Supporting Information

Adhesive RAFT Agents for Controlled Polymerization of Acrylamide: Effect of Catechol-end R Groups

*Olabode O. Oyeneye, William Z. Xu, Paul A. Charpentier**

Department of Chemical and Biochemical Engineering, University of Western Ontario, London ON N6A-5B9 Canada

*Corresponding author: pcharpentier@eng.uwo.ca

Experimental Section Complement

Characterization: 1D (^{1}H and ^{13}C) and 2D (gHSQC, gHMBC) NMR spectra were measured using either a Varian INOVA 600 or a Varian INOVA 400 spectrometer. gHSQC was recorded with multiplicity edited. $CDCl_3$, D_2O, or DMSO-d_6 was used as the solvent and chemical shifts were referenced to tetramethylsilane (TMS; 0.0 ppm). The AM concentration [AM] was determined based on the ^{1}H NMR signals of the olefinic protons. ATR-FTIR spectra were recorded at a resolution of 6 cm^{-1} over 64 scans using a mid-IR spectrometer (Nicolet 6700) equipped with smart diamond ATR (attenuated total reflection). UV-Vis spectra were recorded on a Shimadzu UV-3600 (UV-VIS-NIR) Spectrophotometer equipped with two lamps (halogen and deuterium) and three detectors (photomultiplier tube, InGaAs and cooled PbS) at room temperature. Molecular weight (M_n) and dispersity (Đ) of the synthesized PAM samples were measured by a Viscotek GPC Max VE 2001 gel permeation chromatography equipped with a triple detector array (TDA 302) including a refractive index detector (RI), a viscometer, and two light scattering detectors (low angle and right angle, 670 nm). 0.10 M NaNO3/1.15 mM NaN3 aqueous solution was used as mobile phase at a flow rate of 0.7 mL/min. Two PolyAnalytik columns (A206:

20×10^6 Da, 130 Å) were employed to separate the samples at 35°C, which were calibrated by a polyethylene oxide (PEO, MW: 18600 Da, PDI: 1.03, $\alpha = 0.69$, $K = 3.7 \times 10^{-4}$ dl/g) standard. The dn/dc value of PAM in the eluent was pre-determined to be 0.15 mL/g using a refractometer. The molecular weight averages and dispersities were calculated using OmniSEC software (Ver. 4.5.6.268). The molecular weight (M_n) of catechol end-functionalized polyacrylamide samples was also determined based on end group analysis of the ^{1}H NMR spectra of the sample. Thermal properties of the synthesized materials were evaluated via thermogravimetric analysis (TGA) on a SDT Q600, TA instruments by heating the materials from room temperature to 700°C at a heating rate of 10°C/min under air. A Malvern Zetasizer Nano S (Model: ZEN 1600) was used to characterize the particle size (PS) of the Al_2O_3-PAM nanocomposites based on dynamic light scattering (DLS). The Zetasizer Nano S was equipped with a 633 nm He-NE laser source, and at a scattering angle of 173°. Prior to the PS determination which was done in triplicate, the samples were prepared to a concentration of 10 mg/L using distilled water as the dispersion medium (room temperature), and ultra-sonicated for 5 – 10 min to obtain a well-dispersed suspension.

Supporting Data

Table S2: RAFT Polymerization of acrylamide mediated with Dopa- CTAs

Dopa-CTA (3)	Time (min)	$M_{n,GPC}$	$M_{n,NMR}$*	M_w/M_n
(3a)	60	14800	14400	1.19
(3b)	60	13900	10600	1.21
(3c)	60	9400	8500	1.21

Reaction conditions: $[AM]_0:[Dopa\text{-}CTA]_0:[ACVA]_0$ = 2500:5:1,
Solvent = 24.5 mL DMSO/DMF (97:3, vol%), Temp = 70°C, $[AM]_0$ = 2M.
*Mn values determined by end-group analysis of the ^{1}H NMR spectra

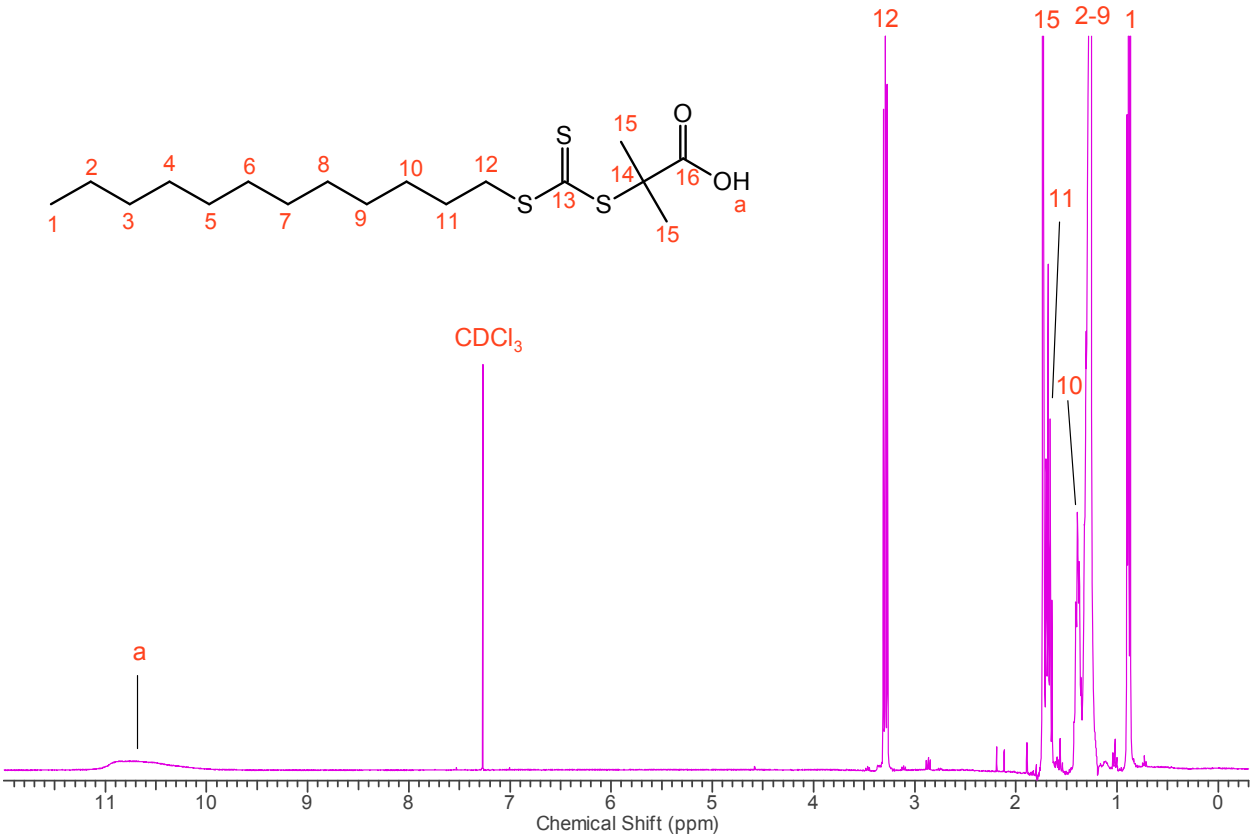

Figure S1. Complete ^{1}H NMR spectra of (**1a**) DDMAT (600 MHz, @ 25°C).

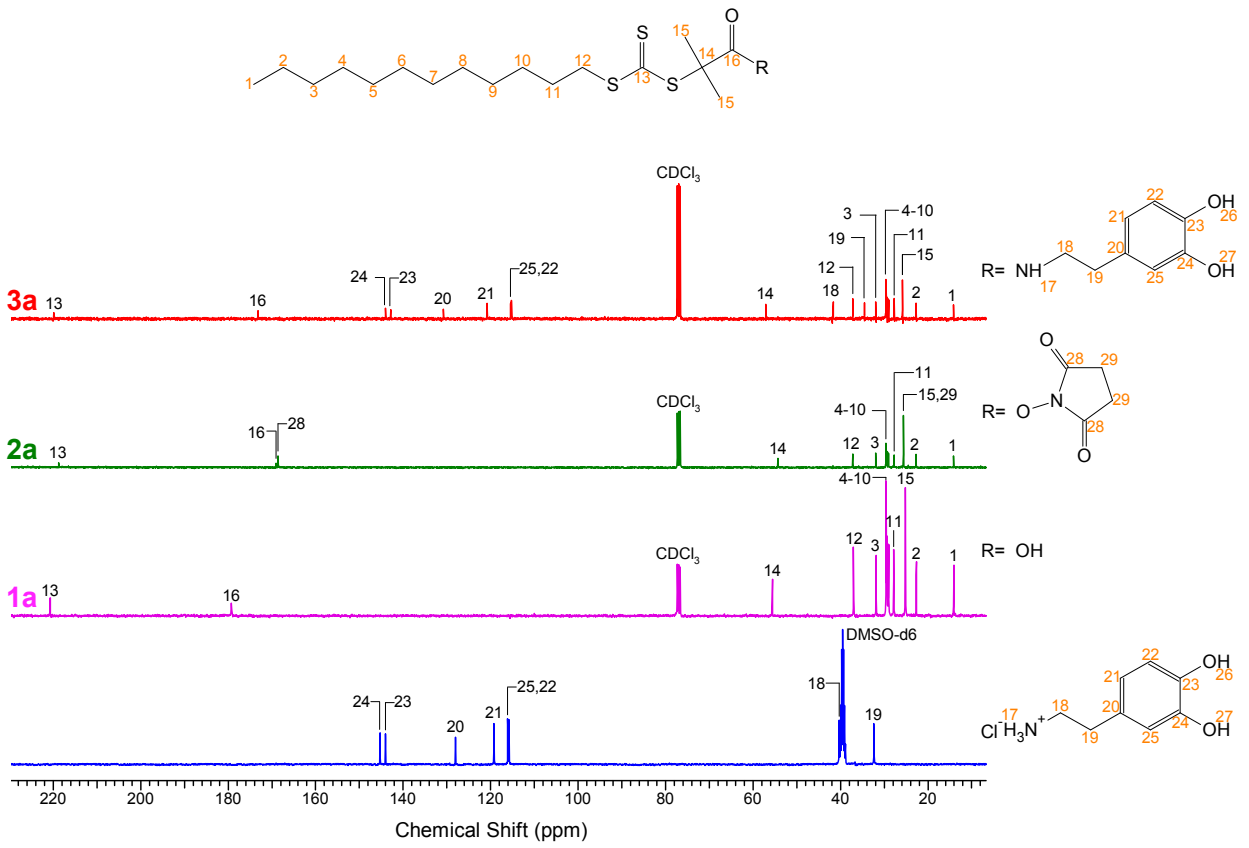

Figure S2. ^{13}C NMR spectra of (bottom) dopamine hydrochloride, (**1a**) DDMAT, (**2a**) Suc-DDMAT and (**3a**) Dopa-DDMAT in $CDCl_3$ (100 MHz, @ 25°C)

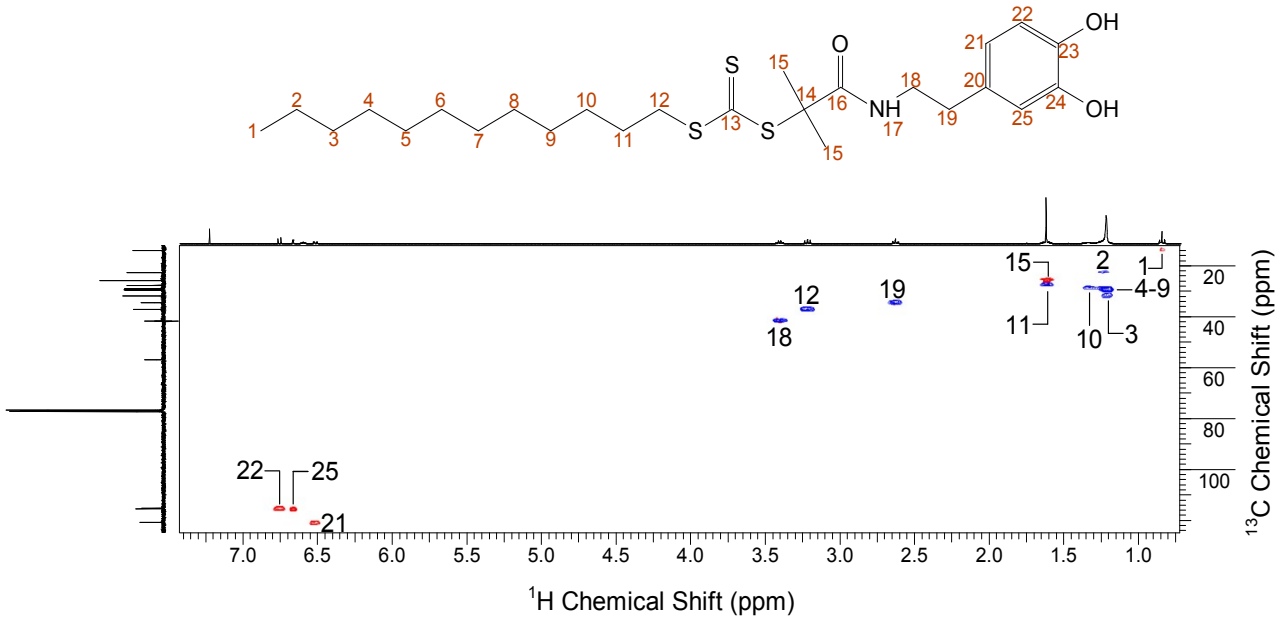

Figure S3. gHSQC NMR spectrum of Dopa-DDMAT (**3a**) in $CDCl_3$ (100 MHz, @ 25°C).

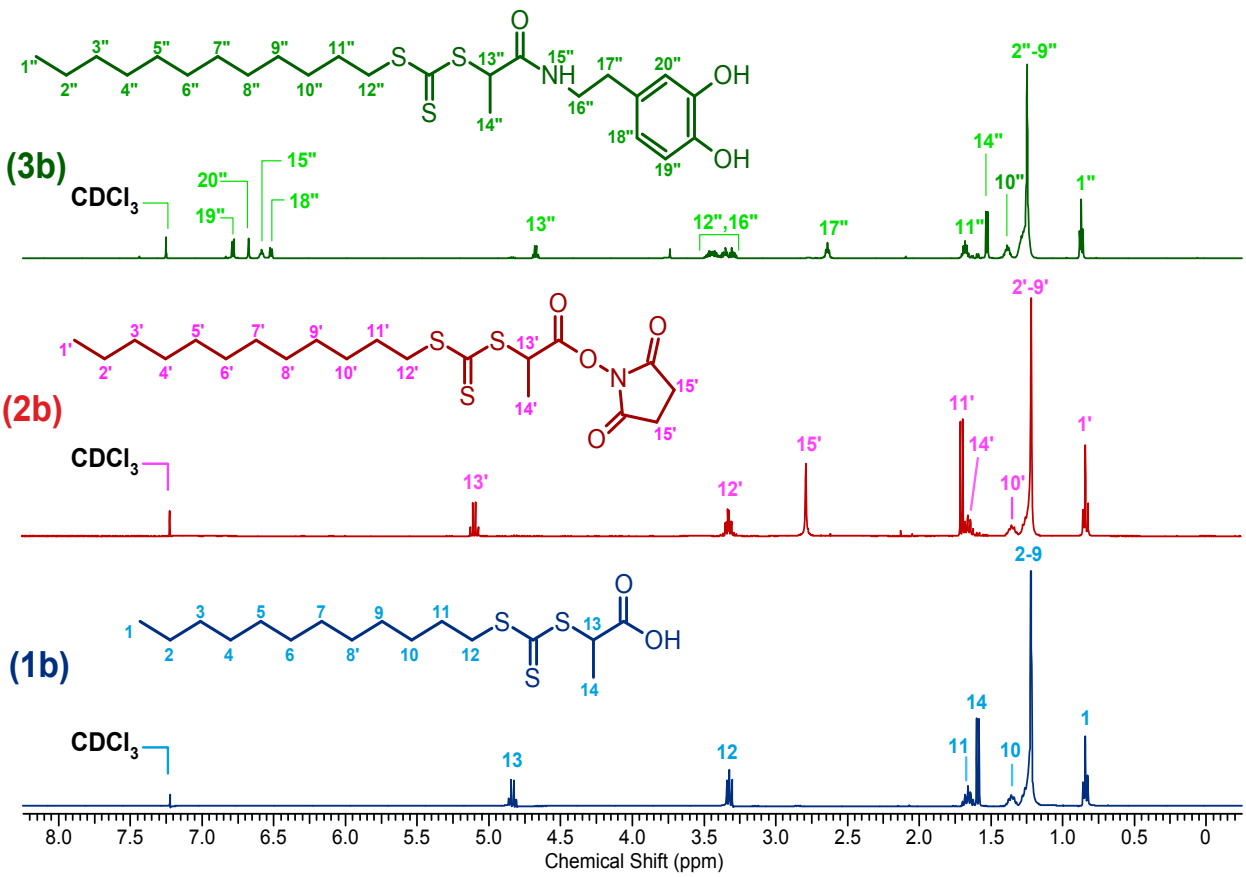

Figure S4.^{1}H NMR Spectra of (**1b**) DoPAT, (**2b**) Suc-DoPAT and (**3b**) Dopa-DoPAT in $CDCl_3$ (600 MHz, @ 25^{o}C)

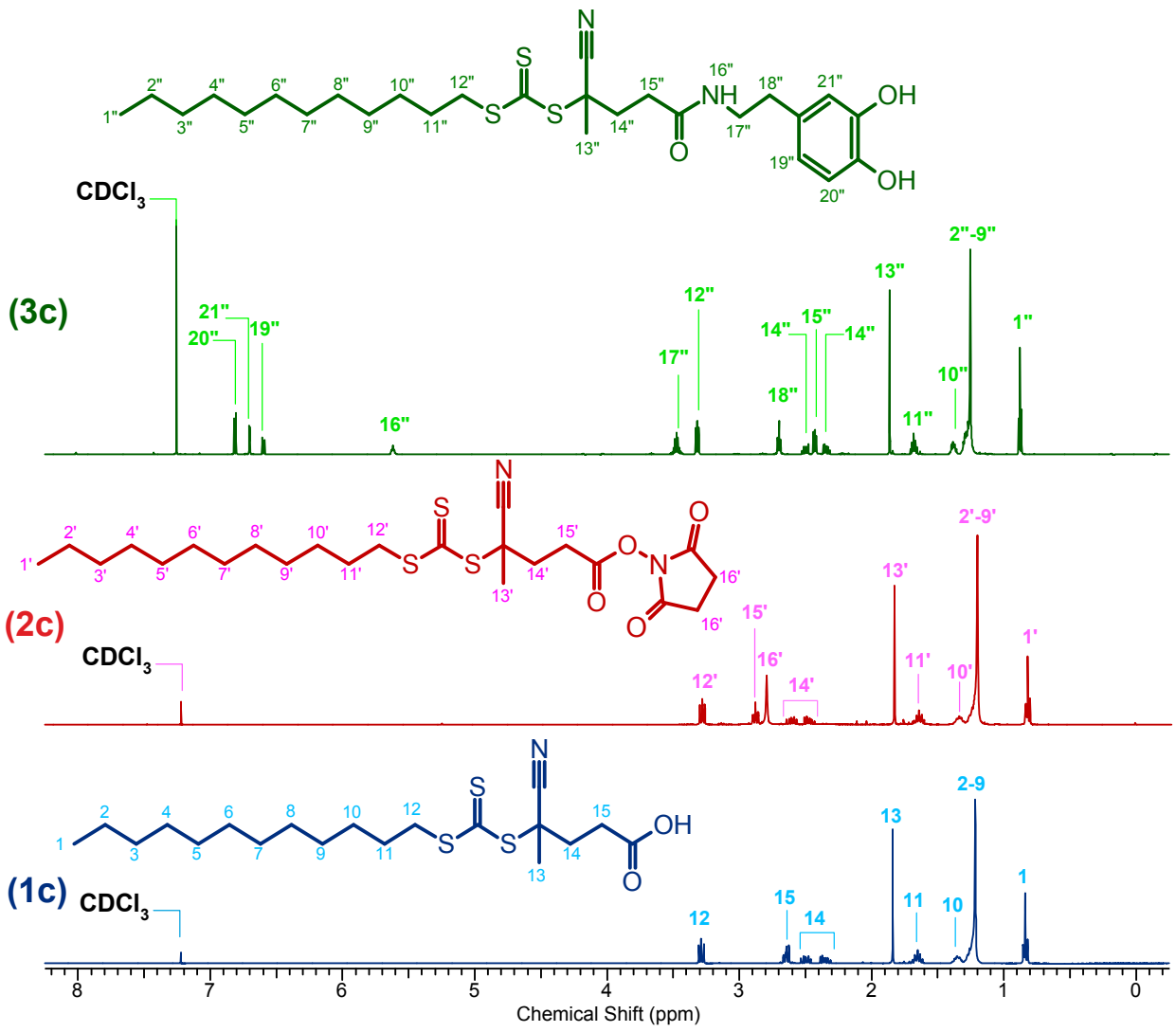

Figure S5. ^{1}H NMR Spectra of (**1c**) CDSPA, (**2c**) Suc-CDSPA and (**3c**) Dopa-CDSPA in $CDCl_3$ (600 MHz, @ 25^{o}C)

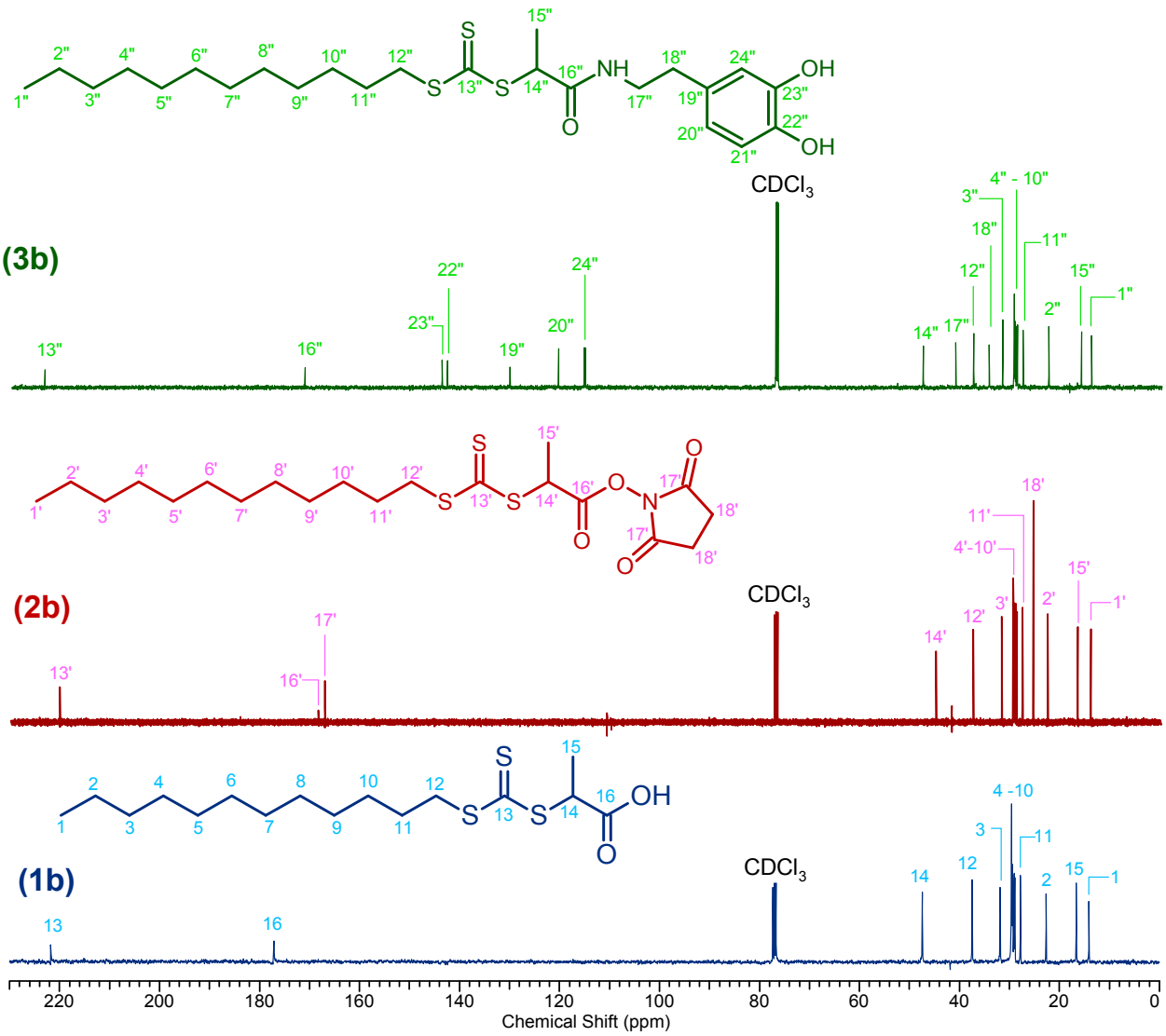

Figure S6. ^{13}C NMR of (**1b**) DoPAT, (**2b**) Suc-DoPAT and (**3b**) Dopa-DoPAT in $CDCl_3$ (100 MHz, @ 25°C)

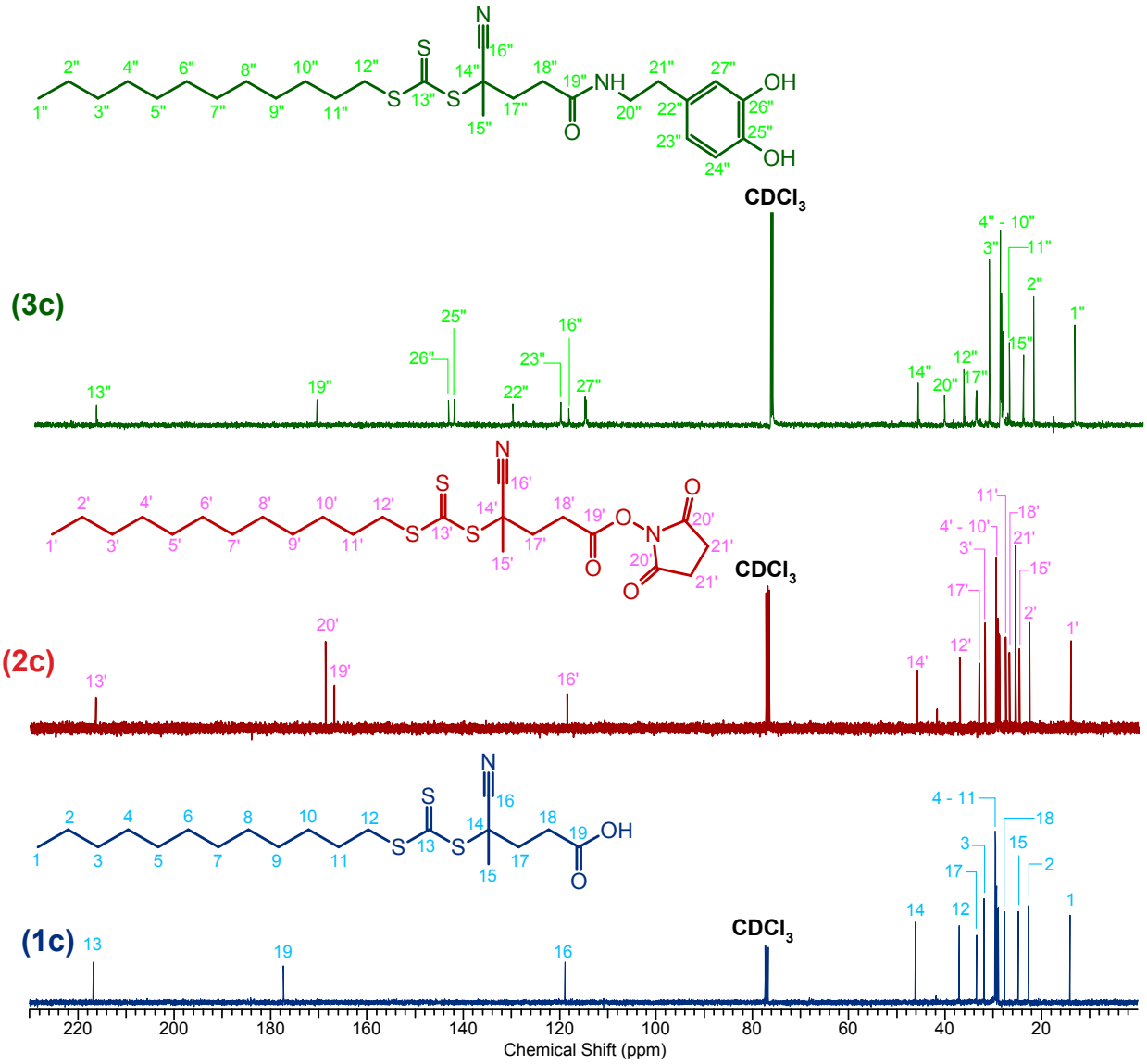

Figure S7. ^{13}C NMR of (**1c**) CDSPA, (**2c**) Suc-CDSPA and (**3c**) Dopa-CDSPA in $CDCl_3$ (100 MHz, @ 25°C)

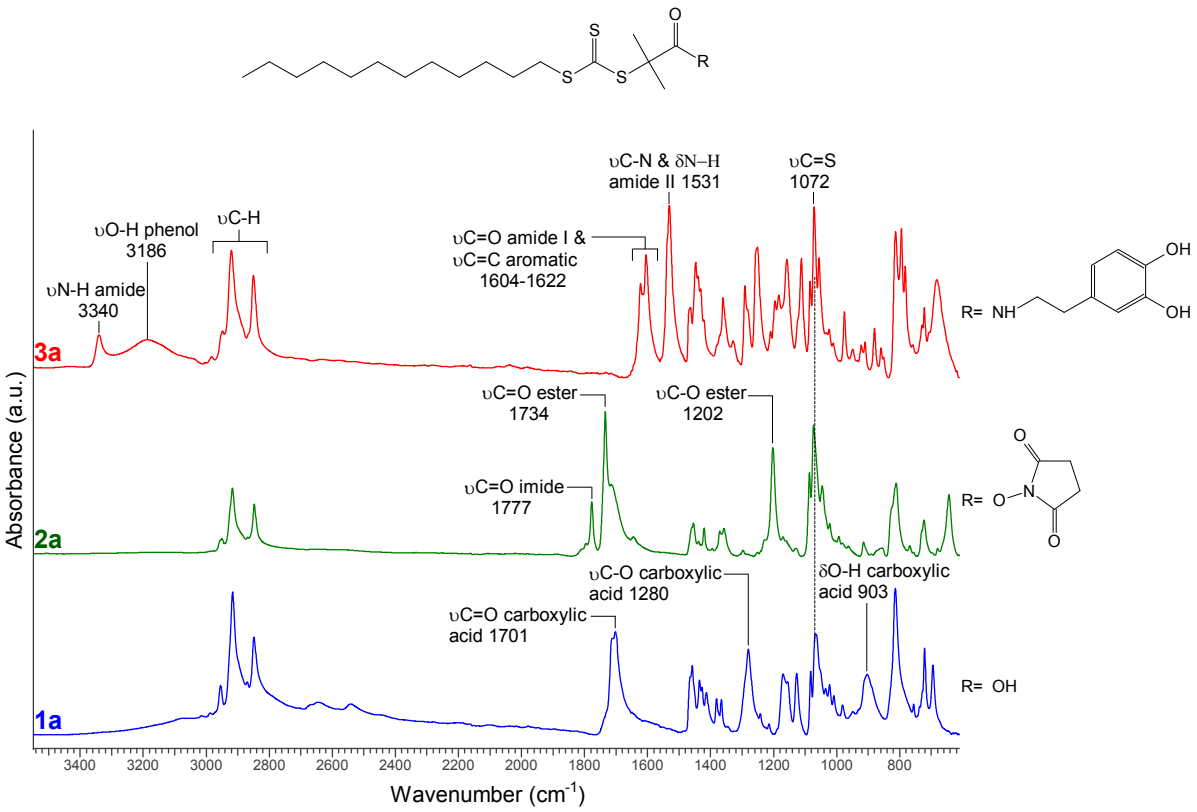

Figure S8. ATR-FTIR spectra of (1a) DDMAT, (2a) Suc-DDMAT and (3a) Dopa-DDMAT.

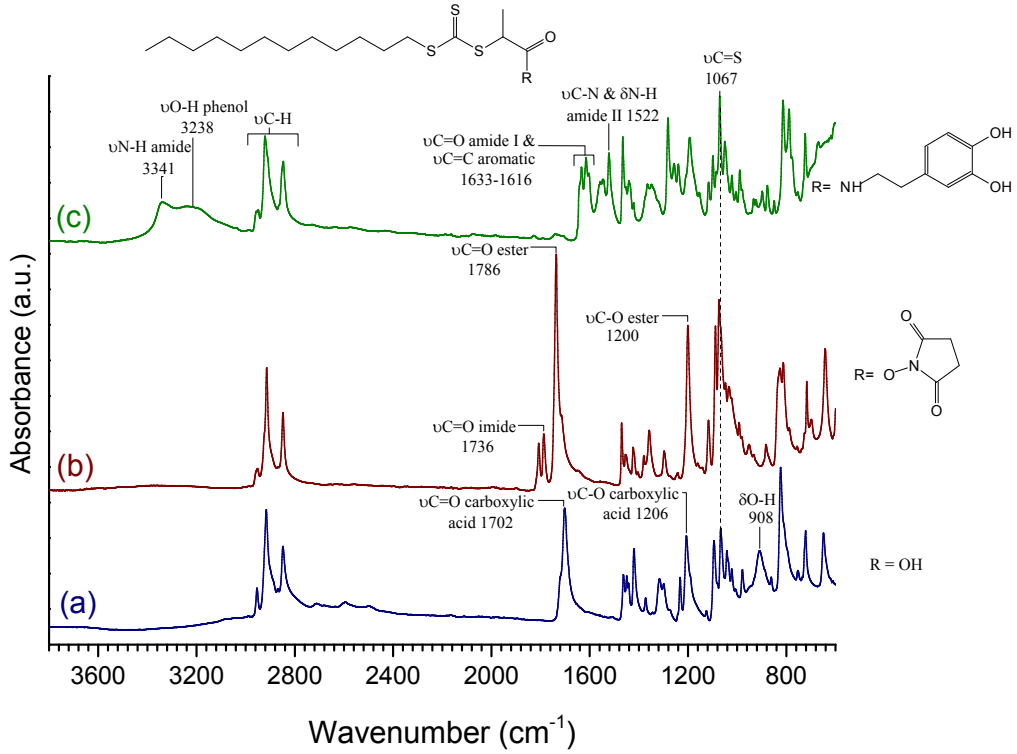

Figure S9. ATR-FTIR Spectra of (**1b**) DoPAT, (**2b**) Suc-DoPAT and (**3b**) Dopa-DoPAT

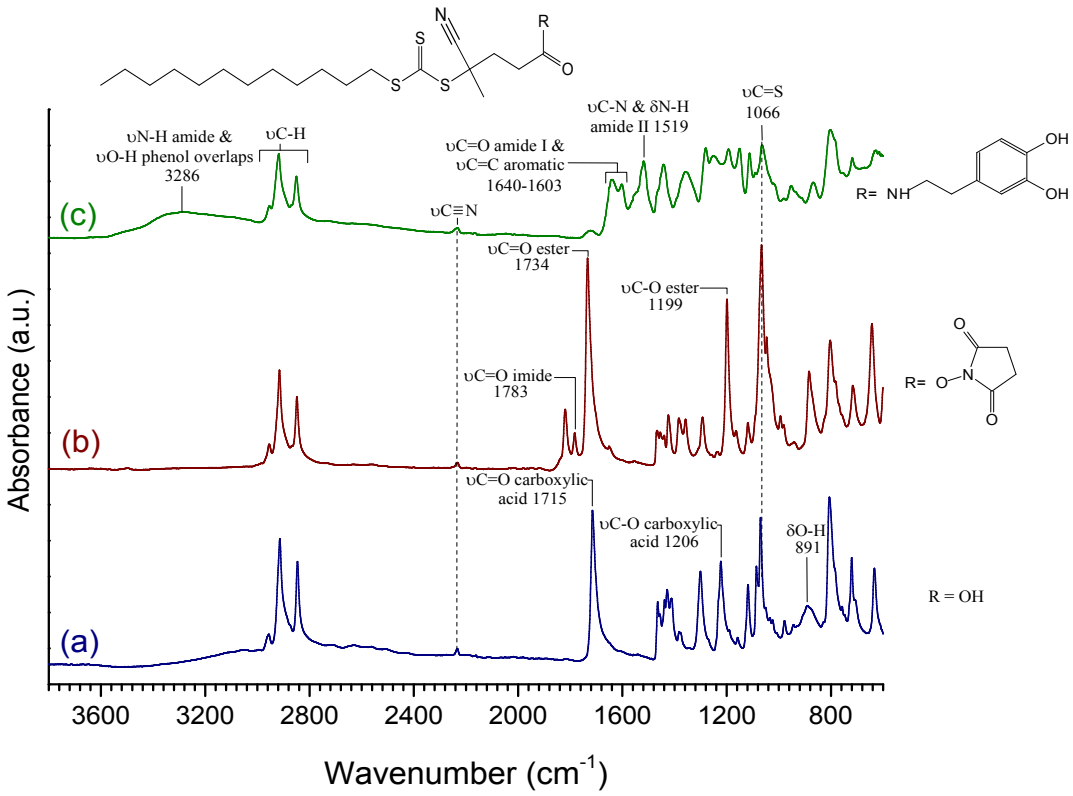

Figure S10. ATR-FTIR Spectra of (**1c**) CDSPA, (**2c**) Suc-CDSPA and (**3c**) Dopa-CDSPA

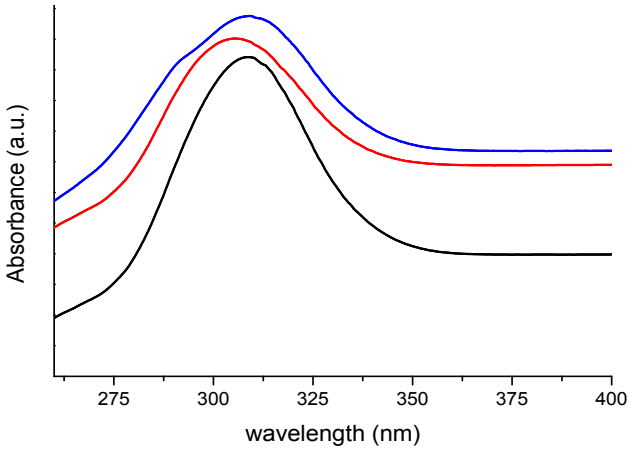

Figure S11. UV-vis absorbance spectra of 0.05 mM each of (**1a**, black) DDMAT, (**2a**, red) Suc-DDMAT and (**3a**, blue) Dopa-DDMAT in MeOH

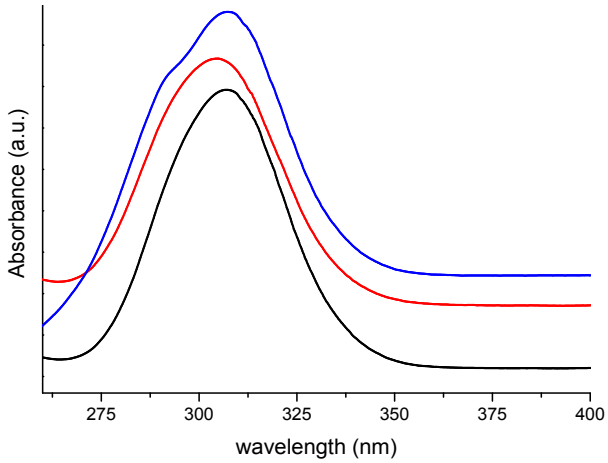

Figure S12. UV-vis absorbance spectra of 0.05 mM each of (**1b**, black) DoPAT, Suc-DoPAT (**2b**, red) and (**3b**, blue) Dopa-DoPAT in MeOH

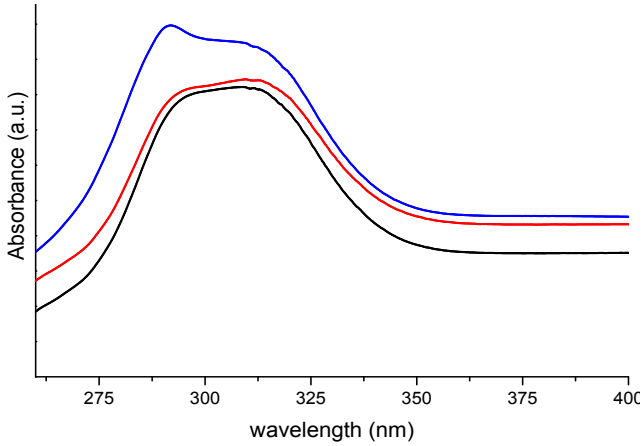

Figure S13. UV-vis absorbance spectra of 0.05 mM each of (**1c**, black) CDSPA, (**2c**, red) Suc-CDSPA and (**3c**, blue) Dopa-CDSPA in MeOH

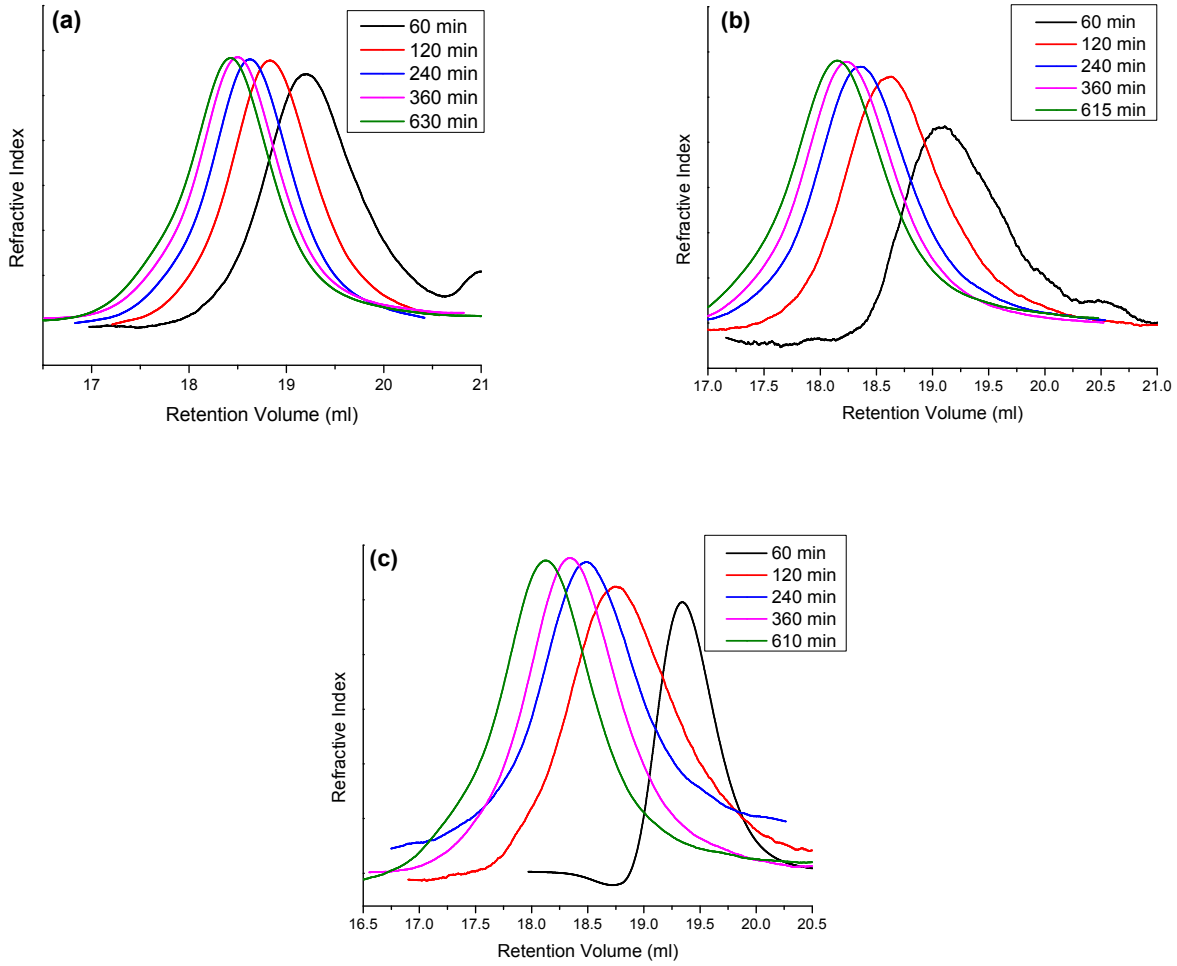

Figure S14: GPC DRI Chromatograms of catechol end-functionalized polyacrylamide (Dopa-PAM) synthesized with (a) Dopa-DDMAT, (b) Dopa-DoPAT and (c) Dopa-CDSPA.

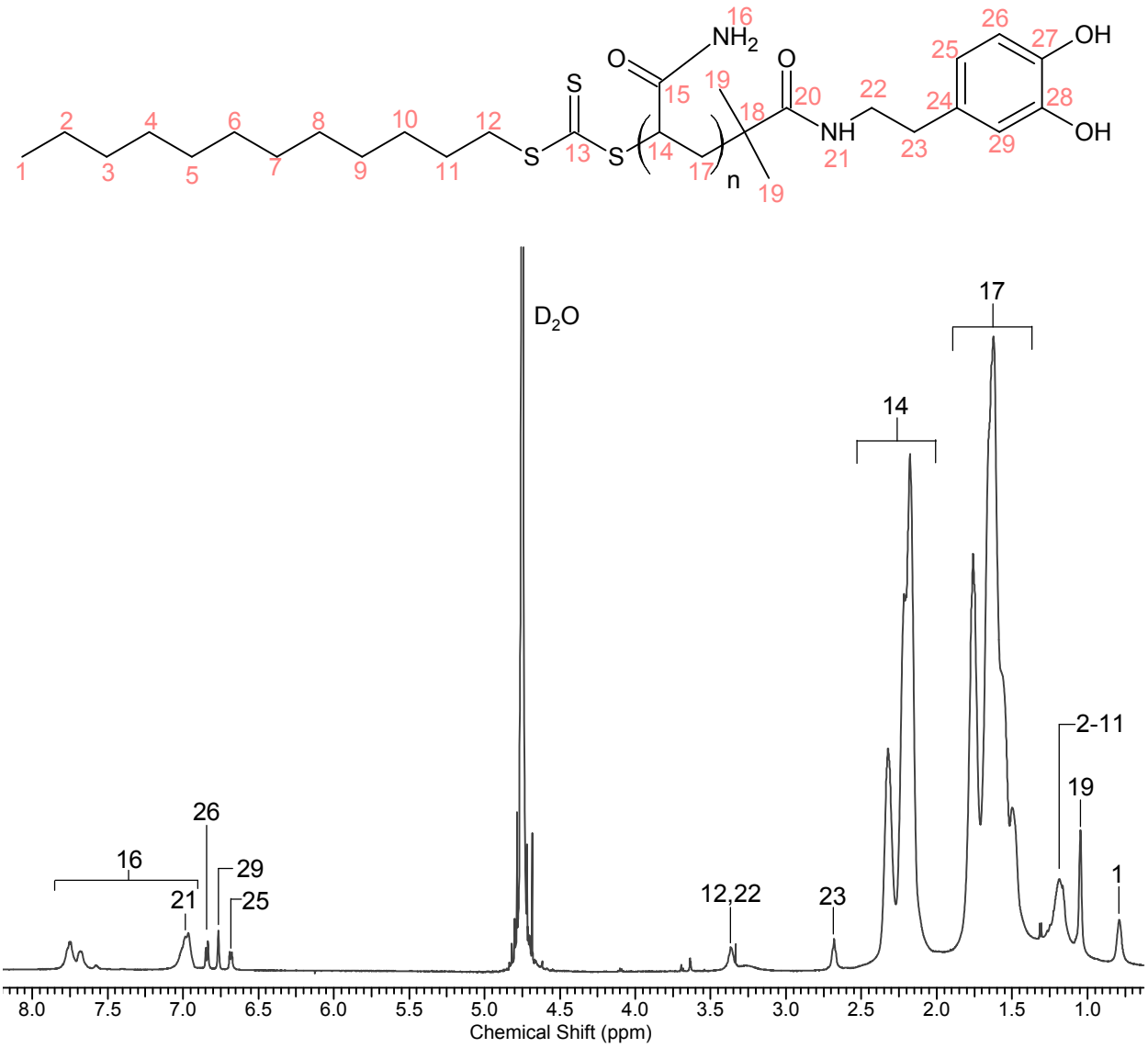

Figure S15. ^{1}HNMR spectrum of the synthesized DPAM (**4a**) in D_2O (600 MHz, @ 25^{o}C)

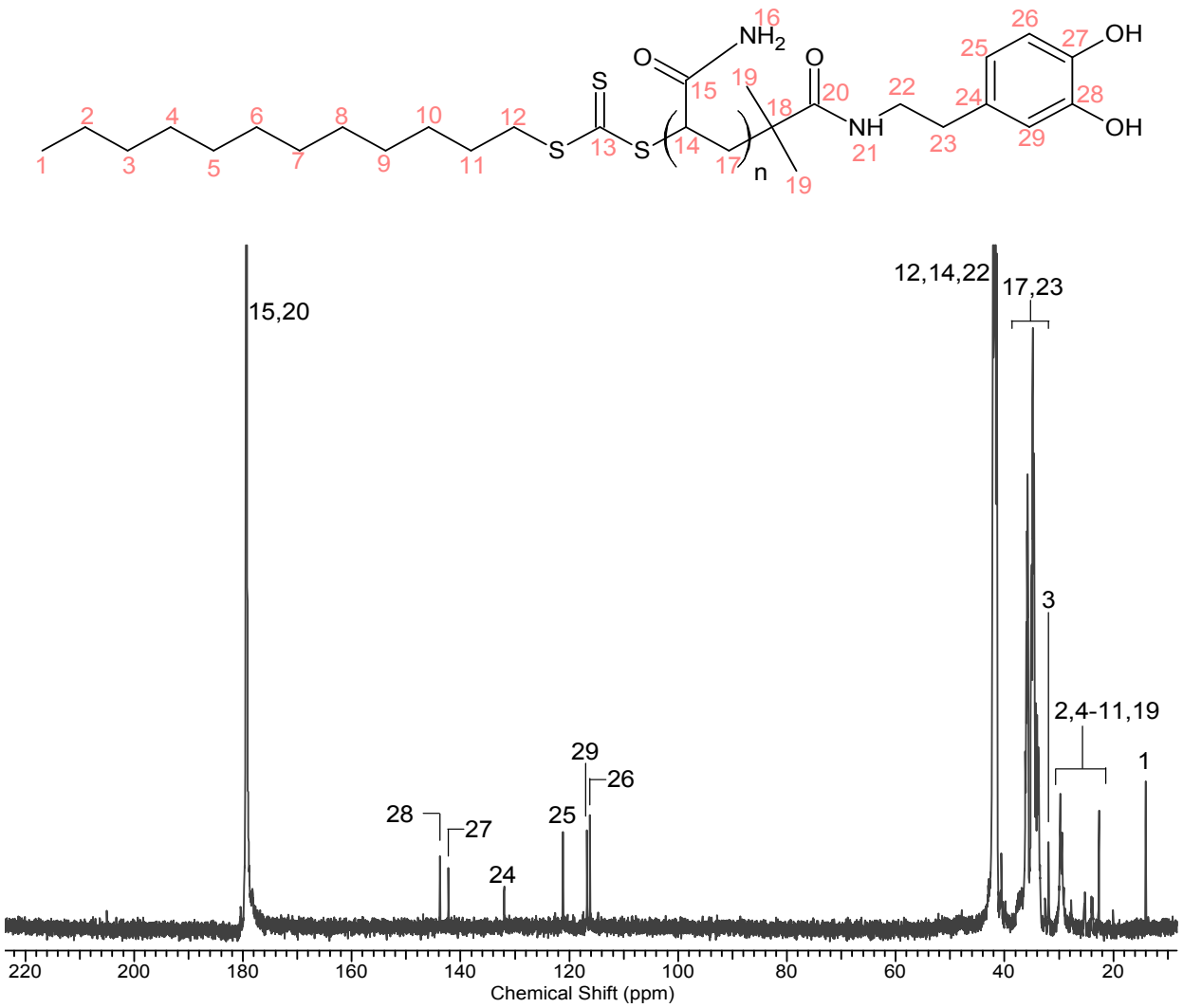

Figure S16. ^{13}C NMR spectrum of the synthesized DPAM (**4a**) in D_2O (100 MHz, @ 25°C)