Supporting Information

Polymorphism of asymmetric catalysts based on amphiphilic lipopeptides in solution

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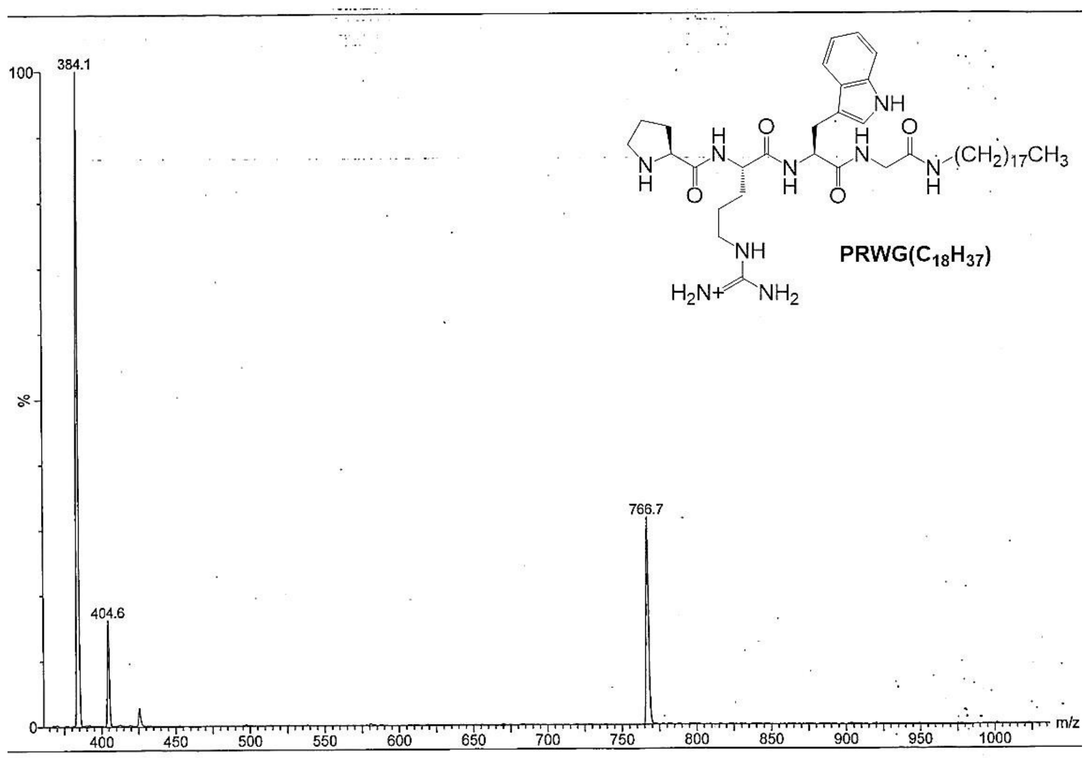
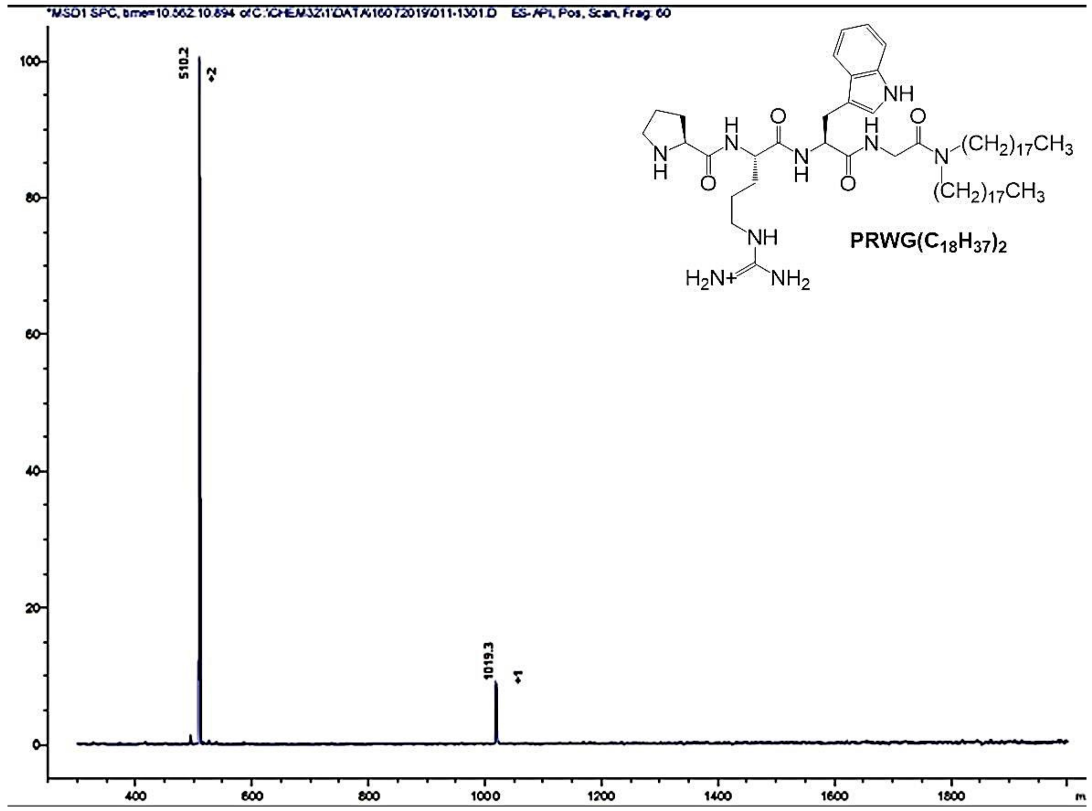

384.1
404.6
766.7
%
m/z
PRWG($C_{18}H_{37}$)


510.2
+2
1019.3
+1
PRWG($C_{18}H_{37}$)$_2$

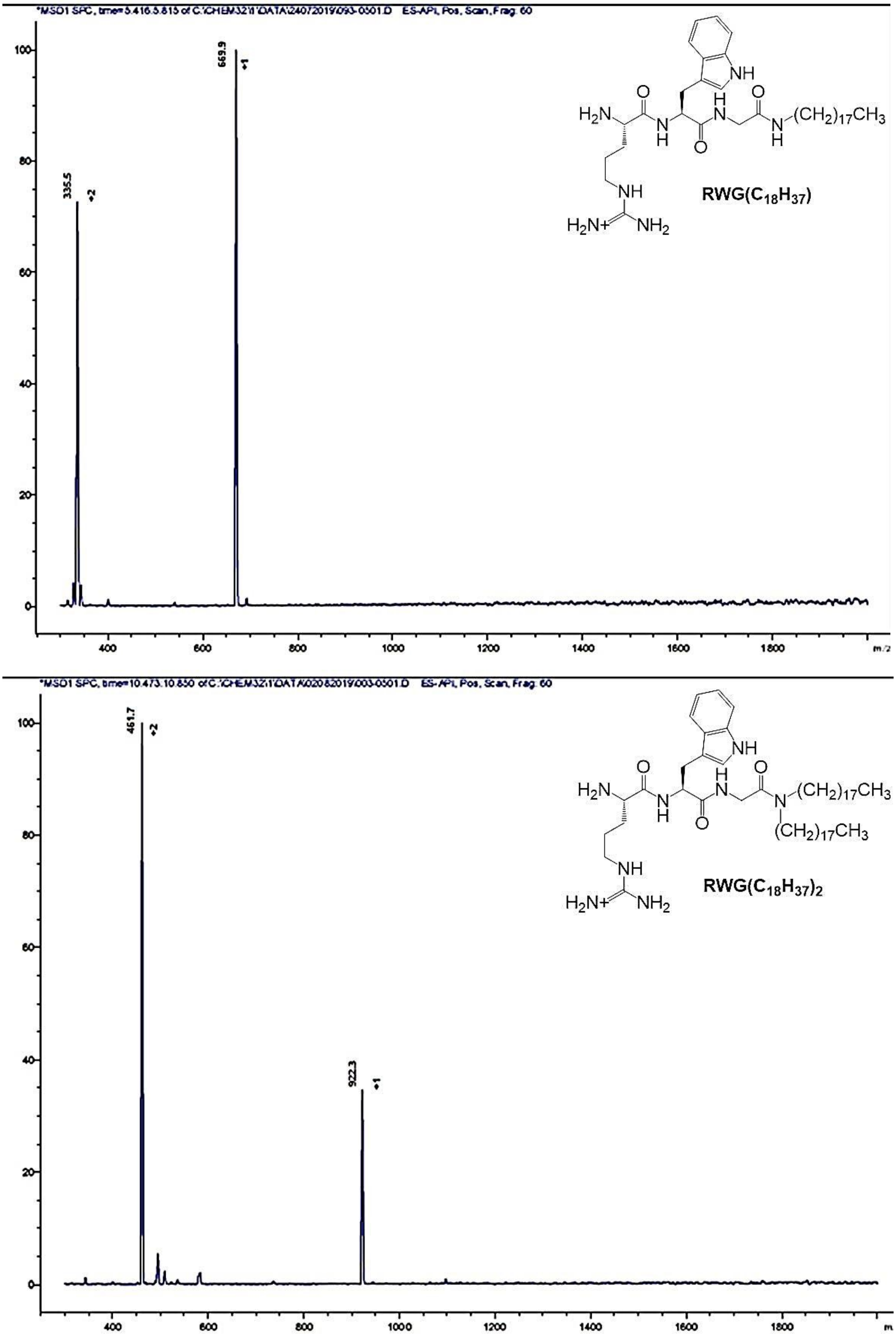


Figure S1. Mass spectrometry analysis of PRWG($C_{18}H_{37}$), PRWG($C_{18}H_{37}$)$_2$, RWG($C_{18}H_{37}$) and RWG($C_{18}H_{37}$)$_2$ lipopeptides.

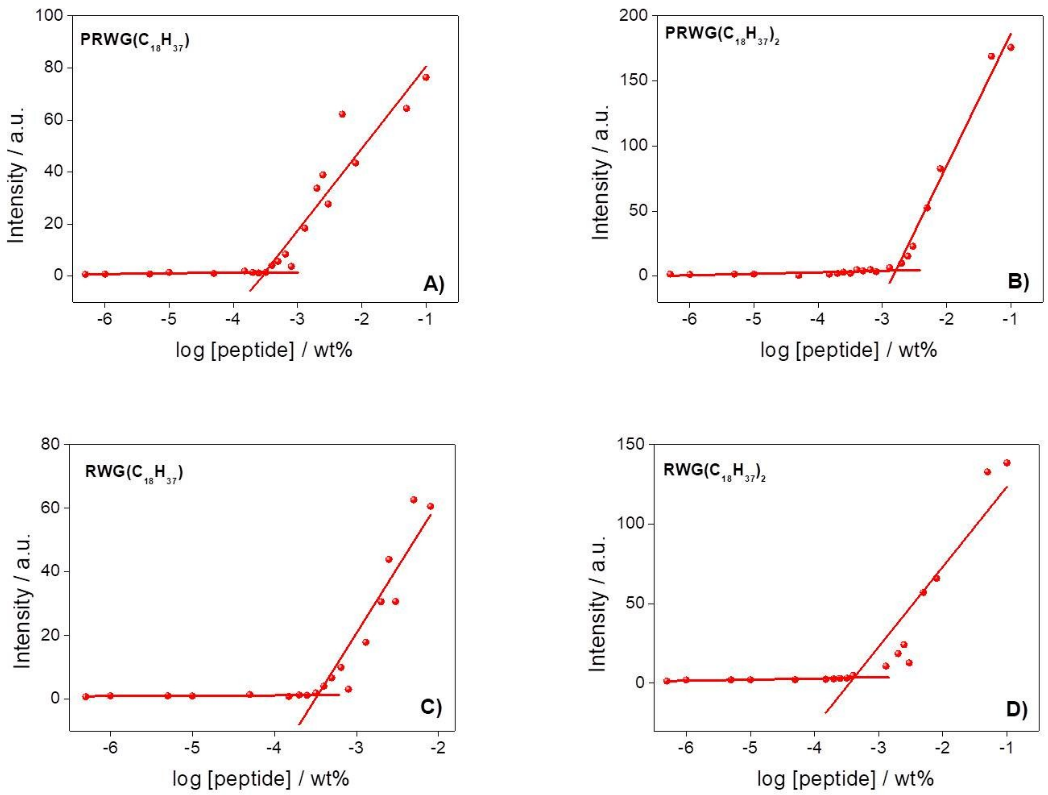


Figure S2. Fluorescence intensity as a function of A) PRWG($C_{18}H_{37}$), B) PRWG($C_{18}H_{37}$)$_2$, C) RWG($C_{18}H_{37}$) and D) RWG($C_{18}H_{37}$)$_2$ concentration, considering the ANS excitation.

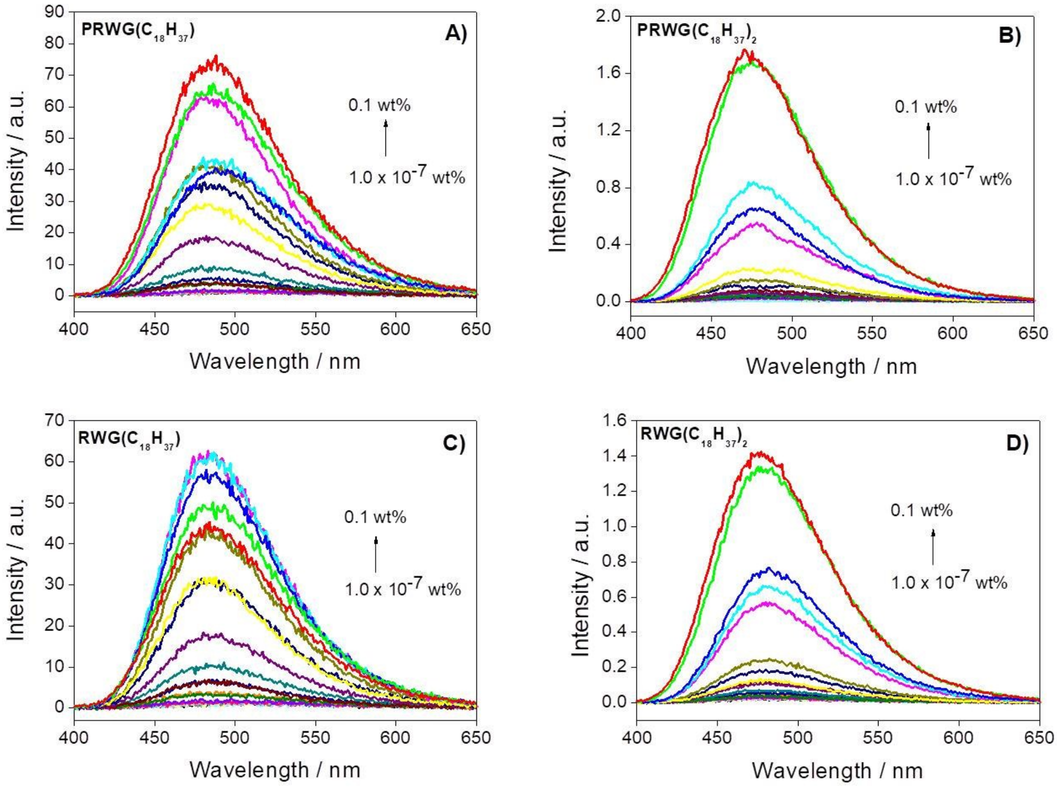


Figure S3. Emission spectra for solutions with different concentration of A) PRWG($C_{18}H_{37}$), B) PRWG($C_{18}H_{37}$)$_2$, C) RWG($C_{18}H_{37}$) and D) RWG($C_{18}H_{37}$)$_2$, in presence of ANS.

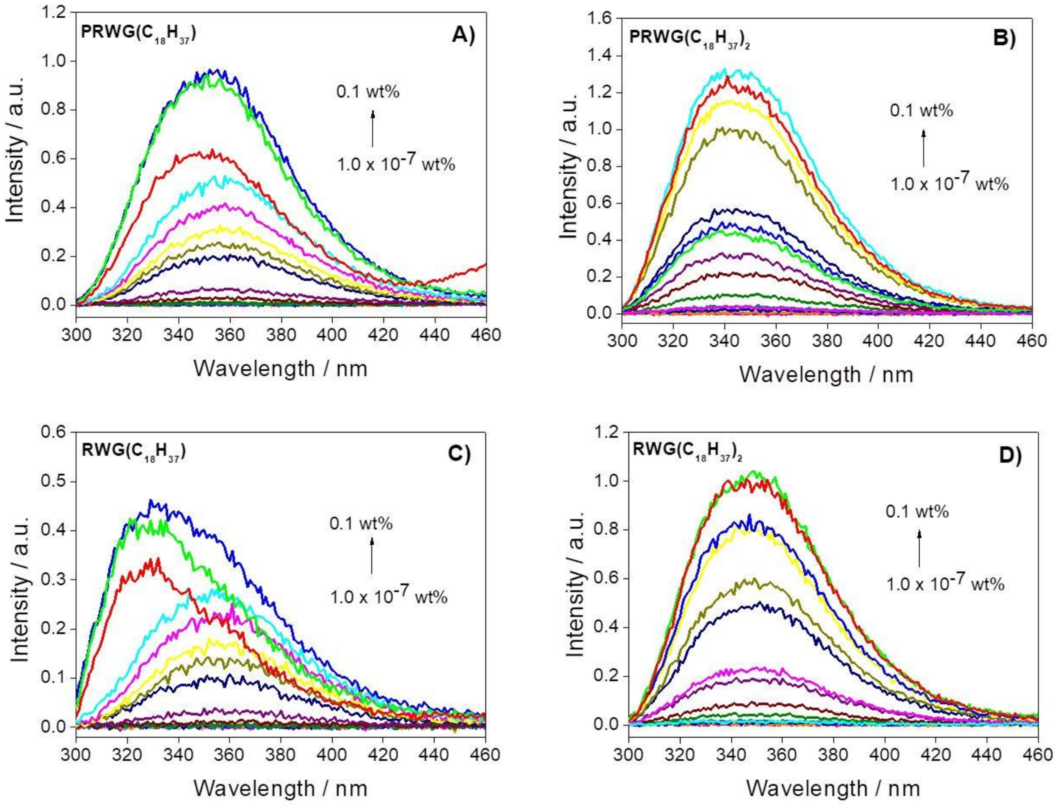


Figure S4. Emission spectra for water solutions with different concentration of A)

PRWG($C_{18}H_{37}$), B) PRWG($C_{18}H_{37}$)$_2$, C) RWG($C_{18}H_{37}$) and D) RWG($C_{18}H_{37}$)$_2$, considering the intrinsic tryptophan emission.

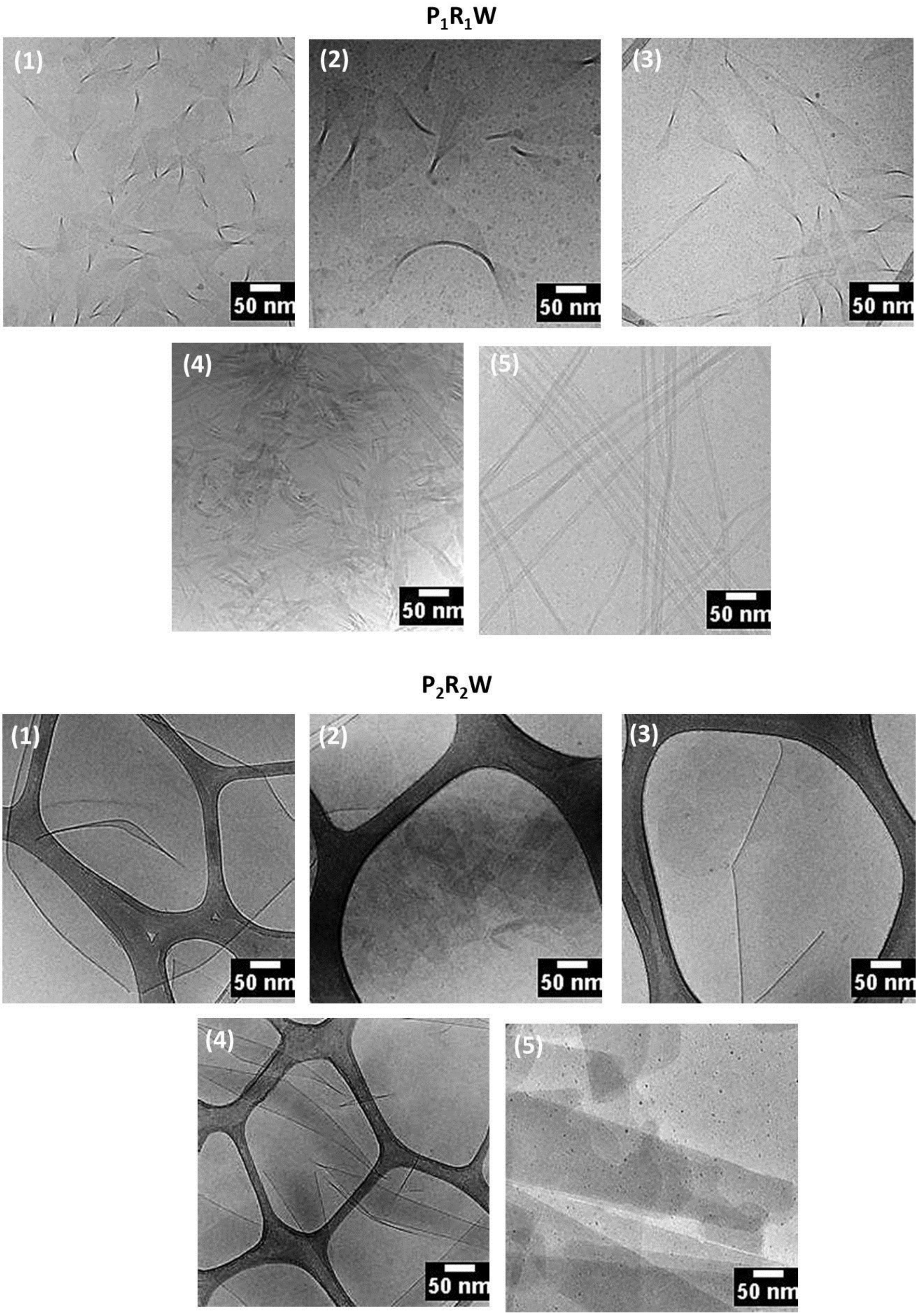


Figure S5. Cryo-TEM images from 1 wt% solutions of **P_1R_1W** (**1-5**) and **P_2R_2W** (**1-5**).

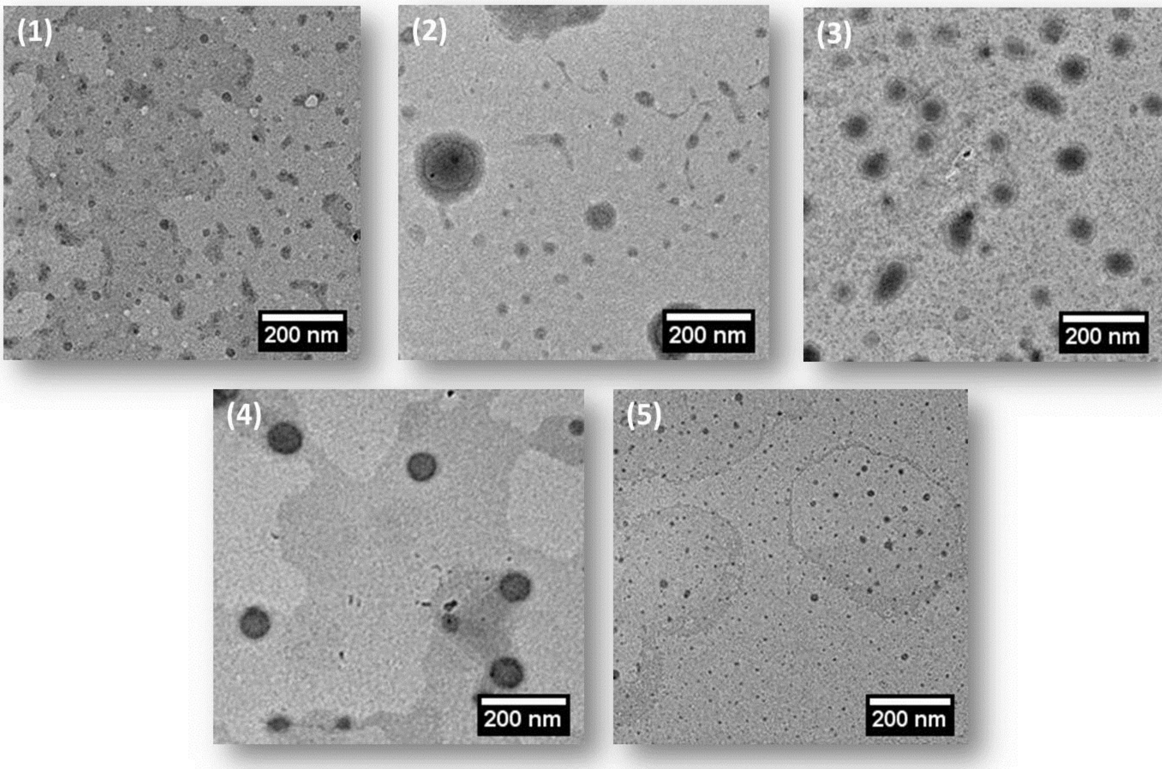


Figure S6. TEM images of 1 wt% solutions of $\mathbf{P_1R_1C}$ (**1-5**).

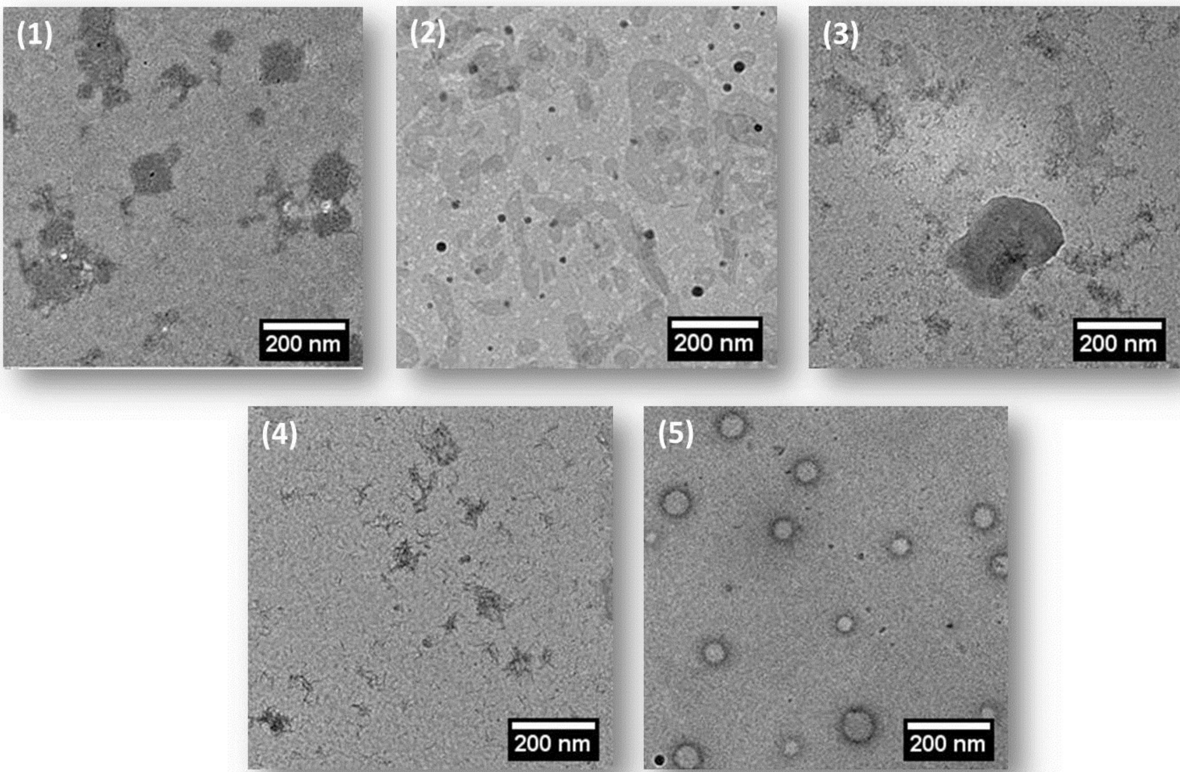
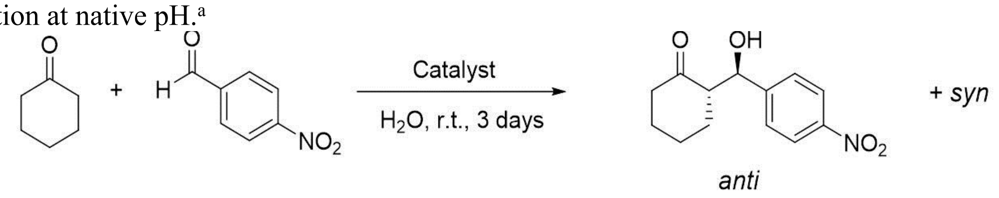


Figure S7. TEM images of 1 wt% solutions of $\mathbf{P_2R_2C}$ (**1-5**).

Table S1. Comparative results of the aldol reactions between *p*-nitrobenzaldehyde and cyclohexanone catalysed by the lipopeptide mixtures in water and cyclohexanone / water condition at native pH.[a]

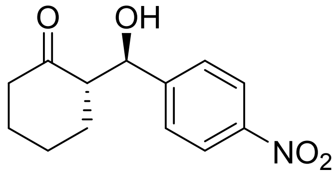


Entry[a]	Sample	Catalyst (mol%)	H_2O[b] (eq.)	Conv.[c] (%)	*anti*:*syn*[c]	Entry[a]	Sample	Catalyst (mol%)	H_2O[b] (eq.)	Conv.[c] (%)	*anti*:*syn*[c]
	P_1R_1W						P_1R_1C				
1	**(1)**	5	2	75.7	89:11	31	**(1)**	5	2	50.7	91:8
2	**(2)**	5	2	78.8	93:7	32	**(2)**	5	2	44.5	94:6
3	**(3)**	5	2	82.9	93:7	33	**(3)**	5	2	43.4	98:2
4	**(4)**	5	2	91.5	93:7	34	**(4)**	5	2	39.3	93:7
5	**(5)**	5	2	94.7	93:7	35	**(5)**	5	2	50.9	93:7
	P_1R_1W						P_1R_1C				
6	**(1)**	20	2	92.0	87:13	36	**(1)**	20	2	73.2	75:25
7	**(2)**	20	2	86.2	88:12	37	**(2)**	20	2	49.6	86:14
8	**(3)**	20	2	90.9	91:9	38	**(3)**	20	2	58.0	81:19
9	**(4)**	20	2	92.5	81:19	39	**(4)**	20	2	60.0	74:26
10	**(5)**	20	2	86.7	85:15	40	**(5)**	20	2	53.7	93:7
	P_1R_1W										
11	**(1)**	20	6	95.9	85:15	-	-	-		-	-
12	**(2)**	20	6	94.1	90:10	-	-	-		-	-
13	**(3)**	20	6	90.3	89:11	-	-	-		-	-
14	**(4)**	20	6	95.7	89:11	-	-	-		-	-
15	**(5)**	20	6	94.0	91:9	-	-	-		-	-
	P_2R_2W						P_2R_2C				
16	**(1)**	5	2	47.6	91:9	41	**(1)**	5	2	20.3	88:12
17	**(2)**	5	2	59.1	88:12	42	**(2)**	5	2	27.0	91:9
18	**(3)**	5	2	60.8	87:13	43	**(3)**	5	2	27.0	89:11
19	**(4)**	5	2	66.4	92:8	44	**(4)**	5	2	22.5	96:4
20	**(5)**	5	2	76.0	93:7	45	**(5)**	5	2	24.5	93:7
	P_2R_2W						P_2R_2C				
21	**(1)**	20	2	50.2	82:18	46	**(1)**	20	2	45.7	73:27
22	**(2)**	20	2	68.8	78:22	47	**(2)**	20	2	42.8	75:25
23	**(3)**	20	2	67.0	75:25	48	**(3)**	20	2	68.7	75:25
24	**(4)**	20	2	59.2	86:14	49	**(4)**	20	2	61.6	64:36
25	**(5)**	20	2	71.8	89:11	50	**(5)**	20	2	31.6	80:20
	P_2R_2W										
26	**(1)**	20	6	77.4	88:12	-	-	-		-	-
27	**(2)**	20	6	91.8	81:19	-	-	-		-	-
28	**(3)**	20	6	88.6	86:14	-	-	-		-	-
29	**(4)**	20	6	85.7	88:12	-	-	-		-	-
30	**(5)**	20	6	88.8	91:9	-	-	-		-	-

[a] The reactions were promoted at room temperature under vigorous stirring for 3 days, using 12 equivalents of cyclohexanone, 1 equivalent of *p*-nitrobenzaldehyde, 5 and 20 mol% of catalyst;
[b] Excess water relative to cyclohexanone (*v* / *v*);

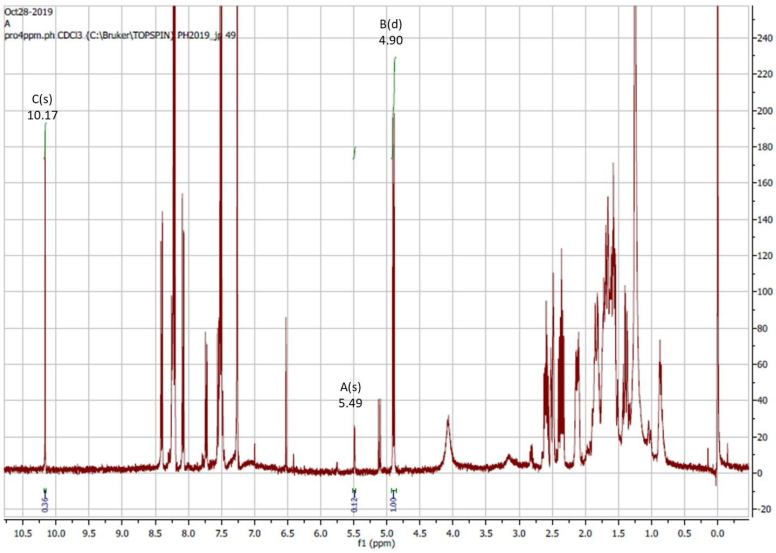
[c] Conversion and diastereoselectivity were determined by ^{1}H-NMR analysis of the crude product.

(*S*)-2-((*R*)-Hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one

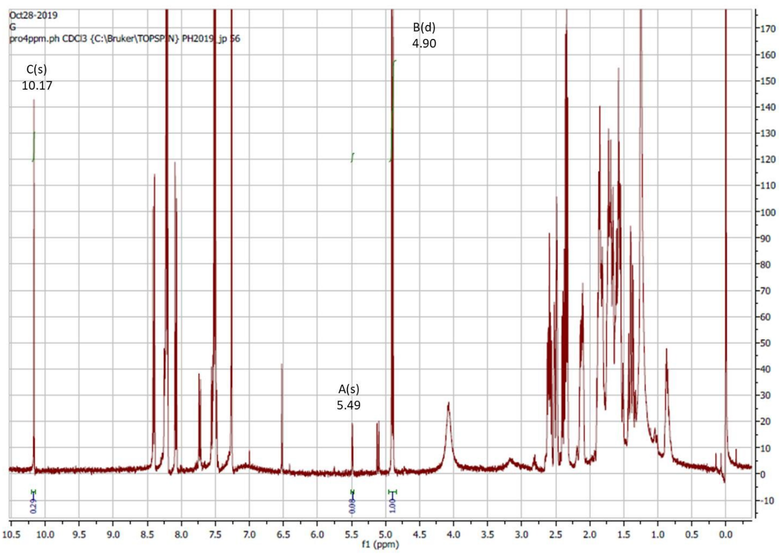


^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22-8.18 (m, 2H, ArH), 7.51-7.47 (m, 2H, ArH), 5.49 (br s, 1H, C*H*OH of *syn* diastereoisomer), 4.90 (dd, J = 7.5 Hz, 3.0 Hz, 1H, CHOH of *anti* diastereoisomer), 2.66-2.30 (m, 1H, C*H*CHOH), 2.66-2.30 (m, 2H, $CH_2C(O)$), 2.16-1.24 (m, 6H, chex-H).

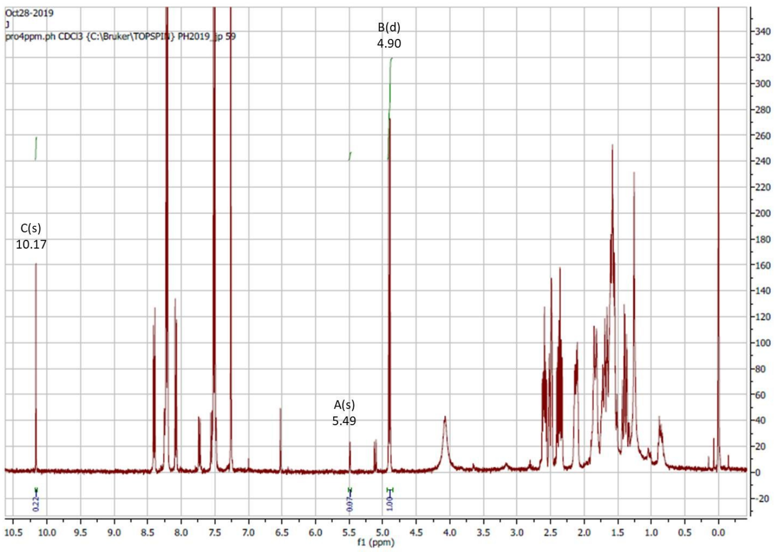
P_1R_1W 1 - 5 mol%



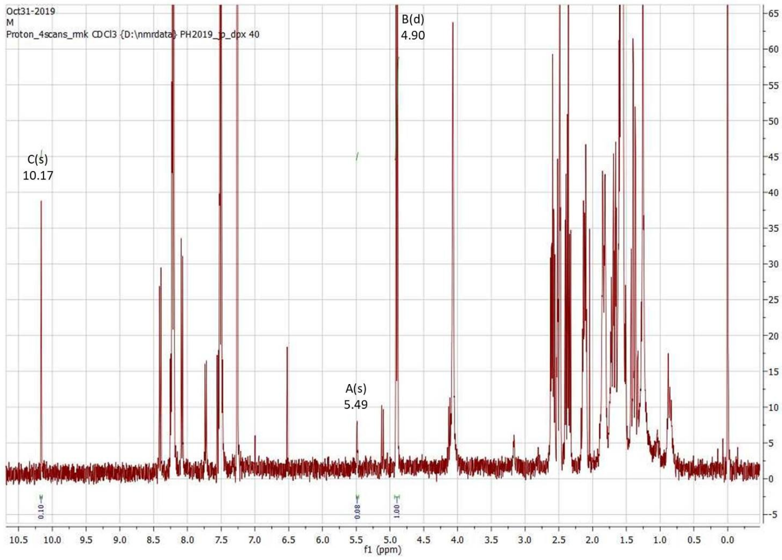
P_1R_1W 2 - 5 mol%



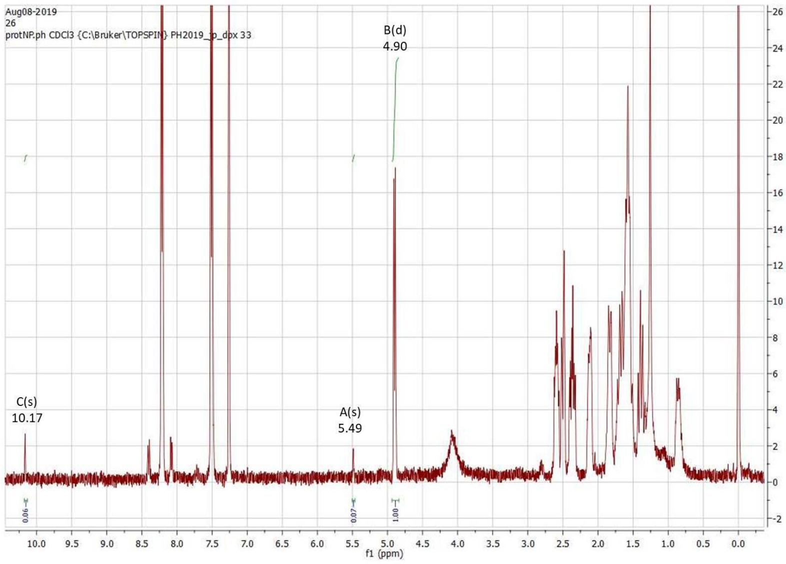
P$_1$R$_1$W 3 - 5 mol%



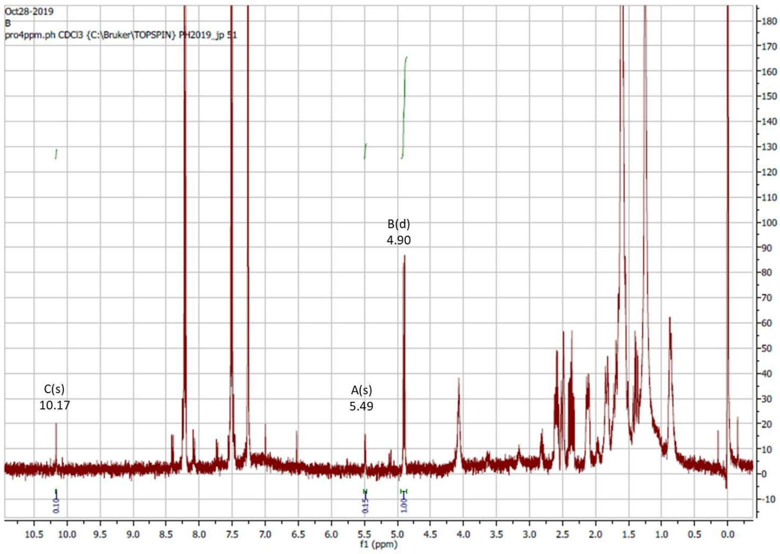
P$_1$R$_1$W 4 - 5 mol%



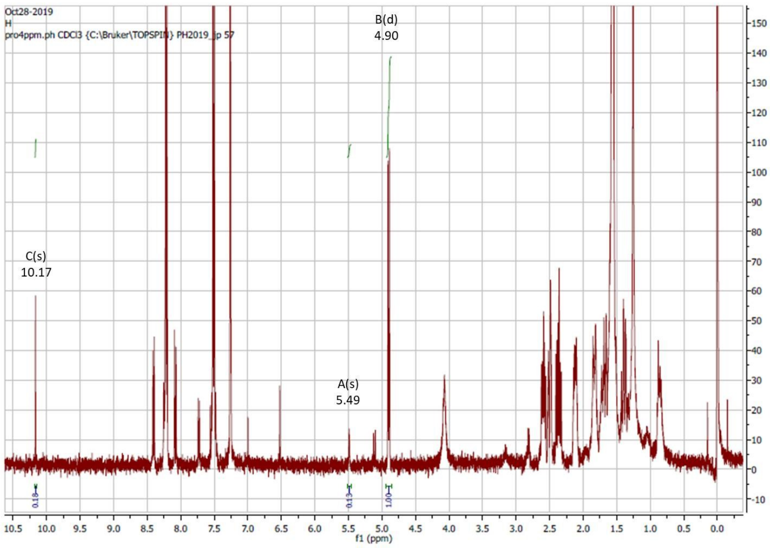
P$_1$R$_1$W 5 - 5 mol%



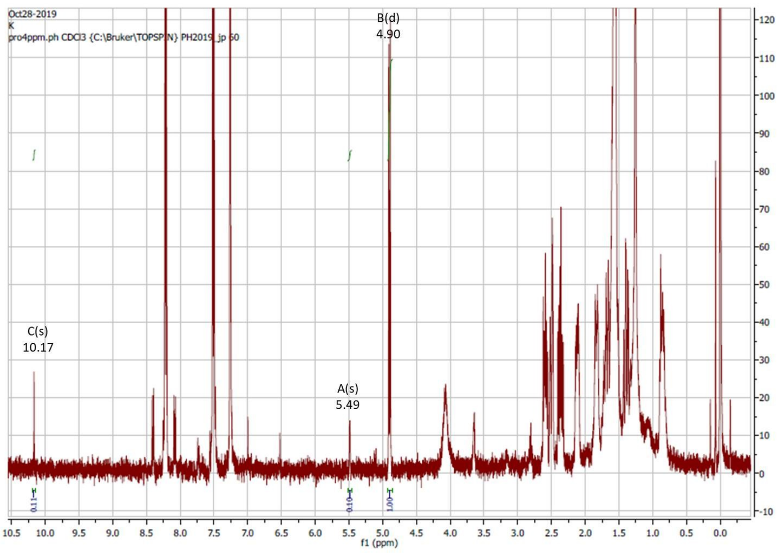
P_1R_1W 1 - 20 mol%



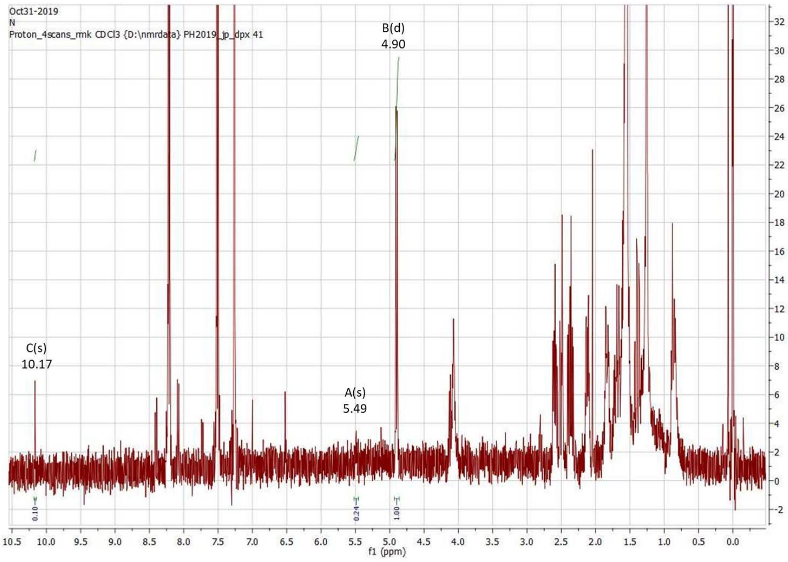
P_1R_1W 2 - 20 mol%



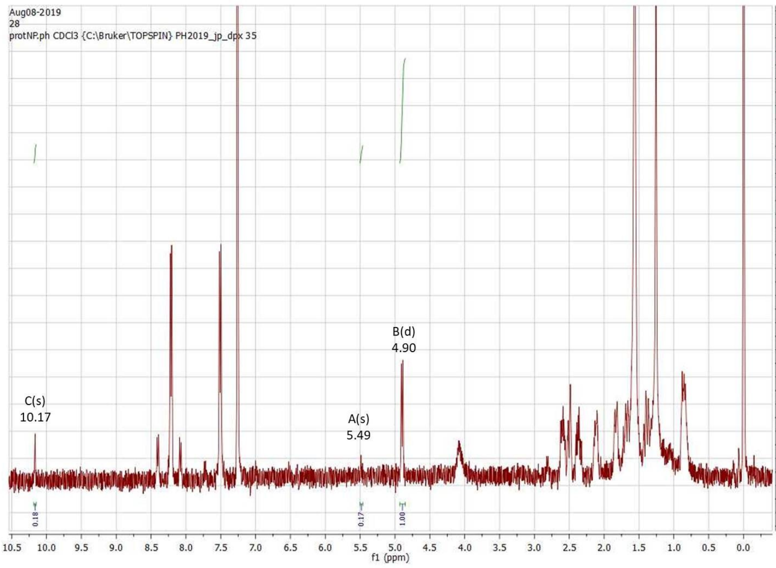
P_1R_1W 3 - 20 mol%



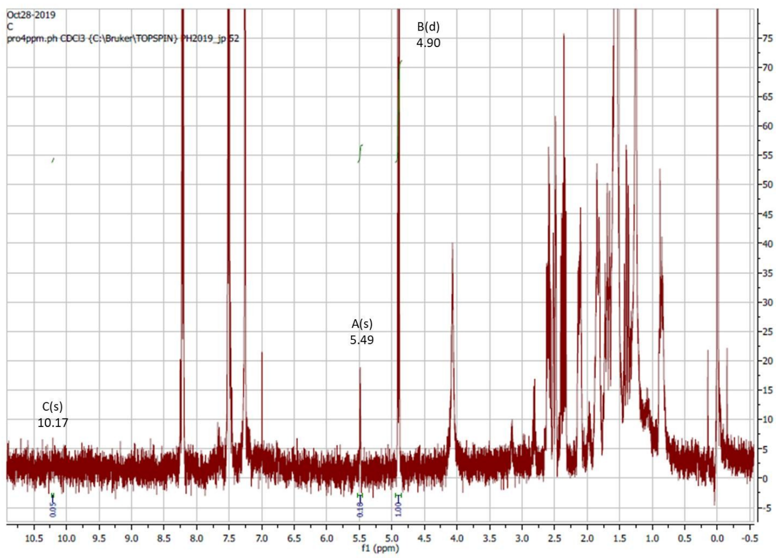
P_1R_1W 4 - 20 mol%



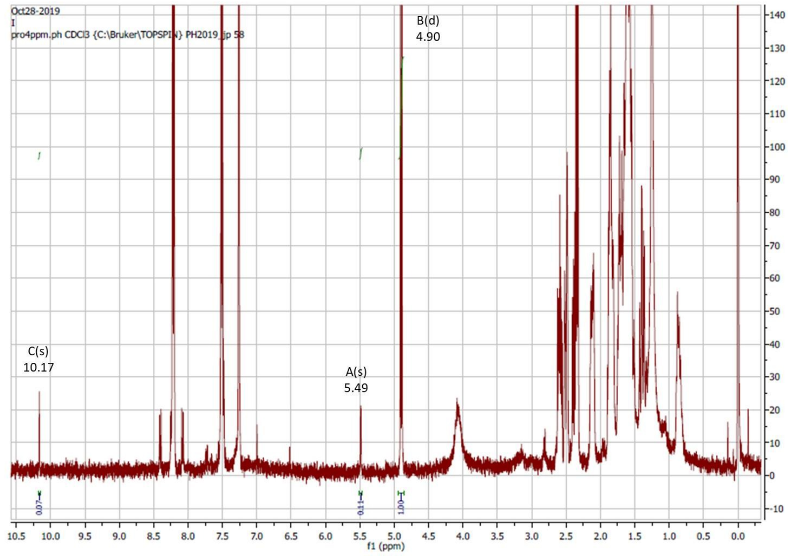
P_1R_1W 5 - 20 mol%



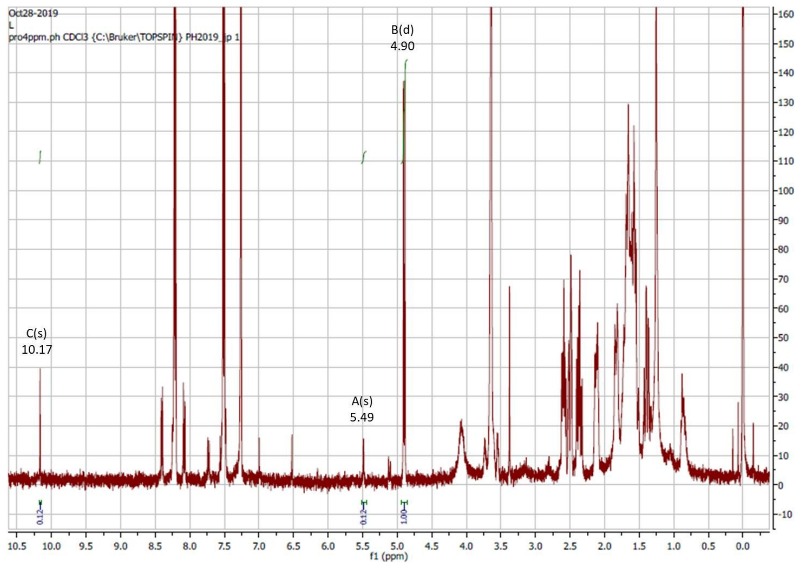
P_1R_1W 1 - 20 mol% water excess



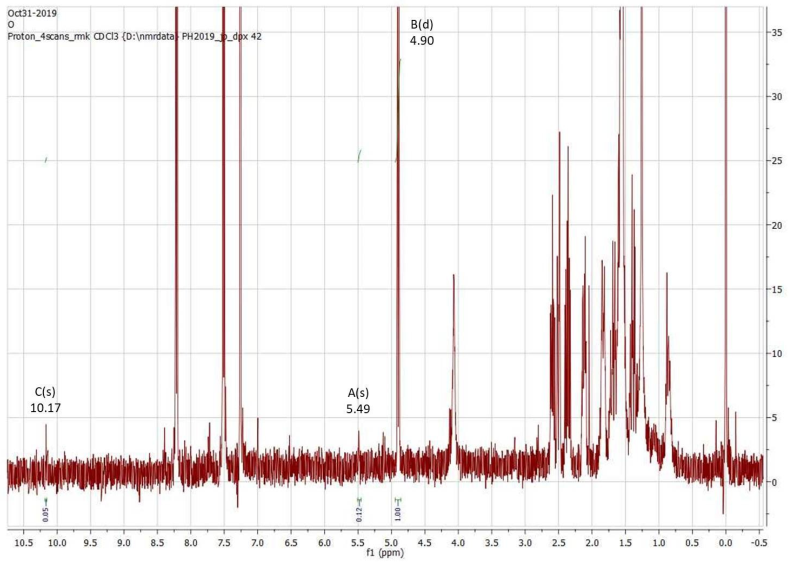
P_1R_1W 2 - 20 mol% water excess



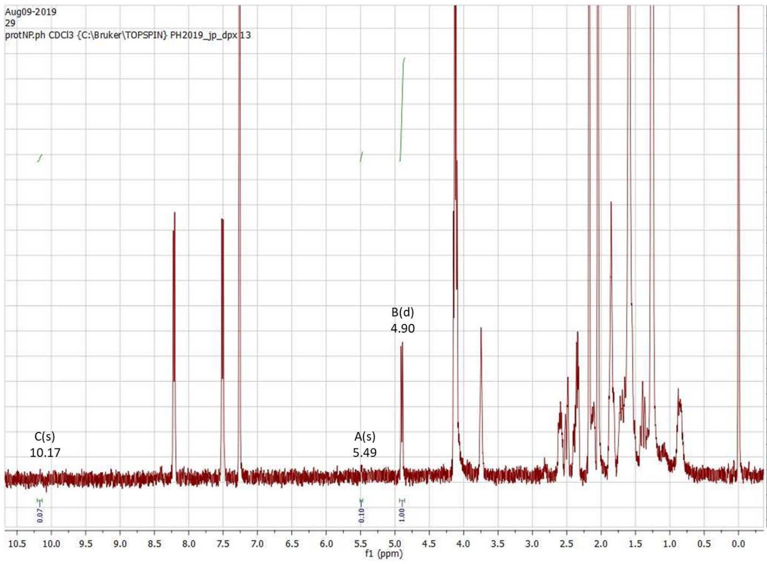
P_1R_1W 3 - 20 mol% water excess



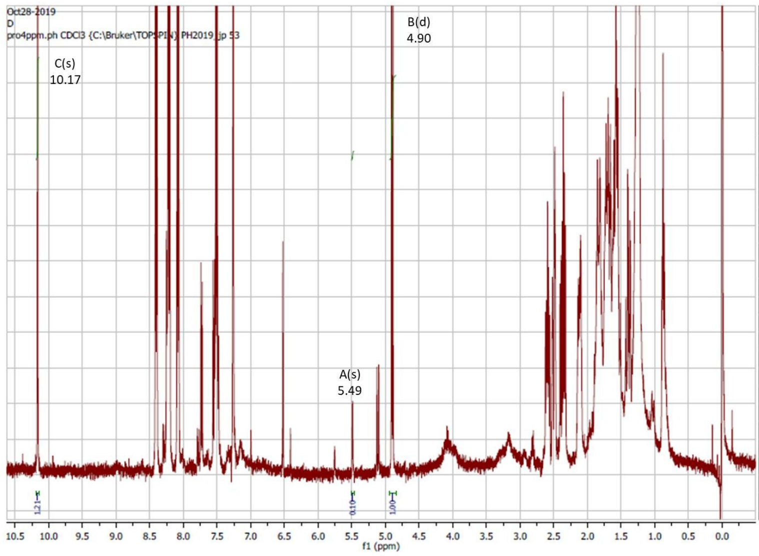
P_1R_1W 4 - 20 mol% water excess



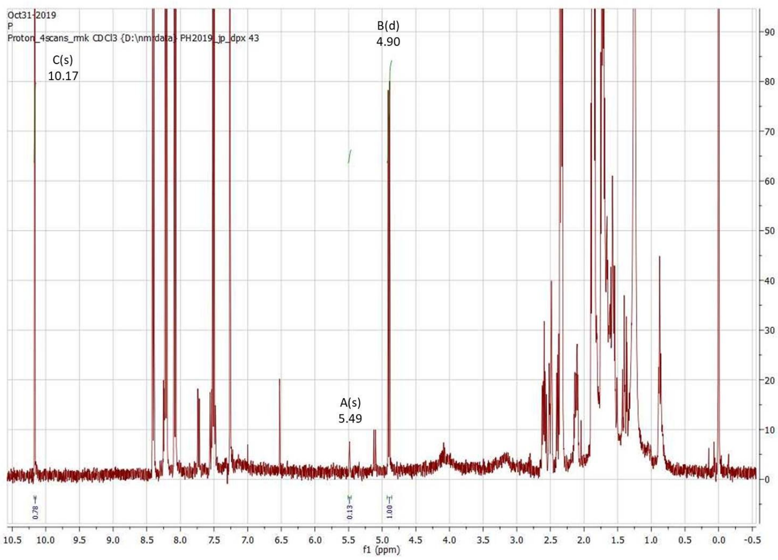
P_1R_1W 5 - 20 mol% water excess



P_2R_2W 1 - 5 mol%



P_2R_2W 2 - 5 mol%



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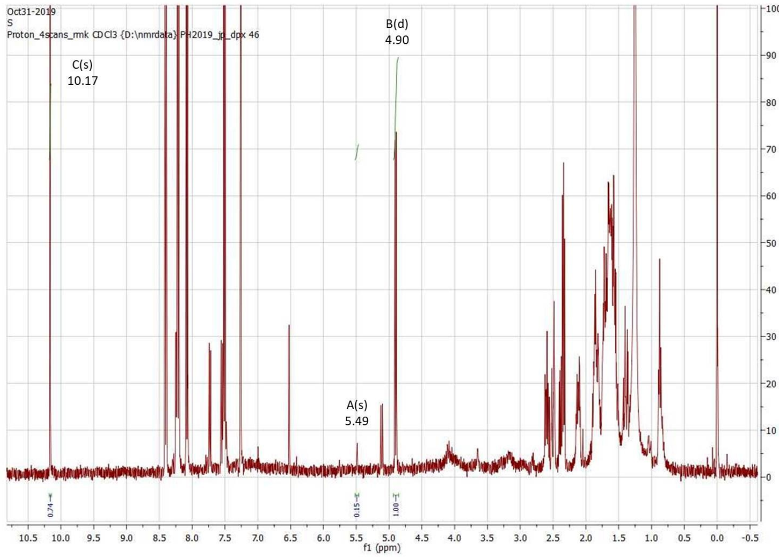
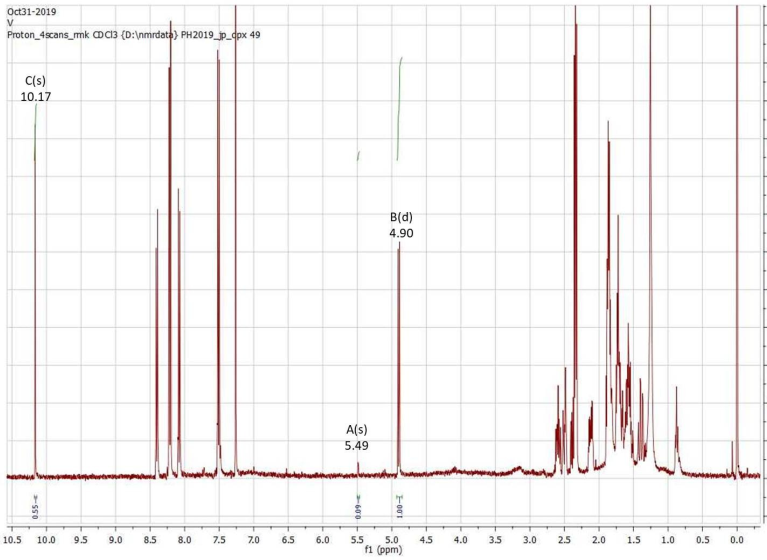
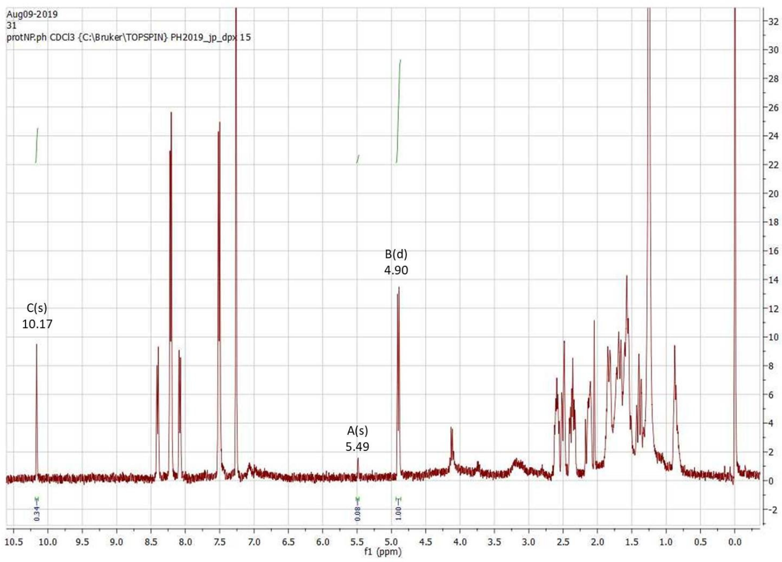


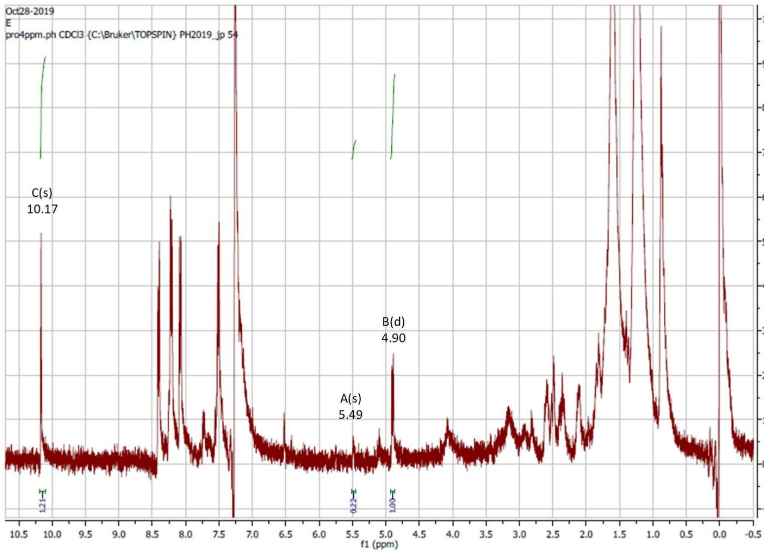
P_2R_2W 4 - 5 mol%



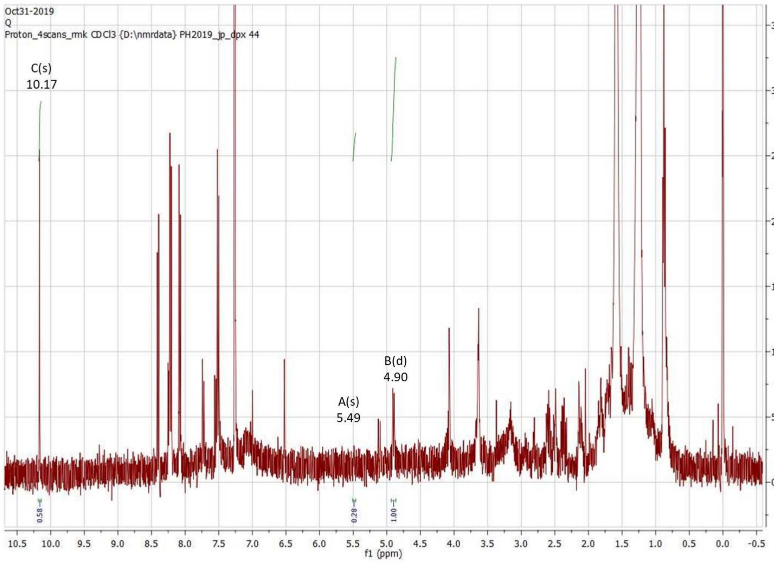
P_2R_2W 5 - 5 mol%



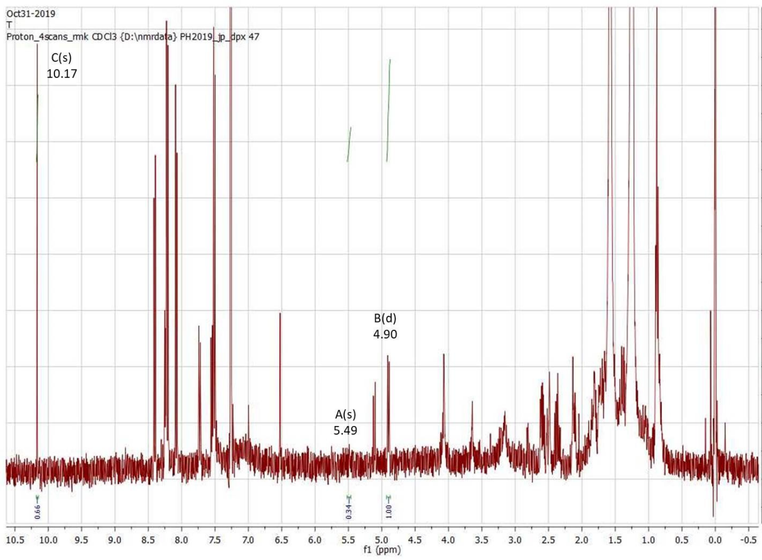
P_2R_2W 1 - 20 mol%



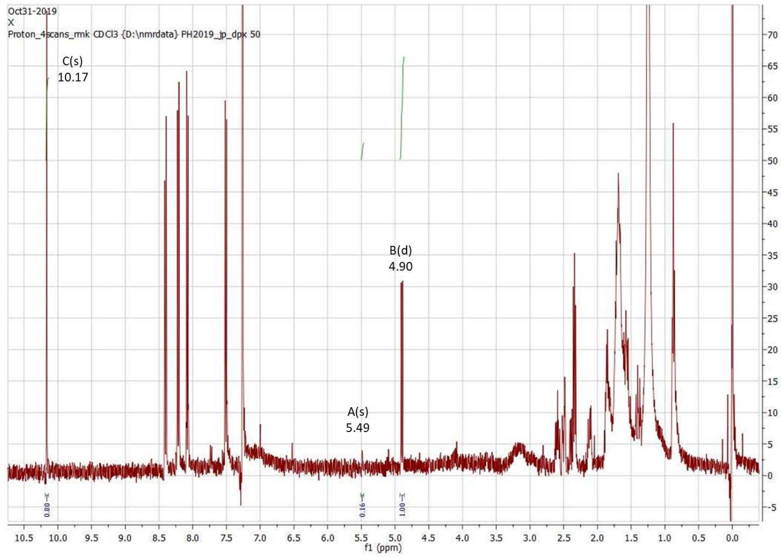
P_2R_2W 2 - 20 mol%



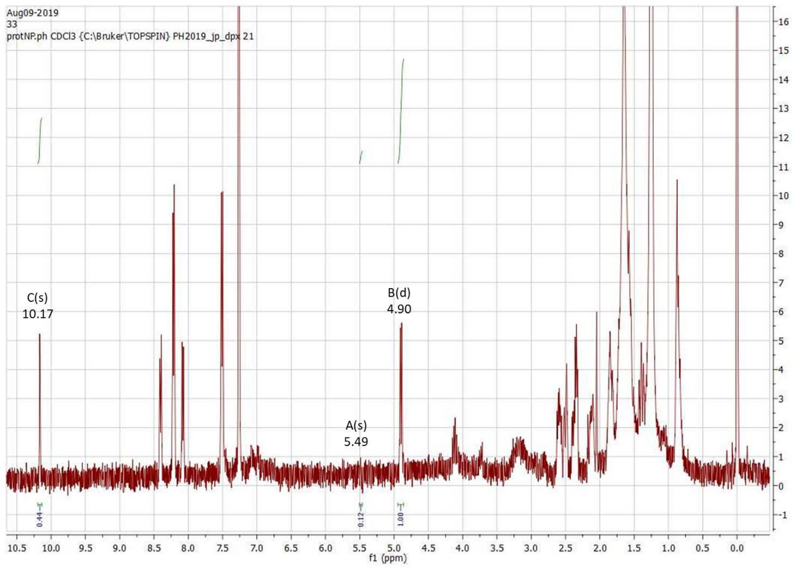
P_2R_2W 3 - 20 mol%



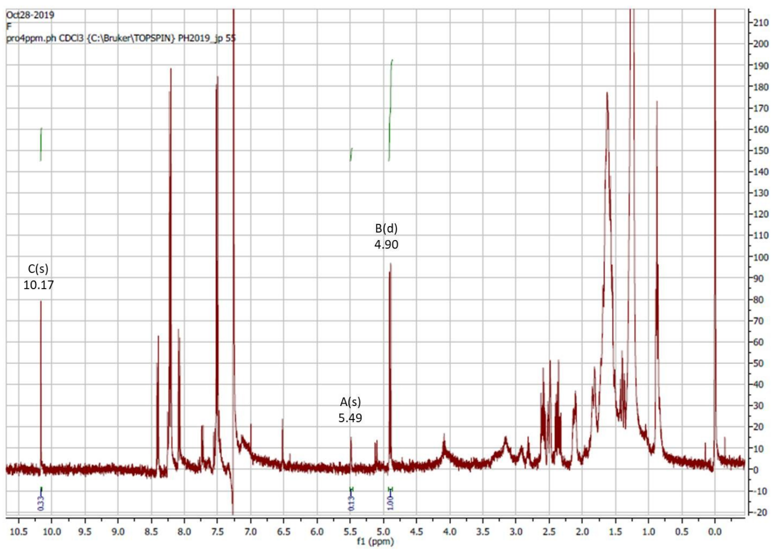
P_2R_2W 4 - 20 mol%



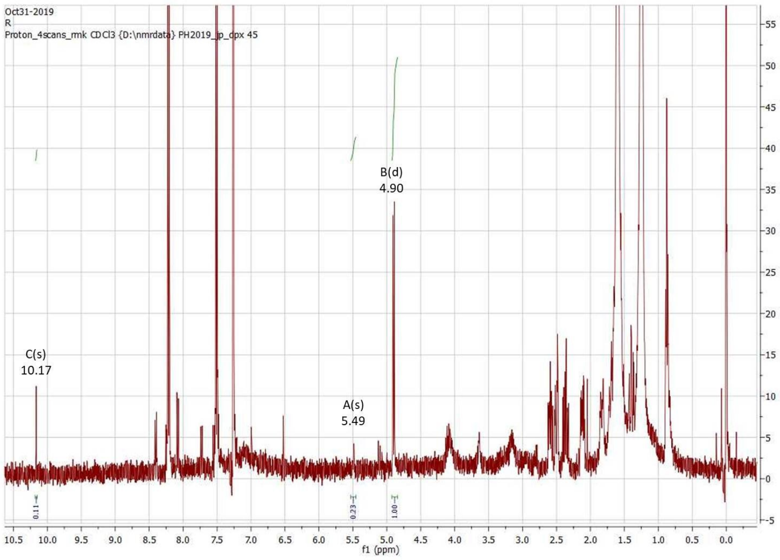
P_2R_2W 5 - 20 mol%



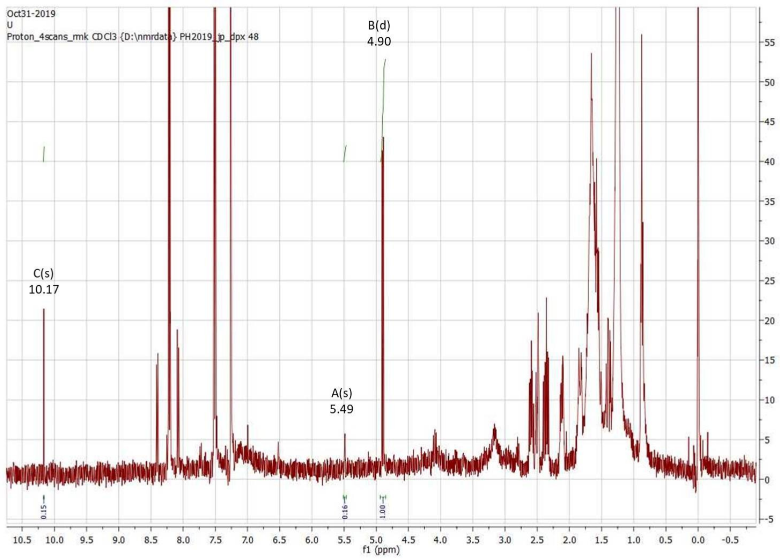
P_2R_2W 1 - 20 mol% water excess



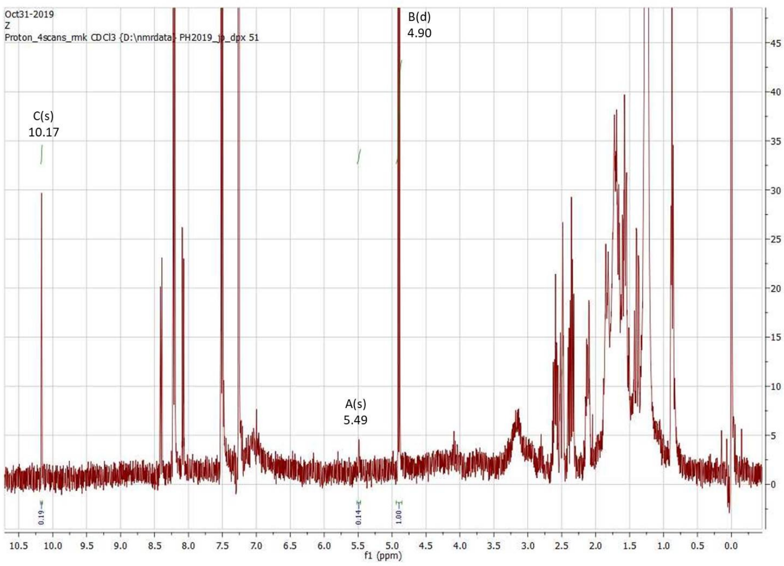
P_2R_2W 2 - 20 mol% water excess



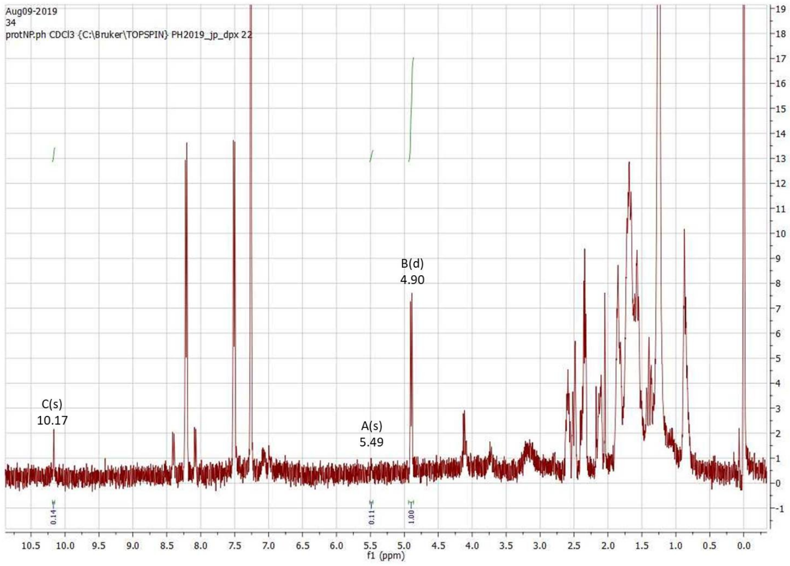
P_2R_2W 3 - 20 mol% water excess



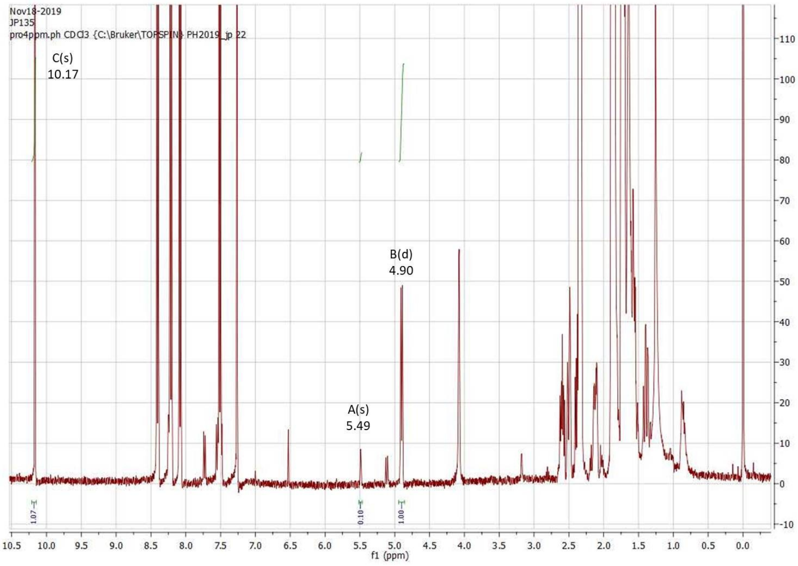
P_2R_2W 4 - 20 mol% water excess



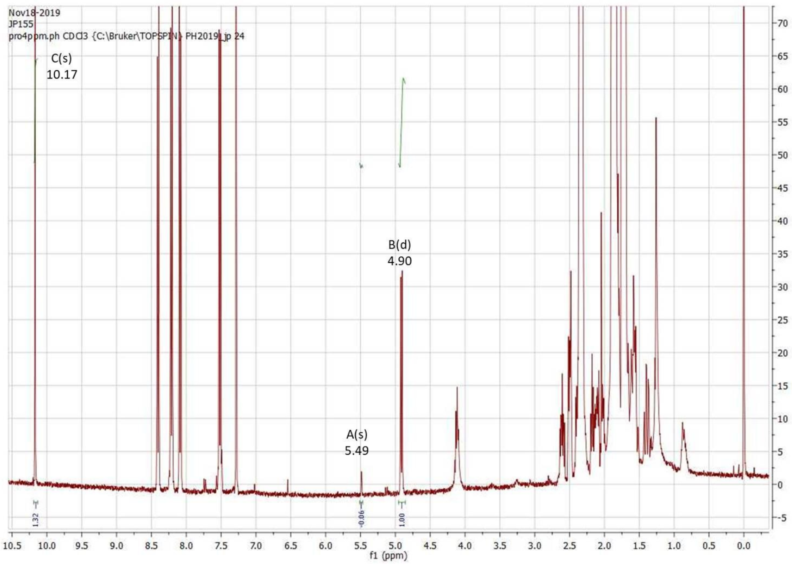
P_2R_2W 5 - 20 mol% water excess



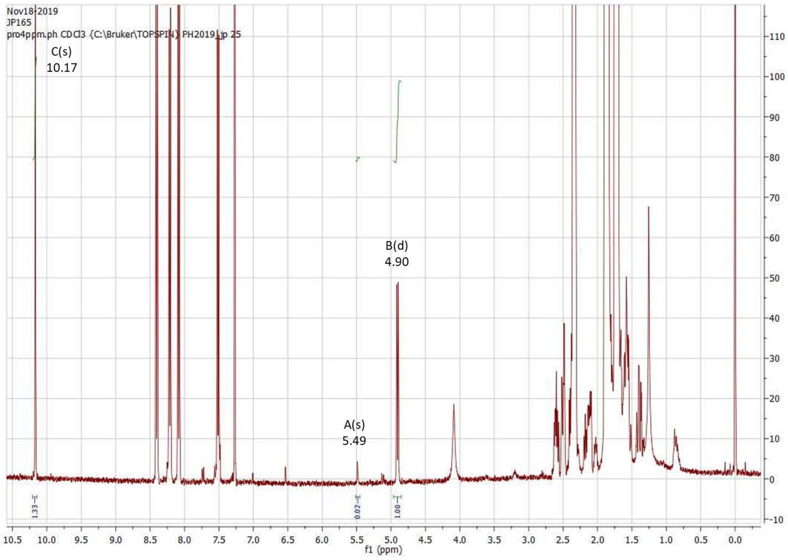
P_1R_1C 1 - 5 mol%



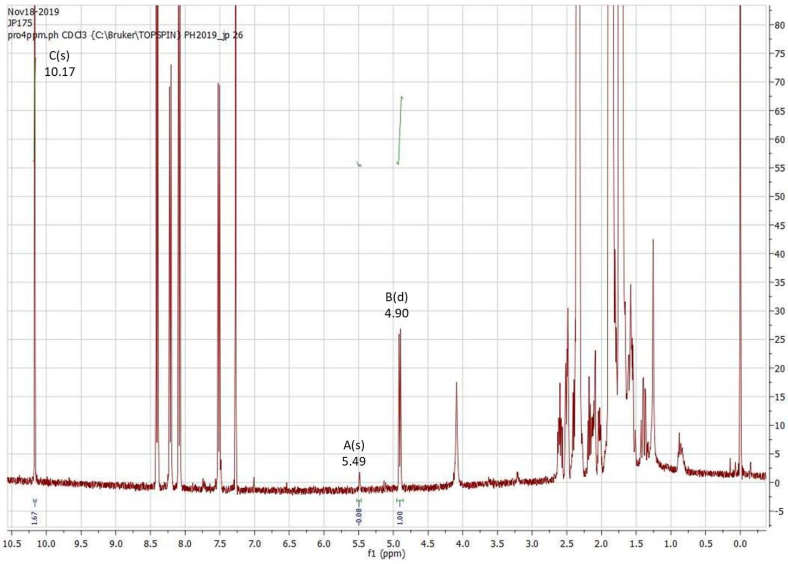
P_1R_1C 2 - 5 mol%



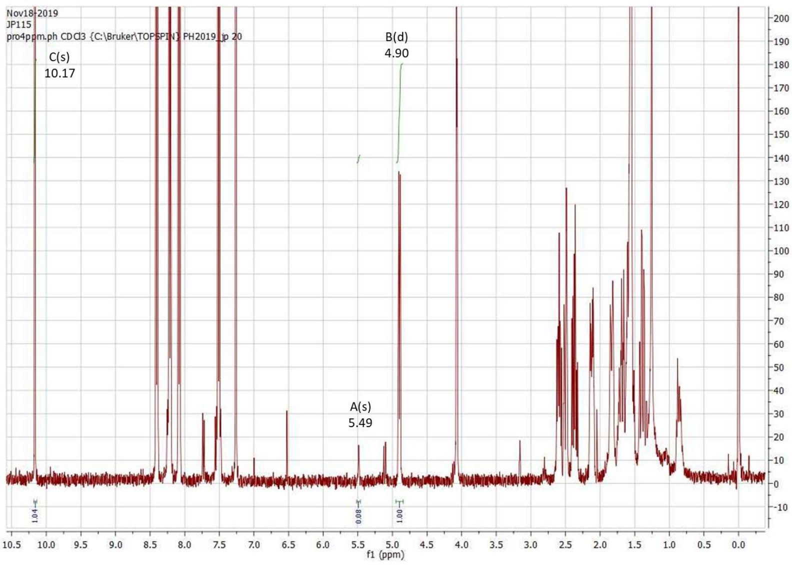
P_1R_1C 3 - 5 mol%



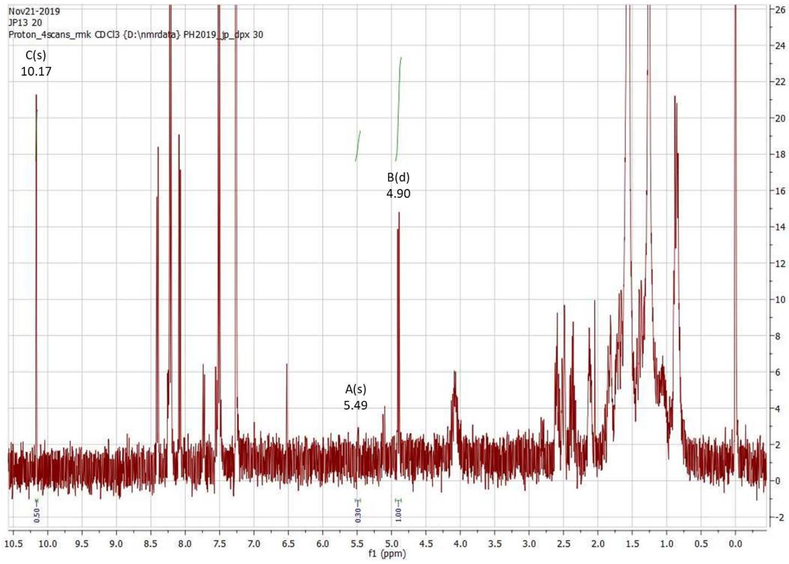
P_1R_1C 4 - 5 mol%



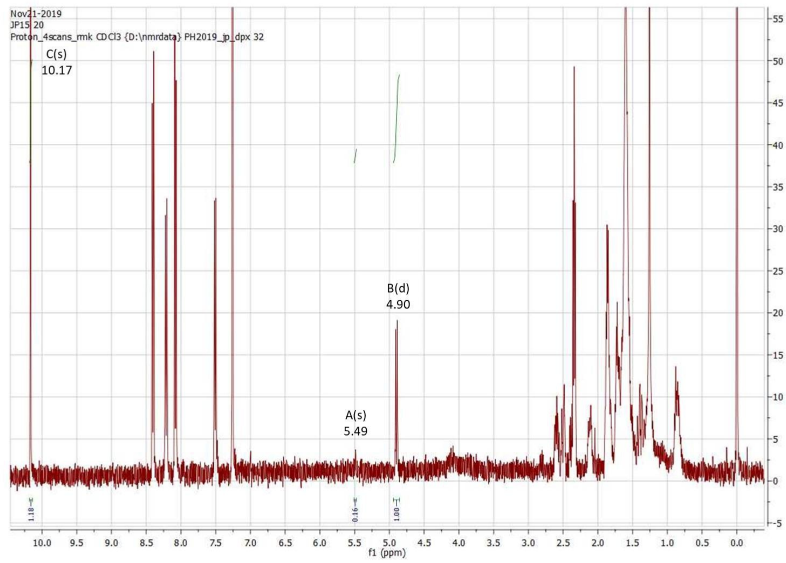
P_1R_1C 5 - 5 mol%



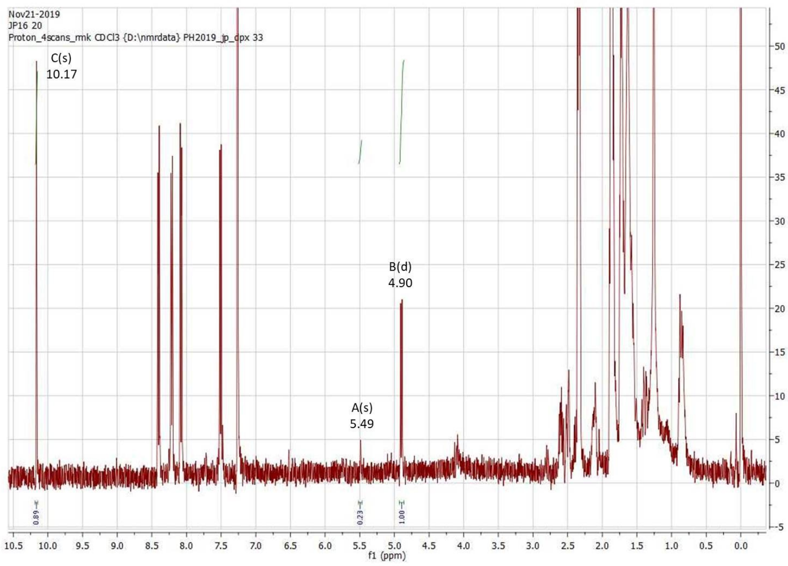
P_1R_1C **1** - 20 mol%



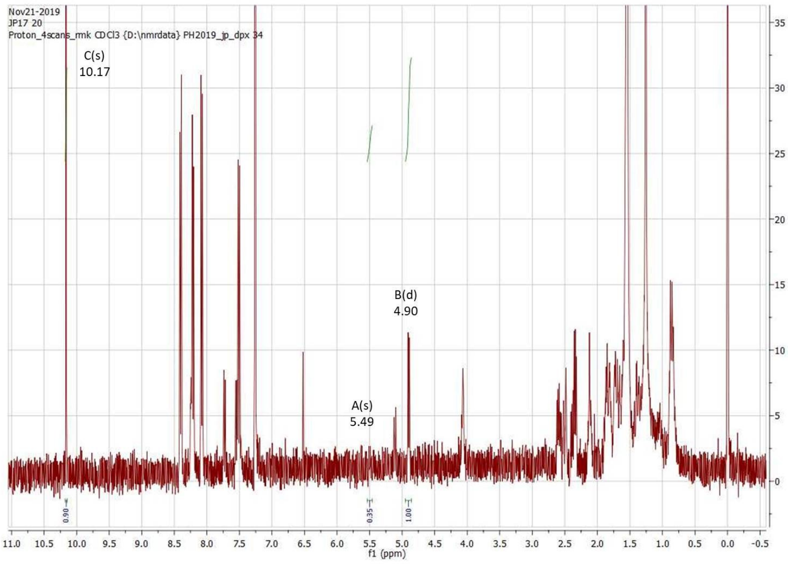
P_1R_1C **2** - 20 mol%



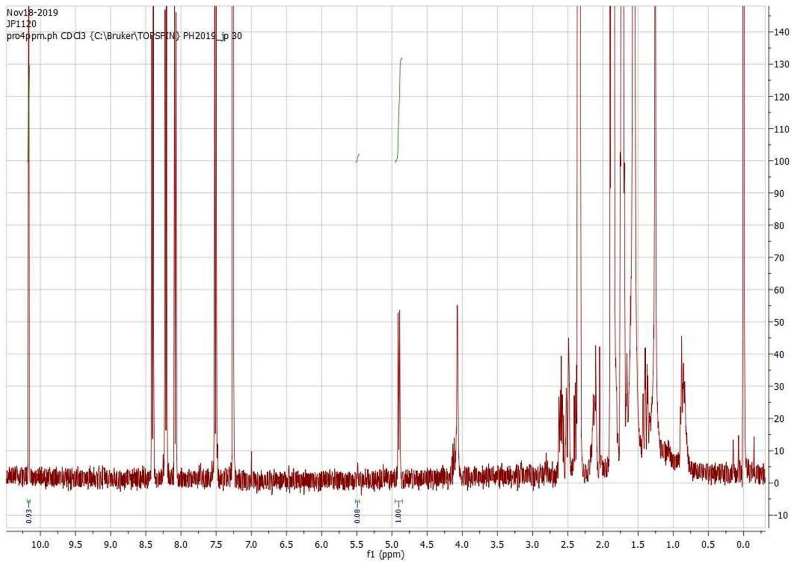
P_1R_1C **3** - 20 mol%



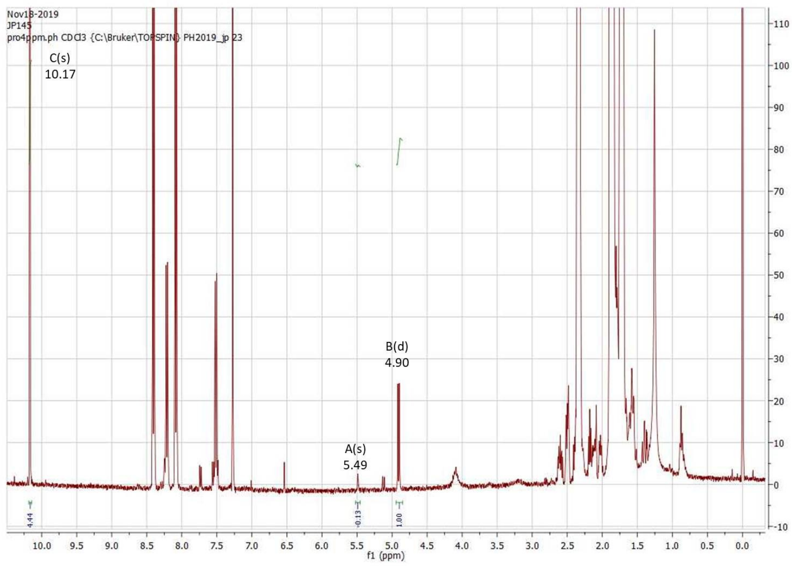
P_1R_1C 4 - 20 mol%



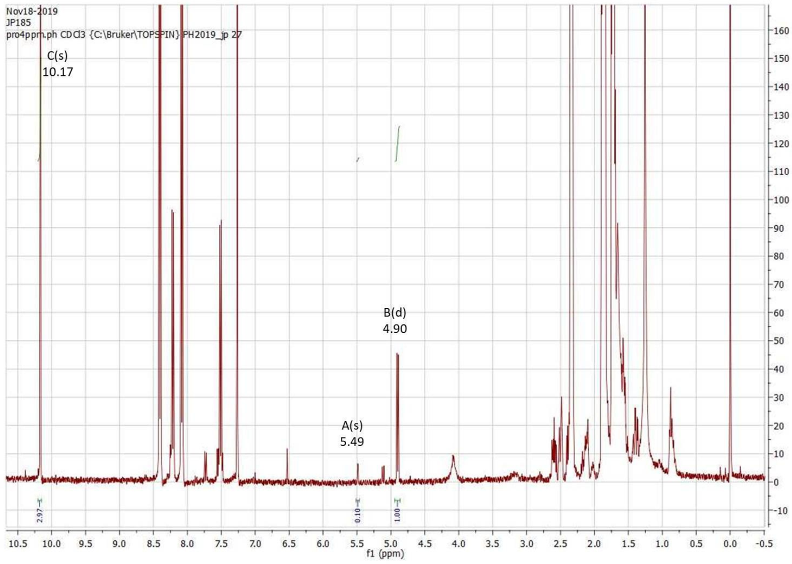
P_1R_1C 5 - 20 mol%



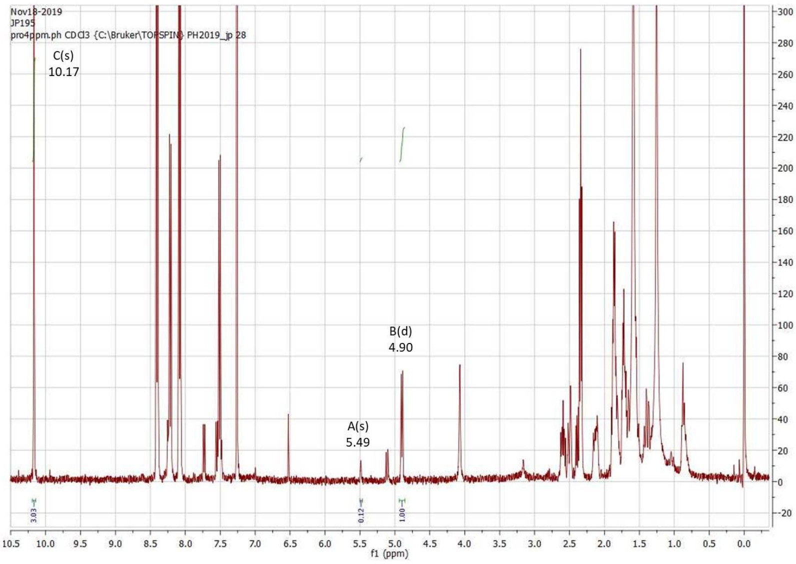
P_2R_2C 1 - 5 mol%



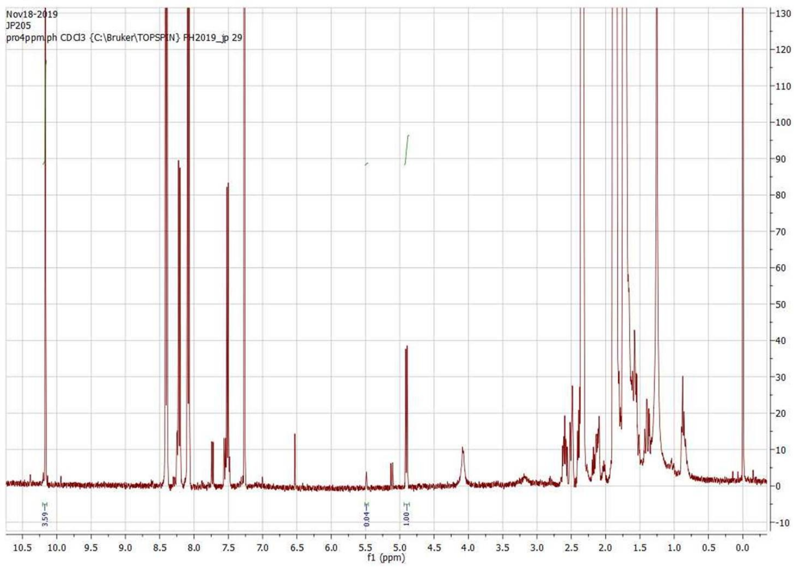
P_2R_2C 2 - 5 mol%



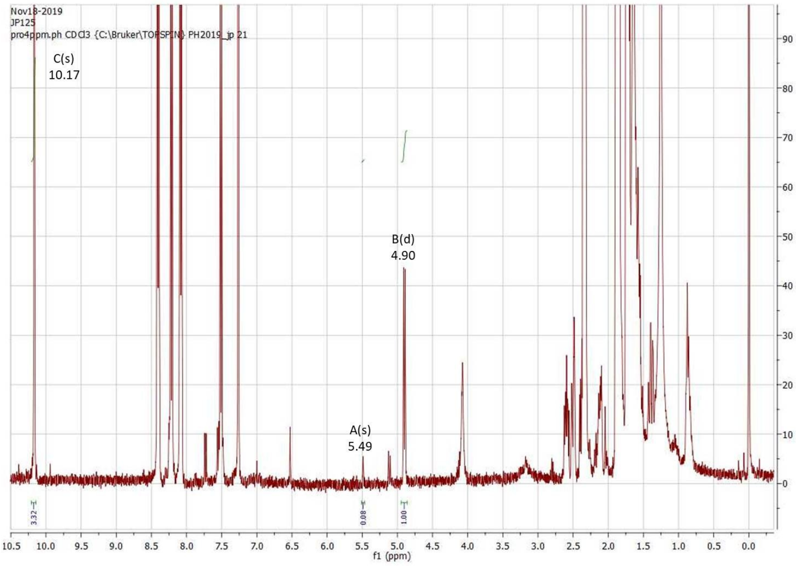
P_2R_2C 3 - 5 mol%



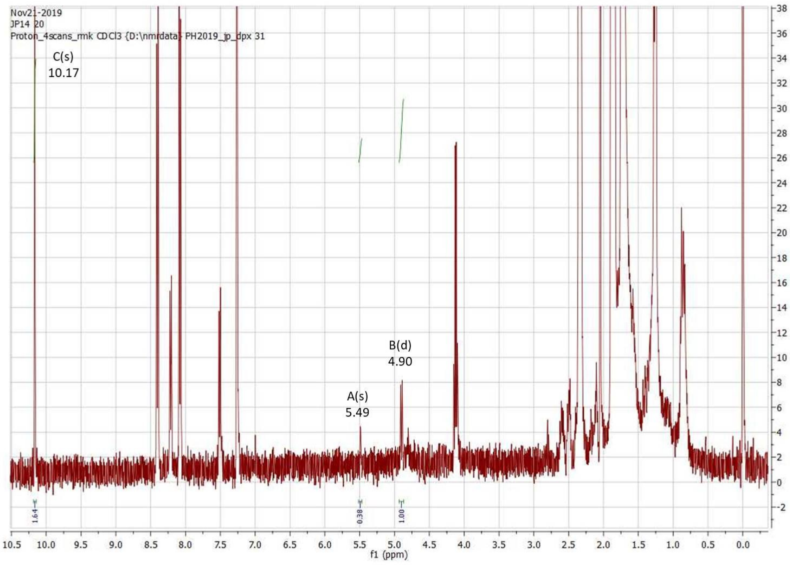
P_2R_2C 4 - 5 mol%



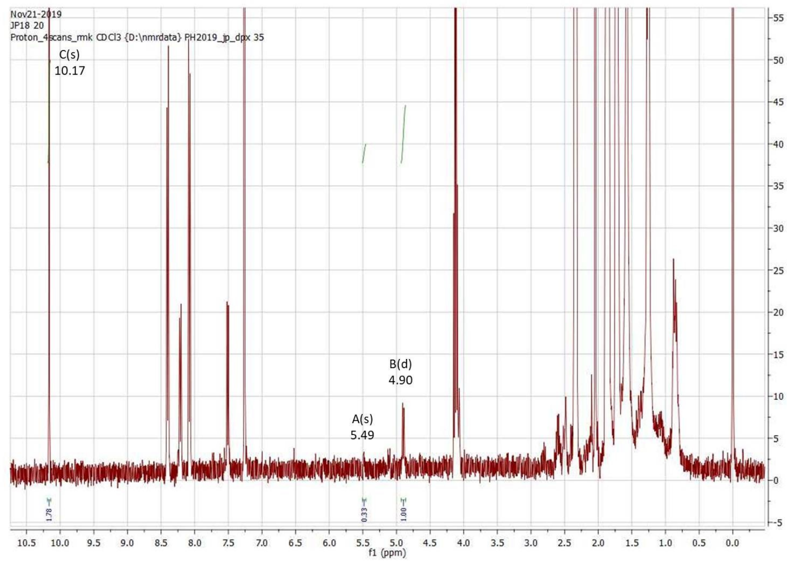
P_2R_2C 5 - 5 mol%



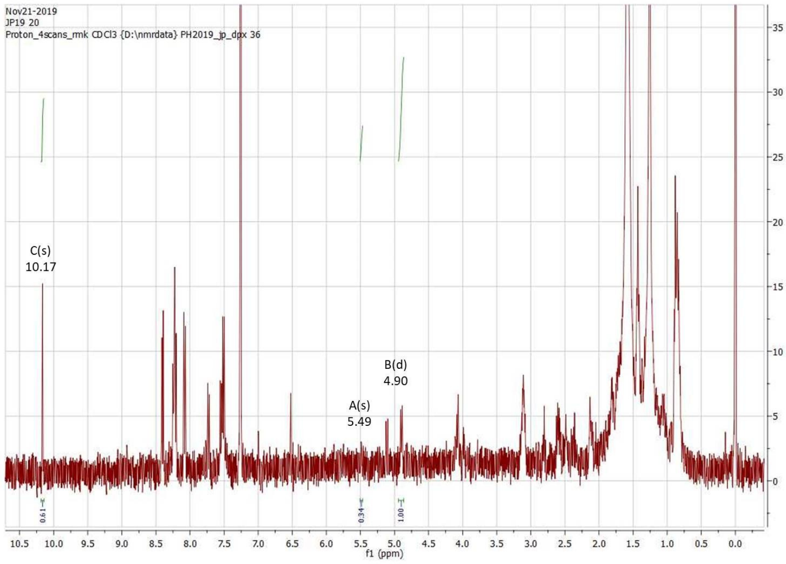
P_2R_2C 1 - 20 mol%



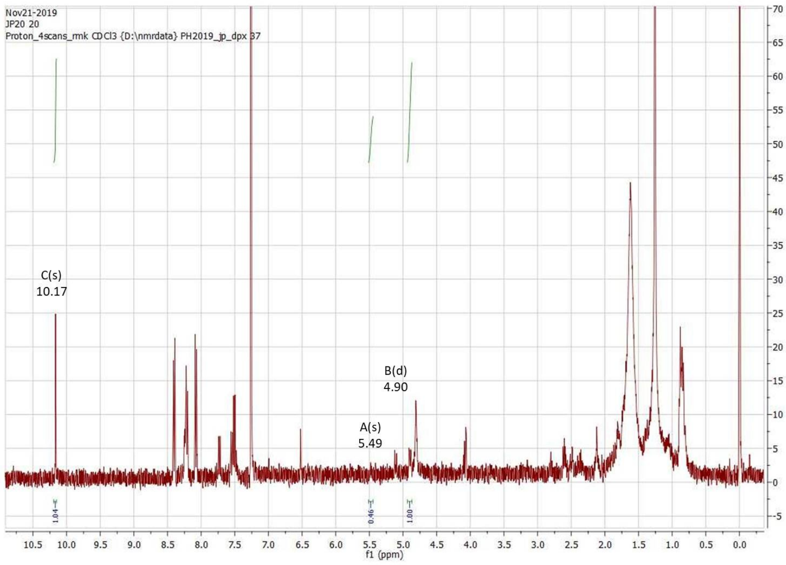
P_2R_2C 2 - 20 mol%



P_2R_2C 3 - 20 mol%



P_2R_2C 4 - 20 mol%



P_2R_2C 5 - 20 mol%

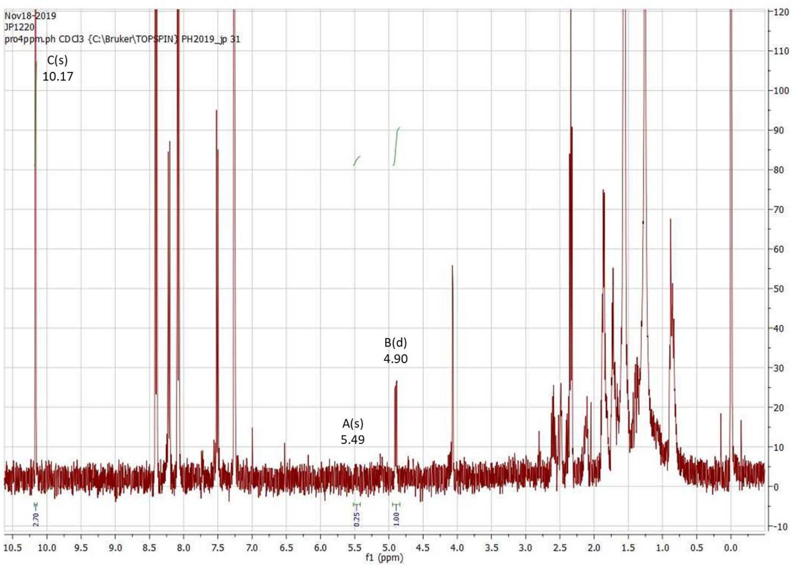


Figure S8. Representative ^1H NMR spectra of crude aldol products described in Table S1.