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ELECTRONIC SUPPORTING INFORMATION

New Journal of Chemistry

Difunctional ammonium ionic liquids with bicyclic cation

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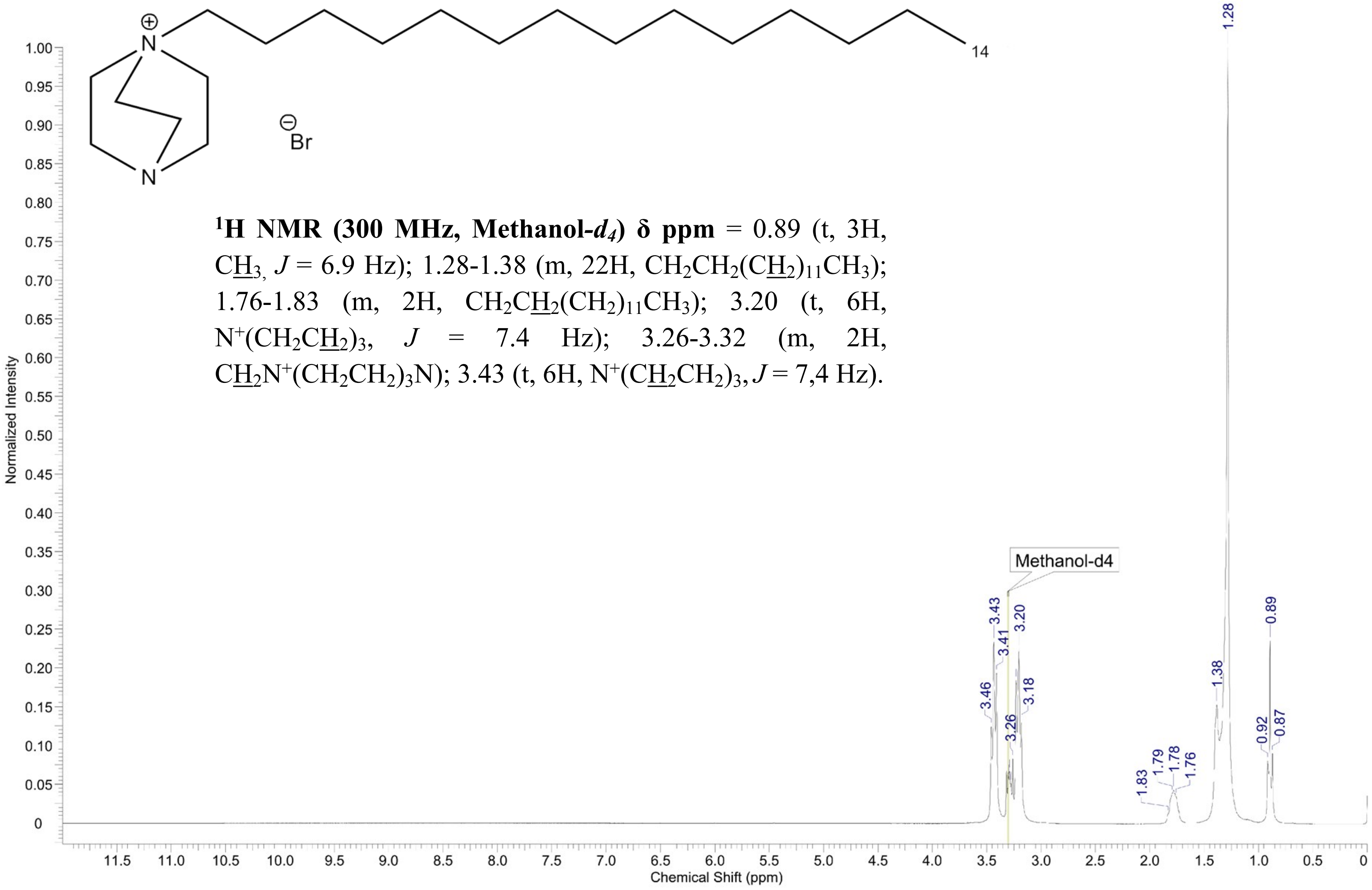
The following abbreviations were used to explain the multiplicities:

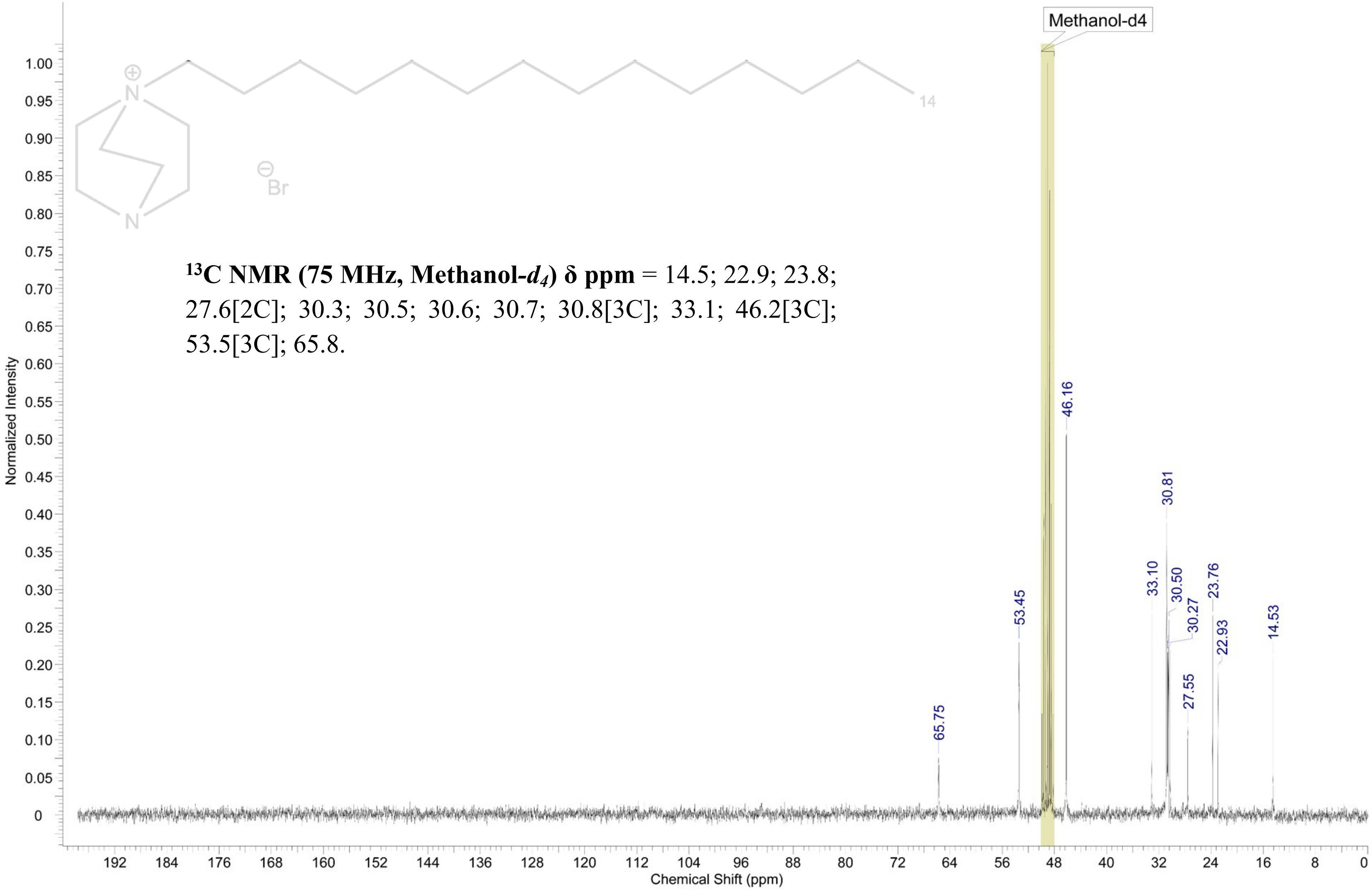
s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets.

Fig. S1 ^{1}H NMR spectrum of 1-tetradecyl-1-azonia-4-azabicyclo[2.2.2]octane bromide **(6)**.



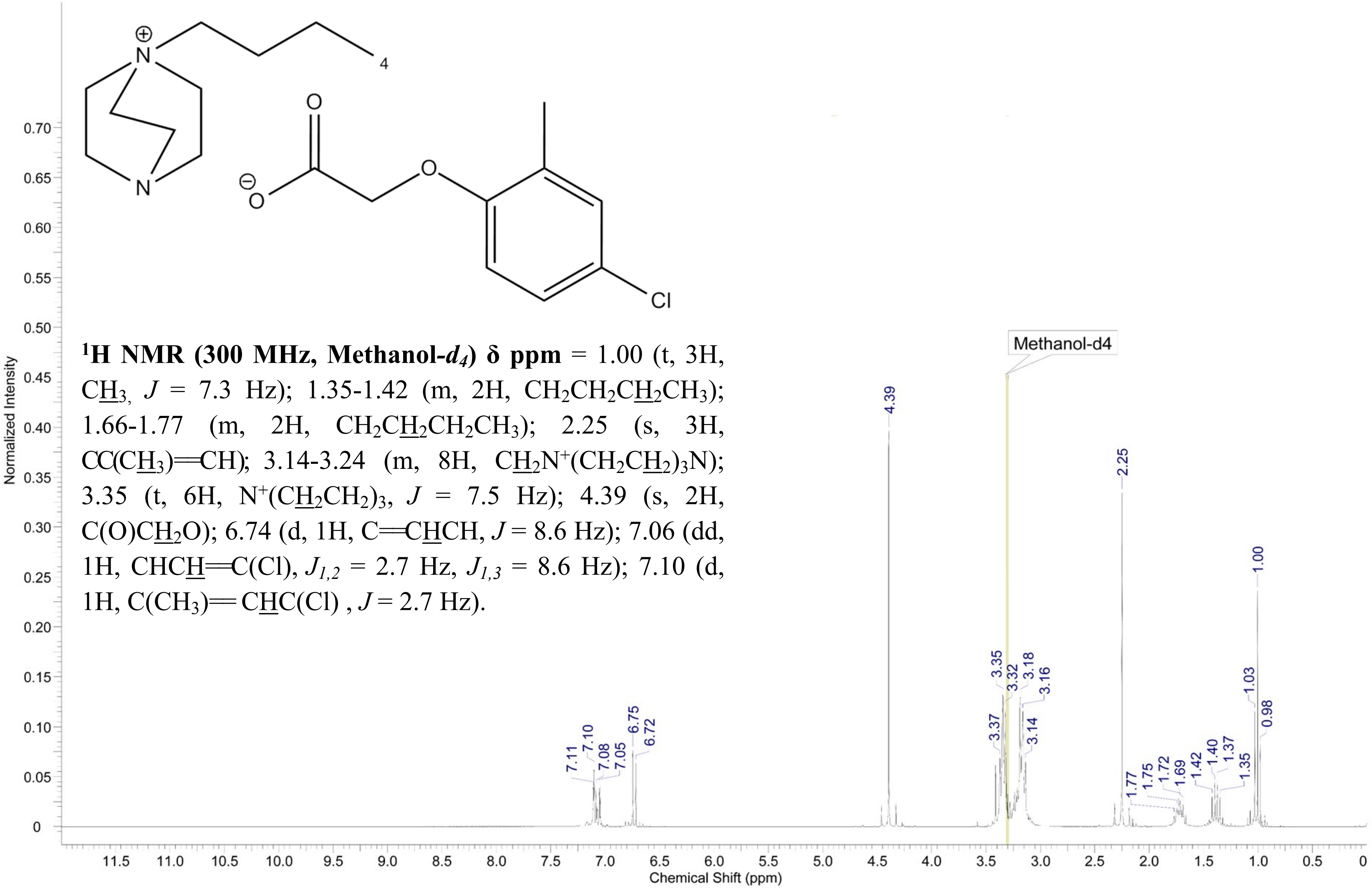
^{1}H NMR (300 MHz, Methanol-d_4) δ ppm = 0.89 (t, 3H, $C\underline{H}_3$, J = 6.9 Hz); 1.28-1.38 (m, 22H, $CH_2CH_2(C\underline{H}_2)_{11}CH_3$); 1.76-1.83 (m, 2H, $CH_2C\underline{H}_2(CH_2)_{11}CH_3$); 3.20 (t, 6H, $N^+(CH_2C\underline{H}_2)_3$, J = 7.4 Hz); 3.26-3.32 (m, 2H, $C\underline{H}_2N^+(CH_2CH_2)_3N$); 3.43 (t, 6H, $N^+(C\underline{H}_2CH_2)_3$, J = 7,4 Hz).

Fig. S2 ^{13}C NMR spectrum of 1-tetradecyl-1-azonia-4-azabicyclo[2.2.2]octane bromide **(6)**.



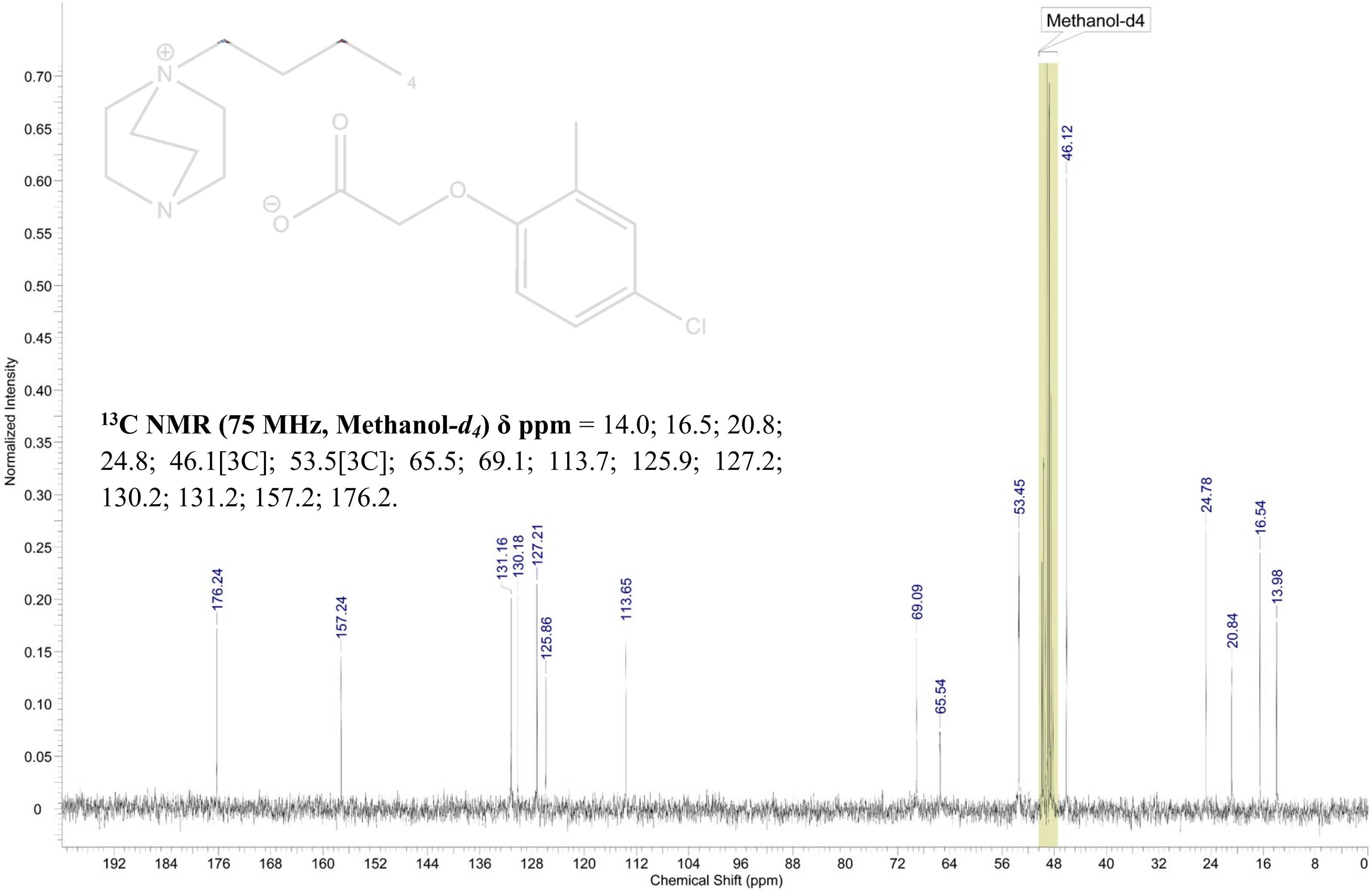
^{13}C NMR (75 MHz, Methanol-d_4) δ ppm = 14.5; 22.9; 23.8; 27.6[2C]; 30.3; 30.5; 30.6; 30.7; 30.8[3C]; 33.1; 46.2[3C]; 53.5[3C]; 65.8.

Fig. S3 ^{1}H NMR spectrum of 1-butyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(9)**.



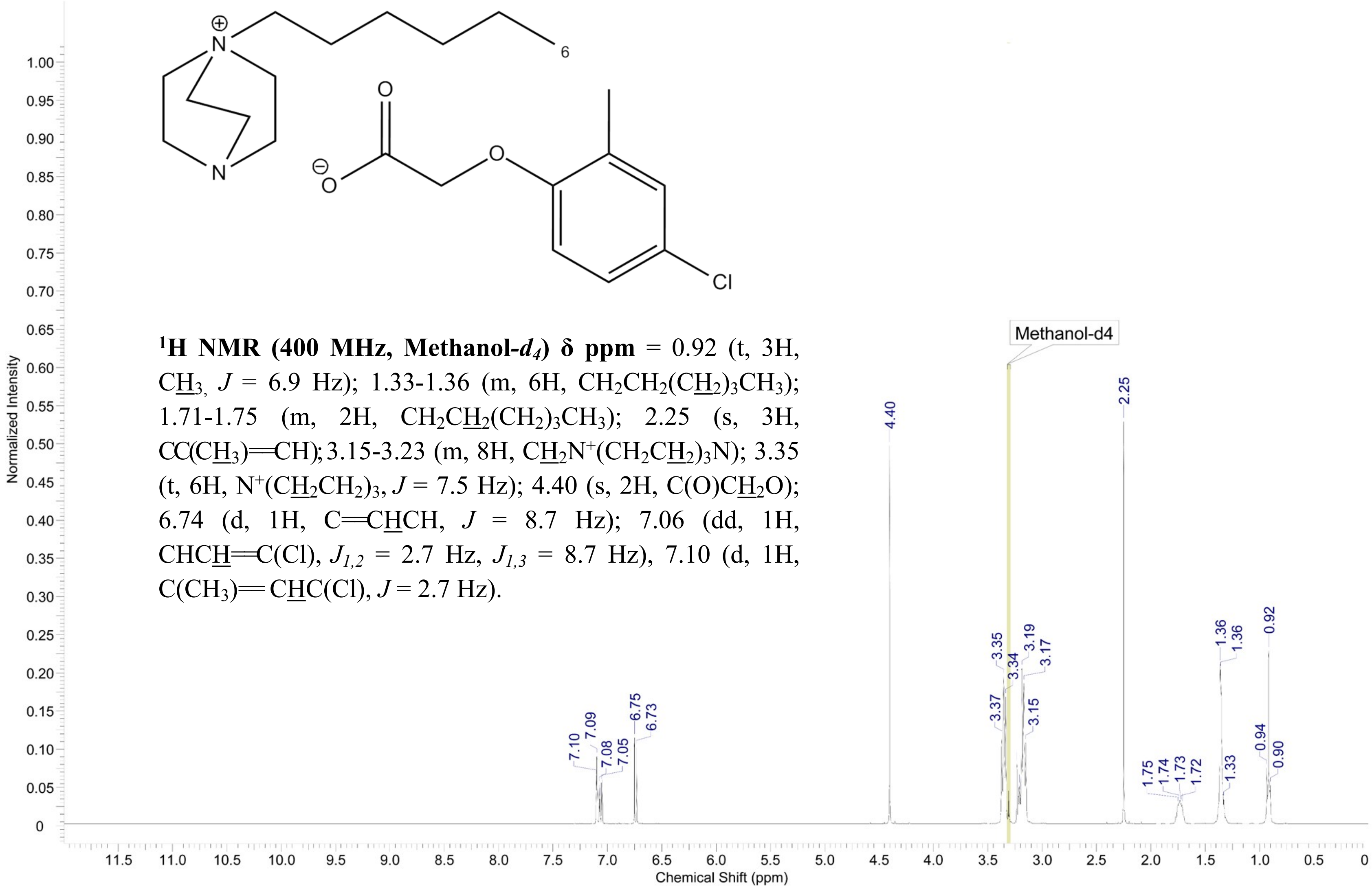
^{1}H NMR (300 MHz, Methanol-d_4) δ ppm = 1.00 (t, 3H, $C\underline{H}_3$, J = 7.3 Hz); 1.35-1.42 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$); 1.66-1.77 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$); 2.25 (s, 3H, $CC(C\underline{H}_3){=}CH$); 3.14-3.24 (m, 8H, $C\underline{H}_2N^+(CH_2C\underline{H}_2)_3N$); 3.35 (t, 6H, $N^+(C\underline{H}_2CH_2)_3$, J = 7.5 Hz); 4.39 (s, 2H, $C(O)C\underline{H}_2O$); 6.74 (d, 1H, $C{=}C\underline{H}CH$, J = 8.6 Hz); 7.06 (dd, 1H, $CHC\underline{H}{=}C(Cl)$, $J_{1,2}$ = 2.7 Hz, $J_{1,3}$ = 8.6 Hz); 7.10 (d, 1H, $C(CH_3){=}C\underline{H}C(Cl)$, J = 2.7 Hz).

Fig. S4 ^{13}C NMR spectrum of 1-butyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(9)**.



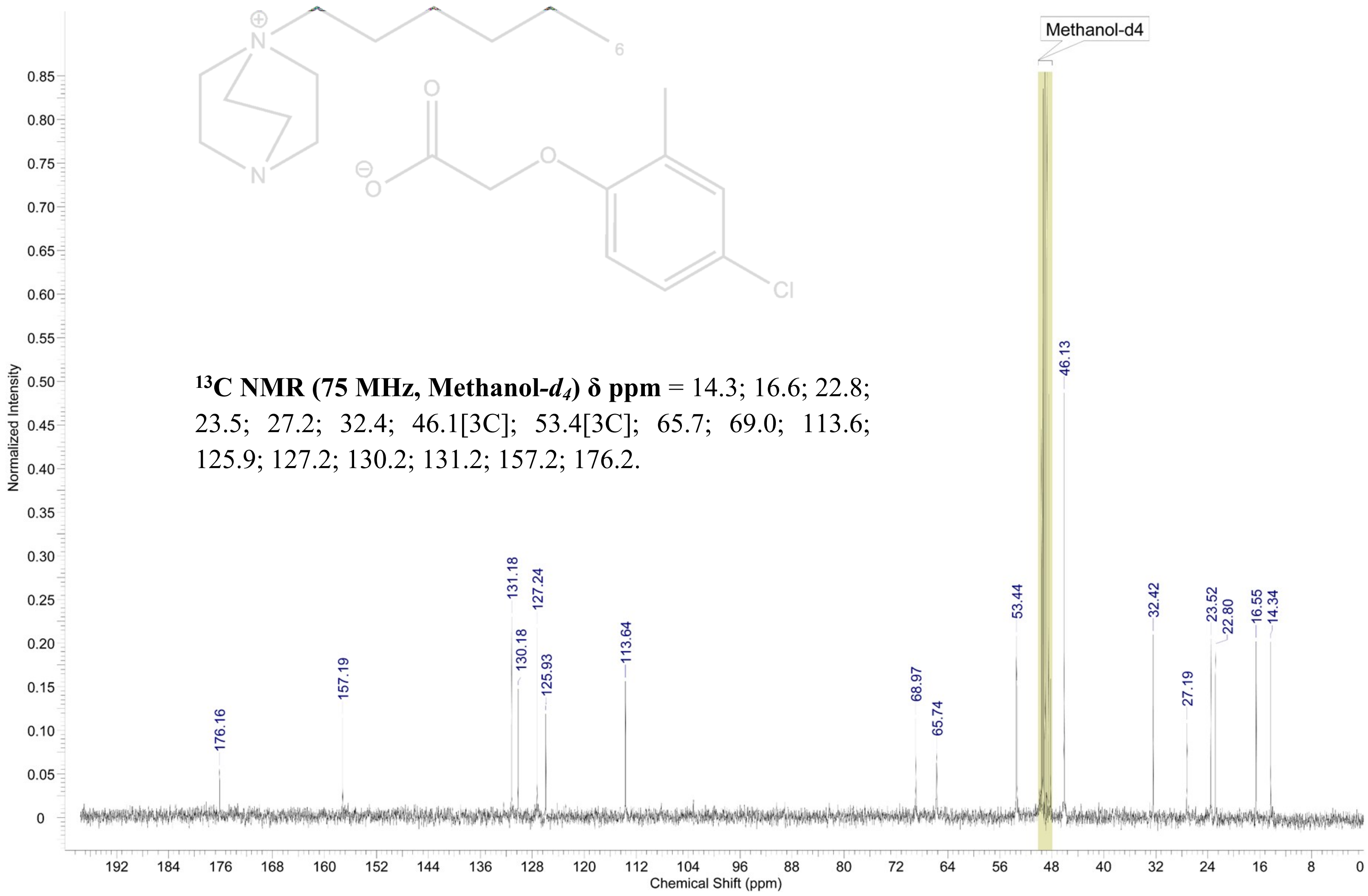
^{13}C NMR (75 MHz, Methanol-d_4) δ ppm = 14.0; 16.5; 20.8; 24.8; 46.1[3C]; 53.5[3C]; 65.5; 69.1; 113.7; 125.9; 127.2; 130.2; 131.2; 157.2; 176.2.

Fig. S5 ^{1}H NMR spectrum of 1-hexyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(10)**.



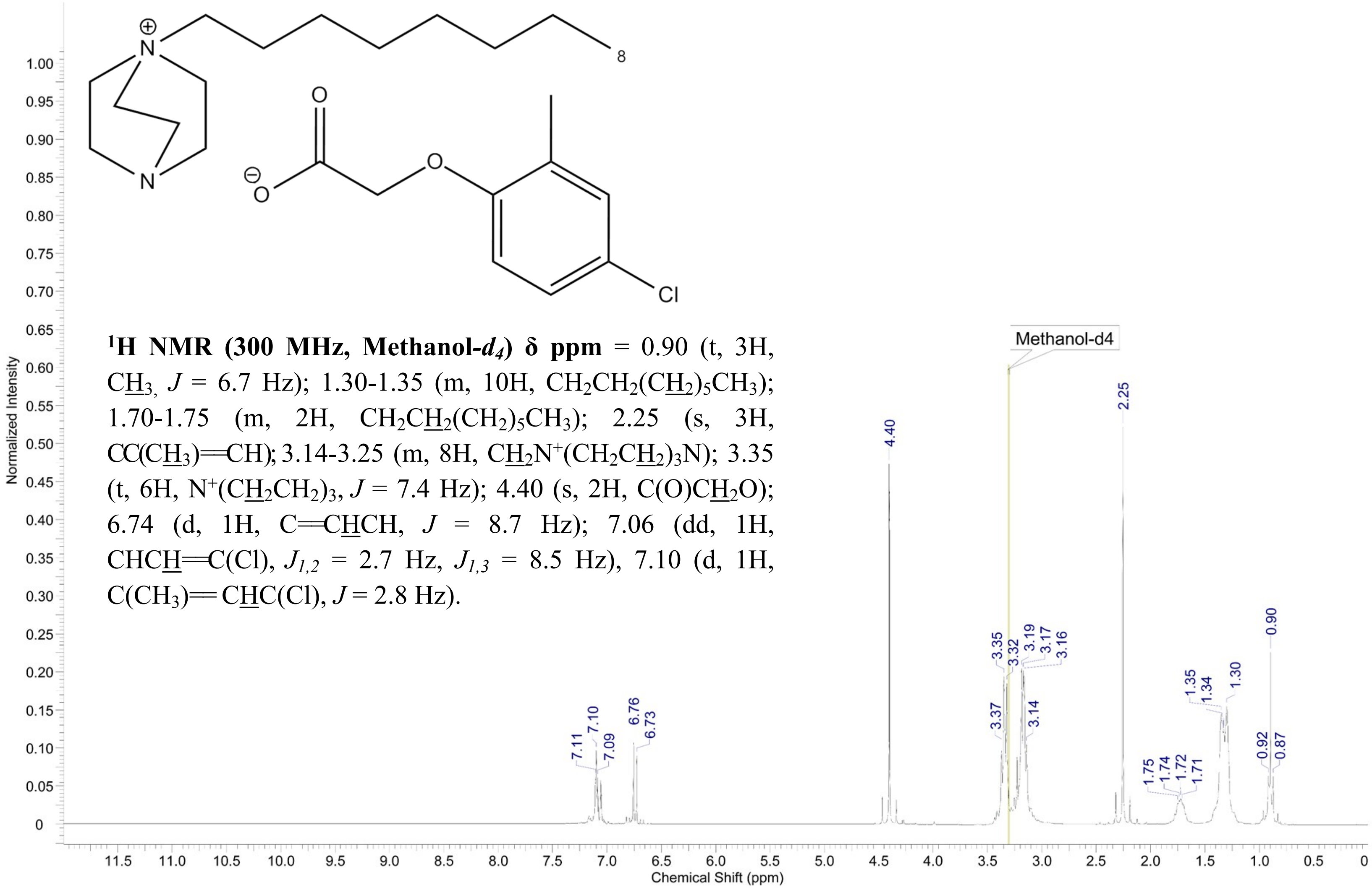
^{1}H NMR (400 MHz, Methanol-*d_4*) δ ppm = 0.92 (t, 3H, $C\underline{H}_3$, J = 6.9 Hz); 1.33-1.36 (m, 6H, $CH_2CH_2(C\underline{H}_2)_3CH_3$); 1.71-1.75 (m, 2H, $CH_2C\underline{H}_2(CH_2)_3CH_3$); 2.25 (s, 3H, $CC(C\underline{H}_3){=}CH$); 3.15-3.23 (m, 8H, $C\underline{H}_2N^+(CH_2C\underline{H}_2)_3N$); 3.35 (t, 6H, $N^+(C\underline{H}_2CH_2)_3$, J = 7.5 Hz); 4.40 (s, 2H, $C(O)C\underline{H}_2O$); 6.74 (d, 1H, $C{=}C\underline{H}CH$, J = 8.7 Hz); 7.06 (dd, 1H, $CHC\underline{H}{=}C(Cl)$, $J_{1,2}$ = 2.7 Hz, $J_{1,3}$ = 8.7 Hz), 7.10 (d, 1H, $C(CH_3){=}C\underline{H}C(Cl)$, J = 2.7 Hz).

Fig. S6 ^{13}C NMR spectrum of 1-hexyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(10)**.



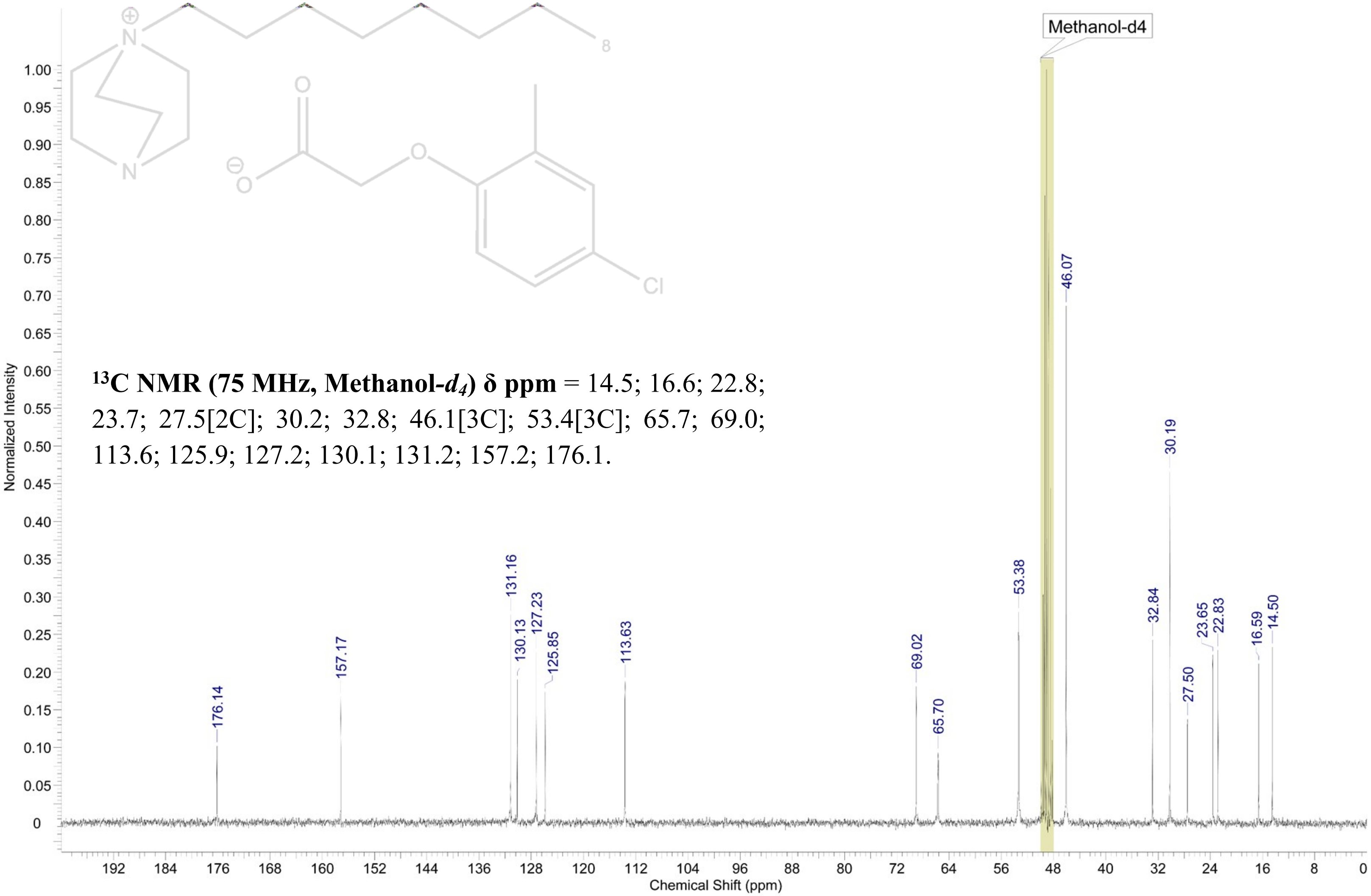
^{13}C NMR (75 MHz, Methanol-d_4) δ ppm = 14.3; 16.6; 22.8; 23.5; 27.2; 32.4; 46.1[3C]; 53.4[3C]; 65.7; 69.0; 113.6; 125.9; 127.2; 130.2; 131.2; 157.2; 176.2.

Fig. S7 ^{1}H NMR spectrum of 1-octyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(11)**.



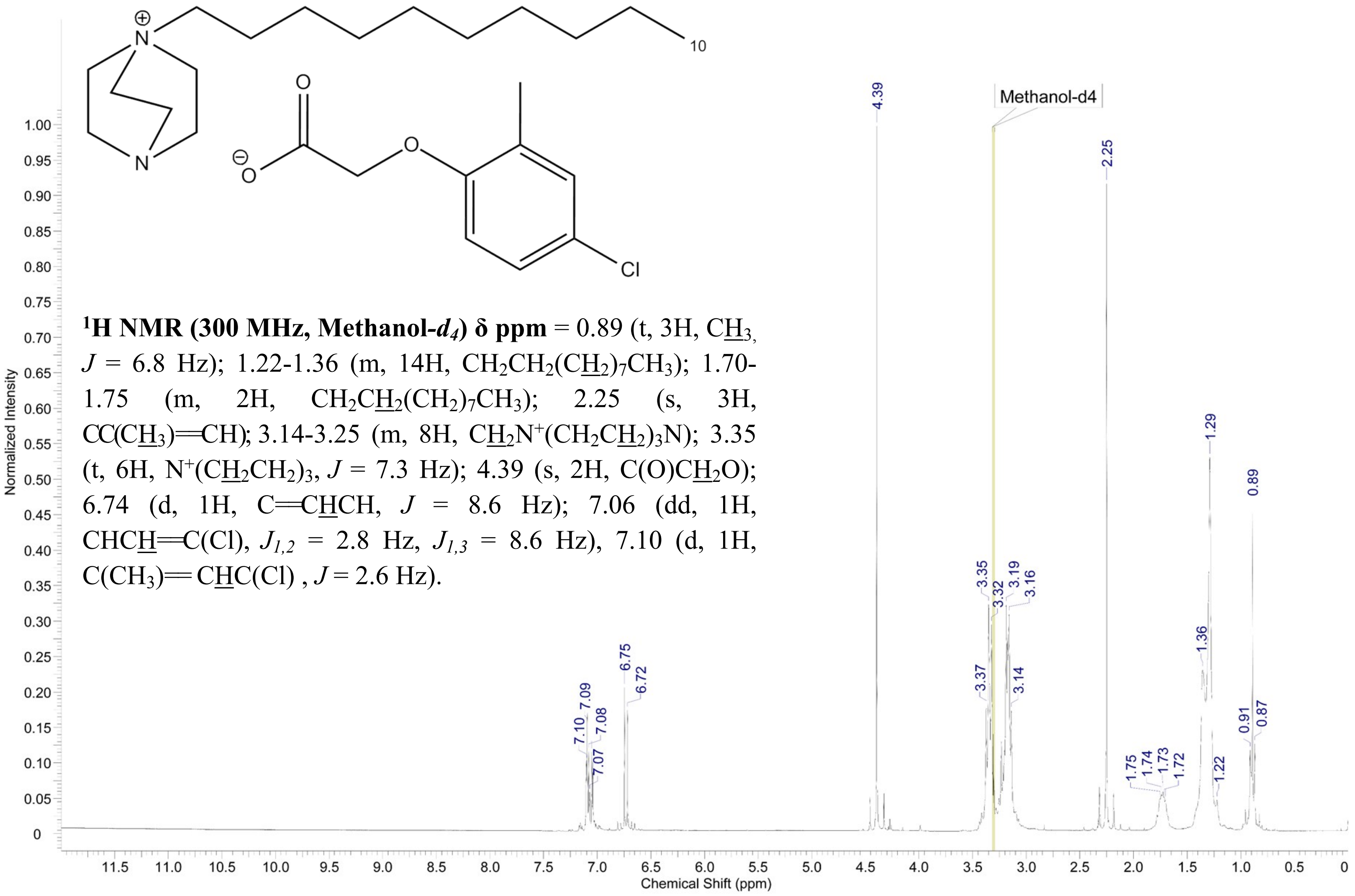
^{1}H NMR (300 MHz, Methanol-d_4) δ ppm = 0.90 (t, 3H, $C\underline{H}_3$, J = 6.7 Hz); 1.30-1.35 (m, 10H, $CH_2CH_2(C\underline{H}_2)_5CH_3$); 1.70-1.75 (m, 2H, $CH_2C\underline{H}_2(CH_2)_5CH_3$); 2.25 (s, 3H, $CC(C\underline{H}_3){=}CH$); 3.14-3.25 (m, 8H, $C\underline{H}_2N^+(CH_2C\underline{H}_2)_3N$); 3.35 (t, 6H, $N^+(C\underline{H}_2CH_2)_3$, J = 7.4 Hz); 4.40 (s, 2H, $C(O)C\underline{H}_2O$); 6.74 (d, 1H, $C{=}C\underline{H}CH$, J = 8.7 Hz); 7.06 (dd, 1H, $CHC\underline{H}{=}C(Cl)$, $J_{1,2}$ = 2.7 Hz, $J_{1,3}$ = 8.5 Hz), 7.10 (d, 1H, $C(CH_3){=}C\underline{H}C(Cl)$, J = 2.8 Hz).

Fig. S8 ^{13}C NMR spectrum of 1-octyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(11)**.



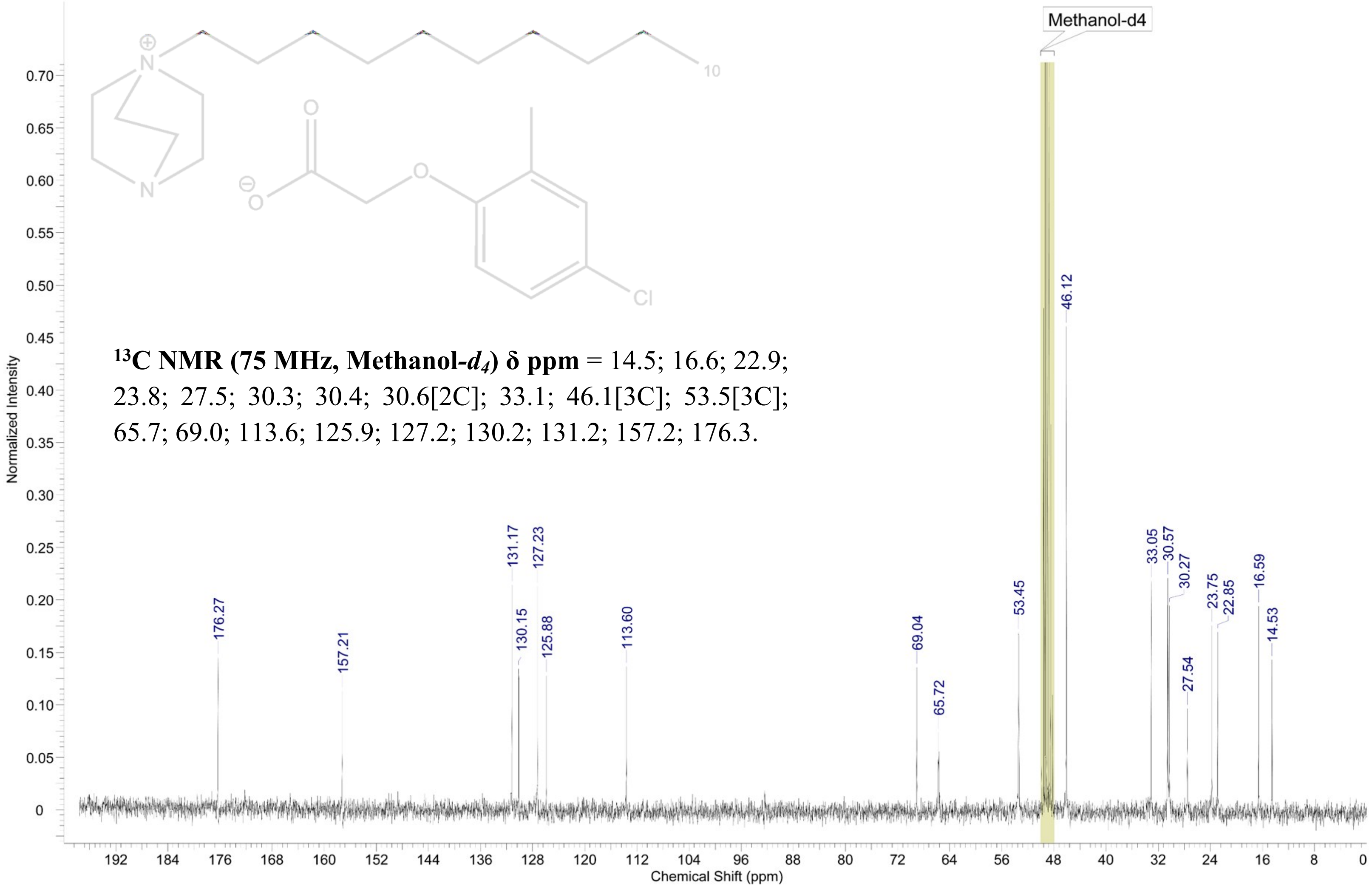
^{13}C NMR (75 MHz, Methanol-d_4) δ ppm = 14.5; 16.6; 22.8; 23.7; 27.5[2C]; 30.2; 32.8; 46.1[3C]; 53.4[3C]; 65.7; 69.0; 113.6; 125.9; 127.2; 130.1; 131.2; 157.2; 176.1.

Fig. S9 ^{1}H NMR spectrum of 1-decyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(12)**.



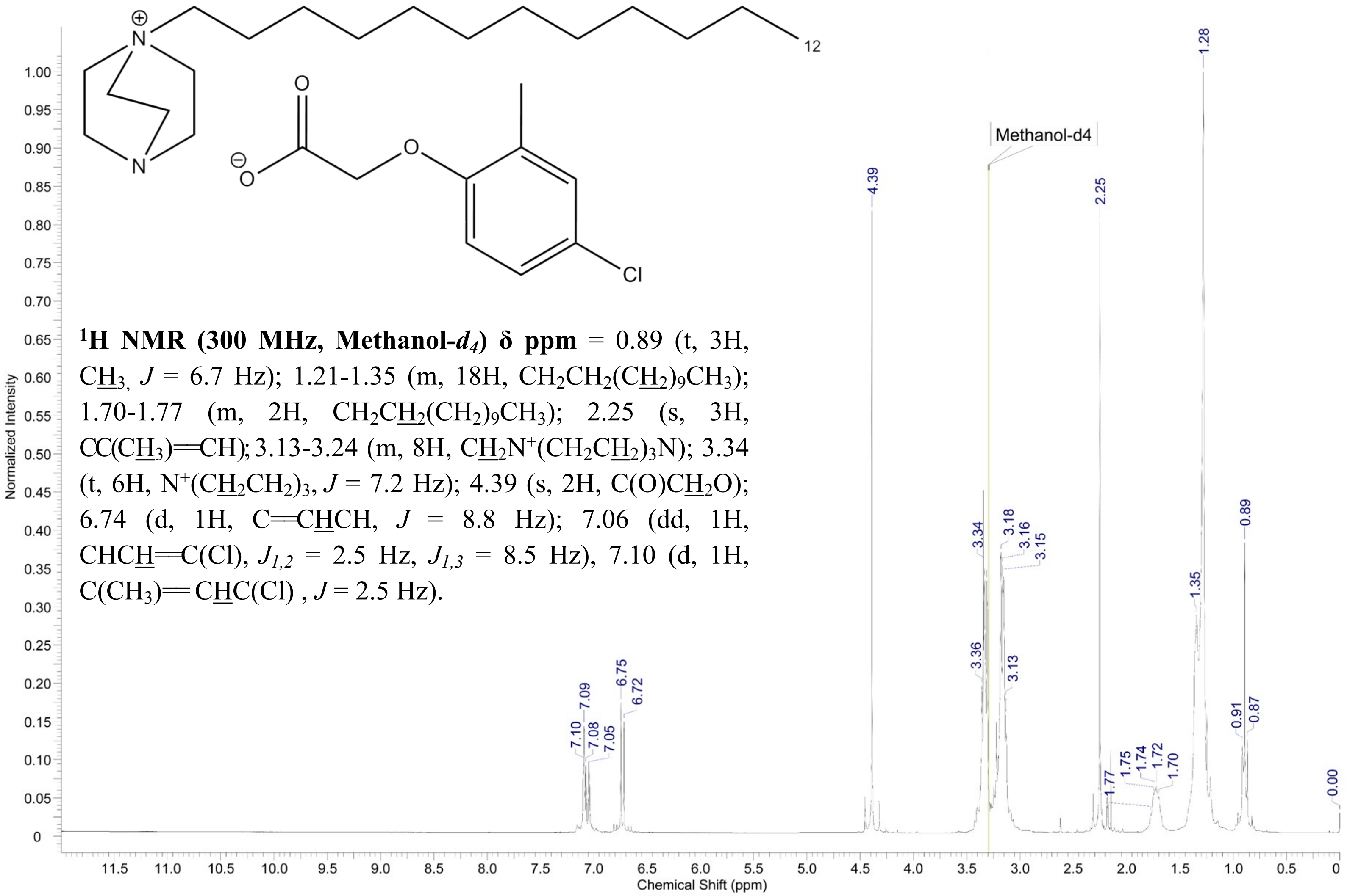
^{1}H NMR (300 MHz, Methanol-d_4) δ ppm = 0.89 (t, 3H, $C\underline{H}_3$, J = 6.8 Hz); 1.22-1.36 (m, 14H, $CH_2CH_2(C\underline{H}_2)_7CH_3$); 1.70-1.75 (m, 2H, $CH_2C\underline{H}_2(CH_2)_7CH_3$); 2.25 (s, 3H, $CC(C\underline{H}_3){=}CH$); 3.14-3.25 (m, 8H, $C\underline{H}_2N^+(CH_2C\underline{H}_2)_3N$); 3.35 (t, 6H, $N^+(C\underline{H}_2CH_2)_3$, J = 7.3 Hz); 4.39 (s, 2H, $C(O)C\underline{H}_2O$); 6.74 (d, 1H, $C{=}C\underline{H}CH$, J = 8.6 Hz); 7.06 (dd, 1H, $CHC\underline{H}{=}C(Cl)$, $J_{1,2}$ = 2.8 Hz, $J_{1,3}$ = 8.6 Hz), 7.10 (d, 1H, $C(CH_3){=}C\underline{H}C(Cl)$, J = 2.6 Hz).

Fig. S10 ^{13}C NMR spectrum of 1-decyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(12)**.



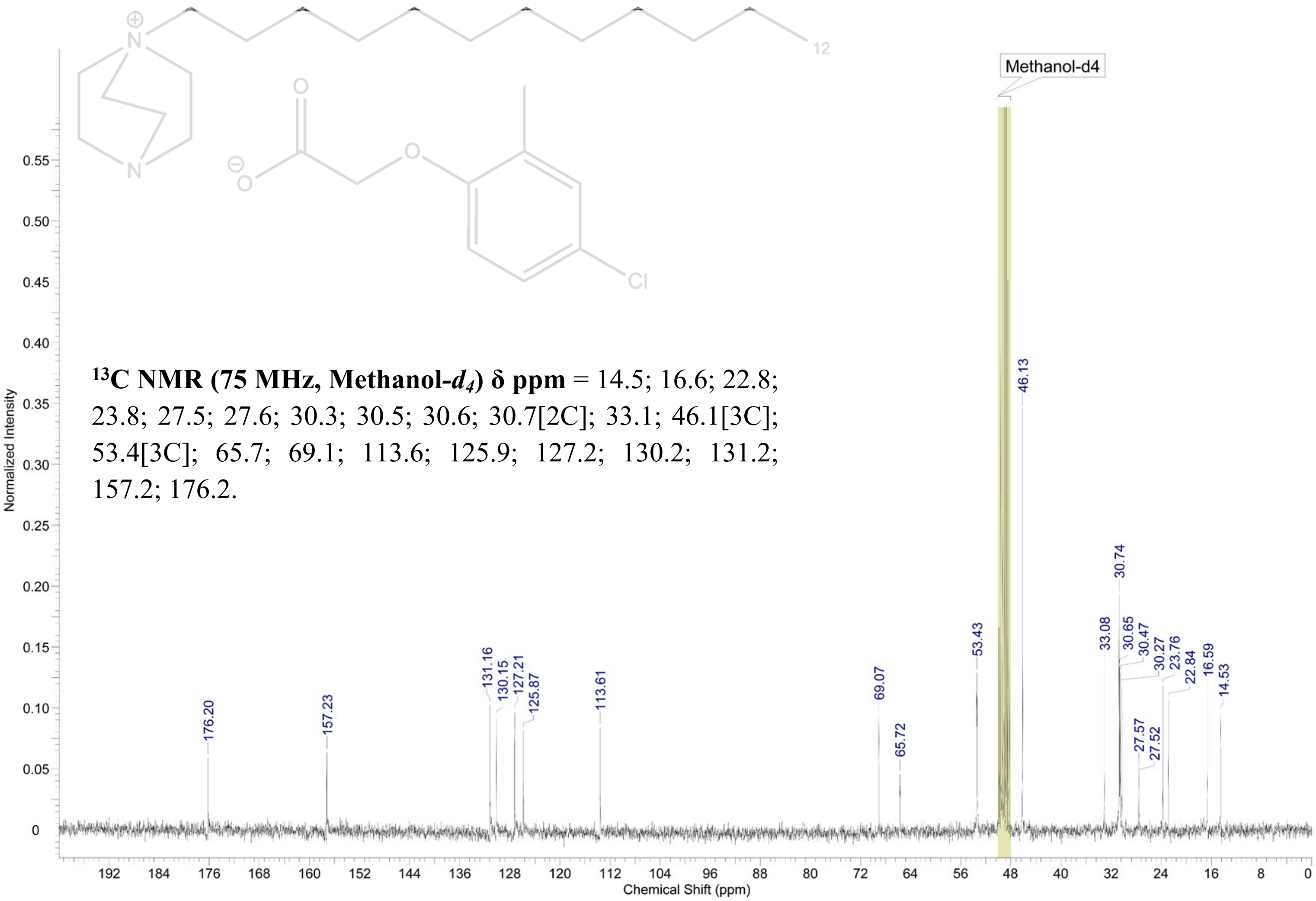
^{13}C NMR (75 MHz, Methanol-d_4) δ ppm = 14.5; 16.6; 22.9; 23.8; 27.5; 30.3; 30.4; 30.6[2C]; 33.1; 46.1[3C]; 53.5[3C]; 65.7; 69.0; 113.6; 125.9; 127.2; 130.2; 131.2; 157.2; 176.3.

Fig. S11 ^{1}H NMR spectrum of 1-dodecyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(13)**.



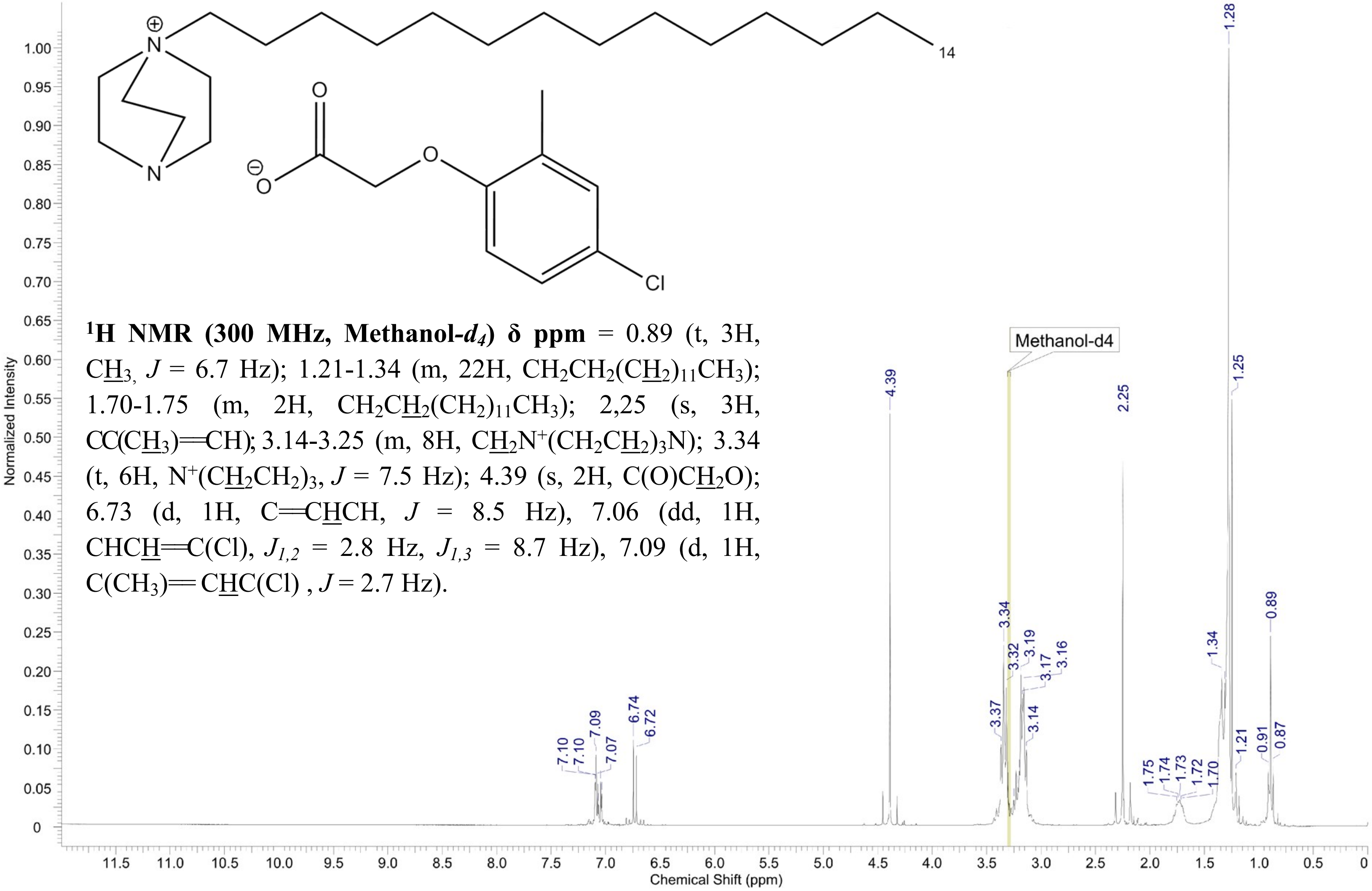
^{1}H NMR (300 MHz, Methanol-d_4) δ ppm = 0.89 (t, 3H, C$\underline{H}_3$, J = 6.7 Hz); 1.21-1.35 (m, 18H, $CH_2CH_2(C\underline{H}_2)_9CH_3$); 1.70-1.77 (m, 2H, $CH_2C\underline{H}_2(CH_2)_9CH_3$); 2.25 (s, 3H, $CC(C\underline{H}_3){=}CH$); 3.13-3.24 (m, 8H, $C\underline{H}_2N^+(CH_2C\underline{H}_2)_3N$); 3.34 (t, 6H, $N^+(C\underline{H}_2CH_2)_3$, J = 7.2 Hz); 4.39 (s, 2H, $C(O)C\underline{H}_2O$); 6.74 (d, 1H, $C{=}C\underline{H}CH$, J = 8.8 Hz); 7.06 (dd, 1H, $CHC\underline{H}{=}C(Cl)$, $J_{1,2}$ = 2.5 Hz, $J_{1,3}$ = 8.5 Hz), 7.10 (d, 1H, $C(CH_3){=}C\underline{H}C(Cl)$, J = 2.5 Hz).

Fig. S12 ^{13}C NMR spectrum of 1-dodecyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(13)**.



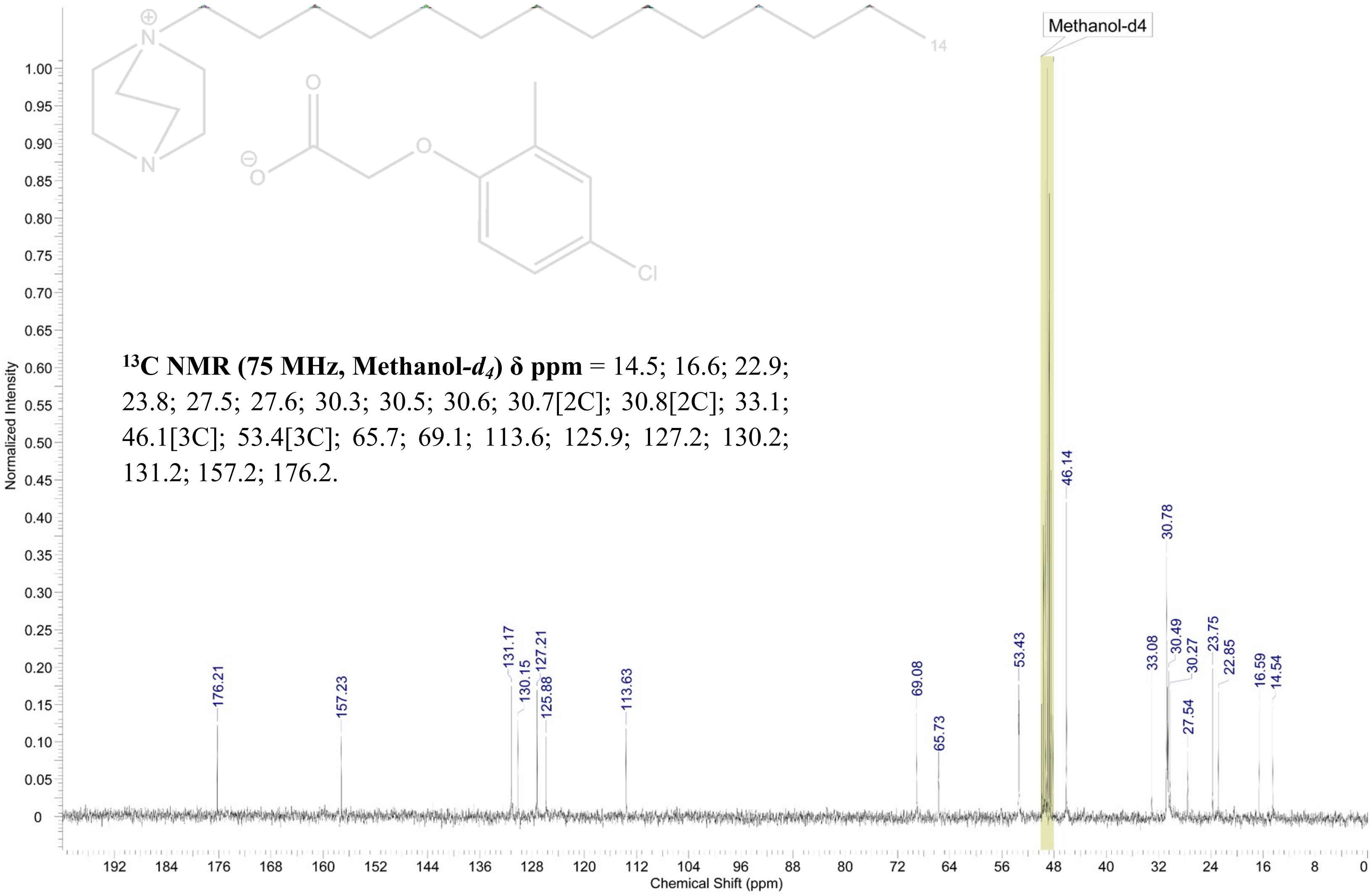
^{13}C NMR (75 MHz, Methanol-d_4) δ ppm = 14.5; 16.6; 22.8; 23.8; 27.5; 27.6; 30.3; 30.5; 30.6; 30.7[2C]; 33.1; 46.1[3C]; 53.4[3C]; 65.7; 69.1; 113.6; 125.9; 127.2; 130.2; 131.2; 157.2; 176.2.

Fig. S13 ^{1}H NMR spectrum of 1-tetradecyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(14)**.



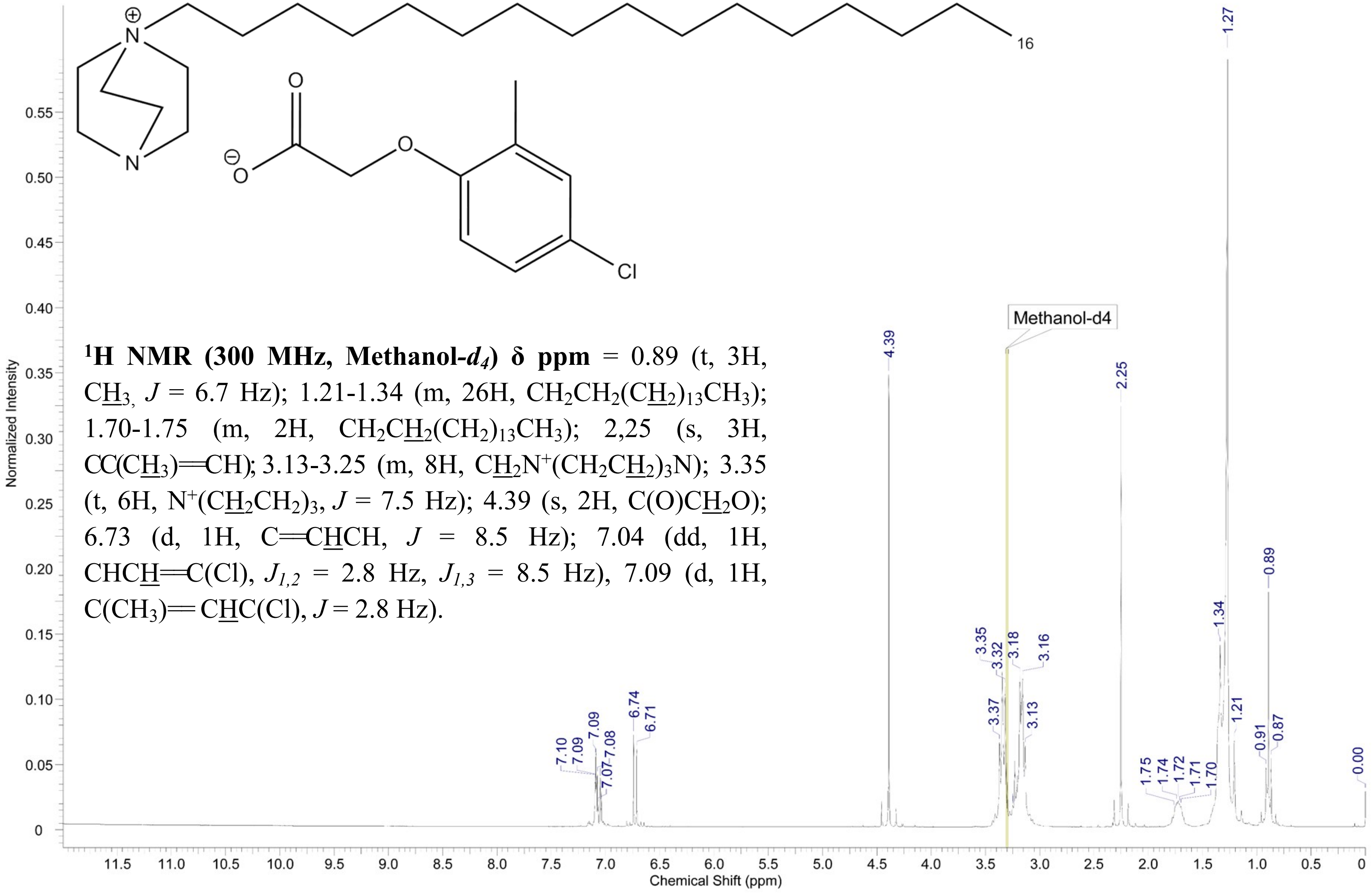
^{1}H NMR (300 MHz, Methanol-d_4) δ ppm = 0.89 (t, 3H, C$\underline{H}_3$, J = 6.7 Hz); 1.21-1.34 (m, 22H, $CH_2CH_2(C\underline{H}_2)_{11}CH_3$); 1.70-1.75 (m, 2H, $CH_2C\underline{H}_2(CH_2)_{11}CH_3$); 2,25 (s, 3H, $CC(C\underline{H}_3){=}CH$); 3.14-3.25 (m, 8H, $C\underline{H}_2N^+(CH_2C\underline{H}_2)_3N$); 3.34 (t, 6H, $N^+(C\underline{H}_2CH_2)_3$, J = 7.5 Hz); 4.39 (s, 2H, $C(O)C\underline{H}_2O$); 6.73 (d, 1H, $C{=}C\underline{H}CH$, J = 8.5 Hz), 7.06 (dd, 1H, $CHC\underline{H}{=}C(Cl)$, $J_{1,2}$ = 2.8 Hz, $J_{1,3}$ = 8.7 Hz), 7.09 (d, 1H, $C(CH_3){=}C\underline{H}C(Cl)$, J = 2.7 Hz).

Fig. S14 ^{13}C NMR spectrum of 1-tertradecyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-bromide **(14)**.



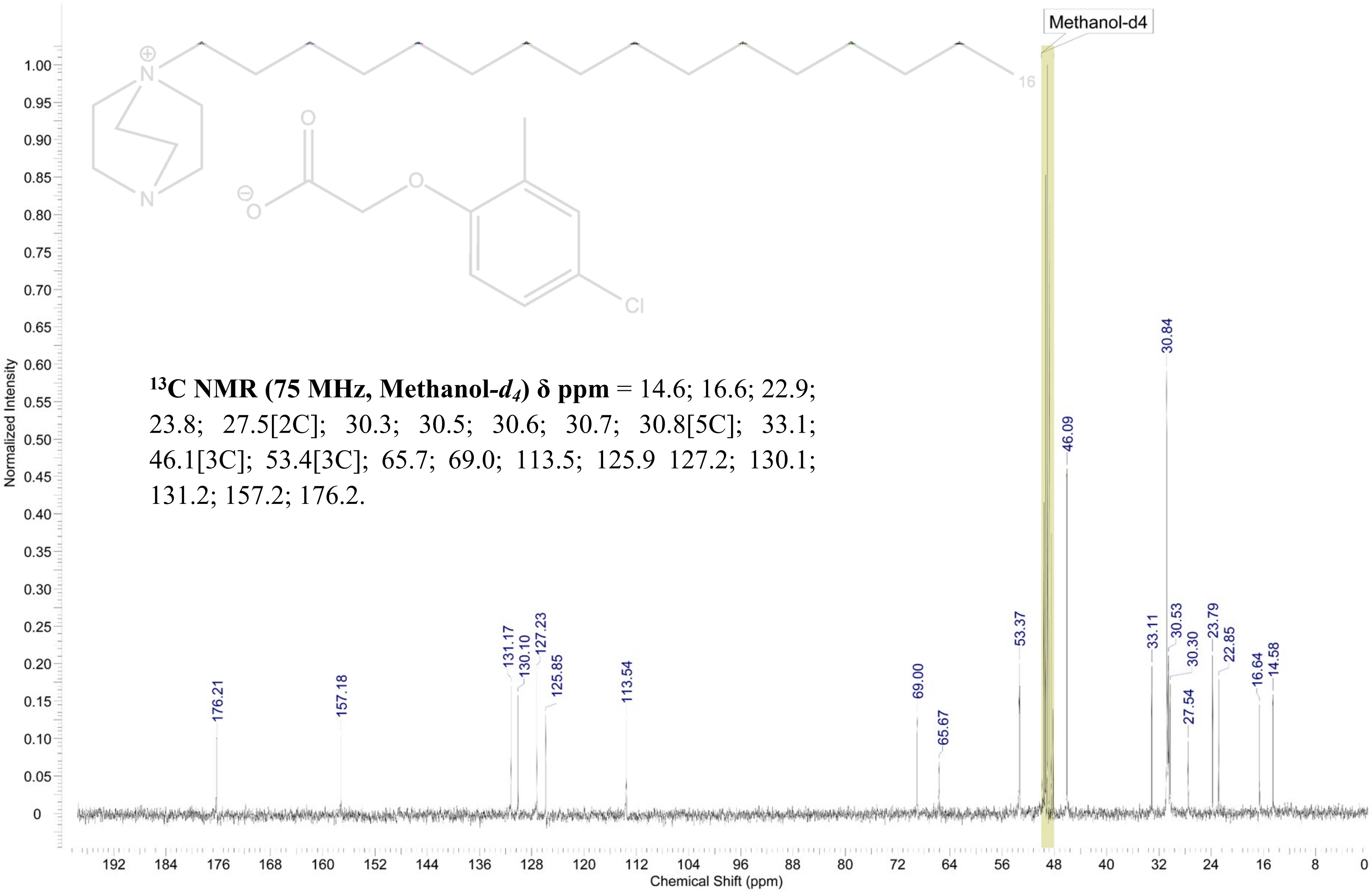
^{13}C NMR (75 MHz, Methanol-d_4) δ ppm = 14.5; 16.6; 22.9; 23.8; 27.5; 27.6; 30.3; 30.5; 30.6; 30.7[2C]; 30.8[2C]; 33.1; 46.1[3C]; 53.4[3C]; 65.7; 69.1; 113.6; 125.9; 127.2; 130.2; 131.2; 157.2; 176.2.

Fig. S15 ^{1}H NMR spectrum of 1-hexadecyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(15)**.



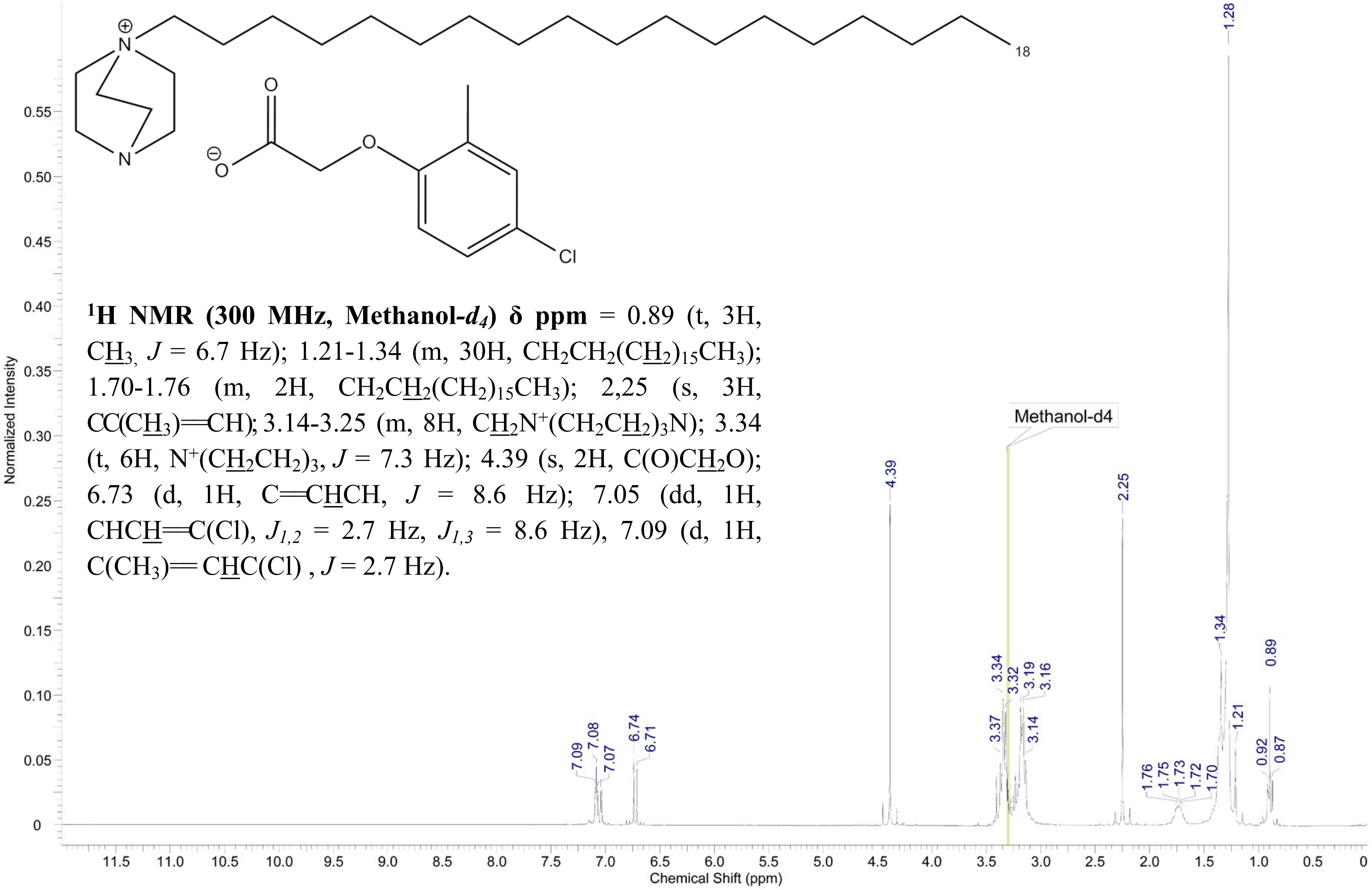
^{1}H NMR (300 MHz, Methanol-d_4) δ ppm = 0.89 (t, 3H, $C\underline{H}_3$, J = 6.7 Hz); 1.21-1.34 (m, 26H, $CH_2CH_2(C\underline{H}_2)_{13}CH_3$); 1.70-1.75 (m, 2H, $CH_2C\underline{H}_2(CH_2)_{13}CH_3$); 2,25 (s, 3H, $CC(C\underline{H}_3){=}CH$); 3.13-3.25 (m, 8H, $C\underline{H}_2N^+(CH_2C\underline{H}_2)_3N$); 3.35 (t, 6H, $N^+(C\underline{H}_2CH_2)_3$, J = 7.5 Hz); 4.39 (s, 2H, $C(O)C\underline{H}_2O$); 6.73 (d, 1H, $C{=}C\underline{H}CH$, J = 8.5 Hz); 7.04 (dd, 1H, $CHC\underline{H}{=}C(Cl)$, $J_{1,2}$ = 2.8 Hz, $J_{1,3}$ = 8.5 Hz), 7.09 (d, 1H, $C(CH_3){=}C\underline{H}C(Cl)$, J = 2.8 Hz).

Fig. S16 ^{13}C NMR spectrum of 1-hexadecyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(15)**.



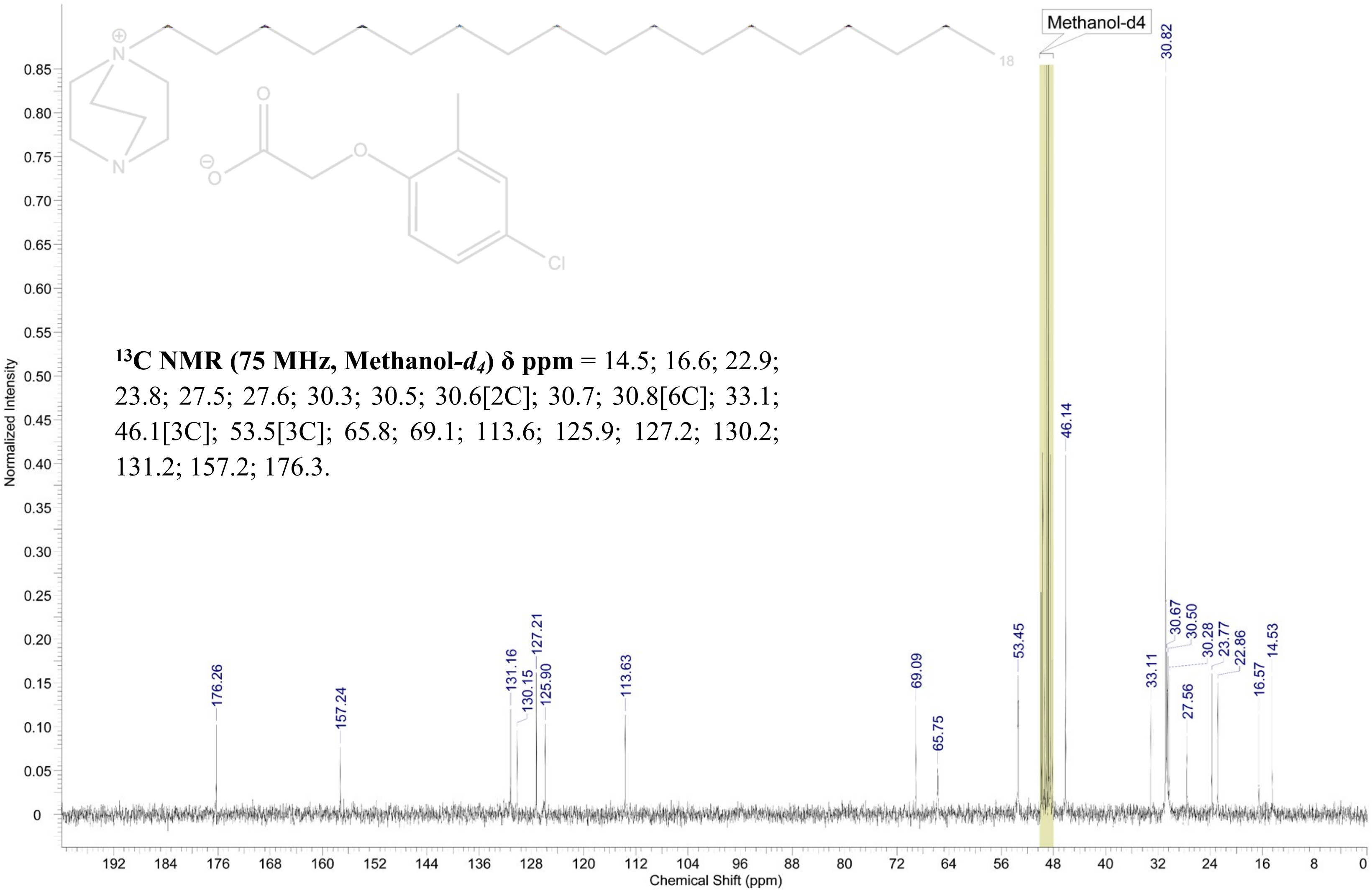
^{13}C NMR (75 MHz, Methanol-d_4) δ ppm = 14.6; 16.6; 22.9; 23.8; 27.5[2C]; 30.3; 30.5; 30.6; 30.7; 30.8[5C]; 33.1; 46.1[3C]; 53.4[3C]; 65.7; 69.0; 113.5; 125.9 127.2; 130.1; 131.2; 157.2; 176.2.

Fig. S17 ^{1}H NMR spectrum of 1-octadecyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(16)**.



^{1}H NMR (300 MHz, Methanol-d_4) δ ppm = 0.89 (t, 3H, $C\underline{H}_3$, J = 6.7 Hz); 1.21-1.34 (m, 30H, $CH_2CH_2(C\underline{H}_2)_{15}CH_3$); 1.70-1.76 (m, 2H, $CH_2C\underline{H}_2(CH_2)_{15}CH_3$); 2,25 (s, 3H, $CC(C\underline{H}_3){=}CH$); 3.14-3.25 (m, 8H, $C\underline{H}_2N^+(CH_2C\underline{H}_2)_3N$); 3.34 (t, 6H, $N^+(C\underline{H}_2CH_2)_3$, J = 7.3 Hz); 4.39 (s, 2H, $C(O)C\underline{H}_2O$); 6.73 (d, 1H, $C{=}C\underline{H}CH$, J = 8.6 Hz); 7.05 (dd, 1H, $CHC\underline{H}{=}C(Cl)$, $J_{1,2}$ = 2.7 Hz, $J_{1,3}$ = 8.6 Hz), 7.09 (d, 1H, $C(CH_3){=}C\underline{H}C(Cl)$, J = 2.7 Hz).

Fig. S18 ^{13}C NMR spectrum of 1-octadecyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate **(16)**.



^{13}C NMR (75 MHz, Methanol-d_4) δ ppm = 14.5; 16.6; 22.9; 23.8; 27.5; 27.6; 30.3; 30.5; 30.6[2C]; 30.7; 30.8[6C]; 33.1; 46.1[3C]; 53.5[3C]; 65.8; 69.1; 113.6; 125.9; 127.2; 130.2; 131.2; 157.2; 176.3.

Table S1 Characteristic shifts in ^1H NMR for precursor and ionic liquid, ppm

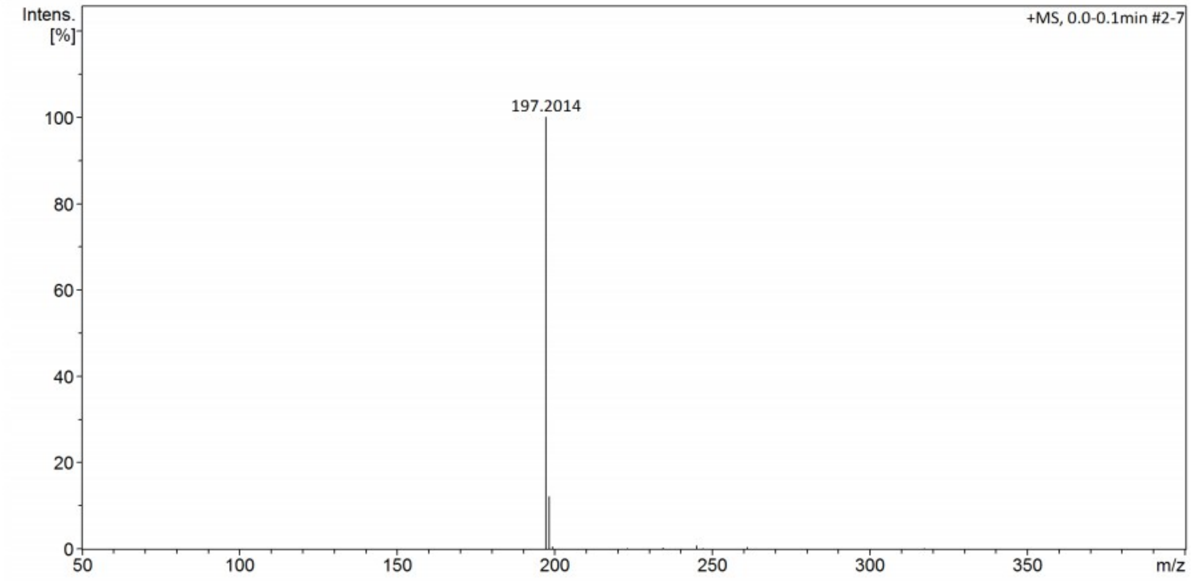
Compound		**Cation – signals from protons**			
		$CH_2CH_2(CH_2)_{11}CH_3$	$N^+(CH_2CH_2)_3$	$CH_2N^+(CH_2CH_2)_3N$	$N^+(CH_2CH_2)_3$
Precursor **(6)**	$[D_{14}][Br]$	1.76-1.83 (m)	3.20 (t)	3.26-3.32 (m)	3.43 (t)
Ionic liquid **(14)**	$[D_{14}][MCPA]$	1.70-1.75 (m)	3.14-3.25 (m)		3.34 (t)

Table S2 Elemental analysis for ILs **(9-16)**

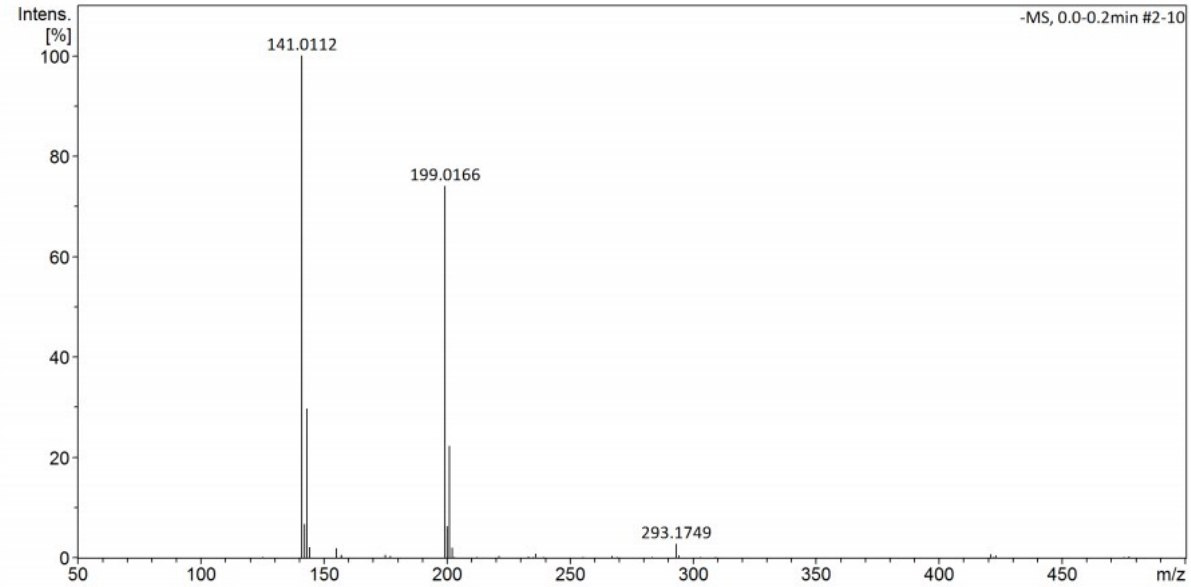
IL	**Short**	**Chemical formula**	**Molecular weight [g mol^{-1}]**	**Calculated values [%]**			**Obtained values [%]**		
				C	**H**	**N**	**C**	**H**	**N**
9	**$[D_4][MCPA]$**	$C_{19}H_{29}ClN_2O_3$	368.90	61.86	7.92	7.59	61.49	7.56	7.20
10	**$[D_6][MCPA]$**	$C_{21}H_{33}ClN_2O_3$	396.95	63.54	8.38	7.06	63.89	8.76	7.38
11	**$[D_8][MCPA]$**	$C_{23}H_{37}ClN_2O_3$	425.00	65.00	8.77	6.59	65.41	8.39	6.99
12	**$[D_{10}][MCPA]$**	$C_{25}H_{41}ClN_2O_3$	453.06	66.28	9.12	6.18	66.61	8.89	6.49
13	**$[D_{12}][MCPA]$**	$C_{27}H_{45}ClN_2O_3$	481.11	67.40	9.43	5.82	67.00	9.83	6.01
14	**$[D_{14}][MCPA]$**	$C_{29}H_{49}ClN_2O_3$	509.16	68.41	9.70	5.50	67.99	10.01	5.89
15	**$[D_{16}][MCPA]$**	$C_{31}H_{53}ClN_2O_3$	537.22	69.31	9.94	5.21	69.00	10.36	4.95
16	**$[D_{18}][MCPA]$**	$C_{33}H_{57}ClN_2O_3$	565.27	70.12	10.16	4.96	70.52	10.56	4.56

The ESI-MS spectrum of 1-hexyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate (10) and 1-hexadecyl-1-azonia-4-azabicyclo[2.2.2]octane 4-chloro-2-methylphenoxyacetate (15).

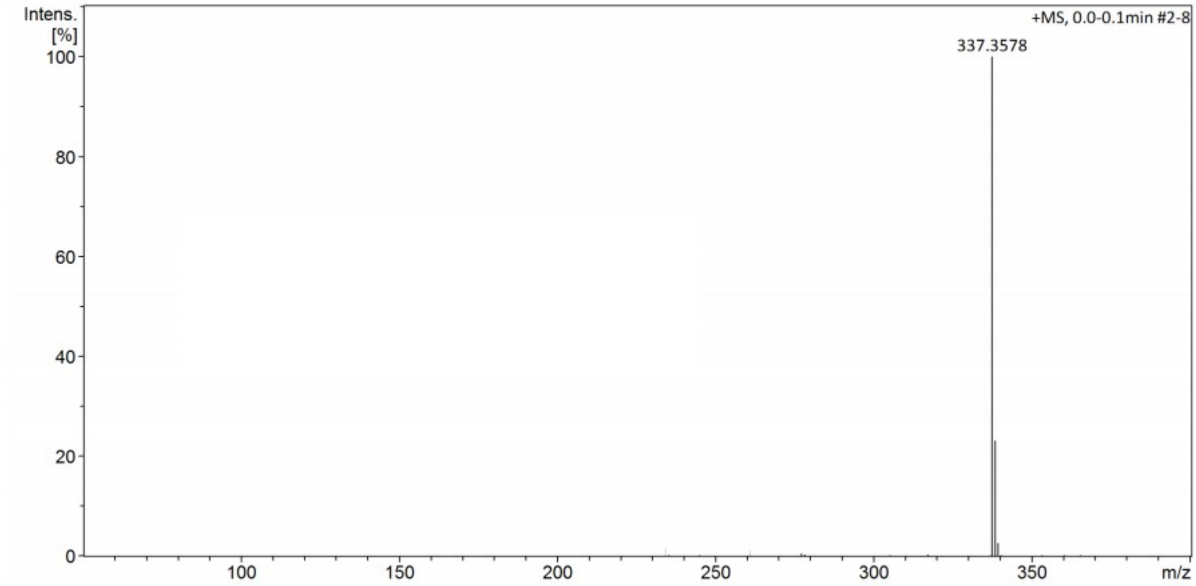
IL 10: HRMS (ESI-Q-TOF), (ES^+) for $C_{12}H_{25}N_2^+$ [m/z] = 197.2012 (calculated), 197.2014 (found)



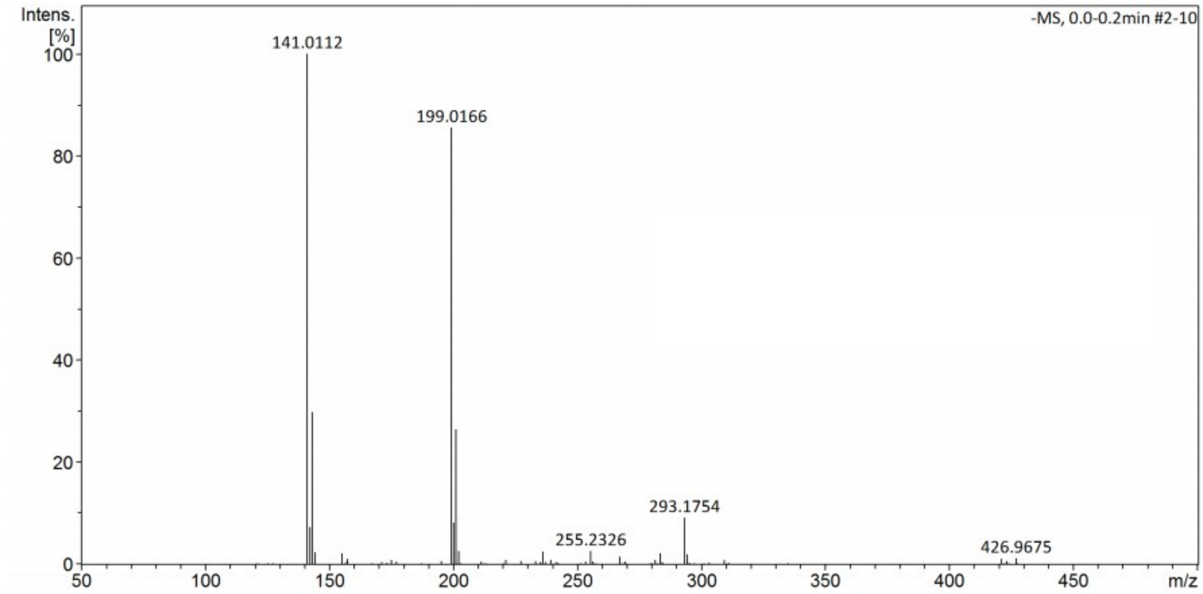
IL 10: HRMS (ESI-Q-TOF), (ES^-) for $C_9H_8ClO_3^-$ [m/z] = 199.0167 (calculated), 199.0166 (found).



IL 15: HRMS (ESI-Q-TOF), (ES$^+$) for $C_{22}H_{45}N_2^+$ [m/z] = 337.3577 (calculated), 337.3578 (found).



IL 15: HRMS (ESI-Q-TOF), (ES$^-$) for $C_9H_8ClO_3^-$ [m/z] = 199.0167 (calculated), 199.0166 (found).



Thermal analysis

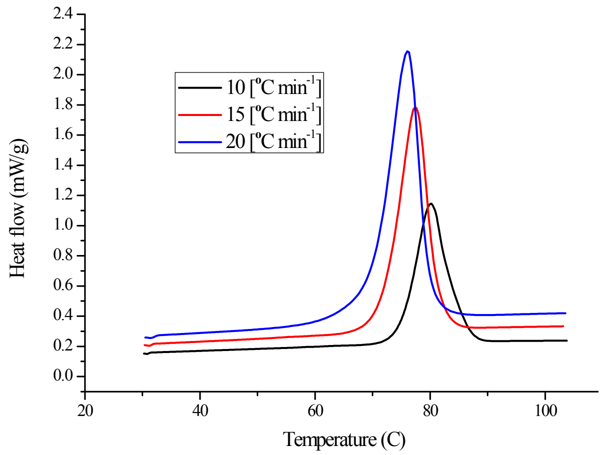
Based on the assumption that the evolution of crystallinity is linearly proportional to the evolution of heat released during crystallization, the relative degree of crystallinity, Xw(t), was calculated by integration of exothermal peaks from eqn (1):

$$X_{W(t)} = \frac{\int_{t_0}^{t} \frac{dH}{dt}}{\int_{t_0}^{t_\infty} \frac{dH}{dt}} \qquad [1]$$

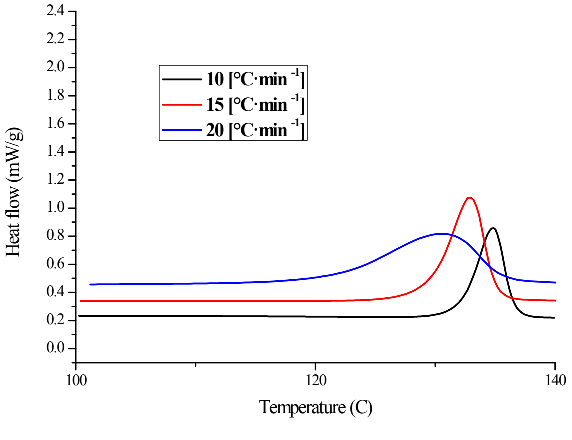
where dH/dt is crystallization heat flow rate at a temperature of t and t_0 and t_∞ correspond to starting and ending temperatures of crystallization, respectively. In eqn (1), Xw(t) at any crystallization temperature is converted to volume fraction relative crystallinity X(t).

Non-isothermal crystallization curves at sample cooling rates of 10 °C min^{-1}, 15 °C min^{-1}, and 20 °C min^{-1} are shown in Fig. S19. It can be seen that as the cooling rate increases.

a)



b)



c)

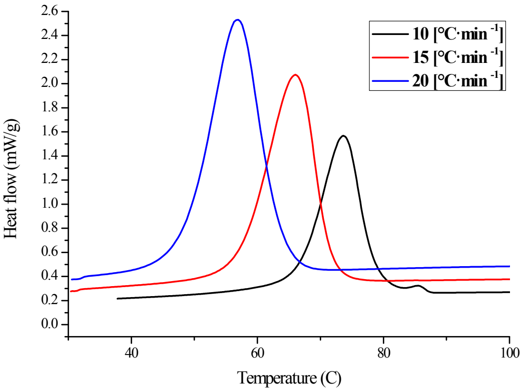
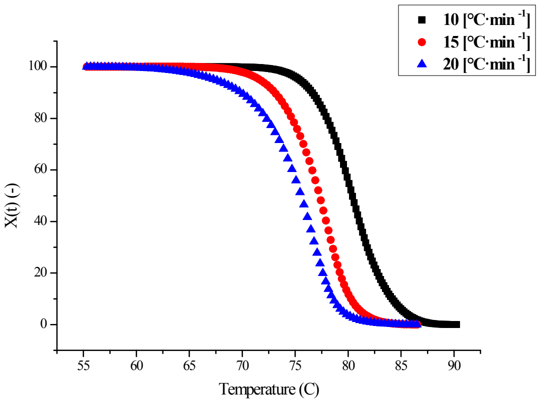
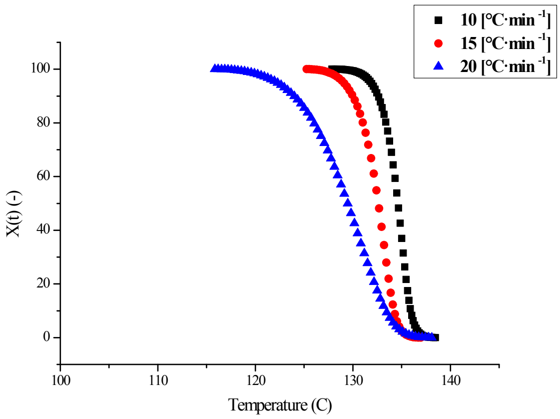


Fig. S19 Non-isothermal crystallization DSC curves for a) [D_6][Br] **(2)** b) [D_{12}][Br] **(5)** c) [D_{16}][Br] **(7)** at different cooling rate.

a)



b)



c)

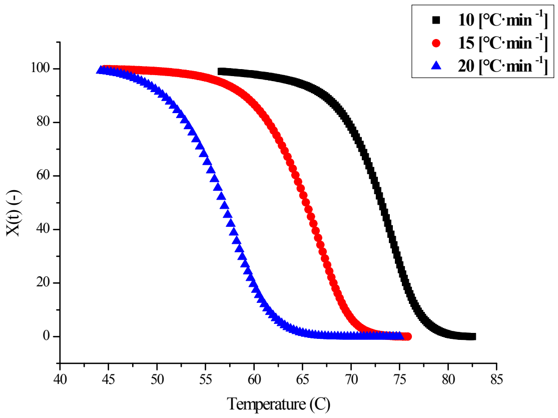


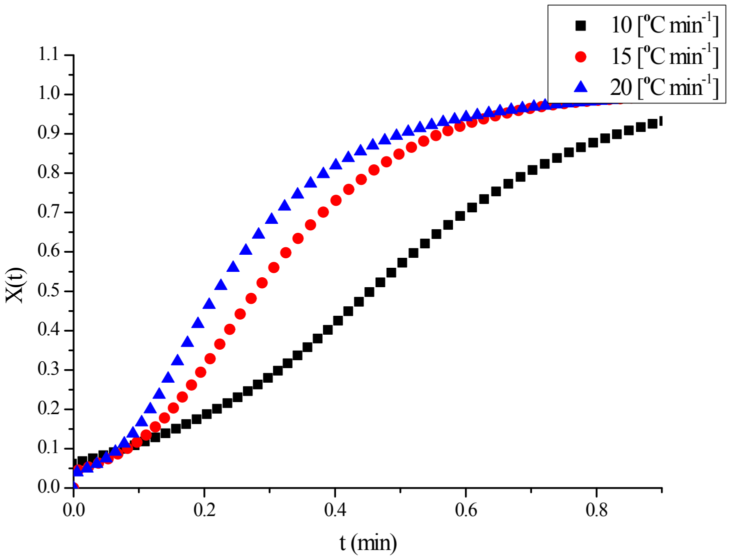
Fig. S20 Relationship between relative crystallinity and crystallization temperature for a) [D$_6$][Br] **(2)** b) [D$_{12}$][Br] **(5)** and c) [D$_{16}$][Br] **(7)** bromides at different cooling rate.

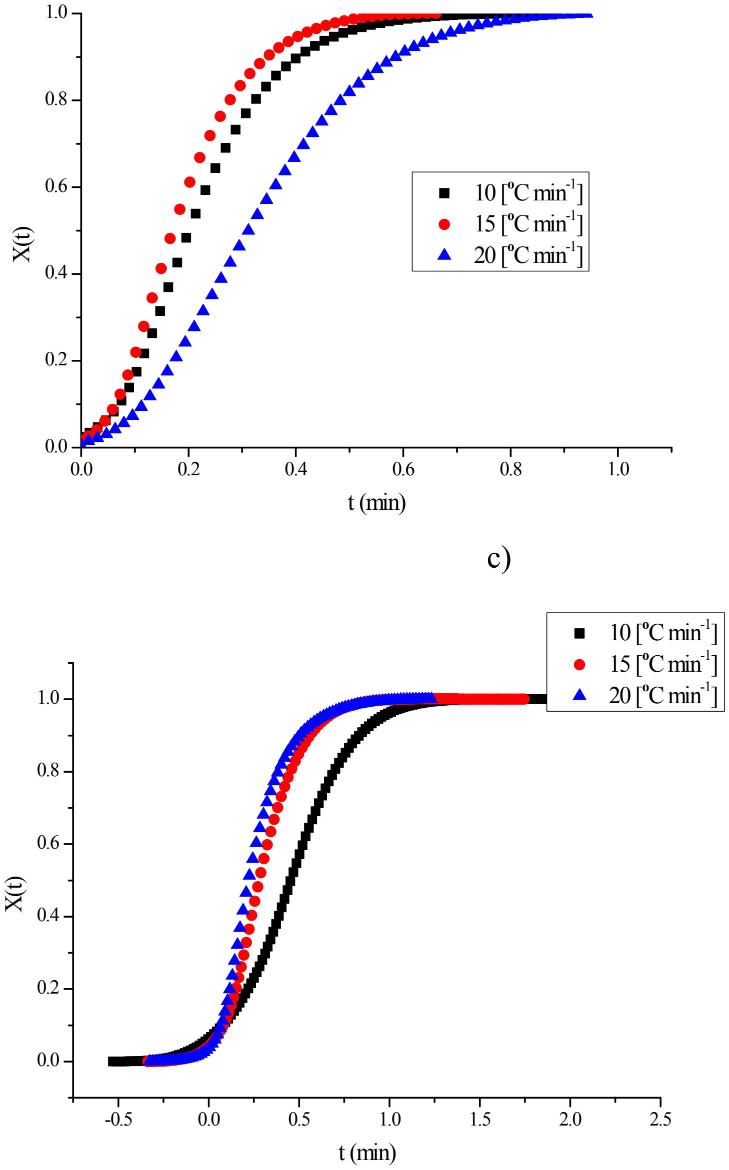
The relationship between crystallinity X(t) and temperature T can be converted to that between crystallinity X(t) and time t, as shown in eqn (2).

$$t = \frac{(T_0 - T)}{\beta} \qquad [2]$$

where β is the cooling rate (Ji et al., 2008).The horizontal temperature axis can be transformed into a time scale. **Fig. S21** shows the variations of relative crystallinity with crystallization time for all compounds. All these curves have the same characteristic sigmoidal shape at various cooling rates due to the spherulite impingement in the later stage of crystallization. It can be seen that, for crystallization completion, a shorter time requires higher cooling rates.

a)





b)

c)

Fig. S21 Relationship between relative crystallity and crystallization time for a) $[D_6][Br]$ **(2)** b) $[D_{12}][Br]$ **(5)** and c) $[D_{16}][Br]$ **(7)** bromides at different cooling rate.

Non-Isothermal Crystallization Kinetics Analysis

Modified Avrami Model (Jeziorny Equation)

The Avrami equation (eqn (3)) describes isothermal crystallization kinetics. The equation describes how solids transform from one state of matter or phase to another at constant temperature and can also describe some types of chemical reactions:

$$X(t) = 1 - \exp(-K \cdot t^n) \qquad [3]$$

where X(t) is time-dependent relative crystallinity, n is Avrami exponent, K is crystallization rate constant, and t is crystallization time. The Avrami exponent n depends on type of nucleation and growth process, and the value of n is between 1 and 4. eqn (3) is typically rearranged in a linear form as double logarithm eqn (4):

$$\log[-\ln(1 - X(t))] = \log K + n\log t \qquad [4]$$

The Jeziorny method modifies the Avrami equation to describe non-isothermal crystallization kinetics. The Jeziorny method is a direct method to apply the Avrami equation to non-isothermal crystallization. It calibrates parameters by taking non-isothermal crystallization as isothermal crystallization, so that non-isothermal crystallization mechanism is determined:

$$\log K_C = \frac{\log K}{\beta} \qquad [5]$$

A corrected form of the rate term (K) used in the Avrami equation assuming a constant cooling/heating rate is proposed.

The relative crystallinity at a set cooling rate (β) is a function of crystallization temperature (T). The plot of log[-ln(1 - X(t))] against log(t) is obtained based on eqn (4). The Avrami index n is obtained from the slope, and log K can be obtained from the intercept. Correction of cooling rate β is made for the obtained K (eqn (5)), where Kc is the modified crystallization rate constant of the non-isothermal crystallization process.

Fig. S22 Influence of ILs **9-16** treatments on cornflower.

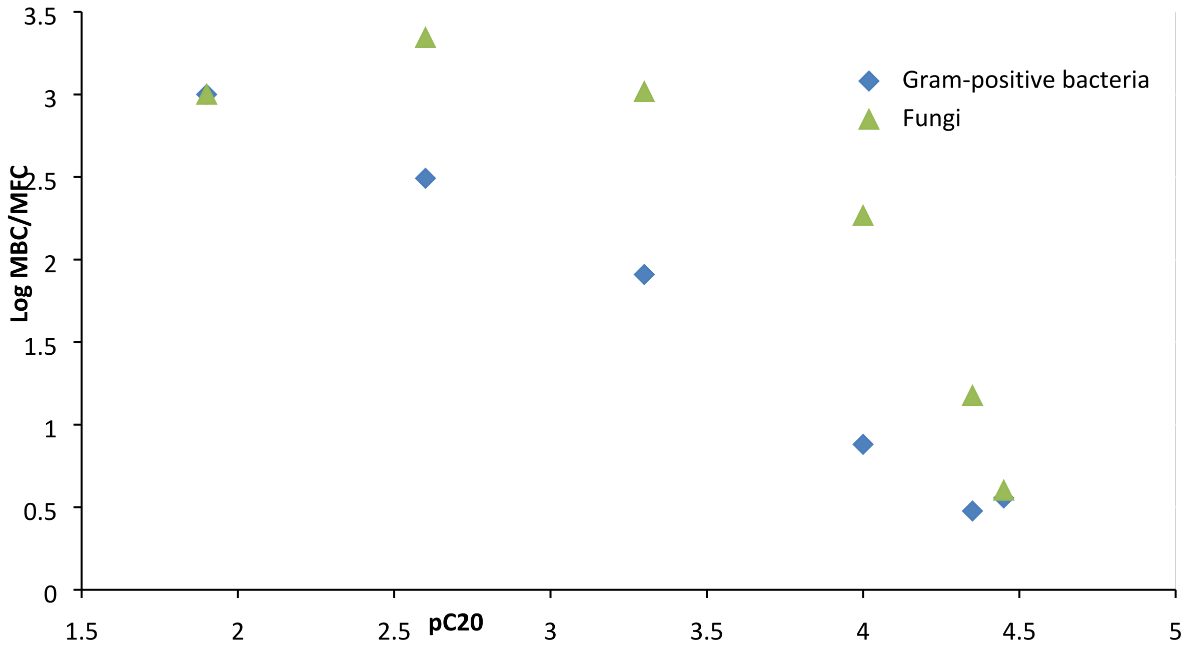


Fig. S23 Relation between pC_{20} and log MBC/MFC for Gram-positive bacteria and fungi for ILs **11-16**.