ELECTRONIC SUPPORTING INFORMATION

RSC Advances

Third generation ionic liquids with *N*-alkylated 1,4-diazabicyclo[2.2.2]octane cation and pelargonate anion

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Number of pages: 21

Number of tables: 2

Number of figures: 17

1. IDENTIFICATION OF COMPOUNDS

The following abbreviations were used to explain the multiplicities:
s = singlet, d = doublet, t = triplet, m = multiplet.

Fig. A.1 ^{1}H NMR spectrum of 1-hexyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(1).**

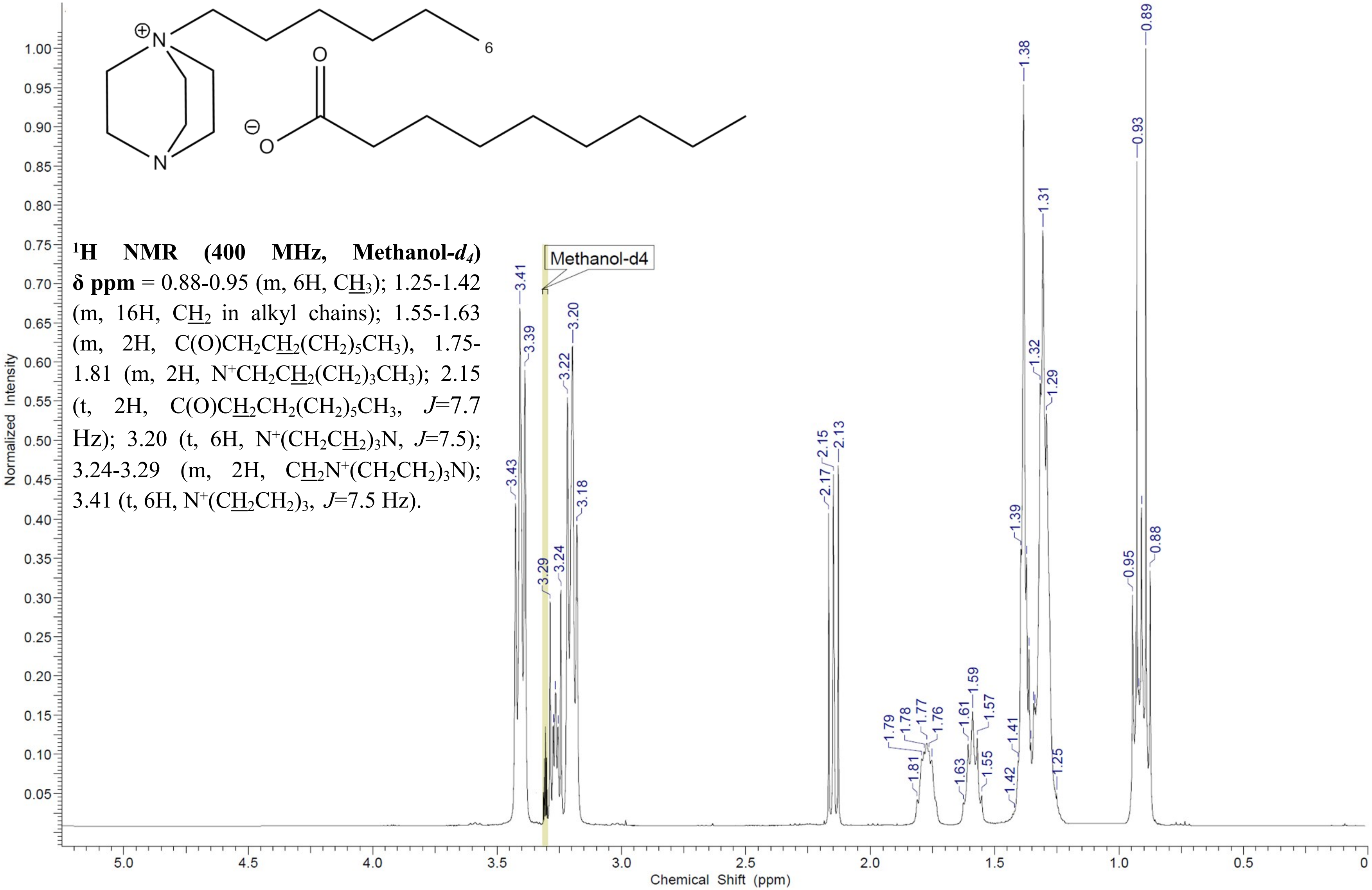


Fig. A.2 ^{13}C NMR spectrum of 1-hexyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(1)**.

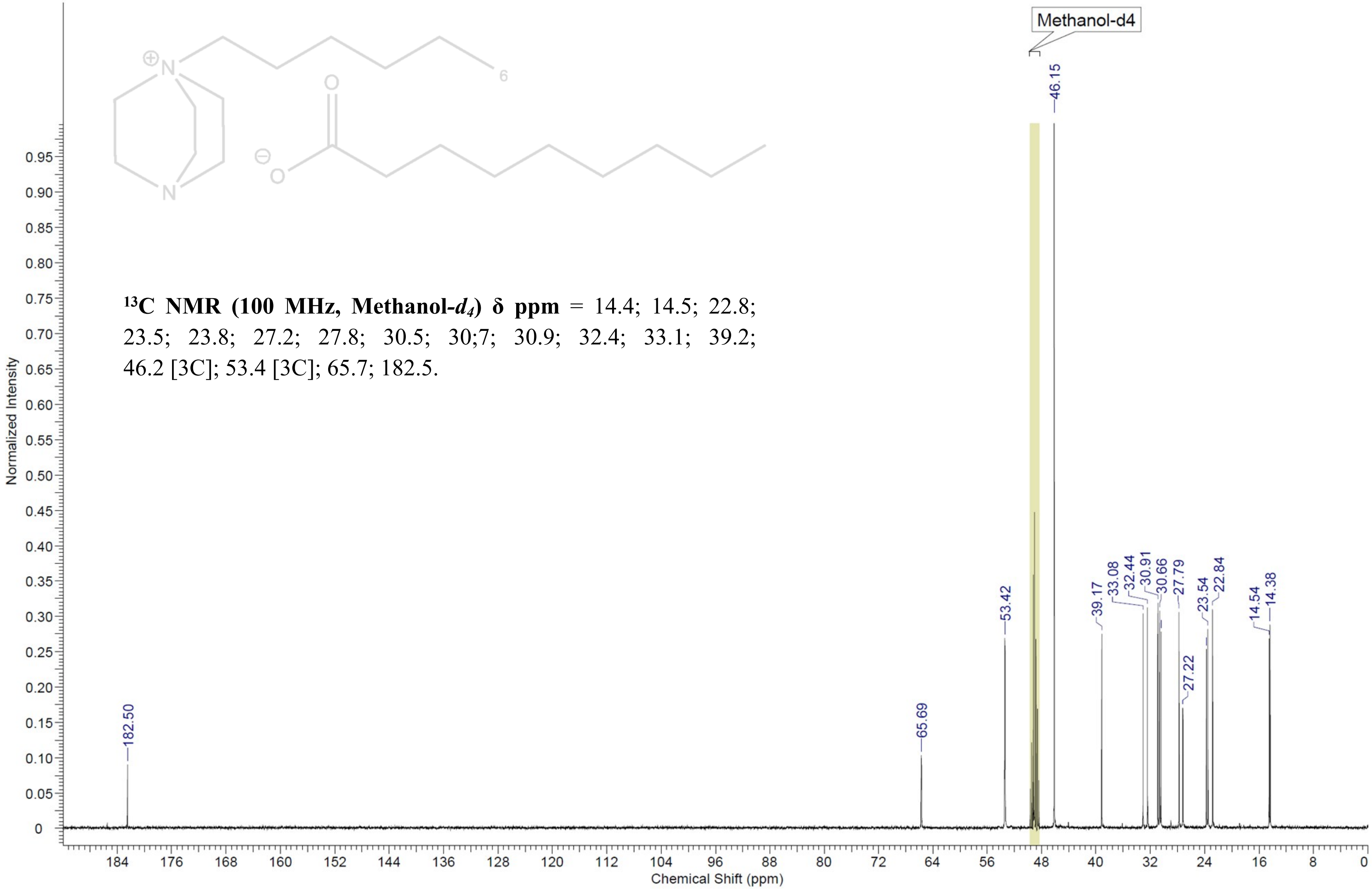


Fig. A.3 ^{1}HNMR spectrum of 1-decyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(4)**.

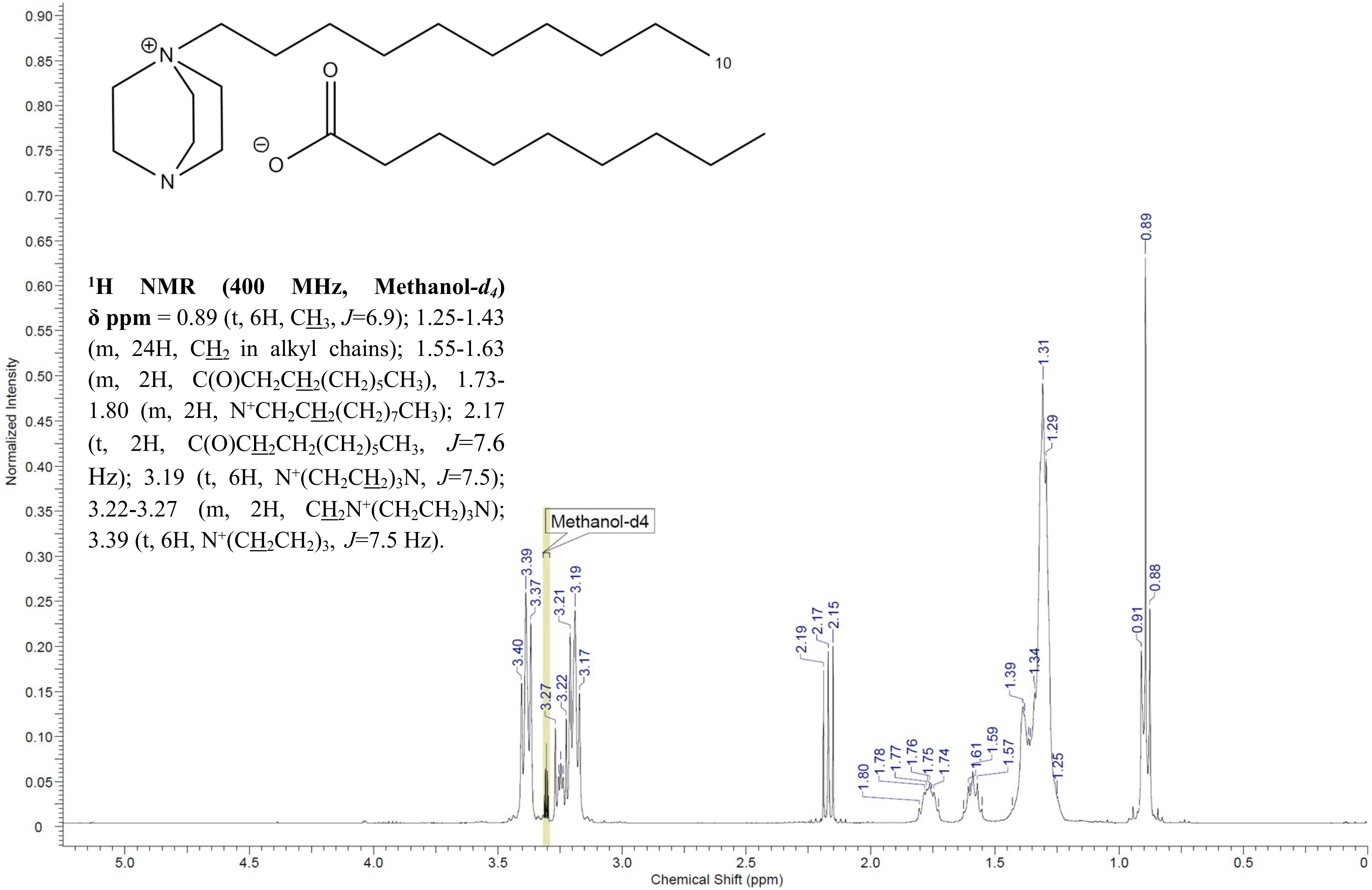


Fig. A.4 ^{13}C NMR spectrum of 1-decyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(4)**.

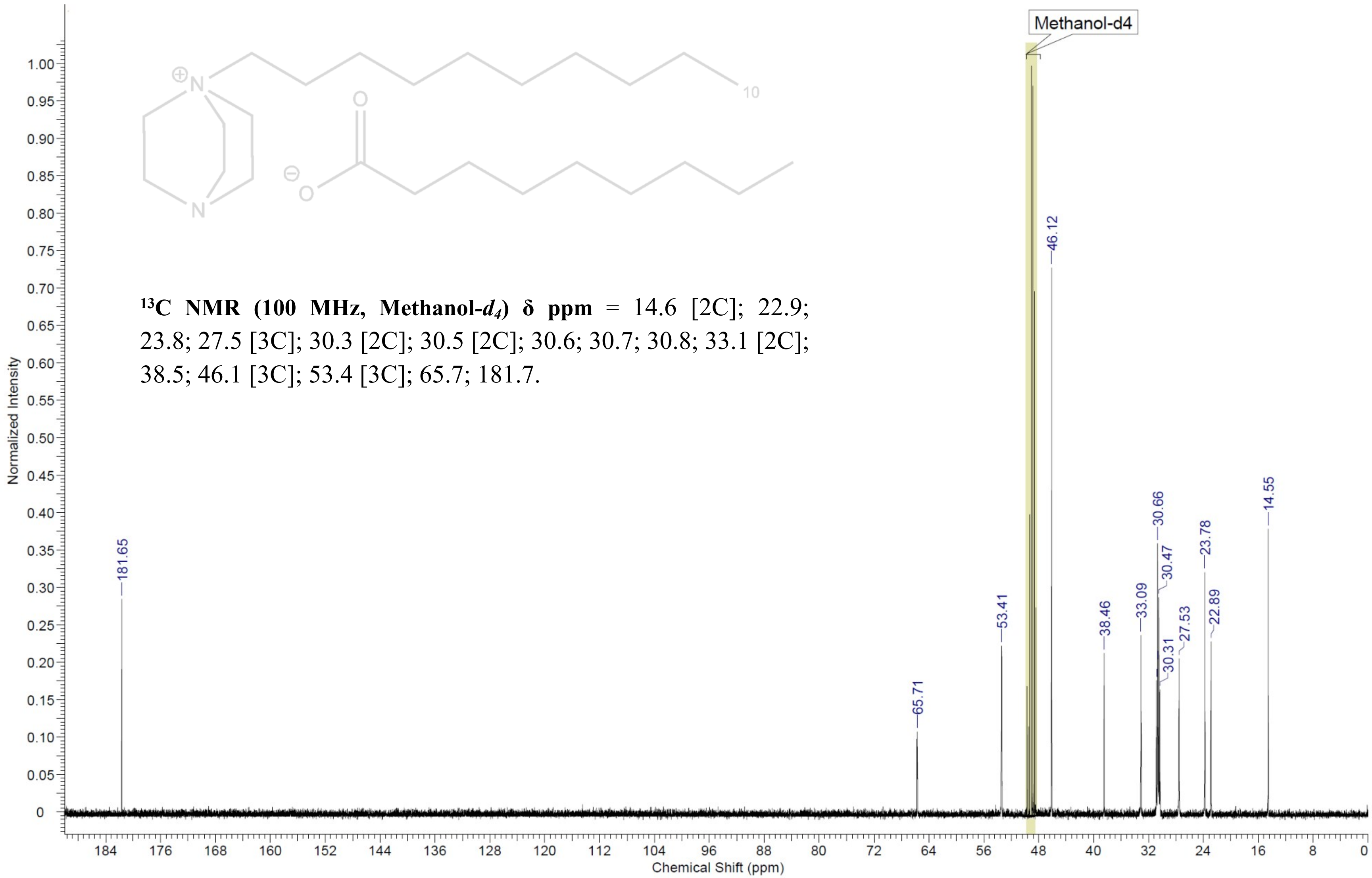


Fig. A.5 ^{1}H NMR spectrum of 1-dodecyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(5)**.

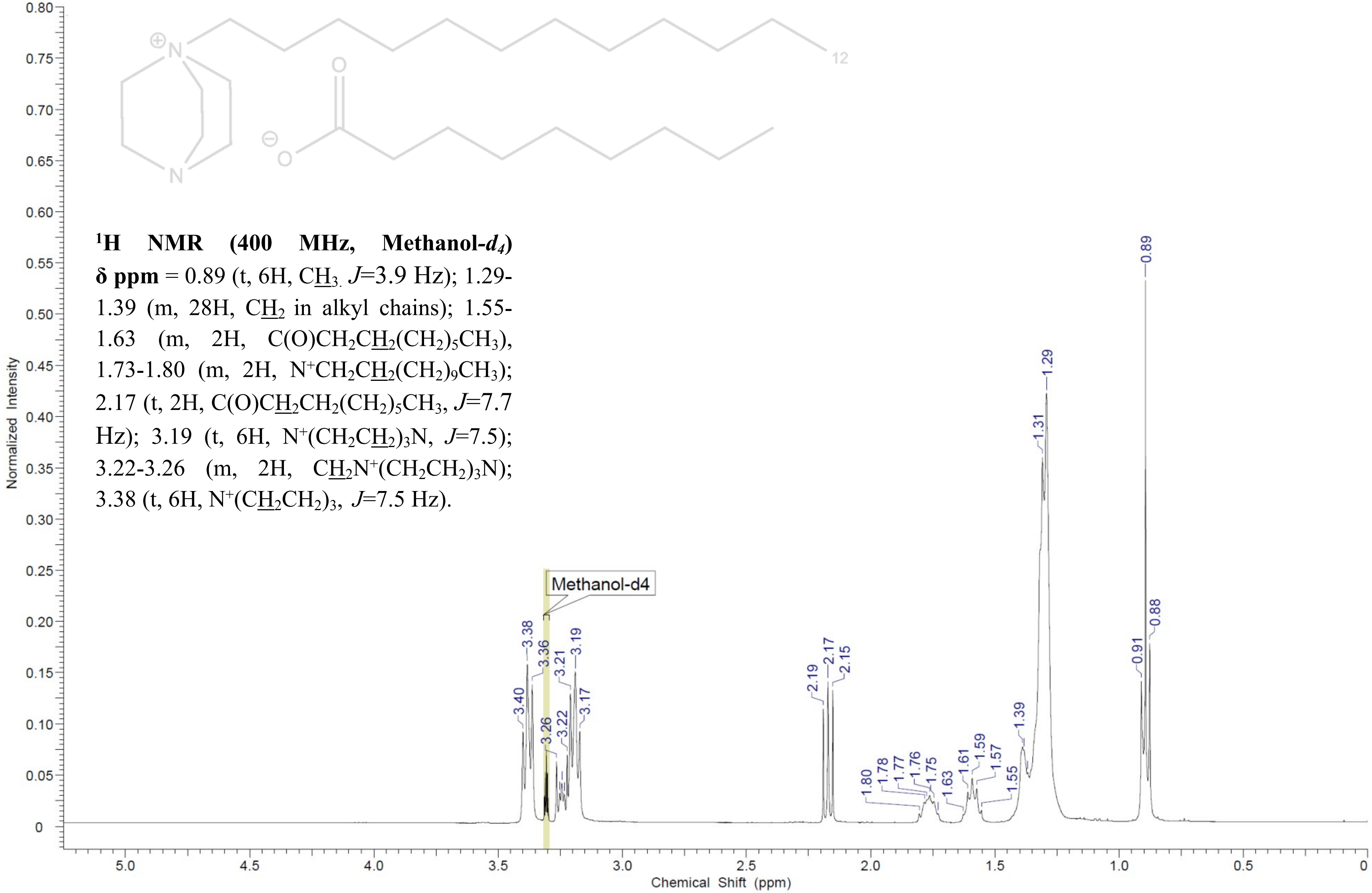


Fig. A.6 ^{13}C NMR spectrum of 1-dodecyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(5)**.

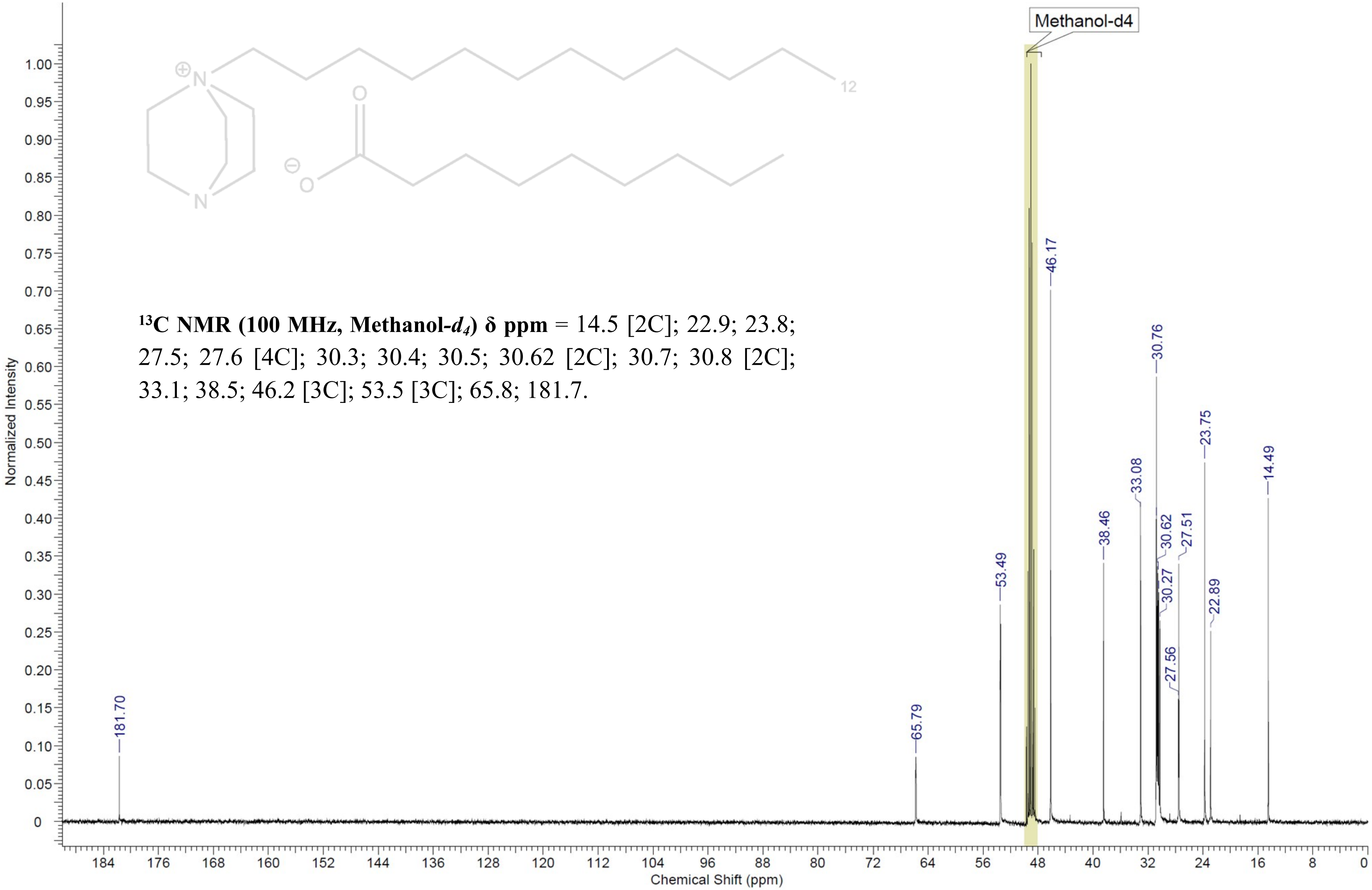


Fig. A.7 ^{1}H NMR spectrum of 1-hexadecyl -1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(7)**.

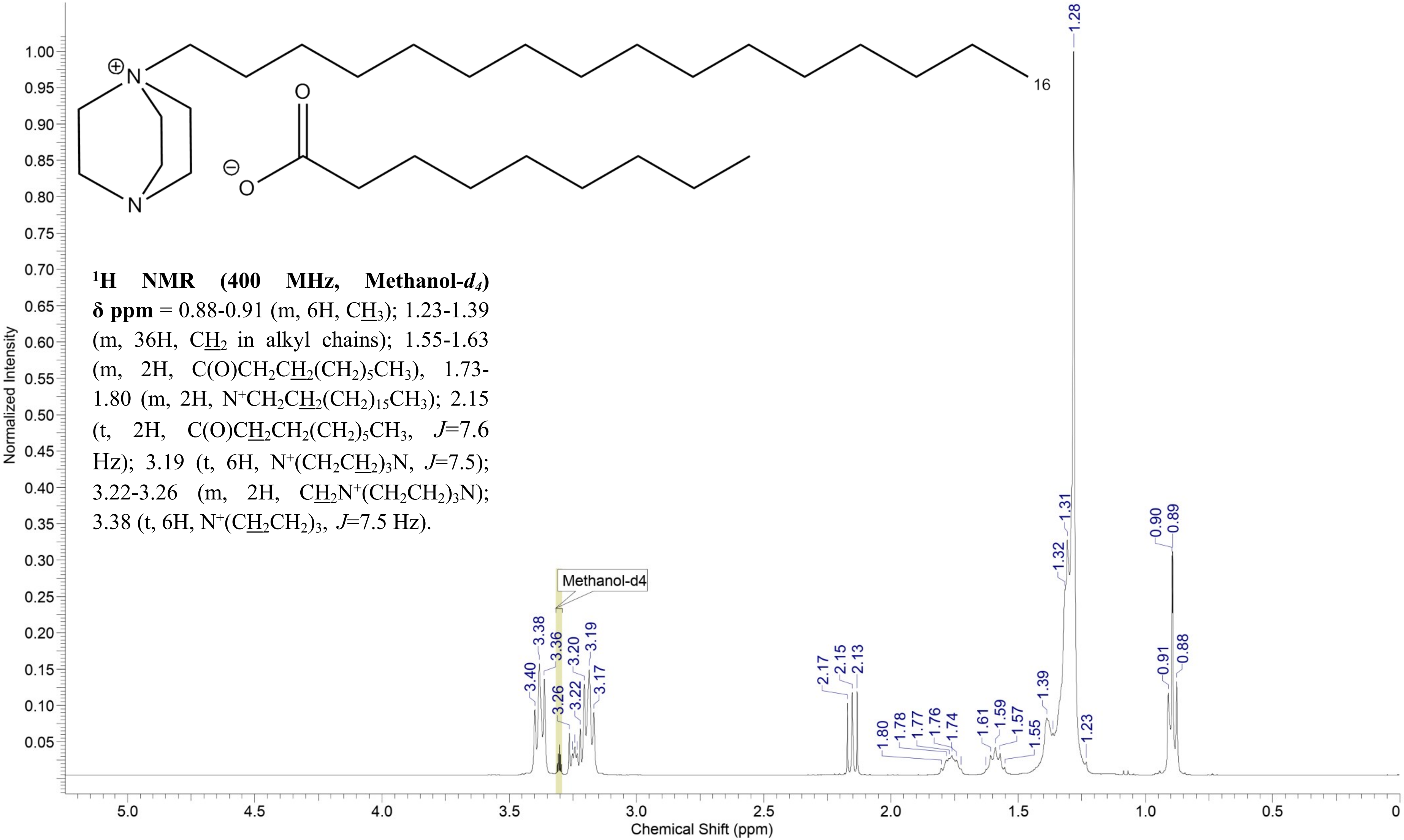


Fig. A.8 ^{13}C NMR spectrum of 1-hexadecyl -1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(7)**.

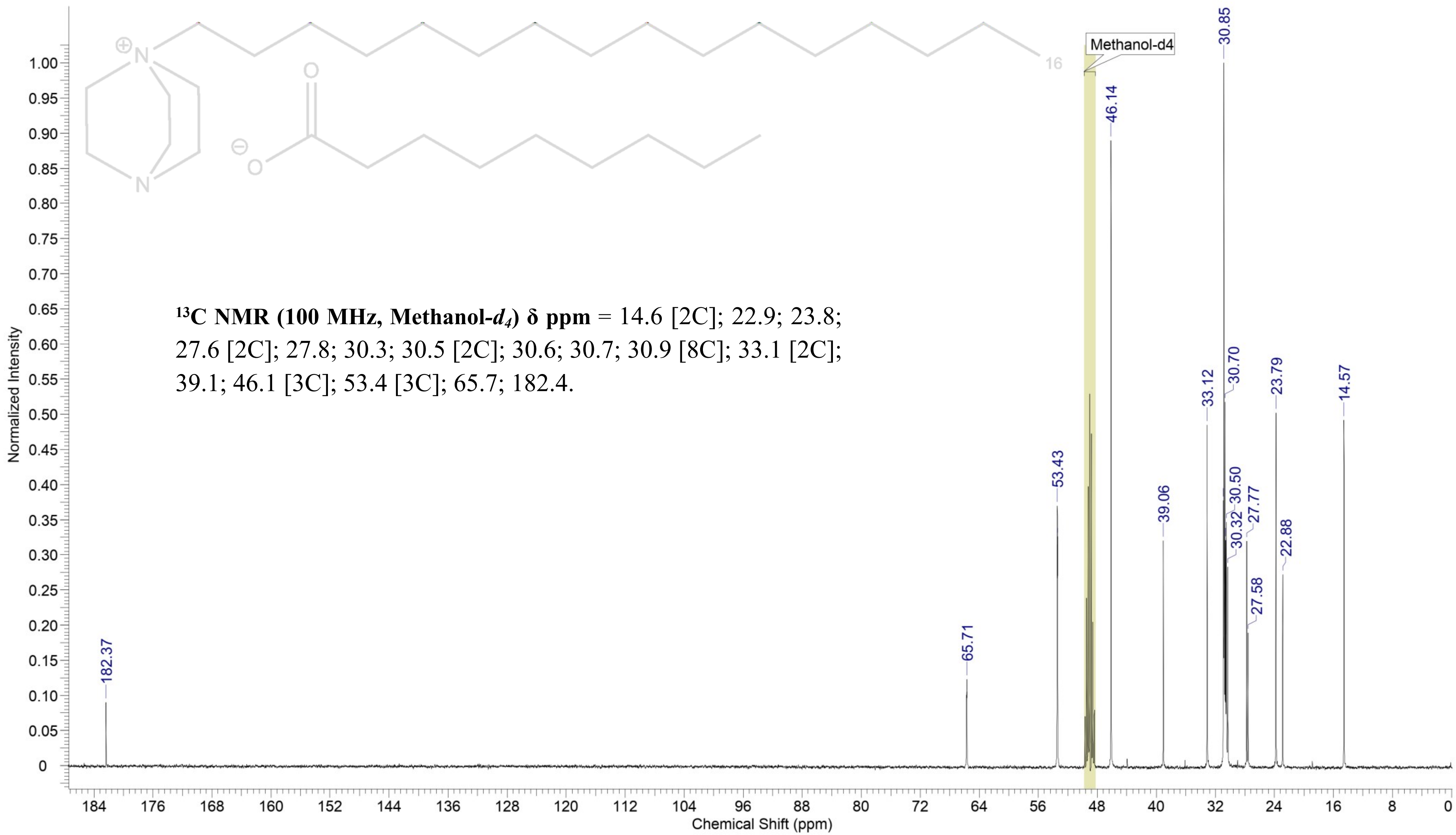


Fig. A.9 ^{1}H NMR spectrum of 1-octadecyl -1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(8)**.

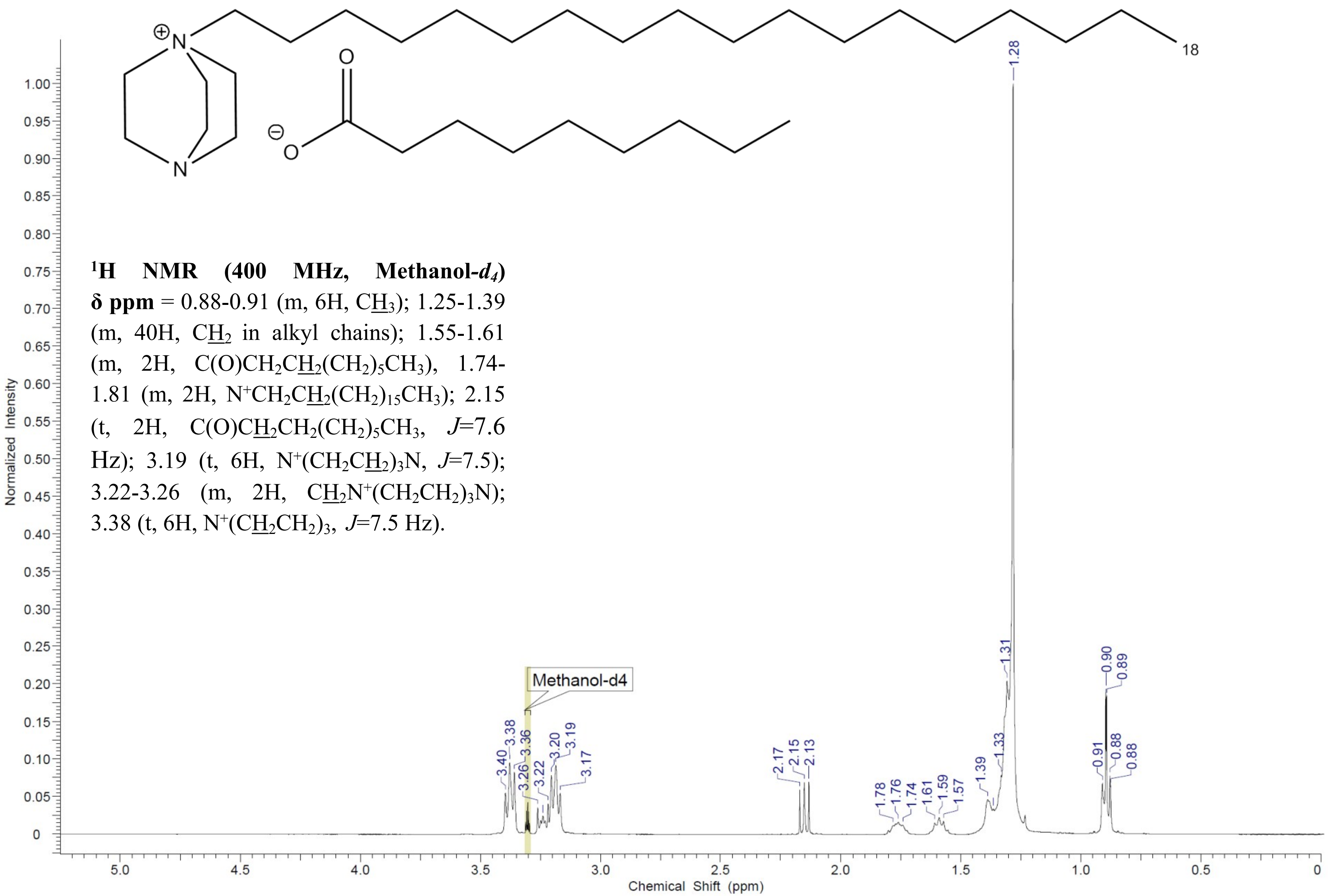
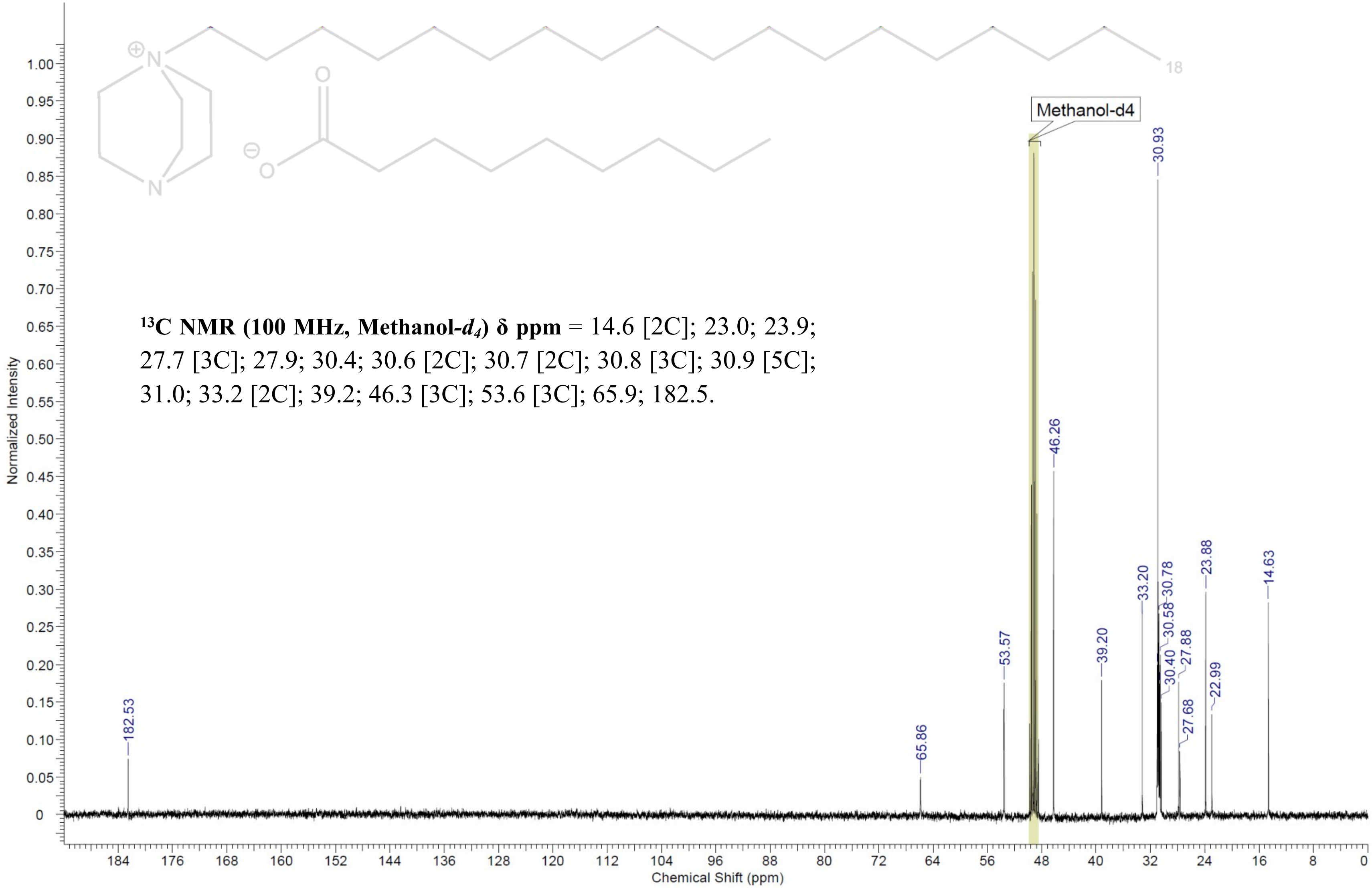


Fig. A.10 ^{13}C NMR spectrum of 1-octadecyl -1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(8)**.



^{13}C NMR (100 MHz, Methanol-*d_4*) δ ppm = 14.6 [2C]; 23.0; 23.9; 27.7 [3C]; 27.9; 30.4; 30.6 [2C]; 30.7 [2C]; 30.8 [3C]; 30.9 [5C]; 31.0; 33.2 [2C]; 39.2; 46.3 [3C]; 53.6 [3C]; 65.9; 182.5.

Fig. A.11 Comparison of the FT-IR spectra of pelargonic acid, 1-tetradecyl-1-azonia-4-azabicyclo[2.2.2]octane bromide and 1-tetradecyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(6)**.

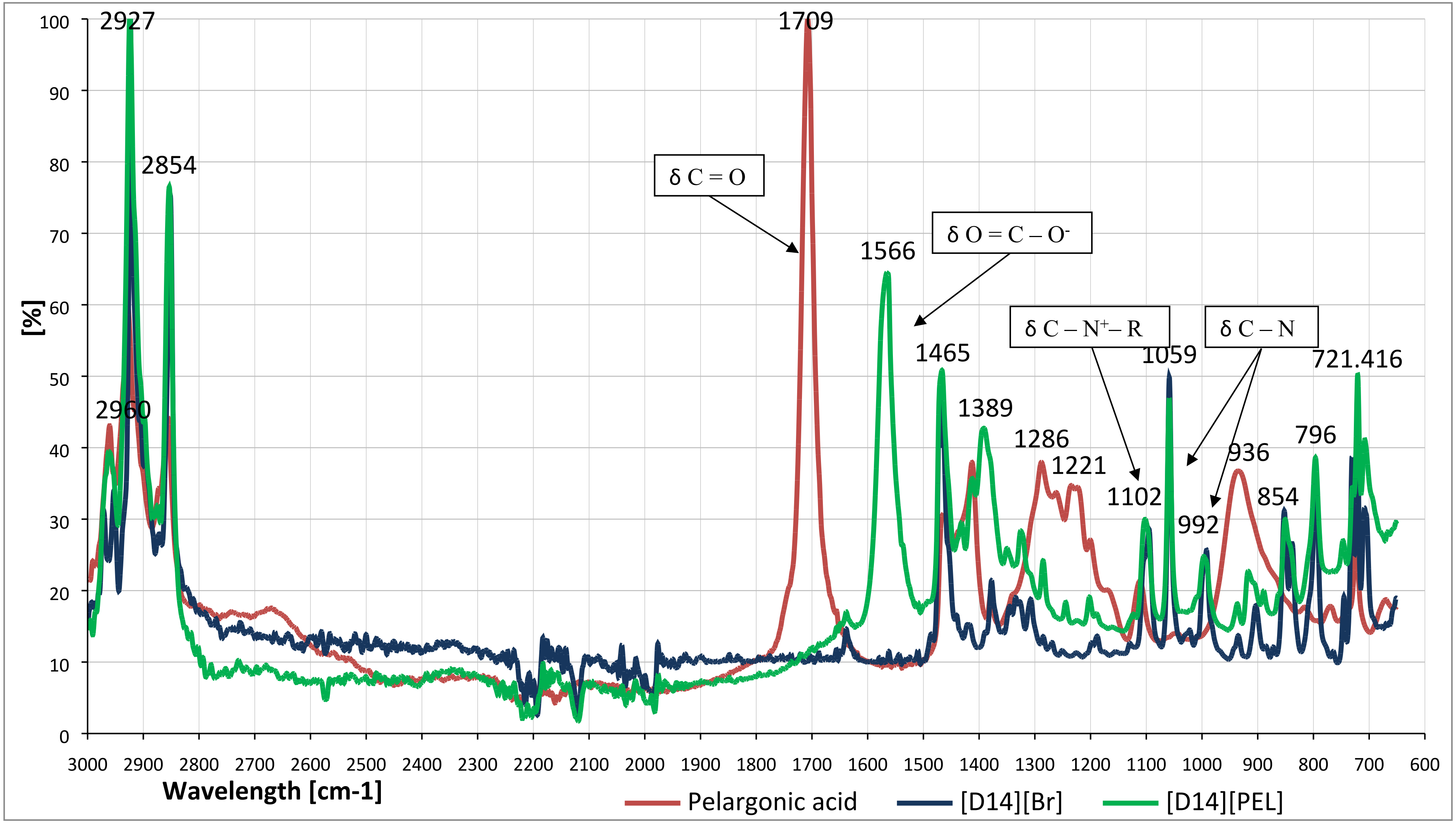
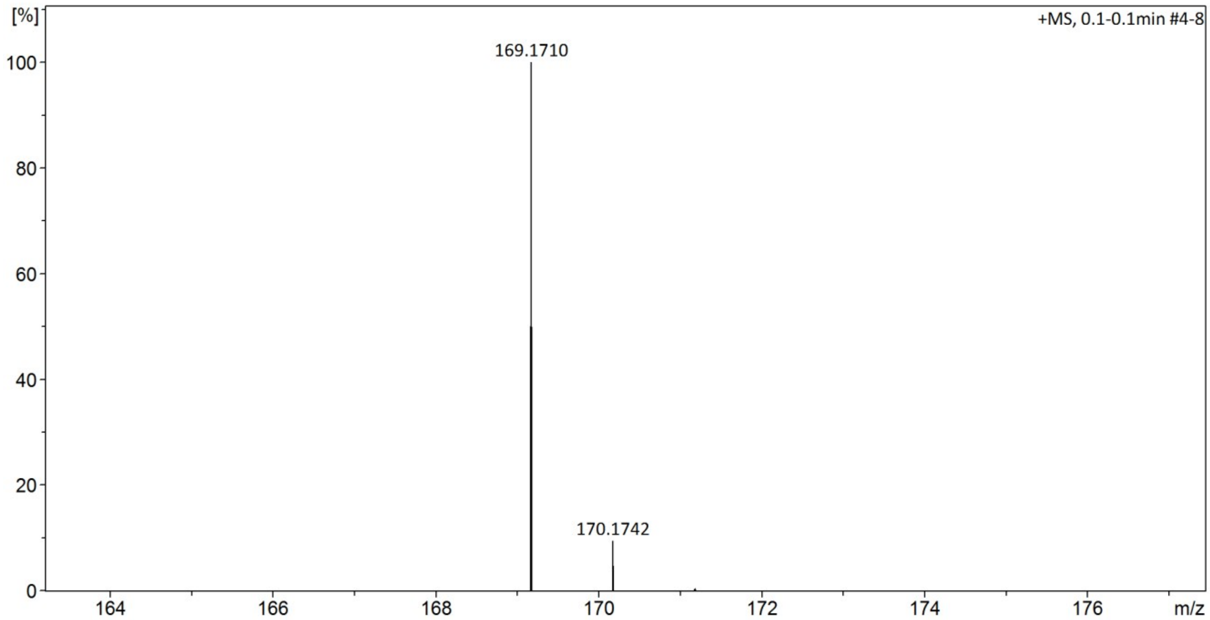


Table A.1 Elemental analysis for 1-alkyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(1-8)**

IL	Short	Chemical formula	Molecular weight [g mol^{-1}]	Calculated values [%]			Obtained values [%]		
				C	H	N	C	H	N
1	**[D$_4$][PEL]**	$C_{19}H_{38}N_2O_2$	326.52	69.89	11.73	8.58	69.56	11.54	8.33
2	**[D$_6$][PEL]**	$C_{21}H_{42}N_2O_2$	354.57	71.14	11.94	7.90	71.02	12.15	7.76
3	**[D$_8$][PEL]**	$C_{23}H_{46}N_2O_2$	382.62	72.20	12.12	7.32	72.14	11.98	7.05
4	**[D$_{10}$][PEL]**	$C_{25}H_{50}N_2O_2$	410.68	73.12	12.27	6.82	73.33	12.01	7.11
5	**[D$_{12}$][PEL]**	$C_{27}H_{54}N_2O_2$	438.73	73.92	12.41	6.39	73.80	12.10	6.56
6	**[D$_{14}$][PEL]**	$C_{29}H_{58}N_2O_2$	466.78	74.62	12.52	6.00	74.98	12.37	6.04
7	**[D$_{16}$][PEL]**	$C_{31}H_{62}N_2O_2$	494.83	75.24	12.63	5.66	75.10	12.42	5.45
8	**[D$_{18}$][PEL]**	$C_{33}H_{66}N_2O_2$	522.89	75.80	12.72	5.36	75.99	12.44	5.23

Fig. A.12 ESI-MS spectra of 1-butyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(1)**.

IL 1: HRMS (ESI-Q-TOF), (ES^+) for $C_{10}H_{21}N_2^+$ [m/z] = 169.1699 (calculated), 169.1710 (found)



IL 1: HRMS (ESI-Q-TOF), (ES^-) for $C_9H_{17}O_2^-$ [m/z] = 157.1234 (calculated), 157.1233 (found)

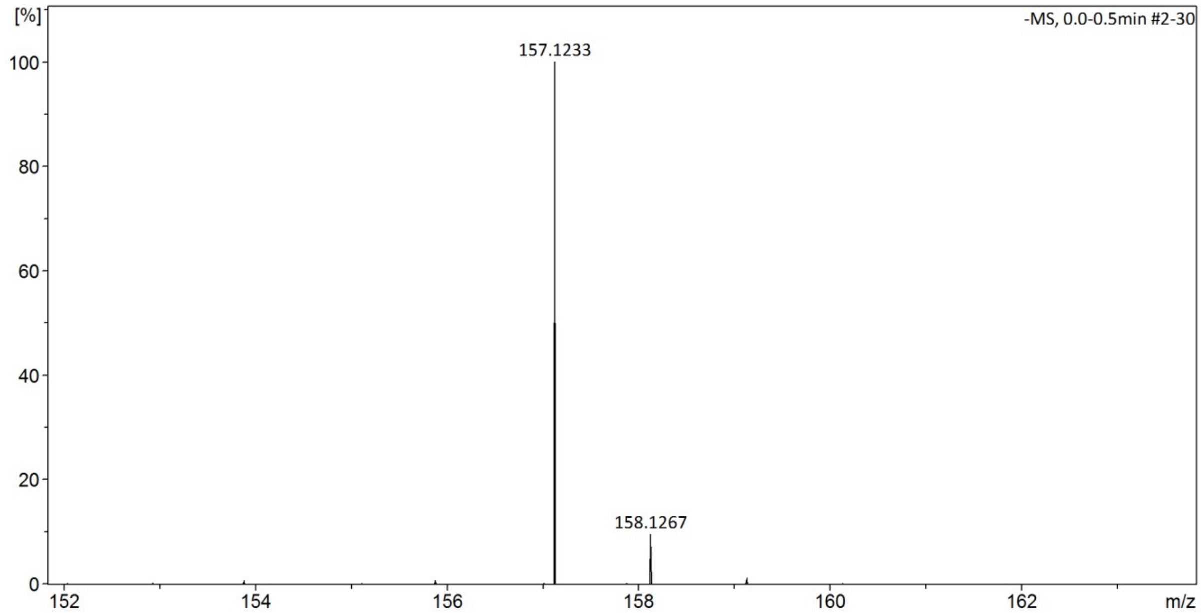
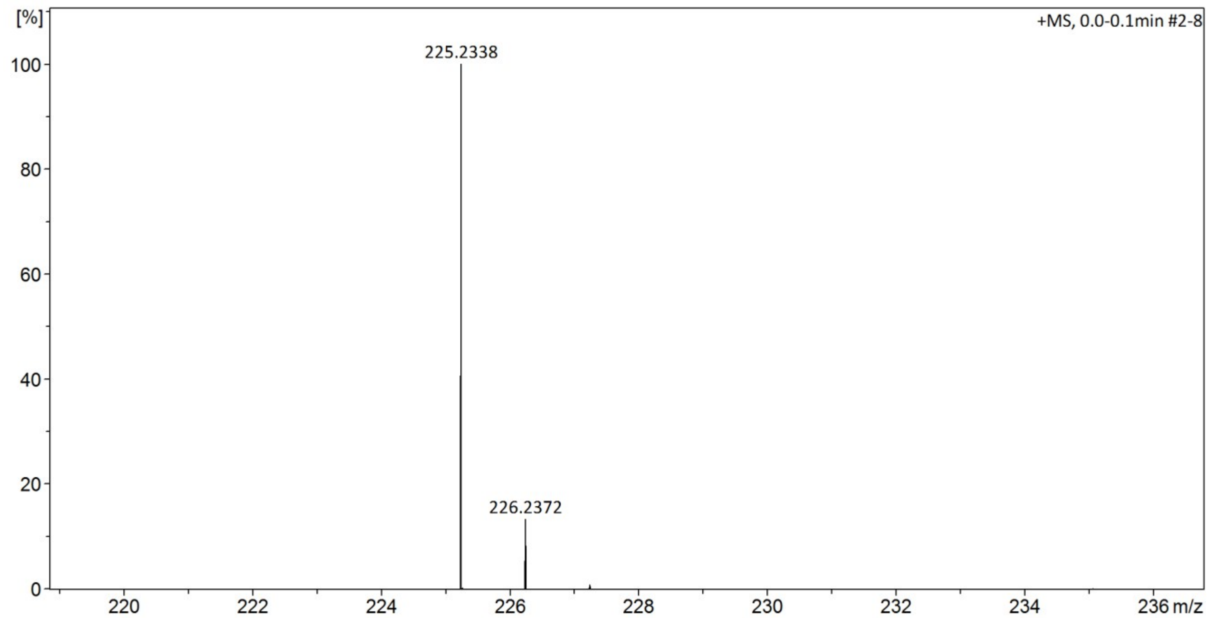


Fig. A.13 ESI-MS spectra of 1-octyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(3)**.

IL 3: HRMS (ESI-Q-TOF), (ES^+) for $C_{14}H_{29}N_2^+$ [m/z] = 225.2325 (calculated), 225.2338 (found)



IL 3: HRMS (ESI-Q-TOF), (ES^-) for $C_9H_{17}O_2^-$ [m/z] = 157.1234 (calculated), 157.1236 (found)

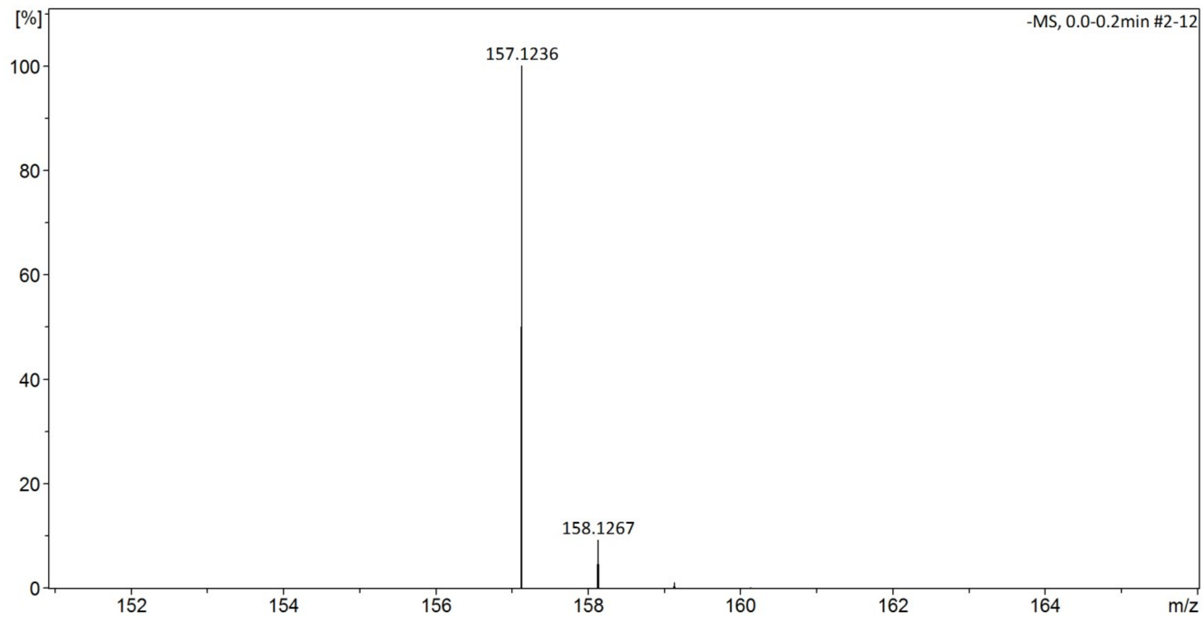
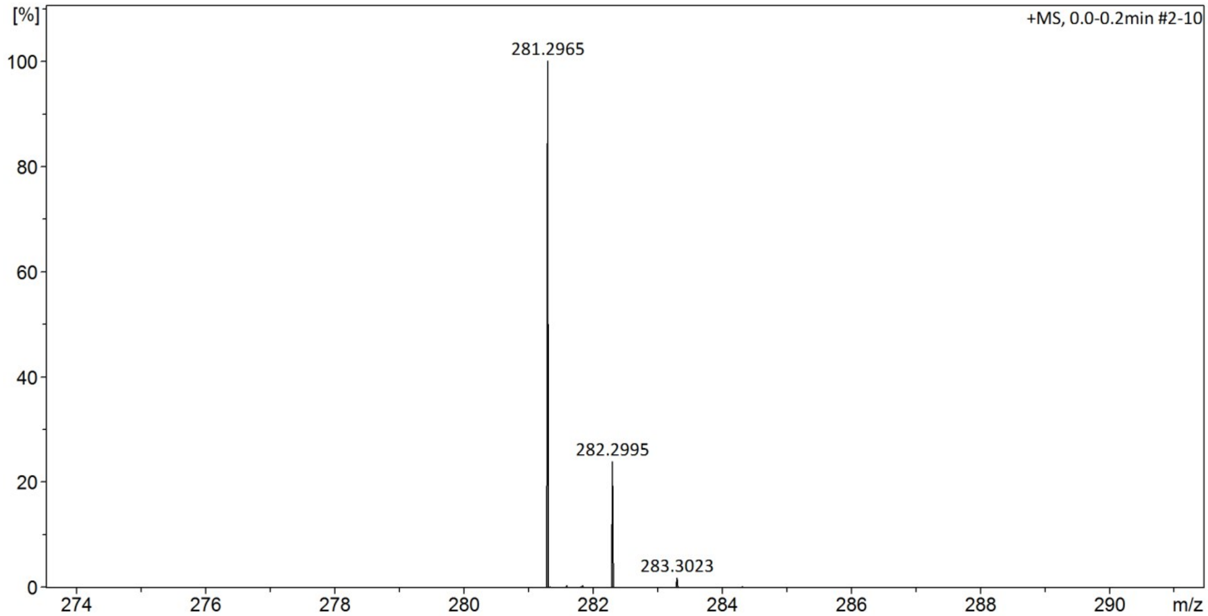


Fig. A.14 ESI-MS spectra of 1-dodecyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(5)**.

IL 5: HRMS (ESI-Q-TOF), (ES^+) for $C_{18}H_{37}N_2^+$ [m/z] = 281.2951 (calculated), 281.2965 (found)



IL 5: HRMS (ESI-Q-TOF), (ES^-) for $C_9H_{17}O_2^-$ [m/z] = 157.1234 (calculated), 157.1235 (found)

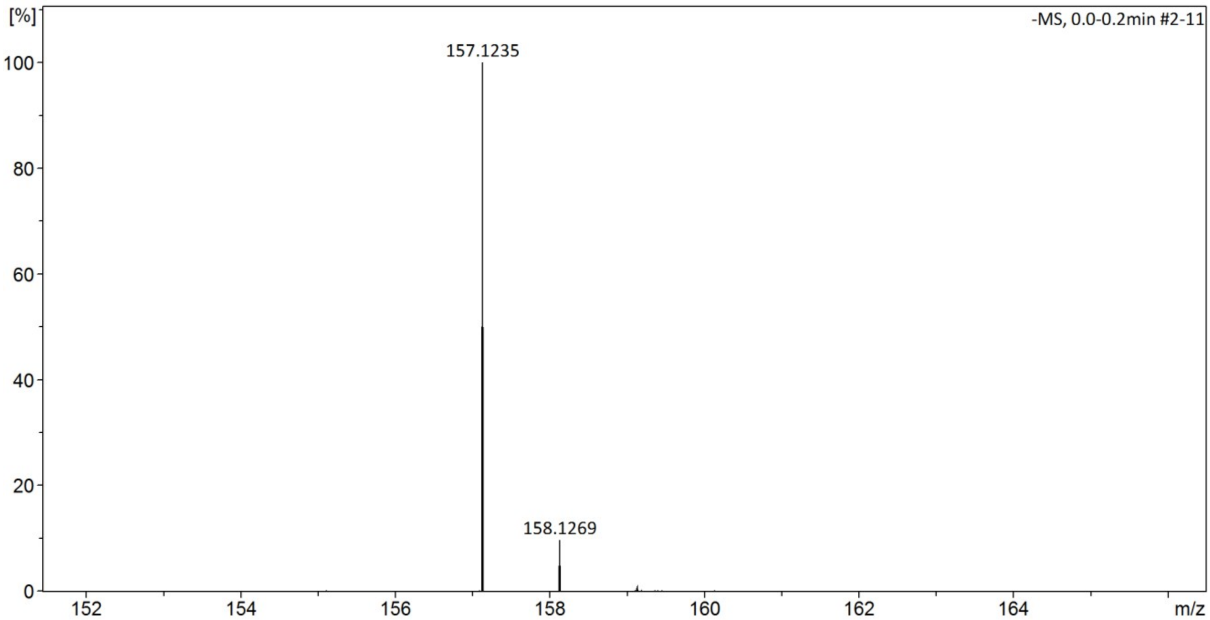
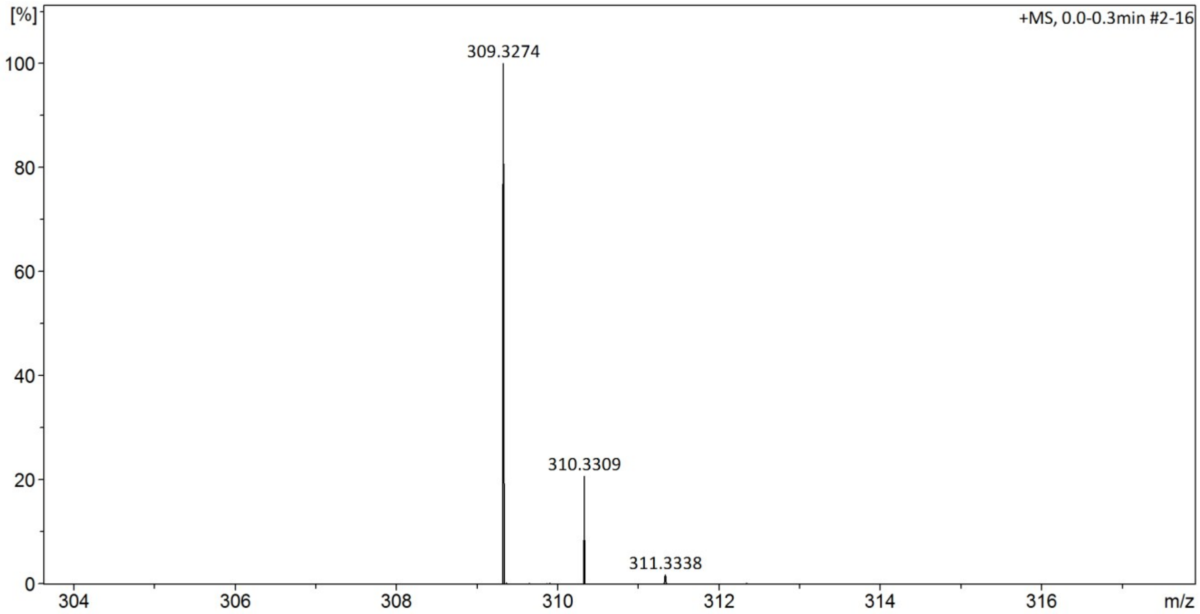


Fig. A.15 ESI-MS spectra of 1-tetradecyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(6)**.

IL 6: HRMS (ESI-Q-TOF), (ES^+) for $C_{20}H_{41}N_2^+$ [m/z] = 309.3264 (calculated), 309.3274 (found)



IL 6: HRMS (ESI-Q-TOF), (ES^-) for $C_9H_{17}O_2^-$ [m/z] = 157.1234 (calculated), 157.1235 (found)

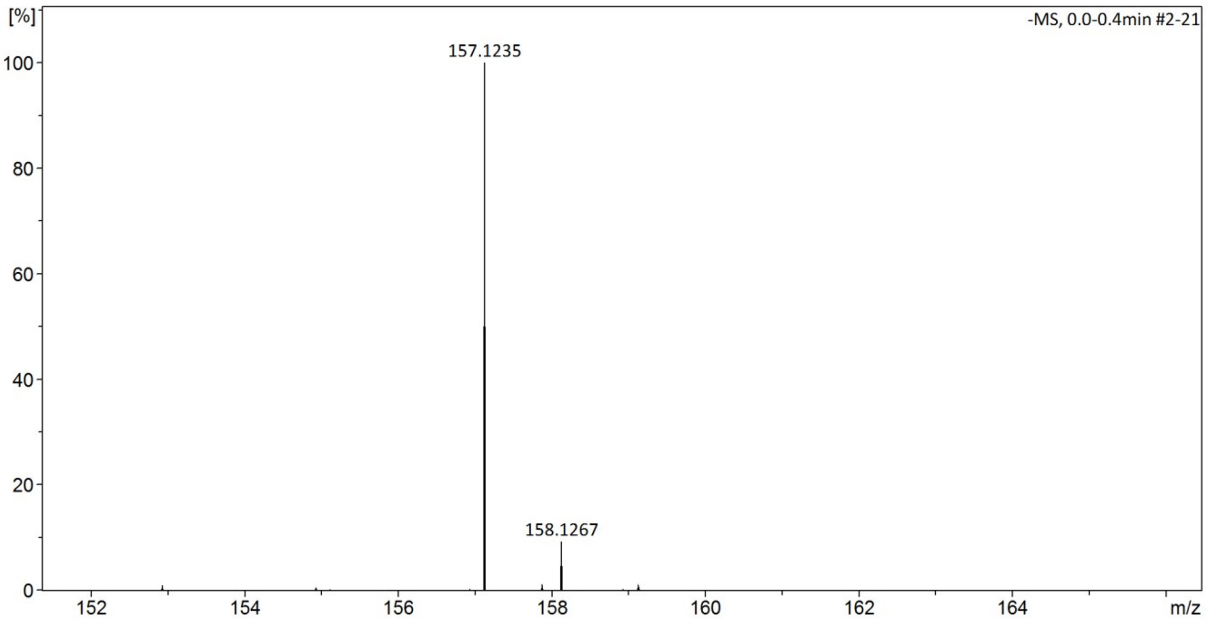
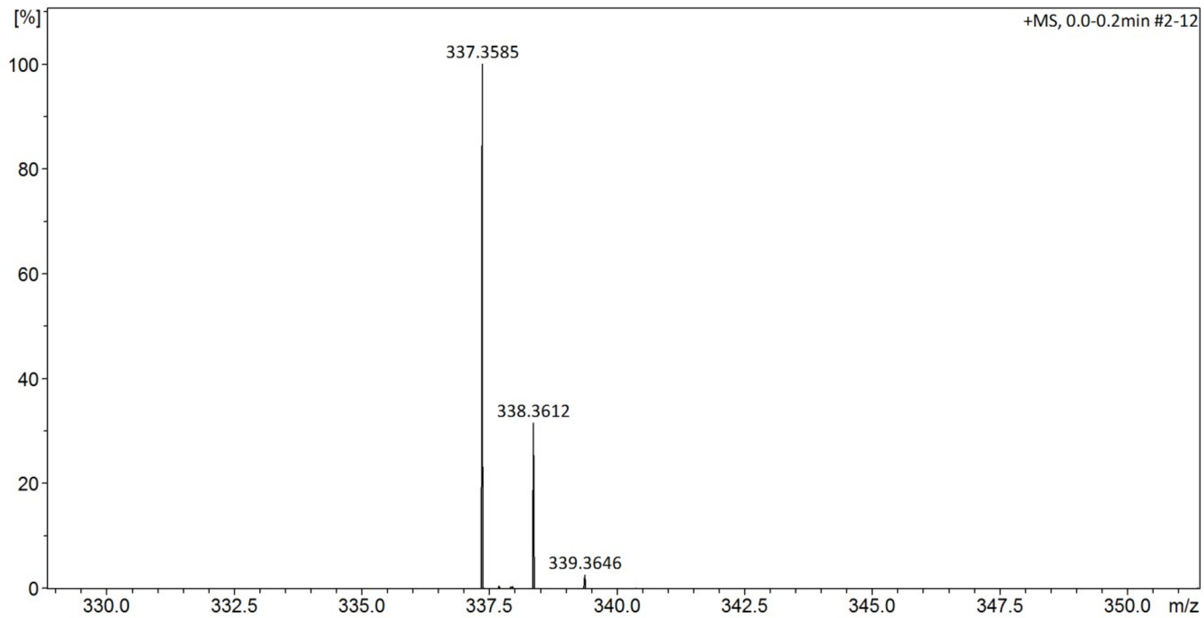
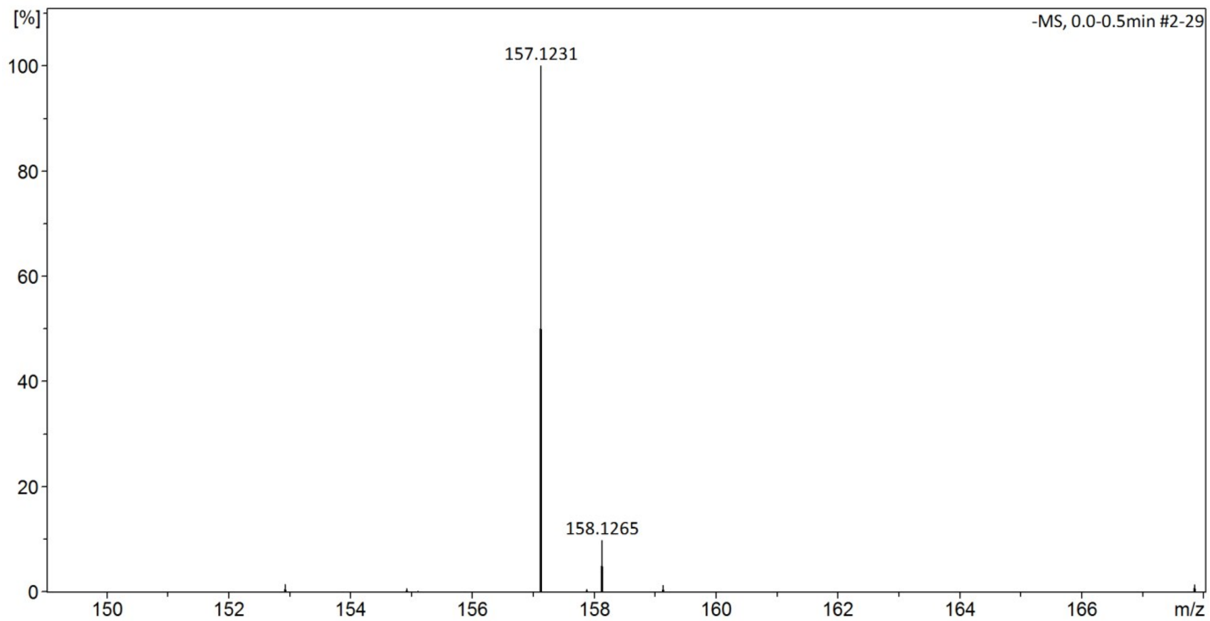


Fig. A.16 ESI-MS spectra of 1-hexadecyl-1-azonia-4-azabicyclo[2.2.2]octane pelargonate **(7)**.

IL 7: HRMS (ESI-Q-TOF), (ES^+) for $C_{22}H_{45}N_2^+$ [m/z] = 337.3577 (calculated), 337.3585 (found)



IL 7: HRMS (ESI-Q-TOF), (ES^-) for $C_9H_{17}O_2^-$ [m/z] = 157.1234 (calculated), 157.1231 (found)



2. FEEDING DETERRENT ACTIVITY

Table A.2 Feeding deterrent activities of the prepared ILs against tested insects

Compound	Granary weevil (*Sitophilus granarius*)			Confused flour beetle (*Tribolium confusum*)						Khapra beetle (*Trogoderma granarium*)		
	Adults			Adults			Larvae			Larvae		
	R	A	T	R	A	T	R	A	T	R	A	T
[D4][PEL]	98.7 b	58.5 a	157.2 ab	-0.5 a	-18.8 a	-19.3 a	22.1 a	-33.1 a	-11.0 a	36.4 a	16.6 ab	53.0 a
[D6][PEL]	43.4 a	66.8 a	110.2 a	12.5 ab	-0.7 ab	11.8 ab	48.8 ab	-27.1 a	21.7 ab	44.6 ab	-0.1 a	44.5 a
[D8][PEL]	98.6 b	56.8 a	155.4 ab	39.2 abc	-18.6 a	20.6 abc	20.2 a	-1.4 a	18.8 ab	44.0 ab	43.5 bc	87.5 ab
[D10][PEL]	100.0 b	84.0 a	184.0 b	41.2 abc	9.7 bc	50.9 bcd	68.2 bc	-25.7 a	42.5 abc	80.9 ab	68.7 c	149.6 bc
[D12][PEL]	97.1 b	71.2 a	168.3 b	44.1 bc	5.1 abc	49.2 bc	22.1 a	-1.9 a	20.2 ab	85.0 ab	73.2 c	158.2 c
[D14][PEL]	100.0 b	79.0 a	179.0 b	32.6 abc	29.4 cd	62.0 cd	64.0 bc	-15.5 a	48.5 abc	94.4 b	80.8 c	175.2 c
[D16][PEL]	100.0 b	90.9 a	190.9 b	65.0 c	-3.0 ab	62.0 cd	90.1 c	-16.6 a	73.5 bc	81.5 ab	77.0 c	158.5 c
[D18][PEL]	100.0 b	79.7 a	179.7 b	61.0 c	37.4 d	98.4 d	95.9 c	14.6 a	110.5 c	82.1 ab	71.8 c	153.9 bc
$LSD_{0.05}$	25.5	34.5	48.5	39.6	23.8	43.5	33.8	51.3	70.7	49.5	36.9	60.6
Azadirachtin[a]	100.0	74.3	174.3	100.0	85.0	185.0	100.0	88.4	188.4	100.0	94.2	194.2

a - J. Pernak, K. Wasiński, T. Praczyk, J. Nawrot, A. Cieniecka-Rosłonkiewicz, F. Walkiewicz, K. Materna, Sweet ionic liquids-cyclamates: Synthesis, properties, and application as feeding deterrents, *Sci. China: Chem*. 55 (2012) 1532–1541. https://doi.org/10.1007/s11426-012-4631-9

3. THE RELATION BETWEEN THE SURFACE TENSION REDUCTION EFFICIENCY pC_{20} AND BIOLOGICAL ACTIVITY

Fig. A.17 Relationship between the plant's fresh weight reduction and pC_{20} for 1/2 N dose of ILs **5-8.**