

ChemPhotoChem

Supporting Information

Synthesis and Photochemical Investigation of Tetraacylgermanes

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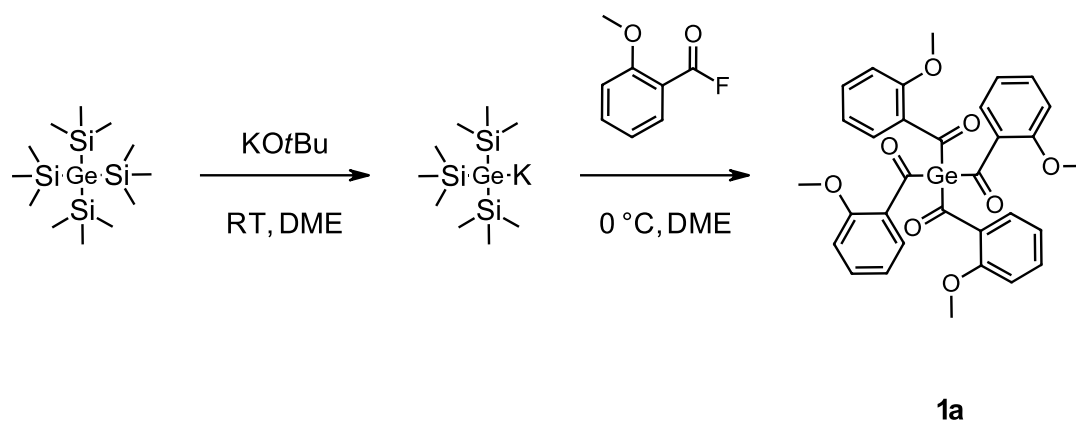
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Synthesis

All of the following syntheses were performed under exclusion of light below 480 nm. Schlenk techniques were used to ensure the exclusion of moisture and oxygen. They follow the general procedure with slightly different purification steps. Tetrakis(trimethylsilyl)germane and the corresponding acid fluoride were synthesized according to literature previously.¹⁻³

Tetrakis(2-methoxybenzoyl)germane (1a)



Scheme ESI 1. Synthesis of tetrakis(2-methoxybenzoyl)germane (1a)

Compound	M / g mol ⁻¹	Eq	n /mmol	m /g
tetrakis(trimethylsilyl)germane	365.39	1	5.47	2.00
potassium <i>tert</i> -butoxide	112.21	1.1	6.02	0.68
2-methoxybenzoyl fluoride	154.14	4.1	22.44	3.46

A predried Schlenk flask was charged with 2.00 g (1 eq., 5.47 mmol) of tetrakis(trimethylsilyl)germane and 676 mg of potassium *tert*-butoxide together with 50 mL dry 1,2-dimethoxy ethane (DME). The mixture was stirred for 1 h to obtain a yellow solution. In a separate Schlenk flask 3.46 g (4.1 eq., 22.44 mmol) of 2-methoxybenzoyl fluoride were dissolved in 30 mL dry DME. The latter mixture was cooled in an ice bath to 0 °C. Using a syringe, the tetrakis(trimethylsilyl)germane solution was added slowly to the dissolved 2-methoxybenzoyl fluoride. The orange reaction mixture was wrapped in aluminum foil and stirred overnight in the ice bath to slowly reach room temperature. The following day a yellow suspension was observed. A separatory funnel was charged with 300 mL of saturated NH₄Cl solution together with the reaction mixture. To provide a better phase separation ~100 mL of dichloromethane (DCM) and 200 mL of distilled water were added. The organic phase was separated and the aqueous phase was extracted with DCM until no yellow discoloration was observed upon further extraction steps with dichloromethane. The combined organic layers were washed two times with ~400 mL distilled water and subsequently dried over sodium

sulfate. The solvent was removed on the rotary evaporator and under high vacuum upon which the formation of a foamy yellow solid was observed. The solid was dissolved in acetone and put in the freezer at -30 °C for precipitation overnight.

The yellow crystalline precipitate was filtered off and washed with -30 °C acetone. The product was then dried under high vacuum, yielding 1.63 g of the yellow crystalline powder (48.6 %). A second fraction was obtained by drying the mother liquor *in vacuo* and washing the remaining solid with n-heptane and acetone. The yellow crystalline solid (301 mg) was obtained *via* filtration.

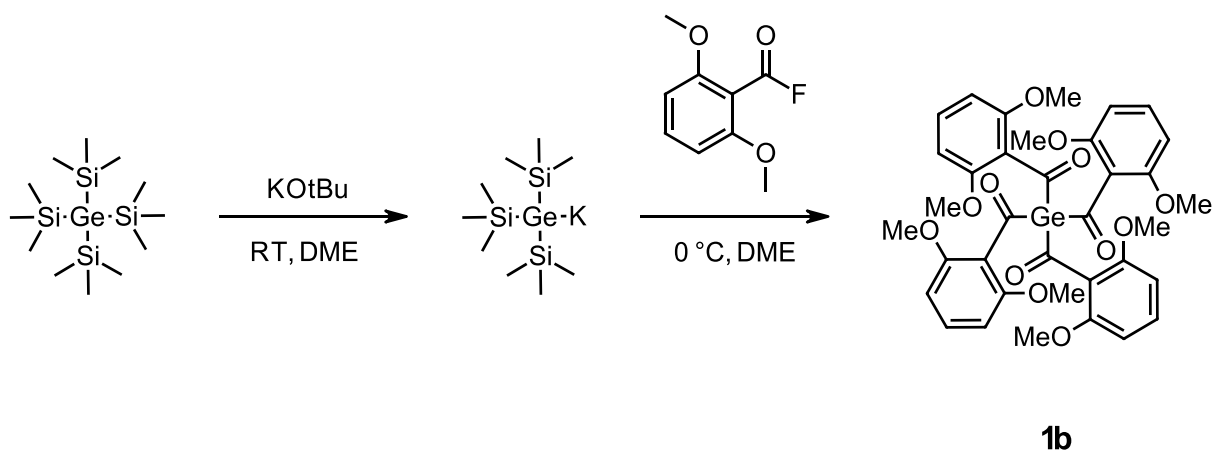
Yield: 1.93 g yellow crystalline powder
58 % of theory
62 % of literature⁴

¹H-NMR (CDCl₃, 300 MHz, ppm) δ: 7.63 (1H, d, Aryl-H), 7.39 (1H, t, Aryl-H), 6.94 (1H, t, Aryl-H), 6.80 (1H, d, Aryl-H), 3.48 (3H, s, Aryl-H).

¹³C-NMR (CDCl₃, 76 MHz, ppm) δ: 221.76 (GeC=O), 160.21, 134.49, 130.01, 126.50, 120.34, 111.46 (Aryl-C), 53.57 (O-CH₃)

m.p.: 170-177°C (lit. 173°C⁴)

Tetrakis(2,6-dimethoxybenzoyl)germane (1b)



Scheme ESI 2. Synthesis of tetrakis(2,6-dimethoxybenzoyl)germane (1b)

Compound	M / g mol ⁻¹	Eq	n / mmol	m / g
tetrakis(trimethylsilyl)germane	365.39	1	5.47	2.00
potassium <i>tert</i> -butoxide	112.21	1.1	6.02	0.68
2,6-dimethoxybenzoyl fluoride	184.17	4.1	22.44	4.13

A predried Schlenk flask was charged with 2.00 g (1 eq., 5.47 mmol) of tetrakis(trimethylsilyl)germane and 676 mg (1.1 eq., 6.02 mmol) of potassium *tert*-butoxide together with 50 mL dry DME. The mixture was stirred for 30 min to obtain a yellow solution. In a separate Schlenk flask 4.13 g (4.1 eq., 22.44 mmol) of 2,6-dimethoxybenzoyl fluoride were dissolved in 30 mL dry DME. The latter mixture was cooled in an ice bath to 0 °C. Using a syringe, the tetrakis(trimethylsilyl)germane solution was added slowly to the solution containing 2,6-dimethoxybenzoyl fluoride. The Schlenk flask was wrapped in aluminum foil for further light protection, and stirred overnight in the ice bath to slowly reach room temperature. The following day a yellow suspension was observed. A separatory funnel was charged with 300 mL of saturated NH₄Cl solution together with the reaction mixture. To provide a better phase separation ~100 mL of DCM and 200 mL of distilled water were added. The organic phase was separated and the aqueous phase was extracted with DCM until no yellow discoloration was observed upon further extraction steps with DCM. The combined organic layers were washed two times with ~250 mL distilled water and subsequently dried over sodium sulfate. The solvent was removed on the rotary evaporator and under high vacuum upon which the formation of a foamy yellow solid was observed. The product was obtained by dissolving the solid in DCM and precipitating it by adding diisopropyl ether [DCM:diisopropyl ether, 1:3]. This way the product was obtained as yellow powder (1.73 g).

Yield: 1.73 g yellow powder
43 % of theory

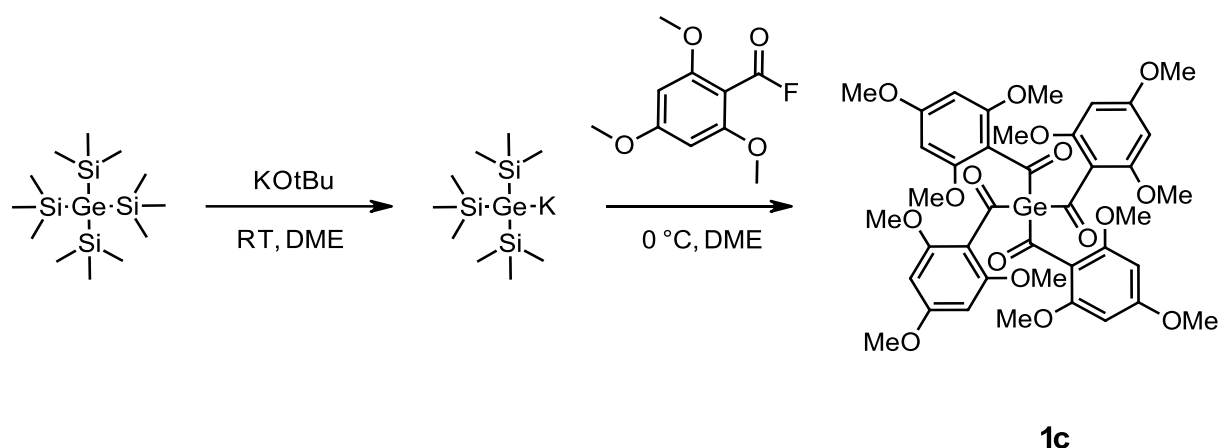
¹H-NMR (CDCl₃, 300 MHz, ppm) δ: 7.10 (1H, t, Aryl-H), 6.34 (2H, d, Aryl-H), 3.74 (6H, s, O-CH₃).

¹³C-NMR (CDCl₃, 76 MHz, ppm) δ: 220.90 (GeC=O), 158.14, 132.37, 120.58, 103.31 (Aryl-C), 55.38 (O-CH₃).

m.p.: 158 – 164 °C

HRMS: [C₃₆H₃₆GeO₁₂]; calc. EM+H: 735.1500 g/mol, found: 735.1514 g/mol

Tetrakis(2,4,6-trimethoxybenzoyl)germane (1c)



Scheme ESI 3. Synthesis of tetrakis(2,4,6-trimethoxybenzoyl)germane (1c)

Compound	M / g mol ⁻¹	Eq	n / mmol	m / g
tetrakis(trimethylsilyl)germane	365.39	1	5.47	2.00
potassium <i>tert</i> -butoxide	112.21	1.1	6.02	0.24
2,4,6-trimethoxybenzoyl fluoride	166.20	4.1	22.44	4.81

A predried Schlenk flask was charged with 2.00 g (1 eq., 5.47 mmol) of tetrakis(trimethylsilyl)germane and 676 mg (1.1 eq., 6.02 mmol) of potassium *tert*-butoxide together with 50 mL dry DME. The mixture was stirred for 30 min to obtain a yellow solution. In a separate Schlenk flask 4.81 g (4.1 eq., 22.44 mmol) of 2,4,6-trimethoxybenzoyl fluoride were dissolved in 30 mL dry DME. The latter mixture was cooled in an ice bath to 0 °C. Using a syringe, the tetrakis(trimethylsilyl)germane solution was added slowly to solution containing 2,4,6-trimethoxybenzoyl fluoride. The Schlenk flask was wrapped in aluminum foil for further light protection, and stirred overnight in the ice bath to slowly reach room temperature. The following day ~10 ml of dry THF were added to the yellow suspension to provide better solubility upon which the mixture turned orange. After stirring for 1 h, a temperature increase was observed. A separatory funnel was charged with 300 mL of saturated NH₄Cl solution together with the reaction mixture. To provide a better phase separation ~100 mL of DCM and 200 mL of distilled water were added. The organic phase was separated and the aqueous phase was extracted with DCM until no yellow discoloration was observed upon further extraction steps with DCM. The combined organic layers were washed two times with ~400 mL distilled water and subsequently dried over sodium sulfate. The solvent was removed on the rotary evaporator and under high vacuum upon which the formation of a foamy yellow solid was observed. The product was obtained by dissolving the solid in DCM and precipitating

it through addition of diisopropyl ether [DCM:diisopropyl ether, 1:3]. This way the product was obtained as yellow powder (2.44 g).

Yield: 2.44 g yellow powder
52 % of theory

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz, ppm) δ : 5.87 (8H, s, Aryl-H), 3.74-3.72 (36H, m, O- CH_3).

$^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz, ppm) δ : 219.14 (GeC=O), 163.26, 160.07, 115.32, 89.76 (Aryl-C), 55.54 (O- CH_3), 55.26 (O- CH_3).

m.p.: 109 – 115 °C

HRMS: [$\text{C}_{40}\text{H}_{44}\text{GeO}_{16}$], calc. EM+H: 855.1924 g/mol, found 855.1943 g/mol

NMR spectra

Tetrakis(2-methoxybenzoyl)germane (1a)

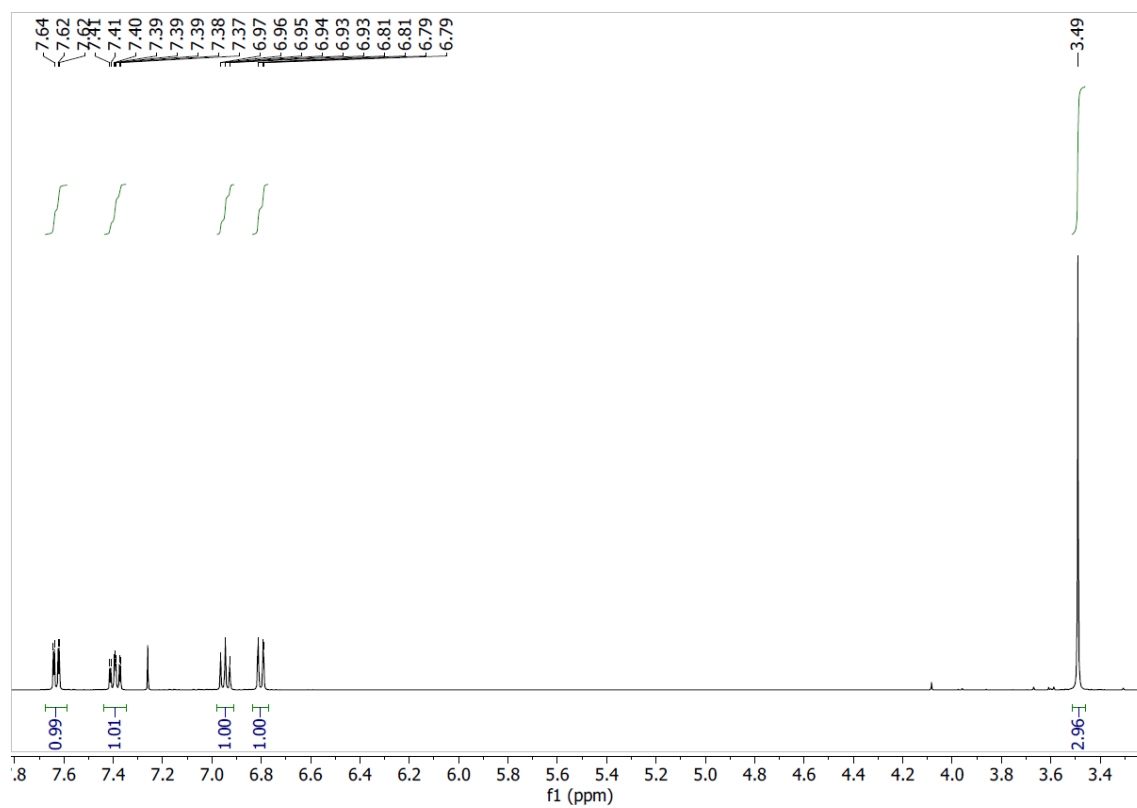


Figure ESI 1. ¹H-NMR spectrum of tetrakis(2-methoxybenzoyl)germane (1a) in CDCl₃

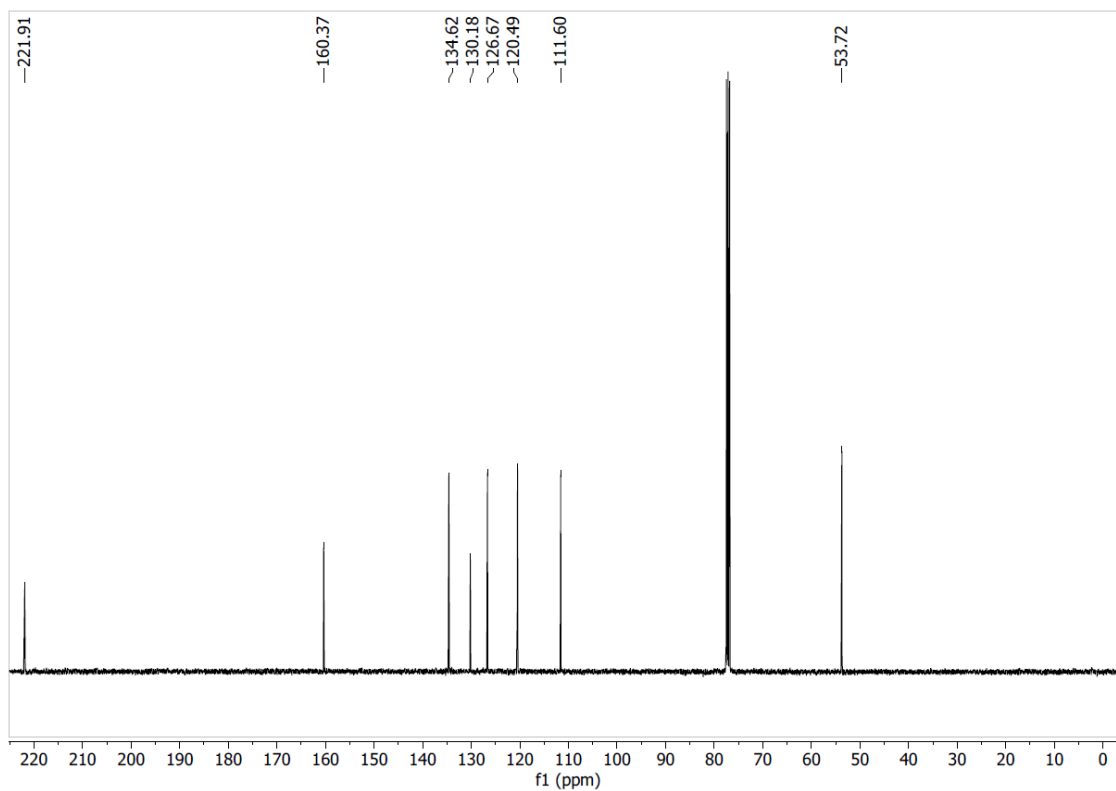


Figure ESI 2. ^{13}C -NMR spectrum of tetrakis(2-methoxybenzoyl)germane (**1a**) in CDCl_3

Tetrakis(2,6-dimethoxybenzoyl)germane (**1b**)

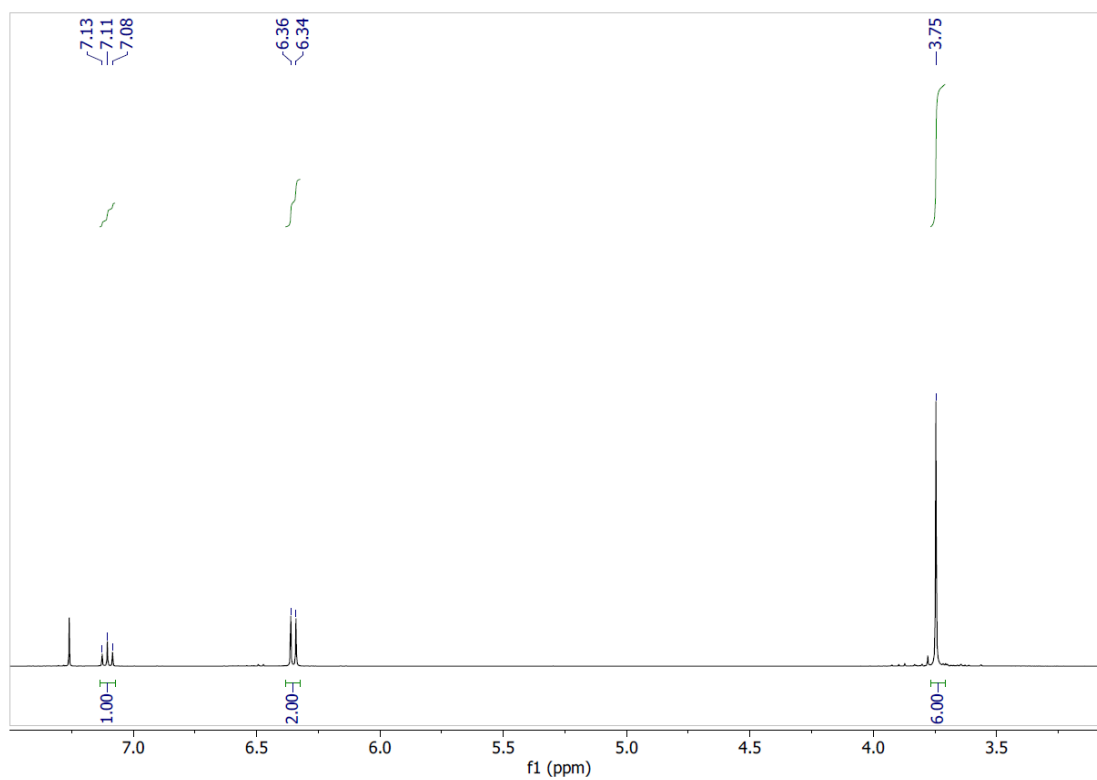


Figure ESI 3. ^1H -NMR spectrum of tetrakis(2,6-dimethoxybenzoyl)germane (**1b**) in CDCl_3

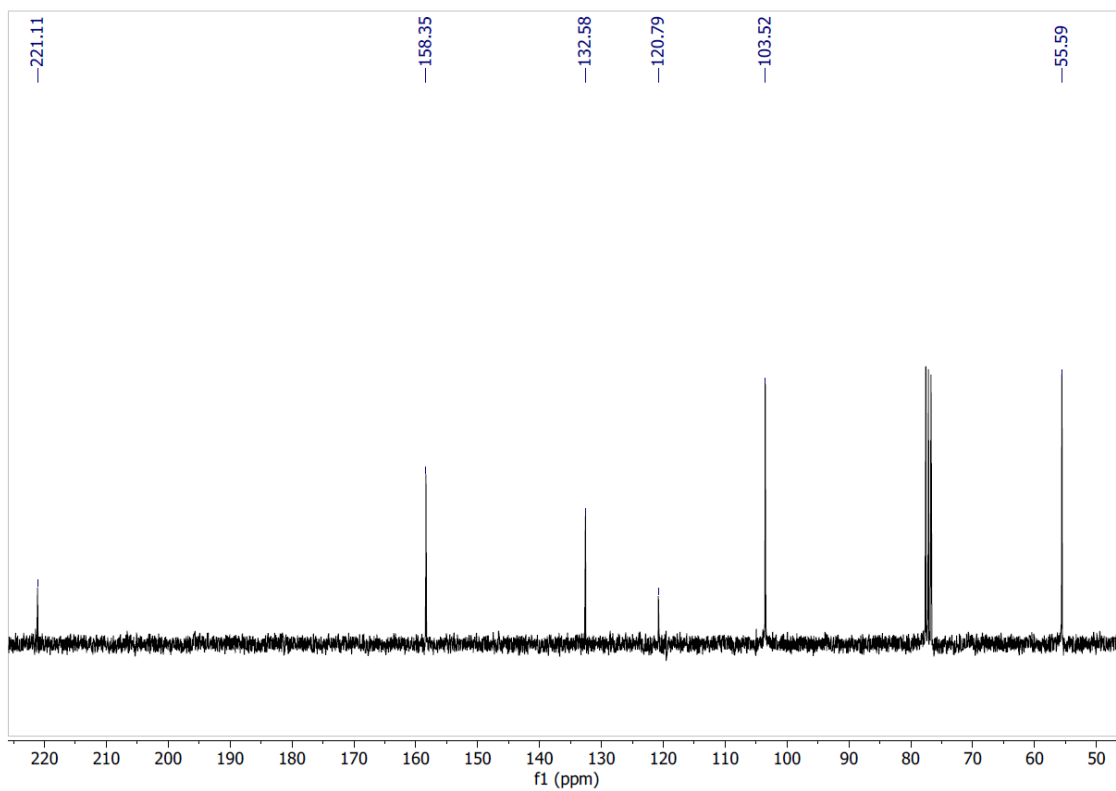


Figure ESI 4. ^{13}C -NMR spectrum of tetrakis(2,6-dimethoxybenzoyl)germane (**1b**) in CDCl_3

Tetrakis(2,4,6-trimethoxybenzoyl)germane (**1c**)

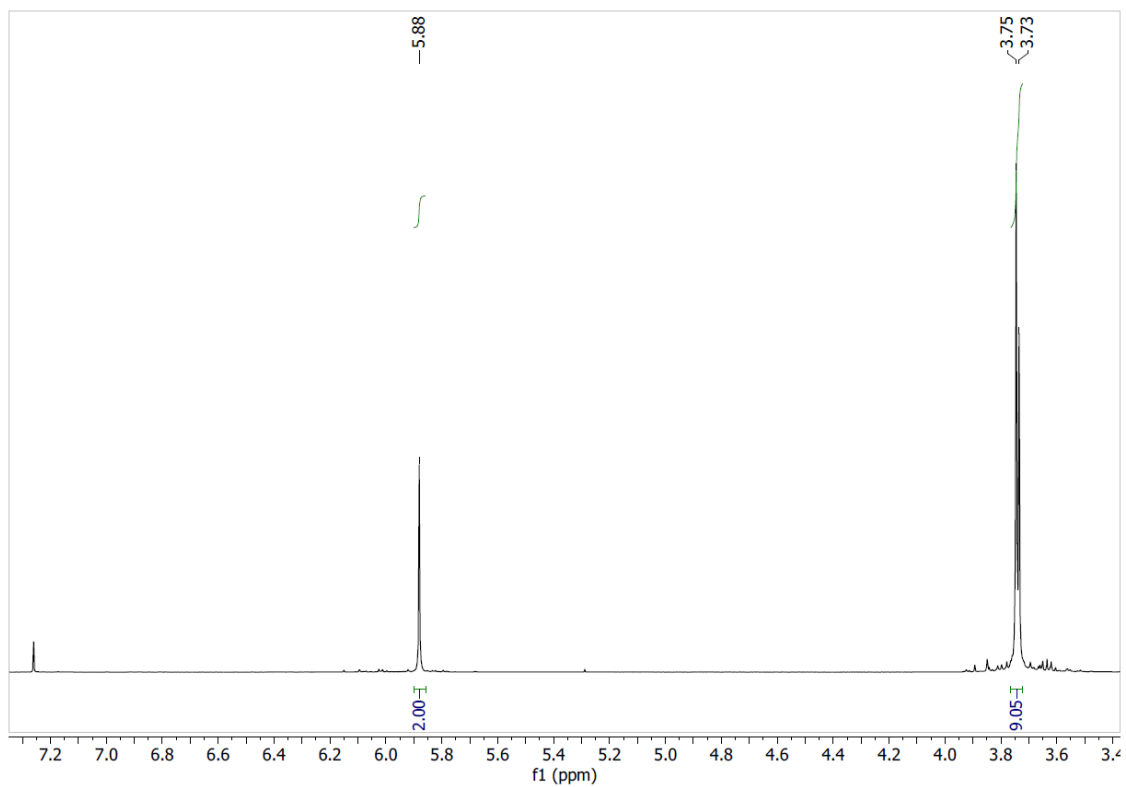


Figure ESI 5. ^1H -NMR spectrum of tetrakis(2,4,6-trimethoxybenzoyl)germane (**1c**) in CDCl_3

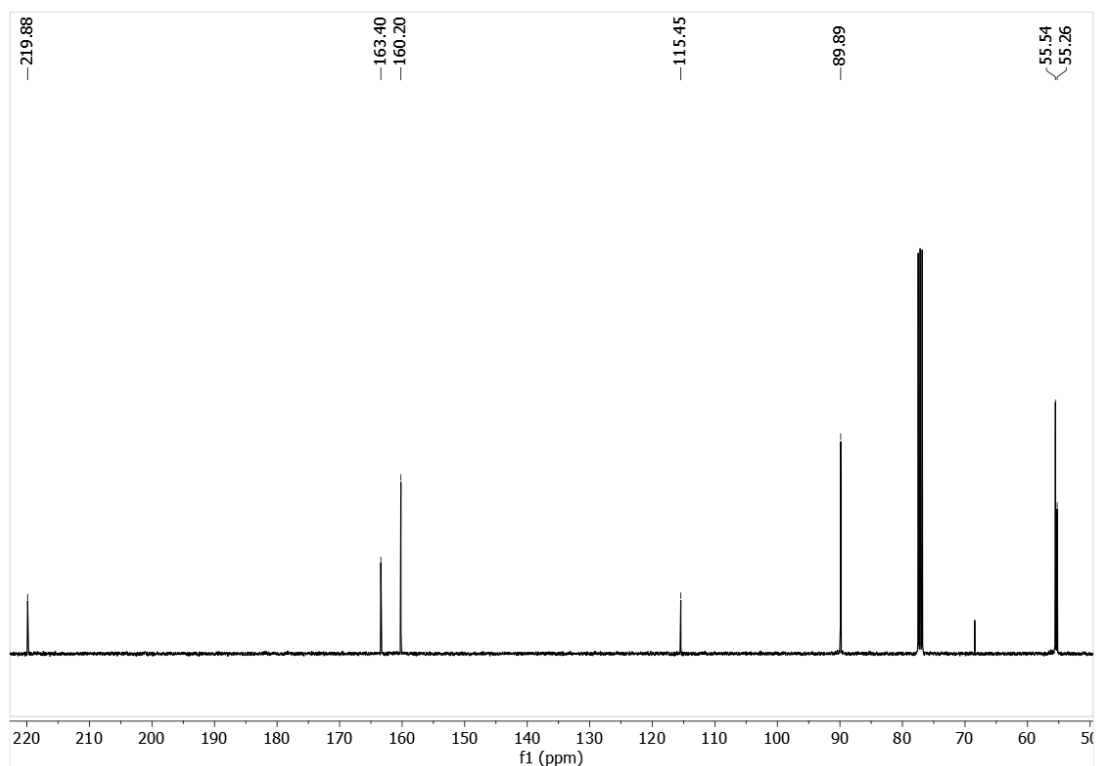


Figure ESI 6. ^{13}C -NMR spectrum of tetrakis(2,4,6-trimethoxybenzoyl)germane (**1c**) in CDCl_3 with remains of diisopropyl ether at 68 ppm.

Steady-state photolysis

For the steady-state photolysis (SSP) experiments, the following steps were performed under light protection. The 385 nm / 460 nm LED was connected to a lightguide using a fitting adapter. The tip of the lightguide was inserted into a quickfit with quartz window on the bottom. The intensity behind the glass window was set to $100 \text{ mW}/\text{cm}^2$ for each LED, using an Ocean Optics 2000+ USB device and the SpectraSuit Software. The set-up is shown in Figure ESI 7 the absorption spectra for each sample are shown in Figure ESI 8 (385 nm) and Figure ESI 9 (460 nm).

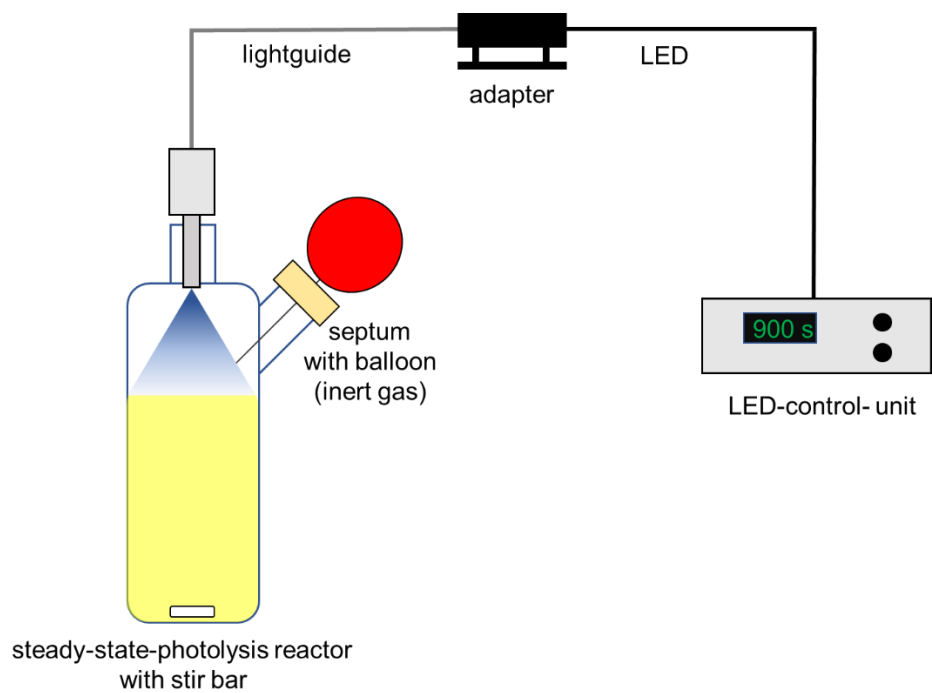
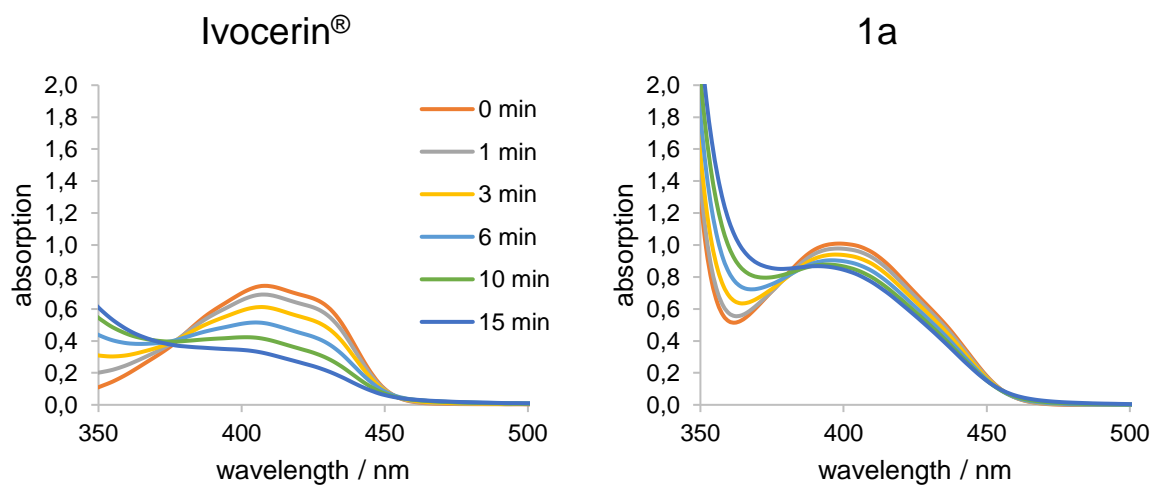


Figure ESI 7. Schematic depiction of the SSP setup



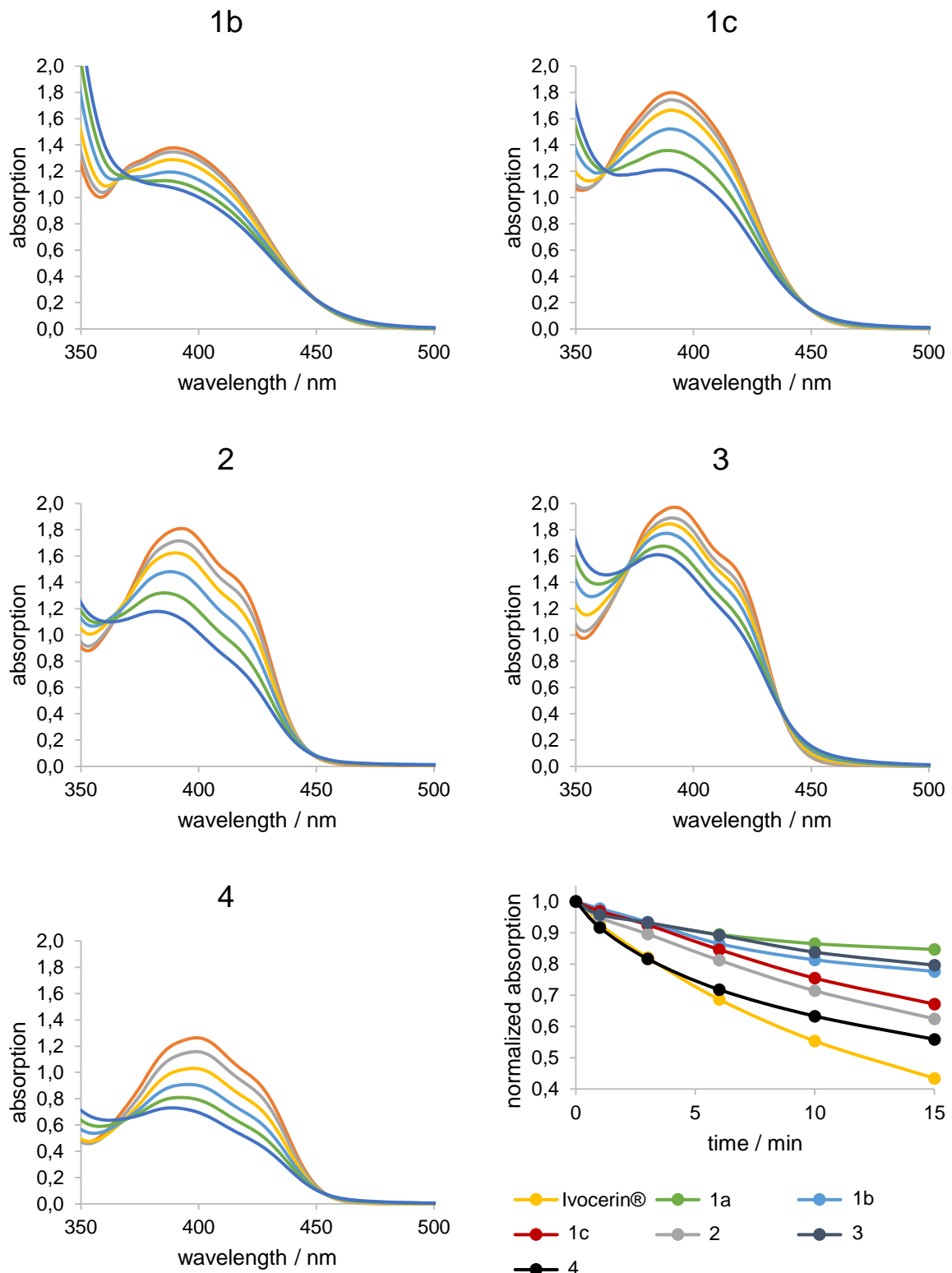
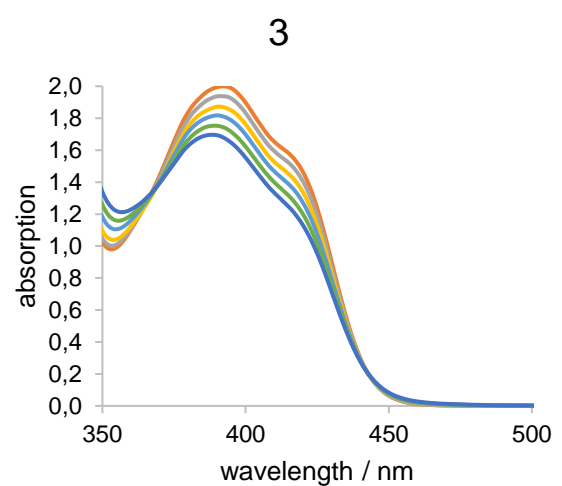
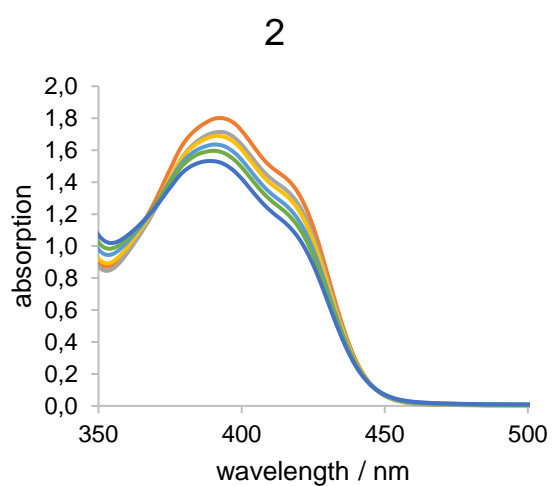
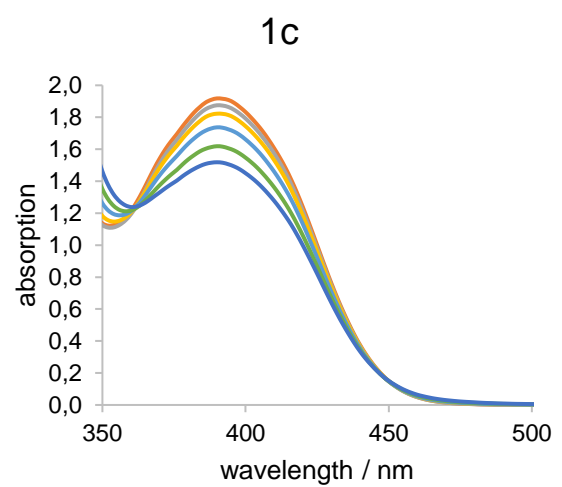
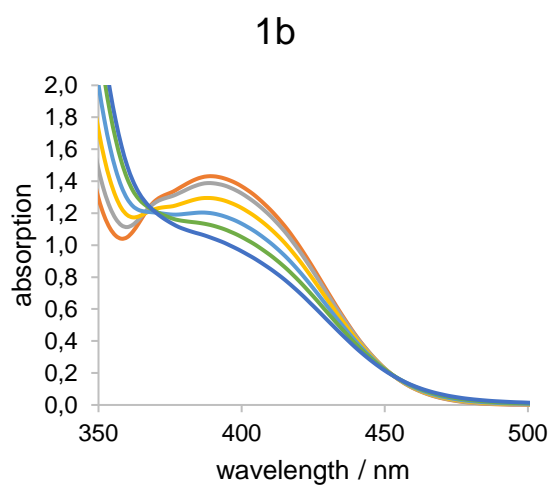
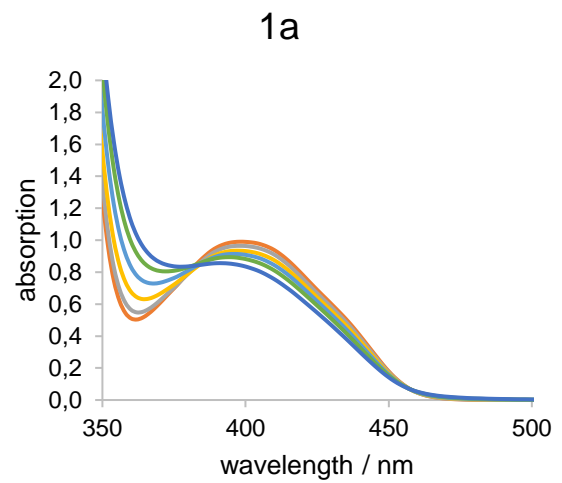
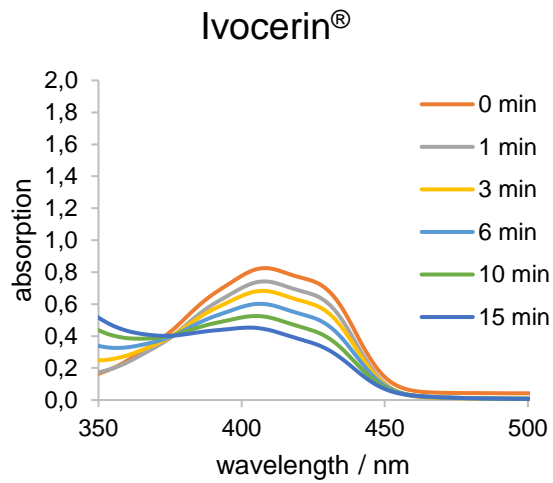


Figure ESI 8. UV-Vis spectra of SSP (385 nm LED) of Ivocerin®, 1a-c, 2, 3 and 4 after 0 min, 1 min, 3 min, 6 min, 10 min and 15 min of irradiation time together with a plot of their normalized absorption over time, monitored at the respective maxima of the $n-\pi^*$ absorption band



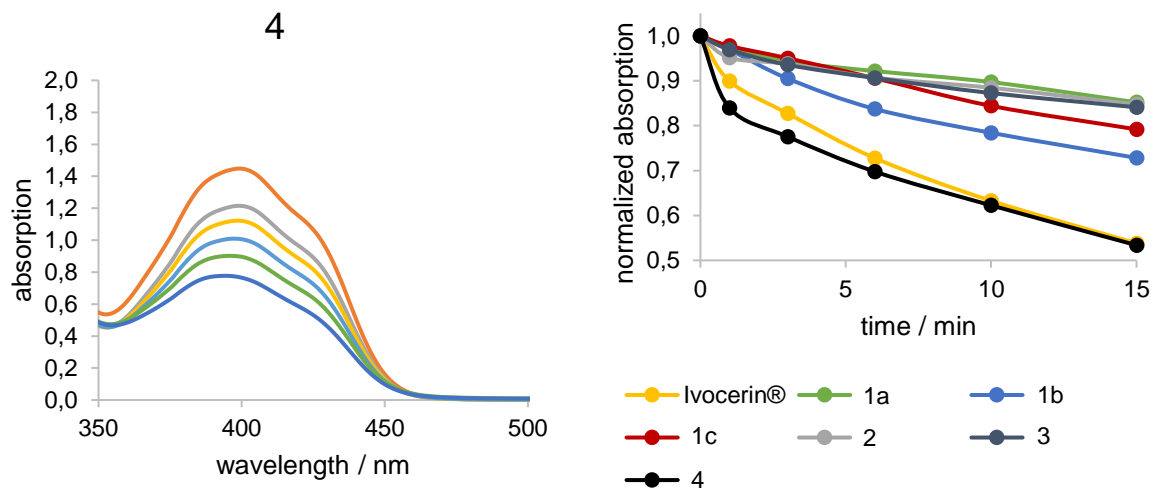


Figure ESI 9. UV-Vis spectra of SSP (460 nm LED) of Ivocerin®, **1a-c**, **2**, **3** and **4** after 0 min, 1 min, 3 min, 6 min, 10 min and 15 min of irradiation time, together with a plot of their normalized absorption over time, monitored at the respective maxima of the $n-\pi^*$ absorption band.

RT-FTIR Photorheology

For the RT-FTIR photorheology measurements, all tested formulations were mixed in brown glass vials with the PI and monomer according to the table below (Table ESI 1). In order to dissolve the PIs, they were dispersed in HDDA, heated up to 55 °C in the water bath, and put in the ultrasonic bath for 15 minutes at room temperature. These steps were repeated until the PIs dissolved completely. In Figure ESI 10 two typical rheology curves with storage and loss modulus of 2x Ivocerin[®] and **1b** are shown as an example.

Table ESI 1. PI content of the mixtures for photorheology in HDDA

	M / g mol⁻¹	mol%	n / μmol	m / mg	wt%
1a	613.2	0.17	7.48	4.59	0.46
1b	733.3	0.17	7.48	5.49	0.55
1c	853.4	0.17	7.48	6.38	0.64
3	669.3	0.17	7.48	5.01	0.50
Ivocerin[®]	401.0	0.17	7.48	3.00	0.30
2x Ivocerin[®]	401.0	0.34	15.0	6.00	0.60
HDDA	226.3	99.83	4·10 ³	-	-

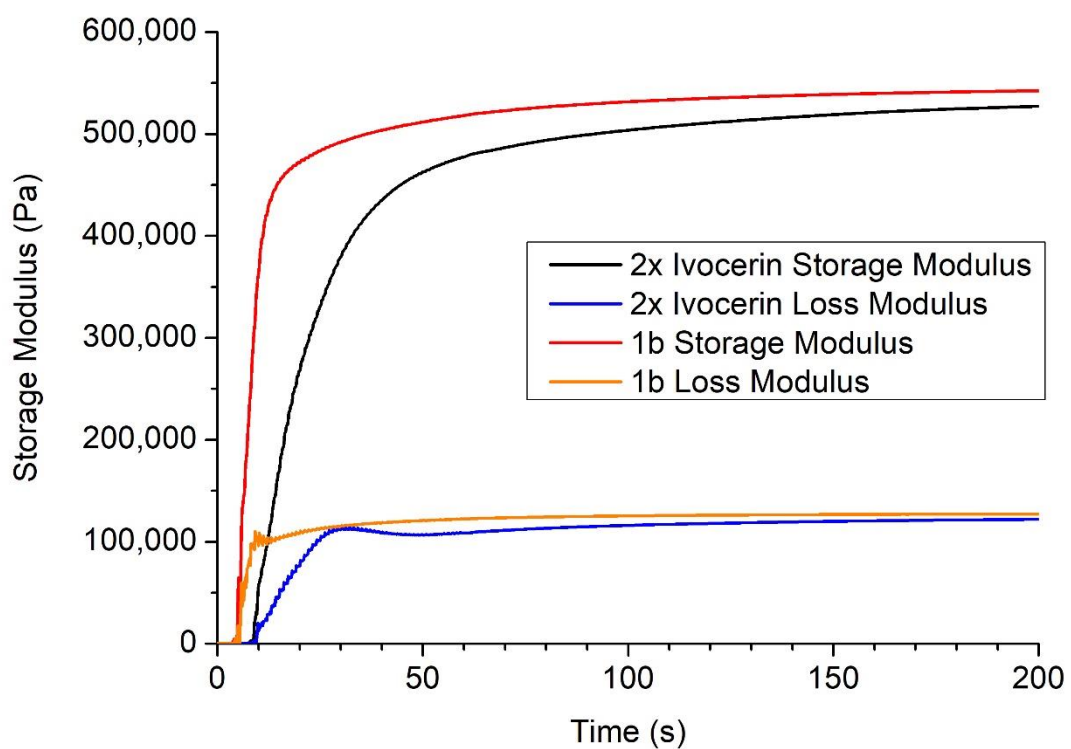


Figure ESI 10. Storage modulus and loss modulus of 2x Ivocerin[®] and **1b** during the photorheology measurements at 460 nm

Literature

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3. Brook, A. G.; Abdesaken, F.; Söllradl, H., Synthesis of some tris(trimethylsilyl)germyl compounds. *Journal of Organometallic Chemistry* **1986**, 299 (1), 9-13.
4. Radebner, J.; Leybold, M.; Eibel, A.; Maier, J.; Schuh, L.; Torvisco, A.; Fischer, R.; Moszner, N.; Gescheidt, G.; Stueger, H.; Haas, M., Synthesis, Spectroscopic Behavior, and Photoinduced Reactivity of Tetraacylgermanes. *Organometallics* **2017**, 36 (18), 3624-3632.