

## Supporting information

### Photoinduced hydroxylperfluoroalkylation of styrenes

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## 1. General Methods

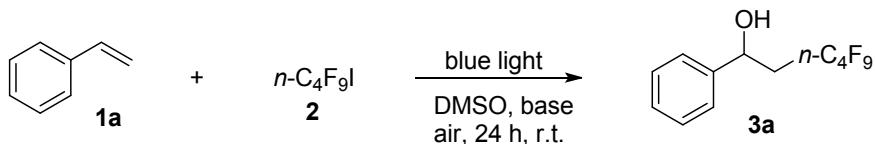
All reagents were used without further purification. Thin layer chromatography (TLC) was visualized by staining with potassium permanganate. Chemical shifts for  $^1\text{H}$  NMR spectra are reported in ppm downfield from TMS or residual  $\text{CHCl}_3$  ( $\delta$  7.26 ppm). Chemical shifts for  $^{19}\text{F}$  NMR are reported in ppm downfield from fluorotrichloromethane ( $\text{CFCl}_3$ ). Chemical shifts for  $^{13}\text{C}$  NMR spectra are recorded in ppm relative to residual chloroform ( $\delta$  77.0 ppm for  $\text{CDCl}_3$ ).  $^{13}\text{C}$  NMR was broad-band decoupled from hydrogen nuclei. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as hertz (Hz). Signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

## General procedures for synthesis of **3**

A 50 mL Schlenk tube equipped with a rubber septum and a magnetic stirring bar was charged with DMSO (5 mL). Then styrene **1** (1 mmol, 1.0 equiv),  $n\text{-C}_4\text{F}_9\text{I}$  (2 mmol, 2.0 equiv), TMEDA (2 mmol, 2.0 equiv) were added. The mixture was stirred under an air atmosphere by irradiation of blue LEDs (15 W  $\times$  2) for 48 h. After the reaction was complete, the solution was added  $\text{CH}_2\text{Cl}_2$  (30 mL) and washed with saturated brine (50 mL  $\times$  3). The organic layer was dried by anhydrous  $\text{Na}_2\text{SO}_4$ . After that, the organic layer was separated and concentrated under vacuum. The residue was purified with silica gel column chromatography to provide the desired product.

## 2. Reaction Condition Optimization

Table S1. Screening of bases



Entry <sup>a</sup>	Base	Yield (%) <sup>b</sup>	Entry <sup>a</sup>	Base	Yield (%) <sup>b</sup>
1	$i\text{Pr}_2\text{NEt}$	81	8	$\text{HOCH}_2\text{CH}_2\text{NH}_2$	38
2	$i\text{Pr}_2\text{NH}$	45	9	$(\text{HOCH}_2\text{CH}_2)_3\text{N}$	84
3	$\text{Et}_2\text{NH}$	9	10	$\text{N} \begin{array}{c}   \\ \text{C}_6\text{H}_4 \end{array} -$	0
4	$\text{Et}_3\text{N}$	58	11	$\text{N} \begin{array}{c}   \\ \text{C}_6\text{H}_4 \end{array} -$	0
5	$\text{Ph}_3\text{N}$	0	12	$\text{N} \begin{array}{c}   \\ \text{C}_6\text{H}_3 \end{array} -$	0
6	DBU	23			
7	TMEDA	91			

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), base (0.4 mmol), anhydrous DMSO (2 mL), blue light (15 W  $\times$  2), 24 h, under an air atmosphere; <sup>b</sup>Yield were determined by  $^{19}\text{F}$  NMR spectroscopy using benzotrifluoride as the internal standard.

Table S2. Screening of concentration and ratios of substrates

blue LEDs solvent, base air, 24 h, r.t.				
Entry <sup>a</sup>	<b>2</b>	TMEDA	DMSO	Yield (%) <sup>b</sup>
1	2 equiv.	2 equiv.	1 mL	99
2	2 equiv.	2 equiv.	2 mL	91
3	2 equiv.	2 equiv.	3 mL	84
4	1.5 equiv.	1.5 equiv.	1 mL	91
5	2 equiv.	1.5 equiv.	1 mL	81
6	1.5 equiv.	2 equiv.	1 mL	83
7	2.5 equiv.	2.5 equiv.	1 mL	96

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2**, TMEDA, anhydrous DMSO, blue light (15W × 2), 24 h, under an air atmosphere; <sup>b</sup>Yield were determined by <sup>19</sup>F NMR spectroscopy using benzotrifluoride as the internal standard.

### 3. Optimization of Condition B (with a photocatalyst)

Table S3. Screening of catalysts and solvents

photocatalyst (1 mol%) white light solvent, air, 24 h, r.t.				
Entry <sup>a</sup>	catalyst	Base	Solvent	Yield (%) <sup>b</sup>
1	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (dtbbpy)(PF <sub>6</sub> )	<i>i</i> Pr <sub>2</sub> NEt	MeCN	18
2	Ir(ppy) <sub>2</sub> (dtbbpy)(PF <sub>6</sub> )	<i>i</i> Pr <sub>2</sub> NEt	MeCN	14
3	[Ir(ppy) <sub>2</sub> Cl] <sub>2</sub>	<i>i</i> Pr <sub>2</sub> NEt	MeCN	16
4	Ru(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>	<i>i</i> Pr <sub>2</sub> NEt	MeCN	20
5	Ir(ppy) <sub>3</sub>	<i>i</i> Pr <sub>2</sub> NEt	MeCN	33
6	Ir(ppy) <sub>3</sub>	<i>i</i> Pr <sub>2</sub> NEt	THF	15
7	Ir(ppy) <sub>3</sub>	<i>i</i> Pr <sub>2</sub> NEt	DMF	53
8	Ir(ppy) <sub>3</sub>	<i>i</i> Pr <sub>2</sub> NEt	DMSO	69

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), photocatalyst (0.002 mmol), base (0.4 mmol), solvent (2 mL), 24 W white fluorescent irradiation, 24 h, under an air atmosphere; <sup>b</sup>Yield were determined by <sup>19</sup>F NMR spectroscopy using benzotrifluoride as the internal standard.

Table S4. Screening of bases

Entry <sup>a</sup>	Base	Yield (%) <sup>b</sup>	Entry <sup>a</sup>	Base	Yield (%) <sup>b</sup>
1	<i>i</i> Pr <sub>2</sub> NEt	90	8	HOCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	46
2	<i>i</i> Pr <sub>2</sub> NH	72	9	(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	40
3	Et <sub>2</sub> NH	69	10		0
4	Et <sub>3</sub> N	72	11		0
5	Ph <sub>3</sub> N	0	12		0
6	DBU	83			
7	TMEDA	83			

<sup>a</sup>Reaction conditions: **1j** (0.2 mmol), **2** (0.4 mmol), base (0.4 mmol), anhydrous DMSO (2 mL), 24 W white fluorescent irradiation, 24 h, under an air atmosphere; <sup>b</sup>Yield were determined by <sup>19</sup>F NMR spectroscopy using benzotrifluoride as the internal standard.

Table S5. Substrate scope of condition B

<b>3a:</b> R <sup>1</sup> = H, R <sup>2</sup> = H, 60%	<b>3n:</b> R <sup>3</sup> = Cl, R <sup>4</sup> = H, 57%
<b>3b:</b> R <sup>1</sup> = F, R <sup>2</sup> = H, 65%	<b>3o:</b> R <sup>3</sup> = Br, R <sup>4</sup> = H, 75%
<b>3c:</b> R <sup>1</sup> = Cl, R <sup>2</sup> = H, 65%	
<b>3d:</b> R <sup>1</sup> = Br, R <sup>2</sup> = H, 68%	
<b>3e:</b> R <sup>1</sup> = <i>t</i> Bu, R <sup>2</sup> = H, 55%	
<b>3f:</b> R <sup>1</sup> = OMe, R <sup>2</sup> = H, 55%	
<b>3g:</b> R <sup>1</sup> = OAc, R <sup>2</sup> = H, 40%	
<b>3j:</b> R <sup>1</sup> = H, R <sup>2</sup> = Me, 85%	
<b>3k:</b> R <sup>1</sup> = F, R <sup>2</sup> = Me, 60%	
<b>3l:</b> R <sup>1</sup> = Cl, R <sup>2</sup> = Me, 57%	
<b>3m:</b> R <sup>1</sup> = H, R <sup>2</sup> = Ph, 60%	
	<b>3s, 66%</b>
	<b>3t, 51%</b>

<sup>a</sup> Reaction conditions: **1** (0.5 mmol), **2** (1 mmol), *i*Pr<sub>2</sub>NEt (1 mmol), anhydrous DMSO (10 mL), 24

W white fluorescent irradiation, 24 h, under an air atmosphere; <sup>b</sup> Isolated yield.

#### 4. NMR spectra and data for all products

Data of 3

**3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhexan-1-ol (3a)**, yellow liquid, 309.4 mg, yield: 91%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.35 (m, 5H), 5.19 (dd, *J* = 8.8, 3.2 Hz, 1H), 2.70-2.55 (m, 1H), 2.49-2.35 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.6, 128.9, 128.4, 125.6, 68.0, 39.8 (t, *J* = 20.2 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -81.2 (t, *J* = 9.4 Hz, 3F), -112.3 to -114.6 (m, 2F), -124.7 (m, 2F), -126.0 to -126.1 (m, 2F); HRMS(EI) Calcd for C<sub>12</sub>H<sub>9</sub>F<sub>9</sub>O (M<sup>+</sup>): 340.0510; found: 340.0520.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-fluorophenyl)hexan-1-ol (3b)**, yellow liquid, 318.6 mg, yield: 89%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39-7.35 (m, 2H), 7.10-7.05 (t, *J* = 8.6 Hz, 2H), 5.21 (dd, *J* = 8.8, 3.2 Hz, 1H), 2.68-2.53 (m, 1H), 2.46-2.24 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.6 (d, *J* = 245.4 Hz), 138.4 (d, *J* = 3.1 Hz), 127.4 (t, *J* = 8.2 Hz), 115.8 (t, *J* = 21.5 Hz), 67.3, 39.9 (t, *J* = 19.5 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -81.1 (tt, *J* = 9.8, 2.6 Hz, 3F), -112.4 to -114.4 (m, 2F), -113.6 (s, 1F), -124.6 (m, 2F), -126.0 (m, 2F); HRMS(EI) Calcd for C<sub>12</sub>H<sub>8</sub>F<sub>10</sub>O (M<sup>+</sup>): 358.0415; found: 358.0410.

**1-(4-chlorophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3c)**, yellow liquid, 336.6 mg, yield: 90%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37-7.31 (m, 4H), 5.21-5.18 (m, 1H), 2.66-2.05 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.0, 134.2, 129.0, 127.0, 67.3, 39.8 (t, *J* = 20.0 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -81.1 to -81.2 (m, 3F), -112.3 to -114.4 (m, 2F), -124.6 (m, 2F), -125.9 to -126.0 (m, 2F); HRMS(EI) Calcd for C<sub>12</sub>H<sub>8</sub>ClF<sub>9</sub>O (M<sup>+</sup>): 374.0120; found: 374.0116.

**1-(4-bromophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3d)**, yellow liquid, 384.5 mg, yield: 92%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 2H), 5.13 (m, 1H), 3.10-2.29 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.7, 131.6, 126.8, 122.1, 67.4, 39.8 (t, *J* = 20.4 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -81.4 (tt, *J* = 9.8, 3.1 Hz, 3F), -112.4 to -114.6 (m, 2F), -124.8 (m, 2F), -126.2 to -126.3 (m, 2F); HRMS(EI) Calcd for C<sub>12</sub>H<sub>8</sub>BrF<sub>9</sub>O (M<sup>+</sup>): 417.9615; found: 417.9607.

**1-(4-(tert-butyl)phenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3e)**, yellow liquid, 368.3 mg, yield: 93%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45-7.32 (m, 4H), 5.19 (dd, *J* = 8.8, 2.8 Hz, 1H), 2.71-2.56 (m, 1H), 2.50-2.40 (m, 2H), 1.36 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 151.5, 139.7, 125.8, 125.4, 67.6, 39.6 (t, *J* = 20.3 Hz), 34.6, 31.2; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -81.2 (t, *J* = 9.8 Hz, 3F), -112.4 to -114.8 (m, 2F), -124.7 (m, 2F), -126.0 (m, 2F); HRMS(EI) Calcd for C<sub>16</sub>H<sub>17</sub>F<sub>9</sub>O (M<sup>+</sup>): 396.1136; found: 396.1139.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hexan-1-ol (3f)**, yellow liquid, 325.6 mg, yield: 88%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.14 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.80 (s, 3H), 2.68-2.53 (m, 1H), 2.42-2.05 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.5, 134.6, 126.8, 114.1, 67.3, 55.1, 39.6 (t, *J* = 20.3 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

$\delta$  -81.1 (tt,  $J$  = 9.4, 3.8 Hz, 3F), -112.4 to -114.7 (m, 2F), -124.7 (m, 2F), -126.0 to -126.1 (m, 2F); HRMS(EI) Calcd for C<sub>13</sub>H<sub>11</sub>F<sub>9</sub>O<sub>2</sub> (M<sup>+</sup>): 370.0615; found: 370.0614.

**4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-hydroxyhexyl)phenyl acetate (3g)**, yellow liquid, 342.3 mg, yield: 86%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (d,  $J$  = 8.4 Hz, 2H), 7.08 (d,  $J$  = 8.0 Hz, 2H), 5.18 (dd,  $J$  = 8.8, 2.8 Hz, 1H), 2.64-2.30 (m, 3H), 2.29 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.6, 150.4, 140.3, 126.8, 121.9, 67.2, 39.7 (t,  $J$  = 20.3 Hz), 21.0; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.2 (t,  $J$  = 7.5 Hz, 3F), -113.1 to -114.6 (m, 2F), -124.7 (m, 2F), -126.1 (m, 2F); HRMS(EI) Calcd for C<sub>14</sub>H<sub>11</sub>F<sub>9</sub>O<sub>3</sub> (M<sup>+</sup>): 398.0564; found: 398.0562.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-(hydroxymethyl)phenyl)hexan-1-ol (3h)**, yellow liquid, 355.0 mg, yield: 96%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 (t,  $J$  = 8.8 Hz, 4H), 5.12 (d,  $J$  = 6.4 Hz, 1H), 4.56 (s, 2H), 3.05-2.65 (br, 2H), 2.60-2.48 (m, 1H), 2.42-2.29 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.1, 140.8, 127.3, 125.8, 67.5, 64.6, 39.6 (t,  $J$  = 20.4 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.3 (d,  $J$  = 2.6 Hz, 3F), -112.3 to -114.7 (m, 2F), -124.7 (m, 2F), -126.1 (m, 2F); HRMS(EI) Calcd for C<sub>13</sub>H<sub>11</sub>F<sub>9</sub>O<sub>2</sub> (M<sup>+</sup>): 370.0615; found: 370.0618.

**4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-hydroxyhexyl)benzonitrile (3i)**, yellow liquid, 255.4 mg, yield: 70%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d,  $J$  = 8.4 Hz, 2H), 7.53 (d,  $J$  = 8.0 Hz, 2H), 5.30 (dd,  $J$  = 2.8, 8.4 Hz, 1H), 2.68-2.32 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.6, 132.7, 126.4, 118.4, 112.2, 67.2, 38.9 (t,  $J$  = 27.8 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.1 (tt,  $J$  = 3.4, 6.4 Hz, 3F), -112.2 to -114.2 (m, 2F), -124.5 (m, 2F), -124.6 to -126.0 (m, 2F); HRMS(EI) Calcd for C<sub>13</sub>H<sub>8</sub>F<sub>9</sub>NO (M<sup>+</sup>): 365.0462; found: 365.0465.

**4,4,5,5,6,6,7,7,7-nonafluoro-2-phenylheptan-2-ol (3j)**, yellow liquid, 325.7 mg, yield: 92%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (d,  $J$  = 8.0 Hz, 2H), 7.41 (t,  $J$  = 8.0 Hz, 2H), 7.32 (t,  $J$  = 7.2 Hz, 1H), 2.76-2.53 (m, 2H), 2.48 (s, 1H), 1.79 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  146.6, 128.4, 127.4, 124.4, 72.8, 42.5 (t,  $J$  = 19.4 Hz), 29.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.4 (t,  $J$  = 11.3 Hz, 3F), -110.4 to -113.7 (m, 2F), -124.8 (m, 2F), -126.0 (m, 2F); HRMS(EI) Calcd for C<sub>13</sub>H<sub>11</sub>F<sub>9</sub>O (M<sup>+</sup>): 354.0666; found: 354.0659.

**4,4,5,5,6,6,7,7,7-nonafluoro-2-(4-fluorophenyl)heptan-2-ol (3k)**, yellow liquid, 327.4 mg, yield: 88%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47-7.44 (m, 2H), 7.04 (t,  $J$  = 8.8 Hz, 2H), 2.71-2.48 (m, 3H), 1.74 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.0 (d,  $J$  = 252.3 Hz), 142.4, 126.3 (t,  $J$  = 8.1 Hz), 115.3, 115.1, 72.5, 42.6 (t,  $J$  = 19.4 Hz), 30.1; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.6 (tt,  $J$  = 11.3 Hz, 3.0 Hz, 3F), -110.6 to -113.9 (m, 2F), -115.8 to -115.9 (m, 1F), -124.9 (m, 2F), -126.1 to -126.2 (m, 2F); HRMS(EI) Calcd for C<sub>13</sub>H<sub>10</sub>F<sub>10</sub>O (M<sup>+</sup>): 372.0572; found: 372.0567.

**2-(4-chlorophenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-2-ol (3l)**, yellow liquid, 345.3 mg, yield: 89%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (d,  $J$  = 8.8 Hz, 2H), 7.34 (d,  $J$  = 8.8 Hz, 2H), 2.70-2.48 (m, 3H), 1.74 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.8, 133.2, 128.4, 72.3, 42.4 (t,  $J$  = 19.3 Hz), 30.0; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.5 (tt,  $J$  = 11.3, 3.0 Hz, 3F), -110.5 to -113.7 (m, 2F), -124.9 (m, 2F), -126.1 to -126.2 (m, 2F); HRMS(EI) Calcd for C<sub>13</sub>H<sub>10</sub>ClF<sub>9</sub>O (M<sup>+</sup>): 388.0276; found: 388.0270.

**3,3,4,4,5,5,6,6,6,6-nonafluoro-1,1-diphenylhexan-1-ol (3m)**, yellow liquid, 386.9 mg, yield: 93%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 8.0$  Hz, 4H), 7.39 (t,  $J = 8.0$  Hz, 4H), 7.32 (t,  $J = 7.2$  Hz, 2H), 3.24 (t,  $J = 18.4$  Hz, 2H), 2.86 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.5, 128.4, 127.5, 125.4, 76.5, 40.8 (t,  $J = 18.9$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.2 (t,  $J = 10$  Hz, 3F), -109.2 to -109.4 (m, 2F), -124.54 (m, 2F), -125.7 to -125.9 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{18}\text{H}_{13}\text{F}_9\text{O} (\text{M}^+)$ : 416.0823; found: 416.0832.

**1-(2-chlorophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3n)**, yellow liquid, 329.1 mg, yield: 88%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67-7.64 (m, 1H), 7.38-7.25 (m, 3H), 5.64 (dd,  $J = 9.2, 2.0$  Hz, 1H), 2.60-2.37 (m, 2H), 2.26 (br, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 131.2, 129.7, 129.3, 127.5, 127.0, 64.7, 38.3 (t,  $J = 20.5$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (tt,  $J = 9.8, 2.6$  Hz, 3F), -111.9 to -115.2 (m, 2F), -124.6 (m, 2F), -126.0 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{12}\text{H}_8\text{ClF}_9\text{O} (\text{M}^+)$ : 374.0120; found: 374.0118.

**1-(2-bromophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3o)**, yellow liquid, 376.1 mg, yield: 90%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 6.8$  Hz, 1H), 7.55 (d,  $J = 7.2$  Hz, 1H), 7.39 (t,  $J = 7.2$  Hz, 1H), 7.19 (t,  $J = 7.2$  Hz, 1H), 5.60 (d,  $J = 9.2$  Hz, 1H), 2.61-2.34 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.4, 133.0, 129.6, 128.1, 127.3, 121.1, 66.9, 38.3 (t,  $J = 20.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (t,  $J = 9.8$  Hz, 3F), -111.8 to -115.2 (m, 2F), -124.7 (m, 2F), -126.0 (q,  $J = 14.3$  Hz, 2F); HRMS(EI) Calcd for  $\text{C}_{12}\text{H}_8\text{BrF}_9\text{O} (\text{M}^+)$ : 417.9615; found: 417.9613.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(o-tolyl)hexan-1-ol (3p)**, yellow liquid, 322.1 mg, yield: 91%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 7.2$  Hz, 1H), 7.28-7.15 (m, 3H), 5.46 (dd,  $J = 9.2, 2.0$  Hz, 1H), 2.63-2.47 (m, 1H), 2.33-2.27 (m, 4H), 2.14 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 133.9, 130.8, 128.1, 126.7, 125.1, 64.2, 38.9 (t,  $J = 20.6$  Hz), 18.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (tt,  $J = 9.8, 2.6$  Hz, 3F), -112.7 to -114.9 (m, 2F), -124.6 (m, 2F), -125.9 to -126.0 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{13}\text{H}_{11}\text{F}_9\text{O} (\text{M}^+)$ : 354.0666; found: 354.0658.

**1-(3-bromophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3q)**, yellow liquid, 355.2 mg, yield: 85%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (s, 1H), 7.46 (dt,  $J = 7.6, 1.2$  Hz, 1H), 7.31-7.23 (m, 2H), 5.18 (dd,  $J = 8.8, 3.2$  Hz, 1H), 2.66-2.31 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.8, 131.5, 130.4, 128.8, 124.2, 122.9, 67.3, 39.9 (t,  $J = 20.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (tt,  $J = 9.8, 3.0$  Hz, 3F), -112.2 to -114.5 (m, 2F), -124.6 (m, 2F), -125.9 to -126.0 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{12}\text{H}_8\text{BrF}_9\text{O} (\text{M}^+)$ : 417.9615; found: 417.9603.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(3-methoxyphenyl)hexan-1-ol (3r)**, yellow liquid, 329.3 mg, yield: 89%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.24 (m, 1H), 6.93-6.92 (m, 2H), 6.84 (d,  $J = 8.4$  Hz, 1H), 5.14 (d,  $J = 8.4$  Hz, 1H), 3.79 (s, 3H), 2.66-2.50 (m, 1H), 2.45-2.32 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.1, 144.2, 130.0, 117.7, 113.5, 111.2, 67.8, 55.0, 39.8 (t,  $J = 20.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.2 (tt,  $J = 12.4, 3.4$  Hz, 3F), -112.2 to -114.7 (m, 2F), -124.7 (m, 2F), -126.0 to -126.1 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{13}\text{H}_{11}\text{F}_9\text{O}_2 (\text{M}^+)$ : 370.0615; found: 370.0607.

**1-(2,6-dimethylphenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3s)**, yellow liquid, 257.6 mg, yield: 70%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (s, 1H), 7.08 (t,  $J = 8.0$  Hz, 2H), 5.44 (d,  $J = 8.8$  Hz, 1H), 2.65-2.50 (m, 1H), 2.43-2.38 (m, 5H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.6, 136.3, 130.7, 128.7, 125.7, 64.2, 38.9 (t,  $J = 20.5$  Hz), 20.9, 18.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.3 (t,  $J = 9.4$  Hz, 3F), -112.7 to -115.0 (m, 2F), -124.7 (m, 2F), -126.1 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{14}\text{H}_{13}\text{F}_9\text{O}$  ( $\text{M}^+$ ): 368.0823; found: 368.0819.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(naphthalen-1-yl)hexan-1-ol (3t)**, yellow liquid, 304.2 mg, yield: 78%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 8.0$  Hz, 1H), 7.92 (d,  $J = 8.0$  Hz, 1H), 7.84 (d,  $J = 8.0$  Hz, 1H), 7.73 (d,  $J = 7.2$  Hz, 1H), 7.61-7.48 (m, 3H), 5.99 (d,  $J = 9.2$  Hz, 1H), 2.77-2.53 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.0, 133.8, 129.4, 129.2, 128.8, 126.7, 125.9, 125.5, 123.1, 122.0, 64.6, 39.2 (t,  $J = 20.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (t,  $J = 9.8$  Hz, 3F), -112.6 to -114.8 (m, 2F), -124.6 (m, 2F), -126.0 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{16}\text{H}_{11}\text{F}_9\text{O}$  ( $\text{M}^+$ ): 390.0666; found: 390.0672.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(naphthalen-2-yl)hexan-1-ol (3u)**, yellow liquid, 296.4 mg, yield: 76%.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  7.98-7.88 (m, 4H), 7.61 (t,  $J = 8.4$  Hz, 1H), 7.53-7.47 (m, 2H), 6.00 (s, 1H), 5.28 (s, 1H), 2.77-2.56 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  142.1, 133.1, 132.8, 128.2, 128.0, 127.7, 126.3, 126.0, 124.7, 124.4, 66.7;  $^{19}\text{F}$  NMR (376 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  -81.4 (m, 3F), -111.2 to -113.9 (m, 2F), -124.5 (s, 2F), -126.1 (s, 2F); HRMS(EI) Calcd for  $\text{C}_{16}\text{H}_{11}\text{F}_9\text{O}$  ( $\text{M}^+$ ): 390.0666; found: 390.0668.

**1-(benzo[b]thiophen-2-yl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3v)**, yellow liquid, 344.5 mg, yield: 87%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84-7.73 (m, 2H), 7.35-7.32 (m, 2H), 7.25 (s, 1H), 5.6 (dd,  $J = 8.4, 3.2$  Hz, 1H), 2.72-2.47 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.6, 139.3, 139.1, 124.8, 124.6, 123.8, 122.6, 120.8, 64.6, 39.8 (t,  $J = 20.5$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (t,  $J = 9.4$  Hz, 3F), -112.2 to -114.6 (m, 2F), -124.6 (m, 2F), -126.0 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{14}\text{H}_9\text{F}_9\text{OS}$  ( $\text{M}^+$ ): 396.0230; found: 396.0233.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methylthiazol-5-yl)hexan-1-ol (3w)**, yellow liquid, 267.1 mg, yield: 74%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (s, 1H), 5.45 (m, 2H), 2.73-2.59 (m, 1H), 2.43-2.34 (m, 1H), 2.23 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.6, 147.7, 135.7, 60.8, 39.8 (t,  $J = 20.4$  Hz), 14.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.4 (d,  $J = 7.1$  Hz, 3F), -112.8 to -115.0 (AB,  $J = 272$  Hz, 2F), -124.8 (s, 2F), -126.2 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{10}\text{H}_8\text{F}_9\text{NOS}$  ( $\text{M}^+$ ): 361.0183; found: 361.0187.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(pyridin-2-yl)hexan-1-ol (3x)**, yellow liquid, 231.1 mg, yield: 68%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (d,  $J = 4.8$  Hz, 1H), 7.68 (td,  $J = 7.6, 1.6$  Hz, 1H), 7.38 (d,  $J = 8.0$  Hz, 1H), 7.20-7.17 (m, 1H), 5.19 (dd,  $J = 8.4, 3.6$  Hz, 1H), 4.80 (s, 1H), 2.68-2.43 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.5, 148.6, 137.3, 123.0, 120.6, 67.3, 38.7 (t,  $J = 20.3$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.5 (tt,  $J = 9.8, 2.6$  Hz, 3F), -112.2 to -114.6 (m, 2F), -124.8 (m, 2F), -126.3 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{11}\text{H}_8\text{F}_9\text{NO}$  ( $\text{M}^+$ ): 340.0384; found: 340.0382.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(pyrazin-2-yl)hexan-1-ol (3y)**, yellow liquid, 215.5 mg, yield:

63%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.76 (s, 1H), 8.53 (s, 2H), 5.33 (dd,  $J = 8.4, 3.6$  Hz, 1H), 4.35-3.65 (m, 1H), 2.84-2.70 (m, 1H), 2.67-2.52 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.0, 144.0, 143.7, 142.7, 66.2, 38.2 (t,  $J = 20.1$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.2 to -81.3 (m, 3F), -111.9 to -114.2 (m, 2F), -124.7 (m, 2F), -126.1 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{10}\text{H}_7\text{F}_9\text{N}_2\text{O}$  ( $\text{M}^+$ ): 342.0415; found: 342.0412.

**(8R,9S,13S,14S)-13-methyl-3-(3,3,4,4,5,5,6,6,6-nonafluoro-1-hydroxyhexyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3z)**, yellow liquid, 428.4 mg, yield: 83%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 8.0$  Hz, 1H), 7.18-7.14 (m, 2H), 5.16 (dd,  $J = 8.4, 2.4$  Hz, 1H), 2.95-2.93 (m, 2H), 2.63-1.96 (m, 10H), 1.68-1.40 (m, 6H), 0.91 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  220.8, 140.2, 140.0, 137.2, 126.2 (d,  $J = 2.9$  Hz), 125.9, 123.0, 67.6, 50.5, 47.9, 44.3, 39.7 (t,  $J = 20.4$  Hz), 38.1, 35.8, 31.4, 29.40, 29.38, 25.7, 21.5, 13.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.2 (t,  $J = 9.8$  Hz, 3F), -110.9 to -111.8 (m, 2F), -124.7 (m, 2F), -125.8 to -125.9 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{24}\text{H}_{25}\text{F}_9\text{O}_2$  ( $\text{M}^+$ ): 516.1711; found: 516.1721

**3,3,4,4,4-pentafluoro-1-phenylbutan-1-ol (3aa)**, yellow liquid, 215.9 mg, yield: 90%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.25 (m, 5H), 5.04 (dd,  $J = 8.8, 3.6$  Hz, 1H), 2.89 (s, 1H), 2.55-2.21 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.7, 128.8, 128.3, 125.6, 67.8, 39.5 (t,  $J = 20.2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -86.1 (m, 3F), -116.1 to -118.3 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{10}\text{H}_9\text{F}_5\text{O}$  ( $\text{M}^+$ ): 240.0574; found: 240.0576.

**4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-phenylnonan-2-ol (3ab)**, yellow liquid, 358.6 mg, yield: 79%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 7.6$  Hz, 2H), 7.40 (t,  $J = 7.6$  Hz, 2H), 7.32 (t,  $J = 7.2$  Hz, 1H), 2.77-2.50 (m, 3H), 1.79 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.6, 128.5, 127.4, 124.4, 72.9, 42.5 (t,  $J = 19.4$  Hz), 29.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.3 (t,  $J = 9.8$  Hz, 3F), -110.2 to -113.6 (m, 2F), -121.9 (s, 2F), -123.2 (s, 2F), -124.0 (s, 2F), -126.5 to -126.6 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{15}\text{H}_{11}\text{F}_{13}\text{O}$  ( $\text{M}^+$ ): 454.0602; found: 454.0598.

#### Data of 3 (under condition B)

**3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhexan-1-ol (3a)**, yellow liquid, 102.1 mg, yield: 60%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.33 (m, 5H), 5.16 (dd,  $J = 8.8, 3.2$  Hz, 1H), 2.68-2.33 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.7, 128.9, 128.4, 125.6, 67.9, 39.8 (t,  $J = 20.5$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.3 (m, 3F), -112.3 to -114.7 (m, 2F), -124.7 (m, 2F), -126.1 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{12}\text{H}_9\text{F}_9\text{O}$  ( $\text{M}^+$ ): 340.0510; found: 340.0508.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-fluorophenyl)hexan-1-ol (3b)**, yellow liquid, 116.4 mg, yield: 65%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.31 (m, 2H), 7.09-7.01 (m, 2H), 5.22-5.16 (m, 1H), 2.68-1.90 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6 (d,  $J = 240.0$  Hz), 138.4 (d,  $J = 3.2$  Hz), 127.4 (d,  $J = 8.2$  Hz), 115.8 (d,  $J = 21.5$  Hz), 67.4, 39.9 (t,  $J = 20.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 to -81.2 (m, 3F), -112.3 to -114.5 (m, 3F), -124.6 (m, 2F), -126.0 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{12}\text{H}_8\text{F}_{10}\text{O}$  ( $\text{M}^+$ ): 358.0415; found: 358.0417.

**1-(4-chlorophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3c)**, yellow liquid, 121.5 mg, yield:

65%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.31 (m, 4H), 5.19 (dd,  $J = 8.8, 3.2$  Hz, 1H), 2.67-2.05 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.0, 134.2, 129.0, 127.0, 67.3, 39.8 (t,  $J = 20.2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 to -81.2 (m, 3F), -112.3 to -114.4 (m, 2F), -124.6 (m, 2F), -126.0 (t,  $J = 11.7$  Hz, 2F); HRMS(EI) Calcd for  $\text{C}_{12}\text{H}_8\text{ClF}_9\text{O}$  ( $\text{M}^+$ ): 374.0120; found: 374.0119.

**1-(4-bromophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3d)**, yellow liquid, 142.0 mg, yield: 68%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.43 (m, 2H), 7.19 (dd,  $J = 8.4, 2.0$  Hz, 2H), 5.14-5.10 (m, 1H), 2.60-1.87 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.5, 132.0, 127.4, 122.3, 67.3, 39.8 (t,  $J = 22.8$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (m, 3F), -112.2 to -114.3 (m, 2F), -124.6 (m, 2F), -125.9 to -126.0 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{12}\text{H}_8\text{BrF}_9\text{O}$  ( $\text{M}^+$ ): 417.9615; found: 417.9612.

**1-(4-(tert-butyl)phenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3e)**, yellow liquid, 108.9 mg, yield: 55%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 8.0$  Hz, 2H), 7.33 (d,  $J = 8.0$  Hz, 2H), 5.19 (dd,  $J = 8.8, 2.8$  Hz, 1H), 2.71-2.56 (m, 1H), 2.50-2.40 (m, 2H), 1.35 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.5, 139.7, 125.8, 125.4, 67.7, 39.7 (t,  $J = 20.4$  Hz), 34.6, 31.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.2 (t,  $J = 9.4$  Hz, 3F), -112.3 to -114.9 (m, 2F), -124.7 (m, 2F), -126.0 to -126.1 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{16}\text{H}_{17}\text{F}_9\text{O}$  ( $\text{M}^+$ ): 396.1136; found: 396.1129.

**3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hexan-1-ol (3f)**, yellow liquid, 101.7 mg, yield: 55%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 8.8$  Hz, 2H), 6.91 (d,  $J = 8.8$  Hz, 2H), 5.16 (dd,  $J = 8.4, 3.2$  Hz, 1H), 3.81 (s, 3H), 2.69-2.54 (m, 1H), 2.46-2.32 (m, 1H), 2.17 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 134.9, 126.9, 114.2, 67.5, 55.2, 39.6 (t,  $J = 19.7$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (m, 3F), -112.4 to -114.7 (m, 2F), -124.7 (m, 2F), -126.0 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{13}\text{H}_{11}\text{F}_9\text{O}_2$  ( $\text{M}^+$ ): 370.0615; found: 370.0621.

**4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-hydroxyhexyl)phenyl acetate (3g)**, yellow liquid, 79.6 mg, yield: 40%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J = 8.4$  Hz, 2H), 7.07 (d,  $J = 8.8$  Hz, 2H), 5.16 (dd,  $J = 8.8, 3.2$  Hz, 1H), 2.65-2.31 (m, 3H), 2.28 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.6, 150.4, 140.3, 126.8, 122.0, 67.3, 39.7 (t,  $J = 20.6$  Hz), 21.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.2 (tt,  $J = 9.8, 3.0$  Hz, 3F), -112.3 to -114.6 (m, 2F), -124.7 (m, 2F), -126.0 to -126.1 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{14}\text{H}_{11}\text{F}_9\text{O}_3$  ( $\text{M}^+$ ): 398.0564; found: 398.0569.

**4,4,5,5,6,6,7,7,7-nonafluoro-2-phenylheptan-2-ol (3j)**, yellow liquid, 150.5 mg, yield: 85%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53-7.50 (m, 2H), 7.42-7.28 (m, 2H), 7.34-7.30 (m, 1H), 2.77-2.54 (m, 2H), 2.42 (s, 1H), 1.79 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.6, 128.4, 127.4, 124.4, 72.8, 42.5 (t,  $J = 19.4$  Hz), 29.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.3 (tt,  $J = 9.8, 3.0$  Hz, 3F), -110.4 to -113.7 (m, 2H), -124.8 (m, 2F), -126.0 (m, 2F); HRMS(EI) Calcd for  $\text{C}_{13}\text{H}_{11}\text{F}_9\text{O}$  ( $\text{M}^+$ ): 354.0666; found: 354.0668.

**4,4,5,5,6,6,7,7,7-nonafluoro-2-(4-fluorophenyl)heptan-2-ol (3k)**, yellow liquid, 111.6 mg, yield: 60%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.42 (m, 2H), 7.01 (t,  $J = 8.4$  Hz, 2H), 2.73-2.48 (m, 3H), 1.73 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.2 (d,  $J = 250.0$  Hz), 142.4 (d,  $J = 3.2$  Hz), 126.4 (d,  $J = 7.5$  Hz), 115.2, 115.0, 72.6, 42.6 (t,  $J = 19.4$  Hz), 30.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

$\delta$  -81.7 (t,  $J$  = 9.8 Hz, 3F), -110.7 to -113.8 (m, 2F), -116.0 to -116.1 (m, 1F), -125.0 (m, 2F), -126.2 (m, 2F); HRMS(EI) Calcd for C<sub>13</sub>H<sub>10</sub>F<sub>10</sub>O (M<sup>+</sup>): 372.0572; found: 372.0558.

**2-(4-chlorophenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-2-ol (3l)**, yellow liquid, 110.6 mg, yield: 57%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (d,  $J$  = 8.4 Hz, 2H), 7.30 (d,  $J$  = 8.4 Hz, 2H), 2.67-2.47 (m, 3H), 1.71 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  145.0, 133.3, 128.5, 126.0, 72.6, 42.4 (t,  $J$  = 19.4 Hz), 29.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.6 (m, 3F), -110.5 to -113.7 (m, 2F), -124.9 (m, 2F), -126.1 to -126.2 (m, 2F); HRMS(EI) Calcd for C<sub>13</sub>H<sub>10</sub>ClF<sub>9</sub>O (M<sup>+</sup>): 388.0276; found: 388.0280.

**3,3,4,4,5,5,6,6,6-nonafluoro-1,1-diphenylhexan-1-ol (3m)**, yellow liquid, 124.8 mg, yield: 60%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50 (d,  $J$  = 7.6 Hz, 4H), 7.39 (t,  $J$  = 7.2 Hz, 4H), 7.31 (t,  $J$  = 7.2 Hz, 2H), 3.24 (t,  $J$  = 18.8 Hz, 2H), 2.82 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  145.5, 128.4, 127.5, 125.4, 76.5, 40.8 (t,  $J$  = 18.8 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.2 (tt,  $J$  = 9.8, 2.6 Hz, 3F), -109.2 to -109.4 (m, 2F), -124.5 (m, 2F), -125.8 (m, 2F); HRMS(EI) Calcd for C<sub>18</sub>H<sub>13</sub>F<sub>9</sub>O (M<sup>+</sup>): 416.0823; found: 416.0811.

**1-(2-chlorophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3n)**, yellow liquid, 106.6 mg, yield: 57%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (d,  $J$  = 7.6 Hz, 1H), 7.37-7.24 (m, 3H), 5.64 (d,  $J$  = 9.6 Hz, 1H), 2.60-2.36 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.5, 132.0, 127.4, 122.3, 67.3, 39.8 (t,  $J$  = 17.9 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.1 (t,  $J$  = 9.8 Hz, 3F), -111.9 to -115.2 (m, 2F), -124.6 (m, 2F), -125.9 (m, 2F); HRMS(EI) Calcd for C<sub>12</sub>H<sub>8</sub>ClF<sub>9</sub>O (M<sup>+</sup>): 374.0120; found: 374.0125.

**1-(2-bromophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3o)**, yellow liquid, 156.7 mg, yield: 75%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (dd,  $J$  = 7.6, 1.6 Hz, 1H), 7.55 (dd,  $J$  = 7.6, 1.2 Hz, 1H), 7.38 (td,  $J$  = 8.0, 1.2 Hz, 1H), 7.19 (td,  $J$  = 7.6, 1.6 Hz, 1H), 5.60 (dd,  $J$  = 9.2, 1.6 Hz, 1H), 2.61-2.34 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.3, 133.0, 129.7, 128.1, 127.3, 121.1, 66.9, 38.3 (t,  $J$  = 20.4 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.1 (t,  $J$  = 9.8 Hz, 3F), -111.8 to -115.1 (m, 2F), -124.6 (m, 2F), -126.0 (m, 2F); HRMS(EI) Calcd for C<sub>12</sub>H<sub>8</sub>BrF<sub>9</sub>O (M<sup>+</sup>): 417.9615; found: 417.9616.

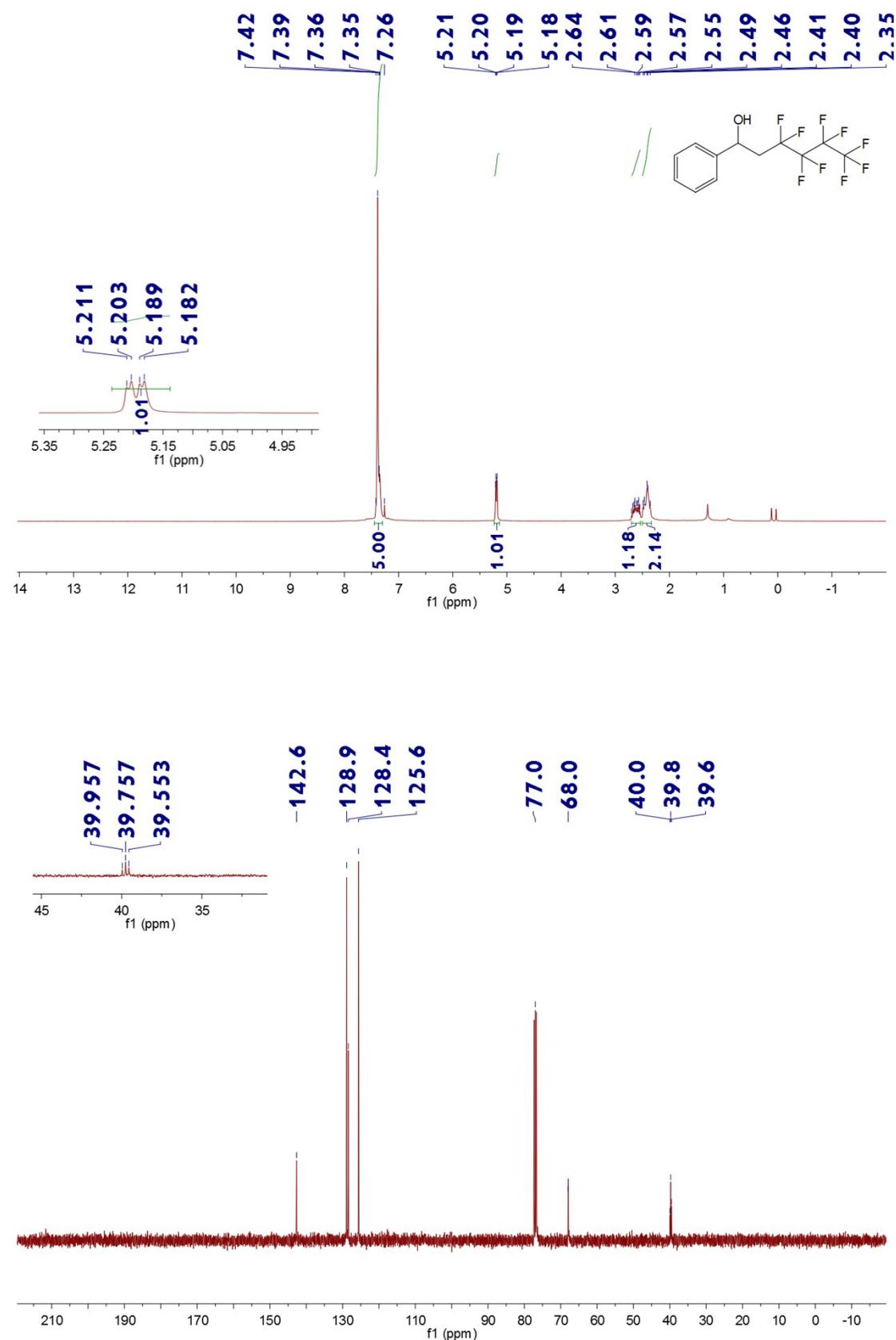
**1-(2,6-dimethylphenyl)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (3s)**, yellow liquid, 121.5 mg, yield: 66%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (s, 1H), 7.00 (s, 2H), 5.36-5.34 (m, 1H), 2.50-2.30 (m, 6H), 2.23 (d,  $J$  = 2.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.6, 136.3, 130.7, 128.7, 125.7, 64.2, 38.9 (t,  $J$  = 20.5 Hz), 20.9, 18.1; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.4 to -81.5 (m, 3F), -112.7 to -115.0 (m, 2F), -124.7 (m, 2F), -126.1 (m, 2F); HRMS(EI) Calcd for C<sub>14</sub>H<sub>13</sub>F<sub>9</sub>O (M<sup>+</sup>): 368.0823; found: 368.0831.

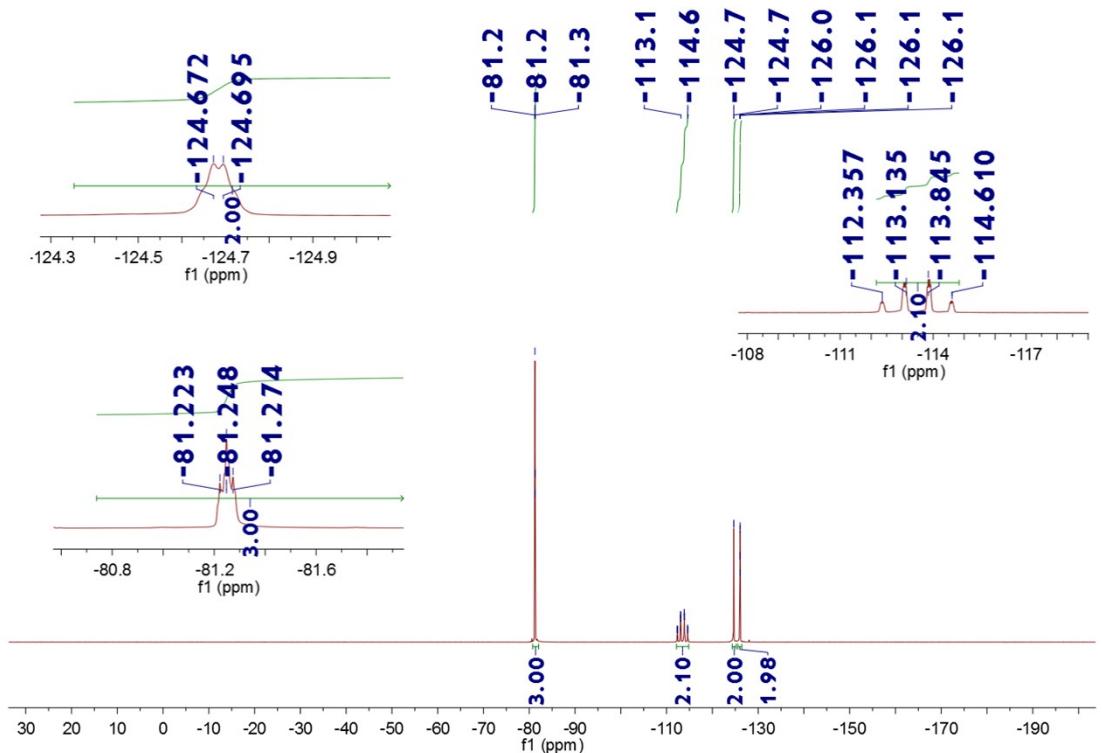
**3,3,4,4,5,5,6,6,6-nonafluoro-1-(naphthalen-1-yl)hexan-1-ol (3t)**, yellow liquid, 99.5 mg, yield: 51%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (d,  $J$  = 8.0 Hz, 1H), 7.92 (d,  $J$  = 7.6 Hz, 1H), 7.84 (d,  $J$  = 8.4 Hz, 1H), 7.73 (d,  $J$  = 6.4 Hz, 1H), 7.60-7.48 (m, 3H), 6.00-5.98 (m, 1H), 2.78-2.41 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.0, 133.9, 129.4, 129.2, 128.8, 126.7, 125.9, 125.5, 123.1, 122.1, 64.6, 39.2 (t,  $J$  = 20.3 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.2 (m, 3F), -112.6 to -114.8

(m, 2F), -124.5 (m, 2F), -125.9 (m, 2F); HRMS(EI) Calcd for C<sub>16</sub>H<sub>11</sub>F<sub>9</sub>O (M<sup>+</sup>): 390.0666; found: 390.0669.

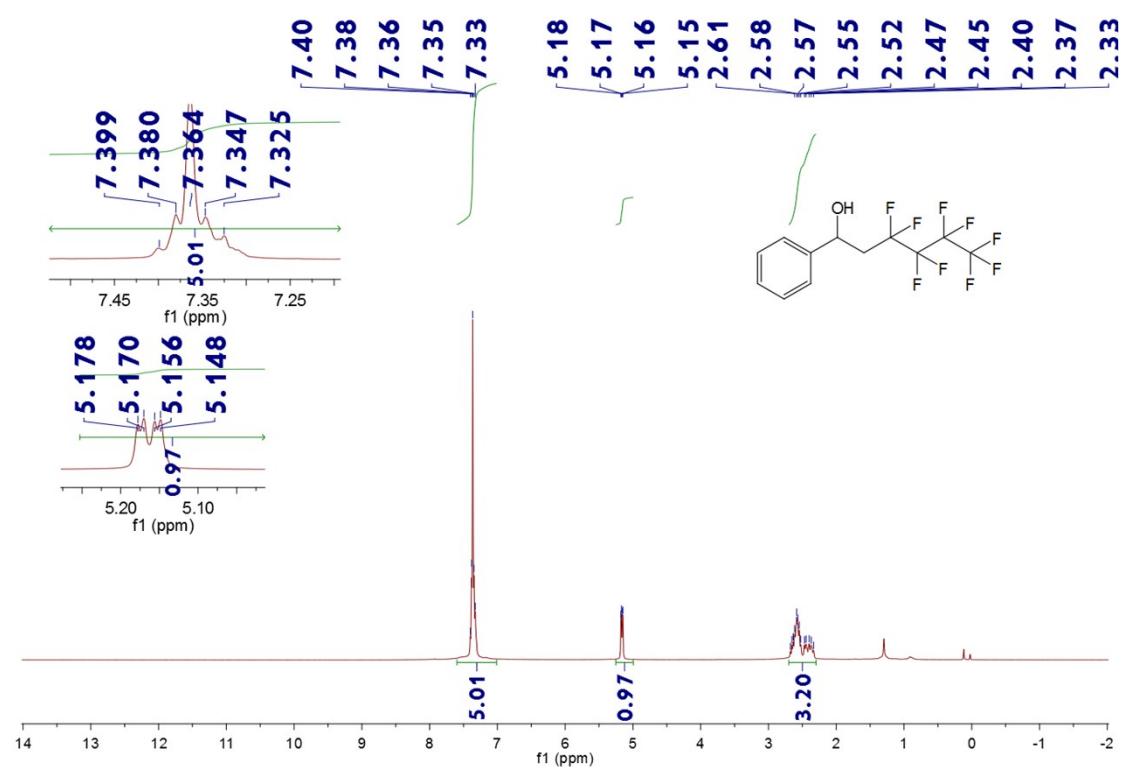
## NMR spectra

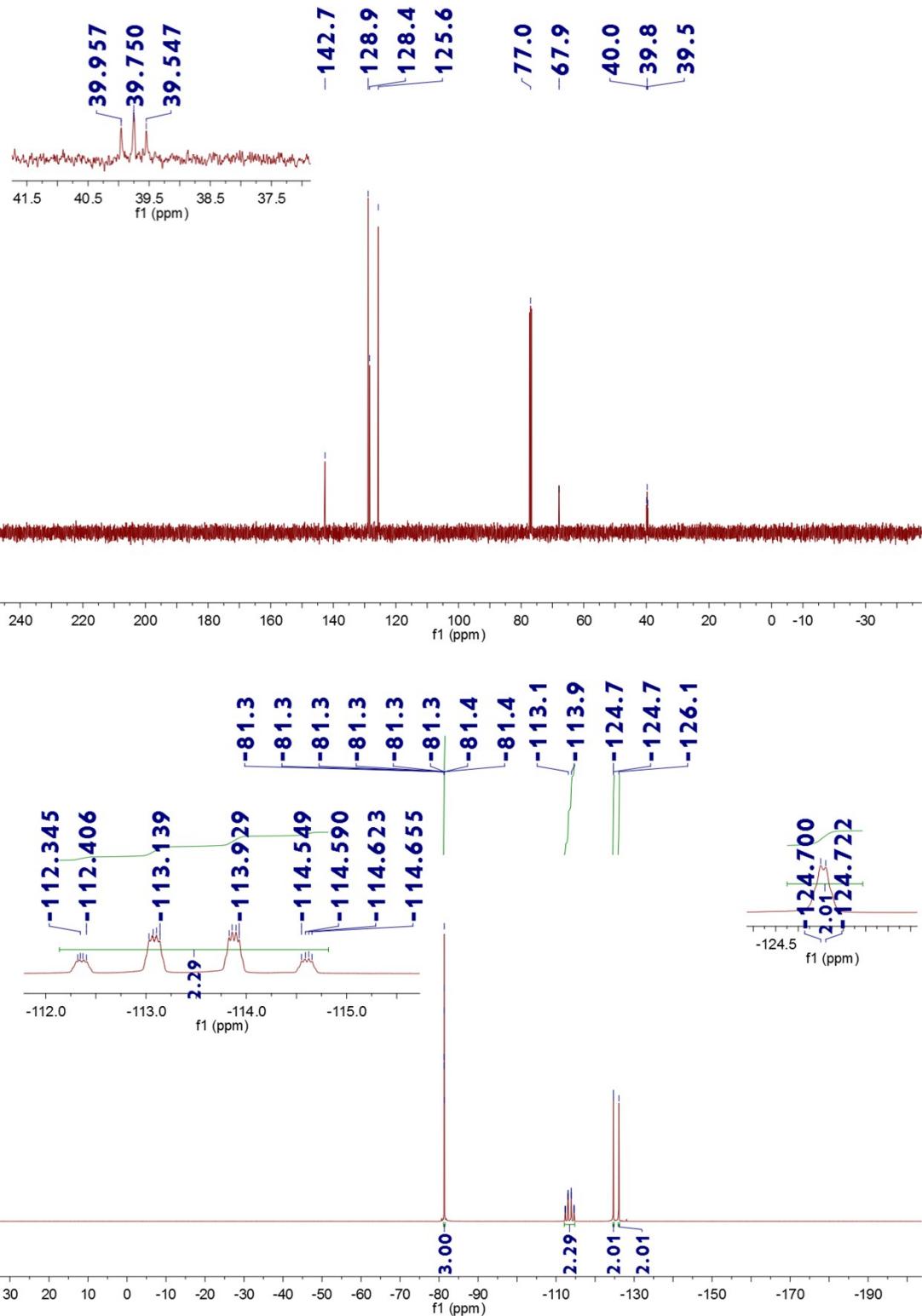
3a



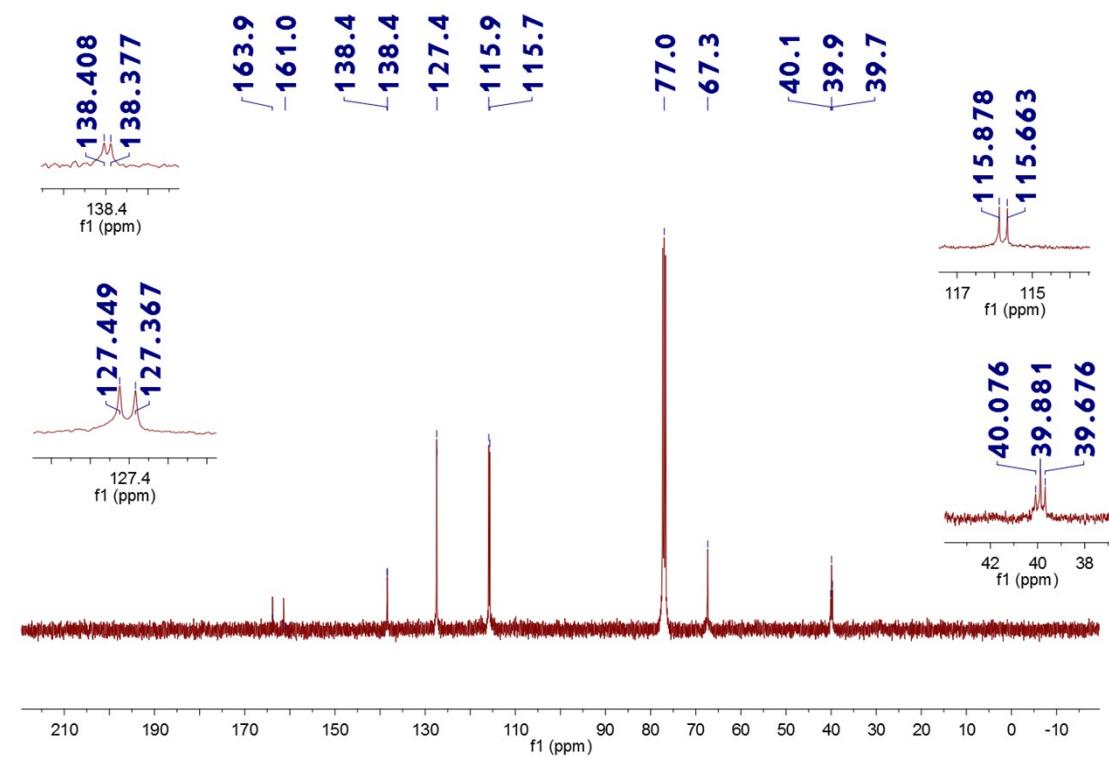
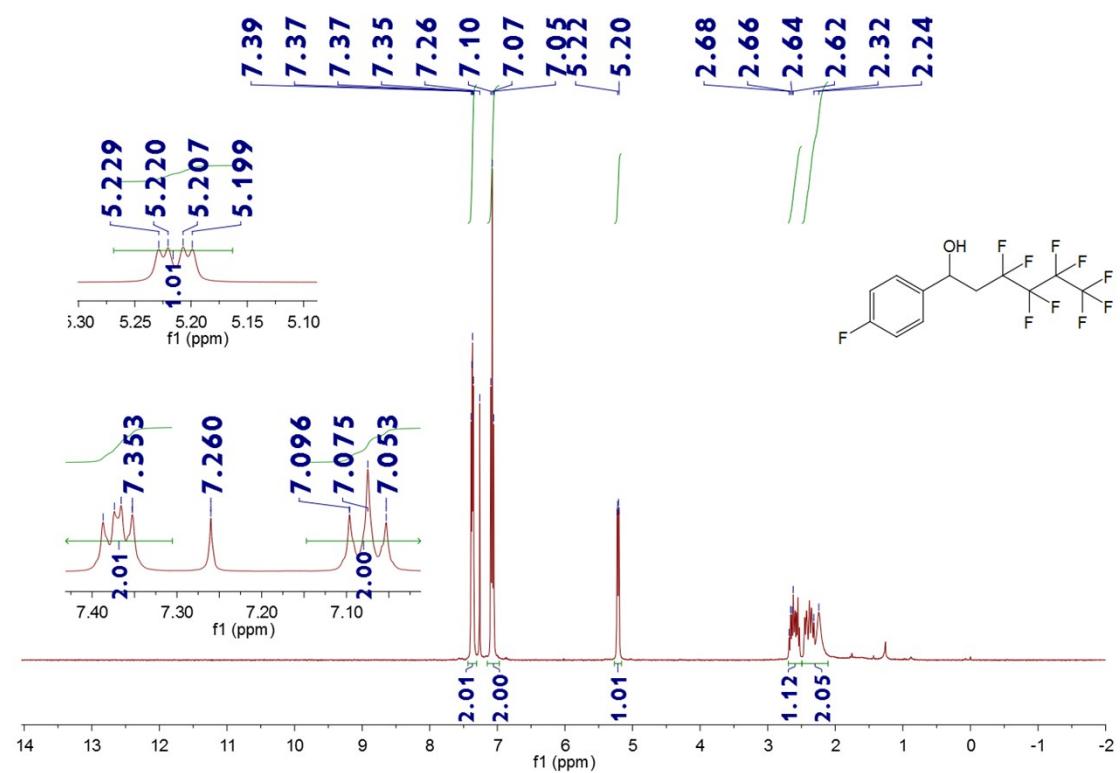


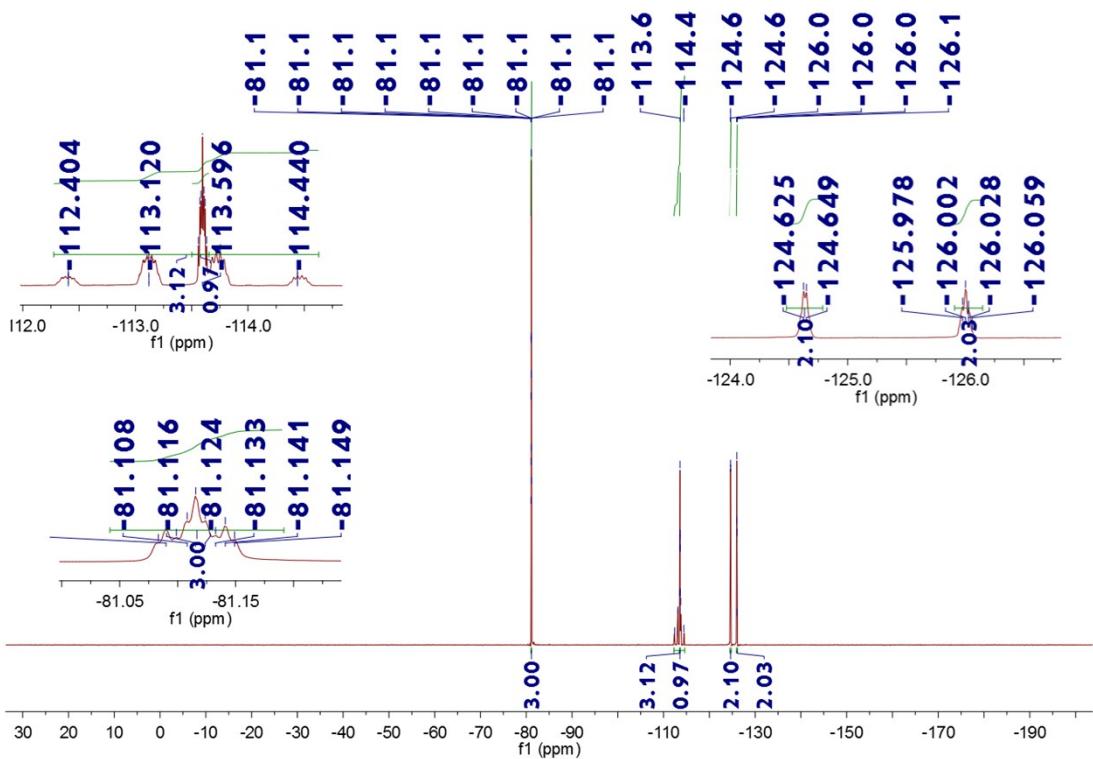
**3a (under condition B)**



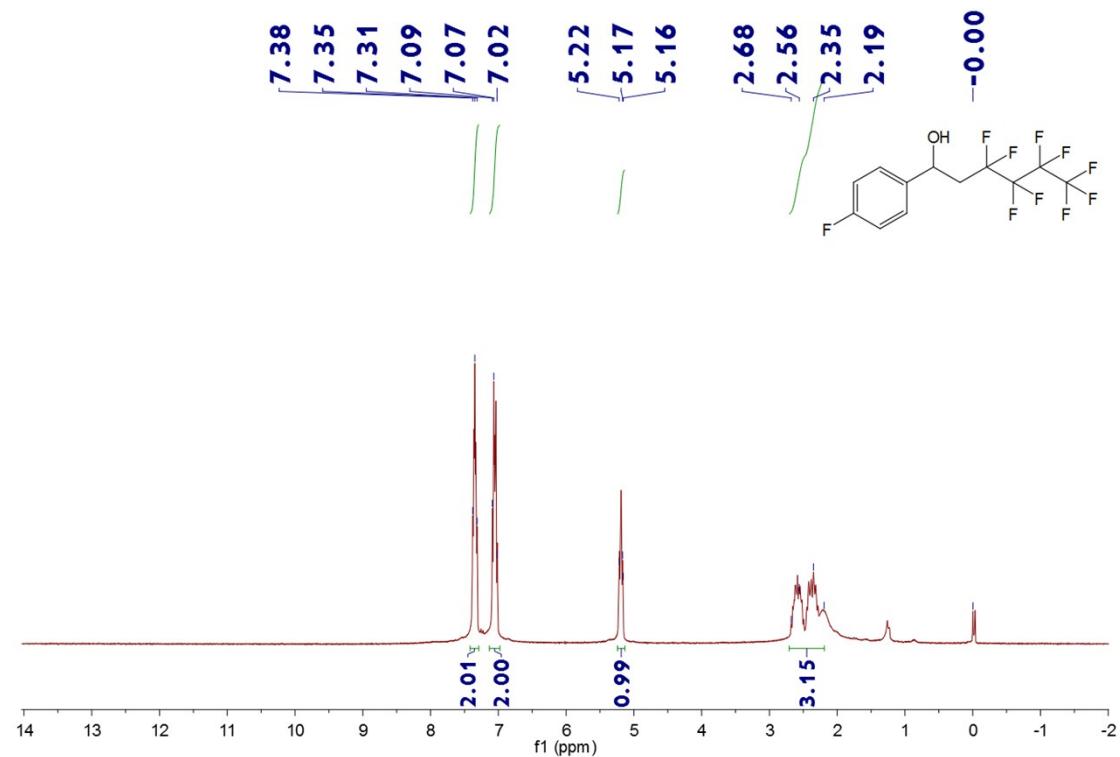


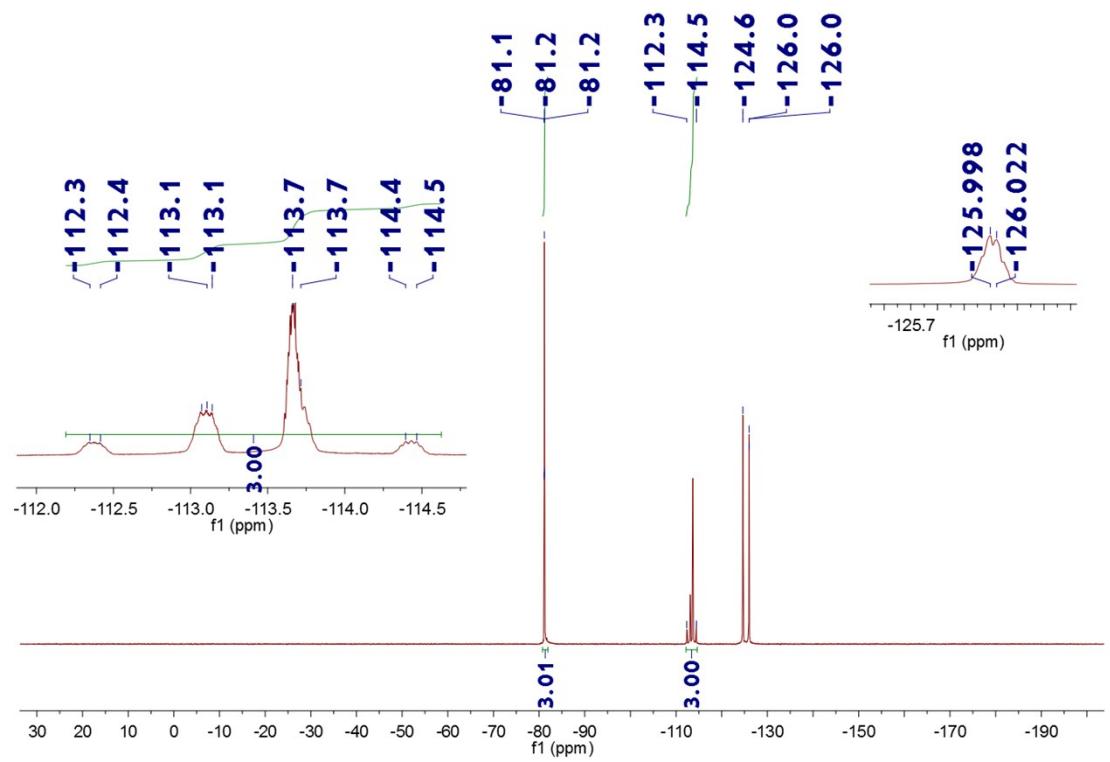
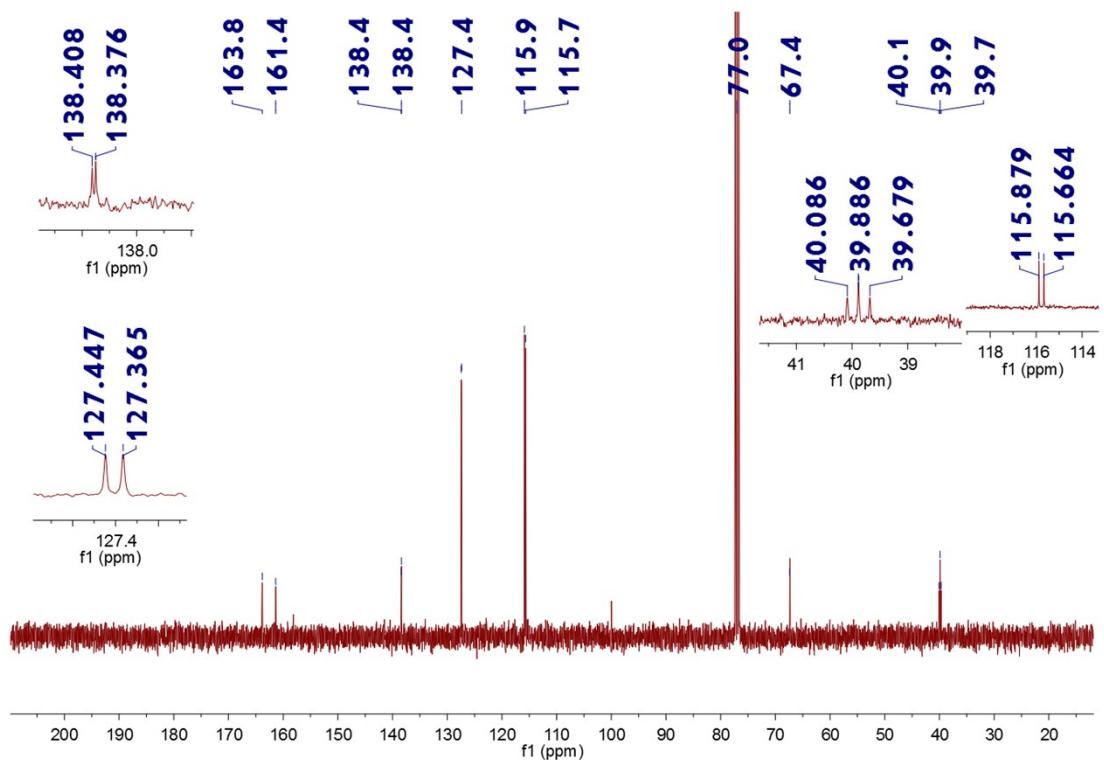
3b



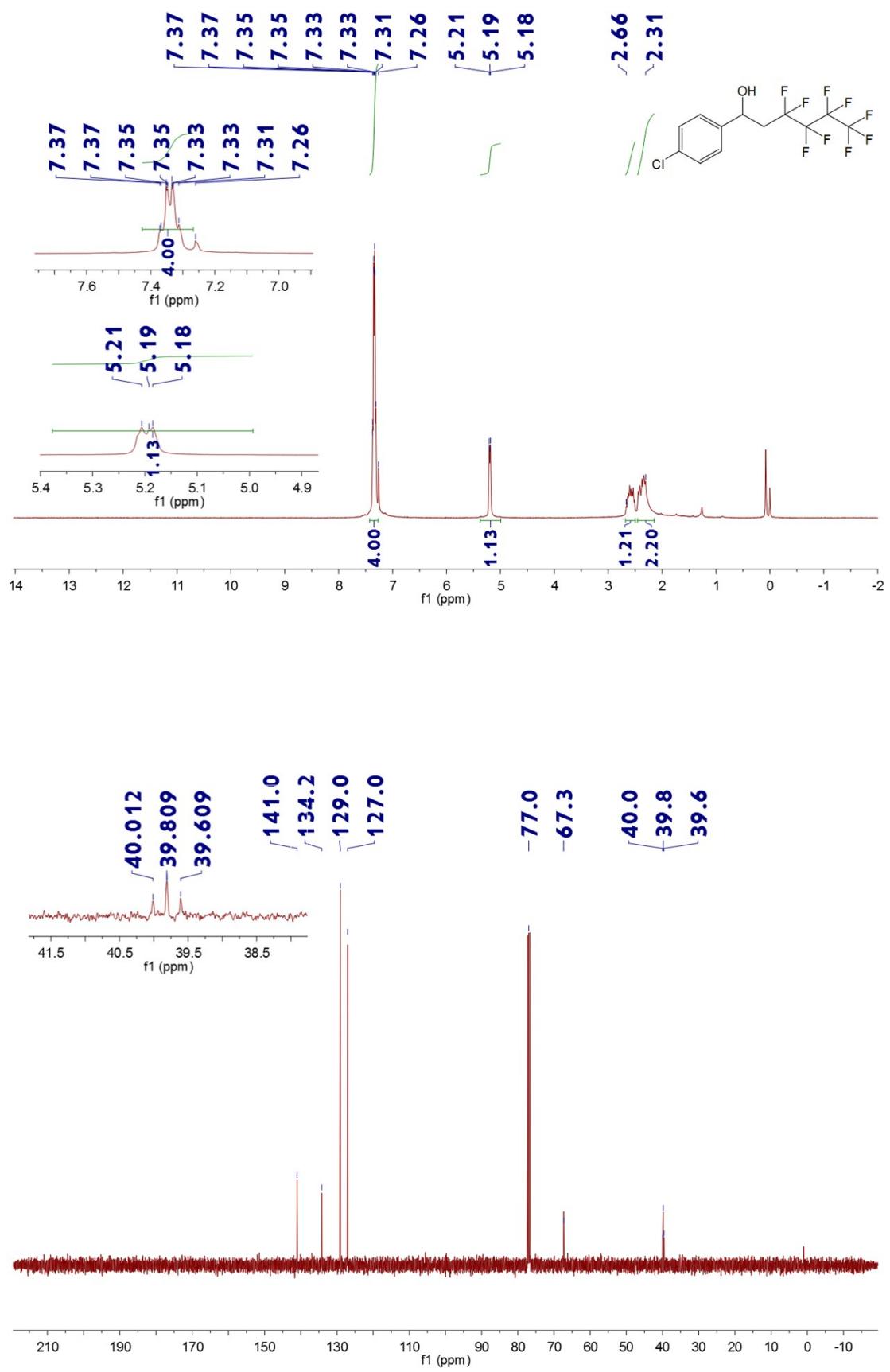


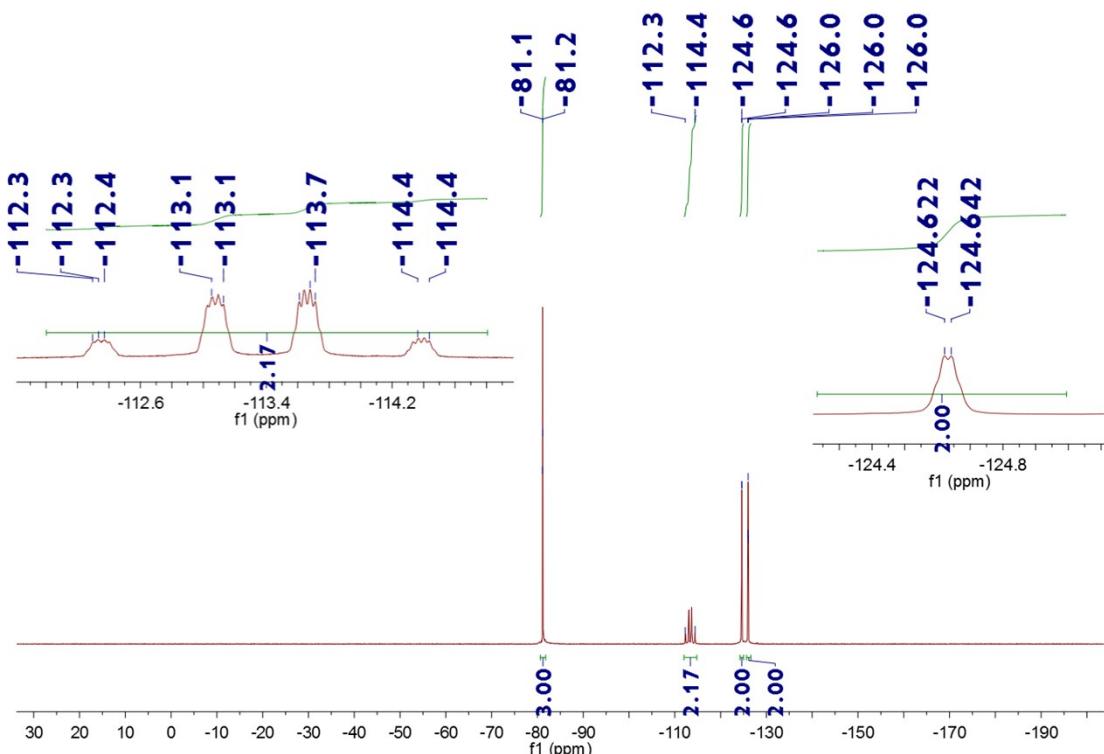
### **3b (under condition B)**



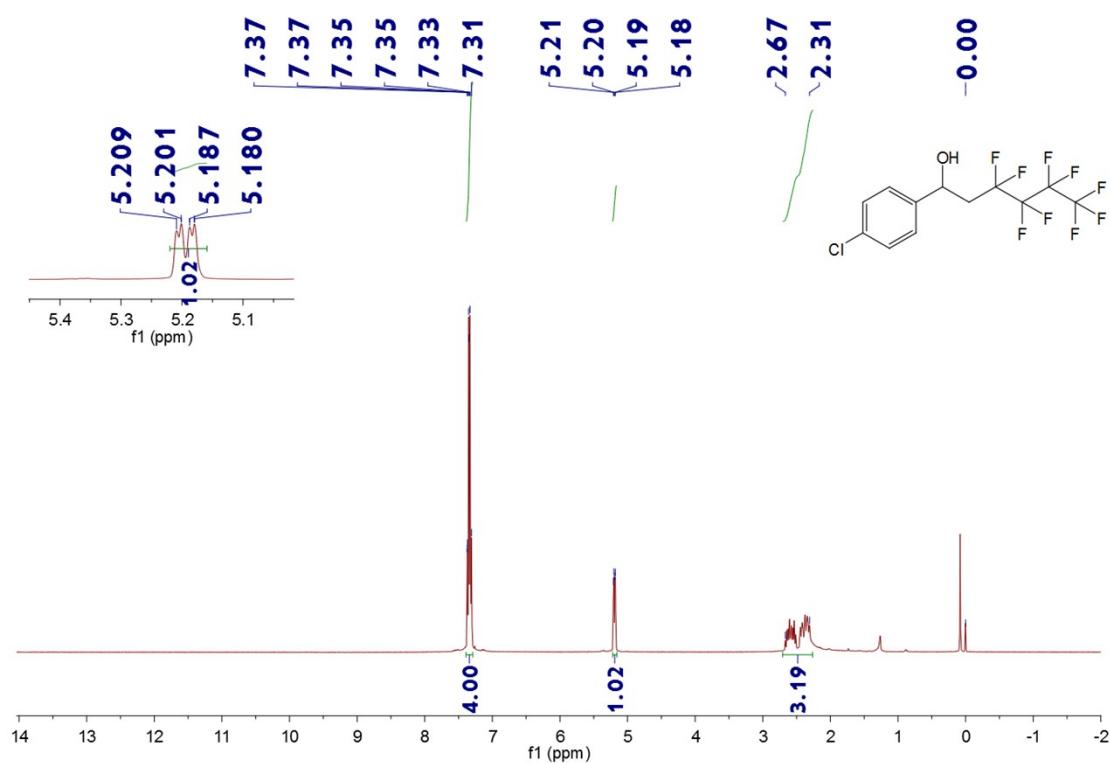


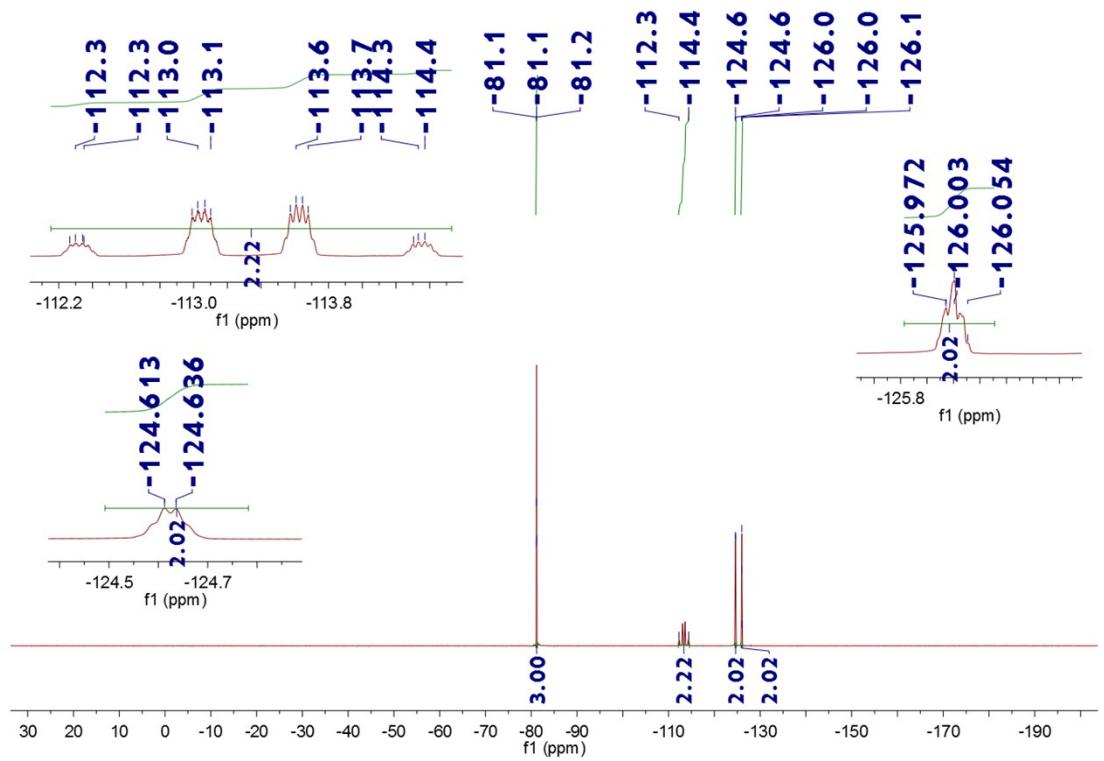
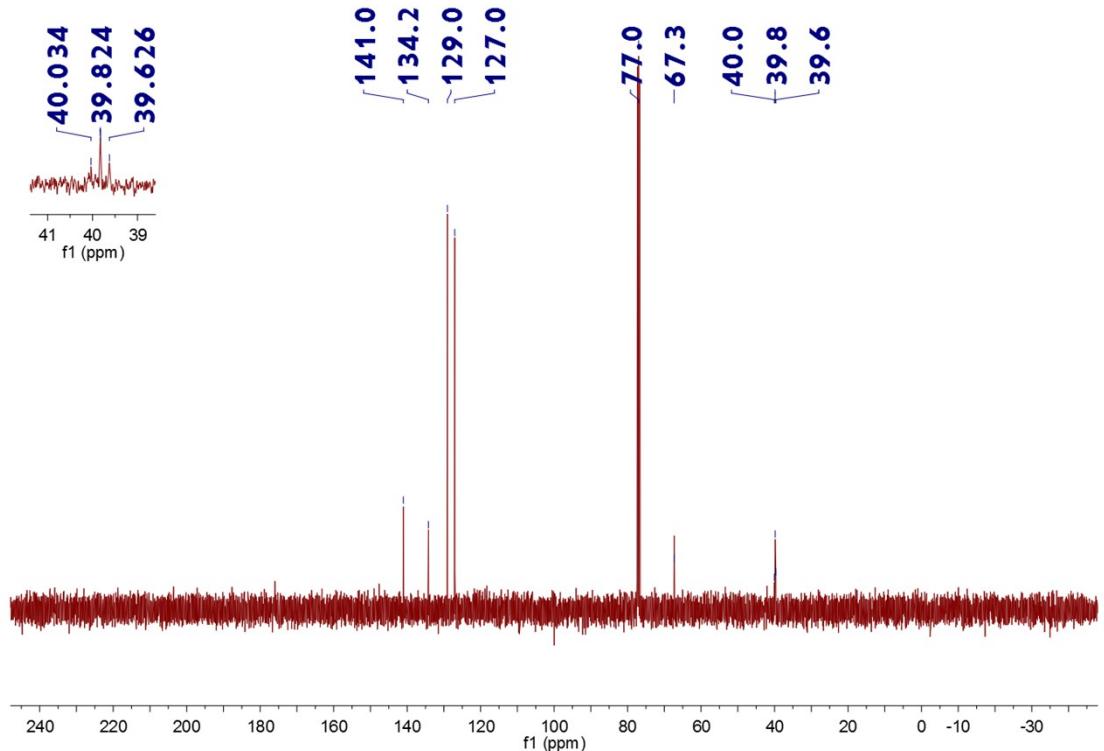
3c



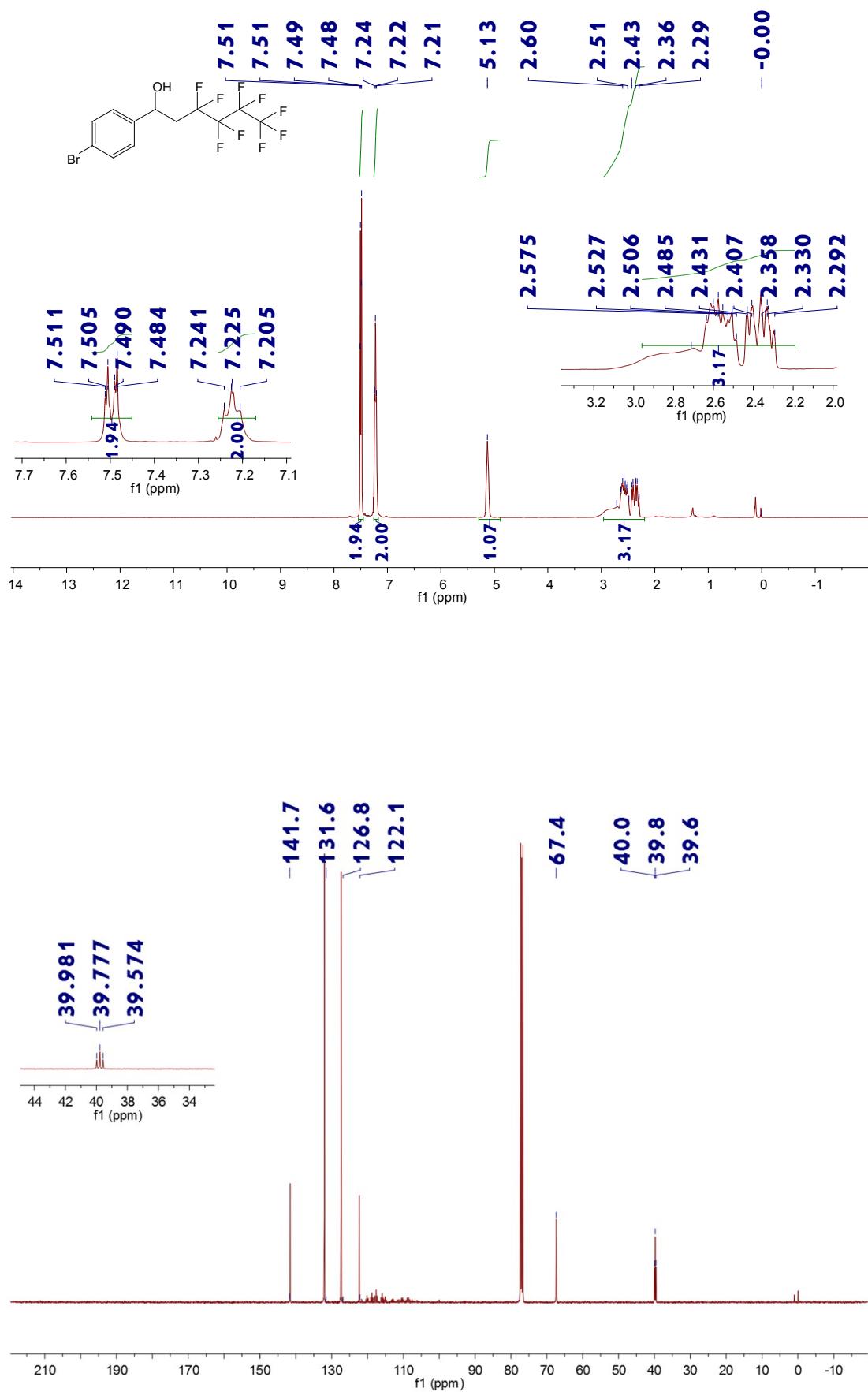


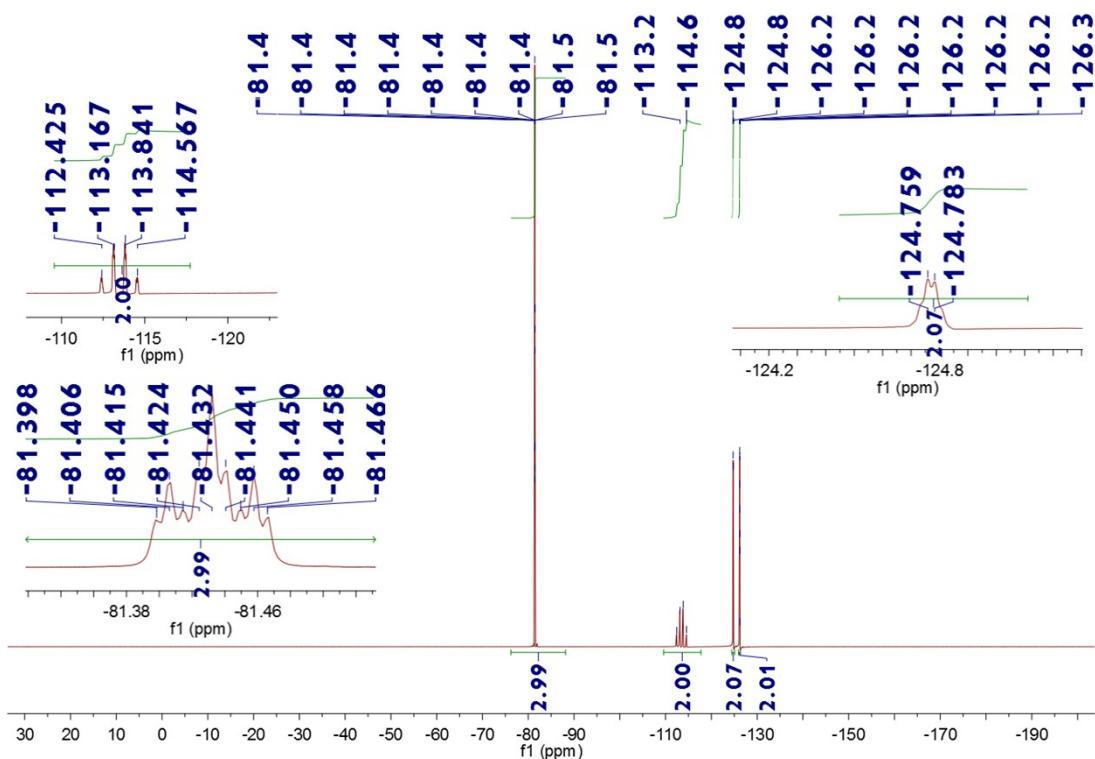
**3c (under condition B)**



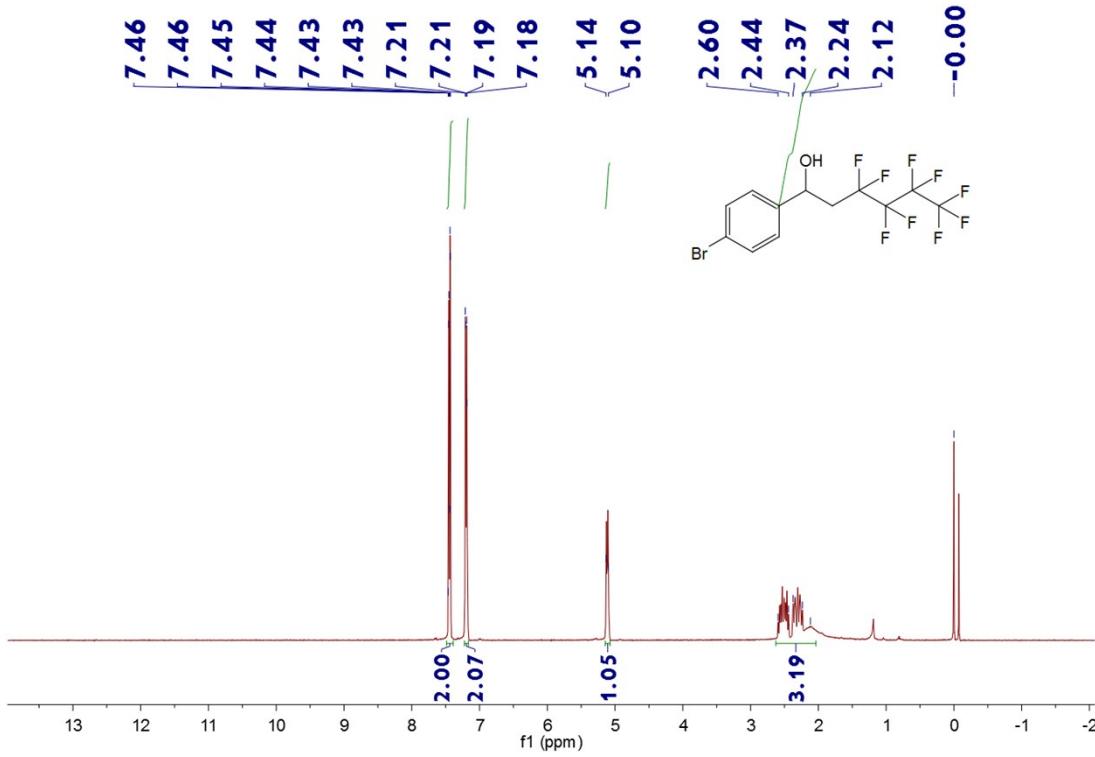


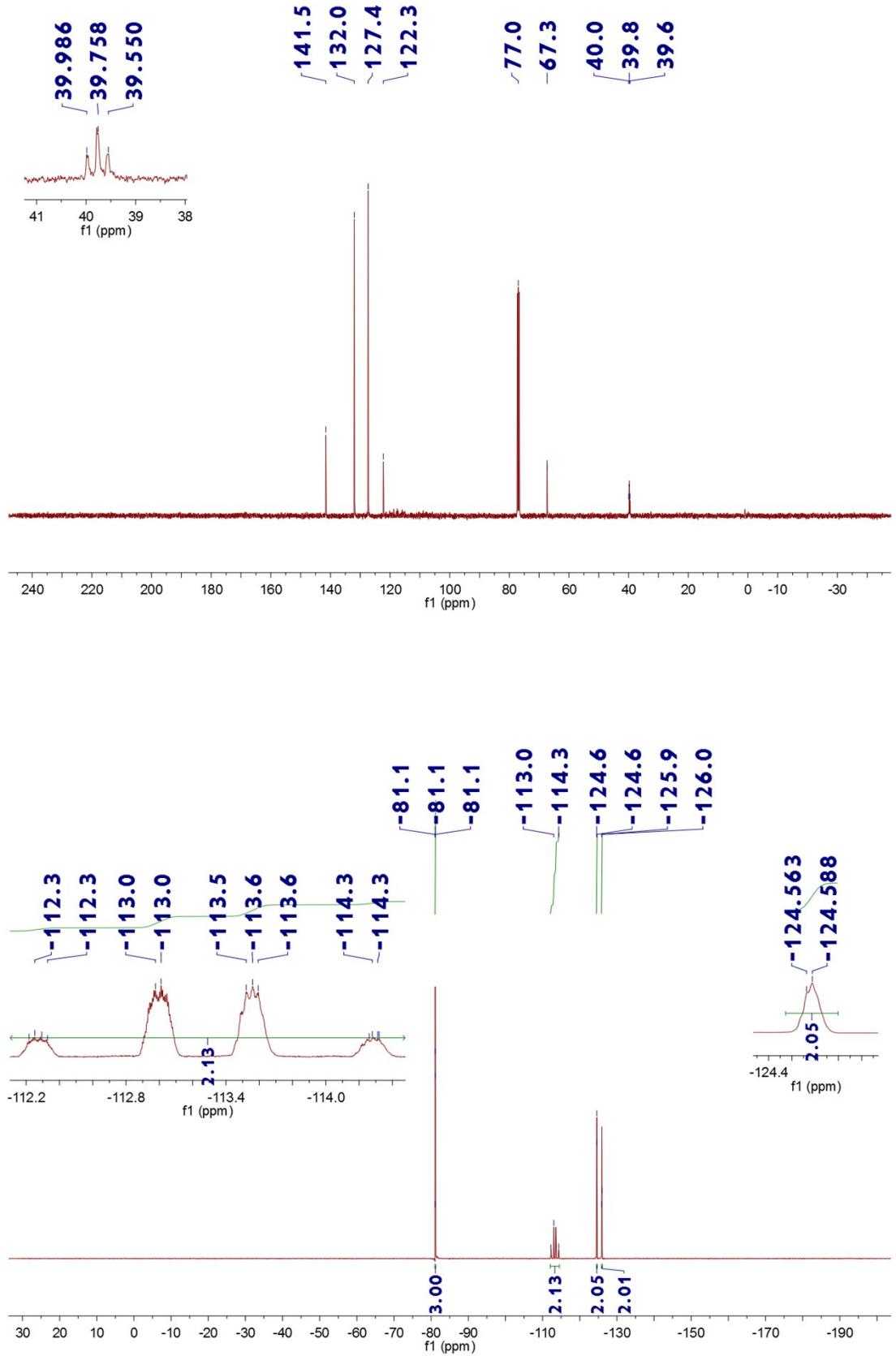
3d



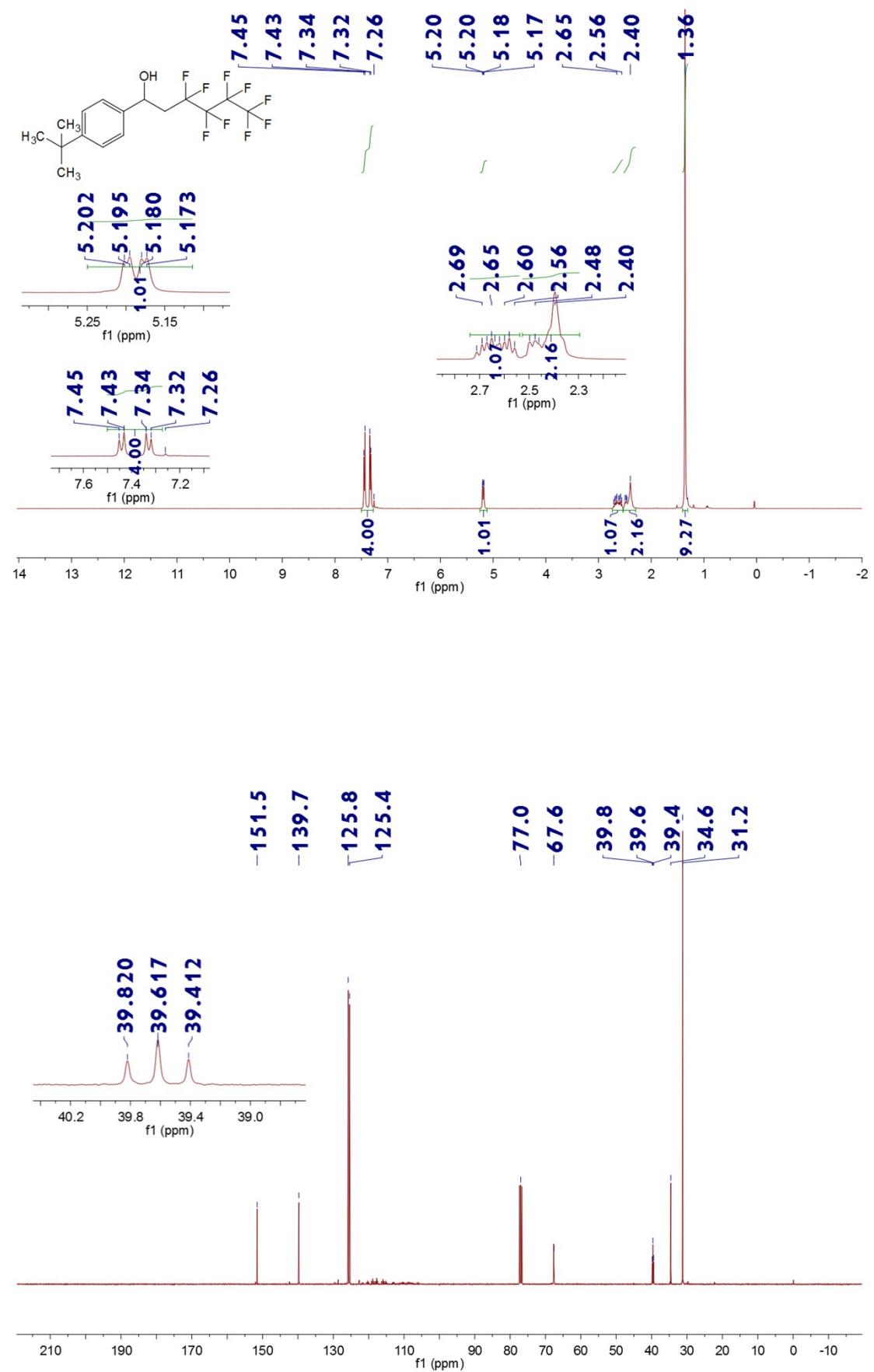


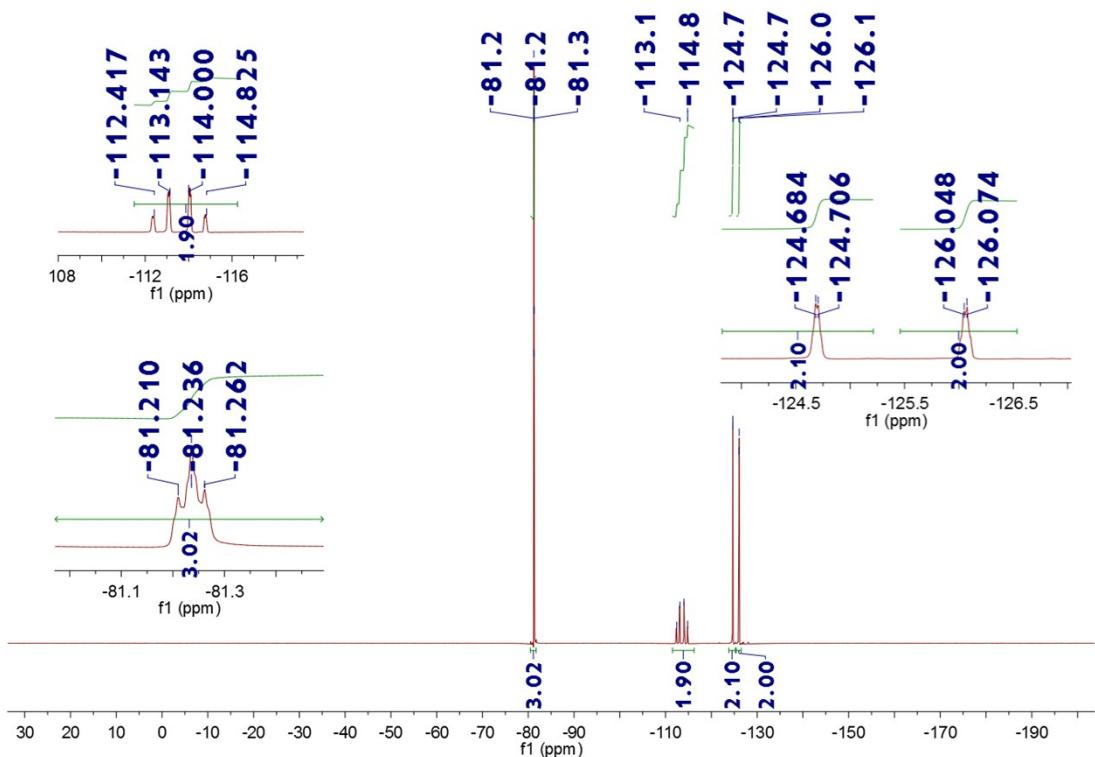
### 3d (under condition B)



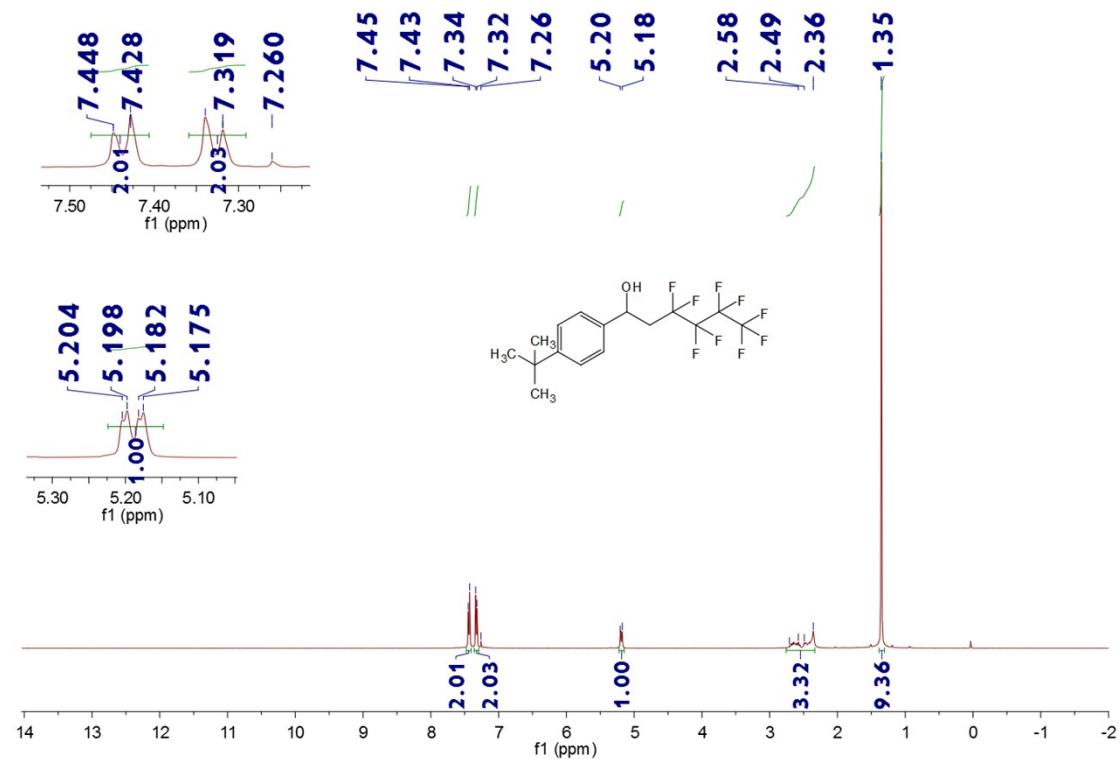


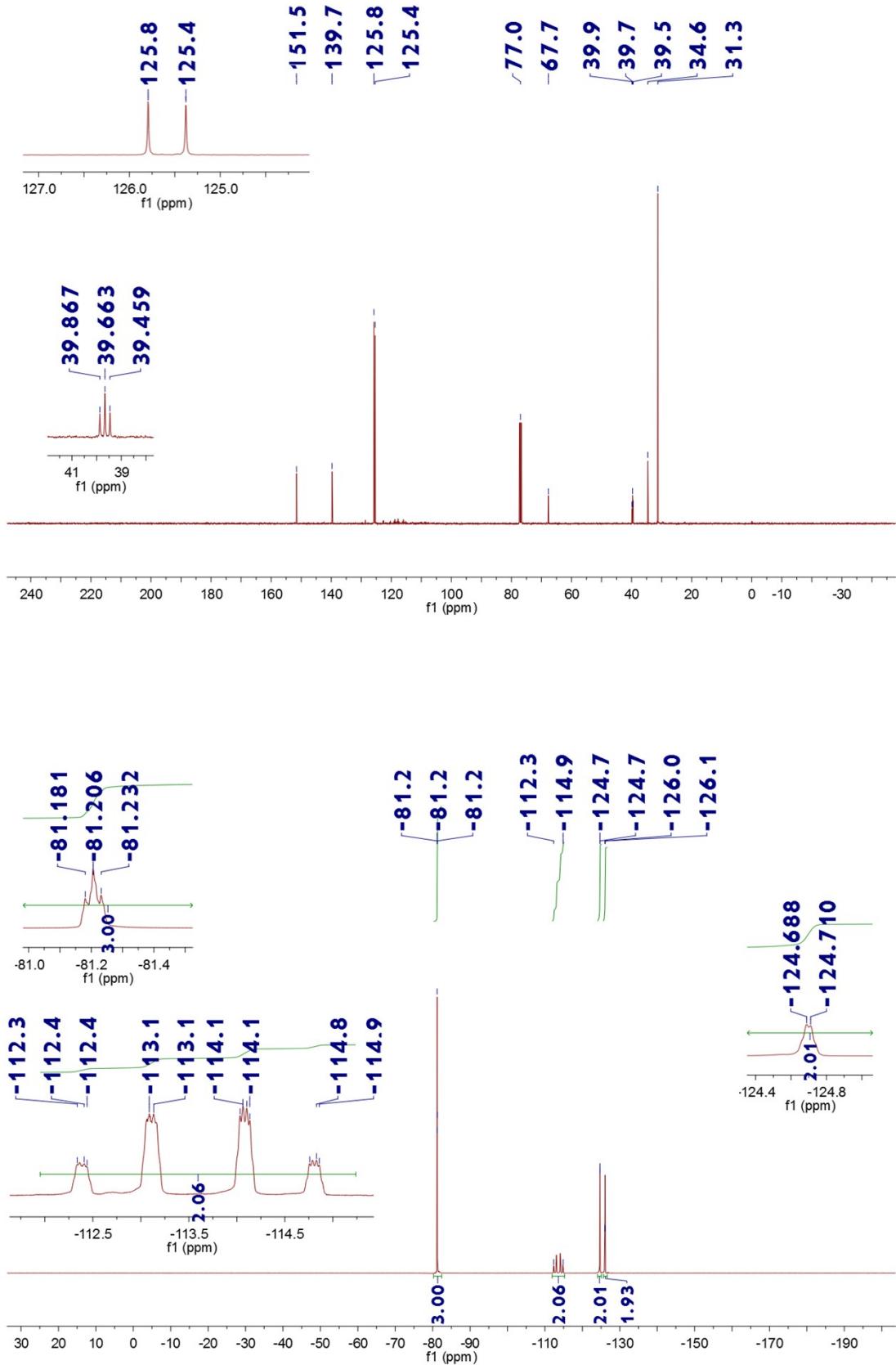
3e



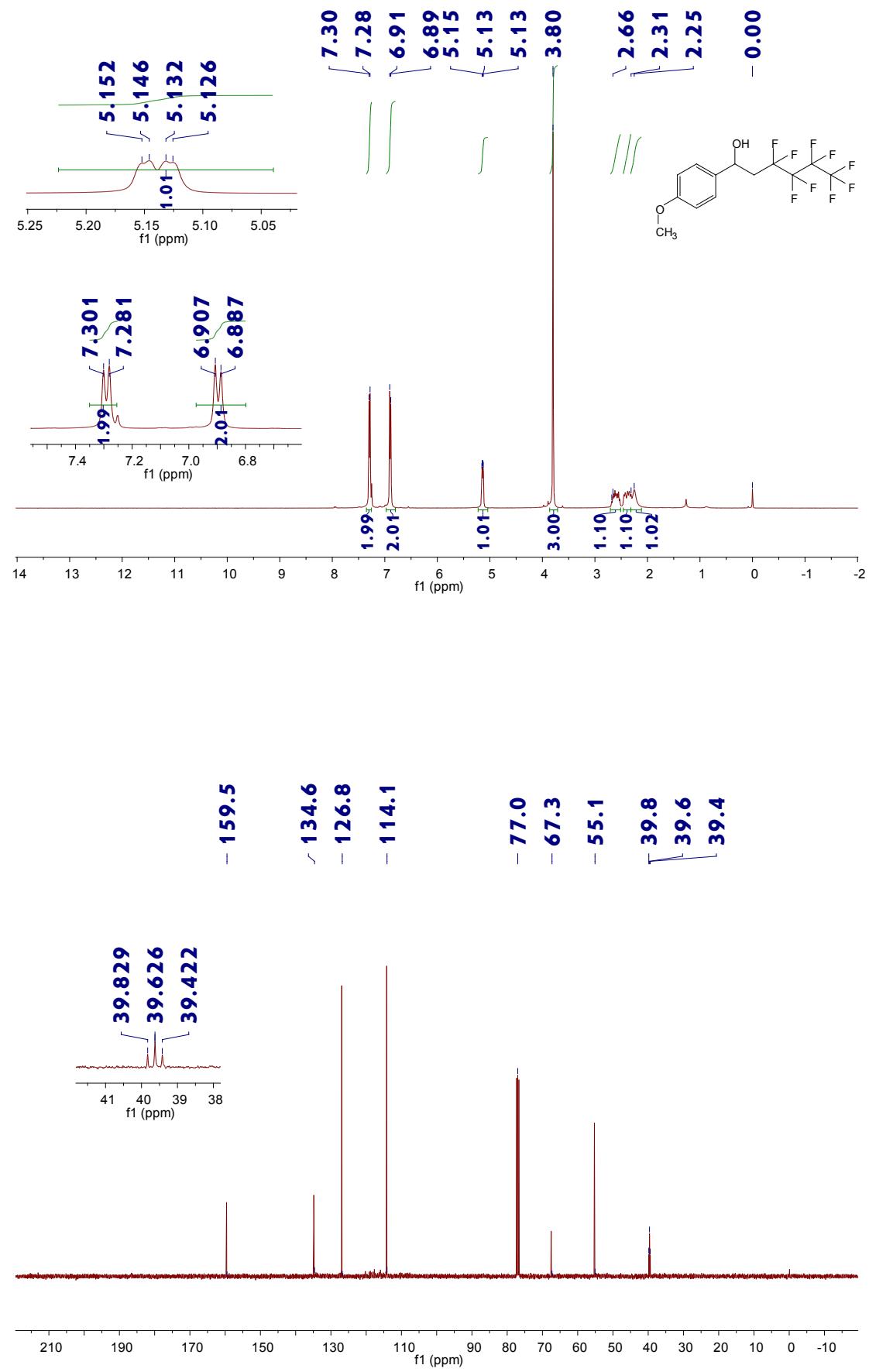


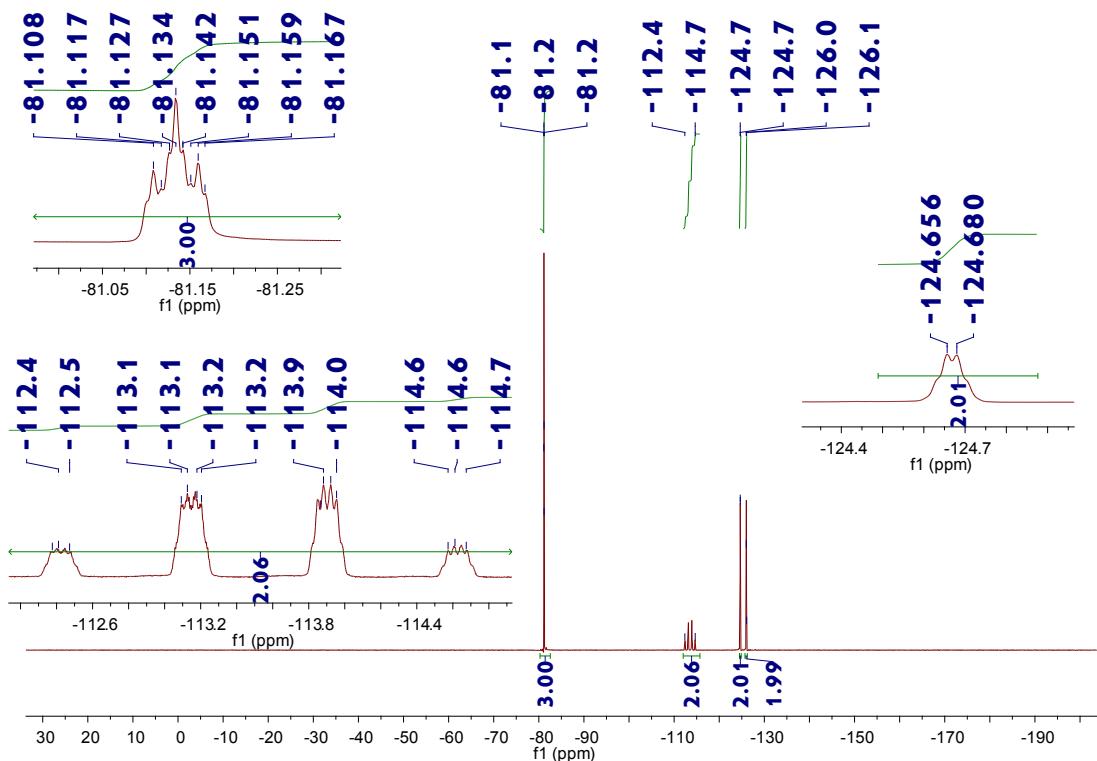
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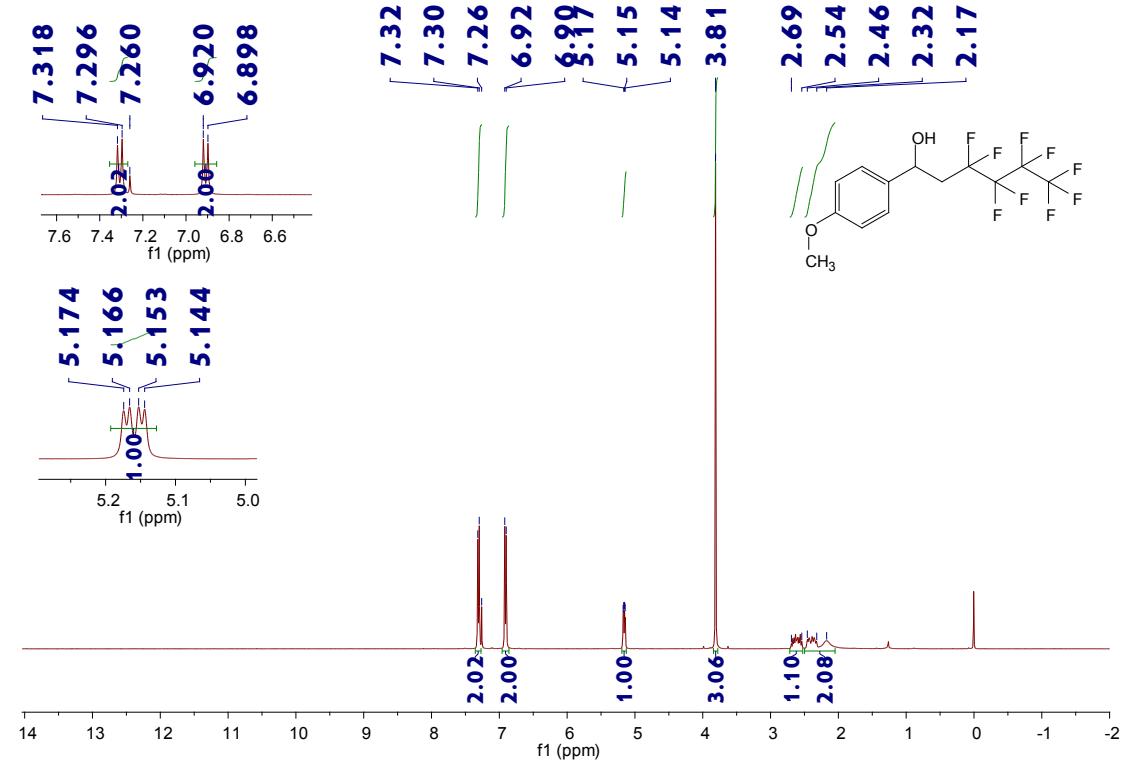


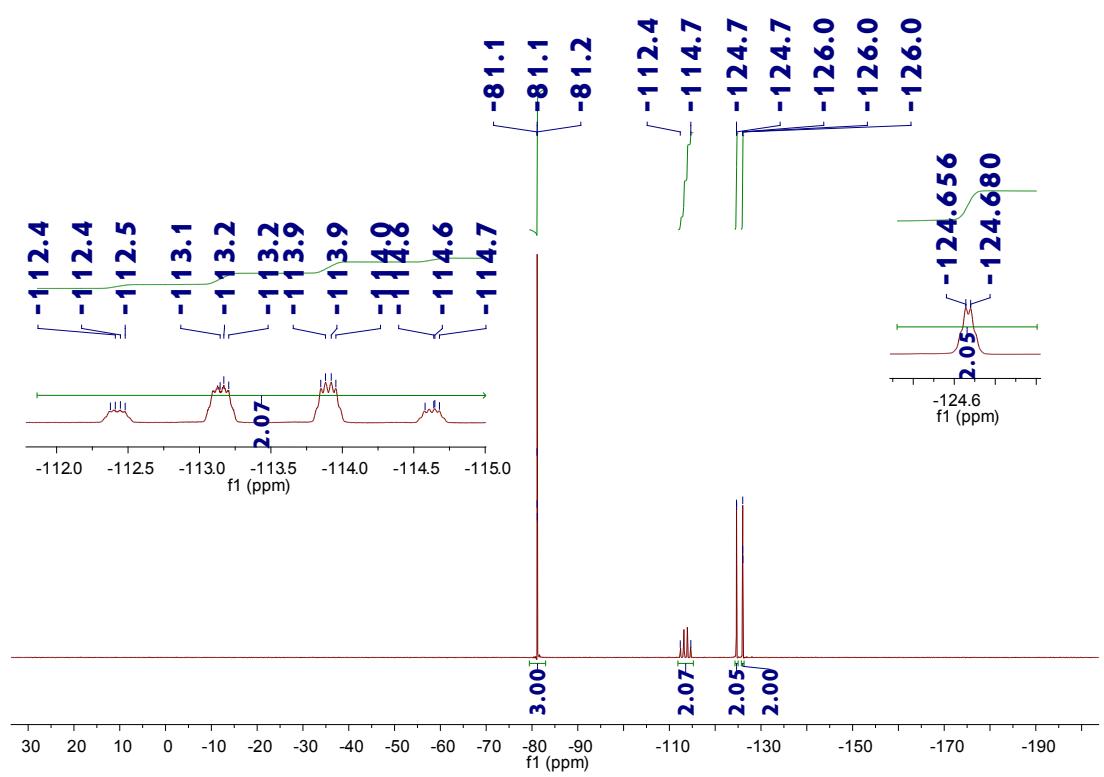
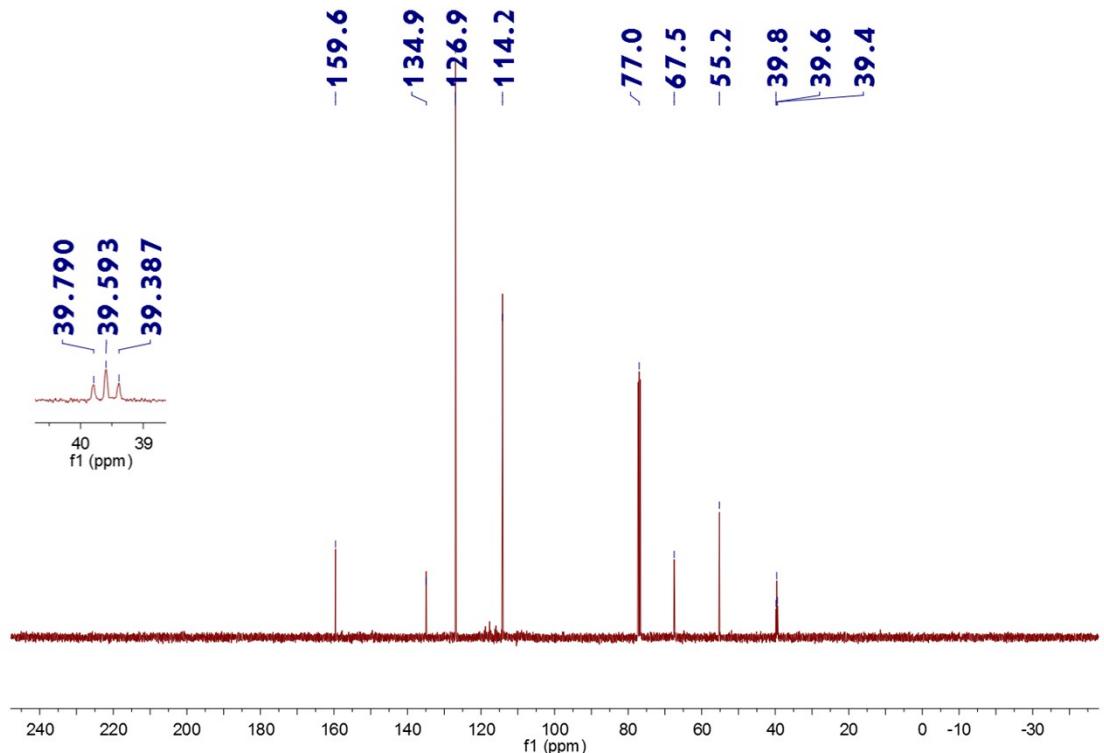
3f



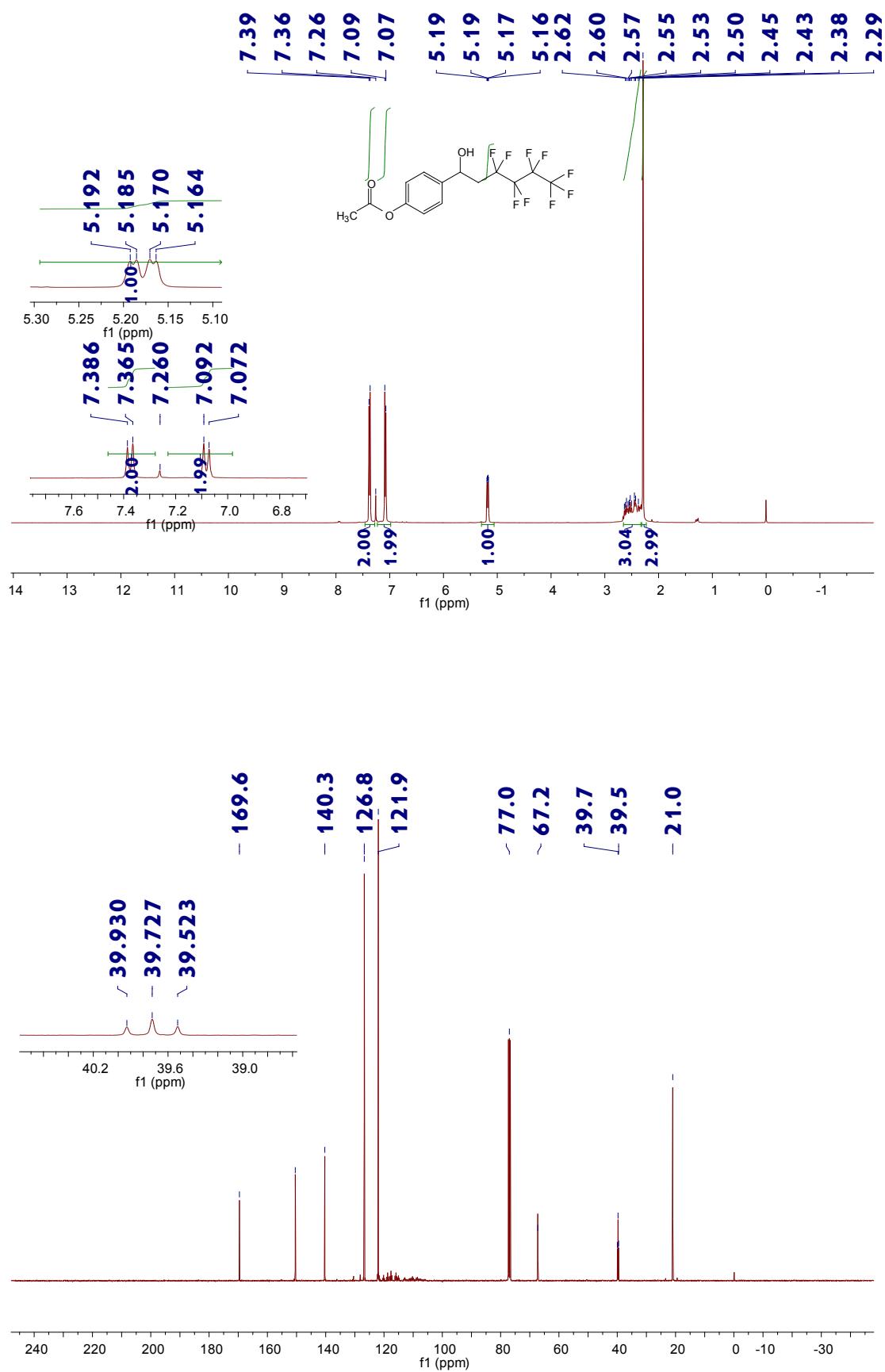


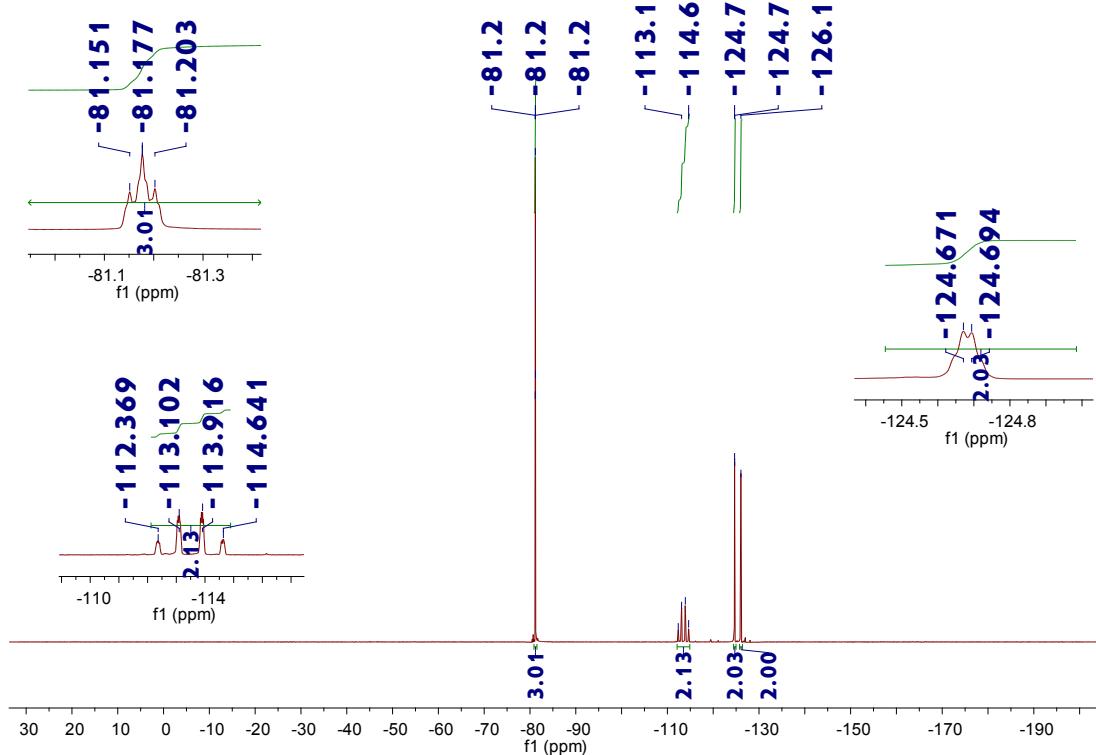
### **3f (under condition B)**



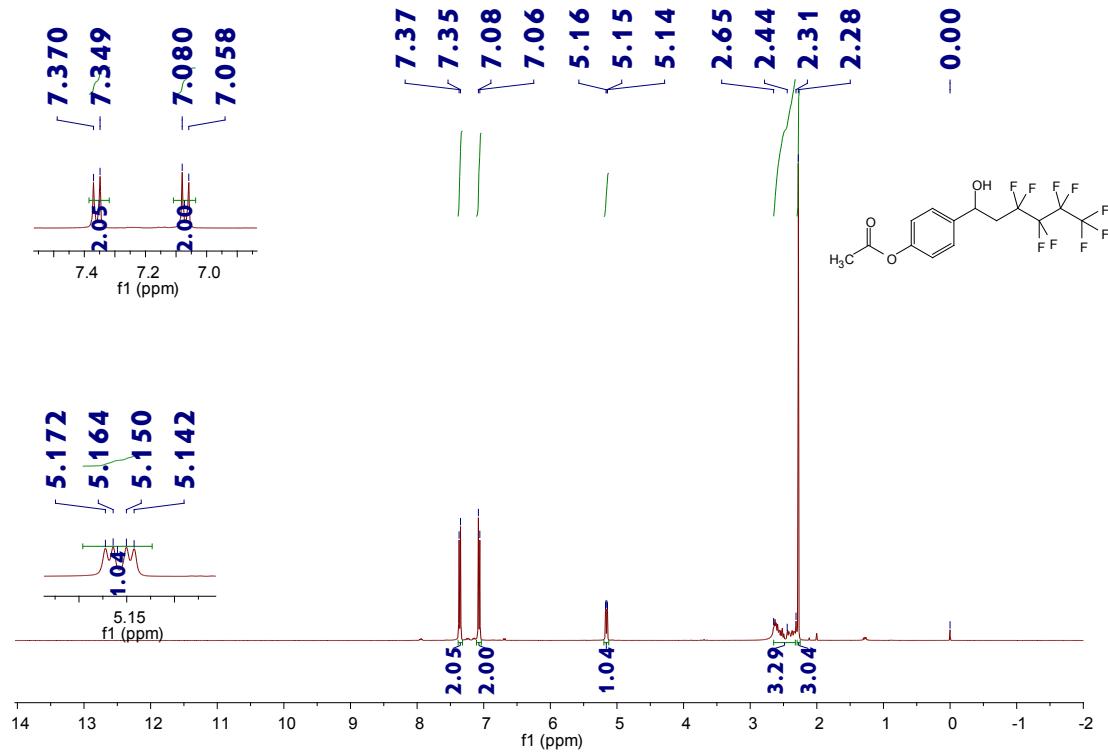


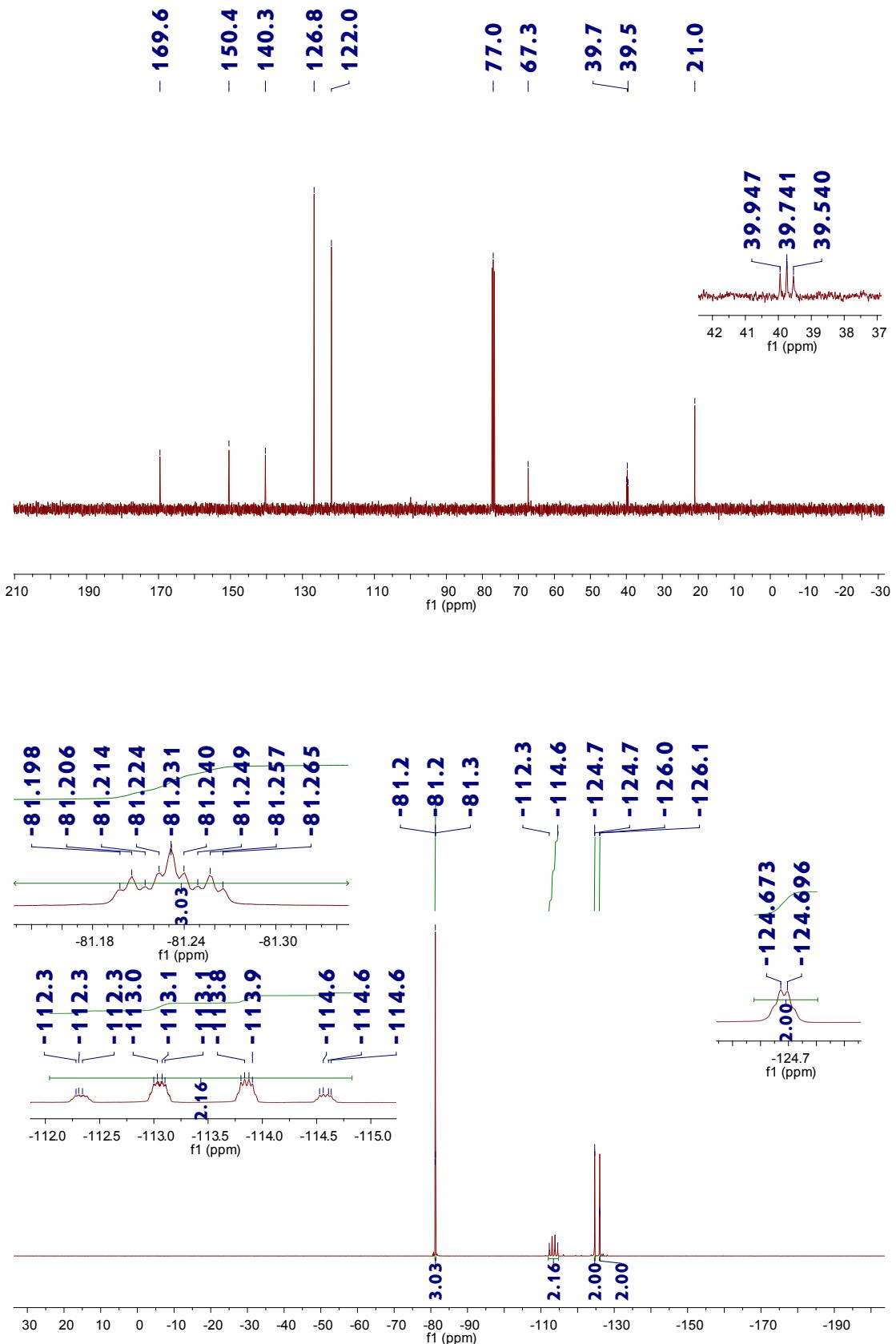
**3g**



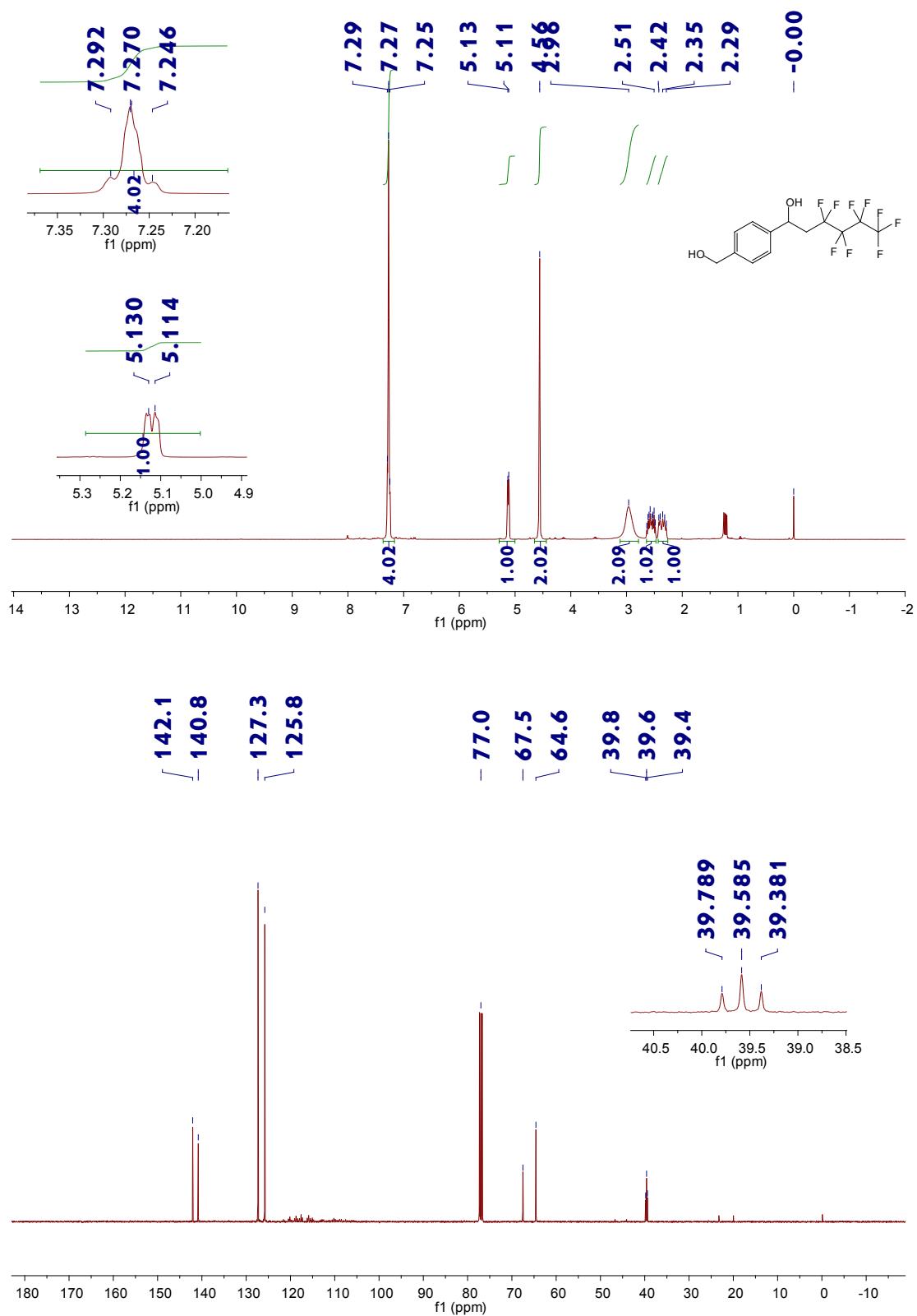


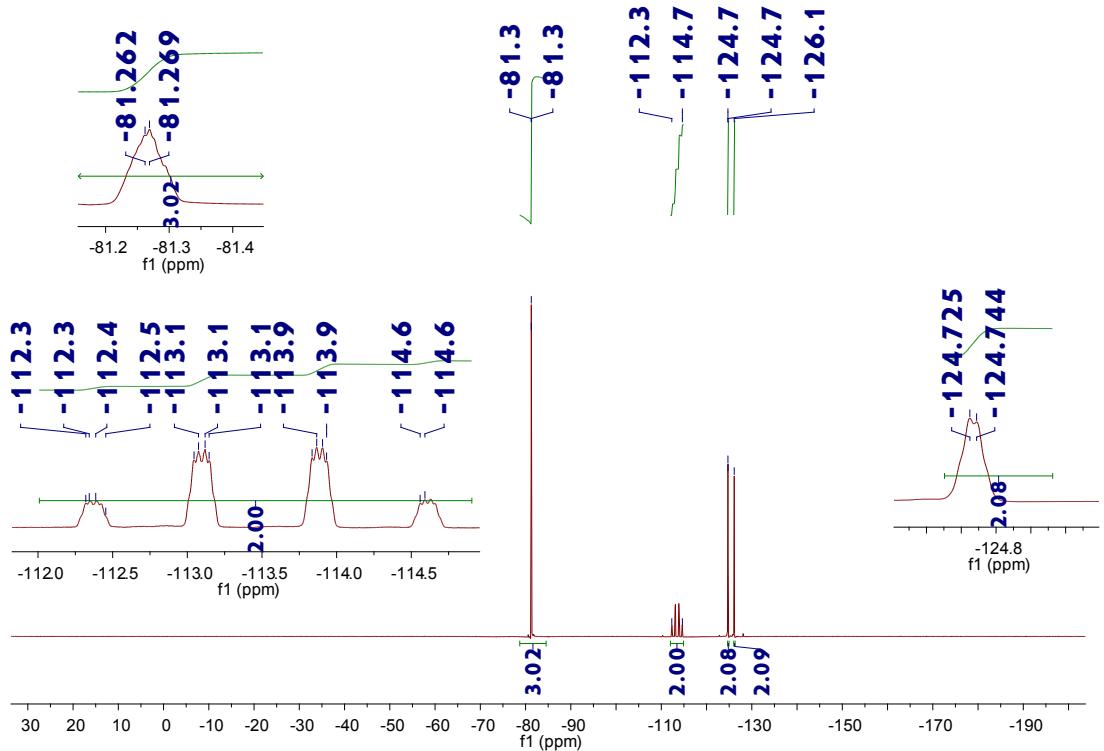
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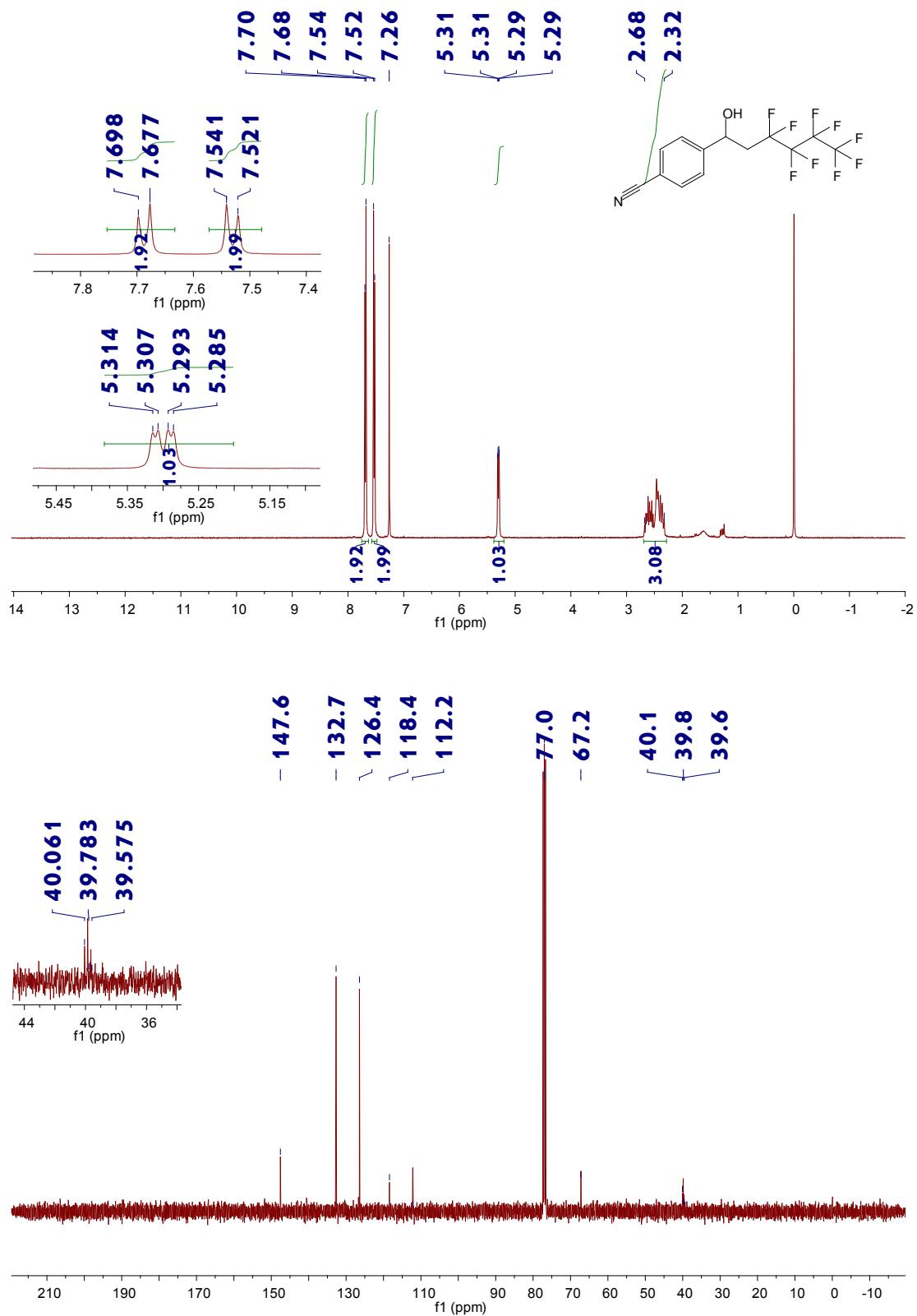


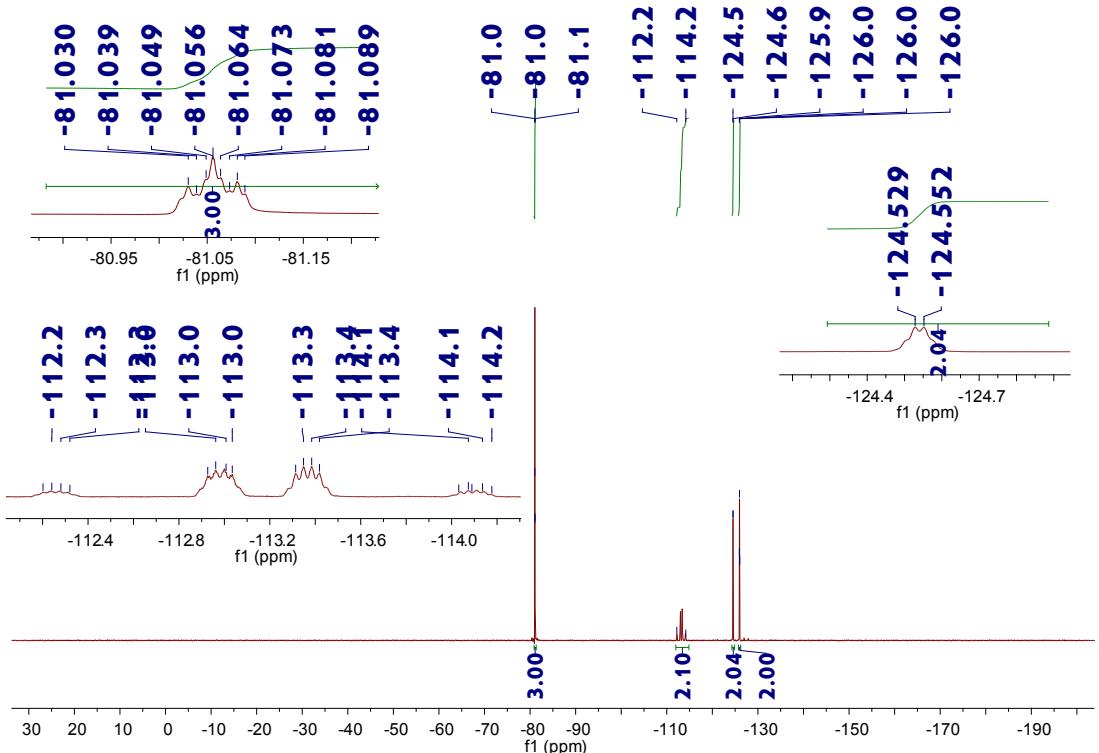
**3h**



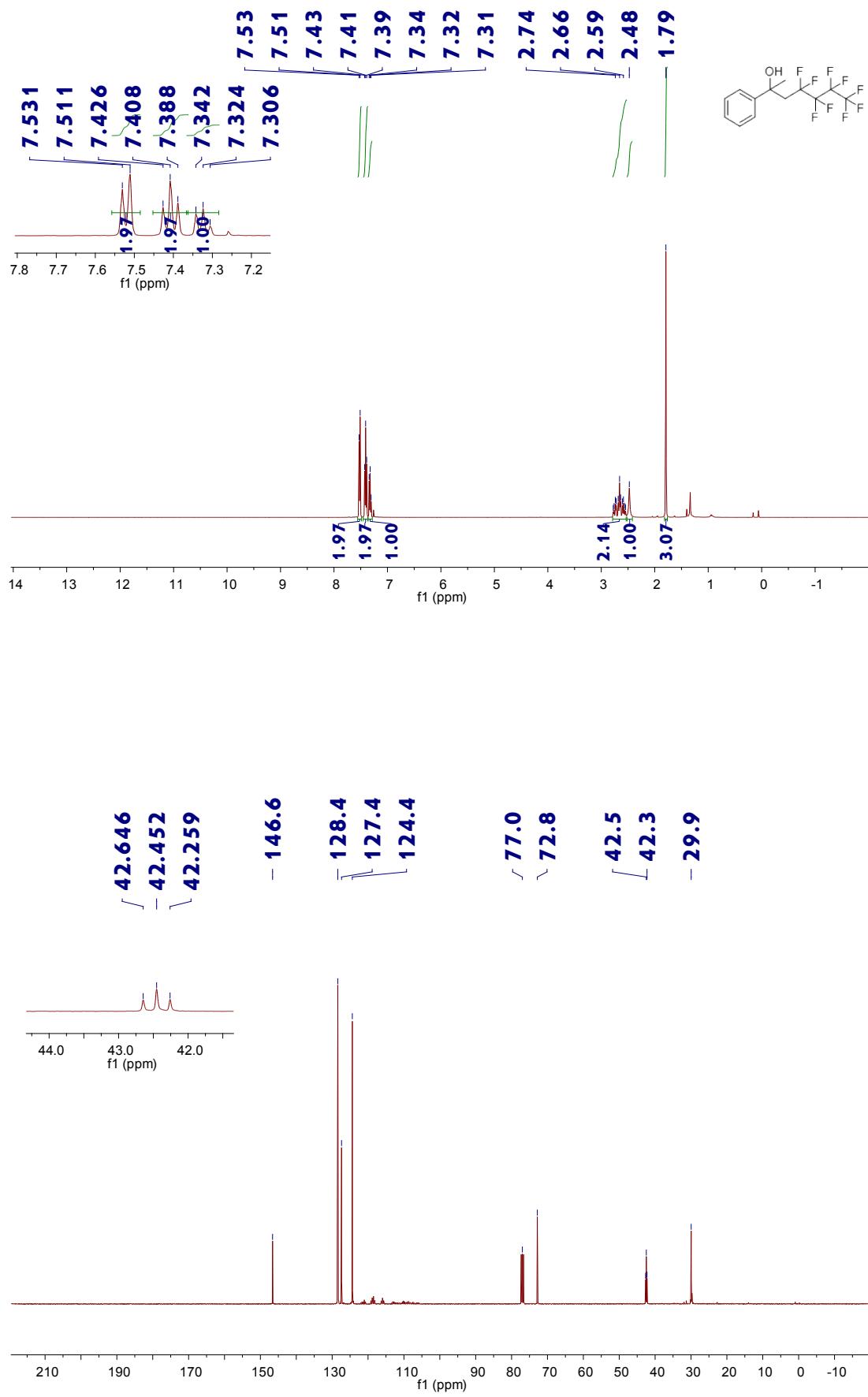


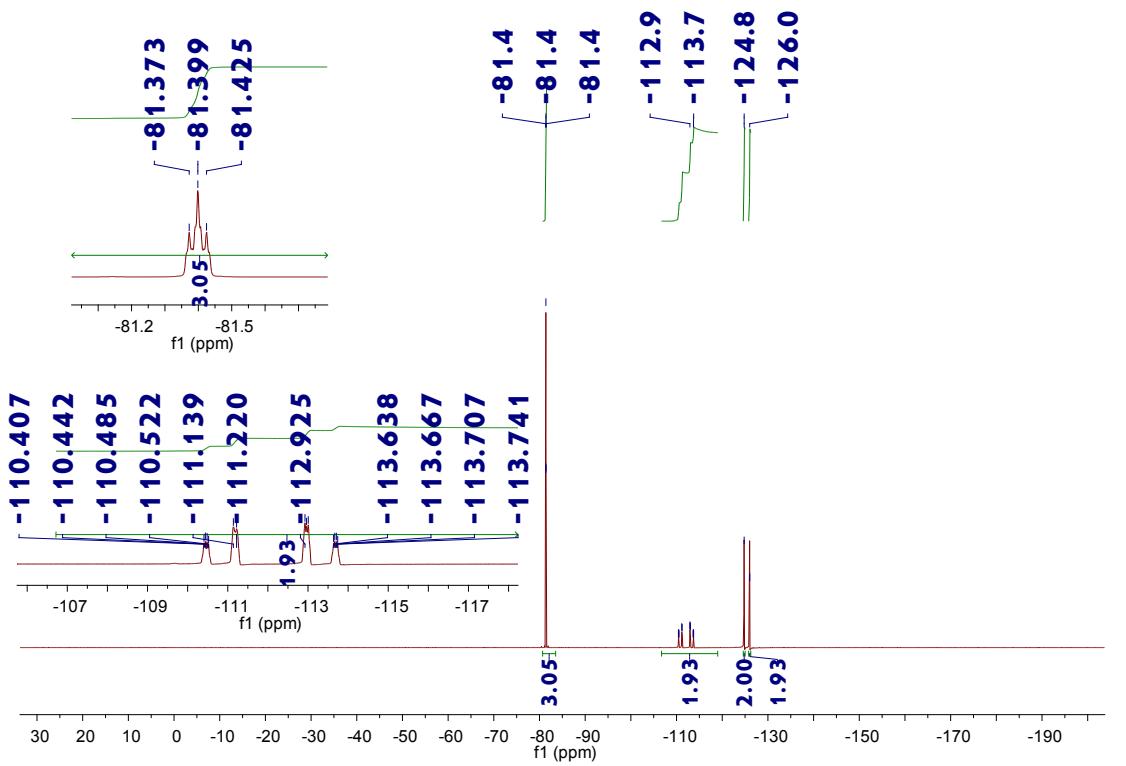
**3i**



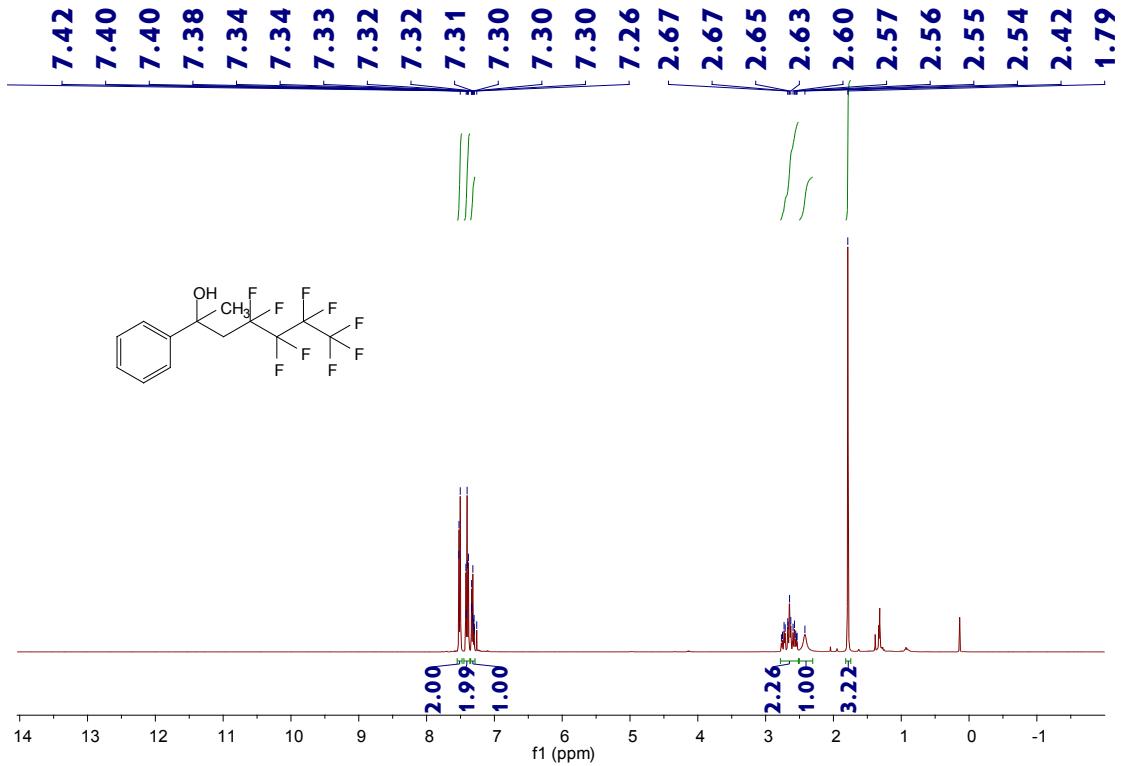


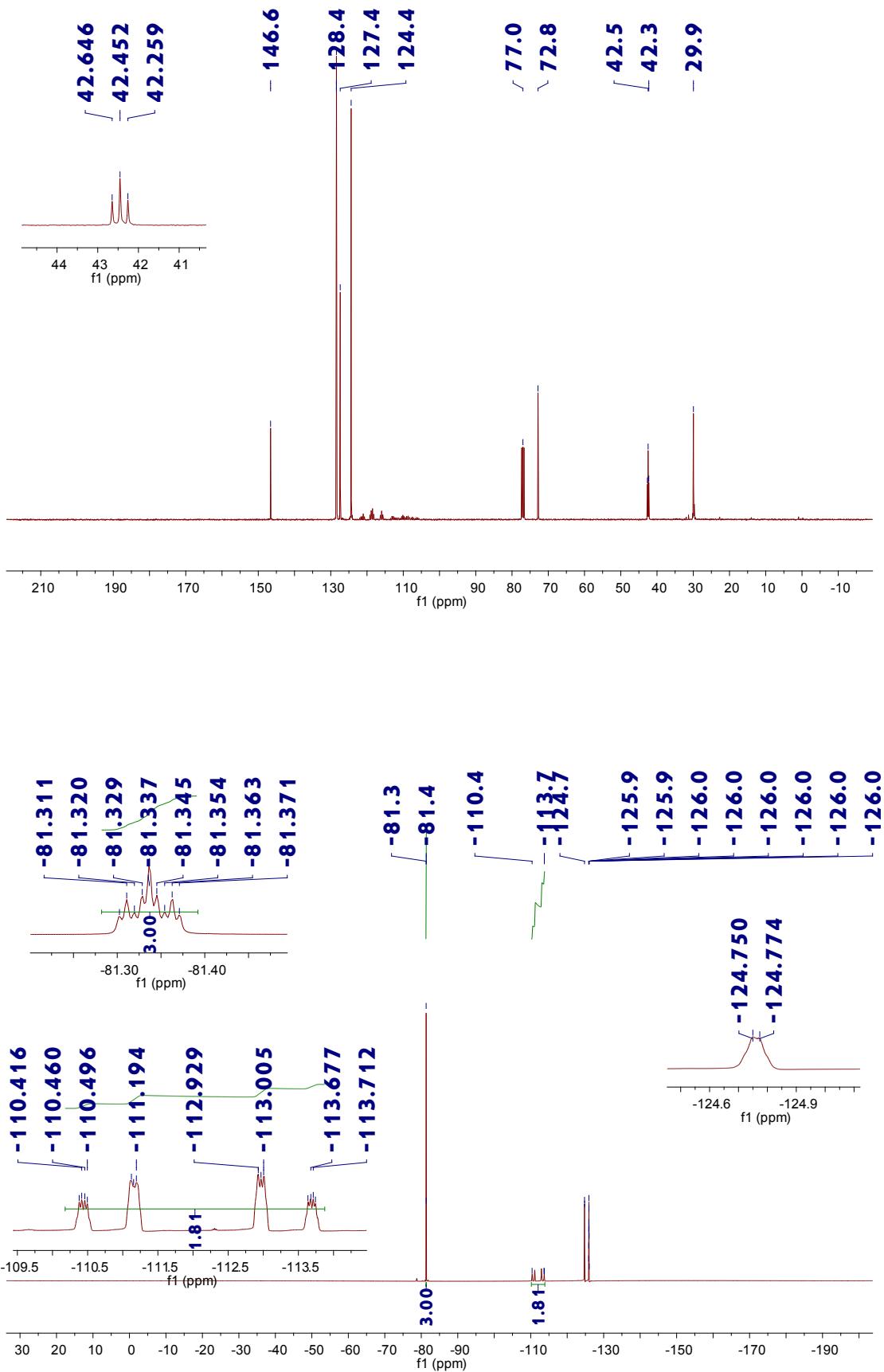
3j



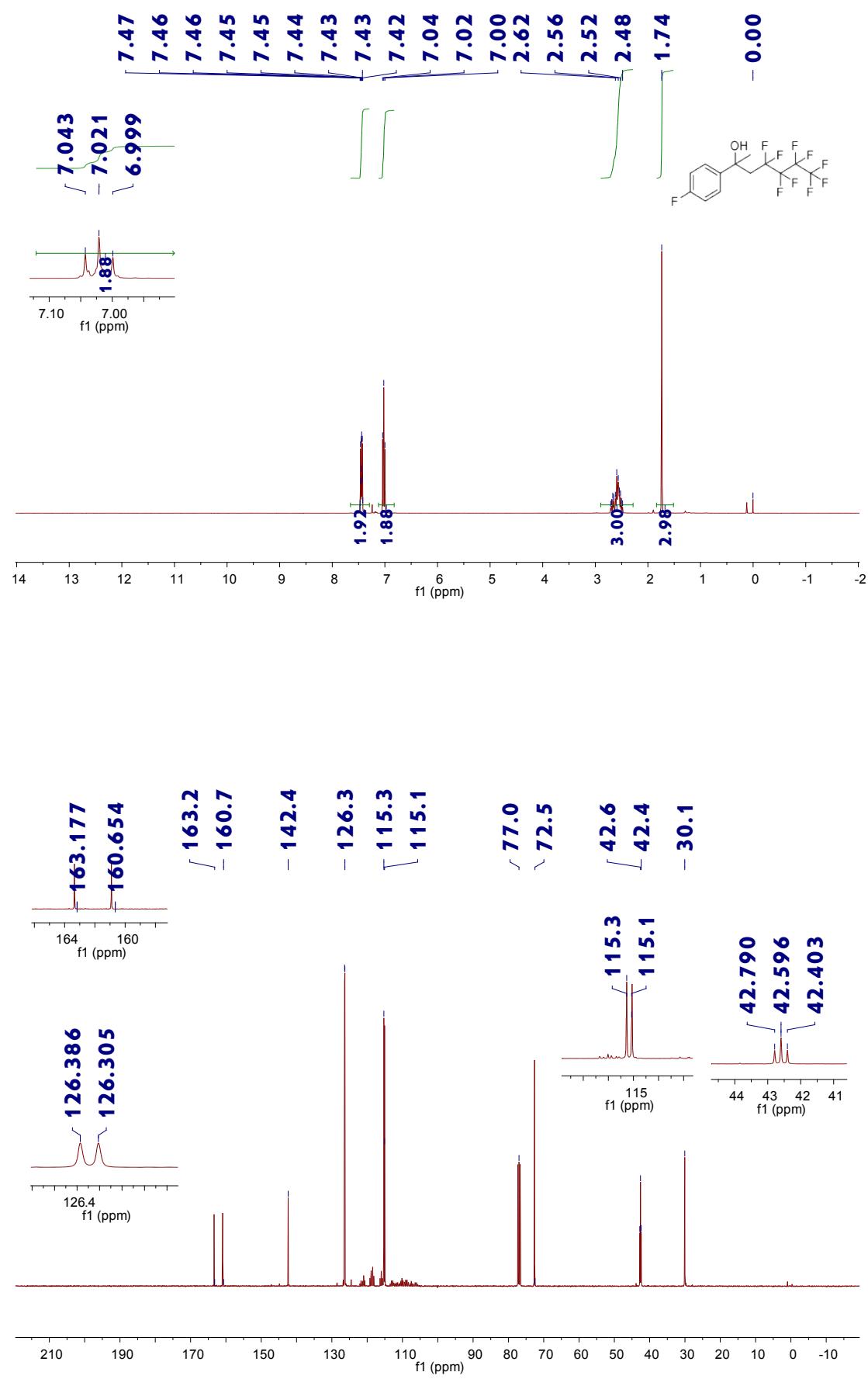


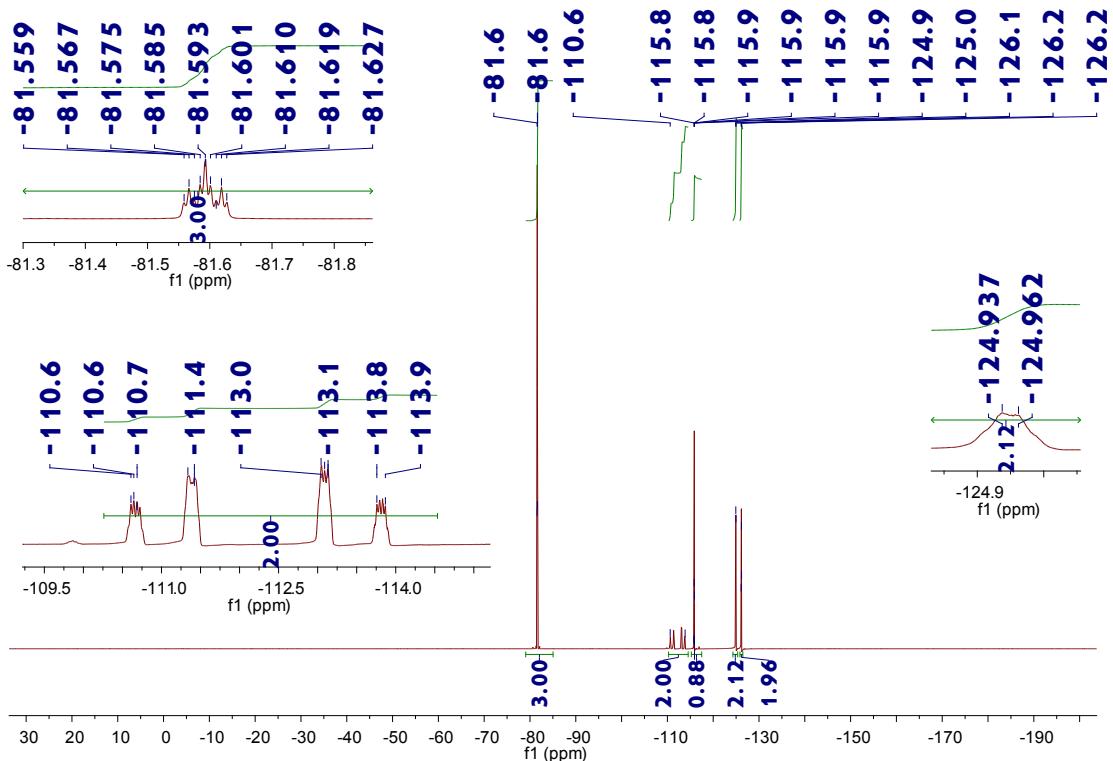
**3j (under condition B)**



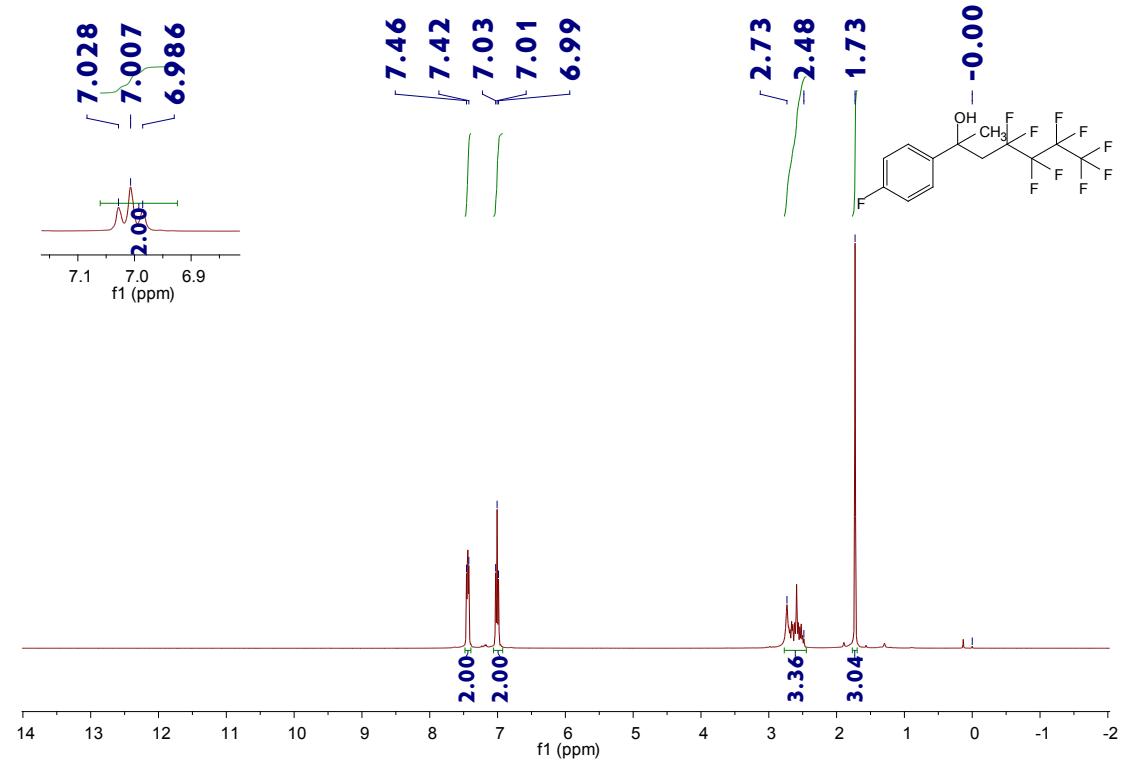


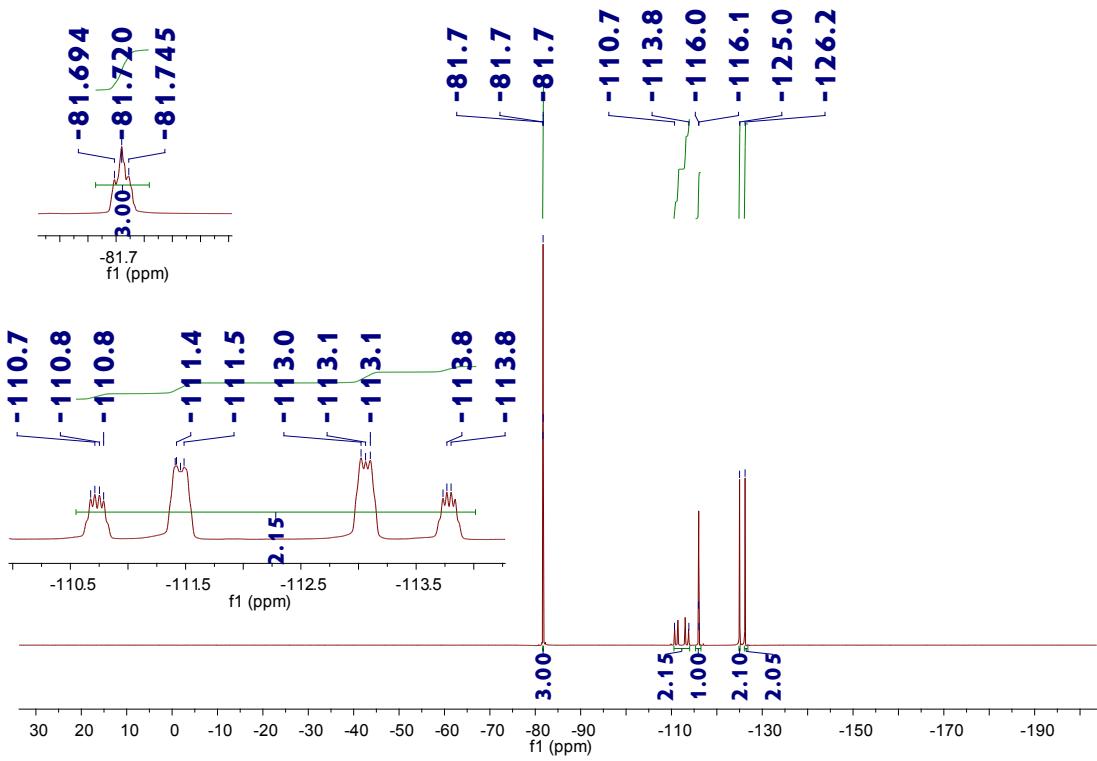
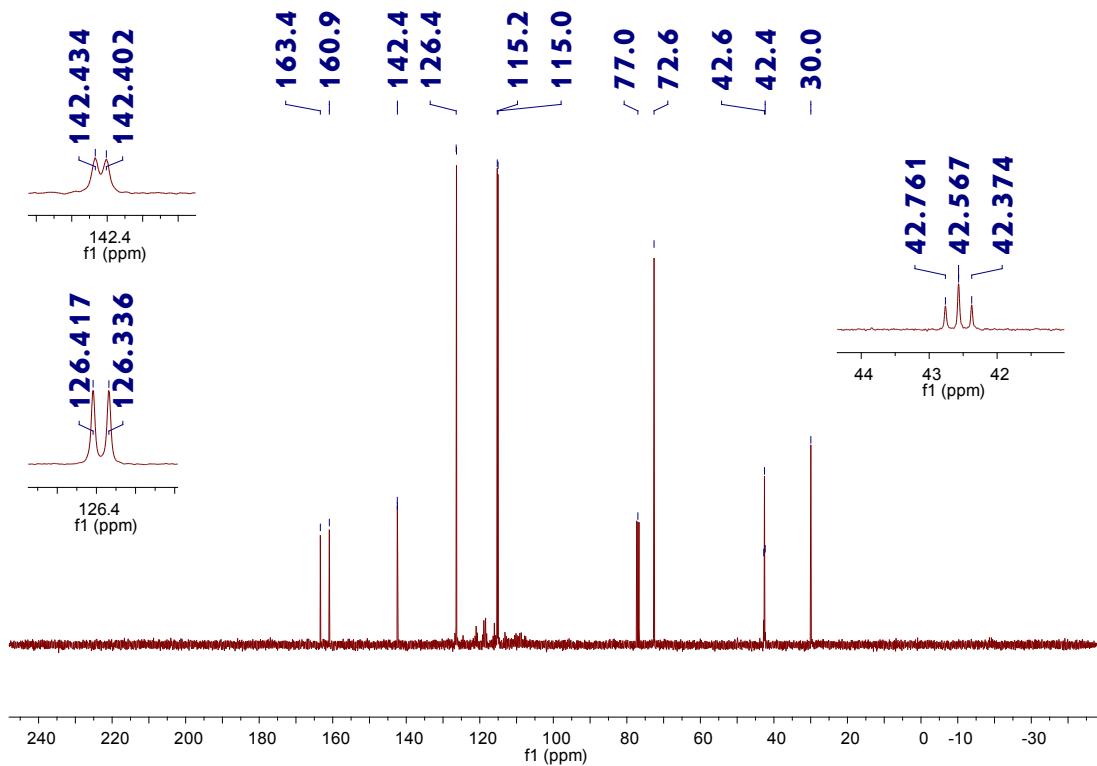
3k

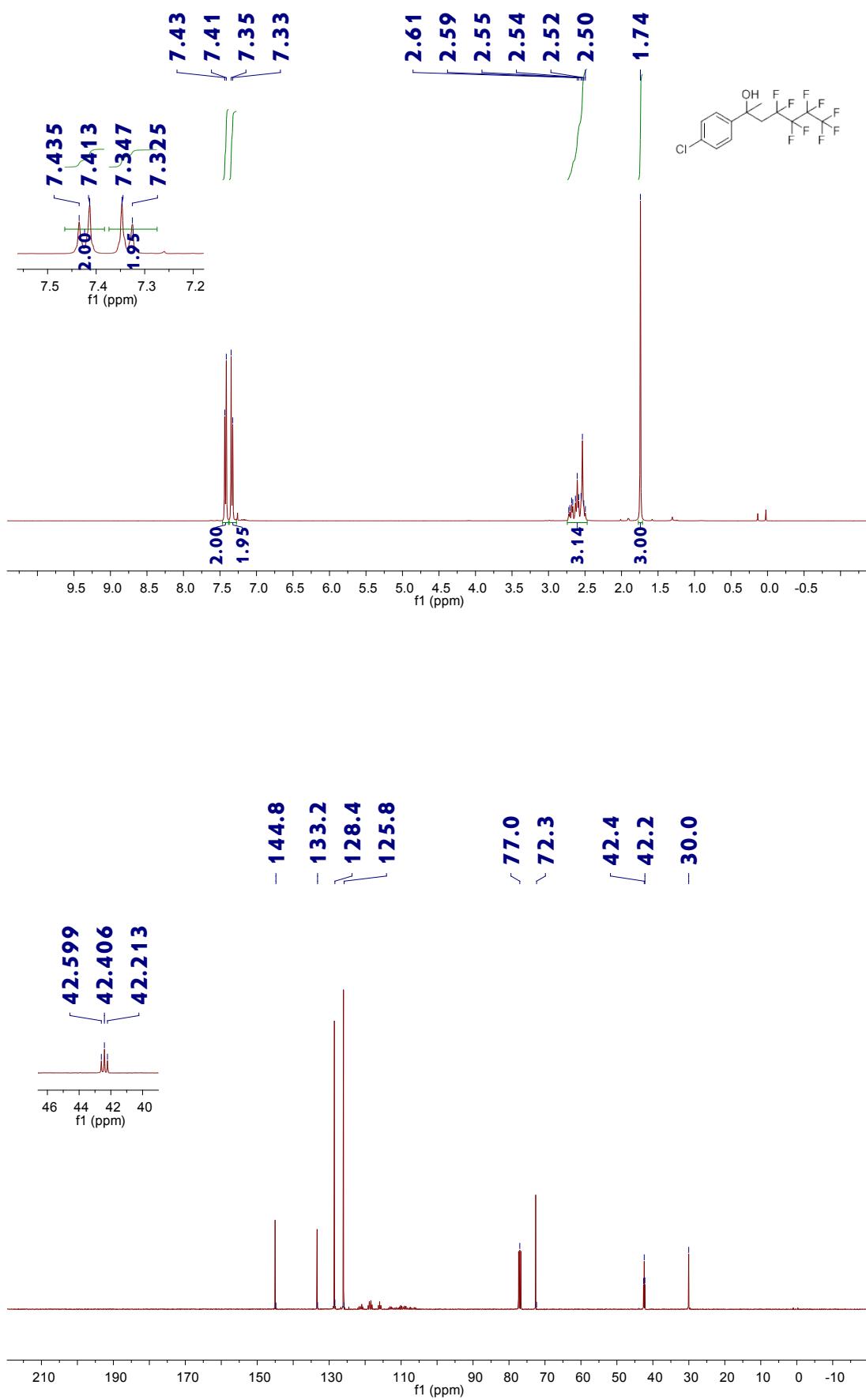


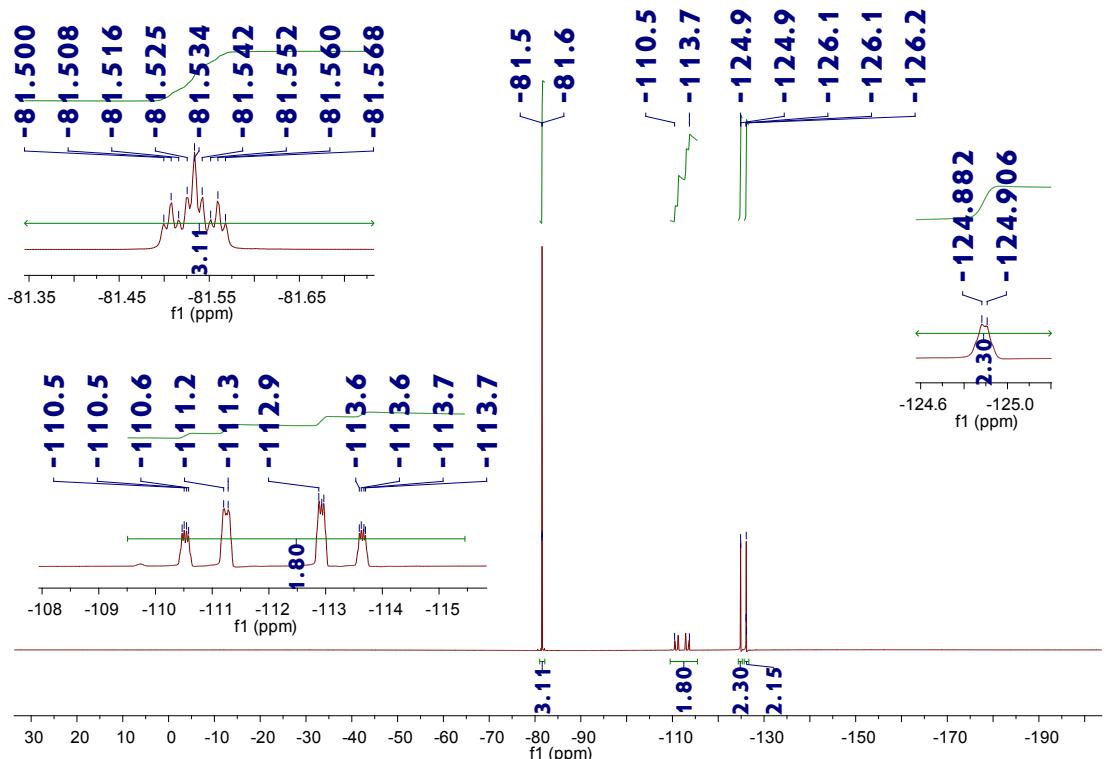


### **3k (under condition B)**

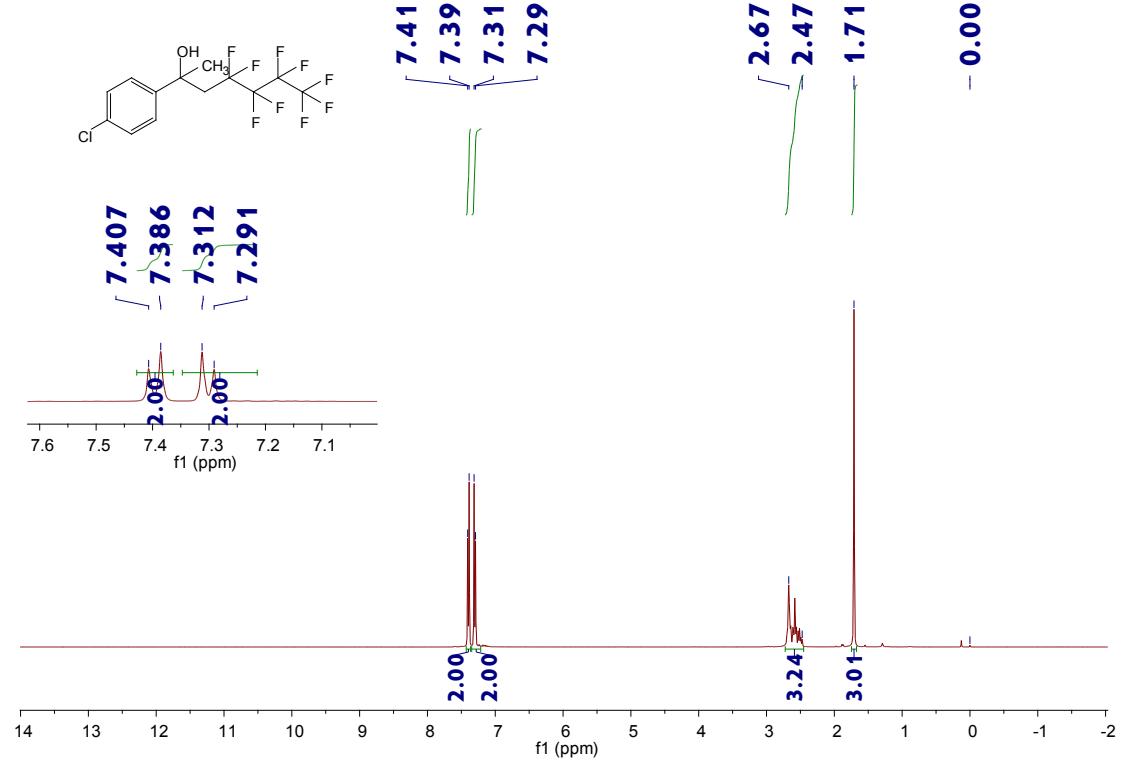


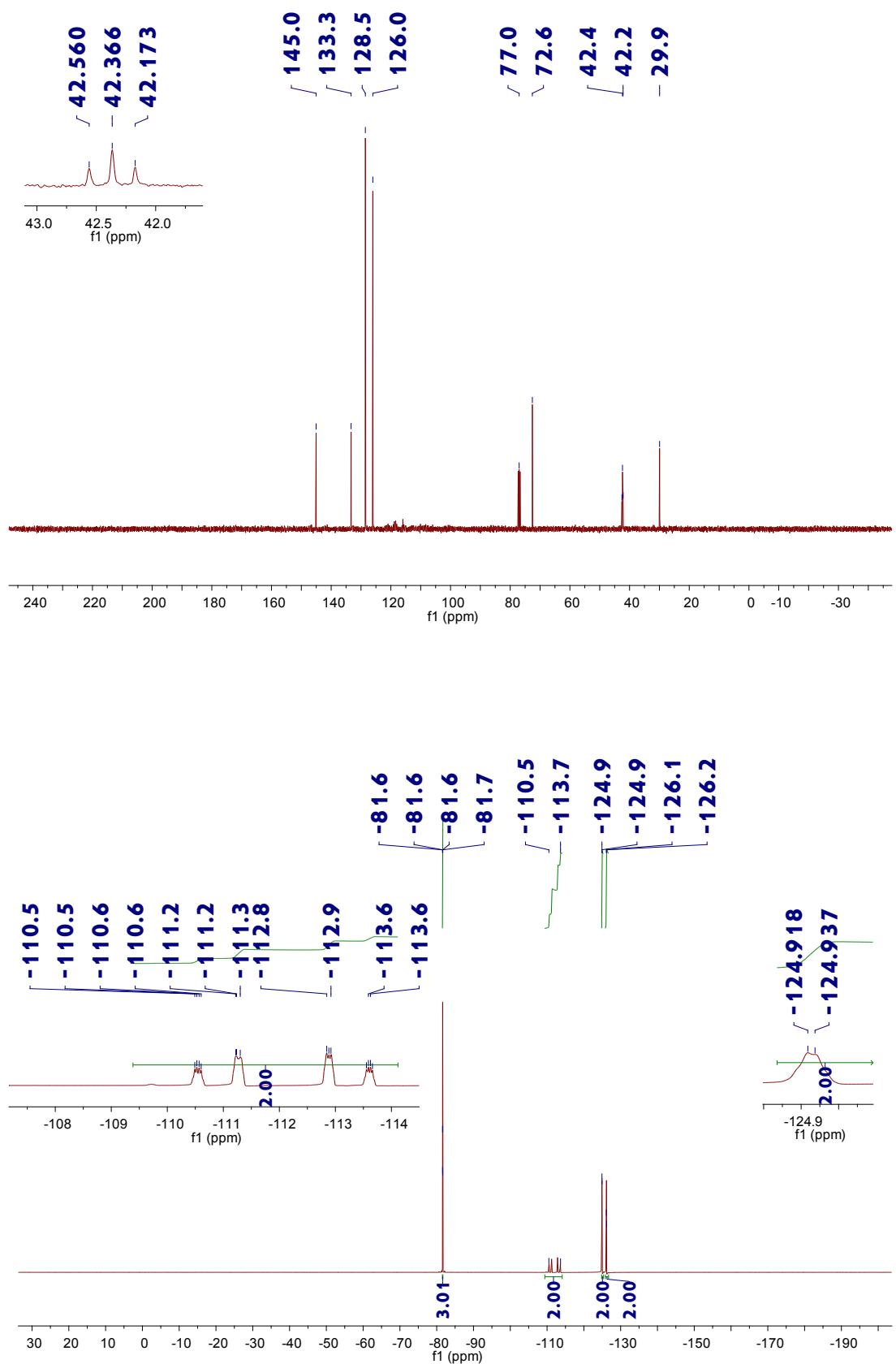




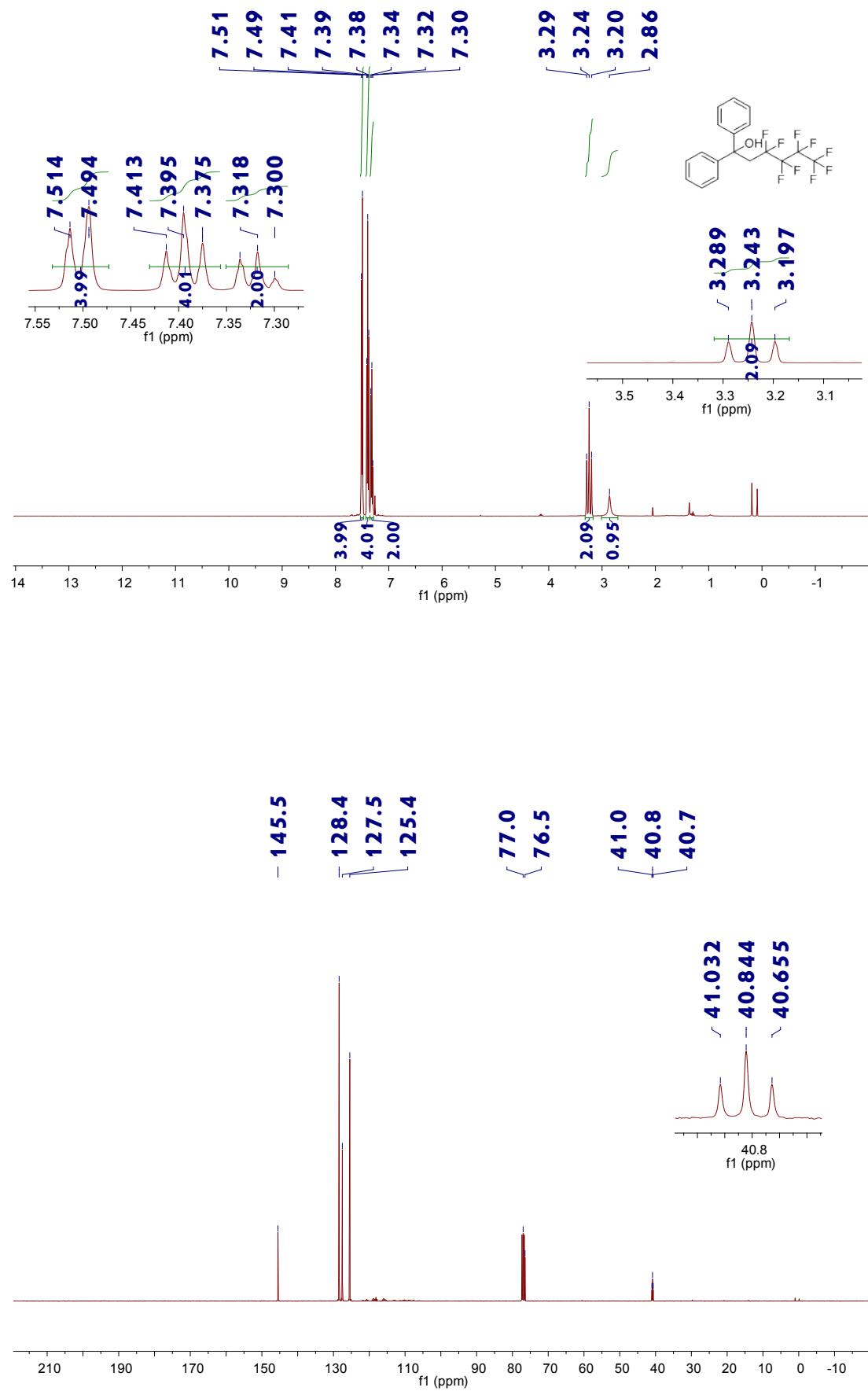


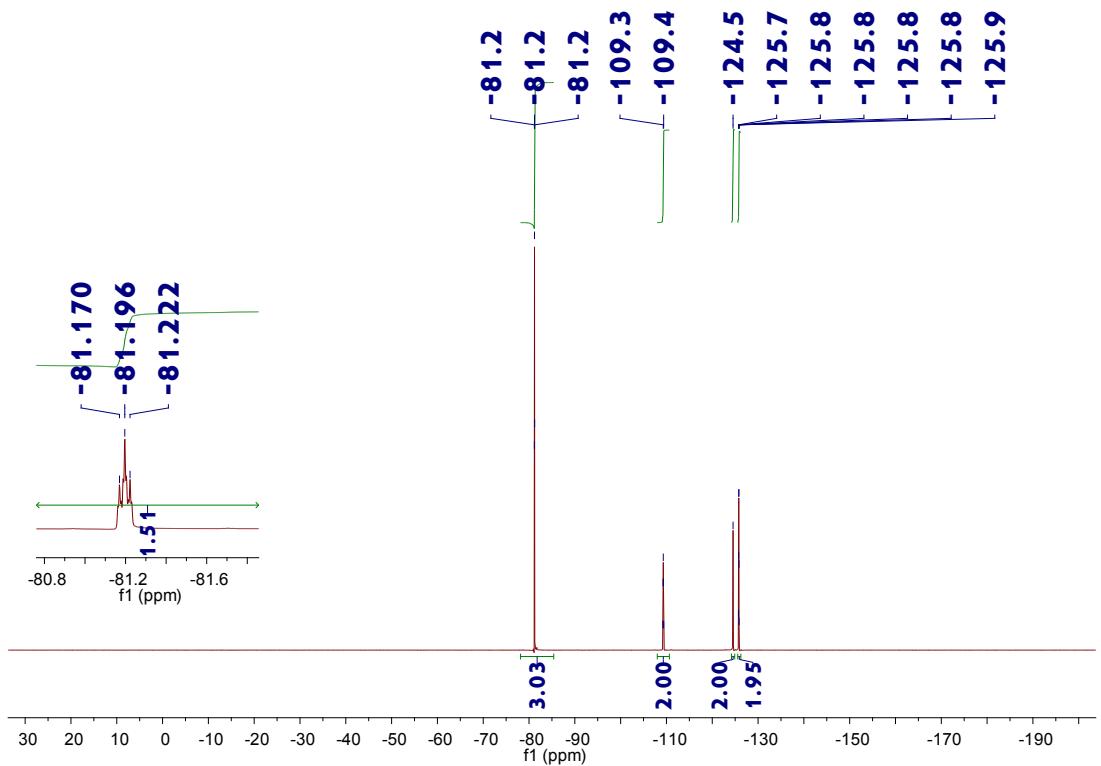
**3l (under condition B)**



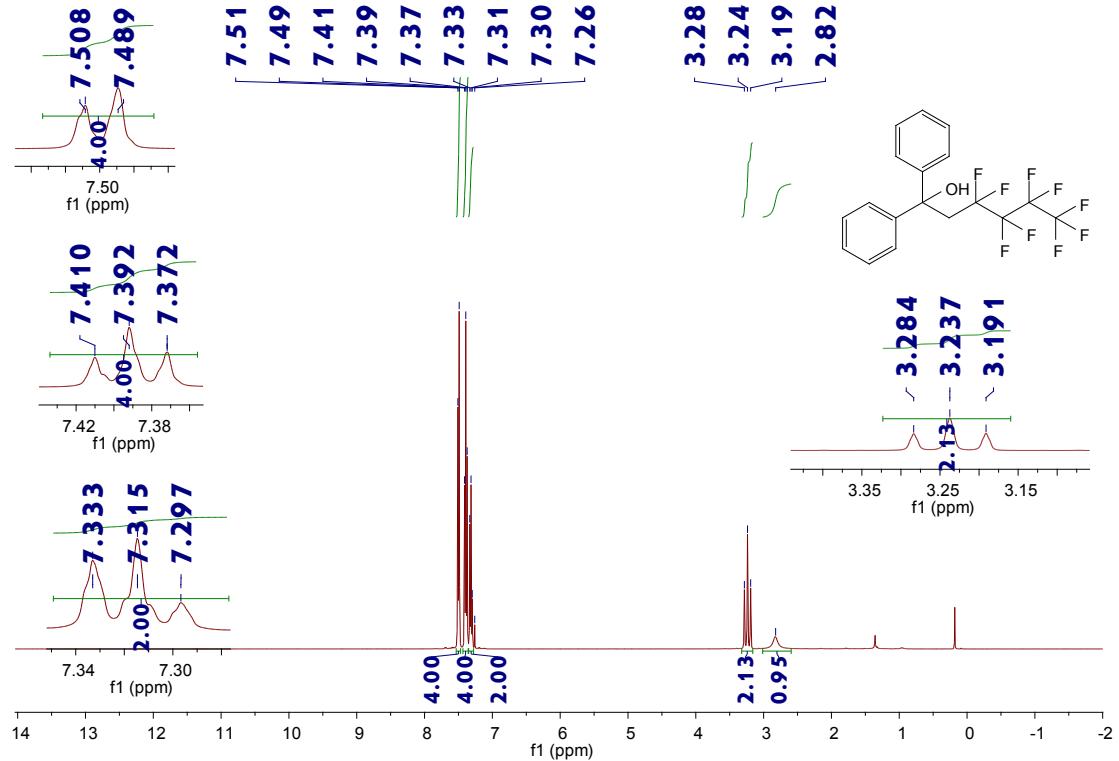


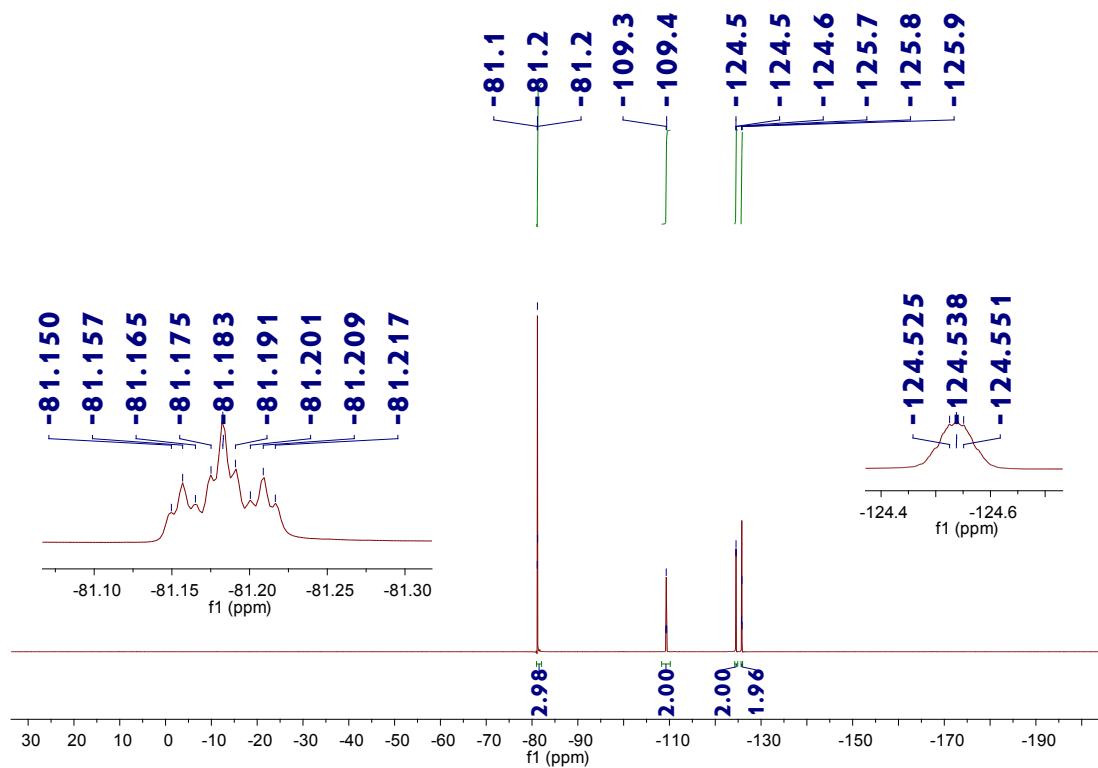
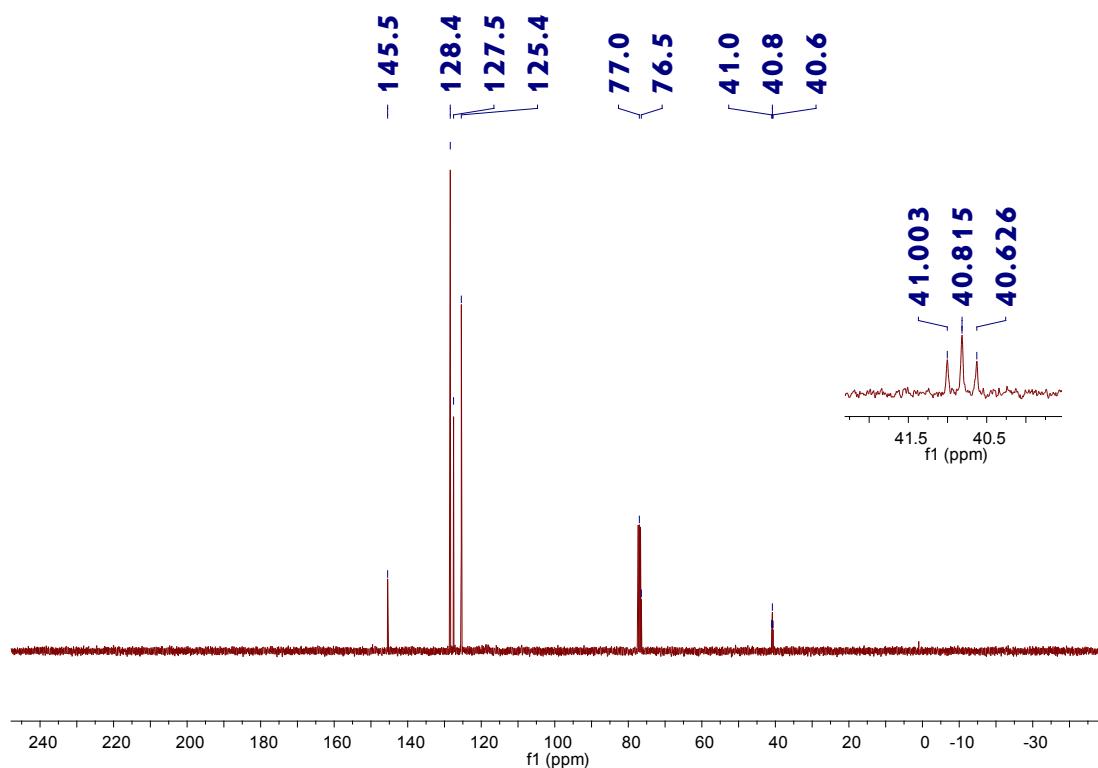
**3m**



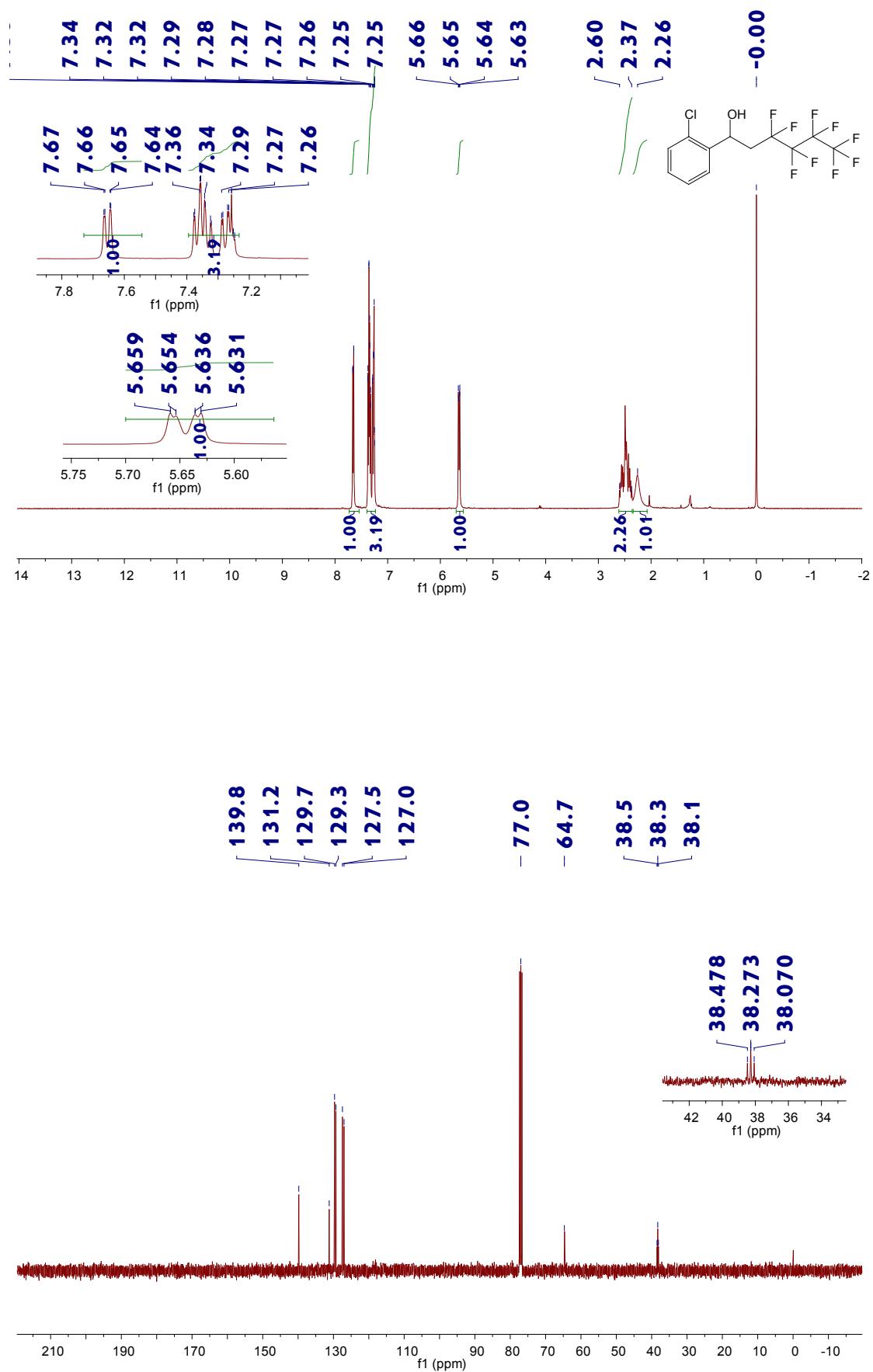


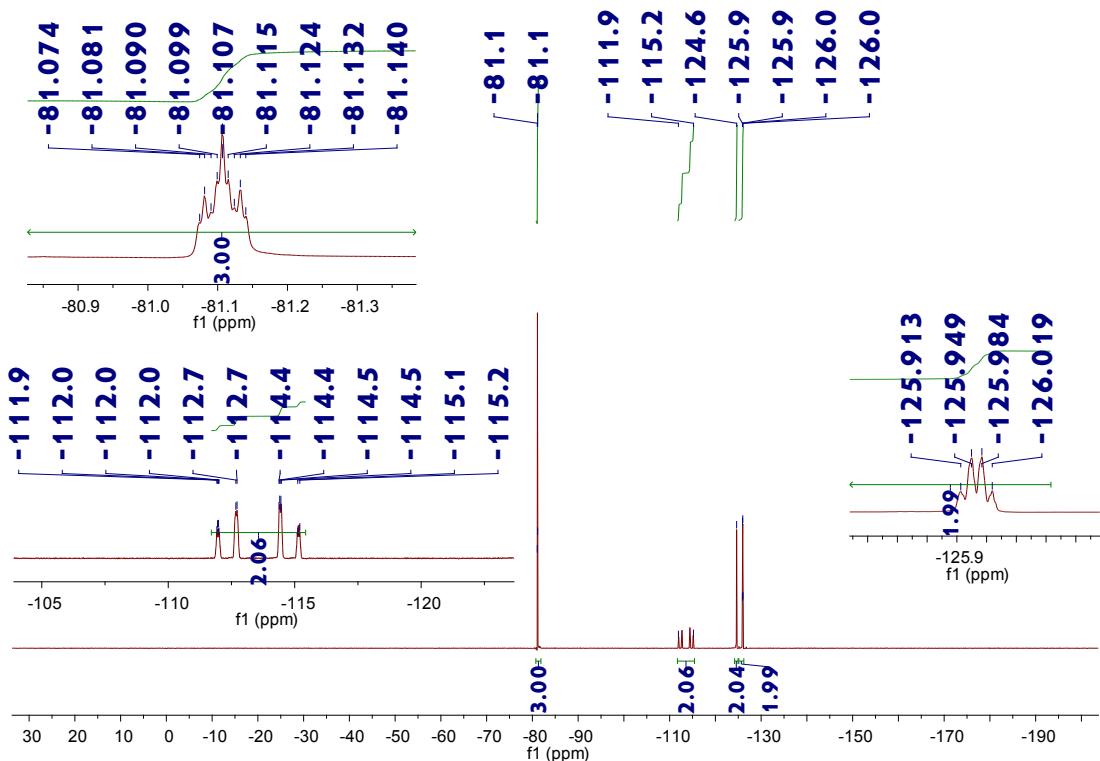
**3m (under condition B)**



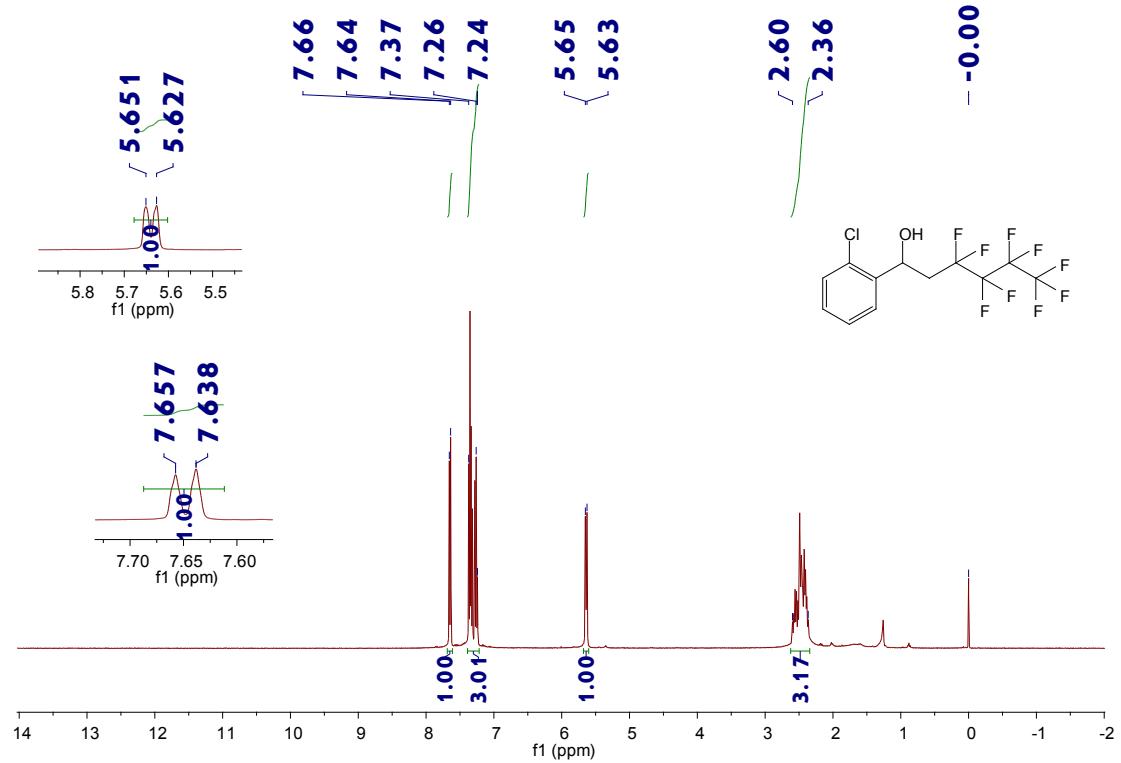


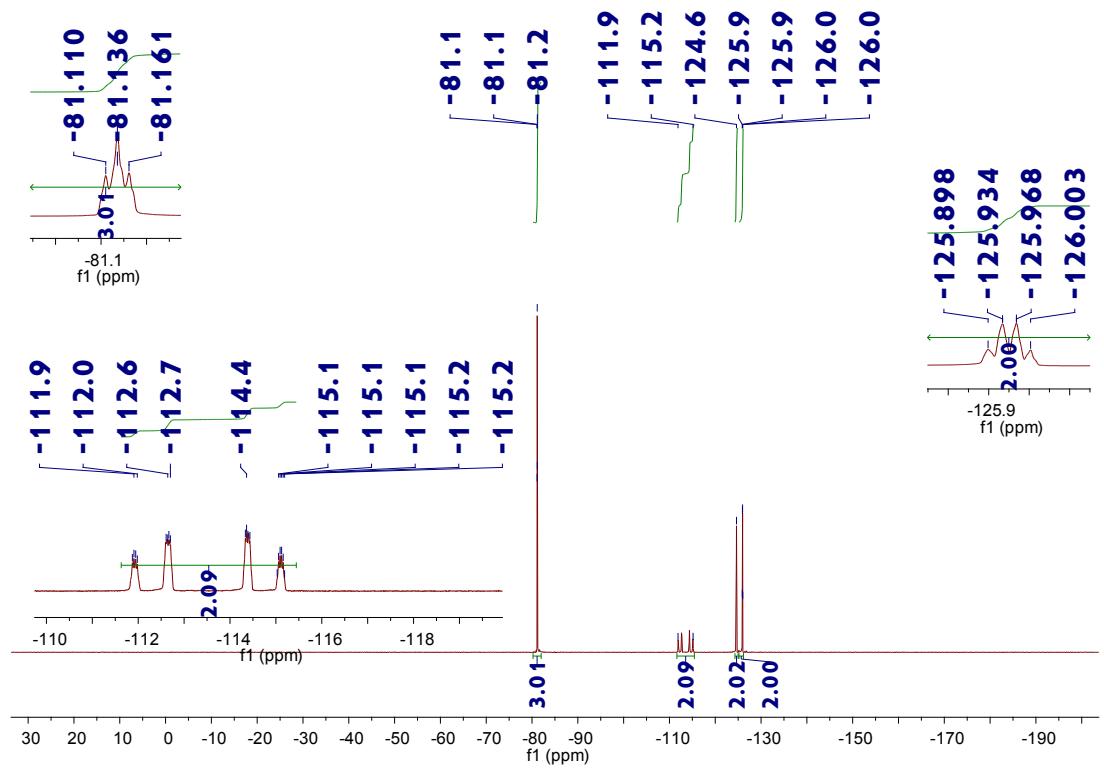
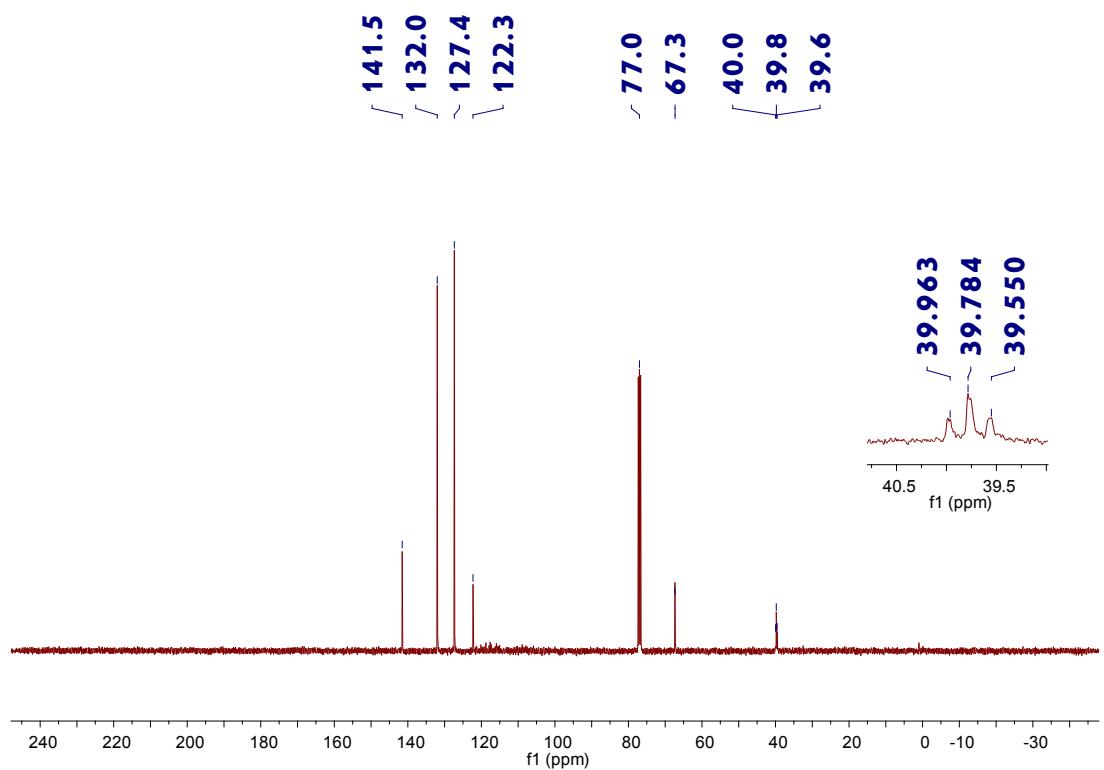
**3n**

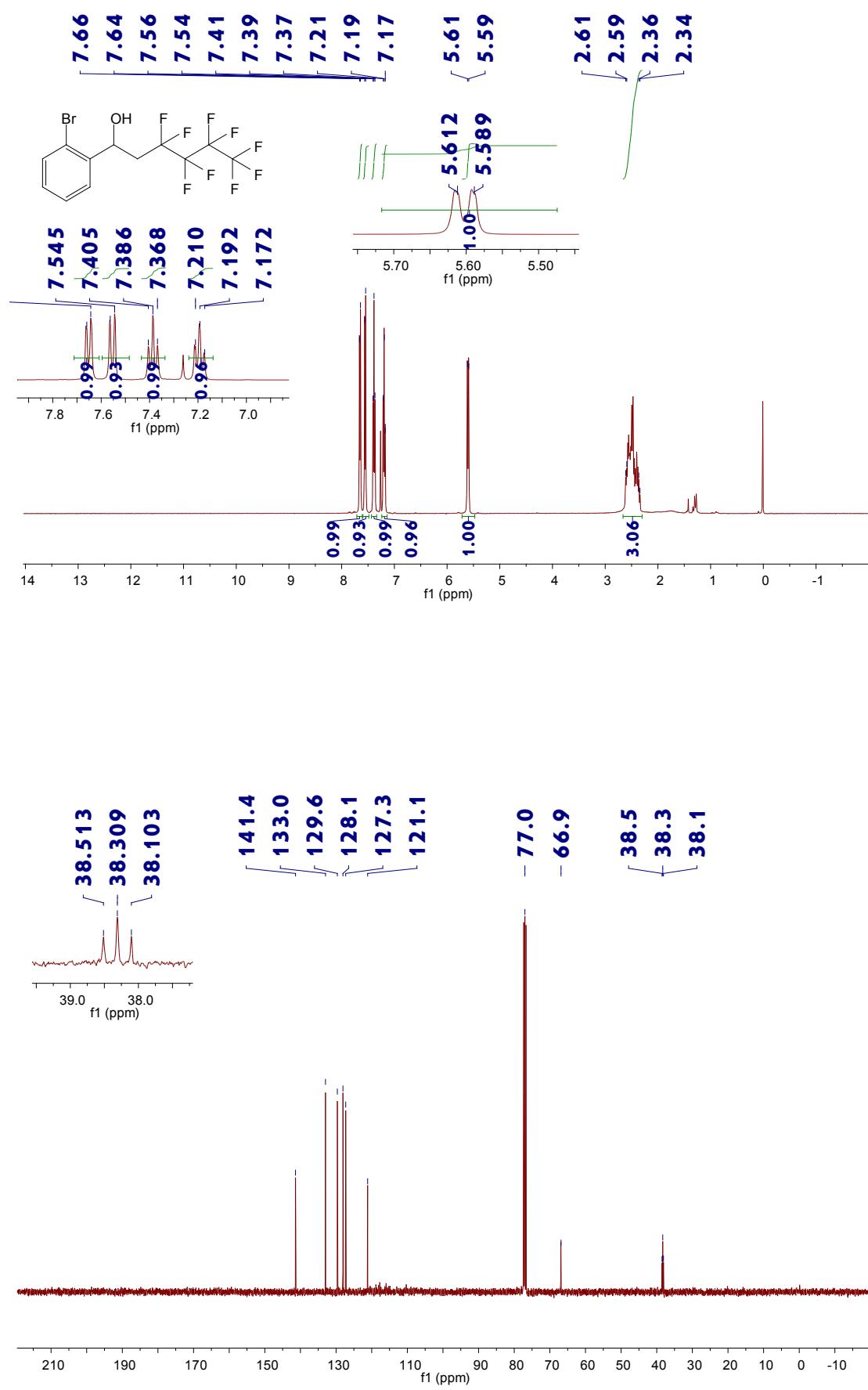


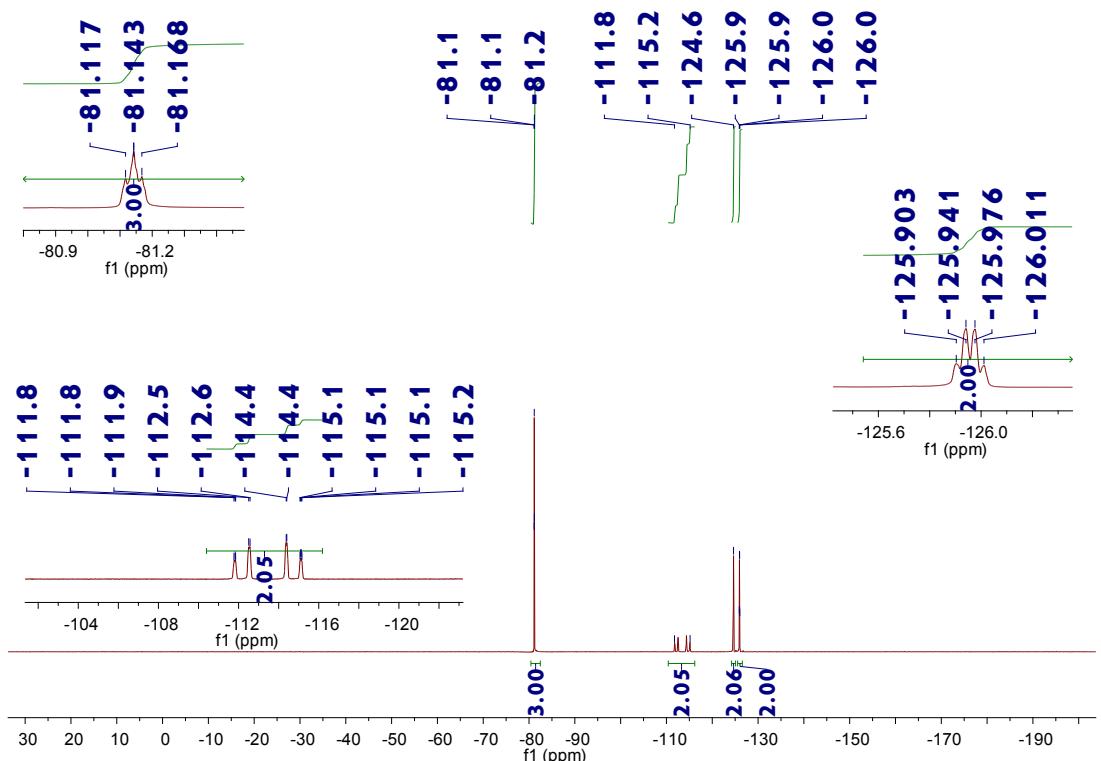


### 3n (under condition B)

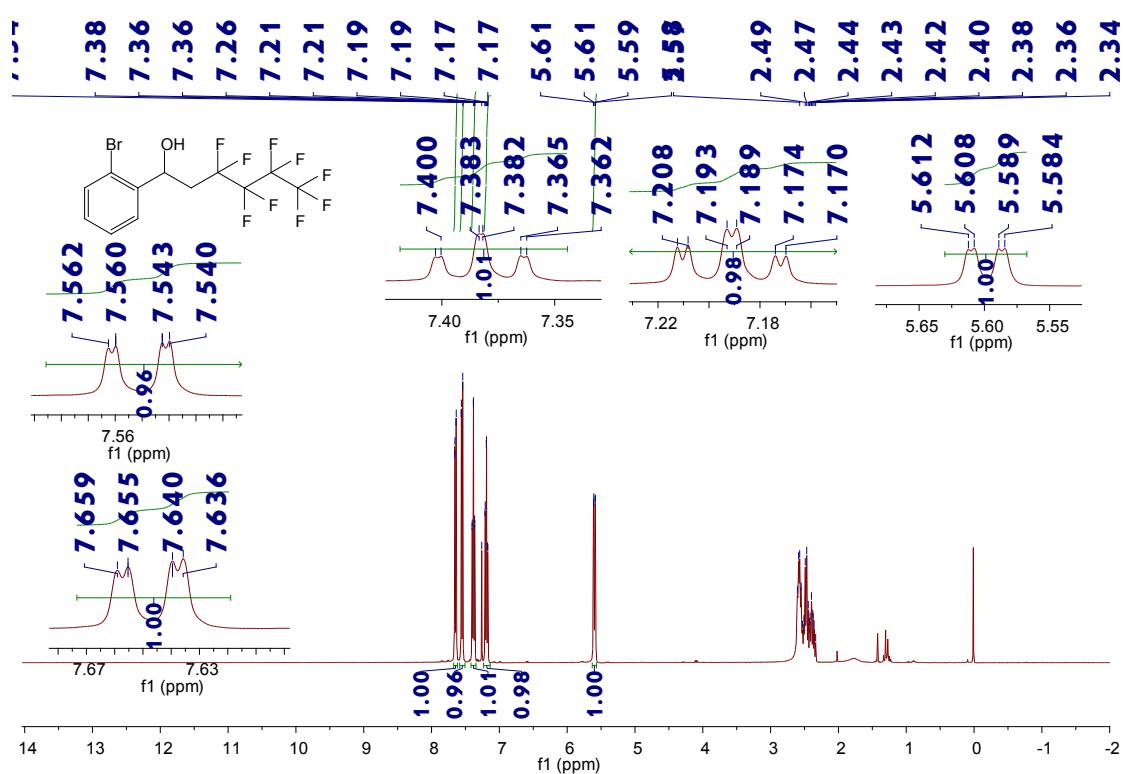


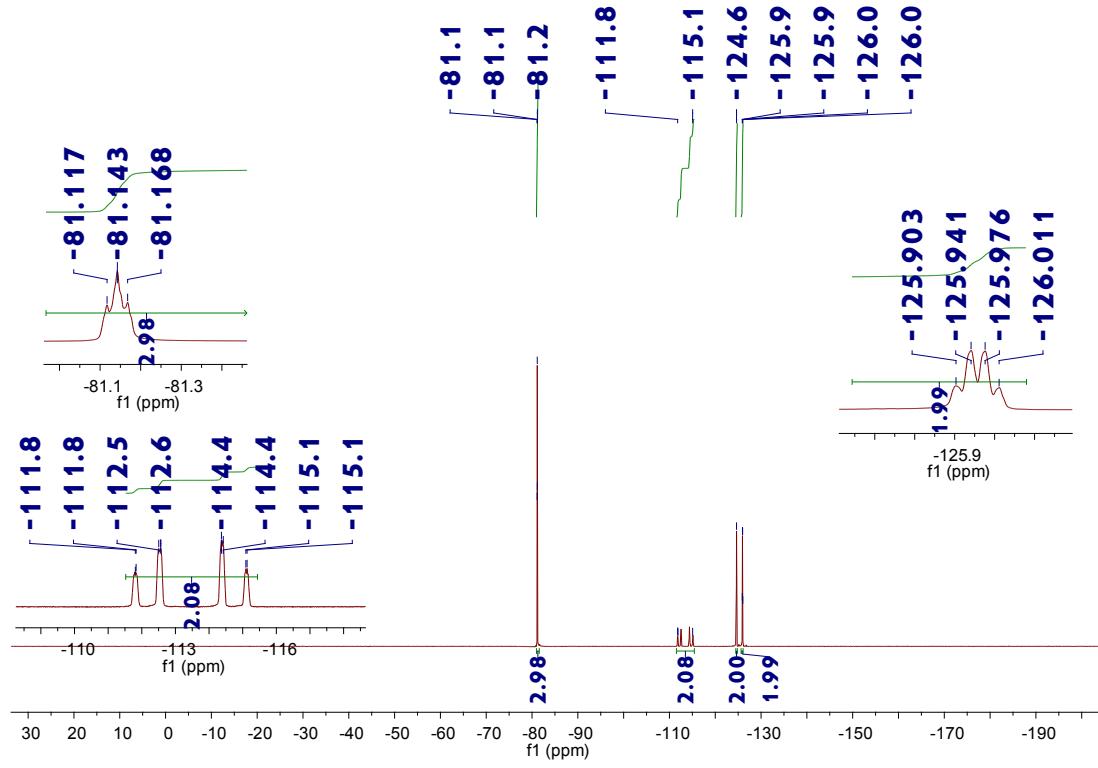
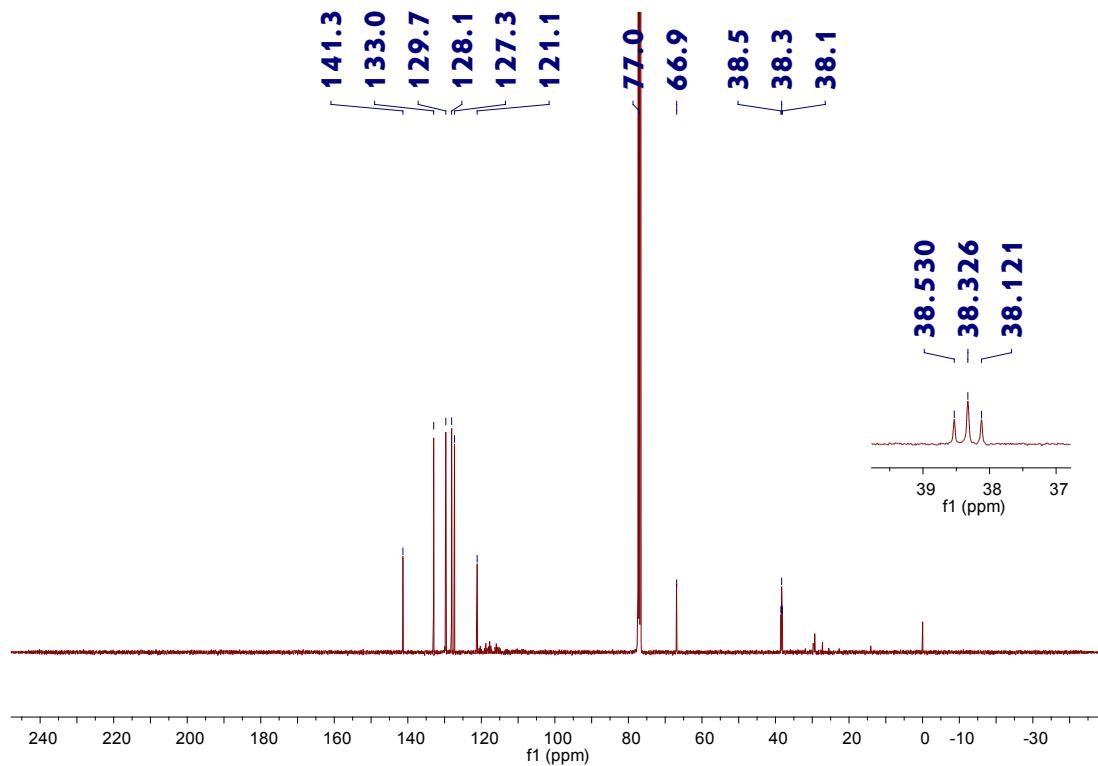




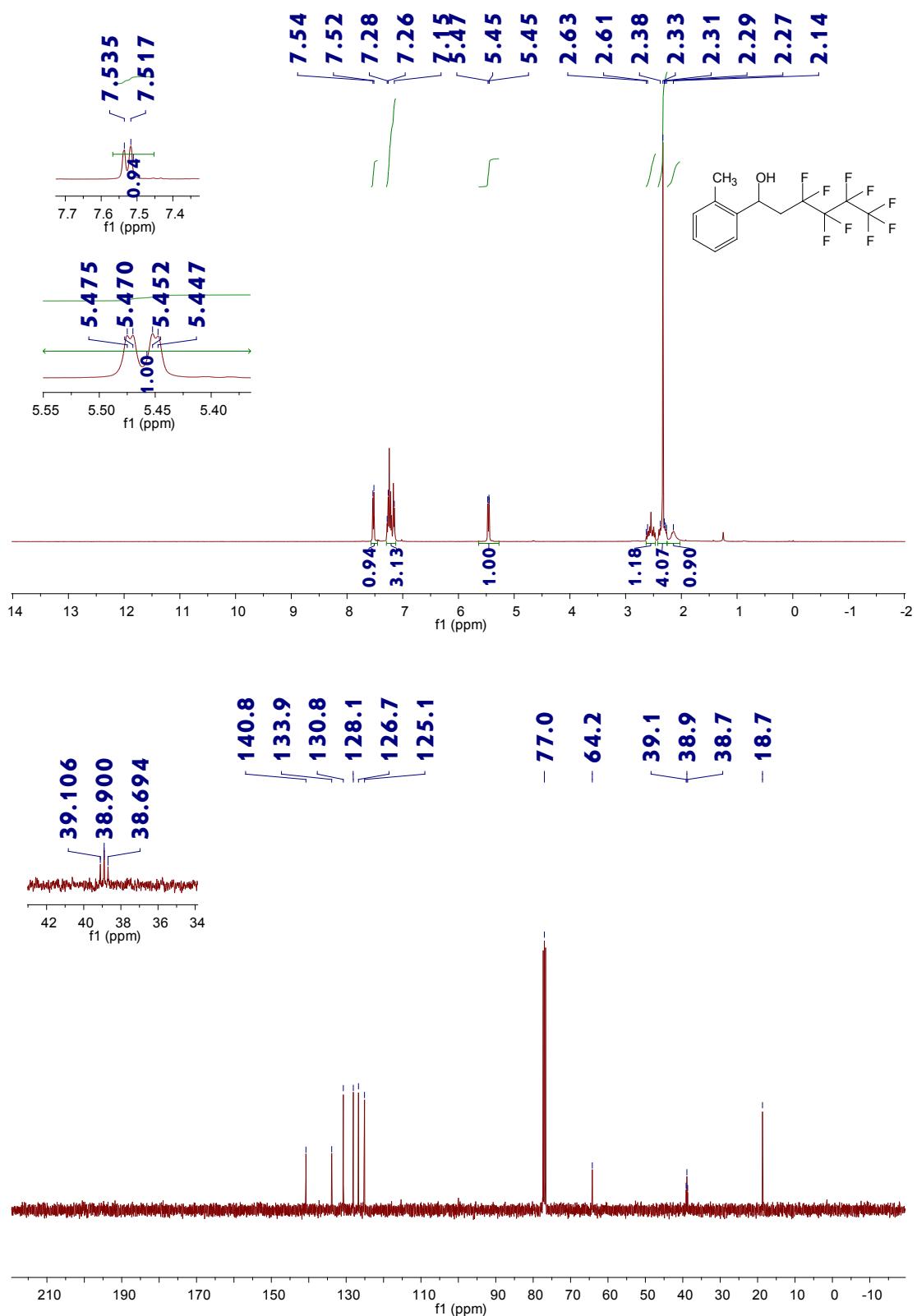


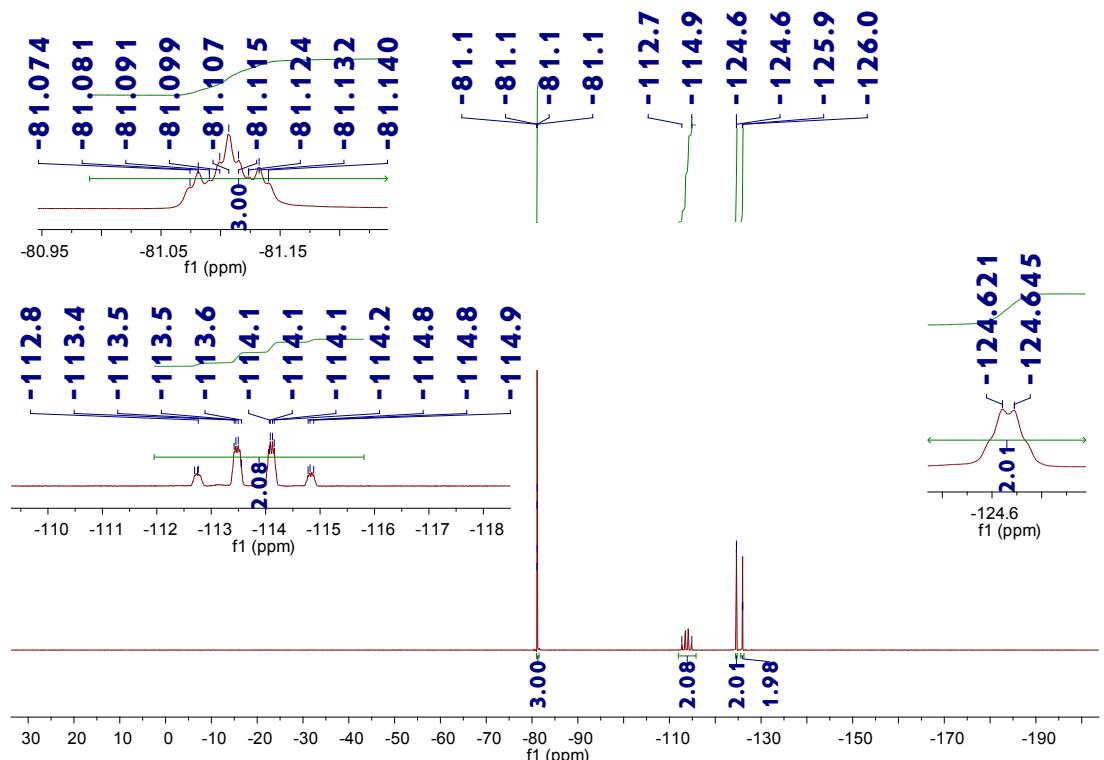
**3o (under condition B)**



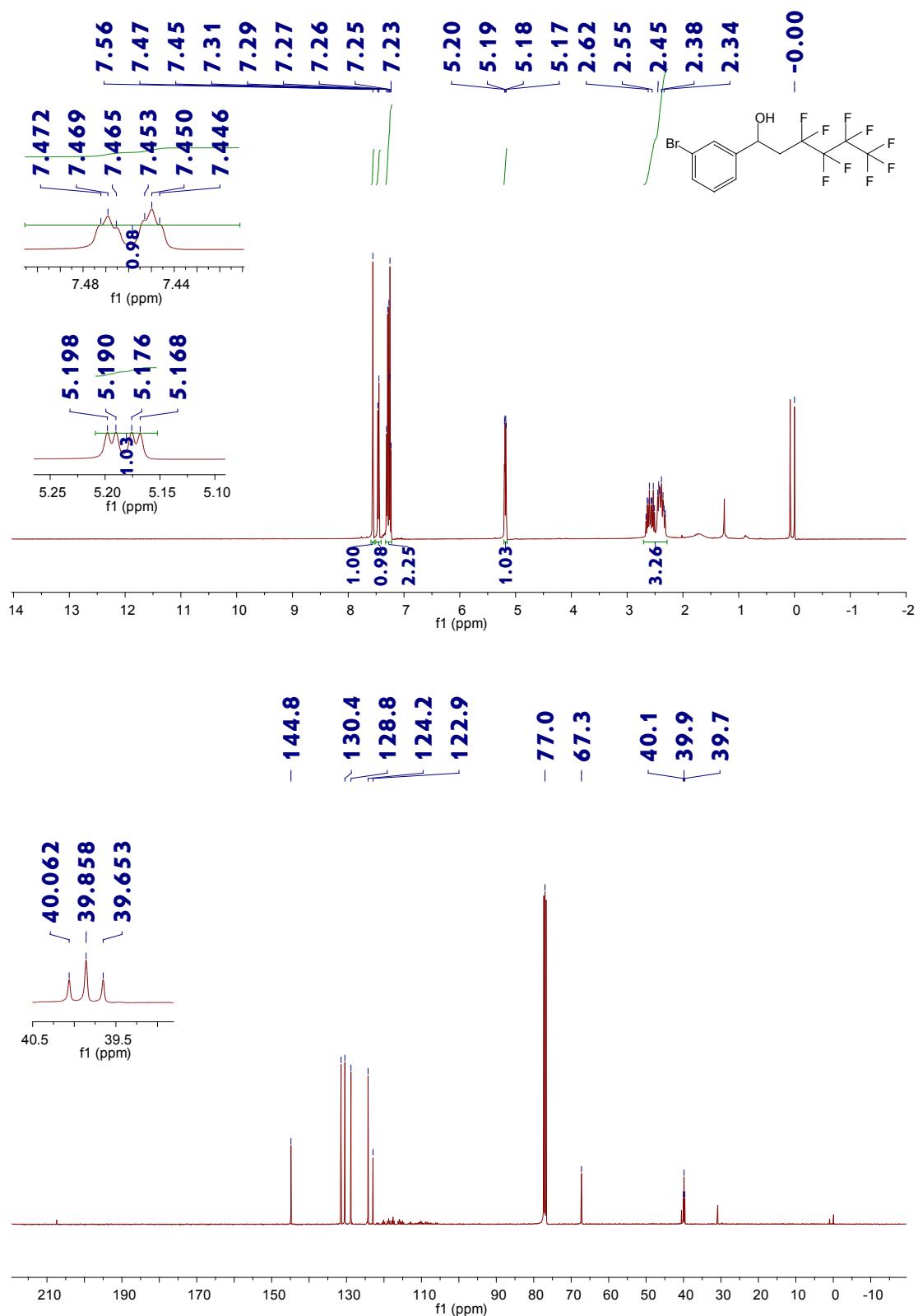


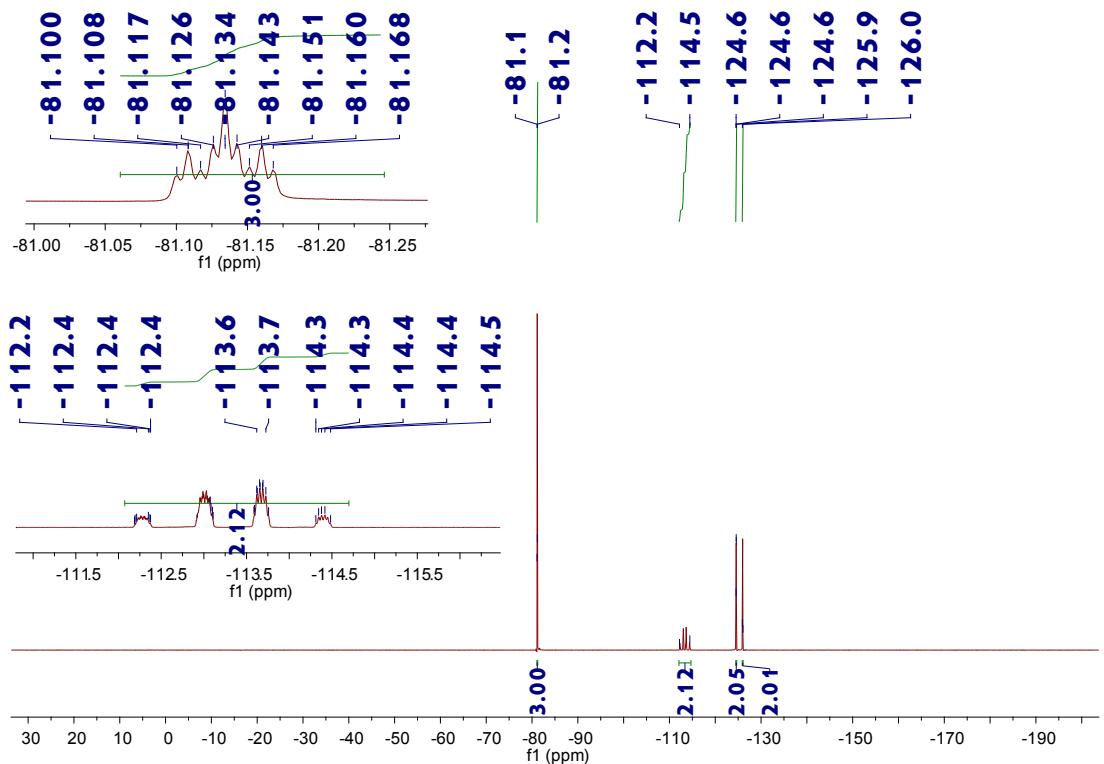
**3p**



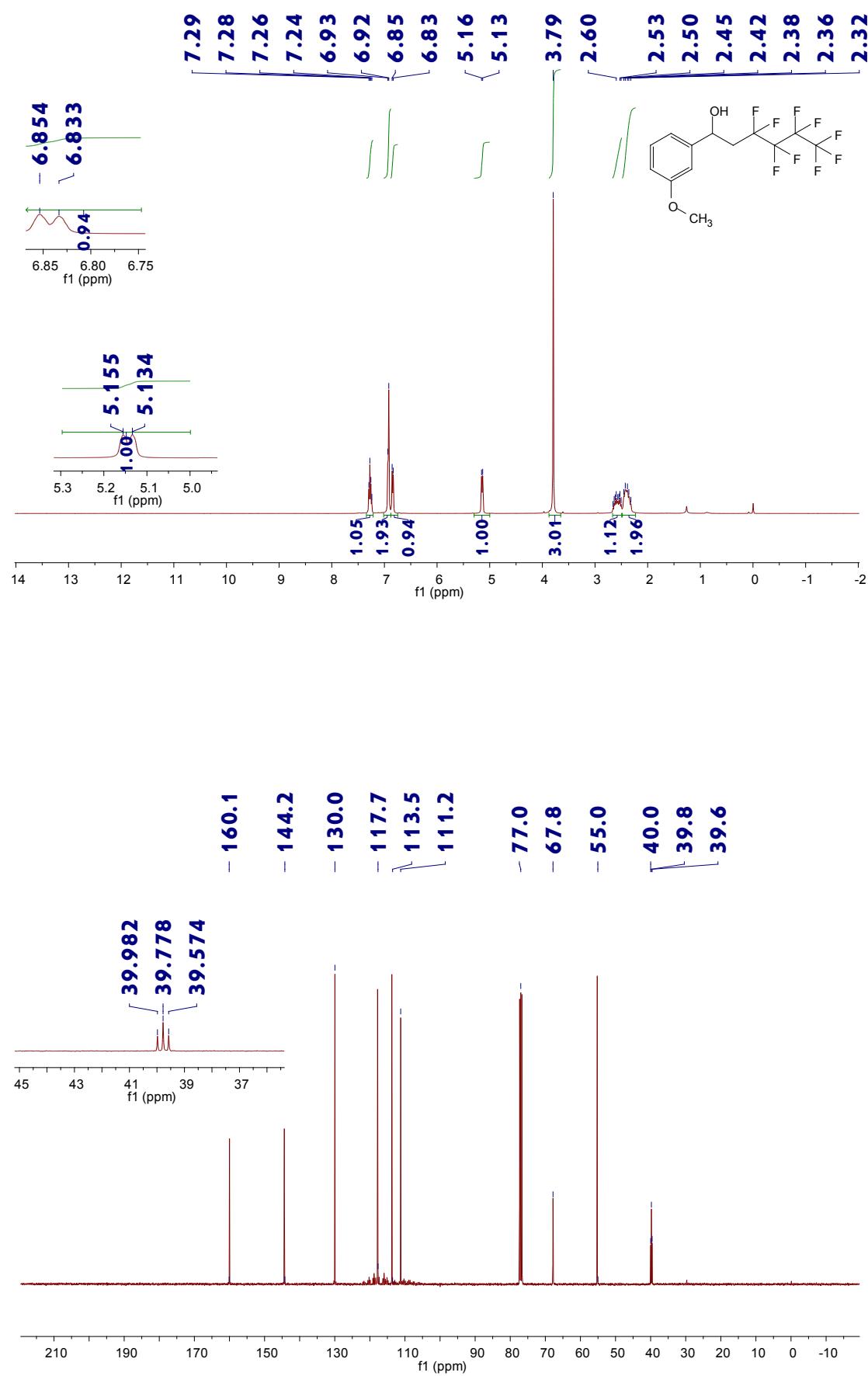


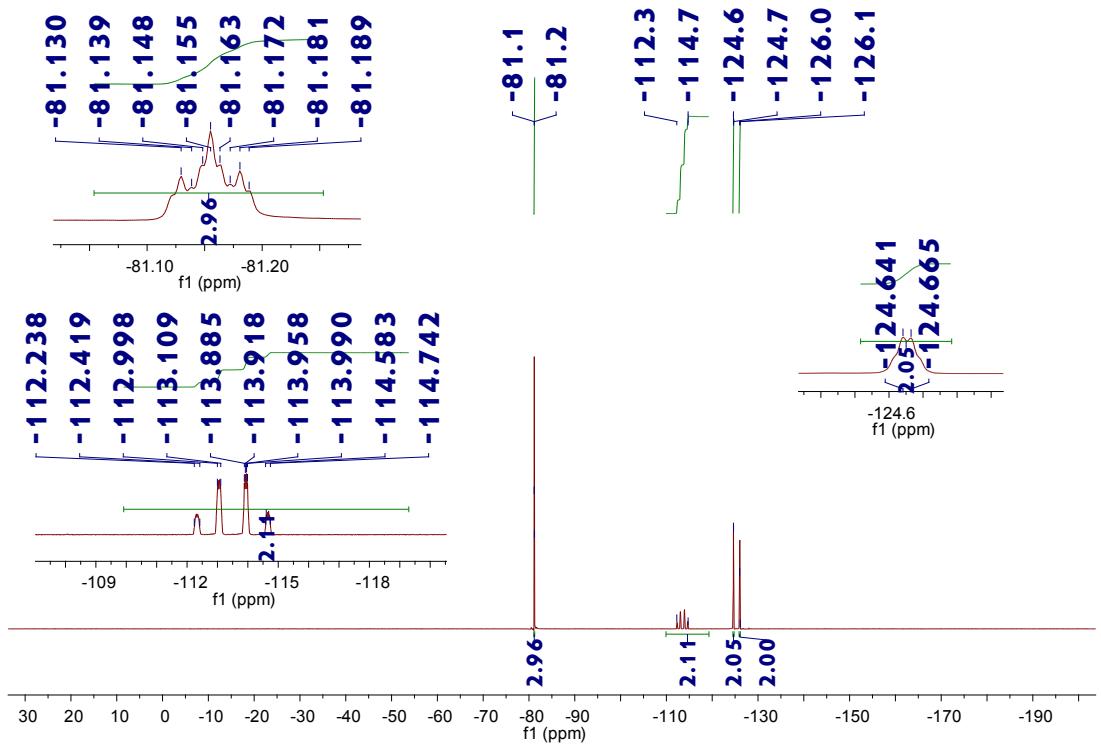
3q



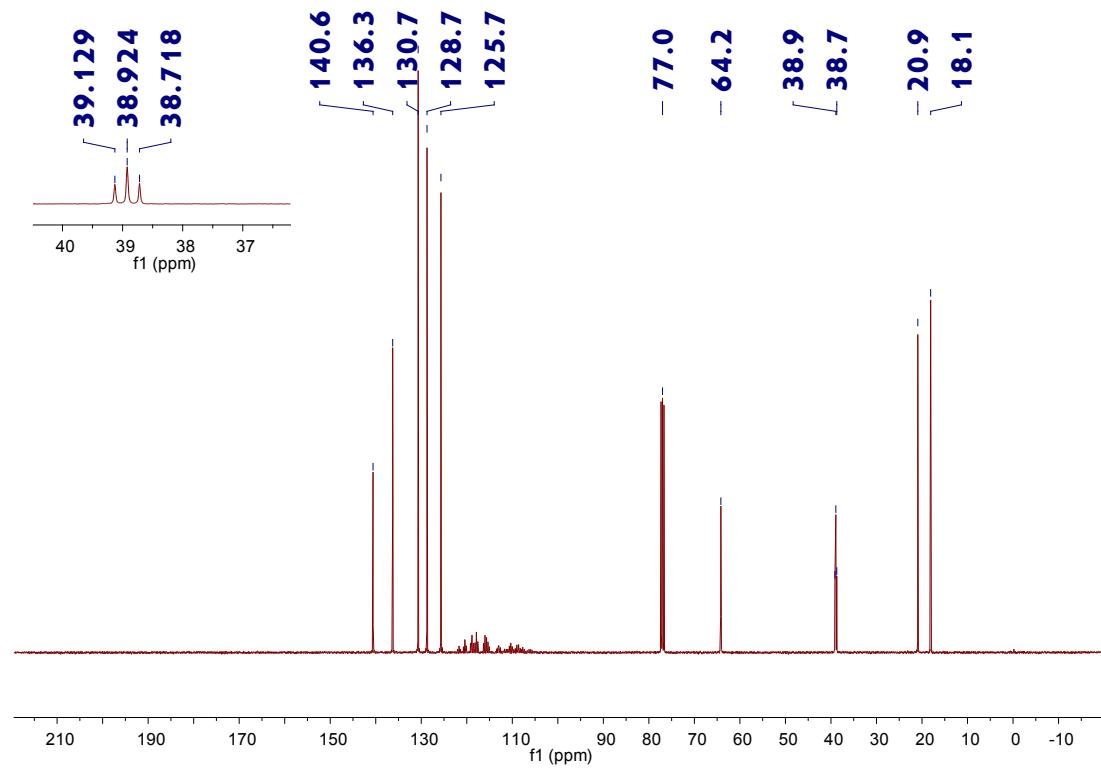
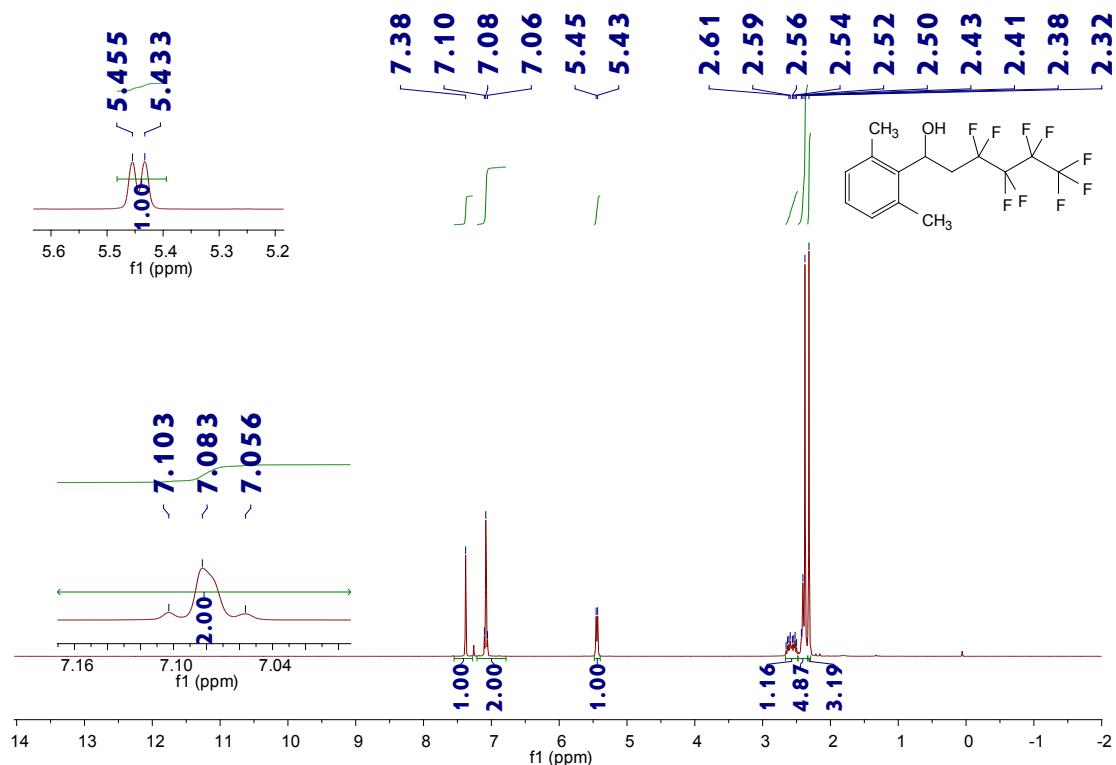


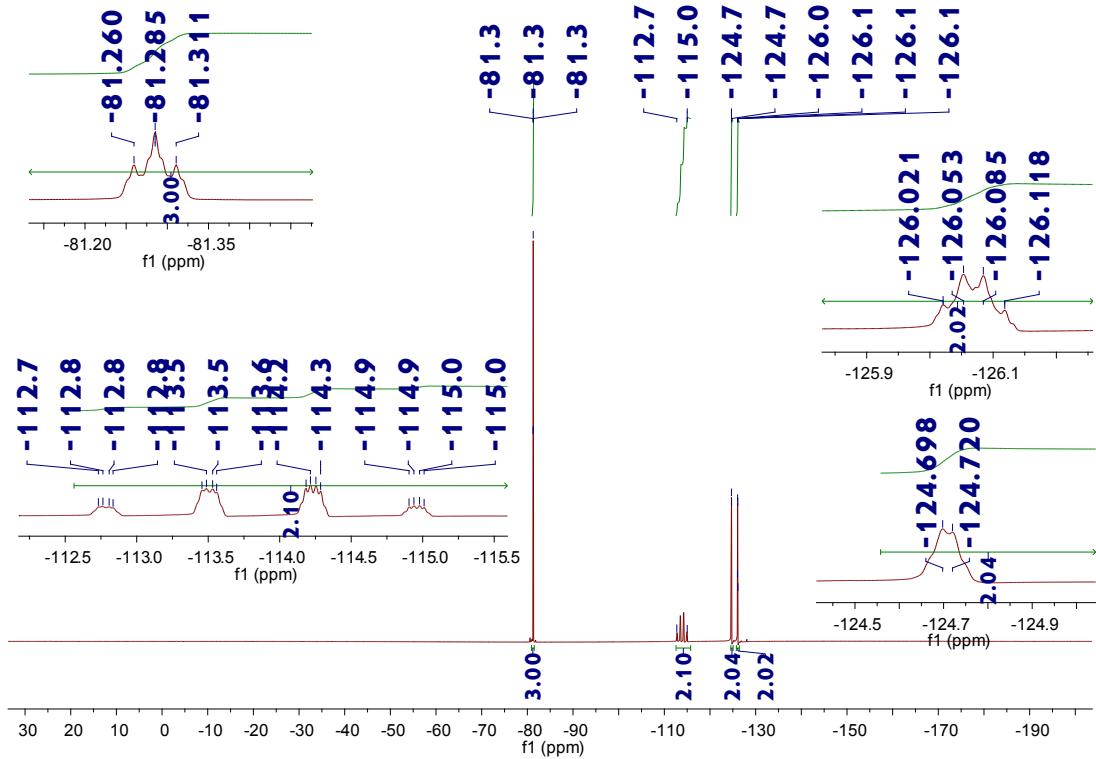
**3r**



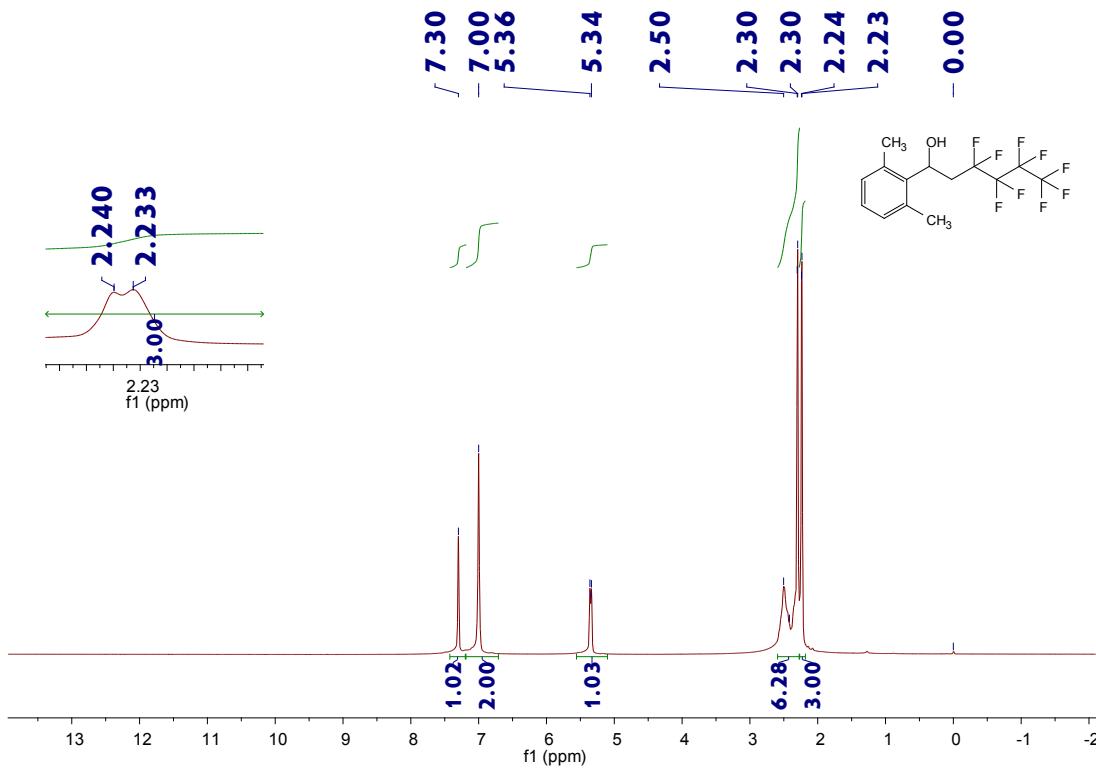


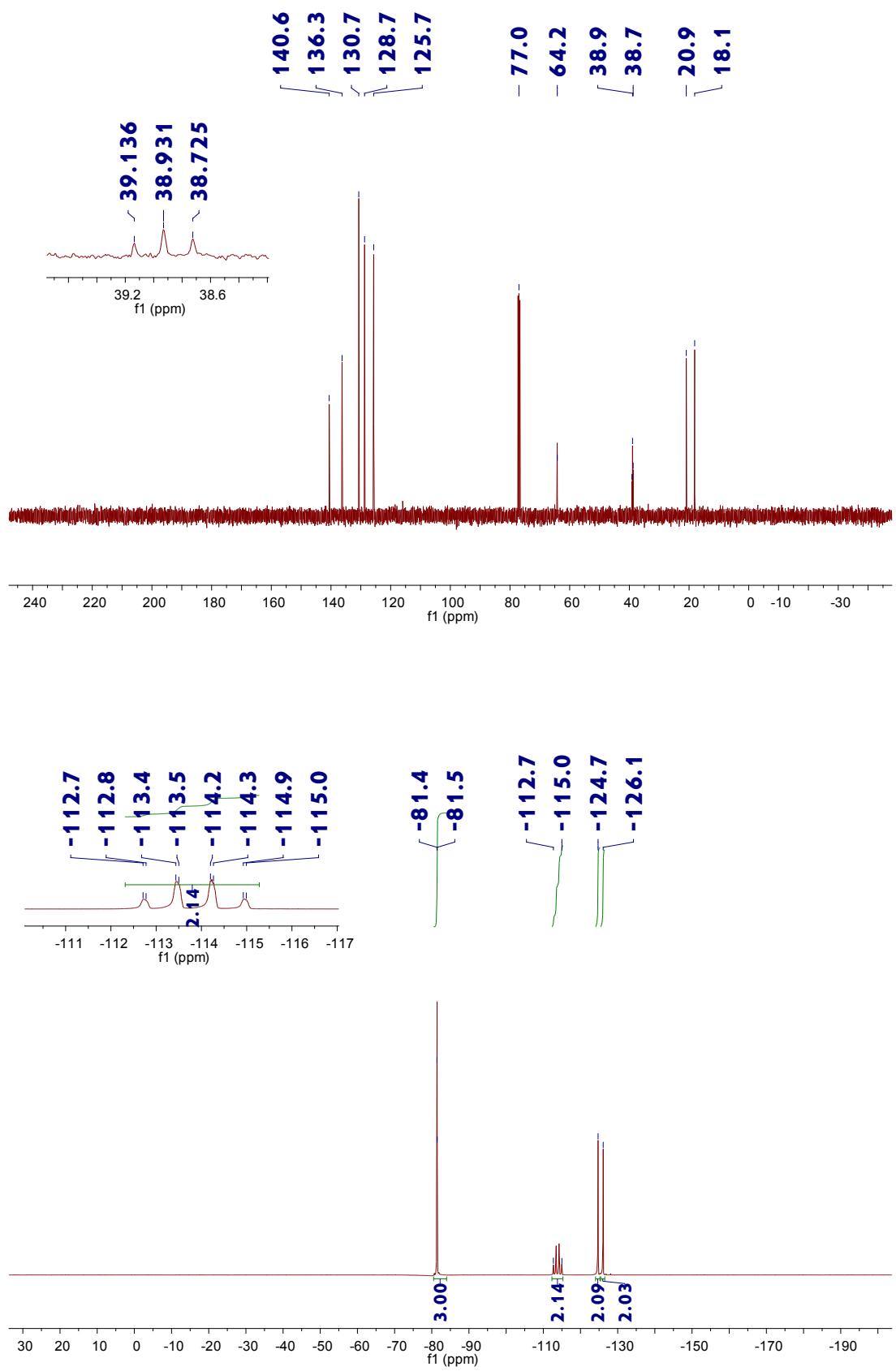
3s



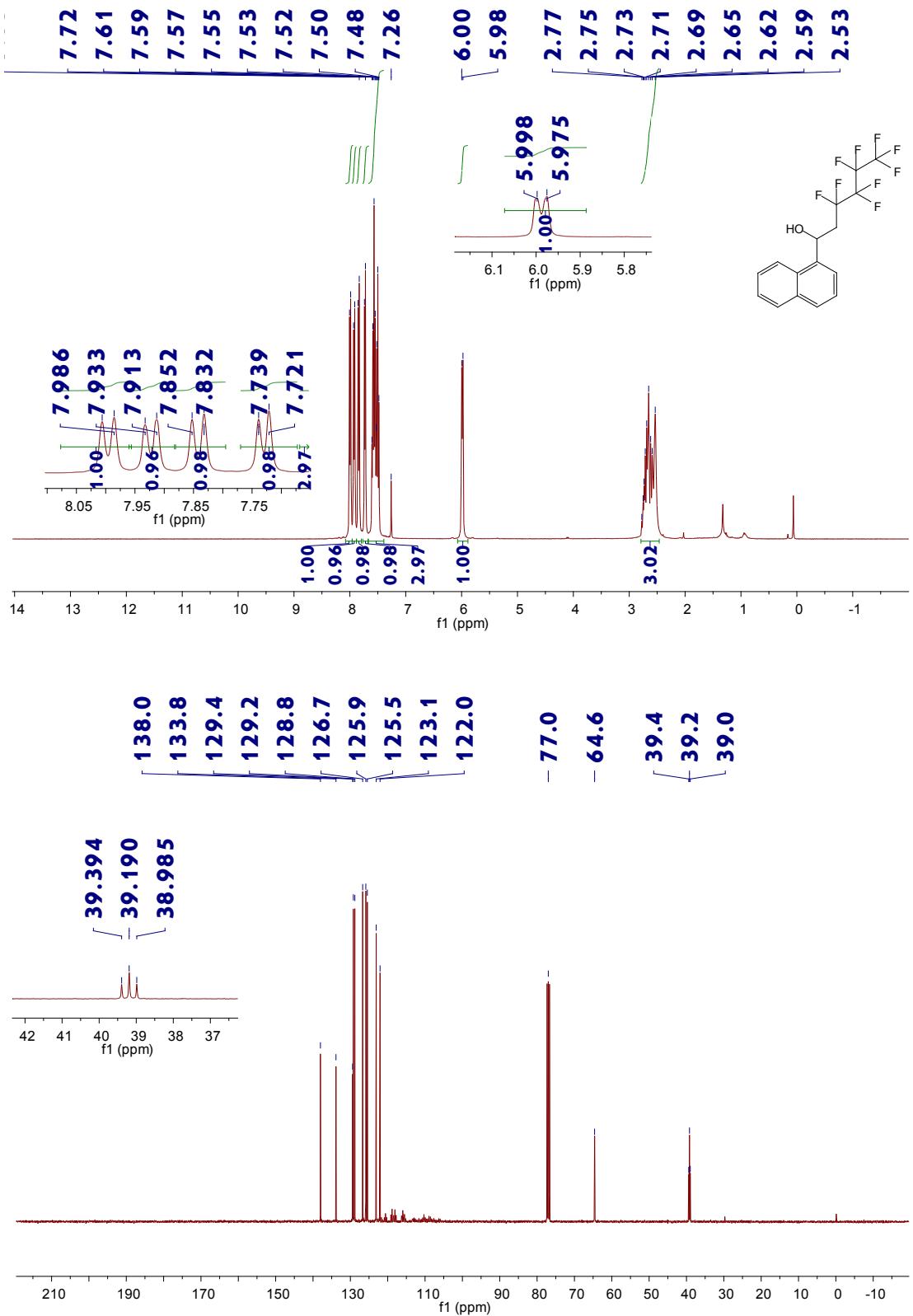


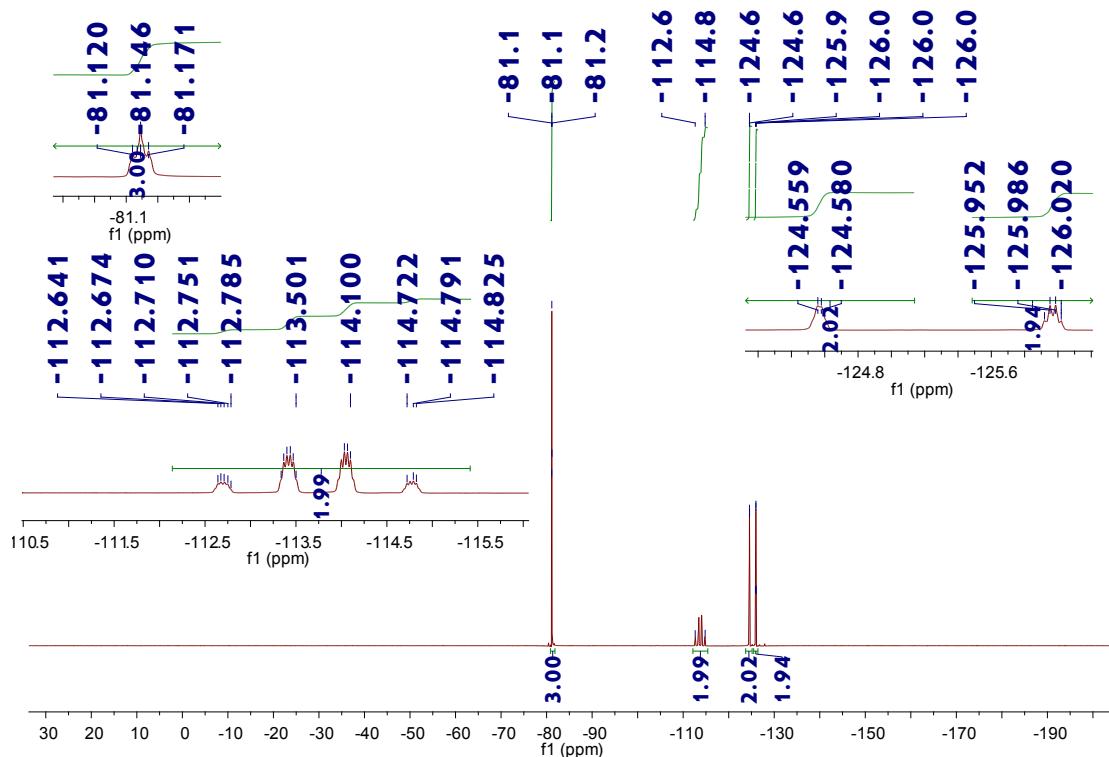
### 3s (under condition B)



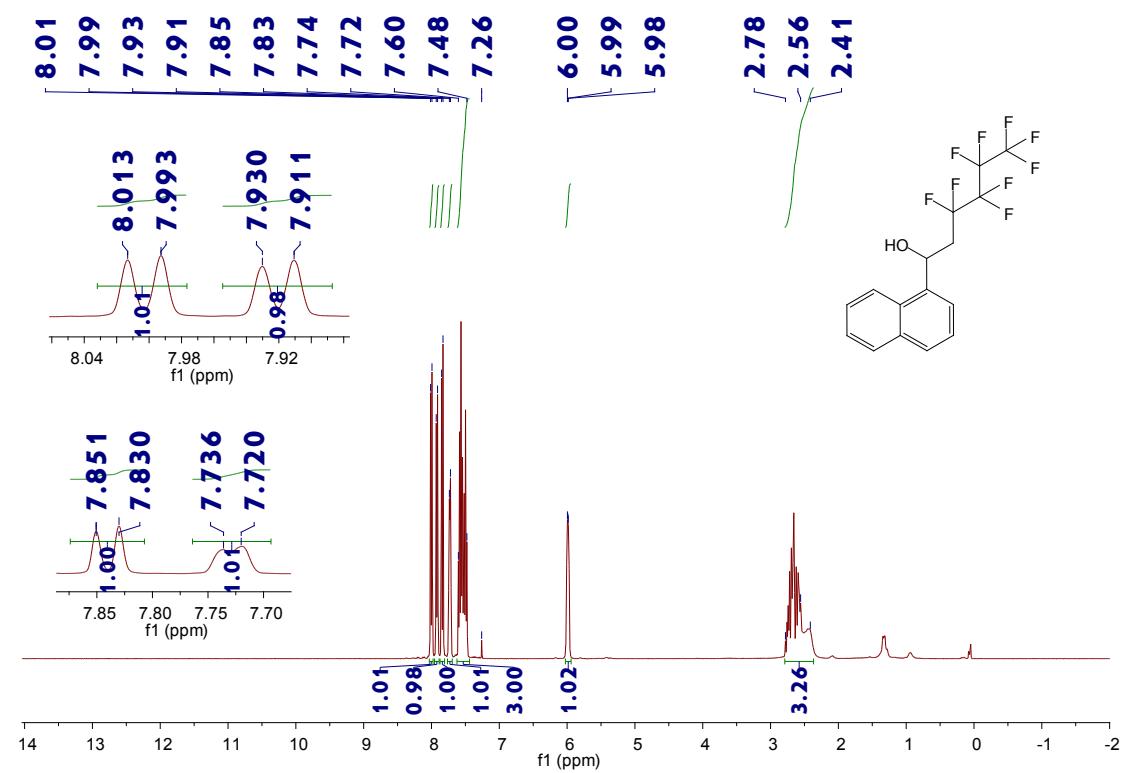


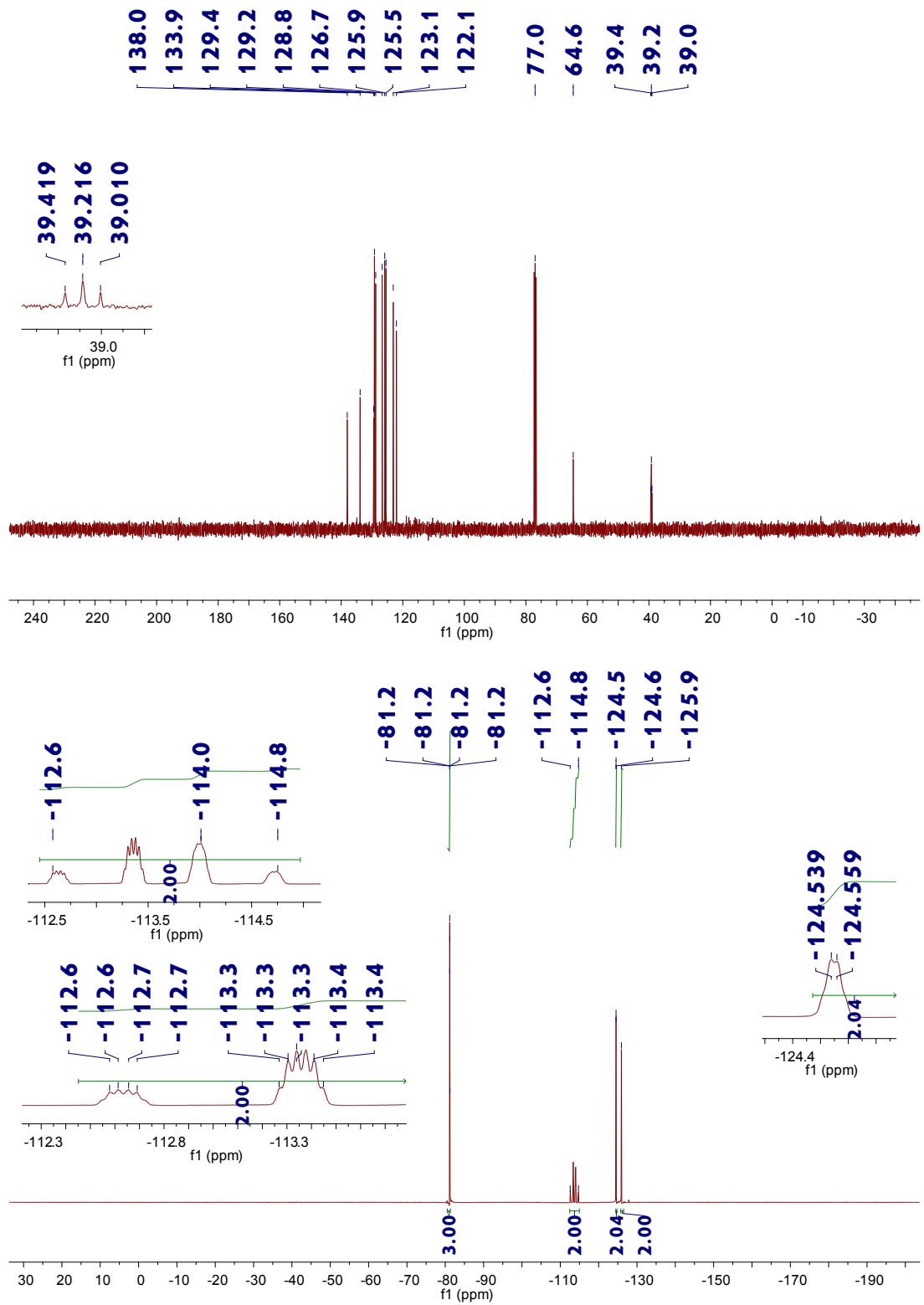
**3t**



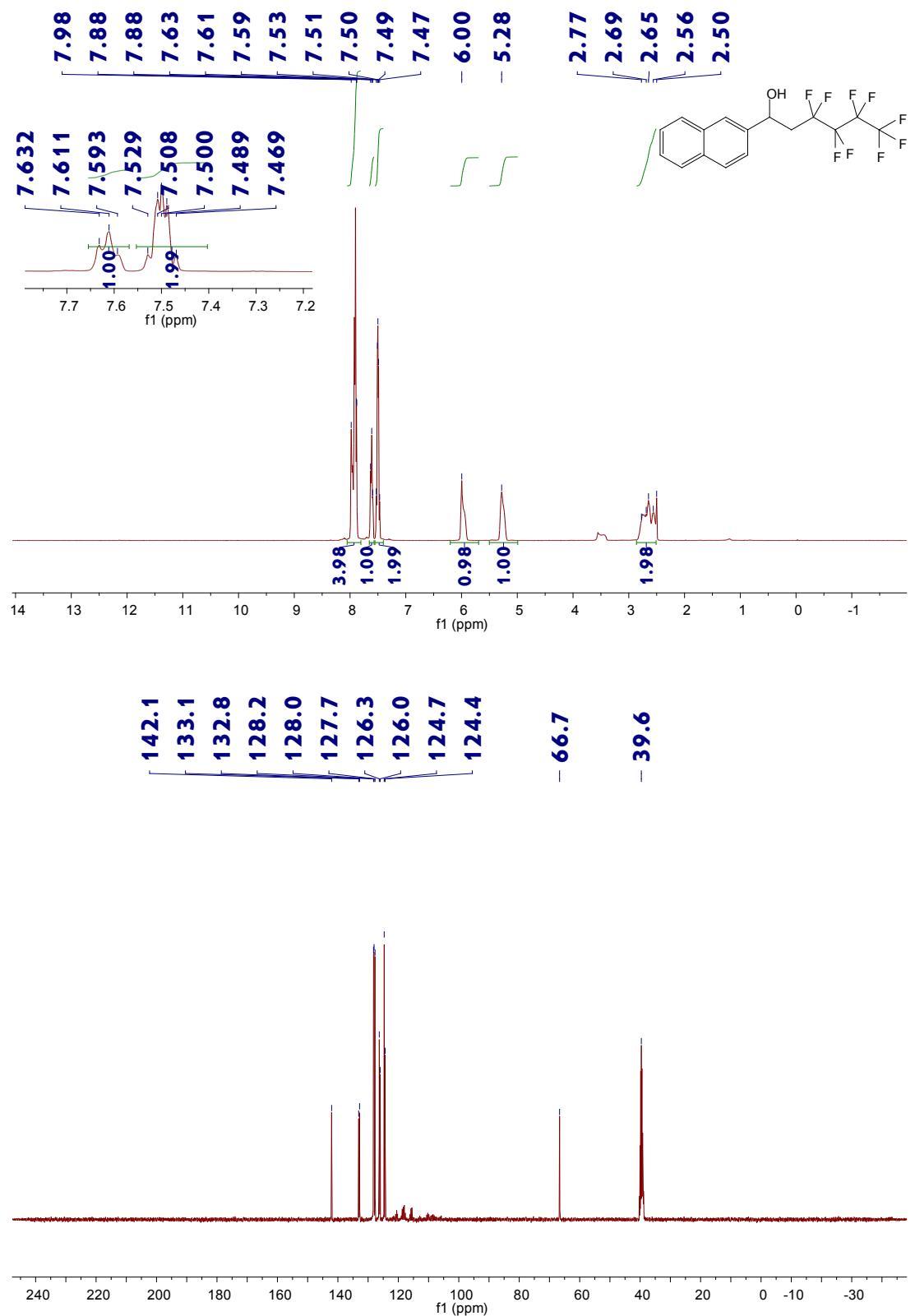


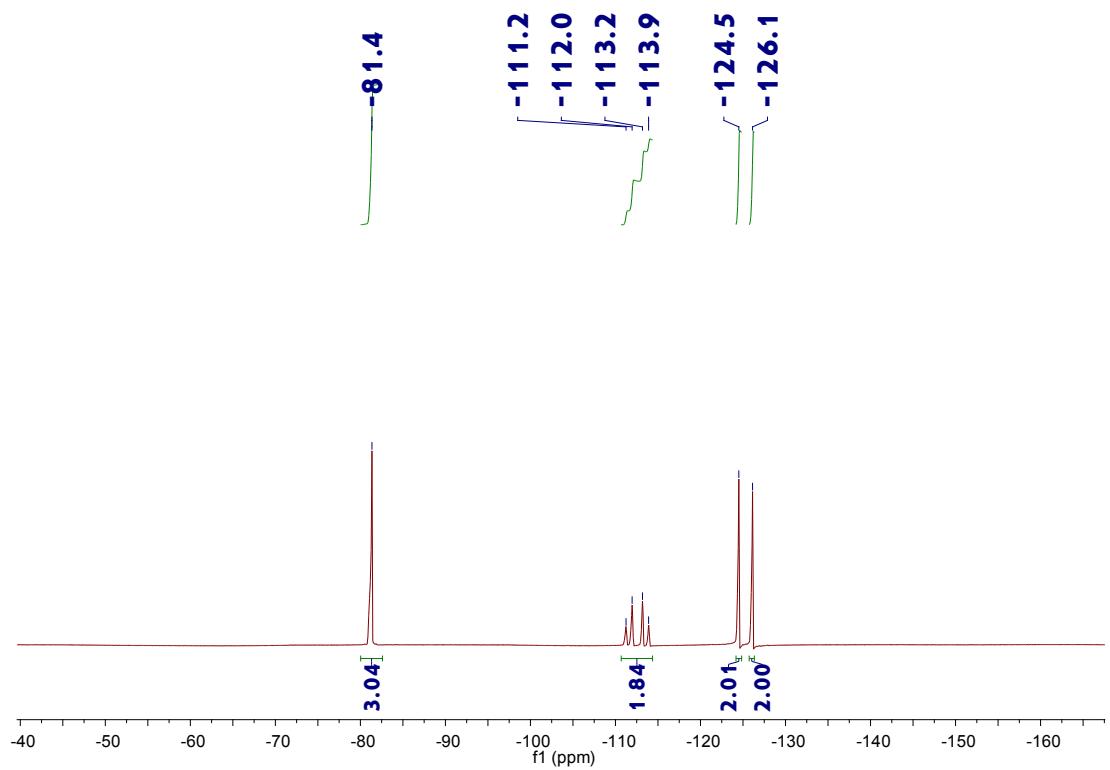
### 3t (under condition B)



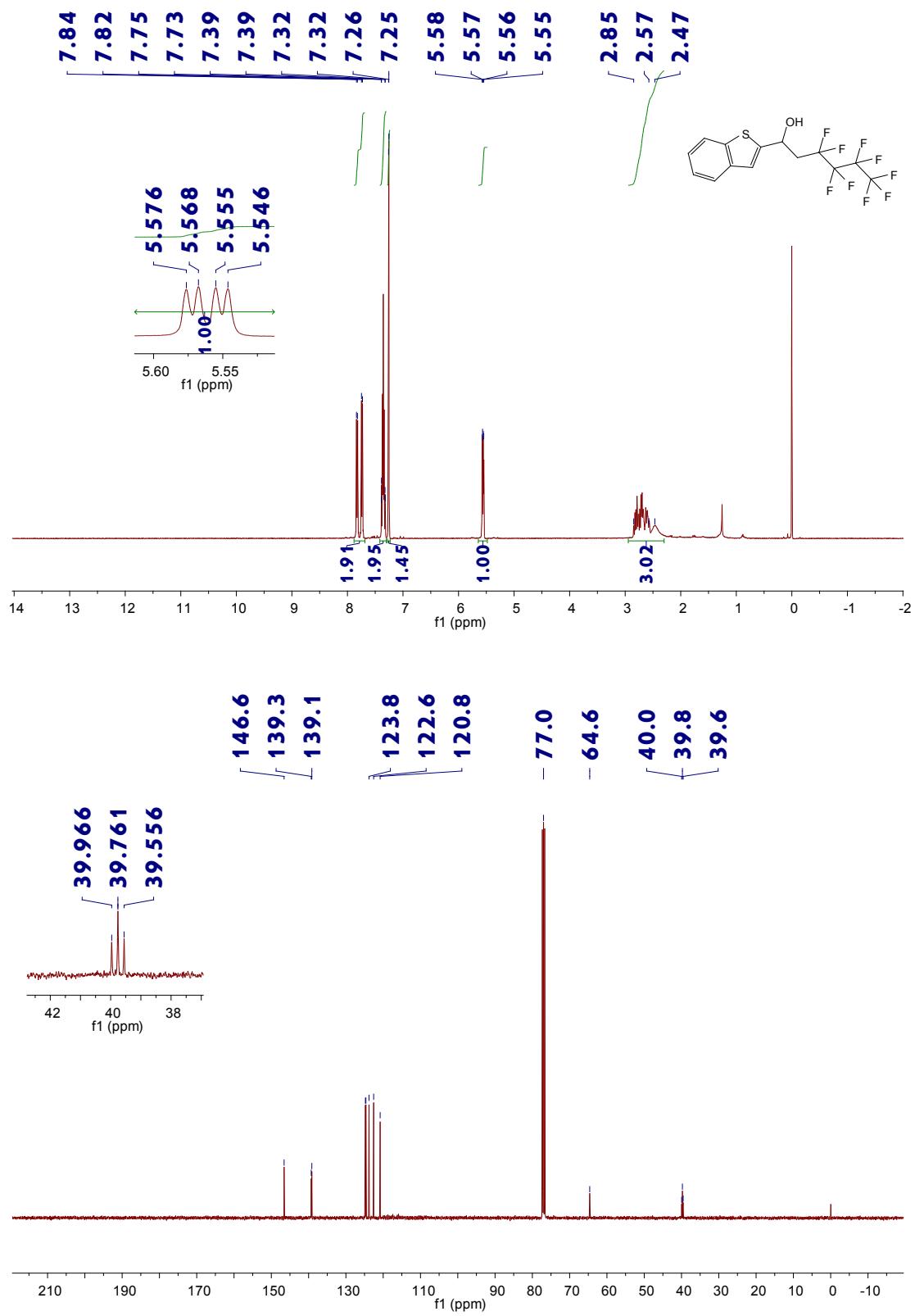


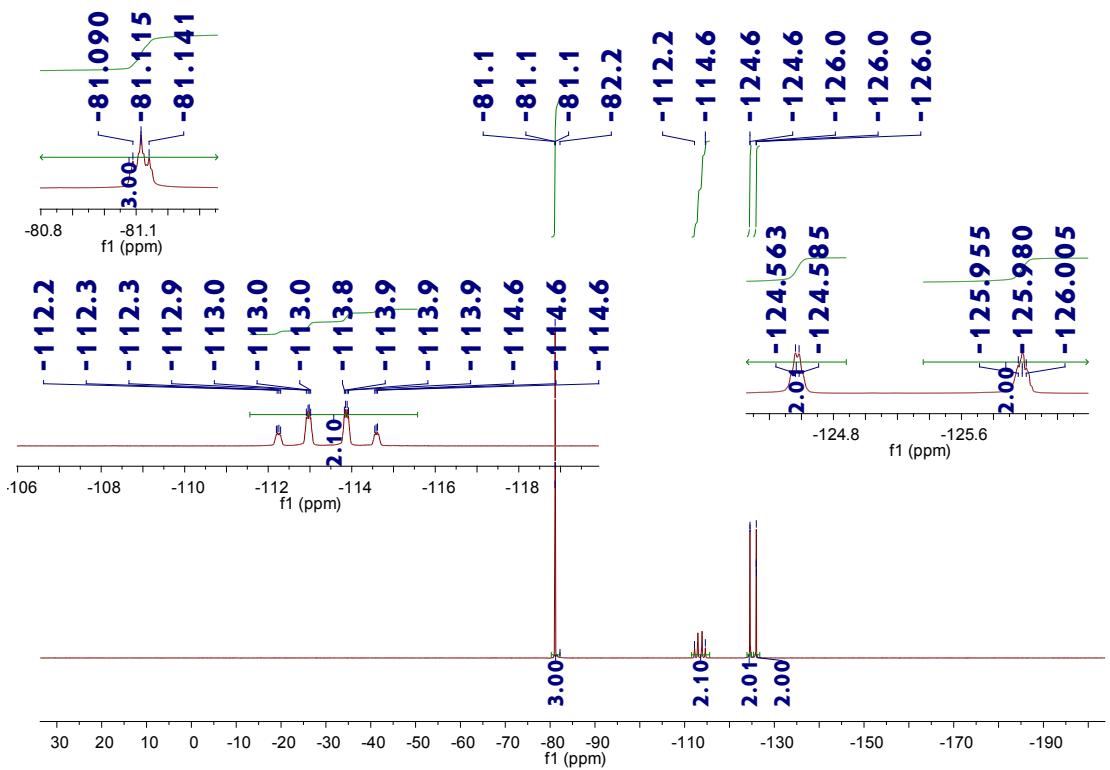
**3u**



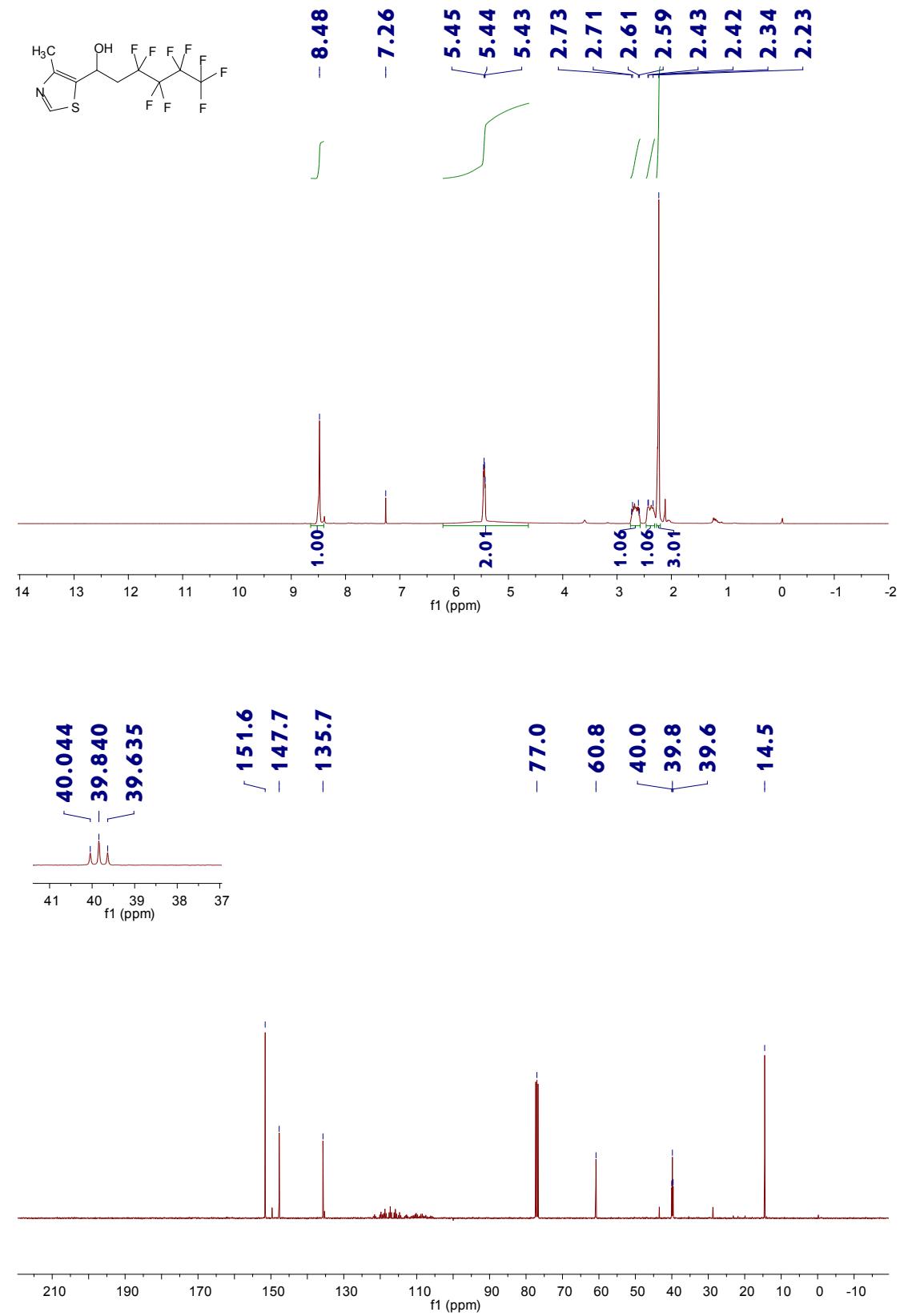


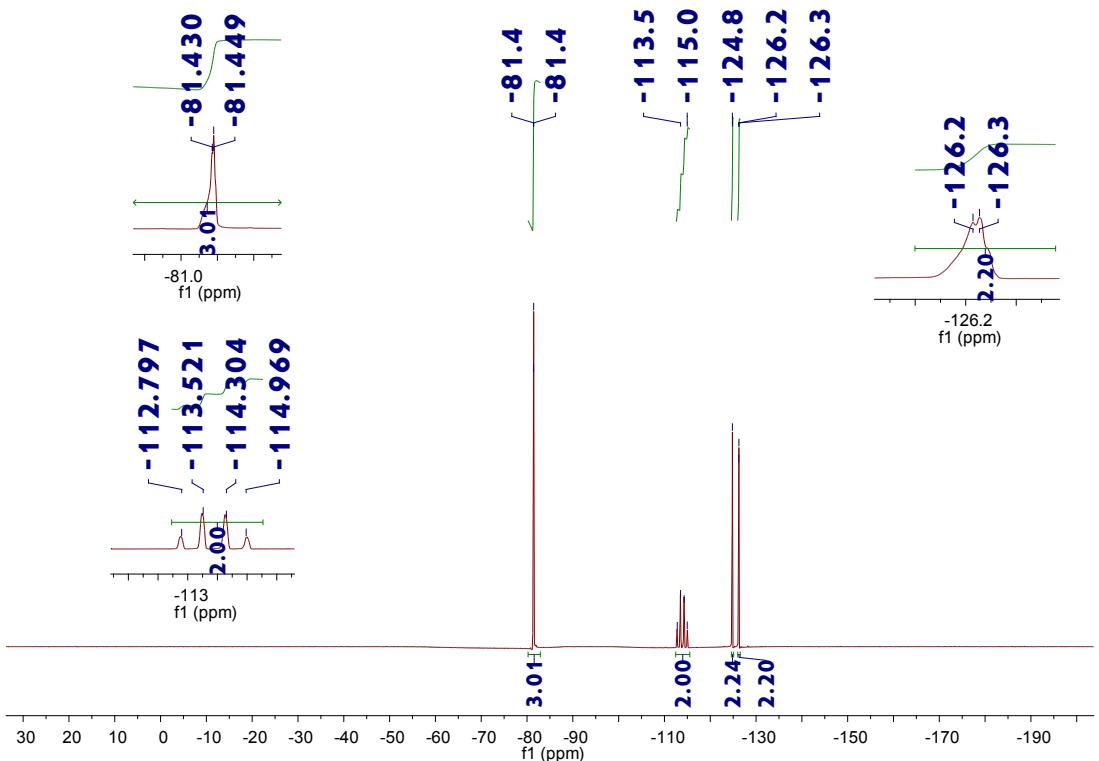
3v



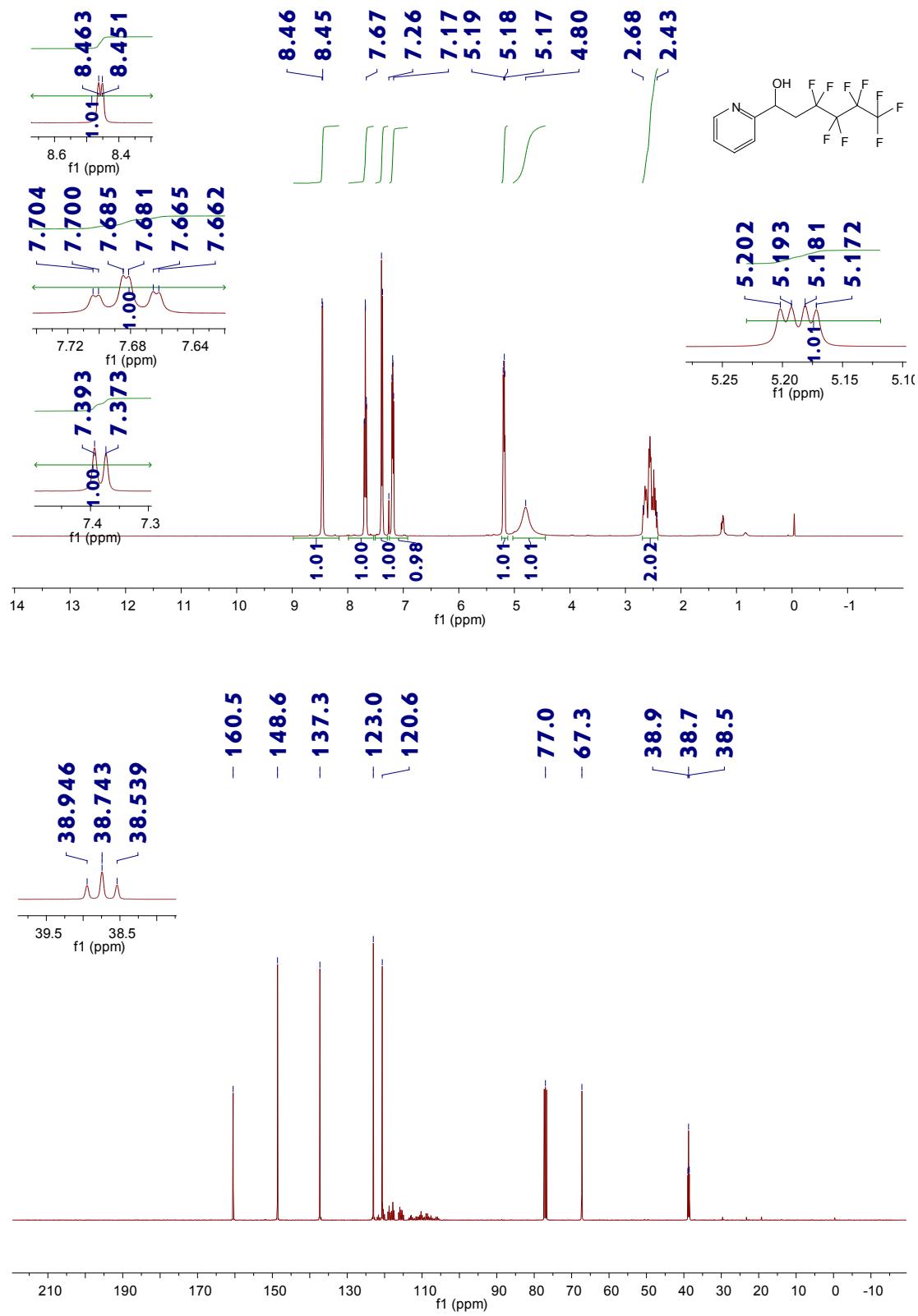


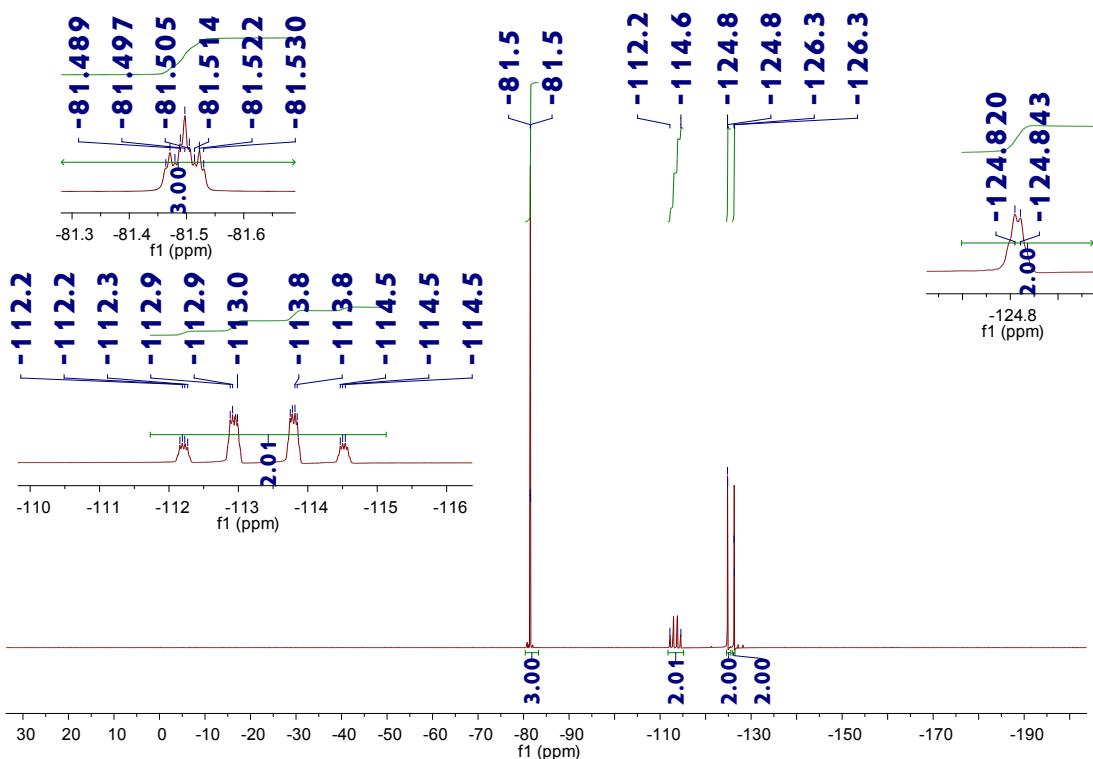
**3w**



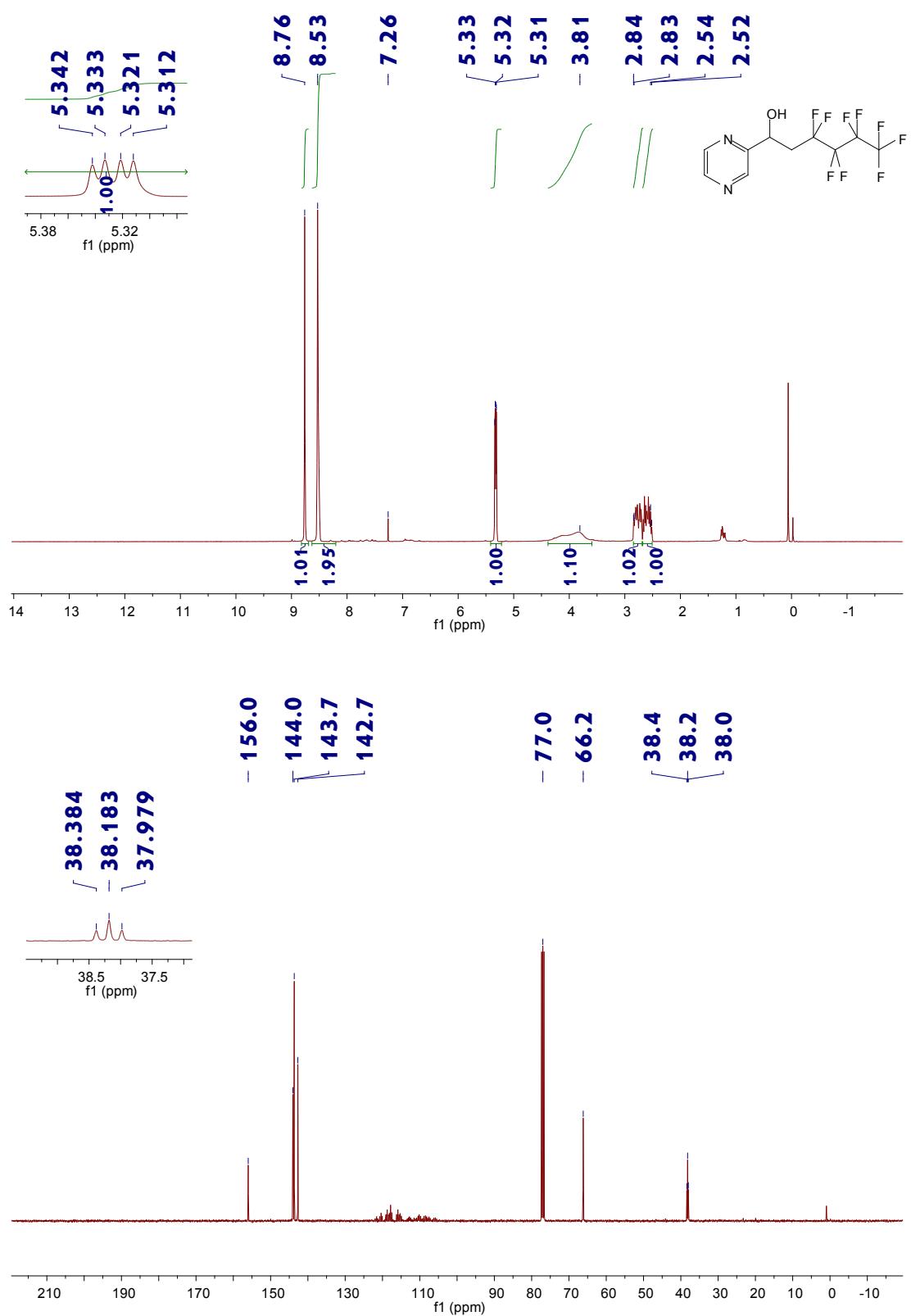


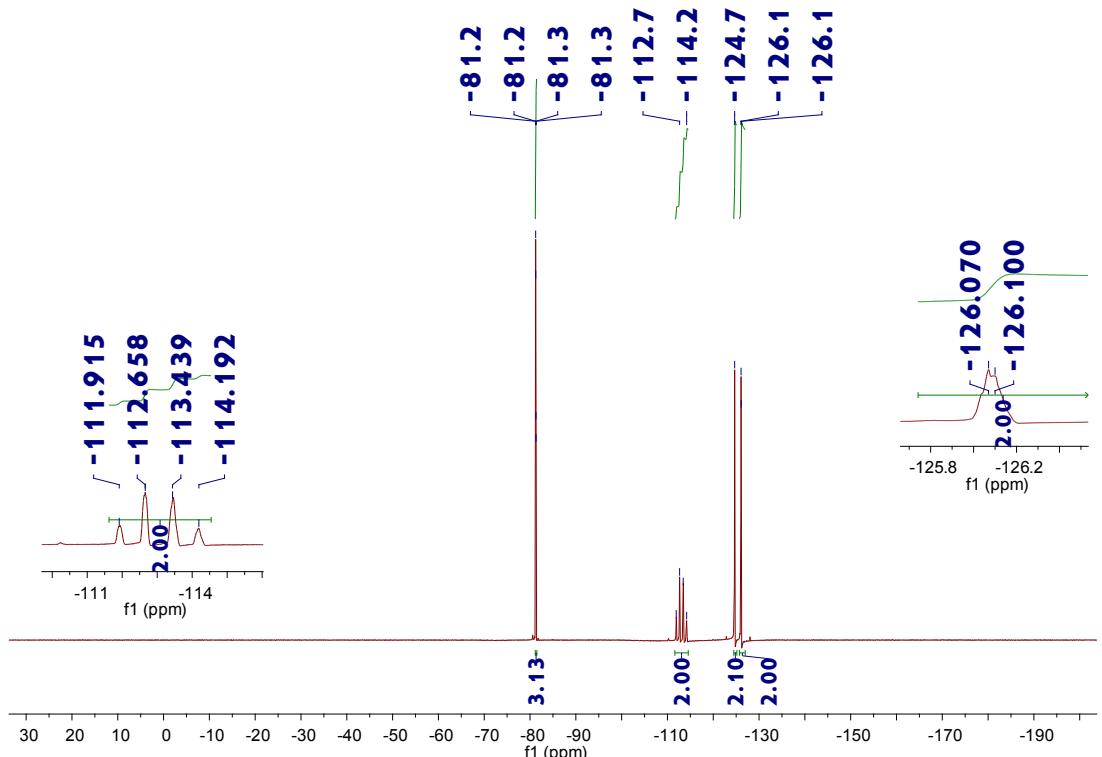
3x



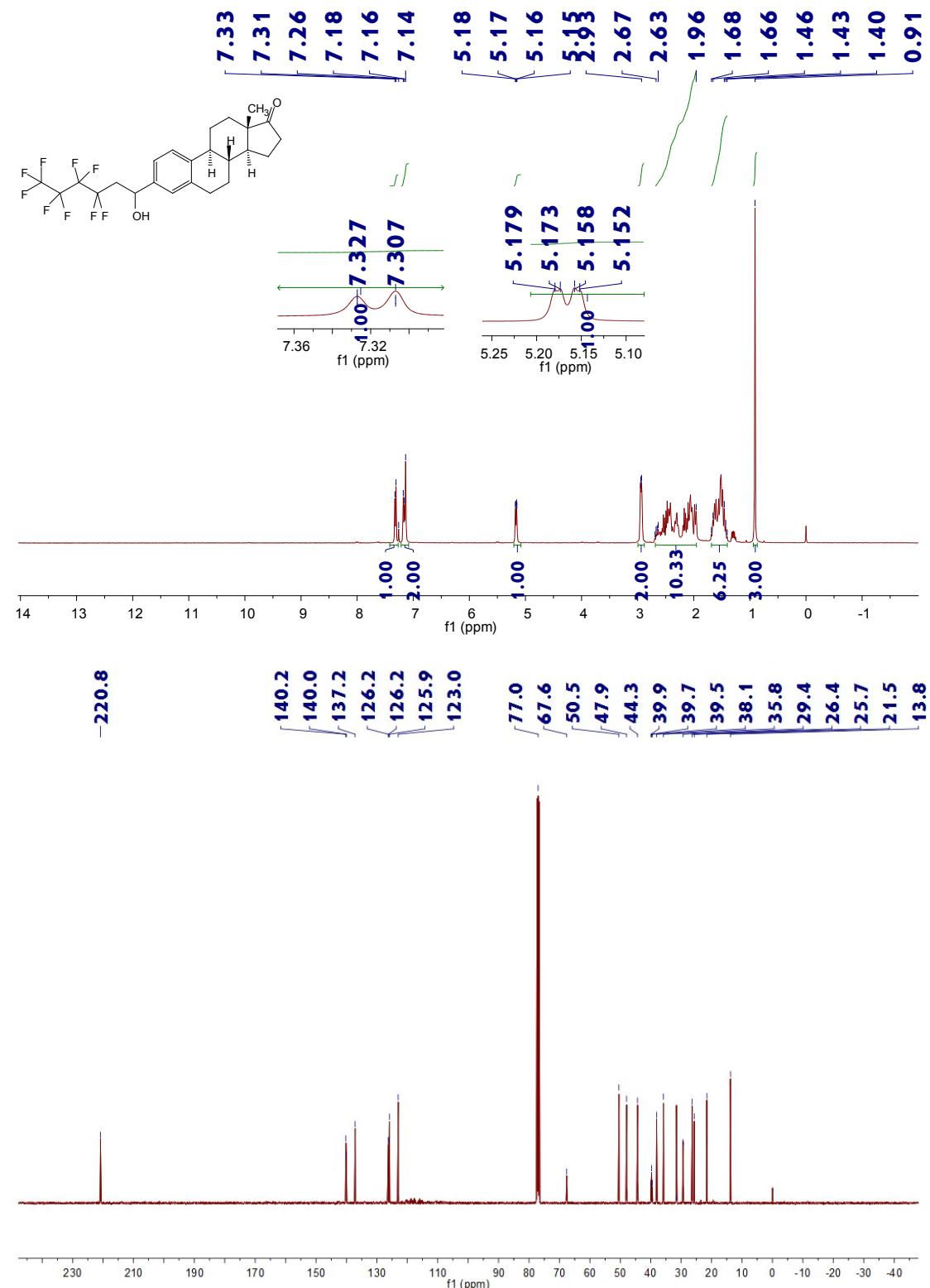


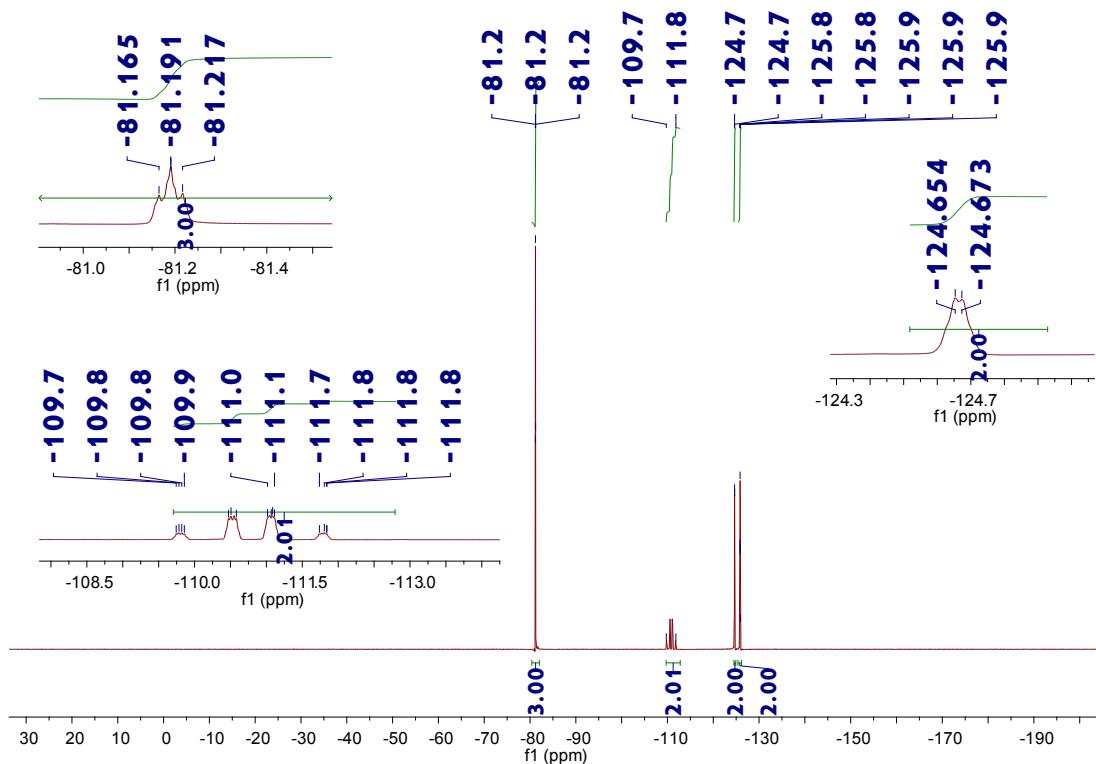
**3y**



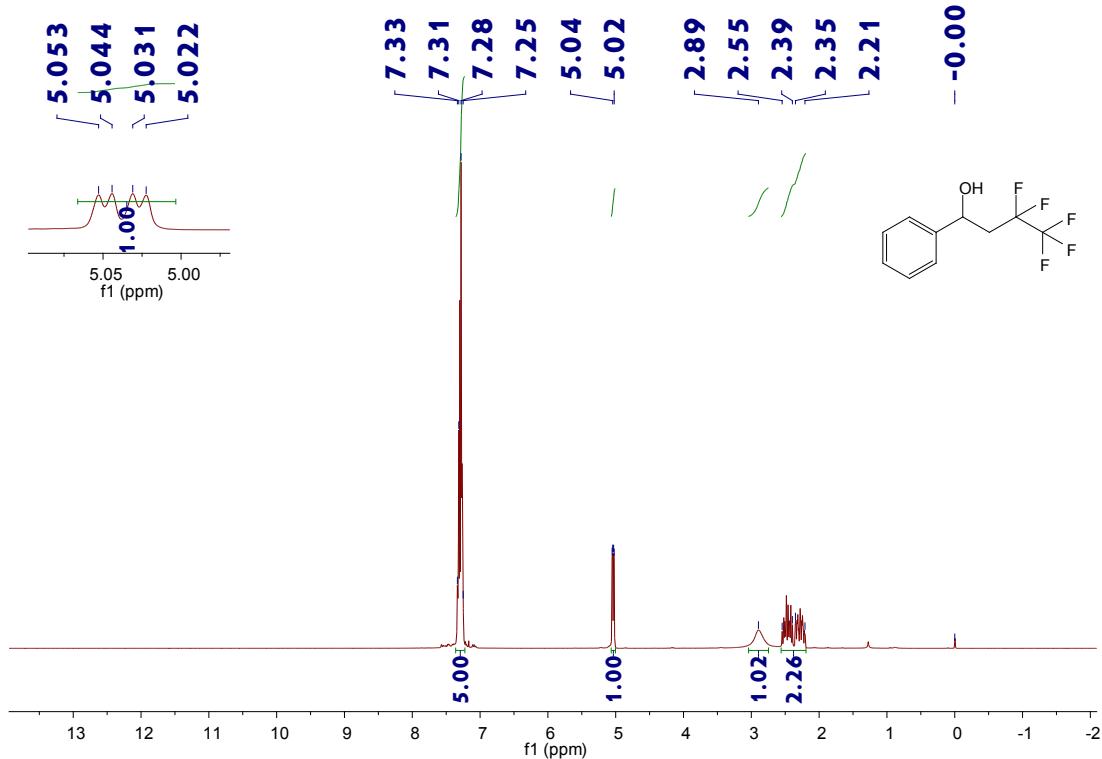


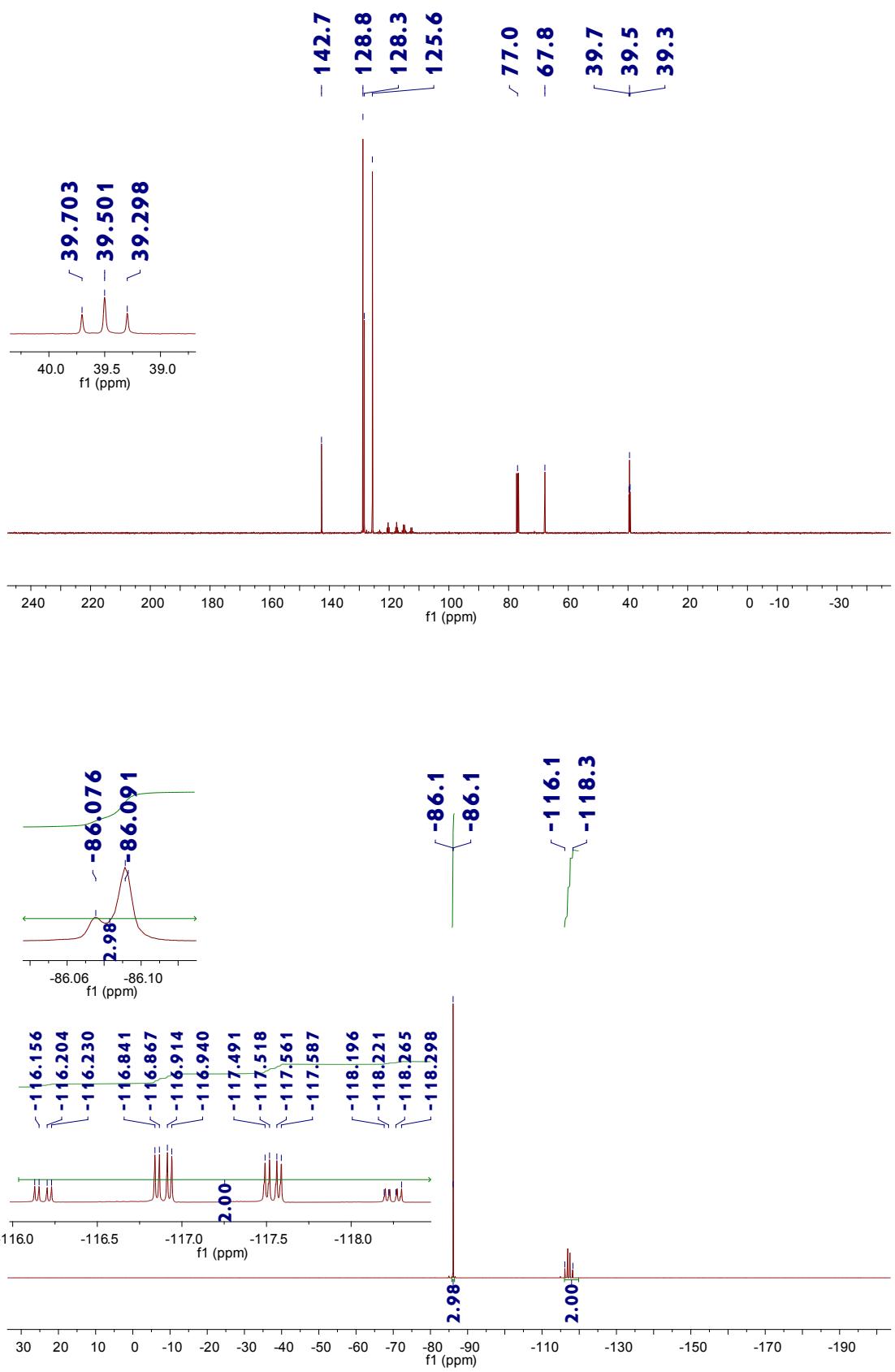
**3z**





**3aa**





**3ab**

