

Study of Aging in Oil Paintings by 1D and 2D NMR Spectroscopy

- [Apostolos Spyros](#), [Demetrios Anglos](#) *Anal. Chem.* 2004, 76, 17, 4929–4936

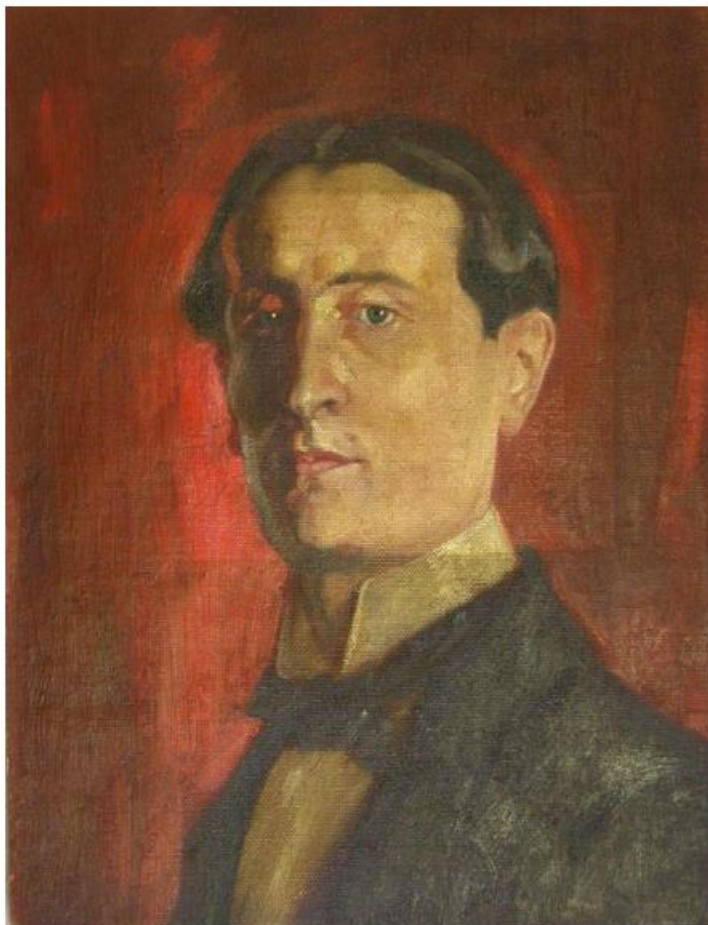
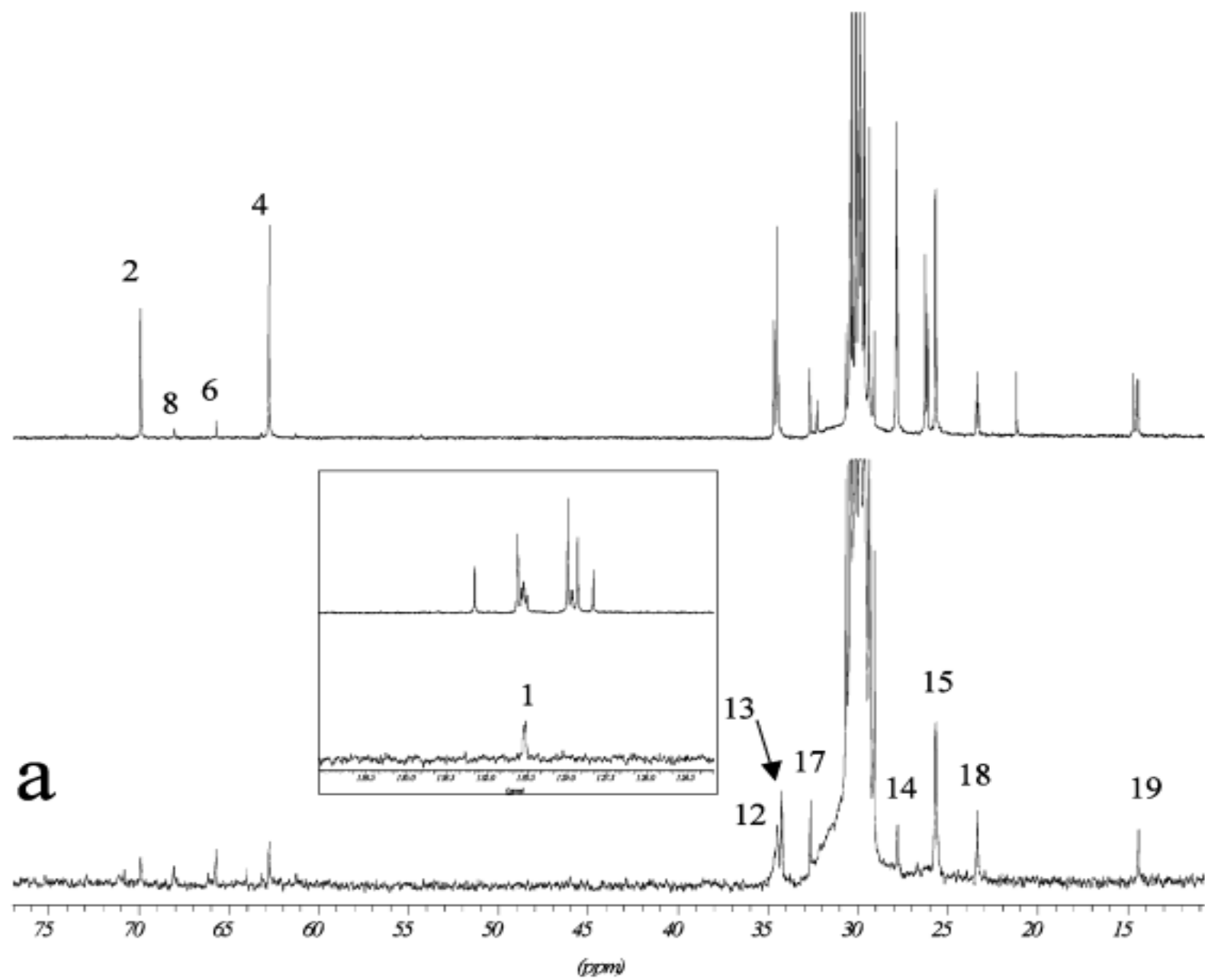


Fig. S-6. (a) “Portrait of young man”, by S. Vandoros, oil on canvas, early 20th century, private collection (b) “The Duke”, unknown artist, oil on canvas, late 17th century, private collection.



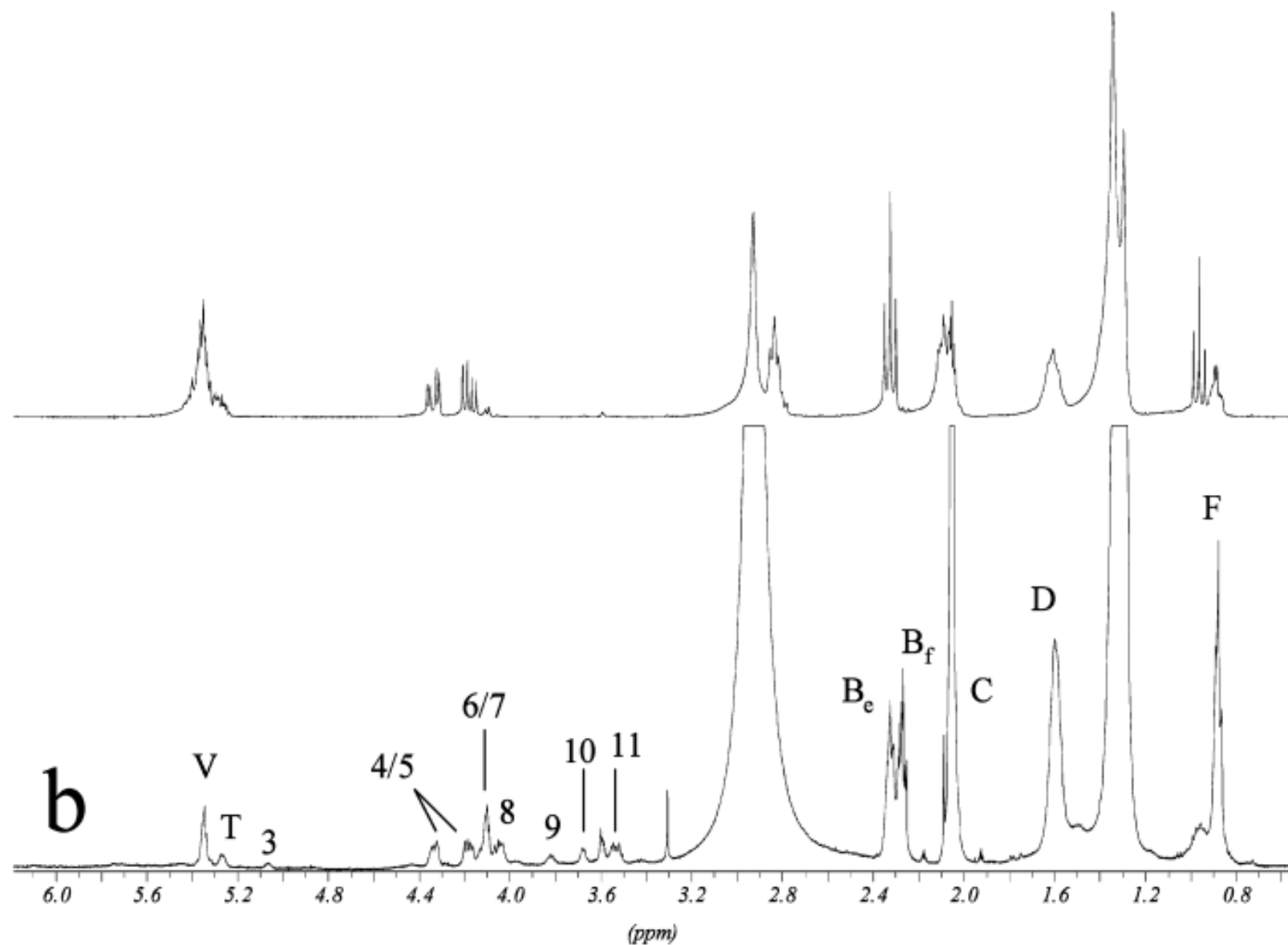


Figure 1. ^{13}C (a) and ^1H NMR spectra (b) of raw (top) and five-year-old (bottom) LB oil paint in acetone- d_6 . Peak numbers and symbols according to Table 1. Peak C is overlapped by the residual solvent peak.

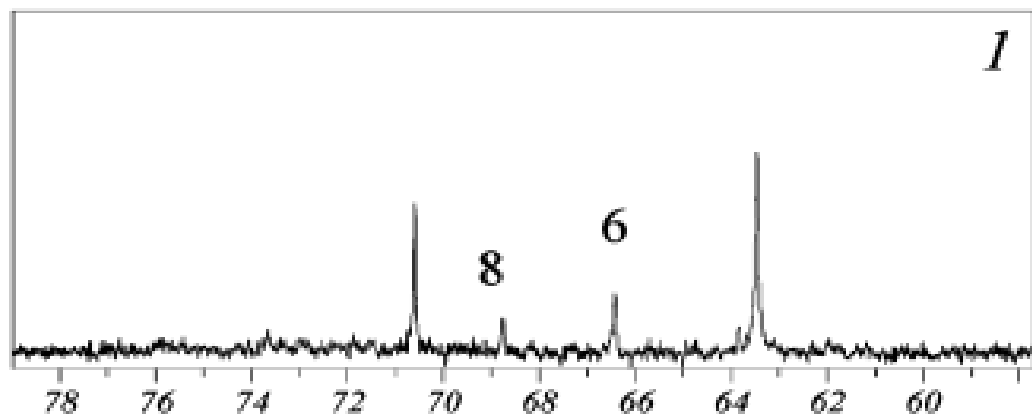
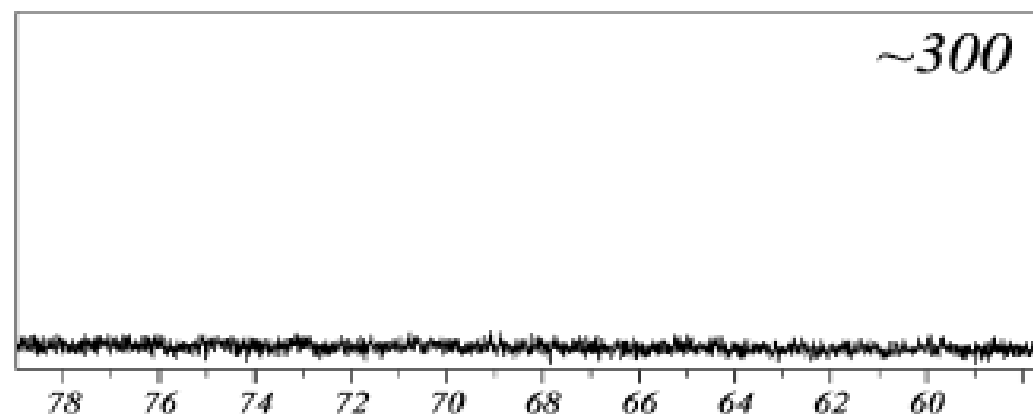
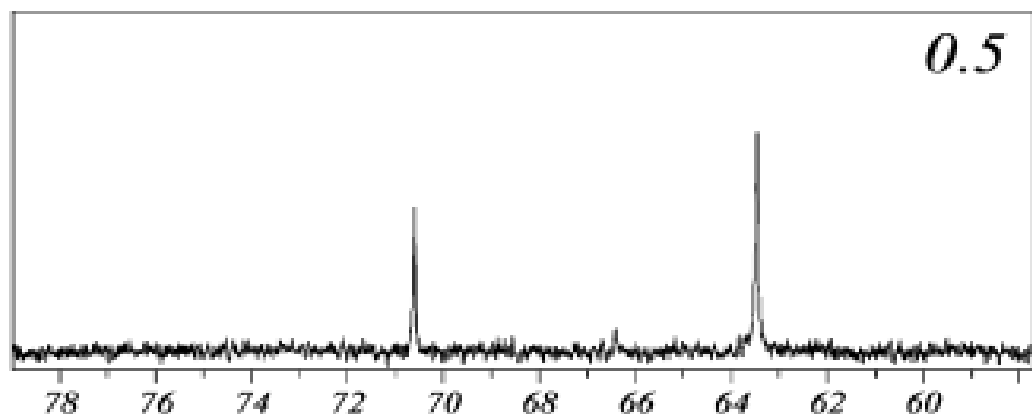
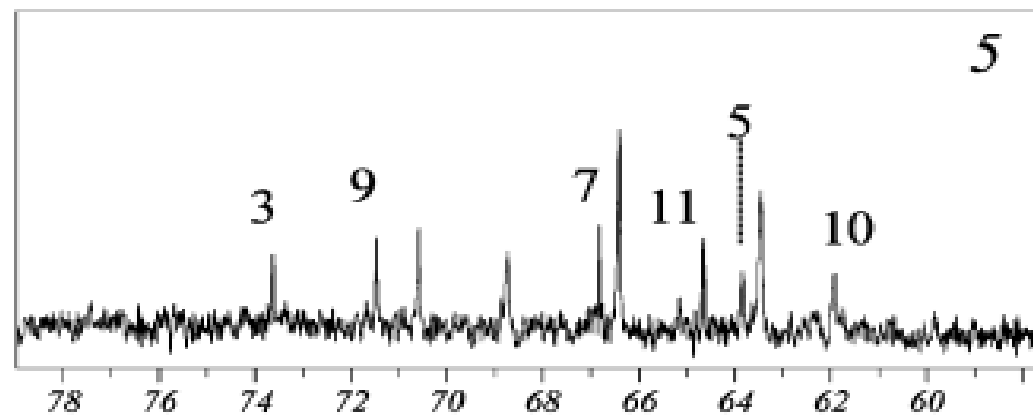
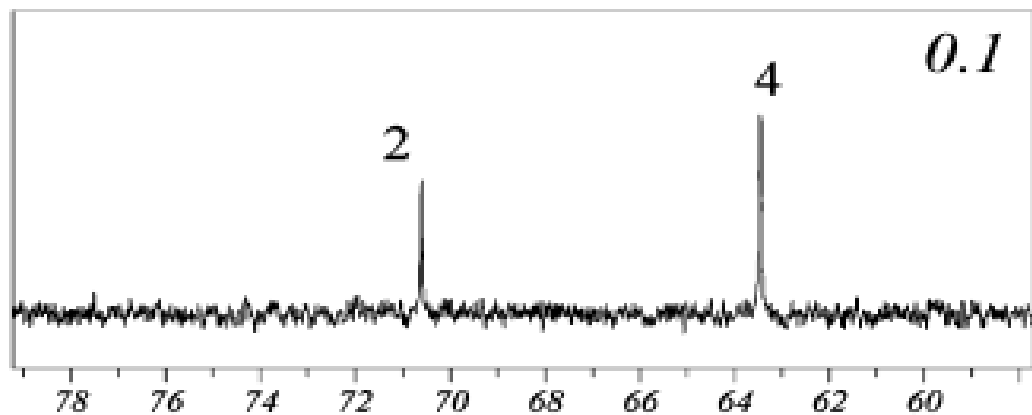
Table 1. Chemical Shifts (δ) of the Main Resonances in the ^1H and ^{13}C NMR Spectra of Binding Material Extracted from Drying Oil Films, Oil Paints, and Paintings in Acetone- d_6 Solvent

	δ (ppm)		group	assignment
	^1H	^{13}C		
1 (V)	5.33	130.5	$\text{CH}=\text{CH}$	unsaturated vinyl protons
2 (I)	5.25	69.9	CHOCOR	triglycerides
3	5.05	73.0	CHOCOR	1,2-diglycerides
4	4.32/4.16	62.8	CH_2OCOR	triglycerides
5	4.34/4.13	63.1	CH_2OCOR	1,2-diglycerides
6	4.1	65.7	CH_2OCOR	1,3-diglycerides
7		66.1		1-monoglycerides
8	4.06	68.1	CHOH $\text{CHO}-$	1,3-diglycerides hydroxy and oxo acids
9	3.8	70.8	CHOH	1-monoglycerides
10	3.66	61.2	CH_2OH	1,2-diglycerides
11	3.5	64.0	CH_2OH	1-monoglycerides
12 (B _e)	2.30	34.6	CH_2COOR	<i>sn</i> -2 esterified acids and diacids
		34.5		<i>sn</i> -1,3
13 (B _f)	2.24	34.2	CH_2COOH	free fatty acids and diacids
14 (C)	2.02	27.8	$\text{CH}_2\text{CH}=\text{}$	unsaturated fatty acids
15 (D)	1.57	26.3	$\text{CH}_2\text{CH}_2\text{COO}-$	all fatty acids and diacids
16 (E)	1.2–1.4	28–30	$(\text{CH}_2)_x$	all fatty acids and diacids
17	1.2–1.4	32.6	$\text{CH}_2\text{CH}_2\text{CH}_3$	oleic/linoleic acid
18	1.2–1.4	23.3	CH_2CH_3	oleic/linoleic acid
19 (F)	0.83–0.98	15.0	CH_3	all fatty acids

Table 2. Characteristic Parameters (Age Markers) Determined from the ^1H and ^{13}C NMR Spectra of Binding Material Extracted from Drying Oil Films, Paints, and Original Paintings with Acetone- d_6 Solvent^a

sample	age (years)	B_f/B^b	HFA ^b	IV	Di/FA	HA/FA	TG/FA
LO	0.1	0.05 (0.01)	0.01 (0.005)	20.9	0.08	0.003	0.64
linseed oil	0.5	0.13 (0.01)	0.03 (0.01)	12.3	0.15	0.01	0.89
	1	0.23 (0.02)	0.10 (0.01)	2.8	0.31	0.015	0.81
	5	0.47 (0.02)	0.32 (0.01)	4.9	0.62	0.09	0.30
	5 ^c	0.48	0.35 (0.01)	4.0	0.47	0.09	0.31
b-LO	0.1	0.08	0.02	8.4	0.13	0.01	0.81
boiled linseed oil	0.5	0.21	0.06	1.4	0.38	0.02	1.1
	1	0.35 (0.04)	0.13 (0.01)	0.4	0.64	0.03	1.0
	5	0.53	0.37	1.3	0.59	0.08	0.23
	5	0.18	0.02	0.3	0.43	0.01	1.2
PO	0.5	0.18	0.02	0.3	0.43	0.01	1.2
poppy seed oil	1	0.29	0.10	0.1	0.56	0.05	1.1
	0	0.04	0.03	173	0.00	0.003	0.87
LB lamp black	0	0.04	0.03	173	0.00	0.003	0.87
LB-1	5	0.46 (0.03)	0.28 (0.04)	15.4	0.19	0.10	0.28
LB-2	5	0.49 (0.02)	0.30 (0.01)	16.9	0.22	0.13	0.31
TW titanium white	0	0.00	0.01	139	0.00	0.00	0.97
TW	5	0.26 (0.02)	0.16 (0.01)	9.8	0.04	0.08	0.48
CR cadmium red	5	0.39	0.18	0.93	0.18	0.10	0.55
LW lead white	5	0.38	0.17	3.4	0.06	0.17	0.49
POYM ^d	~100	0.81 (0.01)	0.56 (0.01)	3.8 (0.6)	0.06 (0.04)	0.21 (0.03)	0.015 (0.008)
The Duke ^d	~300	0.89 (0.03)	0.48 (0.03)	2.0 (0.3)	0.27 (0.03)	0.12 (0.03)	0.016 (0.003)

^a Standard deviations are given in parentheses. For abbreviations used, see the Experimental Section and text. ^b A plot of ^1H vs ^{13}C NMR-determined values of B_f/B and HFA has slope of 1.03, intercept of 0.04, $R^2 = 0.98$, so the average values of these parameters are reported, with standard deviation in parentheses. ^c Extraction with methanol- d_4 . ^d Average values of three separate NMR analyses. POYM: Portrait of Young Man by Vandoros.



(ppm)

a

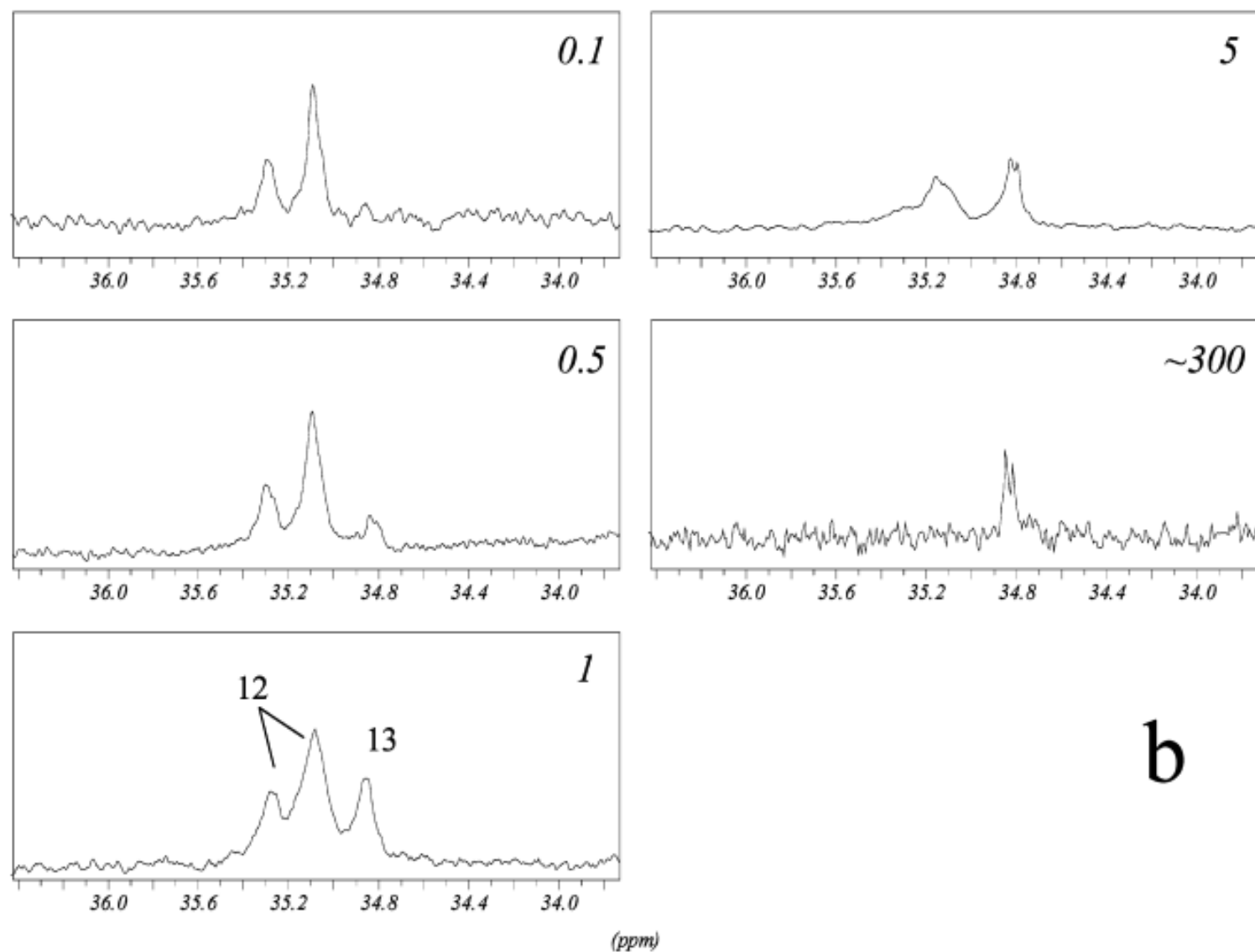


Figure 3. Expansions of the glyceridic and partial aliphatic regions of the ^{13}C NMR spectra of paint extracts in acetone- d_6 , showing the evolution of glycerides (a) and signals 12 and 13 (b), the latter representing esterified and free carboxylic groups respectively, as a function of age in years (numbers in italics on top right of spectra). Peak numbering according to Table 1.