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Supplementary Material

Design of acyl donor for environmental benign acylation of cellulose using an ionic liquid

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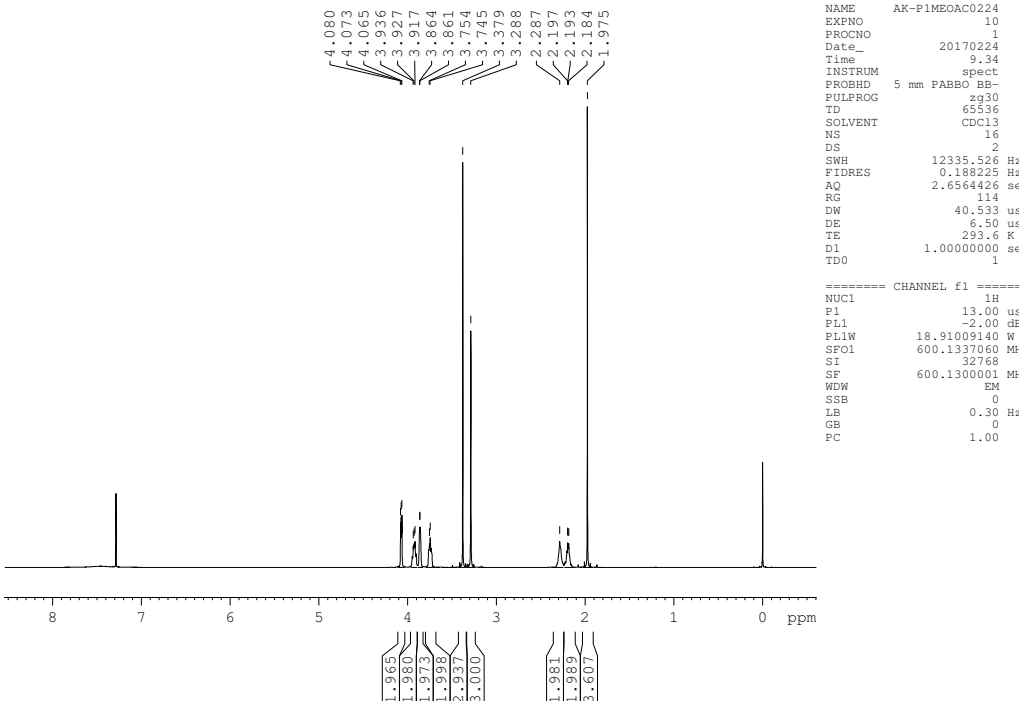


Figure S1-1: ^{1}H NMR of [P_{1ME}][OAc]

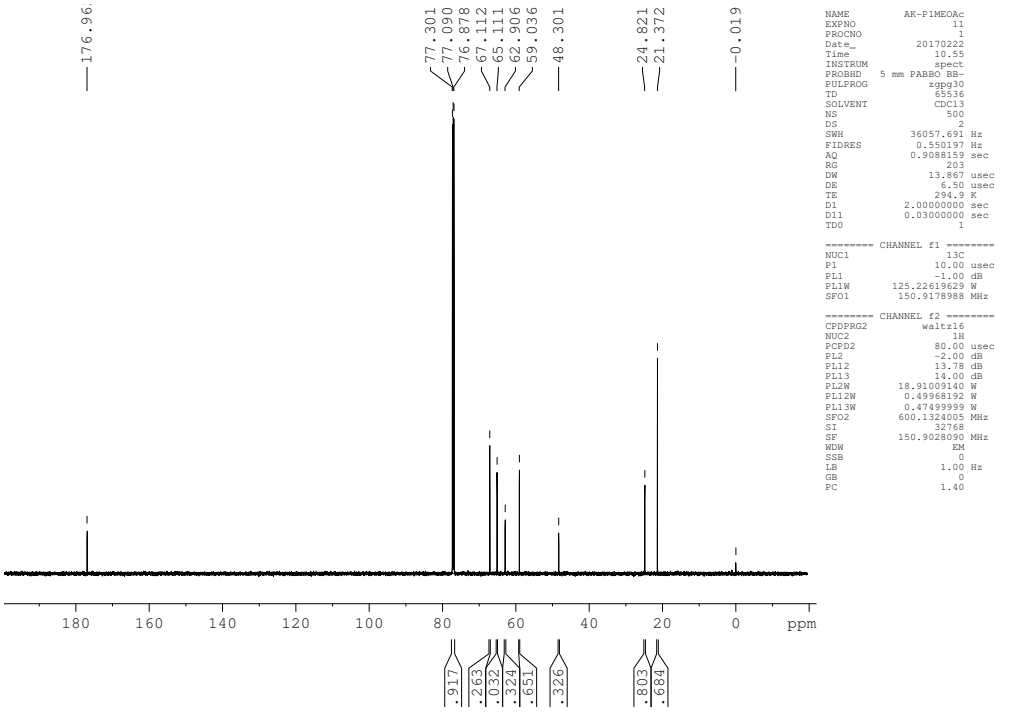


Figure S1-2:^{13}C NMR of [P_{1ME}][OAc]

Table S1. Results of acylation of cellulose using [P_{1ME}][OAc] solvent system

Entry	Acyl donor	R	DS value[(a)]	Products	
				Cellulose ester	Recovered cellulose
1	Vinyl acetate	Methyl	3.0	44 mg	0
2	Vinyl propionate	Ethyl	3.0	32 mg	12 mg
3	Vinyl butyrate	n-C_3H_7	2.9	25 mg	16 mg
4	Vinyl decanoate	n-C_9H_{19}	2.9	101 mg	0
5	Vinyl laurate	n-$C_{11}H_{23}$	3.0	124 mg	0
6	Vinyl palmitate	n-$C_{15}H_{31}$	3.0	141 mg	0
7	Vinyl benzoate	C_6H_5	1.8	46 mg	13 mg
8	2,2,2-trifluoroethyl benzoate	C_6H_5	3.0	70 mg	0

The DS value was determined by ^{1}H NMR analysis following to the equation listed below. We used equations described below for calculating DS [1,2]. Here, AGU means protons at anhydroglucose unit. Since the intensities H2~H4 of cellulose benzoate were not reliable, intensities H1 and H5 were used for the calculating DS values of the cellulose benzoate. Since the integral of ^{1}H NMR spectra was influenced by the n.o.e effect, the DS values are not accurate ones but just estimation values.

DS $_{acetate}$= (I_{acetyl} x 7)/ ($I_{AGU(H1\sim H6)}$ x 9)
DS $_{propionate}$= ($I_{2\text{-}Me}$ x 7)/ ($I_{AGU(H1\sim H6)}$ x 9)
DS $_{butyrate}$= ($I_{4\text{-}Me}$ x 7)/ ($I_{AGU(H1\sim H6)}$ x 9)
DS $_{decanoate}$= ($I_{10\text{-}Me}$ x 7)/ ($I_{AGU(H1\sim H6)}$ x 9)
DS $_{laurate}$= ($I_{12\text{-}Me}$ x 7)/ ($I_{AGU(H1\sim H6)}$ x 9)
DS $_{palmitate}$= ($I_{16\text{-}Me}$ x 7)/ ($I_{AGU\ (H1\sim H6)}$ x 9)
DS $_{benzoate}$= (I_{Phenyl} x 2)/ ($I_{AGU(H1+H5)}$ x 5)

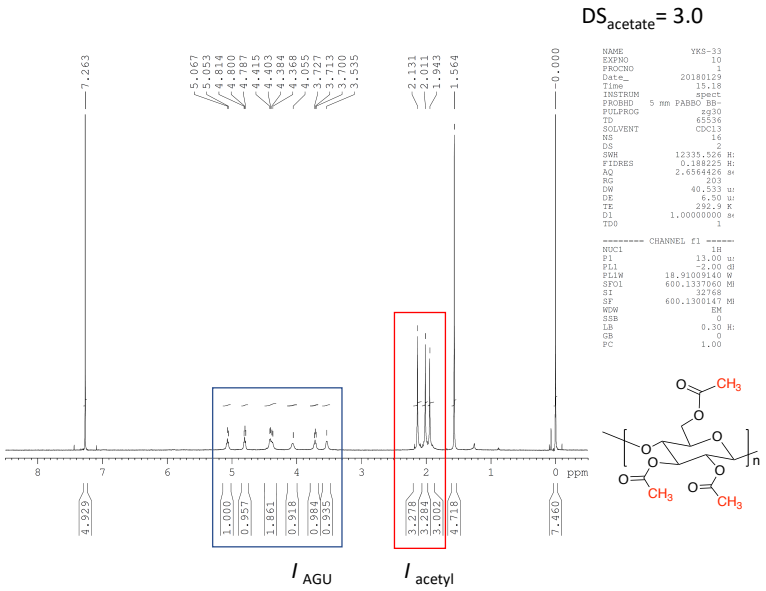


Figure S2:[1]H NMR spectra of Cellulose acetate (DS 3.0)

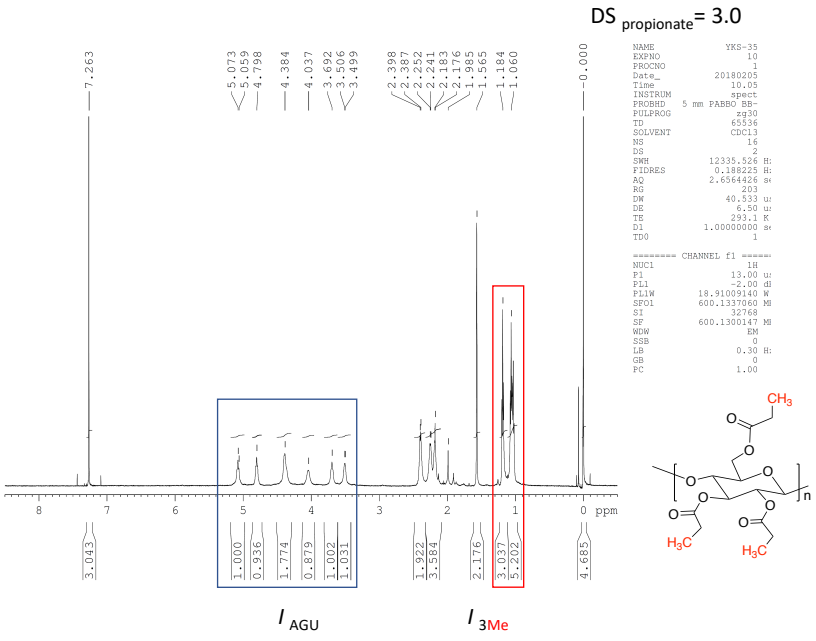


Figure S3:[1]H NMR spectra of Cellulose propionate (DS 3.0)

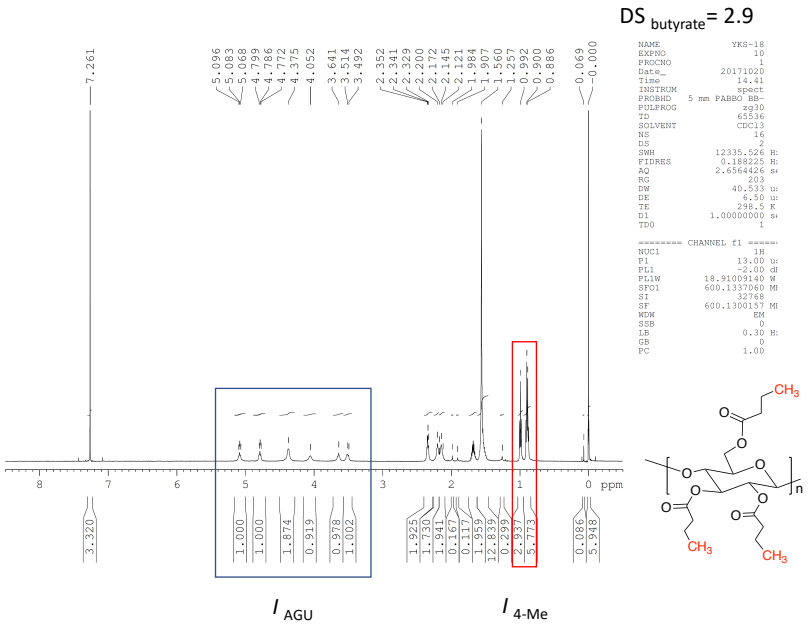


Figure S4:[1]H NMR spectra of Cellulose butyrate (DS 2.9)

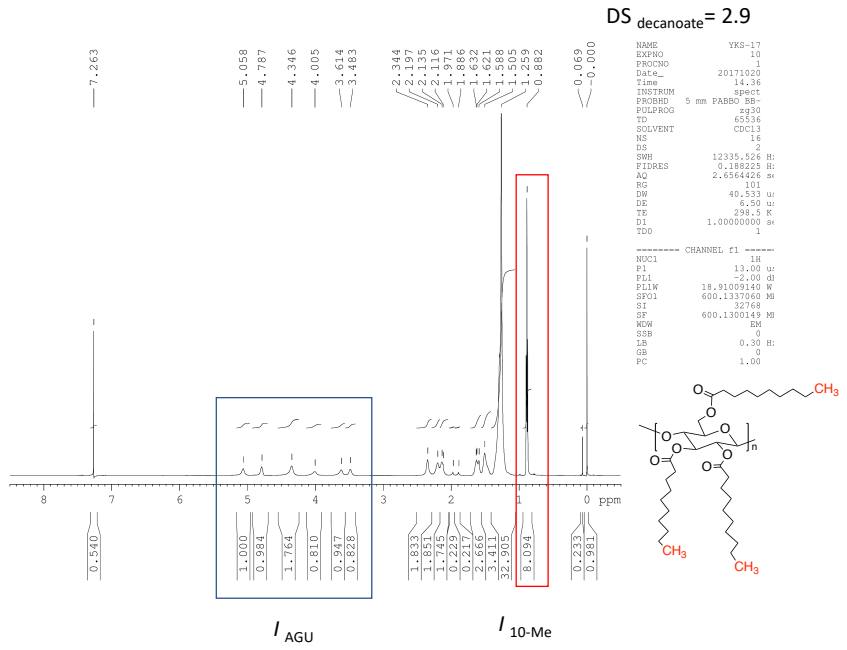


Figure S5:[1]H NMR spectra of Cellulose decanoate (DS 2.9)

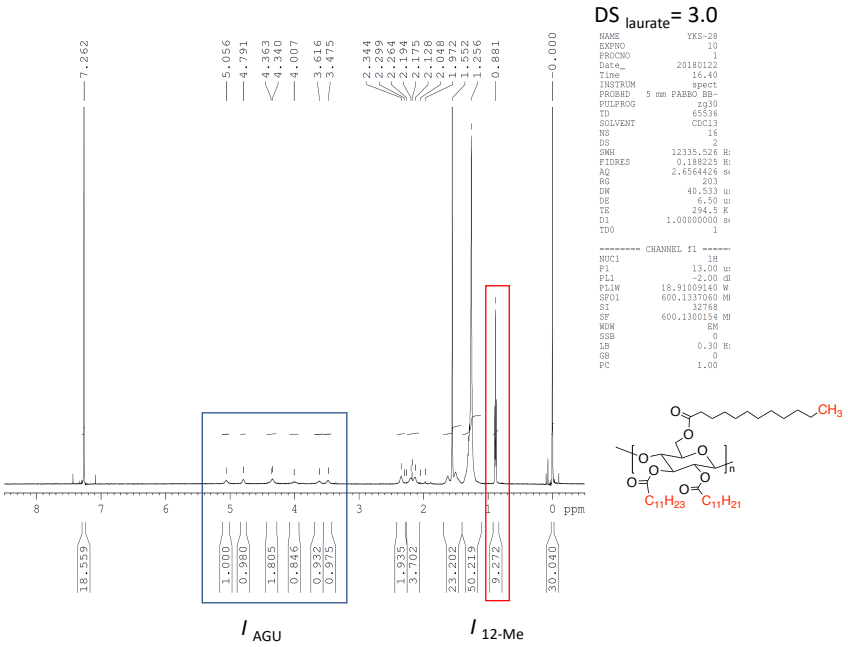


Figure S6:[1]H NMR spectra of Cellulose laurate (DS 3.0)

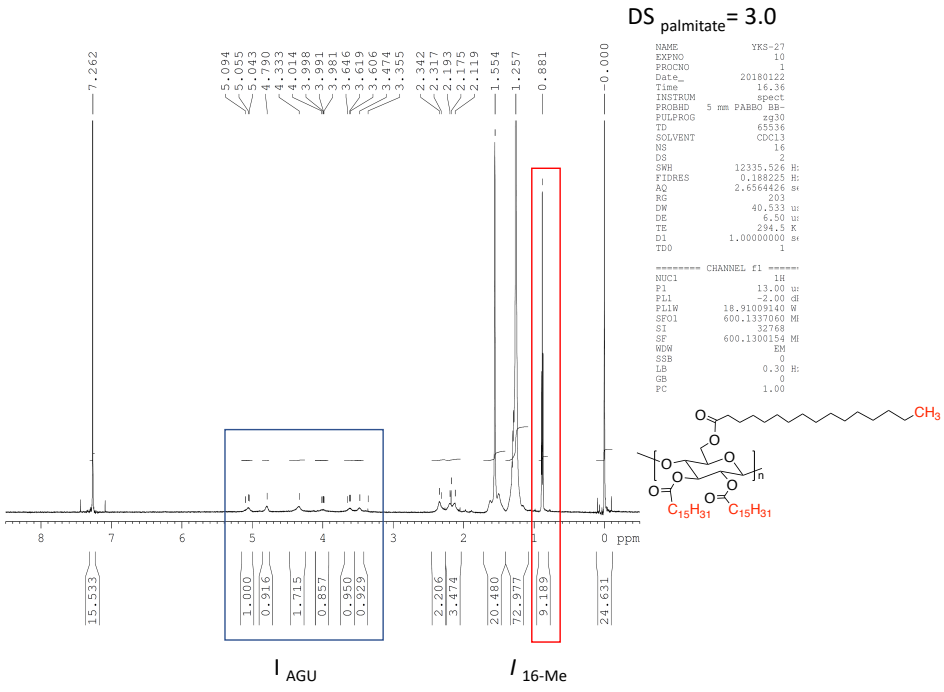


Figure S7:[1]H NMR spectra of Cellulose palmitate (DS 3.0)

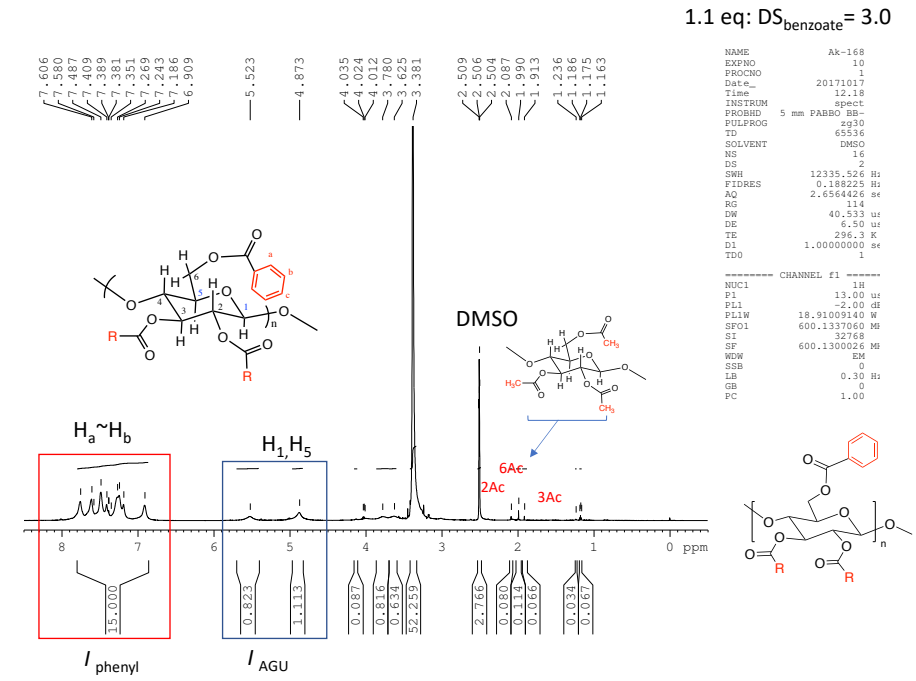


Figure S8-1:[1]H NMR spectra of Cellulose benzoate (DS 3.0)

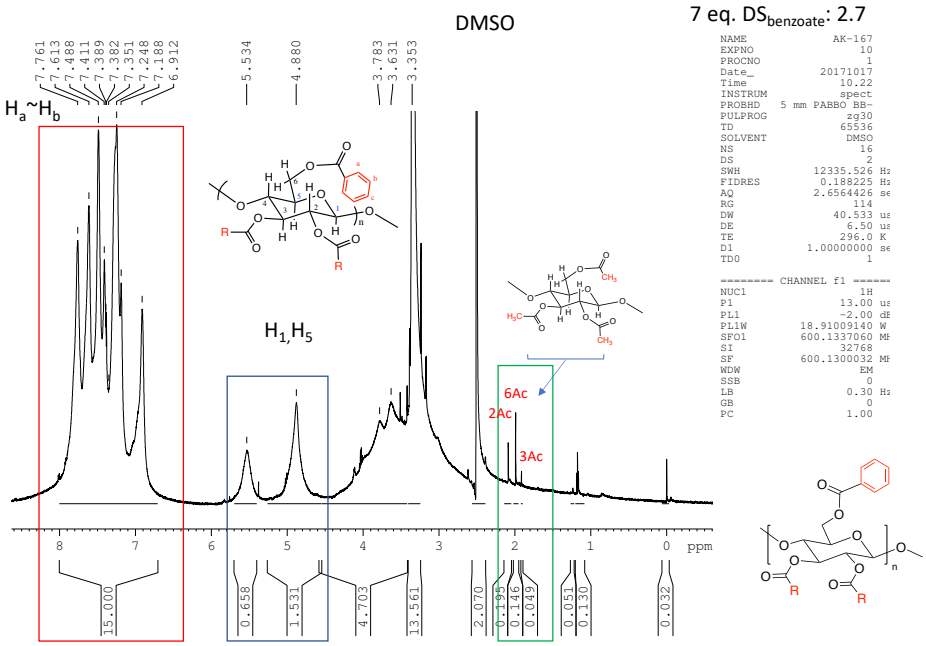
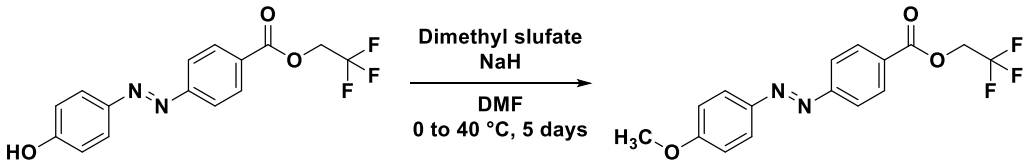


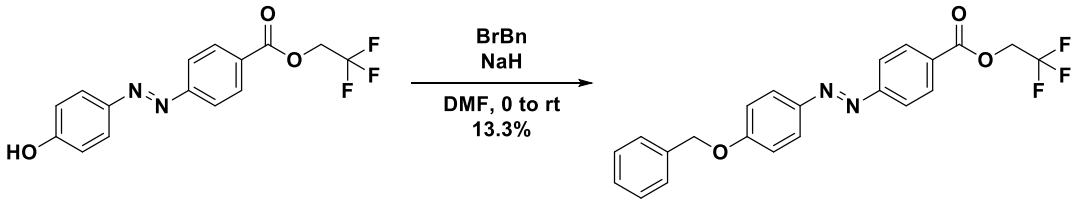
Figure S8-2:[1]H NMR spectra of Cellulose benzoate (DS 2.7)

Synthesis of 2,2,2-trifluoroethyl (*E*)-4-((4-methoxyphenyl)diazenyl)benzoate



To a mixture of 2,2,2-trifluoroethyl (*E*)-4-((4-hydroxyphenyl)diazenyl)benzoate (0.30 g, 0.91 mmol) in dry DMF (9.0 mL) was added 60% NaH (65.4 mg, 1.64 mmol) and dimethylsulfate (0.46 g, 3.63 mmol) at 0°C, then the mixture was stirred at 40°C for 4 days. The reaction was quenched by addition of crashed ice and extracted with CH_2Cl_2. The organic layers were dried under anhydrous MgSO4 and evaporated to dryness. The residue was purified by silica gel chromatography (hexane/ethyl acetate 20:1 to 10:1) to give 2,2,2-trifluoroethyl (*E*)-4-((4-methoxyphenyl)diazenyl)benzoate (0.15 g, 0.44 mmol) in 49% yield.

Synthesis of 2,2,2-trifluoroethyl (E)-4-((4-(benzyloxy)phenyl)diazenyl)benzoate



To a mixture of 2,2,2-trifluoroethyl (*E*)-4-((4-hydroxyphenyl)diazenyl)benzoate(0.33 g, 1.00 mmol) in dry DMF (10 mL) was added 60% NaH (120 mg, 3.04 mmol) and benzyl bromide (0.62 g, 3.64 mmol) at 0°C, then the mixture was stirred at rt for 18 h. The reaction was quenched by addition of iced water and extracted with ethyl acetate. The organic layers were dried under anhydrous $NaSO_4$ and evaporated to dryness. The residue was purified by silica gel chromatography (hexane/ethyl acetate 10:1 to 3:1) to give 2,2,2-trifluoroethyl (*E*)-4-((4-methoxyphenyl)diazenyl)benzoate (3.19 g, 0.77 mmol) in 77% yield.

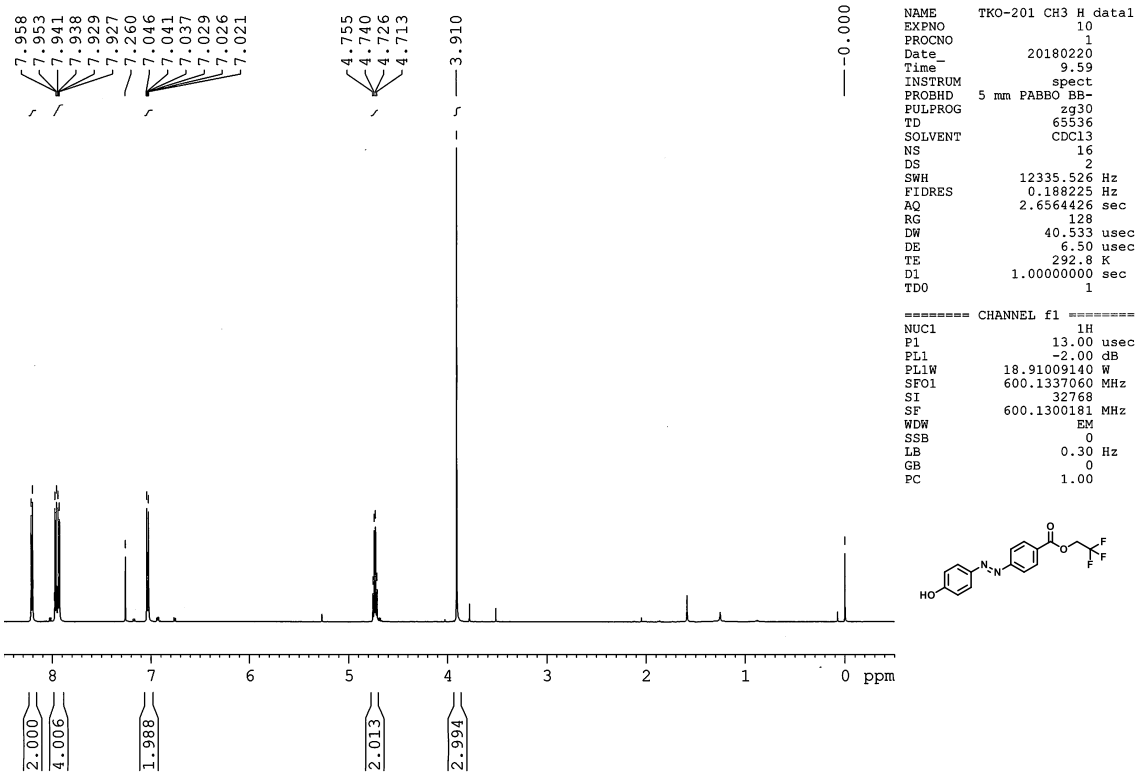


Figure S9-1: 2,2,2-trifluoroethyl (*E*)-4-((4-hydroxyphenyl)diazenyl)benzoate (^{1}H NMR)

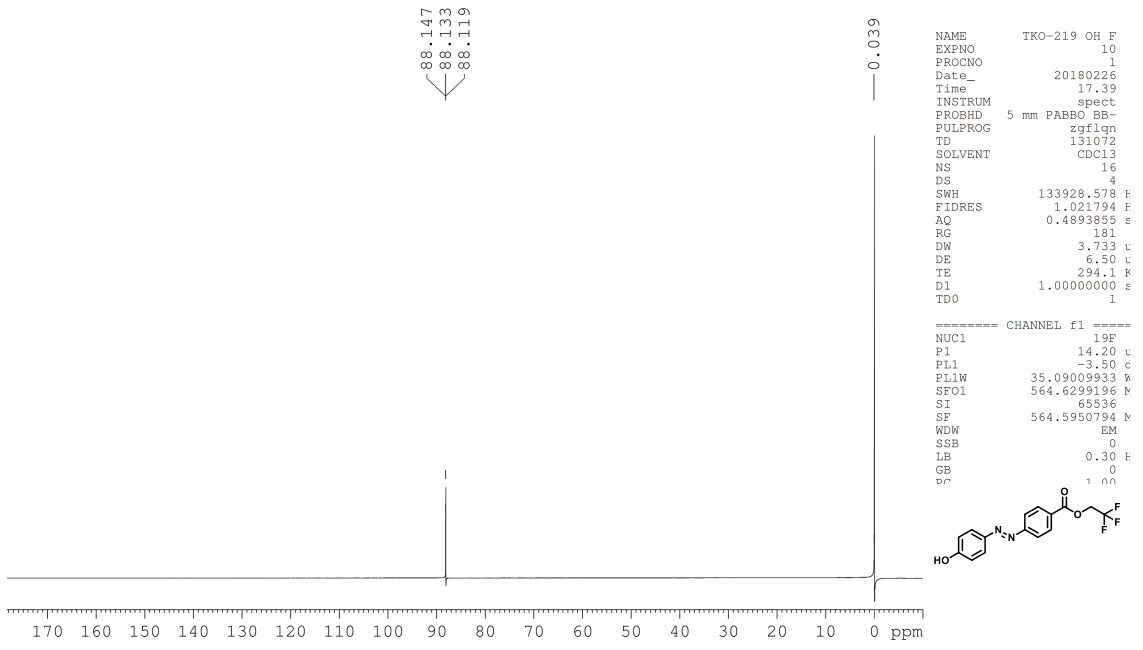


Figure S9-2: 2,2,2-trifluoroethyl (*E*)-4-((4-hydroxyphenyl)diazenyl)benzoate (^{19}F NMR)

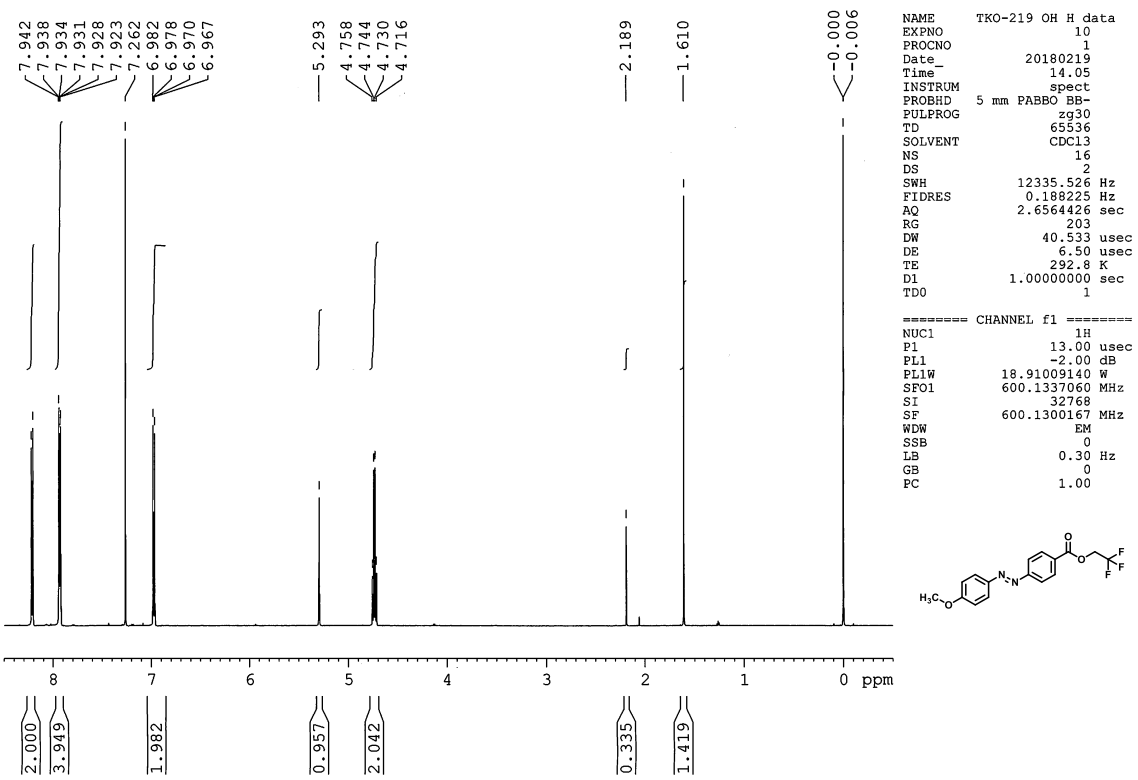


Figure S10-1: 2,2,2-trifluoroethyl (*E*)-4-((4-methoxyphenyl)diazenyl)benzoate (^{1}H NMR)

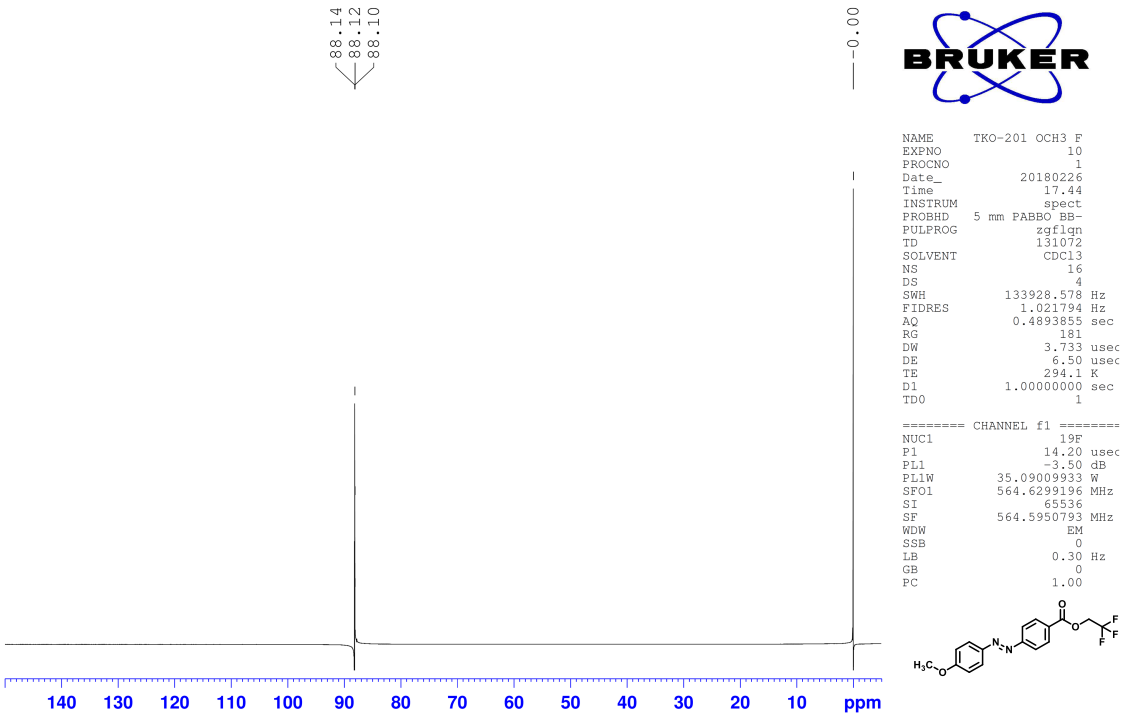


Figure S10-2:2,2,2-trifluoroethyl (*E*)-4-((4-methoxyphenyl)diazenyl)benzoate (^{19}F NMR)

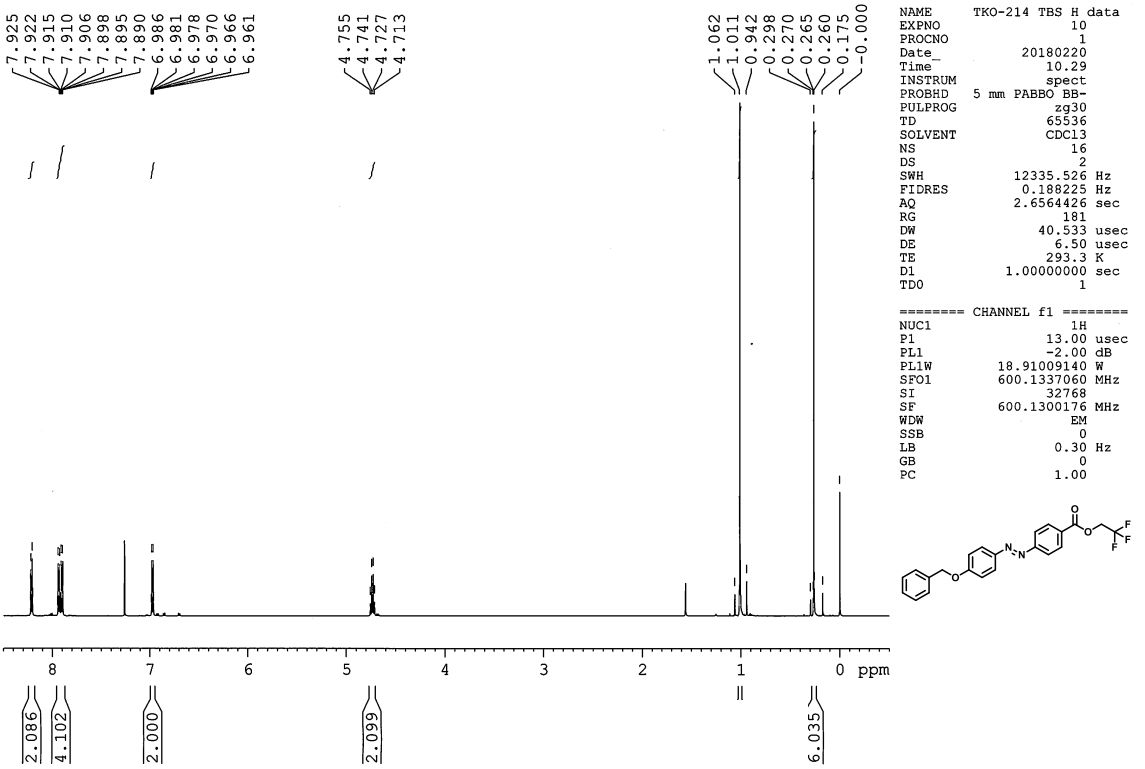


Figure S11-1:2,2,2-trifluoroethyl (E)-4-((4-(benzyloxy)phenyl)diazenyl)benzoate (^{1}H NMR)

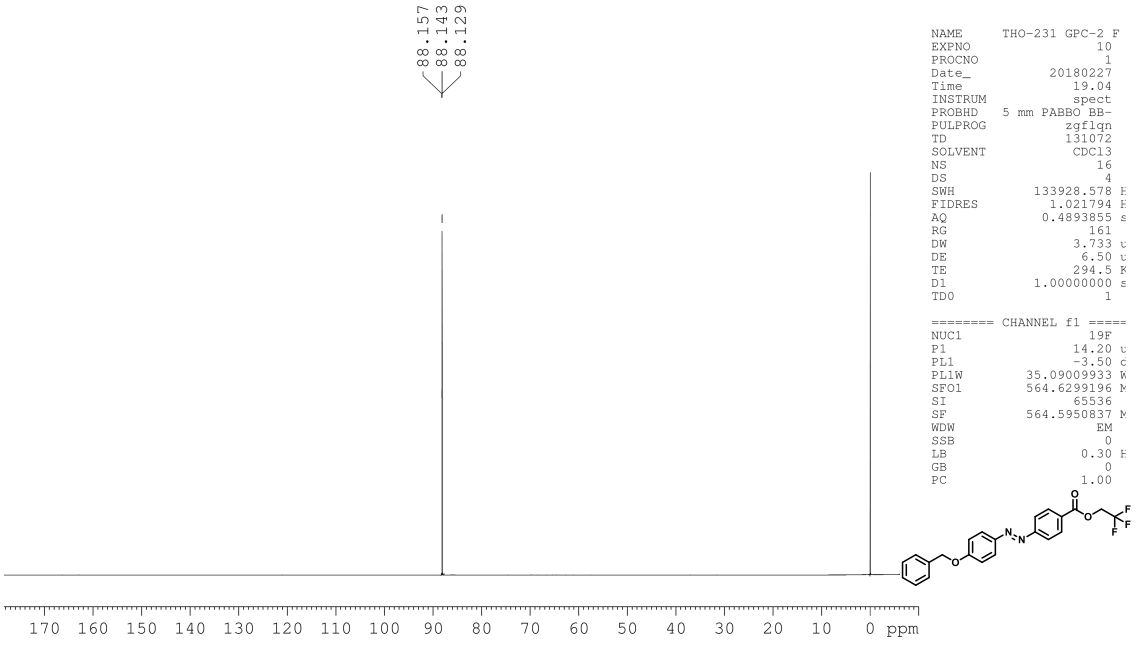


Figure S11-2:2,2,2-trifluoroethyl (E)-4-((4-(benzyloxy)phenyl)diazenyl)benzoate (^{19}F NMR)

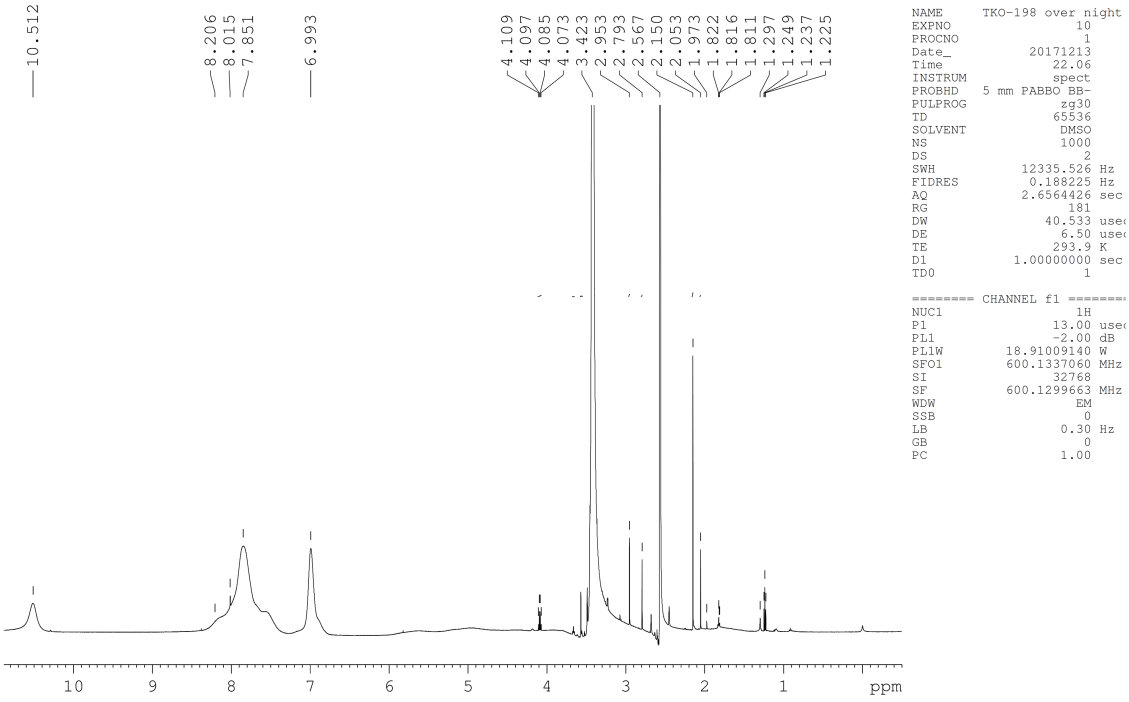


Figure S12:Cellulose (*E*)-4-((4-hydroxyphenyl)diazenyl)benzoate (^{1}H NMR)

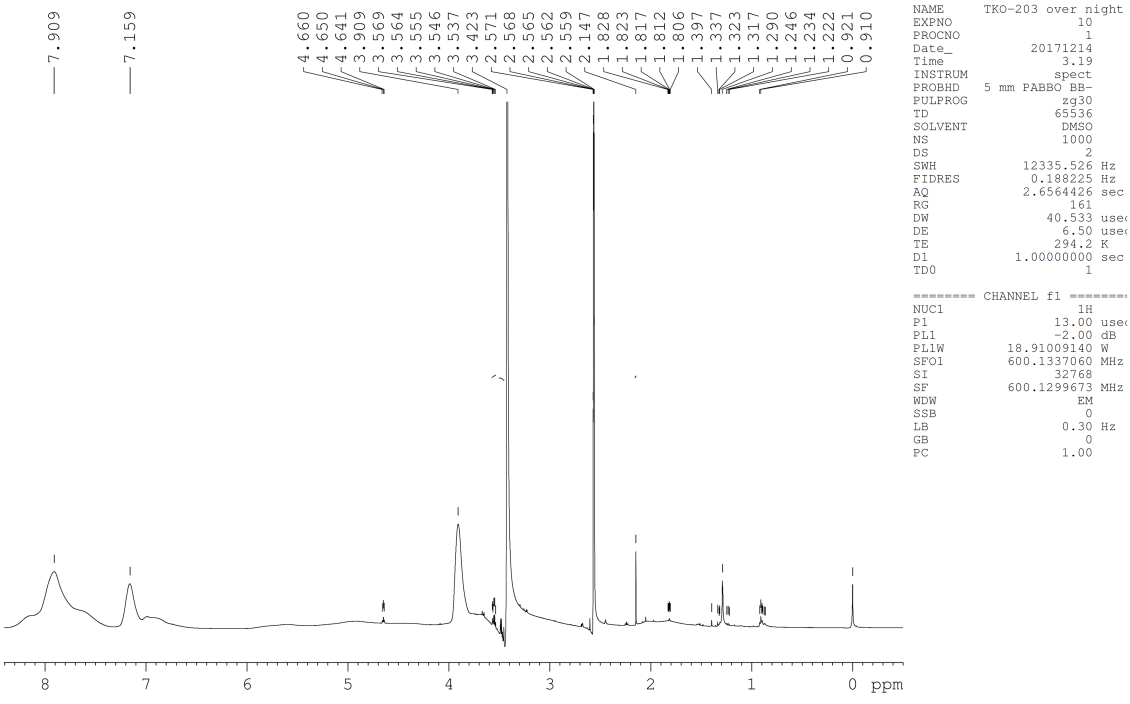


Figure S13:Cellulose (*E*)-4-((4-methoxyphenyl)diazenyl)benzoate (^{1}H NMR)

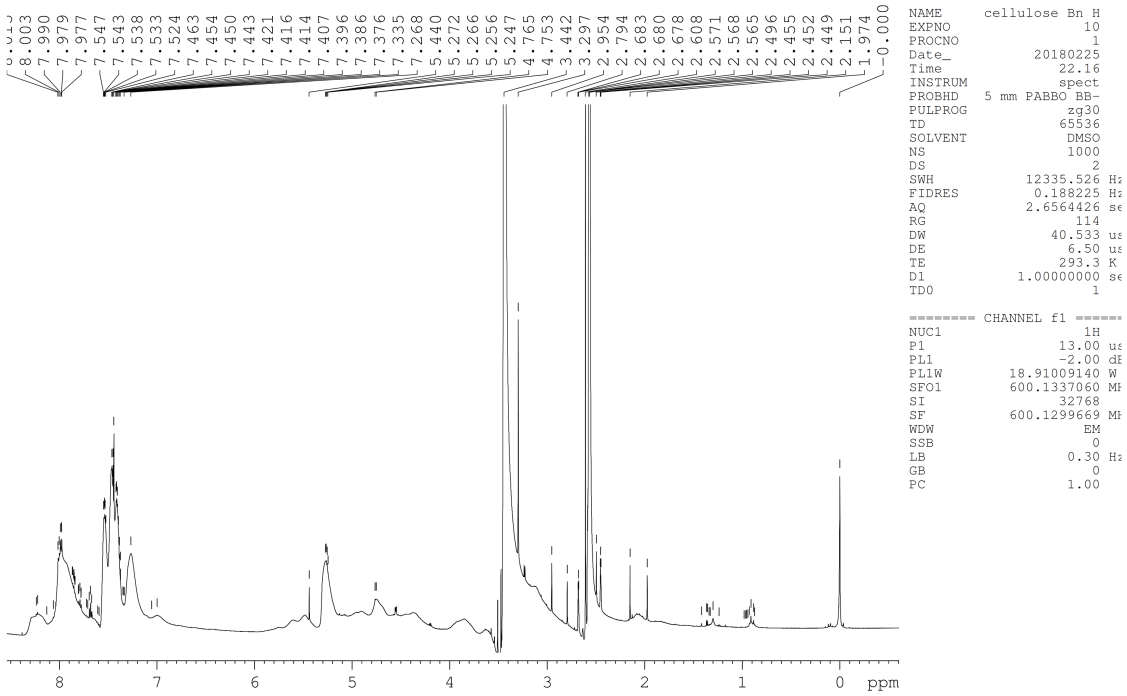


Figure S14:Cellulose (*E*)-4-((4-(benzyloxy)phenyl)diazenyl)benzoate (^{1}H NMR)

References

[1] L. El Hamdaoui, M. El Moussaouiti, S. Gmouth, *Polym. Bull.* **2015**, *72*, 3031–3042.

[2] L.P. Hinner, J. L. Wissner, A. Beurer, B. A. Nebel, B. Hauer, *Green Chem*. **2016**, *18*, 6099–6107.