

Supporting Information for

**Direct Intermolecular Three-Component Aminotrifluoromethylation
of Styrenes by Visible Light Photoredox Catalysis**

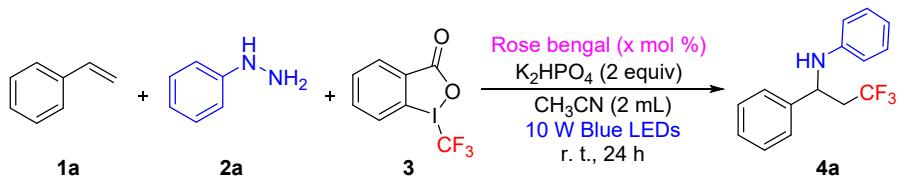
Lvyin Zheng,*‡ Liuhuan Cai,‡ Xiaoya Zhuo, Lei Deng, Yingying Wu,
Bening Yang, Yihan Wang and Wei Guo*

Key Laboratory of Organo-Pharmaceutical Chemistry of Jiangxi Province, Gannan Normal
University, Ganzhou 341000, China
Fax: (+86) 0797-8393536; *E-mail: zhenglvyin@126.com; guoweigw@126.com

Table of Contents	Pages
1. Optimization of the Reaction Conditions.....	S2-S5
2. GC-MS of 4p.....	S6
3. GC-MS of Intermediate 8.....	S7
4. Fluorescence Quenching Experiments.....	S8
5. Cyclic Voltammetry (CV) Experiments.....	S9
6. Light On/off Experiments.....	S10
7. Characterization Data.....	S11-28
8. NMR Spectra.....	S29-S73

1. Optimization of the Reaction Conditions

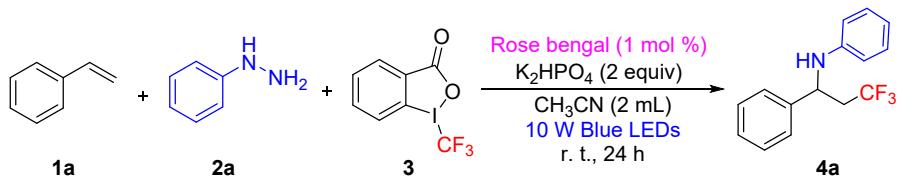
Table S1. The Effect of the Amount of Rose bengal for 4a^a



entry	Rose bengal (x mol %)	yield (%)
1	1	62
2	2	58
3	3	57
4	4	57

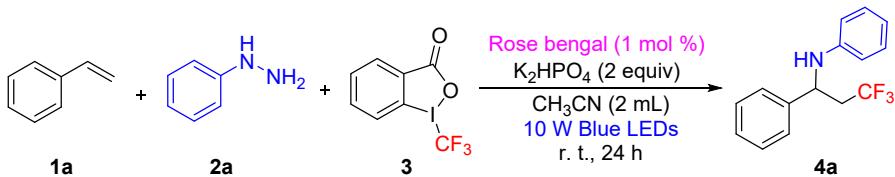
^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), **3** (0.3 mmol), K₂HPO₄ (2 equiv), and Rose bengal (x mol %) in CH₃CN (2 mL), under a 10 W blue LEDs irradiation (465 nm) at room temperature for 24 h in the open air. Isolated yields based on **1a**.

Table S2. The Effect of the Amount of 2a for 4a^a



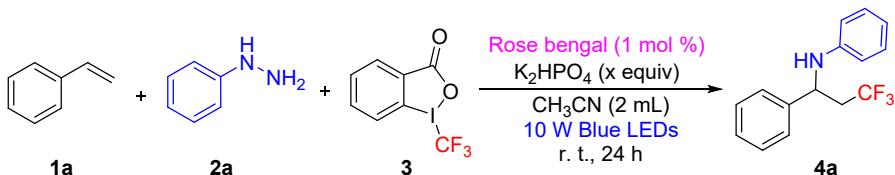
entry	2a (x mmol)	yield (%)
1	0.10	28
2	0.15	33
3	0.20	42
4	0.30	62

^aReaction conditions: **1a** (0.1 mmol), **2a** (x mmol), **3** (0.3 mmol), K₂HPO₄ (2 equiv), and Rose bengal (1 mol %) in CH₃CN (2 mL), under a 10 W blue LEDs irradiation (465 nm) at room temperature for 24 h in the open air. Isolated yields based on **1a**.

Table S3. The Effect of the Amount of 3 for 4a^a

entry	3 (x mmol)	yield (%)
1	0.10	23
2	0.20	50
3	0.30	62
4	0.40	63

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), **3** (x mmol), K₂HPO₄ (2 equiv), and Rose bengal (1 mol %) in CH₃CN (2 mL), under a 10 W blue LEDs irradiation (465 nm) at room temperature for 24 h in the open air. Isolated yields based on **1a**.

Table S4. The Effect of the Amount of K₂HPO₄ for 4a^a

entry	K ₂ HPO ₄ (x equiv)	yield (%)
1	1.0	40
2	1.5	58
3	2.0	62
4	3.0	59

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), **3** (0.3 mmol), K₂HPO₄ (x equiv), and Rose bengal (1 mol %) in CH₃CN (2 mL), under a 10 W blue LEDs irradiation (465 nm) at room temperature for 24 h in the open air. Isolated yields based on **1a**.

Table S5. The Effect of Reaction Temperature for 4a^a

entry	T (°C)	yield (%)
1	25	62
2	40	60
3	60	51
4	80	39

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), **3** (0.3 mmol), K₂HPO₄ (2 equiv), and Rose bengal (1 mol %) in CH₃CN (2 mL), under a 10 W blue LEDs irradiation (465 nm) for 24 h in the open air. Isolated yields based on **1a**.

Table S6. The Effect of Light Sources for 4a^a

entry	light sources (10 W)	yield (%)
1	UV LEDs (385 nm)	25
2	Blue LEDs (440 nm)	34
3	Blue LEDs (465 nm)	62
4	Green LEDs (550 nm)	23
5	White LEDs (6000k)	20

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), **3** (0.3 mmol), K₂HPO₄ (2 equiv), and Rose bengal (1 mol %) in CH₃CN (2 mL), under light irradiation for 24 h in the open air. Isolated yields based on **1a**.

Table S7. The Effect of Reaction Time for 4a^a

1a + **2a** + **3** → **4a**

 Rose bengal (1 mol %)
 K₂HPO₄ (2 equiv)
 CH₃CN (2 mL)
 10 W Blue LEDs
 r. t.

entry	reaction time (h)	yield (%)
1	12	49
2	18	56
3	24	62
4	36	60
5	48	58

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), **3** (0.3 mmol), K₂HPO₄ (2 equiv), and Rose bengal (1 mol %) in CH₃CN (2 mL), under a 10 W blue LEDs irradiation (465 nm) at room temperature in the open air. Isolated yields based on **1a**.

Table S8. Screening Reaction Conditions for 7a^a

1a + **2a** + **6** → **7a**

 photocatalyst (1 mol %)
 base (2 equiv)
 CH₃CN (2 mL)
 10 W Blue LEDs
 r. t.

entry	photocatalyst (1 mol %)	base (2 equiv)	yield (%)
1	Rose Bengal	K ₂ HPO ₄	0
2	Eosin Y	K ₂ HPO ₄	0
3	<i>fac</i> -Ir(ppy) ₃	K ₂ HPO ₄	trace
4	Ru(phen) ₃ Cl ₂	K ₂ HPO ₄	50%
5	Ru(phen) ₃ Cl ₂	DBU	30%
6	Ru(phen) ₃ Cl ₂	NEt ₃	28%
7	Ru(phen) ₃ Cl ₂	K ₂ CO ₃	40%
8	Ru(phen) ₃ Cl ₂	K ₃ PO ₄	45%

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), **6** (0.3 mmol), base (2 equiv), and photocatalyst (1 mol %) in CH₃CN (2 mL), under a 10 W blue LEDs irradiation (465 nm) at room temperature for 24 h in the open air. Isolated yields based on **1a**.

2. GC-MS of 4p

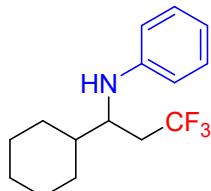
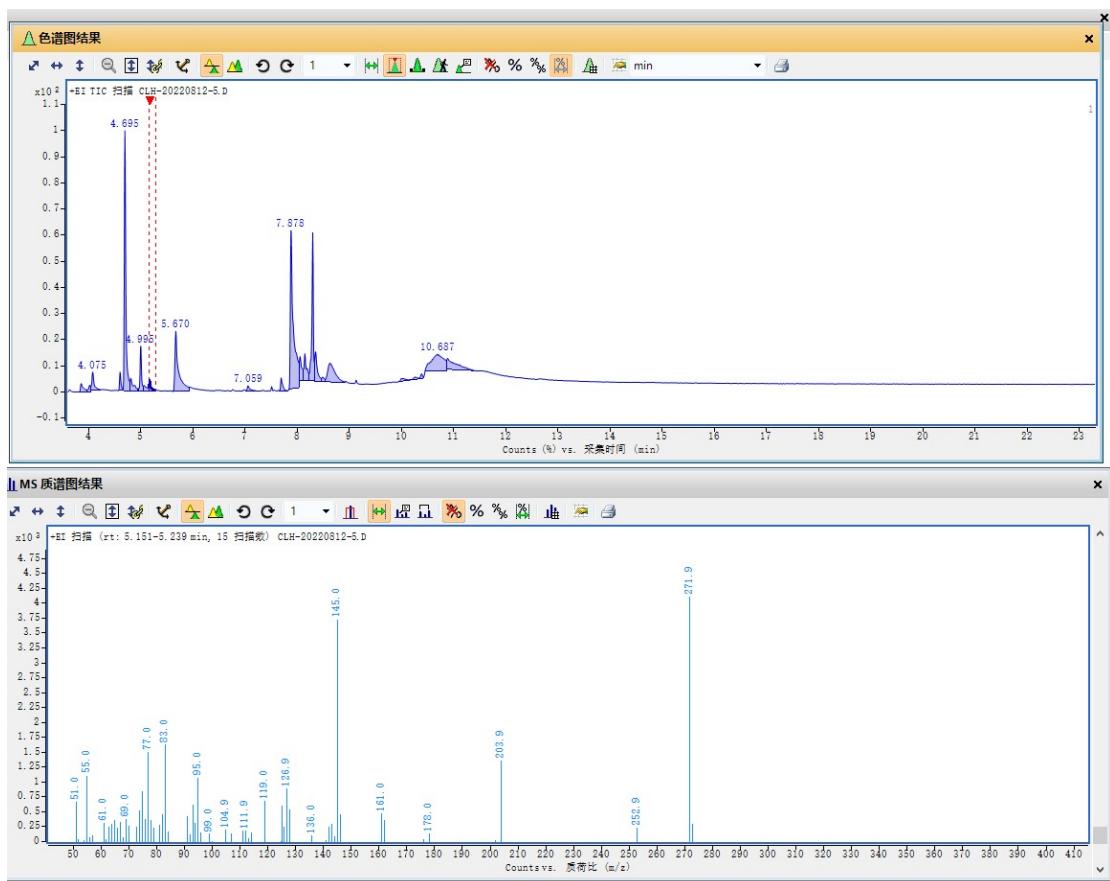


Figure S1: GC-MS of 4p

The retention time: 5.151 min; MS (EI, 70 eV) m/z : 271, 252, 203, 178, 145.

3. GC-MS of Intermediate 8

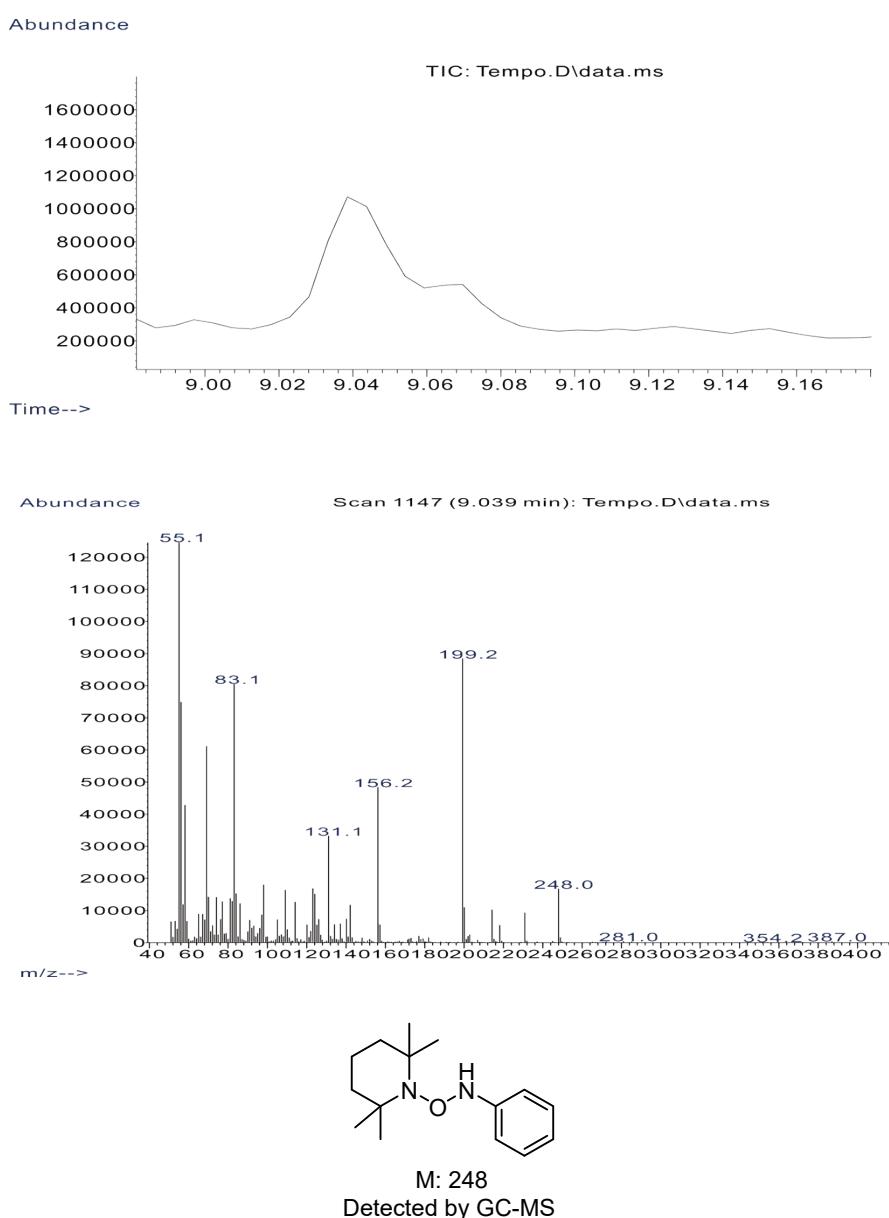


Figure S2: GC-MS of intermediate 8

The retention time: 9.039 min; MS (EI, 70 eV) m/z : 248, 199, 156, 131, 83.

4. Fluorescence Quenching Experiments

Quenched by **2a**: For each quenching experiment, the emission intensity of photocatalyst **Rose bengal** (1×10^{-5} M in THF, $\lambda_{\text{ex}} = 557$ nm, $\lambda_{\text{em}} = 578$ nm) with different concentration of quencher **Rose bengal** (0, 1.0, 2.0, 3.0, 4.0, 5.0 mM) was collected. As shown in Figure S2, compound **2a** was capable of quenching the excited state of photocatalyst **Rose bengal**.

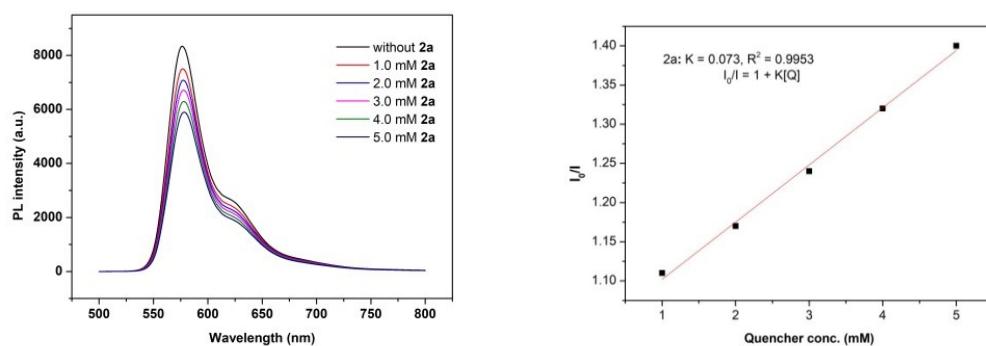


Figure S3 The Fluorescence Emission Spectra of a Solution of **Rose bengal** in THF Containing Different Concentration of Compound **2a** and Stern-Volmer Graph

Quenched by compound **3**: For each quenching experiment, the emission intensity of photocatalyst **Rose bengal** (1×10^{-5} M in THF, $\lambda_{\text{ex}} = 557$ nm, $\lambda_{\text{em}} = 578$ nm) with different concentration of quencher **3** (0, 1.0, 2.0, 3.0, 4.0, 5.0 mM) was collected. As shown in Figure S3, compound **3** was capable of quenching the excited state of photocatalyst **Rose bengal**.

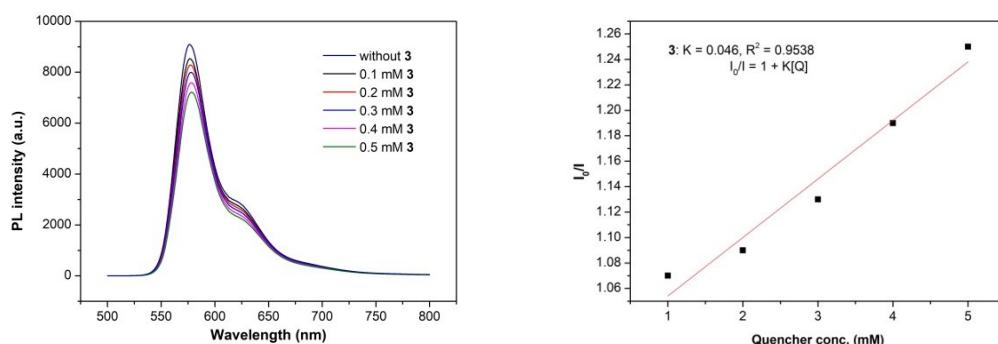


Figure S4 The Fluorescence Emission Spectra of a Solution of **PC 3** in THF Containing Different Concentration of Compound **4** and Stern-Volmer Graph

5. Cyclic Voltammetry (CV) Experiments

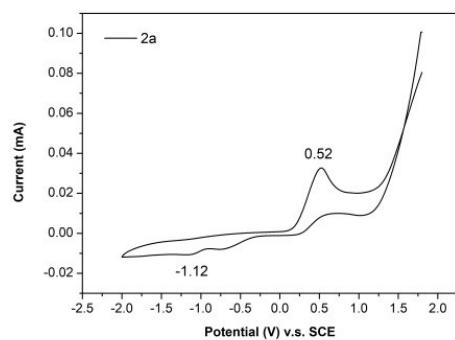


Figure S5 Cyclic Voltammogram of Compound **2a** in CH_3CN at 100 mV/s (v.s. SCE)

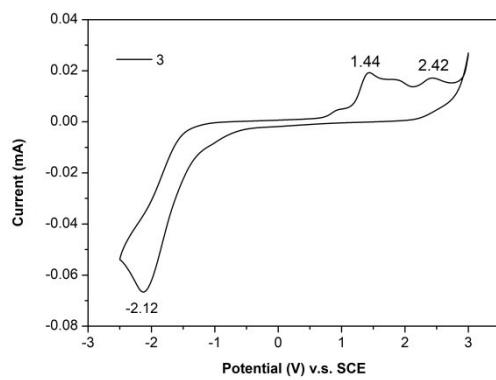


Figure S6 Cyclic Voltammogram of Compound **3** in CH_3CN at 100 mV/s (v.s. SCE)

6. Light On/off Experiments

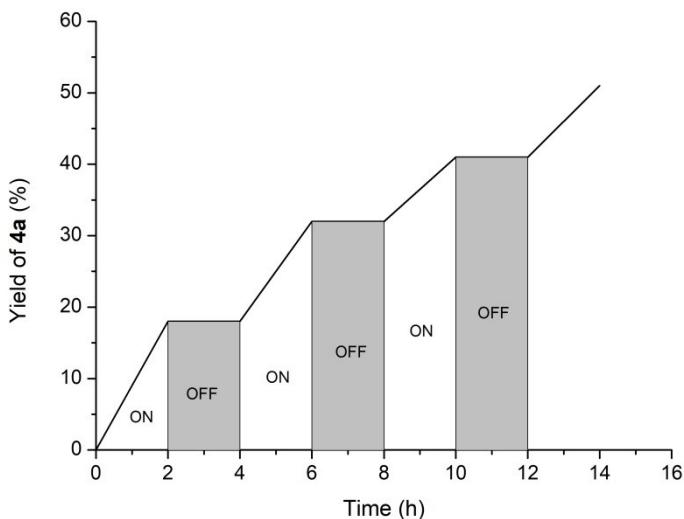
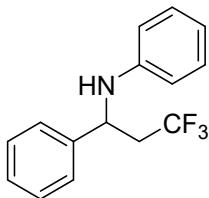


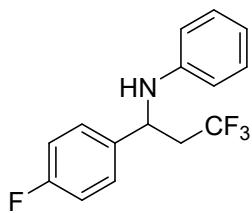
Figure S7 Light On/off Experiments

The procedures for Light On/off experiments: To a mixture of styrene **1a** (0.1 mmol), phenylhydrazine **2a** (0.3 mmol), Togni's reagent **3** (0.3 mmol), Rose bengal (1 mol %), and CH₃CN (2 mL) were successively added into a quartz reaction tube with a stir bar. The reaction mixture was separately stirred and irradiated by 10 W blue LEDs (465 nm) at room temperature for 2 h, 4 h, 6 h and 8 h. The desired product **4a** was isolated in 18%, 32%, 41% and 51%, respectively. Additionally, the reaction mixture was stirred and irradiated by 10 W blue LEDs (465 nm) at room temperature for 2 h, then the reaction mixture was continuously stirred in the dark for 2 h, the corresponding product was also obtained in 18% yield. Additionally, when the reaction mixture was stirred and irradiated by 10 W blue LEDs (465 nm) at room temperature for 4 h, then the reaction mixture was continuously stirred in the dark for 2 h, the corresponding product **4a** was obtained in 32% yield. Additionally, when the reaction mixture was stirred and irradiated by 10 W blue LEDs (465 nm) at room temperature for 6 h, then the reaction mixture was continuously stirred in the dark for 2 h, the corresponding product **4a** was still obtained in 41% yield. Additionally, when the reaction mixture was stirred and irradiated by 10 W blue LEDs (465 nm) at room temperature for 8 h, the corresponding product **4a** was still obtained in 51% yield.

7. Characterization Data

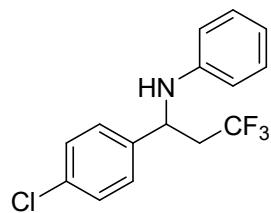


N-(3,3,3-Trifluoro-1-phenylpropyl)aniline (**4a**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 62% yield (16.5 mg, 0.06 mmol); IR (KBr, cm⁻¹) 3030, 2926, 2855, 1603, 1506, 1455, 1318, 1202, 1144, 1031, 905, 866, 750; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.42-7.35 (m, 4H), 7.32-7.28 (m, 1H), 7.14 (t, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 4.75 (dd, *J* = 4.0 Hz, 8.0 Hz, 1H), 4.18 (s, 1H), 2.73-2.55 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 146.3, 141.8, 129.2, 129.1, 127.9, 126.2, 125.8 (q, *J* = 276.0 Hz), 118.3, 113.7, 53.2 (q, *J* = 3.0 Hz), 41.8 (q, *J* = 27.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -63.32; MS (EI, 70 eV) *m/z* 265, 224, 204, 182, 151, 133; HRMS (ESI) *m/z* [M + H]⁺ calcd for C₁₅H₁₅F₃N 266.1151, found 266.1157.

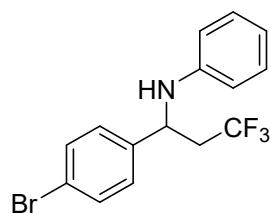


N-(3,3,3-Trifluoro-1-(4-fluorophenyl)propyl)aniline (**4b**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 48% yield (13.6 mg, 0.05 mmol); IR (KBr, cm⁻¹) 3058, 2926, 2855, 1603, 1509, 1432, 1316, 1260, 1201, 1145, 1028, 908, 826; ¹H NMR (400 MHz, CDCl₃) δ ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.38-7.32 (m, 2H), 7.12 (t, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 8.0 Hz, 1H), 6.50 (d,

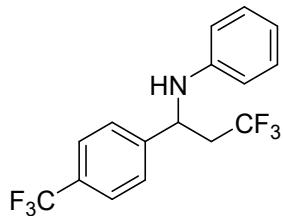
J = 8.0 Hz, 2H), 4.68 (dd, *J* = 4.0 Hz, 8.0 Hz, 1H), 4.15 (s, 1H), 2.67-2.48 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 162.3 (d, *J* = 245.0 Hz), 146.1, 137.4 (d, *J* = 4.0 Hz), 129.3, 127.8 (d, *J* = 8.0 Hz), 125.6 (q, *J* = 276.0 Hz), 118.5, 116.0 (d, *J* = 21.0 Hz), 113.7, 52.6 (q, *J* = 2.0 Hz), 41.9 (q, *J* = 26.0 Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.22, -114.37; MS (EI, 70 eV) *m/z* 283, 200, 191, 151, 127, 104; HRMS (ESI) *m/z* [M + H]⁺ calcd for $\text{C}_{15}\text{H}_{14}\text{F}_4\text{N}$ 284.1057, found 284.1064.



N-(1-(4-Chlorophenyl)-3,3,3-trifluoropropyl)aniline (**4c**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 50% (15.0 mg, 0.05 mmol); IR (KBr, cm^{-1}) 3032, 2956, 2925, 2854, 1673, 1603, 1493, 1379, 1137, 1017, 969, 868, 750; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.35-7.34 (m, 4H), 7.12 (t, *J* = 8.0 Hz, 2H), 6.73 (t, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 2H), 4.70 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 2.66-2.51 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 146.0, 140.2, 133.6, 129.3, 129.3, 127.6, 125.6 (q, *J* = 276.0 Hz), 118.6, 113.7, 52.7 (q, *J* = 3.0 Hz), 41.8 (q, *J* = 27.0 Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.20; MS (EI, 70 eV) *m/z* 299, 248, 231, 216, 180, 151; HRMS (ESI) *m/z* [M + H]⁺ calcd for $\text{C}_{15}\text{H}_{14}\text{ClF}_3\text{N}$ 300.0761, found 300.0765.

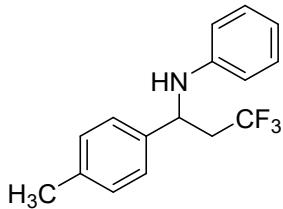


N-(1-(4-Bromophenyl)-3,3,3-trifluoropropyl)aniline (**4d**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 70% (24.1 mg, 0.07 mmol); IR (KBr, cm^{-1}) 3043, 2925, 2854, 1735, 1619, 1533, 1457, 1323, 1202, 1114, 1033, 972, 829, 700; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.40-7.39 (m, 1H), 7.32-7.28 (m, 3H), 7.13 (t, J = 8.0 Hz, 2H), 6.74 (t, J = 8.0 Hz, 1H), 6.54 (d, J = 8.0 Hz, 2H), 4.69 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 2.68-2.54 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 146.0, 140.8, 132.2, 129.3, 127.9, 125.6 (q, J = 276.0 Hz), 121.7, 118.6, 113.7, 52.7 (q, J = 3.0 Hz), 41.8 (q, J = 27.0 Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.20; MS (EI, 70 eV) m/z 343, 260, 251, 187, 151, 132; HRMS (ESI) m/z [M + H] $^+$ calcd for $\text{C}_{15}\text{H}_{14}\text{BrF}_3\text{N}$ 344.0256, found 344.0242.

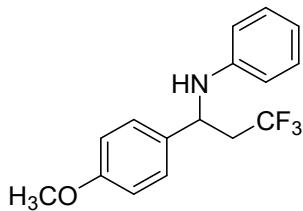


N-(3,3,3-Trifluoro-1-(4-(trifluoromethyl)phenyl)propyl)aniline (**4e**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 51% (17.0 mg, 0.05 mmol); IR (KBr, cm^{-1}) 3048, 2926, 2851, 1724, 1603, 1500, 1420, 1325, 1261, 1131, 1081, 913, 824, 750; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.63 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 8.0 Hz, 2H), 6.74 (t, J = 8.0 Hz, 1H), 6.52 (d, J = 8 Hz, 2H), 4.81 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 4.22 (s, 1H), 2.69-2.52 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 145.8, 130.3 (d, J = 32.0 Hz), 129.8, 129.3, 126.1 (q, J = 4.0 Hz) (CF_3), 125.6 (q, J = 276.0 Hz) (CF_3), 125.3, 122.6, 118.7, 113.7, 52.9 (q, J = 3.0 Hz), 41.8 (q, J = 8.0 Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -62.49, -63.17; MS

(EI, 70 eV) m/z 333, 314, 292, 250, 173, 145; HRMS (ESI) m/z [M + H]⁺ calcd for C₁₆H₁₄F₆N 334.1025, found 334.1014.

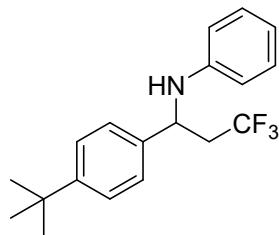


N-(3,3,3-Trifluoro-1-(*p*-tolyl)propyl)aniline (**4f**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 56% (15.8 mg, 0.06 mmol); IR (KBr, cm⁻¹) 3051, 2925, 2855, 1603, 1502, 1460, 1377, 1261, 1138, 1084, 969, 812, 749, 692; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.28-7.27 (m, 2H), 7.17-7.10 (m, 4H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 2H), 4.70 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 4.15 (s, 1H), 2.65-2.54 (m, 2H), 2.33 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 146.4, 138.7, 137.6, 129.7, 129.2, 126.1, 125.8 (d, *J* = 276.0 Hz), 118.2, 113.6, 52.9 (q, *J* = 3.0 Hz), 41.9 (q, *J* = 27.0 Hz), 21.1; ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -63.27; MS (EI, 70 eV) m/z 279, 196, 187, 151, 123, 104; HRMS (ESI) m/z [M + H]⁺ calcd for C₁₆H₁₇F₃N 280.1308, found 280.1319.

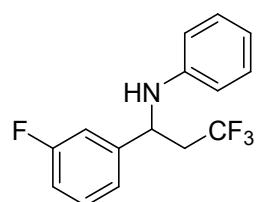


N-(3,3,3-Trifluoro-1-(4-methoxyphenyl)propyl)aniline (**4g**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 58% (17.2 mg, 0.06 mmol); IR (KBr, cm⁻¹) 3035, 2925, 2869, 1603, 1511, 1461, 1378, 1247, 1134, 1033, 908, 826, 751; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 8.0 Hz, 2H),

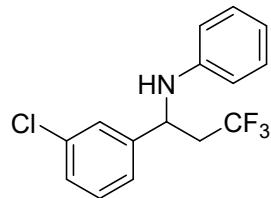
6.88 (d, $J = 8.0$ Hz, 2H), 6.71 (t, $J = 8.0$ Hz, 1H), 6.55 (d, $J = 8.0$ Hz, 2H), 4.69 (dd, $J = 8.0$ Hz, 4.0 Hz, 1H), 4.13 (s, 1H), 3.79 (s, 3H), 2.70-2.49 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 159.2, 146.4, 133.7, 129.2, 127.3, 125.8 (q, $J = 276.0$ Hz), 118.2, 114.4, 113.7, 55.3, 52.6 (q, $J = 3.0$ Hz), 41.8 (q, $J = 27.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.24; MS (EI, 70 eV) m/z 295, 212, 203, 168, 139, 104, 93; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{NO}$ 296.1257, found 296.1249.



N-(1-(4-(*Tert*-butyl)phenyl)-3,3,3-trifluoropropyl)aniline (**4h**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 53% (17.0 mg, 0.05 mmol); IR (KBr, cm^{-1}) 3058, 2962, 2863, 1603, 1505, 1431, 1319, 1210, 1137, 1625, 902, 876, 750; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.37 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.14 (t, $J = 8.0$ Hz, 2H), 6.71 (t, $J = 8.0$ Hz, 1H), 6.57 (d, $J = 8.0$ Hz, 2H), 4.72 (dd, $J = 8.0$ Hz, 4.0 Hz, 1H), 4.14 (s, 1H), 2.68-2.54 (m, 2H), 1.31 (s, 9H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 150.8, 146.4, 138.7, 129.2, 125.9, 125.8 (q, $J = 276.0$ Hz), 118.1, 113.6, 52.7 (q, $J = 3.0$ Hz), 41.7 (q, $J = 27.0$ Hz), 34.5, 31.3; ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.33; MS (EI, 70 eV) m/z 321, 238, 229, 214, 173, 104; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{19}\text{H}_{23}\text{F}_3\text{N}$ 322.1777, found 322.1748.

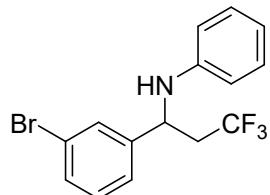


N-(3,3,3-Trifluoro-1-(3-fluorophenyl)propyl)aniline (**4i**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 48% (13.6 mg, 0.05 mmol); IR (KBr, cm^{-1}) 3039, 2923, 2854, 1601, 1513, 1450, 1315, 1247, 1135, 1079, 970, 880, 750; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.35-7.32 (m, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 8.0 Hz, 3H), 6.98 (t, J = 8.0 Hz, 1H), 6.73 (t, J = 8.0 Hz, 1H), 6.53 (d, J = 8.0 Hz, 2H), 4.72 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 4.21 (s, 1H), 2.67-2.50 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 163.3 (d, J = 246.0 Hz), 146.0, 144.6 (d, J = 7.0 Hz), 130.7 (d, J = 8.0 Hz), 129.3, 125.5 (q, J = 289.0 Hz) (CF_3), 121.8 (d, J = 3.0 Hz), 118.5, 114.9 (d, J = 21.0 Hz), 113.7, 113.2 (d, J = 22.0 Hz), 52.9 (q, J = 3.0 Hz), 41.7; ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.26, -111.86; MS (EI, 70 eV) m/z 283, 262, 242, 200, 127, 104; HRMS (ESI) m/z [M + H] $^+$ calcd for $\text{C}_{15}\text{H}_{14}\text{F}_4\text{N}$ 284.1057, found 284.1061.

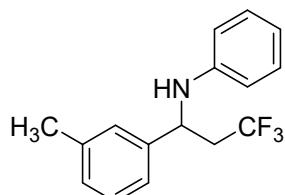


N-(1-(3-Chlorophenyl)-3,3,3-trifluoropropyl)aniline (**4j**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 52% (15.6 mg, 0.05 mmol); IR (KBr, cm^{-1}) 2925, 2855, 1602, 1499, 1379, 1260, 1139, 1081, 972, 854, 753; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.40-7.39 (m, 1H), 7.34-7.28 (m, 3H), 7.13 (t, J = 8.0 Hz, 2H), 6.74 (t, J = 8.0 Hz, 1H), 6.54 (d, J = 8.0 Hz, 2H), 4.70 (dd, J = 8.0, 4.0 Hz, 1H), 2.68-2.54 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 146.0, 144.0, 135.0, 130.4, 129.3, 128.2, 126.3, 125.6 (q, J = 277.0 Hz), 124.4, 118.6, 113.7, 52.9 (q, J = 3.0 Hz), 41.8 (q, J = 27.0 Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.26; MS (EI, 70 eV)

m/z 299, 216, 188, 151, 143, 104; HRMS (ESI) *m/z* [M + H]⁺ calcd for C₁₅H₁₄ClF₃N 300.0761, found 300.0771.

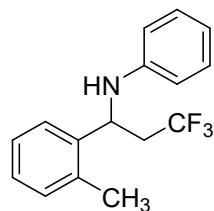


N-(1-(3-Bromophenyl)-3,3,3-trifluoropropyl)aniline (**4k**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 68% (23.3 mg, 0.07 mmol); IR (KBr, cm⁻¹) 3057, 2923, 2856, 1703, 1638, 1509, 1423, 1375, 1084, 995, 868, 747, 697; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.47 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 2H), 6.65 (t, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 2H), 4.60 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 4.08 (s, 1H), 2.59-2.40 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 146.0, 144.3, 131.1, 130.1, 129.3, 129.3, 125.6 (q, *J* = 276.0 Hz), 124.9, 123.2, 118.6, 113.7, 52.9 (q, *J* = 3.0 Hz), 41.9 (q, *J* = 27.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -63.28; MS (EI, 70 eV) *m/z* 343, 260, 189, 151, 104, 77; HRMS (ESI) *m/z* [M + H]⁺ calcd for C₁₅H₁₄BrF₃N 344.0256, found 344.0242.

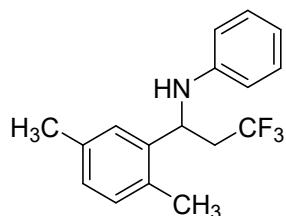


N-(3,3,3-Trifluoro-1-(m-tolyl)propyl)aniline (**4l**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 58% (16.2 mg, 0.06 mmol); IR (KBr, cm⁻¹) 3035, 2924, 2855, 1603, 1503, 1460, 1316, 1261, 1136, 1039, 910, 846, 749, 697; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.24 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.15-

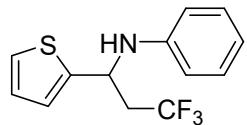
7.09 (m, 3H), 6.71 (t, J = 8.0 Hz, 1H), 6.56 (d, J = 8.0 Hz, 2H), 4.69 (q, J = 8.0 Hz, 4.0 Hz, 1H), 4.17 (s, 1H), 2.66-2.55 (m, 2H), 2.35 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 146.4, 141.8, 138.8, 129.2, 128.9, 128.7, 126.8, 125.8 (d, J = 276.0 Hz), 123.2, 118.2, 113.6, 53.2 (q, J = 3.0 Hz), 41.7 (t, J = 27.0 Hz), 21.5; ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.33; MS (EI, 70 eV) m/z 279, 196, 187, 151, 123, 104; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{N}$ 280.1308, found 280.1308.



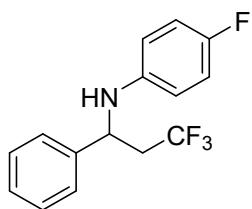
N-(3,3,3-Trifluoro-1-(*o*-tolyl)propyl)aniline (**4m**). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 57% (16.0 mg, 0.06 mmol); IR (KBr, cm^{-1}) 3035, 2926, 2855, 1603, 1504, 1432, 1318, 1213, 1135, 1096, 902, 868, 726, 692; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.45-7.43 (m, 1H), 7.21-7.16 (m, 3H), 7.12 (t, J = 8.0 Hz, 2H), 6.70 (t, J = 8.0 Hz, 1H), 6.48 (d, J = 8.0 Hz, 2H), 4.94 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 4.14 (s, 1H), 2.62-2.47 (m, 2H), 2.45 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 146.4, 139.5, 134.6, 131.1, 129.3, 127.7, 126.9, 125.9 (d, J = 276.0 Hz), 125.1, 118.1, 113.4, 49.2 (q, J = 3.0 Hz), 40.4 (q, J = 27.0 Hz), 18.9; ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.65, MS (EI, 70 eV) m/z 279, 196, 187, 165, 123, 104; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{N}$ 280.1308, found 280.1312.



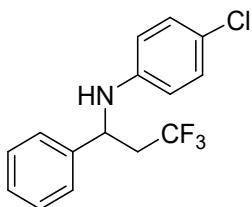
N-(1-(2,5-Dimethylphenyl)-3,3,3-trifluoropropyl)aniline (4n). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 44% (13.0 mg, 0.04 mmol); IR (KBr, cm^{-1}) 3030, 2925, 2869, 1603, 1502, 1460, 1313, 1260, 1136, 1031, 907, 806, 748, 692; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.24 (s, 1H), 7.14-7.07 (m, 3H), 6.99 (d, J = 8.0 Hz, 1H), 6.70 (t, J = 8.0 Hz, 1H), 6.49 (d, J = 8.0 Hz, 2H), 4.89 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 4.10 (s, 1H), 2.60-2.45 (m, 2H), 2.39 (s, 3H), 2.27 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 146.6, 139.4, 136.4, 131.3, 131.0, 129.3, 128.4, 125.7, 118.1, 113.3, 112.9, 49.3 (q, J = 3.0 Hz), 40.4 (q, J = 26.0 Hz), 21.2, 18.5; ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.75; MS (EI, 70 eV) m/z 293, 264, 237, 210, 185, 165; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{17}\text{H}_{19}\text{F}_3\text{N}$ 294.1464, found 294.1454.



N-(3,3,3-Trifluoro-1-(thiophen-2-yl)propyl)aniline (4o). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 56% (15.2 mg, 0.06 mmol); IR (KBr, cm^{-1}) 3038, 2923, 2852, 1735, 1603, 1504, 1432, 1310, 1258, 1133, 1033, 905, 857, 751; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.23-7.22 (m, 1H), 7.17 (t, J = 8.0 Hz, 2H), 7.04 (s, 1H), 6.97 (t, J = 8.0 Hz, 1H), 6.76 (t, J = 8.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 2H), 5.06 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 4.10 (s, 1H), 2.81-2.64 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 146.4, 145.9, 129.3, 127.1, 125.5 (q, J = 276.0 Hz) (CF_3), 124.7, 124.2, 118.8, 113.8, 49.2 (q, J = 3.0 Hz), 42.0 (q, J = 27.0 Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.35; MS (EI, 70 eV) m/z 271, 188, 179, 159, 115, 93; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{13}\text{H}_{13}\text{F}_3\text{NS}$ 272.0715, found 272.0726.

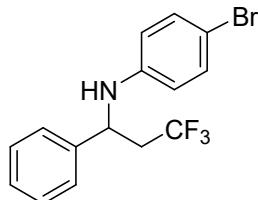


4-Fluoro-N-(3,3,3-trifluoro-1-phenylpropyl)aniline (5a). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 71% (20.1 mg, 0.07 mmol); IR (KBr, cm⁻¹) 3040, 2925, 1614, 1511, 1434, 1380, 1259, 1143, 1031, 904, 821, 701; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.37-7.28 (m, 5H), 6.81 (t, *J* = 8.0 Hz, 2H), 6.48-6.44 (m, 2H), 4.65 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 2.66-2.51 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 156.2 (d, *J* = 235.0 Hz), 142.6 (d, *J* = 2.0 Hz), 142.6, 129.1, 128.0, 126.2, 125.8 (q, *J* = 276.0 Hz), 115.7 (d, *J* = 22.0 Hz), 114.6 (d, *J* = 8.0 Hz), 53.8 (d, *J* = 3.0 Hz), 42.4 (q, *J* = 27.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -63.32, -126.92; MS (EI, 70 eV) *m/z* 283, 200, 173, 133, 122, 109; HRMS (ESI) *m/z* [M + H]⁺ calcd for C₁₅H₁₄F₄N 284.1057, found 284.1051.

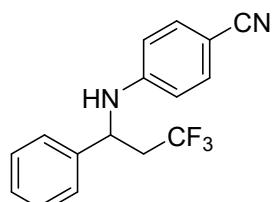


4-Chloro-N-(3,3,3-trifluoro-1-phenylpropyl)aniline (5b). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 40% (12.0 mg, 0.04 mmol); IR (KBr, cm⁻¹) 3033, 2924, 2862, 1601, 1501, 1454, 1381, 1258, 1139, 1031, 905, 816, 701; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.39-7.35 (m, 4H), 7.33-7.27 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.46 (d, *J* = 8.0 Hz, 2H), 4.68 (t, *J* = 8.0 Hz, 1H), 4.21 (s, 1H), 2.66-2.56 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 144.8, 144.2, 129.1, 129.1, 128.1,

126.1, 125.7 (q, $J = 276.0$ Hz), 123.0, 114.8, 53.3 (q, $J = 3.0$ Hz), 41.8 (q, $J = 27.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.37; MS (EI, 70 eV) m/z 299, 216, 188, 151, 143, 104; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{15}\text{H}_{14}\text{ClF}_3\text{N}$ 300.0761, found 300.0769.

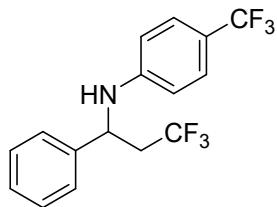


4-Bromo-N-(3,3,3-trifluoro-1-phenylpropyl)aniline (5c). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 75% (26.0 mg, 0.08 mmol); IR (KBr, cm^{-1}) 3033, 2924, 1595, 1497, 1380, 1258, 1146, 1075, 910, 814, 701, 608, 504; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.40-7.34 (m, 4H), 7.33-7.27 (m, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 6.42 (d, $J = 8.0$ Hz, 2H), 4.68 (t, $J = 8.0$ Hz, 1H), 4.21 (s, 1H), 2.69-2.53 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 145.2, 141.2, 132.0, 129.1, 128.1, 126.1, 125.7 (q, $J = 276.0$ Hz), 115.3, 110.1, 53.2 (q, $J = 3.0$ Hz), 41.8 (q, $J = 27.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.37; MS (EI, 70 eV) m/z 343, 260, 189, 151, 104, 77; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{15}\text{H}_{14}\text{BrF}_3\text{N}$ 344.0256, found 344.0268.

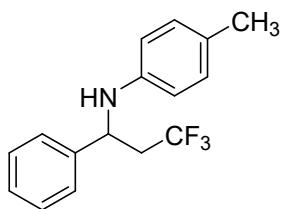


4-((3,3,3-Trifluoro-1-phenylpropyl)amino)benzonitrile (5d). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 78% (23.0 mg, 0.08 mmol); IR (KBr,

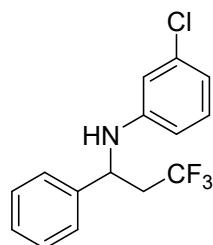
cm^{-1}) 3030, 2926, 2853, 2215, 1606, 1525, 1454, 1337, 1033, 910, 825, 701; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.45-7.29 (m, 7H), 6.53 (d, J = 8.0 Hz, 2H), 4.80-4.75 (m, 2H), 2.69-2.59 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 149.5, 140.3, 133.7, 129.3, 128.4, 125.9, 125.5 (q, J = 276.0 Hz), 120.0, 113.3, 100.2, 52.6 (q, J = 3.0 Hz), 41.7 (q, J = 27.0 Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.36; MS (EI, 70 eV) m/z 290, 207, 173, 109, 77; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}_2$ 291.1104, found 291.1106.



N-(3,3,3-Trifluoro-1-phenylpropyl)-4-(trifluoromethyl)aniline (5e). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 64% (21.3 mg, 0.06 mmol); IR (KBr, cm^{-1}) 3400, 3030, 2926, 2853, 1738, 1619, 1532, 1491, 1324, 1203, 1113, 1068, 938, 826, 701; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.40-7.29 (m, 7H), 6.56 (d, J = 8.0 Hz, 2H), 4.77 (t, J = 8.0 Hz, 1H), 4.50 (s, 1H), 2.68-2.59 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 148.7, 140.8, 129.2, 128.2, 126.6 (q, J = 4.0 Hz), 126.5 (q, J = 86.0 Hz), 126.0, 123.8 (d, J = 78.0 Hz), 119.9 (d, J = 33.0 Hz), 112.9, 52.9 (q, J = 3.0 Hz), 41.8 (q, J = 27.0 Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -61.20, -63.35; MS (EI, 70 eV) m/z 333, 314, 292, 250, 173, 109; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{16}\text{H}_{14}\text{F}_6\text{N}$ 334.1025, found 334.1013.

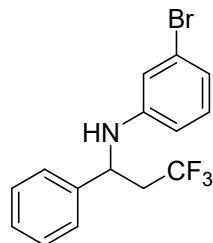


4-Methyl-N-(3,3,3-trifluoro-1-phenylpropyl)aniline (5f). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 43% (12.2 mg, 0.04 mmol); IR (KBr, cm⁻¹) 3401, 3033, 2926, 1619, 1520, 1457, 1381, 1259, 1138, 1034, 910, 809, 701; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.39-7.32 (m, 4H), 7.29-7.27 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.46 (d, *J* = 8.0 Hz, 2H), 4.68 (q, *J* = 8.0 Hz, 4.0 Hz, 1H), 2.67-2.52 (m, 2H), 2.19 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 144.0, 141.9, 129.7, 129.0, 127.9, 127.5, 126.2, 125.8 (q, *J* = 276.0 Hz), 113.9, 53.5 (q, *J* = 3.0 Hz), 41.8 (q, *J* = 27.0 Hz), 20.4; ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -63.32; MS (EI, 70 eV) *m/z* 279, 262, 196, 152, 133, 109; HRMS (ESI) *m/z* [M + H]⁺ calcd for C₁₆H₁₇F₃N 280.1308, found 280.1314.

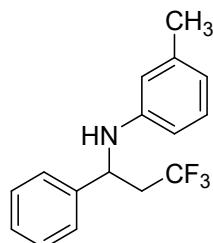


3-Chloro-N-(3,3,3-trifluoro-1-phenylpropyl)aniline (5g). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 56% (17.0 mg, 0.06 mmol); IR (KBr, cm⁻¹) 3400, 3038, 2926, 2853, 1598, 1484, 1380, 1258, 1146, 1031, 930, 851, 763; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.39-7.34 (m, 4H), 7.32-7.28 (m, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.53 (t, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 4.70 (t, *J* = 8.0 Hz, 1H), 4.24 (s, 1H), 2.65-2.55 (m, 2H); ¹³C{¹H} NMR (100

MHz, CDCl₃, ppm) δ 147.4, 141.1, 135.0, 130.2, 129.2, 128.1, 126.1, 125.6 (q, *J* = 276.0 Hz), 118.2, 113.5, 111.8, 53.1 (q, *J* = 3.0 Hz), 41.8 (q, *J* = 27.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -63.30; MS (EI, 70 eV) *m/z* 299, 216, 188, 151, 143, 104; HRMS (ESI) *m/z* [M + H]⁺ calcd for C₁₅H₁₄ClF₃N 300.0761, found 300.0774.

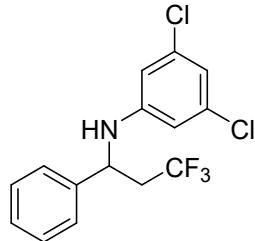


3-Bromo-N-(3,3,3-trifluoro-1-phenylpropyl)aniline (5h). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 66% (22.8 mg, 0.07 mmol); IR (KBr, cm⁻¹) 3395, 3034, 2925, 2854, 1595, 1480, 1379, 1257, 1146, 1031, 986, 849, 762, 683; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.39-7.33 (m, 4H), 7.32-7.28 (m, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 4.70 (t, *J* = 8.0 Hz, 1H), 4.24 (s, 1H), 2.65-2.56 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 147.5, 141.0, 130.5, 129.2, 128.1, 126.1, 125.6 (q, *J* = 276.0 Hz), 123.1, 121.1, 116.5, 112.1, 52.5 (q, *J* = 3.0 Hz), 41.8 (q, *J* = 27.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -63.30; MS (EI, 70 eV) *m/z* 343, 260, 231, 173, 133, 109; HRMS (ESI) *m/z* [M + H]⁺ calcd for C₁₅H₁₄BrF₃N 344.0265, found 344.0254.

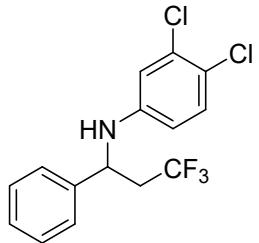


3-Methyl-N-(3,3,3-trifluoro-1-phenylpropyl)aniline (5i). Eluent: petroleum

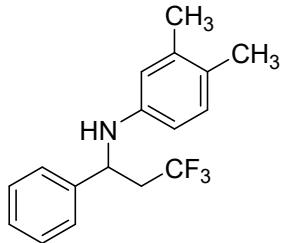
ether/ethyl acetate (v/v = 30:1). Yellow liquid: 55% (15.4 mg, 0.06 mmol); IR (KBr, cm^{-1}) 3430, 3039, 2925, 2855, 1606, 1518, 1454, 1320, 1204, 1137, 1034, 950, 852, 700; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.40-7.34 (m, 4H), 7.30-7.28 (m, 1H), 7.00 (t, J = 8.0 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 6.40 (s, 1H), 6.33 (d, J = 8.0 Hz, 1H), 4.73 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 4.14 (s, 1H), 2.67-2.56 (m, 2H). 2.23 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 146.3, 141.9, 139.0, 129.1, 129.0, 127.8, 126.2, 125.8 (q, J = 276.0 Hz), 119.2, 114.6, 110.6, 53.1 (q, J = 3.0 Hz), 41.8 (q, J = 27.0 Hz), 21.6; ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.26; MS (EI, 70 eV) m/z 279, 196, 173, 133, 109, 77; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{N}$ 280.1308, found 280.1329.



3,5-Dichloro-N-(3,3,3-trifluoro-1-phenylpropyl)aniline (5j). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 45% (15.1 mg, 0.05 mmol); IR (KBr, cm^{-1}) 3395, 3051, 2926, 2853, 1593, 1452, 1315, 1252, 1147, 1095, 964, 826, 701; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.42-7.30 (m, 5H), 6.68-6.66 (m, 1H), 6.41-6.40 (m, 2H), 4.69 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 4.34 (s, 1H), 2.65-2.54 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 147.9, 140.4, 135.5, 129.3, 128.3, 125.9, 125.5 (q, J = 277.0 Hz), 118.1, 111.8, 52.9 (q, J = 3.0 Hz), 41.8 (q, J = 27.0 Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.32; MS (EI, 70 eV) m/z 333, 292, 250, 173, 133, 109; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{F}_3\text{N}$ 334.0372, found 334.0368.

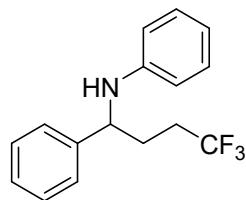


3,4-Dichloro-N-(3,3,3-trifluoro-1-phenylpropyl)aniline (5k). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 48% (15.9 mg, 0.05 mmol); IR (KBr, cm^{-1}) 3403, 3033, 2926, 2855, 1598, 1477, 1380, 1256, 1132, 1023, 930, 846, 700; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.40-7.29 (m, 5H), 7.13 (d, J = 8.0 Hz, 1H), 6.62 (s, 1H), 6.37 (d, J = 8.0 Hz, 1H), 4.68-4.67 (m, 1H), 4.28 (s, 1H), 2.65-2.55 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 145.7, 140.7, 132.8, 130.6, 129.3, 128.3, 126.0, 125.6 (q, J = 276.0 Hz), 121.0, 115.0, 113.2, 53.1 (q, J = 3.0 Hz), 41.8 (q, J = 27.0 Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.32; MS (EI, 70 eV) m/z 333, 250, 173, 161, 133, 109; HRMS (ESI) m/z [M + H] $^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{F}_3\text{N}$ 334.0372, found 334.0380.

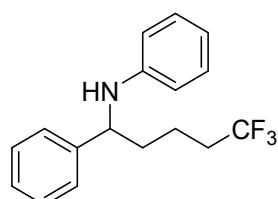


3,4-Dimethyl-N-(3,3,3-trifluoro-1-phenylpropyl)aniline (5l). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid : 59% (17.2 mg, 0.06 mmol); IR (KBr, cm^{-1}) 3396, 3029, 2924, 2868, 1620, 1510, 1458, 1378, 1261, 1137, 1082, 972, 849, 702; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.40-7.33 (m, 4H), 7.30-7.27 (m, 1H), 6.87 (d, J = 8.0 Hz, 1H)), 6.41 (s, 1H), 6.29 (d, J = 8.0 Hz, 1H), 4.70 (q, J = 8.0 Hz, 4.0 Hz,

1H), 2.67-2.55 (m, 2H), 2.14 (s, 3H), 2.12 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 144.4, 142.0, 137.3, 130.2, 129.0, 127.8, 126.3, 126.2, 123.2 (d, $J = 242.0$ Hz), 115.6, 111.0, 53.4 (q, $J = 3.0$ Hz), 41.8 (q, $J = 27.0$ Hz), 20.0, 18.6; ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -63.28; MS (EI, 70 eV) m/z 293, 248, 231, 210, 132, 109; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{17}\text{H}_{19}\text{F}_3\text{N}$ 294.1464, found 294.1475.

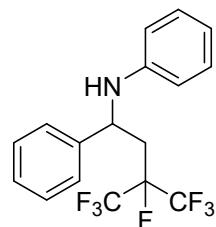


N-(4,4,4-*Trifluoro-1-phenylbutyl)aniline (7a).* Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 50% (14.0 mg, 0.05 mmol); IR (KBr, cm^{-1}) 3395, 3057, 2924, 2869, 1600, 1564, 1457, 1379, 1223, 1182, 1085, 983, 843, 751; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.35-7.30 (m, 4H), 7.25-7.23(m, 1H), 7.10 (t, $J = 8.0$ Hz, 2H), 6.67 (t, $J = 8.0$ Hz, 1H), 6.54 (d, $J = 8.0$ Hz, 2H), 4.38 (t, $J = 8.0$ Hz, 1H), 4.00 (s, 1H), 2.27-1.99 (m, 4H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 146.8, 142.4, 129.3, 129.9, 128.8 (q, $J = 45.0$ Hz), 127.6, 126.3, 117.9, 113.5, 57.0, 31.0 (d, $J = 29.0$ Hz), 30.6 (q, $J = 3.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -66.04; MS (EI, 70 eV) m/z 279, 260, 202, 182, 167; HRMS (ESI) m/z [M + H]⁺ calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{N}$ 280.1308, found 280.1324.



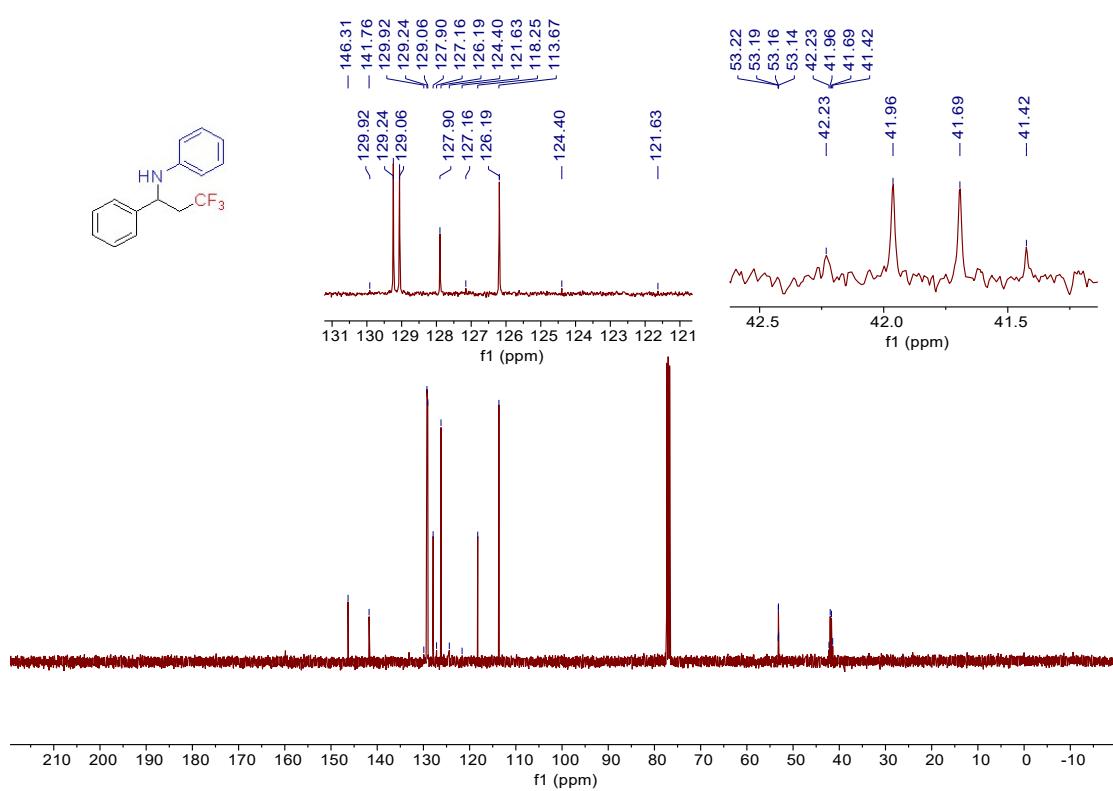
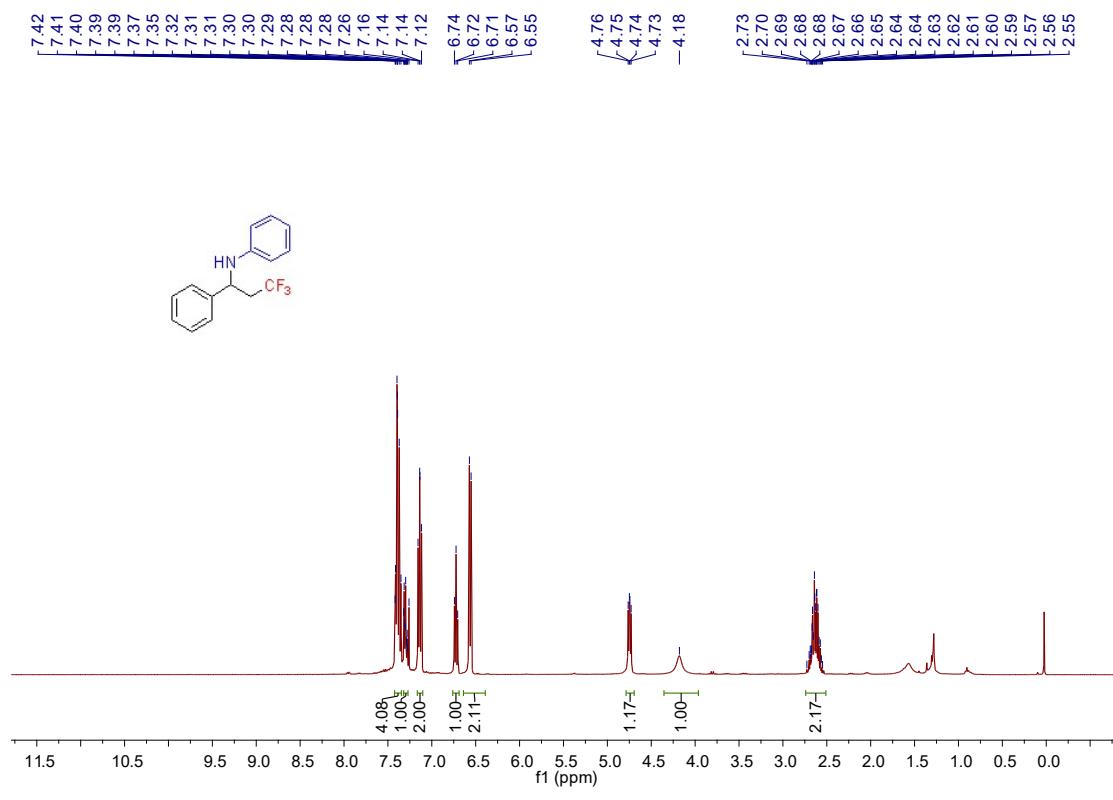
N-(5,5,5-*Trifluoro-1-phenylpentyl)aniline (7b).* Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid : 45% (13.3 mg, 0.05 mmol); IR (KBr, cm^{-1}) 3326,

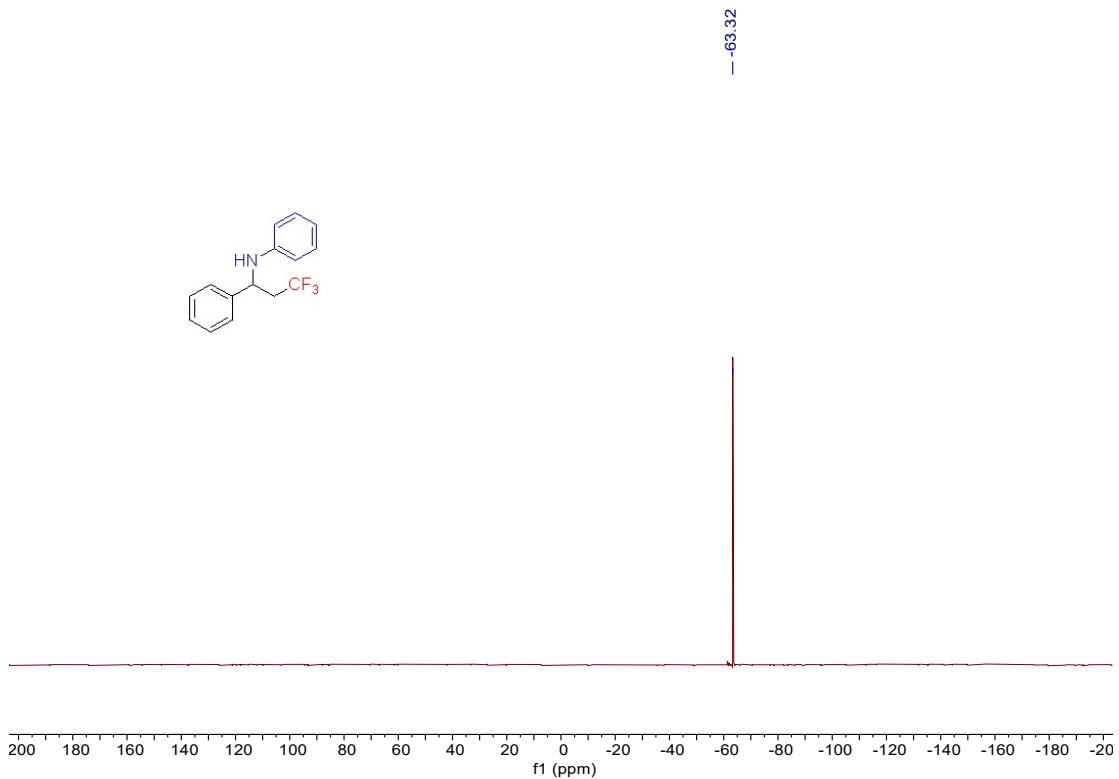
3055, 2923, 2869, 1656, 1500, 1460, 1378, 1257, 1141, 1081, 974, 849, 749, 699; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.33 (d, $J = 8.0$ Hz, 4H), 7.25-7.21(m, 1H), 7.09 (t, $J = 8.0$ Hz, 2H), 6.65 (t, $J = 8.0$ Hz, 1H), 6.52 (d, $J = 8.0$ Hz, 2H), 4.32 (q, $J = 8.0$ Hz, 4.0 Hz, 1H), 4.03(s, 1H) 2.14-2.02 (m, 2H), 1.94-1.79 (m, 2H), 1.75-1.58 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 147.1, 143.3, 129.2, 128.8, 127.5 (q, $J = 172$ Hz), 127.3, 126.3, 117.5, 113.3, 57.8, 37.6, 33.5 (q, $J = 28.0$ Hz), 19.0 (q, $J = 3.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -66.09; MS (EI, 70 eV) m/z 293, 263, 200, 182, 167; HRMS (ESI) m/z [M + H] $^+$ calcd for $\text{C}_{17}\text{H}_{19}\text{F}_3\text{N}$ 294.1464, found 294.1465.



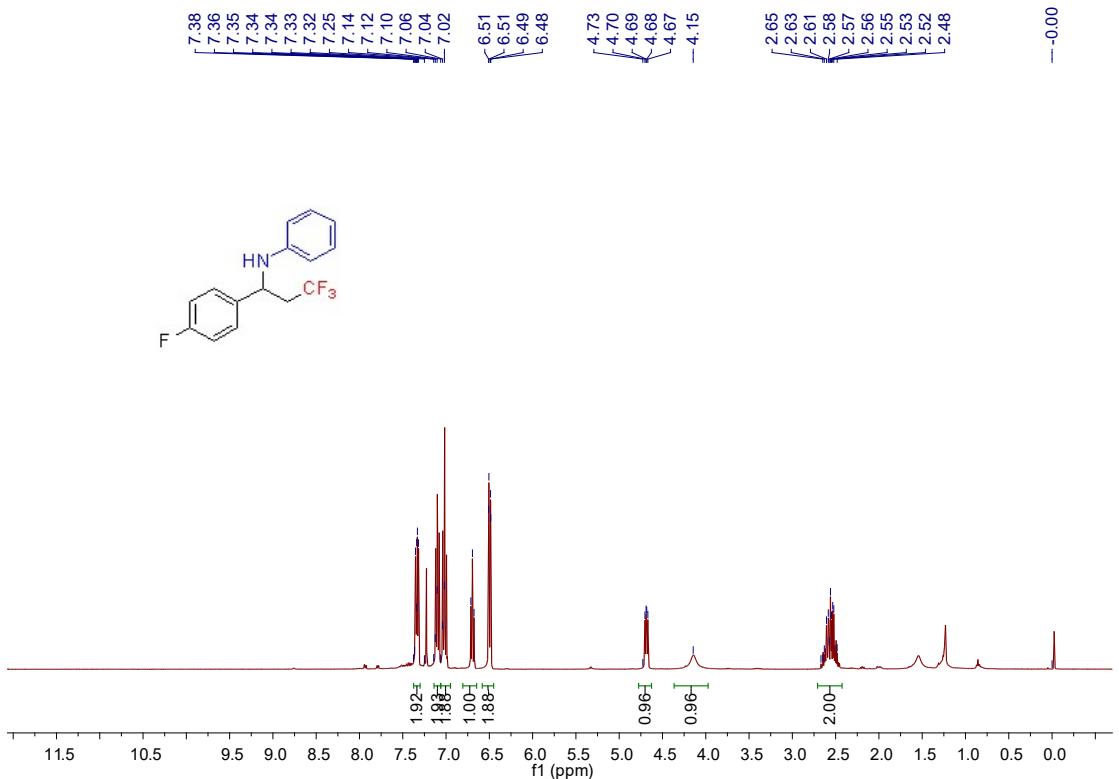
N-(3,4,4,4-Tetrafluoro-1-phenyl-3-(trifluoromethyl)butyl)aniline (7c). Eluent: petroleum ether/ethyl acetate (v/v = 30:1). Yellow liquid: 43% (16.1 mg, 0.04 mmol); IR (KBr, cm^{-1}) 3389, 3029, 2927, 2856, 1603, 1508, 1429, 1317, 1154, 1028, 961, 871, 750, 699; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.40-7.34 (m, 4H), 7.31-7.29 (m, 1H), 7.11 (t, $J = 8.0$ Hz, 2H), 6.71 (t, $J = 8.0$ Hz, 1H), 6.51 (d, $J = 8.0$ Hz, 2H), 4.76 (q, $J = 8.0$ Hz, 4.0 Hz, 1H), 4.15 (s, 1H), 2.65-2.46 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm) δ 146.2, 142.4, 129.4, 129.2 (d, $J = 5.0$ Hz), 128.0, 126.0, 118.3, 117.8, 113.6, 112.9, 53.4, 36.7 (d, $J = 19.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -75.72, -76.94; MS (EI, 70 eV) m/z 365, 337, 306, 273, 182; HRMS (ESI) m/z [M + H] $^+$ calcd for $\text{C}_{17}\text{H}_{15}\text{F}_7\text{N}$ 366.1087, found 366.1075.

8. NMR Spectra

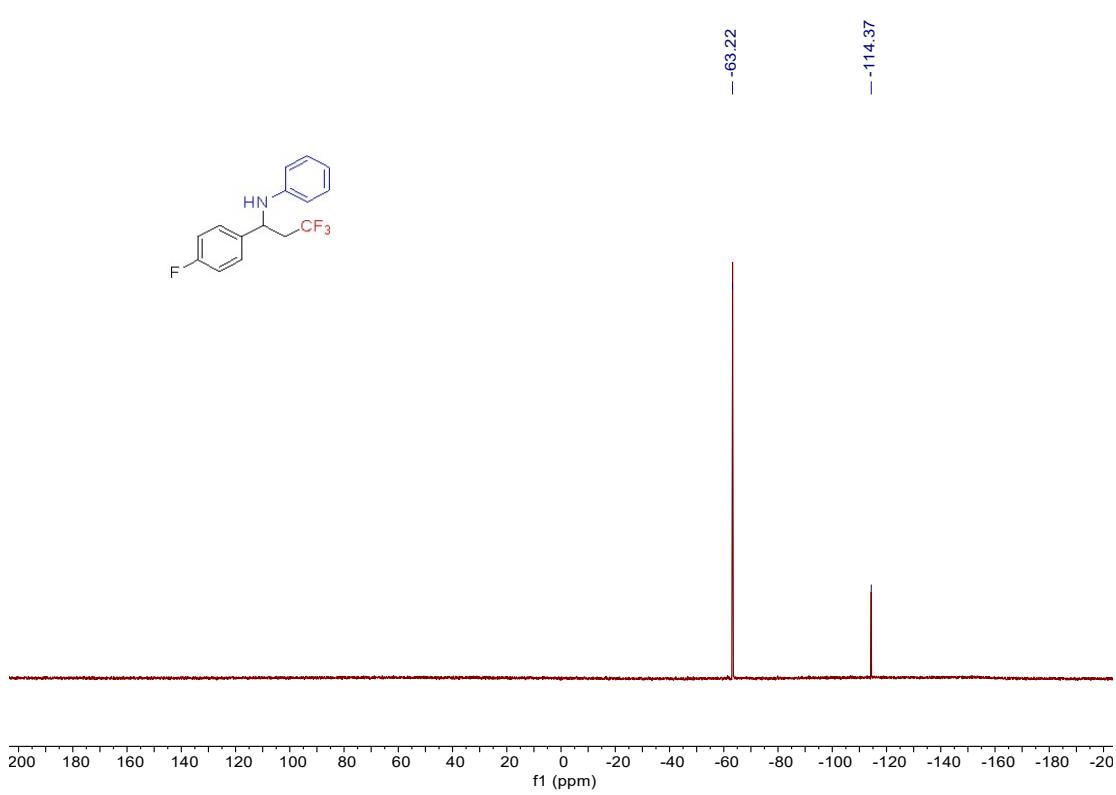
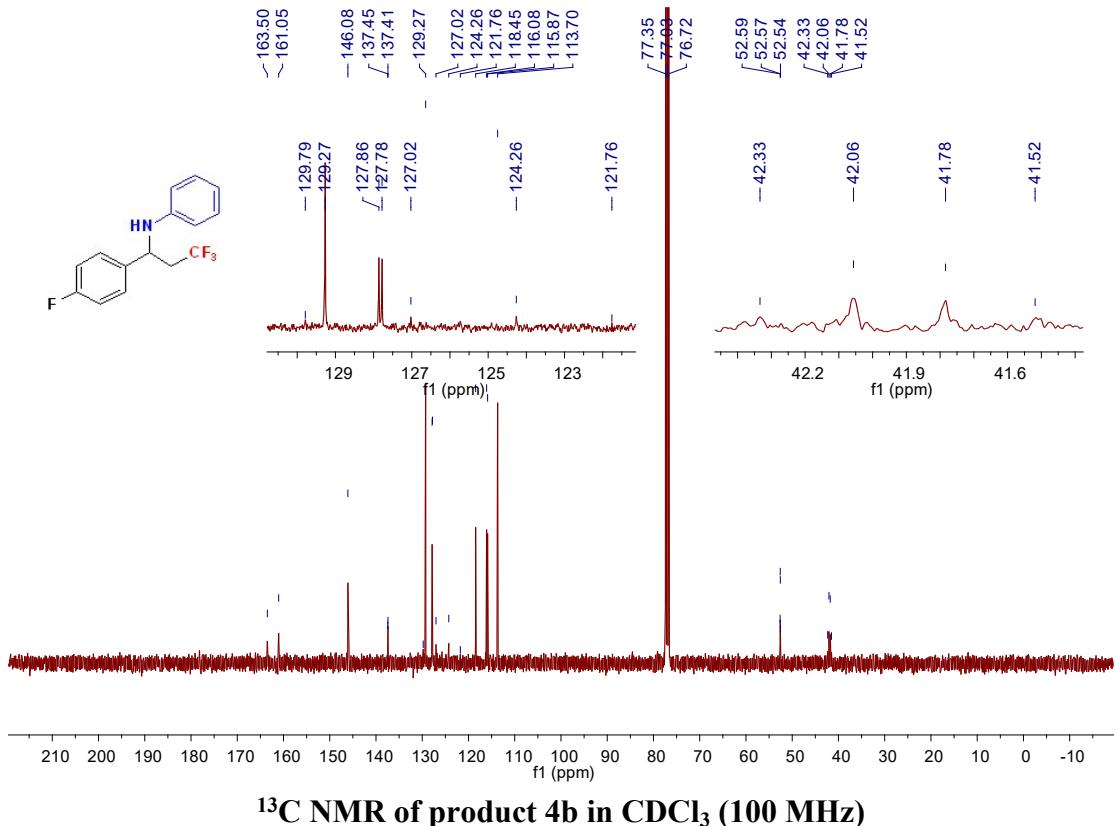


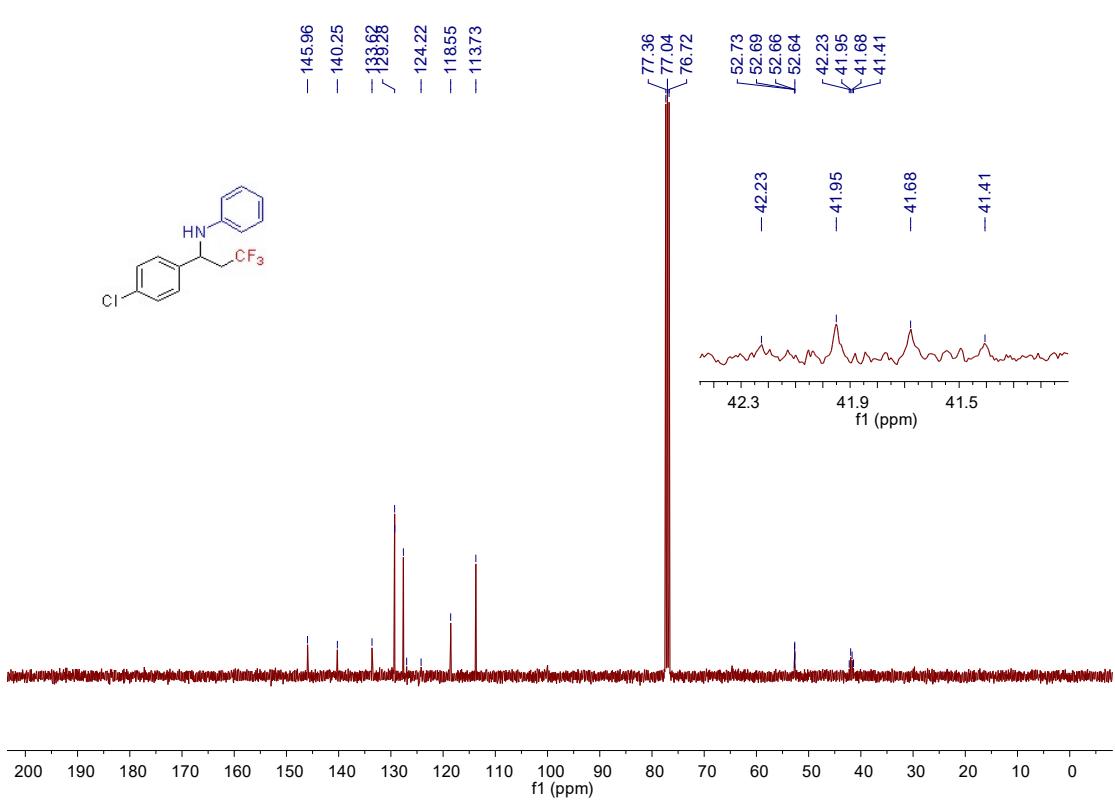
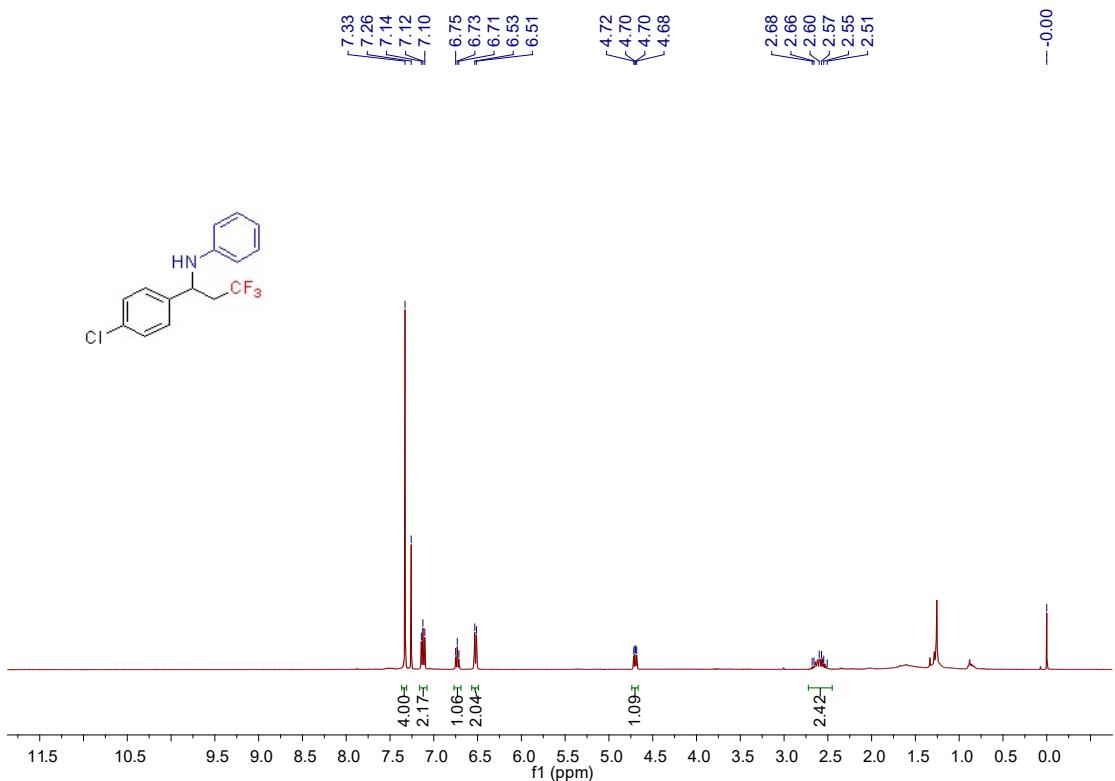


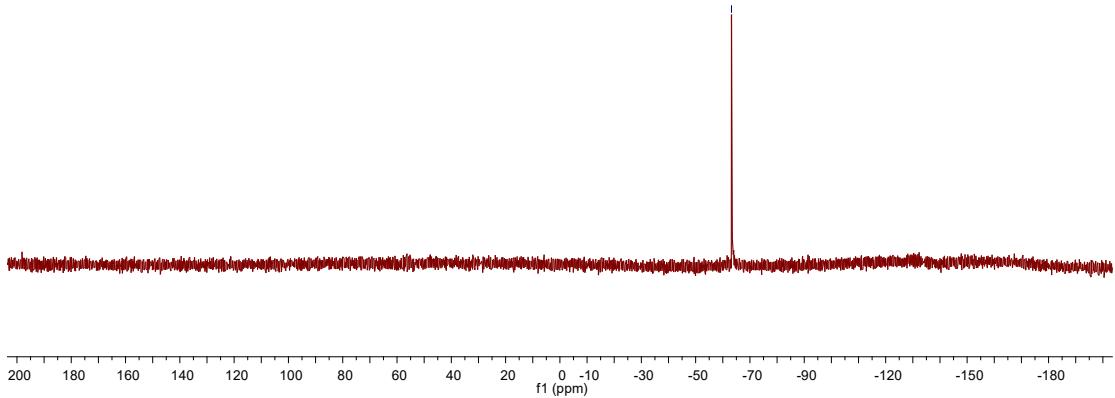
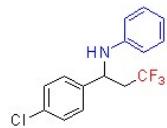
¹⁹F NMR of product 4a in CDCl₃ (376 MHz)



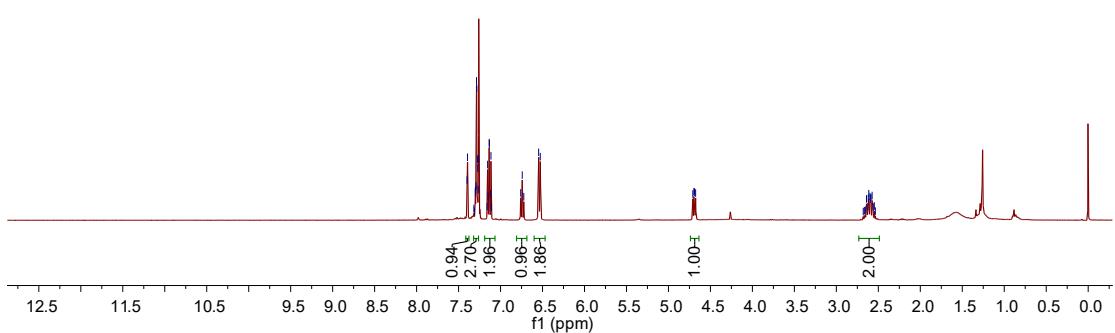
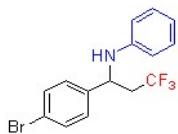
¹H NMR of product 4b in CDCl₃ (400 MHz)



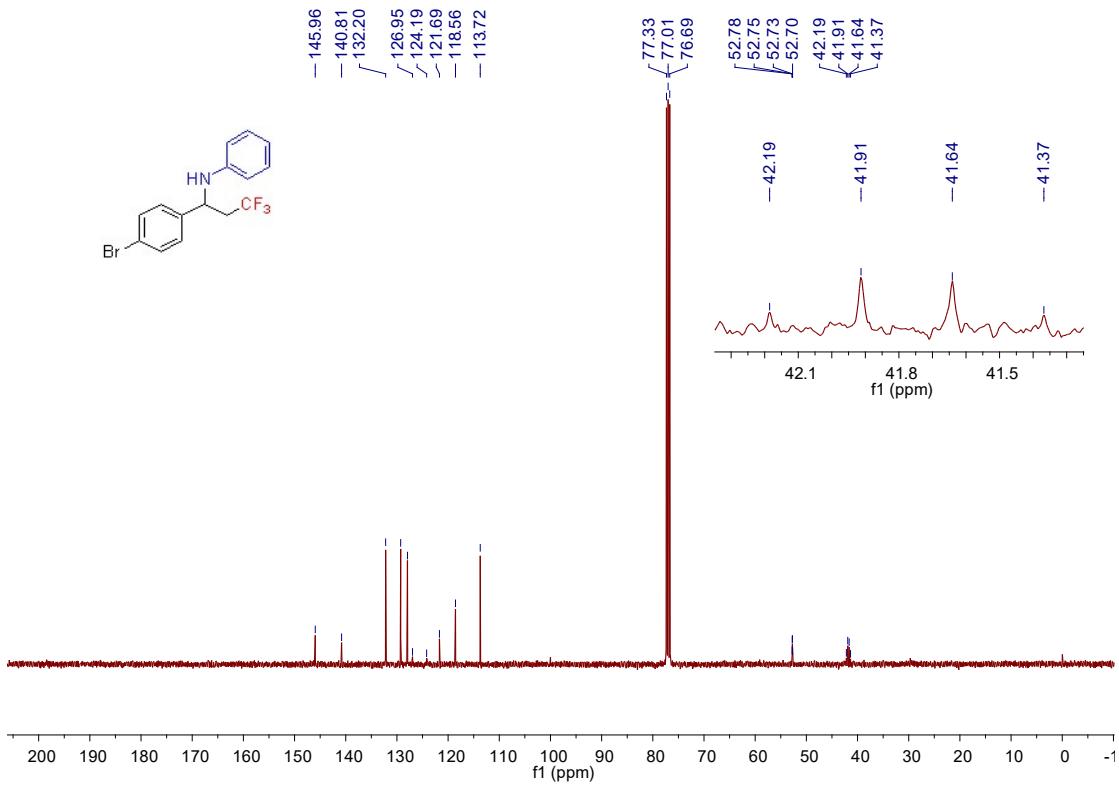




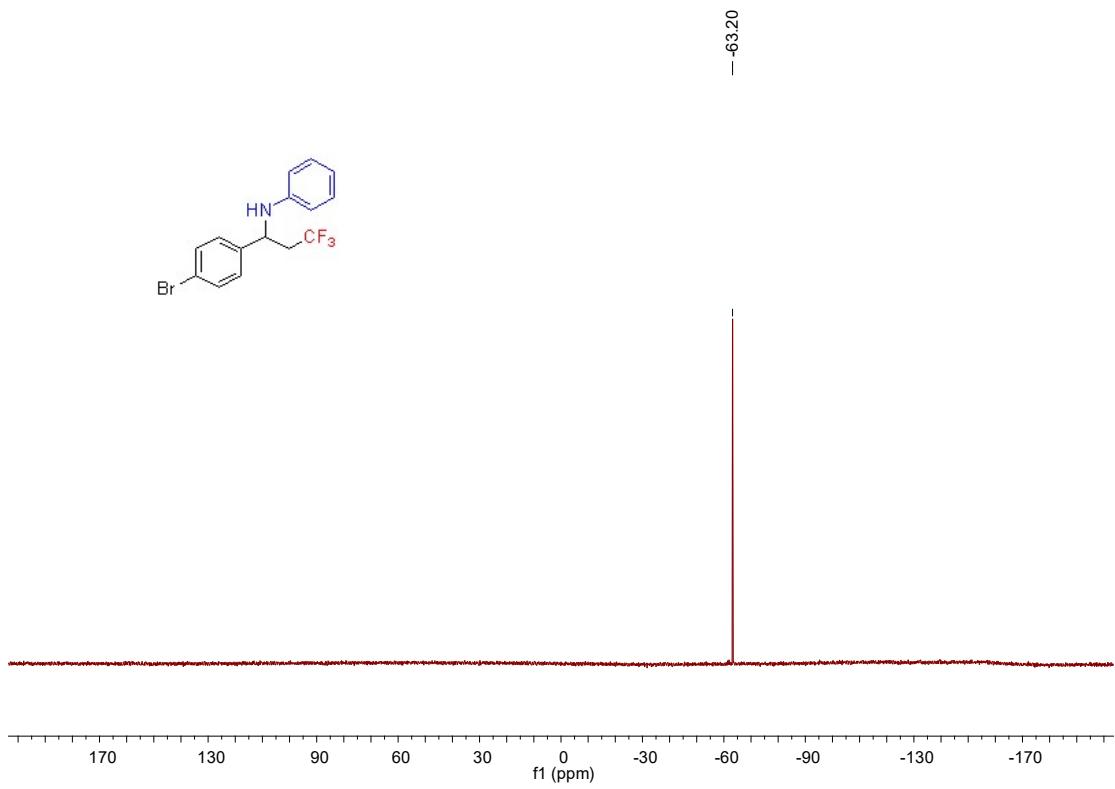
¹⁹F NMR of product 4c in CDCl₃ (376 MHz)



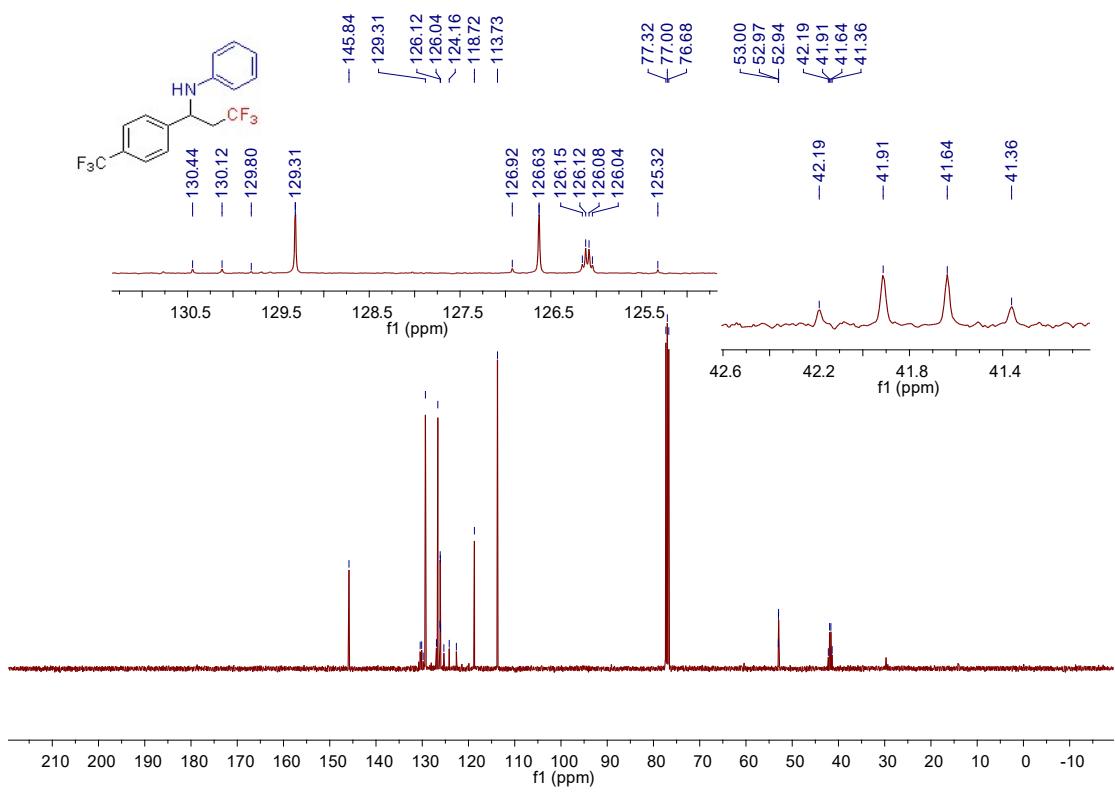
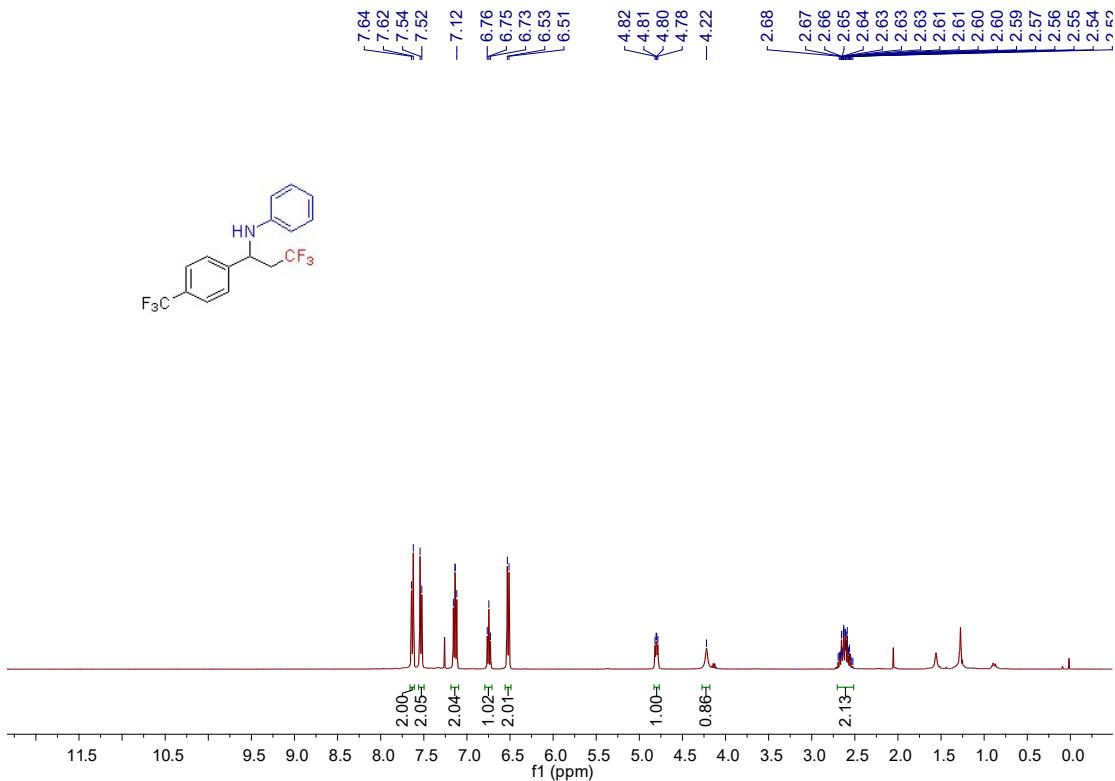
¹H NMR of product 4d in CDCl₃ (400 MHz)

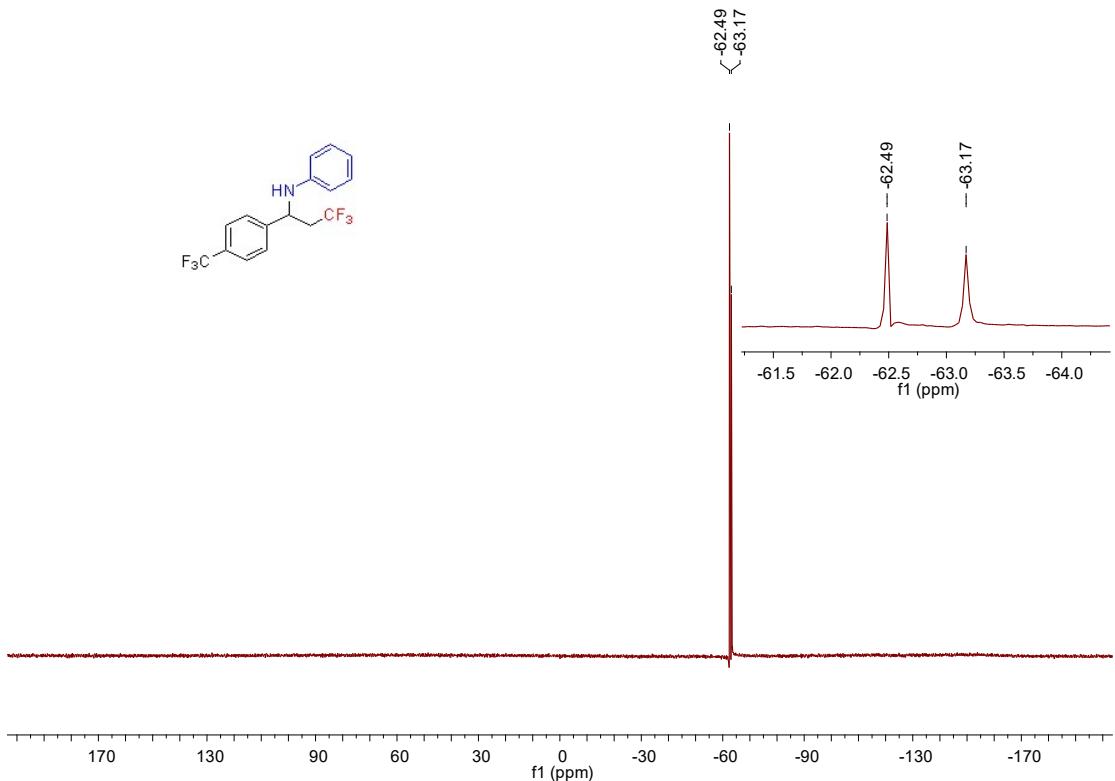


¹³C NMR of product 4d in CDCl₃ (100 MHz)

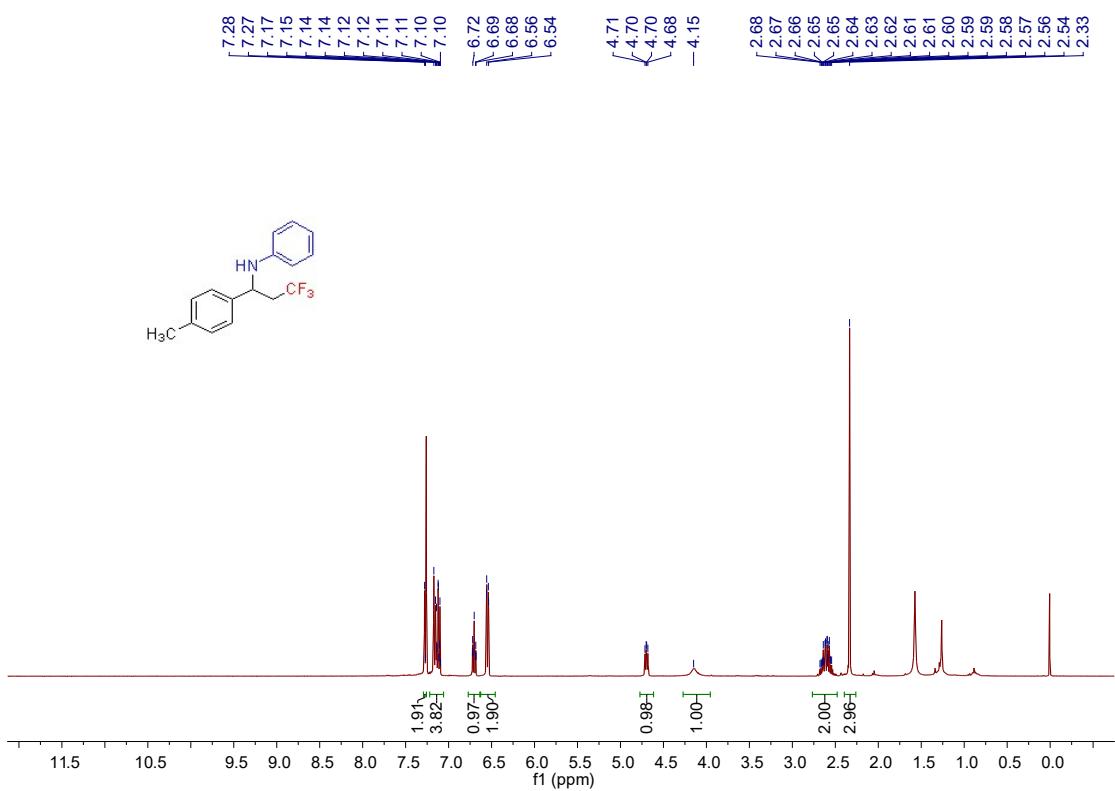


¹⁹F NMR of product 4d in CDCl₃ (376 MHz)

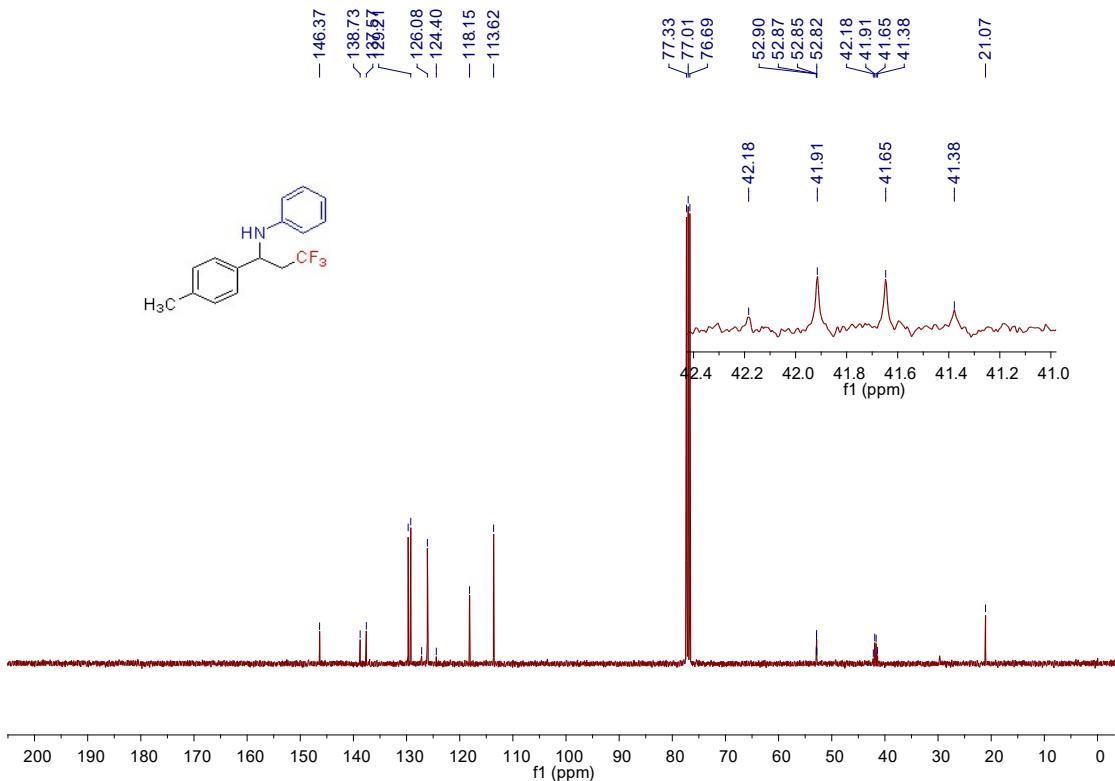




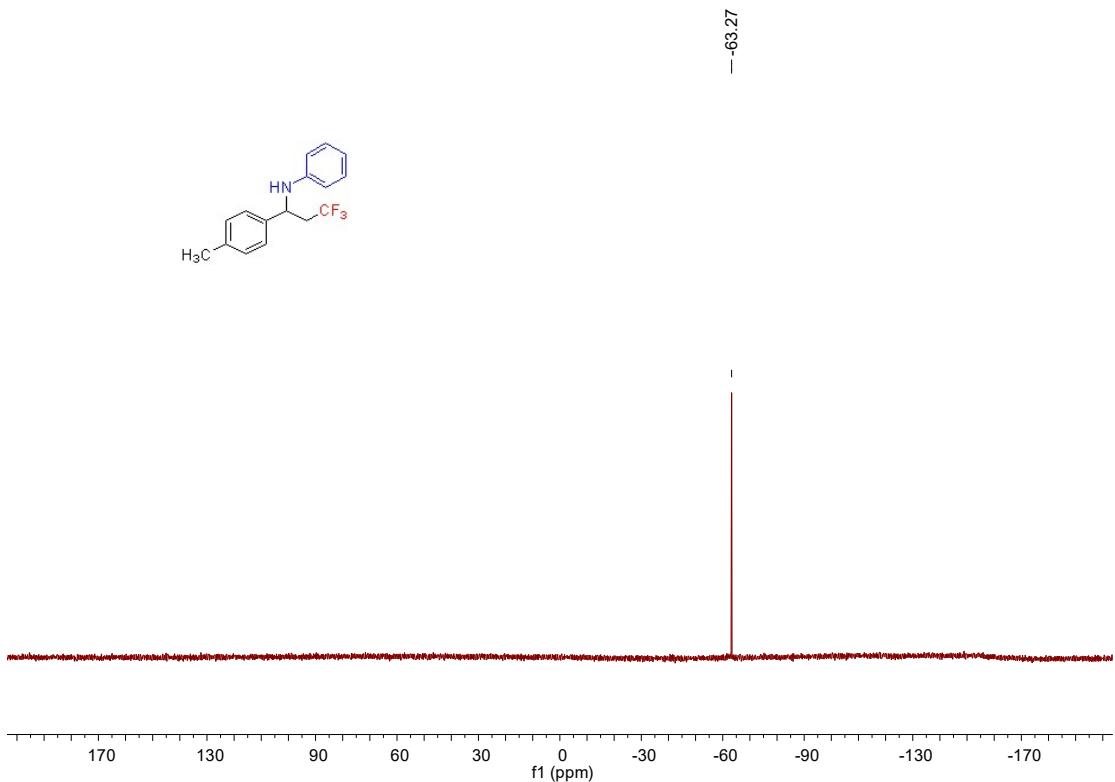
¹⁹F NMR of product 4e in CDCl₃ (376 MHz)



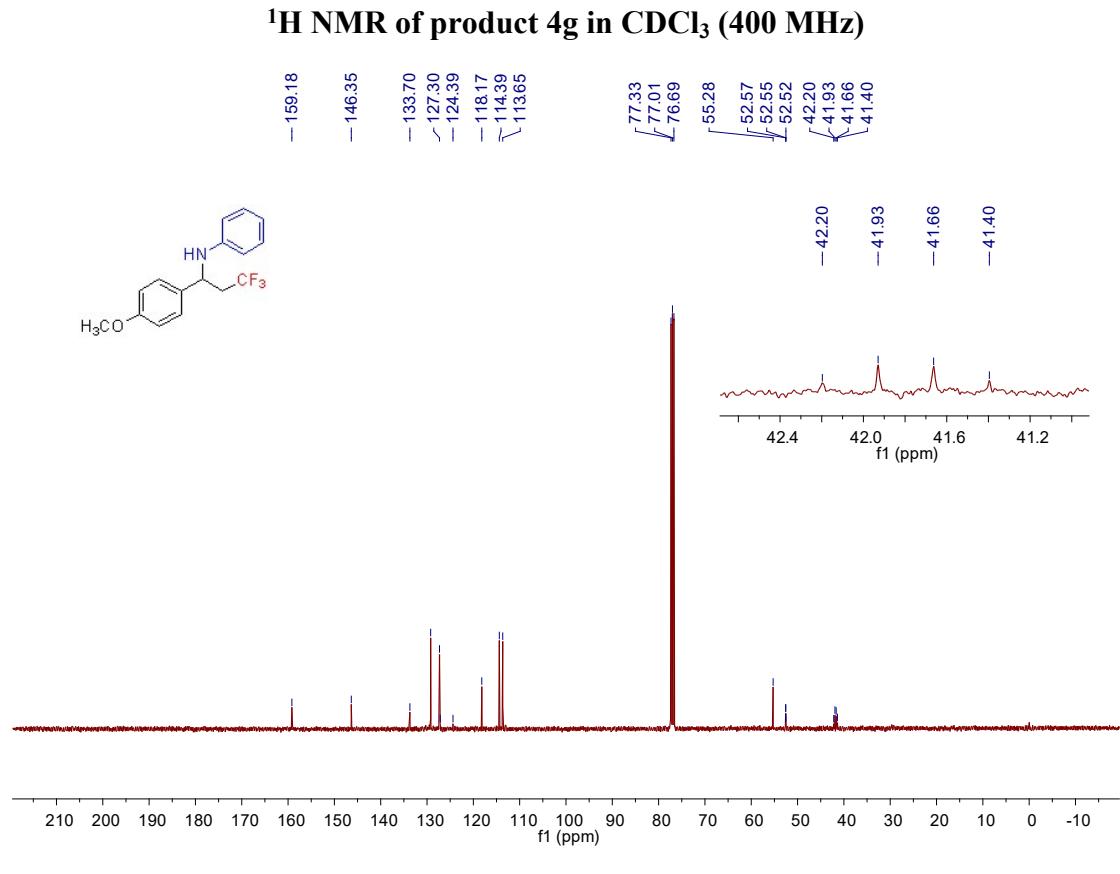
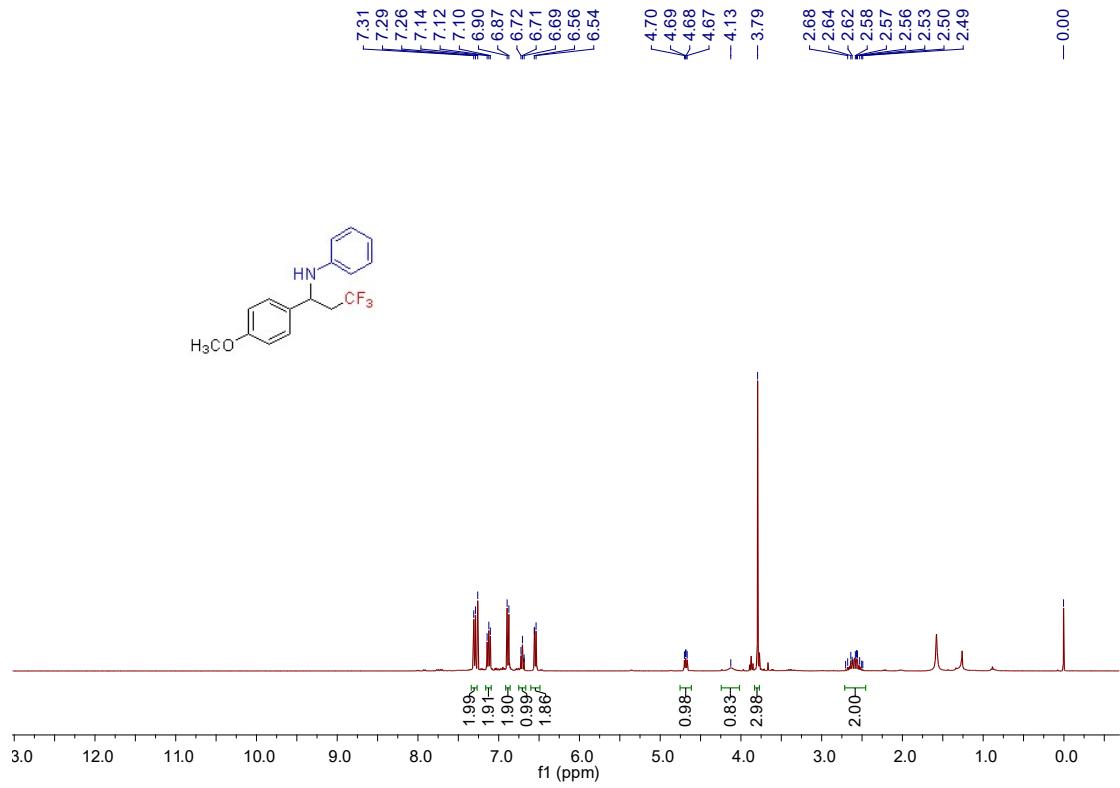
¹H NMR of product 4f in CDCl₃ (400 MHz)

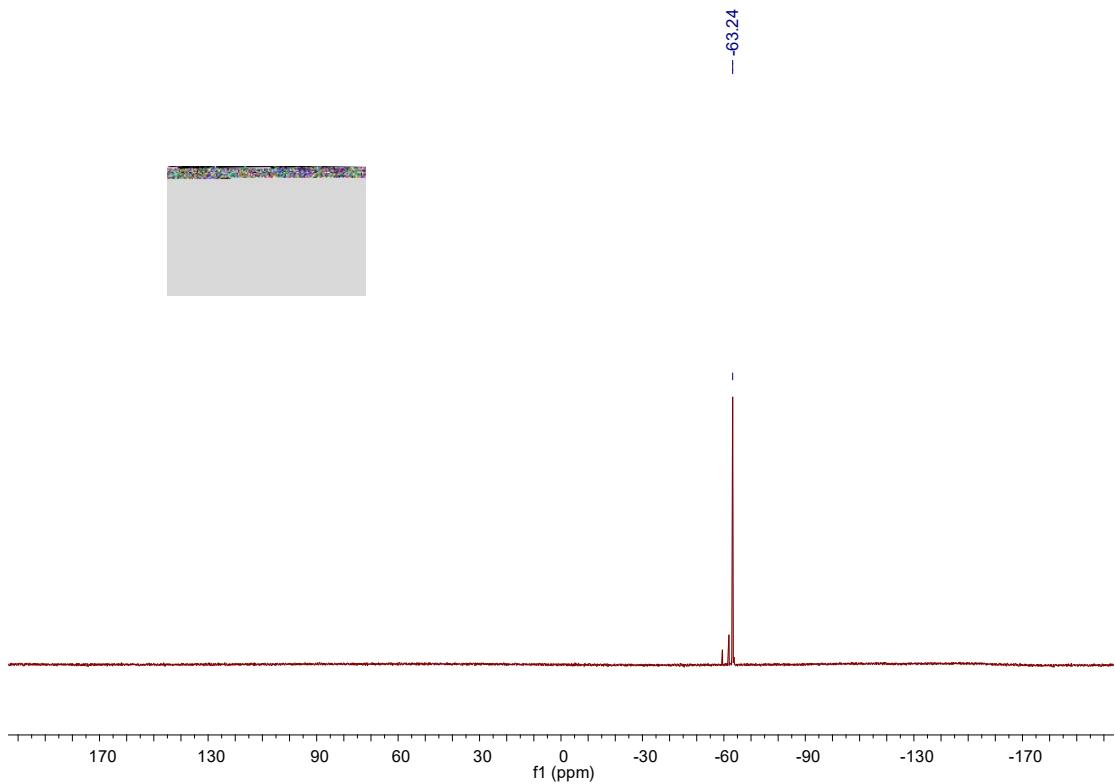


¹³C NMR of product 4f in CDCl₃ (100 MHz)

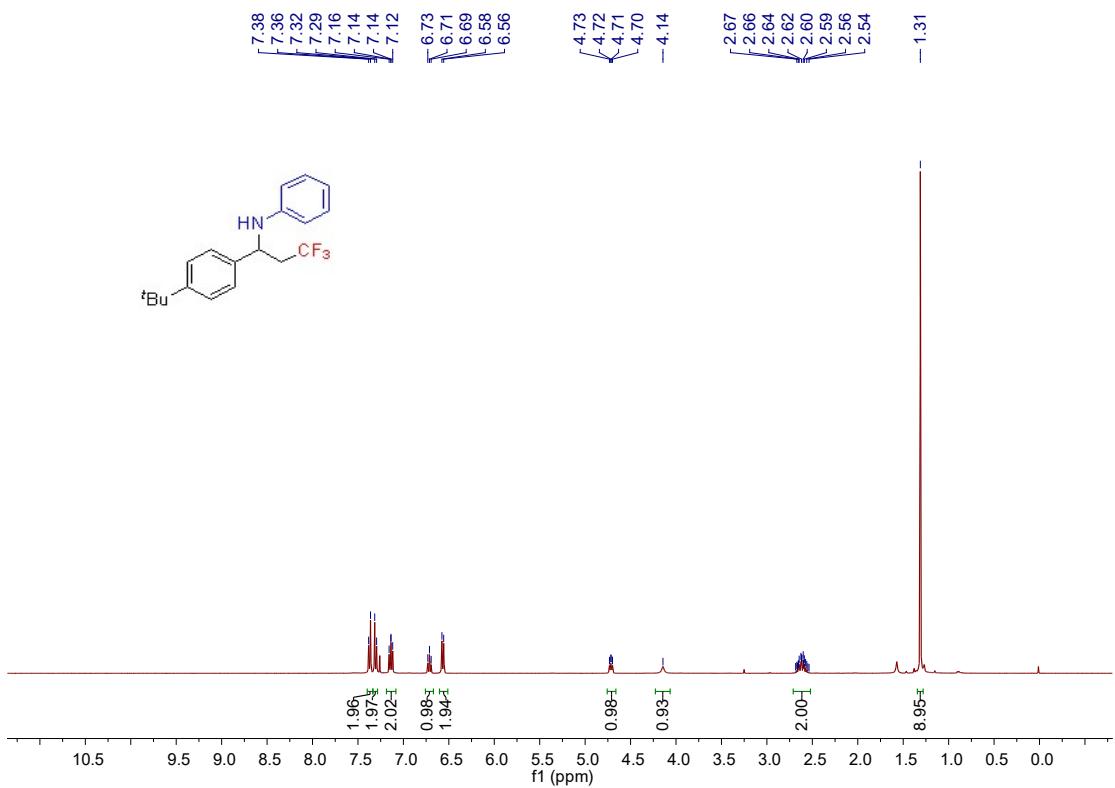


¹⁹F NMR of product 4f in CDCl₃ (376 MHz)

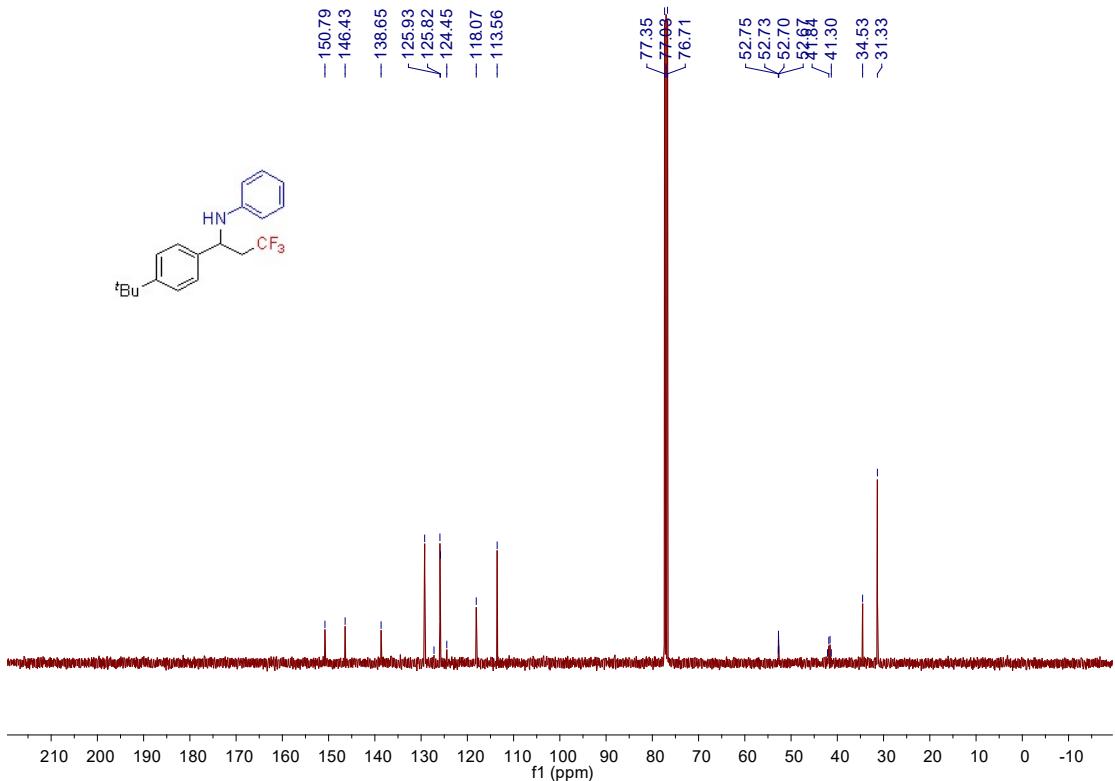




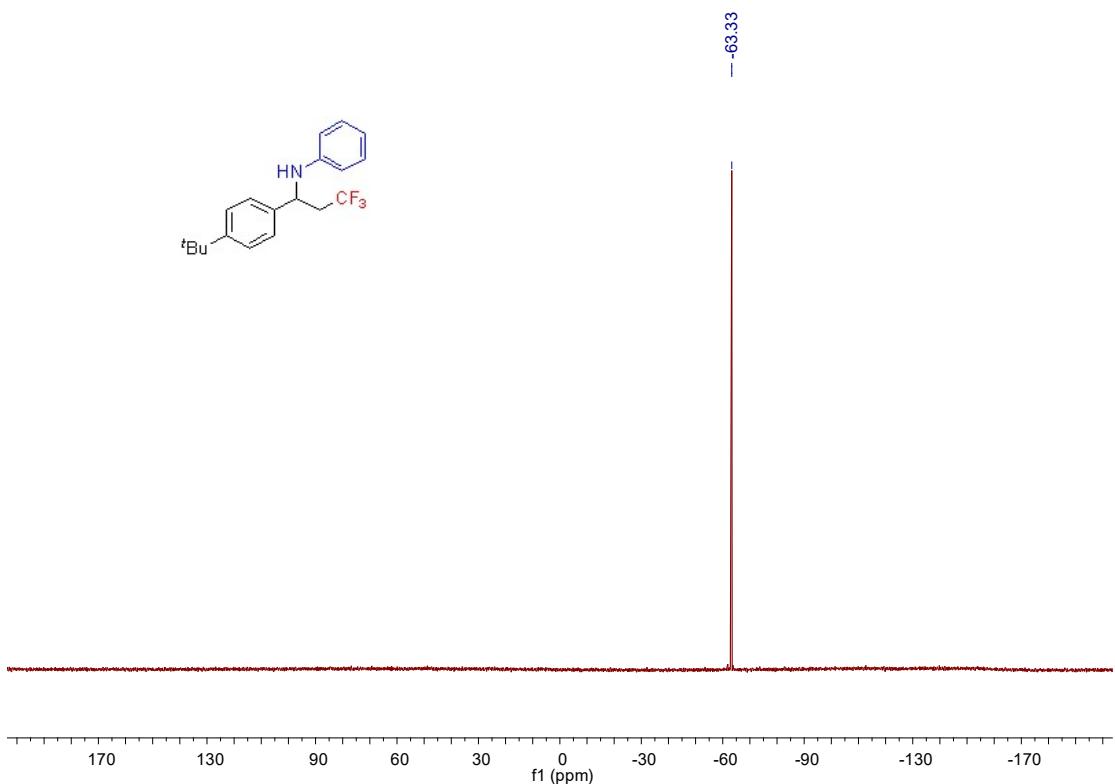
¹⁹F NMR of product 4g in CDCl₃ (376 MHz)



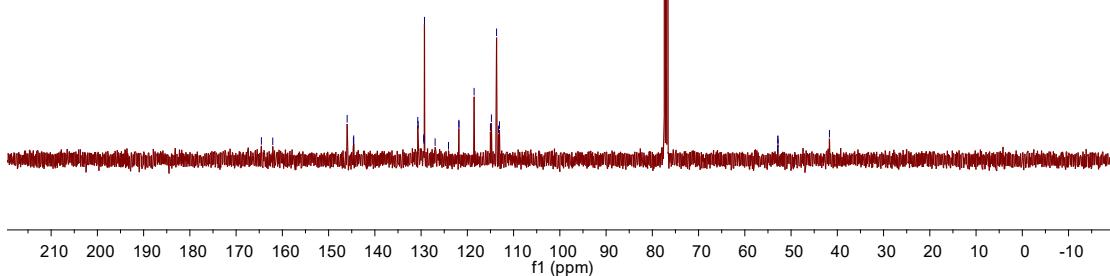
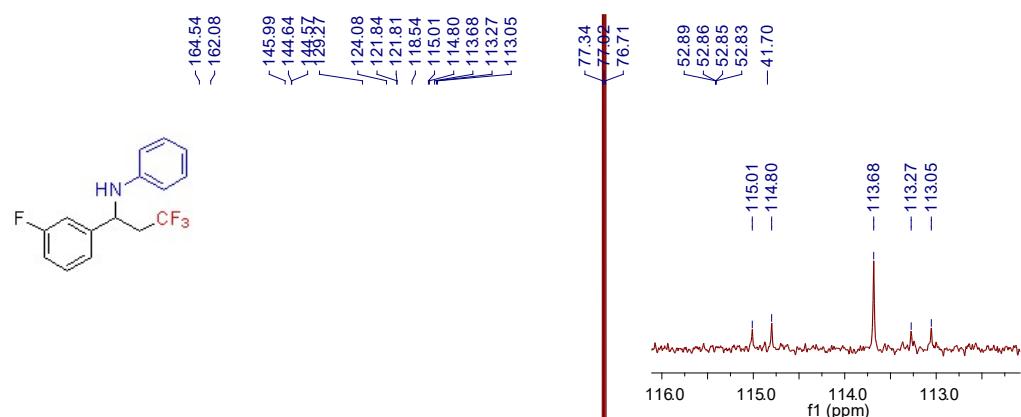
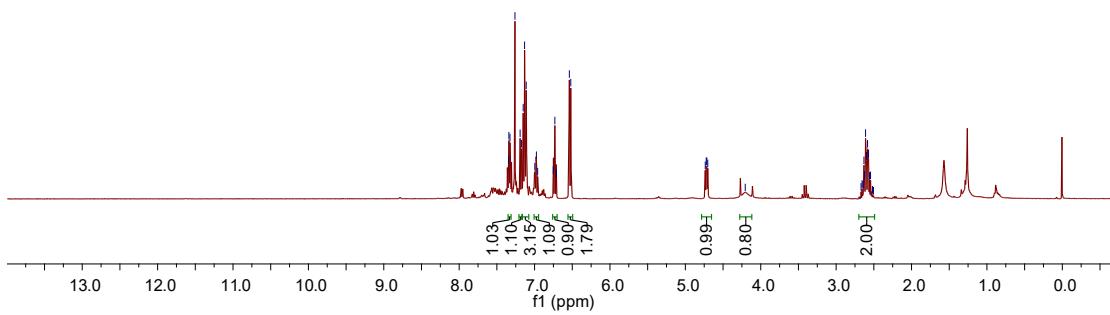
¹H NMR of product 4h in CDCl₃ (400 MHz)



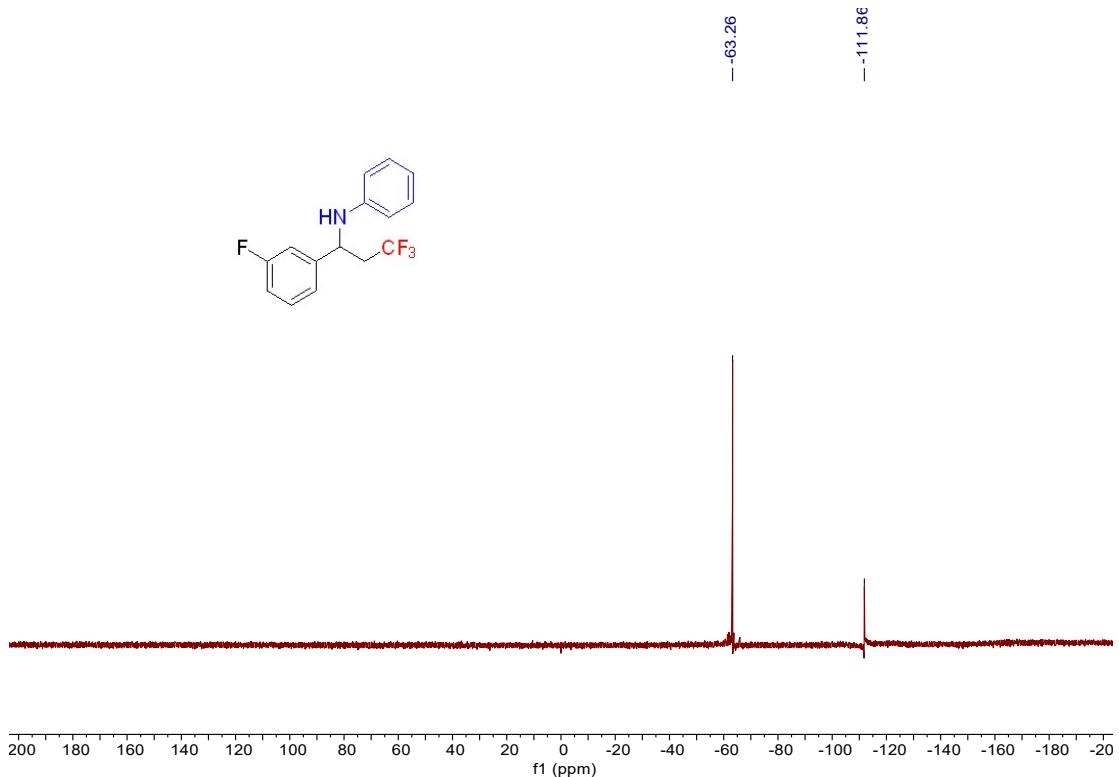
^{13}C NMR of product 4h in CDCl_3 (100 MHz)



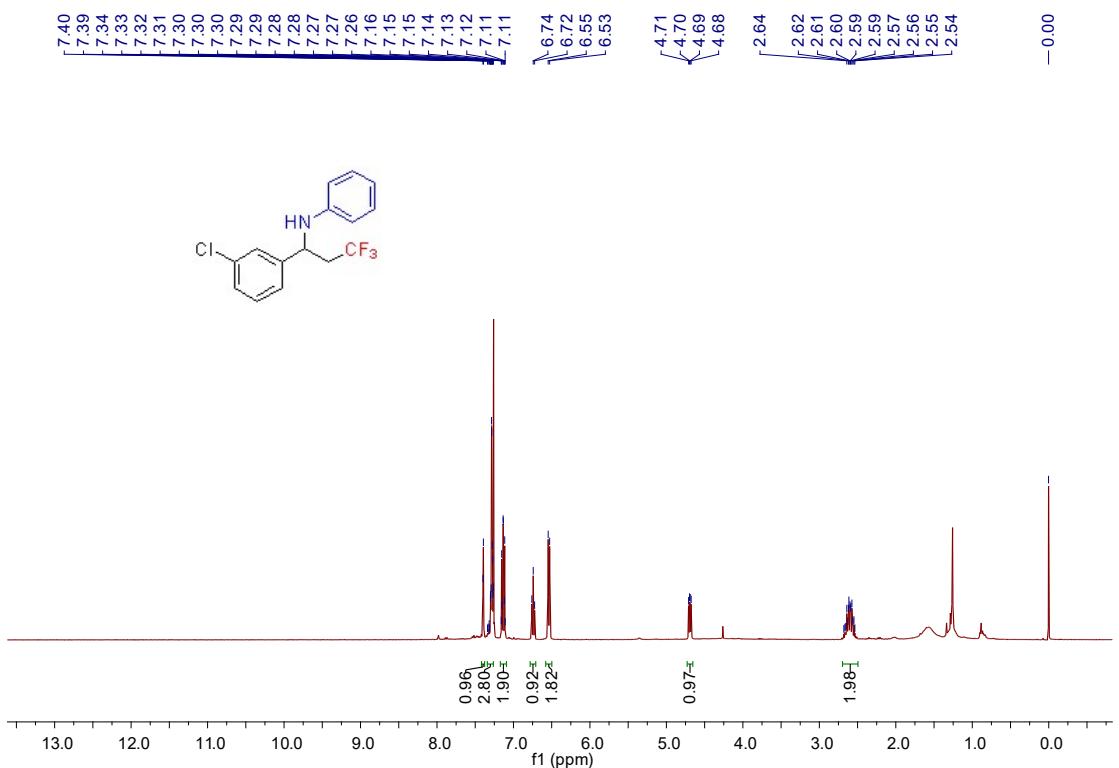
^{19}F NMR of product 4h in CDCl_3 (376 MHz)



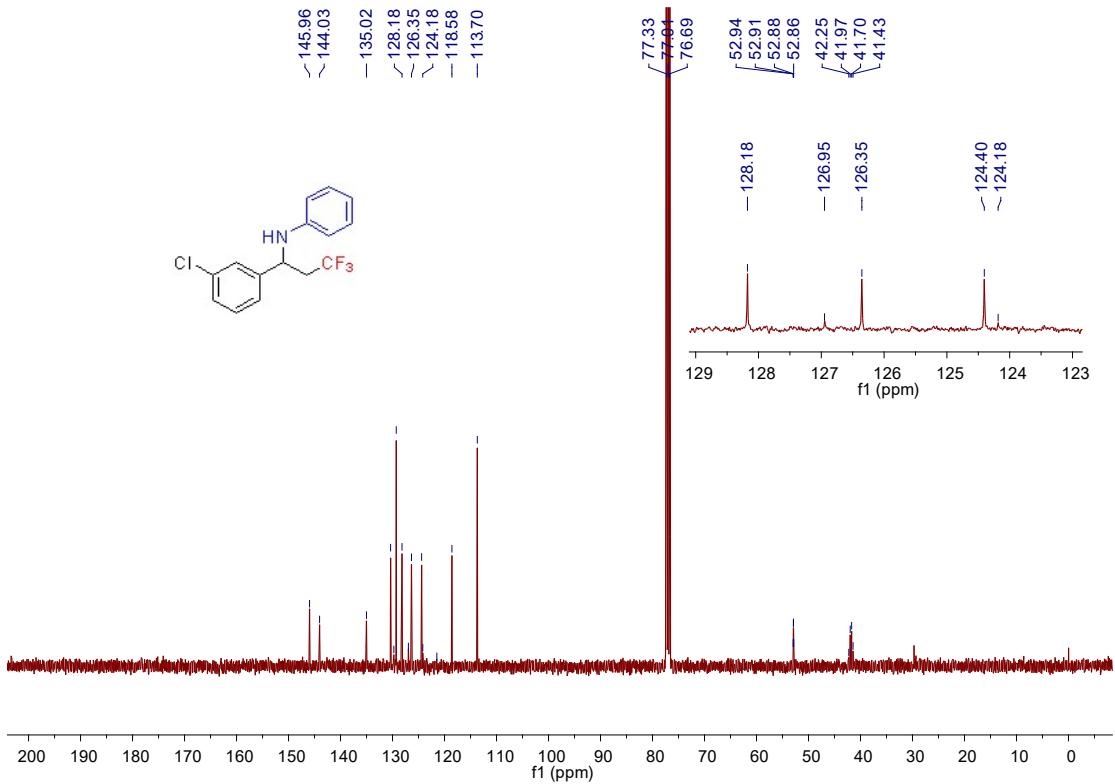
¹³C NMR of product 4i in CDCl₃ (100 MHz)



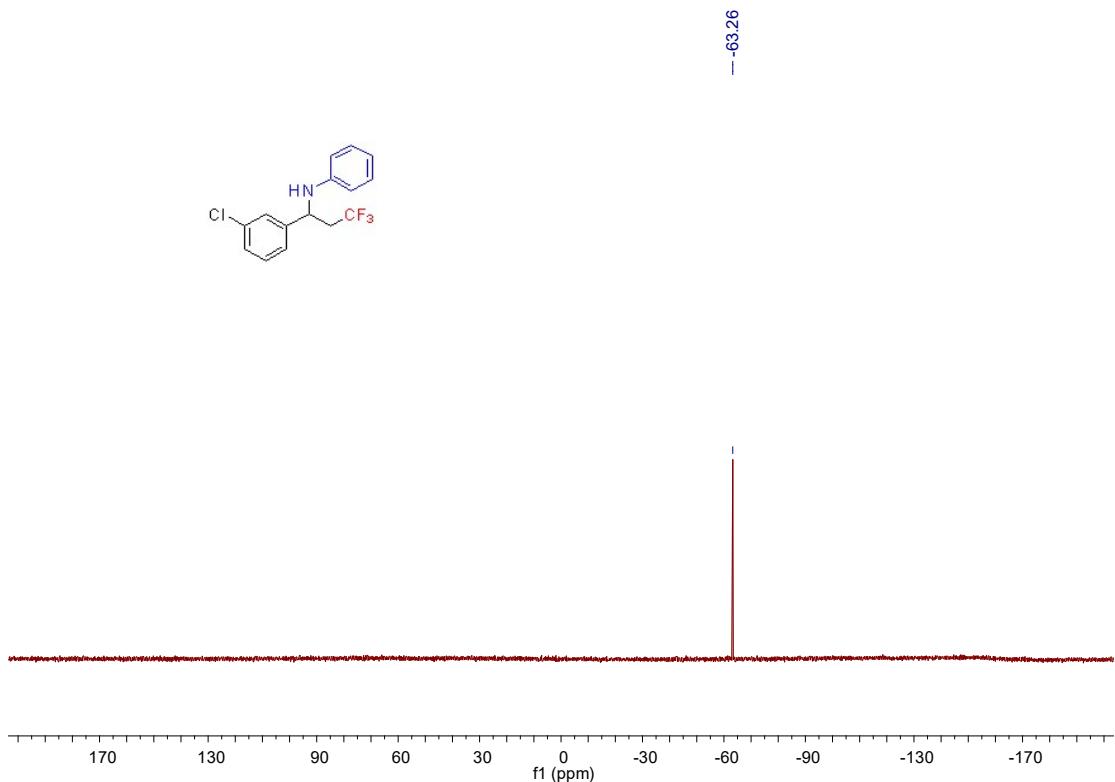
¹⁹F NMR of product 4i in CDCl₃ (376 MHz)



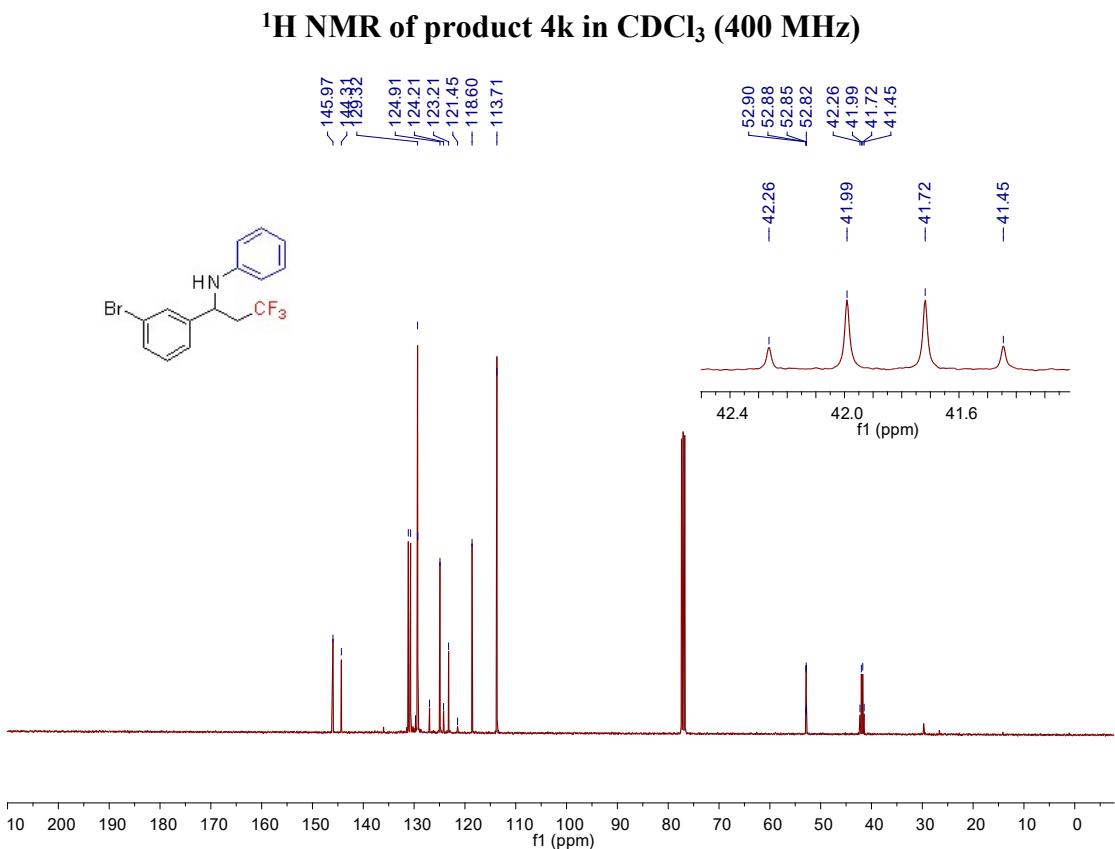
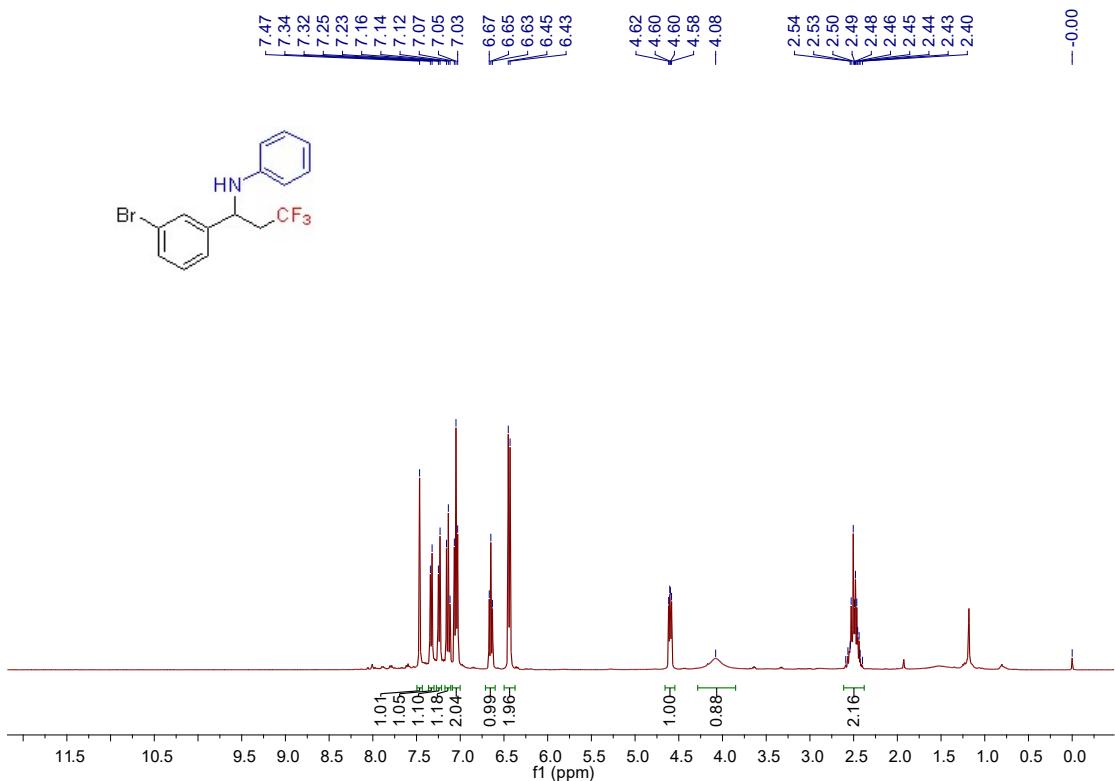
¹H NMR of product 4j in CDCl₃ (400 MHz)



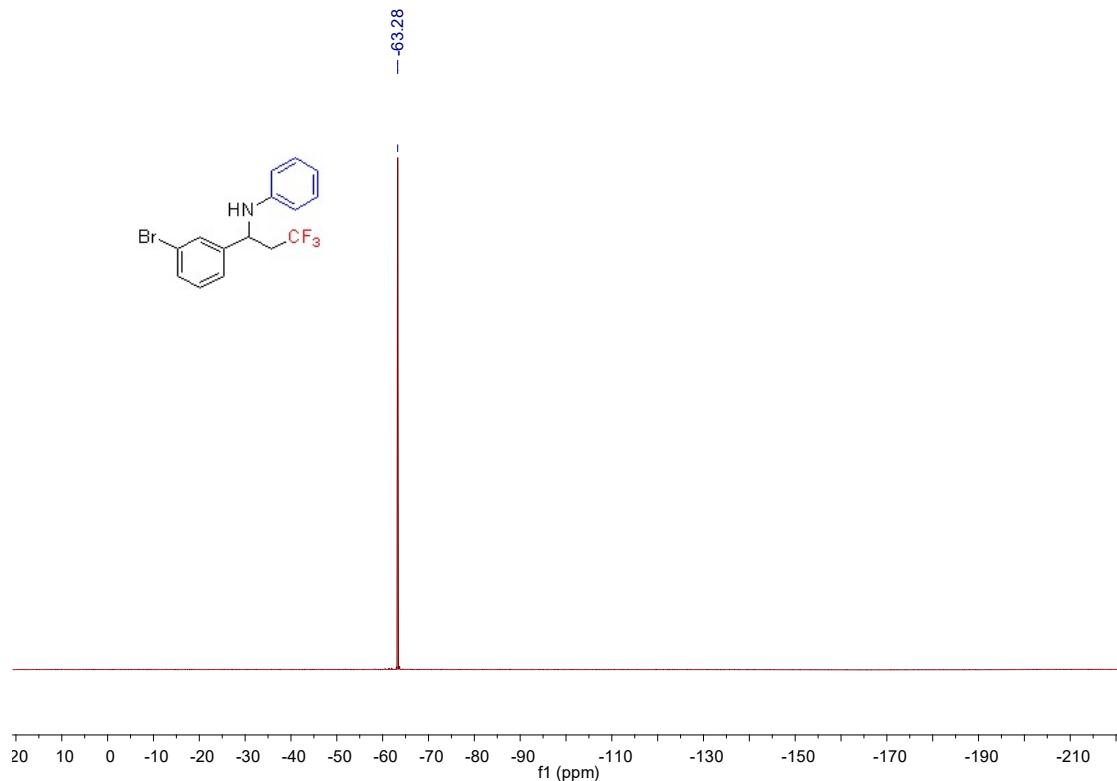
¹³C NMR of product 4j in CDCl₃ (100 MHz)



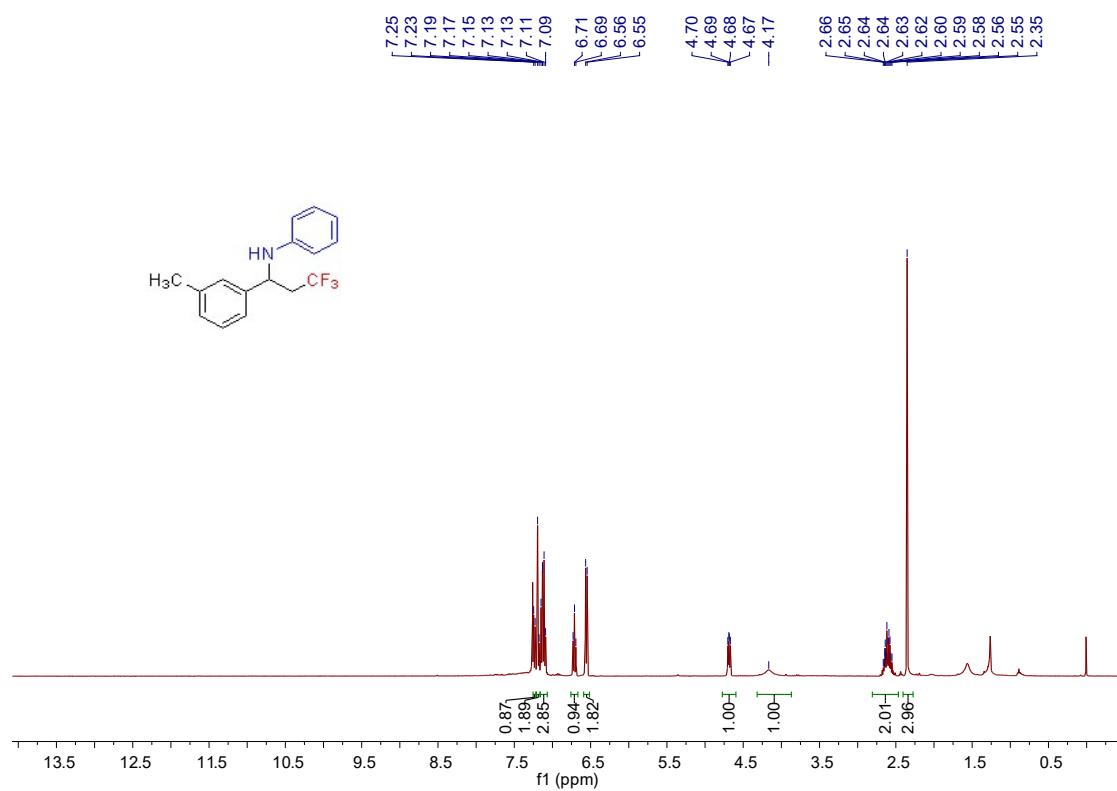
¹⁹F NMR of product 4j in CDCl₃ (376 MHz)



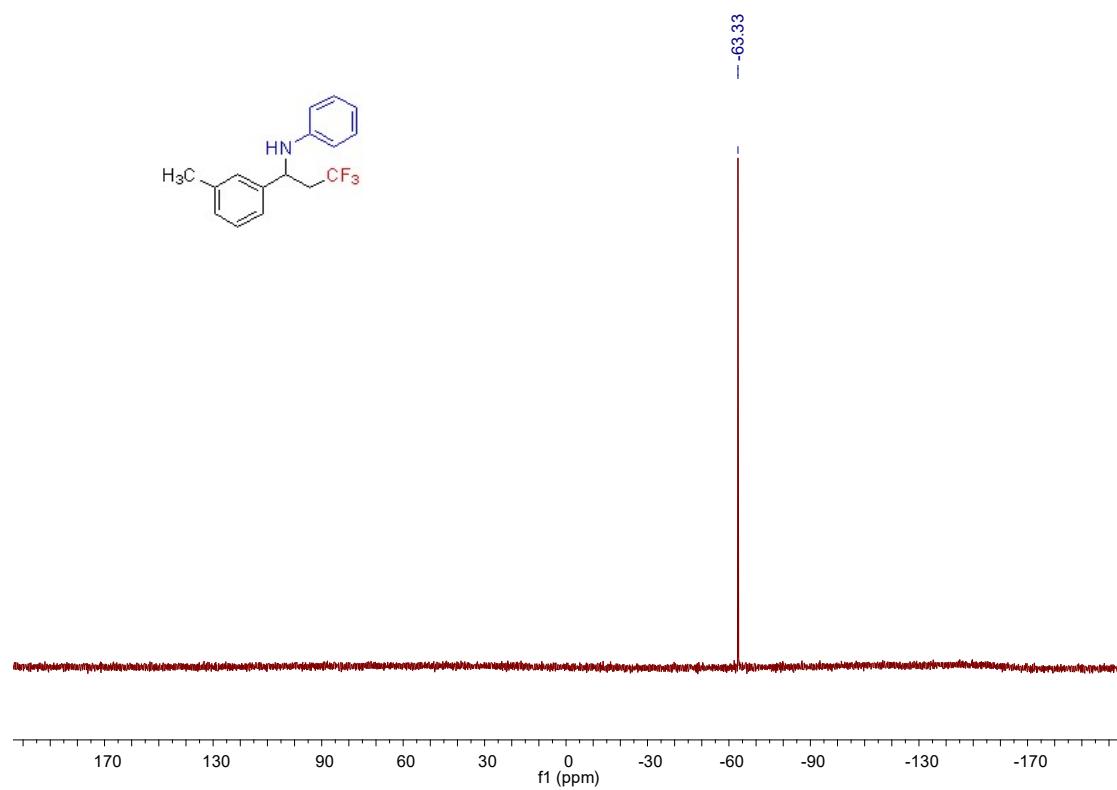
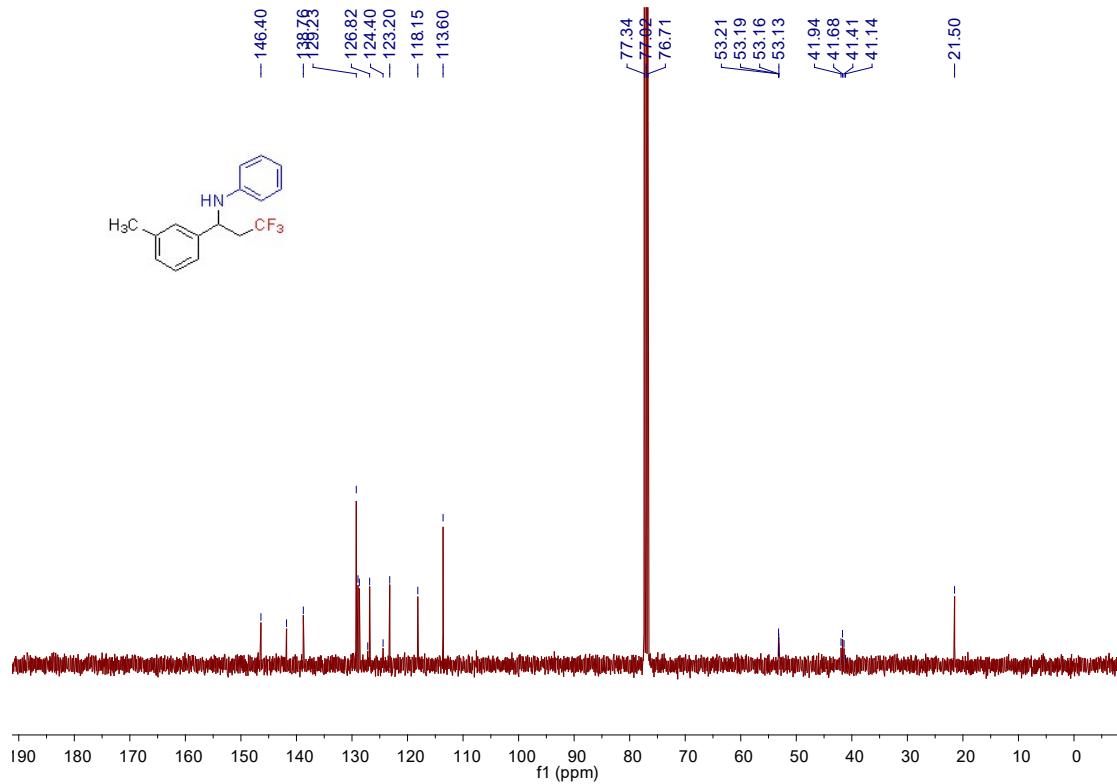
¹³C NMR of product 4k in CDCl₃ (100 MHz)



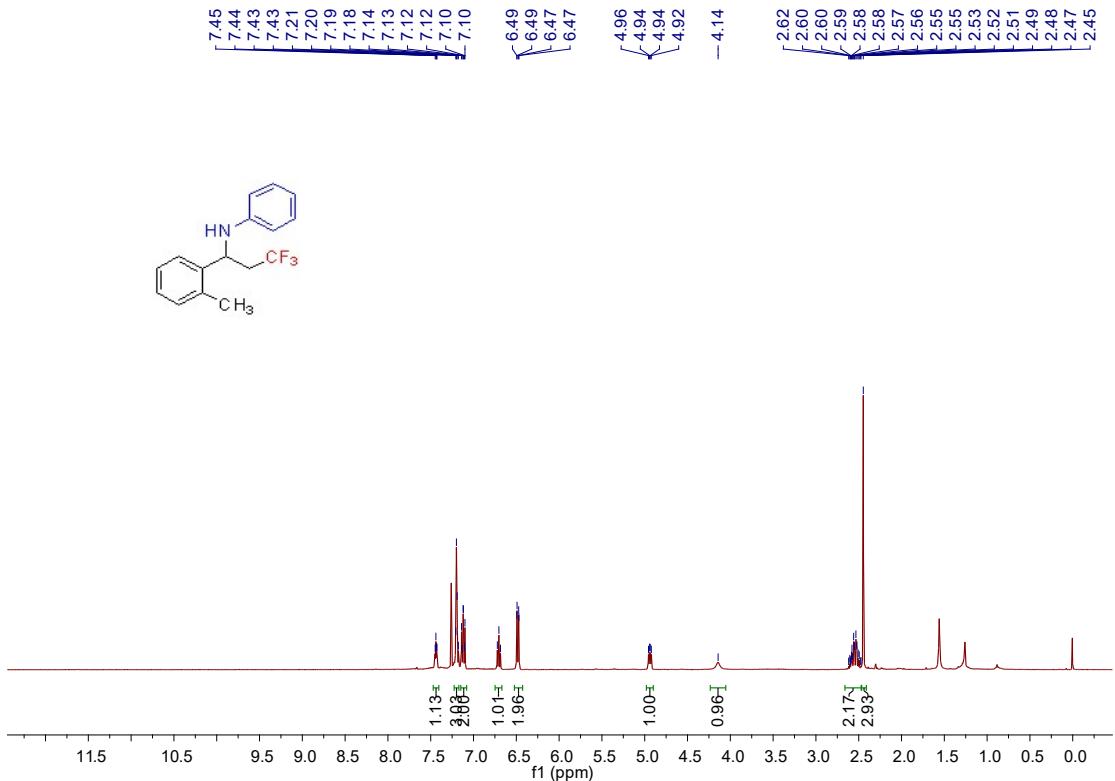
¹⁹F NMR of product 4k in CDCl₃ (376 MHz)



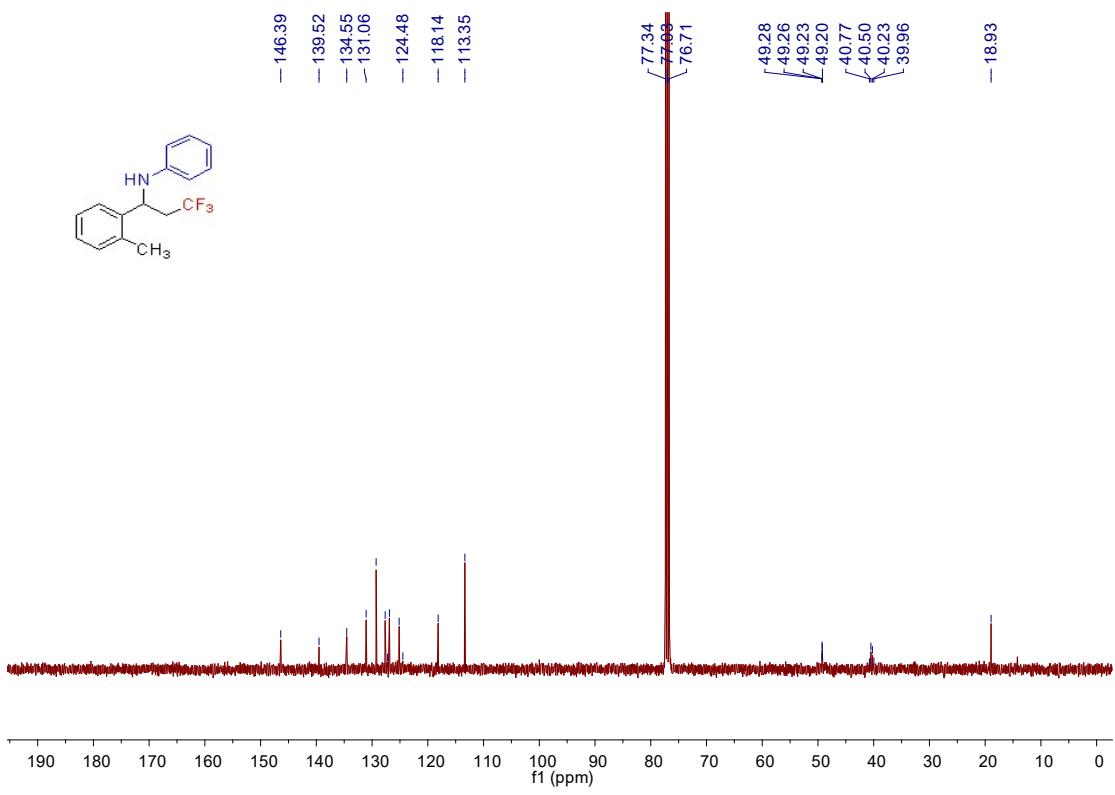
¹H NMR of product 4l in CDCl₃ (400 MHz)



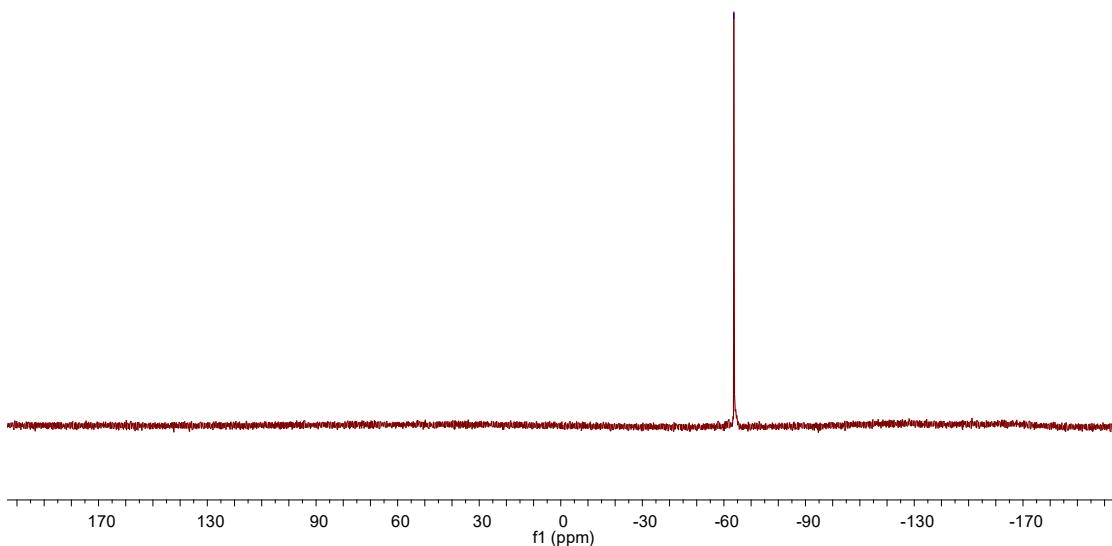
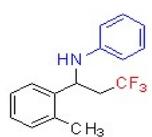
^{19}F NMR of product 4l in CDCl_3 (376 MHz)



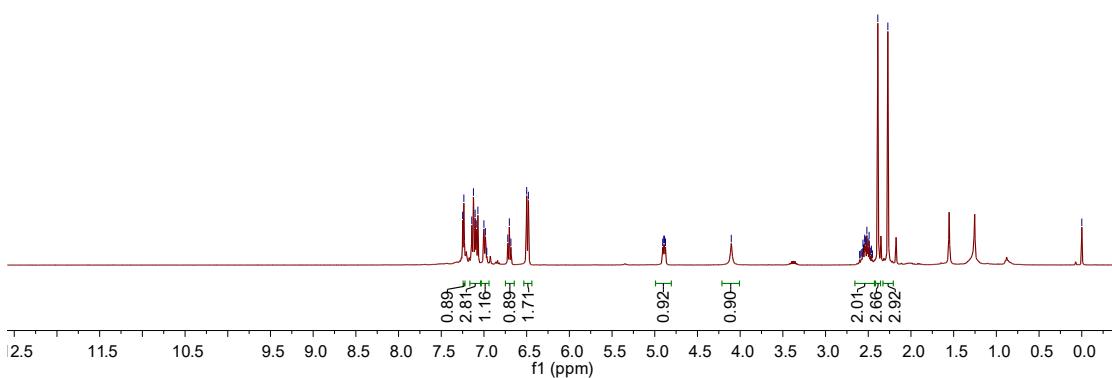
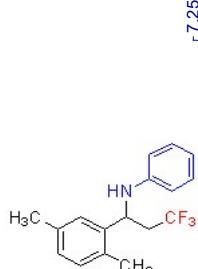
¹H NMR of product 4m in CDCl₃ (400 MHz)



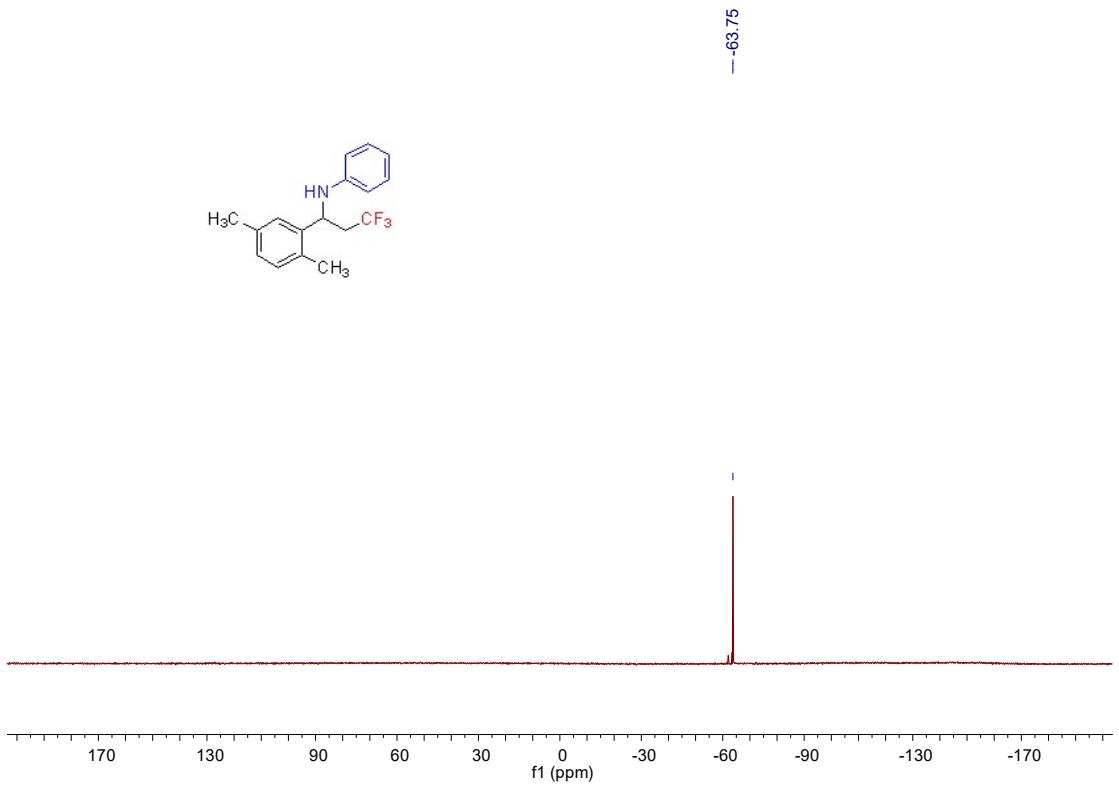
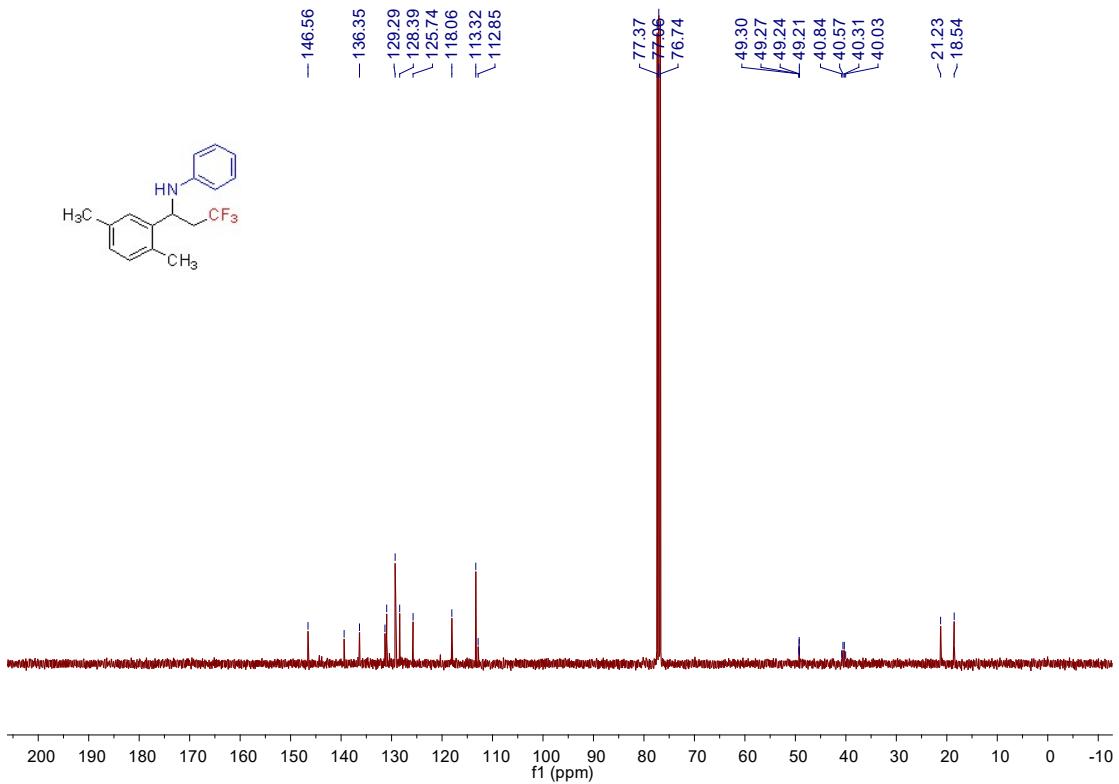
¹³C NMR of product 4m in CDCl₃ (100 MHz)

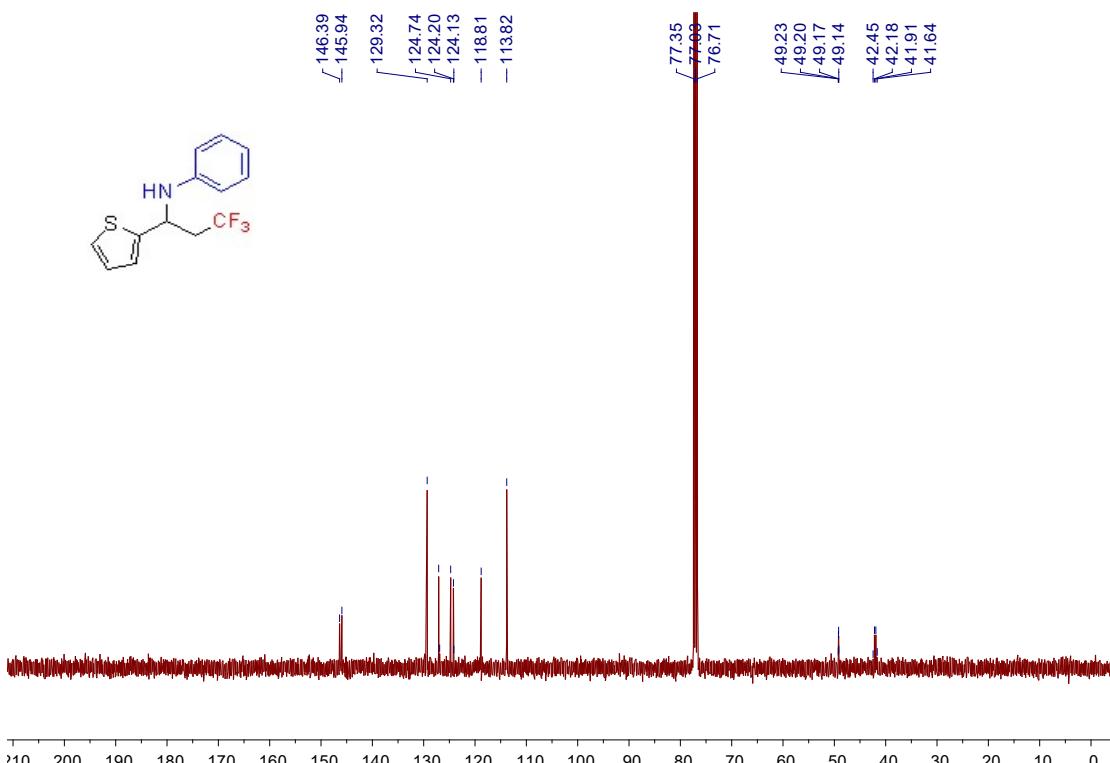
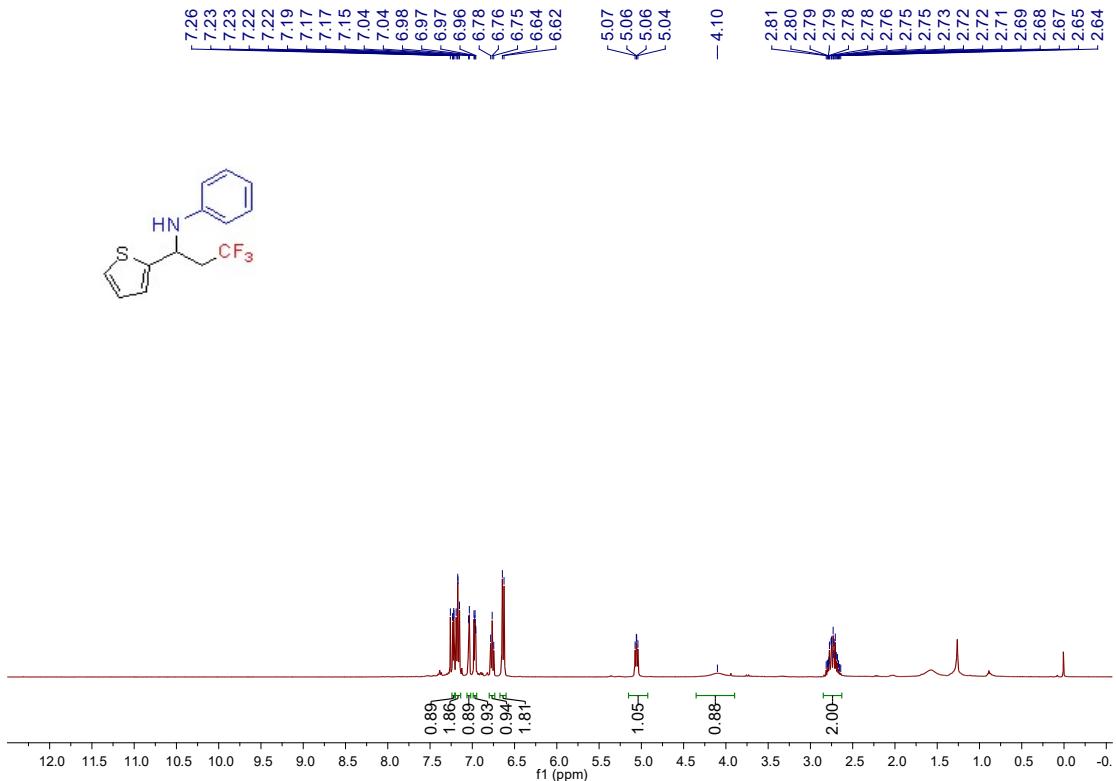


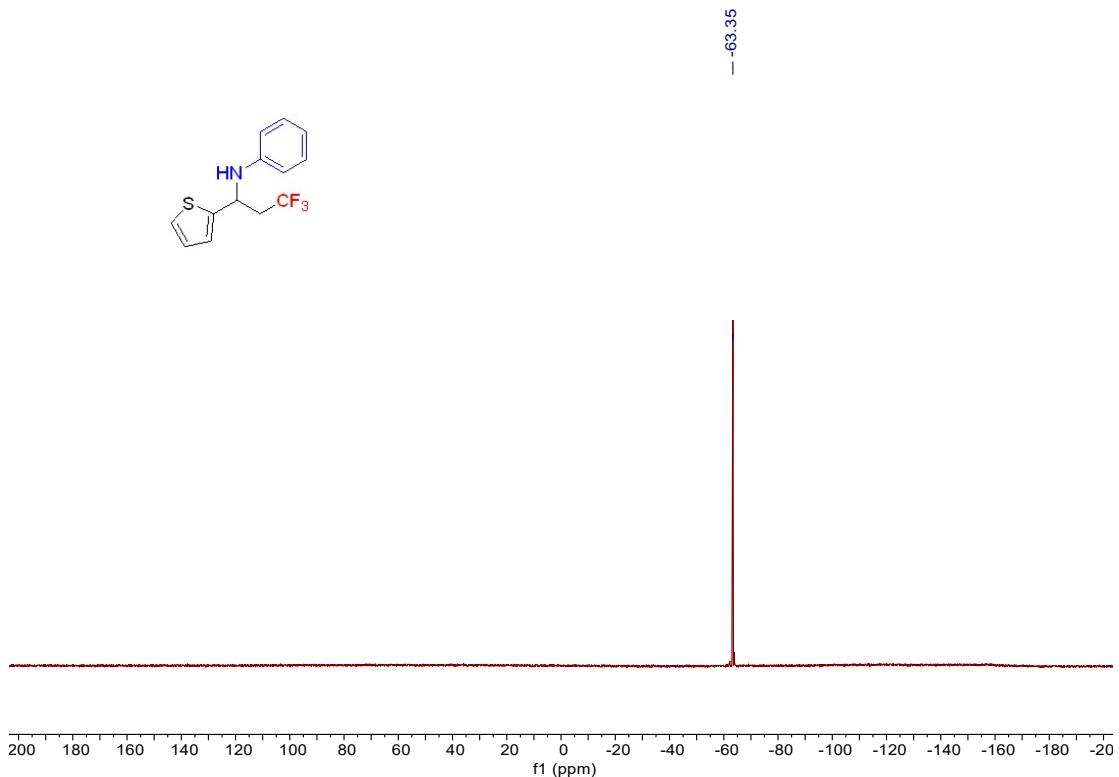
^{19}F NMR of product 4m in CDCl_3 (376 MHz)



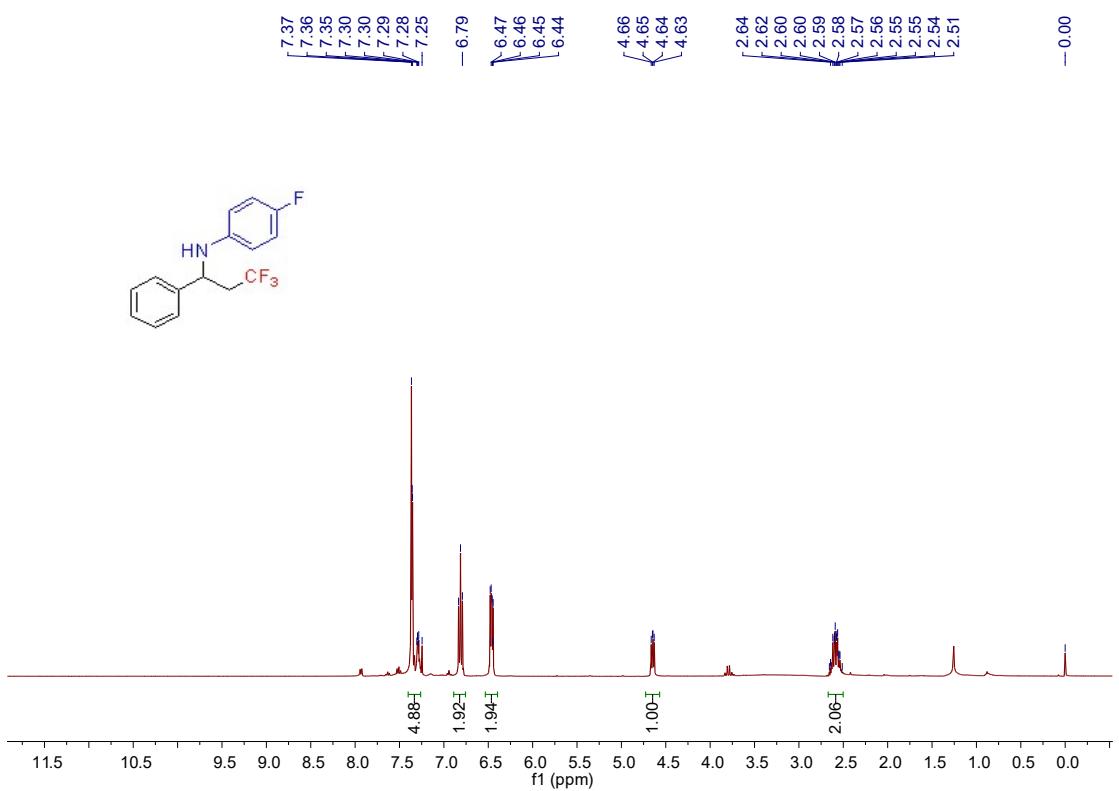
^1H NMR of product 4n in CDCl_3 (400 MHz)



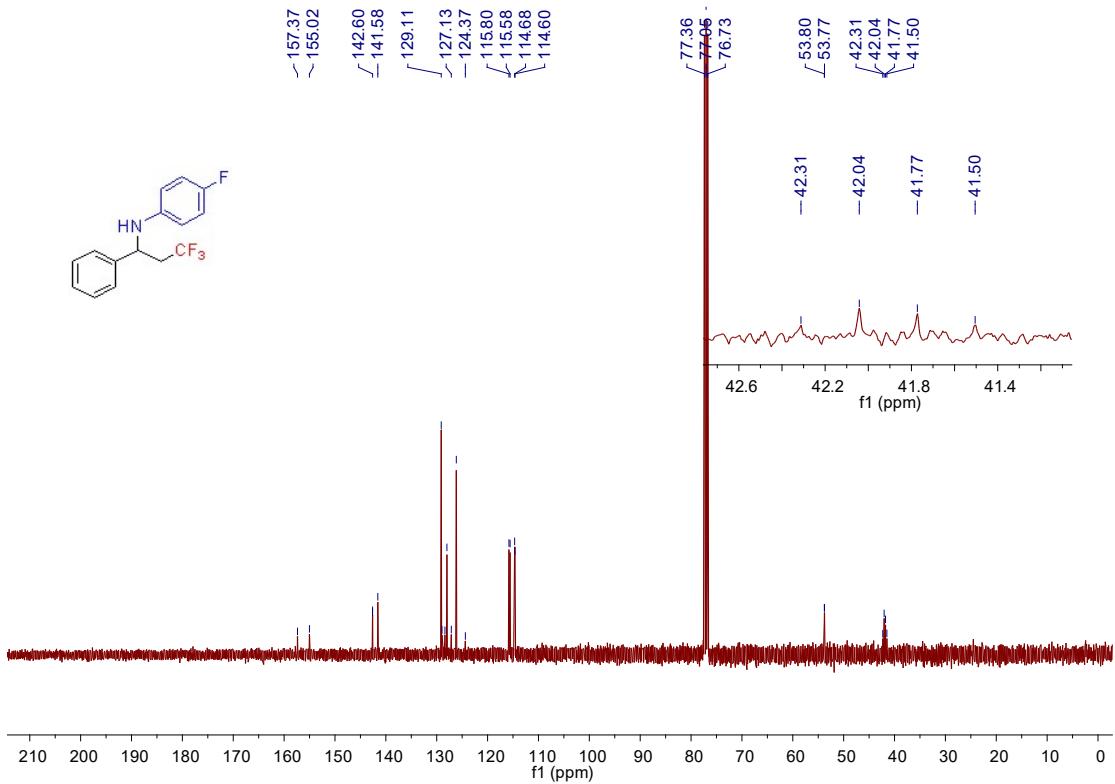




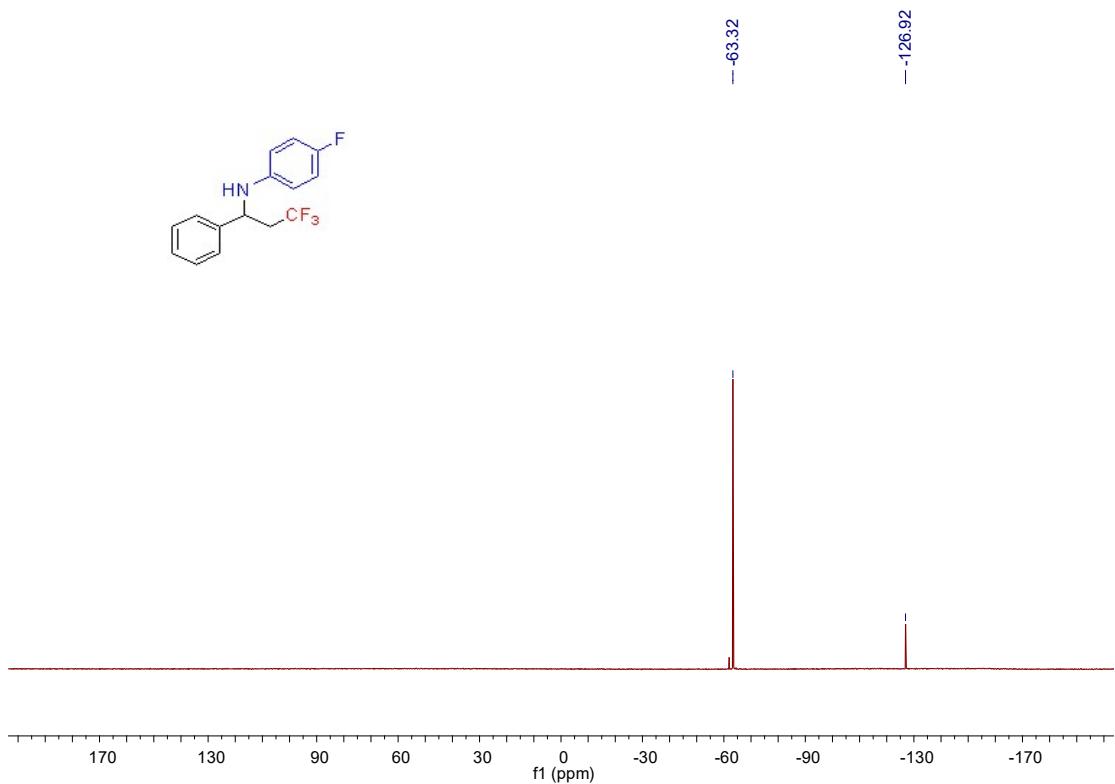
¹⁹F NMR of product 4o in CDCl₃ (376 MHz)



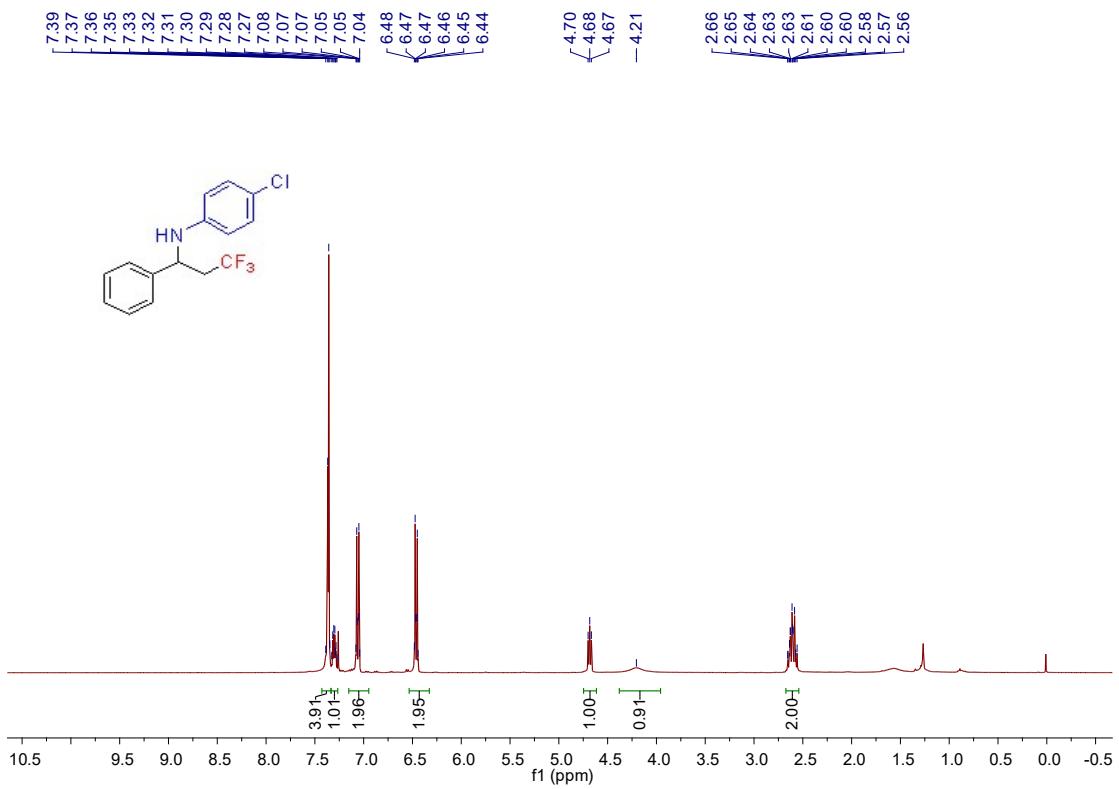
¹H NMR of product 5a in CDCl₃ (400 MHz)



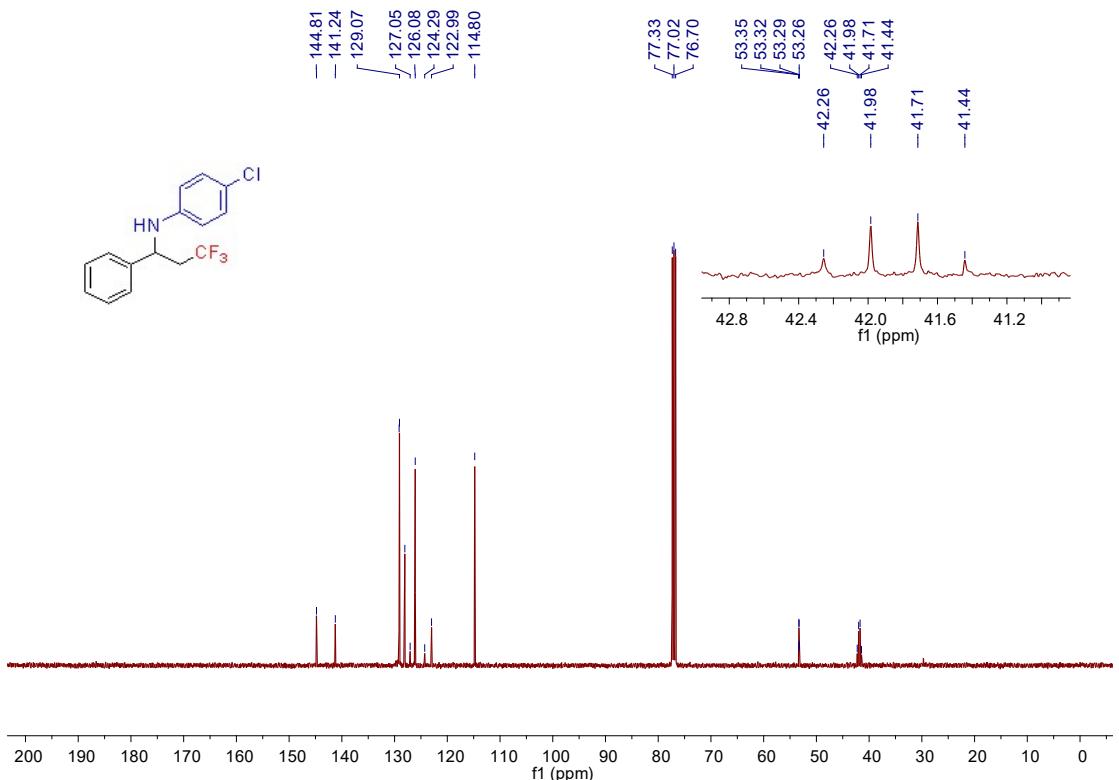
13C NMR of product 5a in CDCl_3 (100 MHz)



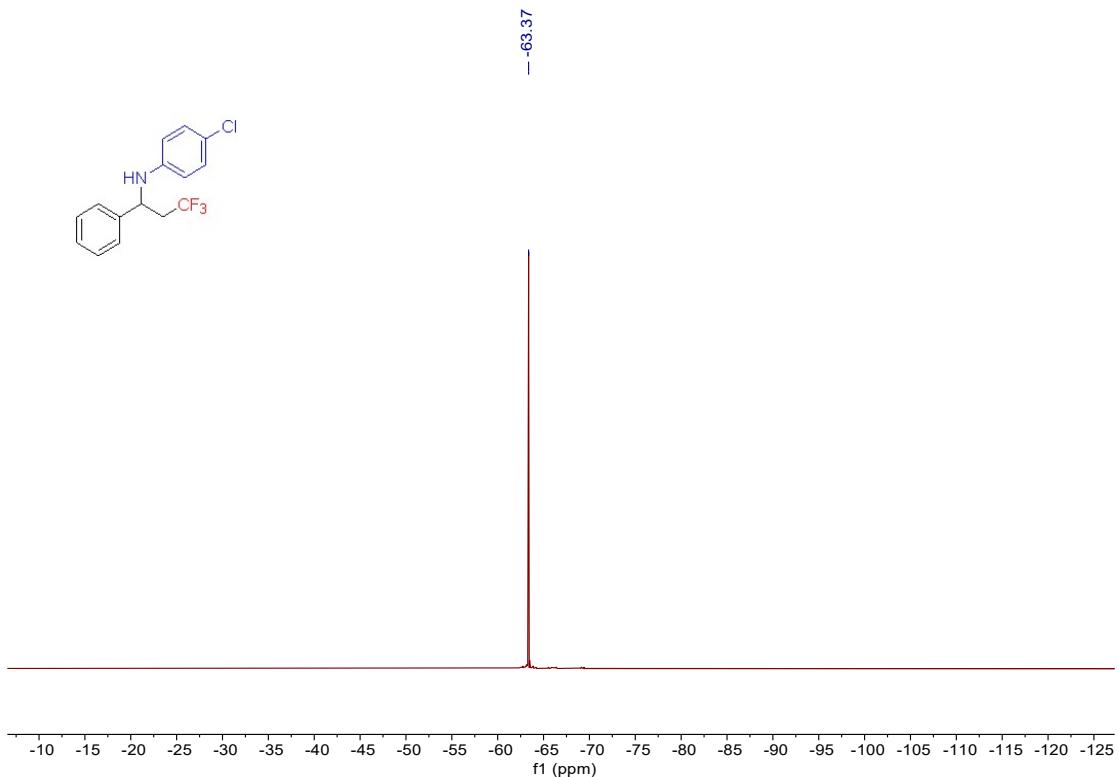
19F NMR of product 5a in CDCl_3 (376 MHz)



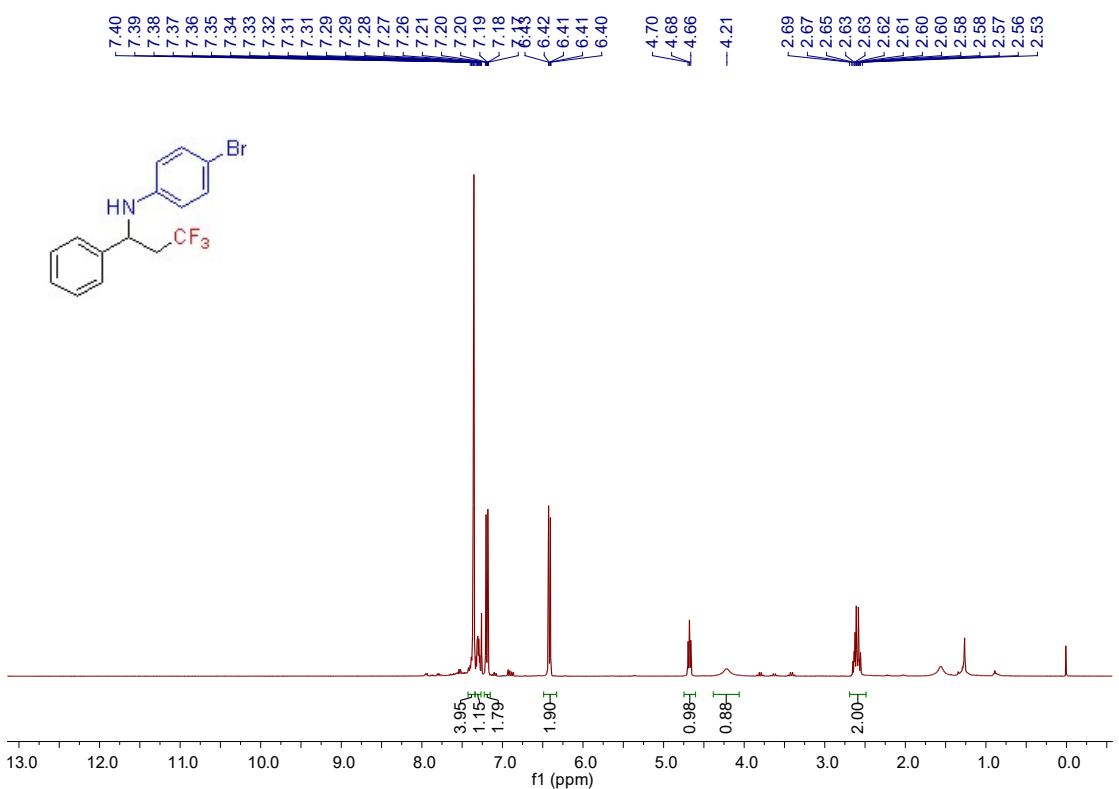
¹H NMR of product 5b in CDCl₃ (400 MHz)



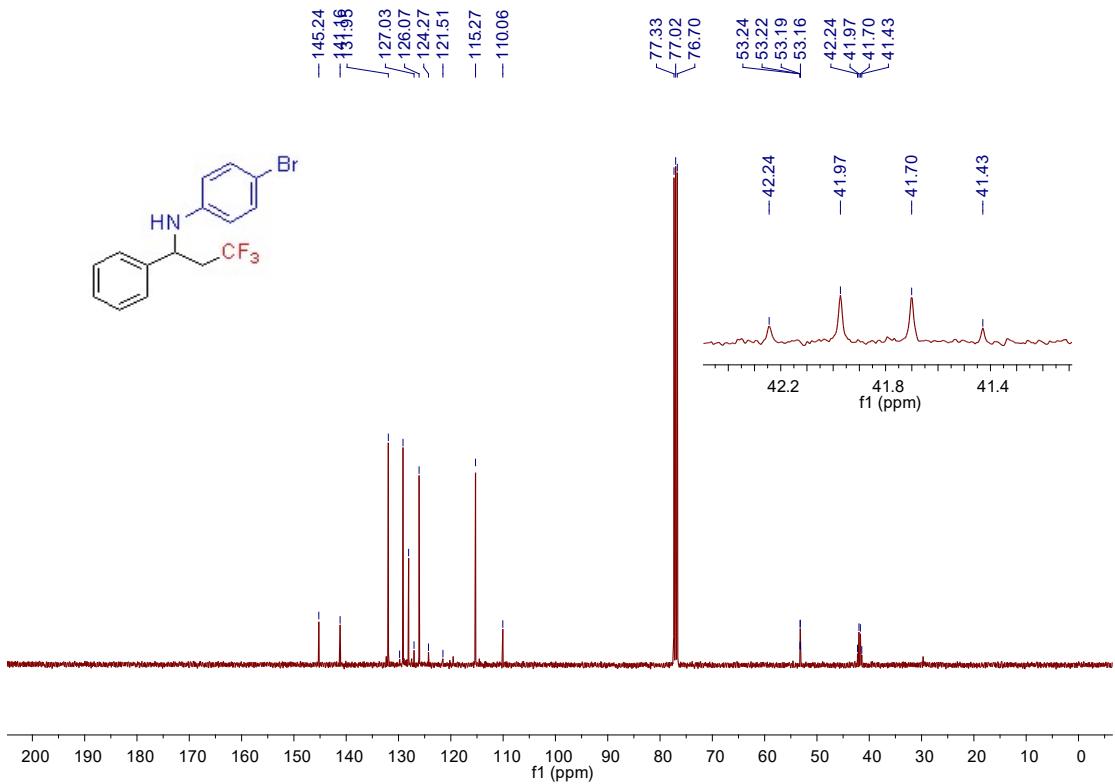
¹³C NMR of product 5b in CDCl₃ (100 MHz)



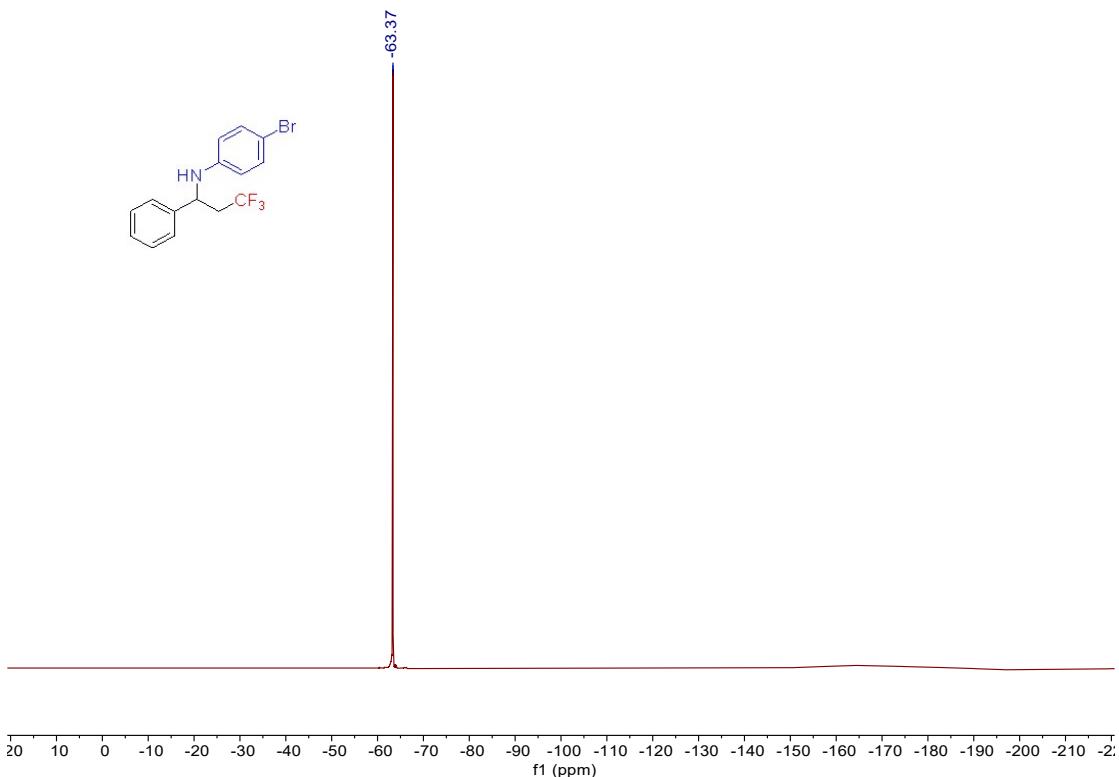
^{19}F NMR of product **5b** in CDCl_3 (376 MHz)



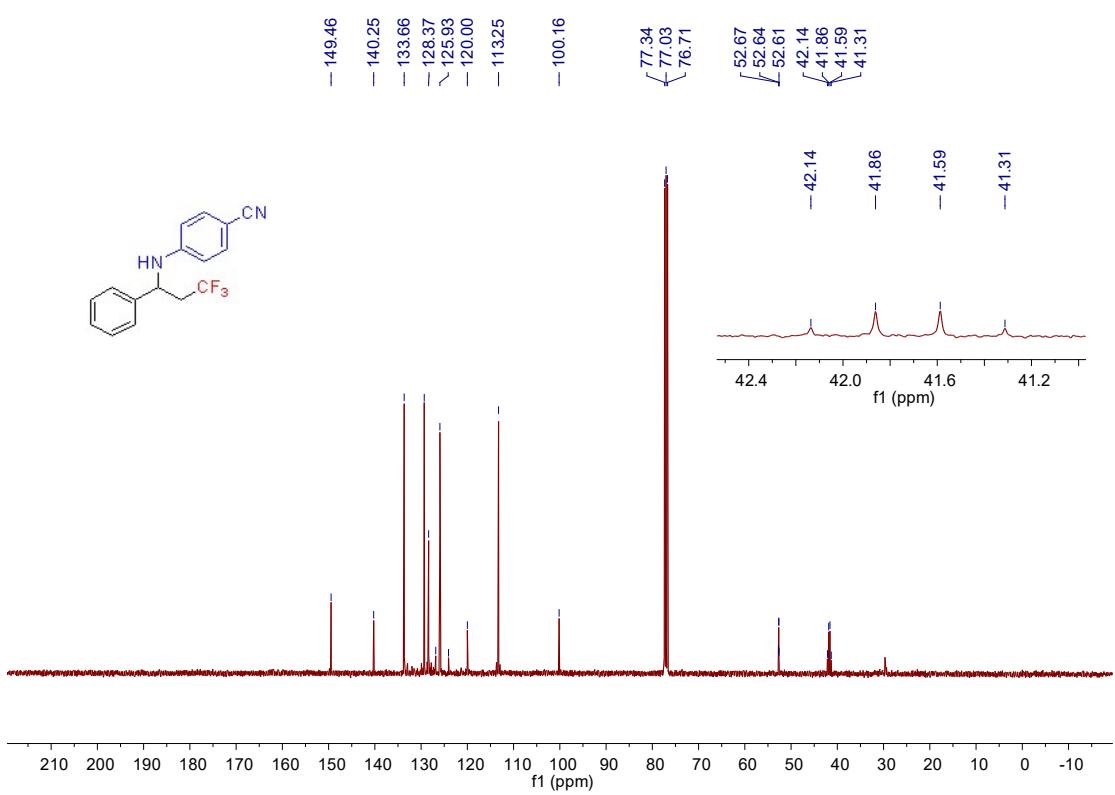
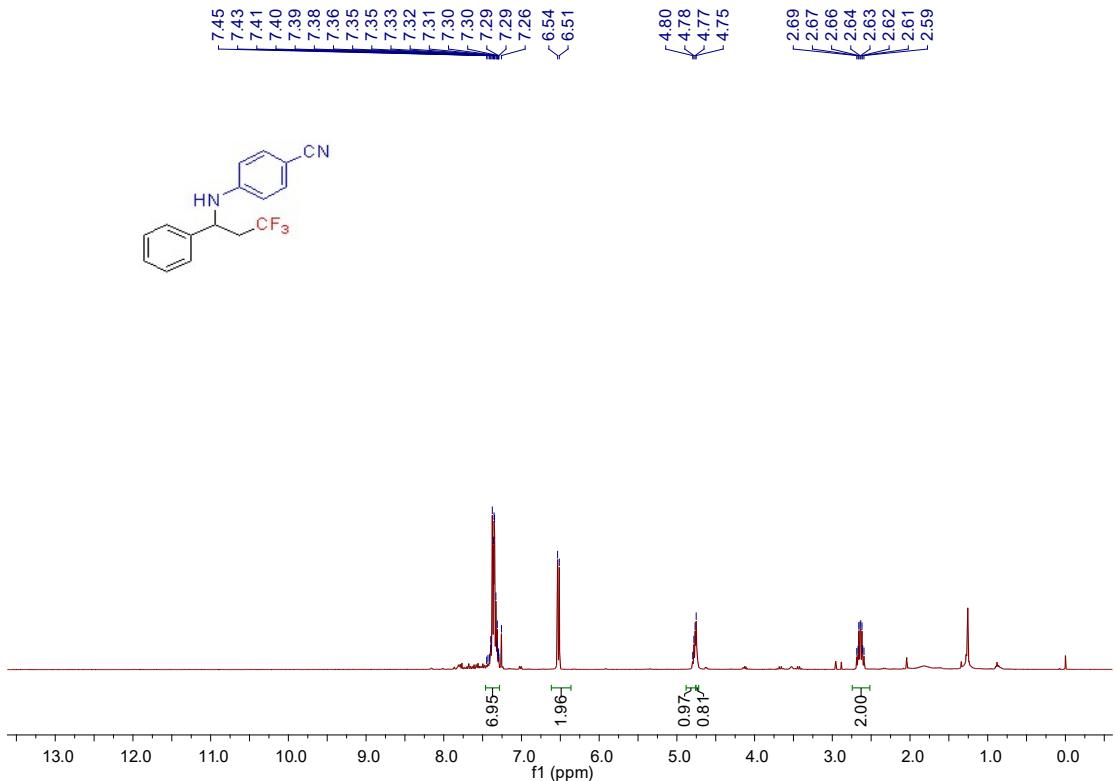
^1H NMR of product **5c** in CDCl_3 (400 MHz)

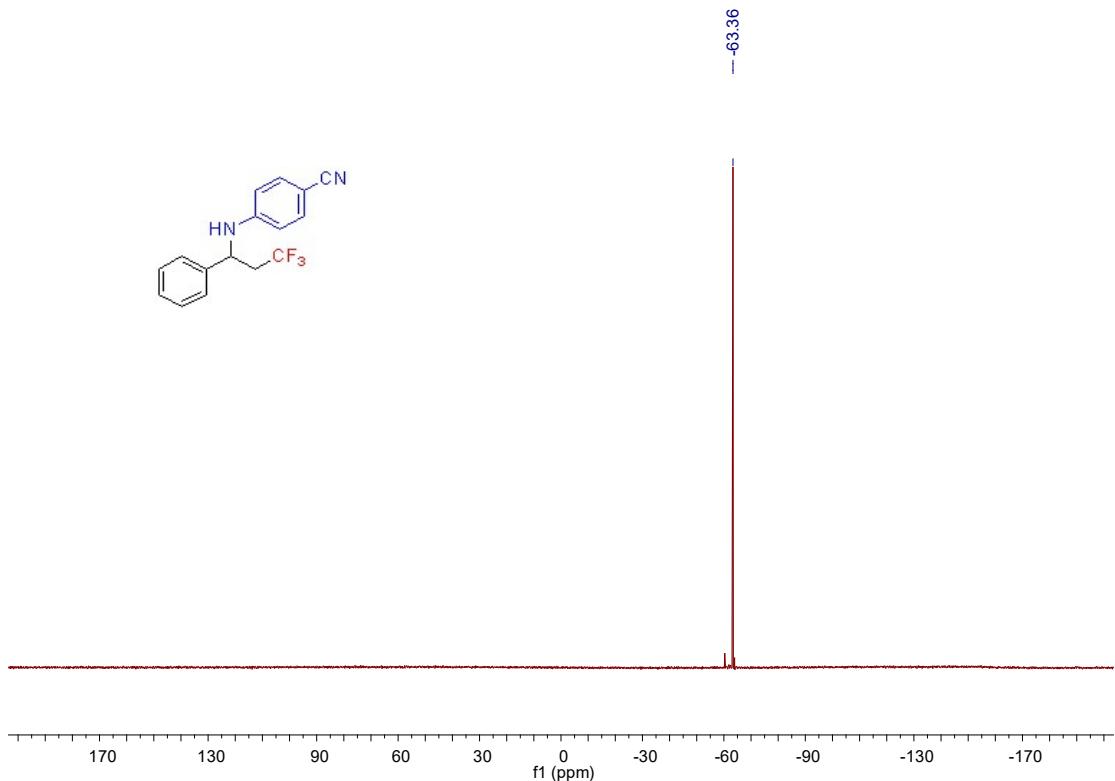


13C NMR of product 5c in CDCl₃ (100 MHz)

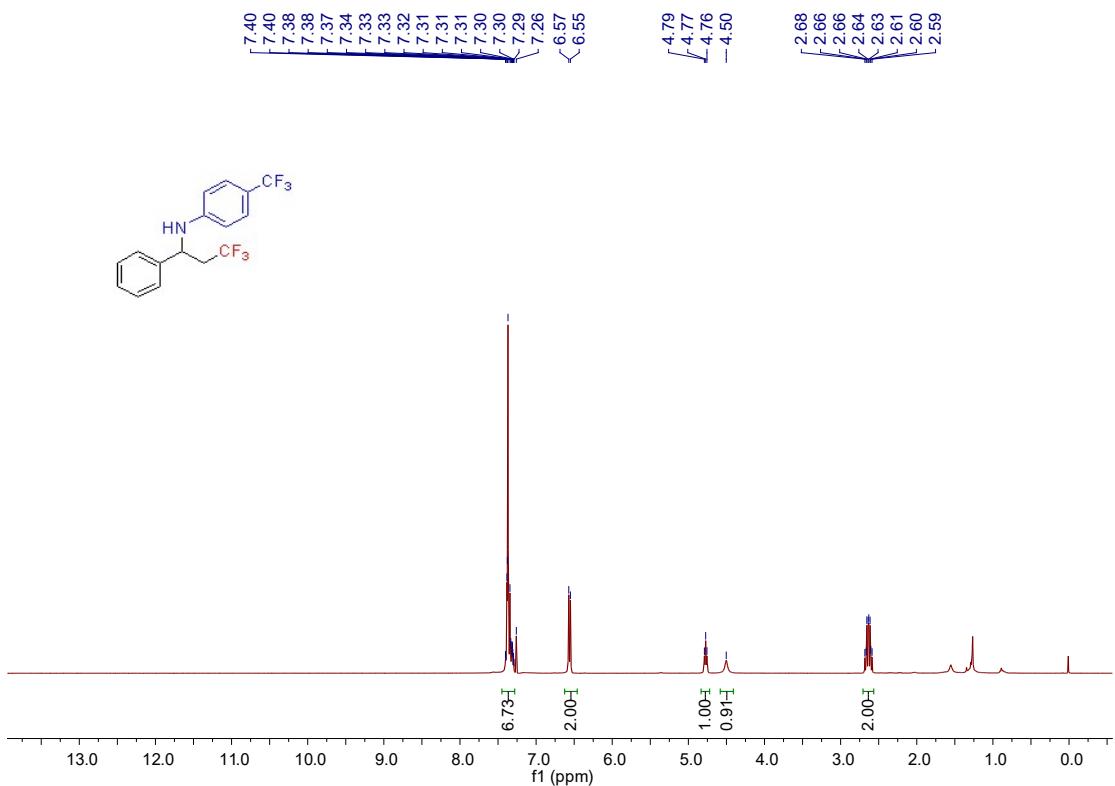


19F NMR of product 5c in CDCl₃ (376 MHz)

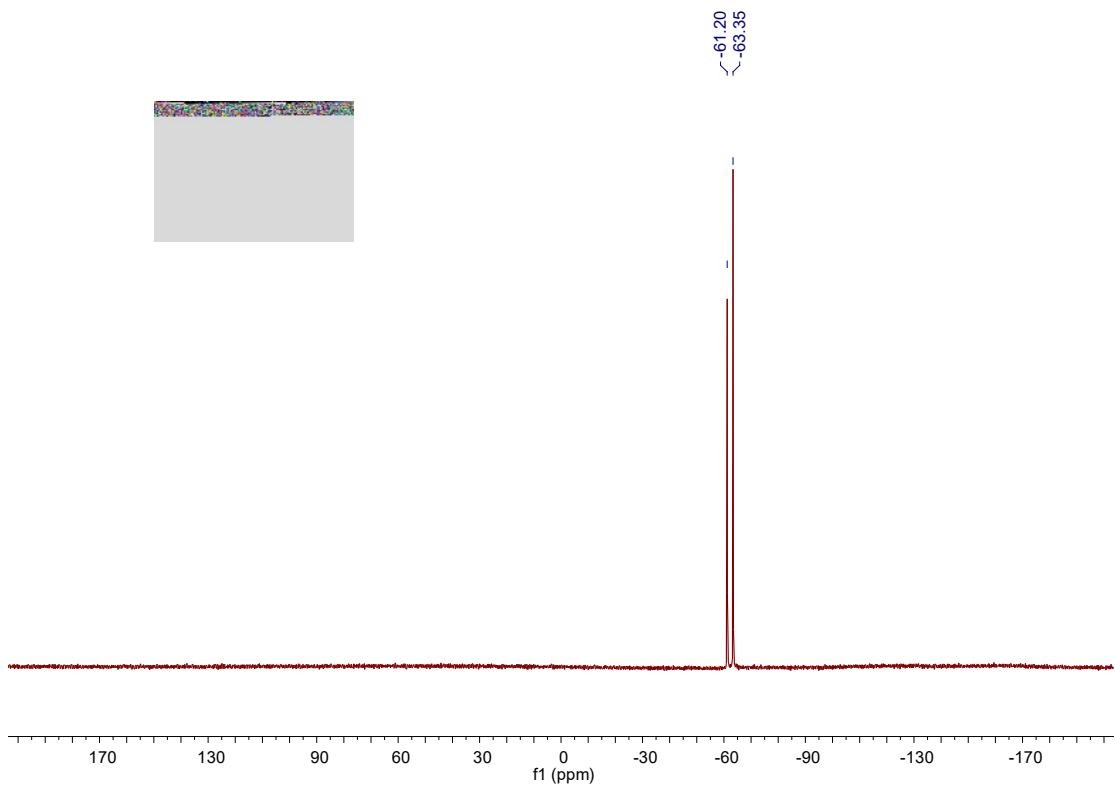
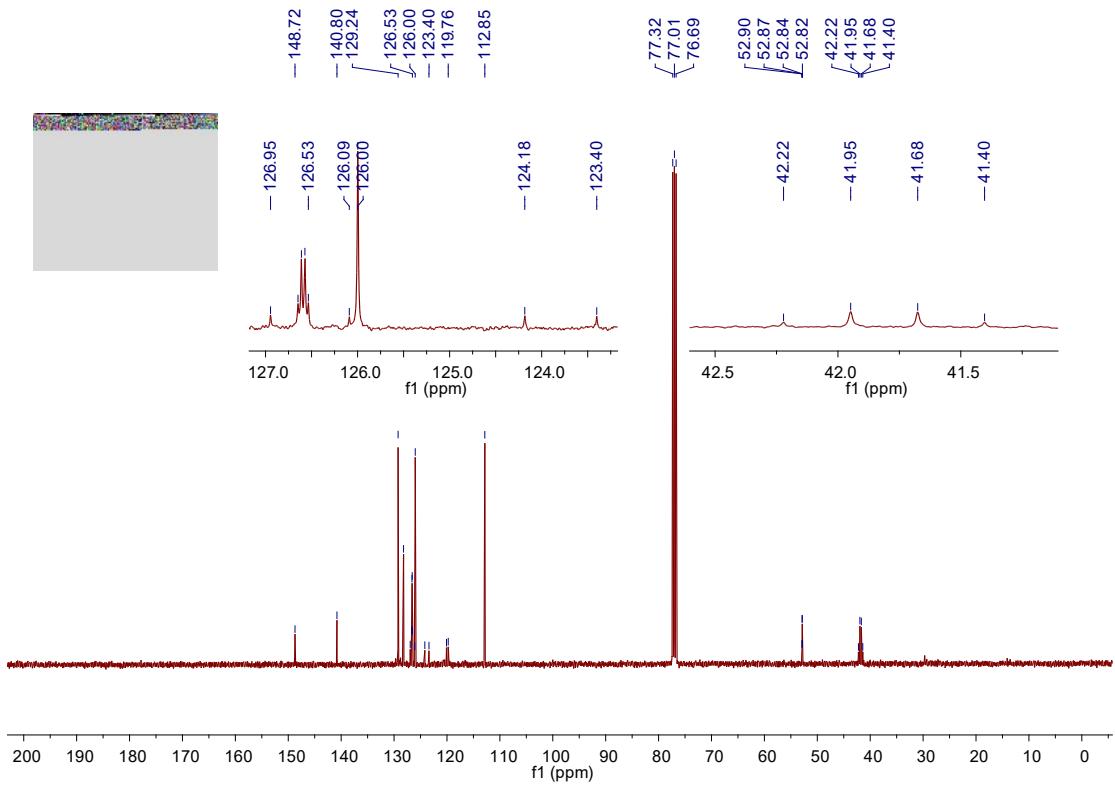


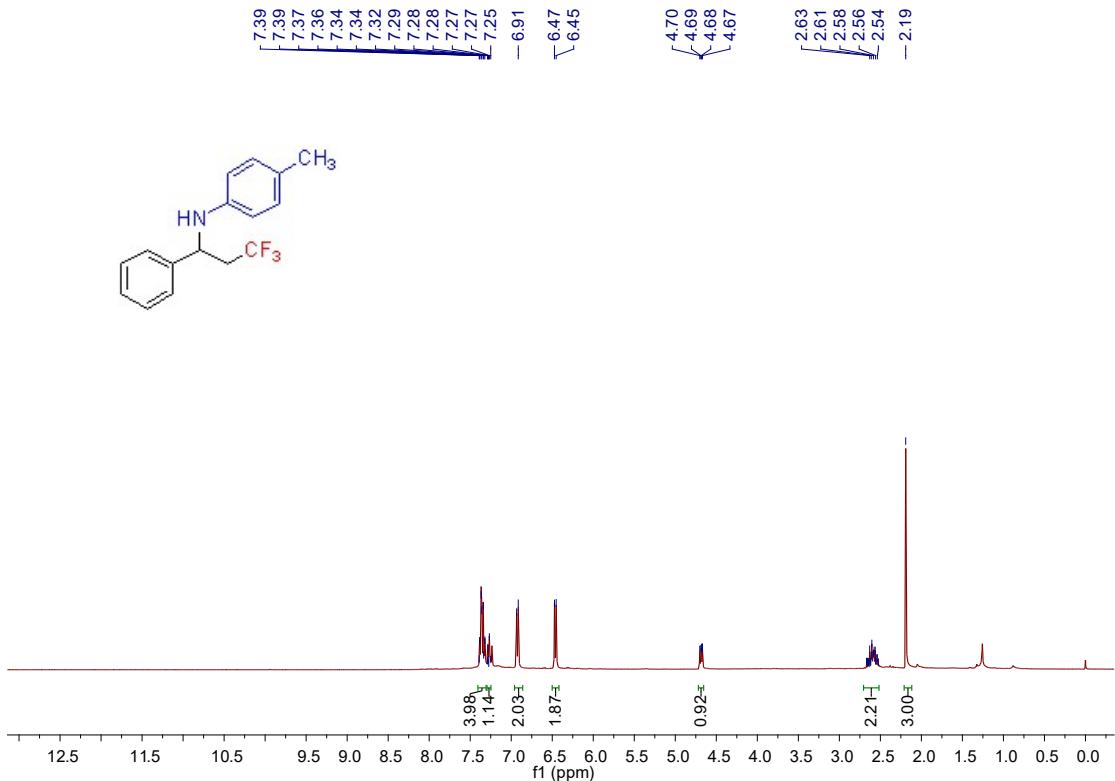


¹⁹F NMR of product 5d in CDCl₃ (376 MHz)

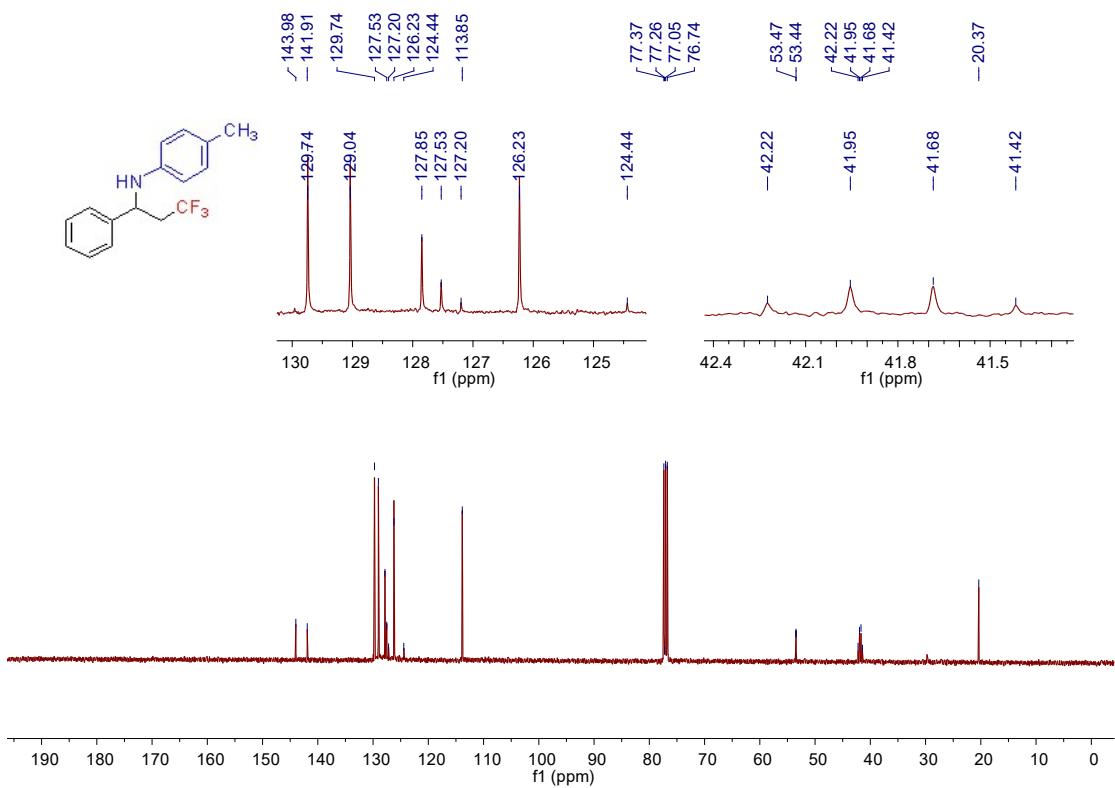


¹H NMR of product 5e in CDCl₃ (400 MHz)

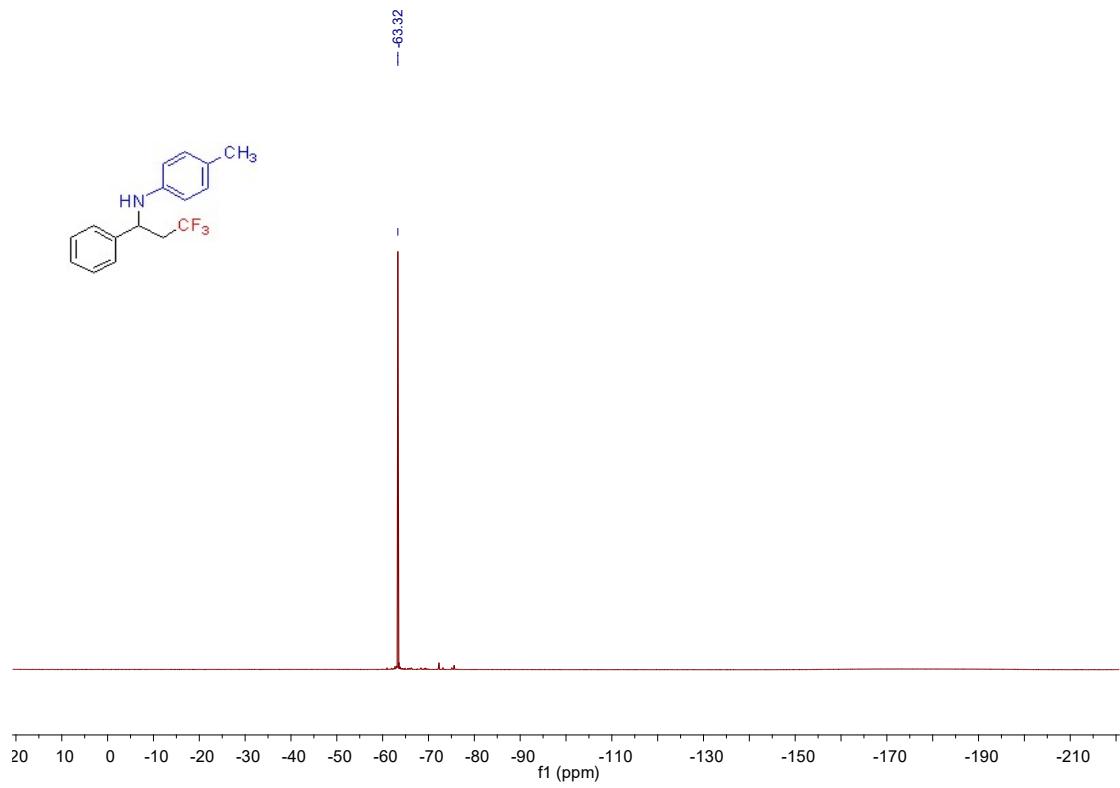




¹H NMR of product 5f in CDCl₃ (400 MHz)

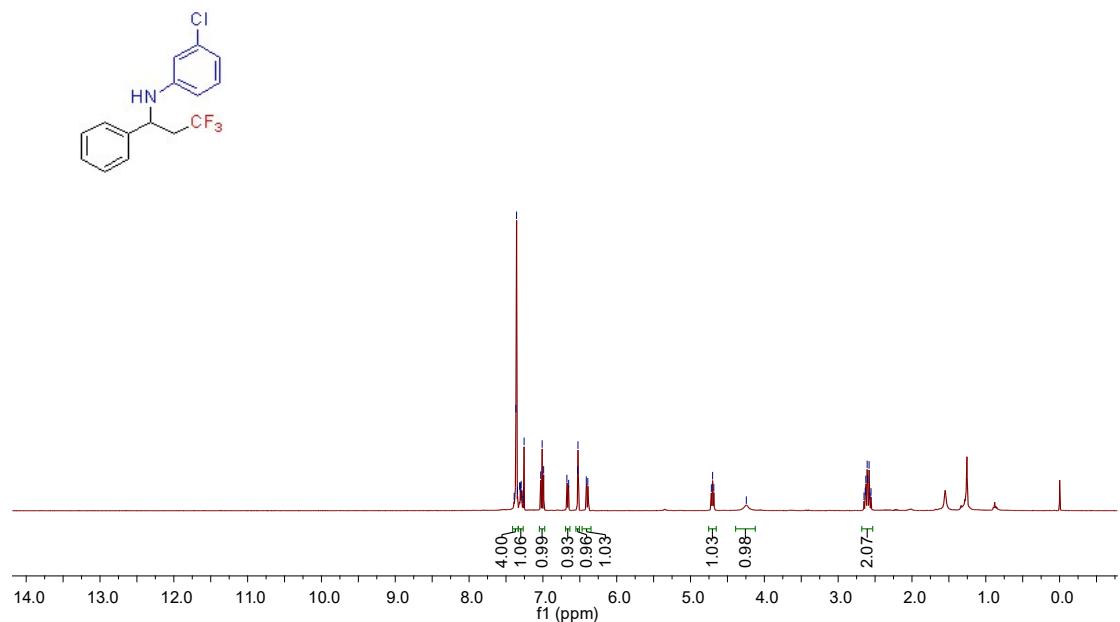


¹³C NMR of product 5f in CDCl₃ (100 MHz)

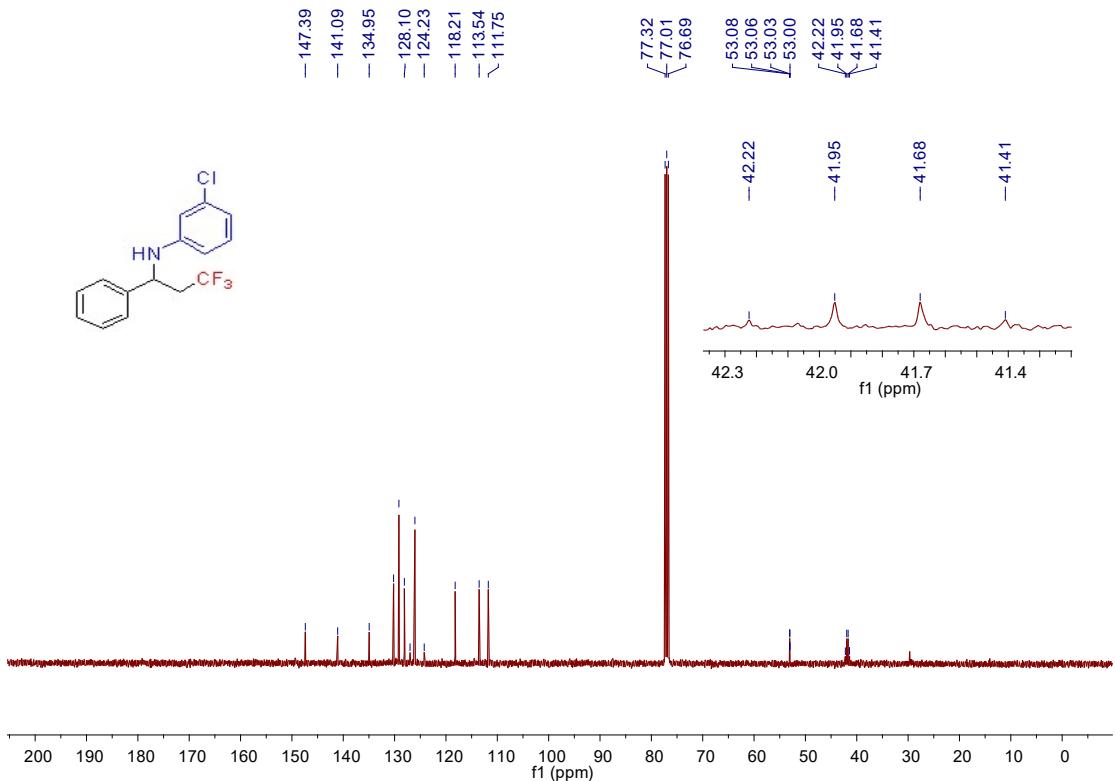


^{19}F NMR of product 5f in CDCl_3 (376 MHz)

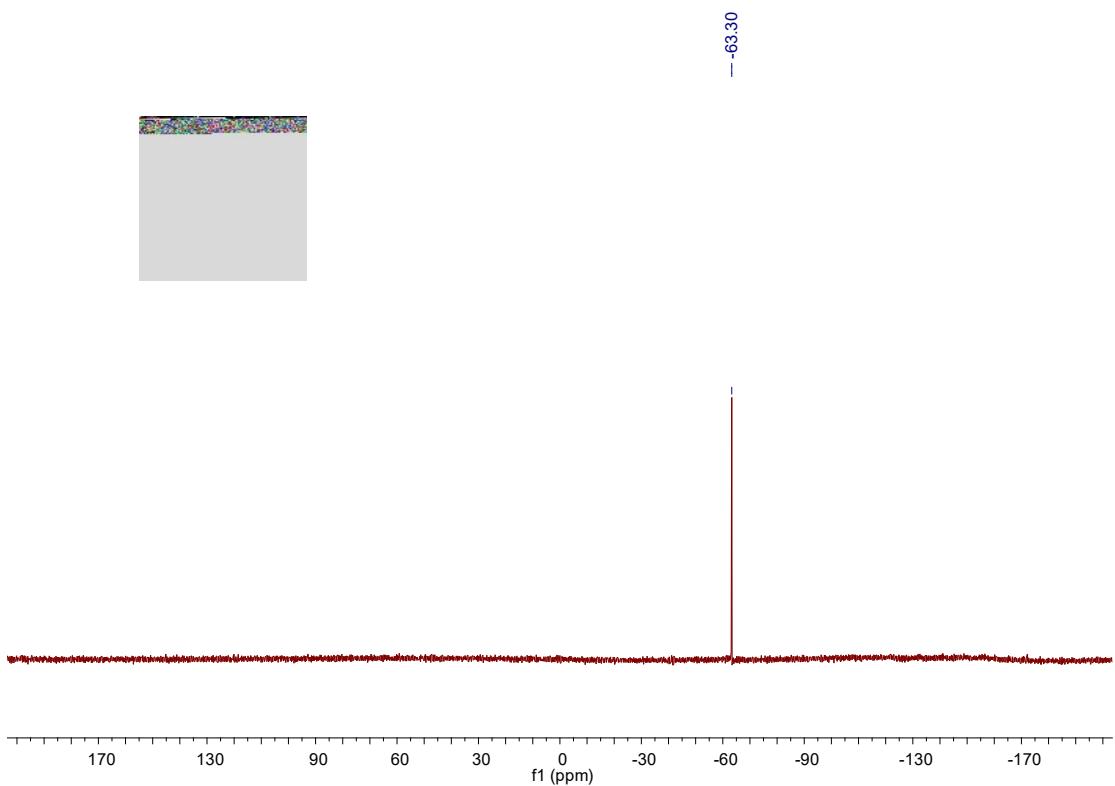
7.39
 7.37
 7.36
 7.34
 7.32
 7.31
 7.31
 7.29
 7.28
 7.27
 7.25
 7.03
 7.01
 6.99
 6.53
 6.52
 6.41
 6.39
 4.72
 4.70
 4.68
 -4.24



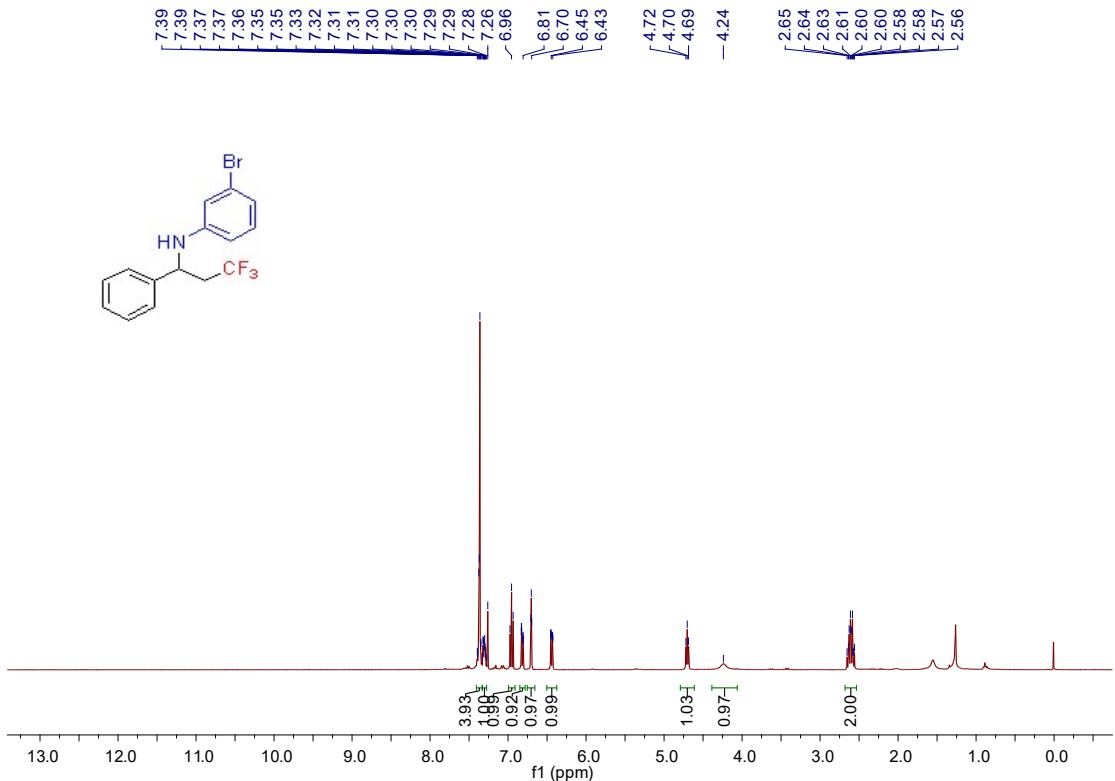
^1H NMR of product 5g in CDCl_3 (400 MHz)



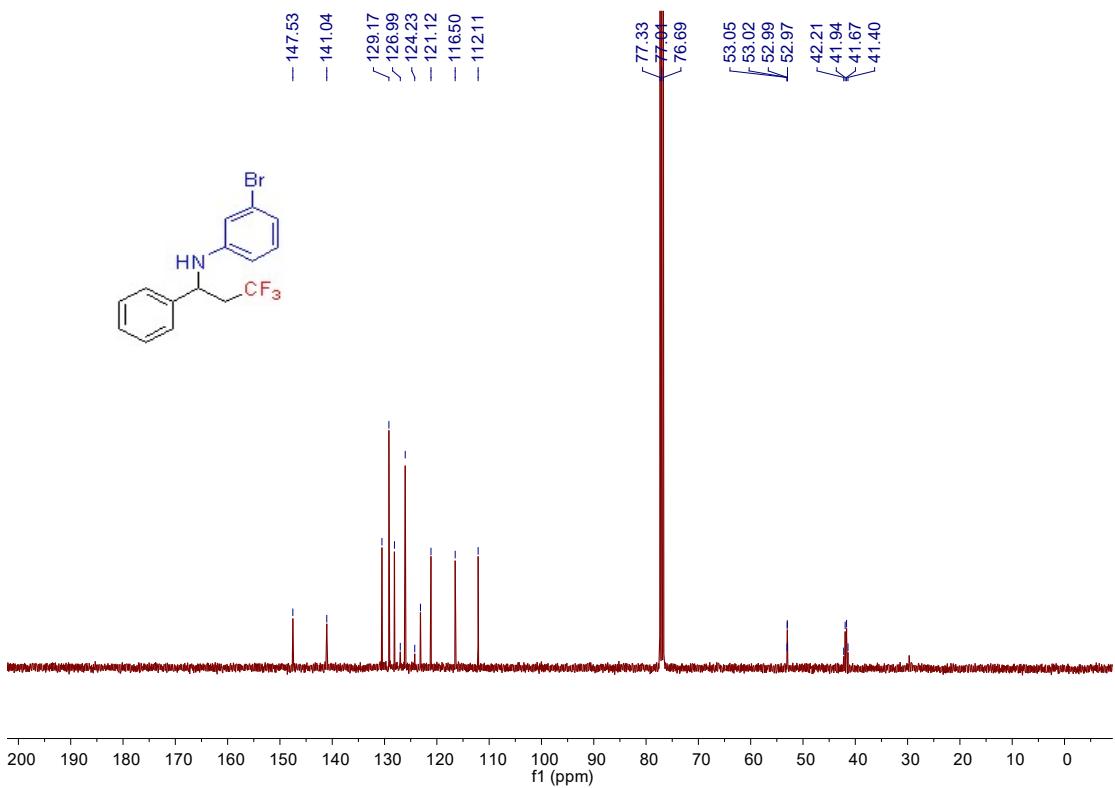
¹³C NMR of product 5g in CDCl₃ (100 MHz)



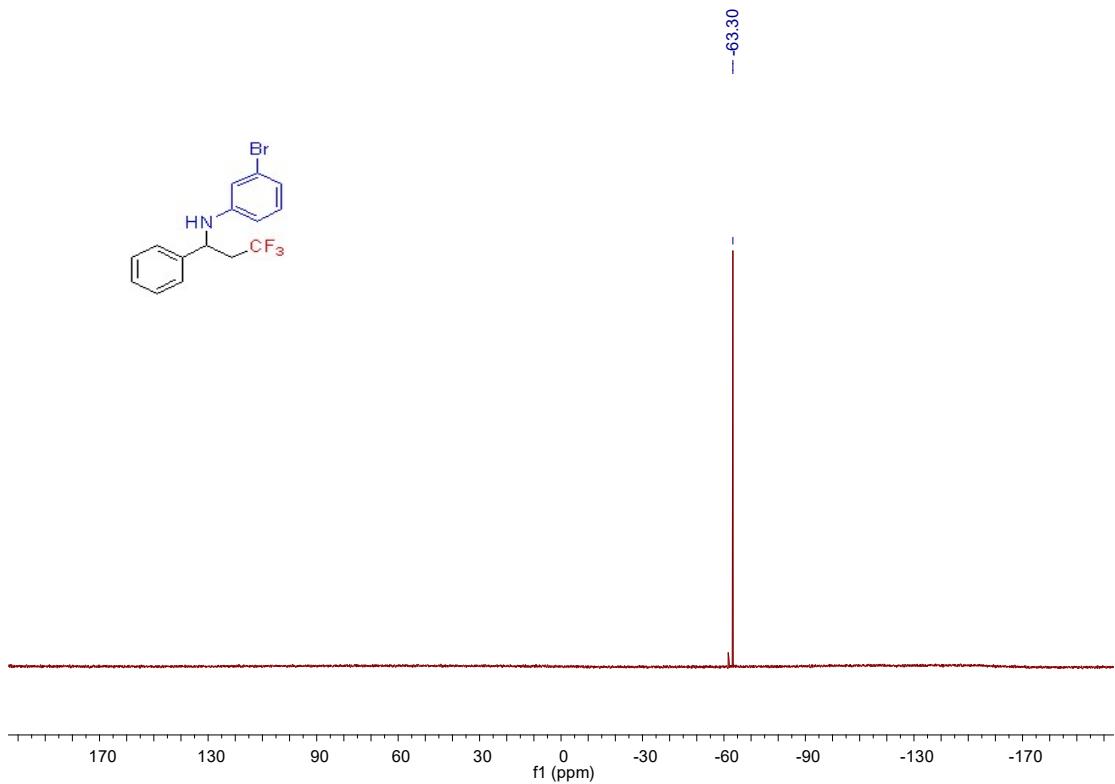
¹⁹F NMR of product 5g in CDCl₃ (376 MHz)



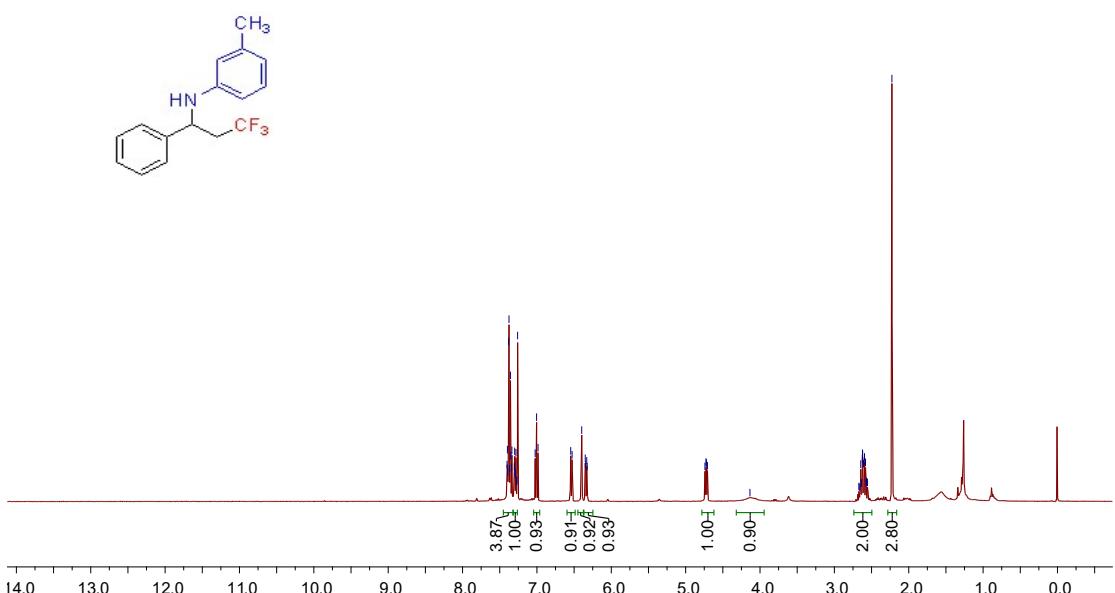
¹H NMR of product 5h in CDCl₃ (400 MHz)



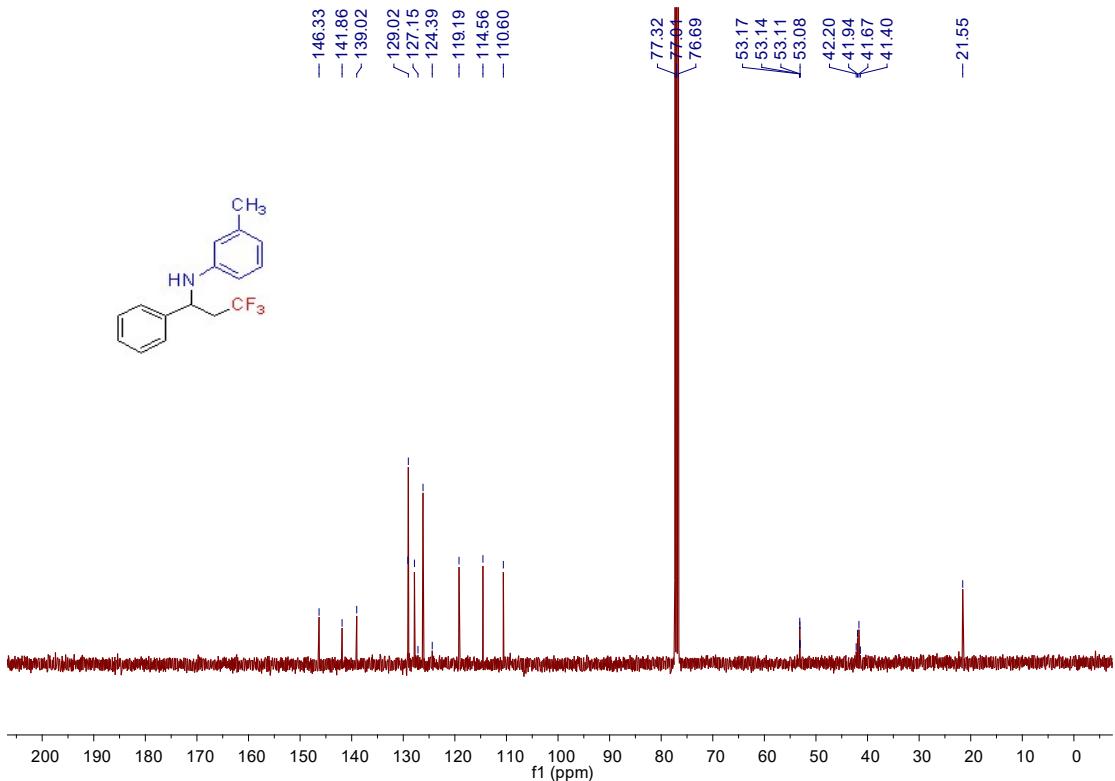
¹³C NMR of product 5h in CDCl₃ (100 MHz)



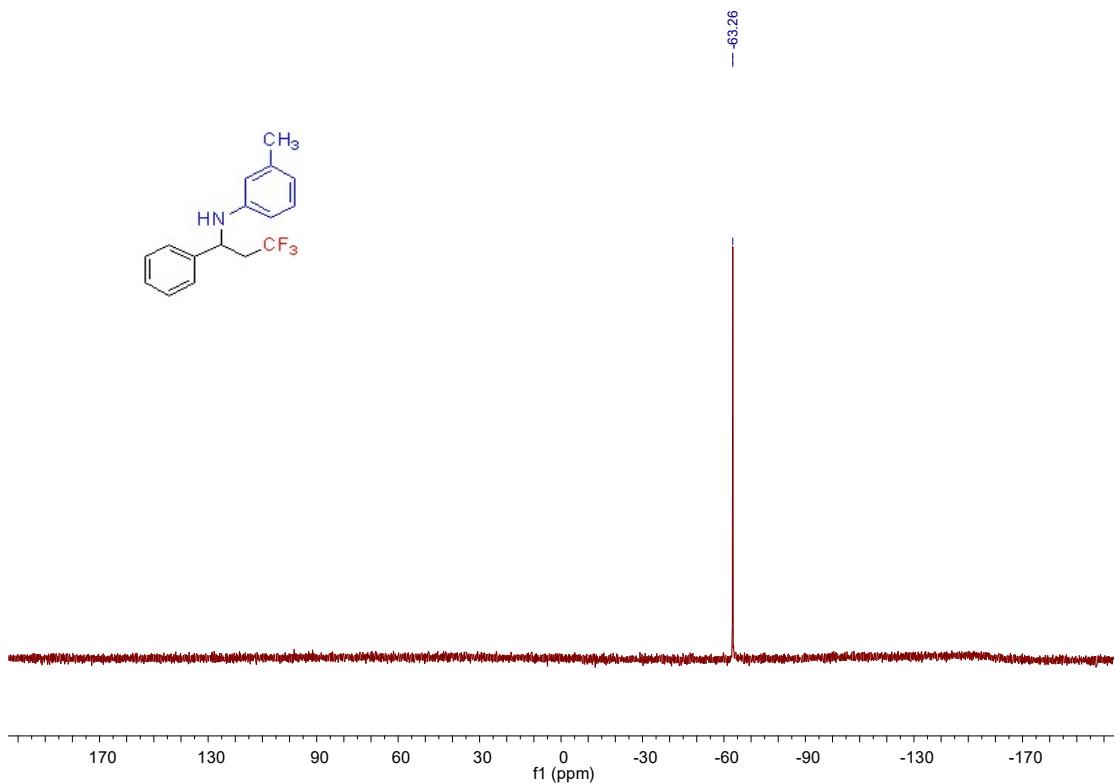
¹⁹F NMR of product 5h in CDCl₃ (376 MHz)



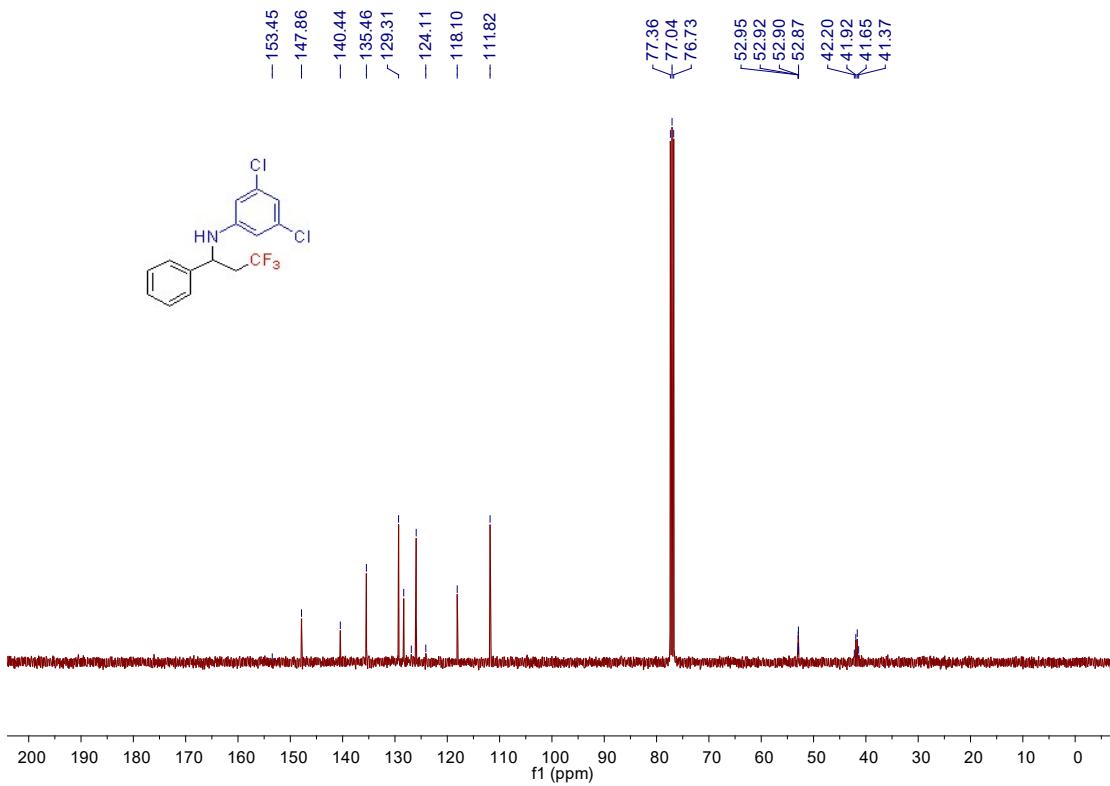
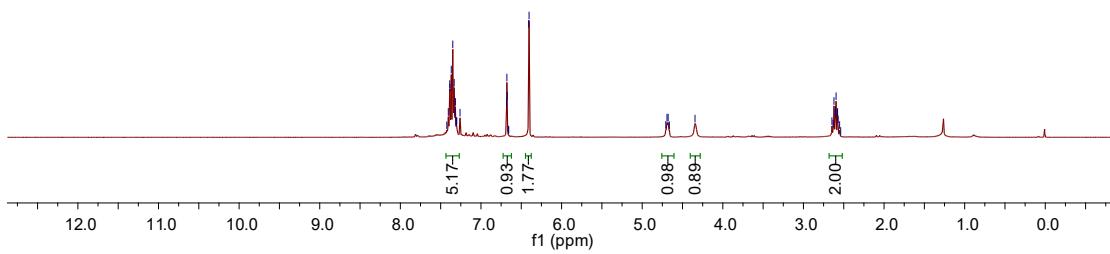
¹H NMR of product 5i in CDCl₃ (400 MHz)

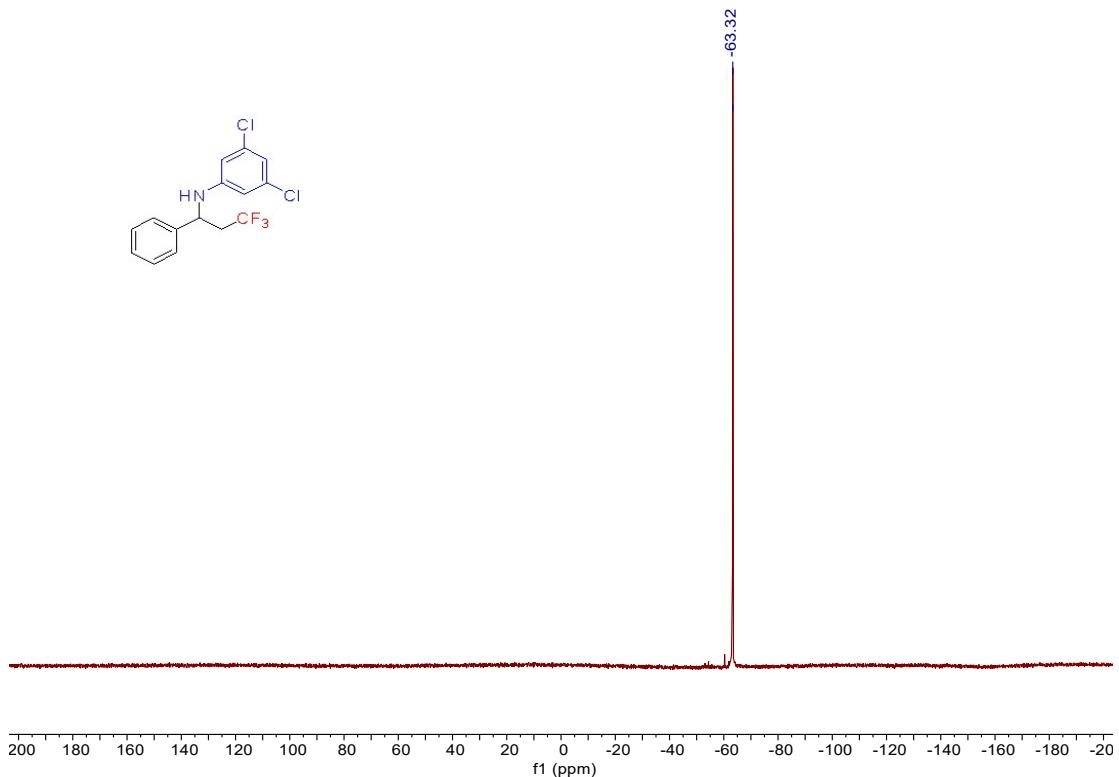


¹³C NMR of product 5i in CDCl₃ (100 MHz)

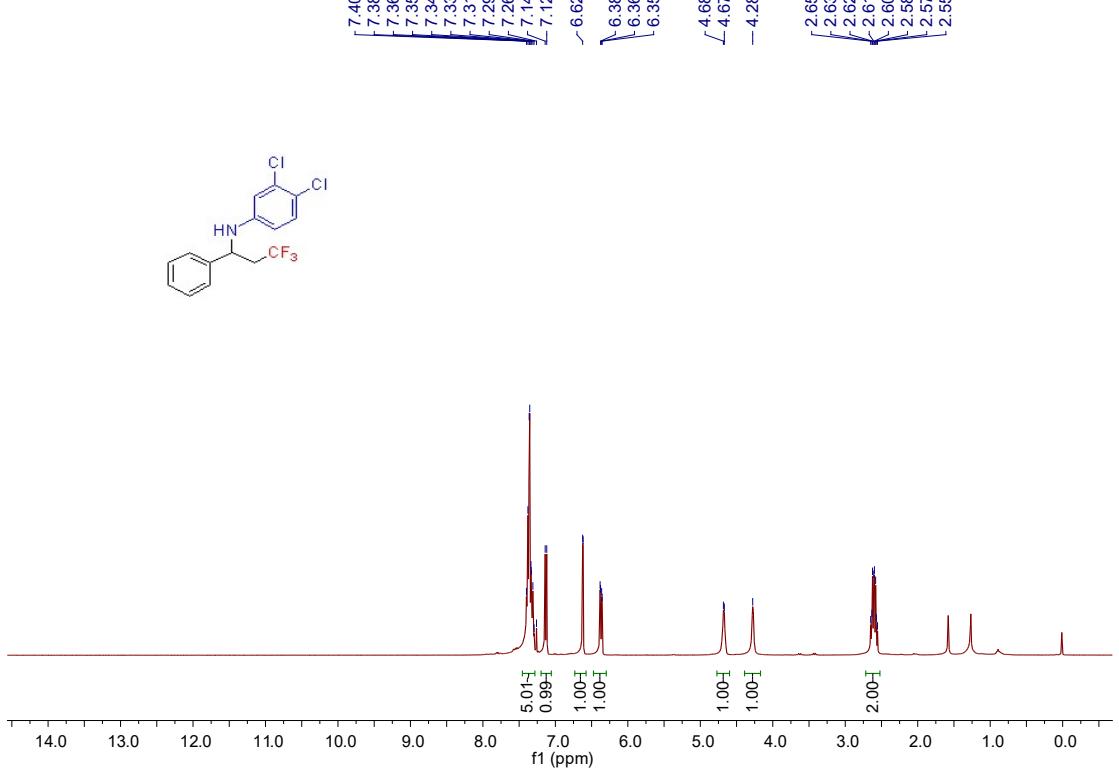


¹⁹F NMR of product 5i in CDCl₃ (376 MHz)

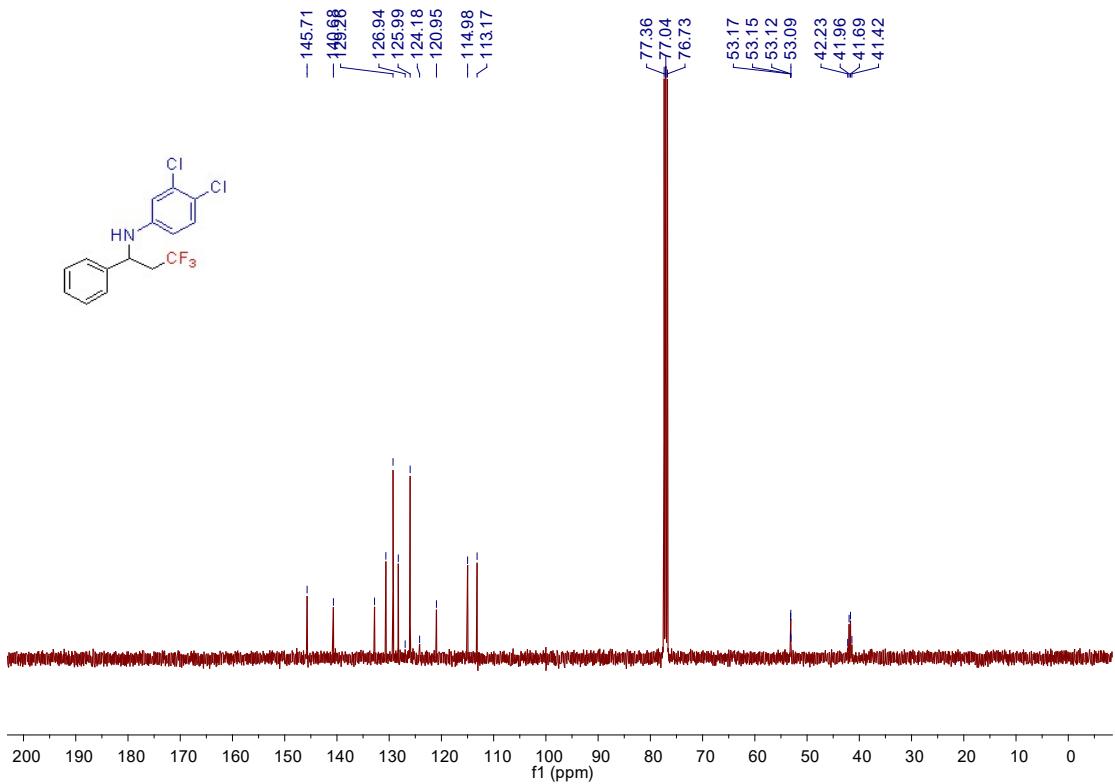




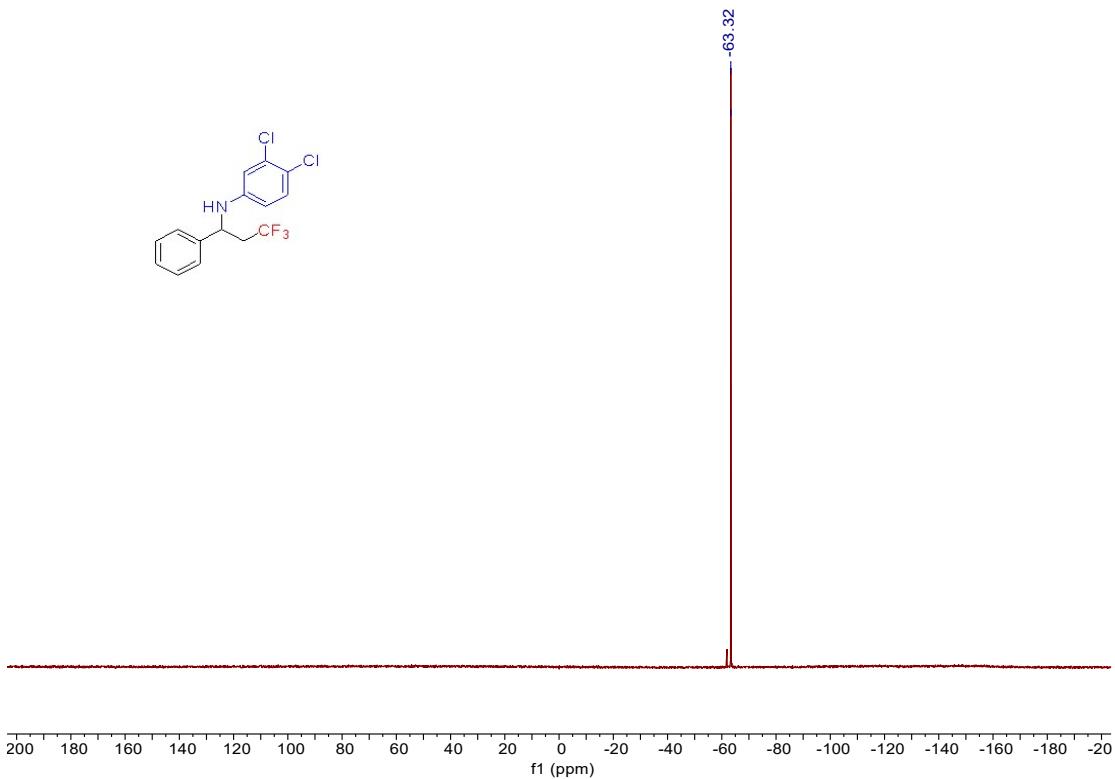
¹⁹F NMR of product 5j in CDCl₃ (376 MHz)



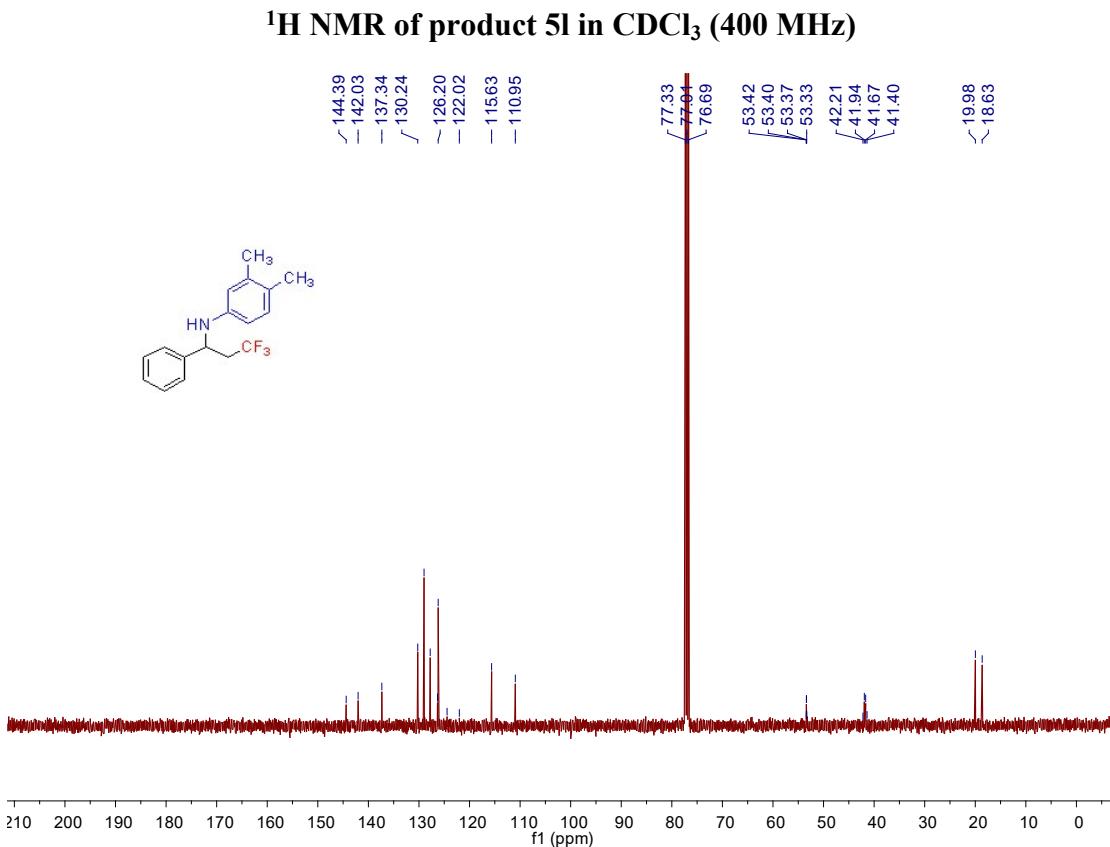
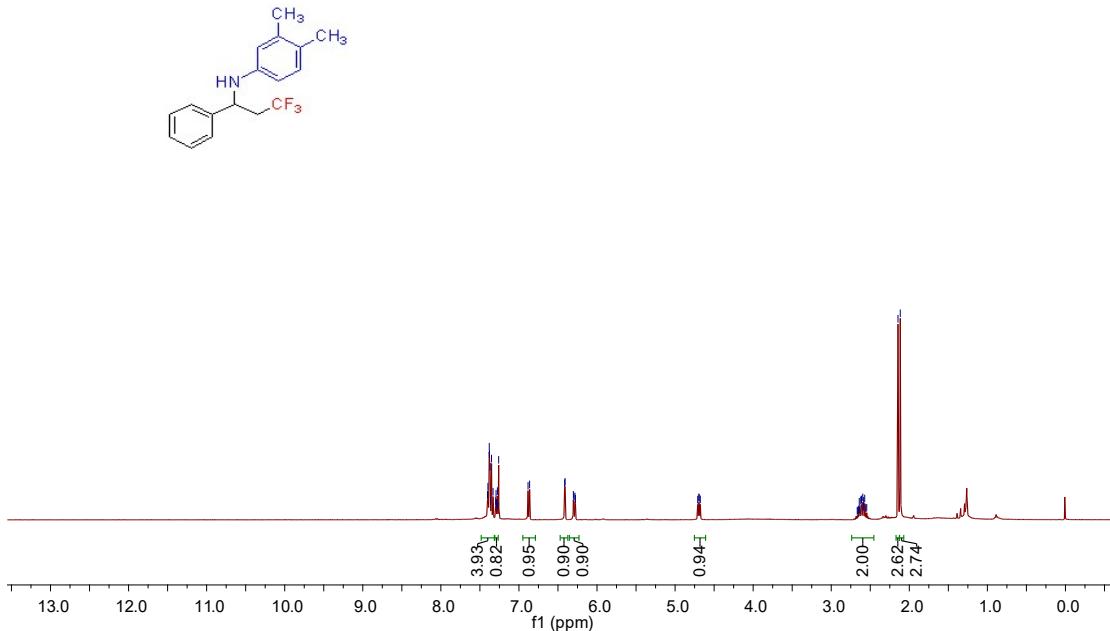
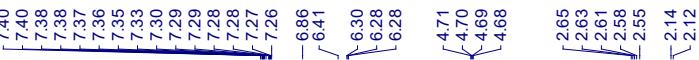
¹H NMR of product 5k in CDCl₃ (400 MHz)

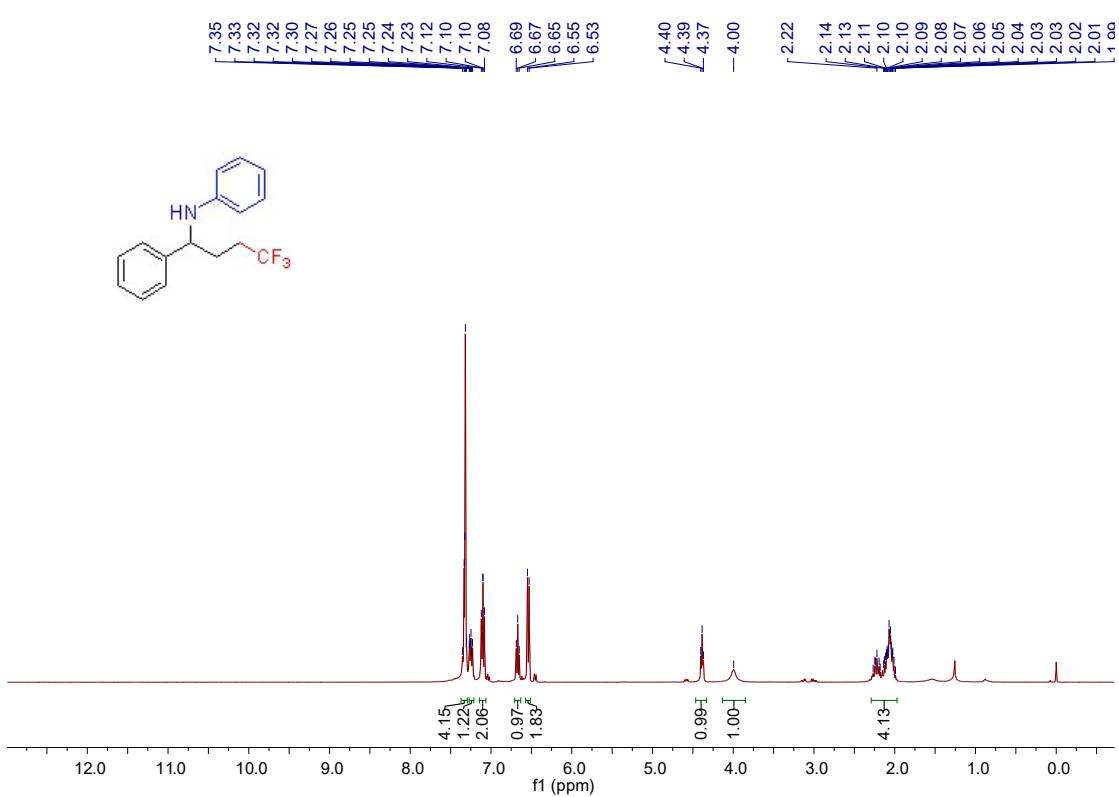
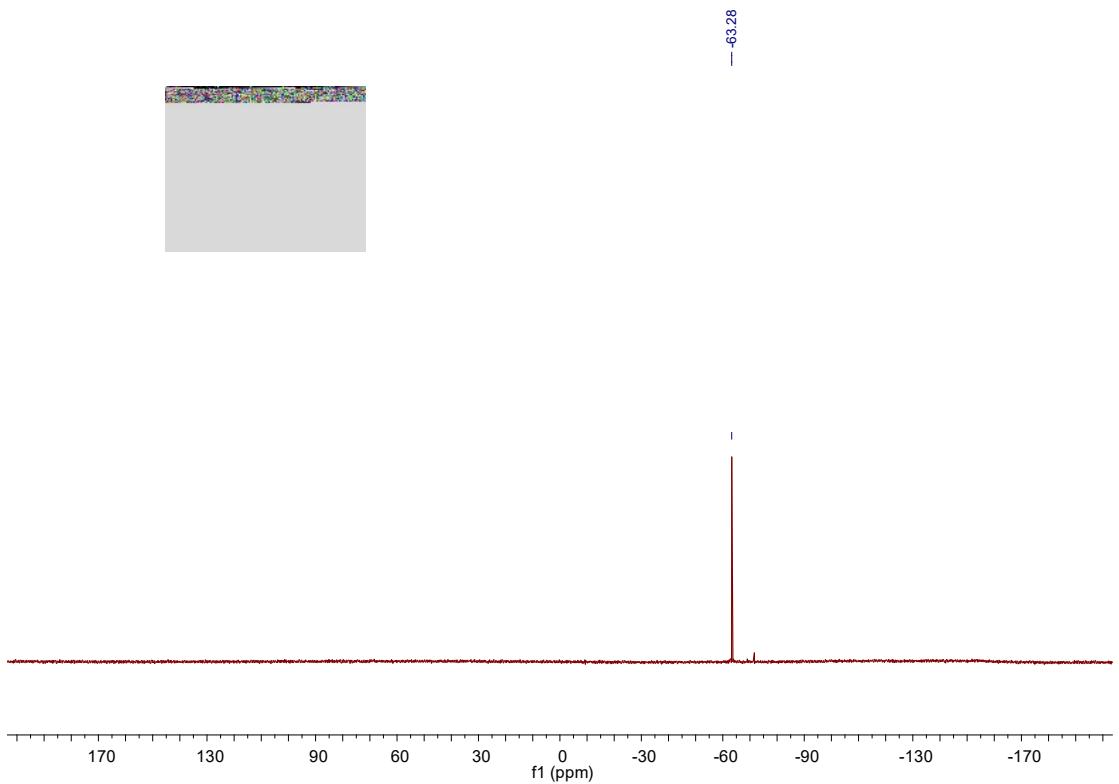


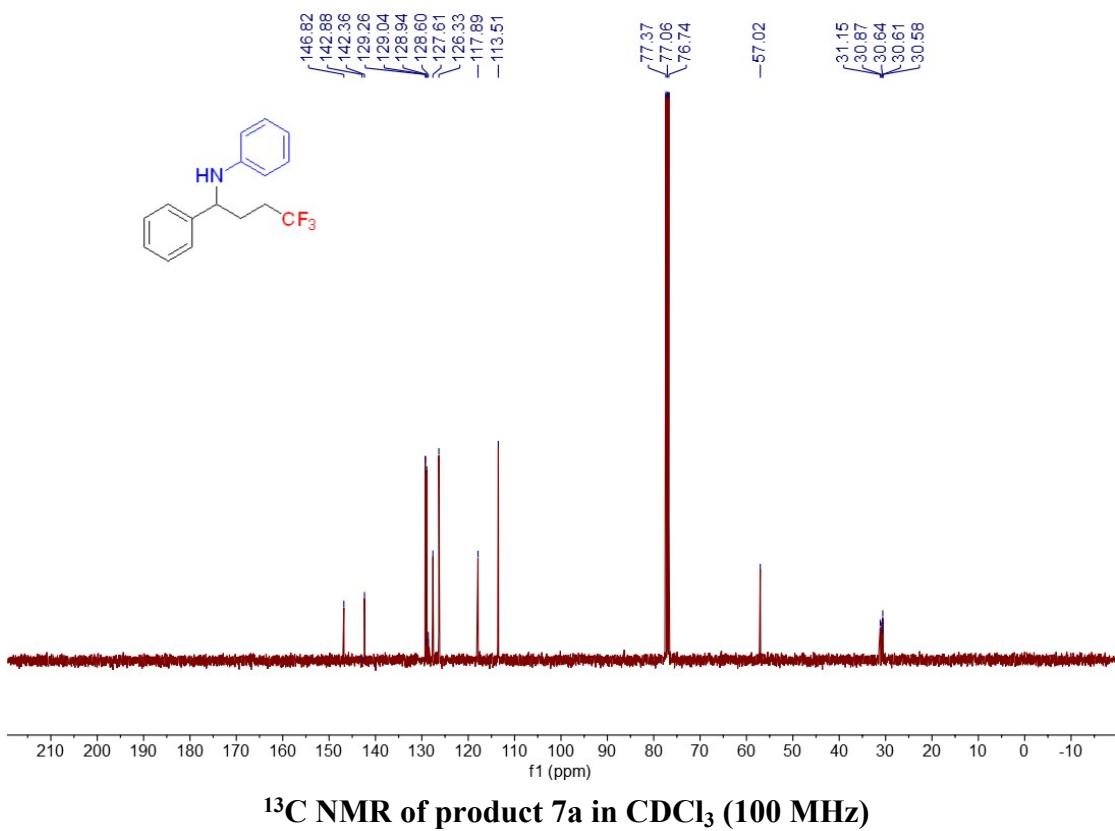
¹³C NMR of product 5k in CDCl₃ (100 MHz)



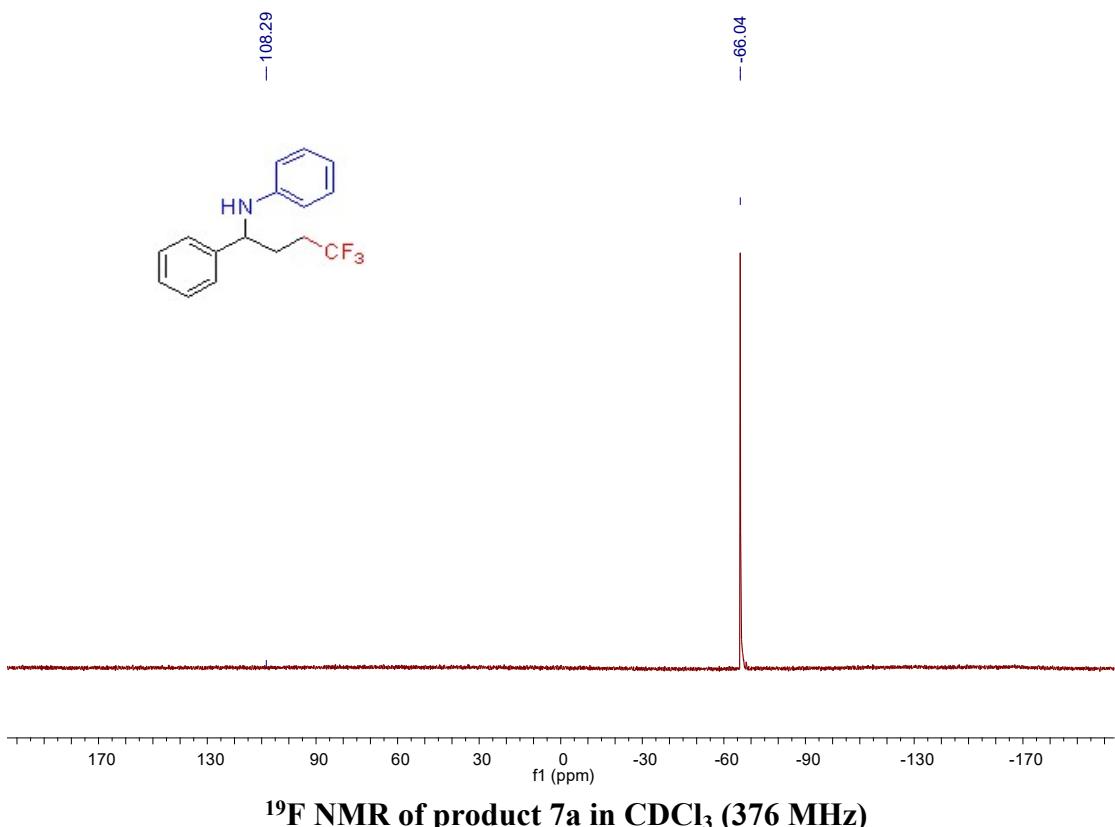
¹⁹F NMR of product 5k in CDCl₃ (376 MHz)



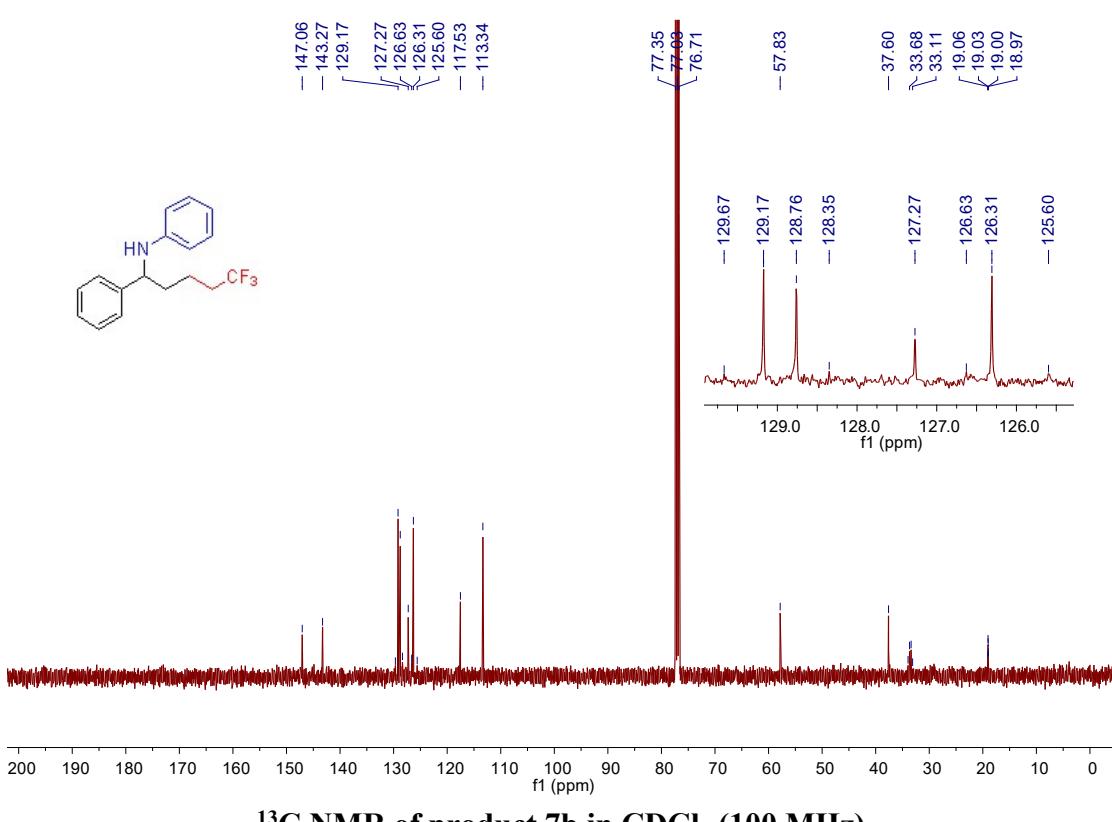
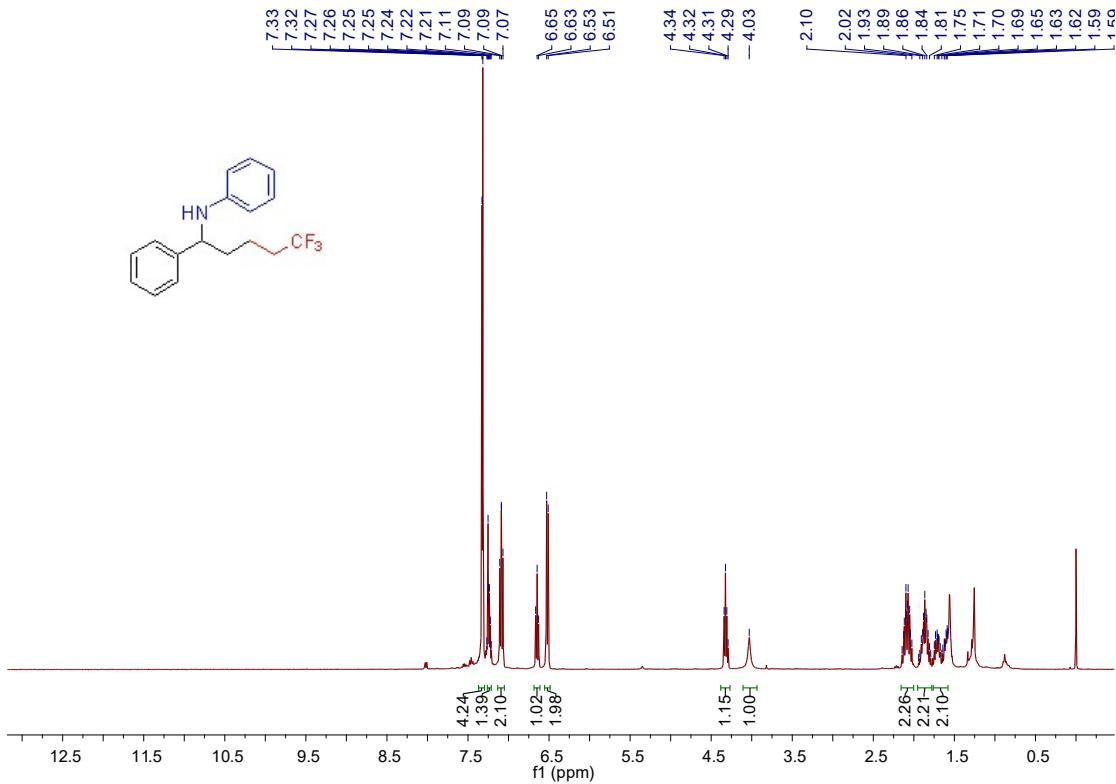


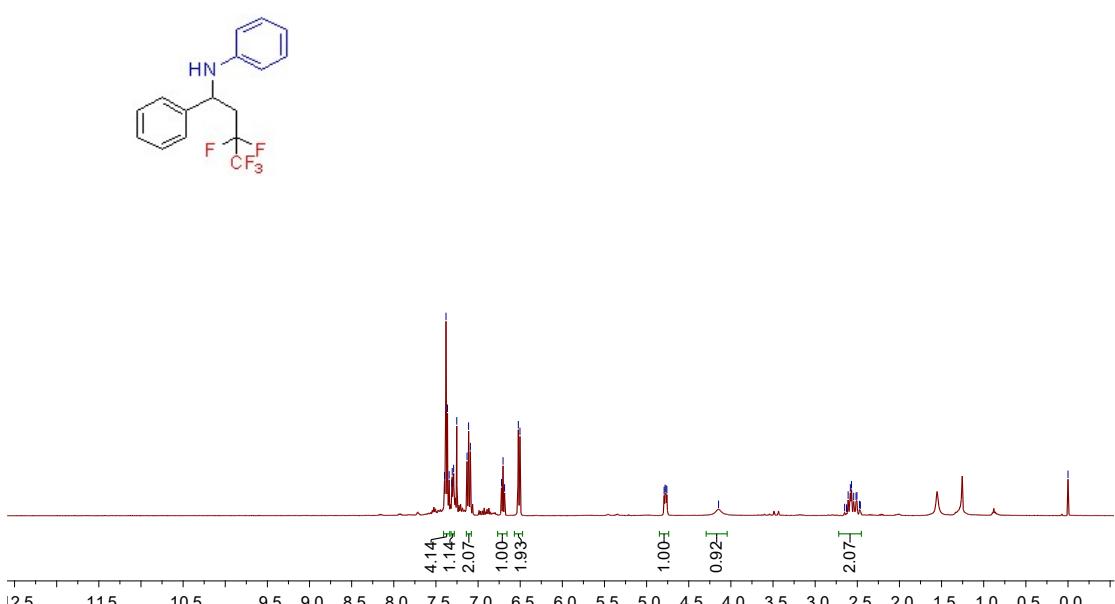
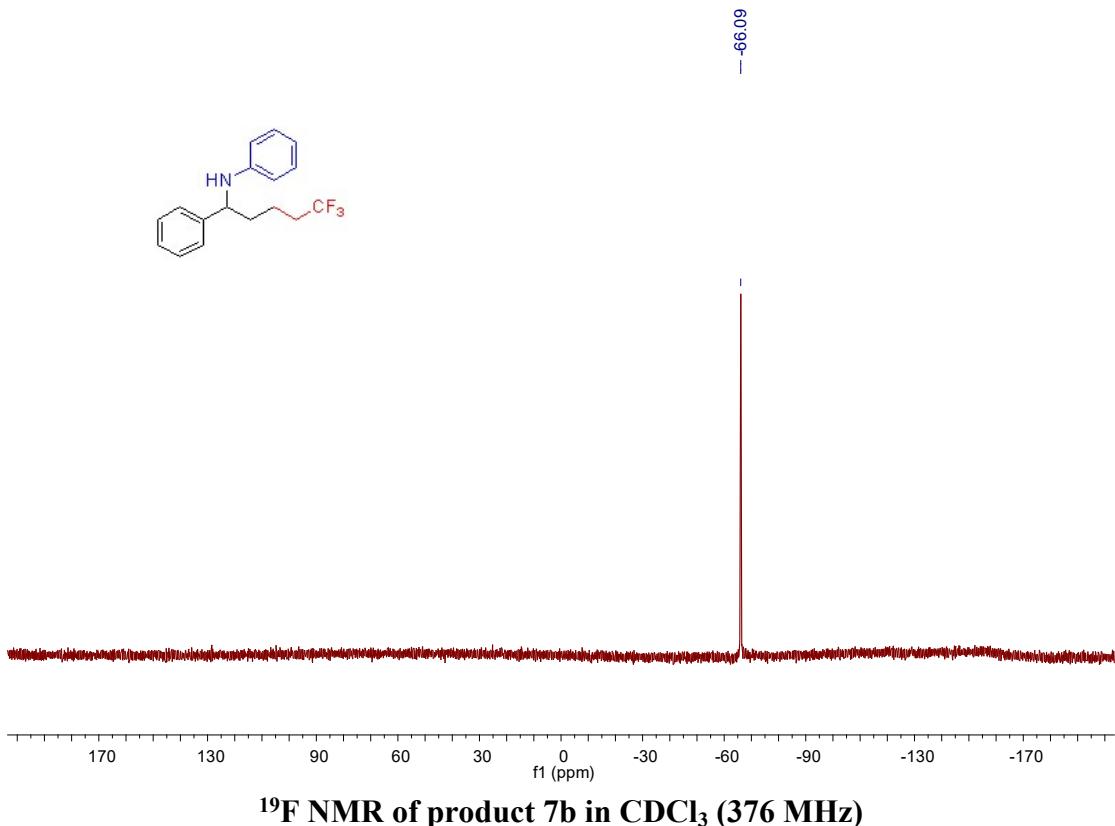


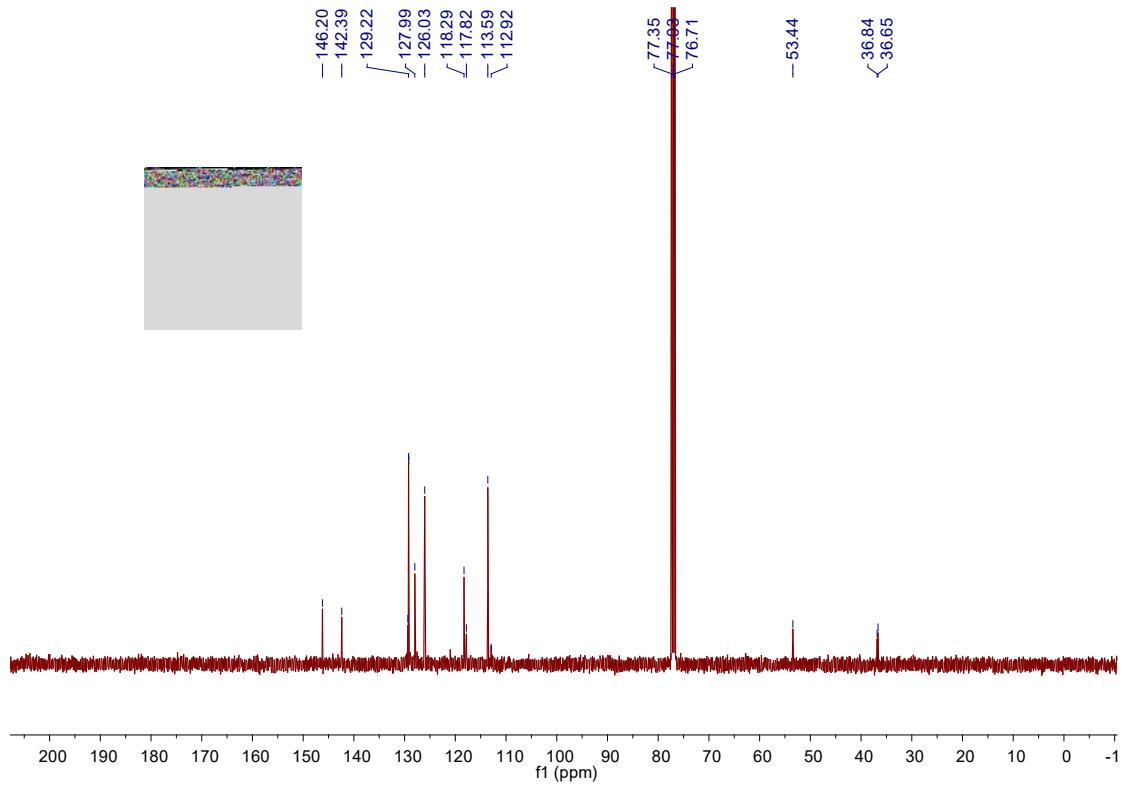
¹³C NMR of product 7a in CDCl₃ (100 MHz)



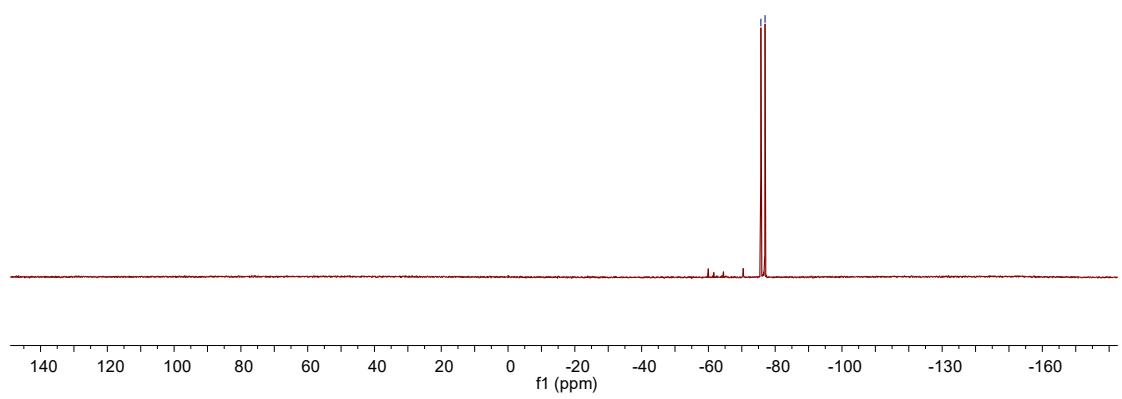
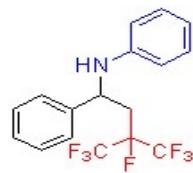
¹⁹F NMR of product 7a in CDCl₃ (376 MHz)







¹³C NMR of product 7c in CDCl₃ (100 MHz)



¹⁹F NMR of product 7c in CDCl₃ (376 MHz)