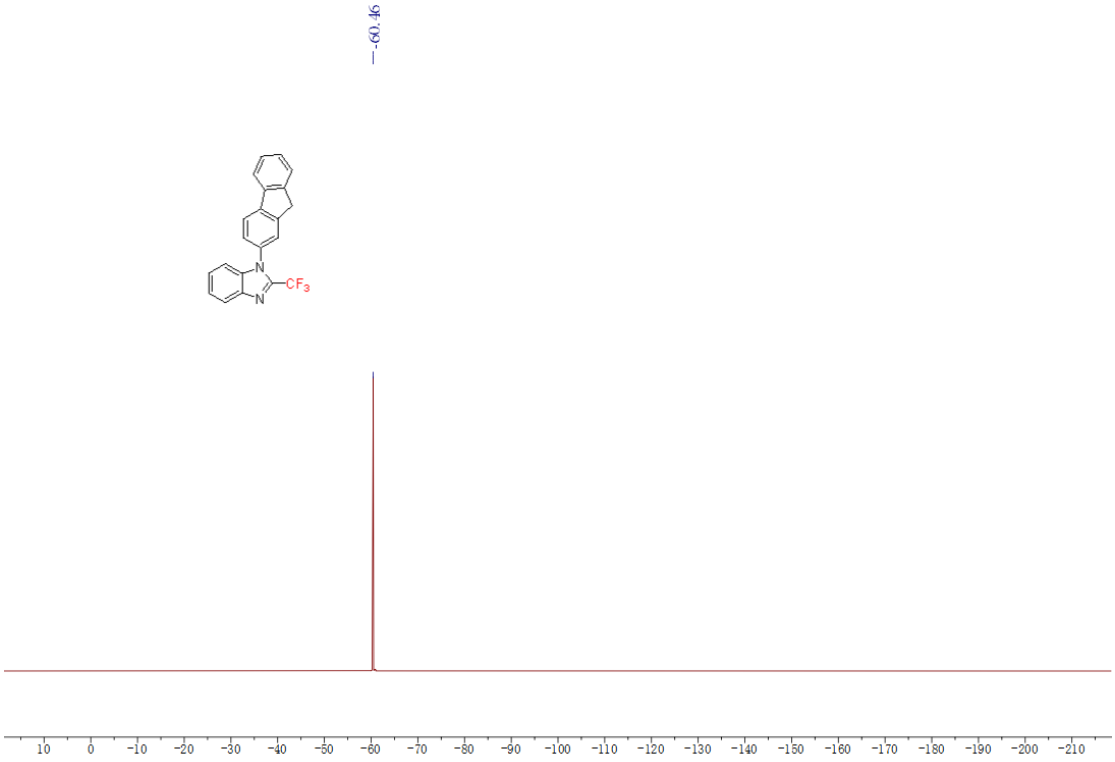
^{13}C NMR spectra of **4y** in $CDCl_3$



^{1}H NMR spectra of **4z** in $CDCl_3$



^{19}F NMR spectra of **4z** in $CDCl_3$



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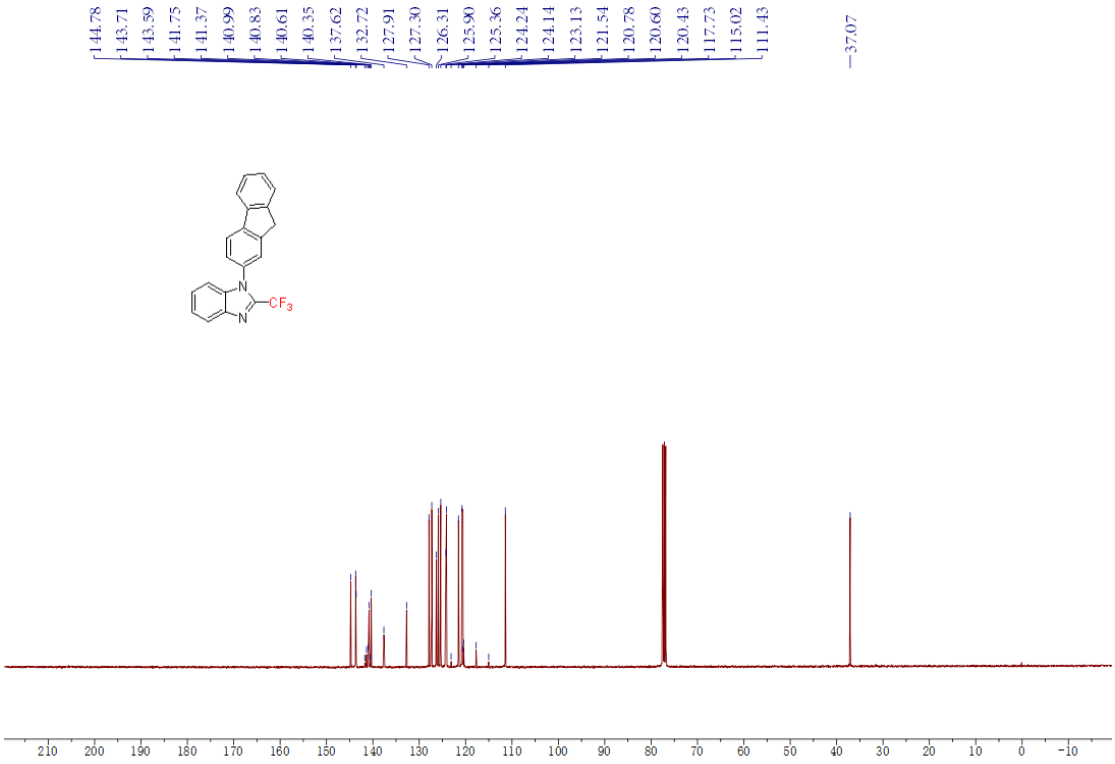
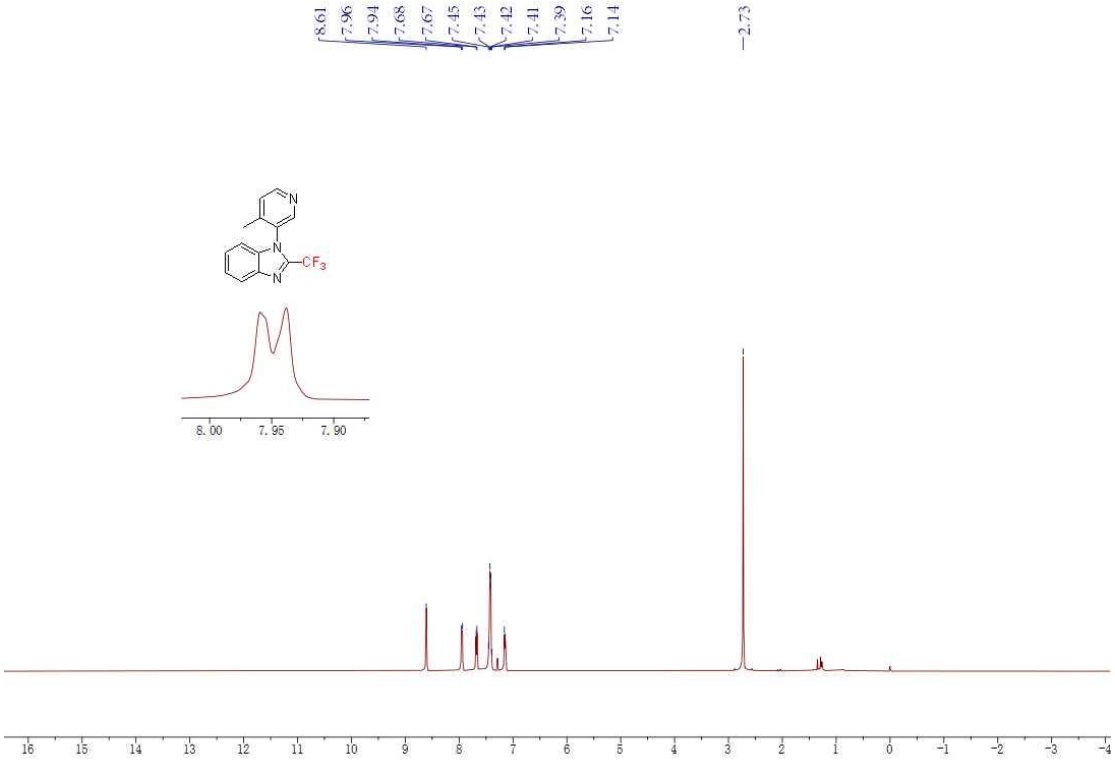
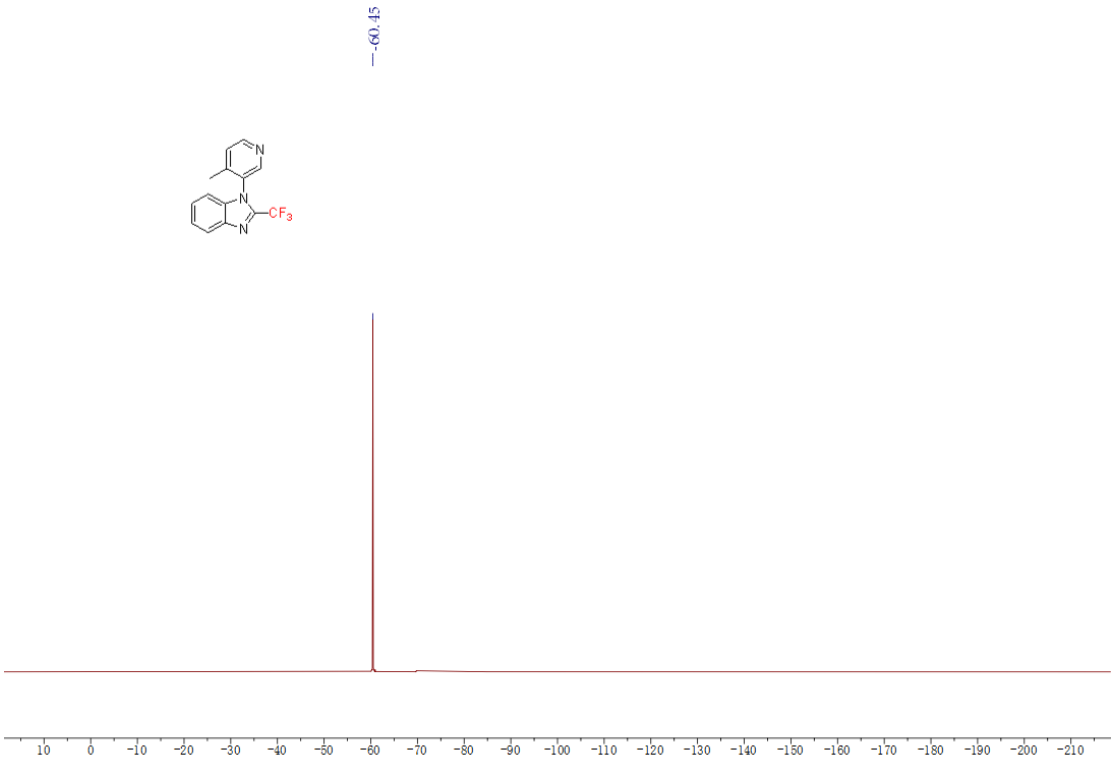


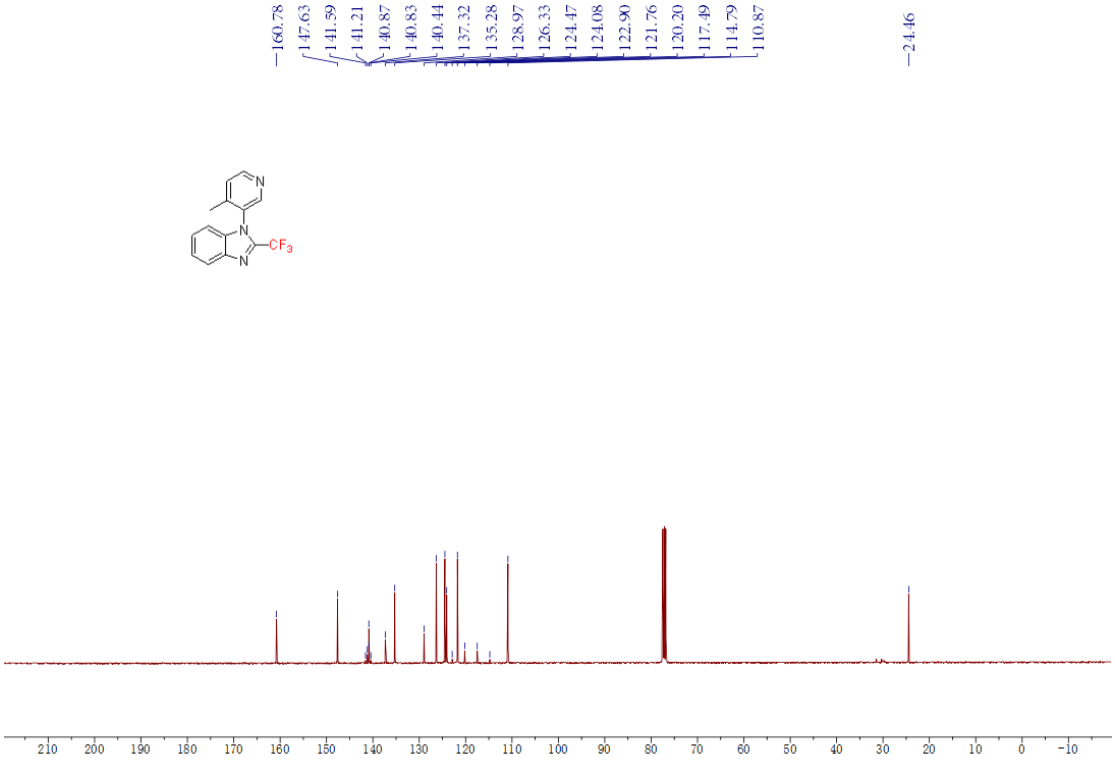
^{1}H NMR spectra of **4aa** in $CDCl_3$



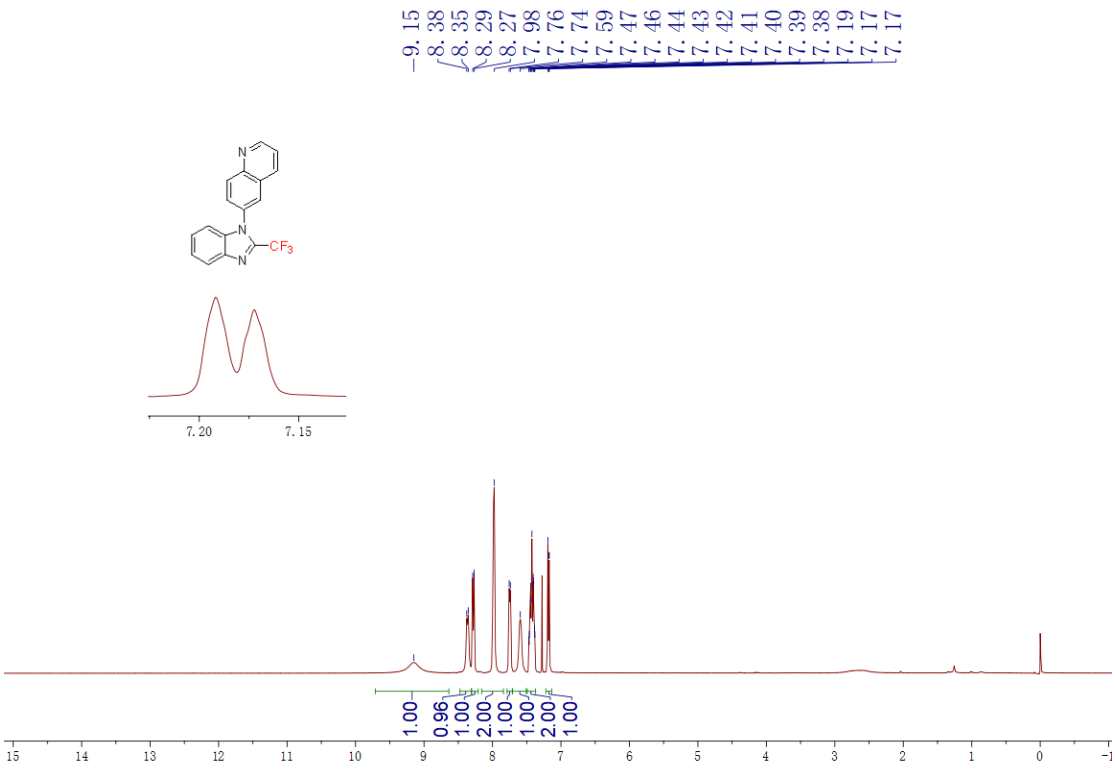
^{19}F NMR spectra of **4aa** in $CDCl_3$



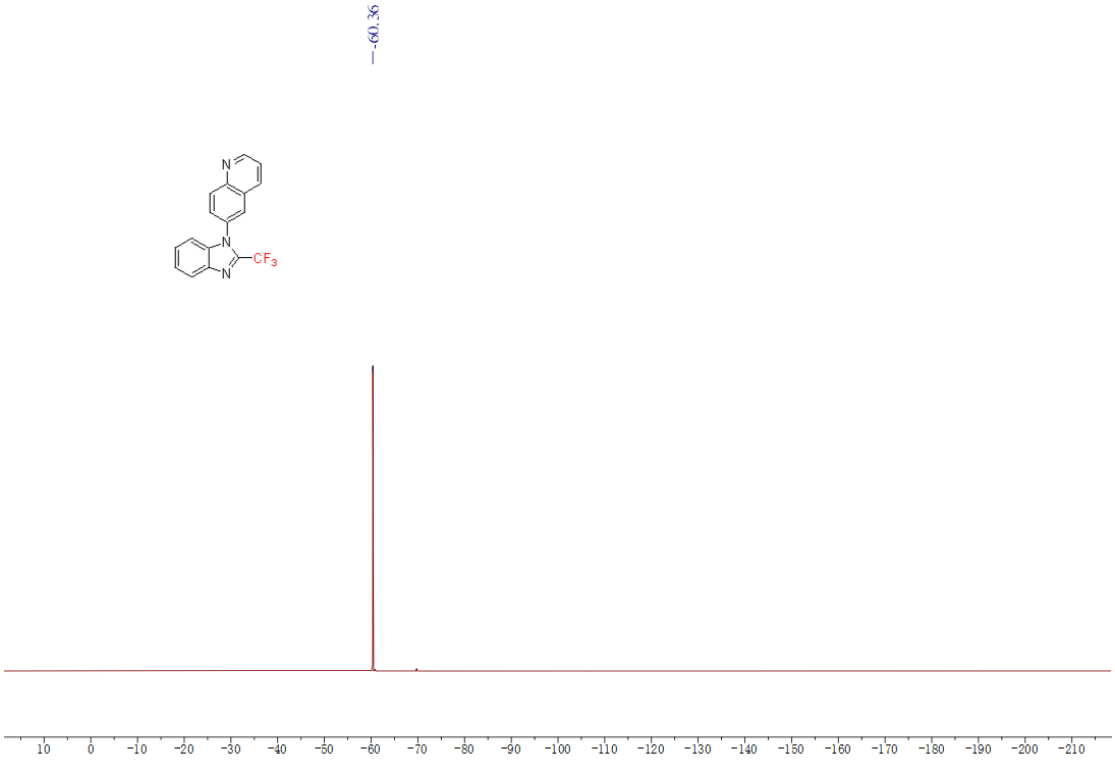
^{13}C NMR spectra of **4aa** in $CDCl_3$



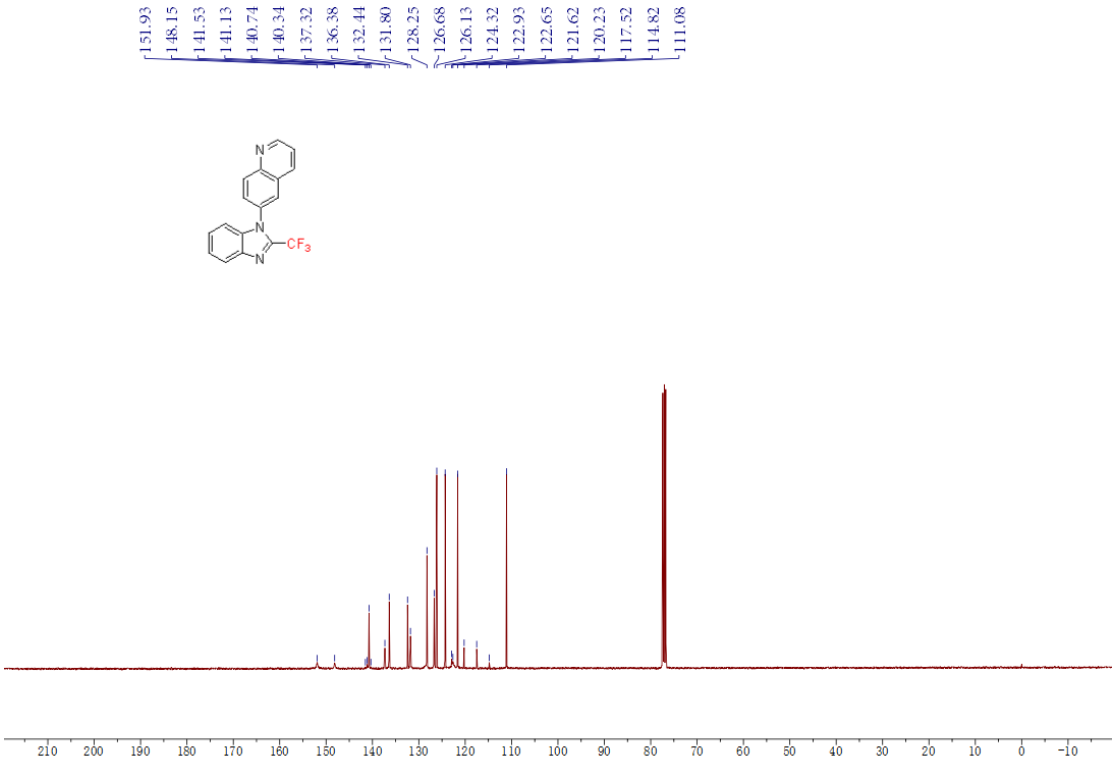
^{1}H NMR spectra of **4ab** in $CDCl_3$



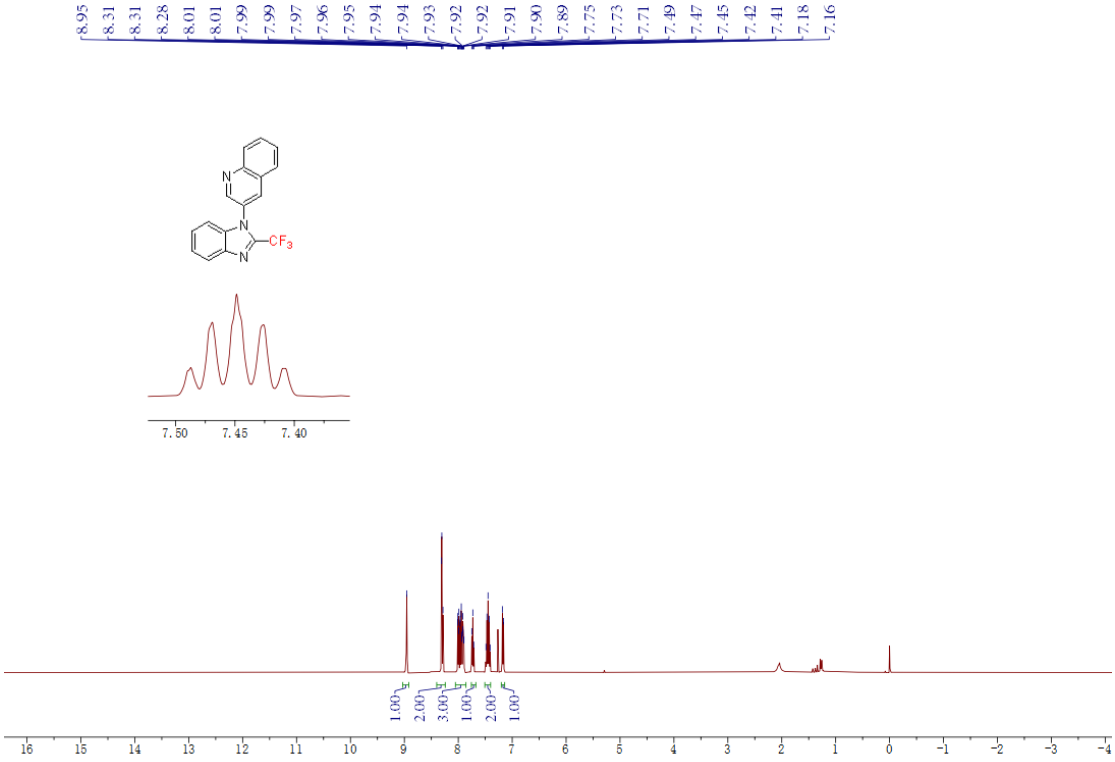
^{19}F NMR spectra of **4ab** in $CDCl_3$



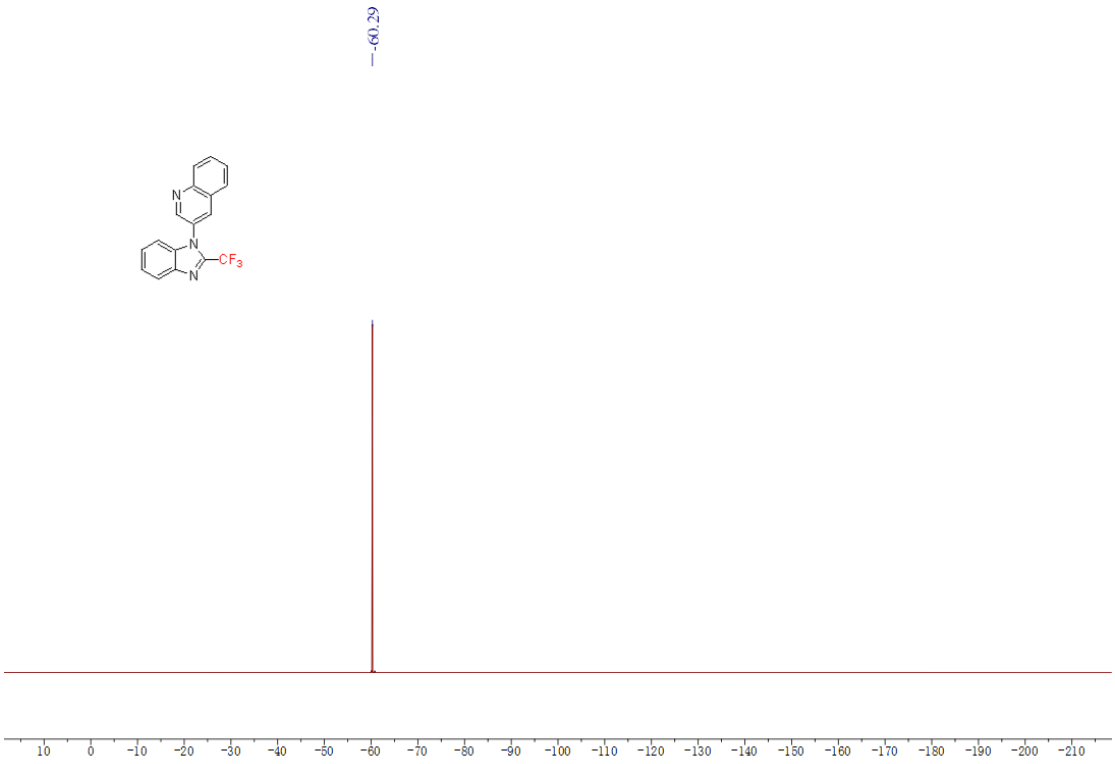
^{13}C NMR spectra of **4ab** in $CDCl_3$



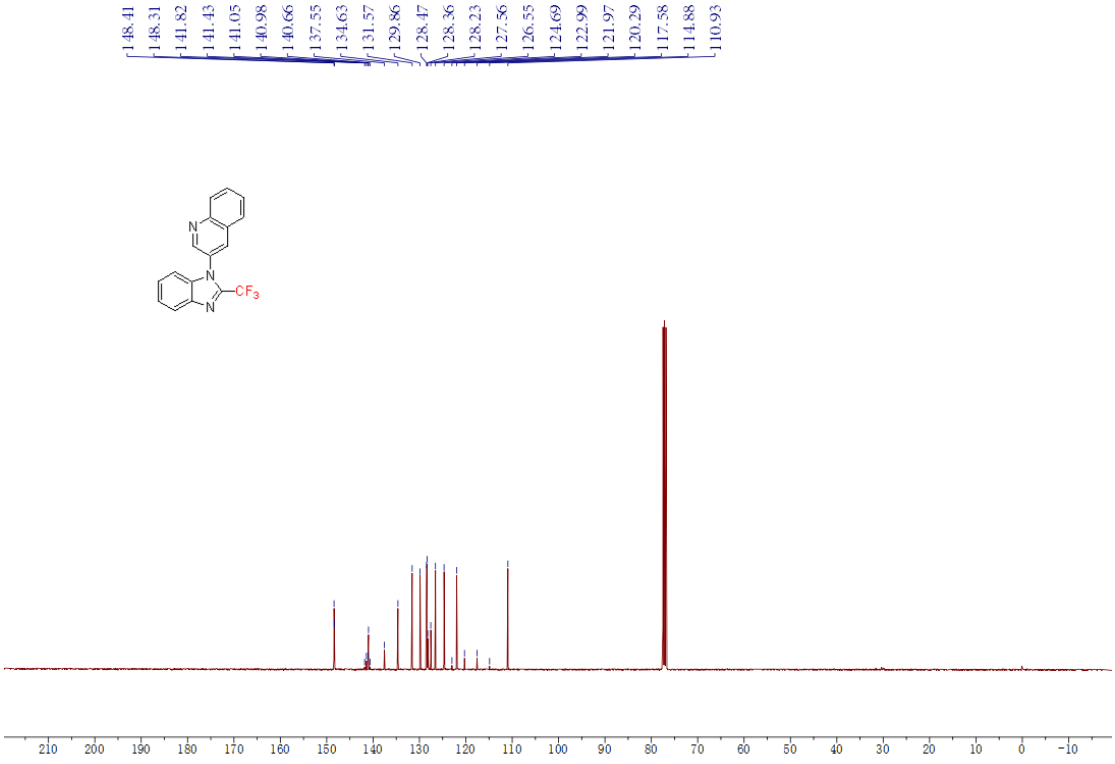
^{1}H NMR spectra of **4ac** in $CDCl_3$



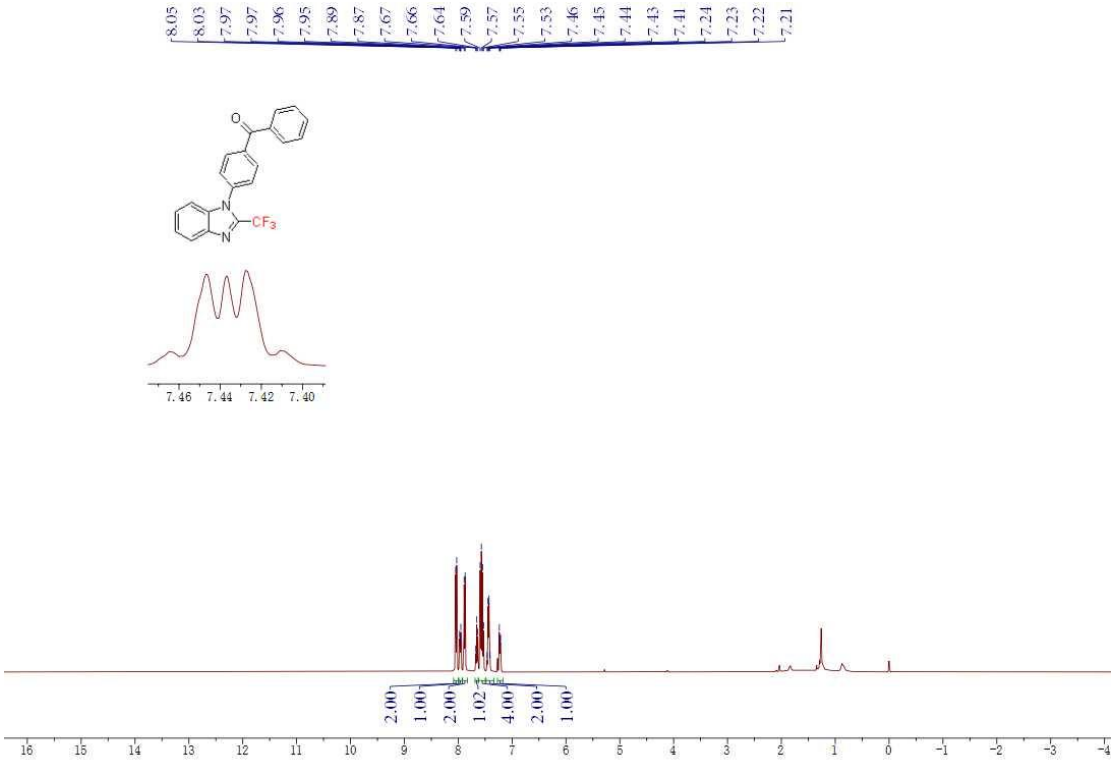
^{19}F NMR spectra of **4ac** in $CDCl_3$



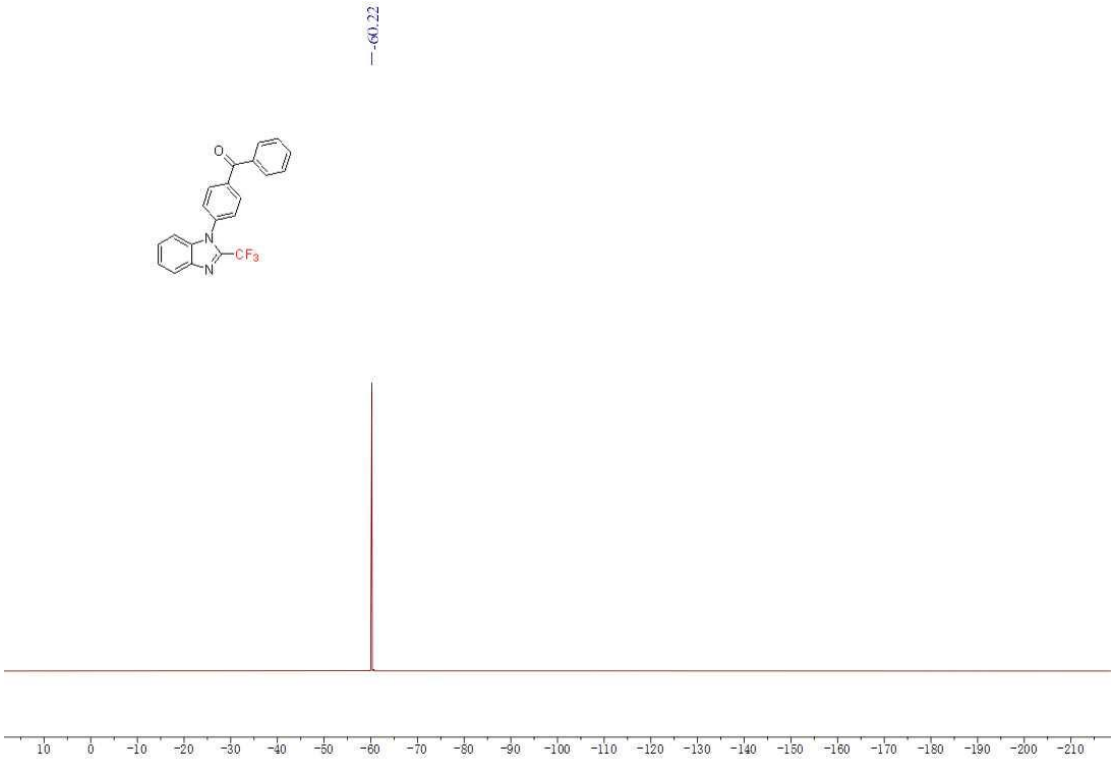
^{13}C NMR spectra of **4ac** in $CDCl_3$



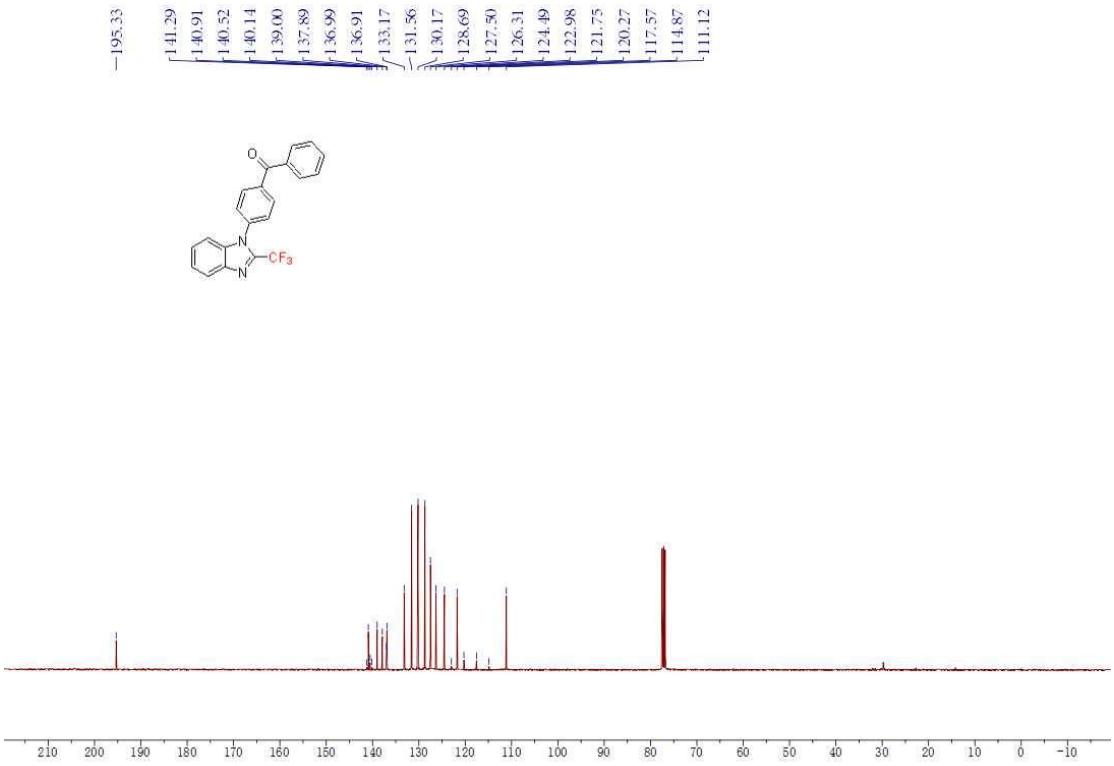
^{1}H NMR spectra of **4ad** in $CDCl_3$



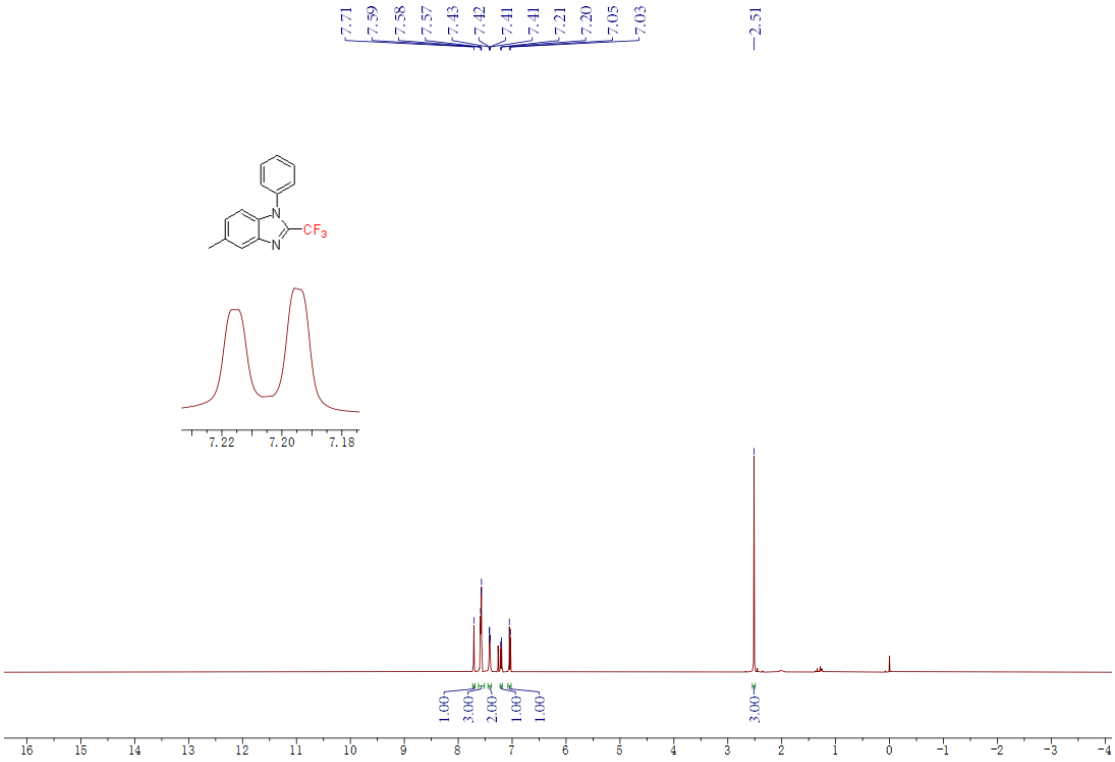
^{19}F NMR spectra of **4ad** in $CDCl_3$



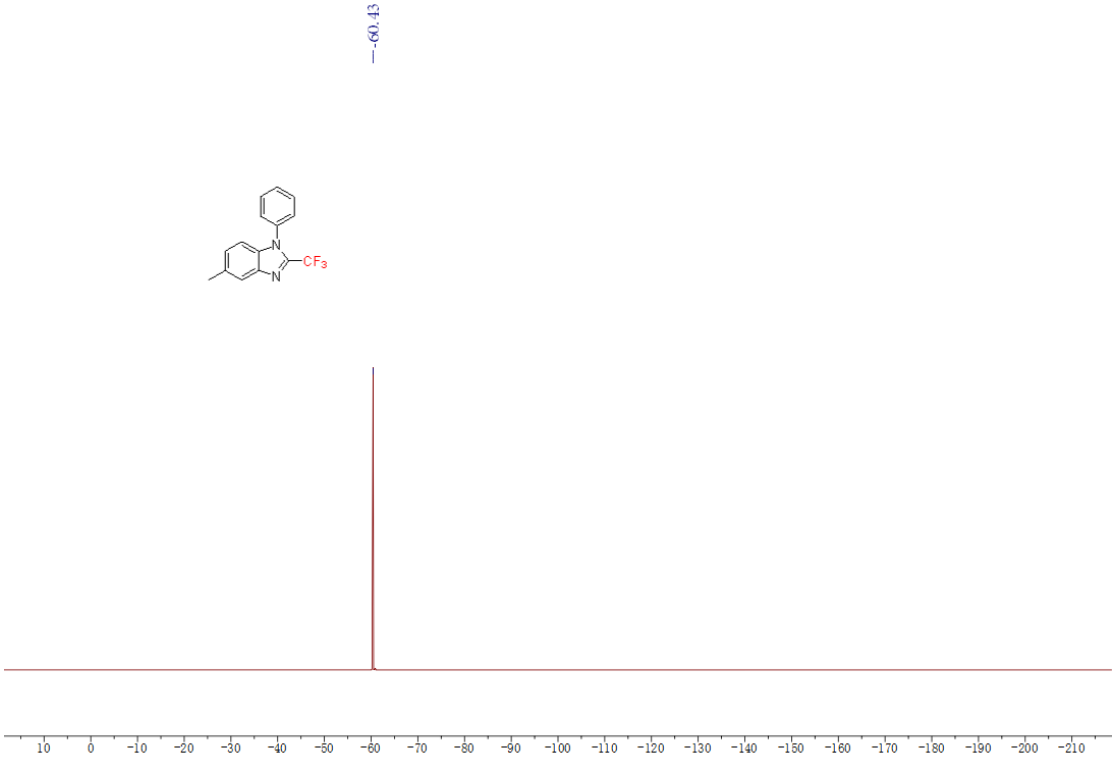
^{13}C NMR spectra of **4ad** in $CDCl_3$



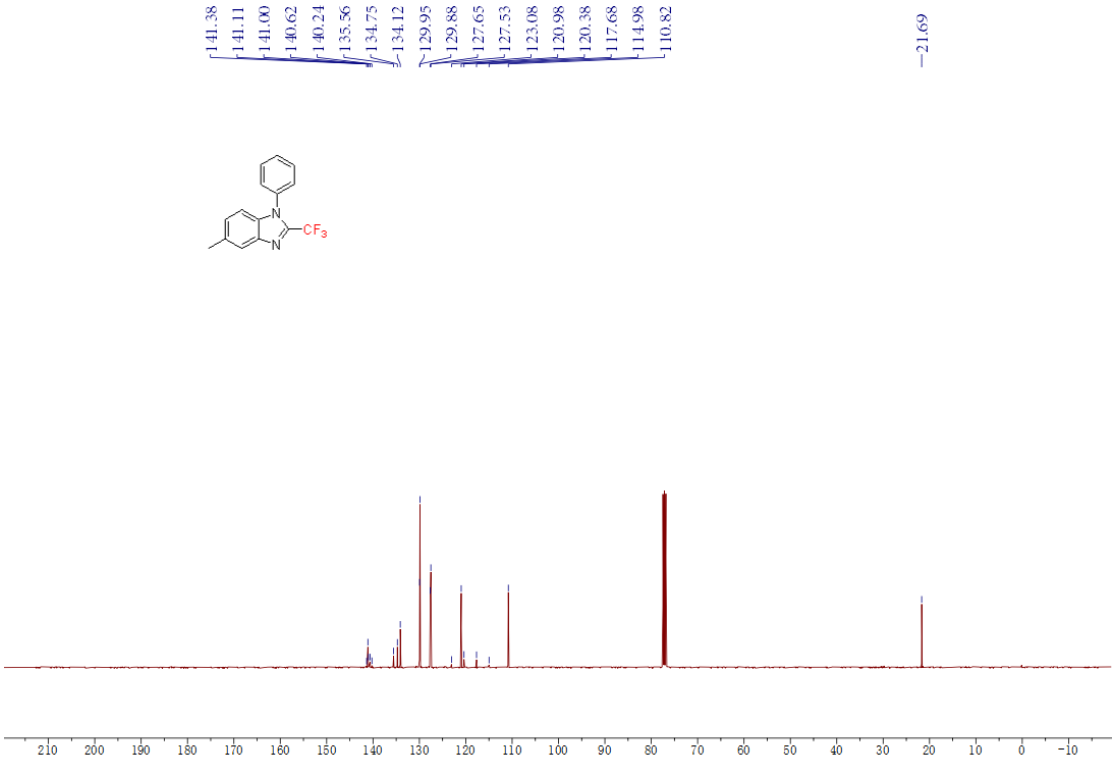
^{1}H NMR spectra of **5a** in $CDCl_3$



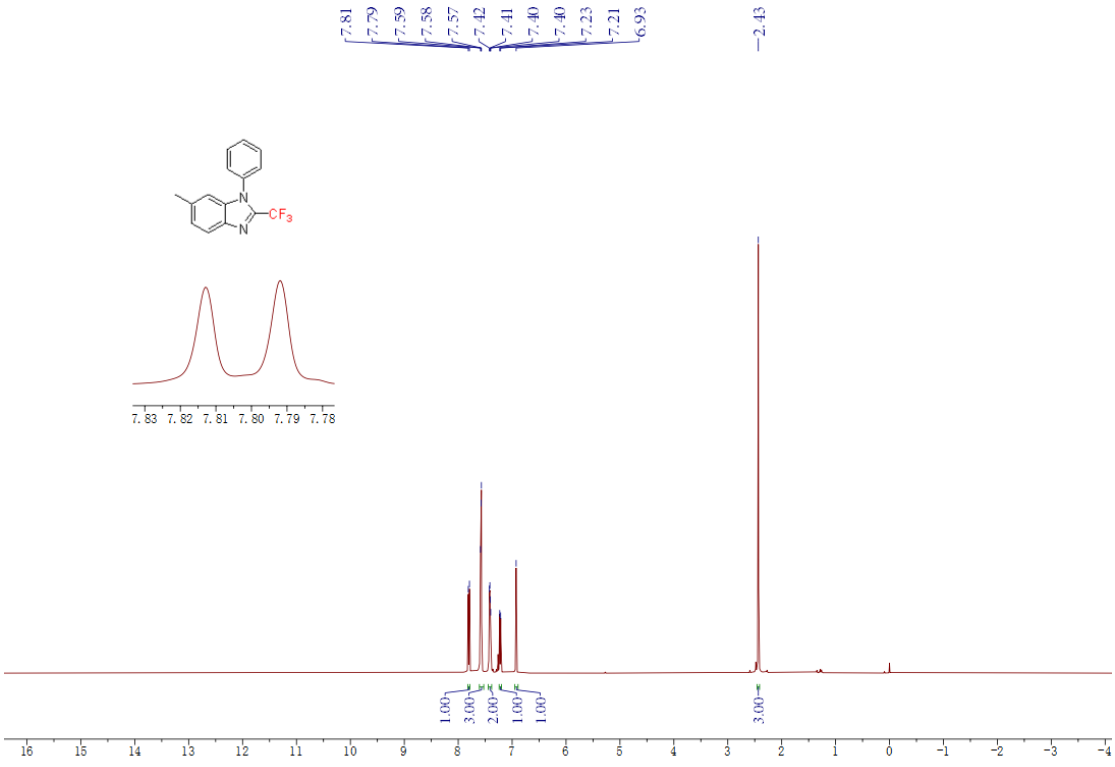
^{19}F NMR spectra of **5a** in $CDCl_3$



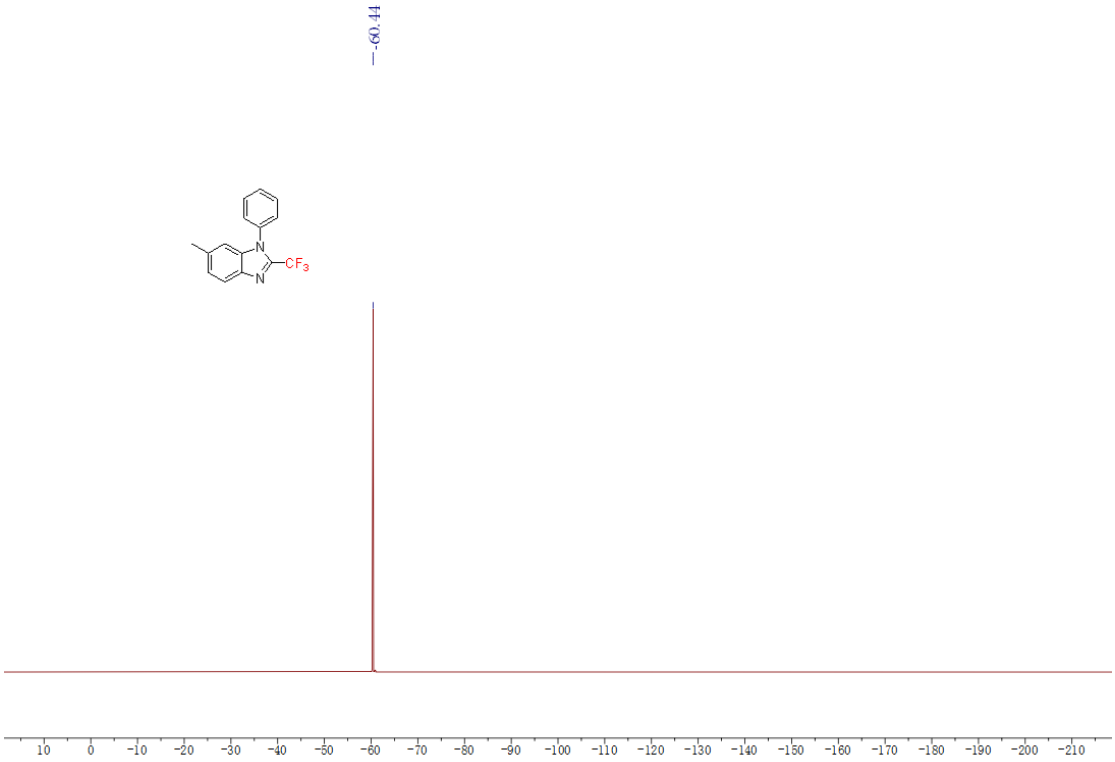
^{13}C NMR spectra of **5a** in $CDCl_3$



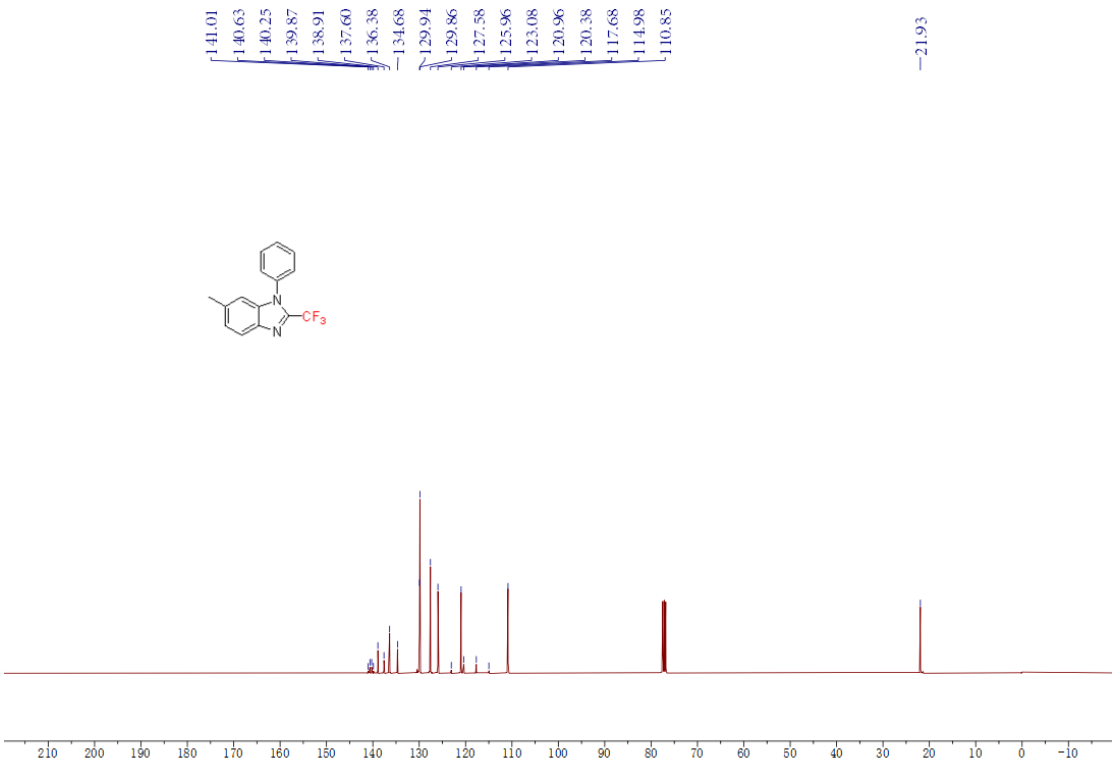
^{1}H NMR spectra of **5b** in $CDCl_3$



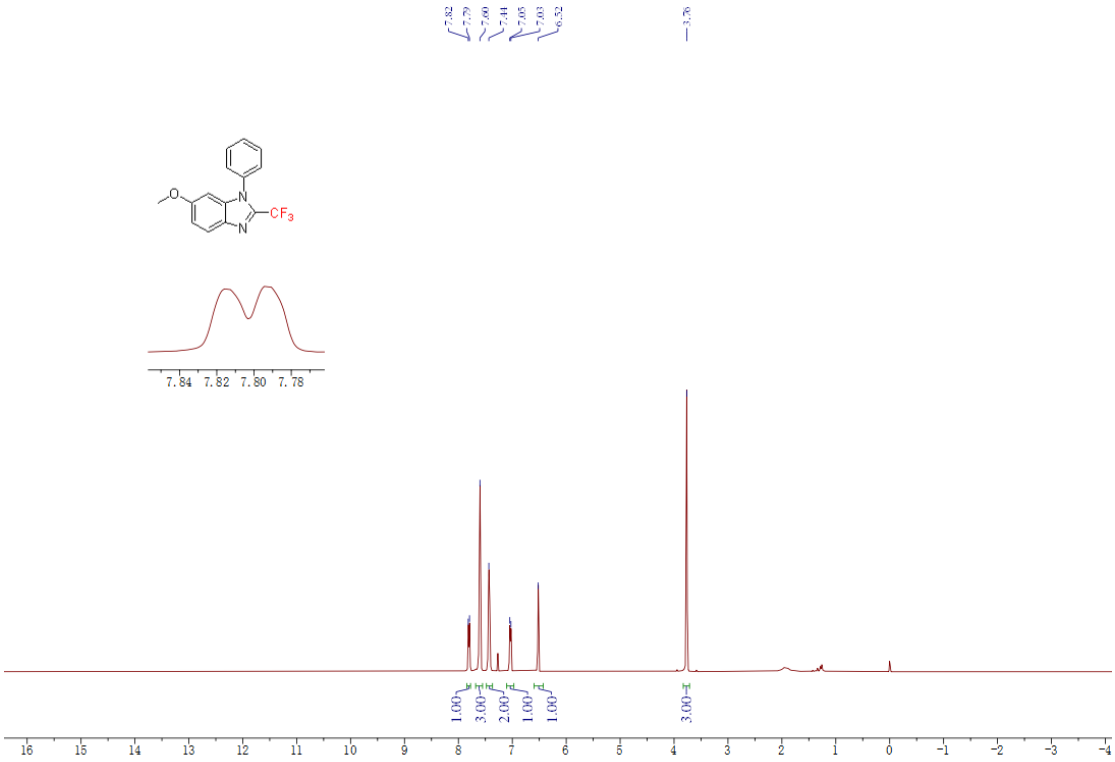
^{19}F NMR spectra of **5b** in $CDCl_3$



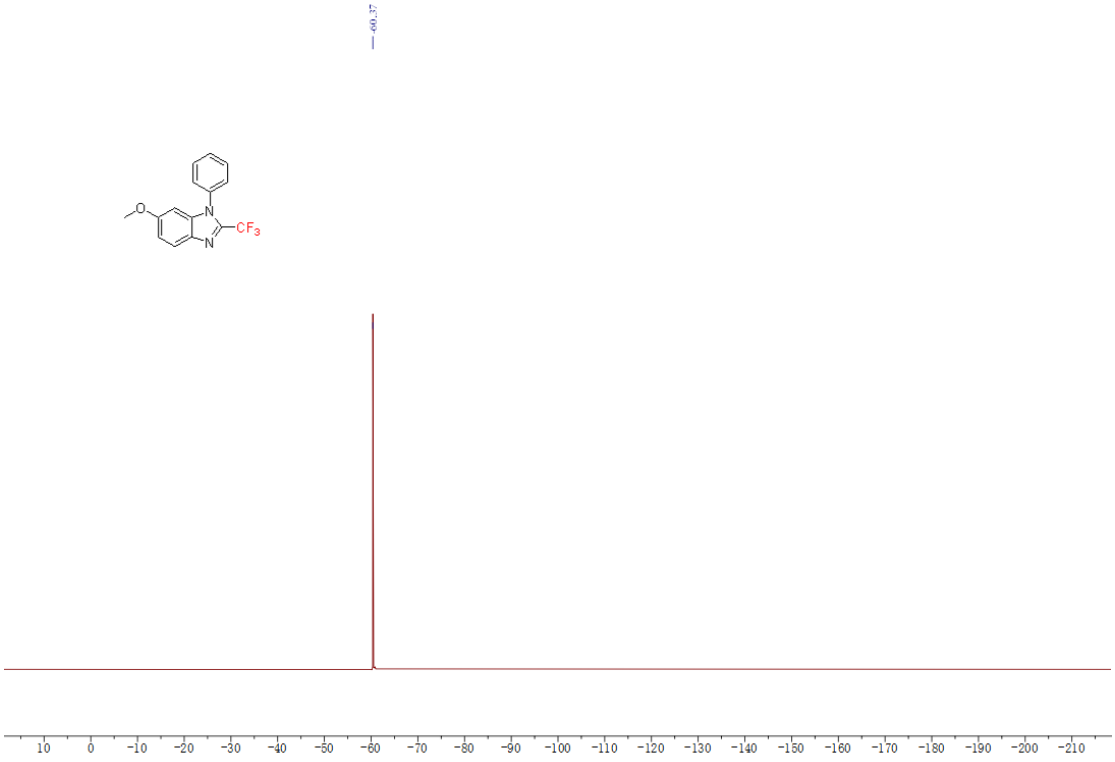
^{13}C NMR spectra of **5b** in $CDCl_3$



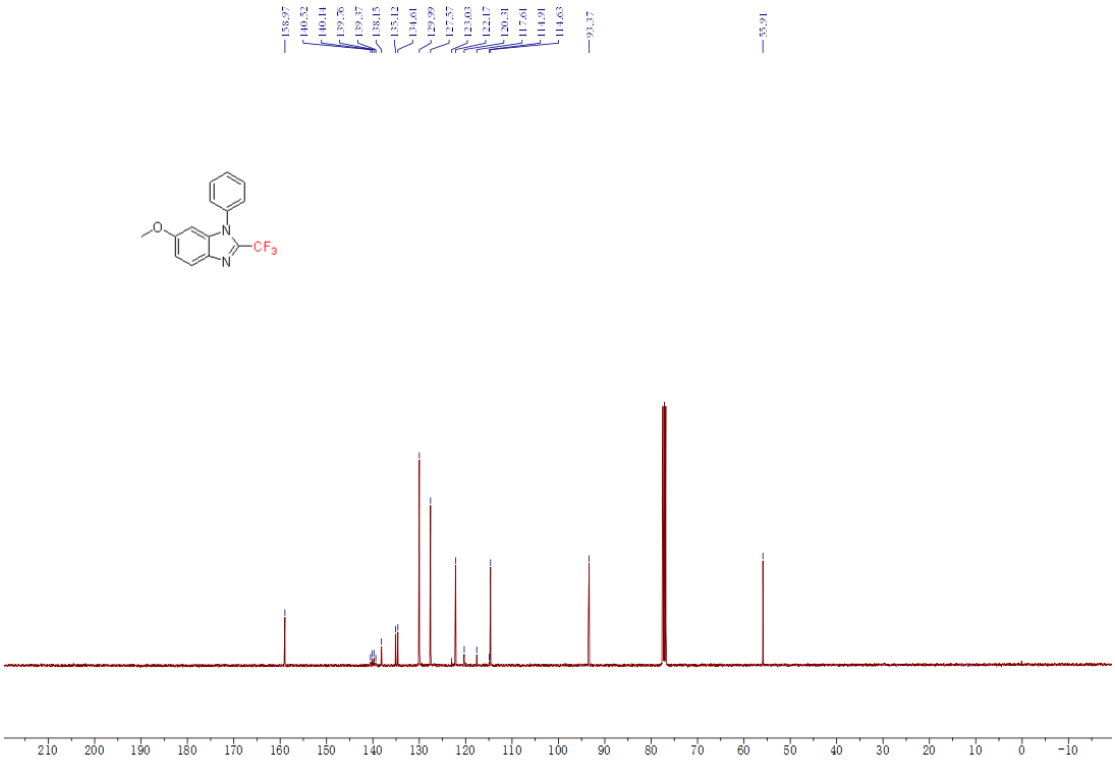
^{1}H NMR spectra of **5c** in $CDCl_3$



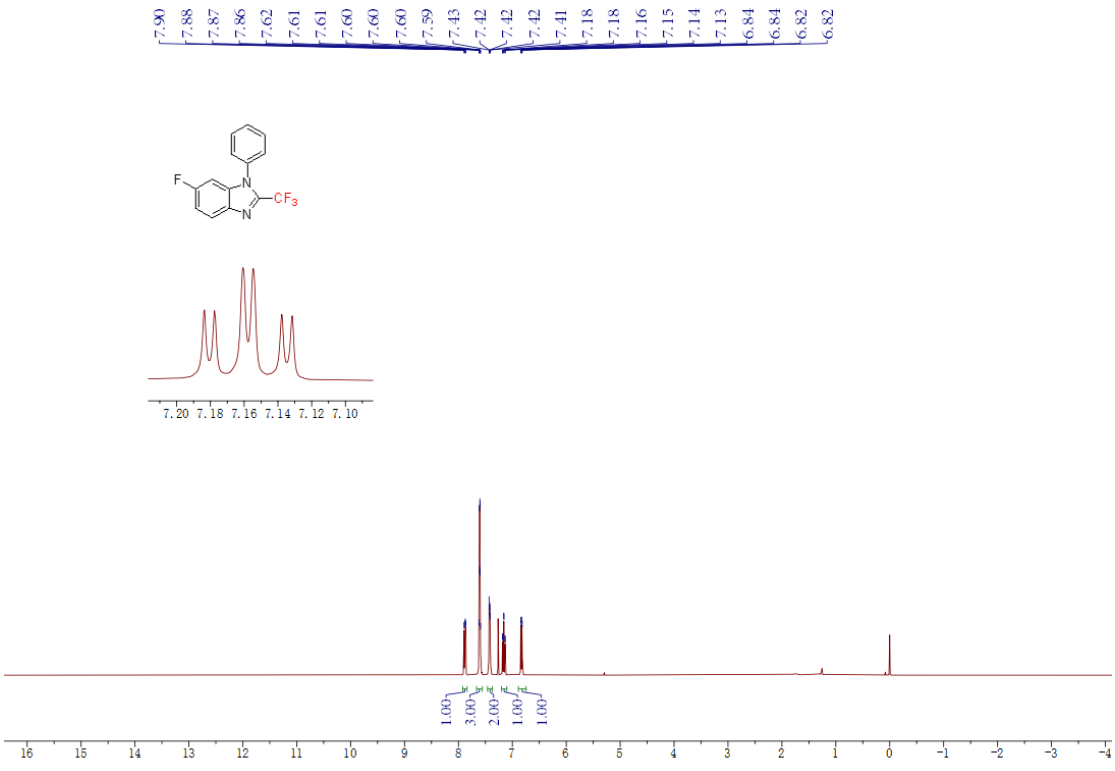
^{19}F NMR spectra of **5c** in $CDCl_3$



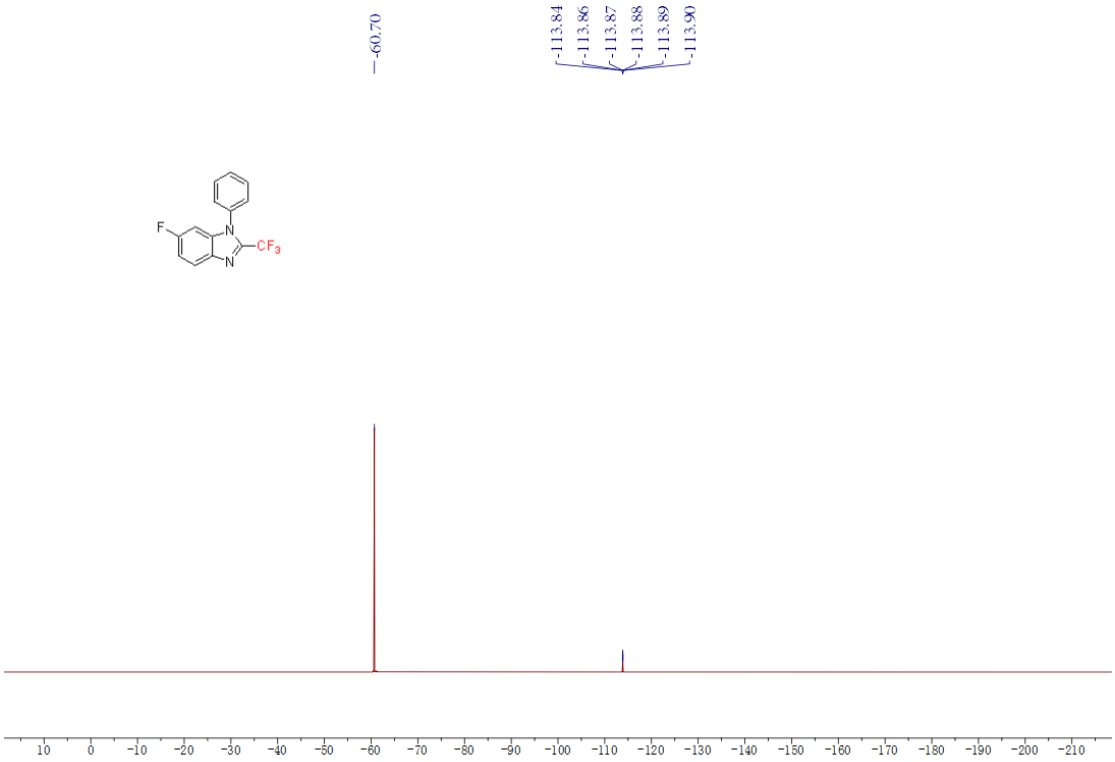
^{13}C NMR spectra of **5c** in $CDCl_3$



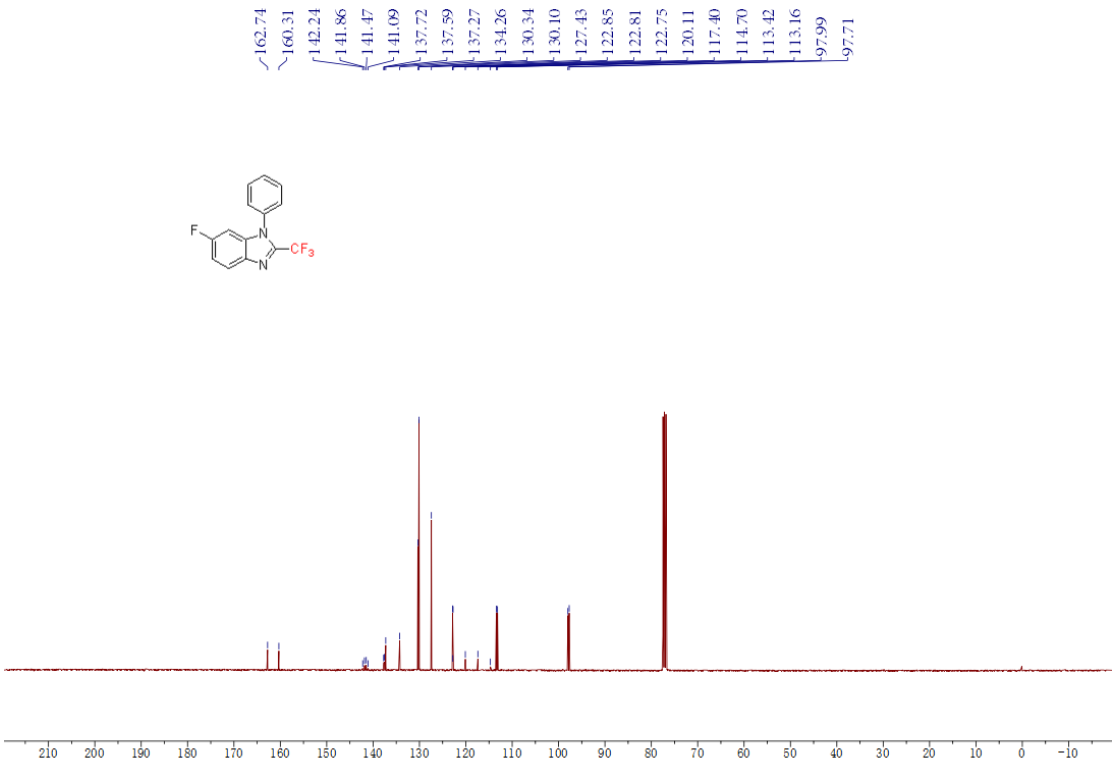
^{1}H NMR spectra of **5e** in $CDCl_3$



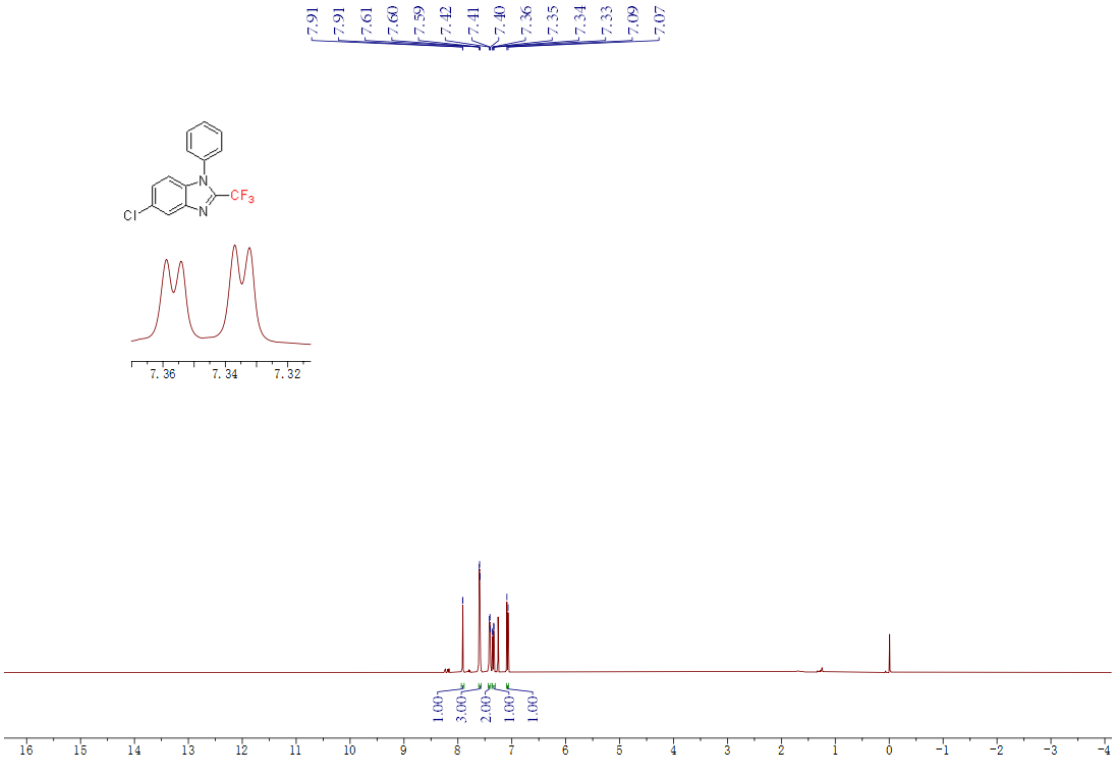
^{19}F NMR spectra of **5e** in $CDCl_3$



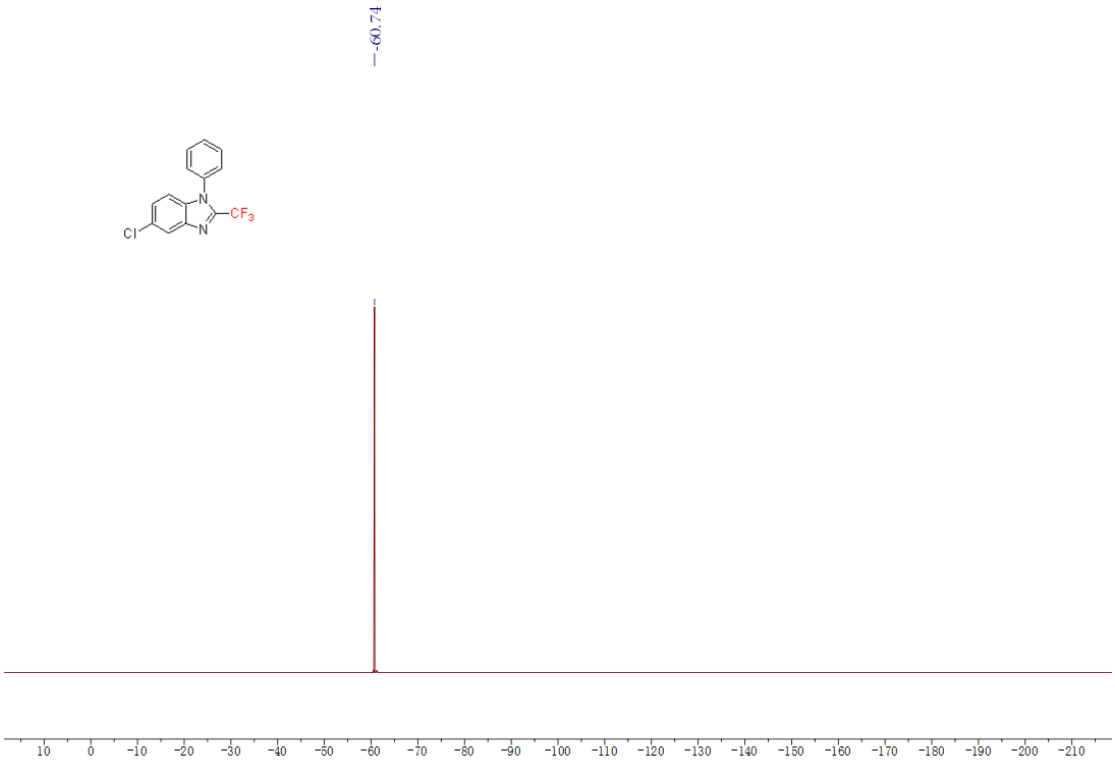
^{13}C NMR spectra of **5e** in $CDCl_3$



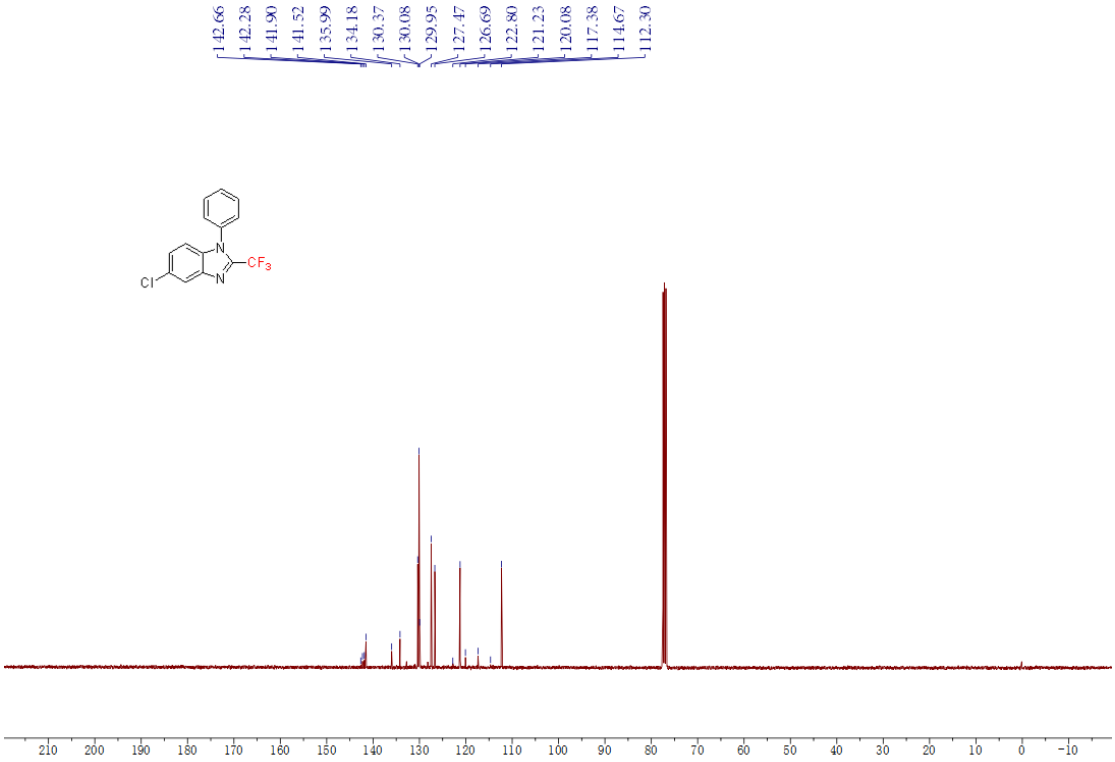
^{1}H NMR spectra of **5f** in $CDCl_3$



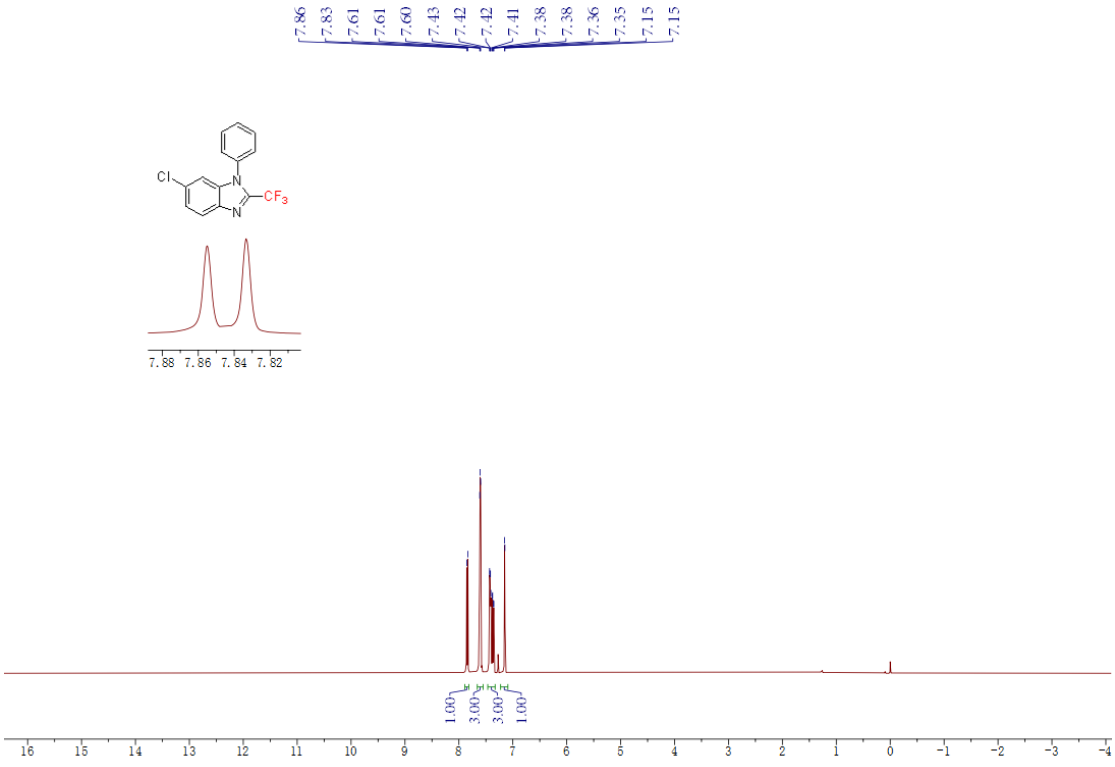
^{19}F NMR spectra of **5f** in $CDCl_3$



^{13}C NMR spectra of **5f** in $CDCl_3$

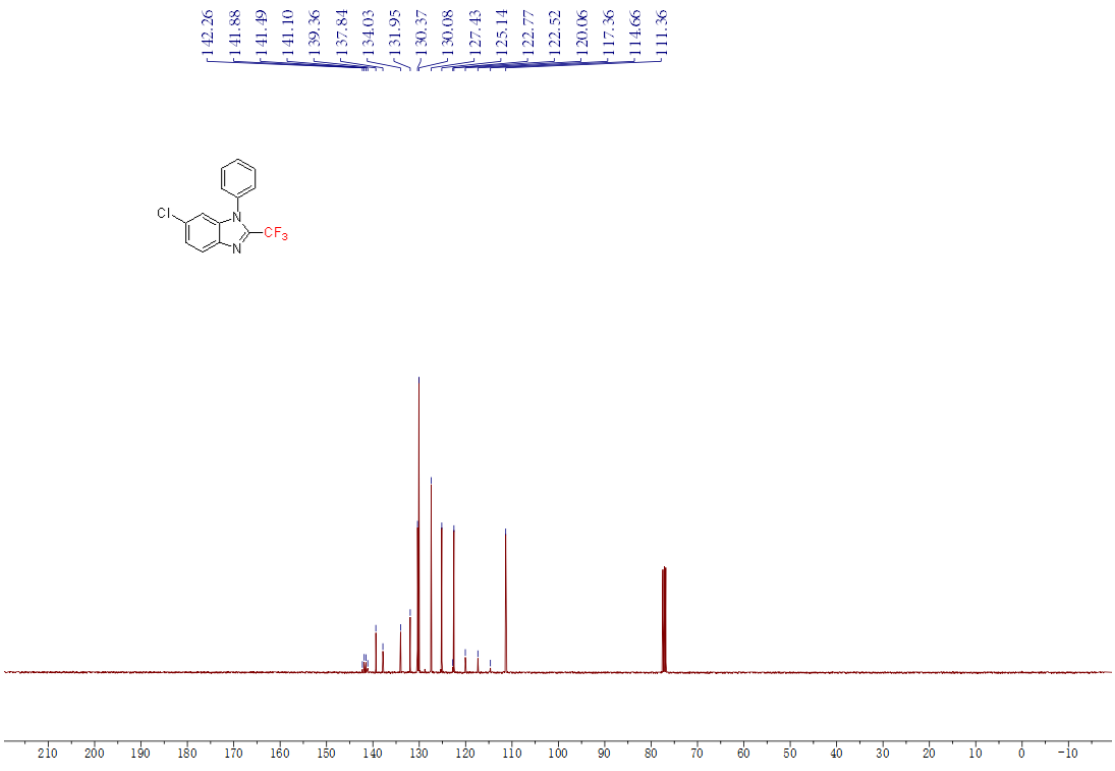


^{1}H NMR spectra of **5g** in $CDCl_3$

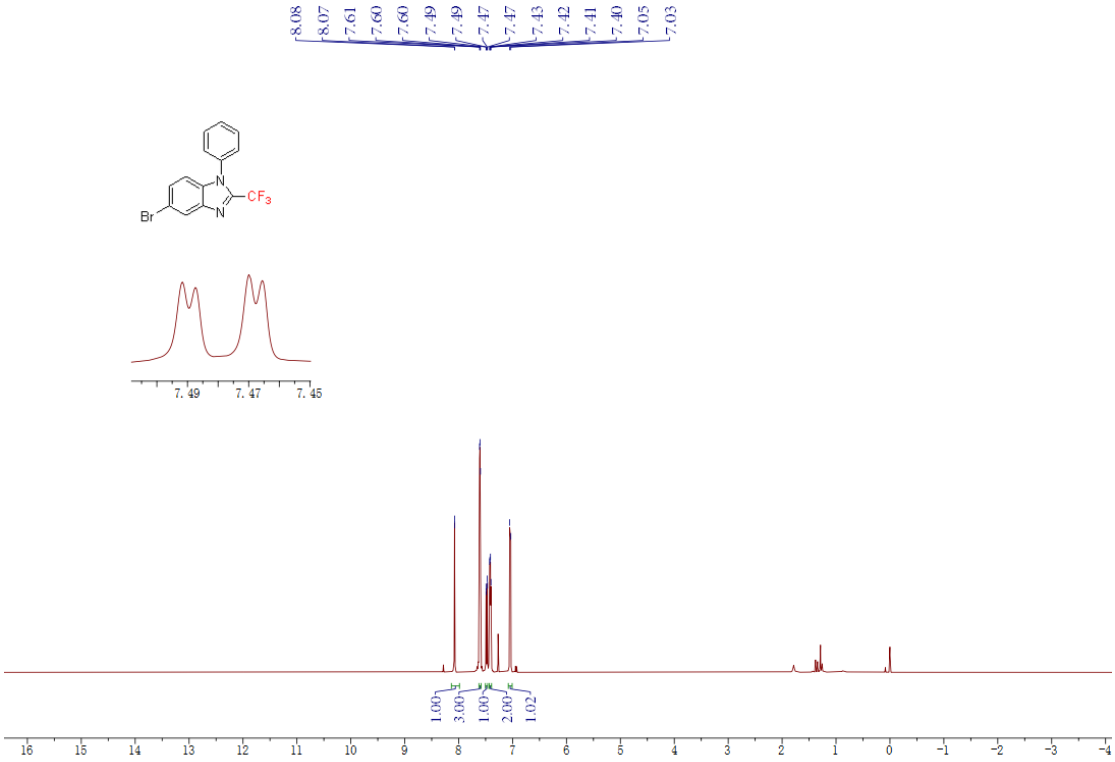


^{19}F NMR spectra of **5g** in $CDCl_3$

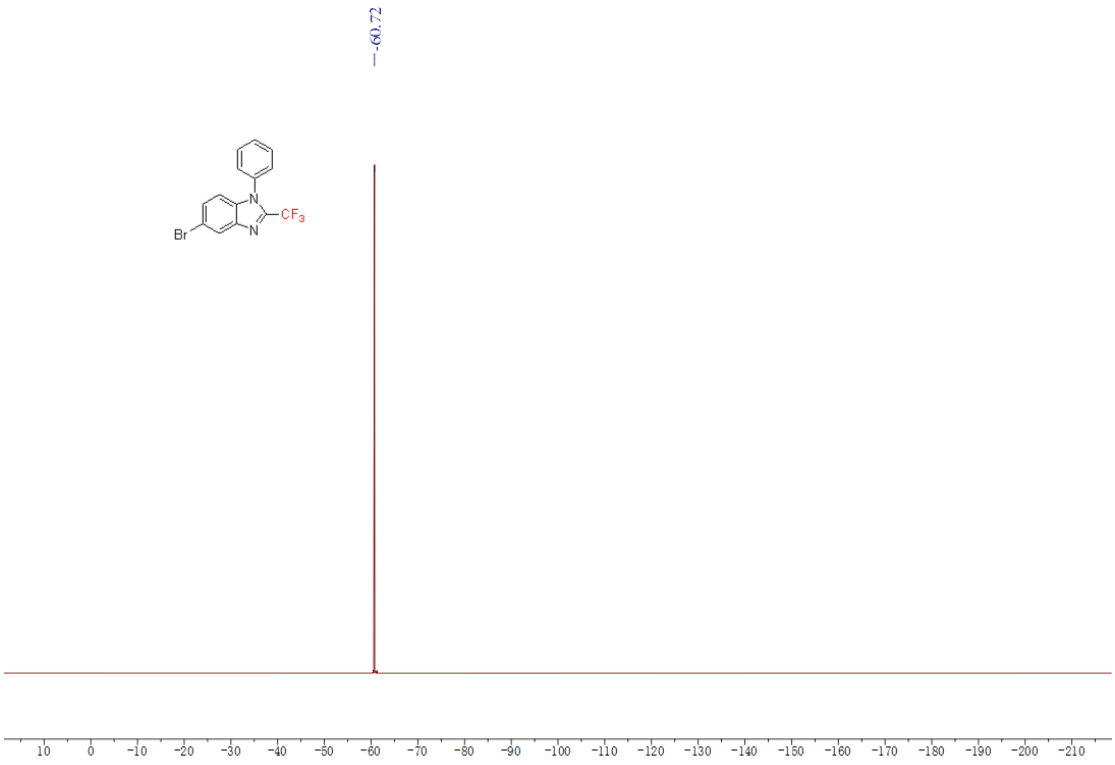
^{13}C NMR spectra of **5g** in $CDCl_3$



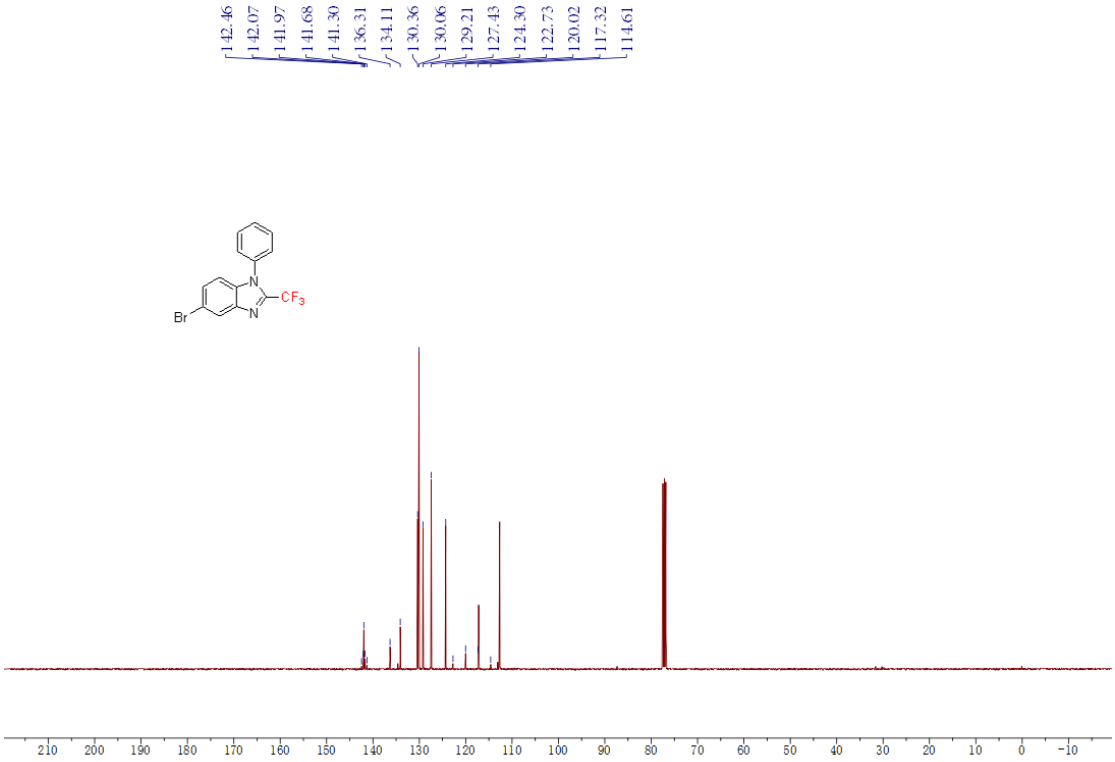
^{1}H NMR spectra of **5h** in $CDCl_3$



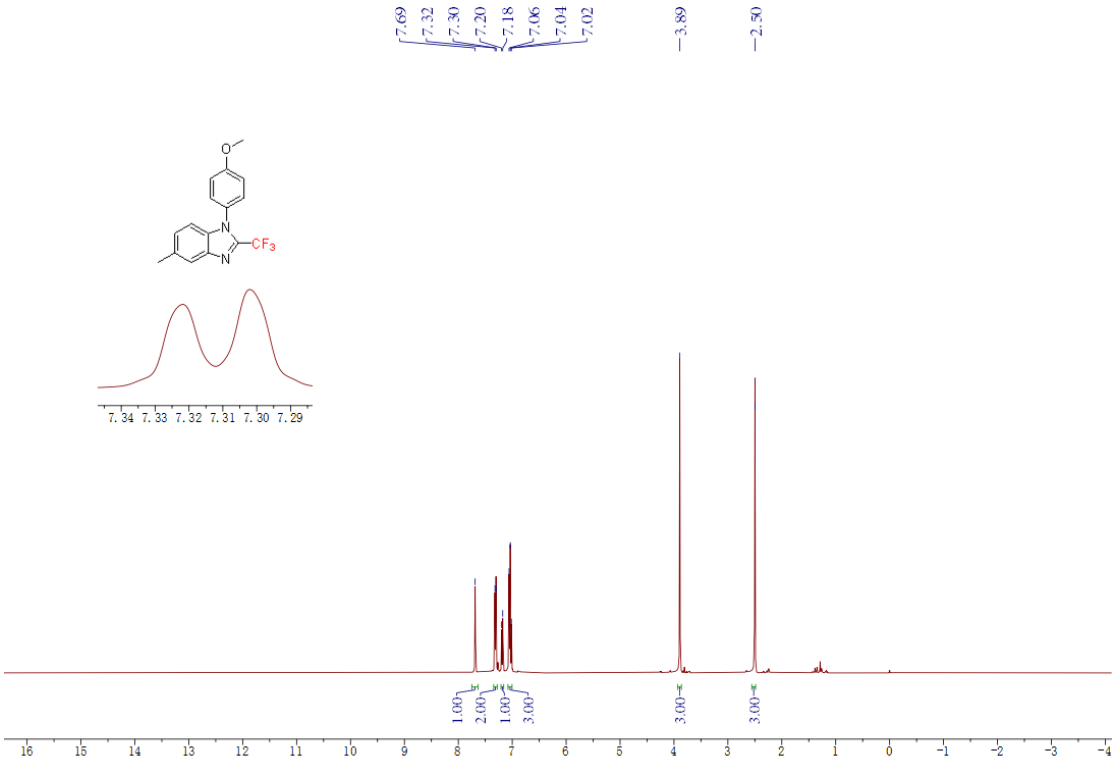
^{19}F NMR spectra of **5h** in $CDCl_3$



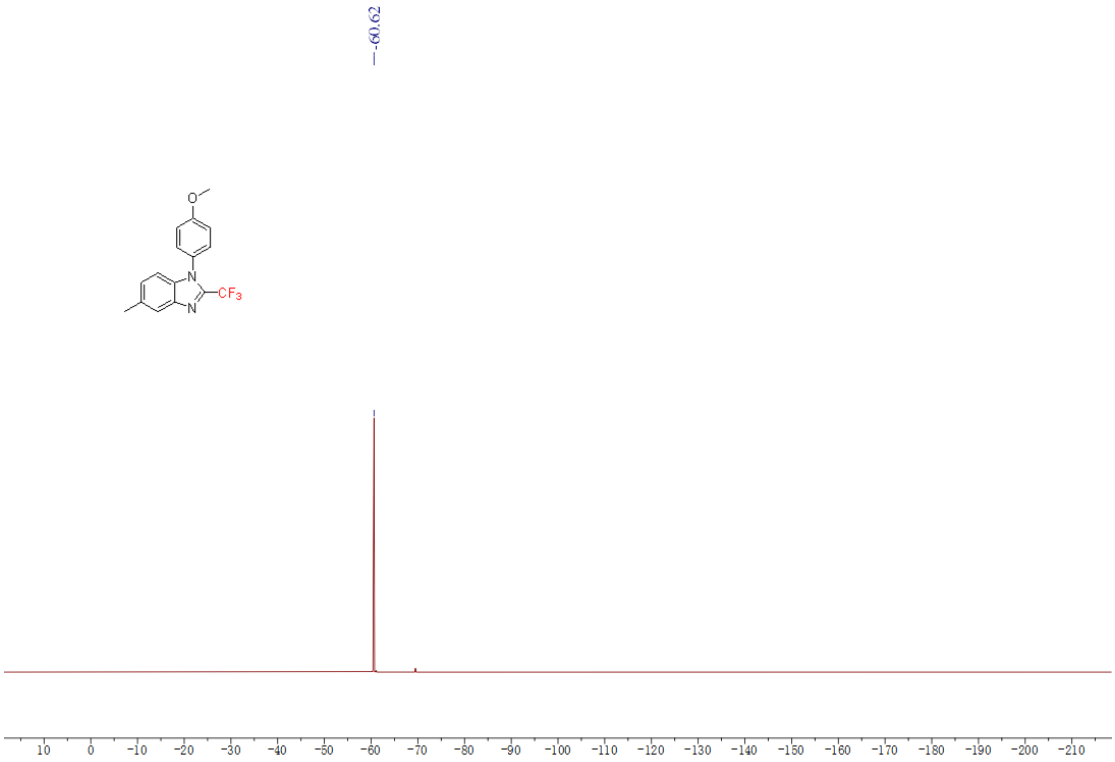
^{13}C NMR spectra of **5h** in $CDCl_3$



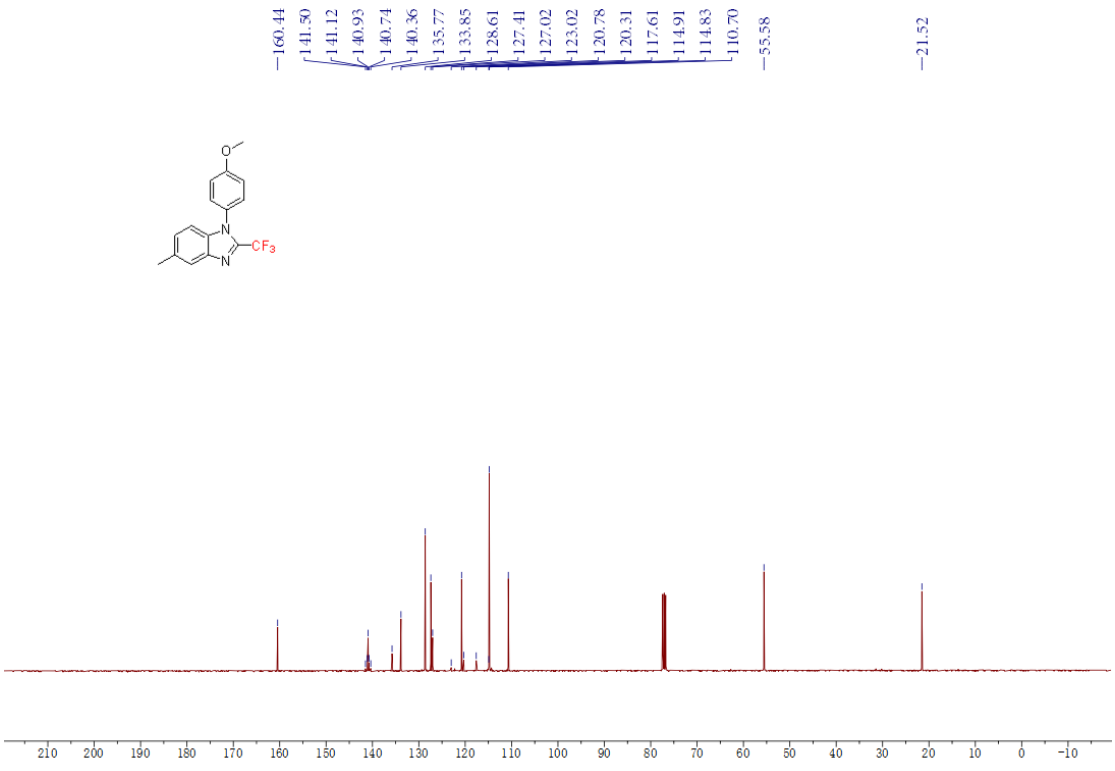
^{1}H NMR spectra of **5i** in $CDCl_3$



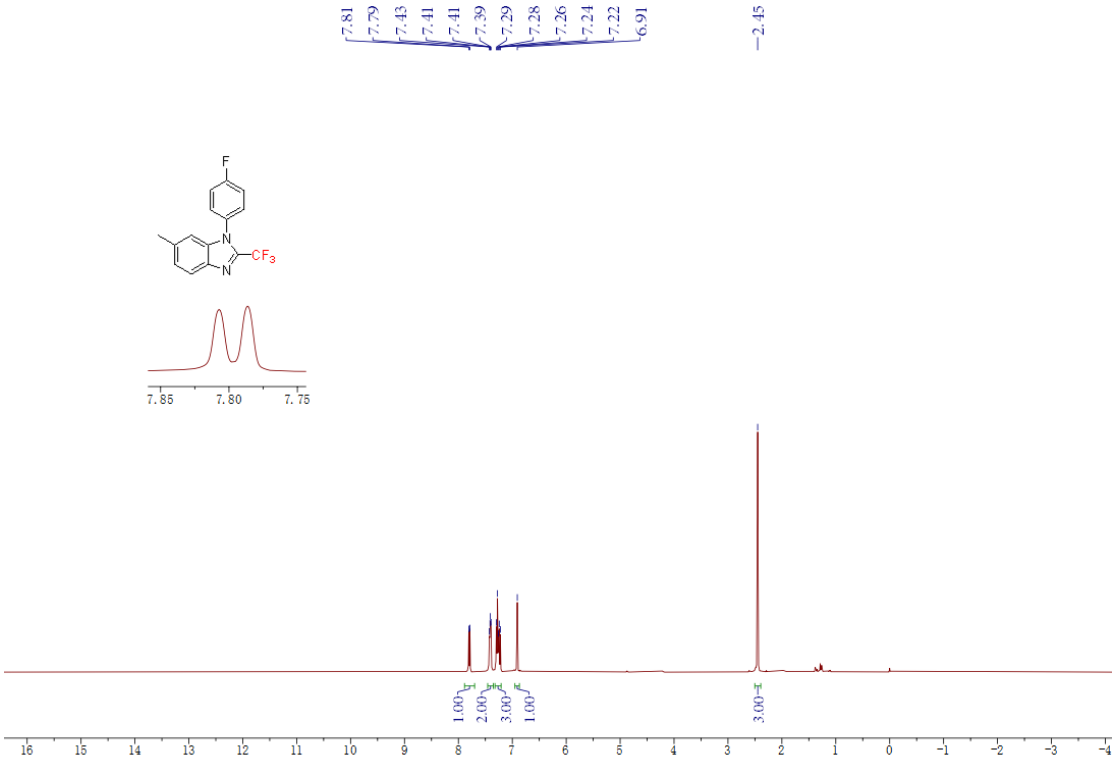
^{19}F NMR spectra of **5i** in $CDCl_3$



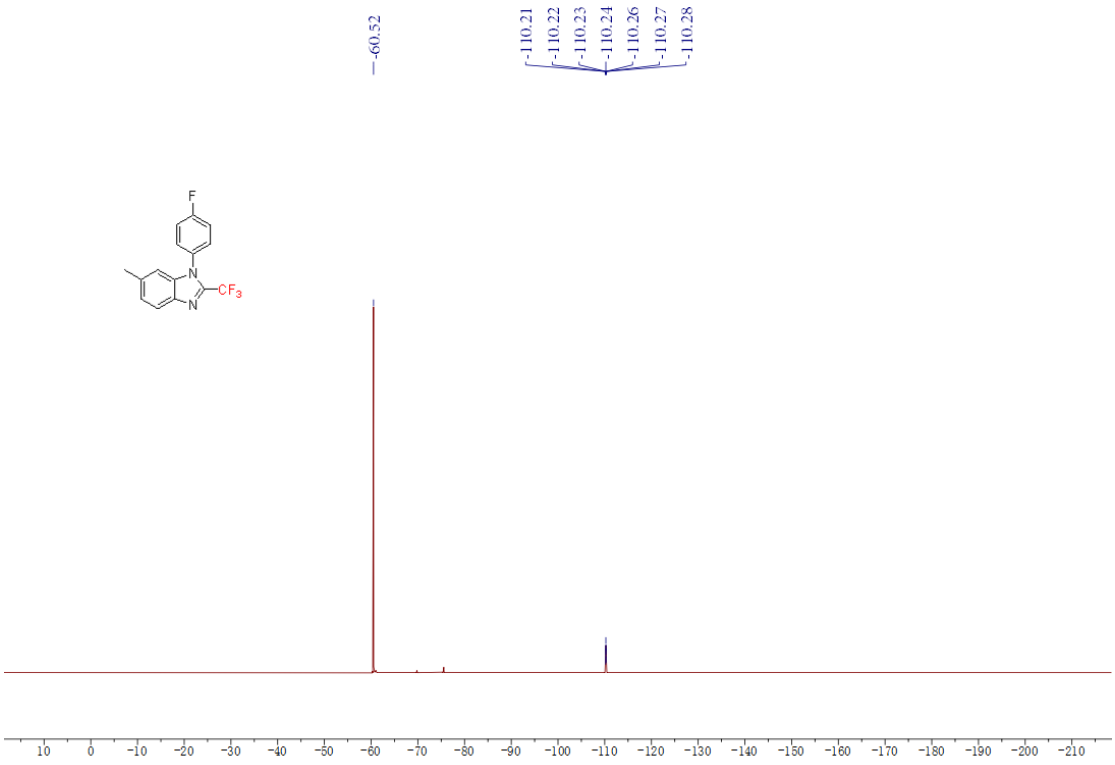
^{13}C NMR spectra of **5i** in $CDCl_3$



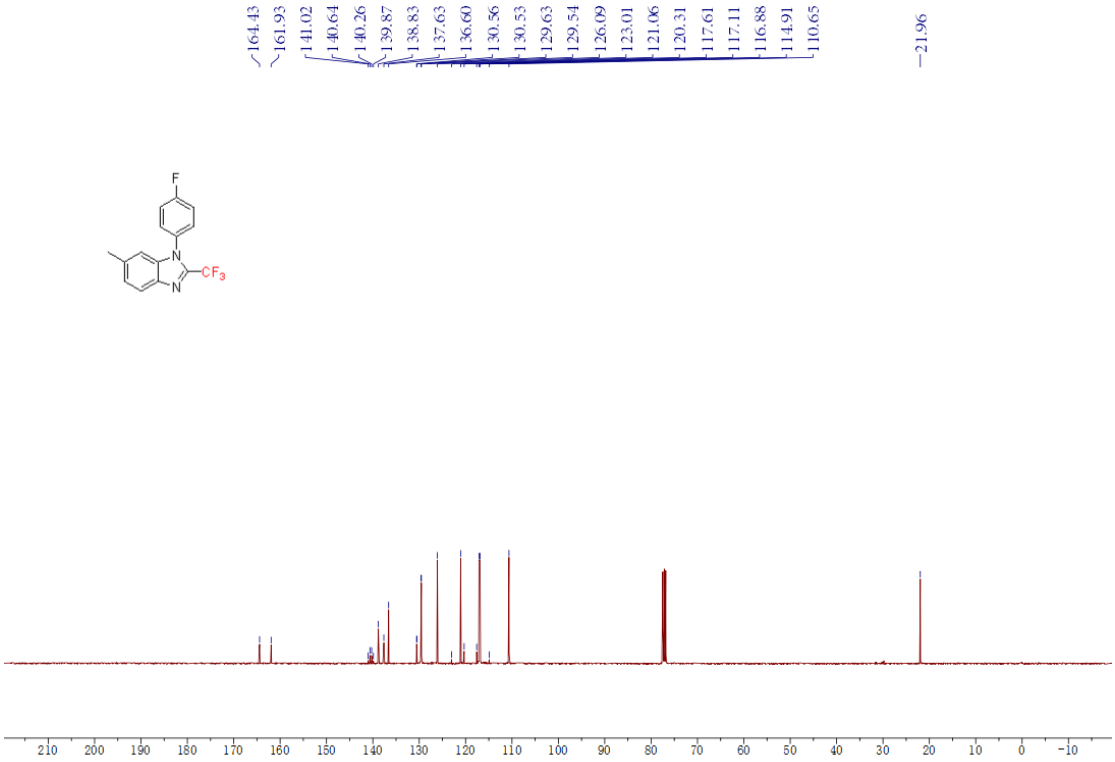
^{1}H NMR spectra of **5j** in $CDCl_3$



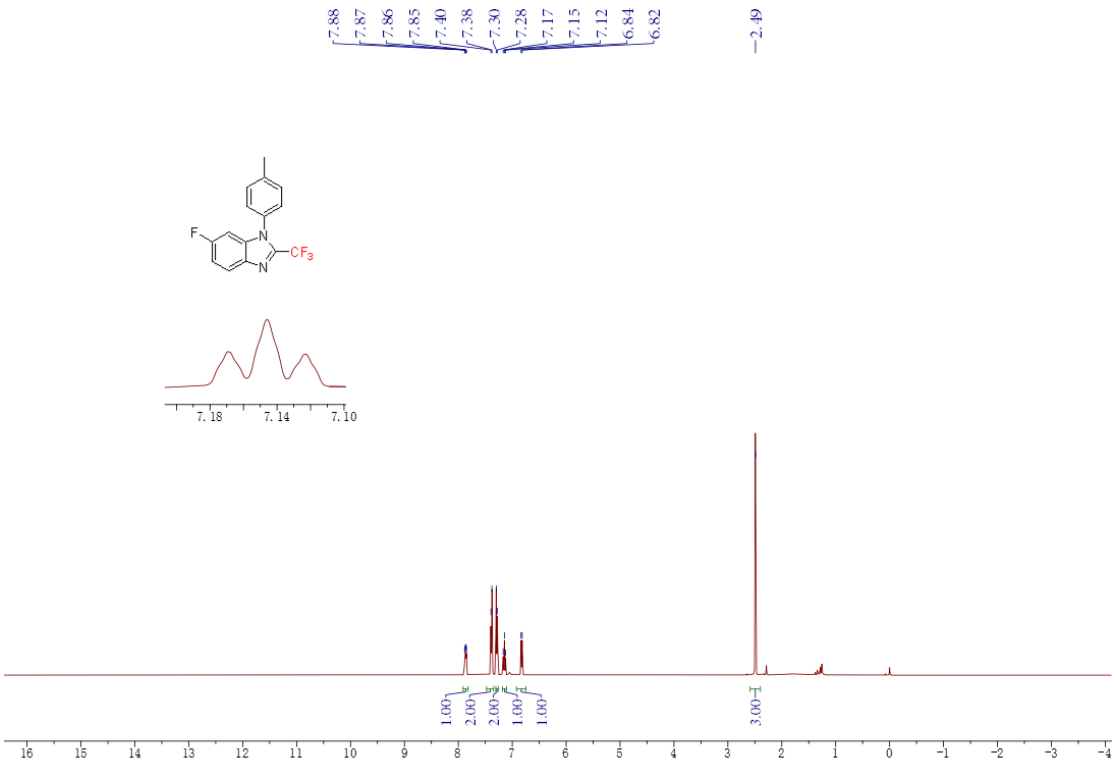
^{19}F NMR spectra of **5j** in $CDCl_3$



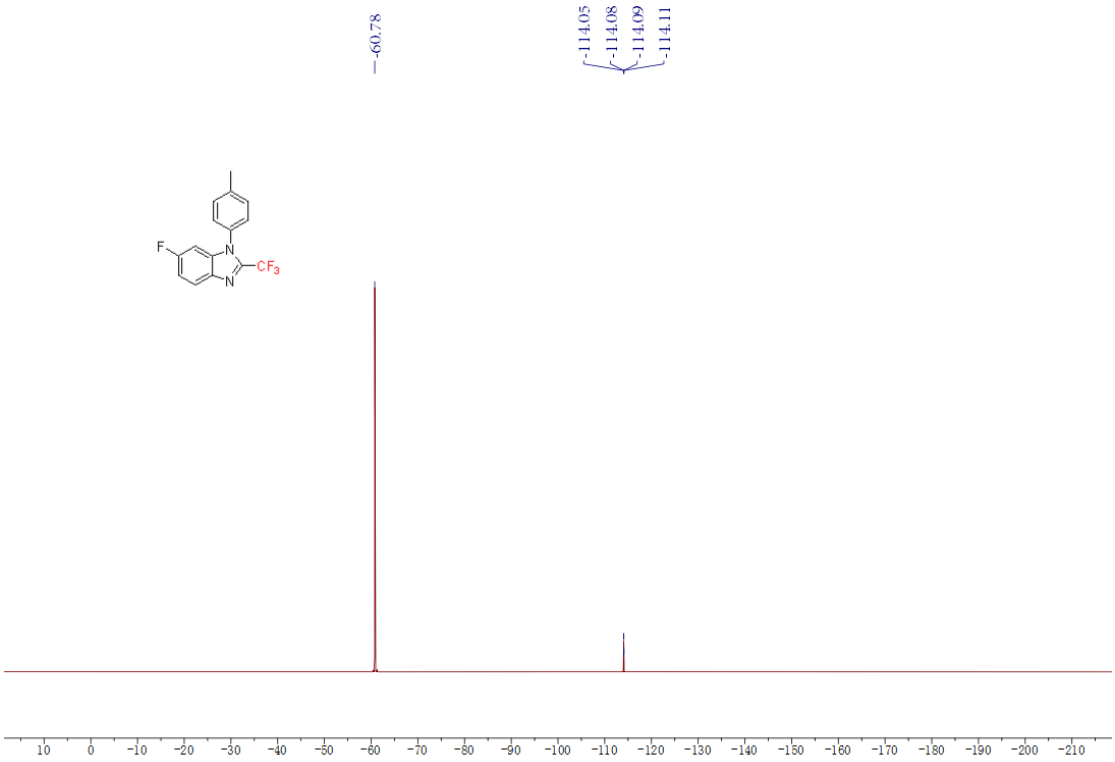
^{13}C NMR spectra of **5j** in $CDCl_3$



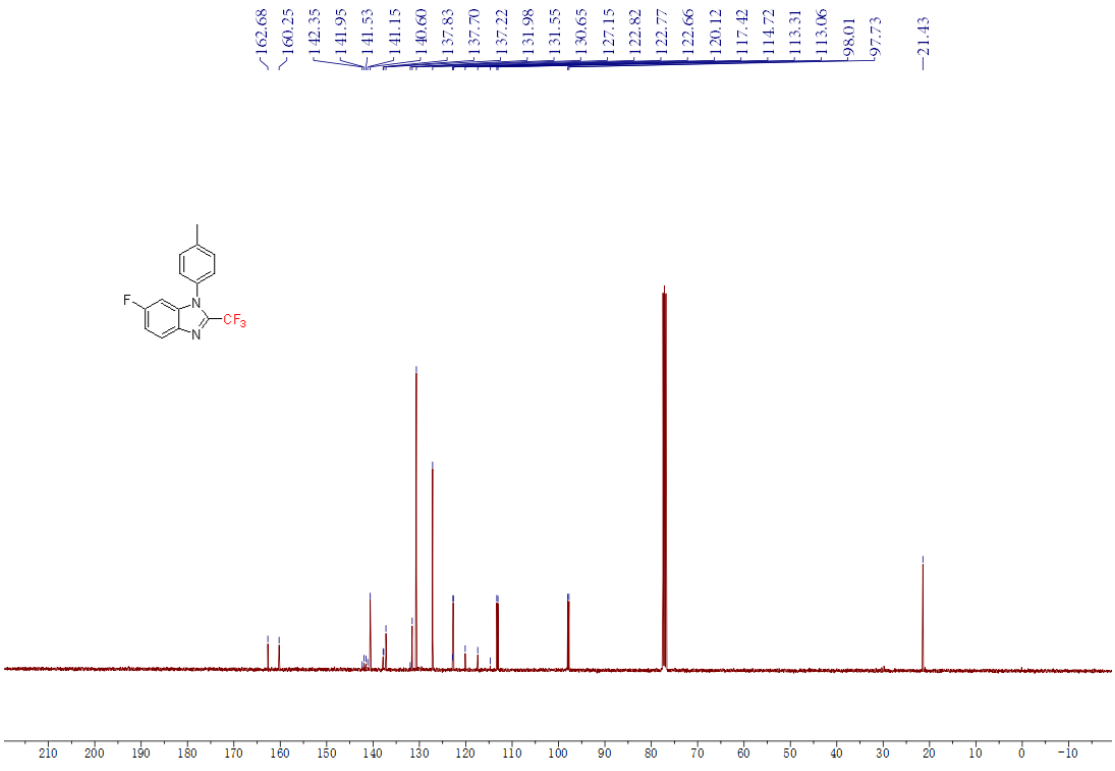
^{1}H NMR spectra of **5k** in $CDCl_3$



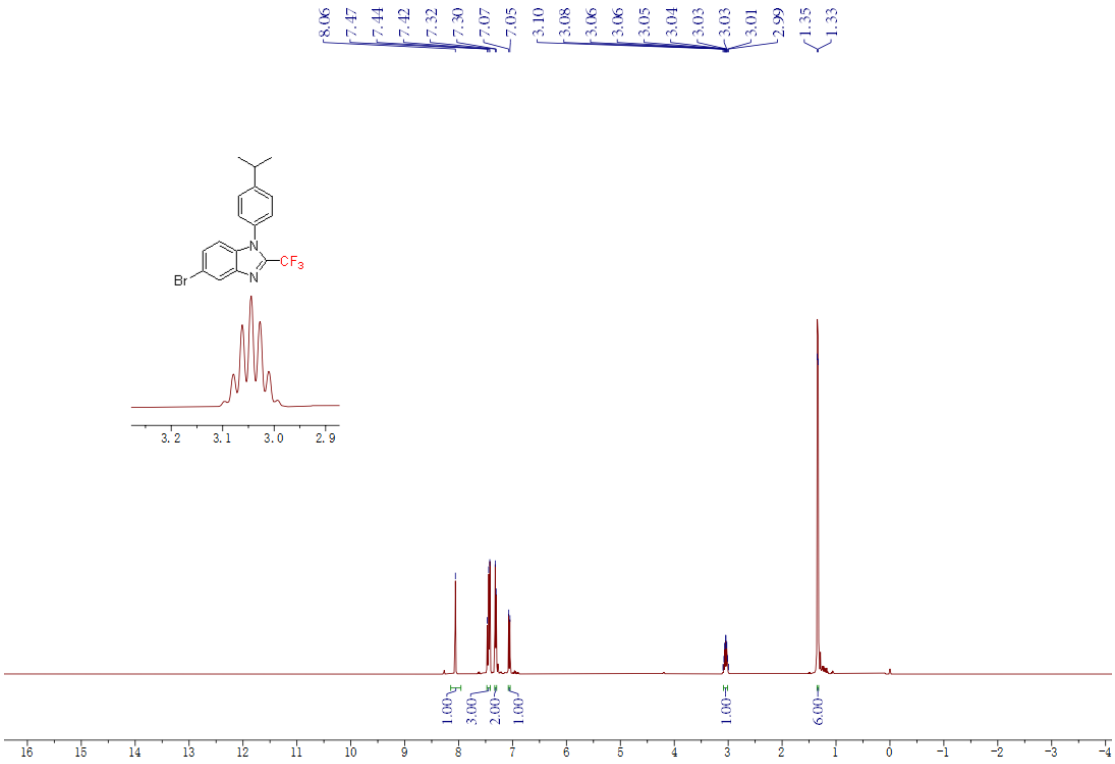
^{19}F NMR spectra of **5k** in $CDCl_3$



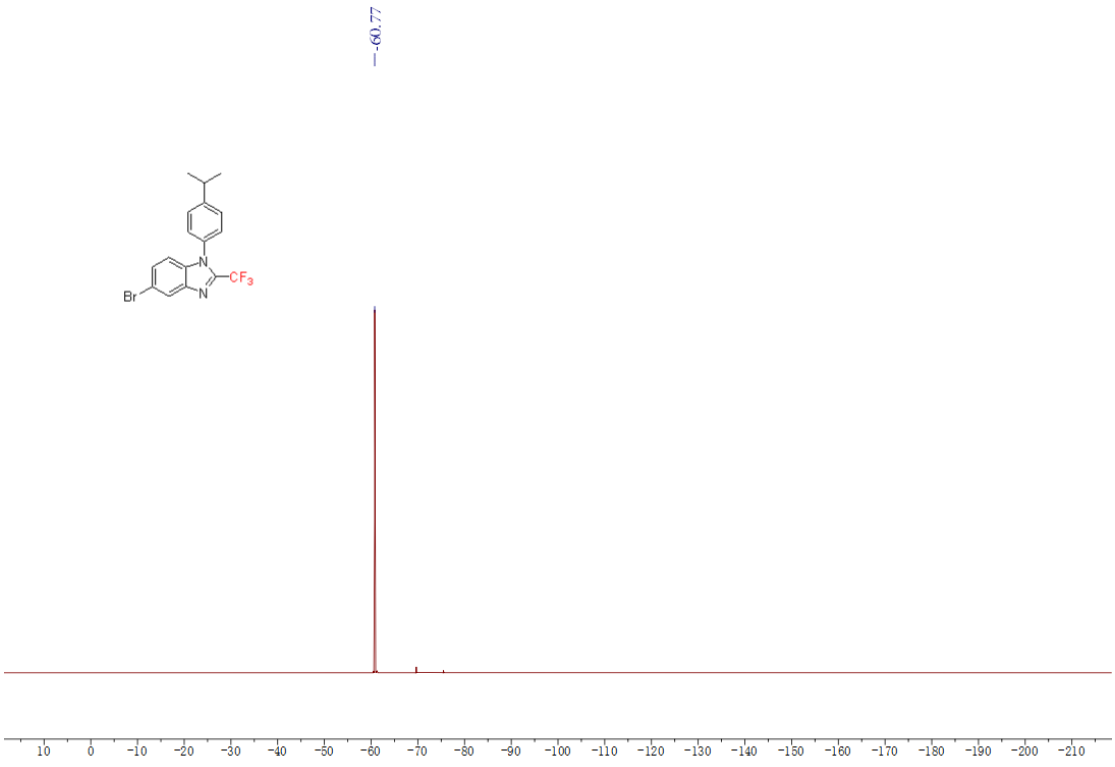
^{13}C NMR spectra of **5k** in $CDCl_3$



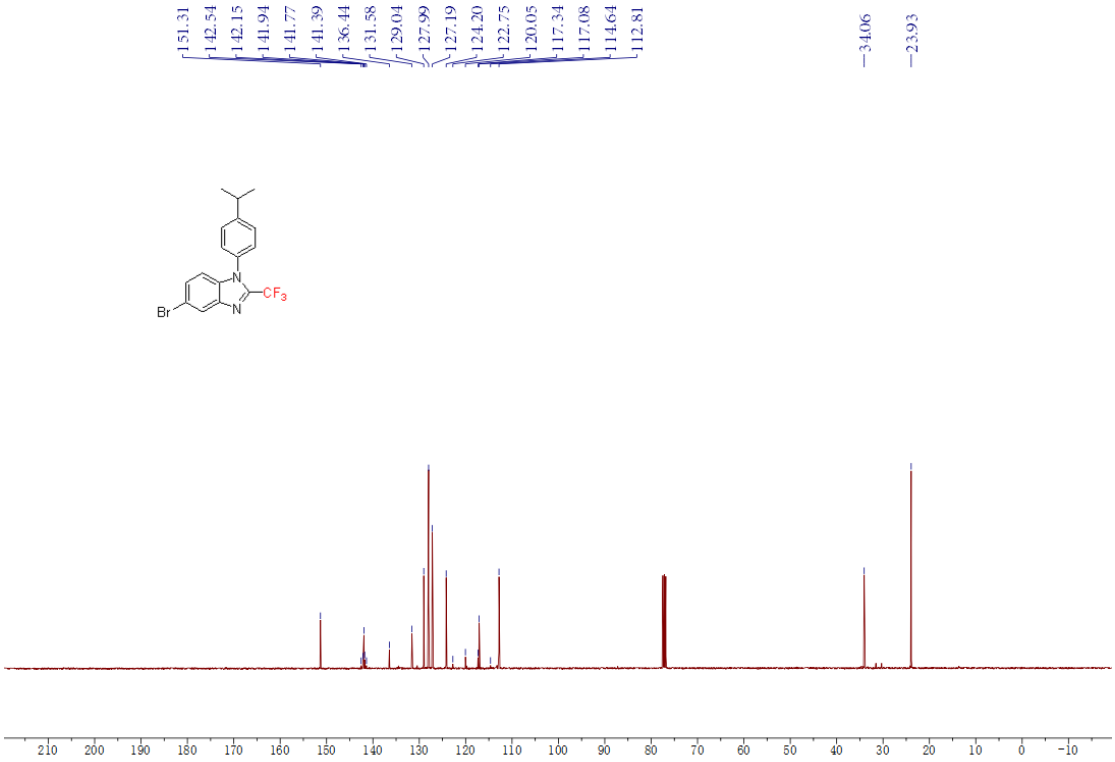
^{1}H NMR spectra of **5l** in $CDCl_3$



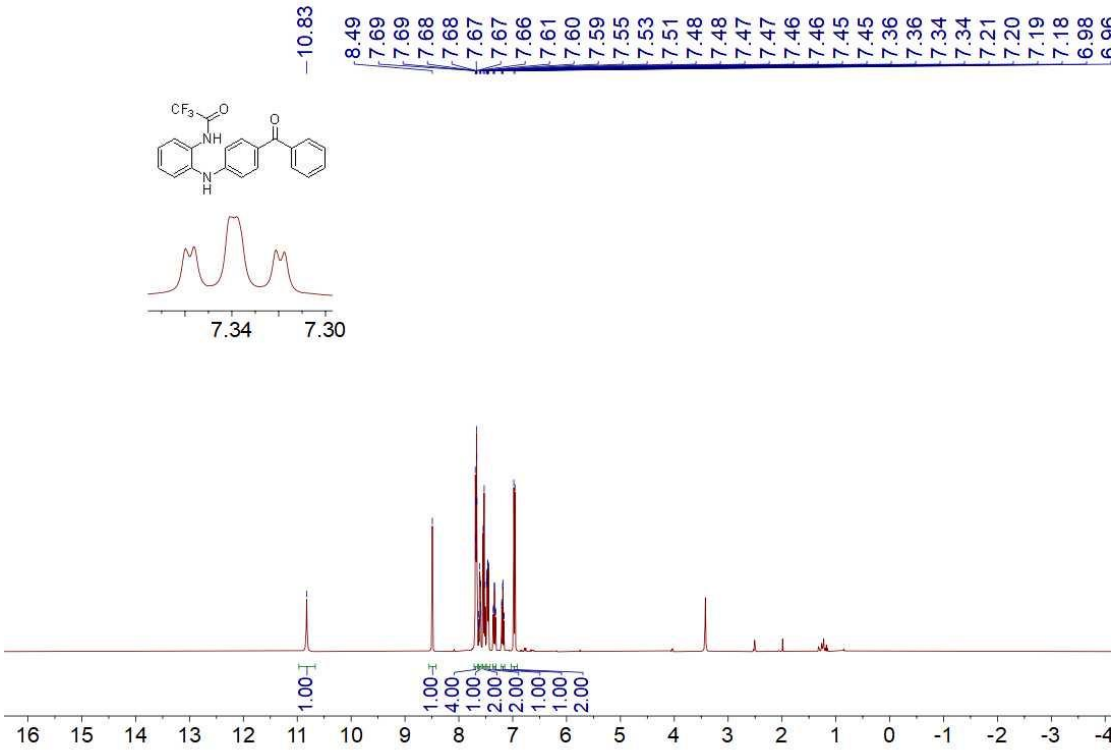
^{19}F NMR spectra of **5l** in $CDCl_3$



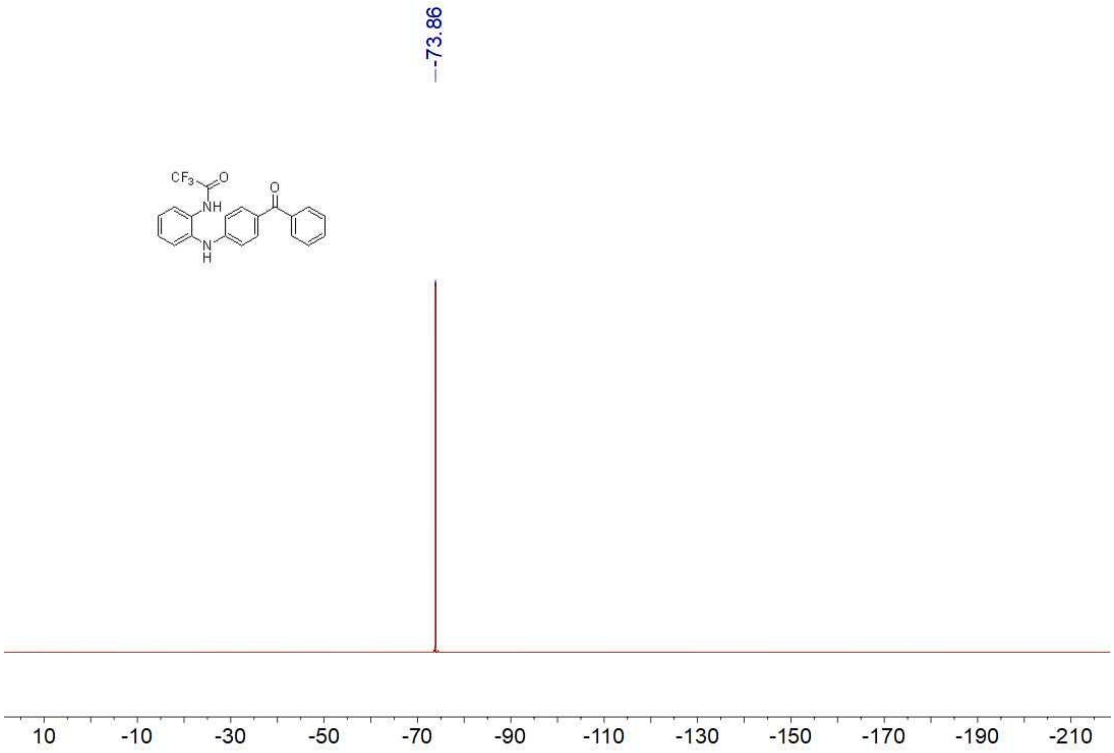
^{13}C NMR spectra of **5l** in $CDCl_3$



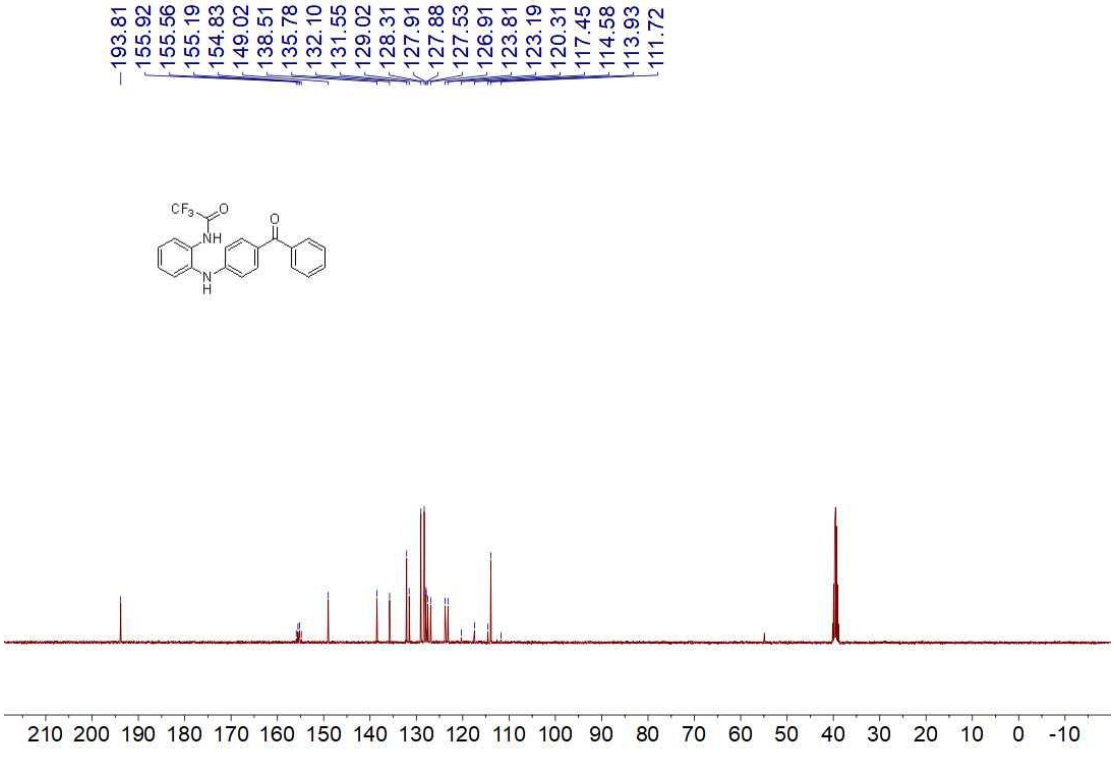
^{1}H NMR spectra of **6** in DMSO-d_6



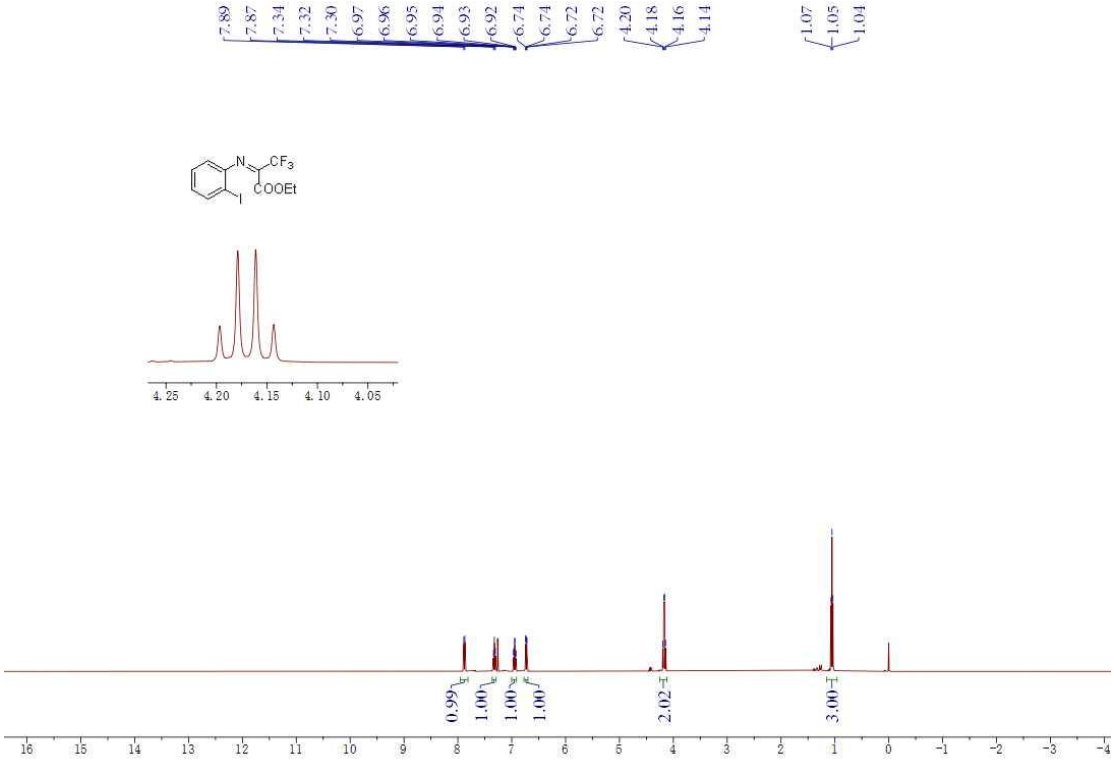
^{19}F NMR spectra of **6** in DMSO-d_6



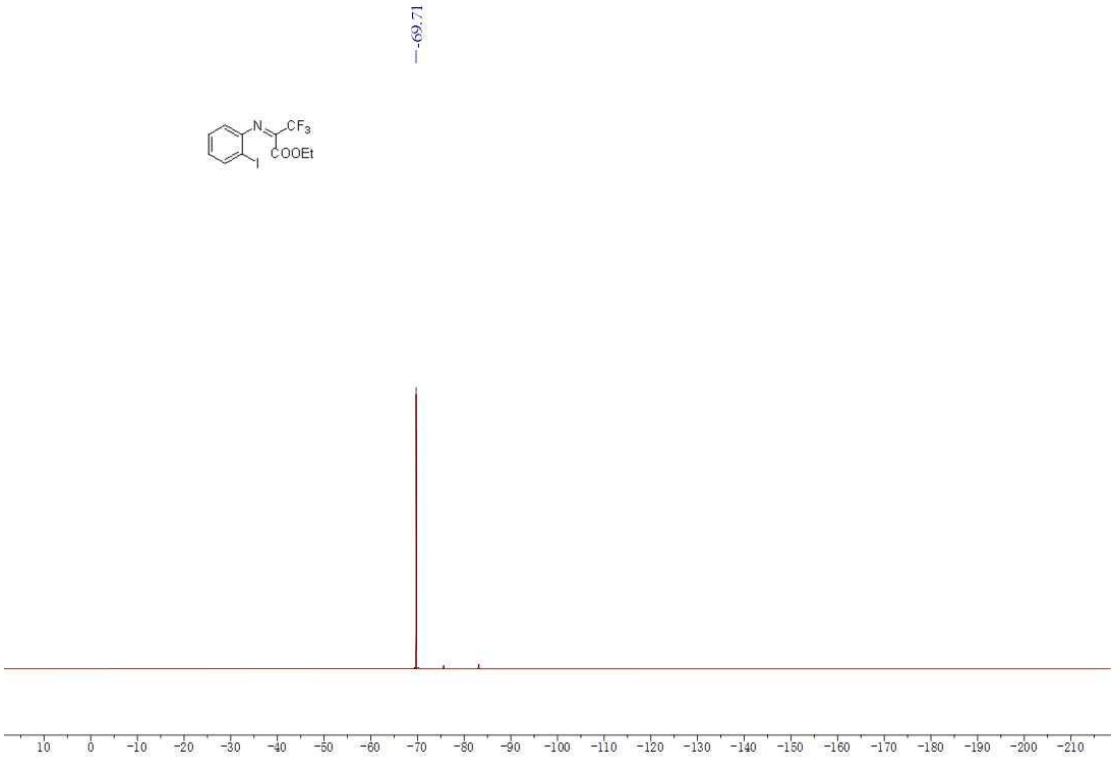
^{13}C NMR spectra of **6** in DMSO-d_6



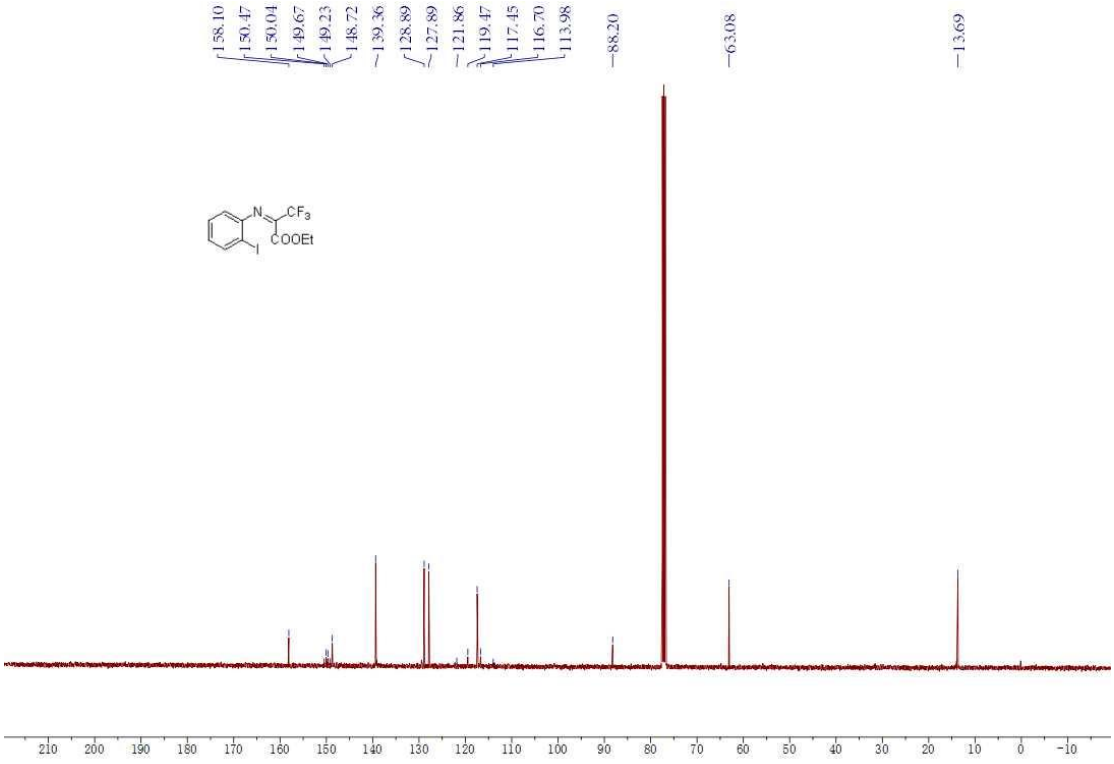
^{1}H NMR spectra of **9** in $CDCl_3$



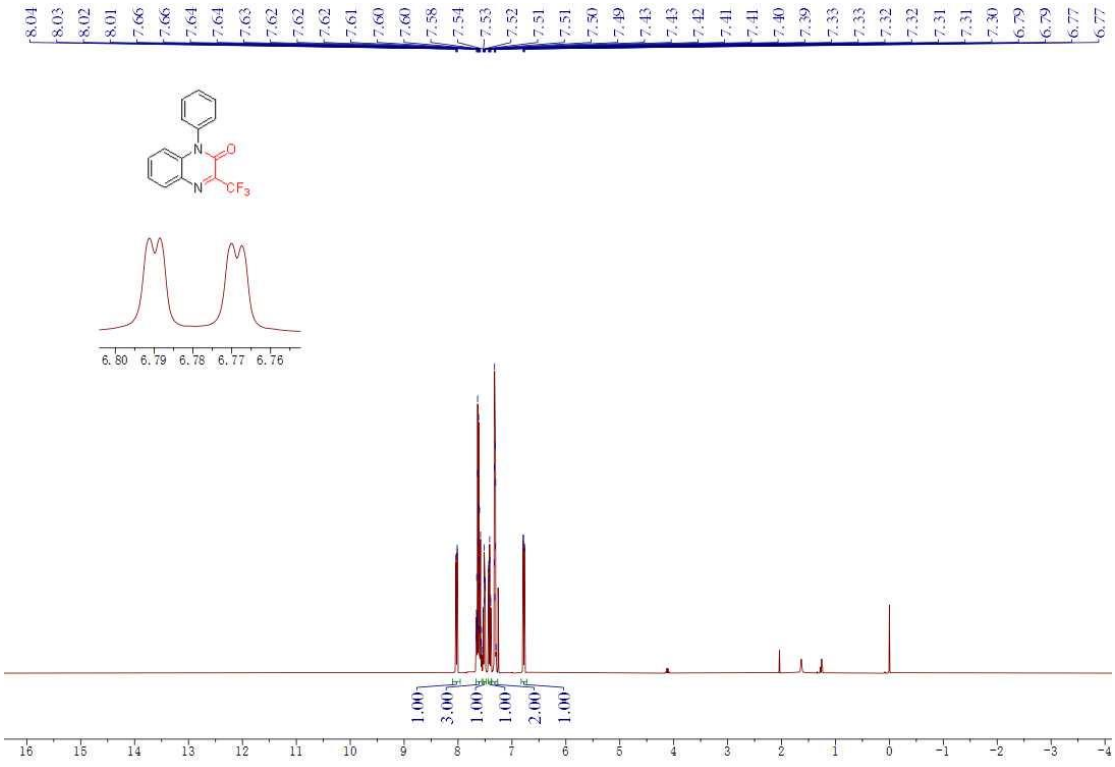
^{19}F NMR spectra of **9** in $CDCl_3$



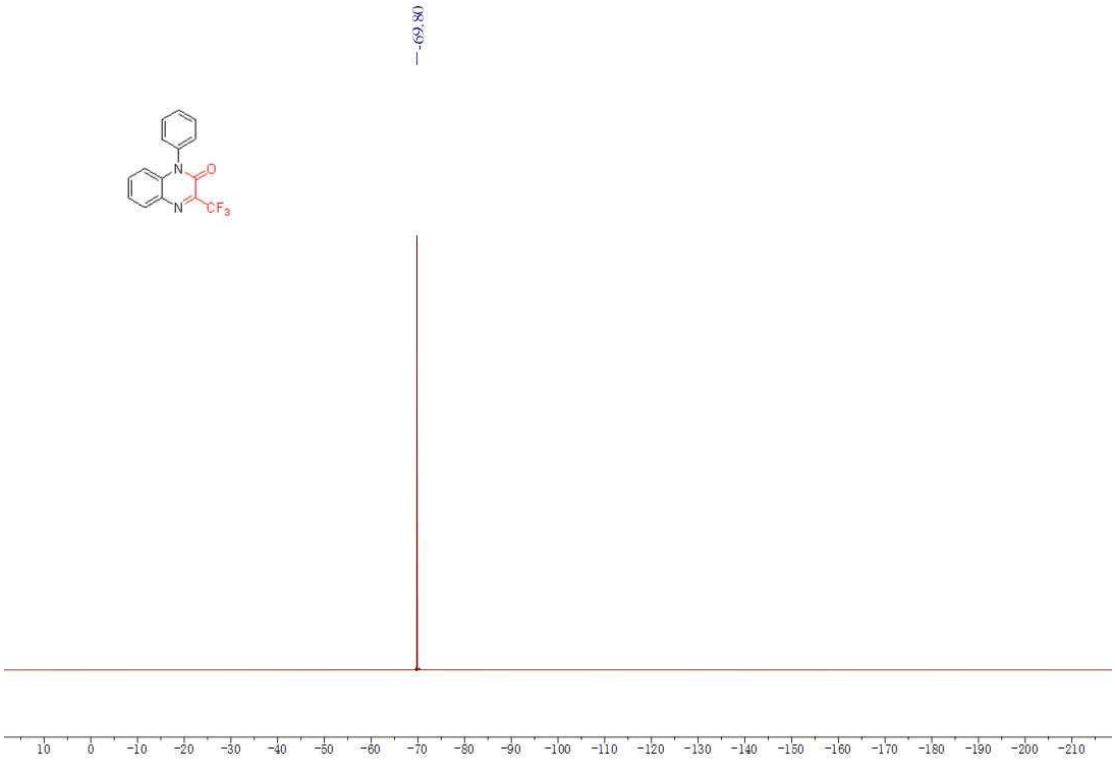
^{13}C NMR spectra of **9** in $CDCl_3$



^{1}H NMR spectra of **4a′** in $CDCl_3$



^{19}F NMR spectra of **4a′** in $CDCl_3$



^{13}C NMR spectra of **4a′** in $CDCl_3$