Selective acetylation of primary amino groups with phenyl acetate; simple synthesis of N,N´-diacetyl polyamines

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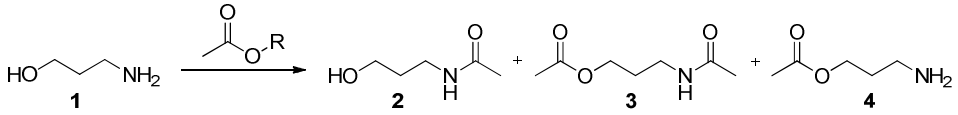
Supplementary Material: Table S1 and S2 for the reactivity of a series of aliphatic and aromatic esters acetates. ^{1}H and ^{13}C spectra of N^{1},N^{8}-Ac$_2$-Spd and N^{1},N^{12}-Ac$_2$-Spm.

General procedure for solvent free acetylation described in tables S1 and S2

3-aminopropanol (1.33 mmol) and the corresponding acetate (13.31 mmol) refluxed with vigorous stirring for 0.25-72h. The progress of the reaction was monitored with ^{1}H NMR taking samples on predetermined time intervals. The solvent free reactions in room temperatures were performed as described above without heating

Table S1 Acetylation of 3-aminopropanol with different acetates[a]



Ester	Time (h)	Reaction temperature (ºC)	Conversion (%)[b] 2	3	4
R = Me	4	57	43	-	-
	24		70	10	-
	48		80	12	-
	72		84	13	-
R = Et	4	77	8	-	-
	24		41	-	-
	48		77	6	-
	72		92	4	-
R = $CHCH_2$	1	73	92	8	-
	4		80	20	-
	24		20	80	-
R = iPr	4	89	3	-	-
	24		12	-	-
	48		24	2	-
	72		44	3	-
R = But	0.5	127	39	-	-
	1.5		62	-	-
	20		94	4	-
	72		86	13	-
R = Bn	0.25	212	93	1	-
	0.5		83	17	-
	1		68	32	-
R = Ph	0.25	196	56	43	-
	0.5		30	70	-
	1		0	100	-

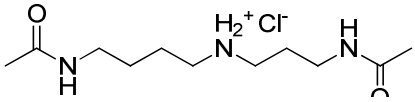
[a] 3-aminopropanol (1 equiv,1.33 mmol), ester (10 equiv,13.30 mmol) under reflux for 0.25-72 h. [b] Determined from ^{1}H-NMR spectra without purification

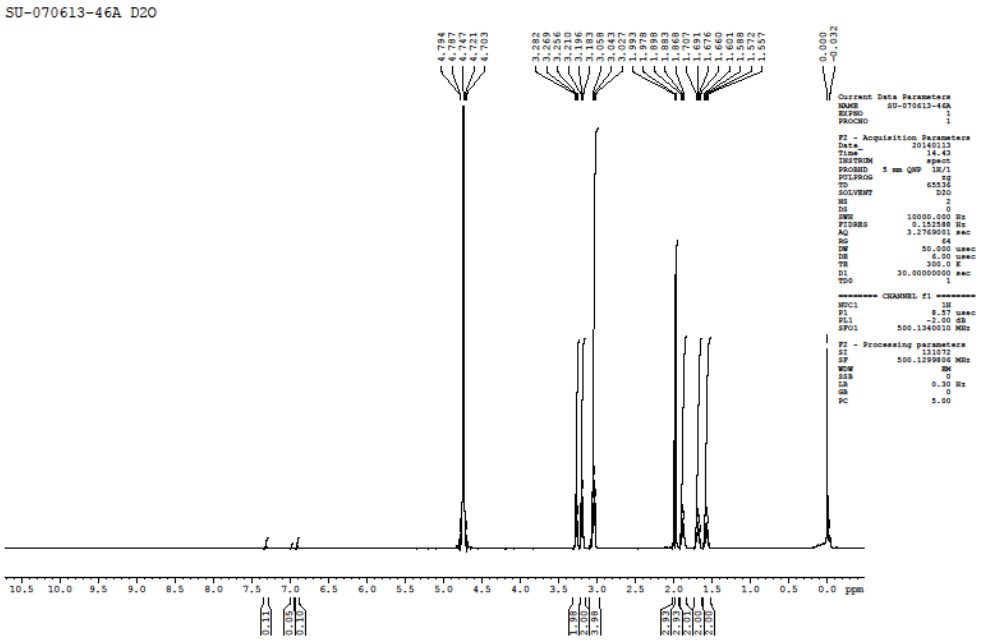
Table S2. Acetylation of 3-aminopropanol with benzyl- and phenyl acetate at room temperature[a]

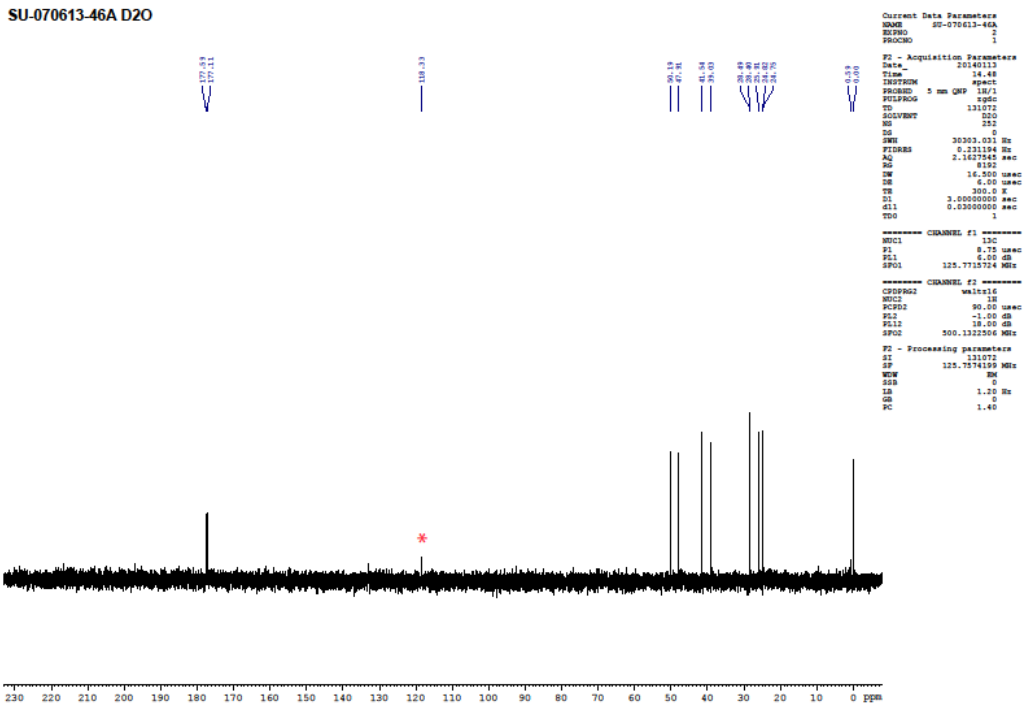
Aminoalcohol	Ester	Time (h)	Conversion (%)[b] 2	3
1	benzyl acetate	0.5	26	-
		1	36	-
		24	59	1.5
1	phenyl acetate	0.5	98	1
		1	99.5	0
		24	95	1.5

[a] 3-aminopropanol (1 equiv,1.33 mmol), ester (10 equiv,13.30 mmol) for 0.5-24 h. [b] Determined from ^{1}H-NMR spectra without purification

^{1}H and ^{13}C NMR Spectra of N^{1},N^{8}-Ac$_2$-Spermidine hydrochloride.

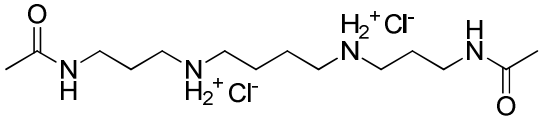


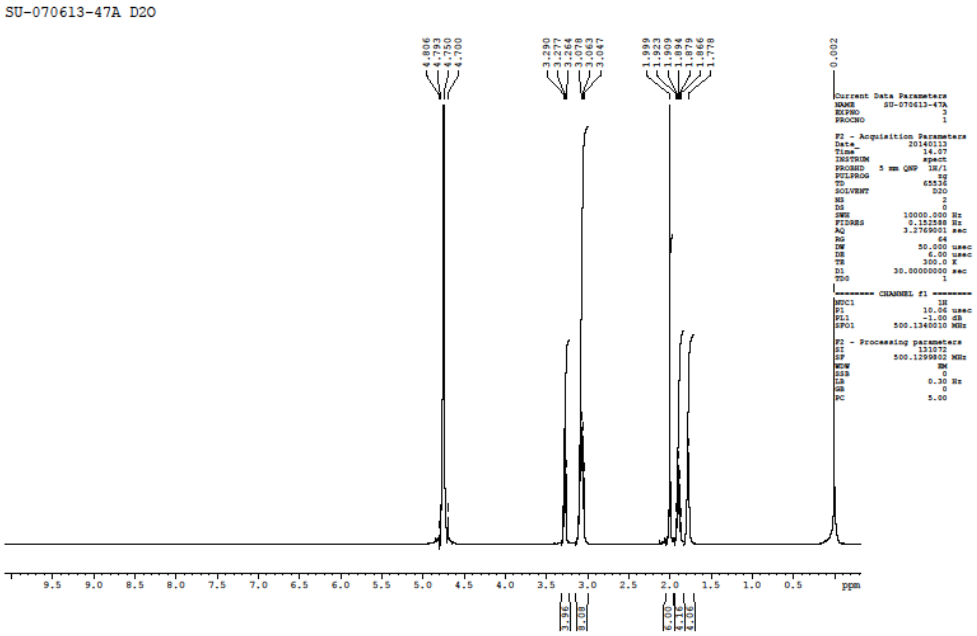


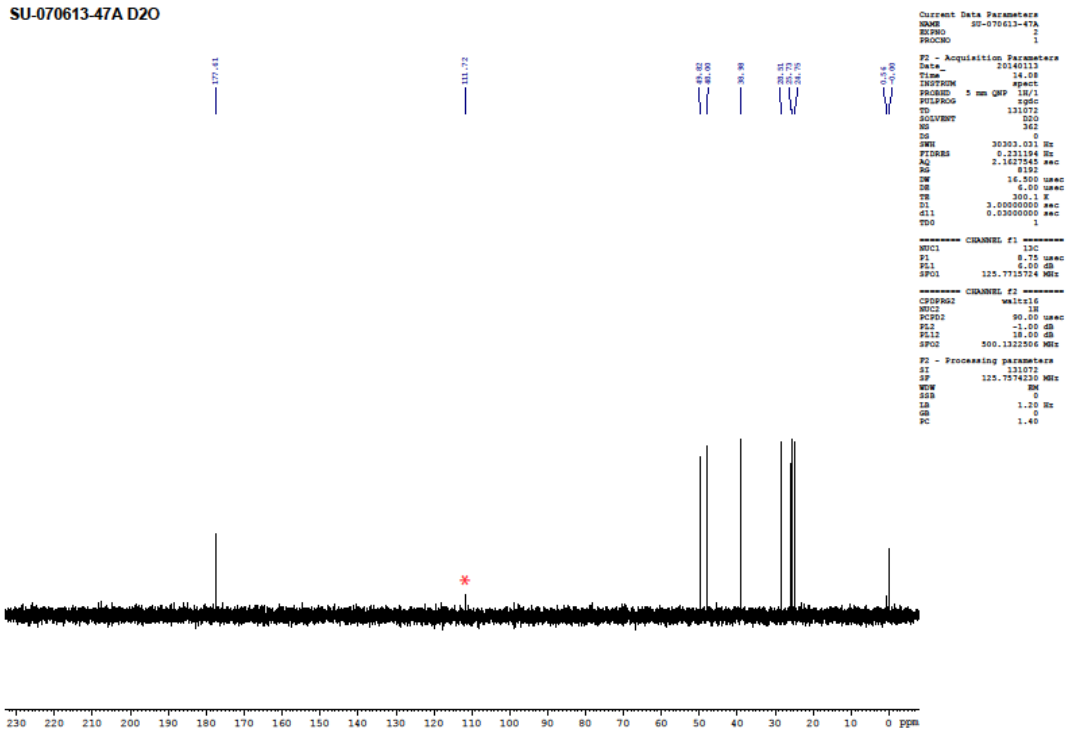


* = Instrument artifact

^{1}H and ^{13}C NMR Spectra of N^{1},N^{12}-Ac$_2$-Spermine dihydrochloride.







* = Instrument artifact