Supporting Information

Photocatalytic Surface Patterning of Cellulose using Diazonium Salts and Visible Light

Peter Schroll,[a] Charlie Fehl,[b] Stephan Dankesreiter[c] and Burkhard König*[a]

(a) *Institut für Organische Chemie, Universität Regensburg, Universitätsstraße 31, D-93053 Regensburg, Germany.*

(b) *Department of Medicinal Chemistry, University of Kansas, Delbert M. Shankel Structural Biology Center, 2034 Becker Drive, Lawrence, Kansas 66047-3761, USA.*

(c) *Institut für Anorganische Chemie, Universität Regensburg, Universitätsstraße 31, D-93053 Regensburg, Germany.*

Email: burkhard.koenig@chemie.uni-regensburg.de

Tel.: +49 941 943 4575 Fax: +49 941 943 1717

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1 Instruments and Materials

NMR-spectra were recorded on a Bruker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz, T = 295 K and a Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz, T = 295 K) spectrometer) equipped with a robotic sampler. Chemical shifts are reported in δ [ppm]. Tetramethylsilane (TMS) was used as an external standard. The spectra were analyzed by first order, the coupling constants *J* are given in Hertz [Hz].

Characterization of the signals: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, dt = doublet of triplets, tt = triplet of triplets, m = multiplet, br. s. = broad singlet), and coupling constants (Hz). Integration is determined as the relative number of protons. Error of reported values: chemical shift: 0.01 ppm for ^{1}H-NMR, 0.1 ppm for ^{13}C-NMR and 0.1 Hz for coupling constants. The solvent used is reported for each spectrum.

Electron-impact (EI-MS) and chemical ionisation (CI-MS) **mass spectra** were measured on a Finnigan TSQ 710 spectrometer, and electronspray ionization (ESI-MS) mass spectra were measured on a ThermoQuest Finnigan TSQ 7000 spectrometer.

UV/Vis spectra in solution were recorded on a Cary BIO 50 UV/Vis/NIR spectrometer (Varian). A 10 mm quartz cuvette from Hellma was used.

Diffuse UV/Vis reflectance spectra for solid samples were recorded using an Omega 20 spectrometer (Bruins Instruments, Puchheim, Germany). Reflectance spectra were transformed into absorption spectra by Kubelka-Munk transformation.

Fluorescence spectra were recorded on a FluoroMax®-4 fluorescence spectrofluorometer (Horiba). Liquid samples were measured using cuvettes. Fluorescence spectra of cellulose sheets were obtained using a solid sample holder, which ensures an accurate positioning of the substrate for the measurement.

IR spectra of solid samples were recorded on a BIO-RAD Excalibur IR spectrometer.

Microscopic pictures have been recorded on a Makroskop M420 (Wild Heerbrugg).

All reactions were monitored by **thin layer chromatography** (TLC) using silica gel 60 F_{254} aluminium sheets (Merck) with detection under 254 nm or 366 nm UV light excitation, by naked eye, or by staining with appropriate stains (anisaldehyde or orthophosphomolybdic acid).

Preparative thin layer chromatography (PTLC) was carried out on homemade glass plates (20x20 cm) coated with silica gel 60 GF254 with ~15% calcium sulfate and fluorescent indicator (20 g, Fluka).

Column chromatography was performed on silica gel (Merck silica gel Si 40 – 63 µm).

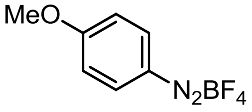
Visible light irradiation was performed with an OSRAM® Oslon SSL 80 LD H9GP-3T3U-35 royal-blue LED lamp (P = 1.12 W, 700 mA, λ_{max} = 455 nm).

Solvents were used as p.a. grade or dried by usual methods[1] and distilled prior to use if required by the experimental procedure. All **reagents and starting materials** were purchased from Aldrich, Fluka, VWR, Acros or Schleicher&Schüll and used without further purification.

2 Synthesis of Substrates

2.1 4-Methoxybenzenediazonium tetrafluoroborate

4-Methoxybenzenediazonium tetrafluoroborate was synthesized according to previous literature reports:[2, 3] 4-methoxyaniline (1.85 g, 15 mmol) was dissolved in a mixture of distilled water (6 mL) and hydrofluoroboric acid (32%, 1 eq., 8.0 mL, 15 mmol). After cooling the reaction mixture to 0°C sodium nitrite (1.0 g, 15 mmol) in water (2.0 mL) was added dropwise. The resulting mixture was stirred for two hours. A thick precipitate was formed, collected by filtration and re-dissolved in a minimum of acetone. The diazonium tetrafluoroborate was precipitated by the addition of diethyl ether. Further purification was achieved by repeating the procedure of dissolving the solid in acetone and precipitating the product by addition of diethyl ether, until the product was obtained as a white solid. The product was filtered, washed three times with diethyl ether and dried in vacuo to yield 1.85 g (56%) of a white solid.



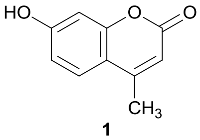
^{1}H-NMR (400 MHz, DMSO-d_6): δ [ppm] = 4.04 (s, 3H), 7.46 – 7.51 (m, 2H), 8.59 – 8.64 (m, 2H).

^{13}C-NMR (101 MHz, DMSO-d_6): δ [ppm] = 57.5, 103.4, 117.3, 136.1, 168.8.

MS (ESI): *m/z* (%) = 135.0 (100) [M^+], 175.9 (14) [M^++MeCN].

2.2 7-Hydroxy-4-methyl-2H-chromen-2-one (1)

7-Hydroxy-4-methyl-2H-cgromen-2-one was synthesized using the Pechmann reaction, as described elsewhere:[4, 5] Recorcinol (9.1 mmol, 1.0 g, 1.0 eq.) and ethyl acetoacetate (9.1 mmol, 1.15 mL, 1.0 eq.) were dissolved in trifluoroacetic acid (6 mL) in a round bottom flask at ambient temperature. The solution was stirred for 24 h. The mixture was quenched by addition of ice-cold water (20 ml). After one hour at 0°C, a precipitate was formed that was filtered off in a sintered filter and washed with water (2x5 mL), and dried under high vacuum. Traces of water were removed by lyophilization. Yield: 1.4 g (89%) of **1** (white solid).



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^{1}H-NMR (300 MHz, DMSO-d$_6$): δ [ppm] = 2.35 (d, *J* = 1.1 Hz, 3H), 6.12 (d, *J* = 1.1 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 10.52 (s, 1H).

^{13}C-NMR (75 MHz, DMSO-d$_6$): δ [ppm] = 18.0, 102.1, 110.1, 111.9, 112.7, 126.5, 153.4, 154.7, 160.2, 161.0.

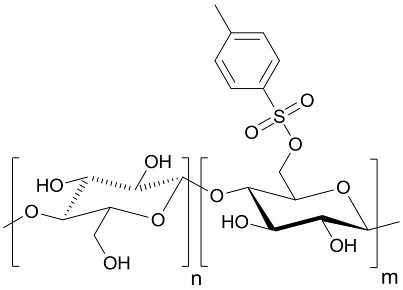
MS (ESI): *m/z* (%) = 176.1 (100) [$M^{\cdot+}$], 148.1 (85) [$M^{\cdot+}$-CO].

2.3 General procedure for photocatalytic experiments in homogeneous solution

A 5 mL reaction vessel with a magnetic stirring bar was equipped with $Ru(bpy)_3Cl_2\cdot 6H_2O$ (1 mol%, 1.5 mg), aryl diazonium tetraflouroborate (1 eq., 0.2 mmol), unsaturated compound **3** (5 eq., 1.0 mmol) and dry DMSO (1 mL). The mixture was degassed by “freeze-pump-thaw” technique (three cycles) and irradiated with a blue high power LED P = 1.12 W, 700 mA, λ_{max} = 455 nm) for 20 minutes at 20°C. The reaction mixture was diluted with water (4 ml) and extracted with diethyl ether (3 x 5 mL). The combined organic layers were concentrated in vacuum. Traces of water were removed by lyophilization. Purification of the crude product was achieved by preparative thin-layer chromatography on silica gel 60 F254 using a mixture of petroleum ether and ethyl acetate (3:1) as eluent.

2.4 Tosylated cellulose (9)

Cellulose was tosylated following a literature-known procedure:[6, 7] Cellulose (filter paper, 45 mm diameter, 110 mg, 0.61 mmol with respect to amount of glucose, 1.0 eq.) was submerged in a mixture of $NaOH_{aq}$ (20%, 20 mL) and THF (10 mL) and cooled to 0°C. Tosyl chloride (0.92 mmol, 175 mg, 1.5 eq.) in THF (10 mL) was added dropwise. The mixture was stirred for 24 hours and allowed to warm to ambient temperature. The filter paper was washed with water (3x15 mL) and acetone (3x15 mL), and dried under high vacuum for three hours.



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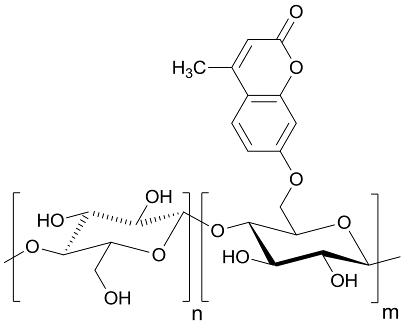
2.5 Coumarin-linked cellulose (7)

A flask was filled with DMF (dry, 30 mL) and coumarin derivative **3** (1.8 mmol, 0.42 g, 3.0 eq. with respect to amount of filter paper), potassium carbonate (3.7 mmol, 0.51 g, 6.0 eq.) and tosylated filter paper and heated to 90°C for 24 hours. After that, it was washed with ethanol (3x15 mL), and dried under high vacuum. The procedure was also performed with arylated coumarin **2**.



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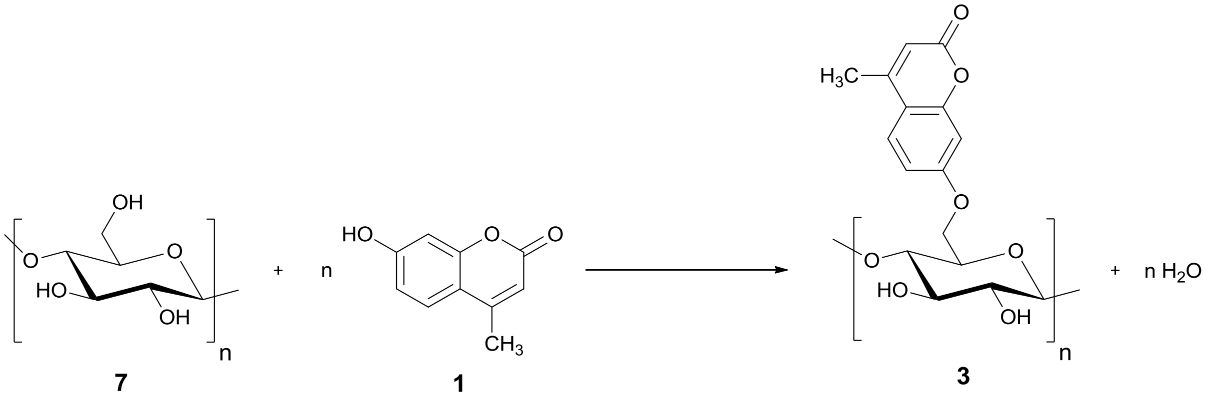
2.6 Determination of filter loading

Equation for immobilization of 7-hydroxy-4-methyl-2H-chromen-2-one **1** on cellulose:



Calculation of filter loading x_i from gravimetric data:

$$x_i = \frac{n(\mathbf{3})}{n(\mathbf{7})}$$

$$x_i = \frac{[m(\mathbf{1}) - m(H_2O)] \cdot M(\mathbf{7})}{[M(\mathbf{1}) - M(H_2O)] \cdot m(\mathbf{7})}$$

Note: Molar mass of glucose in cellulose polymer M(**7**) is 162.05 g·mol^{-1}, since condensation of glucose monomers (M = 180.06 g·mol^{-1}) to give cellulose liberates water.

Results from three independent experiments $x_1 = 24.3\%, x_2 = 20.1\%, x_3 = 18.4\%;$

With x being the arithmetic mean $x = \frac{\sum_{i=1}^{n} x_i}{n} = 21.0\%$

Calculation of standard deviation s $s = \sqrt{\frac{\sum_{i=0}^{n} (x_i - x)^2}{n-1}} = 3.0\%$

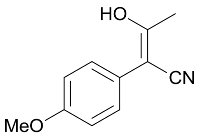
Filter loading is determined to be 21%±3%.

2.7 General procedure for heterogeneous photocatalytic experiments

A dry, coumarin-linked cellulose polymer (filter paper; loading: 21%±3% corresponding to 0.13 mmol of immobilized coumarin derivative **1**) was put on aluminum foil. A solution of Ru(bpy)$_3$Cl$_2$·6H$_2$O (6.4 mg, 8.5 µmol, 6 mol%, 6.4 mg) and *p*-methoxy diazonium tetraflouroborate (33.3 mg, 0.15 mmol) in dry DMSO (0.6 mL) was applied to the paper. A mask was fit over the paper, and a high power blue LED (light emitting diode; P = 1.12 W, 700 mA, $\lambda_{max} = 455$ nm) propped over the setup and initiated for 20 minutes. After that, the mask was removed and the polymer was washed with methanol, water, and acetone, and dried in the air. The pattern was visible on the polymer.

2.8 (Z)-3-Hydroxy-2-(4-methoxyphenyl)but-2-enenitrile (11)

The molecule was synthesized according to literature.[8] A 100 mL flask was dried, filled with nitrogen, and equipped with DMSO (55 mL). NaH (4.0 g, 100 mmol, 60% suspension in paraffin oil) was added in portions and the mixture was heated to 75°C for 30 minutes, until hydrogen evolution had ceased. The solution was cooled to 20°C and *p*-methoxyphenylacetonitrile (13.3 mL, 98 mmol) was added rapidly while keeping the temperature below 25°C. The mixture was stirred for five minutes. Ethyl acetate (9.7 mL, 98 mmol) were added to the yellow solution and the temperature was kept below 20°C. The solution was allowed to warm to ambient temperature and stirred for two hours. The mixture was poured into 280 mL of ice-water and extracted four times with dichloromethane (50 mL each). The turbid aqueous layer was filtered and acidified with acetic acid (8 mL). After one hour in the fridge, the white precipitate was filtered off, washed with water, and dried under vacuo to yield 16.4 g (89%) of product.



11

^{1}H-NMR (300 MHz, DMSO-d_6): δ [ppm] = 2.30 (s, 3H), 3.74 (s, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 11.31 (s, 1H).

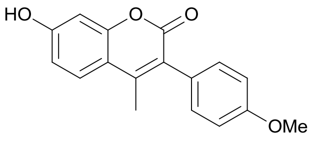
^{13}C-NMR (75 MHz, DMSO-d_6): δ [ppm] = 21.6, 55.1, 86.2, 113.7, 114.1, 125.1, 128.3, 157.5, 166.7.

R_F (PE/EE 5:1) = 0.13

MS (EI): *m/z* (%) = 189.1 (10) [$M^{\cdot+}$], 147.1 (100) [$M^{\cdot+}$ – O=C=CH_2], 132.1 (34) [$M^{\cdot+}$ – O=C=CH_2 – $CH_3^{\cdot}$].

2.9 7-Hydroxy-3-(4-methoxyphenyl)-4-methyl-2H-chromen-2-one (2)

The molecule was synthesized according to literature.[8] A 50 ml double-necked flask, stirring bar and thermometer was filled with sulphuric acid (97%, 11 ml) and cooled to 5 °C. (Z)-3-hydroxy-2-(4-methoxyphenyl)but-2-enenitrile (6.62 g, 35 mmol) and resorcinol (3.85 g, 35 mmol) were mixed in a mortar and added in small portions over 70 minutes with vigorous stirring. The cooling bath was removed and stirring was continued for another 68 h. The viscous mixture was poured into water (60 mL) and ice (60 g). An orange honey-like tar separated. The supernatant was removed and the tar was heated with sulphuric acid (10% in water, 170 mL) to reflux. A clear solution was decanted and refluxed for two hours. After cooling to 0°C, a solid precipitated which was collected and boiled in ethanol (150 mL). After that, the solution was mixed with water (300 mL). Cooling facilitated crystallization. Pale yellow crystals were collected by filtration, and dried under high vacuo to yield 1.1 g (11%) of product.



2

^{1}H-NMR (300 MHz, DMSO-d_6): δ [ppm] = 2.21 (s, 3H), 3.79 (s, 3H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.95 – 7.01 (m, 2H), 7.17 – 7.24 (m, 2H), 7.64 (d, *J* = 8.8 Hz, 1H), 10.51 (s, 1H).

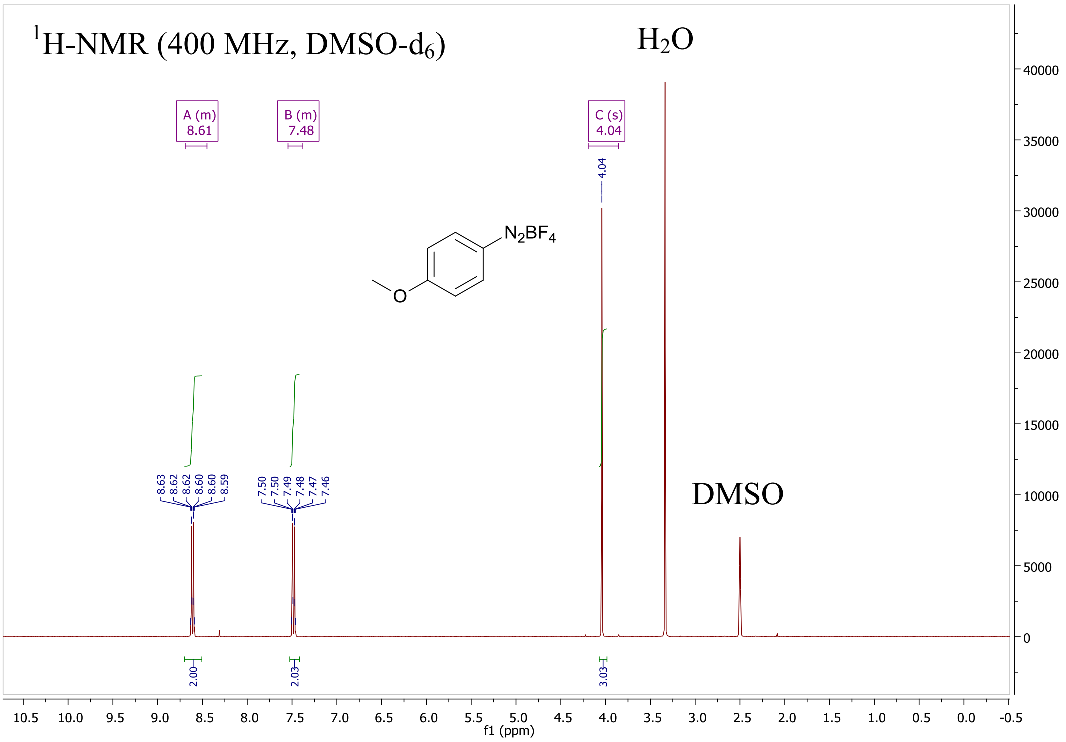
^{13}C-NMR (75 MHz, DMSO-d_6): δ [ppm] = 16.4, 55.1, 101.9, 112.5, 113.0, 113.5, 122.0, 126.9, 127.1, 131.6, 148.1, 153.8, 158.7, 160.5, 160.7.

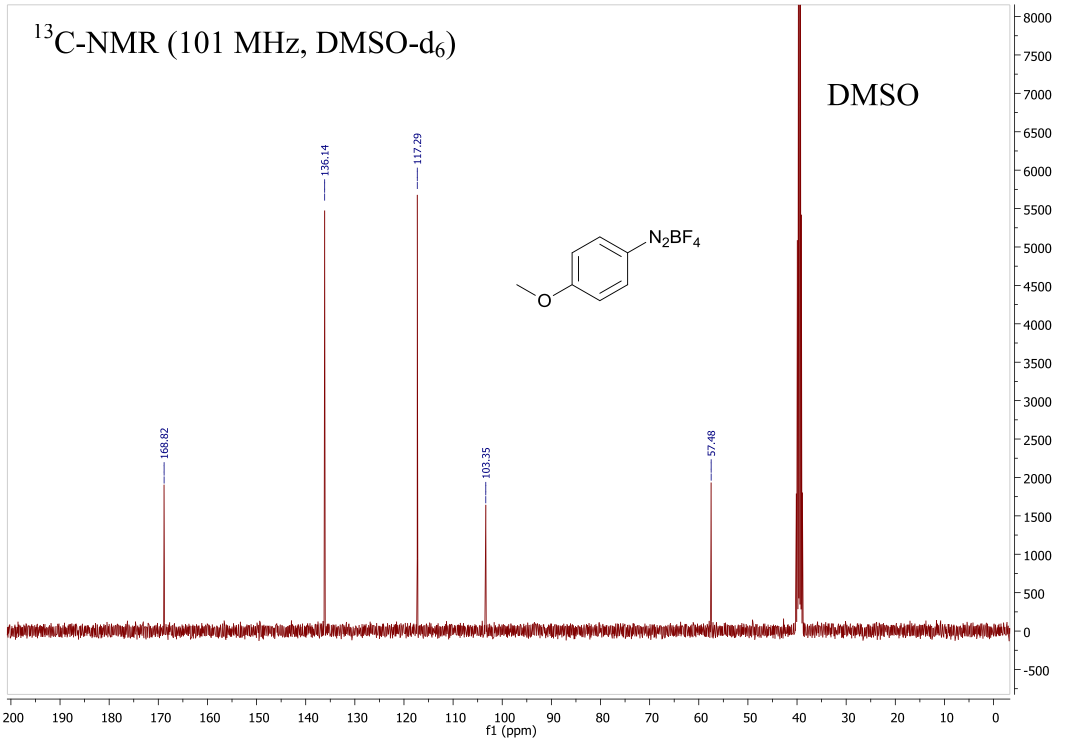
MS (ESI): *m/z* (%) = 283.1 (100) [MH^+], 587.2 (8) [$2MNa^+$].

R_F (PE/EE 3:1) = 0.18

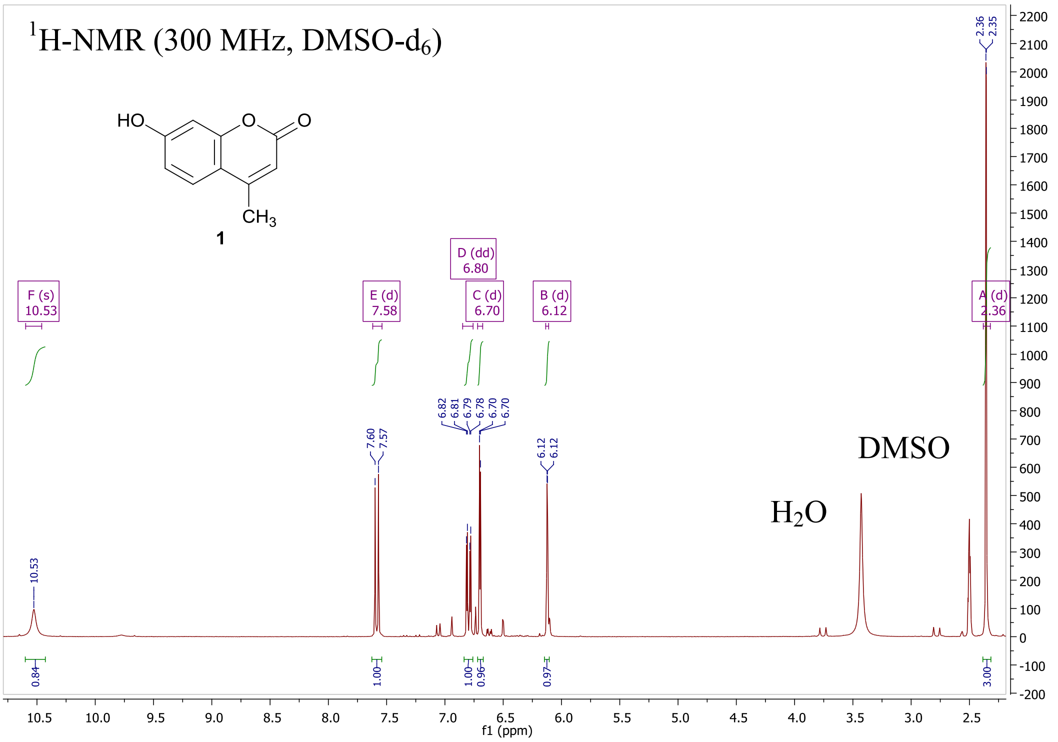
3 Spectroscopic data

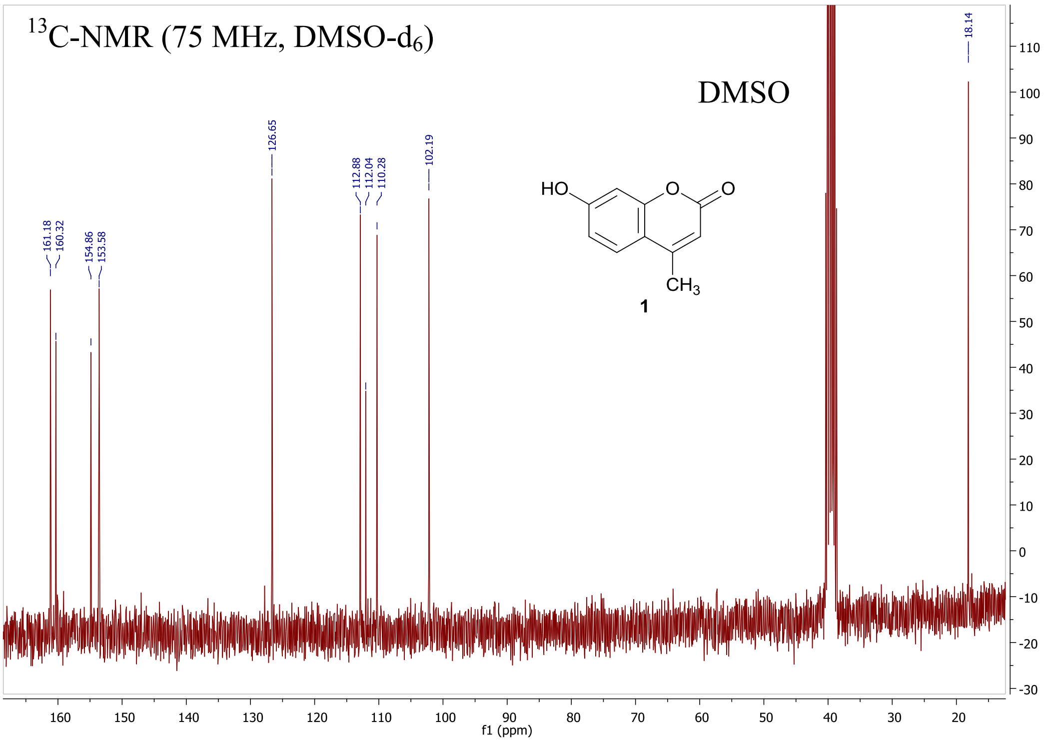
3.1 NMR data of 4-methoxybenzenediazonium tetrafluoroborate



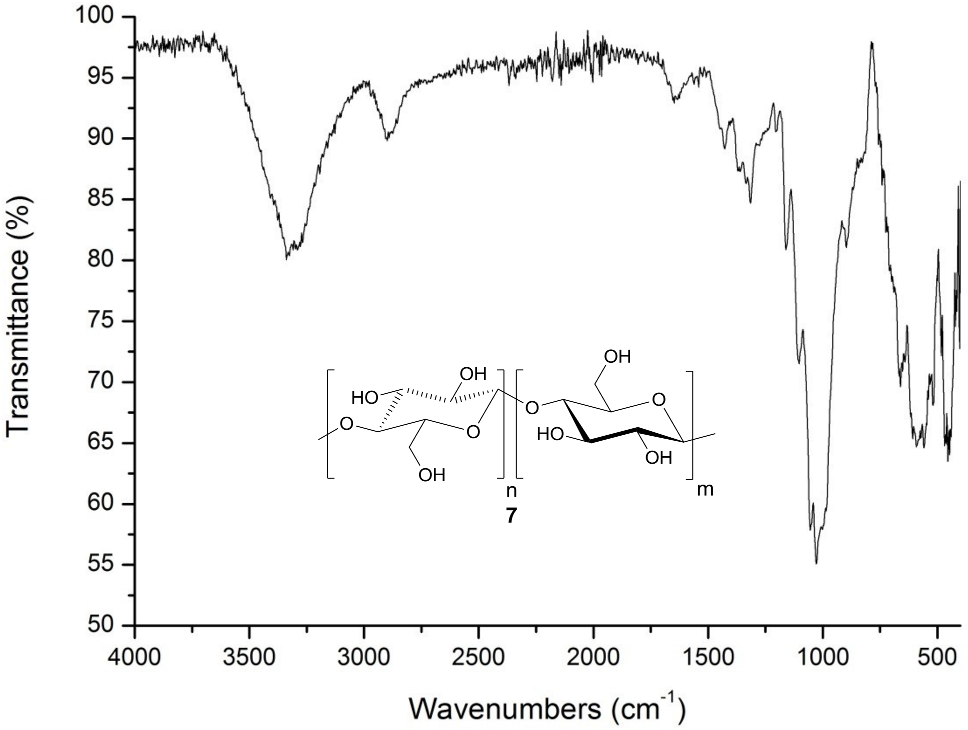


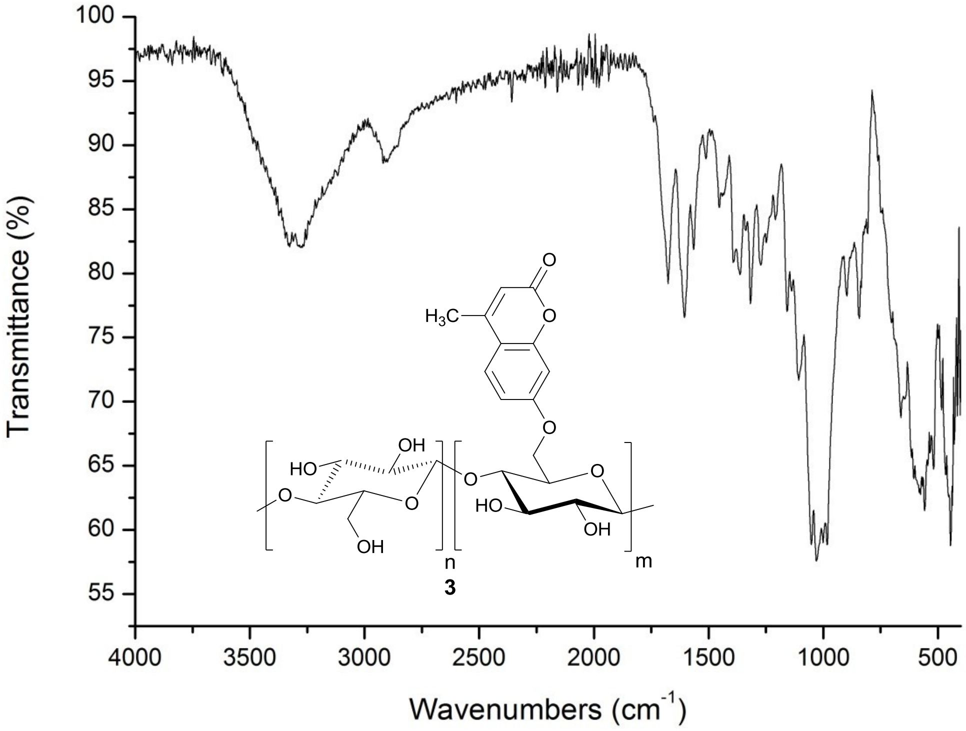
3.2 NMR data of 7-hydroxy-4-methyl-2H-chromen-2-one (1)



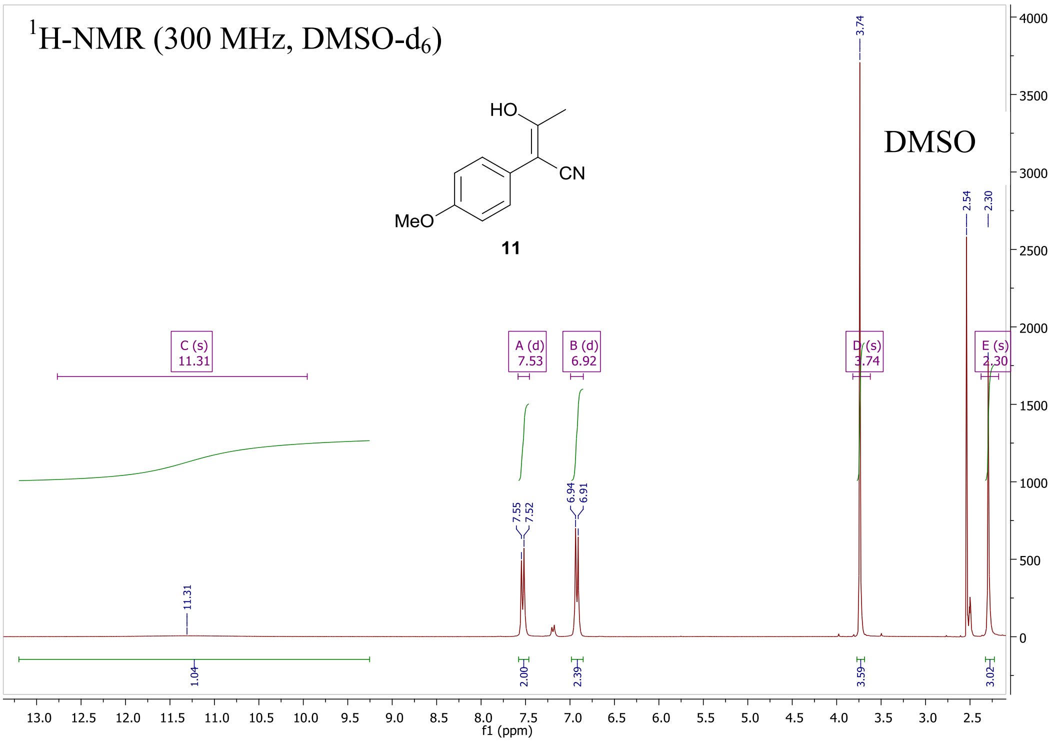


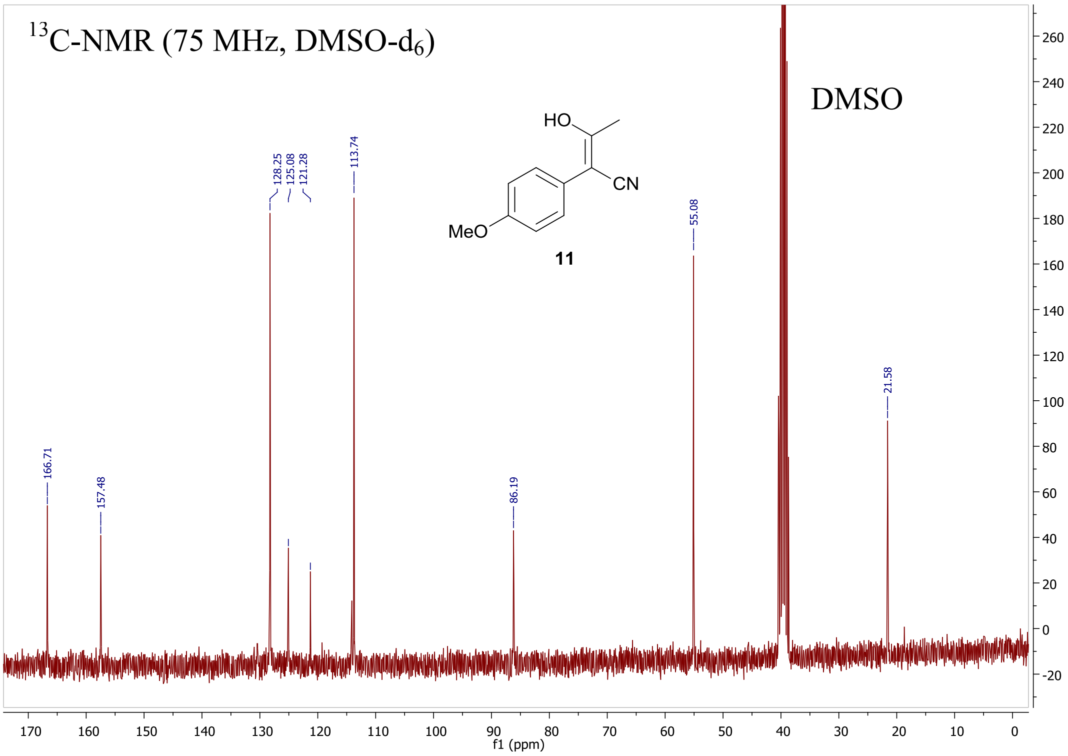
3.3 IR data of cellulose (7) and coumarin-linked cellulose (3)



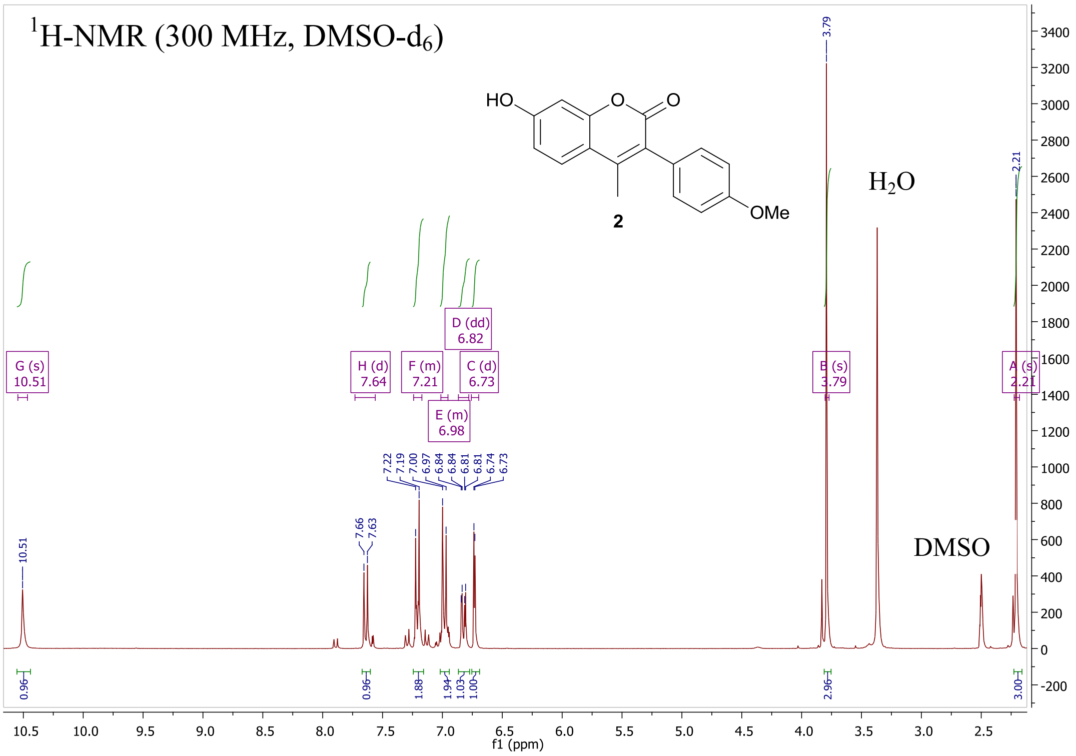


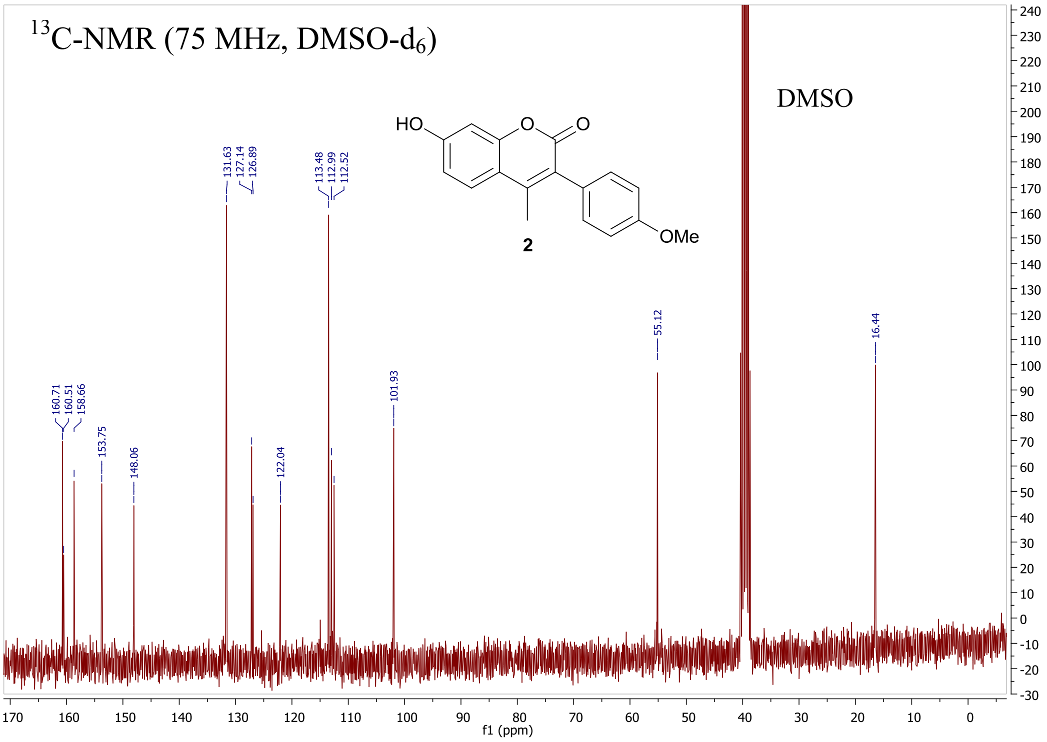
3.4 NMR data of (Z)-3-Hydroxy-2-(4-methoxyphenyl)but-2-enenitrile (11)





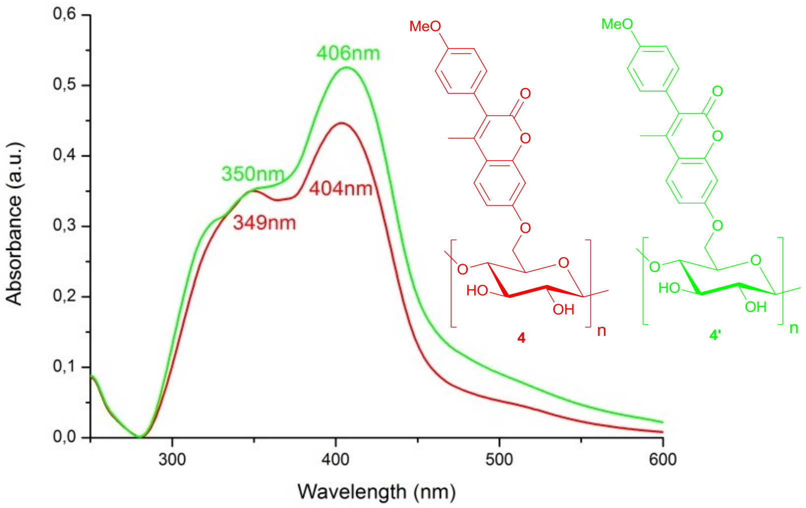
3.5 NMR data of 7-Hydroxy-3-(4-methoxyphenyl)-4-methyl-2H-chromen-2-one (2)





3.6 Absorption spectra of arylated photoproduct (4) and independently prepared authentic sample (4')

Authentic sample 4' has been synthesized by immobilization of **2** in the same manner as described for the immobilization of **1** on cellulose.



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