Supporting Information

Tandem reduction and trifluoroethylation of quinolines and quinoxalines with trifluoroacetic acid and trimethylamine borane

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Contents

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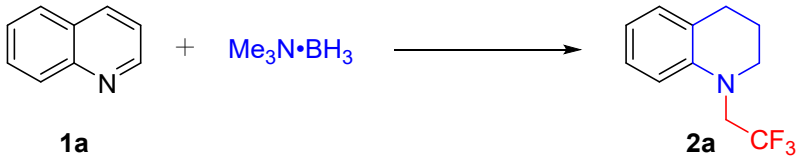
1. General information

All reagents were obtained commercially and used without further purification. Column chromatography was performed on silica gel (200-300 mesh). The reported yields are the actual isolated yields of pure products unless stated otherwise. NMR spectra were recorded on the Bruker Ascend 500 spectrometers at ambient temperature. ^{1}H NMR spectra were obtained in $CDCl_3$ or DMSO-d_6 at 500 MHz. ^{13}C NMR spectra were obtained at 126 MHz. ^{19}F NMR spectra were obtained at 471 MHz. The chemical shifts (δ) were expressed in ppm and coupling constants (*J*) were in Hz.

2. Screening of the reaction solvents



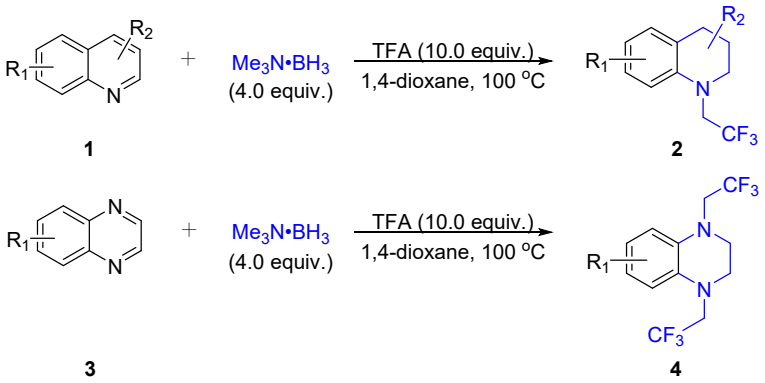
1a **2a**

Table 1 Screening of the reaction solvents [a]

Entry	$Me_3N{\cdot}BH_3$ (equiv.)	Acid (equiv.)	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	4	TFA (10)	THF	100	10	62
2	4	TFA (10)	MeOH	100	10	0
3	4	TFA (10)	Acetone	100	10	0
4	4	TFA (10)	H_2O	100	10	0
5	4	TFA (10)	Toluene	100	10	17
6	4	TFA (10)	DCE	100	10	14
7	4	TFA (10)	DCM	100	10	21
8	4	TFA (10)	EA	100	10	25
9	4	TFA (10)	MeCN	100	10	27
10	4	TFA (10)	DMSO	100	10	26
11	4	TFA (10)	DMF	100	10	49
12	4	TFA (10)	1,4-dioxane	100	10	82

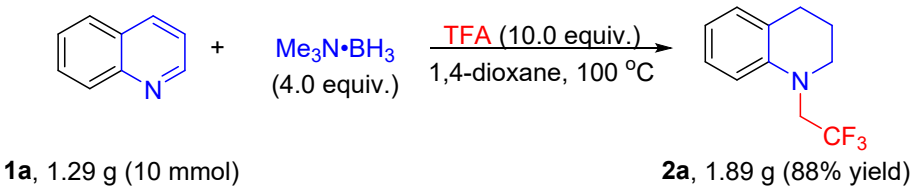
[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), $Me_3N{\cdot}BH_3$ (0.8 mmol, 4.0 equiv.), TFA (2.0 mmol, 10.0 equiv.), solvent (1.0 mL), air; [b] Yields determined by ^{1}H NMR analysis of the crude reaction mixture using 4-benzyloxybenzaldehyde as internal standard.

3. General procedure for tandem reduction/trifluoroethylation of quinolines and quinoxalines



To a Schenk tube equipped with a stirring bar, TFA (2.0 mmol, 10.0 equiv.) was added to the mixture of quinolines **1** or quinoxalines **3** (0.2 mmol, 1.0 equiv.) with $Me_3N{\cdot}BH_3$ (0.8 mmol, 4.0 equiv.) in 1,4-dioxane (1.0 mL). And the mixture was stirred at 100 °C for 3 h. After confirming that the starting material was exhausted by TLC monitoring, NaOH (1.0 mol/L) was added and the mixture was extracted with CH_2Cl_2 (5.0 mL×3). Then the organic solvent layer was obtained and dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the target products.

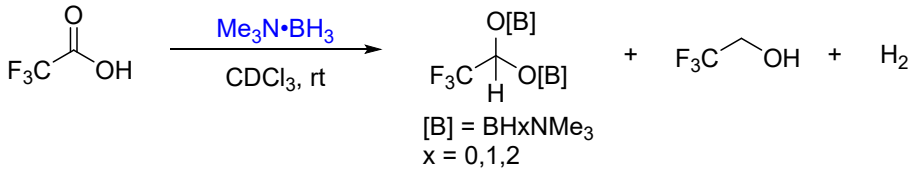
4. Gram-scaled reaction of quinoline



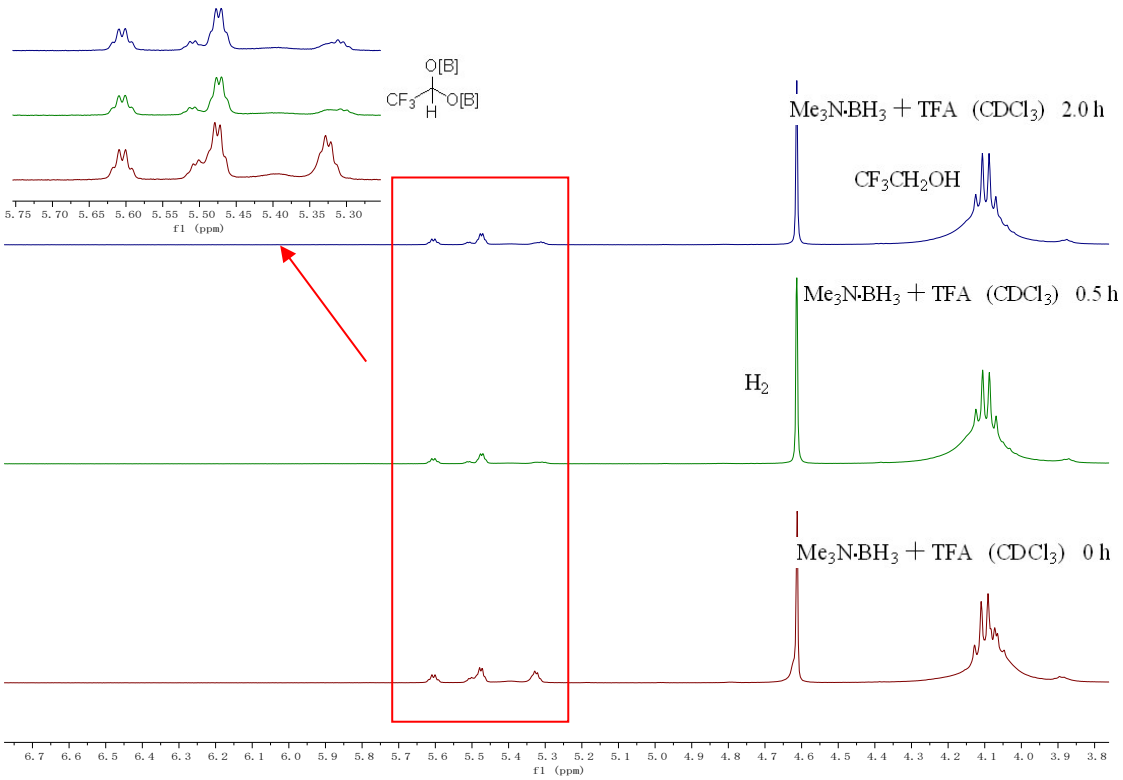
1a, 1.29 g (10 mmol) **2a**, 1.89 g (88% yield)

To a Schenk tube equipped with a stirring bar, TFA (100 mmol, 10.0 equiv.) was added to a solution of quinoline **1a** (10 mmol, 1.0 equiv.) and $Me_3N{\cdot}BH_3$ (40 mmol, 4.0 equiv.) in 1,4-dioxane (50 mL). And the mixture was stirred at 100 °C for 3 h. After confirming that the starting material was exhausted by TLC monitoring, NaOH (1.0 mol/L) was added and the reaction mixture was extracted with CH_2Cl_2 (10.0 mL×3). Then the organic solvent layer was obtained and dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the target products.

5. Reaction process monitoring



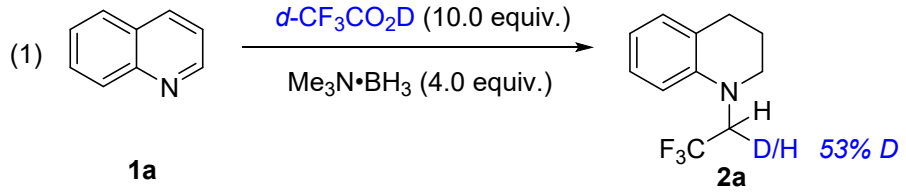
A solution of $Me_3N{\cdot}BH_3$ (0.4 mmol) in $CDCl_3$ (0.5 mL) was added to an NMR tube, and then TFA (1.0 mmol) was added. The reaction mixture was monitored by ^1H NMR at 0 h, 0.5 h and 2.0 h, respectively. The ^1H NMR spectrum was as follows. The reaction proceeded very fast, and CF_3CH_2OH and H_2 were generated as soon as TFA was added. Besides, three quartet peaks were observed from 5.32 to 5.63 ppm (q, J = 4.3 Hz), which were supposed as mixtures of trifluoroacetaldehyde diboryl acetals. Similar silyl acetals (^1H δ 5.10-5.70, J = 4.2 Hz) were reported in ref. 22 (Nat. Commun. 2017, 8, 15913).



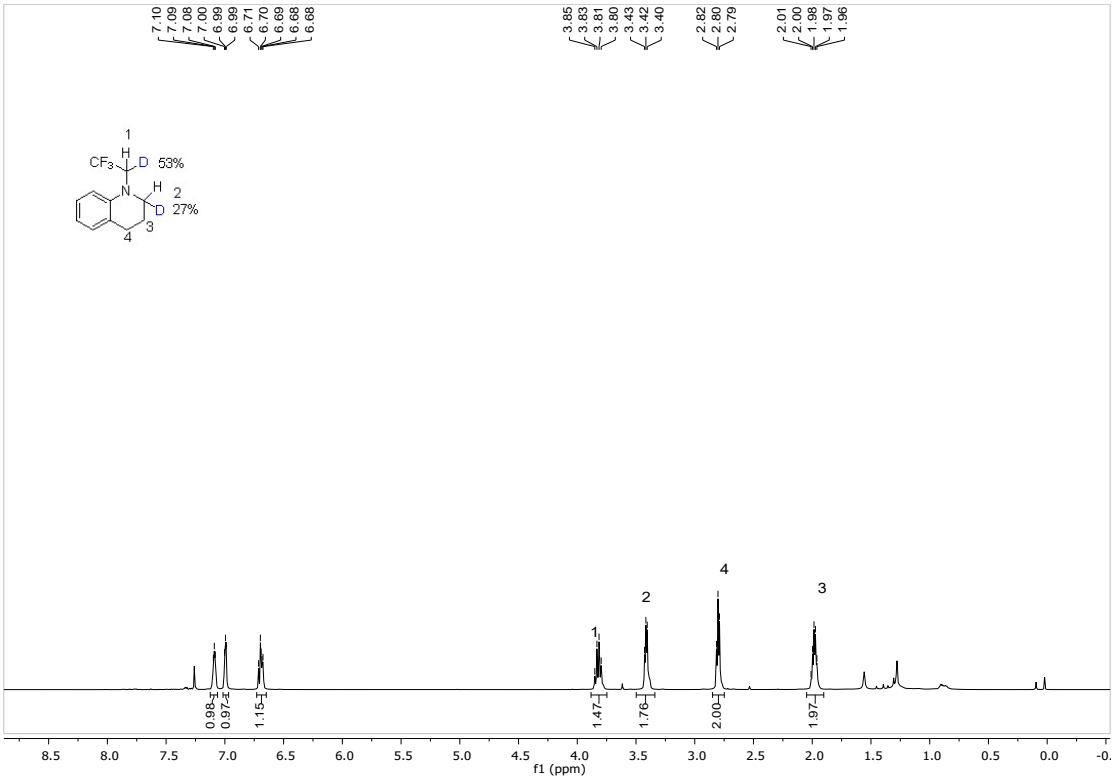
Stacked ^1H NMR spectra at different time

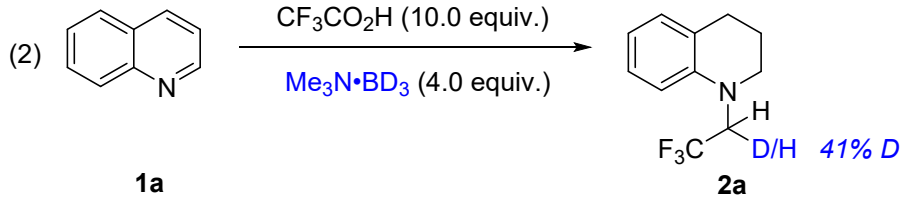
6. Deuterium-labelling experiments

Several deuteration experiments were conducted by using quinoline or tetrahydroquinoline as the substrate. Theoretically, the hydrogen in trifluoroethyl group was supposed to derive from $Me_3N{\cdot}BH_3$. However, the deuterium atom was incorporated in the product whether with $Me_3N{\cdot}BD_3$ or *d*-TFA. It was supposed that a deuterium-hydrogen exchange may occur between the deuterium-labelled reagents (products) with TFA or other reagents bearing active proton (water, solvent). Therefore, we could not ascertain that the source of hydrogen in trifluoroethyl group based on the current experimental results.



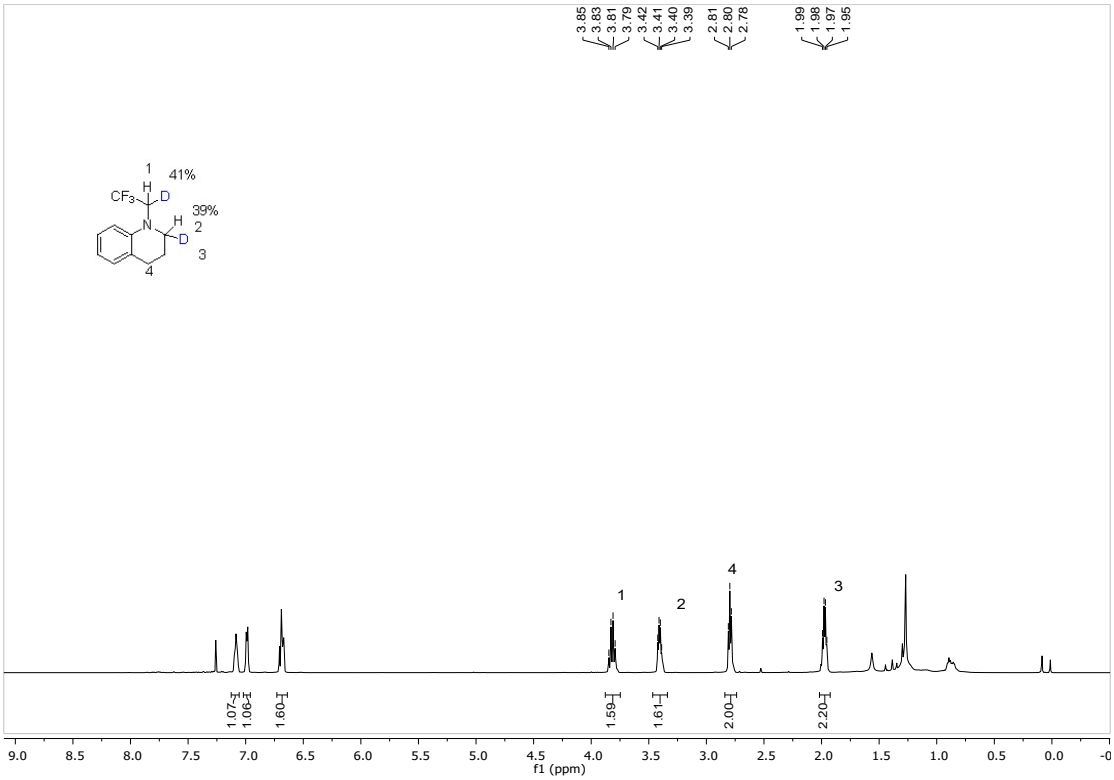
To a Schenk tube, *d*-TFA (2.0 mmol, 10.0 equiv.) was added to a solution of quinoline **1a** (0.2 mmol) and $Me_3N{\cdot}BH_3$ (0.8 mmol, 4.0 equiv.) in 1,4-dioxane (1.0 mL). The mixture was stirred at 100 °C for 3 h. Subsequently, the reaction mixture was neutralized with NaOH (1.0 mol/L) and extracted with CH_2Cl_2 for three times. The combined organic phase was dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the target products. The position and ratio of deuterium were confirmed by ^1H NMR.

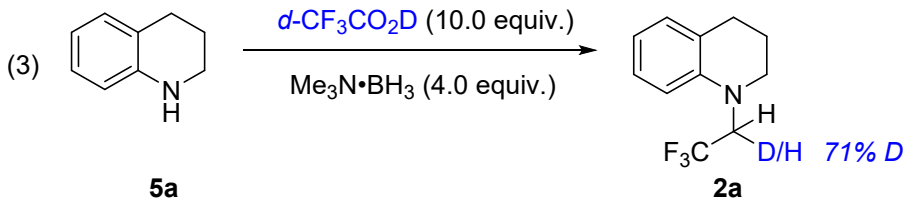




1a **2a**

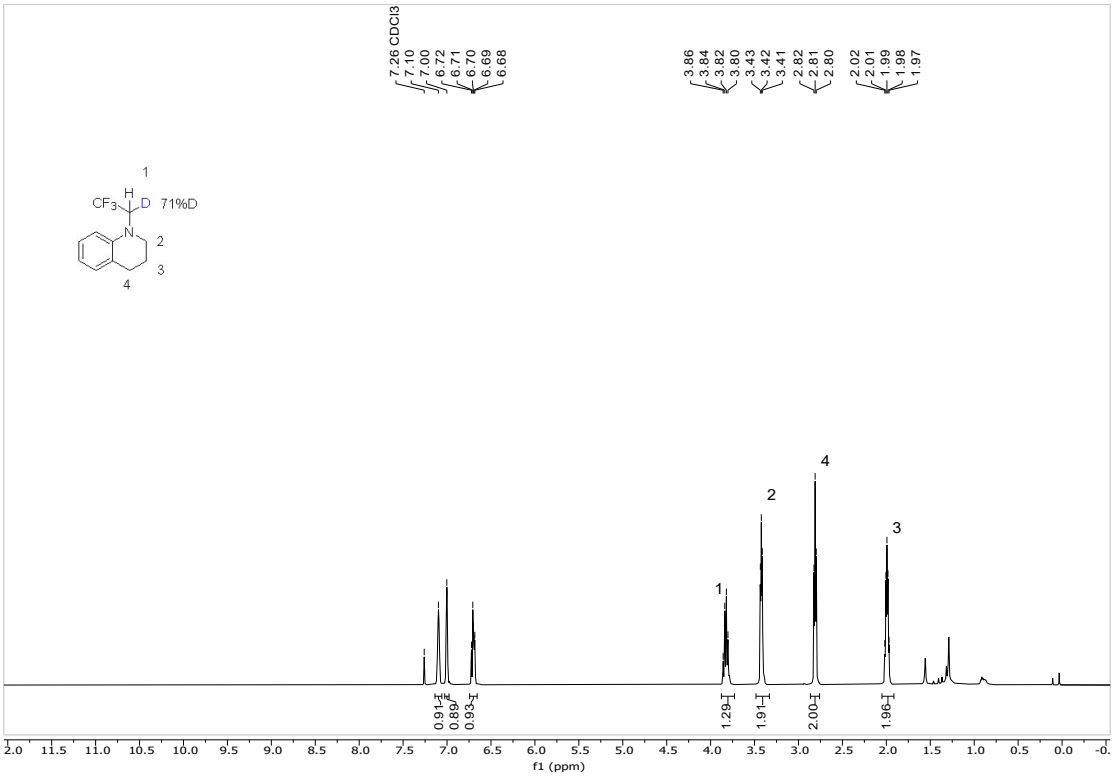
To a Schenk tube, TFA (2.0 mmol, 10.0 equiv.) was added to a solution of quinoline **1a** (0.2 mmol) and $Me_3N{\cdot}BD_3$ (0.8 mmol, 4.0 equiv.) in 1,4-dioxane (1.0 mL). The mixture was stirred at 100 °C for 3 h. Subsequently, the reaction mixture was neutralized with NaOH (1.0 mol/L) and extracted with CH_2Cl_2 for three times. The combined organic phase was dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the target products. The position and ratio of deuterium were confirmed by ^1H NMR.

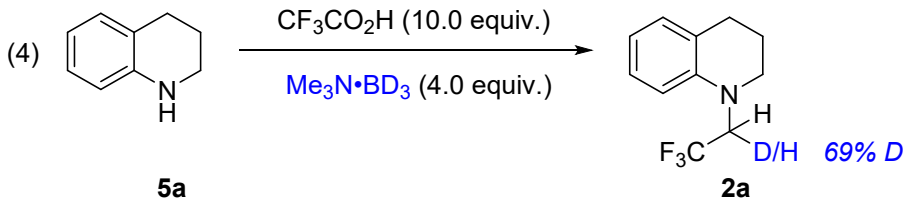




5a **2a**

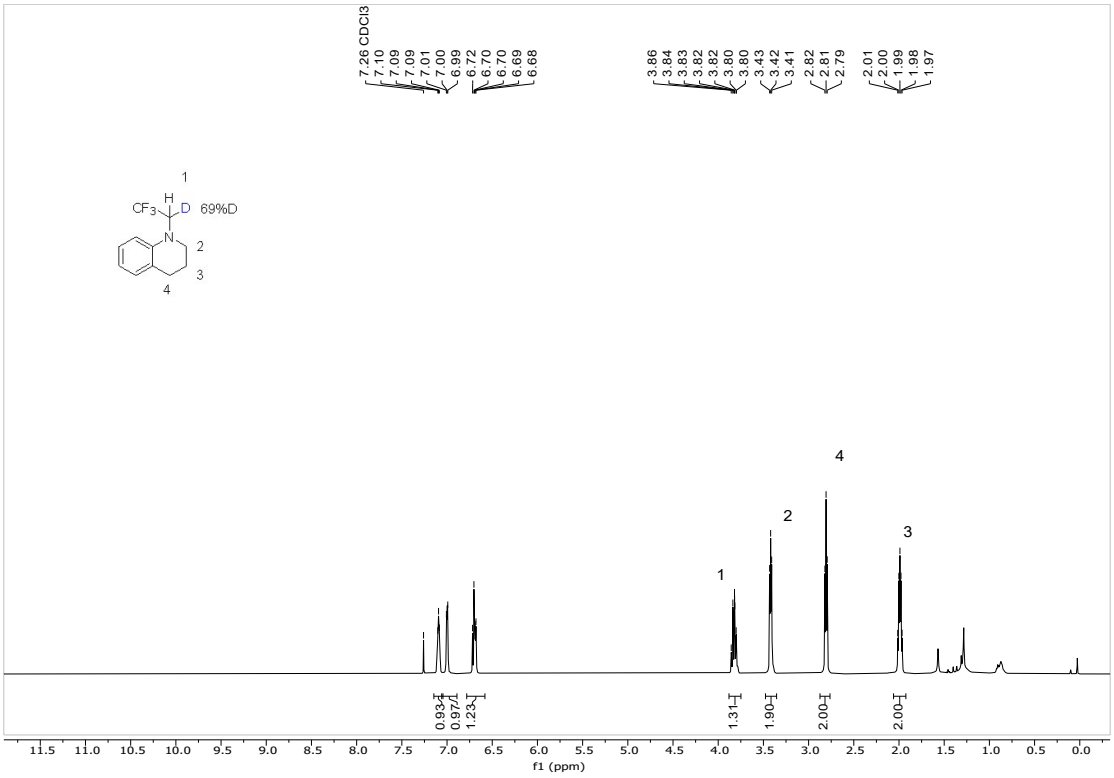
To a Schenk tube, *d*-TFA (2.0 mmol, 10.0 equiv.) was added to a solution of tetrahydroquinoline **5a** (0.2 mmol) and $Me_3N{\cdot}BH_3$ (0.8 mmol, 4.0 equiv.) in 1,4-dioxane (1.0 mL). The mixture was stirred at 100 °C for 3 h. Subsequently, the reaction mixture was neutralized with NaOH (1.0 mol/L) and extracted with CH_2Cl_2 for three times. The combined organic phase was dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the target products. The position and ratio of deuterium were confirmed by ^1H NMR.



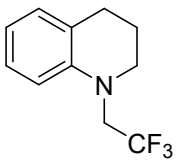


5a **2a**

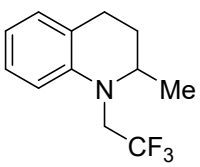
To a Schenk tube, TFA (2.0 mmol, 10.0 equiv.) was added to a solution of tetrahydroquinoline **5a** (0.2 mmol) and $Me_3N{\cdot}BD_3$ (0.8 mmol, 4.0 equiv.) in 1,4-dioxane (1.0 mL). The mixture was stirred at 100 °C for 3 h. Subsequently, the reaction mixture was neutralized with NaOH (1.0 mol/L) and extracted with CH_2Cl_2 for three times. The combined organic phase was dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the target products. The position and ratio of deuterium were confirmed by ^1H NMR.



7. Characterization data of products

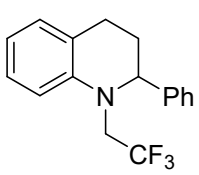


1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2a)[1]: Colorless oil (38.7 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.70 – 6.66 (m, 2H), 3.82 (q, *J* = 9.1 Hz, 2H), 3.43 – 3.38 (m, 2H), 2.79 (t, *J* = 6.3 Hz, 2H), 2.00 – 1.94 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 129.6, 127.3, 125.8 (q, *J* = 283.4 Hz), 123.0, 117.8, 111.7, 53.8 (q, *J* = 32.5 Hz), 51.3, 28.1, 22.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.18.

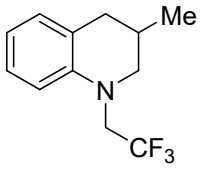


2-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2b): Colorless oil (24.3 mg, 53% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.72 – 6.28 (m, 2H), 3.99 – 3.91 (m, 1H), 3.79 – 3.70 (m, 1H), 3.64 – 3.58 (m, 1H), 2.97 – 2.87 (m, 1H), 2.74 – 2.71 (m, 1H), 2.07 – 1.95 (m, 1H), 1.83 – 1.76 (m, 1H), 1.17 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 129.7, 127.2, 125.8 (q, *J* = 282.4 Hz), 122.3, 117.5, 112.3, 53.7, 51.8 (q, *J* = 32.7 Hz), 27.1, 23.3, 17.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.25. **HRMS (ESI) m/z:** calcd for $C_{12}H_{15}F_3N$ $[M + H]^+$: 230.1157, found: 230.1161.

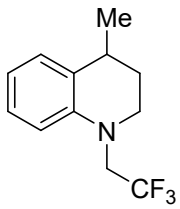
[1] Yamashita T, Sakamoto T, Kikugawa Y, et al. J. Fluorine Chem. 2010, 131(4): 477-486.



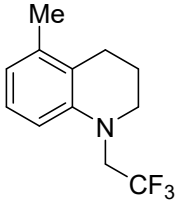
2-phenyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2c): Colorless oil (25.6 mg, 44% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.26-7.23 (m, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 2H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 4.79 (s, 1H), 4.13 – 4.04 (m, 1H), 3.63 – 3.54 (m, 1H), 2.63 – 2.49 (m, 2H), 2.29 – 2.25 (m, 1H), 2.07 – 2.04 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.2, 142.5, 129.6, 128.7, 127.5, 127.4, 126.6, 125.9 (q, *J* = 284.5 Hz), 122.9, 117.6, 110.8, 62.1, 50.9 (q, *J* = 32.9 Hz), 28.9, 23.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.54. **HRMS (ESI) m/z:** calcd for $C_{17}H_{17}F_3N$ $[M + H]^+$: 292.1313, found: 292.1314.



3-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2d): Colorless oil (28.4 mg, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.71 – 6.67 (m, 2H), 3.89 – 3.75 (m, 2H), 3.34 (d, *J* = 11.1 Hz, 1H), 3.05 (t, *J* = 10.4 Hz, 1H), 2.83 – 2.77 (m, 1H), 2.50 – 2.45 (m, 1H), 2.13 – 2.11 (m, 1H), 1.05 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 129.8, 127.2, 125.8 (q, *J* = 283.6 Hz), 122.6, 117.8, 111.4, 58.0, 53.7 (q, *J* = 33.8 Hz), 36.3, 27.0, 18.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.16. **HRMS (ESI) m/z:** calcd for $C_{12}H_{15}F_3N$ $[M + H]^+$: 230.1157, found: 230.1161.

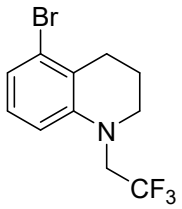


4-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2e): Colorless oil (22.9 mg, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 – 7.08 (m, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 3.91 – 3.77 (m, 2H), 3.51 – 3.43 (m, 1H), 3.39 – 3.33 (m, 1H), 2.96 – 2.90 (m, 1H), 2.06 – 2.00 (m, 1H), 1.74 – 1.71 (m, 1H), 1.30 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 128.7, 128.2, 127.2, 125.9 (q, *J* = 283.1 Hz), 117.8, 111.7, 53.8 (q, *J* = 33.4 Hz), 47.9, 30.9, 29.3, 22.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.06. **HRMS (ESI) m/z:** calcd for $C_{12}H_{15}F_3N$ $[M + H]^+$: 230.1157, found: 230.1159.

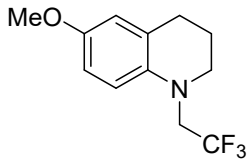


5-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2f): Colorless oil (32.6 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (t, *J* = 7.8 Hz, 1H), 6.63 – 6.57 (m, 2H), 3.81 (q, *J* = 9.1 Hz, 2H), 3.40 – 3.34 (m, 2H), 2.67 (t, *J* = 6.4 Hz, 2H), 2.20 (s, 3H), 2.02 – 1.97 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 137.2, 126.5, 125.9 (q, *J* = 283.9 Hz), 121.8, 119.9, 110.1, 54.3 (q, *J* = 33.1 Hz), 50.8, 24.9,

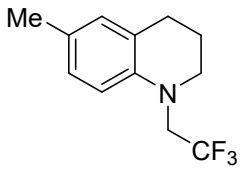
22.0, 20.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.31. **HRMS (ESI) m/z:** calcd for $C_{12}H_{15}F_3N$ [M + H]$^+$: 230.1157, found: 230.1156.



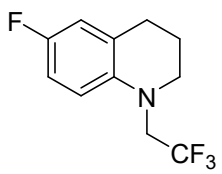
5-bromo-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2g): Colorless oil (47.9 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (d, *J* = 7.7 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 3.82 (q, *J* = 9.0 Hz, 2H), 3.42 – 3.33 (m, 2H), 2.82 (t, *J* = 6.5 Hz, 2H), 2.02 – 1.93 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 127.8, 126.1, 125.6 (q, *J* = 282.6 Hz), 122.6, 122.0, 111.0, 53.9 (q, *J* = 32.9 Hz), 50.8, 28.7, 21.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.13. **HRMS (ESI) m/z:** calcd for $C_{11}H_{12}BrF_3N$ [M + H]$^+$: 294.0105, found: 294.0105.



6-methoxy-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2h): Colorless oil (37.3 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.68 (d, *J* = 8.9 Hz, 1H), 6.64 – 6.60 (m, 2H), 3.79 – 3.71 (m, 5H), 3.38 – 3.33 (m, 2H), 2.78 (t, *J* = 6.3 Hz, 2H), 1.99 – 1.92 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 139.1, 126.0 (q, *J* = 283.3 Hz), 124.6, 115.3, 113.3, 112.7, 55.8, 54.7 (q, *J* = 34.6 Hz), 51.4, 28.3, 22.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.42. **HRMS (ESI) m/z:** calcd for $C_{12}H_{15}F_3NO$ [M + H]$^+$: 246.1106, found: 246.1104.

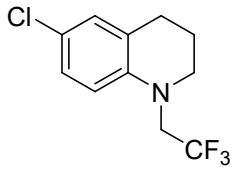


6-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2i): Colorless oil (35.8 mg, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (d, *J* = 8.2 Hz, 1H), 6.82 (s, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 3.79 (q, *J* = 9.1 Hz, 2H), 3.40 – 3.35 (m, 2H), 2.76 (t, *J* = 6.2 Hz, 2H), 2.23 (s, 3H), 2.00 – 1.92 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 130.3, 127.7, 127.0, 125.9 (q, *J* = 283.8 Hz), 123.0, 111.9, 54.0 (q, *J* = 32.6 Hz), 51.3, 28.0, 22.2, 20.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.26. **HRMS (ESI) m/z:** calcd for $C_{12}H_{15}F_3N$ [M + H]$^+$: 230.1157, found: 230.1160.

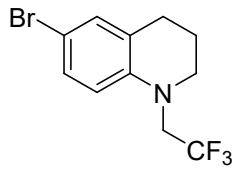


6-fluoro-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2j): Colorless oil (33.6 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (t, *J* = 8.5 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 6.59 – 6.57 (m, 1H), 3.77 (q, *J* = 9.1 Hz, 2H), 3.39 – 3.34 (m, 2H), 2.76 (t, *J* = 6.2 Hz, 2H), 1.99 – 1.92 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7 (d, *J* = 234.8 Hz), 141.0, 125.8 (q, *J* = 283.5 Hz), 124.7 (d, *J* = 6.7 Hz), 115.9 (d, *J* = 22.4 Hz), 113.5 (d, *J* = 22.6 Hz), 112.8 (d, *J* = 8.5 Hz), 54.5 (q, *J* = 35.0 Hz), 51.3, 28.2, 21.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.30, -127.99. **HRMS (ESI) m/z:** calcd for

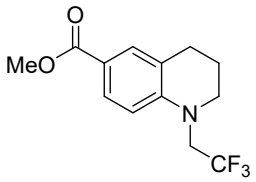
$C_{11}H_{12}F_4N$ [M + H]$^+$: 234.0906, found: 234.0907.



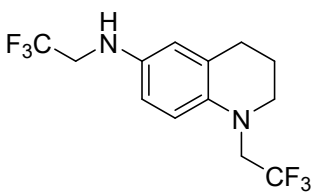
6-chloro-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2k): Colorless oil (35.0 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.8 Hz, 1H), 6.95 (s, 1H), 6.58 (d, *J* = 8.8 Hz, 1H), 3.79 (q, *J* = 9.0 Hz, 2H), 3.42 – 3.35 (m, 2H), 2.75 (t, *J* = 6.2 Hz, 2H), 2.00 – 1.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 129.2, 126.9, 125.7 (q, *J* = 283.7 Hz), 124.7, 122.4, 112.8, 53.8 (q, *J* = 33.8 Hz), 51.2, 28.0, 21.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.07. **HRMS (ESI) m/z:** calcd for $C_{11}H_{12}ClF_3N$ [M + H]$^+$: 250.0610, found: 250.0605.



6-bromo-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2l): Colorless oil (35.9 mg, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.7 Hz, 1H), 7.09 (s, 1H), 6.53 (d, *J* = 8.7 Hz, 1H), 3.79 (q, *J* = 8.9 Hz, 2H), 3.41 – 3.38 (m, 2H), 2.77 – 2.74 (m, 2H), 1.98 – 1.94 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 132.0, 129.9, 125.7 (q, *J* = 283.2 Hz), 125.2, 113.3, 109.6, 53.7 (q, *J* = 34.8 Hz), 51.1, 28.0, 21.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.03. **HRMS (ESI) m/z:** calcd for $C_{11}H_{12}BrF_3N$ [M + H]$^+$: 294.0105, found: 294.0106.

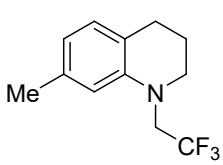


methyl 1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (2m): Red solid (33.9 mg, 62% yield), M.p. 66-67 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.7 Hz, 1H), 7.67 (s, 1H), 6.64 (d, *J* = 8.7 Hz, 1H), 3.93 – 3.81 (m, 5H), 3.47 (d, *J* = 4.6 Hz, 2H), 2.81 (t, *J* = 5.9 Hz, 2H), 2.01 – 1.93 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 148.2, 131.2, 129.5, 125.5 (q, *J* = 282.6 Hz), 122.2, 118.8, 110.5, 53.0 (q, *J* = 33.2 Hz), 51.8, 51.3, 27.9, 21.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.76. **HRMS (ESI) m/z:** calcd for $C_{13}H_{15}F_3NO_2$ [M + H]$^+$: 274.1055, found: 274.1055.

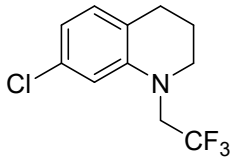


***N*,1-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinolin-6-amine (2n)**: Colorless oil (57.5 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.58 (d, *J* = 8.7 Hz, 1H), 6.50 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 3.76 – 3.63 (m, 4H), 3.52 – 3.50 (m, 1H), 3.33 (t, *J* = 5.5 Hz, 2H), 2.74 (t, *J* = 6.3 Hz, 2H), 1.98 – 1.90 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 138.4, 126.0 (q, *J* = 282.6 Hz), 125.3 (q, *J* = 280.4 Hz), 124.7, 115.6, 113.6, 113.2, 54.8 (q, *J* = 32.7 Hz), 51.4, 47.4 (q, *J* = 33.7 Hz), 28.3, 22.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.47, -

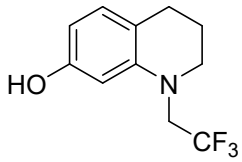
72.35. **HRMS (ESI) m/z:** calcd for $C_{13}H_{14}F_6N_2$ [M + H]$^+$: 313.1139, found: 313.1142.



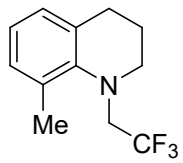
7-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2o): Colorless oil (35.1 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (d, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 7.5 Hz, 1H), 6.49 (s, 1H), 3.81 (q, *J* = 9.1 Hz, 2H), 3.41 – 3.36 (m, 2H), 2.75 (t, *J* = 6.2 Hz, 2H), 2.28 (s, 3H), 1.98 – 1.93 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 137.0, 129.5, 125.9 (q, *J* = 282.4 Hz), 120.2, 118.6, 112.5, 53.9 (q, *J* = 33.0 Hz), 51.4, 27.7, 22.2, 21.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.18. **HRMS (ESI) m/z:** calcd for $C_{12}H_{15}F_3N$ [M + H]$^+$: 230.1157, found: 230.1159.



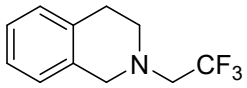
7-chloro-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2p): Colorless oil (44.3 mg, 89% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (d, *J* = 7.8 Hz, 1H), 6.66 – 6.61 (m, 2H), 3.79 (q, *J* = 9.0 Hz, 2H), 3.42 – 3.36 (m, 2H), 2.73 (t, *J* = 6.2 Hz, 2H), 1.98 – 1.93 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 132.7, 130.5, 125.6 (q, *J* = 283.7 Hz), 121.4, 117.6, 111.5, 53.6 (q, *J* = 33.5 Hz), 51.0, 27.6, 21.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.99. **HRMS (ESI) m/z:** calcd for $C_{11}H_{12}ClF_3N$ [M + H]$^+$: 250.0610, found: 250.0607.



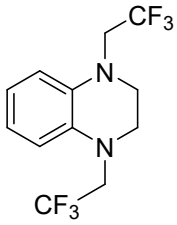
1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinolin-7-ol (2q): White solid (35.1 mg, 76% yield), M.p. 98-99 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (d, *J* = 7.8 Hz, 1H), 6.19-6.16 (m, 2H), 4.88 (s, 1H), 3.77 (q, *J* = 9.1 Hz, 2H), 3.41 – 3.33 (m, 2H), 2.71 (t, *J* = 6.3 Hz, 2H), 1.94 (p, *J* = 6.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 145.6, 130.3, 125.8 (q, *J* = 283.1 Hz), 115.7, 104.6, 99.1, 53.8 (q, *J* = 32.7 Hz), 51.2, 27.3, 22.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.05. **HRMS (ESI) m/z:** calcd for $C_{11}H_{12}F_3NO$ [M + H]$^+$: 232.0949, found: 232.0952.



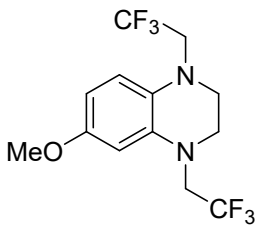
8-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2r): Colorless oil (21.7 mg, 47% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (d, *J* = 6.3 Hz, 1H), 6.91 – 6.88 (m, 2H), 3.41 (q, *J* = 8.9 Hz, 2H), 3.23-3.22 (m, 2H), 2.82 (t, *J* = 6.5 Hz, 2H), 2.32 (s, 3H), 1.89-1.84 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 131.5, 130.1, 129.6, 127.6, 125.6 (q, *J* = 280.6 Hz), 122.9, 55.2 (q, *J* = 29.1 Hz), 48.6, 27.5, 18.7, 17.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -67.87. **HRMS (ESI) m/z:** calcd for $C_{12}H_{15}F_3N$ [M + H]$^+$: 230.1157, found: 230.1160.



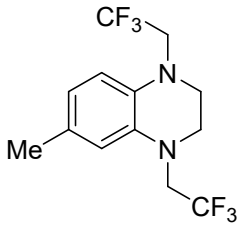
2-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroisoquinoline (2s): Colorless oil (34.0 mg, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.10 (m, 3H), 7.04 – 7.00 (m, 1H), 3.90 (s, 2H), 3.17 (q, *J* = 9.5 Hz, 2H), 3.00 (t, *J* = 5.8 Hz, 2H), 2.93 (t, *J* = 5.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.1, 133.9, 128.9, 126.6, 126.5, 125.9, 125.7 (q, *J* = 279.8 Hz), 58.1 (q, *J* = 27.8 Hz) 56.1, 51.6, 28.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.18.



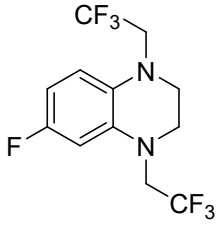
1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4a): Colorless oil (54.5 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 – 6.75 (m, 2H), 6.74 – 6.70 (m, 2H), 3.79 (q, *J* = 9.0 Hz, 4H), 3.45 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.4, 125.6 (q, *J* = 282.7 Hz), 119.8, 113.3, 54.3 (q, *J* = 32.7 Hz), 48.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.32. **HRMS (ESI) m/z:** calcd for $C_{12}H_{13}F_6N_2$ $[M + H]^+$: 299.0983, found: 299.0985.



6-methoxy-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4b): Colorless oil (56.5 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.65 (d, *J* = 8.5 Hz, 1H), 6.33 – 6.31 (m, 2H), 3.79 (q, *J* = 9.0 Hz, 2H), 3.75 (s, 3H), 3.68 (q, *J* = 9.1 Hz, 2H), 3.43 (t, *J* = 4.3 Hz, 2H), 3.36 (t, *J* = 4.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.1, 135.8, 128.7, 125.6 (q, *J* = 281.6 Hz), 125.5 (q, *J* = 283.1 Hz), 115.3, 103.35, 100.4, 55.7, 55.6 (q, *J* = 30.3 Hz), 54.1 (q, *J* = 33.7 Hz), 48.5, 48.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.17, -70.60. **HRMS (ESI) m/z:** calcd for $C_{13}H_{15}F_6N_2O$ $[M + H]^+$: 329.1089, found: 329.1091.

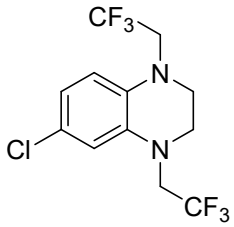


6-methyl-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4c): White solid (52.0 mg, 83% yield), M.p. 98-99 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 8.2 Hz, 1H), 6.52 (s, 1H), 3.81 – 3.72 (m, 4H), 3.44 – 3.33 (m, 4H), 2.25 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.4, 132.1, 129.4, 125.9 (q, *J* = 284.2 Hz), 125.9 (q, *J* = 284.2 Hz), 120.2, 114.1, 113.7, 54.6 (q, *J* = 32.8 Hz), 54.3 (q, *J* = 32.1 Hz), 48.6, 48.5, 21.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.32, -70.39. **HRMS (ESI) m/z:** calcd for $C_{13}H_{15}F_6N_2$ $[M + H]^+$: 313.1139, found: 313.1142.

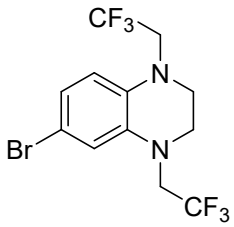


6-fluoro-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4d): White solid (50.6 mg, 80% yield), M.p. 69-70 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.65 – 6.60 (m, 1H), 6.46 – 6.42 (m, 2H), 3.78 (q, *J* = 8.9 Hz, 2H),

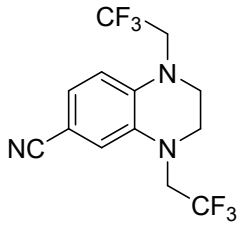
3.71 (q, 9.3 Hz, 2H), 3.44 (t, *J* = 4.3 Hz, 2H), 3.39 (t, *J* = 4.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4 (d, *J* = 237.7 Hz), 135.5 (d, *J* = 9.7 Hz), 130.4, 125.5 (q, *J* = 282.2 Hz), 125.4 (q, *J* = 280.6 Hz), 114.7 (d, *J* = 10.2 Hz), 105.1 (d, *J* = 22.1 Hz), 100.2 (d, *J* = 27.7 Hz), 55.2 (q, *J* = 32.3 Hz), 53.9 (q, *J* = 34.0 Hz), 48.3, 48.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.14, -70.49, -123.07. **HRMS (ESI) m/z:** calcd for $C_{12}H_{12}F_7N_2$ $[M + H]^+$: 317.0889, found: 317.0885.



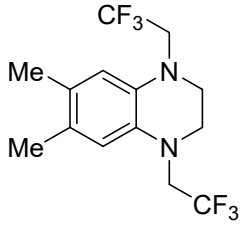
6-chloro-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4e): Yellow solid (55.9 mg, 84% yield), M.p. 61-62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70 (d, *J* = 8.6 Hz, 1H), 6.65 (s, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 3.81 – 3.73 (m, 4H), 3.46 – 3.40 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.2, 132.8, 125.6 (q, *J* = 282.4 Hz), 125.4 (q, *J* = 282.6 Hz), 124.7, 119.1, 114.0, 112.8, 54.3 (q, *J* = 32.9 Hz), 53.9 (q, *J* = 32.8 Hz), 48.4, 48.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.10, -70.18. **HRMS (ESI) m/z:** calcd for $C_{12}H_{12}ClF_6N_2$ $[M + H]^+$: 333.0593, found: 333.0595.



6-bromo-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4f): Yellow solid (61.0 mg, 81% yield), M.p. 64-65 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 – 6.83 (m, 1H), 6.78 (s, 1H), 6.54 (d, *J* = 8.6 Hz, 1H), 3.81 – 3.72 (m, 4H), 3.45 – 3.40 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 133.3, 125.4 (q, *J* = 282.4 Hz), 125.3 (q, *J* = 282.9 Hz), 122.1, 115.6, 114.3, 111.8, 54.1 (q, *J* = 33.3 Hz), 53.9 (q, *J* = 33.3 Hz), 48.4, 48.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.09, -70.14. **HRMS (ESI) m/z:** calcd for $C_{12}H_{12}BrF_6N_2$ $[M + H]^+$: 377.0088, found: 377.0091.

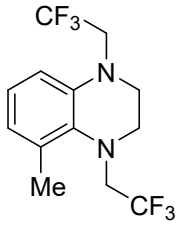


1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline-6-carbonitrile (4g): Light green solid (19.4 mg, 30% yield), M.p. 112-113 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.4 Hz, 1H), 6.87 (s, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 3.88 (q, *J* = 8.8 Hz, 2H), 3.81 (q, *J* = 8.8 Hz, 2H), 3.54 (t, *J* = 4.4 Hz, 2H), 3.49 (t, *J* = 4.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 133.9, 125.2 (q, *J* = 282.5 Hz), 125.1 (q, *J* = 282.7 Hz) ,124.5, 120.1, 115.3, 111.9, 101.6, 53.7 (q, *J* = 33.5 Hz), δ 53.2 (q, *J* = 33.2 Hz), 48.5, 48.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.72, -69.88. **HRMS (ESI) m/z:** calcd for $C_{13}H_{12}F_6N_3$ $[M + H]^+$: 324.0935, found: 324.0941.

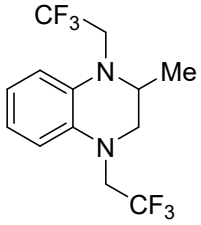


6,7-dimethyl-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4i): Colorless oil (60.7 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.52 (s, 2H), 3.76 (q, *J* = 9.0 Hz, 4H), 3.39 (s, 4H),

2.19 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.4, 127.7,125.7 (q, *J* = 281.7 Hz), 115.3, 54.7 (q, *J* = 32.2 Hz), 48.6, 19.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.44. **HRMS (ESI) m/z:** calcd for $C_{14}H_{17}F_6N_2$ $[M + H]^+$: 327.1296, found: 327.1300.



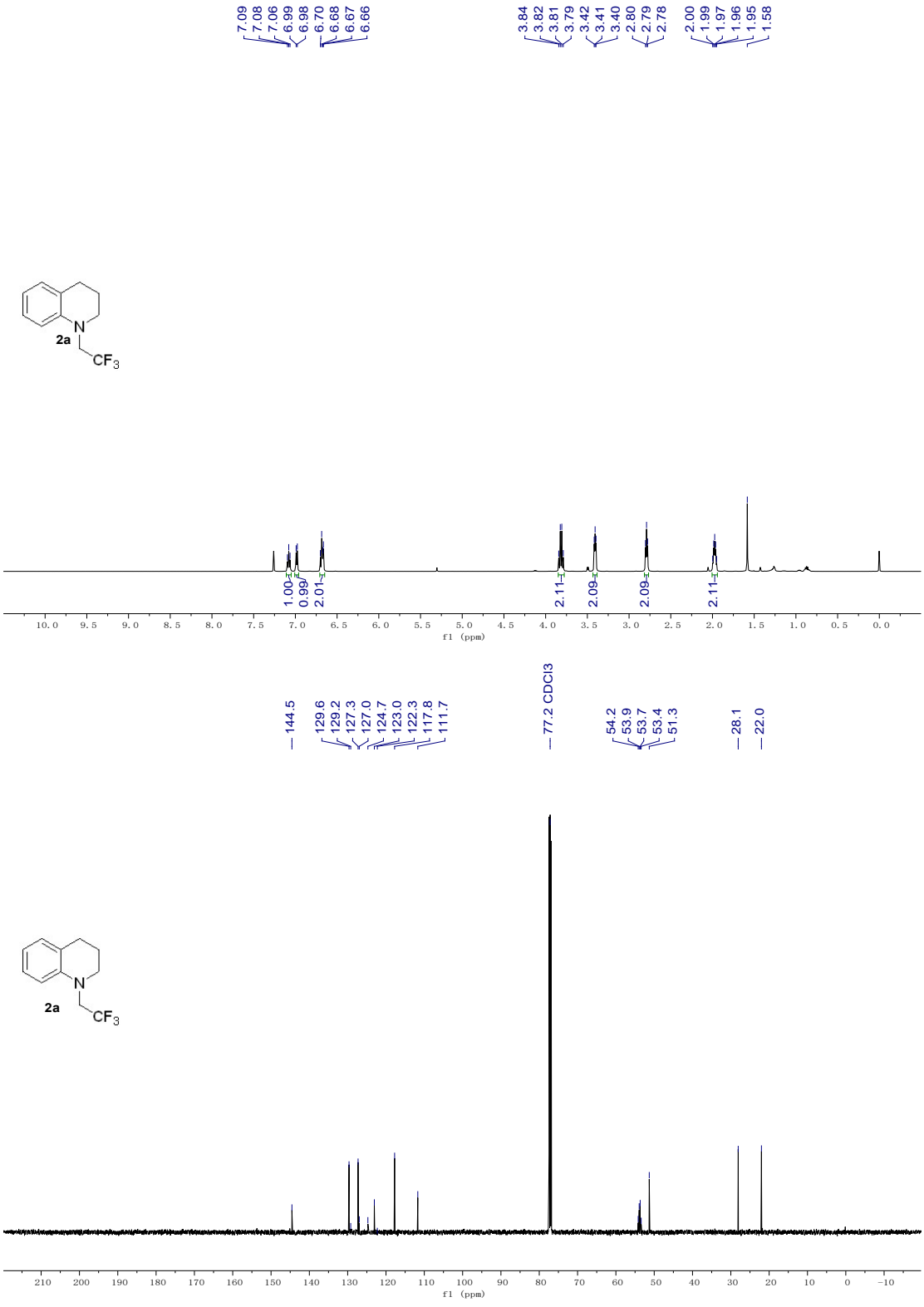
5-methyl-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4j): Colorless oil (29.4 mg, 47% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (t, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 2H), 3.91 (q, *J* = 8.9 Hz, 2H), 3.50 – 3.43 (m, 2H), 3.30 (q, *J* = 9.0 Hz, 2H), 3.23 – 3.17 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 133.6, 133.2, 125.7 (q, *J* = 279.4 Hz), 125.3 (q, *J* = 280.0 Hz), 124.8, 121.3, 110.1, 55.8 (q, *J* = 30.3 Hz), 53.6 (q, *J* = 33.0 Hz), 45.4, 43.4, 18.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -68.10, -69.87. **HRMS (ESI) m/z:** calcd for $C_{13}H_{15}F_6N_2$ $[M + H]^+$: 313.1139, found: 313.1146.

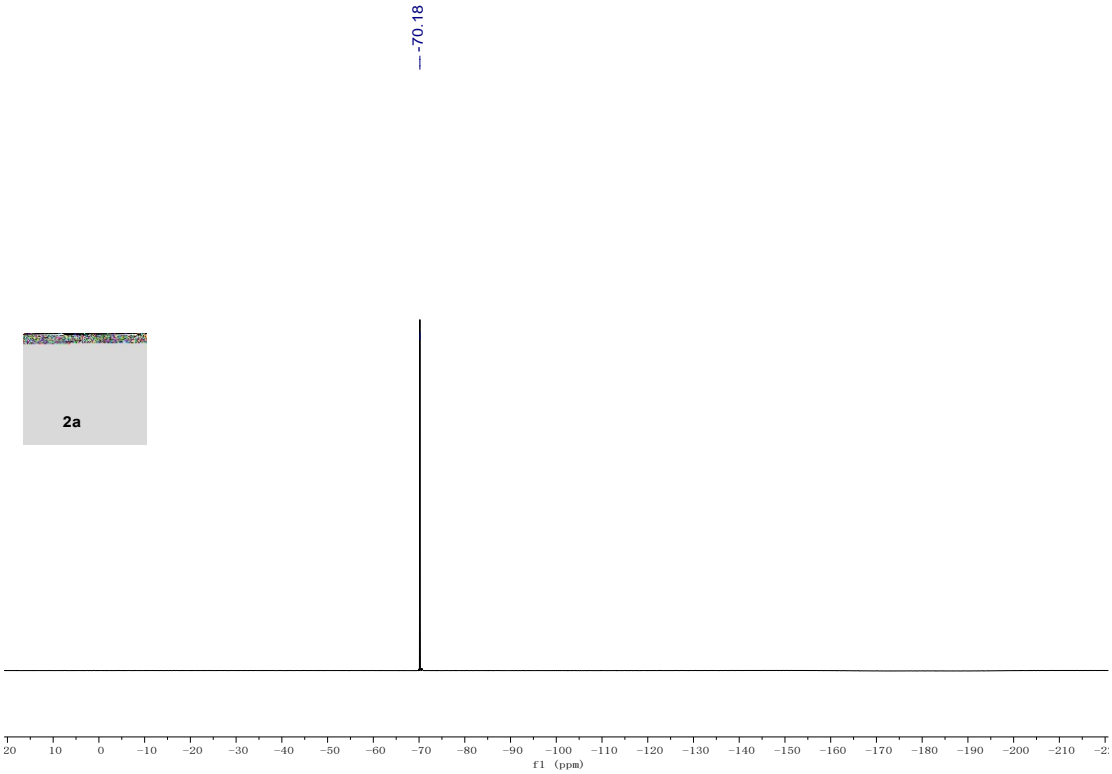


2-methyl-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4k): Colorless oil (12.5 mg, 20% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 – 6.75 (m, 2H), 6.73 – 6.70 (m, 2H), 3.96 – 3.81 (m, 2H), 3.81 – 3.66 (m, 2H), 3.59 – 3.53 (m, 2H), 3.16 (d, *J* = 11.1 Hz, 1H), 1.20 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.8, 132.8, 125.6 (q, *J* = 282.9 Hz), 125.5 (q, *J* = 282.0 Hz), 119.7, 119.5, 114.5, 111.9, 53.7 (q, *J* = 33.2 Hz), 53.7(q, *J* = 33.2 Hz), 53.2, 53.0, 16.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.38, -70.88. **HRMS (ESI) m/z:** calcd for $C_{13}H_{15}F_6N_2$ $[M + H]^+$: 313.1139, found: 313.1137.

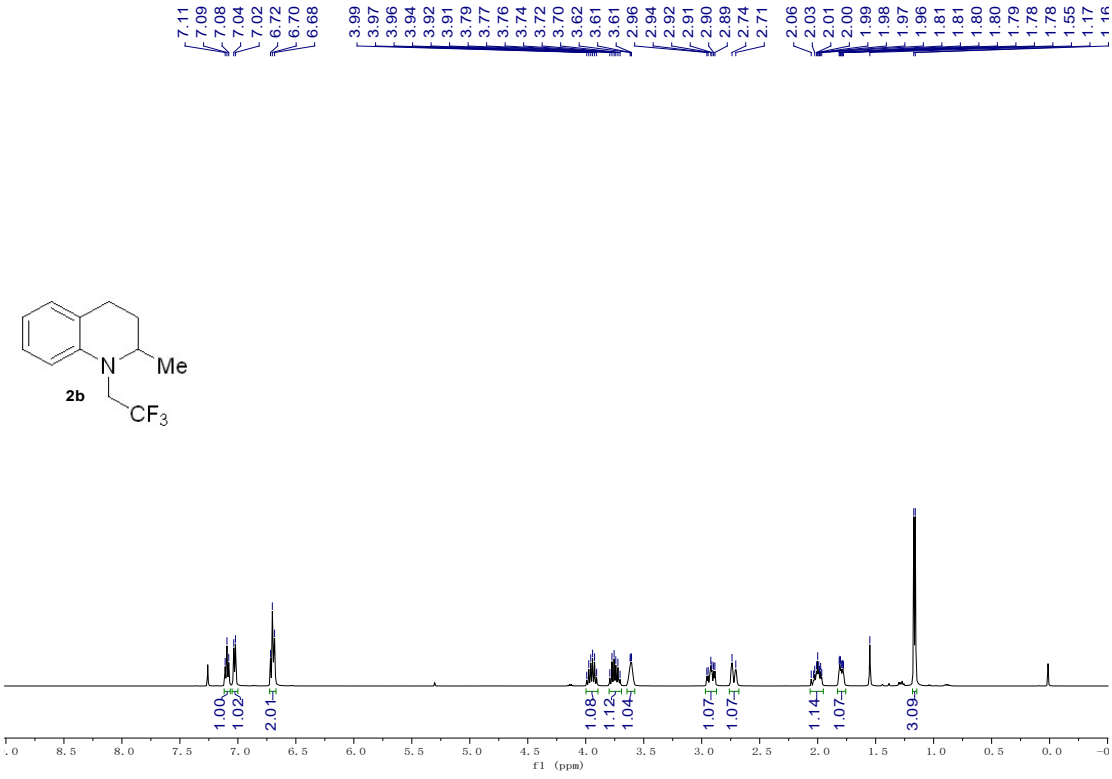
8. NMR spectrum of products

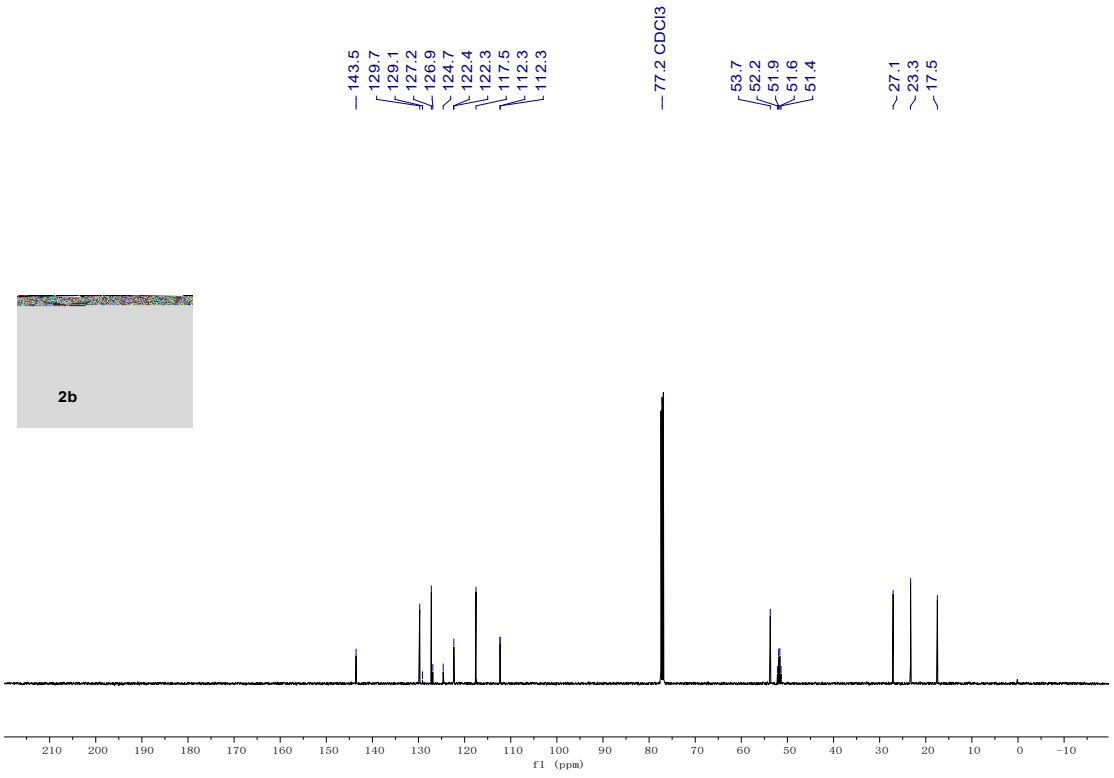
1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2a)

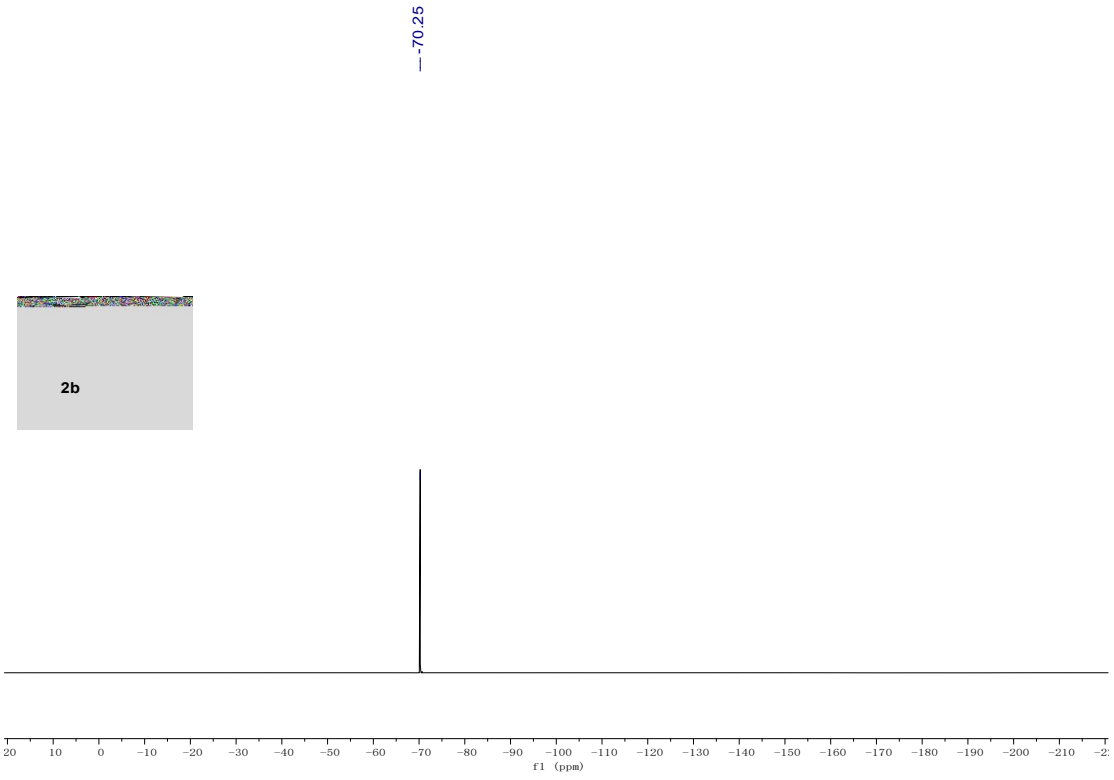




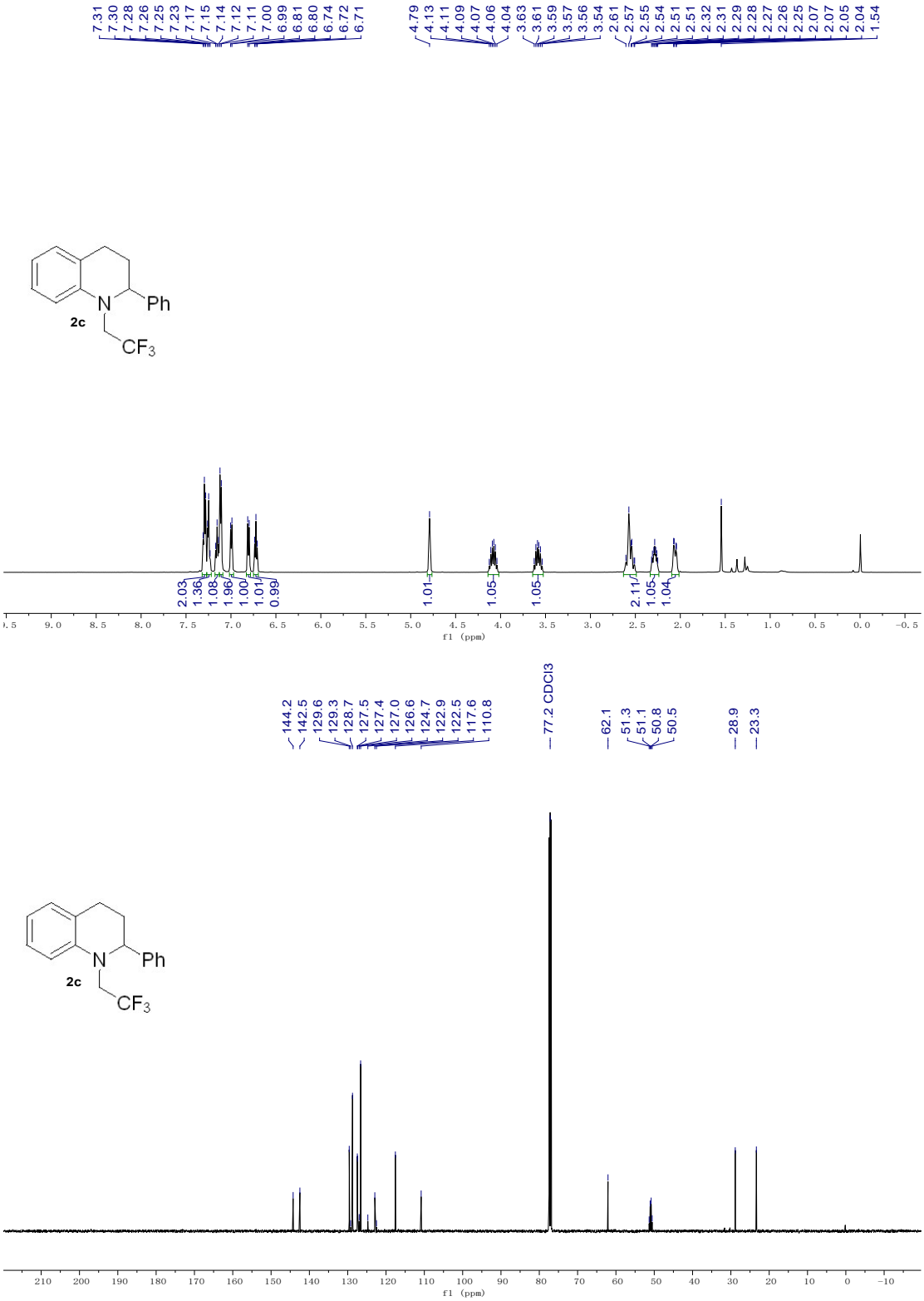
2-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2b)

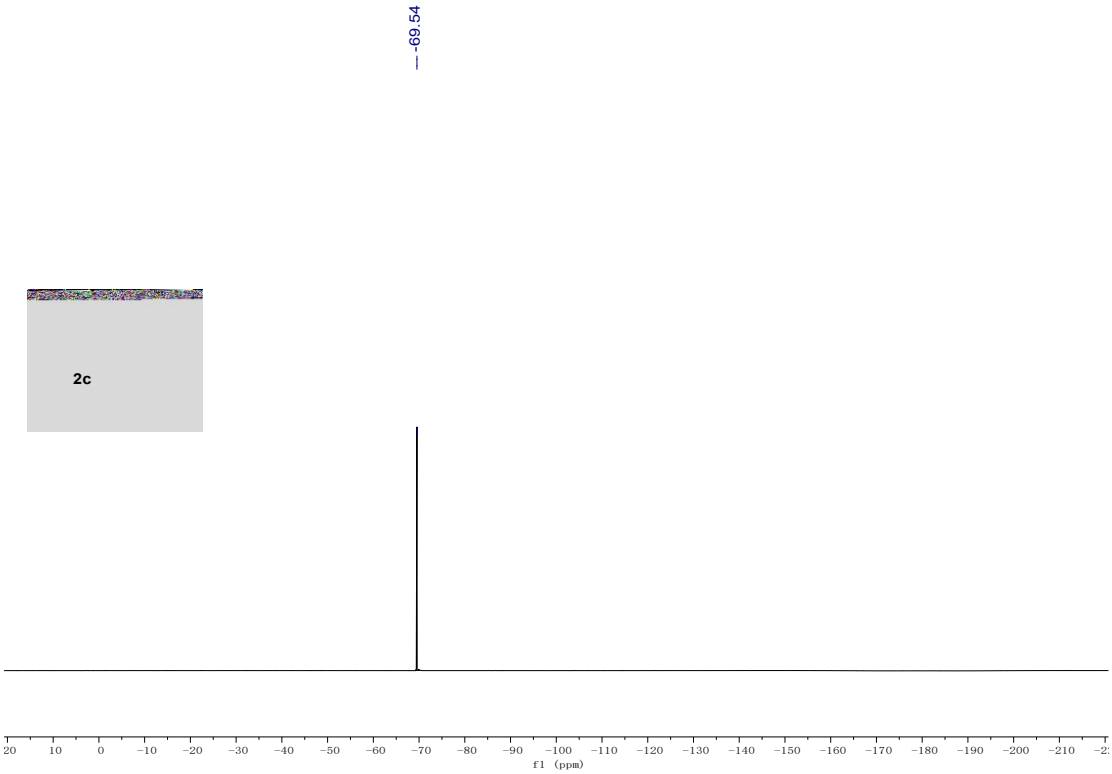



143.5
129.7
129.1
127.2
126.9
124.7
122.4
122.3
117.5
112.3
112.3
77.2 CDCl3
53.7
52.2
51.9
51.6
51.4
27.1
23.3
17.5
2b
f1 (ppm)

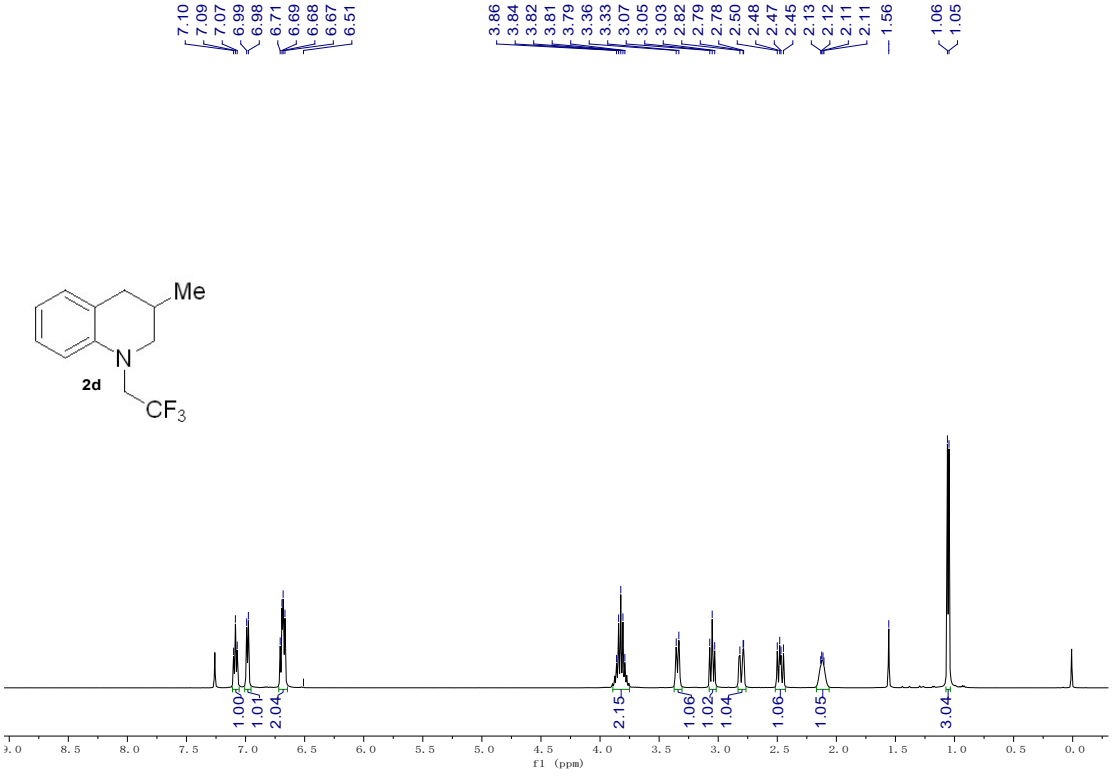

-70.25
2b
f1 (ppm)

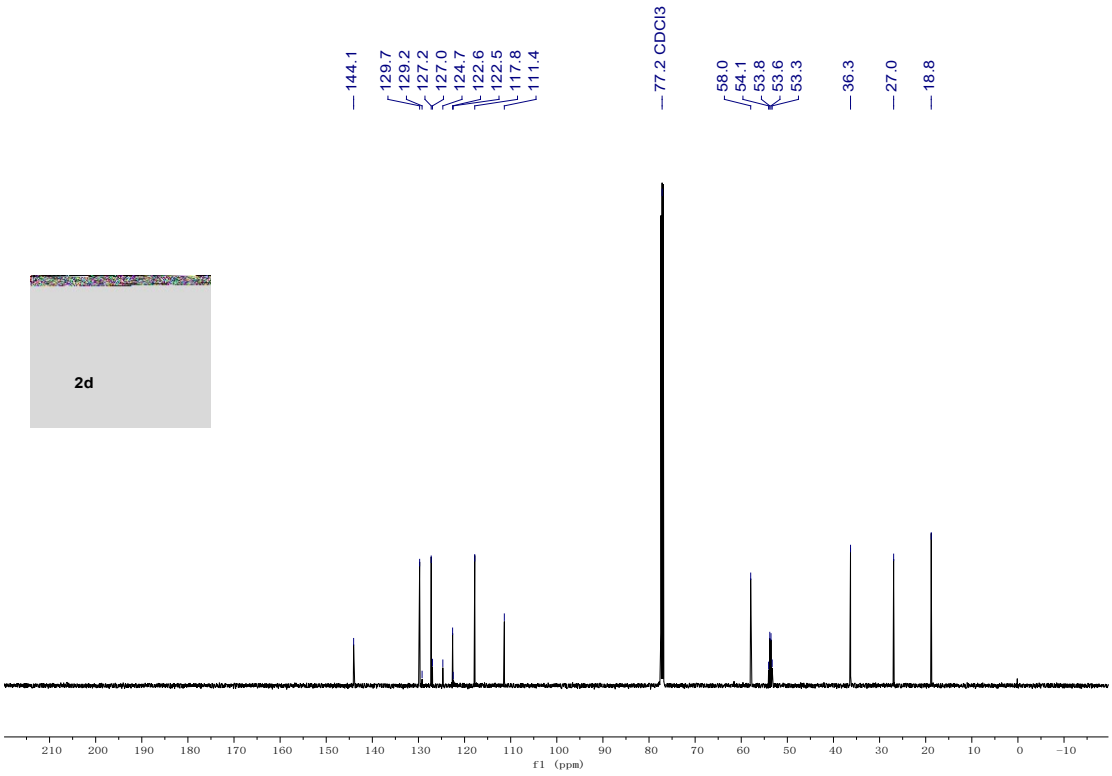
2-phenyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2c)

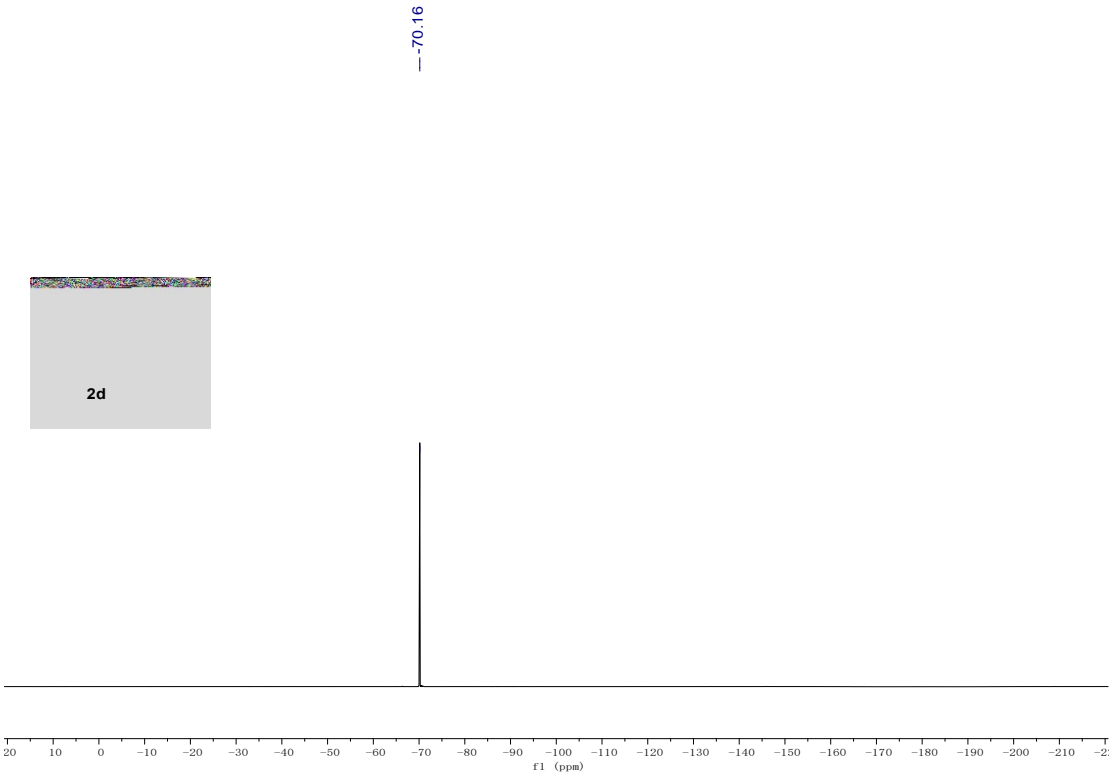




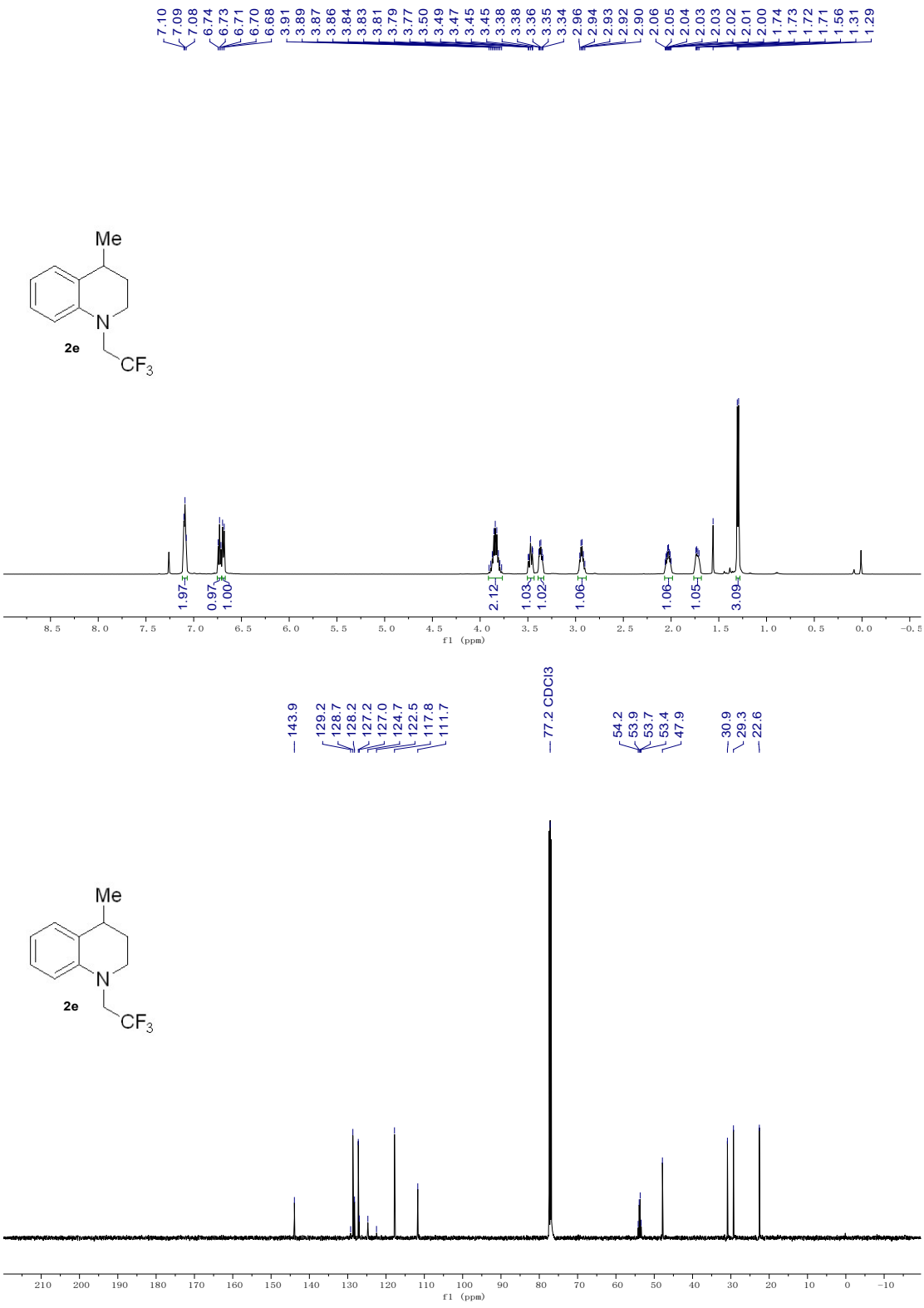
3-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2d)

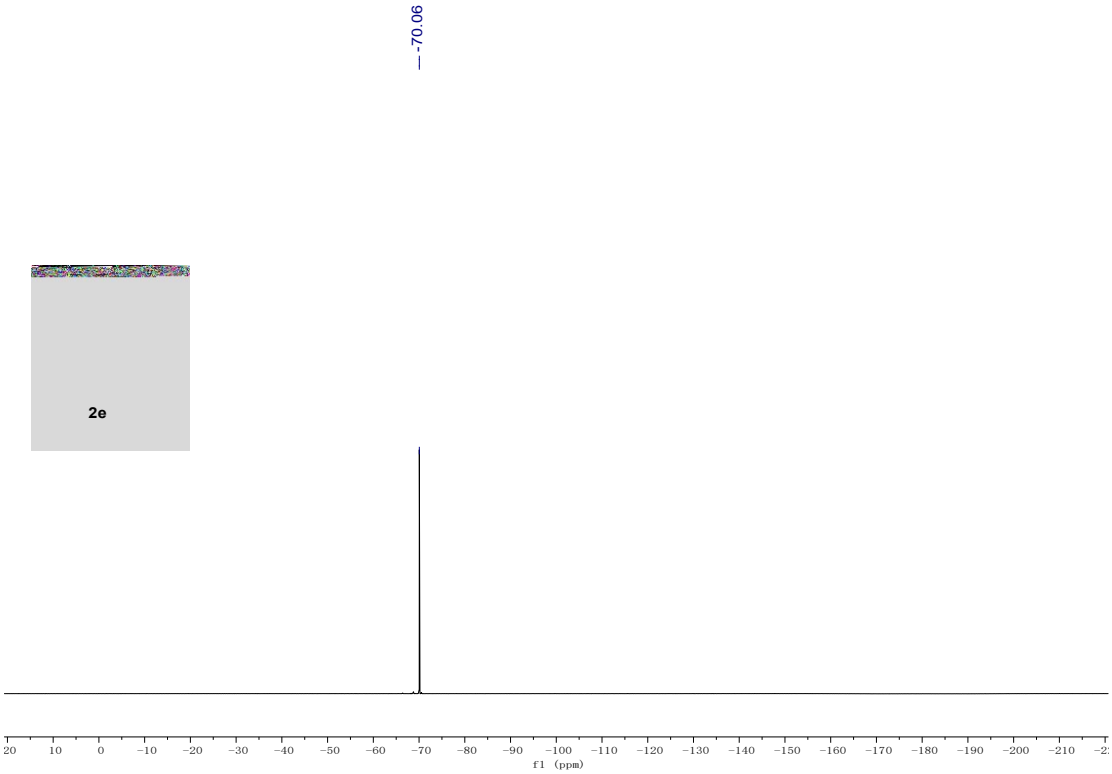



144.1
129.7
129.2
127.2
127.0
124.7
122.6
122.5
117.8
111.4
77.2 CDCl3
58.0
54.1
53.8
53.6
53.3
36.3
27.0
18.8
2d
f1 (ppm)

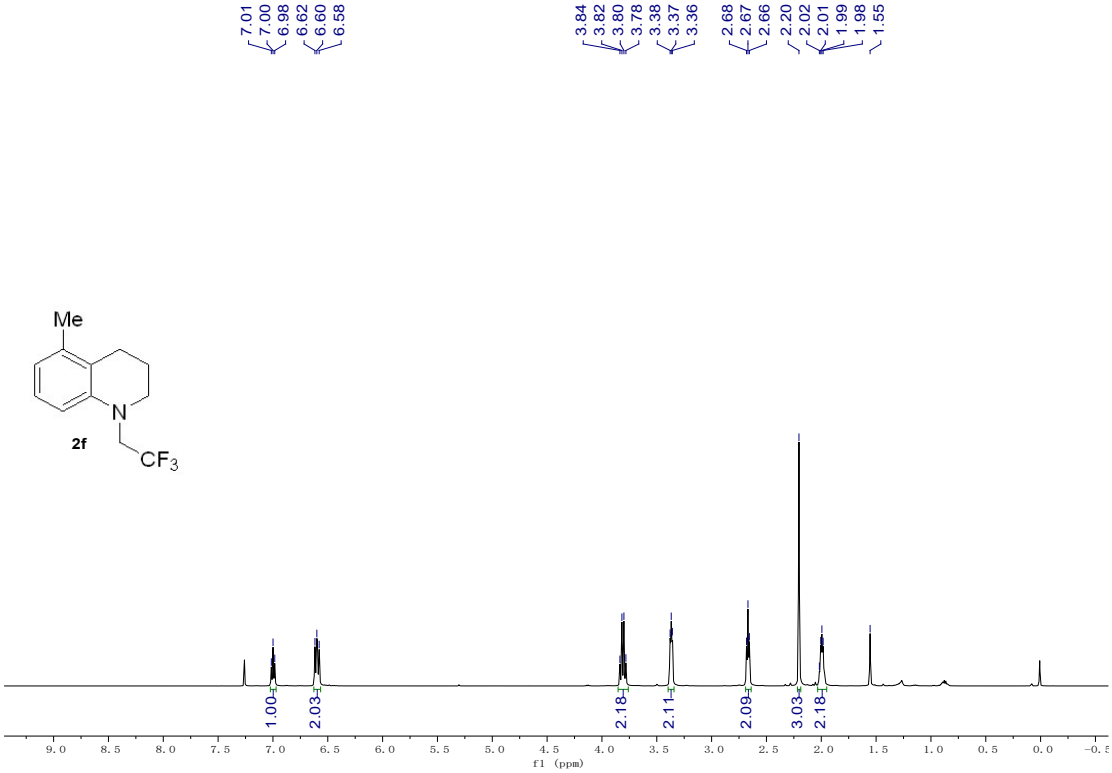

-70.16
2d
f1 (ppm)

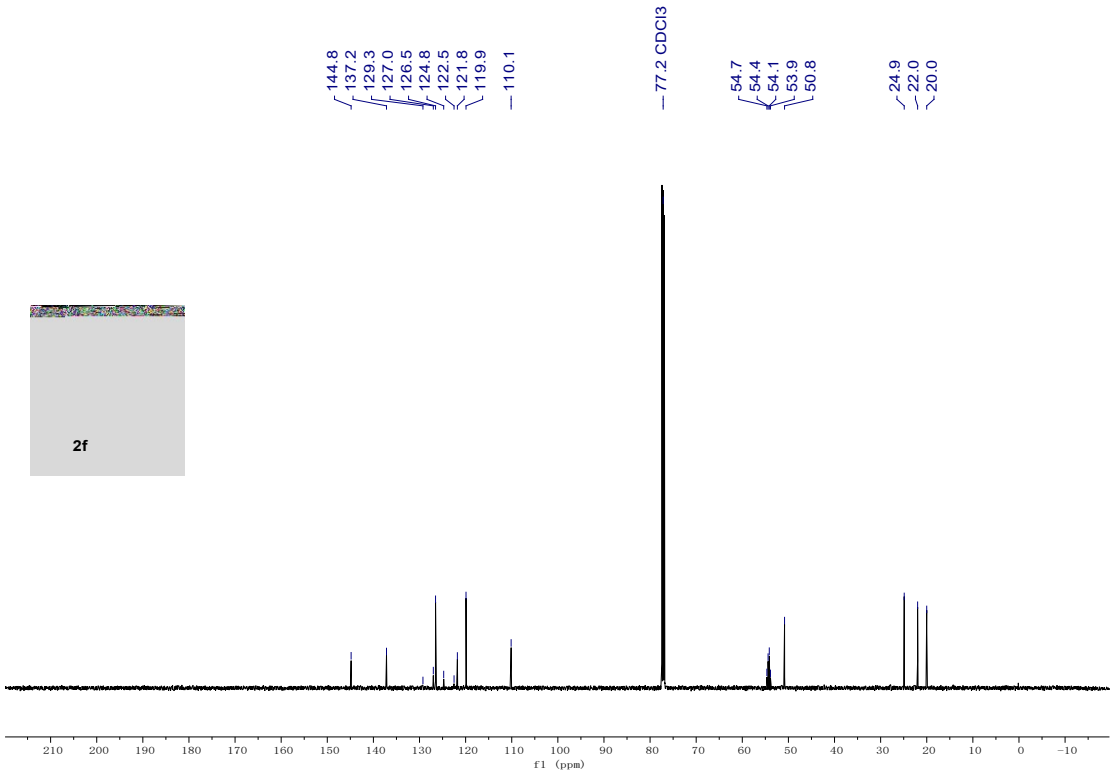
4-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2e)

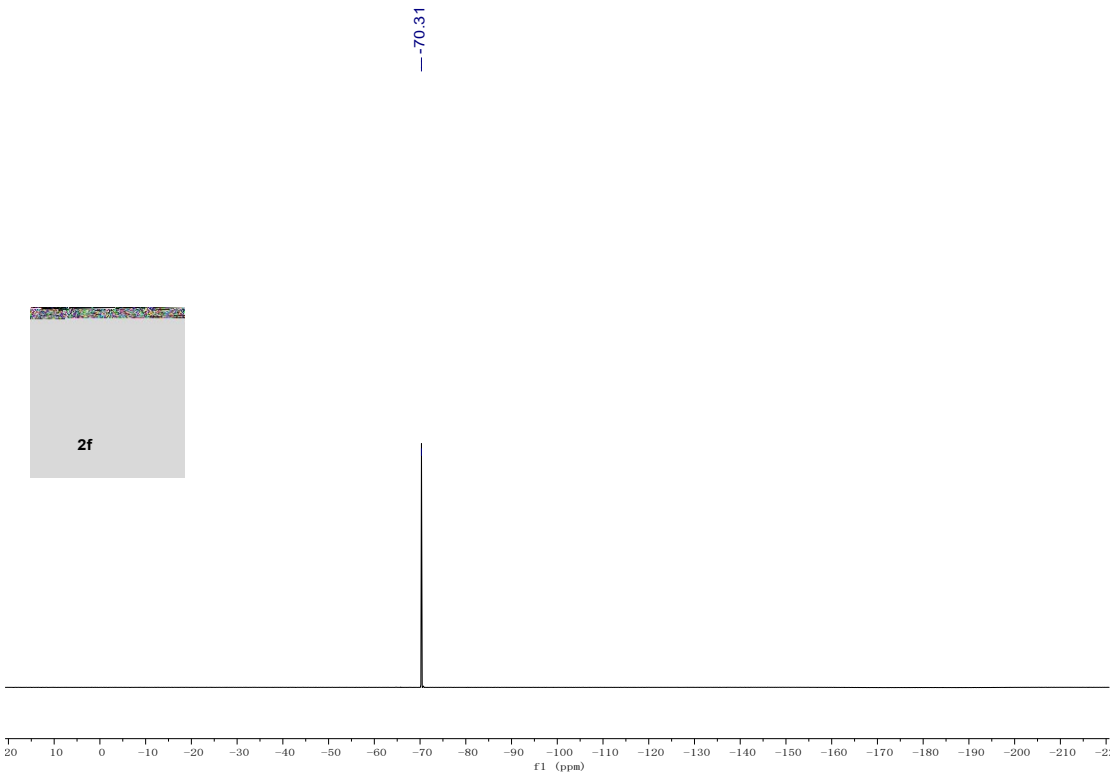




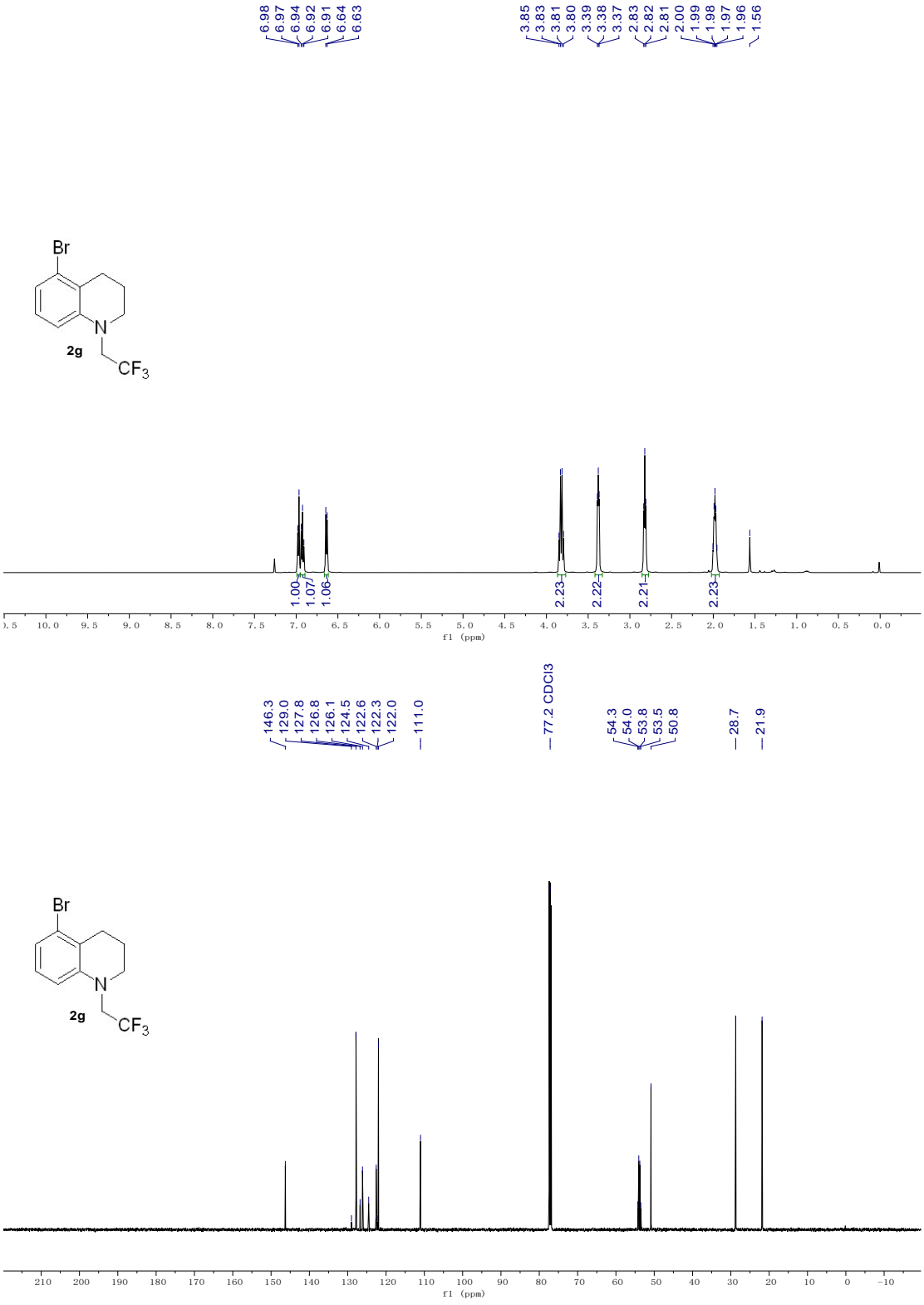
5-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2f)

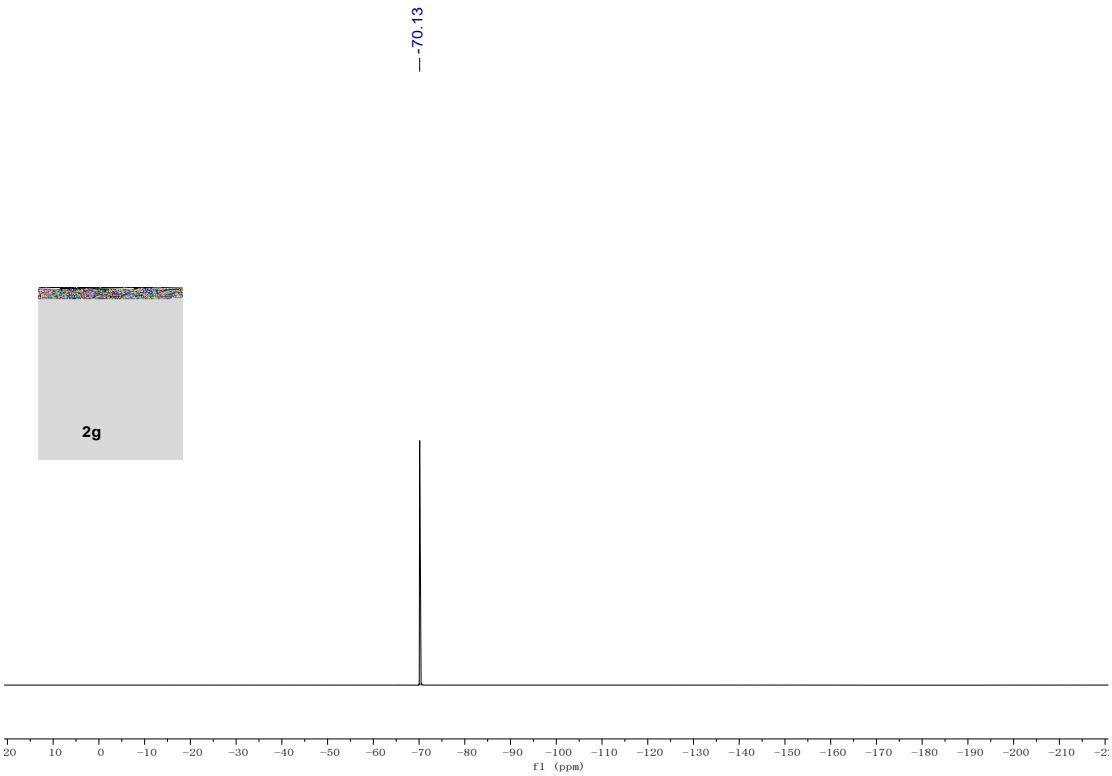



144.8
137.2
129.3
127.0
126.5
124.8
122.5
121.8
119.9
110.1
77.2 CDCl3
54.7
54.4
54.1
53.9
50.8
24.9
22.0
20.0
2f
f1 (ppm)

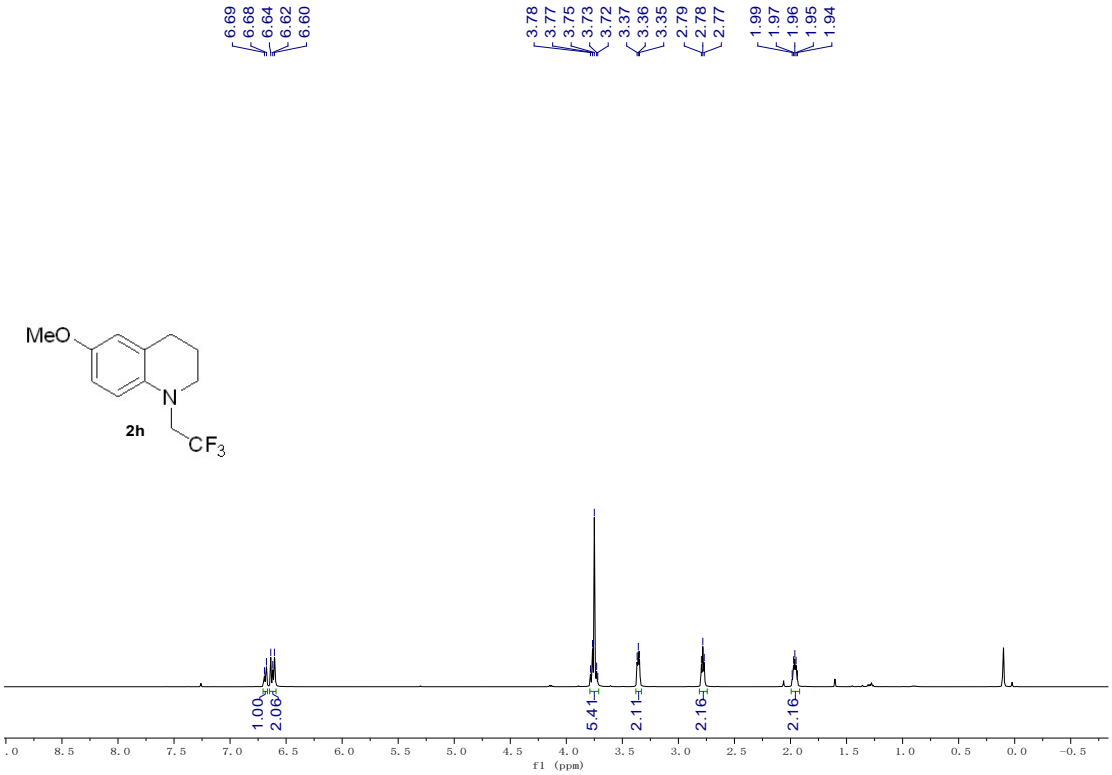

-70.31
2f
f1 (ppm)

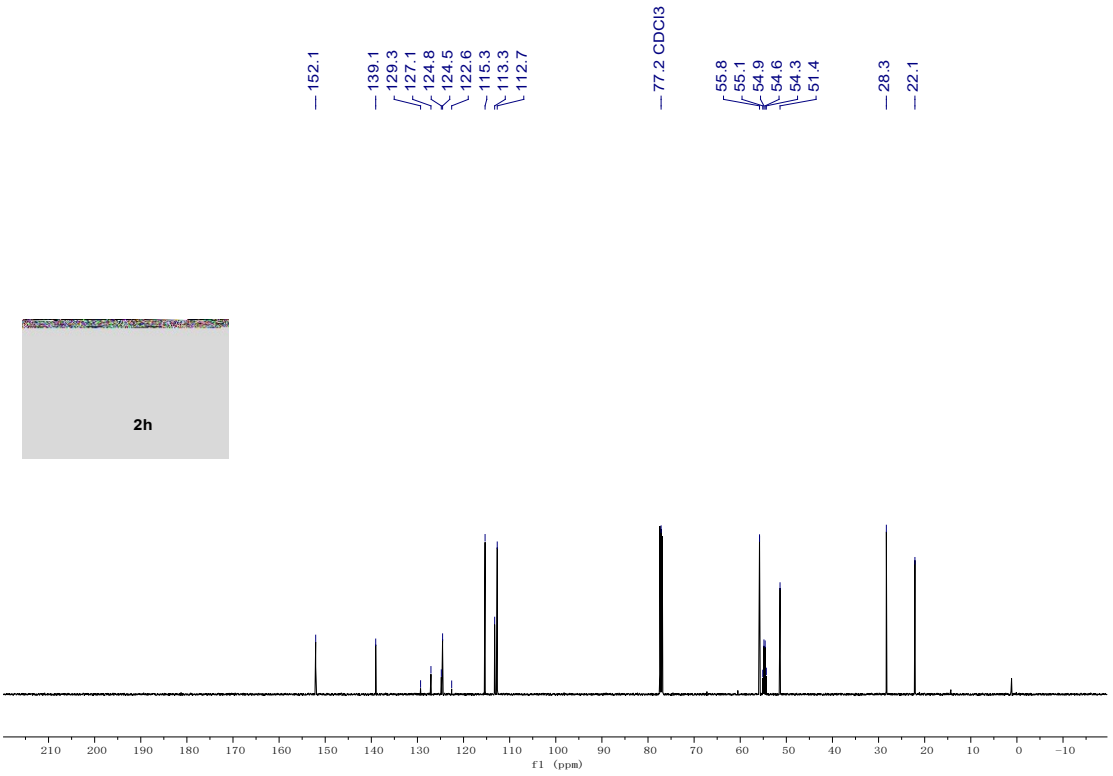
5-bromo-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2g)

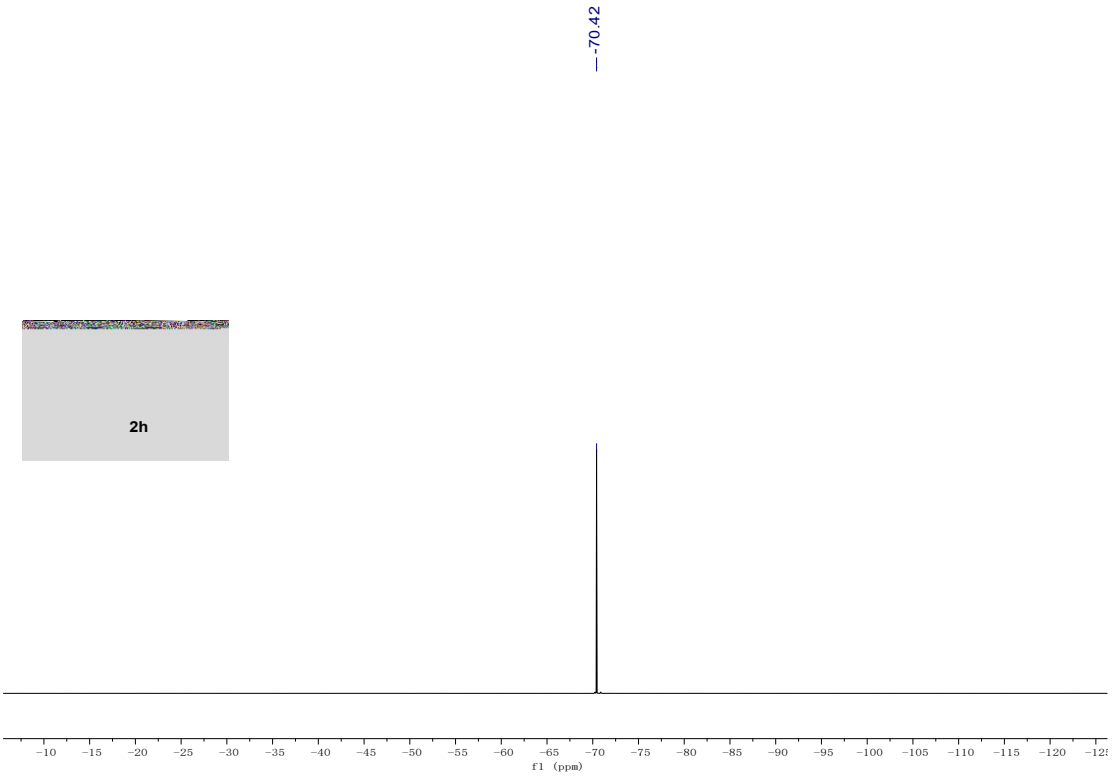




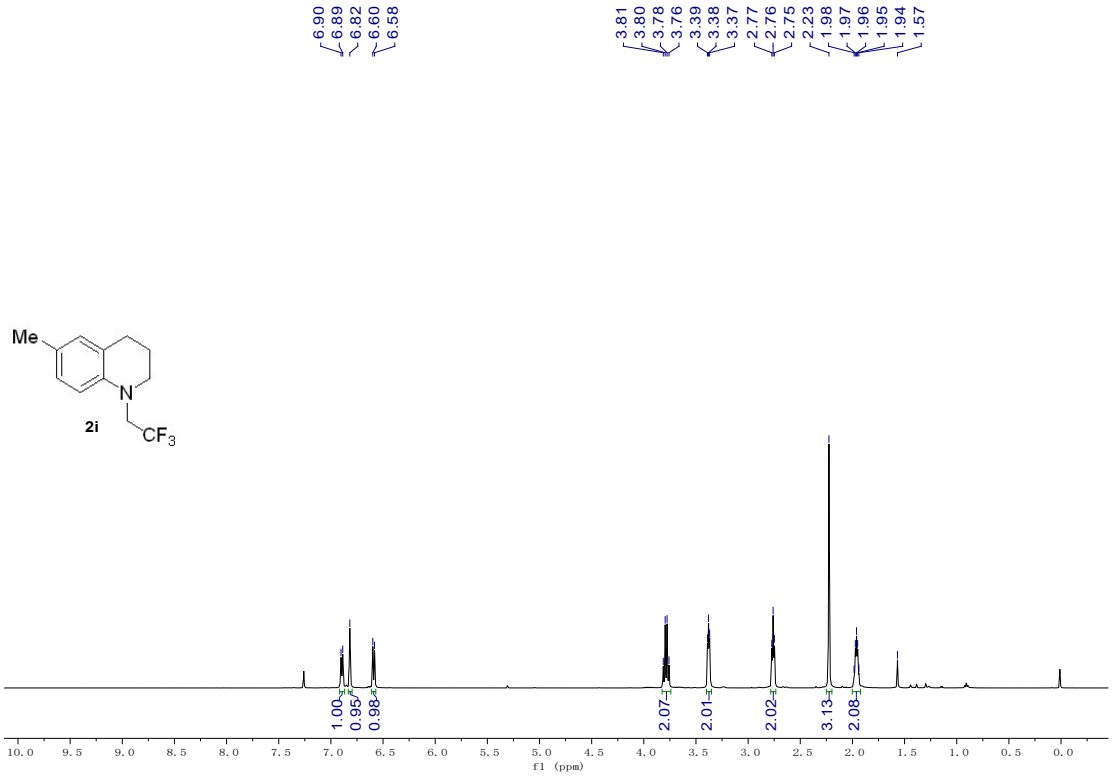
6-methoxy-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2h)

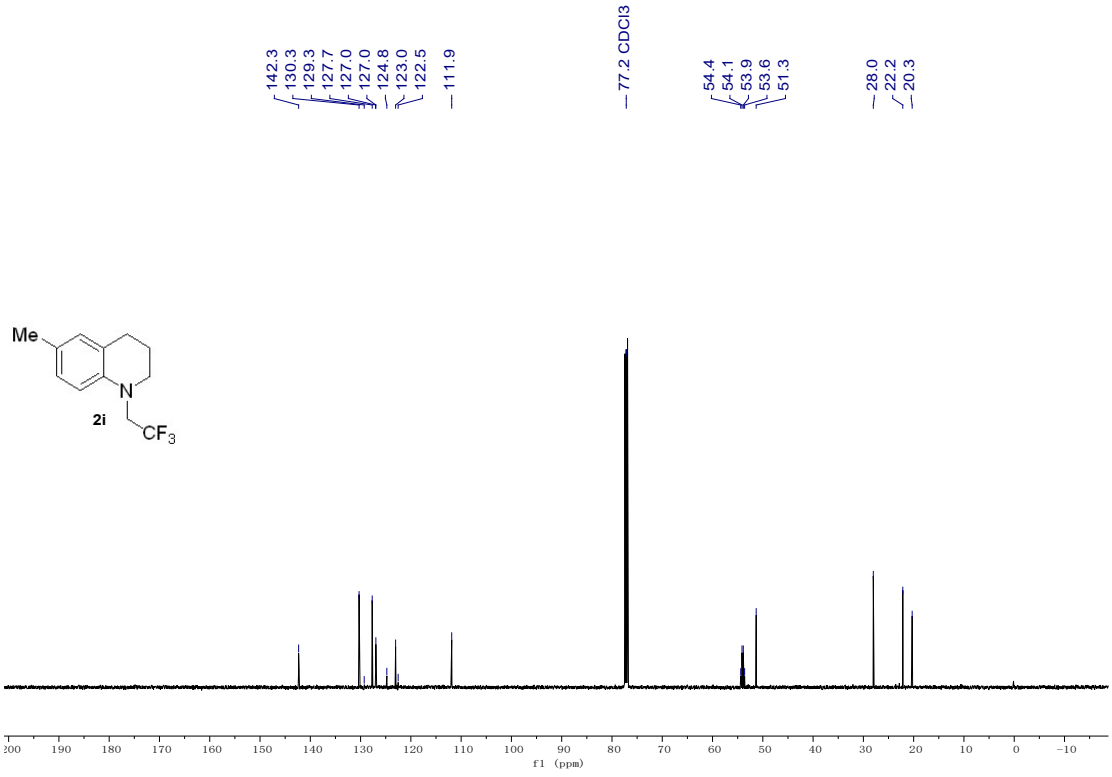


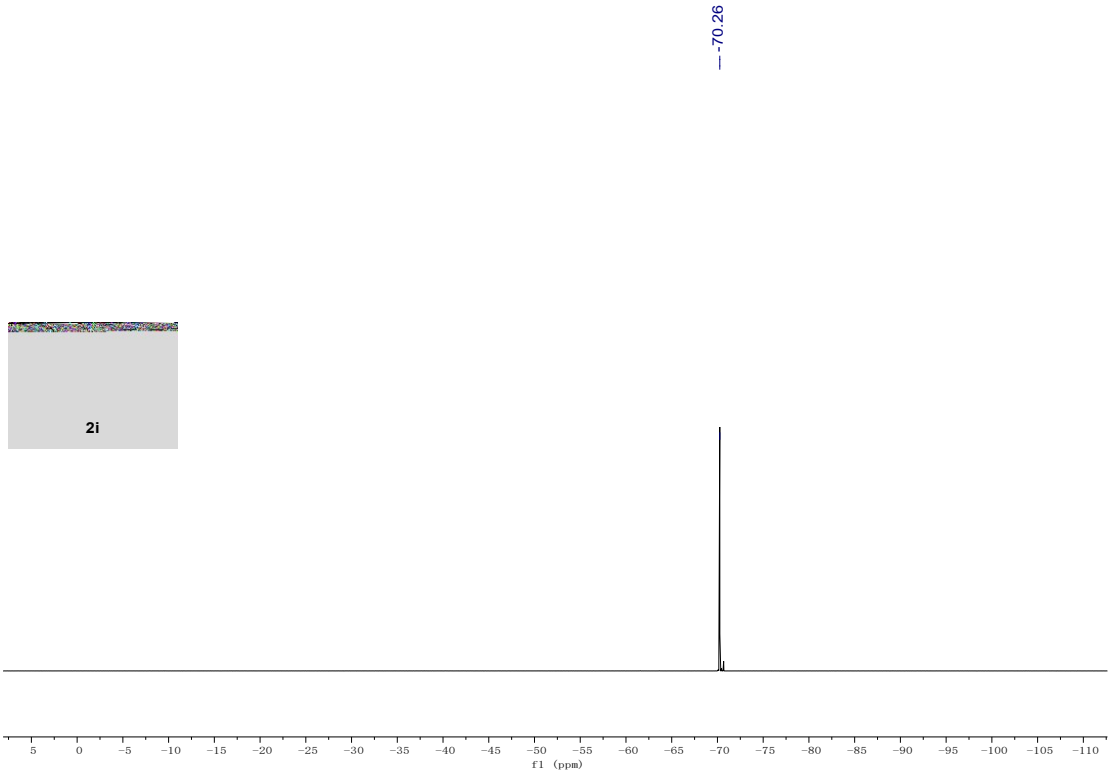

152.1
139.1
129.3
127.1
124.8
124.5
122.6
115.3
113.3
112.7
77.2 CDCl3
55.8
55.1
54.9
54.6
54.3
51.4
28.3
22.1
2h
f1 (ppm)


-70.42
2h
f1 (ppm)

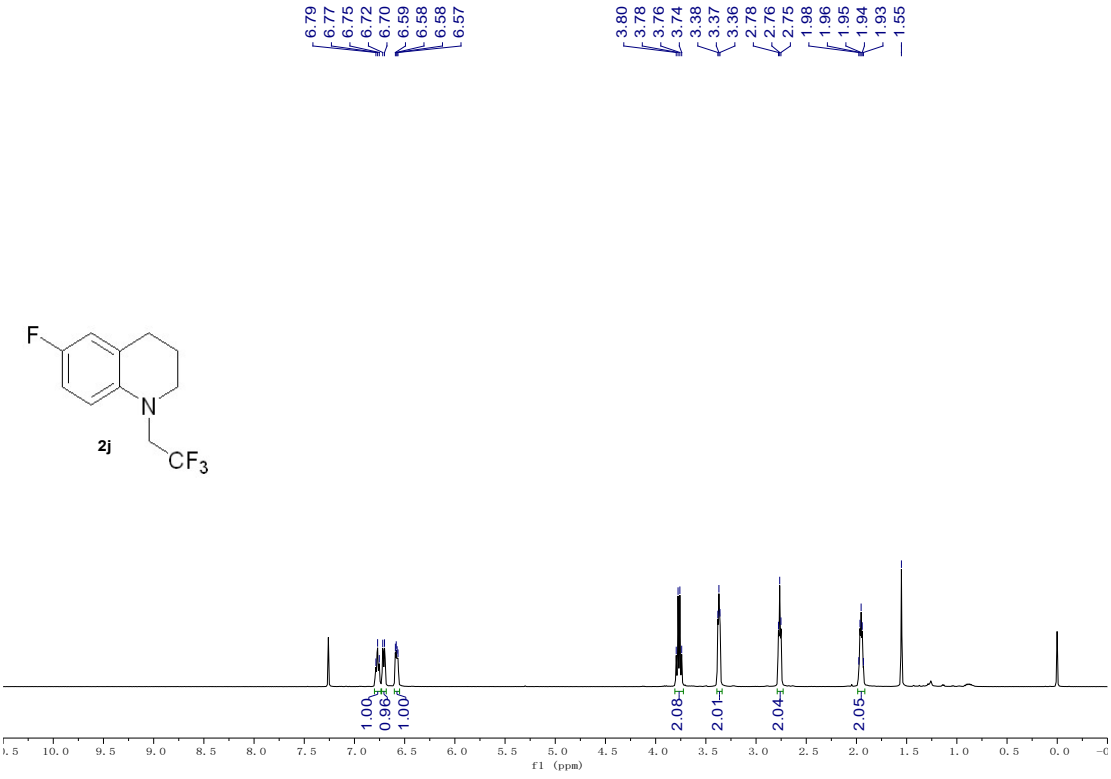
6-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2i)

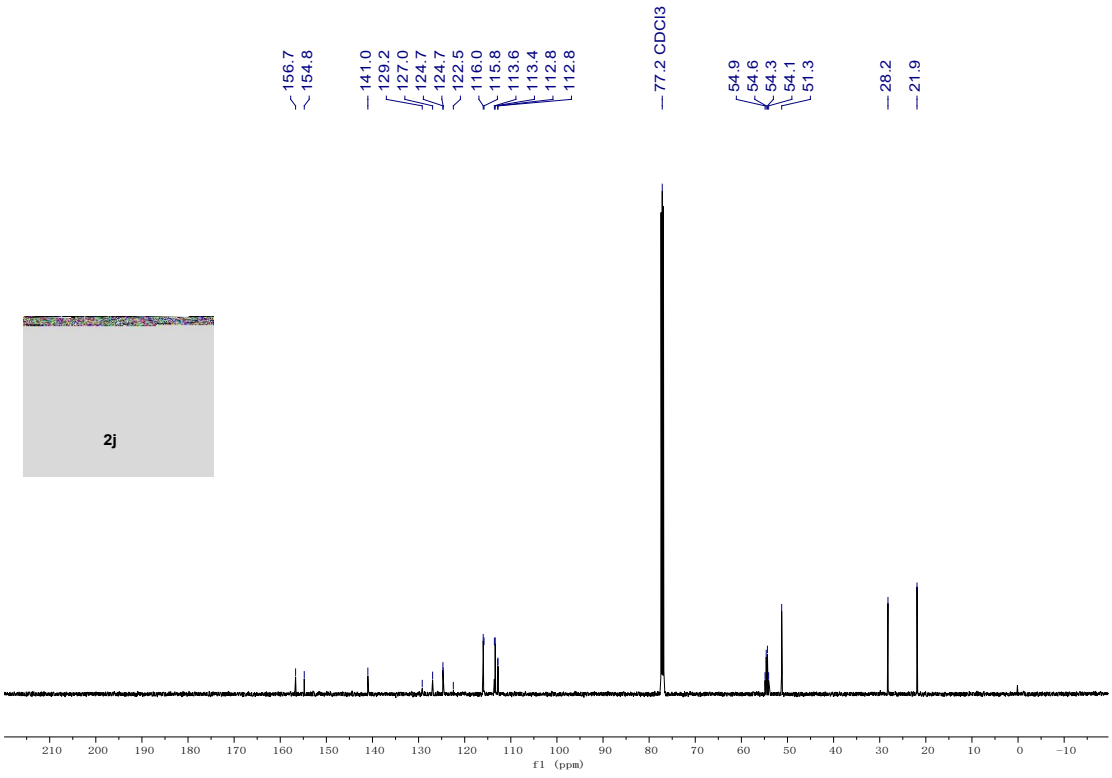


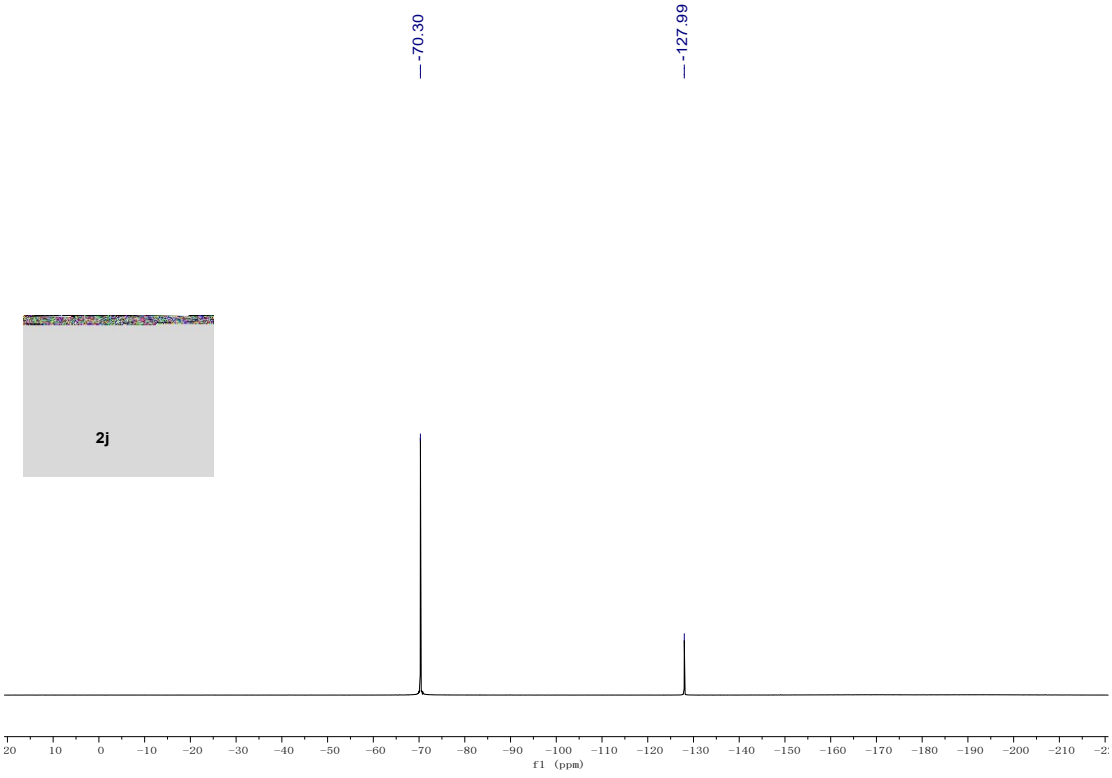




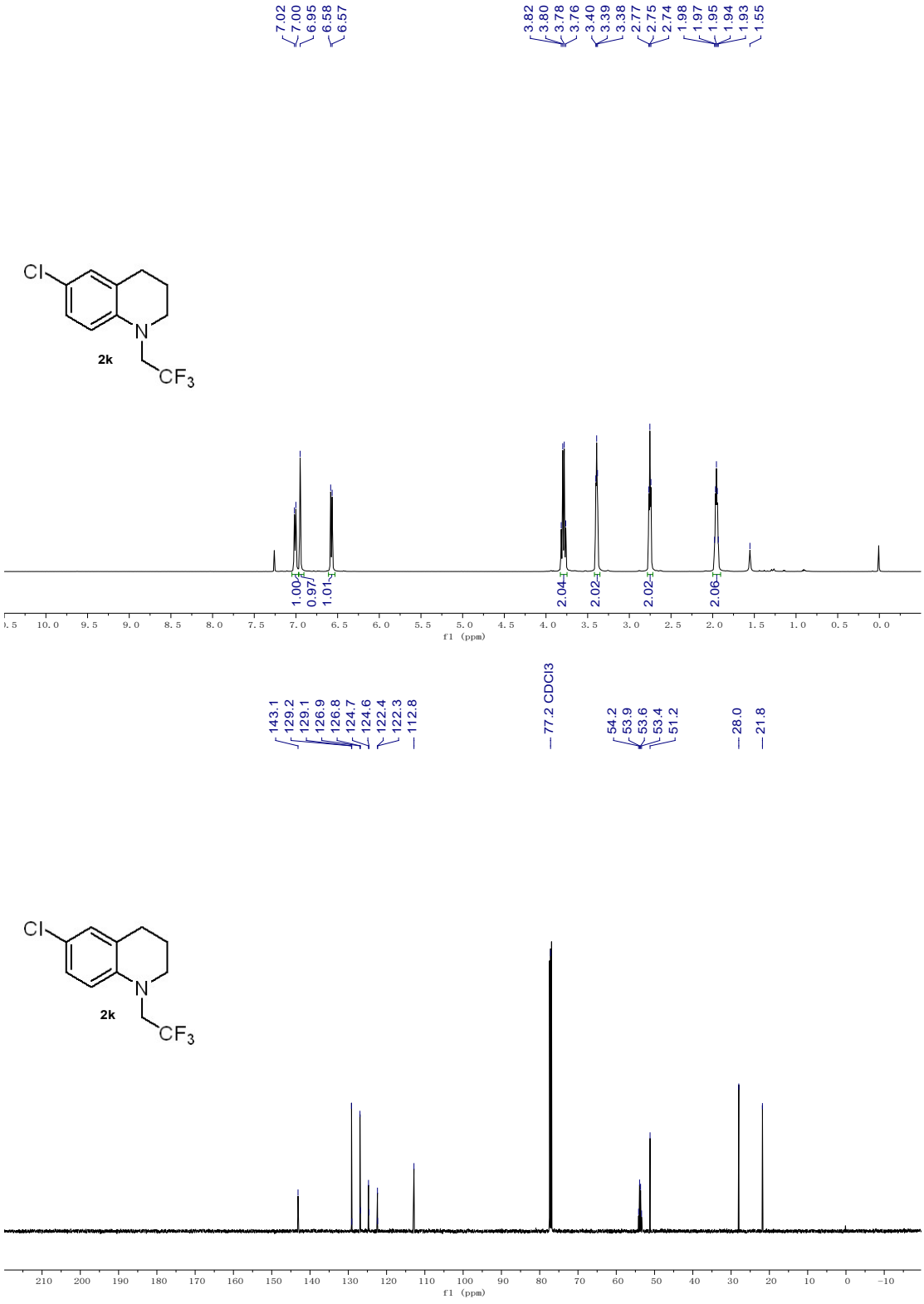
6-fluoro-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2j)

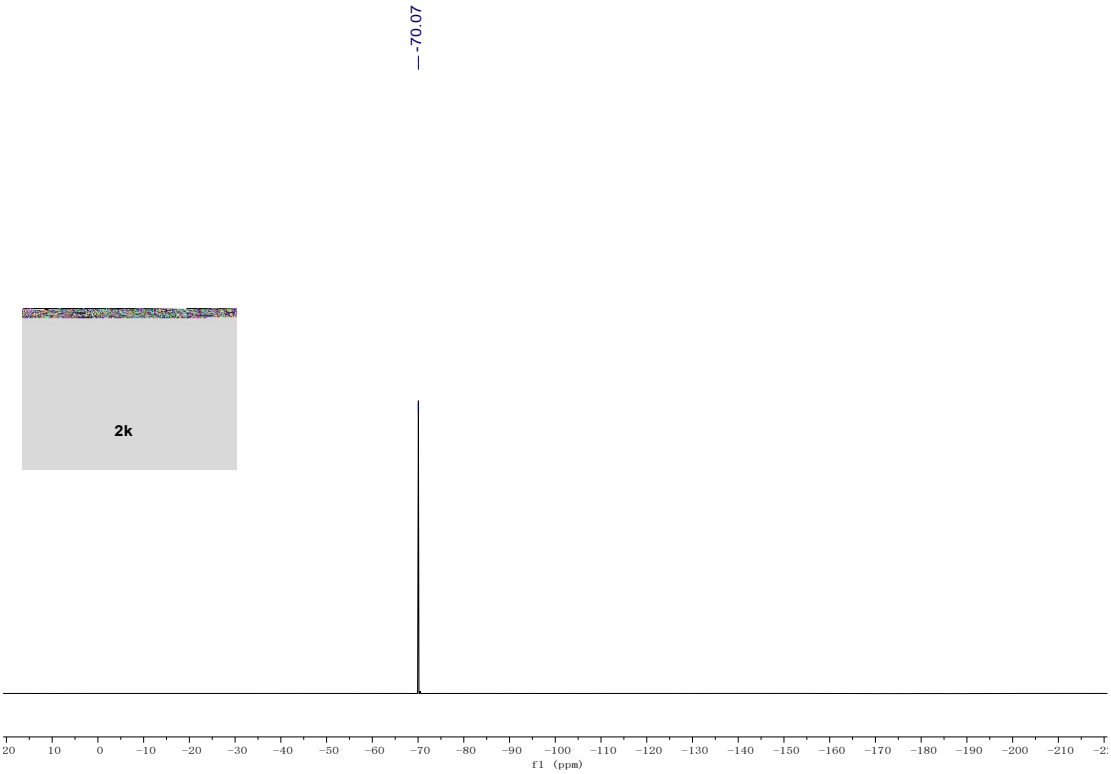



156.7
154.8
141.0
129.2
127.0
124.7
124.7
122.5
116.0
115.8
113.6
113.4
112.8
112.8
77.2 CDCl3
54.9
54.6
54.3
54.1
51.3
28.2
21.9
2j
f1 (ppm)

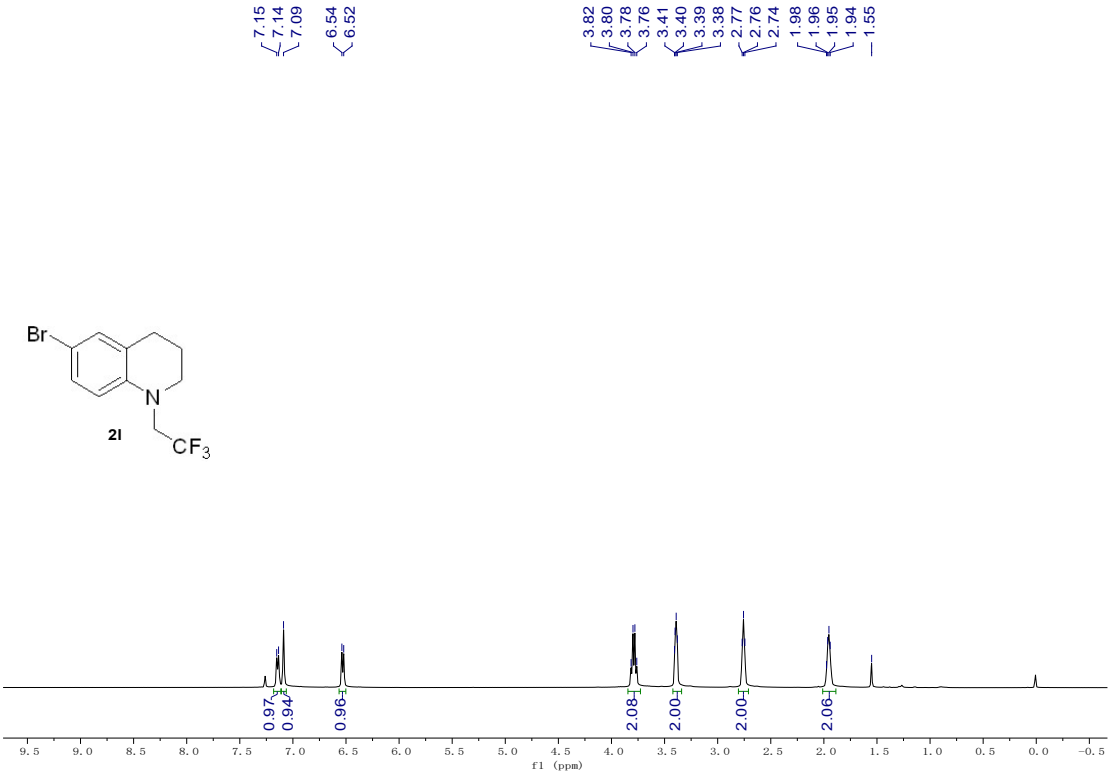

-70.30
-127.99
2j
f1 (ppm)

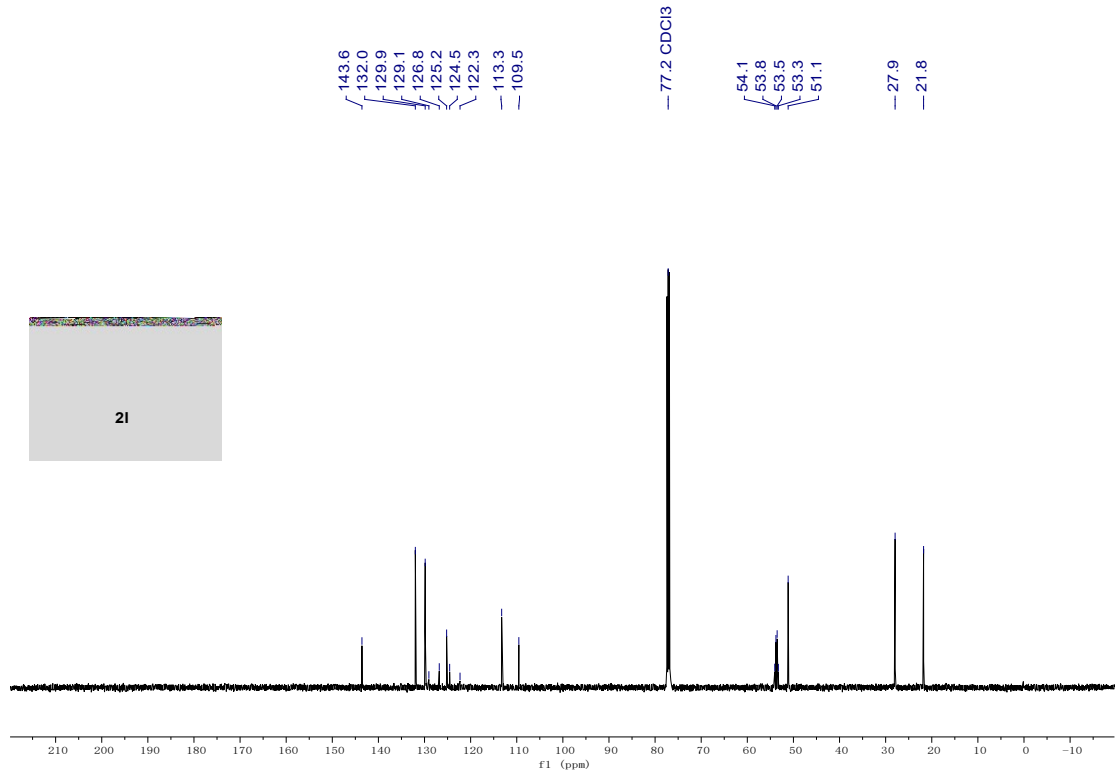
6-chloro-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2k)

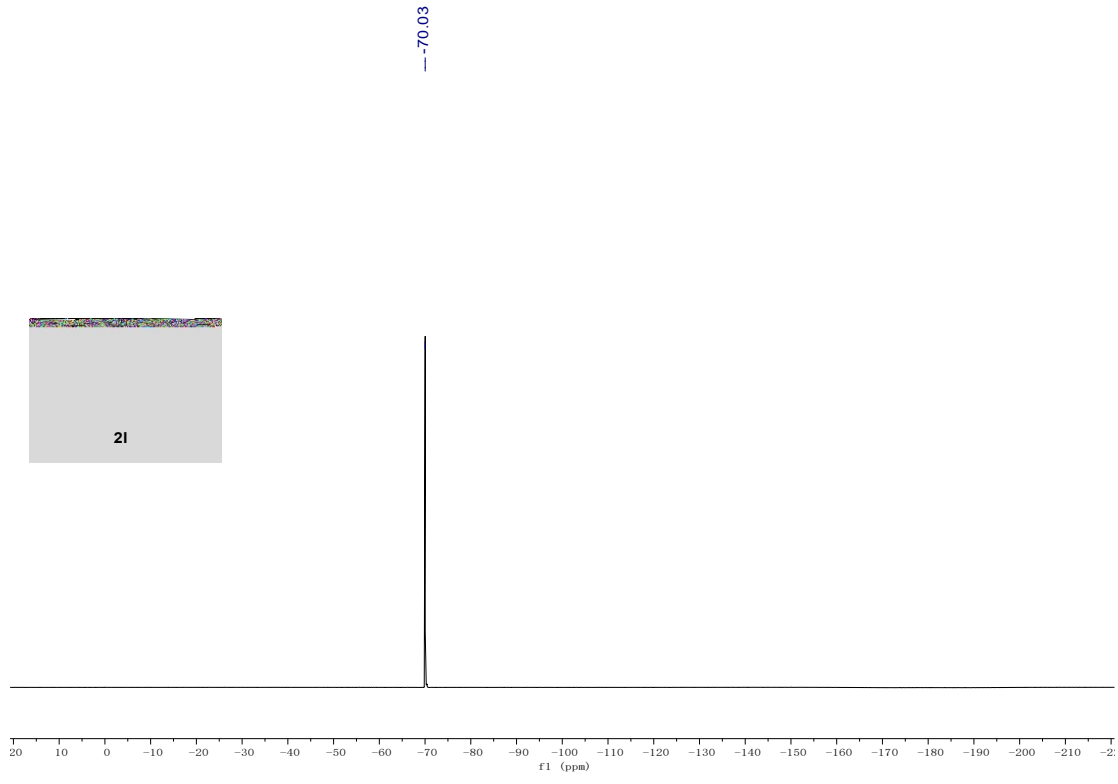




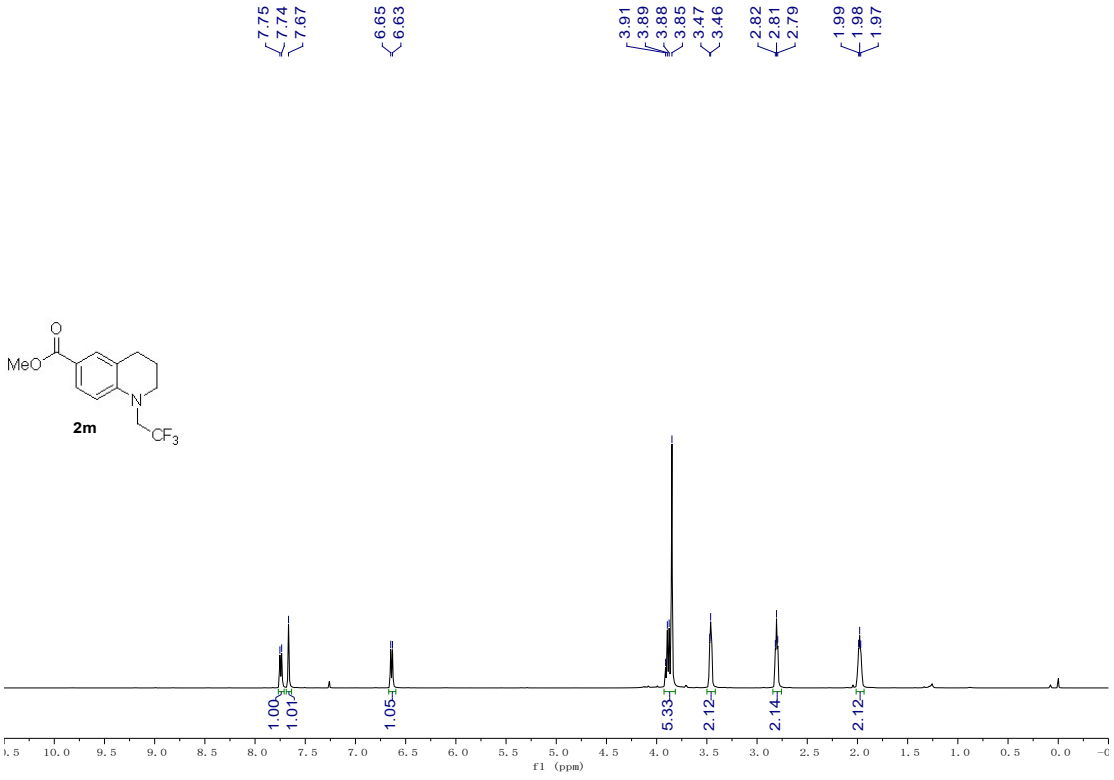
6-bromo-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2l)

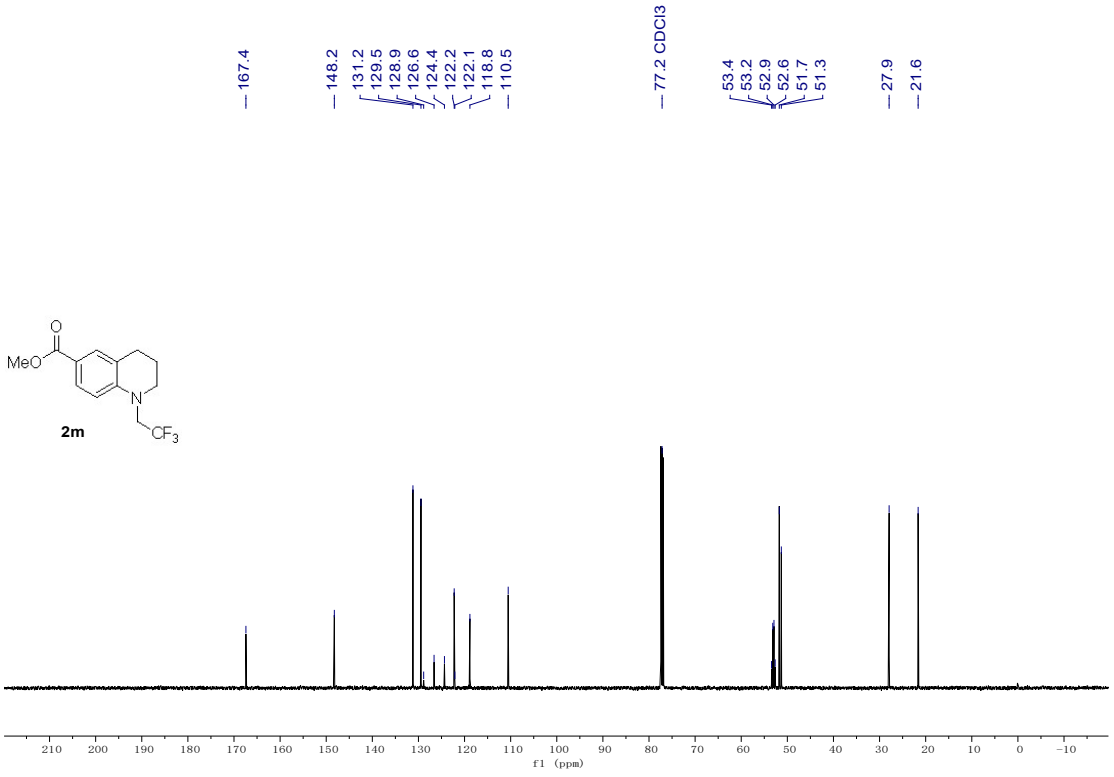


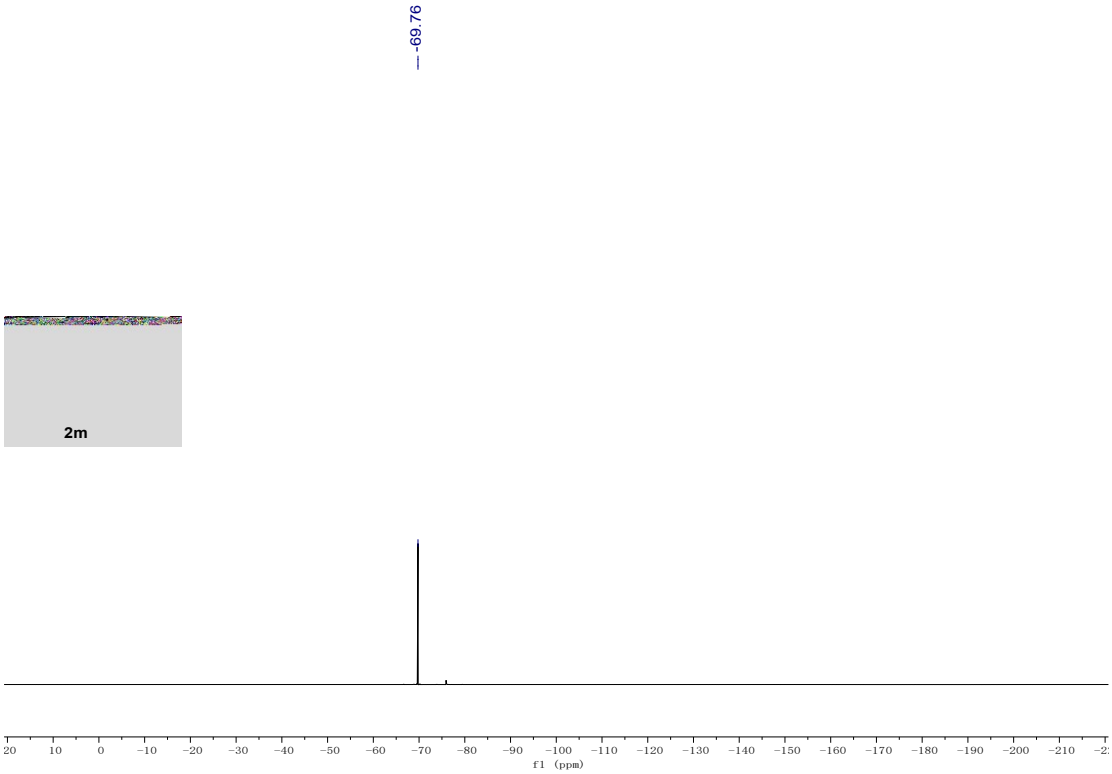

143.6
132.0
129.9
129.1
126.8
125.2
124.5
122.3
113.3
109.5
77.2 CDCl3
54.1
53.8
53.5
53.3
51.1
27.9
21.8
2l
f1 (ppm)


-70.03
2l
f1 (ppm)

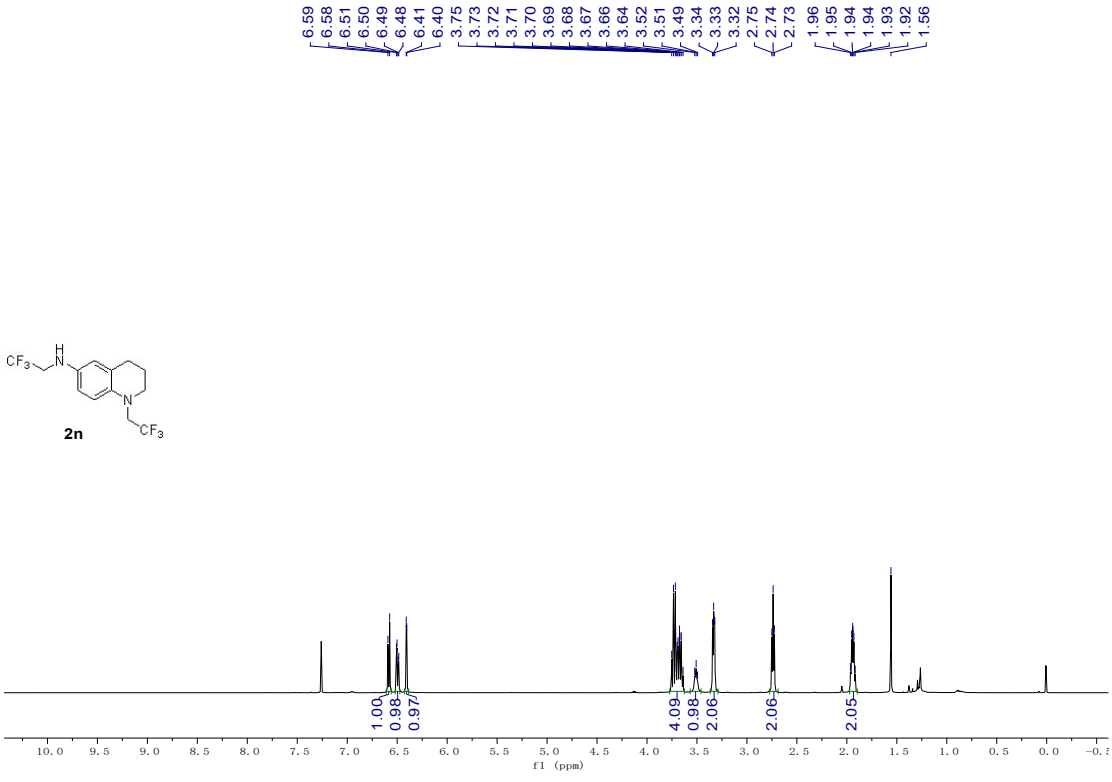
methyl 1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (2m)

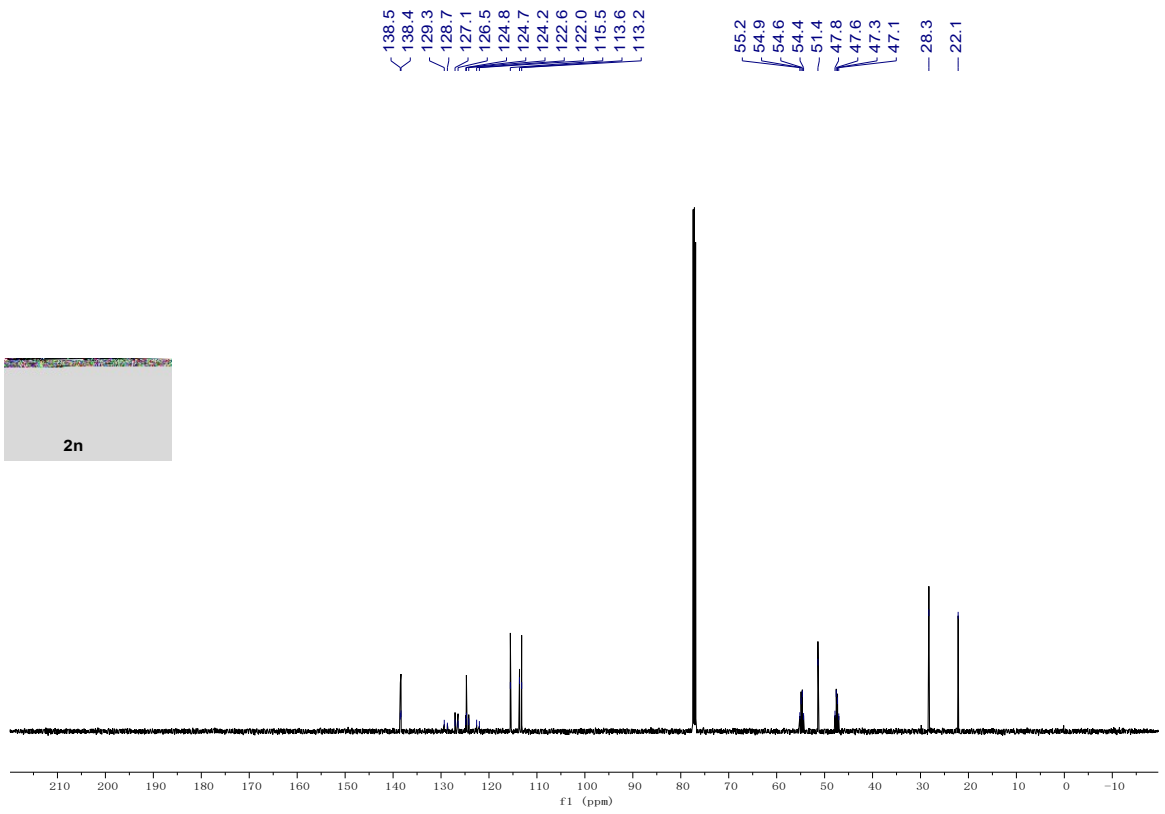


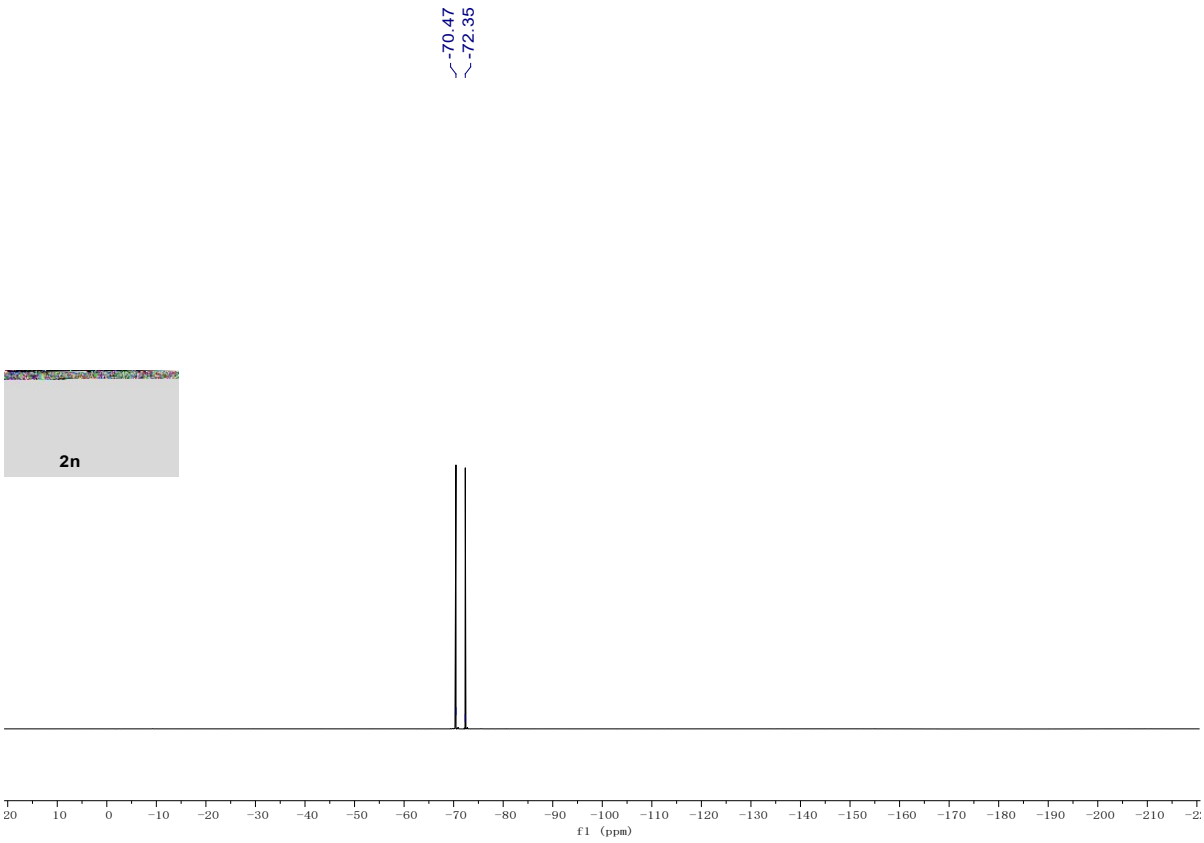




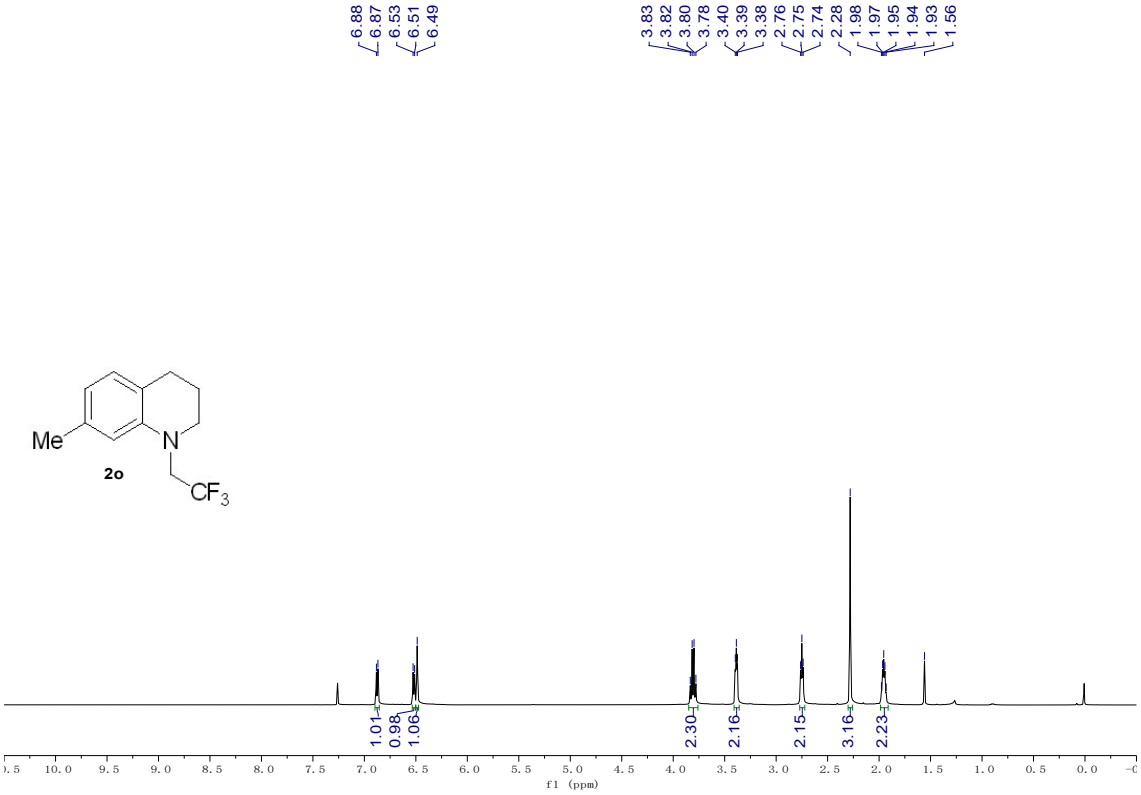
N,1-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinolin-6-amine (2n)

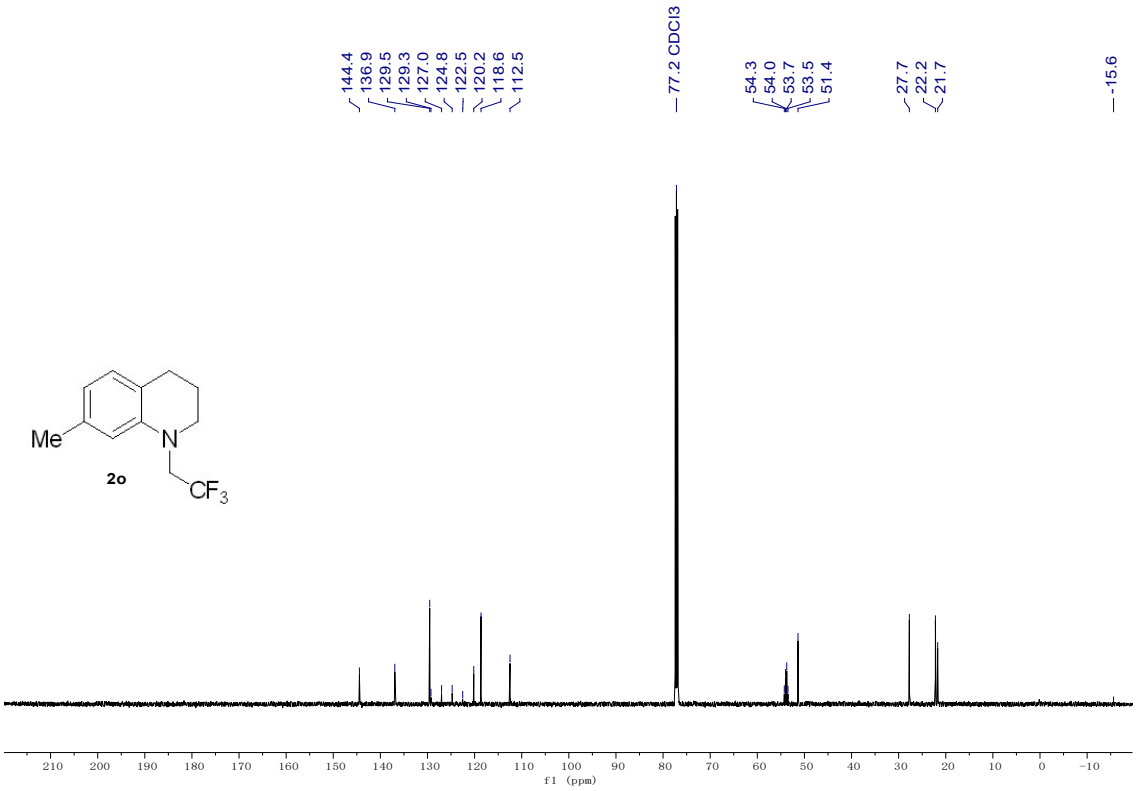


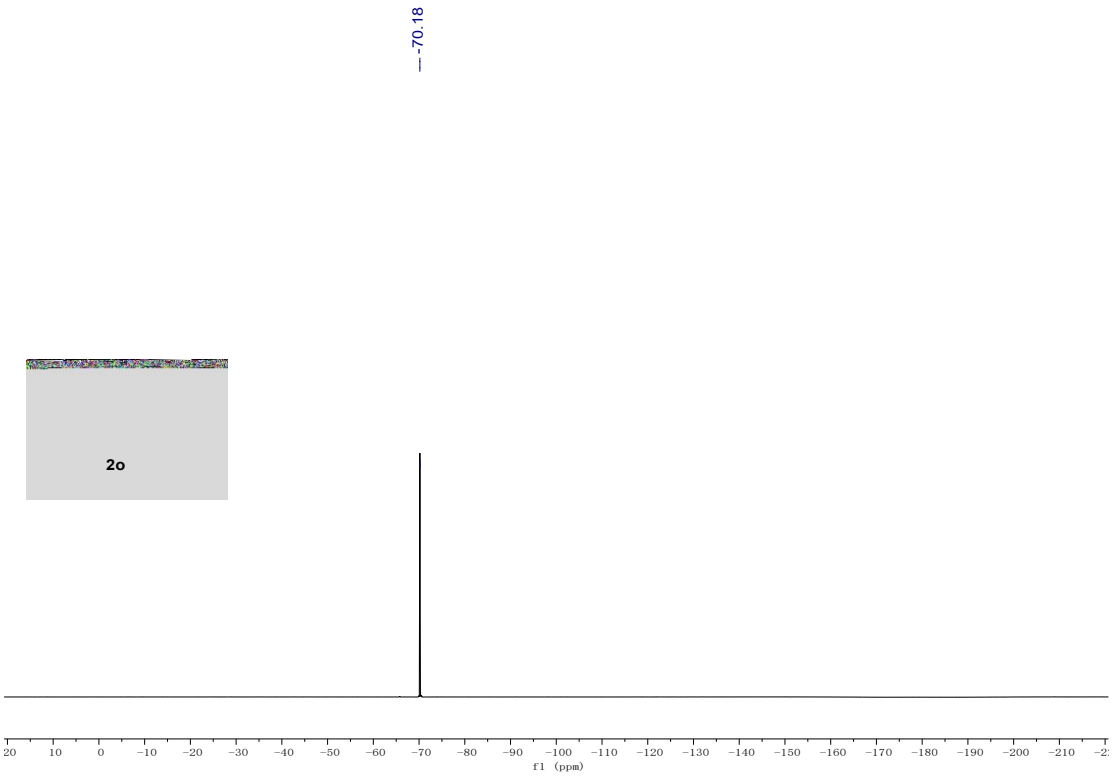

138.5
138.4
129.3
128.7
127.1
126.5
124.8
124.7
124.2
122.6
122.0
115.5
113.6
113.2
55.2
54.9
54.6
54.4
51.4
47.8
47.6
47.3
47.1
28.3
22.1
2n
f1 (ppm)


-70.47
-72.35
2n
f1 (ppm)

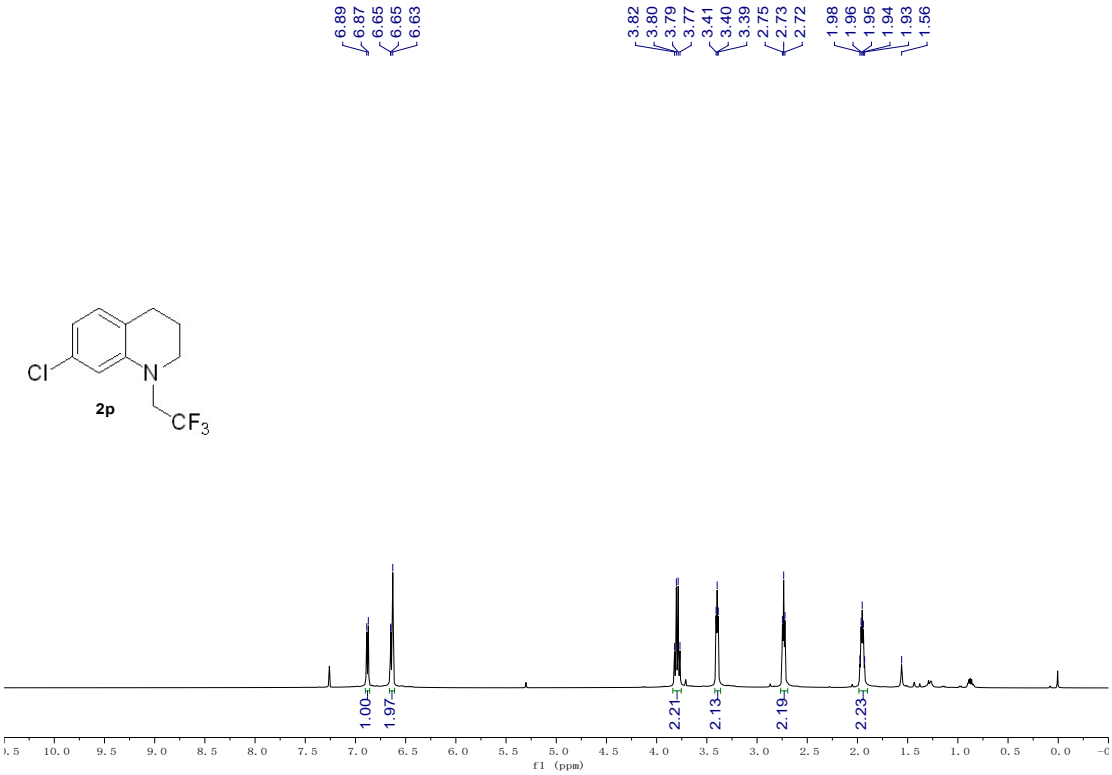
7-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2o)

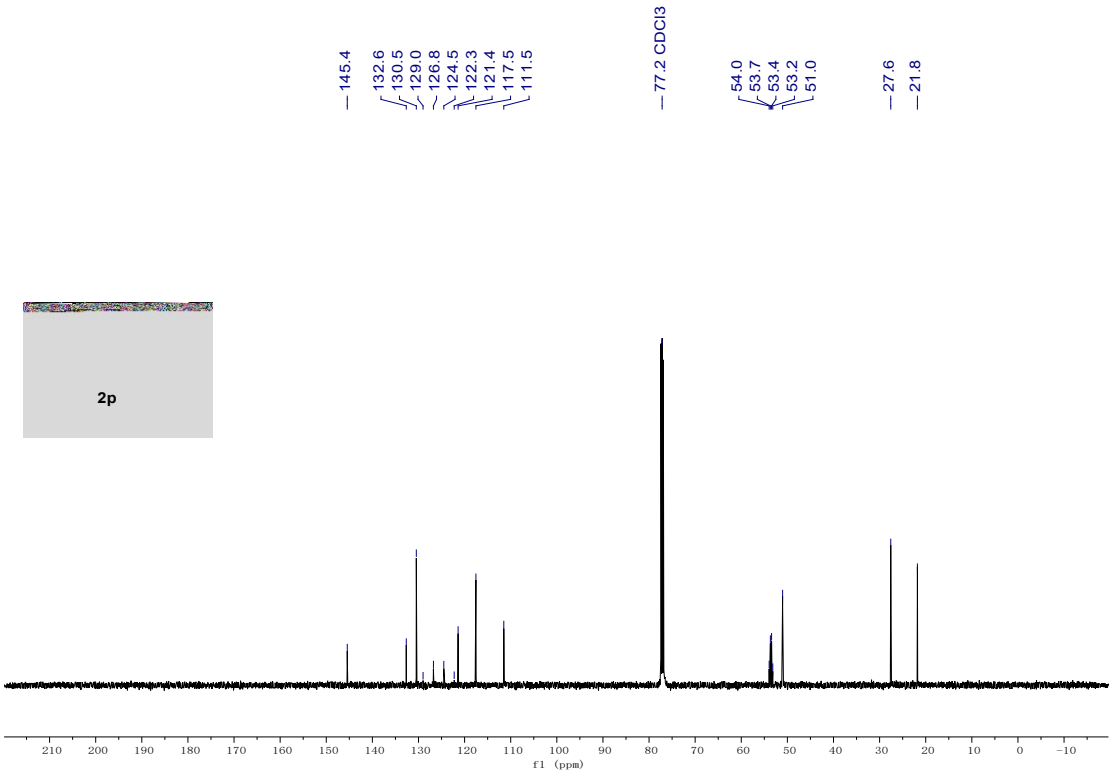


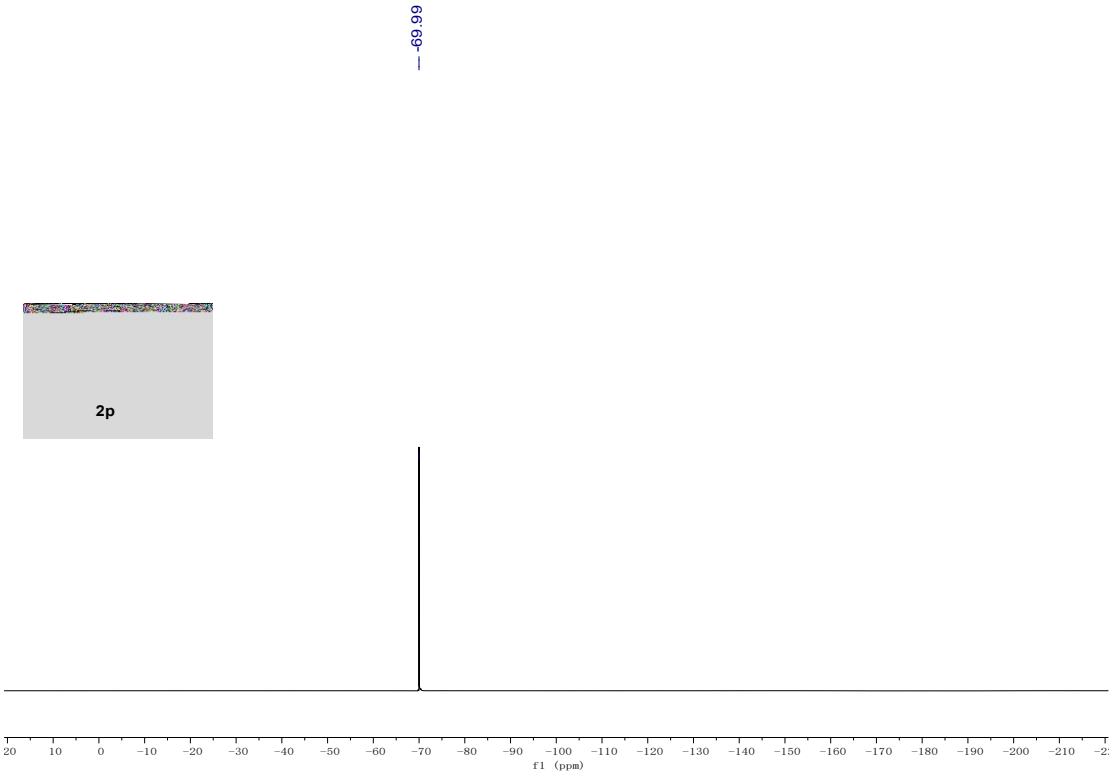




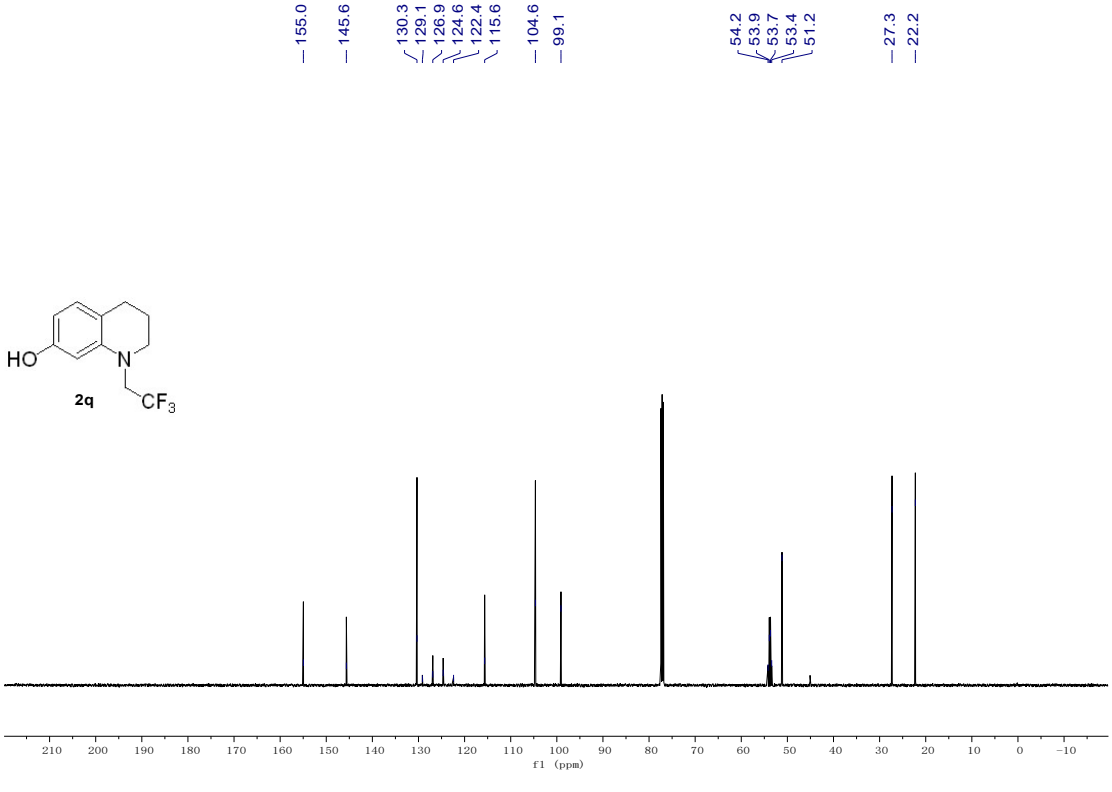
7-chloro-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2p)

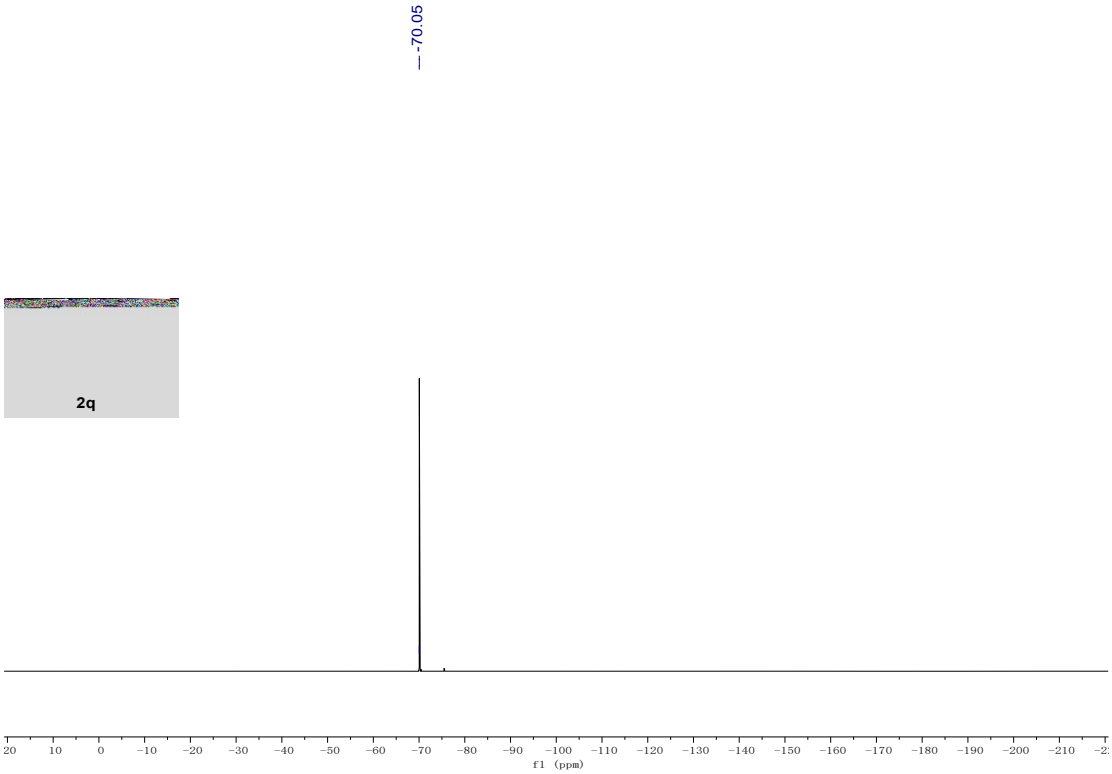



145.4
132.6
130.5
129.0
126.8
124.5
122.3
121.4
117.5
111.5
77.2 CDCl3
54.0
53.7
53.4
53.2
51.0
27.6
21.8
2p
f1 (ppm)

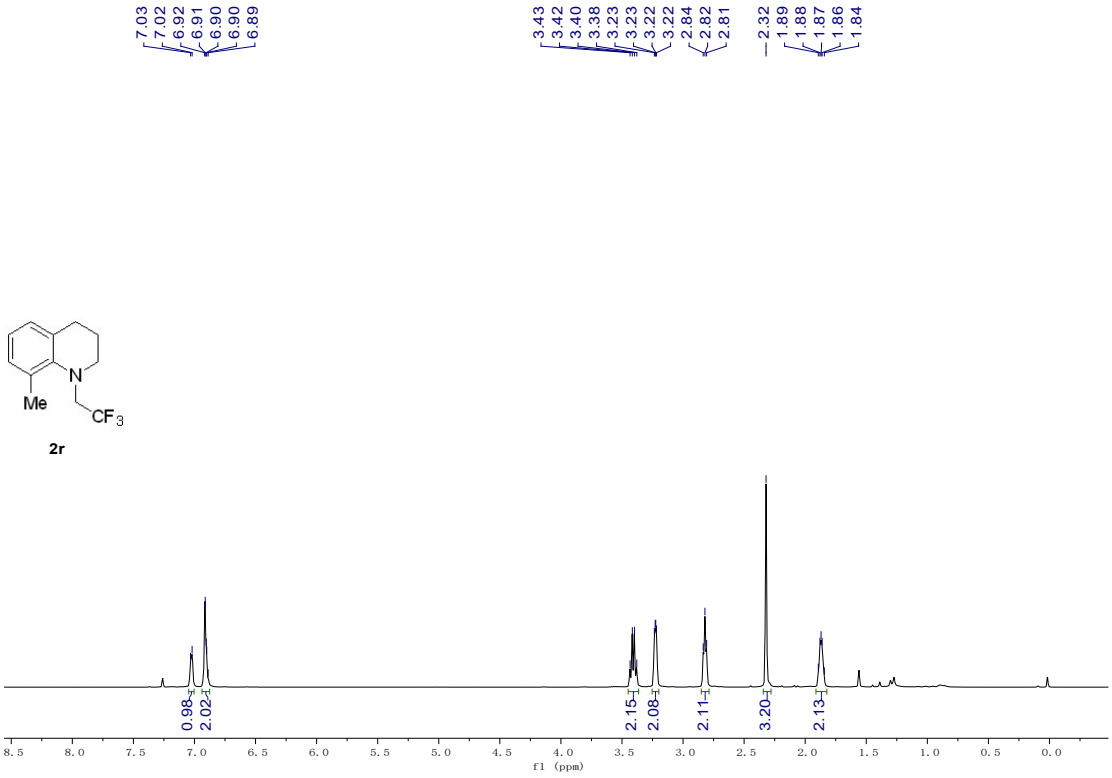

-69.99
2p
f1 (ppm)

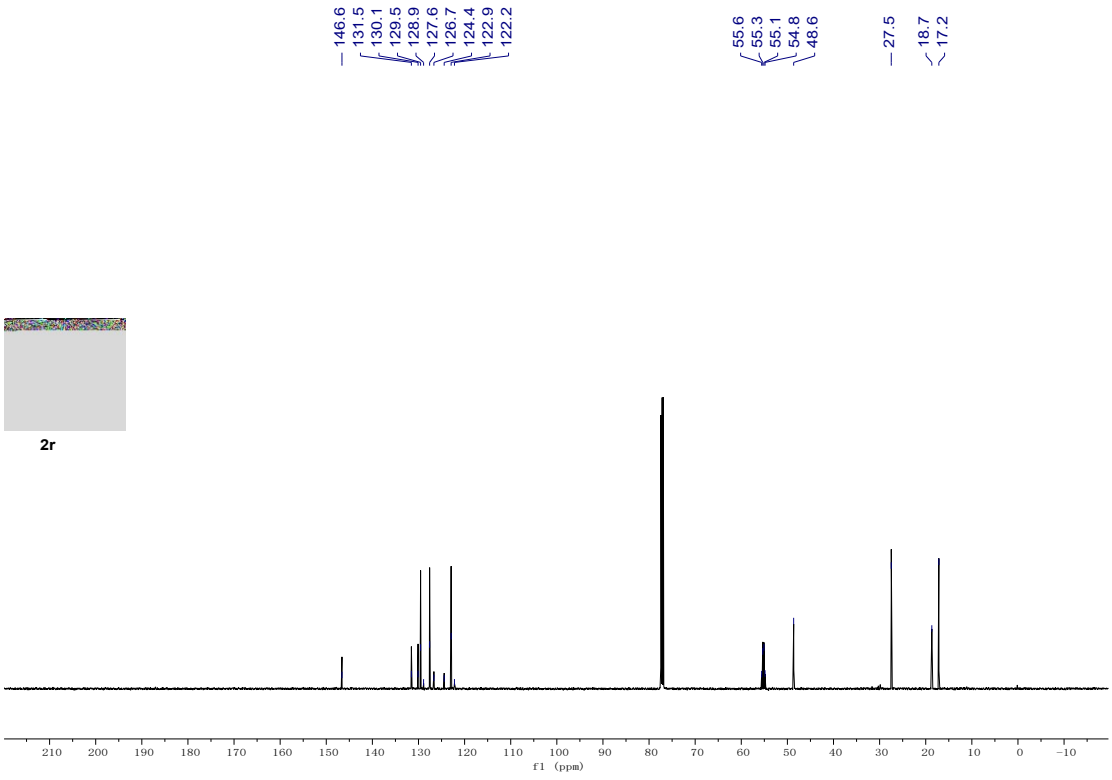
1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinolin-7-ol (2q)

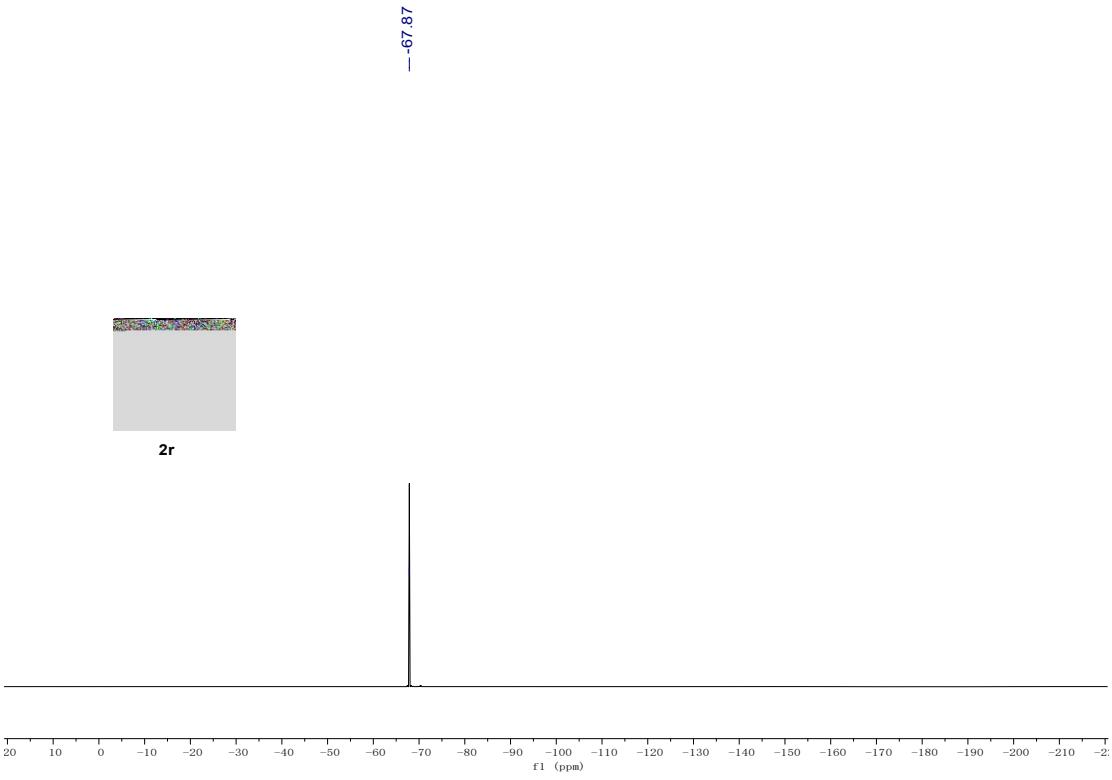




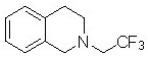
8-methyl-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoline (2r)



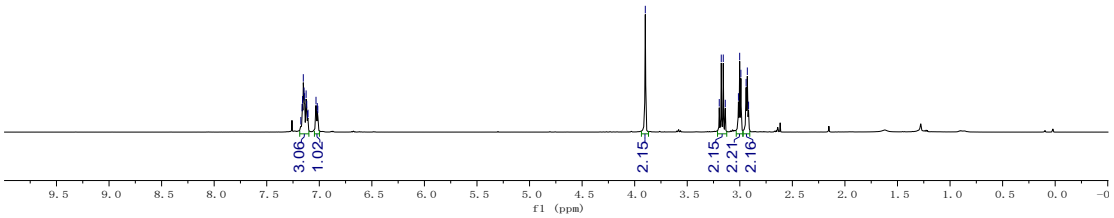

146.6
131.5
130.1
129.5
128.9
127.6
126.7
124.4
122.9
122.2
55.6
55.3
55.1
54.8
48.6
27.5
18.7
17.2
2r
f1 (ppm)

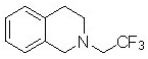

-67.87
2r
f1 (ppm)

2-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroisoquinoline (2s)

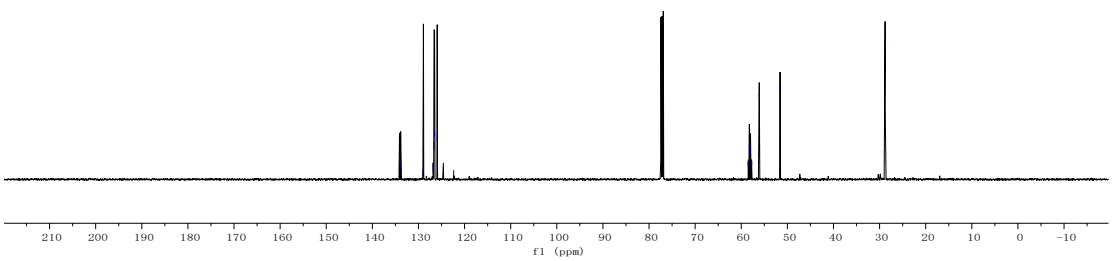


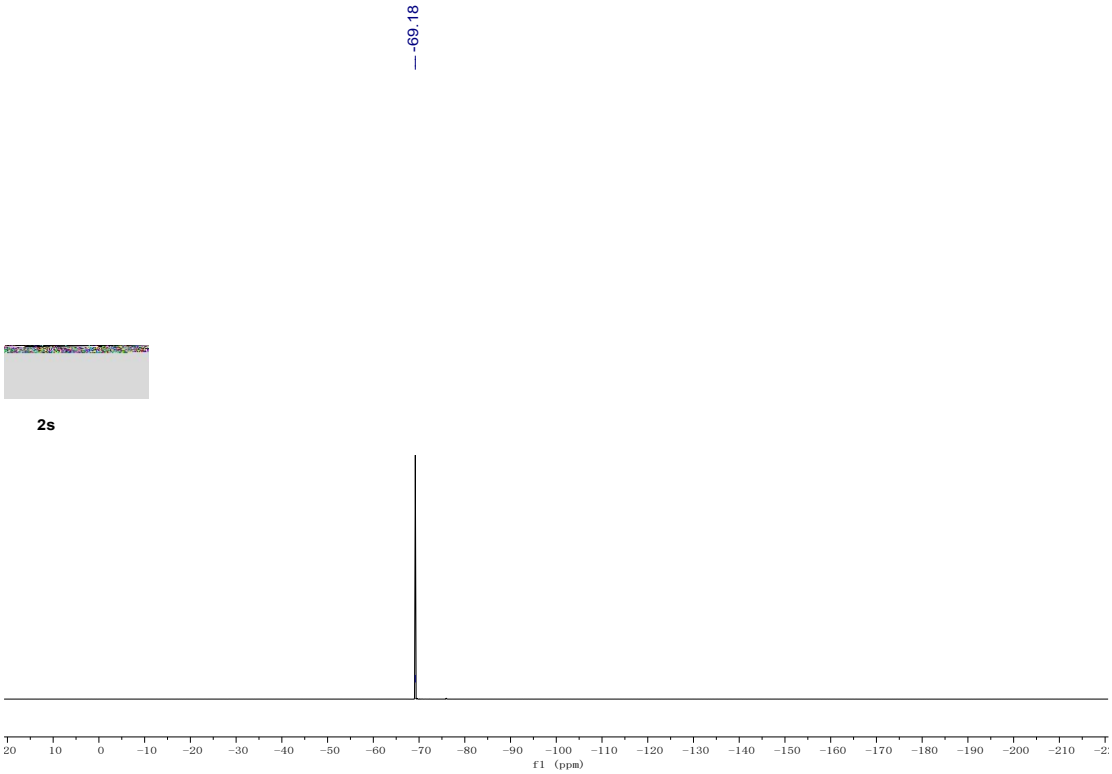
2s



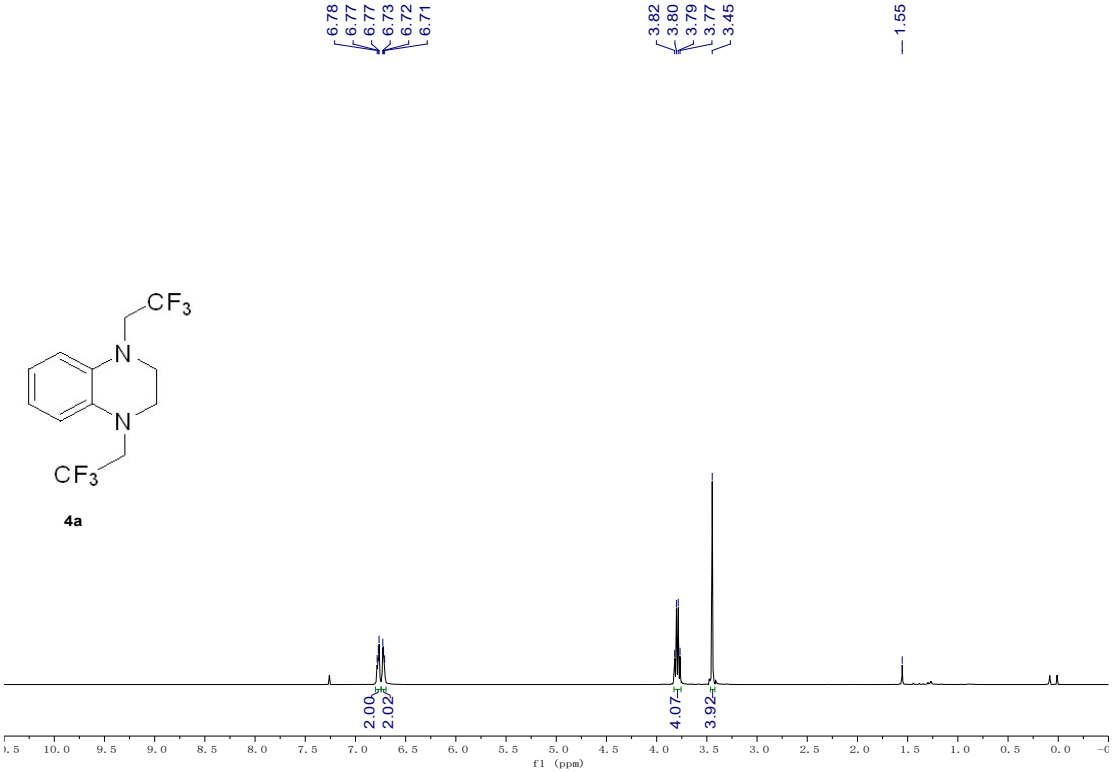


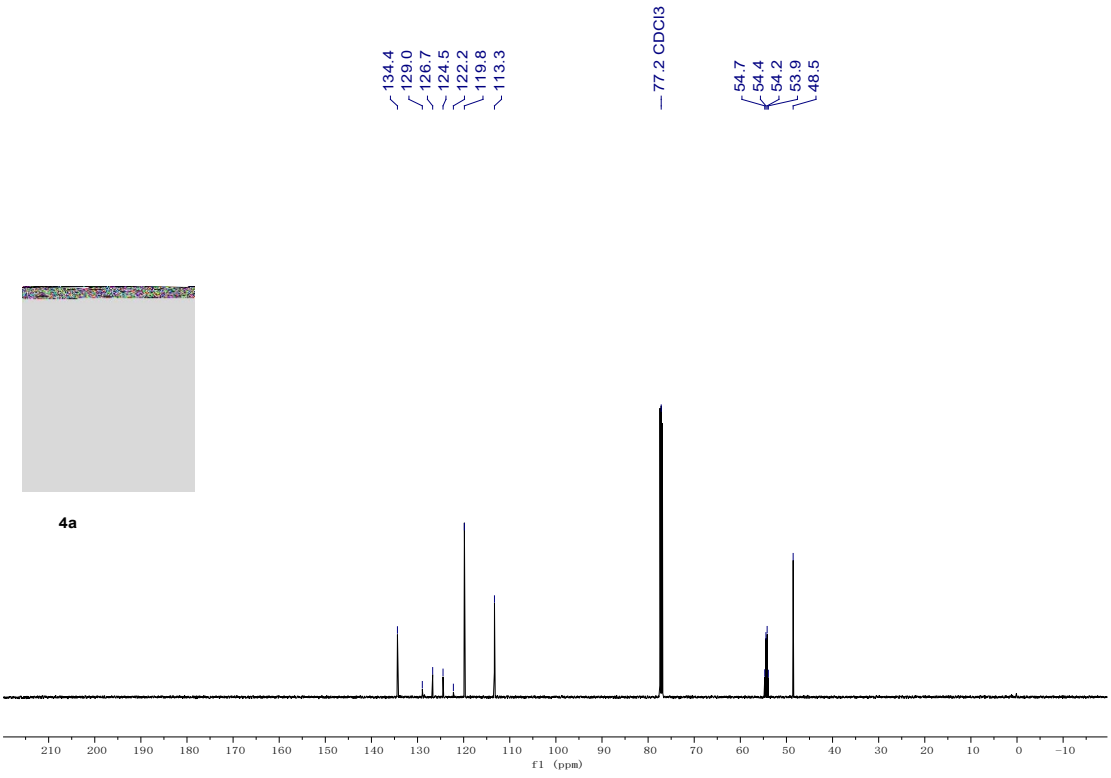
2s

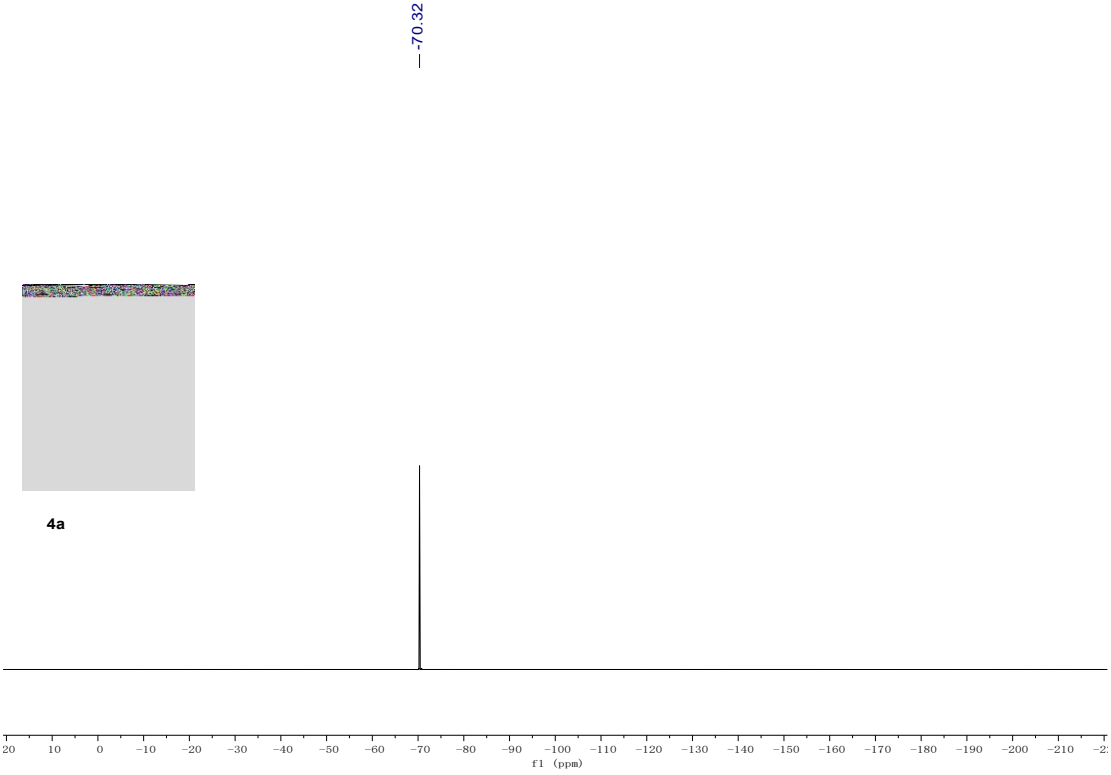




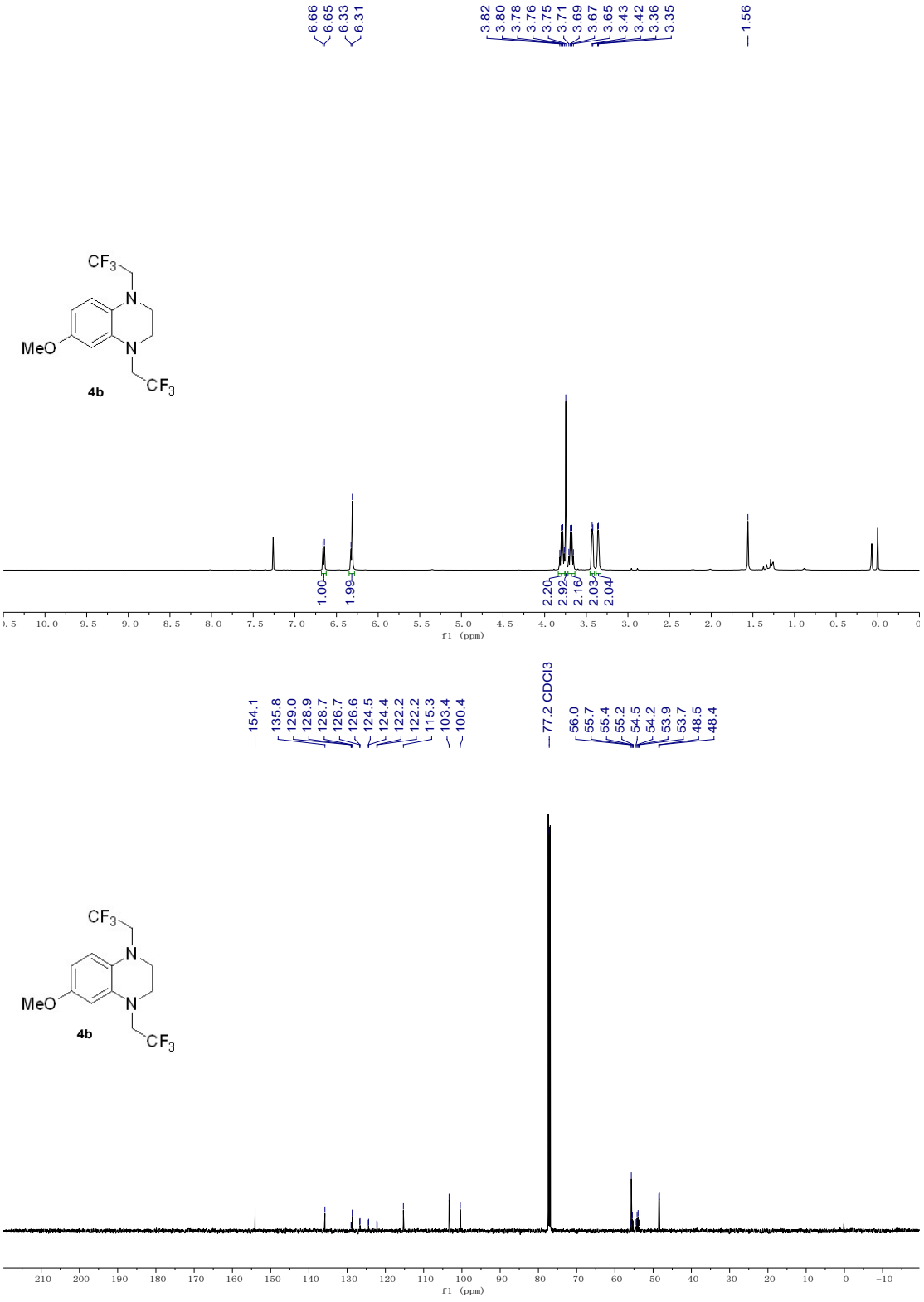
1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4a)

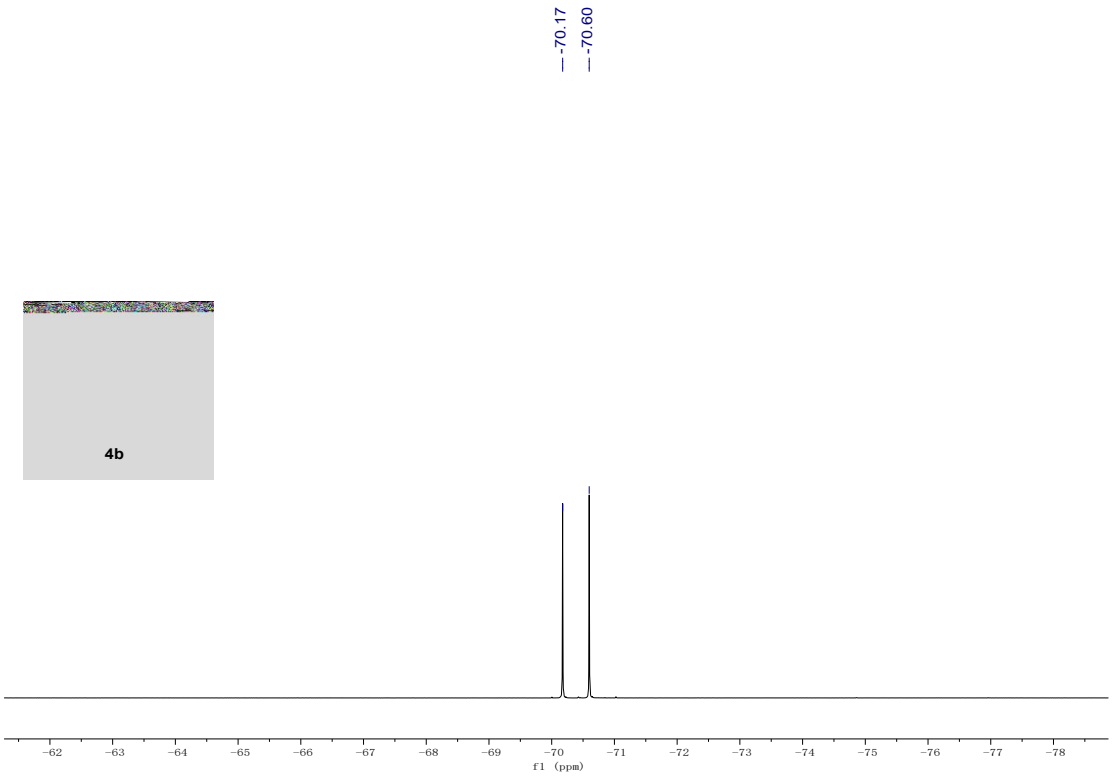



134.4
129.0
126.7
124.5
122.2
119.8
113.3
77.2 CDCl3
54.7
54.4
54.2
53.9
48.5
4a
f1 (ppm)

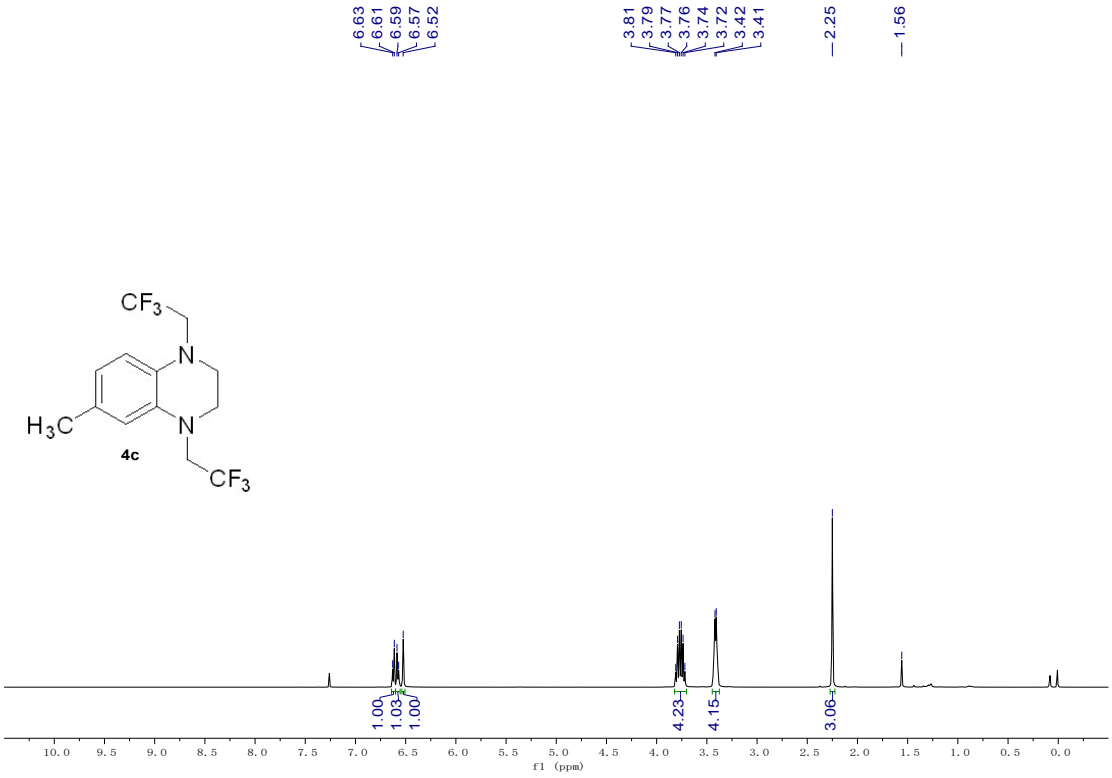

-70.32
4a
f1 (ppm)

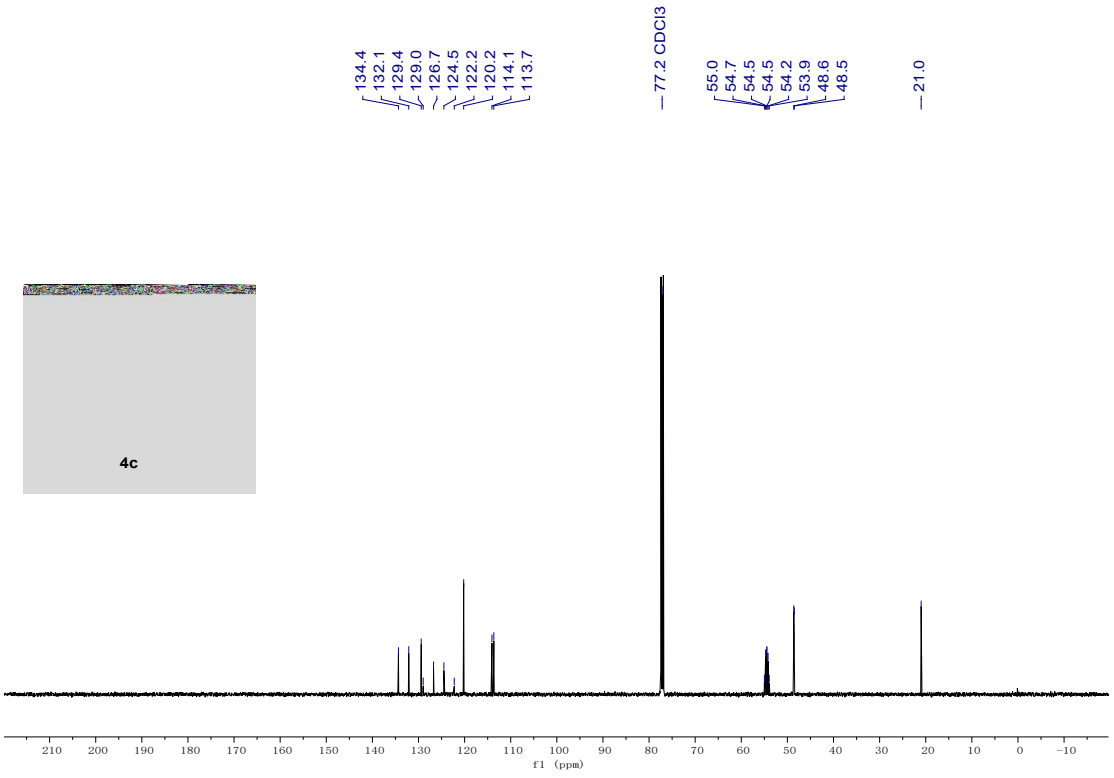
6-methoxy-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4b)

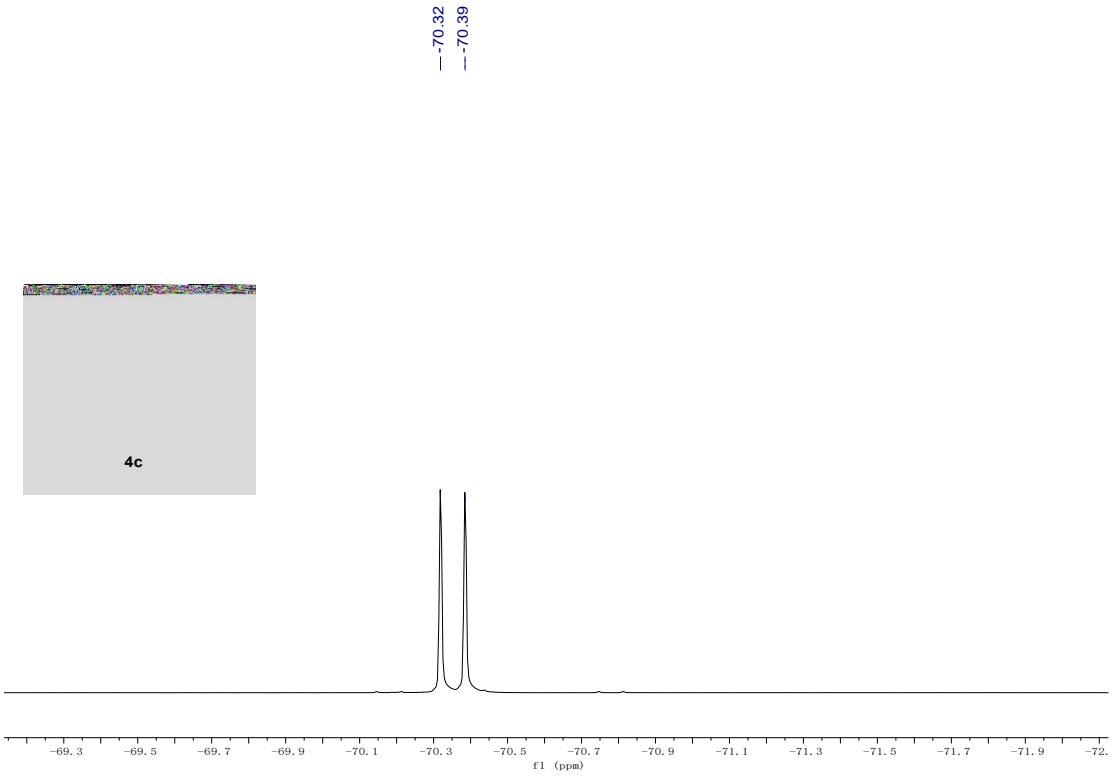




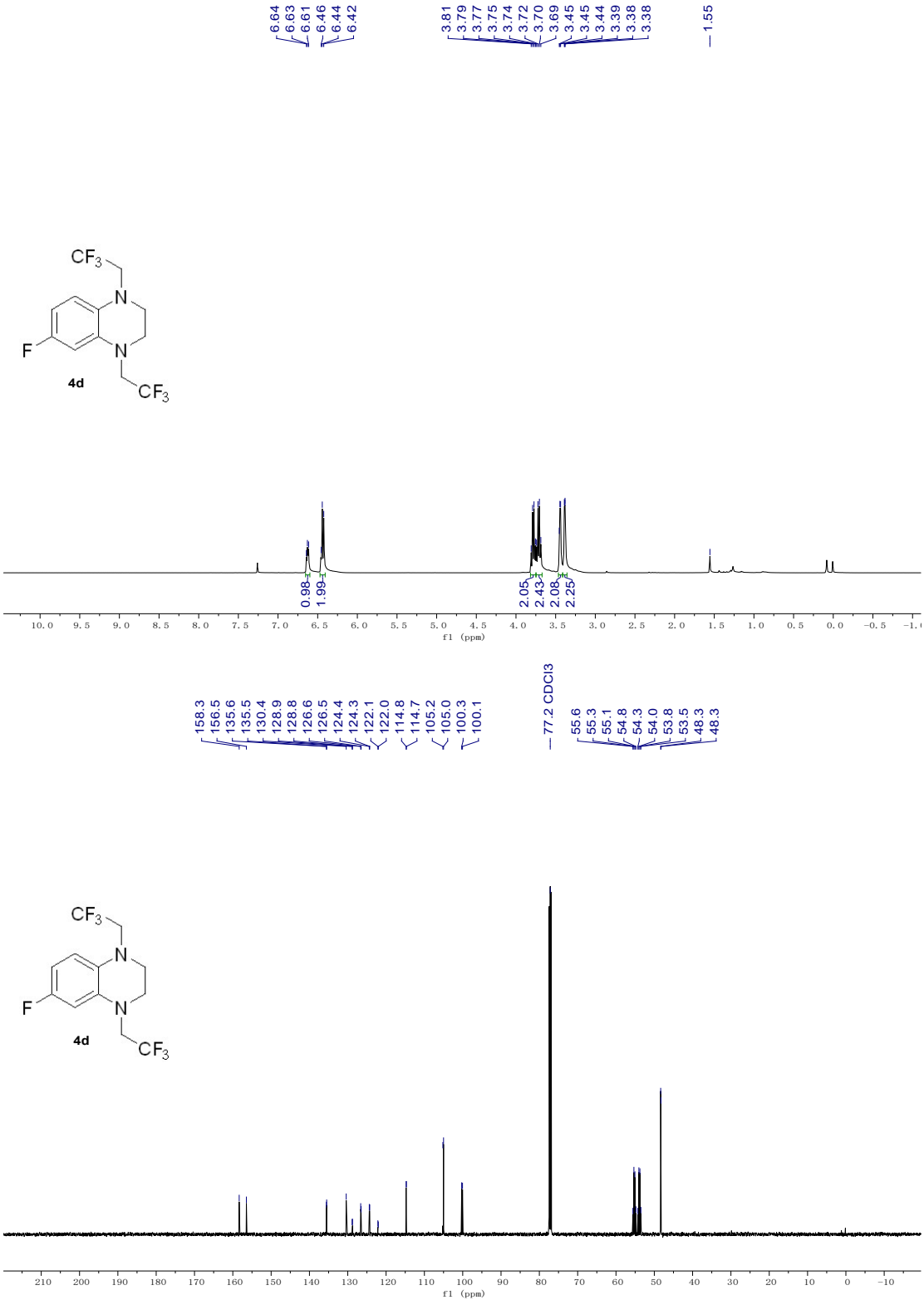
6-methyl-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4c)

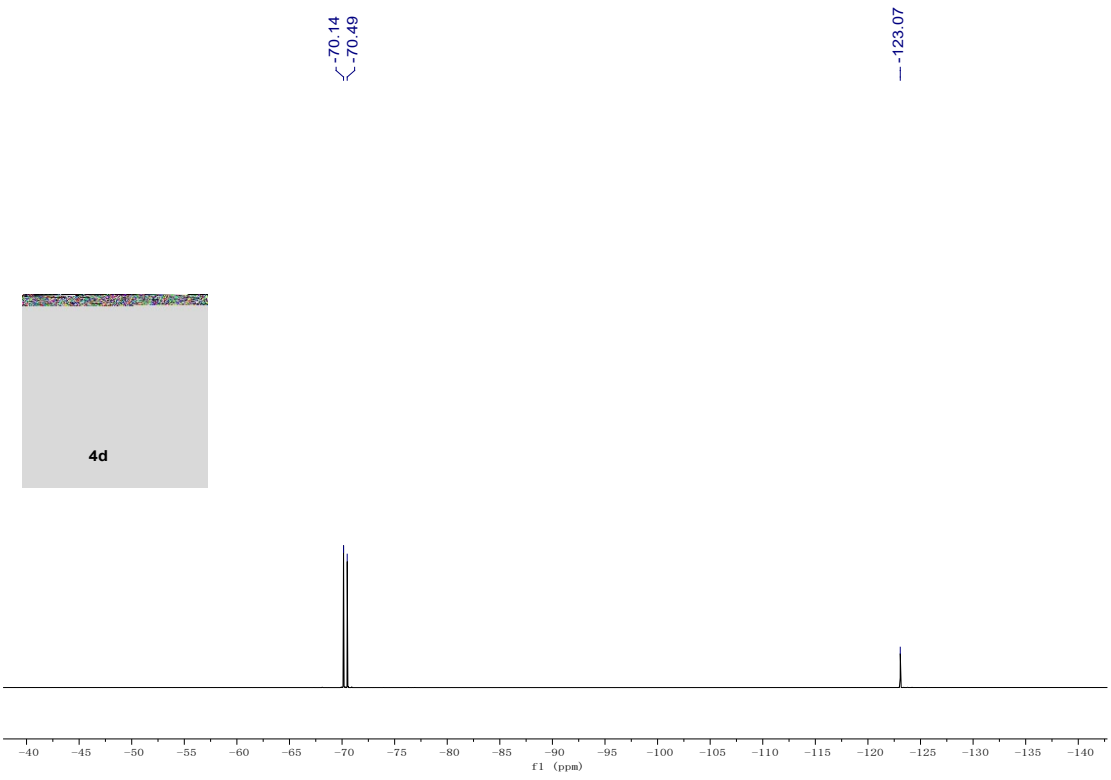



134.4
132.1
129.4
129.0
126.7
124.5
122.2
120.2
114.1
113.7
77.2 CDCl3
55.0
54.7
54.5
54.5
54.2
53.9
48.6
48.5
21.0
4c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

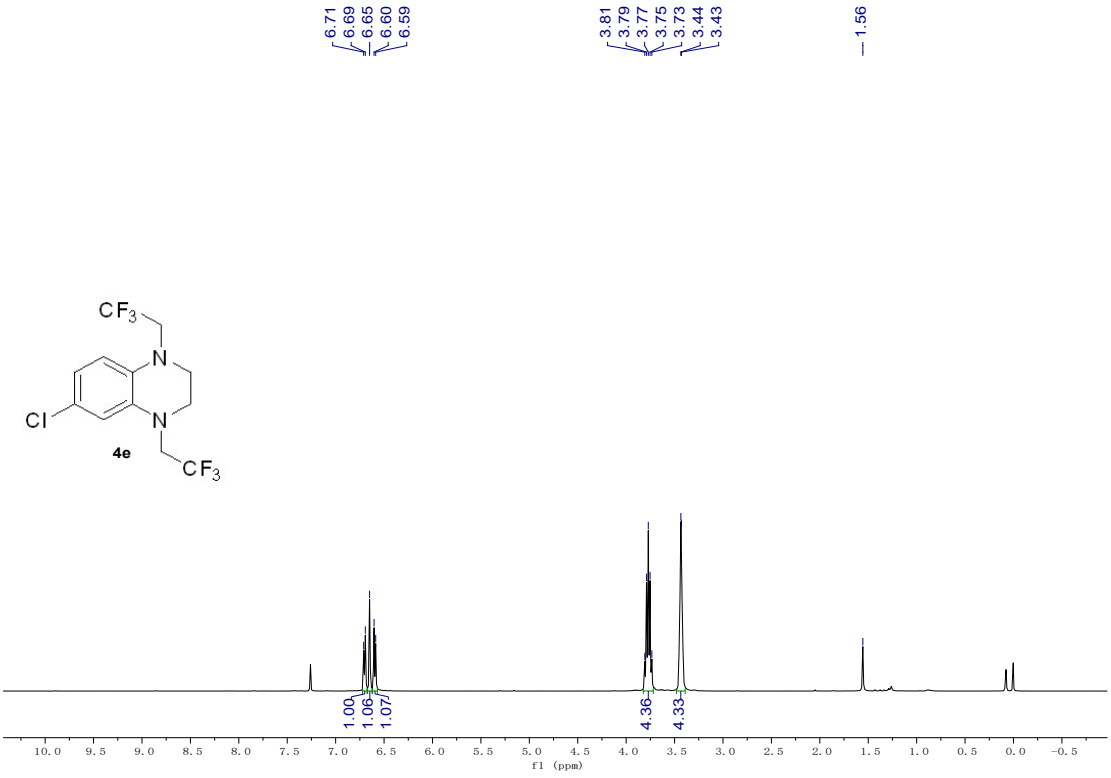

-70.32
-70.39
4c
−69.3 −69.5 −69.7 −69.9 −70.1 −70.3 −70.5 −70.7 −70.9 −71.1 −71.3 −71.5 −71.7 −71.9 −72.
f1 (ppm)

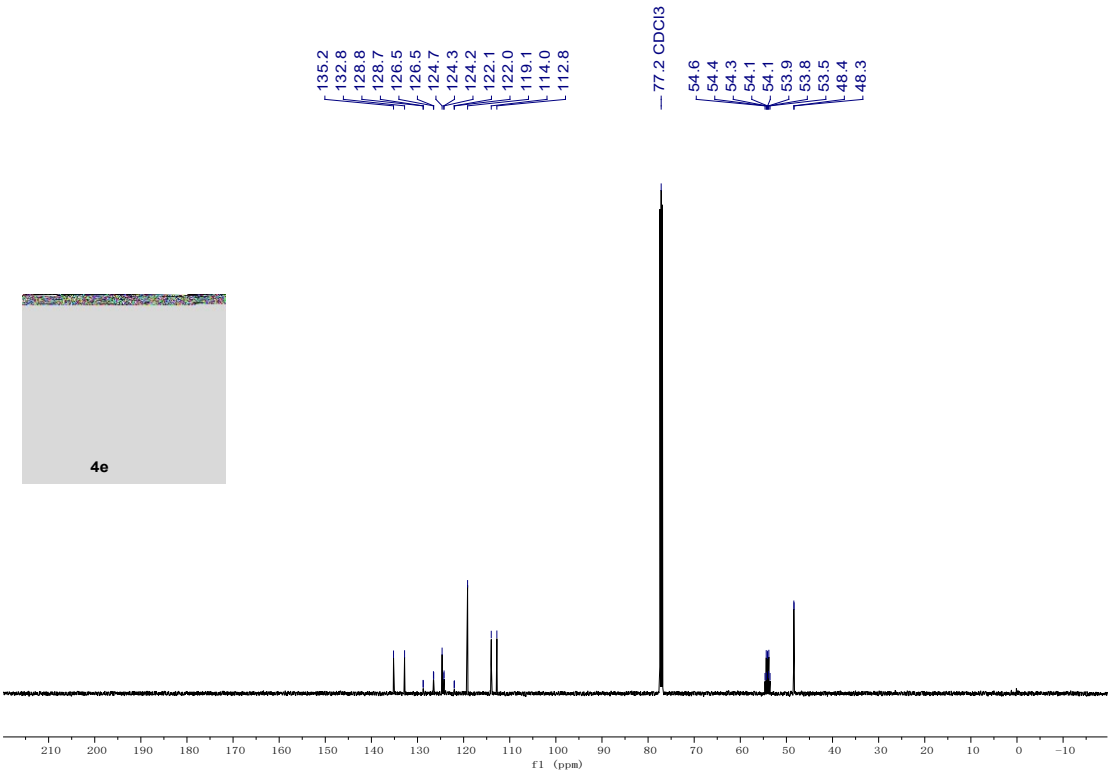
6-fluoro-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4d)

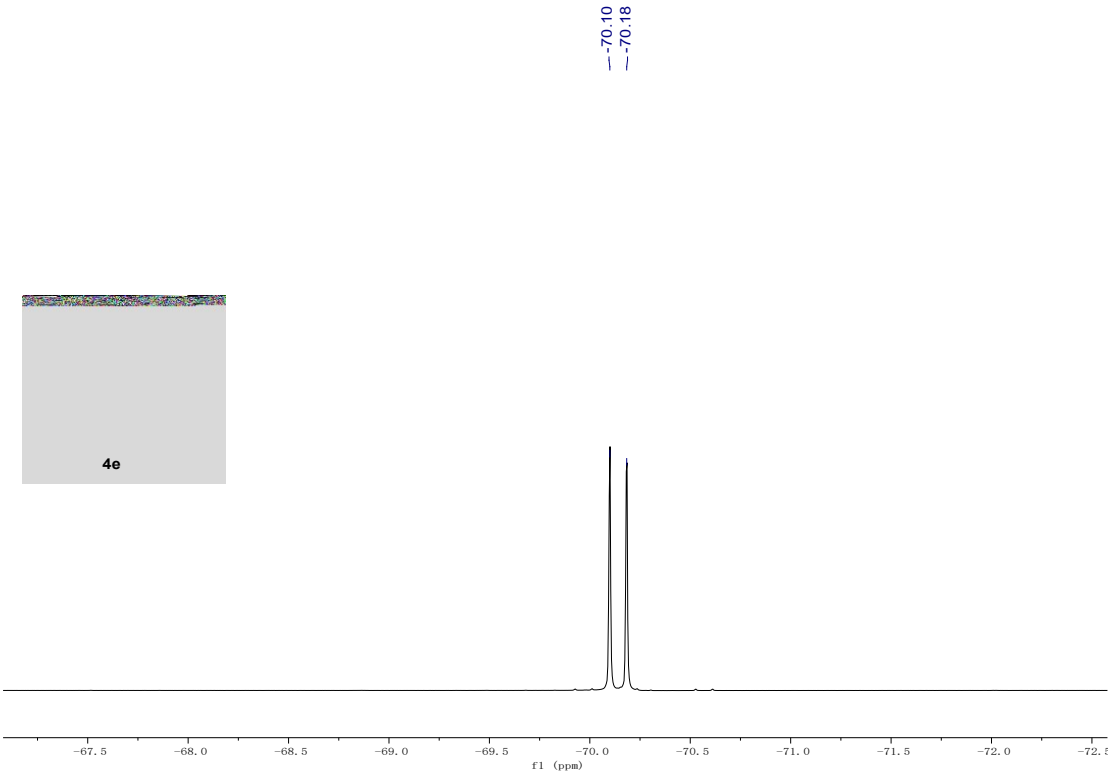




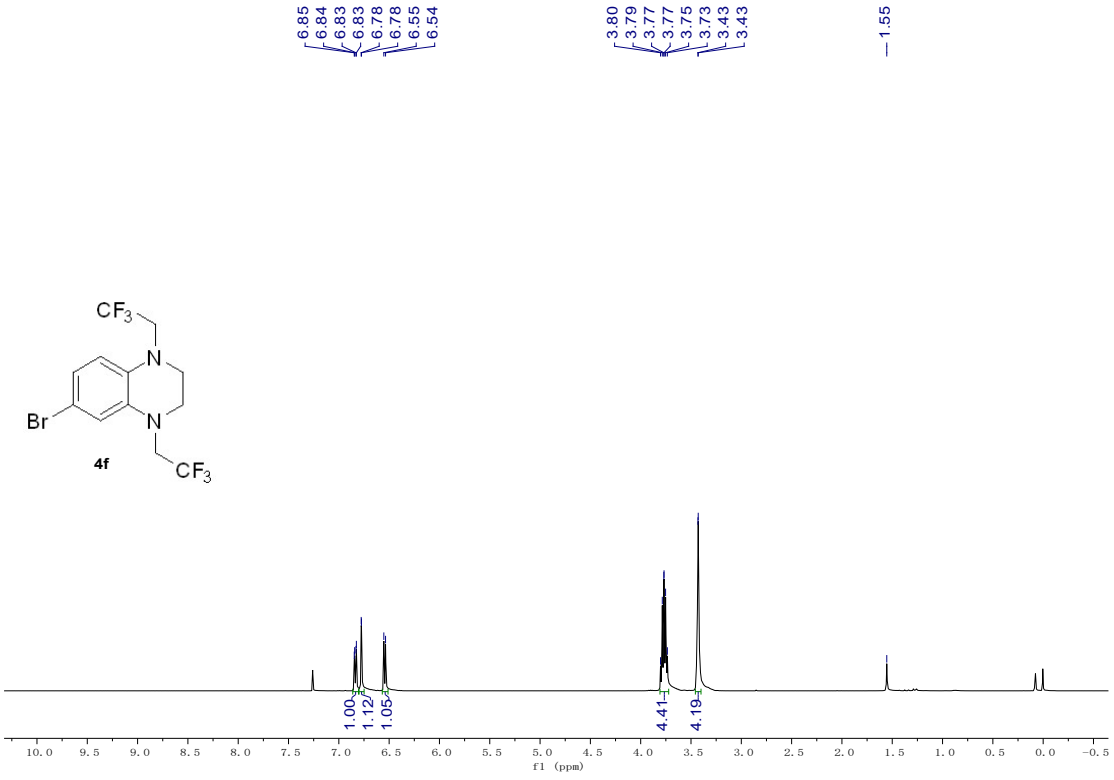
6-chloro-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4e)

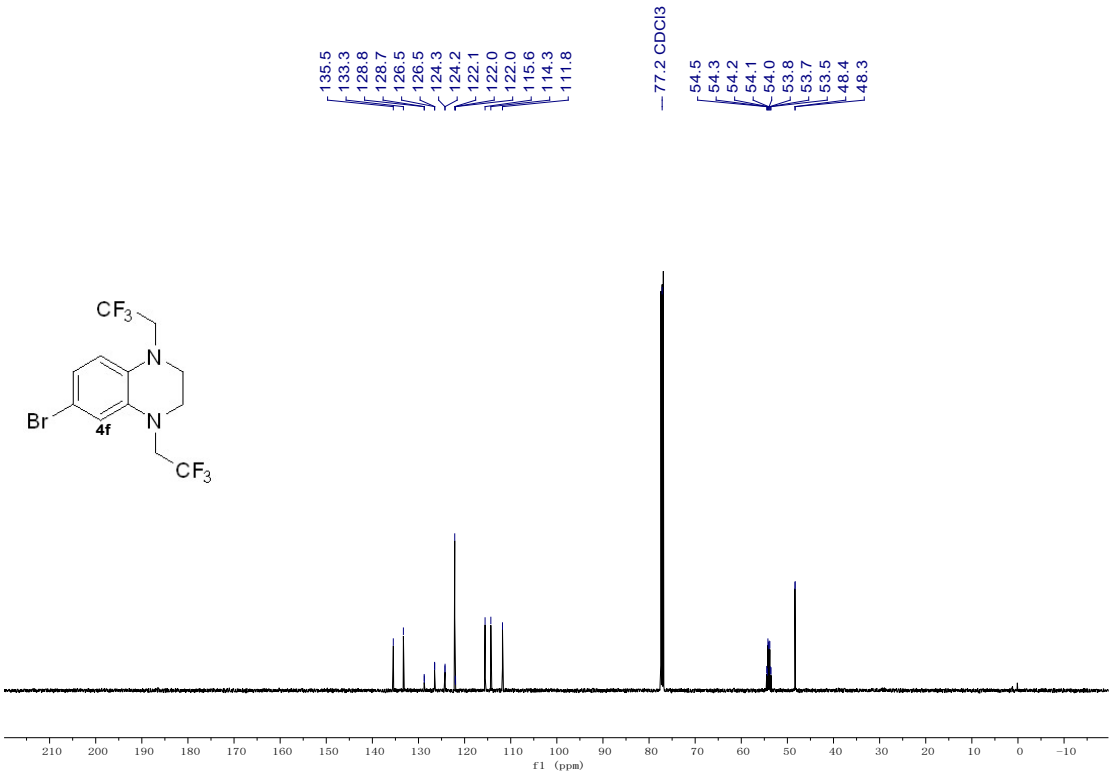


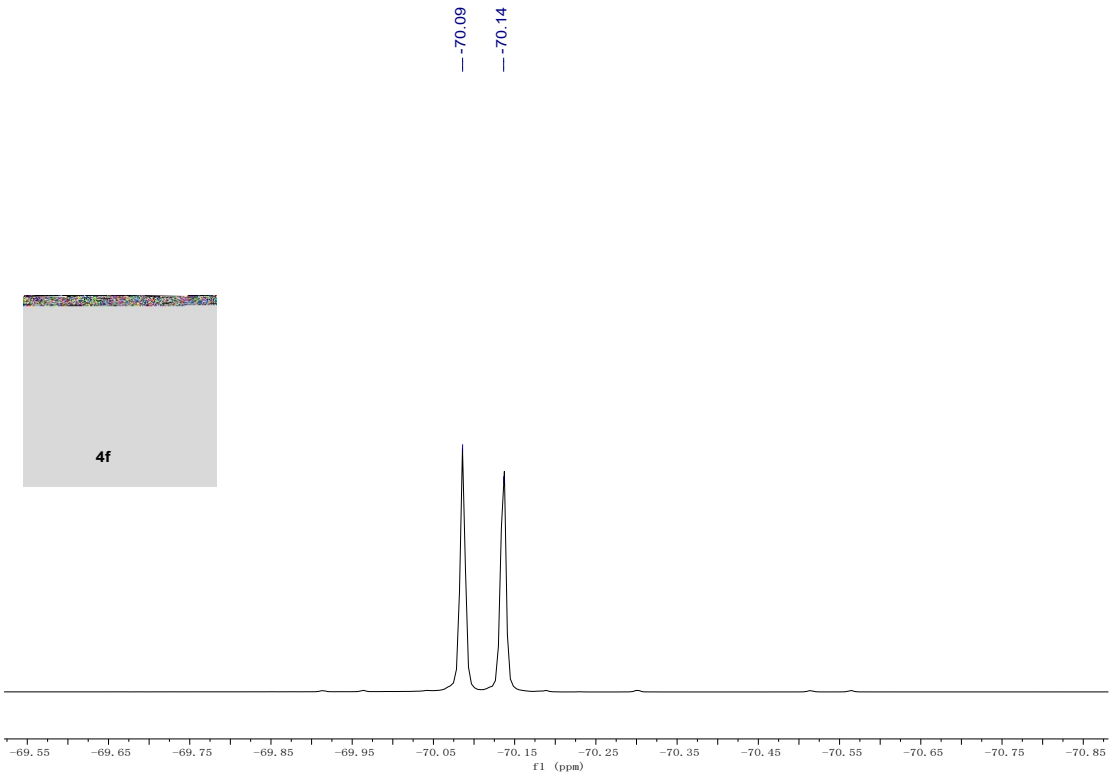

135.2
132.8
128.8
128.7
126.5
126.5
124.7
124.3
124.2
122.1
122.0
119.1
114.0
112.8
77.2 CDCl3
54.6
54.4
54.3
54.1
54.1
53.9
53.8
53.5
48.4
48.3
4e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-70.10
-70.18
4e
−67.5 −68.0 −68.5 −69.0 −69.5 −70.0 −70.5 −71.0 −71.5 −72.0
f1 (ppm)

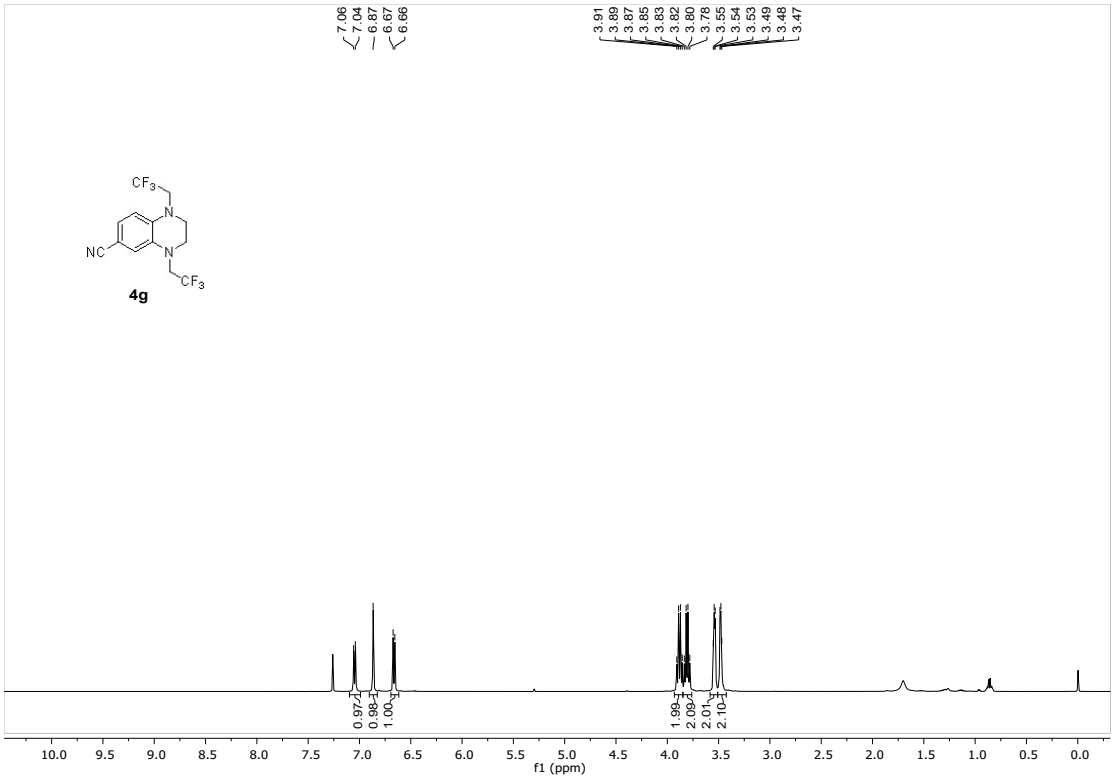
6-bromo-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4f)

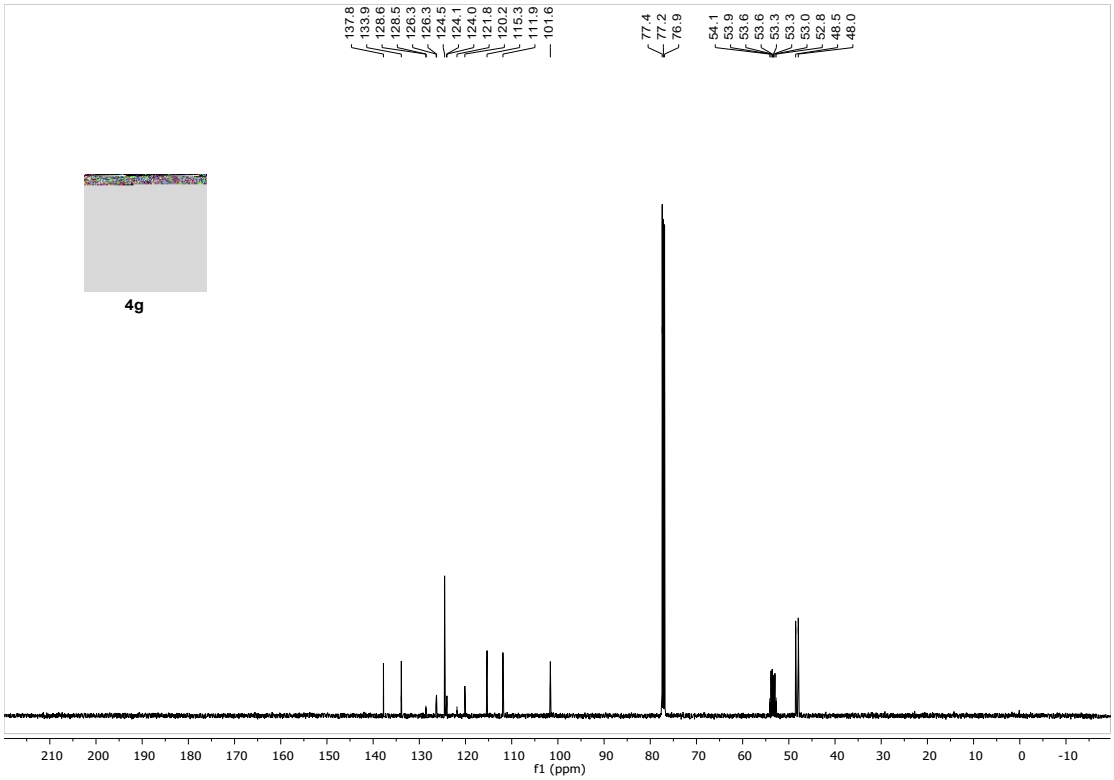


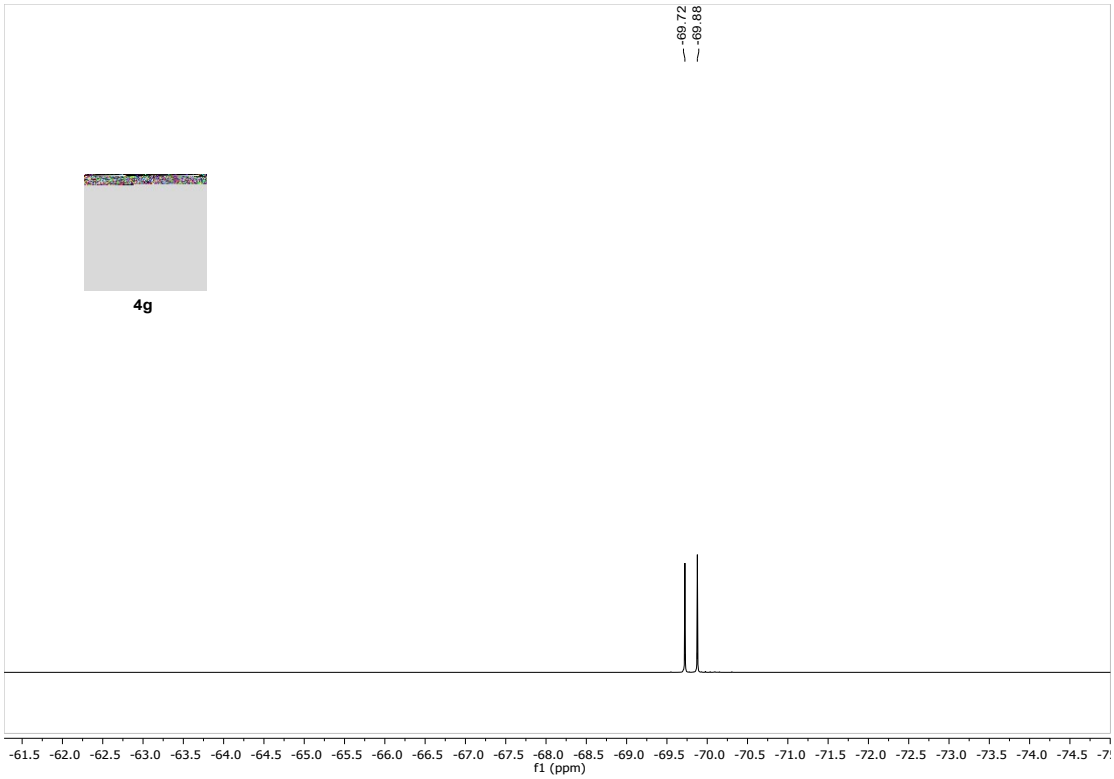




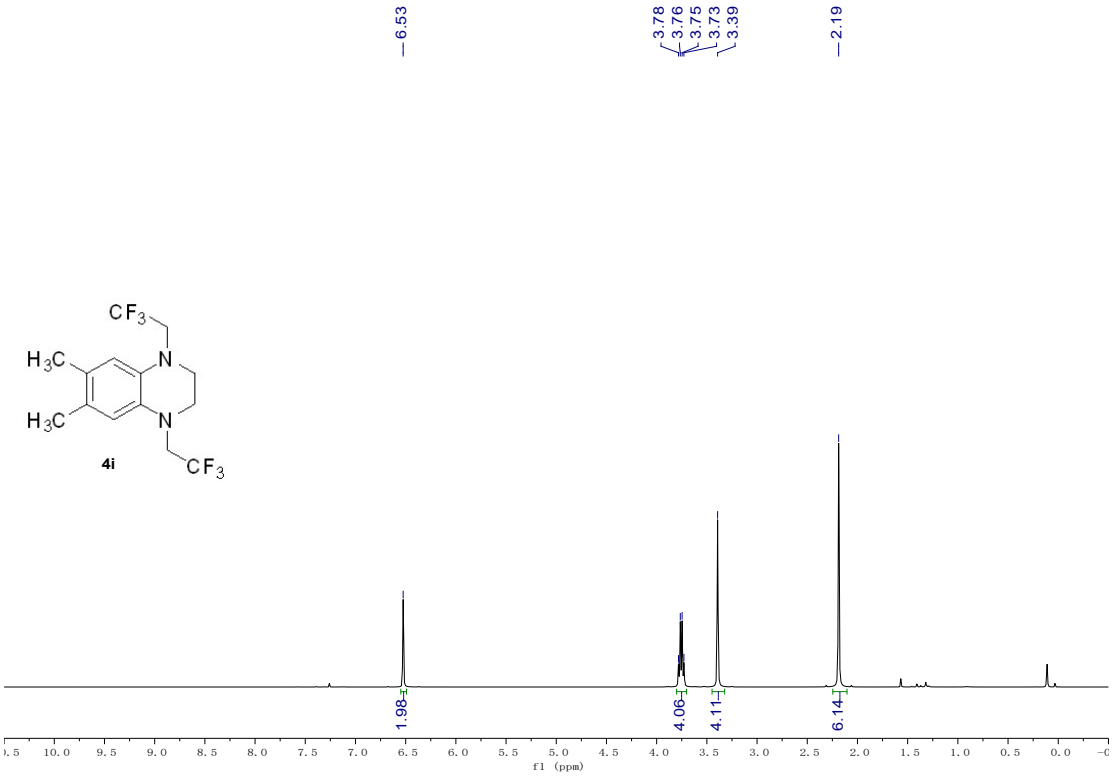
1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline-6-carbonitrile (4g)

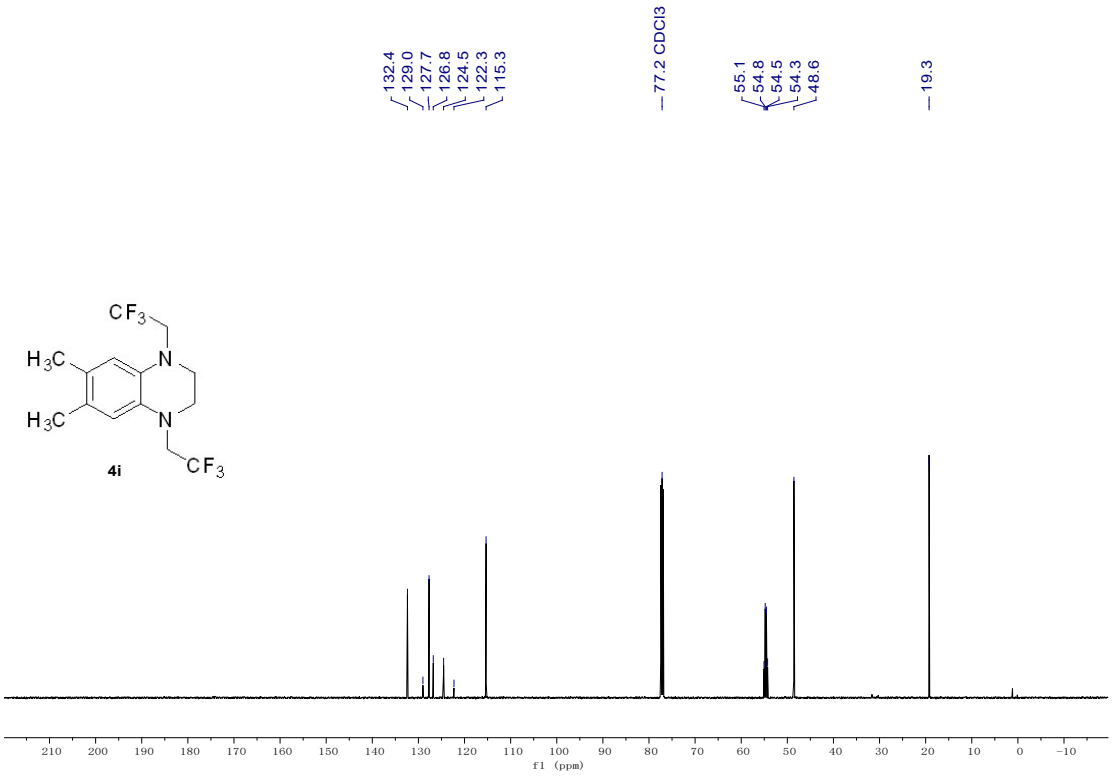


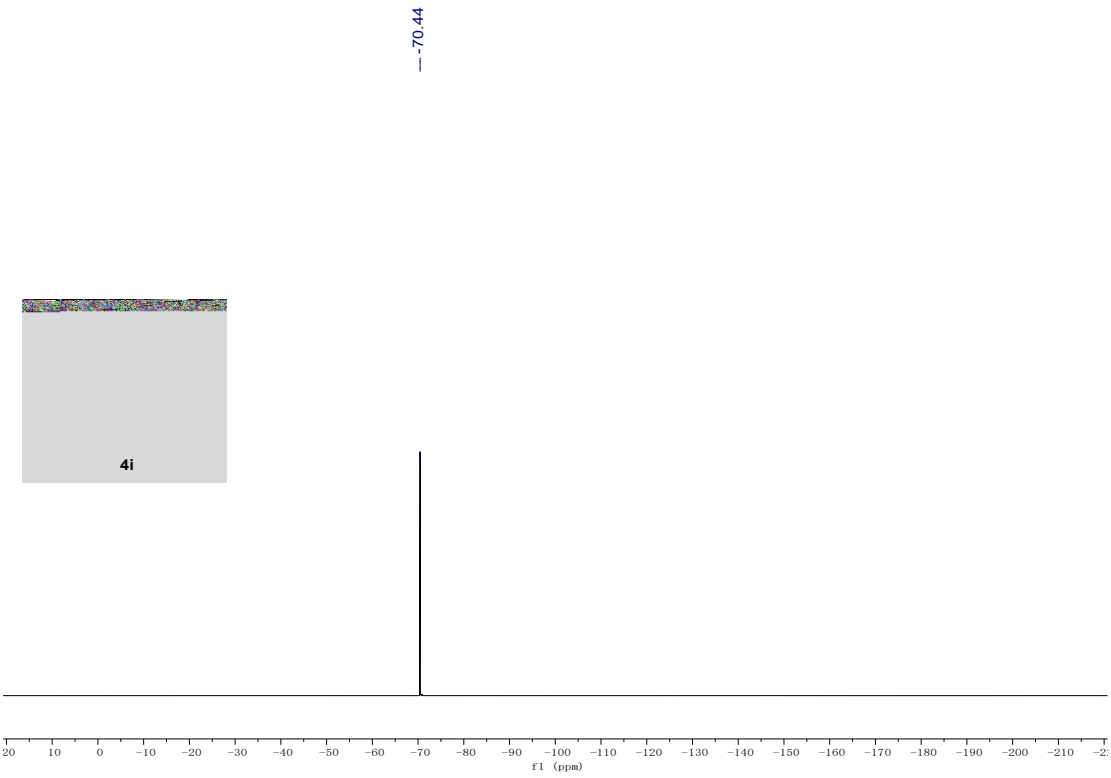

137.8
133.9
128.6
128.5
126.3
126.3
124.5
124.1
124.0
121.8
120.2
115.3
111.9
101.6
77.4
77.2
76.9
54.1
53.9
53.6
53.6
53.3
53.3
53.0
52.8
48.5
48.0
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-69.72
-69.88
4g
-61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0 -70.5 -71.0 -71.5 -72.0 -72.5 -73.0 -73.5 -74.0 -74.5
f1 (ppm)

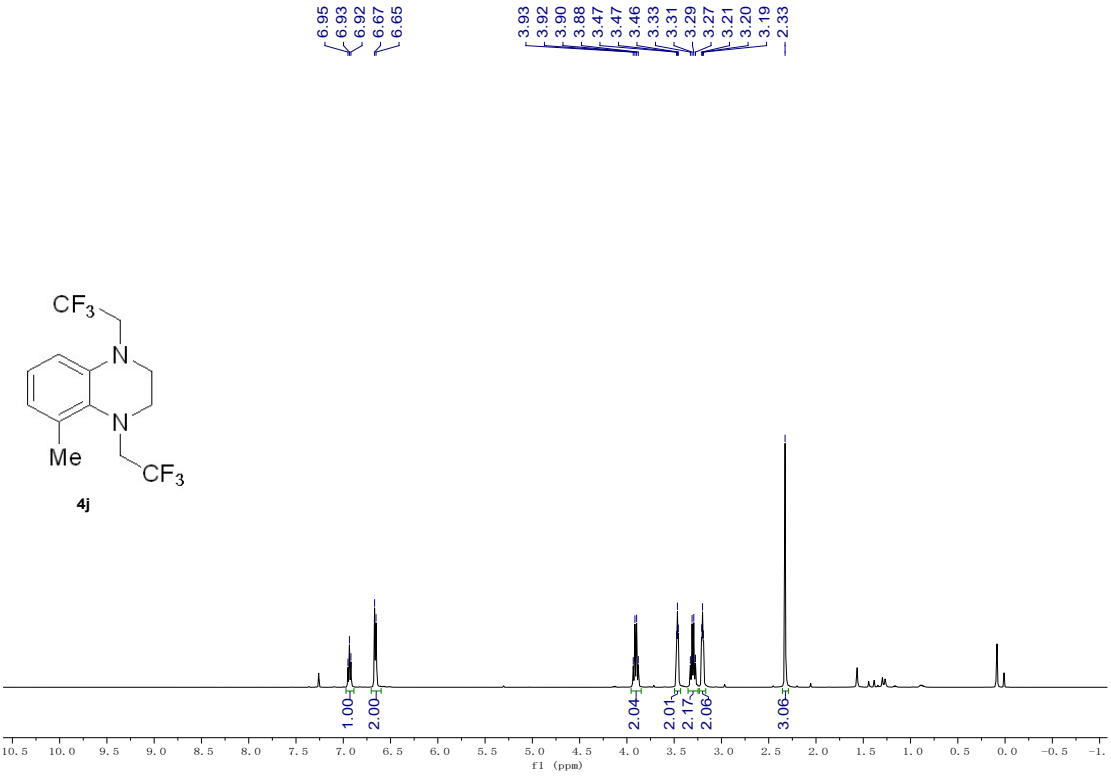
6,7-dimethyl-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4i)

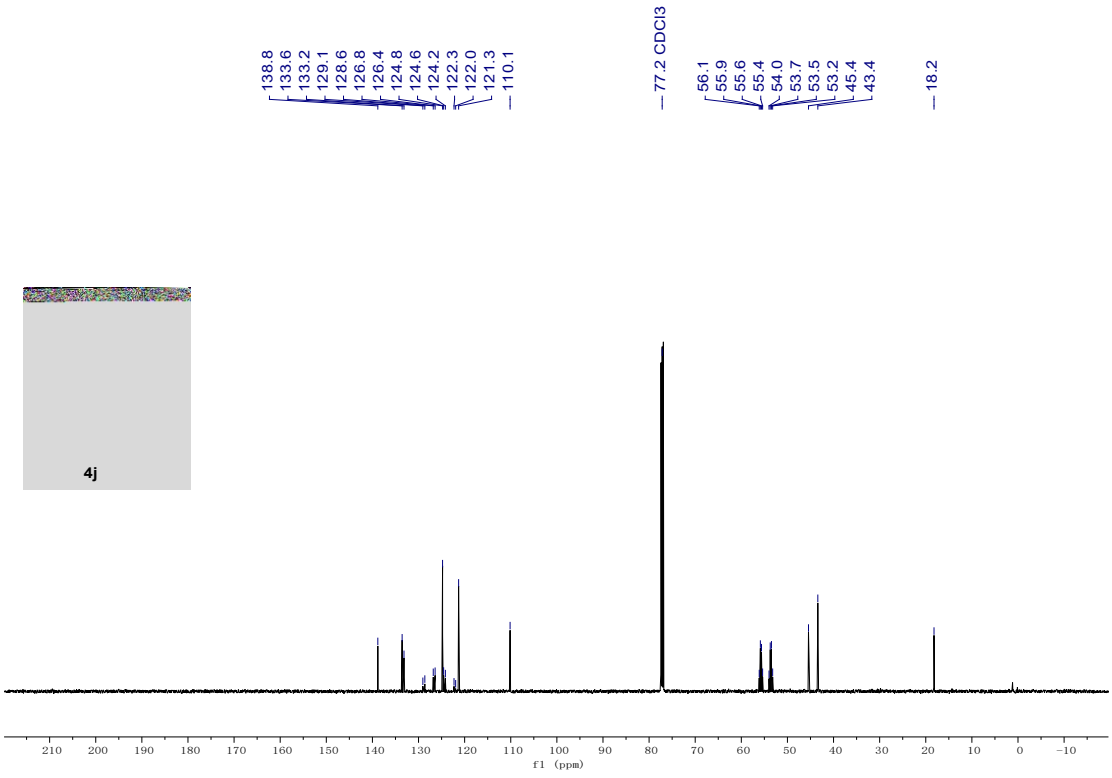


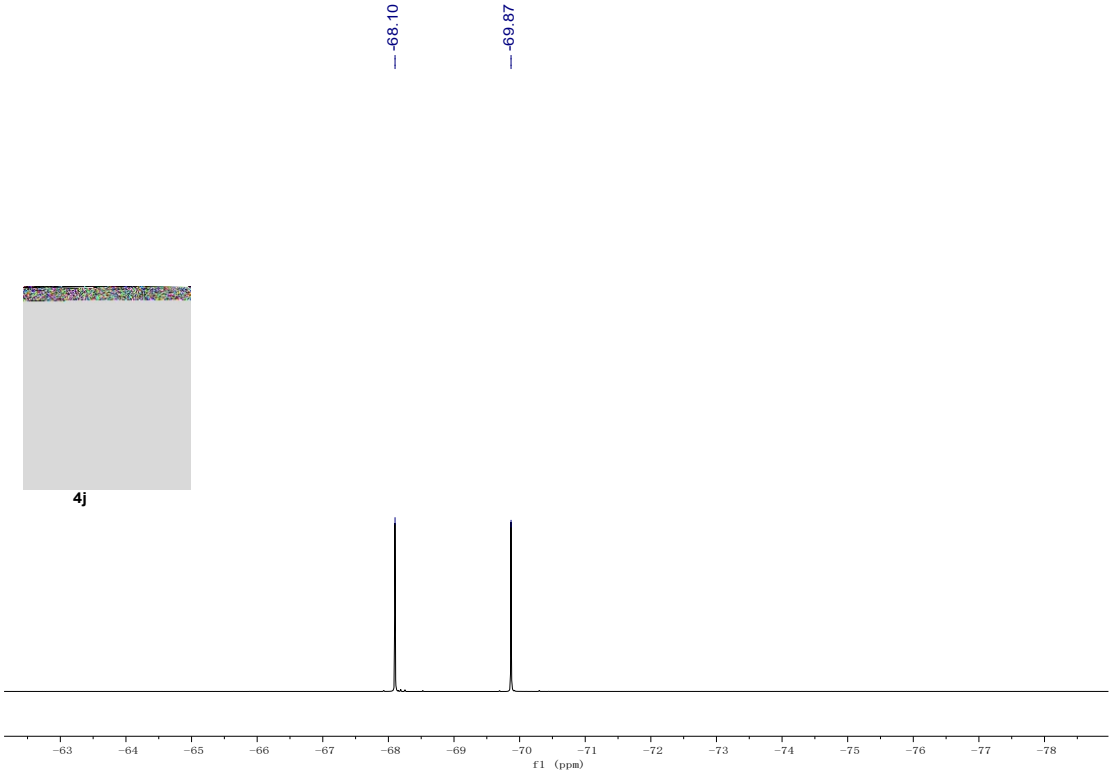




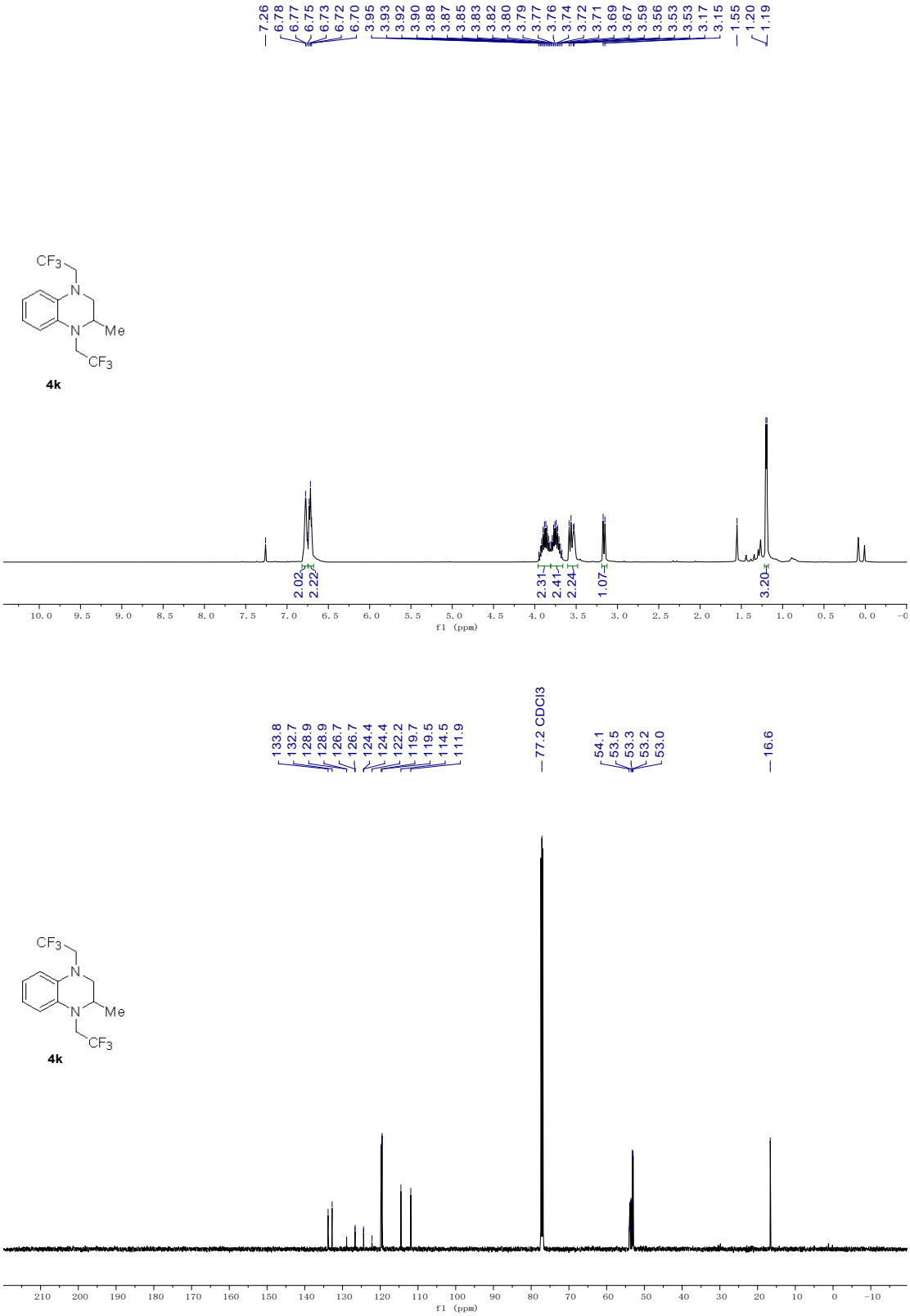
5-methyl-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4j)

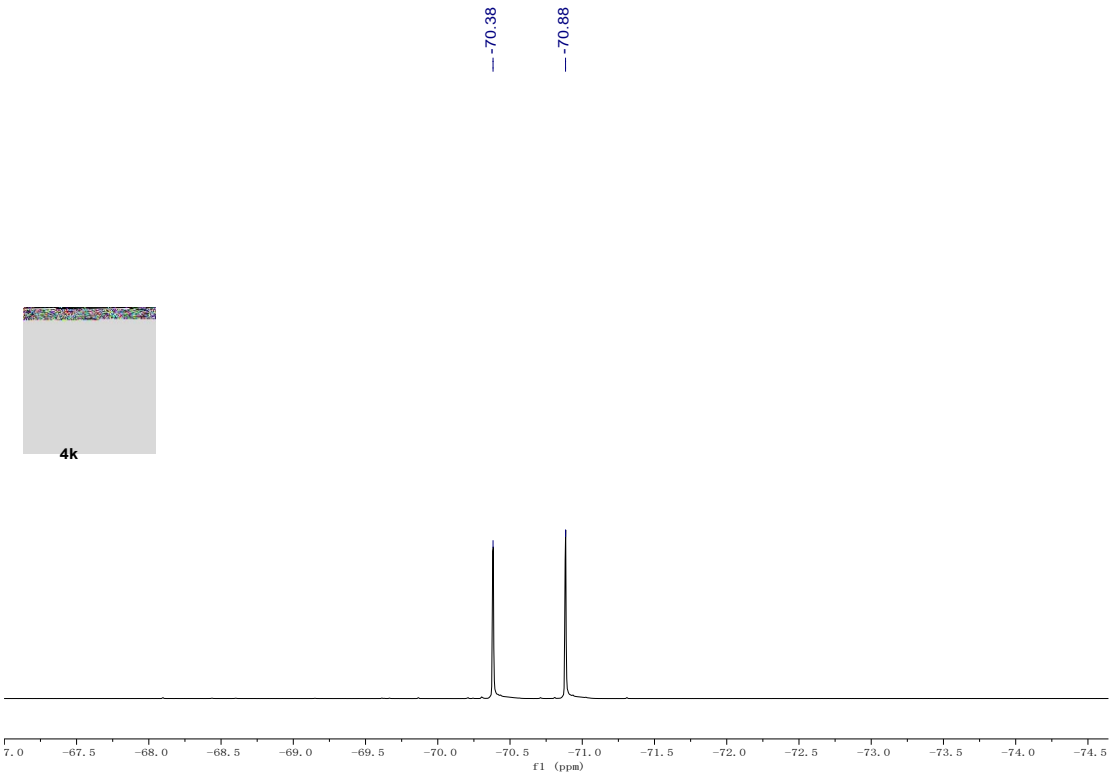



138.8
133.6
133.2
129.1
128.6
126.8
126.4
124.8
124.6
124.2
122.3
122.0
121.3
110.1
77.2 CDCl3
56.1
55.9
55.6
55.4
54.0
53.7
53.5
53.2
45.4
43.4
18.2
4j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-68.10
-69.87
4j
−63 −64 −65 −66 −67 −68 −69 −70 −71 −72 −73 −74 −75 −76 −77 −78
f1 (ppm)

2-methyl-1,4-bis(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydroquinoxaline (4k)




-70.38
-70.88
4k
7.0
-67.5
-68.0
-68.5
-69.0
-69.5
-70.0
-70.5
-71.0
-71.5
-72.0
-72.5
-73.0
-73.5
-74.0
-74.5
f1 (ppm)