Synthesis and characterization of fully biobased polyesters with tunable branched architectures

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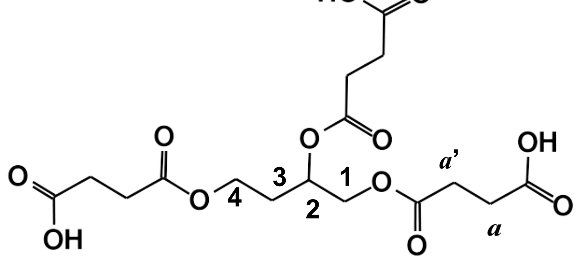
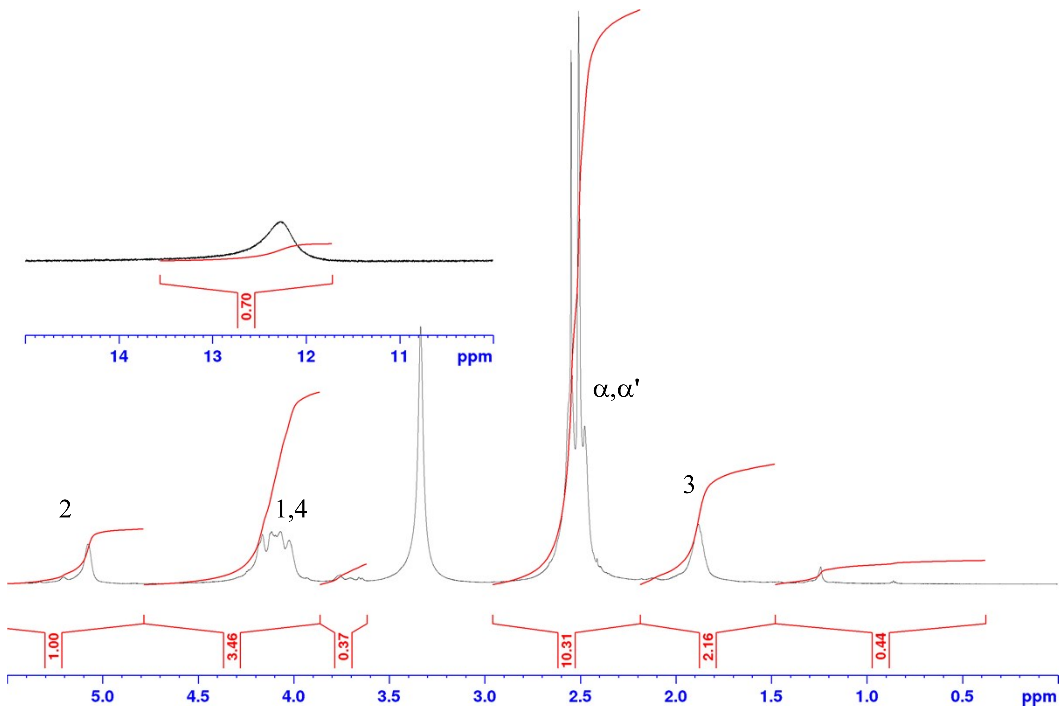
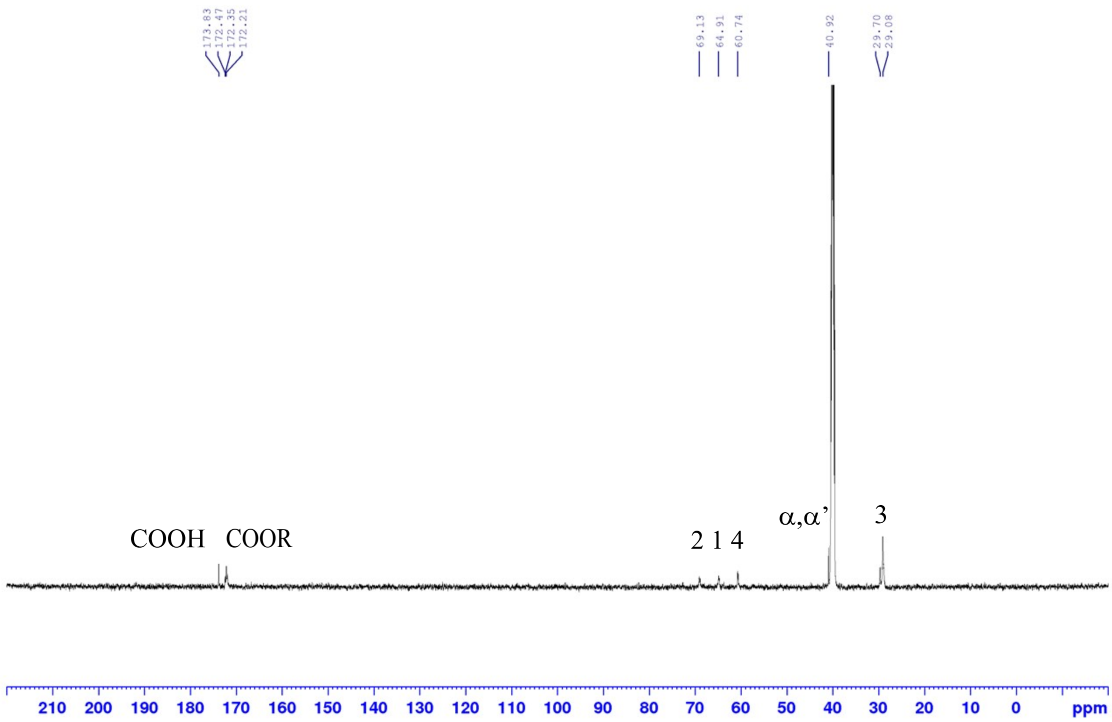
Supplementary Information

Carboxyl terminated SucA/BTO(-COOH)





FigureS1:[1]HNMRspectrumofSucA/BTO(-COOH)indmso-d_6



FigureS2:[13]CNMRspectrumofSucA/BTO(-COOH)indmso-d_6

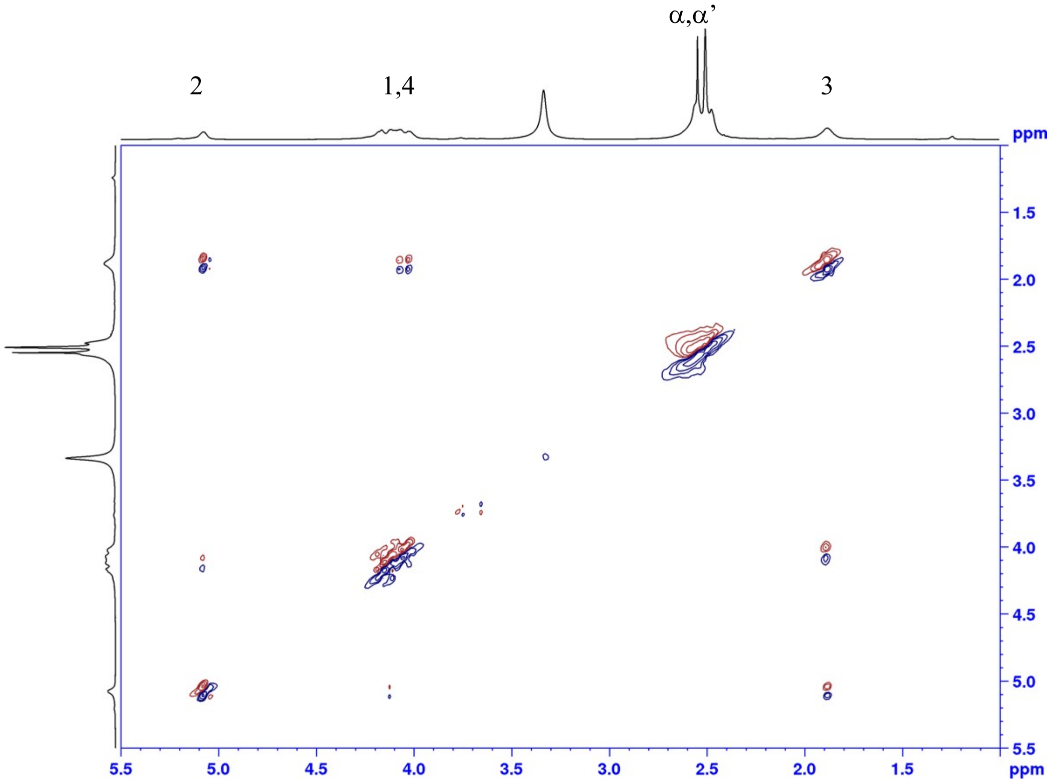


Figure S 3: COSY NMR spectrum of SucA/BTO(-COOH) in dmso-d_6

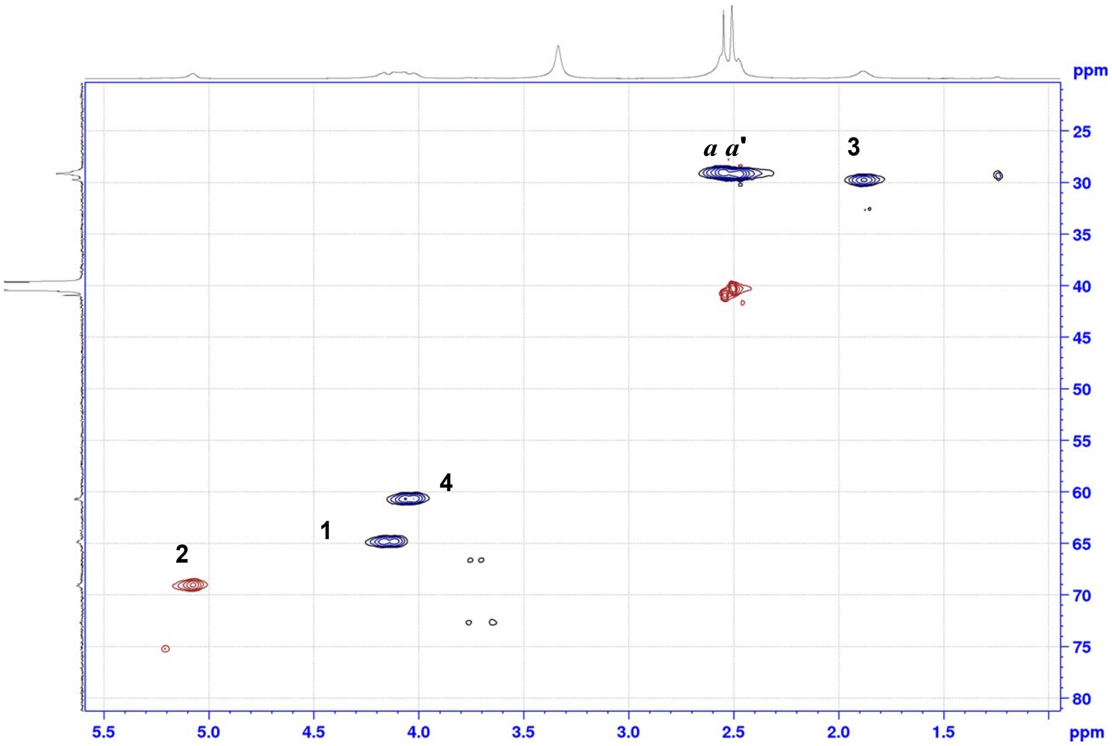


Figure S 4: HSQC NMR spectrum of SucA/BTO(-COOH) in dmso-d_6

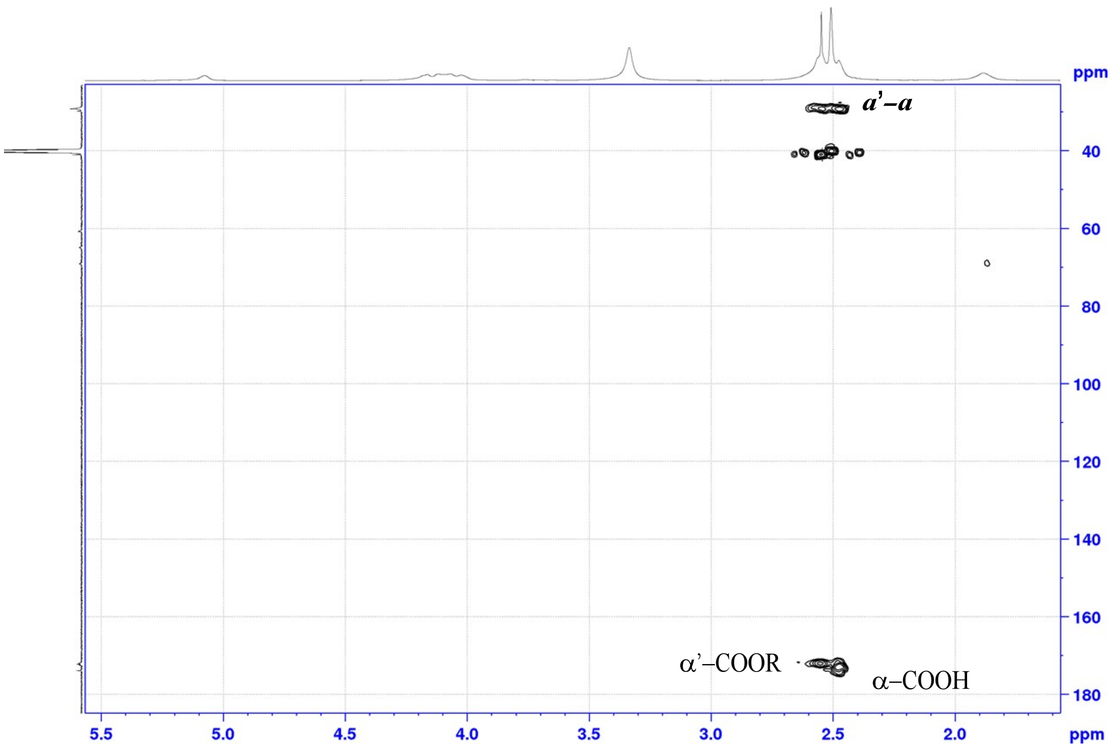
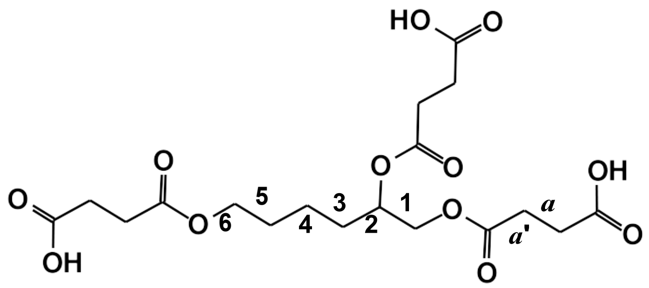


Figure S 5: NMR spectrum of SucA/BTO(-COOH) in dmso-d_6

SucA/HTO(-COOH)



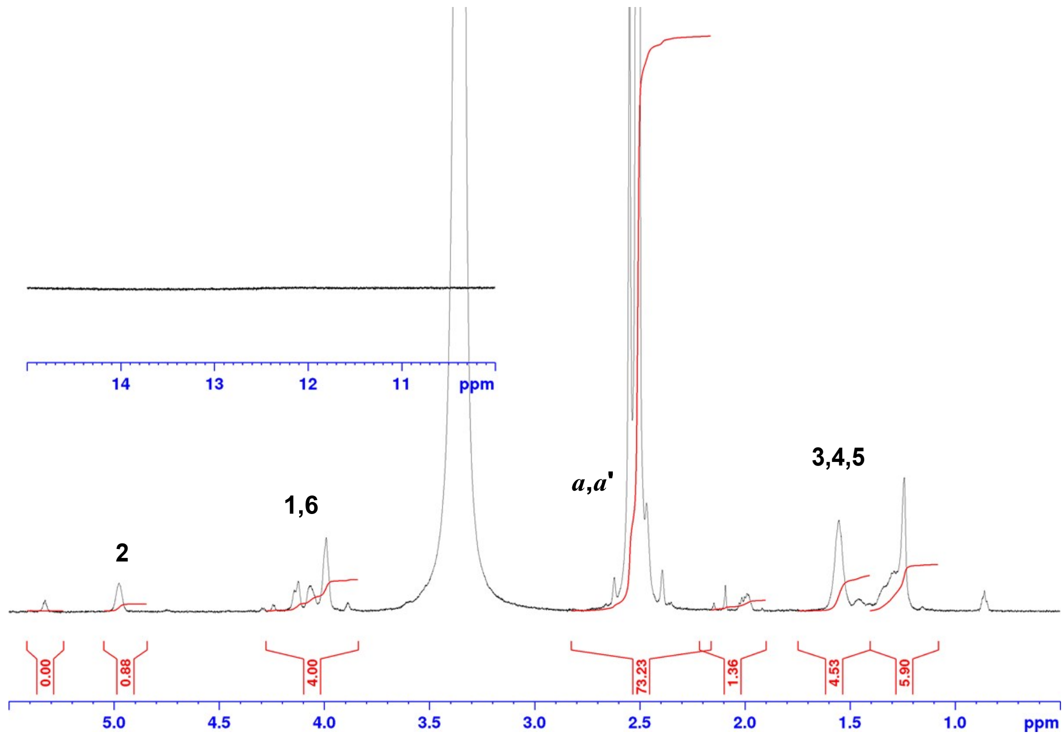
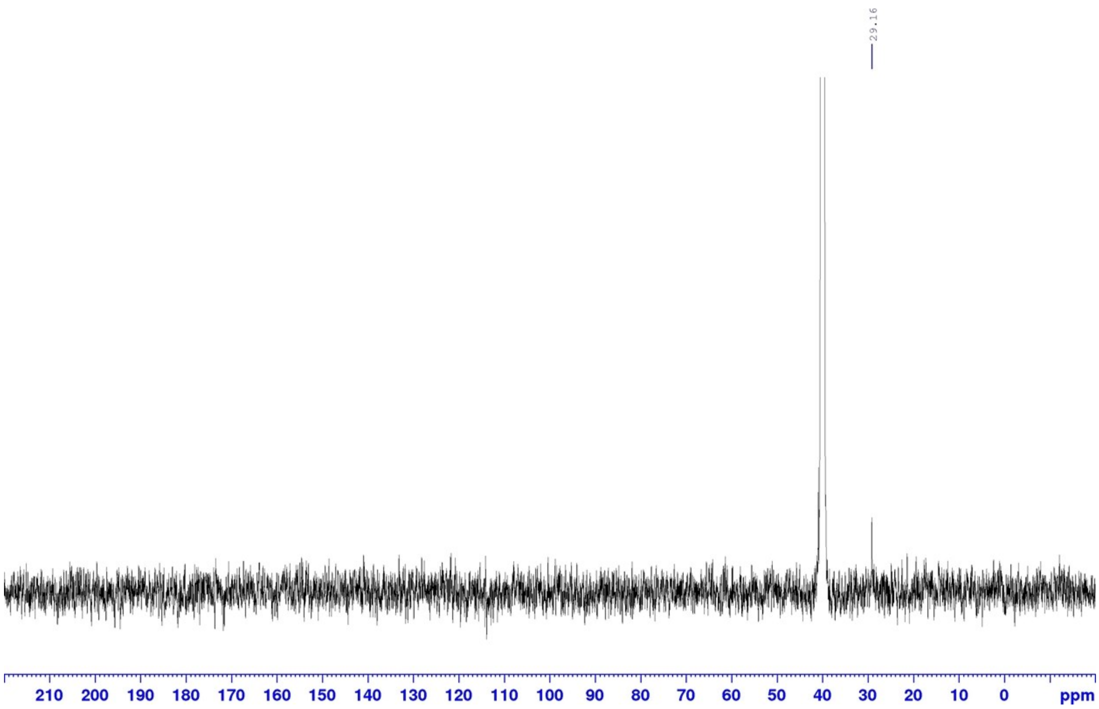
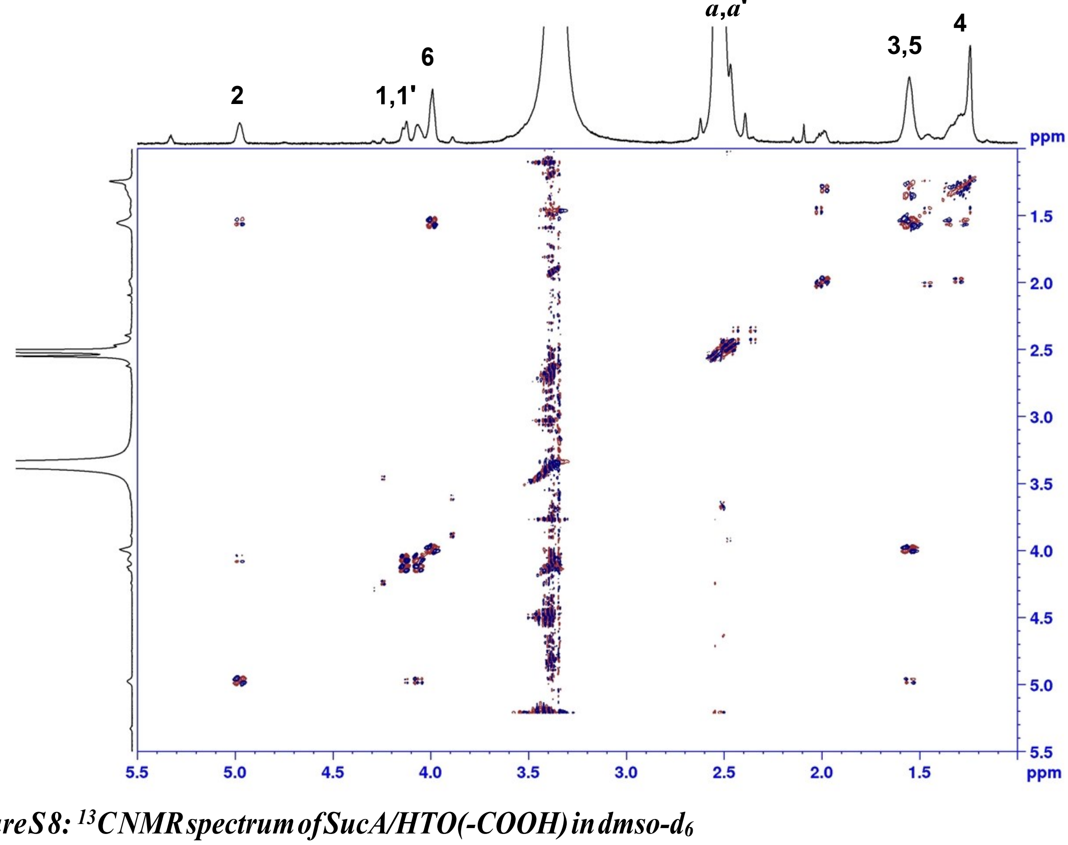


Figure S 6: ^{1}H NMR spectrum of SucA/HTO(-COOH) in dmso-d_6



FigureS7: ^{13}CNMRspectrumofSucA/HTO(-COOH)indmso-d_6



FigureS8: ^{13}CNMRspectrumofSucA/HTO(-COOH)indmso-d_6

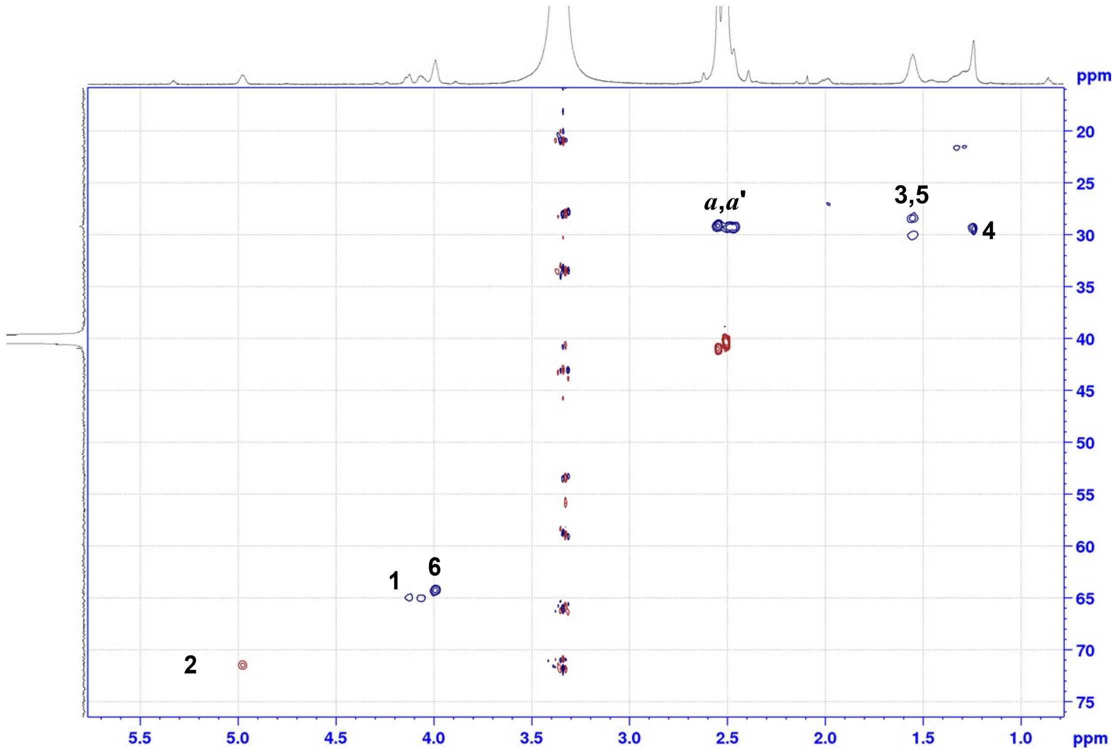


Figure S 9: HSQC NMR spectrum of SucA/HTO(-COOH) in dmso-d_6

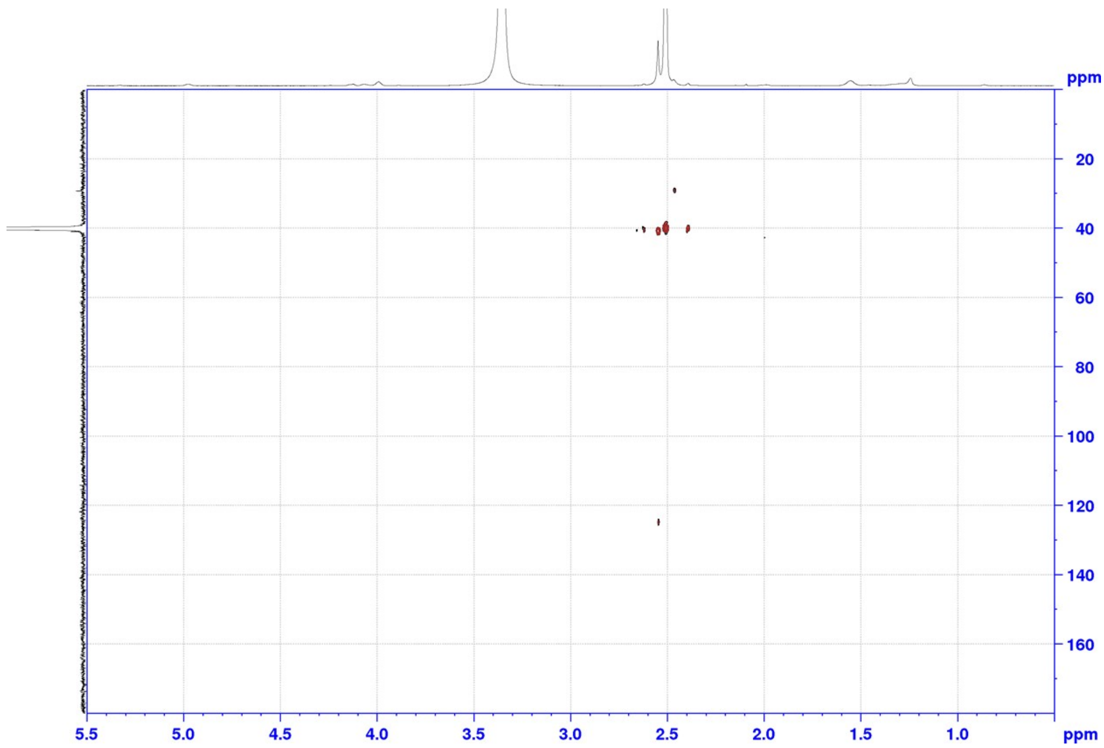
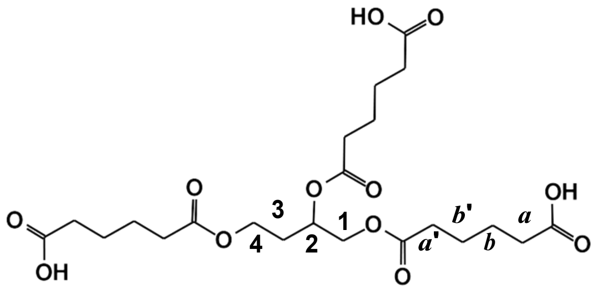


Figure S 10: HMBC NMR spectrum of SucA/HTO(-COOH) in dmso-d_6

AdiA/BTO(-COOH)



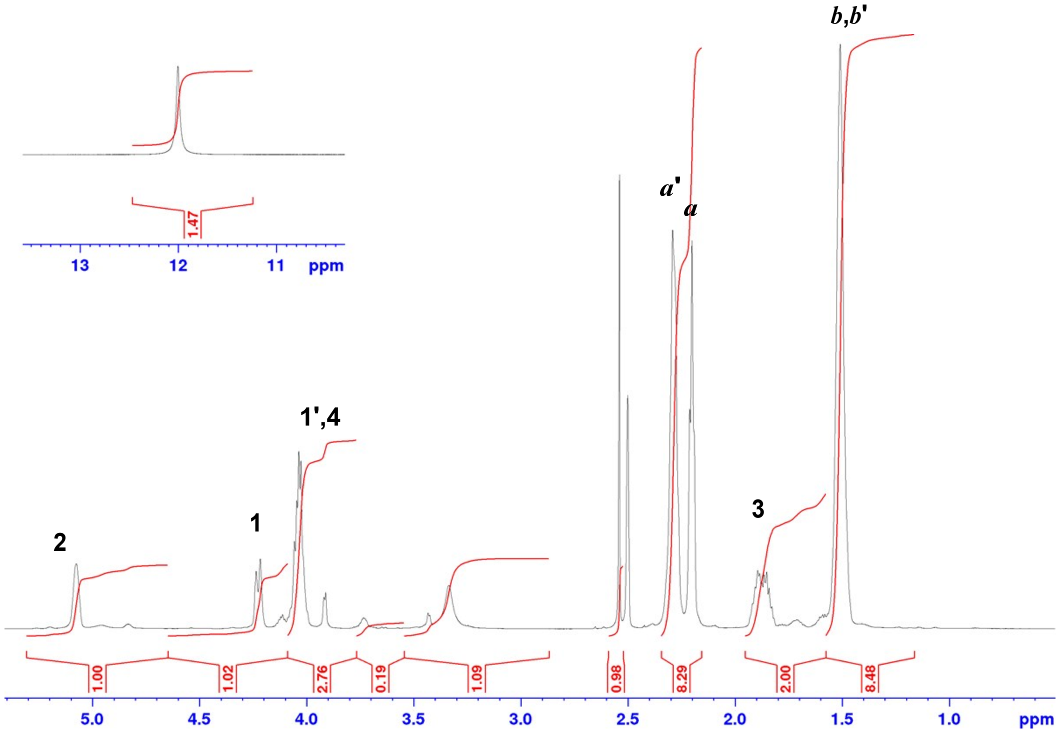


Figure S 11: ^{1}H NMR spectrum of AdiA/BTO(-COOH) in dmso-d_6

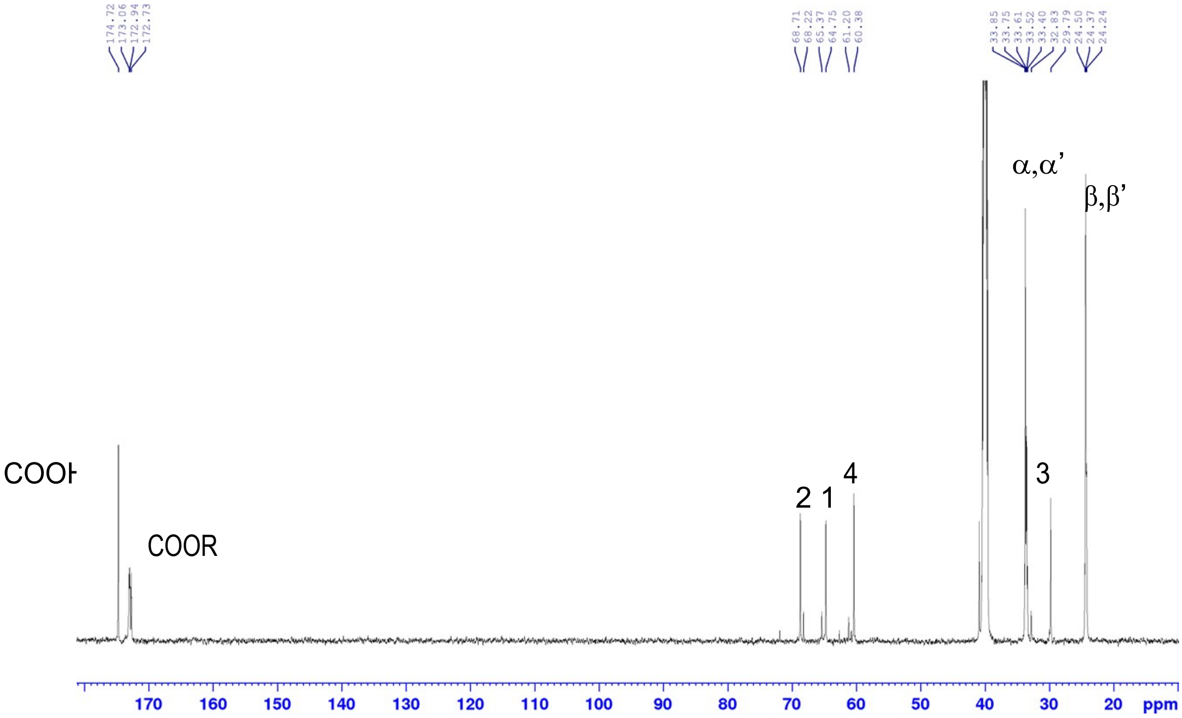


Figure S 12: ^{13}C NMR spectrum of AdiA/BTO(-COOH) in dmso-d_6

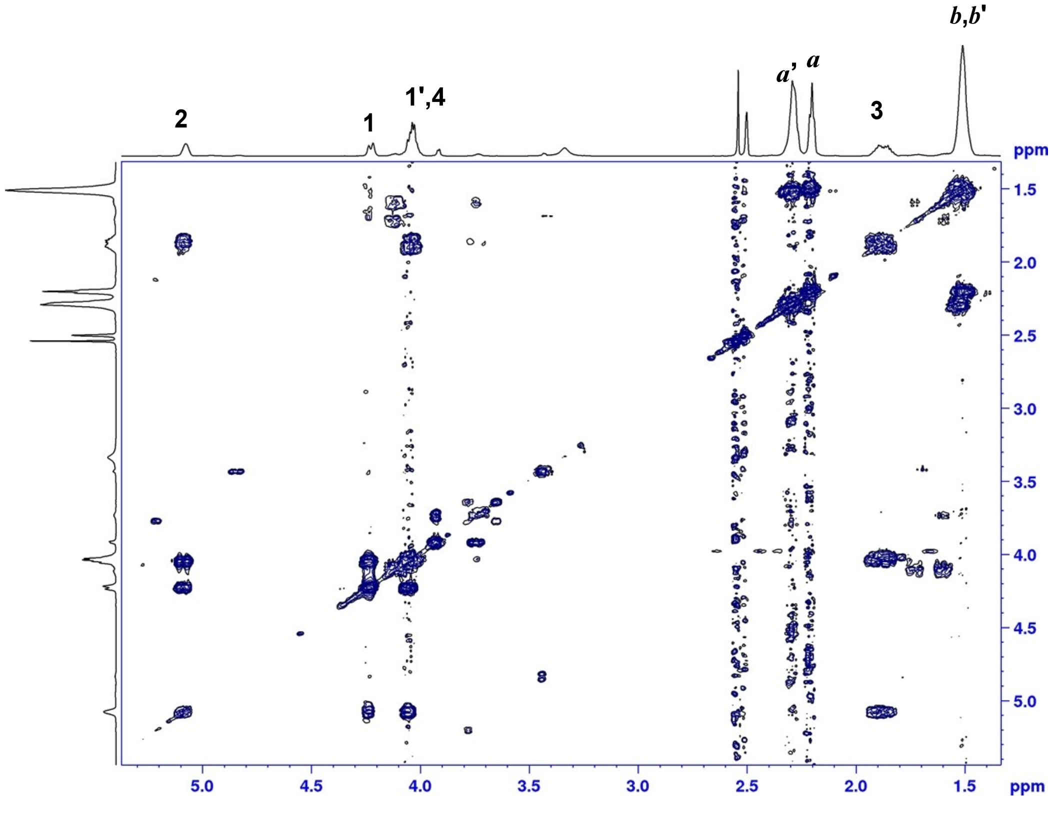


Figure S 13: COSY NMR spectrum of AdiA/BTO(-COOH) in dsmo-d_6

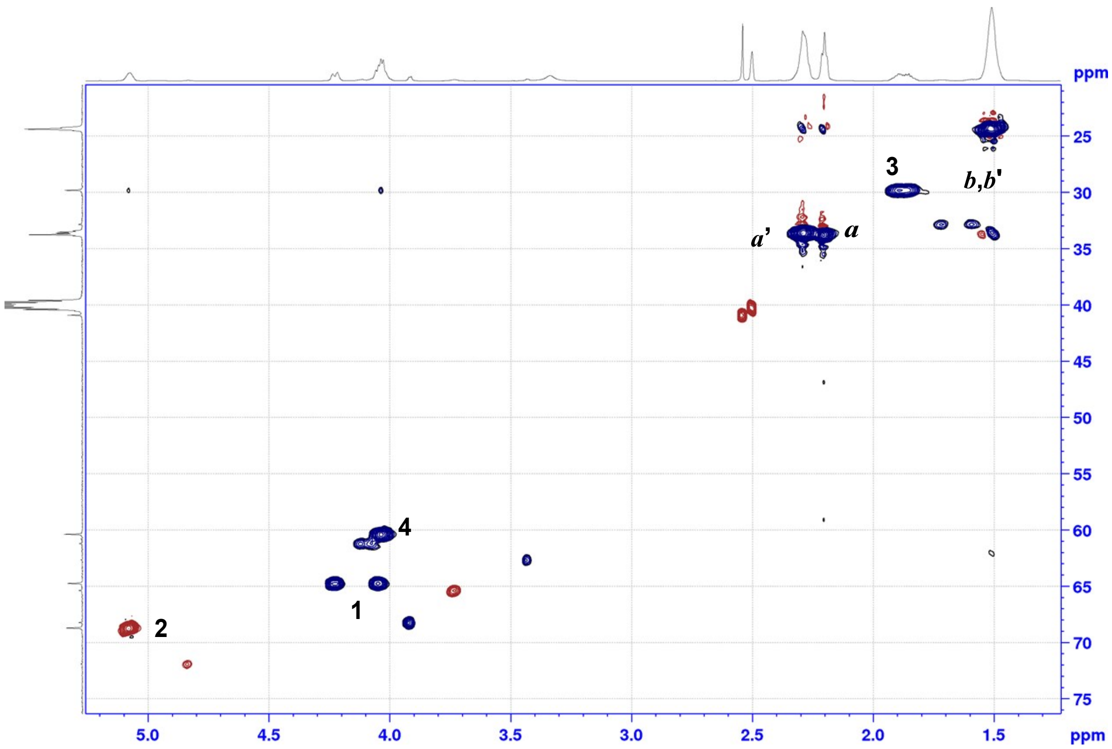


Figure S 14: HSQC NMR spectrum of AdiA/BTO(-COOH) in dmso-d_6

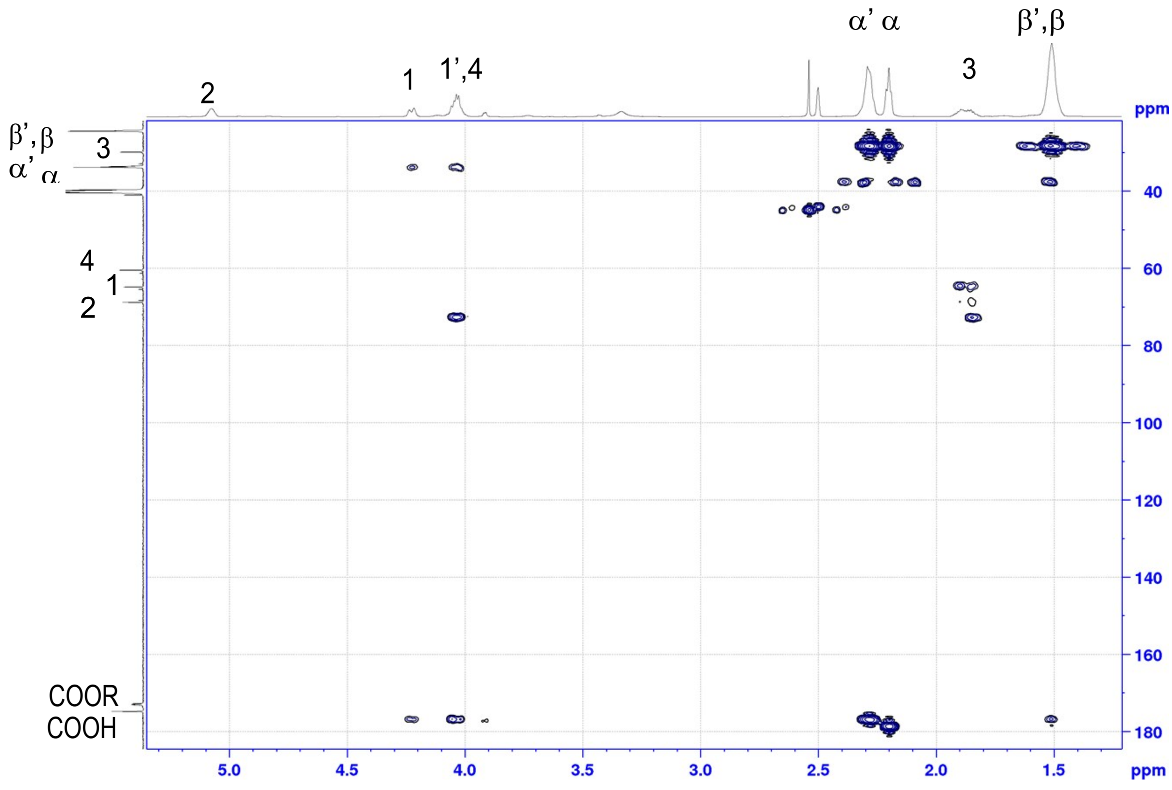
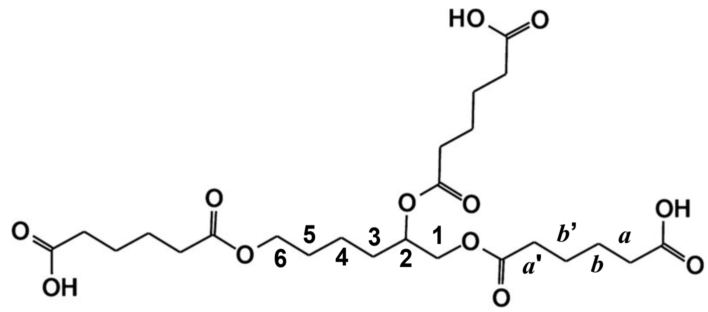


Figure S 15 HMBC NMR spectrum of AdiA/BTO(-COOH) in dmso-d_6

AdA/HTO(-COOH)



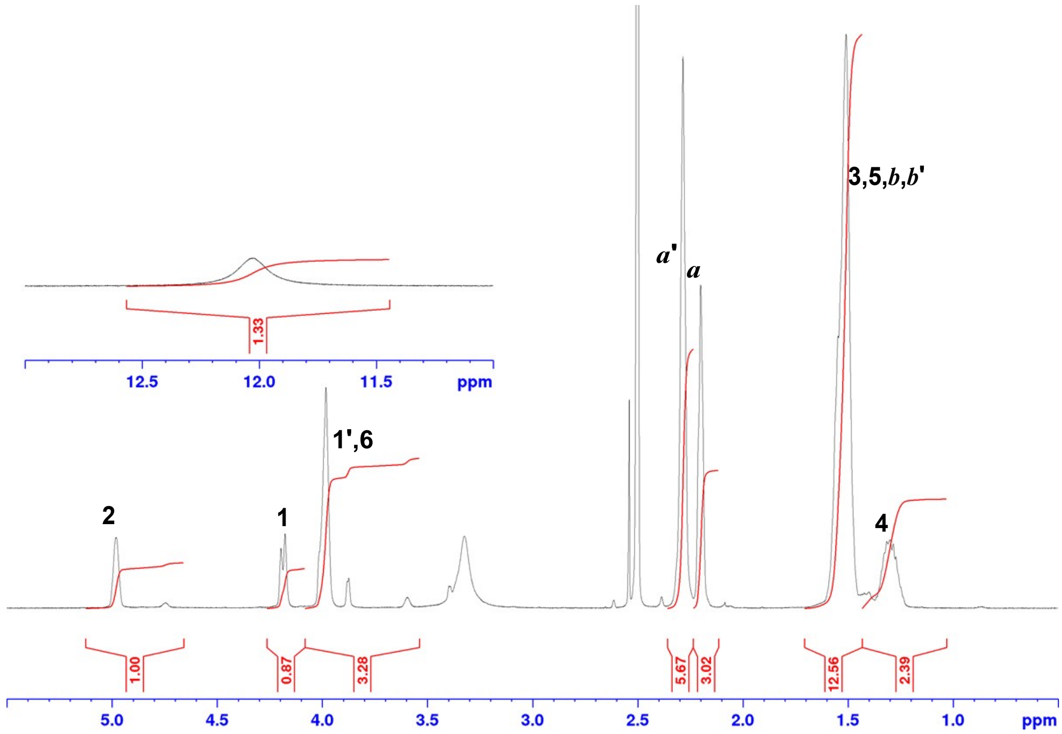


Figure S 16:^{1}H NMR spectrum of AdiA/HTO(-COOH) in dmso-d_6

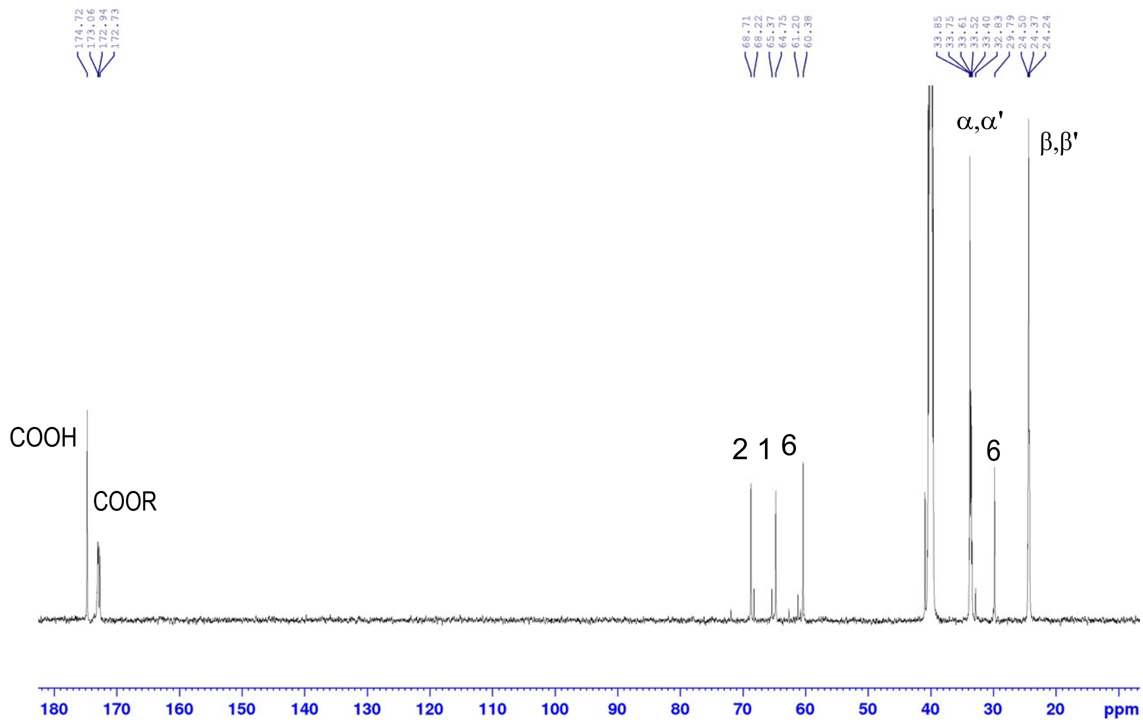


Figure S 17: ^{13}C spectrum of AdiA/HTO(-COOH) in dmso-d_6

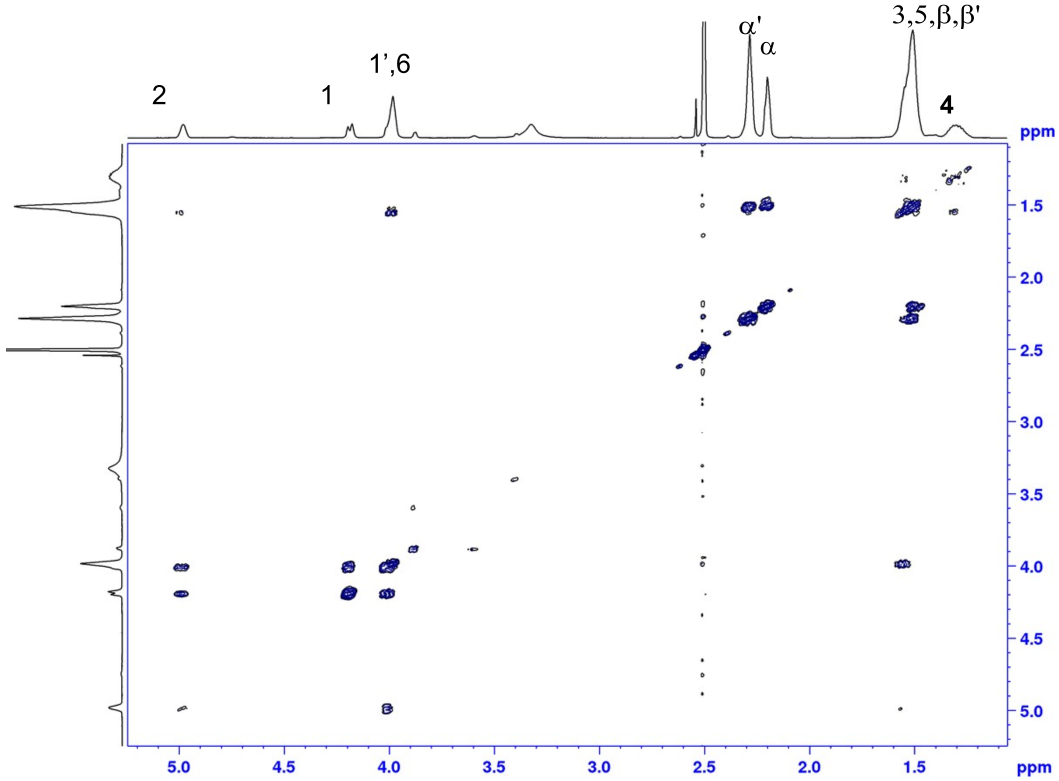


Figure S 18: COSY NMR spectrum of AdiA/HTO(-COOH) in dmso-d_6

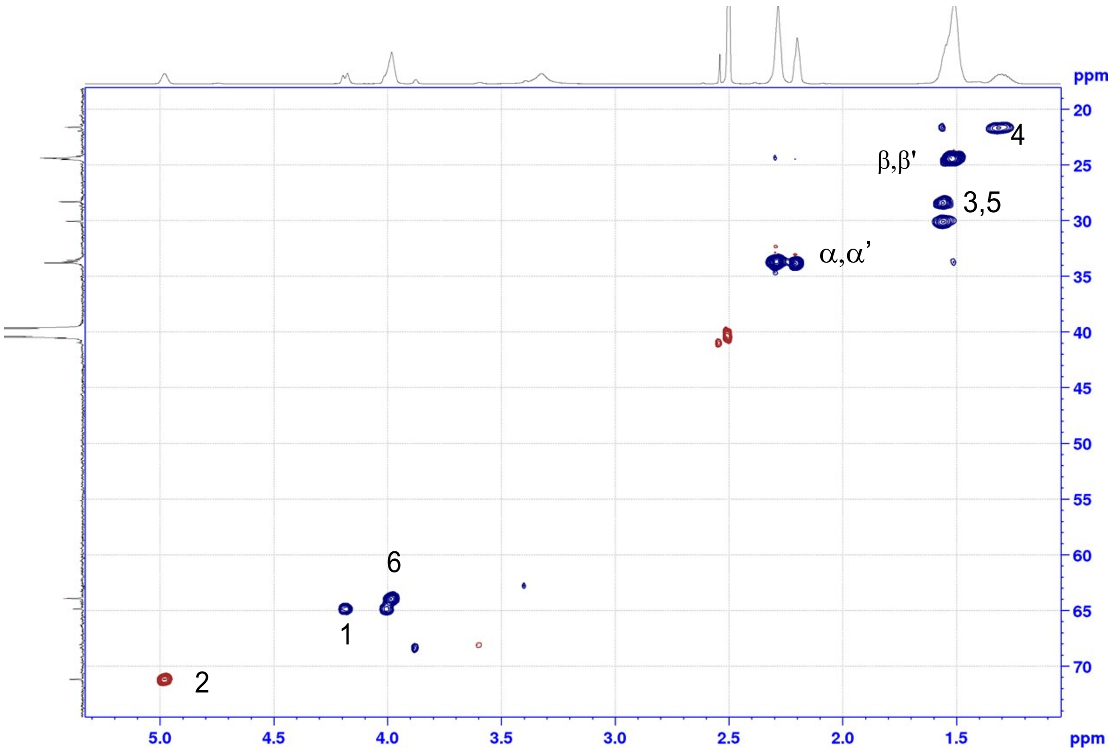


Figure S 19: HSQC NMR spectrum of Adi/HTO(-COOH) in dmso-d_6

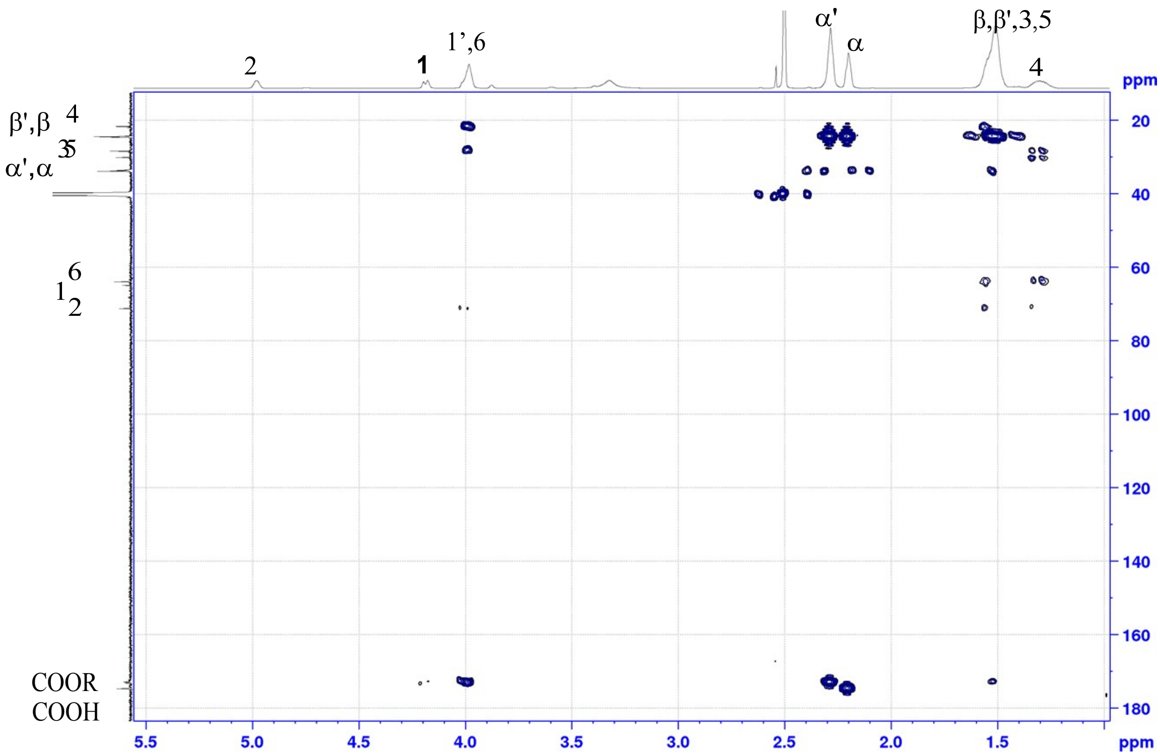
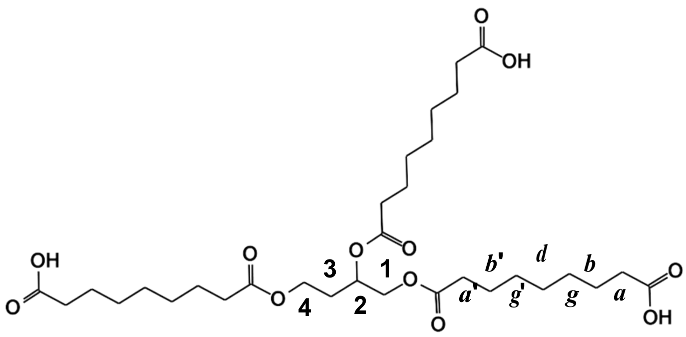


Figure S 20: HMBC NMR spectrum of AdiA/HTO(-COOH) in dmso-d_6

AzA/BTO(-COOH)



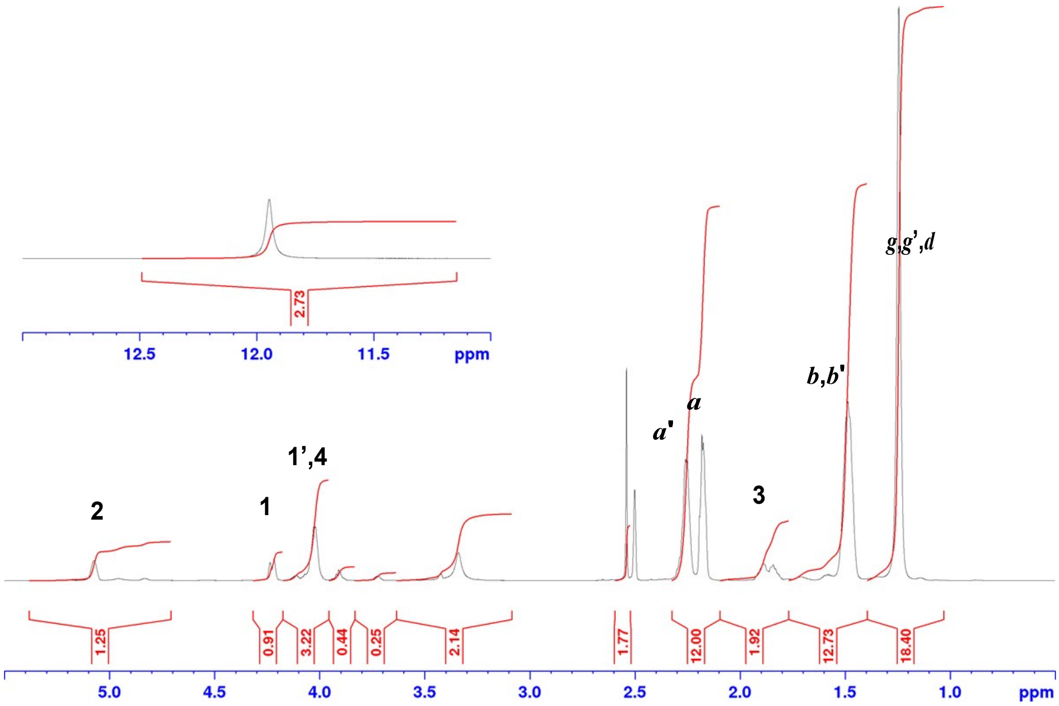


Figure S 21: ^{1}H NMR spectrum of AzeA/BTO(-COOH) in dmso-d_6

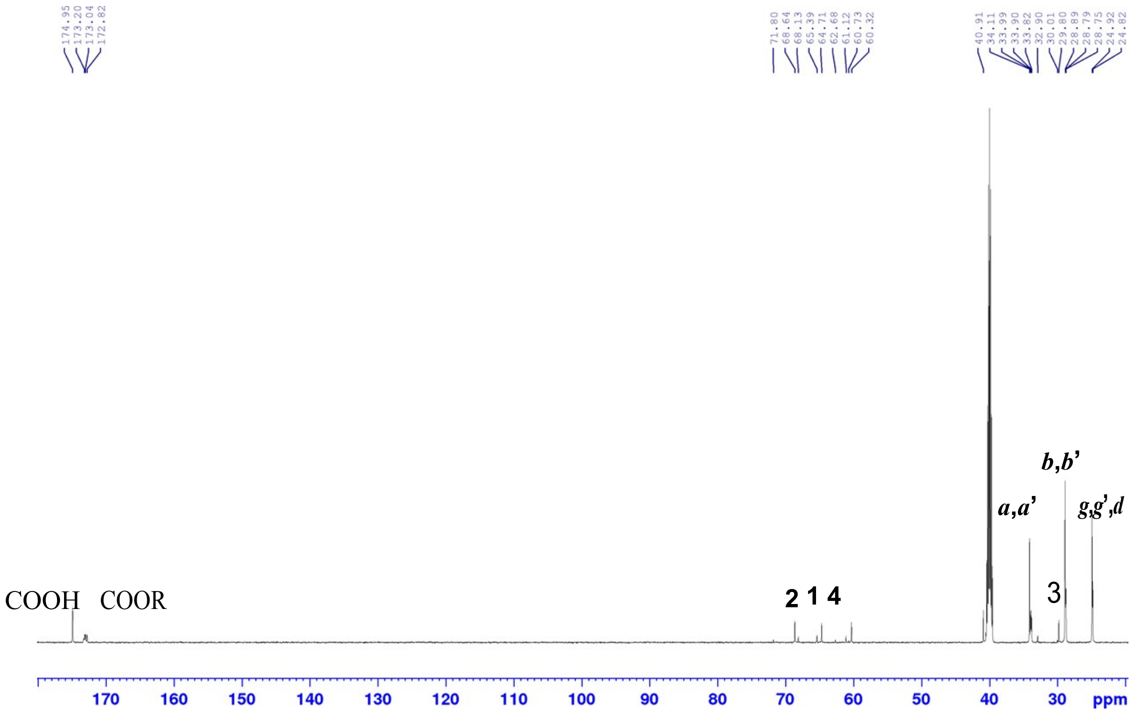


Figure S 22: ^{13}C NMR spectrum of AzeA/BTO(-COOH) in dmso-d_6

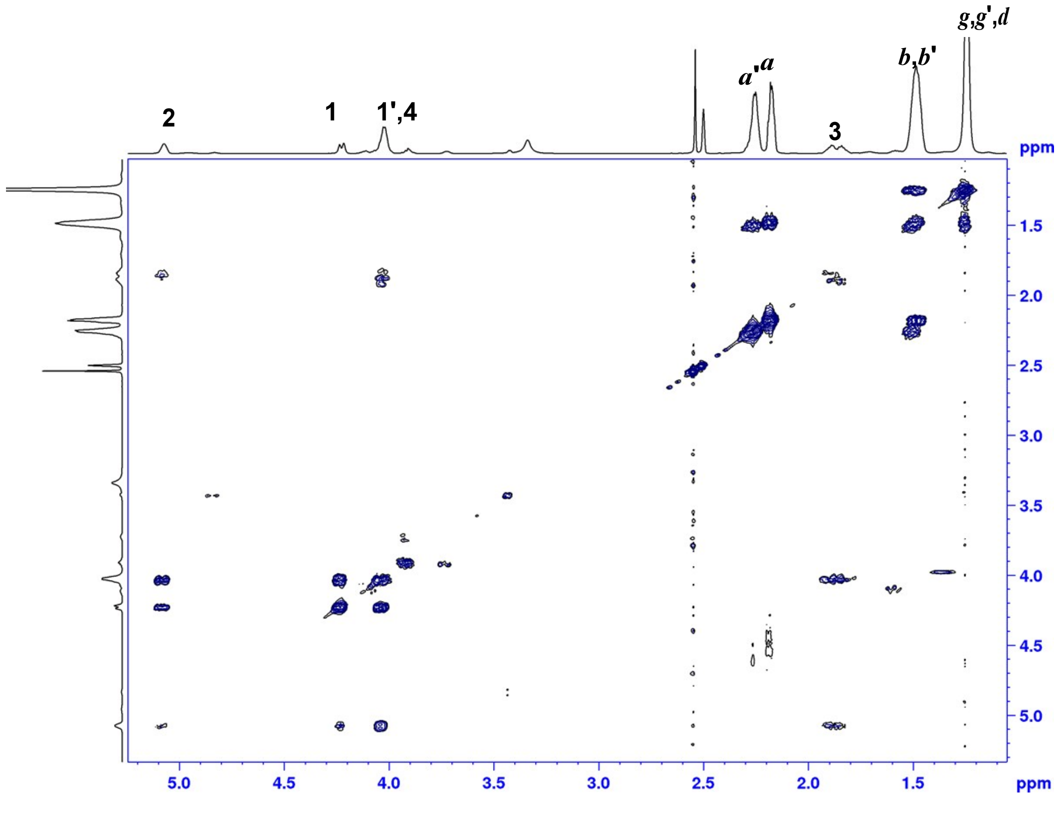


Figure S 23: COSY NMR spectrum of AzeA/BTO(-COOH) in dmso-d_6

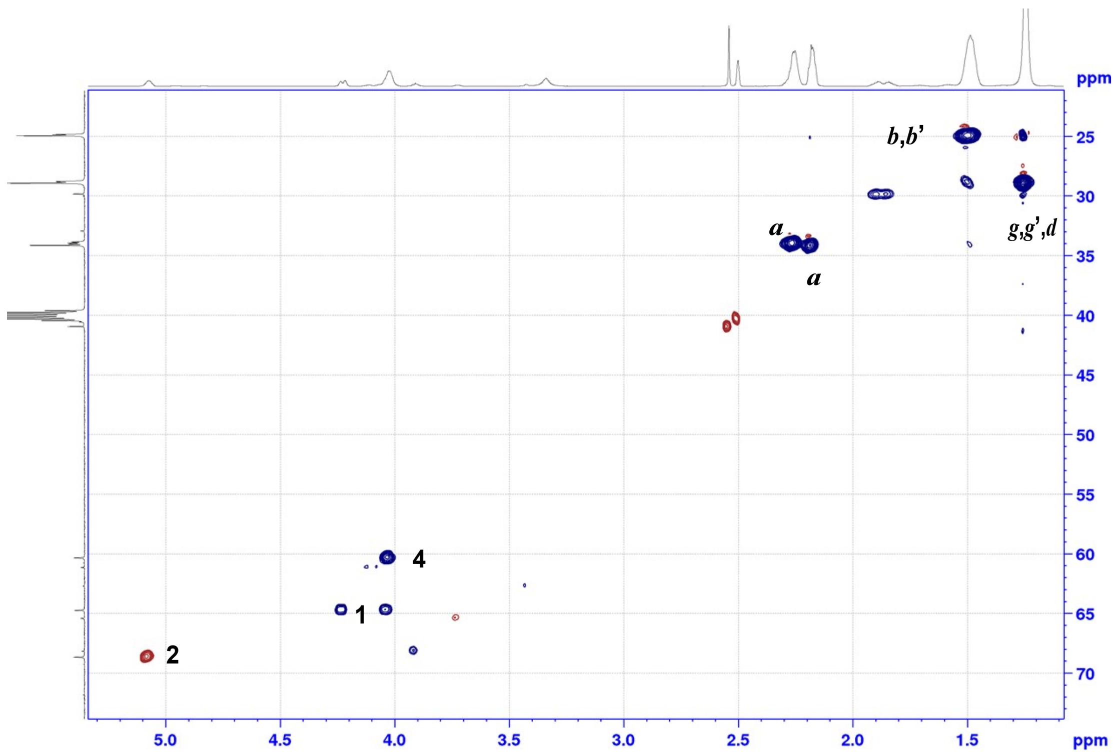


Figure S 24: HSQC spectrum of AzeA/BTO(-COOH) in dmso-d_6

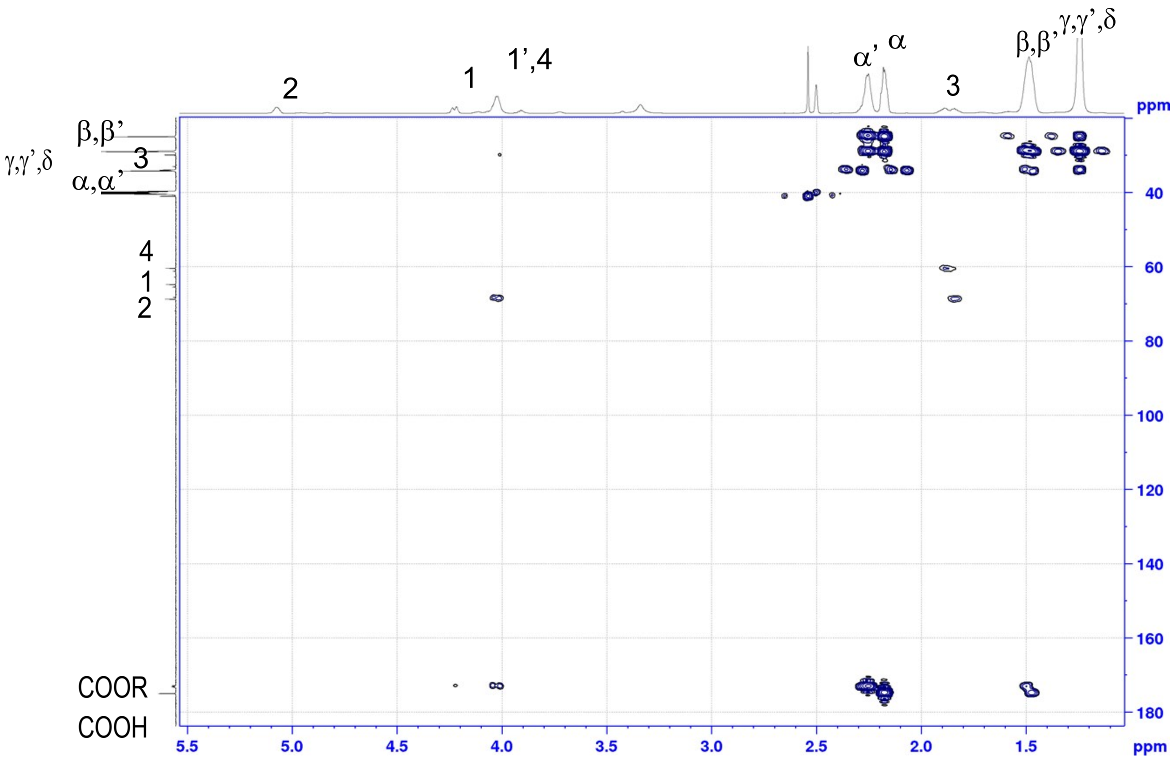


Figure S 25: HMBC NMR spectrum of AzeA/BTO(-COOH) in dmso-d_6

AzeA/HTO(-COOH)

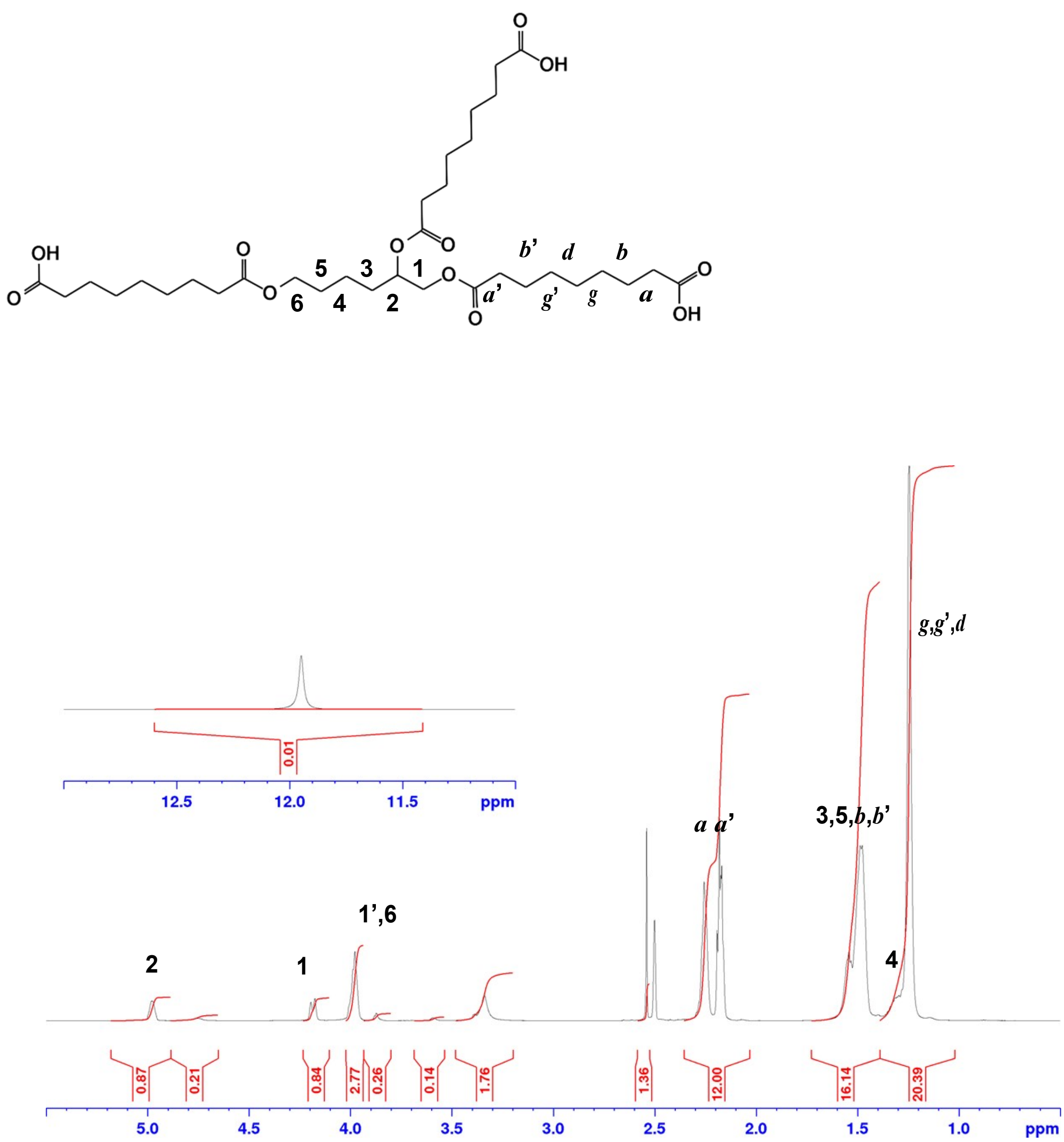


Figure S 26: ^{1}H NMR spectrum of AzeA/HTO(-COOH) in dmso-d_6

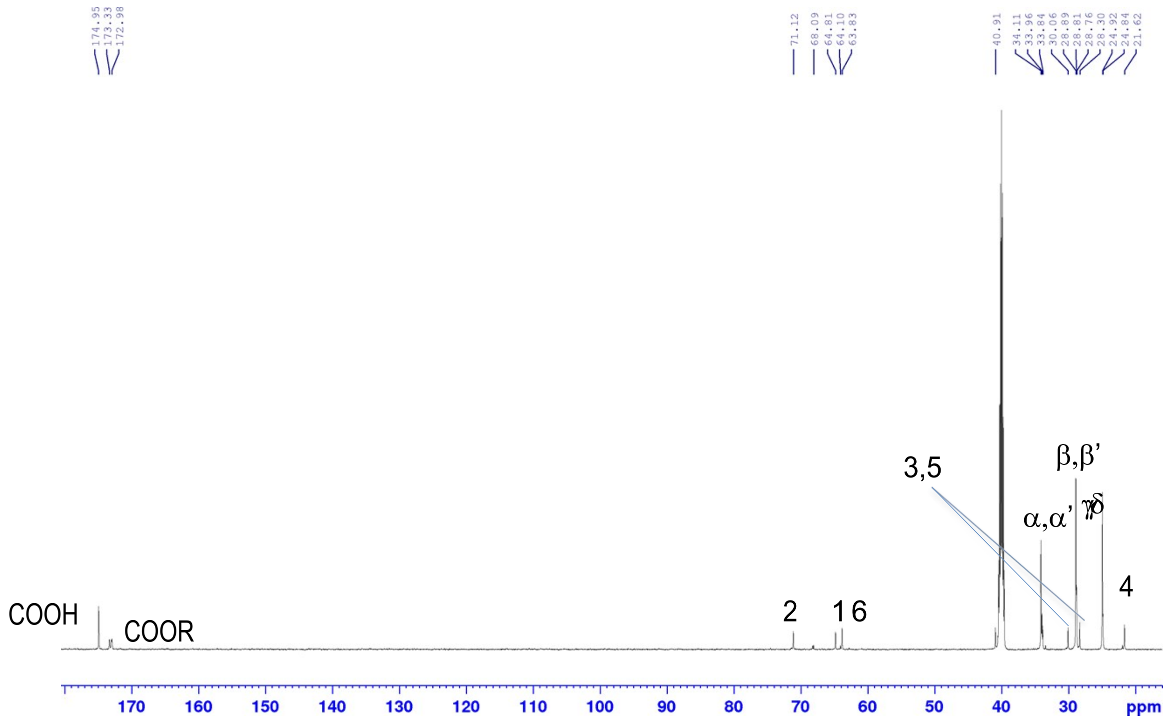


Figure S 27: ^{13}C NMR spectrum of AzeA/HTO(-COOH) in dmso-d$_6$

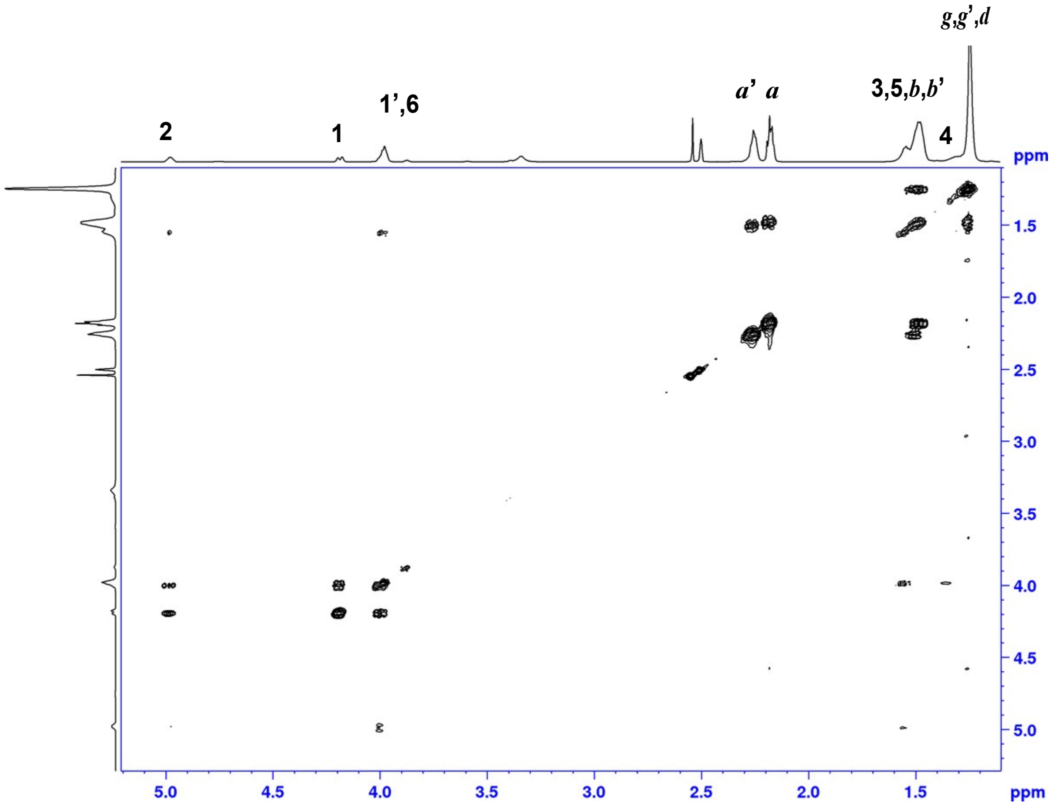


Figure S 28: COSY NMR spectrum of AzeA/HTO(-COOH) in dmso-d$_6$

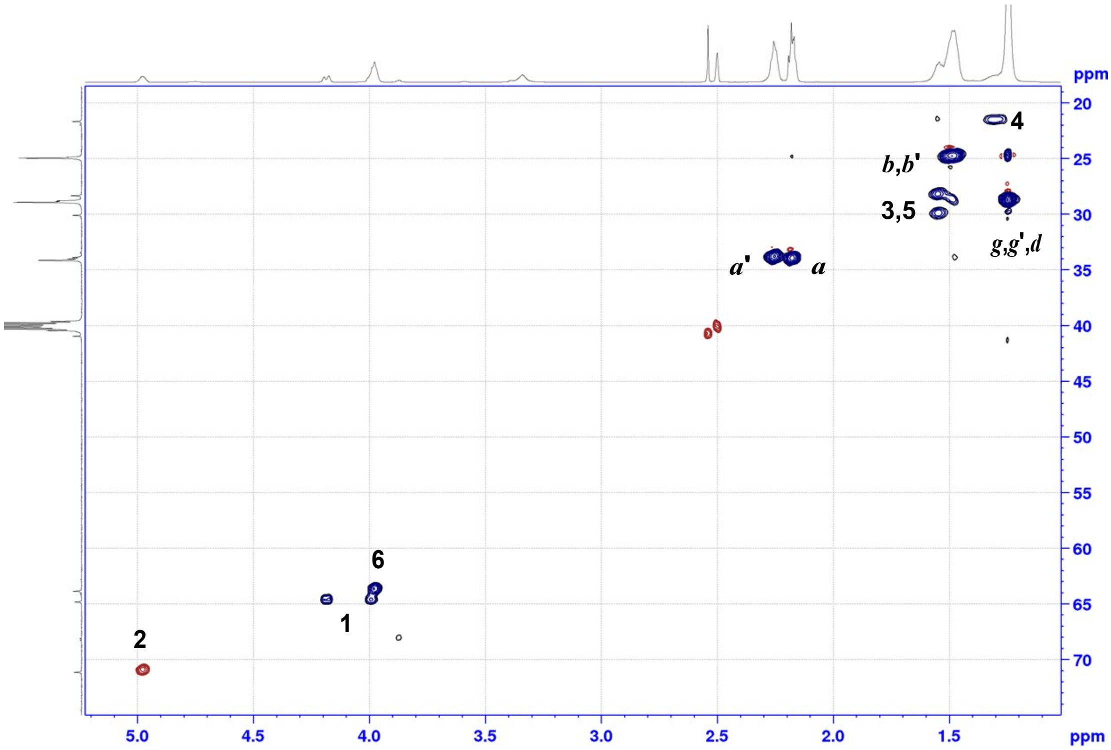


Figure S 29: HSQC spectrum of AzeA/HTO(-COOH) in dmso-d_6

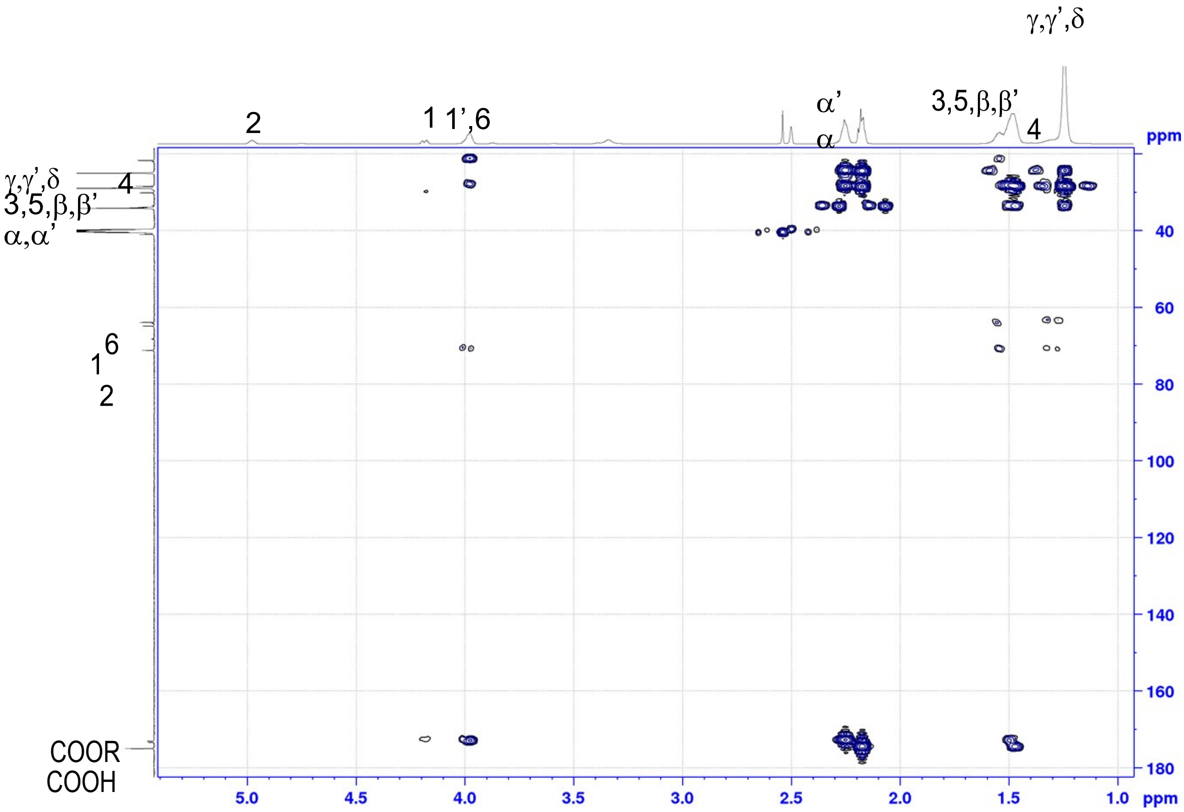


Figure S 30: HMBC NMR spectrum of AzeA/HTO(-COOH) in dsmo-d_6

hydroxyl terminated

SucA/BTO(-OH)

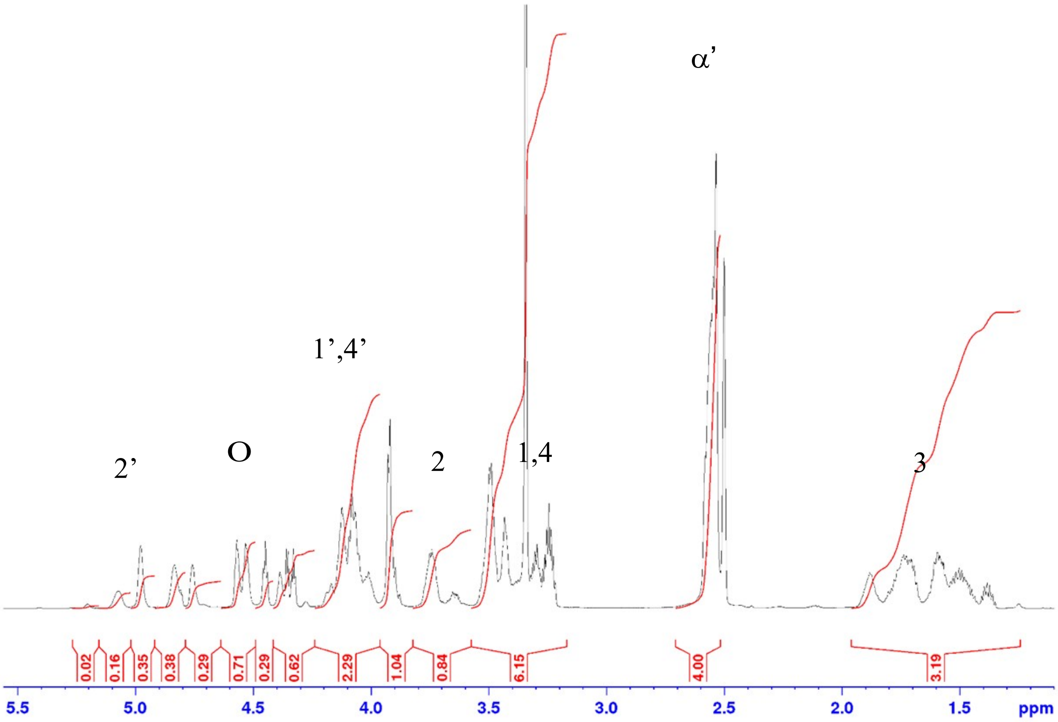


Figure S 31: [1]H NMR spectrum of SucA/BTO(-OH) in dmso-d_6

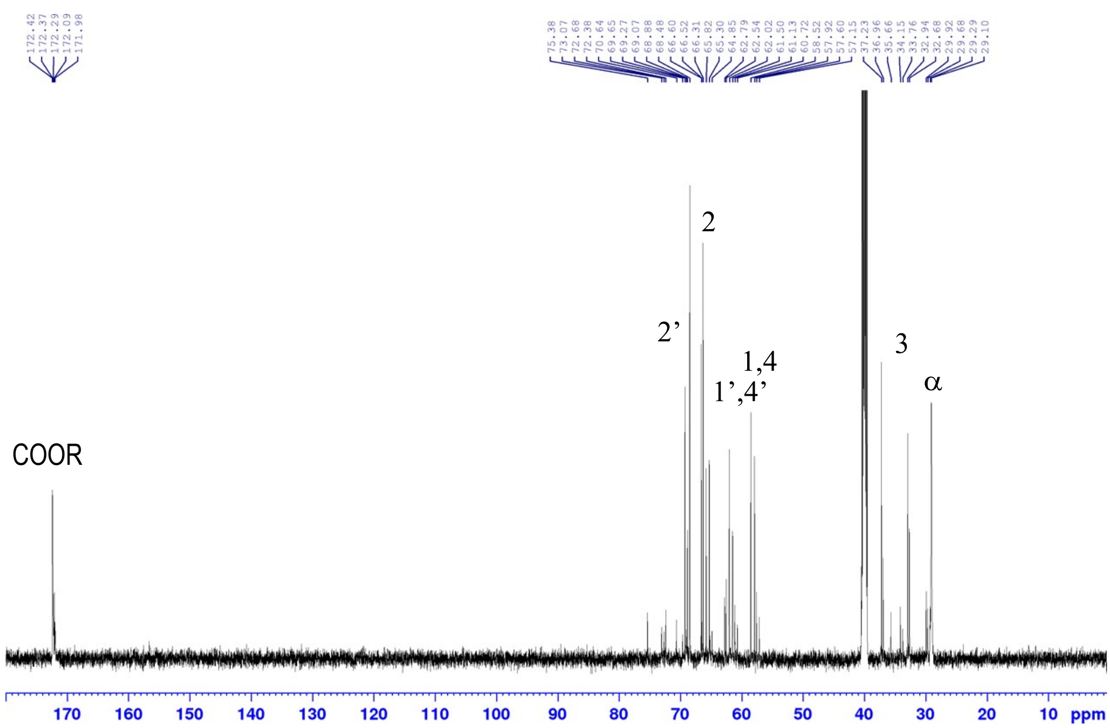


Figure S 32: ^{13}C NMR spectrum of SucA/BTO(-OH) in dmso-d_6

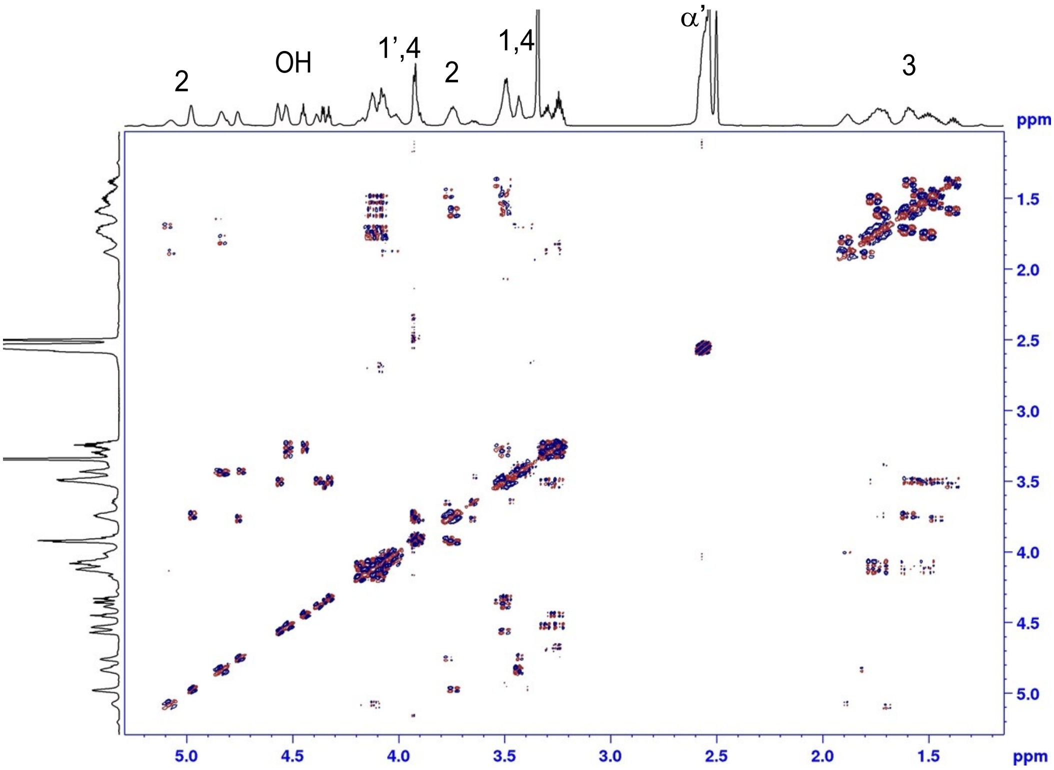


Figure S 33: COSY NMR spectrum of SucA/BTO(-OH) in dmso-d_6

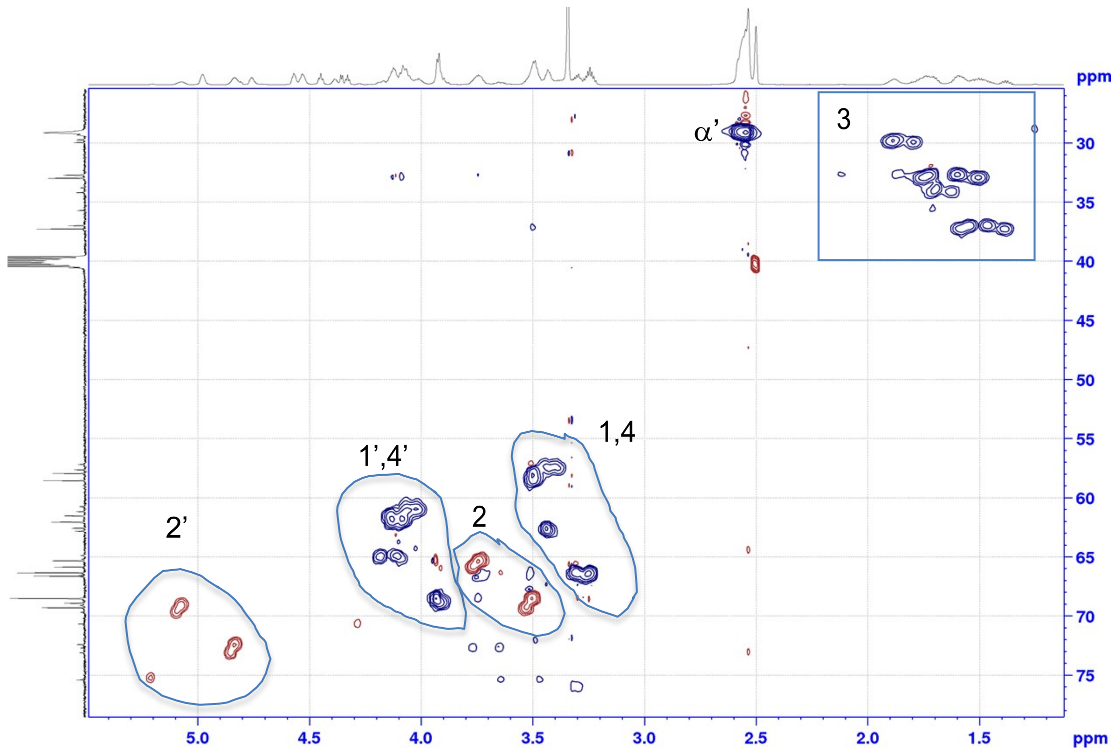


Figure S 34: HSQC NMR spectrum of SucA/BTO(-OH) in dmso-d_6

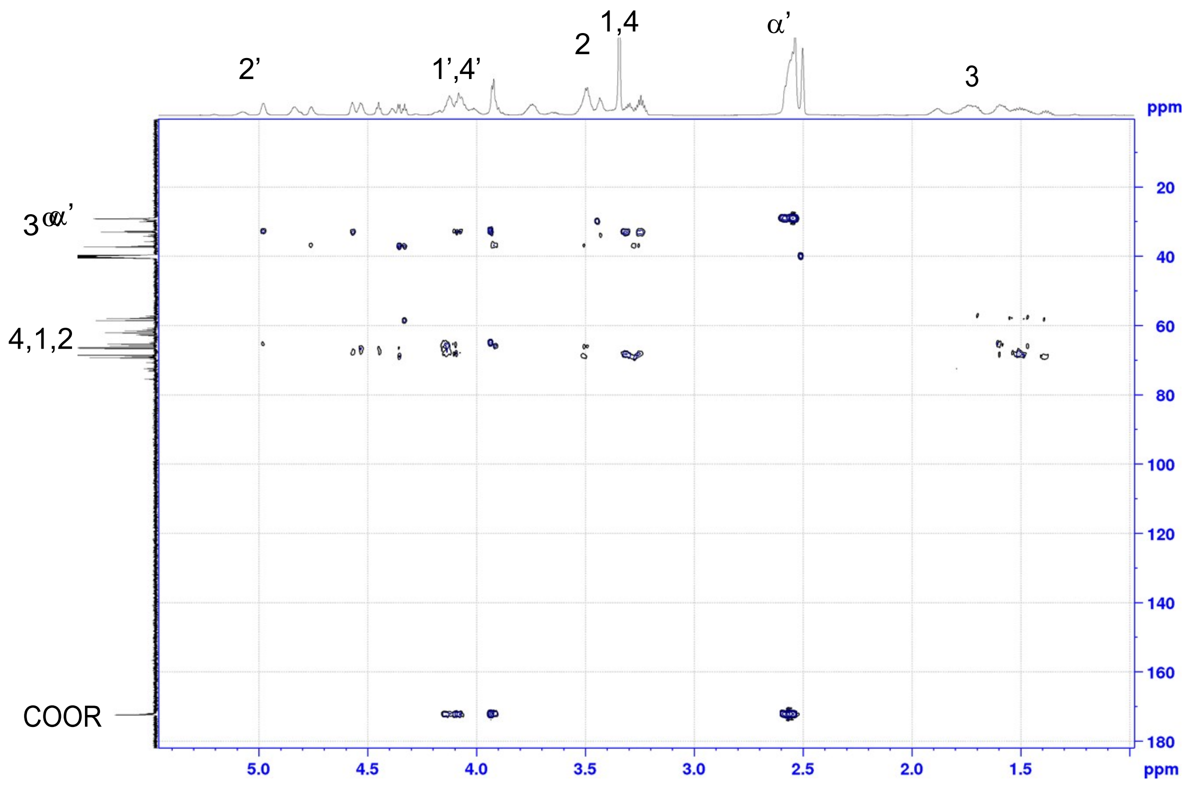


Figure S 35: HMBC NMR spectrum of SucA/BTO(-OH) in dmso-d_6

SucA/HTO(-OH)

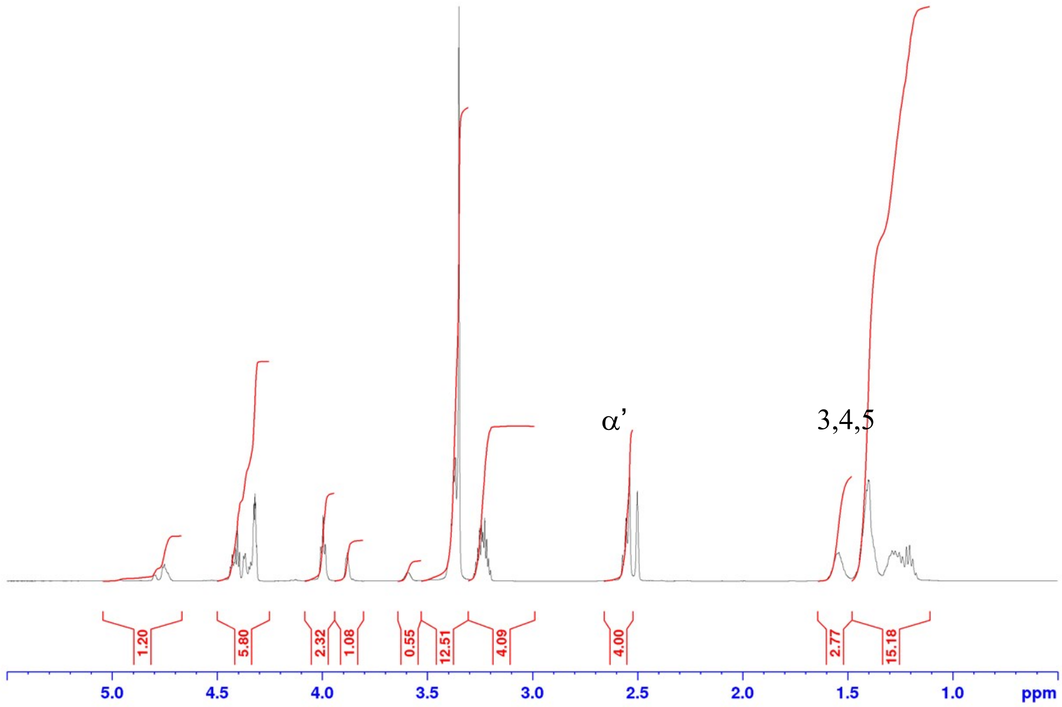


Figure S 36: ^{1}H NMR spectrum of SucA/HTO(-OH) in dmso-d_6

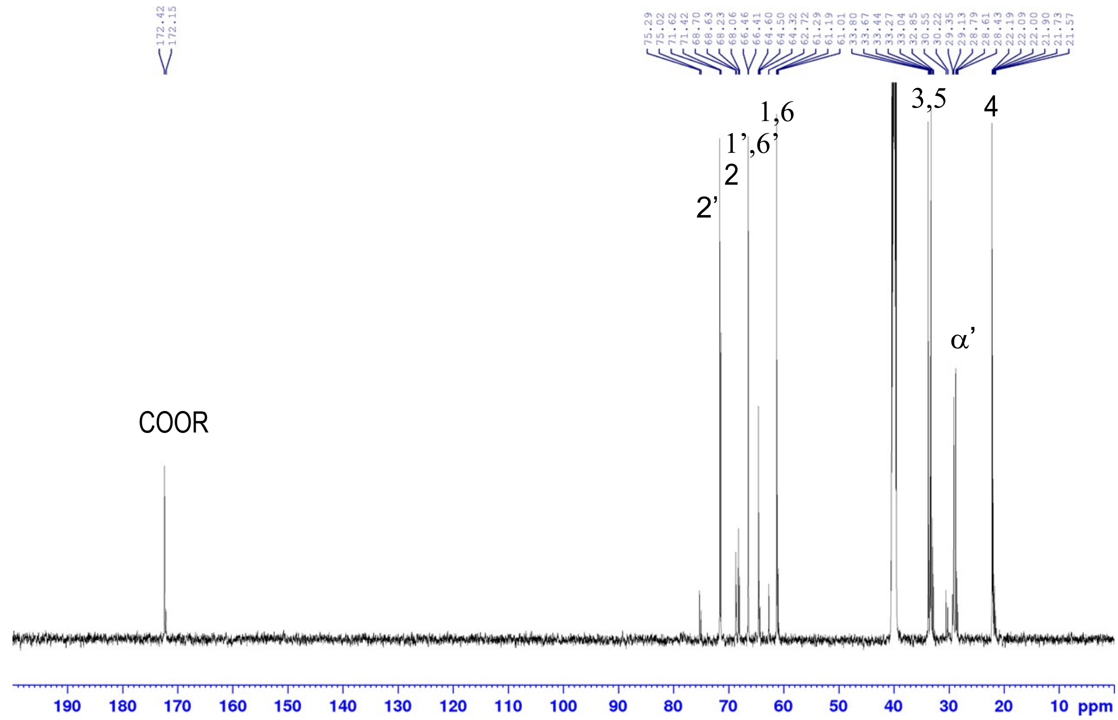


Figure S 37: ^{13}C NMR spectrum of SucA/HTO(-OH) in dmso-d_6

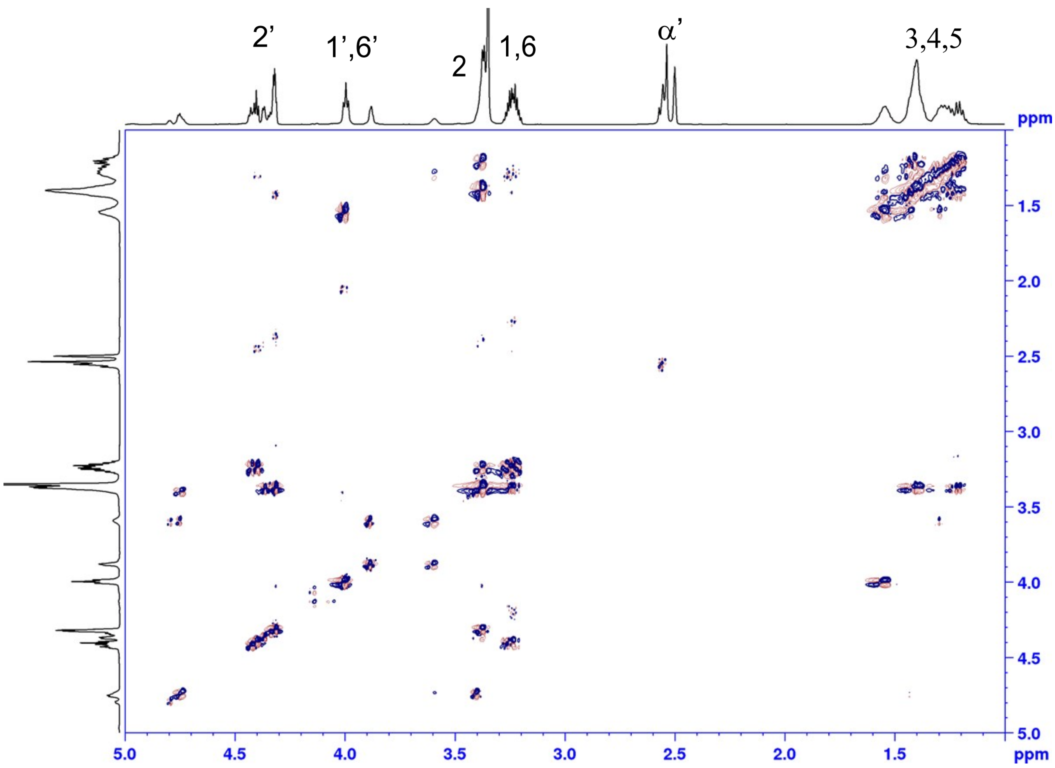


Figure S 38: COSY NMR spectrum of SucA/HTO(-OH) in dmso-d_6

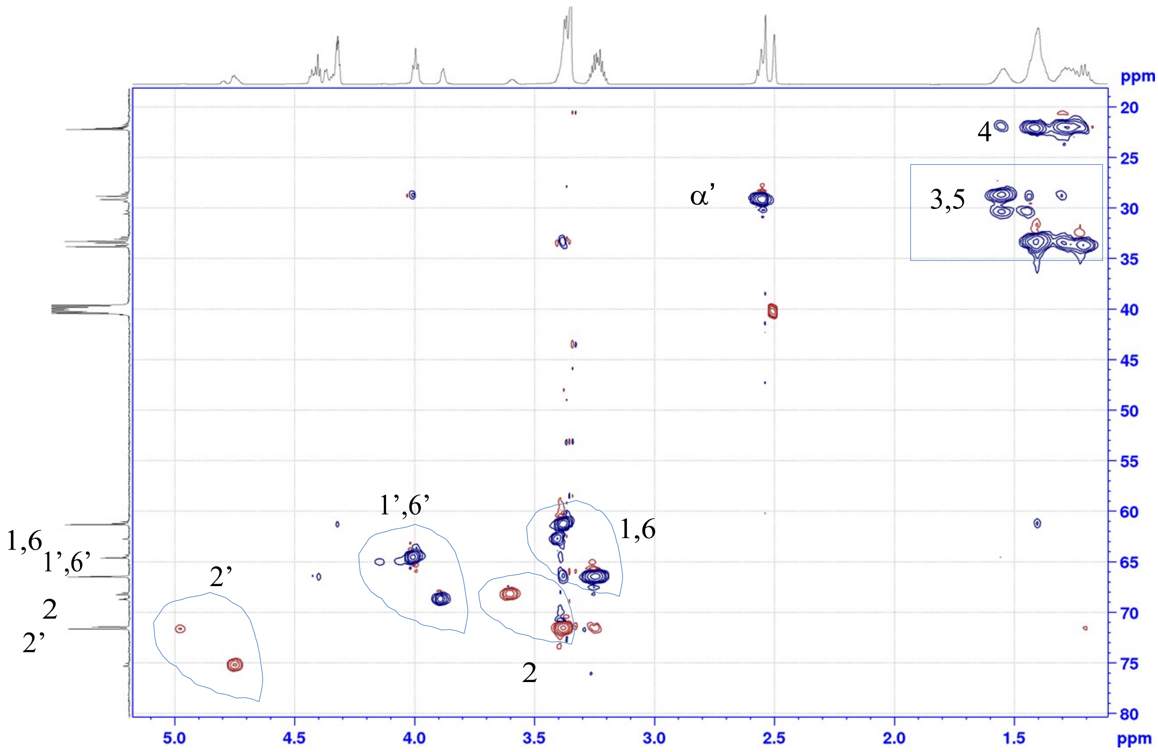


Figure S 39: HSQC NMR spectrum of SucA/HTO(-OH) in dmso-d_6

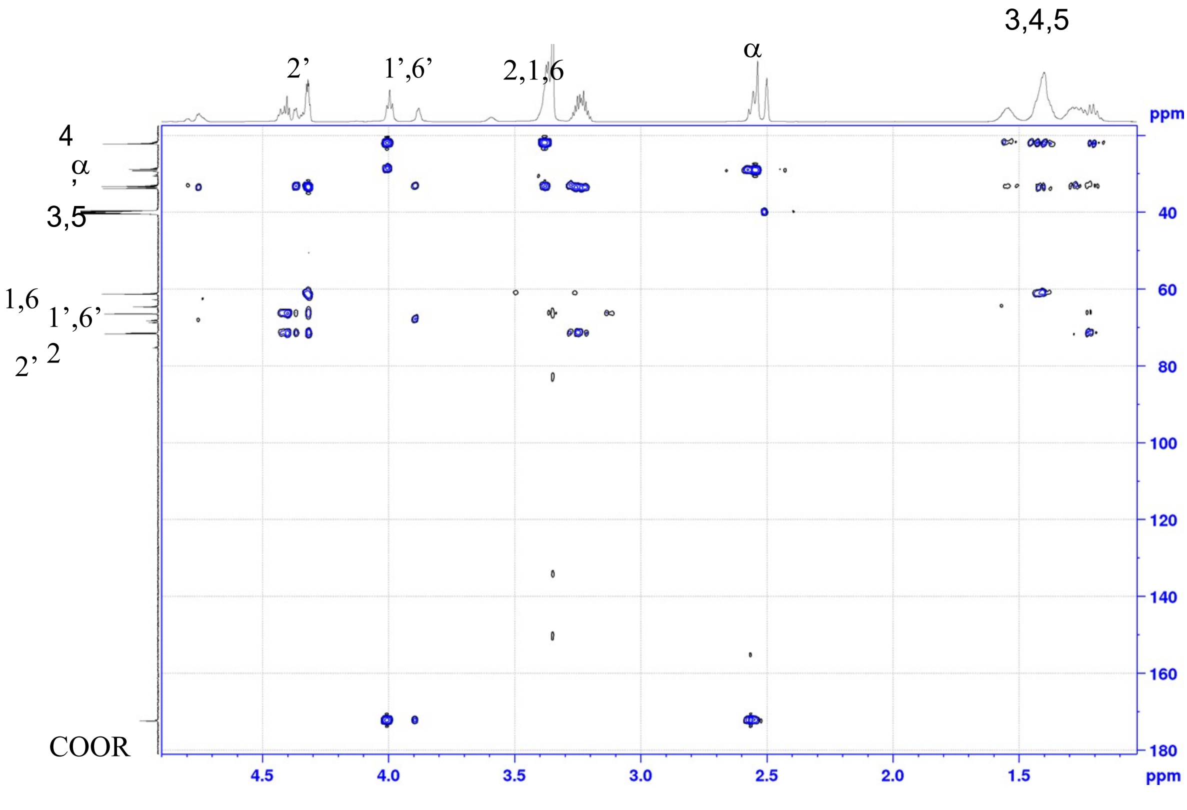


Figure S 40: HMBC NMR spectrum of SucA/HTO(-OH) in dmso-d_6

AdiA/BTO(-OH)

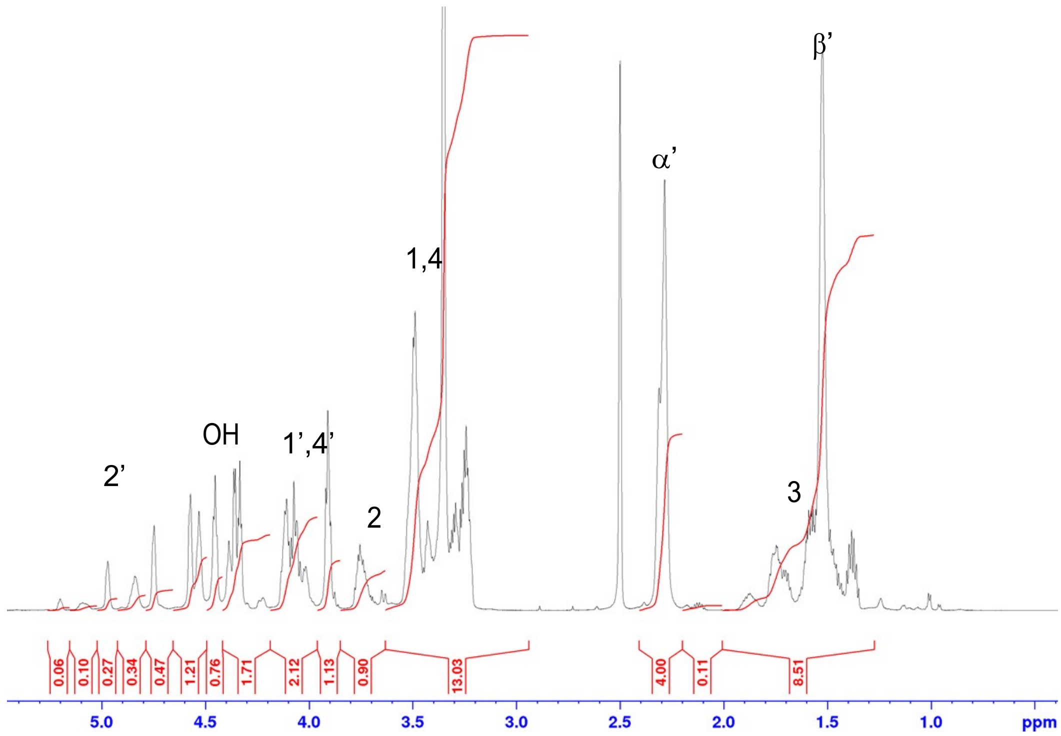


Figure S 41: ^{1}H NMR spectrum of AdiA/BTO(-OH) in dmso-d_6

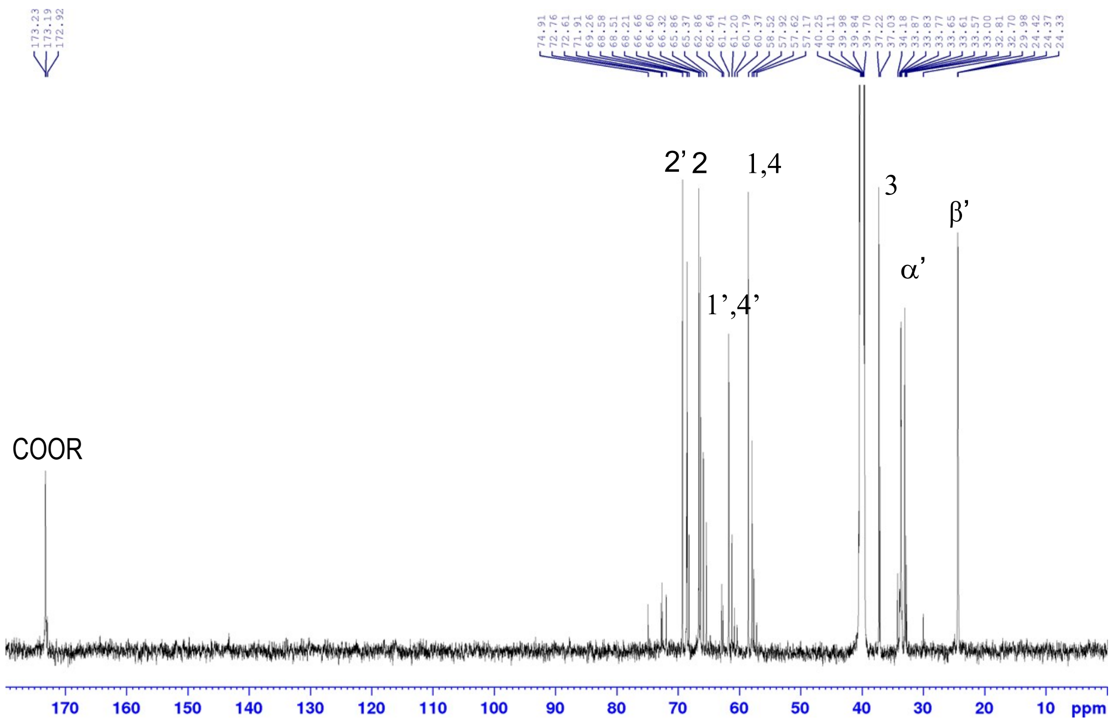


Figure S 42: ^{13}C NMR spectrum of AdiA/BTO(-OH) in dmso-d_6

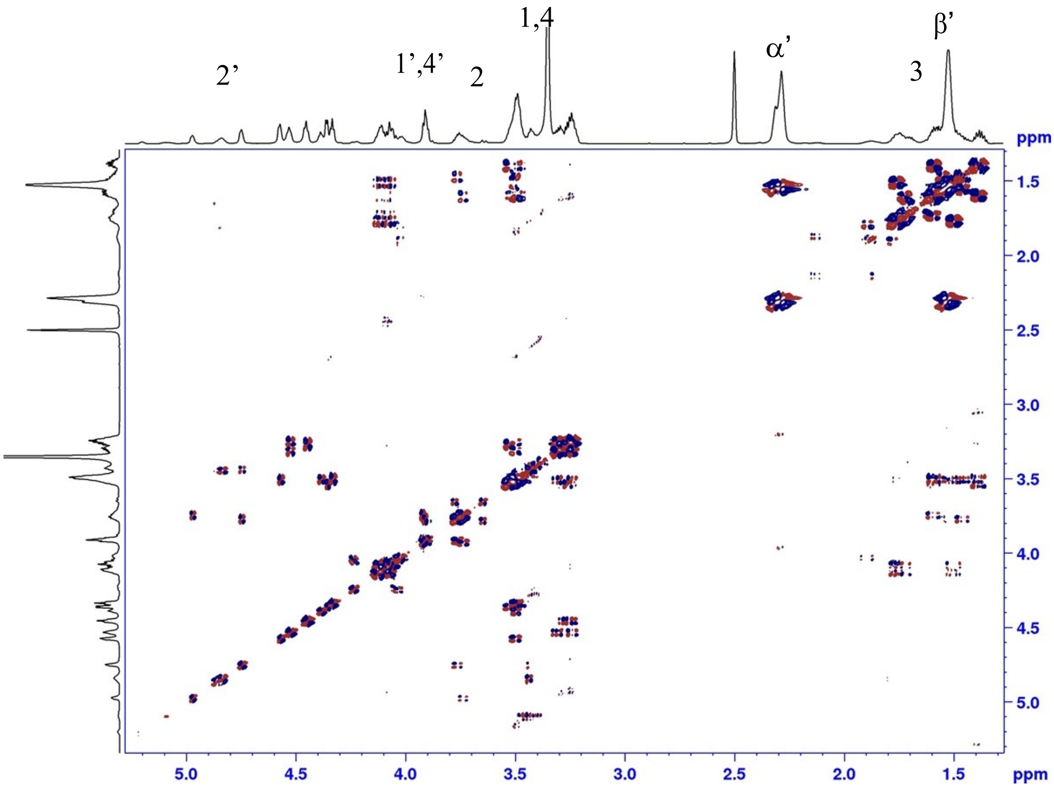


Figure S 43: COSY NMR spectrum of AdiA/BTO(-OH) in dmso-d_6

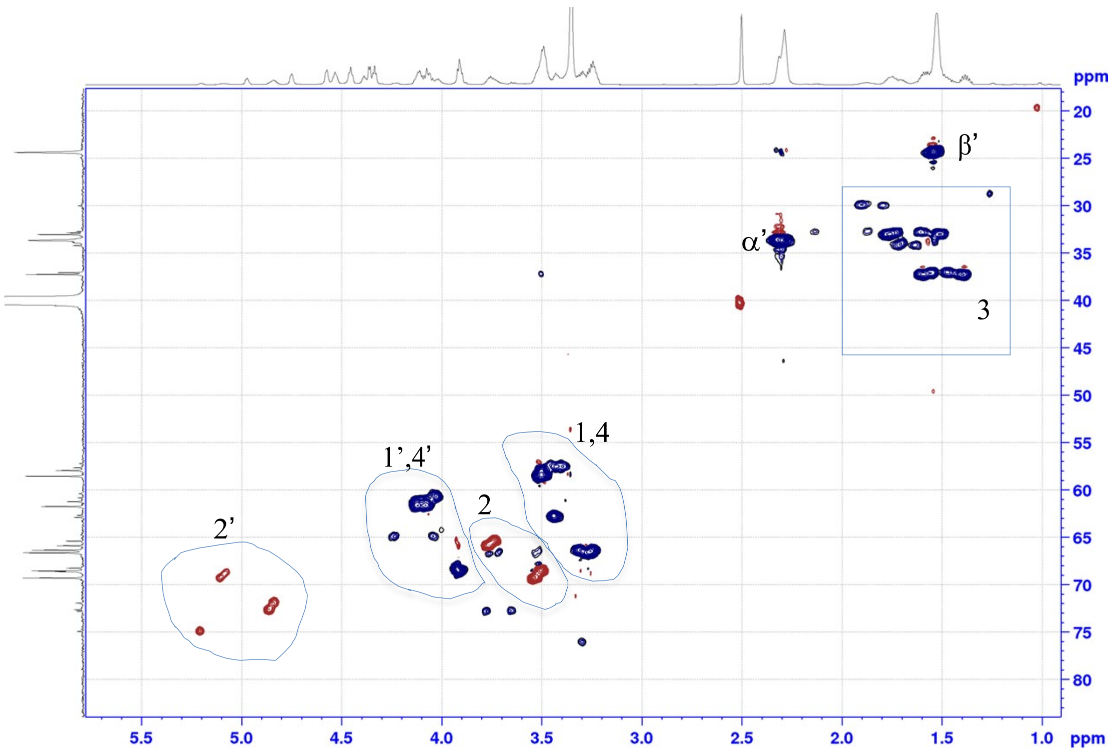


Figure S 44: HSQC NMR spectrum of AdiA/BTO(-OH) in dmso-d6

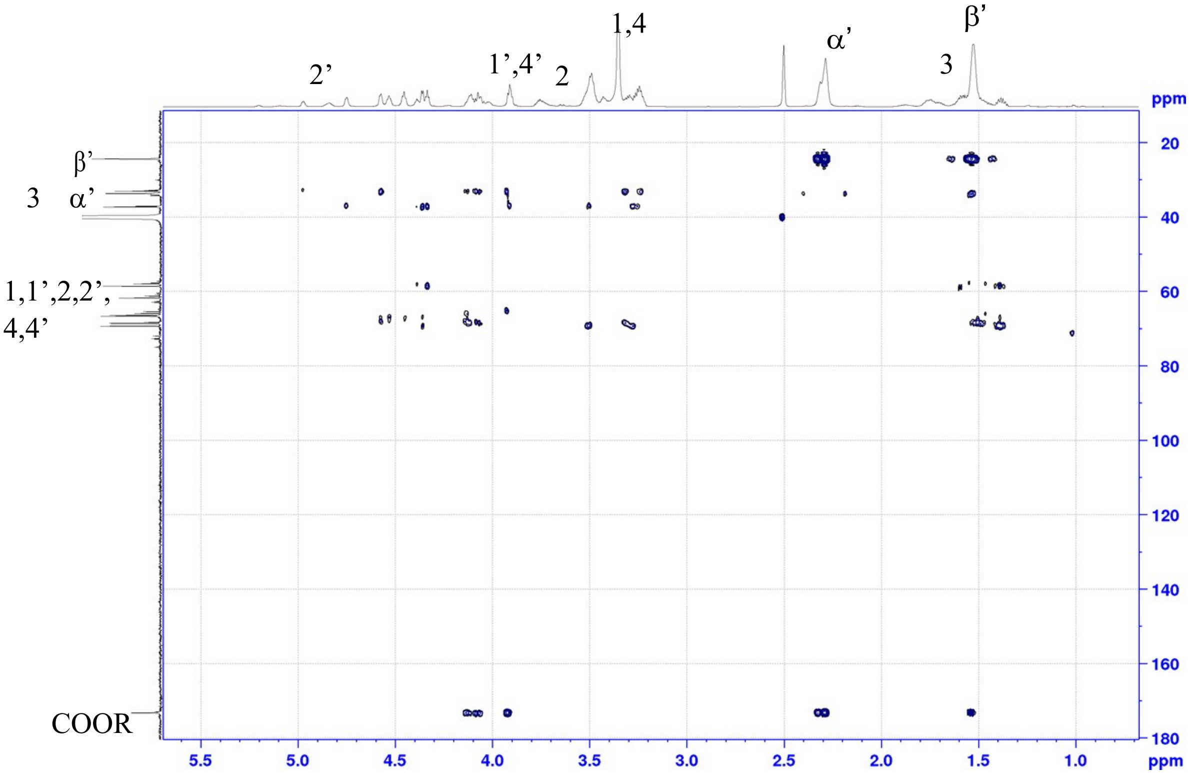


Figure S 45: HMBC NMR Spectrum of AdiA/BTO(-OH) in dmso-d_6

AdiA/HTO(-OH)

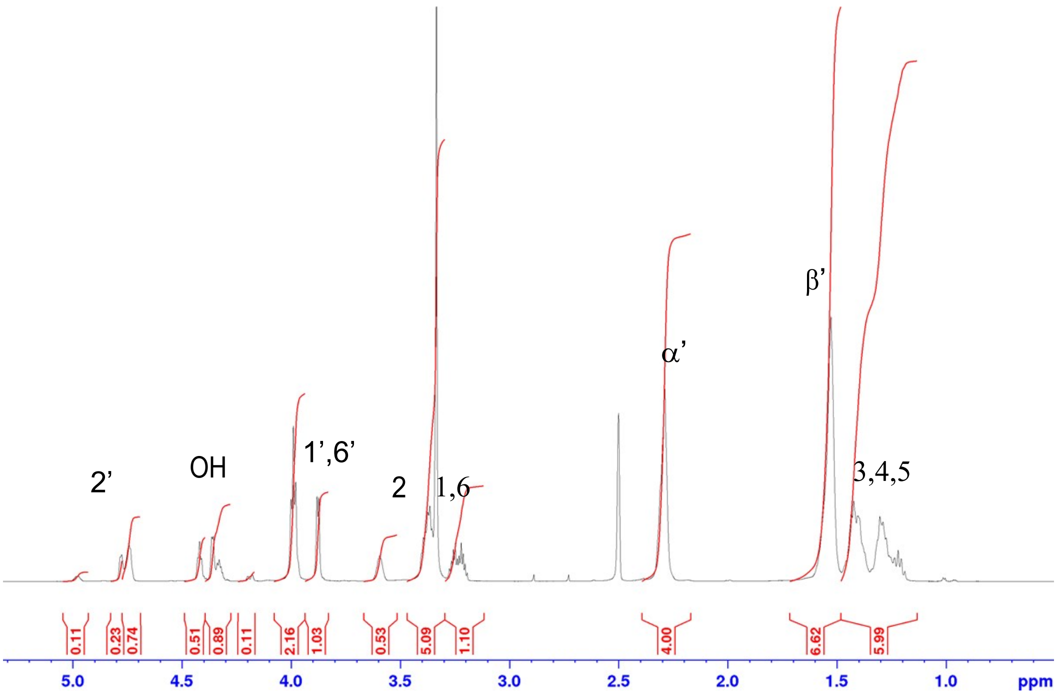


Figure S 46: ^{1}H NMR spectrum of AdiA/HTO(-OH) in dsmo-d_6

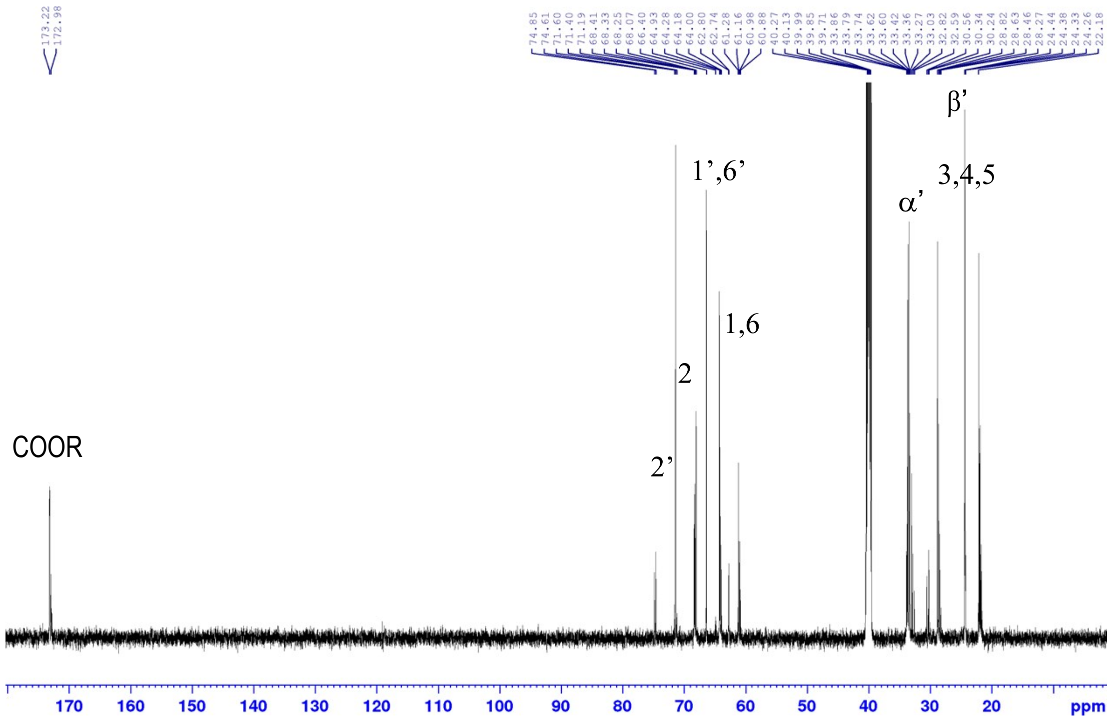


Figure S 47: ^{13}C NMR spectrum of Adi/HTO(-OH) in dmso-d_6

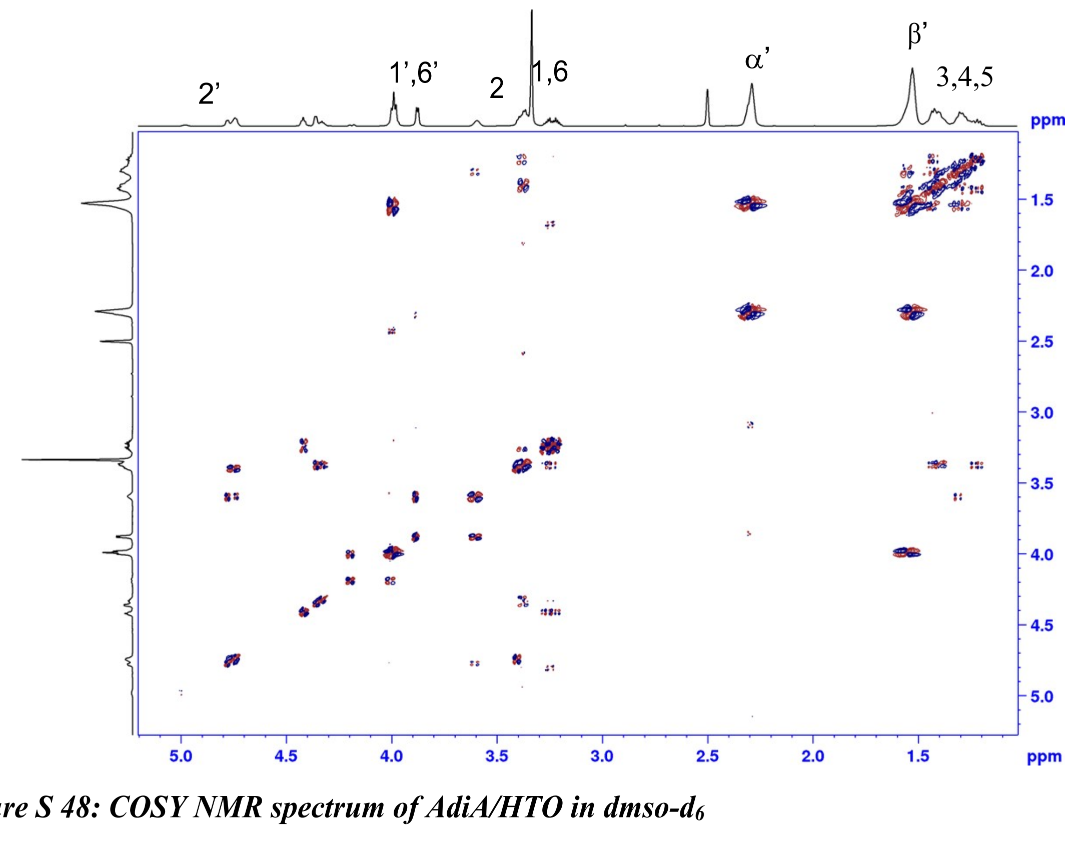


Figure S 48: COSY NMR spectrum of AdiA/HTO in dmso-d_6

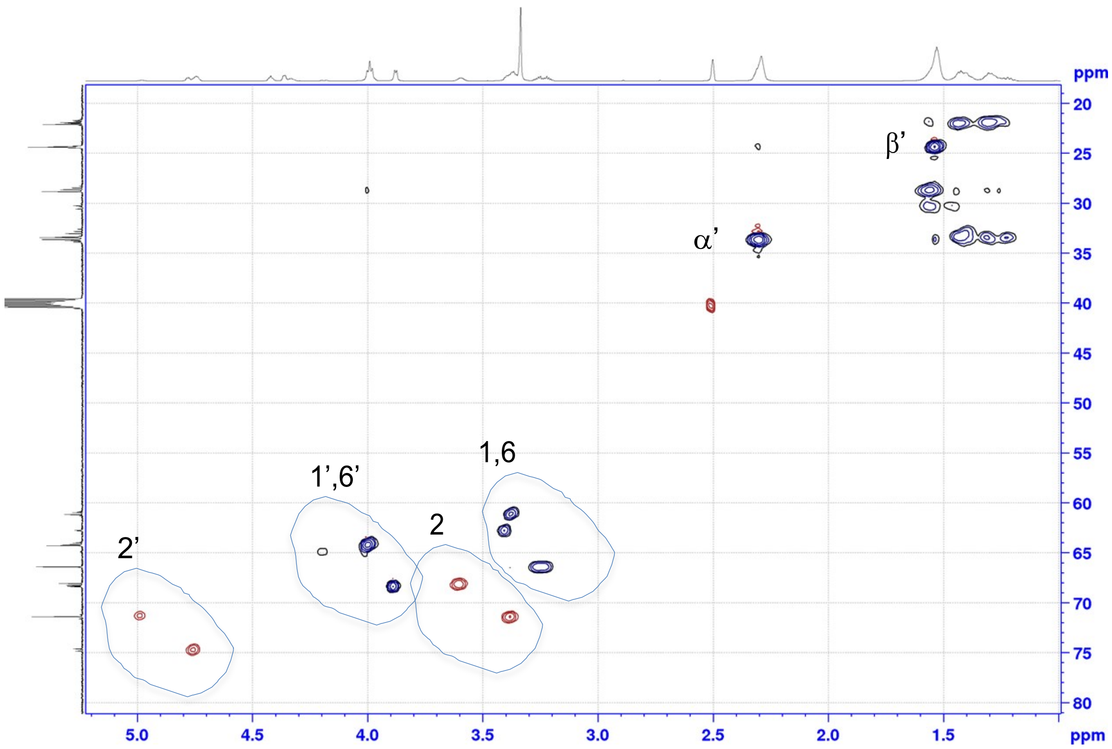


Figure S 49: HSQC NMR spectrum of AdiA/HTO(-OH) in dmso-d_6

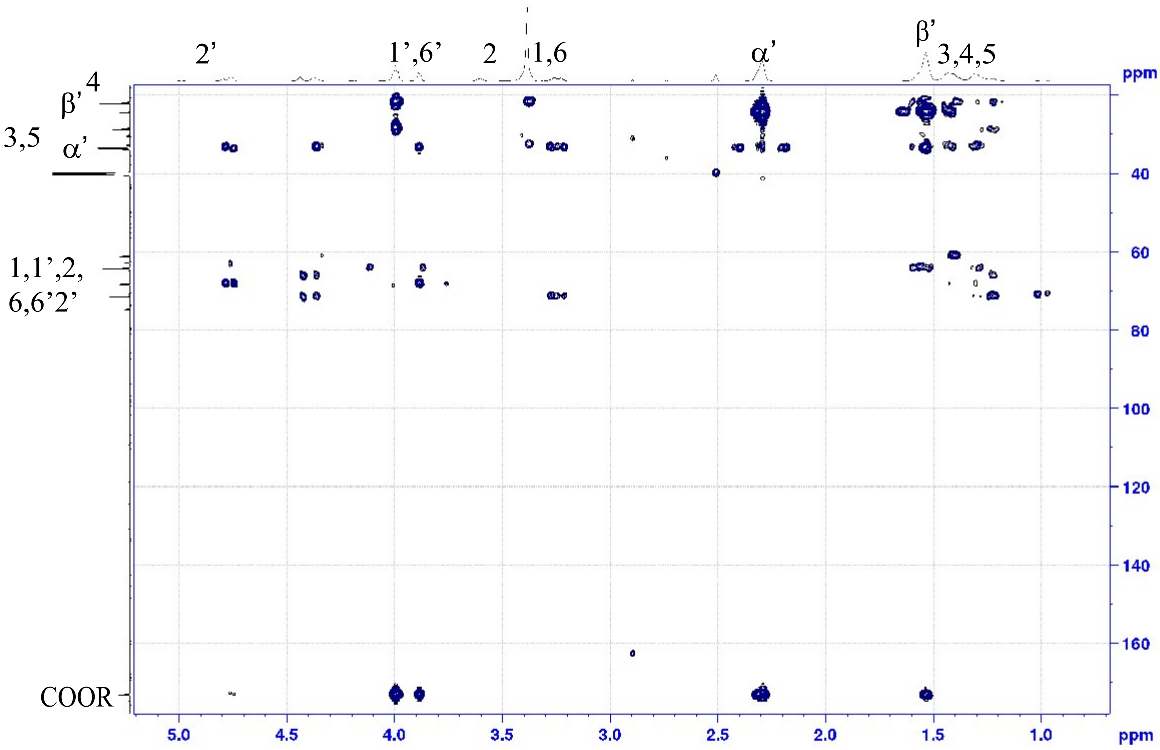


Figure S 50: HMBC NMR spectrum of AdiA/HTO(-OH) in dmso-d_6

AzA/BTO(-OH)

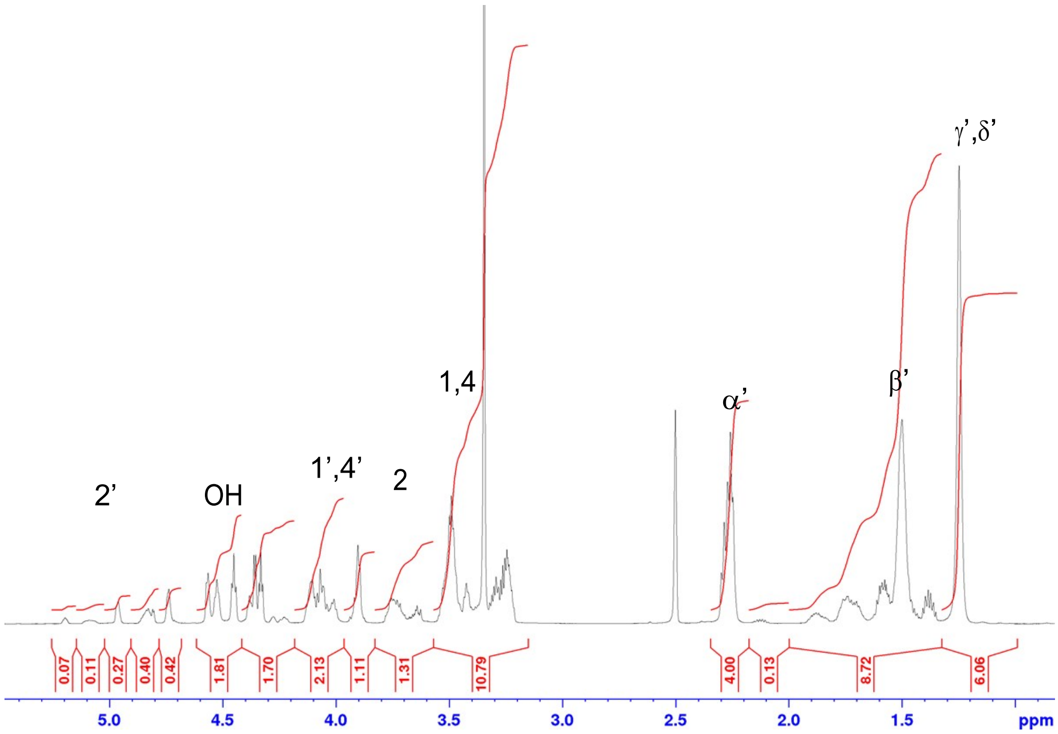


Figure S 51: ^{1}H NMR spectrum of AzeA/BTO(-OH) in dmso-d_6

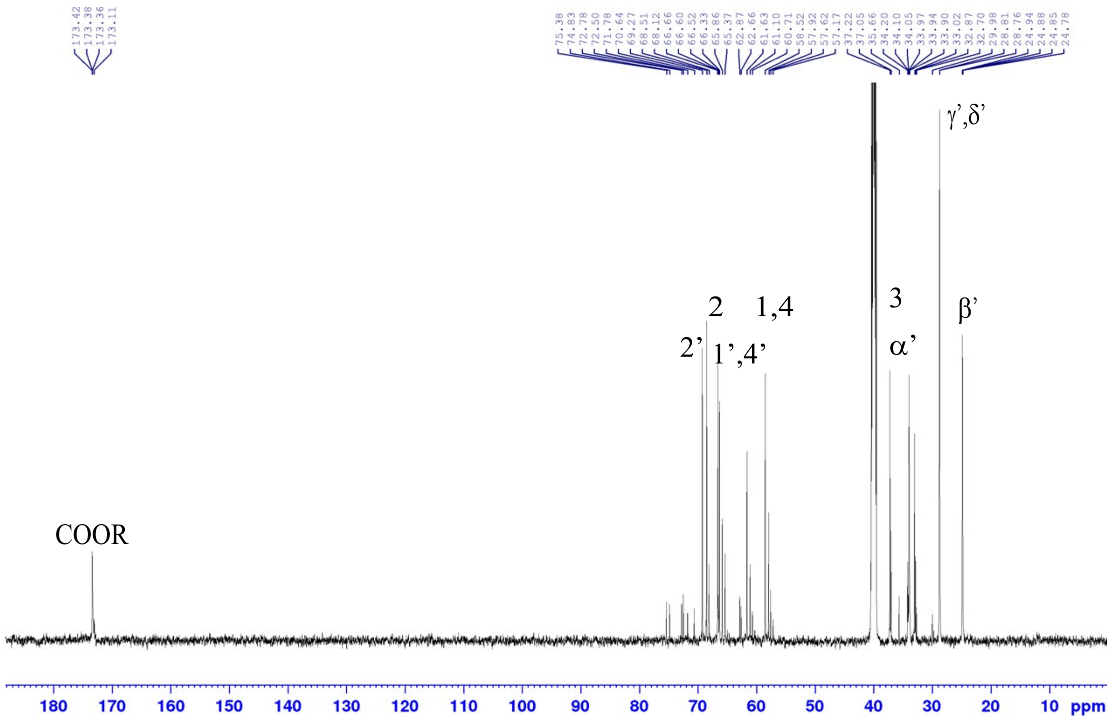


Figure S 52: ^{13}C NMR spectrum of AzeA/BTO(-OH) in dmso-d_6

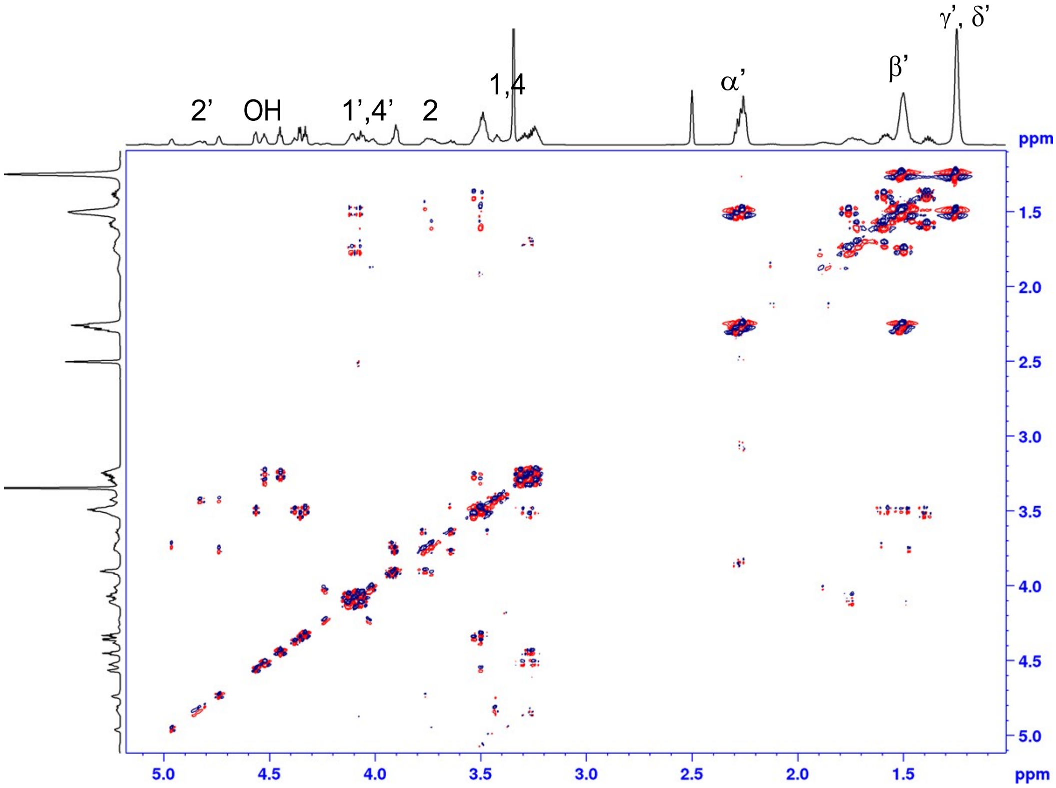


Figure S 53: COSY NMR spectrum of AzeA/BTO(-OH) in dmso-d_6

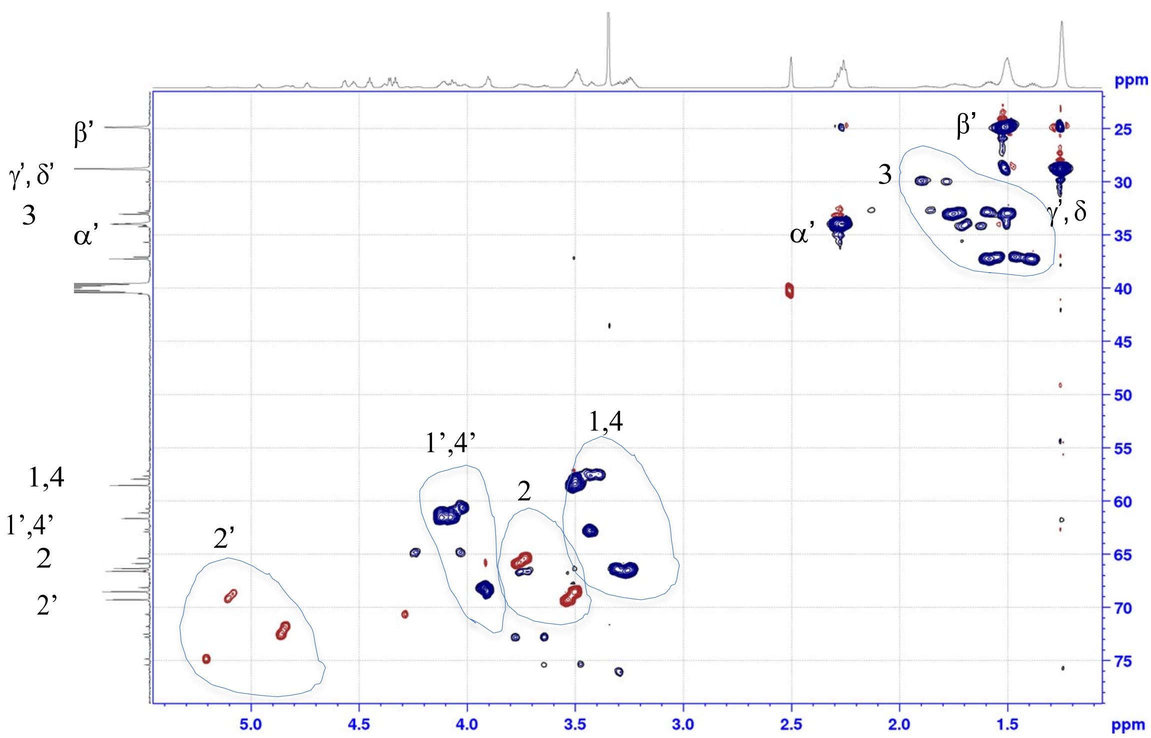


Figure S 54: HSQC NMR spectrum of AzeA/BTO(-OH) in dmso-d_6

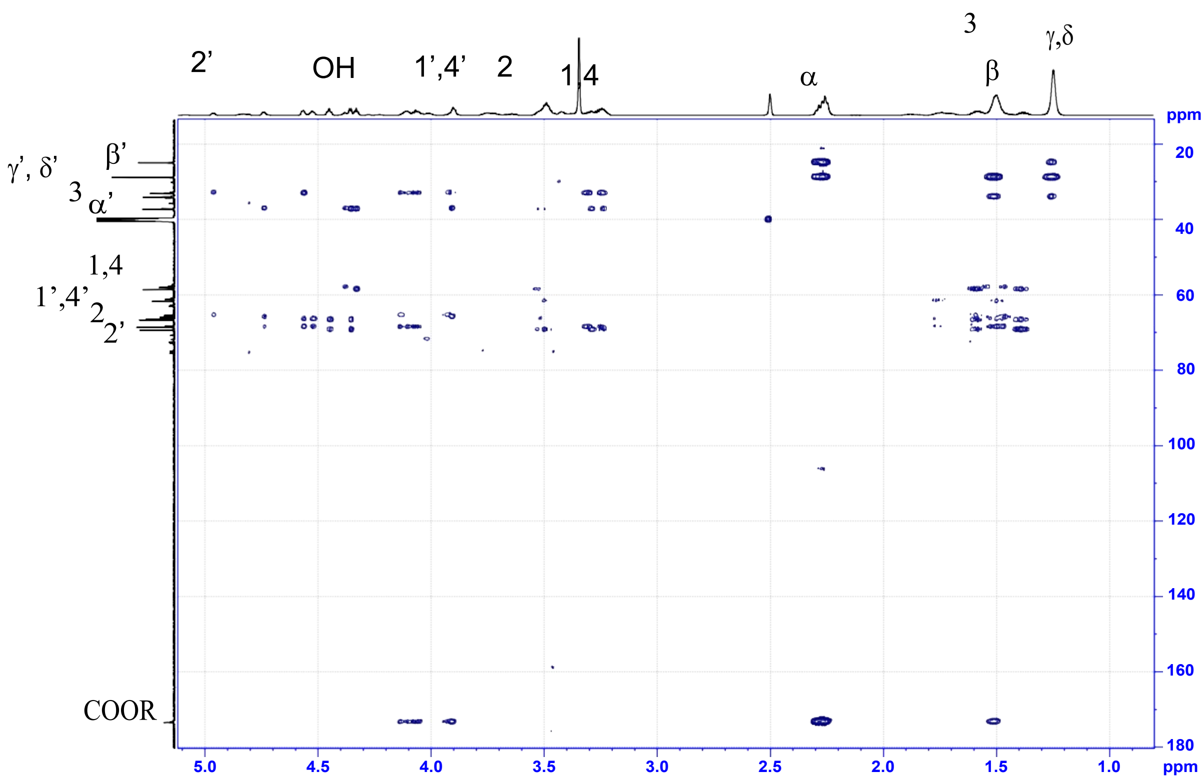


Figure S 55: HMBC NMR spectrum of AzeA/BTO(-OH) in dmso-d_6

AzeA/HTO(-OH)

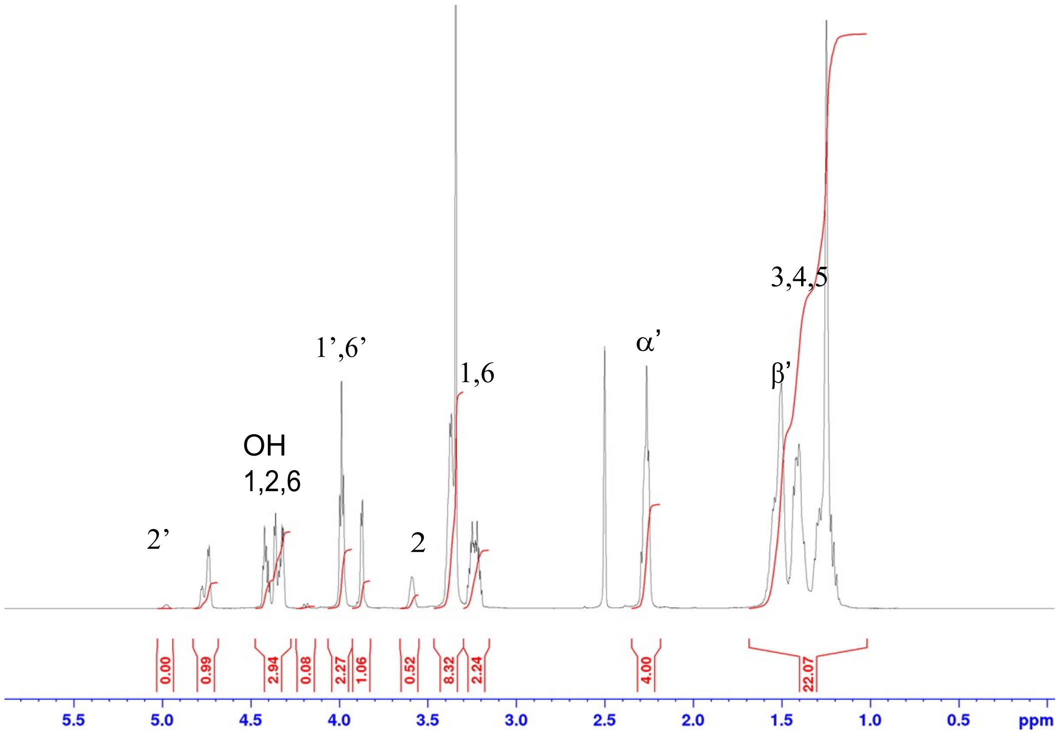


Figure S 56: ^{1}H NMR spectrum of AzeA/HTO(-OH) in dmso-d_6

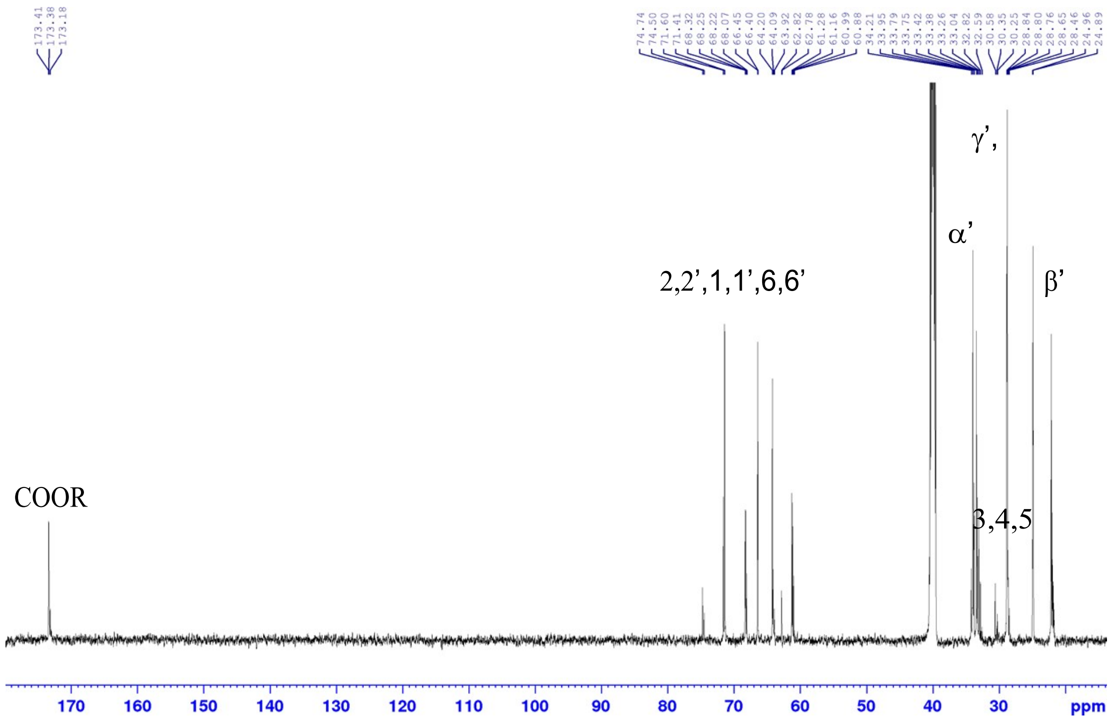


Figure S 57: ^{13}C NMR spectrum of AzeA/HTO in dmso-d_6

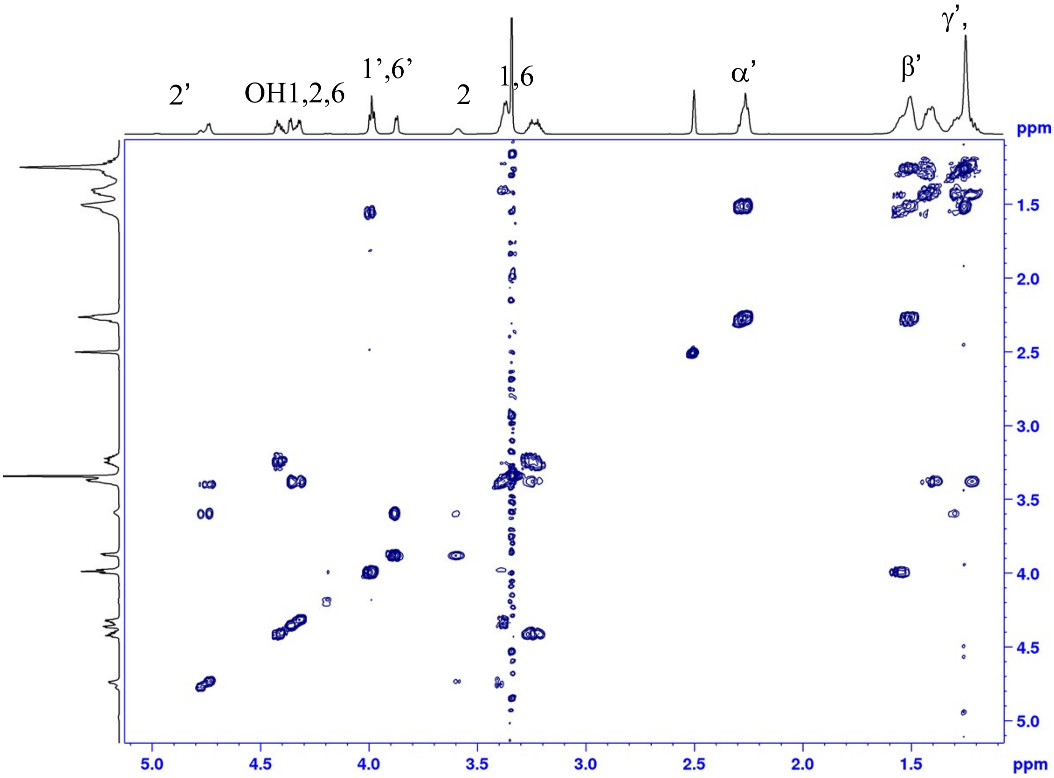


Figure S 58: COSY NMR spectrum of AzeA/HTO(-OH) in dmso-d_6

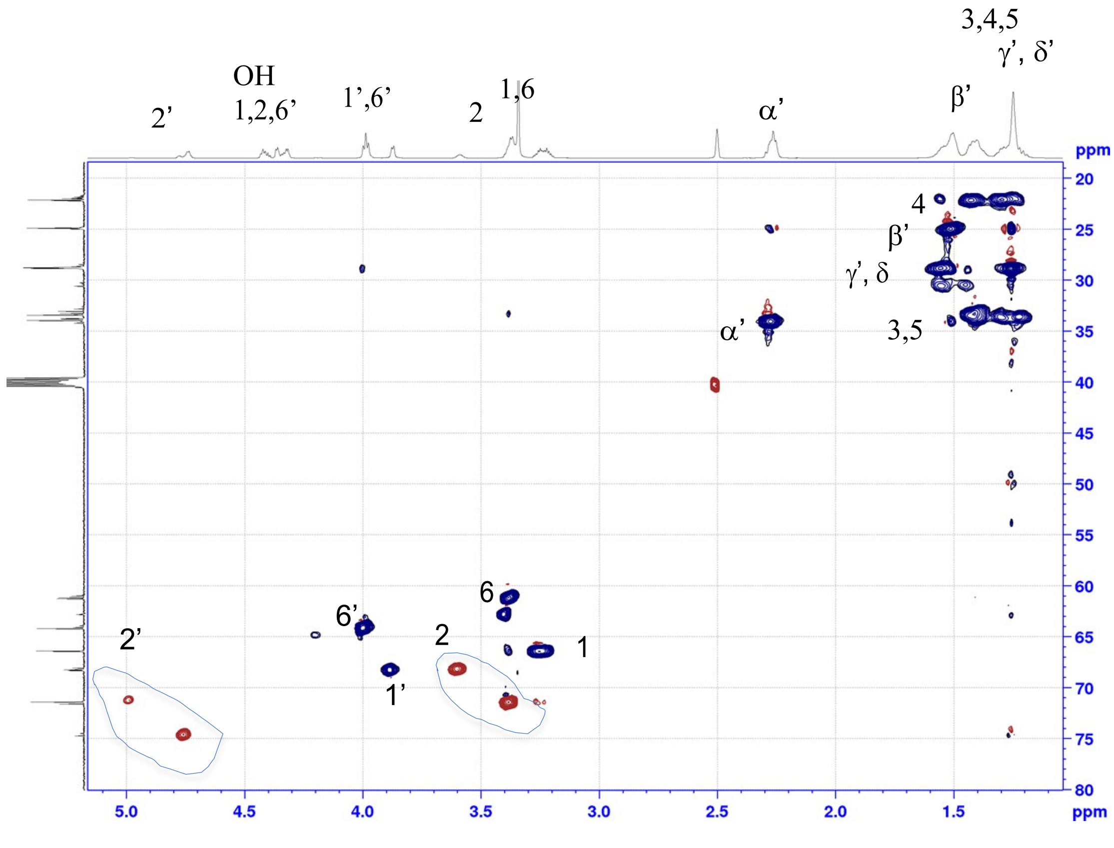


Figure S 59: HSQC NMR spectrum of AzeA/HTO(-OH) in dmso-d_6

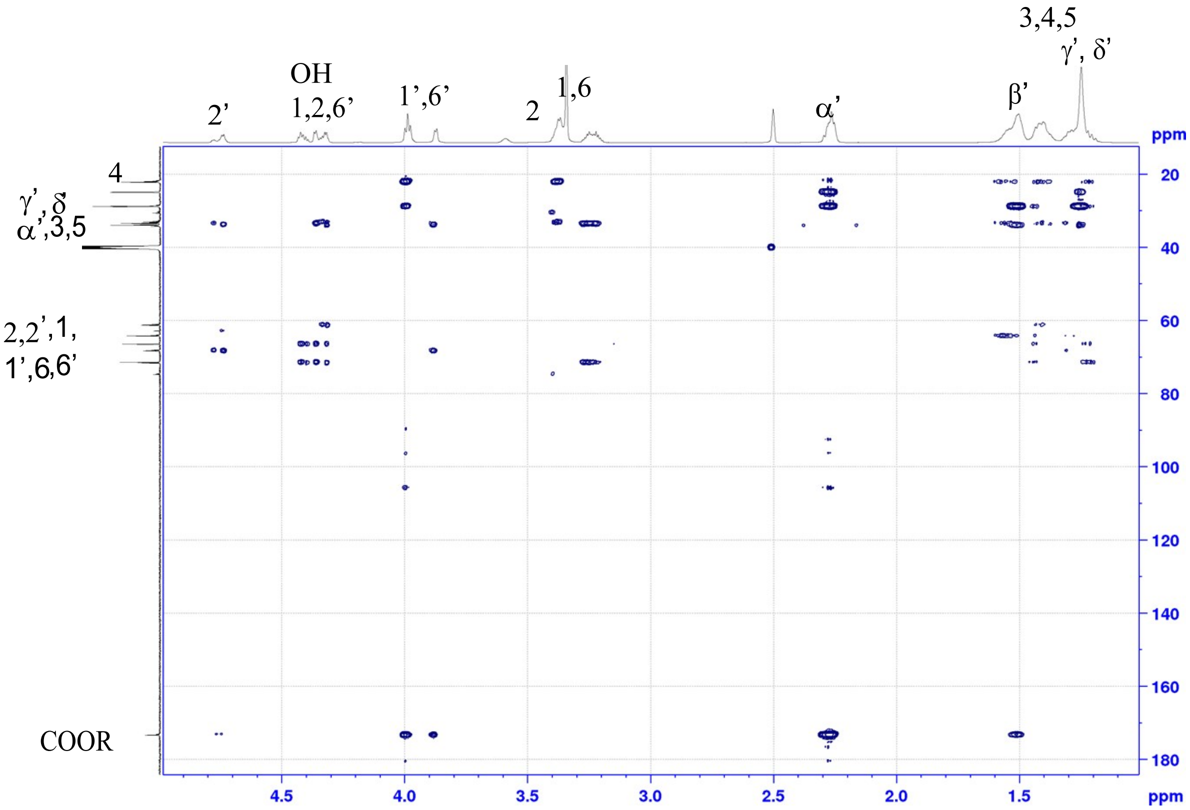


Figure S 60: HMBC NMR spectrum of AzeA/HTO(-OH) in dmso-d_6

Table S1: ^{1}H NMR chemical shifts of acid-ended branched polyesters in DMSO-d_6 (major peaks only). Ranges indicate regions where multiple peaks are found. (*: Chemical shifts read from HSQC; ** not observed)

Compound	1'	2'	3	4	4'	5	6'	□	□'	□□'	□'□ □'	COOH
SucA/BTO (-COOH)	4.15	5.03	1.88		4.05			2.48	2.55			12.29
SucA/HTO (-COOH)	4.13,4.06*	4.98	1.55	1.30		1.55	3.99	2.48	2.55			**
AdiA/BTO (-COOH)	4.23,4.05*	5.08	1.88		4.04			2.21	2.29	1.51		12.01
AdiA/HTO (-COOH)	4.18,4.01*	4.99	1.56	1.31		1.56	3.98	2.20	2.28	1.51		12.01
AzeA/BTO (-COOH)	4.23,4.04*	5.08	1.87		4.03			2.18	2.25	1.49	1.25	11.95
AzeA/HTO (-COOH)	4.18,3.99*	4.98	1.55	1.3		1.55	3.98	2.17	2.26	1.48	1.25	11.95

Table S2: ^{13}C NMR chemical shifts of acid-ended branched polyesters in DMSO-d_6. Ranges indicate regions where multiple peaks are found. (** not observed)

Compound	1'	2'	3	4	4'	5	6'	□□□'	□□□'	□'□ □'	COOH	COOR
SucA/BTO (-COOH)	64.91	69.13	29.70		60.74			29.08			173.82	171.8-172.5
SucA/HTO (-COOH)	65.1	71.5	28.2	21.6		30.0	64.4	29.06-29.15			**	**
AdiA/BTO (-COOH)	63.6-69.0	64.4-72.5	29.80		59.7-63.5			33.4-33.9	24.0-24.6		174.73	172.5-173.2
AdiA/HTO (-COOH)	64.84	71.16	28.26	21.56		30.02	63.89	33.1-34.0	24.0-24.7		174.71	172.7-173.2
AzeA/BTO (-COOH)	61.6-69.1	64.1-72.5	29.80, 32.91		59.9-61.9			33.77-34.0	24.84	28.7-28.85	174.92	172.7-173.4
AzeA/HTO (-COOH)	62.8-68.5	67.7-74.8	30.09	21.64		28.34	63.84	33.77-34.1	24.9	28.8	174.92	172.8-173.4

Table S3: ^{1}H NMR chemical shifts of OH-ended branched polyesters in DMSO-d_6. Ranges indicate regions where multiple peaks are found. (*: Chemical shifts read from HSQC; ** not observed; *** OH group signals are observed at 4.98 (m), 4.76 (m), 4.58(m), 4.54(t), 4.46(t), 4.40(t), 4.37(d), 4.34(t))

Compound	1	1OH	1'	2	2OH	2'	3	4	4OH	4'	5	6'	6	6OH	□'	□'	□'□ □'
SucA/BTO(-OH)	3.2-3.5		3.87-4.21	3.47-3.8		4.8-5.2	1.35-1.93	3.2-3.5		3.87-4.21					2.5-2.6		
SucA/HTO(-OH)	3.24		3.88	3.34-3.63		4.71-5.00	1.55	1.28,1.41			1.18-1.44	4.00	3.34-3.42				
AdiA/BTO(-OH)	3.21-3.54	***	3.88-4.25	3.48-3.79	***	4.82-5.22	1.38-1.94	3.21-3.54	***	3.88-4.25					2.29-2.31	1.53	
AdiA/HTO(-OH)	3.24	4.41	4.21-3.86	3.35-3.63	4.36	4.72-5.01	1.56	1.20,1.43				4.21-3.86	3.35-4.43	4.33	2.29	1.53	
AzeA/BTO(-OH)			3.90	3.46-3.79		4.8-5.20				4.0-4.1							
AzeA/HTO(-OH)	3.25		3.88 [illegible]	3.3-3.6		5.0	1.45	4.7- 1.19-			1.54	3.99			2.27	1.51	1.25

Table S4: ^{13}C NMR chemical shifts of OH-ended branched polyesters in DMSO-d_6. Ranges indicate regions where multiple peaks are found.

Compound	1	1'	2	2'	3	4	4'	5	6'	6	□'	□'	□'□ □'	COOR
SucA/BTO (-OH)	56.9-67.1	60.1-69.5	64.6-69.8	68.3-75.7	29.2-37.7	56.9-67.1	60.1-69.5				29.14			171.8-172.5
SucA/HTO (-OH)	66.43-66.46	68.60-68.75	68.0-71.6	71.4-75.3	32.89-33.9	28.53-29.41		21.56-22.23	64.21-64.62	60.91-62.73				
AdiA/BTO (-OH)	57.2-66.66	60.2-69.2	65.35-69.39	68.58-74.94	29.8-37.4	57.2-66.66	60.2-69.2				33.65	24.38		172.9-173.25
AdiA/HTO (-OH)	66.3	63.8-68.5-	67.9-71.7	71.16-74.90	32.61-34.50	21.59-22.22		28.32-28.85	63.8-68.5-	60.7-60.1	33.58-33.90	24.30-24.48		172.9-173.3
AzeA/BTO (-OH)		68.1-68.7	65-69.3	68.0-75.2		60.2-61.8								172.8-173.2
AzeA/HTO(-OH)	66.41-66.47	66.6-66.8	67.7-72	71.2-75.7	32.6-34.0	21.65-22.45		28.7	64.2-64.6		33.78-34.25	24.88-24.99	28.5-28.9	173.09-173.44