

Supporting Information:

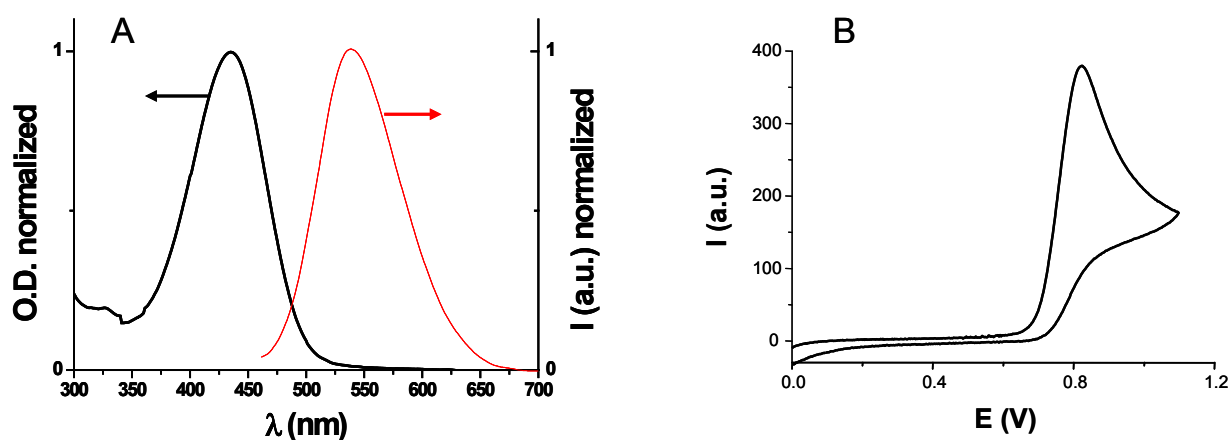
Chalcone Derivatives as Highly Versatile Photoinitiators For Radical, Cationic, Thiol-ene and IPN Polymerization Reactions Upon Visible Lights.

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Figure S1. (A) Absorption and fluorescence spectra for Cal_5 in acetonitrile. (B) Cyclic Voltammogram for Cal_5.



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Figure S2. ESR Spin trapping spectra for the irradiation of a Cal_5/TH solution (a) experimental and (b) simulated spectra ($a_N = 14.1$ G and $a_H = 2.3$ G in agreement with data for Ar^\bullet ref.²⁸).

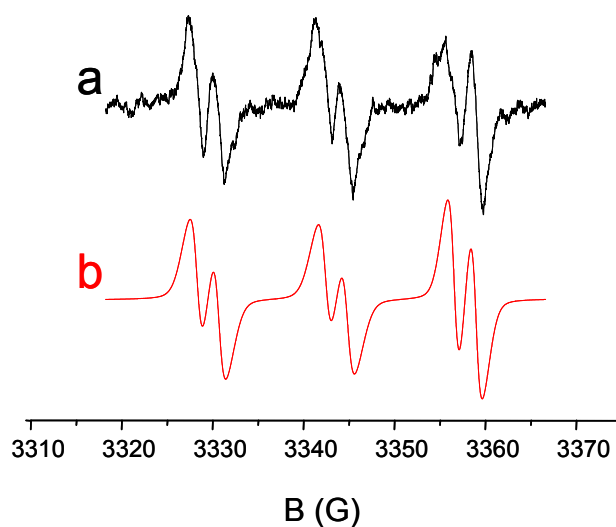
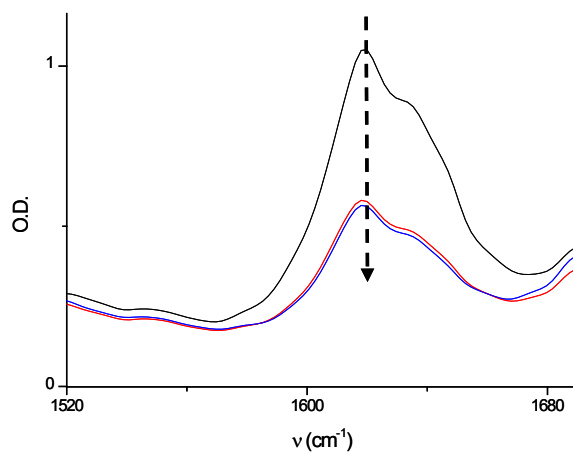


Figure S3. IR spectra recorded in the course of the trithiol/DVE-3 photopolymerization upon sunlight (in laminate; June – 20 - 2013; Mulhouse); initiating system Cal_5/Iod (0.5%/1% w/w); black curve is prior to sunlight exposure; red = 400 s and blue = 600 s.



Synthesis of the chalcone derivatives:

The different chalcone derivatives were synthesized by a base-catalyzed Claisen - Schmidt condensation reaction of 2'-hydroxyacetophenone and the corresponding aldehyde. Cal_3-Cal_5 were synthesized following procedures previously reported in the literature.[M.-A. Tehfe, F. Dumur, P. Xiao, B. Graff, F. Morlet-Savary, J.-P. Fouassier, D. Gignes J. Lalevée, Polym. Chem. 2013, DOI: 10.1039/c3py00536d]

Synthesis of (E)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one Cal_1

An aqueous solution of sodium hydroxide (60%, 80 mL, 48 g in 80 mL of water) was added to a methanolic solution (80 mL) of 2'-hydroxyacetophenone (5.45 g, 4.8 mL, 40 mmol). The obtained solution was cooled to room temperature, benzaldehyde (4.24 g, 4.08 mL, 40 mmol) was added and the reaction mixture was stirred for 12 h. After this period, the reaction mixture was poured into a mixture of water (100 mL), ice and hydrochloric acid (pH adjusted to 2). The obtained solid was filtered, taken in chloroform (200 mL) and washed with a 5% aqueous solution of sodium hydrogen carbonate (2 × 200 mL). The organic layer was collected, dried and evaporated to dryness. The residue was crystallized from ethanol giving the chalcone (7.71 g, 86% yield). ¹H NMR (CDCl₃) δ (ppm): 6.94 (t, 1H, J = 8.0 Hz), 7.03 (d, 1H, J = 8.4 Hz), 7.42-7.44 (m, 3H), 7.50 (td, 1H, J = 8.4 Hz, J = 1.4 Hz), 7.63-7.68 (m, 3H), 7.90-7.95 (m, 2H), 12.52 (brs, 1H, OH); ¹³C NMR (CDCl₃) δ (ppm): 118.6, 118.8, 120.0, 120.1, 128.6, 129.0, 129.6, 130.9, 134.6, 136.4, 145.4, 163.6, 193.7; HRMS (ESI MS) m/z: theor: 247.0730 found: 247.0732 ([M+Na]⁺ detected).

Synthesis of (E)-1-(2-hydroxyphenyl)-3-(p-tolyl)prop-2-en-1-one Cal_2

An aqueous solution of sodium hydroxide (60%, 80 mL, 48 g in 80 mL of water) was added to a methanolic solution (80 mL) of 2'-hydroxyacetophenone (5.45 g, 4.8 mL, 40 mmol). The obtained solution was cooled to room temperature, *p*-tolualdehyde (4.80 g, 4.72 mL, 40 mmol) was added and the reaction mixture was stirred for 12 h. After this period, the reaction mixture was poured into a mixture of water (100 mL), ice and hydrochloric acid (pH adjusted to 2). The obtained solid was filtered, taken in chloroform (200 mL) and washed with a 5% aqueous solution of sodium hydrogen carbonate (2 × 200 mL). The organic layer was collected, dried and evaporated to dryness. The residue was crystallized from ethanol giving the chalcone (8.67 g, 83% yield). ¹H NMR (CDCl₃) δ (ppm): 2.40 (s, 3H), 6.93 (td, 1H, J = 6.1 Hz, J = 1.1 Hz), 7.02 (dd, 1H, J = 8.4 Hz, J = 1.0 Hz), 7.22-7.25 (d, 2H, J = 8.0 Hz), 7.48

(td, 1H, $J = 7.0$ Hz, $J = 1.6$ Hz), 7.56 (d, 2H, $J = 8.2$ Hz), 7.62 (d, 1H, $J = 15.5$ Hz), 7.90 (d, 1H, $J = 15.5$ Hz), 7.92 (dd, 1H, $J = 7.0$ Hz, $J = 1.6$ Hz), 12.9 (s, 1H, OH); ^{13}C NMR (CDCl_3) δ (ppm): 21.6, 118.6, 118.8, 119.0, 120.1, 128.7, 129.6, 129.8, 131.9, 136.3, 141.6, 145.6, 163.6, 193.8; HRMS (ESI MS) m/z : theor: 261.0886 found: 261.0890 ($[\text{M}+\text{Na}]^+$ detected).

Synthesis of (1-(2-hydroxyphenyl)-3-(4-(octyloxy)phenyl)prop-2-en-1-one) Cal_3.

An aqueous solution of sodium hydroxide (60%, 80 mL, 48 g in 80 mL of water) was added to a methanolic solution (80 mL) of 2'-hydroxyacetophenone (5.45 g, 4.8 mL, 40 mmol). The obtained solution was cooled to room temperature, octyloxybenzaldehyde (9.37 g, 40 mmol) was added and the reaction mixture was stirred for 12 h. After this period, the reaction mixture was poured into a mixture of water (100 mL), ice and hydrochloric acid (pH adjusted to 2). The obtained solid was filtered, taken in chloroform (200 mL) and washed with a 5% aqueous solution of sodium hydrogen carbonate (2×200 mL). The organic layer was collected, dried and evaporated to dryness. The residue was crystallized from ethanol giving the chalcone (1-(2-hydroxyphenyl)-3-(4-(octyloxy)phenyl)prop-2-en-1-one) as a light yellow solid (11.56 g, 82% yield). ^1H NMR (CDCl_3) δ (ppm): 0.89 (t, 3H, $J = 6.6$ Hz, CH_3), 1.30-1.47 (m, 10H), 1.81 (qt, 2H, $J = 6.9$ Hz), 4.01 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.92-6.95 (m, 3H), 6.98 (brs, 1H, OH), 7.02 (d, 1H, $J = 8.3$ Hz), 7.49 (td, 1H, $J = 7.1$ Hz, $J = 1.4$ Hz), 7.54 (d, 1H, $J = 15.4$ Hz), 7.62 (d, 2H, $J = 8.7$ Hz), 7.89-7.93 (m, 2H); ^{13}C NMR (CDCl_3) δ (ppm): 14.1, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 68.3, 115.0, 117.4, 118.6, 118.7, 120.2, 127.1, 129.5, 130.5, 136.1, 145.5, 151.7, 163.6, 193.7; HRMS (ESI MS) m/z : theor: 352.2038 found: 352.2035 (M^+ detected); $\text{Mp} = 92^\circ\text{C}$.

Synthesis of (3-(anthracen-9-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one) Cal_4.

An aqueous solution of sodium hydroxide (60%, 80 mL, 48 g in 80 mL of water) was added to a methanolic solution (80 mL) of 2'-hydroxyacetophenone (5.45 g, 4.8 mL, 40 mmol). The obtained solution was cooled to room temperature, 9-anthracenaldehyde (8.25 g, 40 mmol) was added and the reaction mixture was stirred for 12 h. After this period, the reaction mixture was poured into a mixture of water (100 mL), ice and hydrochloric acid (pH adjusted to 2). The obtained solid was filtered, taken in chloroform (200 mL) and washed with a 5% aqueous solution of sodium hydrogen carbonate (2×200 mL). The organic layer was collected, dried and evaporated to dryness. The residue was crystallized from ethanol giving the chalcone (3-(anthracen-9-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one) as a yellow solid (10.77 g, 83% yield). ^1H NMR (CDCl_3) δ (ppm): 7.50-7.56 (m, 5H), 7.65-7.69 (m, 3H), 8.02-

8.06 (m, 3H), 8.28 (d, 1H, J = 7.6 Hz), 8.68 (s, 1H), 8.96 (d, 2H, J = 8.7 Hz), 11.5 (s, 1H); ^{13}C NMR (CDCl_3) δ (ppm): 119.0, 123.6, 124.7, 125.1, 125.5, 125.7, 126.6, 128.6, 128.8, 129.0, 129.1, 129.3, 129.4, 129.7, 129.8, 131.1, 131.3, 132.1, 135.2, 136.6, 142.7, 163.8, 193.0; HRMS (ESI MS) m/z : theor: 324.1150 found: 324.1153 (M^+ detected); $M = 124^\circ\text{C}$ (decomp).

Synthesis of (3-(4-(dimethylamino)phenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one) Cal_5.

An aqueous solution of sodium hydroxide (60%, 80 mL, 48 g in 80 mL of water) was added to a methanolic solution (80 mL) of 2'-hydroxyacetophenone (5.45 g, 4.8 mL, 40 mmol). The obtained solution was cooled to room temperature, *N,N*-dimethylaminobenzaldehyde (5.97 g, 40 mmol) was added and the reaction mixture was stirred for 12 h. After this period, the reaction mixture was poured into a mixture of water (100 mL), ice and hydrochloric acid (pH adjusted to 2). The obtained solid was filtered, taken in chloroform (200 mL) and washed with a 5% aqueous solution of sodium hydrogen carbonate (2×200 mL). The organic layer was collected, dried and evaporated to dryness. The residue was crystallized from ethanol giving the chalcone (3-(4-(dimethylamino)phenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one) as a light yellow solid (7.62 g, 71% yield). ^1H NMR (CDCl_3) δ (ppm): 3.06 (s, 6H), 6.69 (d, 2H, J = 8.9 Hz), 6.92 (t, 1H, J = 8.1 Hz), 6.98 (brs, 1H, OH), 7.01 (d, 1H, J = 8.3 Hz), 7.43-7.48 (m, 2H), 7.58 (d, 2H, J = 8.8 Hz), 7.89-7.94 (m, 2H); ^{13}C NMR (CDCl_3) δ (ppm): 40.1, 111.8, 114.3, 118.5, 118.6, 120.4, 122.4, 129.4, 130.8, 135.6, 146.5, 152.3, 163.5, 193.5; HRMS (ESI MS) m/z : theor: 267.1259 found: 267.1261 (M^+ detected). $M_p = 172\text{-}173^\circ\text{C}$.