Cu-Catalyzed/Mediated Synthesis of *N*-Fluoroalkylanilines from Arylboronic Acids: Fluorine Effect on the Reactivity of Fluoroalkylamines

Hui Wang, Yuan-Hong Tu, De-Yong Liu, Xiang-Guo Hu*

National Engineering Research Center for Carbohydrate Synthesis, Jiangxi Normal University, Nanchang,330022, China.
Email: huxiangg@iccas.ac.cn

Contents

1. General information

All purchased reagents were used without further purification unless otherwise noted. All solvents were dried over activated 4Å molecular sieves. Analytical TLC was performed with 0.2 mm silica gel 60F plates with 254 nm fluorescent indicator. TLC plates were visualized by ultraviolet light or by treatment with a spray off Pancaldi reagent {$Ce(SO_4)_2$}. Column chromatograph was performed on 200-300 mesh silica gal. NMR spectra were measured in $CDCl_3$ (TMS, 1H δ = 0; $CDCl_3$, 1H δ = 7.26, 13C δ = 77.36) (^{1}H at 400 MHz, ^{13}C at 100 MHz, ^{19}F at 376 MHz) magnetic resonance spectrometer Chemical shifs (δ) are reported in ppm, and coupling constants (J) are in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. What should be noted is that all petroleum ether and ethyl acetate (EtOAc) used for flash column chromatography were redistilled twice before using, but the trace amount of residue of impurities such as H-grease and silicone grease could still be seen on NMR spectra of some products

2. General procedure

2.1 Procedure A: Cu-catalyzed reaction of aryl boric acid with $CF_3CH_2NH_2$ or $HCF_2CH_2NH_2$

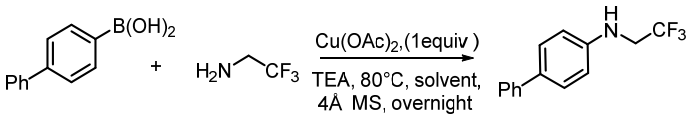
To a reaction tube containing $Cu(OAc)_2$ (9.1 mg, 0.05 mmol, 0.2 equiv), aryl boronic acid (0.25 mmol, 1.0 equiv) and 4 Å MS was added TEA (105 μL, 0.75 mmol, 3 equiv), $CF_3CH_2NH_2$ (40 μL, 0.5 mmol, 2.0 equiv) and CH_3CN (2.5 mL) were added successively via syringe. The mixture was stirred vigorously under 80 ºC overnight. Then the reaction solution was filtered over a sintered-glass funnel with a tightly packed pad of Celite (1 cm thick), and the filter cake was rinsed with DCM (20 mL). The combined filtrates were concentrated. The residue was purified with silica gel column chromatography to provide the desired product.

2.2 Procedure B: Cu-promoted coupling reactions of $CF_3CF_2CH_2NH_2$ or $CF_3CF_2CF_2CH_2NH_2$ with boronic acids

To a reaction tube containing $Cu(OAc)_2$ (45.4 mg, 0.25 mmol, 1.0 equiv), aryl boronic acid (0.25 mmol, 1.0 equiv) and 4 Å MS was added TEA (105 μL, 0.75 mmol, 3 equiv), $CF_3CF_2CH_2NH_2$ (54 μL, 0.5 mmol, 2.0 equiv) and CH_3CN (2.5 mL) were added successively via syringe. The mixture was stirred vigorously under 80 ºC overnight. Then the reaction solution was filtered over a sintered-glass funnel with a tightly packed pad of Celite (1 cm thick), and the filter cake was rinsed with DCM (20 mL). The combined filtrates were concentrated. The residue was purified with silica gel column chromatography to provide the desired product.

2.3 Optimization reaction

Table S1 the effect of solvents

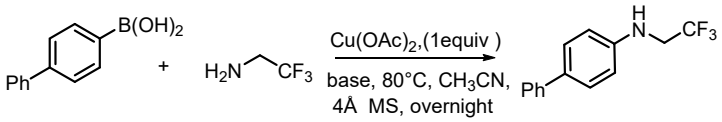


Solvent	Yield (%)
CH_3CN	70%
DCM	17%
toluene	41%
DMF	65%
MeOH	0
dioxane	48%

DCE	35%
THF	45%

4-biphenylboronic acid (0.10 mmol, 1 equiv), $CF_3CH_2NH_2$ (0.20 mmol, 2 equiv), $Cu(OAc)_2$ (0.1 mmol, 1 equiv), solvents (2.0 ml), T= 80 ºC, TEA (0.2 mmol, 2 equiv), 4Å MS, overnight. Yields were determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard.

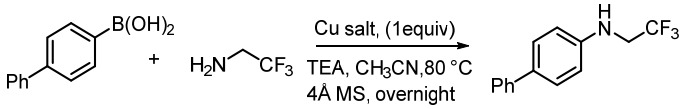
Table S2 Base screen



base	Yield (%)
NaOAc	58%
CsCO3	26%
DBU	16%
DIPEA	63%
TEA	70%
K_3PO_4	58%
pyridine	52%
K_2CO_3	39%
Na_2CO3	47%

4-biphenylboronic acid (0.1 mmol, 1 equiv), $CF_3CH_2NH_2$ (0.2 mmol, 2 equiv), $Cu(OAc)_2$ (0.1 mmol, 1 equiv), CH_3CN (2.0 ml), T= 80 ºC, base (0.2 mmol, 2 equiv), 4 Å MS, overnight. Yields determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard.

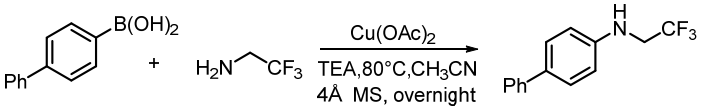
Table S3 Evaluation of copper salts



Cu salts	Yield 3a (%)
$Cu(OAc)_2$	70%
$Cu(OAc)_2•H_2O$	67%
CuCl	2%
CuBr	0
$Cu(OTf)_2$	5%
$Cu(acac)_2$	0
$CuBr_2$	3%
CuCN	0
CuI	0

4-biphenylboronic acid (0.1 mmol, 1 equiv), $CF_3CH_2NH_2$ (0.2 mmol, 2 equiv), **Cu salts** (0.1 mmol, 1equiv), CH_3CN (2.0 ml), T= 80 ºC, TEA (0.2 mmol, 2 equiv), 4Å MS, overnight. Yields were determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard.

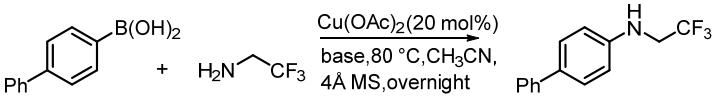
Table S4 Exploration the equivalent of $Cu(OAc)_2$



$Cu(OAc)_2$	yeild
1equiv	70%
0.2equiv	60%
0.1equiv	24%
0.05equiv	23%

4-biphenylboronic acid (0.10 mmol, 1 equiv), $CF_3CH_2NH_2$ (0.20 mmol, 2 equiv), CH_3CN (2.0 ml), T= 80 ºC, TEA (0.2 mmol, 2 equiv), 4Å MS, overnight. Yields were determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard.

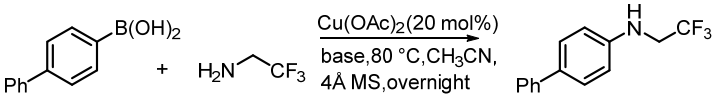
Table S5 The effect of concentration.



4-biphenylboronic acid (mmol)	Yield (%)
0.1	68%
0.2	70%
0.5	52%

The amount of reagents was adjusted while the volume of the solvent was kept constant. 4-biphenylboronic acid (1 equiv), $CF_3CH_2NH_2$ (2 equiv), $Cu(OAc)_2$, (0.2 equiv), TEA (3 equiv), CH_3CN (2.0 ml), T = 80 ºC, base, 4Å MS, overnight. Yields were determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard.

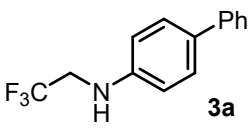
Table S6 Control experiments



entry	Yield(%)
no copper	0
no base	32%

4-biphenylboronic acid (0.10 mmol, 1 equiv), $CF_3CH_2NH_2$ (0.20 mmol, 2 equiv), TEA (0.3 mmol, 3 equiv), CH_3CN (2.0 ml), T = 80 ºC, 4Å MS, overnight. Yields were determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard.

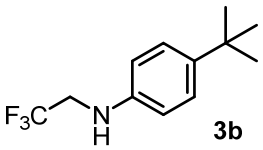
3. Characterization data of Compounds



3a

***N*-(2,2,2-trifluoroethyl)-[1,1'-biphenyl]-4-amine**

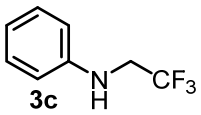
Purified by flash column chromatography (petroleum ether/AcOEt = 100:1), white solid (39.6 mg, 63% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.32 – 7.22 (m, 1H), 6.76 (d, J = 8.4 Hz, 2H), 4.20 (s, 1H), 3.80 (q, J = 9.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.6, 140.8, 132.1, 128.7, 128.1, 126.4, 125.0 (q, J = 280.0 Hz), 113.4, 46.0 (q, J = 33.3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.27 (t, J = 8.9 Hz, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -72.27 (s, 3F). (Consistent with previous reported values.[1])



3b

4-(tert-butyl)-*N*-(2,2,2-trifluoroethyl)aniline

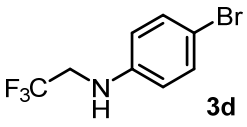
Purified by flash column chromatography (petroleum ether 100%), pale yellow liquid (43 mg, 74% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.7 Hz, 2H), 6.64 (d, J = 8.6 Hz, 2H), 3.83 (s, 1H), 3.79 – 3.67 (m, 2H), 1.28 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.8, 141.9, 126.2, 125.1 (q, J = 280.1 Hz), 112.9, 46.3 (q, J = 33.5 Hz), 34.0, 31.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.32 (t, J = 8.7 Hz, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -72.32 (s, 3F); **HRMS (ESI)** m/z calcd for $C_{12}H_{17}F_3N^+$ $[M+H]^+$ 232.13076, found 232.13084.



3c

***N*-(2,2,2-trifluoroethyl)aniline**

Purified by flash column chromatography (petroleum ether 100%), pale yellow liquid (33.7 mg, 77% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 8.5, 7.3 Hz, 2H), 6.81 (tt, J = 7.4, 1.1 Hz, 1H), 6.69 (d, J = 8.0 Hz, 2H), 3.91 (s, 1H), 3.77 (qd, J = 8.9, 7.0 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.35 (t, J = 8.9 Hz, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -72.35(s, 3F). (Consistent with previous reported values.[1])

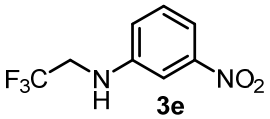


3d

4-bromo-*N*-(2,2,2-trifluoroethyl)aniline

Purified by flash column chromatography (petroleum ether 100%), yellow liquid (49.2 mg, 77% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 8.8 Hz, 2H), 3.96 (s, 1H), 3.88 – 3.58 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.3, 132.2, 124.9 (q, J = 280.0 Hz), 114.7, 110.8, 46.0 (q, J = 33.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.27 (t, J = 8.7 Hz, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -72.27

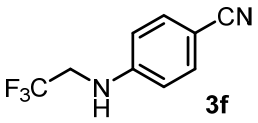
(s, 3F). (Consistent with previous reported values[1].)



3e

3-nitro-*N*-(2,2,2-trifluoroethyl)aniline

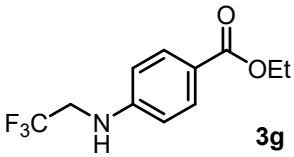
Purified by flash column chromatography (petroleum ether/ Dichloromethane = 5:1), yellow solid (34.9 mg, 63% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 8.2, 2.0 Hz, 1H), 7.52 (s, 1H), 7.35 (t, J = 8.1 Hz, 1H), 6.98 (dd, J = 8.2, 2.4 Hz, 1H), 4.33 (s, 1H), 3.85 (qd, J = 8.7, 1.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.3, 147.0, 130.1, 124.7 (q, J = 280.2 Hz), 119.0, 113.8, 107.0, 45.6 (q, J = 34.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.16 (t, J = 8.8 Hz, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -72.16 (s, 3F). (Consistent with previous reported values.[1])



3f

4-((2,2,2-trifluoroethyl)amino)benzonitrile

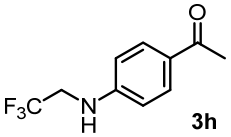
Purified by flash column chromatography (petroleum ether/AcOEt = 10:1), white solid (35.7 mg, 71% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.7 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 4.59 (s, 1H), 3.83 (qd, J = 7.0, 1.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.6, 133.7, 124.4 (q, J = 280.0 Hz), 119.7, 112.6, 100.9, 44.9 (q, J = 34.1 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.11(t, J = 8.7 Hz, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -72.11 (s, 3F). (Consistent with previous reported values.[2])



3g

ethyl 4-((2,2,2-trifluoroethyl)amino)benzoate

Purified by flash column chromatography (petroleum ether/Dichloromethane = 3:1), white solid (39.1 mg, 63% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H), 4.47 (s, 1H), 4.33 (q, J = 7.2 Hz, 2H), 3.82 (q, J = 9.0 Hz, 2H), 1.37 (t, J =7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 150.1, 131.5, 124.7 (q, J = 280.0 Hz), 120.7, 112.0, 60.5, 45.2 (q, 34.0 Hz), 14.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.22 (t, J = 8.7 Hz, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -72.22 (s, 3F). (Consistent with previous reported values.[1])

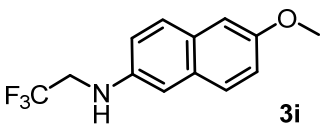


3h

1-(4-((2,2,2-trifluoroethyl)amino)phenyl)ethan-1-one

Purified by flash column chromatography (petroleum ether/ AcOEt = 9:1), white solid (35.2 mg, 65% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.9 Hz, 2H), 6.69 (d, J = 8.7 Hz, 2H), 4.75 (s, 1H), 3.96 – 3.71 (m, 2H), 2.52 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.5, 150.4, 130.7, 128.4, 124.7 (q, J = 280.1 Hz), 112.0, 45.2 (q, J = 34.2 Hz), 26.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.14 (t, J = 8.8 Hz, 3F); **^{19}F {^{1}H} NMR** (376

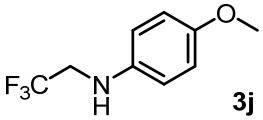
MHz, $CDCl_3$) δ -72.14 (s, 3F). (Consistent with previous reported values.[2])



3i

6-methoxy-*N*-(2,2,2-trifluoroethyl)naphthalen-2-amine

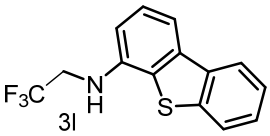
Purified by flash column chromatography (petroleum ether/AcOEt = 100:1), white solid (46.7 mg, 73% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 12.8, 9.1 Hz, 2H), 7.09 (dd, J = 8.9, 2.6 Hz, 1H), 7.04 (d, J = 2.6 Hz, 1H), 6.91 (d, J = 7.9 Hz, 2H), 3.88 (s, 3H), 3.86 – 3.79 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.7, 142.3, 130.0, 129.0, 128.1 127.7, 125.1 (q, J = 280.0 Hz), 119.2, 117.8, 106.4, 106.1, 55.3, 46.4 (q, J = 33.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.05 (t, J = 8.9 Hz, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -72.05 (s, 3F); **HRMS (ESI)** m/z calcd for $C_{13}H_{13}F_3NO^+$ $[M+H]^+$ 256.0944, found 256.0946.



3j

4-methoxy-*N*-(2,2,2-trifluoroethyl)aniline

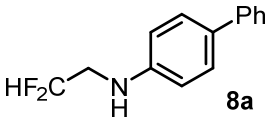
Purified by flash column chromatography (petroleum ether/AcOEt = 50:1), yellow liquid (37 mg, 72% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.80 (d, J = 9.0 Hz, 2H), 6.66 (d, J = 8.9 Hz, 2H), 3.75 (s, 3H), 3.70 (q, J = 8.9 Hz, 2H), 3.50(s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 140.3, 125.2 (q, J = 280.0 Hz), 114.9, 114.7, 55.7, 47.1 (q, J = 33.1 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.27 (t, J = 9.0 Hz, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -72.7 (s, 3F). (Consistent with previous reported values.[1])



3l

***N*-(2,2,2-trifluoroethyl)dibenzo[b,d]thiophen-4-amine**

Purified by flash column chromatography (petroleum ether, 100%), white solid (15.1 mg, 21% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 5.8, 3.2 Hz, 1H), 7.84 (dd, J = 5.9, 3.1 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.43 (dd, J = 5.9, 3.1 Hz, 2H), 7.36 (t, J = 7.8 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 4.03 – 3.82 (m, 3H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ 141.0, 138.3, 136.8, 136.4, 126.8, 126.1, 125.9, 125.0 (q, J = 278.8 Hz), 124.7, 123.0, 122.1, 113.1, 108.2, 46.1 (q, J = 33.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.93 (t, J = 8.3 Hz, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -71.93 (s, 3F); **HRMS (ESI)**: calcd. for $C_{14}H_{11}F_3NS^+$ $[M+H]^+$ 282.05588, found 282.05591.

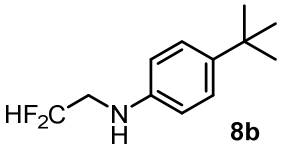


8a

N-(2,2-difluoroethyl)-[1,1'-biphenyl]-4-amine

Purified by flash column chromatography (petroleum ether, 100%), white solid (48.1 mg, 81% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.45 (J = 8.6 Hz, 2H), 7.39 (t, J = 7.7 Hz, 2H), 7.30 – 7.24 (m, 1H), 6.71 (d, J =

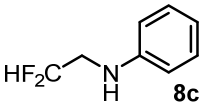
8.6 Hz, 2H), 5.92 (tt, *J* = 56.2, 4.4 Hz, 1H), 3.92 (s, 1H), 3.55 (tdd, *J* = 14.3, 6.6, 4.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 146.2, 140.9, 131.7, 128.7, 128.2, 126.4, 126.4, 114.5, (t, *J* = 241.8 Hz), 113.4, 46.5 (t, *J* = 25.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -122.61 (dt, *J* = 56.3, 14.5 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) *δ* -122.61 (s, 2F); **HRMS (ESI)** m/z calcd for $C_{14}H_{14}F_2N^+$ $[M+H]^+$ 234.10888, found 234.10902.



8b

4-(tert-butyl)-*N*-(2,2-difluoroethyl)aniline

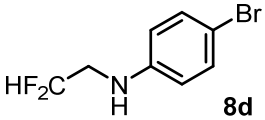
Purified by flash column chromatography (petroleum ether, 100%), yellow liquid (45.8 mg, 86% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.23 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 5.88 (tt, *J* = 56.1, 4.2 Hz, 1H), 3.76 (s, 1H), 3.49 (td, *J* = 14.3, 4.3 Hz, 2H), 1.28 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 144.4, 141.6, 126.3, 114.7 (t, *J* = 241.8 Hz), 112.9, 46.8 (t, *J* = 26.2 Hz), 34.0, 31.6; **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -122.57 (dt, *J* = 56.3, 14.3 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) *δ* -122.57 (s, 2F); **HRMS (ESI)** m/z calcd for $C_{12}H_{18}F_2N^+$ $[M+H]^+$ 214.1402, found 214.1400.



8c

***N*-(2,2-difluoroethyl)aniline**

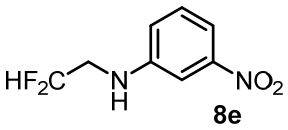
Purified by flash column chromatography (petroleum ether, 100%), pale yellow liquid (36.6 mg, 93% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.21 (dd, *J* = 8.5, 7.3 Hz, 2H), 6.83 – 6.74 (m, 1H), 6.66 (m, 2H), 5.91 (tt, *J* = 56.1, 4.0 Hz, 2H), 3.85 (s, 1H), 3.53 (tdd, *J* = 14.4, 6.7, 4.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 146.8*,* 129.5, 118.7, 114.5 (t, *J* =241.2 Hz), 113.1, 46.5 (t, *J* = 26.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -122.67 (dt, J = 56.0, 14.4 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) *δ* -122.67 (s, 2F). **HRMS (ESI)** m/z calcd for $C_8H_9BrF_2N^+$ $[M+H]^+$, 158.0776, found 158.0772.



8d

4-bromo-N-(2,2-difluoroethyl)aniline

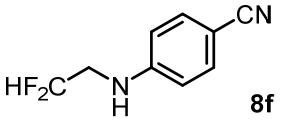
Purified by flash column chromatography (petroleum ether, 100%), yellow liquid (54.6 mg, 92% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.28 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H),5.89 (tt, *J* = 55.9, 14.2 Hz, 1H), 3.89 (s, 1H), 3.50 (td, *J* = 14.5, 4.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 145.8, 132.2, 114.7, 114.3 (t, *J* = 242.5 Hz), 110.4, 46.4 (t, *J* = 26.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -122.64 (dt, *J* = 56.2, 14.5 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) *δ* -122.64 (s, 2F); **HRMS (ESI)** m/z calcd for $C_8H_9BrF_2N^+$ $[M+H]^+$ 235.9881, found 235.9883.



8e

N-(2,2-difluoroethyl)-3-nitroaniline

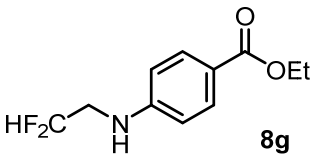
Purified by flash column chromatography (petroleum ether / Dichloromethane = 5:1), yellow solid (34.7 mg, 69% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 8.1, 2.0 Hz, 1H), 7.48 (t, J = 2.3 Hz, 1H), 7.33 (t, J = 8.1 Hz, 1H), 6.96 (dd, J = 8.1, 2.4 Hz, 1H), 5.96 (tt, J = 55.6, 3.9 Hz, 1H), 4.29 (s, 1H), 3.63 (tdd, J = 14.6, 6.7, 4.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.4, 147.8, 130.1, 119.1, 114.1 (t, J = 242.5 Hz), 113.3, 106.7, 46.0 (t, J = 25.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.68 (dt, J = 55.6, 14.4 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -122.68 (s, 2F); **HRMS (ESI)** m/z calcd for $C_8H_9F_2N_2O_2^+$ $[M+H]^+$ 203.0627, found 203.0628.



8f

4-((2,2-difluoroethyl)amino)benzonitrile

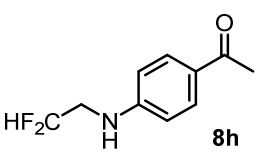
Purified by flash column chromatography (petroleum ether / EtOAc = 10:1), white solid (36.3 mg, 80% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.9 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 5.93 (tt, J = 55.5, 4.0 Hz, 1H), 4.51 (s, 1H), 3.60 (tdd, J = 14.8, 6.5, 4.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.3, 133.9, 120.0, 114.0 (t, J = 242.8 Hz), 112.6, 100.4, 45.5 (t, J = 25.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.52 (dt, J = 55.9, 14.4 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -122.52 (s, 2F). (Consistent with previous reported values.[2])。



8g

ethyl 4-((2,2-difluoroethyl)amino)benzoate

Purified by flash column chromatography (petroleum ether / Dichloromethane = 3:1), white solid (47.7 mg, 83% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.9 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 5.92 (tt, J = 55.4, 4.1 Hz, 1H), 4.39 (s, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.60 (tdd, J = 14.5, 6.6, 4.0 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 150.6, 131.6, 120.3, 114.1 (t, J = 242.4 Hz), 111.8, 60.4, 45.7 (t, J = 26.1 Hz), 14.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.58 (dt, J = 55.8, 14.4 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -122.58 (s, 2F); **HRMS (ESI)** m/z calcd for $C_{11}H_{14}F_2NO_2^+$ $[M+H]^+$ 230.09871, found 230.09882.

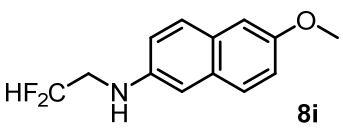


8h

1-(4-((2,2-difluoroethyl)amino)phenyl)ethan-1-one

Purified by flash column chromatography (petroleum ether / Dichloromethane = 1:1), white solid (36.7 mg, 74% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.9 Hz, 2H), 6.65 (d, J = 8.5 Hz, 2H), 6.23 – 5.66 (m, 1H), 4.58

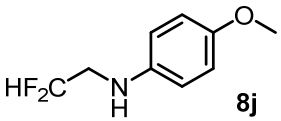
(s, 1H), 3.62 (tdd, *J* = 14.6, 6.7, 4.0 Hz, 2H), 2.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.5, 151.0, 130.8, 127.9, 114.1 (t, *J* = 243.1 Hz), 111.8, 45.6 (t, *J* = 26.2 Hz), 26.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.50 (dt, *J* = 55.8, 14.4 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -122.50 (s, 2 F); **HRMS (ESI)** m/z calcd for $C_{10}H_{12}F_2NO^+$ $[M+H]^+$ 200.0881, found 200.0884.



8i

***N*-(2,2-difluoroethyl)-6-methoxynaphthalen-2-amine**

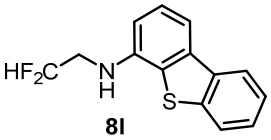
Purified by flash column chromatography (petroleum ether / EtOAc = 50:1), white solid (40.3 mg, 68% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 11.9, 8.7 Hz, 2H), 7.13 – 7.00 (m, 2H), 6.93 – 6.82 (m, 2H), 5.97 (tt, *J* = 56.2, 4.2 Hz, 1H), 3.87 (s, 3H), 3.60 (td, *J* = 14.4, 4.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.6, 142.9, 130.1, 128.8, 128.2, 127.6, 119.1, 118.1, 114.5 (t, *J* = 241.9 Hz), 106.2, 105.8, 55.5, 46.7 (t, *J* = 26.3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.49(dt, *J* = 55.7, 14.6 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -122.49 (s, 2F); **HRMS (ESI)** m/z calcd for $C_{13}H_{14}F_2NO^+$ $[M+H]^+$ 238.1038, found 238.1036.



8j

***N*-(2,2-difluoroethyl)-4-methoxyaniline**

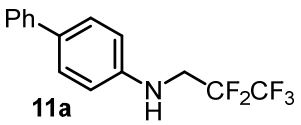
Purified by flash column chromatography (petroleum ether / EtOAc = 50:1), yellow liquid (46.6 mg, 71% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.80 (d, *J* = 9.1 Hz, 2H), 6.63 (d, *J* = 9.1 Hz, 2H), 5.91 (tt, *J* = 56.2, 4.1 Hz, 1H), 3.75 (s, 3H), 3.62 (s, 1H), 3.47 (td, *J* = 14.4, 4.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 140.8, 115.0, 114.8 (t, *J* = 242.0 Hz), 114.6, 55.8, 47.5 (t, *J* = 25.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.76 (dt, *J* = 56.4, 14.4 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -122.76 (s, 2F). (Consistent with previous reported values.[2])



8l

***N*-(2,2-difluoroethyl)dibenzo[b,d]thiophen-4-amine**

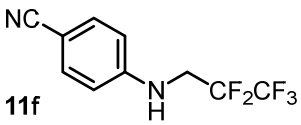
Purified by flash column chromatography (petroleum ether, 100%), white solid (24 mg, 36% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.86 (dd, *J* = 5.8, 3.2 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.45 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H), 6.02 (tt, *J* = 56.0, 4.2 Hz, 1H), 3.85 (s, 1H), 3.79 – 3.65 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.5, 138.4, 136.8, 136.4, 126.8, 126.1, 125.9, 124.6, 123.0, 122.1, 114.5 (t, *J* = 242.1 Hz), 112.8, 107.8, 46.6 (t, *J* = 26.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.26 (tt, *J* = 56.1, 14.1 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -122.26 (s, 2F); **HRMS (ESI)** m/z calcd for $C_{14}H_{12}F_2NS^+$ $[M+H]^+$ 264.06530, found 264.06546.



11a

***N*-(2,2,3,3,3-pentafluoropropyl)-[1,1'-biphenyl]-4-amine**

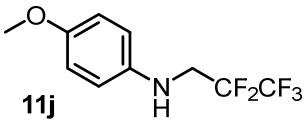
Purified by flash column chromatography (petroleum ether, 100%), white solid (51.1 mg, 68% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.31 – 7.26 (m, 1H), 6.76 (d, J = 8.6 Hz, 2H), 3.94 (t, J = 6.5 Hz, 1H), 3.86 (td, J = 14.6, 6.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.7, 140.8, 132.2, 128.7, 128.1, 126.5, 126.5, 119.0 (qt, J = 286.0, 35.3 Hz), 113.9 (tq, J = 254.4, 36.6 Hz), 113.5, 44.21 (t, J = 23.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -83.92 (s, 3F), -121.85 (t, J = 14.6 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -83.92 (s, 3F), -121.85 (s, 2F); **HRMS (ESI)** m/z calcd for $C_{15}H_{13}F_5N^+$ $[M+H]^+$ 302.09627, found 302.09662.



11f

4-((2,2,3,3,3-pentafluoropropyl)amino)benzonitrile

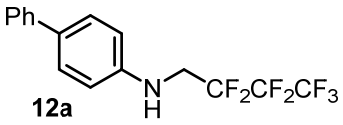
Purified by flash column chromatography (petroleum ether / EtOAc = 15:1), white solid (44 mg, 70% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 4.44 (t, J = 7.0 Hz, 1H), 4.05 – 3.67 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.8, 133.8, 119.7, 118.8 (qt, J = 286.1, 35.1 Hz), 113.5 (tq, J = 254.7, 36.8 Hz), 112.9, 101.3, 43.2 (t, J = 24.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -83.98 (s, 3F), -121.74 (t, J = 14.7 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -83.98 (s, 3F), -121.74 (s, 2F). (Consistent with previous reported values.[2])



11j

4-methoxy-N-(2,2,3,3,3-pentafluoropropyl)aniline

Purified by flash column chromatography (petroleum ether / EtOAc = 50:1), yellow liquid (39.1mg, 61% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.80 (d, J = 8.9 Hz, 2H), 6.65 (d, J = 8.9 Hz, 2H), 3.79 –3.72 (m, 5H), 3.61 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 140.4, 119.0 (qt, J = 286.0, 35.4 Hz), 115.0, 114.8, 114.0 (tq, J = 256.1, 36.5 Hz), 55.7, 45.4 (t, J = 23.7 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz, 25 ºC) δ -83.98 (s, 3F), -121.94 (t, J = 29.8 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -83.98 (s, 3F), -121.94 (s, 2F). (Consistent with previous reported values.[2])

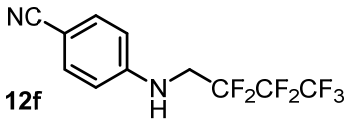


12a

N-(2,2,3,3,4,4,4-heptafluorobutyl)-[1,1'-biphenyl]-4-amine

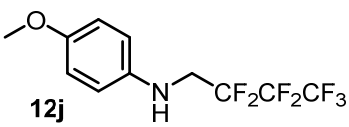
Purified by flash column chromatography (petroleum ether, 100%), white solid (57 mg, 65% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 8.3, 1.3 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.40 (dd, J = 8.4, 7.0 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 8.6 Hz, 2H), 4.08 – 3.72 (m, 3H); **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 145.8, 140.9, 132.2, 128.7, 128.1, 126.5, 126.5, 117.8 (qt, J = 286.3, 33.7 Hz), 115.8 (tt, J = 254.6, 30.5 Hz), 113.5, 109.5 (m), 44.2 (t, J = 23.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.68 (t, J = 9.3 Hz, 3F), -118.99 (dqd, J = 20.2, 9.1, 5.0 Hz, 2F), -127.57 (d, J = 4.2 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -80.68 (t, J = 9.3 Hz, 3F), -118.91 – -119.07 (m, 2F), -127.46 – -127.64 (m, 2F); **HRMS (ESI)** m/z calcd for $C_{16}H_{13}F_7N^+$ $[M+H]^+$ 352.09307, found 352.09332.



4-((2,2,3,3,4,4,4-heptafluorobutyl)amino)benzonitrile

Purified by flash column chromatography (petroleum ether / EtOAc = 15:1), white solid (49.2 mg, 65% yield); **^{1}H NMR** ($CDCl_3$, 400 MHz, 25 ºC) δ 7.49 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 4.40 (s, 1H), 3.92 (tdt, J = 15.2, 7.1, 1.3 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz, 25 ºC) δ 149.9, 133.8, 119.7, 117.6 (qt, J = 288.5, 33.8 Hz), 115.4 (tt, J = 256.7, 30.7 Hz), 112.9, 109.5(m), 101.2, 43.2 (t, J = 23.7 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz, 25 ºC) δ -80.64 (t, J = 9.3 Hz, 3F), -118.87 (dtt, J = 15.0, 9.2, 5.6 Hz, 2F), -127.52 (d, J = 5.4 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -80.64 (t, J = 9.4 Hz, 3F), -118.87 (ttd, J = 9.4, 5.6, 2.7 Hz, 2F), -125.44 – -128.88 (m, 2F); **HRMS (ESI)** m/z calcd for $C_{11}H_6F_7N_2^-$ $[M-H]^-$ 299.04247, found 299.04263.

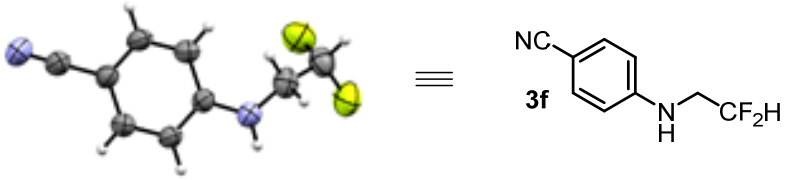


N-(2,2,3,3,4,4,4-heptafluorobutyl)-4-methoxyaniline

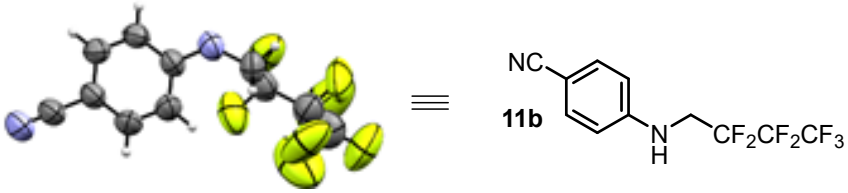
Purified by flash column chromatography (petroleum ether / EtOAc = 50:1), yellow liquid (47.8mg, 62% yield); **^{1}H NMR** ($CDCl_3$, 400 MHz, 25 ºC) δ 6.80 (d, J = 8.9 Hz, 2H), 6.66 (d, J = 8.9 Hz, 2H), 3.81 (dt, J = 15.2, 5.0 Hz, 2H), 3.75 (s, 3H), 3.62 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz, 25 ºC) δ 153.3, 140.4,117.7 (qt, J = 286.7, 34.5 Hz), 115.9 (tt, J = 255.2, 30.4 Hz), 114.9, 114.8, 109.1 (m), 55.7, 45.4 (t, J = 23.3 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz, 25 ºC) δ -80.75 (t, J = 9.5 Hz, 3F), -119.10 (tddd, J = 15.2, 11.6, 7.4, 4.0 Hz, 2F), -127.65 (d, J = 4.8 Hz, 2F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -80.75 (t, J = 9.3 Hz, 3F), -116.32 – -121.56 (m, 2F), -127.65 (d, J = 4.8 Hz, 2F). (Consistent with previous reported values.[3])

4. X-ray structure of 3f and 11b

Compound 3f (CCDC 1853090)



Compound 11b (CCDC 1853088)



5. Refeence

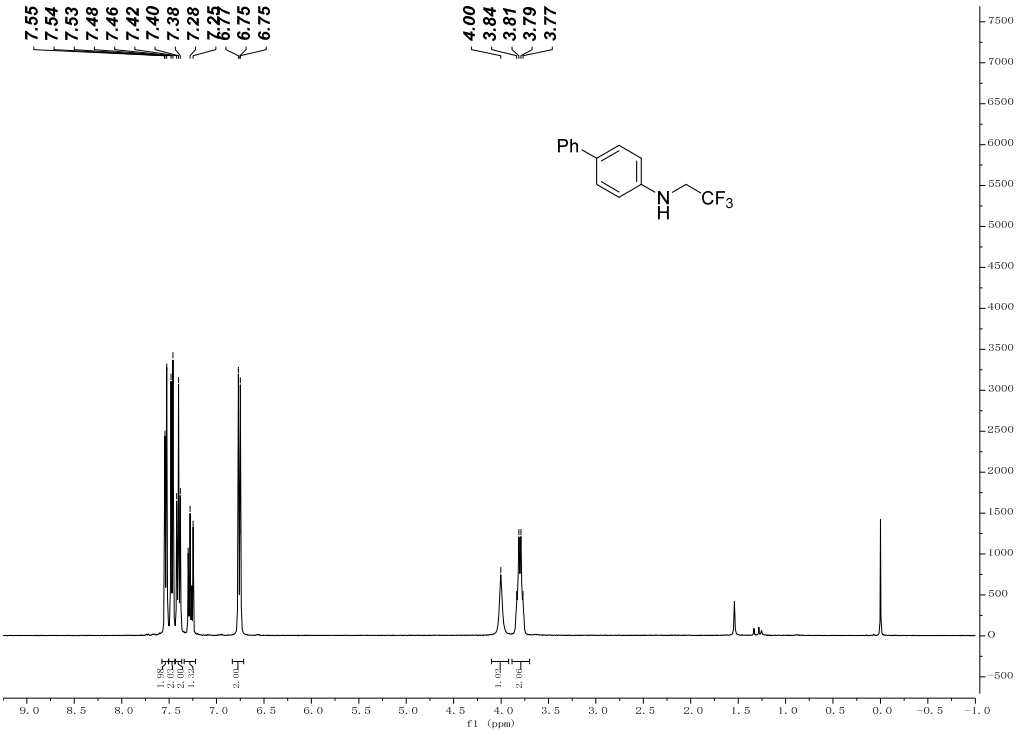
1. Luo, H.; Wu, G.; Zhang, Y.; Wang, J., Silver(I)-Catalyzed N-Trifluoroethylation of Anilines and O-Trifluoroethylation of Amides with 2,2,2-Trifluorodiazoethane. *Angew. Chem. Int. Ed. Engl.* **2015,** *54* (48), 14503-7.

2. Brusoe, A. T.; Hartwig, J. F., Palladium-Catalyzed Arylation of Fluoroalkylamines. *J. Am. Chem. Soc.* **2015,** *137* (26), 8460-8.

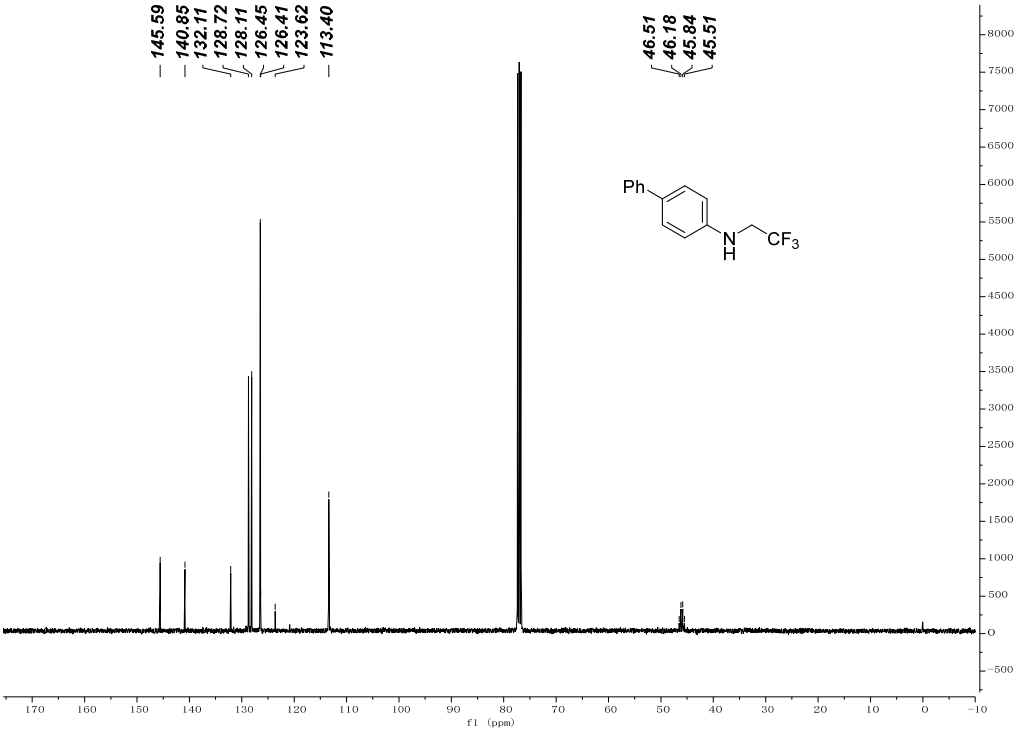
3. Berzina, B.; Sokolovs, I.; Suna, E., Copper-Catalyzed para-Selective C–H Amination of Electron-Rich Arenes. *ACS Catalysis* **2015,** *5* (11), 7008-7014.

6. NMR spectra of novel compounds

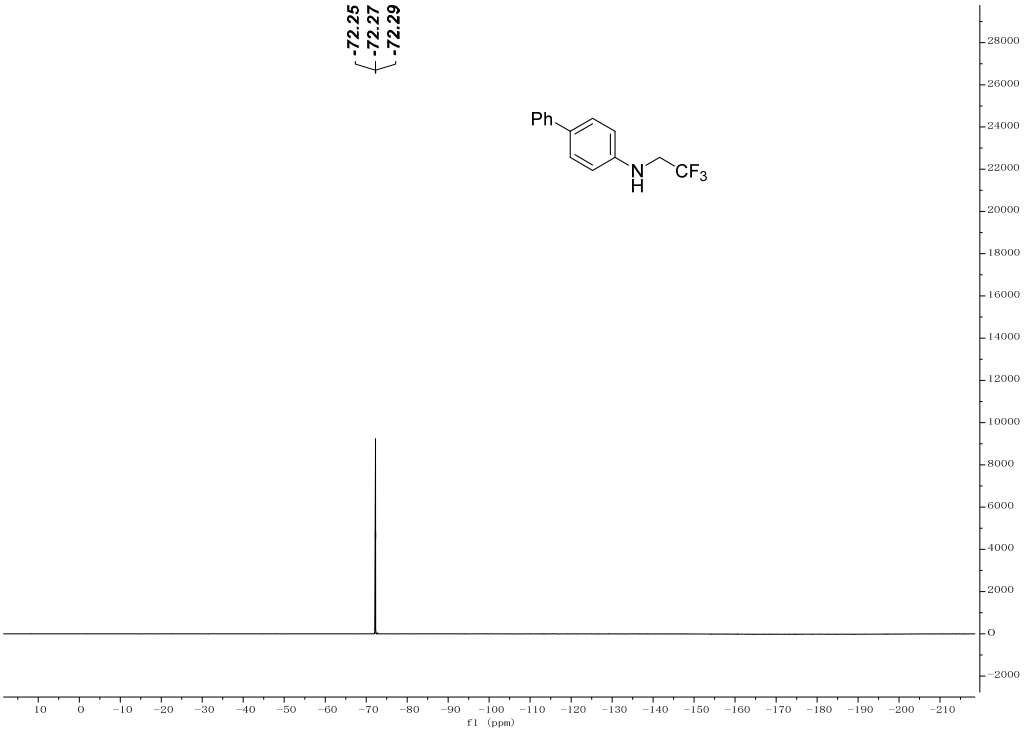
^{1}H NMR ($CDCl_3$, 400 MHz) of **3a**



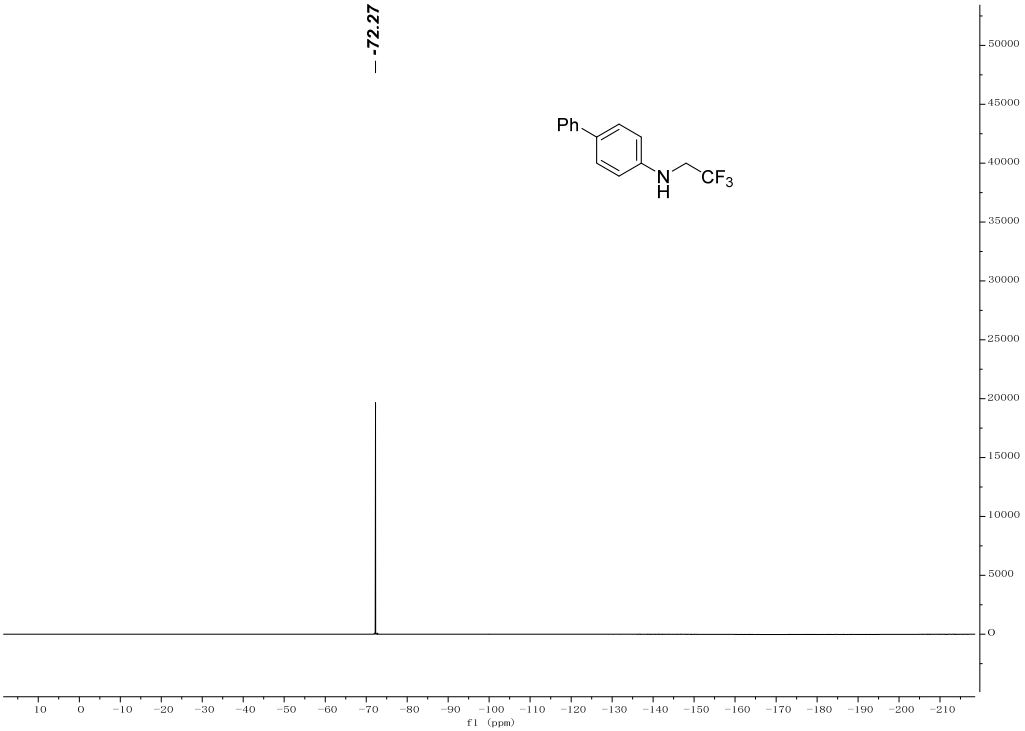
^{13}C NMR ($CDCl_3$, 100 MHz) of **3a**



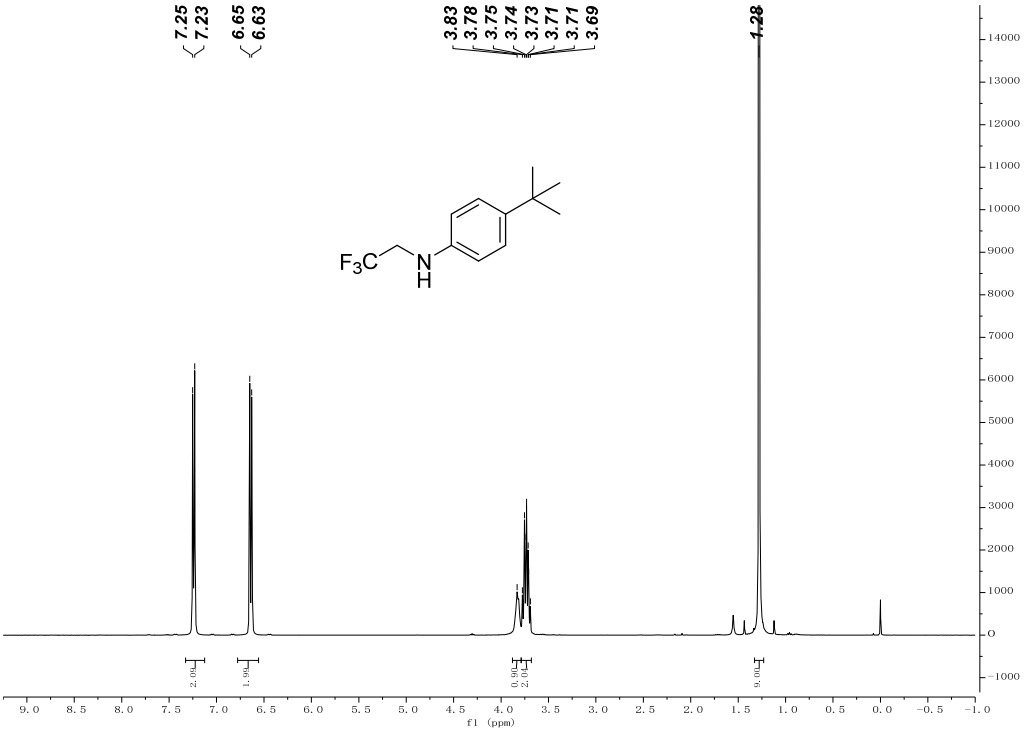
^{19}F NMR ($CDCl_3$, 376 MHz) of **3a**



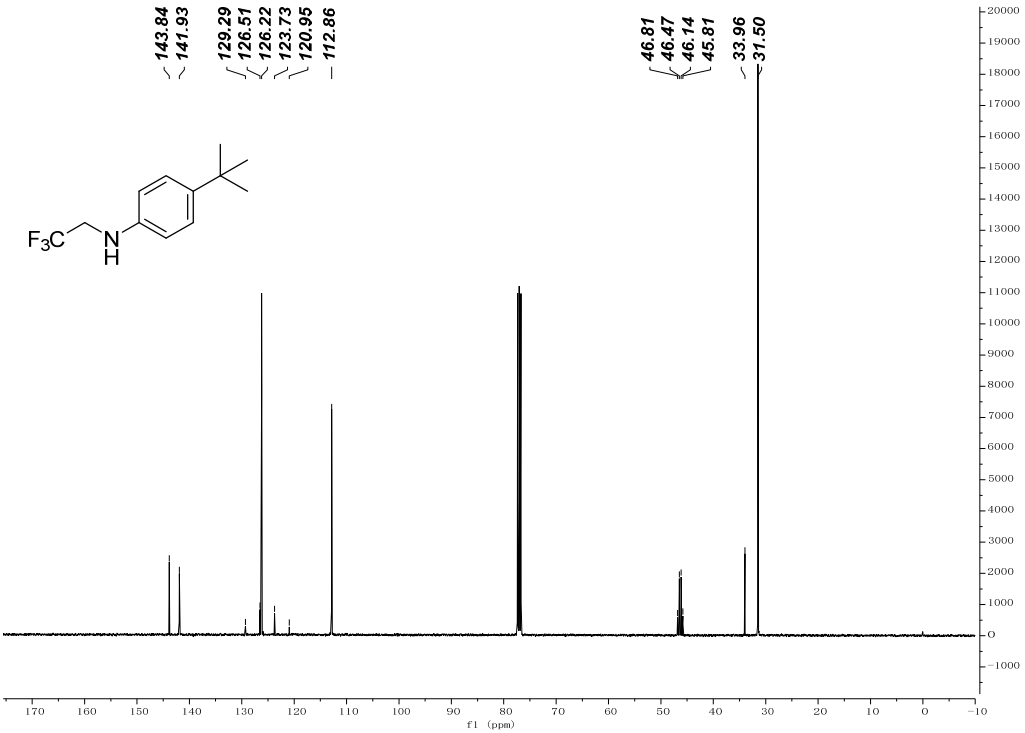
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **3a**



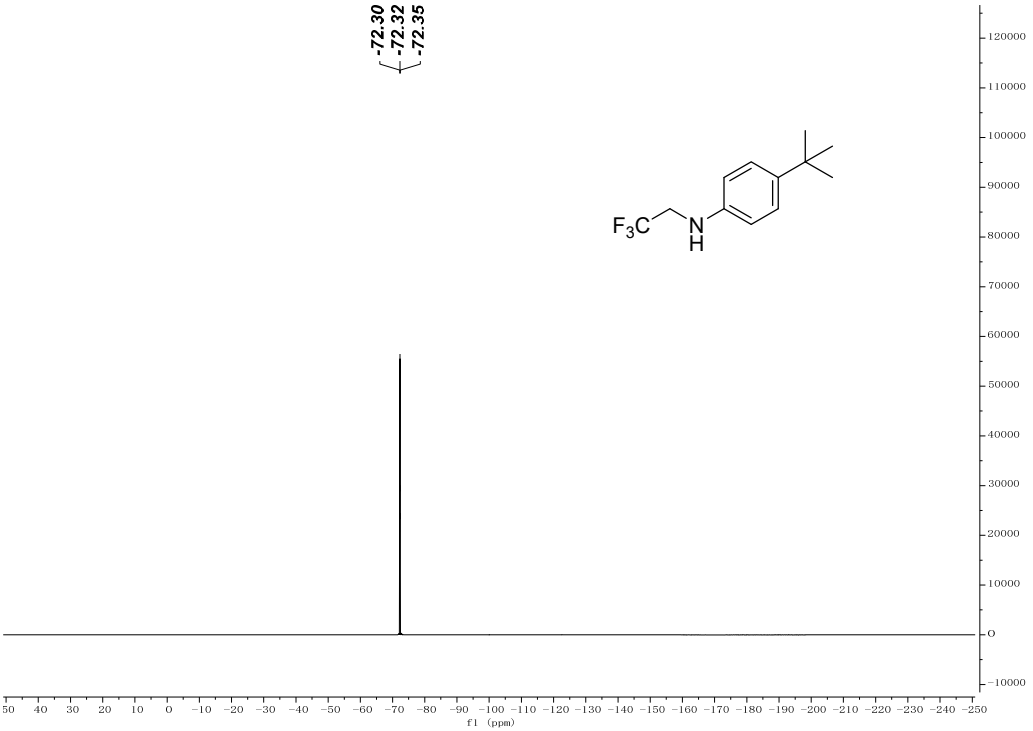
^{1}H NMR ($CDCl_3$, 400 MHz) of **3b**



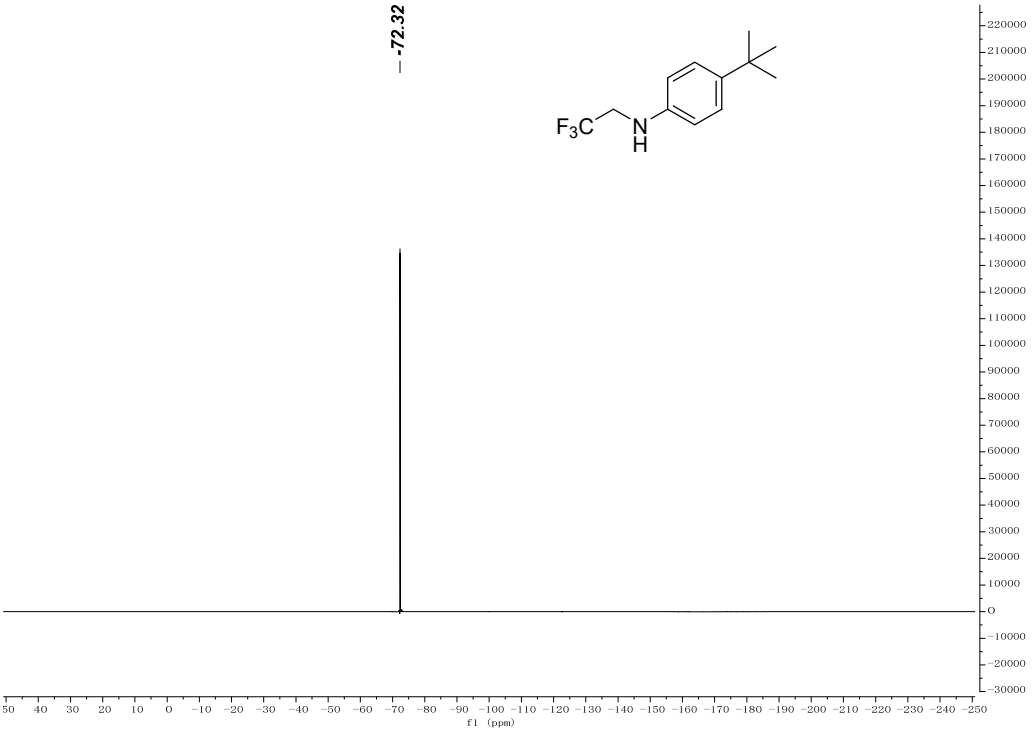
^{13}C NMR ($CDCl_3$, 100 MHz) of **3b**



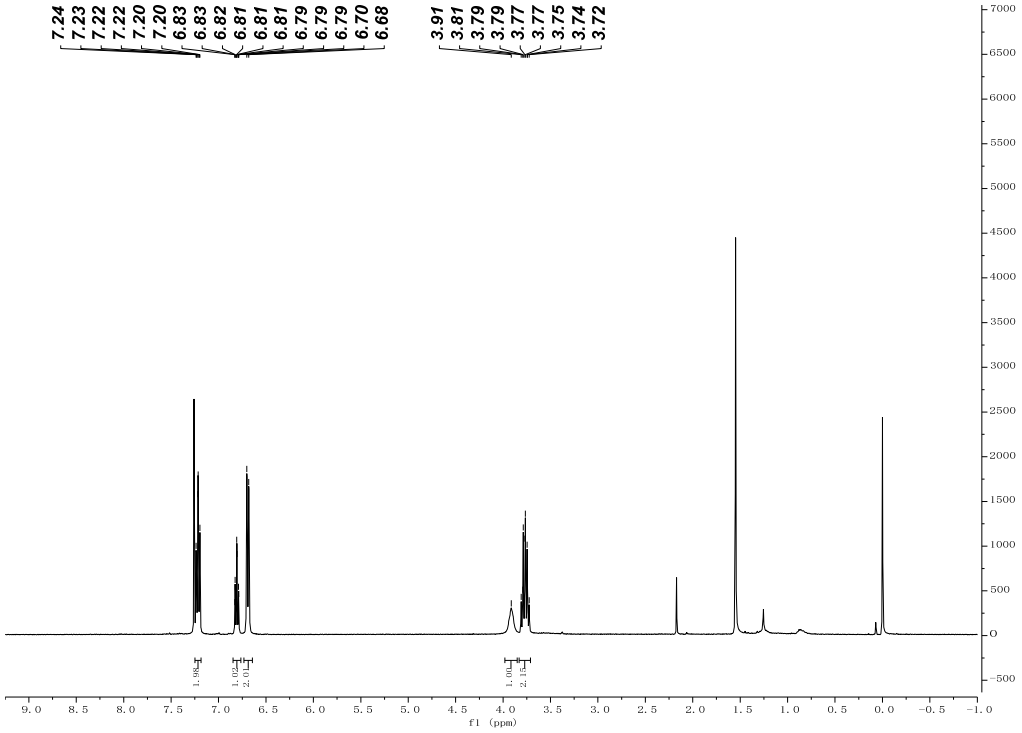
^{19}F NMR ($CDCl_3$, 376 MHz) of **3b**



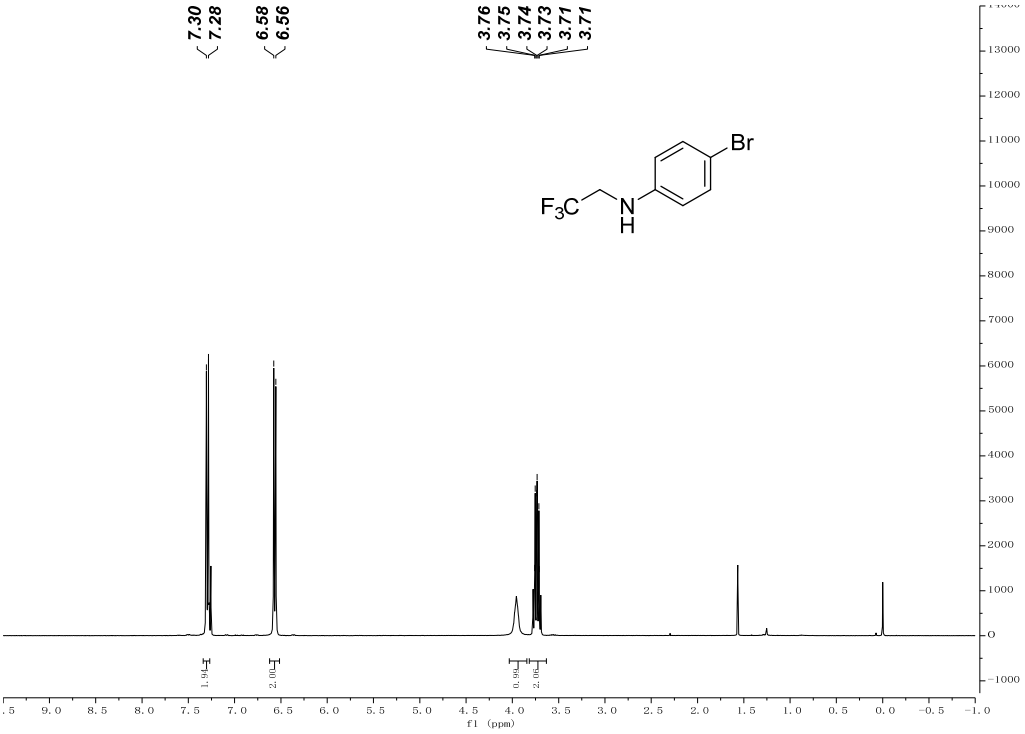
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **3b**



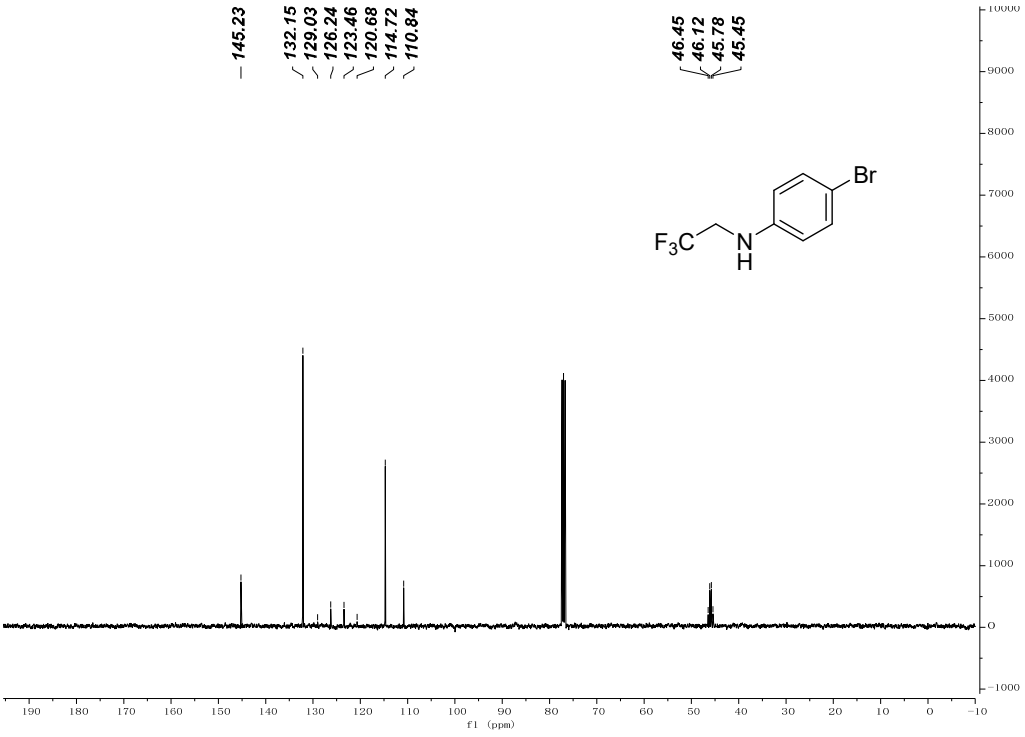
^{1}H NMR ($CDCl_3$, 400 MHz) of **3c**



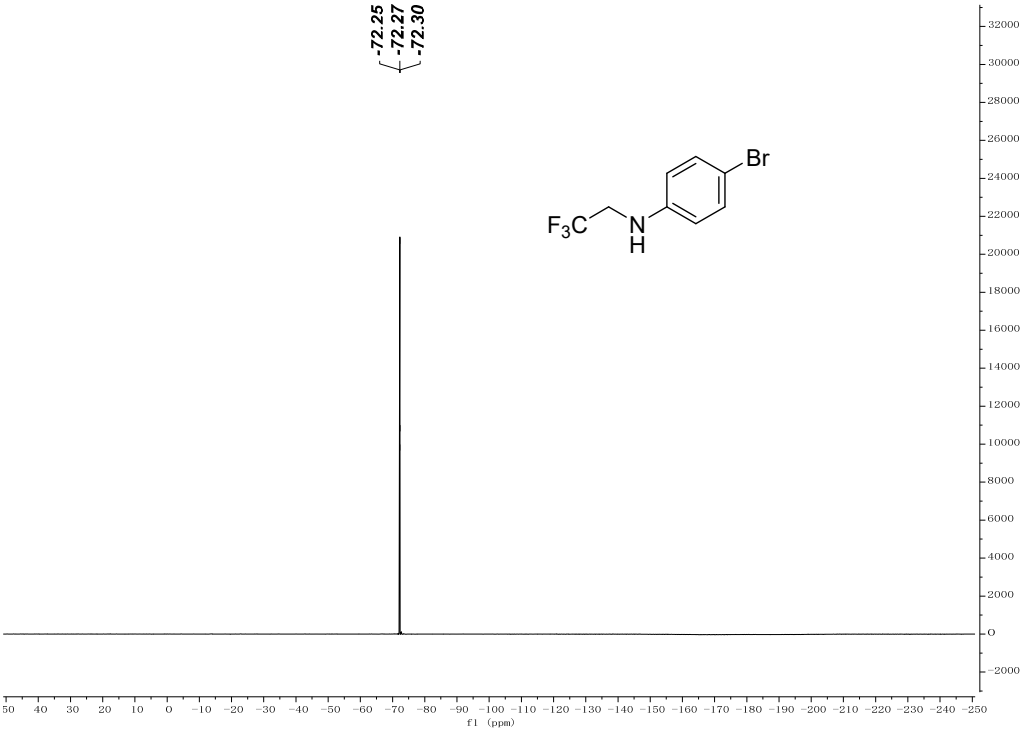
^{1}H NMR ($CDCl_3$, 400 MHz) of **3d**



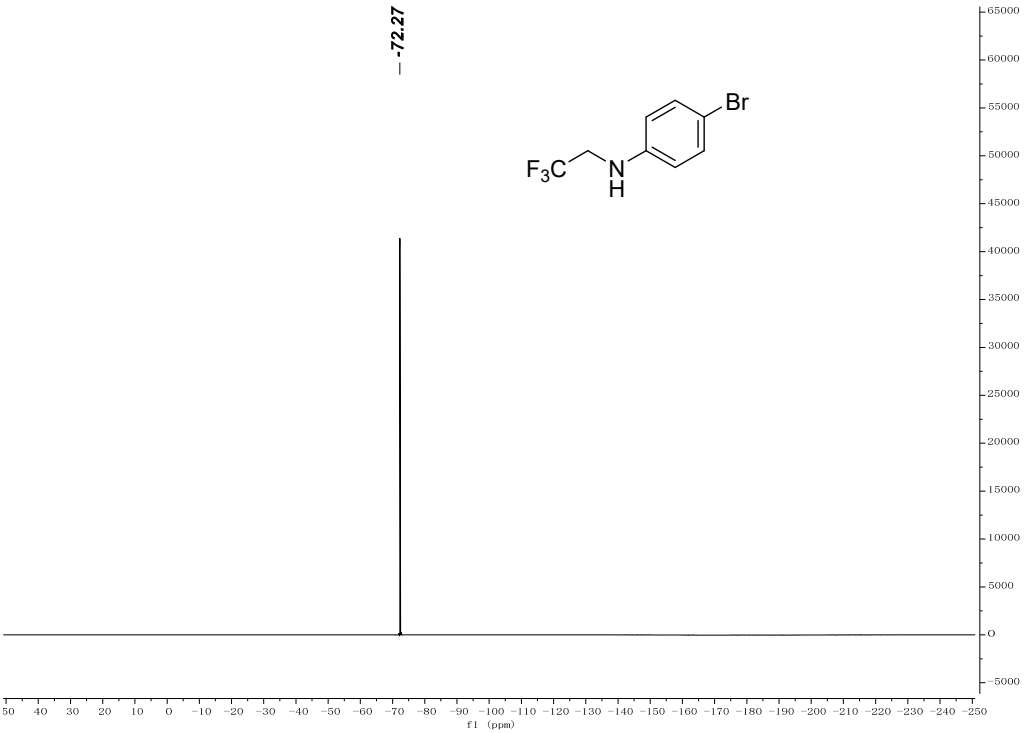
^{13}C NMR ($CDCl_3$, 100 MHz) of **3d**



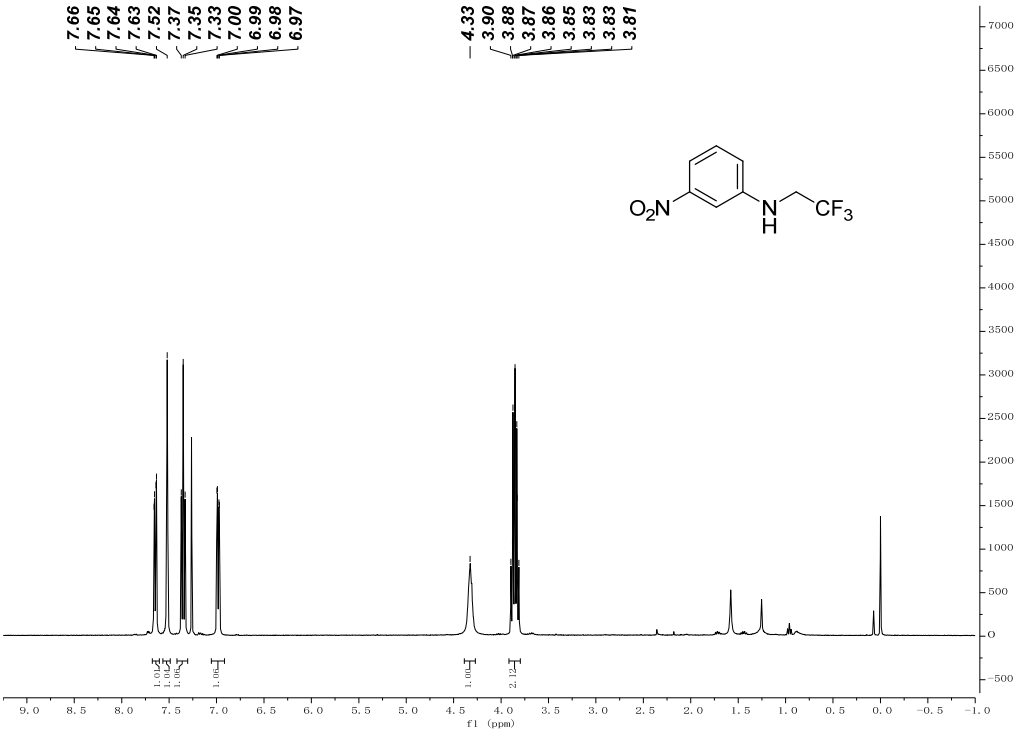
^{19}F NMR ($CDCl_3$, 376 MHz) of **3d**



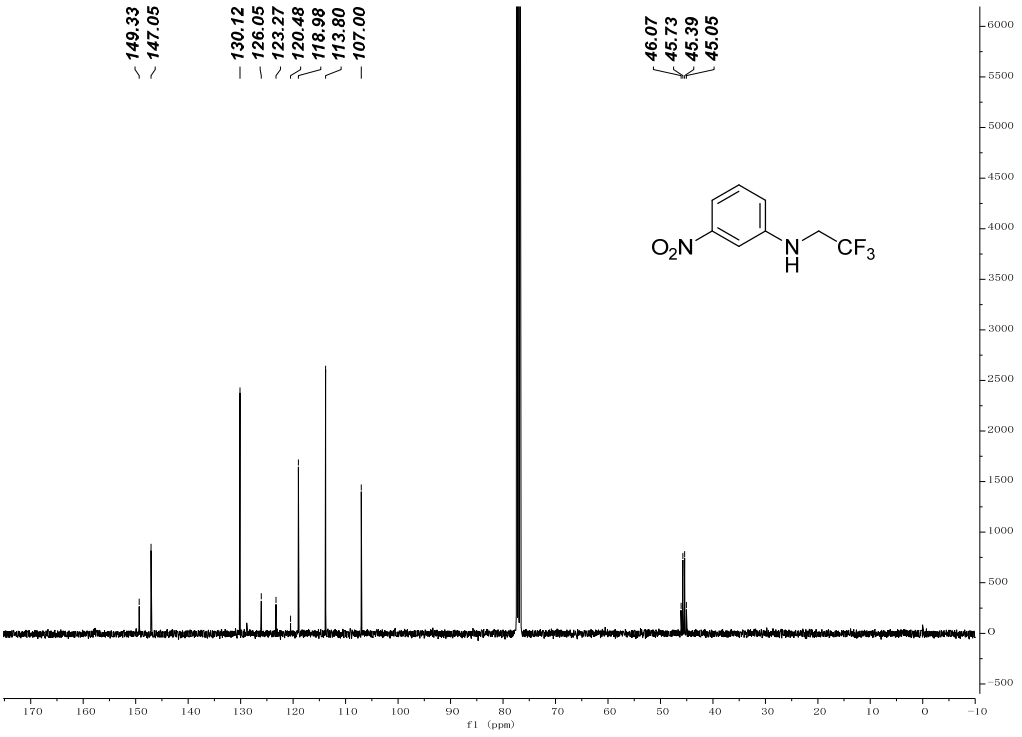
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **3d**



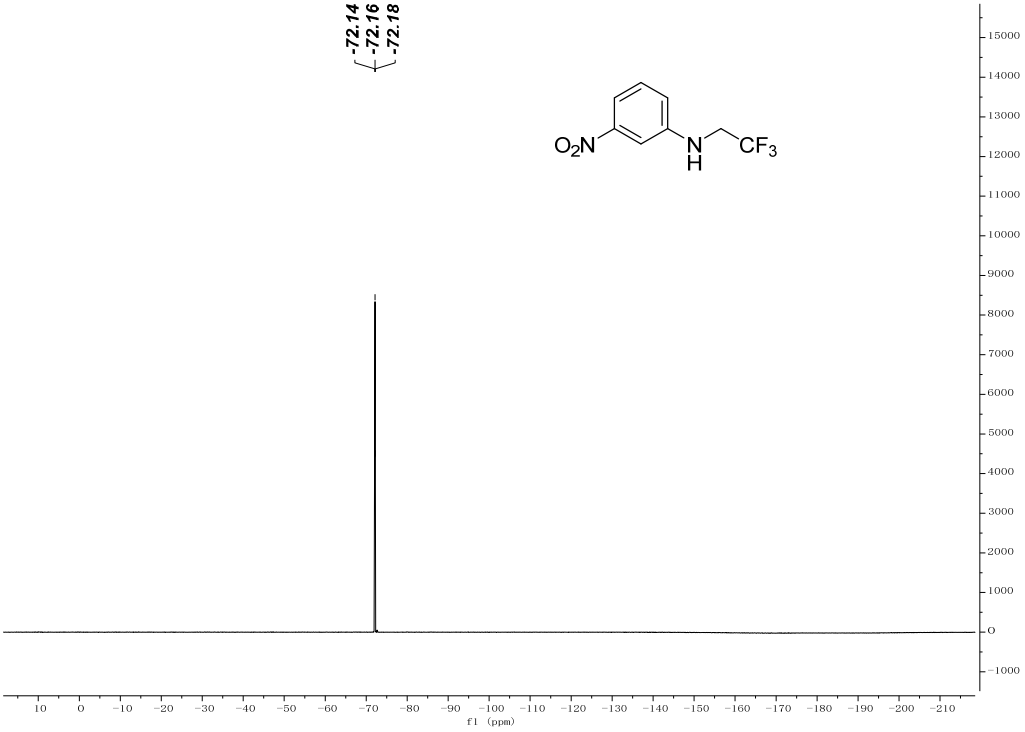
^{1}H NMR ($CDCl_3$, 400 MHz) of **3e**



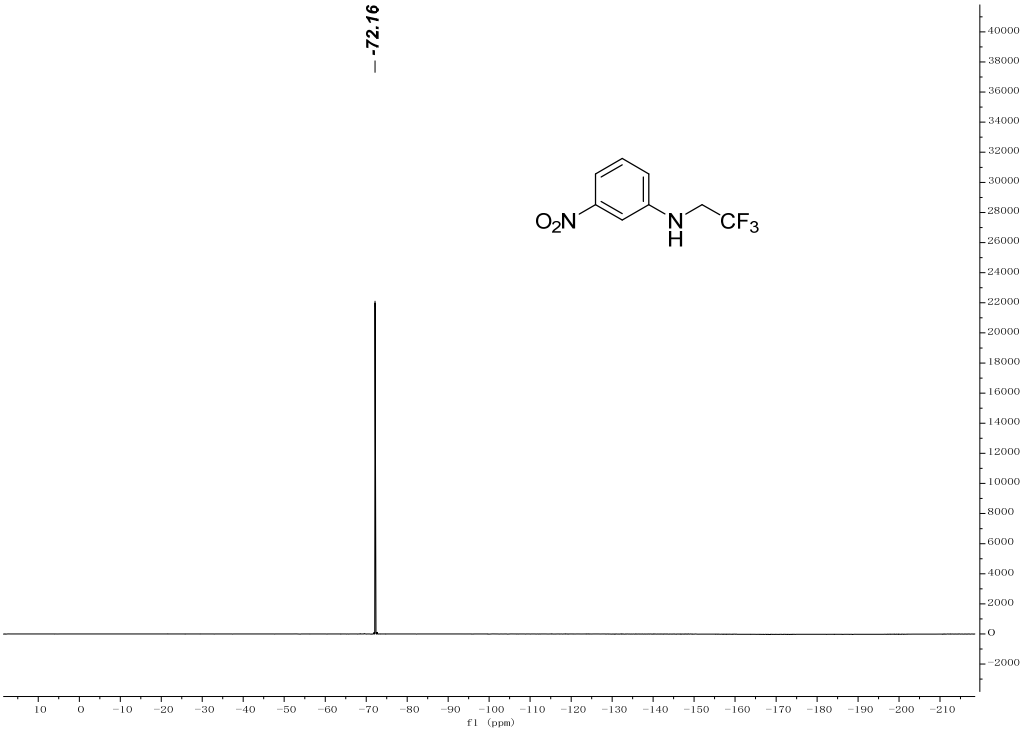
^{13}C NMR ($CDCl_3$, 100 MHz) of **3e**



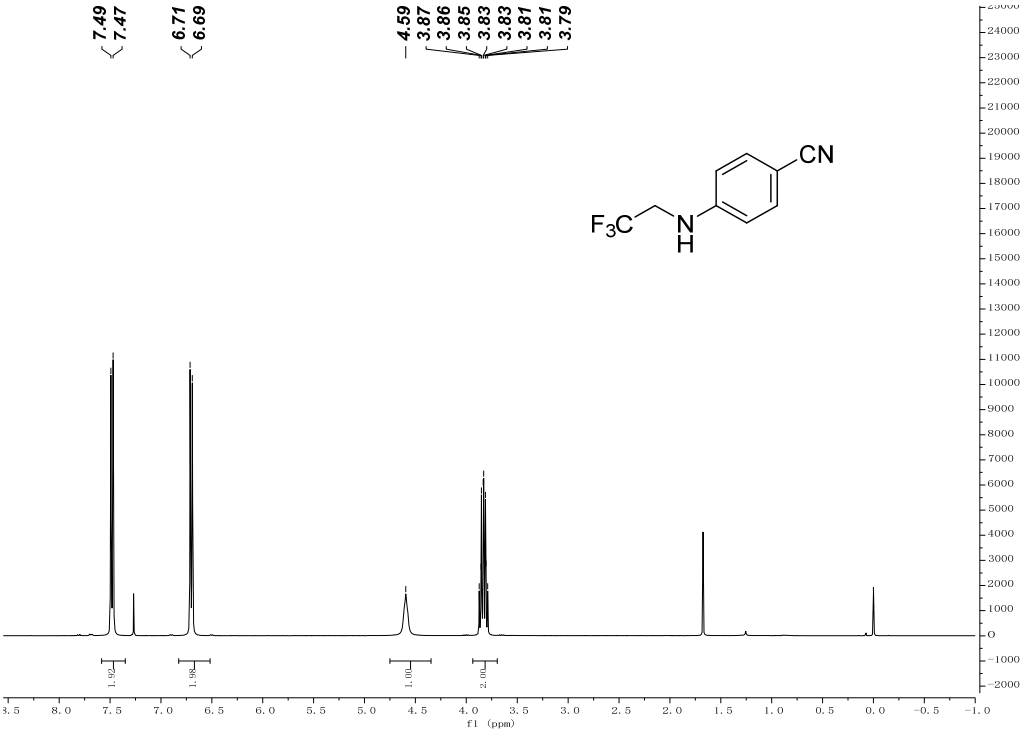
^{19}F NMR ($CDCl_3$, 376 MHz) of **3e**



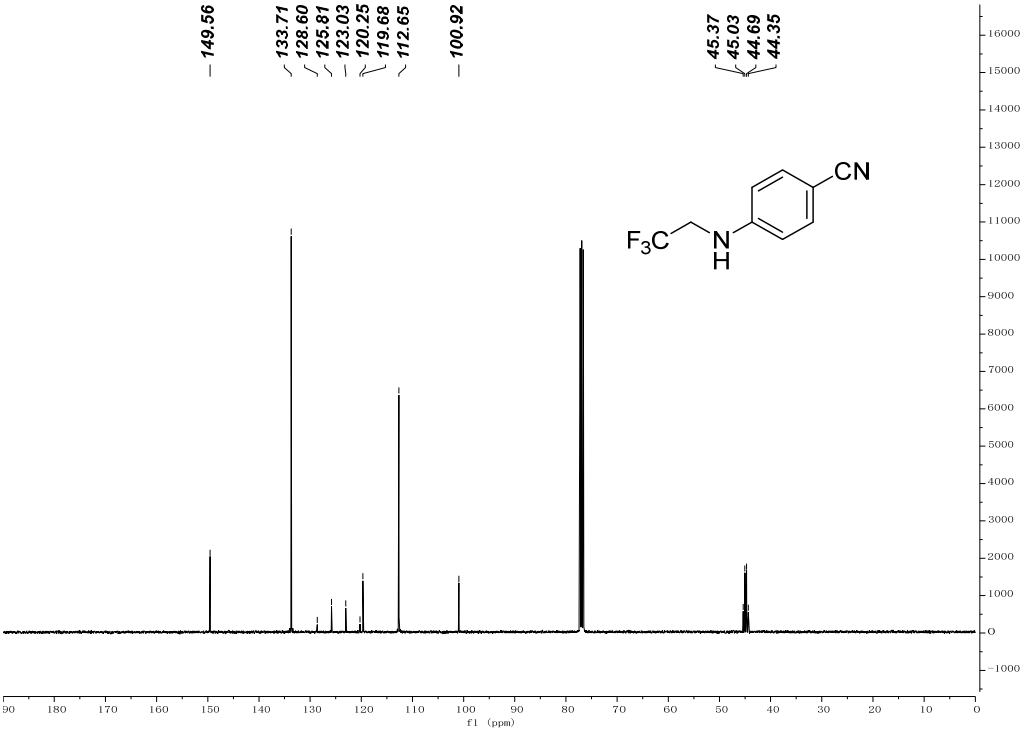
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **3e**



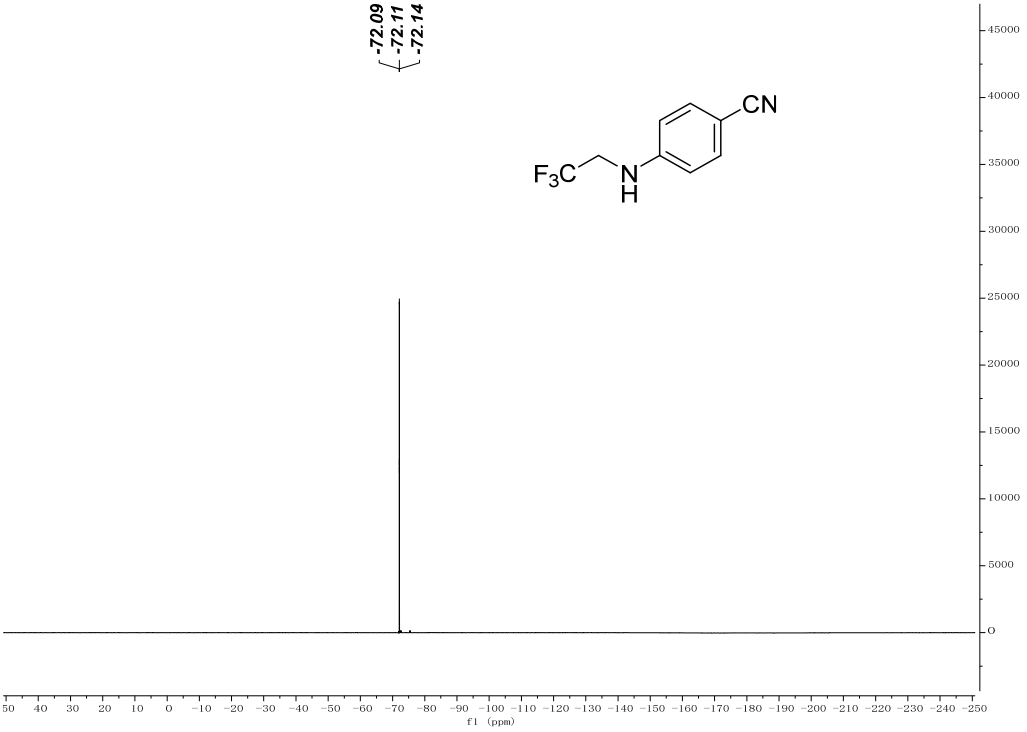
^{1}H NMR ($CDCl_3$, 400 MHz) of **3f**



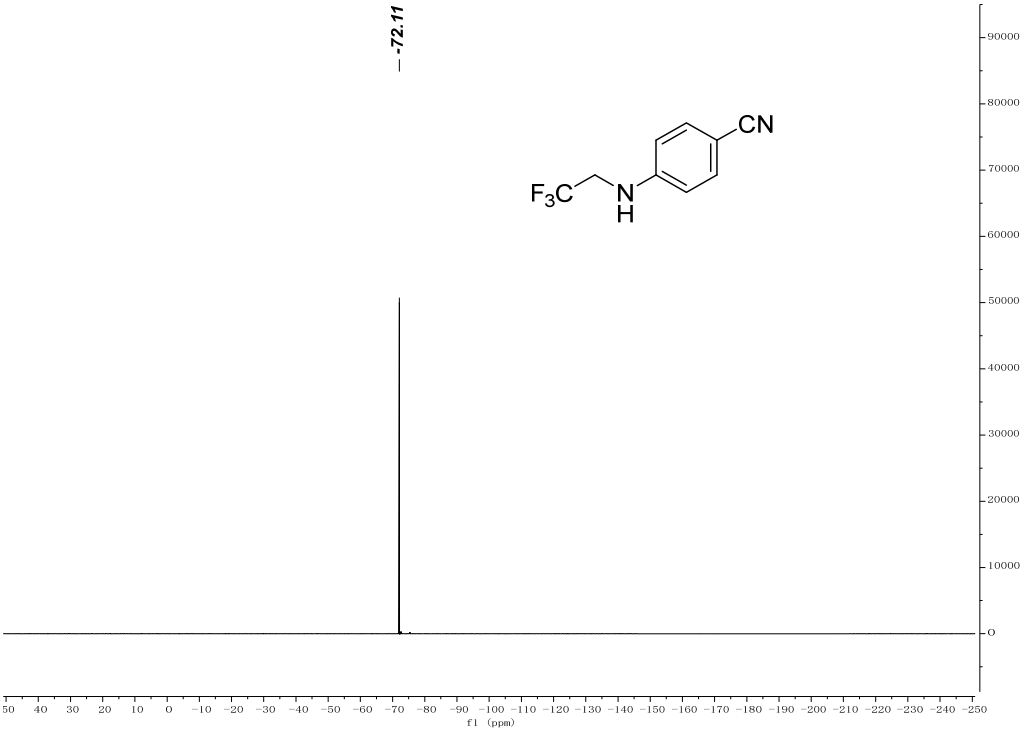
^{13}C NMR ($CDCl_3$, 100 MHz) of **3f**



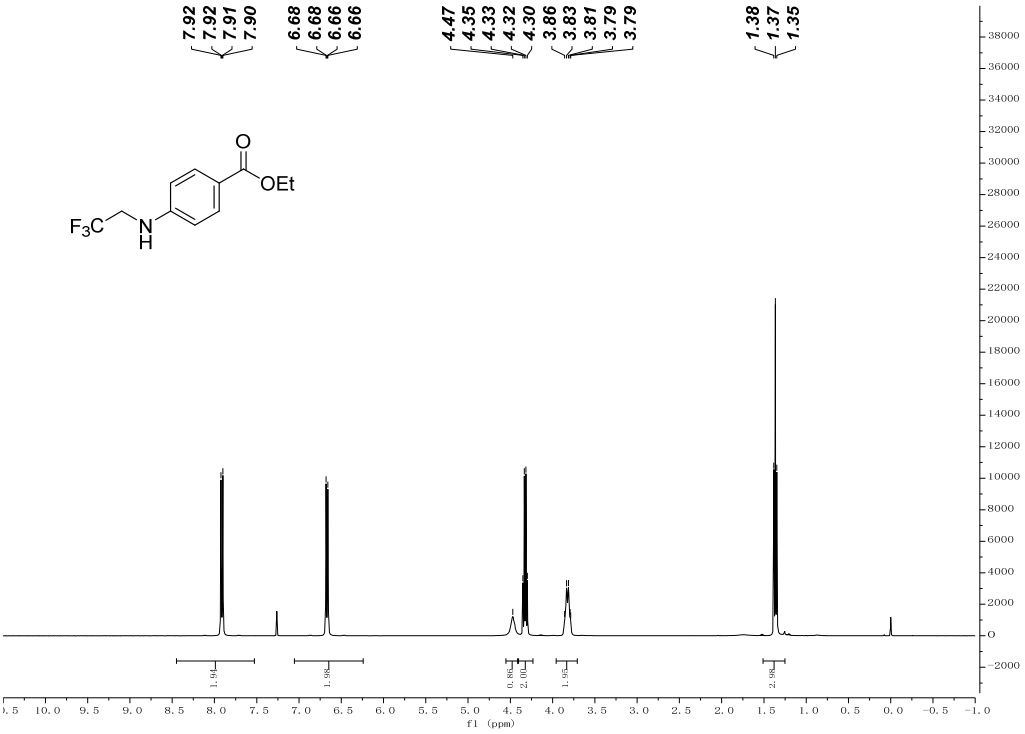
^{19}F NMR ($CDCl_3$, 376 MHz) of **3f**



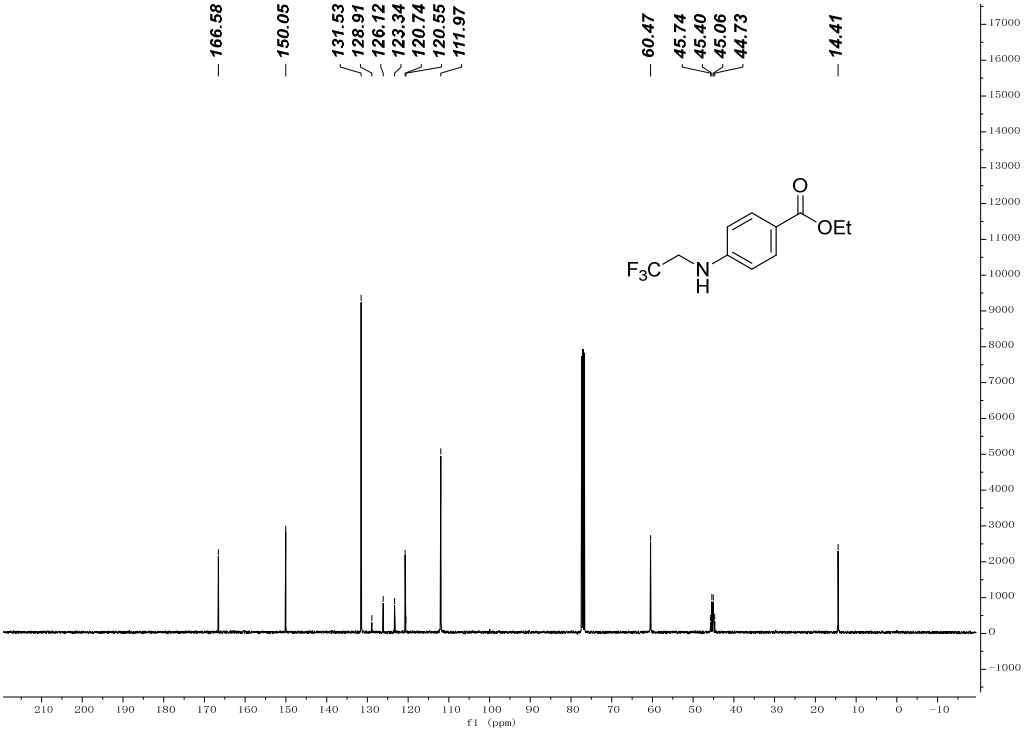
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **3f**



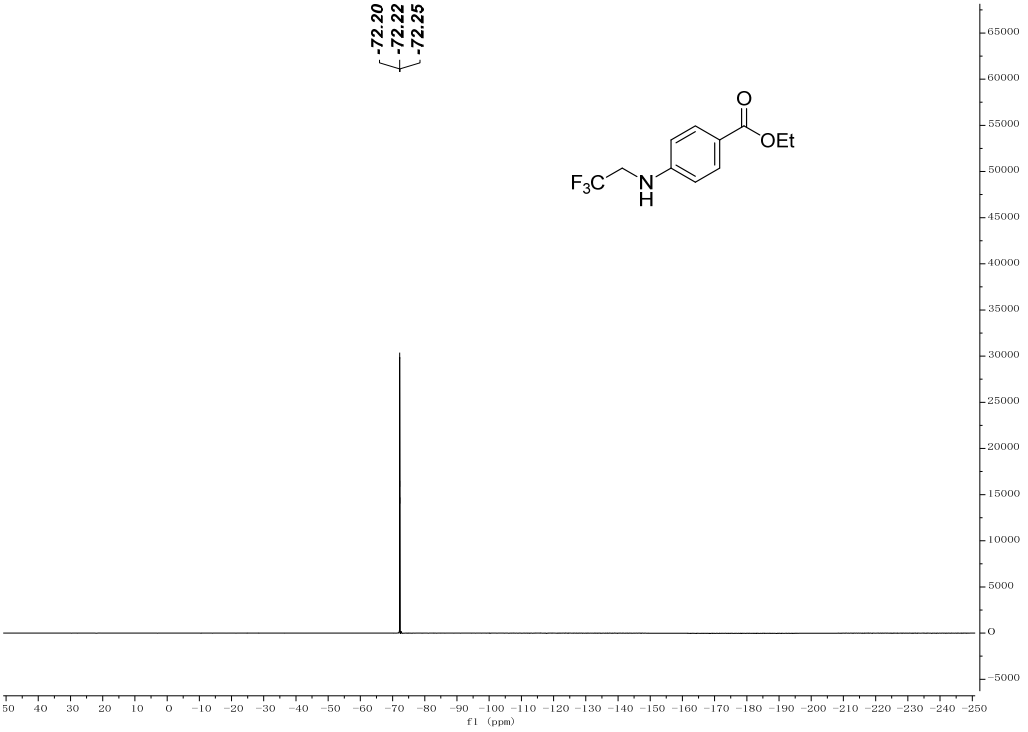
^{1}H NMR ($CDCl_3$, 400 MHz) of **3g**



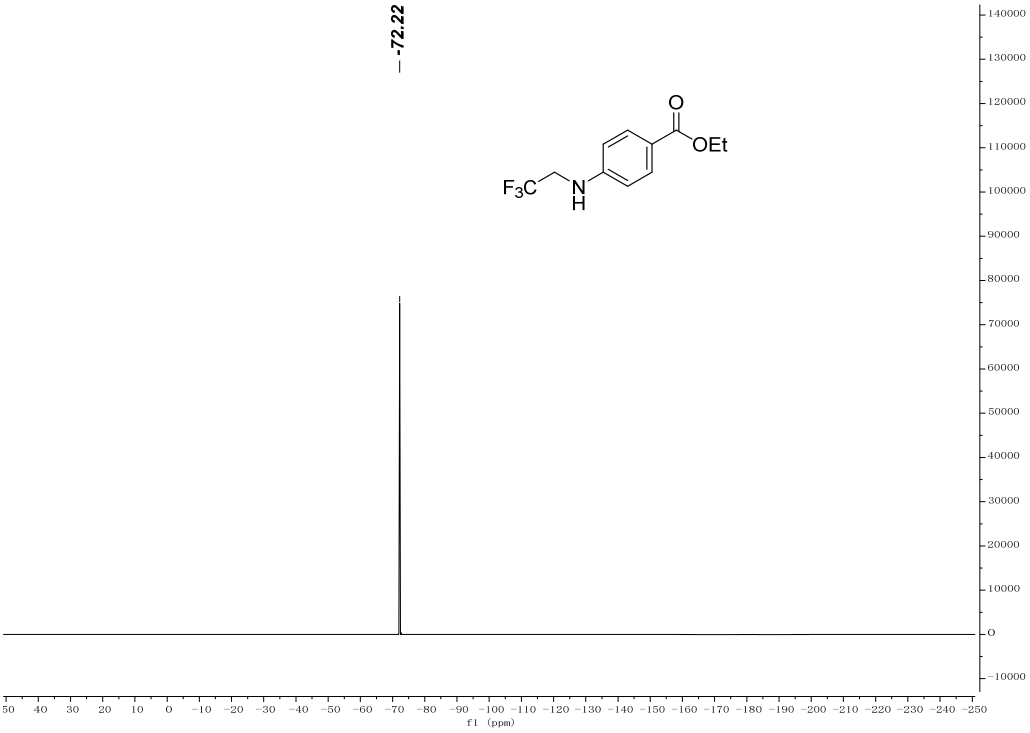
^{13}C NMR ($CDCl_3$, 100 MHz) of **3g**



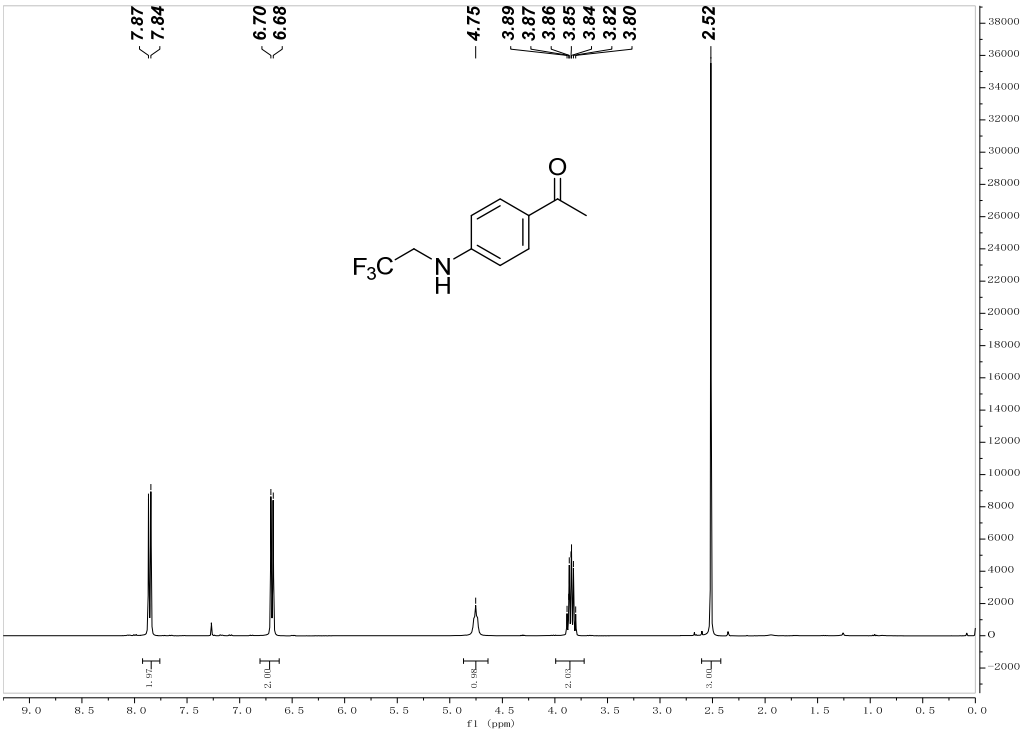
^{19}F NMR ($CDCl_3$, 376 MHz) of **3g**



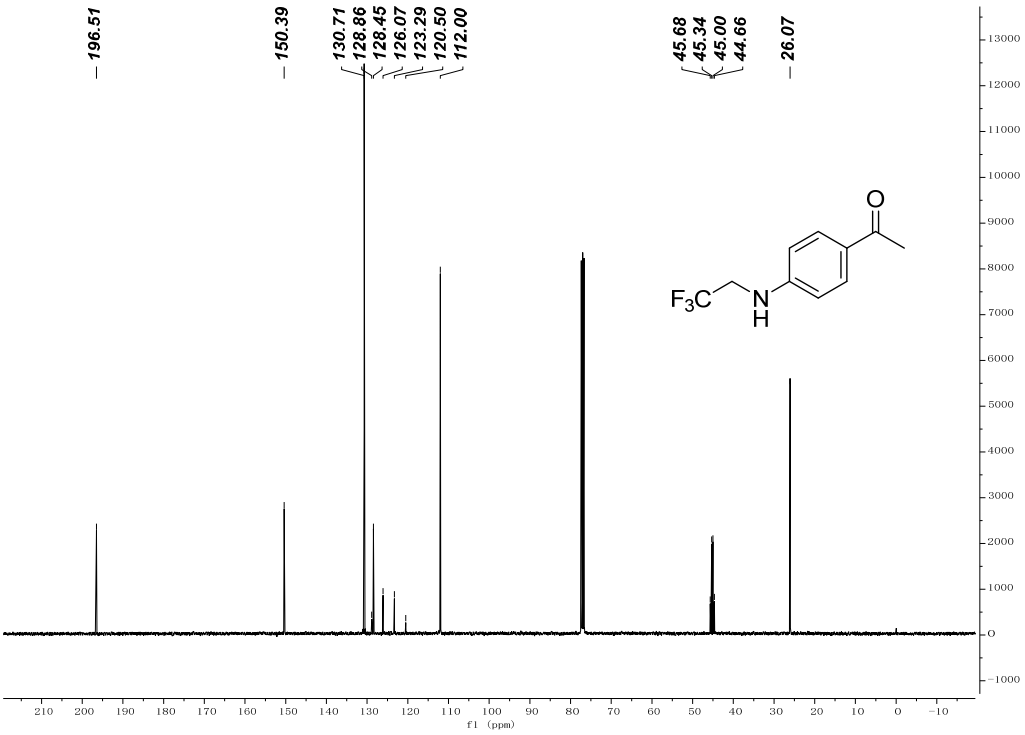
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **3g**



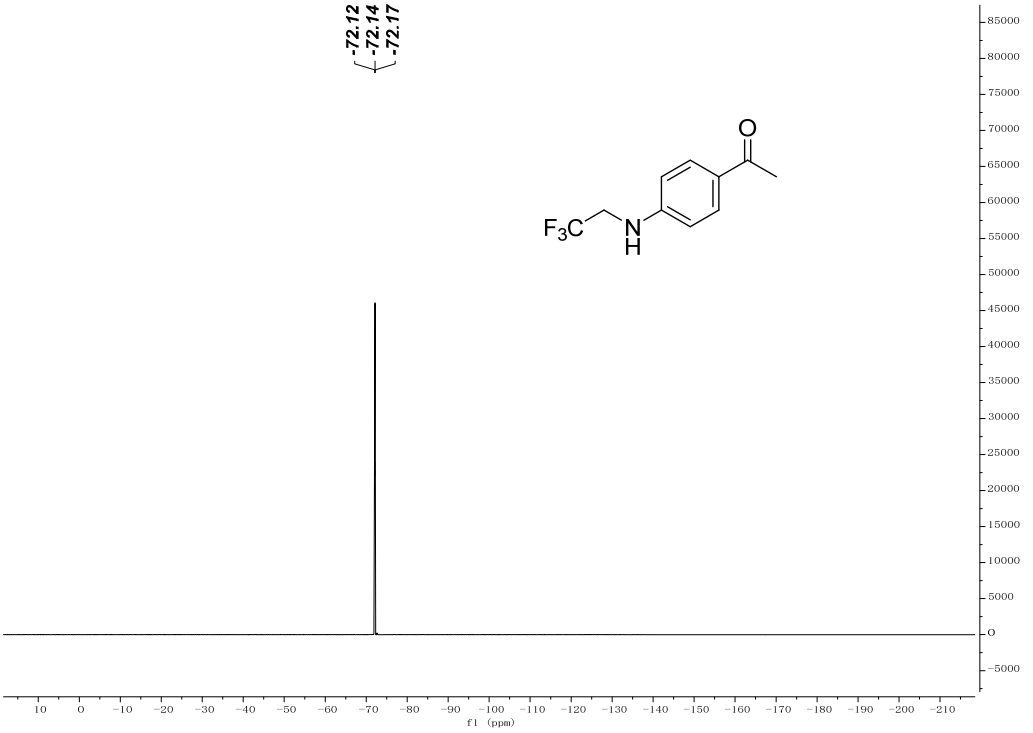
^{1}H NMR ($CDCl_3$, 400 MHz) of **3h**



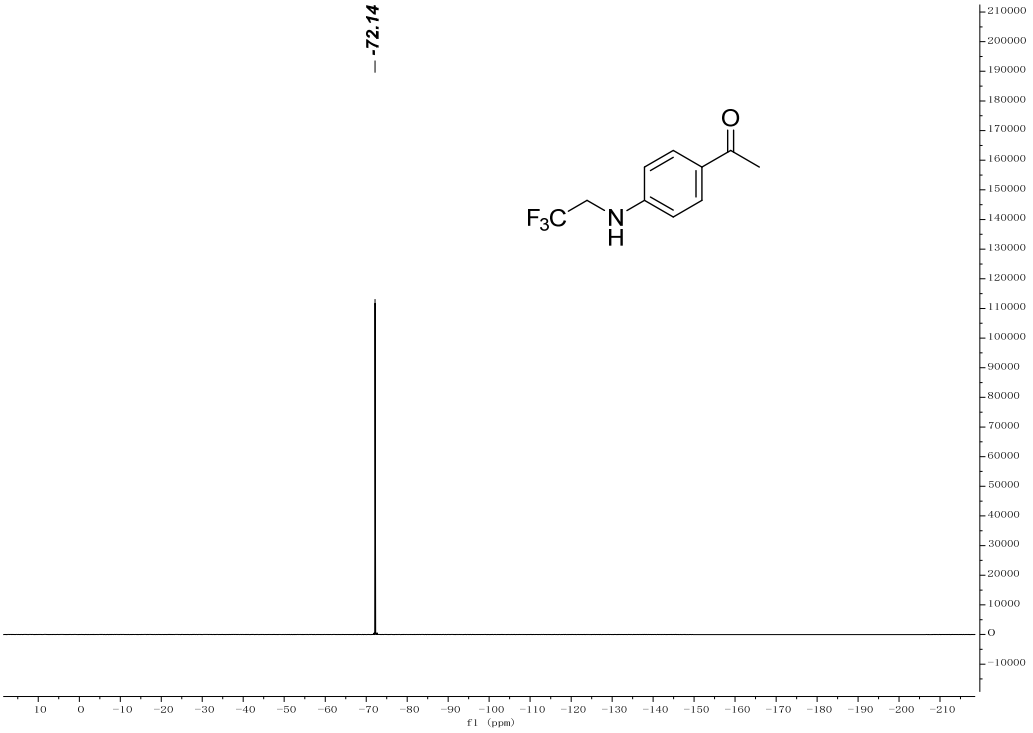
^{13}C NMR ($CDCl_3$, 100 MHz) of **3h**



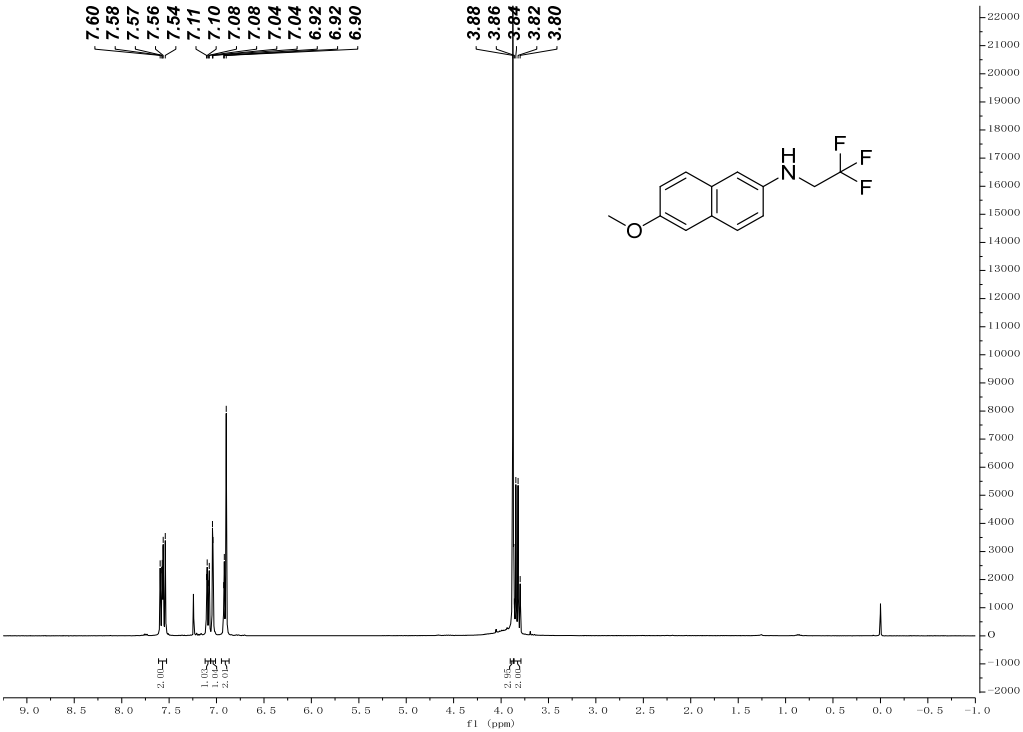
^{19}F NMR ($CDCl_3$, 376 MHz) of **3h**



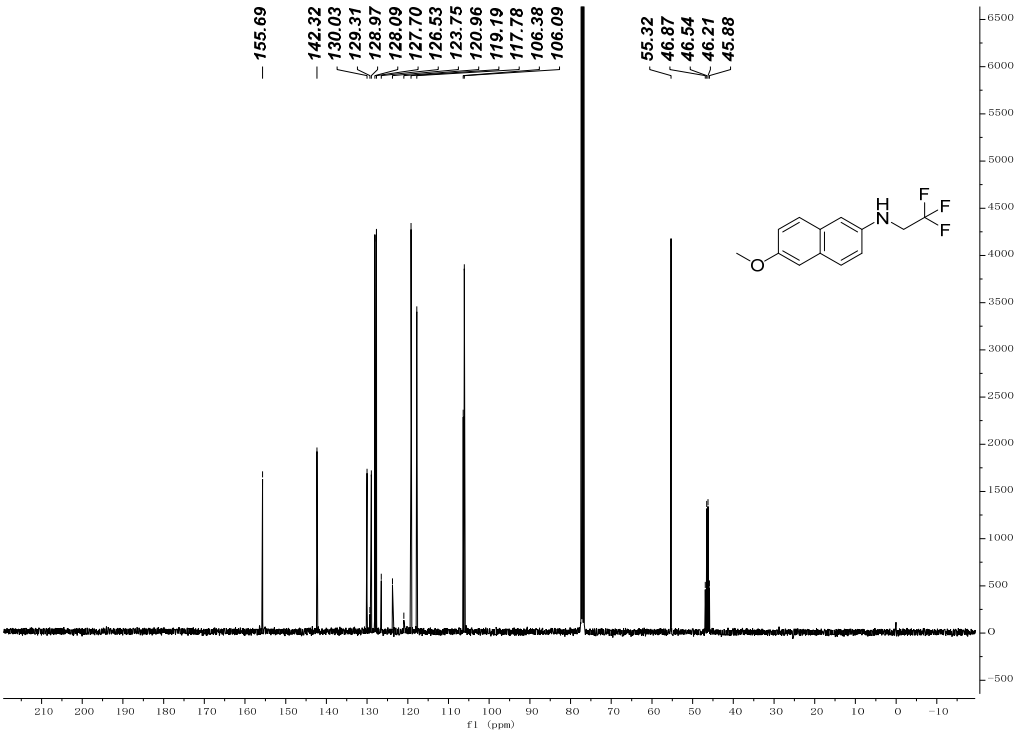
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **3h**



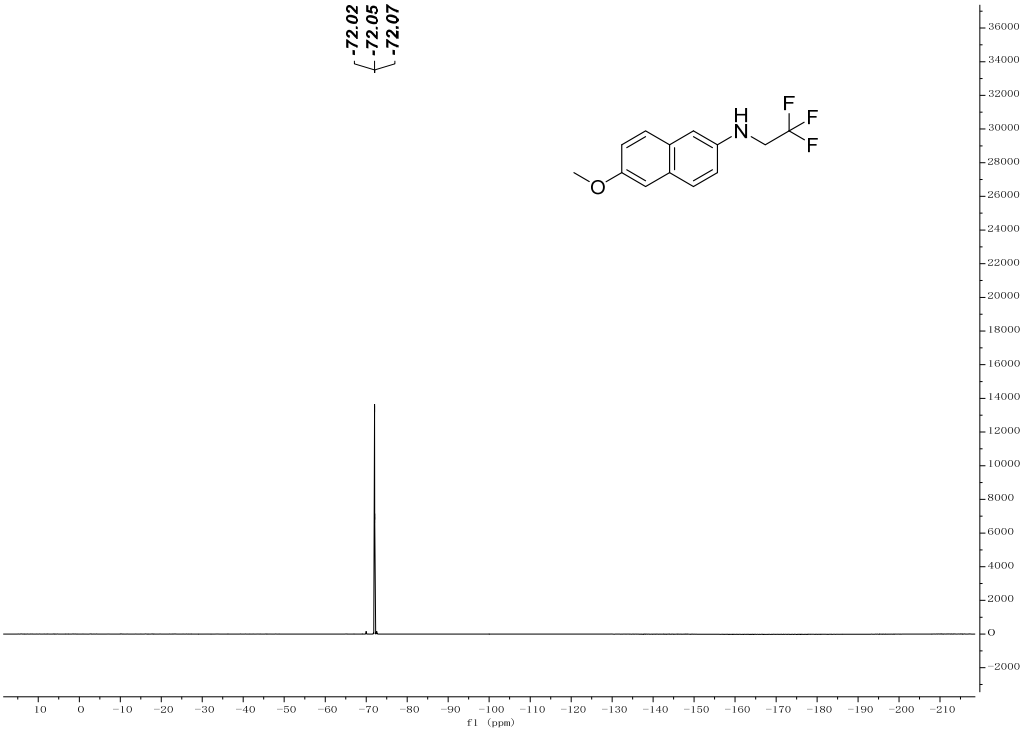
^{1}H NMR ($CDCl_3$, 400 MHz) of **3i**



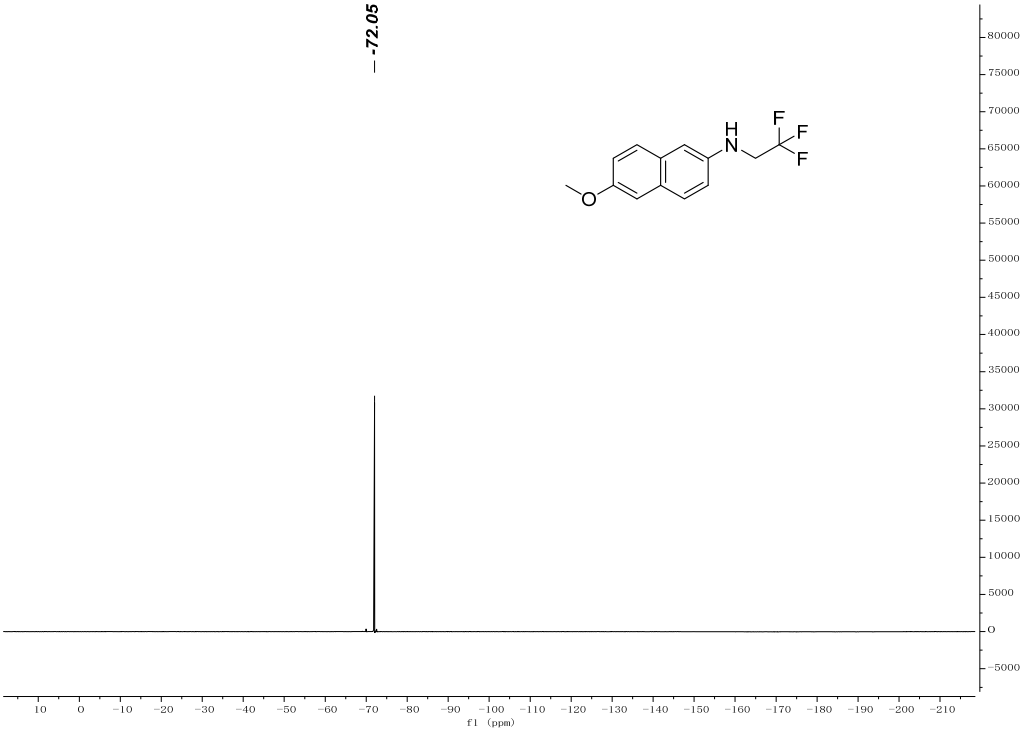
^{13}C NMR ($CDCl_3$, 100 MHz) of **3i**



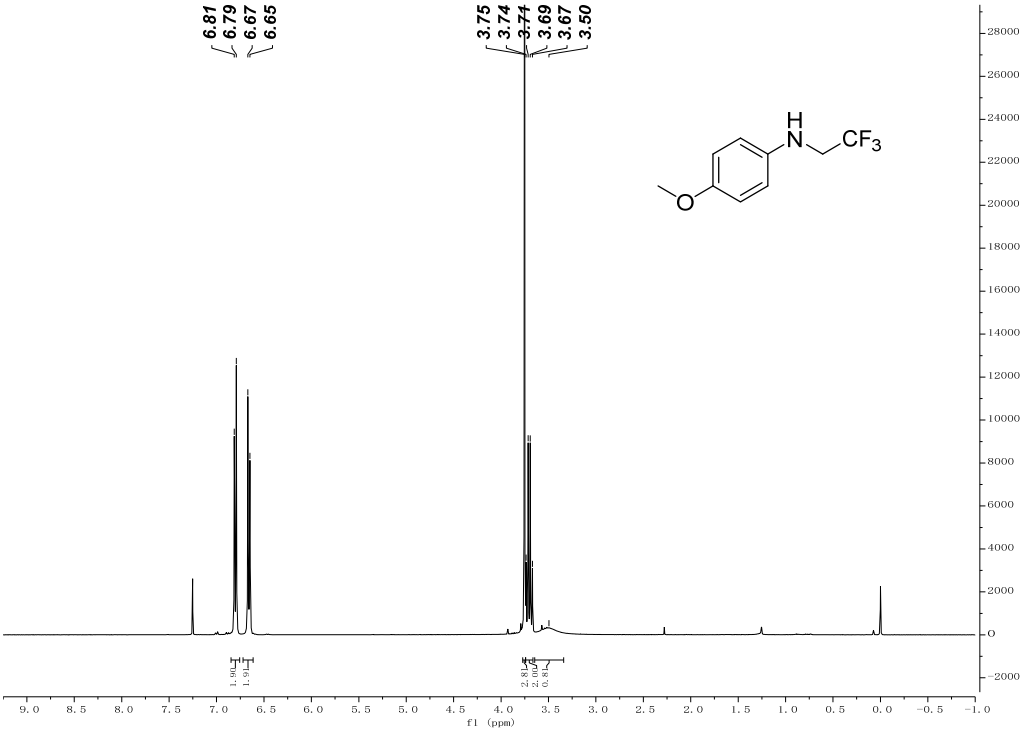
^{19}F NMR ($CDCl_3$, 376 MHz) of **3i**



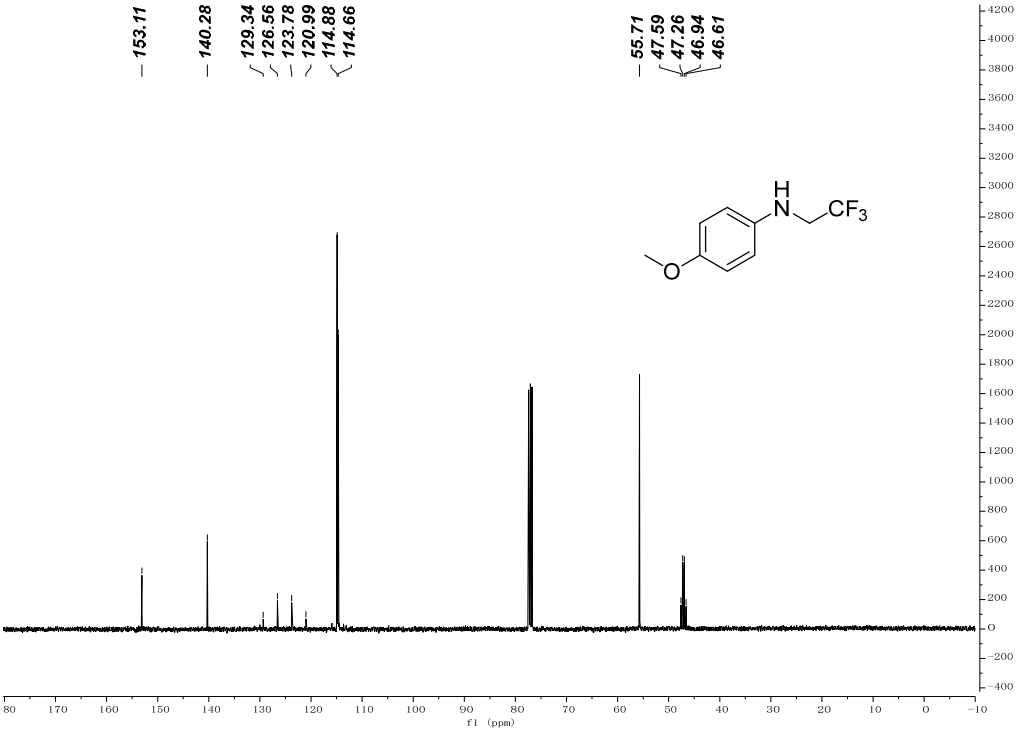
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **3i**



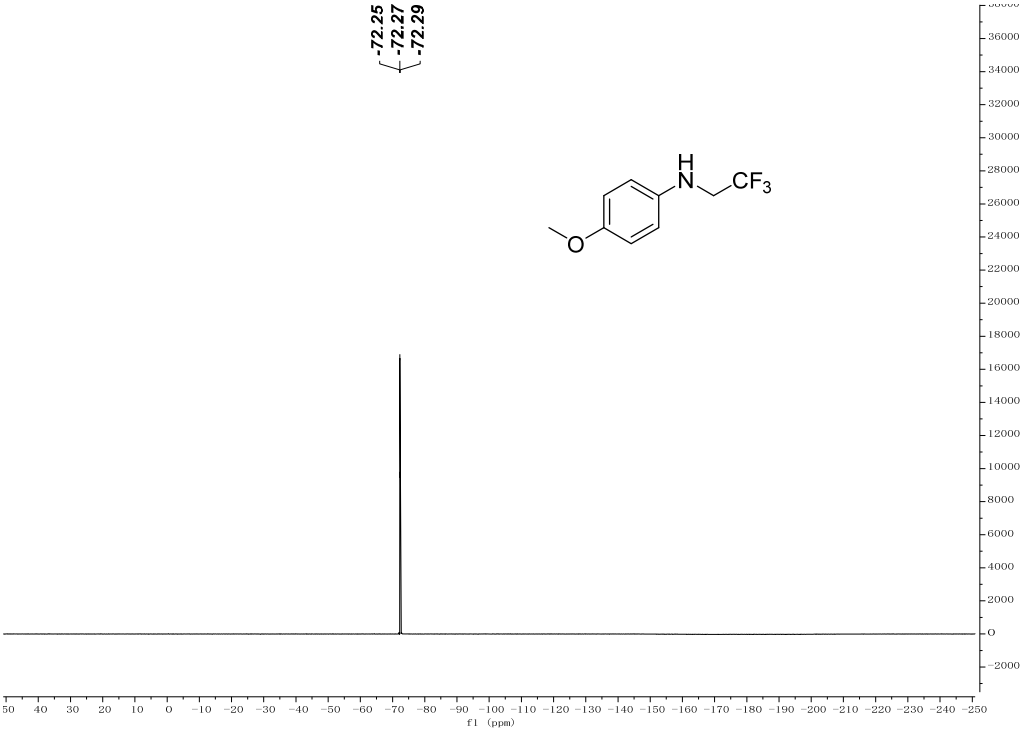
^{1}H NMR ($CDCl_3$, 400 MHz) of **3j**



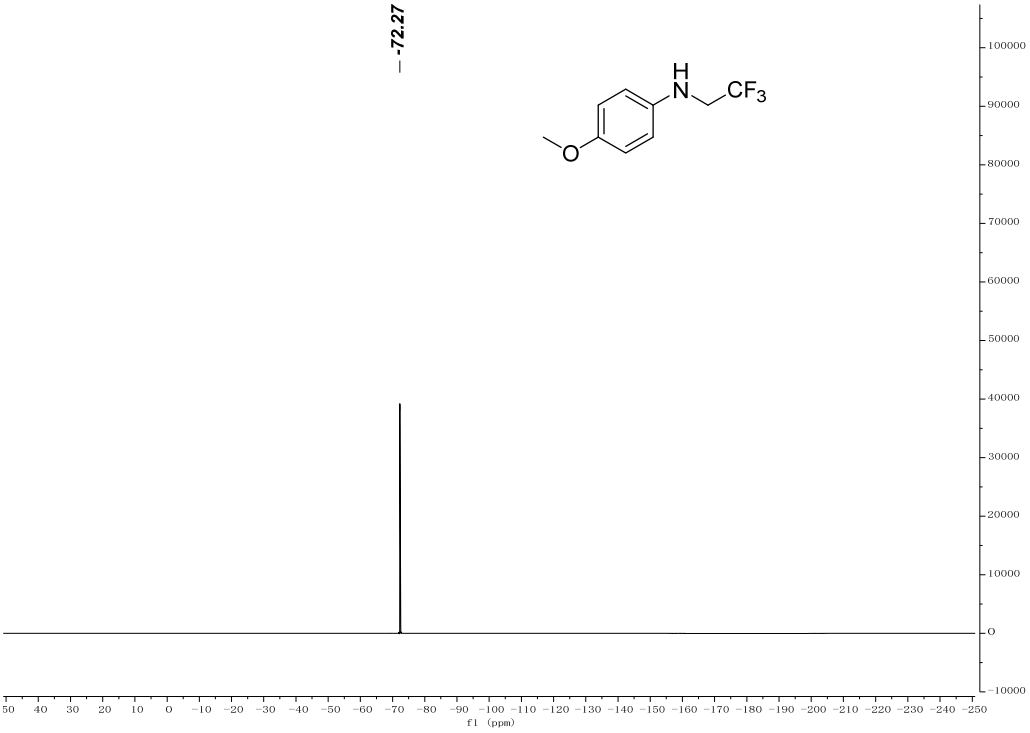
^{13}C NMR ($CDCl_3$, 100 MHz) of **3j**



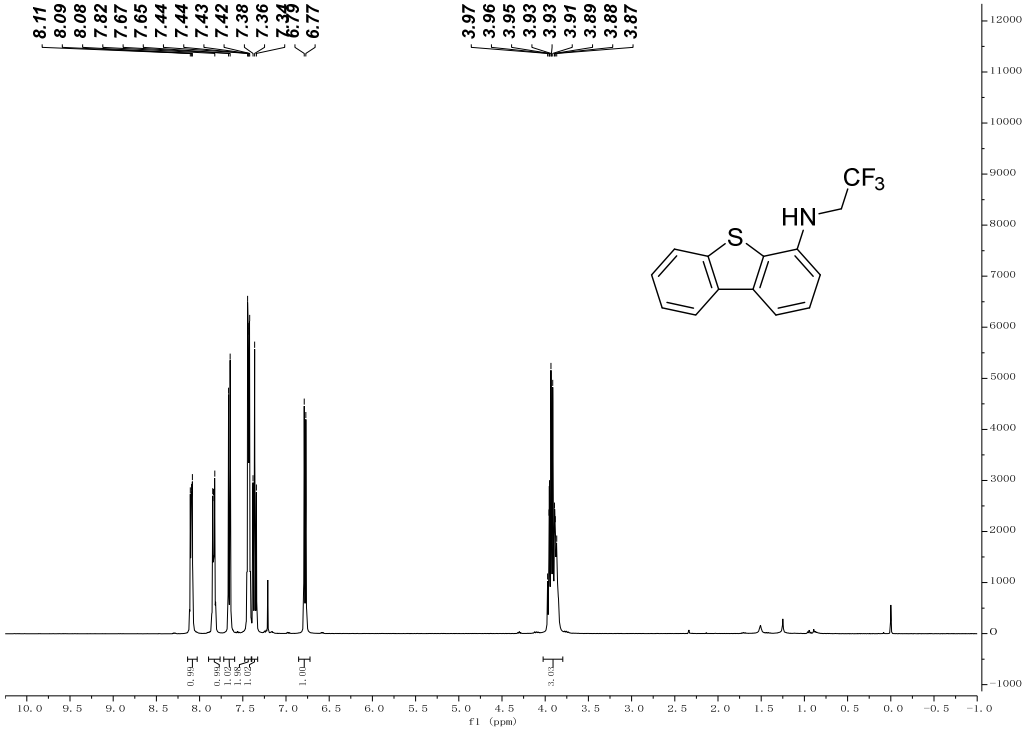
^{19}F NMR ($CDCl_3$, 376 MHz) of **3j**



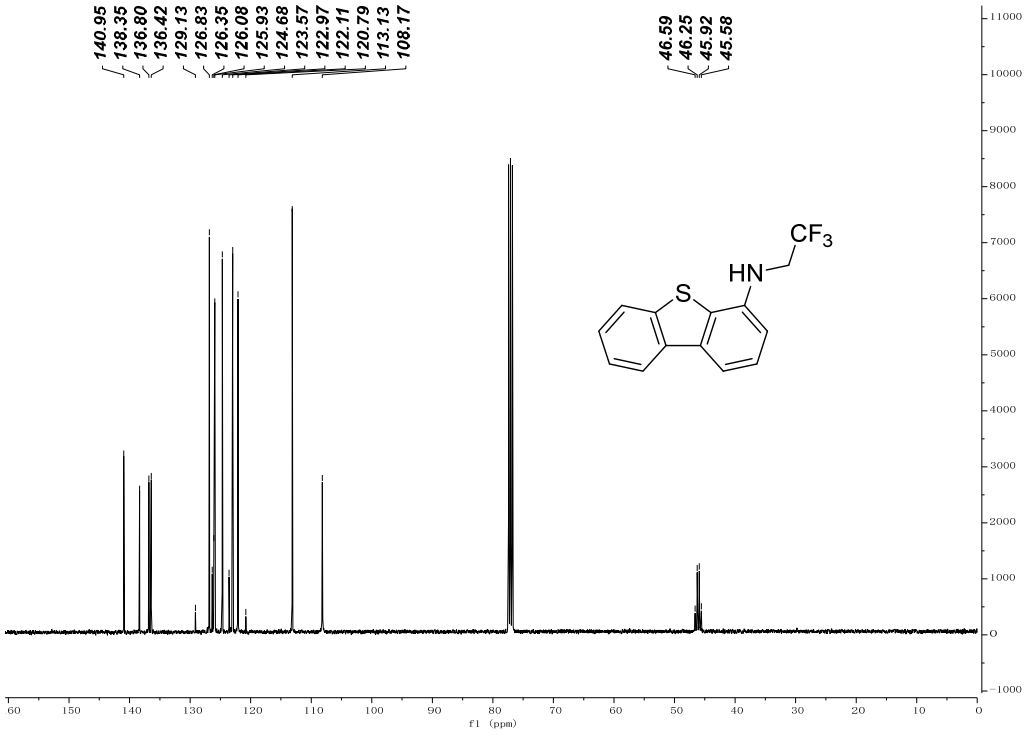
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **3j**



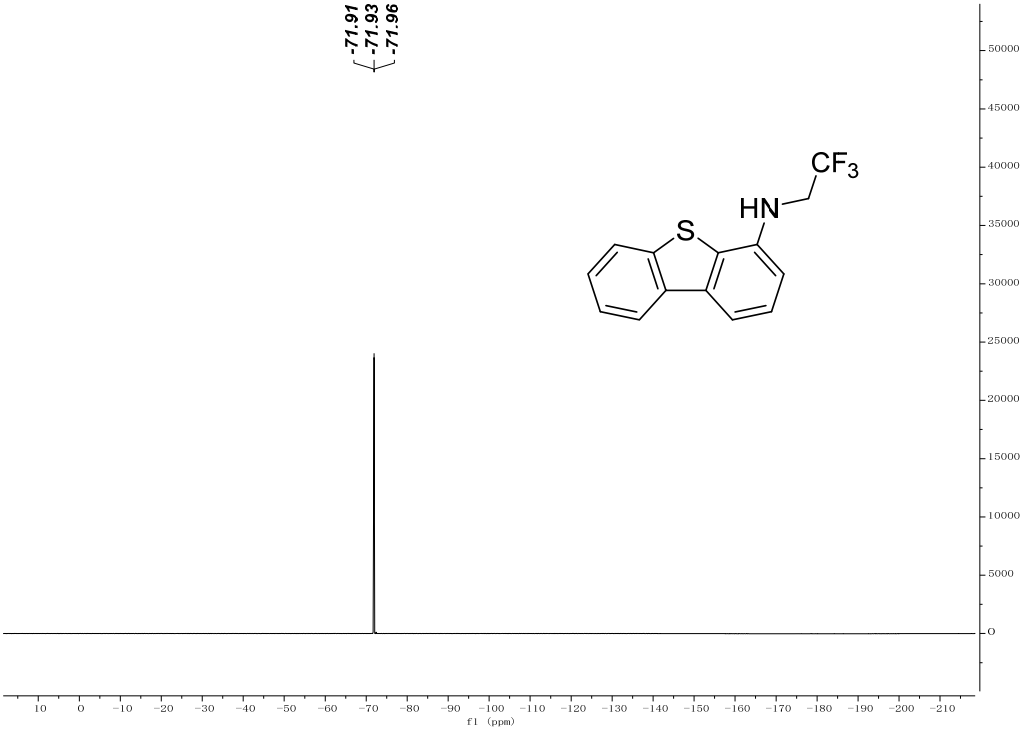
^{1}H NMR ($CDCl_3$, 400 MHz) of **3l**



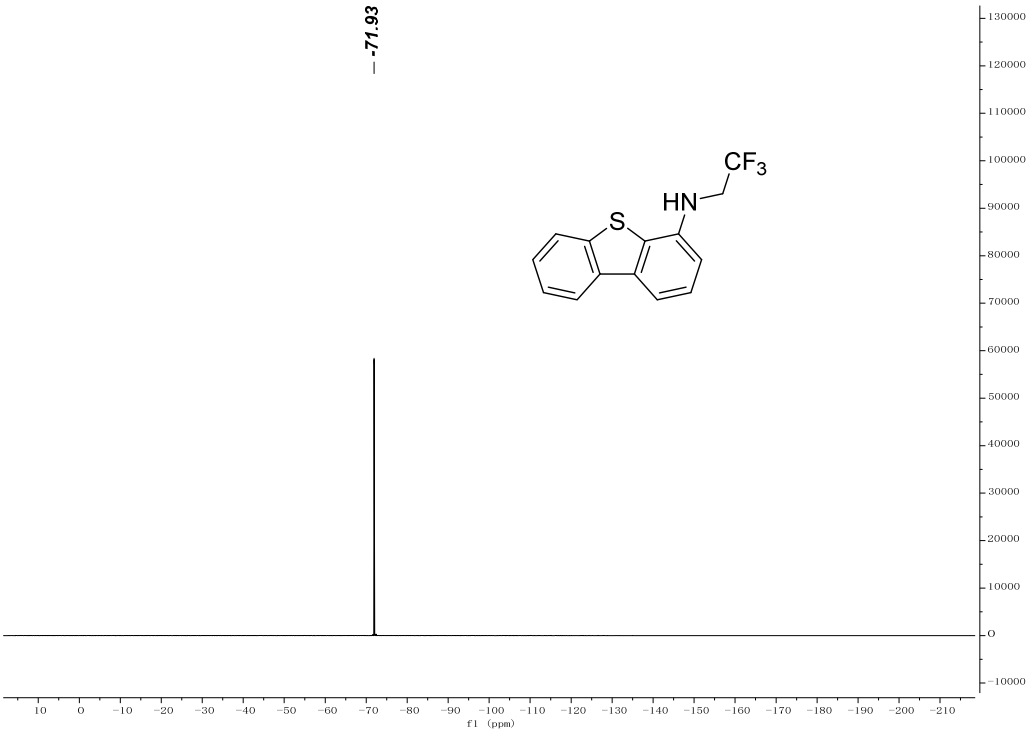
^{13}C NMR ($CDCl_3$, 100 MHz) of **3l**



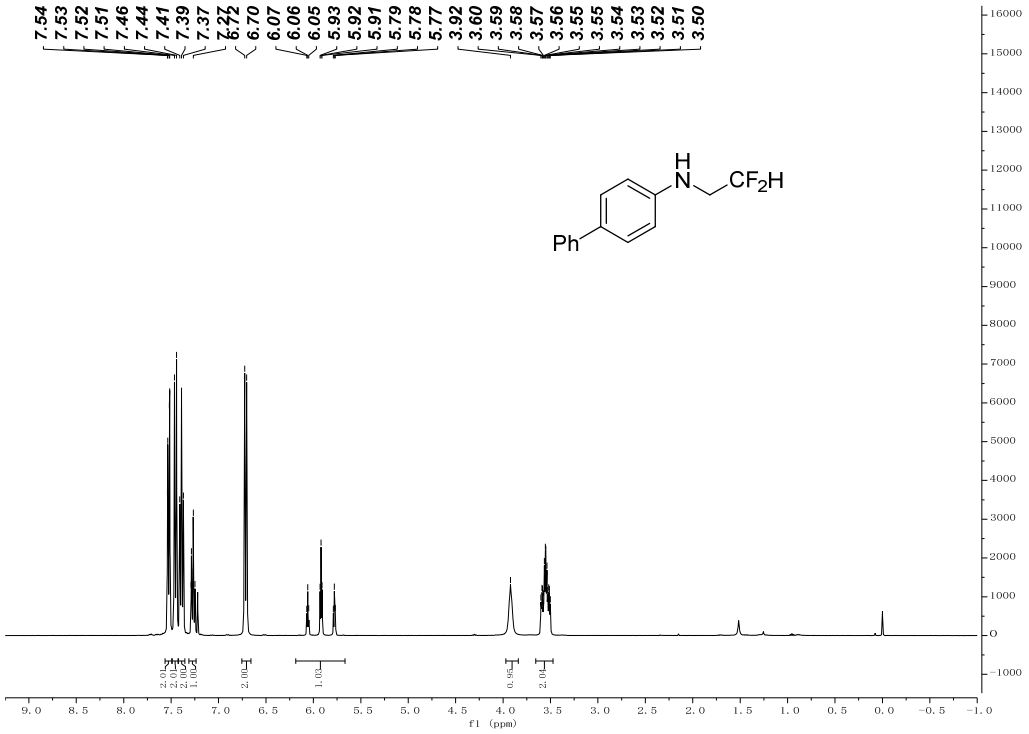
^{19}F NMR ($CDCl_3$, 376 MHz) of **3l**



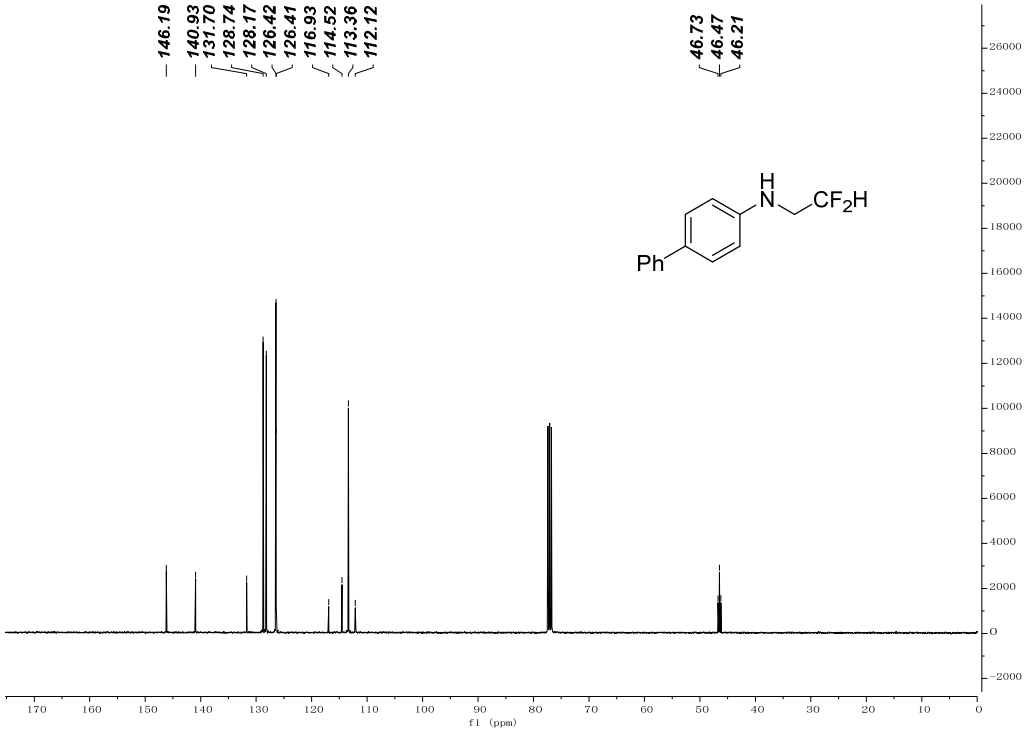
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **3l**



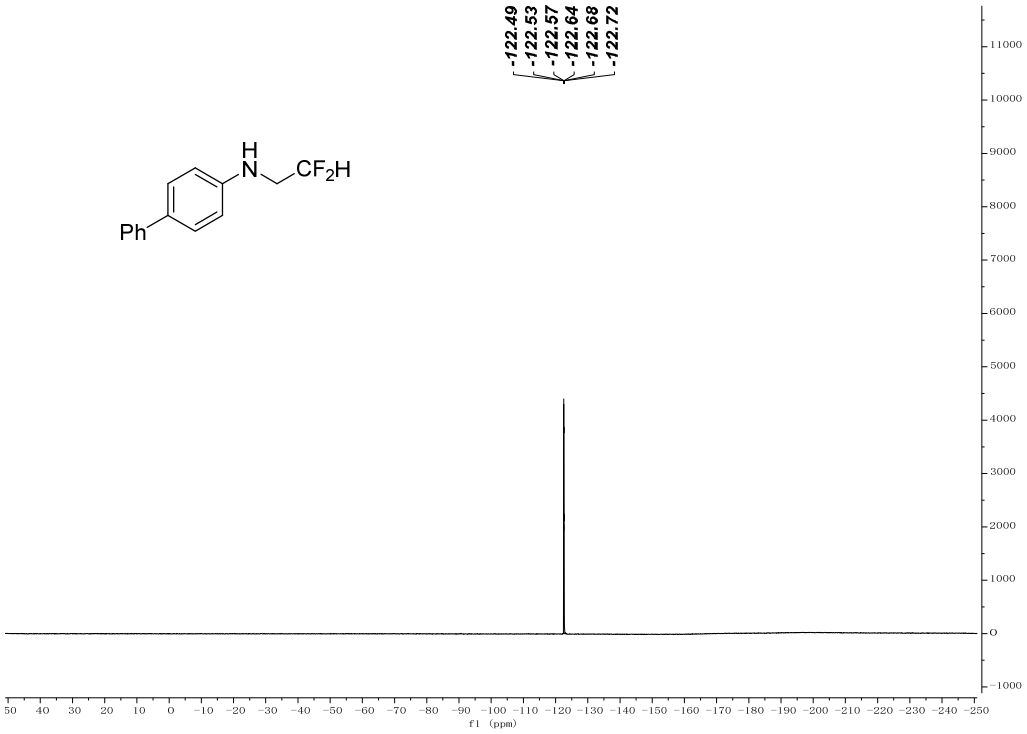
^{1}H NMR ($CDCl_3$, 400 MHz) of **8a**



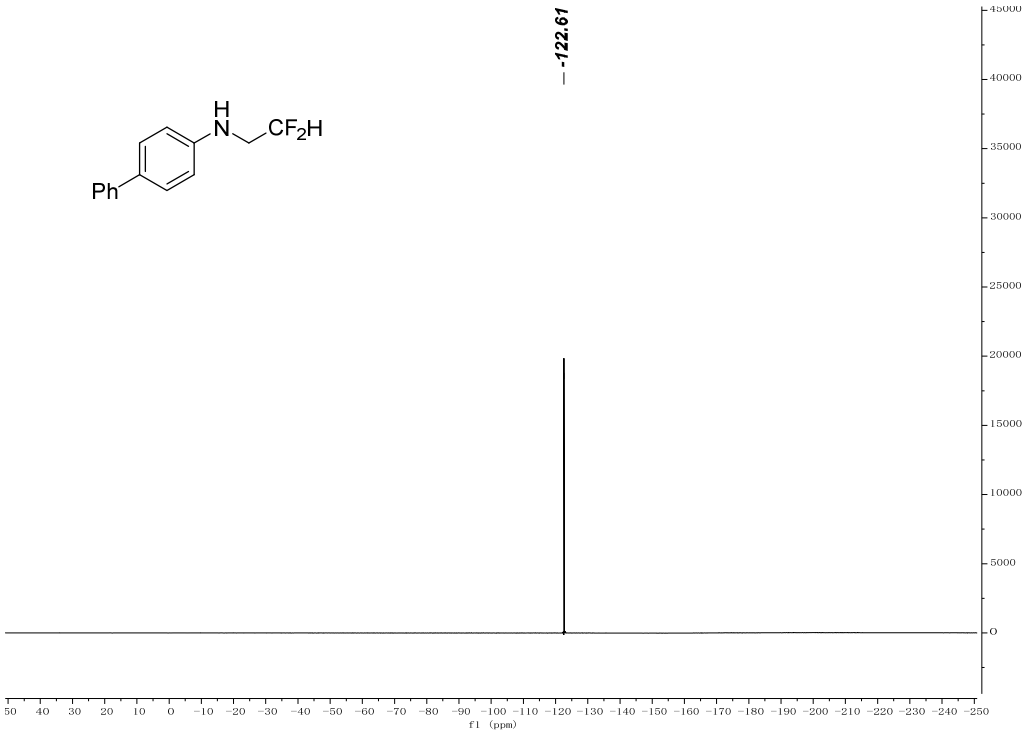
^{13}C NMR ($CDCl_3$, 100 MHz) of **8a**



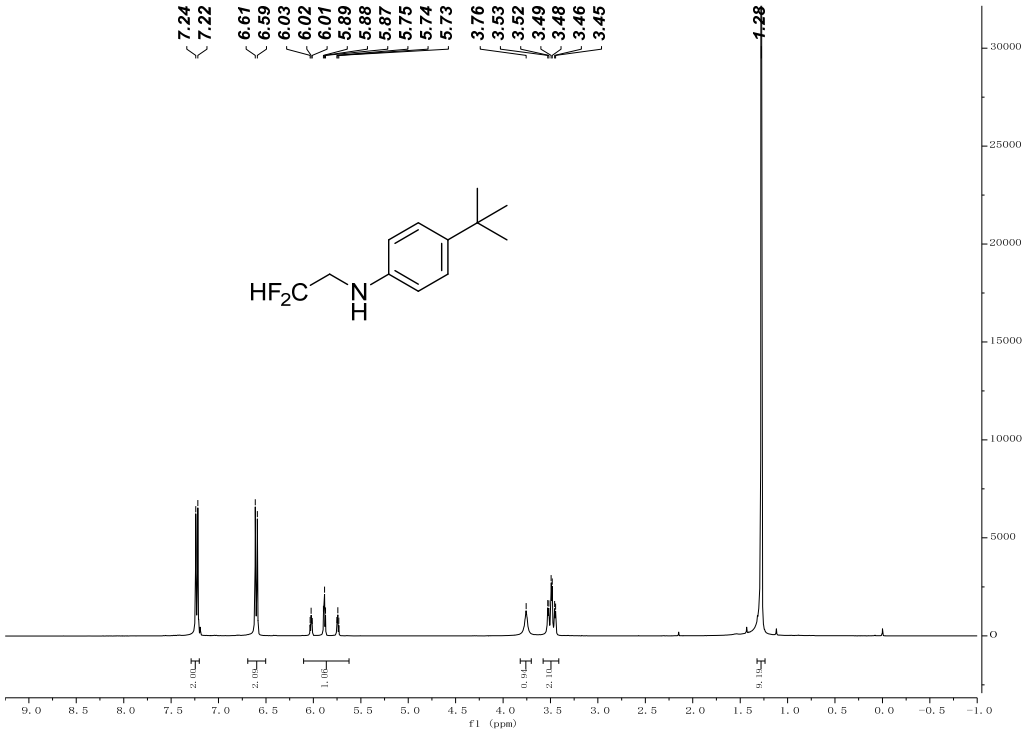
^{19}F NMR ($CDCl_3$, 376 MHz) of **8a**



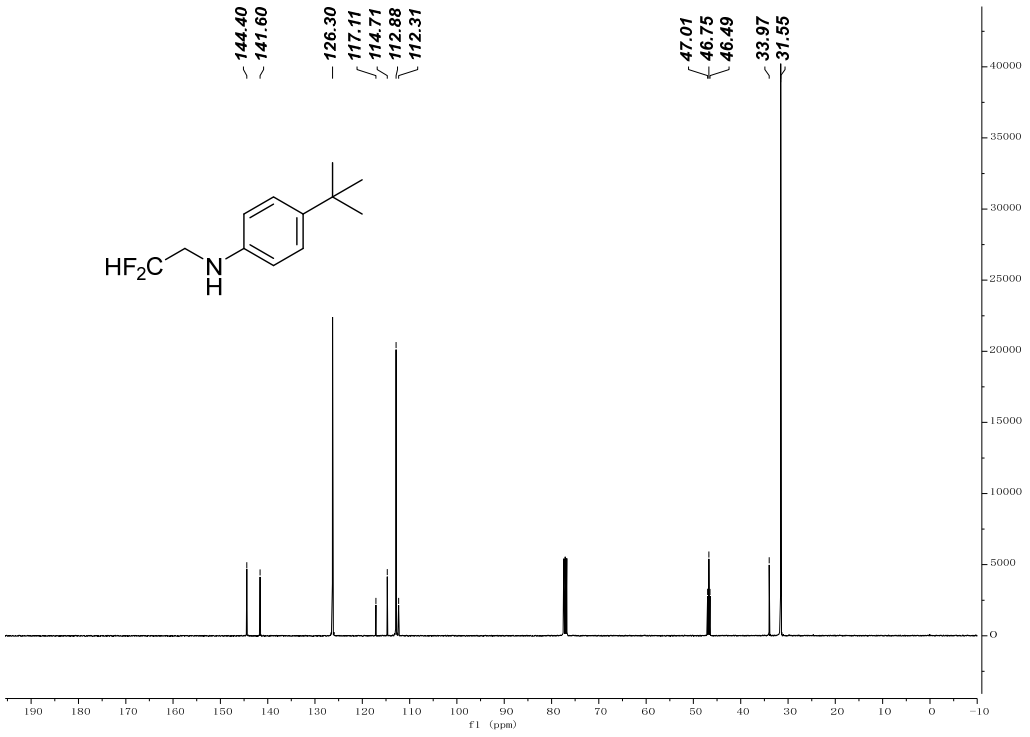
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **8a**



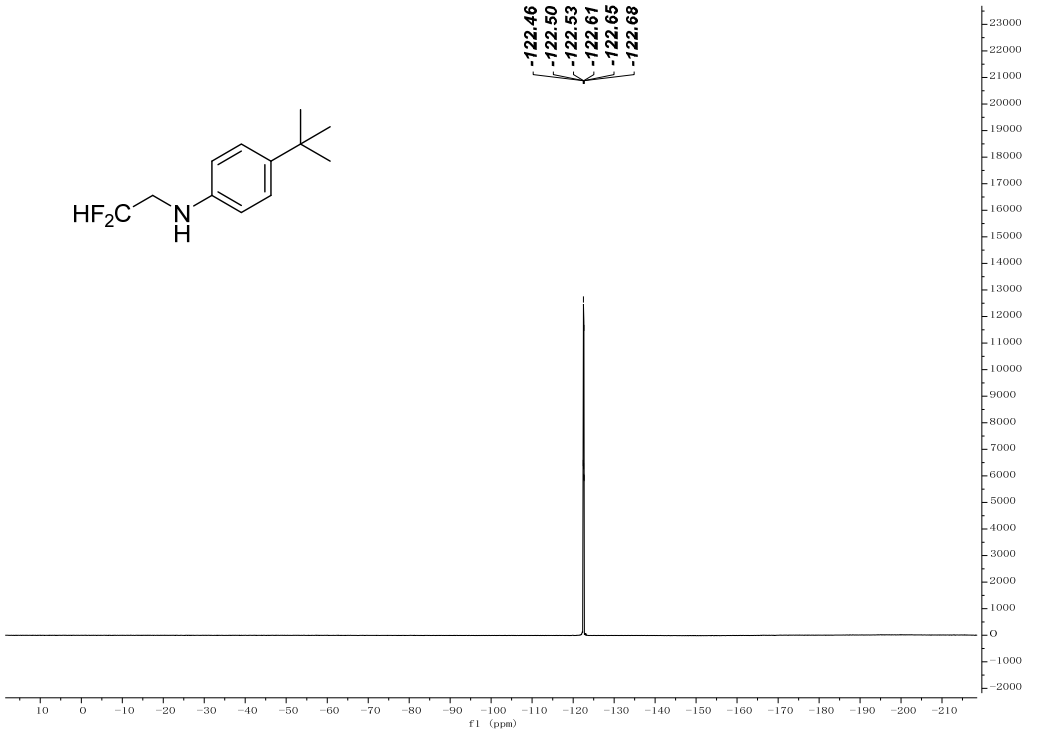
^{1}H NMR ($CDCl_3$, 400 MHz) of **8b**



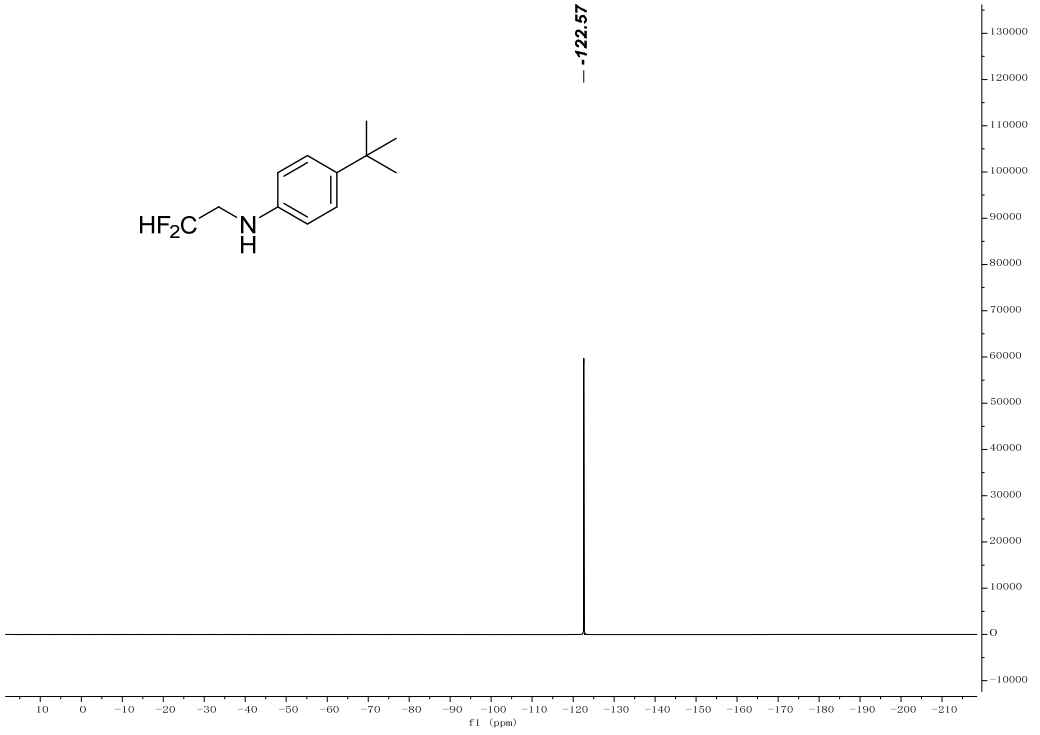
^{13}C NMR ($CDCl_3$, 100 MHz) of **8b**



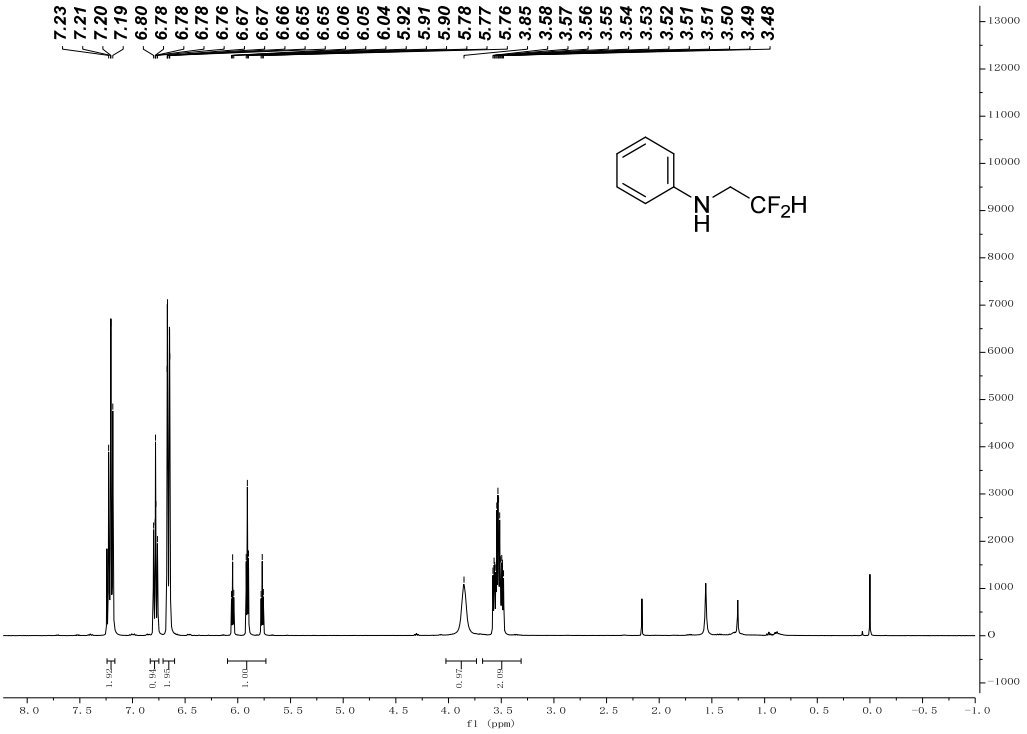
^{19}F NMR ($CDCl_3$, 376 MHz) of **8b**



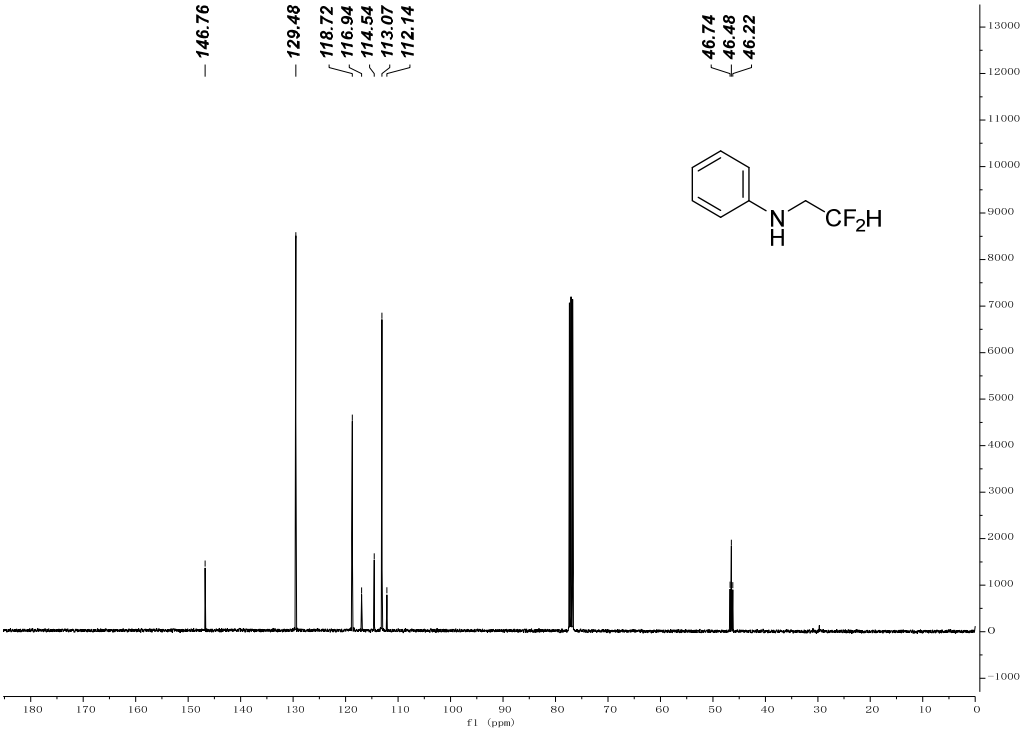
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **8b**



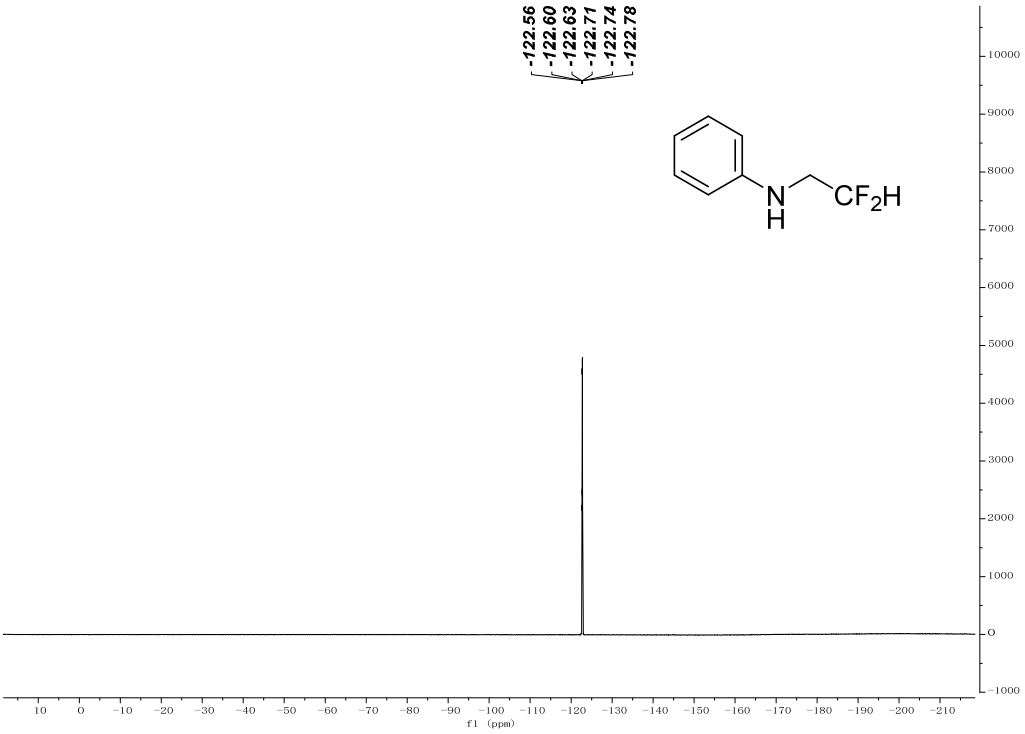
^{1}H NMR ($CDCl_3$, 400 MHz) of **8c**



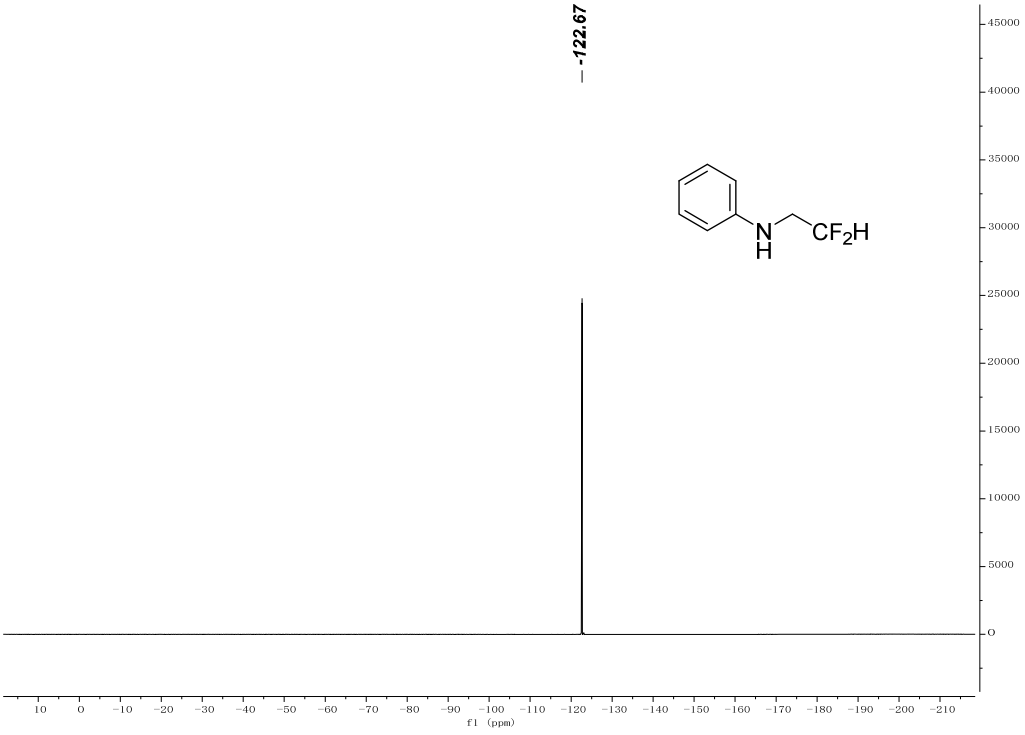
^{13}C NMR ($CDCl_3$, 100 MHz) of **8c**



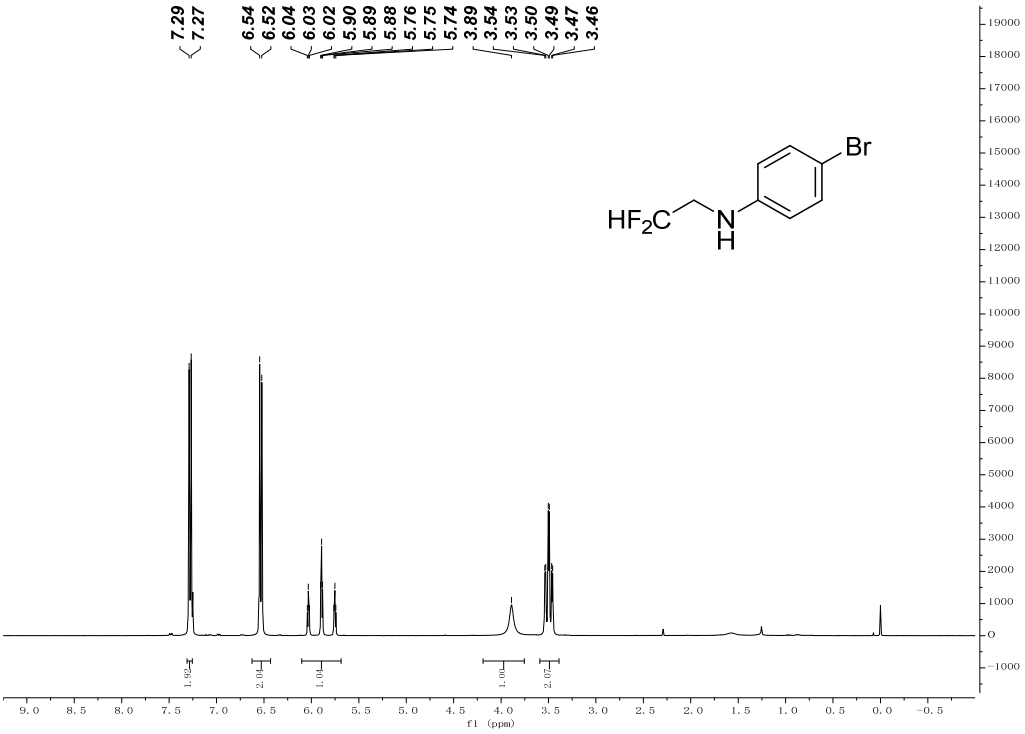
^{19}F NMR ($CDCl_3$, 376 MHz) of **8c**



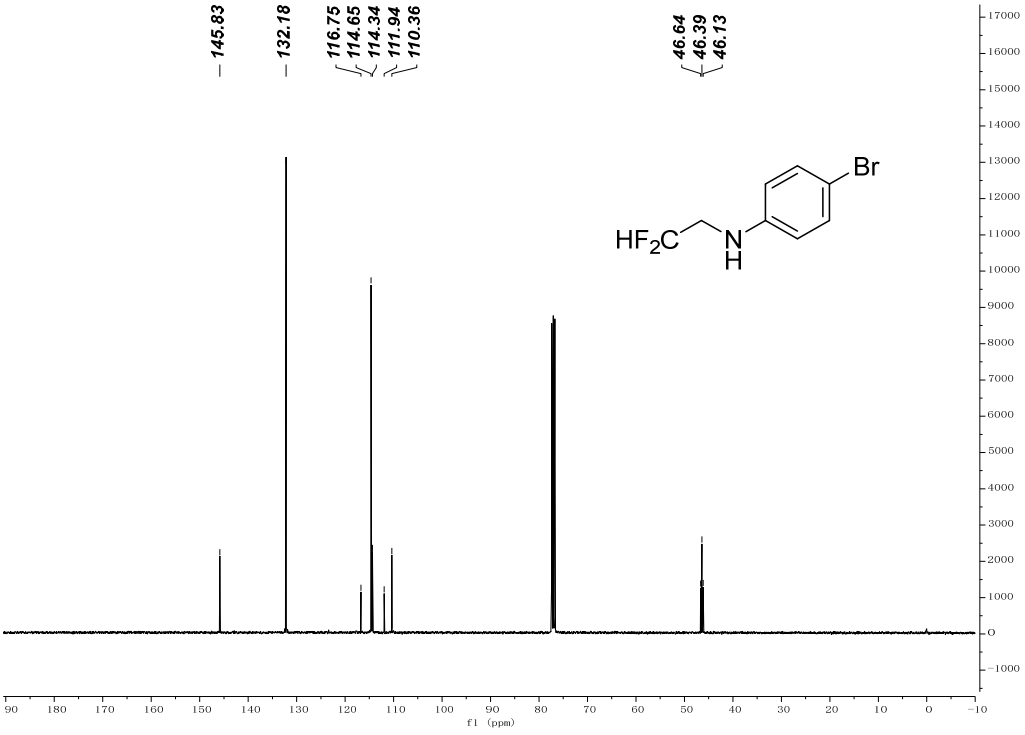
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **8c**



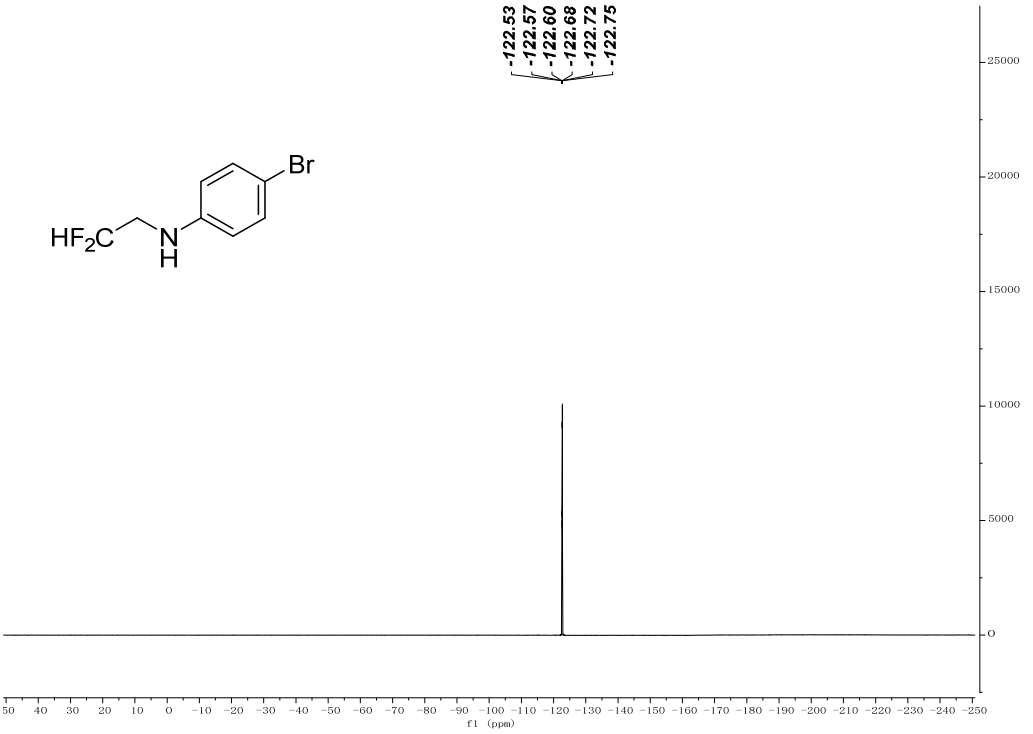
^{1}H NMR ($CDCl_3$, 400 MHz) of **8d**



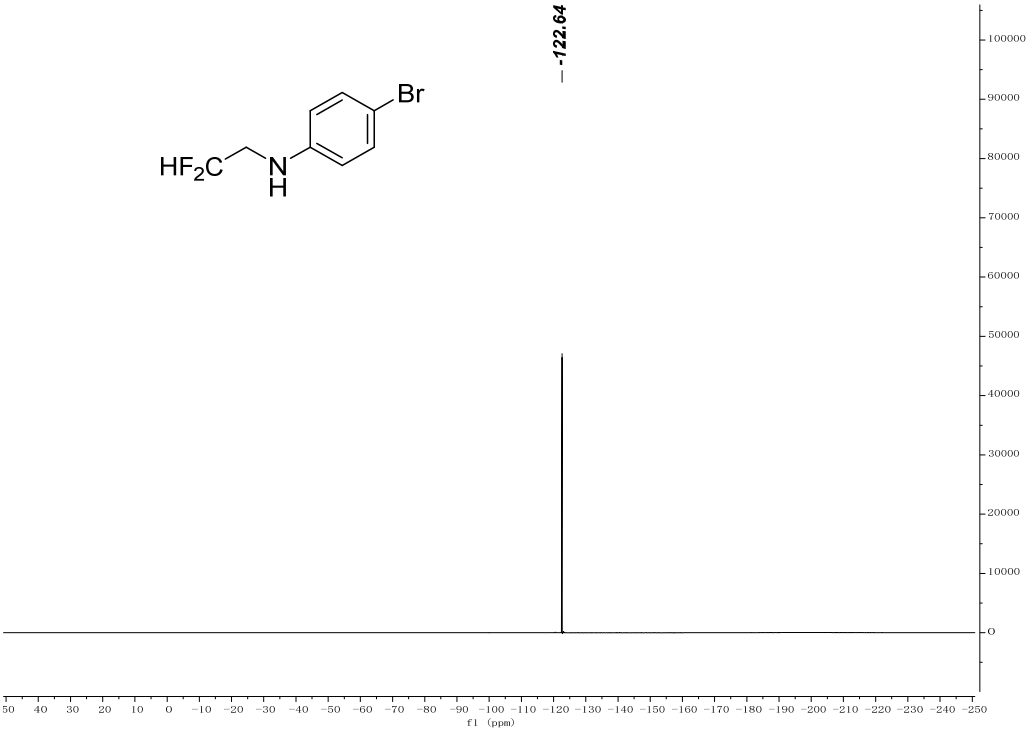
^{13}C NMR ($CDCl_3$, 100 MHz) of **8d**



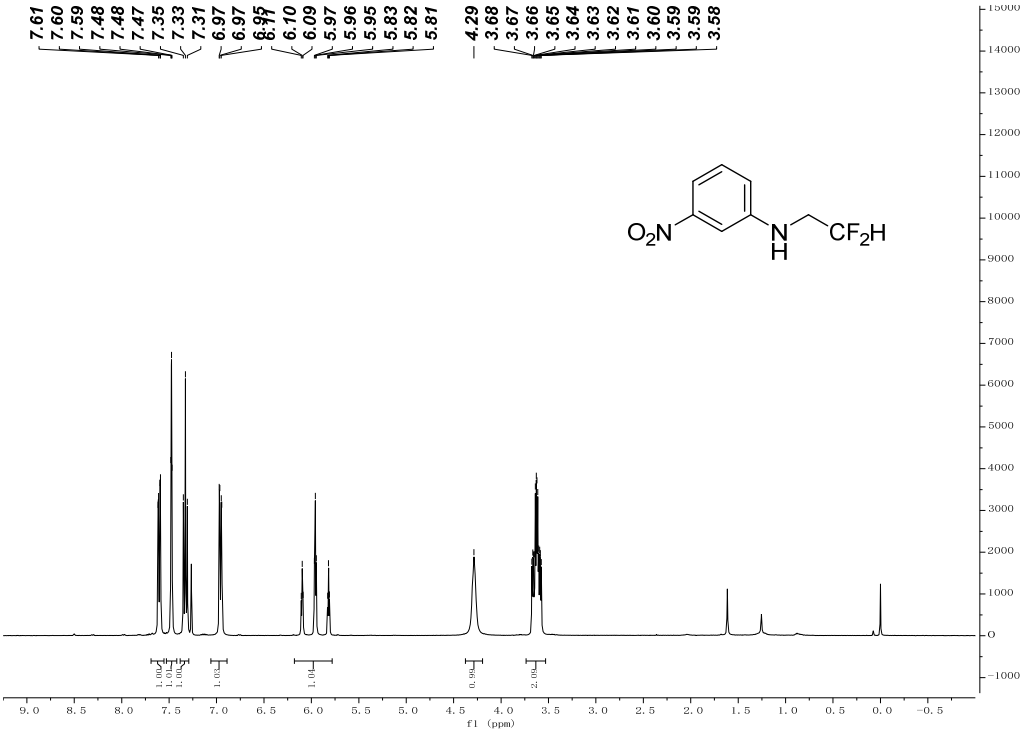
^{19}F NMR ($CDCl_3$, 376 MHz) of **8d**



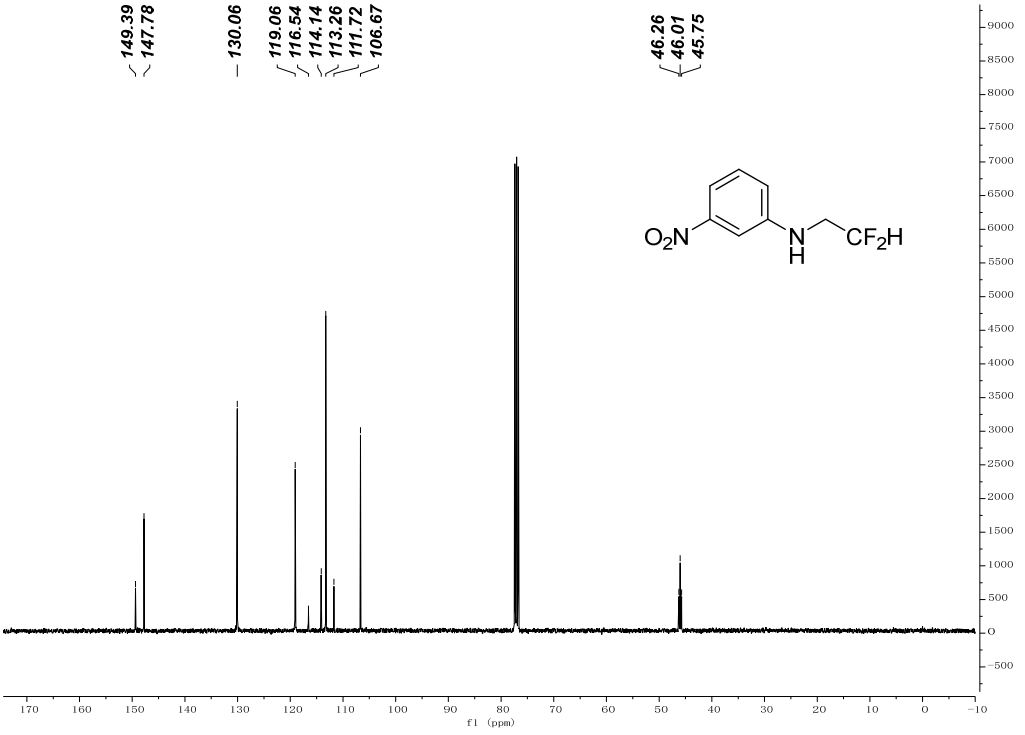
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **8d**



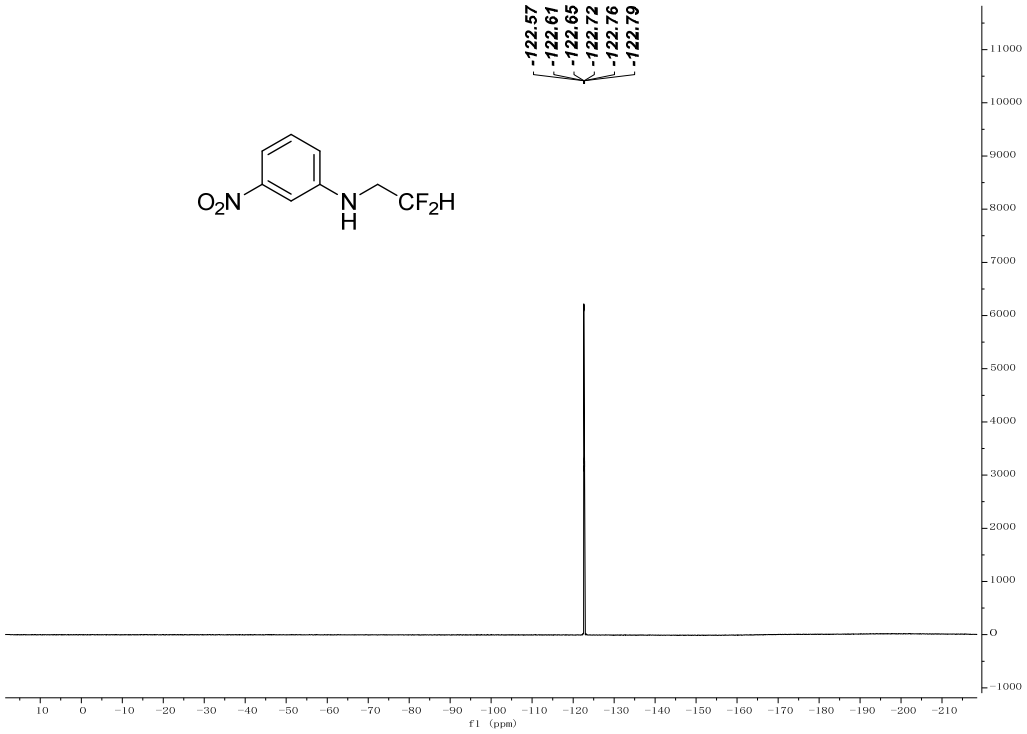
^{1}H NMR ($CDCl_3$, 400 MHz) of **8e**



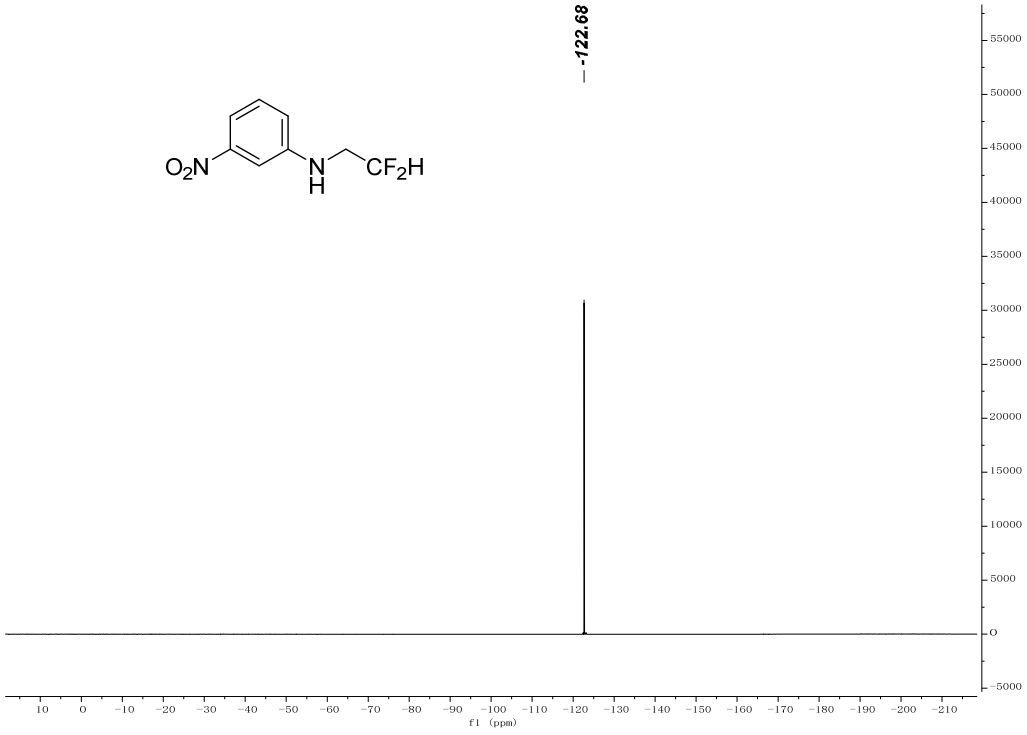
^{13}C NMR ($CDCl_3$, 100 MHz) of **8e**



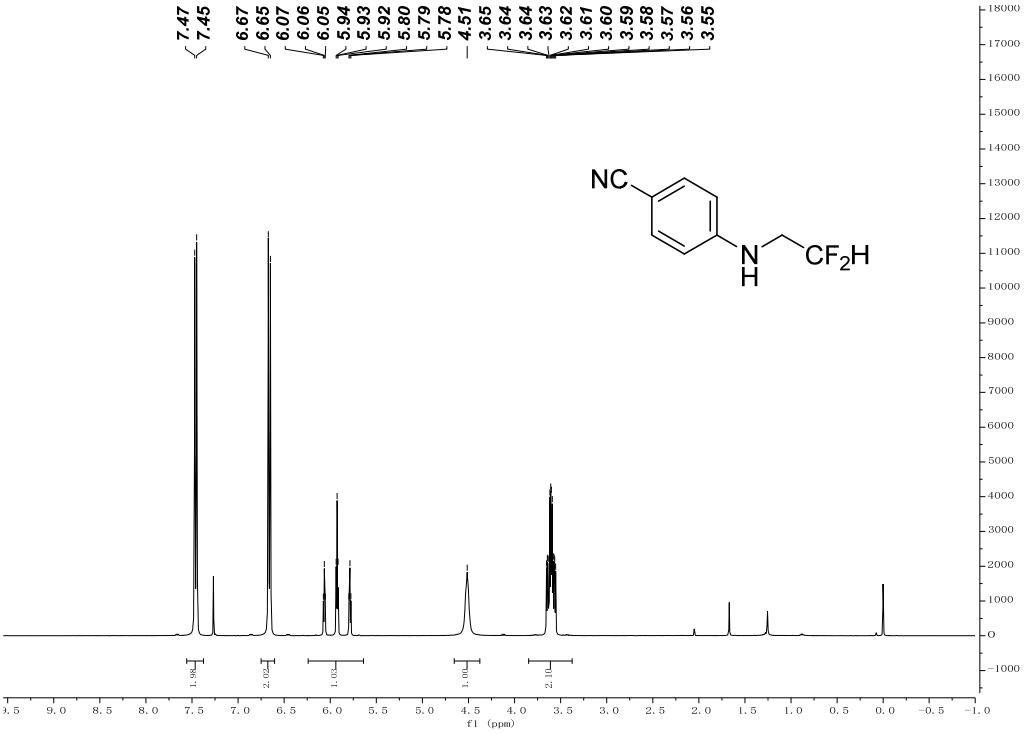
^{19}F NMR ($CDCl_3$, 376 MHz) of **8e**



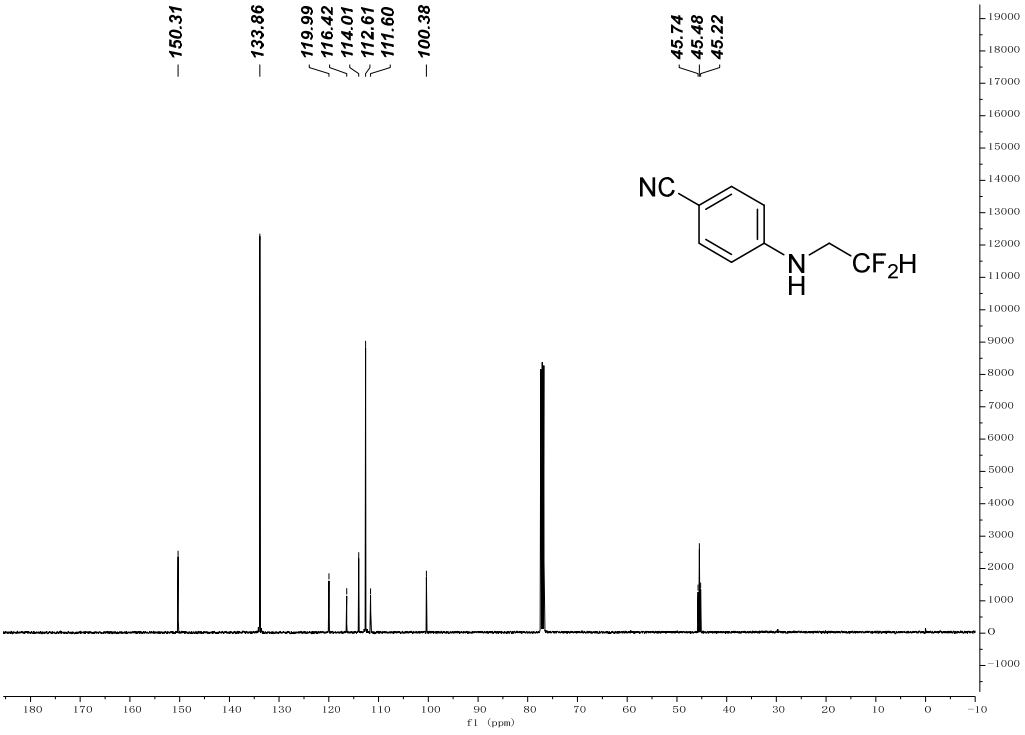
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **8e**



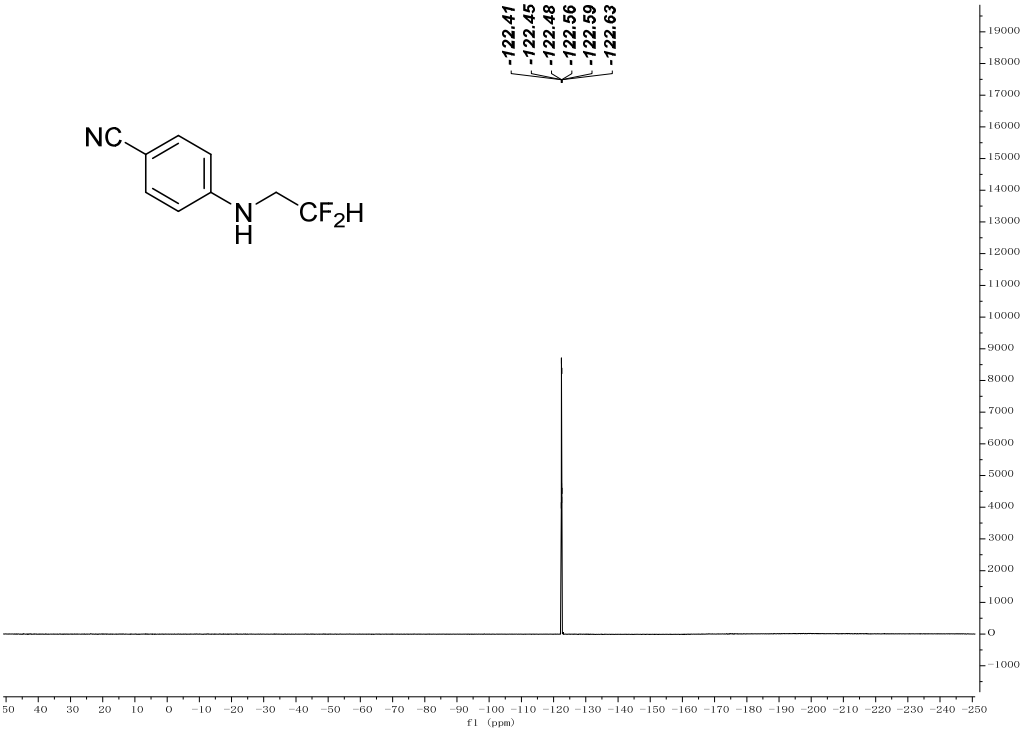
^{1}H NMR ($CDCl_3$, 400 MHz) of **8f**



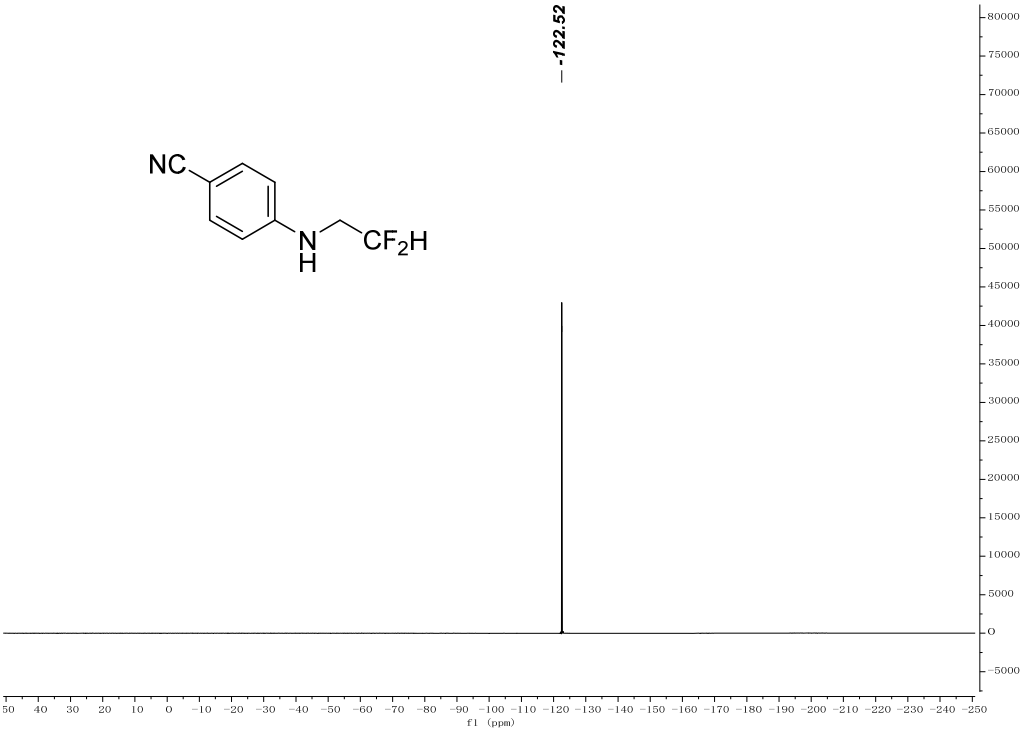
^{13}C NMR ($CDCl_3$, 100 MHz) of **8f**



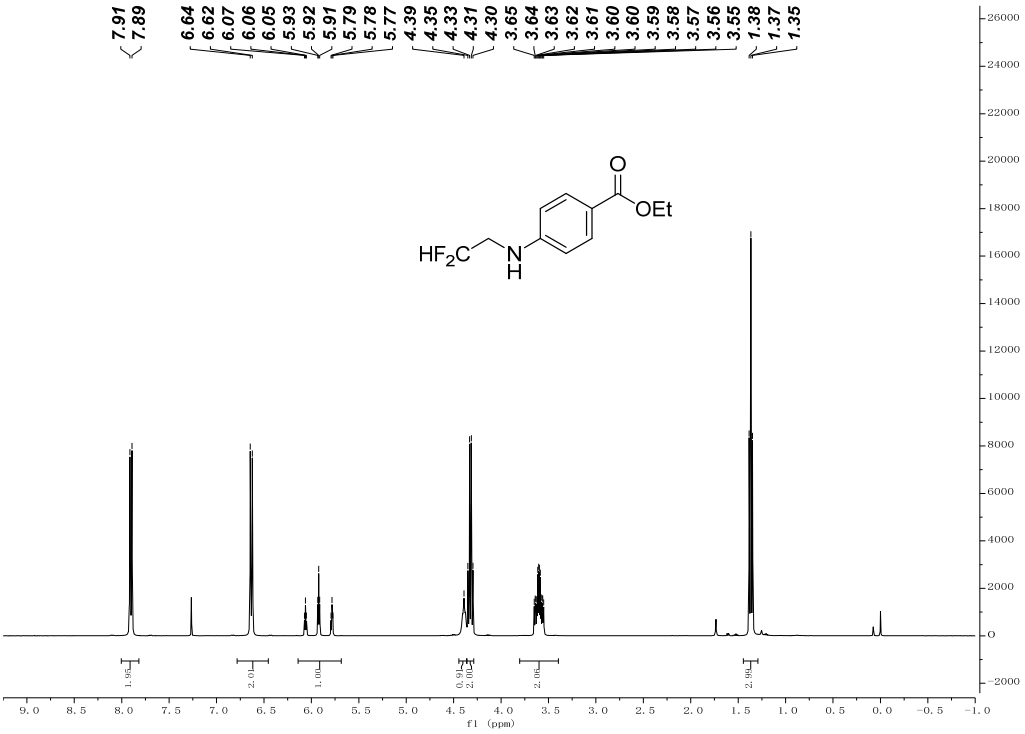
^{19}F NMR ($CDCl_3$, 376 MHz) of **8f**



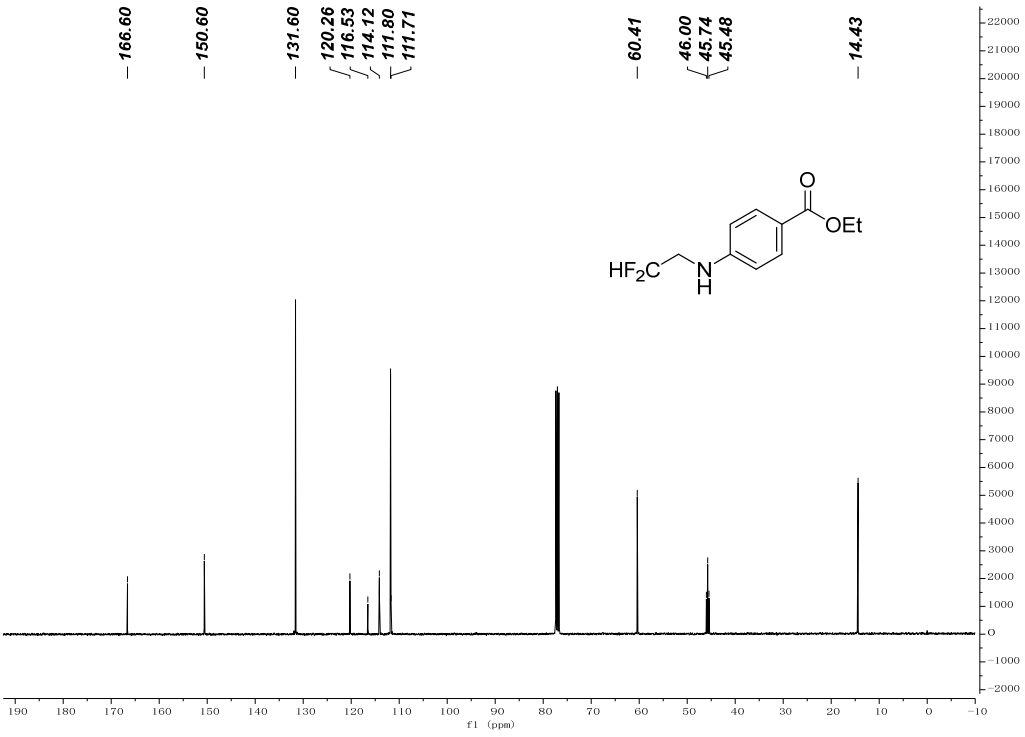
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **8f**



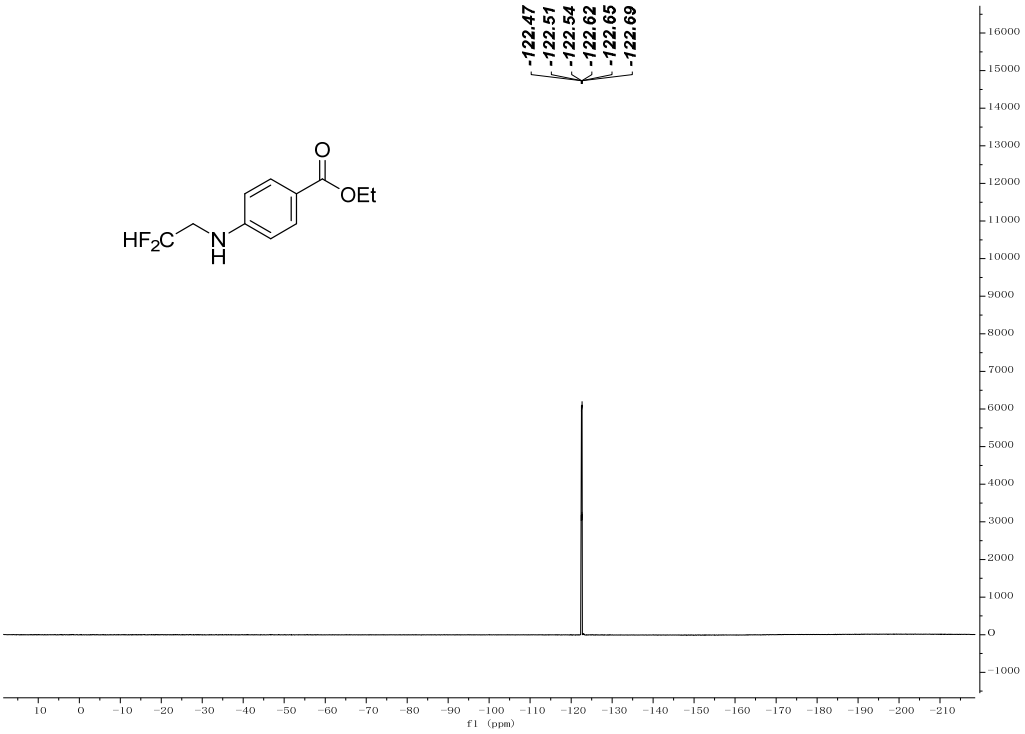
^{1}H NMR ($CDCl_3$, 400 MHz) of **8g**



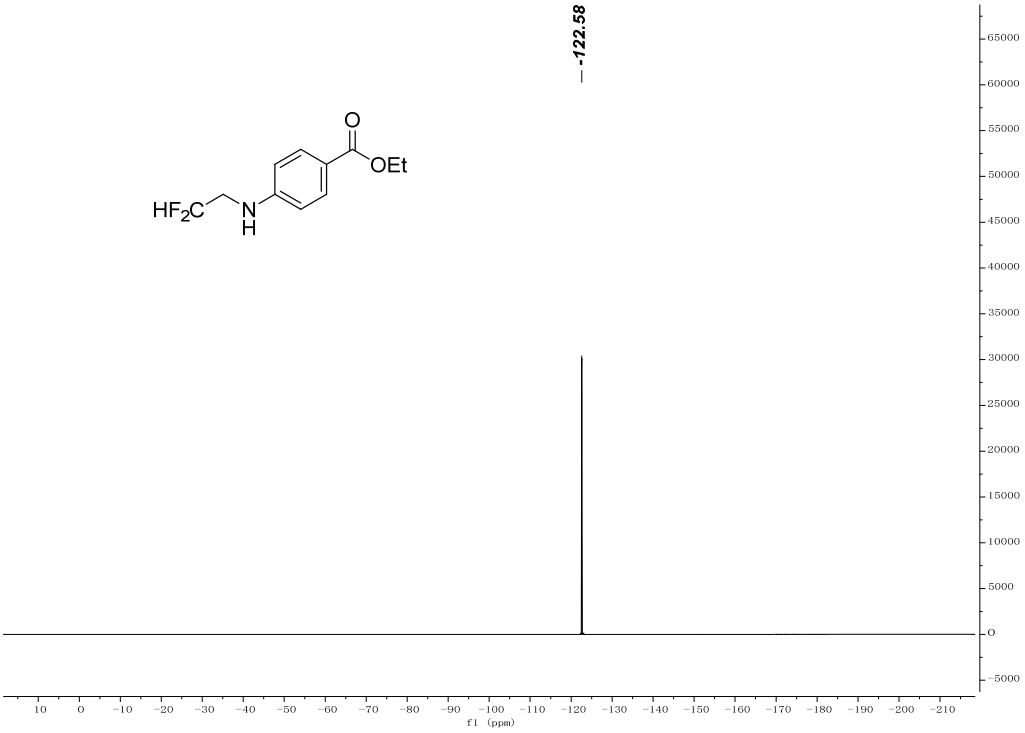
^{13}C NMR ($CDCl_3$, 100 MHz) of **8g**



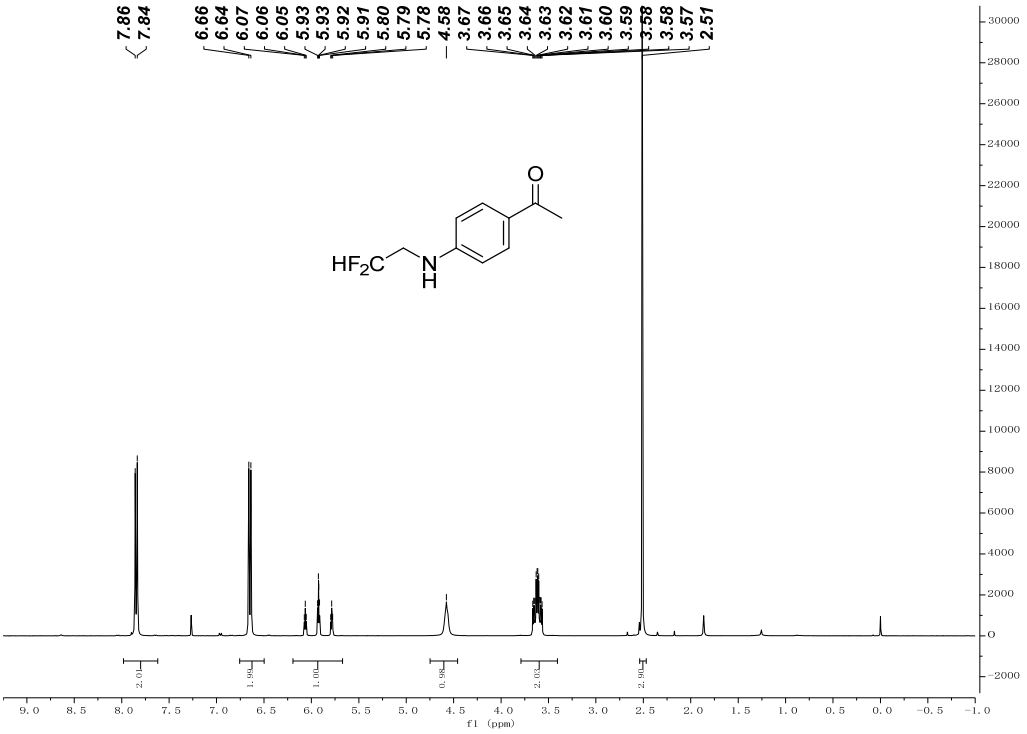
^{19}F NMR ($CDCl_3$, 376 MHz) of **8g**



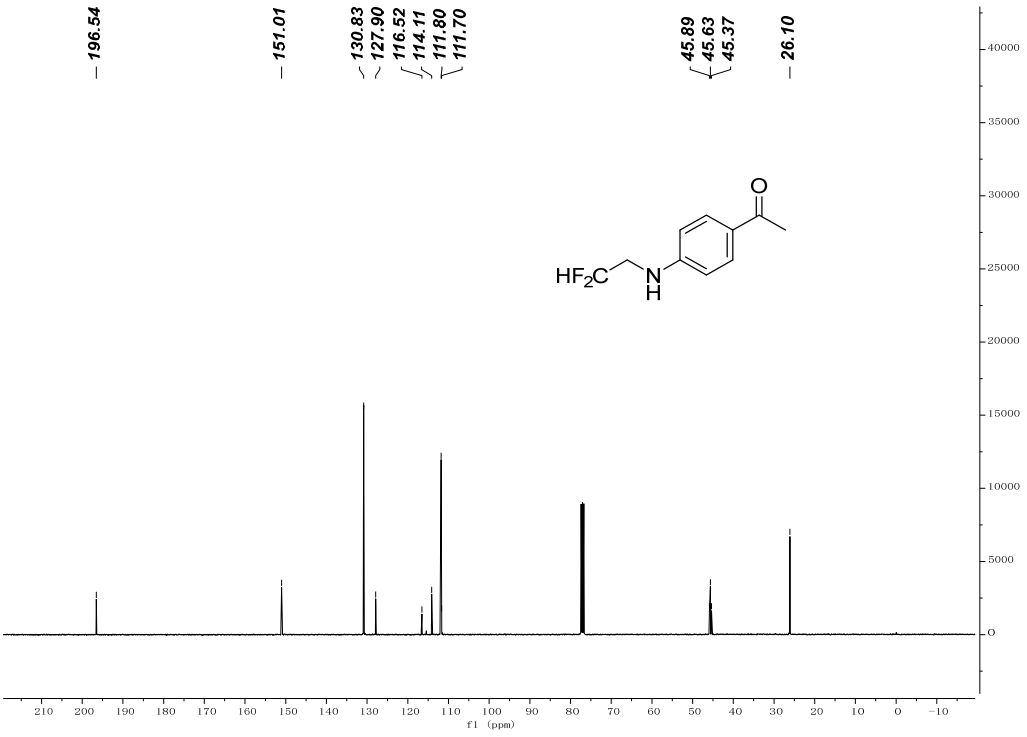
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **8g**



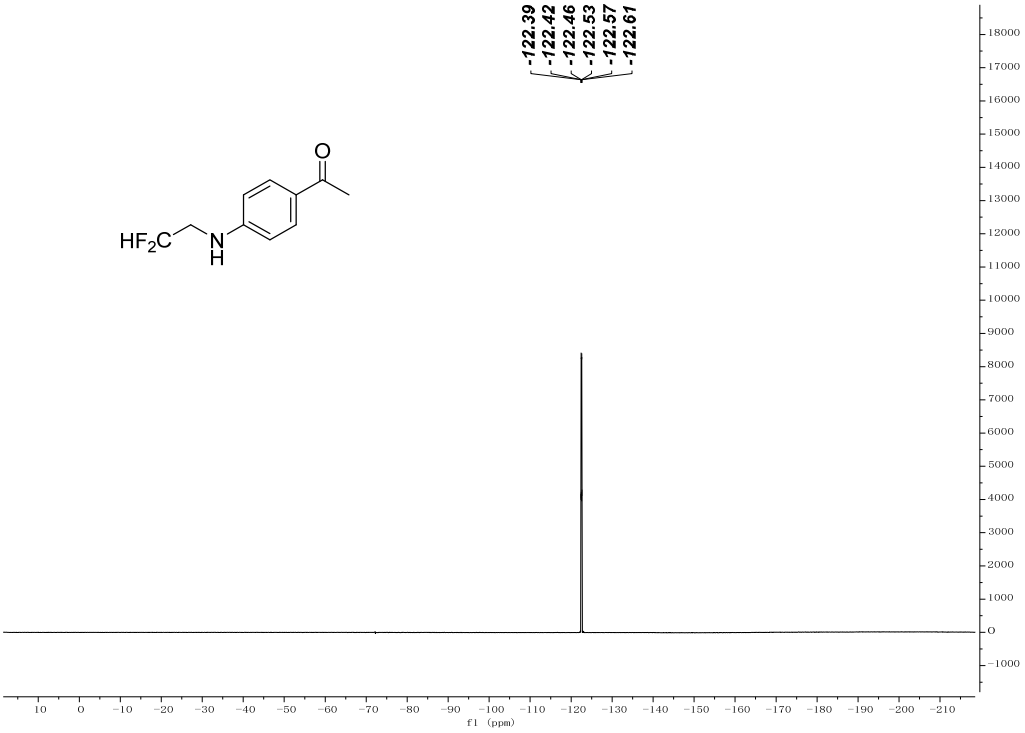
^{1}H NMR ($CDCl_3$, 400 MHz) of **8h**



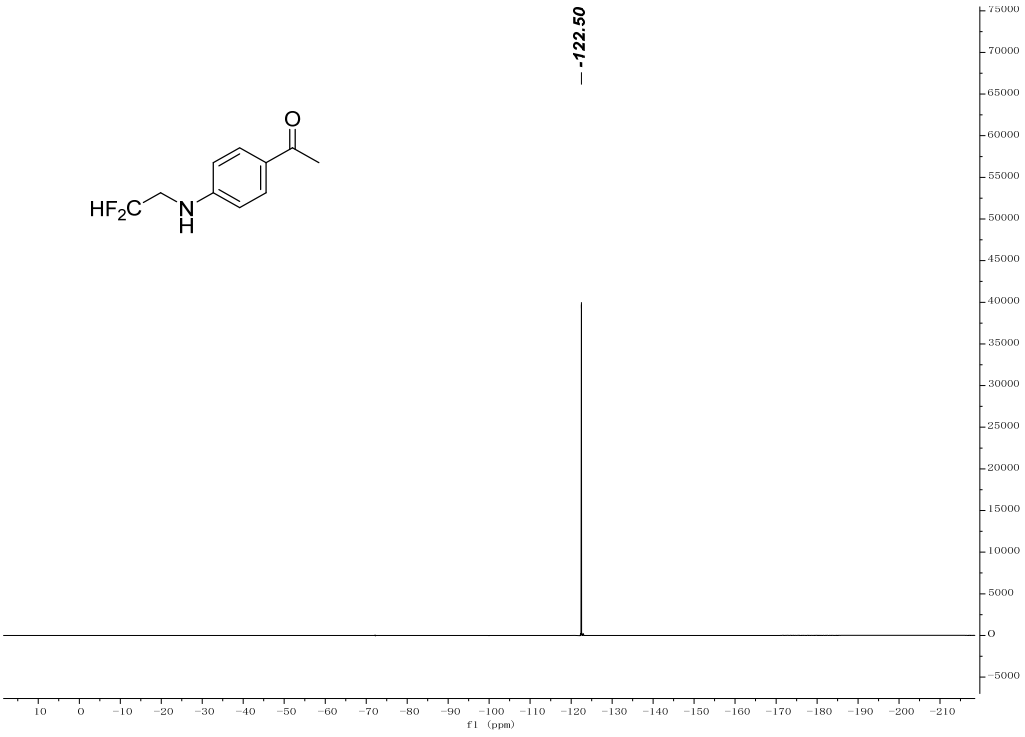
^{13}C NMR ($CDCl_3$, 100 MHz) of **8h**



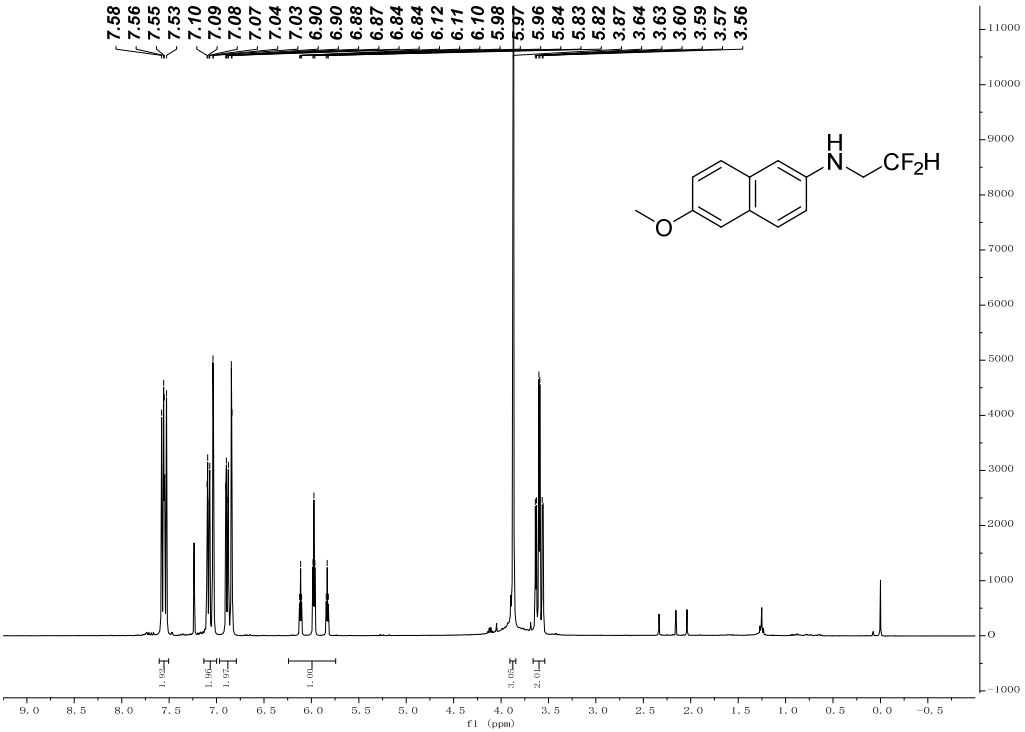
^{19}F NMR ($CDCl_3$, 376 MHz) of **8h**



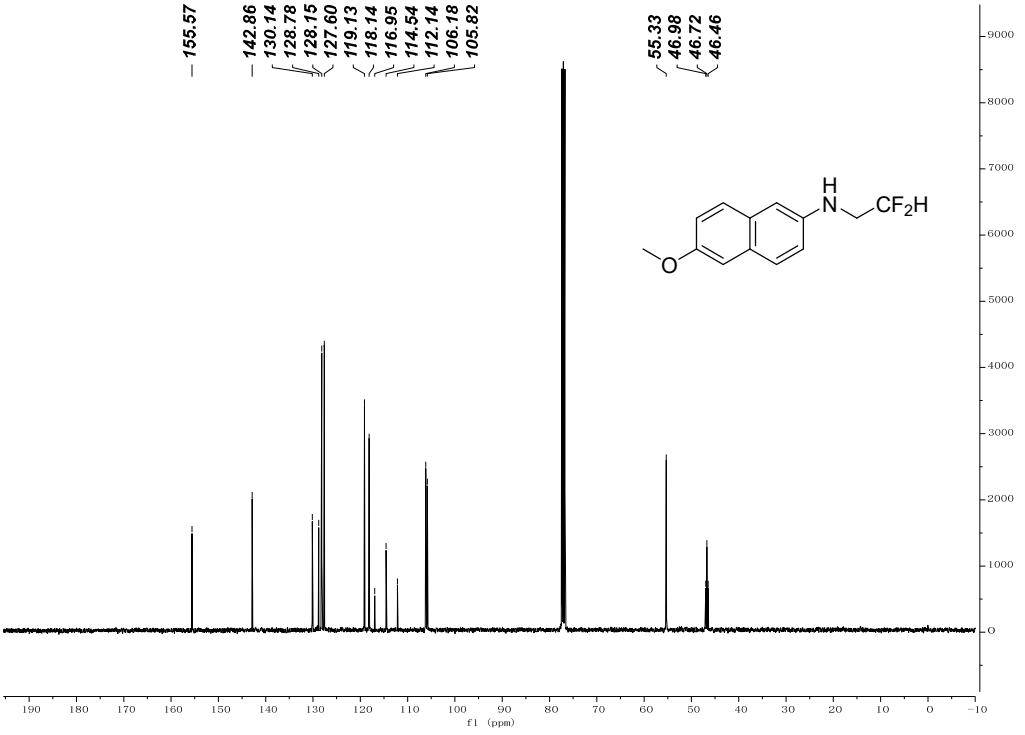
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **8h**



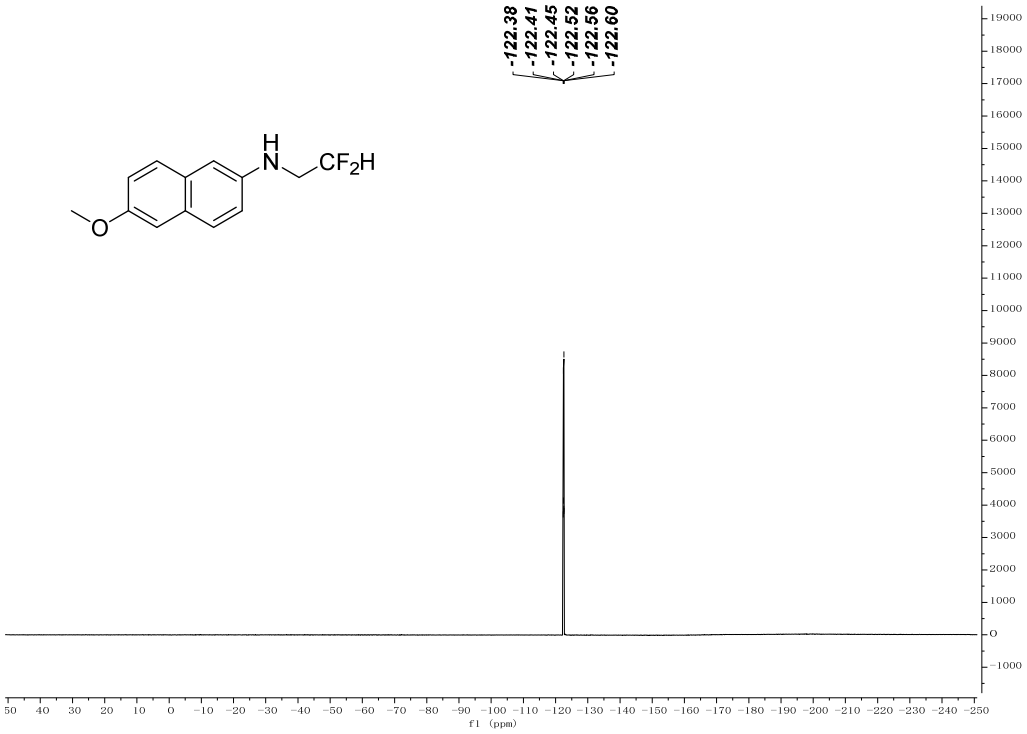
^{1}H NMR ($CDCl_3$, 400 MHz) of **8i**



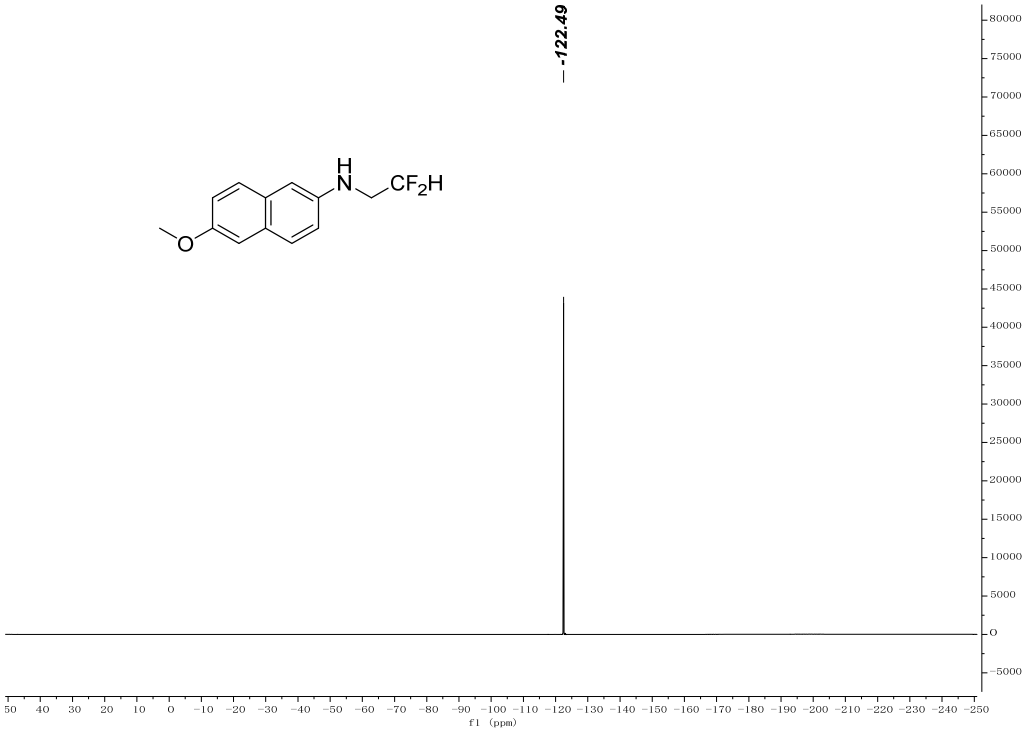
^{13}C NMR ($CDCl_3$, 100 MHz) of **8i**



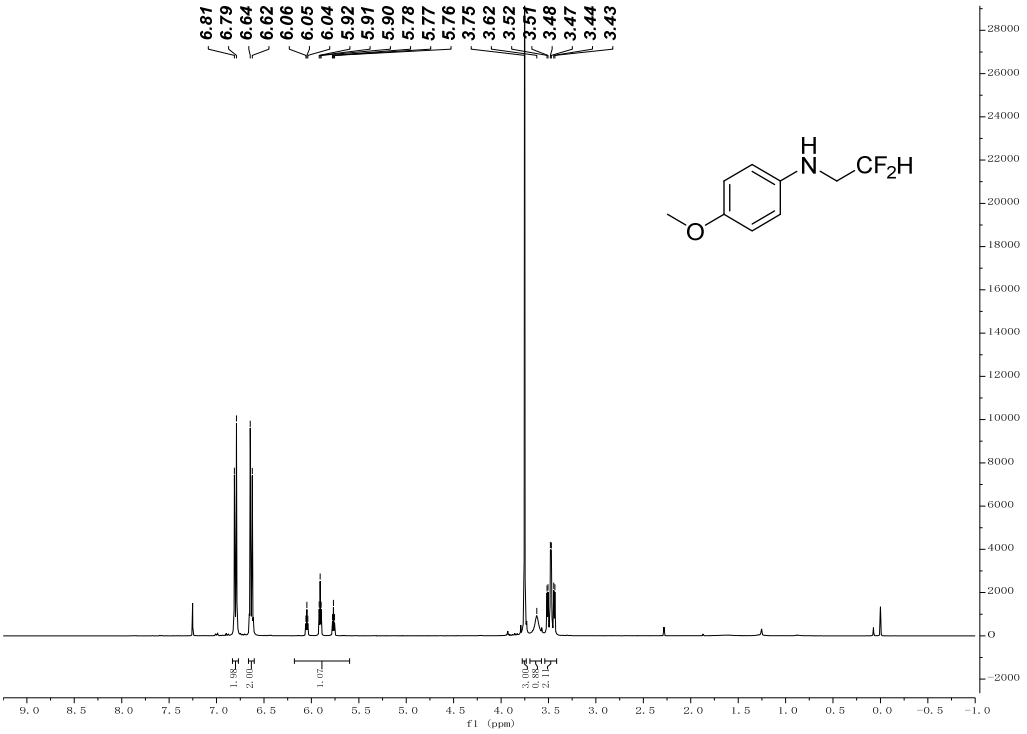
^{19}F NMR ($CDCl_3$, 376 MHz) of **8i**



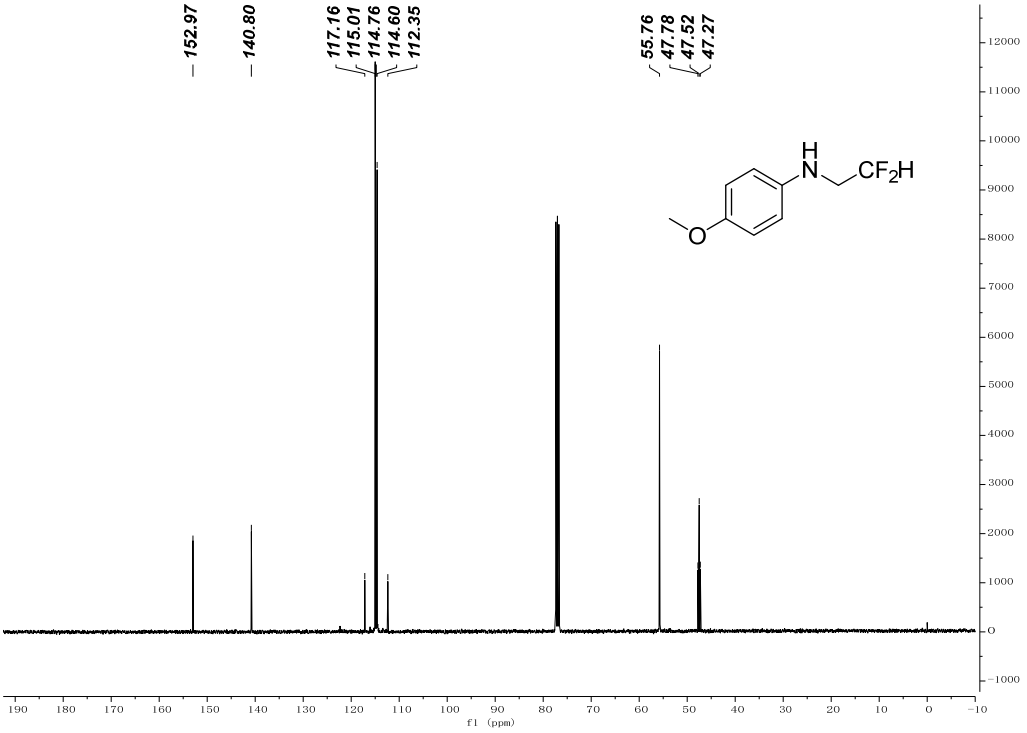
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **8i**



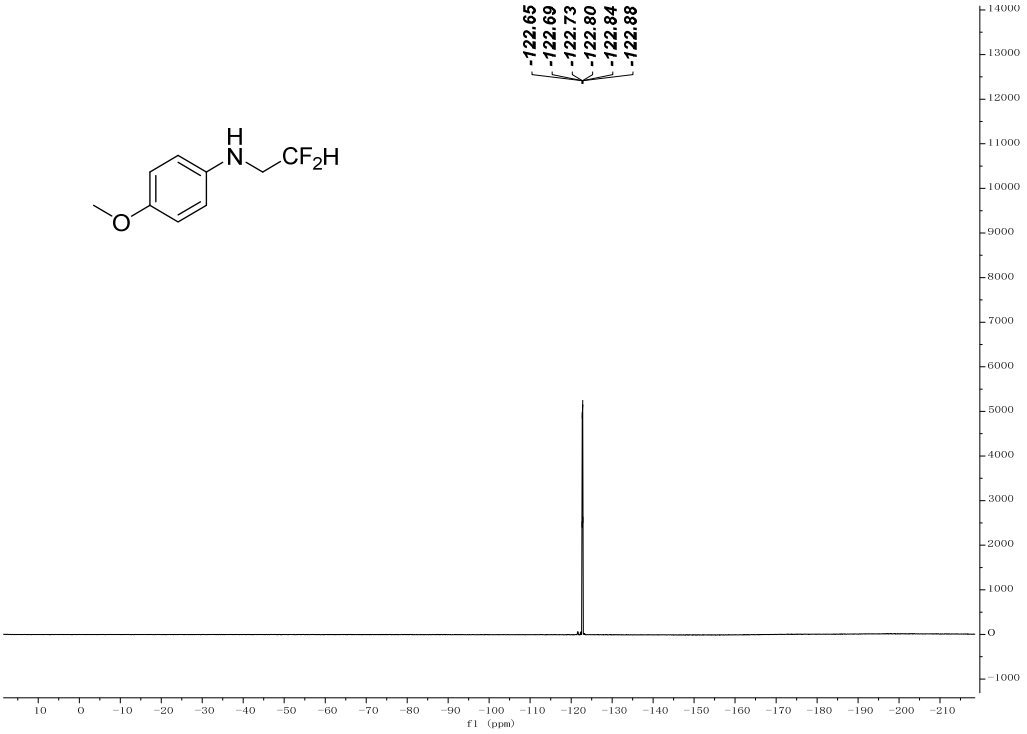
^{1}H NMR ($CDCl_3$, 400 MHz) of **8j**



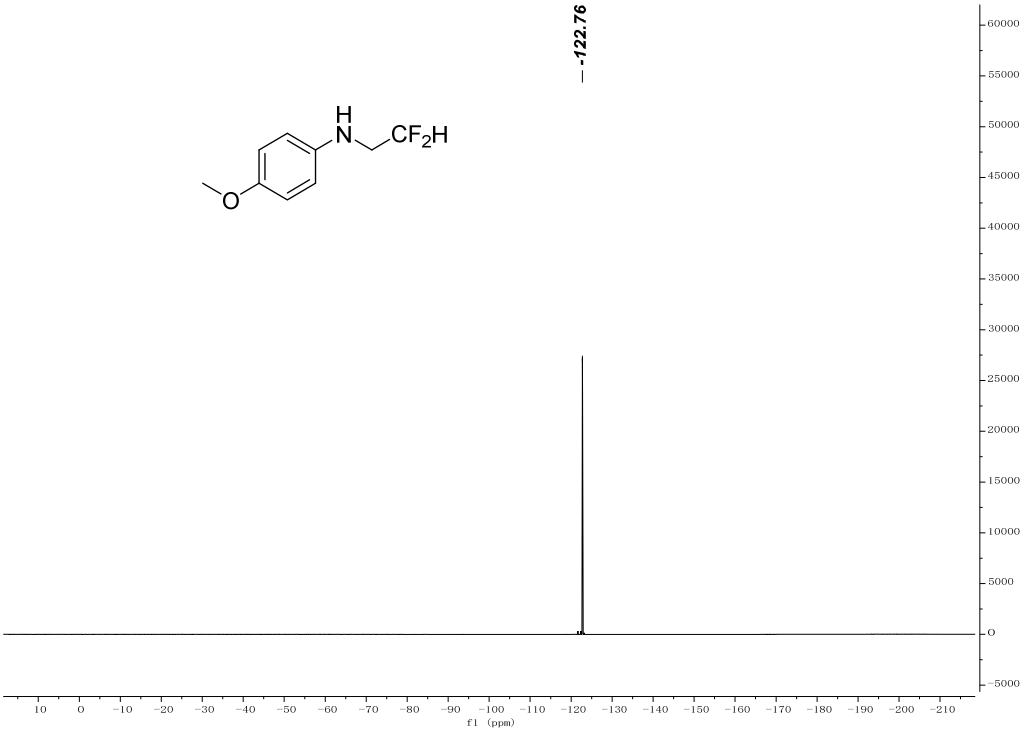
^{13}C NMR ($CDCl_3$, 100 MHz) of **8j**



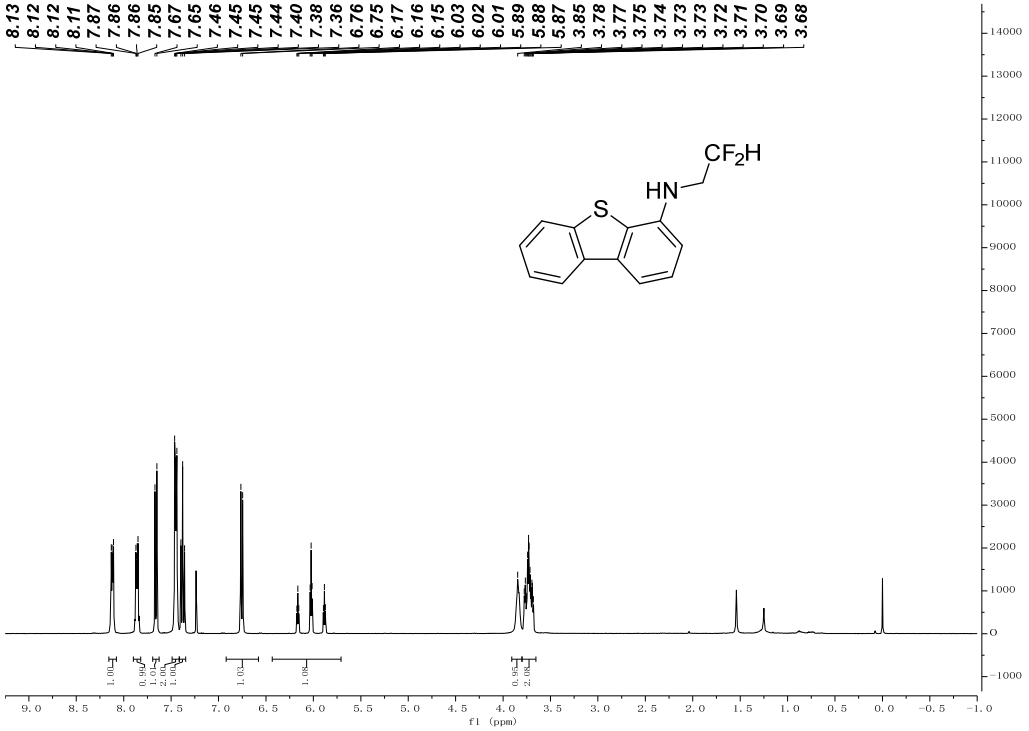
^{19}F NMR ($CDCl_3$, 376 MHz) of **8j**



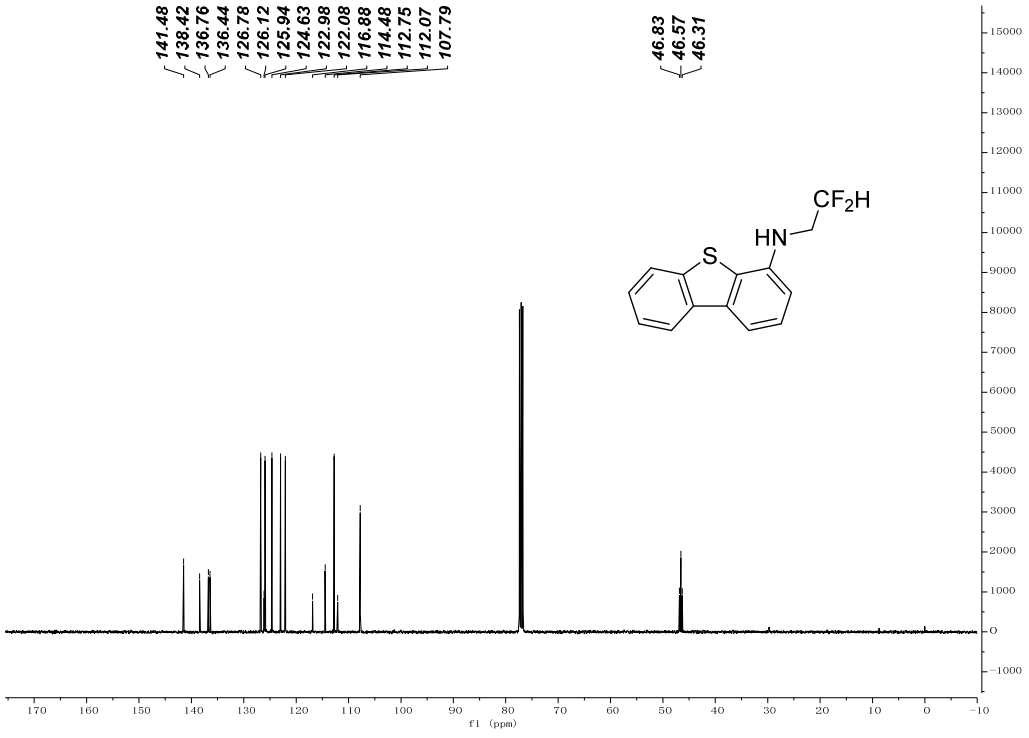
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **8j**



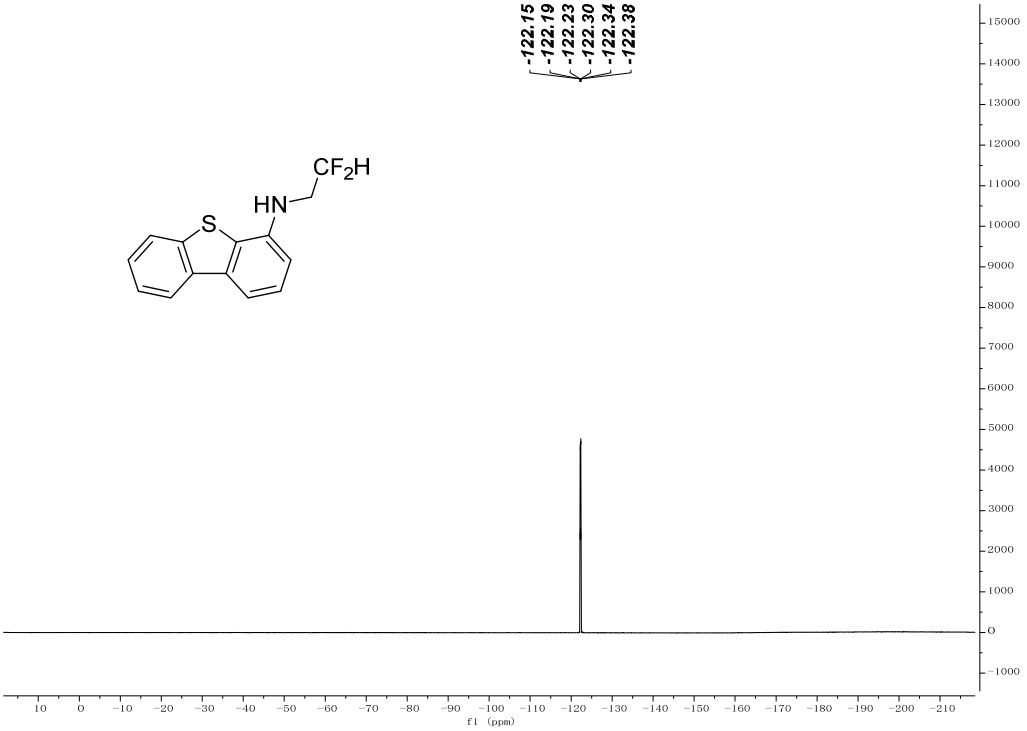
^{1}H NMR ($CDCl_3$, 400 MHz) of **8l**



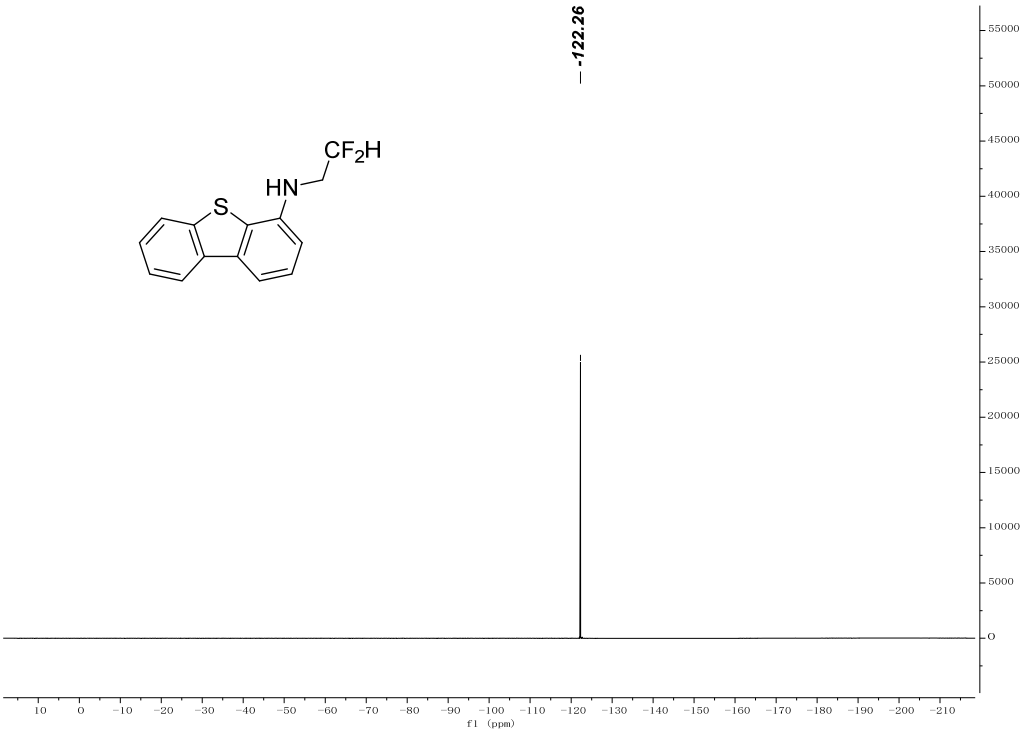
^{13}C NMR ($CDCl_3$, 100 MHz) of **8l**



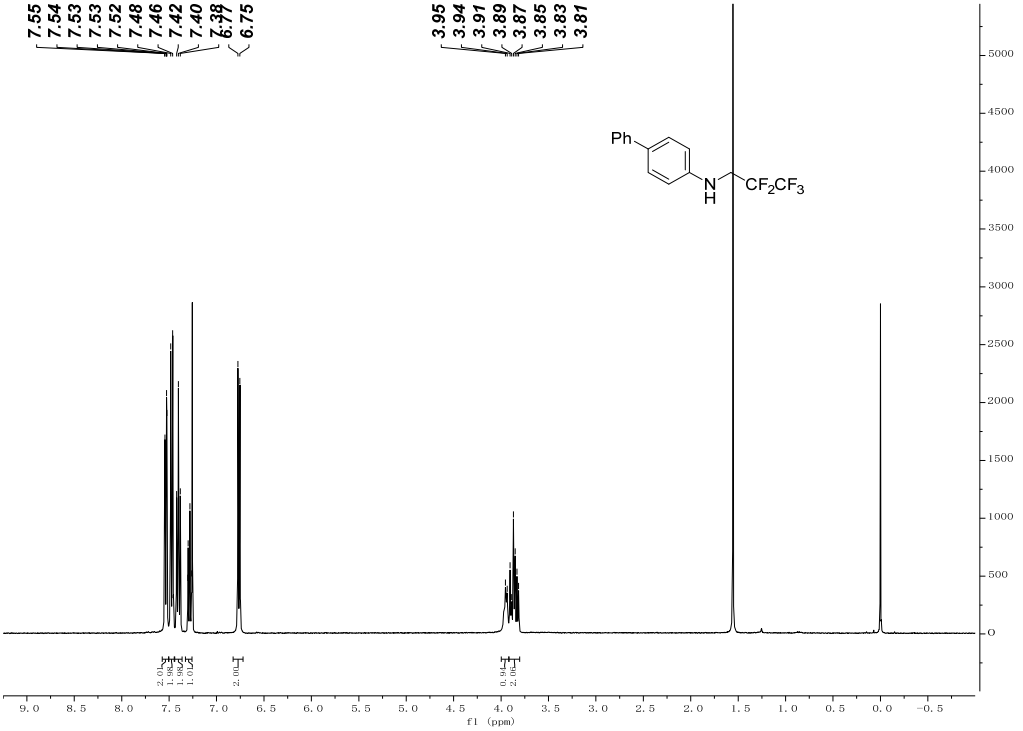
^{19}F NMR ($CDCl_3$, 376 MHz) of **8l**



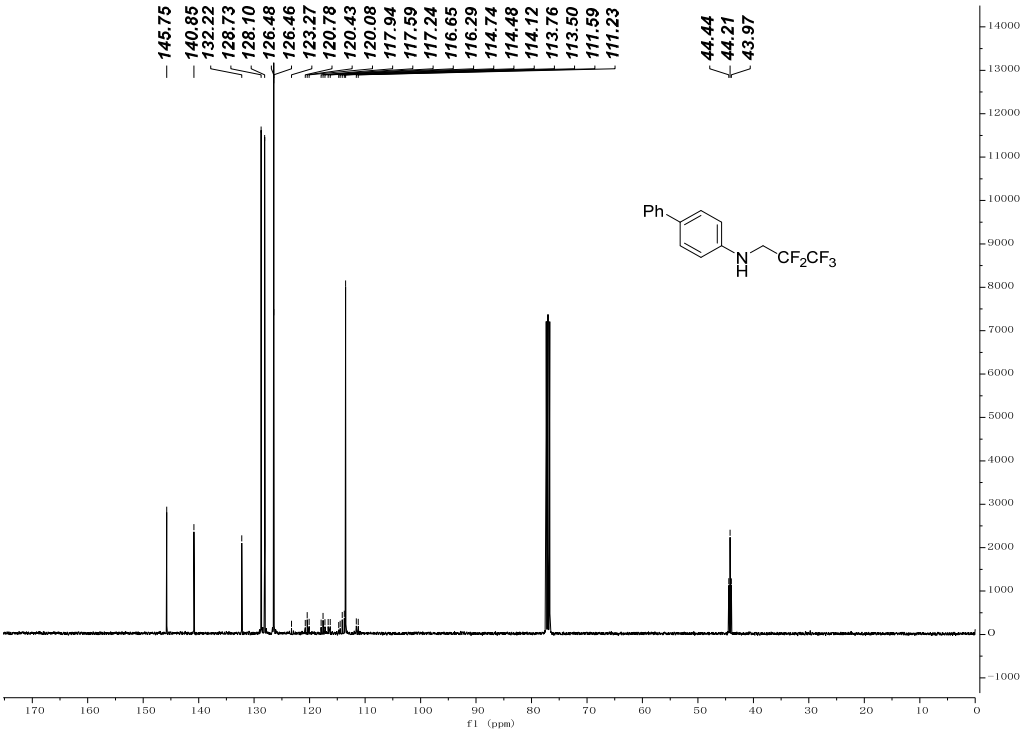
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **8l**



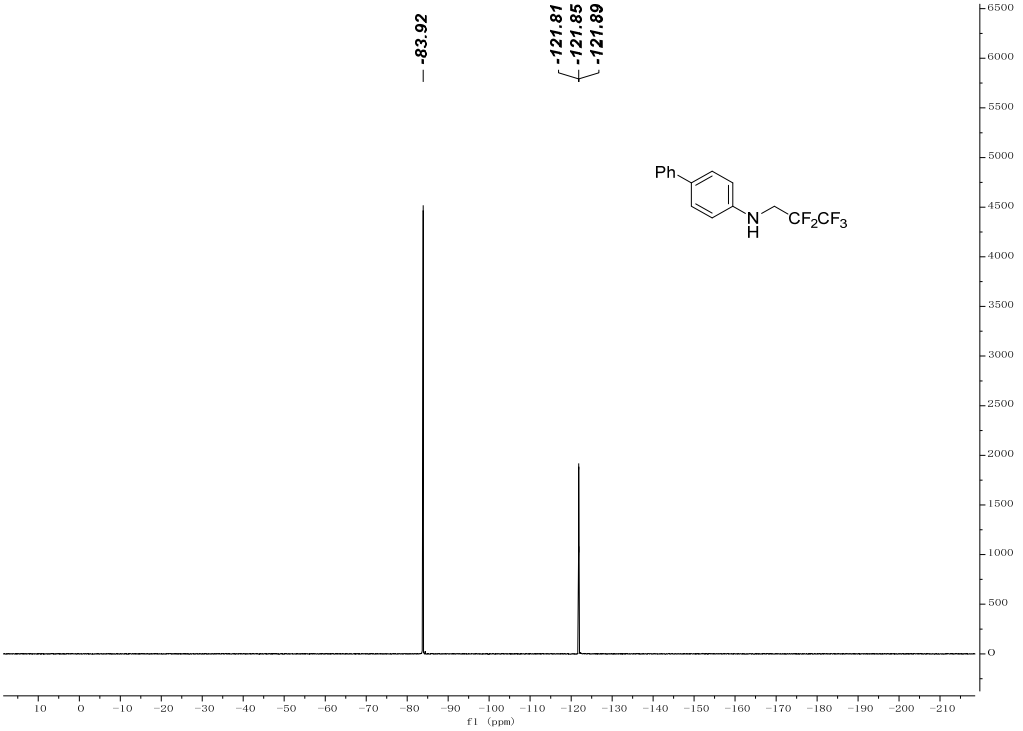
^{1}H NMR ($CDCl_3$, 400 MHz) of **11a**



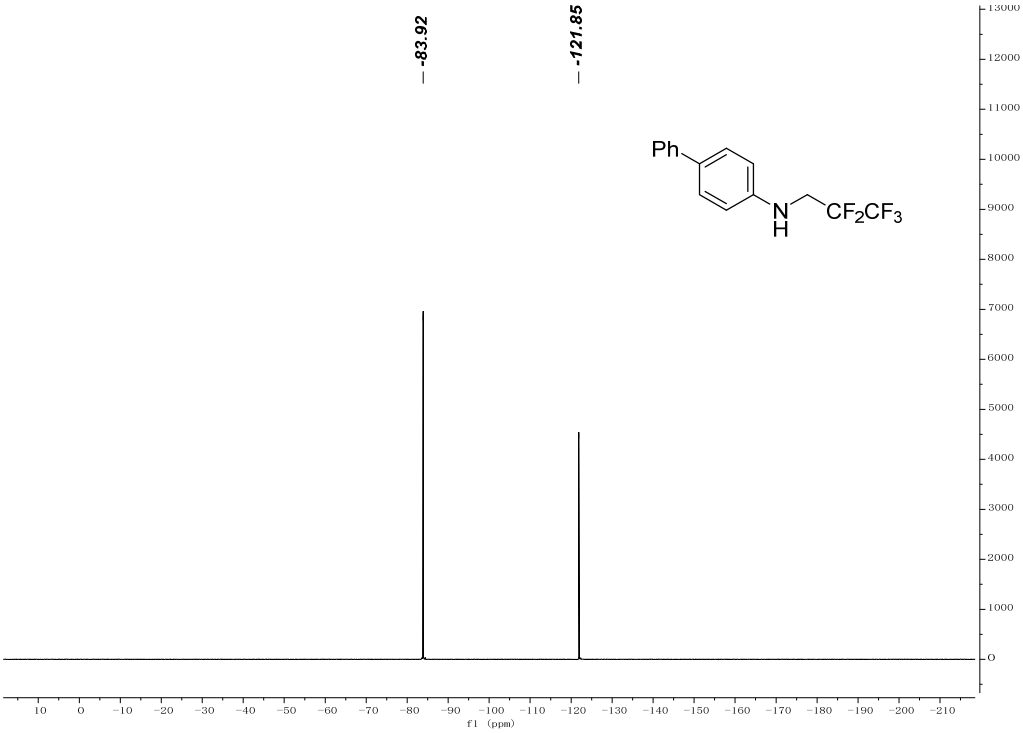
^{13}C NMR ($CDCl_3$, 100 MHz) of **11a**



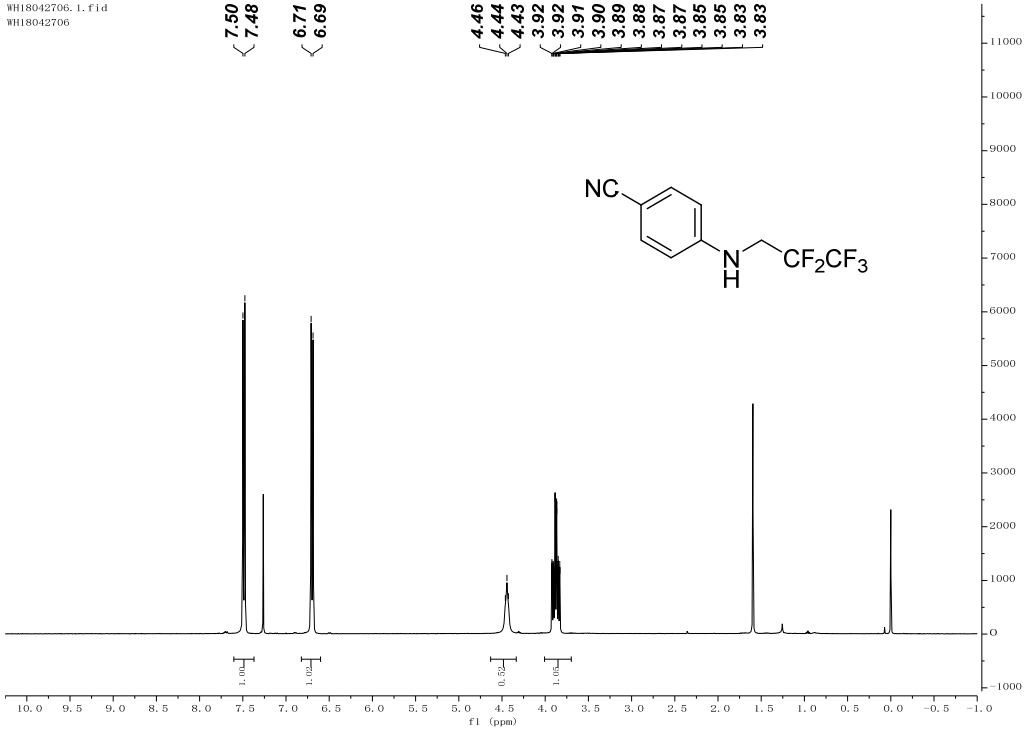
^{19}F NMR ($CDCl_3$, 376 MHz) of **11a**



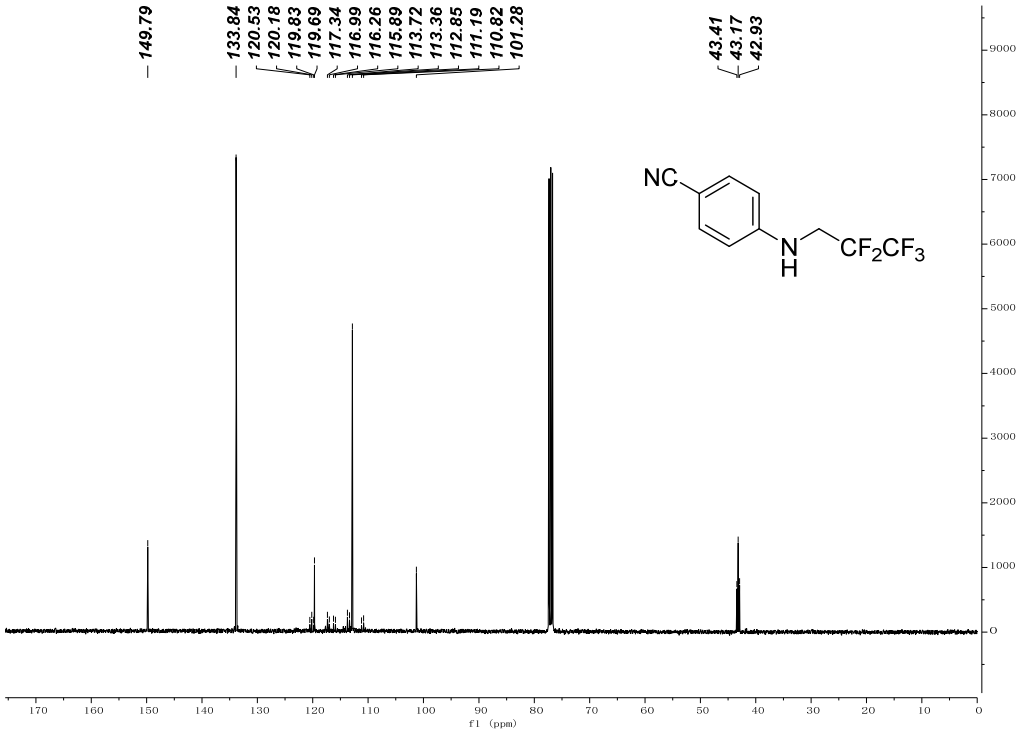
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **11a**



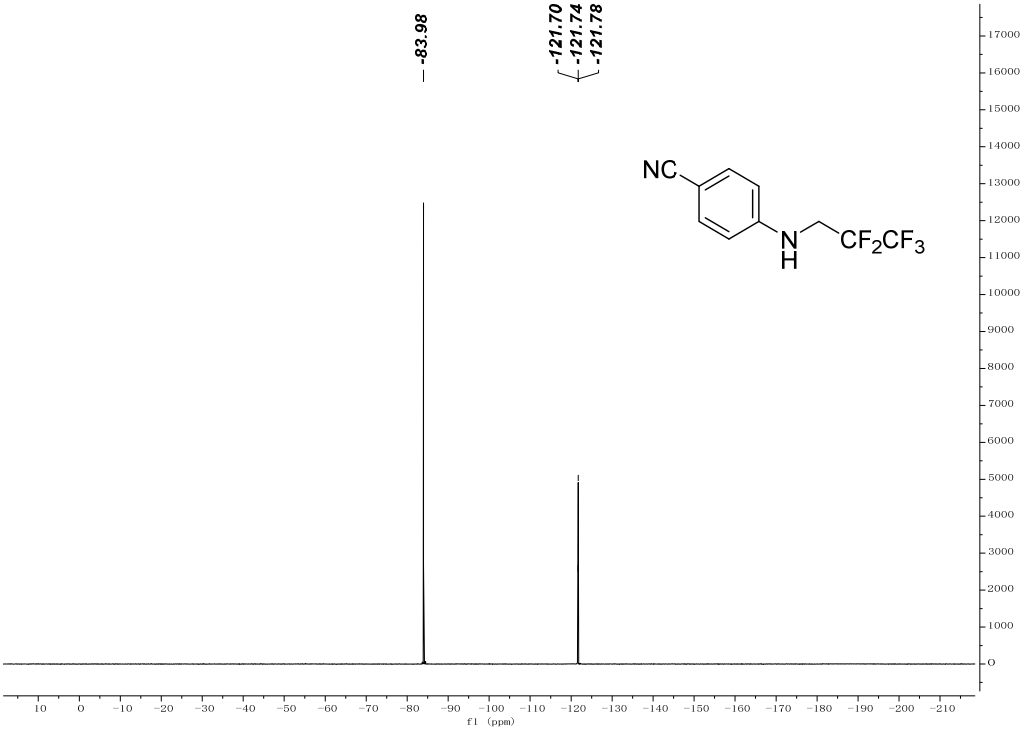
^{1}H NMR ($CDCl_3$, 400 MHz) of **11f**



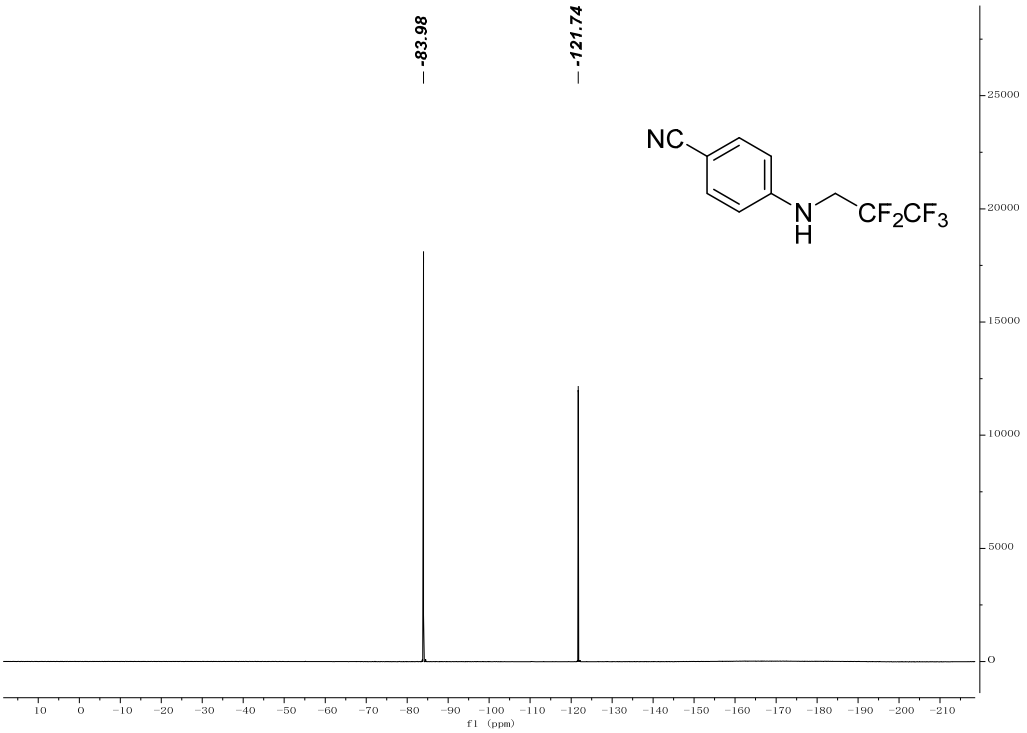
^{13}C NMR ($CDCl_3$, 100 MHz) of **11f**



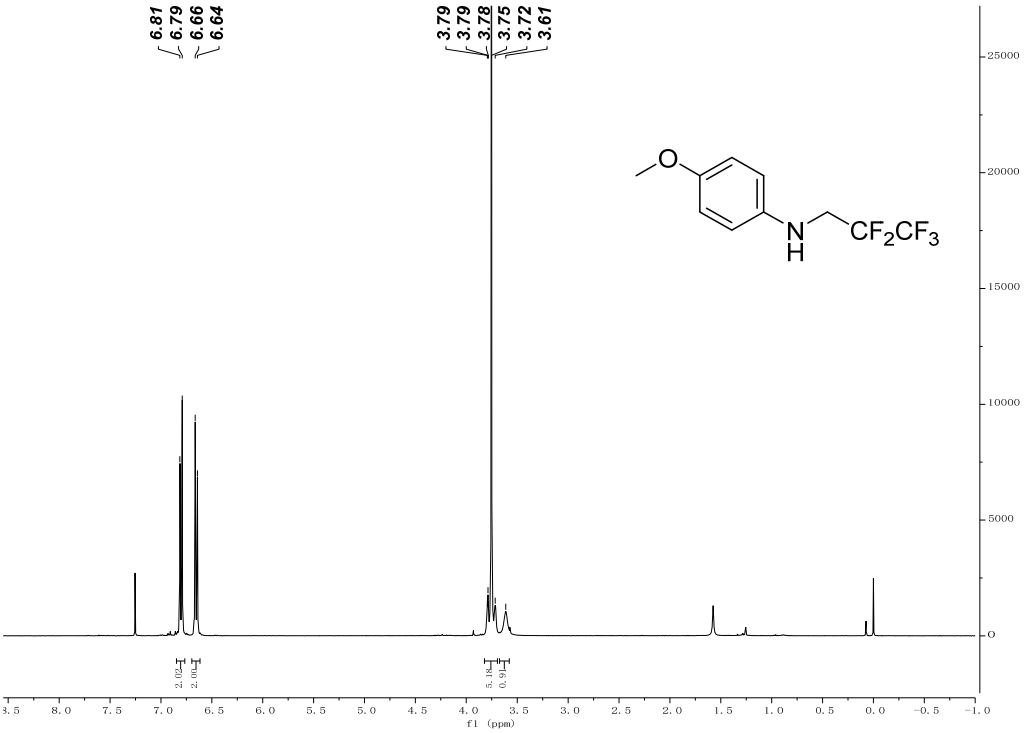
^{19}F NMR ($CDCl_3$, 376 MHz) of **11f**



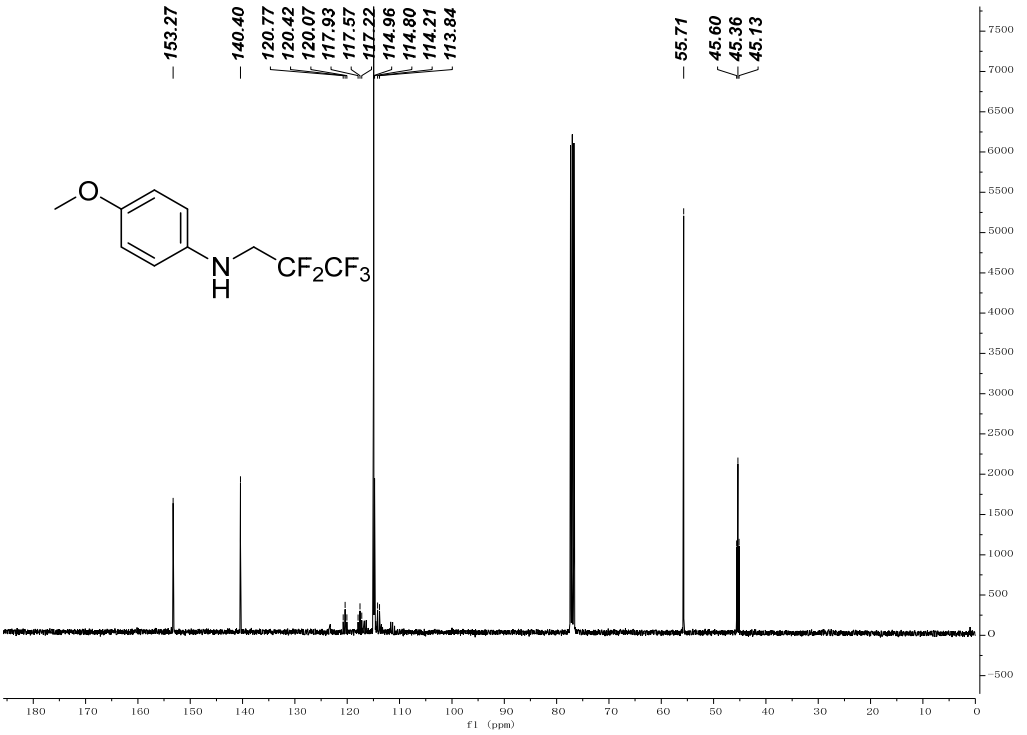
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **11f**



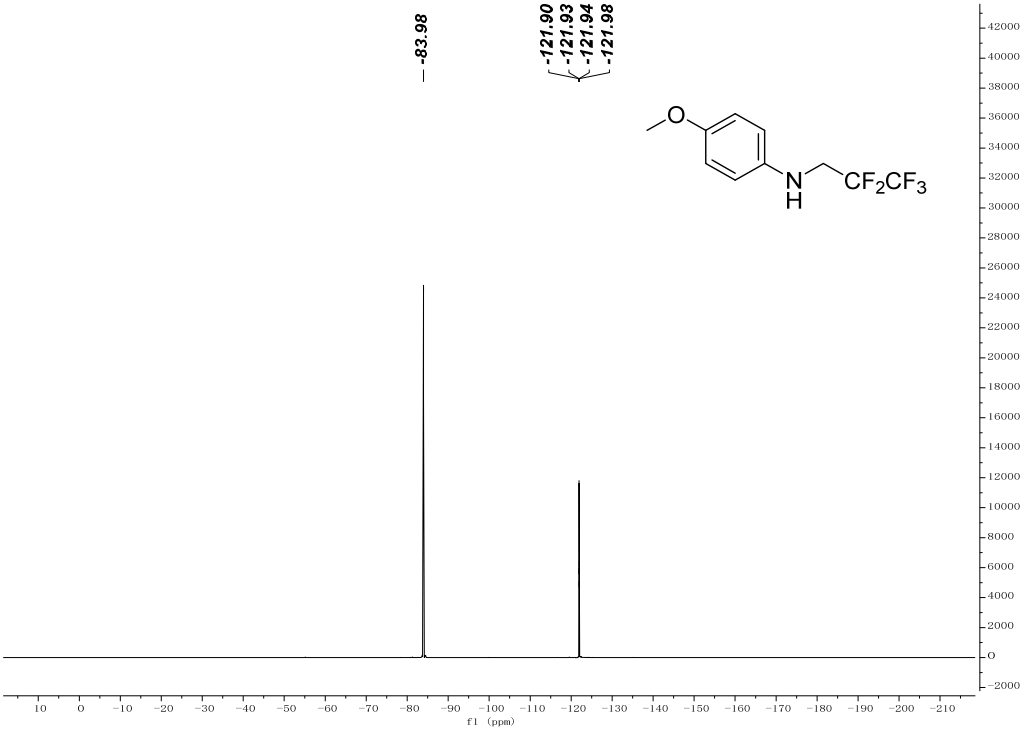
^{1}H NMR ($CDCl_3$, 400 MHz) of **11j**



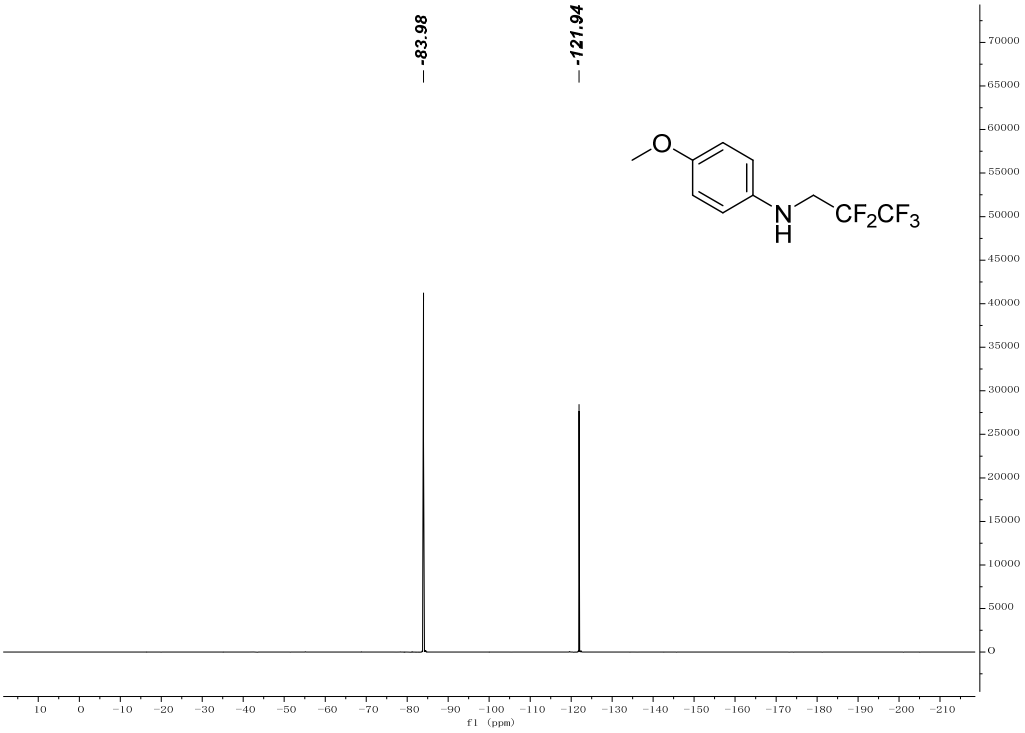
^{13}C NMR ($CDCl_3$, 100 MHz) of **11j**



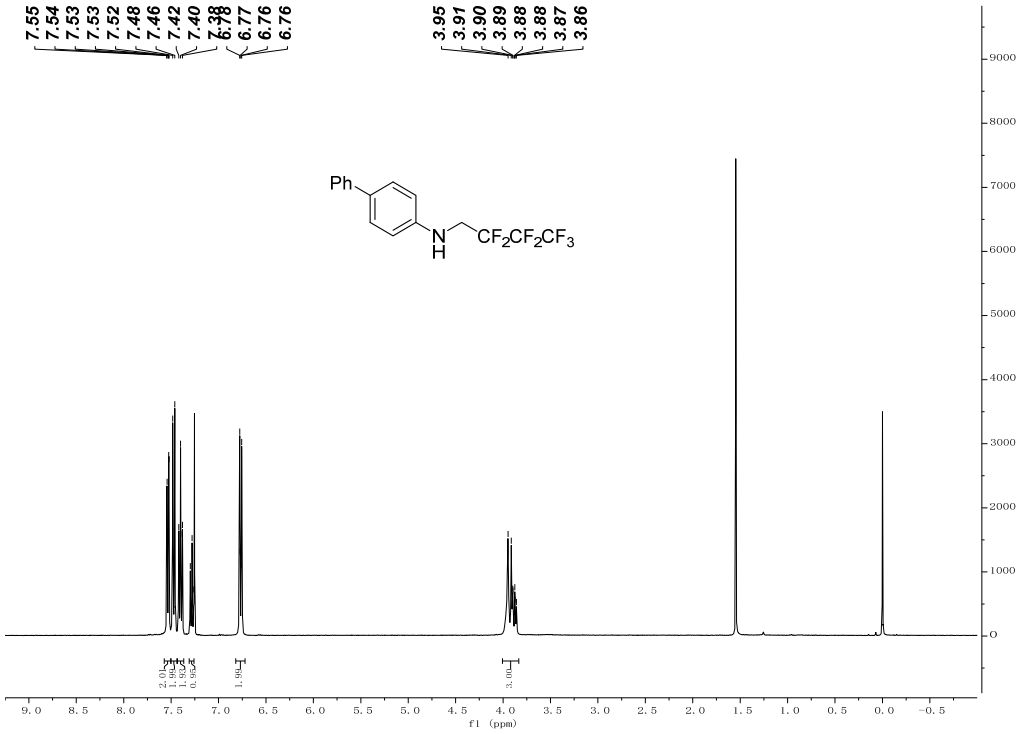
^{19}F NMR ($CDCl_3$, 376 MHz) of **11j**



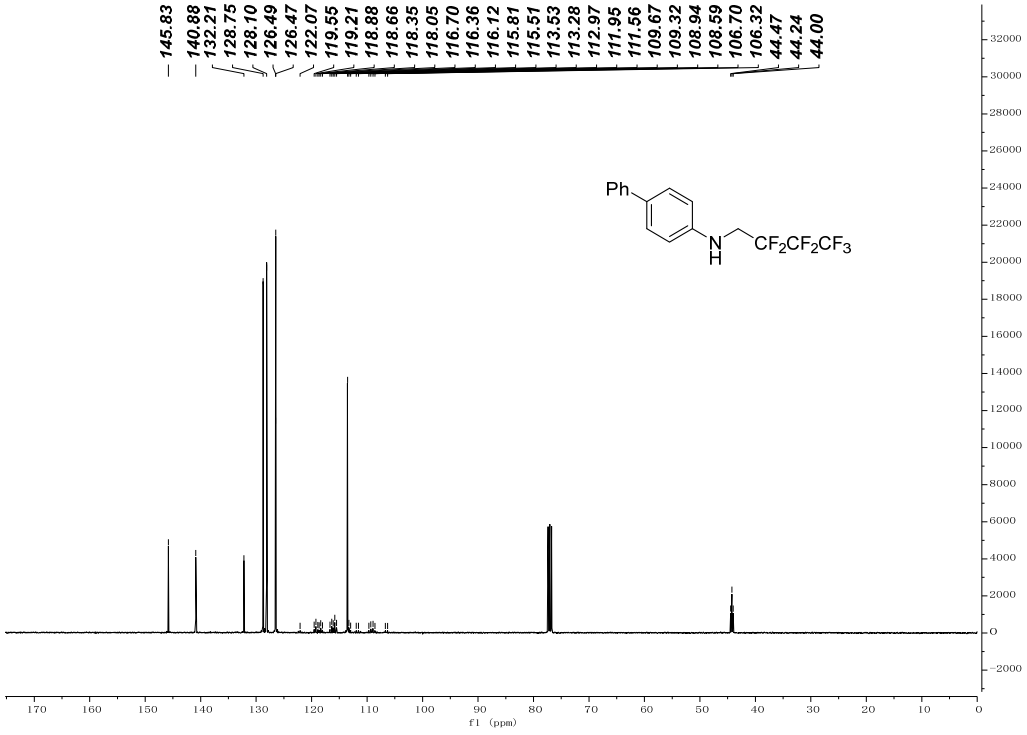
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **11j**



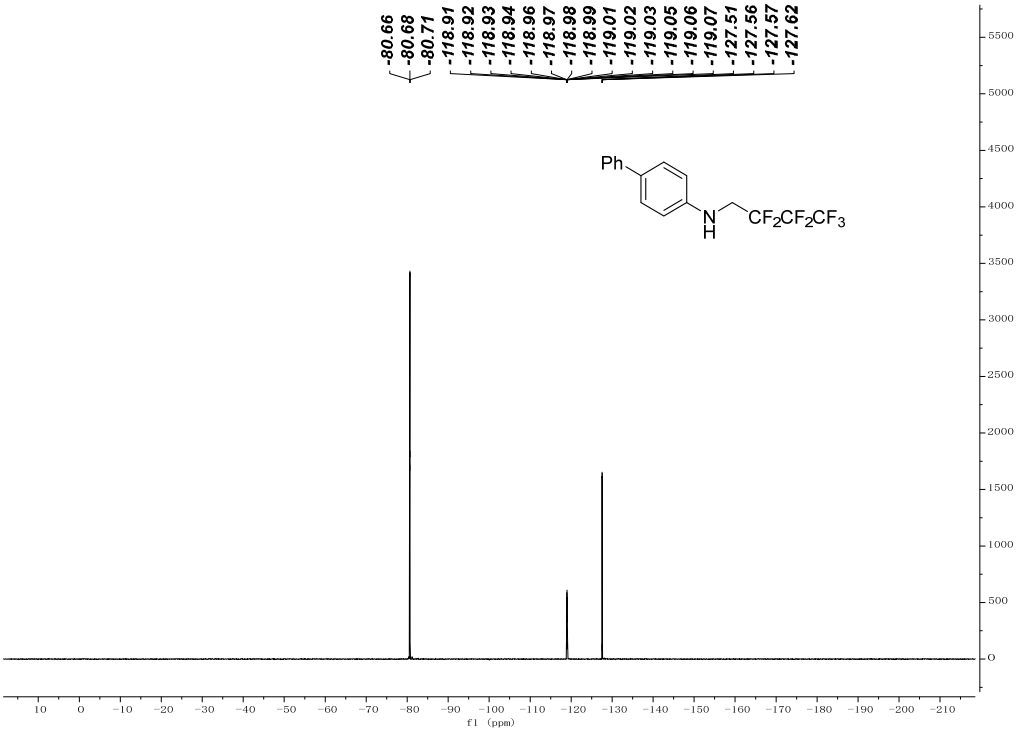
^{1}H NMR ($CDCl_3$, 400 MHz) of **12a**



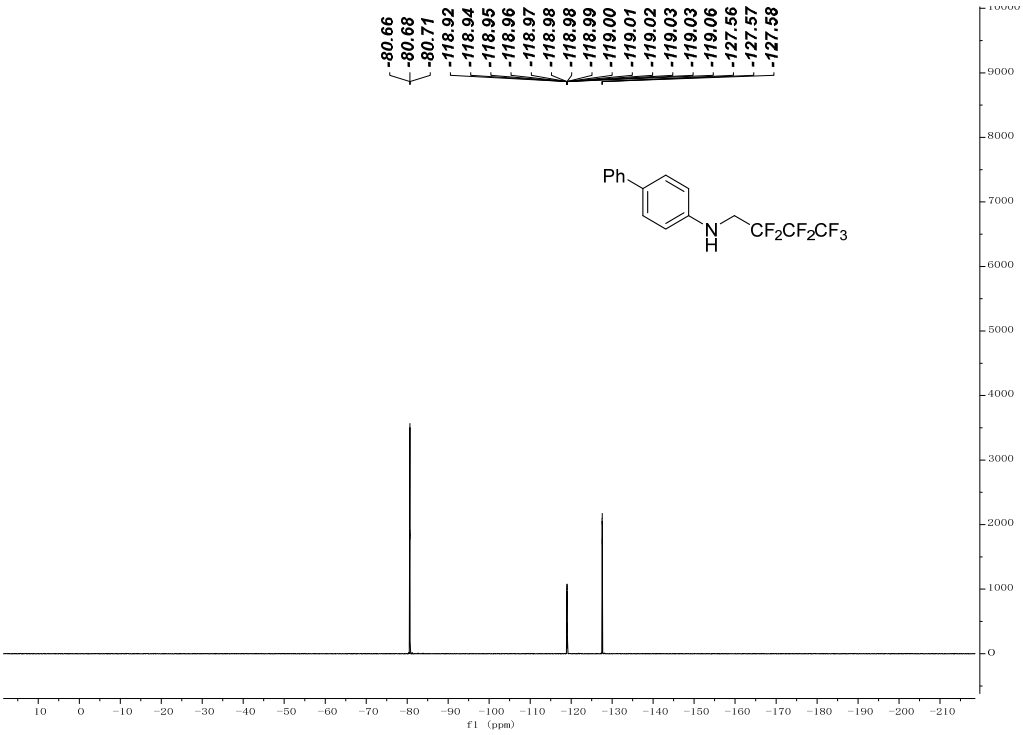
^{13}C NMR ($CDCl_3$, 100 MHz) of **12a**



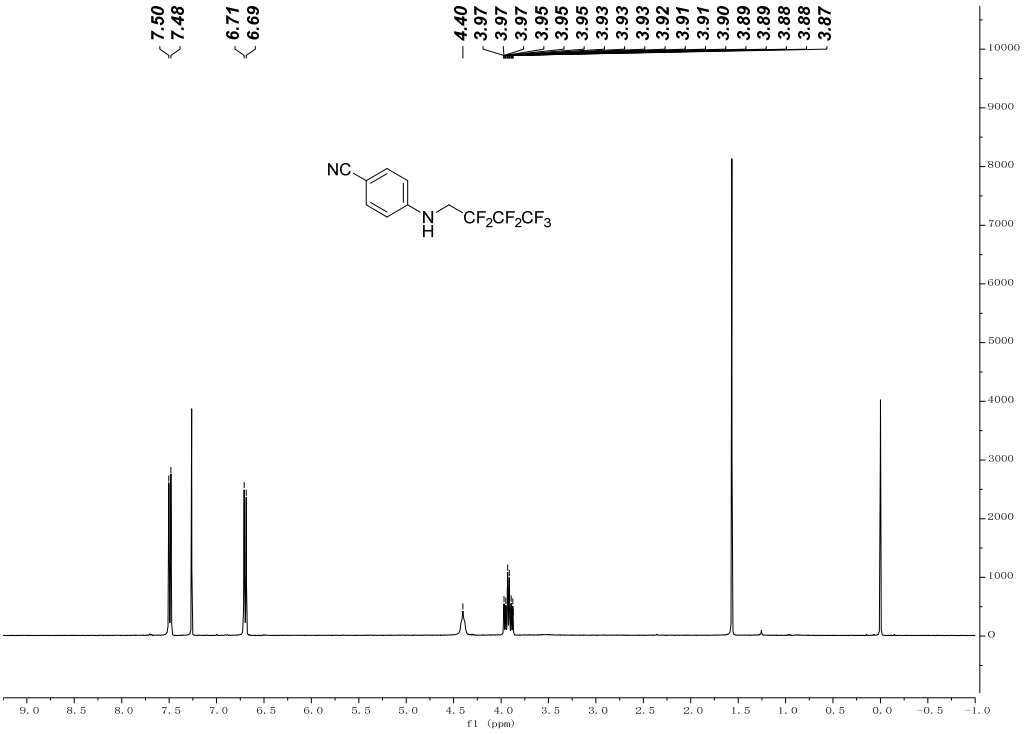
^{19}F NMR ($CDCl_3$, 376 MHz) of **12a**



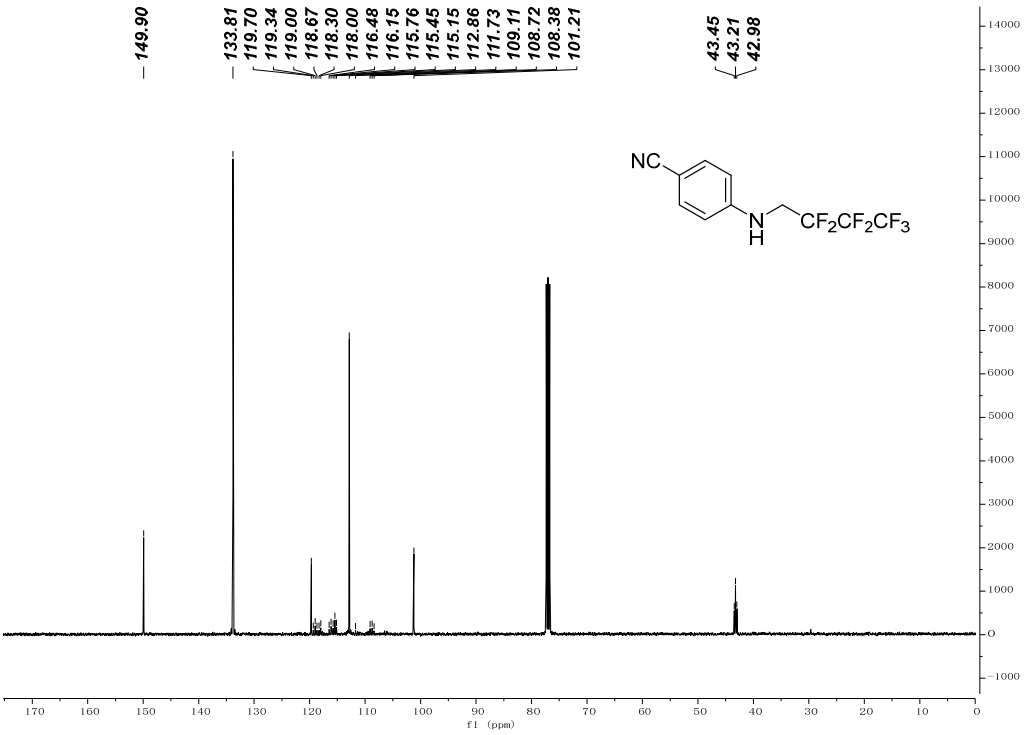
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **12a**



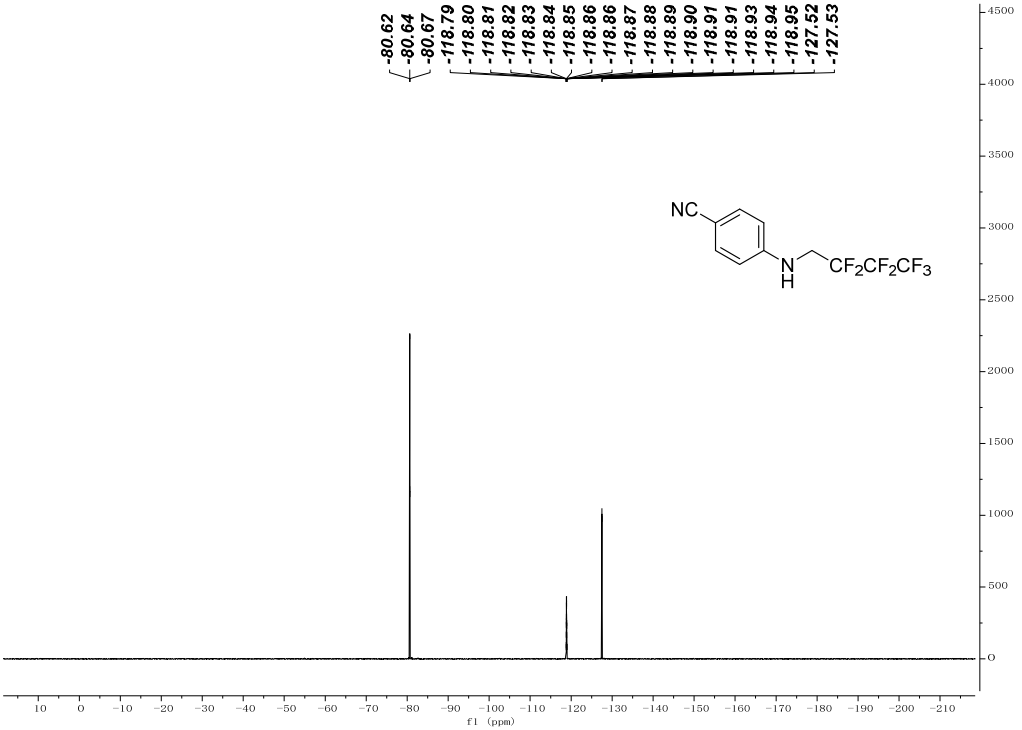
^{1}H NMR ($CDCl_3$, 400 MHz) of **12f**



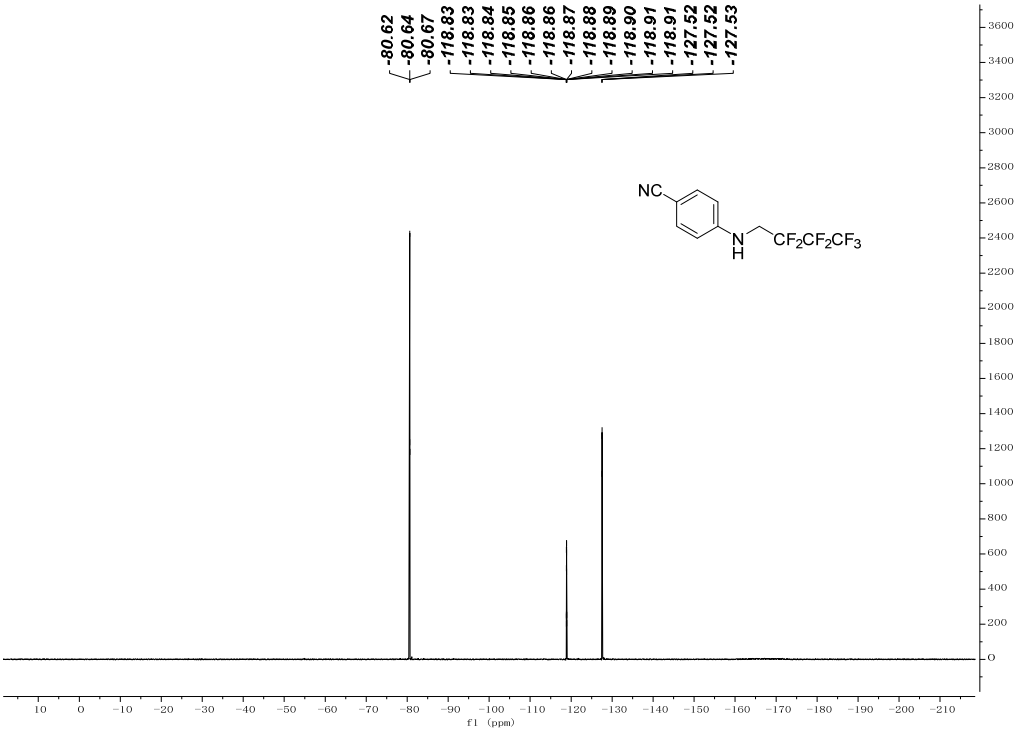
^{13}C NMR ($CDCl_3$, 100 MHz) of **12f**



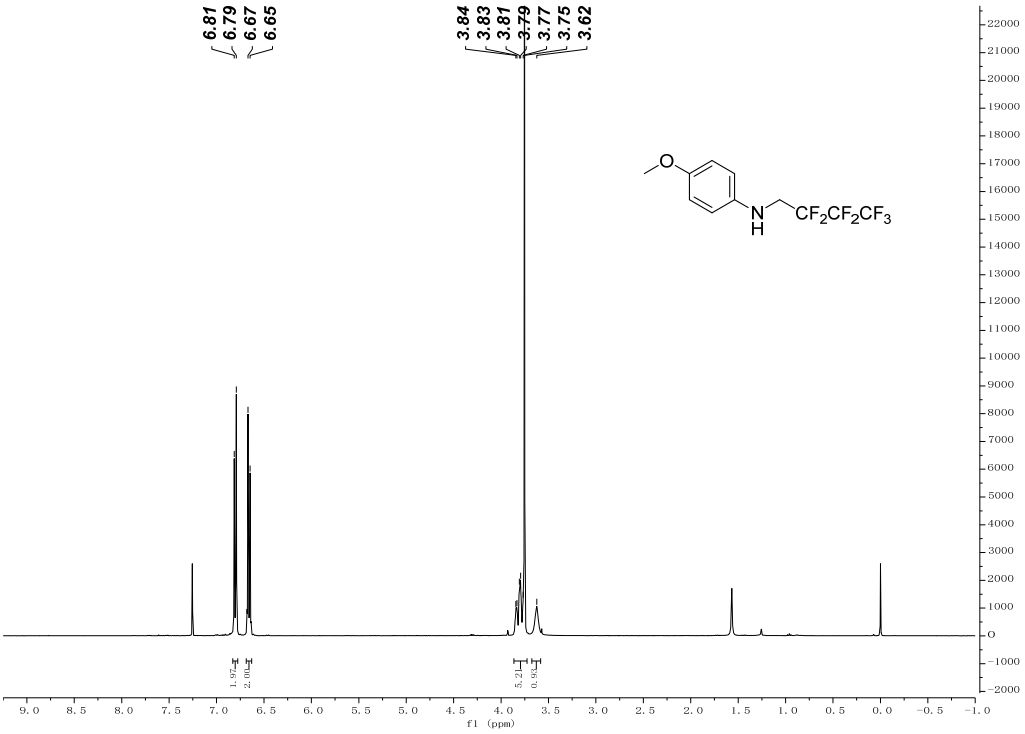
^{19}F NMR ($CDCl_3$, 376 MHz) of **12f**



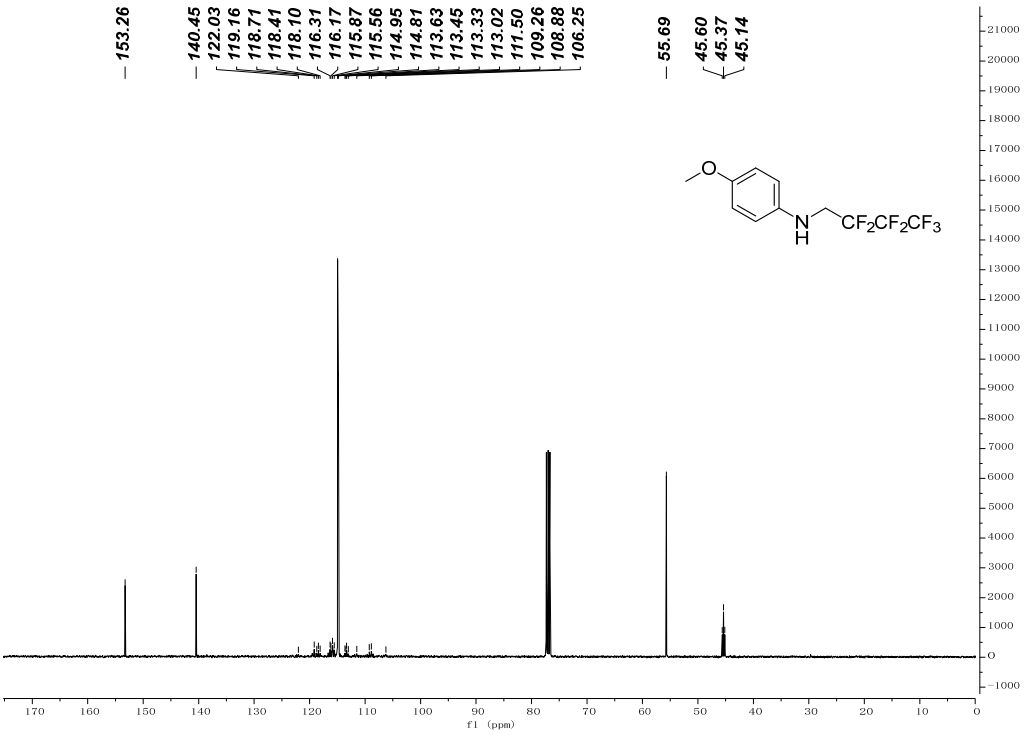
^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **12f**



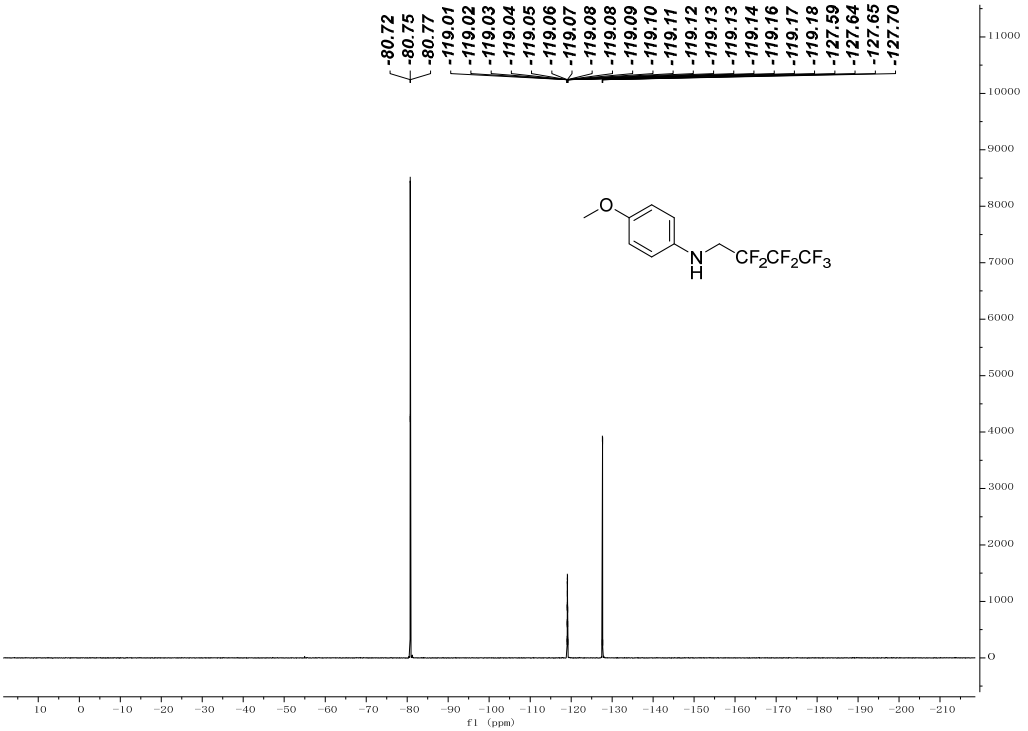
^{1}H NMR ($CDCl_3$, 400 MHz) of **12j**



^{13}C NMR ($CDCl_3$, 100 MHz) of **12j**



^{19}F NMR ($CDCl_3$, 376 MHz) of **12j**



^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) of **12j**