Electronic Supplementary Material (ESI) for New Journal of Chemistry.

ELECTRONIC SUPPORTING INFORMATION

Biodegradable herbicidal ionic liquids based on synthetic auxins and analogues of betaine

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Table S1. Elemental analysis for salts with dodecylbetainium cation

Salt	Alkyl	Anion	Chemical formula	Molecular weight [g mol^{-1}]	Calculated values [%]			Obtained values [%]		
					C	H	N	C	H	N
[C_{12}Bet][Cl]	$C_{12}H_{25}$	Cl	$C_{16}H_{34}ClNO_2$	307.9	62.41	11.13	4.55	62.77	10.88	4.79
1	$C_{12}H_{25}$	2,4-D	$C_{13}H_{17}Cl_2NO_5$	338.1	46.17	5.07	4.14	46.49	5.22	3.89
2	$C_{12}H_{25}$	MCPA	$C_{14}H_{20}ClNO_5$	317.8	52.92	6.34	4.41	52.77	6.16	4.72
3	$C_{12}H_{25}$	MCPP	$C_{15}H_{22}ClNO_5$	331.8	54.30	6.68	4.22	54.03	6.46	4.50
4	$C_{12}H_{25}$	Dicamba	$C_{13}H_{17}Cl_2NO_5$	338.1	46.17	5.07	4.14	45.90	5.37	4.29

The following abbreviations were used to explain the multiplicities:

s = singlet, d = doublet, q – quartet, m = multiplet, dd - doublet of doublets.

Figure S1. ^{1}H NMR spectrum of dodecylbetainium chloride - [C_{12}Bet][Cl].

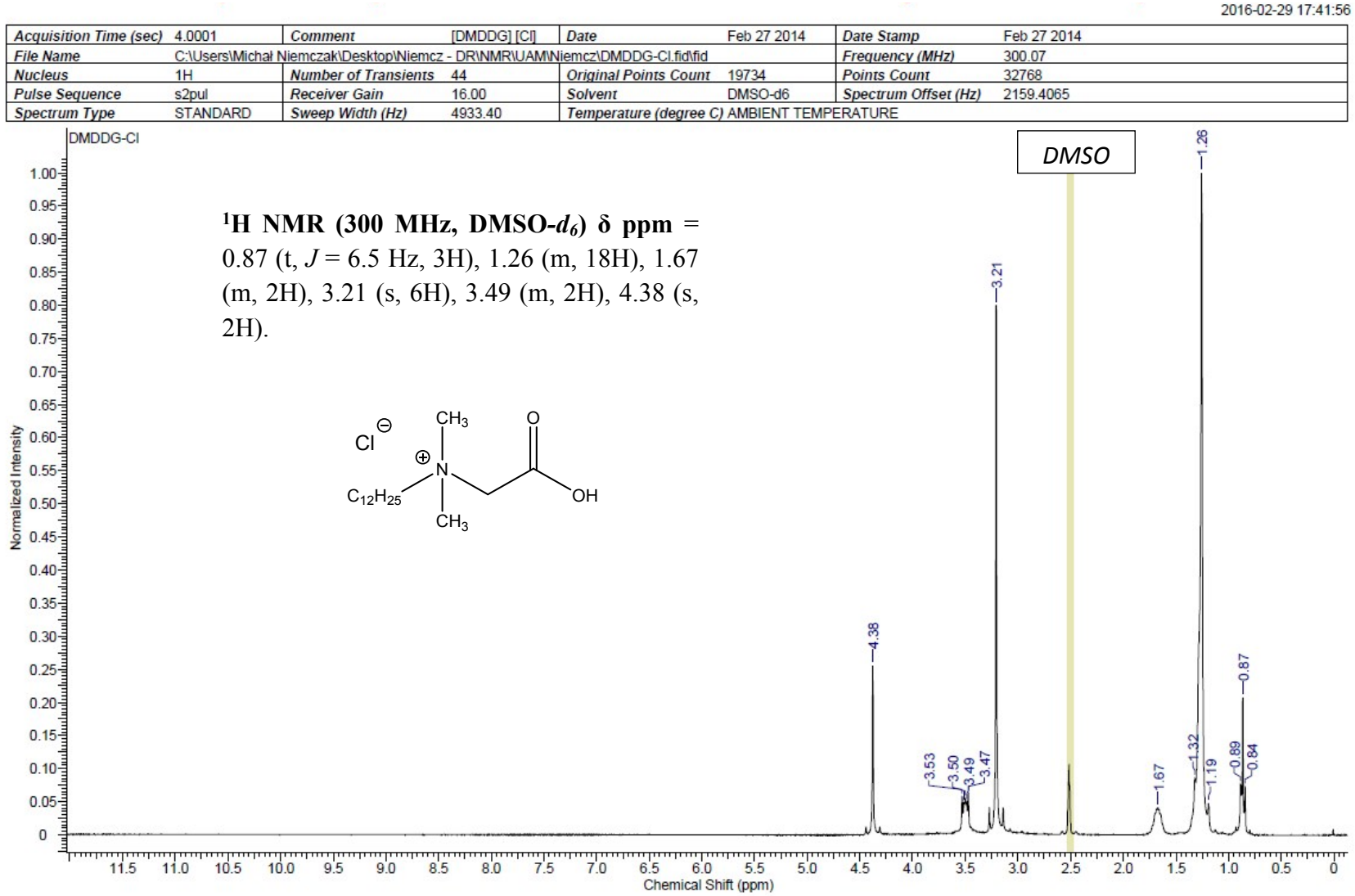

Figure S2. ^{13}C NMR spectrum of dodecylbetainium chloride - $[C_{12}Bet][Cl]$.

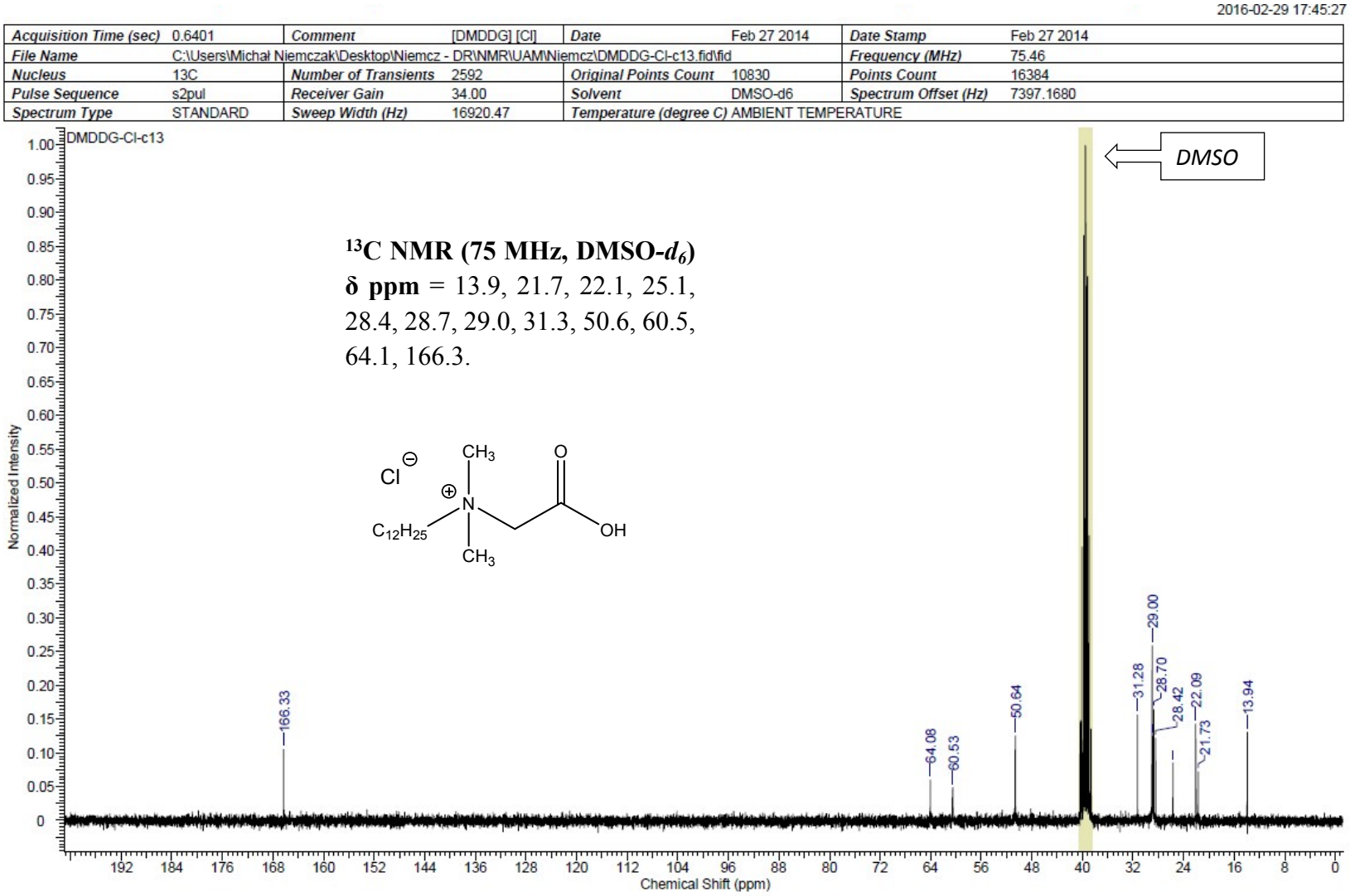

Figure S3. ^{1}H NMR spectrum of cocoamidopropylbetainium chloride - [CAPBet][Cl].

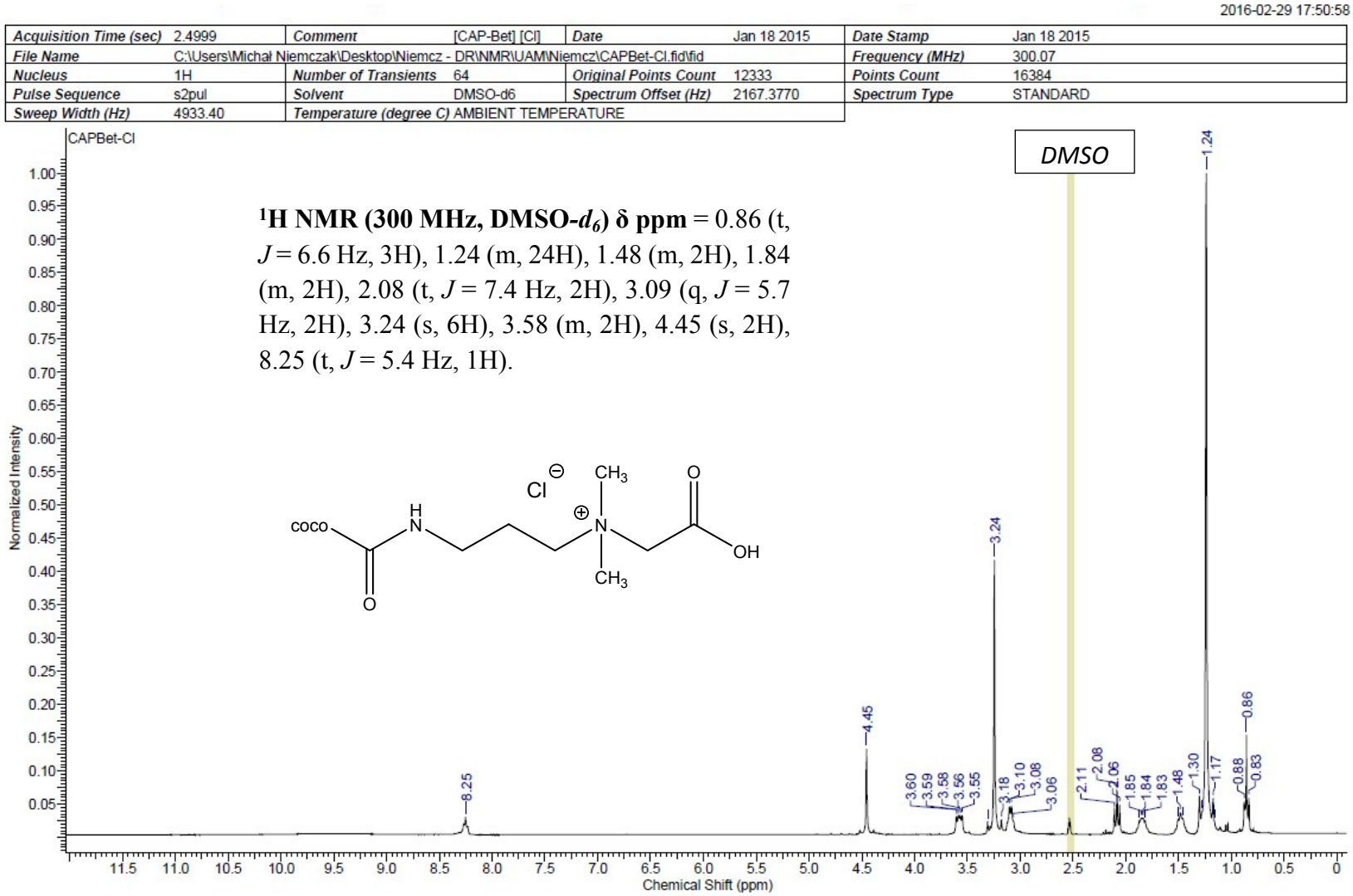

Figure S4. ^{13}C NMR spectrum of cocoamidopropylbetainium chloride - [CAPBet][Cl].

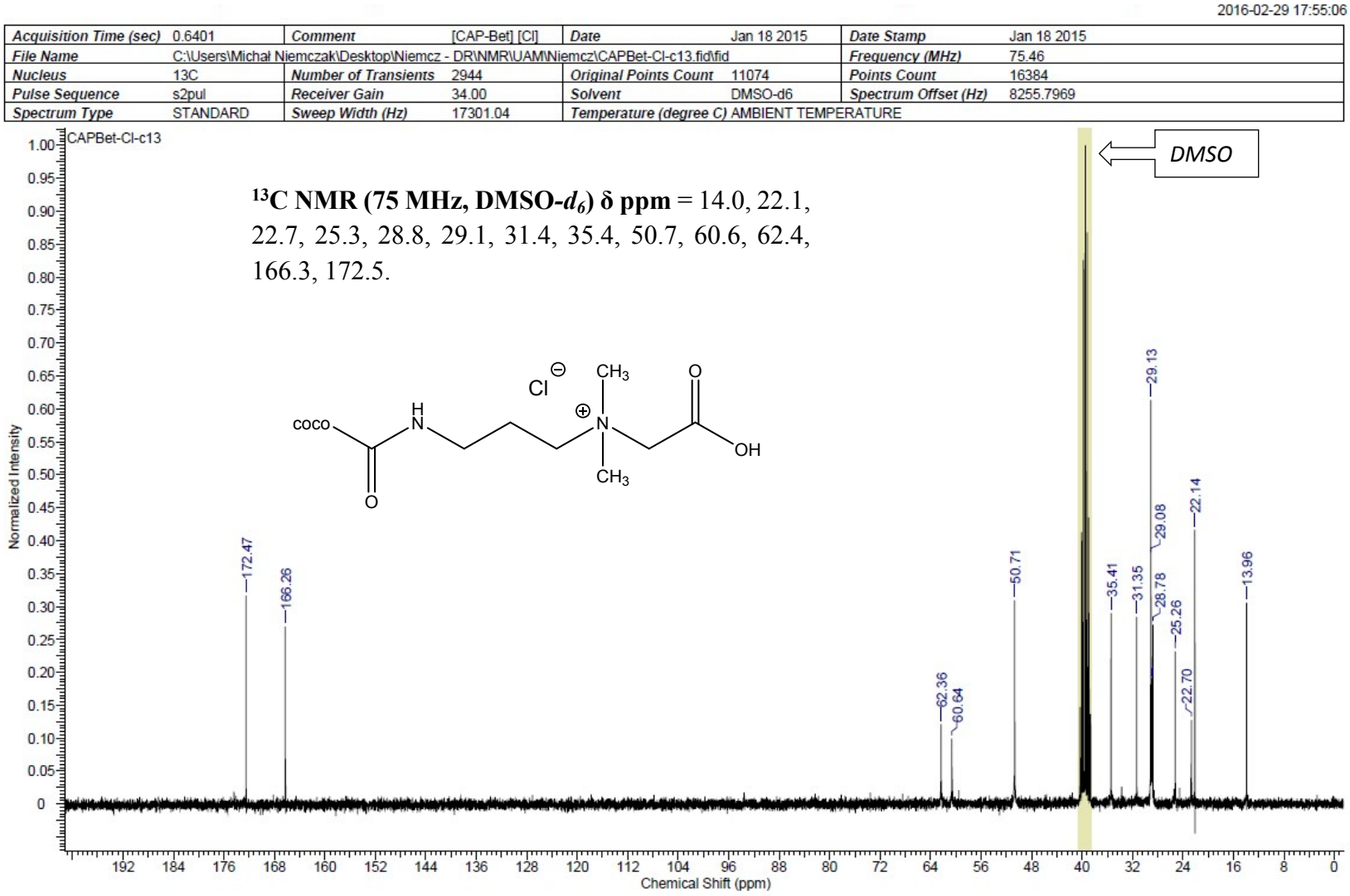

Figure S5. ^{1}H NMR spectrum of dodecylbetainium 2,4-dichlorophenoxyacetate (**1**).

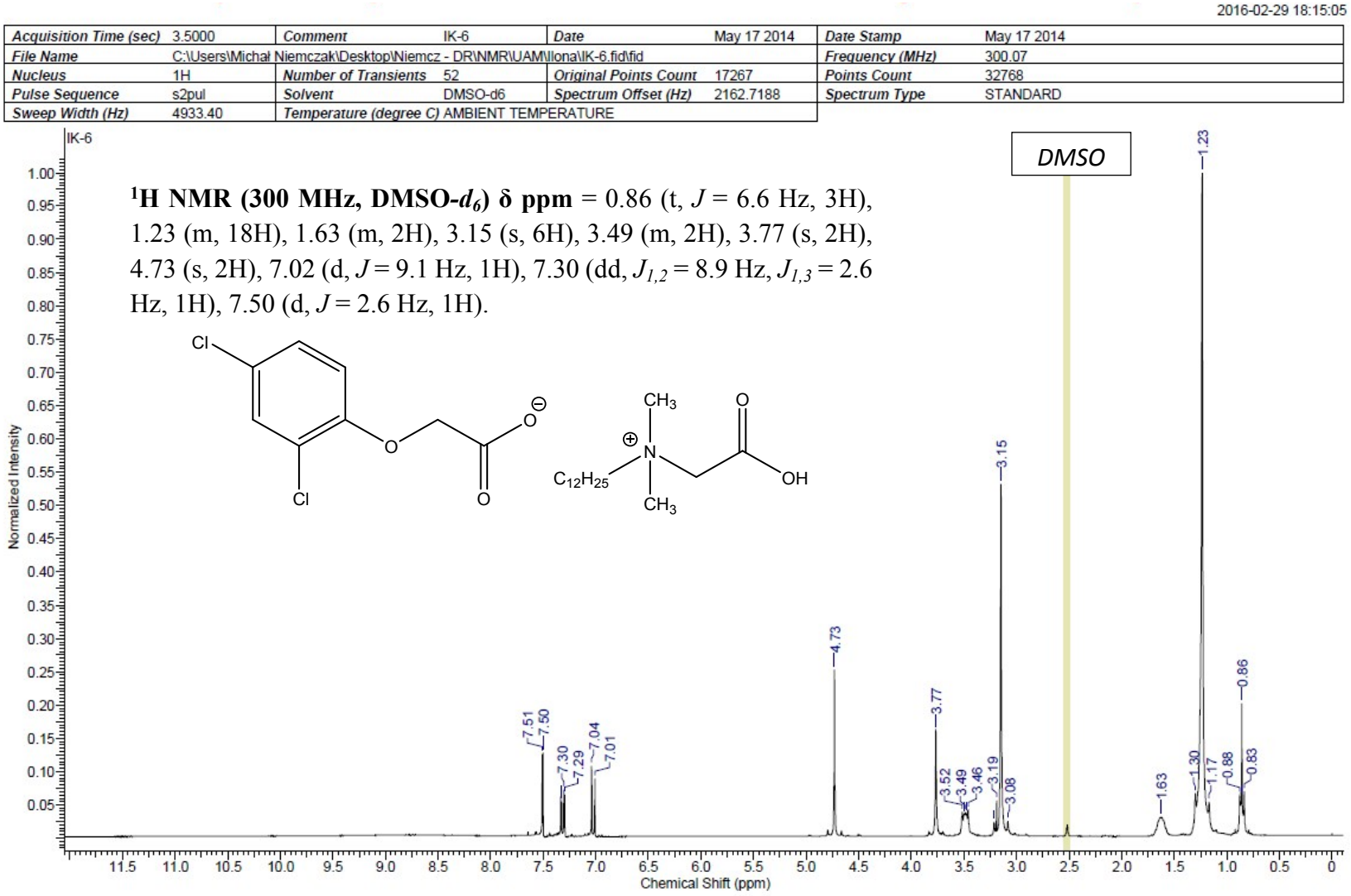

Figure S6. ^{13}C NMR spectrum of dodecylbetainium 2,4-dichlorophenoxyacetate (**1**).

2016-02-29 18:18:19

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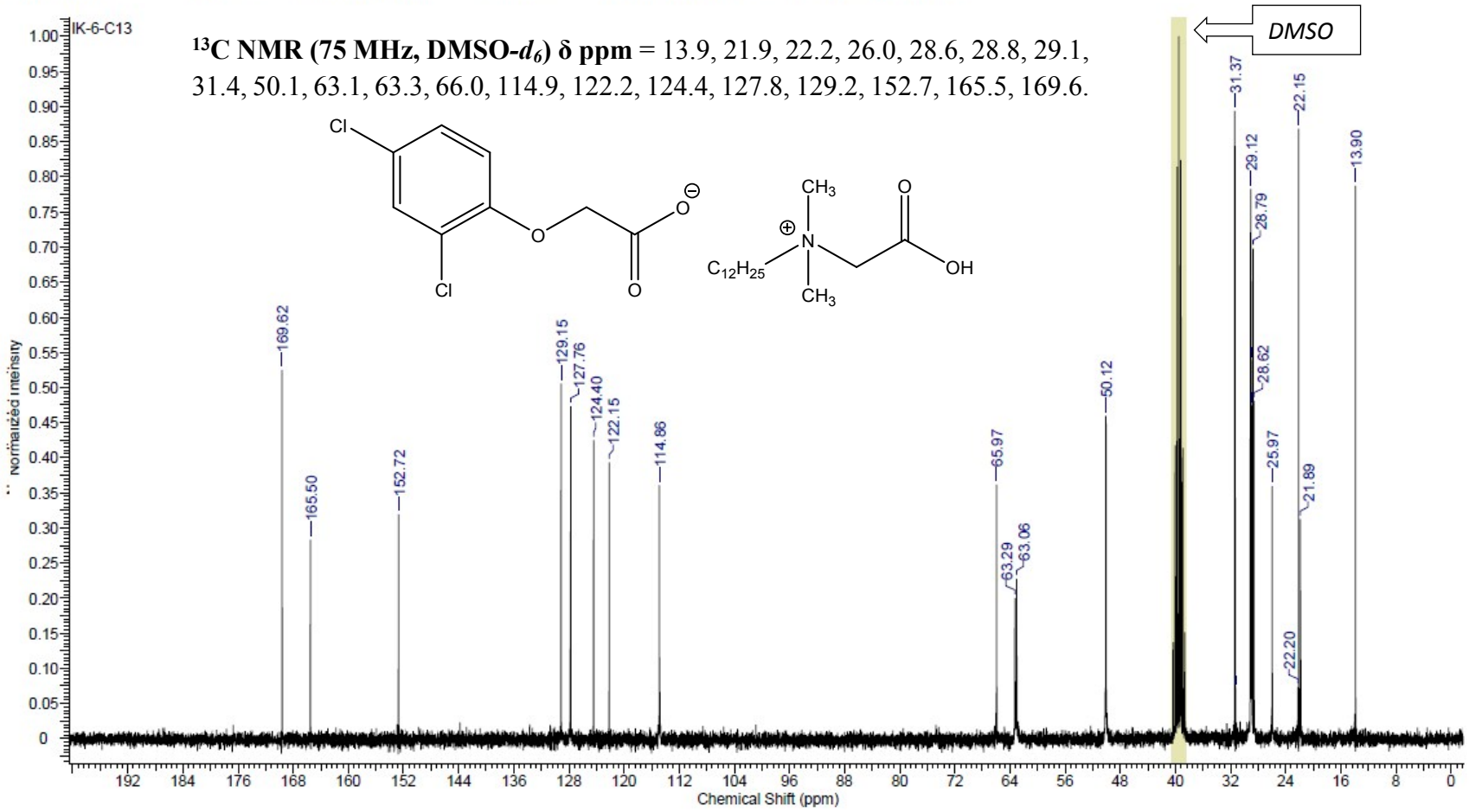
Pulse Sequence	s2pul	*Receiver Gain*	34.00	*Solvent*	DMSO-d6	*Spectrum Offset (Hz)*	7264.3770
Spectrum Type	STANDARD	*Sweep Width (Hz)*	16077.17	*Temperature (degree C)*	AMBIENT TEMPERATURE		



^{13}C NMR (75 MHz, DMSO-d_6) δ ppm = 13.9, 21.9, 22.2, 26.0, 28.6, 28.8, 29.1, 31.4, 50.1, 63.1, 63.3, 66.0, 114.9, 122.2, 124.4, 127.8, 129.2, 152.7, 165.5, 169.6.

Figure S7. ^{1}H NMR spectrum of dodecylbetainium 4-chloro-2-methylphenoxyacetate (**2**).

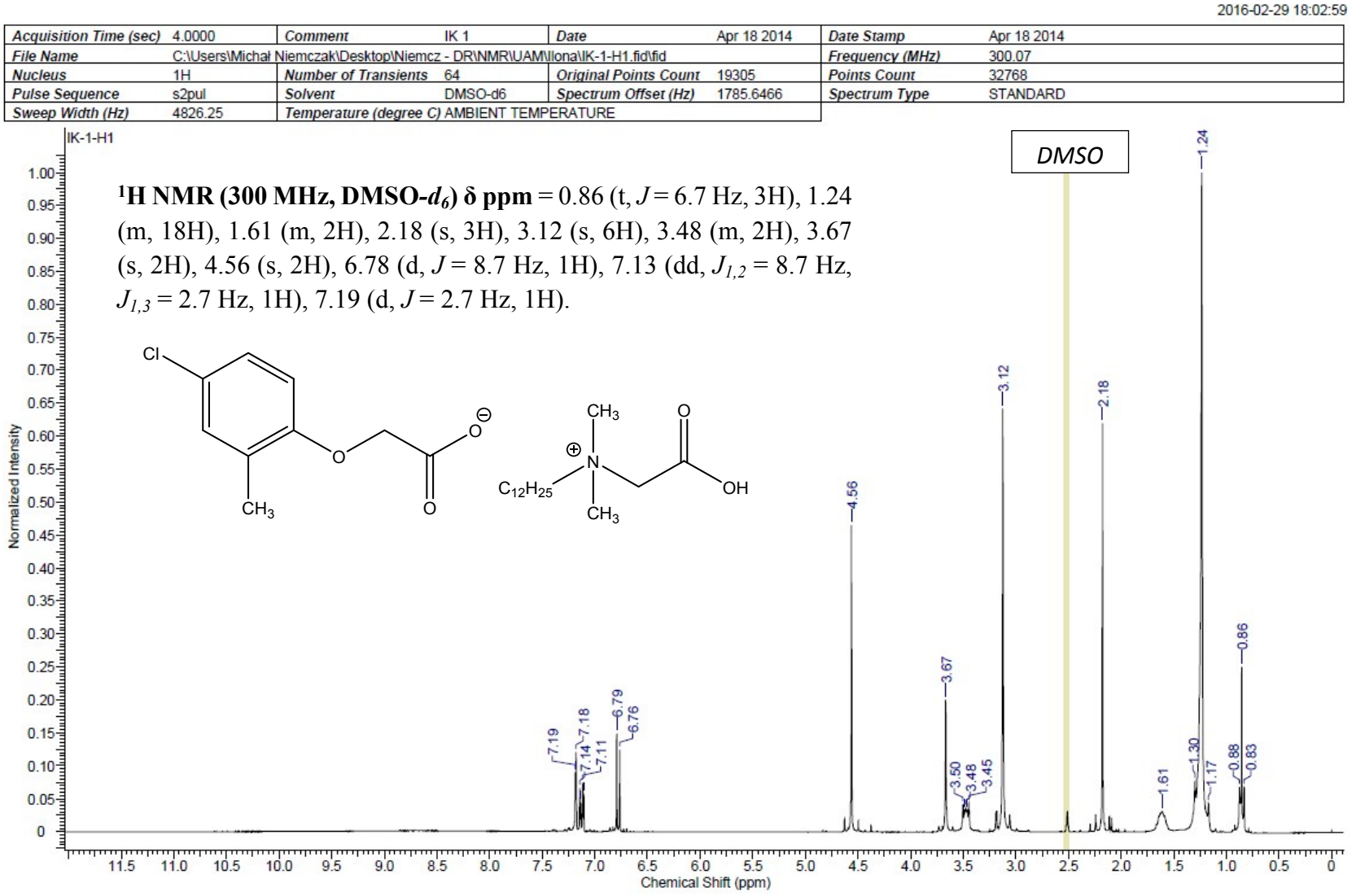


Figure S8. ^{13}C NMR spectrum of dodecylbetainium 4-chloro-2-methylphenoxyacetate (**2**).

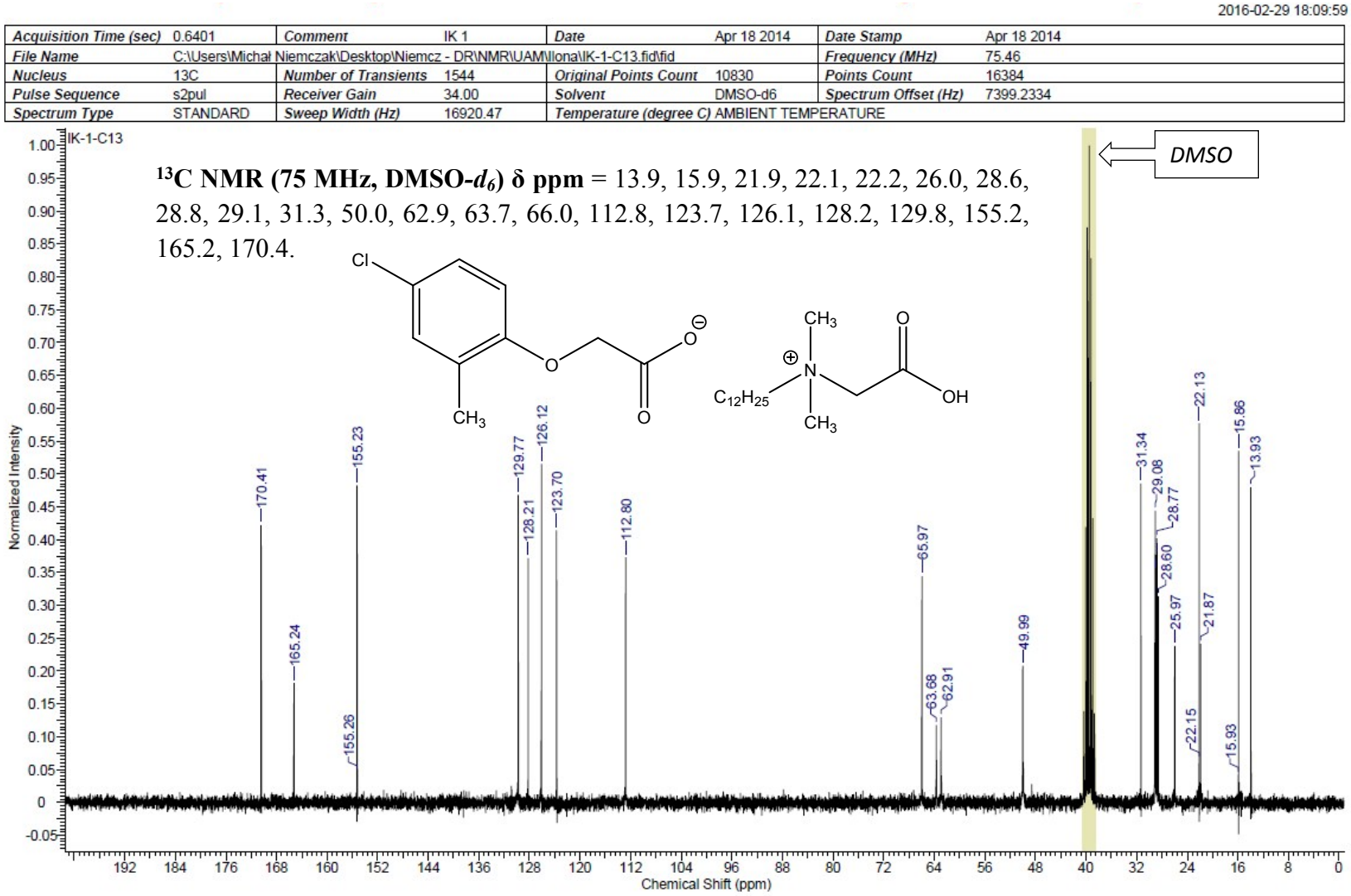


Figure S9. [1]H NMR spectrum of dodecylbetainium 2-(4-chloro-2-methylphenoxy)propionate (**3**).

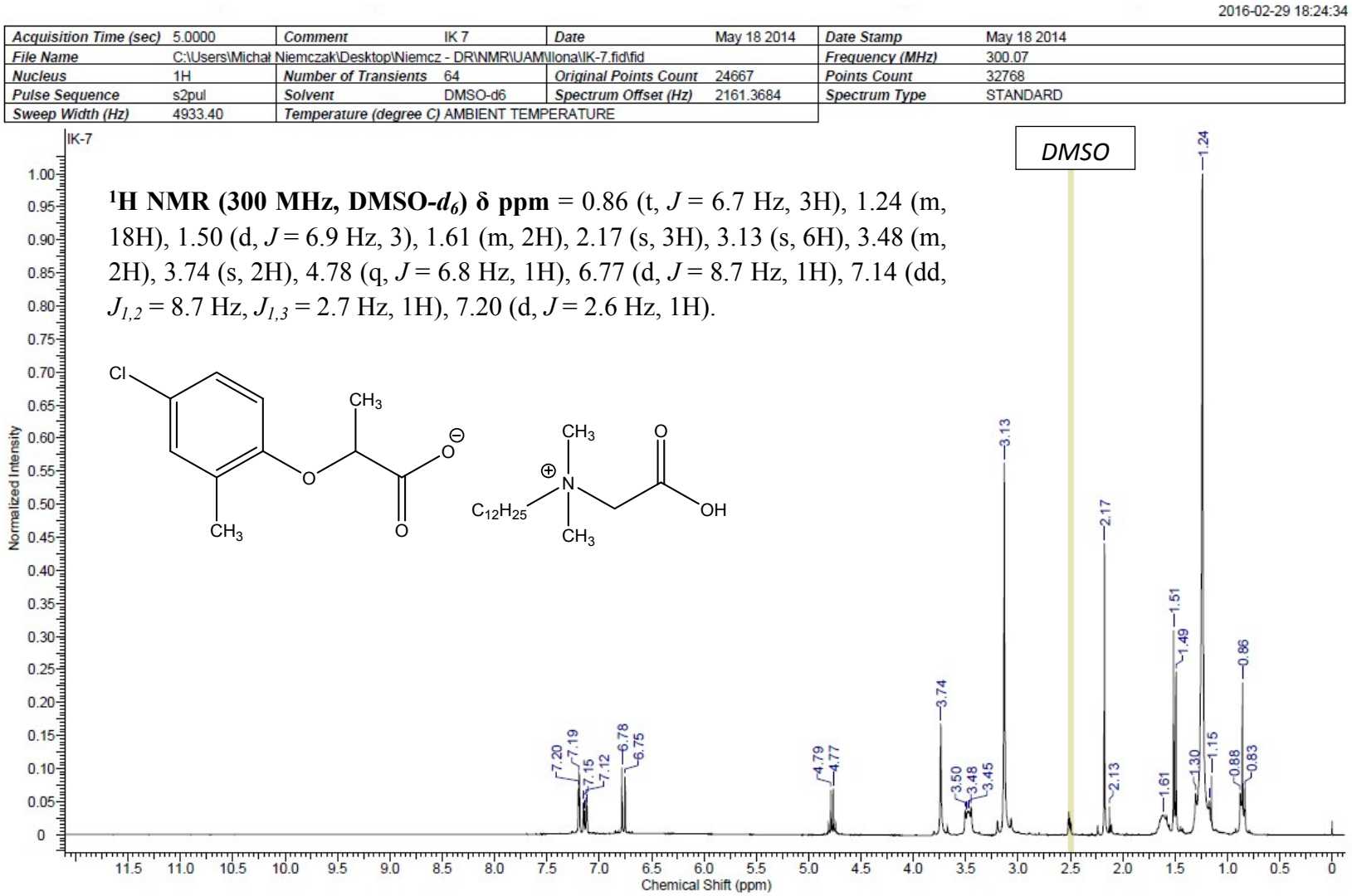


Figure S10. ^{13}C NMR spectrum of dodecylbetainium 2-(4-chloro-2-methylphenoxy)propionate (**3**).

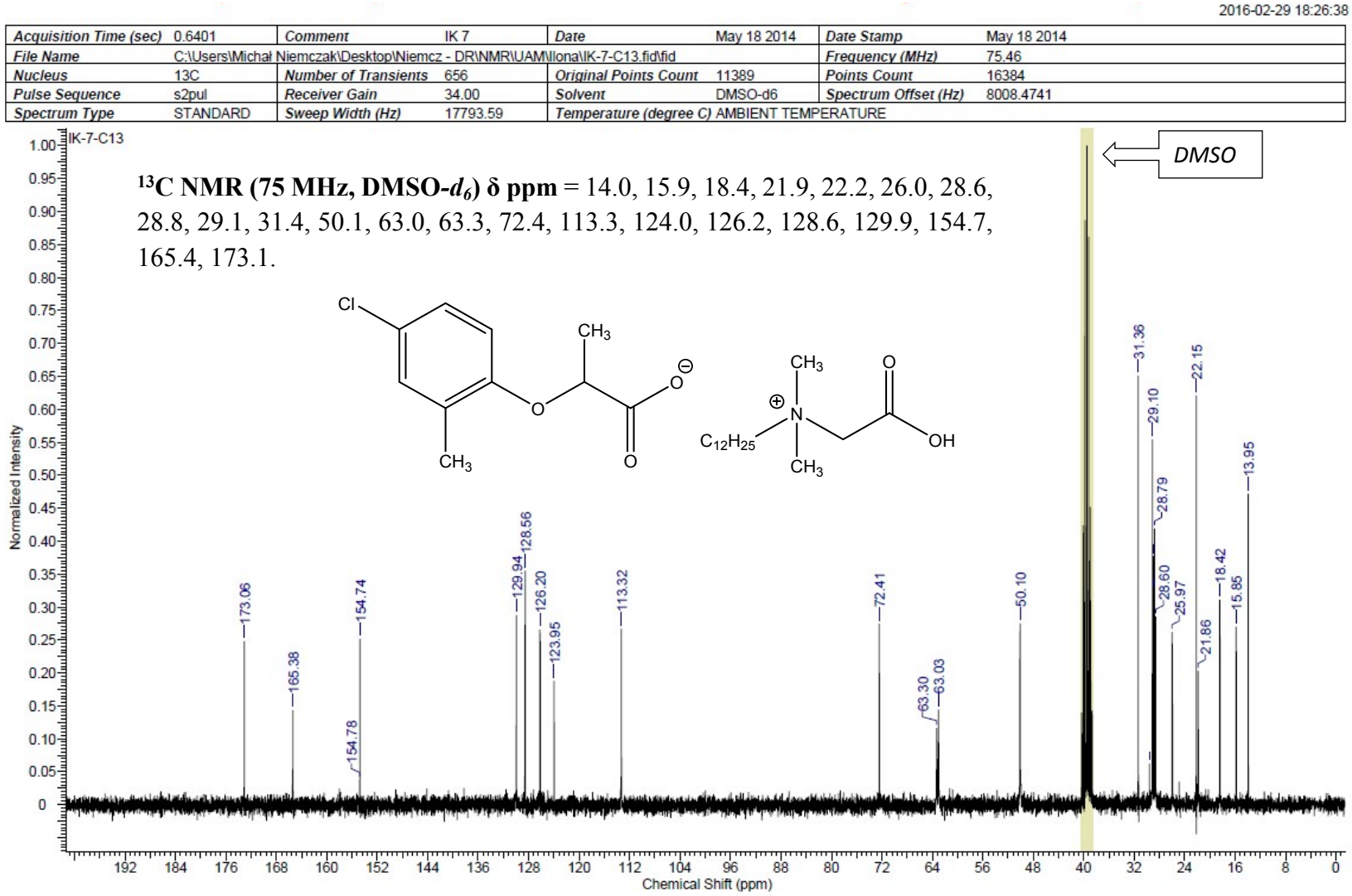
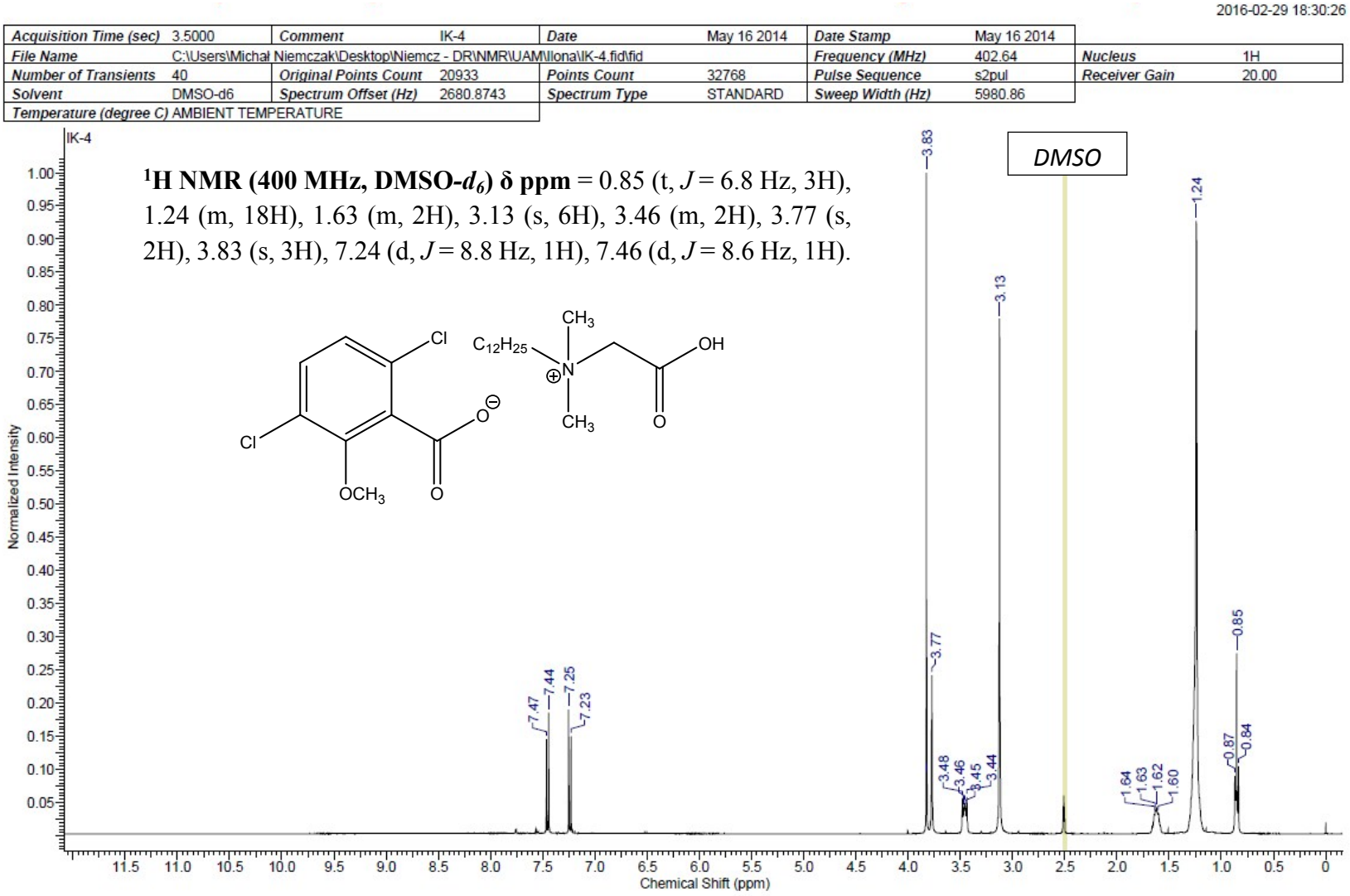


Figure S11. [1]H NMR spectrum of dodecylbetainium 3,6-dichloro-2-methoxybenzoate (**4**).



[1]H NMR (400 MHz, DMSO-d_6) δ ppm = 0.85 (t, J = 6.8 Hz, 3H), 1.24 (m, 18H), 1.63 (m, 2H), 3.13 (s, 6H), 3.46 (m, 2H), 3.77 (s, 2H), 3.83 (s, 3H), 7.24 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 8.6 Hz, 1H).

Figure S12. ^{13}C NMR spectrum of dodecylbetainium 3,6-dichloro-2-methoxybenzoate (**4**).

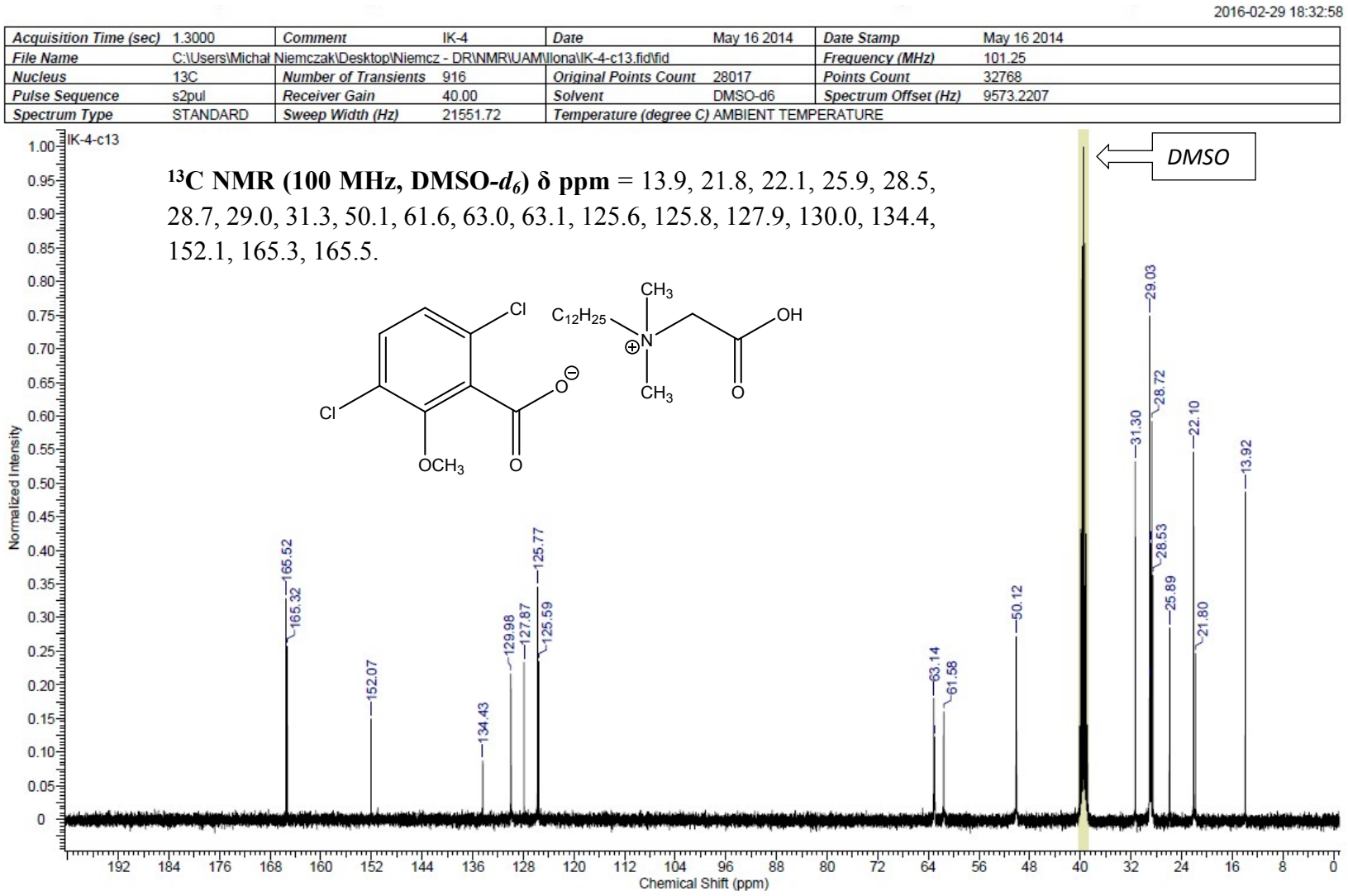


Figure S13. [1]H NMR spectrum of cocoamidopropylbetainium 2,4-dichlorophenoxyacetate (**5**).

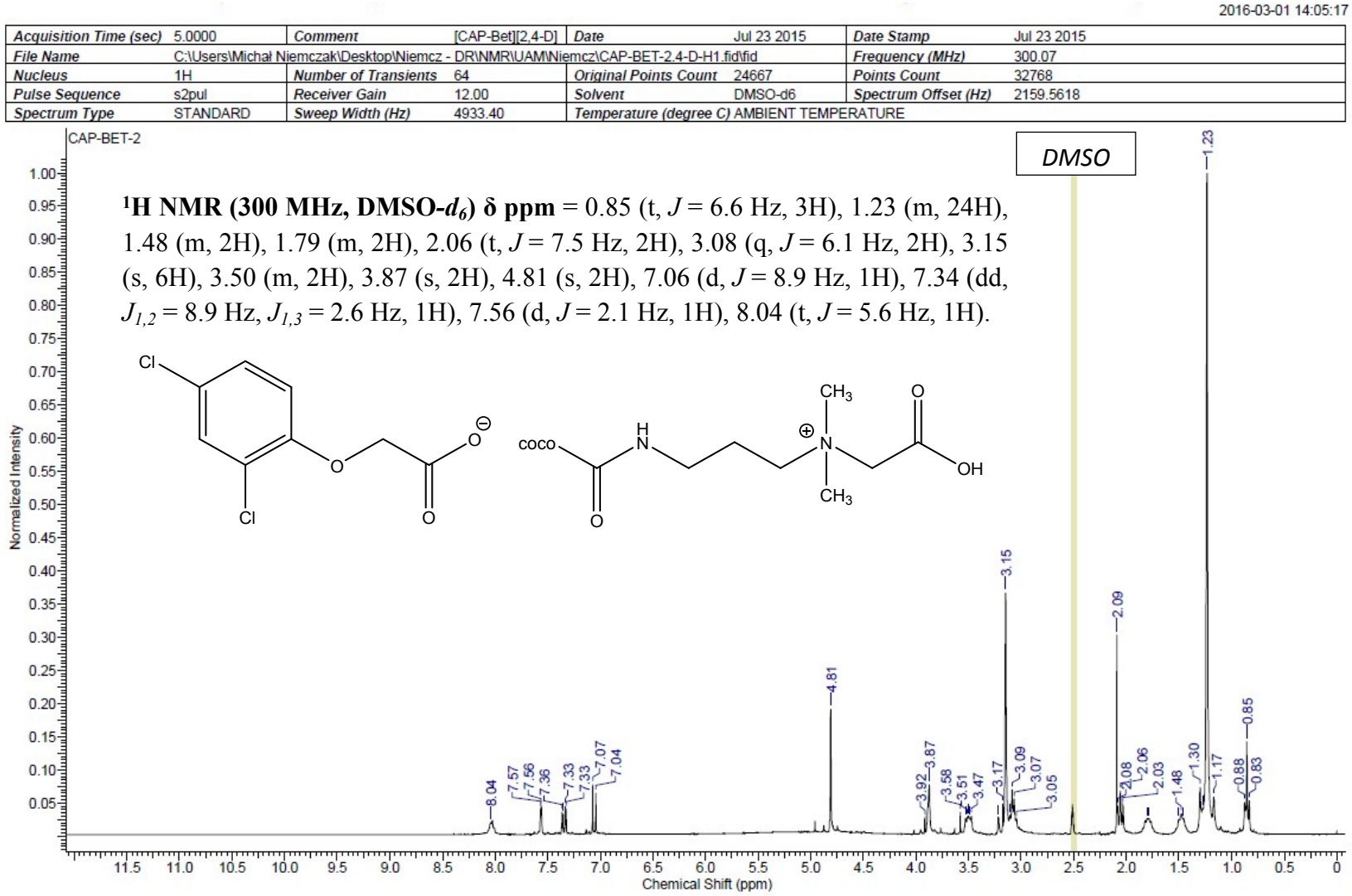


Figure S14. ^{13}C NMR spectrum of cocoamidopropylbetainium 2,4-dichlorophenoxyacetate (**5**).

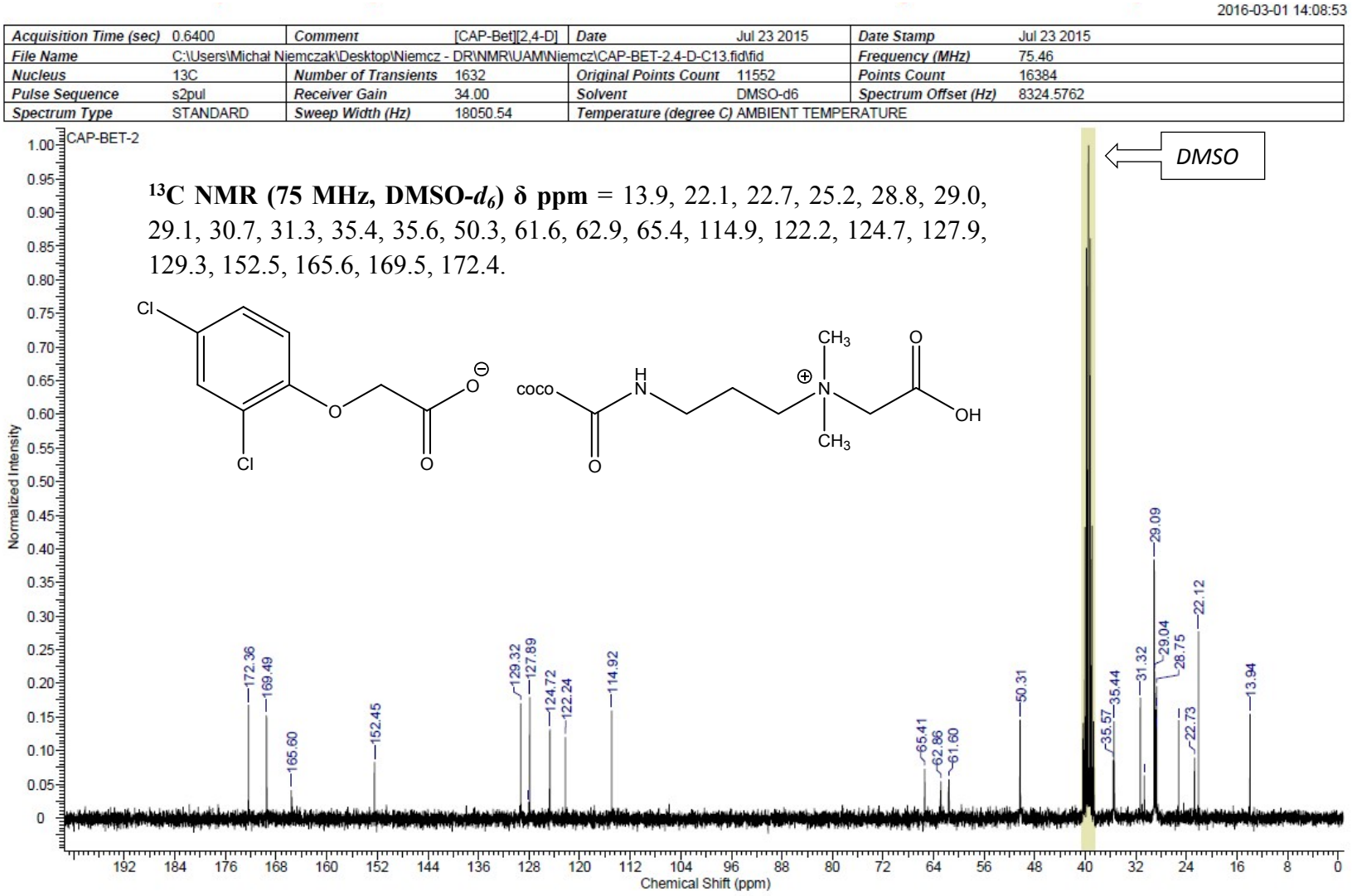


Figure S15. ^{1}H NMR spectrum of cocoamidopropylbetainium 4-chloro-2-methylphenoxyacetate (**6**).

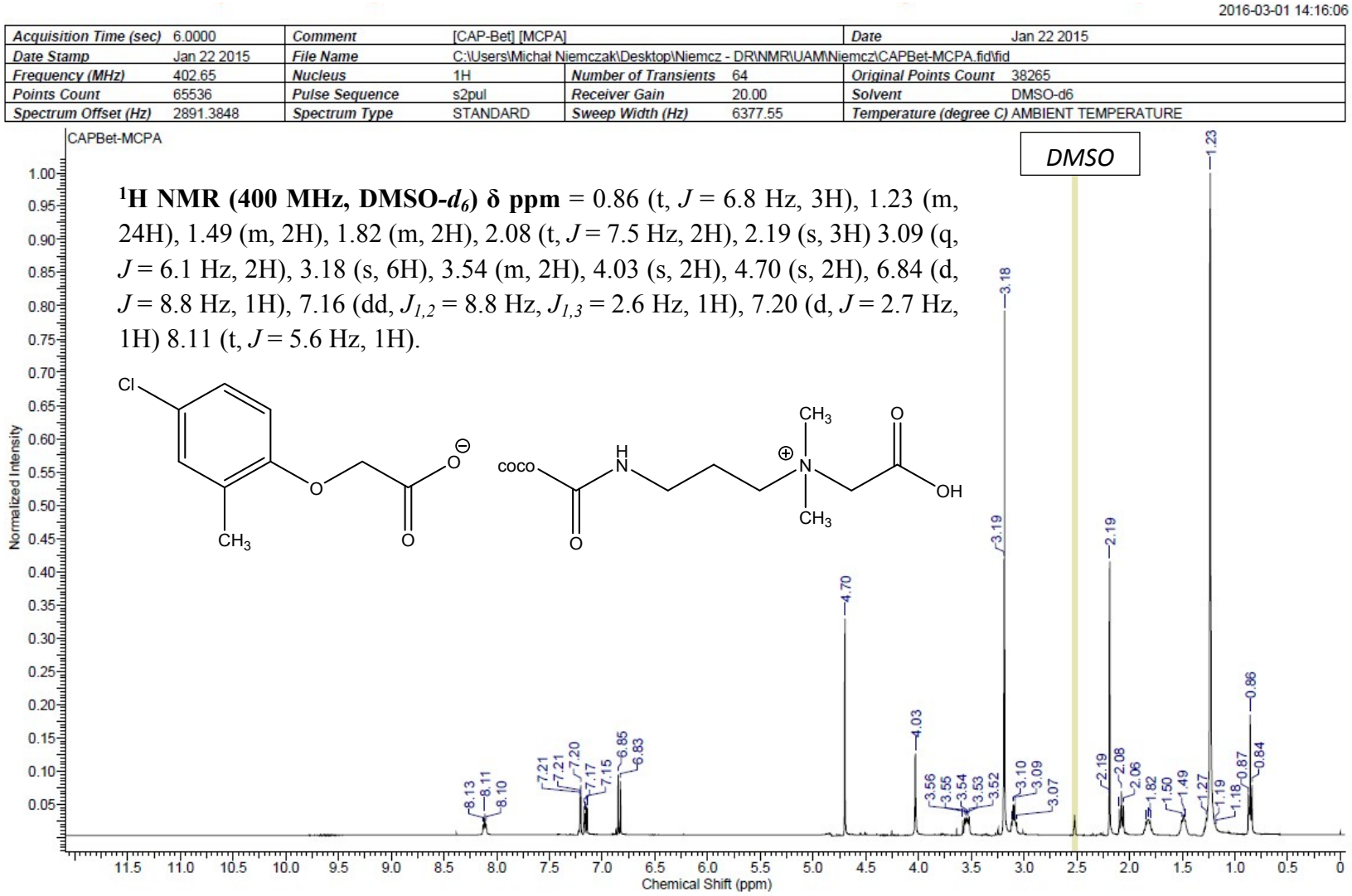


Figure S16. ^{13}C NMR spectrum of cocoamidopropylbetainium 4-chloro-2-methylphenoxyacetate (**6**).

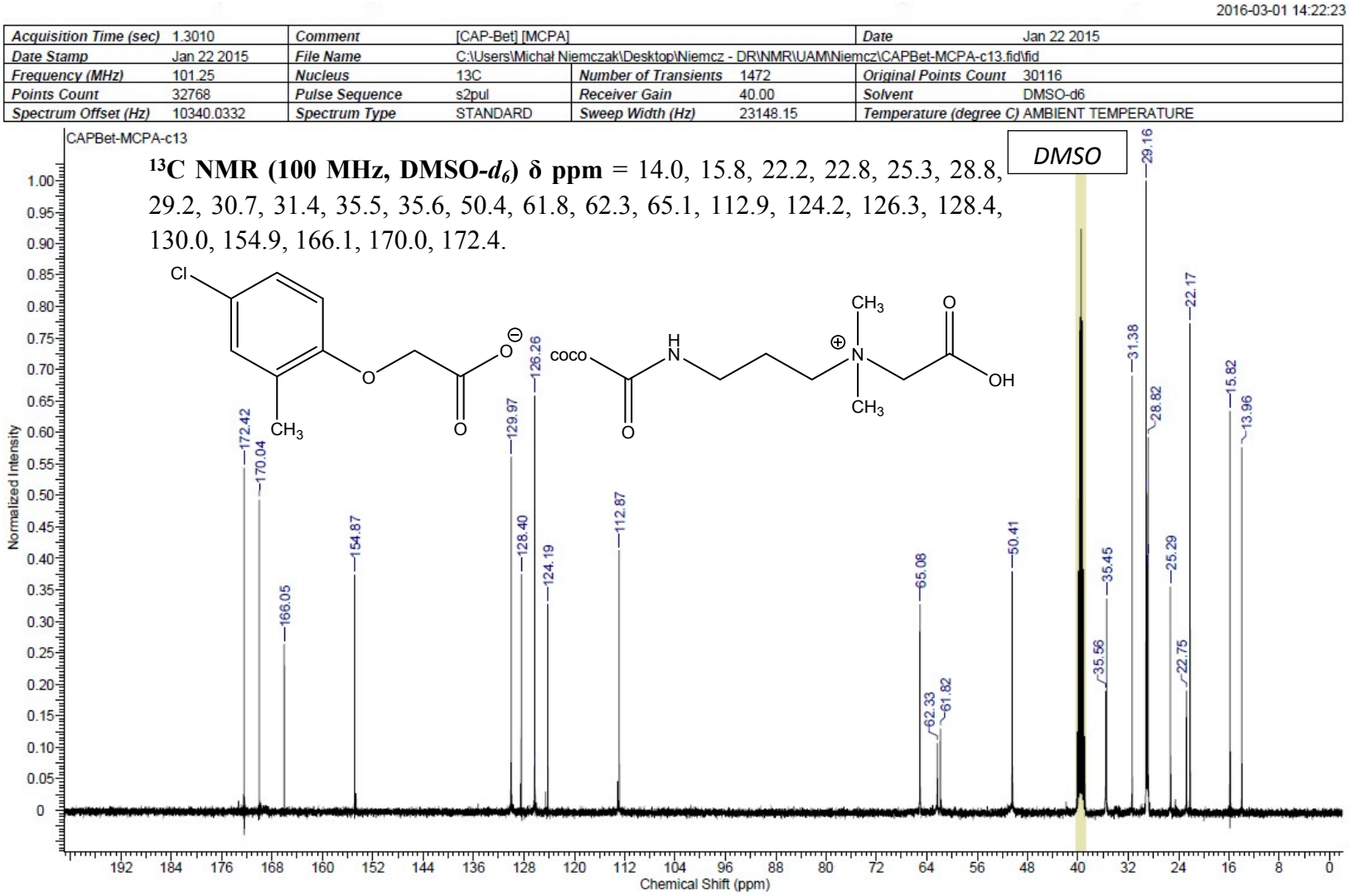


Figure S17. ^{1}H NMR spectrum of cocoamidopropylbetainium 2-(4-chloro-2-methylphenoxy)propionate (**7**).

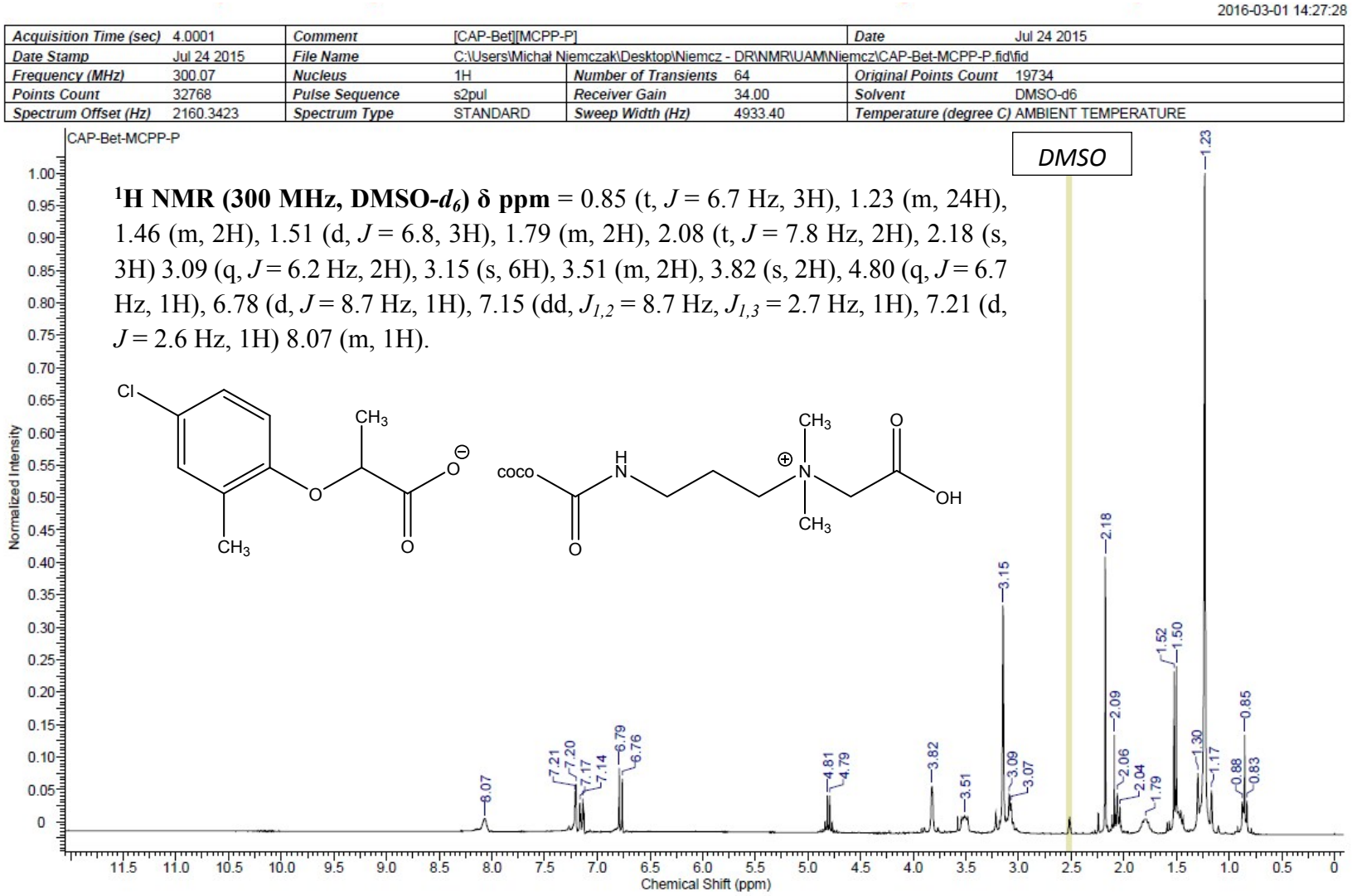


Figure S18. ^{13}C NMR spectrum of cocoamidopropylbetainium 2-(4-chloro-2-methylphenoxy)propionate (**7**).

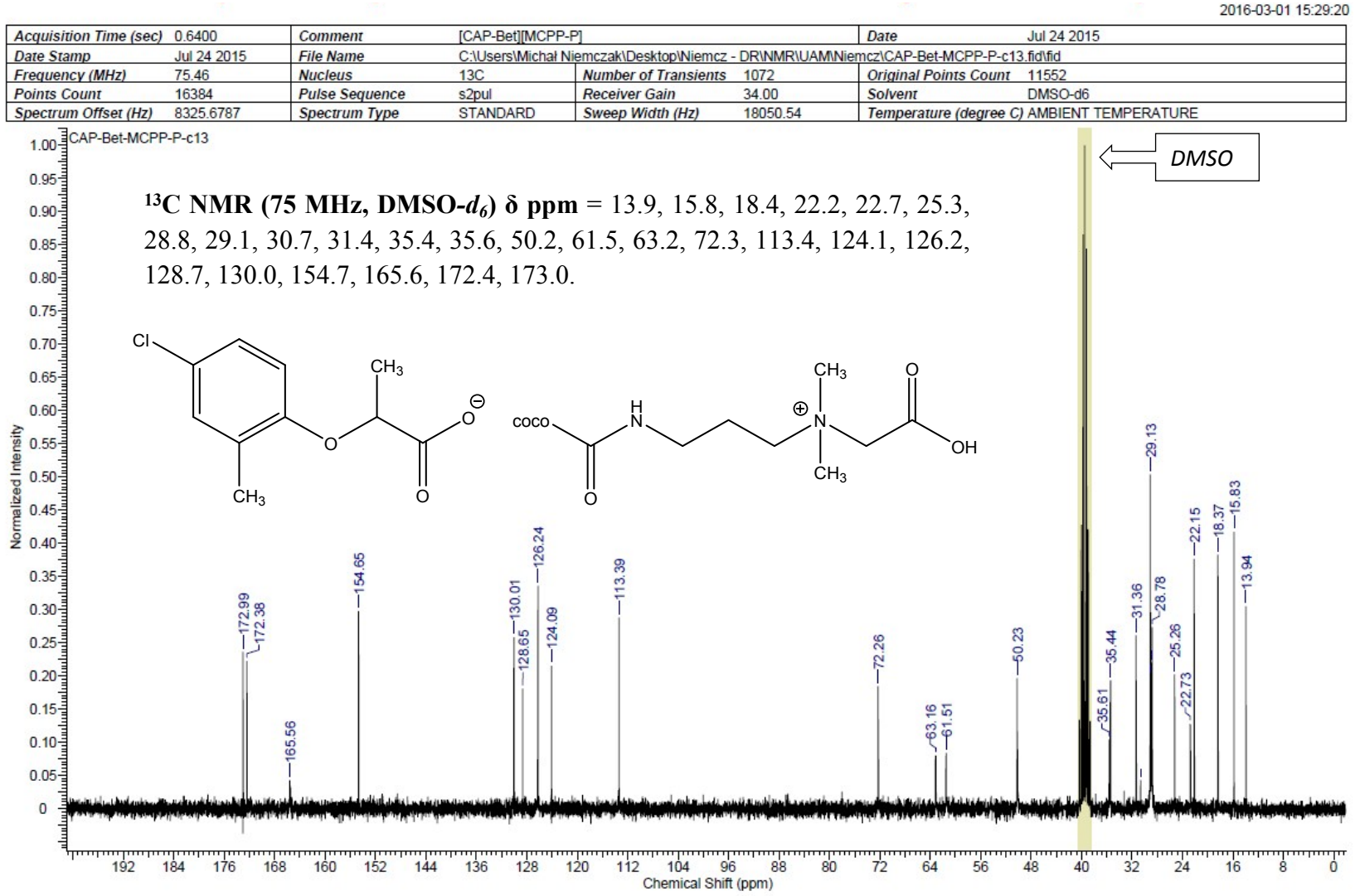
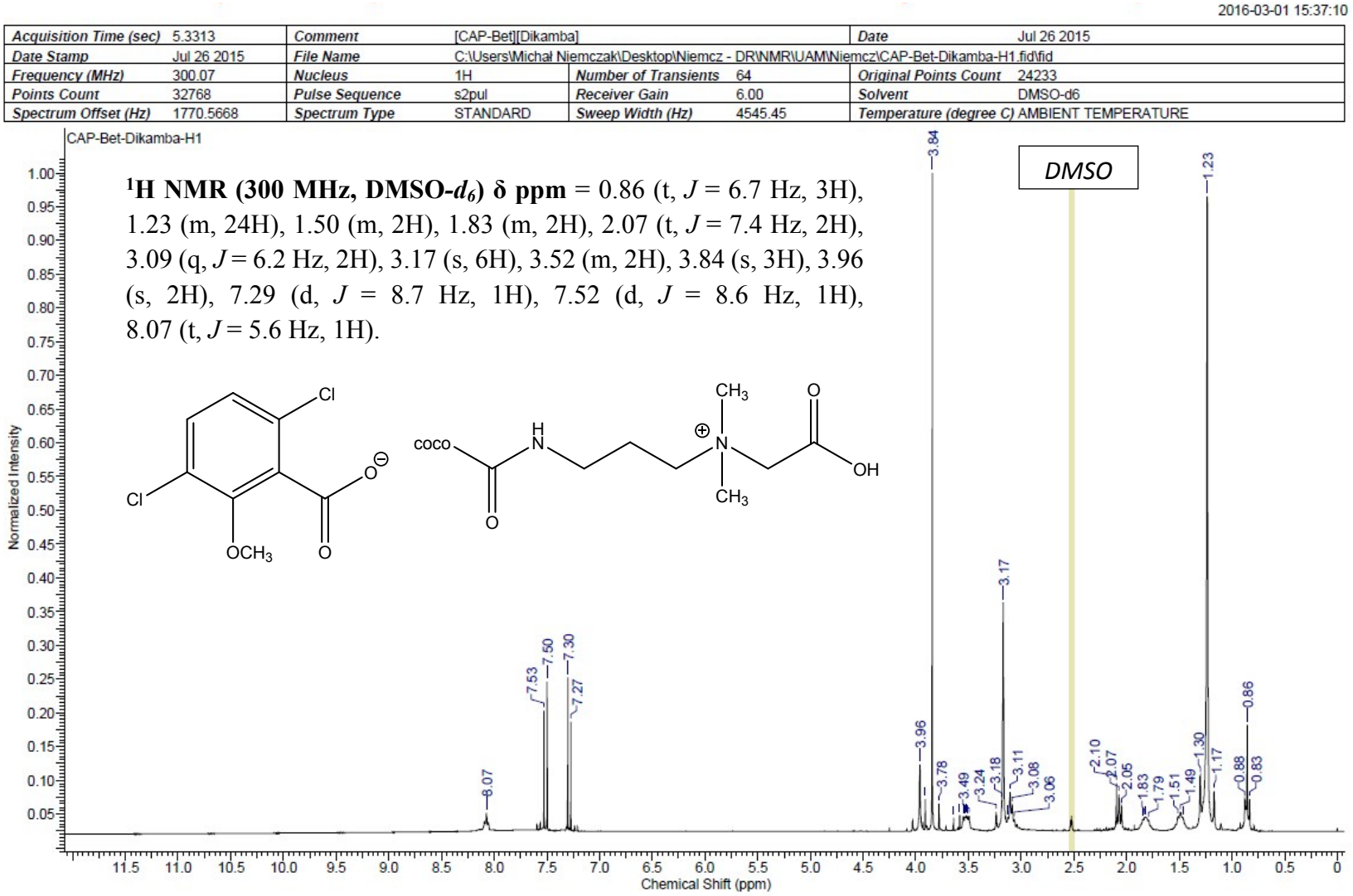


Figure S19. [1]H NMR spectrum of cocoamidopropylbetainium 3,6-dichloro-2-methoxybenzoate (**8**).



^{1}H NMR (300 MHz, DMSO-d_6) δ ppm = 0.86 (t, *J* = 6.7 Hz, 3H), 1.23 (m, 24H), 1.50 (m, 2H), 1.83 (m, 2H), 2.07 (t, *J* = 7.4 Hz, 2H), 3.09 (q, *J* = 6.2 Hz, 2H), 3.17 (s, 6H), 3.52 (m, 2H), 3.84 (s, 3H), 3.96 (s, 2H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 8.07 (t, *J* = 5.6 Hz, 1H).

Figure S20. ^{13}C NMR spectrum of cocoamidopropylbetainium 3,6-dichloro-2-methoxybenzoate (**8**).

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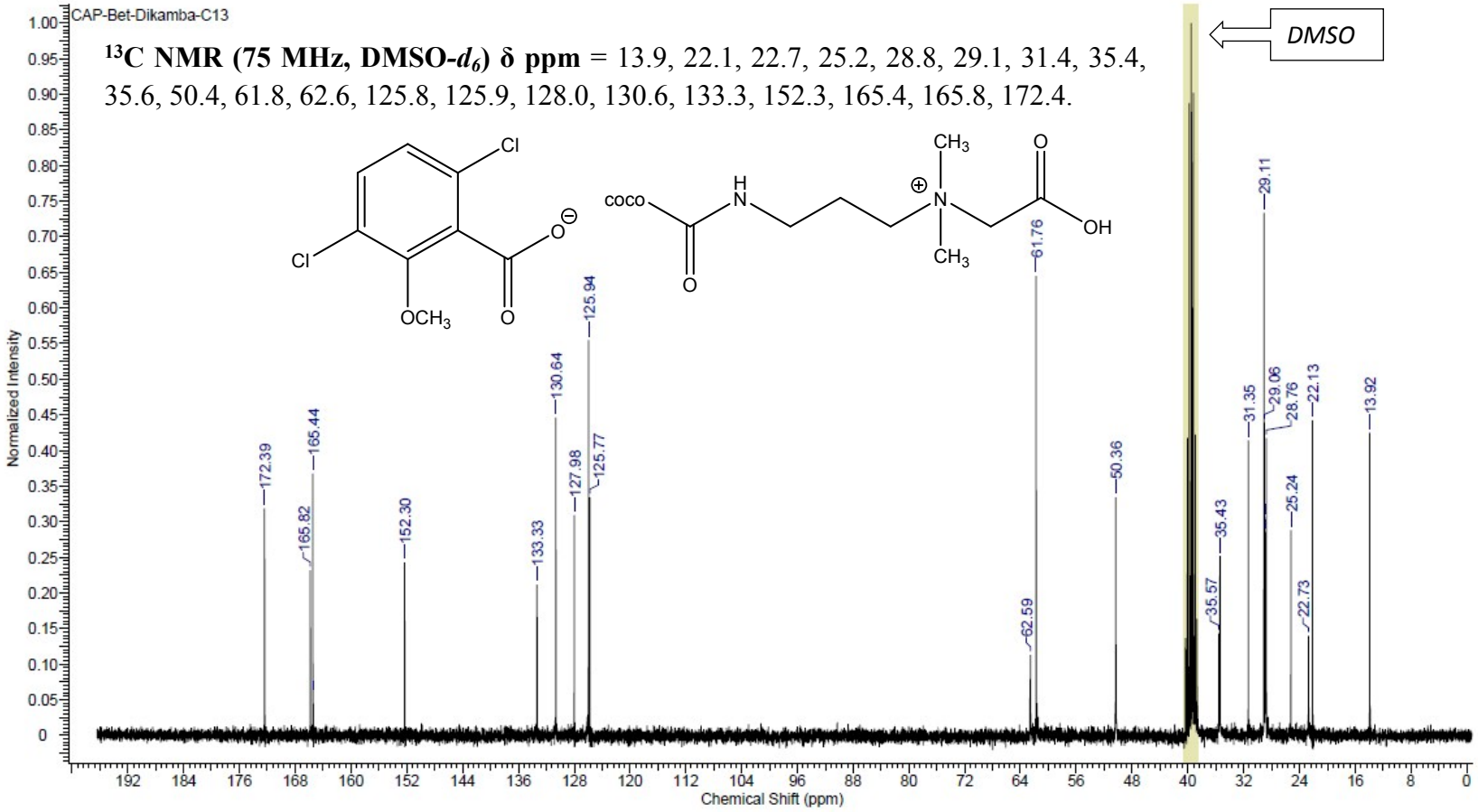

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm = 13.9, 22.1, 22.7, 25.2, 28.8, 29.1, 31.4, 35.4, 35.6, 50.4, 61.8, 62.6, 125.8, 125.9, 128.0, 130.6, 133.3, 152.3, 165.4, 165.8, 172.4.

Table S2. Shifts in ^{1}H NMR, ppm

Salt	Alkyl	Anion	Cation – signals from protons			
			C-C<u>H</u>$_2$-N	N-C<u>H</u>$_3$	N-C<u>H</u>$_2$-C	N<u>H</u>-CO
[C_{12}Bet][Cl]	$C_{12}H_{25}$	Cl	3.49(m)	3.21(s)	4.38(s)	---
1	$C_{12}H_{25}$	2,4-D	3.49(m)	3.15(s)	3.77(s)	---
2	$C_{12}H_{25}$	MCPA	3.48(m)	3.12(s)	3.67(s)	---
3	$C_{12}H_{25}$	MCPP	3.48(m)	3.13(s)	3.74(s)	---
4	$C_{12}H_{25}$	Dicamba	3.46(m)	3.13(s)	3.77(s)	---
[CAPBet][Cl]	CAP[a]	Cl	3.58(m)	3.24(s)	4.45(s)	8.25(t)
5	CAP[a]	2,4-D	3.50(m)	3.15(s)	3.87(s)	8.04(t)
6	CAP[a]	MCPA	3.54(m)	3.18(s)	4.03(s)	8.11(t)
7	CAP[a]	MCPP	3.51(m)	3.15(s)	3.82(s)	8.07(t)
8	CAP[a]	Dicamba	3.52(m)	3.17(s)	3.96(s)	8.07(t)

[a] cocoamidopropyl; s - singlet; t - triplet; m - multiplet

Table S3. Shifts in ^{13}C NMR, ppm

Salt	Alkyl	Anion	Cation – signals from carbon atoms				
			C-<u>C</u>H$_2$-N	N-<u>C</u>H$_3$	N-<u>C</u>H$_2$-C	NH-<u>C</u>O	C-<u>C</u>OOH
[C_{12}Bet][Cl]	$C_{12}H_{25}$	Cl	64.1	50.6	60.5	---	166.3
1	$C_{12}H_{25}$	2,4-D	63.3	50.1	63.1	---	165.5
2	$C_{12}H_{25}$	MCPA	63.7	50.0	62.9	---	165.2
3	$C_{12}H_{25}$	MCPP	63.3	50.1	63.0	---	165.4
4	$C_{12}H_{25}$	Dicamba	63.1	50.1	63.0	---	165.3
[CAPBet][Cl]	CAP[a]	Cl	62.4	50.7	60.6	172.5	166.3
5	CAP[a]	2,4-D	61.6	50.3	62.9	172.4	165.6
6	CAP[a]	MCPA	61.8	50.4	62.3	172.4	166.1
7	CAP[a]	MCPP	61.5	50.2	63.2	172.4	165.6
8	CAP[a]	Dicamba	61.8	50.4	62.6	172.4	165.8

[a] 3-cocoamidopropyl

Table S4. Viscosity values (Pa·s) for ILs **1-4**, **6-8**

IL	Alkyl	Anion	Temperature [°C]						
			20	**30**	**40**	**50**	**60**	**70**	**80**
1	$C_{12}H_{25}$	2,4-D	---	---	---	---	---	1.7646	0.9038
2	$C_{12}H_{25}$	MCPA	---	---	---	3.2349	1.4484	0.7164	0.3936
3	$C_{12}H_{25}$	MCPP	64.679	19.573	6.9902	2.8573	1.3081	0.6574	0.3677
4	$C_{12}H_{25}$	Dicamba	---	---	318.80	80.371	25.173	9.3479	3.8929
6	CAP[a]	MCPA	495.83	123.84	37.152	13.069	5.2461	2.4611	1.2336
7	CAP[a]	MCPP	300.11	76.929	23.794	8.6983	3.5709	1.6944	0.8782
8	CAP[a]	Dicamba	3461.8	714.79	186.06	57.487	20.381	8.3412	3.7911

[a] 3-cocoamidopropyl

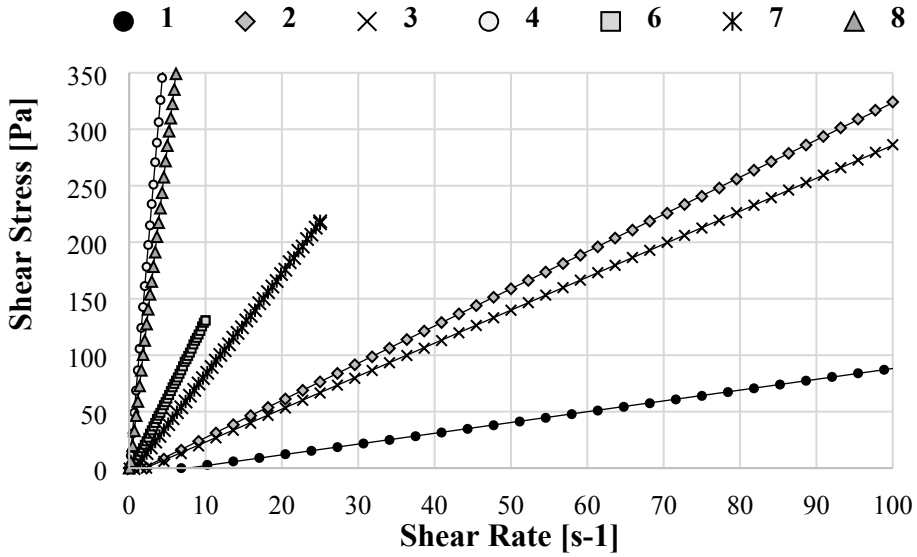

Figure S21. Shear stress versus shear rate for ILs **1-4**, **6-8**

Table S5. Density values ($g \cdot cm^{-3}$) for ILs **1-4**, **6-8**

IL	Alkyl	Anion	Temperature [°C]						
			20	**30**	**40**	**50**	**60**	**70**	**80**
1	$C_{12}H_{25}$	2,4-D	---	---	---	---	---	1.09541	1.08787
2	$C_{12}H_{25}$	MCPA	---	---	---	1.09733	1.08919	1.08227	1.07441
3	$C_{12}H_{25}$	MCPP	1.06764	1.06063	1.05362	1.04652	1.03944	1.03222	1.02489
4	$C_{12}H_{25}$	Dicamba	---	---	1.14047	1.13314	1.12584	1.11866	1.11126
6	CAP[a]	MCPA	1.09165	1.08453	1.07745	1.07024	1.06293	1.05515	1.04707
7	CAP[a]	MCPP	1.08930	1.08197	1.07459	1.06711	1.05937	1.05087	1.04081
8	CAP[a]	Dicamba	1.15646	1.14947	1.14242	1.13527	1.12787	1.12043	1.11302

[a] 3-cocoamidopropyl

Table S6. Summary of straight lines coefficients *a* and *b* obtained by linear regression and correlation coefficients (R^2) for density measurements

IL	Alkyl	Anion	Equation of a straight line (y = a·x + b)		Correlation coefficient (R^2)
			a	**b**	
2	$C_{12}H_{25}$	MCPA	-0.00076	1.1350	0.9991
3	$C_{12}H_{25}$	MCPP	-0.00071	1.0820	0.9999
4	$C_{12}H_{25}$	Dicamba	-0.00073	1.1696	0.9999
6	CAP[a]	MCPA	-0.00074	1.1068	0.9995
7	CAP[a]	MCPP	-0.00080	1.1061	0.9969
8	CAP[a]	Dicamba	-0.00072	1.1712	0.9998

[a] 3-cocoamidopropyl

Table S7. Refractive index values for ILs **1-8**

IL	Alkyl	Anion	Temperature [°C]						
			20	30	40	50	60	70	80
1	$C_{12}H_{25}$	2,4-D	---	---	---	---	---	1.49442	1.49109
2	$C_{12}H_{25}$	MCPA	---	---	---	1.50102	1.49729	1.49419	1.49122
3	$C_{12}H_{25}$	MCPP	1.49941	1.49622	1.49293	1.48958	1.48621	1.48285	1.47958
4	$C_{12}H_{25}$	Dicamba	---	---	1.50909	1.50585	1.50261	1.49941	1.49631
5	CAP[a]	2,4-D	1.50500	1.50053	1.49702	1.49333	1.4901	1.48682	1.48334
6	CAP[a]	MCPA	1.49895	1.49530	1.49174	1.48920	1.48637	1.48293	1.47999
7	CAP[a]	MCPP	1.50375	1.49913	1.49601	1.49221	1.48925	1.48569	1.48231
8	CAP[a]	Dicamba	1.51450	1.51132	1.50816	1.50502	1.50187	1.49927	1.49631

[a] 3-cocoamidopropyl

Table S8. Summary of straight lines coefficients *a* and *b* obtained by linear regression and correlation coefficients (R^2) for refractive index measurements

IL	Alkyl	Anion	Equation of a straight line (y = a·x + b)		Correlation coefficient (R^2)
			a	b	
2	$C_{12}H_{25}$	MCPA	-0.00033	1.5171	0.9970
3	$C_{12}H_{25}$	MCPP	-0.00033	1.5061	0.9999
4	$C_{12}H_{25}$	Dicamba	-0.00032	1.5219	0.9999
5	CAP[a]	2,4-D	-0.00035	1.5115	0.9977
6	CAP[a]	MCPA	-0.00031	1.5048	0.9978
7	CAP[a]	MCPP	-0.00035	1.5101	0.9975
8	CAP[a]	Dicamba	-0.00030	1.5204	0.9991

[a] 3-cocoamidopropyl

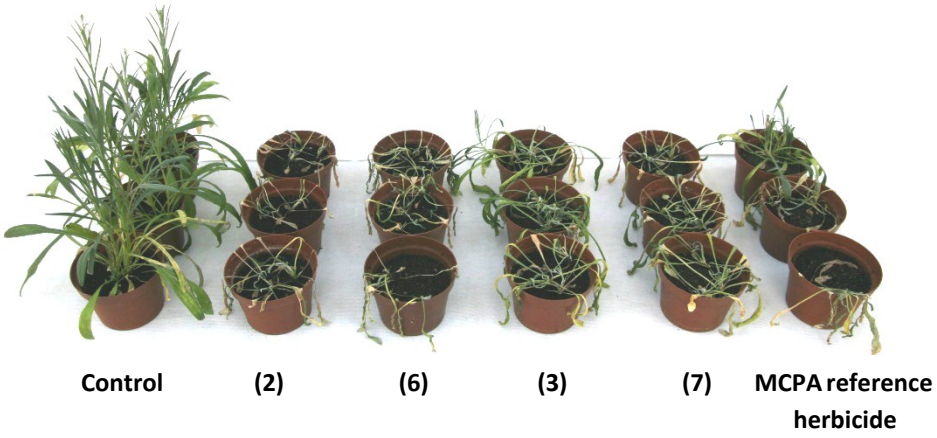

Figure S22. Herbicidal activity of **2**, **3**, **6** and **7** against cornflower (*Centaurea cyanus*)

Table S9. Collected values of surface tension (γ) and contact angle (CA) of spray solutions containing HILs (**1**-**8**) and reference herbicides

IL	Alkyl	Anion	Surface tension [mN m^{-1}]	Contact angle [°]
1	$C_{12}H_{25}$	2,4-D	31.71 ± 0.10	58.95 ± 0.94
2	$C_{12}H_{25}$	MCPA	31.83 ± 0.16	60.28 ± 1.36
3	$C_{12}H_{25}$	MCPP	31.66 ± 0.09	57.51 ± 2.19
4	$C_{12}H_{25}$	Dicamba	32.66 ± 0.17	62.22 ± 0.91
5	CAP[a]	2,4-D	31.47 ± 0.04	51.74 ± 1.87
6	CAP[a]	MCPA	31.62 ± 0.12	52.79 ± 1.87
7	CAP[a]	MCPP	31.63 ± 0.08	50.40 ± 0.90
8	CAP[a]	Dicamba	30.41 ± 0.03	50.33 ± 1.39
---	2,4-D ref. herbicide		71.70 ± 0.14	107.96 ± 0.66
---	MCPA ref. herbicide		71.70 ± 0.12	107.86 ± 0.67
---	Dicamba ref. herbicide		65.32 ± 0.13	103.70 ± 0.93

[a] 3-cocoamidopropyl

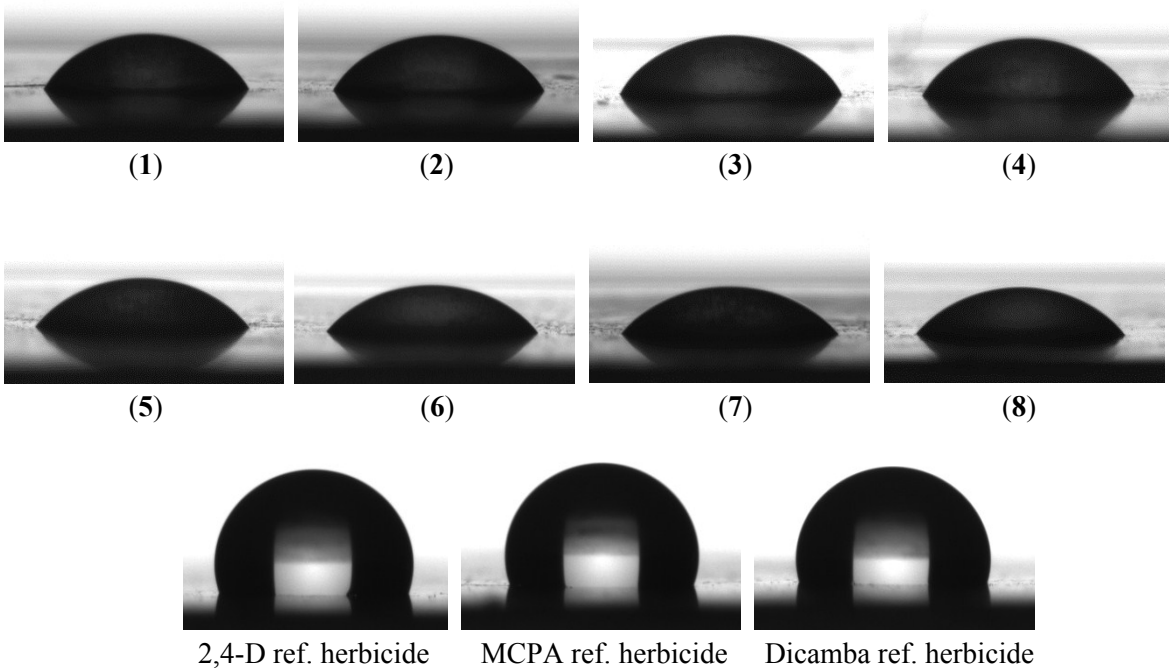

Figure S23. Shape of drop of the studied ILs (**1**-**8**) and reference herbicides