Supporting Information

# Optical Control of pH *via* Chromoselective Photodosimetry

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# 1. General information

Commercially available chemicals were used as received. Dry solvents were obtained commercially unless otherwise noted.

7-(Diethylamino)-4-(hydroxymethyl)-2*H*-chromen-2-one (coumarin alcohol),[1] PAD2,[2] and PBD2[3] were synthesized according to literature procedures.

Flash column chromatography was performed using silica gel (pore size 60 Å, 400 mesh, 40-63 µm particle size) on a Biotage Isolera One using eluent gradients or by manual flash column chromatography as stated with the procedures.

$^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker Avance Neo 400, Avance III HD 400, Avance III 400 or Avance III HD 300 at 25 °C. Chemical shifts (δ) are given in parts per million (ppm) relative to the residual solvent signal (for $^{1}$H detection, δ = 7.26 ppm ($CDCl_3$) and 2.50 (DMSO-$d_6$); for $^{13}$C detection, δ = 77.16 ppm ($CDCl_3$) and 39.52 (DMSO-$d_6$)).[4] The splitting pattern of peaks is designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), or combinations of these signals.

LC-MS was performed on an Agilent 1260 Infinity II combined with an InfinityLab LC/MSD iQ mass detector (ESI) using an Infinity Lab Poroshell 120 EC-C18 column at 40 °C eluted with MeCN/$H_2O$ + 0.1% formic acid. Electron spray ionization mass spectrometry (ESI-MS) and high resolution ESI (HR-MS) were performed on a maXis or MicroTOF spectrometer from Bruker (Bremen Germany). Values are given in m/z.

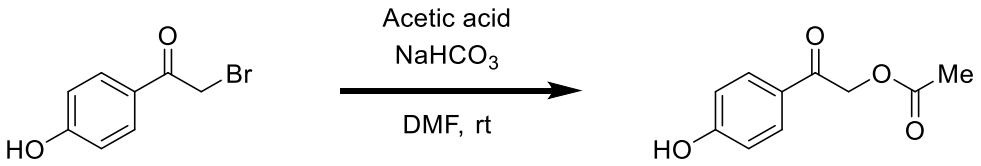
UV-Vis absorption spectroscopy was done on a Specord S600 in quartz cuvettes (path 1.00 cm) at a controlled temperature of 20 °C. Molar attenuation coefficients (ε) were determined by fitting the slope of absorbance vs. concentration taken from at least three separate dilutions.

Irradiation was either performed with a home-built LED setup at a fixed distance, orthogonal to the detector light path, with an Alonefire SV003 (365 nm), with an OptoWell irradiation device at 368 nm (mean irradiance in 3 mm distance to the emissive surface: 3.62 mW/cm$^2$, https://optobiolabs.com/products/optowell/), or with a Thorlabs M310L3 LED and an OptoWell irradiation device at 448 nm (mean irradiance in 3 mm distance to the emissive surface: 12.89 mW/cm$^2$). pH measurements were performed using a Mettler-Toledo pH/Ion meter SevenDirect SD50 with a 5 s read-out rate. The pH meter was calibrated in aqueous buffers (pH values 4.01, 7.00, and 9.21).

Abbreviations used: PADs – photoacid donors, PBDs – photobase donors, DMF – *N*,*N*′-dimethylformamide, DCM – dichloromethane, THF – tetrahydrofuran, DCC – *N*,*N*′-dicyclohexylcarbodiimide, DMAP – 4-dimethylaminopyridine.

# 2. Synthesis and characterization of PADs and PBDs

## Synthesis of 2-(4-hydroxyphenyl)-2-oxoethyl acetate (PAD1)[5]:

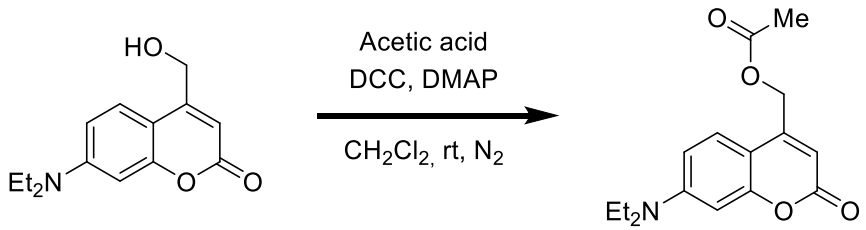



2-Bromo-1-(4-hydroxyphenyl)ethan-1-one (300 mg, 1.39 mmol, 1.0 equiv), acetic acid (90 µL, 1.67 mmol), and $NaHCO_3$ (140 mg, 1.67 mmol) were stirred in DMF (2 mL) for 2 h at room temperature. The reaction was then quenched with brine. The resulting mixture was extracted with DCM. The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure by rotary evaporation. The crude product was purified by column chromatography (30% EtOAc in pentane) to obtain an off-white solid (yield: 230 mg, 85%).

**$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 10.48 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.35 (s, 2H), 2.13 (s, 3H).

**$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 190.6, 169.9, 162.6, 130.3, 125.4, 115.4, 66.0, 20.4.

## Synthesis of (7-(diethylamino)-2-oxo-2*H*-chromen-4-yl)methyl acetate (PAD3):



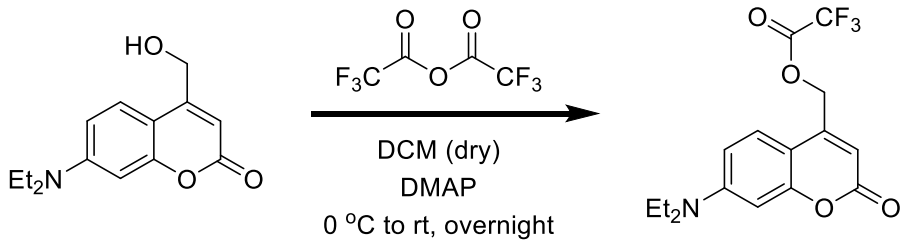

DMAP (48 mg, 0.396 mmol) and DCC (404 mg, 1.955 mmol) were added to 15.0 mL of dry DCM under an inert atmosphere. To this, 0.3 mL of acetic acid (5.245 mmol) was added, and the reaction was stirred for 30 min, until 182 mg of 7-(diethylamino)-4-(hydroxymethyl)-2*H*-chromen-2-one (0.737 mmol, 1.0 equiv) was added. The reaction was stirred for 6 h, at which point full conversion was observed by TLC (30% EtOAc in pentane). The reaction was filtered and concentrated by rotary evaporation, after which residual dicyclohexylurea was removed by redissolution of the product in cold acetonitrile. Purification by column chromatography (3% EtOAc in DCM) afforded the desired product in good yield (161 mg, 75%).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.0 Hz, 1H), 6.58 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.51 (d, *J* = 2.6 Hz, 1H), 6.13 (t, *J* = 1.3 Hz, 1H), 5.21 (d, *J* = 1.3 Hz, 2H), 3.41 (q, *J* = 7.1 Hz, 4H), 2.19 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 170.4, 162.0, 156.4, 150.8, 149.5, 124.5, 108.8, 106.6, 106.1, 98.0, 61.5, 44.9, 20.9, 12.6.

**HRMS** (ESI) m/z: $[M+H]^+$: 290.1385 (calcd 290.1387).

## Synthesis of (7-(diethylamino)-2-oxo-2*H*-chromen-4-yl)methyl 2,2,2-trifluoroacetate (PAD4)[6,7]:



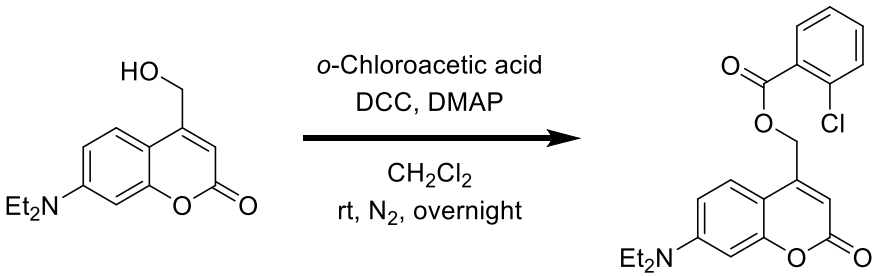

DMAP (38 mg, 0.314 mmol) and 7-(diethylamino)-4-(hydroxymethyl)-2*H*-chromen-2-one (150 mg, 0.607 mmol, 1.0 equiv) were added to 3.0 mL of dry DCM under inert atmosphere. The reaction was cooled to 0 °C and trifluoroacetic acid anhydride (TFAA, 0.15 mL, 0.5 mmol) was added dropwise. The reaction was stirred at 0 °C for 30 min., after which the reaction was allowed to warm up to room temperature. After 1 h, a further 0.1 mL of TFAA (0.3 mmol) was added and the reaction was stirred overnight. The reaction was quenched by dropwise addition of water (3.0 mL), after which the layers were separated and the organic phase was washed with aq. HCl (1M, 3.0 mL), aq. $NaHCO_3$ (sat., 3.0 mL), and brine (3.0 mL). The organic phase was dried over $MgSO_4$, concentrated by rotary evaporation and purified by column chromatography (15 to 50% EtOAc in pentane).

The instability of the product precluded full characterization.

**$^{1}$H NMR** (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 9.1 Hz, 1H), 6.60 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.53 (d, *J* = 2.5 Hz, 1H), 6.18 – 6.11 (m, 1H), 5.44 (d, *J* = 1.2 Hz, 2H), 3.43 (q, *J* = 7.1 Hz, 4H), 1.21 (t, *J* = 7.1, 4.0 Hz, 6H).

**$^{19}$F NMR** (282 MHz, $CDCl_3$) δ -74.58.

## Synthesis of (7-(diethylamino)-2-oxo-2*H*-chromen-4-yl)methyl 2-chlorobenzoate (PAD5):



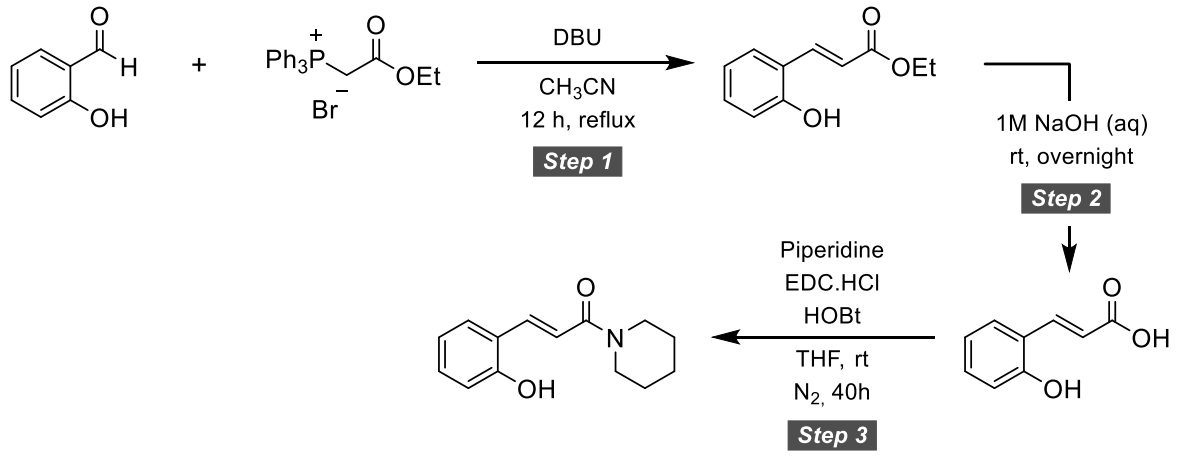

7-(Diethylamino)-4-(hydroxymethyl)-2*H*-chromen-2-one (97 mg, 0.39 mmol, 1.0 equiv), DMAP (6 mg, 0.051 mmol), DCC (96 mg, 0.46 mmol), and *ortho*-chlorobenzoic acid (143 mg, 0.912 mmol) were dissolved in dry DCM (2.0 mL) under inert atmosphere. The reaction was stirred overnight, filtered, and concentrated by rotary evaporation. Redissolution in acetonitrile removed residual dicyclohexylurea from the mixture. The crude product was purified by column chromatography (5 to 50% EtOAc in pentane) to obtain the product in decent yield. (102 mg, 68%).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.38 – 7.34 (m, 2H), 6.60 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.53 (d, *J* = 2.6 Hz, 1H), 6.27 (d, *J* = 1.2 Hz, 1H), 5.47 (d, *J* = 1.2 Hz, 1H), 3.42 (q, *J* = 7.1 Hz, 4H), 1.22 (t, J = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 169.4, 164.9, 162.0, 156.5, 150.9, 149.1, 133.4, 131.9, 131.5, 129.0, 126.9, 124.6, 108.9, 107.0, 106.1, 98.0, 77.5, 77.4, 77.2, 76.8, 62.5, 44.9, 12.6.

**HRMS** (ESI) m/z: $[M+Na]^+$: 408.0979 (calcd 408.0973).

**Synthesis of (*E*)-3-(2-hydroxyphenyl)-1-(piperidin-1-yl)prop-2-en-1-one (PBD1)[8–11]:**




## Step 1:

A solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.46 mL, 9.82 mmol), salicylaldehyde (1.0 g, 8.18 mmol, 1.0 equiv) and substituted triphenylphosphonium salt (3.62 g, 8.3 mmol) in $CH_3CN$ (12.0 mL) was stirred for 12 h under reflux. After removal of the solvent, the residue was redissolved in dichloromethane, and washed with water, 1N HCl, and brine. The organic layer was dried over $MgSO_4$ and concentrated by rotary evaporation. Purification by column chromatography (10% EtOAc in pentane) yielded 1.34 g of ethyl 2-hydroxycinnamate (79%).

**$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 10.23 (s, 1H), 7.86 (d, *J* = 16.2 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.2, 1.7 Hz, 1H), 6.91 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.83 (ddd, *J* = 7.8, 7.2, 1.1 Hz, 1H), 6.59 (d, *J* = 16.2 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

## Step 2:

Ethyl 2-hydroxycinnamate (156 mg, 0.812 mmol, 1.0 equiv) was dissolved in 5.0 mL 1M NaOH aqueous solution and stirred overnight. The reaction was filtered and acidified with 2M HCl aqueous solution until the pH was below 3 and a solid formed. This solid was collected by filtration, washed with chloroform, and dried under vacuum to obtain 2-hydroxycinnamic acid (108 mg, 0.658 mmol, 81%).

**$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 12.21 (s, 1H), 10.18 (s, 1H), 7.79 (d, *J* = 15.8 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.21 (td, *J* = 7.9, 1.7 Hz, 1H), 6.90 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 16.1 Hz, 1H)

## Step 3:

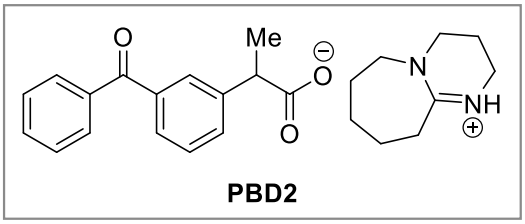
To an oven-dried vial, 2-hydroxycinnamic acid (102 mg, 0.623 mmol, 1.0 equiv), EDCxHCl (146 mg, 0.761 mmol), and HOBt (99 mg, 0.731 mmol) were added. The vial was put under nitrogen and dry THF (7.0 mL) was added. Then, of piperidine (0.1 mL, 1.0 mmol) was added to the stirring solution dropwise and the reaction was stirred for 40 h. Then, the reaction was concentrated and EtOAc (15.0 mL) was added. The crude solution was washed twice with consecutively NaOH (aq., 1M, 15.0 mL), HCl (aq., 1M, 15.0 mL), $NaHCO_3$ (aq., sat. 15.0 mL), and brine (15.0 mL). The combined aqueous fraction was extracted with EtOAc (2 x 10.0 mL). The combined organic fraction was then washed with brine (20.0 mL), dried over $NaSO_4$, and concentrated by rotary evaporation. Purification by column chromatography (2 to 15% MeOH in DCM) yielded the desired product (43 mg, 0.187 mmol, 30%).

**$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 9.96 (s, 1H), 7.74 (d, *J* = 15.5 Hz, 1H), 7.66 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.21 – 7.13 (m, 2H), 6.87 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.81 (td, *J* = 7.5, 1.2 Hz, 1H), 3.65 – 3.49 (m, 4H), 1.66 – 1.57 (m, 2H), 1.55 – 1.42 (m, 4H).

**$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 164.7, 156.1, 136.6, 130.5, 128.1, 122.0, 119.2, 117.3, 116.0, 46.1, 42.5, 26.5, 25.5, 24.2.

**HRMS** (ESI) m/z: $[M+H]^+$: 232.1339 (calcd 232.1332).

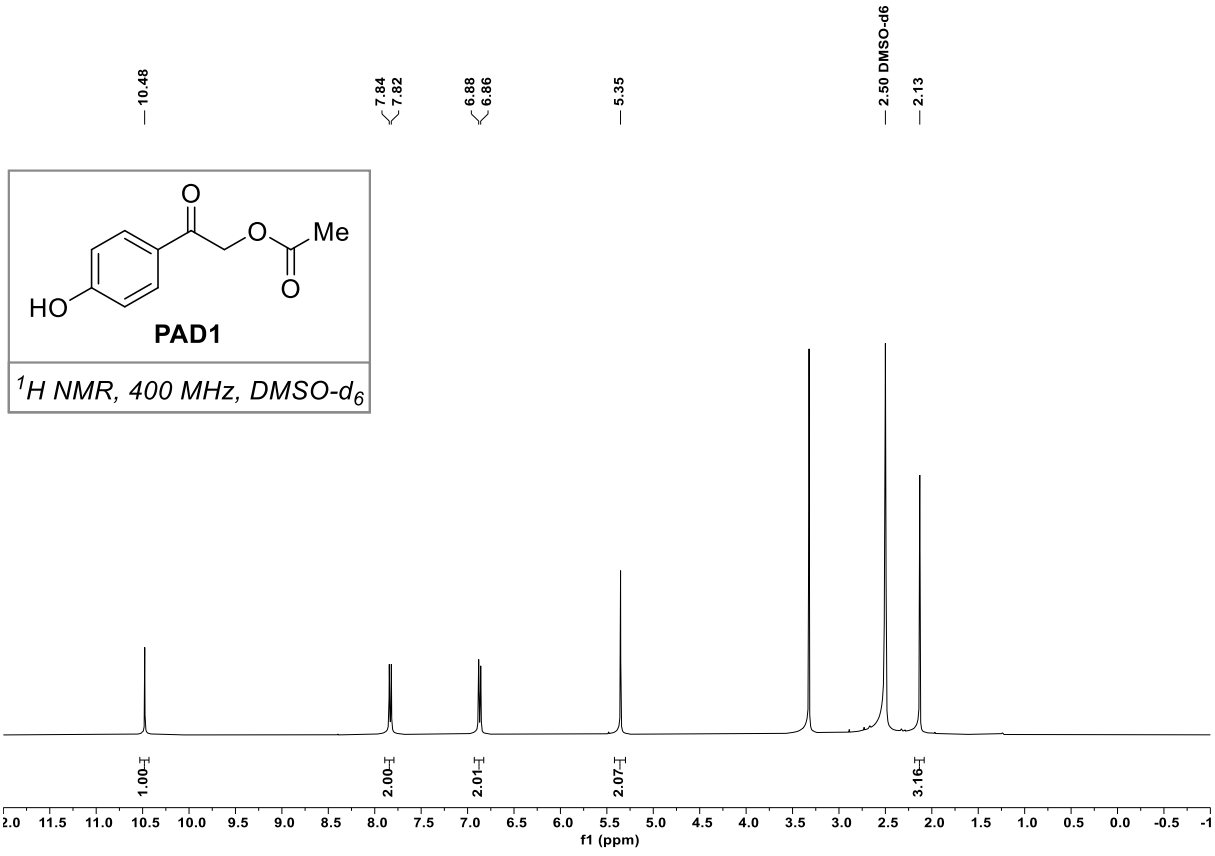
## Characterization of PBD2[3]:

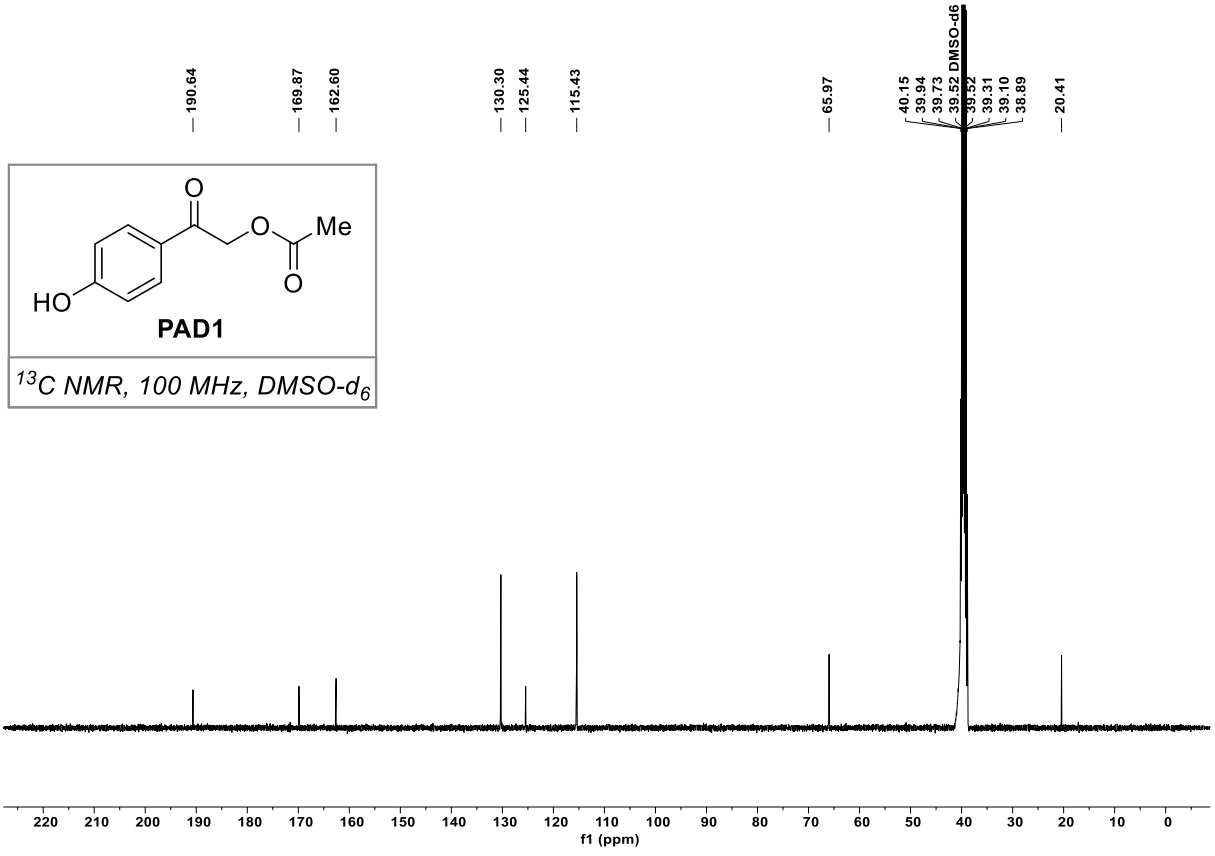


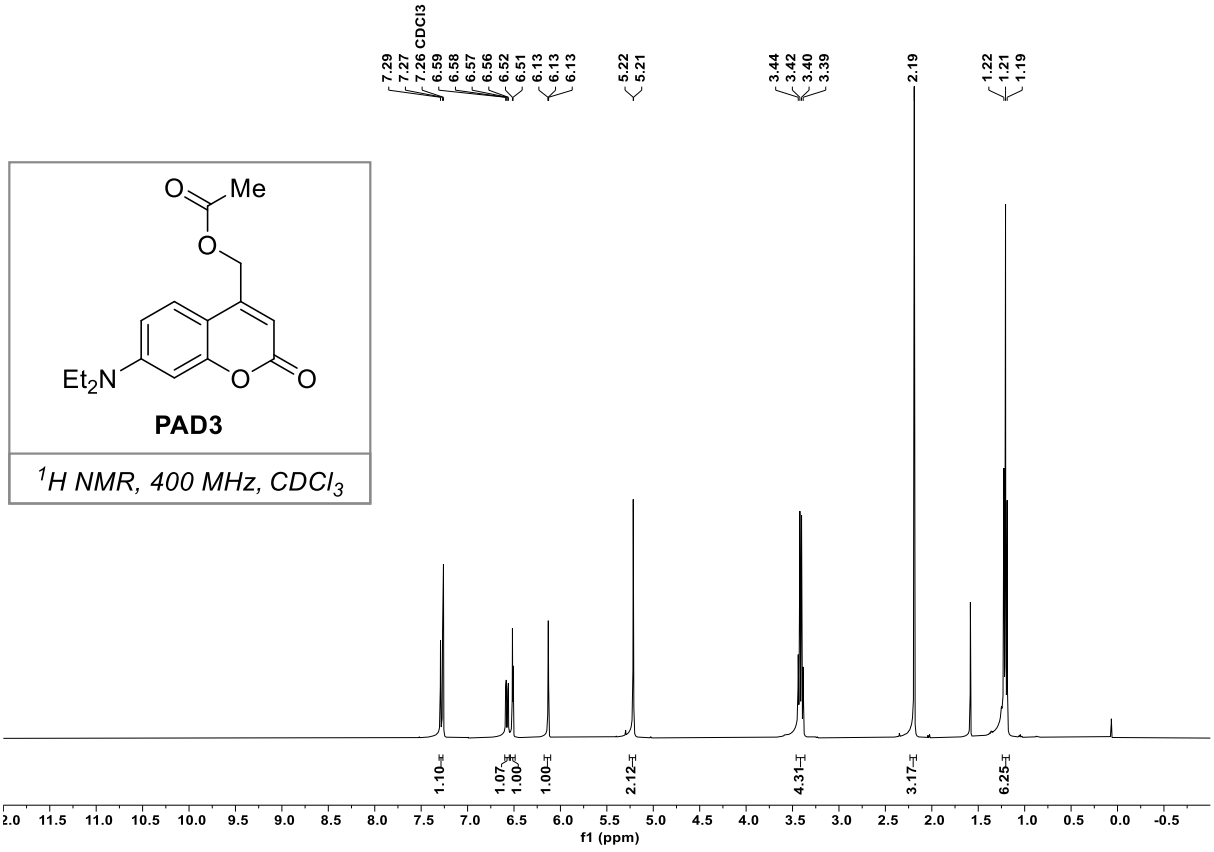
**PBD2**

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.86 – 7.75 (m, 3H), 7.67 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.45 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 1H), 3.70 (q, *J* = 7.1 Hz, 1H), 3.42 – 3.31 (m, 6H), 2.73 (d, *J* = 10.0 Hz, 2H), 1.92 (p, *J* = 6.0 Hz, 2H), 1.72 – 1.58 (m, 6H), 1.50 (d, *J* = 7.1 Hz, 3H).

# 3. NMR spectra of the synthesized compounds



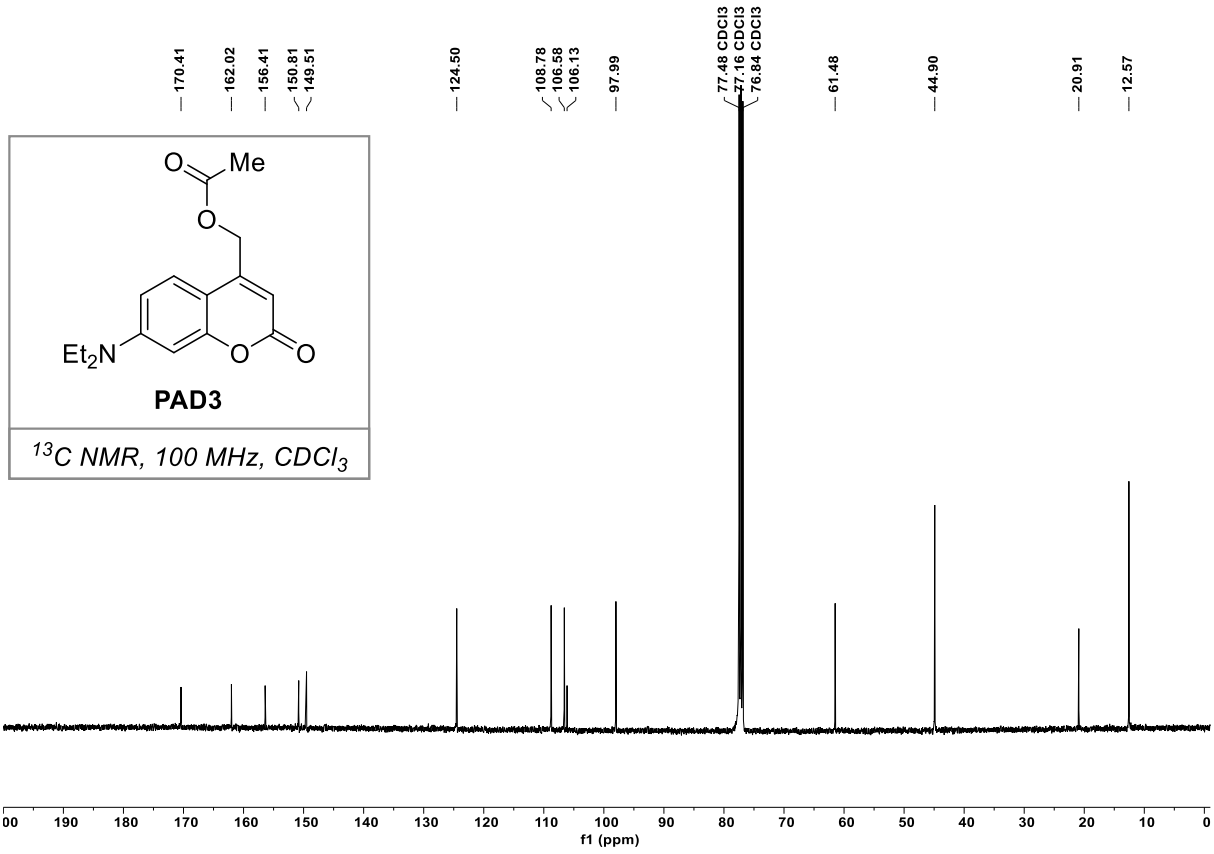






**PAD3**

*$^{1}H$ NMR, 400 MHz, $CDCl_3$*

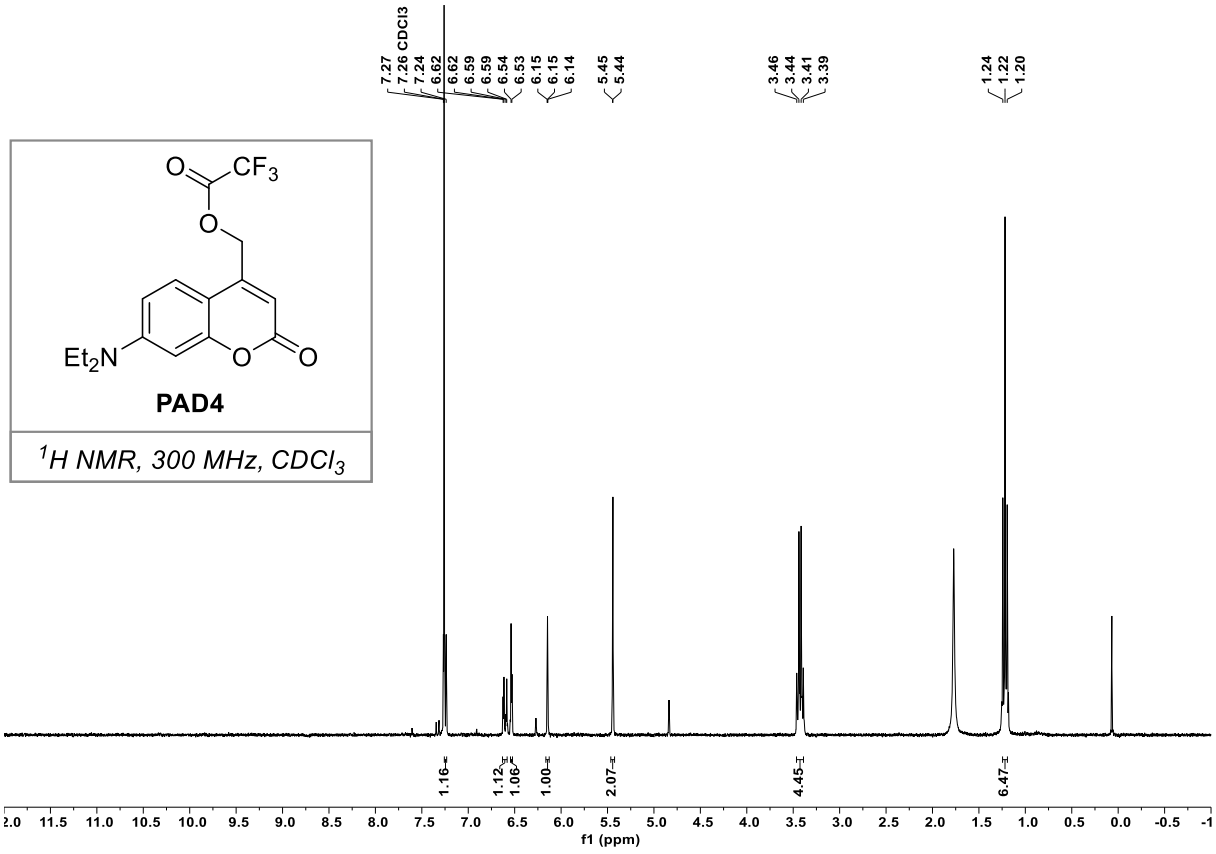






**PAD3**

*$^{13}C$ NMR, 100 MHz, $CDCl_3$*

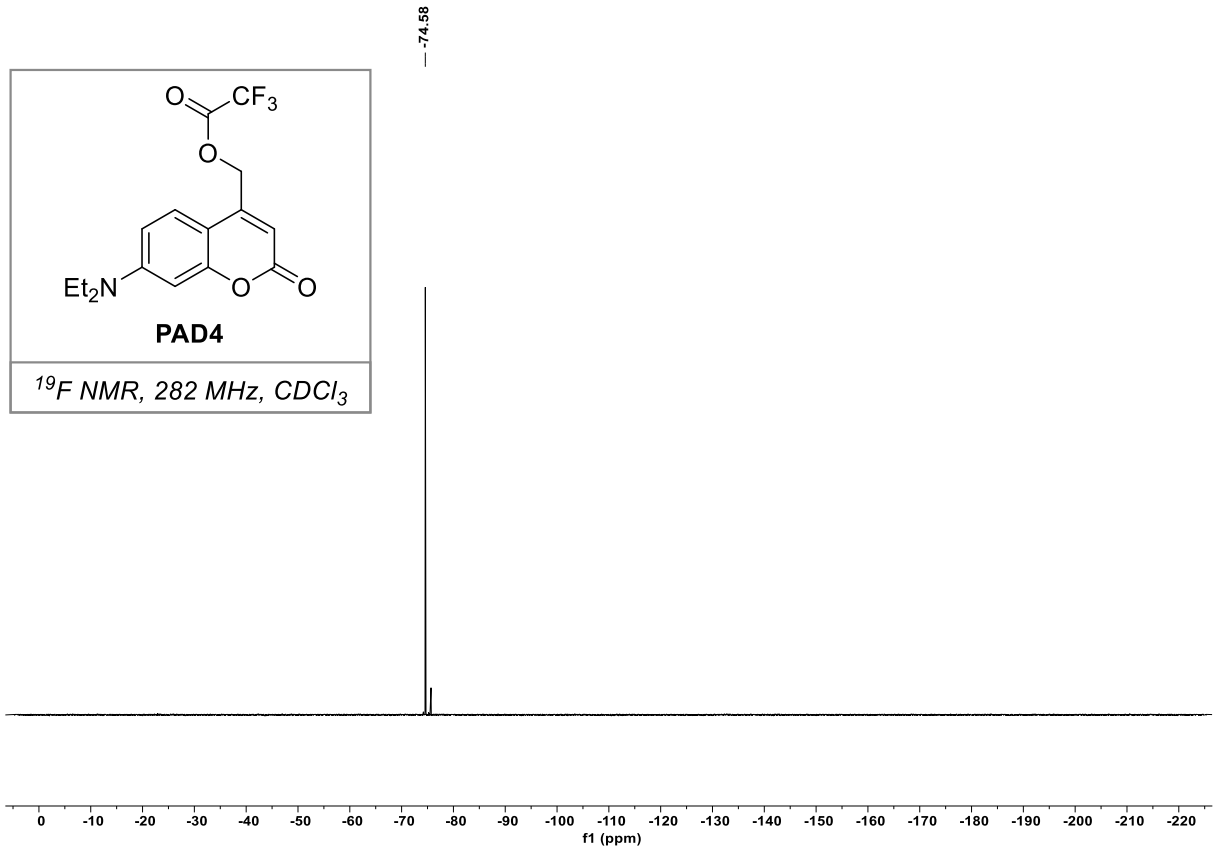






**PAD4**

*$^{1}H$ NMR, 300 MHz, $CDCl_3$*

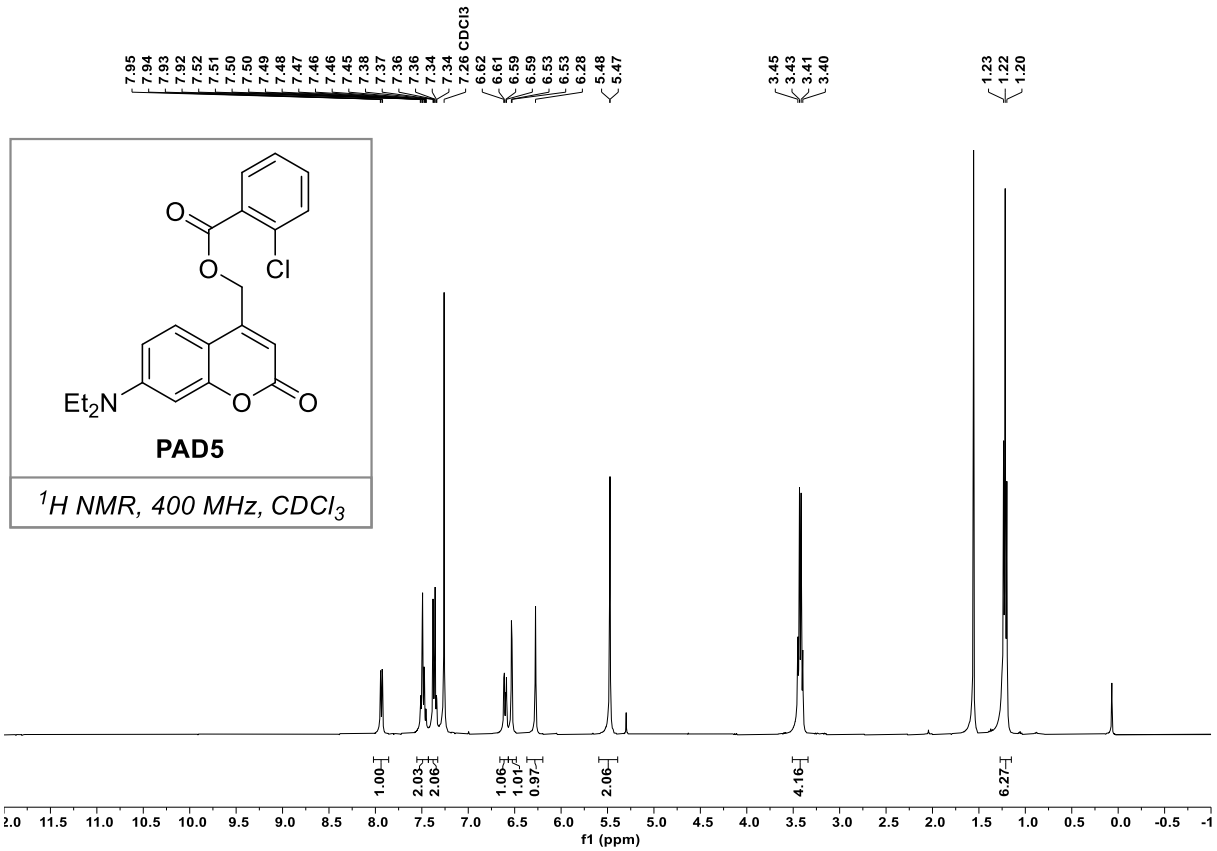






**PAD4**

*$^{19}F$ NMR, 282 MHz, $CDCl_3$*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7.93
7.92
7.52
7.51
7.50
7.50
7.49
7.48
7.47
7.46
7.46
7.45
7.38
7.37
7.36
7.36
7.34
7.34
7.26 CDCl3
6.62
6.61
6.59
6.59
6.53
6.53
6.28
5.48
5.47
3.45
3.43
3.41
3.40
1.23
1.22
1.20
O
O
Cl
Et2N
O
O
PAD5
1H NMR, 400 MHz, CDCl3
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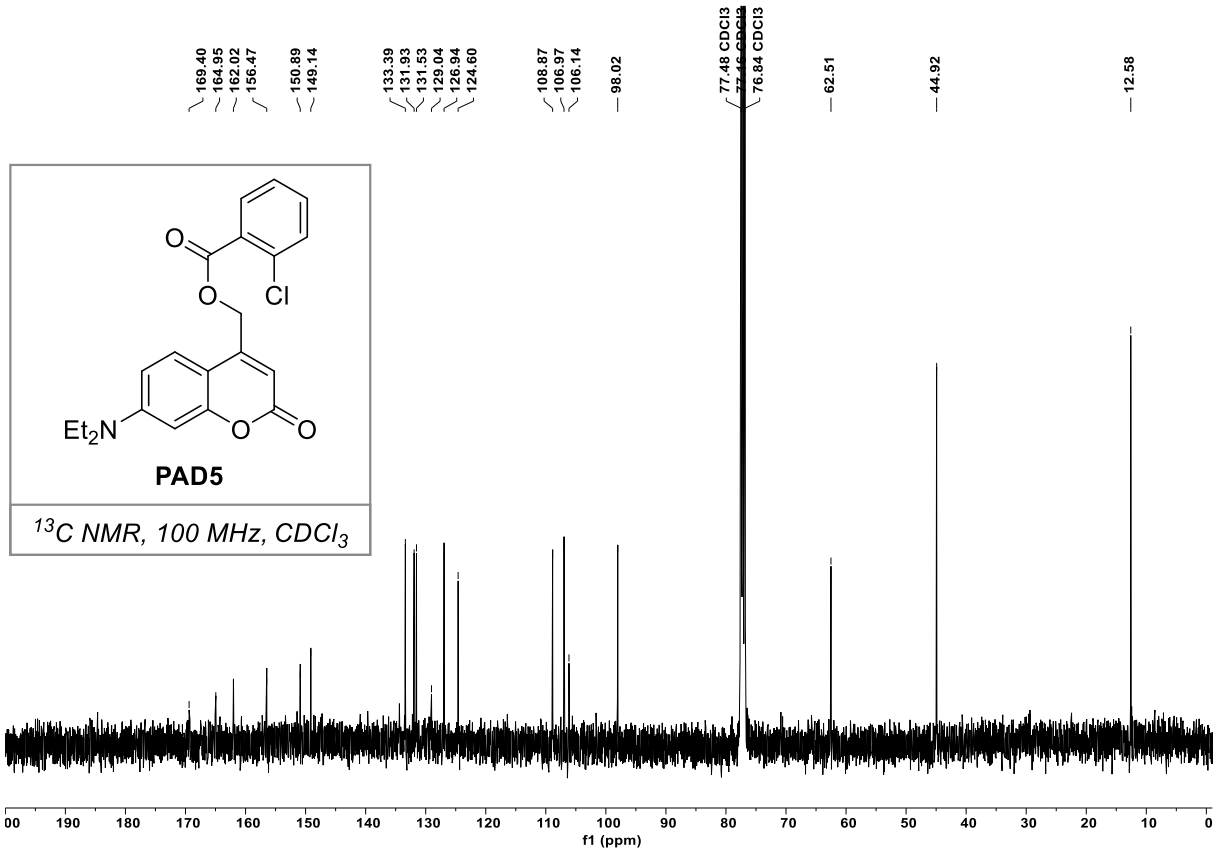
2.03
2.06
1.06
1.01
0.97
2.06
4.16
6.27
f1 (ppm)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150.89
149.14
133.39
131.93
131.53
129.04
126.94
124.60
108.87
106.97
106.14
98.02
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.51
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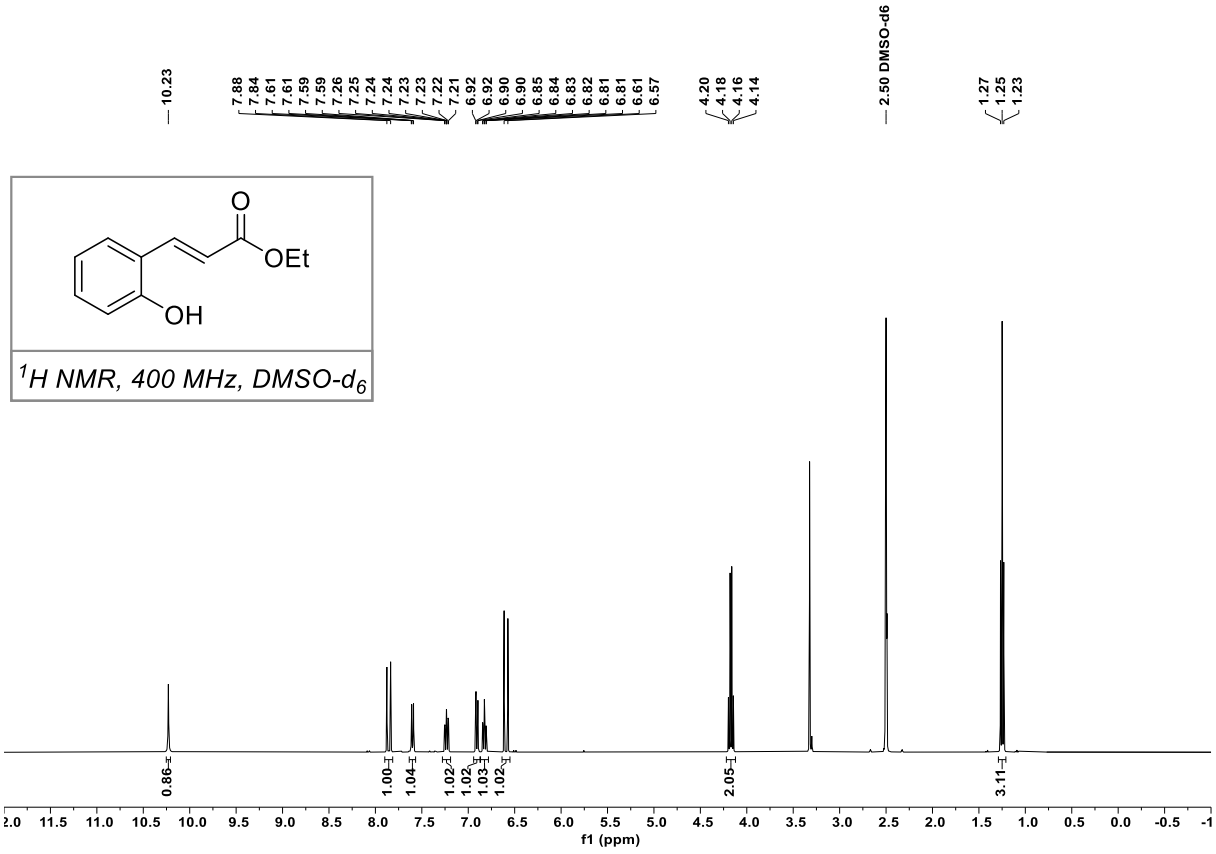
12.58
O
O
Cl
Et2N
O
O
PAD5
13C NMR, 100 MHz, CDCl3
f1 (ppm)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7.59
7.59
7.26
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7.24
7.24
7.23
7.22
7.21
6.92
6.92
6.90
6.90
6.85
6.84
6.83
6.82
6.81
6.81
6.61
6.57
4.20
4.18
4.16
4.14
2.50 DMSO-d6
1.27
1.25
1.23
O
OEt
OH
1H NMR, 400 MHz, DMSO-d6
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1.00
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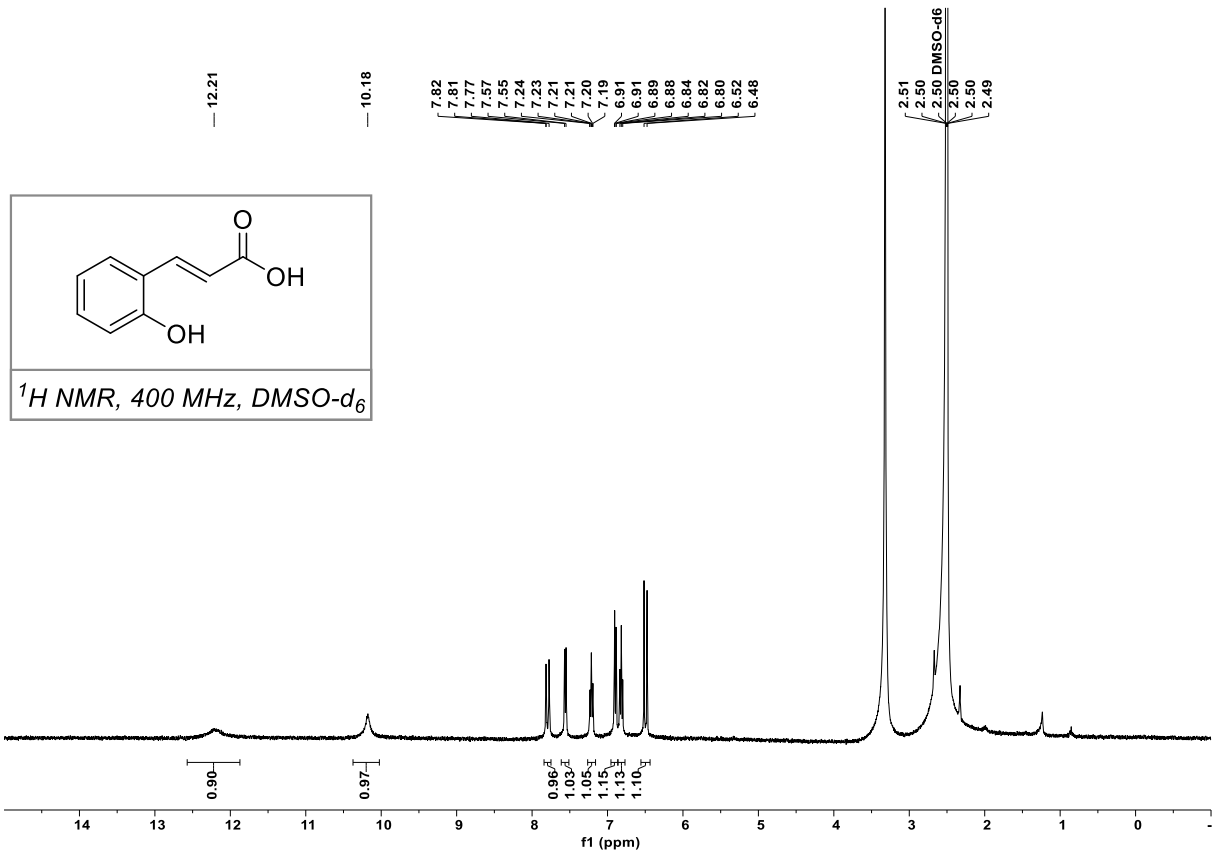
1.02
1.02
1.03
1.02
2.05
3.11
f1 (ppm)


12.21
10.18
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7.81
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7.57
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7.24
7.23
7.21
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7.20
7.19
6.91
6.91
6.89
6.88
6.84
6.82
6.80
6.52
6.48
2.51
2.50
2.50 DMSO-d6
2.50
2.50
2.49
O
OH
OH
1H NMR, 400 MHz, DMSO-d6
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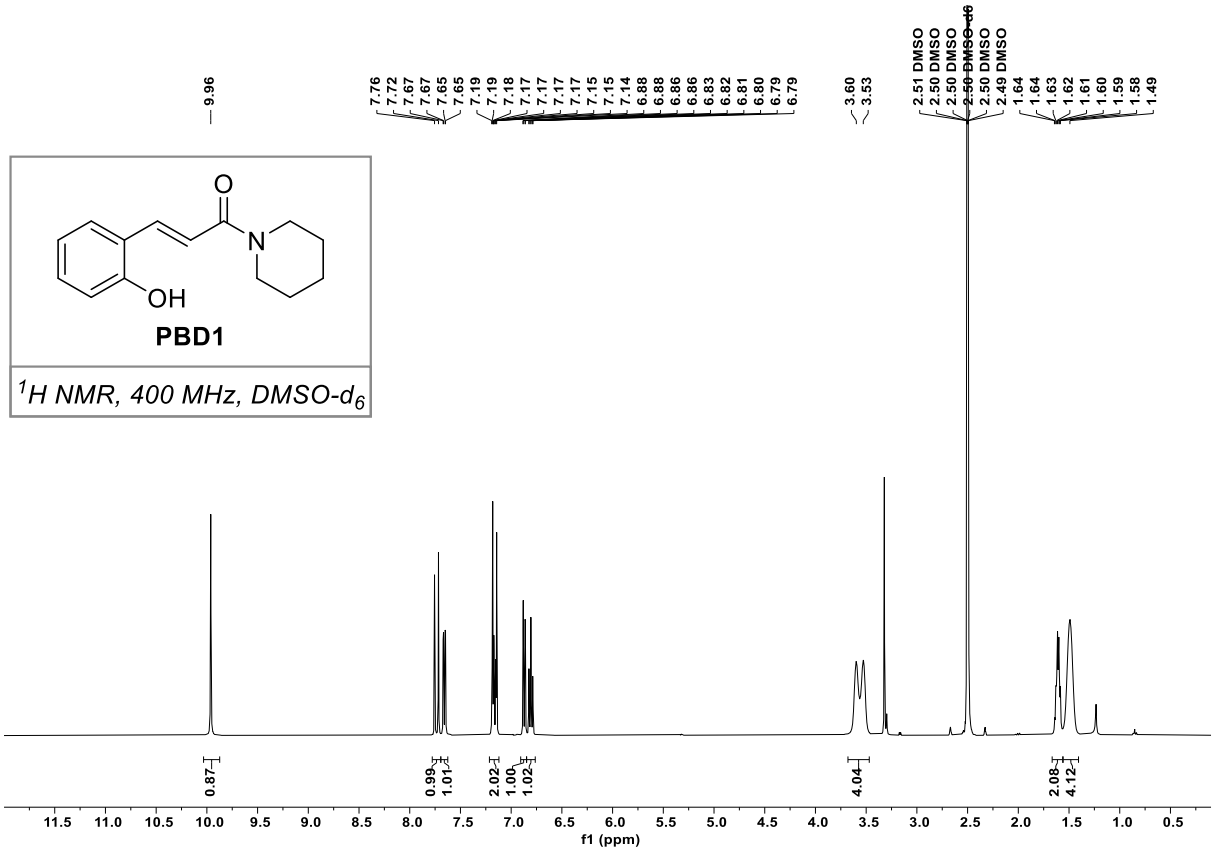
0.97
0.96
1.03
1.05
1.15
1.13
1.10
f1 (ppm)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7.65
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7.17
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7.17
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7.15
7.14
6.88
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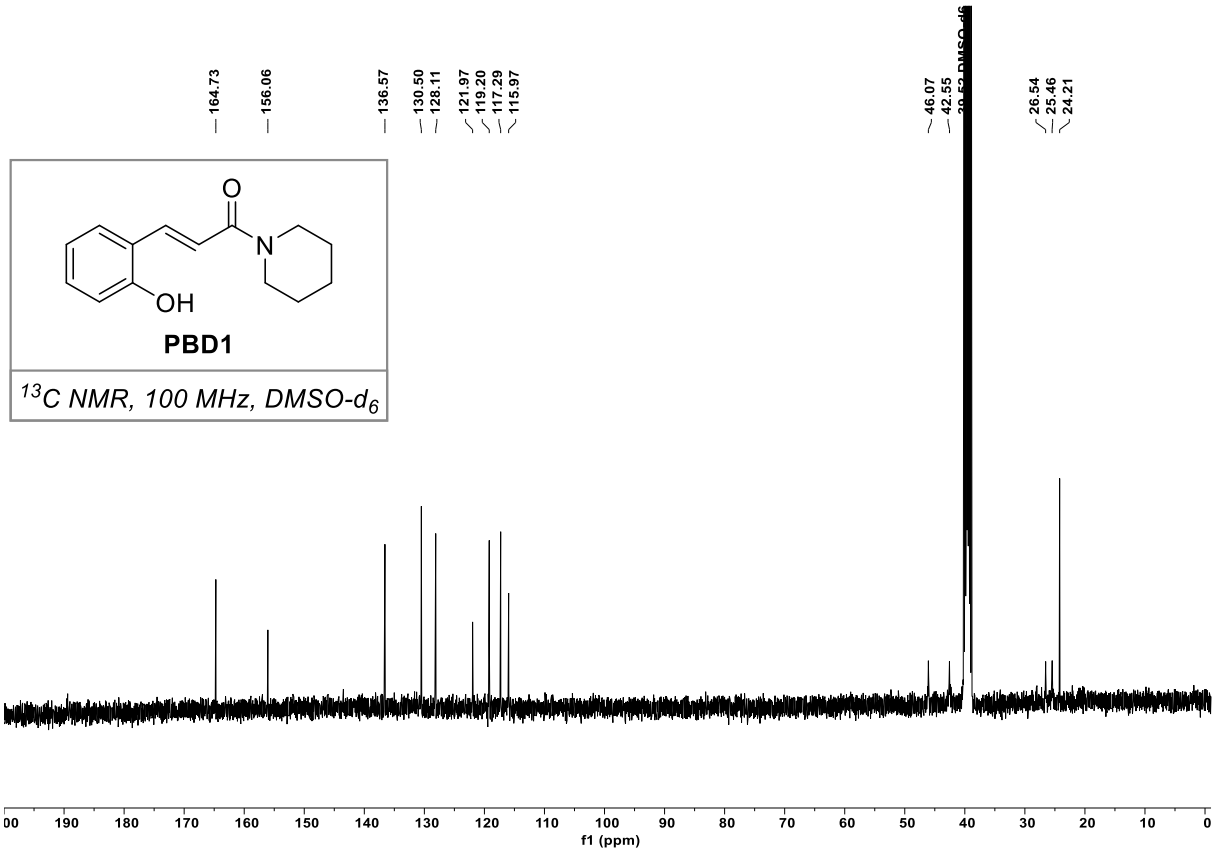
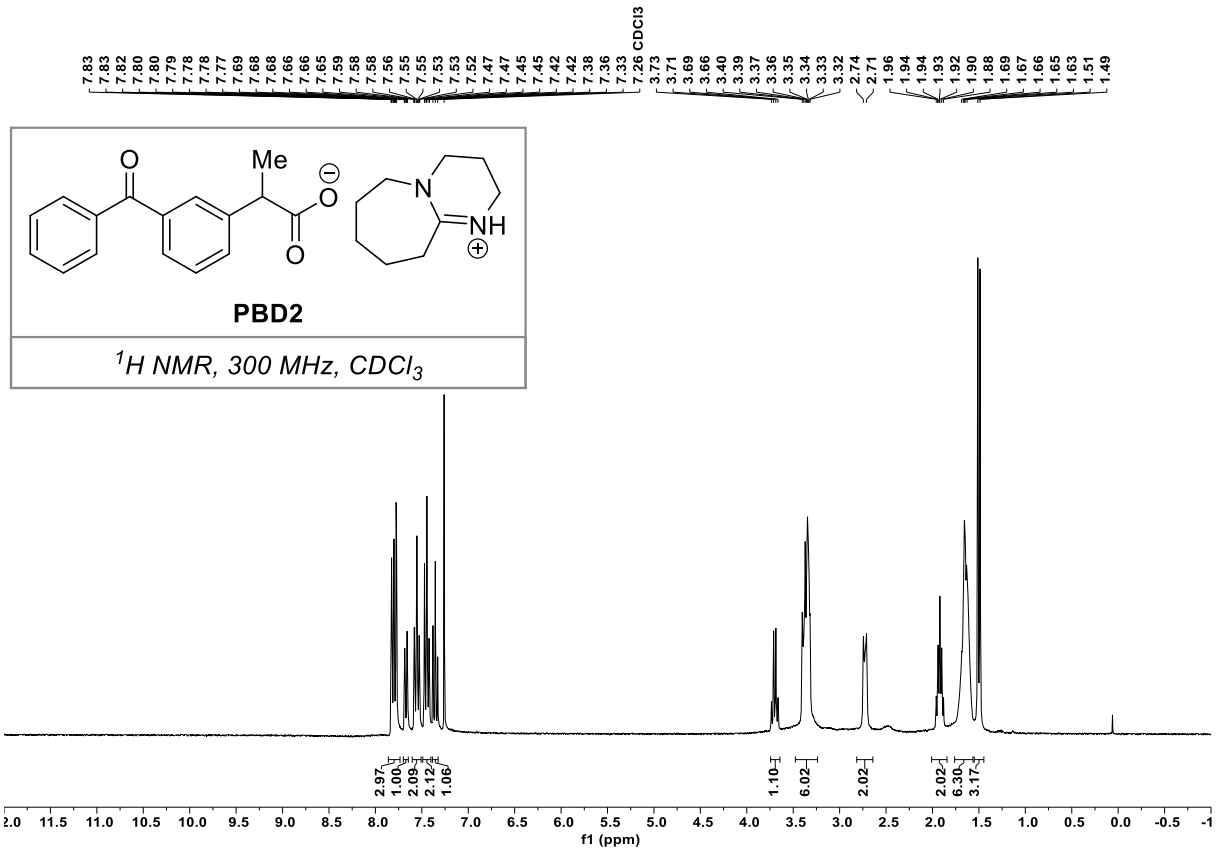
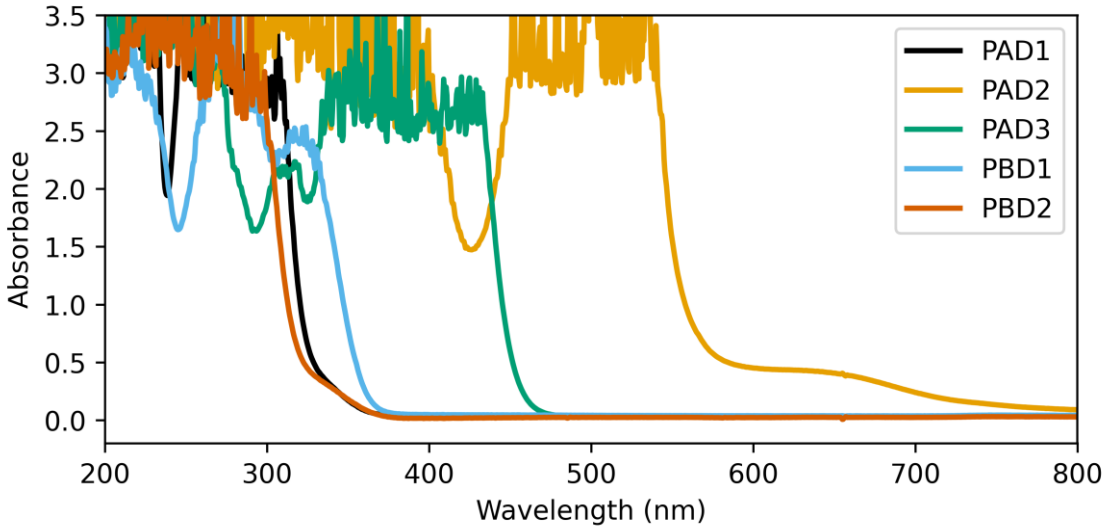
6.82
6.81
6.80
6.79
6.79
3.60
3.53
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO-d6
2.50 DMSO
2.49 DMSO
1.64
1.64
1.63
1.62
1.61
1.60
1.59
1.58
1.49
O
N
OH
PBD1
$^{1}H$ NMR, 400 MHz, DMSO-$d_6$
0.87
0.99
1.01
2.02
1.00
1.02
4.04
2.08
4.12
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


164.73
156.06
136.57
130.50
128.11
121.97
119.20
117.29
115.97
46.07
42.55
26.54
25.46
24.21
O
N
OH
PBD1
$^{13}C$ NMR, 100 MHz, DMSO-$d_6$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.83 7.83 7.82 7.80 7.80 7.79 7.78 7.78 7.77 7.69 7.68 7.68 7.66 7.66 7.65 7.59 7.58 7.58 7.56 7.55 7.55 7.53 7.53 7.52 7.47 7.47 7.45 7.45 7.42 7.42 7.38 7.36 7.33 7.26 CDCl3 3.73 3.71 3.69 3.66 3.40 3.39 3.37 3.36 3.35 3.34 3.33 3.32 2.74 2.71 1.96 1.94 1.94 1.93 1.92 1.90 1.88 1.69 1.67 1.66 1.65 1.63 1.51 1.49
O
Me
O
O
N
NH
PBD2
$^1H$ NMR, 300 MHz, $CDCl_3$
2.97 1.00 2.09 2.12 1.06 1.10 6.02 2.02 2.02 6.30 3.17
f1 (ppm)

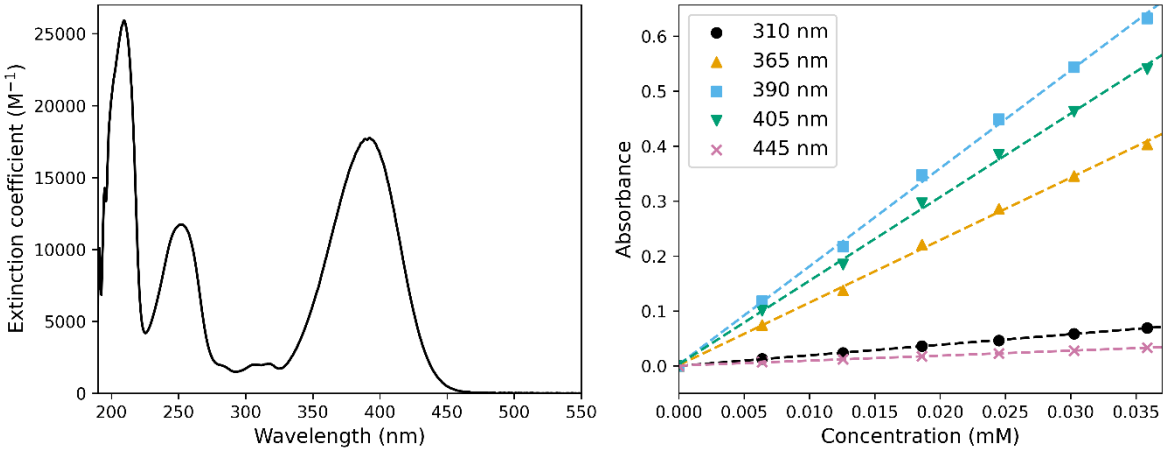
# 4. Photochemical characterization of PADs and PBDs

## High concentration UVVis spectra



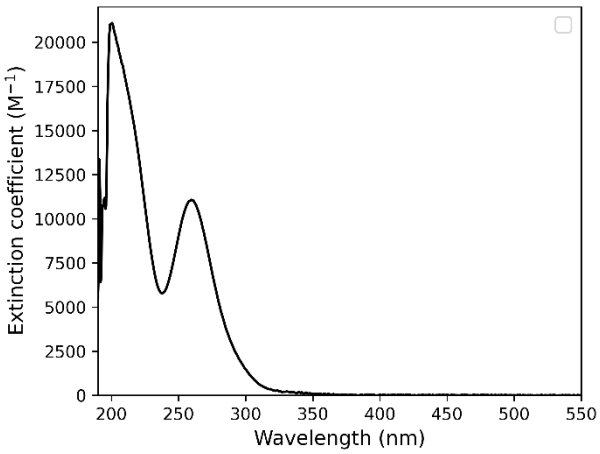

UV-Vis spectra of **PAD**s and **PBD**s in 50% methanol in water at a concentration of 2 mM of as a saturated solution, whichever is lower.

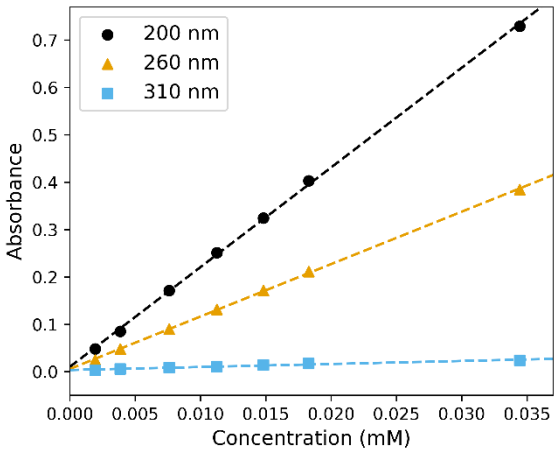
## Determination of molar absorption coefficients of PAD3:




| *Wavelength* | ***ε (M$^{-1}$)*** |
|---|---|
| *390 nm* | 17.8 (± 0.3) x10$^3$ |
| *310 nm* | 1.97 (± 0.05) x10$^3$ |
| *365 nm* | 11.4 (± 0.2) x10$^3$ |
| *405 nm* | 15.2 (± 0.3) x10$^3$ |
| *445 nm* | 0.9 (± 0.03) x10$^3$ |

## Determination of molar absorption coefficients of PBD2:

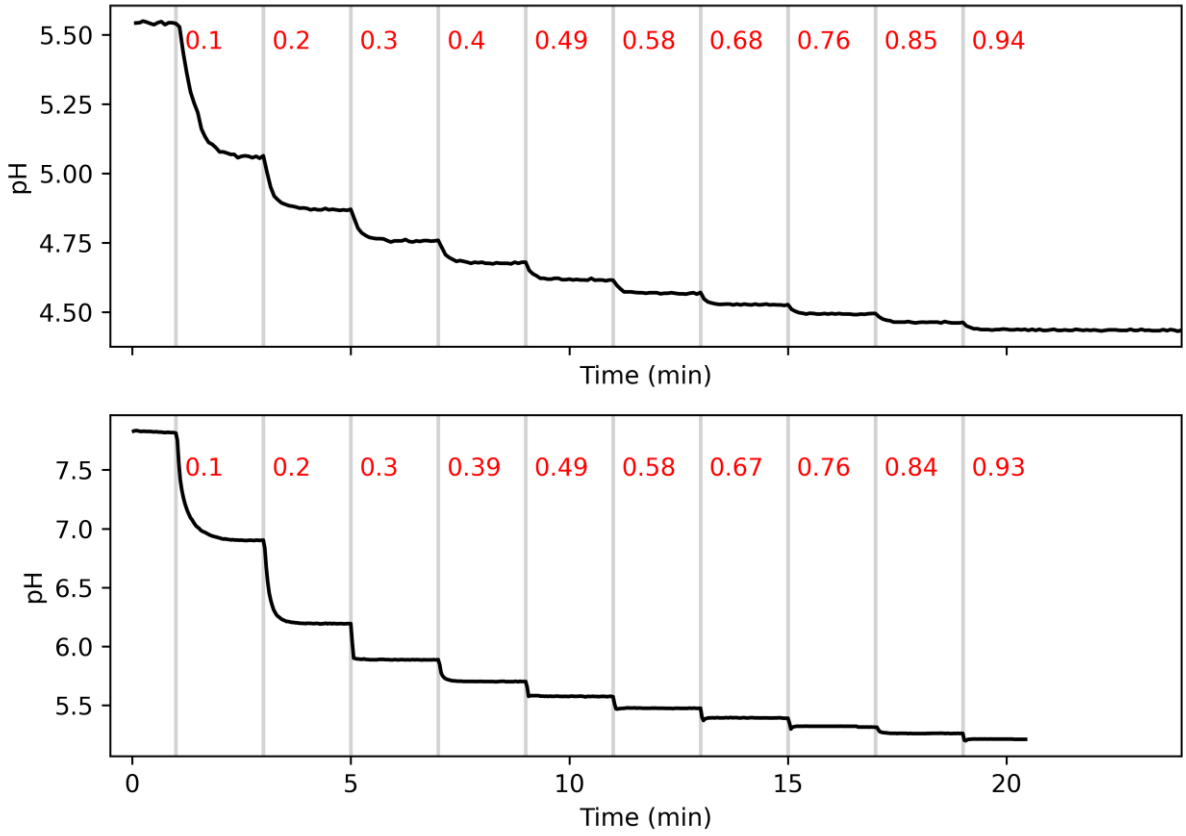



| *Wavelength* | ***ε (M$^{-1}$)*** |
|---|---|
| *260 nm* | 11.06 (± 0.08) x10$^3$ |
| *310 nm* | 0.64 (± 0.06) x10$^3$ |

## Acetic acid titrations:

**Top:** The pH of a 10.0 mL solution of 50% methanol in water was measured. To this, 1.0 mL of a 10 mM solution of acetic acid in methanol/water (3.1 mg (52 µmol) in 5.0 mL) was added in 10 steps. The red text gives the concentration of acetic acid (in mM) for that specific interval (between grey lines).




**Bottom:** To a 10.0 mL solution of 50% methanol in water was added 1 µL of LiOH 1 M (aq.) solution, and 100 µL of Britton-Robinson buffer. The pH of the solution was measured over 10 sequential additions of 100 µL of a 10 mM solution of acetic acid in methanol/water. The red text gives the concentration of acetic acid (in mM) for that specific interval (between grey lines).

## Photochemical release of acetate from PAD2 in methanol/water:

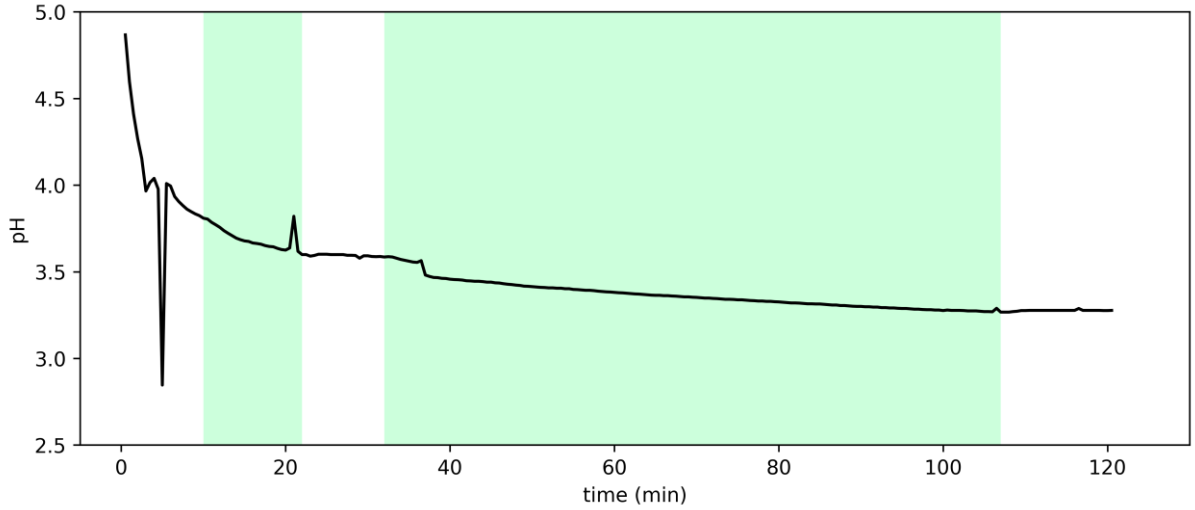



**Figure S1:** Of 1.6 mL of saturated **PAD2** solution in methanol/water (50%, filtered through a cotton plug before use) the pH was measured, while the sample was irradiated with 505 nm light (Thorlabs LED) for 12 min followed by 75 min, during which no irradiation-related change in pH was observed and after which deposition of the starting material was observed.

## Photochemical release of acetate from PAD3 in methanol/water:

A small amount of **PAD3** was dissolved in 2.0 mL of methanol and 2.0 mL of water. The residual solid indicated a saturated solution. Of this solution, approximately 1.8 mL were transferred to a cuvette, of which both the UV-Vis spectrum and the pH were monitored. After stabilization of the pH measurement (approx. 5 min), irradiation was started: 5x (Prismatix 365 nm, 100%, 120s, 600 s pause).

## Piperidine titration:

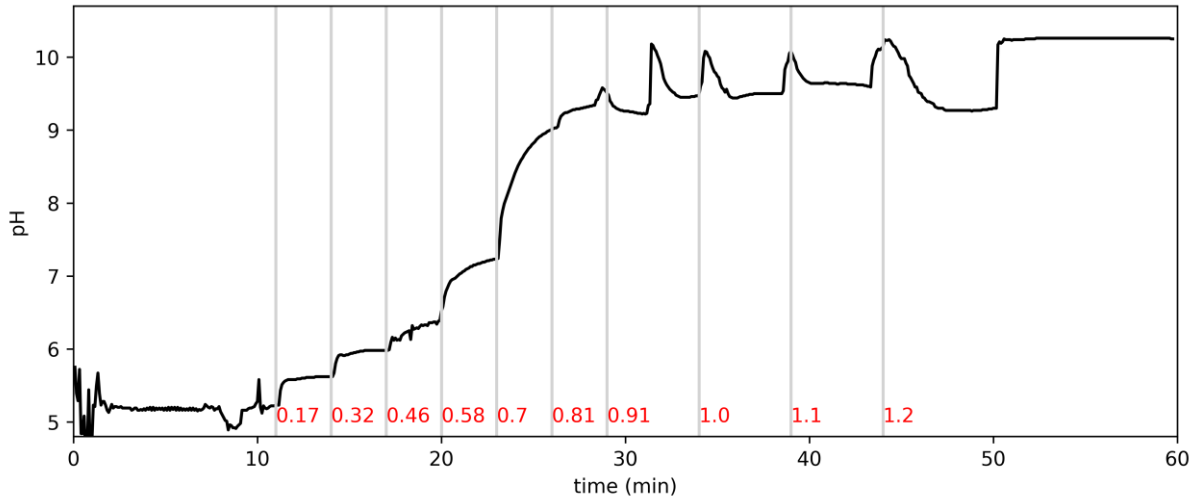



**Figure S2:** The pH of a 2.0 mL solution of 50% methanol in water was measured. To this, 1.0 mL of a 3.5 mM solution of piperidine in methanol/water (1.5 mg (18 µmol) in 5.0 mL) was added in 10 steps. Every time after addition and mixing, 100 µL of solution was removed to keep the volume constant. The red text gives the concentration of piperidine (in mM) for that specific interval (between grey lines).

## Photochemical release of piperidine from PBD1 in methanol/water:

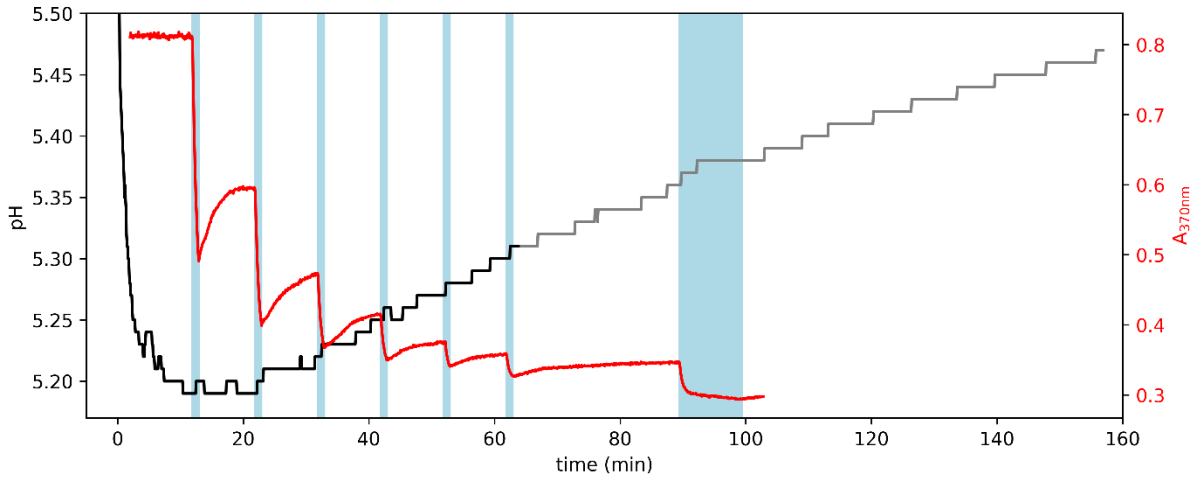



**Figure S3:** 0.5 mg of **PBD1** (2 µmol) was dissolved in 2.0 mL of methanol, 1.98 mL of water, and 20 uL of 0.1 M NaOAc/AcOH buffer pH 5.6 (final conc. 0.5 mM). Of this solution, 1.6 mL was transferred to a cuvette, of which the UV-Vis spectrum and the pH were monitored. The sample was irradiated 6 times for 1 min at λ = 310 nm (100% LED power), with 9 min intervals. Subsequently, the sample was irradiated for 10 min (λ = 310 nm, 100% LED power). No irradiation-related change in pH was observed.

## Photochemical release of DBU from PBD2 in methanol/water:

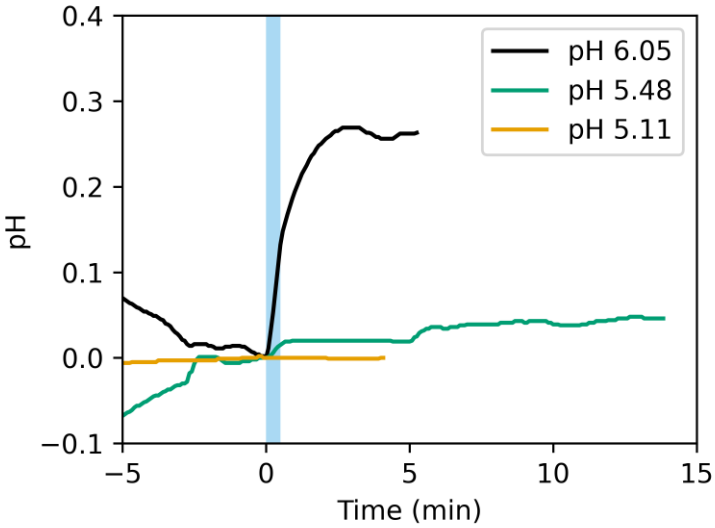
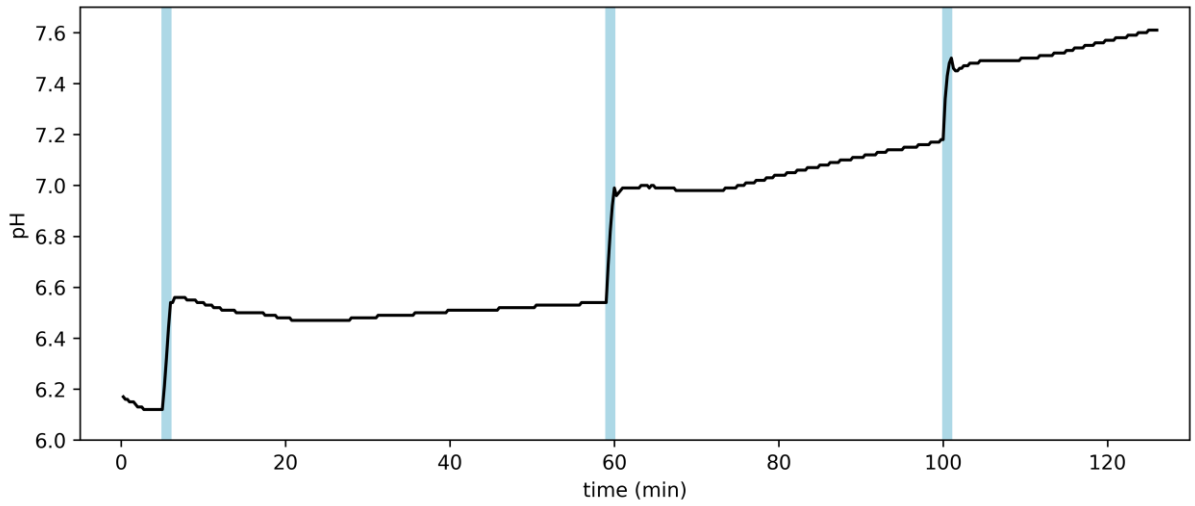


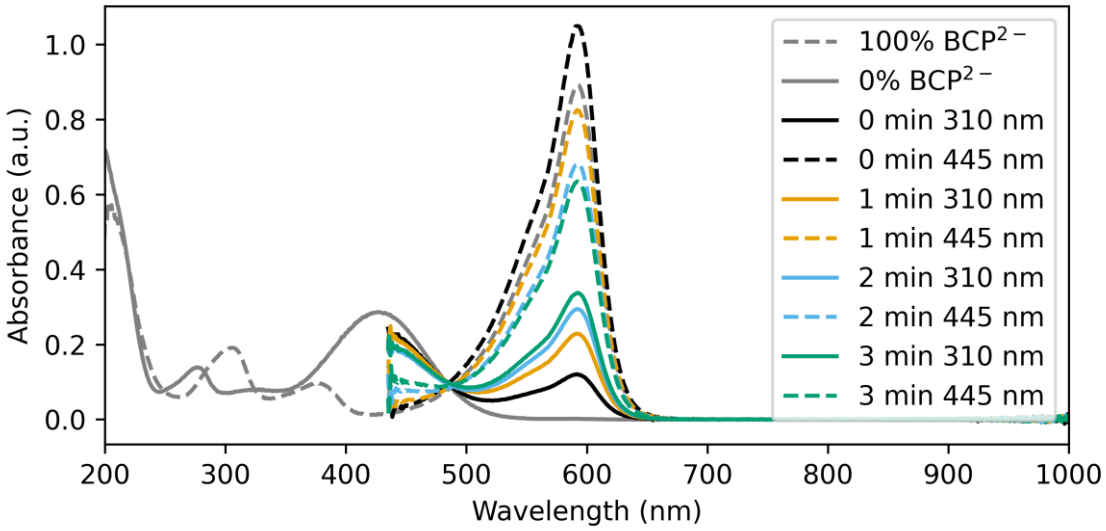

**Figure S4:** Of three aliquots of a solution of **PAD5** and **PBD2** (0.56 and 0.43 mM, resp.) in 50% methanol in water the pH was adjusted by the addition of a small amount of acetic acid and triethylamine. The aliquots were irradiated separately for 1 min each, during which the pH was measured at 5 s intervals.

## Influence of addition of buffer:




**PBD2** (1.8 mM) in 50% methanol, 50% demi water with 1% 0.1M NaOAc/AcOH pH 5.6 buffer, irradiated with 3x 1 minute 310 nm light.

## Spectroscopic determination of [$BCP^{2-}$]:

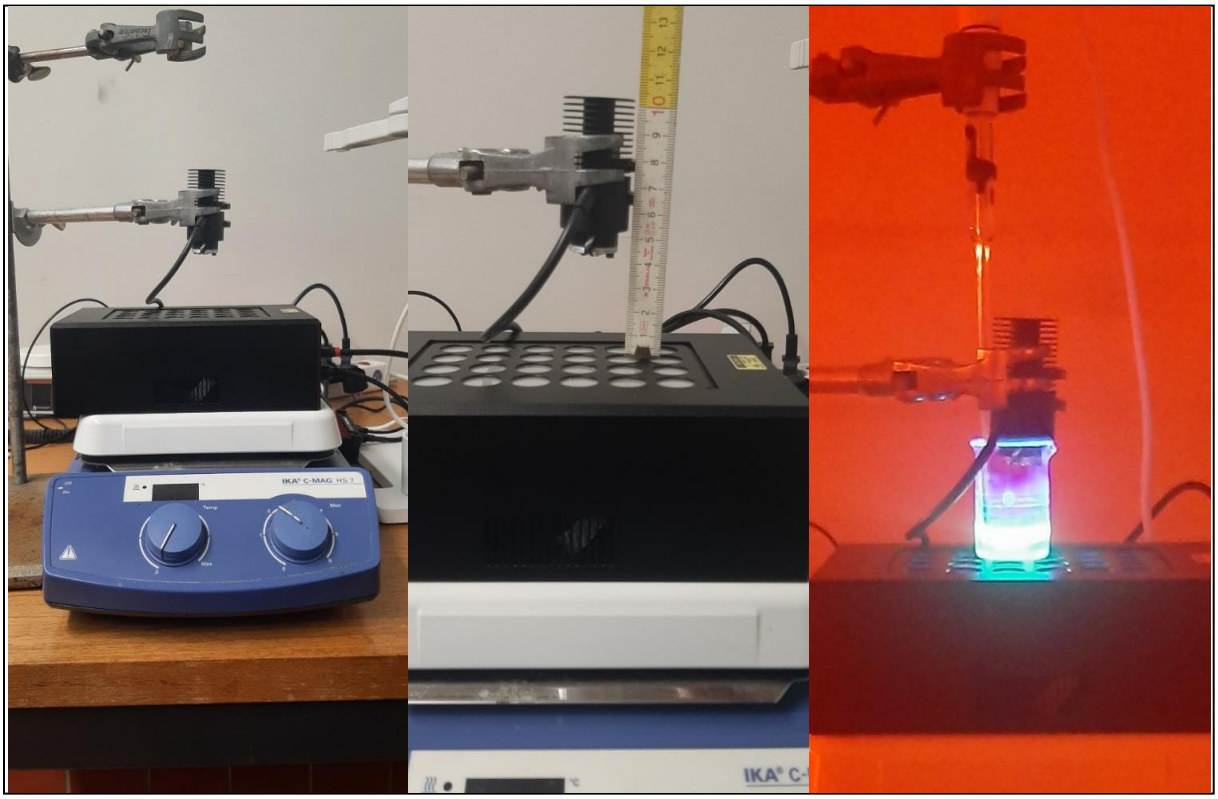



The absorption spectrum was measured after addition of **BCP** to the reaction mixture. The amount of **$BCP^{2-}$** was determined from the absorption at the isosbestic point (487 nm) and the absorption maximum (593 nm) via the following formula:

$$\frac{\frac{A_{593nm}}{A_{487nm}} - \frac{A_{593nm,0\%BCP^{2-}}}{A_{487nm,0\%BCP^{2-}}}}{\frac{A_{593nm,100\%BCP^{2-}}}{A_{487nm,100\%BCP^{2-}}} - \frac{A_{593nm,0\%BCP^{2-}}}{A_{487nm,0\%BCP^{2-}}}} * 100\%$$

| SAMPLE | $A_{593NM}$ | $A_{487NM}$ | % $BCP^{2-}$ |
|---|---|---|---|
| **0 MIN 310 NM** | 0.11949 | 0.087956 | 12.85823 |
| **1 MIN 310 NM** | 0.22744 | 0.094114 | 23.01724 |
| **2 MIN 310 NM** | 0.29393 | 0.089776 | 31.24905 |
| **3 MIN 310 NM** | 0.3371 | 0.095497 | 33.70609 |
| **0 MIN 445 NM** | 1.0489 | 0.10209 | 98.45802 |
| **1 MIN 445 NM** | 0.82337 | 0.088128 | 89.51587 |
| **2 MIN 445 NM** | 0.68246 | 0.085093 | 76.81647 |
| **3 MIN 445 NM** | 0.63406 | 0.09102 | 66.697 |
| **100% $BCP^{2-}$** | 0.89094 | 0.085381 | 100 |
| **0% $BCP^{2-}$** | 0.0016441 | 0.085381 | 0 |

## Sequential release of acid and base in methanol/water:



A Thorlabs M310L3 LED was mounted over a beaker, at a distance of approximately 4 cm from the liquid surface. This beaker was put on an Optowell block (irradiation wavelength 448.4 nm, E = 12.89 mW/cm$^2$), which was then in it's totally put on a stirring plate. In the beaker, the METTLER TOLEDO pH probe was mounted. The pH was logged with a 5 s interval over a maximum of 100 min.

In a typical experiment, 34.1 mg of **PBD2** (83.9 µmol) and 23.6 mg of **PAD3** (81.6 µmol) were dissolved in 40.0 mL methanol/water (1:1 ratio), resulting in a final concentration of approximately 2 mM. Unfortunately, not all **PAD3** dissolved and thus a saturated solution is assumed, and the solution was filtered through a simple cotton plug before use.

# 5. References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