Supporting Information *for*

An alternative metal-free amination approach to 3-trifluoromethyl anilines: the major products under Kröhnke pyridine synthesis conditions

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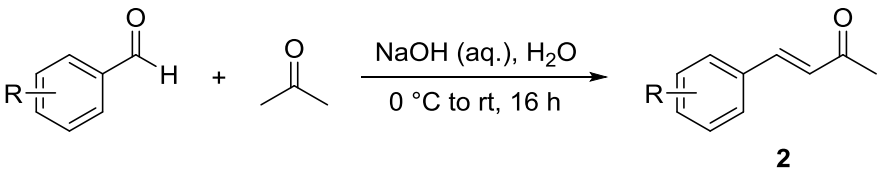
General information

^{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. HRMS data were recorded on a high-resolution Thermo Scientific Exactive Plus instrument. IR (ATR) were recorded on Nicolet IS50 (Thermo). Unless otherwise mentioned, all solvents and reagents were purchased from commercial sources. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60.

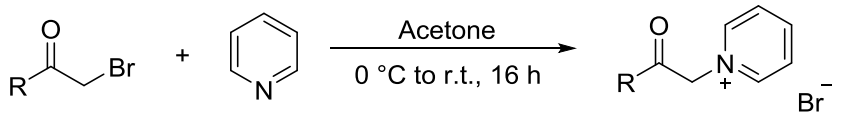
General procedure of the synthesis of *α,β*-unsaturated ketones 2:[1, 2]



2

A solution of aryl aldehyde (10.0 mmol, 1.0 equiv) in acetone (100 mL) was added dropwise 2 M NaOH (aq.) (10 mL, 2.0 equiv) at 0 ℃, and then the mixture was stirred at room temprature for 16 hours. The reaction solution was quenched with 20 mL NH_4Cl (aq.) and extracted with EtOAc (50 mL × 3). The organic phase was combined, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed by rotary evaporation. The resulting *α,β*-unsaturated ketones were purified by column chromatography on silica gel with petroleum ether/ethyl acetate.

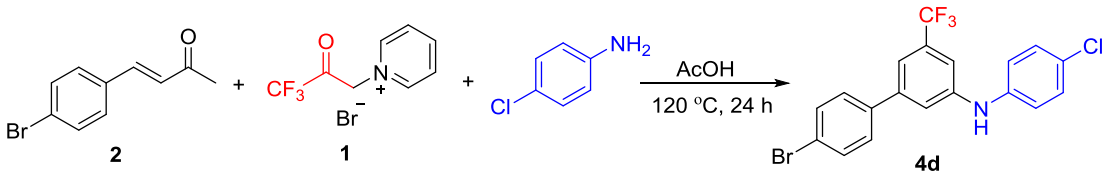
General procedure of the synthesis of pyridinium bromides (1 and 1'):[3, 4]



R = CF_3: **1**
R = CH_3: **1'**

A solution of 3-bromo-1,1,1-trifluoropropan-2-one (1.9 g, 10.0 mmol, 1.0 equiv) or 1-bromopropan-2-one (1.4 g, 10.0 mmol, 1.0 equiv) in acetone (20 mL) was added dropwise pyridine (0.79 g, 10.0 mmol, 1.0 equiv) in acetone (10 mL) at 0 °C, and the mixture was stirred at room temprature for 16 hours. The resulting solid products were filtered, collected, washed with acetone (3 mL × 3) and dried under vacuum to obtain **1** and **1'**.

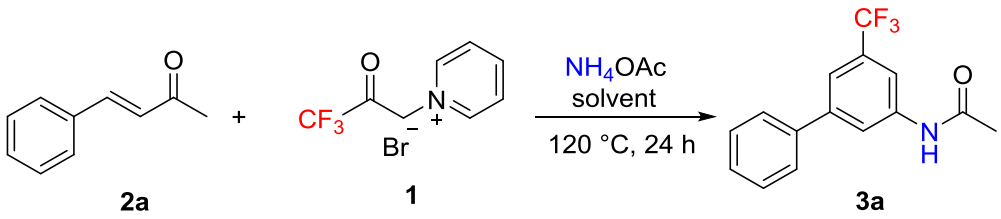
The effect of amount of amine on the reaction



Entry	Amount of amine (equiv)	Temp. (℃)	Yield(%)[b]
1	3	120	54
2	5	120	65
3	7	120	82
4	10	120	**92**

[a] Reaction conditions: **1** (0.30 mmol, 3.0 equiv), **2** (0.10 mmol, 1.0 equiv), AcOH (2.0 mL), under air atmosphere. [b] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard.

The effect of solvent on the reaction

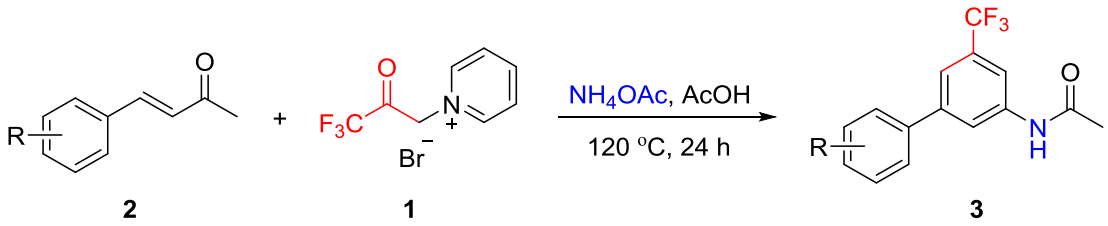


2a **1** **3a**

Entry	Solvent	Additive	Yield(%)[b]
1	HOAc	/	**77**
2	HCOOH	/	0
3	PhMe	/	0
4	DMF	/	0
5	DMSO	/	0
6	Dioxane	/	0
7	PhMe	HOAc[c]	21
8	DMF	HOAc[c]	0
9	DMSO	HOAc[c]	0
10	Dioxane	HOAc[c]	0

[a] Reaction conditions: **1** (0.30 mmol, 3.0 equiv), **2a** (0.10 mmol, 1.0 equiv), solvent (2.0 mL), under air atmosphere. [b] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard.[c] Total volume of acid and solvent was 0.5 mL (1:1).

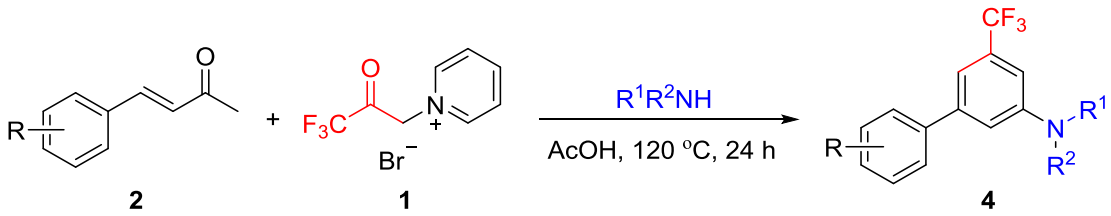
General procedure of the synthesis of 3-(trifluoromethyl)phenyl acetamides 3a–3t:



2 **1** **3**

To an oven-dried 5 mL pressure tube was added *α*,*β*-unsaturated ketones **2** (0.30 mmol, 1.0 equiv), 1-(3,3,3-trifluoro-2-oxopropyl)pyridinium bromides **1** (242.1 mg, 0.90 mmol, 3.0 equiv), NH_4OAc (231.0 mg, 3.0 mmol, 10.0 equiv) and AcOH (2 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 120 °C for 24 h. After the completion of the reaction, the solution was diluted with ethyl acetate (20 mL) and neutralized by cold saturated $NaHCO_3$ (20 mL) to pH > 7. The mixture solution was extracted with EtOAc (20 mL × 2). The organic phase was combined, dried over anhydrous Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting 3-(trifluoromethyl)phenyl acetamides were purified by column chromatography on silica gel with petroleum ether/ethyl acetate.

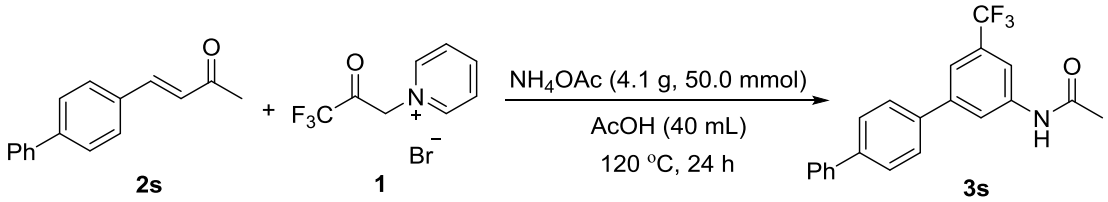
General procedure of the synthesis of 3-(trifluoromethyl)phenyl anilines 4a–4v:



2 **1** **4**

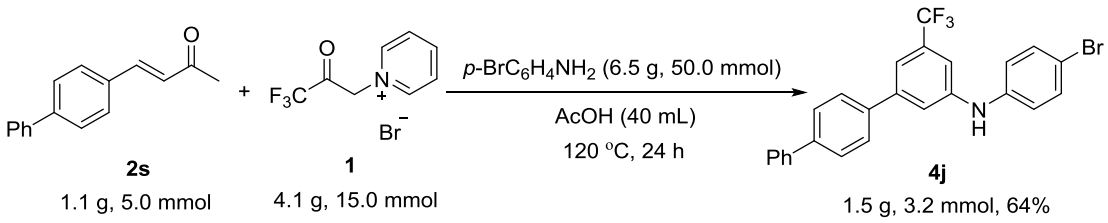
To an oven-dried 5 mL pressure tube was added *α*,*β*-unsaturated ketones **2** (0.30 mmol, 1.0 equiv), 1-(3,3,3-trifluoro-2-oxopropyl)pyridinium bromides **1** (242.1 mg, 0.90 mmol, 3.0 equiv), amines (3.0 mmol, 10.0 equiv) and AcOH (2 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 120 °C for 24 h. After the completion of the reaction, the solution was diluted with ethyl acetate (20 mL) and neutralized by cold saturated $NaHCO_3$ (20 mL) to pH > 7. The mixture solution was extracted with EtOAc (20 mL × 2). The organic phase was combined, dried over anhydrous Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting 3-(trifluoromethyl)phenyl anilines were purified by column chromatography on silica gel with petroleum ether/ethyl acetate.

Procedure for gram scale reaction for synthesis of 3s:



To an oven-dried 100 mL pressure tube was added **2s** (1.1 g, 5.0 mmol, 1.0 equiv), 1-(3,3,3-trifluoro-2-oxopropyl)pyridinium bromides **1** (4.0 g, 15.0 mmol, 3.0 equiv), NH_4OAc (3.9 g, 50.0 mmol, 10.0 equiv) and AcOH (40 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 120 °C for 24 h. After the completion of the reaction, the solution was diluted with ethyl acetate (120 mL) and neutralized by cold saturated $NaHCO_3$ (150 mL) to pH > 7. The organic phase was collected and the aqueous was extracted with EtOAc (100 mL × 2). The organic phase was combined, dried over anhydrous Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting product was purified by column chromatography on silica gel with petroleum ether : ethyl acetate (20 : 1) to obtain **3s** (1.2 g, 65% yield) as a yellow solid.

Procedure for gram scale reaction for synthesis of 4j:

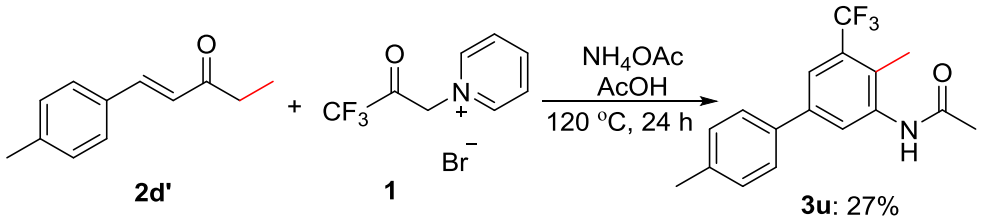


To an oven-dried 100 mL pressure tube was added **2s** (1.1 g, 5.0 mmol, 1.0 equiv), 1-(3,3,3-trifluoro-2-oxopropyl)pyridinium bromides **1** (4.0 g, 15.0 mmol, 3.0 equiv), 4-bromoaniline (8.6 g, 50.0 mmol, 10.0 equiv) and AcOH (40 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 120 °C for 24 h. After the completion of the reaction, the solution was diluted with ethyl acetate (120 mL) and neutralized by cold saturated $NaHCO_3$ (150 mL) to pH > 7. The organic phase was collected and the aqueous was extracted with EtOAc (100 mL × 2). The organic phase

was combined, dried over anhydrous Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting product was purified by column chromatography on silica gel with petroleum ether : ethyl acetate (20 : 1) to obtain **4j** (1.5 g, 64% yield) as a yellow solid.

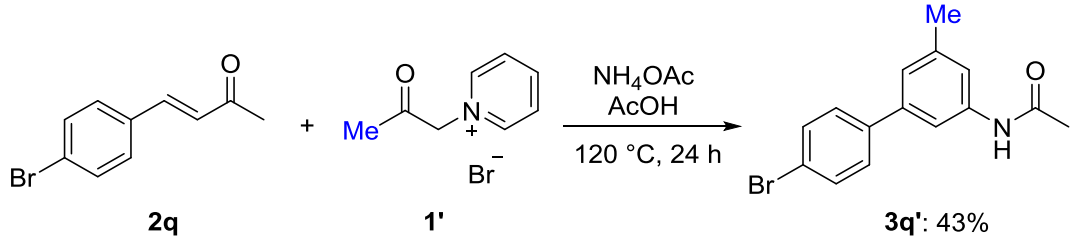
Follow-up studies

(1) Synthesis of four-substituted compound 3u



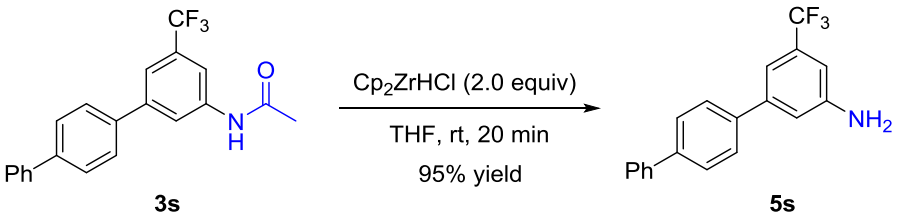
To an oven-dried 5 mL pressure tube was added 1-(*p*-tolyl)pent-1-en-3-one **2d′** (52.2 mg, 0.30 mmol, 1.0 equiv), 1-(3,3,3-trifluoro-2-oxopropyl)pyridinium bromides **1** (242.1 mg, 0.90 mmol, 3.0 equiv), NH_4OAc (231.0 mg, 3.0 mmol, 10.0 equiv) and AcOH (2 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 120 °C for 24 h. After the completion of the reaction, the solution was diluted with ethyl acetate (20 mL) and neutralized by cold saturated $NaHCO_3$ (20 mL) to pH > 7. The mixture solution was extracted with EtOAc (20 mL × 2). The organic phase was combined, dried over anhydrous Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting *N*-(4,4'-dimethyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide **3u** was purified by column chromatography on silica gel with petroleum ether/ethyl acetate.

(2) Synthesis of *N*-(4'-bromo-5-methyl-[1,1'-biphenyl]-3-yl)acetamide (3q')



To an oven-dried 5 mL pressure tube was added 4-(4-bromophenyl)but-3-en-2-one **2q** (67.0 mg, 0.30 mmol, 1.0 equiv), 1-(2-oxopropyl)pyridinium bromides **1'** (193.0 mg, 0.90 mmol, 3.0 equiv), NH_4OAc (231.0 mg, 3.0 mmol, 10.0 equiv) and AcOH (2 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 120 °C for 24 h. After the completion of the reaction, the solution was diluted with ethyl acetate (20 mL) and neutralized by cold saturated $NaHCO_3$ (20 mL) to pH > 7. The mixture solution was extracted with EtOAc (20 mL × 2). The organic phase was combined, dried over anhydrous Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting product was purified by column chromatography on silica gel with petroleum ether : ethyl acetate (3 : 1) to obtain *N*-(4'-bromo-5-methyl-[1,1'-biphenyl]-3-yl)acetamide **3q'** (39.0 mg, 43% yield) as a white solid.

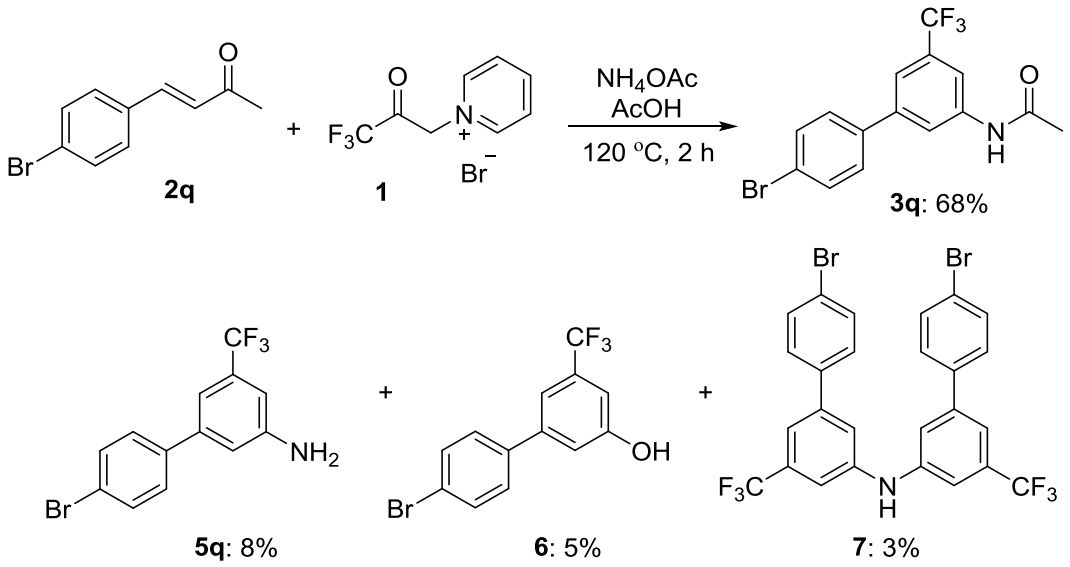
(3) Synthetic transformation of 3s to 5s



3s **5s**

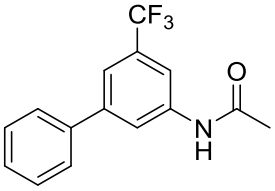
To an oven-dried 5 mL pressure tube was added *N*-(5-(trifluoromethyl)-[1,1':4',1''-terphenyl]-3-yl)acetamide **3s** (35.5 mg, 0.10 mmol, 1.0 equiv), Cp_2ZrHCl (51.5 mg, 0.20 mmol, 2.0 equiv) and THF (2 mL). The tube was sealed with Teflon screw cap and the solution was stirred at room temperature for 20 min. The crude mixture was diluted with ethyl acetate (15 mL) and washed by saturated NH_4Cl (4 mL × 3). The organic phase was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting product was purified by column chromatography on silica gel with petroleum ether : ethyl acetate (5 : 1) to obtain 5-(trifluoromethyl)-[1,1':4',1''-terphenyl]-3-amine **5s** (30.0 mg, 95% yield) as a white solid.

Detection of potential intermediate



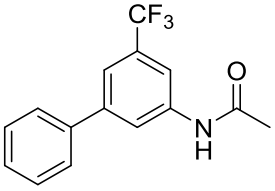
To an oven-dried 25 mL pressure tube was added 4-(4-bromophenyl)but-3-en-2-one **2q** (110.0 mg, 0.50 mmol, 1.0 equiv), 1-(3,3,3-trifluoro-2-oxopropyl)pyridinium bromides **1** (404.0 mg, 1.5 mmol, 3.0 equiv), NH_4OAc (385.0 mg, 5.0 mmol, 10.0 equiv) and AcOH (4 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 120 °C for 2 h. The solution was diluted with ethyl acetate (30 mL) and neutralized by cold saturated $NaHCO_3$ (30 mL) to pH 7-8. The organic phase was collected and the aqueous was extracted with EtOAc (30 mL × 2). The organic phase was combined, dried over anhydrous Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting product was purified by column chromatography on silica gel with petroleum ether : ethyl acetate (from 20 : 1 to 2 : 1) to obtain *N*-(4'-bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide **3q** (121 mg, 68% yield), 4'-bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine **5q** (13 mg, 8% yield), 4'-bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-3-ol **6** (8 mg, 5% yield), and bis(4'-bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)amine **7** (9 mg, 3% yield).

Data for compounds 3–7



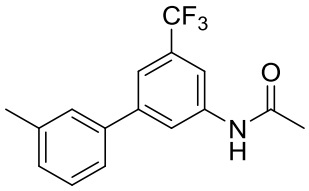
***N*-(5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3a)**

Obtained as a white solid in 75% yield (63 mg). Mp: 104.2 – 106.0 °C. R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.98 (s, 1H), 7.81 (s, 1H), 7.59 – 7.52 (m, 3H), 7.46 – 7.39 (m, 3H), 2.23 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 143.0, 139.3, 139.0, 131.7 (q, J = 32.8 Hz), 129.0, 128.2, 127.1, 123.8 (q, J = 272.7 Hz), 121.6, 119.6 (q, J = 3.7 Hz), 115.4 (q, J = 3.9 Hz), 24.5. IR (ATR): ν 3063, 2986, 1744, 1671, 1597, 1582, 1519, 1450, 1380, 1360, 1296, 1264, 1224, 1154, 1124, 1098, 1073, 1012, 1001, 984, 956, 934, 878, 861, 842, 817, 756, 729, 708, 686, 675, 632, 615 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{13}ONF_3$ $[M + H]^+$: 280.0944; found: 280.0940.



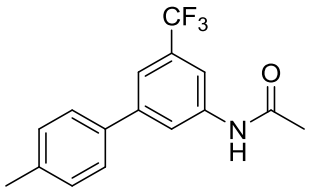
***N*-(2'-methyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3b)**

Obtained as a yellow oil in 64% yield (56 mg). R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.84 (s, 1H), 7.72 (s, 1H), 7.34 – 7.19 (m, 5H), 2.27 (s, 3H), 2.21 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 143.6, 140.0, 138.4, 135.2, 131.1 (q, J = 32.5 Hz), 130.5, 129.6, 128.0, 126.0, 123.8 (q, J = 273.2 Hz), 123.6, 121.6 (q, J = 3.8 Hz), 115.0 (q, J = 3.8 Hz), 24.5, 20.3. IR (ATR): ν 3282, 3066, 2959, 2928, 1671, 1615, 1563, 1492, 1457, 1360, 1317, 1288, 1253, 1222, 1205, 1167, 1121, 1073, 1035, 1014, 973, 919, 905, 882, 842, 760, 727, 707, 683, 634 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{16}H_{15}ONF_3$ $[M + H]^+$: 294.1100; found: 294.1097.



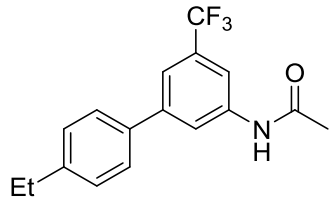
***N*-(3'-methyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3c)**

Obtained as a yellow oil in 67% yield (59 mg). R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.83 – 7.79 (m, 2H), 7.57 (s, 1H), 7.39 – 7.33 (m, 3H), 7.22 (d, J = 6.9 Hz, 1H), 2.43 (s, 3H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 143.1, 139.3, 138.8, 138.7, 131.7 (q, J = 32.1 Hz), 129.0, 128.9, 127.9, 124.3, 123.8 (q, J = 272.7 Hz), 121.5, 119.6 (q, J = 3.7 Hz), 115.2 (q, J = 3.8 Hz), 24.6, 21.5. IR (ATR): ν 3284, 3108, 2925, 1670, 1606, 1564, 1491, 1456, 1359, 1325, 1307, 1268, 1212, 1162, 1120, 1079, 1019, 1002, 975, 926, 873, 784, 738, 716, 699 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{16}H_{15}ONF_3$ $[M + H]^+$: 294.1100; found: 294.1095.



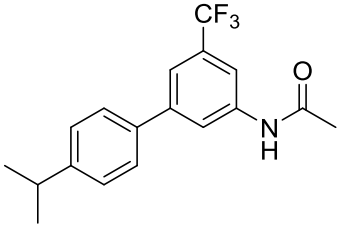
***N*-(4'-methyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3d)**

Obtained as a yellow oil in 74% yield (64 mg). R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.89 (s, 1H), 7.78 (s, 1H), 7.56 (s, 1H), 7.48 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 7.0 Hz, 2H), 2.41 (s, 3H), 2.23 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 142.9, 138.9, 138.2, 131.7 (q, J = 32.4 Hz), 129.7, 127.0, 123.7 (q, J = 272.9 Hz), 121.3, 119.4 (q, J = 3.7 Hz), 118.6, 115.0 (q, J = 3.8 Hz), 24.6, 21.1. IR (ATR): ν 3401, 3033, 2960, 2934, 2866, 2358, 1685, 1601, 1580, 1516, 1494, 1464, 1393, 1367, 1312, 1276, 1258, 1202, 1166, 1123, 1075, 995, 950, 908, 862, 813, 762, 722, 701, 668, 625, cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{16}H_{15}ONF_3$ $[M + H]^+$: 294.1100; found: 294.1096.



***N*-(4'-ethyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3e)**

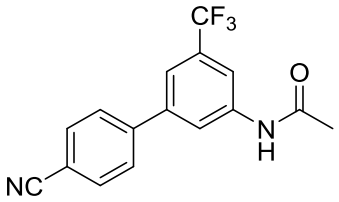
Obtained as a yellow solid in 77% yield (68 mg). Mp: 70.3 – 71.8 °C. R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.78 (s, 1H), 7.70 (br, 1H), 7.58 – 7.56 (m, 1H), 7.51 (dt, J = 8.1, 2.3 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 2.72 (q, J = 7.6 Hz, 2H), 2.24 (s, 3H), 1.29 (t, J = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 144.6, 143.0, 138.8, 136.7, 131.7 (q, J = 32.2 Hz), 128.5, 127.1, 123.8 (q, J = 273.9 Hz), 121.2, 119.5 (q, J = 3.8 Hz), 118.3, 115.0 (q, J = 3.8 Hz), 28.5, 24.6, 15.5. IR (ATR): ν 3281, 3172, 3109, 3032, 2966, 2933, 2874, 1670, 1610, 1564, 1515, 1457, 1435, 1406, 1361, 1321, 1290, 1260, 1164, 1121, 1076, 1012, 968, 919, 879, 828, 768, 737, 701, 683, 653, 619 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{17}H_{17}ONF_3$ $[M + H]^+$: 308.1257; found: 308.1252.



***N*-(4'-isopropyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3f)**

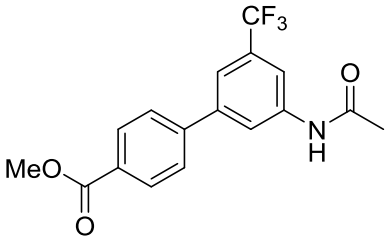
Obtained as a yellow oil in 70% yield (68 mg). R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.87 (br, 1H), 7.80 (s, 1H), 7.57 (s, 1H), 7.51 (dt, J = 8.3, 1.9 Hz, 2H), 7.32 (dt, J = 8.3, 1.9 Hz, 2H), 3.02 – 2.92 (m, 1H), 2.24 (s, 3H), 1.30 (d, J = 7.2, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 149.2, 142.9, 138.9, 136.8, 131.7 (q, J = 32.2 Hz), 127.1, 127.1, 123.8 (q, J = 272.3 Hz), 121.3, 119.4 (q, J = 3.9 Hz), 115.0 (q, J =

3.9 Hz), 33.8, 24.6, 23.9. IR (ATR): ν 3283, 3109, 2961, 2929, 2871, 1669, 1615, 1563, 1515, 1458, 1435, 1407, 1361, 1320, 1289, 1260, 1215, 1201, 1164, 1121, 1077, 1054, 1014, 973, 879, 739, 701, 684, 653, 621 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{18}H_{19}ONF_3$ $[M + H]^+$: 322.1413; found: 322.1409.



***N*-(4'-cyano-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3g)**

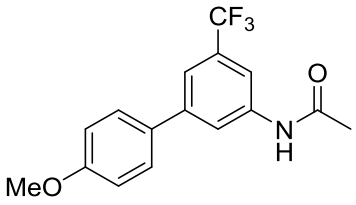
Obtained as a yellow solid in 84% yield (77 mg). Mp: 186.2 – 188.0 °C. R_f (petroleum ether : ethyl acetate = 2 : 1) = 0.25. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.44 (s, 1H), 8.13 (s, 1H), 8.10 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 7.72 (s, 1H), 2.11 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.3 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.6, 143.5, 141.3, 140.6, 133.5, 130.8 (q, J = 31.6 Hz), 128.4, 124.3 (q, J = 272.9 Hz), 121.3, 119.1, 118.4 (q, J = 3.7 Hz), 115.5 (q, J = 3.9 Hz), 111.4, 24.5. IR (ATR): ν 3290, 3031, 2959, 2923, 2866, 1602, 1565, 1515, 1490, 1457, 1387, 1365, 1321, 1277, 1256, 1203, 1164, 1121, 1105, 1069, 1010, 995, 951, 908, 863, 818, 762, 727, 700, 671, 612, 586, 491, 471, 450, 443, 420, 403 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{16}H_{12}ON_2F_3$ $[M + H]^+$: 305.0896; found: 305.0895.



methyl 3'-acetamido-5'-(trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate (3h)

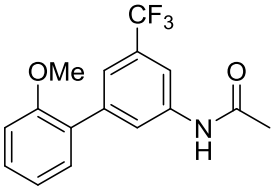
Obtained as a yellow solid in 78% yield (52 mg). Mp: 91.4 – 92.9 °C. R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 2H), 8.04 (s, 1H), 7.91 (s, 1H), 7.83 (s, 1H), 7.64 (d, J = 8.1 Hz, 2H), 7.59 (s, 1H),

3.96 (s, 3H), 2.25 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 166.9, 143.7, 141.8, 139.1, 132.0 (q, J = 32.5 Hz), 130.3, 129.8, 127.2, 123.6 (q, J = 272.9 Hz), 121.6, 119.6 (q, J = 3.9 Hz), 116.0 (q, J = 4.0 Hz), 52.3, 24.6. IR (ATR): ν 3312, 3111, 2954, 1704, 1675, 1609, 1563, 1513, 1459, 1436, 1401, 1363, 1279, 1259, 1167, 1123, 1076, 1017, 970, 910, 884, 853, 815, 773, 731, 703, 670, 648, 584, 543 cm^{-1}. HRMS (ESI) m/z: calcd. for: $C_{17}H_{15}F_3NO_3$ [M + H]$^+$: 338.0998; found: 338.0992.



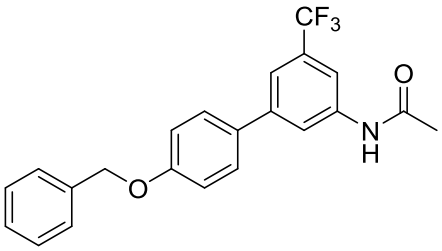
***N*-(4'-methoxy-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3i)**

Obtained as a white solid in 45% yield (42 mg). Mp: 103.0 – 105.0 °C. R_f (petroleum ether : ethyl acetate = 2 : 1) = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.73 (s, 2H), 7.58 – 7.46 (m, 3H), 6.98 (d, J = 8.7, 2H), 3.87 (s, 3H), 2.23 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 159.8, 142.6, 138.8, 131.8, 131.7 (q, J = 32.3 Hz), 128.3, 123.6 (q, J = 272.0 Hz), 121.0, 119.2 (q, J = 3.7 Hz), 114.6 (q, J = 3.9 Hz), 114.4, 55.4, 24.6. IR (ATR): ν 3416, 2962, 2931, 2858, 2335, 1989, 1732, 1686, 1665, 1568, 1543, 1492, 1455, 1412, 1389, 1364, 1317, 1261, 1226, 1167, 1125, 1105, 1093, 1076, 1014, 997, 970, 933, 870, 731, 700, 684, 637, 619, 587, 564, 550, 540, 466, 410 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{16}H_{15}O_2NF_3$ [M + H]$^+$: 310.1049; found: 310.1044.



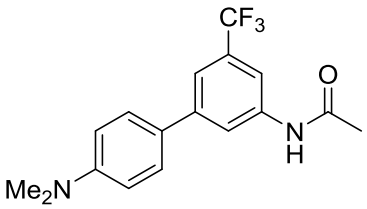
***N*-(2'-methoxy-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3j)**

Obtained as a yellow solid in 54% yield (34 mg). Mp: 96.0 – 97.3 °C. R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.82 (s, 1H), 7.73 (s, 1H), 7.54 (s, 1H), 7.37 (t, J = 8.4 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.3 Hz, 1H), 3.83 (s, 3H), 2.21 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 156.3, 140.2, 138.0, 130.9 (q, J = 32.4 Hz), 130.7, 129.6, 128.7, 124.0, 123.8 (q, J = 271.5 Hz), 122.2 (q, J = 3.9 Hz), 121.0, 115.2 (q, J = 4.0 Hz), 111.4, 55.6, 24.5. IR (ATR): ν 3415, 3033, 2938, 2836, 1718, 1600, 1586, 1520, 1490, 1464, 1437, 1374, 1317, 1260, 1229, 1162, 1115, 1074, 992, 945, 908, 855, 762, 733, 697, 630, 609 cm^{-1}. HRMS (ESI) m/z: calcd. for: $C_{16}H_{15}F_3NO_2$ $[M + H]^+$: 310.1049; found: 310.1044.



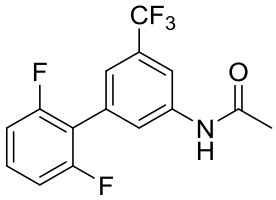
***N*-(4'-(benzyloxy)-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3k)**

Obtained as a yellow solid in 59% yield (68 mg). Mp: 132.0 – 134.0 °C. R_f (petroleum ether : ethyl acetate = 2 : 1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.73 (s, 1H), 7.69 (br s, 1H), 7.56 – 7.49 (m, 3H), 7.48 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.06 (d, J = 8.1 Hz, 2H), 5.12 (s, 2H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 159.0, 142.6, 138.8, 136.7, 132.0, 131.7 (q, J = 32.5 Hz), 128.7, 128.3, 128.1, 127.5, 123.8 (q, J = 272.6 Hz), 121.0, 119.1 (q, J = 3.8 Hz), 115.3, 114.7 (q, J = 3.6 Hz), 70.1, 24.6. IR (ATR): ν 3276, 3110, 3038, 2930, 2867, 1670, 1607, 1564, 1514, 1567, 1437, 1407, 1361, 1324, 1285, 1261, 1245, 1202, 1178, 1166, 1120, 1077, 1016, 918, 877, 861, 828, 807, 736, 696, 632, 616, 586, 557, 537, 507, 476, 458, 451, 443, 430, 419, 410, 401 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{19}O_2NF_3$ $[M + H]^+$: 386.1362; found: 386.1357.



***N*-(4'-(dimethylamino)-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3l)**

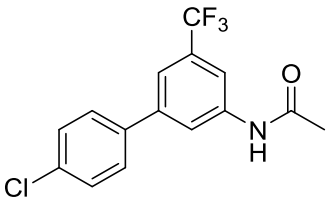
Obtained as a yellow solid in 42% yield (41 mg). Mp: 97.9 – 99.7 °C. R_f (petroleum ether : ethyl acetate = 2 : 1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.72 (s, 1H), 7.58 (br s, 1H), 7.54 (s, 1H), 7.51 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 3.03 (s, 6H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 150.3, 142.9, 138.7, 131.6 (q, J = 32.4 Hz), 127.8, 127.2, 123.9 (q, J = 272.7 Hz), 120.3, 118.7 (q, J = 3.7 Hz), 114.0 (q, J = 3.6 Hz), 112.9, 40.6, 24.7. IR (ATR): ν 3291, 3102, 2895, 1669, 1607, 1565, 1526, 1458, 1440, 1407, 1362, 1314, 1284, 1263, 1228, 1200, 1166, 1120, 1076, 1017, 999, 971, 948, 919, 876, 815, 736, 684, 586, 574, 565, 551, 542, 536, 527, 519, 511, 488, 471, 433, 410, 403 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{17}H_{18}ON_2F_3$ $[M + H]^+$: 323.1366; found: 323.1361.



***N*-(2',6'-difluoro-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3m)**

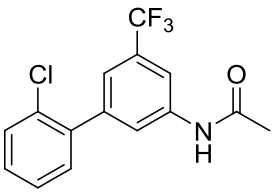
Obtained as a yellow solid in 51% yield (48 mg). Mp: 87.2 – 89.0 °C. R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 3H), 7.52 (s, 1H), 7.16 – 7.02 (m, 3H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F), -118.3 (d, J = 17.8 Hz, 1F), -123.8 (d, J = 17.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 158.7 (dd, J = 243.4, 2.5 Hz), 155.5 (dd, J = 244.7, 2.4 Hz), 138.8, 136.4, 131.7 (q, J = 32.6 Hz), 128.4 (dd, J = 7.8, 15.3 Hz), 123.5 (q, J = 273.8

Hz), 123.2 (d, *J* = 2.0 Hz), 121.3 – 121.2 (m), 117.4 (dd, *J* = 25.6, 8.5 Hz), 116.5 (dd, *J* = 24.6, 3.4 Hz), 116.3 (dd, *J* = 23.9, 8.6 Hz), 116.2 (q, *J* = 4.1 Hz), 24.5. IR (ATR): ν 3285, 3109, 1673, 1615, 1564, 1497, 1458, 1434, 1413, 1354, 1290, 1270, 1243, 1226, 1200, 1164, 1123, 1064, 1037, 1017, 982, 936, 907, 869, 815, 760, 738, 714, 700, 684, 653, 626, 590, 567, 539, 521, 506, 467, 447, 424, 401 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{11}ONF_5$ $[M + H]^+$: 316.0755; found: 316.0753.



***N*-(4'-chloro-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3n)**

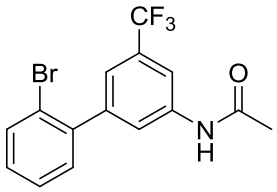
Obtained as a yellow solid in 63% yield (59 mg). Mp: 117.9 – 119.8 °C. R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.81 (br s, 1H), 7.75 (s, 1H), 7.52 (s, 1H), 7.50 (dt, *J* = 8.6, 2.1 Hz, 2H), 7.42 (dt, *J* = 8.6, 2.0 Hz, 2H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 141.8, 139.0, 137.7, 134.5, 131.9 (q, *J* = 32.5 Hz), 129.2, 128.4, 123.7 (q, *J* = 272.8 Hz), 121.3, 119.4 (q, *J* = 3.7 Hz), 115.5 (q, *J* = 3.8 Hz), 24.6. IR (ATR): ν 3282, 3174, 3104, 1673, 1617, 1609, 1563, 1497, 1456, 1434, 1395, 1361, 1323, 1288, 1203, 1166, 1124, 1094, 1075, 1037, 1013, 973, 909, 880, 738, 719, 701, 682, 649, 434, 617, 484, 642, 522, 480, 462, 449, 425, 413, 405 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{12}ONClF_3$ $[M + H]^+$: 314.0554; found: 314.0550.



***N*-(2'-chloro-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3o)**

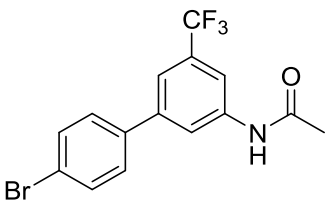
Obtained as a yellow oil in 66% yield (62 mg). R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (br s, 1H), 7.89 (s, 1H), 7.80 (s, 1H),

7.50 – 7.47 (m, 1H), 7.45 (s, 1H), 7.35 – 7.30 (m, 3H), 2.21 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 140.9, 138.6, 138.3, 132.3, 131.2, 131.1 (q, J = 32.4 Hz), 130.1, 129.4, 127.1, 123.9, 123.6 (q, J = 272.8 Hz), 121.9 (q, J = 3.7 Hz), 115.8 (q, J = 3.9 Hz), 24.5. IR (ATR): ν 3285, 3114, 1673, 1618, 1593, 1565, 1481, 1455, 1439, 1362, 1318, 1281, 1245, 1202, 1168, 1124, 1089, 1049, 1037, 1014, 973, 920, 882, 836, 757, 736, 704, 682, 651, 628, 589, 548, 516, 468, 435, 425, 417, 405 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{12}ONClF_3$ $[M + H]^+$: 314.0554; found: 314.0551.



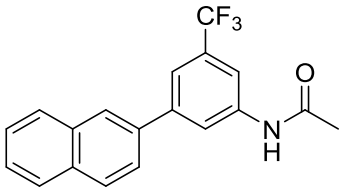
***N*-(2'-bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3p)**

Obtained as a yellow oil in 68% yield (68 mg). R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.76 (s, 1H), 7.69 (dd, J = 7.0, 1.0 Hz, 1H), 7.61 (br s, 1H), 7.44 – 7.36 (m, 2H), 7.33 (dd, J = 7.6, 1.9 Hz, 1H), 7.25 (dd, J = 7.4, 1.9 Hz, 1H), 2.23 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 142.6, 140.7, 138.2, 133.3, 131.2 (q, J = 32.6 Hz), 131.1, 129.5, 127.6, 123.7, 123.5 (q, J = 272.5 Hz), 122.3, 122.0 (q, J = 3.7 Hz), 115.7 (q, J = 3.8 Hz), 24.6. IR (ATR): ν 3284, 3053 ,1671, 1617, 1565, 1454, 1363, 1264, 1169, 1127, 1087, 1027, 895, 882, 730, 703, 656, 587, 549, 536, 505, 460, 455, 428, 420, 411, 405, 401 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{12}ONBrF_3$ $[M + H]^+$: 358.0049; found: 358.0046.



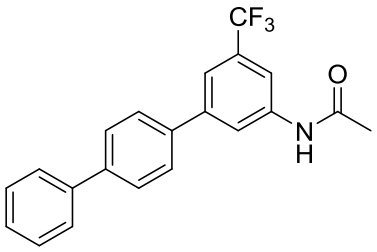
***N*-(4'-bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3q)**

Obtained as a yellow solid in 71% yield (76 mg). Mp: 143.0 – 145.0 °C. R_f (petroleum ether : ethyl acetate = 4 : 1) = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.84 (br s, 1H), 7.76 (s, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.52 (s, 1H), 7.43 (d, J = 8.4 Hz, 2H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 141.8, 139.0, 138.2, 132.1, 131.9 (q, J = 32.4 Hz), 128.7, 123.5 (q, J = 272.8 Hz), 122.7, 121.7, 119.4 (q, J = 3.7 Hz), 114.0 (q, J = 3.6 Hz), 24.6. IR (ATR): ν 3280, 3172, 3100, 1671, 1615, 1562, 1491, 1455, 1433, 1390, 1360, 1323, 1288, 1257, 1222, 1204, 1165, 1121, 1070, 1037, 1008, 974, 919, 906, 880, 733, 716, 700, 686, 670, 633, 616, 484, 542, 521, 512, 460, 427, 409 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{12}ONBrF_3$ $[M + H]^+$: 358.0049; found: 358.0047.



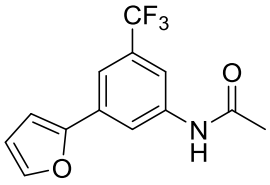
***N*-(3-(naphthalen-2-yl)-5-(trifluoromethyl)phenyl)acetamide (3r)**

Obtained as a yellow solid in 72% yield (71 mg). Mp: 217.0 – 219.0 °C. R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.05 (s, 1H), 7.97 – 7.86 (m, 3H), 7.82 (s, 1H), 7.75 – 7.69 (m, 2H), 7.62 (br s, 1H), 7.57 – 7.50 (m, 2H), 2.27 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 142.9, 138.9, 136.6, 133.5, 133.0, 131.9 (q, J = 32.5 Hz), 128.8, 128.3, 127.7, 126.6, 126.5, 126.3, 125.1, 123.7 (q, J = 273.5 Hz), 121.7, 119.9 (q, J = 3.8 Hz), 115.3 (q, J = 3.8 Hz), 24.7. IR (ATR): ν 3286, 3056, 2965, 2930, 1672, 1611, 1564, 1477, 1457, 140, 1363, 1340, 1324, 1275, 1262, 1233, 1166, 1122, 1074, 1060, 1016, 977, 922, 881, 856, 831, 818, 783, 748, 701, 686, 669, 627, 611, 586, 562, 539, 478, 429, 419, 410 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{19}H_{15}ONF_3$ $[M + H]^+$: 330.1100; found: 330.1096.



***N*-(5-(trifluoromethyl)-[1,1':4',1''-terphenyl]-3-yl)acetamide (3s)**

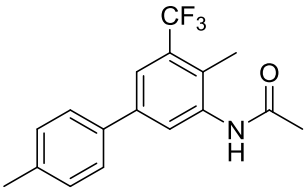
Obtained as a yellow solid in 76% yield (81 mg). Mp: 188.0 –189.8 °C. R_f (petroleum ether : ethyl acetate = 2 : 1) = 0.28. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.41 (s, 1H), 8.13 (s, 1H), 8.07 (s, 1H), 7.86 – 7.71 (m, 6H), 7.68 (s, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.44 – 7.37 (m, 1H), 2.12 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.3 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.5, 141.9, 141.2, 140.5, 139.8, 130.7 (q, J = 31.6 Hz), 129.5, 128.2, 127.9, 127.8, 127.1, 124.4 (q, J = 272.6 Hz), 120.8, 117.8 (q, J = 3.9 Hz), 114.4 (q, J = 4.0 Hz), 24.6. IR (ATR): ν 3396, 3030, 2918, 2859, 1699, 1601, 1558, 1504, 1485, 1457, 1444, 1412, 1395, 1364, 1338, 1322, 1270, 1236, 1209, 1164, 1120, 1105, 1035, 1007, 993, 960, 942, 907, 857, 834, 786, 765, 730, 696, 649, 620, 609, 594, 577, 554, 520, 500, 474, 461, 447, 431, 418, 402 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{21}H_{17}ONF_3$ $[M + H]^+$: 356.1257; found: 356.1253.



***N*-(3-(furan-2-yl)-5-(trifluoromethyl)phenyl)acetamide (3t)**

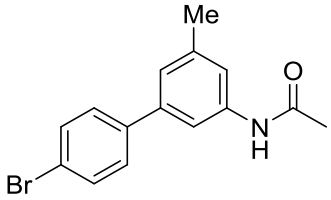
Obtained as a white solid in 80% yield (64 mg). Mp: 116.0 – 118.0 °C. R_f (petroleum ether : ethyl acetate = 2 : 1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.71 (s, 1H), 7.65 (s, 1H), 7.61 (br s, 1H), 7.50 (s, 1H), 6.75 (d, J = 3.4 Hz, 1H), 6.51 (s, 1H), 2.25 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 152.1, 142.9, 138.9, 132.4, 131.9 (q, J = 32.7 Hz), 123.6 (q, J = 272.7 Hz), 117.6, 116.2 (q, J = 3.8 Hz), 114.9 (q, J = 3.6 Hz), 112.0, 106.8, 24.6. IR (ATR): ν 3295, 3169, 3115, 2927, 1767, 1673, 1621, 1584, 1558, 1498, 1460, 1430,

1354, 1323, 1286, 1263, 1168, 1019, 998, 977, 908, 876, 795, 737, 695, 684, 593, 565, 542, 514, 491, 451, 423, 409 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{13}H_{11}O_2NF_3$ $[M + H]^+$: 270.0736; found: 270.0733.



***N*-(4,4'-dimethyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetamide (3u)**

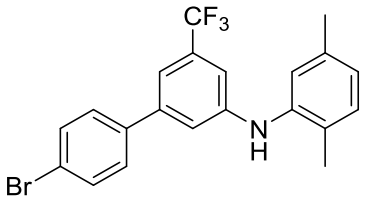
Obtained as a white solid in 27% yield (25 mg). Mp: 182.0–183.6 °C. R_f (ethyl acetate) = 0.68. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.70 (s, 1H), 7.89 (s, 1H), 7.72 (s, 1H), 7.57 (d, J = 7.7 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 2.12 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -59.3 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.2, 139.3, 138.5, 138.0, 135.9, 130.2, 129.9, 129.3 (q, J = 28.9 Hz), 128.0, 126.9, 124.9 (q, J = 274.0 Hz), 120.8 (q, J = 5.8 Hz), 23.7, 21.1, 14.0. IR (ATR): ν 3382, 3265, 2922, 1661, 1538, 1514, 1368, 1343, 1223, 1133, 1107, 808, 694, 485 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{17}H_{17}F_3NO$ $[M + H]^+$: 308.1257; found: 308.1254.



***N*-(4'-bromo-5-methyl-[1,1'-biphenyl]-3-yl)acetamide (3q')**

Obtained as a white solid in 43% yield (39 mg). Mp: 50.5 – 51.7 °C. R_f (petroleum ether : ethyl acetate = 1 : 1) = 0.42. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.99 (s, 1H), 7.69 (s, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.42 (s, 1H), 7.15 (s, 1H), 2.34 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 140.4, 140.0, 139.7, 139.2, 132.3, 129.1, 122.6, 121.3, 119.4, 114.9, 24.6, 21.7. IR (ATR): ν 3293,

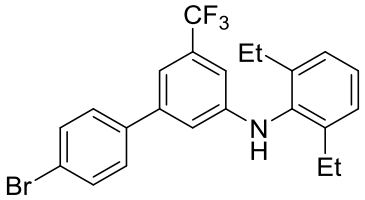
2959, 2920, 2850, 1667, 1611, 1561, 1490, 1457, 1387, 1286, 1073, 1009 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{15}BrNO$ $[M + H]^+$: 304.0332; found: 304.0331.



4'-bromo-*N*-(2,5-dimethylphenyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine

(4a)

Obtained as a yellow oil in 84% yield (105 mg). R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.75. ^{1}H NMR (400 MHz, $CDCl_3$)) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.28 (s, 1H), 7.21 – 7.16 (m, 2H), 7.14 – 7.09 (m, 2H), 6.94 (d, *J* = 7.7 Hz, 1H), 5.62 (br s, 1H), 2.35 (s, 3H), 2.27 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 142.0, 139.2, 139.0, 136.9, 132.3 (q, *J* = 32.1 Hz), 132.0, 131.2, 128.8, 127.7, 125.0, 123.9 (q, *J* = 272.4 Hz), 122.3, 117.0, 114.6 (q, *J* = 3.9 Hz), 111.5 (q, *J* = 3.8 Hz), 21.1, 17.6. IR (ATR): ν 3402, 3021, 2921, 2961, 1733, 1605, 1578, 1523, 1505, 1486, 1454, 1386, 1362, 1321, 1245, 1216, 1164, 1119, 1103, 1067, 1309, 1009, 999, 956, 908, 862, 837, 820, 731, 716, 701, 671, 650, 600, 584, 554, 511, 468, 442, 420, 414, 402 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{21}H_{18}NBrF_3$ $[M + H]^+$: 420.0569; found: 420.0566.

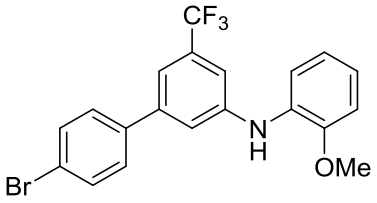


4'-bromo-*N*-(2,6-diethylphenyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine

(4b)

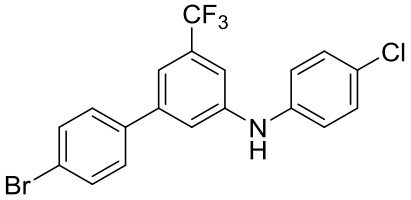
Obtained as a yellow oil in 85% yield (113 mg). R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.76. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.58 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.28 – 7.26 (m, 2H), 7.20 (s, 1H), 6.80 (d, *J* = 16.2 Hz, 2H), 5.50 (s, 1H), 2.66 (q, *J* = 7.5 Hz, 4H), 1.23 (t, *J* = 7.6 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 142.5, 142.0, 139.3, 135.5, 132.3 (q, *J* = 31.8 Hz), 132.0, 131.2, 128.3, 127.5, 127.1, 124.2 (q, *J* =

272.8 Hz), 122.2, 114.1, 113.2 (q, J = 3.9 Hz), 108.8 (q, J = 3.7 Hz), 24.8, 14.8. IR (ATR): ν 3403, 2967, 2933, 2873, 1608, 1589, 1564, 1508, 1487, 1454, 1410, 1388, 1363, 1321, 1299, 1273, 1257, 1221, 1162, 1120, 1102, 1067, 1037, 1099, 993, 950, 907, 861, 818, 768, 718, 702, 670, 642, 594, 424, 491, 468, 448, 428, 414 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{23}H_{22}NBrF_3$ $[M + H]^+$: 448.0882; found: 448.0880.



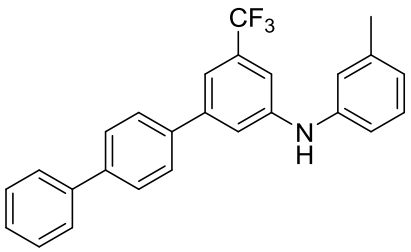
4'-bromo-*N*-(2-methoxyphenyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4c)

Obtained as a yellow oil in 88% yield (111 mg). R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.71. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.45 (s, 1H), 7.40 – 7.36 (m, 2H), 7.33 (s, 1H), 7.02 – 6.96 (m, 3H), 6.36 (br s, 1H), 3.94 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 144.3, 142.0, 138.9, 132.3 (q, J = 31.8 Hz), 132.0, 131.2, 128.8, 124.1 (q, J = 273.7 Hz), 122.4, 121.8, 120.9, 118.5, 116.5, 115.6 (q, J = 3.8 Hz), 112.7 (q, J = 3.8 Hz), 110.9, 55.6. IR (ATR): ν 3410, 3034, 1610, 1592, 1565, 1517, 1488, 1456, 1396, 1384, 1363, 1321, 1276, 1205, 1164, 1120, 1104, 1068, 1009, 996, 869, 817, 735, 713, 699, 670, 645, 629, 620, 600, 584, 523, 513, 696, 468, 447, 436, 425, 415, 404 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{20}H_{16}ONBrF_3$ $[M + H]^+$: 422.0362; found: 422.0360.



4'-bromo-*N*-(4-chlorophenyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4d)

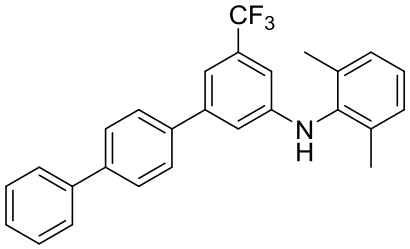
Obtained as a yellow solid in 90% yield (115 mg). Mp: 82.8 – 84.5 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.71. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.33 – 7.30 (m, 4H), 7.23 (s, 1H), 7.09 (d, J = 8.8 Hz, 2H), 5.92 (br s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 142.3, 140.2, 138.7, 132.5 (q, J = 32.2 Hz), 132.1, 129.7, 128.7, 127.5, 123.8 (q, J = 272.8 Hz), 122.5, 120.5, 118.0, 115.6 (q, J = 3.8 Hz), 112.4 (q, J = 3.8 Hz). IR (ATR): ν 3409, 2943, 2838, 1731, 1593, 1565, 1529, 1486, 1455, 1416, 1389, 1323, 1278, 1244, 1221, 1162, 1115, 1103, 1067, 1047, 1026, 1009, 995, 953, 868, 818, 785, 740, 717, 700, 671, 646, 630, 594, 586, 558, 549, 541, 524, 516, 508, 481, 464, 456, 448, 442, 434, 418, 406 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{19}H_{13}BrClF_3N$ $[M + H]^+$: 425.9867; found: 425.9870.



_N_-(_m_-tolyl)-5-(trifluoromethyl)-[1,1':4',1''-terphenyl]-3-amine (4e)

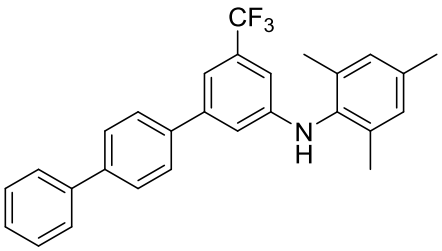
Obtained as a yellow solid in 72% yield (87 mg). Mp: 74.0 – 76.0 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 6H), 7.53 – 7.47 (m, 2H), 7.46 (s, 1H), 7.44 – 7.38 (m, 2H), 7.28 – 7.27 (m, 2H), 7.04 – 7.00 (m, 2H), 6.90 (d, J = 7.6 Hz, 1H), 5.92 (br s, 1H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 142.8, 141.7, 140.9, 140.5, 139.7, 138.8, 132.2 (q, J = 32.1 Hz), 129.5, 128.9, 127.7, 127.6, 127.5, 127.1, 124.0 (q, J = 274.0 Hz), 123.4, 120.1, 118.1, 116.3, 115.7 (q, J = 3.8 Hz), 112.0 (q, J = 3.8 Hz), 21.6. IR (ATR): ν 3402, 3032, 2961, 2922, 2683, 1702, 1601, 1589, 1531, 1518, 1488, 1458, 1444, 1387, 1365, 1311, 1277, 1259, 1217, 1164, 1122, 1075, 1077, 996, 961, 913, 866, 836, 765, 731, 695, 637, 624, 606, 584, 511, 494, 477, 460,

441, 424, 405 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{26}H_{21}NF_3$ $[M + H]^+$: 404.1620; found: 404.1621.



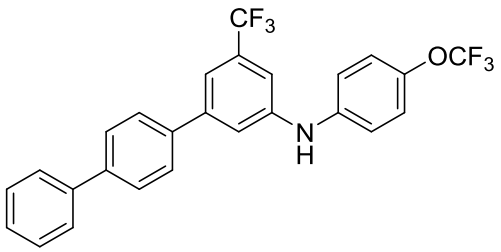
***N*-(2,6-dimethylphenyl)-5-(trifluoromethyl)-[1,1':4',1''-terphenyl]-3-amine (4f)**

Obtained as a yellow oil in 80% yield (100 mg). R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.80. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 6H), 7.51 – 7.55 (m, 2H), 7.46 – 7.41 (m, 1H), 7.33 (s, 1H), 7.25 – 7.22 (m, 3H), 6.92 (t, J = 1.9 Hz, 1H), 6.80 (t, J = 1.9 Hz, 1H), 5.49 (br s, 1H), 2.33 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 142.7, 140.8, 140.6, 139.2, 137.0, 136.2, 132.3 (q, J = 31.4 Hz), 128.9, 128.8, 128.2, 127.6, 127.5, 127.1, 126.6, 124.3 (q, J = 272.5 Hz), 114.5, 113.6 (q, J = 4.0 Hz), 108.8 (q, J = 3.8 Hz), 18.4. IR (ATR): ν 3395, 3030, 2948, 2919, 2856, 1716, 1607, 1591, 1557, 1526, 1505, 1486, 1457, 1444, 1412, 1395, 1322, 1272, 1258, 1230, 1200, 1118, 1074, 1035, 1007, 993, 968, 946, 917, 861, 835, 763, 731, 695, 644, 619, 608, 592, 579, 558, 558, 531, 521, 512, 501, 492, 483, 472, 462, 453, 444, 433, 414, 406 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{27}H_{23}F_3N$ $[M + H]^+$: 418.1777; found: 418.1768.



***N*-mesityl-5-(trifluoromethyl)-[1,1':4',1''-terphenyl]-3-amine (4g)**

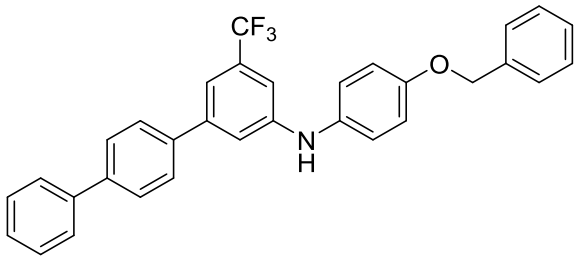
Obtained as a yellow oil in 77% yield (99 mg). R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.76. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 6H), 7.57 – 7.50 (m, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.33 (s, 1H), 7.07 (s, 2H), 6.92 (s, 1H), 6.79 (s, 1H), 5.42 (br s, 1H), 2.41 (s, 3H), 2.30 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 142.7, 140.7, 140.6, 139.3, 136.3, 136.1, 134.3, 132.2 (q, J = 31.7 Hz), 129.6, 128.9, 127.6 (2C), 127.1, 124.4 (q, J = 272.8 Hz), 114.3, 113.3 (q, J = 3.9 Hz), 108.5 (q, J = 3.9 Hz), 21.0, 18.3. IR (ATR): ν 3396, 3030, 2918, 2859, 1699, 1601, 1558, 1504, 1485, 1457, 1444, 1395, 1364, 1338, 1322, 1310, 1270, 1236, 1209, 1120, 1073, 1035, 1007, 993, 960, 942, 907, 857, 834, 786, 765, 730, 649, 620, 609, 594, 577, 520, 499, 474, 447, 418, 402 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{28}H_{25}NF_3$ $[M + H]^+$: 432.1934; found: 432.1935.



_N_-(4-(trifluoromethoxy)phenyl)-5-(trifluoromethyl)-[1,1':4',1''-terphenyl]-3-amin e (4h)

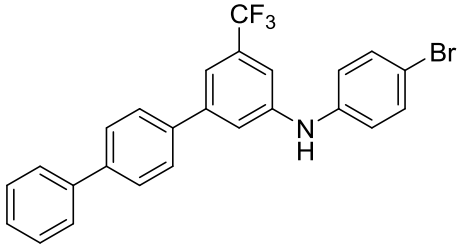
Obtained as a yellow solid in 78% yield (111 mg). Mp: 147.0 – 148.9 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.62 (m, 6H), 7.50 (t, J = 7.5 Hz, 2H), 7.46 (s, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.27 (s, 1H), 7.23 – 7.16 (m, 4H), 5.97 (br s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.2 (s, 3F), -62.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.9 (q, J = 1.9 Hz), 143.1, 141.1, 140.7, 140.4, 138.6, 132.4 (q, J = 32.2 Hz), 128.9, 127.7, 127.6, 127.5, 127.1, 123.9 (q, J = 272.0 Hz), 122.6, 120.5 (q, J = 255.0 Hz), 119.7, 118.5, 116.5 (q, J = 3.9 Hz), 112.5 (q, J = 3.8 Hz). IR (ATR): ν 3399, 3084, 2982, 2947, 2933, 2920, 1601, 1508, 1488, 1463, 1405, 1367, 1256, 1224, 1024, 1074, 1008, 996, 954, 920, 836, 792, 766, 752, 742, 698, 677, 658, 609, 592, 547, 538, 528, 518, 479, 471, 460, 447, 432,

432, 418, 405 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{26}H_{18}ONF_6$ $[M + H]^+$: 474.1287; found: 474.1282.



***N*-(4-(benzyloxy)phenyl)-5-(trifluoromethyl)-[1,1':4',1''-terphenyl]-3-amine (4i)**

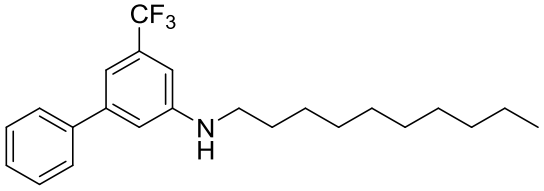
Obtained as a yellow solid in 75% yield (112 mg). Mp: 161.2 – 162.8 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 6H), 7.52 – 7.49 (m, 4H), 7.46 – 7.38 (m, 4H), 7.34 (s, 1H), 7.29 (s, 1H), 7.17 (d, J = 6.8 Hz, 2H), 7.11 (s, 1H), 7.03 (d, J = 7.8 Hz, 2H), 5.77 (br s, 1H), 5.11 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 146.4, 142.8, 140.9, 140.5, 139.0, 137.0, 134.5, 132.3 (q, J = 31.9 Hz), 128.9, 128.7, 128.1, 127.6 (2C), 127.5, 127.1, 124.0 (q, J = 273.5 Hz), 123.5, 116.3, 116.0, 114.6 (q, J = 3.9 Hz), 110.3 (q, J = 3.8 Hz), 70.5. HRMS (ESI) m/z: calcd. for $C_{32}H_{25}ONF_3$ $[M + H]^+$: 496.1883; found: 496.1878.



***N*-(4-bromophenyl)-5-(trifluoromethyl)-[1,1':4',1''-terphenyl]-3-amine (4j)**

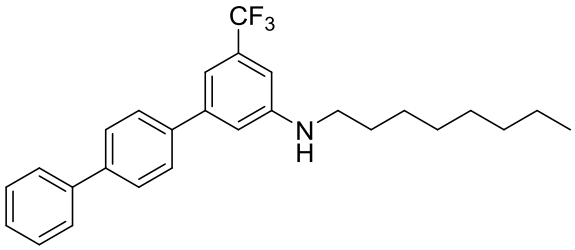
Obtained as a yellow solid in 70% yield (98 mg). Mp: 159.3–161.0 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 2H), 7.67 – 7.64 (m, 4H), 7.52 – 7.45 (m, 7H), 7.25 (s, 1H), 7.06 (d, J = 8.9 Hz, 2H), 5.92 (br s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 144.0, 143.0, 141.1, 141.0, 140.4, 138.6, 132.6, 132.3 (q, *J* = 31.7 Hz), 128.9, 127.7, 127.6, 127.5, 127.1, 123.9 (q, *J* = 272.5 Hz), 120.5, 118.5, 116.4 (q, *J* = 3.9 Hz), 114.5, 112.5 (q, *J* = 3.9 Hz). IR (ATR): ν 3400, 3019, 2919, 2959, 1735, 1607, 1579, 1505, 1488, 1455, 1360, 1319, 1244, 1120, 1066, 1000, 956, 908, 860, 839, 818, 731, 715, 699, 673, 585, 554, 420, 413, 403 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{25}H_{18}BrF_3N$ $[M + H]^+$: 468.0569; found: 468.0573.



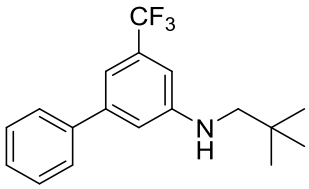
***N*-decyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4k)**

Obtained as a yellow solid in 85% yield (96 mg). Mp: 83.4 – 85.0 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.62 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.40 (m, 1H), 7.19 (s, 1H), 6.97 (s, 1H), 6.84 (s, 1H), 3.96 (br s, 1H), 3.22 (t, *J* = 7.1 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.54 – 1.25 (m, 14H), 0.95 (t, *J* = 6.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 143.1, 140.6, 132.0 (q, *J* = 31.5 Hz), 128.8, 127.8, 127.2, 124.4 (q, *J* = 272.6 Hz), 114.3, 112.6 (q, *J* = 4.0 Hz), 107.7 (q, *J* = 3.8 Hz), 43.9, 32.0, 29.6, 29.6, 29.5, 29.4 (2C), 27.2, 22.7, 14.2. IR (ATR): ν 3425, 2924, 2854, 1609, 1579, 1520, 1494, 1446, 1412, 1364, 1317, 1277, 1261, 1120, 992, 908, 853, 699, 626 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{23}H_{31}F_3N$ $[M + H]^+$: 378.2403; found: 378.2399.



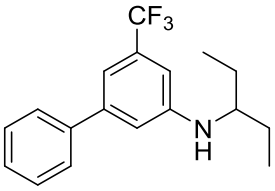
***N*-octyl-5-(trifluoromethyl)-[1,1':4',1''-terphenyl]-3-amine (4l)**

Obtained as a yellow solid in 83% yield (106 mg). Mp: 168.0 – 169.7 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 6H), 7.52 – 7.47 (m, 2H), 7.42 – 7.38 (m, 1H), 7.21 (s, 1H), 7.01 (s, 1H), 6.84 (s, 1H), 4.21 (br s, 1H), 3.24 – 3.20 (m, 2H), 1.76 – 1.66 (m, 2H), 1.48 – 1.44 (m, 2H), 1.39 – 1.29 (m, 8H), 0.94 – 0.90 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 142.6, 140.7, 140.6, 139.4, 132.1 (q, J = 31.8 Hz), 128.9, 127.5 (2C), 127.1, 124.4 (q, J = 272.2 Hz), 114.3, 112.7, 108.0, 44.1, 31.8, 29.4, 29.3, 29.3, 27.1, 22.7, 14.1. IR (ATR): ν 3426, 2926, 2853, 1518, 1490, 1445, 1361, 1318, 1118, 1077, 993, 910, 855, 733, 700, 673, 625, 419 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{27}H_{31}F_3N$ $[M + H]^+$: 426.2403; found: 426.2408.



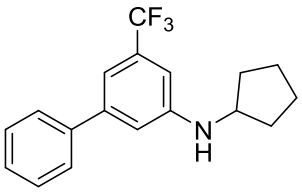
***N*-neopentyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4m)**

Obtained as a yellow solid in 84% yield (76 mg). Mp: 84.0 – 85.8 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.76. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.42 (t, J = 7.3 Hz, 1H), 7.18 (s, 1H), 7.00 (s, 1H), 6.87 (s, 1H), 4.00 (br s, 1H), 3.03 (s, 2H), 1.08 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 143.1, 140.7, 132.0 (q, J = 31.5 Hz), 128.8, 127.8, 127.2, 124.4 (q, J = 272.7 Hz), 114.3, 112.5 (q, J = 4.0 Hz), 107.7 (q, J = 3.9 Hz), 55.6, 32.0, 27.6. IR (ATR): ν 3430, 2956, 2868, 1609, 1579, 1523, 1495, 1446, 1414, 1377, 1347, 1317, 1277, 1261, 1230, 1120, 1075, 991, 936, 853, 760, 711, 697, 634 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{18}H_{21}F_3N$ $[M + H]^+$: 308.1621; found: 308.1616.



_N_-(pentan-3-yl)-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4n)

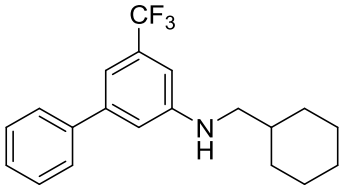
Obtained as a yellow solid in 75% yield (69 mg). Mp: 87.3 – 89.0 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.42 (t, J = 7.3 Hz, 1H), 7.15 (s, 1H), 6.95 (s, 1H), 6.82 (s, 1H), 3.78 (br s, 1H), 3.42 – 3.36 (m, 1H), 1.77 – 1.64 (m, 2H), 1.62 – 1.52 (m, 2H), 1.02 (t, J = 7.5 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 143.1, 140.7, 132.1 (q, J = 31.8 Hz), 128.8, 127.8, 127.2, 124.5 (q, J = 272.2 Hz), 114.5, 112.1 (q, J = 4.0 Hz), 108.0 (q, J = 4.0 Hz), 55.5, 26.8, 10.1. IR (ATR): ν 3413, 2965, 2932, 2877, 1601, 1578, 1521, 1495, 1465, 1442, 1412, 1375, 1319, 1267, 1227, 1117, 1076, 1000, 933, 852, 761, 713, 699, 644, 624 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{18}H_{21}F_3N$ $[M + H]^+$: 308.1621; found: 308.1616.



_N_-cyclopentyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4o)

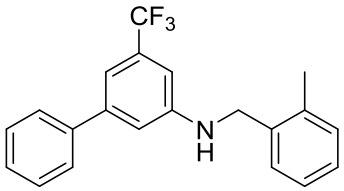
Obtained as a yellow solid in 81% yield (74 mg). Mp: 96.0 – 97.6 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.7 Hz, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.46 (d, J = 7.3 Hz, 1H), 7.23 (s, 1H), 7.00 (s, 1H), 6.88 (s, 1H), 4.01 (br s, 1H), 3.97 – 3.90 (m, 1H), 2.19 – 2.11 (m, 2H), 1.88 – 1.79 (m, 2H), 1.78 – 1.76 (m, 2H), 1.62 – 1.54 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 143.1, 140.7, 132.0 (q, J = 31.7 Hz), 128.9, 127.8, 127.2, 124.5 (q, J = 272.5 Hz), 114.7, 112.4 (q, J = 4.0 Hz), 108.3 (q, J = 4.0 Hz), 54.7, 33.5, 24.1. IR (ATR): ν 3416, 2957, 2870, 1609, 1578, 1518, 1493, 1464, 1444, 1411, 1376, 1309, 1277, 1260, 1231, 1161, 1116, 1075, 991, 907, 852, 732, 714,

698, 650, 629 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{18}H_{19}F_3N$ $[M + H]^+$: 306.1464; found: 306.1459.



_N_-(cyclohexylmethyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4p)

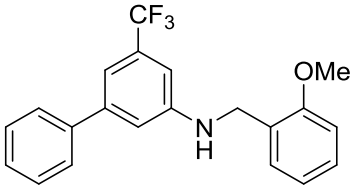
Obtained as a yellow solid in 80% yield (80 mg). Mp: 99.3 – 100.9 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.1 Hz, 1H), 7.17 (s, 1H), 6.95 (s, 1H), 6.82 (s, 1H), 3.80 (br s, 1H), 3.07 (d, J = 6.7 Hz, 2H), 1.90 – 1.86 (m, 2H), 1.83– 1.97 (m, 2H), 1.76 – 1.72 (m, 1H), 1.68 – 1.59 (m, 1H), 1.40 – 1.19 (m, 3H), 1.11 – 1.01 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 143.1, 140.7, 132.0 (q, J = 31.2 Hz), 128.8, 127.8, 127.2, 124.4 (q, J = 271.0 Hz), 114.2, 112.4 (q, J = 3.9 Hz), 107.7 (q, J = 4.0 Hz), 50.5, 37.7, 31.3, 26.5, 25.9. IR (ATR): ν 3431, 2923, 2851, 1698, 1609, 1578, 1520, 1494, 1465, 1447, 1413, 1385, 1358, 1318, 1231, 1117, 1076, 1026, 991, 942, 907, 853, 761, 732, 698, 627 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{20}H_{23}F_3N$ $[M + H]^+$: 334.1777; found: 334.1772.



_N_-(2-methylbenzyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4q)

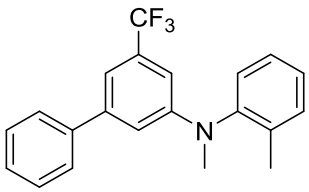
Obtained as a yellow solid in 76% yield (78 mg). Mp: 110.0 – 111.8 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.43 (d, J = 7.3 Hz, 1H), 7.39 (d, J = 7.3 Hz, 1H), 7.30 – 7.25 (m, 4H), 7.00 (s, 1H), 6.89 (s, 1H), 4.39 (s, 2H), 4.15 (br s, 1H), 2.45 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ

148.8, 143.2, 140.5, 136.5, 136.2, 132.1 (q, *J* = 31.0 Hz), 130.7, 128.9, 128.5, 127.9 (2C), 127.2, 126.3, 124.4 (q, *J* = 272.7 Hz), 114.3, 113.0 (q, *J* = 3.9 Hz), 107.8 (q, *J* = 3.9 Hz), 46.4, 19.0. IR (ATR): ν 3409, 3028, 2925, 1695, 1610, 1579, 1518, 1493, 1462, 1445, 1376, 1350, 1317, 1277, 1261, 1165, 1117, 1073, 991, 950, 855, 762, 730, 699, 649, 627, 604 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{21}H_{19}F_3N$ $[M + H]^+$: 342.1464; found: 342.1462.



_N_-(2-methoxybenzyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4r)

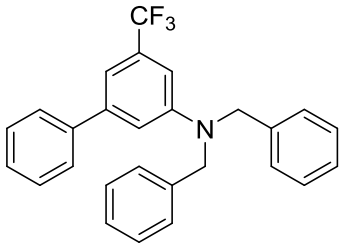
Obtained as a white solid in 73% yield (78 mg). Mp: 113.9 – 115.7 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.21 (s, 1H), 7.06 – 6.92 (m, 3H), 6.91 – 6.84 (m, 2H), 4.41 (s, 2H), 3.85 (s, 3H), N*H* was not observed. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 148.6, 143.1, 140.5, 140.2, 132.0 (q, *J* = 31.0 Hz), 129.9, 128.8, 127.9, 127.2, 124.3 (q, *J* = 270.1 Hz), 119.8, 114.4, 113.2, 113.1 (q, *J* = 3.7 Hz), 113.0, 108.0 (q, *J* = 3.8 Hz), 55.3, 48.2. IR (ATR): ν 3415, 2938, 2836, 1718, 1599, 1519, 1490, 1464, 1436, 1414, 1374, 1317, 1075, 1047, 995, 908, 855, 762, 733, 697, 630 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{21}H_{19}OF_3N$ $[M + H]^+$: 358.1413; found: 358.1408.



_N_-methyl-_N_-(_o_-tolyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4s)

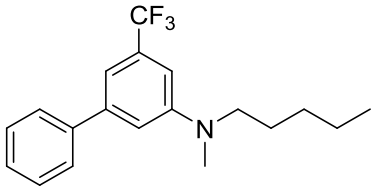
Obtained as a yellow solid in 60% yield (61 mg). Mp: 153.2 – 155.0 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 –

7.52 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.33 – 7.28 (m, 2H), 7.22 – 7.20 (m, 2H), 6.84 (s, 1H), 6.78 (s, 1H), 3.34 (s, 3H), 2.21 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 145.7, 142.9, 140.8, 136.6, 131.9 (q, *J* = 31.6 Hz), 131.7, 128.8, 128.3, 127.9, 127.7, 127.3, 127.2, 124.3 (q, *J* = 272.6 Hz), 114.3, 112.4 (q, *J* = 3.9 Hz), 107.6 (q, *J* = 3.9 Hz), 39.3, 17.8. IR (ATR): ν 2960, 2829, 1717, 1600, 1501, 1491, 1410, 1371, 1310, 1076, 1045, 996, 907, 855, 763, 734, 699, 629 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{21}H_{19}F_3N$ $[M + H]^+$: 342.1464; found: 342.1461.



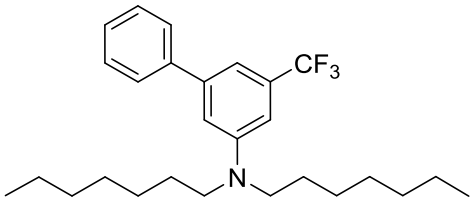
_N_,_N_-dibenzyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4t)

Obtained as a yellow solid in 61% yield (76 mg). Mp: 161.0 – 163.0 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.76. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.46 – 7.34 (m, 9H), 7.30 – 7.28 (m, 6H), 7.17 (s, 1H), 7.09 (s, 1H), 6.99 (s, 1H), 4.75 (s, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 143.1, 140.8, 137.2, 132.0 (q, *J* = 31.6 Hz), 128.9, 128.8, 127.8, 127.3 (2C), 126.7, 124.4 (q, *J* = 272.4 Hz), 114.3, 112.5 (q, *J* = 3.9 Hz), 107.7 (q, *J* = 3.9 Hz), 54.4. IR (ATR): ν 3030, 2923, 1605, 1578, 1494, 1482, 1452, 1403, 1354, 1327, 1297, 1260, 1219, 1166, 1120, 1076, 1051, 1028, 989, 962, 855, 763, 733, 696, 632 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{27}H_{23}F_3N$ $[M + H]^+$: 418.1777; found: 418.1770.



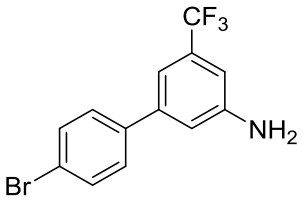
_N_-methyl-_N_-pentyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4u)

Obtained as a yellow solid in 52% yield (50 mg). Mp: 110.2 – 112.0 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.78. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.14 (s, 1H), 7.02 (s, 1H), 6.89 (s, 1H), 3.42 (t, J = 7.5 Hz, 2H), 3.05 (s, 3H), 1.69 – 1.62 (m, 2H), 1.44 – 1.32 (m, 4H), 0.95 (t, J = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 143.0, 141.2, 131.9 (q, J = 31.3 Hz), 128.8, 127.7, 127.3, 124.6 (q, J = 270.5 Hz), 113.6, 111.4, 107.2, 52.8, 38.6, 29.3, 26.4, 22.6, 14.4. IR (ATR): ν 2956, 2928, 2860, 1605, 1578, 1455, 1427, 1392, 1319, 1256, 1197, 1166, 1116, 1075, 1031, 995, 964, 849, 761, 699, 631, 610 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{19}H_{23}F_3N$ $[M + H]^+$: 322.1777; found: 322.1772.



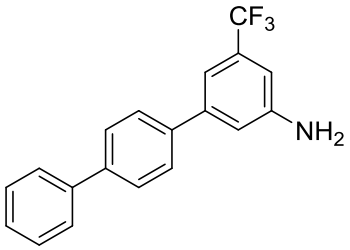
***N,N*-diheptyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (4v)**

Obtained as a yellow solid in 42% yield (55 mg). Mp: 127.3 – 129.1 °C. R_f (petroleum ether : ethyl acetate = 20 : 1) = 0.77. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 7.08 (s, 1H), 6.95 (s, 1H), 6.83 (s, 1H), 3.36 (t, J = 7.7 Hz, 4H), 1.66 – 1.60 (m, 4H), 1.39 – 1.29 (m, 16H), 0.92 (t, J = 6.6 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 143.0, 141.3, 131.9 (q, J = 31.1 Hz), 128.8, 127.7, 127.3, 124.5 (q, J = 272.4 Hz), 113.3, 110.7, 106.8, 51.1, 31.8, 29.1, 27.1, 22.6, 14.1. IR (ATR): ν 2926, 2856, 1609, 1579, 1490, 1468, 1427, 1392, 1319, 1258, 1166, 1119, 1076, 995, 950, 761, 701, 631 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{27}H_{39}F_3N$ $[M + H]^+$: 434.3029; found: 434.3026.



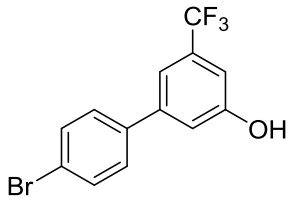
4'-bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (5q)

Obtained as a yellow oil in 8% yield (13 mg). R_f (petroleum ether : ethyl acetate = 4 : 1) = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.18 (s, 1H), 6.98 (s, 1H), 6.92 (s, 1H), 3.97 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 142.0, 139.0, 132.3 (q, *J* = 32.0 Hz), 132.0, 128.7, 124.1 (q, *J* = 272.6 Hz), 122.2, 116.3, 113.7 (q, *J* = 3.9 Hz), 110.6 (q, *J* = 3.8 Hz). IR (ATR): ν 3479, 3389, 2958, 2922, 2850, 1625, 1607, 1453, 1372, 1163, 1119, 1086, 1009, 864, 820, 717 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{13}H_{10}BrF_3N$ $[M + H]^+$: 315.9944; found: 315.9941.



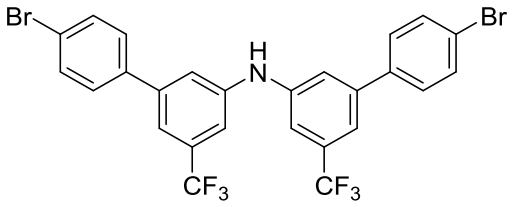
5-(trifluoromethyl)-[1,1':4',1''-terphenyl]-3-amine (5s)

Obtained as a white solid in 95% yield (30 mg). Mp: 115.8 – 117.2 °C. R_f (petroleum ether : ethyl acetate = 4 : 1) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.56 (m, 7H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.07 (s, 1H), 6.90 (s, 1H), 3.94 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 142.7, 140.8, 140.5, 138.9, 132.1 (q, *J* = 31.9 Hz), 128.8, 127.5 (3C), 127.0, 124.2 (q, *J* = 272.5 Hz), 116.4, 114.0 (q, *J* = 4.0 Hz), 110.3 (q, *J* = 3.9 Hz). IR (ATR): ν 3380, 3031, 2929, 1622, 1457, 1375, 1269, 1166, 1122, 836, 766 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{19}H_{15}F_3N$ $[M + H]^+$: 314.1152; found: 314.1148.



4'-bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-3-ol (6)

Obtained as a yellow oil in 5% yield (8 mg). R_f (petroleum ether : ethyl acetate = 4 : 1) = 0.59. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.38 (s, 1H), 7.20 (s, 1H), 7.10 (s, 1H), 5.60 (br s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 142.7, 138.4, 132.6 (q, *J* = 32.4 Hz), 132.1, 128.7, 123.7 (q, *J* = 272.5 Hz), 122.6, 117.2, 116.2 (q, *J* = 3.9 Hz), 111.5 (q, *J* = 3.8 Hz). IR (ATR): ν 3357, 2958, 2925, 2853, 1698, 1605, 1448, 1367, 1269, 1167, 1126, 1103, 1010, 931, 821, 718 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{13}H_9BrF_3O$ $[M + H]^+$: 316.9784; found: 316.9781.



bis(4'-bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)amine (7)

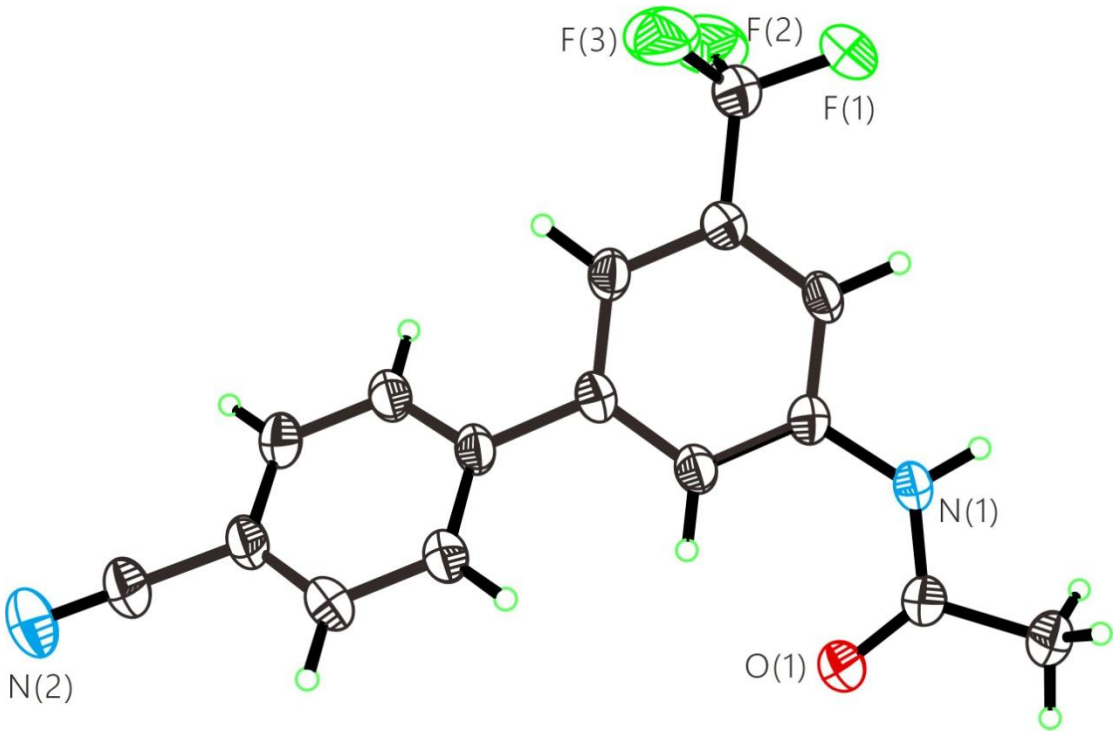
Obtained as a yellow solid in 3% yield (9 mg). Mp: 50.5 – 52.2 °C. R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 4H), 7.50 – 7.41 (m, 8H), 7.37 (s, 2H), 6.14 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 142.6, 138.4, 132.8 (q, *J* = 32.4 Hz), 132.2, 128.7, 123.8 (q, *J* = 272.7 Hz), 122.7, 119.5, 117.2 (q, *J* = 3.9 Hz), 113.8 (q, *J* = 3.8 Hz). IR (ATR): ν 3411, 2917, 2849, 1599, 1455, 1386, 1362, 1263, 1167, 1125, 1069, 1010, 969, 821 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{26}H_{16}Br_2F_6N$ $[M + H]^+$: 615.9528; found: 615.9519.

Crystal structure analyses

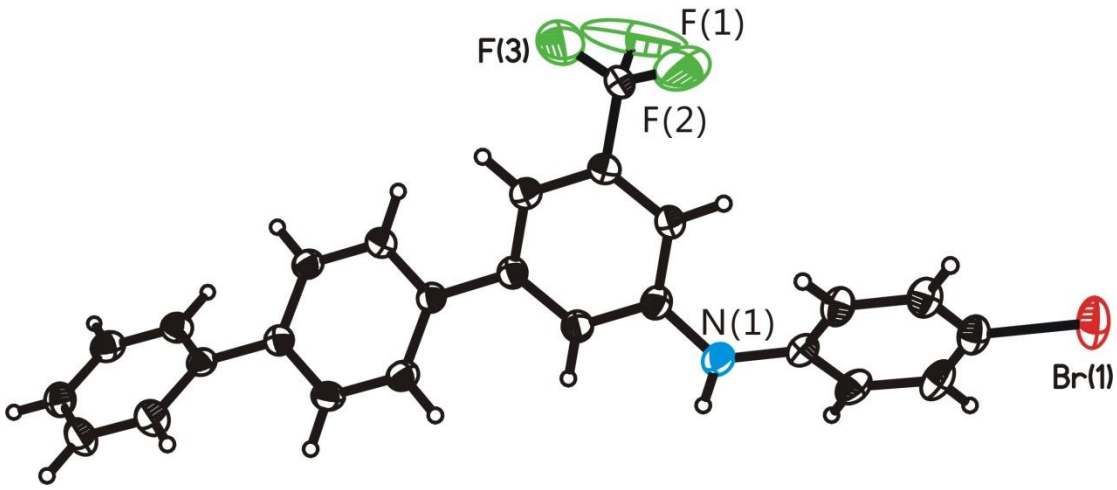
The crystal samples of **3g** and **4j** were prepared by slow volatilization in a $CH_2Cl_2/CDCl_3$ (3:1) solvent mixture. The suitable crystals of **3g** (CCDC 2180121) and **4j** (CCDC 2170084) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 ℃, 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.[5] Structure solution and refinement were carried out with the SHELXTL suite of programs. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

Crystal data and structure refinement for **3g** and **4j**.

Compound	**3g** (CCDC 2180121)	**4j** (CCDC 2170084)
Empirical formula	$C_{16}H_{11}F_3N_2O$	$C_{25}H_{17}BrF_3N$
Formula weight	304.27	468.31
Temperature/K	296	296
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
a/Å	12.9125(12)	9.9303(7)
b/Å	7.5482(8)	16.2965(11)
c/Å	15.0653(17)	12.8568(9)
α/°	90	90
β/°	104.114(4)	98.523(2)
γ/°	90	90
Volume/$Å^3$	1424.0(3)	2057.6(2)
Z	4	4
Density (calc.)/cm^3	1.419	1.512
Absorption coefficient /mm^{-1}	0.117	2.036
F(000)	624.0	944.0
Crystal size/mm	0.1 ×0.1 ×0.1	0.10 × 0.10 × 0.05
Theta range for data collection / °	4.77 to 50.18	4.06 to 50.14
Reflections collected	13918	33763
Independent reflections	2514 [Rint = 0.0691]	3657 [Rint = 0.0576]
Data/restraints/parameters	2514/0/200	3657/6/271
Goodness-of-fit on F^2	1.027	1.053
Final R indexes [I>=2σ (I)]	1.027	0.0888
Final R indexes [all data]	wR_2 =0.1287	wR2 = 0.1474
Largest diff. peak and hole / e $Å^{-3}$	0.26/-0.23	1.05/-0.83



ORTEP diagram of compound 3g. Thermal ellipsoids are drawn at 40% probability



ORTEP diagram of compound 4j. Thermal ellipsoids are drawn at 40% probabilityReferences

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1. H.-Y. Hao, Y.-J. Mao, Z.-Y. Xu, S.-J. Lou and D.-Q. Xu, Selective Cross-Dehydrogenative C(sp3)–H Arylation with Arenes, *Org. Lett.*, 2020, **22**, 2396-2402.
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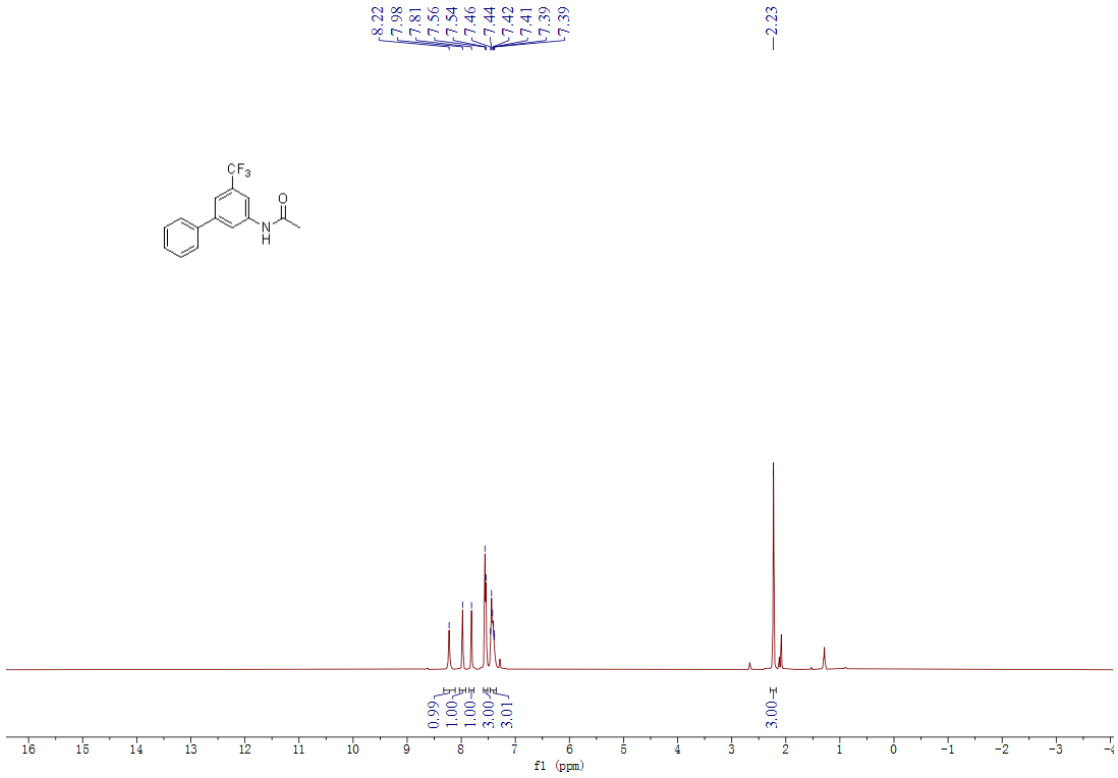
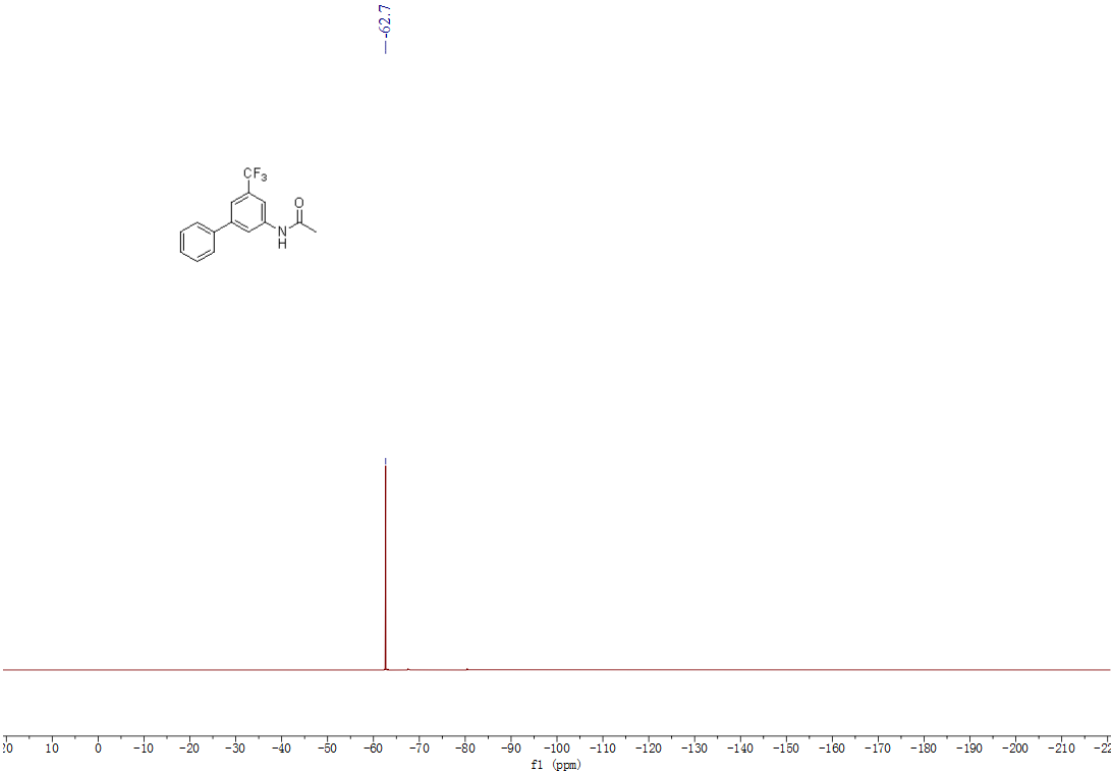
3. N. C. Lungu, A. Dépret, F. Delattre, G. G. Surpateanu, F. Cazier, P. Woisel, P. Shirali and G. Surpateanu, Synthesis of a new fluorinated fluorescent β-cyclodextrin sensor, *J. Fluorine Chem.*, 2005, **126**, 385-388.
4. Y. Fukazawa, V. Y. Vaganov, S. A. Shipilovskikh, A. E. Rubtsov and A. V. Malkov, Stereoselective Synthesis of Atropisomeric Bipyridine N,N′-Dioxides by Oxidative Coupling, *Org. Lett.*, 2019, **21**, 4798-4802.
5. 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

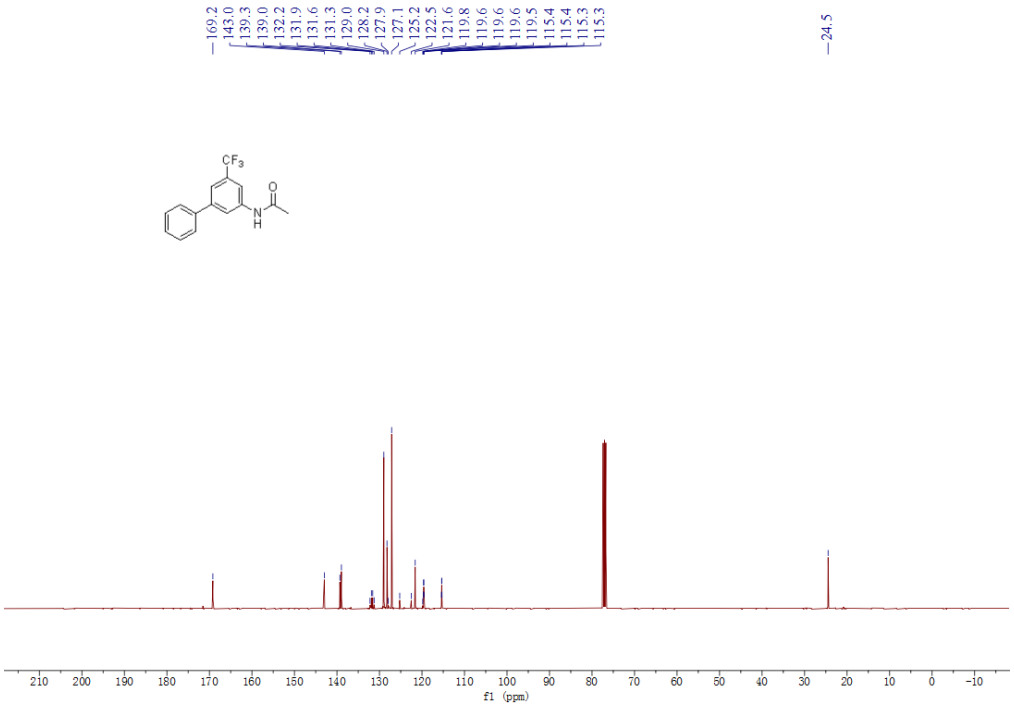
^{1}H NMR spectrum of **3a** in $CDCl_3$



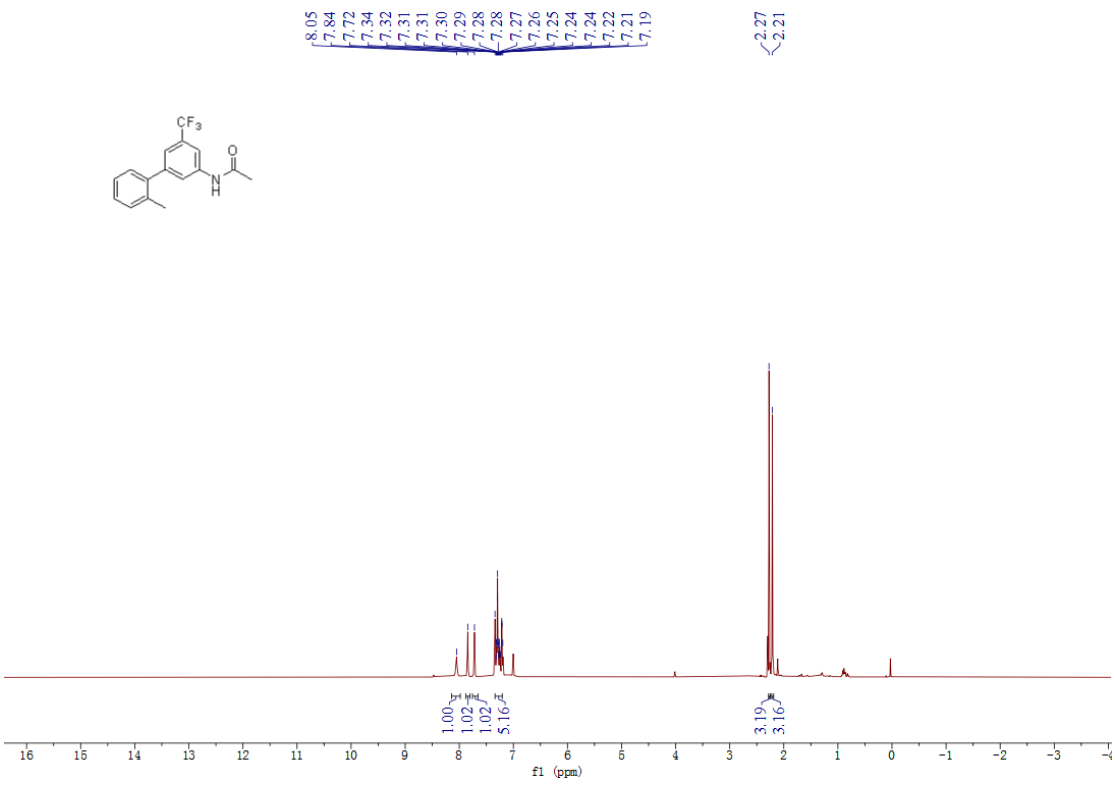
^{19}F NMR spectrum of **3a** in $CDCl_3$



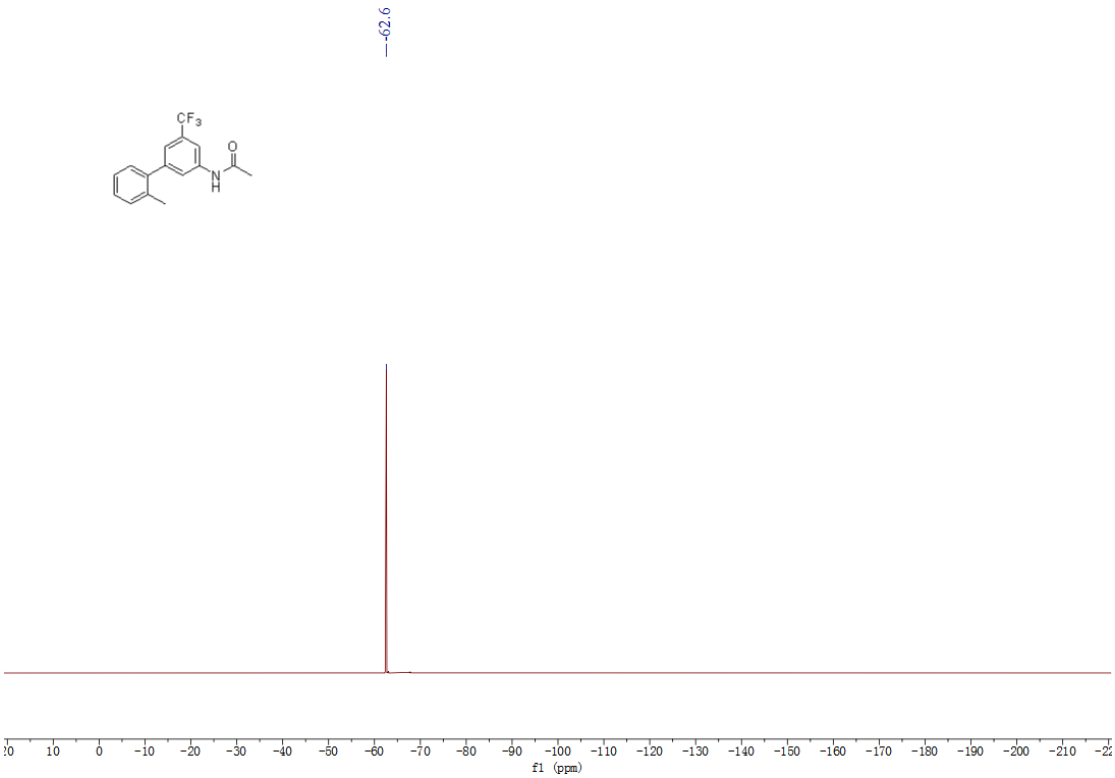
101 MHz ^{13}C NMR spectrum of **3a** in $CDCl_3$



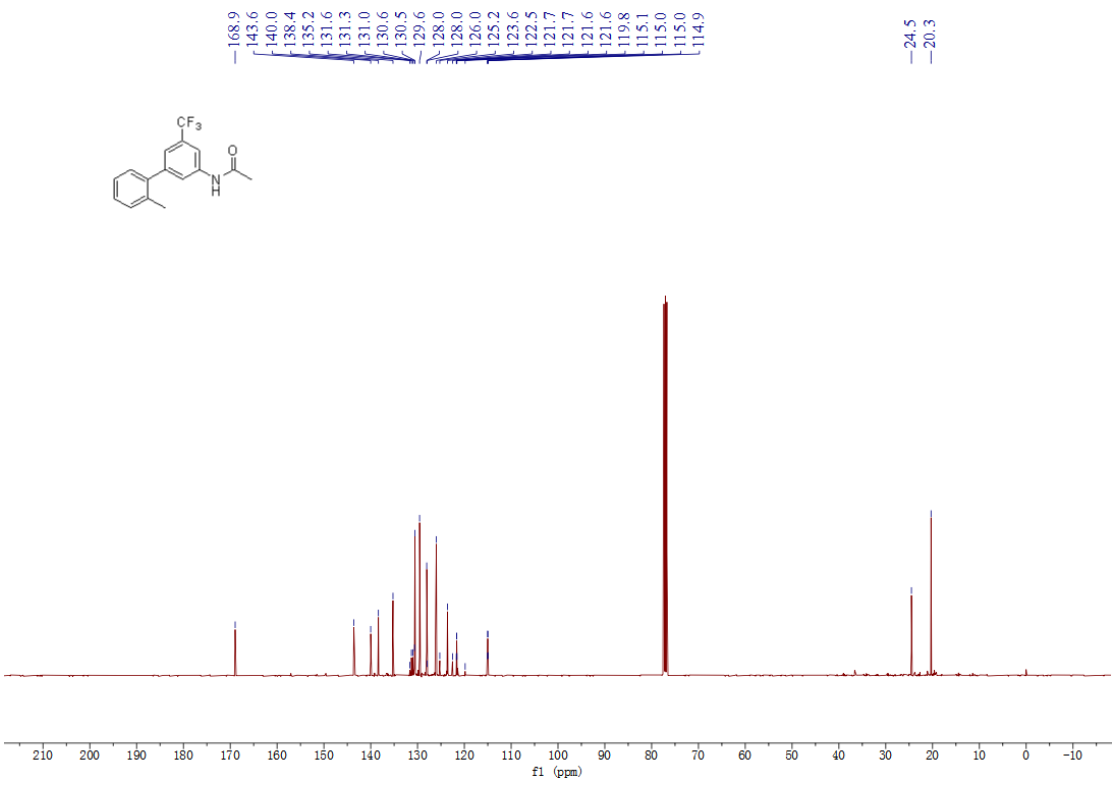
^{1}H NMR spectrum of **3b** in $CDCl_3$



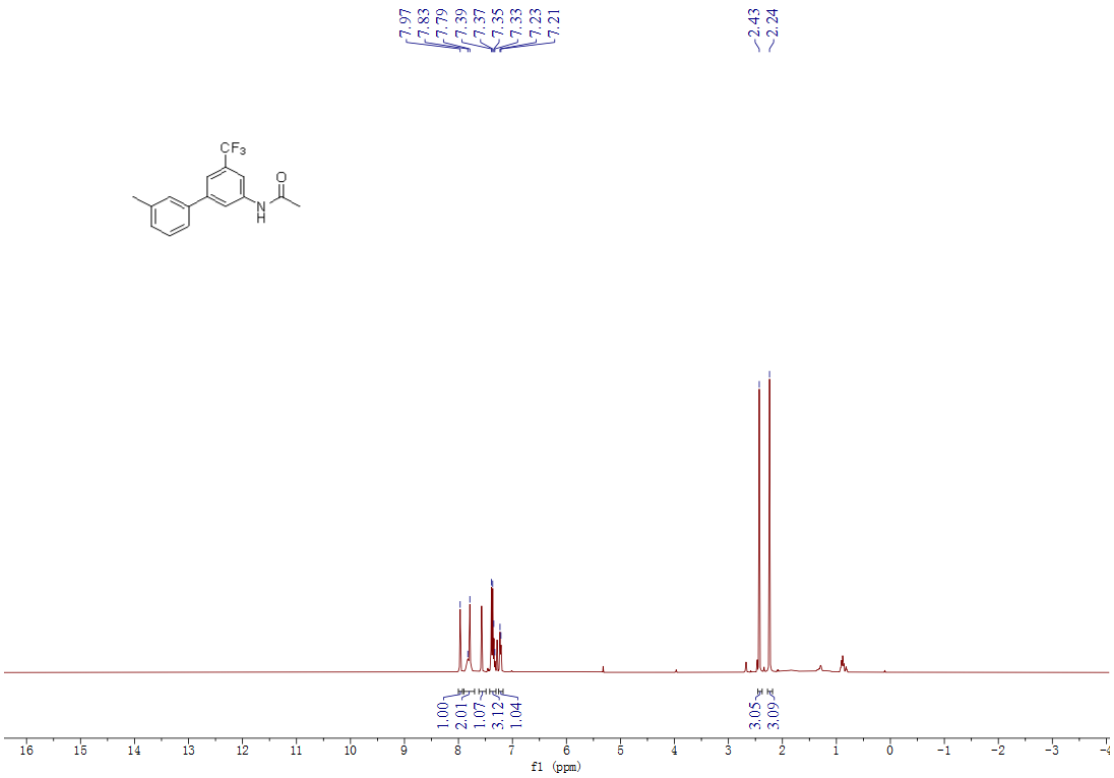
^{19}F NMR spectrum of **3b** in $CDCl_3$



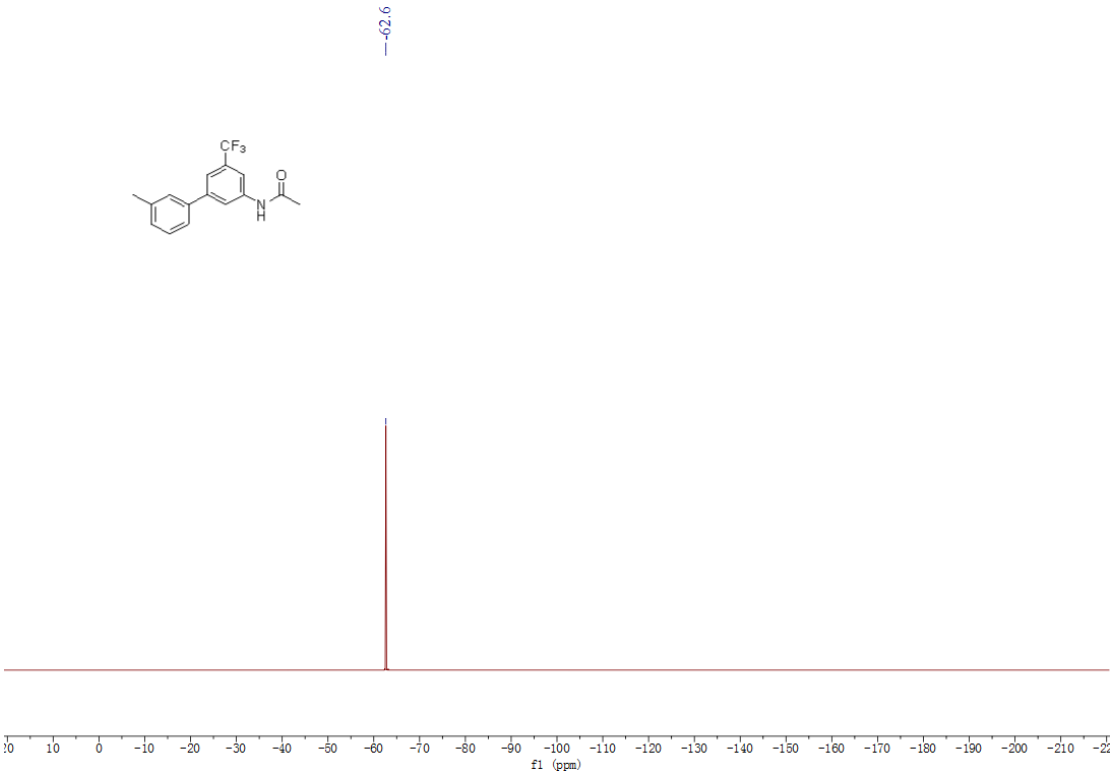
^{13}C NMR spectrum of **3b** in $CDCl_3$



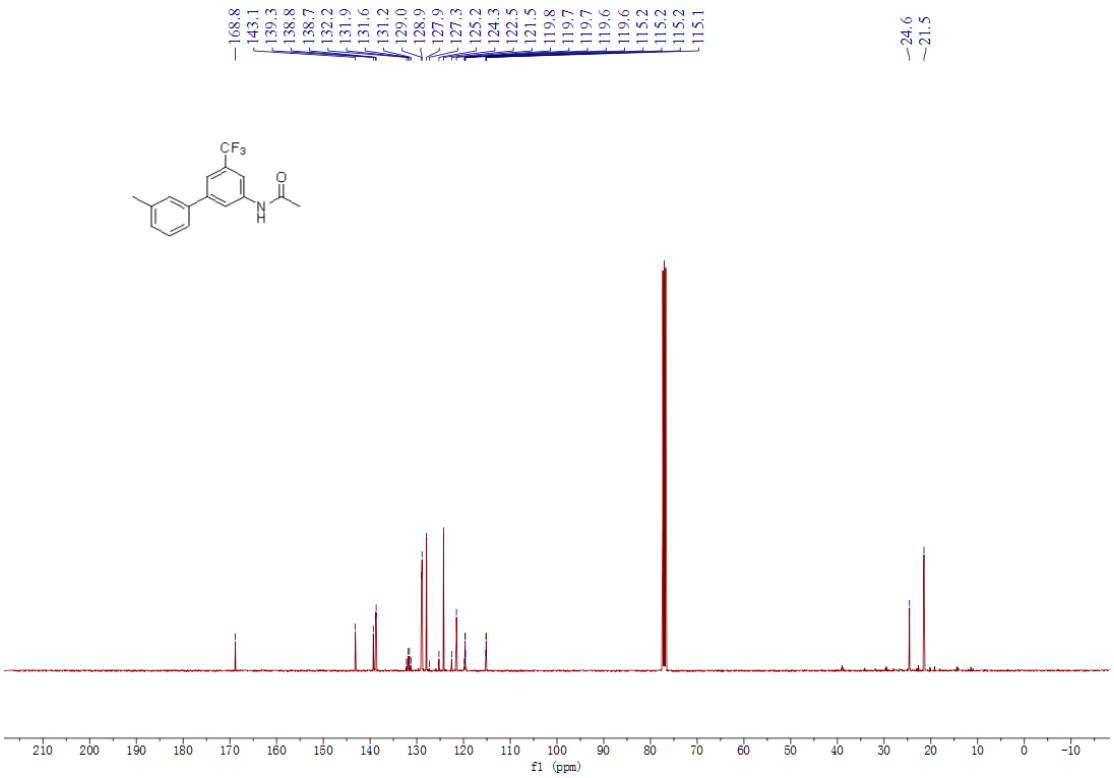
^{1}H NMR spectrum of **3c** in $CDCl_3$



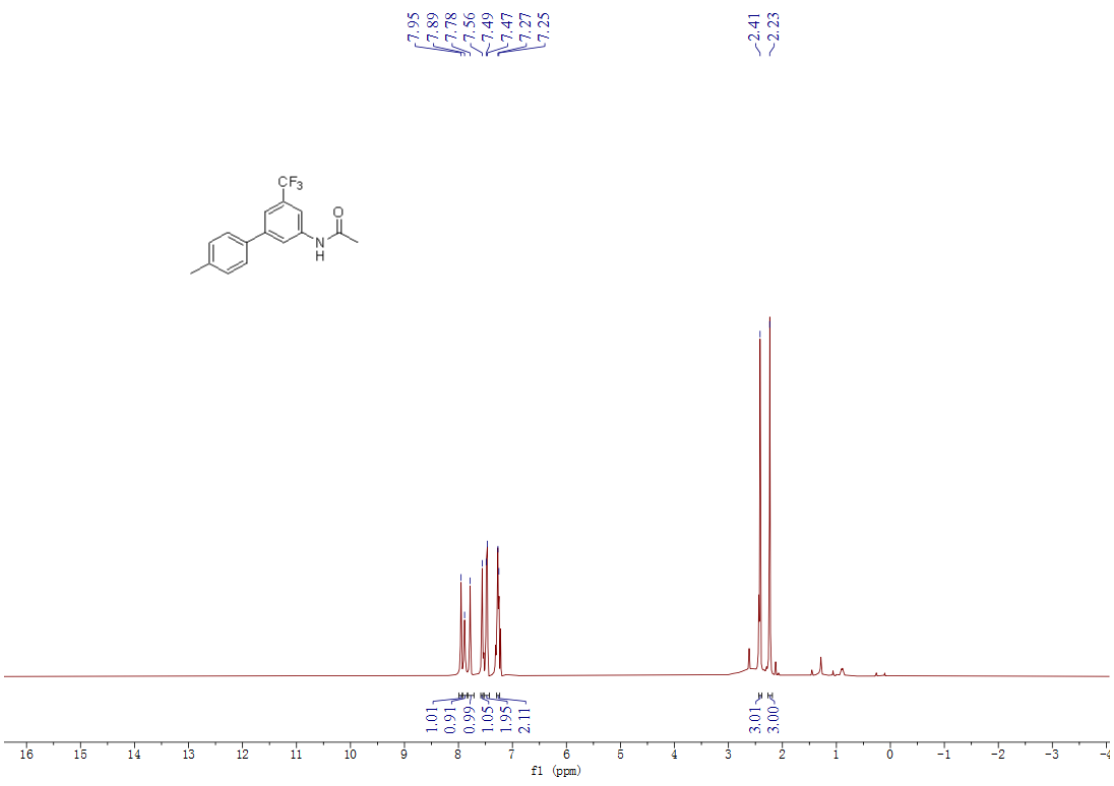
^{19}F NMR spectrum of **3c** in $CDCl_3$



^{13}C NMR spectrum of **3c** in $CDCl_3$



^{1}H NMR spectrum of **3d** in $CDCl_3$



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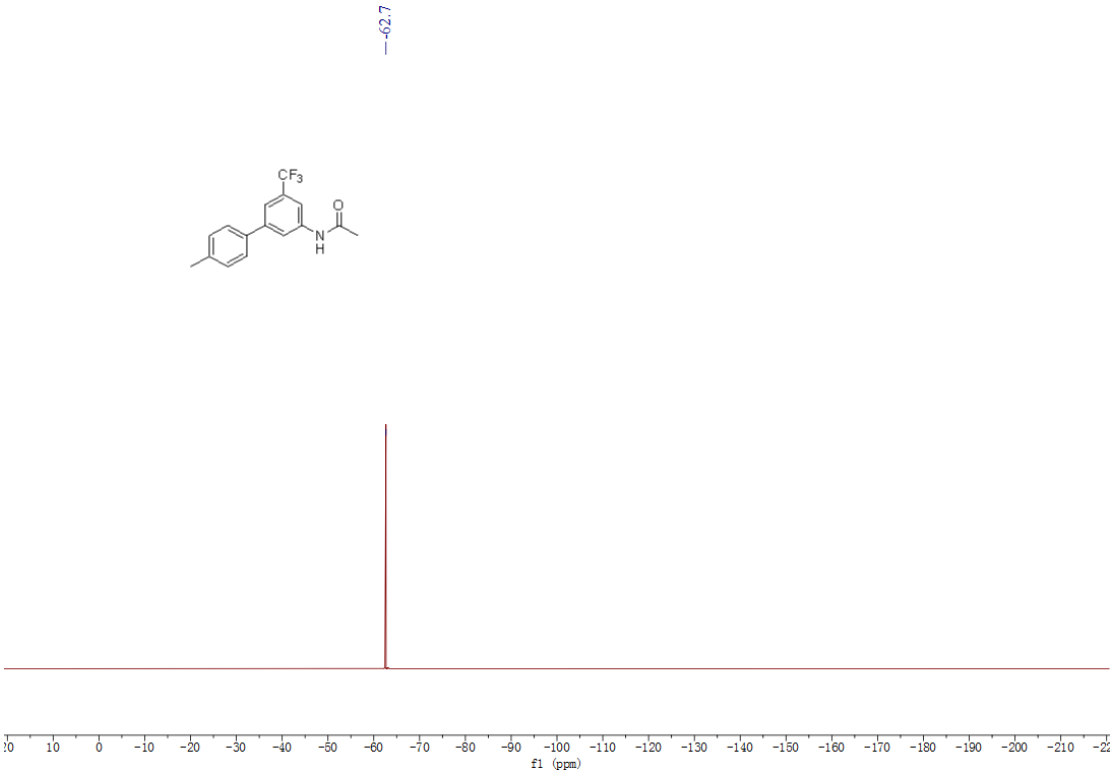

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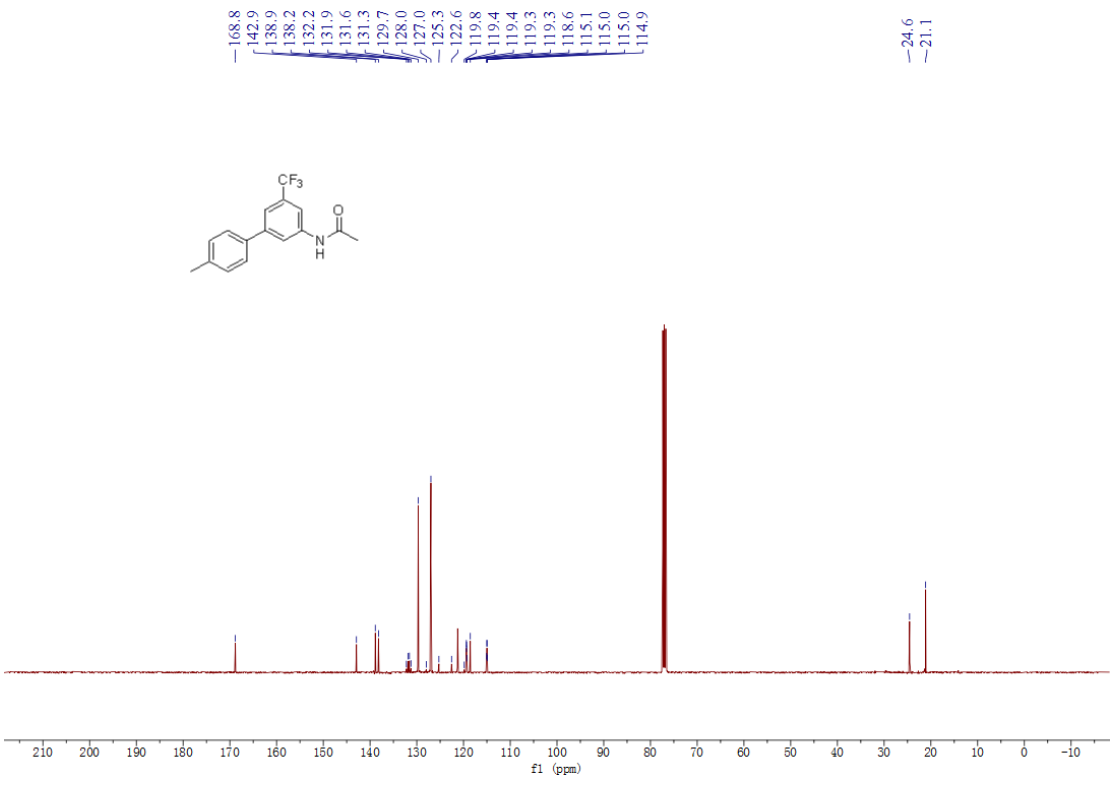
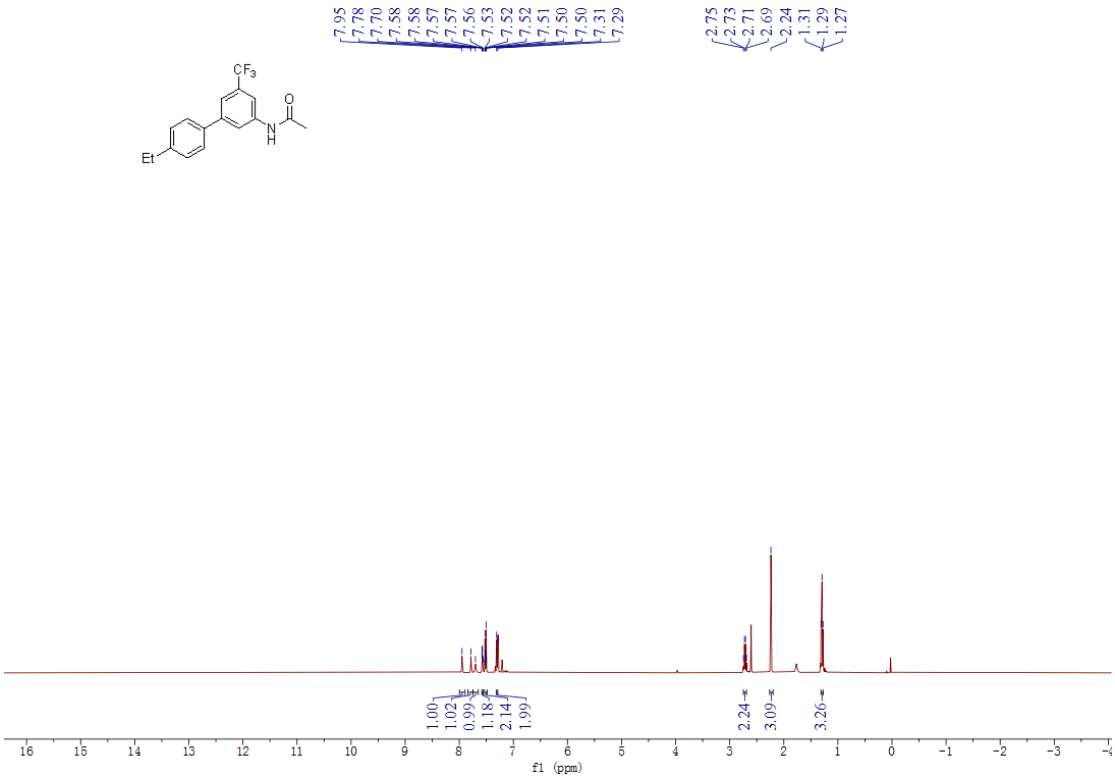
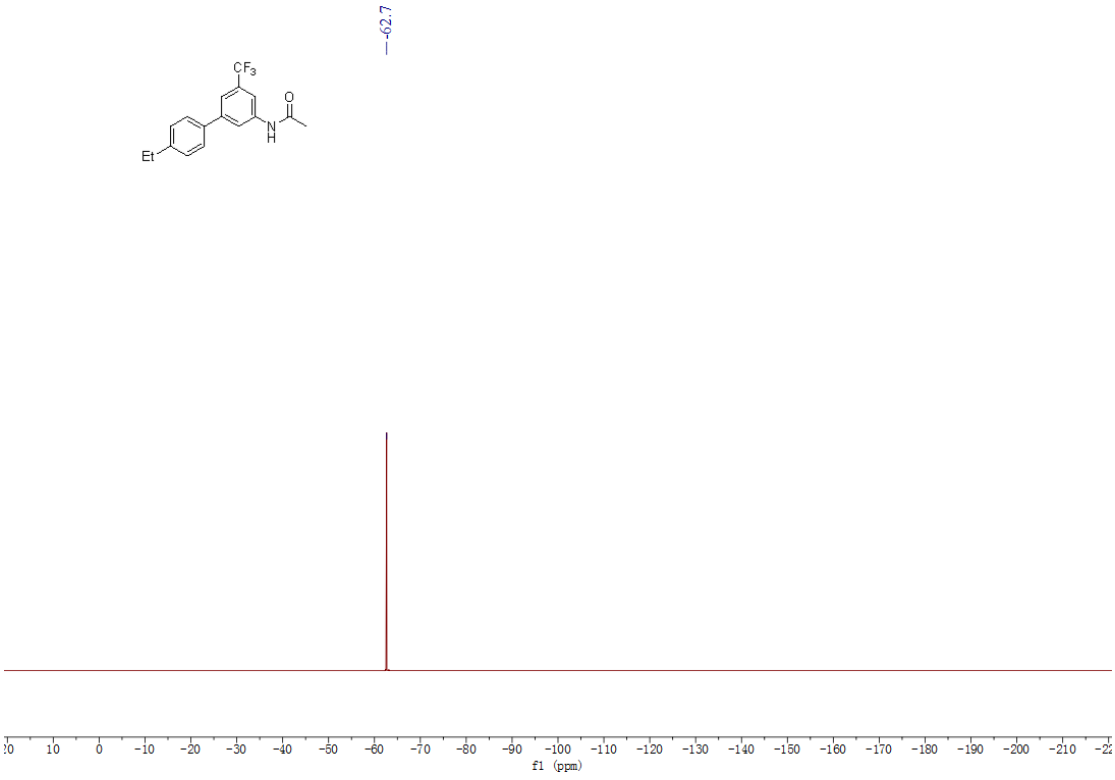


^{1}H NMR spectrum of **3e** in $CDCl_3$



^{19}F NMR spectrum of **3e** in $CDCl_3$



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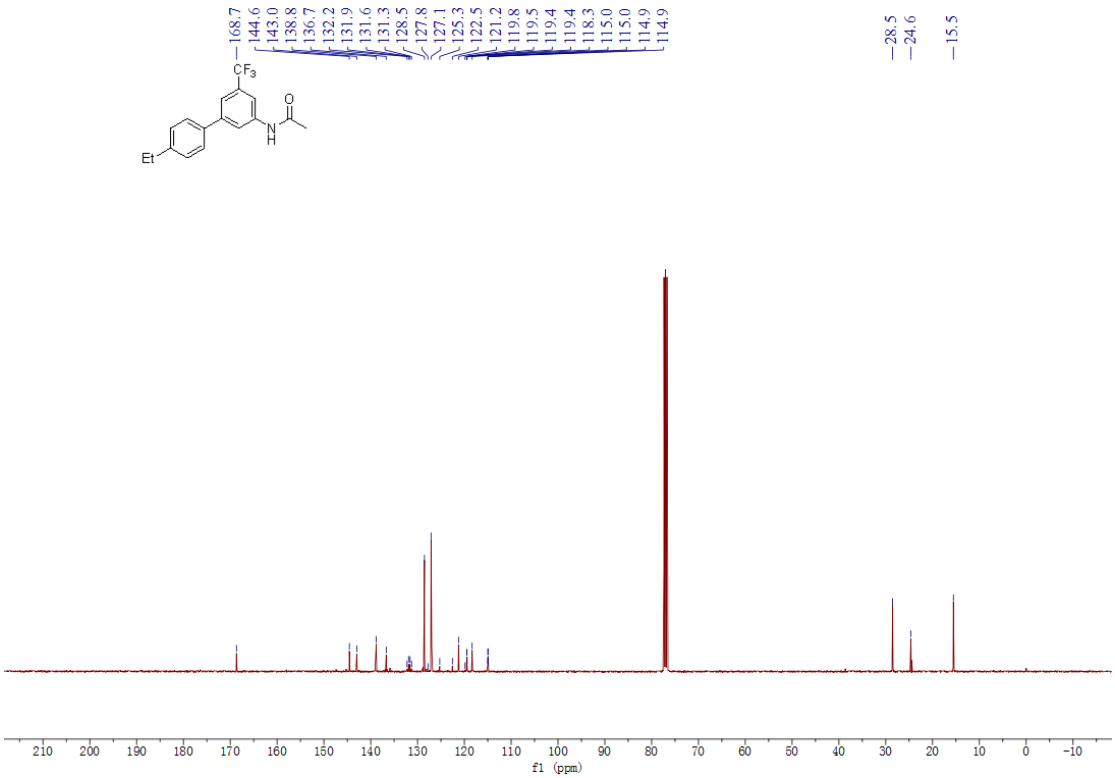
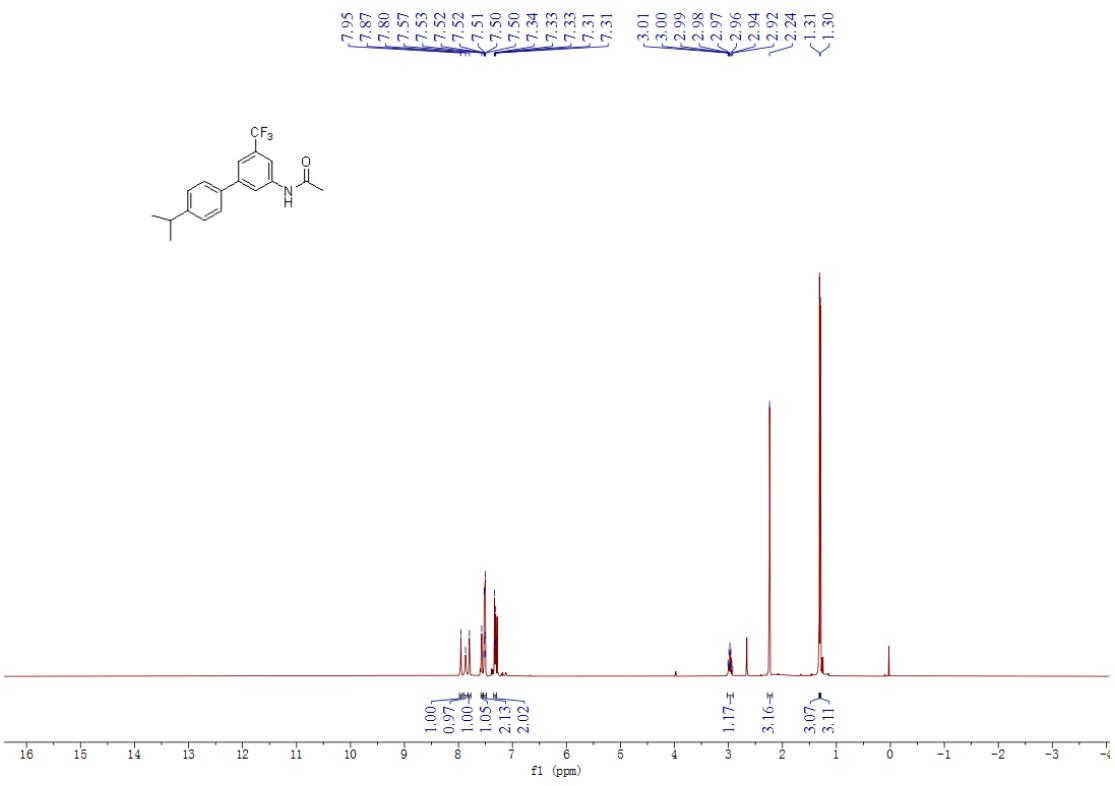


^{1}H NMR spectrum of **3f** in $CDCl_3$



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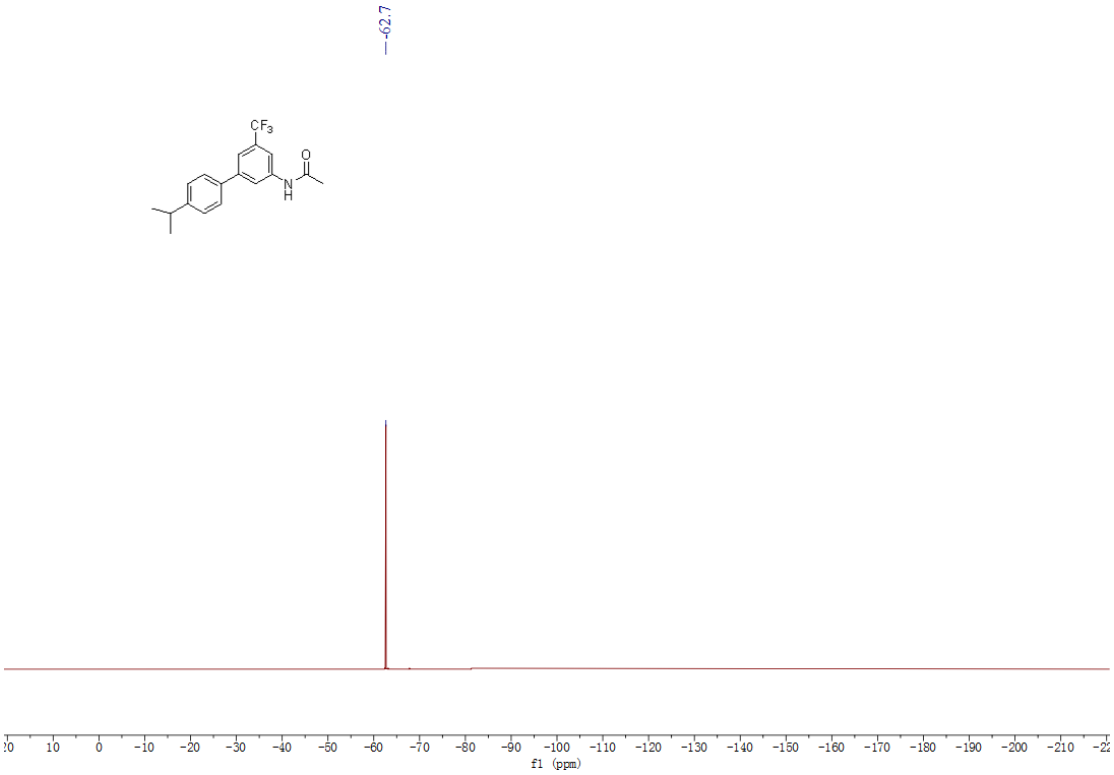

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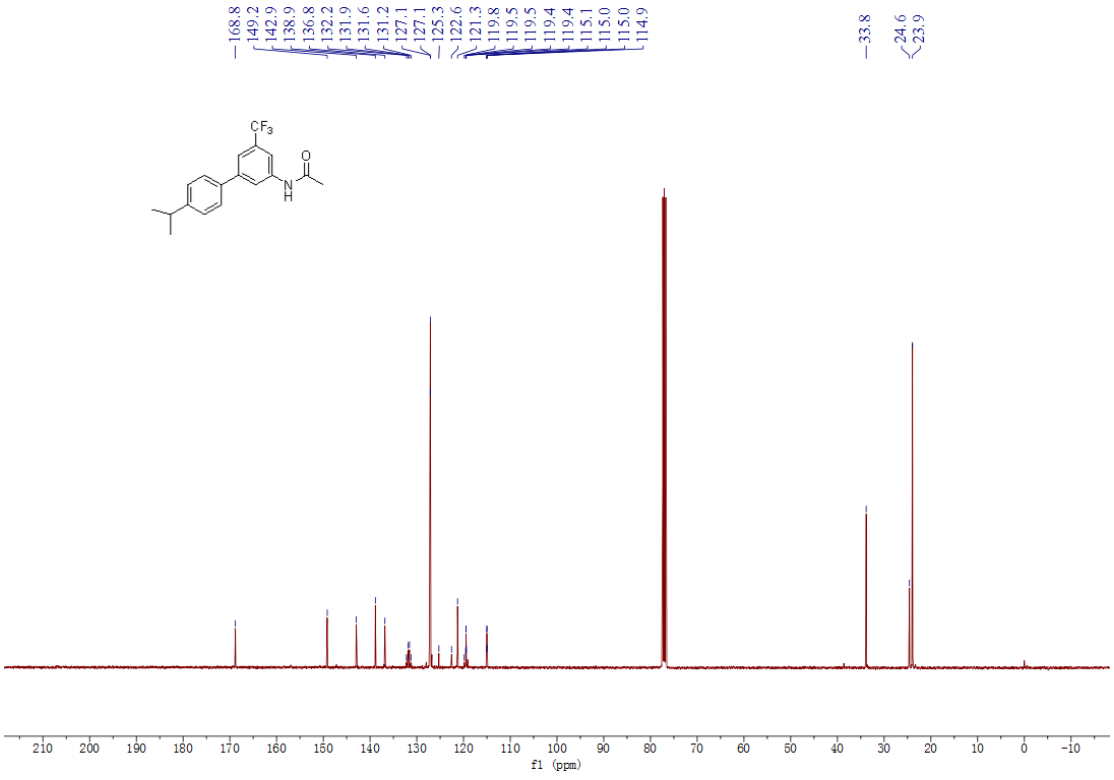
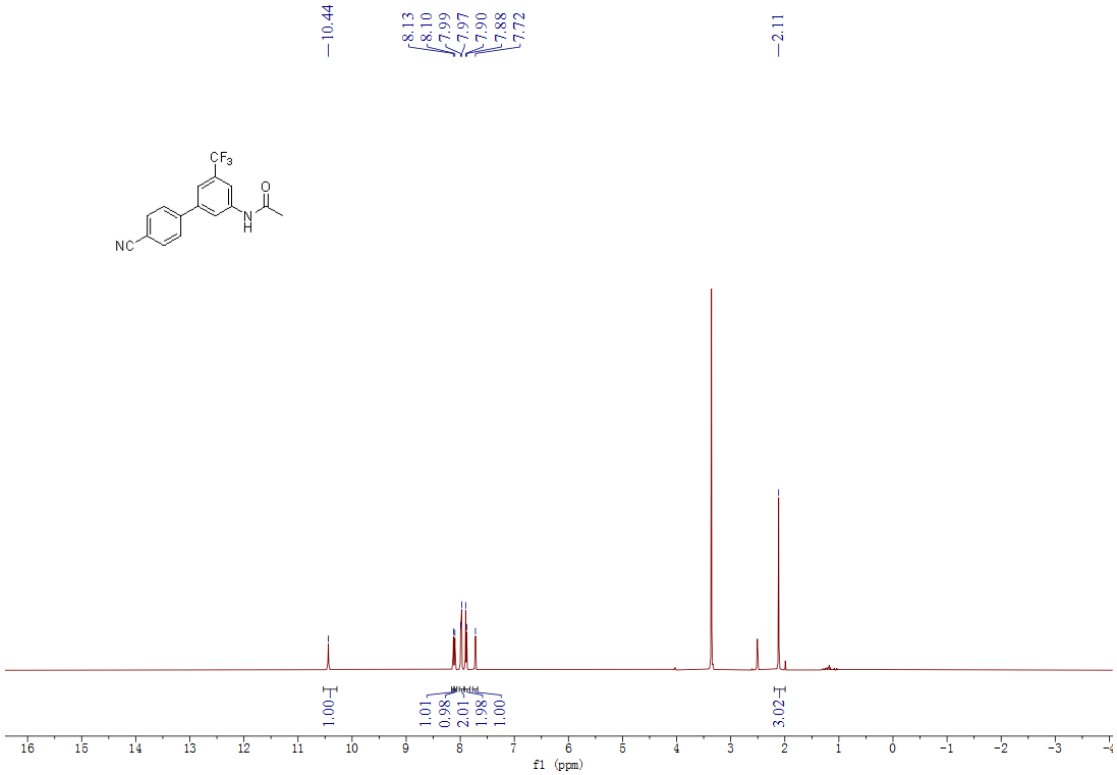


^{1}H NMR spectrum of **3g** in DMSO-d_6



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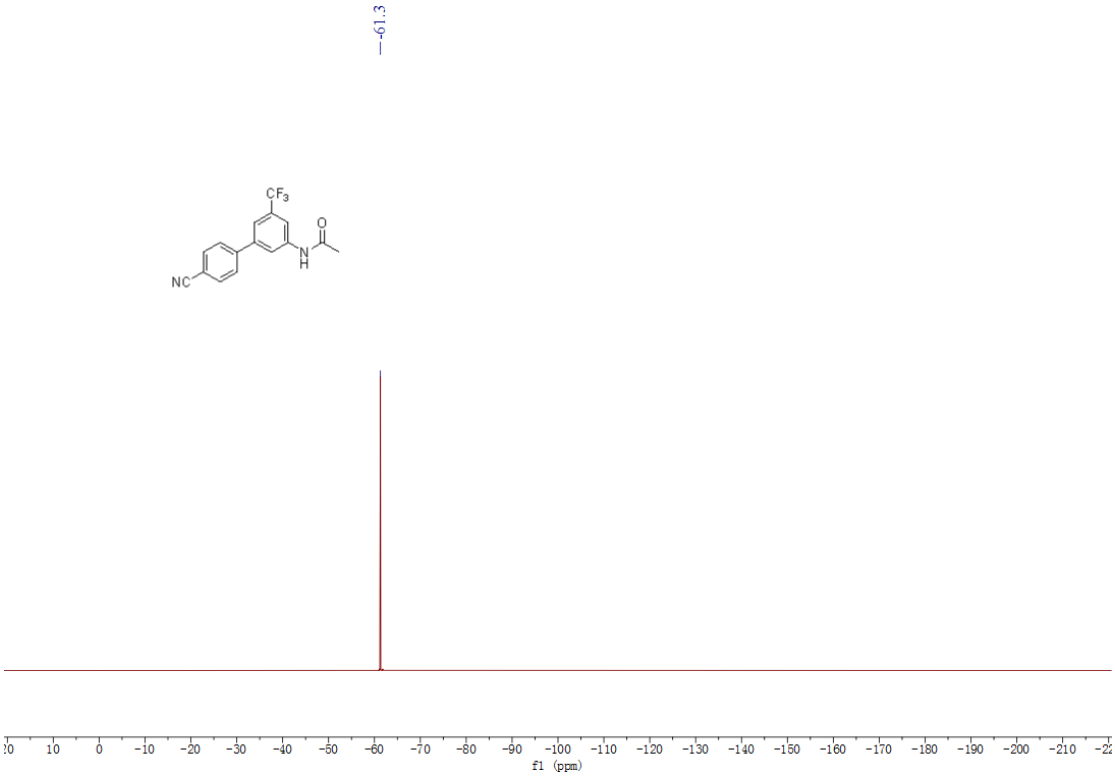

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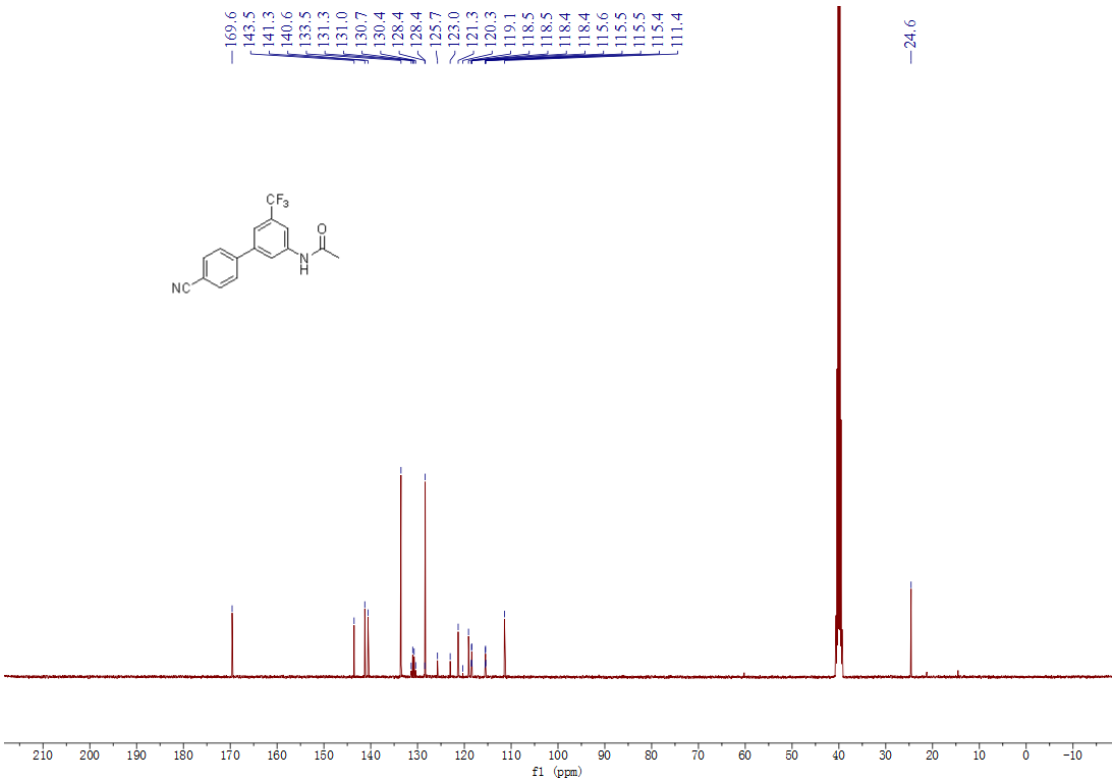
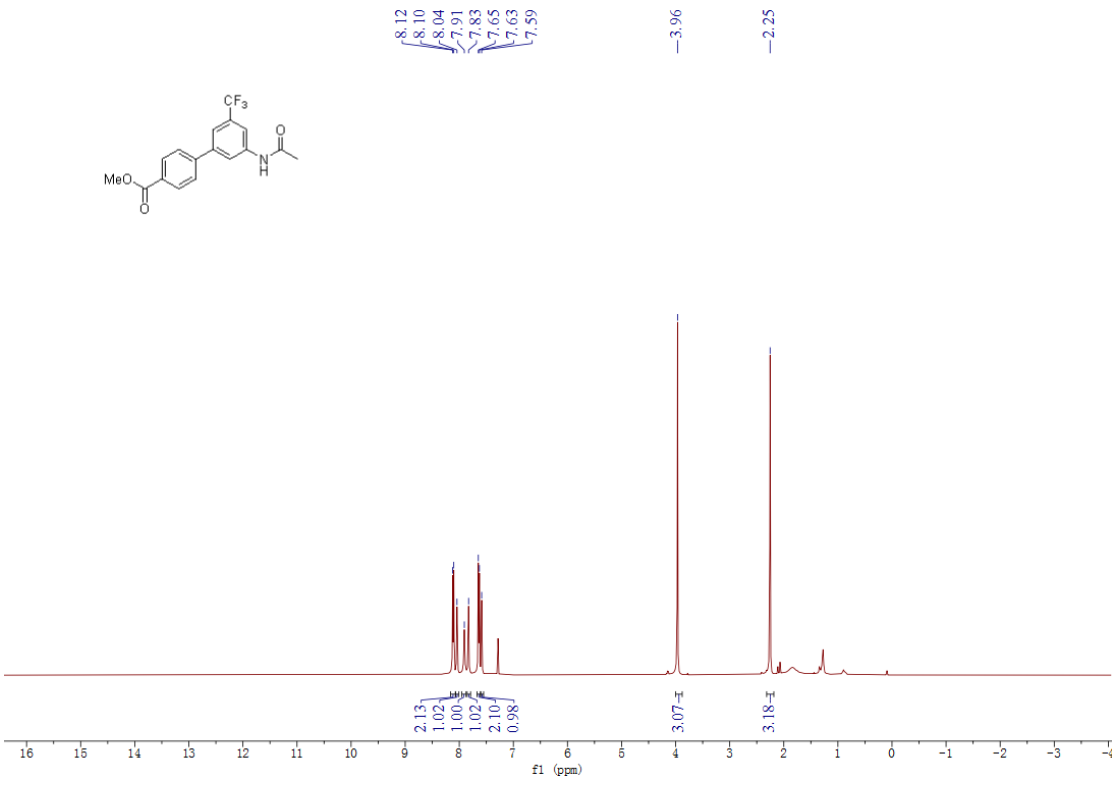
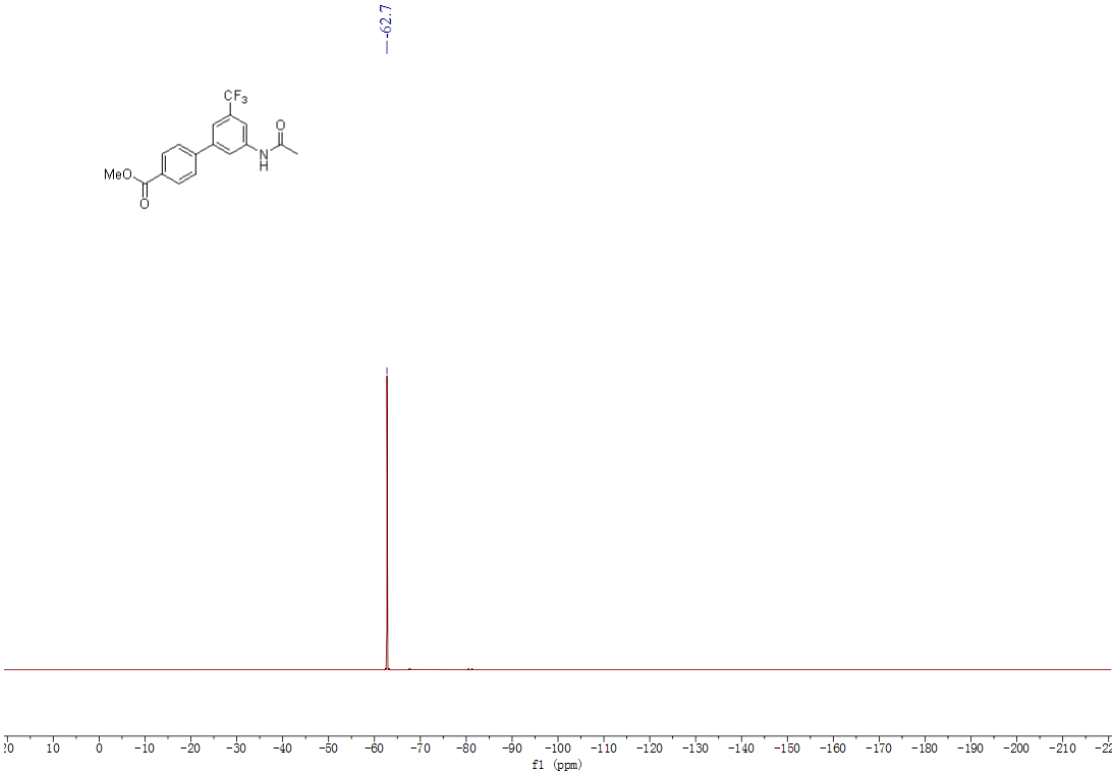


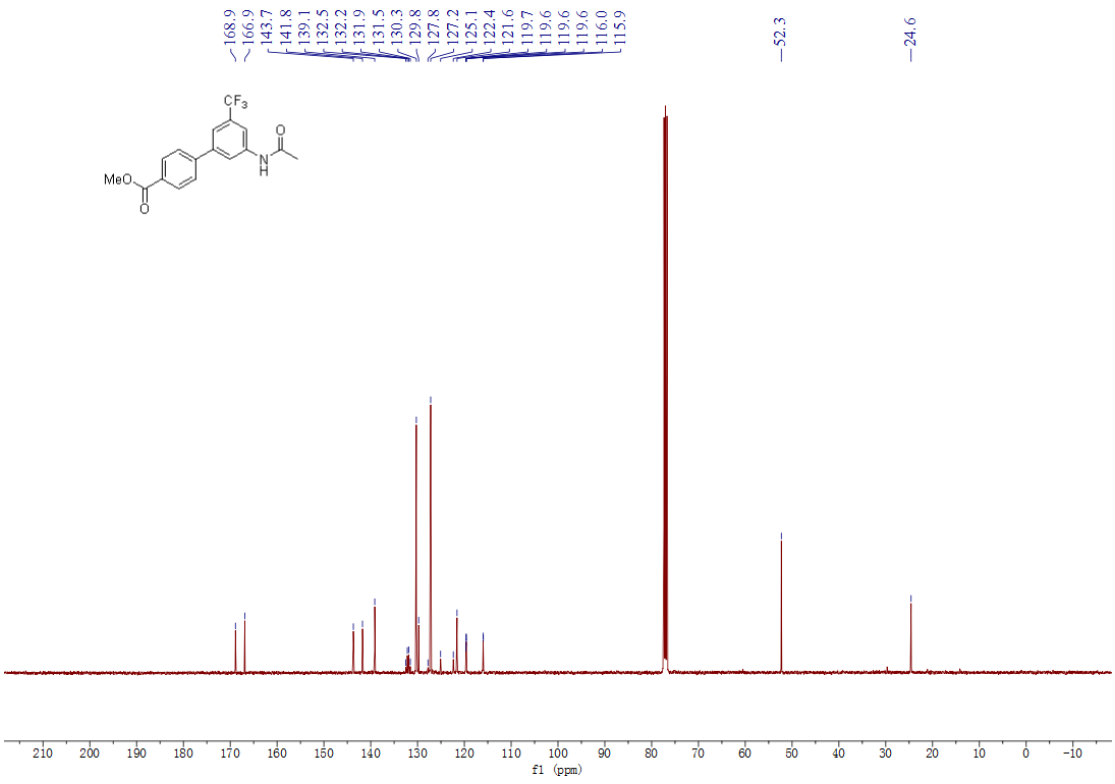
^{1}H NMR spectrum of **3h** in $CDCl_3$



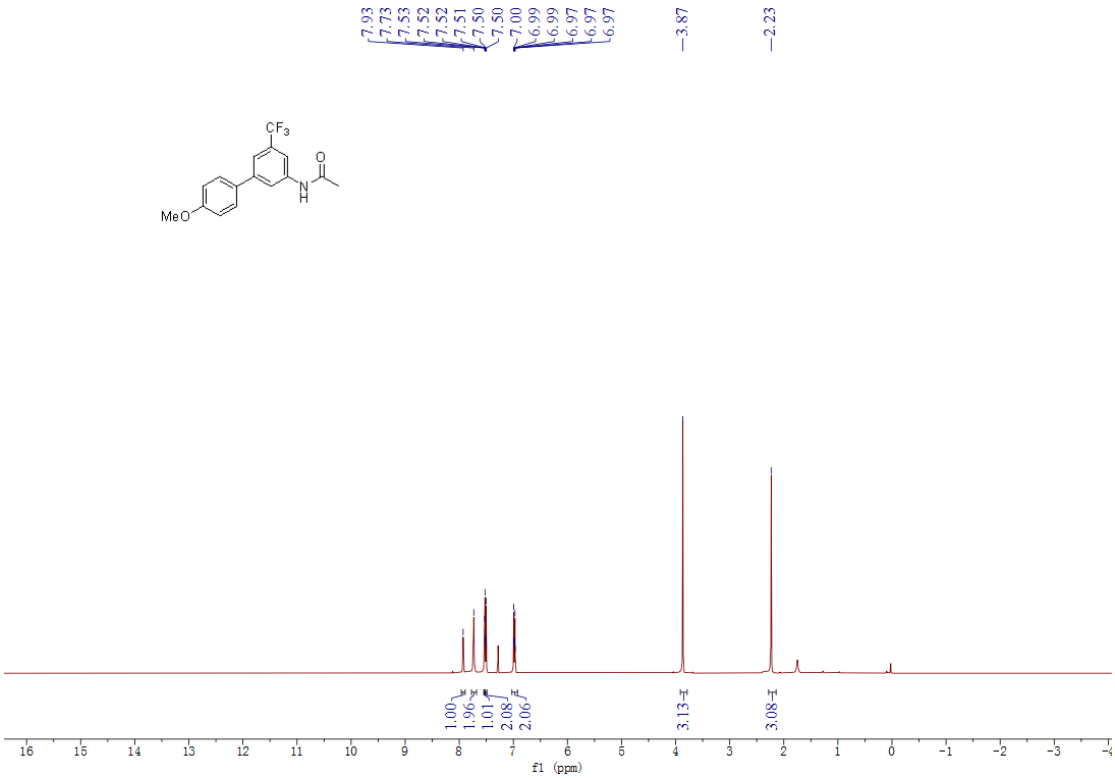
^{19}F NMR spectrum of **3h** in $CDCl_3$



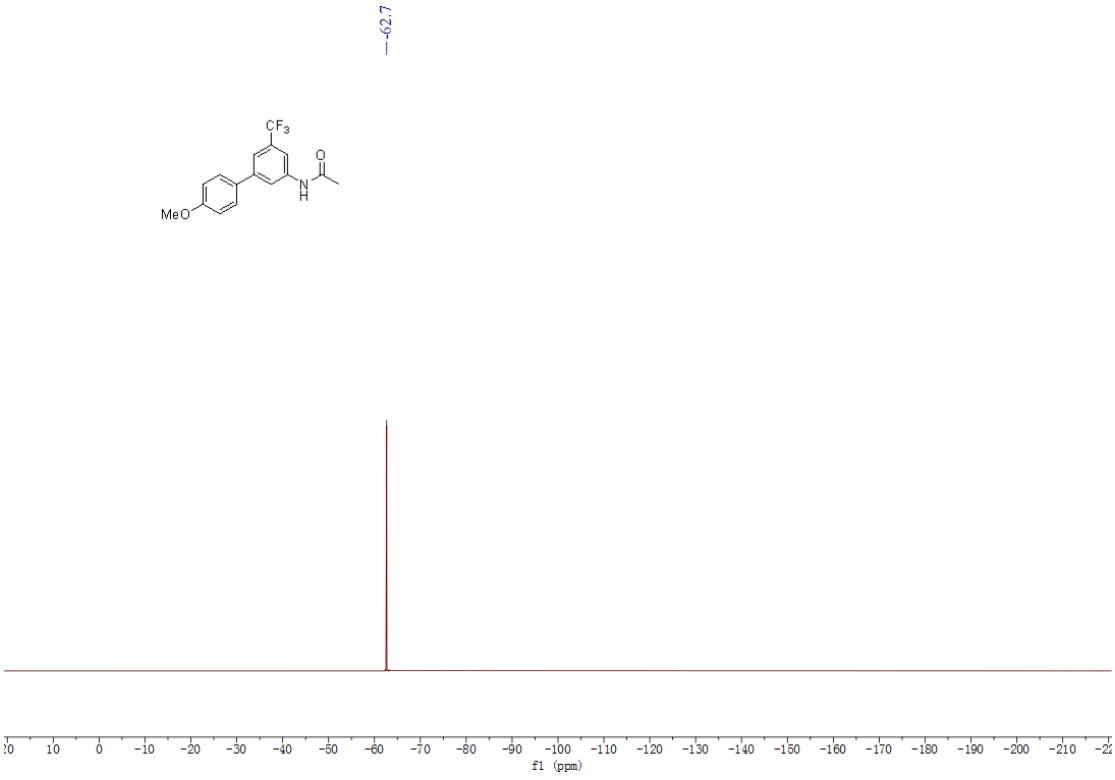
^{13}C NMR spectrum of **3h** in $CDCl_3$



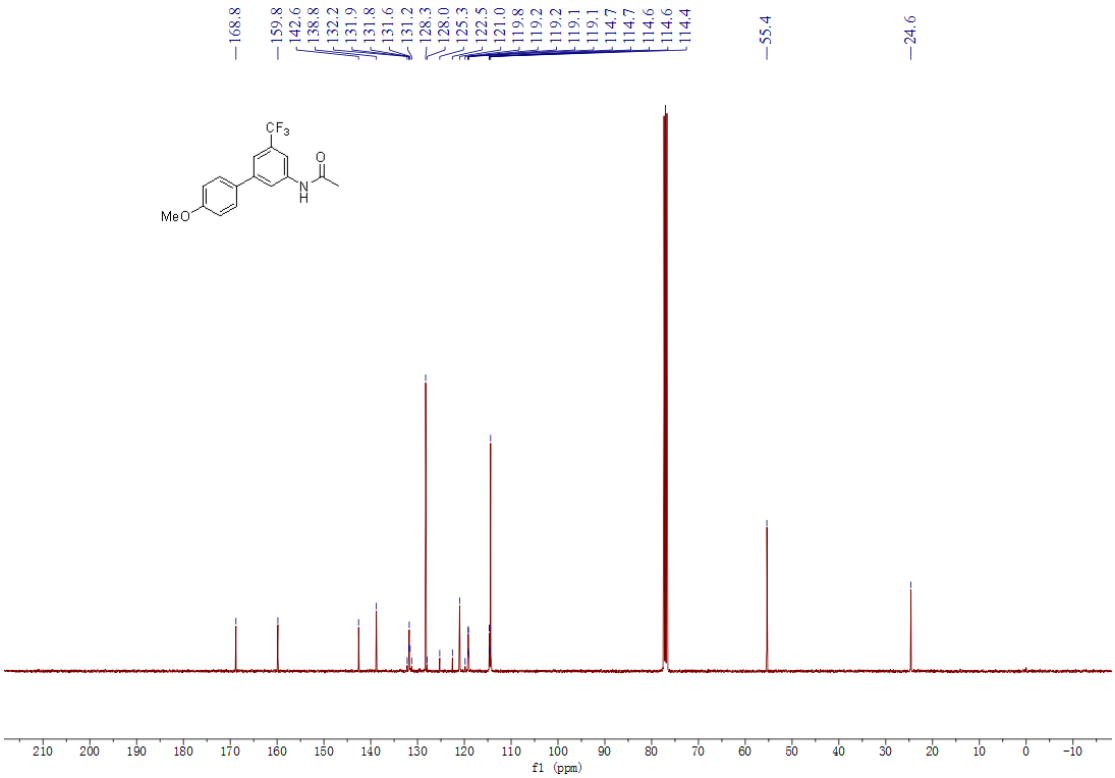
^{1}H NMR spectrum of **3i** in $CDCl_3$



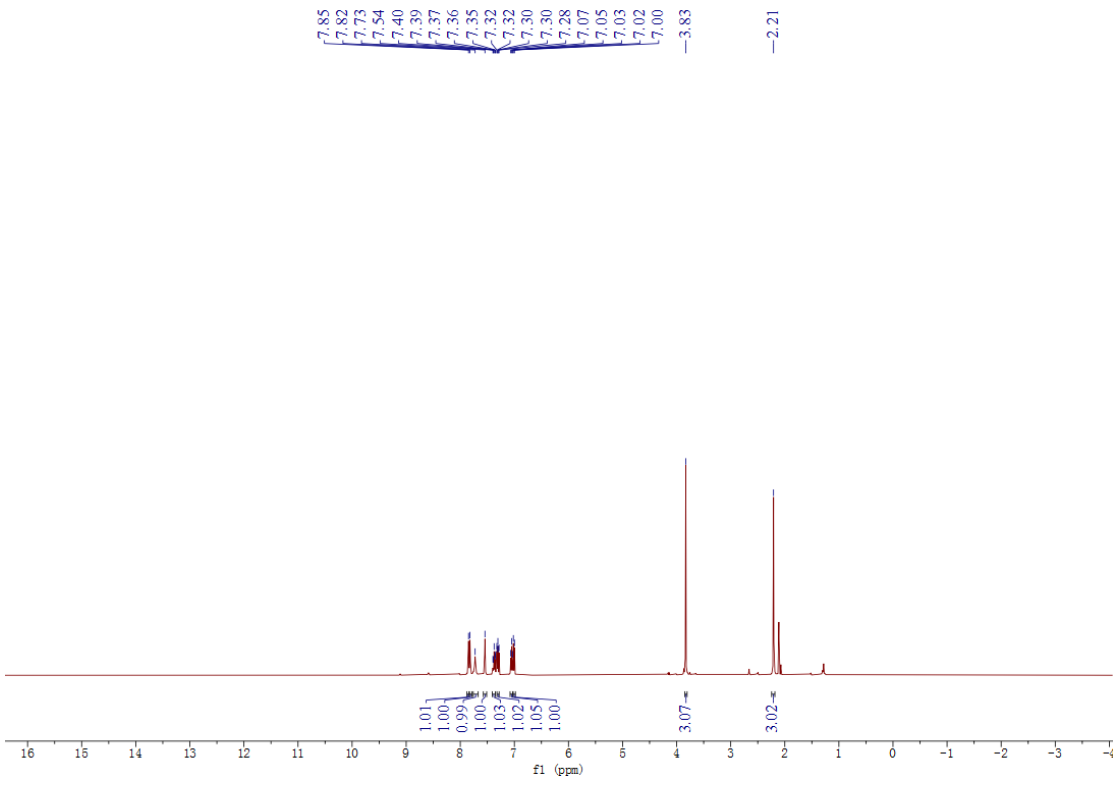
^{19}F NMR spectrum of **3i** in $CDCl_3$



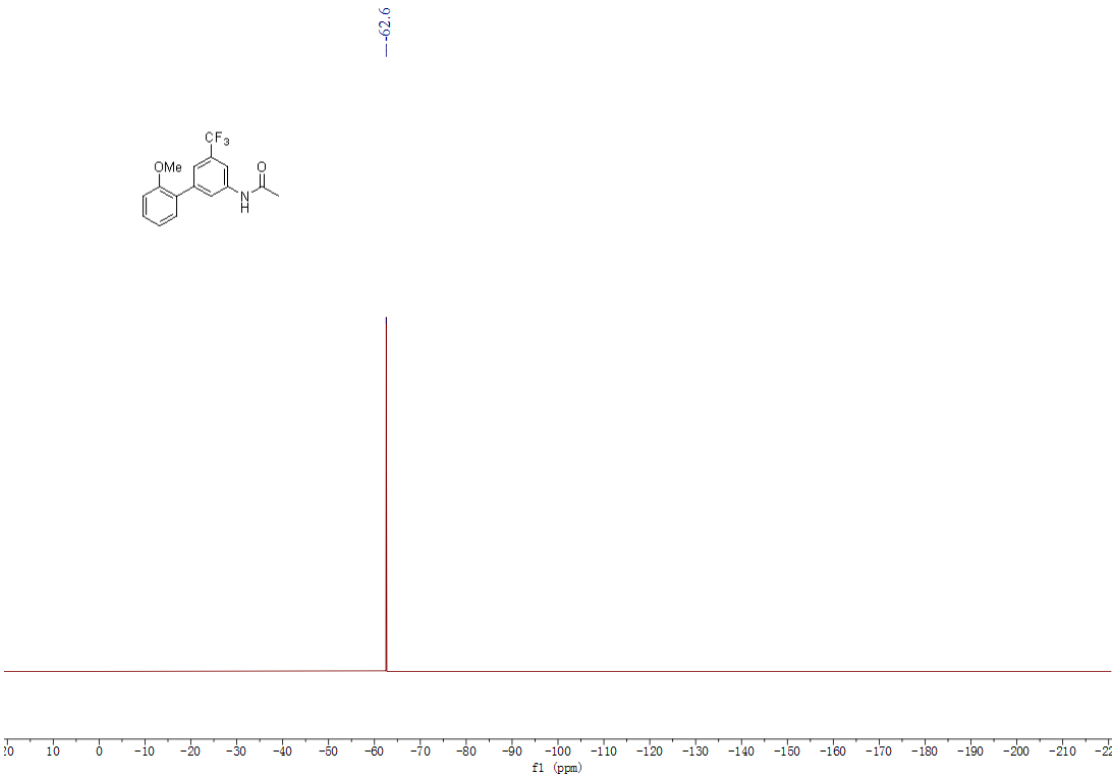
^{13}C NMR spectrum of **3i** in $CDCl_3$



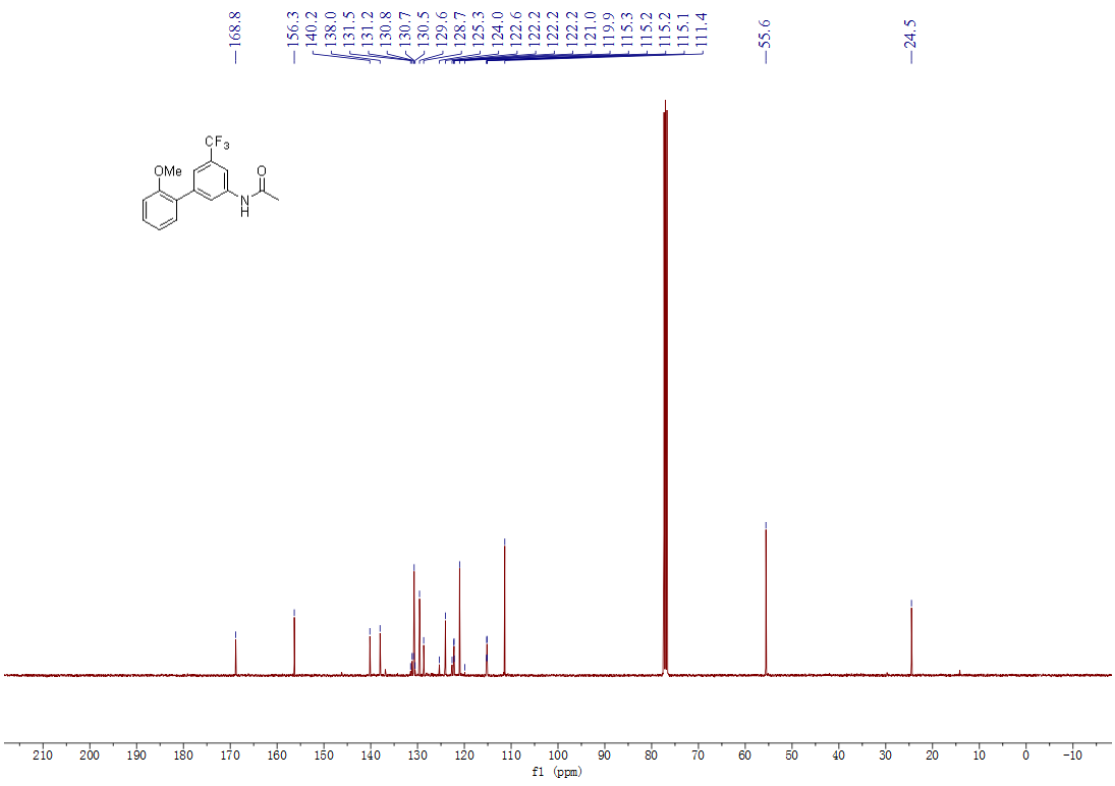
^{1}H NMR spectrum of **3j** in $CDCl_3$



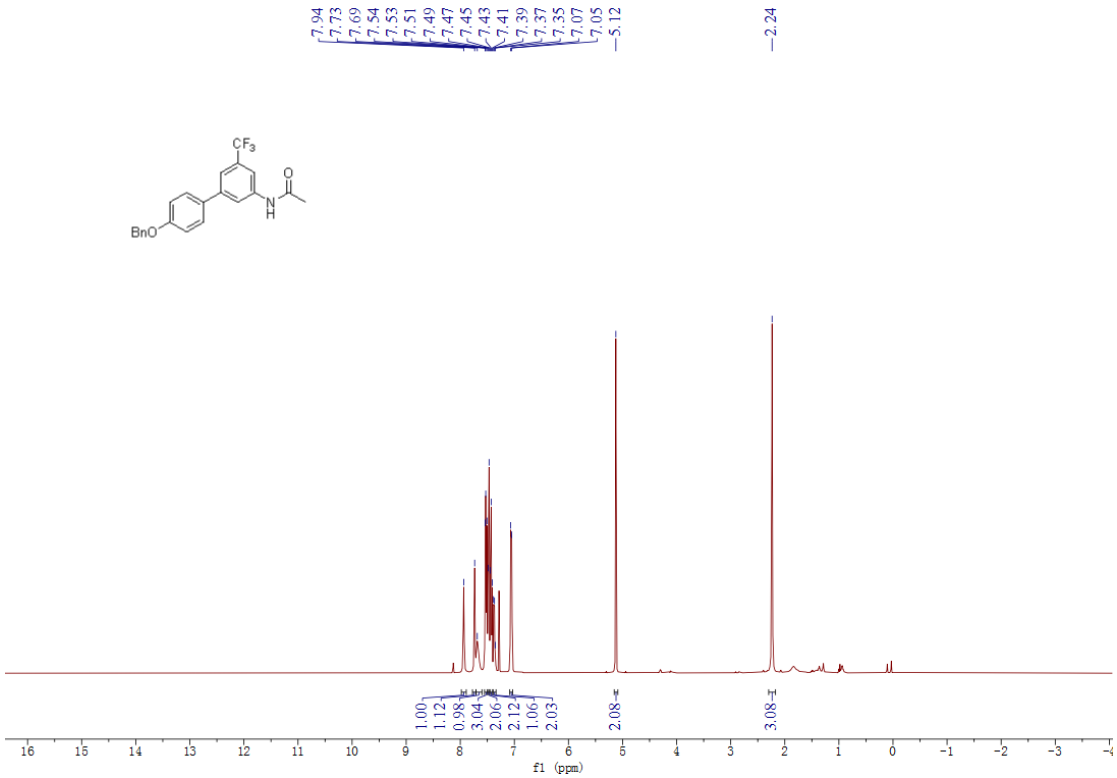
^{19}F NMR spectrum of **3j** in $CDCl_3$



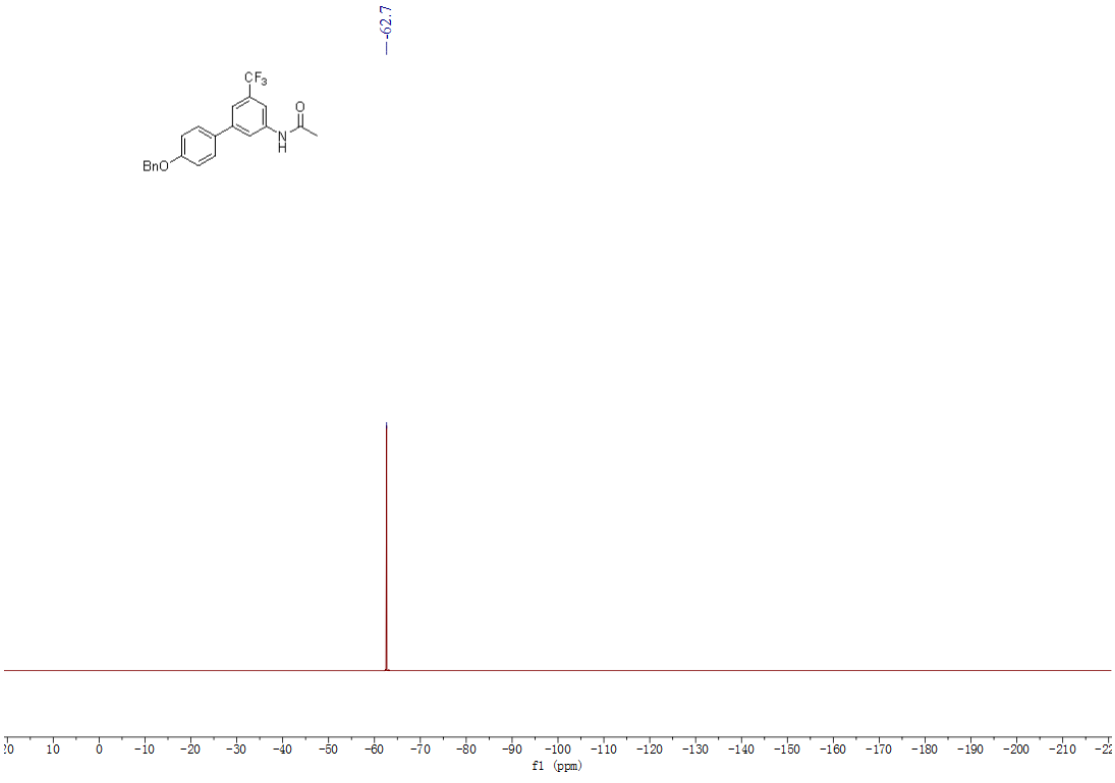
^{13}C NMR spectrum of **3j** in $CDCl_3$



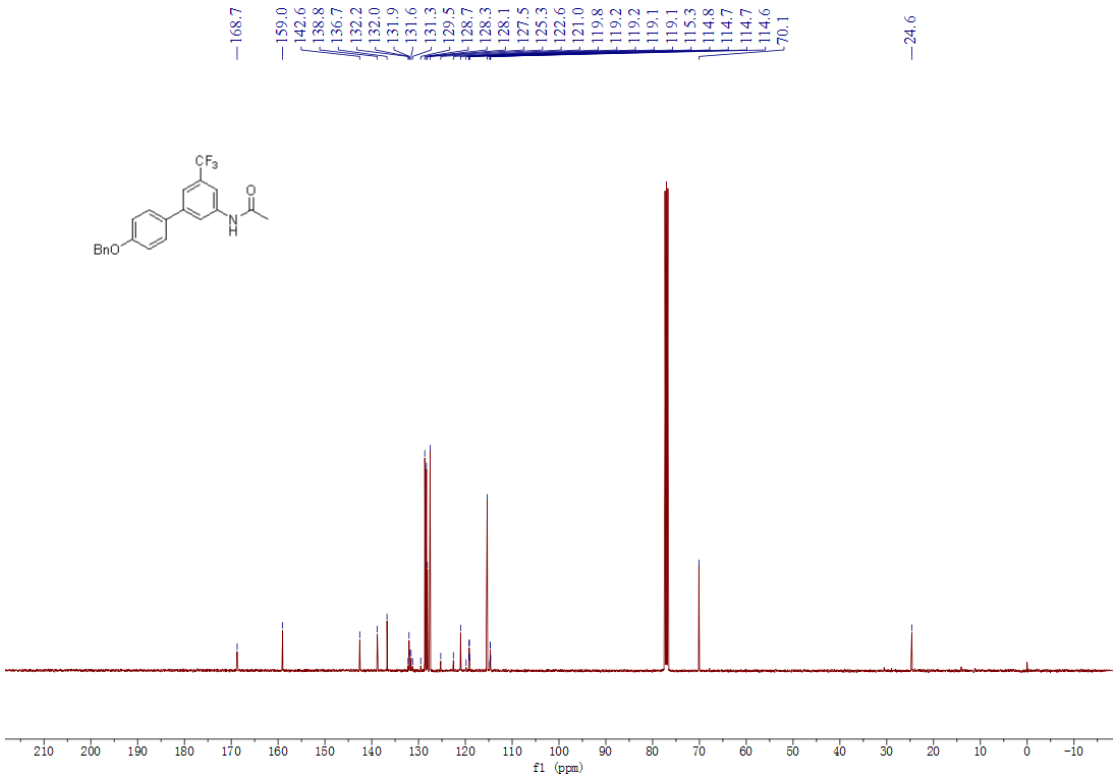
^{1}H NMR spectrum of **3k** in $CDCl_3$



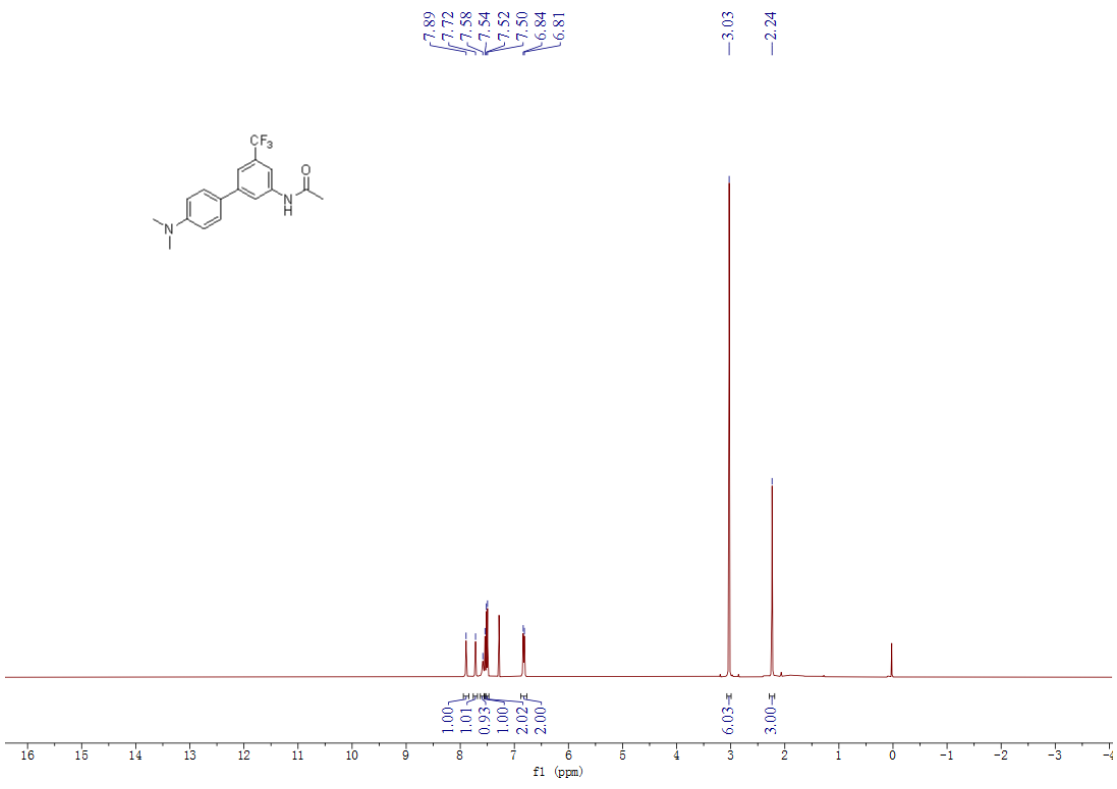
^{19}F NMR spectrum of **3k** in $CDCl_3$



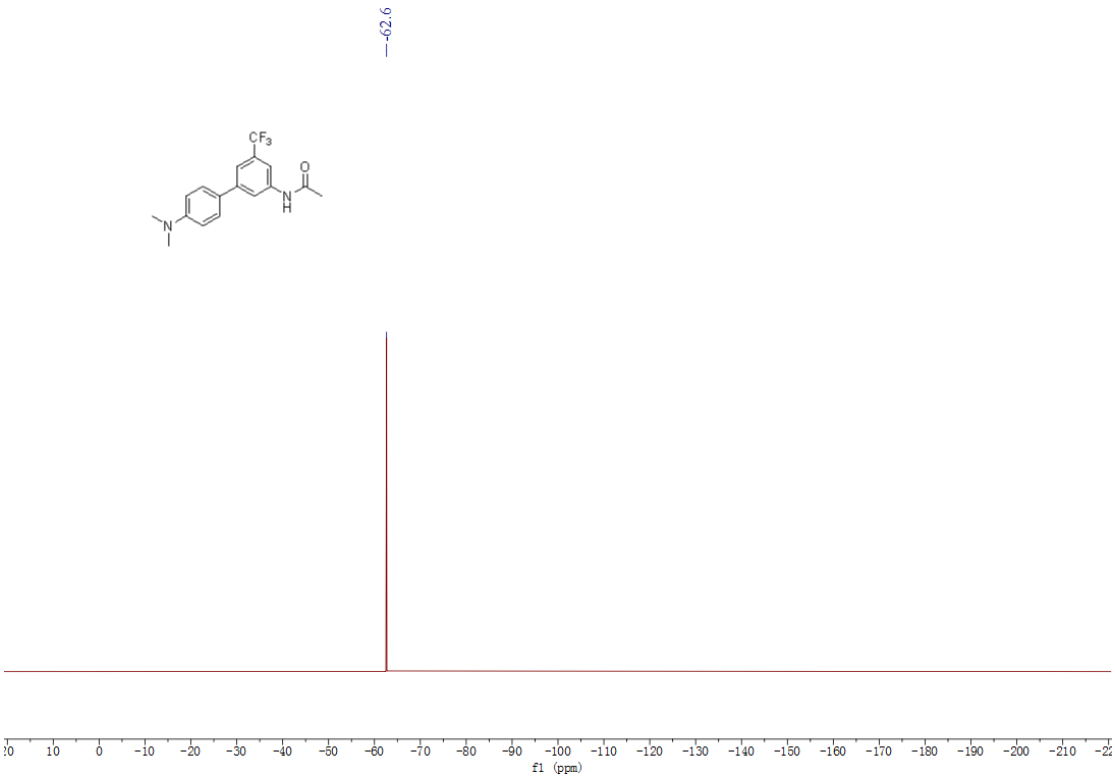
^{13}C NMR spectrum of **3k** in $CDCl_3$



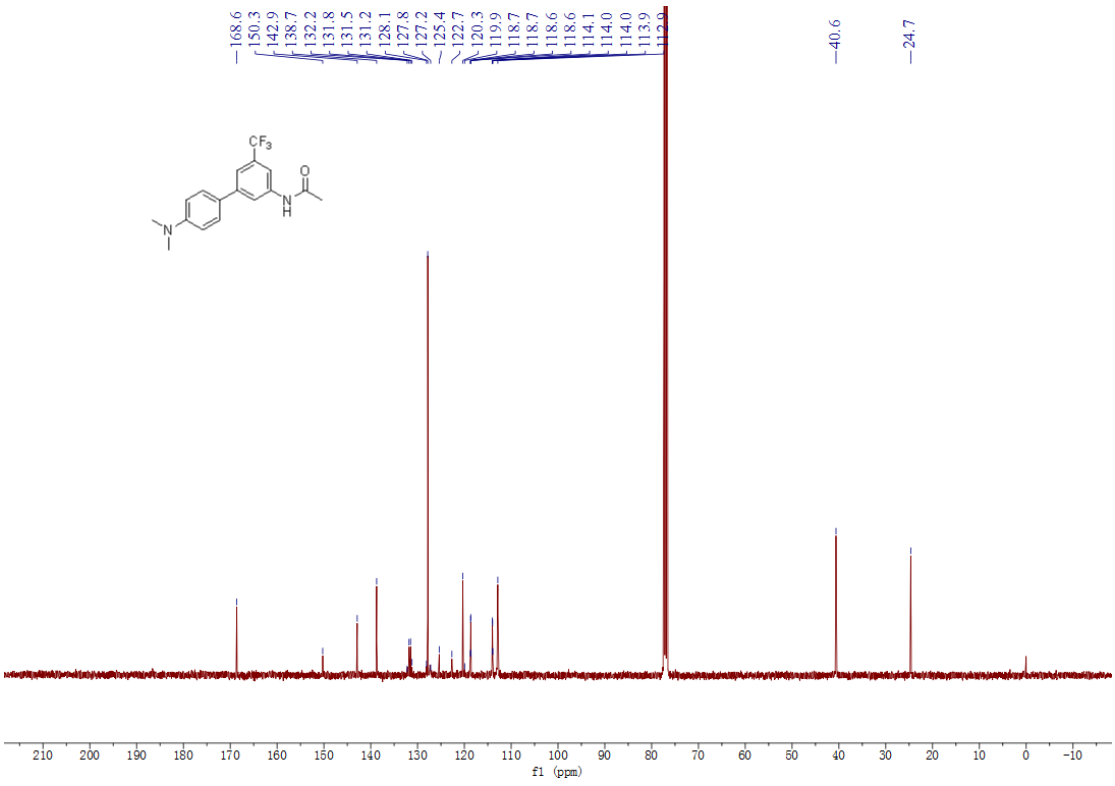
^{1}H NMR spectrum of **3l** in $CDCl_3$



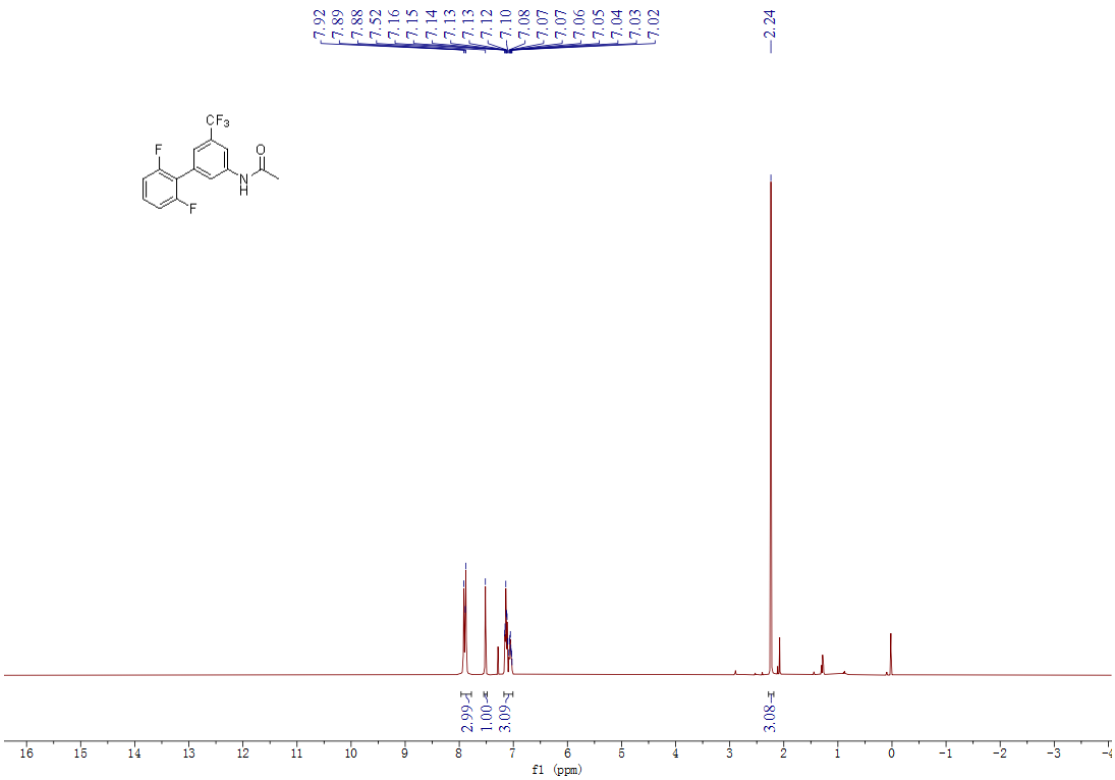
^{19}F NMR spectrum of **3l** in $CDCl_3$



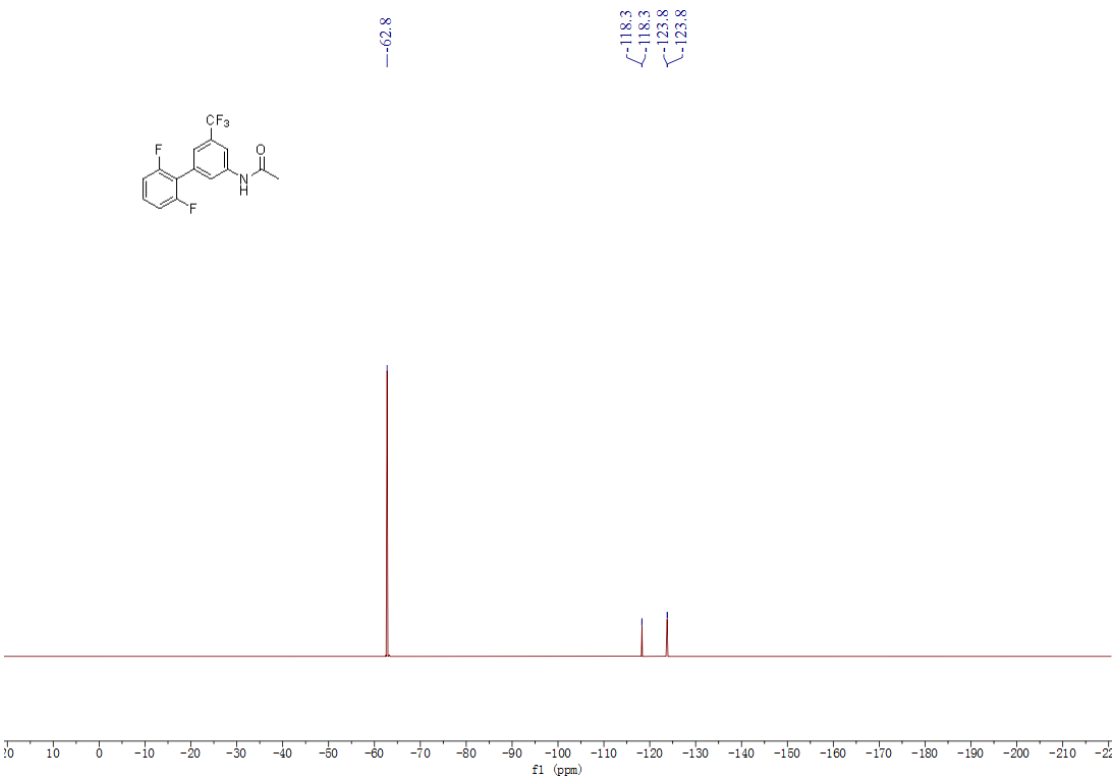
^{13}C NMR spectrum of **3l** in $CDCl_3$



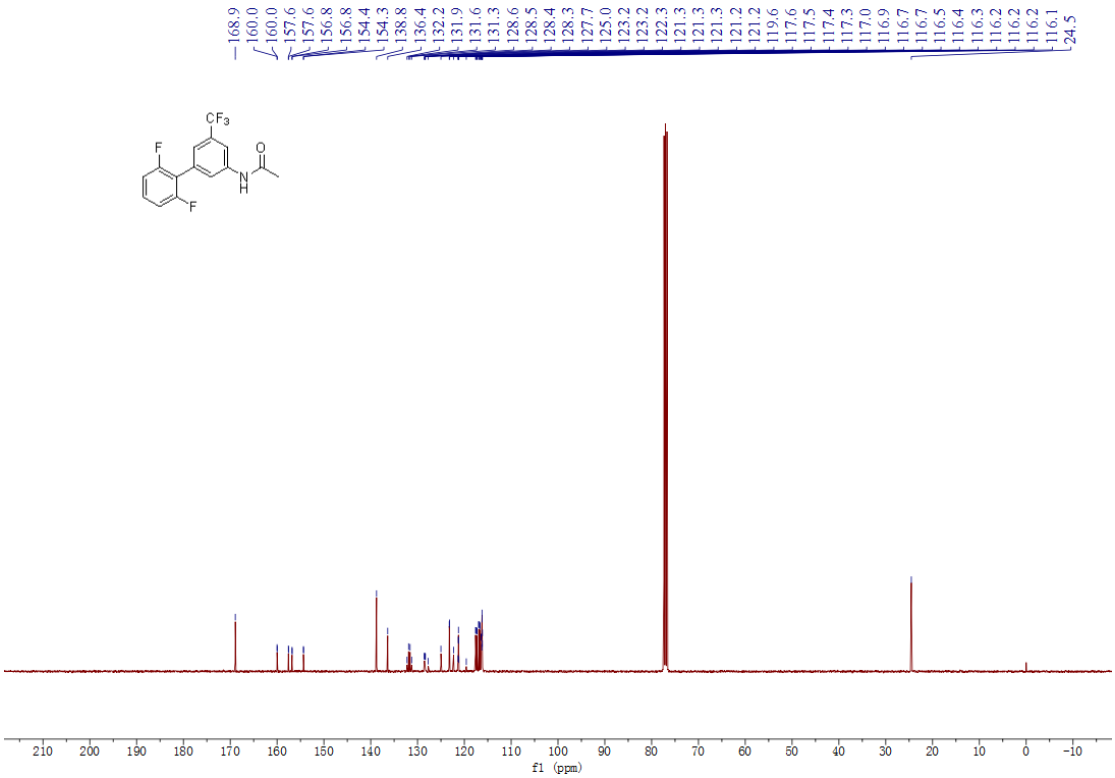
^{1}H NMR spectrum of **3m** in $CDCl_3$



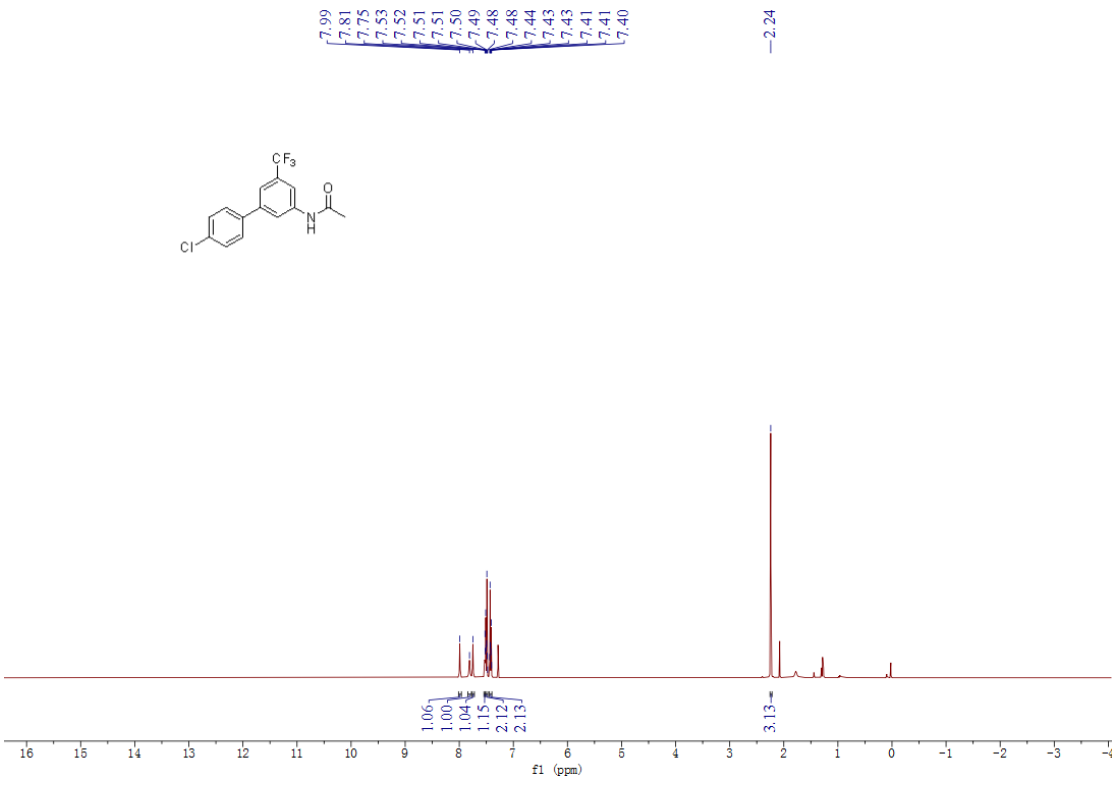
^{19}F NMR spectrum of **3m** in $CDCl_3$



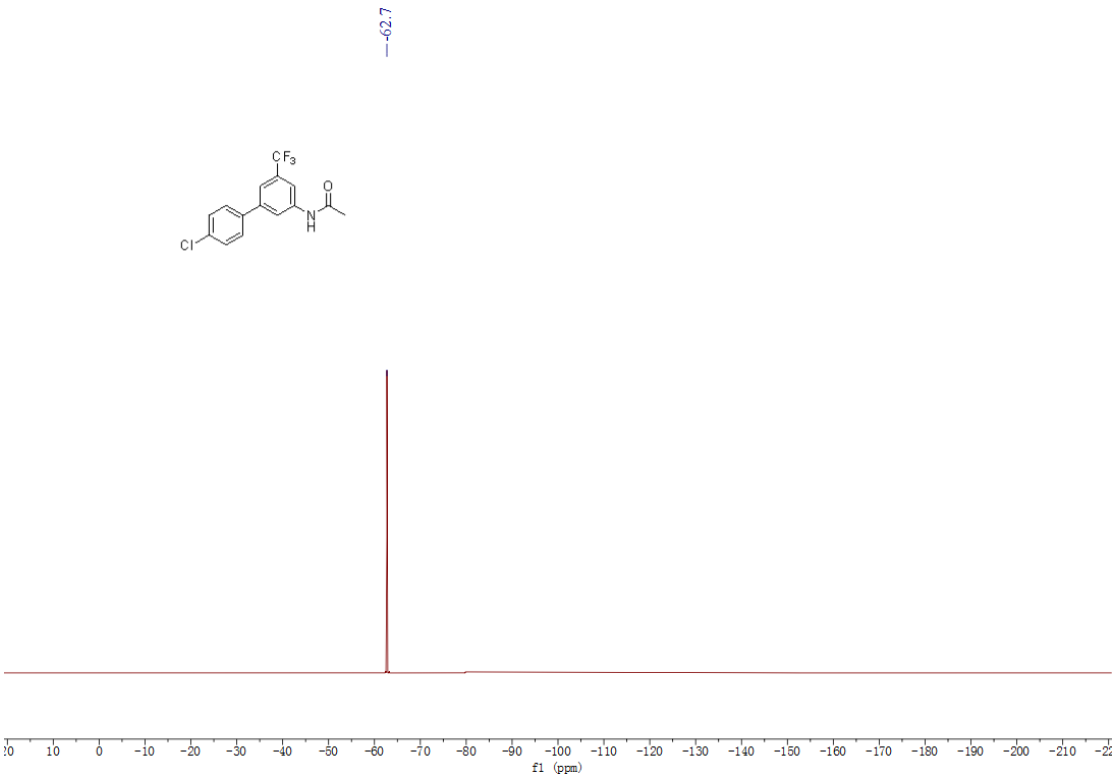
^{13}C NMR spectrum of **3m** in $CDCl_3$



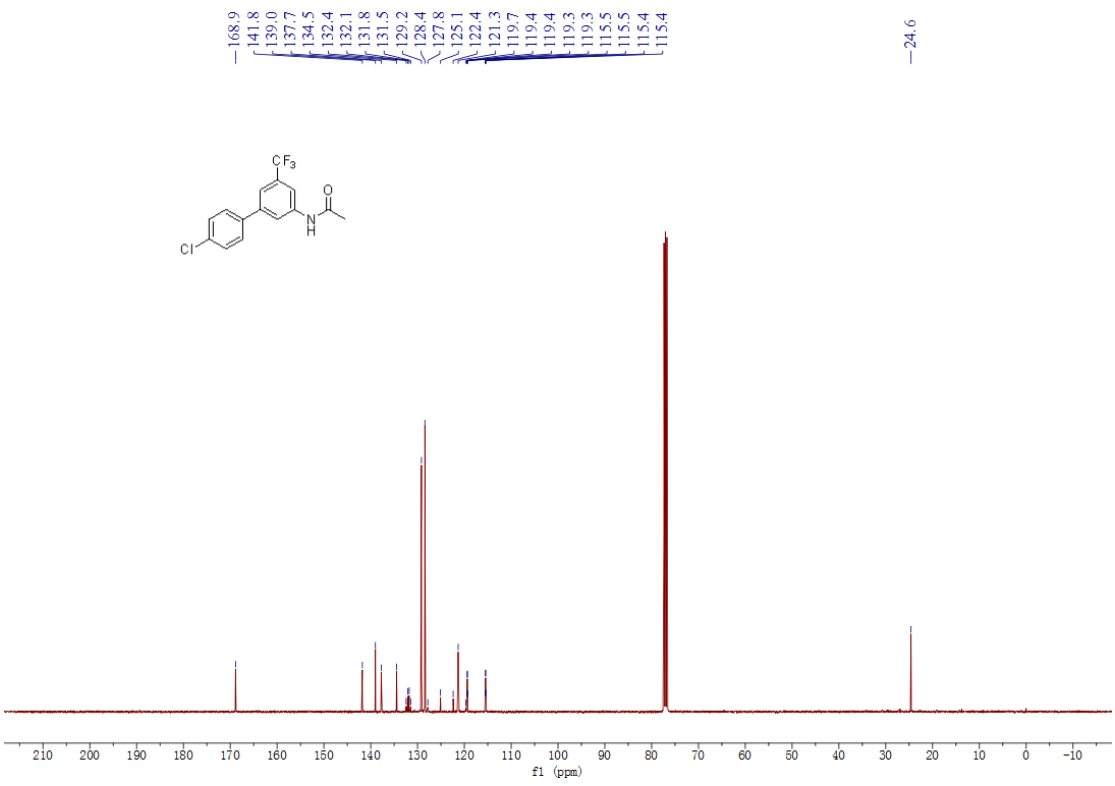
^{1}H NMR spectrum of **3n** in $CDCl_3$



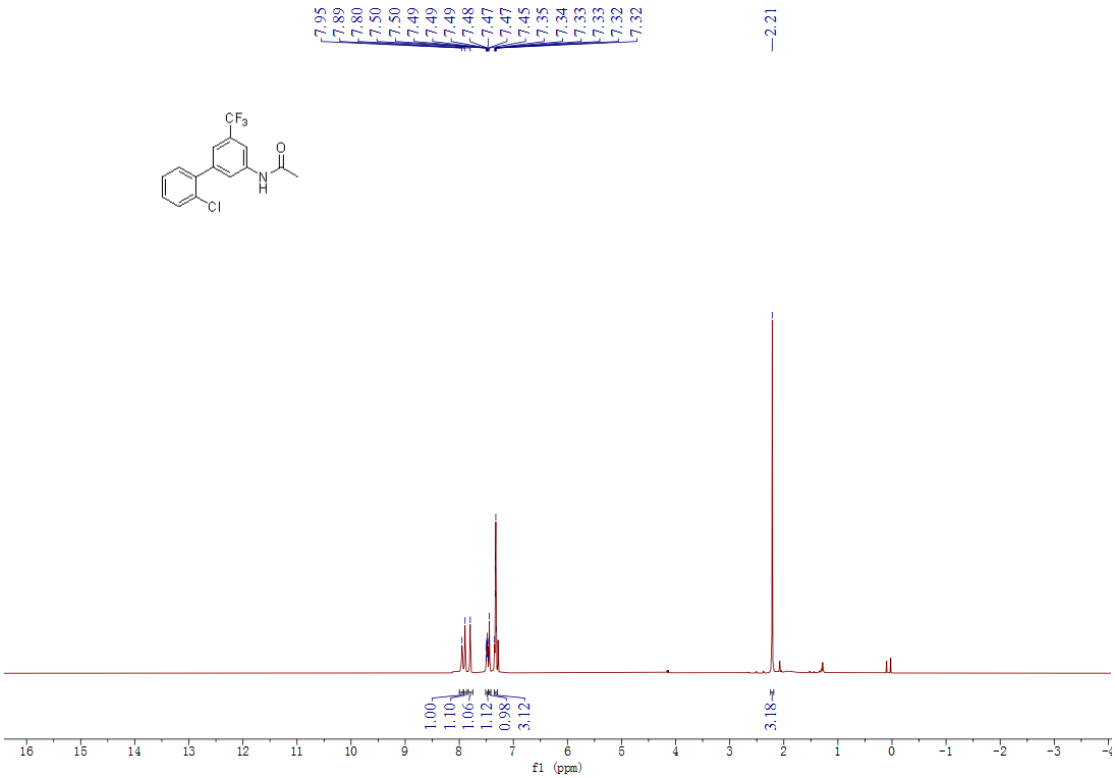
^{19}F NMR spectrum of **3n** in $CDCl_3$



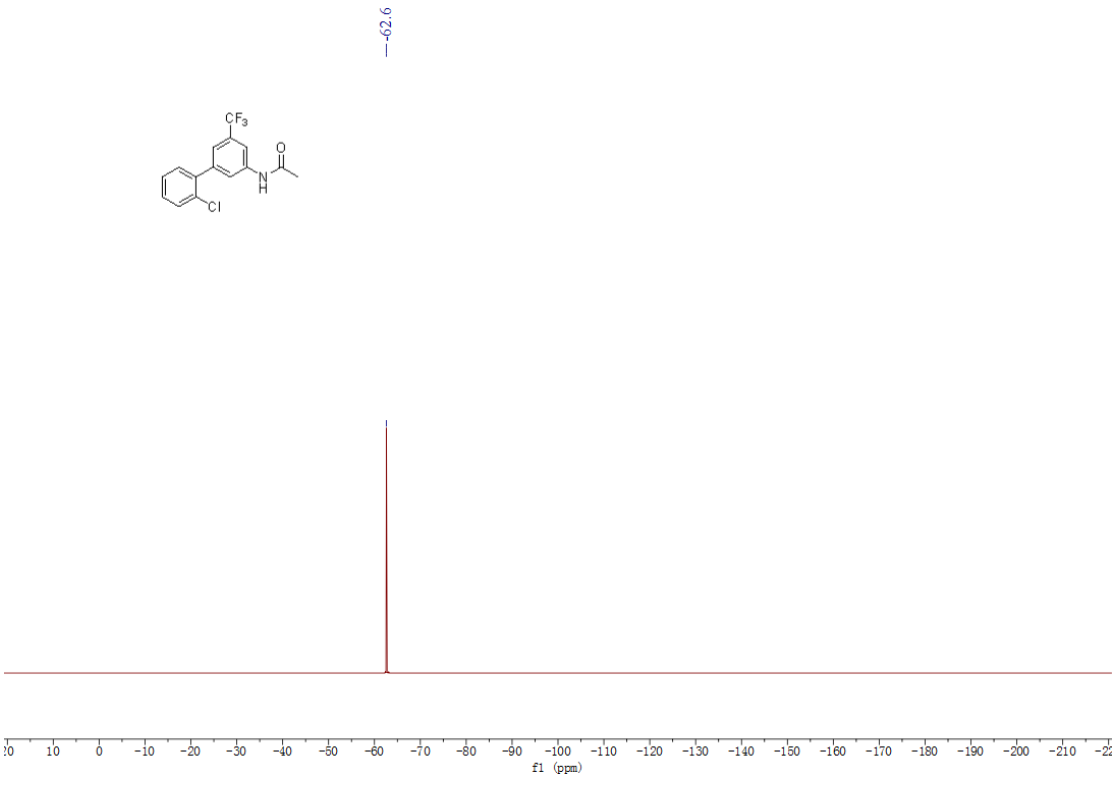
^{13}C NMR spectrum of **3n** in $CDCl_3$



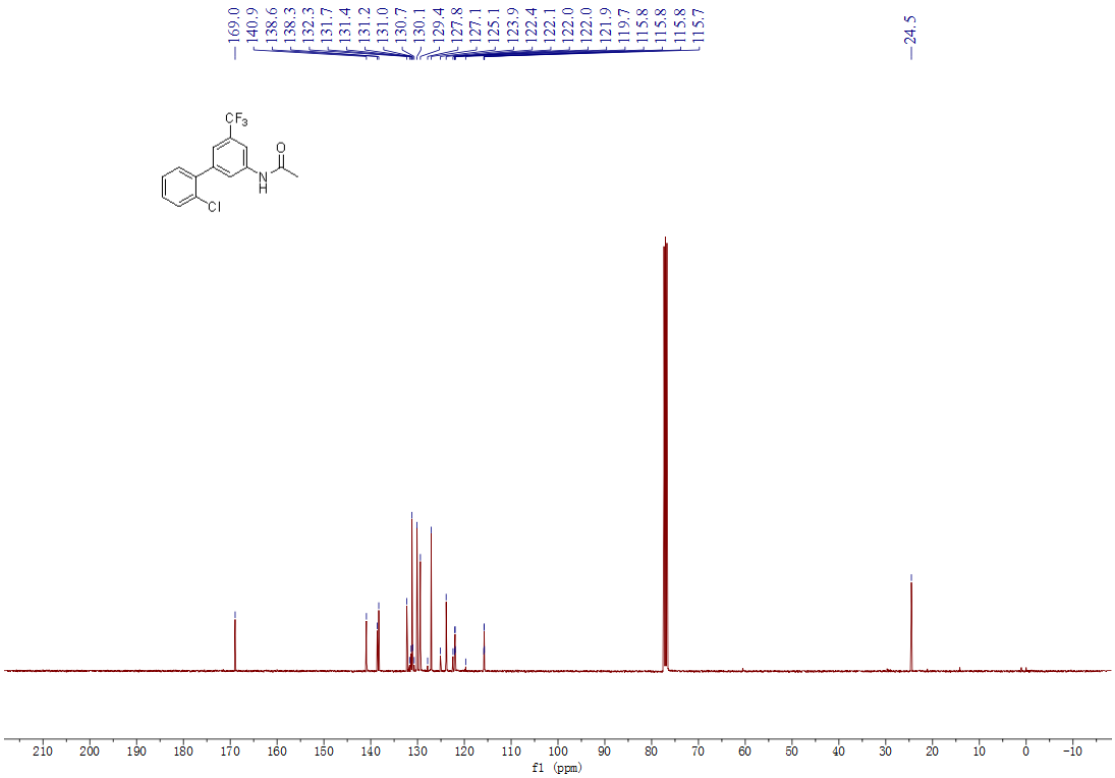
^{1}H NMR spectrum of **3o** in $CDCl_3$



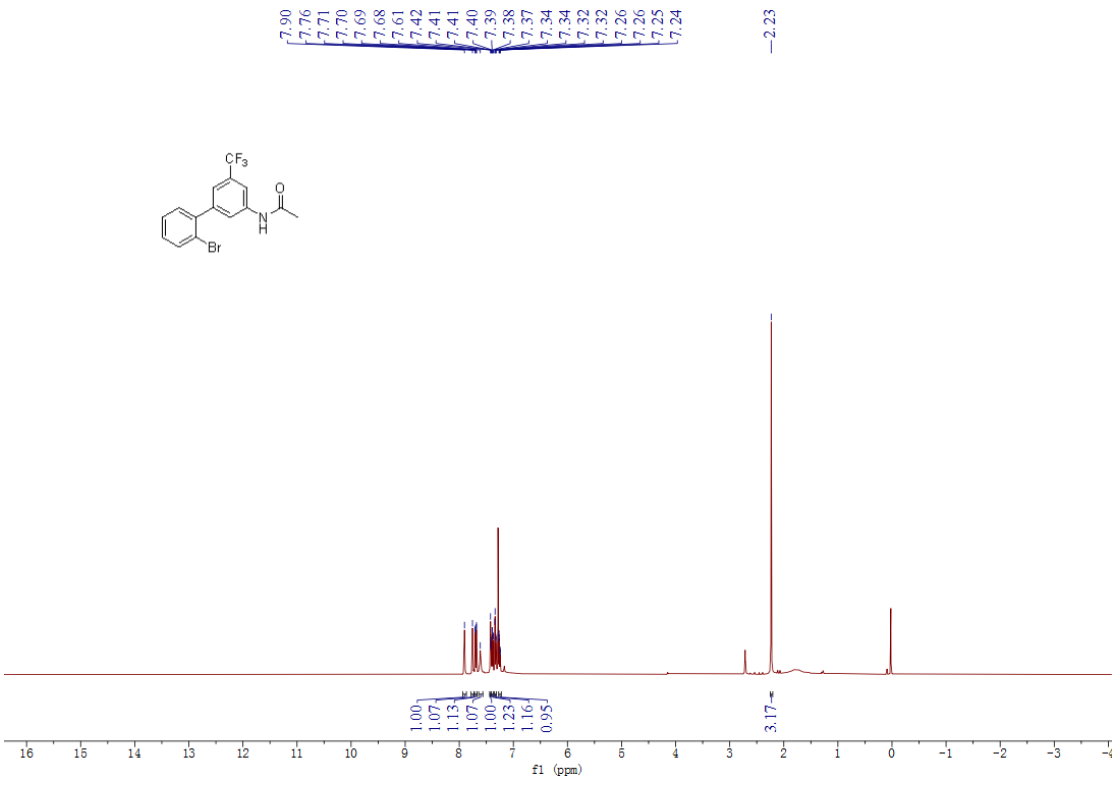
^{19}F NMR spectrum of **3o** in $CDCl_3$



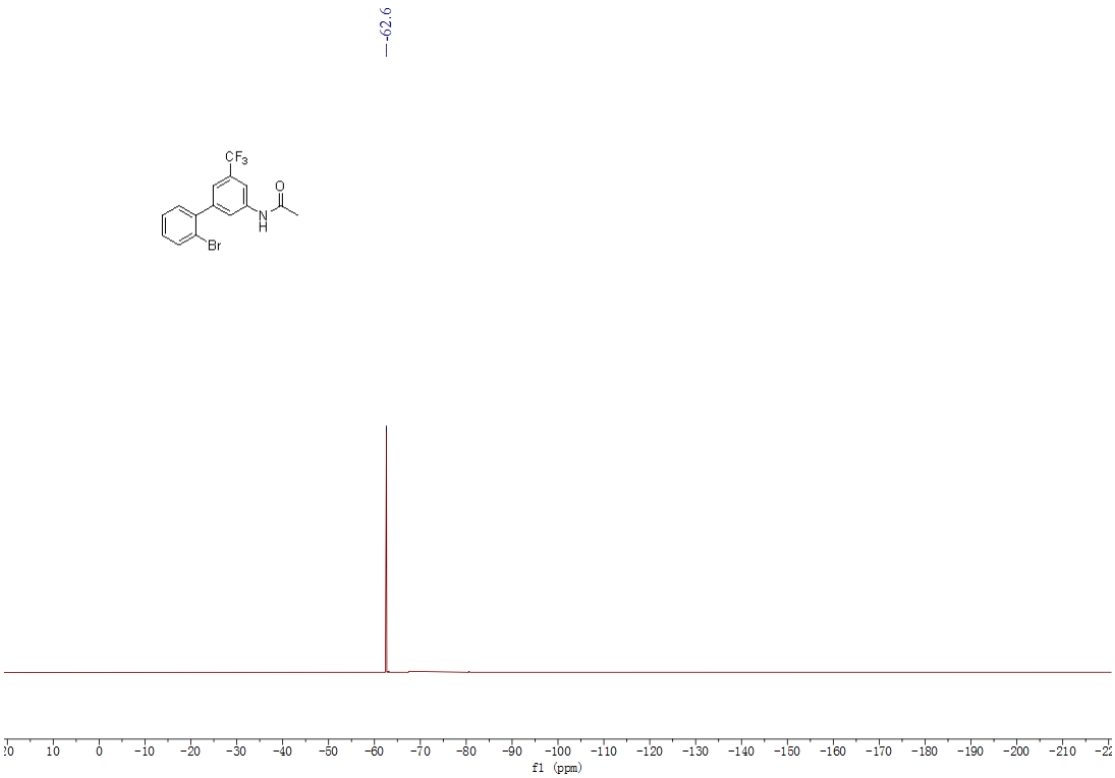
^{13}C NMR spectrum of **3o** in $CDCl_3$



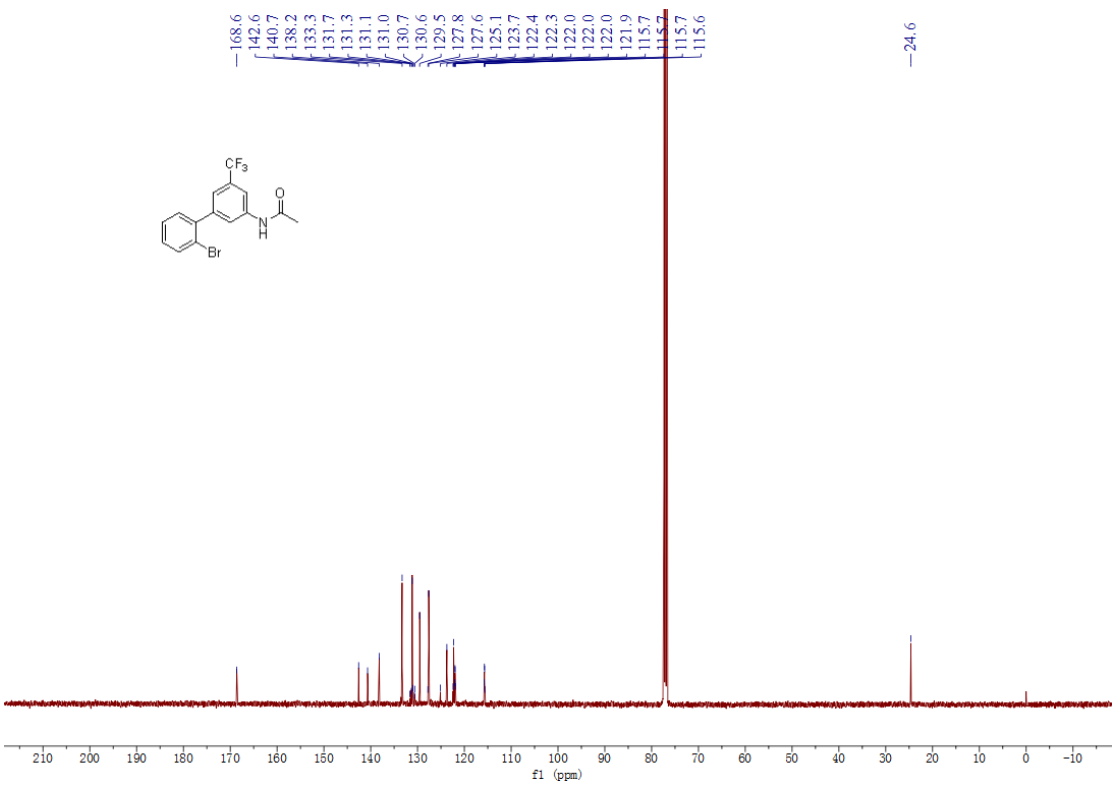
^{1}H NMR spectrum of **3p** in $CDCl_3$



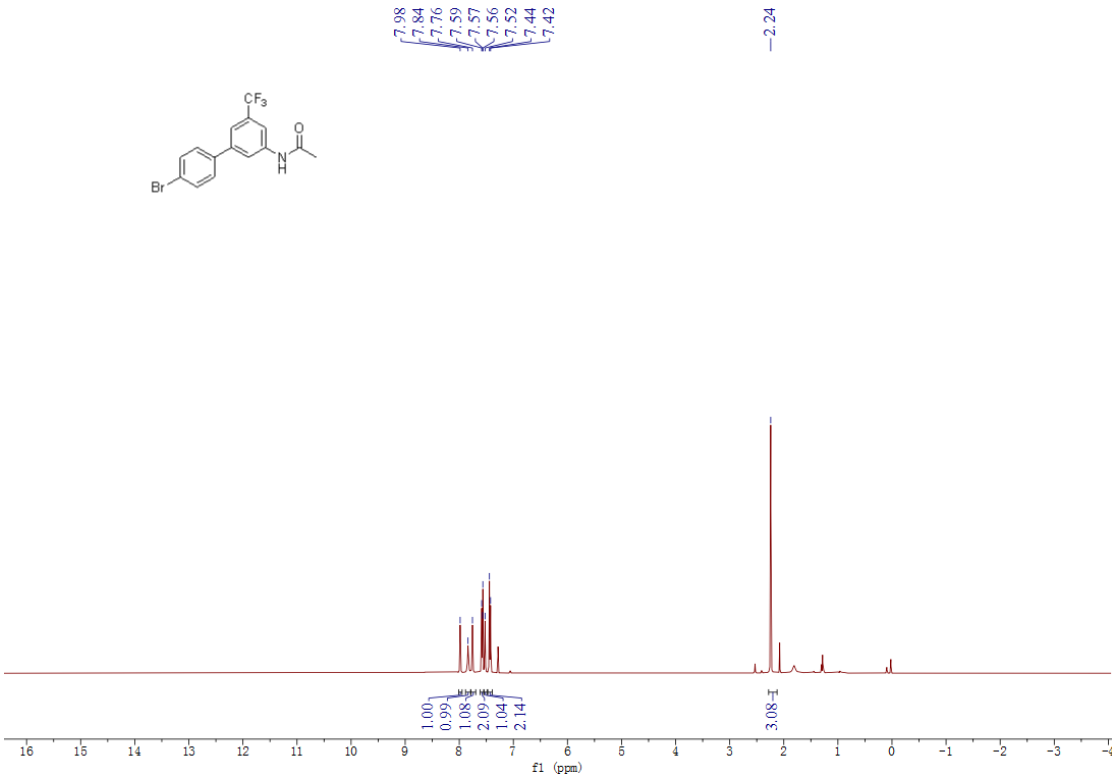
^{19}F NMR spectrum of **3p** in $CDCl_3$



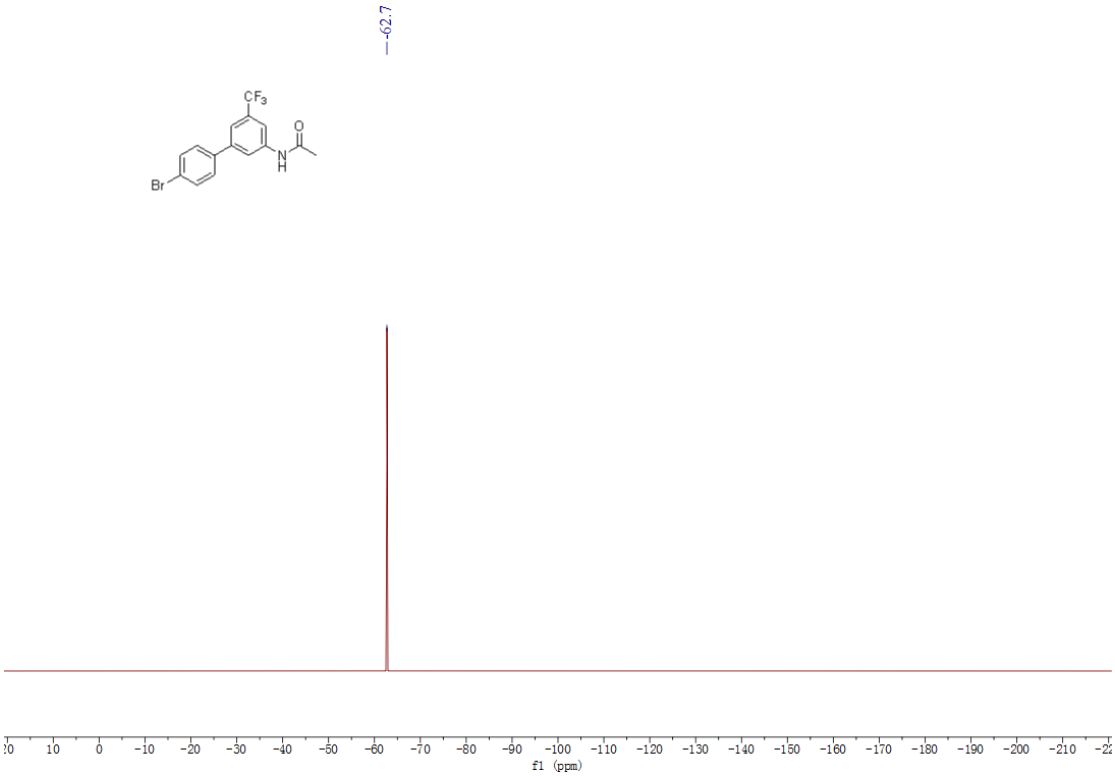
^{13}C NMR spectrum of **3p** in $CDCl_3$



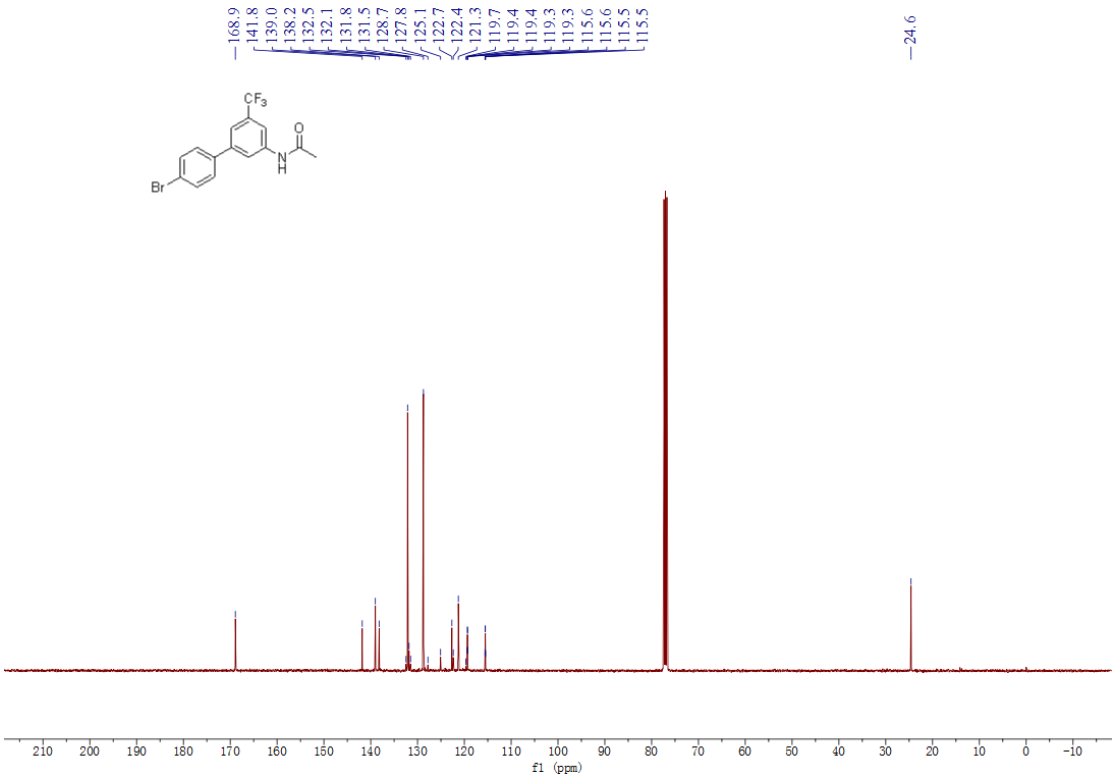
^{1}H NMR spectrum of **3q** in $CDCl_3$



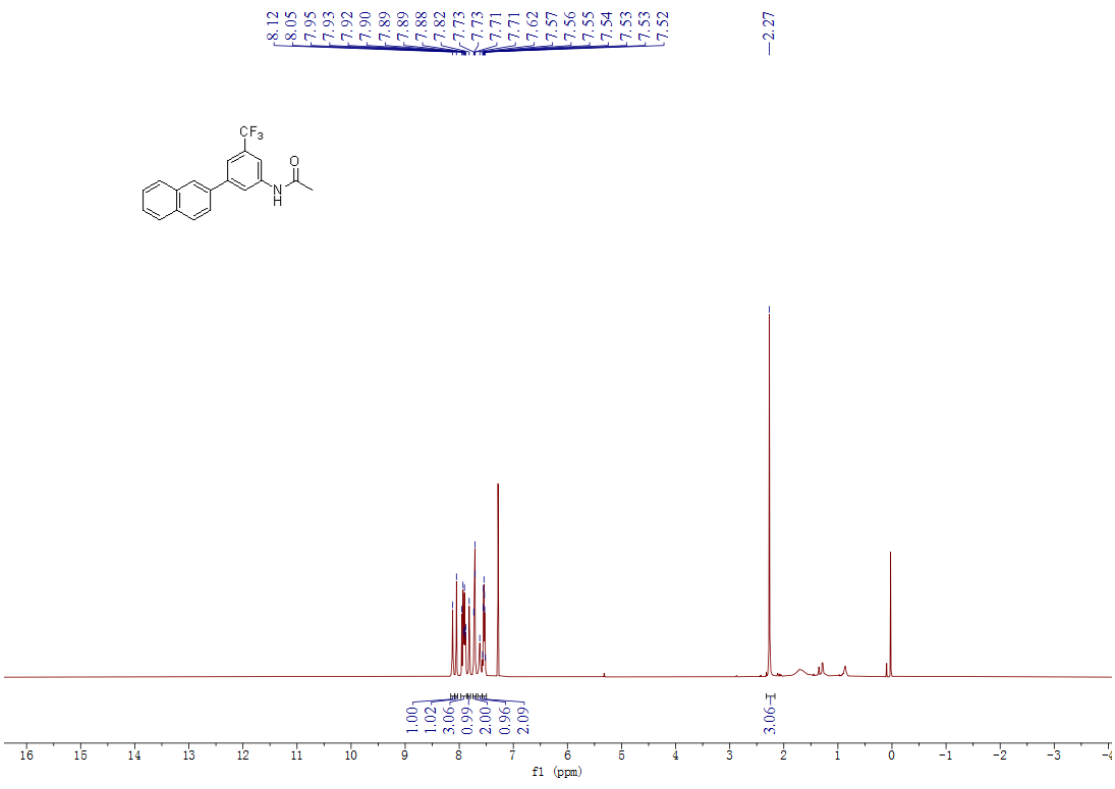
^{19}F NMR spectrum of **3q** in $CDCl_3$



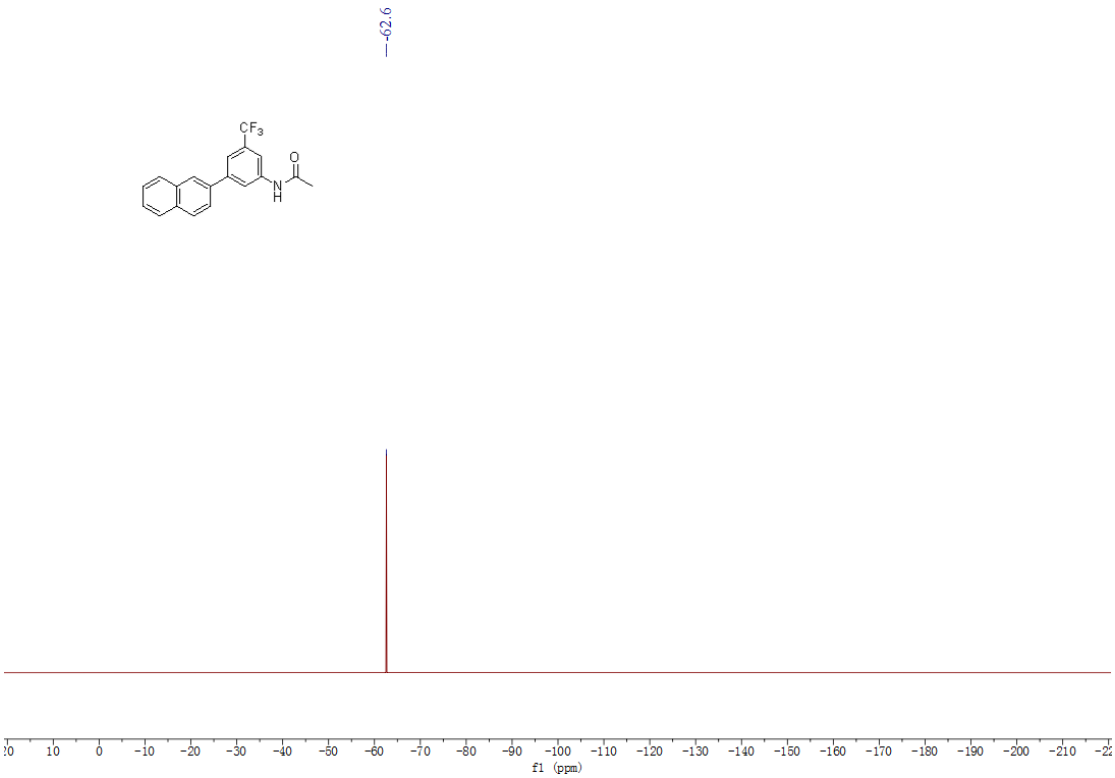
^{13}C NMR spectrum of **3q** in $CDCl_3$



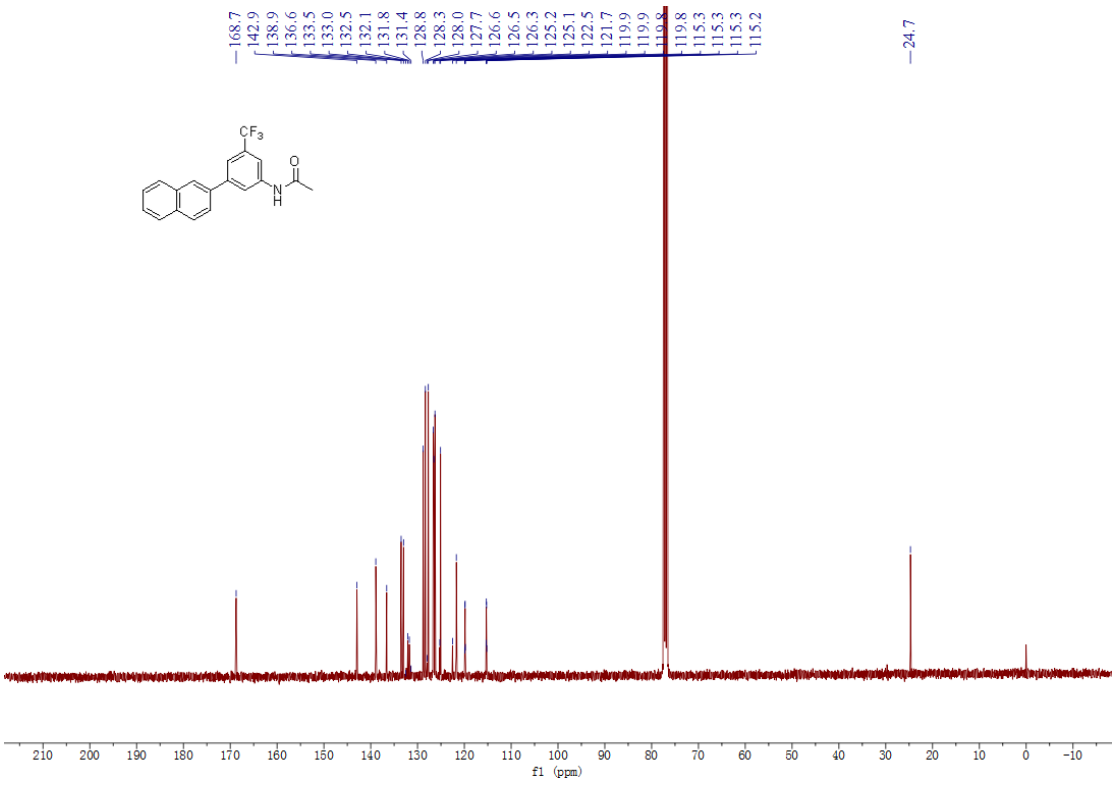
^{1}H NMR spectrum of **3r** in $CDCl_3$



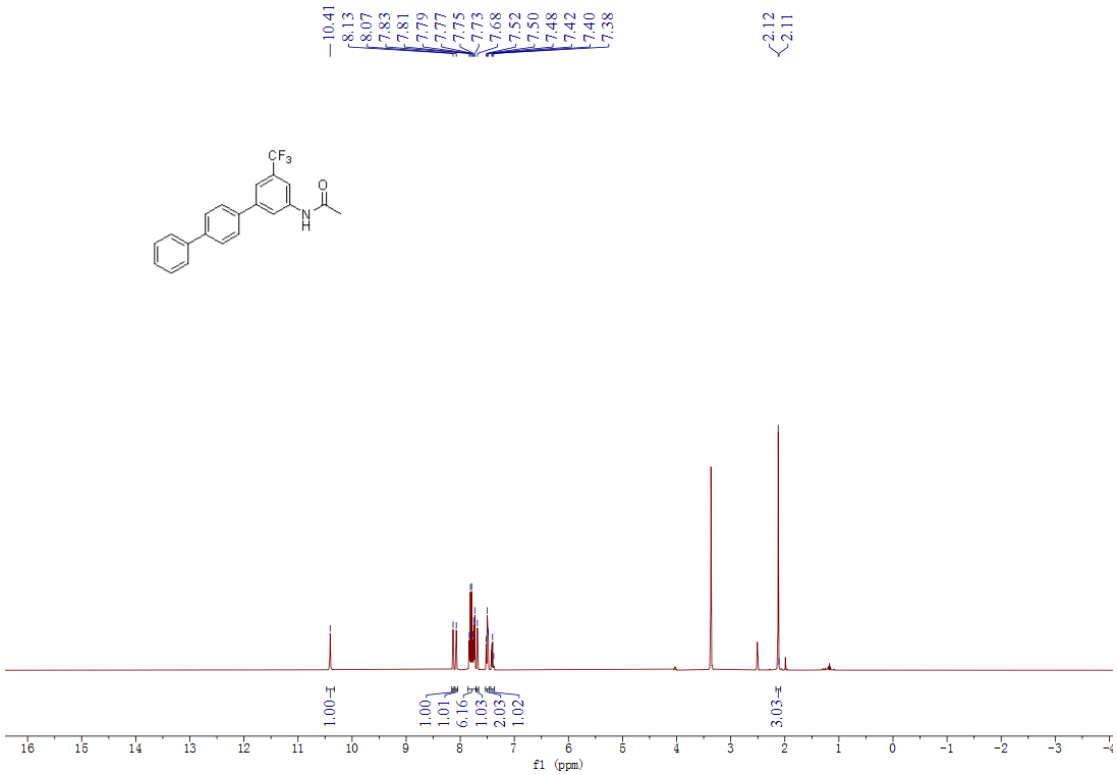
^{19}F NMR spectrum of **3r** in $CDCl_3$



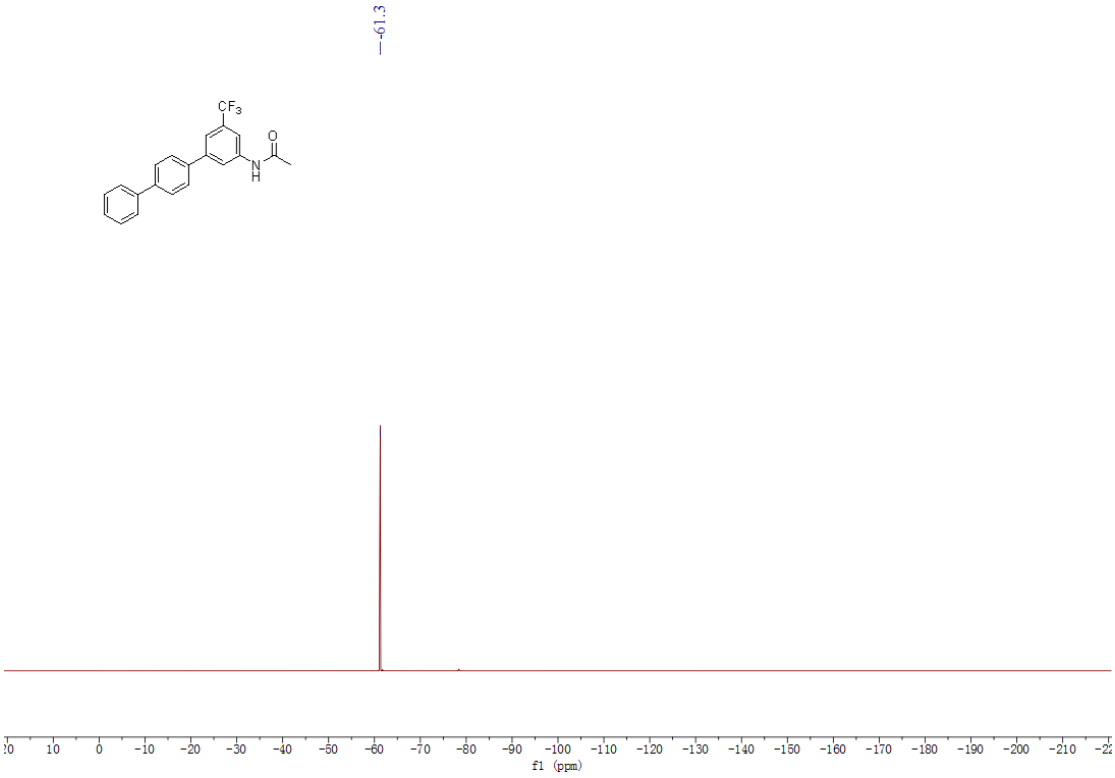
^{13}C NMR spectrum of **3r** in $CDCl_3$



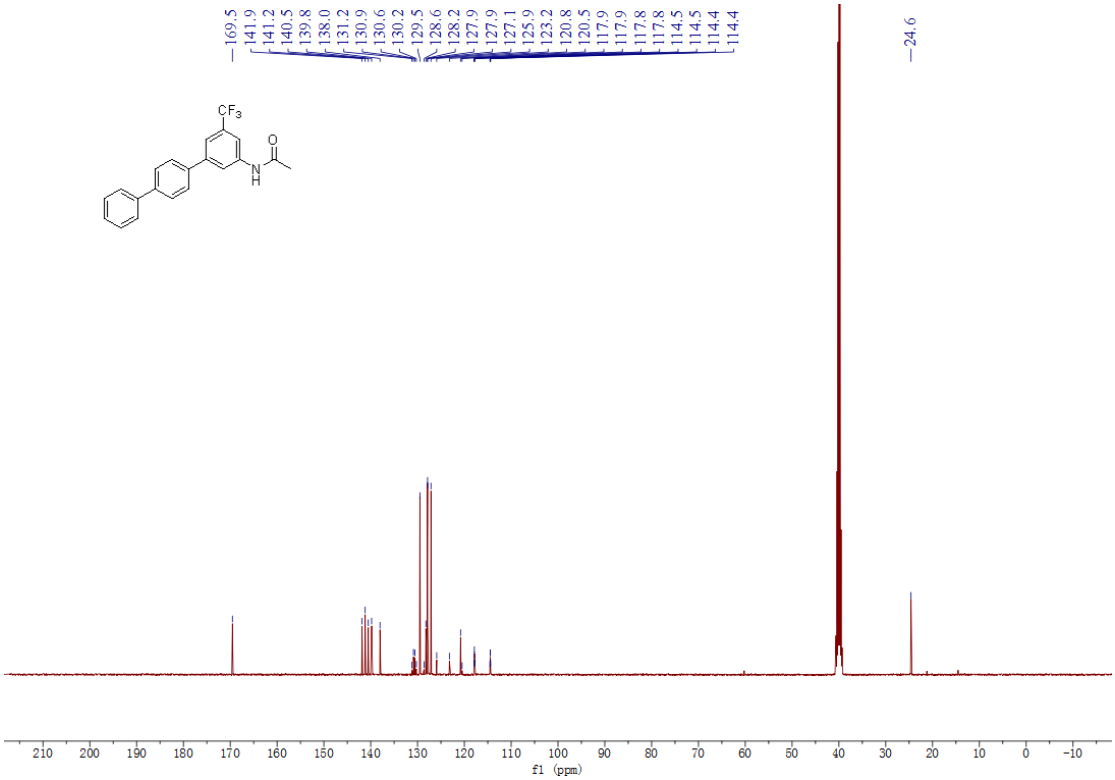
^{1}H NMR spectrum of **3s** in DMSO-d_6



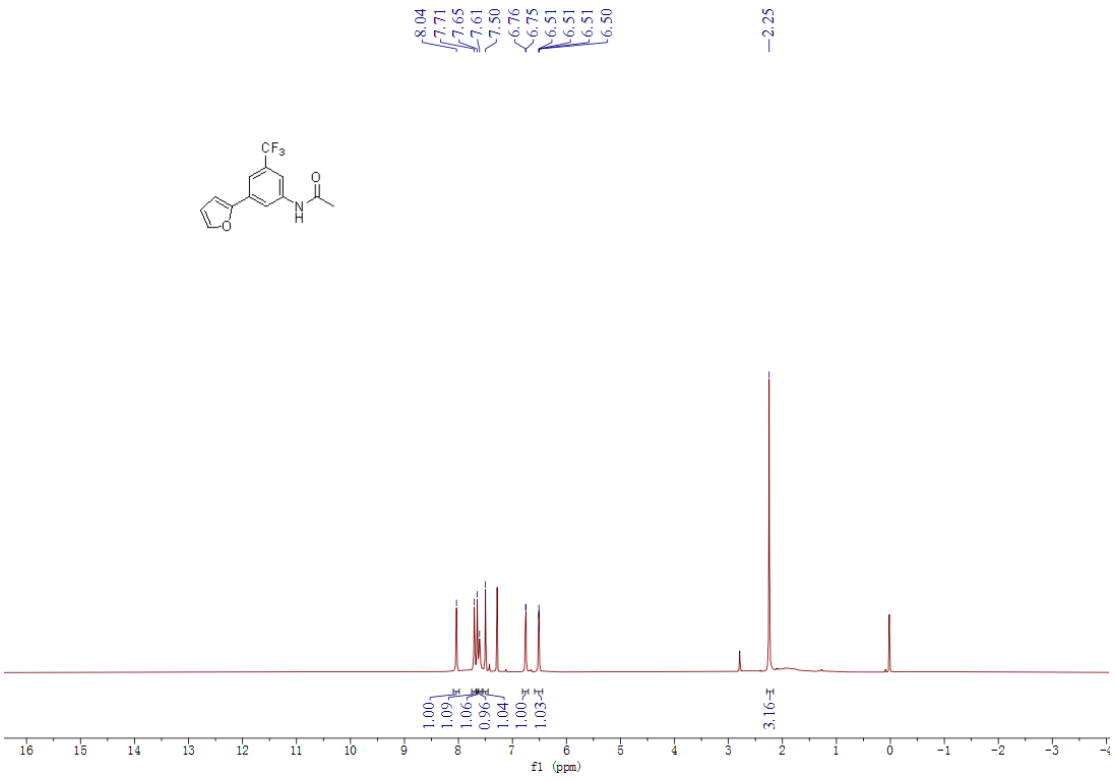
^{19}F NMR spectrum of **3s** in DMSO-d_6



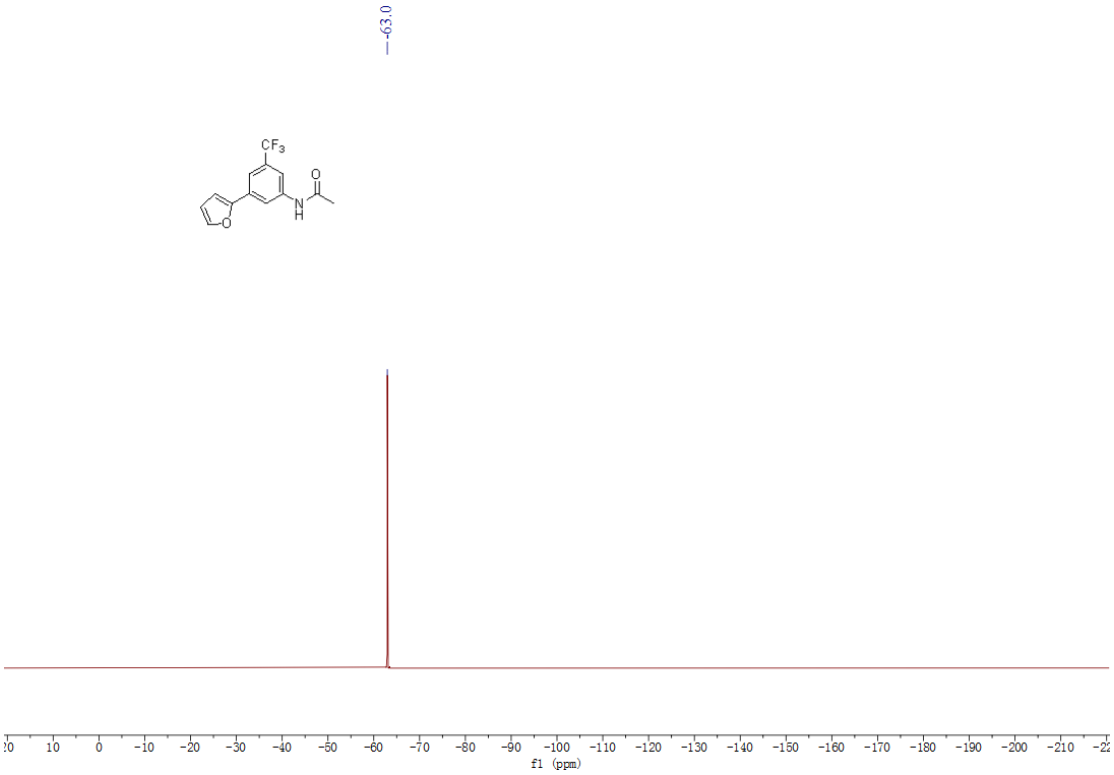
^{13}C NMR spectrum of **3s** in DMSO-d_6



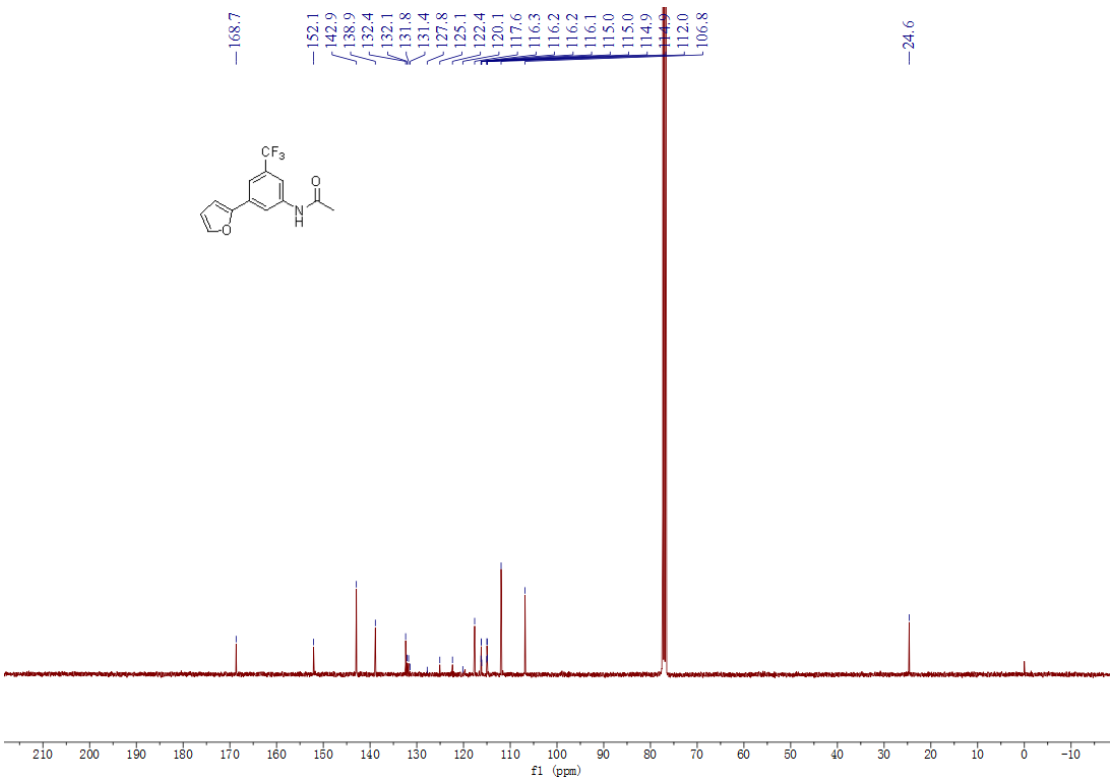
^{1}H NMR spectrum of **3t** in $CDCl_3$



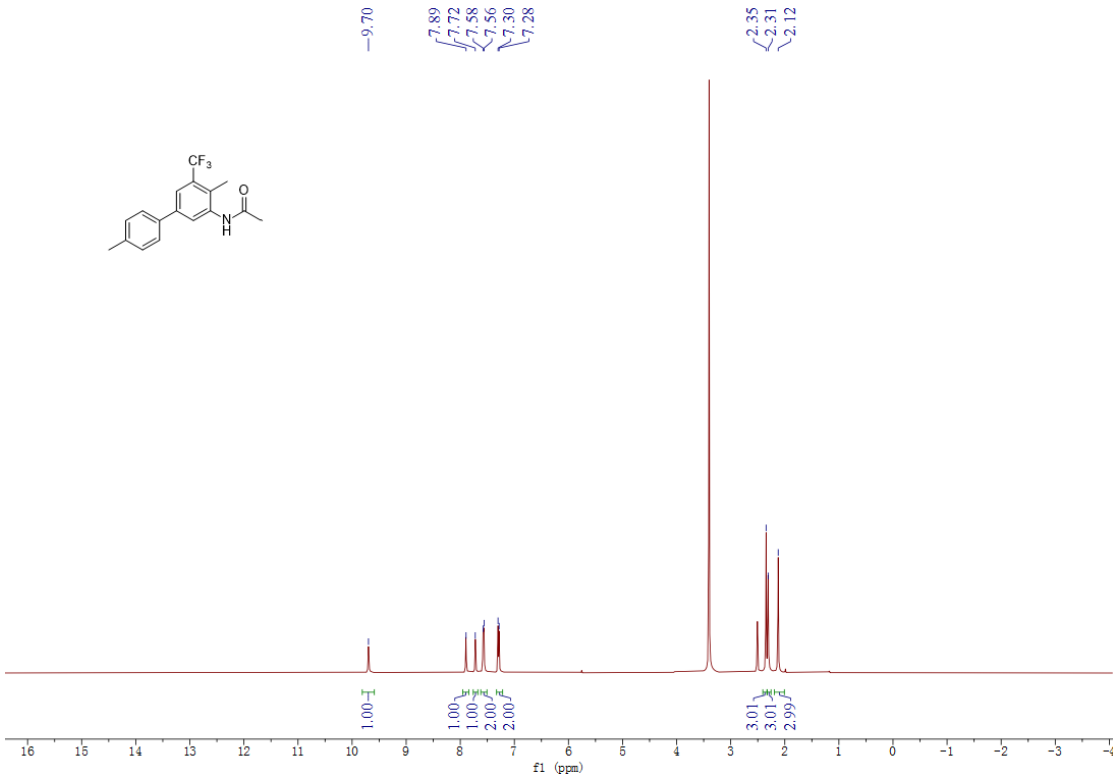
^{19}F NMR spectrum of **3t** in $CDCl_3$



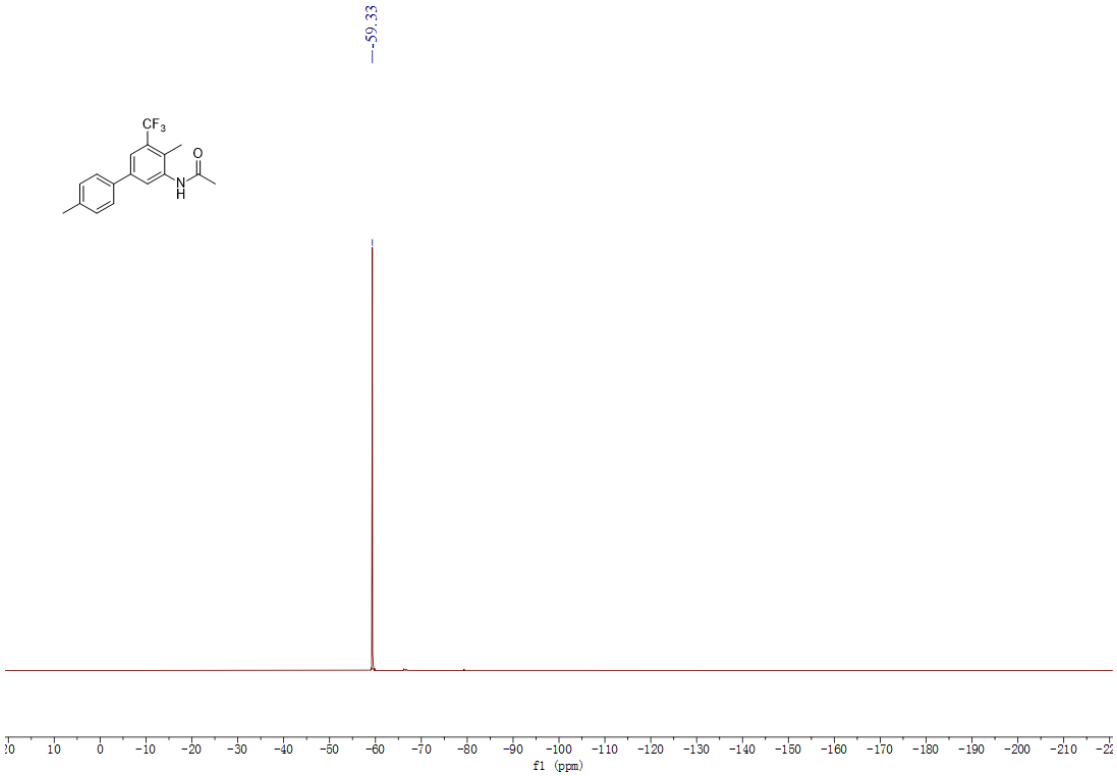
^{13}C NMR spectrum of **3t** in $CDCl_3$



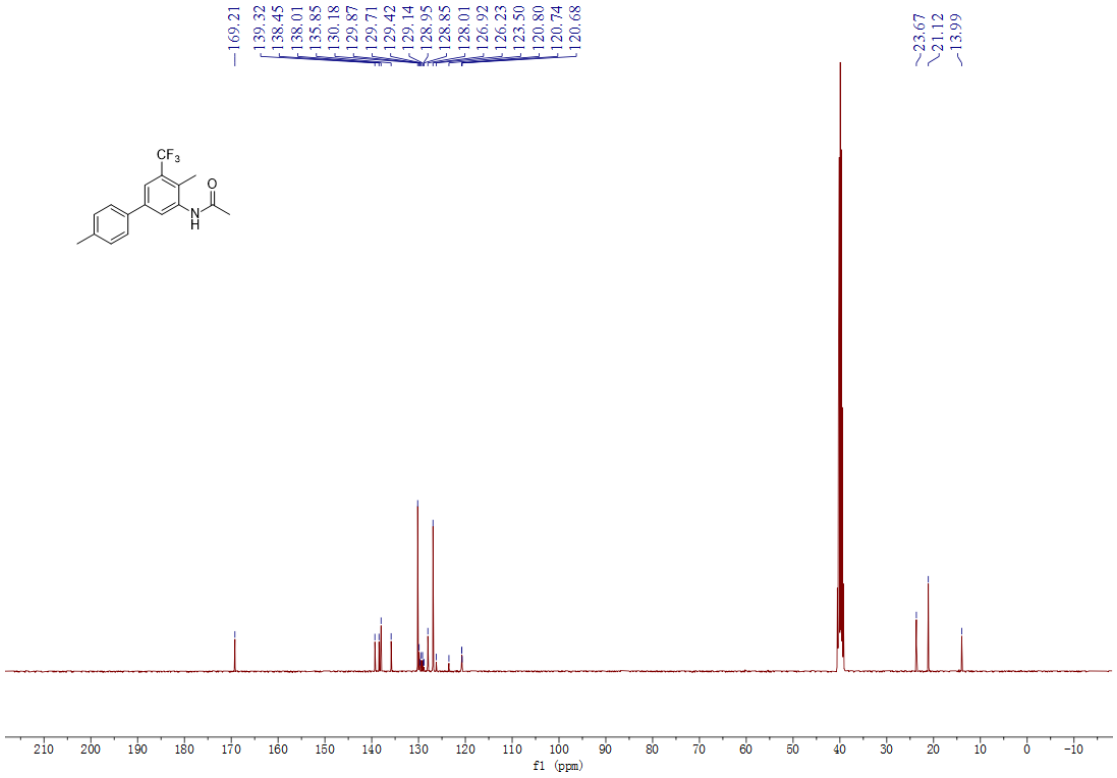
^{1}H NMR spectrum of **3u** in DMSO-d_6



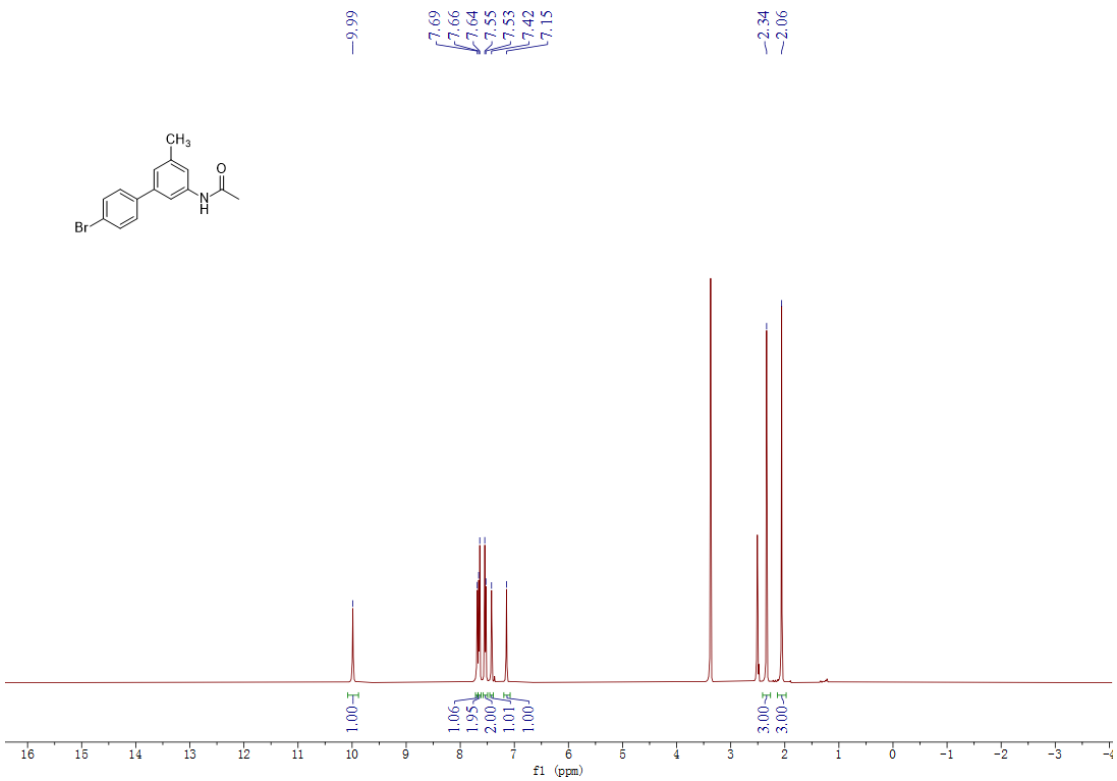
^{19}F NMR spectrum of **3u** in DMSO-d_6



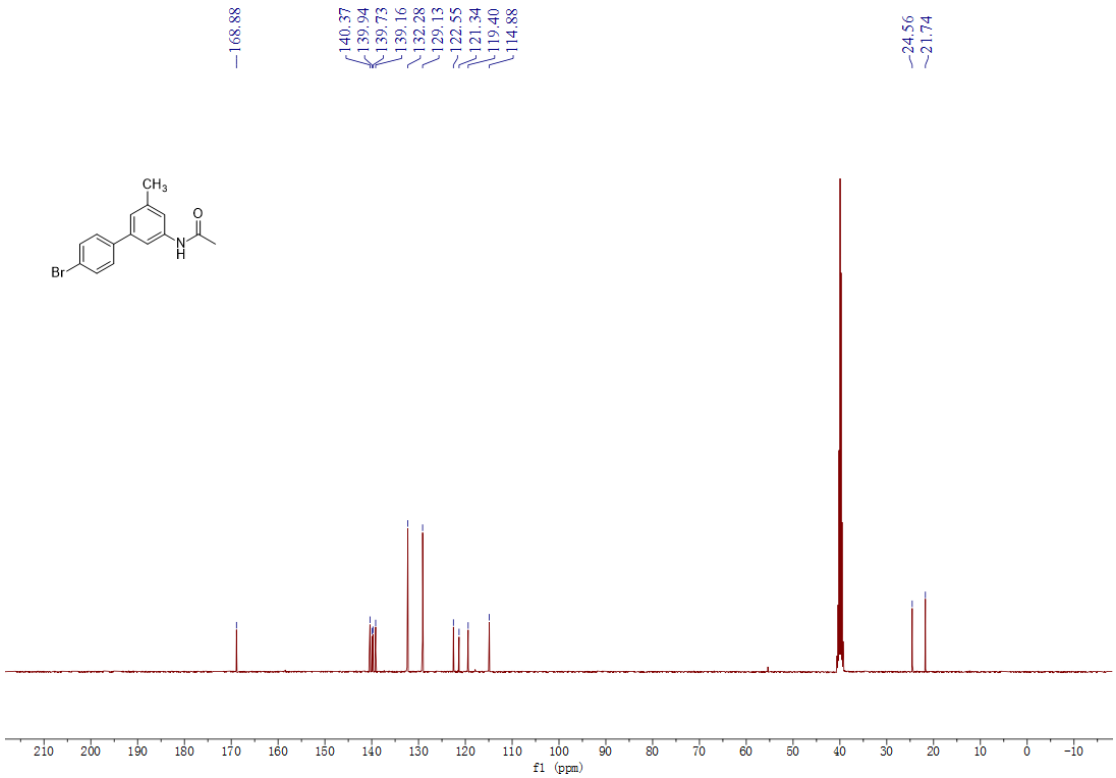
^{13}C NMR spectrum of **3u** in DMSO-d_6



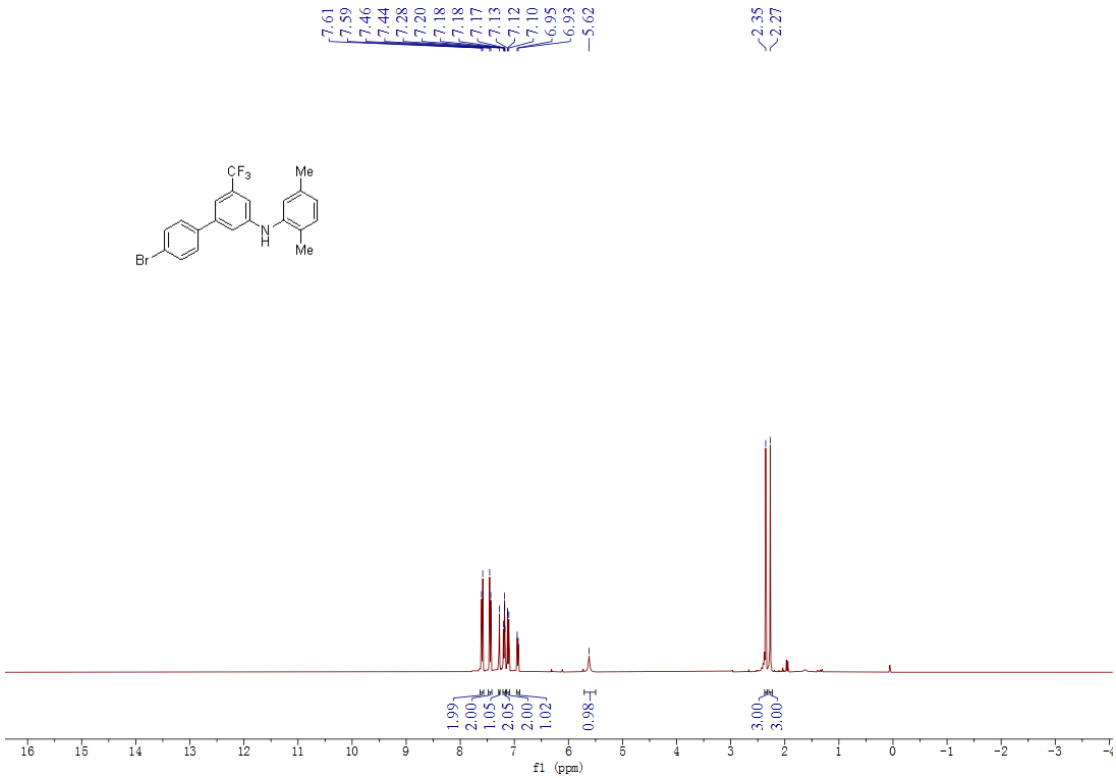
^{1}H NMR spectrum of **3q'** in DMSO-d_6



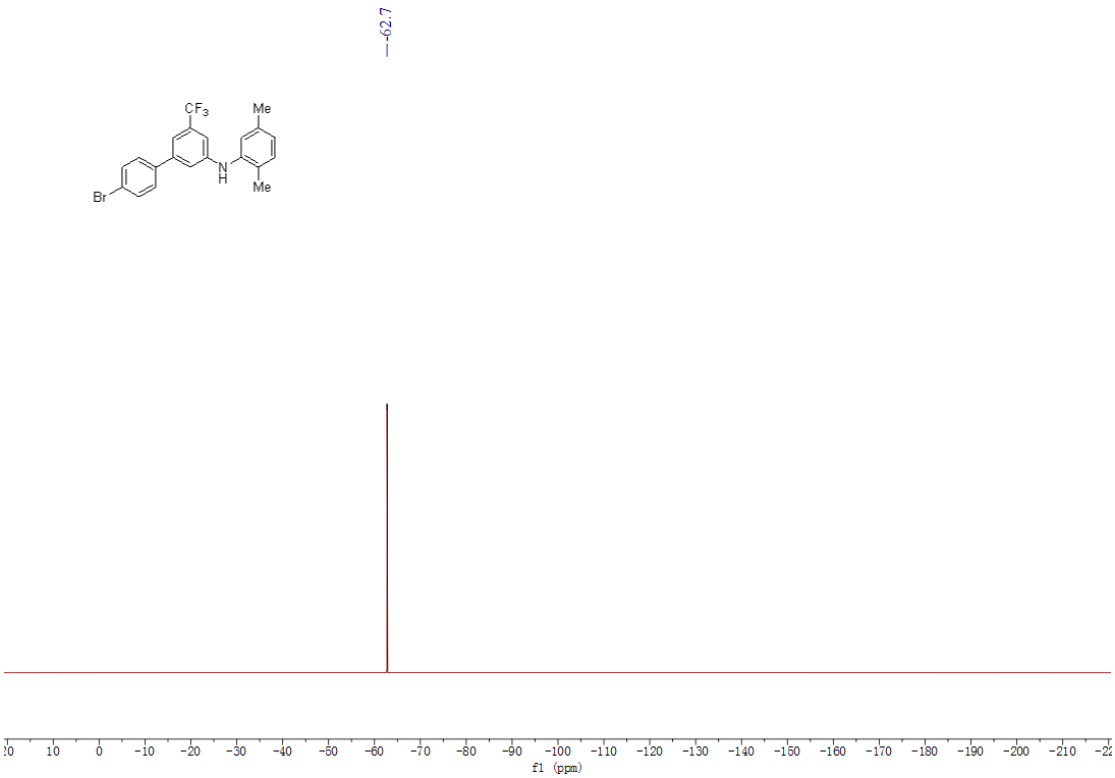
^{13}C NMR spectrum of **3q'** in DMSO-d_6



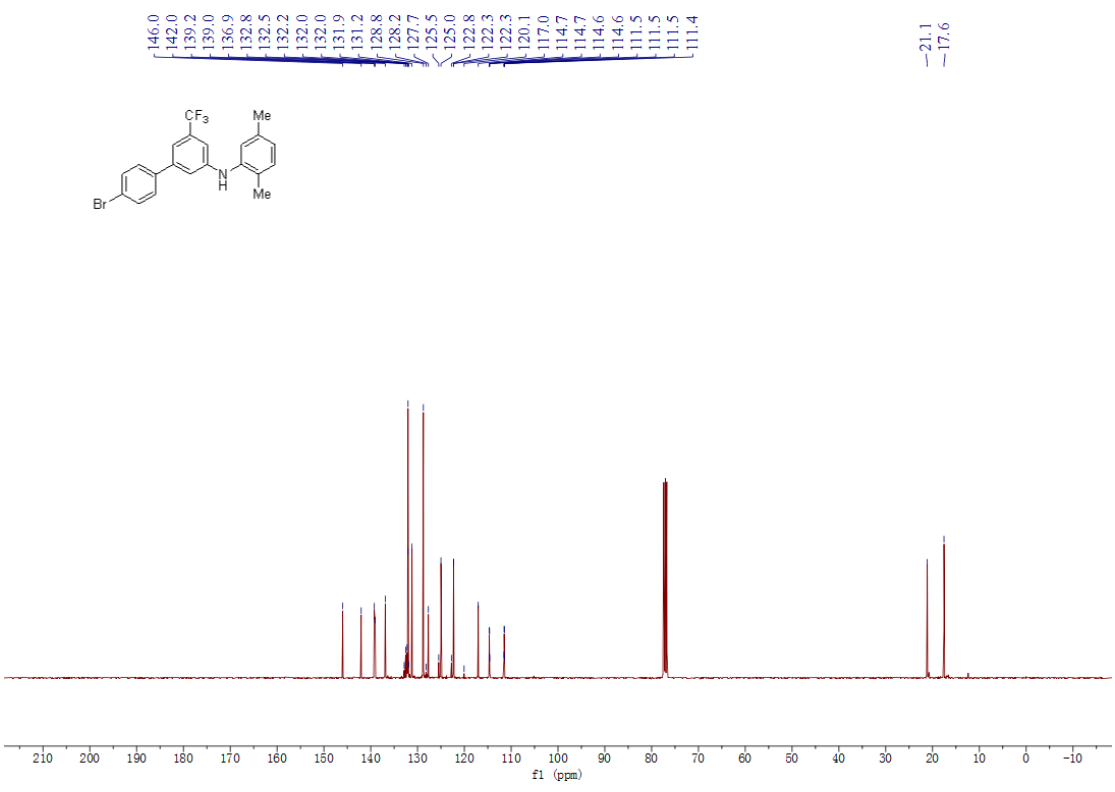
^{1}H NMR spectrum of **4a** in $CDCl_3$



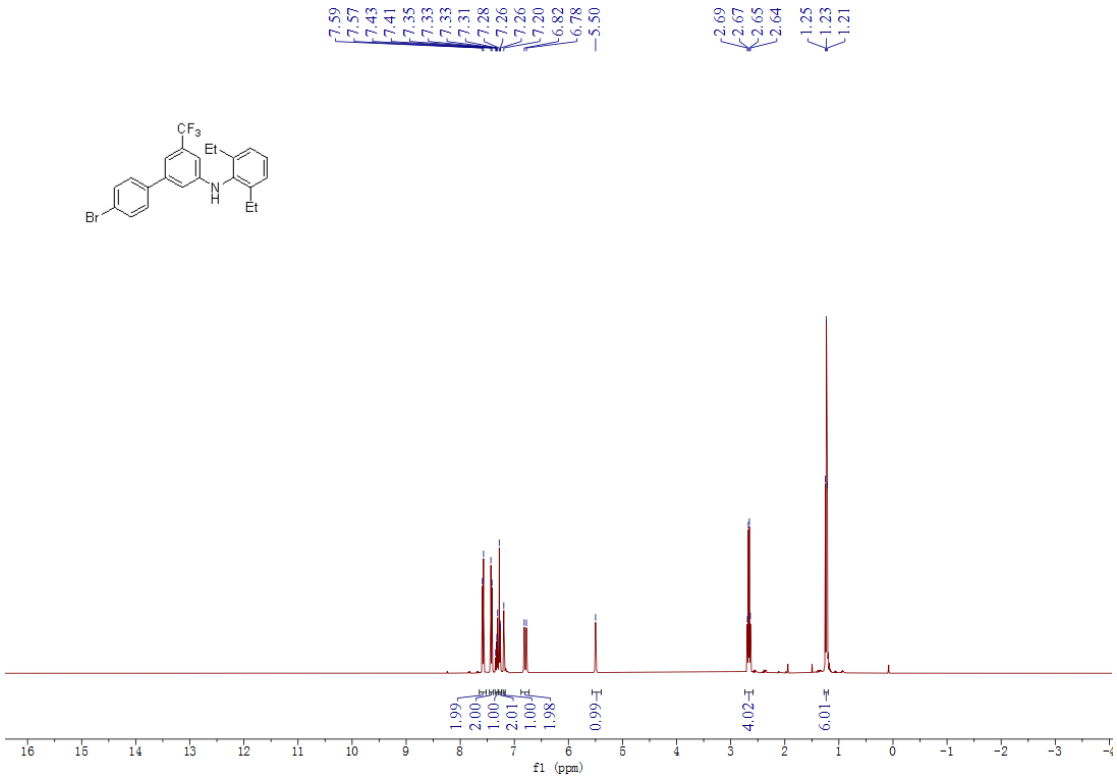
^{19}F NMR spectrum of **4a** in $CDCl_3$



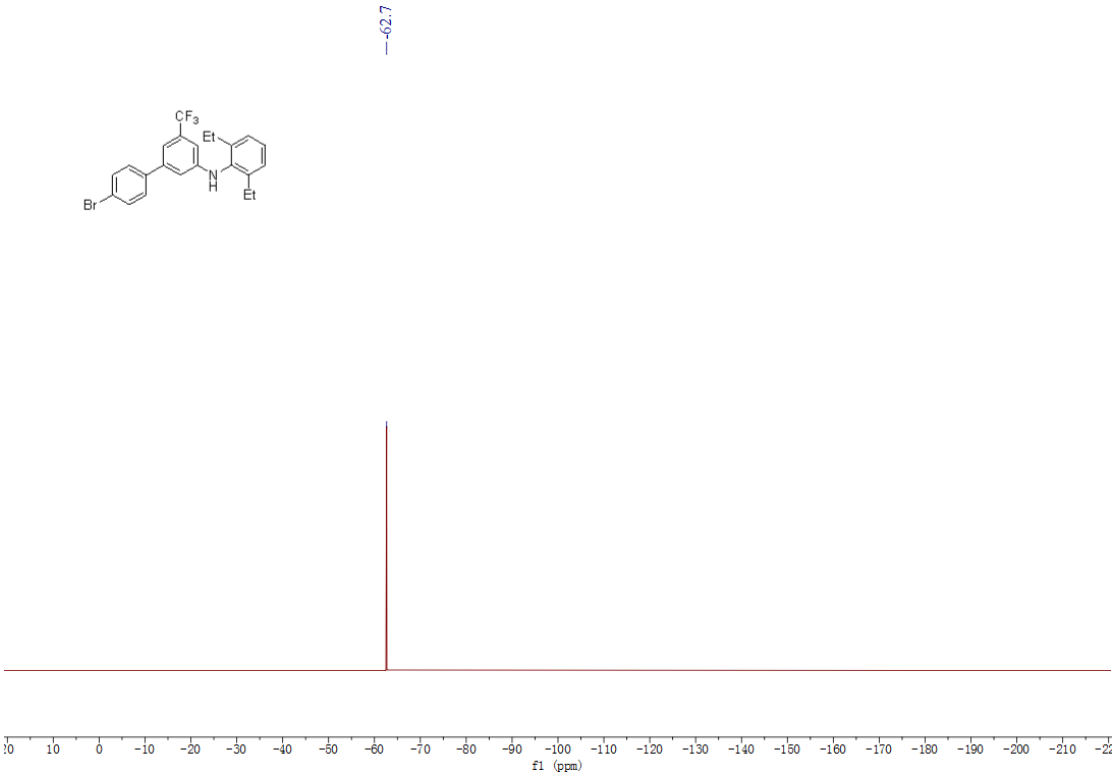
^{13}C NMR spectrum of **4a** in $CDCl_3$



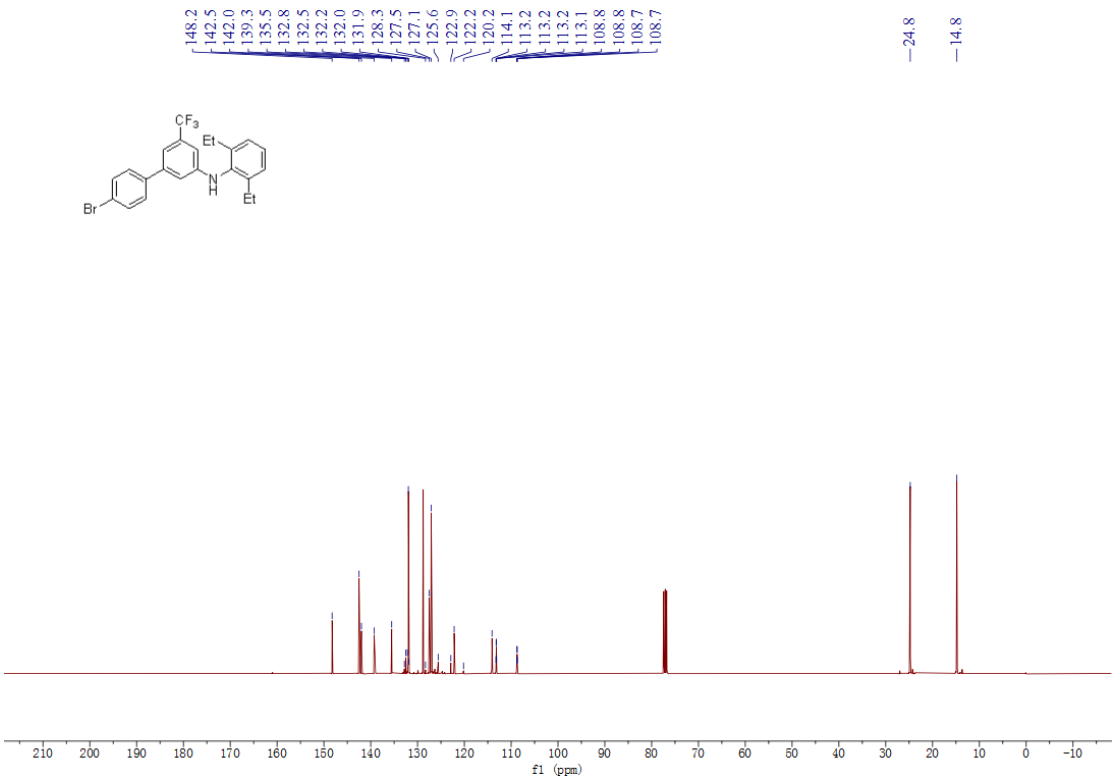
^{1}H NMR spectrum of **4b** in $CDCl_3$



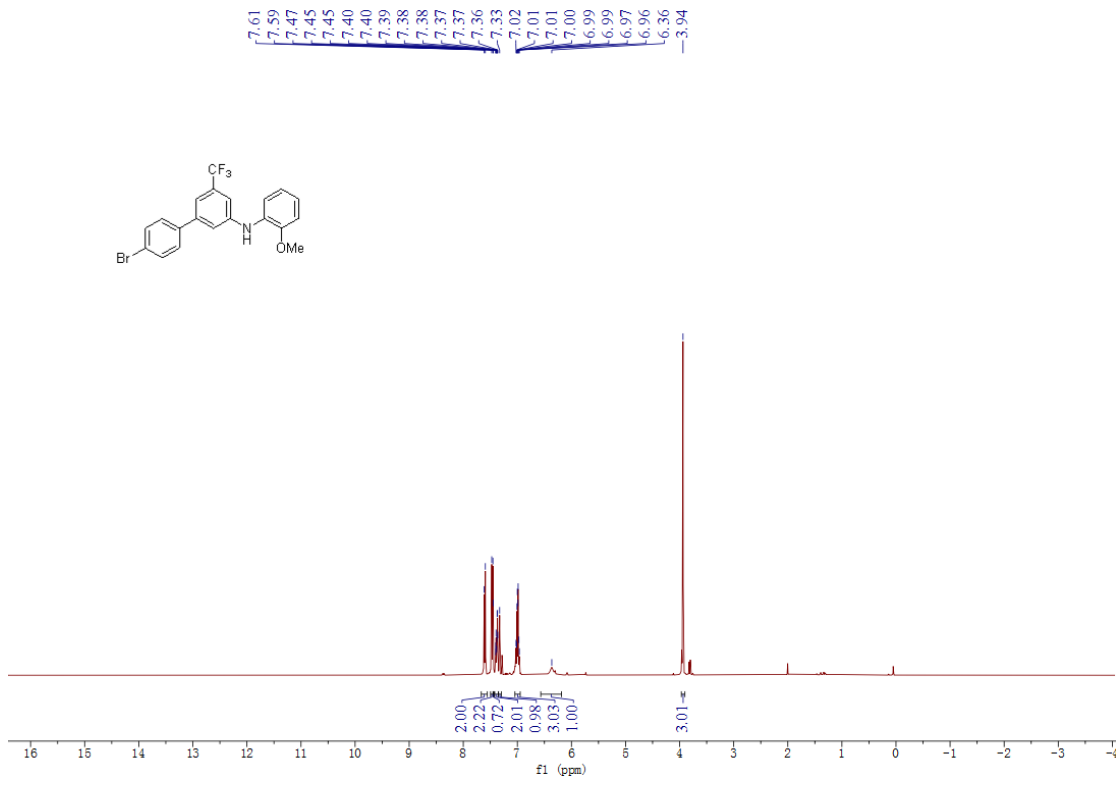
^{19}F NMR spectrum of **4b** in $CDCl_3$



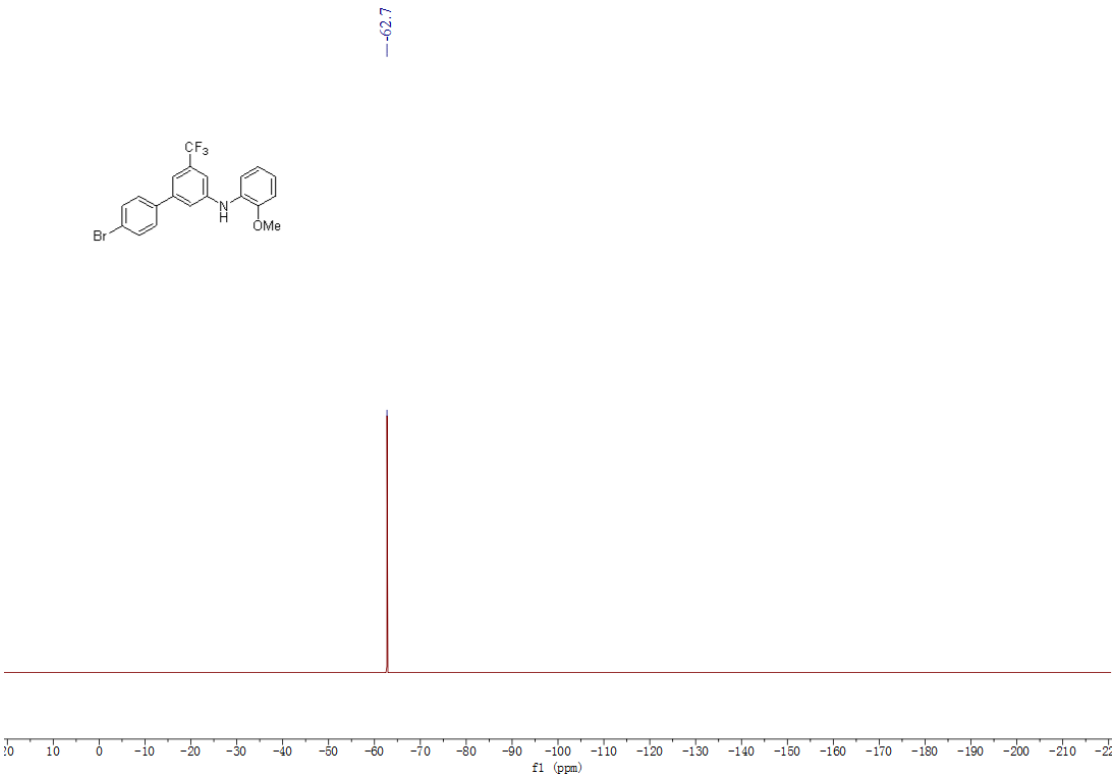
^{13}C NMR spectrum of **4b** in $CDCl_3$



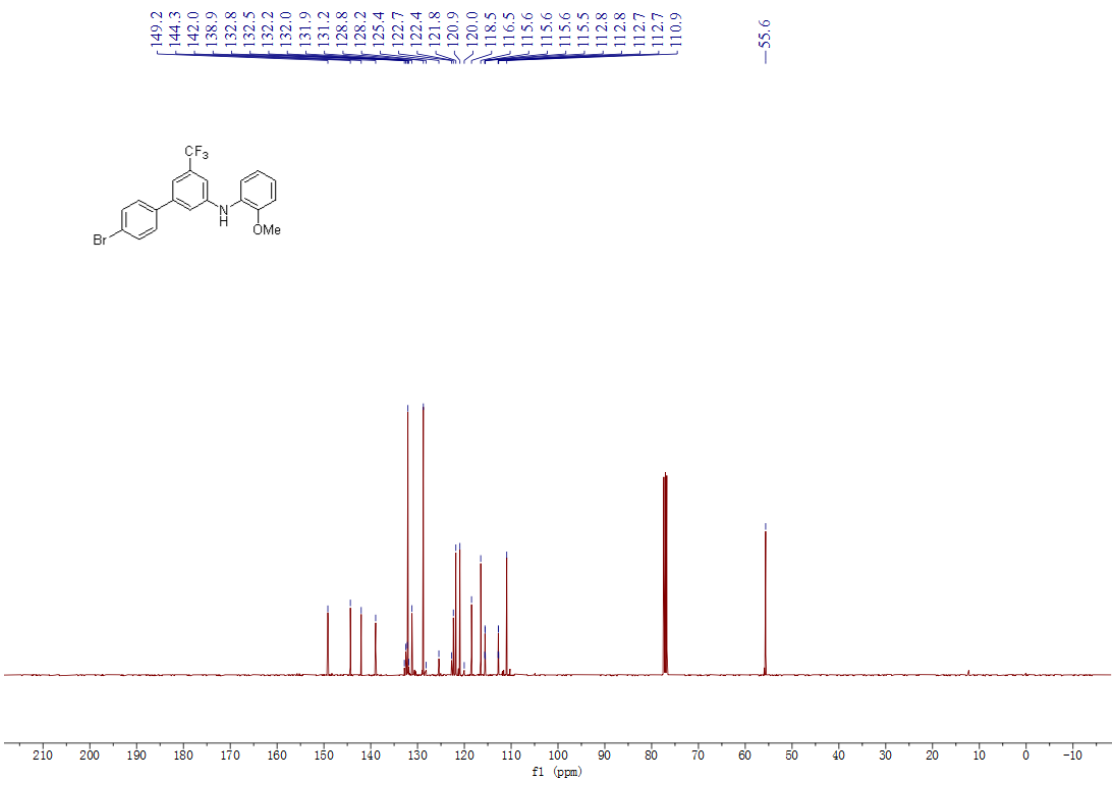
^{1}H NMR spectrum of **4c** in $CDCl_3$



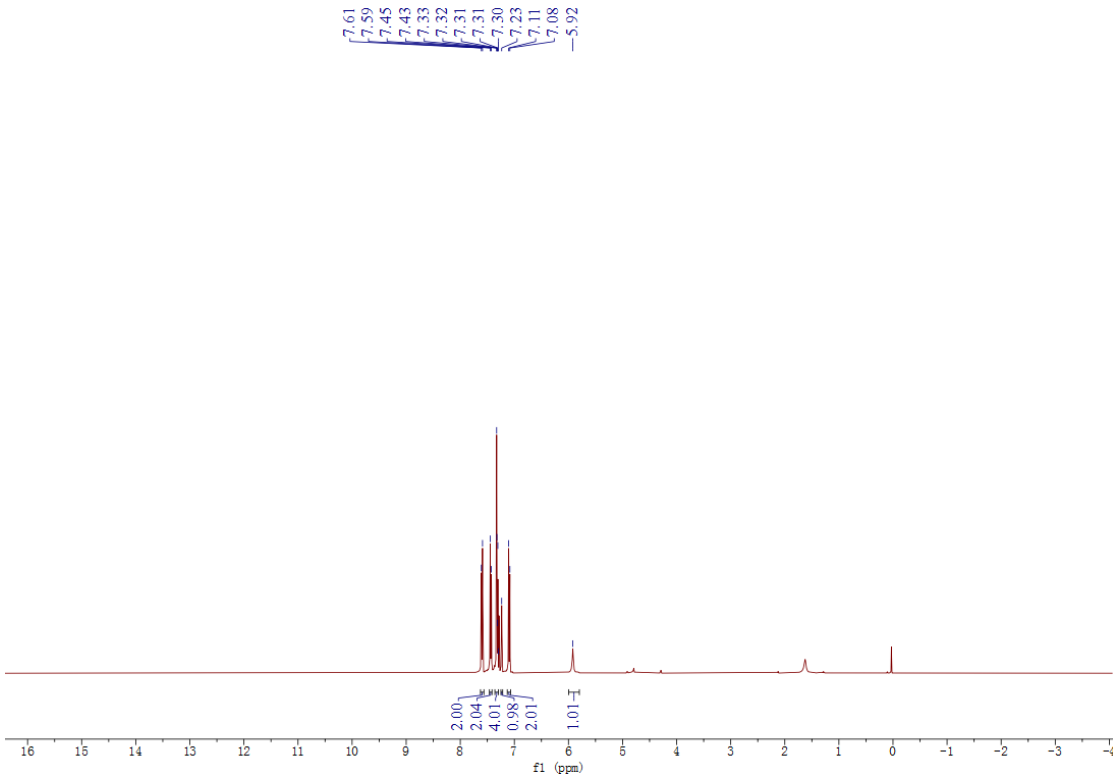
^{19}F NMR spectrum of **4c** in $CDCl_3$



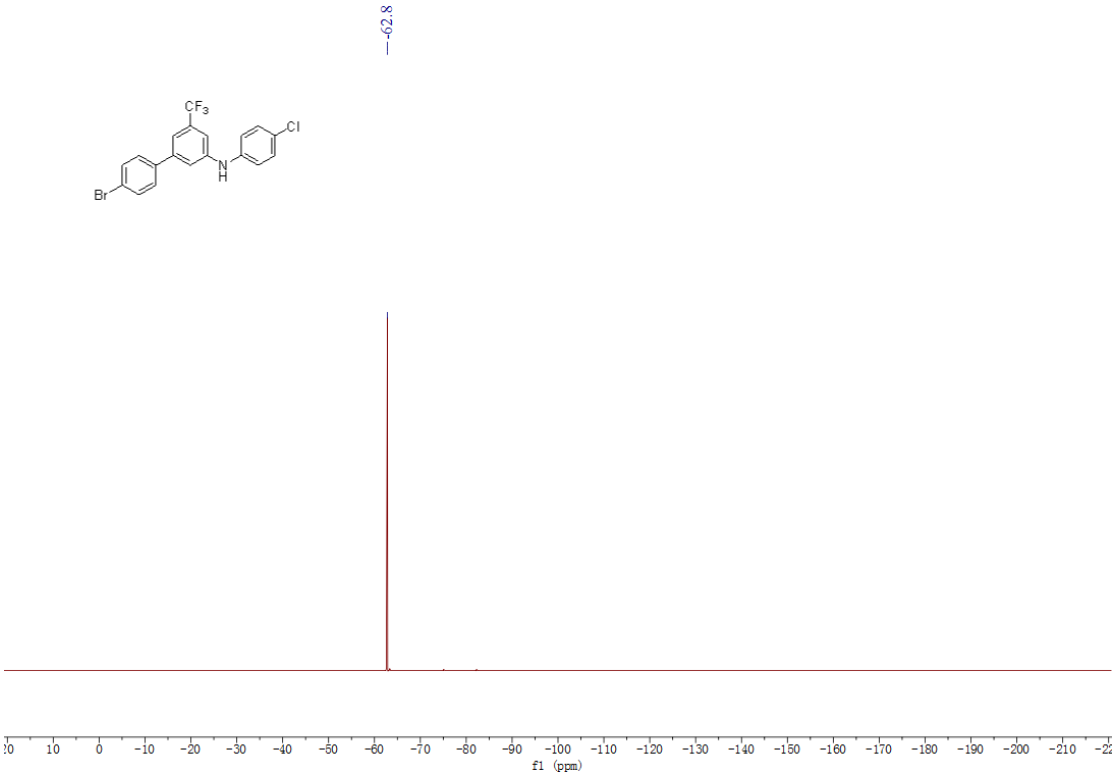
^{13}C NMR spectrum of **4c** in $CDCl_3$



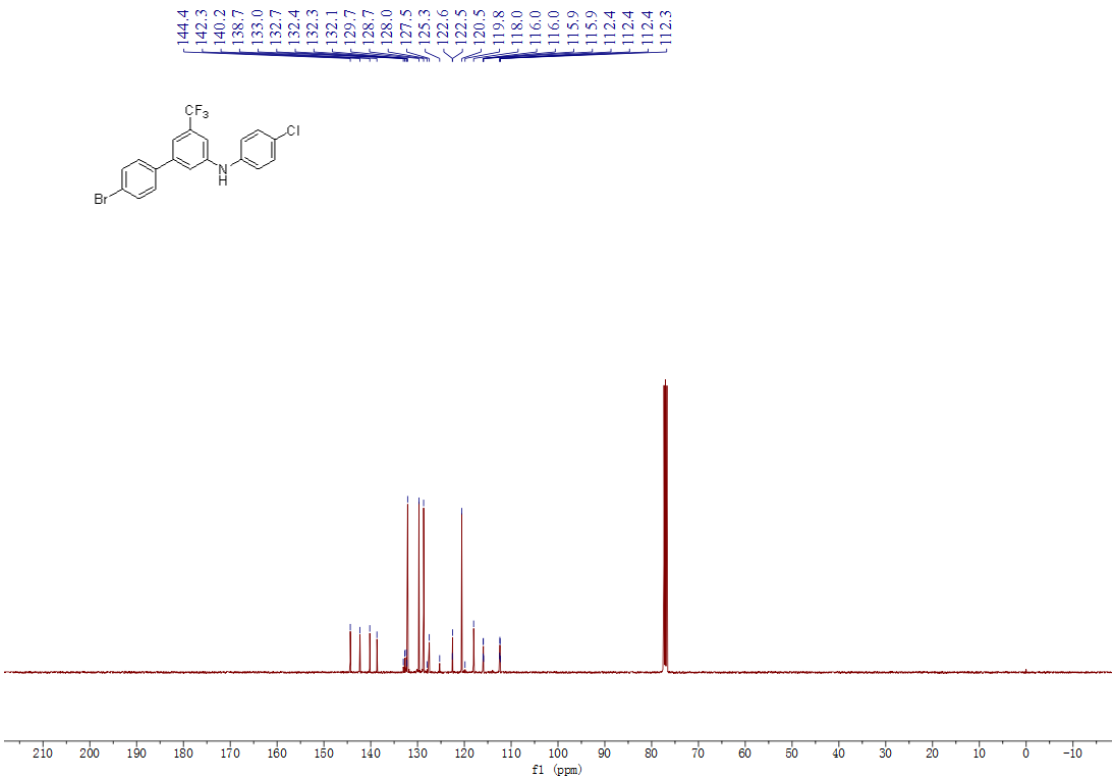
^{1}H NMR spectrum of **4d** in $CDCl_3$



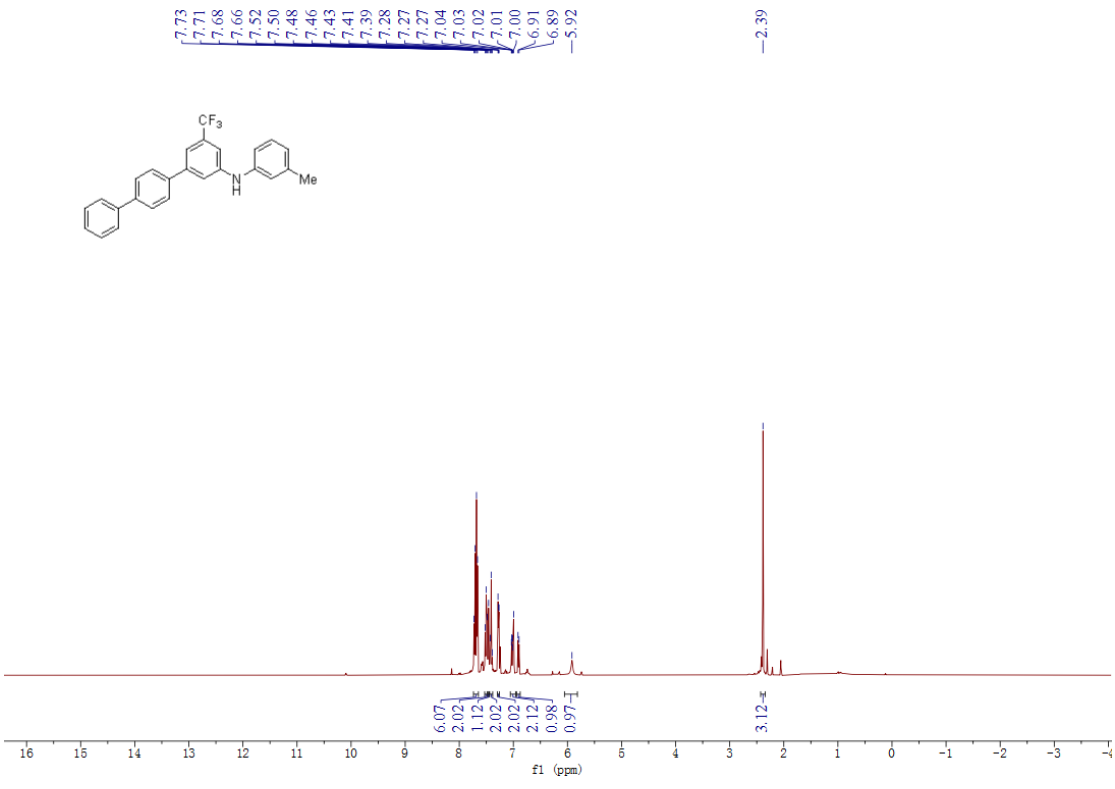
^{19}F NMR spectrum of **4d** in $CDCl_3$



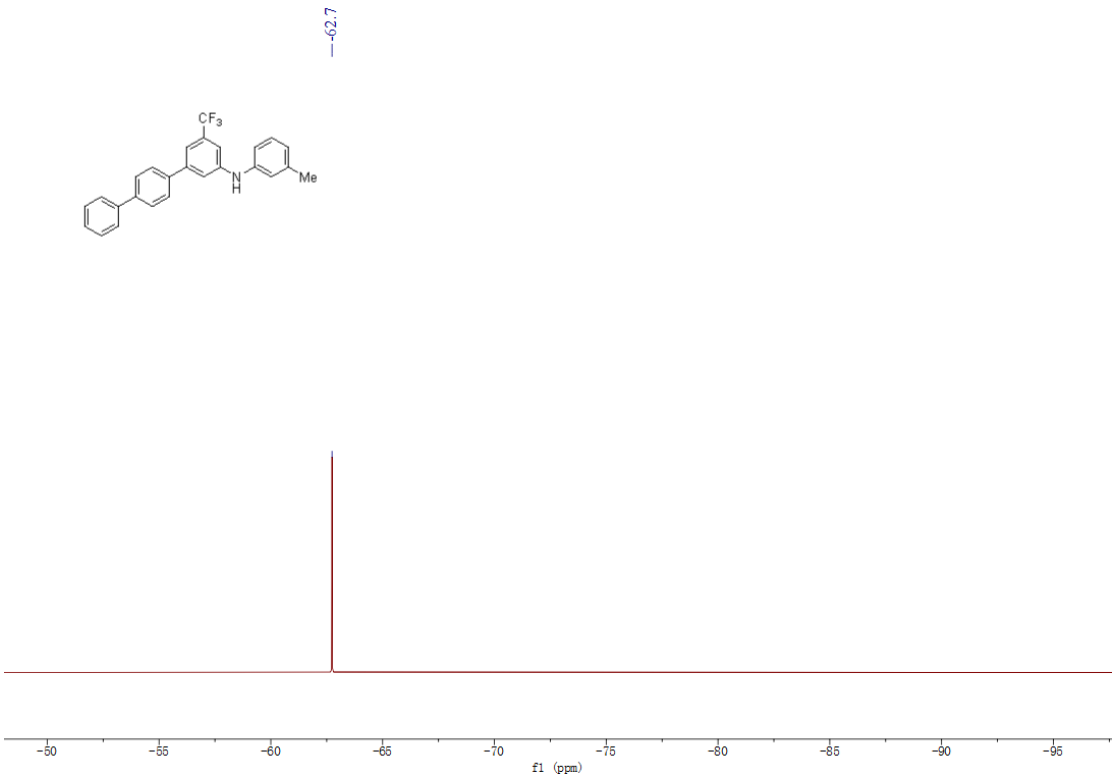
^{13}C NMR spectrum of **4d** in $CDCl_3$



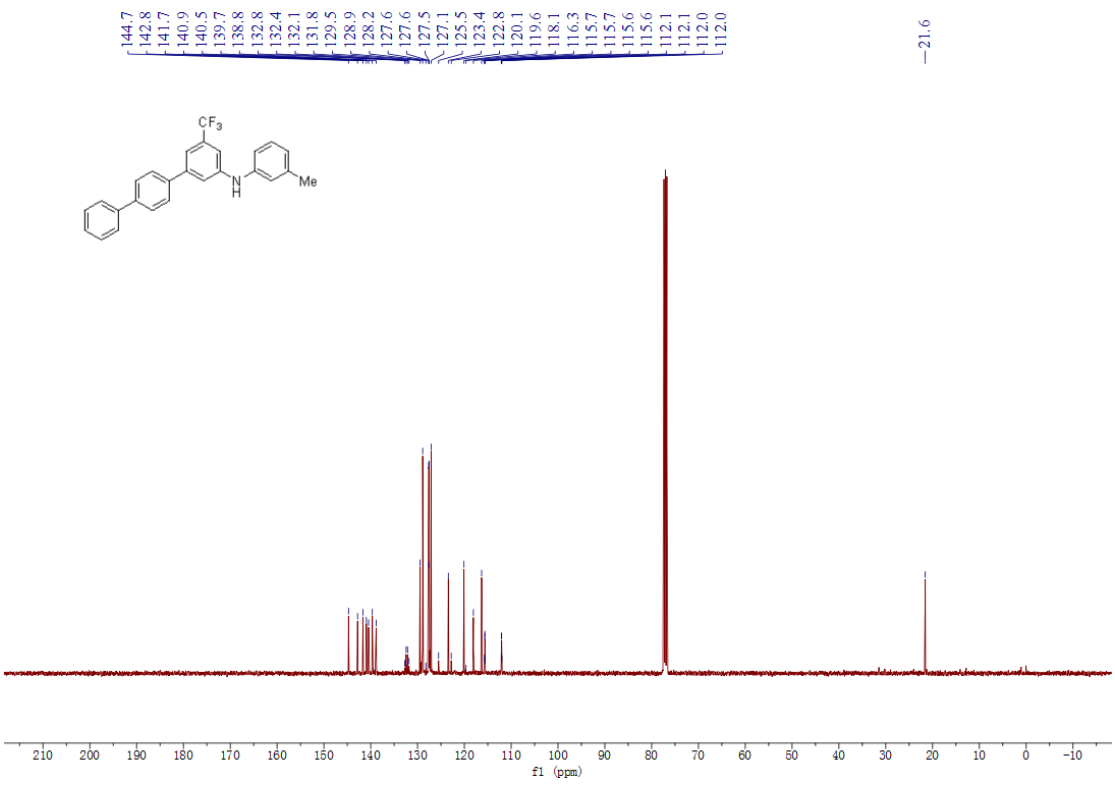
^{1}H NMR spectrum of **4e** in $CDCl_3$



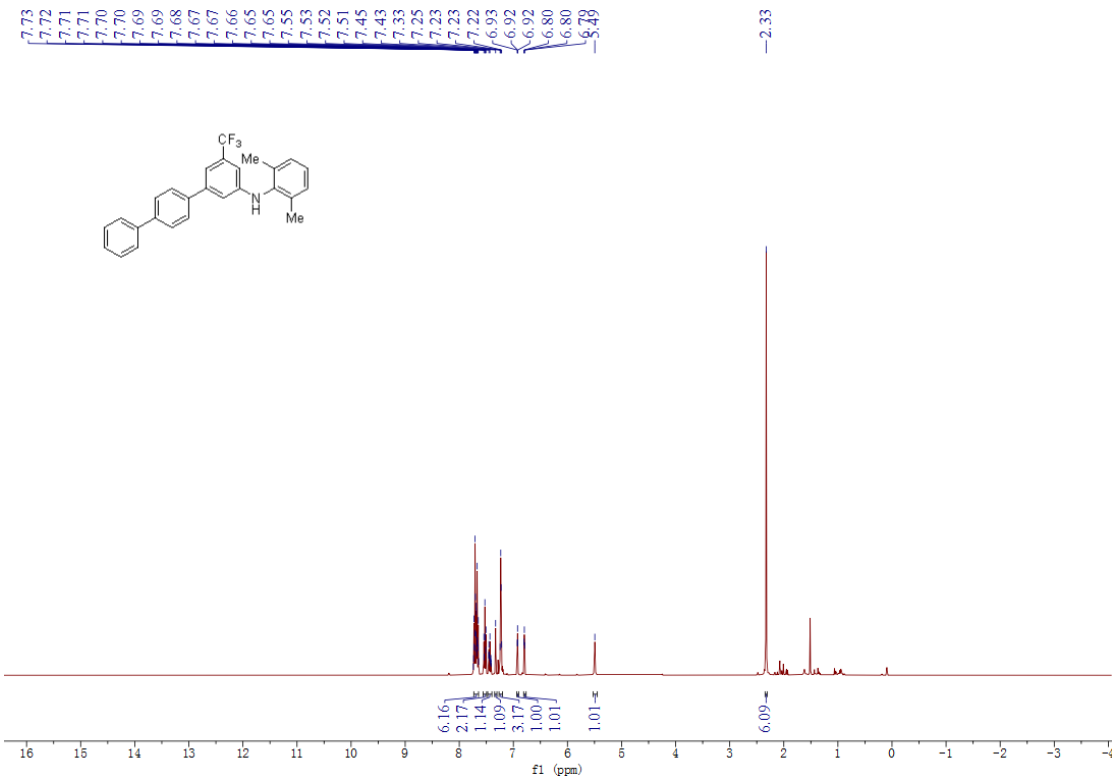
^{19}F NMR spectrum of **4e** in $CDCl_3$



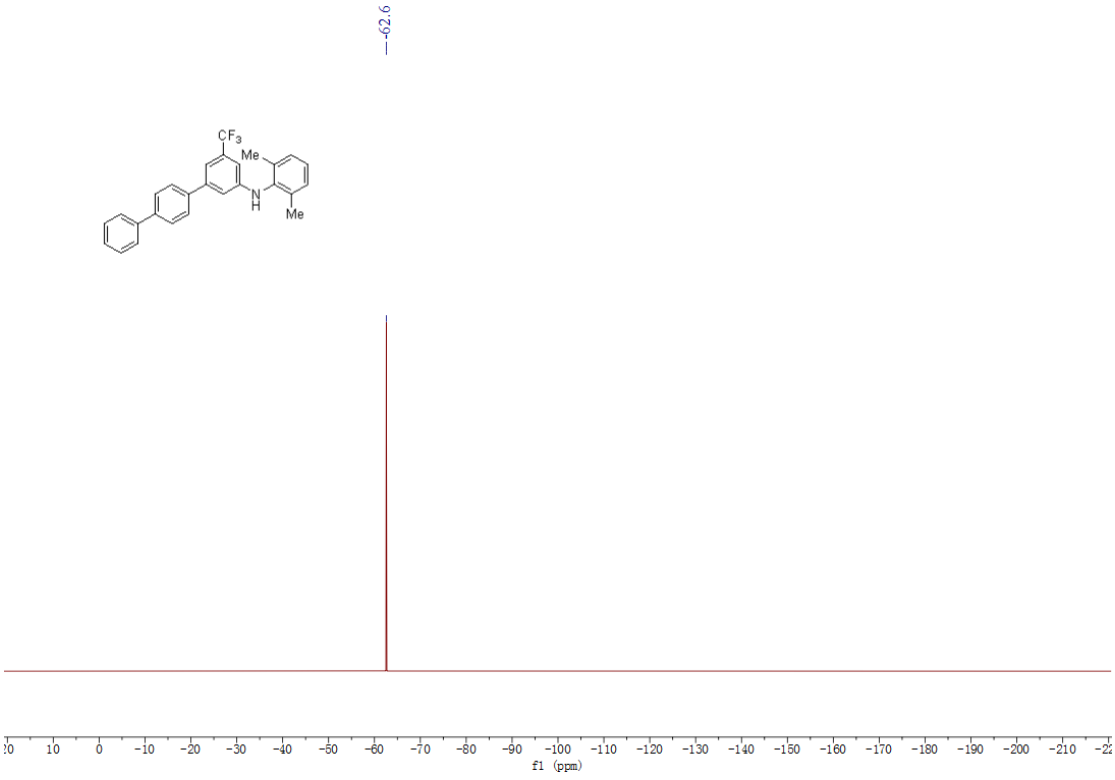
^{13}C NMR spectrum of **4e** in $CDCl_3$



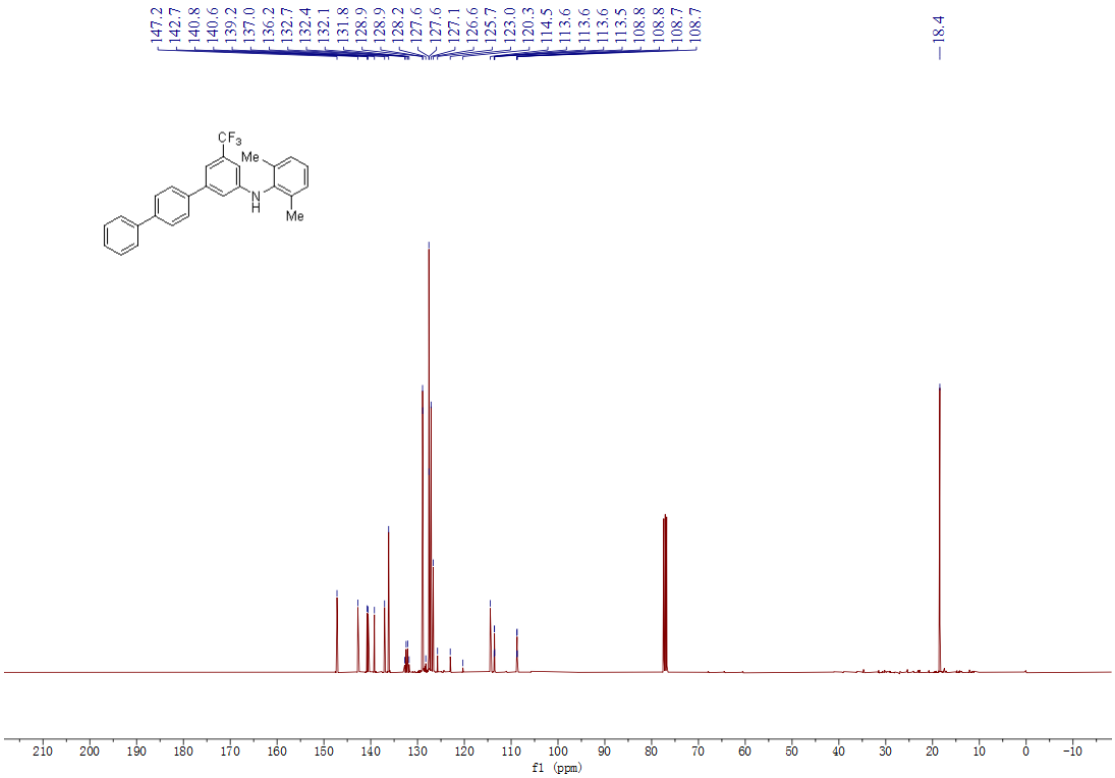
^{1}H NMR spectrum of **4f** in $CDCl_3$



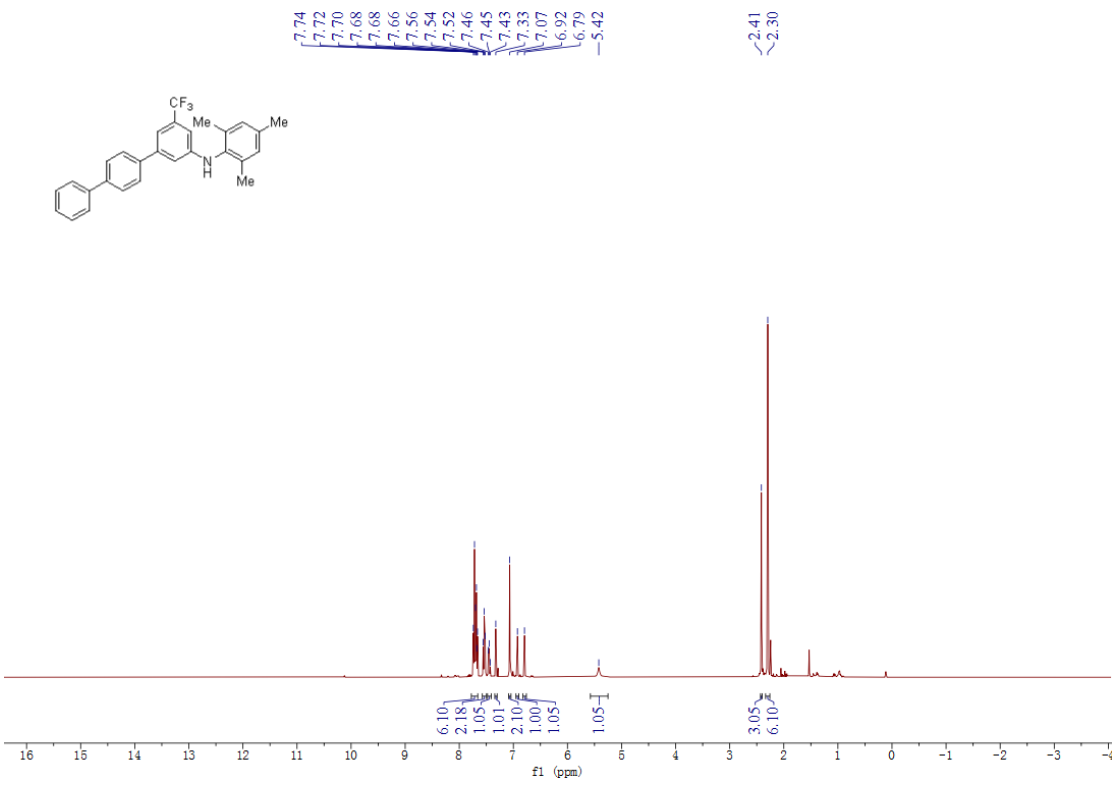
^{19}F NMR spectrum of **4f** in $CDCl_3$



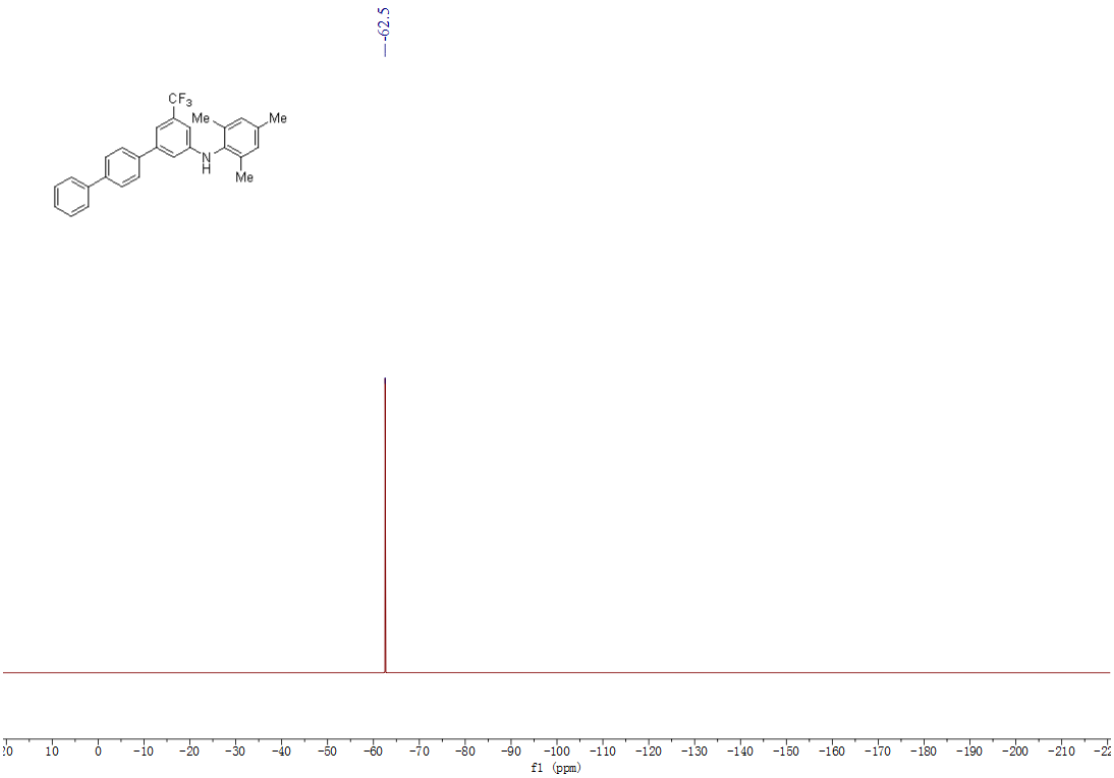
^{13}C NMR spectrum of **4f** in $CDCl_3$



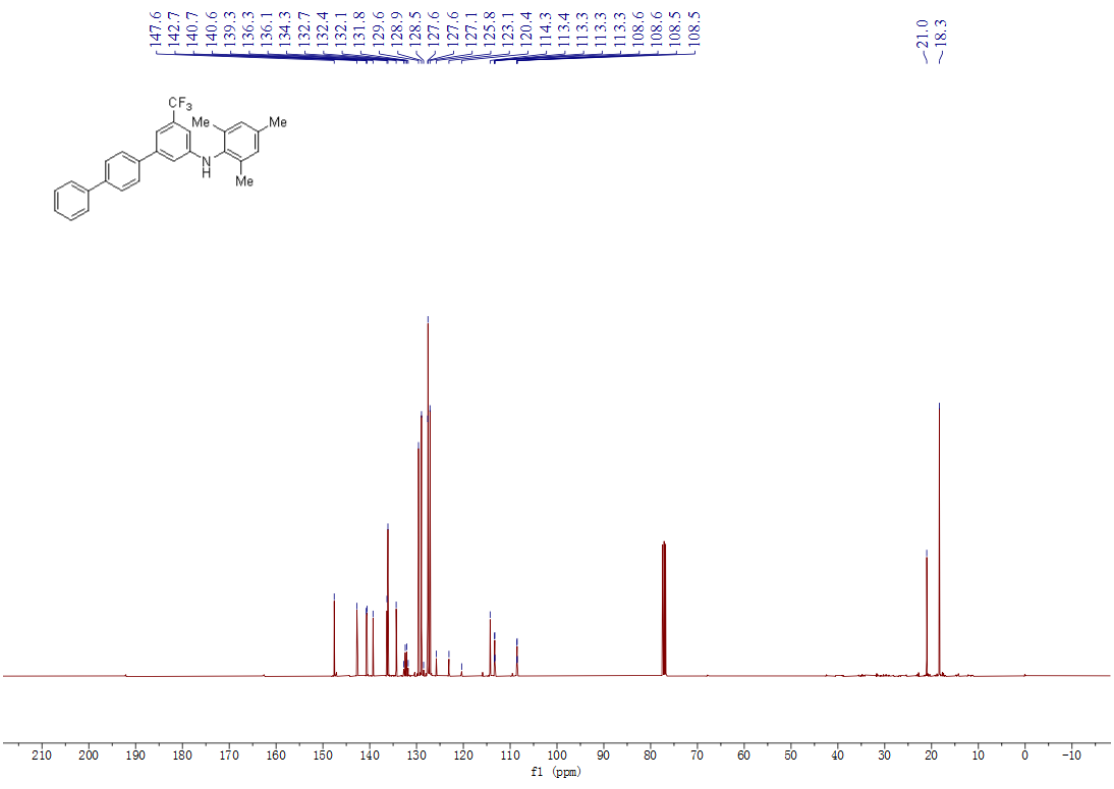
^{1}H NMR spectrum of **4g** in $CDCl_3$



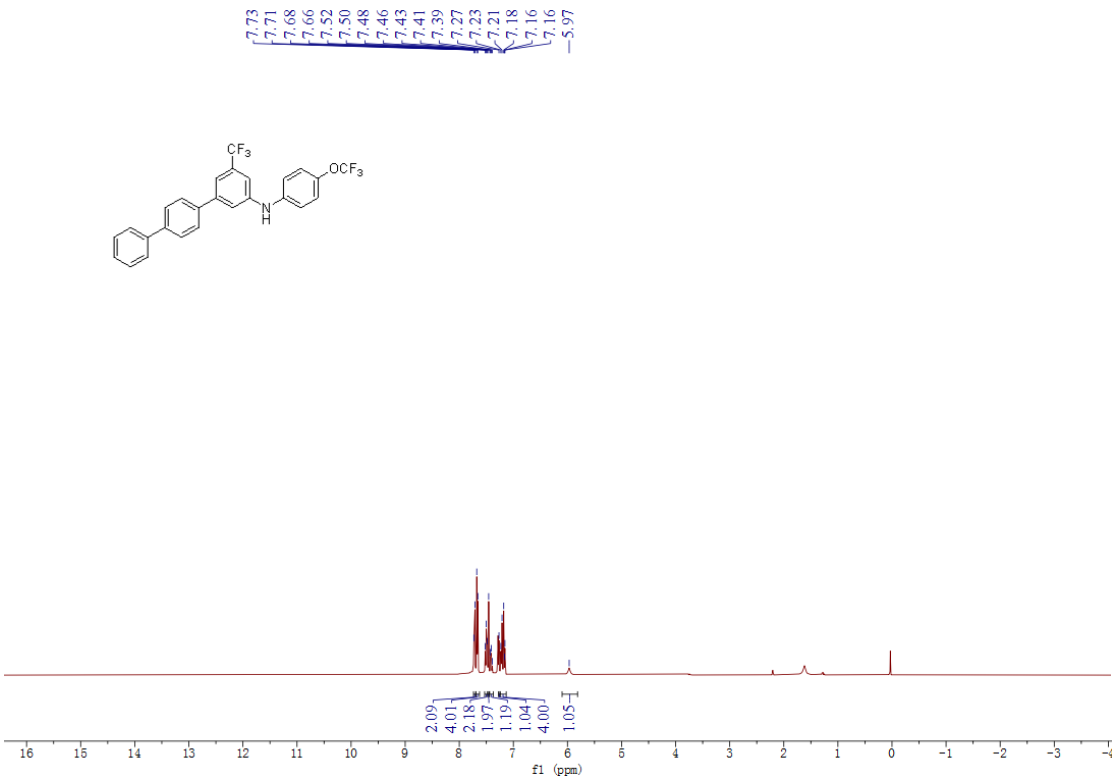
^{19}F NMR spectrum of **4g** in $CDCl_3$



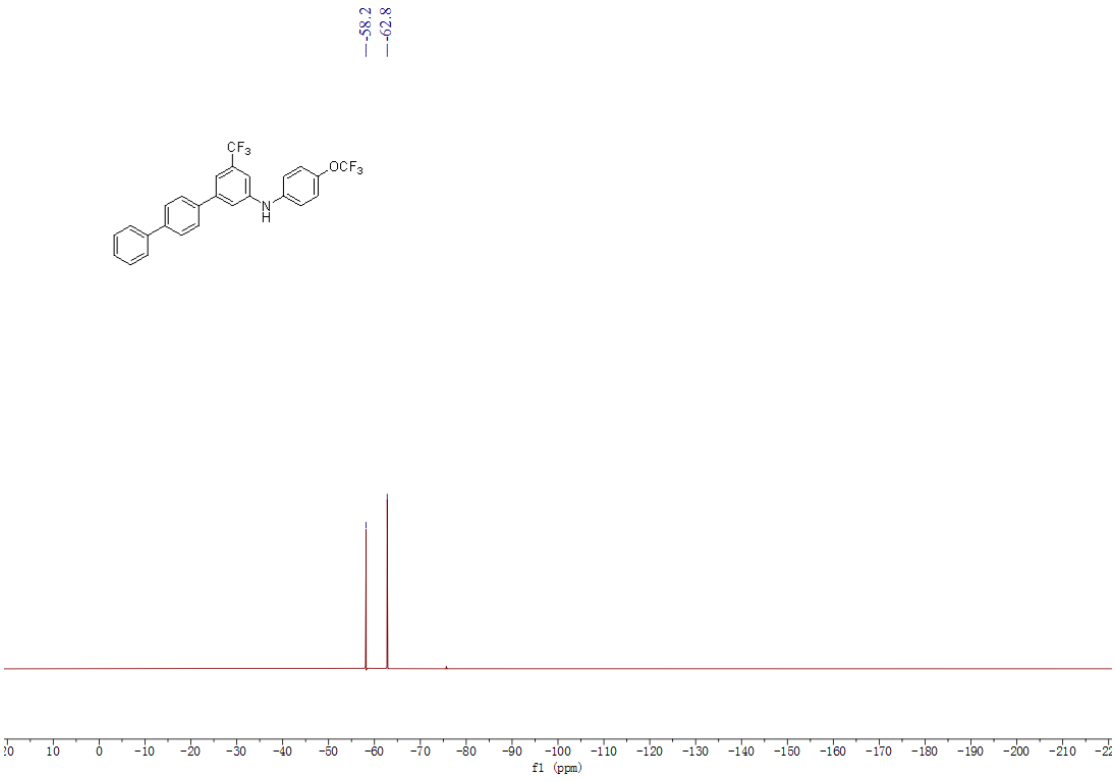
^{13}C NMR spectrum of **4g** in $CDCl_3$



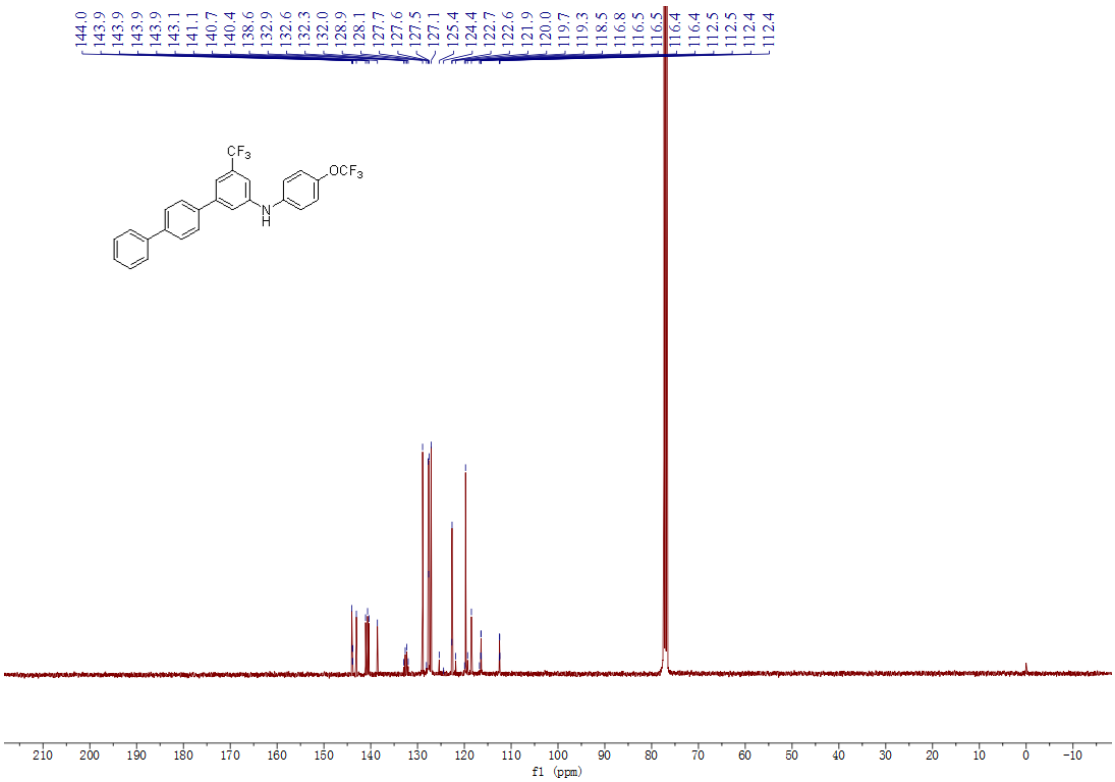
^{1}H NMR spectrum of **4h** in $CDCl_3$



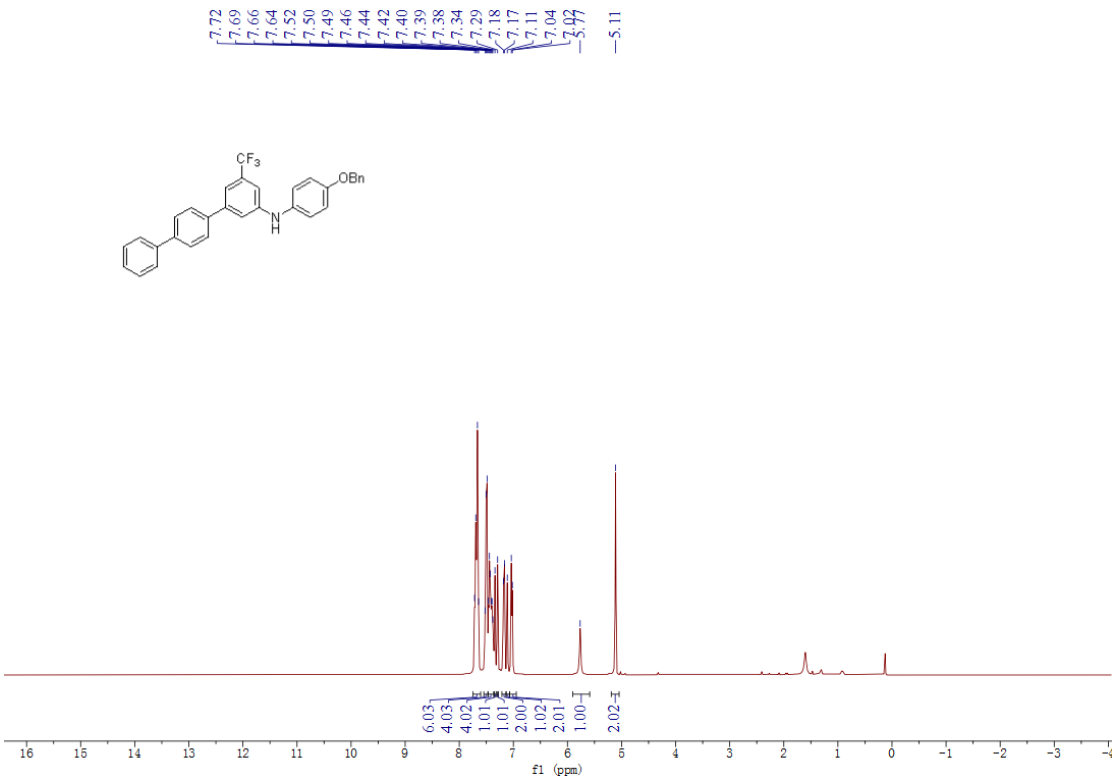
^{19}F NMR spectrum of **4h** in $CDCl_3$



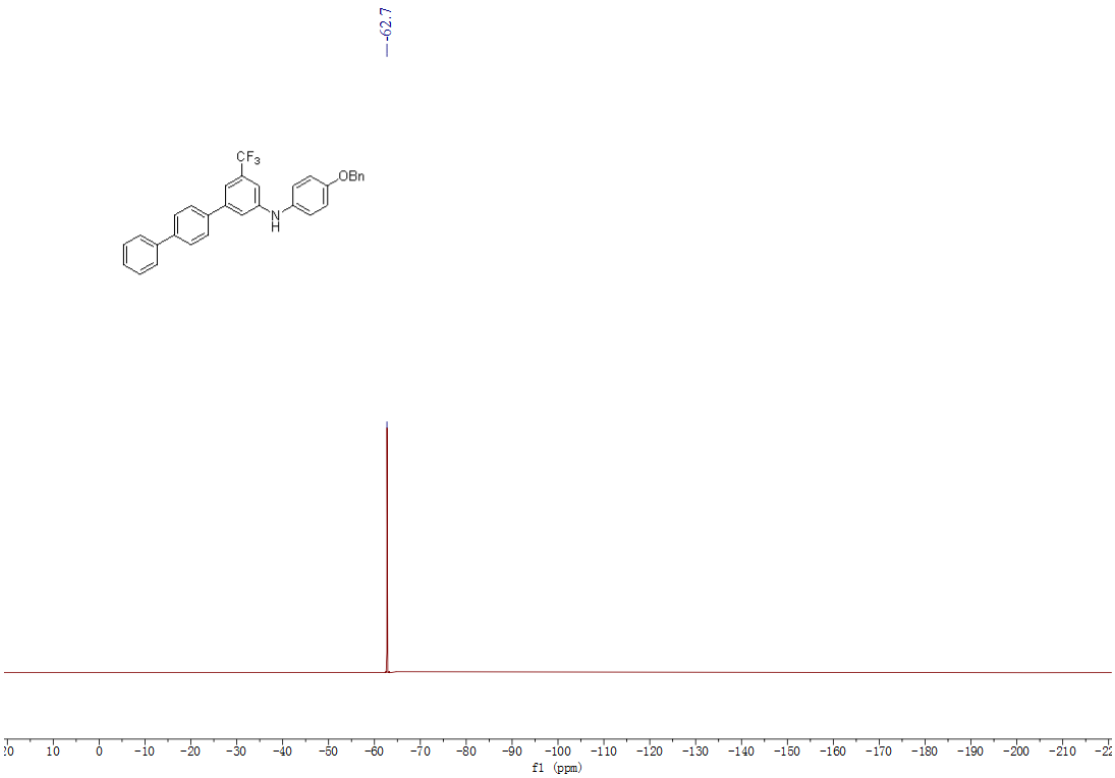
^{13}C NMR spectrum of **4h** in $CDCl_3$



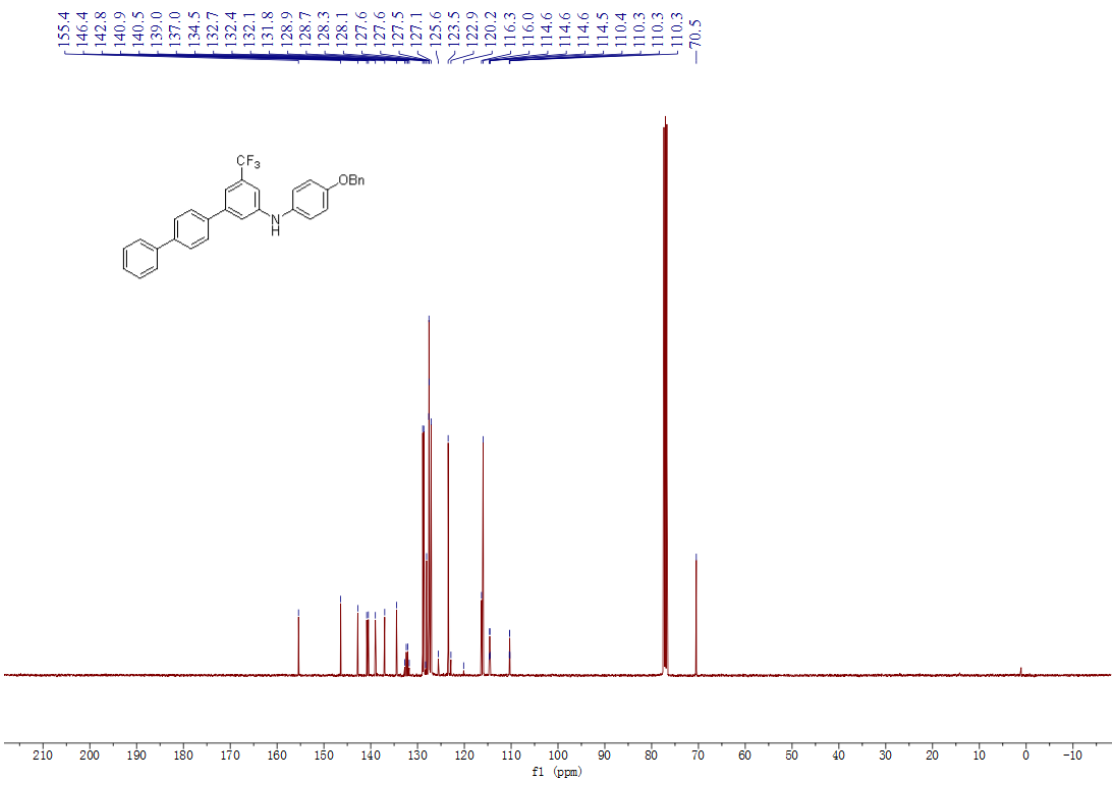
^{1}H NMR spectrum of **4i** in $CDCl_3$



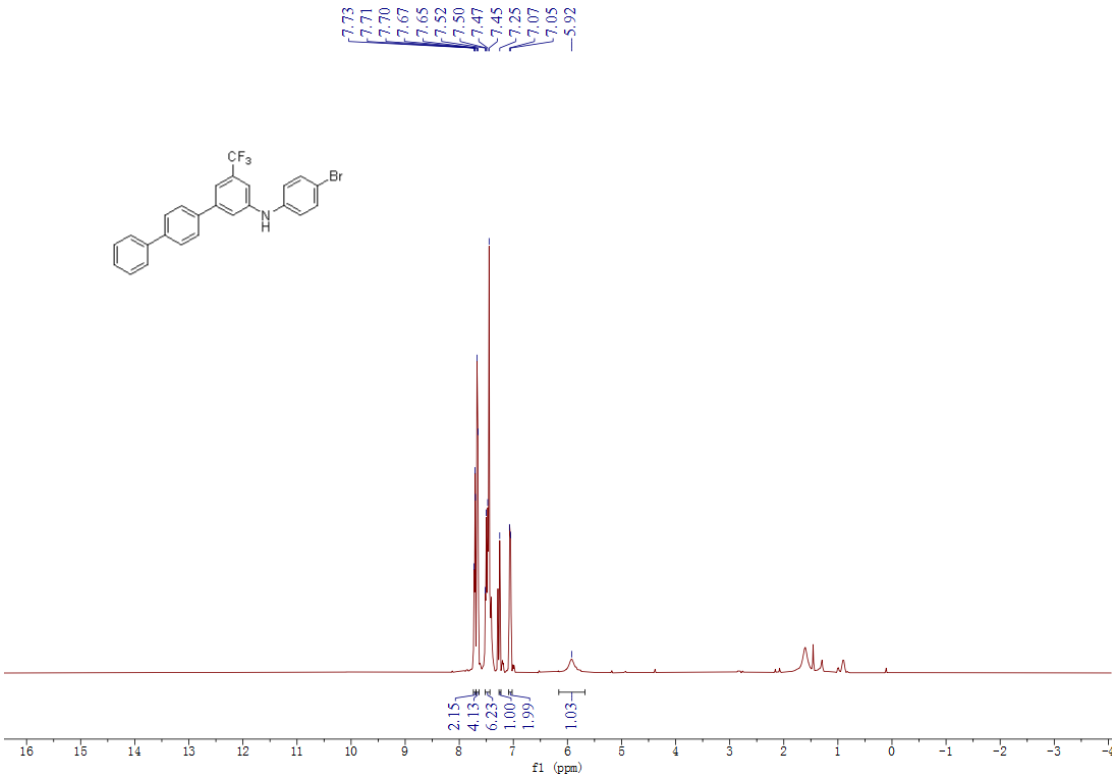
^{19}F NMR spectrum of **4i** in $CDCl_3$



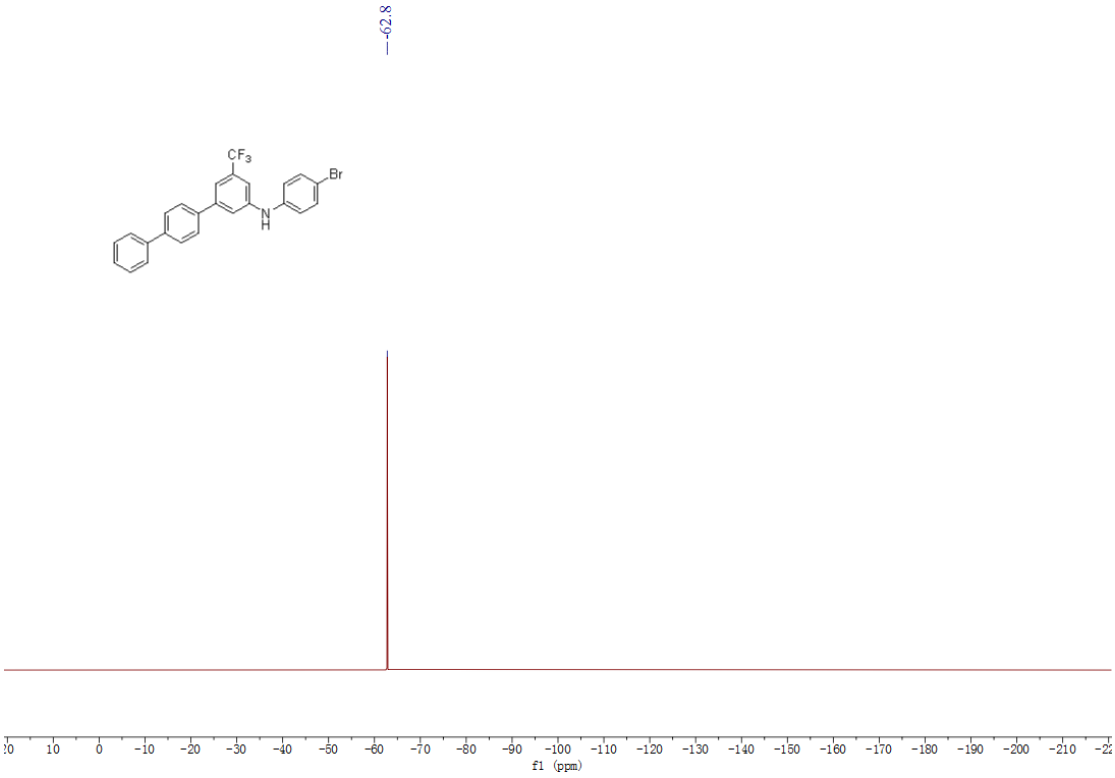
^{13}C NMR spectrum of **4i** in $CDCl_3$



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



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



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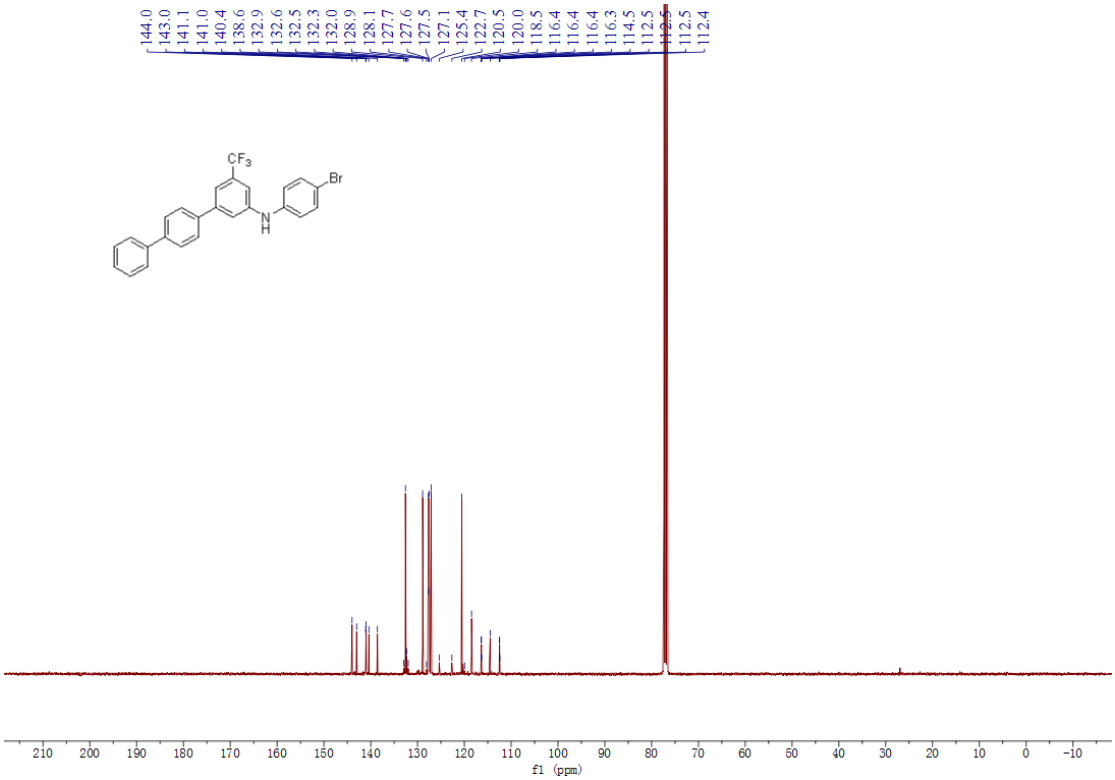
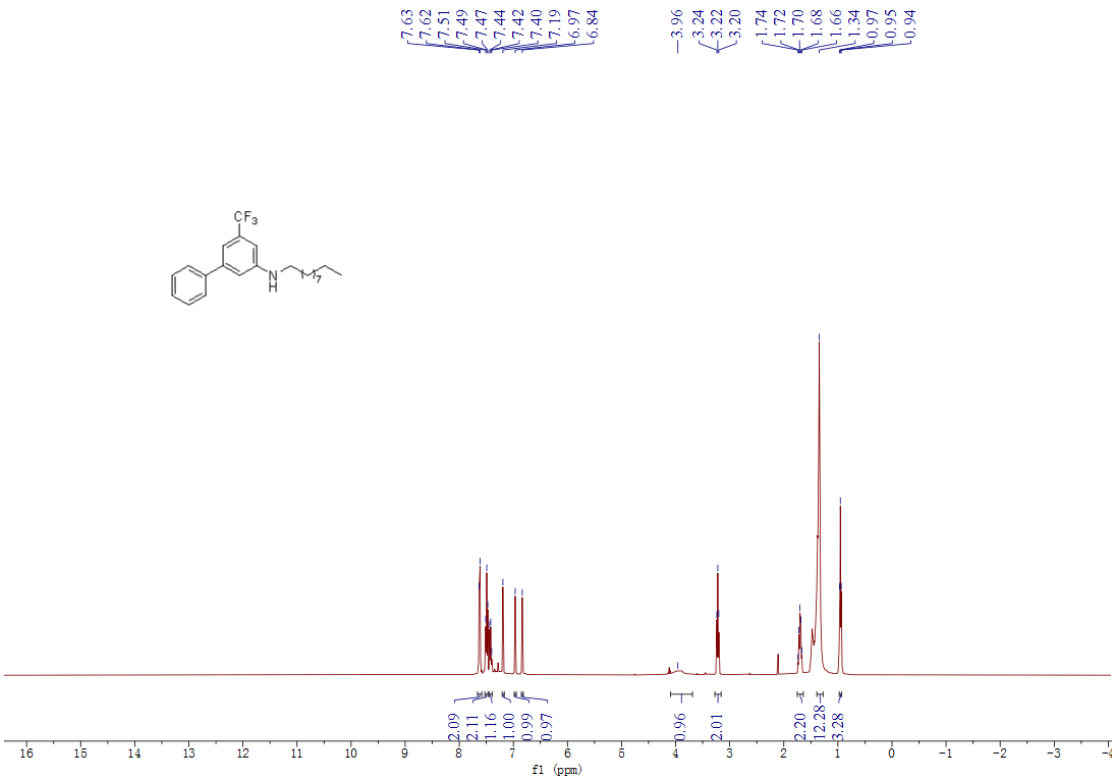
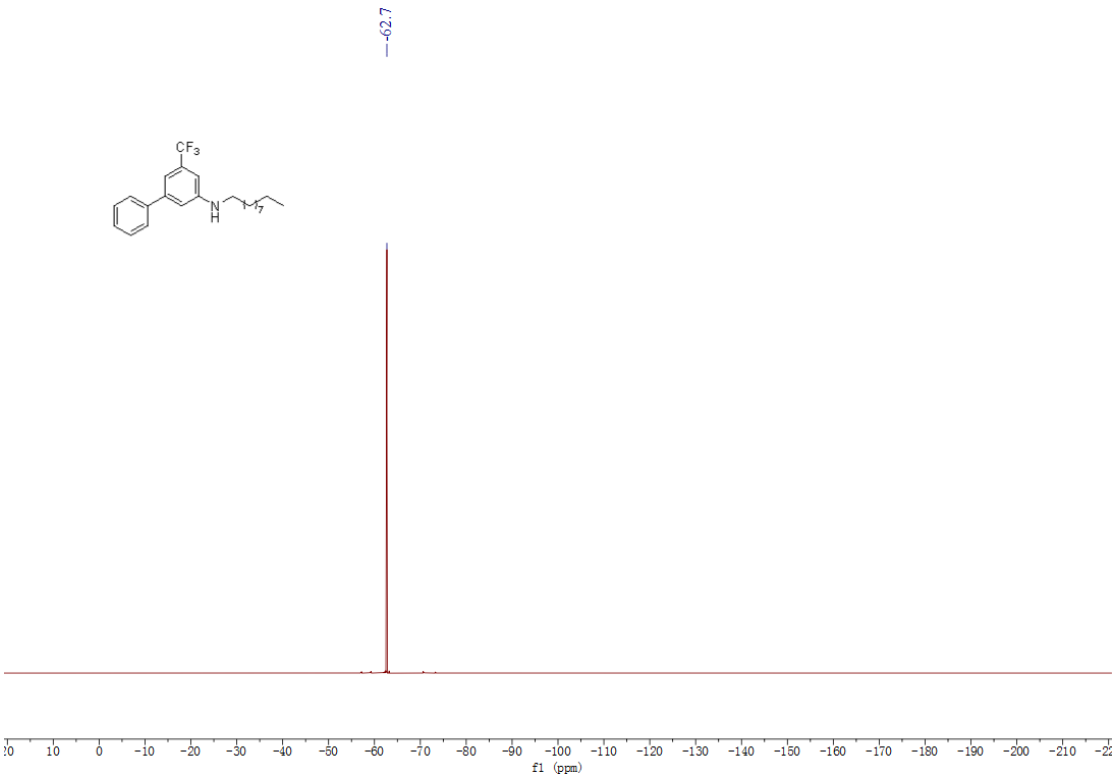


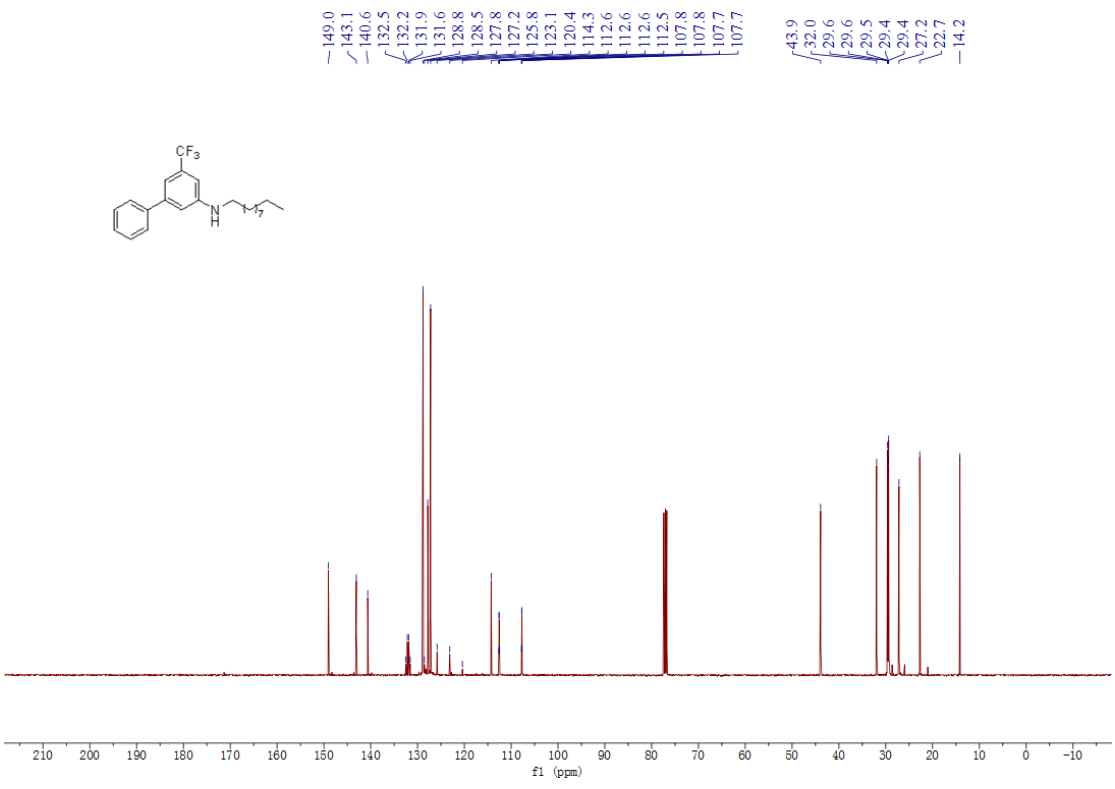
^{1}H NMR spectrum of **4k** in $CDCl_3$



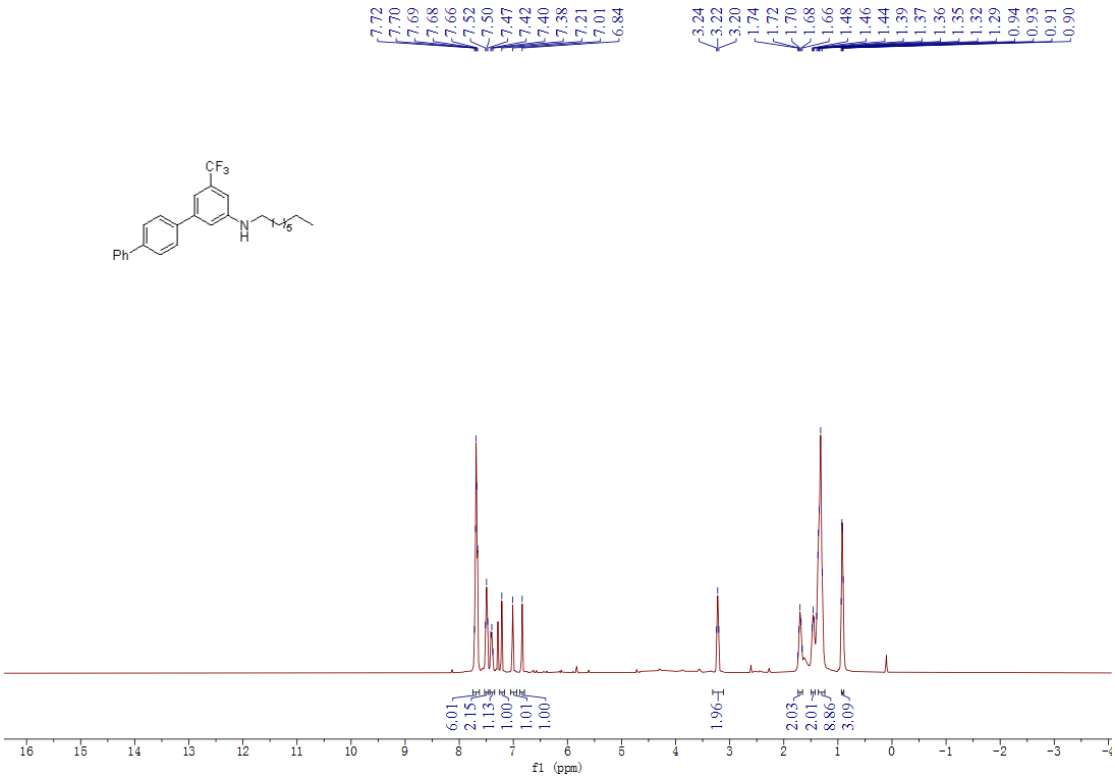
^{19}F NMR spectrum of **4k** in $CDCl_3$



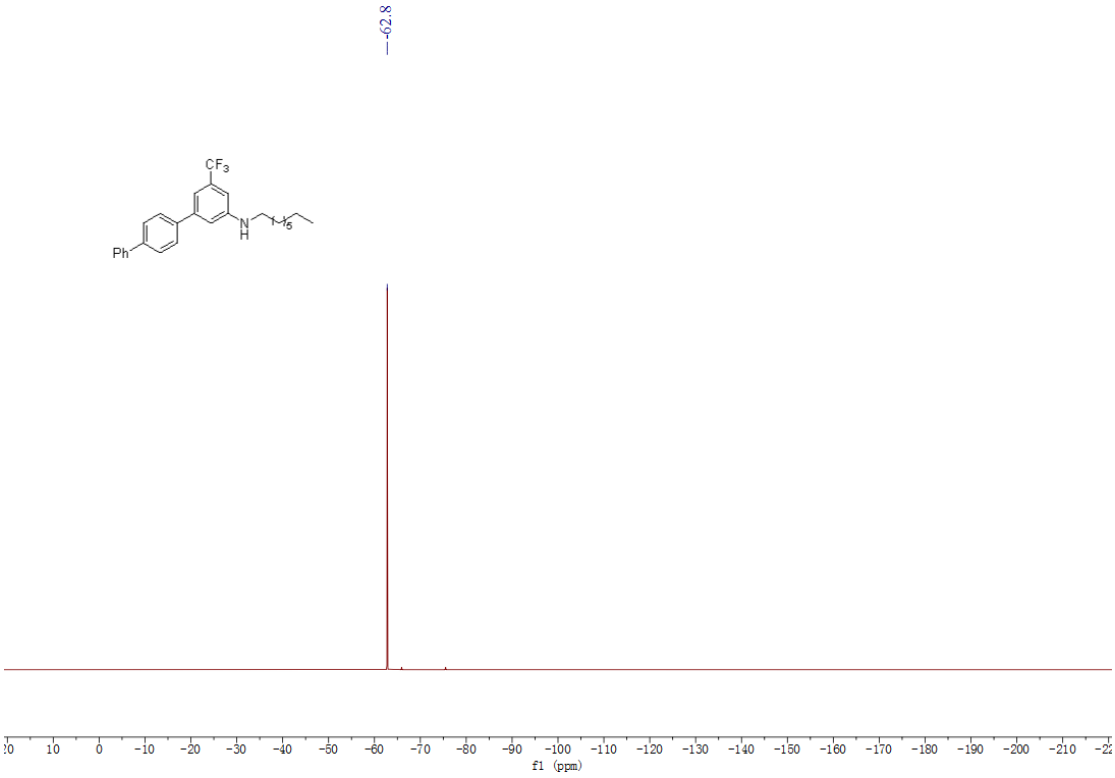
^{13}C NMR spectrum of **4k** in $CDCl_3$



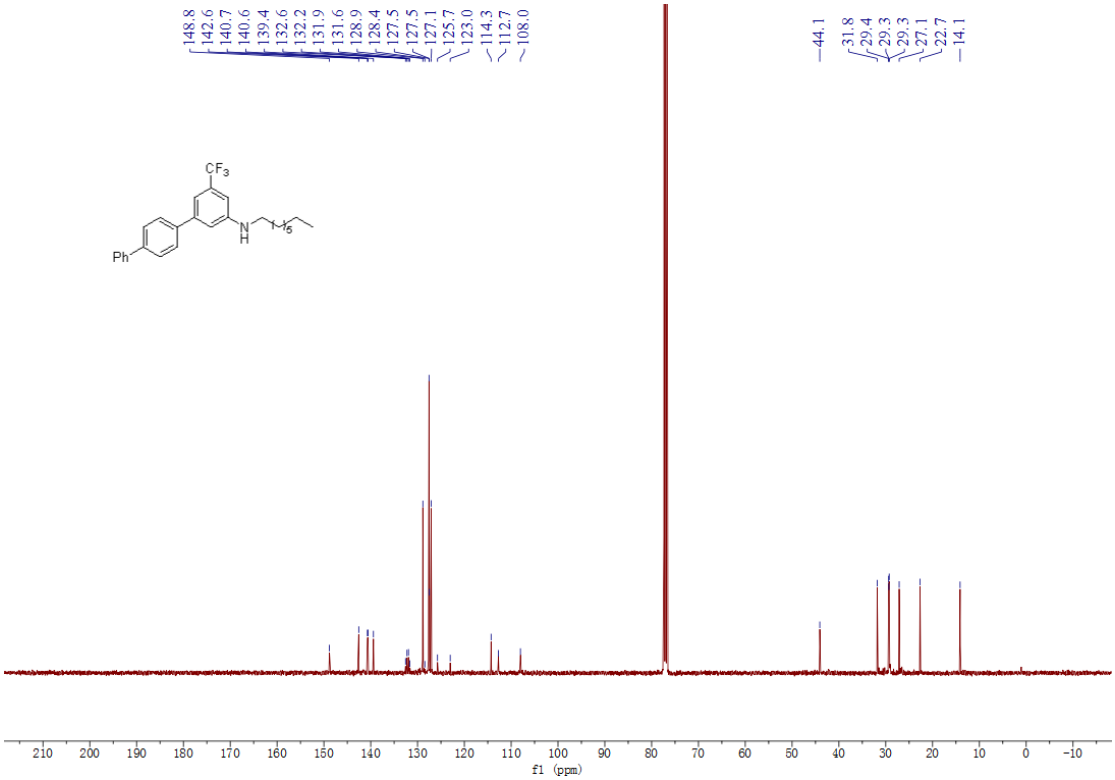
^{1}H NMR spectrum of **4l** in $CDCl_3$



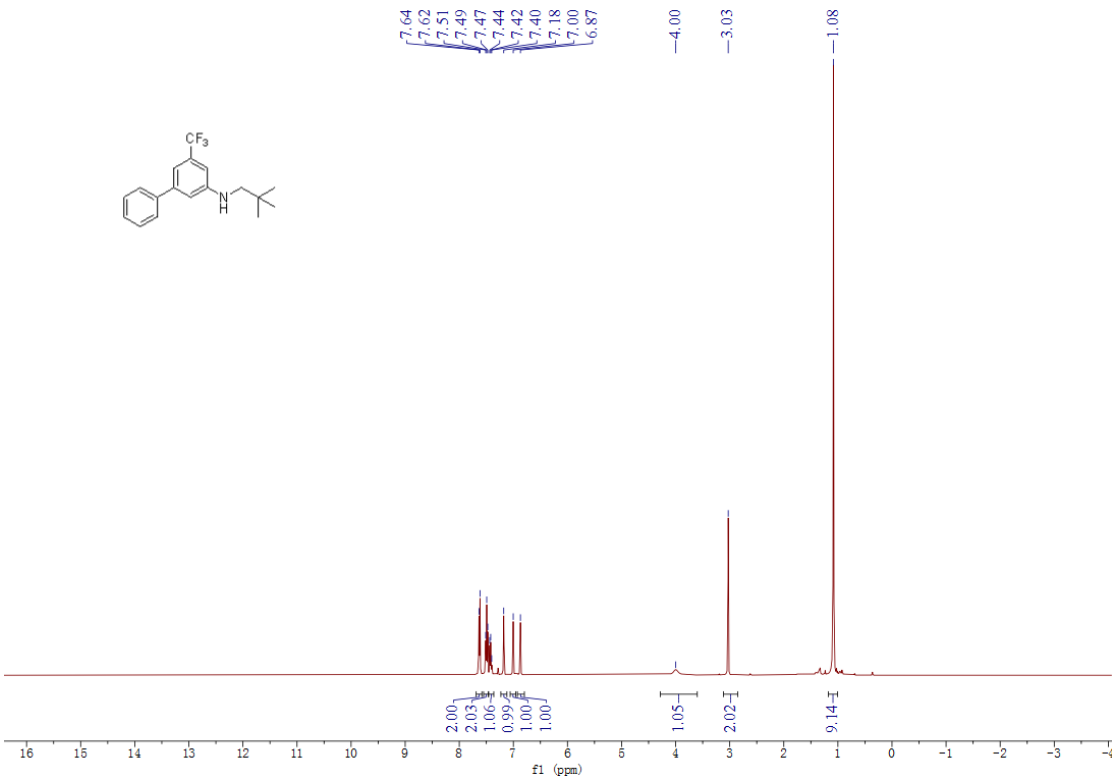
^{19}F NMR spectrum of **4l** in $CDCl_3$



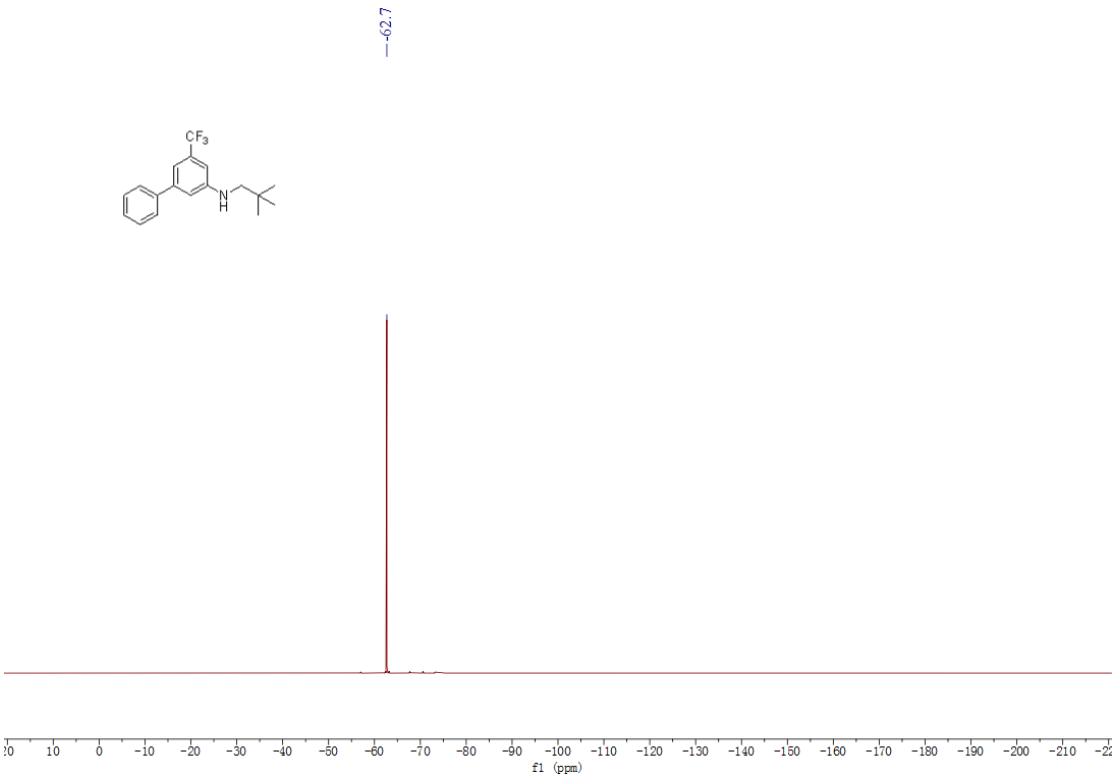
^{13}C NMR spectrum of **4l** in $CDCl_3$



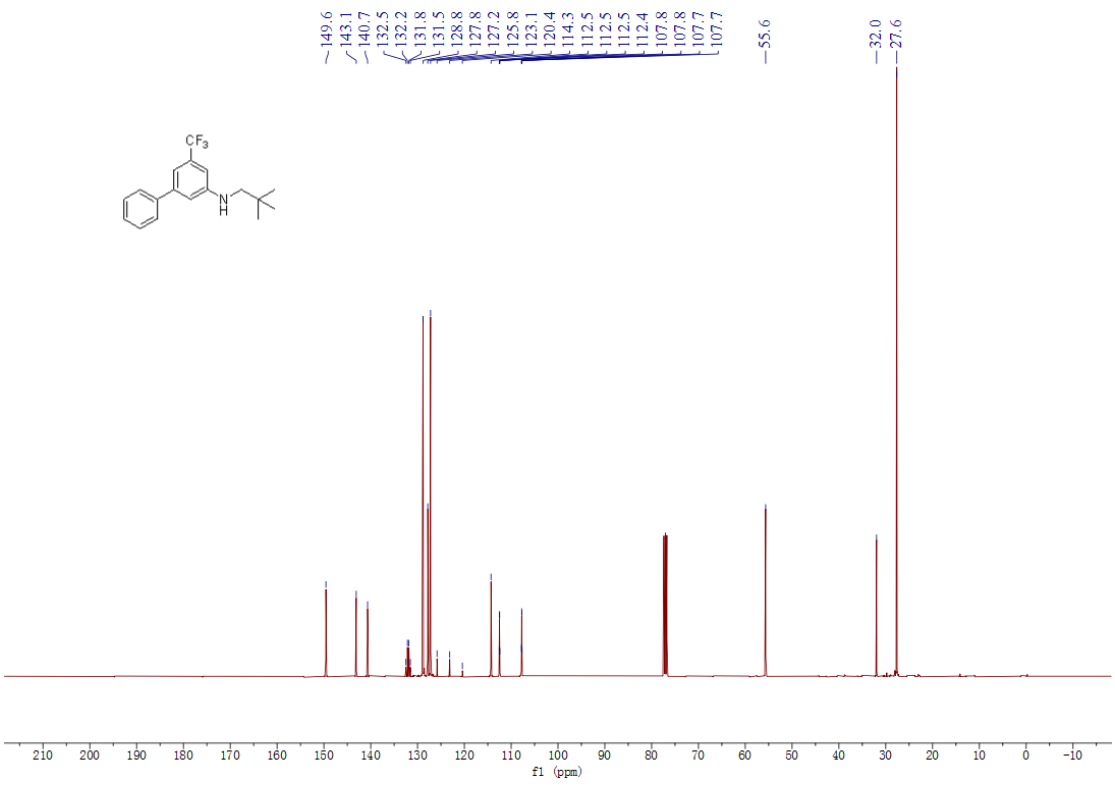
^{1}H NMR spectrum of **4m** in $CDCl_3$



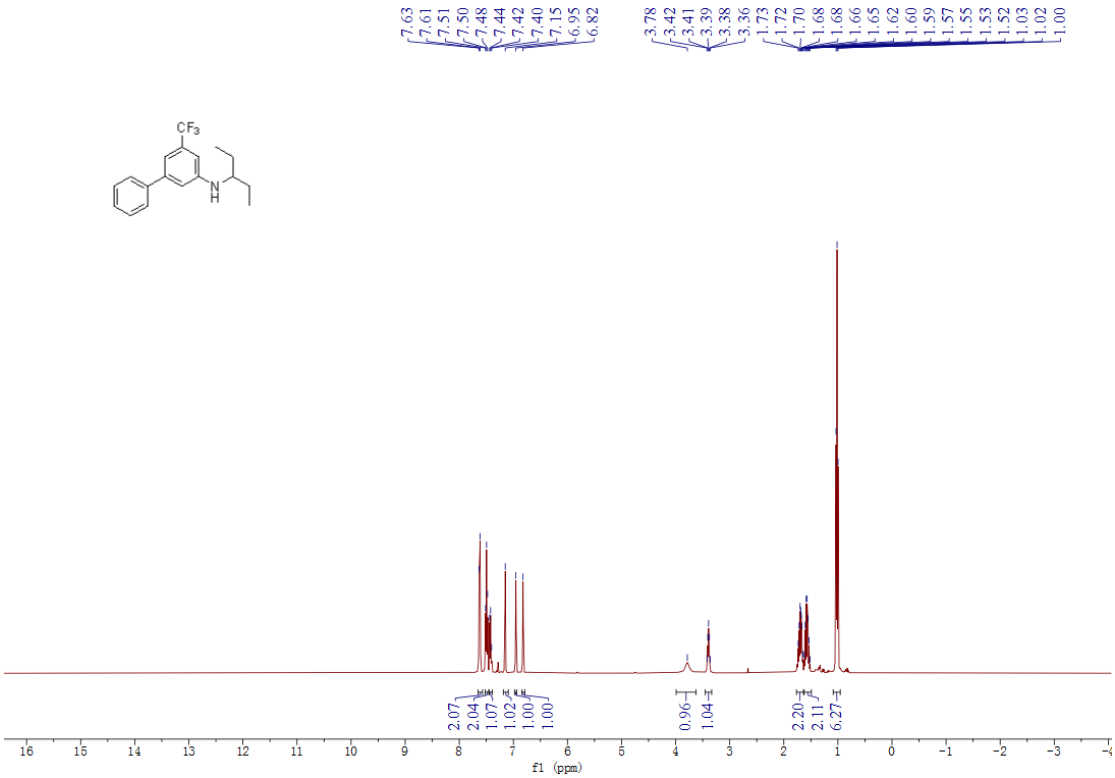
^{19}F NMR spectrum of **4m** in $CDCl_3$



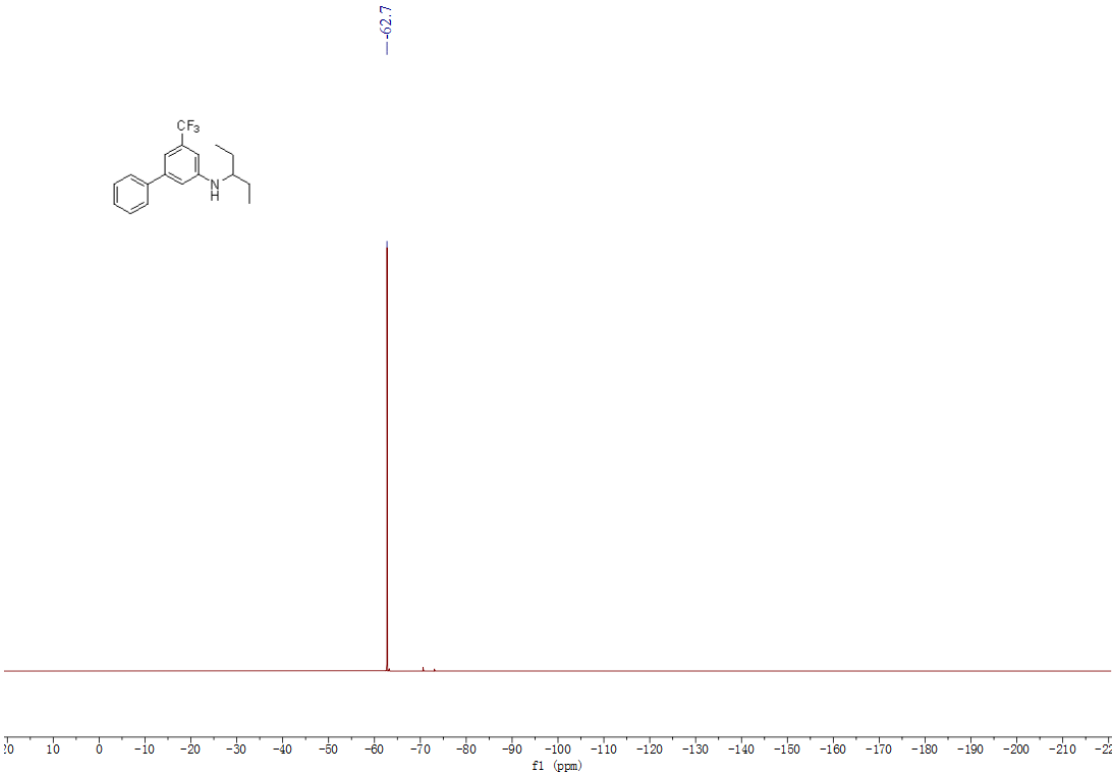
^{13}C NMR spectrum of **4m** in $CDCl_3$



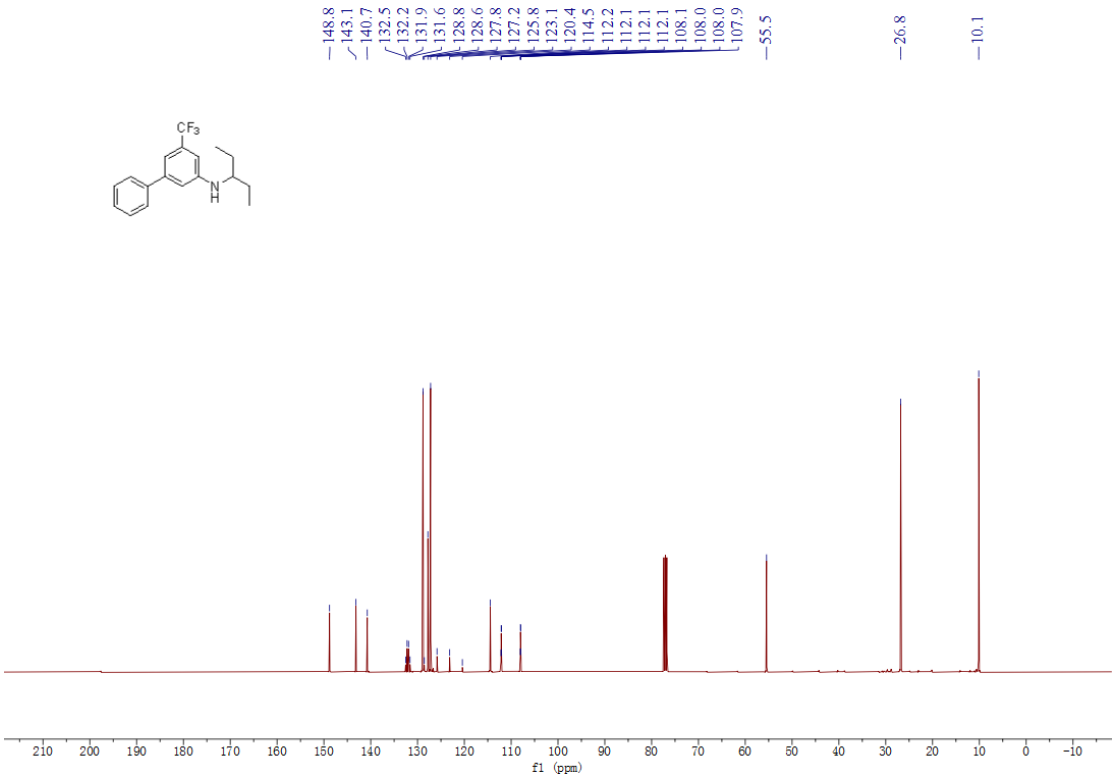
^{1}H NMR spectrum of **4n** in $CDCl_3$



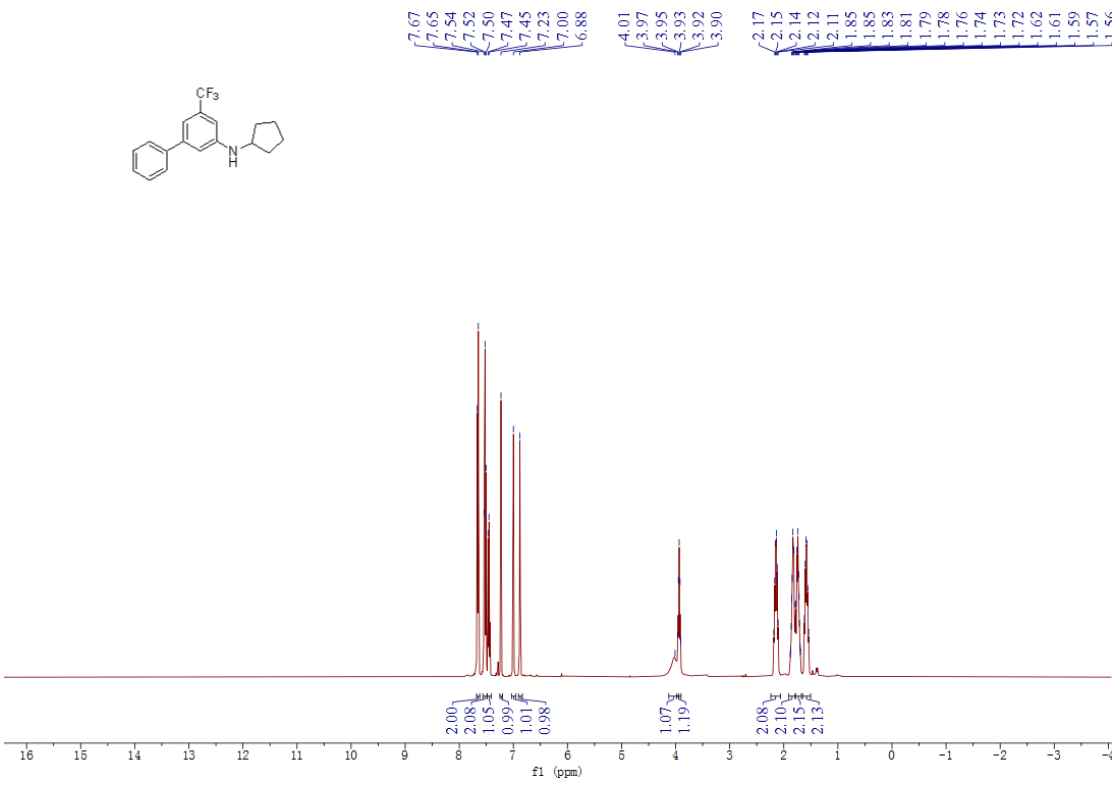
^{19}F NMR spectrum of **4n** in $CDCl_3$



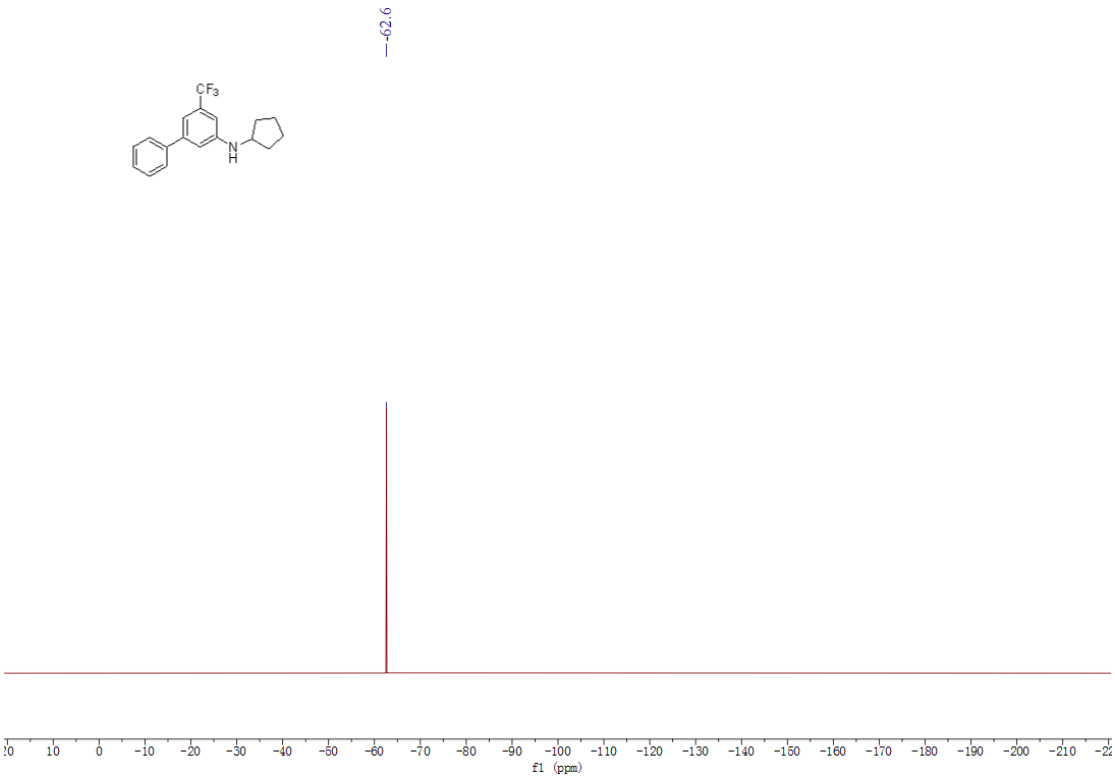
^{13}C NMR spectrum of **4n** in $CDCl_3$



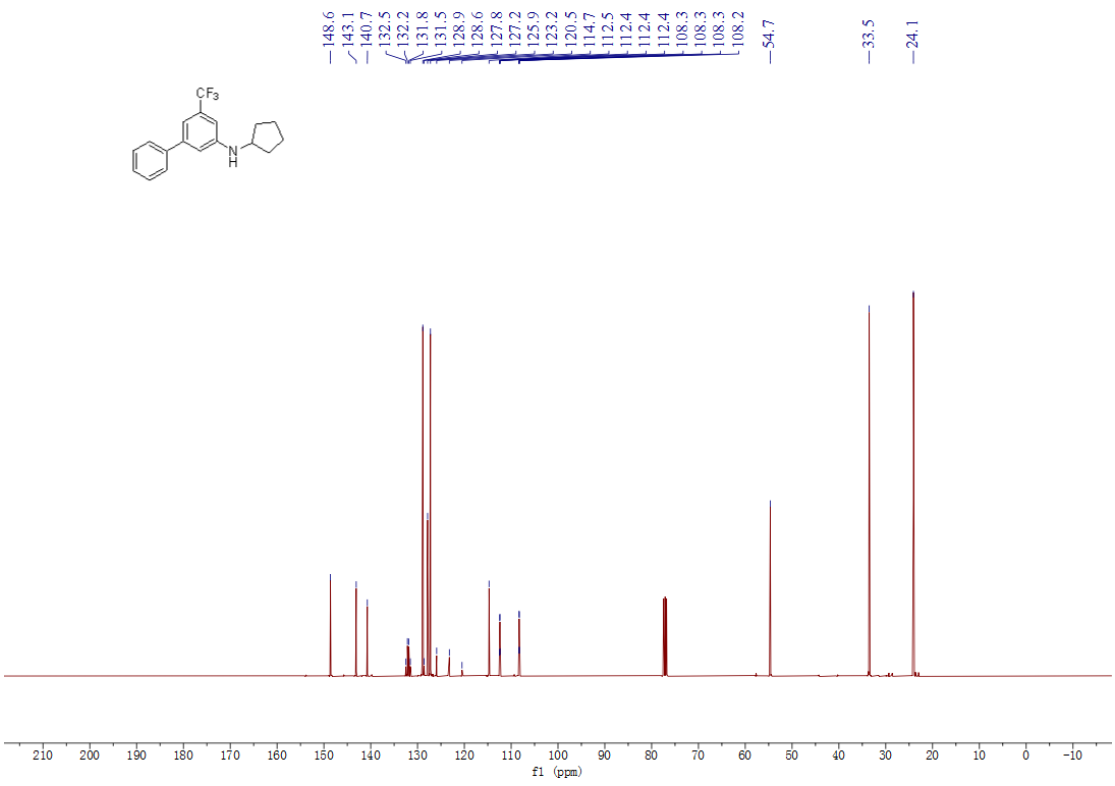
^{1}H NMR spectrum of **4o** in $CDCl_3$



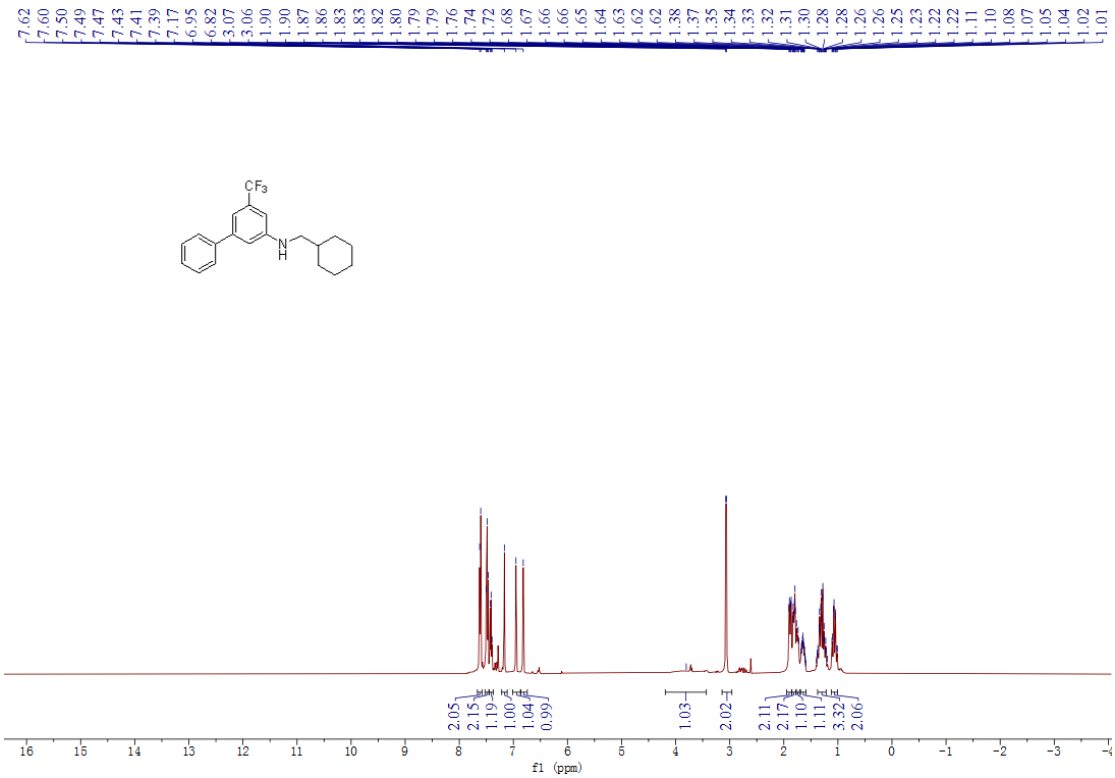
^{19}F NMR spectrum of **4o** in $CDCl_3$



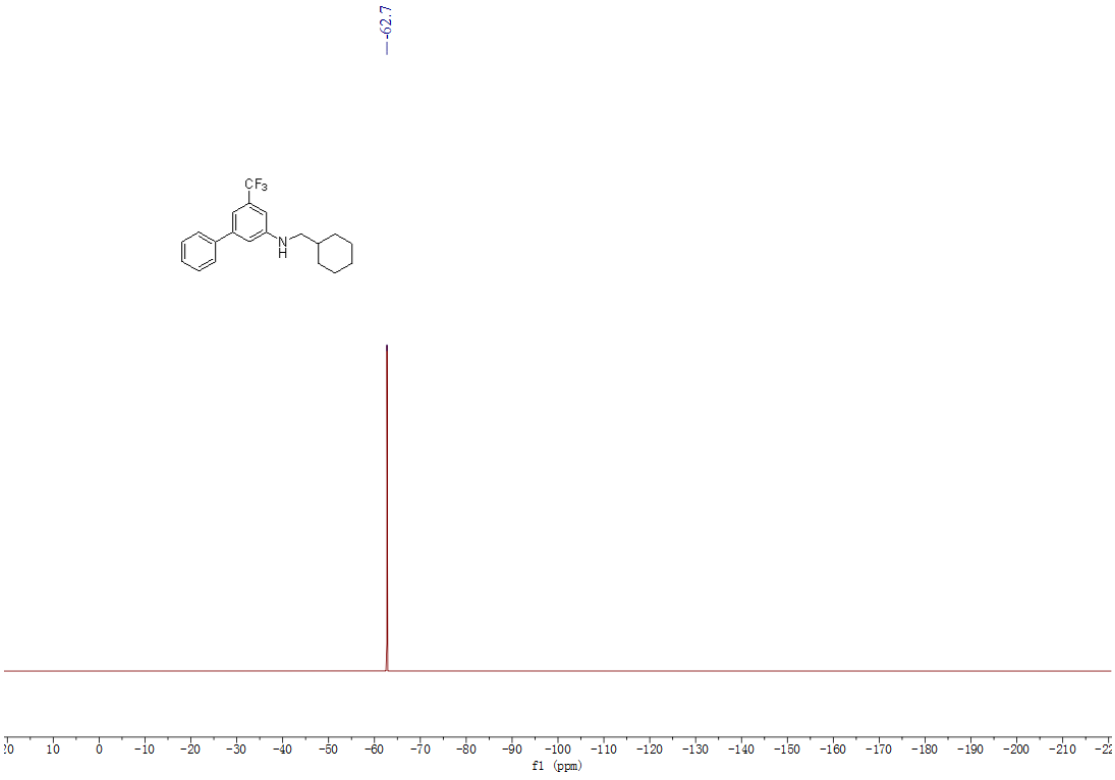
^{13}C NMR spectrum of **4o** in $CDCl_3$



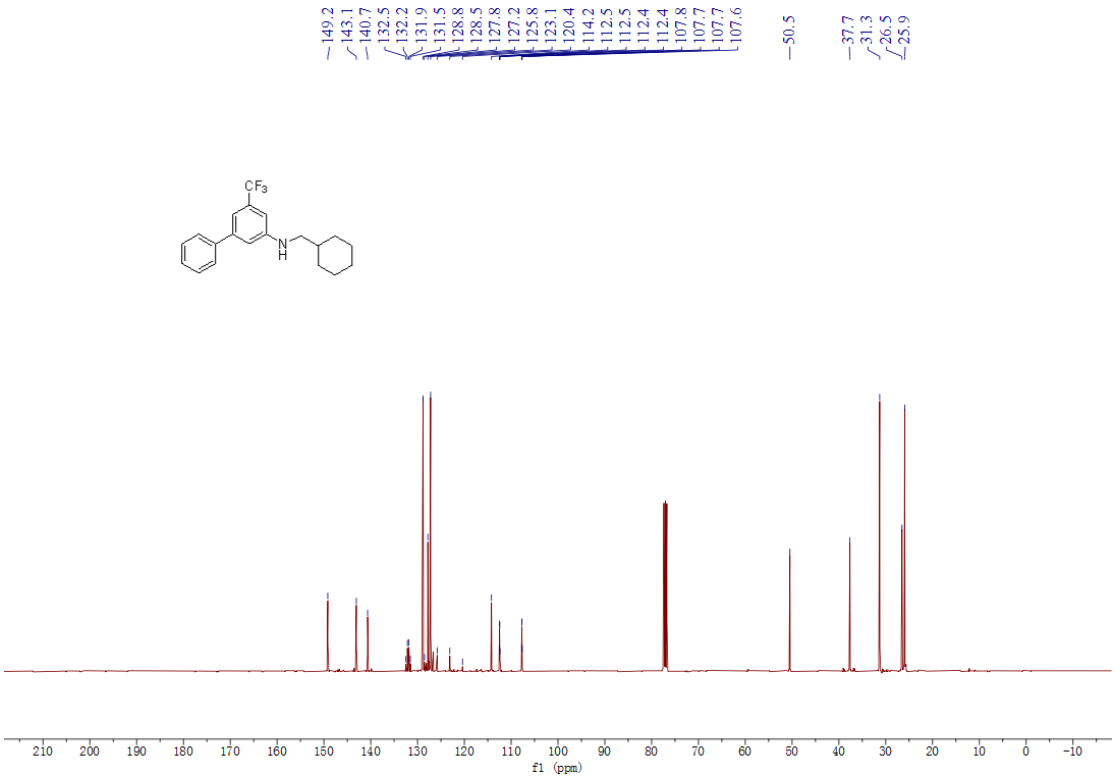
^{1}H NMR spectrum of **4p** in $CDCl_3$



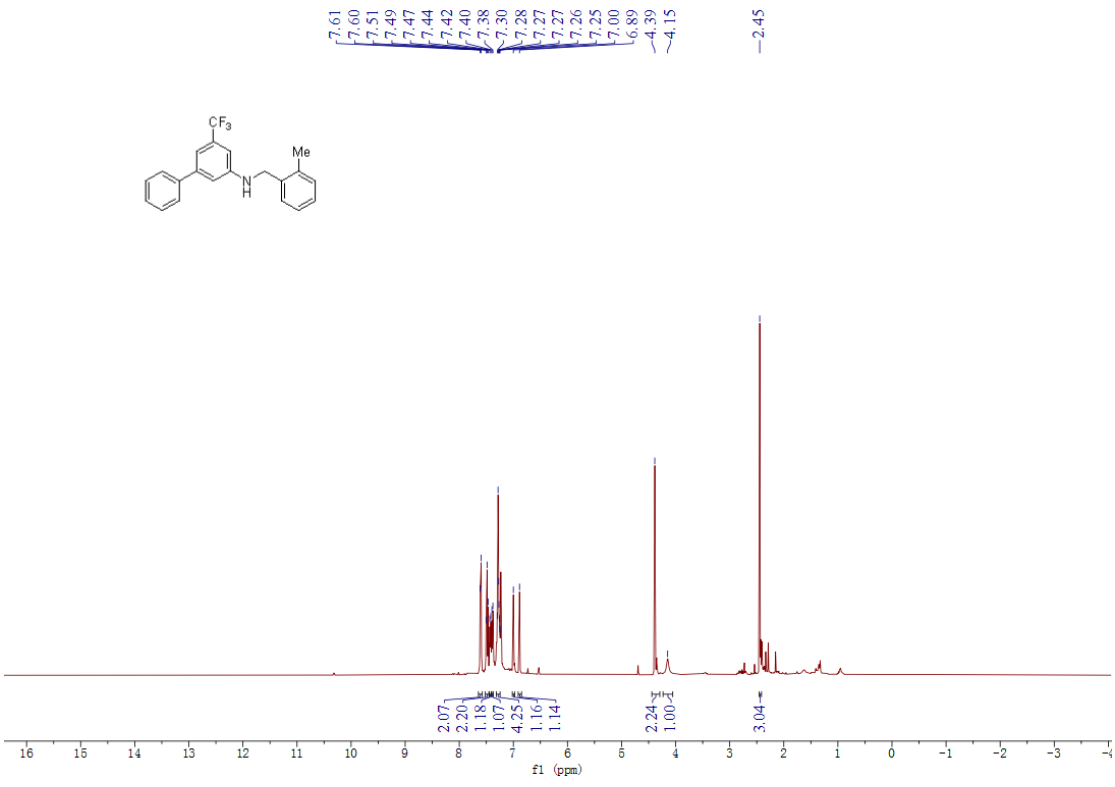
^{19}F NMR spectrum of **4p** in $CDCl_3$



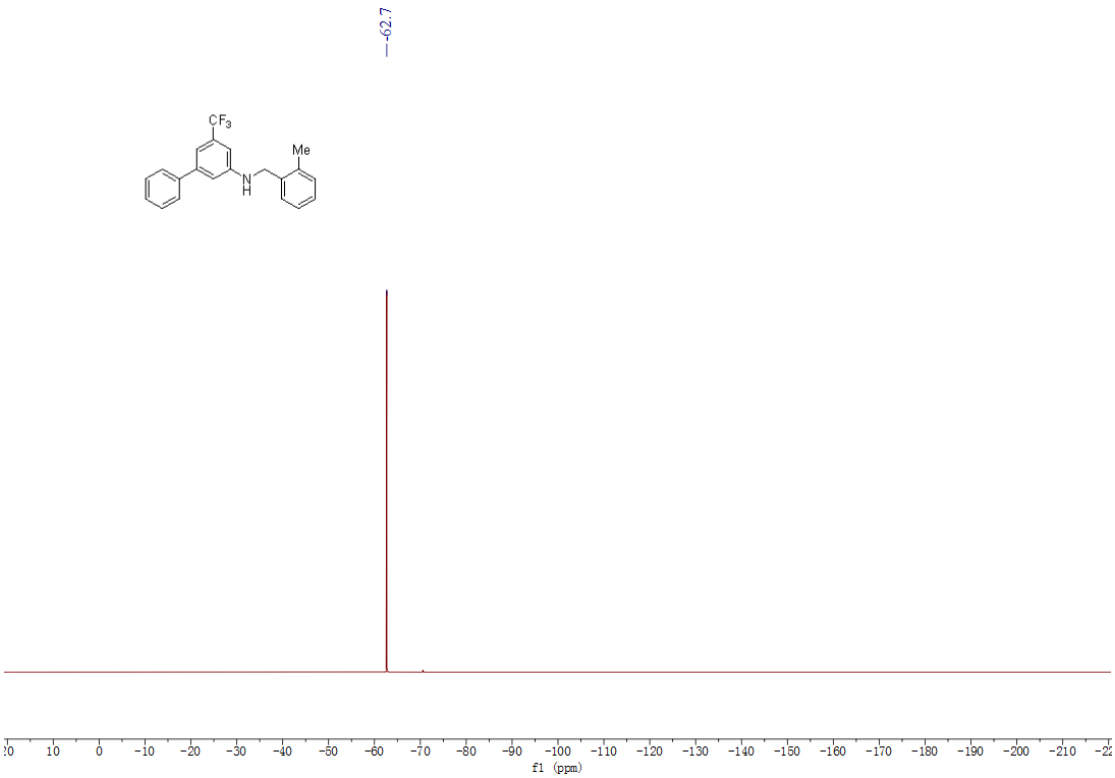
^{13}C NMR spectrum of **4p** in $CDCl_3$



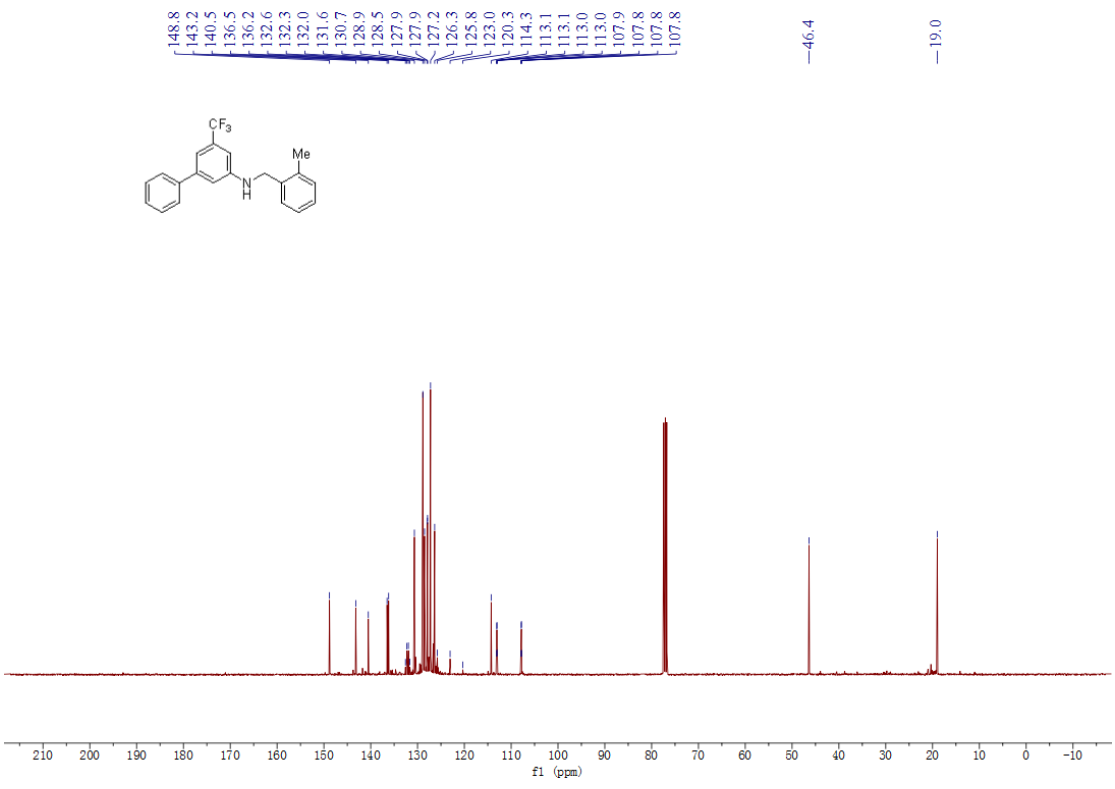
^{1}H NMR spectrum of **4q** in $CDCl_3$



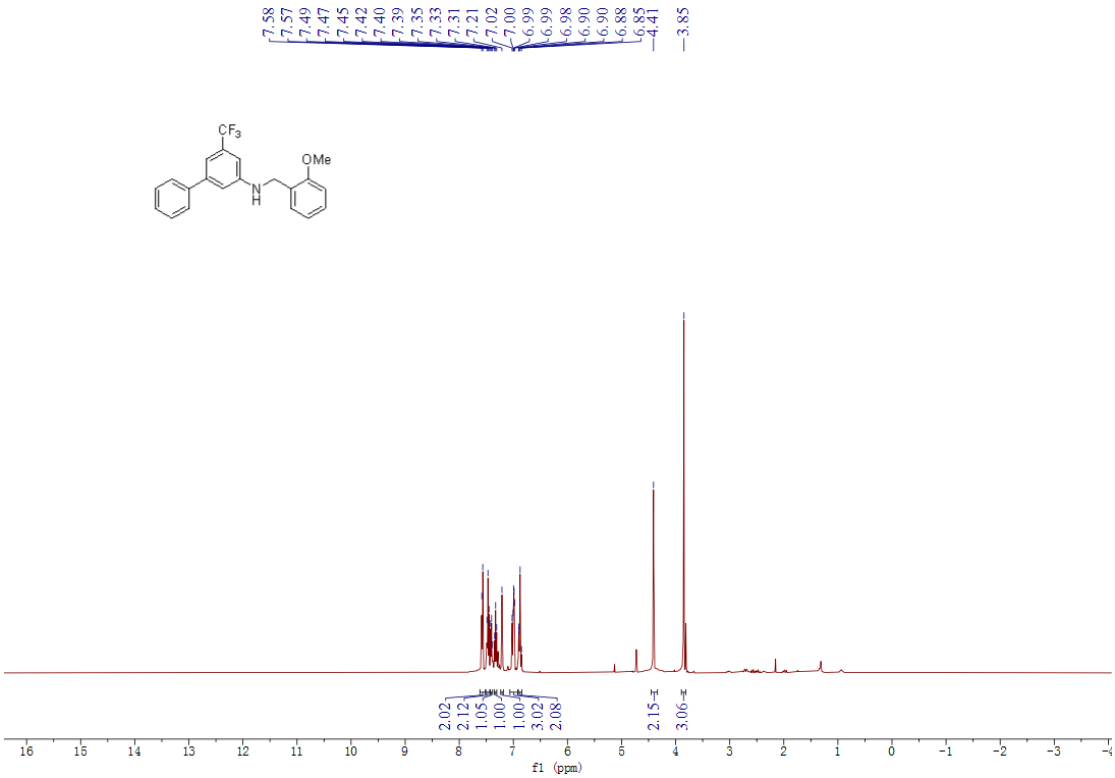
^{19}F NMR spectrum of **4q** in $CDCl_3$



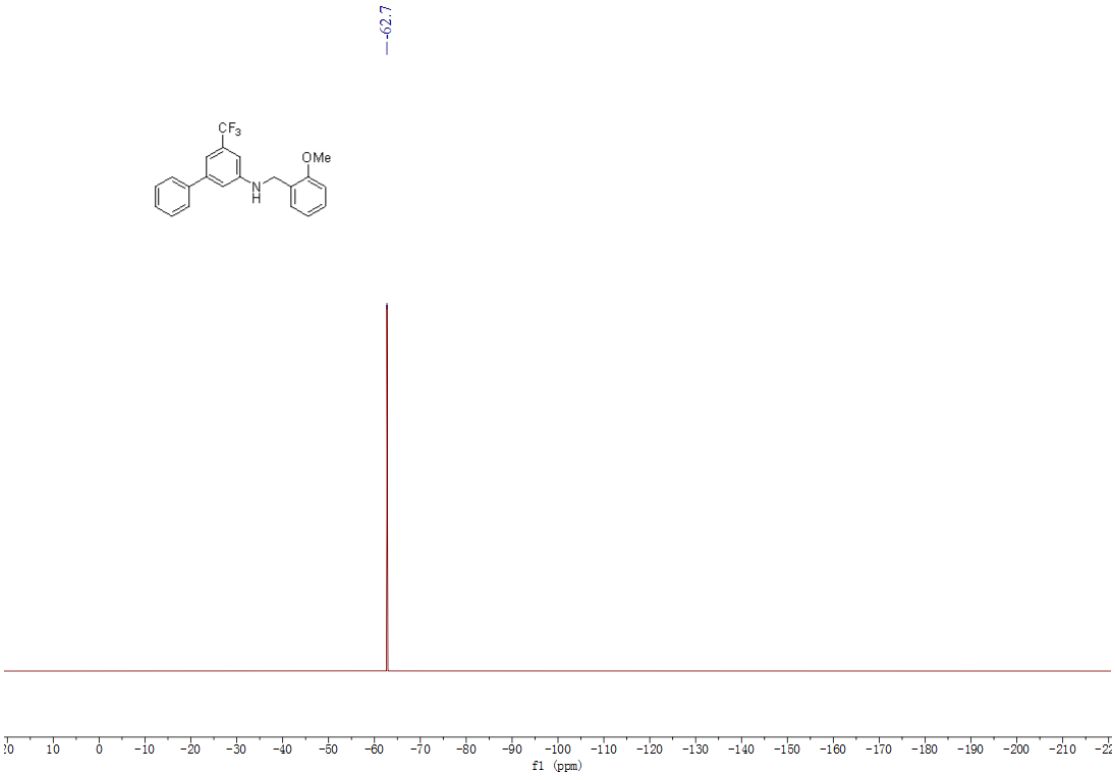
^{13}C NMR spectrum of **4q** in $CDCl_3$



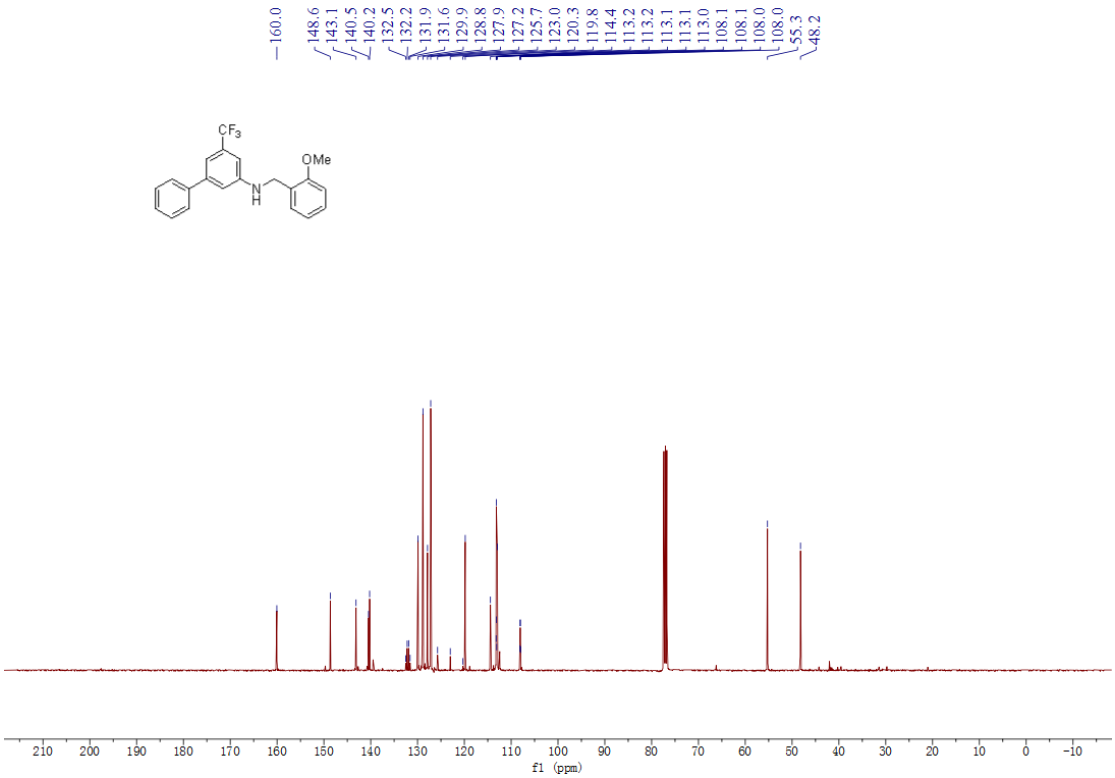
^{1}H NMR spectrum of **4r** in $CDCl_3$



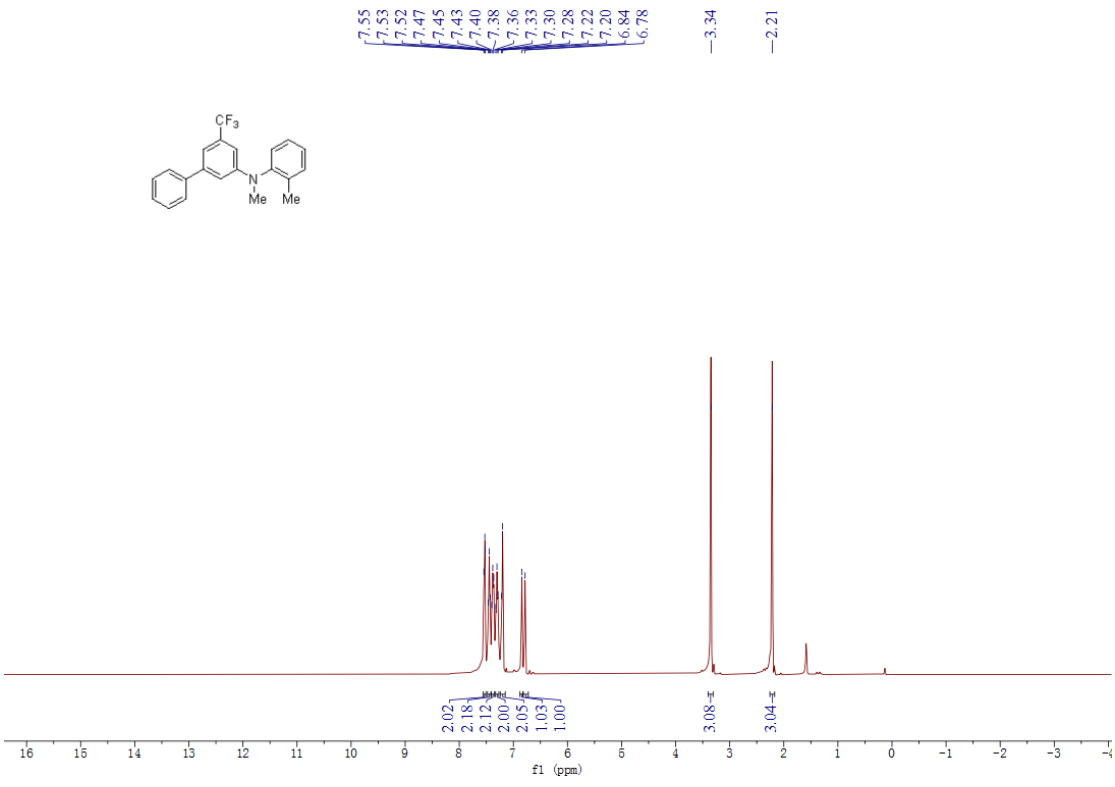
^{19}F NMR spectrum of **4r** in $CDCl_3$



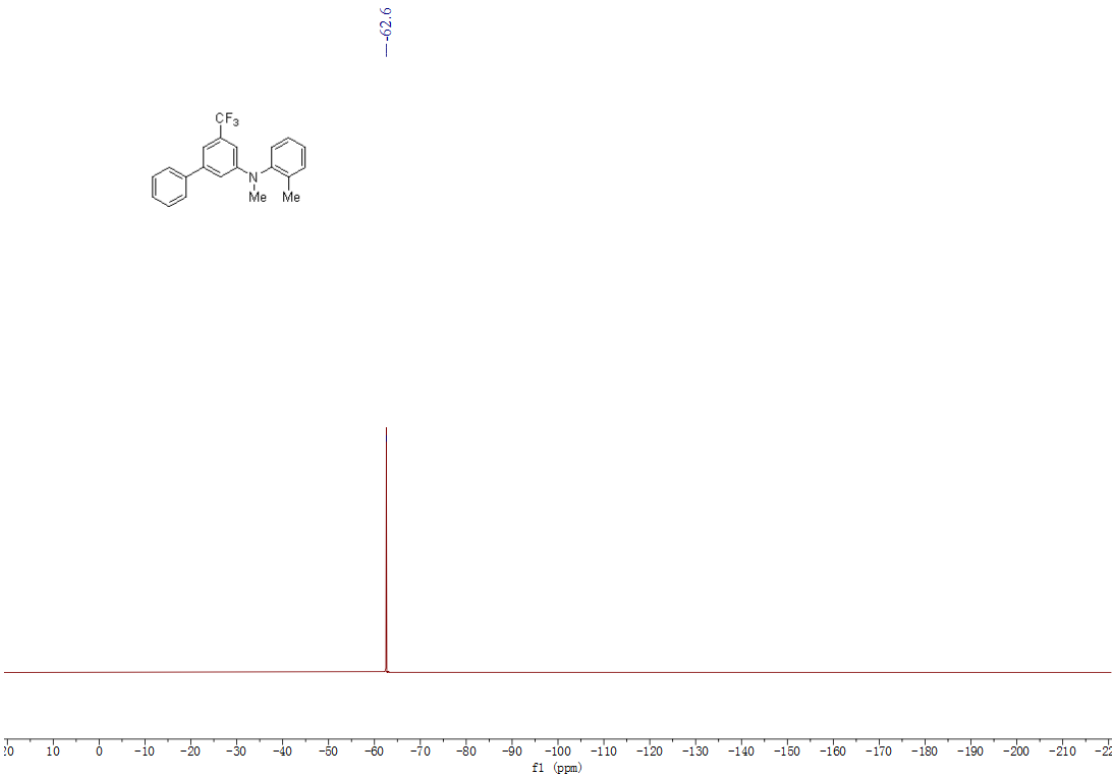
^{13}C NMR spectrum of **4r** in $CDCl_3$



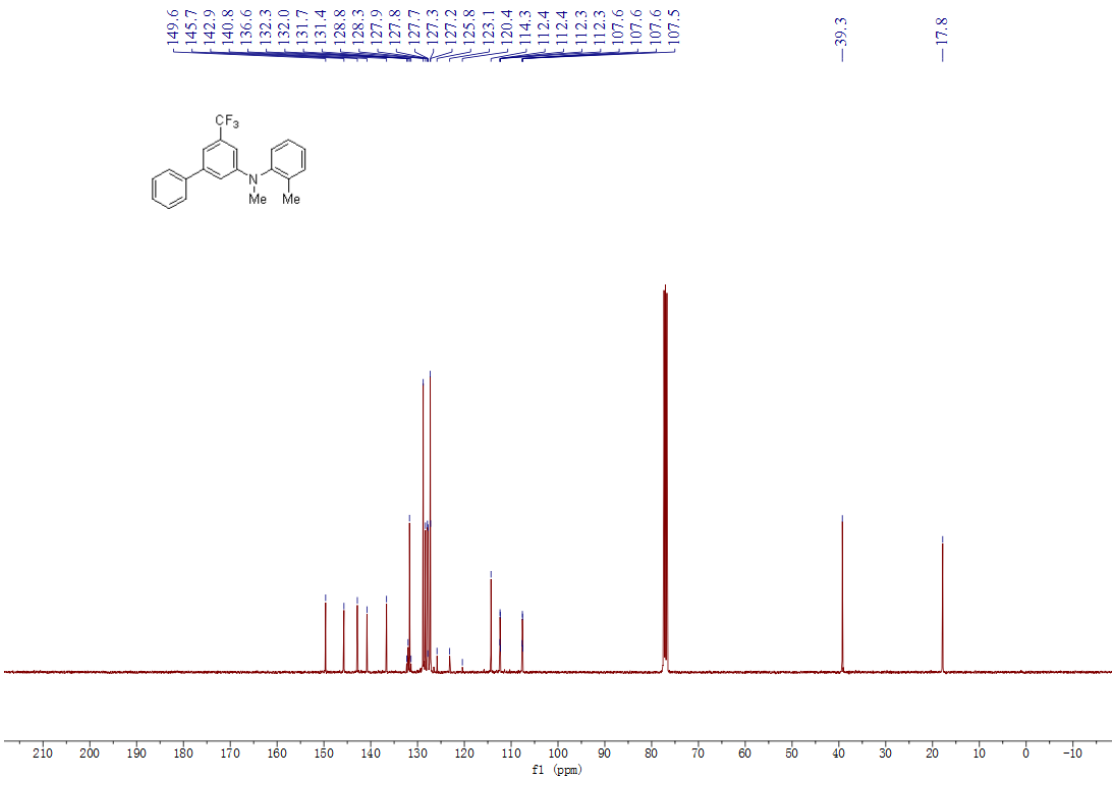
^{1}H NMR spectrum of **4s** in $CDCl_3$



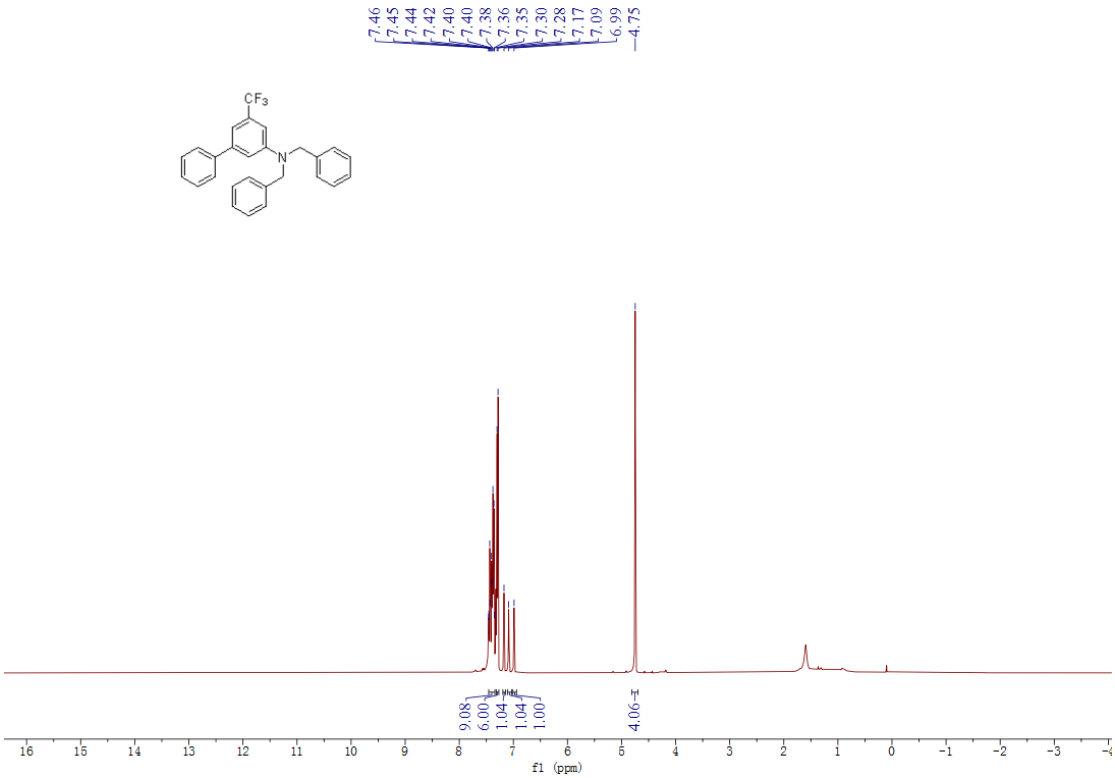
^{19}F NMR spectrum of **4s** in $CDCl_3$



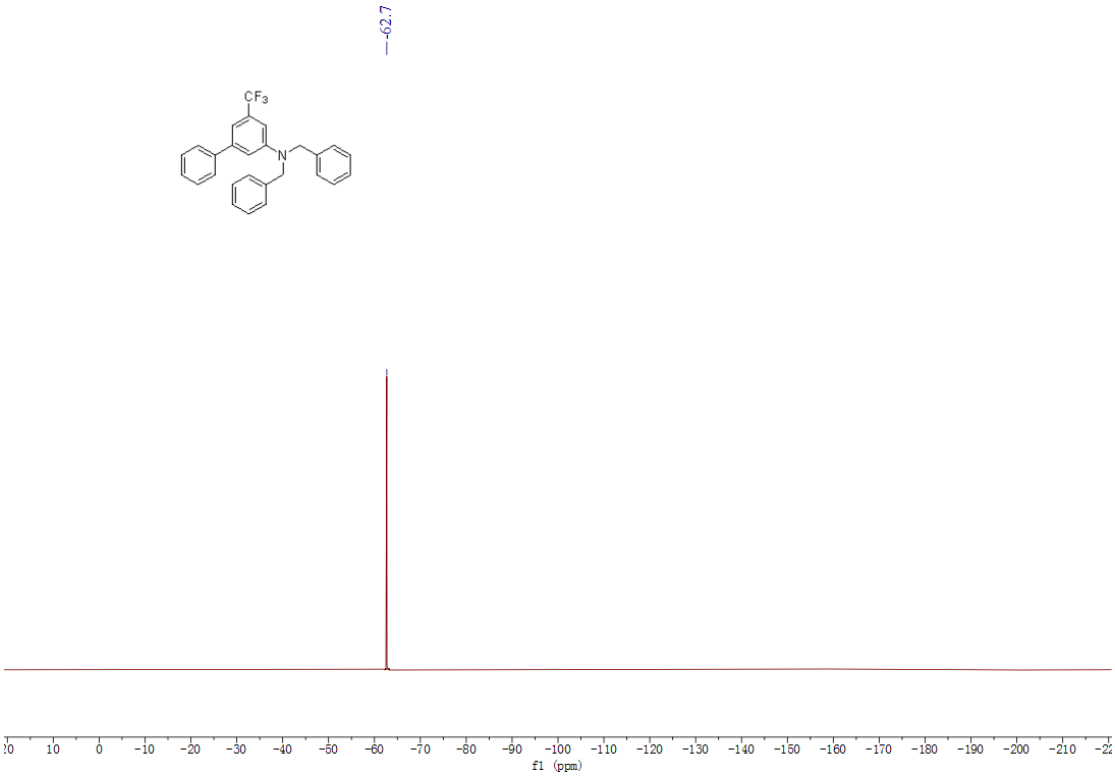
^{13}C NMR spectrum of **4s** in $CDCl_3$



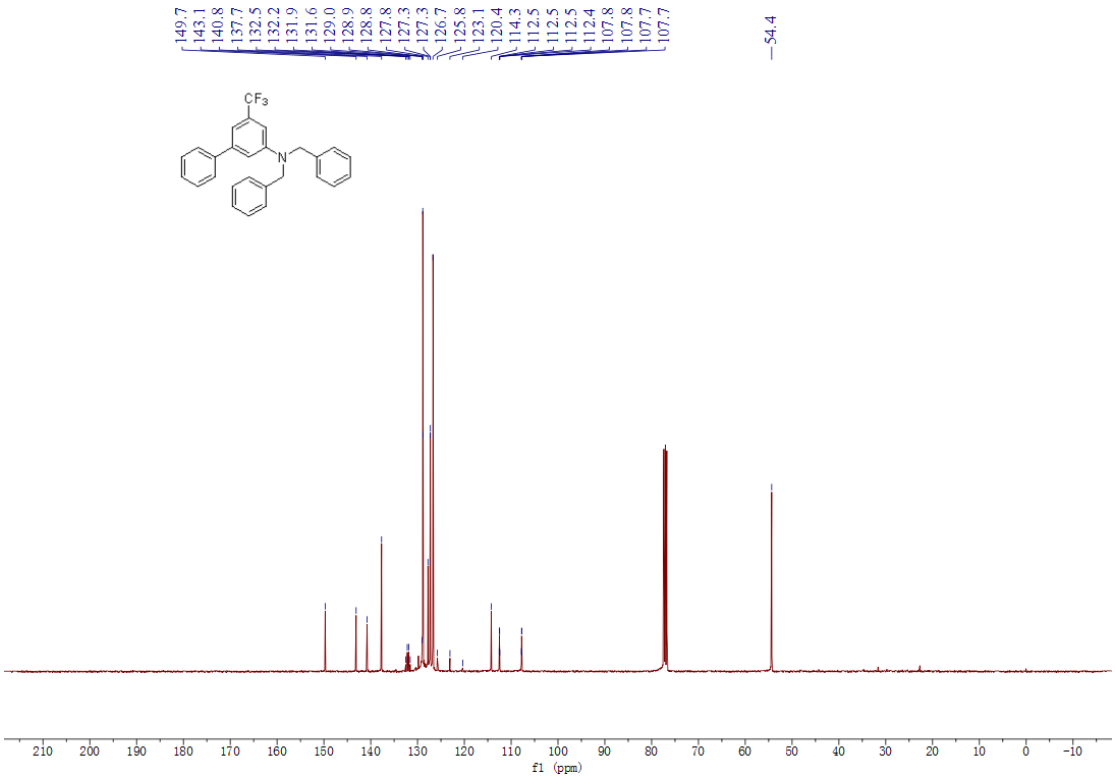
^{1}H NMR spectrum of **4t** in $CDCl_3$



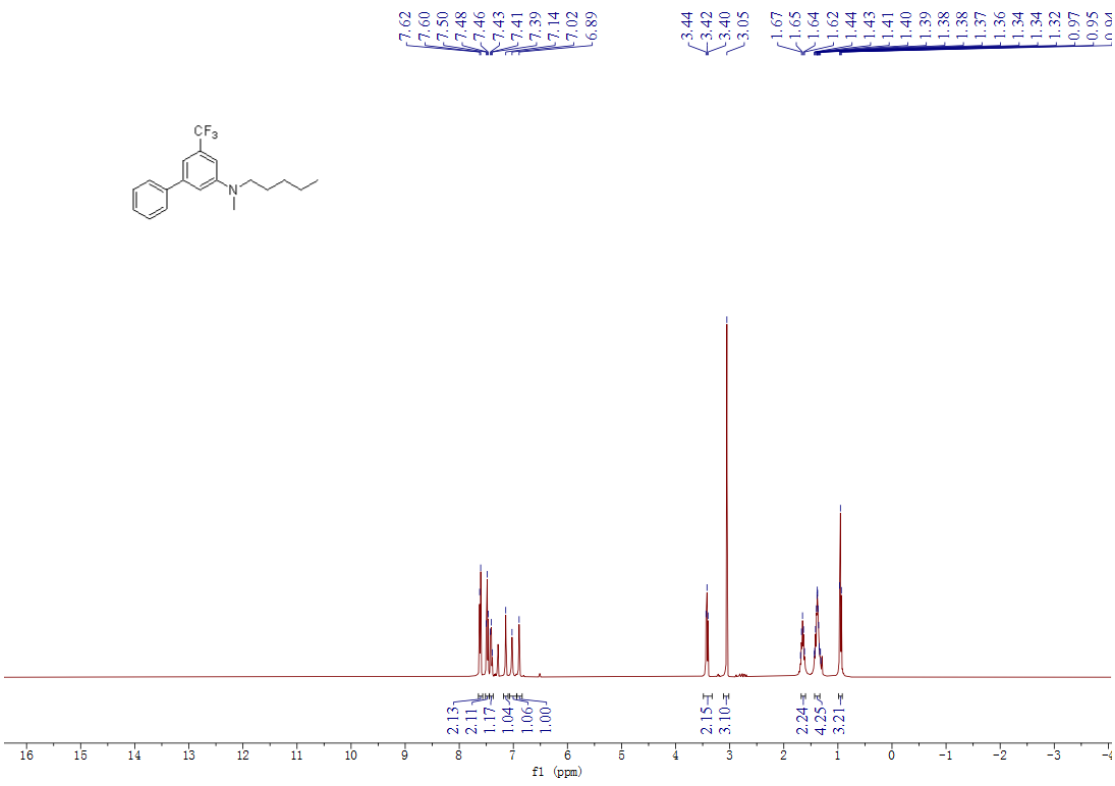
^{19}F NMR spectrum of **4t** in $CDCl_3$



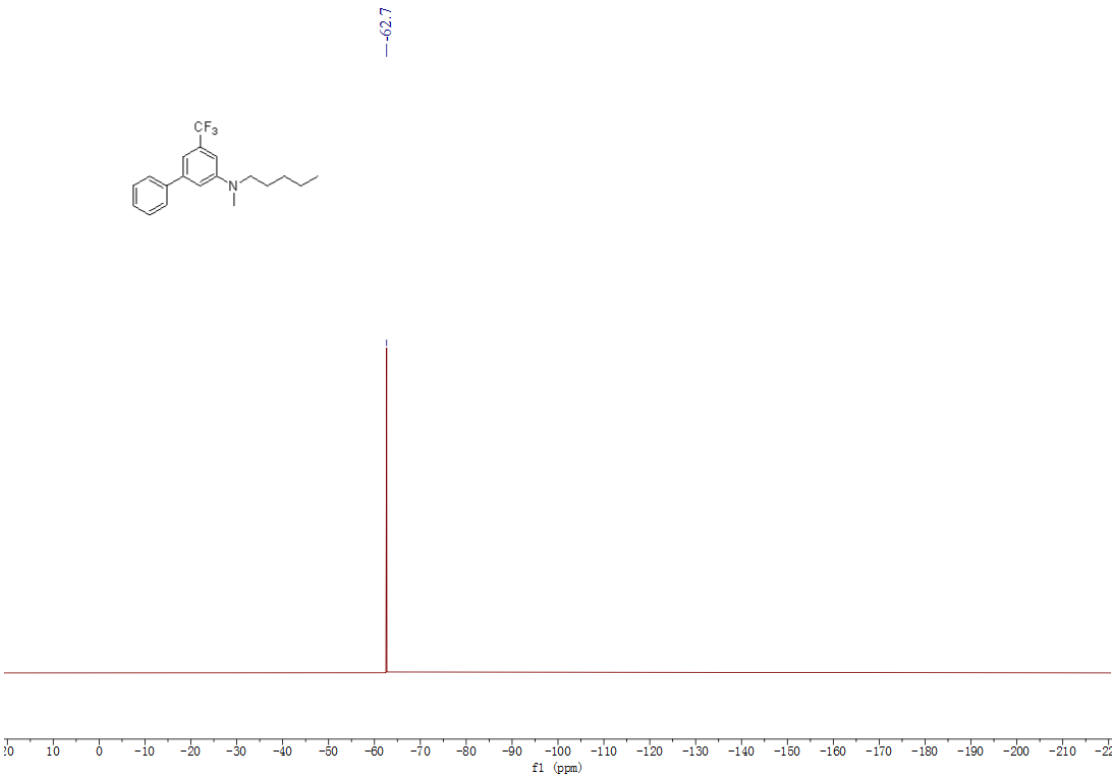
^{13}C NMR spectrum of **4t** in $CDCl_3$



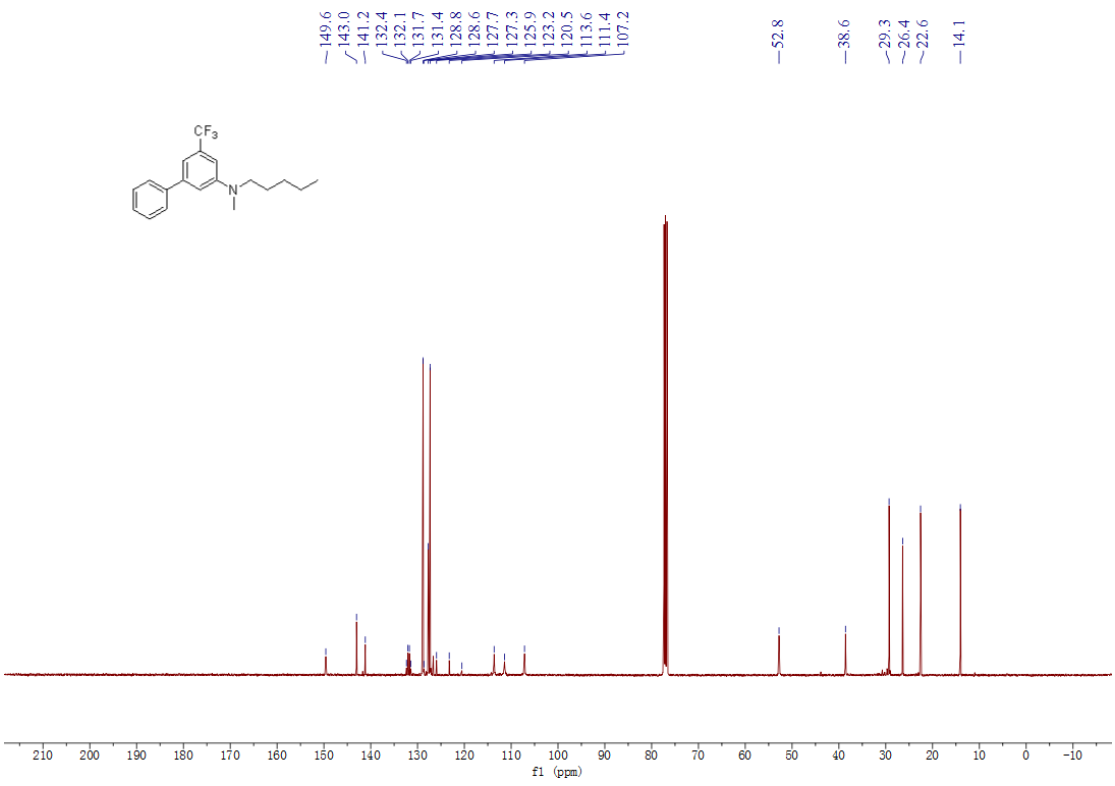
^{1}H NMR spectrum of **4u** in $CDCl_3$



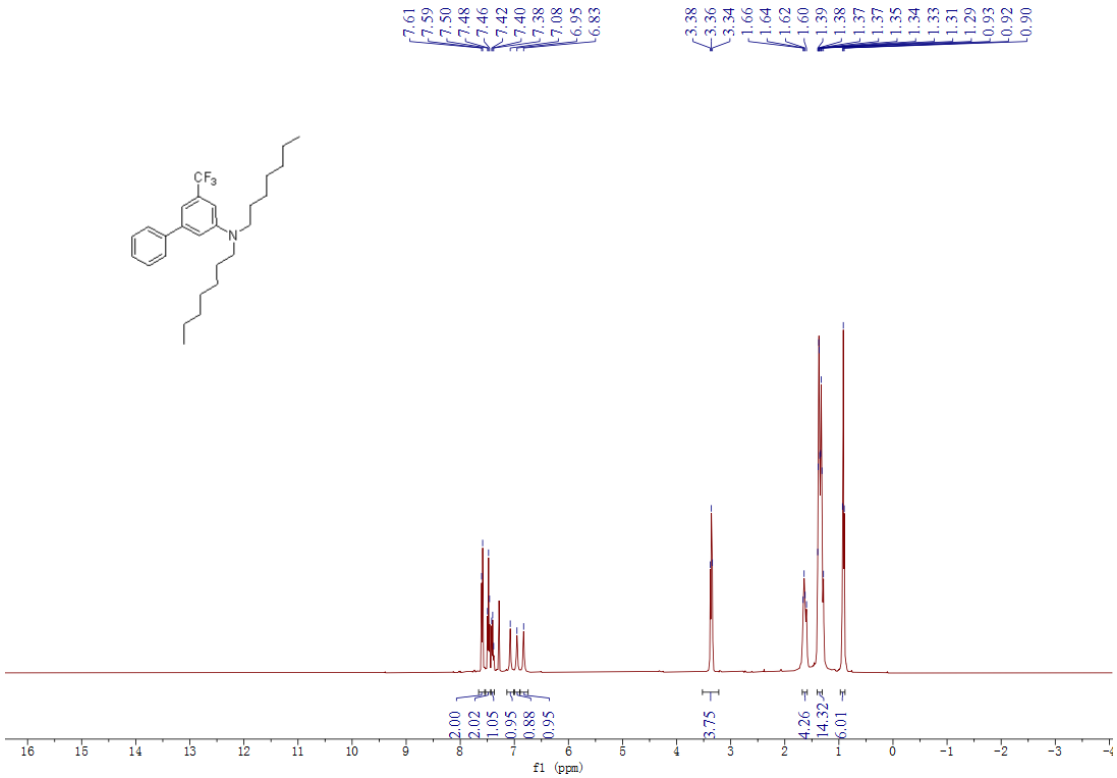
^{19}F NMR spectrum of **4u** in $CDCl_3$



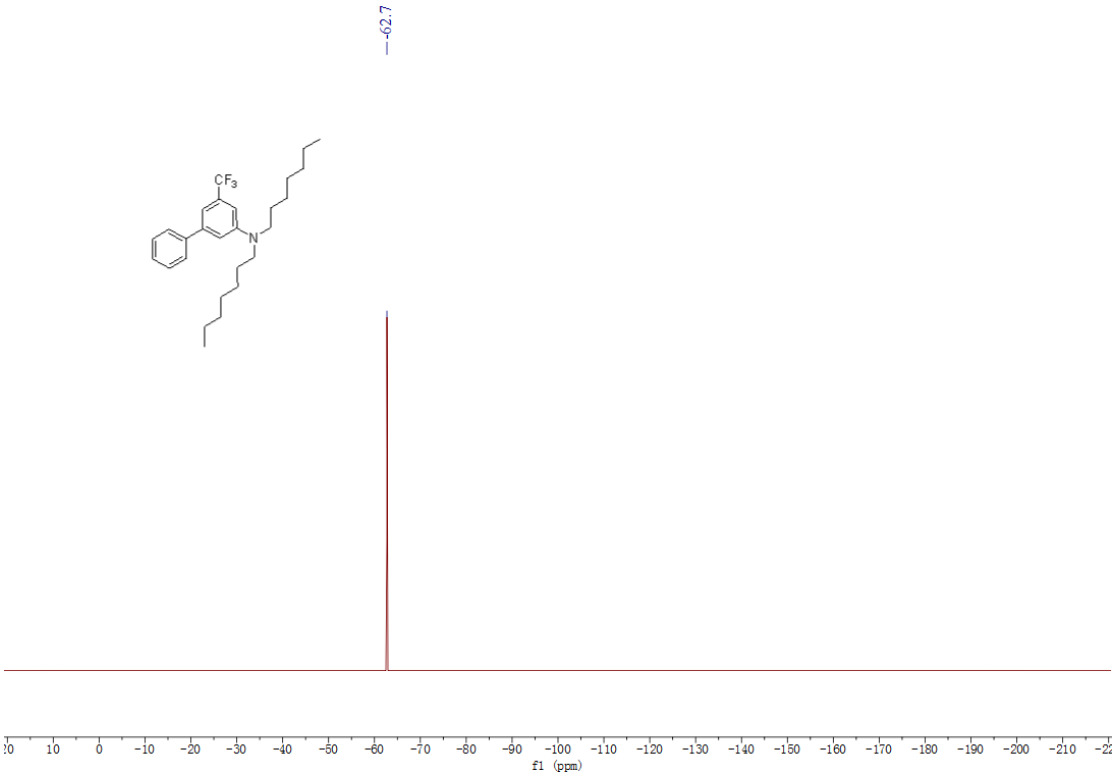
^{13}C NMR spectrum of **4u** in $CDCl_3$



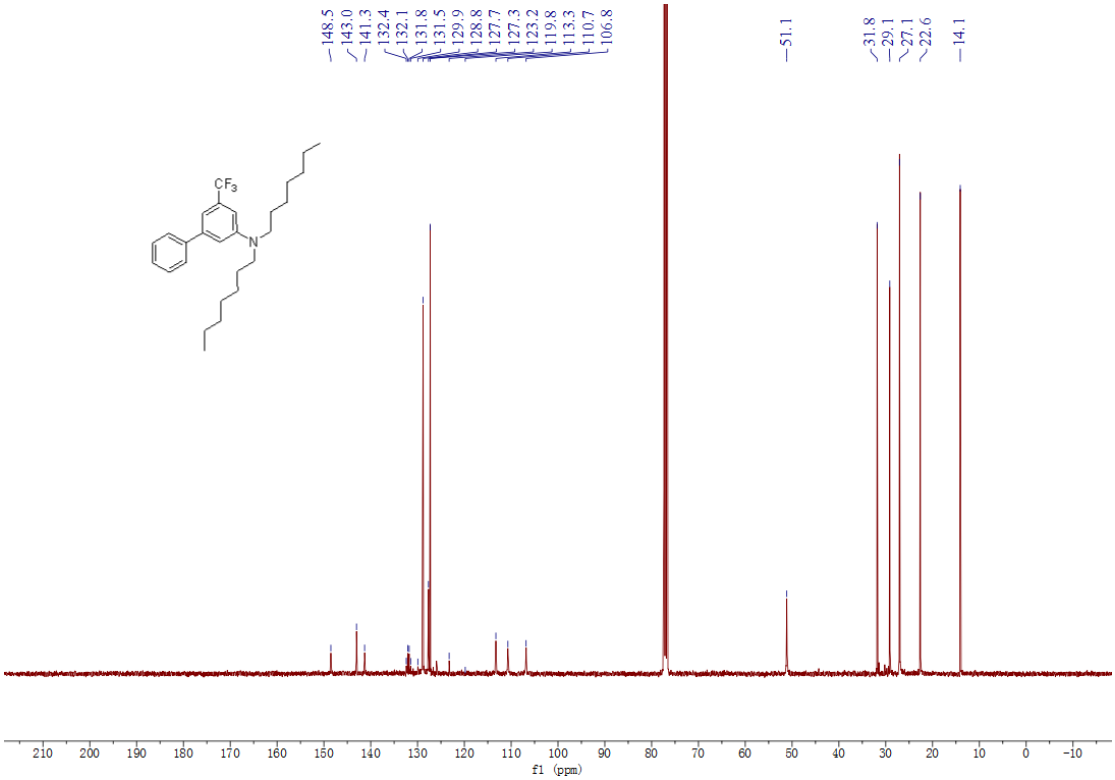
^{1}H NMR spectrum of **4v** in $CDCl_3$



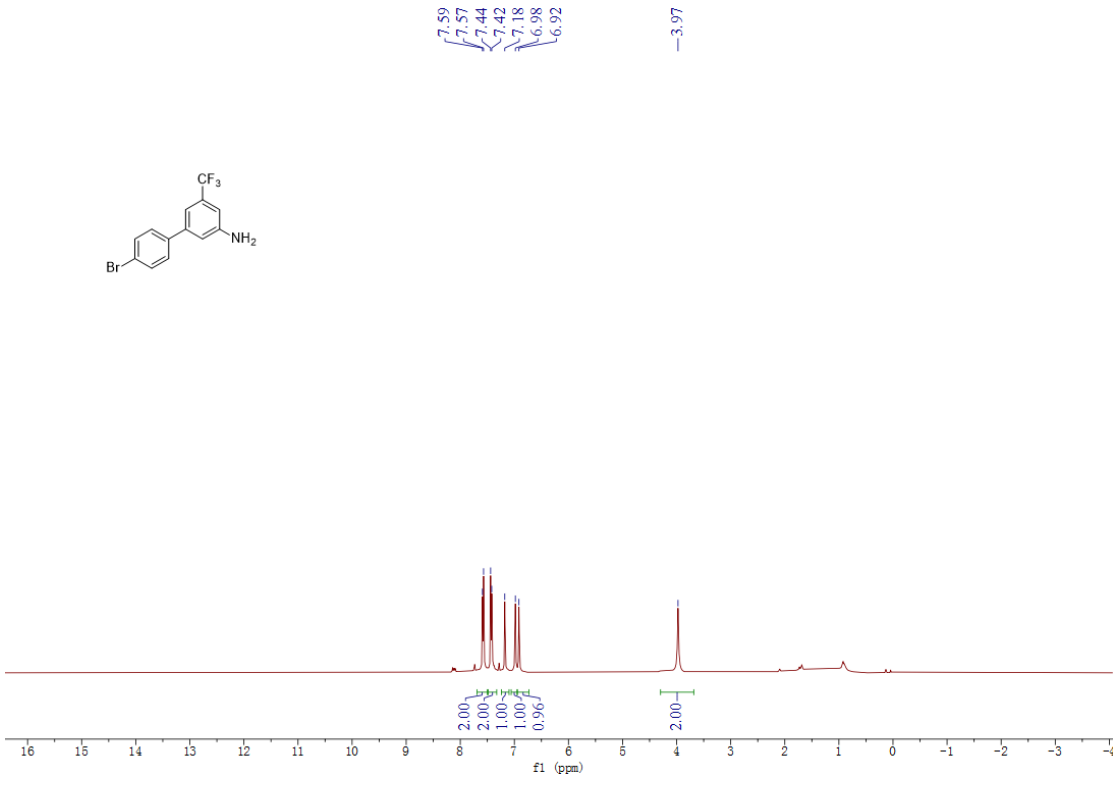
^{19}F NMR spectrum of **4v** in $CDCl_3$



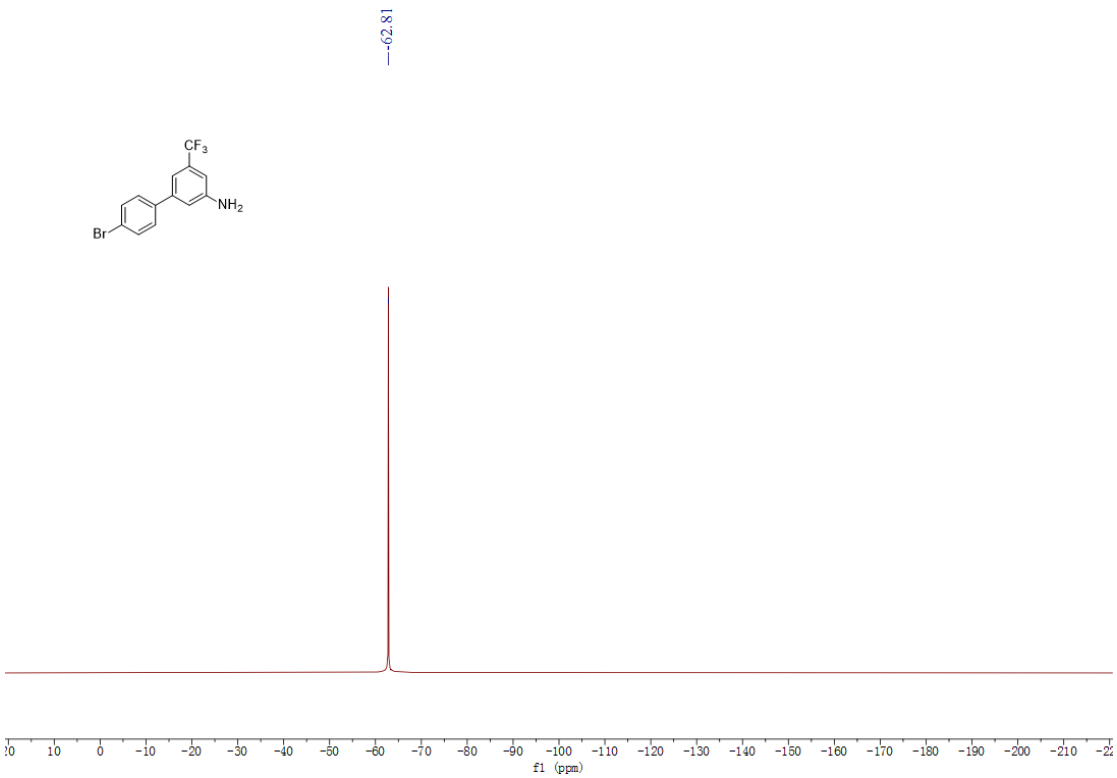
^{13}C NMR spectrum of **4v** in $CDCl_3$



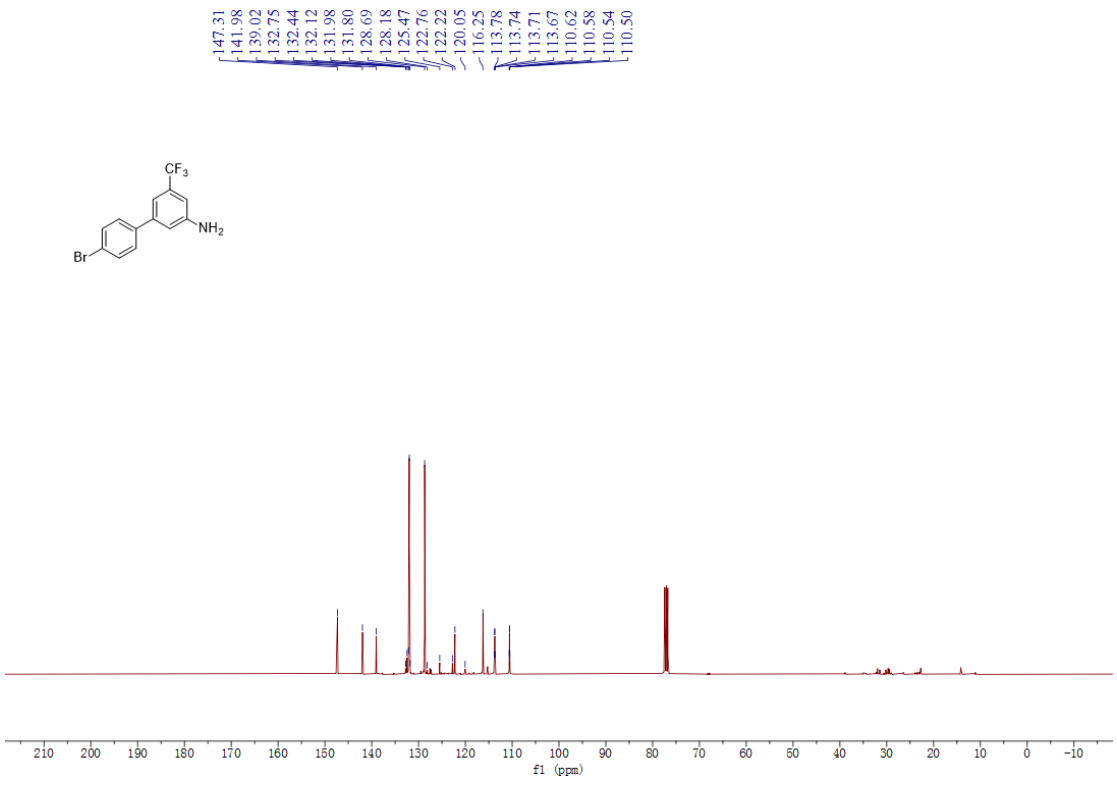
^{1}H NMR spectrum of **5q** in $CDCl_3$



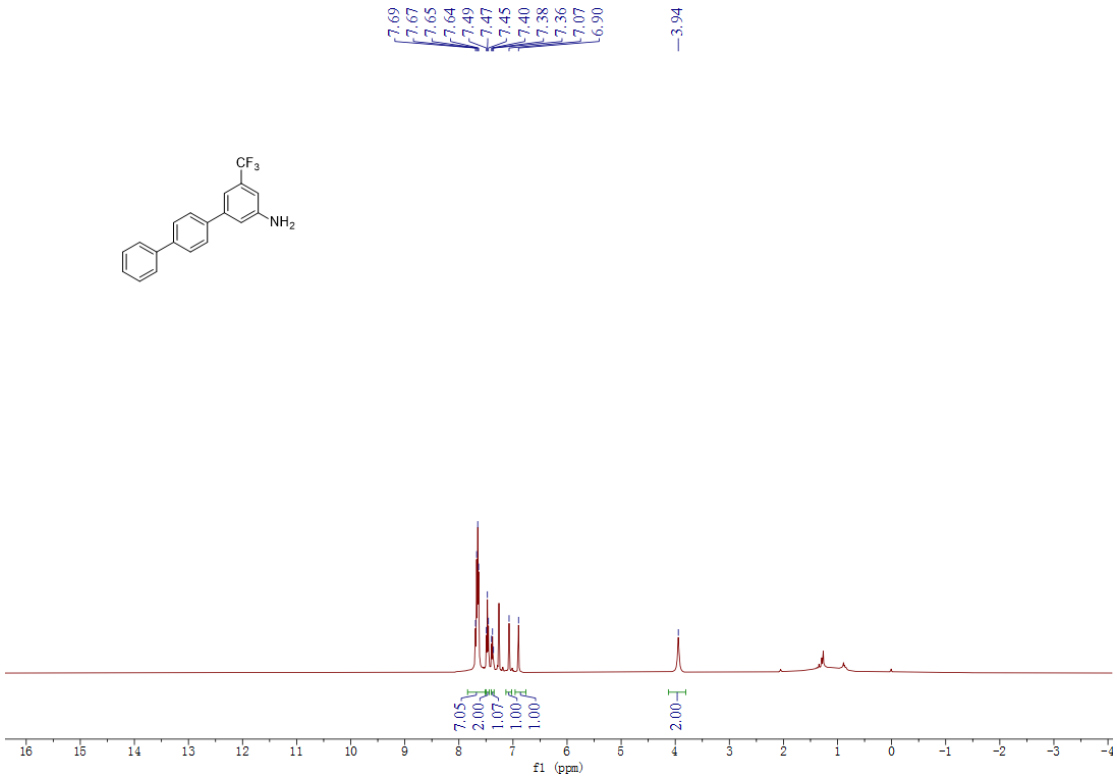
^{19}F NMR spectrum of **5q** in $CDCl_3$



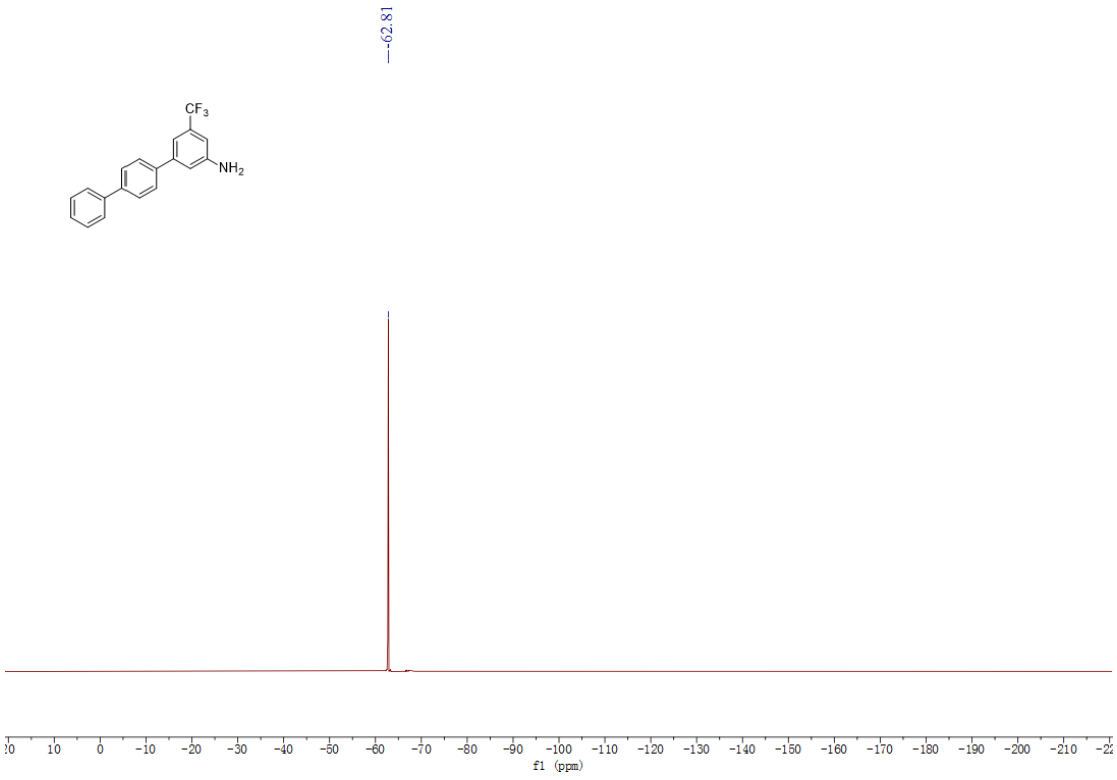
^{13}C NMR spectrum of **5q** in $CDCl_3$



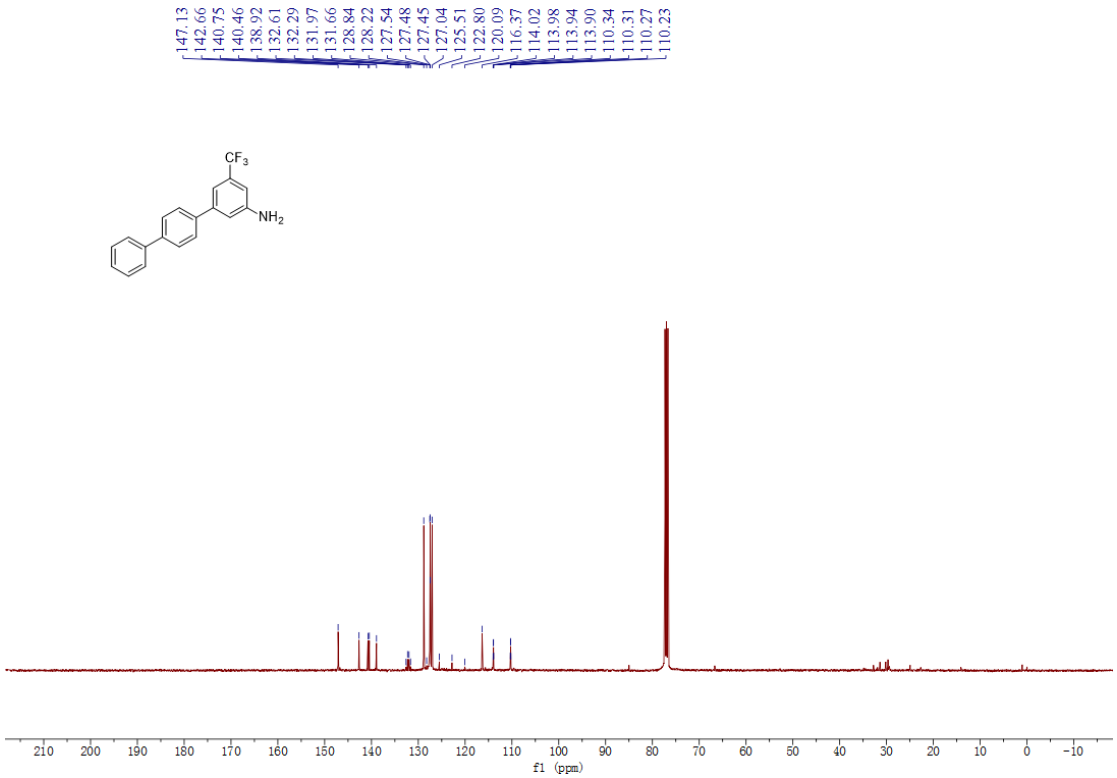
^{1}H NMR spectrum of **5s** in $CDCl_3$



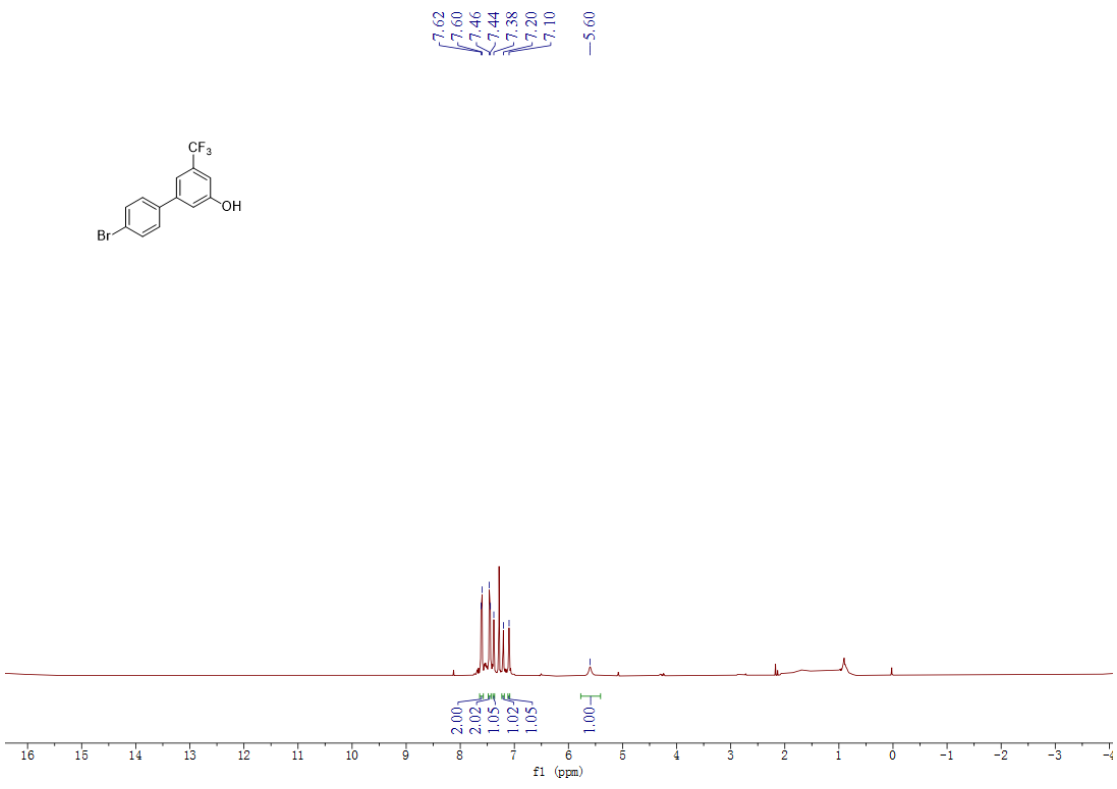
^{19}F NMR spectrum of **5s** in $CDCl_3$



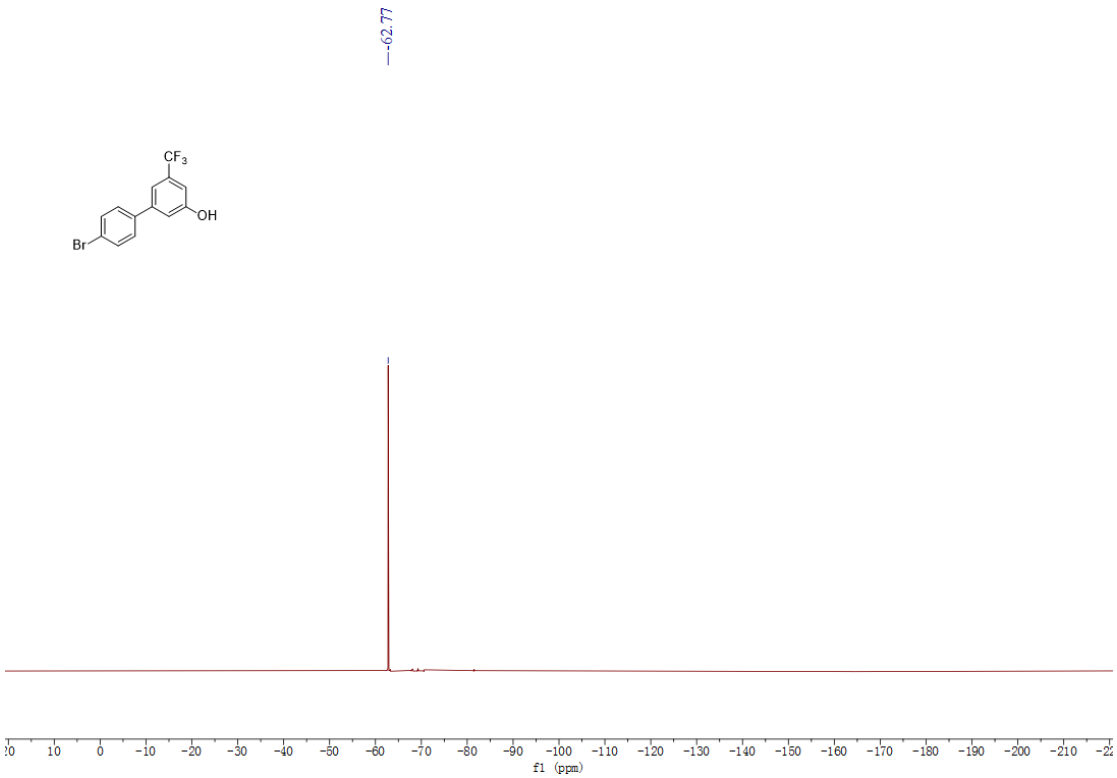
^{13}C NMR spectrum of **5s** in $CDCl_3$



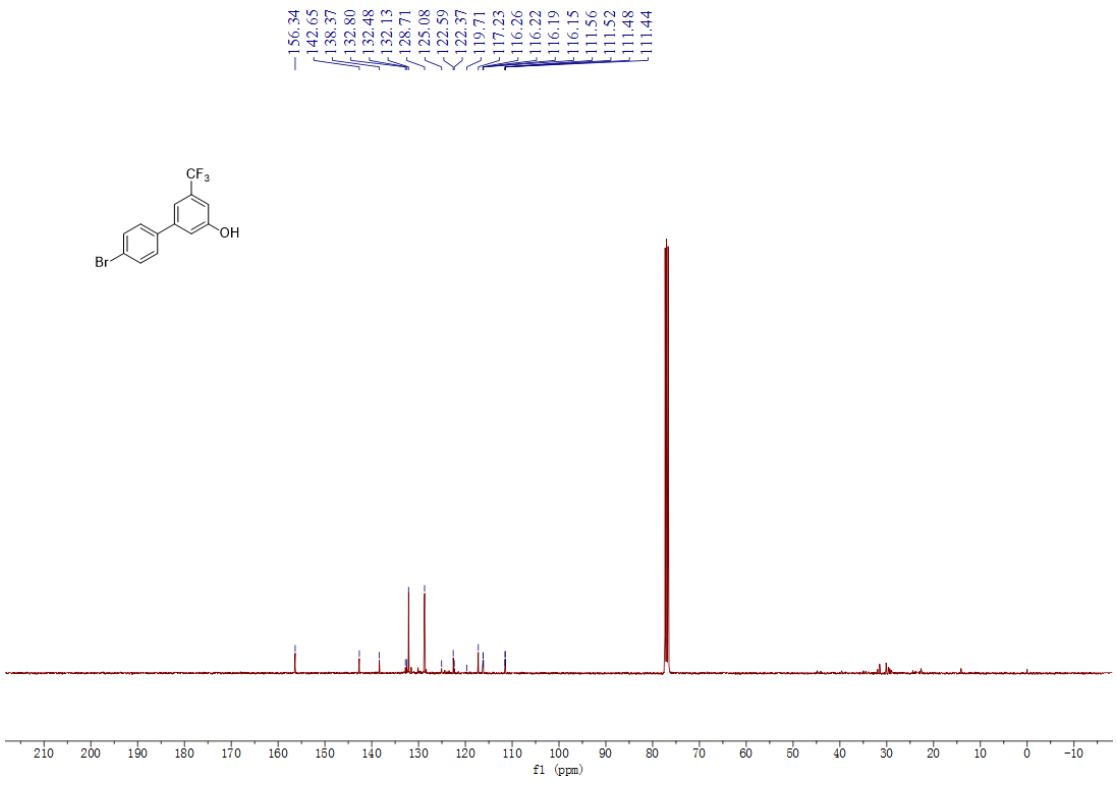
400MHz ^{1}H NMR spectrum of **6** in $CDCl_3$



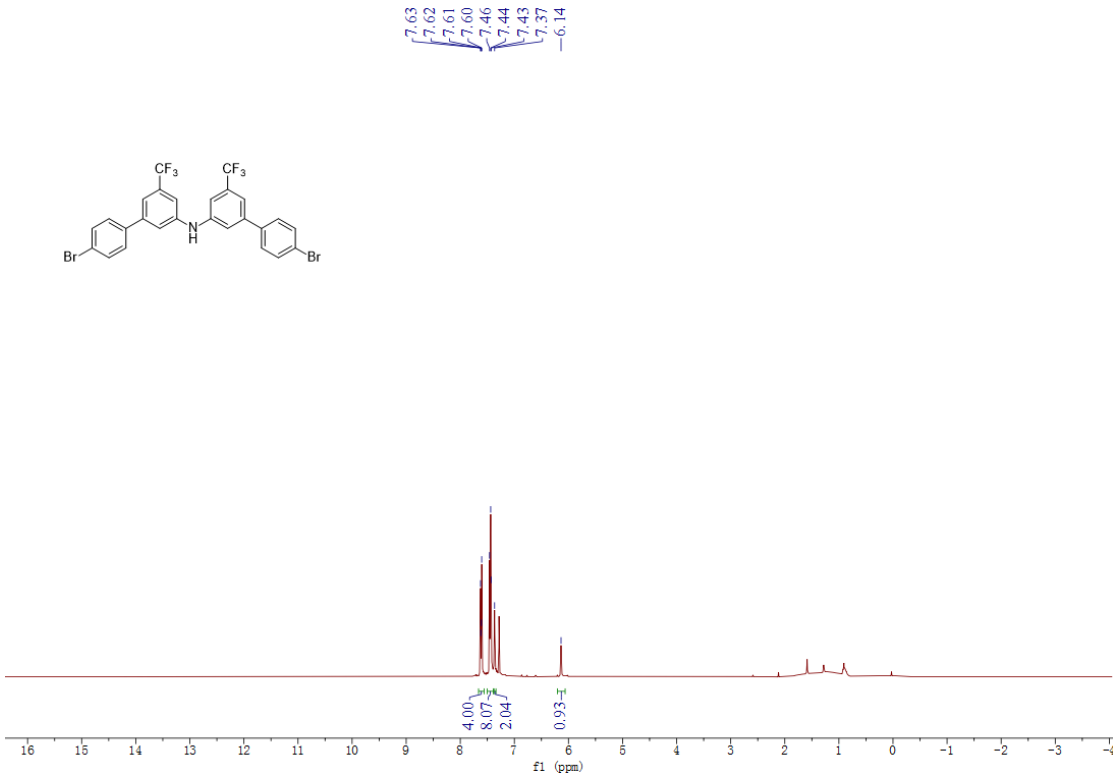
^{19}F NMR spectrum of **6** in $CDCl_3$



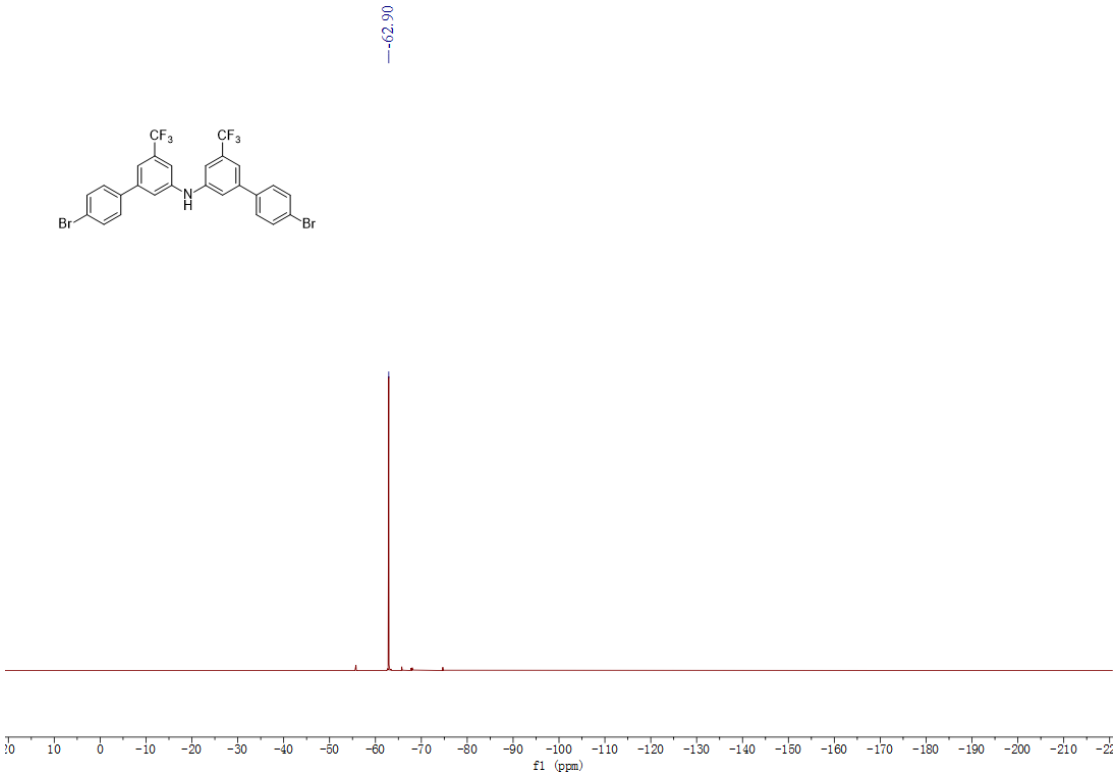
^{13}C NMR spectrum of **6** in $CDCl_3$



^{1}H NMR spectrum of **7** in $CDCl_3$



^{19}F NMR spectrum of **7** in $CDCl_3$



^{13}C NMR spectrum of **7** in $CDCl_3$