

## ELECTRONIC SUPPORTING INFORMATION

### **Synthesis, properties and evaluation of biological activity of herbicidal ionic liquids with 4-(4-chloro-2-methylphenoxy)butanoate anion**

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*1-Ethyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (1)*

Elemental analysis calculated for C<sub>19</sub>H<sub>30</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 355.90 g mol<sup>-1</sup>) (%): C = 64.12, H = 8.50, N = 3.94; found: C = 64.33, H = 8.78, N = 3.70.

*1-Methyl-1-propylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (2)*

Elemental analysis calculated for C<sub>20</sub>H<sub>32</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 369.93 g mol<sup>-1</sup>) (%): C = 64.94, H = 8.72, N = 3.79; found: C = 64.85, H = 8.89, N = 3.53.

*1-Butyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (3)*

Elemental analysis calculated for C<sub>21</sub>H<sub>34</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 383.95 g mol<sup>-1</sup>) (%): C = 65.69, H = 8.93, N = 3.65; found: C = 65.49, H = 8.71, N = 3.53.

*1-Methyl-1-pentylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (4)*

Elemental analysis calculated for C<sub>22</sub>H<sub>36</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 397.98 g mol<sup>-1</sup>) (%): C = 66.39, H = 9.12, N = 3.52; found: C = 66.79, H = 8.88, N = 3.74.

*1-Hexyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (5)*

Elemental analysis calculated for C<sub>23</sub>H<sub>38</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 412.01 g mol<sup>-1</sup>) (%): C = 67.05, H = 9.30, N = 3.40; found: C = 66.75, H = 9.04, N = 3.62.

*1-Heptyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (6)*

Elemental analysis calculated for C<sub>24</sub>H<sub>40</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 426.03 g mol<sup>-1</sup>) (%): C = 67.66, H = 9.46, N = 3.29; found: C = 67.91, H = 9.12, N = 3.53.

*1-Methyl-1-octylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (7)*

Elemental analysis calculated for C<sub>25</sub>H<sub>42</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 440.06 g mol<sup>-1</sup>) (%): C = 68.23, H = 9.62, N = 3.18; found: C = 67.99, H = 9.48, N = 3.45.

*1-Methyl-1-nonylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (8)*

Elemental analysis calculated for C<sub>26</sub>H<sub>44</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 454.09 g mol<sup>-1</sup>) (%): C = 68.77, H = 9.77, N = 3.08; found: C = 68.43, H = 9.60, N = 3.23.

*1-Decyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (9)*

Elemental analysis calculated for C<sub>27</sub>H<sub>46</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 468.11 g mol<sup>-1</sup>) (%): C = 69.28, H = 9.90, N = 2.99; found: C = 69.05, H = 9.68, N = 3.21.

*I-Methyl-1-undecylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (10)*

Elemental analysis calculated for C<sub>28</sub>H<sub>48</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 482.14 g mol<sup>-1</sup>) (%): C = 69.75, H = 10.03, N = 2.91; found: C = 69.98, H = 10.35, N = 3.30.

*I-Dodecyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (11)*

Elemental analysis calculated for C<sub>29</sub>H<sub>50</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 496.17 g mol<sup>-1</sup>) (%): C = 70.20, H = 10.16, N = 2.82; found: C = 69.99, H = 9.88, N = 3.03.

*I-Methyl-1-tetradecylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (12)*

Elemental analysis calculated for C<sub>31</sub>H<sub>54</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 524.22 g mol<sup>-1</sup>) (%): C = 71.03, H = 10.38, N = 2.67; found: C = 71.24, H = 10.13, N = 2.91.

*I-Hexadecyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (13)*

Elemental analysis calculated for C<sub>33</sub>H<sub>58</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 552.27 g mol<sup>-1</sup>) (%): C = 71.77, H = 10.59, N = 2.54; found: C = 71.51, H = 10.37, N = 2.82.

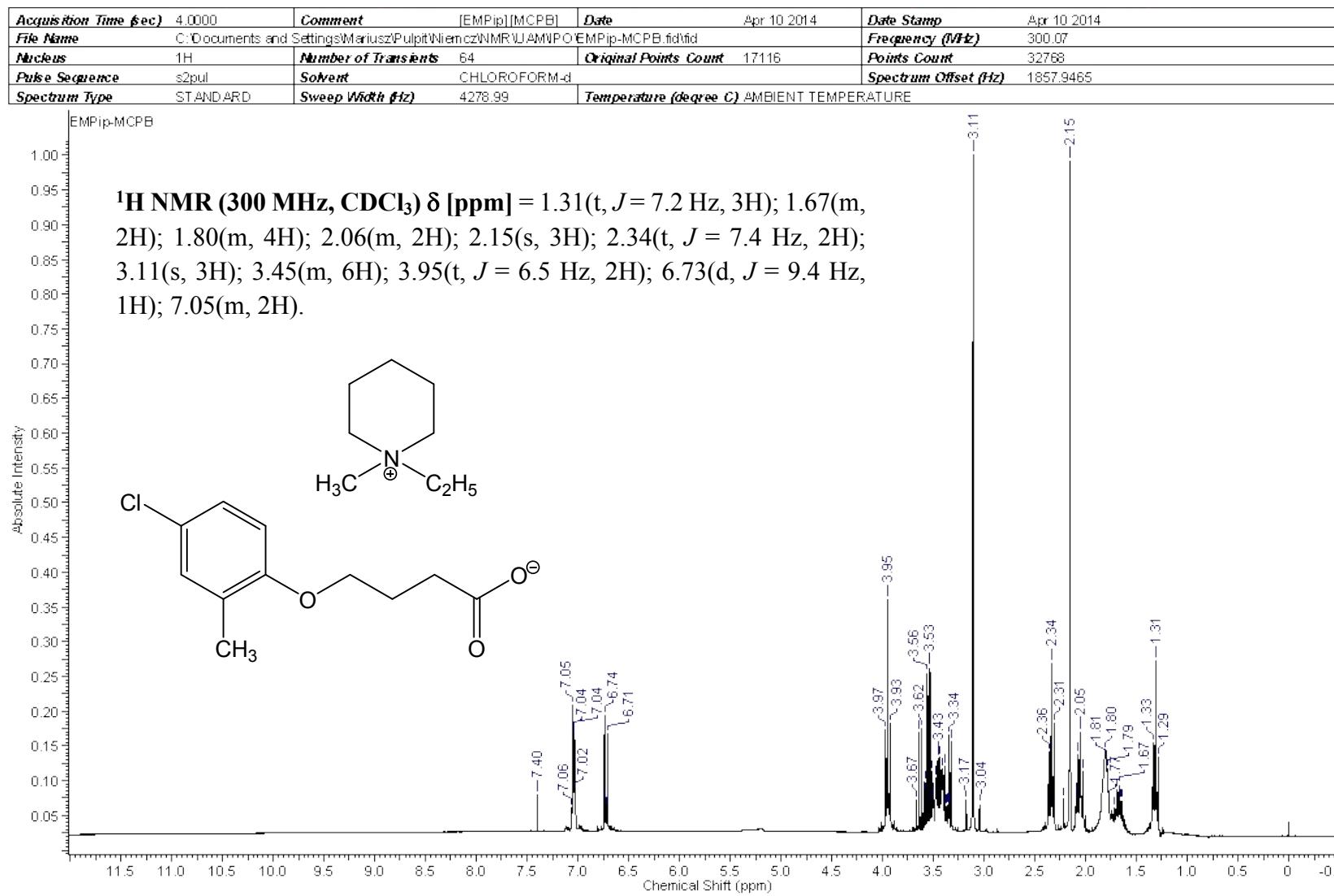
*I-Methyl-1-octadecylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (14)*

Elemental analysis calculated for C<sub>35</sub>H<sub>62</sub>ClNO<sub>3</sub> (M<sub>mol</sub> = 580.32 g mol<sup>-1</sup>) (%): C = 72.44, H = 10.77, N = 2.41; found: C = 72.59, H = 10.93, N = 2.61.

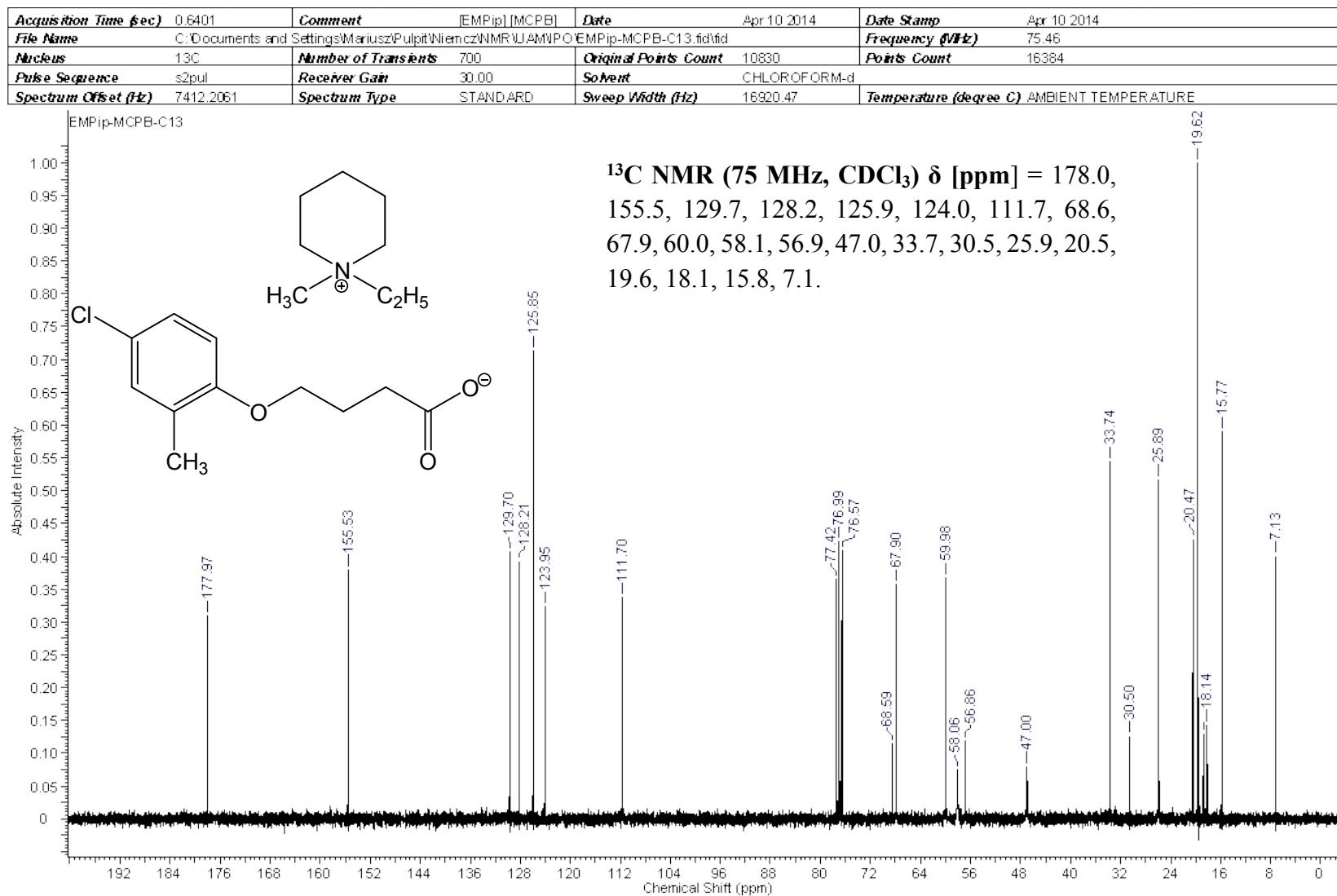
The following abbreviations were used to explain the multiplicities:

s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintuplet, sext = sextet, sep = septet.

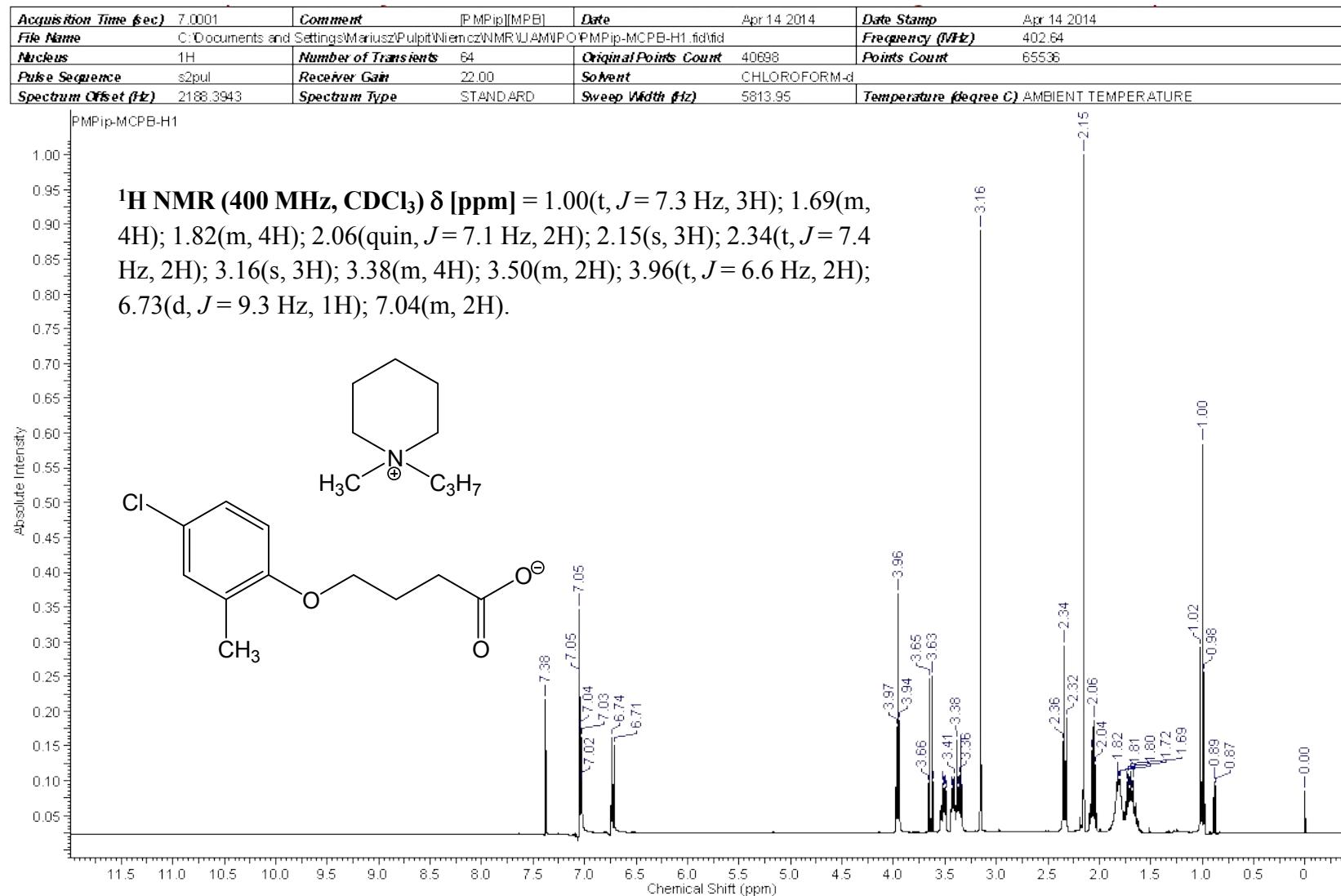
**Figure S1.**  $^1\text{H}$  NMR spectrum of 1-ethyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**1**).



**Figure S2.**  $^{13}\text{C}$  NMR spectrum of 1-ethyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**1**).

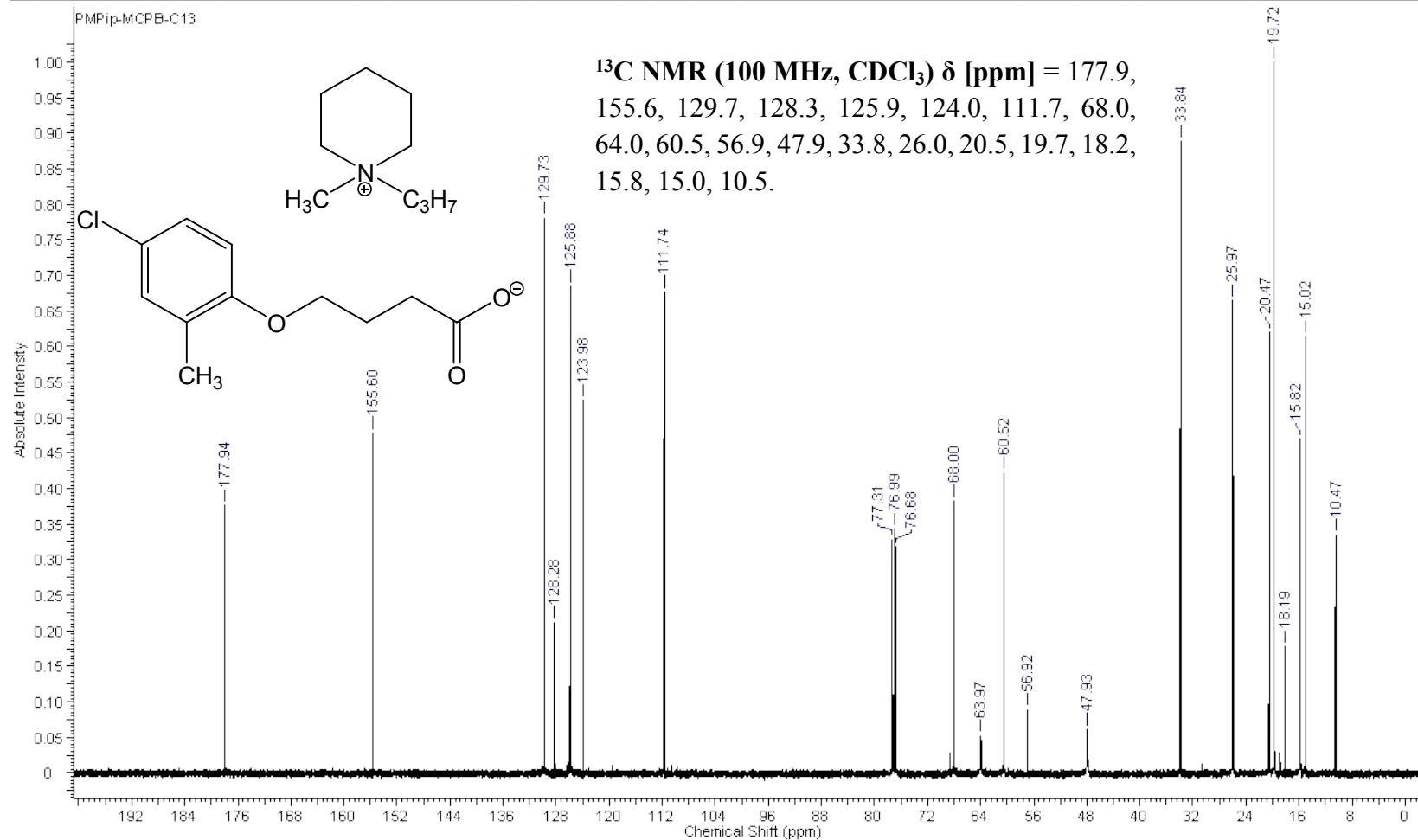


**Figure S3.**  $^1\text{H}$  NMR spectrum of 1-methyl-1-propylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**2**).

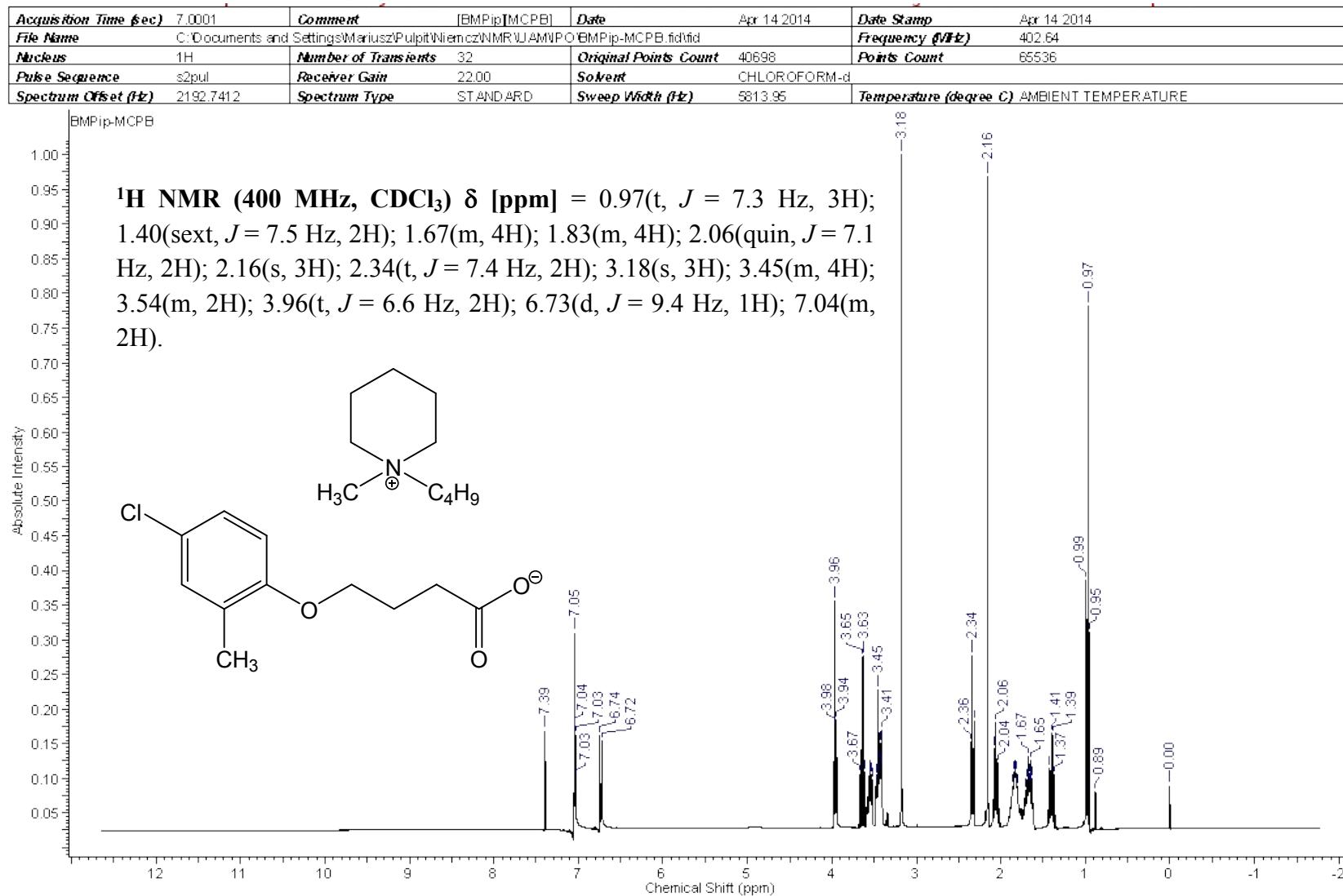


**Figure S4.**  $^{13}\text{C}$  NMR spectrum of 1-methyl-1-propylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**2**).

Acquisition Time (sec)	1.3006	Comment	[PMPip][MCPB]	Date	Apr 14 2014	Date Stamp	Apr 14 2014
File Name	C:\Documents and Settings\Marusz\Pulpit\NiemczNMR\JAMNPO\MPip-MCPB-C13.fidfid					Frequency (MHz)	101.26
Nucleus	$^{13}\text{C}$	Number of Transients	1024	Original Points Count	31878	Points Count	32768
Pulse Sequence	s2pul	Receiver Gain	36.00	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	11115.3262	Spectrum Type	STANDARD	Sweep Width (Hz)	24509.80	Temperature (degree C)	AMBIENT TEMPERATURE

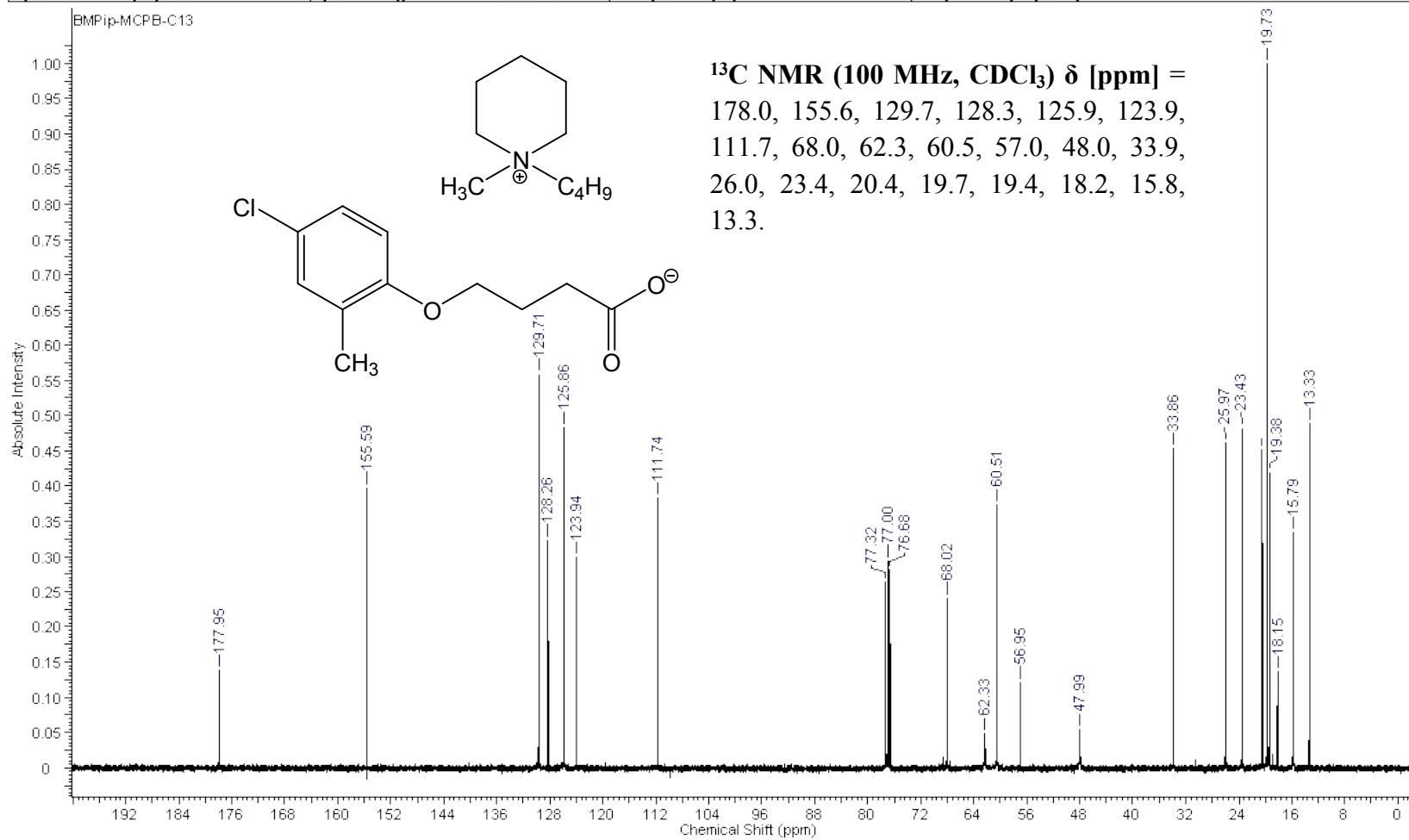


**Figure S5.**  $^1\text{H}$  NMR spectrum of 1-butyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**3**).

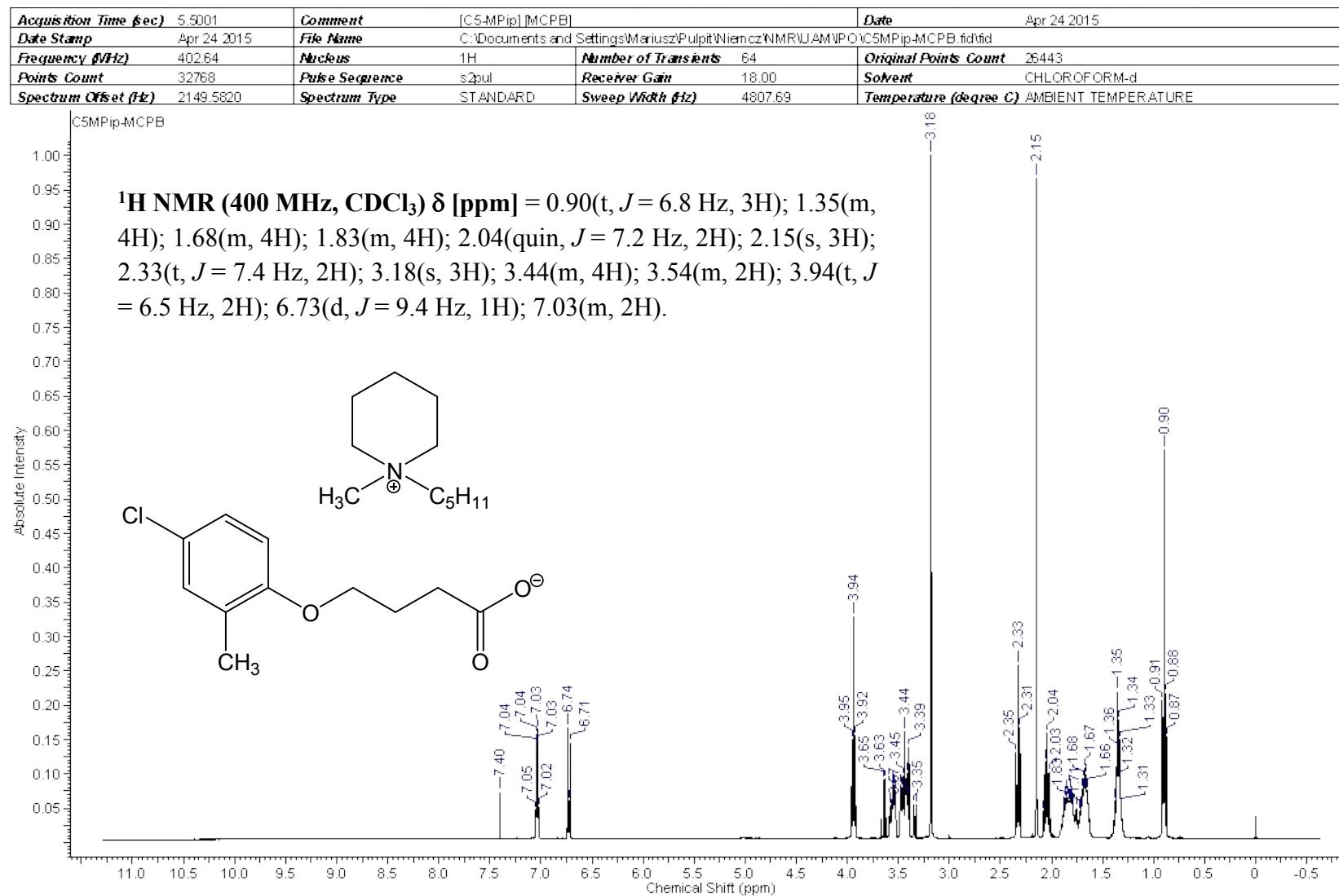


**Figure S6.**  $^{13}\text{C}$  NMR spectrum of 1-butyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**3**).

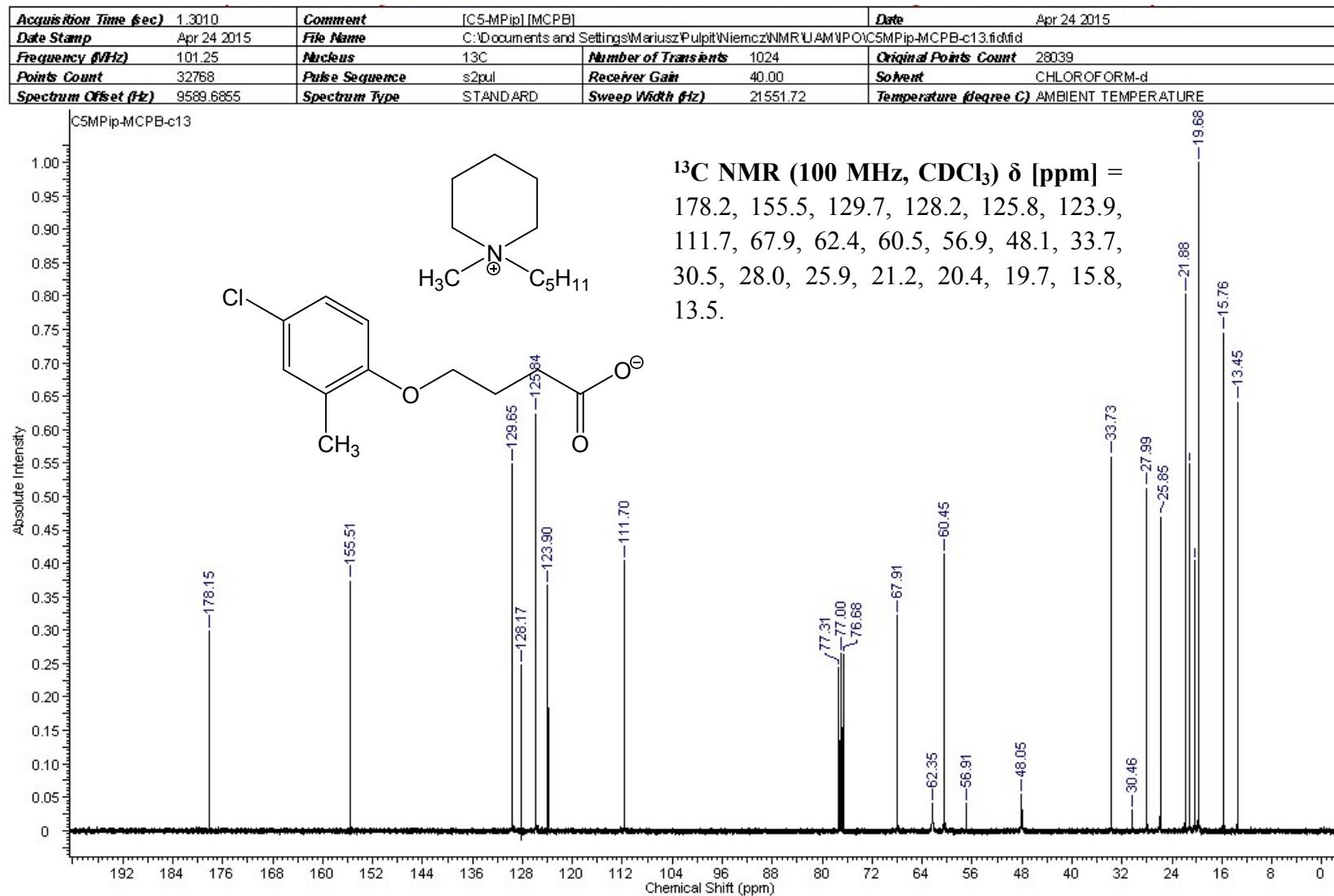
Acquisition Time (sec)	1.3006	Comment	[BMPip][MCPB]	Date	Apr 14 2014	Date Stamp	Apr 14 2014
File Name	C:\Documents and Settings\Marusz\Pulpit\Niencz\NMR\UAM\PO\BMPip-MCPB-C13.fidfid					Frequency (MHz)	101.26
Nucleus	$^{13}\text{C}$	Number of Transients	904	Original Points Count	31878	Points Count	32768
Pulse Sequence	s2pul	Receiver Gain	36.00	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	11114.2031	Spectrum Type	STANDARD	Sweep Width (Hz)	24509.80	Temperature (degree C)	AMBIENT TEMPERATURE



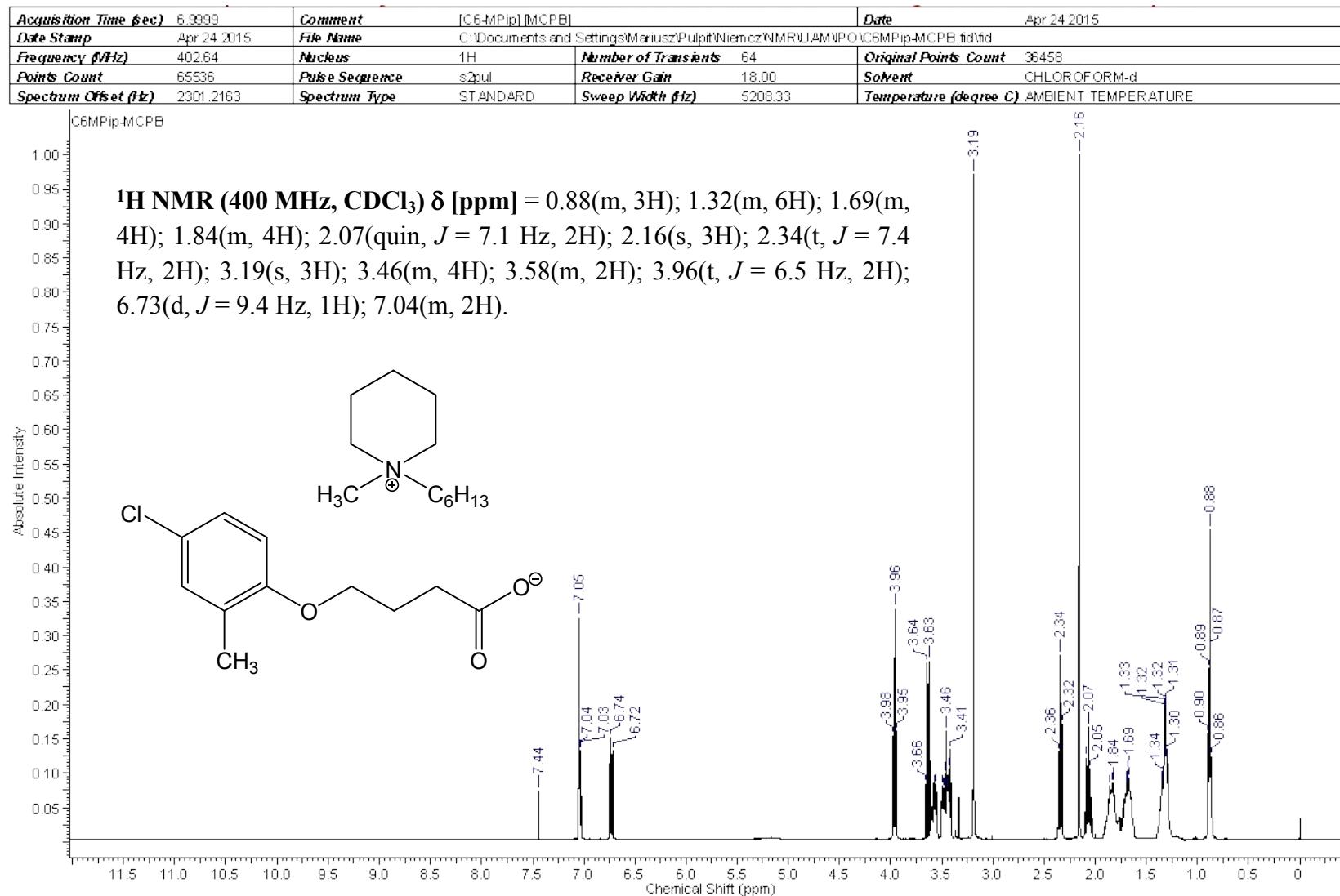
**Figure S7.**  $^1\text{H}$  NMR spectrum of 1-methyl-1-pentylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**4**).



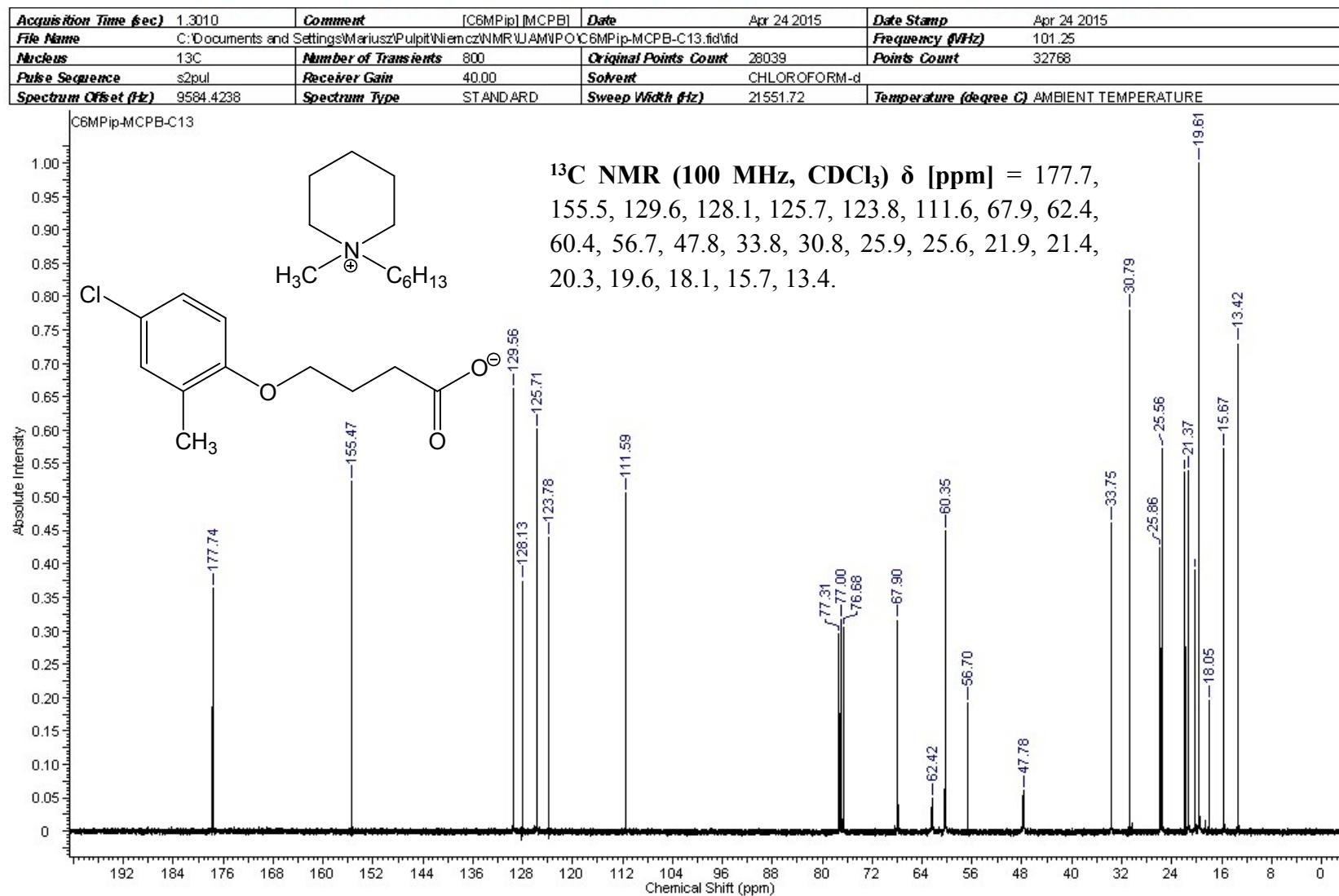
**Figure S8.**  $^{13}\text{C}$  NMR spectrum of 1-methyl-1-pentylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**4**).



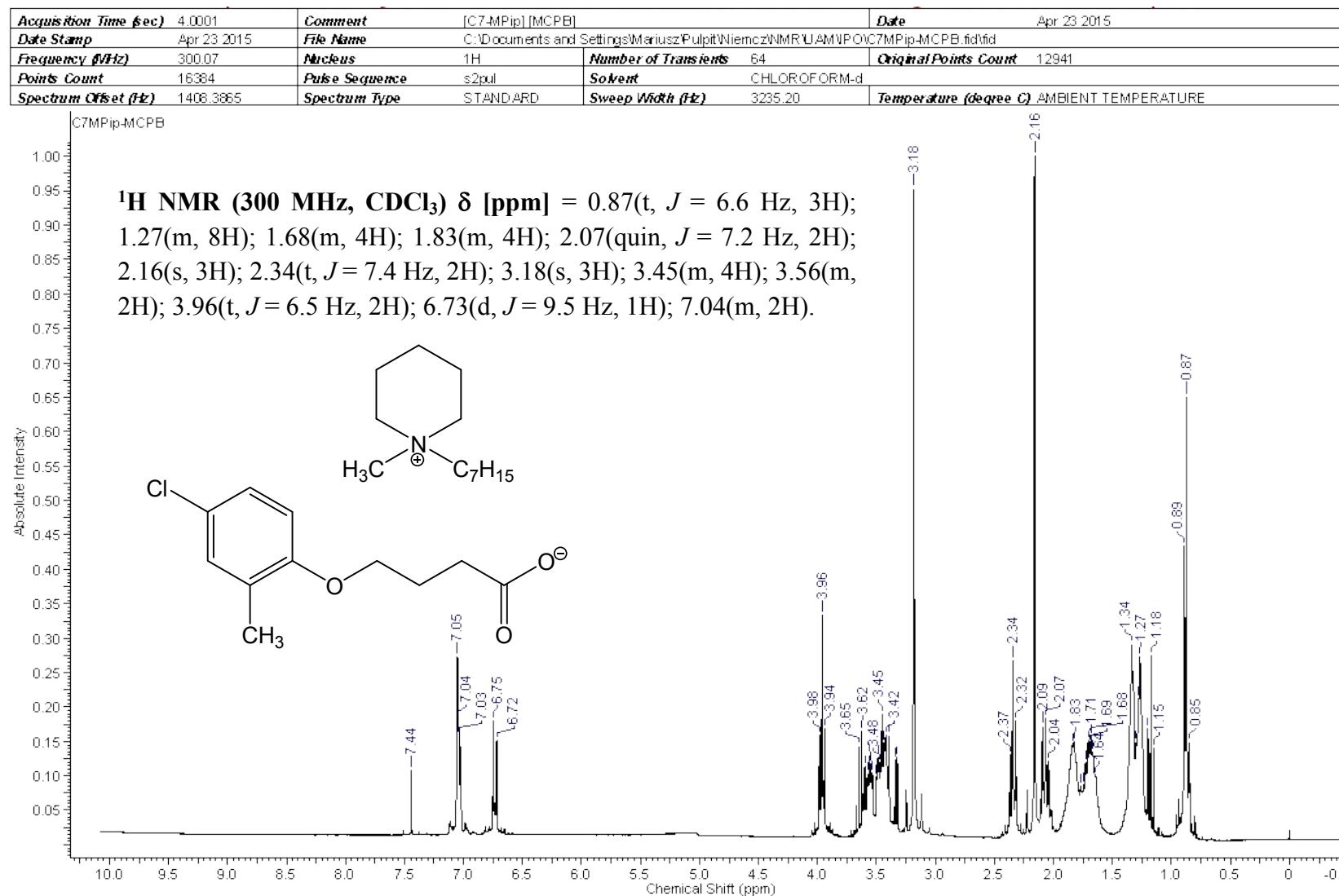
**Figure S9.**  $^1\text{H}$  NMR spectrum of 1-hexyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**5**).



**Figure S10.**  $^{13}\text{C}$  NMR spectrum of 1-hexyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**5**).



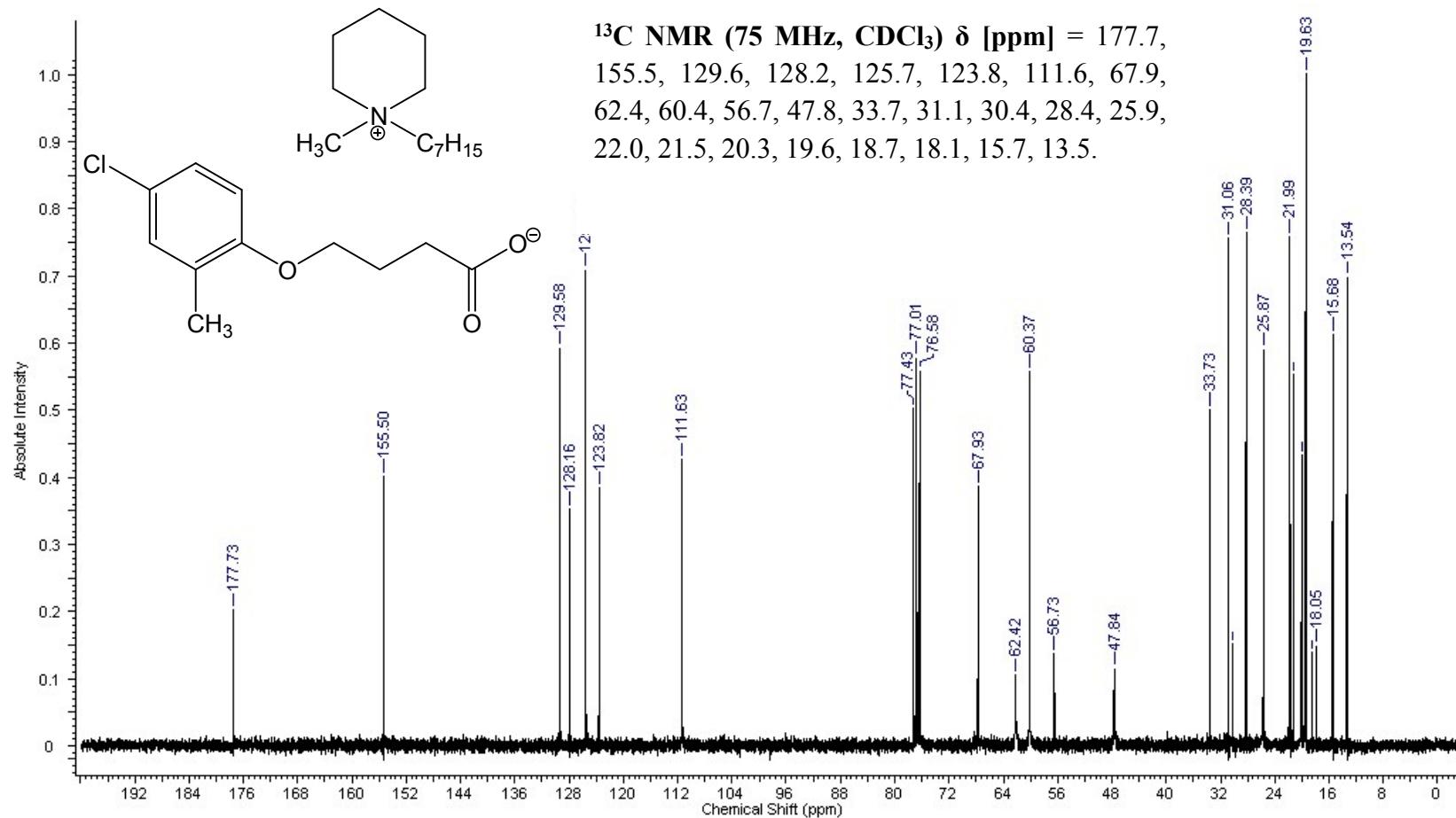
**Figure S11.**  $^1\text{H}$  NMR spectrum of 1-heptyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**6**).



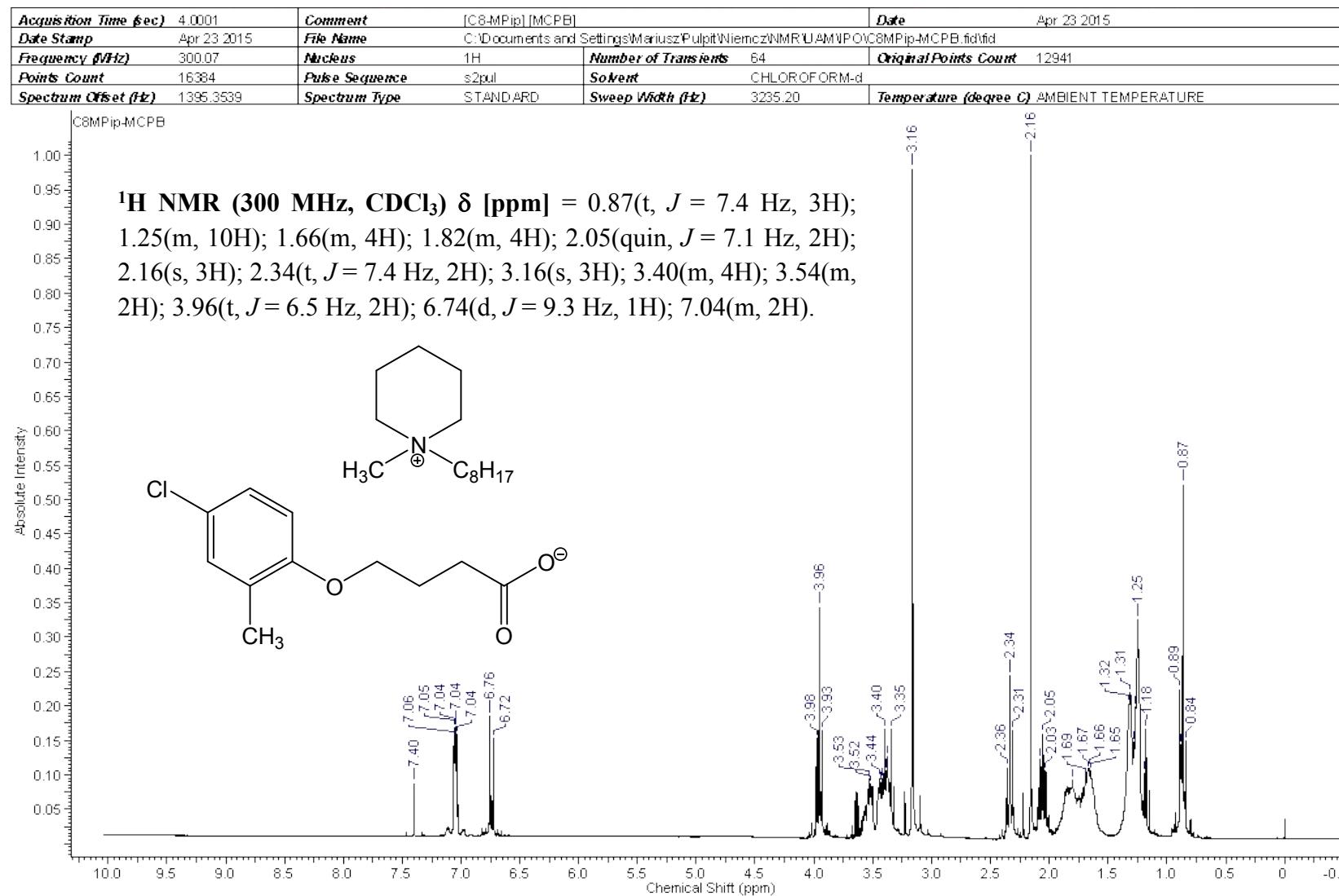
**Figure S12.**  $^{13}\text{C}$  NMR spectrum of 1-heptyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**6**).

<b>Acquisition Time (sec)</b>	0.6400	<b>Comment</b>	[C7-MPip][MCPB]	<b>Date</b>	Apr 23 2015
<b>Date Stamp</b>	Apr 23 2015	<b>File Name</b>	C:\Documents and Settings\Marusz\Pulpit\Niemcz\NMR\J\AMNPO\13C7MPip-MCPB-c13.fidfid		
<b>Frequency (MHz)</b>	75.46	<b>Nucleus</b>	$^{13}\text{C}$	<b>Number of Transients</b>	1452
<b>Points Count</b>	16384	<b>Pulse Sequence</b>	s2pul	<b>Receiver Gain</b>	34.00
<b>Spectrum Offset (Hz)</b>	7082.9160	<b>Spectrum Type</b>	STANDARD	<b>Sweep Width (Hz)</b>	16025.64
				<b>Original Points Count</b>	10257
				<b>Solvent</b>	CHLOROFORM-d
				<b>Temperature (degree C)</b>	AMBIENT TEMPERATURE

C7MPip-MCPB-c13



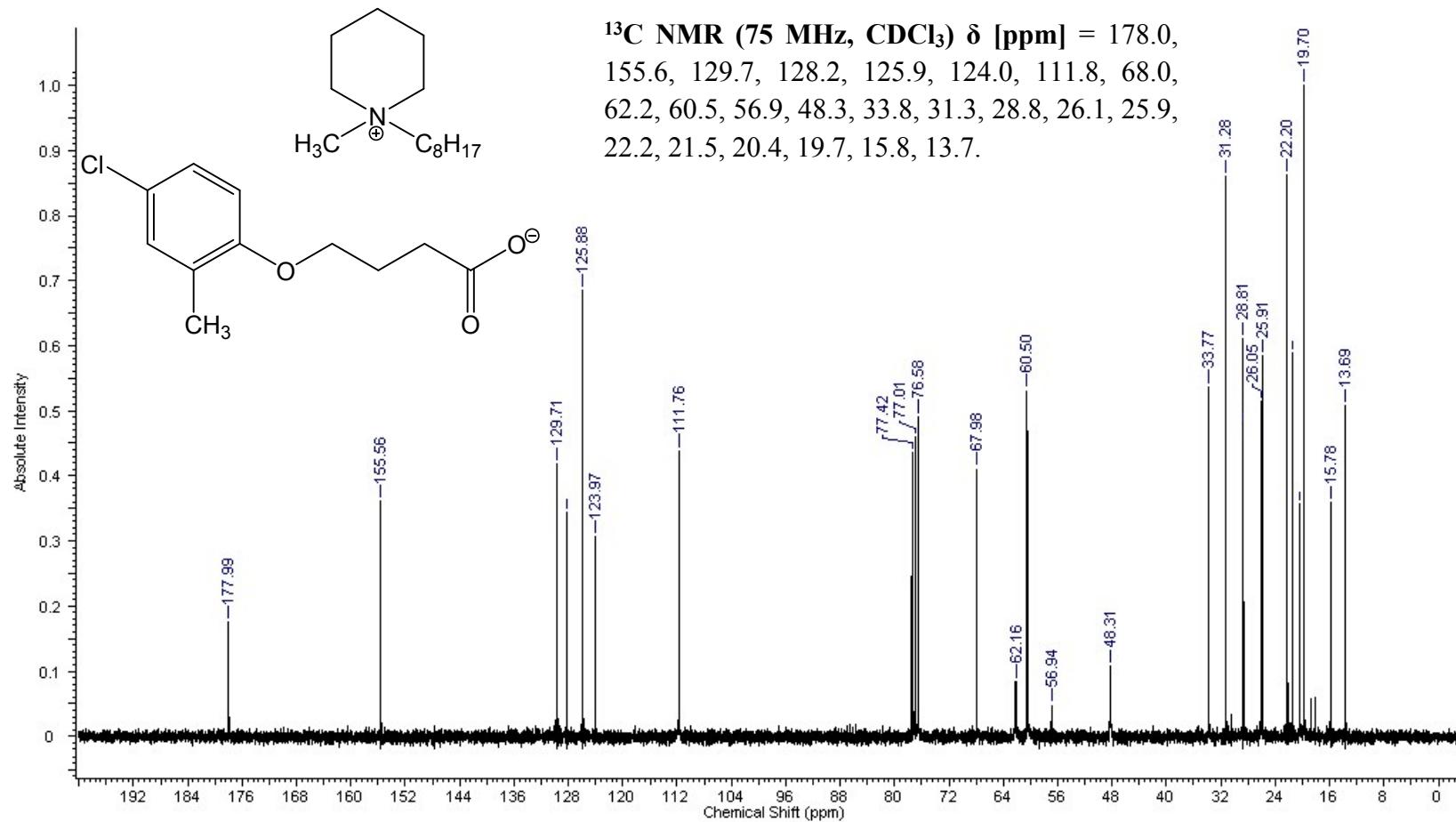
**Figure S13.**  $^1\text{H}$  NMR spectrum of 1-methyl-1-octylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**7**).



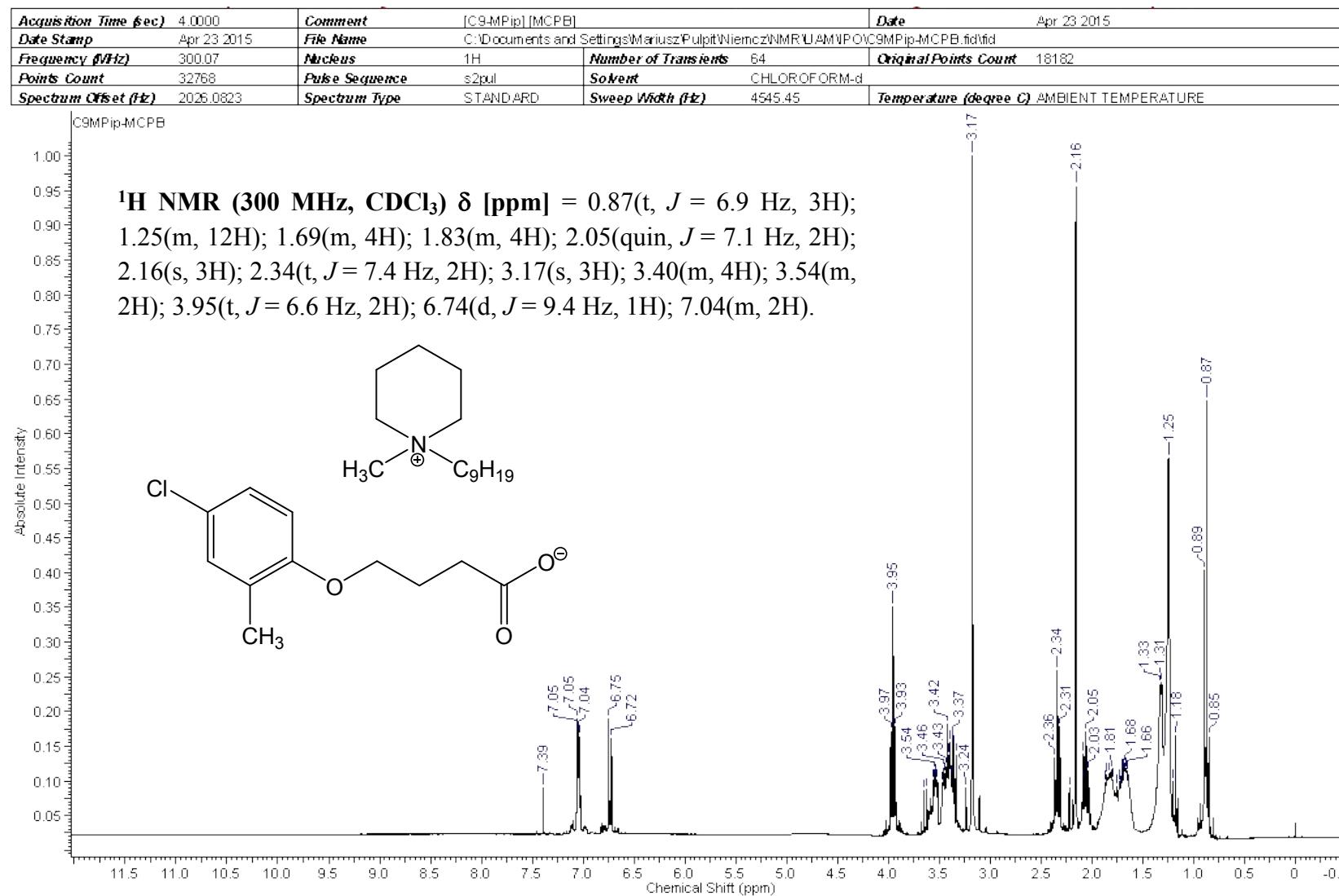
**Figure S14.**  $^{13}\text{C}$  NMR spectrum of 1-methyl-1-octylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (7).

Acquisition Time (sec)	0.6400	Comment	[C8-MPip] [MCPB]	Date	Apr 23 2015
Date Stamp	Apr 23 2015	File Name	C:\documents and settings\mariusz\Pulpit\NiemczNMR\1J\AM\POIC8MPip-MCPB-c13.fid.fid		
Frequency (Hz)	75.46	Nucleus	$^{13}\text{C}$	Number of Transients	1148
Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	34.00
Spectrum Offset (Hz)	7087.8071	Spectrum Type	STANDARD	Sweep Width (Hz)	16025.64
				Original Points Count	10257
				Solvent	CHLOROFORM-d
				Temperature (degree C)	AMBIENT TEMPERATURE

C8MPip-MCPB-c13



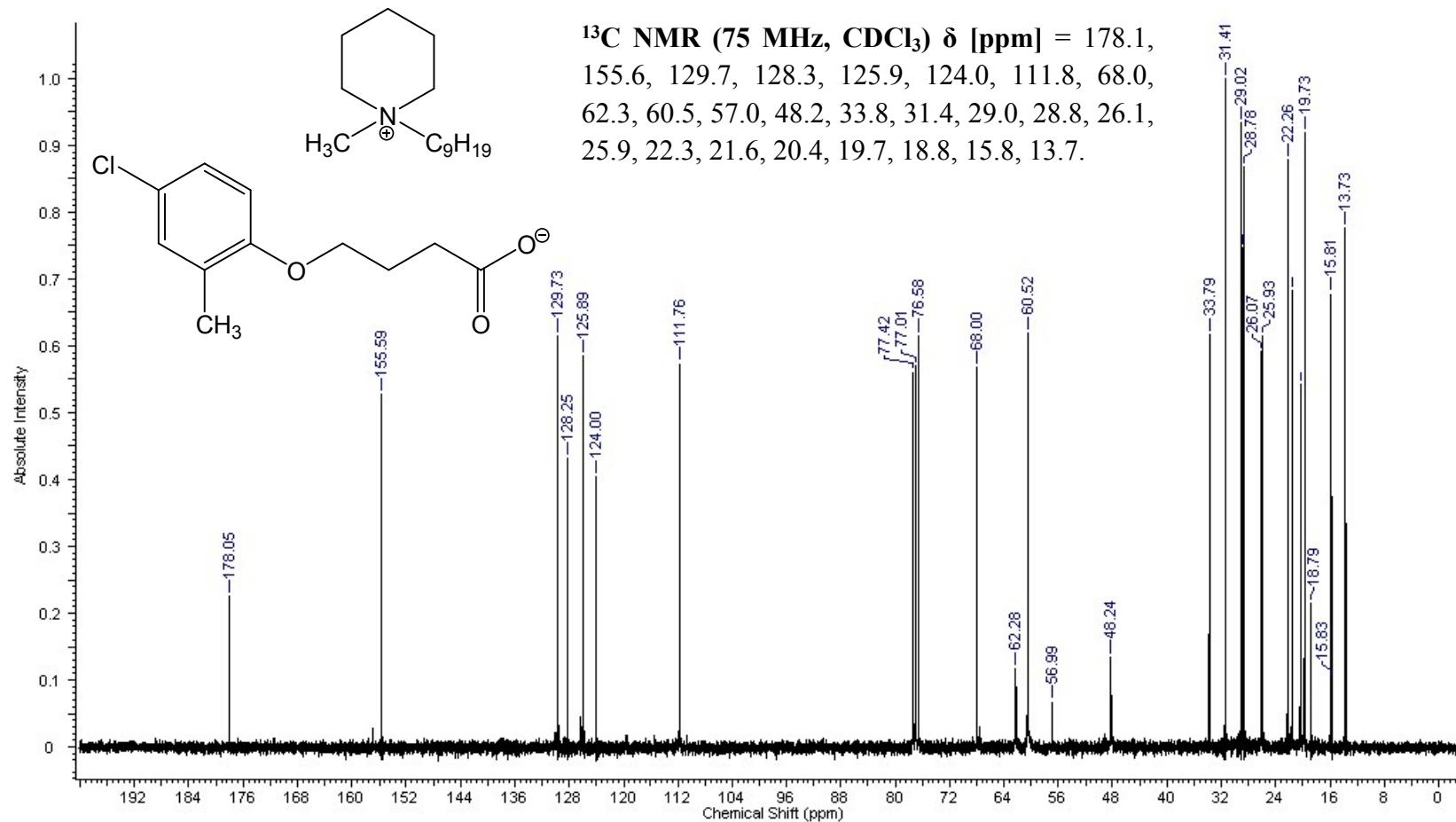
**Figure S15.**  $^1\text{H}$  NMR spectrum of 1-methyl-1-nonylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**8**).



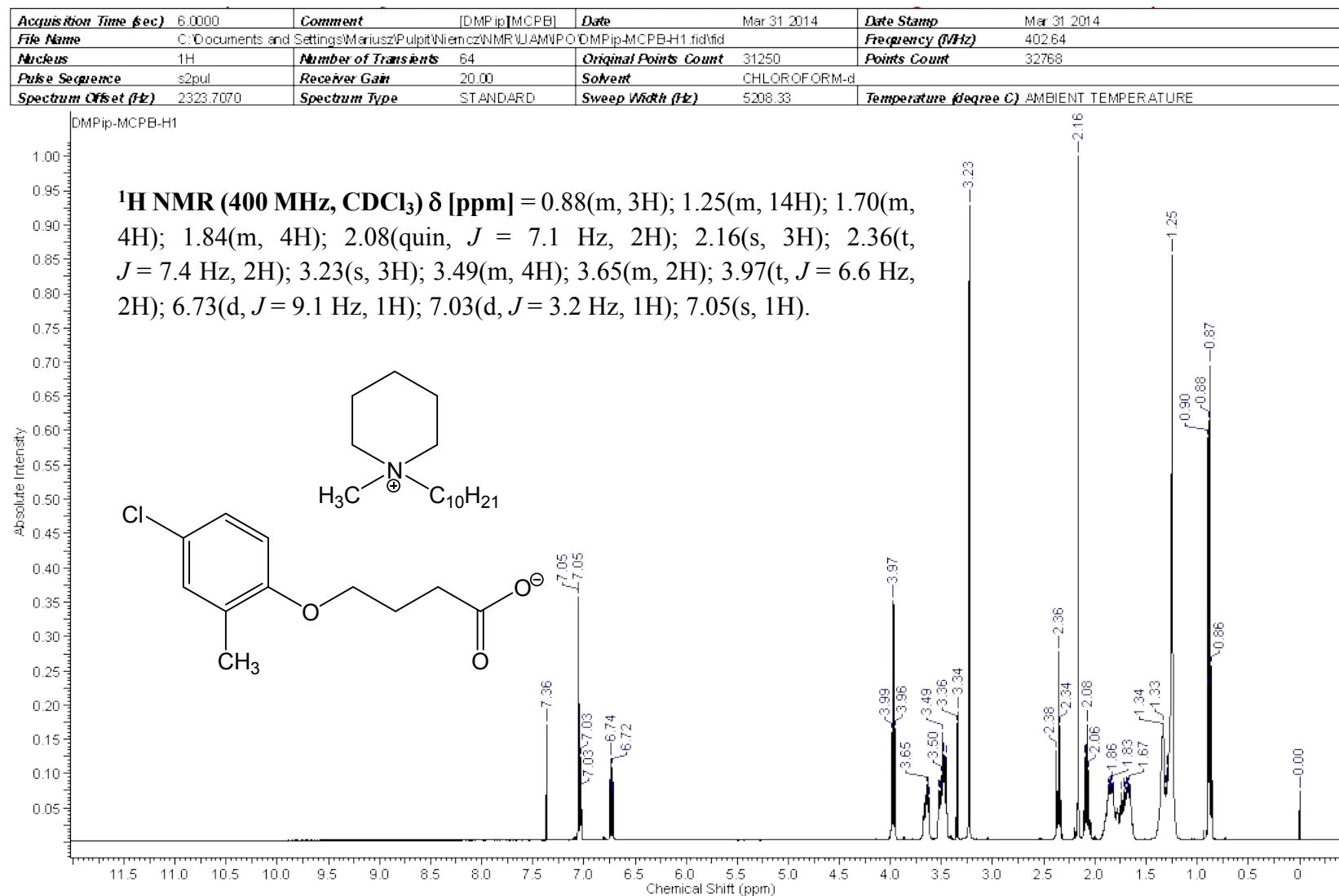
**Figure S16.**  $^{13}\text{C}$  NMR spectrum of 1-methyl-1-nonylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**8**).

<b>Acquisition Time (sec)</b>	0.6400	<b>Comment</b>	[C9-MPip][MCPB]	<b>Date</b>	Apr 23 2015
<b>Date Stamp</b>	Apr 23 2015	<b>File Name</b>	C:\Documents and Settings\Kamil\Pulpit\Niemcz\NMR\UAM\PO\13C\C9-MPip-MCPB-C13.fid\fid		
<b>Frequency (MHz)</b>	75.46	<b>Nucleus</b>	$^{13}\text{C}$	<b>Number of Transients</b>	2000
<b>Points Count</b>	16384	<b>Pulse Sequence</b>	s2pul	<b>Receiver Gain</b>	34.00
<b>Spectrum Offset (Hz)</b>	7088.7847	<b>Spectrum Type</b>	STANDARD	<b>Sweep Width (Hz)</b>	16025.64
					<b>Temperature (Degree C)</b> AMBIENT TEMPERATURE

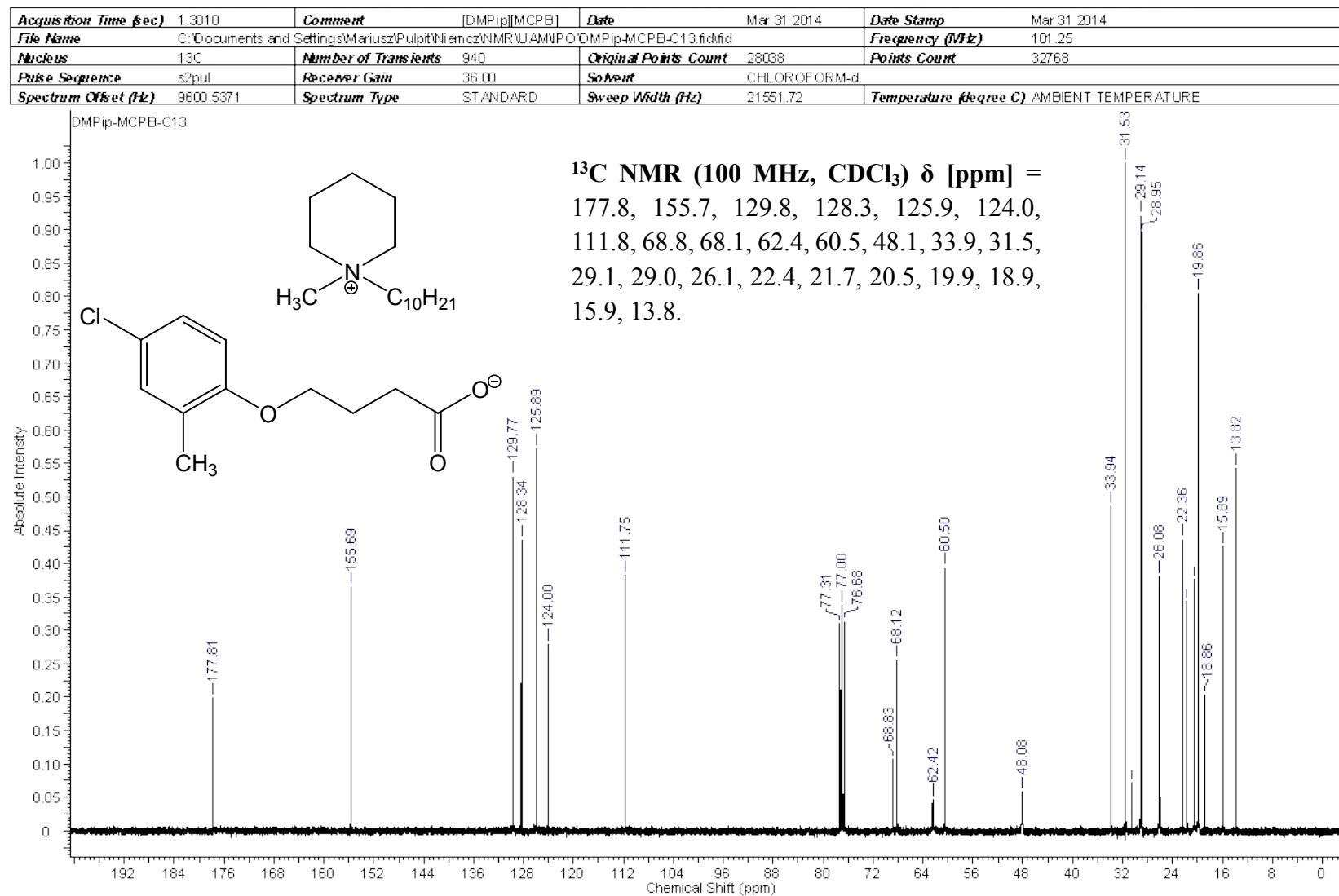
C9-MPip-MCPB-C13



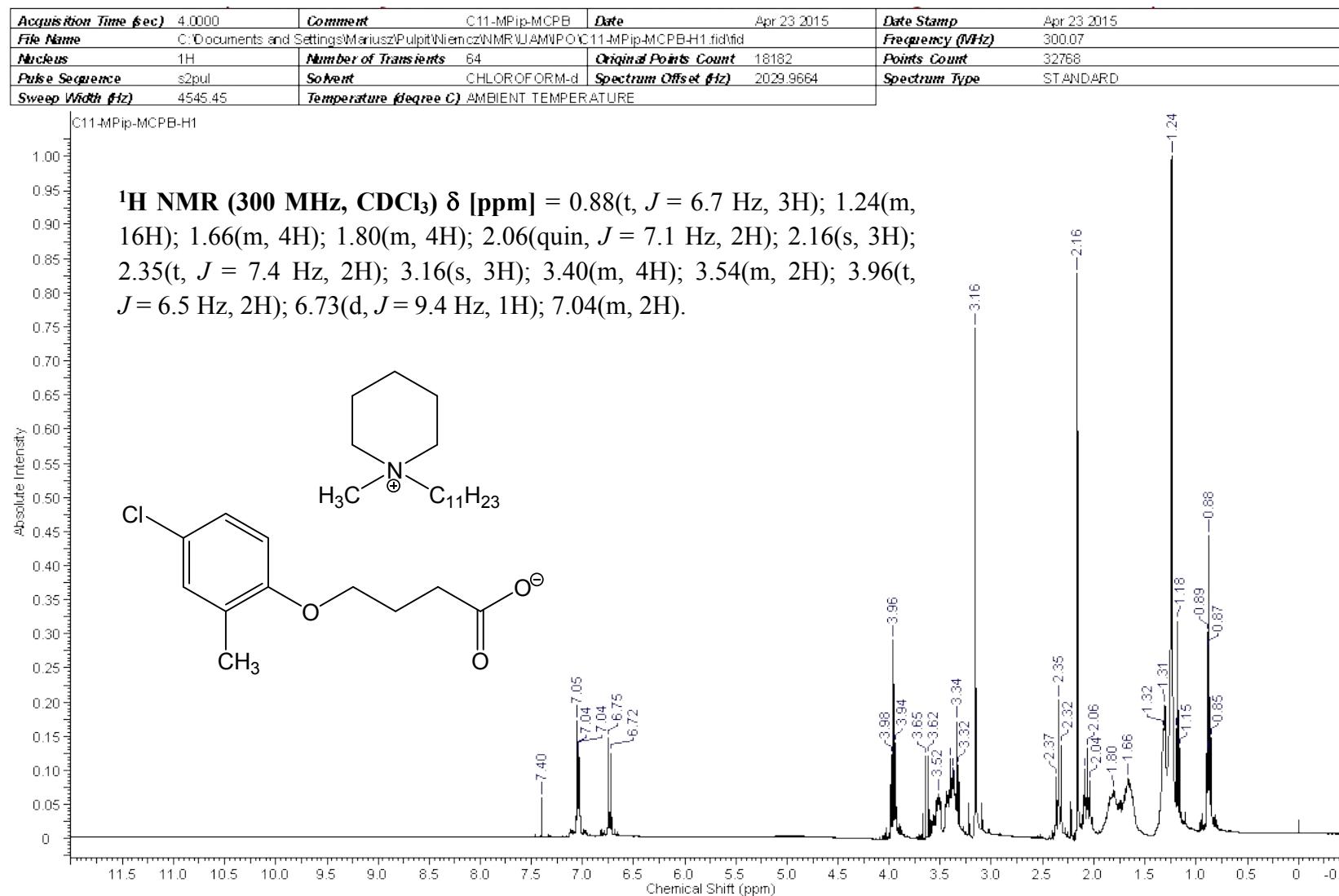
**Figure S17.**  $^1\text{H}$  NMR spectrum of 1-decyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**9**).



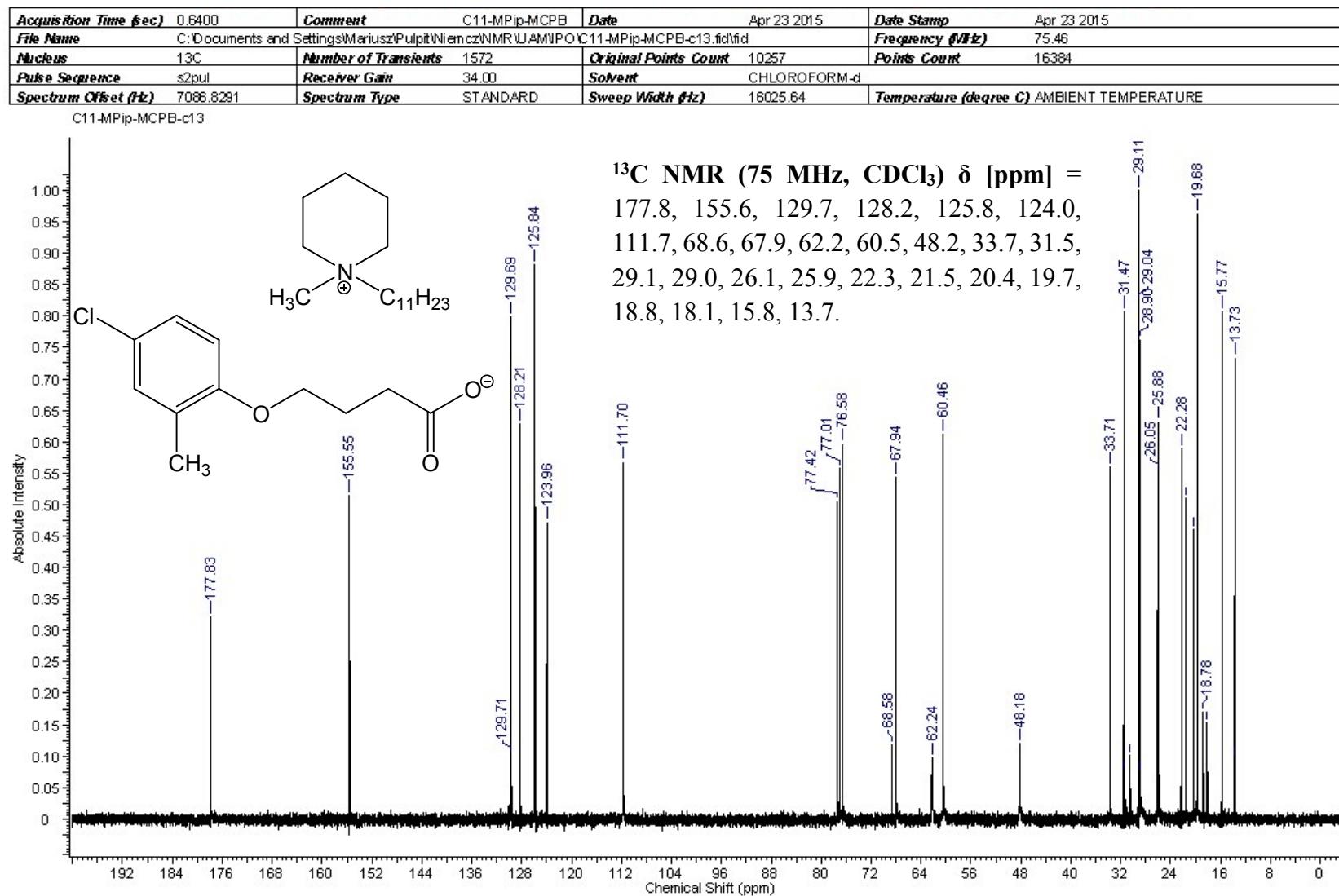
**Figure S18.**  $^{13}\text{C}$  NMR spectrum of 1-decyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**9**).



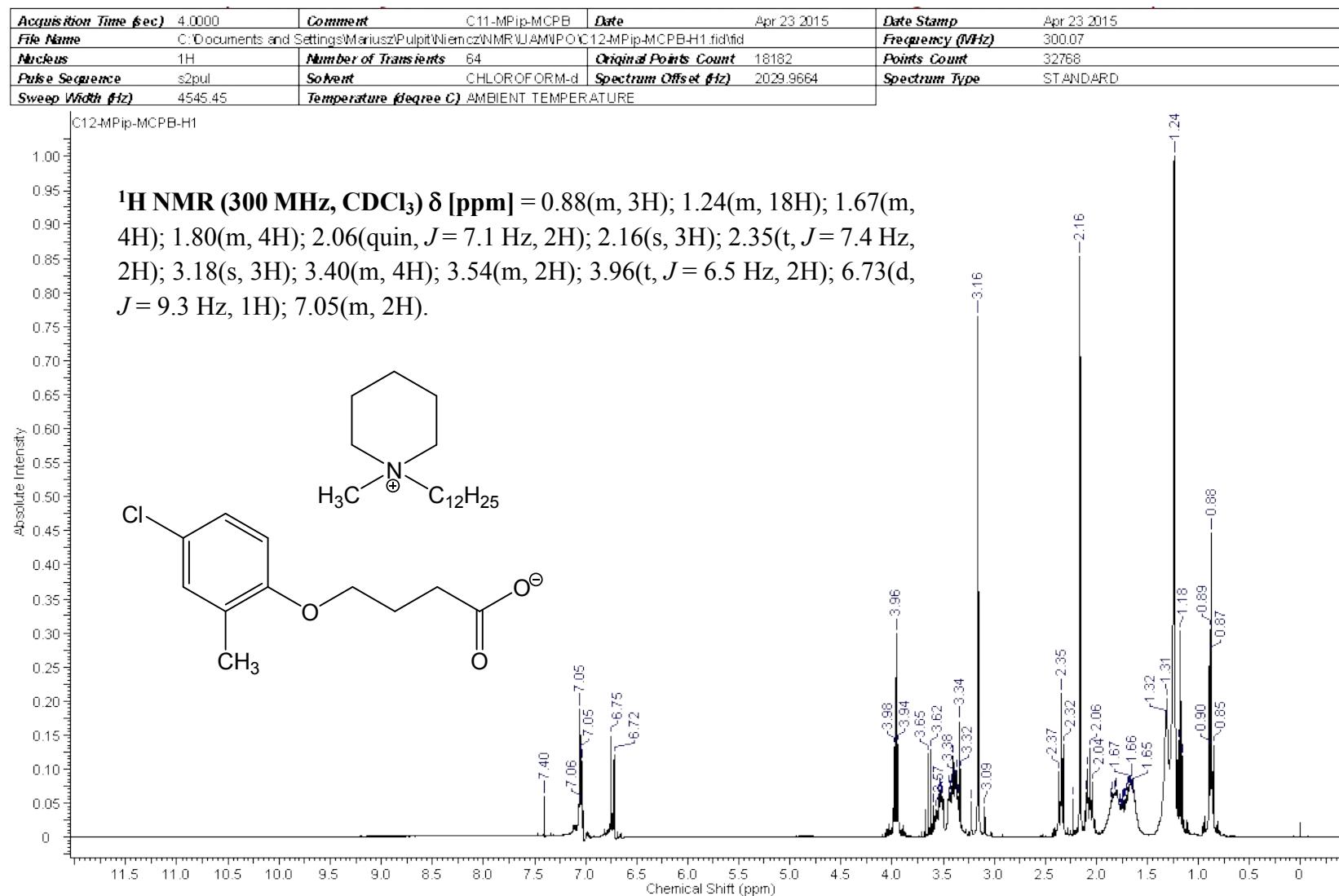
**Figure S19.**  $^1\text{H}$  NMR spectrum of 1-methyl-1-undecylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**10**).



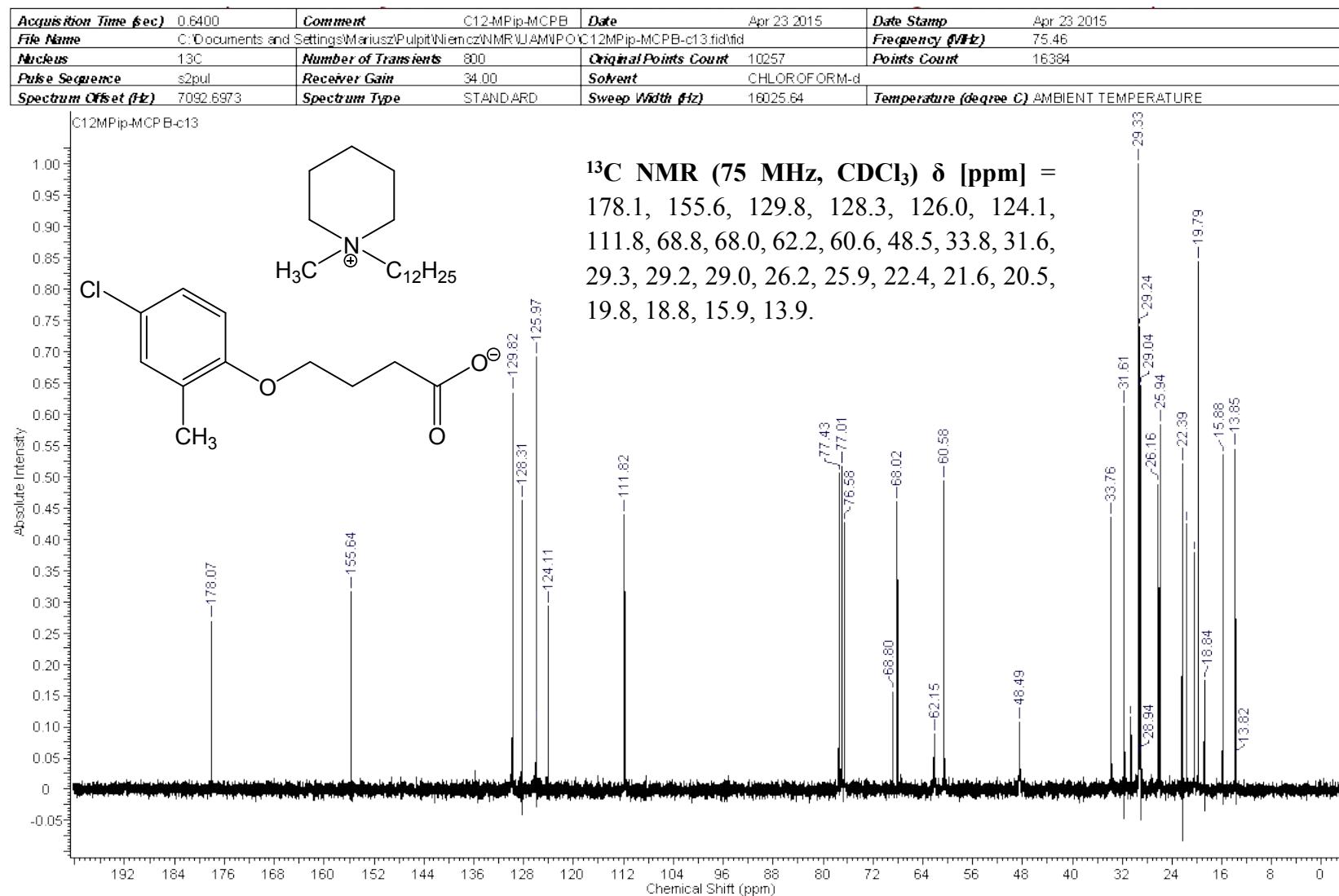
**Figure S20.**  $^{13}\text{C}$  NMR spectrum of 1-methyl-1-undecylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**10**).



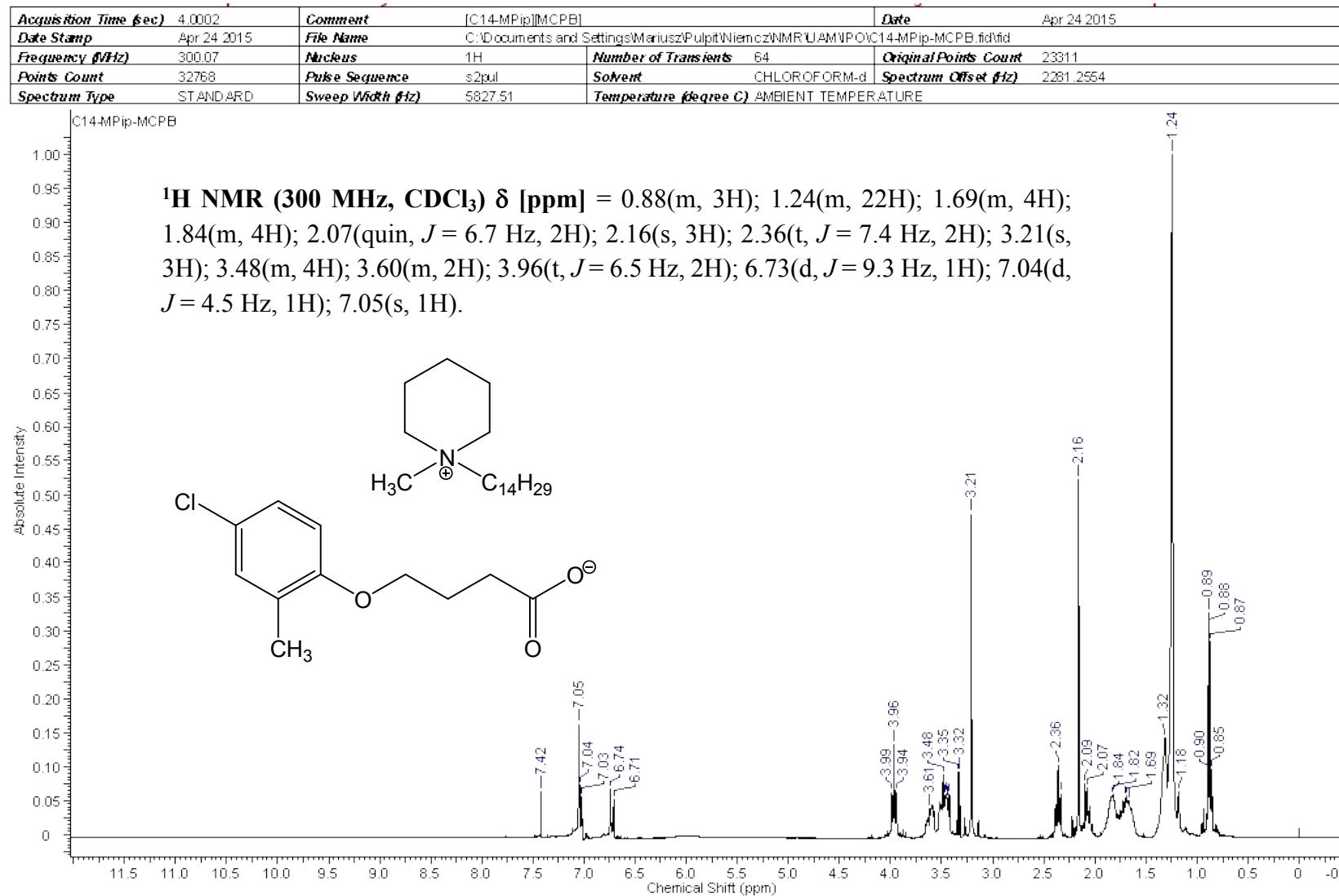
**Figure S21.**  $^1\text{H}$  NMR spectrum of 1-dodecyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**11**).



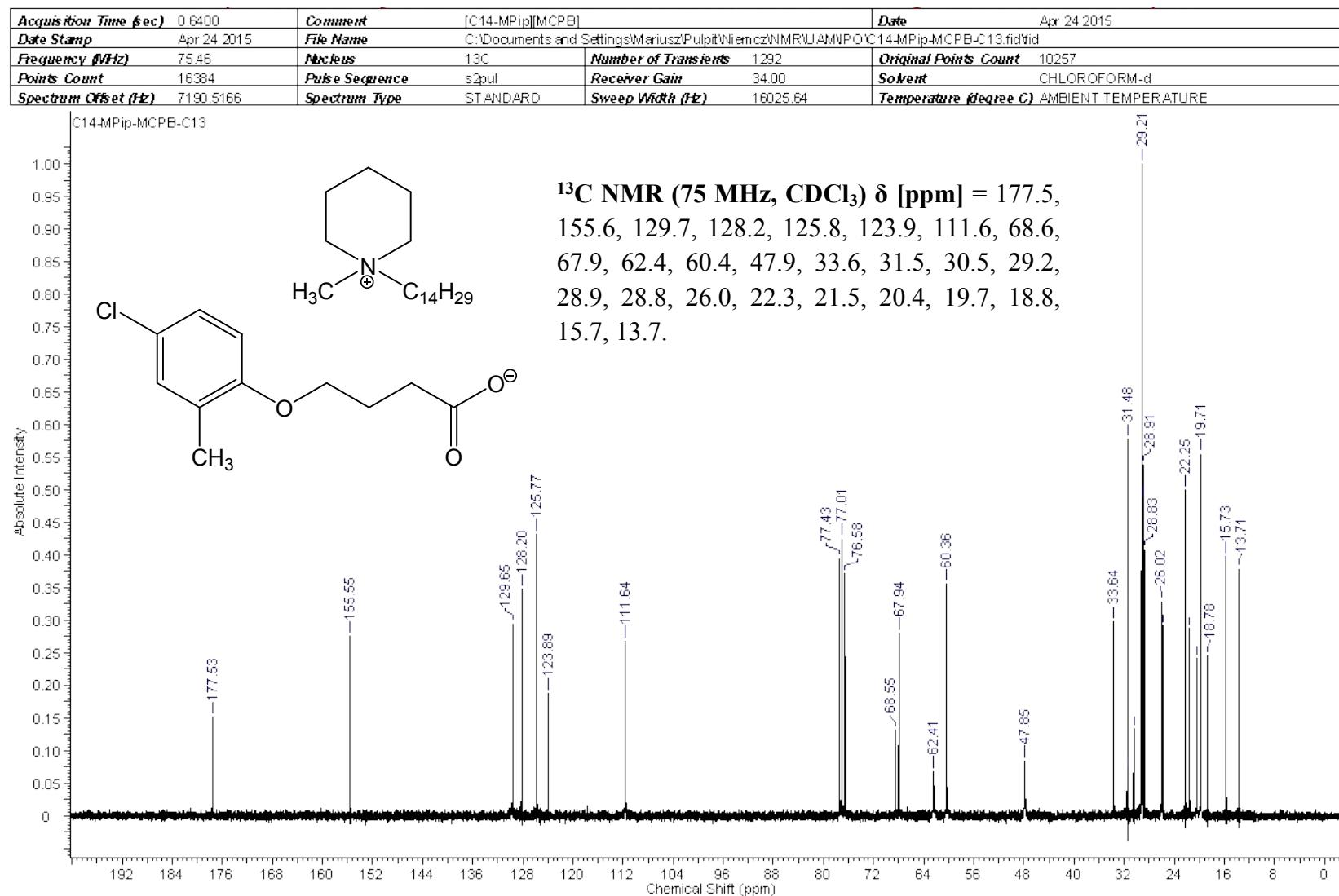
**Figure S22.**  $^{13}\text{C}$  NMR spectrum of 1-dodecyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**11**).



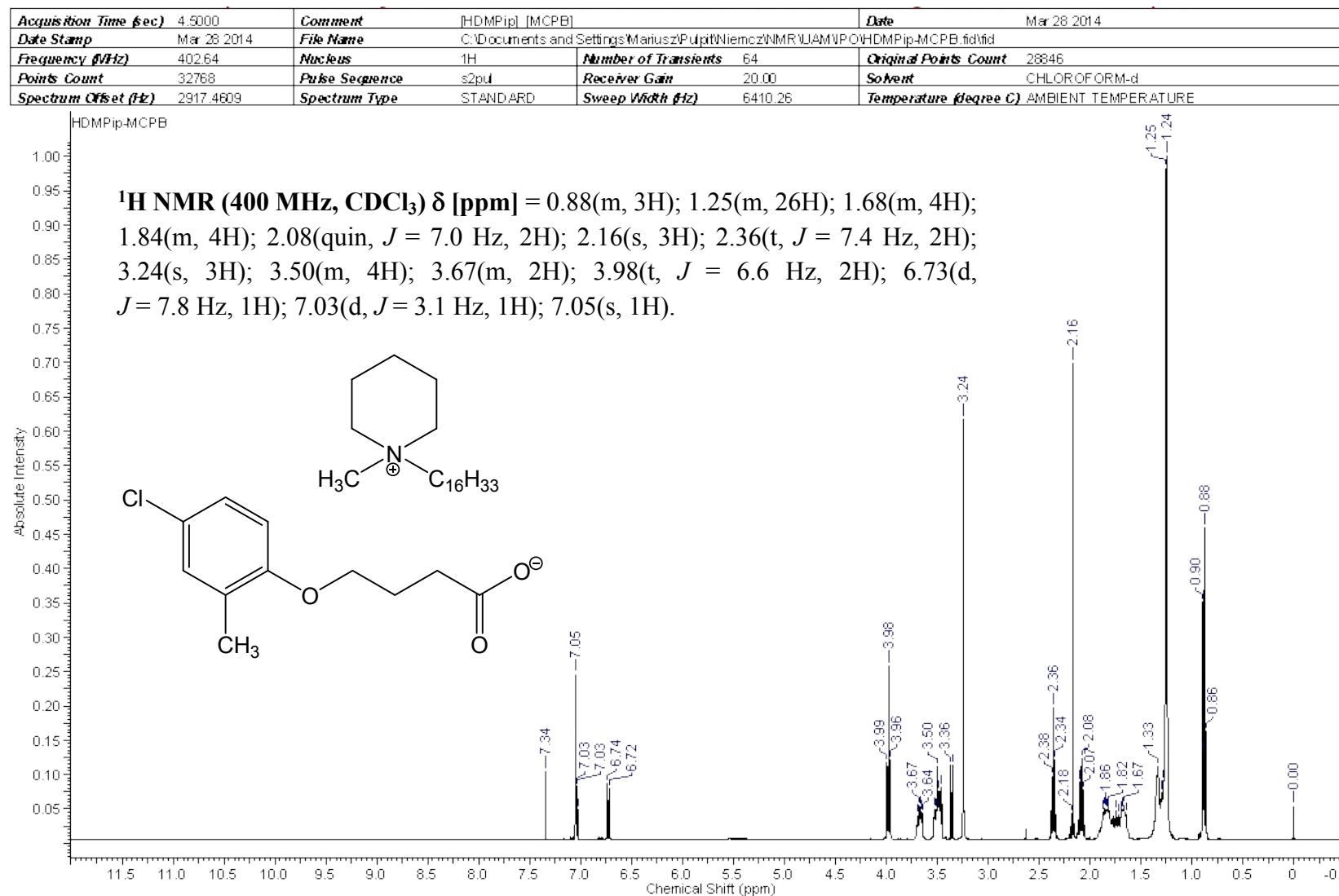
**Figure S23.**  $^1\text{H}$  NMR spectrum of 1-methyl-1-tetradecylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**12**).



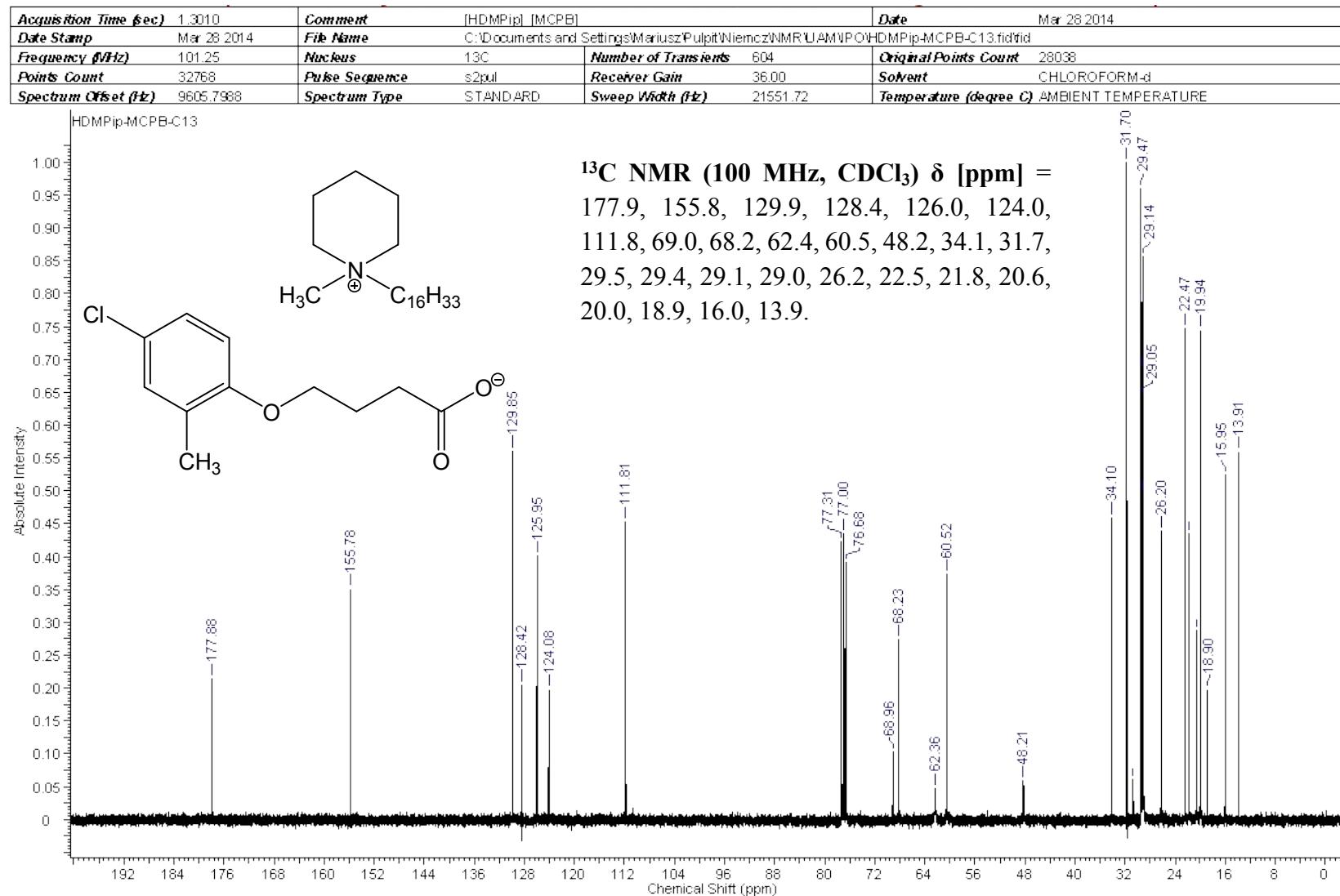
**Figure S24.**  $^{13}\text{C}$  NMR spectrum of 1-methyl-1-tetradecylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**12**).



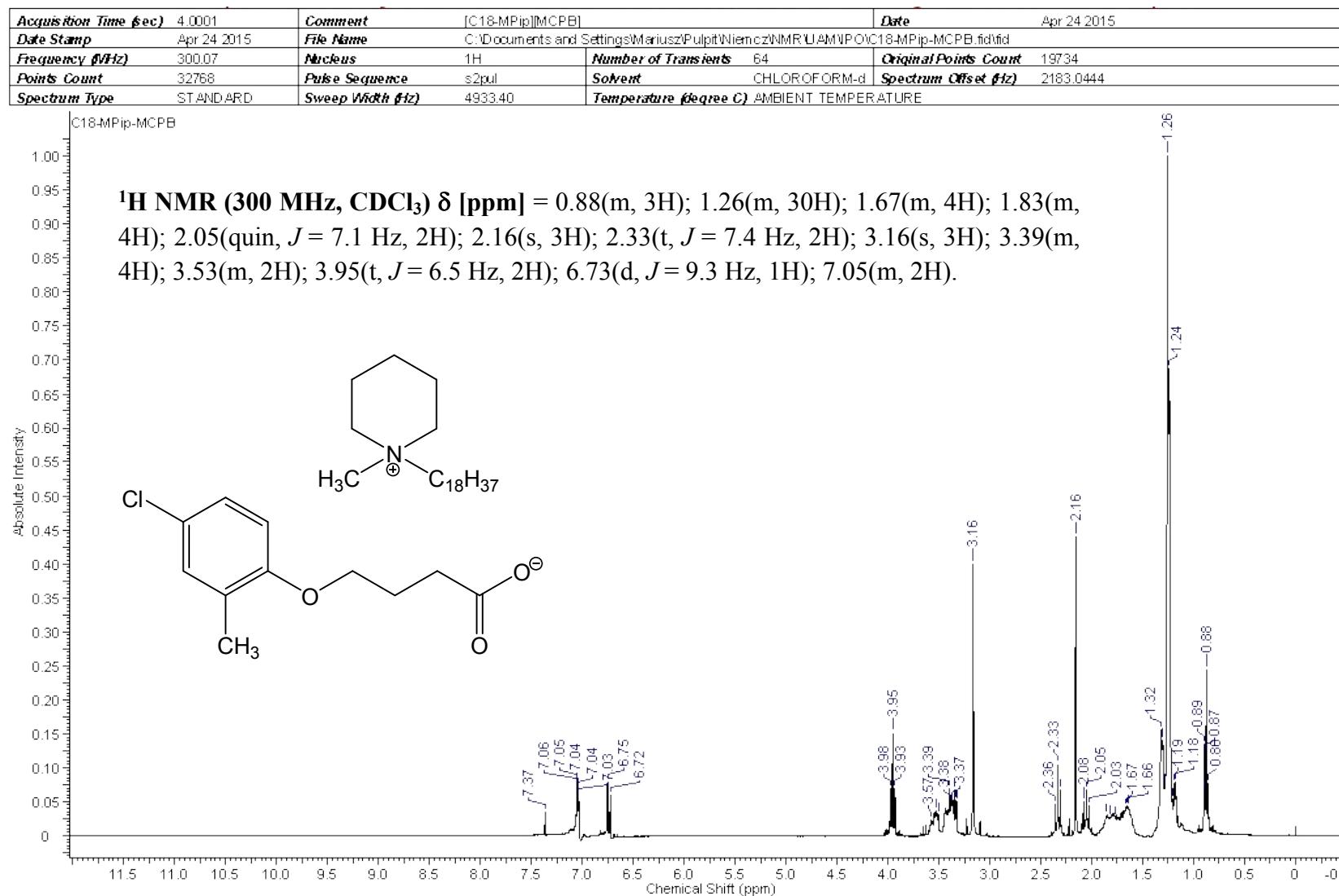
**Figure S25.**  $^1\text{H}$  NMR spectrum of 1-hexadecyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**13**).



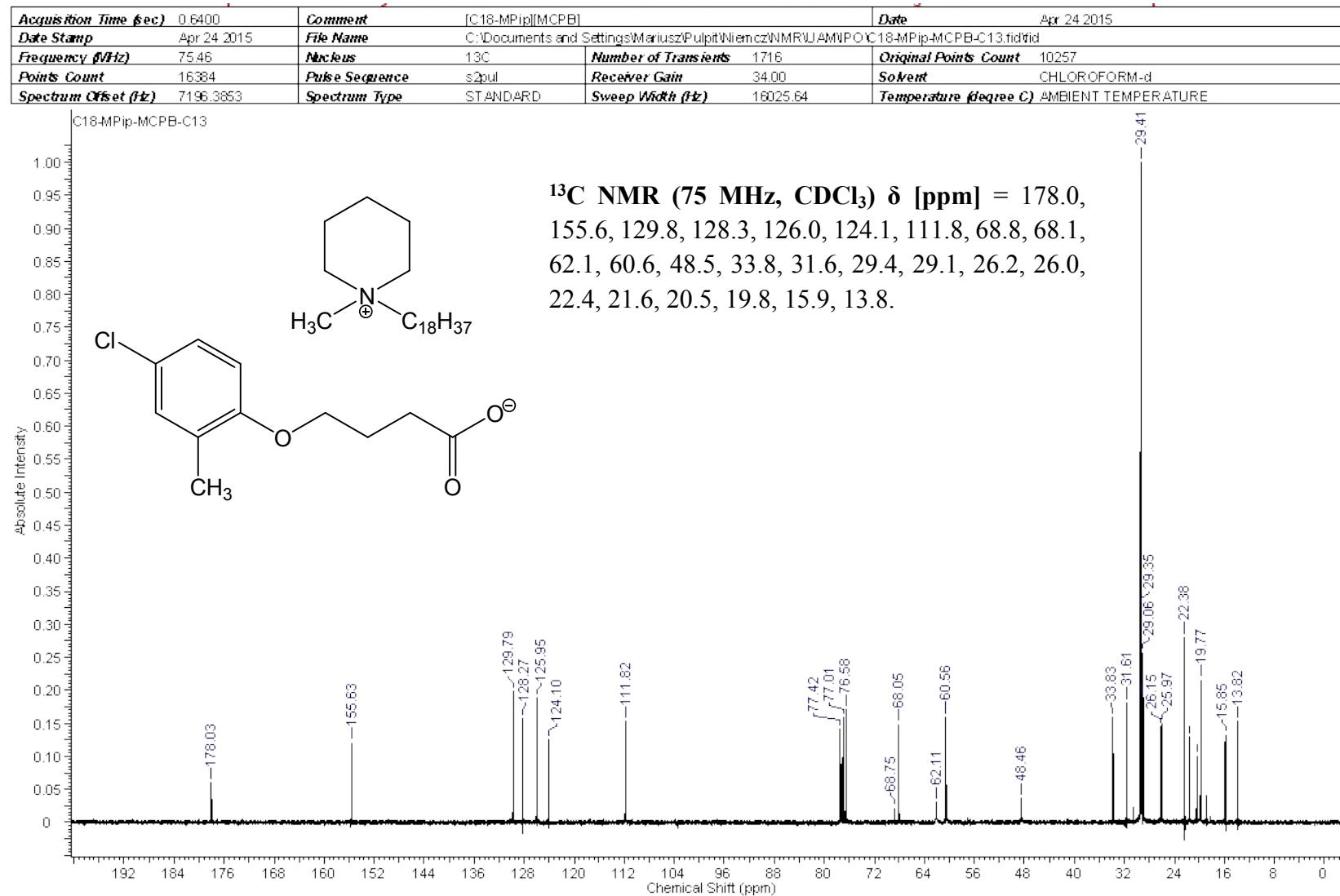
**Figure S26.**  $^{13}\text{C}$  NMR spectrum of 1-hexadecyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**13**).



**Figure S27.**  $^1\text{H}$  NMR spectrum of 1-methyl-1-octadecylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**14**).



**Figure S28.**  $^{13}\text{C}$  NMR spectrum of 1-methyl-1-octadecylpiperidinium 4-(4-chloro-2-methylphenoxy)butanoate (**14**).



**Table S1.** Viscosity values (Pa·s) for of the HILs (**5-10**)

HIL	R	Temperature [°C]						
		20	30	40	50	60	70	80
<b>5</b>	C <sub>6</sub> H <sub>13</sub>	1.4293	0.5685	0.2646	0.1359	0.0821	0.0559	0.0426
<b>6</b>	C <sub>7</sub> H <sub>15</sub>	1.5138	0.4896	0.2266	0.1355	0.0800	0.0502	0.0406
<b>7</b>	C <sub>8</sub> H <sub>17</sub>	2.2696	0.8712	0.3842	0.1827	0.1083	0.0701	0.0535
<b>8</b>	C <sub>9</sub> H <sub>19</sub>	1.5092	0.6217	0.2857	0.1492	0.0861	0.0568	0.0422
<b>9</b>	C <sub>10</sub> H <sub>21</sub>	13.0937	1.3535	0.4887	0.2520	0.1383	0.0840	0.0578
<b>10</b>	C <sub>11</sub> H <sub>23</sub>	1.6705	0.6456	0.3122	0.1650	0.1036	0.0673	0.0519

**Table S2.** Density values (g·cm<sup>-3</sup>) for of the HILs (**5-10**)

HIL	R	Temperature [°C]						
		20	30	40	50	60	70	80
<b>5</b>	C <sub>6</sub> H <sub>13</sub>	1.10650	1.09956	1.09280	1.08587	1.07875	1.07147	1.06420
<b>6</b>	C <sub>7</sub> H <sub>15</sub>	1.09183	1.08484	1.07798	1.07104	1.06401	1.05703	1.04988
<b>7</b>	C <sub>8</sub> H <sub>17</sub>	1.08652	1.07973	1.07325	1.06664	1.05968	1.05256	1.04539
<b>8</b>	C <sub>9</sub> H <sub>19</sub>	1.07489	1.06795	1.06107	1.05414	1.04724	1.04034	1.03304
<b>9</b>	C <sub>10</sub> H <sub>21</sub>	1.06717	1.06039	1.05409	1.04732	1.04038	1.03344	1.02621
<b>10</b>	C <sub>11</sub> H <sub>23</sub>	1.05584	1.04955	1.04254	1.03559	1.02868	1.02155	1.01441

**Table S3.** Refractive index values for of the HILs (**5-10**)

HIL	R	Temperature [°C]						
		20	30	40	50	60	70	80
<b>5</b>	C <sub>6</sub> H <sub>13</sub>	1.51434	1.51118	1.50801	1.50485	1.50169	1.49961	1.49706
<b>6</b>	C <sub>7</sub> H <sub>15</sub>	1.51291	1.50973	1.50657	1.50335	1.50017	1.49733	1.49492
<b>7</b>	C <sub>8</sub> H <sub>17</sub>	1.51387	1.51067	1.50751	1.50435	1.50115	1.49802	1.49508
<b>8</b>	C <sub>9</sub> H <sub>19</sub>	1.50879	1.50565	1.50211	1.49856	1.49534	1.49275	1.48975
<b>9</b>	C <sub>10</sub> H <sub>21</sub>	1.51322	1.50997	1.50619	1.50166	1.49903	1.49610	1.49386
<b>10</b>	C <sub>11</sub> H <sub>23</sub>	1.50711	1.50377	1.5003	1.49653	1.49354	1.49114	1.48864