

## 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. <sup>1</sup>H and <sup>13</sup>C spectra of *N*<sup>1</sup>,*N*<sup>8</sup>-Ac<sub>2</sub>-Spd and *N*<sup>1</sup>,*N*<sup>12</sup>-Ac<sub>2</sub>-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  $^1\text{H}$  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<sup>a</sup>

Ester	Time (h)	Reaction temperature ( $^\circ\text{C}$ )	Conversion (%) <sup>b</sup>		
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 = CH <sub>2</sub> CH <sub>3</sub>	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	-

<sup>a</sup> 3-aminopropanol (1 equiv, 1.33 mmol), ester (10 equiv, 13.30 mmol) under reflux for 0.25-72 h.

<sup>b</sup> Determined from  $^1\text{H}$ -NMR spectra without purification

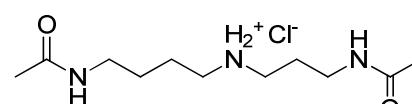
**Table S2.** Acetylation of 3-aminopropanol with benzyl- and phenyl acetate at room temperature<sup>a</sup>

Aminoalcohol	Ester	Time (h)	Conversion (%) <sup>b</sup>	
			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

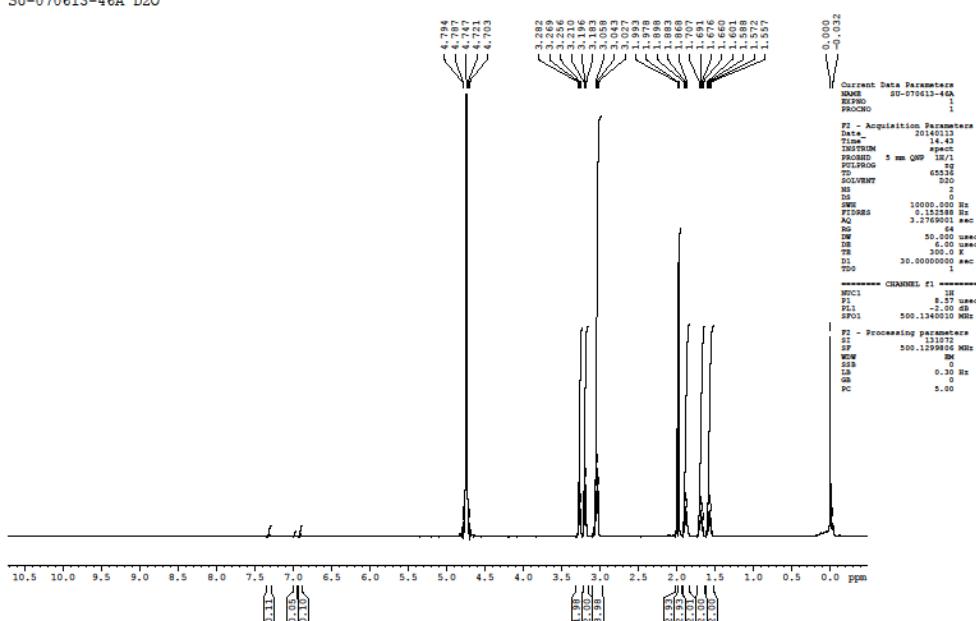
<sup>a</sup> 3-aminopropanol (1 equiv, 1.33 mmol), ester (10 equiv, 13.30 mmol) for 0.5-24 h.

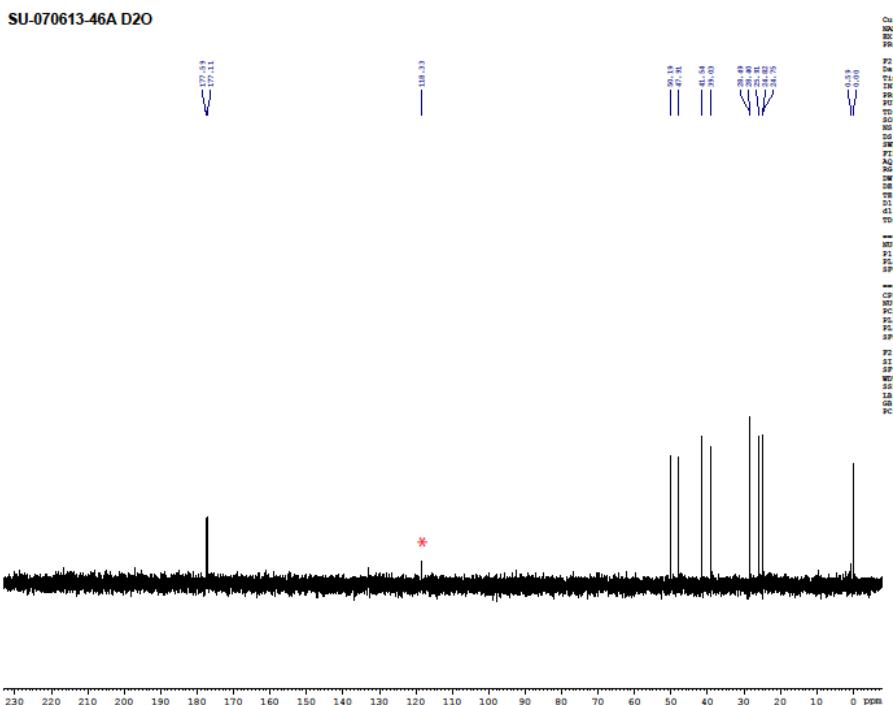
<sup>b</sup> Determined from <sup>1</sup>H-NMR spectra without purification

**<sup>1</sup>H and <sup>13</sup>C NMR Spectra of *N<sup>1,N<sup>8</sup></sup>*-Ac<sub>2</sub>-Spermidine hydrochloride.**



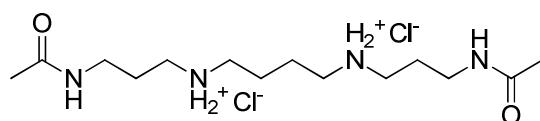
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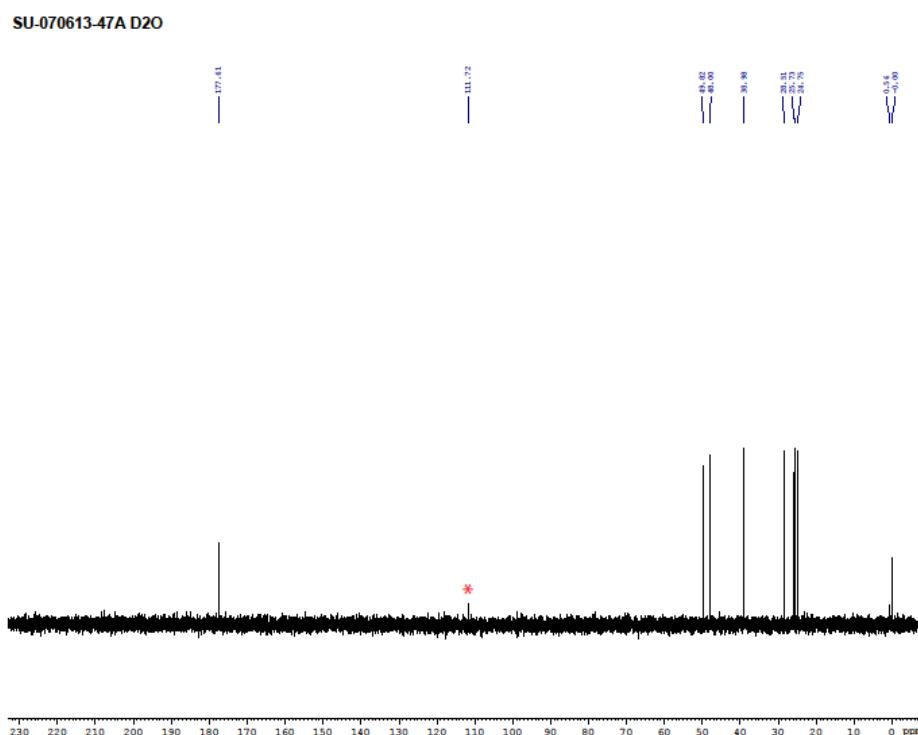
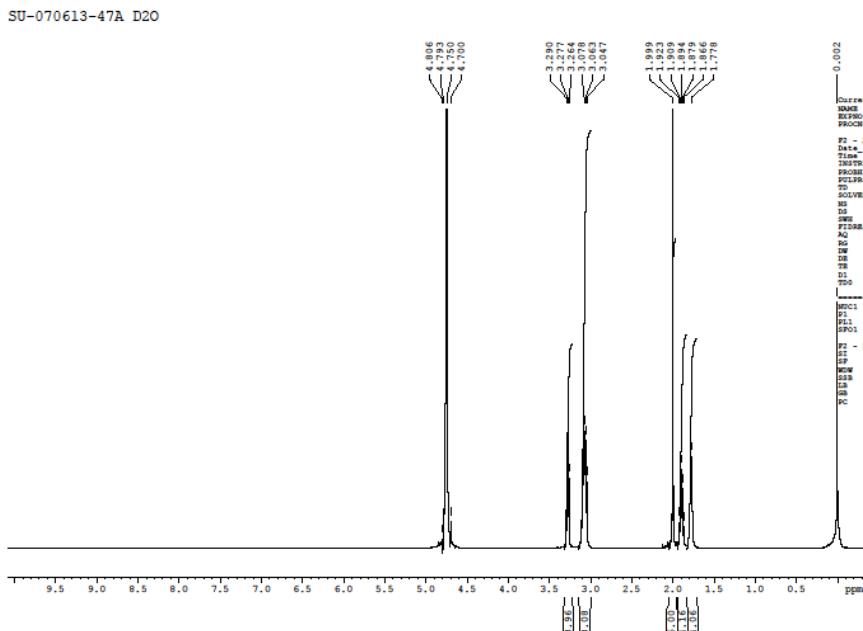




\* = Instrument artifact

### <sup>1</sup>H and <sup>13</sup>C NMR Spectra of *N*<sup>1</sup>,*N*<sup>12</sup>-Ac<sub>2</sub>-Spermine dihydrochloride.





\* = Instrument artifact