SUPPORTING INFO

Visible light excitation of CdSe nanocrystals triggers the release of coumarin from cinnamate surface ligands

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EXPERIMENTAL PROCEDURES FOR NANOCRYSTAL SYNTHESIS, LIGAND EXCHANGE, PHOTOLYSES AND ELECTROCHEMISTRY

General materials and methods. Unless indicated otherwise, all reactions were carried out under an inert atmosphere. All handling of cinnamates and nanocrystals was performed in a darkroom illuminated by red light. All purifications by column chromatography were carried out with silica gel from Sorbent Technologies. TLC plates were purchased from EM Science. Spots were visualized by UV light, treatment with I_2 or treatment with phosphomolybdic acid. THF, ether and CH_2Cl_2 were dried using a Solvent Purification System from Solvtek. MeCN and H_2O for HPLC analysis were of HPLC quality. All other solvents were used as received. All chemicals were purchased from Aldrich Company. When KO_2 in DMF was used, 2 equivalents (with respect to KO_2) of 18-crown-6 were added to solubilize the salt. All centrifugations were performed with a Fisher Scientific Centrific Model 228. Membrane size-exclusion centrifugations utilized Centriplus 50 centrifuge tubes (Millipore). NMR spectra were taken on a Bruker 300 or 400 MHz NMR instruments. Signals were calibrated on $CDCl_3$ and are reported with respect to TMS. ^{31}P shifts are reported with respect to 80 % H_3PO_4. In the ^{13}C spectra, some alkyl carbons overlapped. If visible, ^{1}H-NMR shifts for phenolic protons are reported. UV-visible absorption spectra were recorded on a Hewlett Packard 8452A spectrometer. Fluorescence measurements were recorded on an ISS PC1 Photon Counting Spectrometer (excitation and emission slit: 0.5 mm). Elemental analyzes were carried out by Atlantic Microlabs. Unless stated otherwise, all HRMS spectra were recorded using the electrospray technique. ES-HRMS measurements (positive ion mode) were performed at Ohio State University, FAB-HRMS at Duke University. Analysis by GC was carried out using a Hewlett Packard 5980 Series II chromatograph (30 m x 0.32 mm HP50 column, T_{init}=100 °C, t_{init}=1 min, rate=20 °C/min, T_{final}=250 °C). Melting points were taken on a Thomas Hoover Melting Point Apparatus. HPLC analyses for

bulk electrolysis were performed with a Waters 600 Controller, 717 Autosampler and 996 Photodiode Array using a Supelco 5 μM LC-18-DB column (4.6 mm x 25 cm) reverse phase column. Electrochemistry experiments were performed on a CH Instruments CHI660A Electrochemical Workstation. Platinum electrodes (1.57 mm^2 effective area) were purchased from CH instruments, platinum wires from VWR. Systematic names for molecules according to IUPAC rules were generated using the Beilstein AutoNom program version 2.02.118 and/or by using the ACD/I-Lab Web service (ACD/IUPAC Name Free 7.06).

Retention times. GC-analysis: biphenyl at 4.4 min, **1** at 9.1 min, **6** at 3.9 min, **7** at 6.6 min. HPLC analysis: benzophenone at 9 min, **9a** at 20 min, **9b** at 29 min (broad).

Pyridine coated nanocrystals (py-NC). In a centrifuge tube, TOPO coated NC (ca. 40 mg) were heated at 90 ºC in distilled pyridine (2 mL) overnight in a glove box. After cooling, excess hexanes were added and the vial was shaken and centrifuged. The supernatant liquid was decanted. Hexanes were added to the residue and the process was repeated once more. The resulting hexane-wet nanocrystals were used as such, as extensive drying led to loss of ligands and formation of insoluble material. The py-NC (as a solution in pyridine) could be stored for months in the glove box. On one occasion, pentane was used as the washing solvent (3x) and after brief air-drying the pyridine coated nanocrystals were dissolved in $CDCl_3$ for NMR analysis; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.61 (br m, 2H, pyr-H2), 7.83 (br m, 1H, pyr-H4), 7.30 (br m, 2H, pyr-H3), 2.17 (br s, 12H, TOPO-$C^{1,2}\underline{H}_2$), 1.61 (br s, 30H, TOPO-$C^{3\text{-}8}\underline{H}_2$), 0.86 (br m, 9H, TOPO-$C\underline{H}_3$), NMR shifts for unbound TOPO: δ 1.6, 1.21, 0.82. Comparing the integration of the pyridine and TOPO NMR peaks indicated that roughly 60 % of the original TOPO ligands had been replaced by pyridine on that occasion.

Ligand exchange procedure. Hexane-wet, pyridine coated NC were dissolved in $CHCl_3$ or $CDCl_3$ (treated with neutral alumina just before use) and degassed with nitrogen. To this was added a

concentrated solution of the synthetic thiol(s) (typically 0.5 – 1.0 M) in degassed $CHCl_3$ (treated with neutral alumina just before use). The mixture was stirred in the dark under an inert atmosphere for 2-3 d. After the indicated time, excess solvent was added (ether for all cinnamate-coated NC, hexanes for all others) to precipitate the NC. The vial was then shaken and centrifuged. The supernatant liquid was decanted. More solvent was added to the residue and the process was repeated 4 times. The washings were concentrated and analyzed by GC to make sure all free ligand had been washed out. The washed NC were dried under high-vacuum and stored at –78 ºC. Alternatively, they were dissolved in DMF by stirring for 2 days, followed by filtering through Celite. These solutions were stored at lower temperatures to avoid decomposition, although the quality decreased slowly upon prolonged storage (> 6 months).

General photolysis procedure. Irradiations were carried out in circular quartz tubes (diameter 0.9 mm, height 13 cm), equipped with a vacuum-adapter side-arm, that were left open to air or degassed by three freeze-pump-thaw cycles to remove air and traces of $HNMe_2$ (no significant leaking of the vacuum was observed after 24 h). All analyses using UV-visible absorption and fluorescence spectroscopy were recorded in this tube. All photolysis solutions with the 31 Å nanocrystals had an absorbance of ~0.15 at the first excitation peak of the nanocrystal. For irradiation, a high pressure mercury lamp (1000 W, Hanovia 528B-1) in conjunction with a Spectral Energy GM 252 high intensity grating monochromator was used. The metal sample chamber was at ca. 40 cm distance from the source. Irradiation was performed at ambient temperature and care was taken to prevent any exposure to incidental ambient light. At intervals the tube was removed from the beam and subjected to UV-visible absorption spectroscopy (300 nm – 700 nm) and fluorescence spectroscopy (excitation at 374 nm/ emission at 438 nm) for no longer than a few seconds. Although they were shown to have no effect on the outcome of the photolysis, these intermediate analyses were <u>not</u> conducted during

quantitative photolysis experiments (see below). In some cases, the nanocrystals were separated from the solution after photolysis, as described below. Absorption of adrenochrome was recorded at 486 nm.

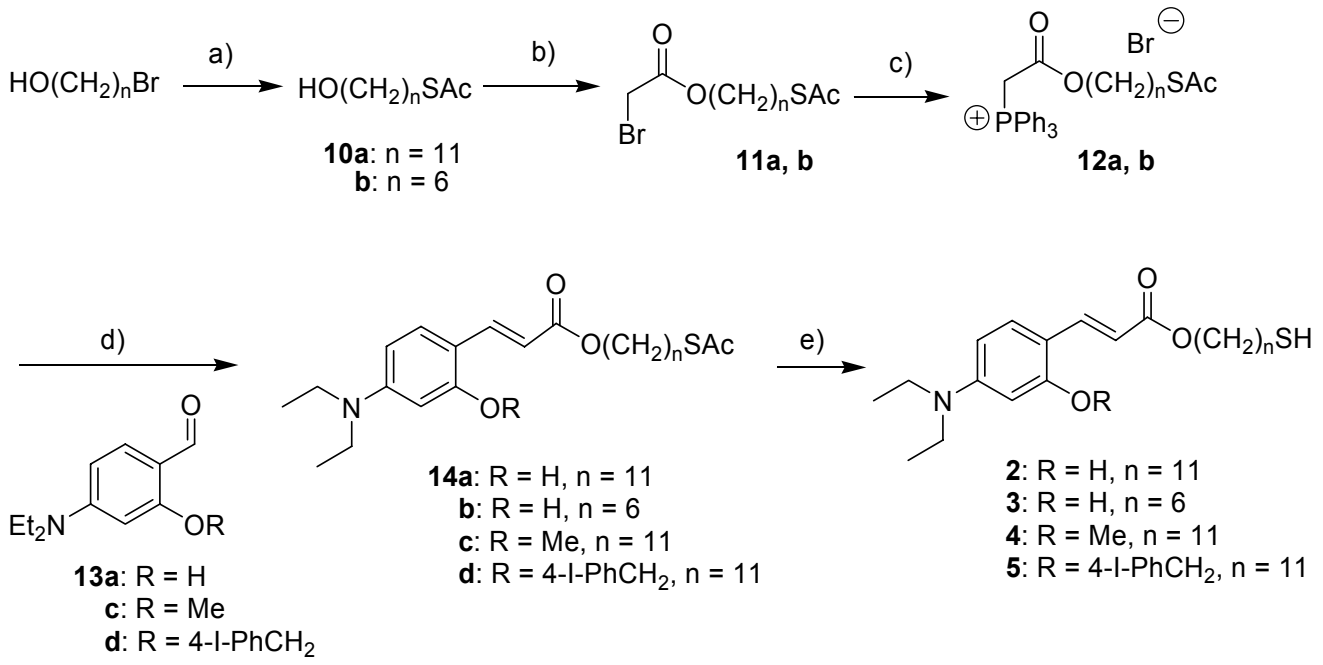
Quantitative analysis of photolysis mixtures. NC solutions were freeze-pump-thawed (3 cycles) to remove air and $HNMe_2$. After >24 h irradiation time without any intermediate analysis, irradiation was stopped and the solution was analyzed by UV-visible absorption and fluorescence spectroscopy. The photolysis tube was then opened, internal standard (biphenyl, 1 mM) in DMF was added and the contents of the tube were transferred (incl. 1 wash with DMF) into a Millipore centrifuge tube. The tube was spun at 3300 rpm for 1 h and the filtrate collected. More DMF was then added to the Millipore tube and it was spun again. The two filtrates were combined and adjusted to exactly 10.0 mL DMF. This solution was analyzed by UV-visible absorption spectroscopy (374 nm), to determine the combined amount of coumarin and cinnamates, and by fluorescence (excitation at 374 nm/ emission at 438 nm) spectroscopy to quantify the amount of coumarin formed. Subsequently, the solution was poured into a vial containing ether (20 mL) and water (20 mL), the vial was shaken and the ether layer was separated. After drying with $MgSO_4$, the ether was removed (all this was done to concentrate the DMF solution without applying any heat). The residue was redissolved in a very small amount of DMF (50-100 μL) and analyzed by GC for formed coumarin (confirmed by spiking with authentic material). In all cases, a blank solution (with composition and volume equal to the solution that had been photolyzed) was left in the dark for the duration of the photolysis and subsequently was worked up exactly as described above. The blank numbers thus obtained were used as correction, since some thiols tend to go into solution upon prolonged storage of the nanocrystals.

Cyclic voltammetry measurements. All handling was conducted in the dark. An electrochemical cell equipped with a vacuum-adapter side-arm was used. The cell utilized a platinum

working- and counter-electrode and a silver-reference electrode. The signal for the ferrocene (Fc/Fc^+) couple (set at 0.47 V versus HNE) served as the calibration signal for the cell. The supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate (TBAHP) was dissolved in freshly distilled DMF (5 mL, [TBAHP]=50 mM), the solution was degassed (three freeze-pump-thaw cycles) and the background CV measured. Then the cell was opened, a concentrated solution of the analyte added (to about 1 mM) and the solution was degassed again. Substrate CVs were then measured and compared to the obtained background signals.

Bulk electrolysis. All handling was conducted in the dark. The working- and counter-electrode for the cell were coiled long platinum wires (471 mm^2 surface area each). The reference electrode was an $Ag/AgBF_4$ (15 mM) couple in DMF. The signal for the Fc/Fc+ couple (set at 0.47 V versus HNE) served as the calibration signal for the cell. Nitrogen was bubbled through the electrolysis solution at all times, except during the recording of a CV. The supporting electrolyte TBAHP was dissolved in freshly distilled DMF (5 mL, [TBAHP]=50 mM). Cyclic voltammograms were recorded for the background signal. A concentrated solution of the analyte was added (to give a final concentration of about 0.5 – 1.0 mM) and cyclic voltammograms were recorded to establish reduction/oxidation peaks. Bulk electrolysis was performed (at either +0.9 V or –1.5 V) with continuous measurement of the current and with continuous stirring. At intervals, 50 μL aliquots were taken. Internal standard (benzophenone) was added and without any further manipulation the DMF aliquots were analyzed by reverse phase HPLC using 40 % aq. CH_3CN (flow rate = 1.0 mL/min) and UV detection (374 and 254 nm). A vial containing a solution, identical to the solution that was electrolyzed, was placed next to the electrochemical cell and aliquots from this blank were analyzed as to correct for any background isomerization.

SYNTHESIS OF LIGANDS



Scheme S1. Synthesis of thiol-containing cinnamate ligands. Key: a) KSAc, DMF, r.t., 20 h; b) $BrCH_2COBr$, DMAP, pyridine, CH_2Cl_2, 0 ºC, 15-30 min; c) PPh_3, EtOAc, r.t., 3 d; d) [1] Et_3N, PhH, 15 min; [2] aldehyde **13**, PhH, r.t. or Δ, 1 –3 d; e) NaSMe, MeOH, 0 ºC, 2 h. For yields, see below.

S-(11-Hydroxy-undecyl) thioacetate (10a). 11-Bromoundecanol (7.8 g, 31 mmol), potassium thioacetate (7.1 g, 60 mmol) and dry DMF (70 mL) were stirred at room temperature for 20 h in the presence of molecular sieves (4 Å). The brown suspension was diluted with ether and water, the organic layer was collected and the aqueous layer was extracted with ether. The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The resulting solid was recrystallized from hexanes to give off white crystals (7.2 g, 93 %). m.p. 49 °C; ^{1}H NMR ($CDCl_3$, 400 MHz)[1] δ 3.55 (t, 2H, OCH_2, J=6.6 Hz), 2.79 (t, 2H, SCH_2, J=7.2 Hz), 2.25 (s, 3H, $COCH_3$), 2.17 (s, 1H, OH), 1.49 – 1.45 (m, 4H, SCH_2CH_2 + OCH_2CH_2), 1.35 – 1.15 (m, 14H, alkyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ

196.5, 63.1, 33.1, 30.92, 29.88, 29.80, 29.76, 29.46, 29.41, 29.11, 26.1; HRMS for $C_{13}H_{26}O_2S$ [M+H] 247.1732, found 247.1727.

S-(6-Hydroxy-hexyl) thioacetate (10b). This compound was prepared from 6-bromohexanol (2.5 g, 13.8 mmol), potassium thioacetate (3.16 g, 27.8 mmol) and dry DMF (20 mL) using the same procedure as for **10a**. The product was obtained as an orange oil (2.17 g, 93 %). ^{1}H NMR ($CDCl_3$, 300 MHz)[2] δ 3.54 (t, 2H, OCH_2, J=6.6 Hz), 2.82 (t, 2H, SCH_2, J=7.5 Hz), 2.46 (s, 1H, OH), 2.26 (s, 3H, $COCH_3$), 1.57 – 1.45 (m, 4H, alkyl), 1.33 – 1.29 (m, 4H, alkyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.5, 62.9, 32.8, 30.9, 29.84, 29.33, 28.84, 25.66.

11-Acetylsulfanyl-undecyl bromoacetate (11a). A mixture of alcohol **10a** (6.97 g, 28.3 mmol), pyridine (2.95 mL, 36.5 mmol) and DMAP (1.7 g, 14 mmol) in CH_2Cl_2 (50 mL) was stirred at 0 °C. Bromoacetyl bromide (2.95 mL, 33.6 mmol) was added dropwise, after which the mixture was stirred for 30 min at 0 °C. The yellow suspension was diluted with CH_2Cl_2 and extracted successively with water, 1.0 M aq. HCl, satd. aq. $NaHCO_3$-soln. and water. The organic layer was dried with $MgSO_4$, filtered and concentrated to give an orange oil (8.86 g, 85 %) which was sufficiently pure for the next step. An analytical sample was obtained by column chromatography (4:1 hexanes:EtOAc) to afford a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.09 (t, 2H, OCH_2, J=6.7 Hz), 3.77 (s, 2H, $BrCH_2$), 2.79 (t, 2H, SCH_2, J=7.2 Hz), 2.24 (s, 3H, $COCH_3$), 1.59 (p, 2H, OCH_2CH_2, J=6.8 Hz), 1.50 (p, 2H, SCH_2CH_2, J=7.5 Hz, 1.28 – 1.20 (m, 14H, alkyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.2, 167.6, 66.7, 31.00, 29.84, 29.75, 29.45, 29.41, 29.13, 28.98, 28.75, 26.2, 26.10; HRMS for $C_{13}H_{26}BrO_3S$ [M+H] 367.0943, found 367.0933.

6-Acetylsulfanyl-hexyl bromoacetate (11b). This compound was prepared from alcohol **10b** (1.0 g, 5.7 mmol), pyridine (0.6 mL, 7.4 mmol), DMAP (0.34 g, 2.78 mmol, CH_2Cl_2 (15 mL) and bromoacetyl bromide (0.6 mL, 6.8 mmol) using the same procedure as for **11a**. The product was

obtained as a brown oil (1.3 g, 77 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.09 (t, 2H, OCH_2, J=6.6 Hz), 3.75 (s, 2H, $BrCH_2$), 2.80 (t, 2H, SCH_2, J=7.5 Hz), 2.25 (s, 3H, $COCH_3$), 1.57 (p, 2H, OCH_2CH_2, J=6.6 Hz), 1.51 (p, 2H, SCH_2CH_2, J=6.9 Hz), 1.37 (m, 4H, alkyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.1, 167.6, 66.5, 30.9, 29.70, 29.25, 28.78, 28.59, 26.28, 25.62; HRMS for $C_{10}H_{17}BrO_3S$ [M+Na] 318.9974, found 318.9954.

(11-Acetylsulfanyl-undecyloxycarbonymethyl)-triphenylphosphonium bromide (12a). A mixture of crude bromide **11a** (8.36 g, 22.7 mmol) and PPh_3 (12.2 g, 45.0 mmol) in EtOAc (70 mL) was stirred for 3 d at room temperature. The solvent was evaporated to give a red oil which was dissolved in EtOAc (30 mL). To this ether (250 mL) was added dropwise at 0 °C. The solid was filtered, washed with copious amounts of ether and dried. The resulting light-brown solid (12.5 g, 85 %) was sufficiently pure for further reactions and proved stable for at least 2 years at room temperature. An analytical sample was obtained by column chromatography (9:1 CH_2Cl_2:MeOH) to afford a colorless glass. m.p. 90 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 – 7.61 (m, 15H, -PPh_3), 5.43 (d, 2H, PCH_2, J=14 Hz), 3.89 (t, 2H, OCH_2, J=6.4 Hz), 2.79 (t, 2H, SCH_2, J=7.2 Hz), 2.24 (s, 3H, $COCH_3$), 1.49 (p, 2H, OCH_2CH_2, J=7.2 Hz), 1.34 – 1.03 (m, 16H, alkyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.3, 164.6, 135.7 – 130.3 (multiple carbons), 118.0 (J=352 Hz), 67.2, 33.0, 31.0, 29.68, 29.60, 29.53, 29.31, 29.25, 28.95, 28.30, 25.8; ^{31}P NMR ($CDCl_3$, 400 MHz) δ 21.82; HRMS for $C_{33}H_{42}O_3PS$ [M] 549.2592, found 549.2592. The corresponding ylid **11-Acetylsulfanyl-undecyl (triphenyl-λ^5-phosphanylidene)-acetate** was always prepared *in situ* (see next reaction), but it could be obtained quantitatively by dissolving the salt in CH_2Cl_2 and washing 3 x with satd. aq. Na_2CO_3-soln. followed by drying and concentrating the organic layer to give a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58 – 7.22 (m, 15H, -PPh_3), 3.80 (t, 2H, OCH_2, J=6.3 Hz), 2.77 (t, 2H, SCH_2, J=7.5 Hz),

2.18 (s, 3H, $COCH_3$), 1.48 (p, 2H, OCH_2CH_2), 1.34 – 1.08 (m, 16H, alkyl), the vinylic proton (pK_a usually around 7.5) was sometimes observed as a broad peak around 2.0 ppm.

(6-Acetylsulfanyl-hexyloxycarbonymethyl)-triphenylphosphonium bromide (12b). Crude bromide **11b** (1.15 g, 3.88 mmol) and PPh_3 (2.1 g, 7.76 mmol) were stirred in EtOAc (20 mL) for 3 d at room temperature. The solvent was evaporated to give a thick oil. This oil was stirred vigorously with ether and then allowed to settle after which the ether was decanted. This process was repeated 4 more times to wash away all the excess PPh_3. The resulting crude product was a very thick oil (1.95 g, 89 %) that could not be crystallized but that was sufficiently pure for further reactions. An analytical sample was obtained by column chromatography (5 % -> 15 % MeOH in CH_2Cl_2) to afford a colorless thick oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.86 – 7.61 (m, 15H, -PPh_3), 5.40 (br d, 2H, PCH_2, J=14 Hz), 3.89 (t, 2H, OCH_2, J=6.8 Hz), 2.73 (t, 2H, SCH_2, J=7.4 Hz), 2.23 (s, 3H, $COCH_3$), 1.42 – 1.31 (m, 4H, alkyl), 1.20 –1.1 (m, 4H, alkyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.2, 164.6, 135.5, 134.35, 130.72, 128.88, 118.0 (J=384 Hz), 66.9, 33.3, 31.01, 29.40, 28.98, 28.24, 25.25; ^{31}P NMR ($CDCl_3$, 300 MHz) δ 21.94; HRMS for $C_{28}H_{32}O_3PS$ [M] 479.1804, found 479.1838.

4-Diethylamino-2-(4-iodo-phenylmethyloxy)benzaldehyde (13d). 4-Diethylamino-salicyl-aldehyde (1.5 g, 7.77 mmol) was dissolved in DMF (20 mL) and cooled in an ice bath. To this solid KO*t*-Bu (0.91 g, 8.1 mmol) was added. After stirring in the ice bath for 15 min, a clear brown solution was obtained. A solution of 4-iodobenzyl bromide (2.8 g, 9.43 mmol) in DMF (20 mL) was slowly added and stirring was continued for 3 h after which TLC indicated completion of the reaction. Excess water was added and the crude product was filtered and dried. Further purification was achieved by column chromatography (3:1 hexanes:EtOAc) to afford the product as a pink solid (1.3 g, 41 %). m.p. 130 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.2 (s, 1H, CHO), 7.73 (d, 2H, ICH, J=6.9 Hz), 7.73 (1H, Ar-H6, J=8.8 Hz), 7.20 (d, 2H, ICHCH, L=6.9 Hz), 6.28 (d, 1H, Ar-H5, J_1=8.7 Hz), 6.00 (app. s, 1H, Ar-

H3), 5.09 (s, 2H, OCH_2Ar), 3.37 (q, 4H, NCH_2, J=6.9 Hz), 1.16 (t, 6H, NCH_2CH_3, J=6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 187.3, 163.3, 154.1, 138.2, 136.8, 131.0, 129.3, 114.8, 105.1, 94.4, 94.0, 69.9, 45.2, 12.9; HRMS for $C_{18}H_{20}INO_2$ [M+Na] 432.0431, found 432.0427.

11-Acetylsulfanyl-undecyl *E*-3-(4-diethylamino-2-hydroxy-phenyl)propenoate (14a). Salt **12a** (1.02 g, 1.5 mmol) was dissolved in benzene (3 mL) and the solution was stirred until almost homogeneous. Then Et_3N (230 μL, 1.65 mmol) was added and stirring was continued for 15 min, resulting in a solution of the ylid and a precipitate of $Et_3N.HBr$. To this suspension was added 4-diethylaminosalicylaldehyde **13a** (0.26 g, 1.3mmol) and the mixture was stirred in the dark at room temperature for 18 h. The benzene was removed by concentration and the resulting oil was applied to a silica column. All colored bands (mostly product, but also traces of coumarin and aldehyde) were eluted as one fraction with 2:1 hexanes:EtOAc to give an orange oil. This oil was dissolved in hexanes (30 mL) and minimal EtOAc at reflux and then cooled to room temperature while stirring vigorously. After reaching room temperature, the mixture was left at –30 °C for 15 h. The yellow precipitate was filtered, washed with hexanes and dried yielding a yellow powder (0.45 g, 75 %) of very good purity. If an orange color was present in the solid, a second crystallization using the above protocol was employed. m.p. 58 °C; λ_{max} (DMF) 374 nm; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, 2H, ArCH=C, J=16.0 Hz), 7.30 (d, 2H, Ar-H6, J=8.8 Hz), 7.10 (br s, 1H, OH), 6.40 (d, 2H, ArC=CH, J=16.0 Hz), 6.22 (d, 2H, Ar-H5, J=8.8 Hz), 6.11 (app. s, 1H, Ar-H3), 4.18 (t, 2H, OCH_2, J=6.3 Hz), 3.33 (q, 4H, NCH_2, J=6.9 Hz), 2.86 (t, 2H, SCH_2, J=7.2 Hz), 2.32 (s, 3H, $COCH_3$), 1.67 (p, 2H, OCH_2CH_2, J=7.1 Hz), 1.54 (p, 2H, SCH_2CH_2, J=7.2 Hz), 1.4 – 1.20 (m, 14H, alkyl), 1.15 (t, 6H, NCH_2CH_3, J=6.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.0, 167.0, 158.0, 151.1, 141.7, 131.2, 112.0, 110.1, 105.1, 98.5, 64.8, 44.8, 31.0, 29.86, 29.82, 29.65, 29.61, 29.49, 29.23, 29.19, 26.4, 13.1; HRMS (FAB) for

$C_{26}H_{41}NO_4S$ [M] 463.2756, found 463.2765; Anal. calc. for $C_{26}H_{41}NO_4S$ (%): C 67.35, H 8.91, N 3.02, found: C 67.26, H 8.96, N 3.00.

6-Acetylsulfanyl-hexyl *E*-3-(4-diethylamino-2-hydroxy-phenyl)propenoate (14b). This compound was prepared from phosphonium salt **12b** (500 mg, 1.1 mmol), benzene (3 mL), Et_3N (175 μL, 1.26 mmol) and 4-diethylaminosalicylaldehyde **13a** (174 mg, 0.9 mmol) using the same procedure as for **14a**. The crude oil was purified by column chromatography (3:1 hexanes:EtOAc) to give the product as an orange oil (275 mg, 65 %). λ_{max} (DMF) 374 nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.90 (d, 1H, ArCH=C, J=16.0 Hz), 7.46 (br s, 1H, OH), 7.22 (d, 1H, Ar-H6, J=9 Hz), 6.30 (d, 1H, ArC=CH, J=16.0 Hz), 6.13 (dd, 1H, Ar-H5, J_1=8.8 Hz, J_2=2.2 Hz), 6.05 (d, 1H, Ar-H3, J=2.3 Hz), 4.10 (t, 2H, OCH_2, J=6.6 Hz), 3.24 (q, 4H, NCH_2, J=7.0 Hz), 2.79 (t, 2H, SCH_2, J=7.1 Hz), 2.24 (s, 3H, $COCH_3$), 1.61 (p, 2H, OCH_2CH_2, J=6.5 Hz, 1.50 (p, 2H, SCH_2CH_2, J=6.5 Hz), 1.34 – 1.30 (m, 4H, alkyl), 1.06 (t, 6H, NCH_2CH_3, J=7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 197.0, 170.1, 158.6, 151.1, 142.2, 131.2, 111.4, 110.1, 104.9, 98.5, 64.6, 44.9, 31.0, 29.7, 29.4, 29.0, 28.8, 25.8, 12.9; HRMS for $C_{21}H_{31}NO_4S$ [M+Na] 416.1866, found 416.1832.

11-Acetylsulfanyl-undecyl *E*-3-(4-diethylamino-2-methoxy-phenyl)propenoate (14c). Salt **12a** (760 mg, 1.2 mmol) was dissolved in benzene (3 mL) and the mixture was stirred until almost homogeneous. Then Et_3N (190 μL, 1.34 mmol) was added and stirring was continued for 15 min, resulting in a solution of the ylid and a precipitate of Et_3N.HBr. To this suspension was added 4-diethylamino-2-methoxy-benzaldehyde **13c** (207 mg, 1.0 mmol) and the mixture was heated in the dark at 55 °C for 3 d. The benzene was removed by concentration and the resulting oil was applied onto a silica column. The product was eluted with 2:1 hexanes:EtOAc to give an orange oil (198 mg, 41 %) having an *E/Z* ratio of 13/1 (by NMR). Clearly distinguishable peaks for the *Z*-isomer will be reported. ***E*-isomer**: λ_{max} (DMF) 376 nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.92 (d, 1H, ArCH=C,

J=15.9 Hz), 7.36 (d, 1H, Ar-H6, J=8.7 Hz), 6.32 (d, 1H, ArC=CH, J=15.9 Hz), 6.25 (dd, 1H, Ar-H5, J_1=8.7 Hz, J_2=1.8 Hz), 6.12 (d, 1H, Ar-H3, J=1.5 Hz), 4.18 (t, 2H, OCH_2, J=6.6 Hz), 3.86 (s, 3H, OMe), 3.37 (q, 4H, NCH_2, J=6.9 Hz), 2.86 (t, 2H, SCH_2, J=7.2 Hz), 2.32 (s, 3H, $COCH_3$), 1.72 (p, 2H, OCH_2CH_2, J=6.9 Hz), 1.56 (p, 2H, SCH_2CH_2, J=7.2 Hz), 1.3 – 1.20 (m, 14H, alkyl), 1.19 (t, 6H, NCH_2CH_3, J=6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.2, 169.0, 160.7, 151.0, 141.0, 131.1, 112.4, 111.4, 104.5, 94.1, 64.3, 55.5, 44.9, 30.9, 29.62, 29.59, 29.56, 29.41, 29.20, 29.00, 28.90, 26.3, 13.0; HRMS for $C_{27}H_{43}NO_4S$ [M + Na] 500.2805, found 500.2772; ***Z*-isomer**: λ_{max} (DMF) 374 nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.99 (d, 1H, Ar-H6, J=8.9 Hz), 7.20 (d, 1H, ArCH=C, J=12.7 Hz), 5.56 (d, 1H, ArC=CH, J=12.7 Hz), 4.11 (t, 2H, OCH_2), 3.83 (s, 3H, OMe); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.2, 167.6, 160.0, 150.8, 139.3, 133.1, 128.7, 112.5, 103.7, 93.6, 64.9, 55.6.

11-Acetylsulfanyl-undecyl *E*-3-(4-diethylamino-2-(4-iodo-phenylmethyloxy)-phenyl)-propenoate (14d). This compound was prepared from phosphonium salt **12a** (1.5 g, 2.4 mmol), benzene (12 mL), Et_3N (350 μL, 2.5 mmol) and iodo-aldehyde **13d** (0.8 g, 1.95 mmol) using the same procedure as for **14c**. The crude product was purified by column chromatography (5:1 hexanes:EtOAc) to give an orange solid (0.6 g, 45 %) having an *E/Z* ratio of 11/1 (by NMR). Clearly distinguishable peaks for the *Z*-isomer will be reported. m.p. 64 °C; λ_{max} (DMF) 374 nm (ε= 27,349 $cm^{-1}M^{-1}$); ***E*-isomer:** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.96 (d, 1H, ArCH=C, J=15.9 Hz), 7.69 (d, 2H, ICH, J=8.2 Hz), 7.37 (d, 1H, Ar-H6, J=8.8 Hz), 7.18 (d, 2H, ICHCH, L=8.2 Hz), 6.30 (d, 1H, ArC=CH, J=15.9 Hz), 6.25 (dd, 1H, Ar-H5, J_1=8.8 Hz, J_2=2.0 Hz), 6.05 (d, 1H, Ar-H3, J=2.3 Hz), 5.08 (s, 2H, OCH_2Ar), 4.16 (t, 2H, OCH_2, J=6.7 Hz), 3.33 (q, 4H, NCH_2, J=6.9 Hz), 2.84 (t, 2H, SCH_2, J=7.2 Hz), 2.32 (s, 3H, $COCH_3$), 1.66 (m, 2H, OCH_2CH_2), 1.56 (m, 2H, SCH_2CH_2), 1.3 – 1.20 (m, 14H, alkyl), 1.15 (t, 6H, NCH_2CH_3, J=6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.4, 168.9, 159.3, 150.9, 140.5, 138.1, 137.2, 130.8, 129.3, 112.8, 111.8, 105.1, 96.1, 93.7, 70.0, 64.5, 45.0, 31.0, 29.90,

29.86, 29.71, 29.63, 29.57, 29.27, 29.22, 26.4, 13.0; HRMS $C_{33}H_{46}INO_4S$ [M+Na] 702.2085, found 702.2096. ***Z*-isomer**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.96 (d, 1H, ArCH=C, J=12.7 Hz), 5.65 (d, 1H, ArC=CH, J=12.7 Hz), 5.01 (s, 2H, OCH_2Ar), 4.05 (q, 2H, OCH_2, J=6.7 Hz).

11-Mercapto-undecyl *E*-3-(4-diethylamino-2-hydroxy-phenyl)propenoate (2). Cinnamate **14a** (230 mg, 0.498 mmol) was dissolved in MeOH (2.5 mL) and this solution was deoxygenated with nitrogen. The solution was cooled to 0 °C and NaSMe (70 mg, 0.99 mmol)[3] was added. Stirring at 0 °C was continued for 1 – 2 h and then the mixture was quenched with satd. aq. NH_4Cl-soln. This mixture was extracted 4 x with CH_2Cl_2 and the combined organic layers were dried ($MgSO_4$), filtered and concentrated to give a yellow solid (140 mg, ~67 %). This crude material was of good purity but may contain traces of the disulfide. A careful column (2:1 hexanes:EtOAc, N_2 as pressure gas) gave virtually disulfide-free product as a yellow solid. m.p. 78 °; λ_{max} (DMF) 374 nm (ε= 35,191 $cm^{-1}M^{-1}$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, 2H, ArCH=C, J=16.0 Hz), 7.30 (d, 2H, Ar-H6, J=8.8 Hz), 7.0 (br s, 1H, OH), 6.40 (d, 2H, ArC=CH, J=16.0 Hz), 6.22 (d, 2H, Ar-H5, J=8.8 Hz), 6.11 (s, 1H, Ar-H3), 4.19 (t, 2H, OCH_2, J=6.3 Hz), 3.33 (q, 4H, NCH_2, J=6.9 Hz), 2.51 (app. q, 2H, $HSCH_2$, J=7.2 Hz), 1.67 (p, 2H, OCH_2CH_2, J=7.6 Hz), 1.54 (p, 2H, SCH_2CH_2, J=6.8 Hz), 1.4 – 1.2 (m, 14H, alkyl), 1.15 (t, 6H, NCH_2CH_3, J=6.88 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.2, 158.1, 151.1, 141.7, 131.2, 112.0, 110.1, 105.1, 98.5, 64.8, 44.8, 34.4, 29.88, 29.67, 29.46, 29.22, 28.77, 26.4, 25.0, 13.1; HRMS (FAB) for $C_{24}H_{39}NO_3S$ [M] 421.2651, found 421.2635.

6-Mercapto-hexyl *E*-3-(4-diethylamino-2-hydroxy-phenyl)propenoate (3). This compound was prepared from cinnamate **14b** (260 mg, 0.64 mmol), MeOH (5 mL) and NaSMe (90 mg, 1.3 mmol)[3] using the same procedure as for **2**. The crude oil was purified by column chromatography (3:1 hexanes:EtOAc) affording 150 mg of a yellow oil. The compound seemed rather unstable and always contained (in addition to unreacted starting material) amounts of coumarin, *Z*-isomer and disulfides, all

of which could not be removed on two different occasions. λ_{max} (DMF) 374 nm (ε= 35,191 $cm^{-1}M^{-1}$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.93 (d, 1H, ArCH=C, J= 16Hz), 7.30 (d, 1H, Ar-H6, J=8.9 Hz), 6.63 (br s, 1H, OH), 6.37 (d, 1H, ArC=CH, J= 16 Hz), 6.22 (dd, 1H, Ar-H5, J_1=8.9 Hz, J_2=1.9 Hz), 6.07 (d, 1H, Ar-H3, J=2.0 Hz), 4.17 (t, 2H, OCH_2, J=5.8 Hz), 3.34 (q, 4H, NCH_2, J=6.88 Hz), 2.50 (app. q, 2H, $HSCH_2$, J=7.4 Hz), 1.7 – 1.55 (m, 4H, alkyl), 1.4 – 1.2 (m, 4H, alkyl), 1.15 (t, 6H, NCH_2CH_3, J=7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.0, 158.0, 151.2, 141.7, 131.3, 112.1, 110.2, 105.4, 98.6, 64.7, 45.0.9, 34.4, 29.2, 28.6, 26.1, 25.1, 13.2 HRMS for $C_{19}H_{29}NO_3S$ [M+Na] 374.1766, found 374.1781.

11-Mercapto-undecyl *E*-3-(4-diethylamino-2-methoxy-phenyl)propenoate (4). This compound was prepared from cinnamate **14c** (198 mg, 0.407 mmol, *E/Z* 13/1), MeOH (5 mL) and NaSMe (57 mg, 0.82 mmol)[3] using the same procedure as for **2**. The resulting yellow oil (173 mg, 95 %) had satisfactory purity. The *E/Z* ratio of the product was 11/1 by NMR. Clearly distinguishable ^1H peaks for the *Z*-isomer will be reported. ***E*-isomer**: λ_{max} (DMF) 376 nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.92 (1, 2H, ArCH=C, J=15.9 Hz), 7.36 (d, 1H, Ar-H6, J=8.7 Hz), 6.32 (d, 1H, ArC=CH, J=15.9 Hz), 6.25 (dd, 1H, Ar-H5, J_1=8.7 Hz, J_2=2.3 Hz), 6.12 (d, 1H, Ar-H3, J=2.3 Hz), 4.18 (t, 2H, OCH_2, J=6.6 Hz), 3.84 (s, 3H, OMe), 3.37 (q, 4H, NCH_2, J=6.9 Hz), 2.48 (app q, 2H, SCH_2, J=7.0 Hz), 1.72 (p, 2H, OCH_2CH_2, J=7.4 Hz), 1.56 (p, 2H, SCH_2CH_2, J=6.3 Hz), 1.3 – 1.20 (m, 14H, alkyl), 1.19 (t, 6H, NCH_2CH_3, J=6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.0, 160.7, 151.0, 141.0, 131.1, 112.4, 111.4, 104.5, 94.1, 64.3, 55.5, 45.0, 34.5, 29.75, 29.56, 29.33, 29.13, 28.64, 26.3, 13.0; HRMS for $C_{25}H_{41}NO_3S$ [M + Na] 458.2699, found 458.2658. ***Z*-isomer**: λ_{max} (DMF) 374 nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.99 (d, 1H, Ar-H6, J=8.9 Hz), 7.20 (d, 1H, ArCH=C, J=12.7 Hz), 5.66 (d, 1H, ArC=CH, J=12.7 Hz), 4.11 (t, 2H, OCH_2), 3.83 (s, 3H, OMe).

11-Mercapto-undecyl *E*-3-(4-diethylamino-2-(4-iodo-phenylmethyloxy)-phenyl)propenoate (5). Cinnamate **14d** (270 mg, 0.4 mmol) was suspended in MeOH (20 mL) and

this mixture was deoxygenated with nitrogen. Then NaSMe (87 mg, 1.2 mmol)[3] was added. Stirring was continued for 3 h and then the mixture was quenched with satd. aq. NH_4Cl-soln. This mixture was extracted with CH_2Cl_2 (3 x) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated to give a yellow oil. NMR analysis revealed that the reaction had only proceeded halfway, presumably because of the very low solubility of the starting material. Therefore this material was resubjected to the same conditions as described above with 2:1 MeOH:*i*-PrOH as solvent. This led to a quick reaction and after usual work-up and column chromatography (6:1 hexanes:EtOAc) the product was obtained as a yellow oily solid (200 mg, 79 %) of satisfactory purity. The *E/Z* ratio of the product was 11/1. Clearly distinguishable ^1H peaks for the *Z*-isomer will be reported. λ_{max} (DMF) 374 nm; (ε= 27,349 $cm^{-1}M^{-1}$). ***E*-isomer:** ^1H NMR ($CDCl_3$, 300 MHz) δ 7.96 (d, 1H, ArCH=C, J=15.9 Hz), 7.69 (d, 2H, ICH, J=8.2 Hz), 7.37 (d, 1H, Ar-H6, J=8.8 Hz), 7.18 (d, 2H, ICHCH, J=8.2 Hz), 6.30 (d, 1H, ArC=CH, J=15.9 Hz), 6.25 (dd, 1H, Ar-H5, J_1=8.8 Hz, J_2=2.2 Hz), 6.05 (d, 1H, Ar-H3, J=2.2 Hz), 5.08 (s, 2H, OCH_2Ar), 4.16 (t, 2H, OCH_2, J=6.7 Hz), 3.33 (q, 4H, NCH_2, J=6.9 Hz), 2.51 (q, 2H, $HSCH_2$, J=7.2 Hz), 1.66 (m, 2H, OCH_2CH_2), 1.56 (m, 2H, SCH_2CH_2), 1.3 – 1.20 (m, 14H, alkyl), 1.15 (t, 6H, NCH_2CH_3, J=6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.9, 159.3, 150.9, 140.6, 138.1, 137.2, 130.8, 129.3, 112.8, 111.8, 105.2, 96.1, 93.7, 70.0, 64.5, 45.0, 34.4, 29.89, 29.69, 29.46, 29.24, 28.78, 26.4, 25.0, 13.0; HRMS $C_{31}H_{44}INO_3S$ [M+Na] 660.1979, found 660.2013. ***Z*-isomer**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.96 (d, 1H, ArCH=C, J=12.7 Hz), 5.65 (d, 1H, ArC=CH, J=12.7 Hz), 5.01 (s, 2H, OCH_2Ar), 4.05 (q, 2H, OCH_2, J=6.7 Hz).

Ethyl *E*-3-(4-diethylamino-2-hydroxy-phenyl)propenoate (8). Ethyl (triphenyl-λ^5-phosphanylidene)acetate (2.09 g, 5.5 mmol) and 4-diethylaminosalicaldehyde (1 g, 5 mmol) were stirred in benzene (5 mL) in the dark at room temperature for 20 h. Benzene was removed by concentration and the residue applied to a silica column. The product was eluted with 2:1

EtOAc:hexanes and then recrystallized from a hexanes/EtOAc mixture to afford the product as a yellow solid (1.01 g, 78 %). m.p. 154 °C; λ_{max} (DMF) 376 nm (ε= 35,191 $cm^{-1}M^{-1}$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.93 (d, 1H, ArCH=C, J=15.7 Hz), 7.31 (d, 1H, Ar-H6, J=8.9 Hz), 6.4 (br s, 1H, OH), 6.38 (d, 1H, ArC=CH, J=15.7 Hz), 6.24 (dd, 1H, Ar-H5, J_1=8.9 Hz, J_2=2.4 Hz), 6.06 (d, 1H, Ar-H3, J=2.4 Hz), 4.25 (q, 2H, OCH_2, J=7.1 Hz), 3.34 (q, 4H, NCH_2, J=7.1 Hz), 1.32 (t, 2H, OCH_2CH_2, J=7.1 Hz), 1.16 (t, 6H, NCH_2CH_3, J=7.1 Hz); ^{13}C NMR ($CDCl_3$ / d^6-DMSO, 75 MHz) δ 167.6, 158.0, 149.8, 140.4, 129.7, 110.3, 108.7, 103.3, 97.1, 58.7, 43.6, 13.8, 12.0; HRMS for $C_{15}H_{21}NO_3$ [M + Na] 286.1436, found 286.1420; Anal. calc. for $C_{15}H_{21}NO_3$ (%): C 68.42, H 8.04, N 5.32, found: C 68.36, H 7.98, N 5.27.

7-Diethylamino-chromen-2-one (1). Ethyl (triphenyl-λ^5-phosphanylidene)acetate (3.45 g, 9.9 mmol) and 4-diethylaminosalicaldehyde (1.5 g, 7.75 mmol) were heated at 180 ºC for 1 h. The mixture was cooled and then purified by column chromatography (2:1 hexanes:EtOAc). The product was collected and recrystallized from *i*-Pr_2O to give an orange solid (0.88 g, 52 %). m.p. 84 °C; λ_{max} (DMF) 380 nm (ε= 25,339 $cm^{-1}M^{-1}$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50 (d, 1H, ArCH=C, J=10.6 Hz), 7.24 (d, 1H, Ar-H6, J=8.8 Hz), 6.55 (dd, 1H, Ar-H5, J_1=8.8 Hz, J_2=2.5 Hz), 6.48 (d, 1H, Ar-H3, J=2.5 Hz), 6.00 (d, 1H, ArC=CH, J=10.6 Hz), 3.38 (q, 4H, NCH_2, J=7.1 Hz), 1.22 (t, 6H, NCH_2CH_3, J=7.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.6, 157.1, 151.1, 144.1, 129.2, 109.4, 109.1, 108.6, 97.8, 45.2, 12.8; HRMS for $C_{13}H_{15}NO_2$ [M+Na] 240.0995, found 240.0981. NMR data matched with previously reported literature data.[4]

2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethanethiol (6). This compound was prepared from tris(ethyleneglycol)monomethyl ether according to a 3-step patent procedure.[5] The crude orange oil was subjected to vacuum-distillation and the lowest boiling fraction was collected to give the product as a clear colorless liquid. No NMR or MS data for this compound were reported in the patent. ^{1}H

NMR ($CDCl_3$, 300 MHz) δ 3.66 – 3.53 (m, 10H), 3.37 (s, 3H, OMe), 2.7 (q, 2H, SCH_2), 1.62 (t, 1H, SH, J=8.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 73.1, 72.2, 70.8-70.4, 59.2, 24.5; HRMS (as disulfide) for $C_{14}H_{30}O_6S_2$ [M+Na] 381.1376, found 381.1376.

Ethyl 3-(4-Diethylamino-2-methoxy-phenyl)propenoate (9a,b). A mixture of ethyl (triphenyl-λ^5-phosphanylidene)acetate (470 mg, 1.24 mmol) and 4-diethylamino-2-methoxy-benzaldehyde (230 mg, 1.1 mmol) were heated at 160 °C for 1 h. The mixture was then cooled and subjected to careful column chromatography (2:1 hexanes:EtOAc) to give the *E*-isomer (200 mg, 60 %) and the *Z*-isomer (10 mg, 6 %, contained ca. 10% of the E-isomer) as yellow oils. ***E*-isomer 9a**: λ_{max} (DMF) 376 nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.92 (d, 1H, ArCH=C, J=15.9 Hz), 7.34 (d, 1H, Ar-H6, J=9 Hz), 6.32 (d, 1H, ArC=CH, J=15.9 Hz), 6.25 (dd, 1H, Ar-H5, J_1=9 Hz, J_2=2.3 Hz), 6.10 (d, 1H, Ar-H3, J=2.3 Hz), 4.21 (q, 2H, OCH_2, J=7.2 Hz), 3.84 (s, 3H, OMe), 3.36 (q, 4H, NCH_2, J=7.2 Hz), 1.31 (t, 3H, OCH_2CH_3, J=7.2 Hz), 1.18 (t, 6H, NCH_2CH_3, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.9, 159.7, 150.1, 140.1, 130.3, 111.8, 110.7, 103.9, 93.6, 59.8, 55.2, 44.7, 14.8, 12.9; HRMS for $C_{16}H_{23}NO_3$ [M+Na] 300.1570, found 300.1565. ***Z*-isomer 9b**: λ_{max} (DMF) 374 nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.96 (d, 1H, Ar-H6, J=8.8 Hz), 7.17 (d, 1H, ArCH=C, J=12.7 Hz), 6.25 (dd, 1H, Ar-H5, J_1=8.8 Hz, J_2=2.4 Hz), 6.08 (d, 1H, Ar-H3, J=2.4 Hz), 5.58 (d, 1H, ArC=CH, J=12.7 Hz), 4.16 (q, 2H, OCH_2, J=7.1 Hz), 3.82 (s, 3H, OMe), 3.39 (q, 4H, NCH_2, J=7.2 Hz), 1.31 (t, 3H, OCH_2CH_3, J=7.1 Hz), 1.18 (t, 6H, NCH_2CH_3, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.5, 159.9, 150.8, 139.3, 133.1, 113.8, 111.7, 103.8, 93.9, 60.0, 55.7, 44.9, 14.7, 13.1; HRMS for $C_{16}H_{23}NO_3$ [M+Na] 300.1570, found 300.1576.

SELECTED NMR SPECTRA

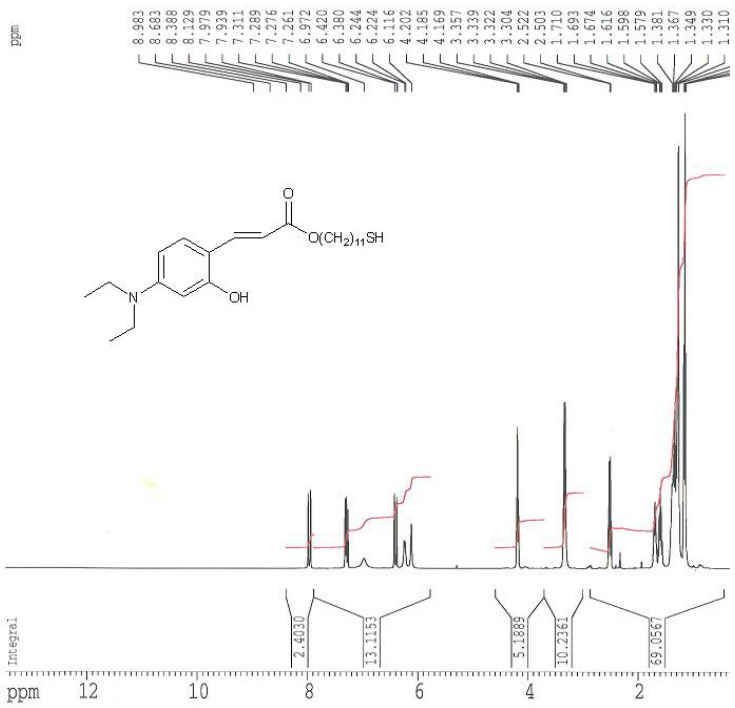


Figure S1. ^{1}H-NMR spectrum of compound **2** in $CDCl_3$**.**

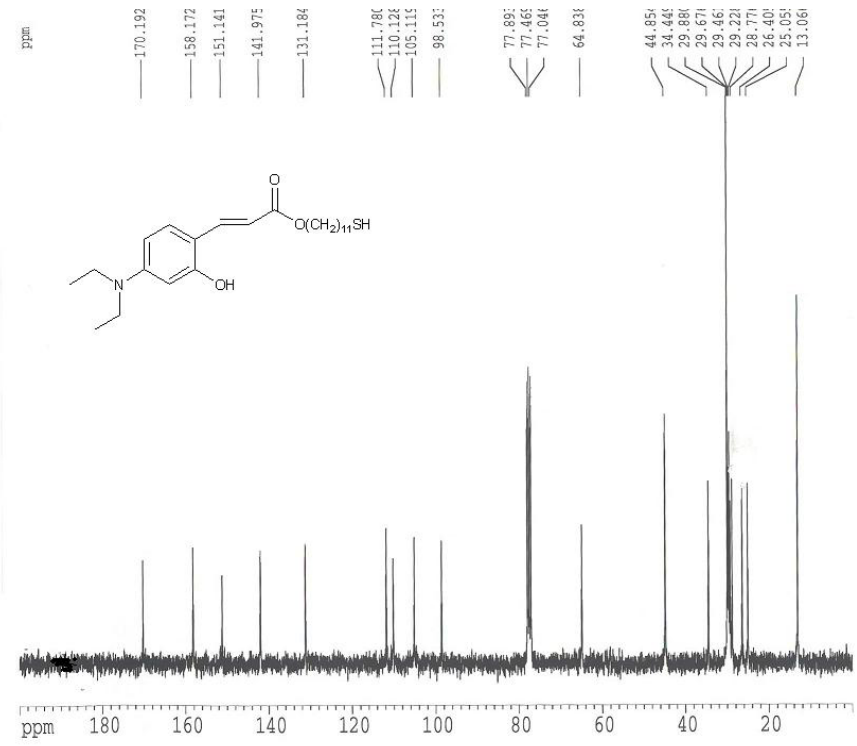


Figure S2. ^{13}C-NMR spectrum of compound **2** in $CDCl_3$**.**

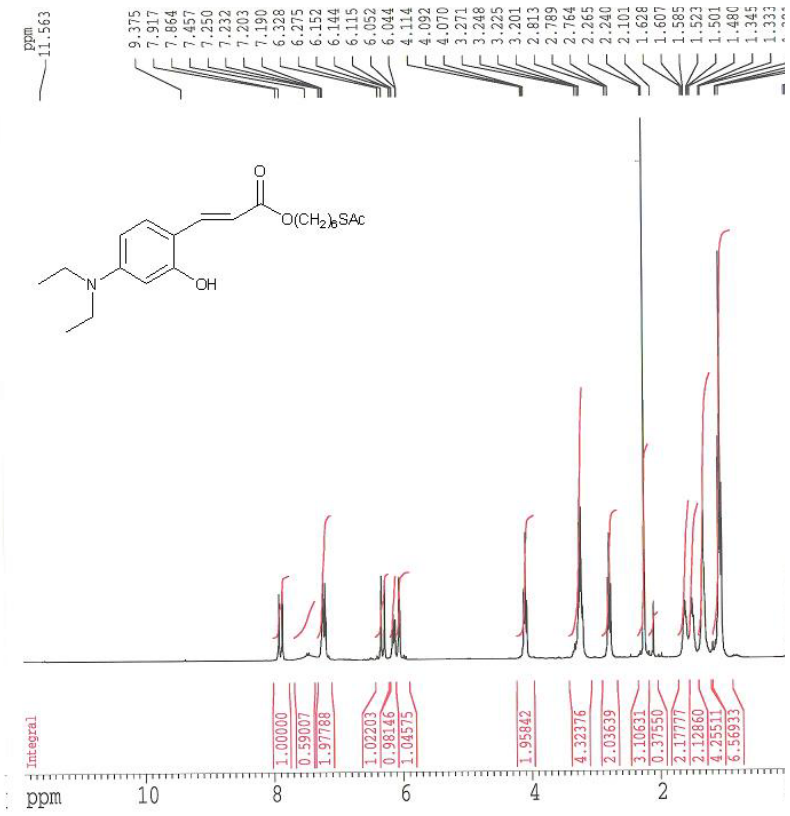


Figure S3. ^{1}H-NMR spectrum of compound **14b** in $CDCl_3$**.**

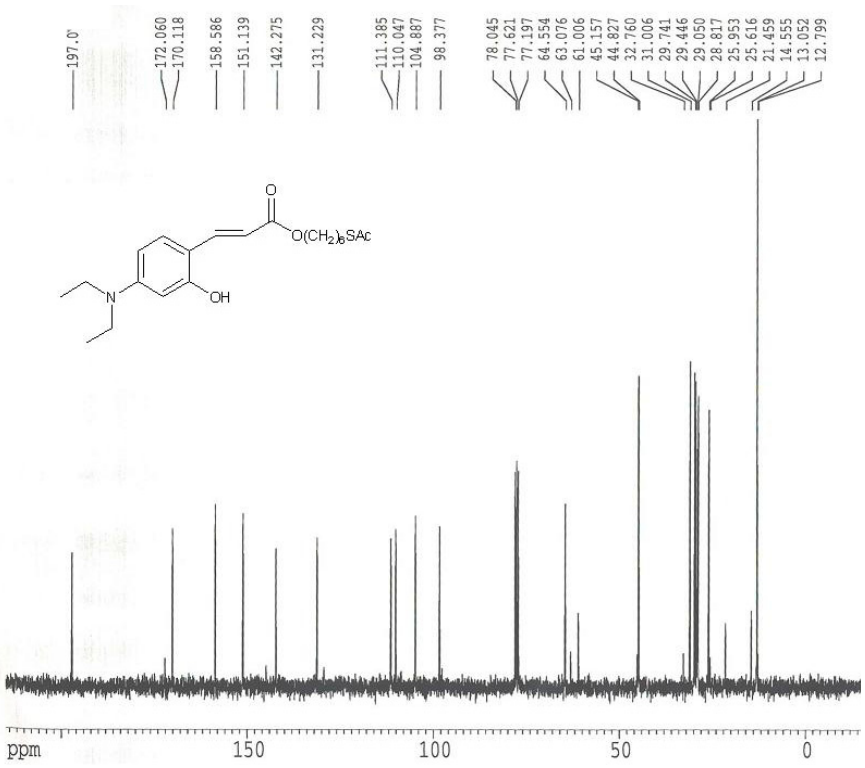


Figure S4. ^{13}C-NMR spectrum of compound **14b** in $CDCl_3$**.**

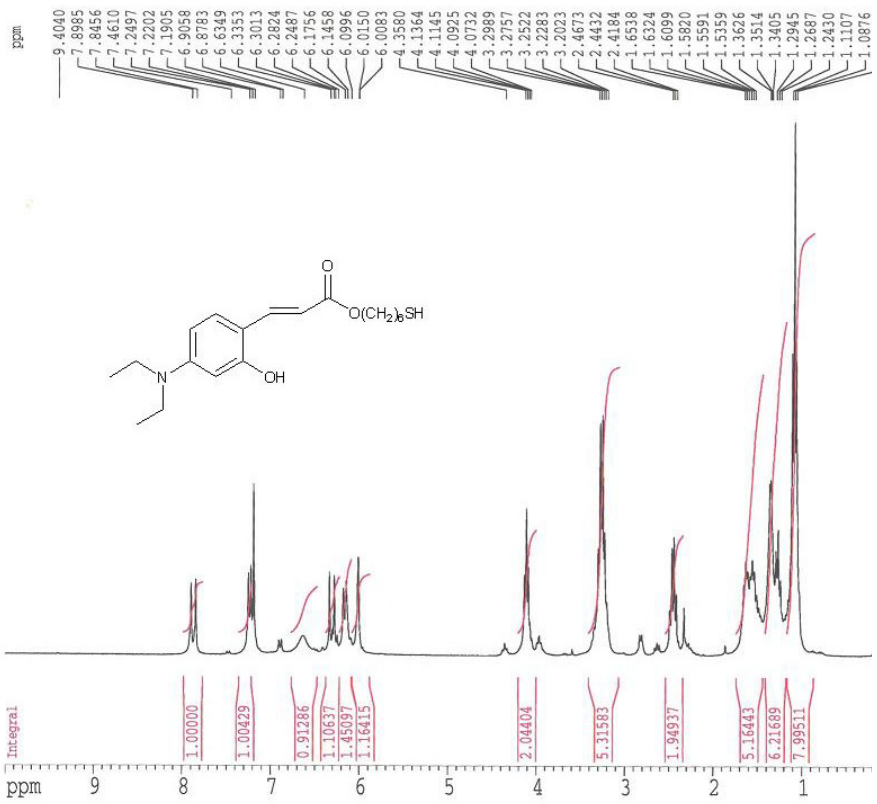


Figure S5. ^{1}H-NMR spectrum of compound **3** in $CDCl_3$. Amounts of starting material **14b** and coumarin **1** are visible. The compound seemed rather unstable and could not be purified further on two different occasions.

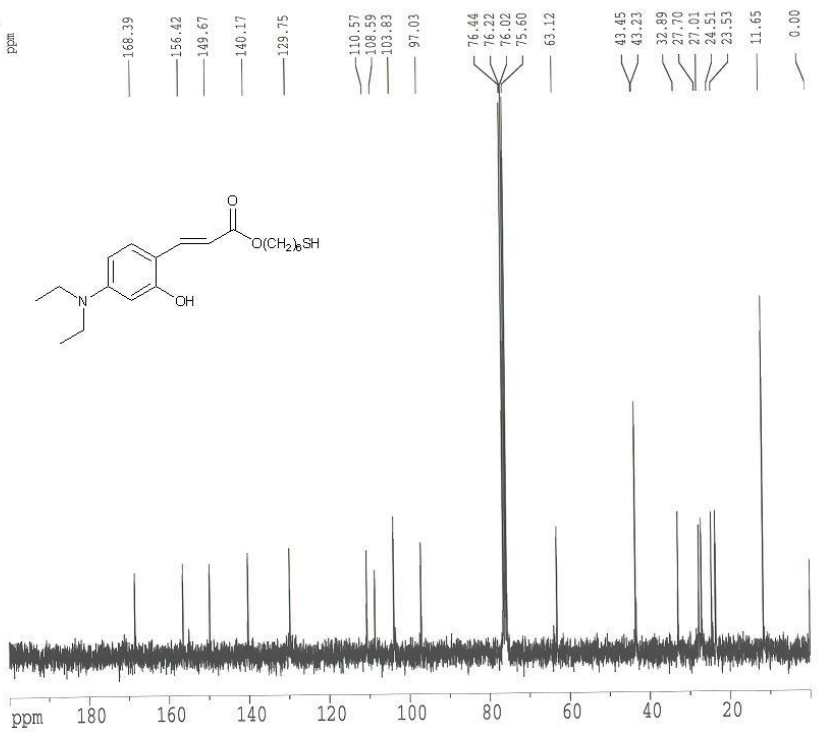


Figure S6. ^{13}C-NMR spectrum of compound **3** in $CDCl_3$. Compound could not be purified further.

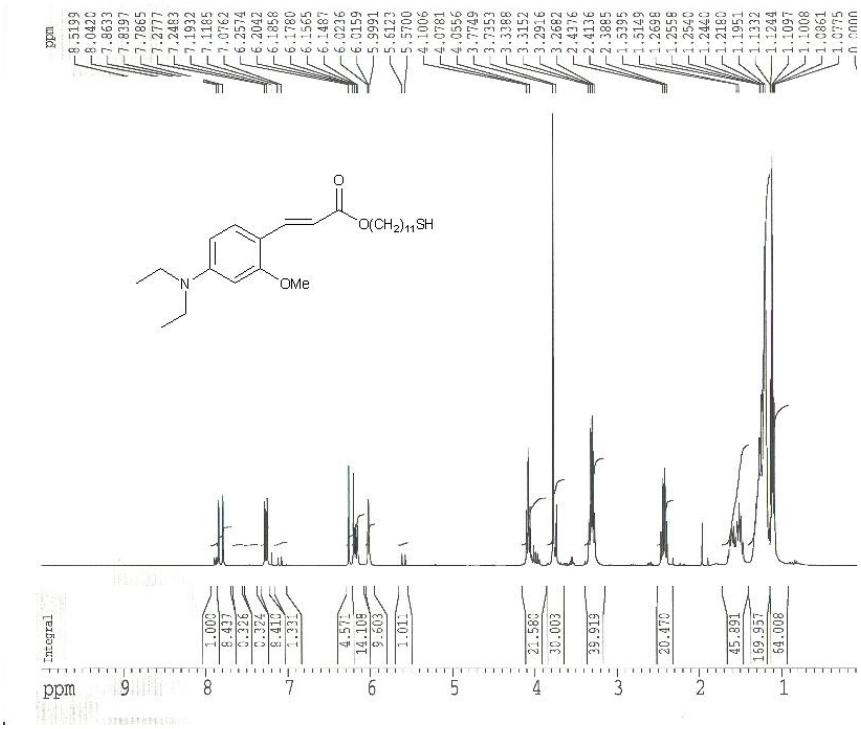


Figure S7. ^{1}H-NMR spectrum of compound **4** in $CDCl_3$. The inseparable *Z*-isomer is visible.

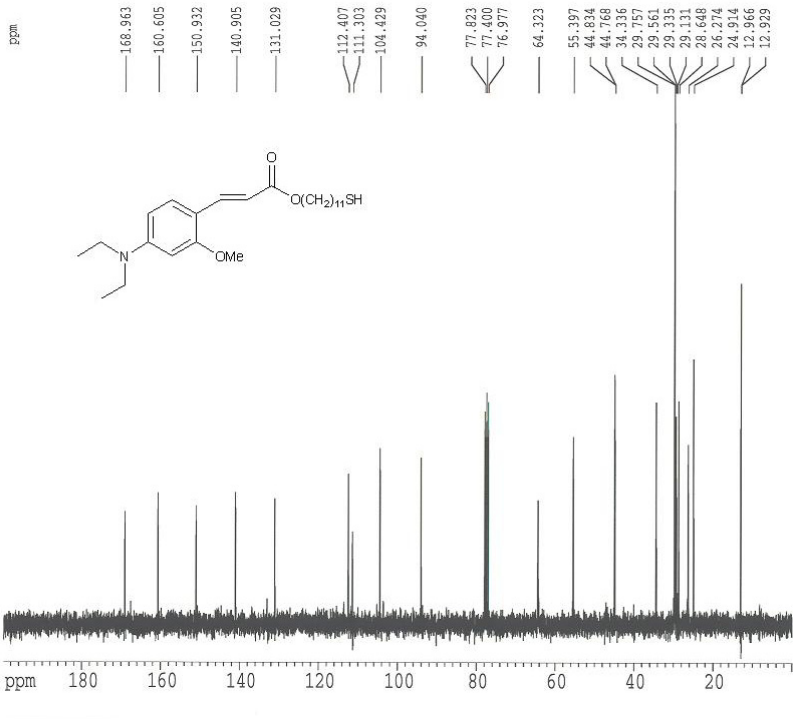


Figure S8. ^{13}C-NMR spectrum of compound **4** in $CDCl_3$. The inseparable *Z*-isomer is visible.

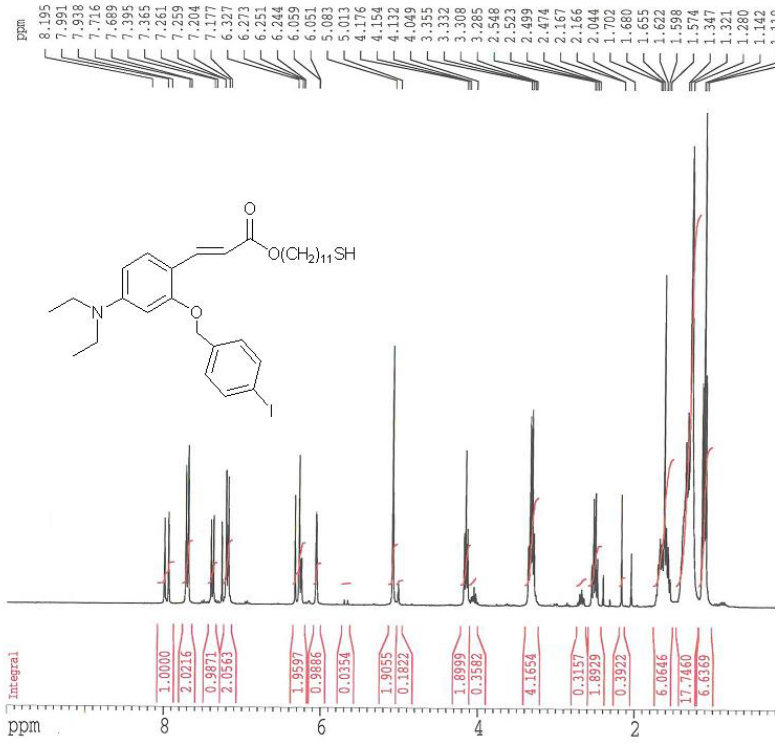


Figure S9. ^{1}H-NMR spectrum of compound **5** in $CDCl_3$. The inseparable *Z*-isomer is visible.

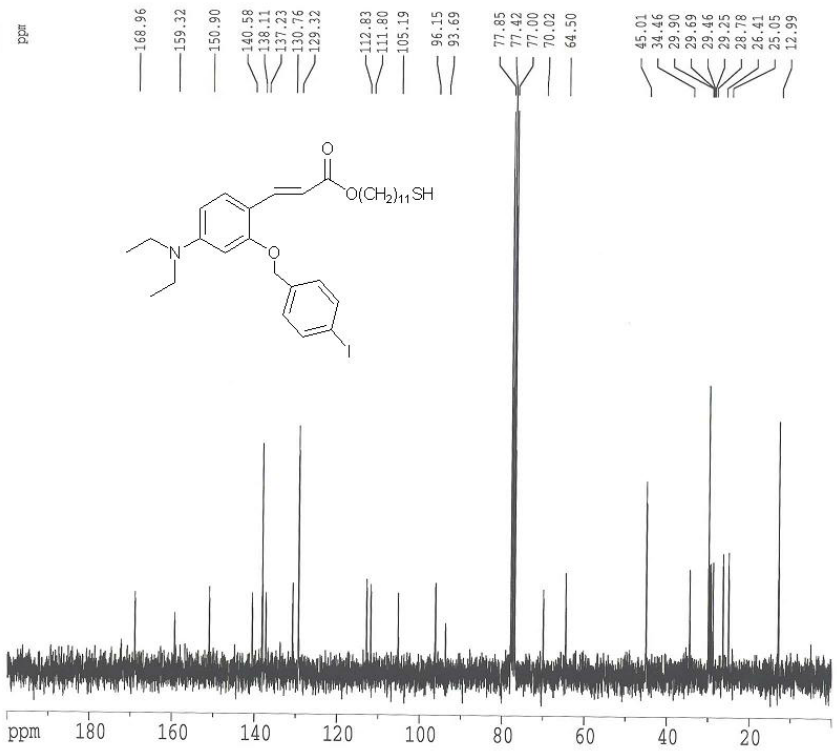


Figure S10. ^{13}C-NMR spectrum of compound **5** in $CDCl_3$. The inseparable *Z*-isomer is visible.

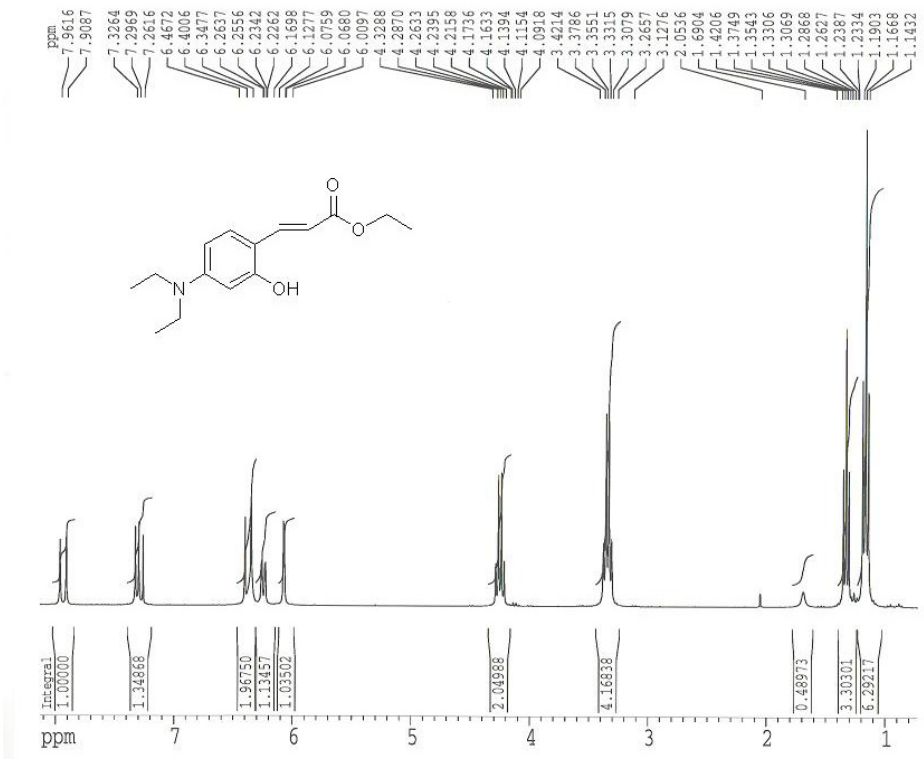


Figure S11. ^{1}H-NMR spectrum of compound **8** in $CDCl_3/d_6$-DMSO.

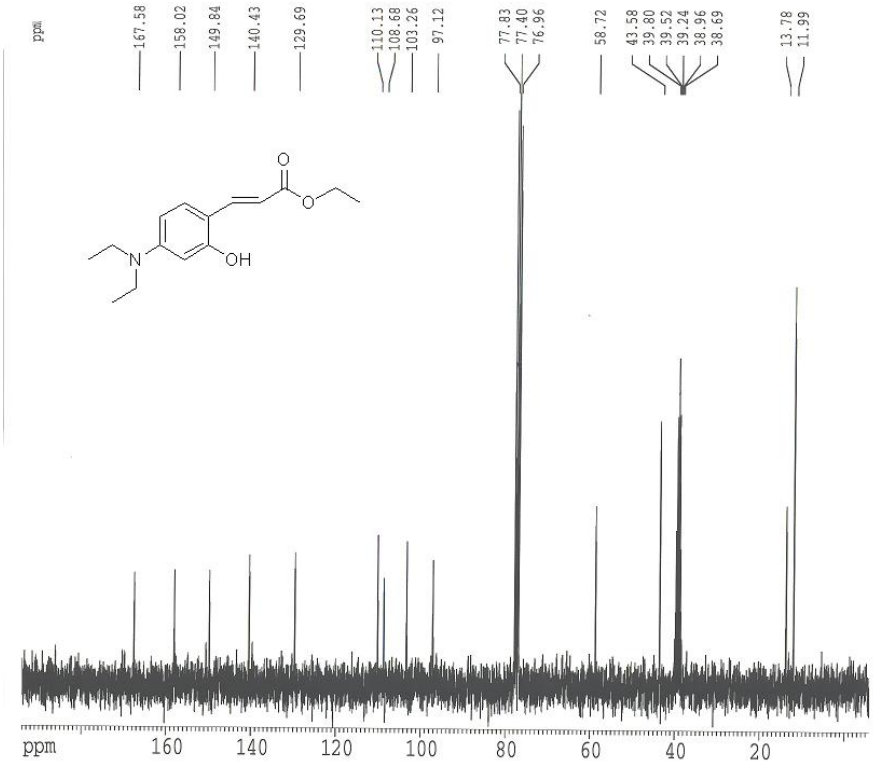


Figure S12. ^{13}C-NMR spectrum of compound **8** in $CDCl_3/d_6$-DMSO.

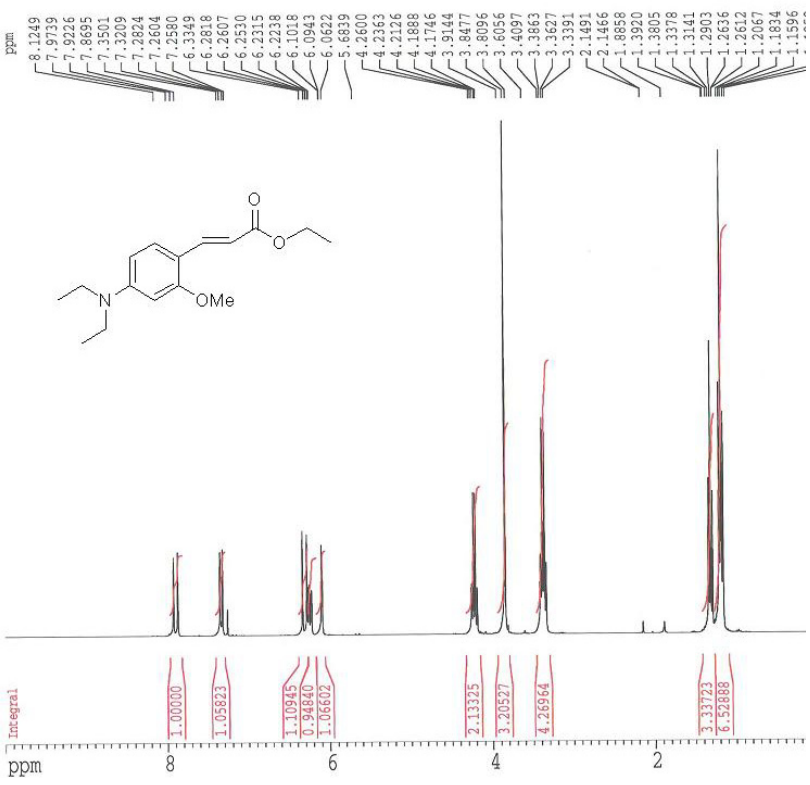


Figure S13. ^{1}H-NMR spectrum of compound **9a** in $CDCl_3$.

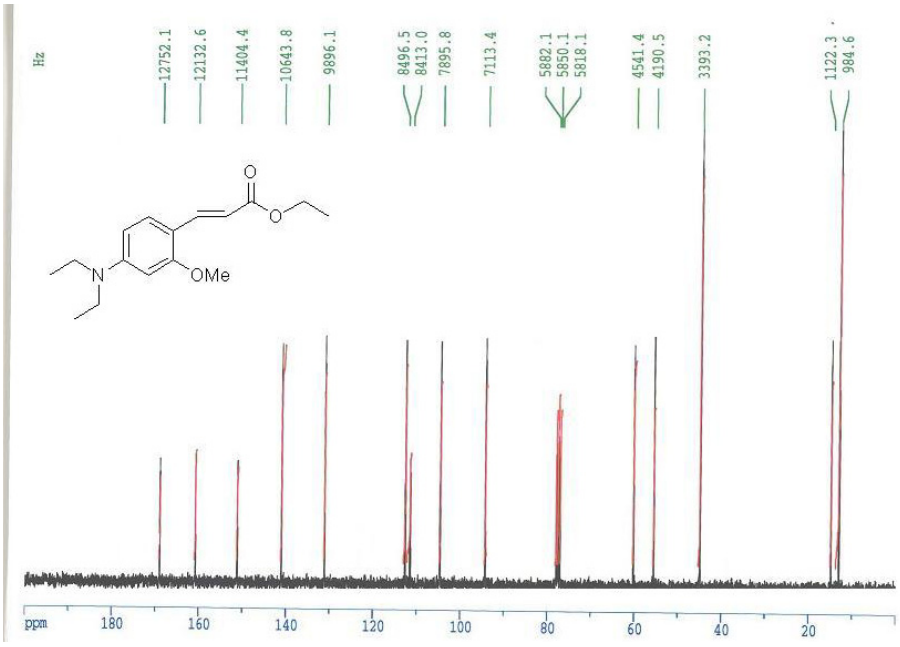


Figure S14. ^{13}C-NMR spectrum of compound **9a** in $CDCl_3$.

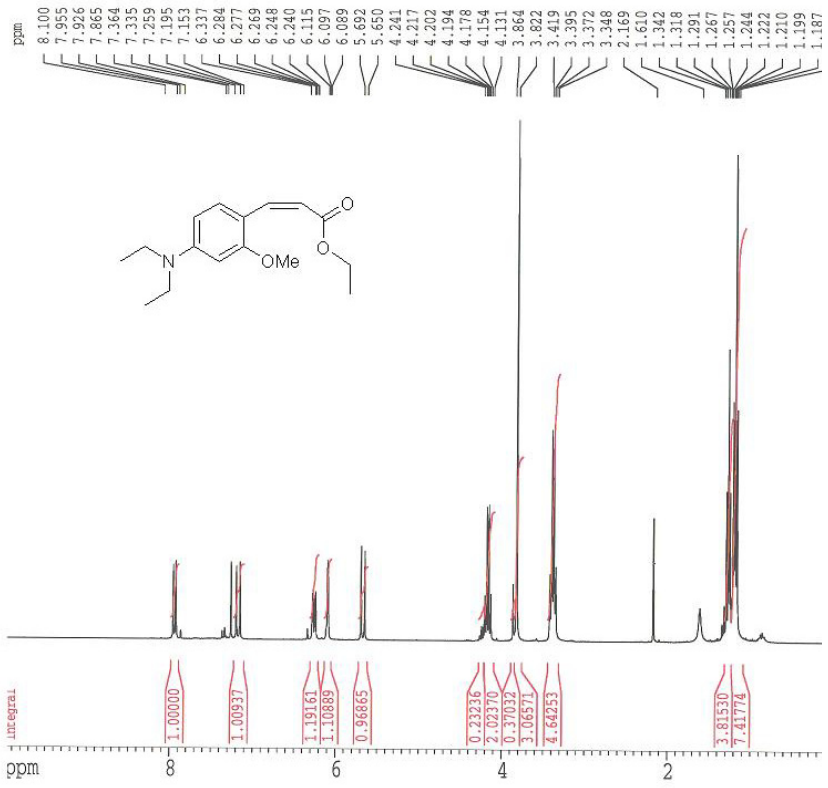


Figure S15. ^{1}H-NMR spectrum of compound **9b** in $CDCl_3$. Traces of *E*-isomer **9a** are visible.

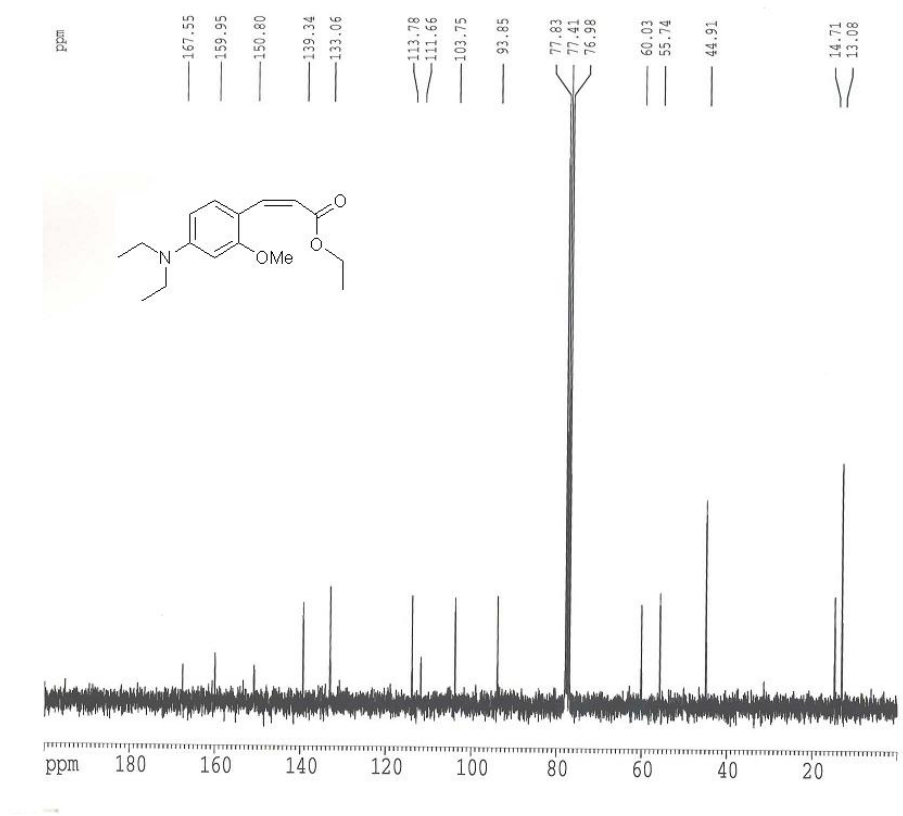


Figure S16. ^{13}C-NMR spectrum of compound **9b** in $CDCl_3$.

Figure S17. ^{1}H-NMR spectrum of compound **6** in $CDCl_3$.

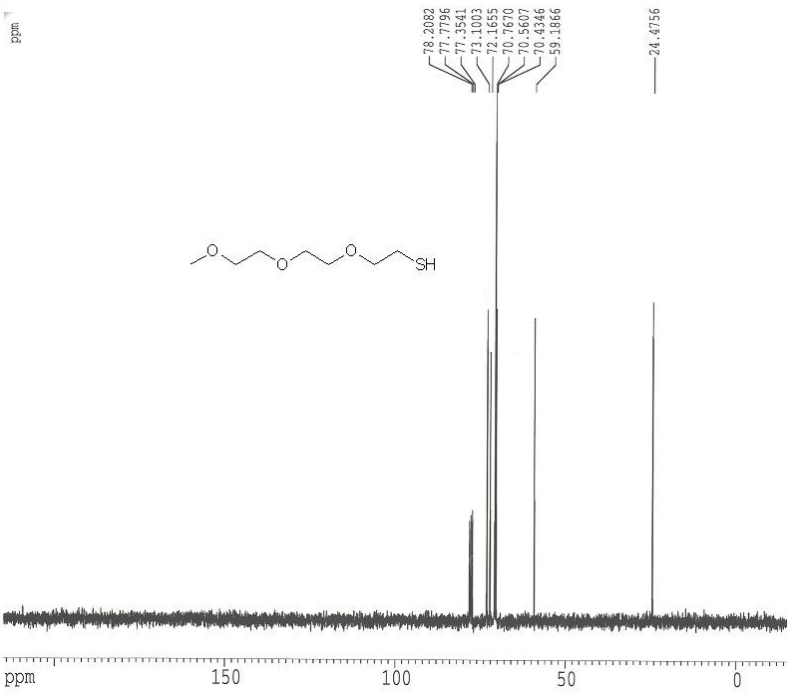


Figure S18. ^{13}C-NMR spectrum of compound **6** in $CDCl_3$.

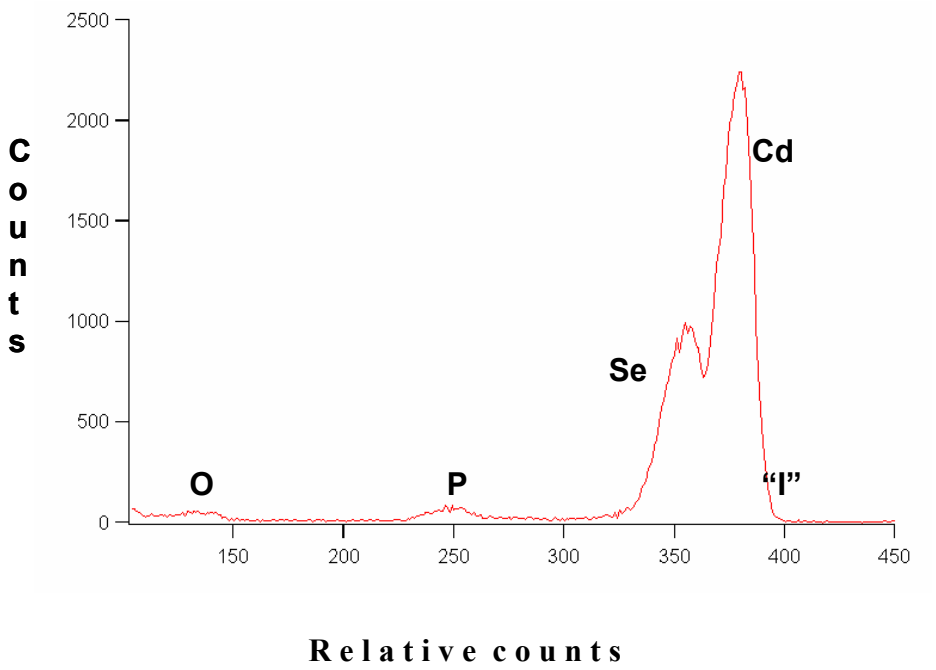


Figure S19. Rutherford Back Scattering spectrum of Type V NC.[6] Clearly visible are the signals for P (remaining TOPO ligands) and the Cd and Se signals. The I signal can be observed as a small shoulder on the Cd peak but was too small to be useful. The P signal also contains traces of S signal but it can still be used for reliable approximation of phosphorous content.

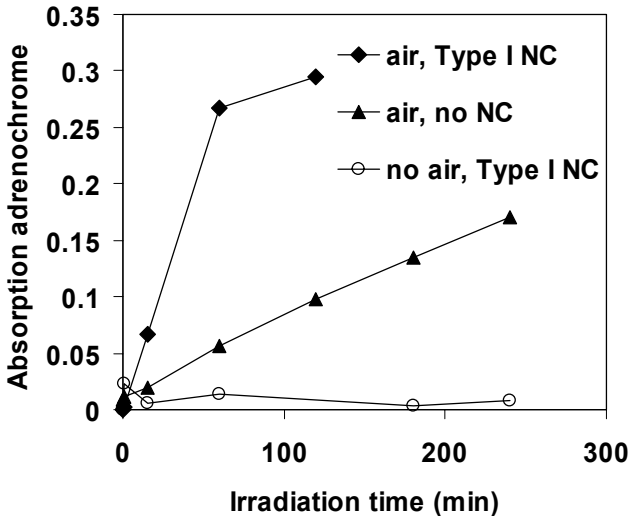


Figure S20. Formation of adrenochrome during irradiations of 100 μM epinephrine in DMF at 374 nm with and without Type I NC or air present

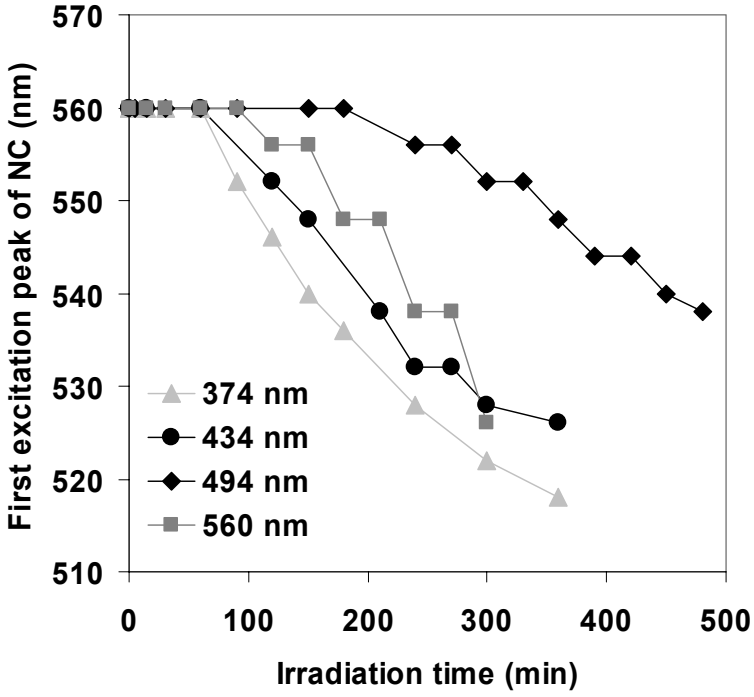


Figure S21. Decomposition of Type I NC during aerobic irradiation at different wavelengths.

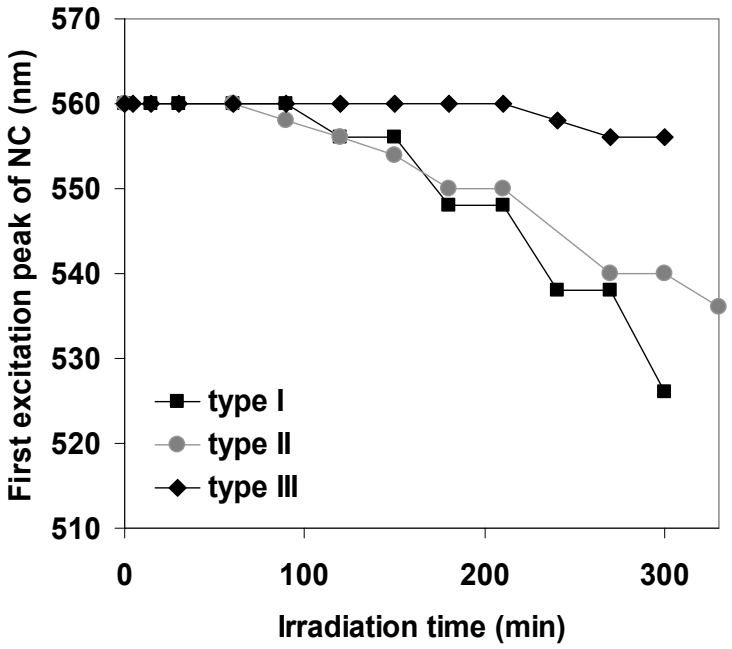


Figure S22. Aerobic irradiation at 560 nm of NC covered with a variety of structurally different cinnamate ligands.

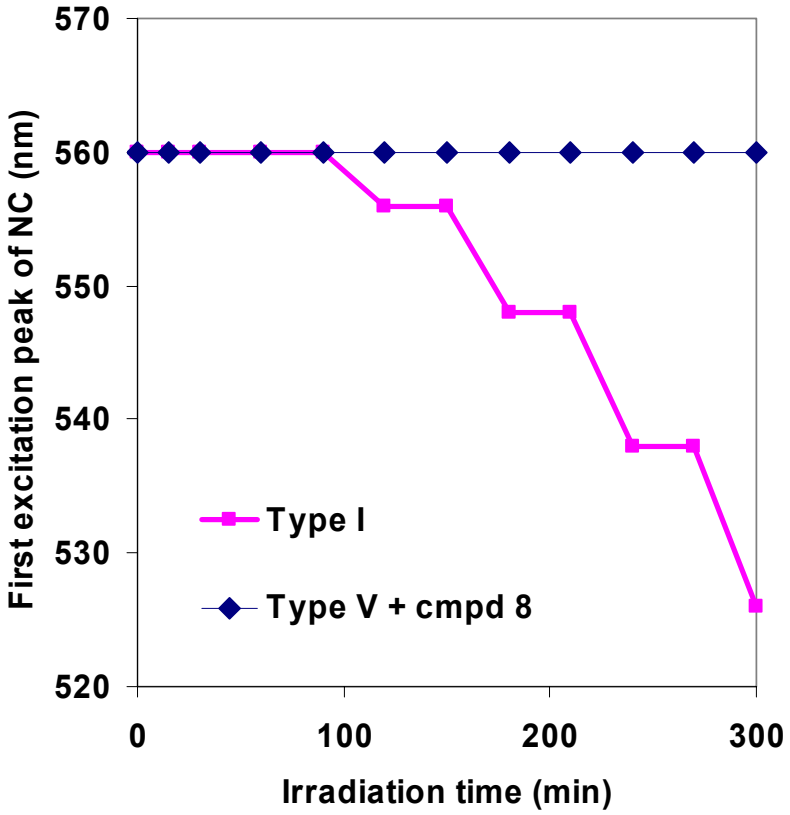


Figure S23. Aerobic irradiation at 560 nm of Type I NC, and of Type V NC in the presence of 7.5 μM of compound **8**. This particular concentration of compound **8** represents the calculated amount of cinnamates present in the used solution of Type I, thereby providing a fair comparison between the two experiments.

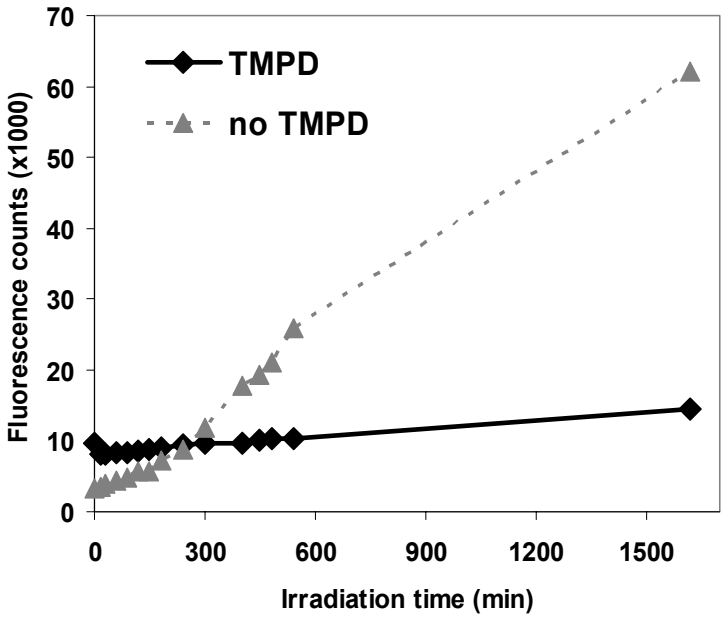


Figure S24. Coumarin formation during aerobic irradiation at 560 nm of Type I NC in DMF with and without 1 mM TMPD present.

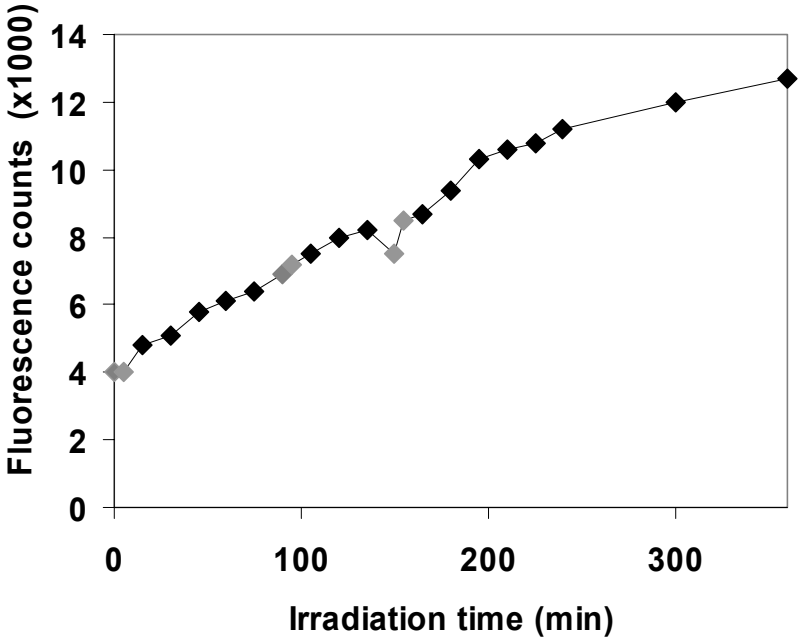


Figure S25. Coumarin formation during 'flash photolysis' of Type I NC. Between two time points, indicated by grey points, the 560 nm light was turned on. At all other time points, it was turned off.

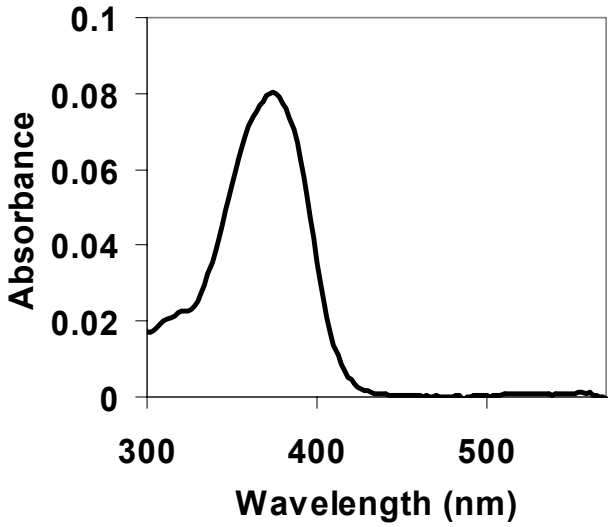


Figure S26. Typical UV-visible absorption spectrum of filtrate after O_2-free irradiation of Type II NC at 560 nm and subsequent separation of NC by size-exclusion membrane centrifugation.

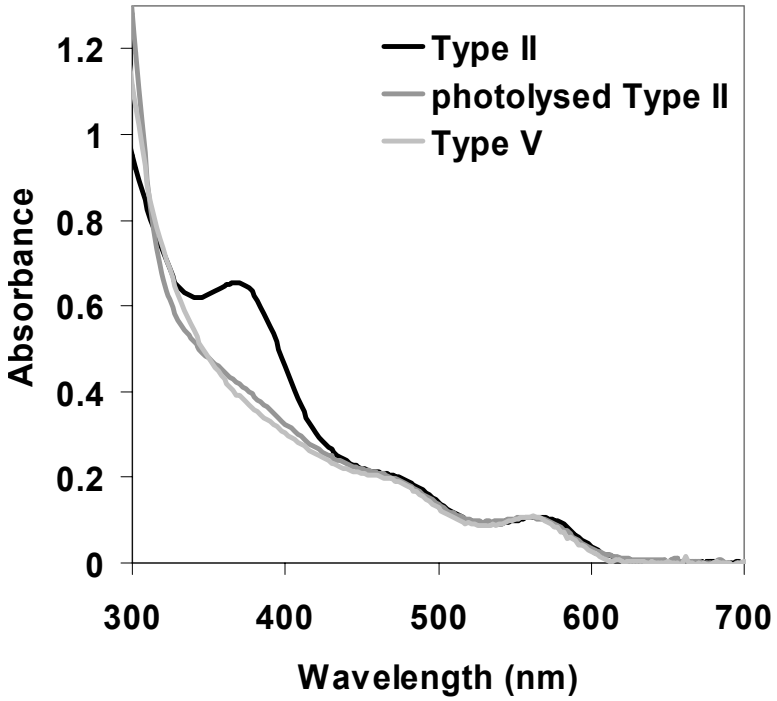


Figure S27. Typical UV-visible absorption spectrum of reconstituted NC in DMF after O_2-free irradiation of Type II NC at 560 nm and subsequent separation of NC by size-exclusion membrane centrifugation. For reference, the normalized UV-visible absorption spectrum of Type V and non-photolyzed Type II NC are shown.

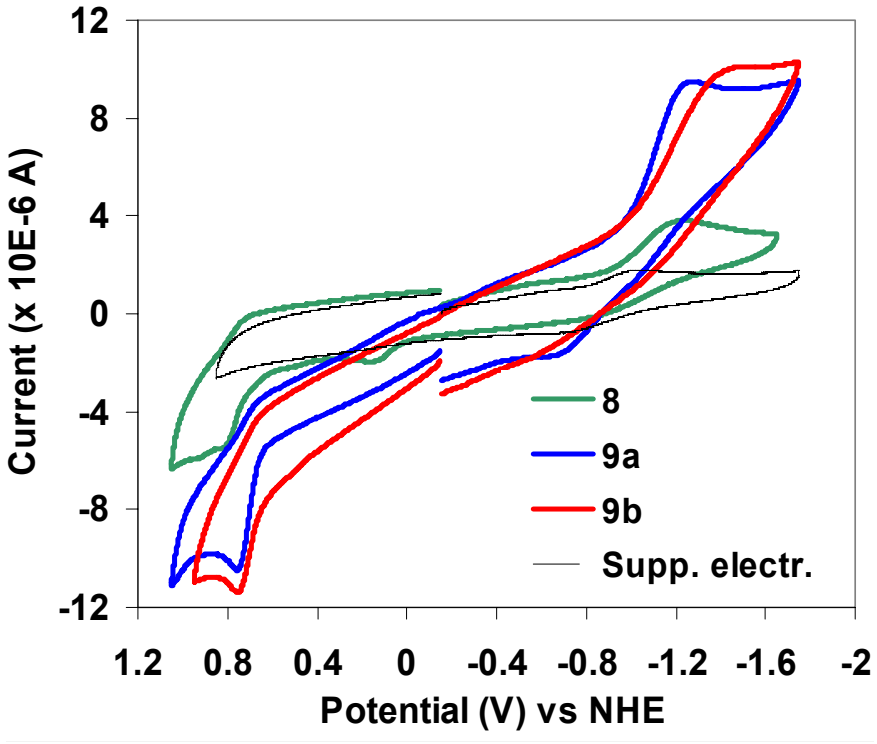


Figure S28. Cyclic voltammograms of cinnamates **8** and **9a,b** in dry, deoxygenated DMF; concentrations of substrate and supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate) were 0.4 – 0.75 mM and 50 mM respectively (scan rate=100 mV/s ; initial scan direction: negative).

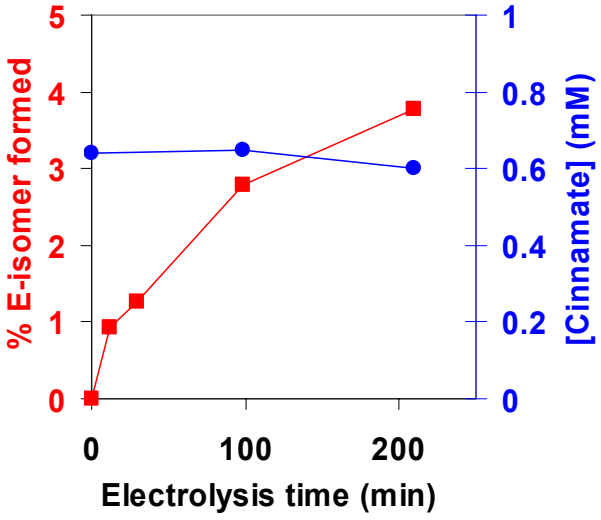


Figure S29. Percentage formation of *E*-isomer **9a** (red squares) and total cinnamate concentration (**9a** + **9b**, blue circles) during bulk electrolysis of **9b** at –1.5 V in DMF in the dark.

REFERENCES

[1] Brown, J. M.; Ramsden, J. A. *J. Chem. Soc. Chem. Comm*. **1996**, *18*, 2117.

[2] Kumar, P.; Bhatia, D.; Rastogi, R. C.; Gupta, K. C. *Bioorg. Med. Chem. Lett*. **1996**, *6*, 683.

[3] Wallace, O. B.; Springer, D. M. *Tetrahedron Lett*. **1998**, *39*, 2693.

[4] Yufit, D. S.; Kirpichenok, M. A.; Struchkov, Yu. T.; Karandashova, L. A.; Grandberg, I. I. *Bull. Acad. Sci. USSR Div. Chem. Sci.(Engl. Transl.)* **1991**, *40*, 702.

[5] Di Domenico, R.; Castoldi, D.; Spinelli, S.; Tofanetti, O.; Tognella, S.; Gandolfi, C. A. *Eur. Patent* 287042, **1988**.

[6] Taylor, J.; Kippeny, T.; Rosenthal, S. J. *J. Clust. Sci*. **2001**, *12*, 571