Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Electrochemical Vicinal Aminotrifluoromethylation of Alkenes: High Regioselective Acquisition of *β*-Trifluoromethylamines

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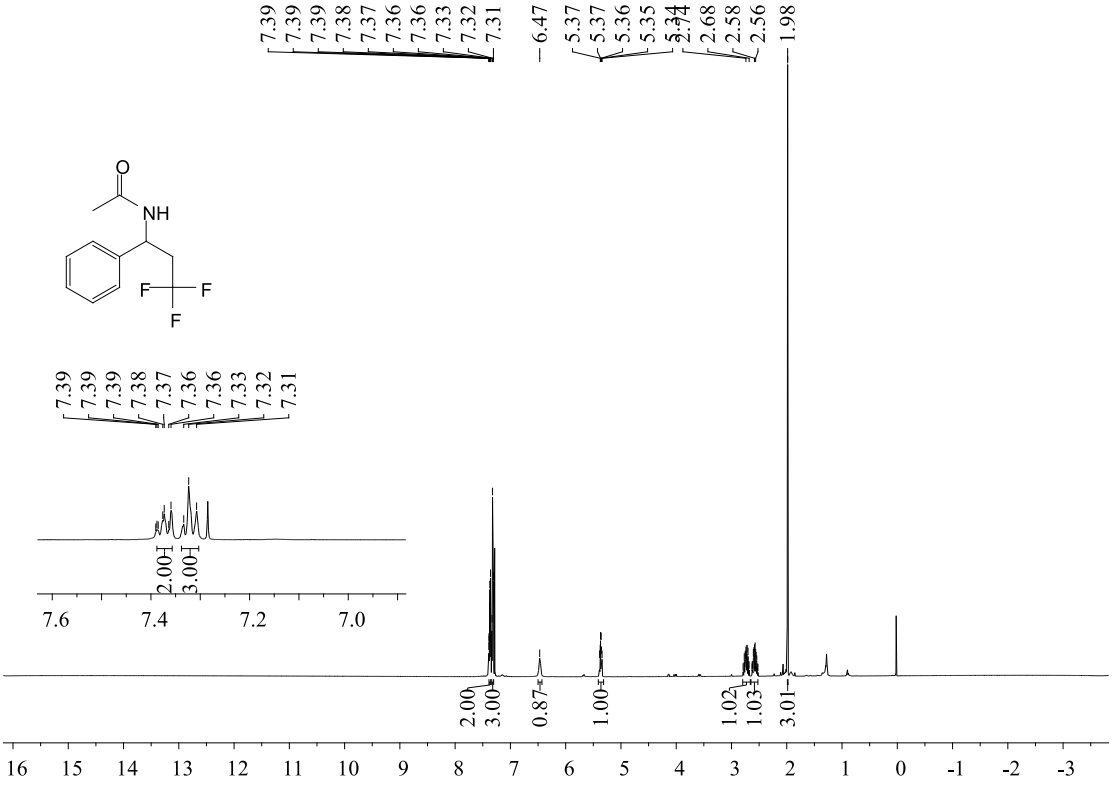
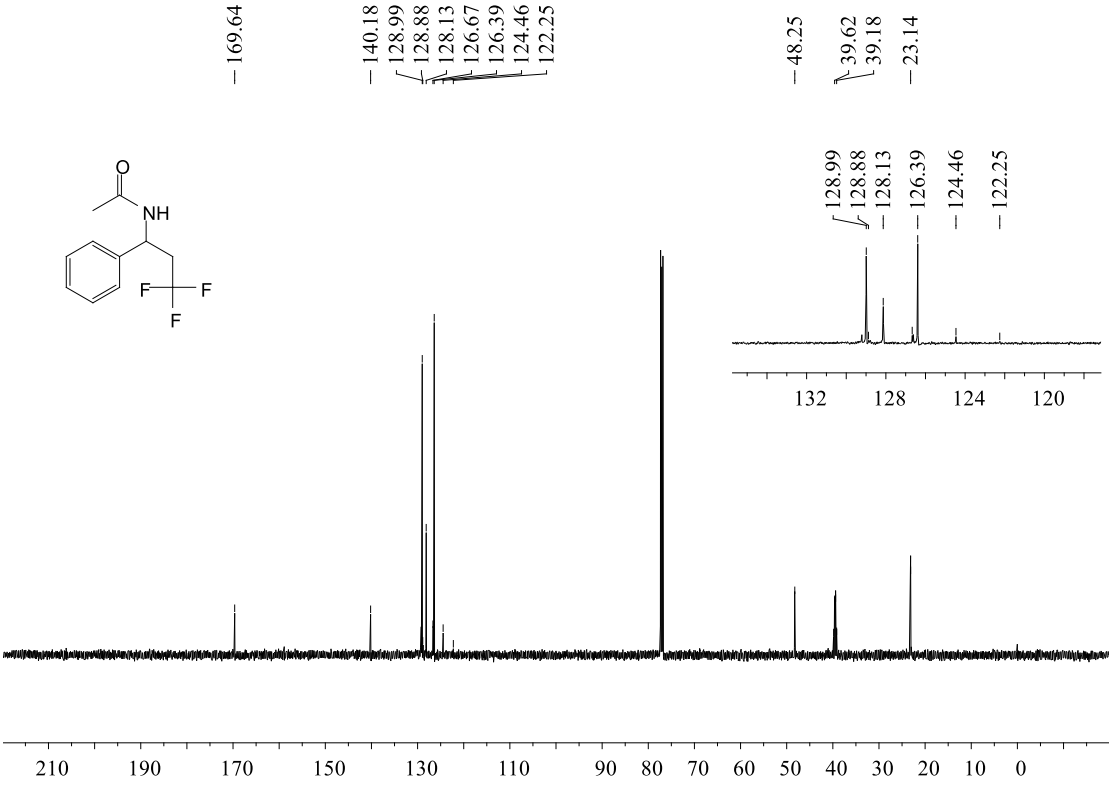
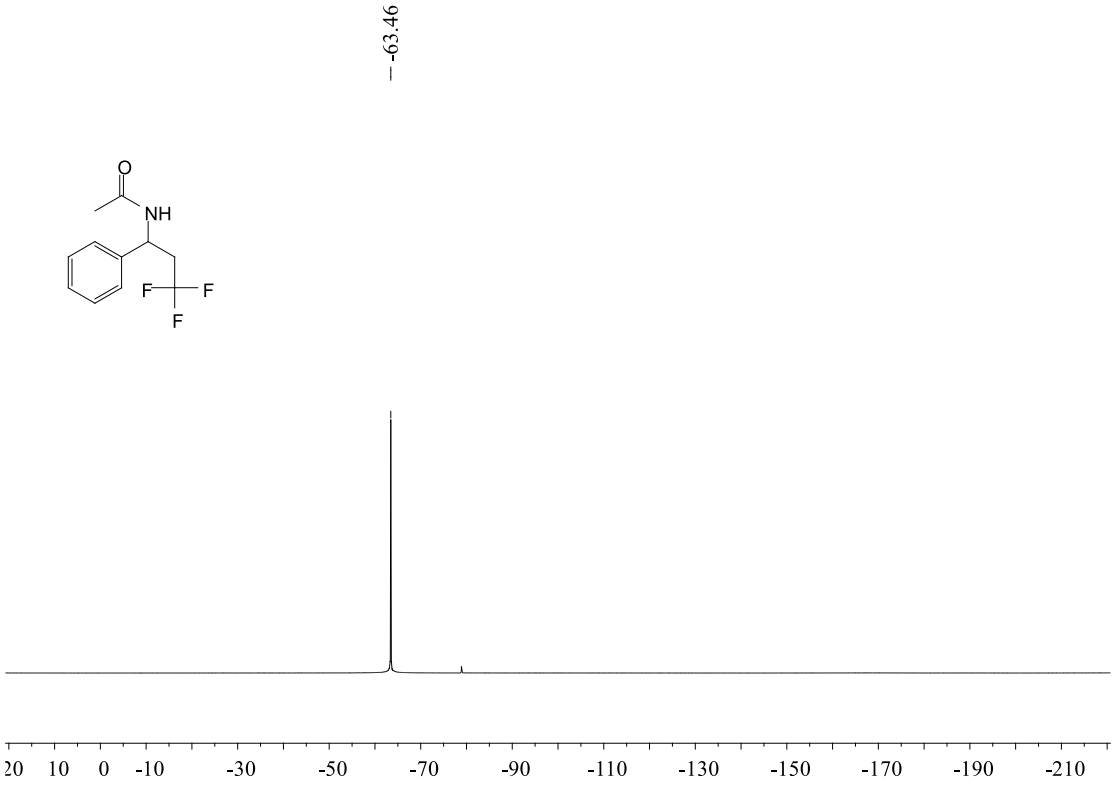


^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3a



^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound 3a



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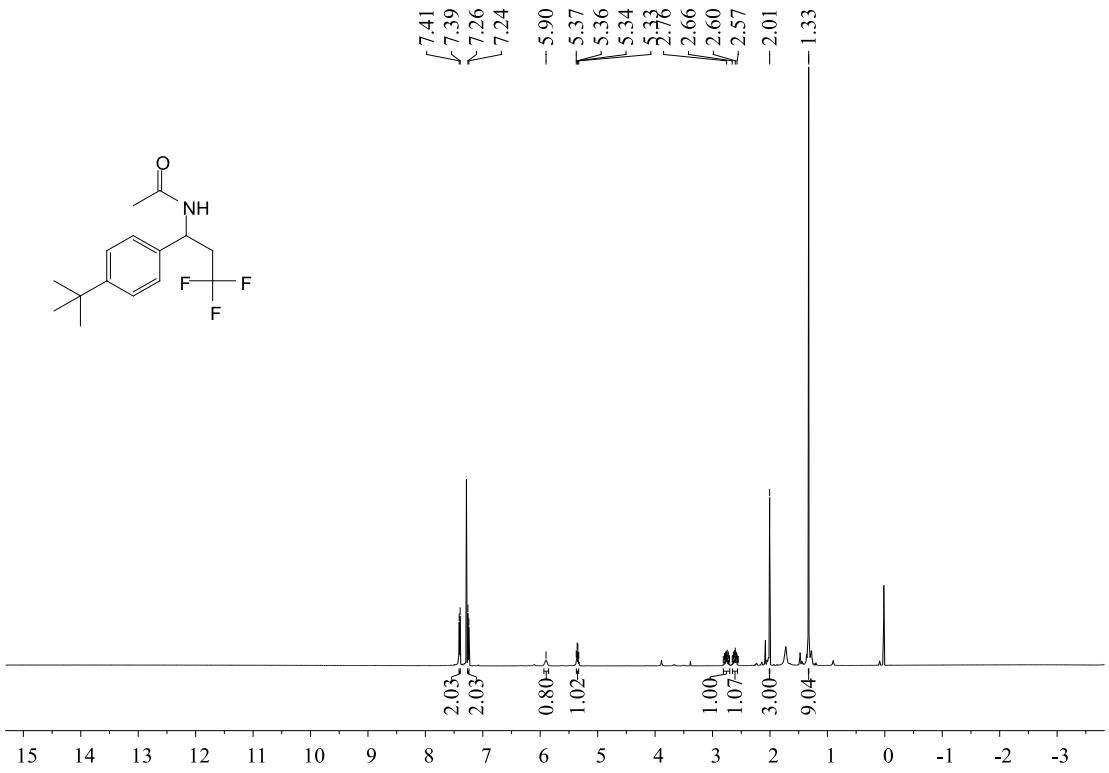
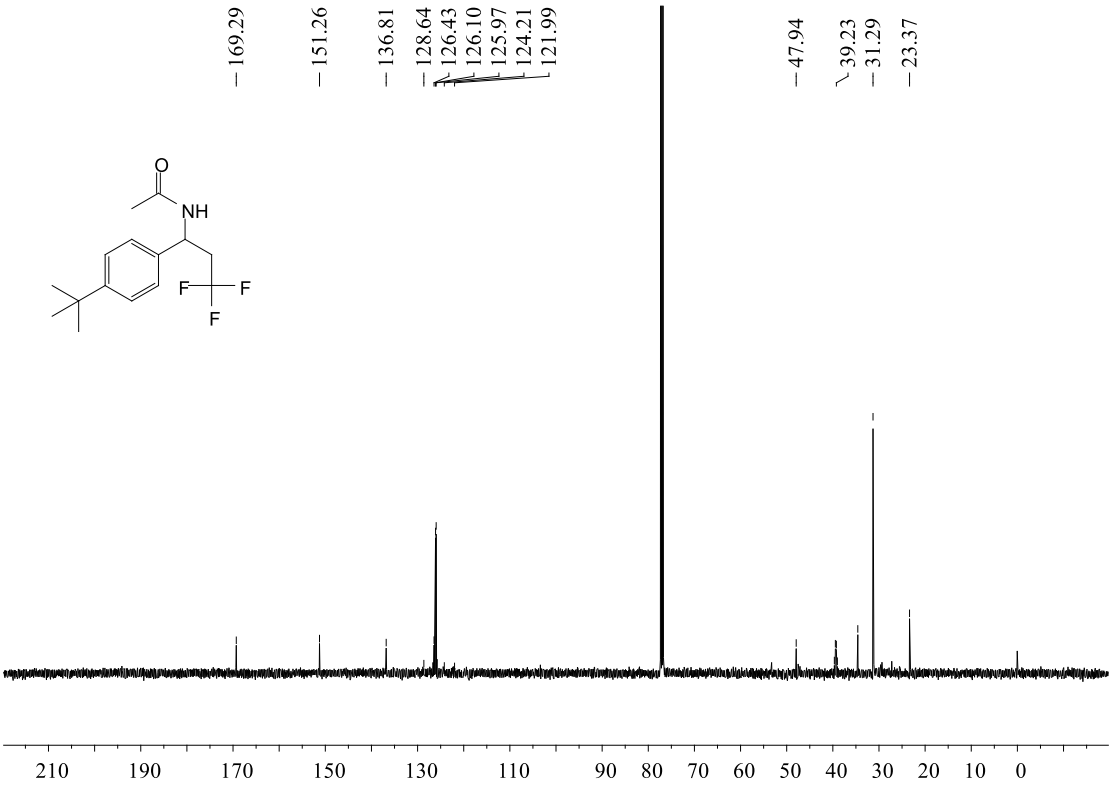
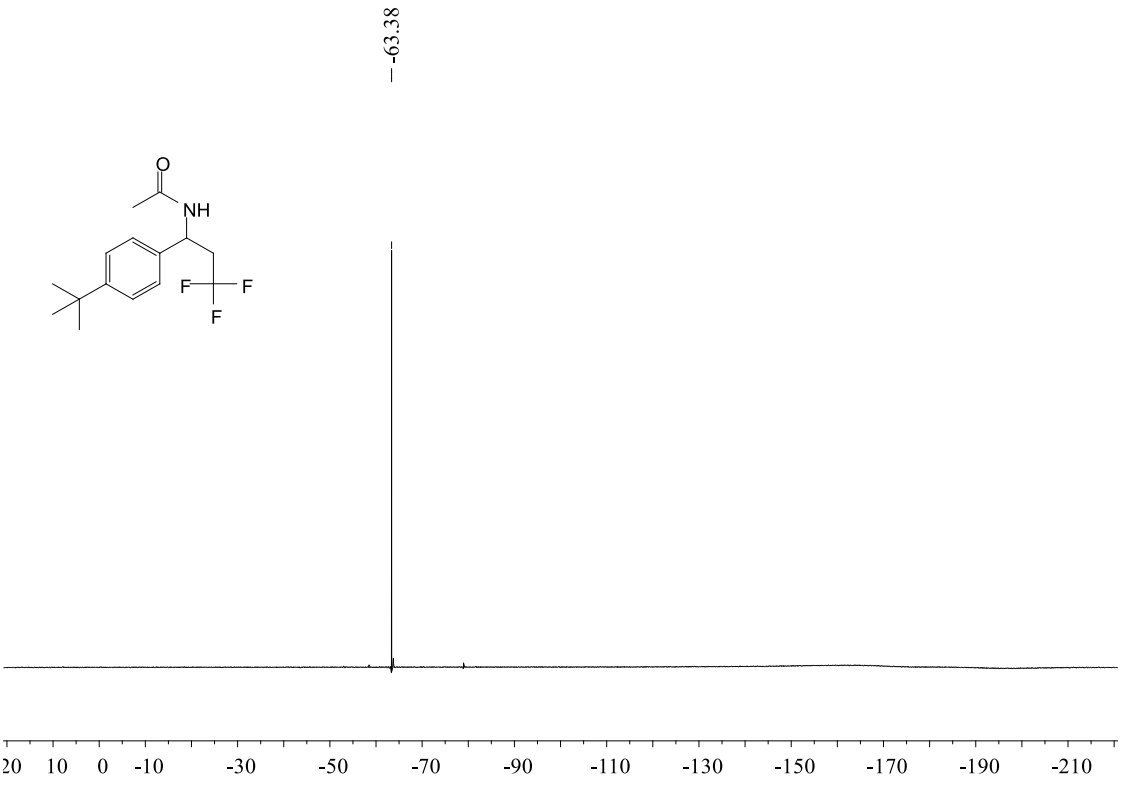


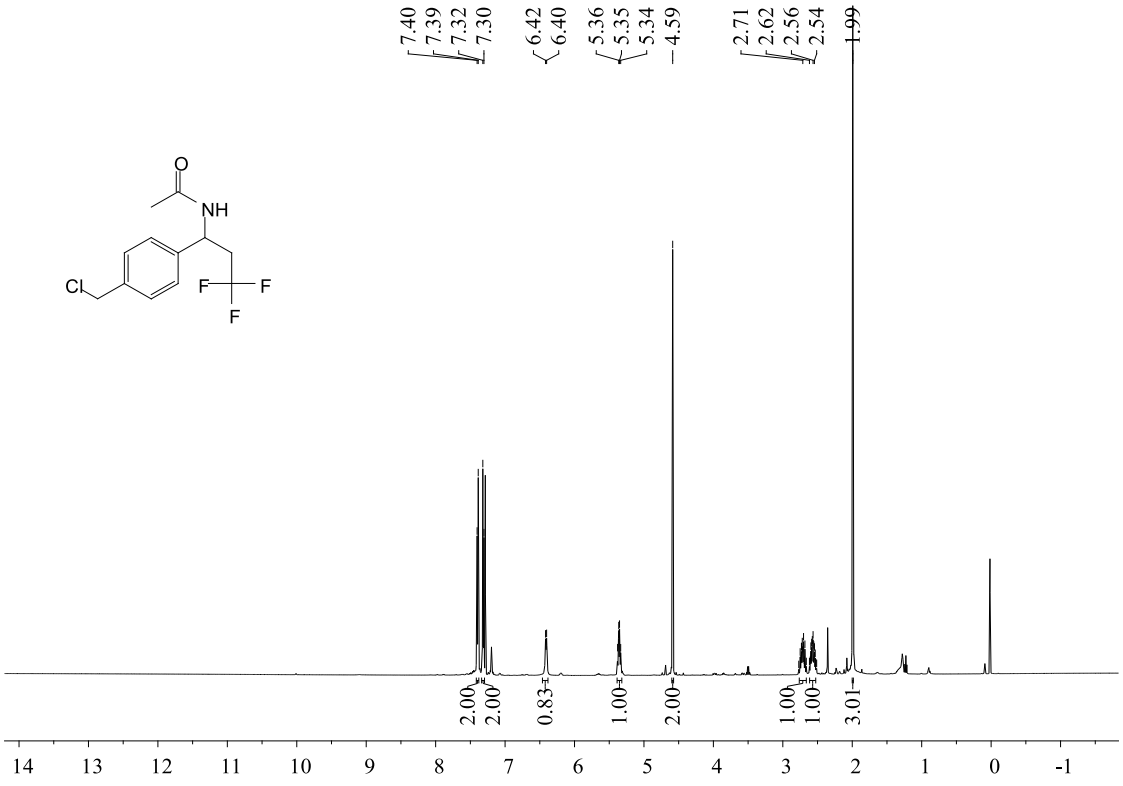
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3b



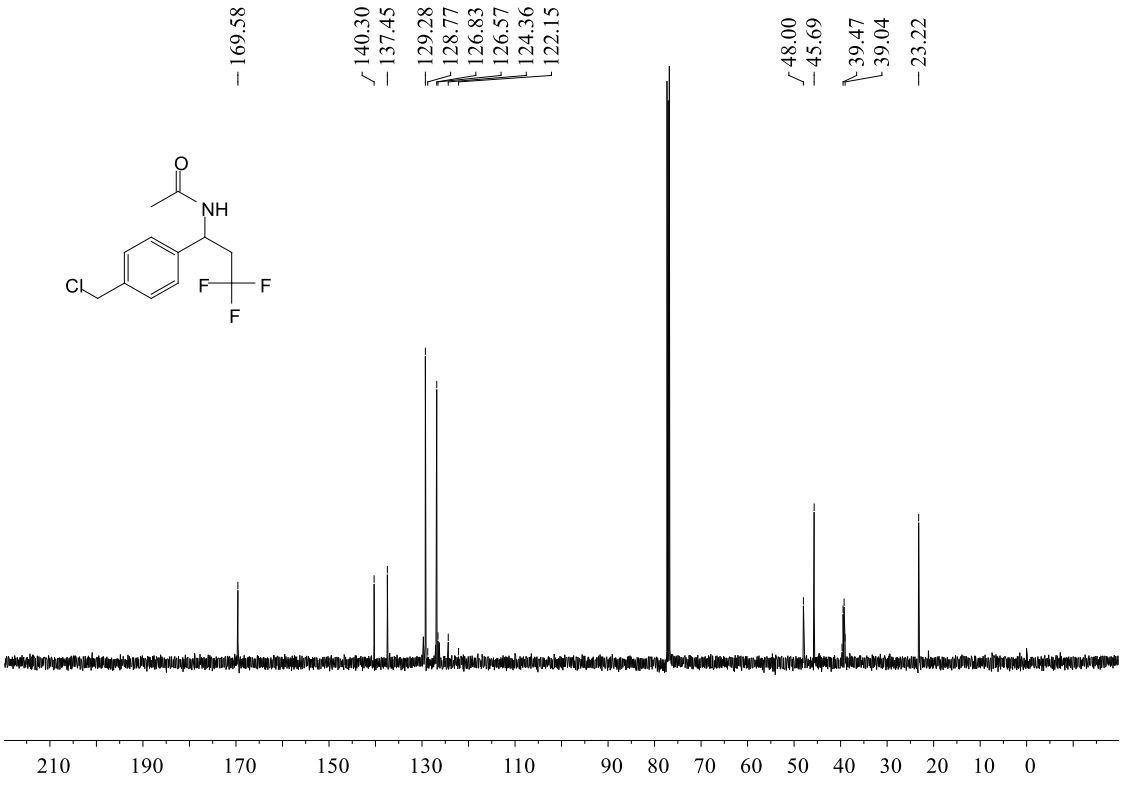
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound 3b



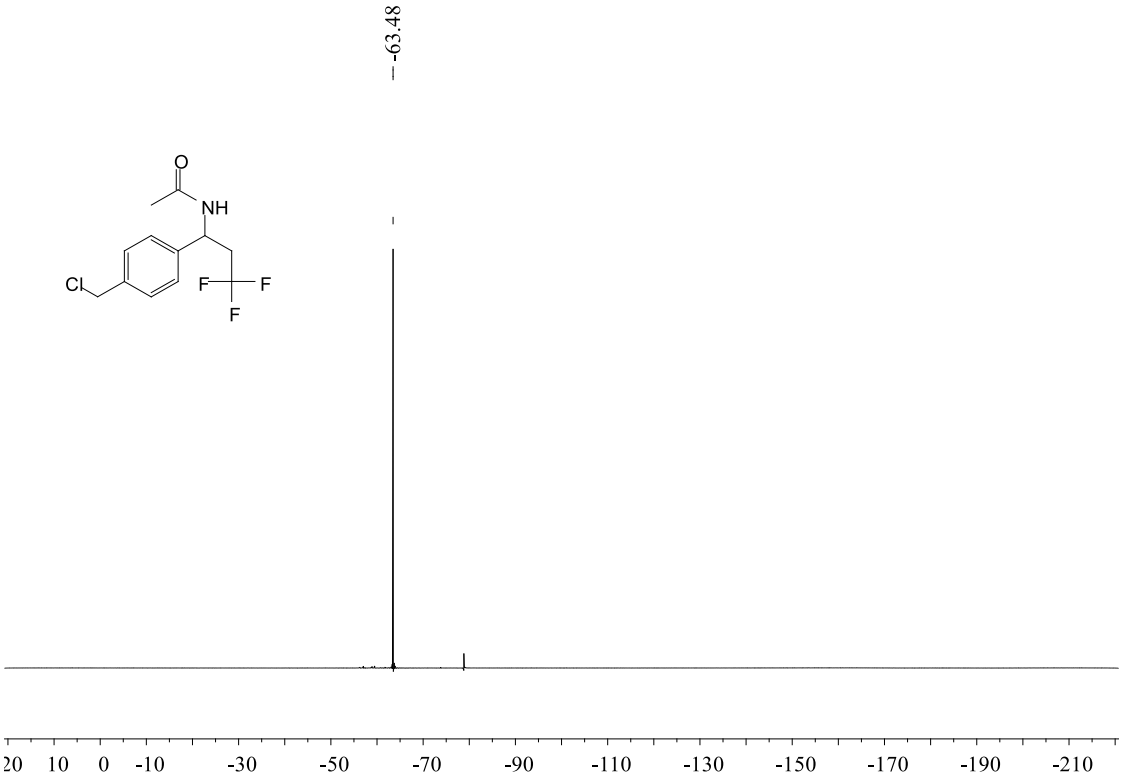
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3c



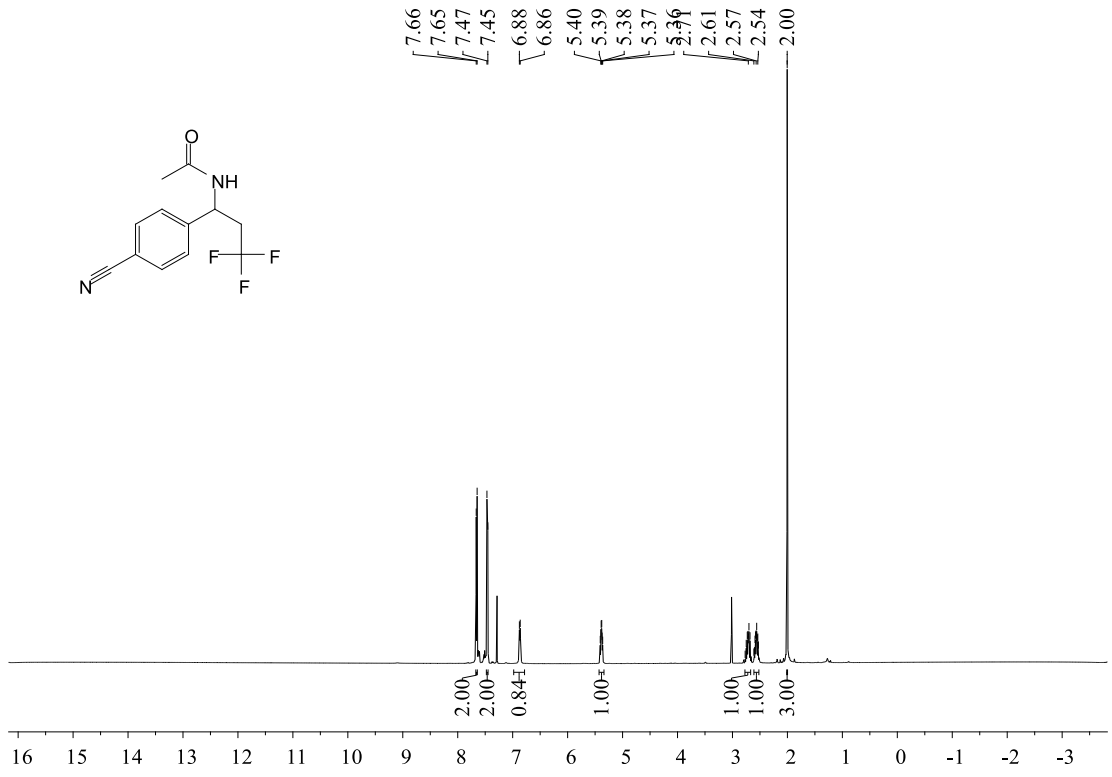
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3c



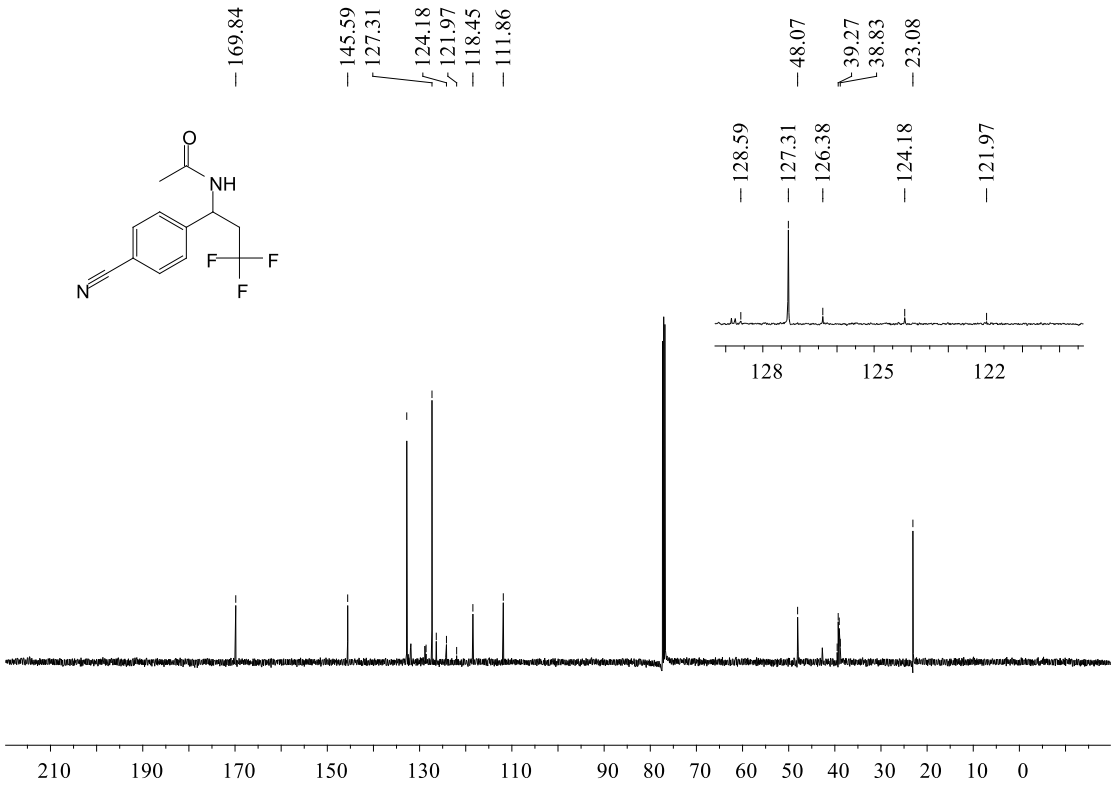
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound 3c



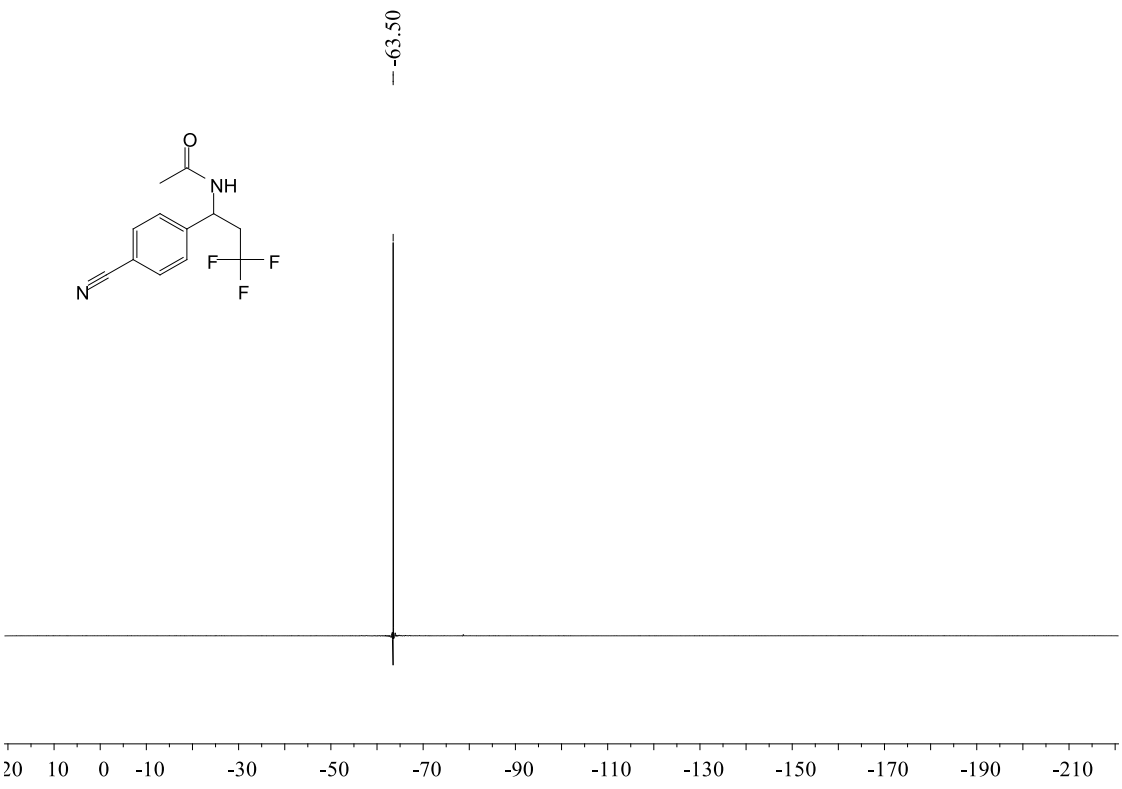
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3d



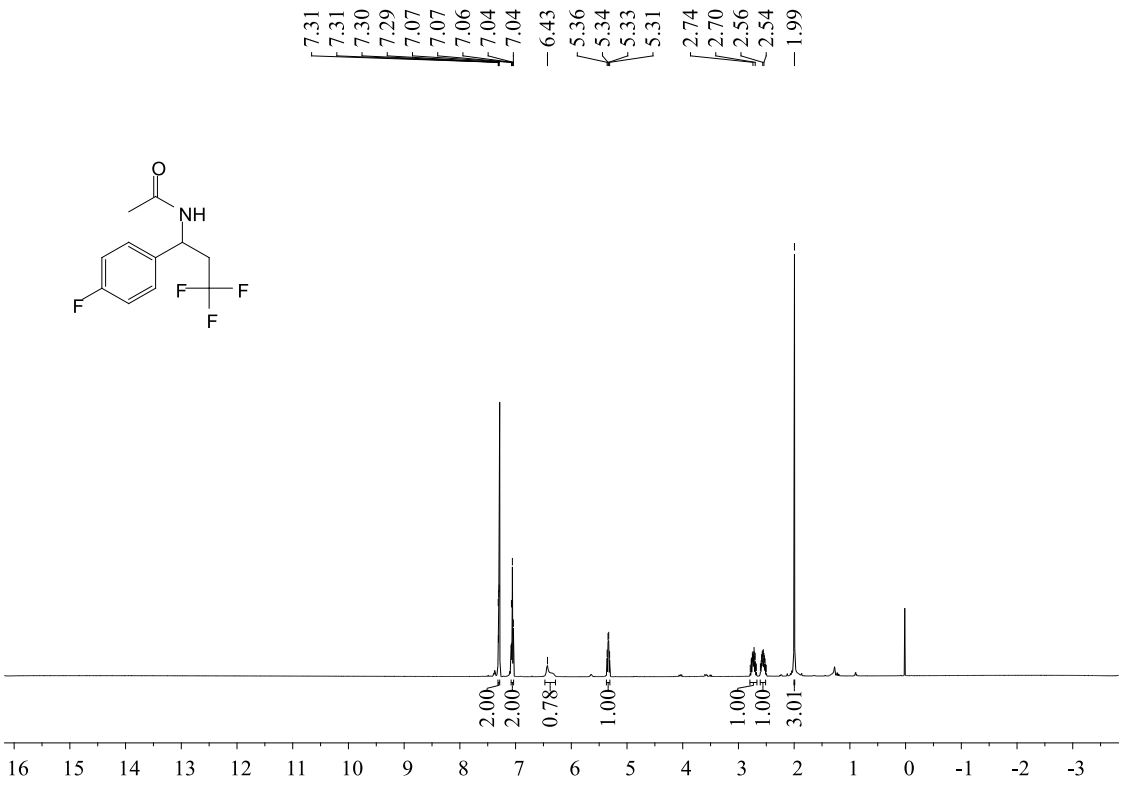
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3d



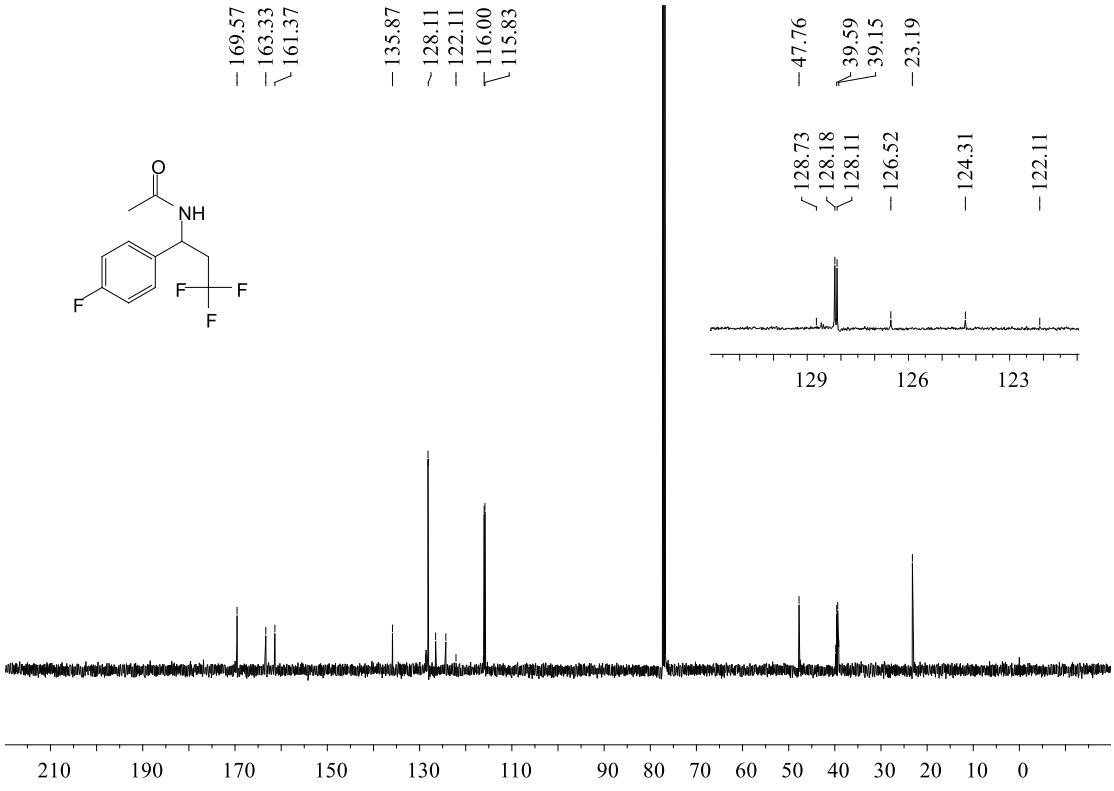
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound 3d



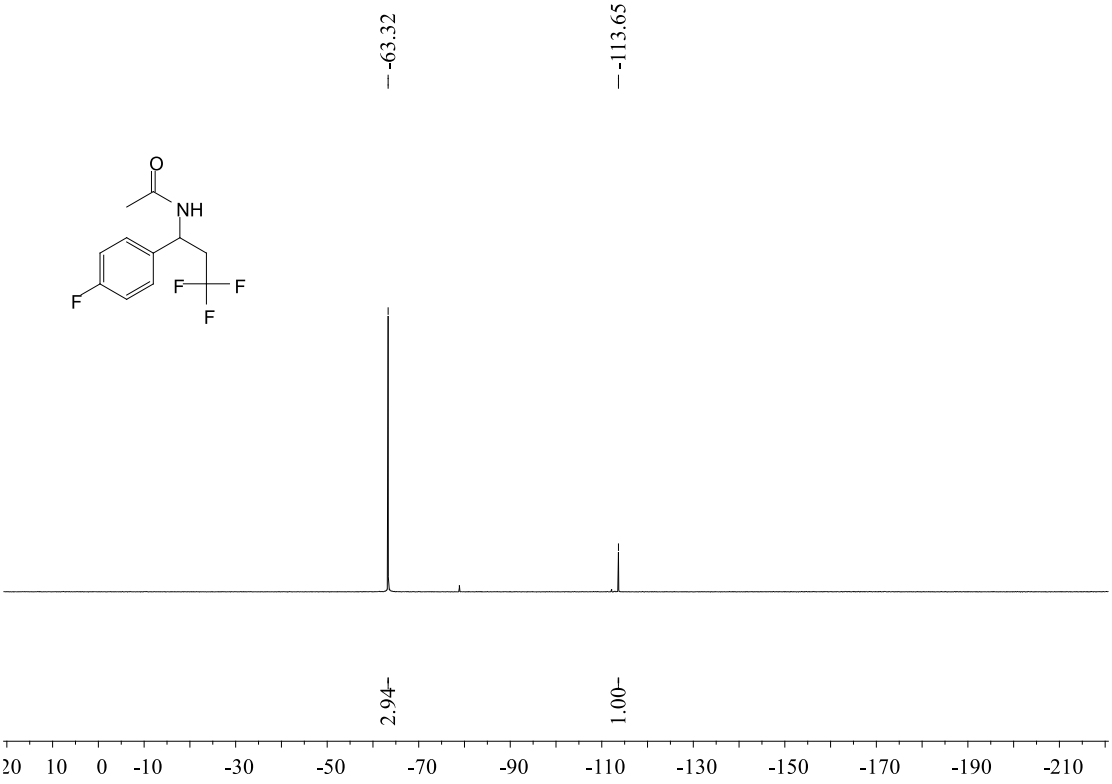
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3e



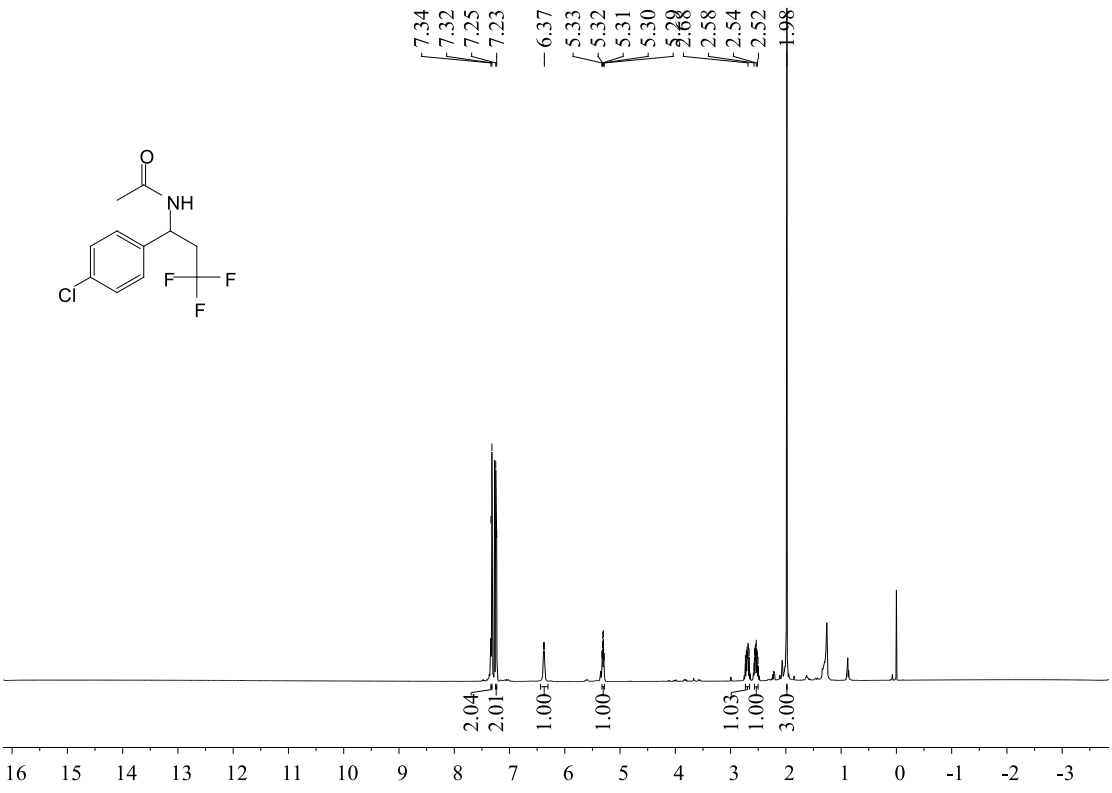
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3e



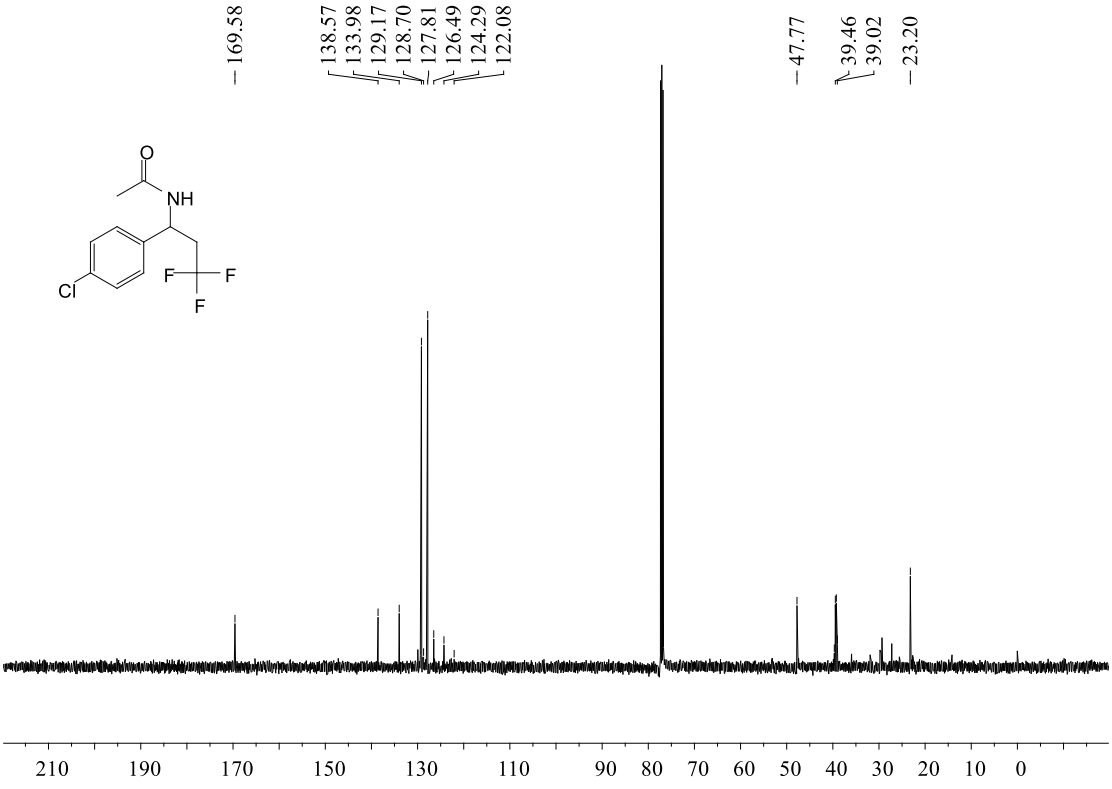
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound 3e



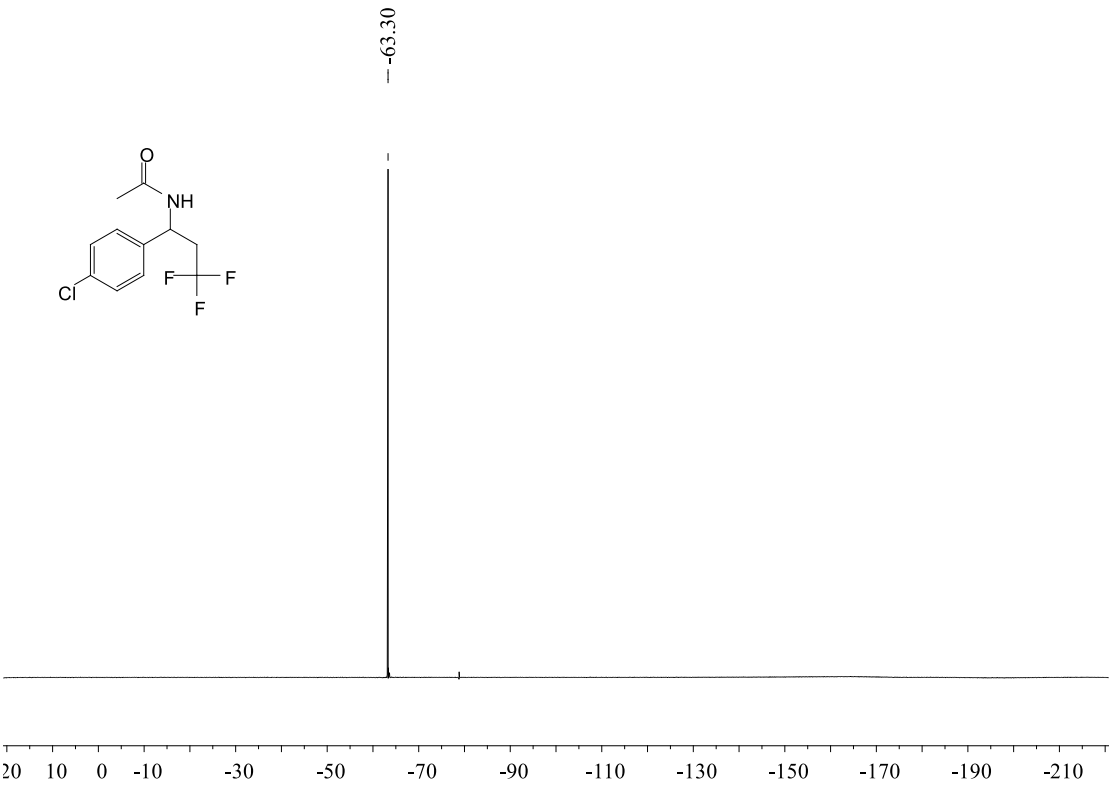
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3f



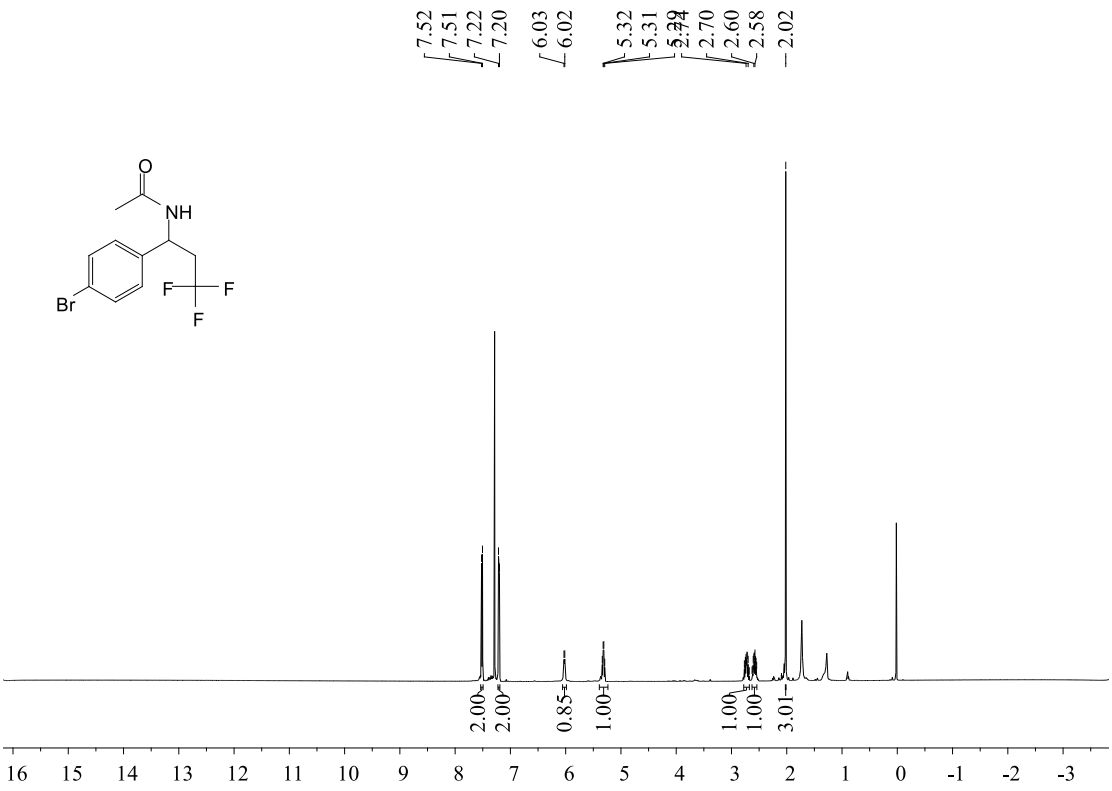
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3f



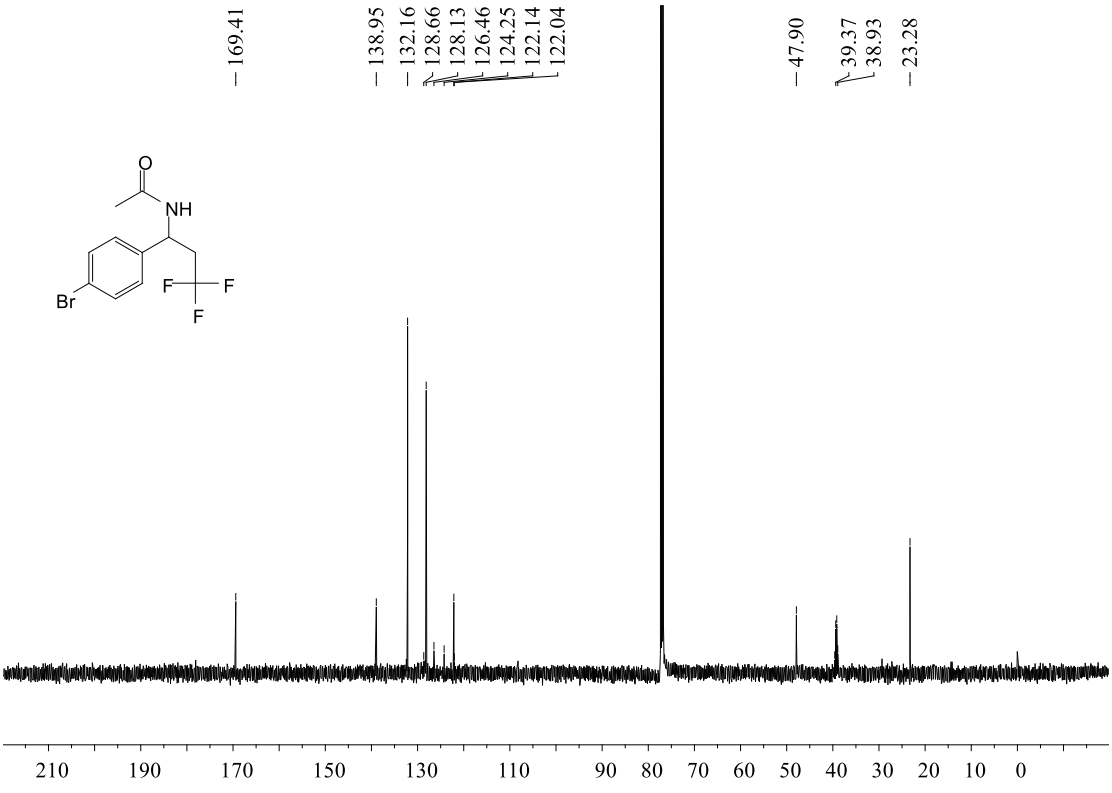
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound 3f



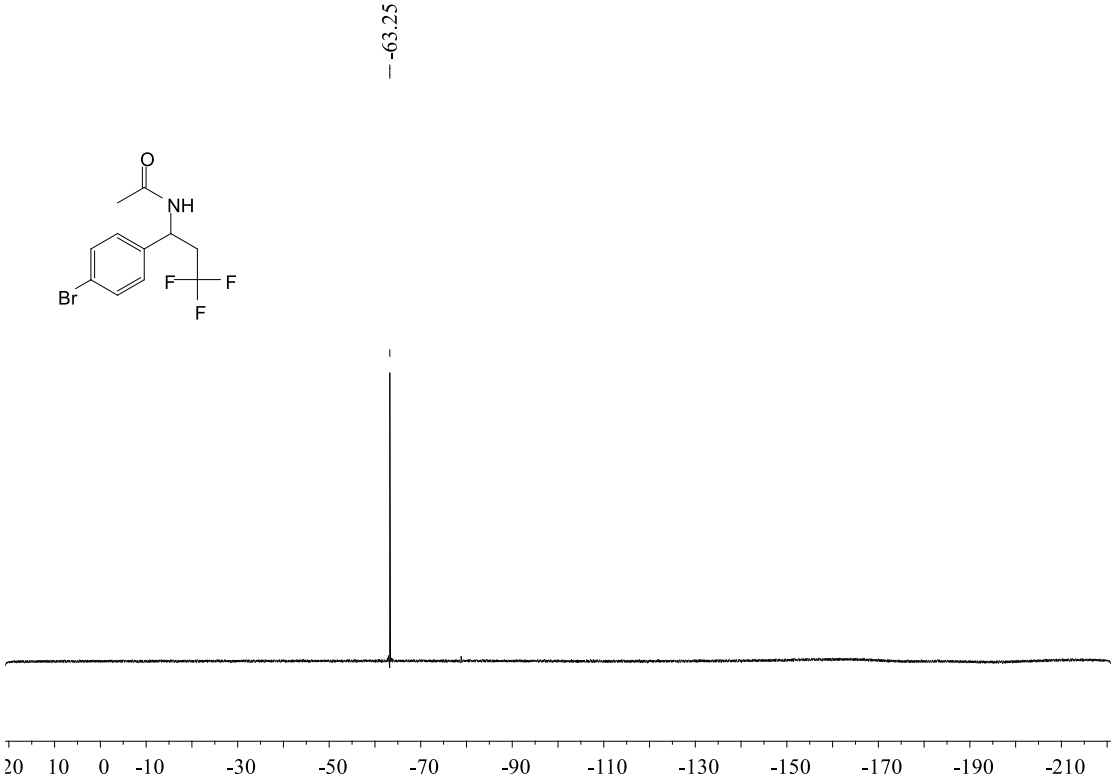
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3g



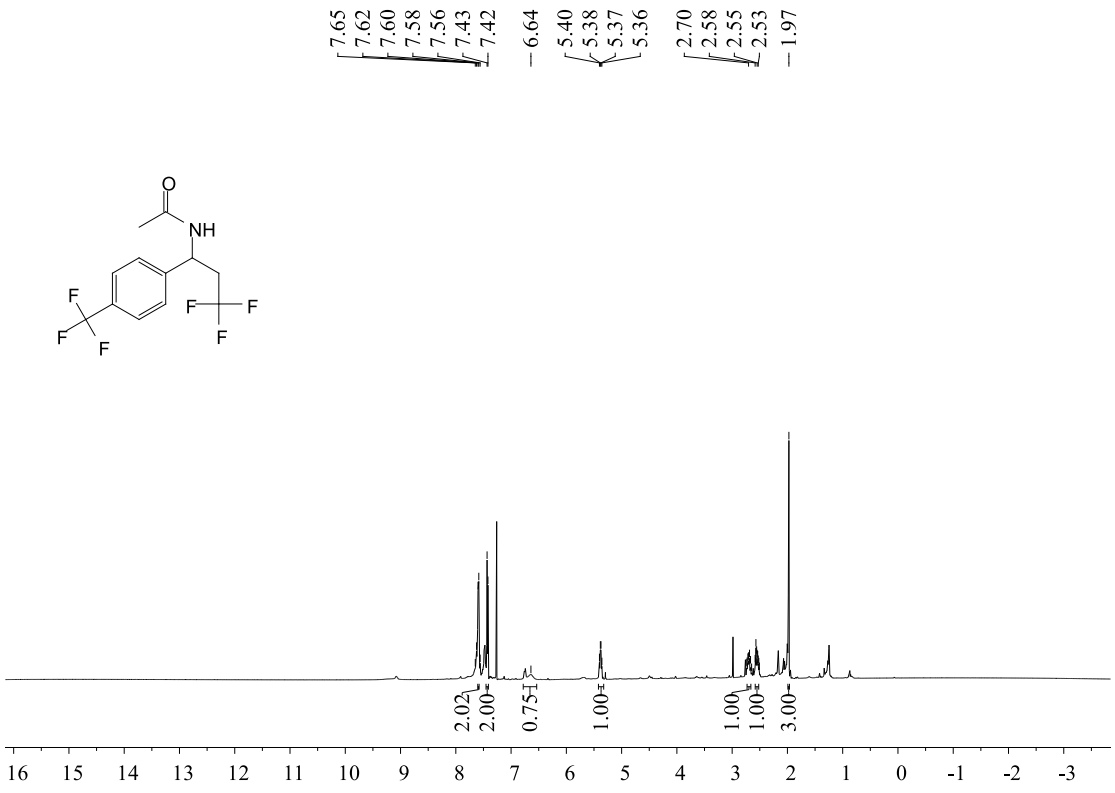
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3g



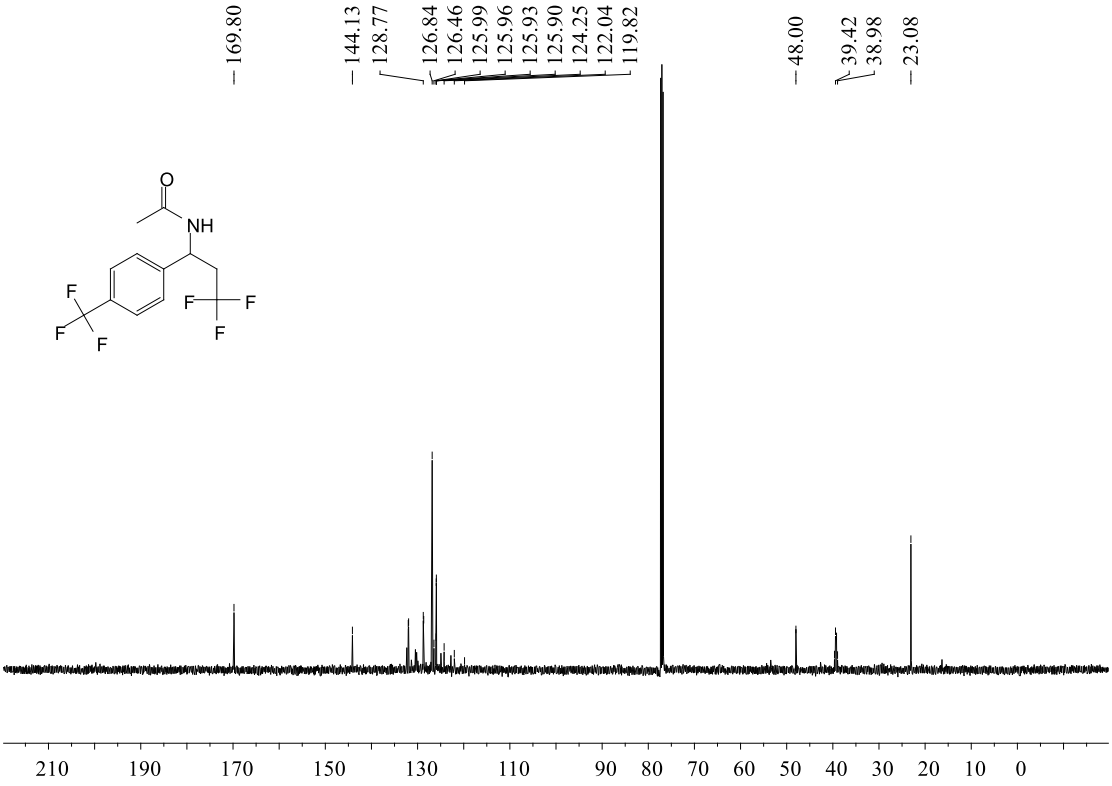
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound 3g



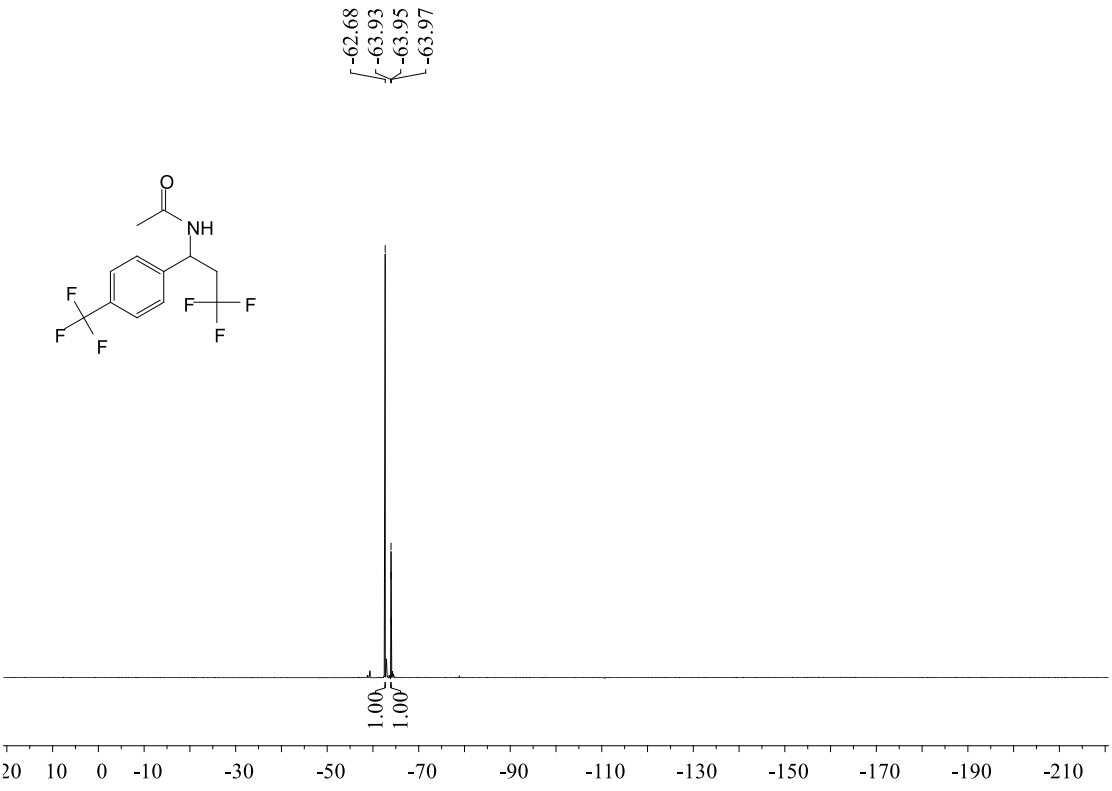
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3h



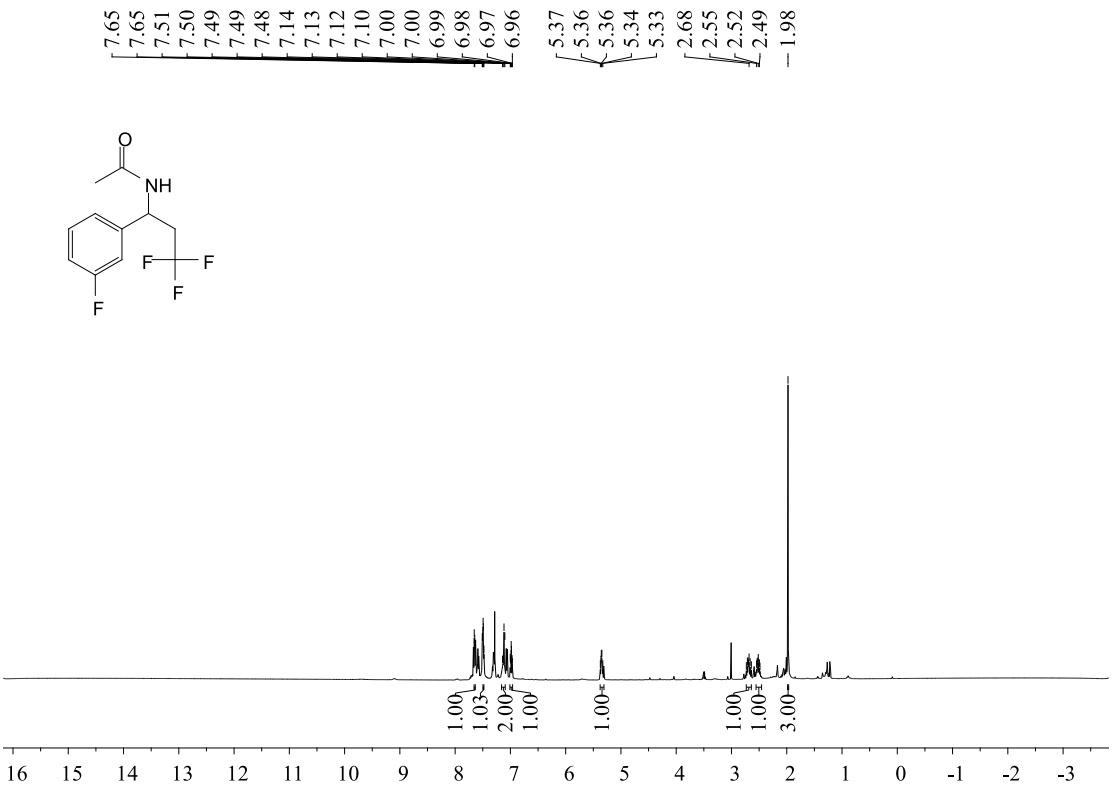
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3h



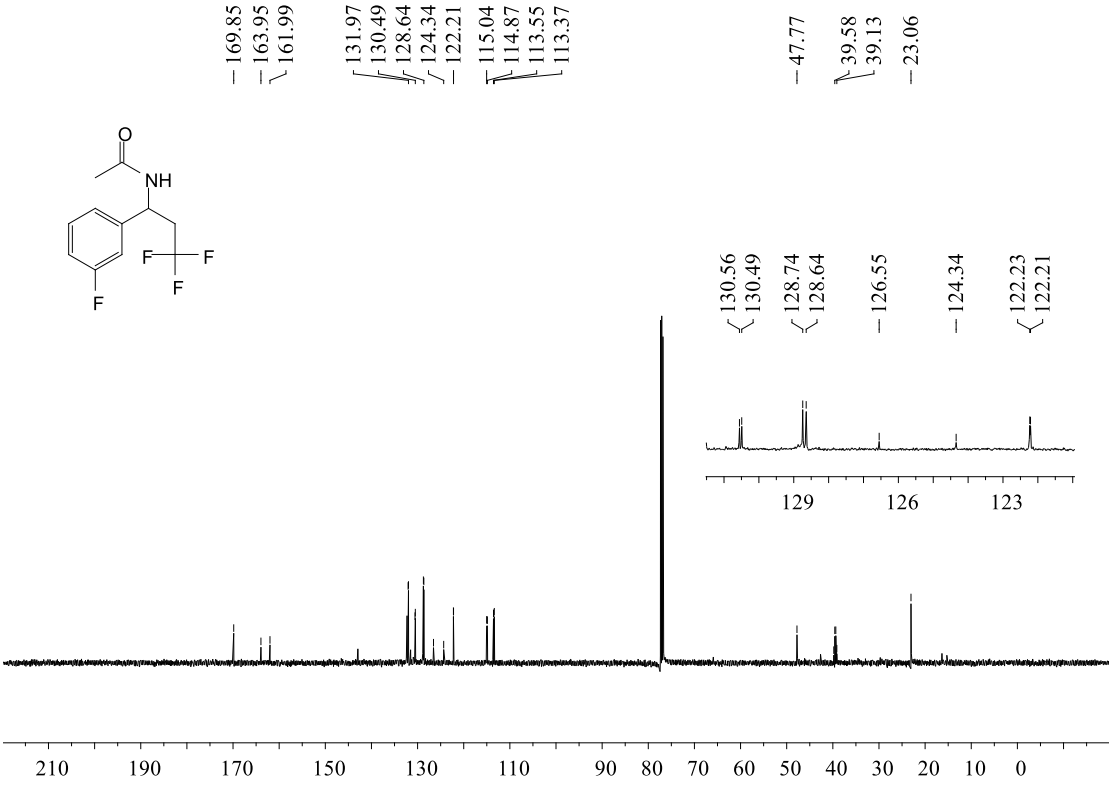
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound 3h



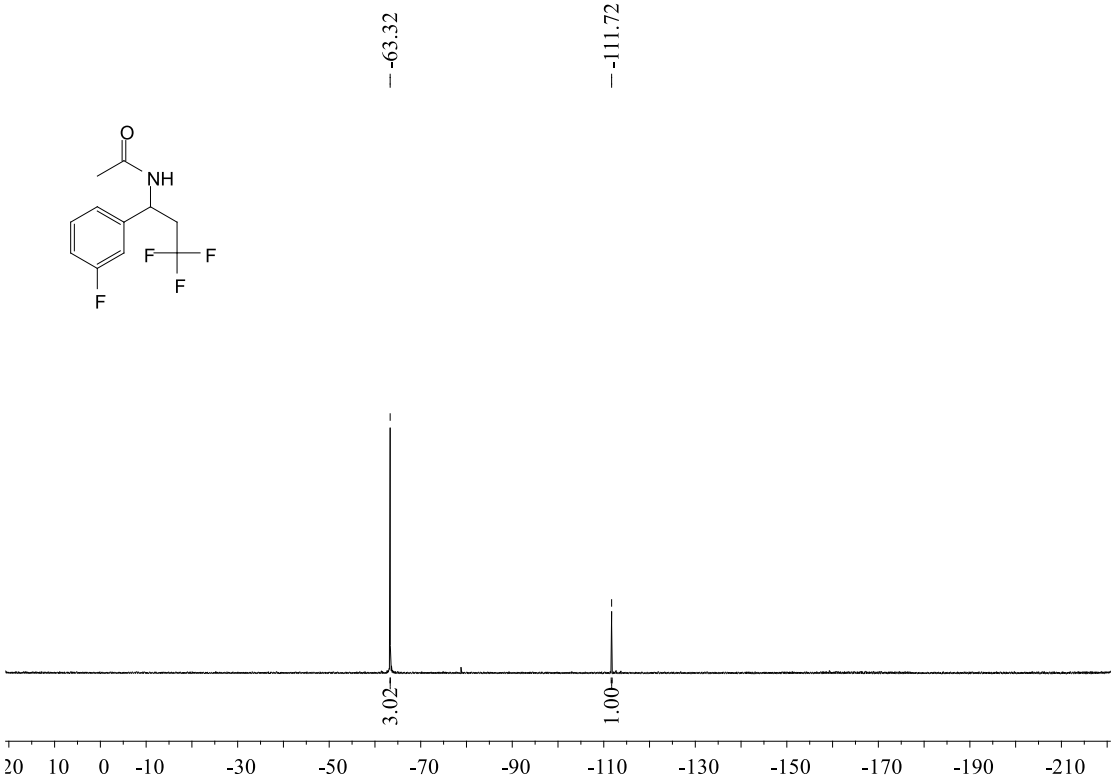
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3i



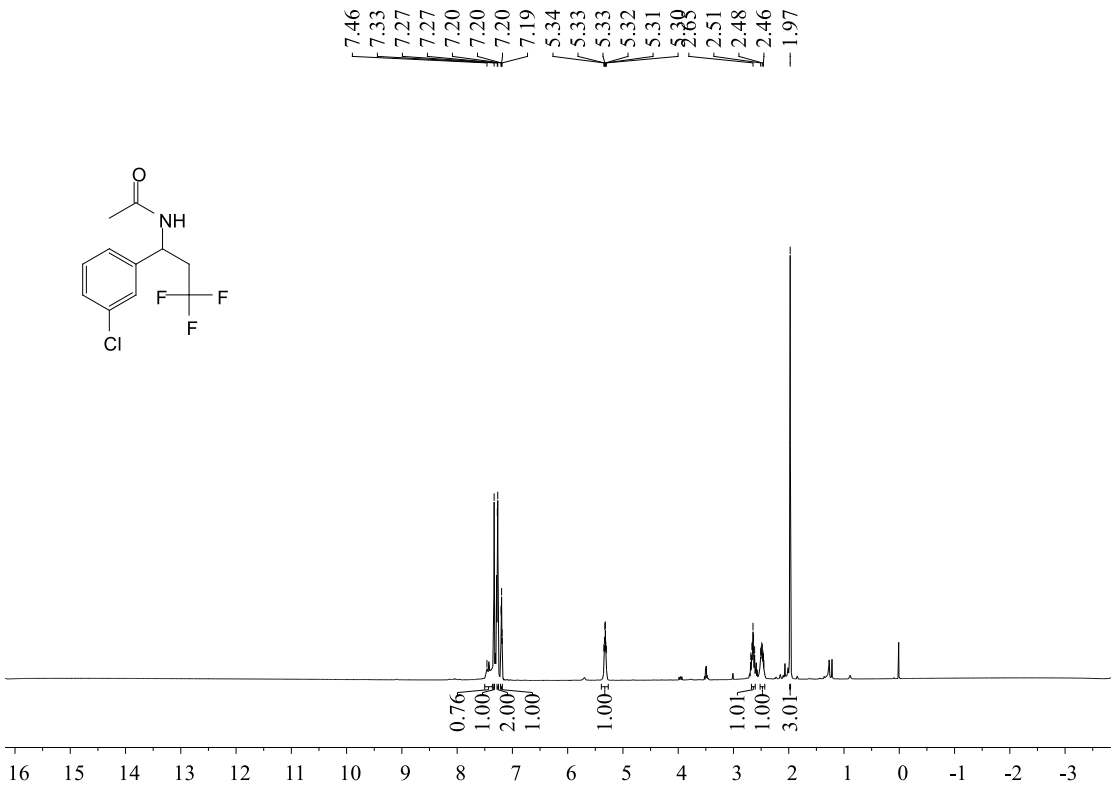
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3i



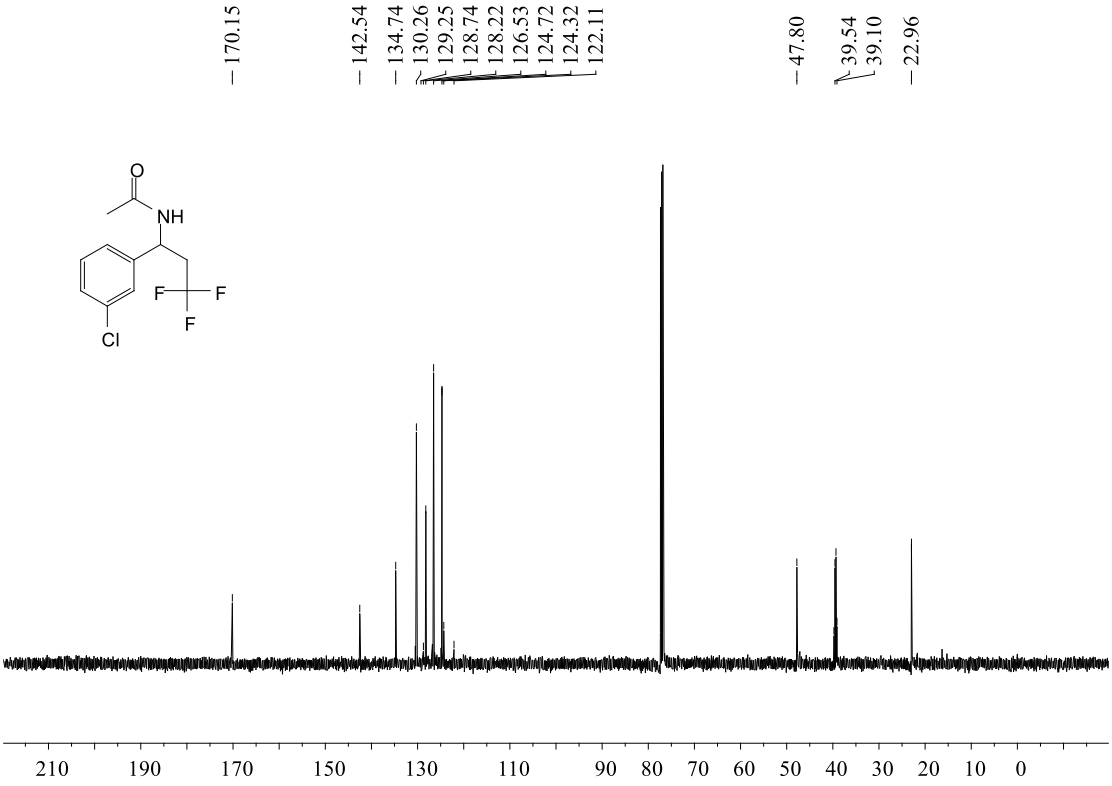
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound 3i



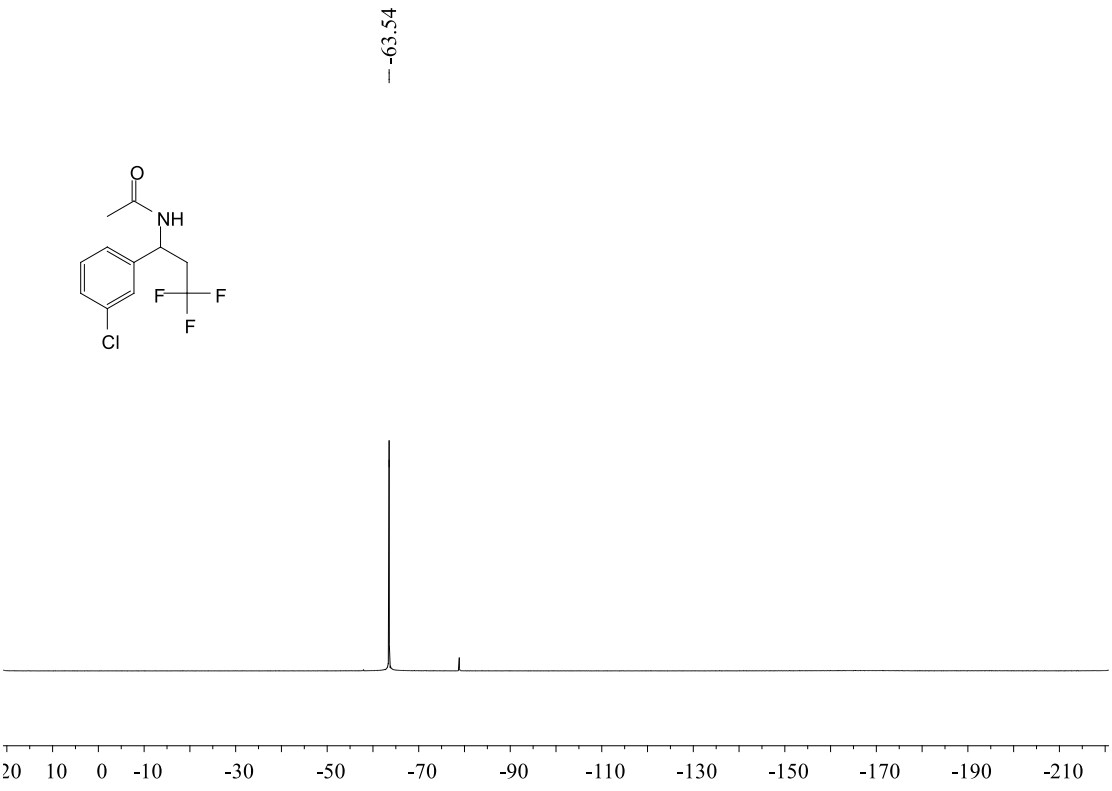
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3j



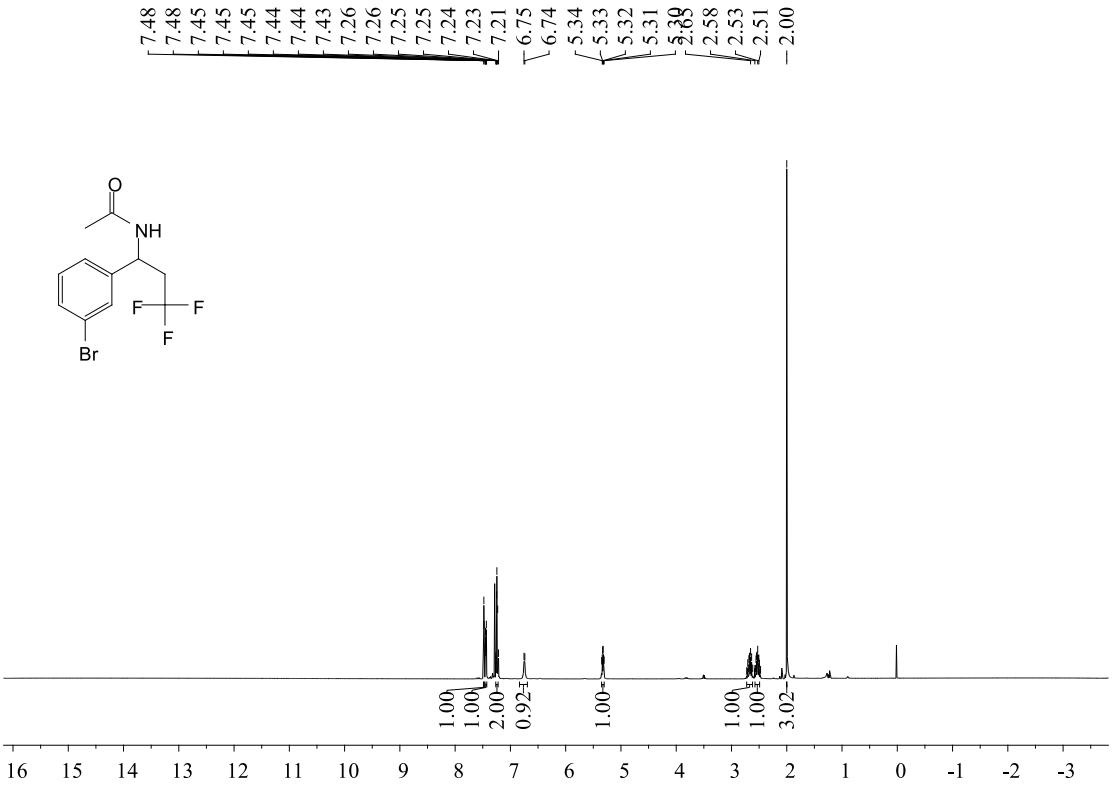
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3j



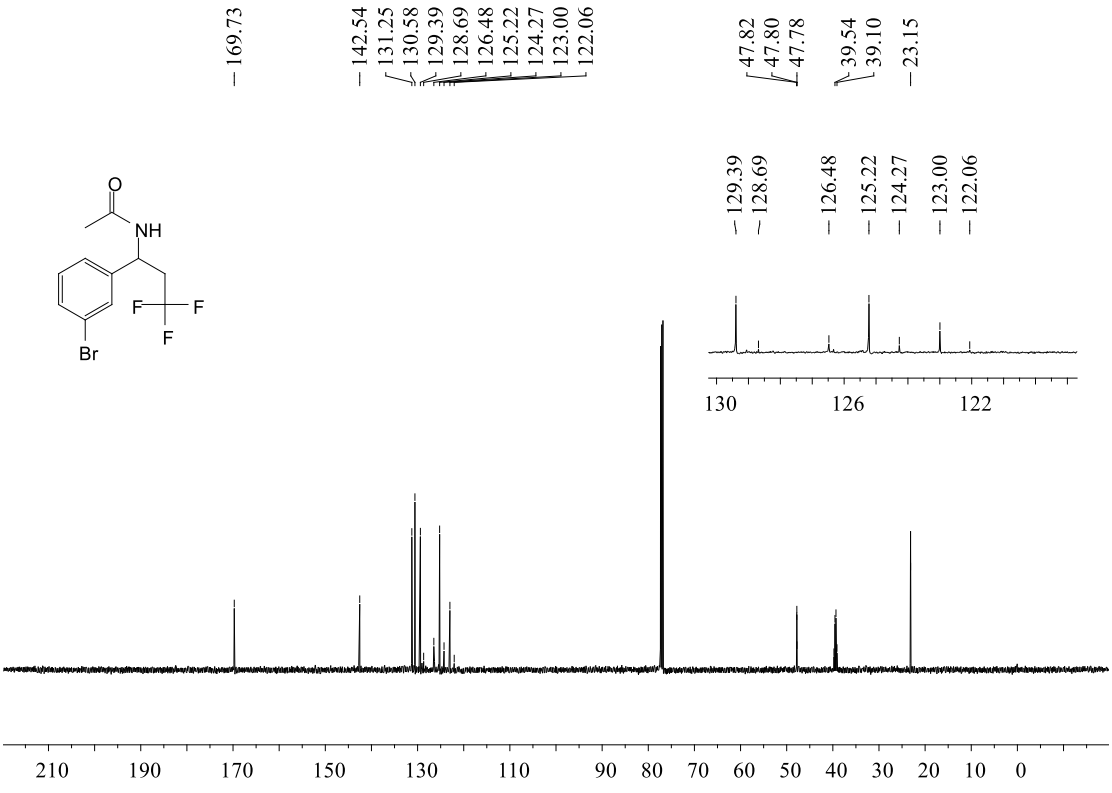
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound 3j



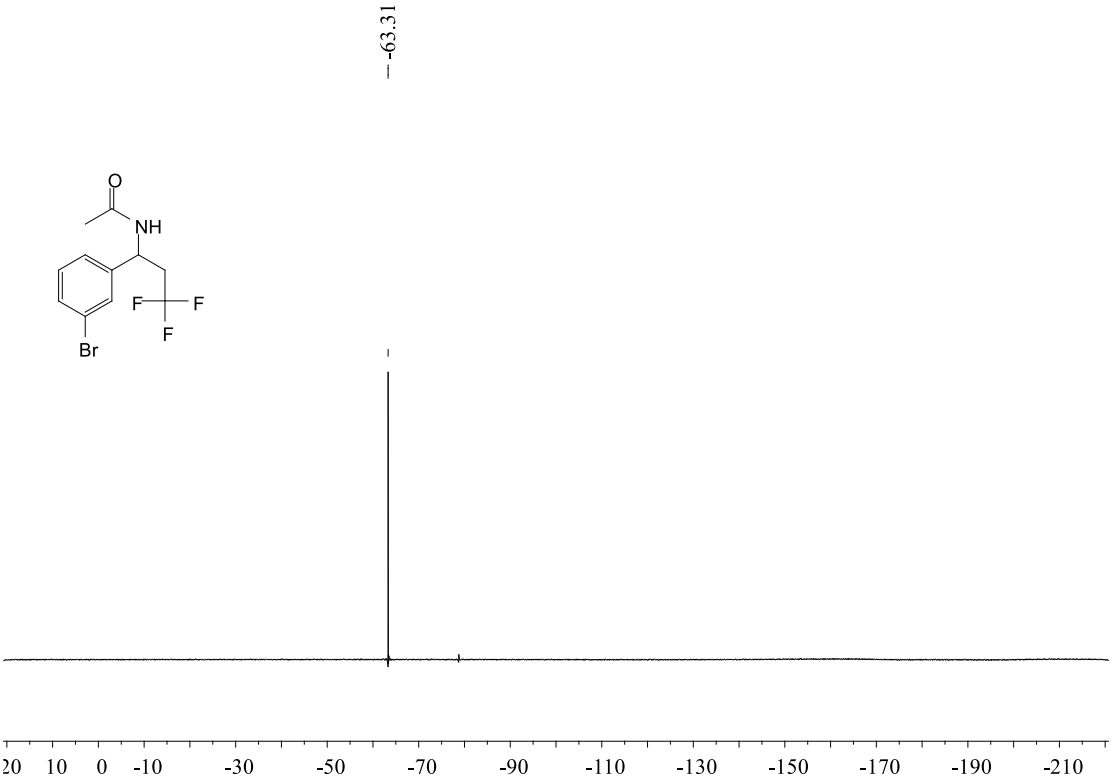
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3k



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3k

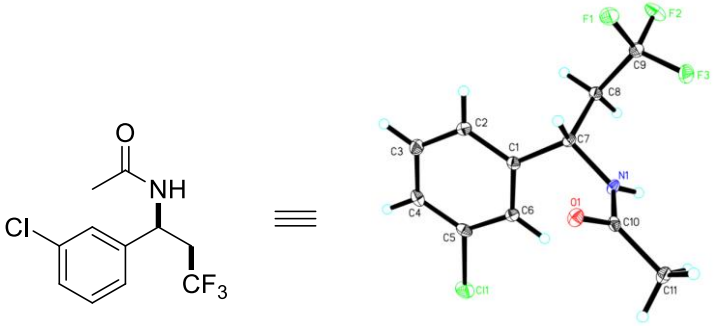


^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound 3k



2. X-ray Crystallographic Data

The X-ray crystallographic structures for **3j**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1905218.



3j crystallographic structure of **3j**

Table 1. Crystal Data and Structure Refinement for 3j.

Identification code	**3j**
Empirical formula	$C_{11}H_{11}ClF_3NO$
Formula weight	265.66
Temperature/K	100.00(10)

Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.4474(19)
b/Å	9.1512(10)
c/Å	9.2001(12)
α/	90
β/	103.529(13)
γ/	90
Volume/Å^3	1182.6(3)
Z	4
ρ_{calc}g/cm^3	1.492
μ/mm^{-1}	0.344
F(000)	544.0
Crystal size/mm^3	0.14 × 0.12 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/	5.312 to 59.022
Index ranges	-13 ≤ h ≤ 18, -12 ≤ k ≤ 8, -12 ≤ l ≤ 12
Reflections collected	6107
Independent reflections	2821 [R_{int} = 0.0300, R_{sigma} = 0.0511]
Data/restraints/parameters	2821/0/155
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0476, wR_2 = 0.0988
Final R indexes [all data]	R_1 = 0.0646, wR_2 = 0.1088
Largest diff. peak/hole / e Å^{-3}	0.32/-0.41

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3j.

Atom	*x*	*y*	*z*	U(eq)
Cl1	-63.5(4)	6921.0(7)	-1448.5(7)	33.81(18)
F1	-5199.4(9)	2961.9(15)	-3101.7(14)	31.9(3)
F2	-5377.6(10)	3716.6(15)	-973.5(16)	34.4(4)
F3	-4472.9(10)	1881.7(13)	-1099.5(15)	30.0(3)
O007	-2244.1(11)	1452.7(15)	-3489.0(14)	20.0(3)
N1	-2544.7(12)	2634.1(18)	-1498.4(18)	15.5(4)
C1	-2608.2(14)	5026(2)	-2778(2)	16.0(4)
C2	-3059.2(16)	5953(2)	-3935(2)	22.4(5)
C3	-2591.0(17)	7164(2)	-4312(3)	24.6(5)
C4	-1664.3(16)	7474(2)	-3548(2)	22.2(5)
C5	-1226.7(15)	6554(2)	-2413(2)	19.9(4)

C6	-1680.9(15)	5334(2)	-2016(2)	17.4(4)
C7	-3159.5(14)	3722(2)	-2390(2)	15.3(4)
C8	-3913.7(14)	4238(2)	-1565(2)	17.1(4)
C9	-4727.1(15)	3202(2)	-1670(2)	19.7(4)
C10	-2115.1(14)	1588(2)	-2121(2)	15.4(4)
C11	-1469.0(15)	580(2)	-1065(2)	19.9(5)

Table 3. Anisotropic Displacement Parameters ($Å^2×10^3$) for 3j.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	22.7(3)	42.3(4)	34.4(3)	-3.2(3)	2.5(2)	-12.1(3)
F1	25.0(8)	44.1(8)	22.0(7)	1.9(6)	-3.7(5)	-9.7(6)
F2	24.7(8)	38.5(8)	45.6(8)	-6.7(7)	19.5(6)	-6.3(6)
F3	29.9(8)	23.5(7)	34.3(8)	8.2(6)	3.0(6)	-5.9(6)
O007	26.0(9)	23.0(8)	11.0(7)	-1.3(6)	4.2(6)	2.1(6)
N1	19.7(9)	16.4(8)	9.7(8)	1.3(7)	2.2(6)	3.0(7)
C1	17.7(11)	16.2(10)	15.3(10)	-1.6(8)	6.6(8)	1.6(8)
C2	17.5(11)	23.8(11)	25.1(11)	4.8(9)	3.6(9)	1.4(9)
C3	27.0(13)	21.5(11)	26.3(12)	6.3(9)	8.4(10)	4.5(9)
C4	27.6(13)	18.0(10)	24.9(11)	-1.4(9)	13.9(9)	-3.5(9)
C5	16.3(11)	24.2(11)	20.3(10)	-7.9(9)	6.5(8)	-3.2(9)
C6	18.1(11)	19.0(10)	14.9(10)	-2.0(8)	3.8(8)	2.5(8)
C7	16.2(10)	16.3(9)	12.3(9)	-0.2(8)	1.2(7)	1.5(8)
C8	18.3(11)	16.5(9)	17.1(10)	0.8(8)	5.0(8)	0.8(8)
C9	19.0(11)	21.3(11)	18.0(10)	0.0(9)	2.9(8)	-0.8(9)
C10	16.3(10)	15.1(9)	15.0(10)	0.9(8)	3.8(8)	-4.8(8)
C11	25.3(12)	18.4(10)	16.1(10)	2.5(8)	5.0(8)	4.7(9)

Table 4. Bond Lengths for 3j.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C5	1.740(2)	C1	C7	1.523(3)
F1	C9	1.352(2)	C2	C3	1.384(3)
F2	C9	1.341(2)	C3	C4	1.388(3)
F3	C9	1.334(2)	C4	C5	1.374(3)
O007	C10	1.235(2)	C5	C6	1.387(3)
N1	C7	1.453(2)	C7	C8	1.541(3)
N1	C10	1.340(3)	C8	C9	1.495(3)
C1	C2	1.397(3)	C10	C11	1.497(3)

C1	C6	1.388(3)

Table 5. Bond Angles for 3j.

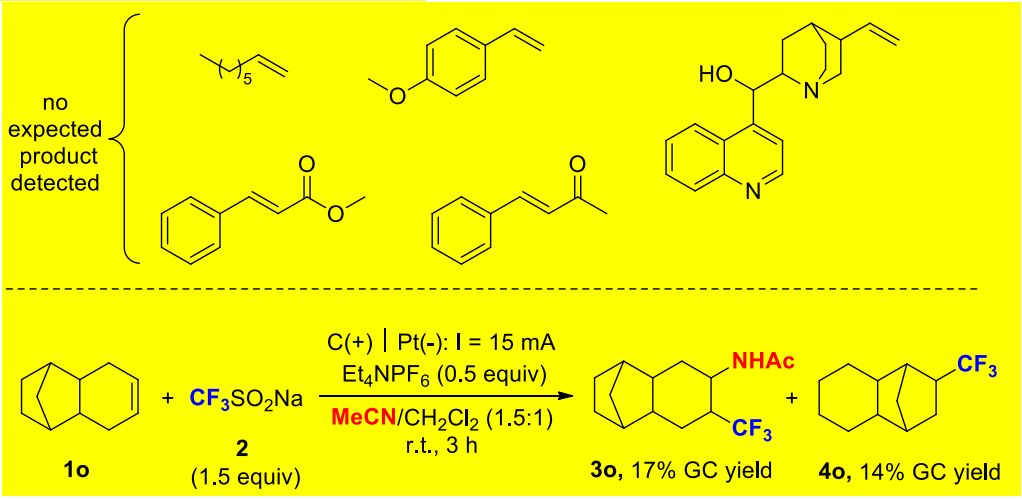
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	N1	C7	122.09(16)	N1	C7	C8	109.94(15)
C2	C1	C7	118.57(18)	C1	C7	C8	110.16(16)
C6	C1	C2	118.97(19)	C9	C8	C7	114.17(17)
C6	C1	C7	122.46(18)	F1	C9	C8	112.09(17)
C3	C2	C1	120.6(2)	F2	C9	F1	105.80(17)
C2	C3	C4	120.4(2)	F2	C9	C8	111.98(17)
C5	C4	C3	118.5(2)	F3	C9	F1	105.44(17)
C4	C5	Cl1	119.15(17)	F3	C9	F2	106.81(17)
C4	C5	C6	122.1(2)	F3	C9	C8	114.13(18)
C6	C5	Cl1	118.75(17)	O007	C10	N1	122.21(18)
C5	C6	C1	119.38(19)	O007	C10	C11	121.44(18)
N1	C7	C1	112.64(16)	N1	C10	C11	116.36(16)

Table 6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3j.

Atom	*x*	*y*	*z*	U(eq)
H1	-2444.93	2680.83	-540.5	19
H2	-3692.84	5750.56	-4466.82	27
H3	-2906.04	7787.86	-5098.68	29
H4	-1339.68	8303.18	-3803.33	27
H6	-1360.25	4714.18	-1229.55	21
H7	-3498.73	3248.62	-3346.02	18
H8A	-3601.44	4387.18	-496.63	21
H8B	-4167.32	5193.56	-1980.19	21
H11A	-1681.26	-431.04	-1279.36	30
H11B	-1485.61	825.38	-35.01	30
H11C	-817.17	685.18	-1191.15	30

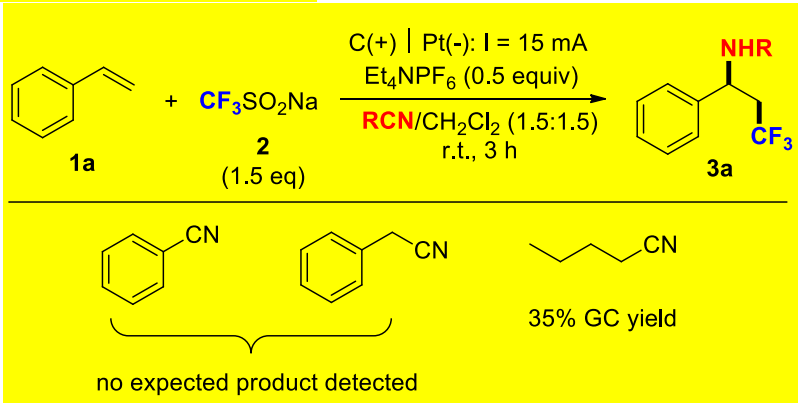
3. Other Alkenes and Nitriles Examined

Scheme 1. Other alkenes examined



In order to expand the scope of the substrates, we examined different types of alkenes (Scheme 1). Other terminal olefins were tried and found, such as 1-octene, *p*-methoxystyrene and cinchonine, and no desired products were detected in the reaction. Among them, *p*-methoxystyrene was speculated to polymerize in reaction before electrolysis. In addition, different internal alkenes had also been examined, including methyl cinnamate, (*E*)-4-phenylbut-3-en-2-one and tricyclo[6.2.1.0(2,7)]undeca-4-ene. When methyl cinnamate and (*E*)-4-phenylbut-3-en-2-one were used as substrates, no expected product was detected in the reaction, and meanwhile, the substrates were partially decomposed. When tricyclo[6.2.1.0(2,7)]undeca-4-ene was used as a substrate, the expected product was detected with a GC yield of 17%, meanwhile, we could also detected the trifluoromethylation product **4o** with a GC yield of 14%.

Scheme 2. Other nitriles examined



In addition, we had also tried to replace acetonitrile with different nitriles to further expand the scope of the substrates (Scheme 2). During the reaction, we found that the use of benzonitrile or phenylacetonitrile instead of acetonitrile could decrease the conductivity of the reaction system, making it difficult for the current to meet the reaction requirements, and no expected product was detected after the reaction. When valeronitrile was used as reaction substrates, we only detected the corresponding products in the reaction with yield of 35%.