

Supporting Information

Copper-Mediated Trifluoromethylation of Aryl-, Heteroaryl-, and Vinyltrifluoroborates with Langlois' Reagent

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EXPERIMENTAL

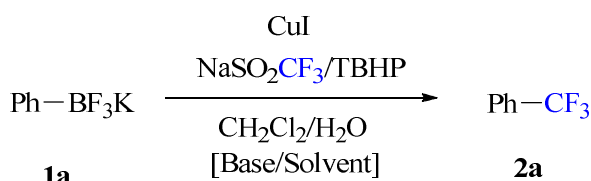
General information: ^1H NMR Spectra, ^{19}F NMR and ^{13}C NMR were recorded on Bruker 400 MHz or 300 MHz in the solvents indicated; chemical shifts are reported in units (ppm) by assigning CDCl_3 resonance in the ^1H spectrum as 7.26 ppm and CDCl_3 resonance in the ^{13}C spectrum as 77.0 ppm. ^{19}F NMR chemical shifts were determined relative to CFCl_3 as internal standard and are measured proton decoupled. All coupling constants (J values) were reported in Hertz (Hz). GC-MS spectra were measured on Shimadzu. Column chromatography was performed on silica gel 200-300 mesh on Combiflash. If not specially mentioned, all the solvents and reagents were used as purchased and without further purification.

Reagents' commercial sources: Reactants (boronic acids or trifluoroborates) were purchased from Combi-Blocks, Tokyo chemical industry (TCI) Japan, Frontier Scientific and Aldrich and used without purification. Commercial sources for other relevant reagents are shown below.

Chemical name	Commercial source	CAS no	Product no
Copper (I) chloride	Aldrich	7758-89-6	61168
NaSO_2CF_3 (Langlois Reagent)	Tokyo chemical industry (TCI)	2926-29-6	T2033
<i>tert</i> -Butyl Hydroperoxide (TBHP) (70% in Water)	Tokyo chemical industry (TCI)	75-91-2	B3153

Experimental Details:

Base and solvent screen for Cu-Mediated for Trifluoromethylation of phenyltrifluoroborate (PhBF₃K, **1a**) with NaSO₂CF₃/TBHP.



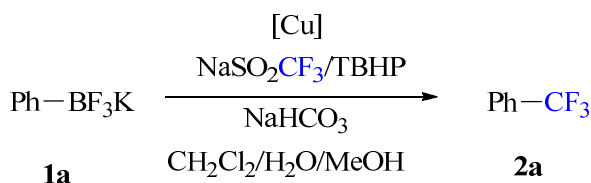
A mixture of the PhBF₃K (27.6 mg, 0.15 mmol, 1.0 equiv), CuI (28.6 mg, 0.15 mmol, 1.0 equiv), NaSO₂CF₃ (70.2 mg, 0.45 mmol, 3.0 equiv), Base (0.15 mmol, 3.0 equiv) in CH₂Cl₂ (0.7 mL), and H₂O (0.5 mL) was cooled to 0 °C, and TBHP (70% solution in water) (104 μL, 5.0 equiv, 0.75 mmol) was added under vigorous stirring. Stirring was continued for overnight at room temperature. To this, 4-fluorobenzonitrile (0.15 mmol) was added as reference to the reaction mixture, stirred for 5 min, an aliquot of the organic phase was withdrawn for the ¹⁹F NMR measurement in CDCl₃. The yields of **2a** as a function of bases and solvents are listed in **Table S1**.

Table S1. Base and solvent screen for Cu-Mediated for Trifluoromethylation of phenyltrifluoroborate (**1a**) with NaSO₂CF₃/TBHP.

Entry	Bases	%Yield
1	Et ₃ N	traces
2	Na ₂ CO ₃	15
3 ^c	Cs ₂ CO ₃	20
4	NaHCO ₃	50
5	NaOAc	28
6	K ₃ PO ₄	31
7	NaHCO ₃	5 ^a
8	NaHCO ₃ /MeOH (0.7 mL)	51
9	NaHCO ₃ /1,4-Dioxane (0.7 mL)	45
10	NaHCO ₃ /1,2-dimethoxyethane (0.7 mL)	45

^a reaction carried out without H₂O and TBHP (5.5 M in decane)

**Copper salt screen for Cu-Mediated for Trifluoromethylation of PhBF₃K (1a)
with NaSO₂CF₃/TBHP.**



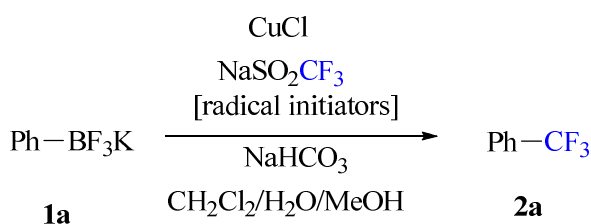
A mixture of the PhBF₃K (27.6 mg, 0.15 mmol, 1.0 equiv), Cu salt (0.15 mmol, 1.0 equiv), NaSO₂CF₃ (70.2 mg, 0.45 mmol, 3.0 equiv), NaHCO₃ (12.6 mg, 0.15 mmol, 3.0 equiv) in CH₂Cl₂ (0.7 mL), MeOH (0.7 mL), and H₂O (0.5 mL) was cooled to 0 °C, and TBHP (70% solution in water) (104 μL, 5.0 equiv, 0.75 mmol) was added under vigorous stirring. Stirring was continued for overnight at room temperature. To this, 4-fluorobenzonitrile (0.15 mmol) was added as reference to the reaction mixture, stirred for 5 min, an aliquot of the organic phase was withdrawn for the ¹⁹F NMR measurement in CDCl₃. The yields of **2a** as a function of copper salts are listed in **Table S2**.

Table S2. Copper salt screen for Cu-Mediated for Trifluoromethylation of phenyltrifluoroborate (**1a**) with NaSO₂CF₃/TBHP.

Entry	Cu Salts	%Yield
1	Cu(I) acetate	10
2	Cu(II) acetate	traces
3	Cu(OCOFCF ₃)	40
4	Cu(OCOFCF ₃) ₂	20
5 ^a	Cu(OSO ₂ CF ₃)	50
6	Cu(OSO ₂ CF ₃) ₂	20
7	(CH ₃ CN) ₄ CuPF ₆	traces
8	CuBr	10
9 ^b	CuTc	50
10	CuCl	80
11	CuCl/1,10-Phen	(8) ^c (15) ^d
12	catalytic	(8) ^e

^aUsed as benzene complex. ^dCopper(I)-thiophene-2-carboxylate; ^c20% CuCl; ^d20% CuCl and 20% 1,10-phenanthroline. ^e**1a** (1.0 equiv., 0.15 mmol), Cu(OAc)₂ (0.2 equiv.), imidazole (0.2 equiv.), 2,4,6-collidine (2.0 equiv.), NH₄Cl (2.5 equiv.), NaSO₂CF₃ (7.0 equiv.), TBHP (70% in H₂O, 16.0 equiv.), CH₂Cl₂/H₂O, air, rt, 15 h.

Radical initiators screen for Cu-Mediated for Trifluoromethylation of PhBF₃K (1a) with NaSO₂CF₃.



A mixture of the PhBF₃K (27.6 mg, 0.15 mmol, 1.0 equiv), CuCl (14.8 mg, 0.15 mmol, 1.0 equiv), NaSO₂CF₃ (70.2 mg, 0.45 mmol, 3.0 equiv), NaHCO₃ (12.6 mg, 0.15 mmol, 3.0 equiv) in CH₂Cl₂ (0.7 mL), MeOH (0.7 mL), and H₂O (0.5 mL) was cooled to 0 °C, and radical initiators (5.0 equiv, 0.75 mmol) was added under vigorous stirring. Stirring was continued for overnight at room temperature. To this, 4-fluorobenzonitrile (0.15 mmol) was added as reference to the reaction mixture, stirred for 5 min, an aliquot of the organic phase was withdrawn for the ¹⁹F NMR measurement in CDCl₃. The yields of **2a** as a function of radical initiators are listed in **Table S3**.

Table S3. Radical initiators screen for Cu-Mediated for Trifluoromethylation of phenyltrifluoroborate (**1a**) with NaSO₂CF₃.

Entry	Radical initiators	%Yield
1	H ₂ O ₂	0
2	NaOCl	traces
3	O ₂	8
4	DDQ	0
5	PhI(OAc) ₂	traces
6	BzOOBz	20

General procedure for the Synthesis of Aryl-CF₃ compounds: (Table 2).

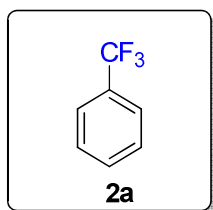
A mixture of the trifluoroborate (0.25 mmol, 1.0 equiv), CuCl (24.8 mg, 0.25 mmol, 1.0 equiv), NaSO₂CF₃ (117 mg, 0.75 mmol, 3.0 equiv), NaHCO₃ (21.0 mg, 0.25 mmol, 3.0 equiv) in CH₂Cl₂ (1.5 mL), MeOH (1.5 mL), and H₂O (1.2 mL) was cooled to 0 °C, and TBHP (70% solution in water) (172 μL, 5.0 equiv, 1.25 mmol, (86 μL, 2.5 equiv, 0.625 mmol for **2i**, and 138 μL, 4.0 equiv, 1.0 mmol for **2j**)) was added under vigorous stirring. Stirring was continued for 6–12h at room temperature.

For the compounds reported as isolated yields (**2b**, **2n**, and **2r**), the organic phase was separated, the aqueous phase was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄, the solvent was removed at 1 atm and the residue was purified by column chromatography on Combiflash with hexanes to afford the desired compounds.

The volatile products were not isolated and their yields were determined only by ¹⁹F NMR of the reaction mixture. For the compounds reported with ¹⁹F NMR yields, 4-fluorobenzonitrile (0.25 mmol) was added as reference to the reaction mixture, stirred for 5 min, an aliquot of the organic phase was withdrawn for the ¹⁹F NMR measurement in CDCl₃.

Spectral data of Aryl-CF₃ compounds (Table 2):

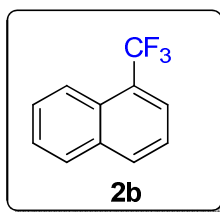
1-(Trifluoromethyl)benzene (**2a**):



The yield (80%) of **2a** was determined by ¹⁹F NMR. The ¹⁹F NMR spectral data for **2a** matched that of an authentic sample (Aldrich, s, -62.3 ppm).

¹⁹F NMR (CDCl₃, 376 M Hz): δ -62.75 (s, 3F); GC-MS *m/z*, 146 (M⁺).

1-(Trifluoromethyl)naphthalene (**2b**):¹

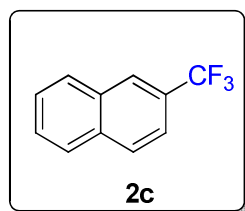


Compound **2b** was isolated in 60% yield (49 mg) and 82% yield was determined by ^{19}F NMR.

^1H NMR (CDCl_3 , 400 MHz): δ 8.18 (d, $J = 8.6$ Hz, 1H), 8.0 (d, $J = 8.2$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H); 7.86 (d, $J = 7.3$ Hz, 1H), 7.55-7.65 (m, 2H), 7.50 (t, $J = 7.7$ Hz, 1H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 133.9 (s, 1C), 132.7 (s, 1C), 129.0 (s, 1C), 128.7 (s, 1C), 127.6 (s, 1C), 127.4 (q, $J = 269.8$ Hz, 1C), 126.6 (s, 1C), 124.6 (q, $J = 6.2$ Hz, 1C), 124.2 ($J = 2.2$ Hz, 1C), 124.1 (s, 1C), 123.3 (s, 1C).

^{19}F NMR (CDCl_3 , 282 M Hz): δ -60.43 (s, 3F); GC-MS m/z , 196 (M^+).

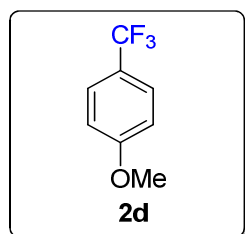
2-(Trifluoromethyl)naphthalene (**2c**):²



The yield (59%) of **2c** was determined by ^{19}F NMR.

^{19}F NMR (CDCl_3 , 282 M Hz): δ -62.86 (s, 3F); GC-MS m/z , 196 (M^+).

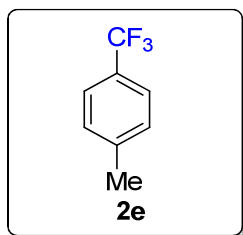
1-Methoxy-4-(trifluoromethyl)benzene (**2d**):³



The yield (74%) of **2d** was determined by ^{19}F NMR.

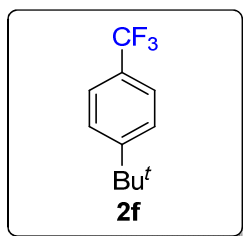
^{19}F NMR (CDCl_3 , 282 M Hz): δ -62.20 (s, 3F); GC-MS m/z , 176 (M^+).

1-Methyl-4-(trifluoromethyl)benzene (**2e**):⁴



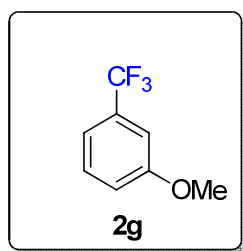
The yield (79%) of **2e** was determined by ¹⁹F NMR.
¹⁹F NMR (CDCl₃, 282 M Hz): δ -62.98 (s, 3F); GC-MS *m/z*, 160 (M⁺).

1-(*Tert*-Butyl)-4-(trifluoromethyl)benzene (**2f**):^{2,4}



The yield (77%) of **2f** was determined by ¹⁹F NMR.
¹⁹F NMR (CDCl₃, 282 M Hz): δ -62.98 (s, 3F); GC-MS *m/z*, 202 (M⁺).

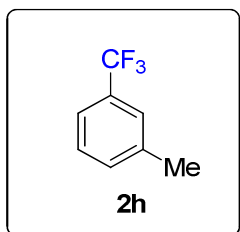
1-Methoxy-3-(trifluoromethyl)benzene (**2g**):^{3,4}



Compound **2g** was isolated in 56% yield (25.0 mg) and 60% yield was determined by ¹⁹F NMR.

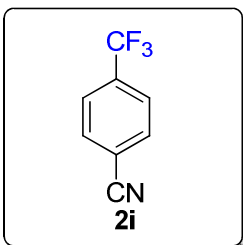
¹H NMR (CDCl₃, 400 MHz): δ 7.39 (d, *J* = 8.0 Hz, 1H), 7.21 (dt, *J* = 7.6 Hz, *J* = 0.9 Hz, 1H), 7.12 (br.s, 1H); 7.07 (dd, *J* = 8.0 Hz, *J* = 0.9 Hz, 1H); ¹⁹F NMR (CDCl₃, 282 M Hz): δ -63.34 (s, 3F); GC-MS *m/z*, 176 (M⁺).

1-Methyl-3-(trifluoromethyl)benzene (2h):^{3,4}



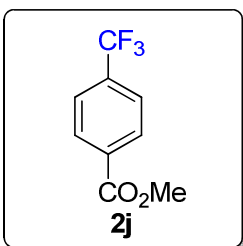
The yield (51%) of **2h** was determined by ¹⁹F NMR.
¹⁹F NMR (CDCl₃, 282 M Hz): δ -63.25 (s, 3 F); GC-MS *m/z*, 160 (M⁺).

4-(trifluoromethyl)benzonitril (2i):⁵



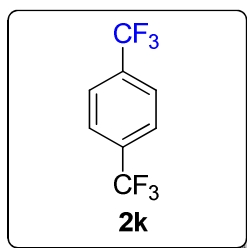
The yield (40%) of **2i** was determined by ¹⁹F NMR.
¹⁹F NMR (CDCl₃, 282 M Hz): δ -64.17 (s, 3F); GC-MS *m/z*, 171 (M⁺).

Methyl 4-(trifluoromethyl)benzoate (2j):⁵



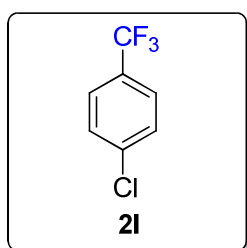
The yield (41%) of **2j** was determined by ¹⁹F NMR.
¹⁹F NMR (CDCl₃, 282 M Hz): δ -63.79 (s, 3F); GC-MS *m/z*, 204 (M⁺).

1,4-Bis(trifluoromethyl)benzene (2k):⁵



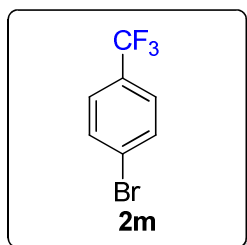
Traces product of **2k** was determined by GC-MS.

1-Chloro-4-(trifluoromethyl)benzene (**2l**):⁵



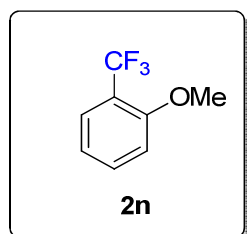
The yield (45%) of **2l** was determined by ¹⁹F NMR.
¹⁹F NMR (CDCl₃, 282 M Hz): δ -63.18 (s, 3F); GC-MS *m/z*, 180 (M⁺).

1-Bromo-4-(trifluoromethyl)benzene (**2m**):⁵



The yield (57%) of **2m** was determined by ¹⁹F NMR.
¹⁹F NMR (CDCl₃, 282 M Hz): δ -63.48 (s, 3F); GC-MS *m/z*, 224 (M⁺).

1-Methoxy-2-(trifluoromethyl)benzene (**2n**):⁵

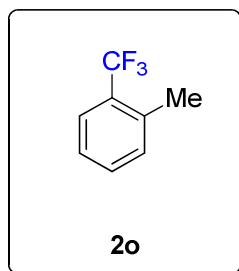


Compound **2n** was isolated in 65% yield (29 mg) and 89% yield was determined by ¹⁹F NMR.

¹H NMR (CDCl₃, 400 MHz): δ 7.56 (d, 1H, *J* = 7.8 Hz), 7.49 (t, 1H, *J* = 7.8 Hz), 7.05-6.95 (m, 3H), 3.90 (s, 3H); ¹³CNMR (CDCl₃, 100 MHz): δ 157.5 (s, 1C), δ

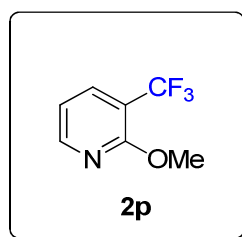
133.2 (s, 1C), 127.1 (q, $J = 5.2$ Hz, 1C), 123.5 (q, $J = 277.1$ Hz, 1C), 120.0 (s, 1C), 118.7 (q, $J = 30.1$ Hz, 1C), 111.9 (s, 1C), 55.9 (s, 1C); ^{19}F NMR (CDCl_3 , 282 MHz): $\delta -63.05$ (s, 3F); GC-MS m/z , 176 (M^+).

1-Methyl-2-(trifluoromethyl)benzene (**2o**):⁵



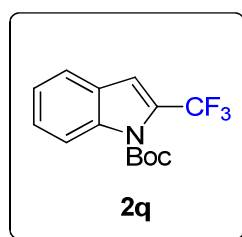
The yield (55%) of **2o** was determined by ^{19}F NMR.
 ^{19}F NMR (CDCl_3 , 282 M Hz): $\delta -63.21$ (s, 3 F); GC-MS m/z , 160 (M^+).

2-Methoxy-3-(trifluoromethyl)pyridine (**2p**):²



The yield (85%) of **2p** was determined by ^{19}F NMR.
 ^{19}F NMR (CDCl_3 , 282 M Hz): $\delta -64.47$ (s, 3F); GC-MS m/z , 177 (M^+).

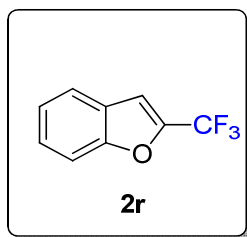
Tert-Butyl-2-(trifluoromethyl)-1*H*-indole-1-carboxylate (**2q**):²



Compound **2r** was isolated in 53% yield (37.8 mg) and 55% yield was determined by ^{19}F NMR.

^1H NMR (CDCl_3 , 400 MHz): δ 8.29 (dd, $J = 8.4$ Hz, $J = 0.8$ Hz, 1H), 7.62 (d, $J = 7.8$ Hz, 1H), 7.45 (td, $J = 7.8$ Hz, $J = 1.2$ Hz, 1H), 7.29 (td, $J = 7.1$ Hz, $J = 1.1$ Hz, 1H); 7.14 (br.s), 1.67 (s, 3H); ^{19}F NMR (CDCl_3 , 376 M Hz): $\delta -58.29$ (s, 3F); GC-MS m/z , 185 (M-Boc).

2-(Trifluoromethyl)benzofuran (2r):²

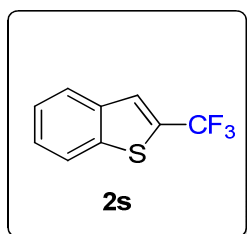


Compound **2r** was isolated in 75% yield (34.8 mg) and 91% yield was determined by ¹⁹F NMR.

¹H NMR (CDCl₃, 300 MHz): δ 7.66 (d, *J* = 8.05 Hz, 1H), 7.56 (dq, *J* = 8.4 Hz, *J* = 0.9 Hz, 1H), 7.44 (td, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H); 7.32 (td, *J* = 8.4 Hz, *J* = 0.9 Hz, 1H), 7.17-7.13 (m, 1H); ¹³CNMR (CDCl₃, 100 MHz): δ 155.2 (s, 1C), δ 143.5 (q, *J* = 48.5 Hz, 1C), 126.9 (s, 1C), 126.9 (s, 1C), 126.0 (s, 1C), 124.2 (s, 1C), 122.5 (s, 1C), 119.4 (q, *J* = 268.2 Hz, 1C), 112.1 (s, 1C), 108.1 (q, *J* = 2.9 Hz, 1C).

¹⁹F NMR (CDCl₃, 282 MHz): δ -66.09 (s, 3 F); GC-MS *m/z*, 186 (M⁺).

2-(Trifluoromethyl)benzo[b]thiophene (2s):²

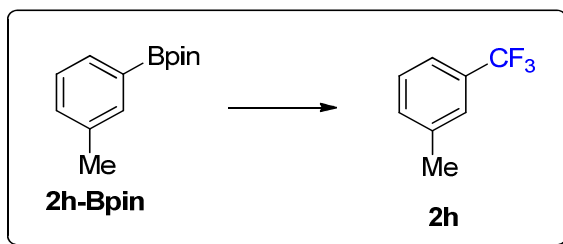


Compound **2r** was isolated in 52% yield (26.2 mg) and 54% yield was determined by ¹⁹F NMR.

¹H NMR (CDCl₃, 400 MHz): δ 7.89-7.85 (m, 2H), 7.70 (s, 1H), 7.47-7.43 (m, 2H).

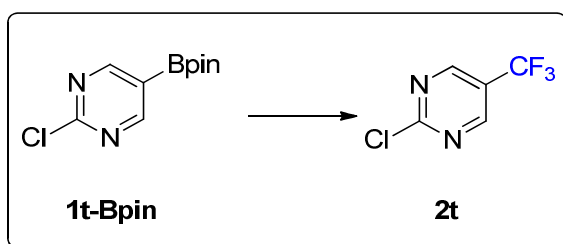
¹⁹F NMR (CDCl₃, 282 MHz): δ -57.04 (s, 3F); GC-MS *m/z*, 202 (M⁺).

1-Methyl-3-(trifluoromethyl)benzene (2h) from 2h-Bpin:^{3,4}



The yield (28%) of **2h** was determined by ^{19}F NMR.
 ^{19}F NMR (CDCl_3 , 282 MHz): δ -63.27 (s, 3 F); GC-MS m/z , 160 (M^+).

2-Chloro-5-(trifluoromethyl)pyrimidine (**2t**) from **1t-Bpin**:^{3,4}

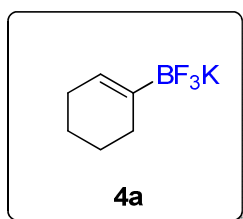


The yield (30%) of **2t** was determined by ^{19}F NMR.
 ^{19}F NMR (CDCl_3 , 282 MHz): δ -62.80 (s, 3F); GC-MS m/z , 182 (M^+).

General Procedure for the Synthesis of Potassium Alkenyltrifluoroborates: Synthesis of compounds **3a-d** (Scheme 2).

To a solution of the boronic acid (1.4 mmol, 1.0 equiv) in MeOH (1.0 mL) was added 4.5 M aq. KHF_2 (933 μL , 4.2 mmol, 3.0 equiv) at 0 °C, the resulting mixture was stirred at the same temperature for 1 h. Solvent was removed by distillation; residue was dissolved in hot acetone (20 mL) and filtered. The filtrate was concentrated and dissolved in minimum amount of acetone, precipitated by adding MTBE. The precipitate was collected by filtration to get products as white solids.⁶

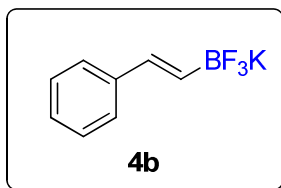
Cyclohex-1-en-1-yltrifluoroborate (4a**)**. The title compound was isolated as a colourless solid in 84% yield (220 mg). The physical data matched with the literature data.⁶



^1H NMR (CD_3OD , 300 MHz): δ ppm 5.75 (s, 1H), 2.0-3.39 (m, 4H), 1.57-1.52 (m,

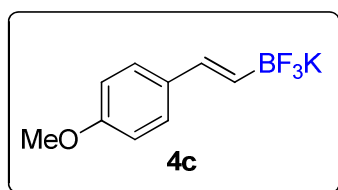
4H); ^{13}C NMR (CD_3OD , 100 MHz): δ ppm 126.5 (q, $J = 3.5$ Hz, 1C), 126.22 (s, 1C), 27.52 (s, 1C), 27.09 (s, 1C), 24.61 (s, 1C), 24.41 (s, 1C); ^{19}F NMR (CD_3OD , 282 MHz): δ ppm -147.9 .

Potassium trans-styryltrifluoroborate (4b). The title compound was isolated as a colourless solid in 81% yield (240 mg). The physical data matched with the literature data.⁶



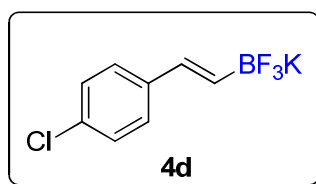
^1H NMR (CD_3OD , 300 MHz): δ ppm 7.46–7.34 (m, 5H), 6.67 (d, $J = 18.0$ Hz, 1H), 6.27–6.19 (m, 1H); ^{19}F NMR (CD_3OD , 282 MHz): δ ppm -143.5 .

Potassium 4-methoxy trans-styryltrifluoroborate (4c). The title compound was obtained as a colorless solid in 73% yield (245 mg). physical data matched with the literature data.⁶



^1H NMR ($\text{DMSO}-d_6$, 300 MHz): δ ppm 7.22 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 8.4$ Hz, 2H), 6.39 (d, $J = 18.0$ Hz, 1H), 6.01–5.92 (m, 1H); ^{19}F NMR ($\text{DMSO}-d_6$, 282 MHz): δ ppm -138.0 .

Potassium 4-chloro trans-styryltrifluoroborate (4d). The title compound was obtained as a colorless solid in 62% yield (215 mg). physical data matched with the literature data.⁶



^1H NMR ($\text{DMSO}-d_6$, 300 MHz): δ ppm 7.34–7.25 (m, 4H), 6.44 (d, $J = 18.3$ Hz, 1H), 6.21–5.93 (m, 1H); ^{19}F NMR ($\text{DMSO}-d_6$, 282 MHz): δ ppm -138.53 .

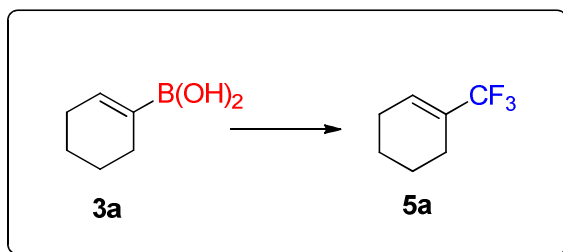
General procedure for the Synthesis of Alkenyl-CF₃ compounds: Synthesis of compounds **5a** to **5d** (Scheme 2).

A mixture of boronic acids or trifluoroborates (0.25 mmol, 1.0 equiv), CuCl (24.8 mg, 0.25 mmol, 1.0 equiv), NaSO₂CF₃ (117 mg, 0.75 mmol, 3.0 equiv), NaHCO₃ (21.0 mg, 0.25 mmol, 3.0 equiv) in CH₂Cl₂ (1.5 mL), MeOH (1.5 mL), and H₂O (1.2 mL) was cooled to 0 °C, and TBHP (70% solution in water) (172 μL, 5.0 equiv, 1.25 mmol) was added under vigorous stirring. Stirring was continued for 6–12h at room temperature.

For the compounds reported as isolated yields, the organic phase was separated, the aqueous phase was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄, the solvent was removed at 1 atm and the residue was purified by column chromatography on Combiflash with hexanes to afford the desired compounds.

The volatile products were not isolated and their yields were determined only by ¹⁹F NMR of the reaction mixture. For the compounds reported with ¹⁹F NMR yields, 4-fluorobenzonitrile (0.25 mmol) was added as reference to the reaction mixture, stirred for 5 min, an aliquot of the organic phase was withdrawn for the ¹⁹F NMR measurement in CDCl₃.

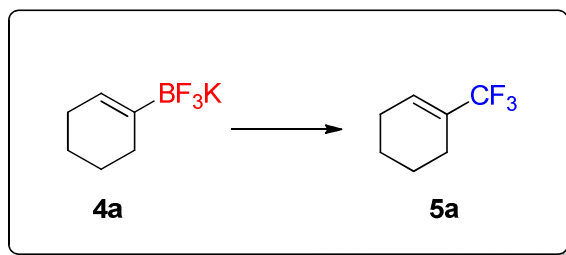
1-(Trifluoromethyl)cyclohex-1-ene (5a)¹⁰ from **3a**:



According to the general procedure; compound **5a** was formed in 64% yield by ¹⁹F NMR.

¹⁹F NMR (CDCl₃, 282 MHz): δ -70.30 (s, 3F); GC-MS *m/z*, 150 (M⁺).

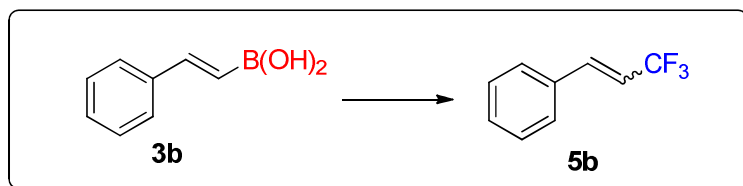
1-(Trifluoromethyl)cyclohex-1-ene (5a)⁷ from **4a**:



According to the general procedure; compound **5a** was formed in 60% yield by ^{19}F NMR.

^{19}F NMR (CDCl_3 , 282 MHz): δ -70.30 (s, 3F); GC-MS m/z , 150 (M^+).

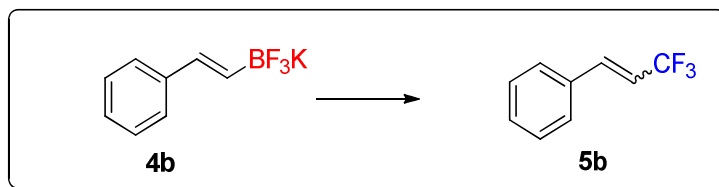
(E)-(3,3,3-Trifluoro-1-en-1-yl)benzene (5b)⁸ from **3b**:



According to the general procedure compound **5b** was obtained in 80% (35 mg) yield and 92% yield was determined by ^{19}F NMR. A ratio of E/Z = 25:1 was determined by ^1H NMR

^1H NMR (CDCl_3 , 400 MHz): δ 7.46-7.42 (m, 2H, mixed signal of *E* and *Z* isomers), 7.40-7.34 (m, 3H, mixed signal of *E* and *Z* isomers), 7.14 (dq, $J = 16.2, 2.2$ Hz, 1H, *E*-isomer), 6.91 (d, $J = 12.7$ Hz, *Z*-isomer), 6.19 (dq, $J = 16.4, 7.3$ Hz, 1H, *E*-isomer), 5.76 (d, $J = 12.7, 9.2$ Hz, *Z*-isomer); ^{19}F NMR (CDCl_3 , 282 MHz): δ -64.05 (s, 3F, *E*-isomer); GC-MS m/z , 172 (M^+).

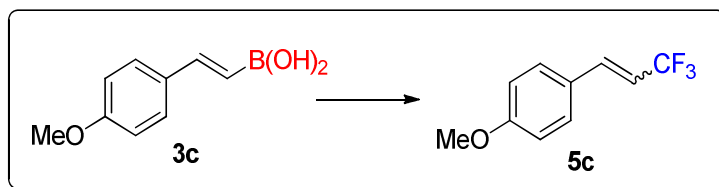
(E)-(3,3,3-Trifluoro-1-en-1-yl)benzene (5b) from **4b**:



According to the general procedure; compound **5b** was formed in 98% yield by ^{19}F NMR. A ratio of E/Z = 20:1 was determined by ^1H NMR.

^{19}F NMR (CDCl_3 , 282 MHz). δ -64.03 (s, 3F, *E*-isomer); GC-MS m/z , 172 (M^+).

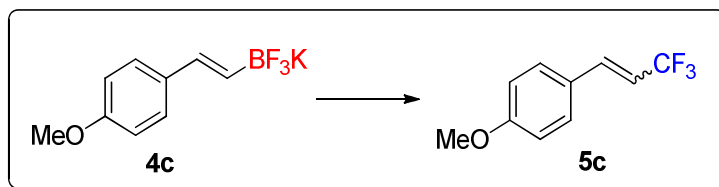
(E)-1-methoxy-4-(3,3,3-Trifluoro-1-en-1-yl)benzene (5c)⁹ from 3c:



According to the general procedure compound **5c** was isolated in 85% yield (43mg) and 93% yield was determined by ¹⁹F NMR. A ratio of E/Z = 16:1 was determined by ¹H NMR

¹H NMR (CDCl₃, 400 MHz): δ 7.39 (d, *J* = 8.8 Hz, 2H, mixed signals of *E* and *Z* isomers), 7.08 (dq, *J* = 16.2, 2.3 Hz, 1H, *E*-isomer), 6.90 (d, *J* = 8.8 Hz, 2H, mixed signals of *E* and *Z* isomers), 6.81 (d, *J* = 12.8 Hz, *Z*-isomer), 6.05 (dq, *J* = 16.2, 6.6 Hz, 1H, *E*-isomer), 5.62 (dq, *J* = 12.8, 9.4 Hz, *Z*-isomer), 3.82 (s, 3H, mixed signals of *E* and *Z* isomers); ¹⁹F NMR (CDCl₃, 282 MHz): δ -63.49 (s, 3 F, *E*-isomer); GC-MS *m/z*, 202 (M⁺).

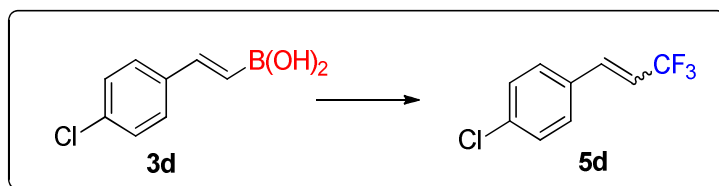
(E)-1-methoxy-4-(3,3,3-Trifluoro-1-en-1-yl)benzene (5c)⁹ from 4c:



According to the general procedure; compound **5c** was formed in 94% yield by ¹⁹F NMR. A ratio of E/Z = 13:1 was determined by ¹H NMR.

¹⁹F NMR (CDCl₃, 282 MHz): δ -63.36 (s, 3F, *E*-isomer); GC-MS *m/z*, 202 (M⁺).

(E)-1-chloro-4-(3,3,3-Trifluoro-1-en-1-yl)benzene (5d)⁹ from 3d:

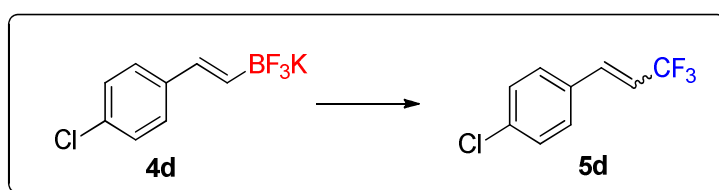


According to the general procedure compound **5d** was isolated in 62% yield

(32mg) and 86% yield was determined by ^{19}F NMR. A ratio of E/Z = 12:1 was determined by ^1H NMR.

^1H NMR (DMSO d_6 , 300 MHz): δ 7.37–7.32 (m, 4H, mixed signals of *E* and *Z* isomers), 7.09 (dq, $J = 16.2, 2.2$ Hz, 1H, *E*-isomer), 6.86 (d, $J = 12.4$ Hz, *E*-isomer), 6.17 (dq, $J = 16.2, 6.6$ Hz, 1H, *E*-isomer), 5.78 (dq, $J = 12.4, 9.0$ Hz, *Z*-isomer); ^{19}F NMR (CDCl_3 , 282 M Hz): δ -64.08 (s, 3F, *E*-isomer); GC-MS m/z , 206 (M^+).

(*E*)-1-chloro-4-(3,3,3-Trifluoro-1-en-1-yl)benzene (5d)⁹ from **4d**:



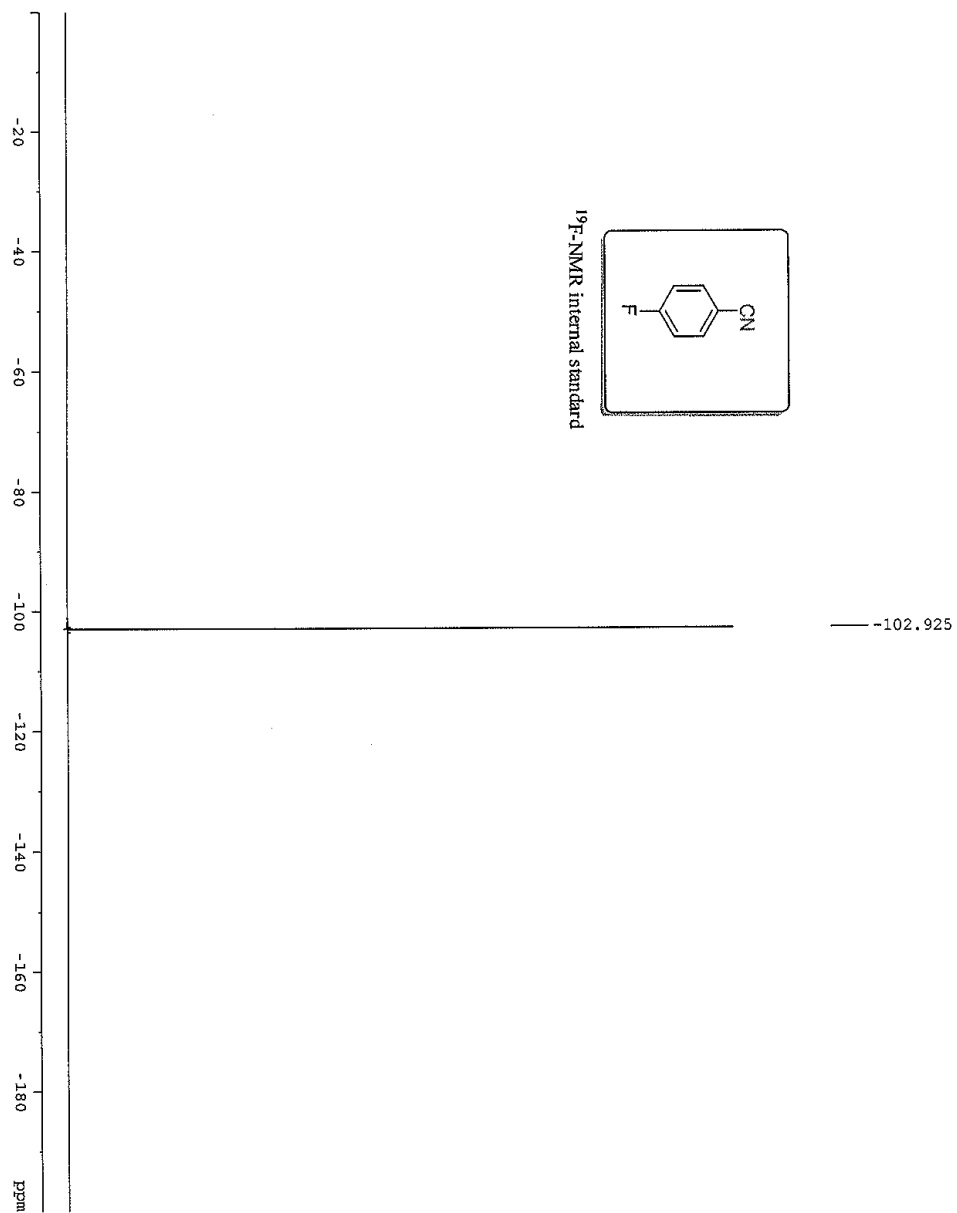
According to the general procedure compound **5d** was formed in 74% yield by ^{19}F NMR. A ratio of E/Z = 3:1 was determined by ^1H NMR.

^{19}F NMR (CDCl_3 , 282 M Hz): δ -63.98 (s, 3F, *E*-isomer); GC-MS m/z , 206 (M^+).

References

1. Xu, J.; Luo, D.-F.; Xiao, B.; Liu, Z.-J.; Gong, T.-J.; Fu, Y.; Liu, L. *Chem. Commun.* **2011**, 4300.
2. Liu, T.; Shen, Q. *Org. Lett.* **2011**, 13, 2342; Chu, L.; Qing, F.-L. *Org. Lett.* **2010**, 12, 5060
3. (a) Khan, B. A.; Buba, A. E.; Gooßen, L. J. *Chem. — Eur. J.* **2011**, 17, 2689. (b) Novàk, P.; Lishchynskyi, A.; Grushin, V. V. *Angew. Chem., Int. Ed.* **2012**, 51, 7767.
4. Huang, Y.; Fang, X.; Li, H.; H, W.; Huang, K.-W.; Yuan, Y.; Weng, Z. *Tetrahedron Lett.* **2012**, 68, 9949.
5. (a) Ye, Y.; Künzi, S. A.; Sanford, M. S. *Org. Lett.* **2012**, 14, 4979. (b) Ye, Y.; Sanford, M. S. *J. Am. Chem. Soc.* **2012**, 134, 9034.
6. (a) Brak, K.; Ellman, J. A. *J. Am. Chem. Soc.* **1999**, 121, 3850 and references therein. (b) Molander, G. A.; Petrillo, D. E. *J. Am. Chem. Soc.* **2006**, 128, 9634. (c) Vedejs, E.; Fields, S. C.; Hayashi, R.; Hithcock, S. R.; Powell, D. R.; Schrimpf, M. R. *J. Am. Chem. Soc.* **1999**, 121, 2460
7. Cho, E. J.; Buchwald, S. L. *Org. Lett.* **2011**, 13, 6552.
8. Prakash, G. K. S.; Krishnan, H. S.; Jog, P. V.; Lyer, A. P.; Olah, G. A. *Org. Lett.* **2012**, 14, 1146.
9. (a) Liu, T.; Shen, Q. *Org. Lett.* **2011**, 13, 2342; (b) Hanamoto, T.; Morita, N.; Shindo, K. *Eur. J. Org. Chem.* **2003**, 21, 4279.

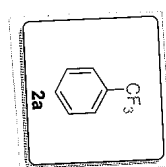
^{19}F NMR of 4-fluorobenzonitrile (internal standard) in CDCl_3



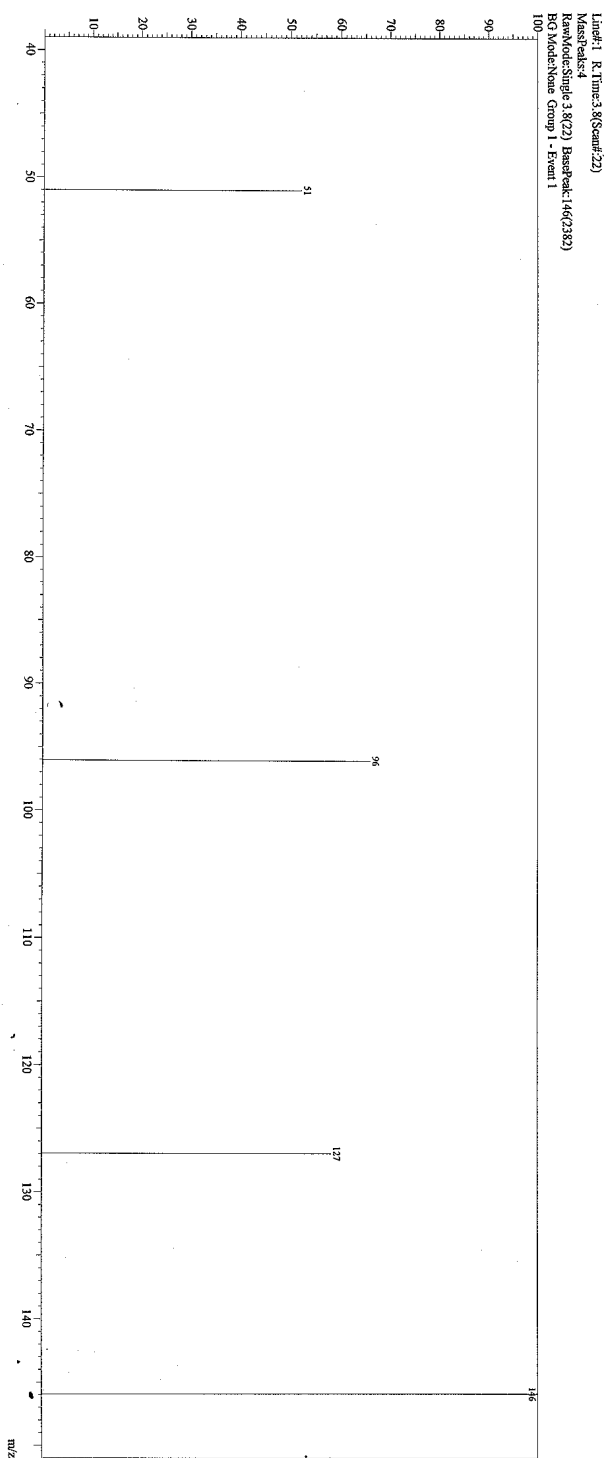
GC-MS of crude 2a

Analytic : GC/MS
Instrument : Shimadzu GC-2010
Analyzed by : Adina
Analyzed : 7/27/2013 11:39:15 PM
Sample Type : Unknown
Level # : 1
Sample Name : SG-NSD-P2-2-NAHCO3-t
Sample ID : SG-NSD-P2-2-NAHCO3-t
IS Amount : [1]=1
Sample Amount : 1
Standard Factor : 1
Yield : 1
Injection Volume : 1

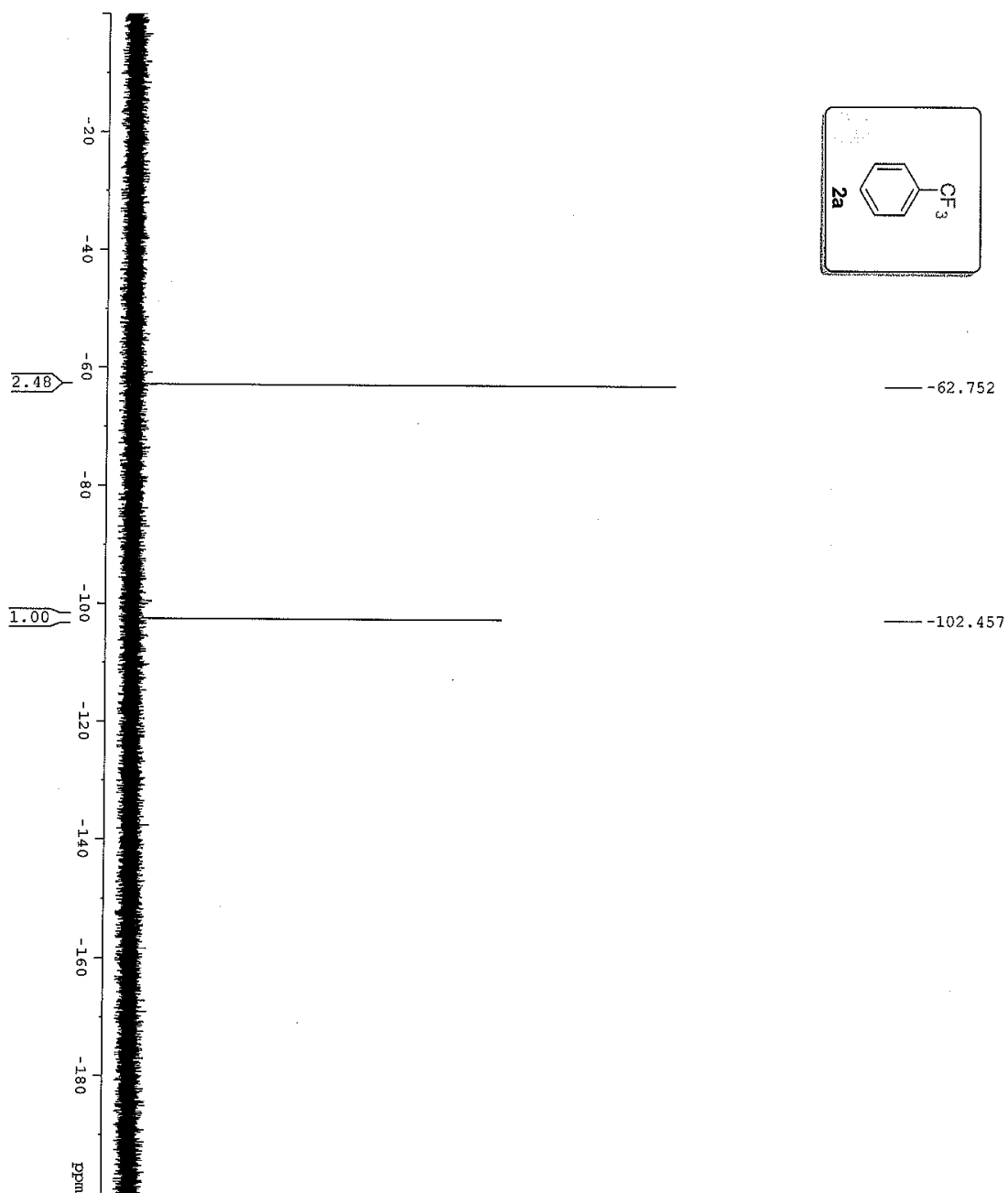
Sample Information



Spectrum



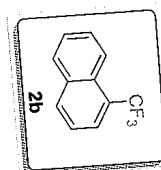
^{19}F NMR yield of compound 2a $(2.48/(1 \times 3) \times 100\% = 82\%)$ in CDCl_3



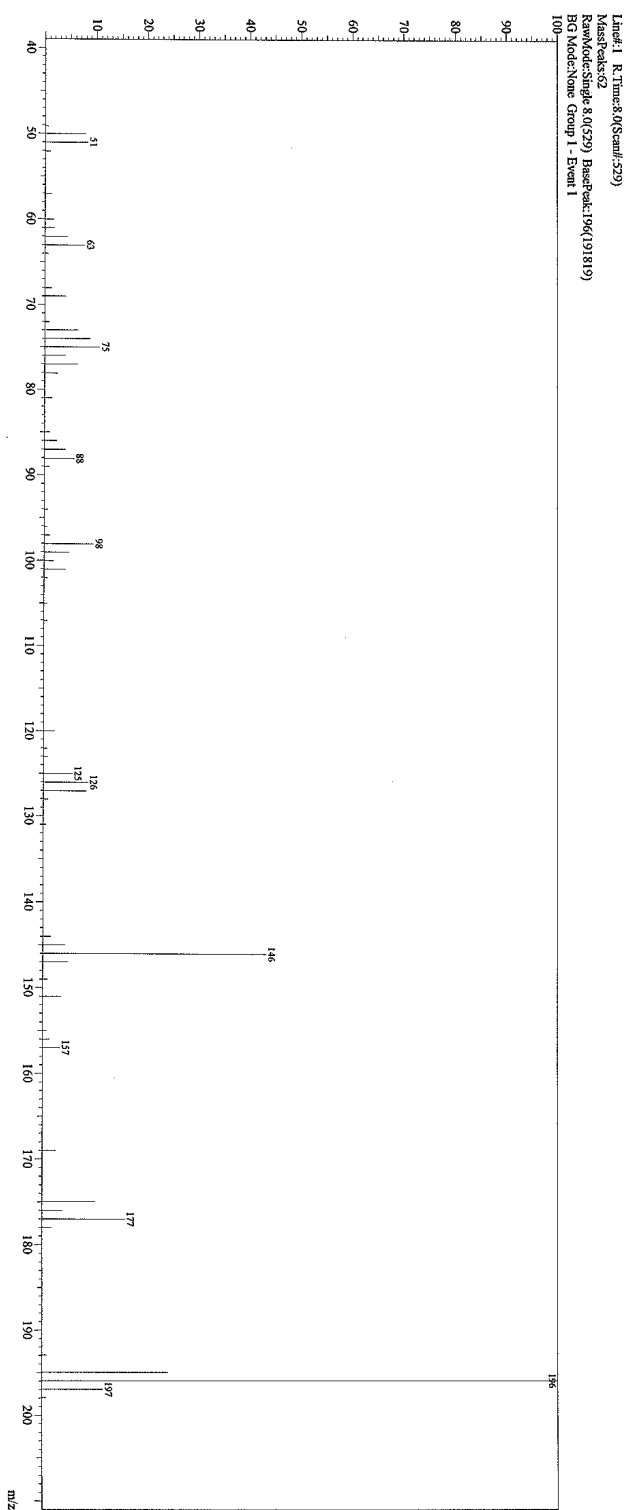
GC-MS of crude 2b

Analyte : GCMS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 8/2/2013 12:09:25 PM
Sample Type : Unknown
Level # : 1
Sample Name : SG-NSD-1-11
Sample ID : SG-NSD-1-11
IS Amount : 1
Sample Amount : 1
Dilution Factor : 1
Vial # : 4
Injection Volume : 3

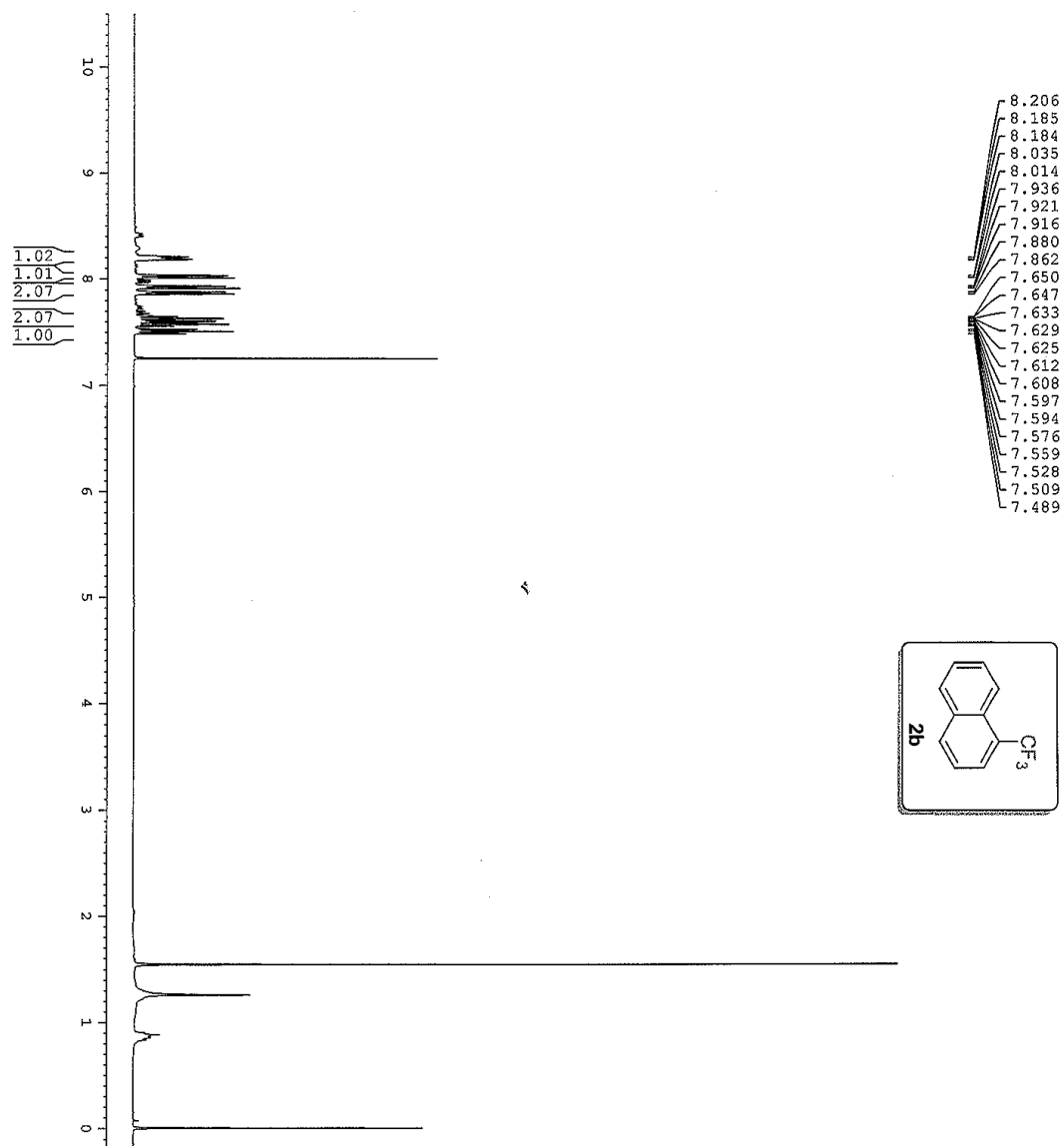
Sample Information



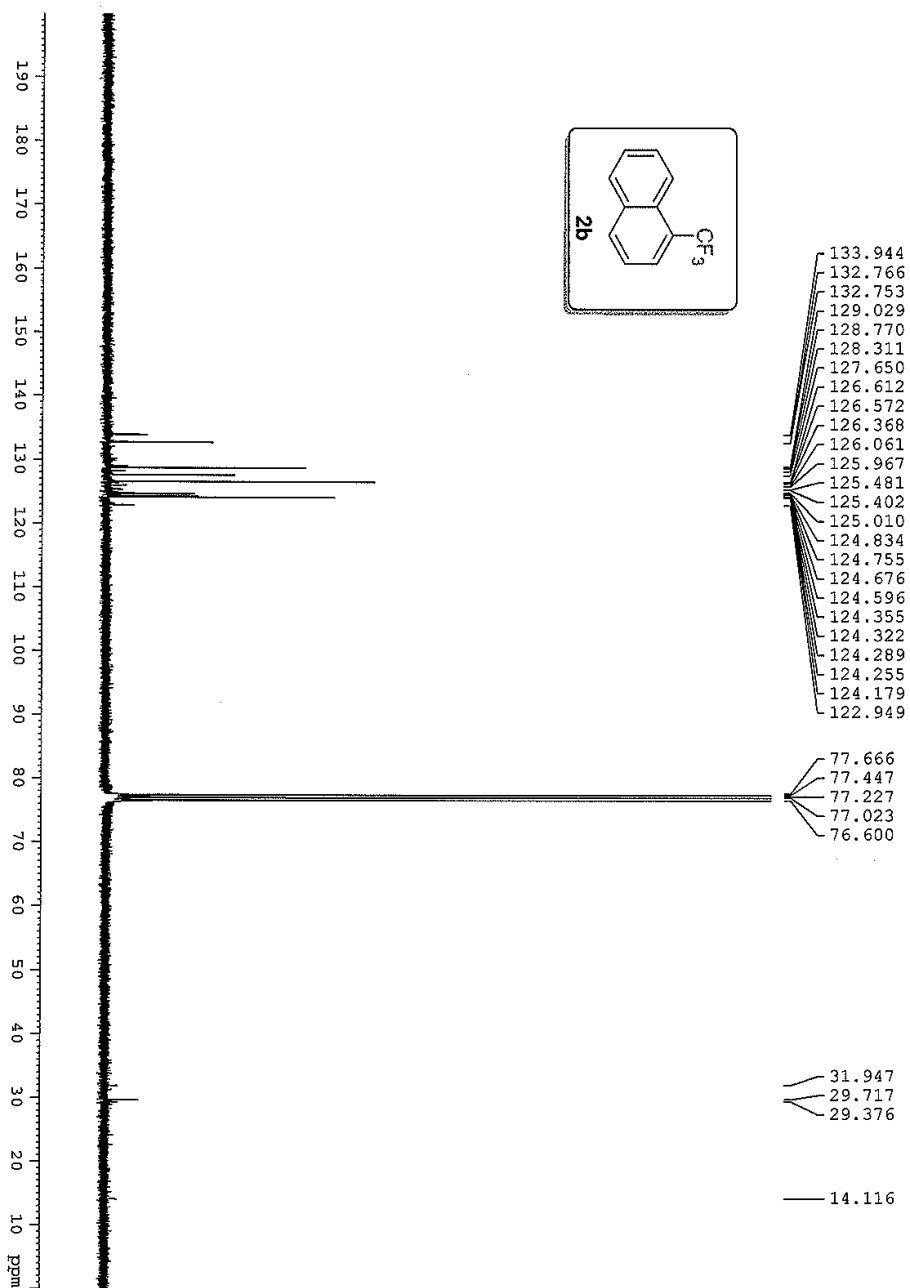
Spectrum



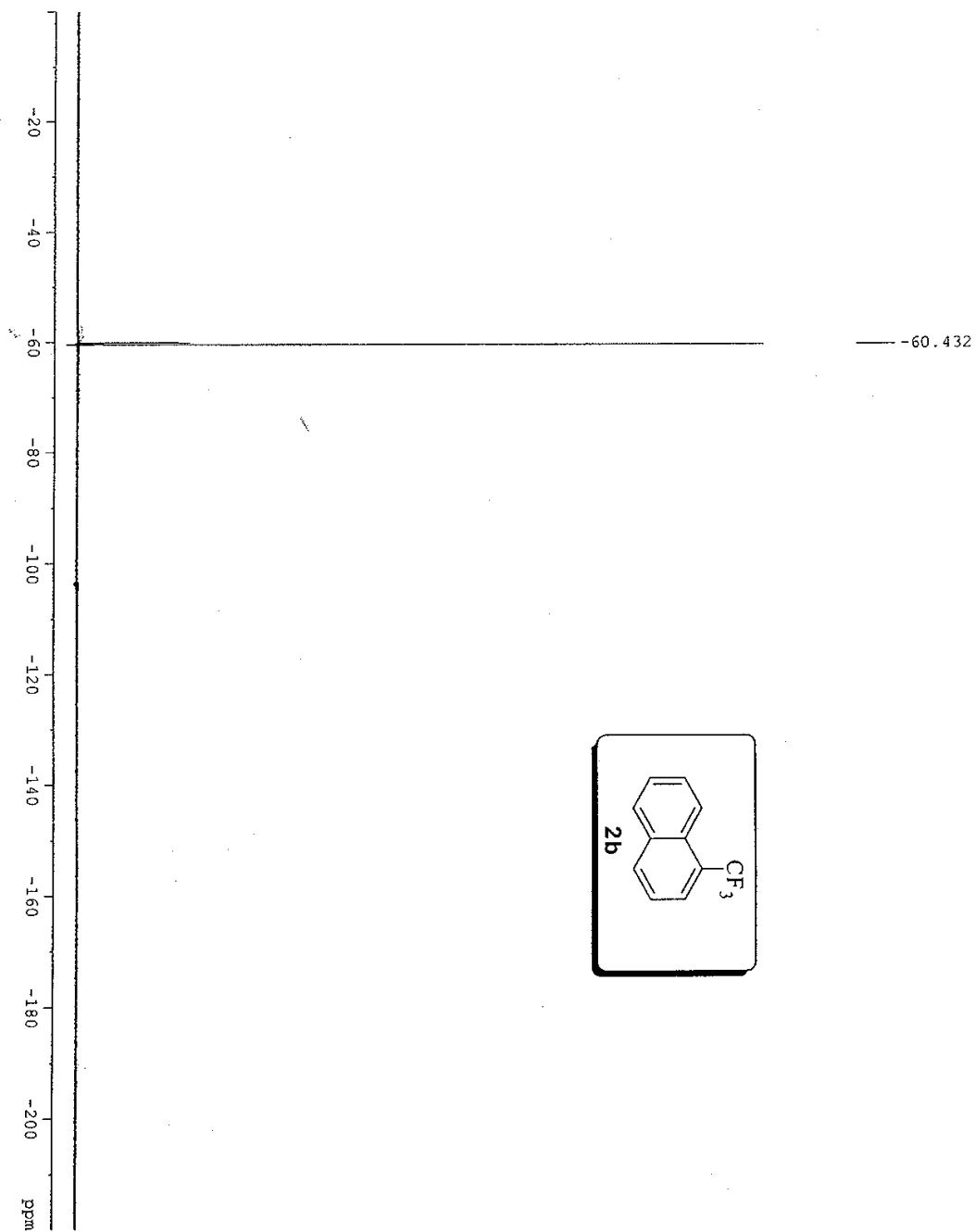
^1H NMR of compound 2b



¹³C NMR of compound 2b



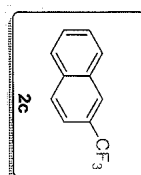
^{19}F NMR of isolated 2b in CDCl_3



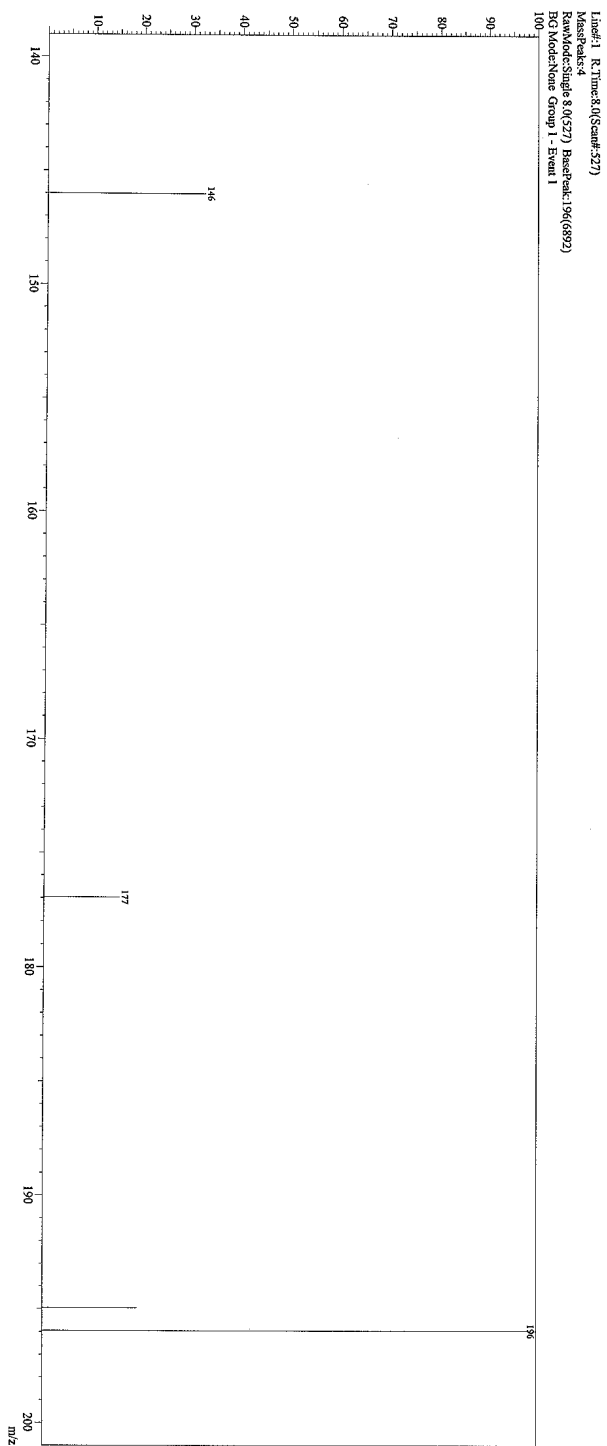
GC-MS of crude 2c

Analysis : GC/MS
Instrument : Shimadzu GC-2010
Acquisition Method : GC/MS
Analyzed By : 8/15/2013 8:15:26 AM
Sample Type : Unknown
Level # : 1
Sample Name : SGC-NSD-I-19
Sample ID : SGC-NSD-I-19
IS Amount : [1]=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 1
Injection Volume : 3

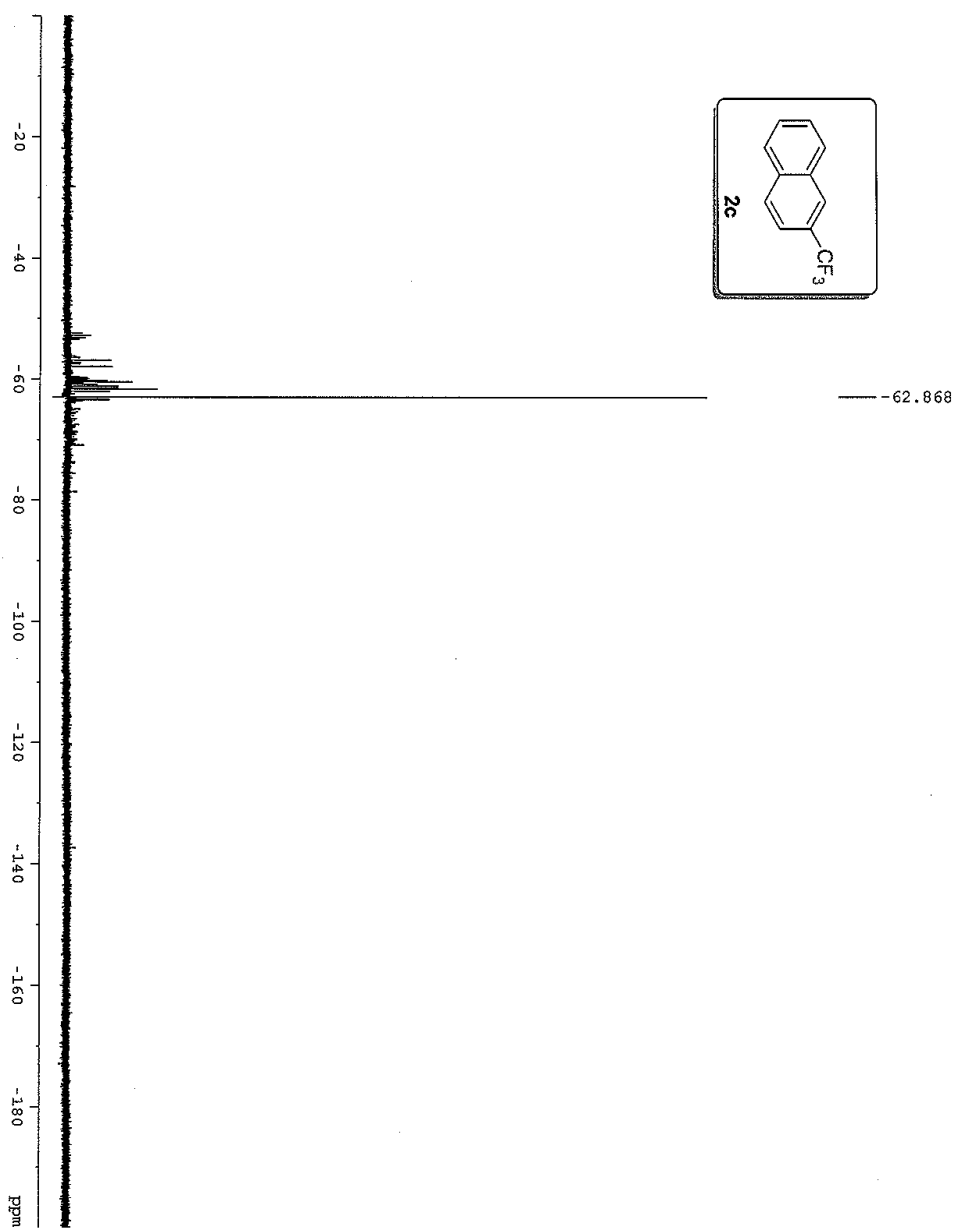
Sample Information



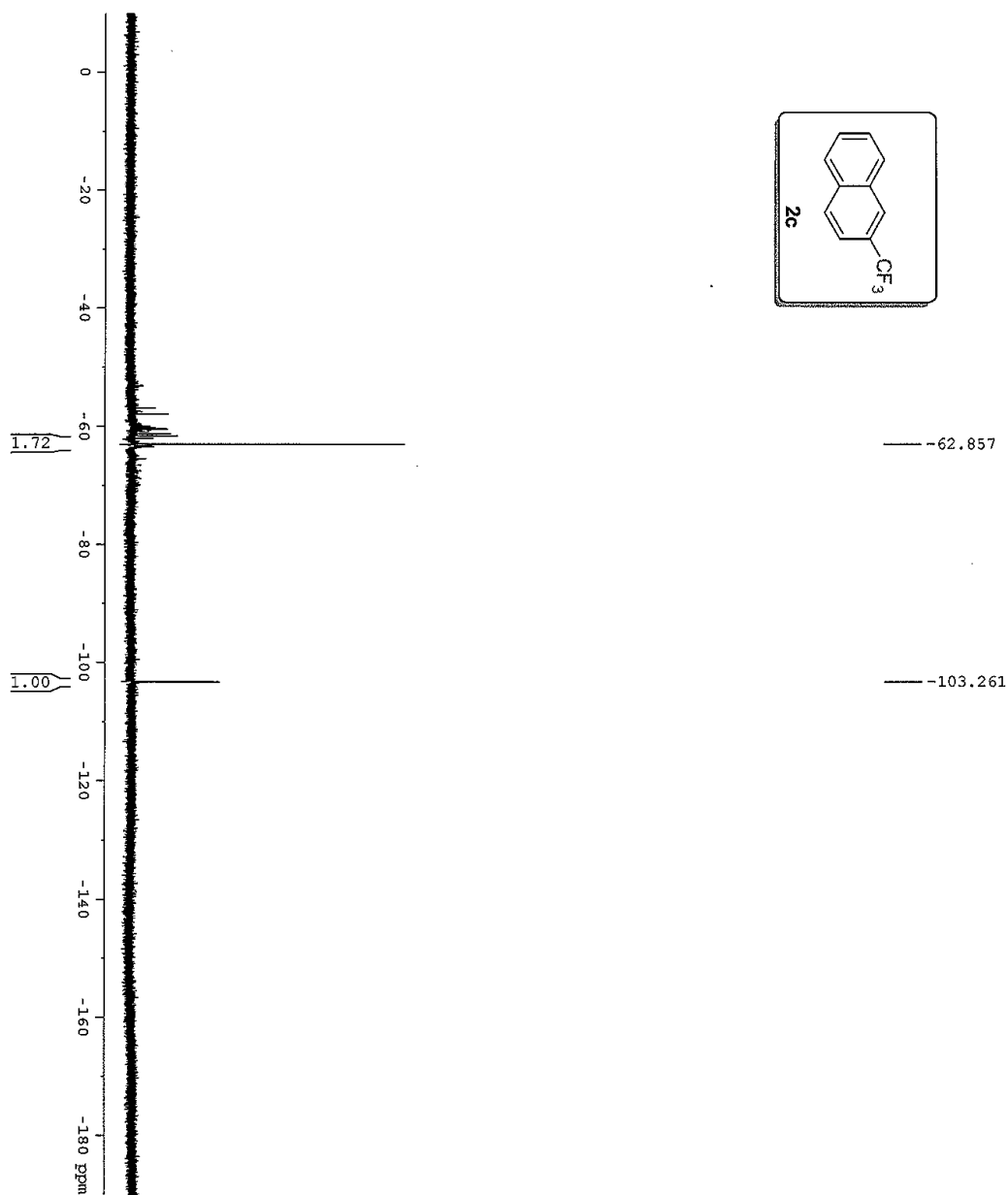
Spectrum



^{19}F NMR of crude **2c** in CDCl_3



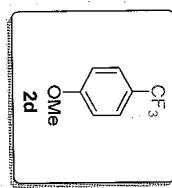
^{19}F NMR yield of compound 2c $(1.72/(1 \times 3) \times 100\% = 57\%)$ in CDCl_3



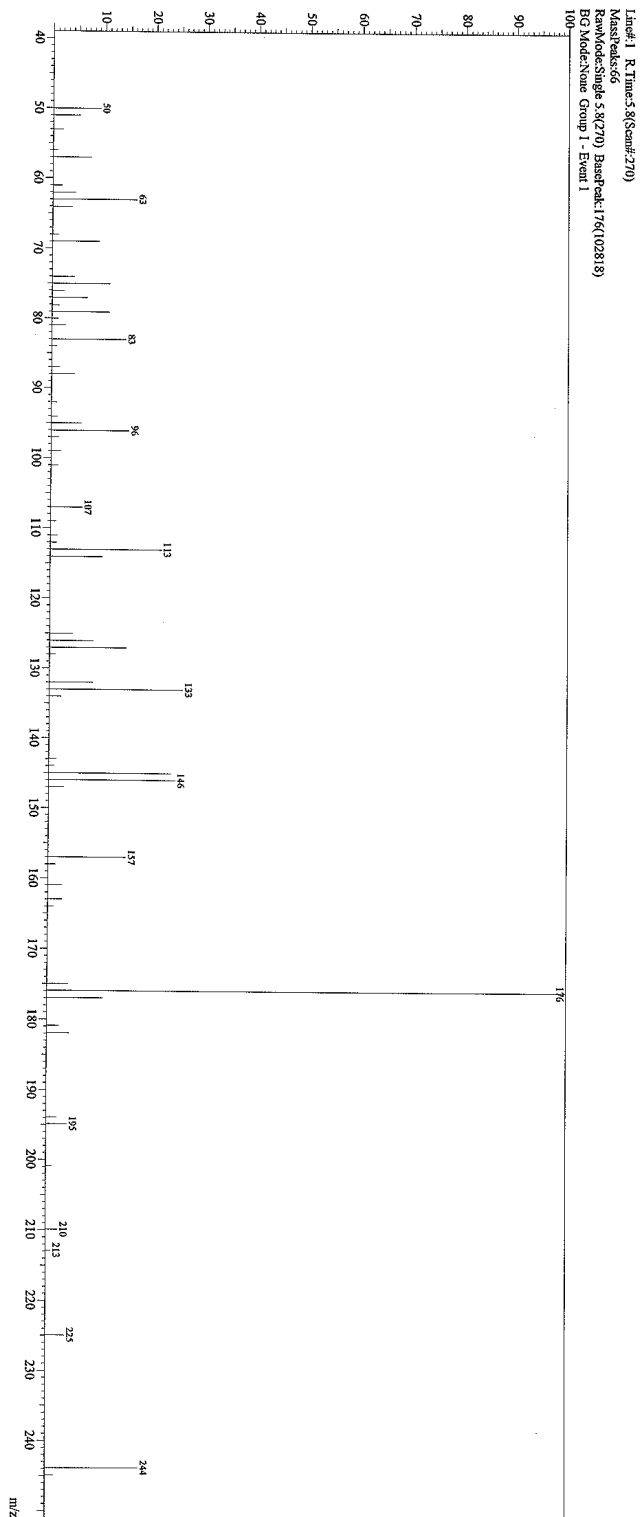
GC-MS of crude 2d

Analysis : GC/MS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 8/9/2013 12:19:56 PM
Sample Type : Unknown
Level # : 1
Sample Name : SG-MNNS-I-17
Sample ID : SG-MNNS-I-17
IS Amount : 1 µl
Sample Amount : 1
Dilution Factor : 1
Vial # : 5
Injection Volume : 3

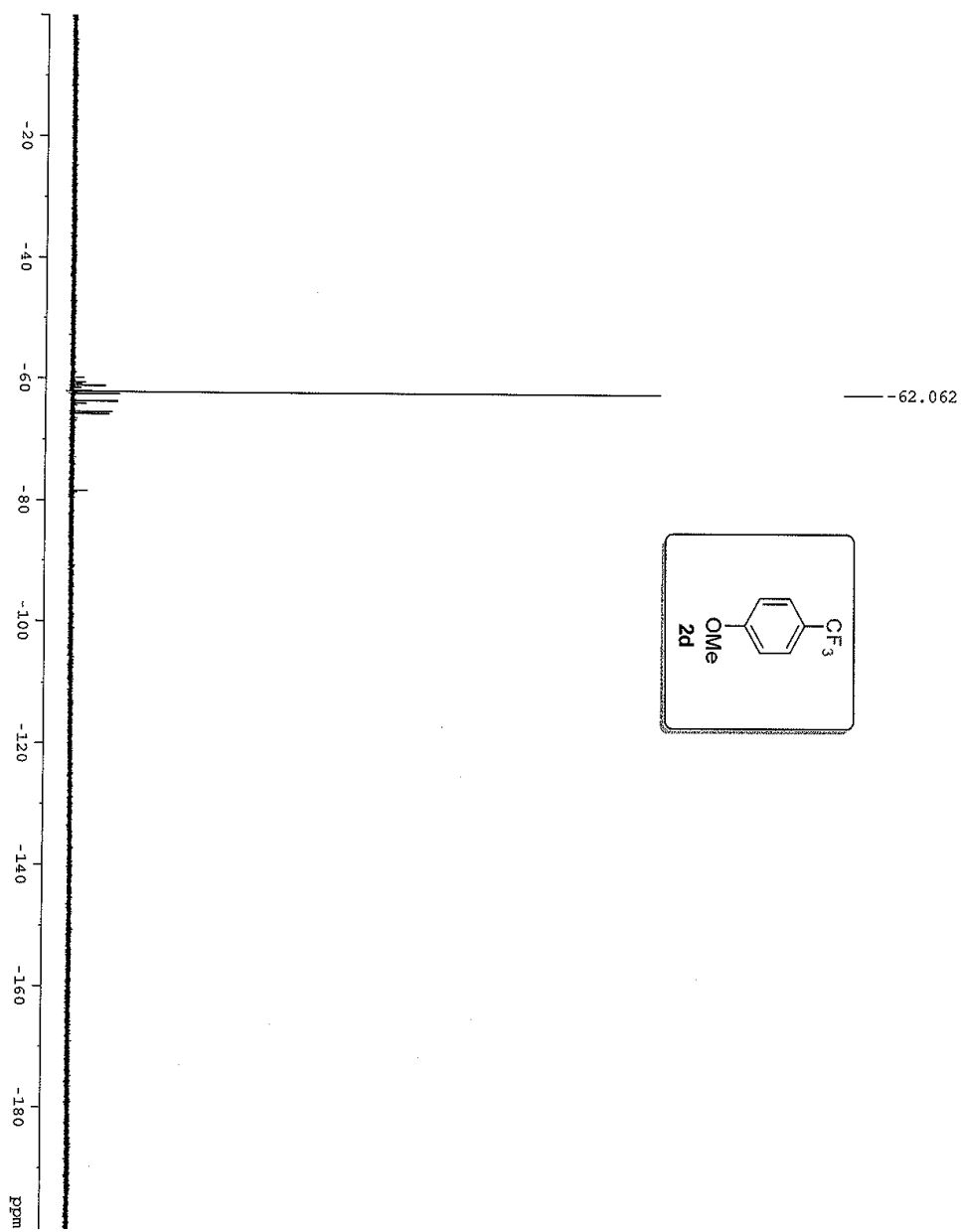
Sample Information



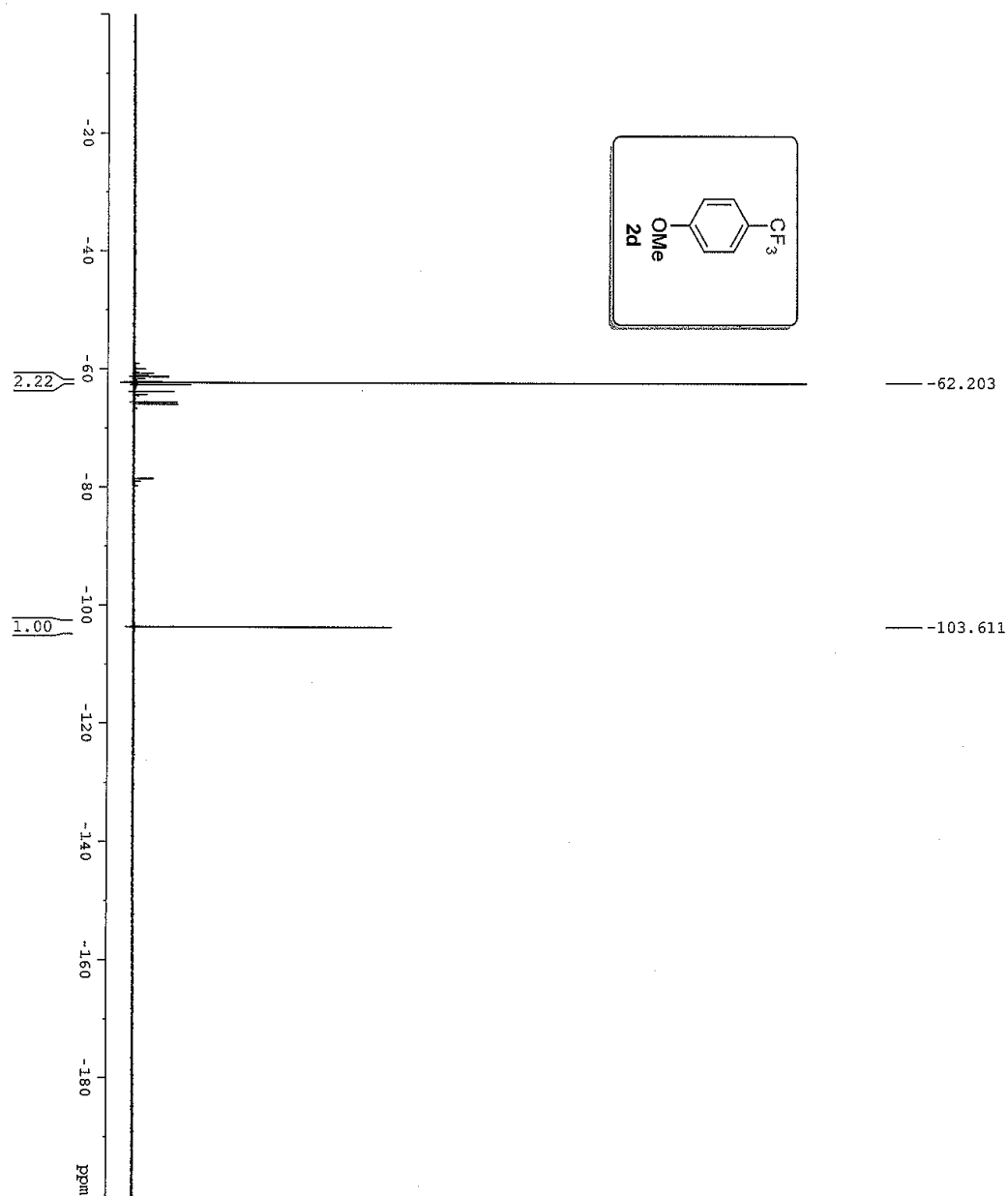
Spectrum



^{19}F NMR of crude 2d in CDCl_3



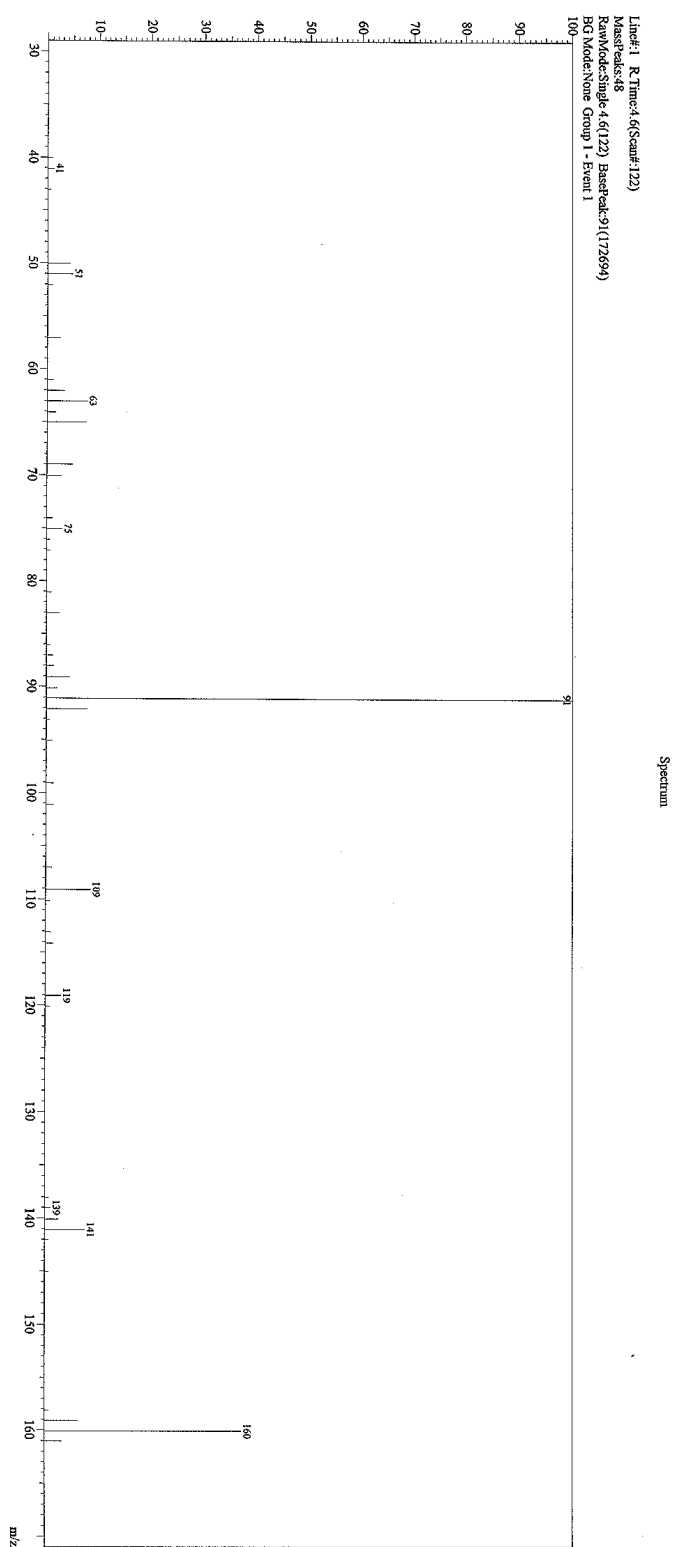
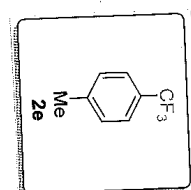
^{19}F NMR yield of compound 2d $(2.22/(1 \times 3) \times 100\% = 74\%)$ in CDCl_3



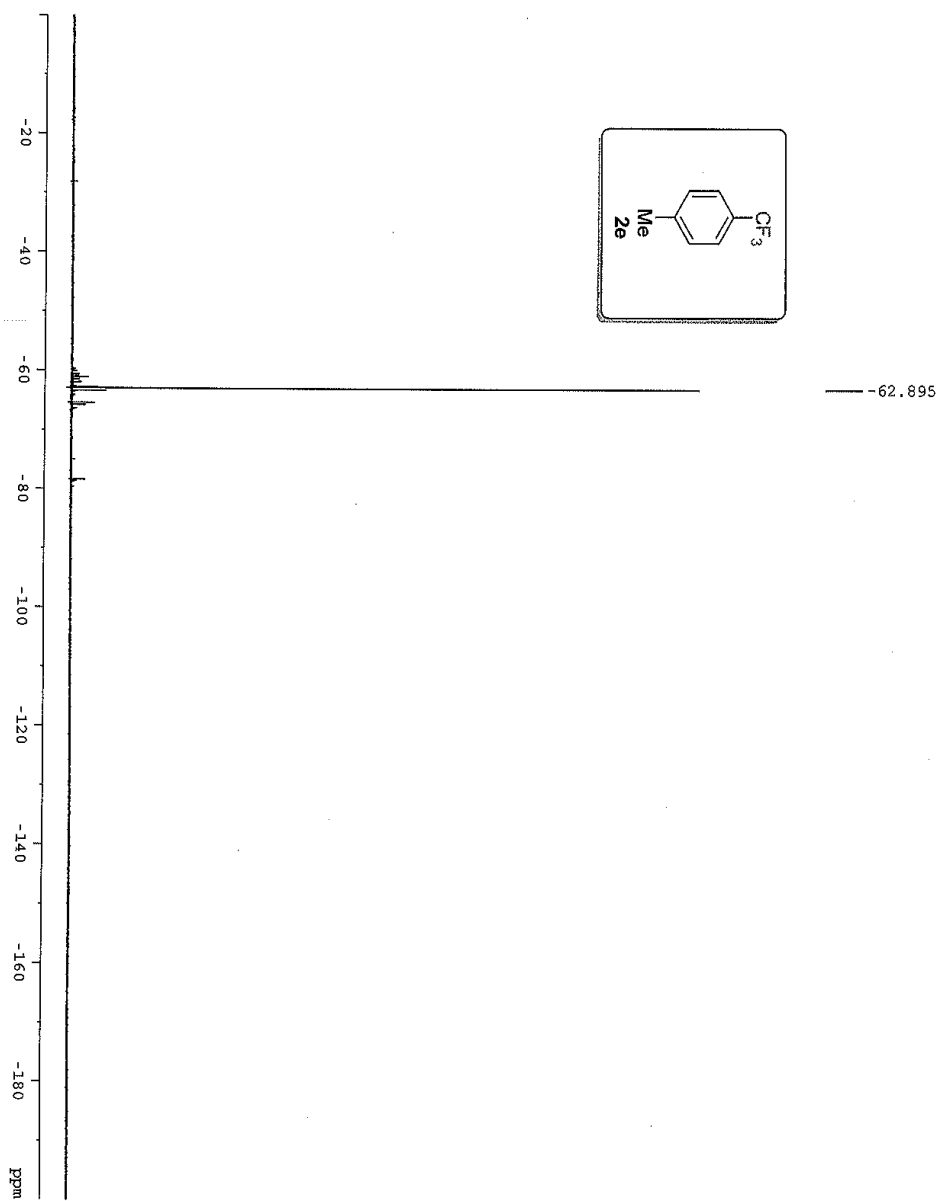
GC-MS of crude 2e

Sample Information

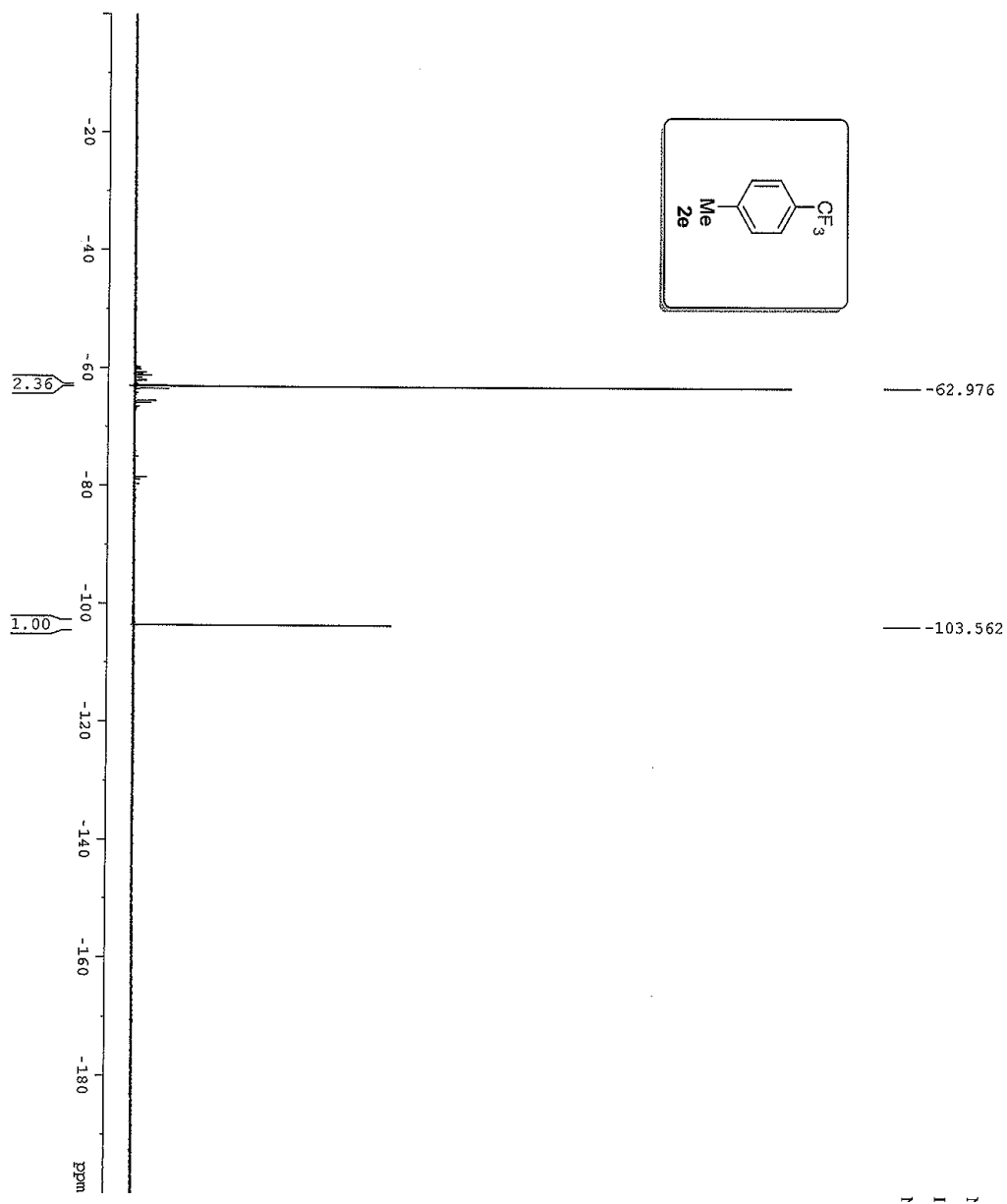
Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 8/8/2013 2:57:29 PM
Sample Type : Unknown
Level # : 1
Sample Name : SG-MNS-1-9
Sample ID : SG-MNS-1-9
IS Amount : [1]=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 6
Injection Volume : 3



^{19}F NMR of crude 2e in CDCl_3



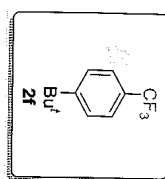
^{19}F NMR yield of compound 2e $(2.36/(1 \times 3) \times 100\% = 79\%)$ in CDCl_3



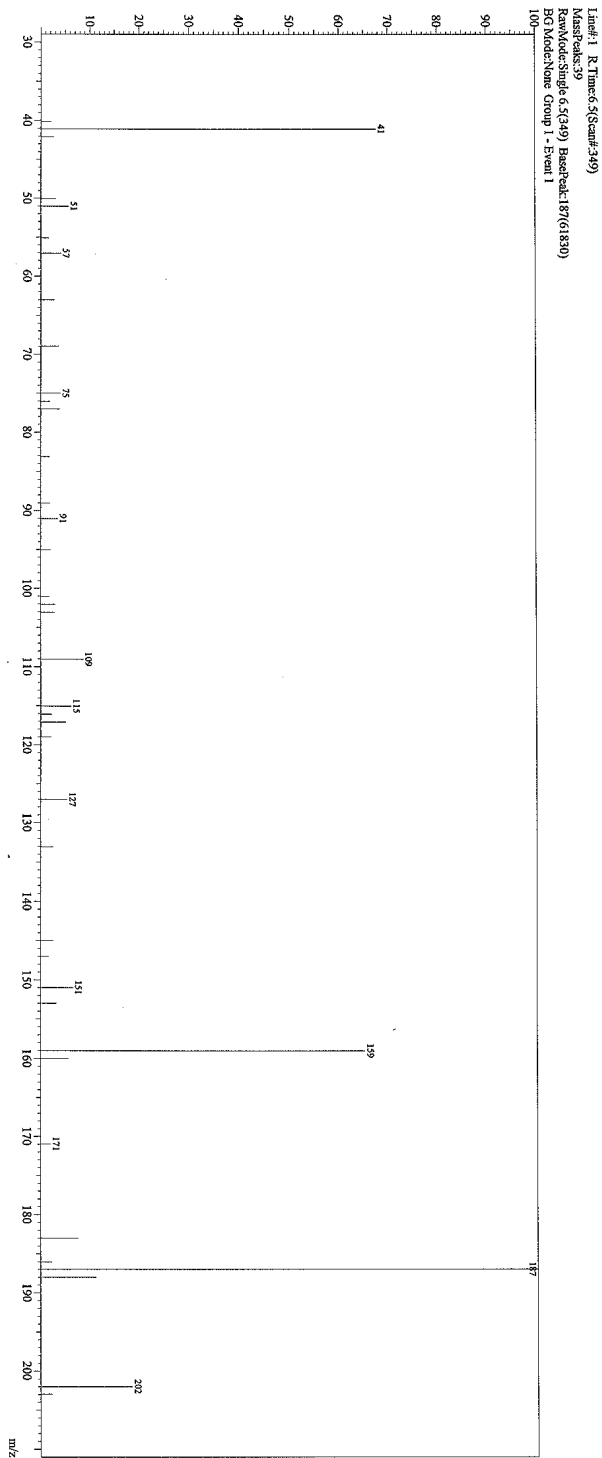
GC-MS of crude 2f

Analysis : GC/MS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 8/15/2013 11:10:59 AM
Sample Type : Unknown
Level # : 1
Sample Name : SG-MNS-4-20
Sample ID : SG-MNS-4-20
IS Amount : 1 µl
Sample Amount : 1
Dilution Factor : 1
Vial # : 6
Injection Volume : 3

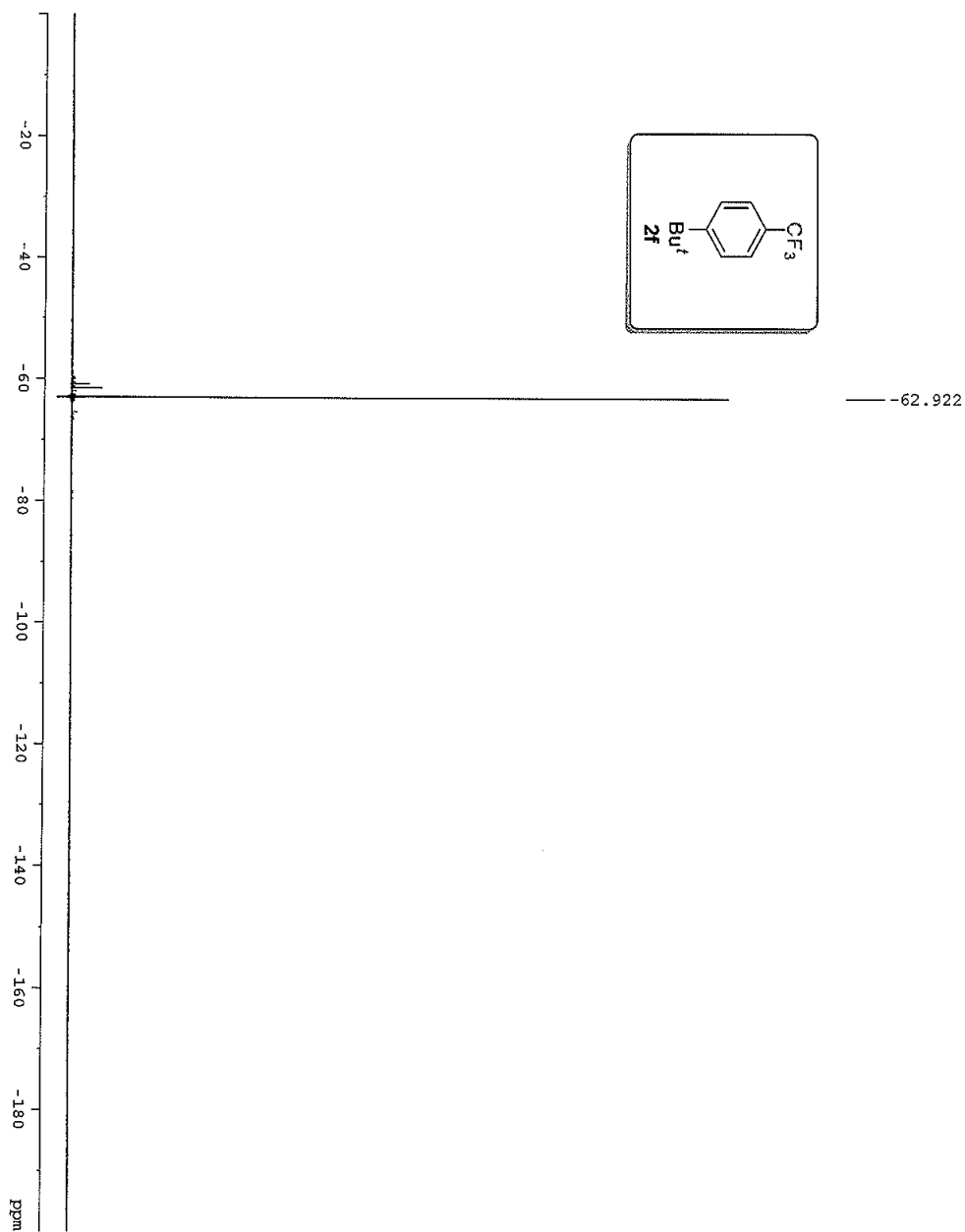
sample unknown



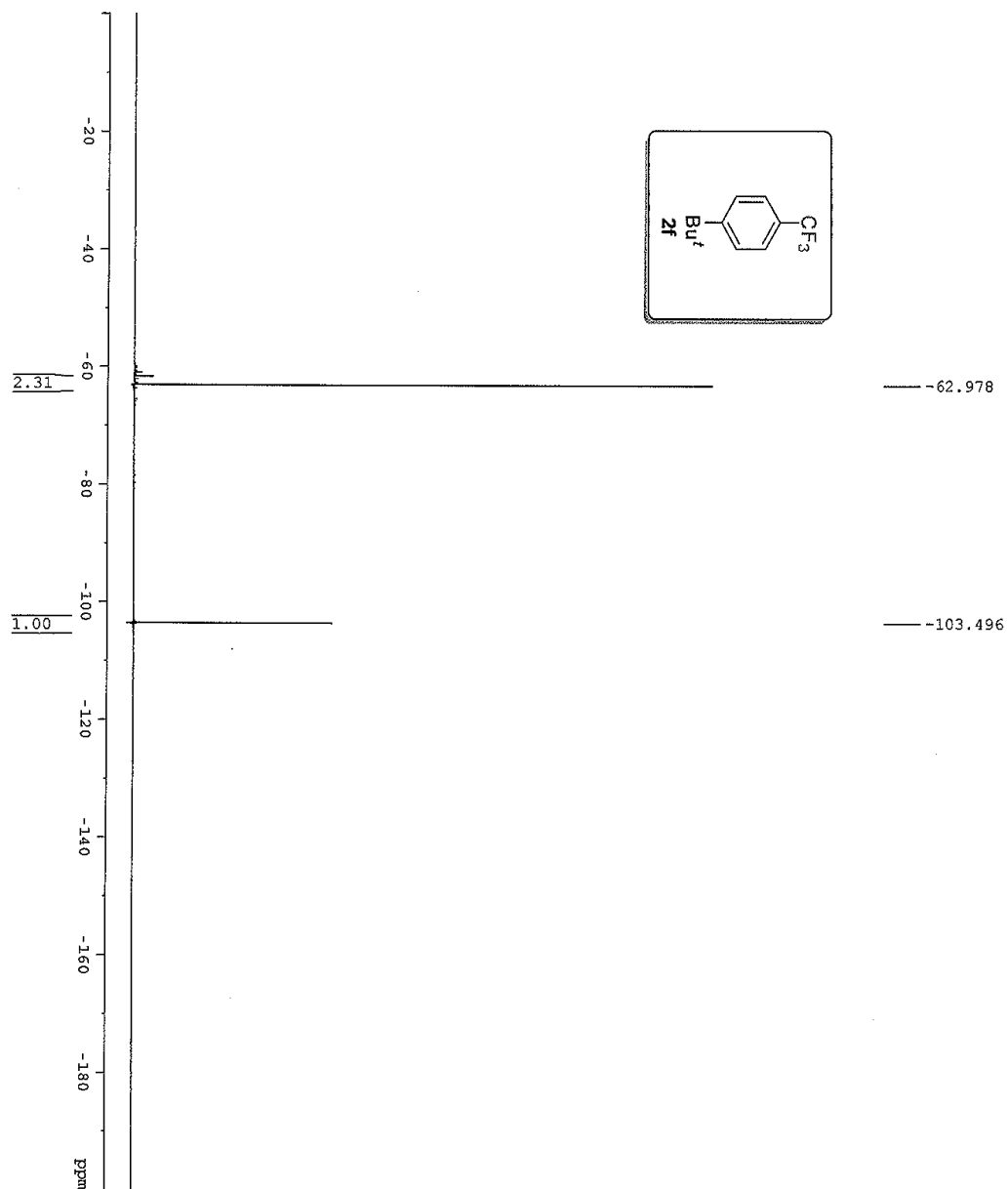
Spectrum



^{19}F NMR of crude 2f in CDCl_3



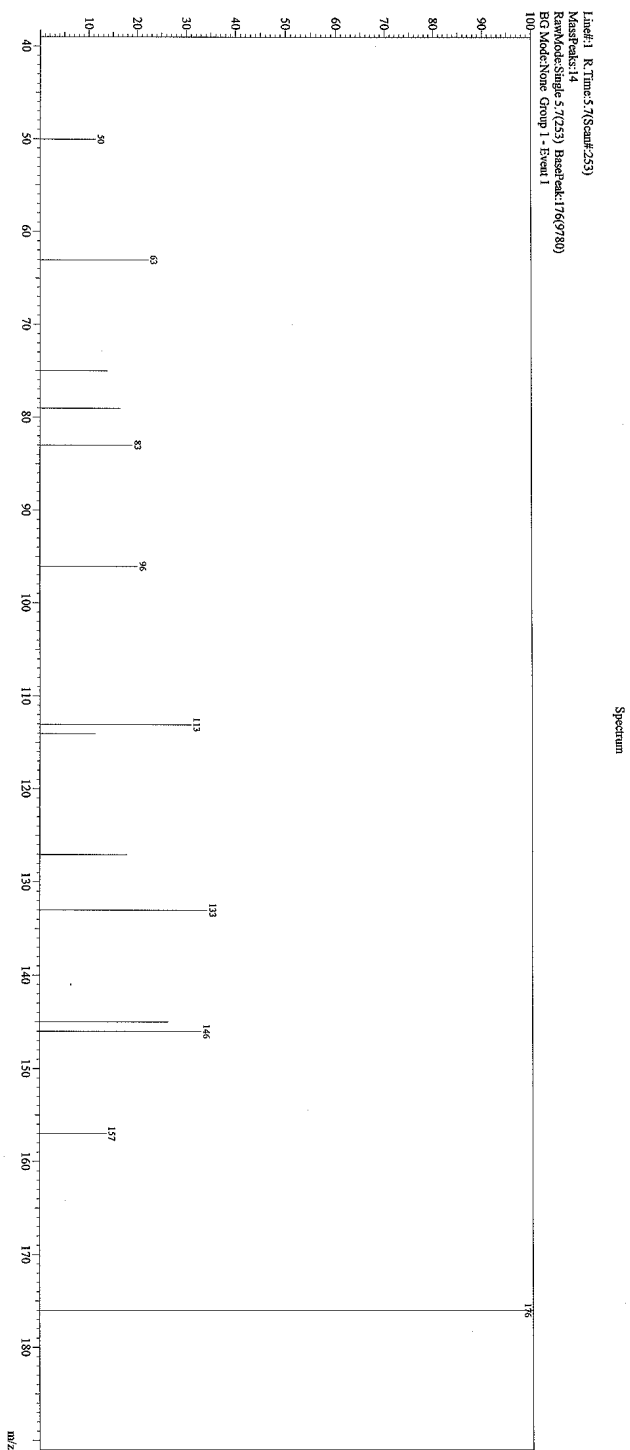
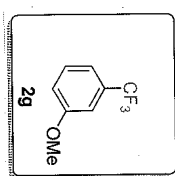
^{19}F NMR yield of compound 2f ($2.31/(1 \times 3) \times 100\% = 77\%$) in CDCl_3



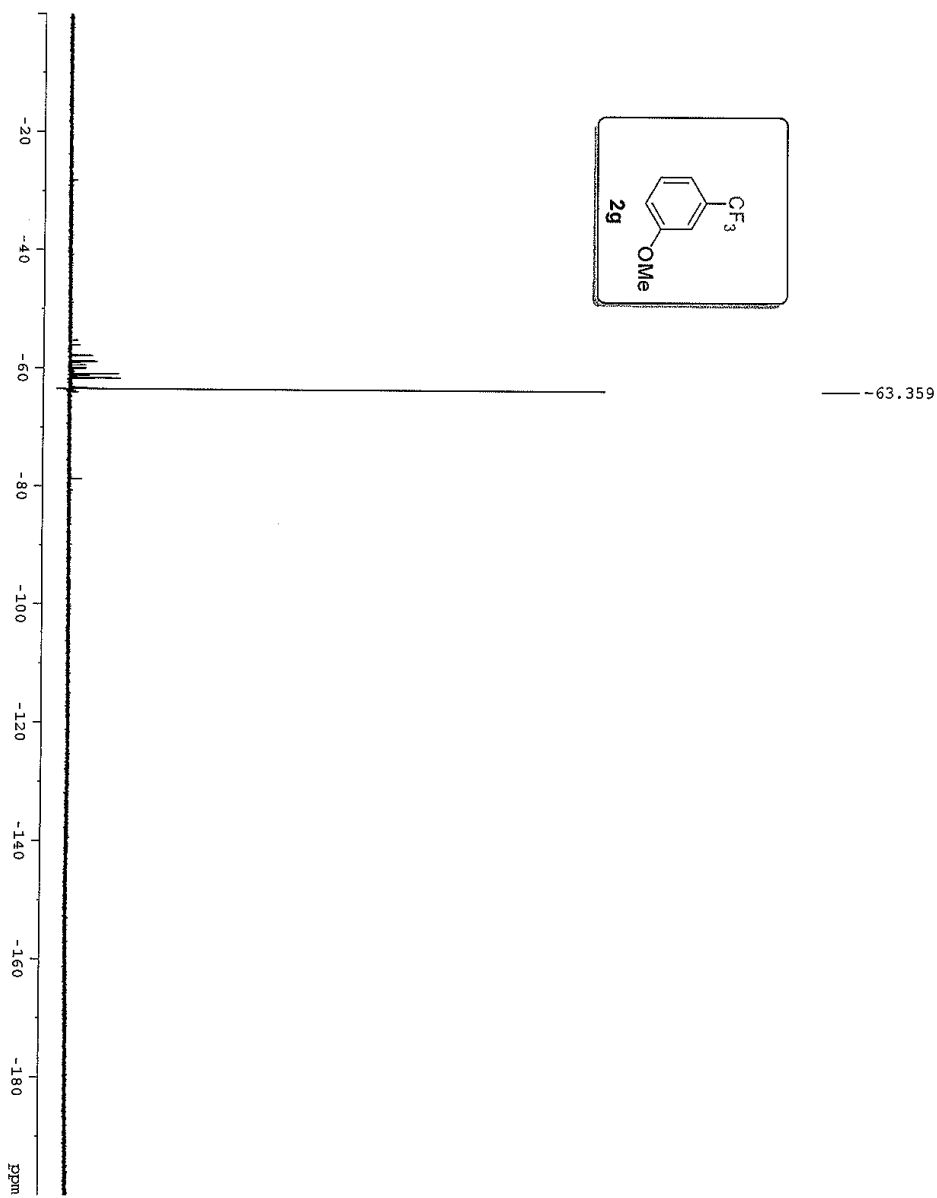
GC-MS of crude 2g

Analysis : GC-MS
Sample Name : Sample 1
Sample ID : [1]-1
Injection Volume : 3

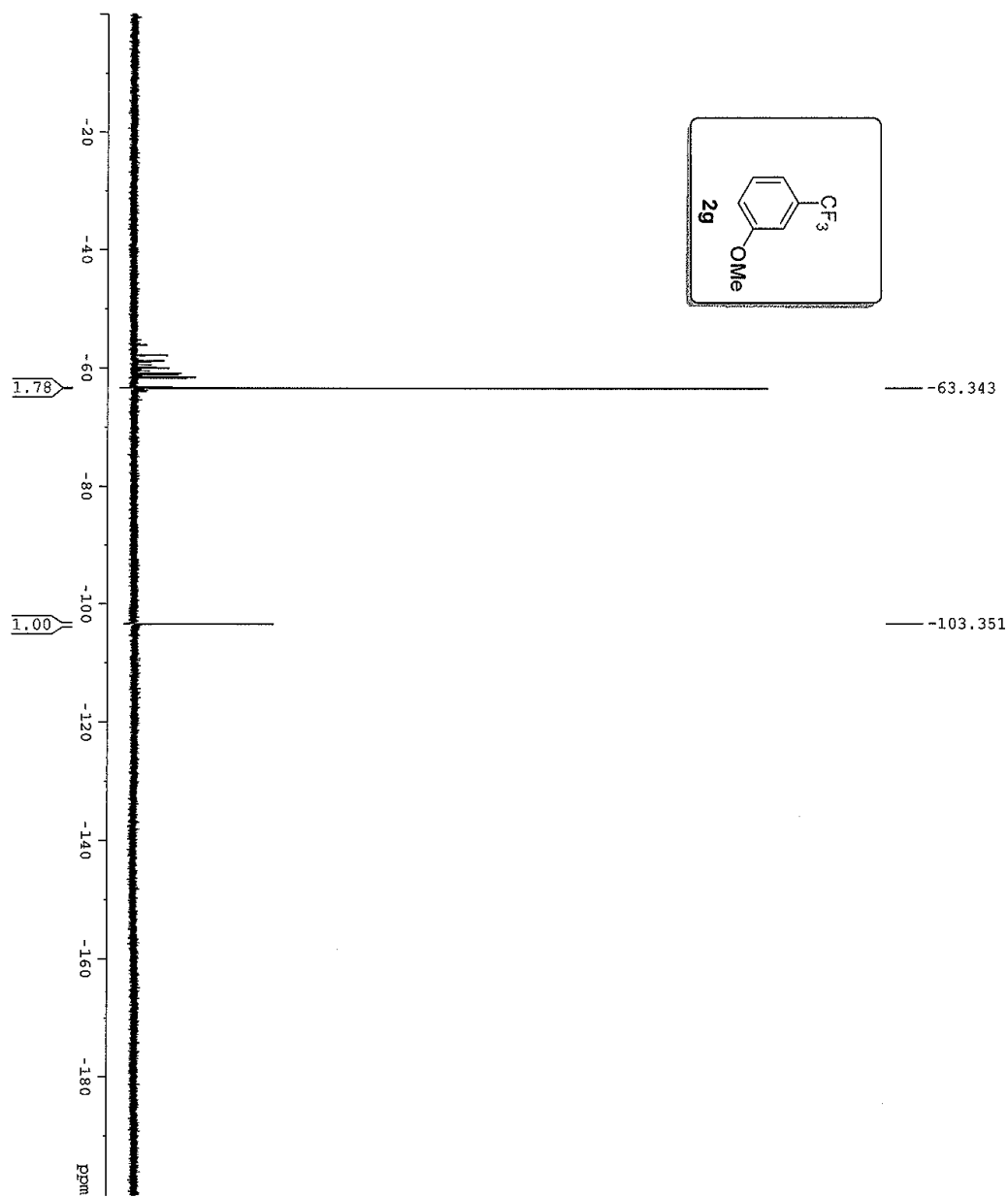
Sample Information
Sample Name : GC-MS
Sample ID : 815/2013 8:50:30 AM
Sample Type : Unknown
Sample Name : SC-NSD-1-20
Sample ID : SC-NSD-1-20
IS Amount : 1
Sample Amount : 1
Injection Volume : 3



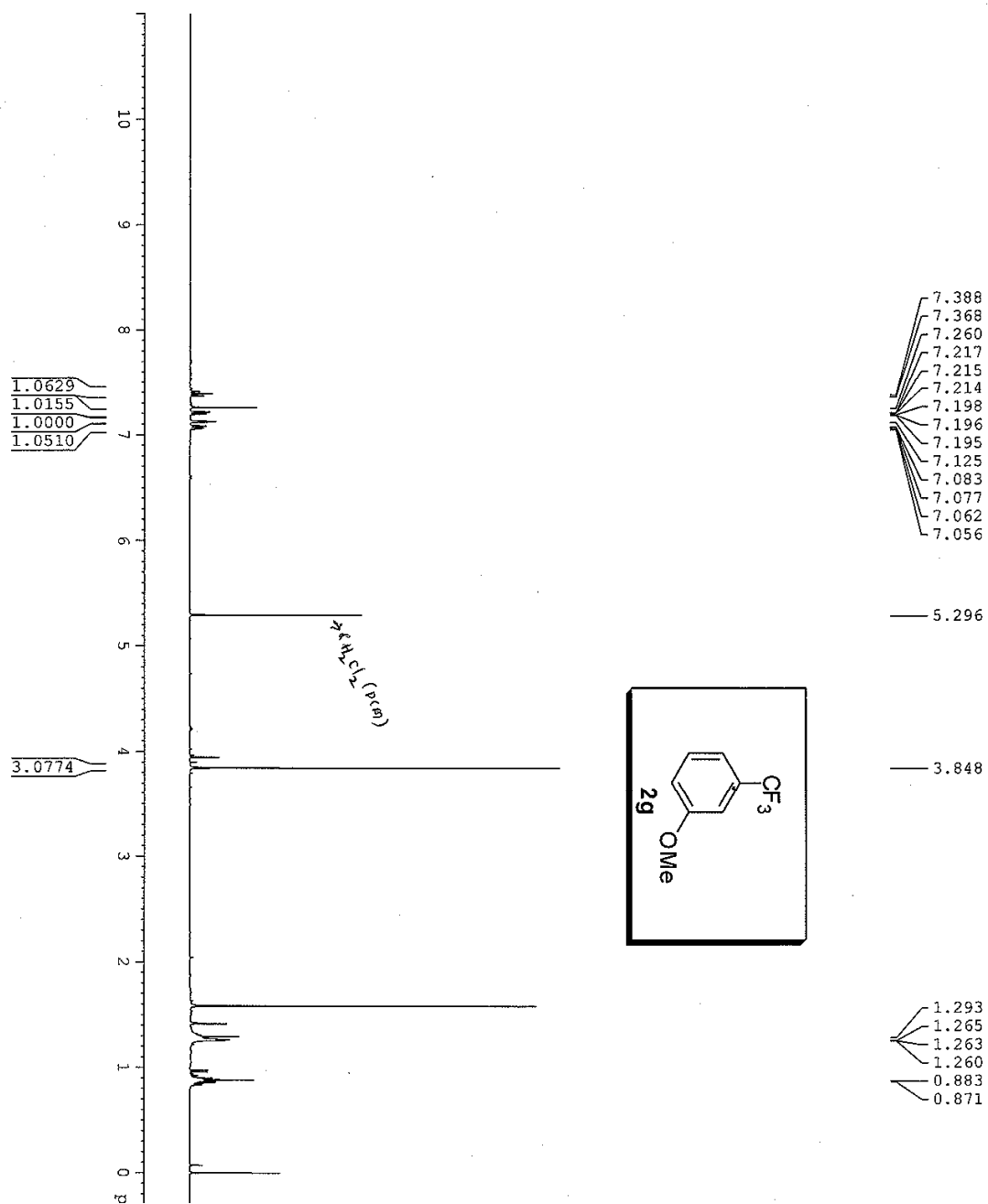
^{19}F NMR of crude 2g in CDCl_3



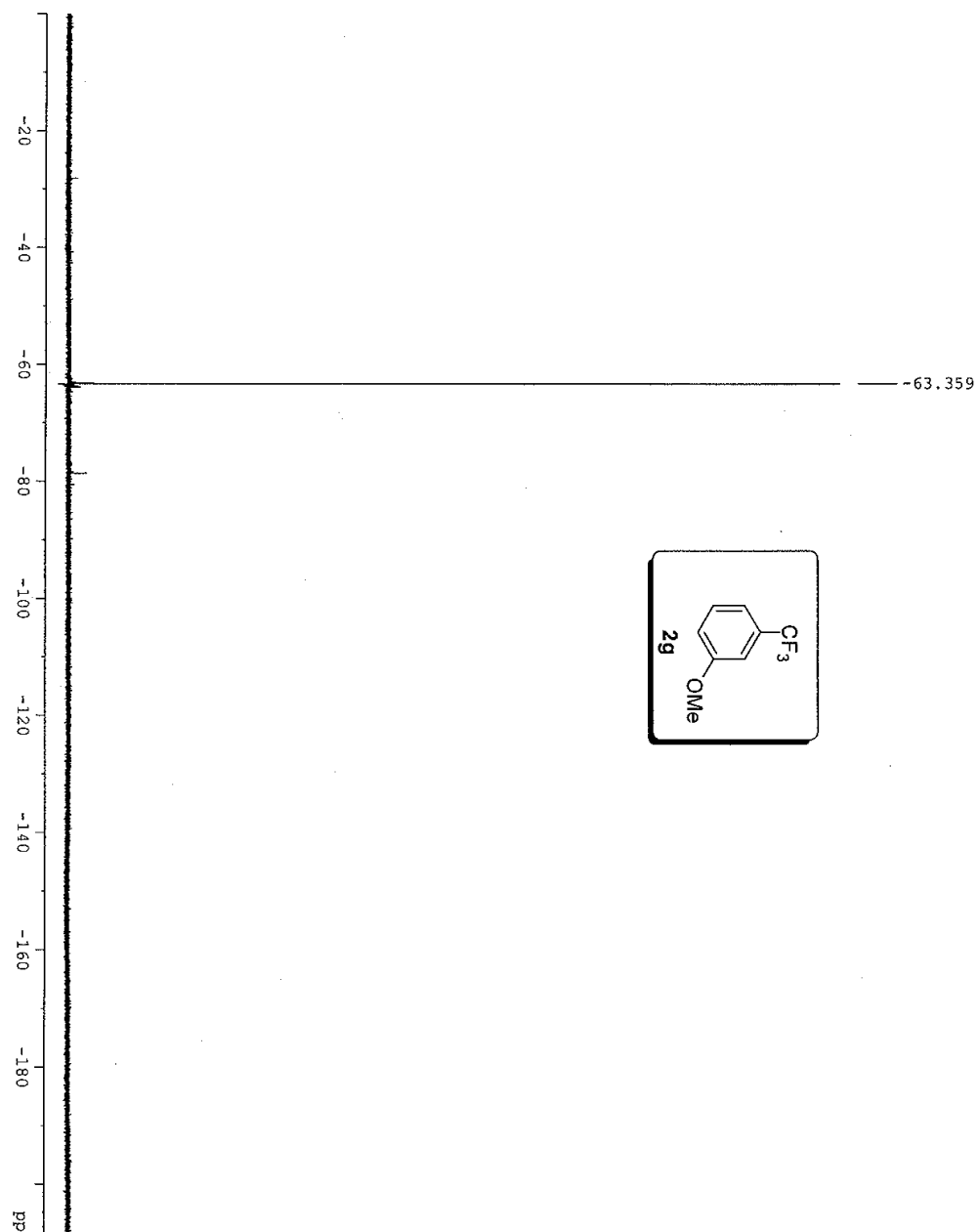
^{19}F NMR yield of compound **2g** $(1.78/(1 \times 3) \times 100\% = 60\%)$ in CDCl_3



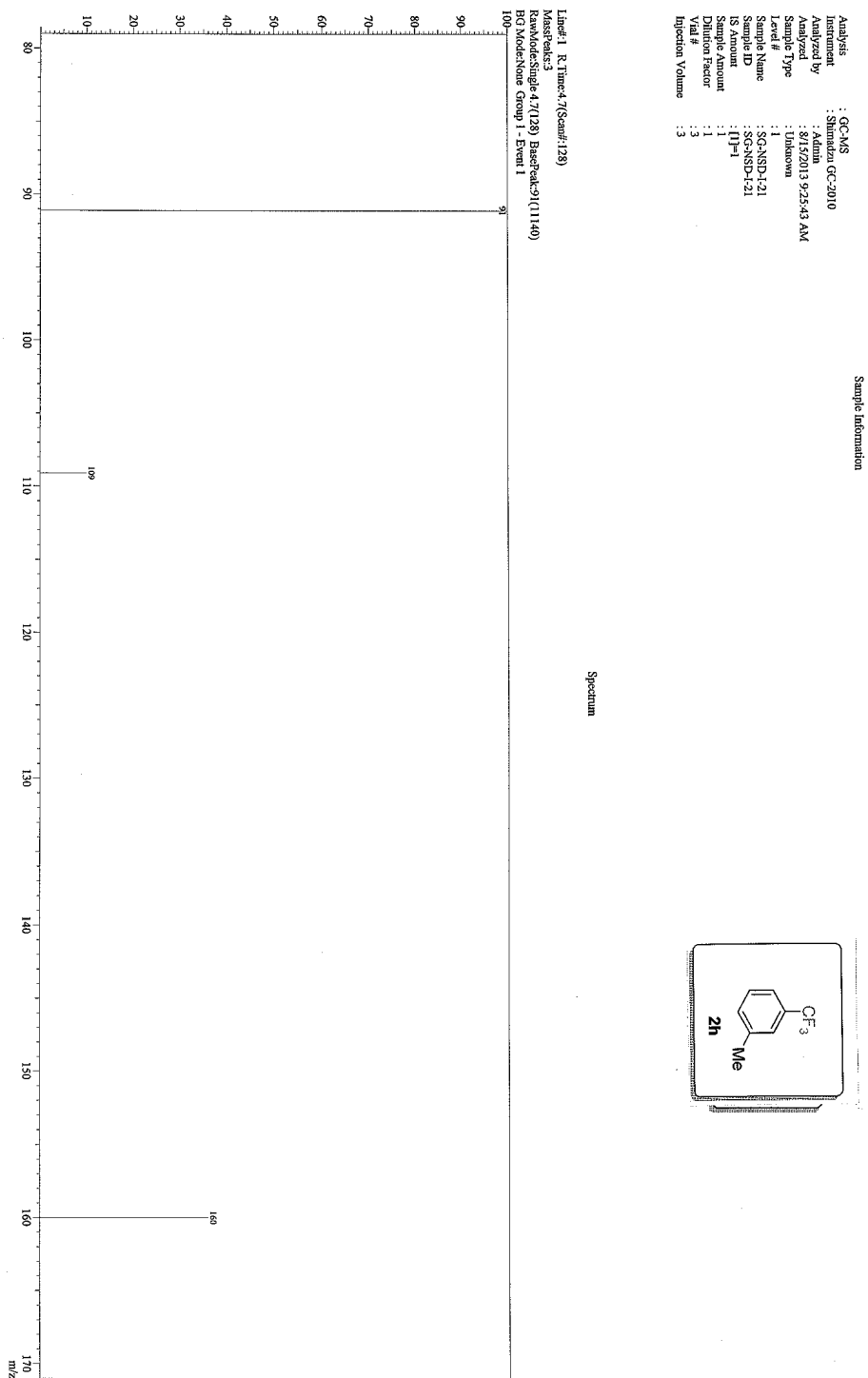
¹H NMR of compound 2g



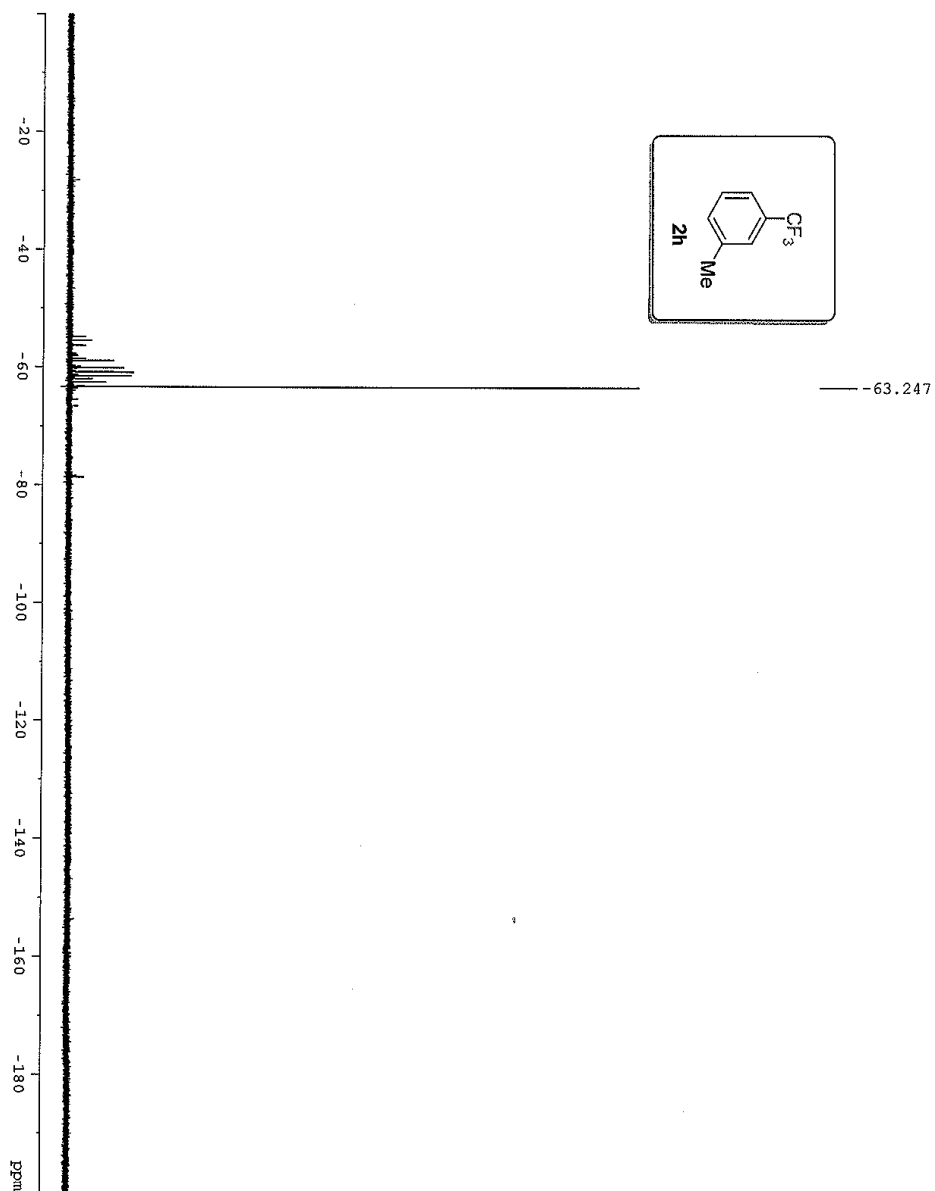
¹⁹F NMR of isolated of 2g in CDCl₃



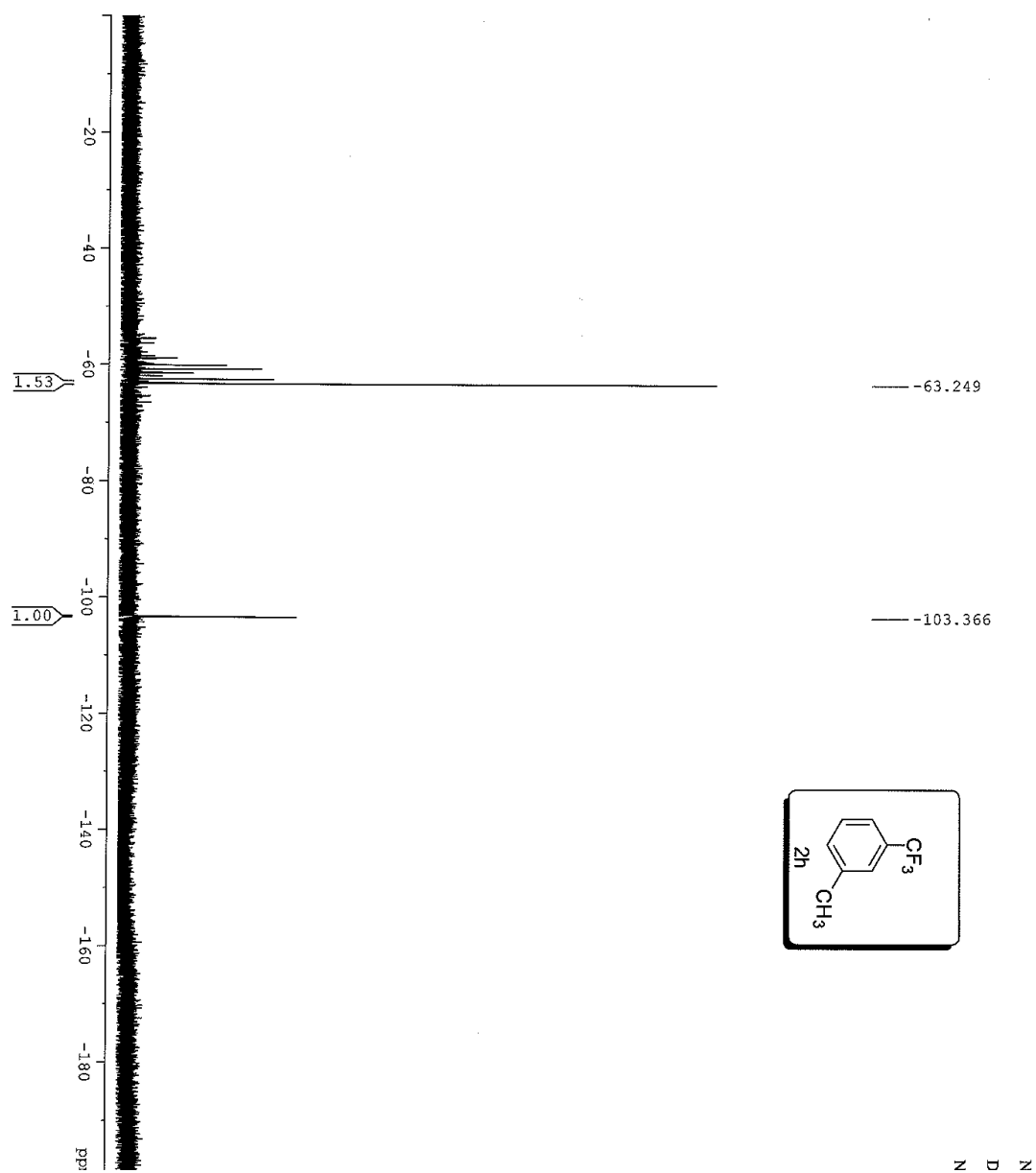
GC-MS of crude 2h



^{19}F NMR of crude 2h in CDCl_3



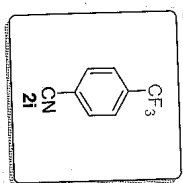
^{19}F NMR yield of compound 2h $(1.53/(1 \times 3) \times 100\% = 51\%)$ in CDCl_3



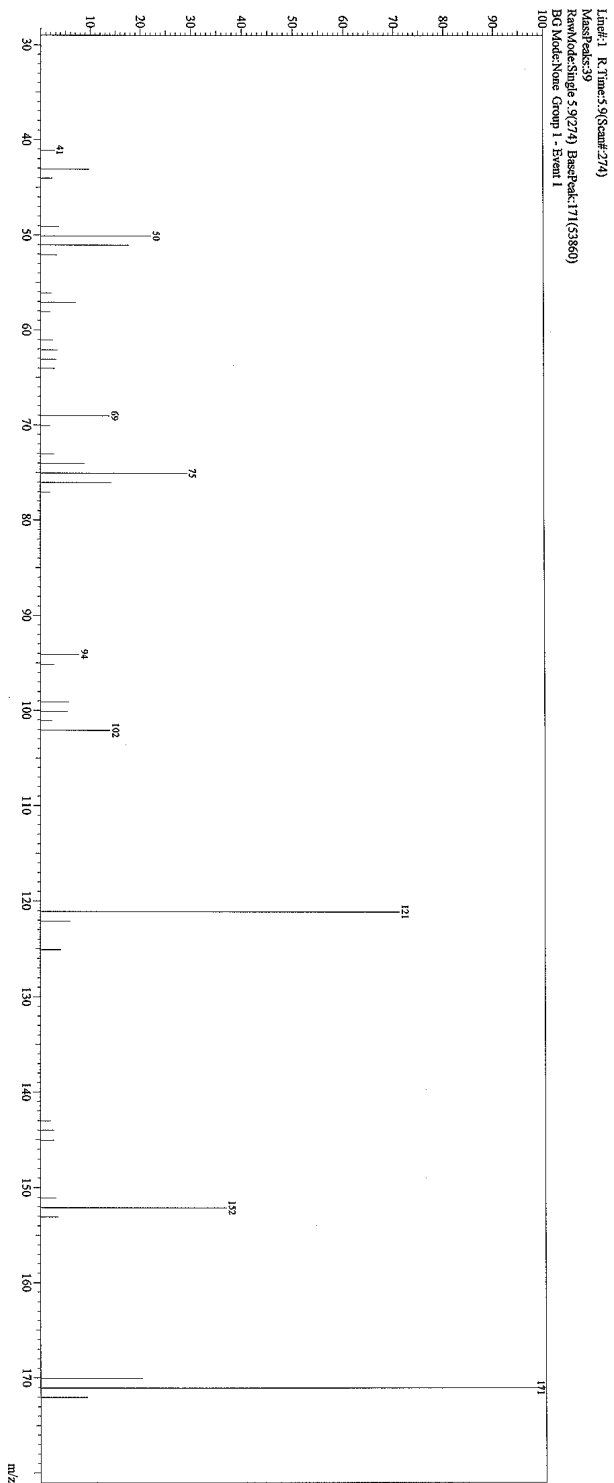
GC-MS of crude 2i

Sample Information

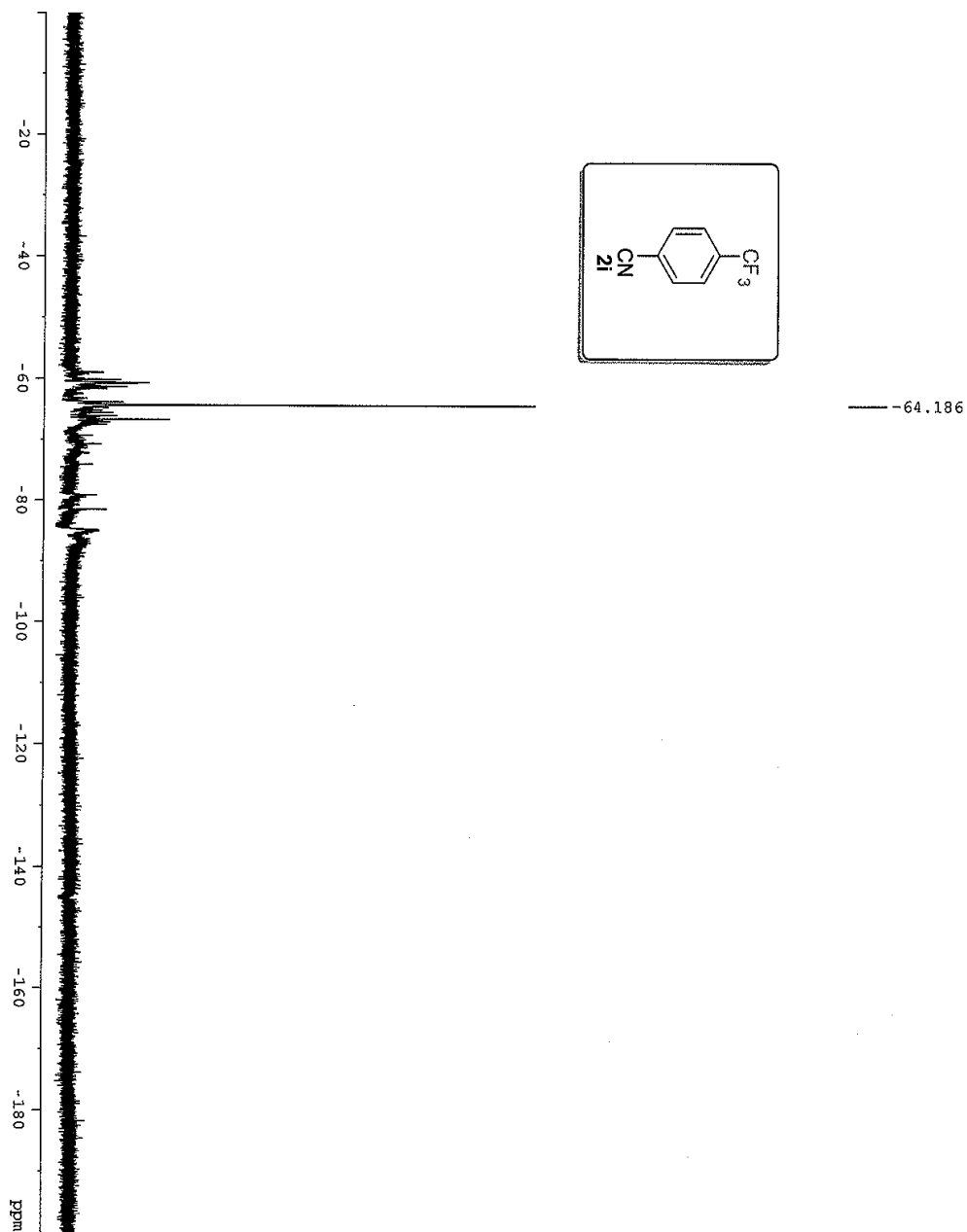
Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 8/3/2013 1:11:18 PM
Sample Type : Unknown
Level # : 1
Sample Name : SO-RBS-F-58
Sample ID : SO-RBS-F-58
S Parameter : 1171
S Parameter : 1
Dilution Factor : 1
Vial # : 3
Injection Volume : 3



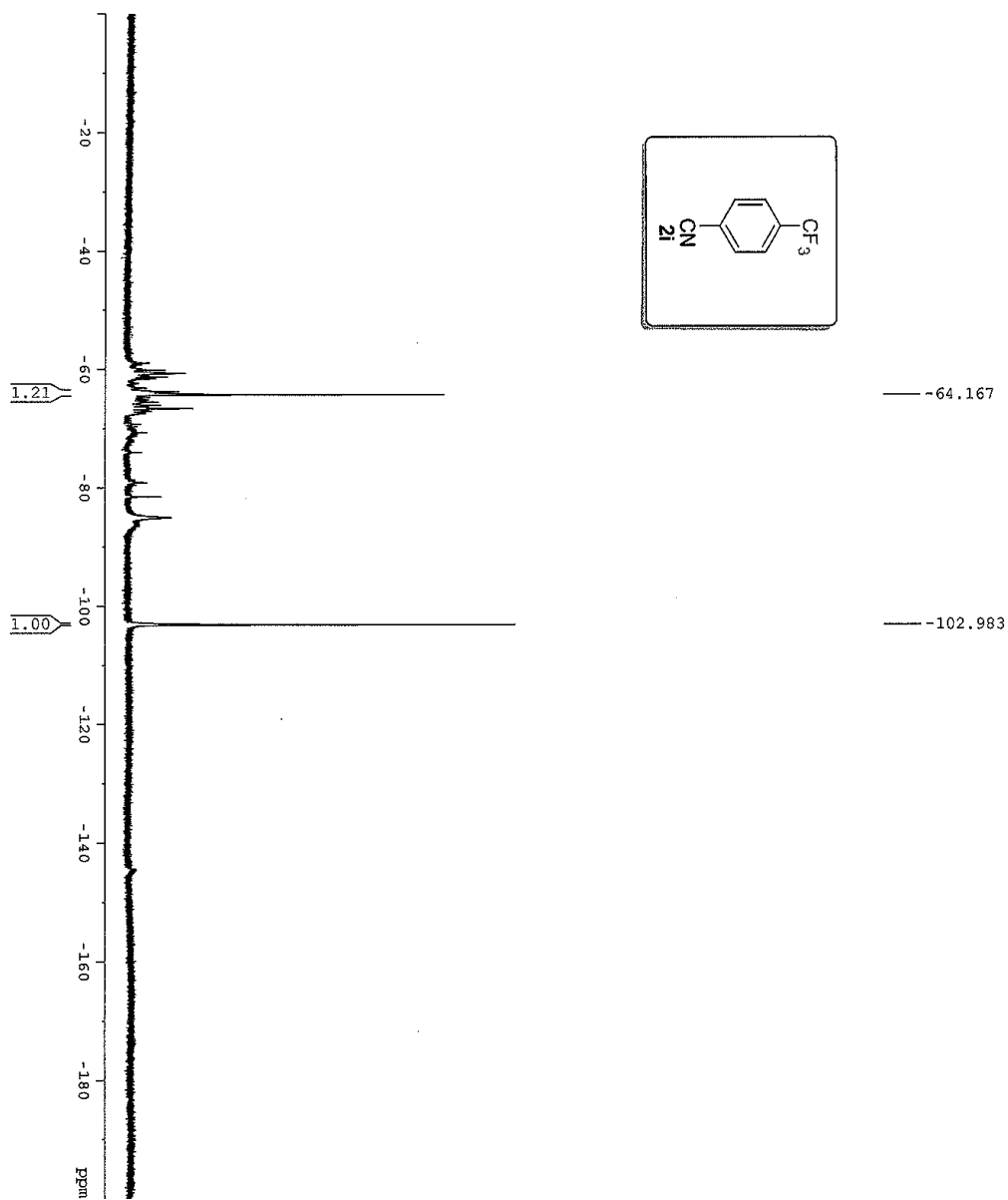
Spectrum



^{19}F NMR of crude **2i** in CDCl_3



^{19}F NMR yield of compound **2i** ($1.21/(1 \times 3) \times 100\% = 40\%$) in CDCl_3

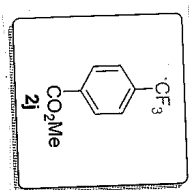
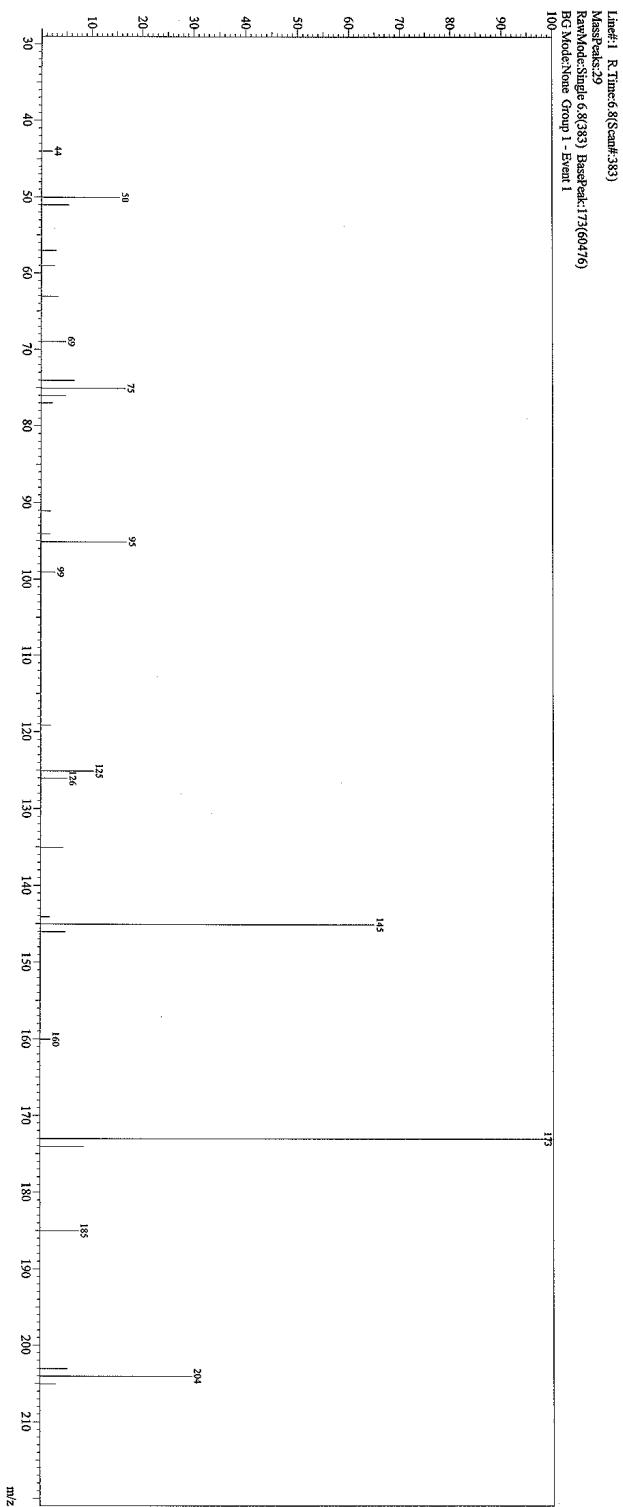


GC-MS of crude 2j

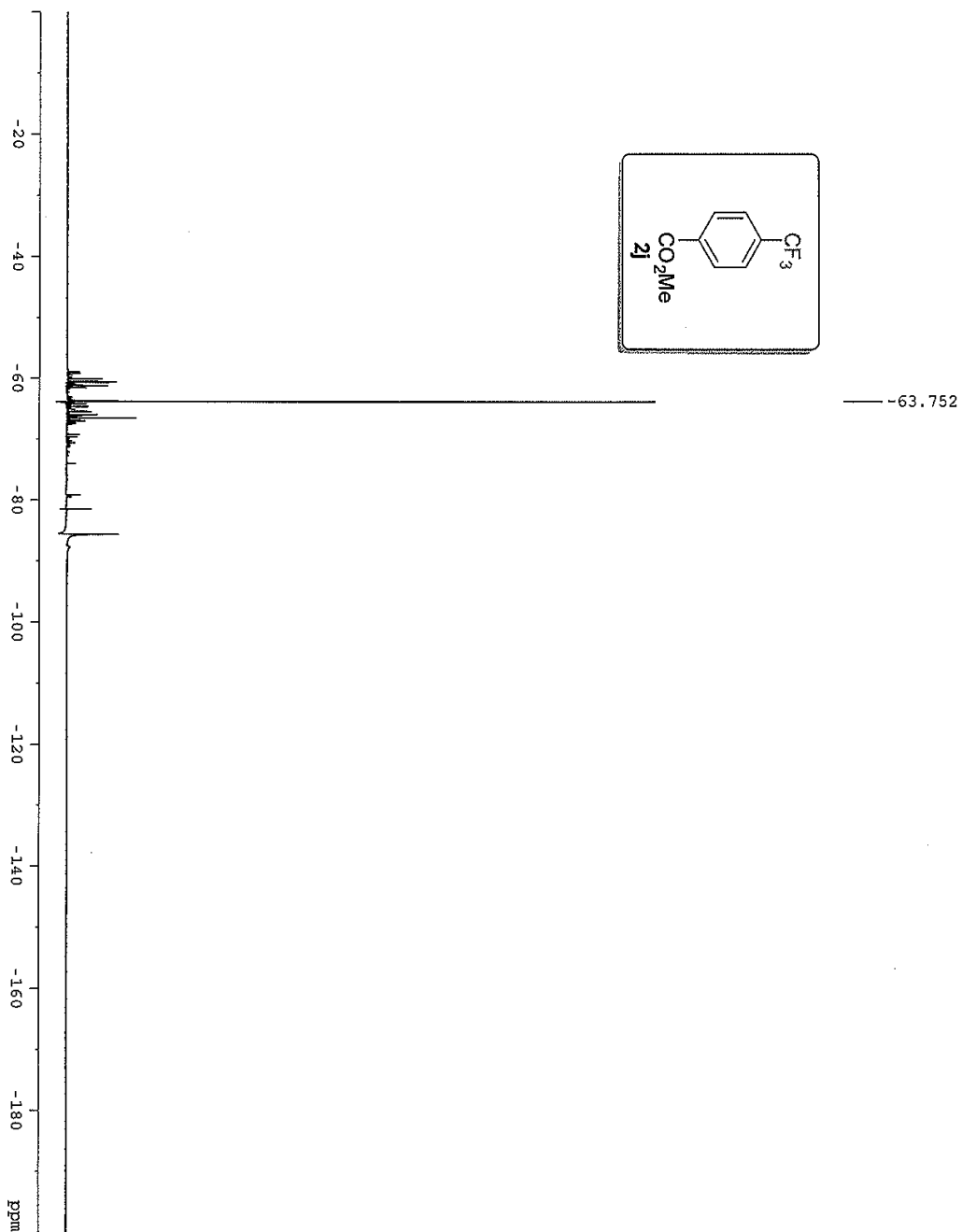
Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Adimu
Analyzed : 8/2/2013 1:46:42 PM
Sample Type : Unknown
Level # : 1
Sample Name : SG-RBS-F-59
Sample ID : SG-RBS-F-59
IS Amount : [1]=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 4
Injection Volume : 3

Sample Information

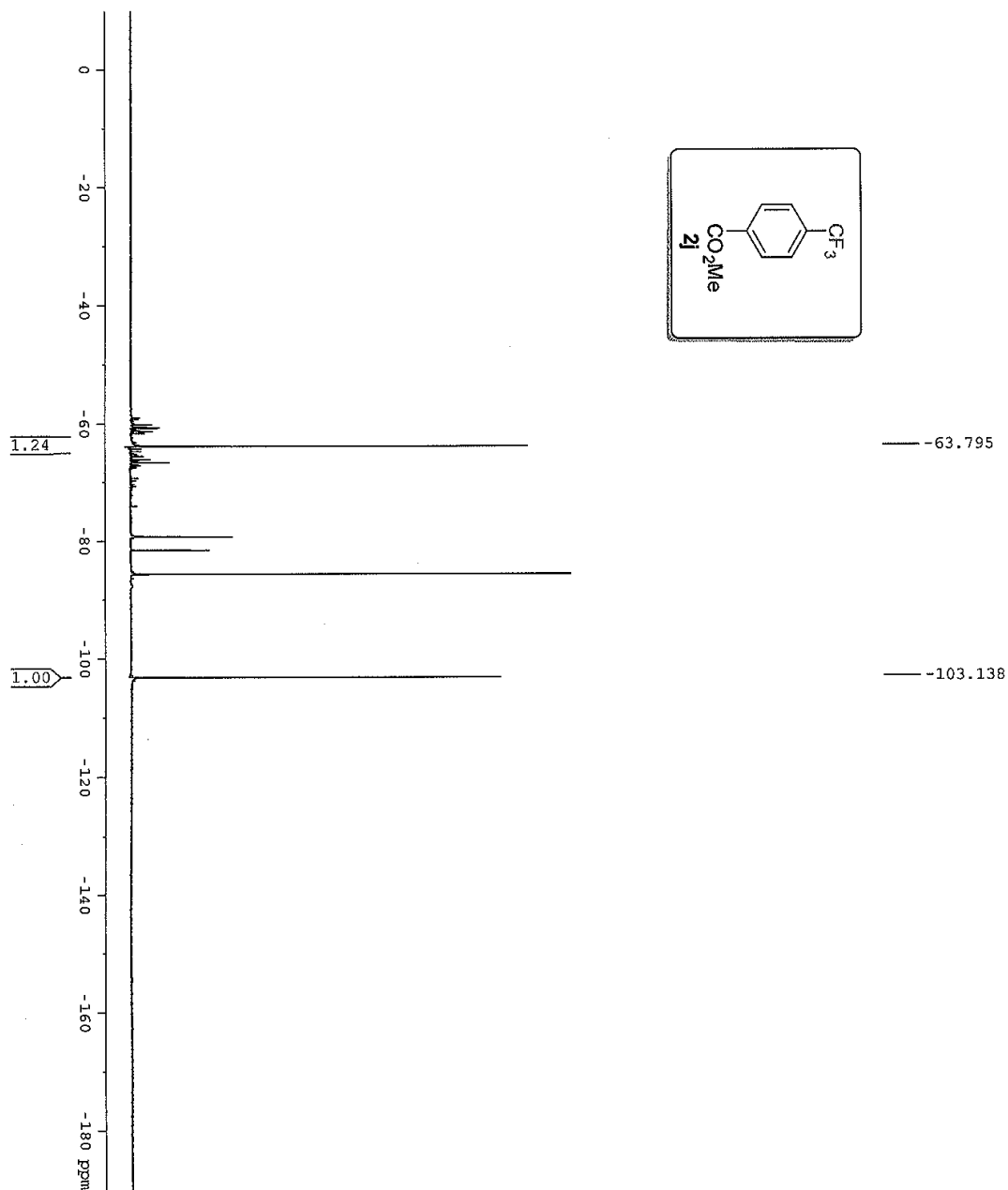
Spectrum



^{19}F NMR of crude 2j in CDCl_3



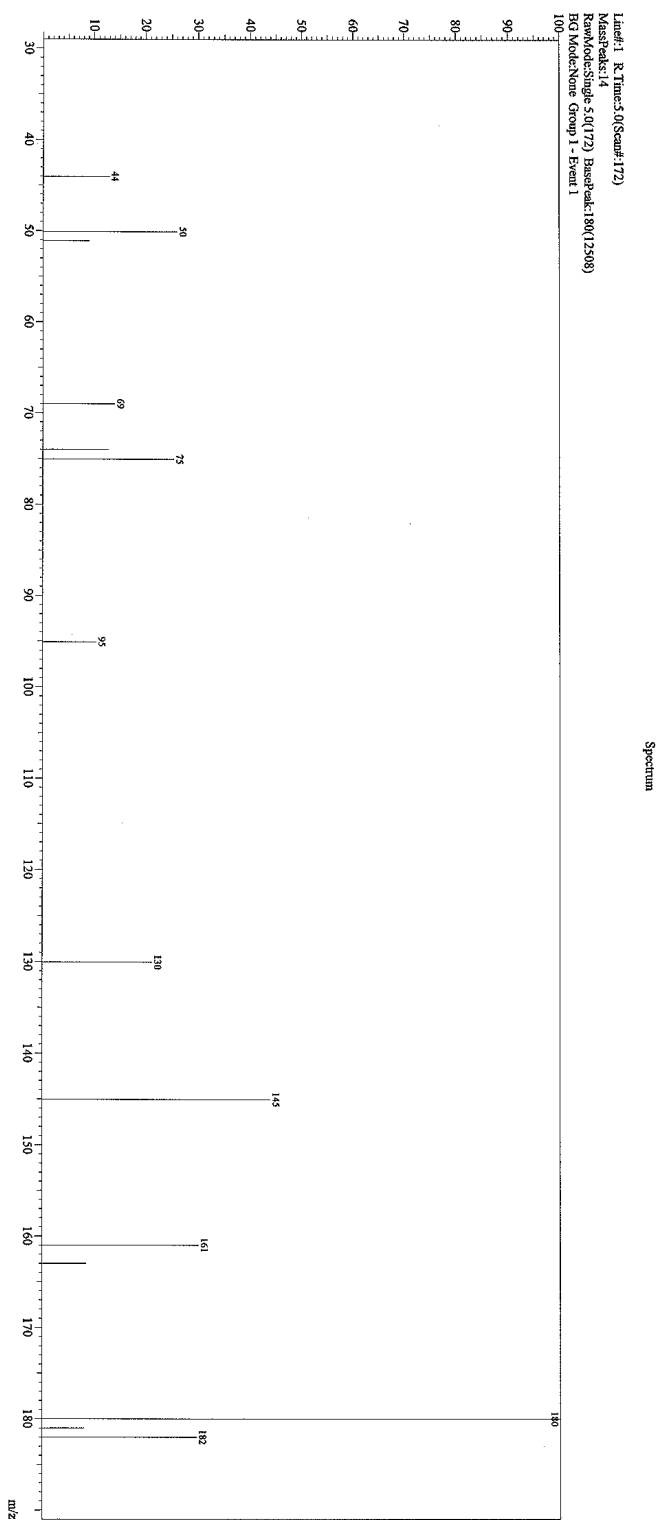
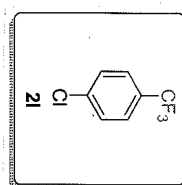
^{19}F NMR yield of compound **2j** ($1.24/(1 \times 3) \times 100\% = 41\%$) in CDCl_3



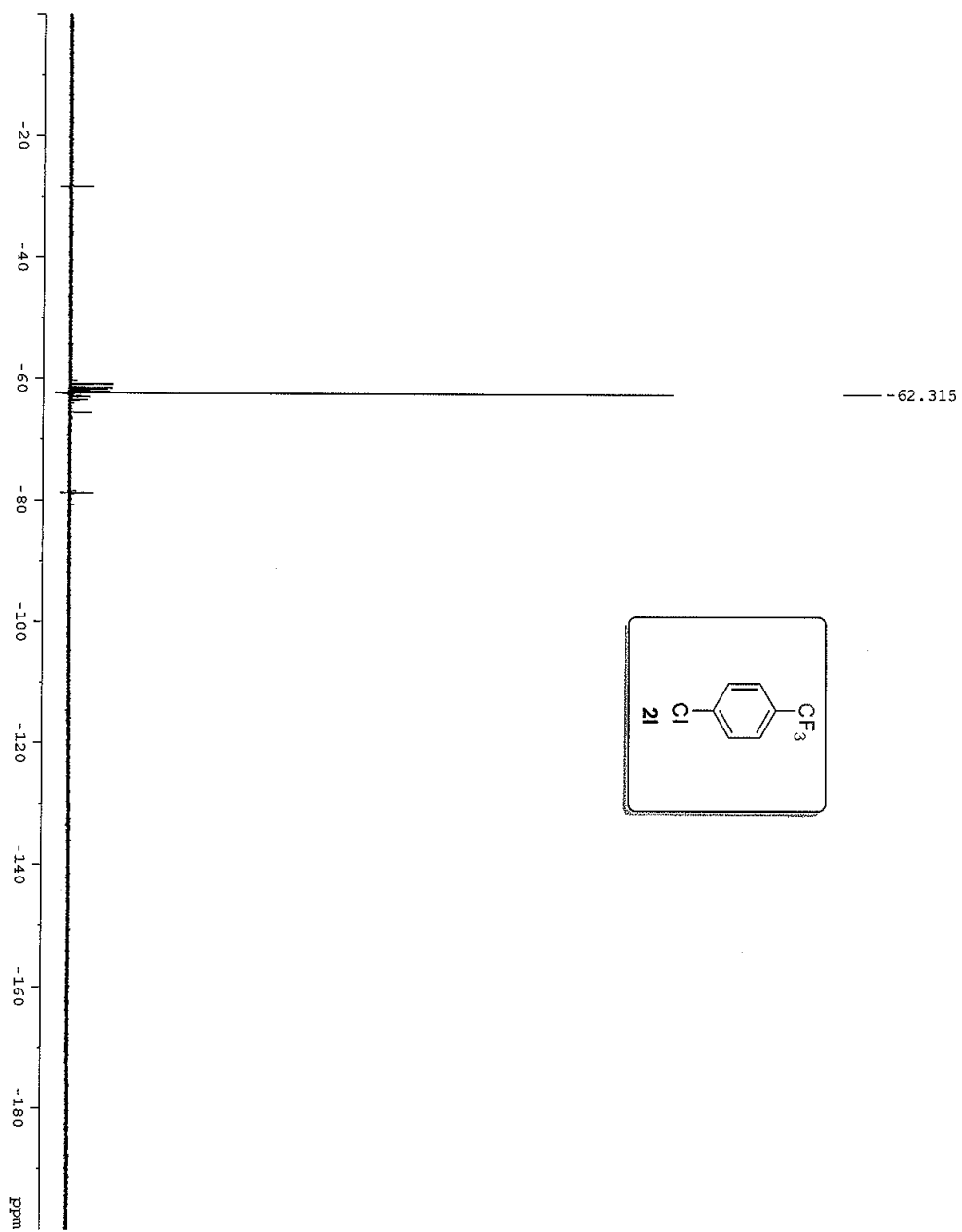
GC-MS of crude 2l

Sample Information

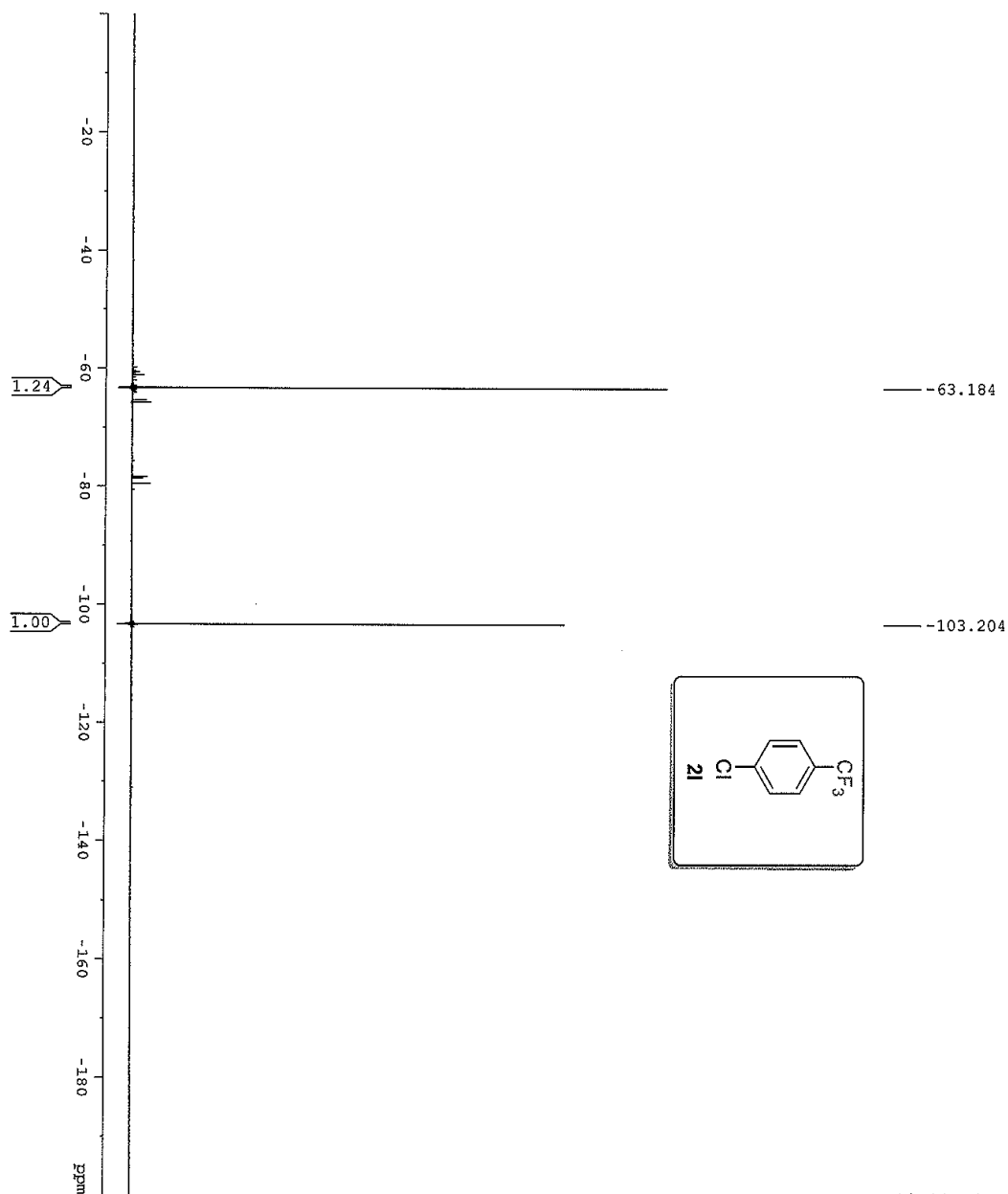
Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 07/2013 10:37:28 AM
Sample Type : Unknown
Injection # : 1
Sample Name : SCANSD-4-12-1
Sample ID : SCANSD-4-12-1
IS Amount : [1]=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 2
Injection Volume : 3



^{19}F NMR of crude 2l in CDCl_3



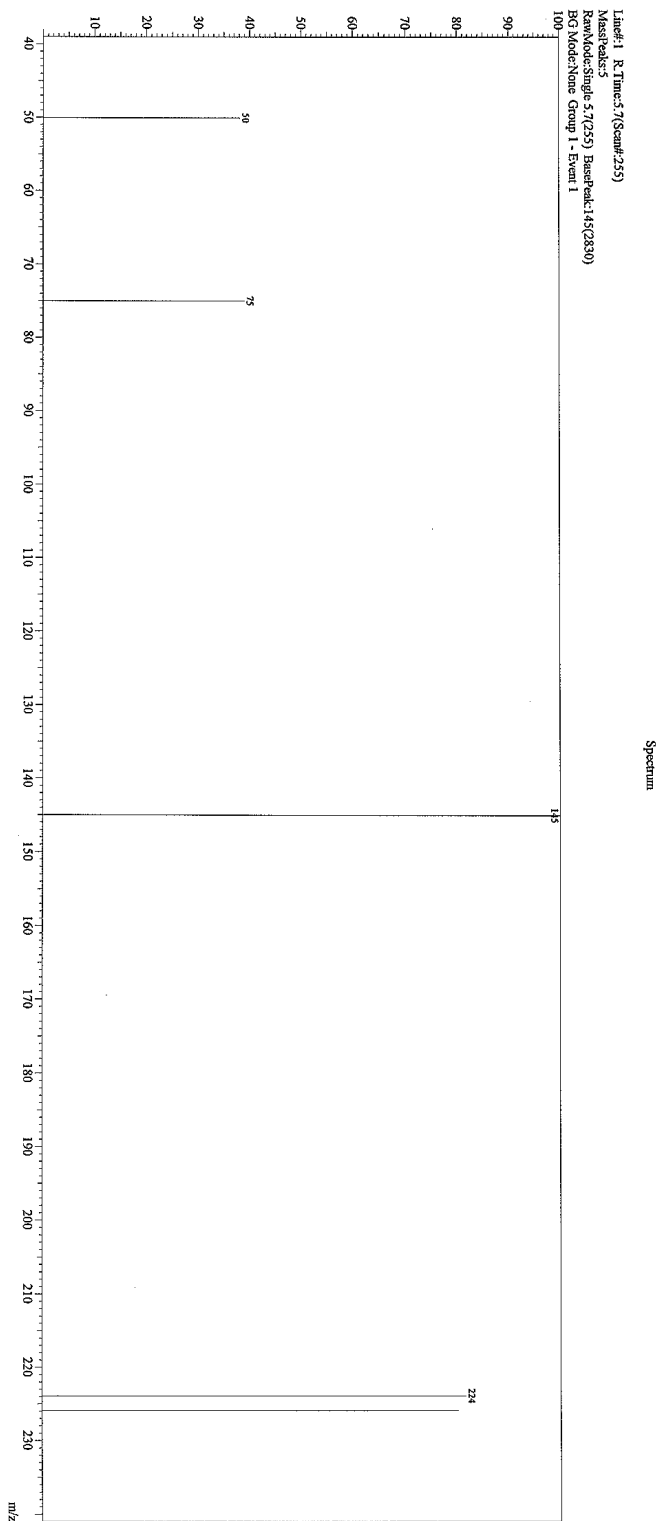
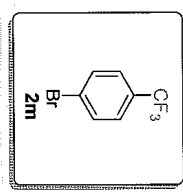
^{19}F NMR yield of compound 2l ($1.24/(1 \times 3) \times 100\% = 41\%$) in CDCl_3



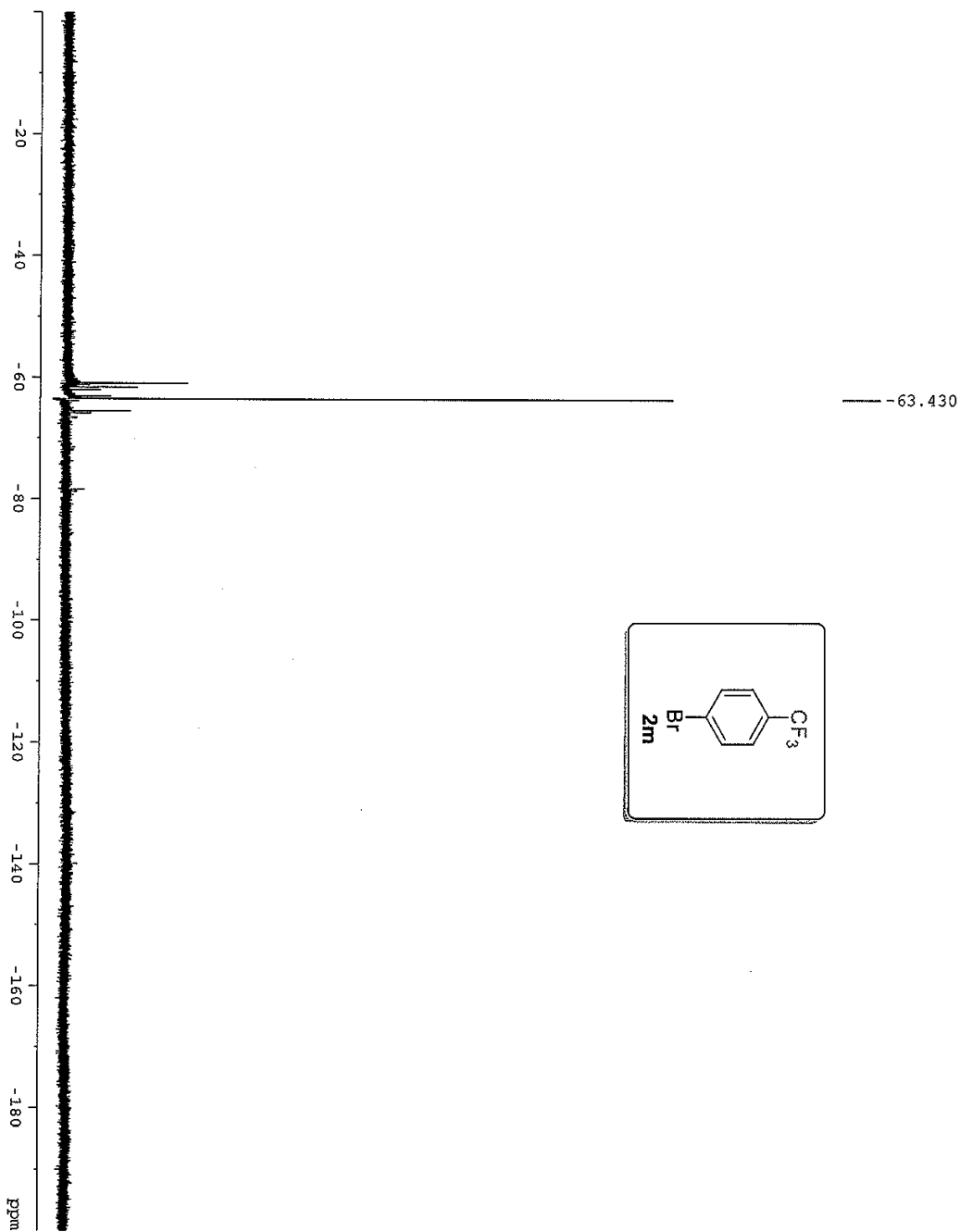
GC-MS of crude 2m

Sample Information

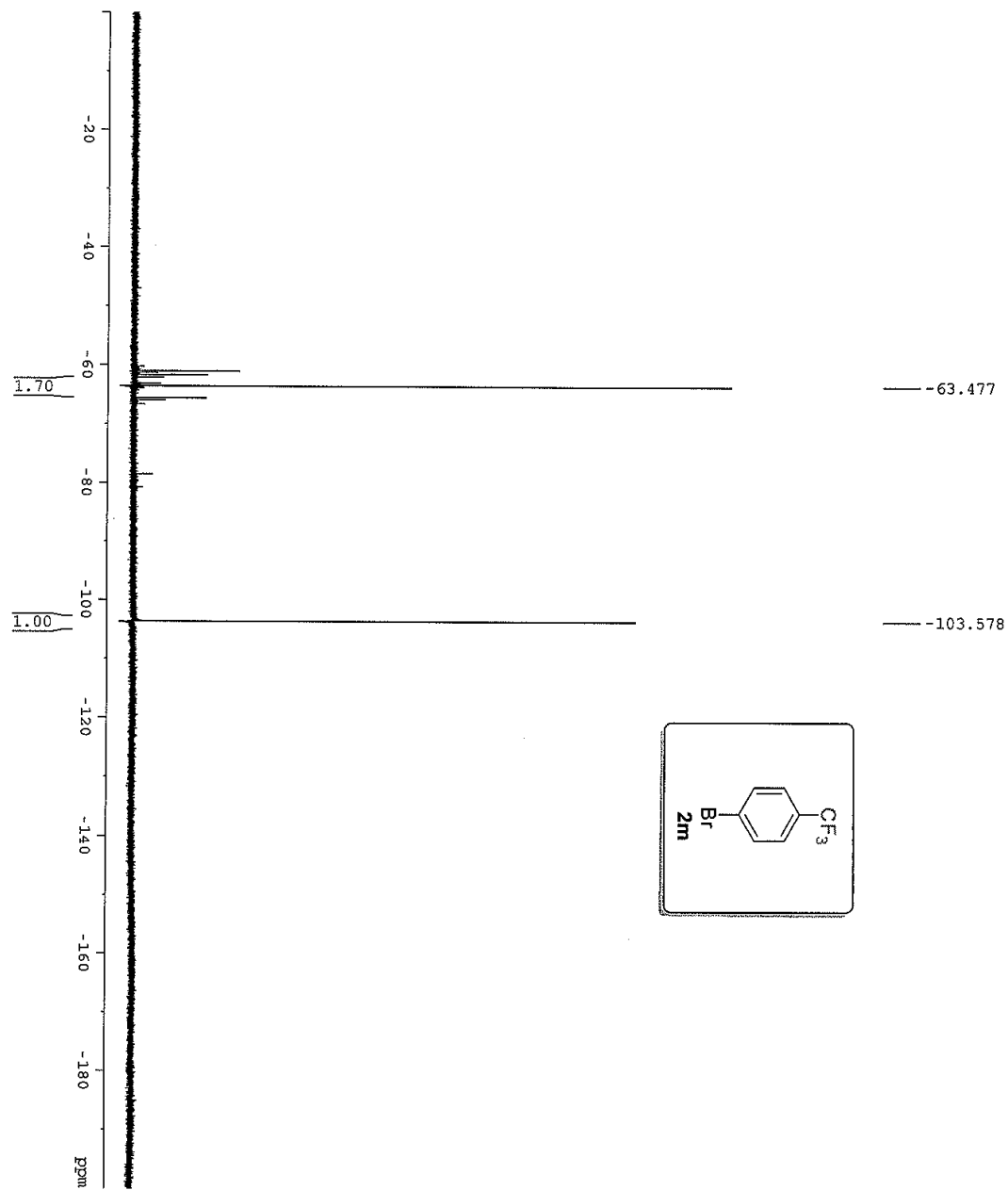
Analysis	: GC-MS
Instrument	: Shimadzu GC-2010
Analyzed by	: Admin
Analyzed	: 8/19/2013 3:14:05 PM
Sample Type	: Unknown
Level #	: 1
Sample Name	: S-GA-MS-1-23
Sample ID	: S-GA-MS-1-23
S Number	: 1171
Sample Amount	: 1
Dilution Factor	: 1
Vial #	: 4
Injection Volume	: 3



^{19}F NMR of crude 2m in CDCl_3



^{19}F NMR yield of compound **2m** ($1.70/(1 \times 3) \times 100\% = 57\%$) in CDCl_3

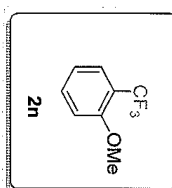
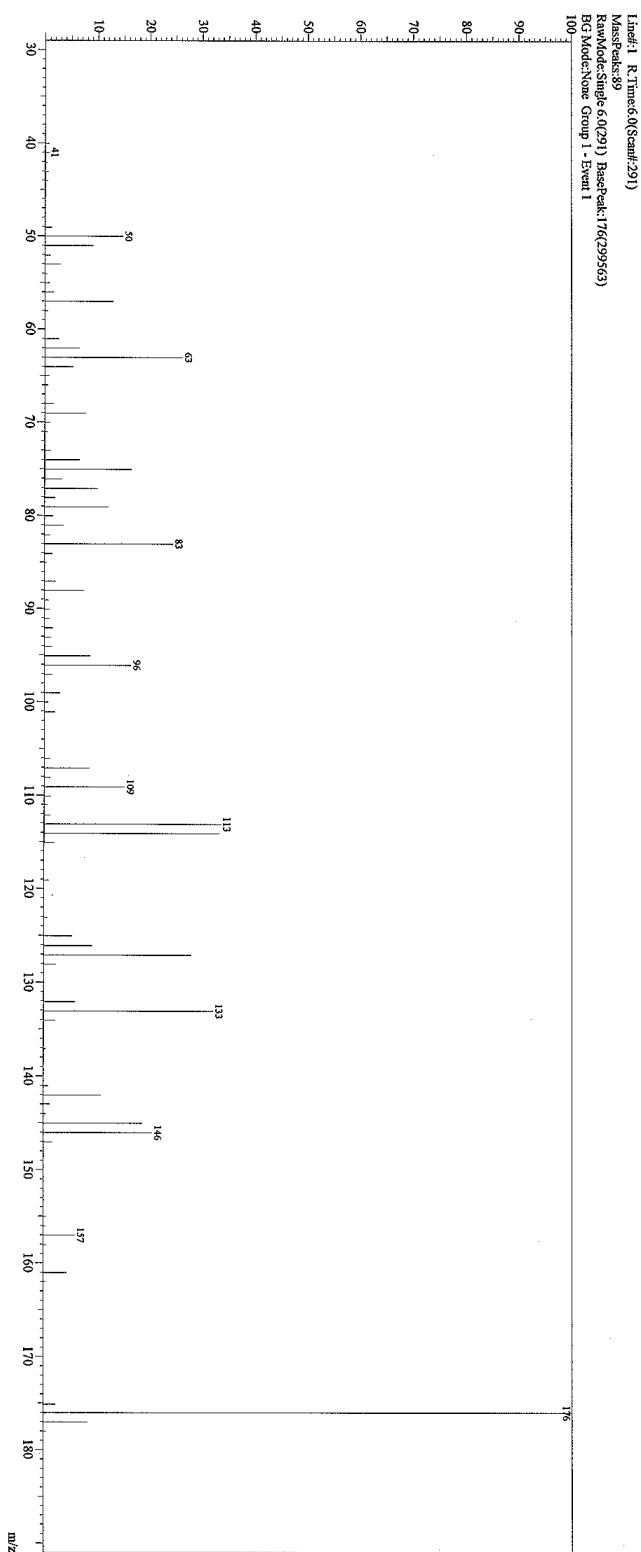


GC-MS of crude 2n

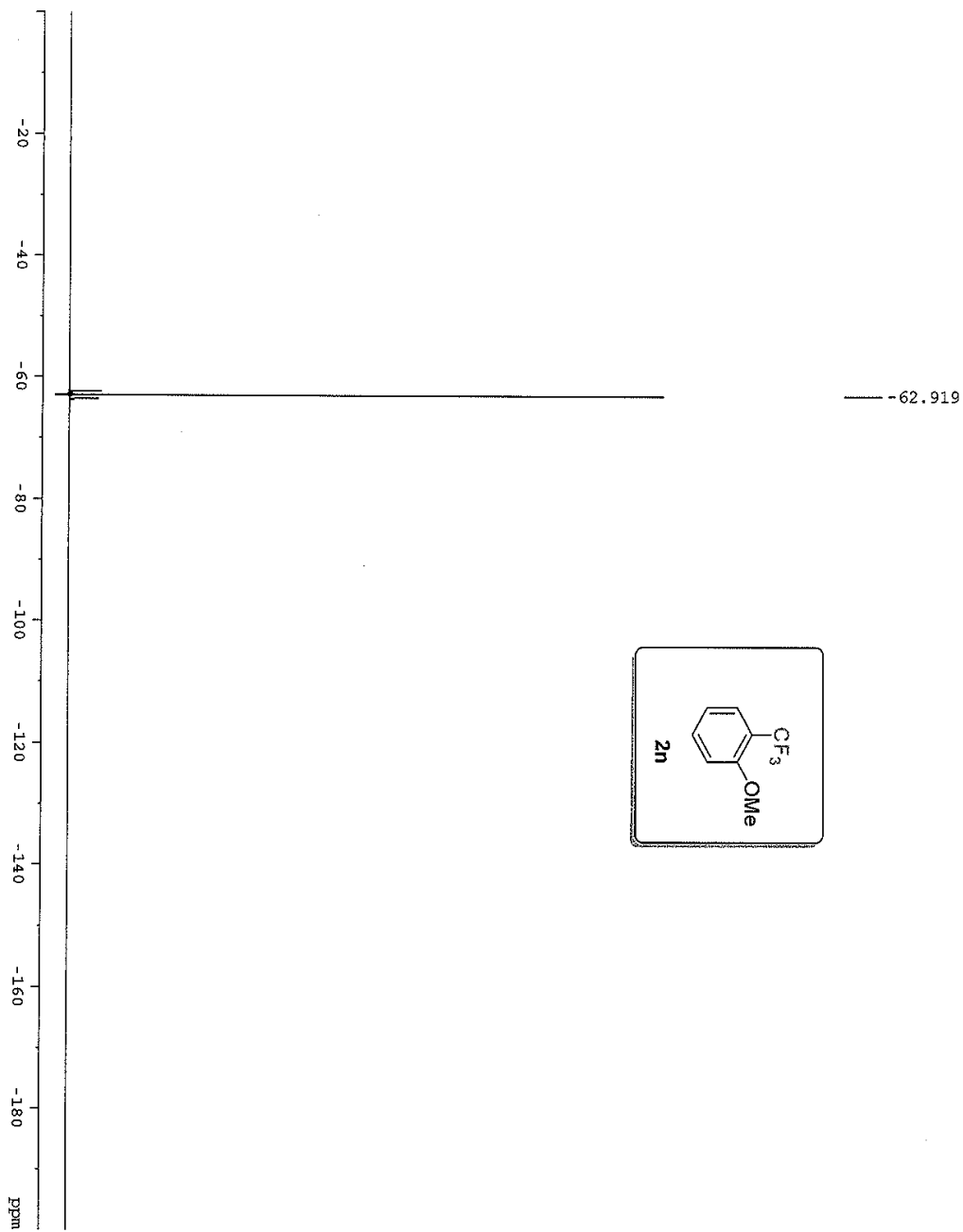
Sample Information

Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Adam
Analyzed : 8/3/2013 2:22:02 PM
Sample Type : Unknown
Level #: 1
Sample Name : SG-ANS-1-8
Sample ID : SG-ANS-1-8
S Amount : [1]-1
Sample Amount : 1
Dilution Factor : 1
Vial #: 5
Injection Volume : 3

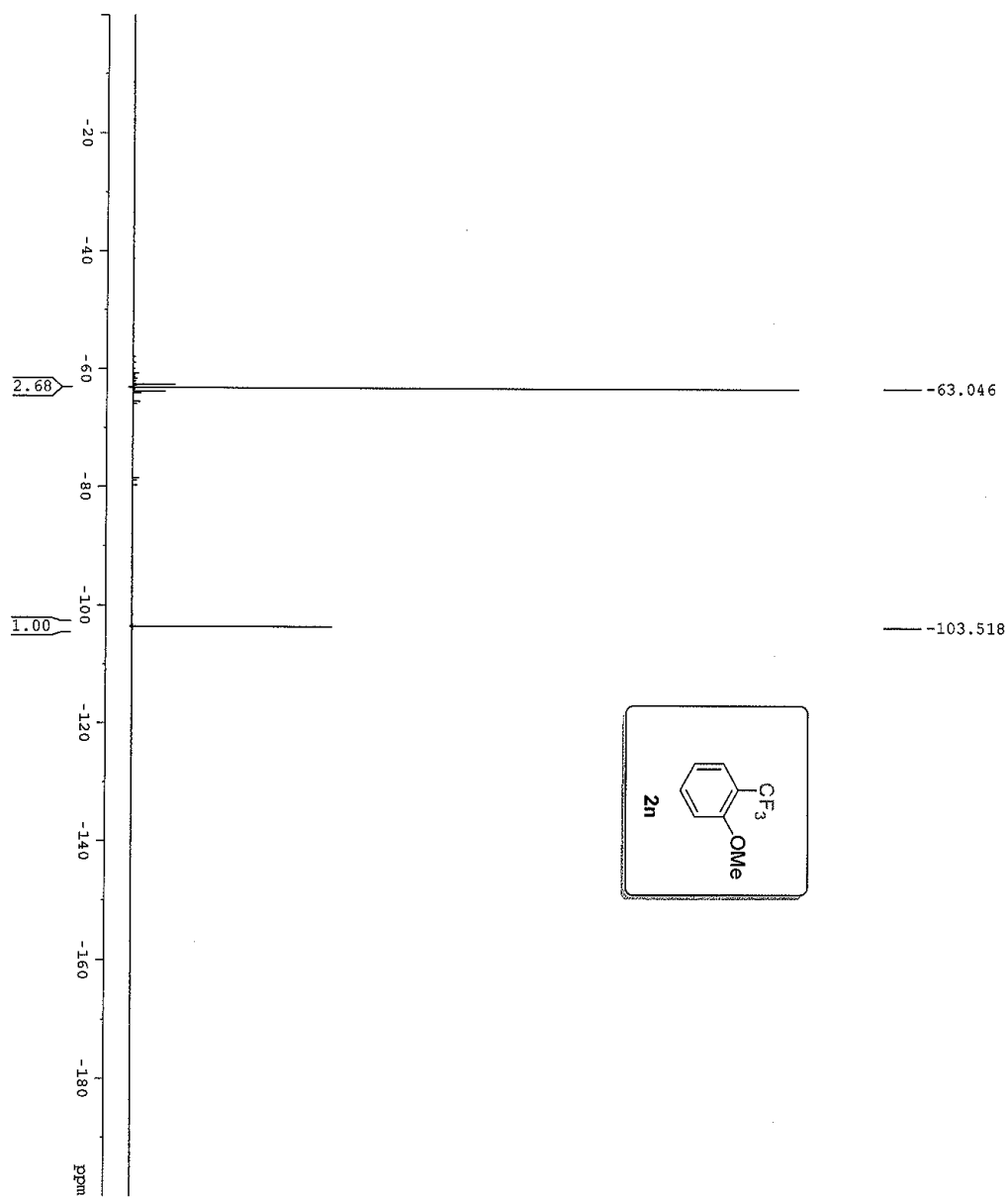
Spectrum



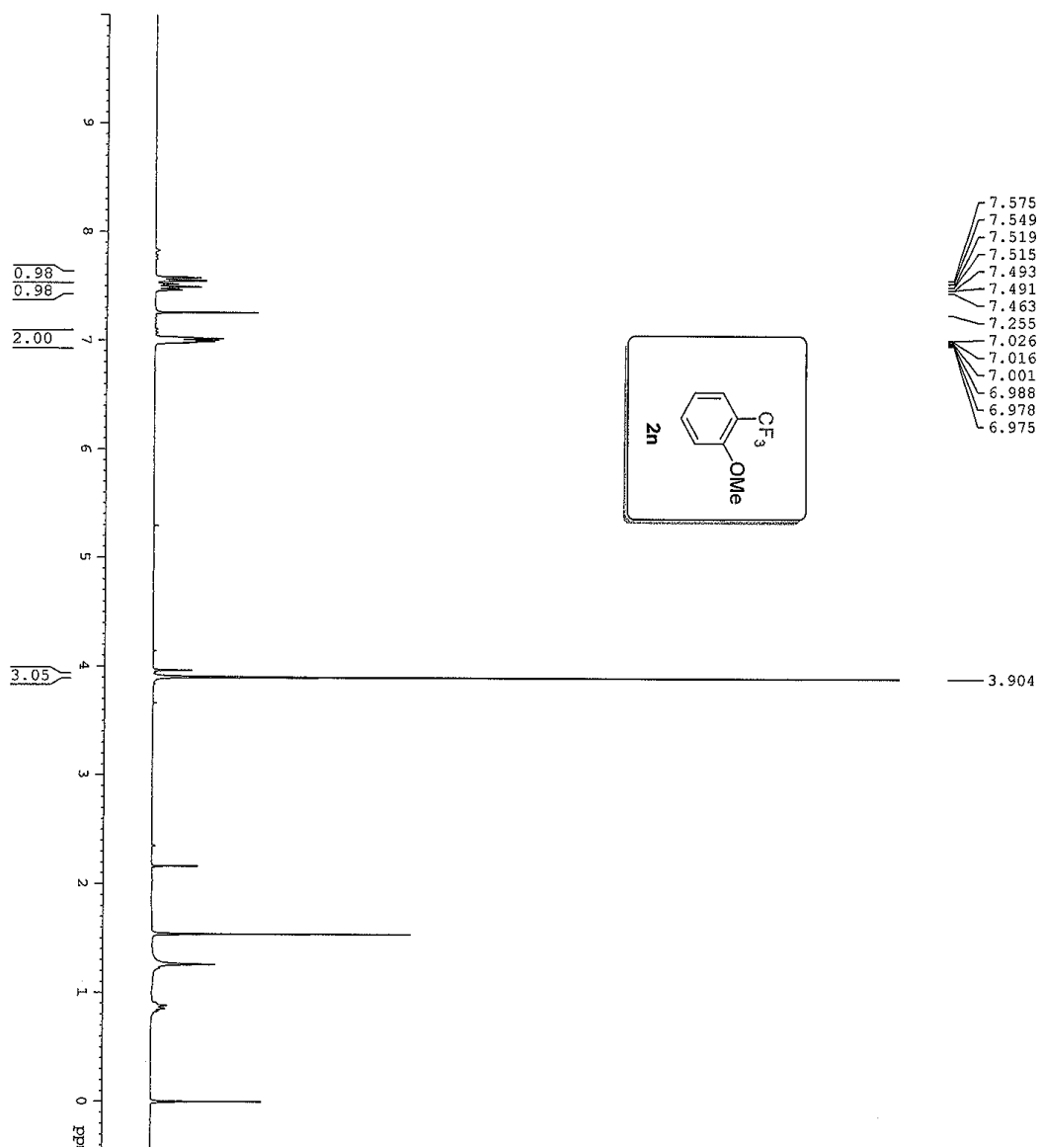
^{19}F NMR of crude **2n** in CDCl_3



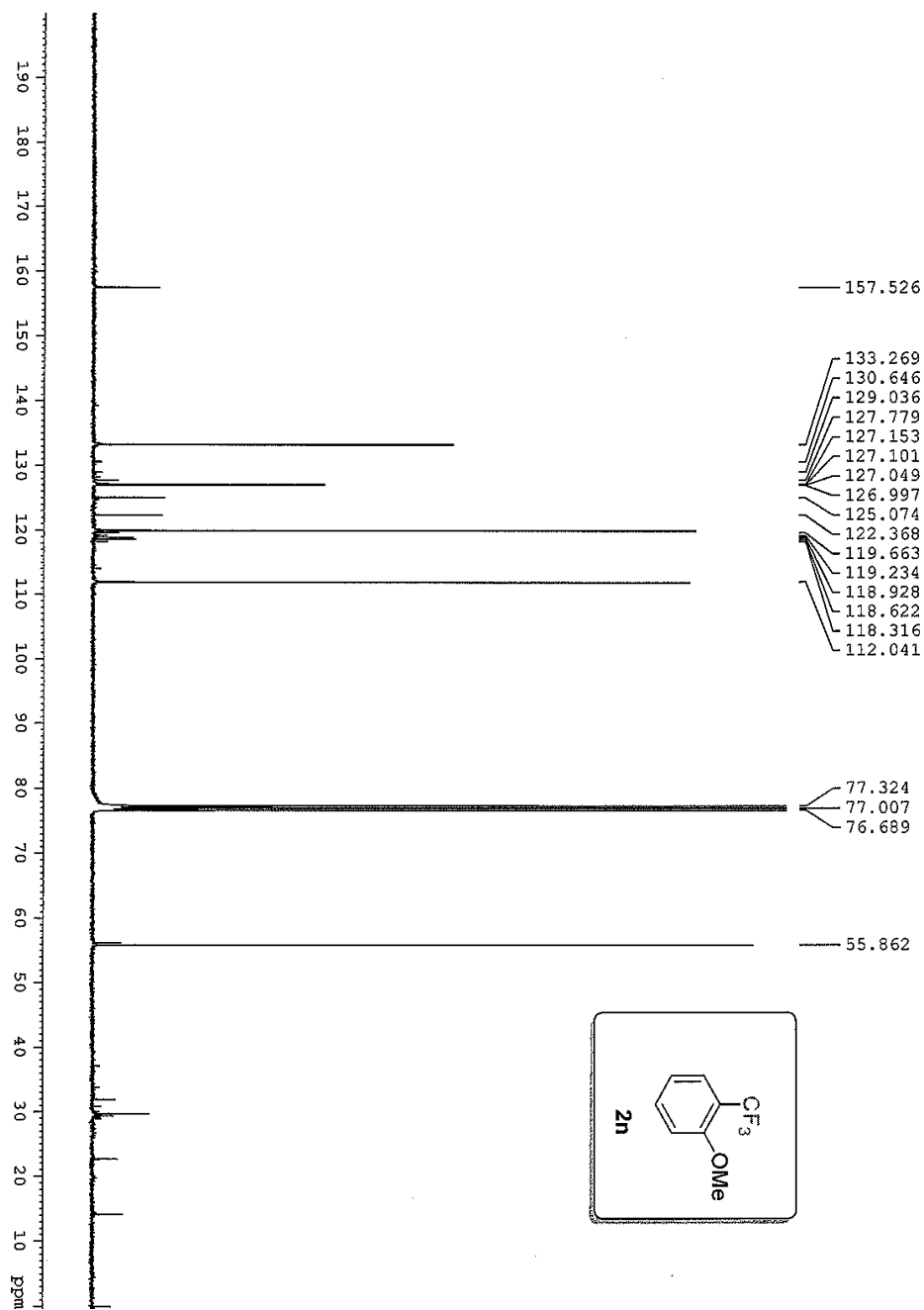
^{19}F NMR yield of compound **2n** ($2.68/(1 \times 3) \times 100\% = 89\%$) in CDCl_3



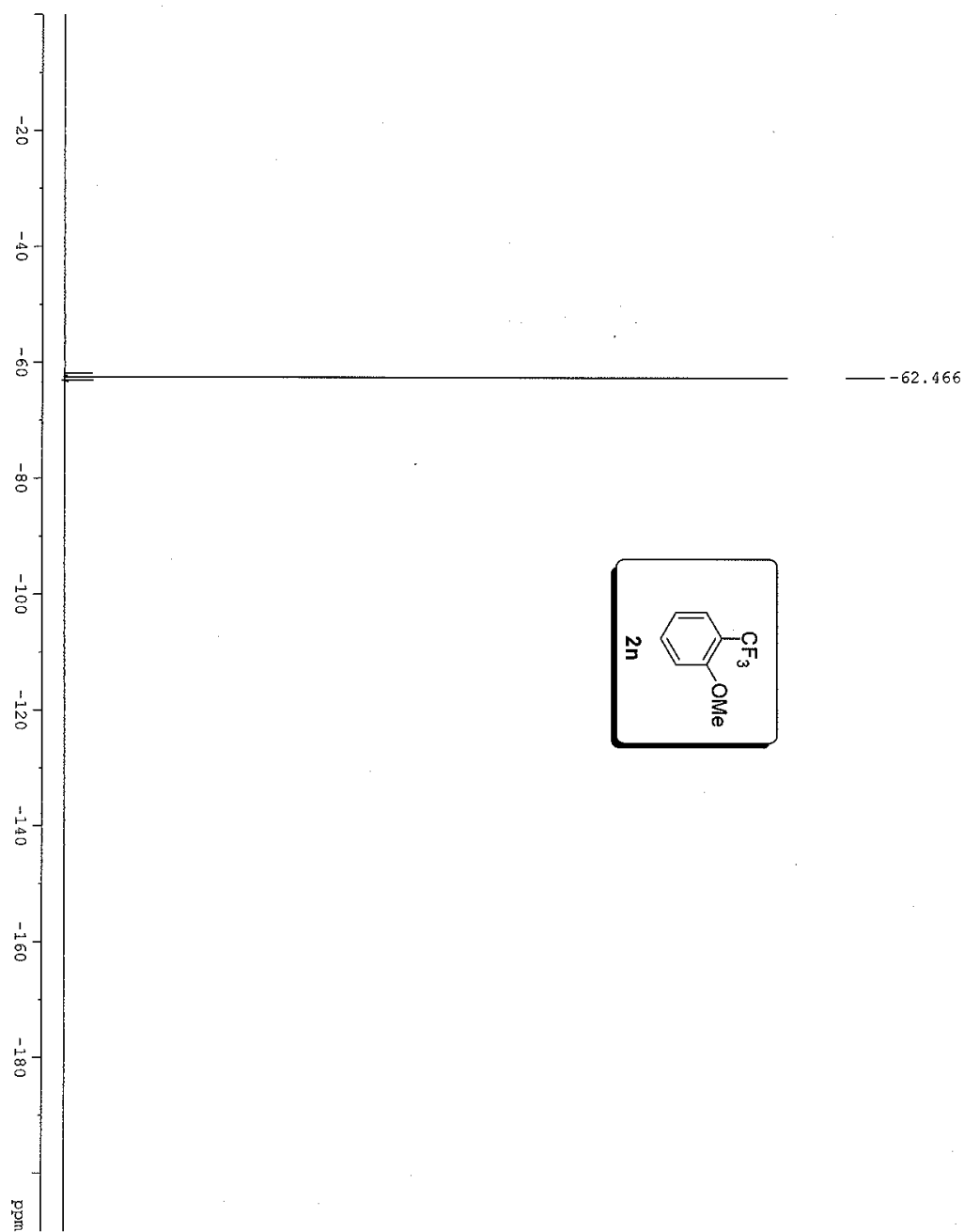
^1H NMR of 2n in CDCl_3



^{13}C NMR of 2n in CDCl_3



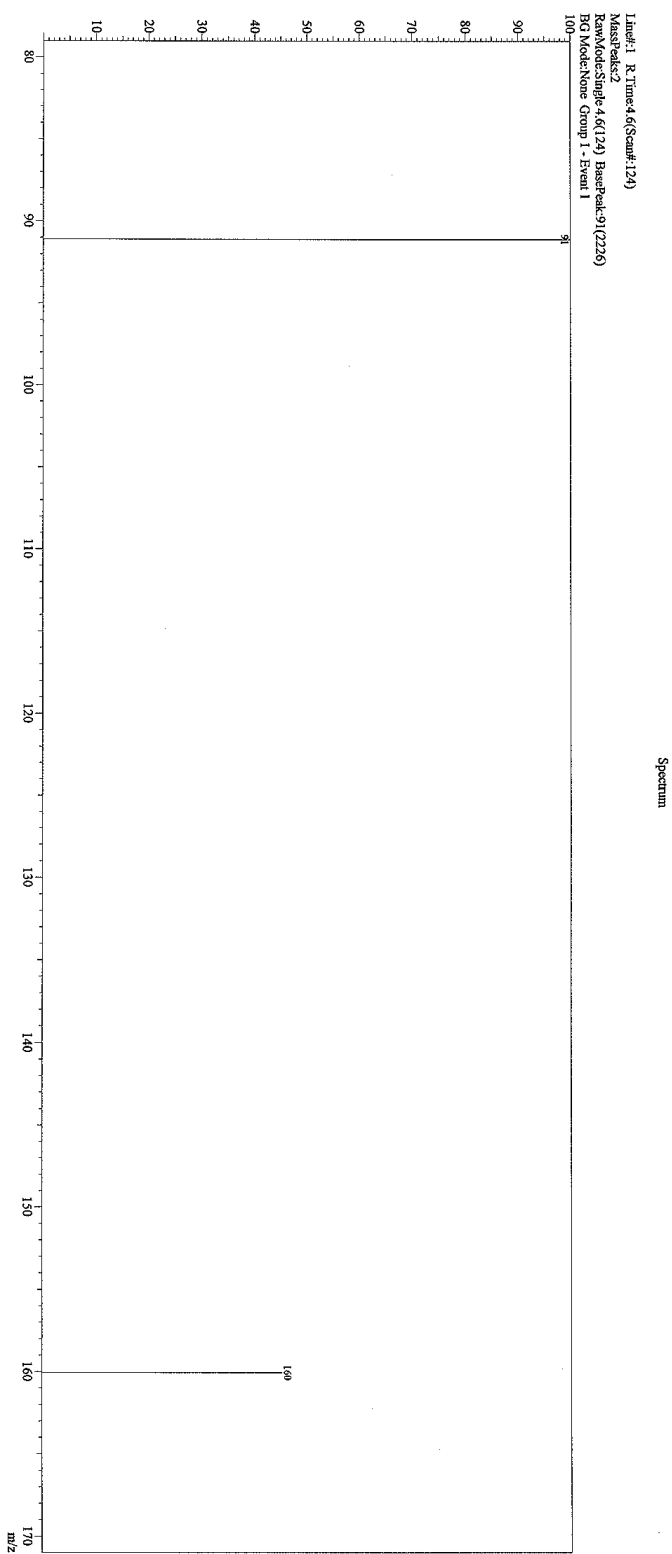
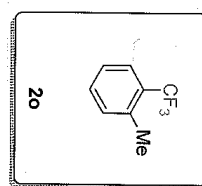
^{19}F NMR of isolated 2n in CDCl_3



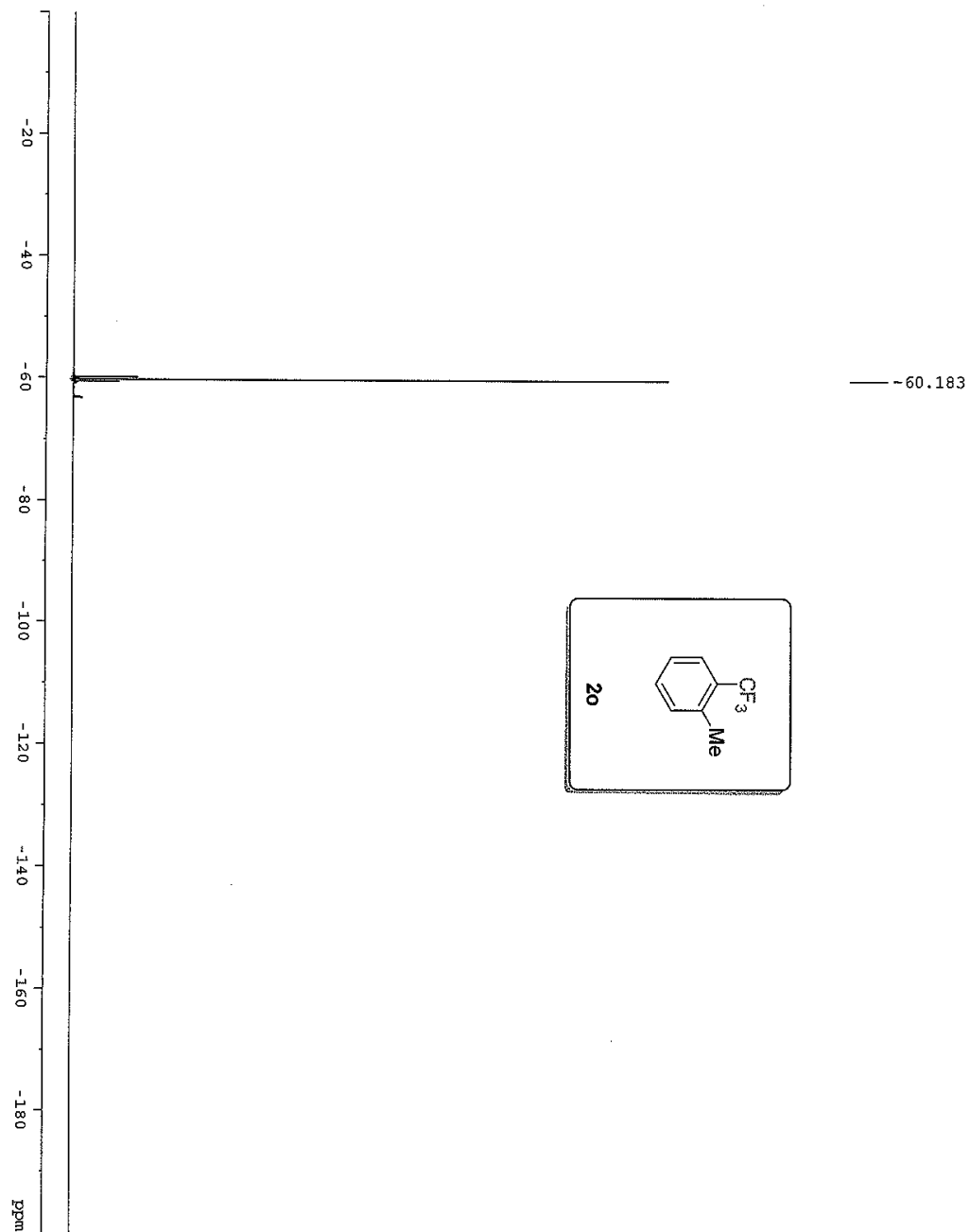
GC-MS of crude 2o

Analysis : GC/MS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 8/7/2013 12:36:04 PM
Sample Type : Unknown
Level # : 1
Sample Name : SC-NSD-I-13
Sample ID : SC-NSD-I-13
IS Amount : [I]=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 2
Injection Volume : 3

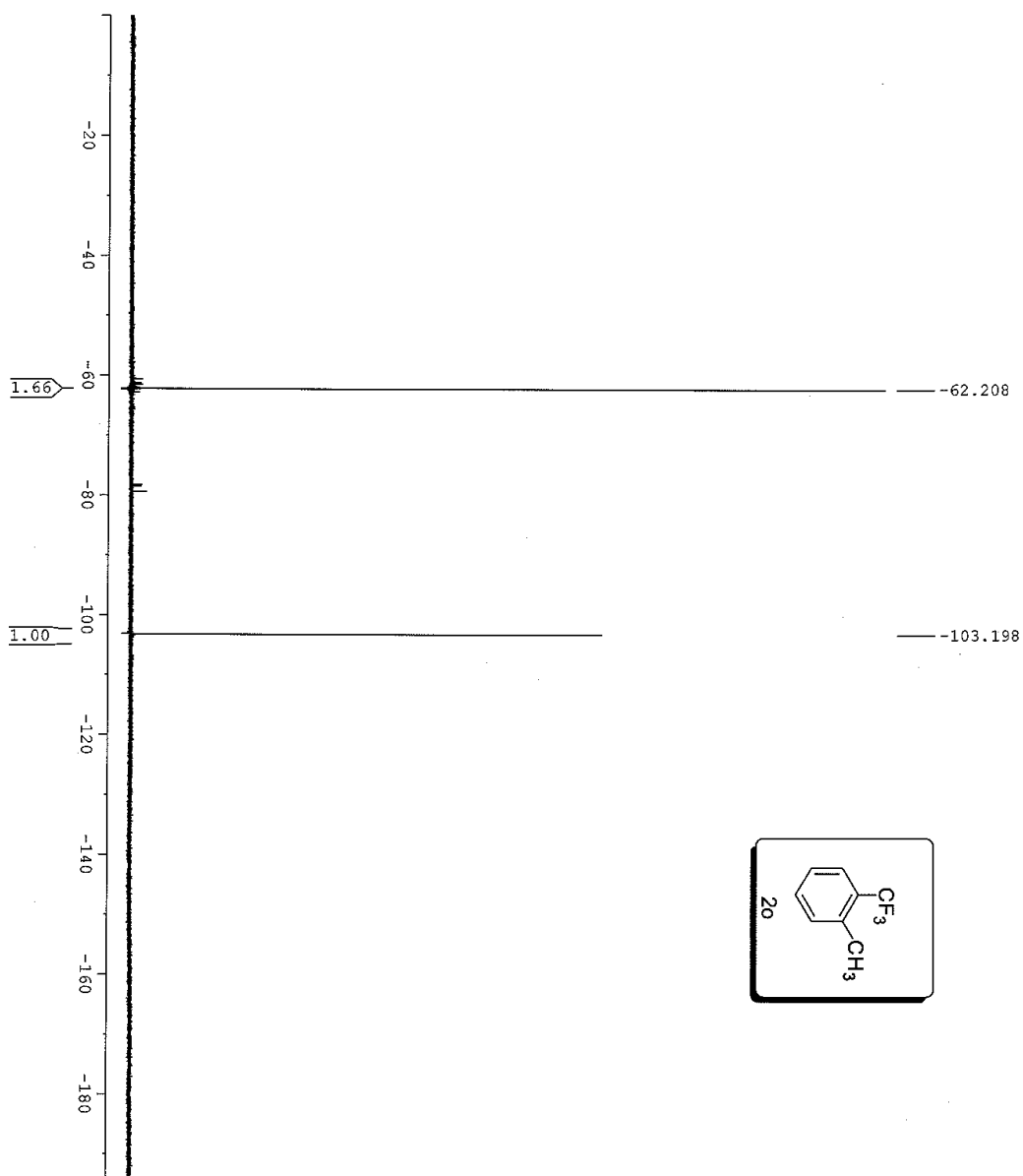
Sample Information



^{19}F NMR of crude 2o in CDCl_3



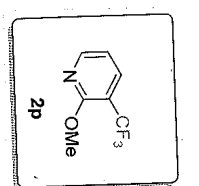
^{19}F NMR yield of compound 2o ($1.66/(1 \times 3) \times 100\% = 55\%$) in CDCl_3



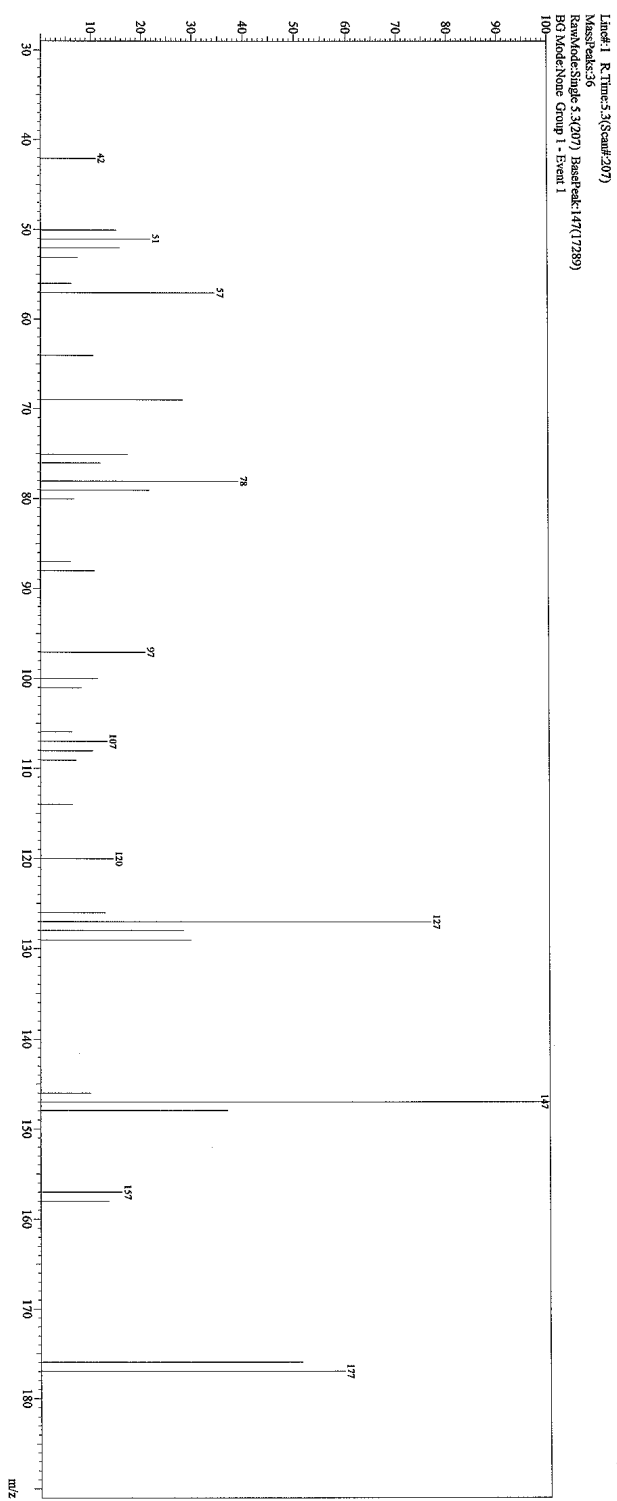
GC-MS of crude 2p

Analysis : GC-MS
Instrument : Shimadzu GC-2010
Acquired by : 82572013 11:29:11 AM
Acquisition :
Sample Type : Unknown
Level # : 1
Sample Name : SG-NSD-132-SUNDAY
Sample ID : SG-NSD-132-SUNDAY
IS Amount : [1]=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 3
Injection Volume : 5

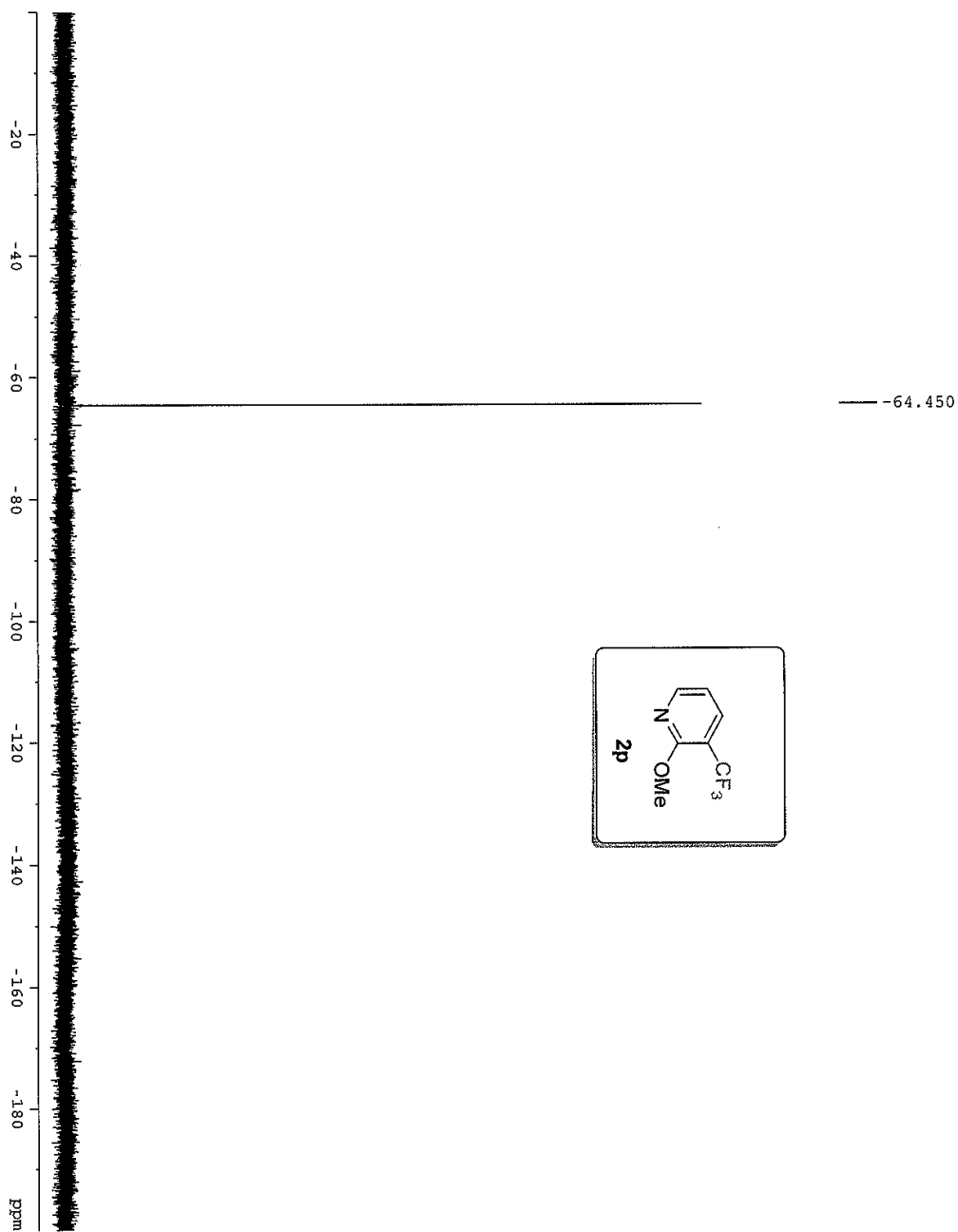
Sample Information



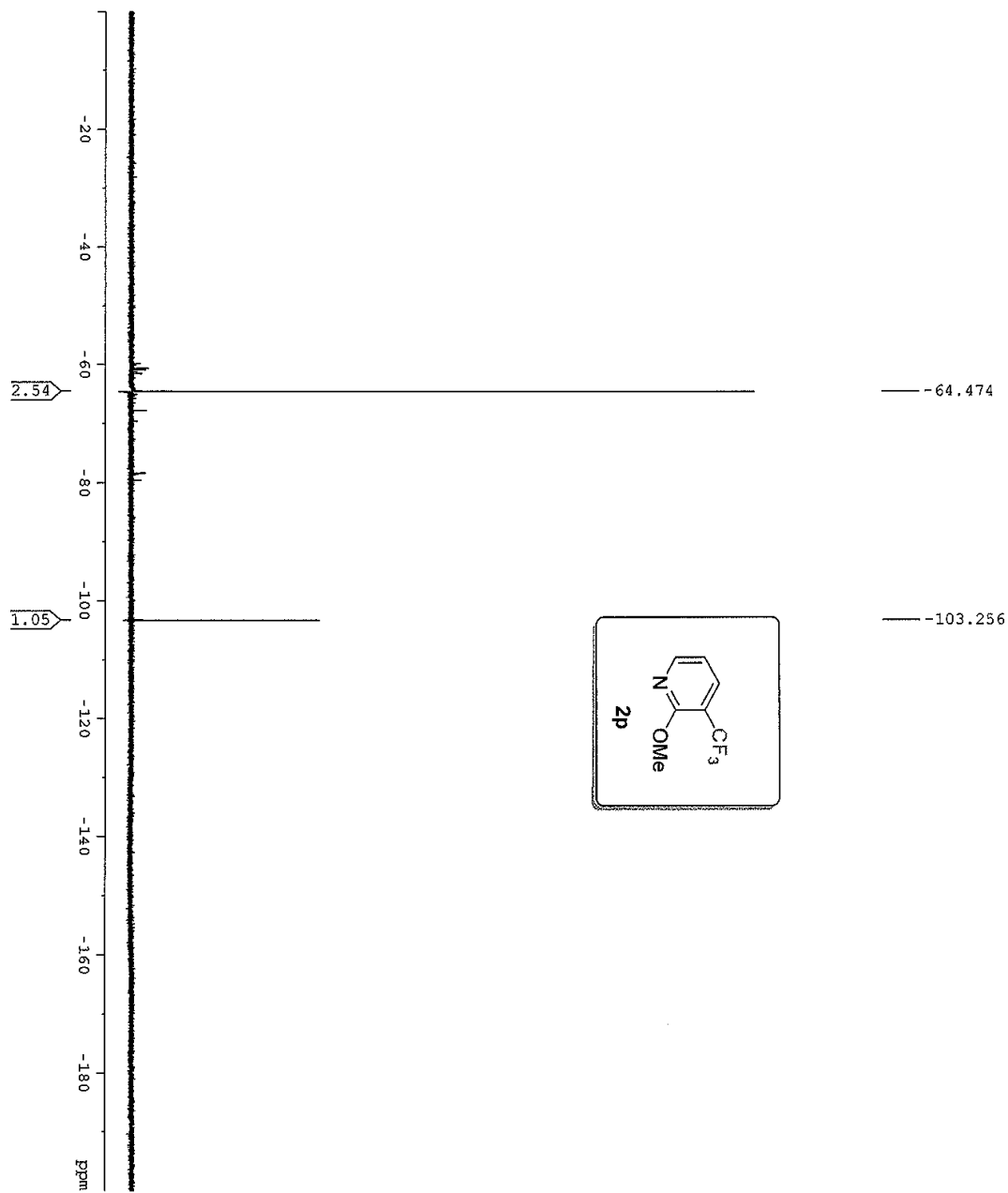
Spectrum



^{19}F NMR of crude 2p in CDCl_3



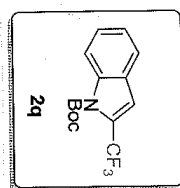
^{19}F NMR yield of compound **2p** ($2.54/(1 \times 3) \times 100\% = 85\%$) in CDCl_3



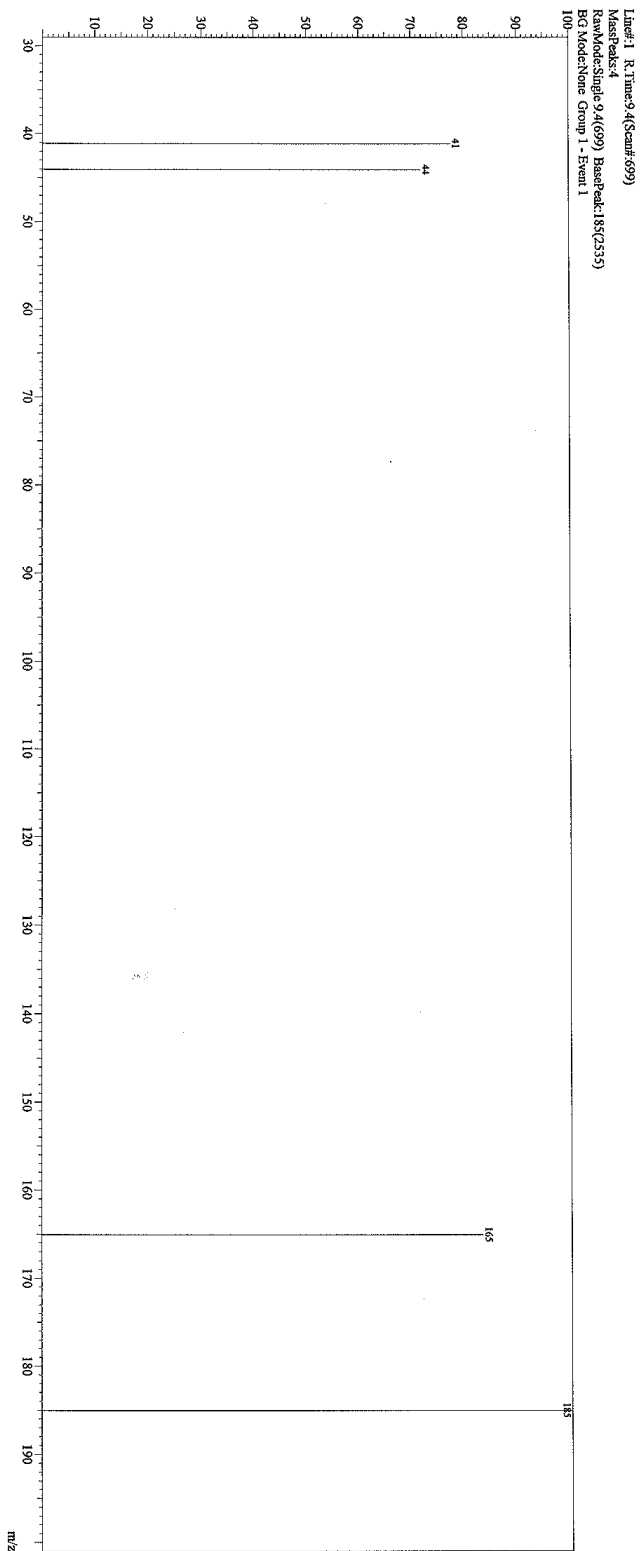
GC-MS of crude 2q

Analysis : GC/MS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 8/29/2013 4:36:37 PM
Sample Type : Unknown
Sample # : 1
Sample Name : SG-MNS1-37
Sample ID : SG-MNS1-37
IS Amount : [1]=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 1
Injection Volume : 5

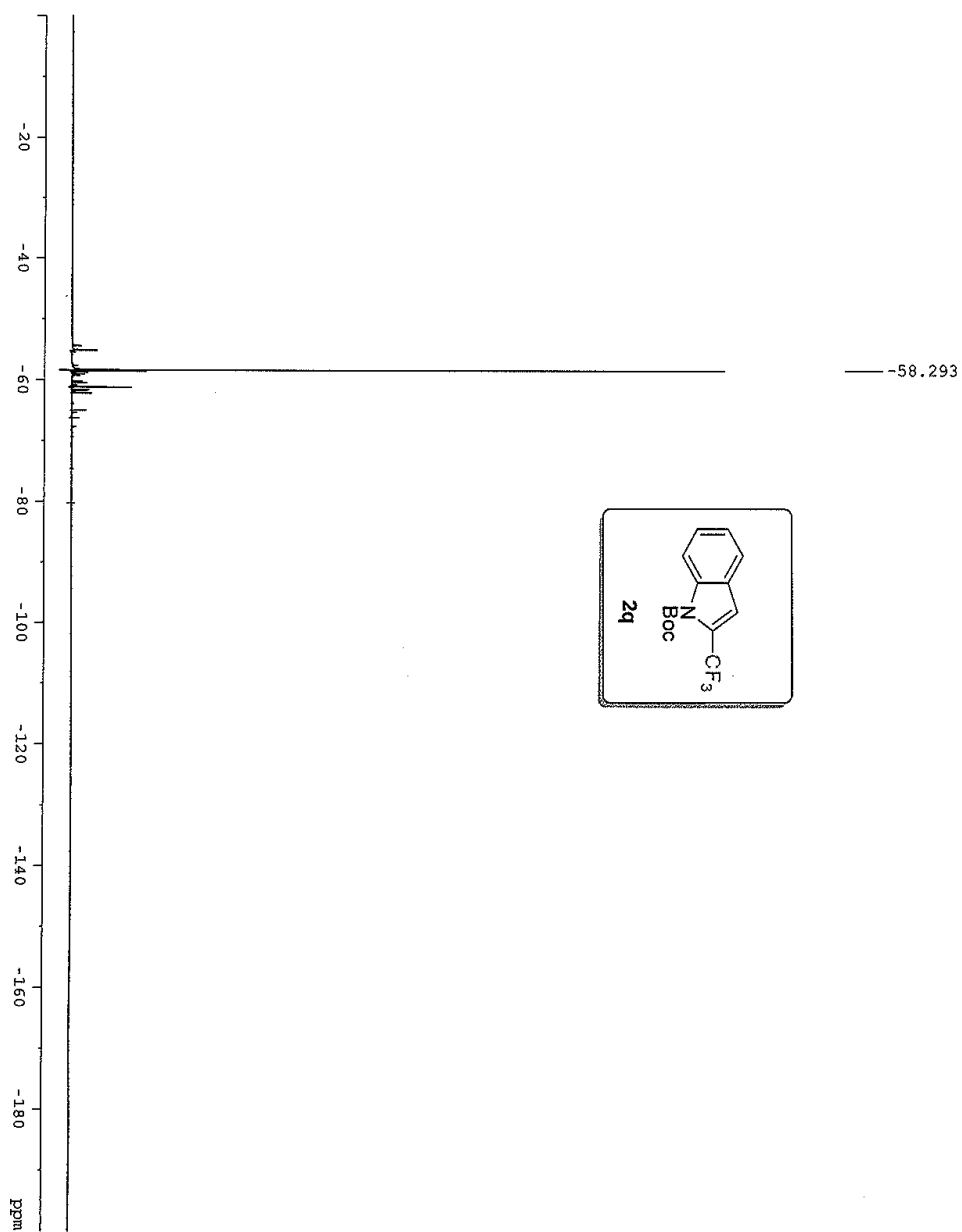
Sample Information



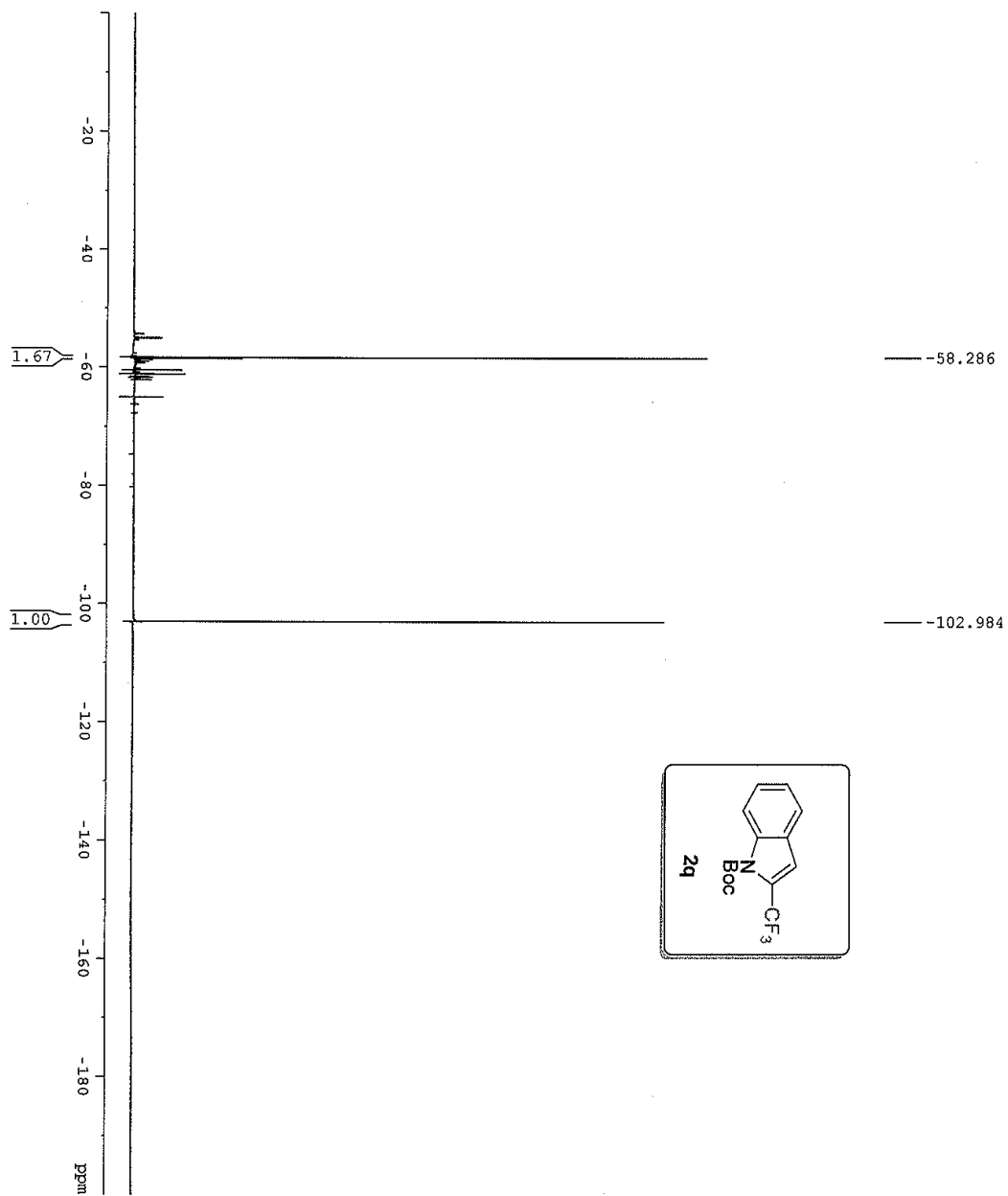
Spectrum



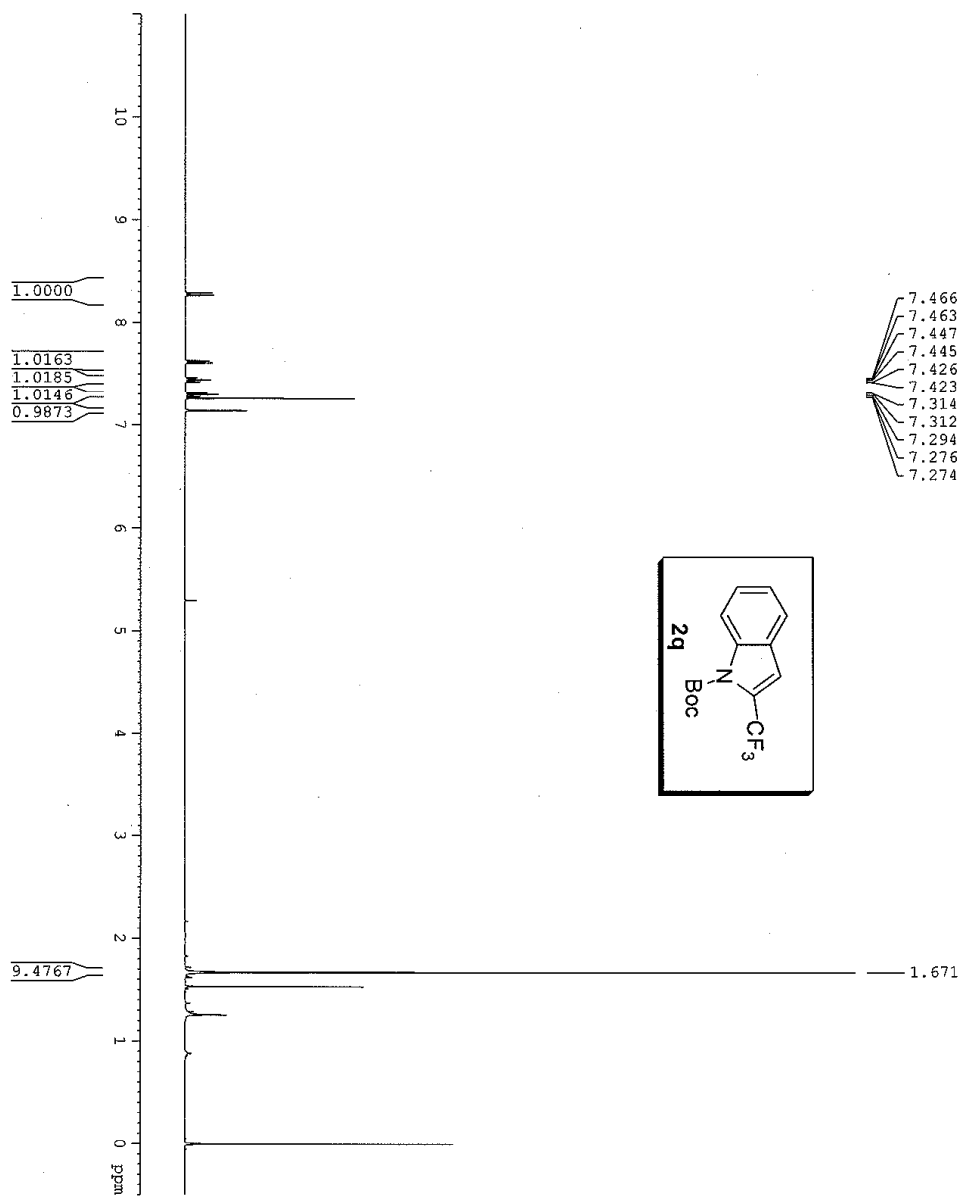
^{19}F NMR of crude 2q in CDCl_3



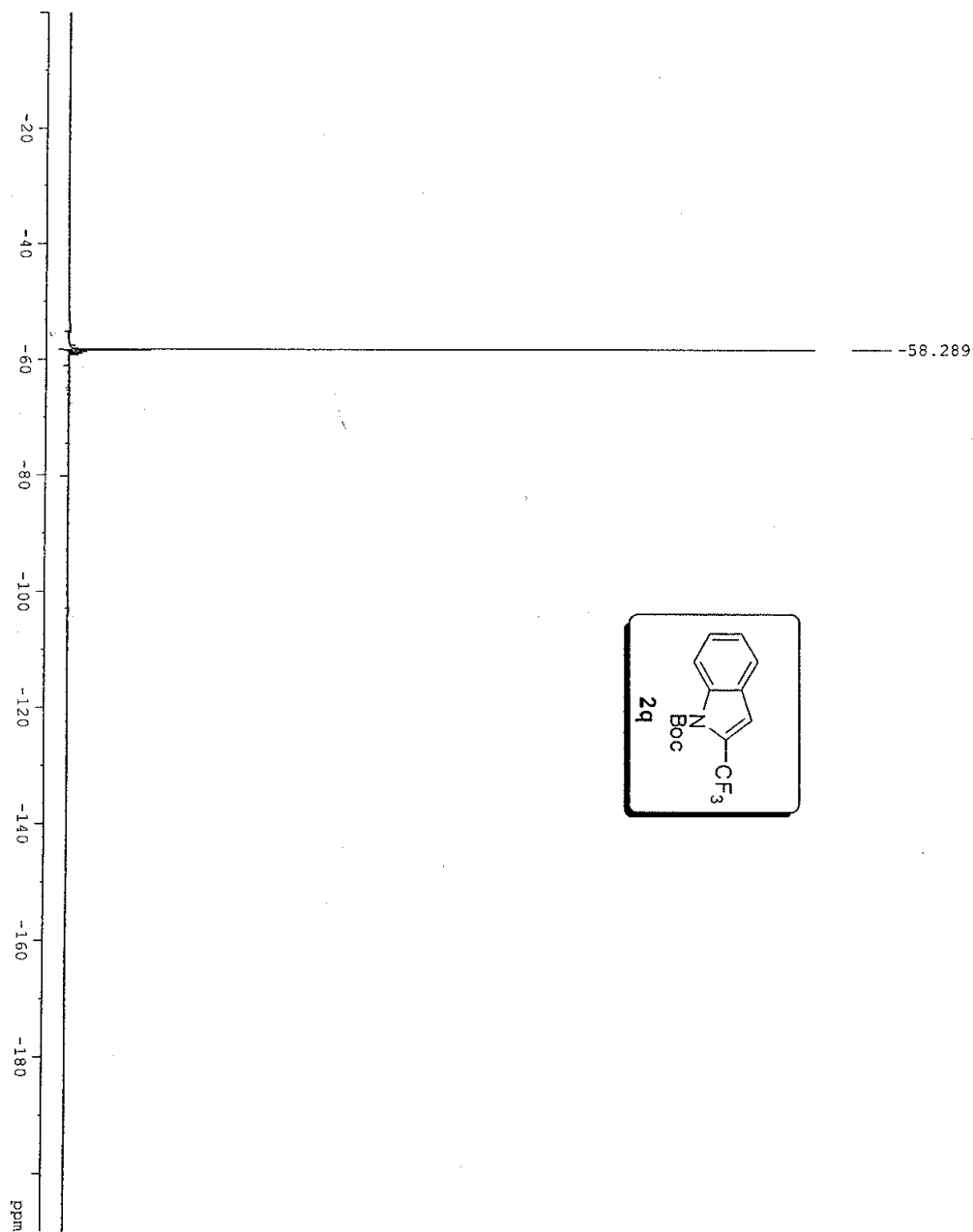
^{19}F NMR yield of compound 2q $(1.67/(1 \times 3) \times 100\% = 55\%)$ in CDCl_3



^1H NMR of compound 2q



^{19}F NMR of isolated 2q in CDCl_3

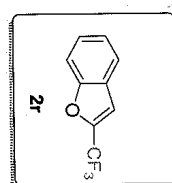
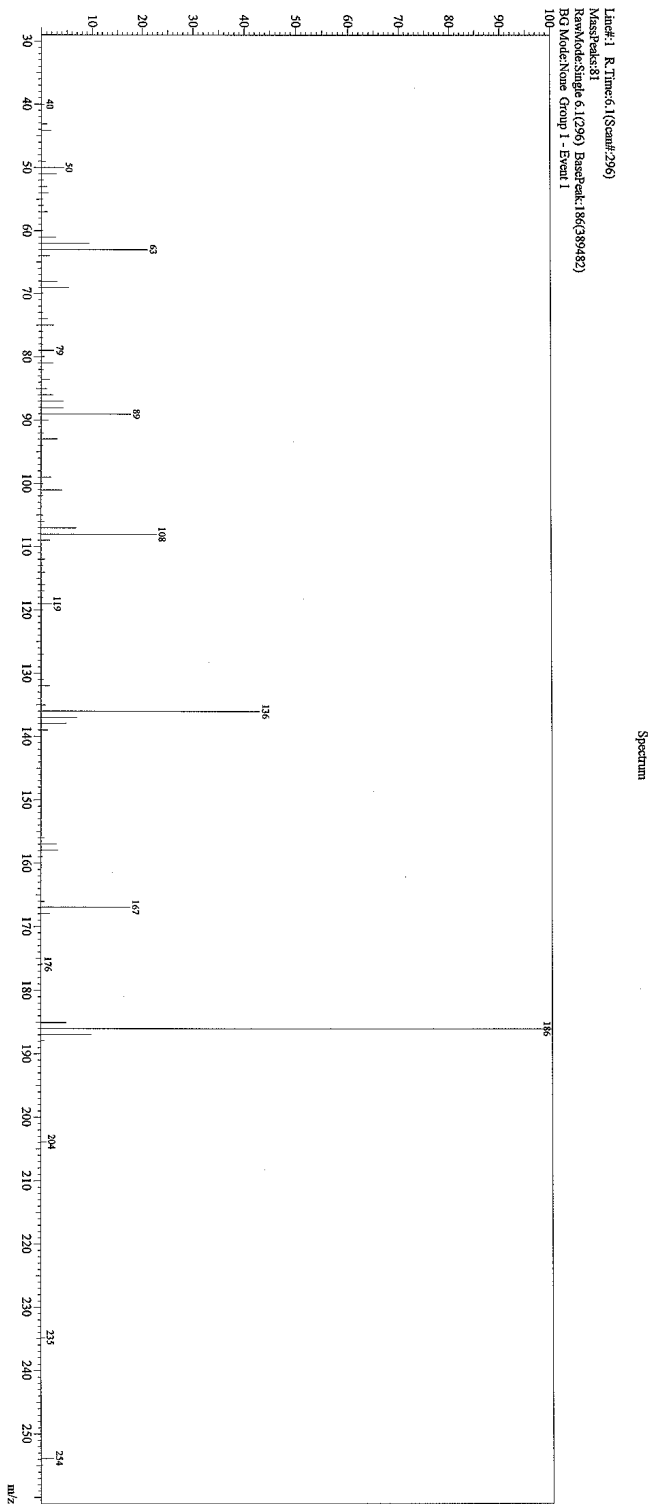


GC-MS of crude 2r

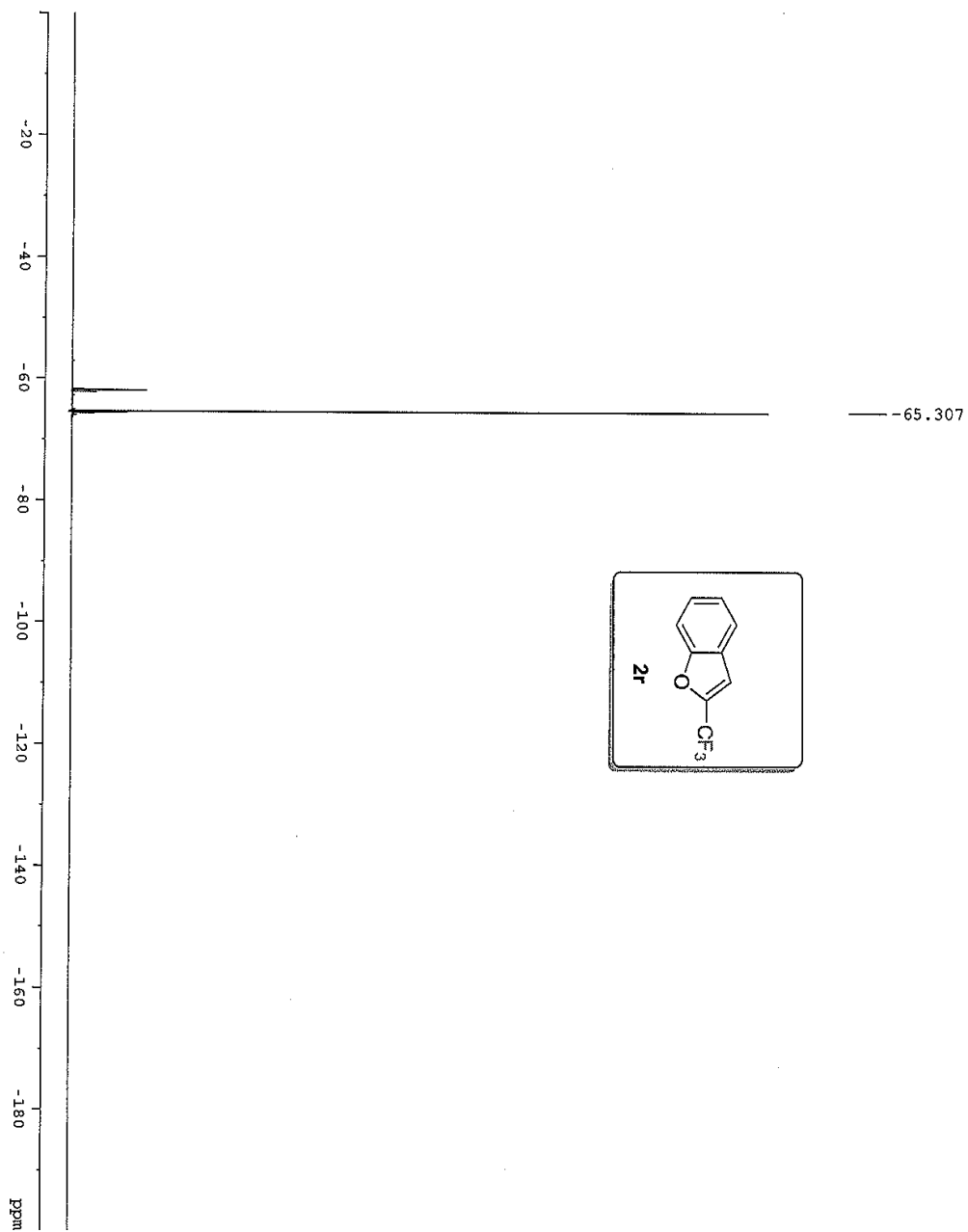
Sample Information

Analyte : GC-MS
Instrument : Shimadzu GC-2010
Analyzed By : Admin
Analyzed : 8/20/2013 5:32:11 PM
Sample Type : Unknown
Level # : 1
Sample Name : SG-NSD-424
Sample ID : SG-NSD-424
IS Amount : 11 µl
Sample Amount : 1
Dilution Factor : 1
Vial # : 1
Injection Volume : 5

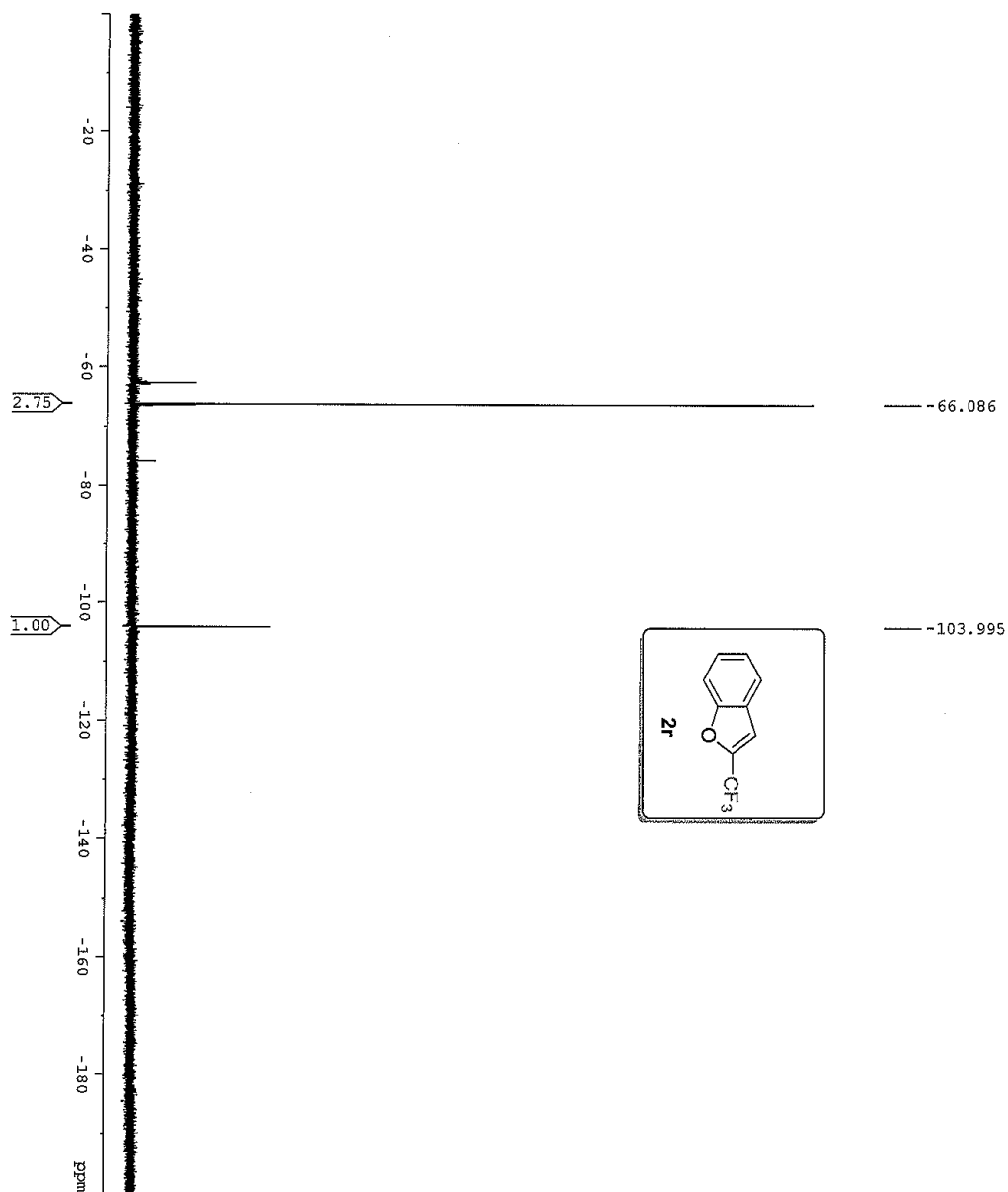
Link# 1 R_Time:6.1 (Scan#:296)
MassPeak:31
Retention:Single 6.1(296) BasePeak:186(389482)
Mode:None Group 1 - Event 1



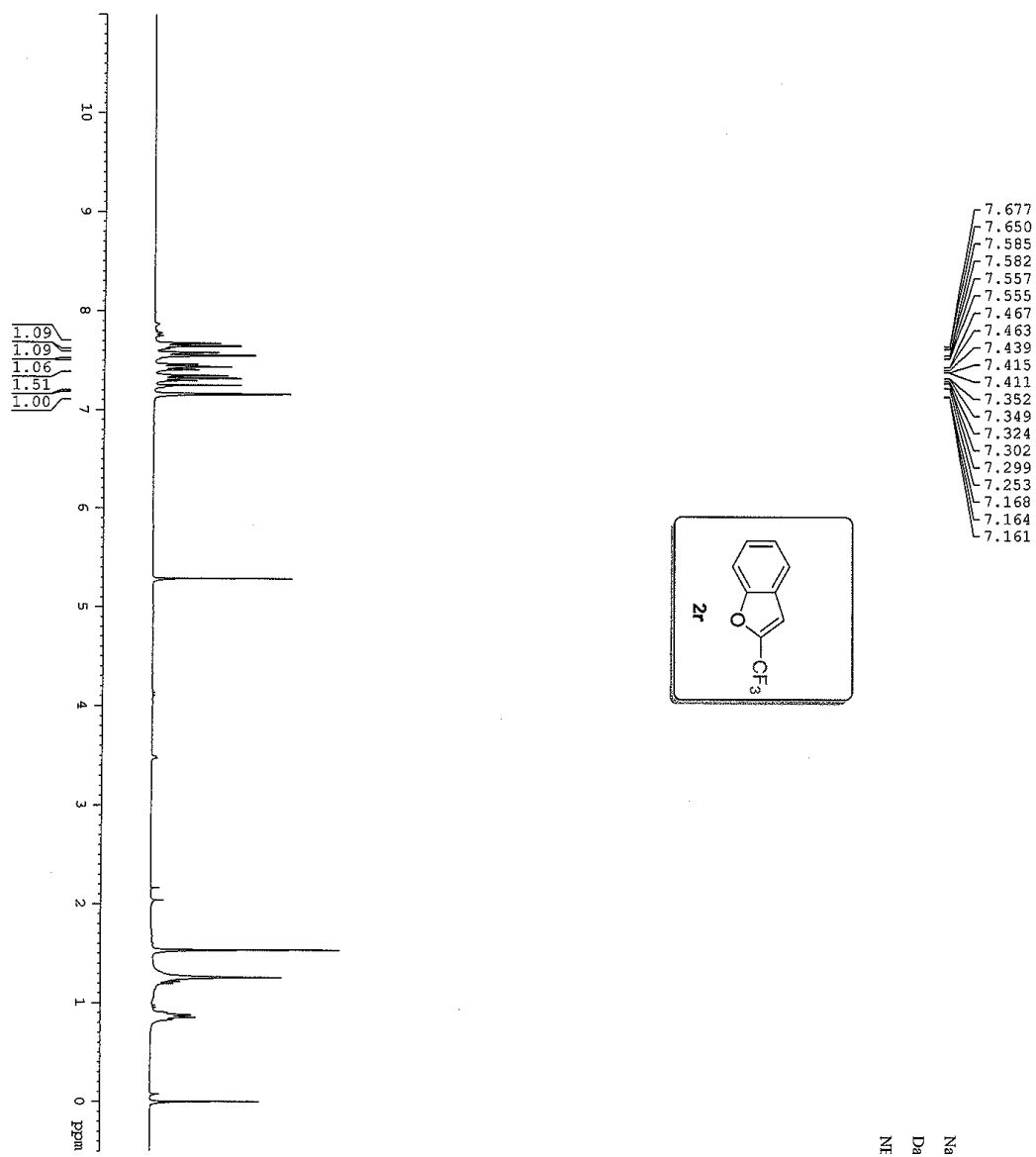
^{19}F NMR of crude 2r in CDCl_3



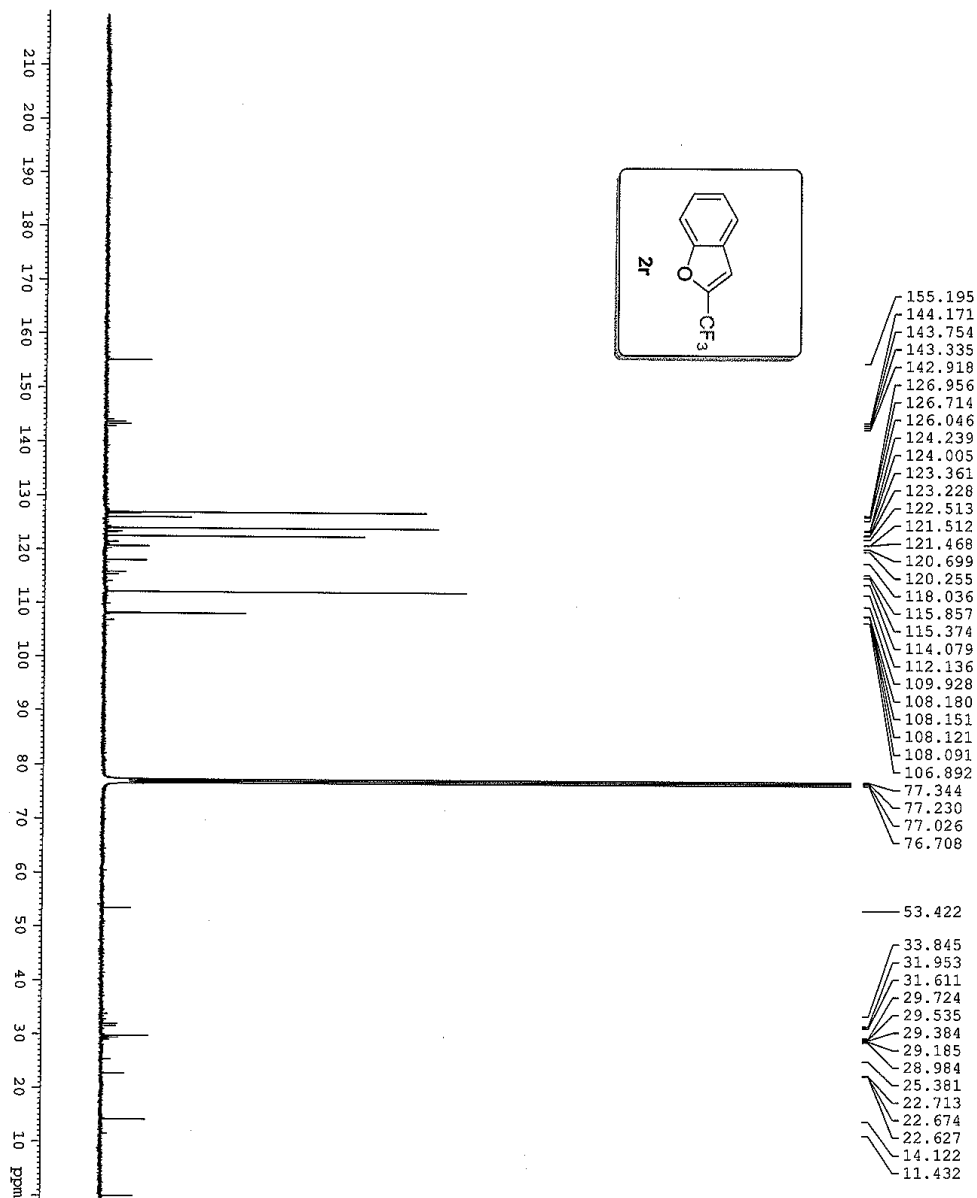
^{19}F NMR yield of compound 2r ($2.75/(1 \times 3) \times 100\% = 91\%$) in CDCl_3



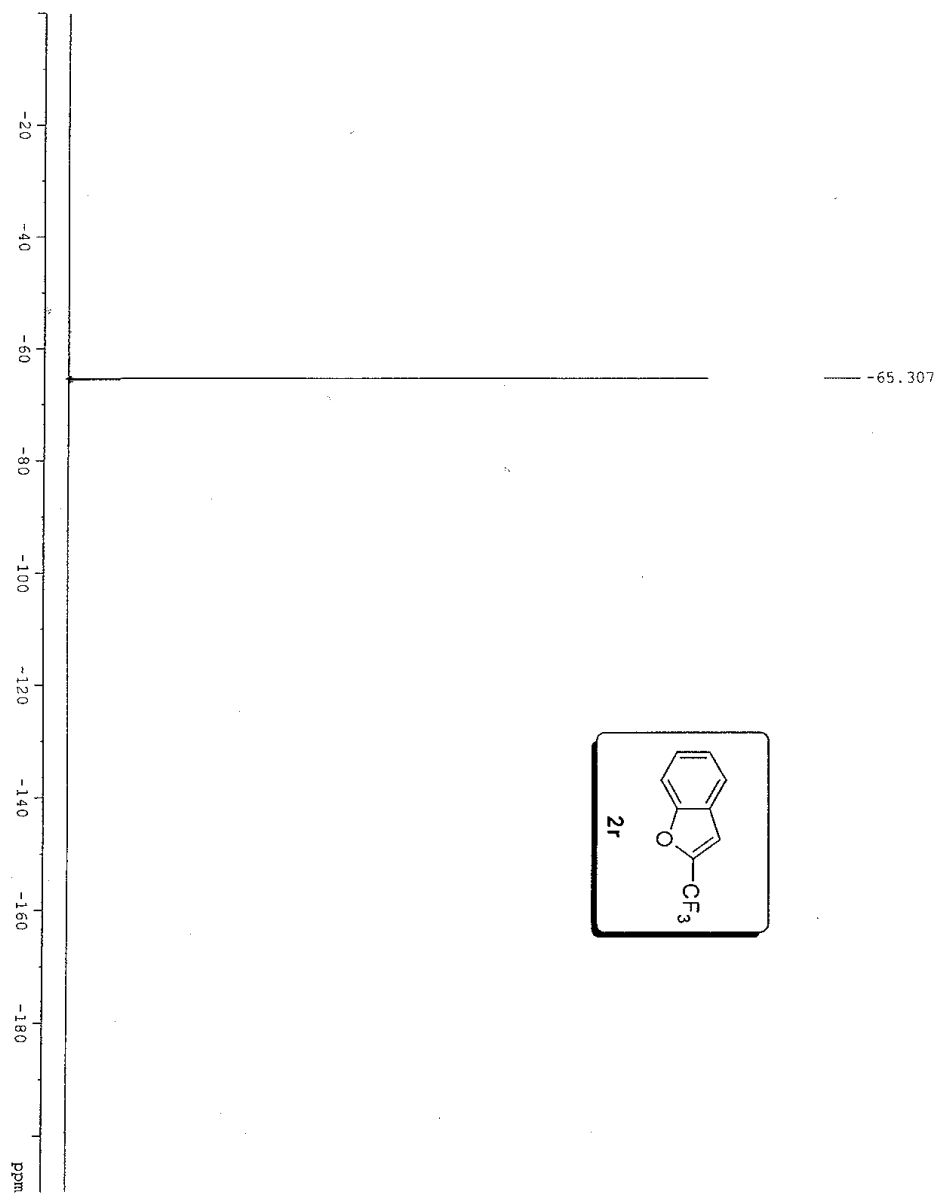
^1H NMR of 2r in CDCl_3



^{13}C NMR of 2r in CDCl_3



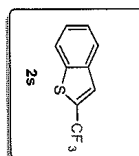
^{19}F NMR of isolated 2r in CDCl_3



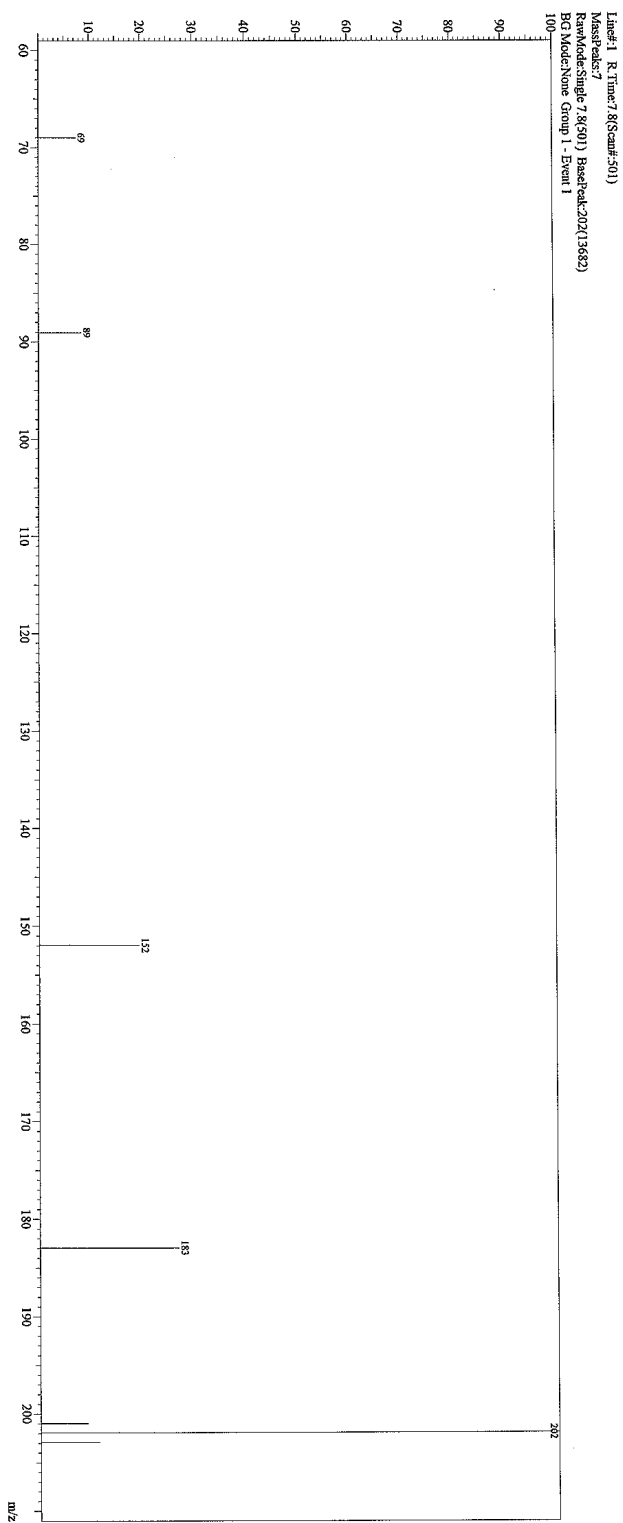
GC-MS of crude 2s

Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 8/19/2013 4:24:22 PM
Sample Type : Unknown
Level # : 1
Sample Name : SG-MNS-125
Sample ID : SG-MNS-125
IS Amount : [I]=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 6
Injection Volume : 3

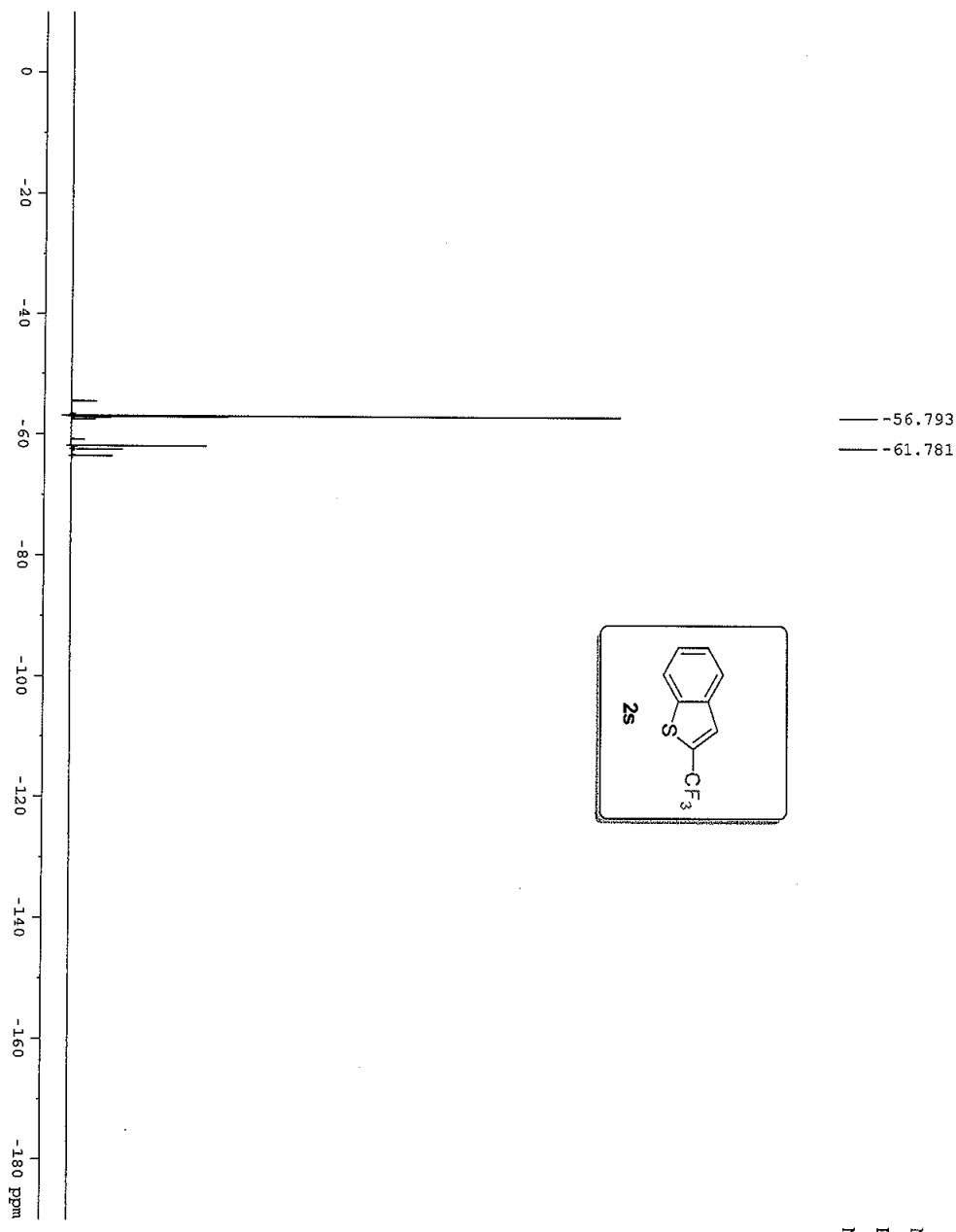
Sample Information



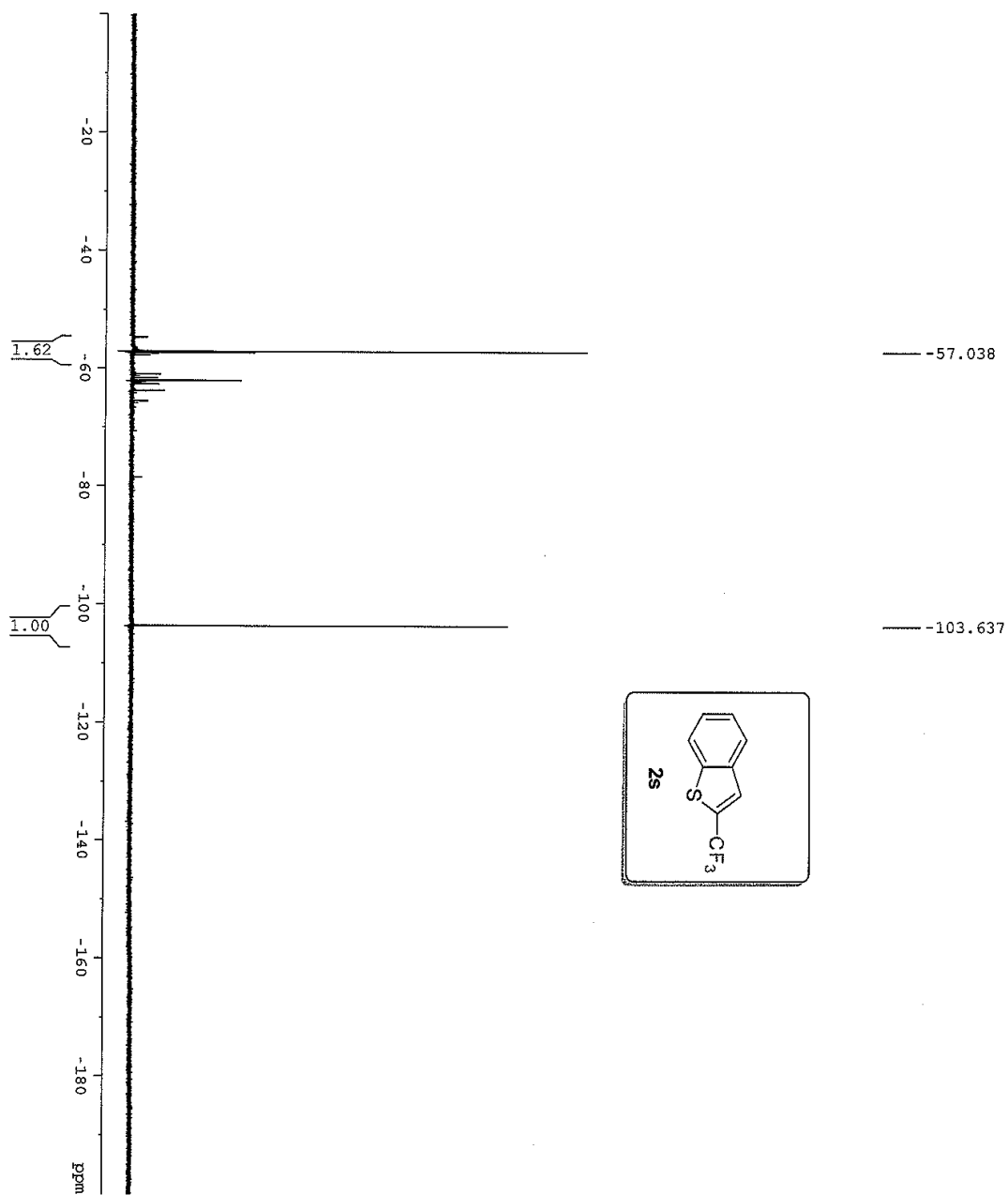
Spectrum



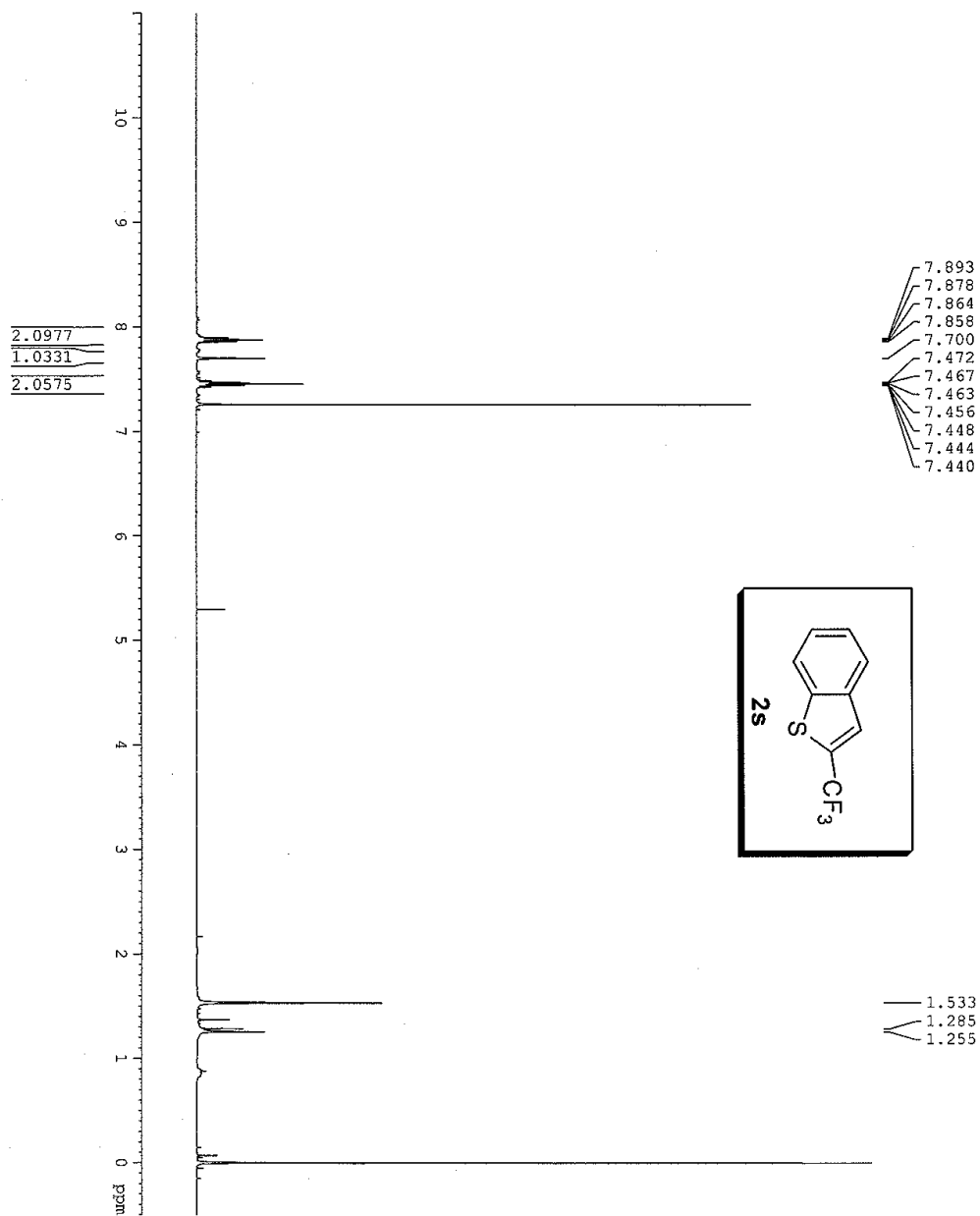
^{19}F NMR of crude **2s** in CDCl_3



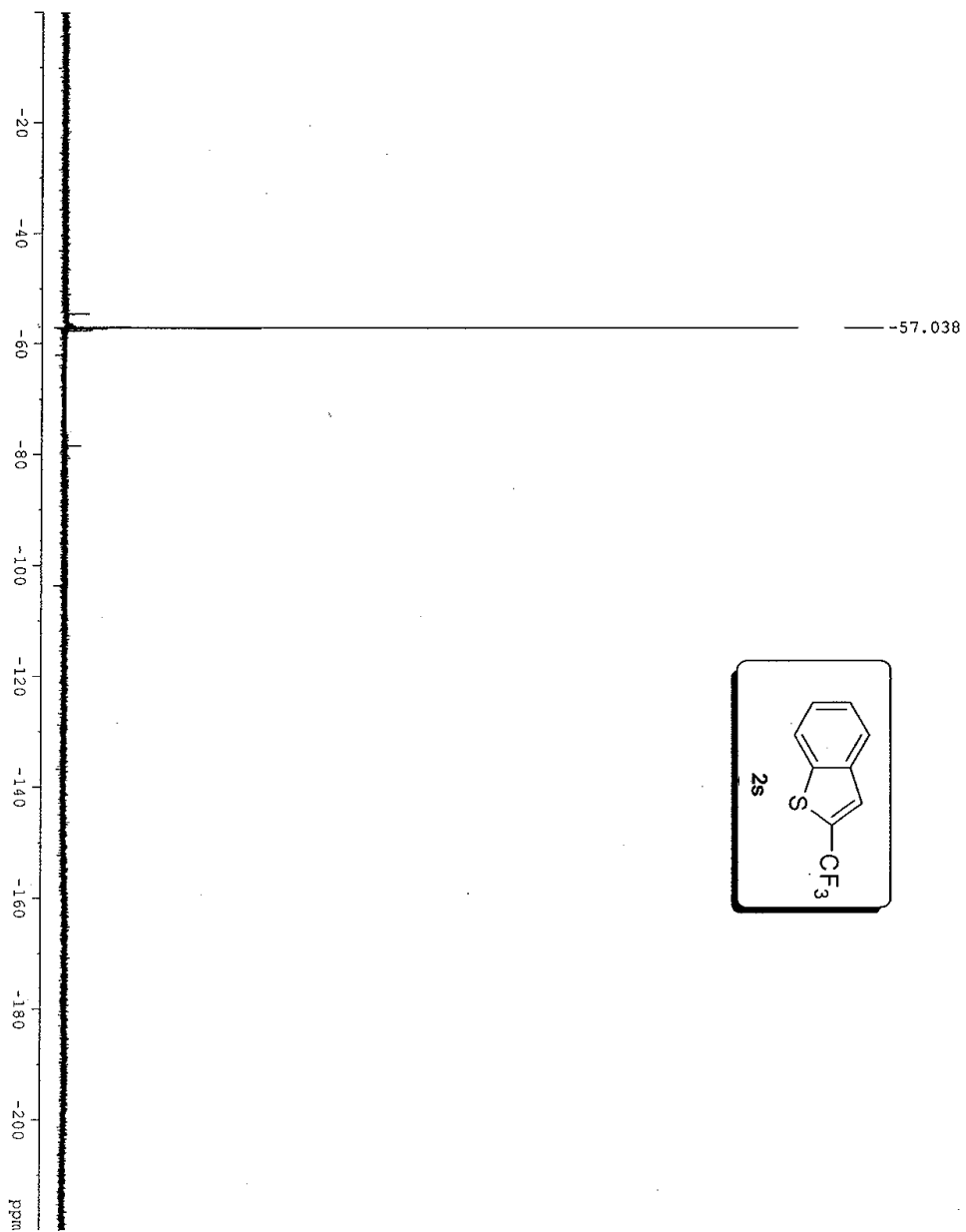
^{19}F NMR yield of compound 2s ($1.62/(1 \times 3) \times 100\% = 54\%$) in CDCl_3



^1H NMR of compound 2s



^{19}F NMR of isolated **2s** in CDCl_3

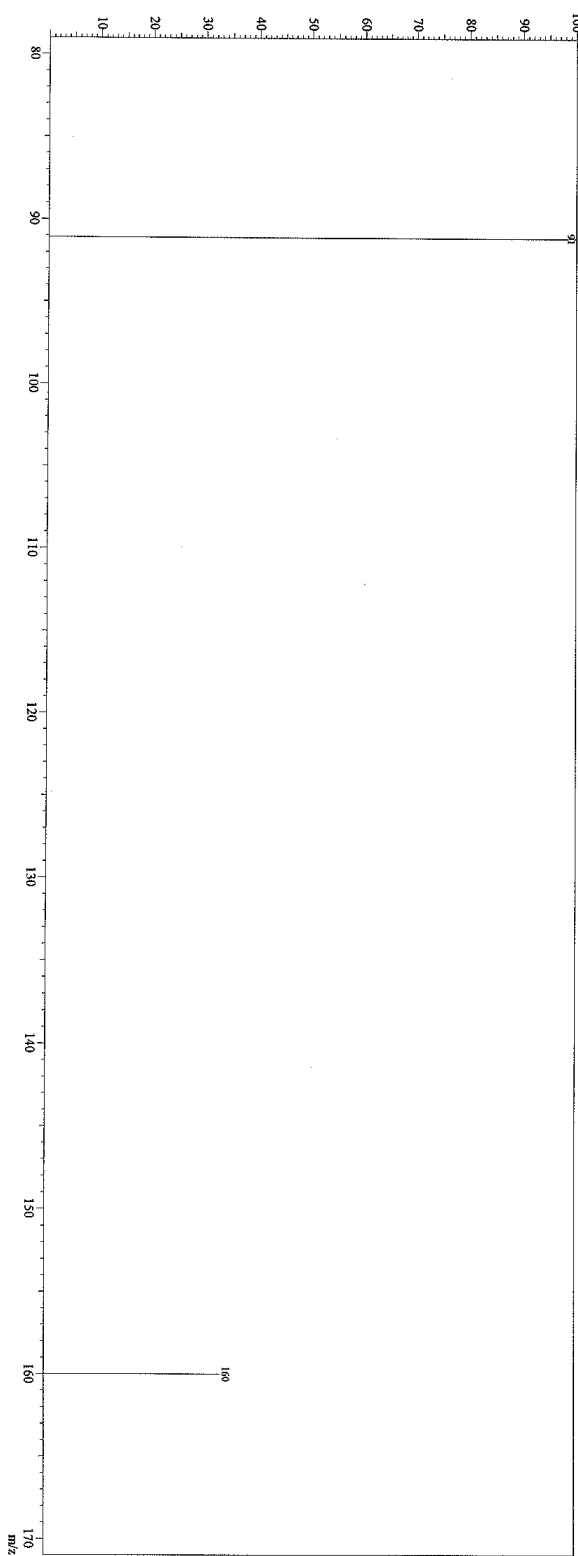


GC-MS of crude 2h

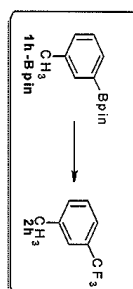
Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 8/25/2013 10:53:05 AM
Sample Type : Unknown
Level # : 1
Sample Name : SG-MNS-1-35
Sample ID : SG-MNS-1-35
IS Amount : [1]=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 2
Injection Volume : 5

Sample Information

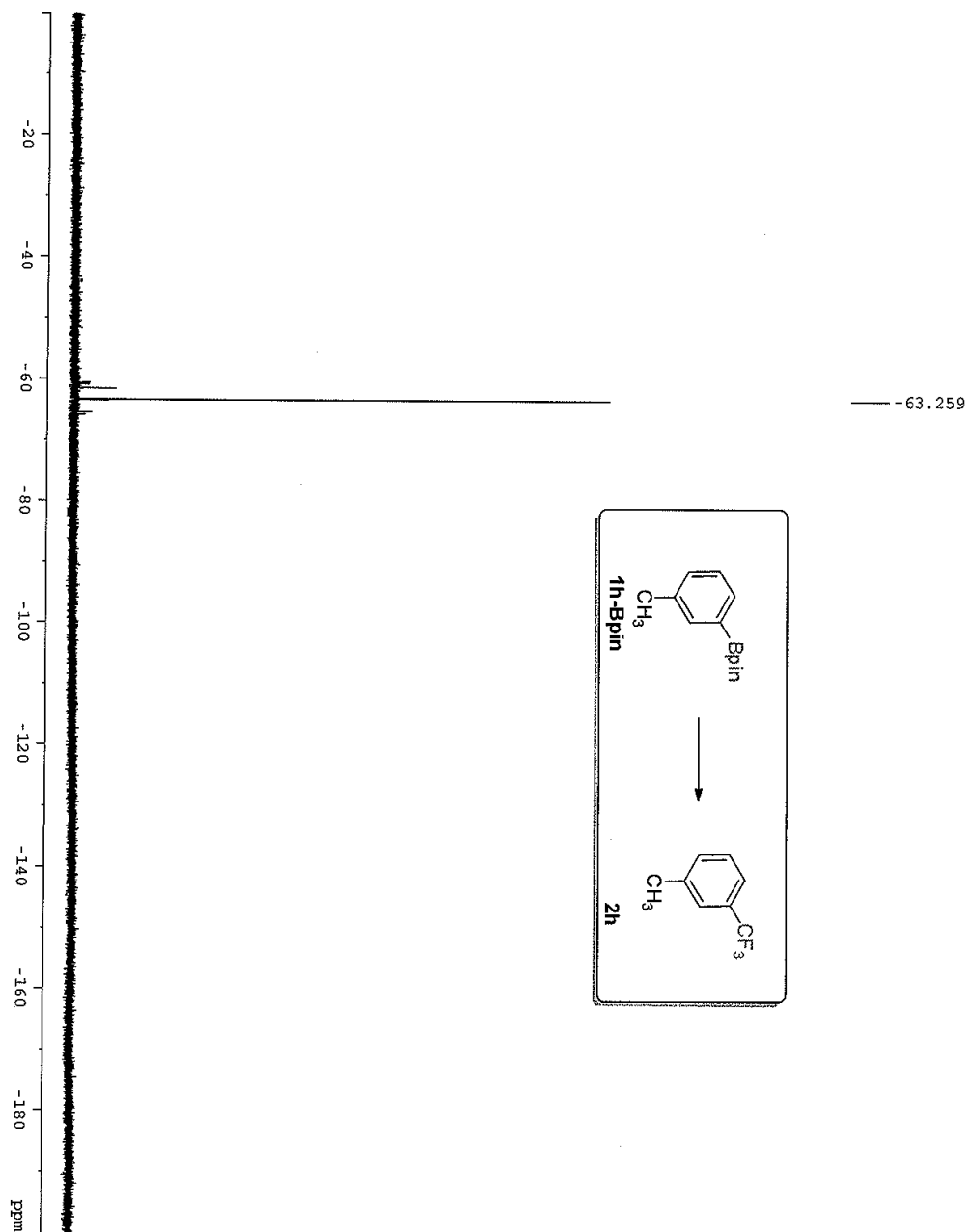
Level: 1, RetTime: 47.5 (Scan#: 109)
MassPeak: 2
RetentionTime: 47.5 (109) BasePeak: 91 (5134)
BG Mode: None Group 1 - Event 1



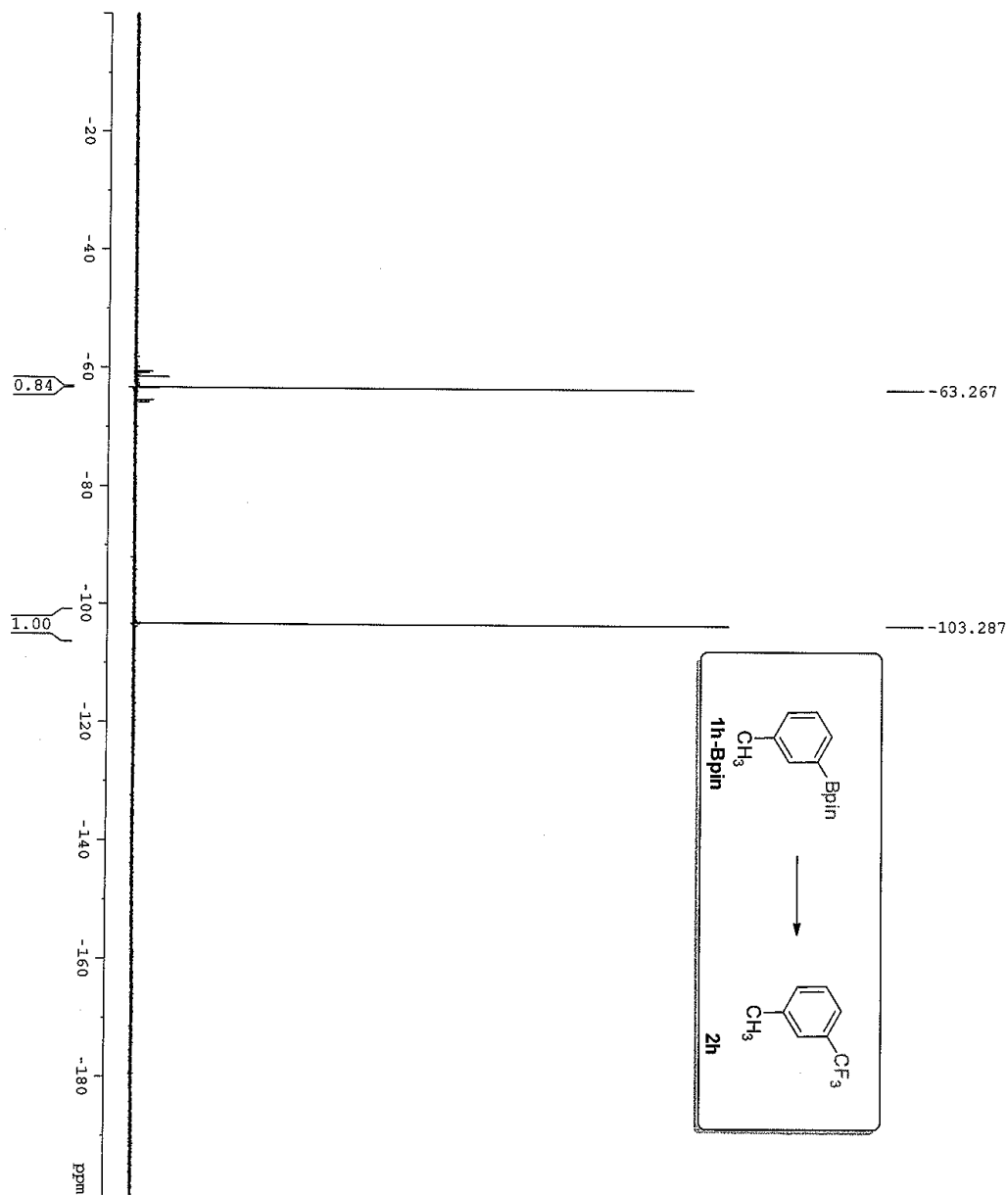
Spectrum



^{19}F NMR of crude 2h in CDCl_3



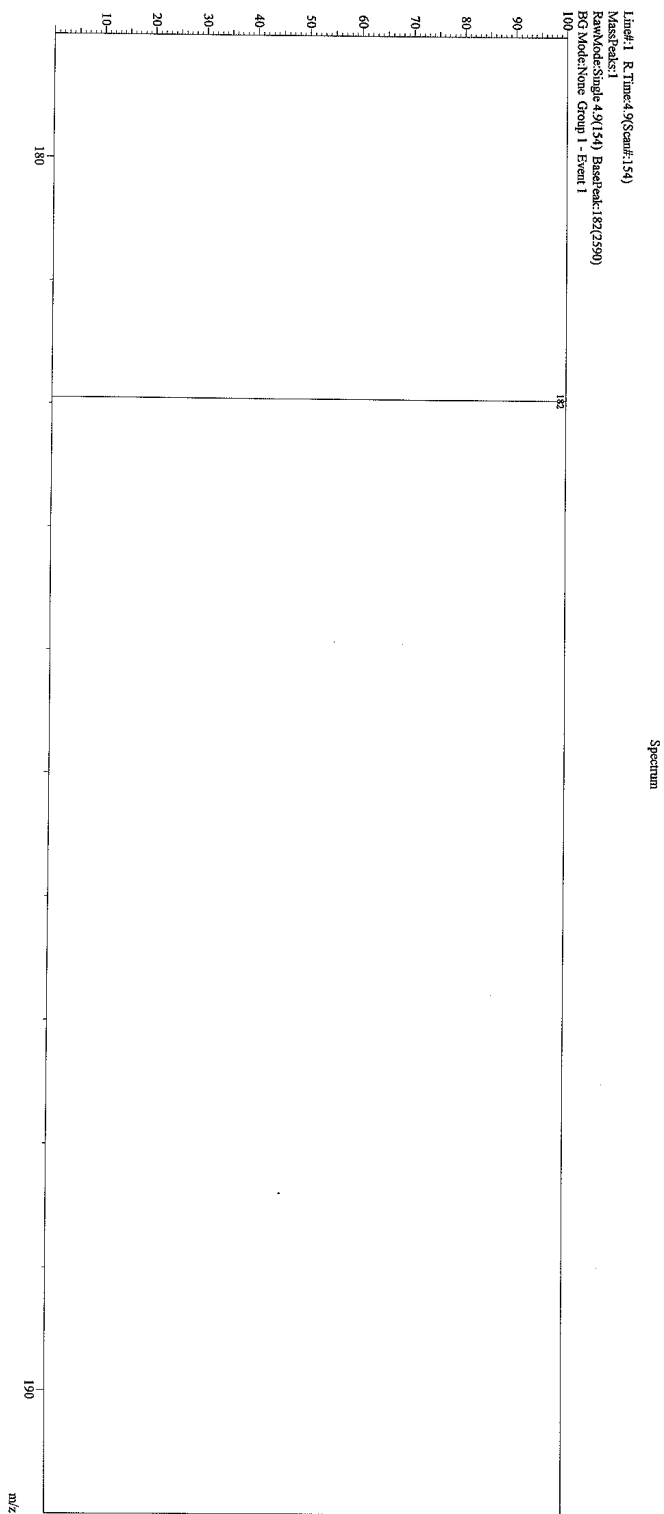
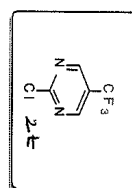
^{19}F NMR yield of compound **2h** $(0.84/(1 \times 3) \times 100\% = 28\%)$ in CDCl_3



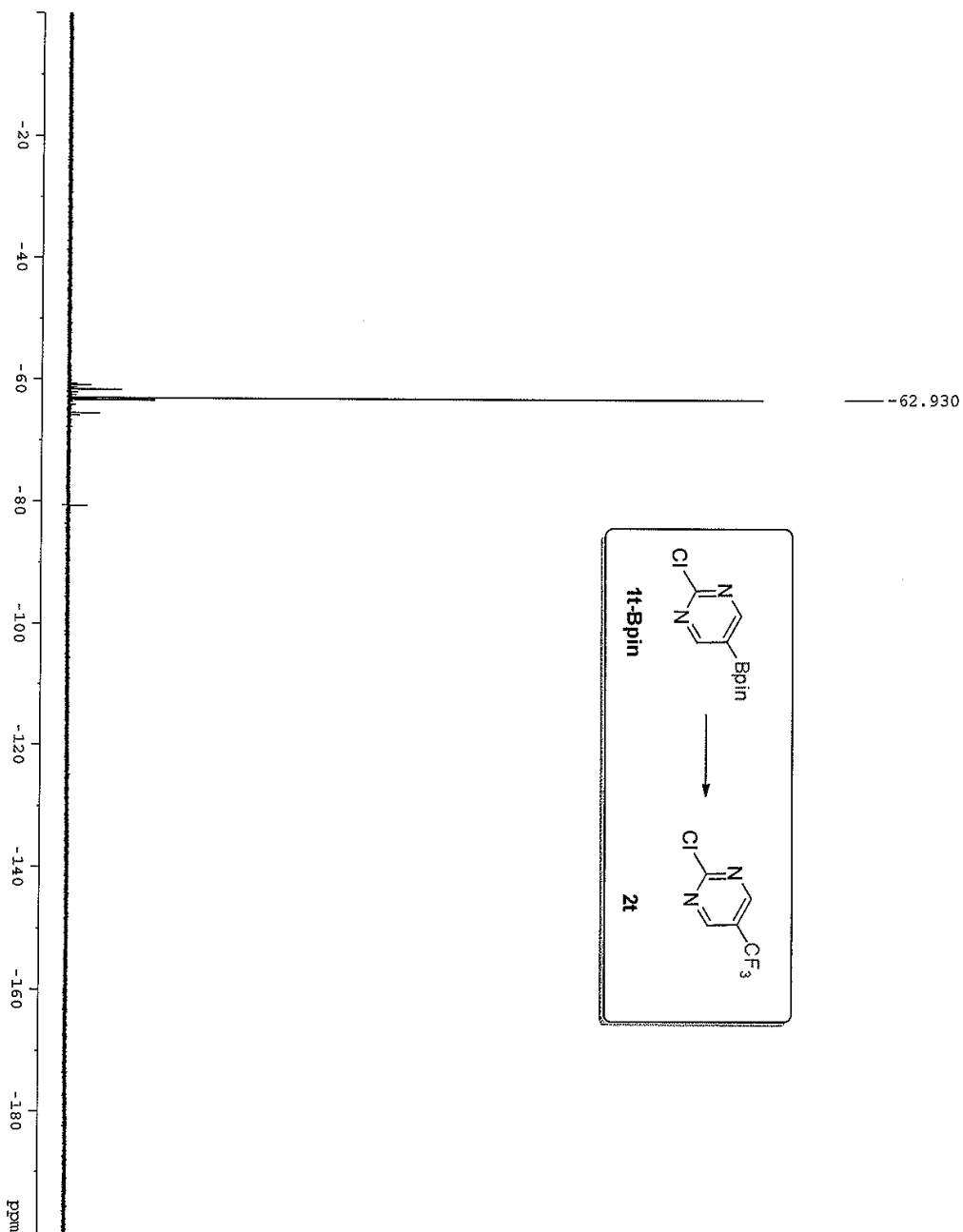
GC-MS of crude 2t

Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Adama
Analyzed : 8/20/2013 3:24:00 PM
Sample Type : Unknown
Level # : 1
Sample Name : SG-VANS-I-28
Sample ID : SG-VANS-I-28
IS Amount : [1]=1
Sample Amount : 1
Injection Factor : 1
Year # : 1
Injection Volume : 5

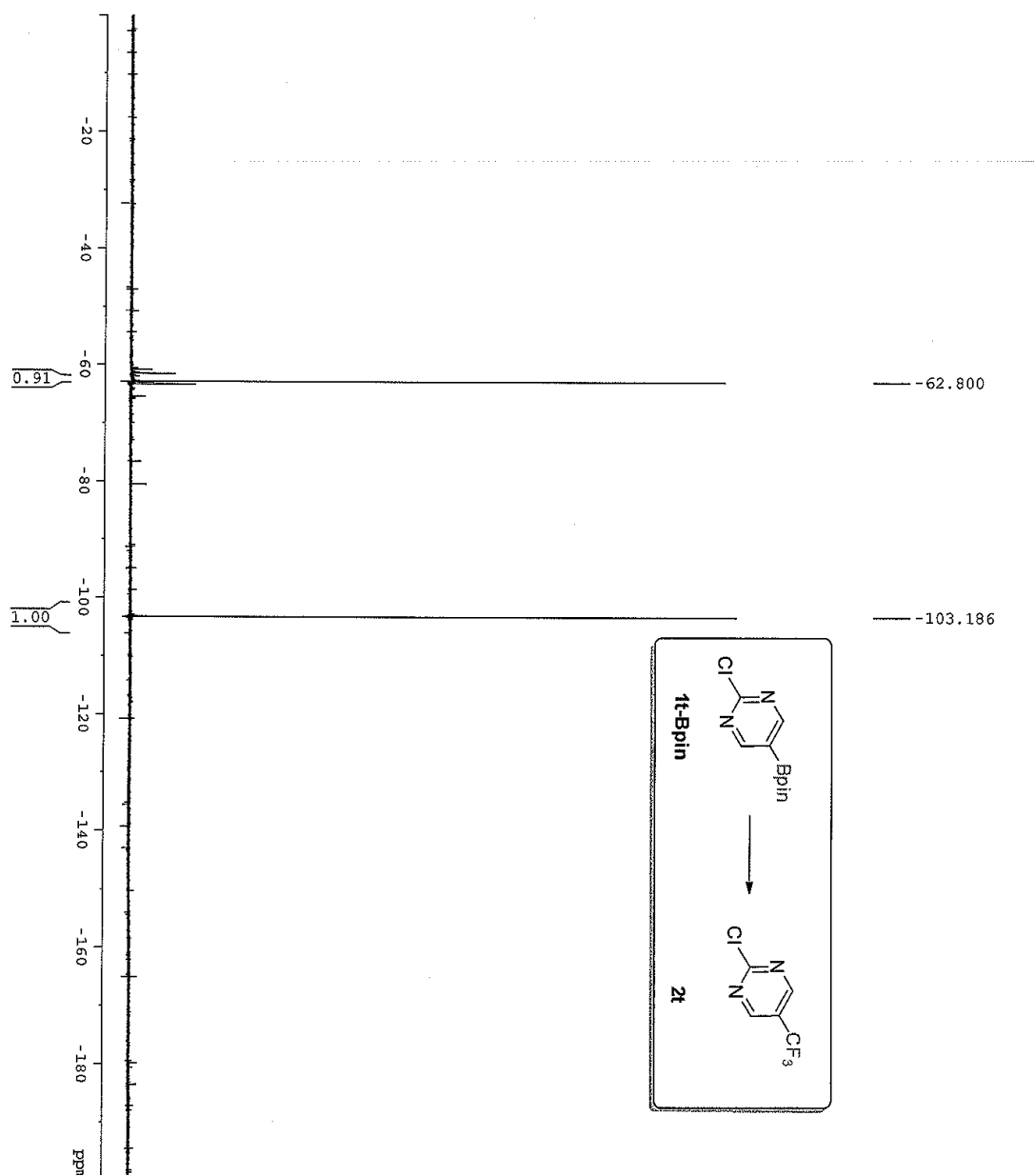
Sample Information



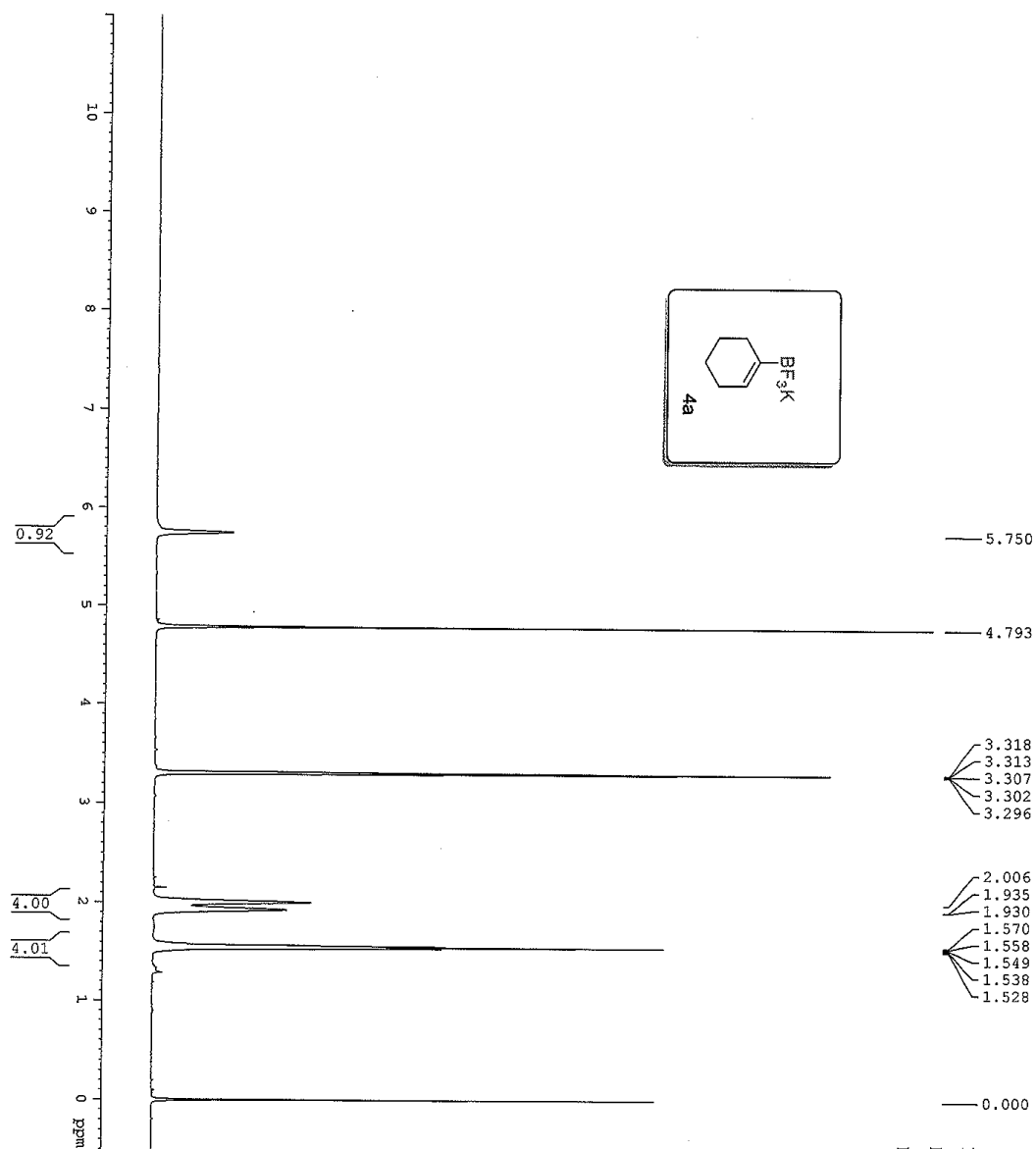
^{19}F NMR of crude **2t** in CDCl_3



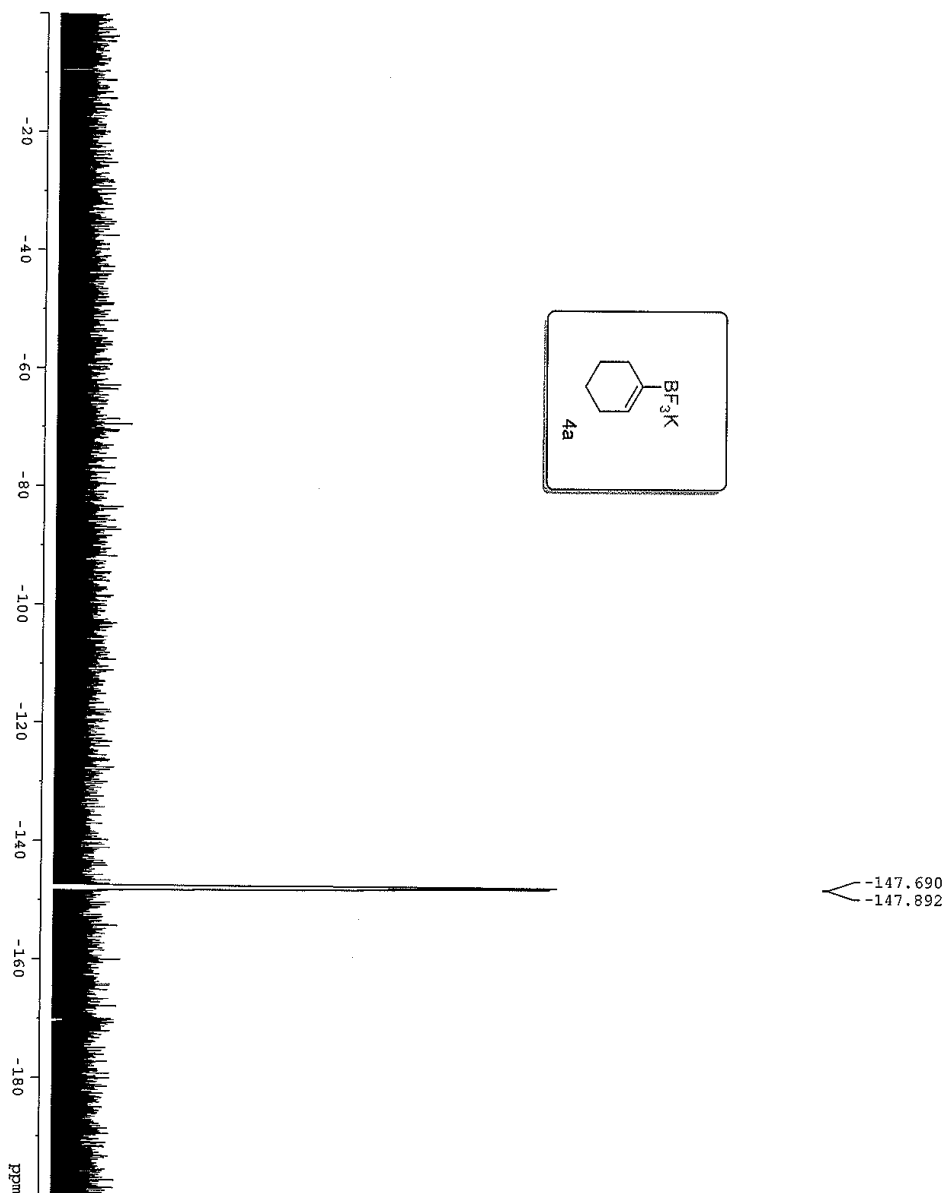
^{19}F NMR yield of compound **2t** ($0.91/(1 \times 3) \times 100\% = 30\%$) in CDCl_3



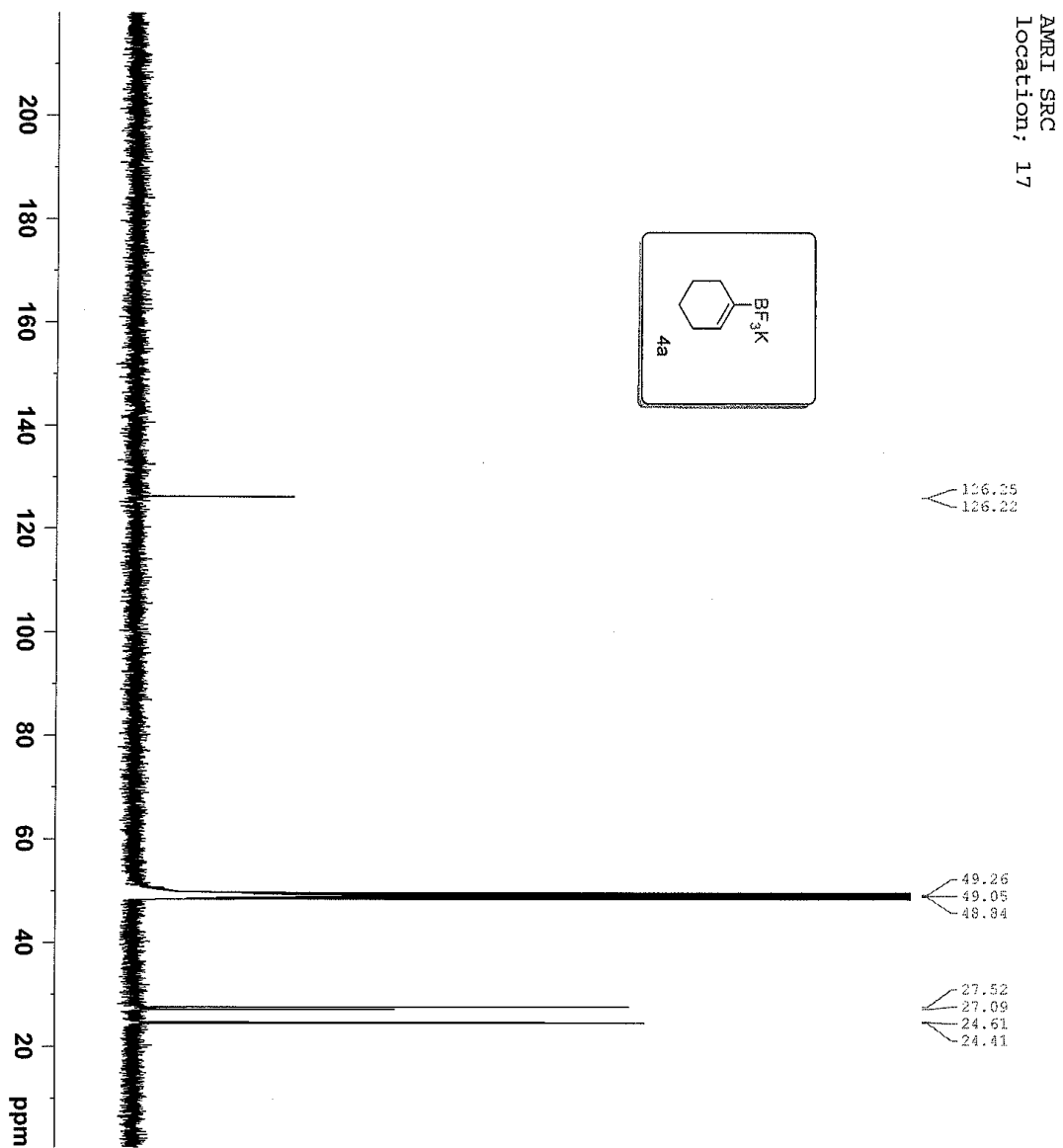
^1H NMR of 4a in CD_3OD



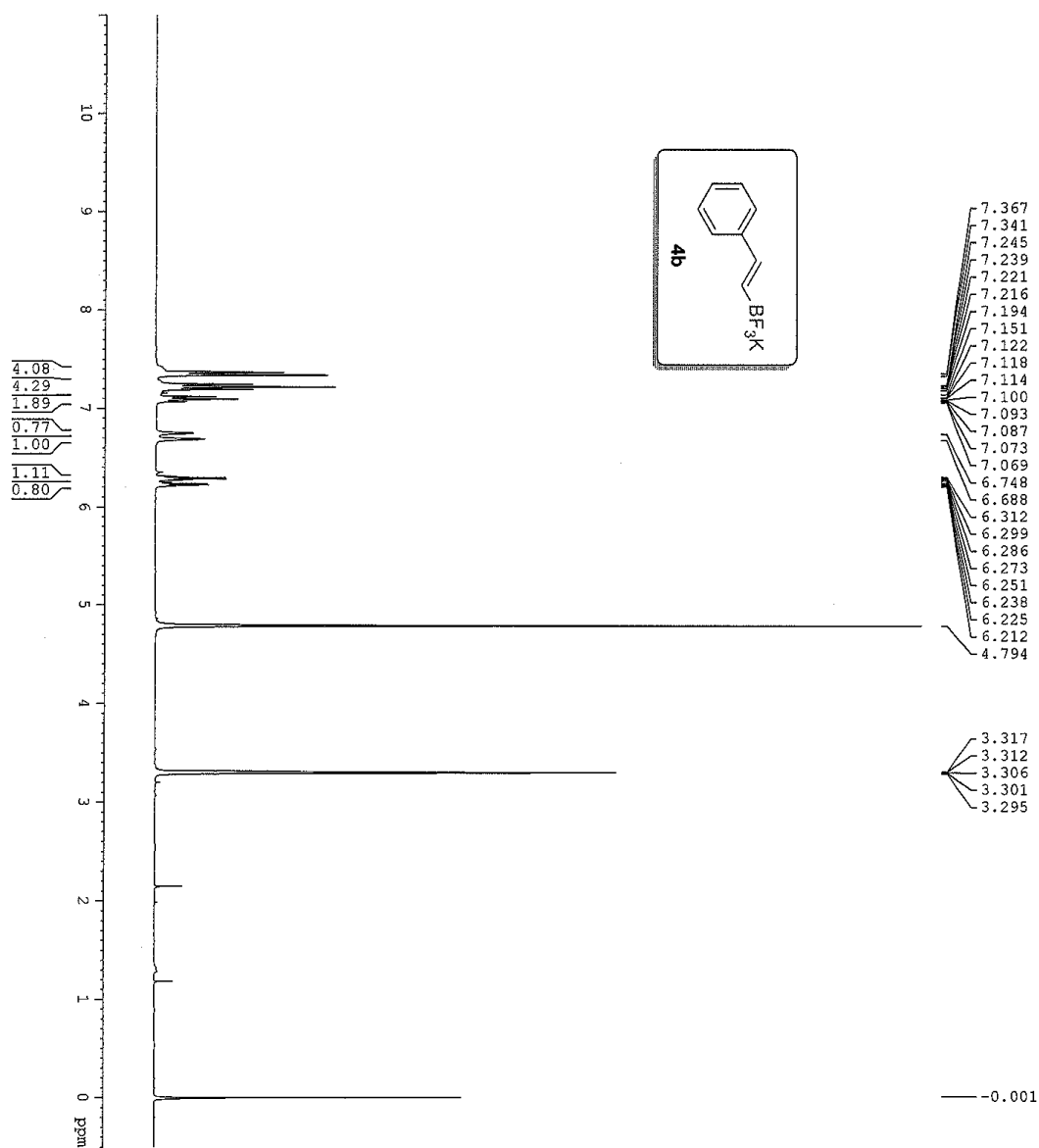
^{19}F NMR of 4a in CD_3OD



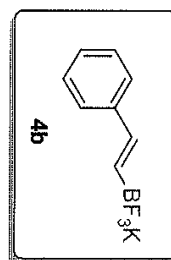
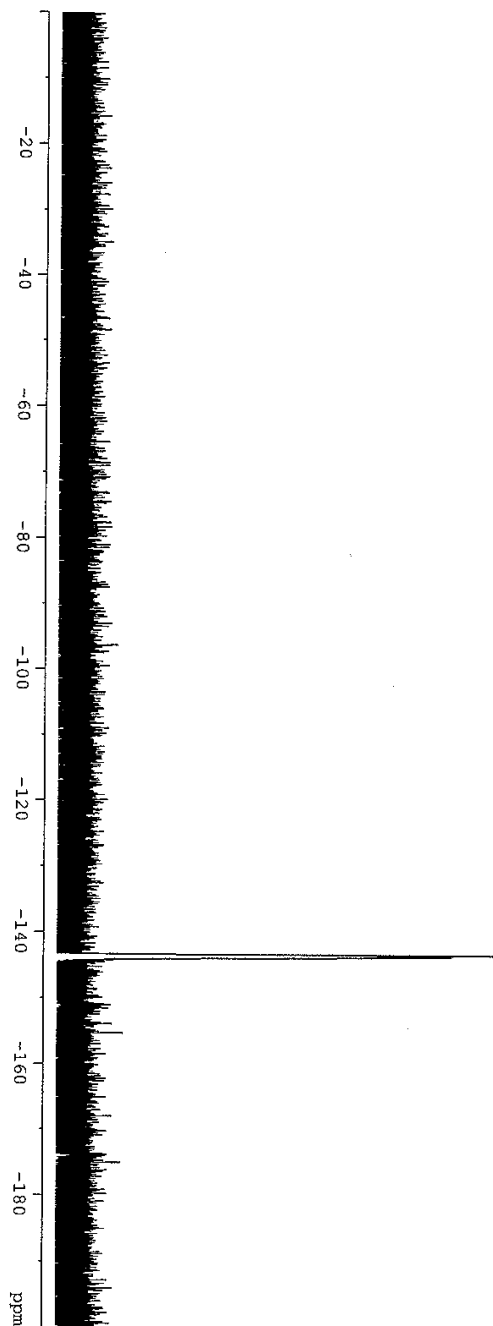
^{13}C NMR of 4a in CD_3OD



^1H NMR of 4b in CD_3OD

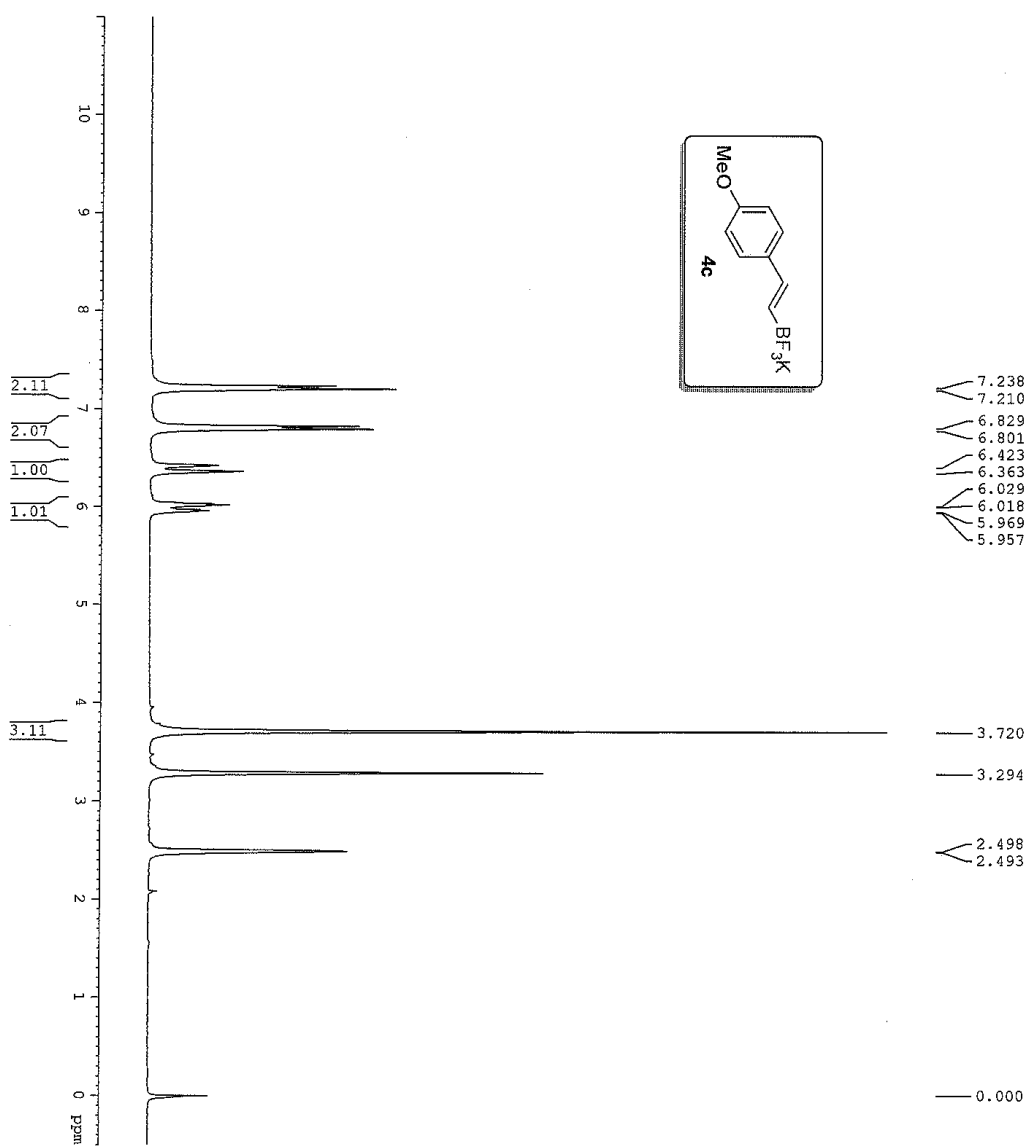


^{13}F NMR of 4b in CD_3OD

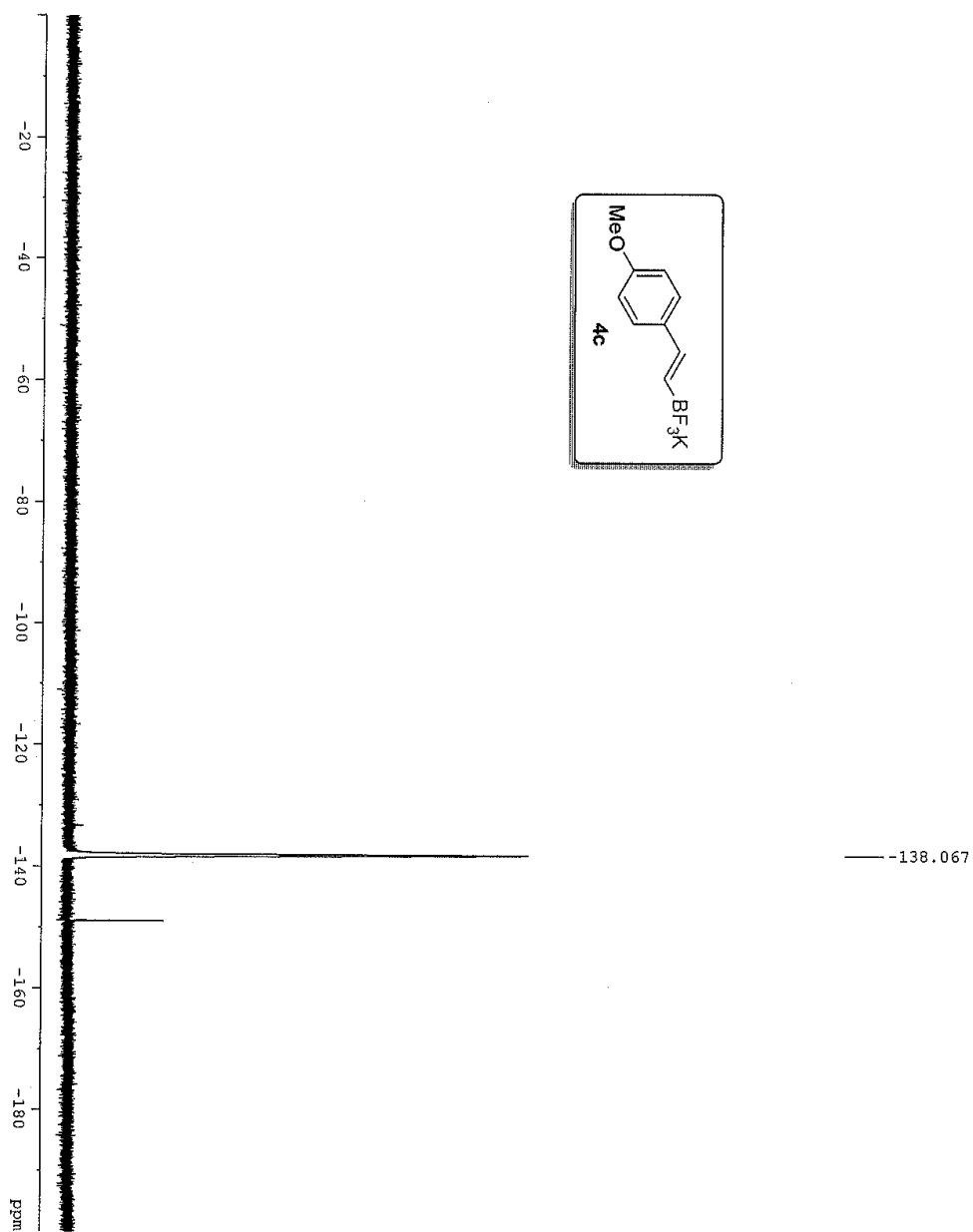


-143.482
-143.514
-143.732

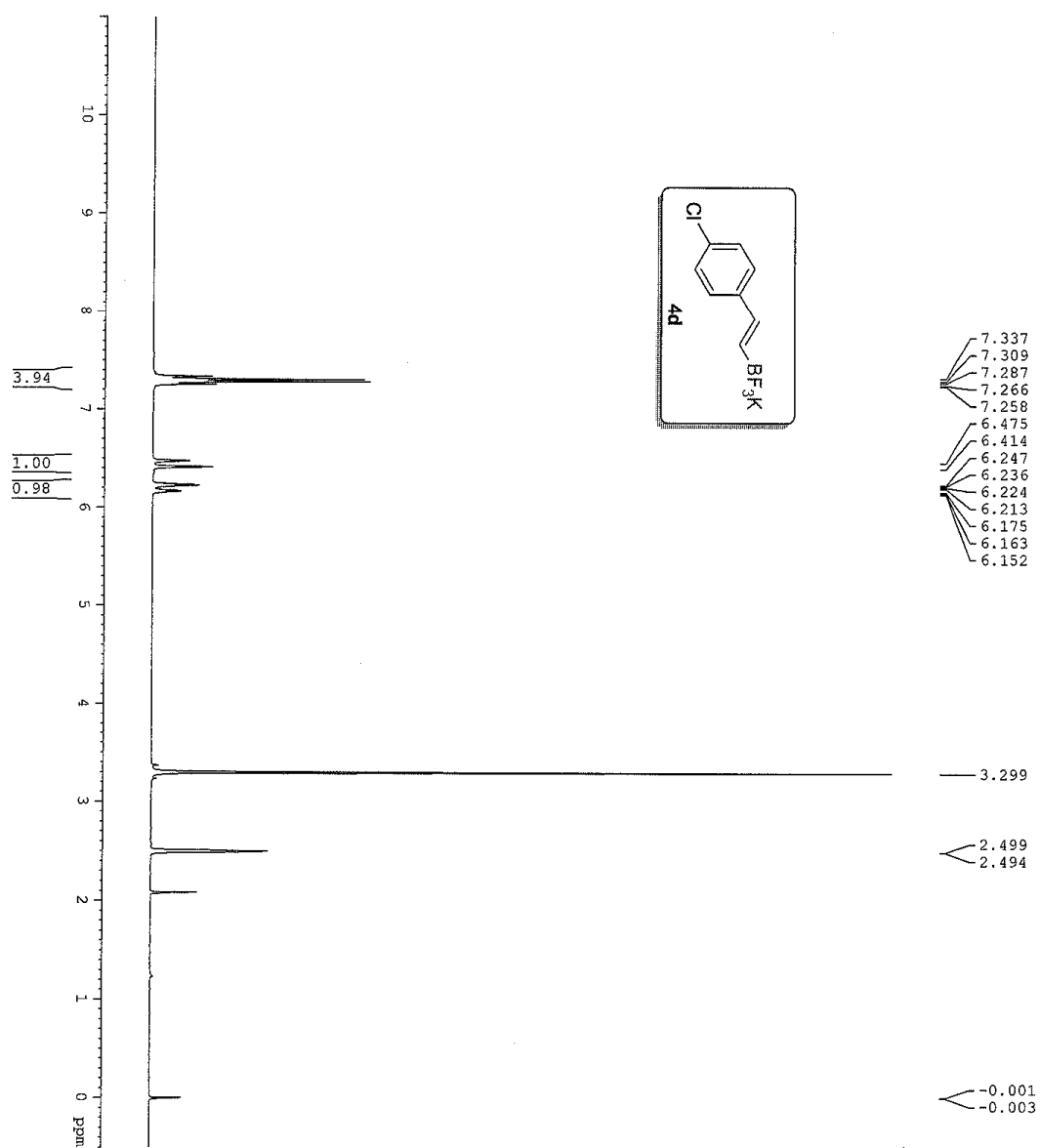
^1H NMR of 4c in $\text{DMSO-}d_6$



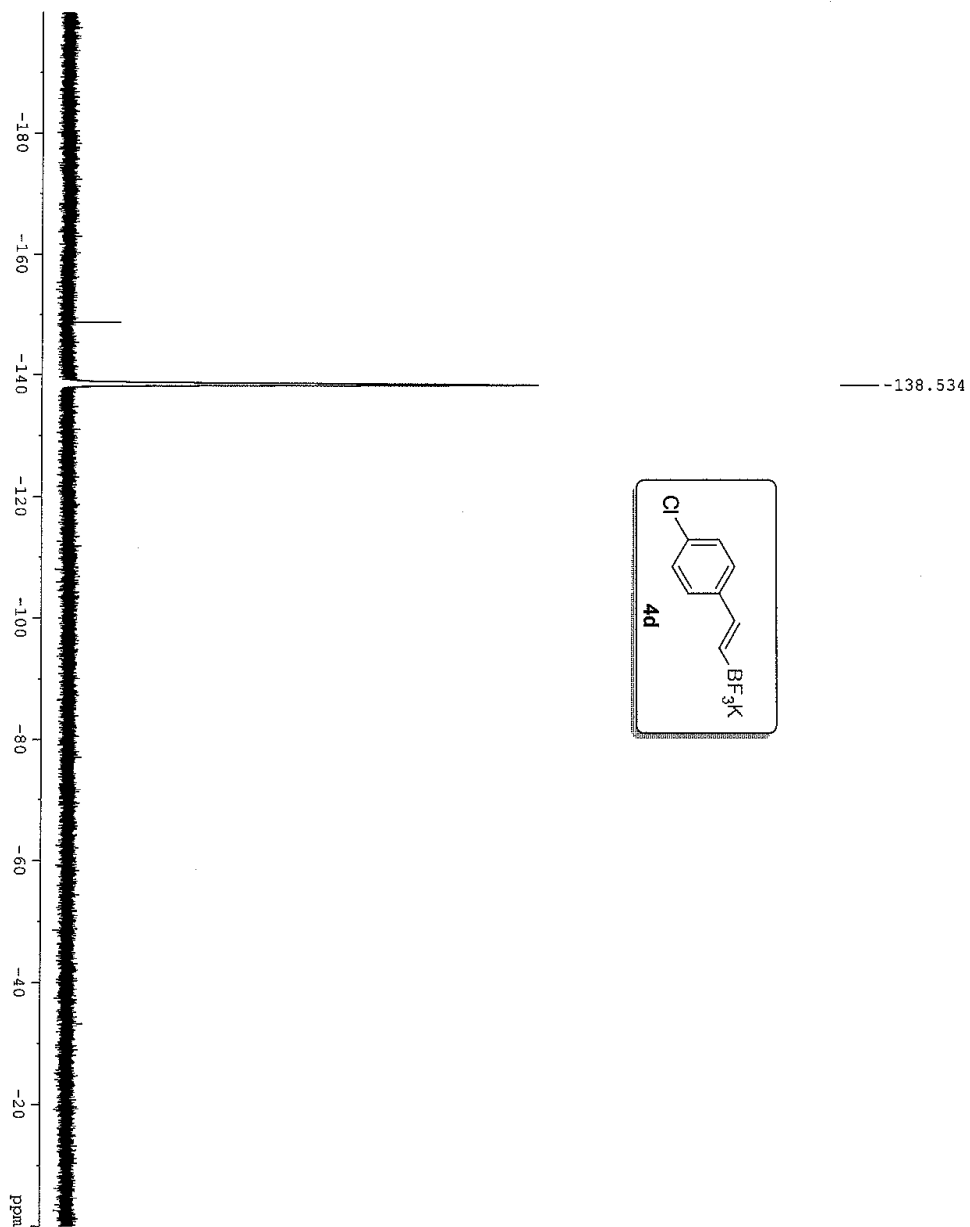
^{19}F NMR of 4c in $\text{DMSO-}d_6$



^1H NMR of 4d in $\text{DMSO-}d_6$



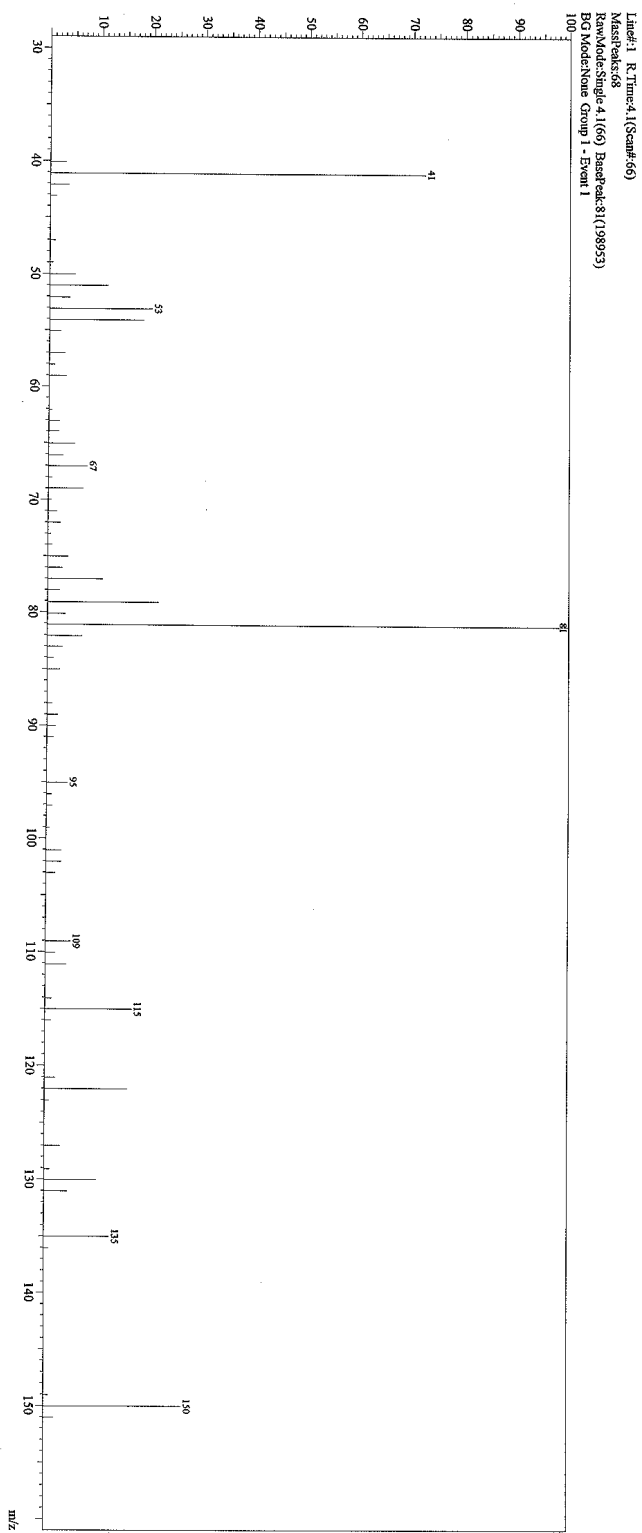
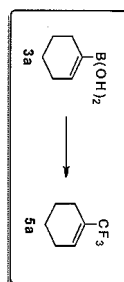
^{19}F NMR of 4d in $\text{DMSO-}d_6$



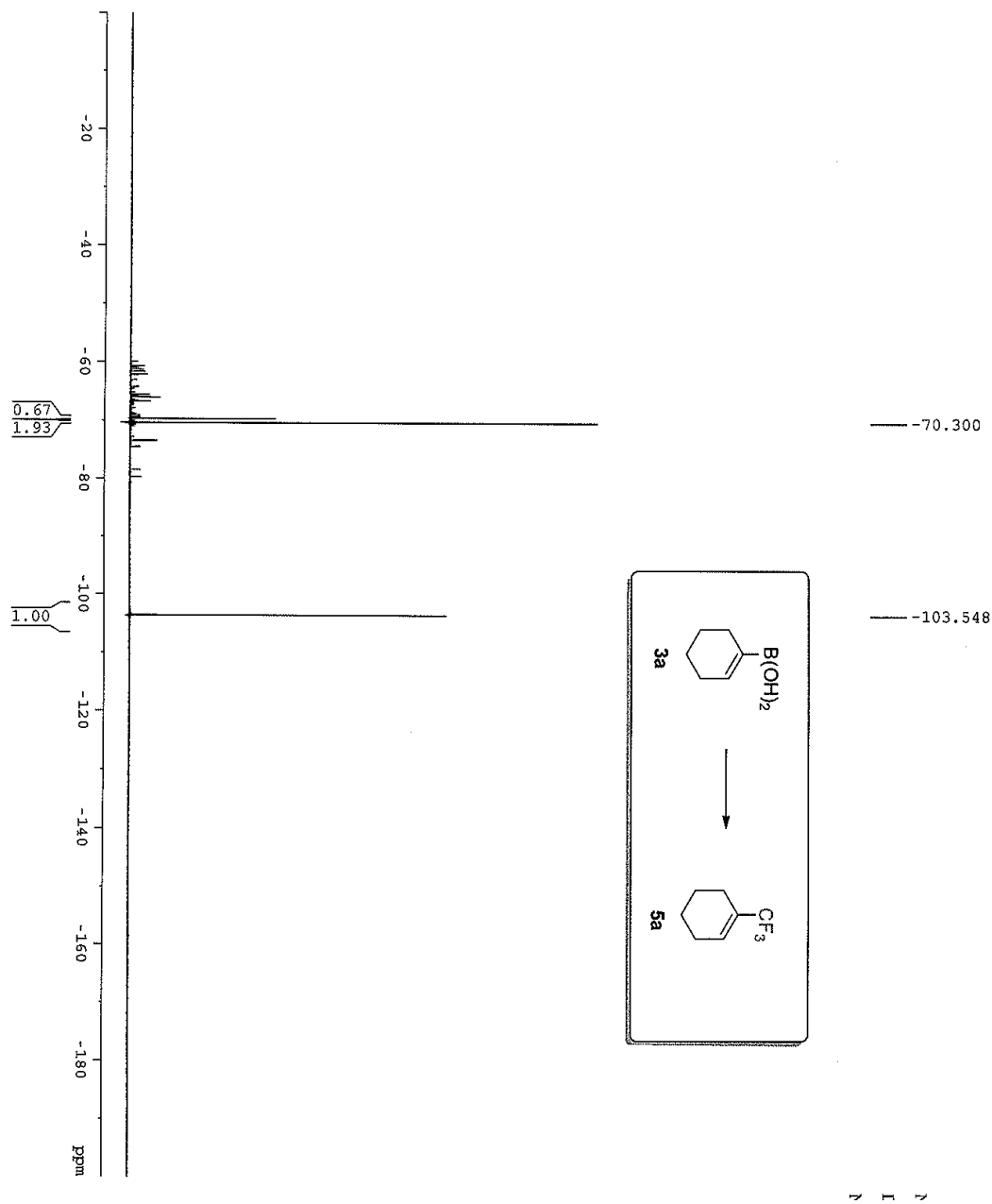
GC-MS of crude 5a

Sample Information

Analysis : GC-MS
Instrument : Shimadzu GC-2010
Sited Admin :
Analyzed by : 8/8/2013 12:15:50 PM
Sample Type : Unknown
Level # : 1
Sample # :
Sample Name : SC-MANS-I-12-1
Sample ID : SC-MANS-I-12-1
IS Amount : [1]=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 4
Injection Volume : 3



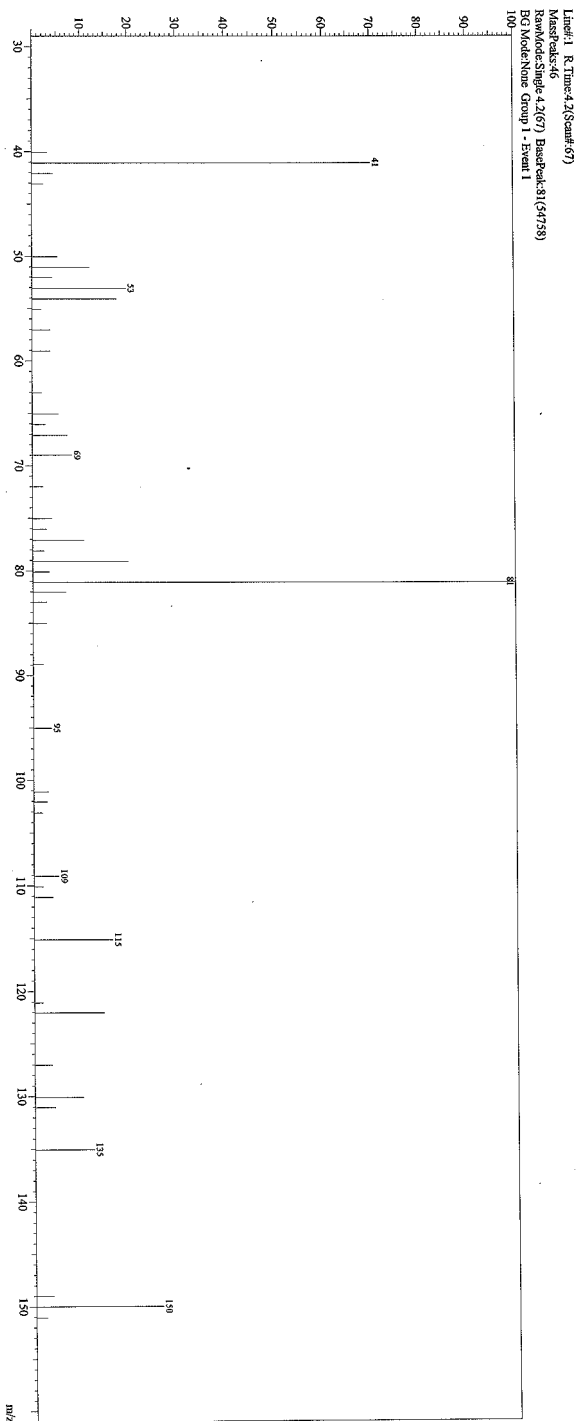
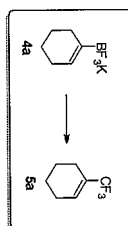
^{19}F NMR yield of compound 5a $(1.93/(1 \times 3) \times 100\% = 64\%)$ in CDCl_3



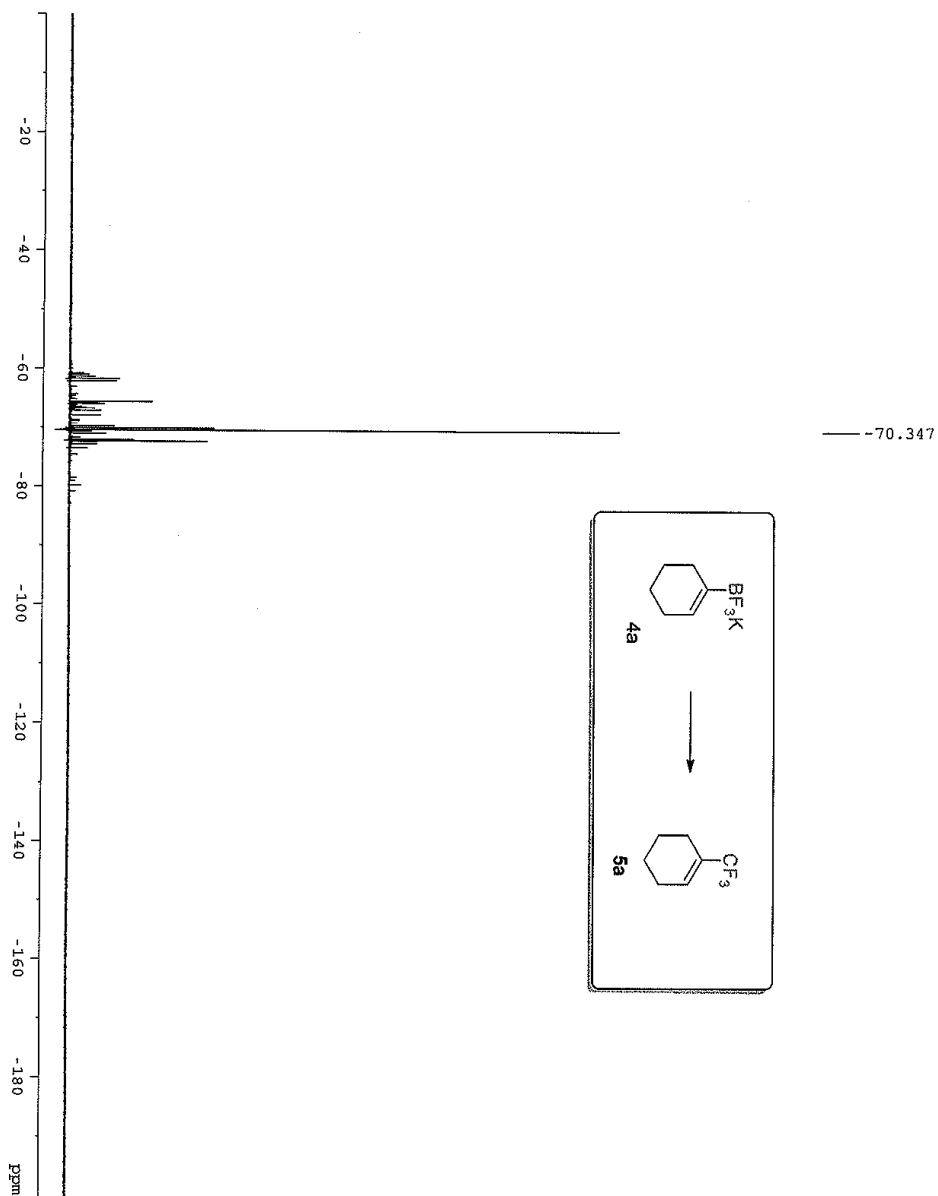
GC-MS of crude 5a

Sample Information

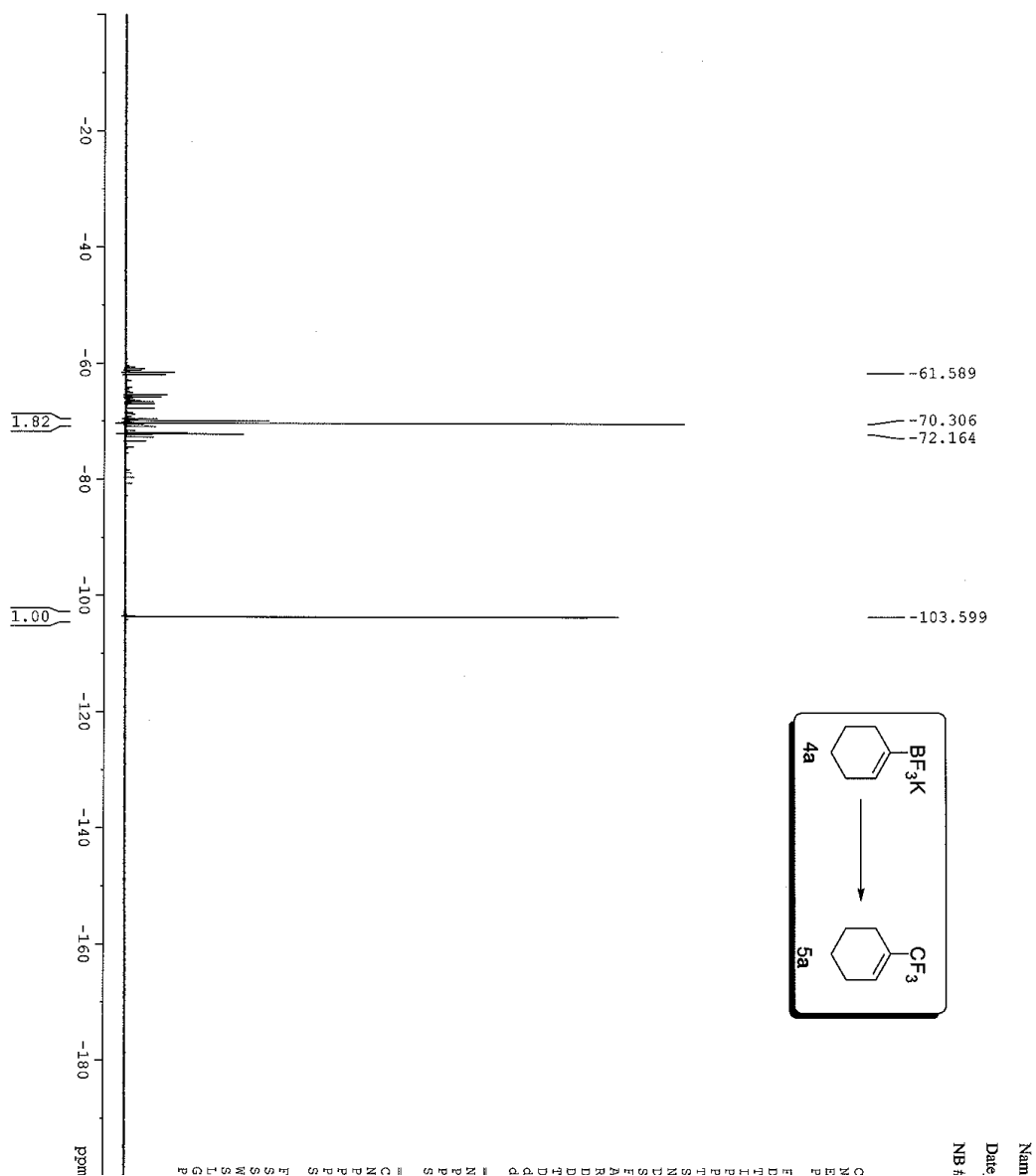
Analysis : GC-MS
Instrument : Shimadzu GC-2010
Acquired by :
Acquisition : 8/27/13 11:44:39 AM
Sample Type : Unknown
Level # : 1
Sample Name : SC-MNS-I-16
Sample ID : SC-MNS-I-16
IS Amount : [1]=1
Sample Amount :
Dilution Factor : 1
Vial # : 1
Injection Volume : 3



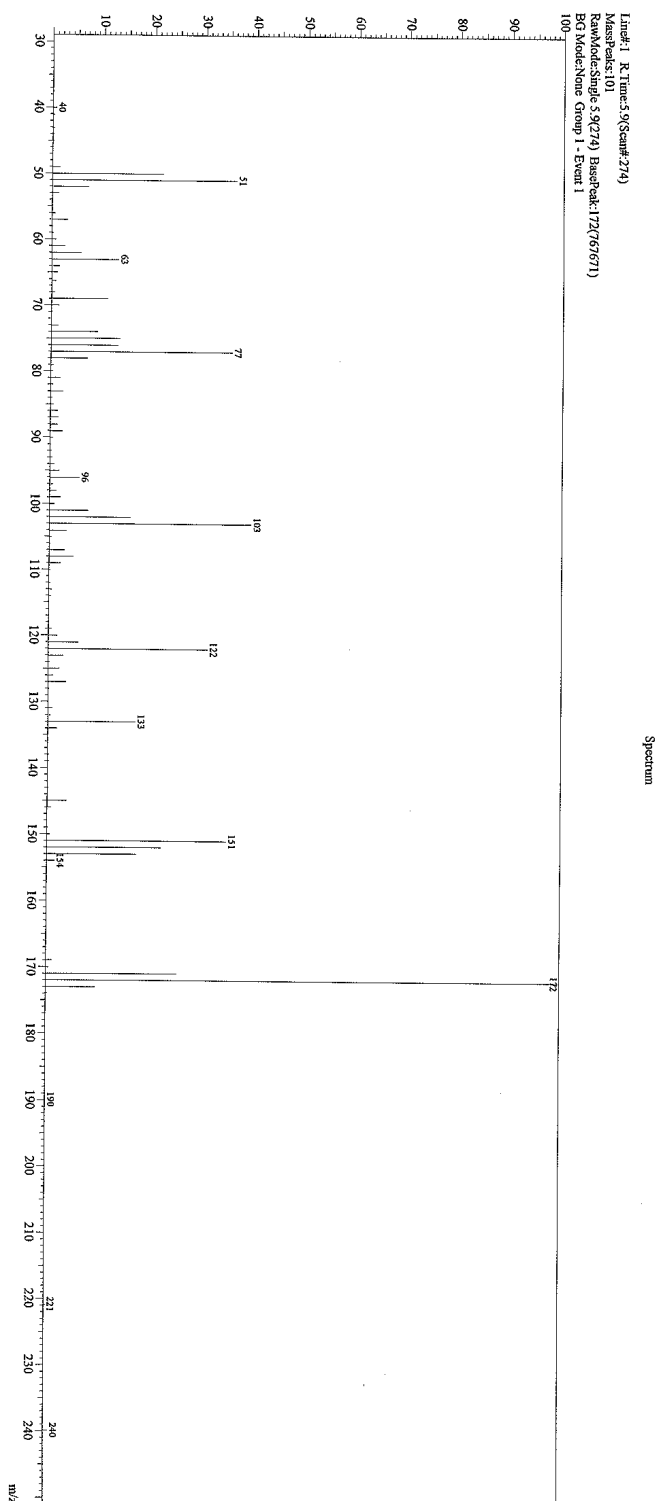
^{19}F NMR of crude 5a in CDCl_3



^{19}F NMR yield of compound 2h $(1.82/(1 \times 3) \times 100\% = 60\%)$ in CDCl_3



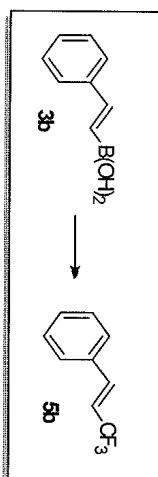
GC-MS of crude 5b



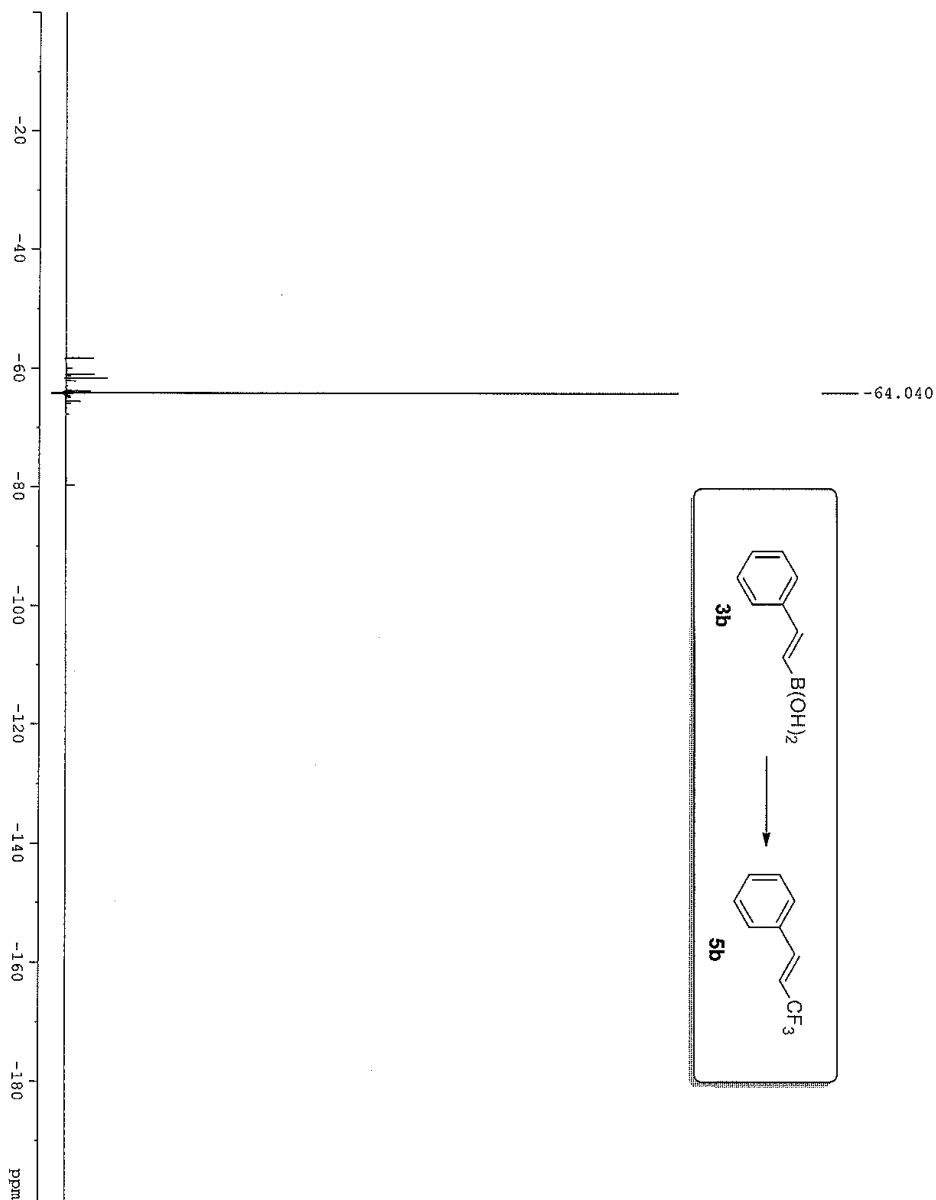
Sample Information

Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 8/8/2013 12:51:08 PM
Sample Type : Unknown
Level # : 1
Sample Name : SG-RBS-F-61-1
Sample ID : SG-RBS-F-61-1
IS Amount : [1]=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 5
Injection Volume : 3

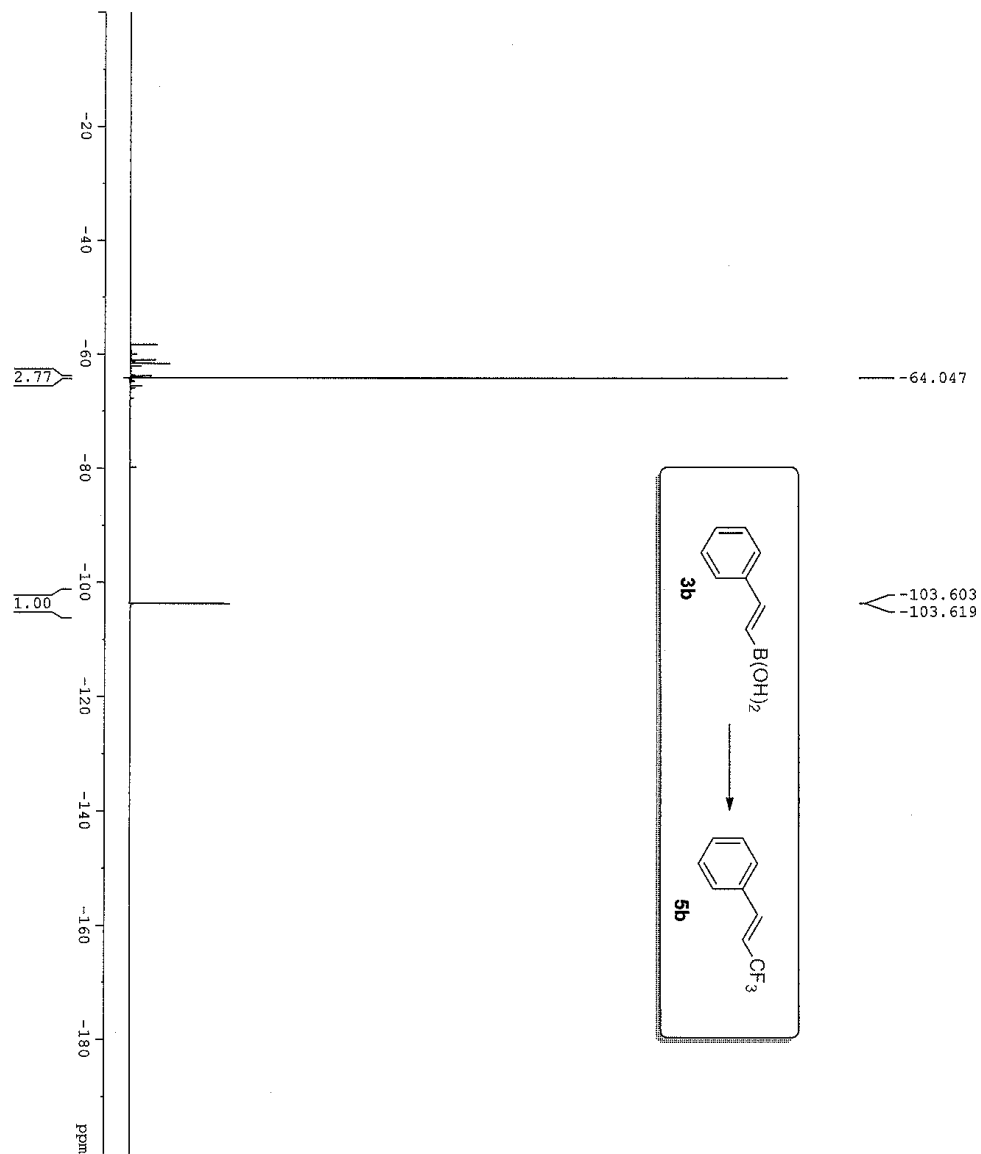
Spectrum



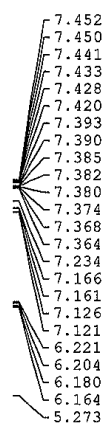
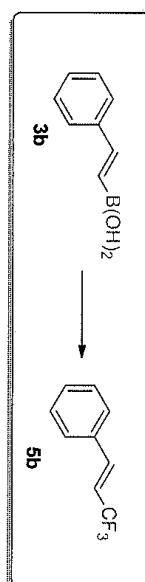
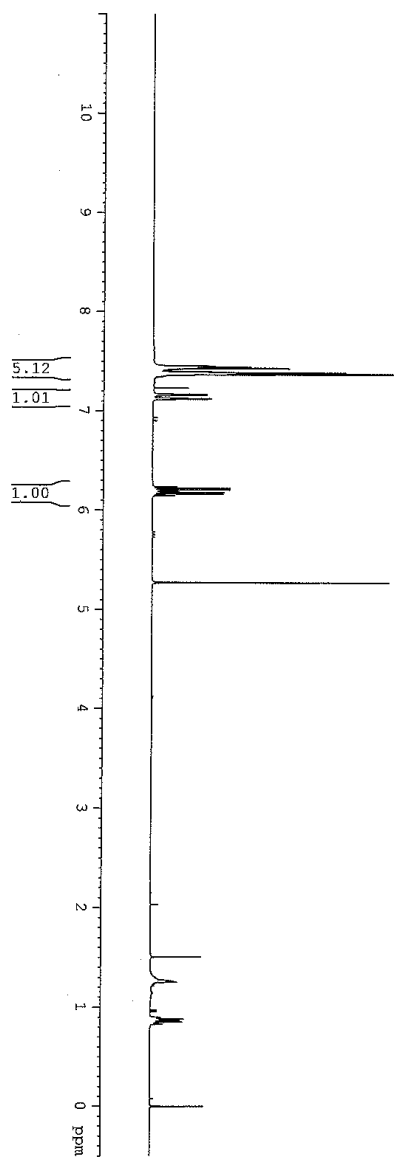
^{19}F NMR of crude 5b in CDCl_3



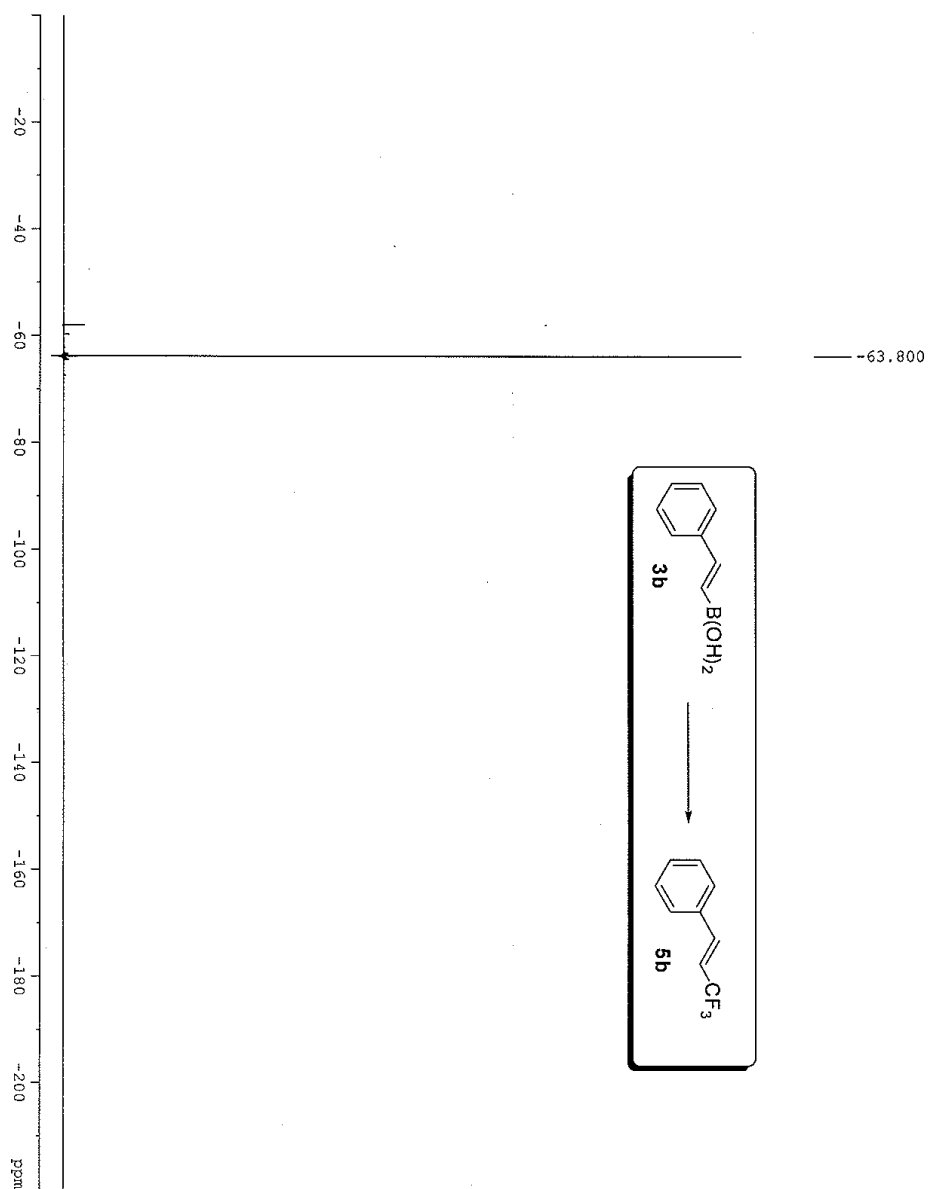
^{19}F NMR yield of compound **5b** ($2.77/(1 \times 3) \times 100\% = 92\%$) in CDCl_3



^1H NMR of 5b in CDCl_3



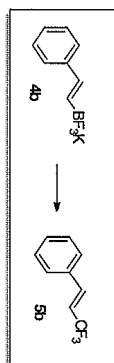
¹⁹F NMR of isolated 5b in CDCl₃



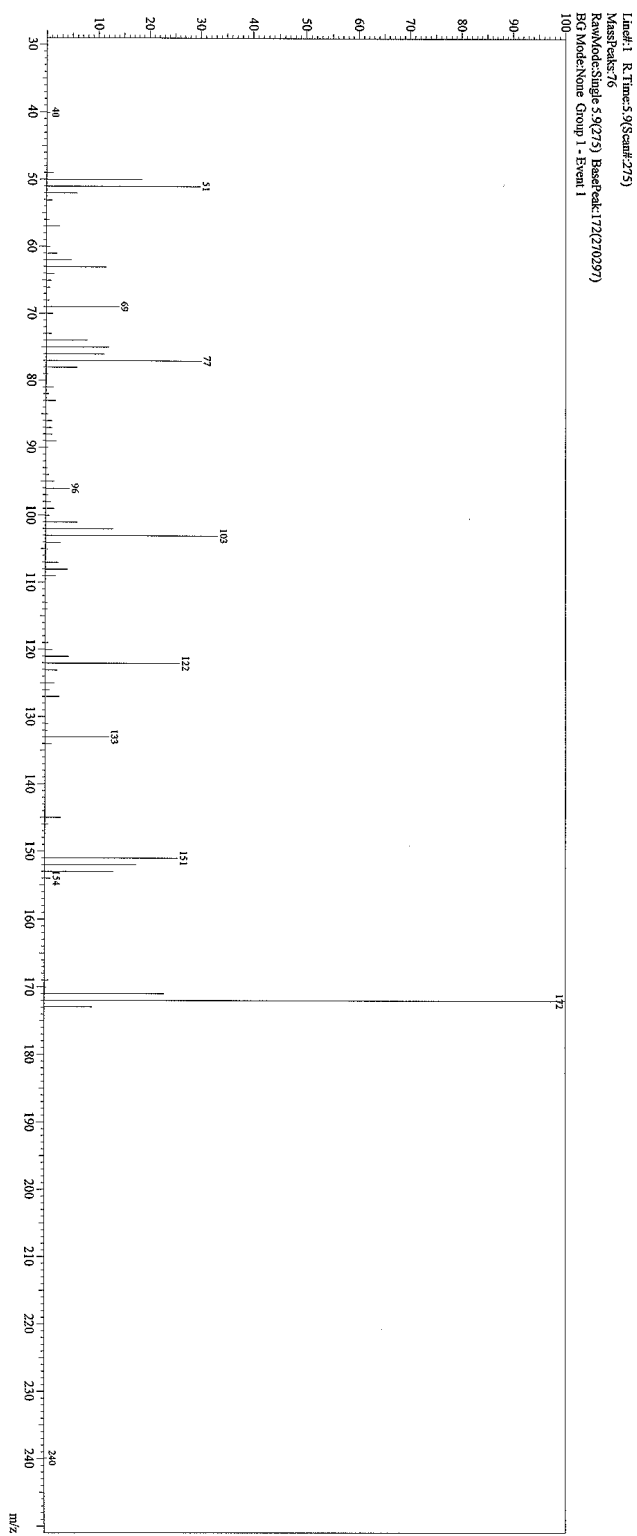
GC-MS of crude 5b

Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analysis by : Shimadzu
Analysis Date : 20/2013 12:55:19 PM
Sample Name : Unknown
Sample # : 1
Sample Name : SG-RRS-F-63
Sample ID : SG-RRS-F-63
IS Amount : []=1
Sample Amount : 1
Dilution Factor : 1
Vial # : 1
Injection Volume : 3

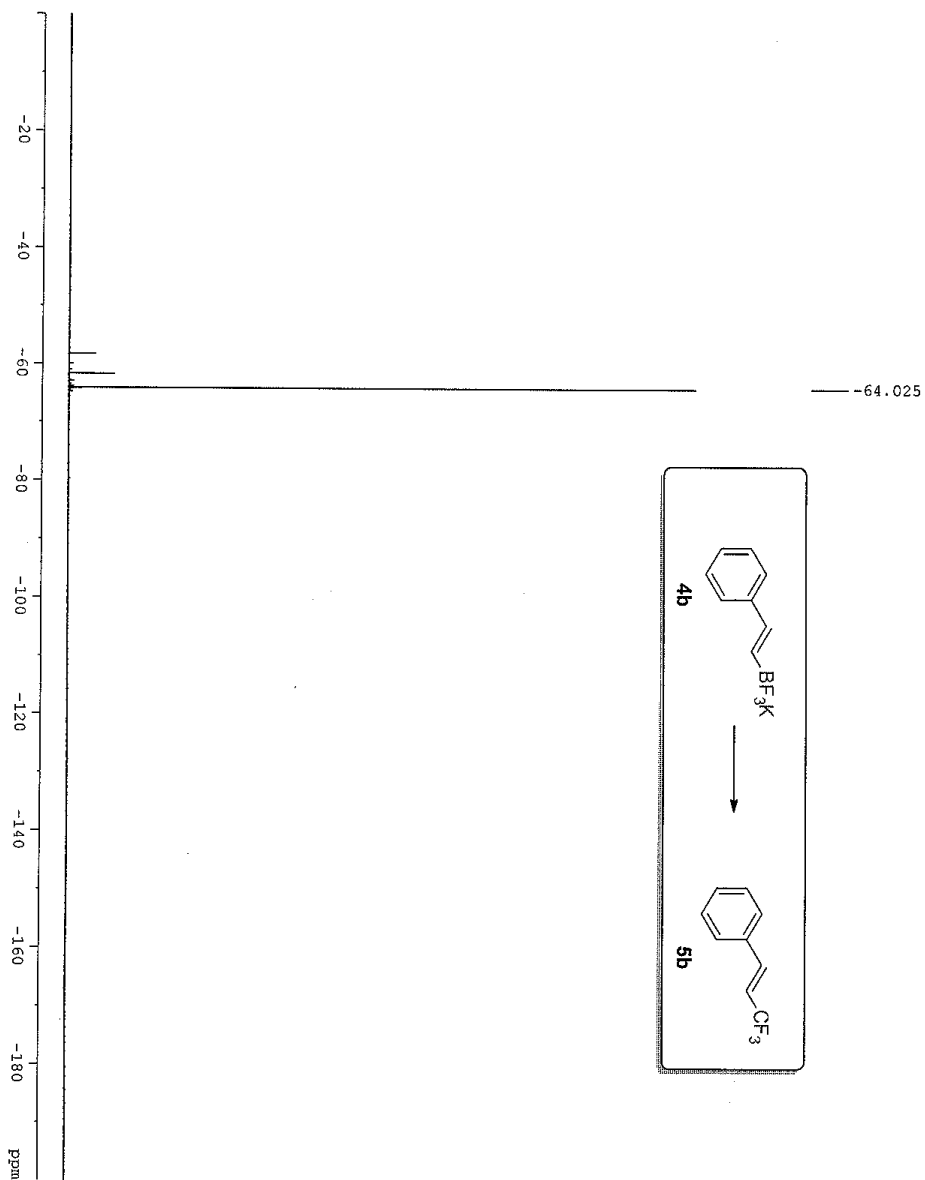
Sample Information



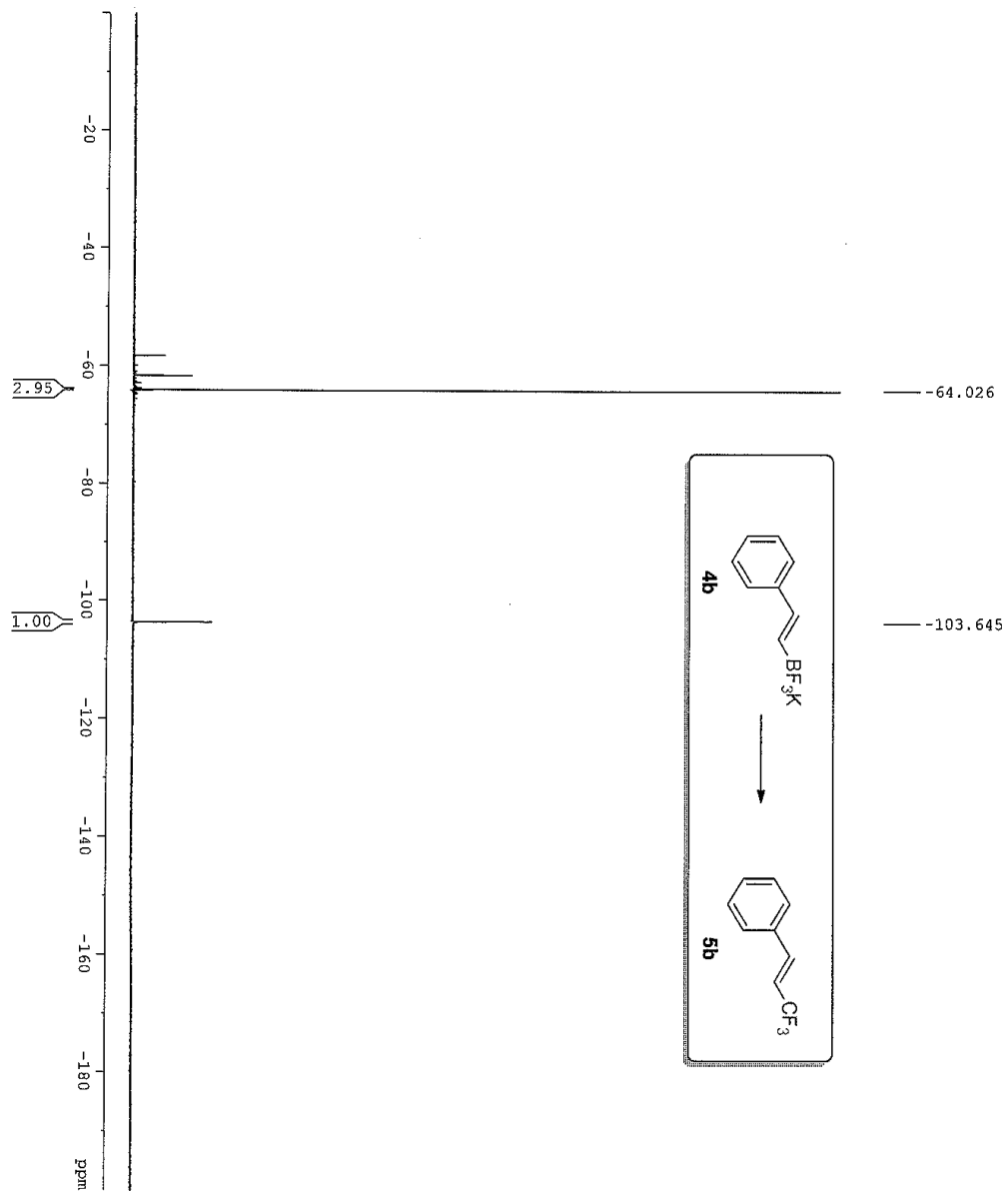
Spectrum



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



^{19}F NMR yield of compound **5b** $(2.95/(1 \times 3) \times 100\% = 98\%)$ in CDCl_3

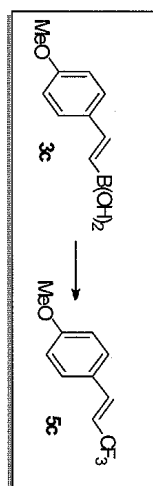
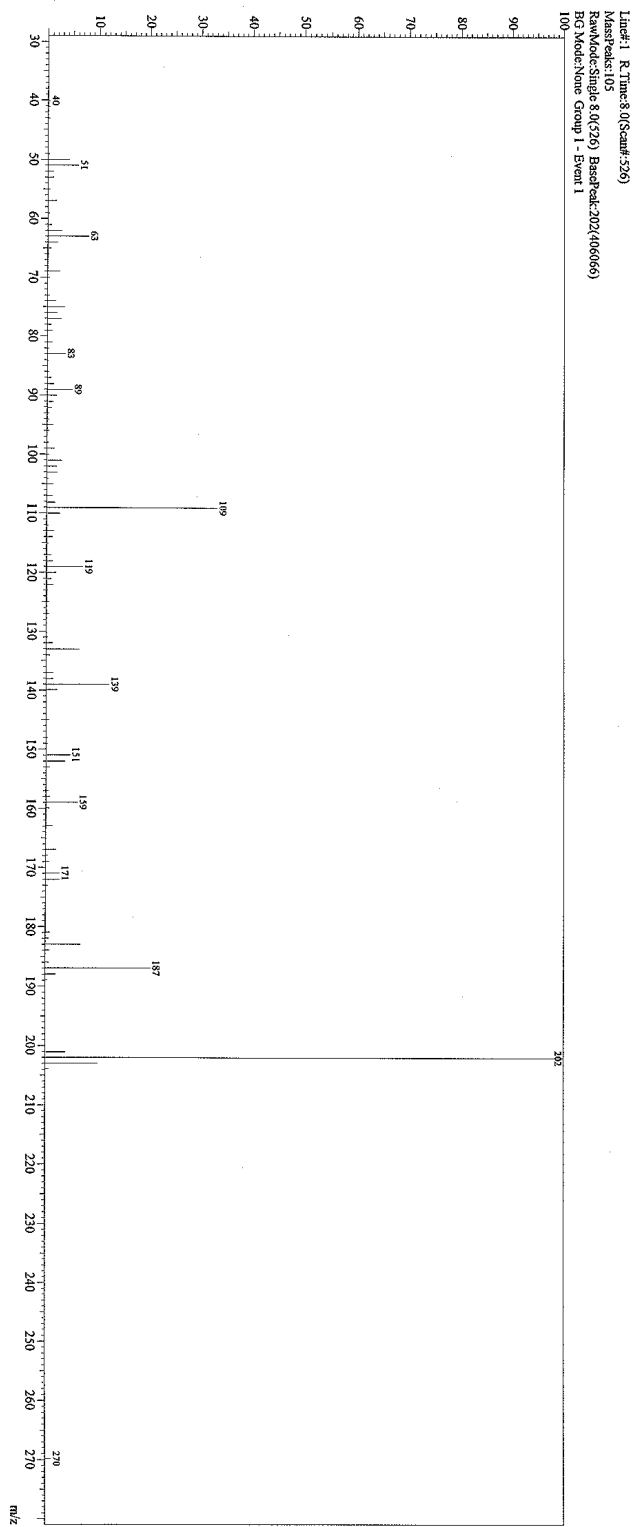


GC-MS of crude 5c

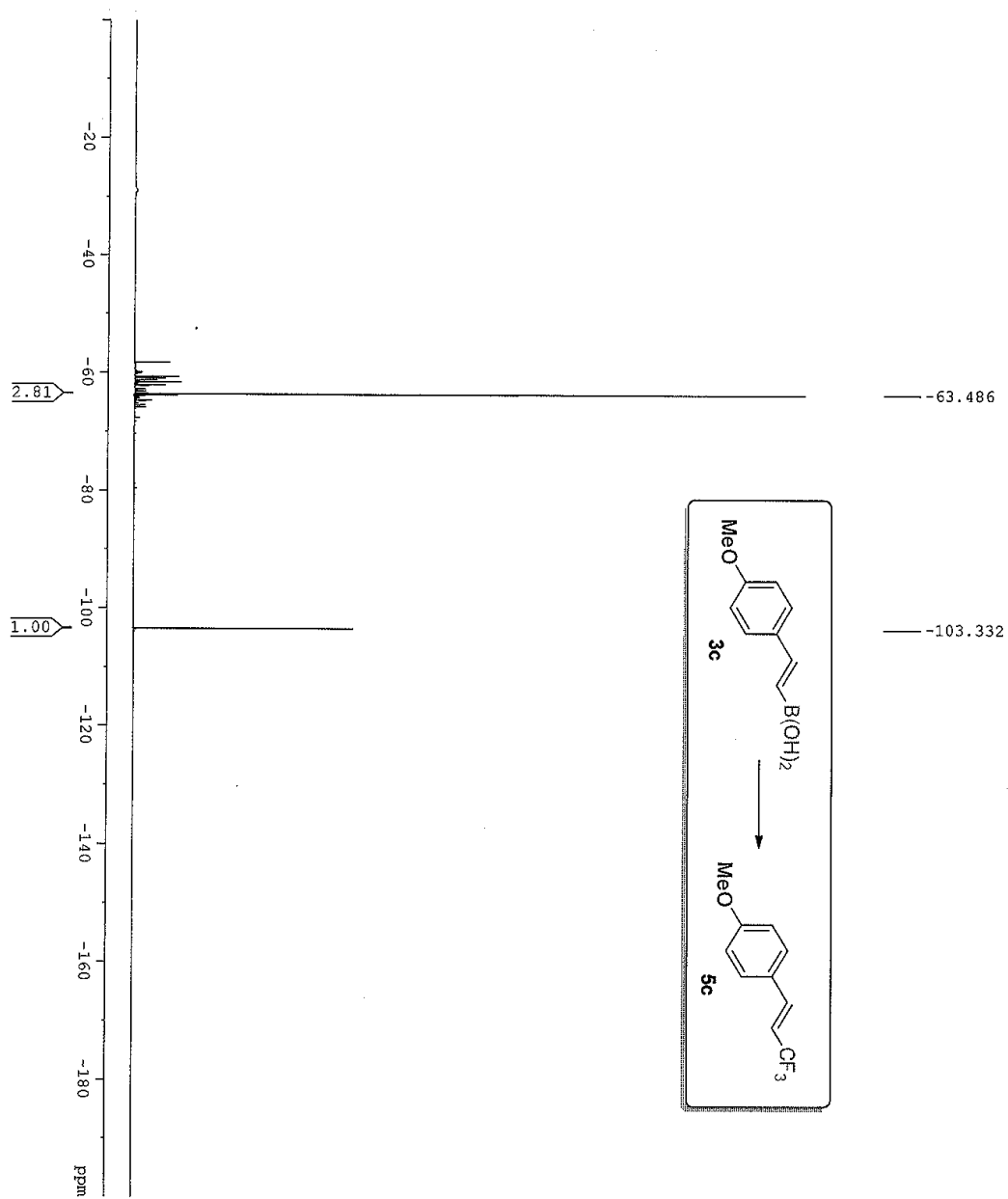
Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Admin
Analyzed : 8/30/2013 1:06:58 PM
Sample Type : Unknown
Level # : 1
Sample Name : SG-RJSS-F-64
Sample ID : SG-RJSS-F-64
IS Amount : [1]-1
Sample Amount : 1
Injection Factor : 1
Injection Volume : 5

Sample Information

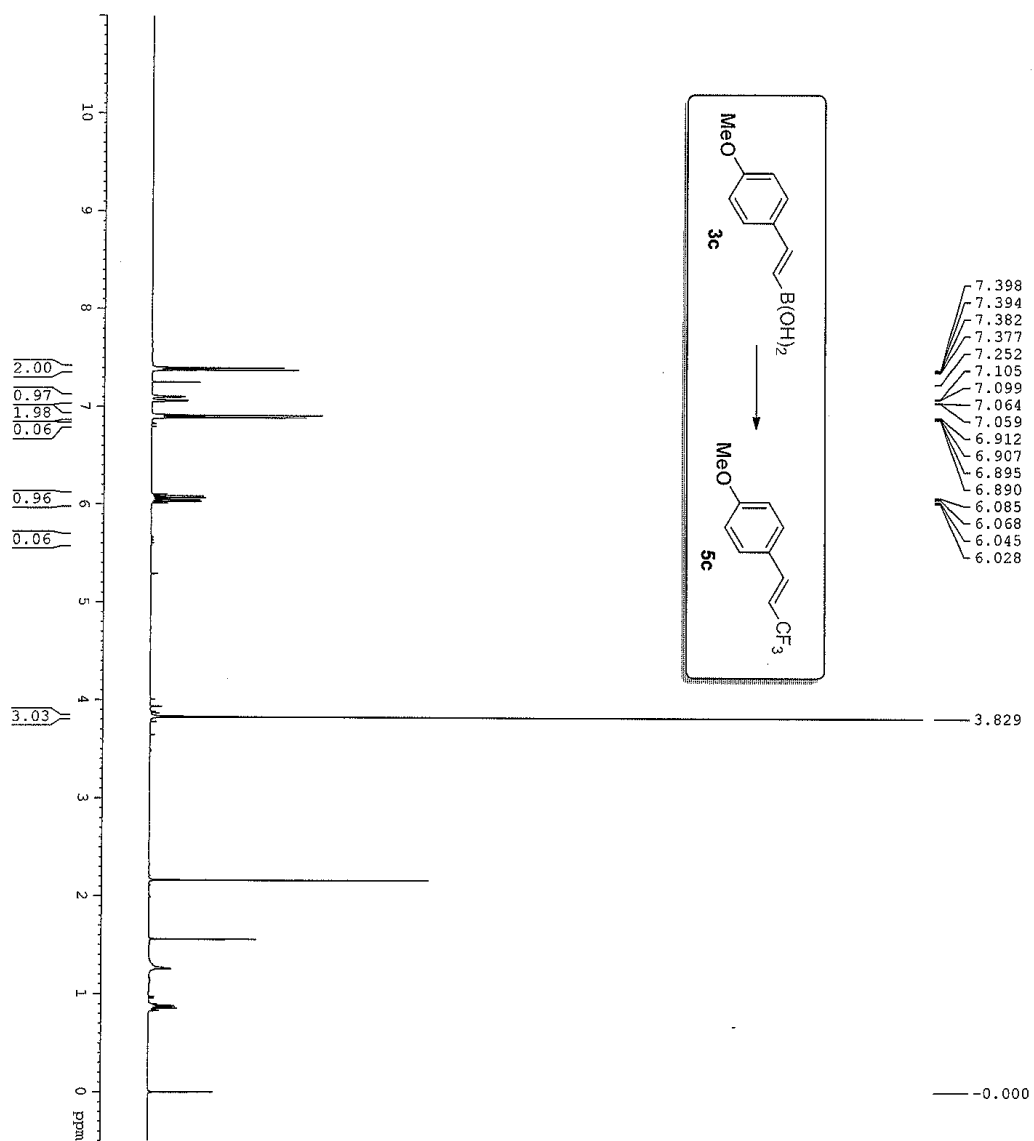
Spectrum



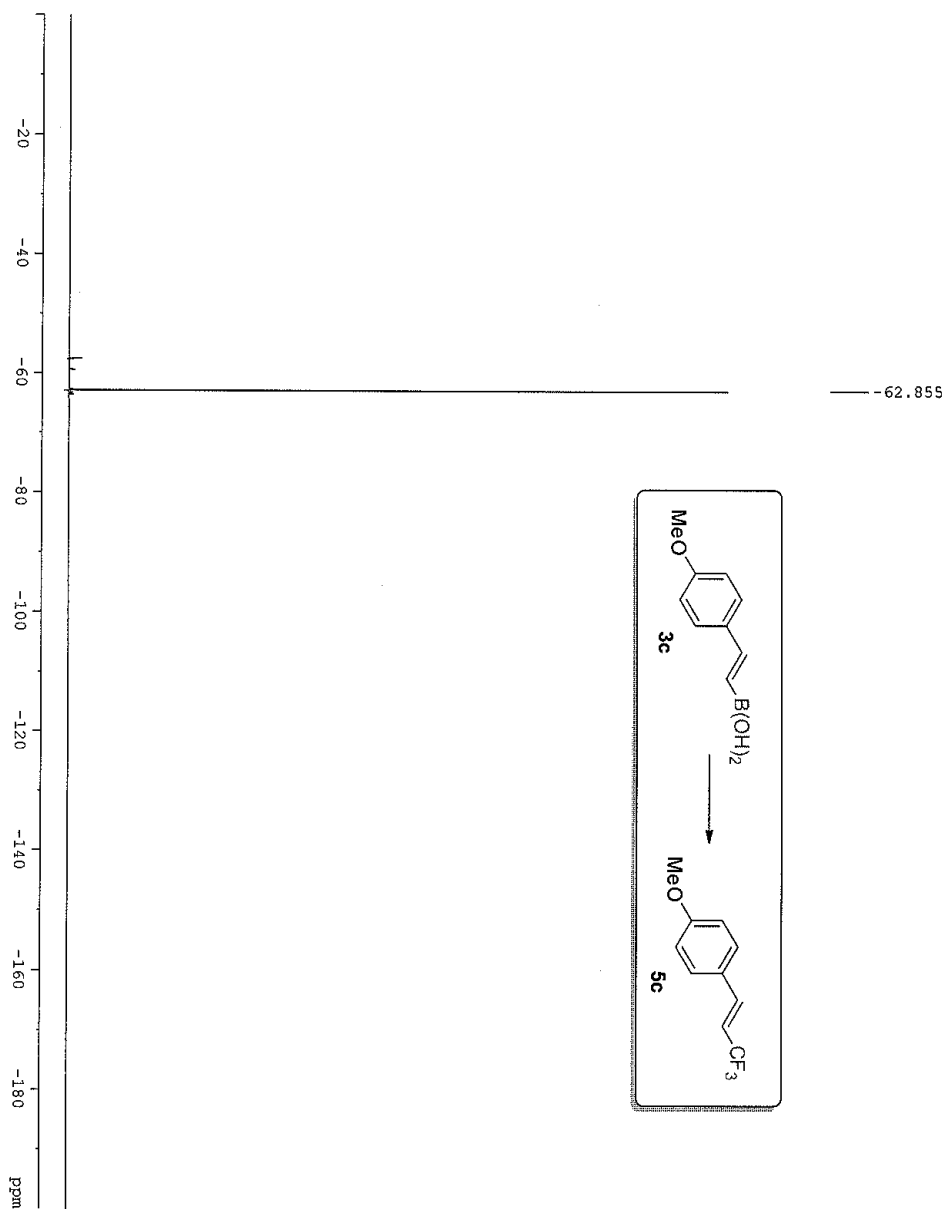
^{19}F NMR yield of compound 5c $(2.81/(1 \times 3) \times 100\% = 93\%)$ in CDCl_3



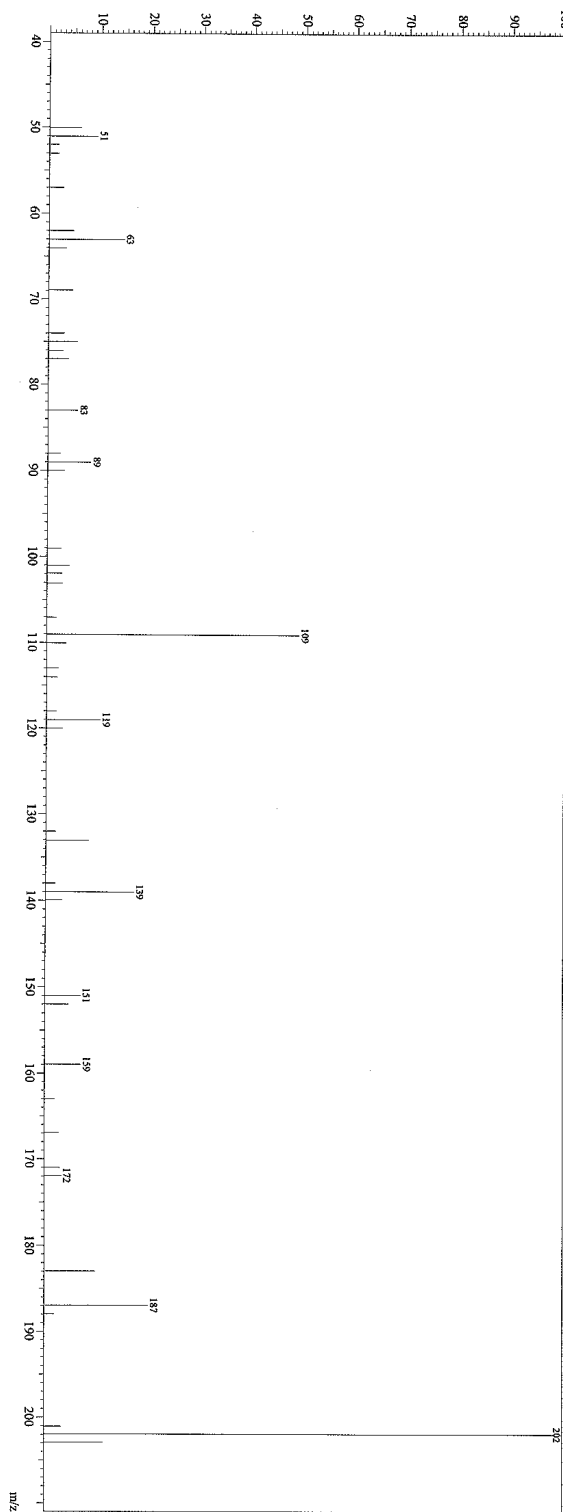
^1H NMR of 5c in CDCl_3



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



GC-MS of crude 5c

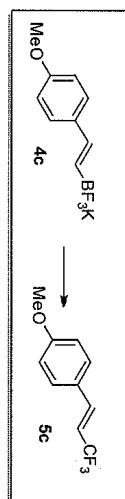


Line# 1, R-Time: 7.9 (Scan# 317)
MassPeaks: 47
RawMode: Simple 7.9(617) BasePeak: 202(54339)
BG Model: None Group 1 - Event 1

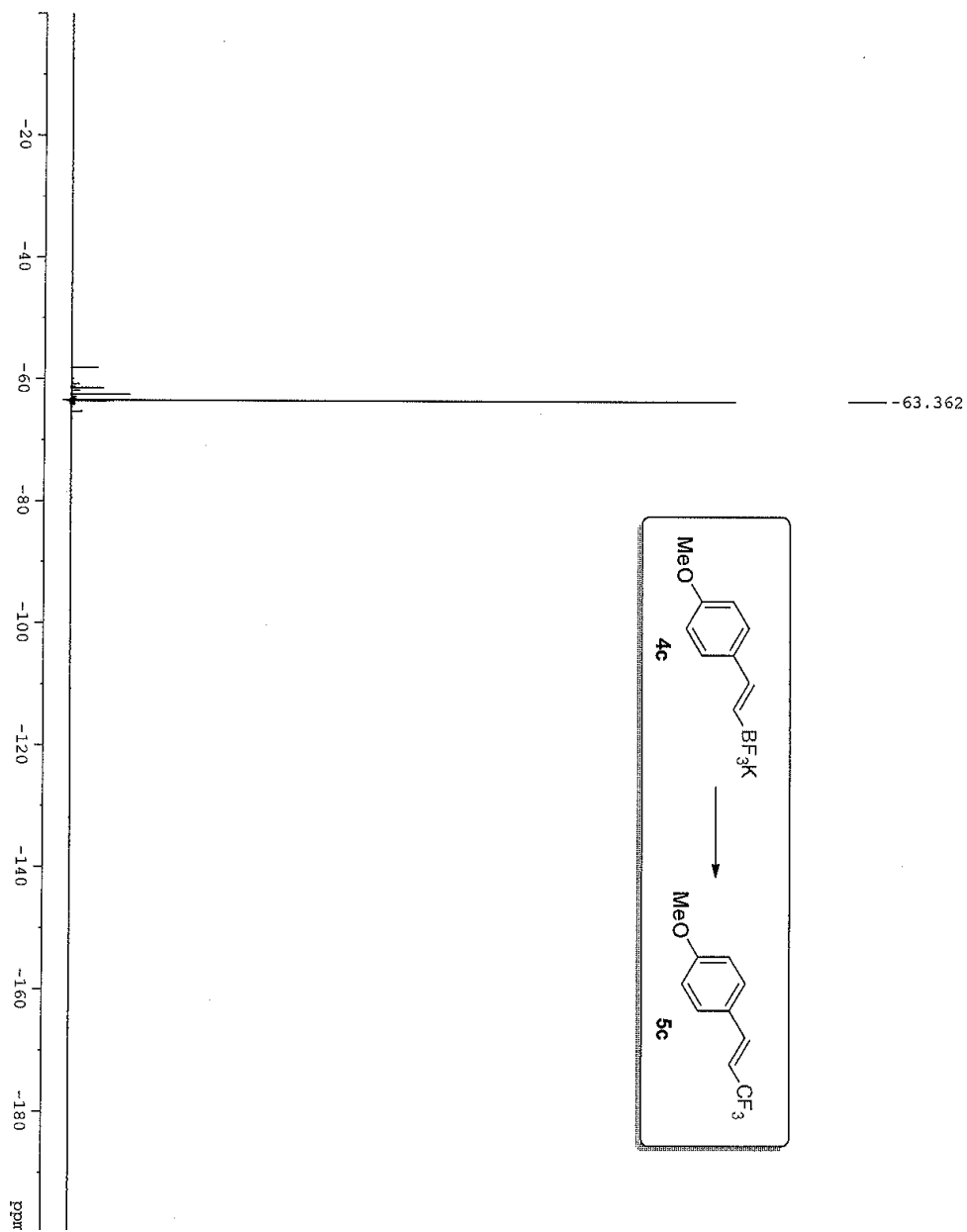
Spectrum

Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Adina
Analyzed : 8/30/2013 1:41:34 PM
Sample Type : Unknown
Level # : 1
Sample Name : SG-RBS-F-68
Sample ID : SG-RBS-F-68
IS Amount : [0] ml
Sample Amount : 1
Dilution Factor : 1
Val # : 2
Injection Volume : 5

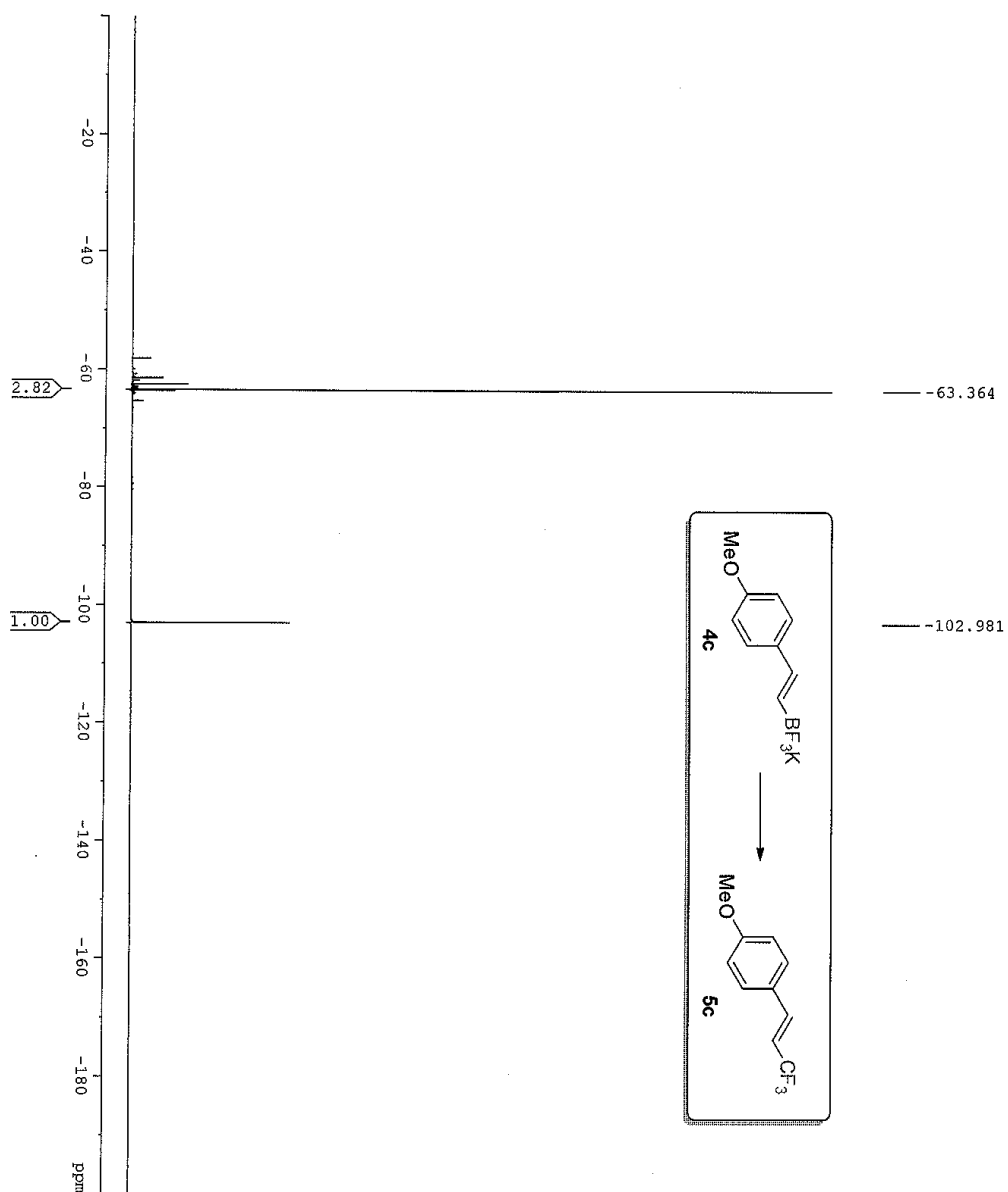
Sample Information



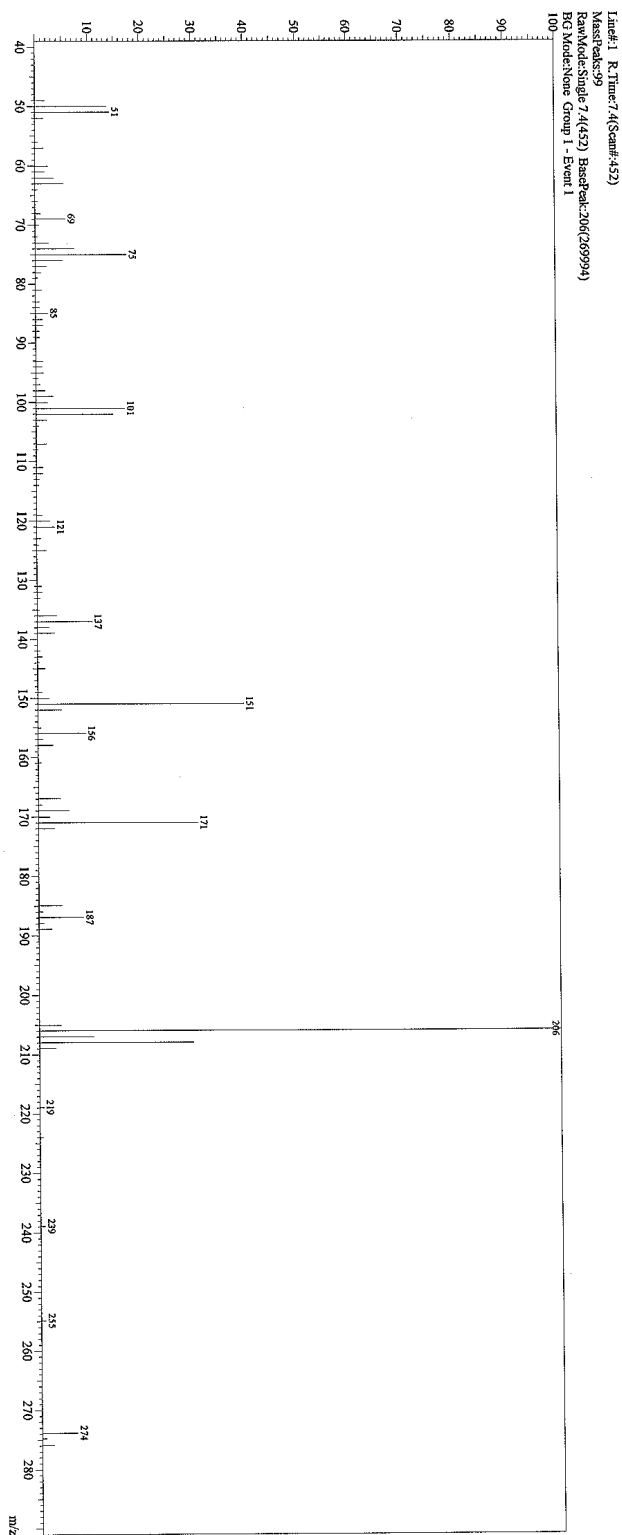
^{19}F NMR of crude **5c** in CDCl_3



^{19}F NMR yield of compound **5c** ($2.82/(1 \times 3) \times 100\% = 94\%$) in CDCl_3



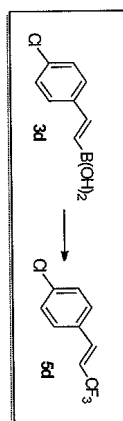
GC-MS of crude 5d



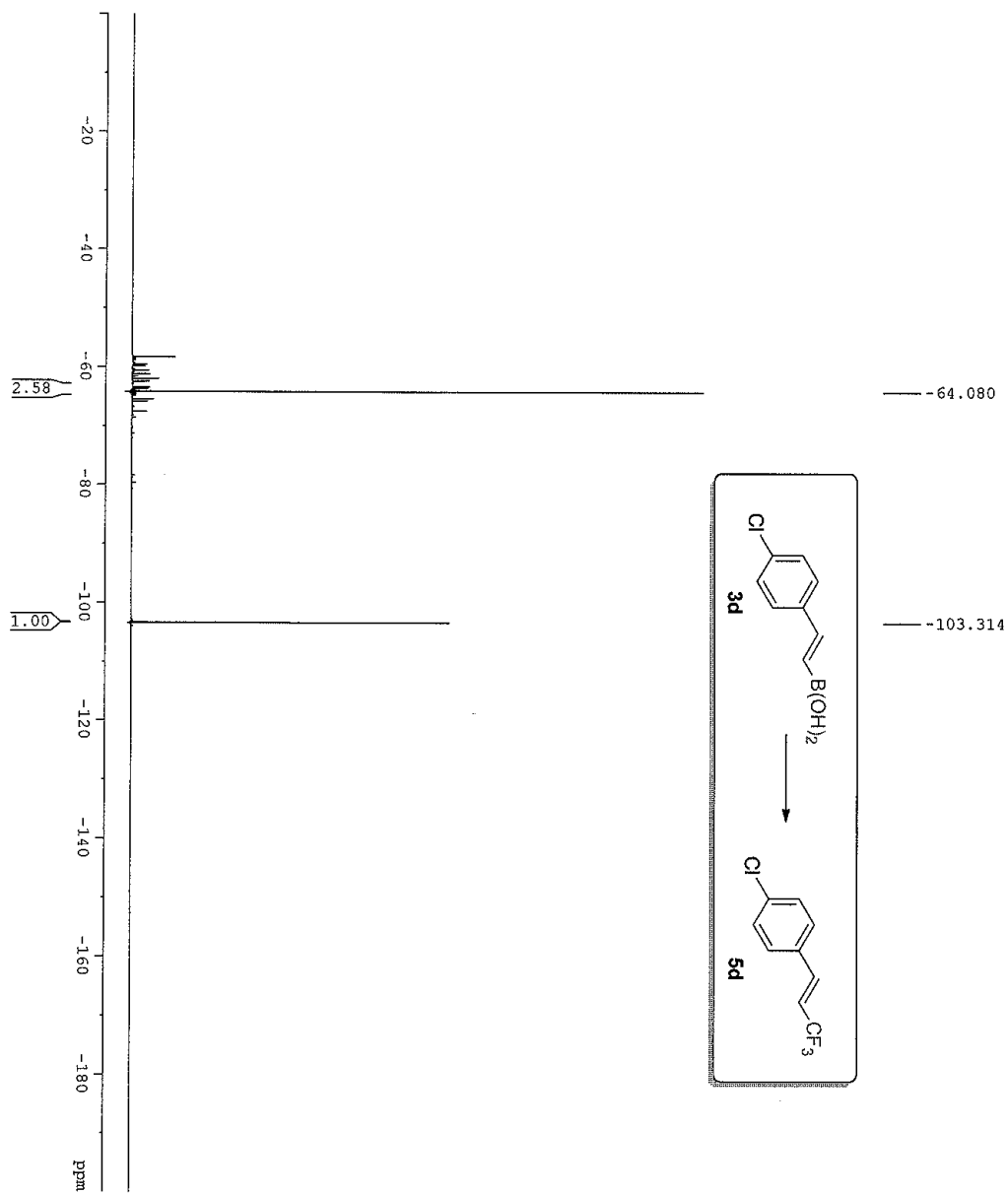
Spectrum

Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Adam
Analyzed : 7/6/2013 5:17:23 PM
Sample Name : Unknown
Sample Type : 1
Sample Name : SG-RBS-F-65-1
Sample ID : SG-RBS-F-65-1
IS Amount : [1]-1
Sample Amount : 1
Dilution Factor : 1
Val # : 2
Injection Volume : 5

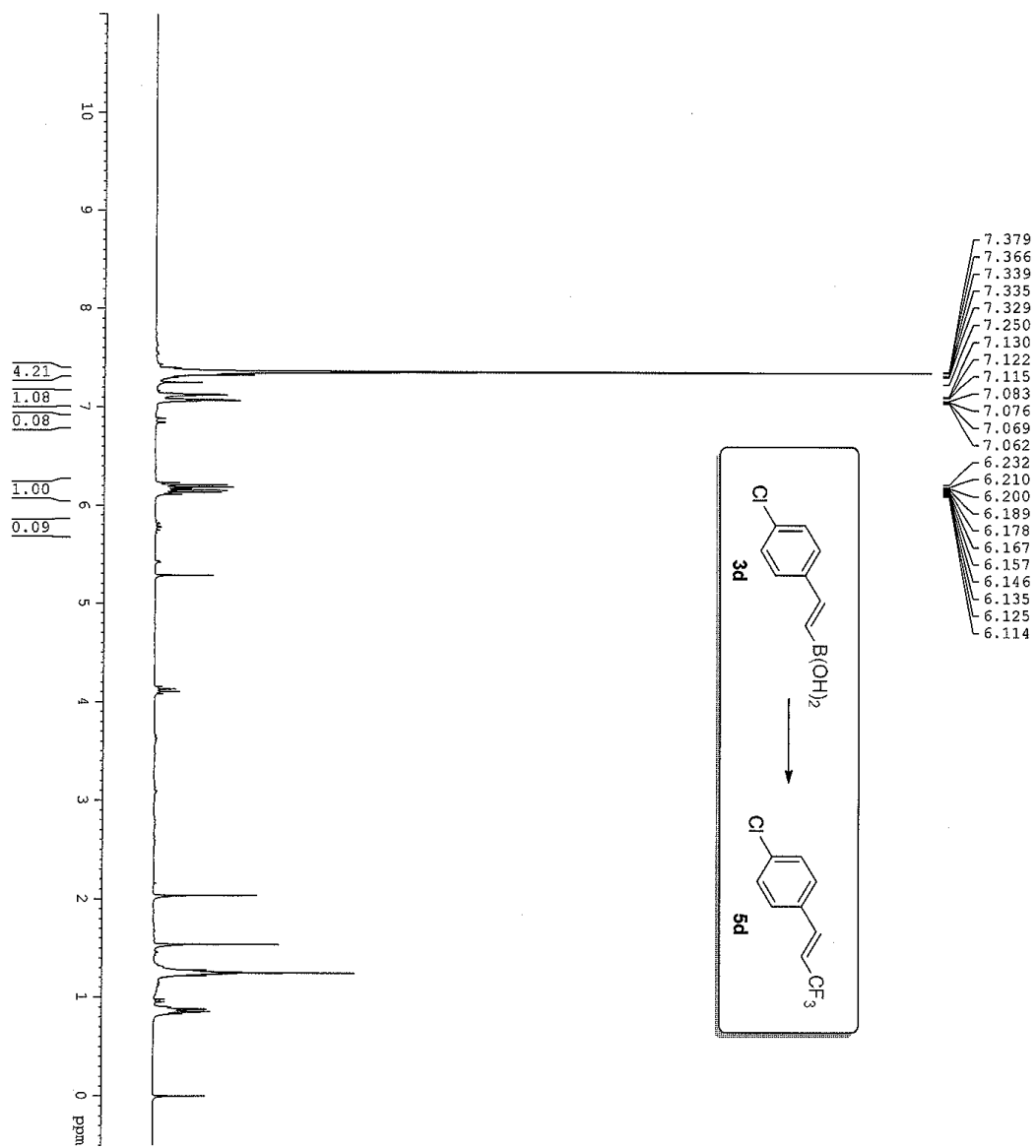
Sample Information



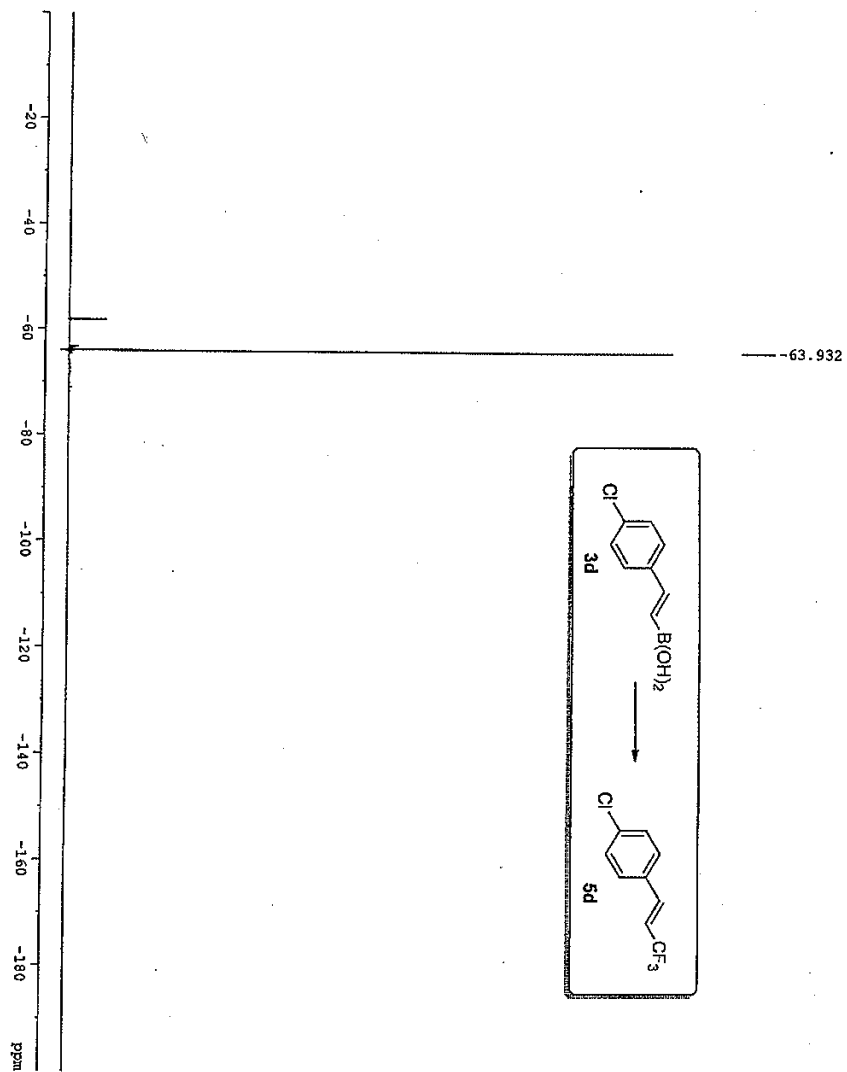
^{19}F NMR yield of compound 5d $(2.58/(1 \times 3) \times 100\% = 86\%)$ in CDCl_3



^1H NMR of 5c in CDCl_3



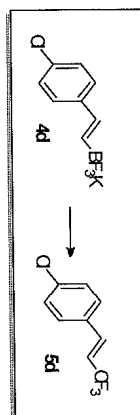
^{19}F NMR of isolated 5d in CDCl_3



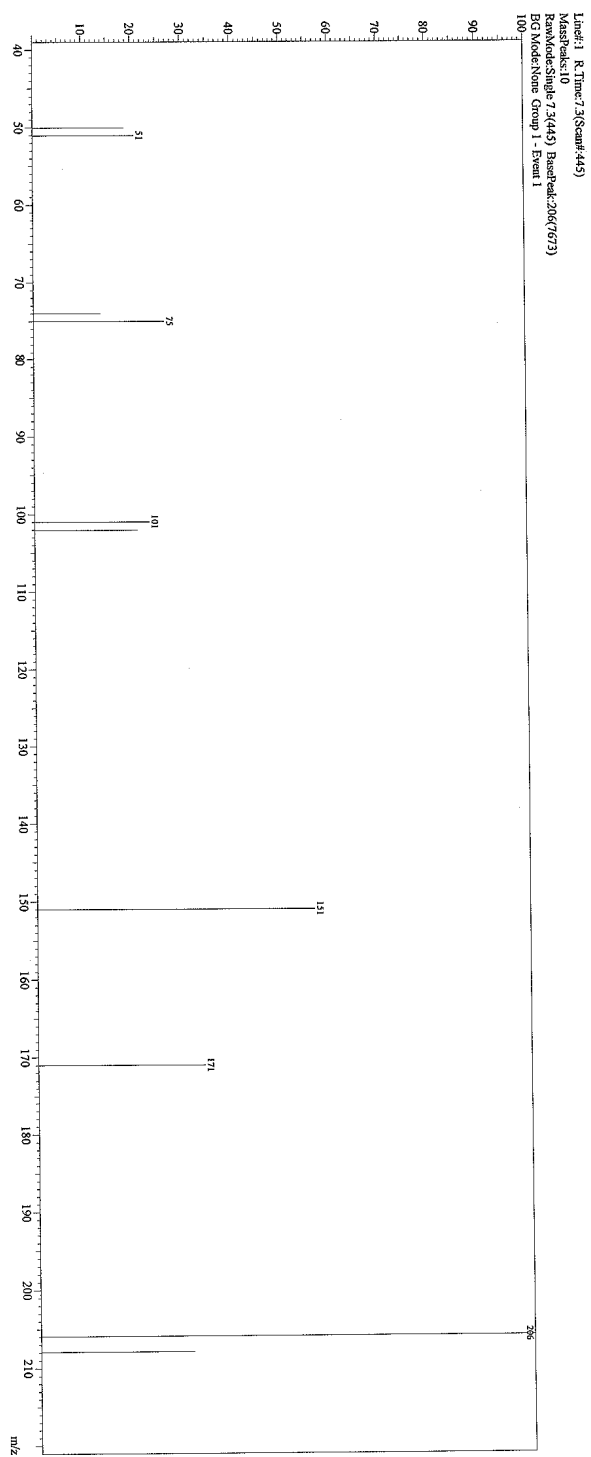
GC-MS of crude 5d

Analysis : GC-MS
Instrument : Shimadzu GC-2010
Analyzed by : Admit
Analyzed : 8/30/2013 2:16:48 PM
Sample Type : Unknown
Level # :
Sample Name : GC-RIS-F-69
Sample ID : GC-RIS-F-69
Injection : 11-1
Sample Amount : 1
Dilution Factor : 1
Val # : 3
Injection Volume : 5

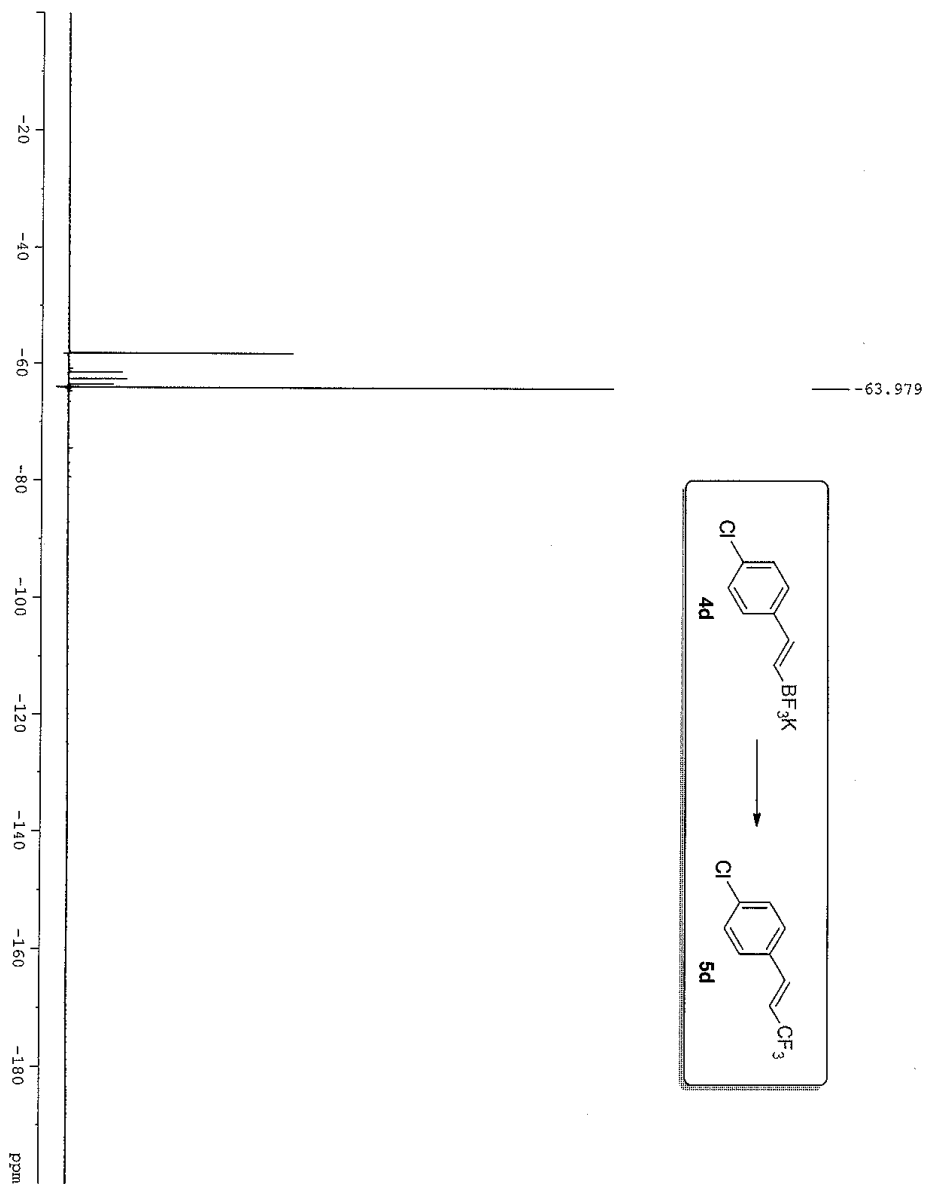
Sample Information



Spectrum



^{19}F NMR of crude 5d in CDCl_3



^{19}F NMR yield of compound 5d $(2.22/(1 \times 3)) \times 100\% = 74\%$ in CDCl_3

