Mechanistic Insight into the Photocontrolled Cationic Polymerization of Vinyl Ethers

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Supporting Information

Experimental Procedures

General Reagent Information

All polymerizations were set up in an Unilab MBraun glovebox with a nitrogen atmosphere and irradiated with blue LED light under nitrogen atmosphere outside the glovebox. Isobutyl vinyl ether (IBVE) (99%, TCI), ethyl vinyl ether (EVE) (99%, Sigma Aldrich), 2-chloroethyl vinyl ether (Cl-EVE) (97%, TCI), *n*-propyl vinyl ether (PVE) (99%, Sigma Aldrich), and *n*-butyl vinyl ether (BVE) (98%, Sigma Aldrich) were dried over calcium hydride (CaH_2) (ACROS organics, 93% extra pure, 0–2 mm grain size) for 12 h and distilled under nitrogen and degassed by three freeze-pump-thaw cycles or by vigorously sparging with nitrogen for 30 min. Ethanethiol (97%, Alfa Aesar) and carbon disulfide (99.9+%, Alfa Aesar) were distilled before use. 2.0 M HCl in diethylether (Sigma Aldrich) and sodium hydride (60%, dispersion in mineral oil, Sigma Aldrich) were used as received. Sodium *N,N*-diethylcarbamate trihydrate (98%, Alfa Aesar) was azeotropically dried with toluene. Dichloromethane (DCM), acetonitrile (MeCN), diethylether (Et_2O), tetrahydrofuran (THF), benzene (PhH), and toluene (PhMe) were purchased from J.T. Baker and were degassed by vigorous purging with argon for 2 h, followed by passing through two packed columns of neutral alumina under argon pressure. Nitromethane (Sigma Aldrich) was distilled over CaH_2. All dried solvents were degassed for 20 min before being transferred into the glovebox. 2,4,6-Triphenylpyrylium tetrafluoroborate (98%, Alfa Aesar) was used as received. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F-254), using UV light as the visualizing agent and an acidic solution of p-anisaldehyde and heat or $KMnO_4$ and heat as developing agents. Flash silica gel chromatography was performed using E. Merck silica gel (60, particle size 0.040–0.063 mm).

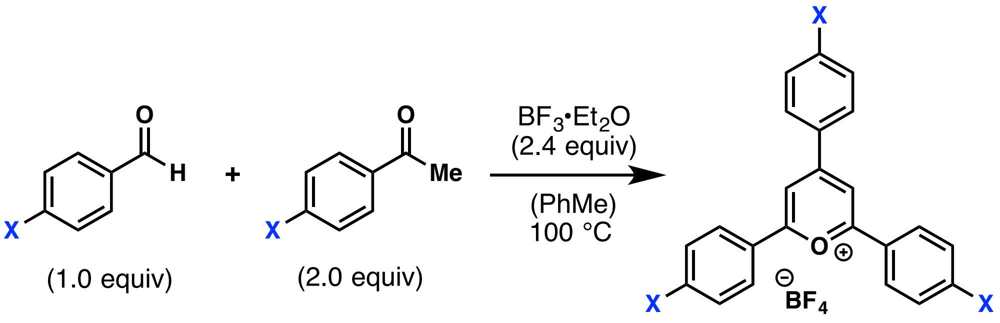
General Analytical Information

All polymer samples were analyzed using a Tosoh EcoSec HLC 8320GPC system with two SuperHM-M columns in series at a flow rate of 0.350 mL/min. THF was used as the eluent and all number-average molecular weights (M_n), weight-average molecular weights (M_w), and dispersities ($Đ$) for poly(vinyl ether)s were calculated from refractive index chromatograms against TSKgel polystyrene standards. Nuclear magnetic resonance (NMR) spectra were recorded on a Mercury 300 MHz, a Varian 400 MHz, a Bruker 500 MHz, or a Varian 600 MHz instrument. Time-resolved fluorescence data were taken using 440 nm pulsed excitation (Becker&Hickl BDL-SMN-440 pulsed diode laser with ~100 ps FWHM pulsewidth) and a Becker & Hickl SPC-830 Time-Correlated Single Photon Counting (TCSPC) card (Becker & Hickl GmbH, Berlin, Germany). Fluorescence was detected by a R3809U-50 microchannel plate photomultiplier tube with a 25 ps transit time spread (Hamamatsu, Bridgewater, NJ). Fluorescence decay curves were collected from samples in 1 cm path-length quartz cuvettes at 90 degrees through Glan-Thompson polarizer set at the magic angle (54.7 degrees) relative to the excitation beam and a 480/50 bandpass filter (Chroma Technology, Bellows Falls, VT). ESR spectra were recorded on a continuous wave X-band Brüker ElexSys E500 EPR spectrometer. UV-Visible spectra were recorded on an Agilent 8453 UV-Vis spectrometer. HRMS data were obtained on a Thermo Fisher Scientific Exactive series DART Mass Spectrometer.

General Reaction Setup

Irradiation of photochemical reactions was done using blue diode led® BLAZE™ lights (450 nm, 2.88 W/ft) or a 9 W Kobi Electric (460–470 nm) bulb. For light intensity modulation, Rangers® CLARITY series full neutral density filters ND2 (50% transmission) and ND4 (25% transmission) were used.

Synthesis of Pyrylium Photocatalysts



S1a: X = OMe
S1c: X = Me
S1d: X = Br

S2a: X = OMe
S2c: X = Me
S2d: X = Br

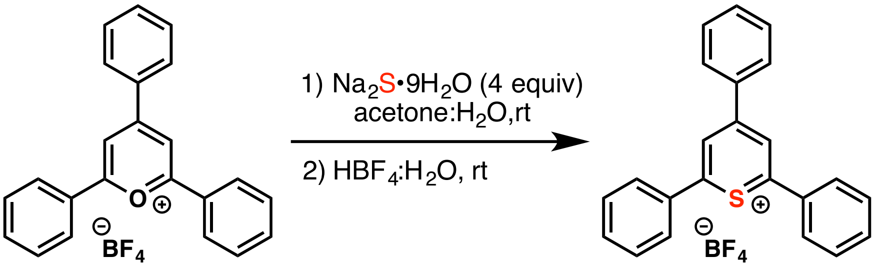
1a: X = OMe
1c: X = Me
1d: X = Br

Pyrylium compounds **1a,c–d** were synthesized according to a literature procedure.[1] At room temperature, freshly distilled BF_3•OEt_2 (2.4 equiv) was slowly added to a mixture of benzaldehyde **S1a,c–d** (1.0 equiv) and acetophenone **S2a,c–d** (2.0 equiv). If both starting materials were solids, they were dissolved in a small amount of toluene before addition of BF_3•OEt_2. The mixture was then vigorously stirred at 100 °C for 2 h. Upon cooling to room temperature, acetone was added until full dissolution of all solids. Diethyl ether was then added, which resulted in precipitation of the desired product. The solid was filtered, washed with Et_2O, and dried *in vacuo*. Multiple recrystallizations in MeCN afforded the pure pyrylium salt (5–35%). The spectroscopic data for these compounds were consistent with those reported in the literature (in d6-DMSO or CD_3CN shown below).[1]

2,4,6-Tris(4-methoxyphenyl)pyrylium tetrafluoroborate (**1a**): ^1H NMR (CD_3CN, 500 MHz) δ 8.28–8.22 (m, 8 H), 7.22–7.17 (m, 6 H), 3.96 (s, 3 H), 3.95 (s, 6 H) ppm. ^{13}C NMR (CD_3CN, 126 MHz) δ 169.5, 166.8, 166.2, 163.5, 132.8, 131.5, 125.6, 122.2, 116.5, 116.4, 112.1, 56.8 ppm.

2,4,6-Tris(4-methylphenyl)pyrylium tetrafluoroborate (**1c**): ^1H NMR (CD_3CN, 500 MHz) δ 8.51 (s, 2 H), 8.25 (d, J = 8.5 Hz, 4 H), 8.17 (d, J = 8.0 Hz, 2 H), 7.56 (d, J = 8.0 Hz, 6 H), 2.51 (s, 9 H) ppm. ^{13}C NMR (CD_3CN, 126 MHz) δ 171.1, 166.0, 148.3, 148.2, 131.7, 131.6, 130.9, 130.5, 129.4, 127.2, 114.8, 22.0 ppm.

2,4,6-Tris(4-bromophenyl)pyrylium tetrafluoroborate (**1d**): ^1H NMR (CD_3CN, 500 MHz) δ 8.71 (s, 2 H), 8.33–8.30 (m, 4 H), 8.24–8.20 (m, 2 H), 8.00–7.96 (m, 6 H), 2.51 (s, 9 H) ppm. ^{13}C NMR (CD_3CN, 126 MHz) δ 171.1, 166.3, 134.3, 132.7, 132.2, 131.5, 131.5, 131.2, 128.9, 117.0 ppm.



1b **1e**

2,4,6-triphenylthiopyrylium tetrafluoroborate (**1e**) was synthesized according to a literature procedure.[1] An aqueous solution of Na_2S (1.14 g, 4.75 mmol, 4 equiv) was added dropwise to a stirred solution of **1b** (0.47 g, 1.19 mmol, 1 equiv). The mixture was stirred at room temperature for 1 h, upon which the color had changed to red. The red solution was then added to an Erlenmeyer flask containing aqueous HBF_4 (20 mL, 48 wt.%) and stirred for 1 h. The yellow precipitate was filtered, washed with Et_2O and recrystallized from MeCN to afford **1e** as yellow crystals (0.18 g, 38%). The spectroscopic data for these compounds were consistent with those reported in the literature.[1]

2,4,6-triphenylthiopyrylium tetrafluoroborate (**1e**): ^1H NMR (CD_3CN, 500 MHz) δ 9.02 (s, 2 H), 8.21–8.18 (m, 2 H), 8.13–8.10 (m, 4 H), 7.86–7.72 (m, 9 H) ppm. ^{13}C NMR (CD_3CN, 126 MHz) δ: ^{13}C NMR (126 MHz, CD_3CN) δ 170.5, 163.1, 137.6, 135.1, 134.8, 134.5, 132.1, 131.3, 130.9, 130.7, 129.7 ppm.

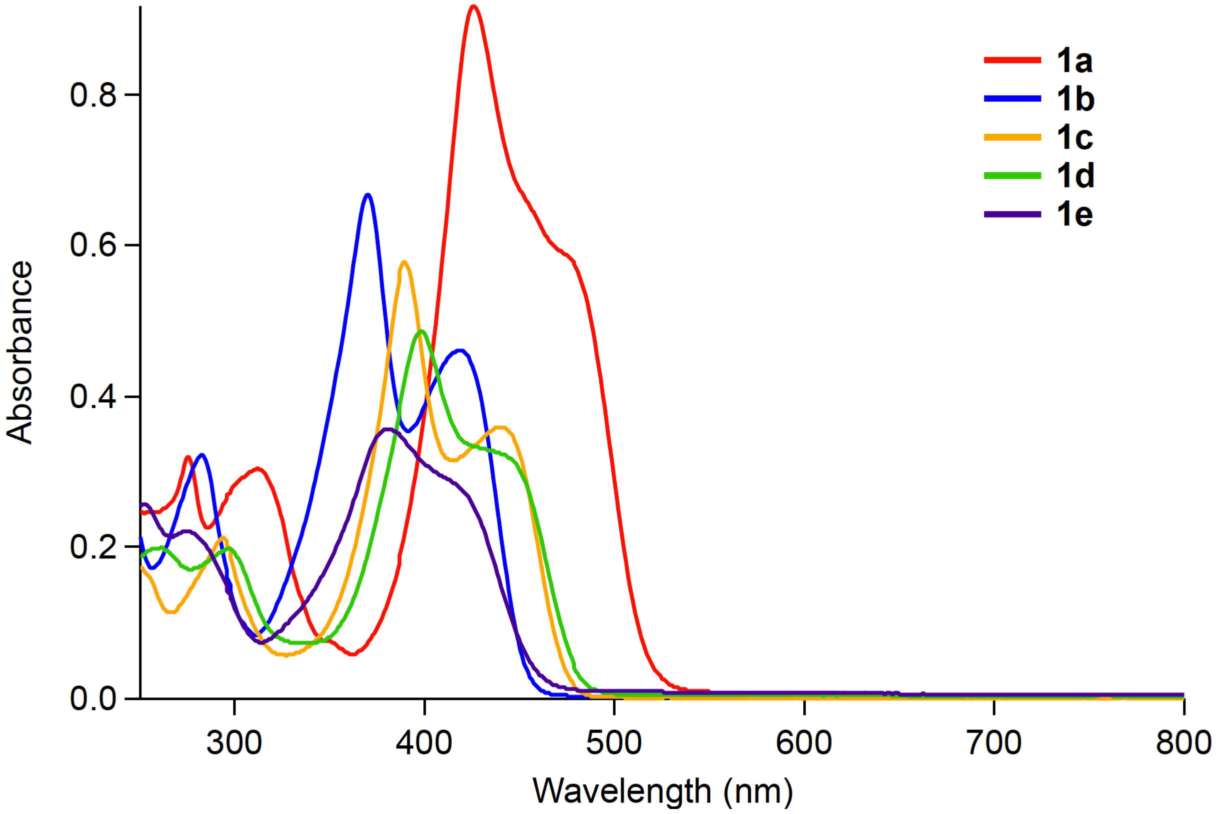
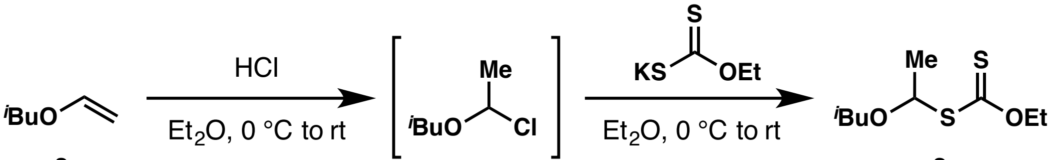


Figure S1. UV-visible spectra of pyryliums 1a–e (0.01 mM).

Synthesis of Chain-Transfer Agents

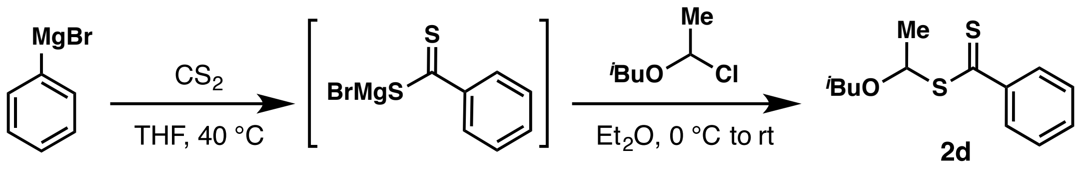
S-1-isobutoxyethyl N,N-diethyl dithiocarbamate (**2a**) and S-1-isobutoxylethyl S′-ethyl trithiocarbonate (**2b**) were prepared as previously reported by our laboratory.[2]



3a **2c**

*Synthesis of S-1-isobutoxyethyl O-ethyl xanthate (**2c**)*

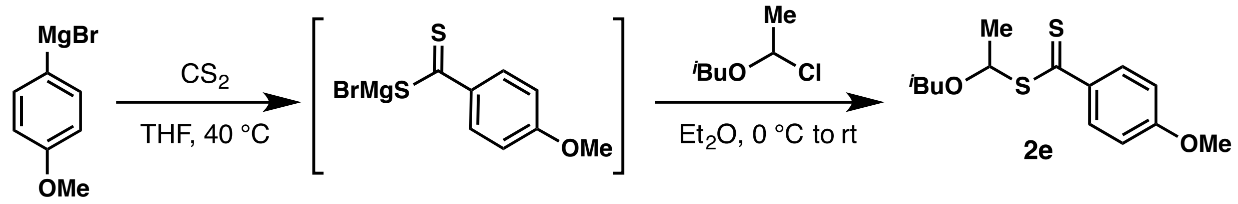
2c was synthesized according to a slightly modified literature procedure.[3] In a flame dried flask, a solution of HCl in Et_2O (5.15 mL, 2.0 M, 10.3 mmol, 1.2 equiv) was added dropwise to a solution of isobutyl vinyl ether (1.15 mL, 8.8 mmol, 1.0 equiv) in Et_2O (10 mL) over 10 min at –78 °C and stirred for 1 h under nitrogen. This solution was then added dropwise to a solution of potassium ethylxanthate (11.8 mmol, 1.3 equiv) in Et_2O (30 mL) over 30 min at 0 °C. Stirring was continued for 1 h at 0 °C, followed by 1.5 h at room temperature. The reaction was diluted with Et_2O (30 mL) and saturated aqueous sodium bicarbonate (30 mL) was added. The layers were separated, and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with water (10 mL), brine (10 mL), then diluted with hexanes (40 mL), dried over $MgSO_4$, and evaporated to dryness *in vacuo*. The brown oil was further purified by column chromatography (SiO_2, gradient from 10:0 to 99:1 hexanes:ethyl ether) to yield **2c** as a pale yellow oil (1.16 g, 59%). The spectroscopic data for this compound were consistent with those reported in the literature.[4] ^1H NMR ($CDCl_3$, 500 MHz) δ 5.58 (q, J = 6.3 Hz, 1 H), 4.71–4.61 (m, 2 H), 3.47 (dd, J = 9.1, 6.8 Hz, 1 H), 3.28 (dd, J = 9.1, 6.4 Hz, 1 H), 1.85 (sept, J = 6.7 Hz, 1 H), 1.68 (d, J = 6.3 Hz, 3 H), 1.43 (t, J = 7.1 Hz, 3 H), 0.90 (d, J = 6.7 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ 214.3, 88.7, 76.3, 69.7, 28.4, 23.0, 19.5, 19.4, 13.9 ppm.



*Synthesis of S-1-isobutoxyethyl benzodithioate (**2d**)*

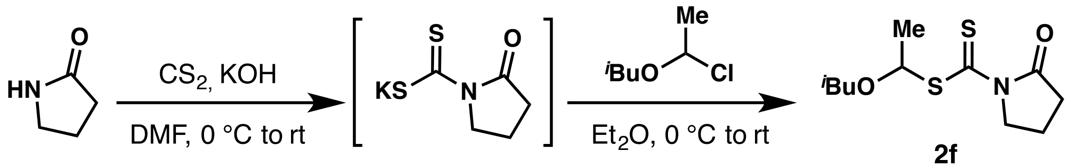
2d was synthesized according to a modified literature procedure.[3] In a flame-dried flask under nitrogen, carbon disulfide (0.36 mL, 6.0 mmol, 1.2 equiv) in THF (4 mL) was heated to 40 °C. To the solution, a solution of phenylmagnesium bromide in THF (1.67 mL, 3.0 M, 5.0 mmol, 1.0 equiv) was added slowly over 15 min and the resulting solution was stirred at 40 °C for 2 h. To a separate flame-dried flask, a solution of HCl in Et_2O (2.3 mL, 2.0 M, 4.6 mmol, 1.2 equiv) was added dropwise to a solution of isobutyl vinyl ether (0.5 mL, 3.8 mmol, 1.0 equiv) in Et_2O (5 mL) over 10 min at –78 °C, stirred for 1.5 h under nitrogen, and warmed to 0 °C over 30 min. The cold solution was then added dropwise to the solution of benzodithioate over 10 min. The resulting mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with H_2O (40 mL) and extracted with DCM (3 x 20 mL). The combined organic phases were washed with water (3 x 30 mL), dried over $MgSO_4$, and evaporated to dryness *in vacuo*. Purification by column chromatography (SiO_2, hexanes) afforded **2d** as a red oil (330 mg, 34%).

The spectroscopic data for this compound were consistent with those reported in the literature.[3] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (d, *J* = 8.4, 1.3 Hz, 2 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 8.4 Hz, 2 H), 5.83 (q, *J* = 6.2 Hz, 1 H), 3.49 (dd, *J* = 9.2, 6.9 Hz, 1 H), 3.34 (dd, *J* = 9.2, 6.4 Hz, 1 H), 1.88 (sept, *J* = 6.7 Hz, 1 H), 1.77 (d, *J* = 6.2 Hz, 3 H), 0.91 (dd, *J* = 6.7, 1.8 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ 229.9, 145.6, 132.6, 128.4, 127.0, 89.6, 76.9, 28.5, 22.5, 19.5, 19.4 ppm.



*Synthesis of S-1-isobutoxyethyl 4-methoxybenzodithioate (**2e**)*

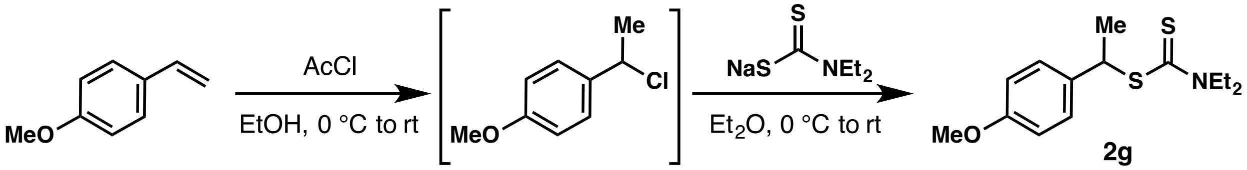
In a flame-dried flask under nitrogen, carbon disulfide (0.36 mL, 6.0 mmol, 1.2 equiv) in THF (8 mL) was heated to 40 °C. To the solution, a solution of 4-methoxyphenylmagnesium bromide in THF (10.0 mL, 0.5 M, 5.0 mmol, 1.0 equiv) was added slowly over 15 min. The resulting solution was stirred at 40 °C for 2 h. To a separate flame-dried flask, a solution of HCl in Et_2O (2.3 mL, 2.0 M, 4.6 mmol,1.2 equiv) was added dropwise to a solution of isobutyl vinyl ether (0.5 mL, 3.8 mmol, 1.0 equiv) in Et_2O (5 mL) over 10 min at –78 °C, stirred for 1.5 h under nitrogen, and warmed to 0 °C over 30 min. Subsequently, the cold solution was added dropwise to the solution of 4-methoxybenzodithioate over 10 min. The resulting mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with H_2O (40 mL) and extracted with DCM (3 x 20 mL). The combined organic phases were washed with water (3 x 30 mL), dried over $MgSO_4$, and evaporated to dryness *in vacuo*. Purification by column chromatography (SiO_2, 8:2 hexanes:toluene) afforded **2e** as a red oil (610 mg, 56%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.10–8.06 (m, 2 H), 6.89–6.86 (m, 2 H), 5.85 (q, *J* = 6.2 Hz, 1 H), 3.87 (s, 3 H), 3.48 (dd, *J* = 9.3, 6.9 Hz, 1 H), 3.33 (dd, *J* = 9.2, 6.4 Hz, 1 H), 1.87 (sept., *J* = 6.7 Hz, 1 H), 1.76 (d, *J* = 6.2 Hz, 3 H), 0.90 (dd, *J* = 6.7, 2.0 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ 227.2, 163.9, 138.6, 129.2, 113.6, 89.4, 76.7, 55.7, 28.5, 22.7, 19.5, 19.4 ppm. HRMS (DART-MS): calc'd for $C_{14}H_{21}O_2S_2$ [M + H$^+$] 285.0977, found 285.0974. IR (neat): $\tilde{\nu}$ = 2957, 2928, 2909, 2871, 2838, 1596, 1571, 1501, 1261, 1170 ($\tilde{\nu}_{max}$), 1047 cm^{-1}.



2f

*Synthesis of S-1-isobutoxyethyl-2-pyrrolidinone-1-carbodithioate (**2f**)*

2f was synthesized according to a slightly modified literature procedure.[3] In a flame-dried flask under nitrogen, potassium hydroxide (0.36 g, 6.4 mmol, 1.25 equiv) and 2-pyrrolidinone (0.46 mL, 6.1 mmol, 1.2 equiv) were combined in anhydrous DMF (15 mL) and left to stir for 20 min. The solution was cooled to 0 °C before carbon disulfide (1.10 mL, 18.3 mmol, 3.6 equiv) was added dropwise over 10 min. The resulting dark red solution was stirred at room temperature for 3 h. To a separate flame-dried flask, a solution of HCl in Et_2O (3.1 mL, 2.0 M, 6.2 mmol, 1.2 equiv) was added dropwise to a solution of isobutyl vinyl ether (0.67 mL, 5.1 mmol, 1.0 equiv) in Et_2O (5 mL) over 10 min at –78 °C, stirred for 1.5 h under nitrogen, and warmed to 0 °C over 30 min. The cold solution was then added dropwise to the solution of potassium 2-pyrrolidinone-1-carbodithioate over 10 min. The resulting mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with H_2O (40 mL) and extracted with DCM (3 x 20 mL). The combined organic phases were washed with water (3 x 30 mL), dried over $MgSO_4$, and evaporated to dryness *in vacuo*. Purification by column chromatography (SiO_2, gradient from 9:1 to 7:3 hexanes:ethyl acetate) afforded **2f** as a yellow oil (610 mg, 46%). The spectroscopic data for this compound were consistent with those reported in the literature.[3] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.77 (q, *J* = 6.1 Hz, 1 H), 4.29–4.20 (m, 2 H), 3.51 (dd, *J* = 9.1, 6.9 Hz, 1 H), 3.28 (dd, *J* = 9.1, 6.5 Hz, 1 H), 2.74 (t, *J* = 8.0 Hz, 2 H), 2.15–2.07 (m, 2 H), 1.85 (sept, *J* = 6.7 Hz, 1 H), 1.71 (d, *J* = 6.1 Hz, 3 H), 0.89 (d, *J* = 6.7 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ 201.1, 173.2, 89.0, 76.6, 53.3, 33.9, 28.5, 22.5, 19.5, 19.4, 17.5 ppm.



*Synthesis of 1-(4-methoxyphenyl)ethyl N,N-diethyldithiocarbamate (**2g**)*

In a flame-dried flask, a solution of *p*-methoxystyrene (0.13 mL, 1.0 mmol, 1.0 equiv) in anhydrous ethanol (0.47 mL, 8.0 mmol, 8.0 equiv) was cooled to 0 °C. To the solution, acetyl chloride (0.57 mL, 8.0 mmol, 8.0 equiv) was added dropwise and the solution was left to stir at room temperature. Once the reaction was complete (as determined by TLC analysis), solvents were removed *in vacuo*. The residues were dissolved in Et_2O (1 mL) and this solution was then added dropwise to a solution of sodium diethyldithiocarbamate (205 mg, 1.2 mmol, 1.2 equiv) in Et_2O (4 mL) at 0 °C. Stirring was continued for 1 h at 0 °C, followed by 1.5 h at room temperature. The reaction was diluted with Et_2O (15 mL) and saturated aqueous sodium bicarbonate (15 mL) was added. The layers were separated, and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with water (10 mL), brine (10 mL), then diluted with hexanes (20 mL), dried over $MgSO_4$, and evaporated to dryness *in vacuo*. The brown oil was further purified by column chromatography (SiO_2, gradient from 10:0 to 7:3 hexanes:ethyl acetate) to afford a pale yellow oil (190 mg, 67%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36 (d, J = 8.7 Hz, 2 H), 6.86 (d, J = 8.7 Hz, 2 H), 5.22 (q, J = 7.0 Hz, 1 H), 4.02 (q, J = 7.1 Hz, 2 H), 3.79 (s, 3 H), 3.69 (q, J = 7.1 Hz, 2 H), 1.77 (d, J = 7.0 Hz, 3 H), 1.29–1.20 (m, 6 H). ^{13}C NMR ($CDCl_3$, 126 MHz,) δ 195.0, 158.9, 134.3, 129.1, 114.0, 55.4, 50.5, 49.3, 46.7, 22.3, 12.6, 11.8 ppm. HRMS (DART-MS): calc'd for $C_{14}H_{22}NOS_2$ [M + H^+] 284.1137, found 284.1137. IR (neat): $\tilde{\nu}$ = 2976, 2932, 2906, 2871, 2835, 1610, 1582, 1511 ($\tilde{\nu}_{max}$), 1249, 1032, 829 cm^{-1}.

General Procedure for Photocontrolled Cationic Polymerization of Isobutyl Vinyl Ether (Tables 2 and 3)

In a nitrogen-filled glove box, an oven-dried one-dram vial was equipped with a stir bar and charged with isobutyl vinyl ether (0.26 mL, 2.00 mmol, 100 equiv), 0.020 mL of a stock solution of CTA in DCM (1.0 M, 0.02 mmol, 1 equiv), and 0.20 mL of a stock solution of photocatalyst in DCM (2.0 mM, 0.40 µmol, 0.02 mol% relative to IBVE). For reactions with 0.01 mol% of photocatalyst, only 0.1 mL of the stock solution of photocatalyst was used and 0.1 mL of DCM was added to maintain the same overall concentration. The vial was sealed with a cap containing a teflon septum under an atmosphere of nitrogen, placed 2 cm away from the Kobi Electric bulb (460–470 nm, 9 W, Table 2) or LED strips (450 nm, 2.88 W/ft, Table 3) outside of the glove box, and stirred while cooling by blowing compressed air over the reaction vial. Following the desired amount of reaction time, irradiation was halted and aliquots for NMR and GPC analysis were taken.

A typical ^{1}H NMR and GPC traces for poly(isobutyl vinyl ether) are shown in Figure S2 and S3–S11. The small shoulder around 17 min (Figures S3–S11) is a GPC artifact. For a picture of the experimental setup, see Figure S12.

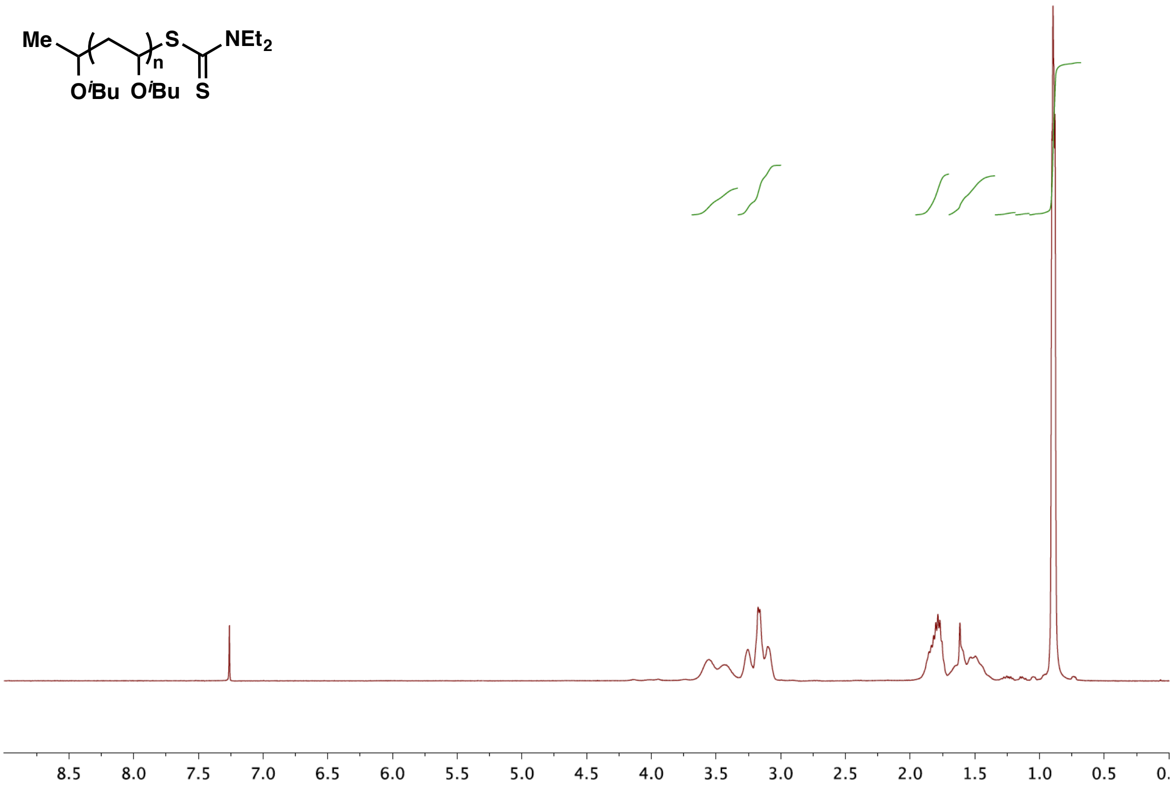


Figure S2. ^{1}H NMR of poly(isobutyl vinyl ether); M_n = 10.7 kg/mol, $Đ$ = 1.19 (Table 2, entry 1) .

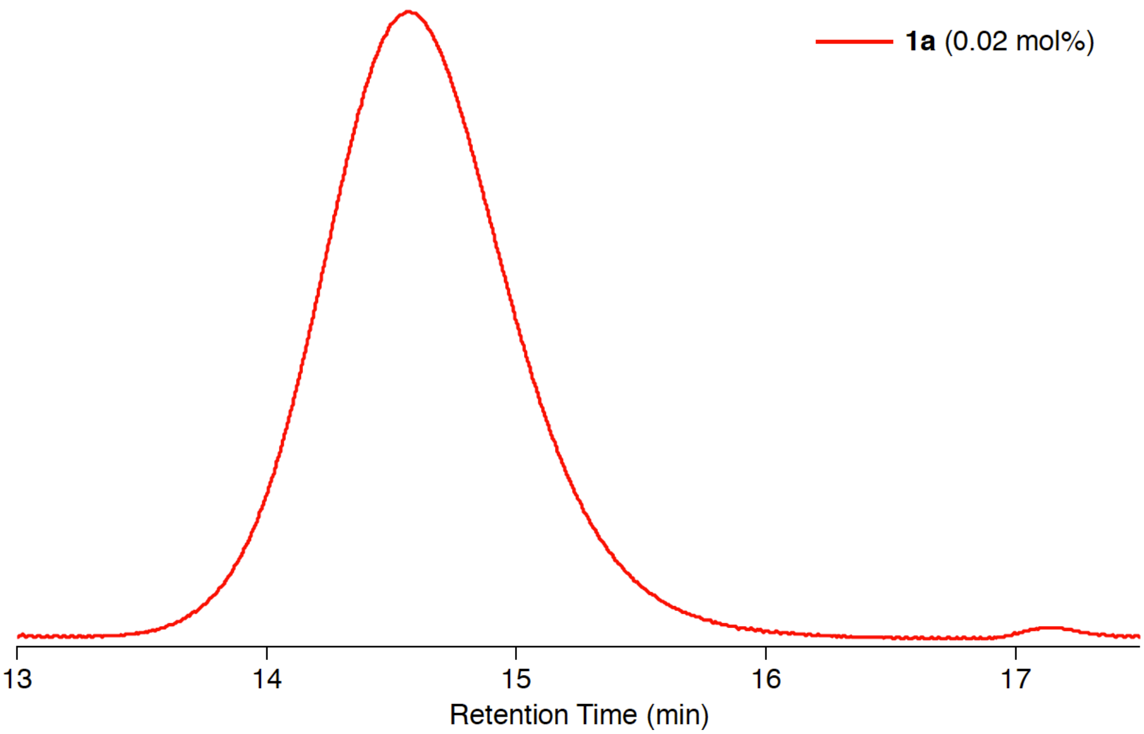


Figure S3. GPC trace of poly(isobutyl vinyl ether); M_n = 10.7 kg/mol, Đ = 1.19 (Table 2, entry 1).

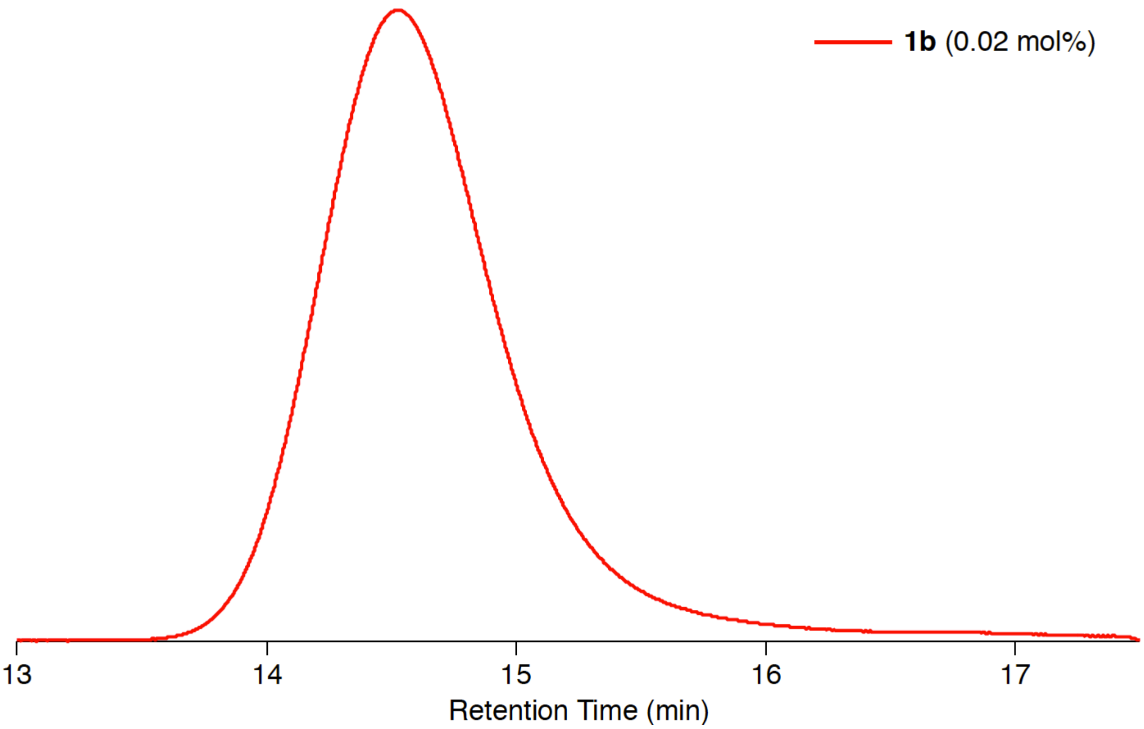


Figure S4. GPC trace of poly(isobutyl vinyl ether); M_n = 10.5 kg/mol, Đ = 1.23 (Table 2, entry 2).

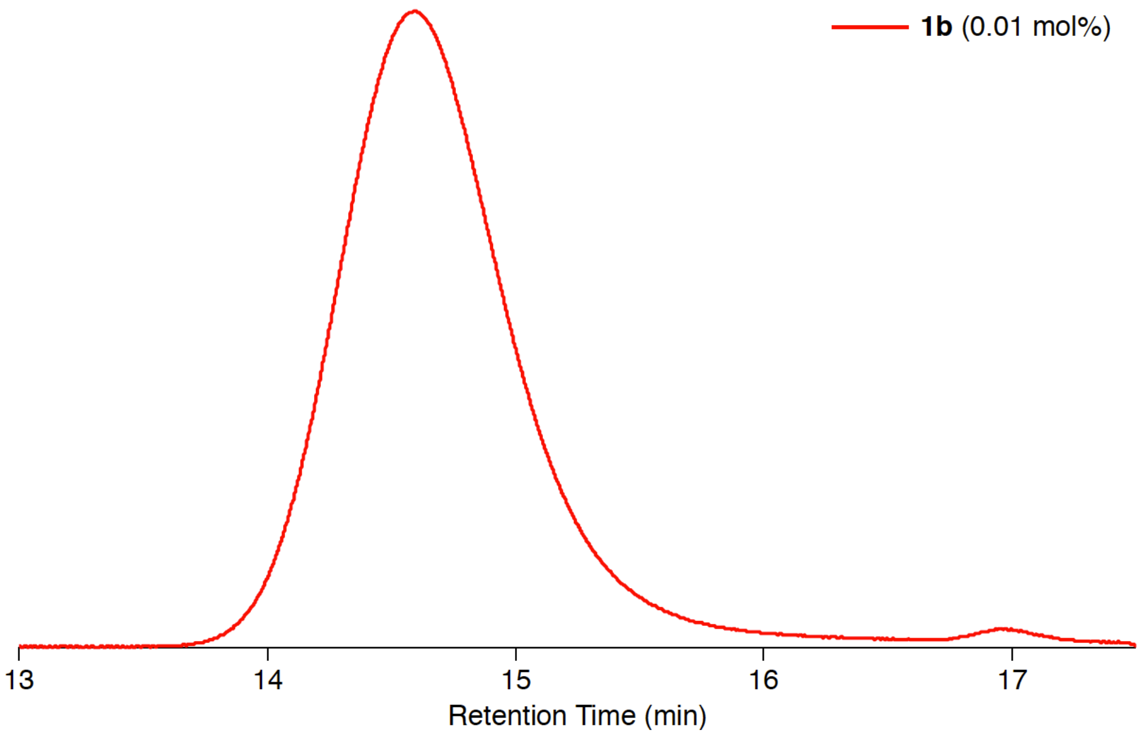


Figure S5. GPC trace of poly(isobutyl vinyl ether); M_n = 10.2 kg/mol, Đ = 1.19 (Table 2, entry 3).

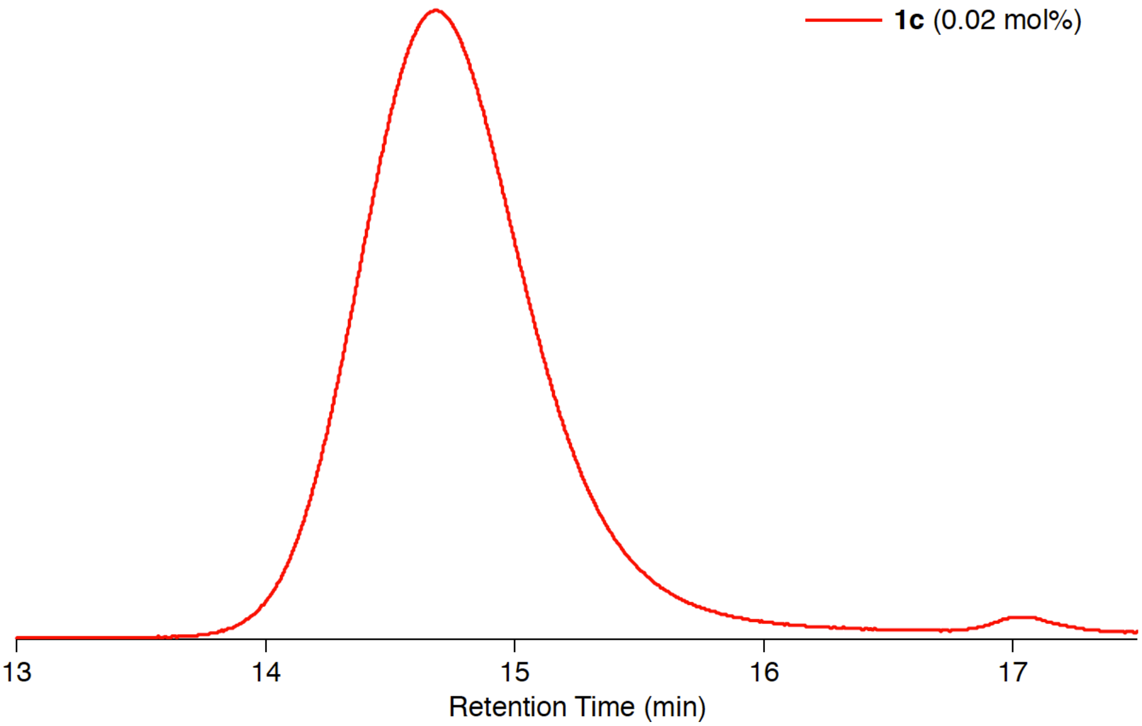


Figure S6. GPC trace of poly(isobutyl vinyl ether); M_n = 11.1 kg/mol, Đ = 1.17 (Table 2, entry 4).

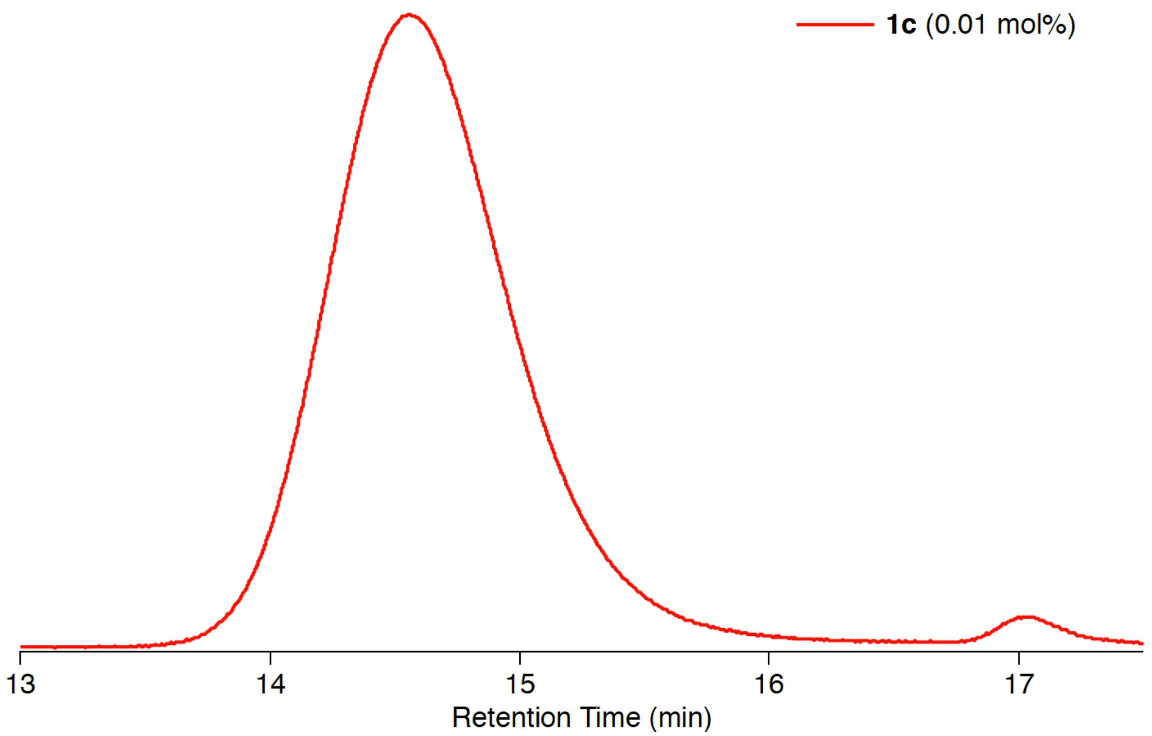


Figure S7. GPC trace of poly(isobutyl vinyl ether); M_n = 10.7 kg/mol, *Đ* = 1.17 (Table 2, entry 5).

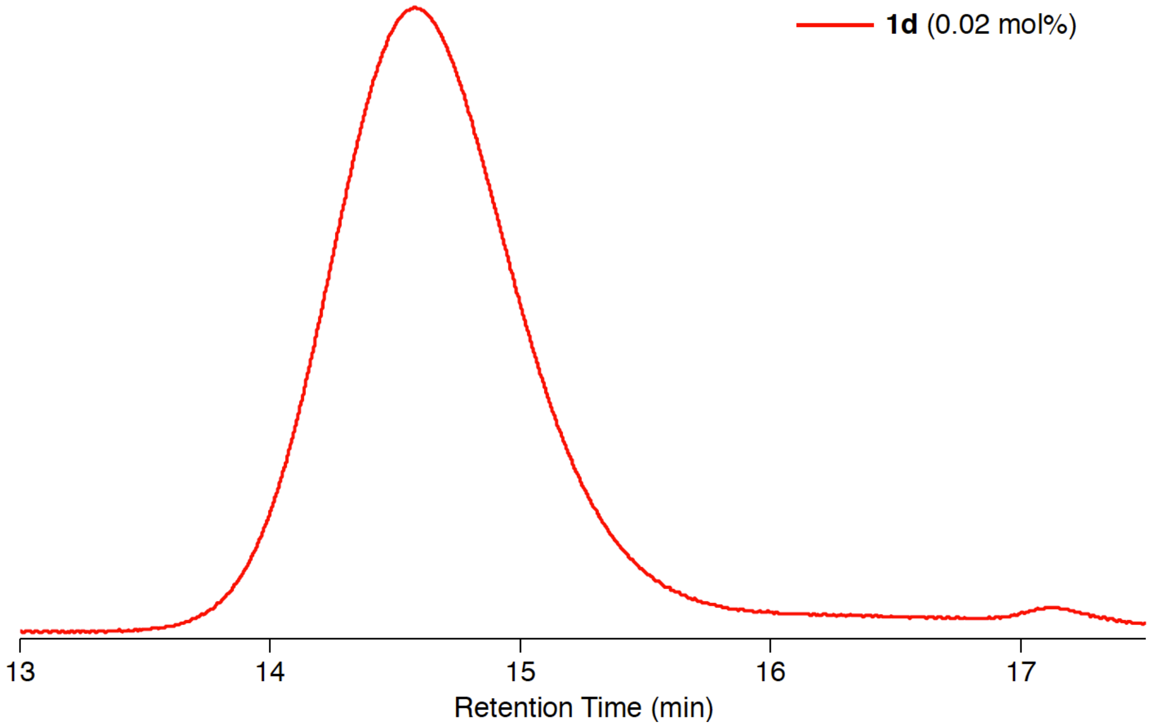


Figure S8. GPC trace of poly(isobutyl vinyl ether); M_n = 10.5 kg/mol, *Đ* = 1.18 (Table 2, entry 6).

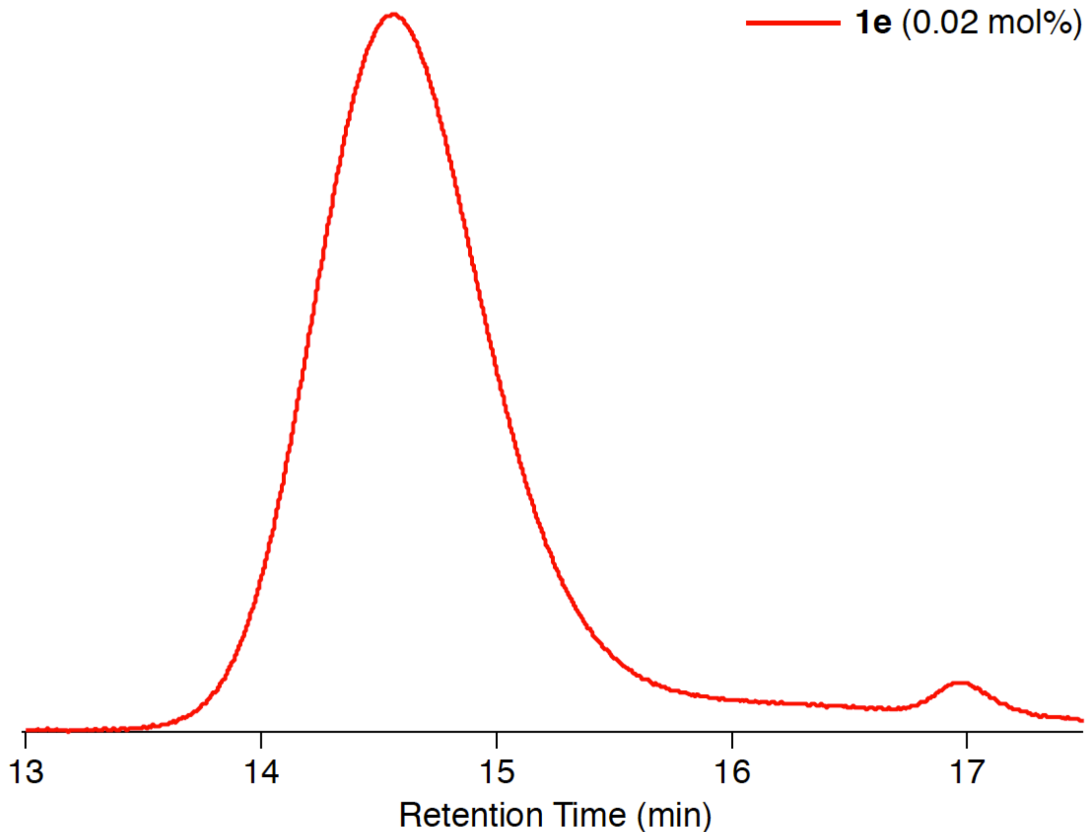


Figure S9. GPC trace of poly(isobutyl vinyl ether); M_n = 10.3 kg/mol, $Đ$ = 1.21 (Table 2, entry 7).

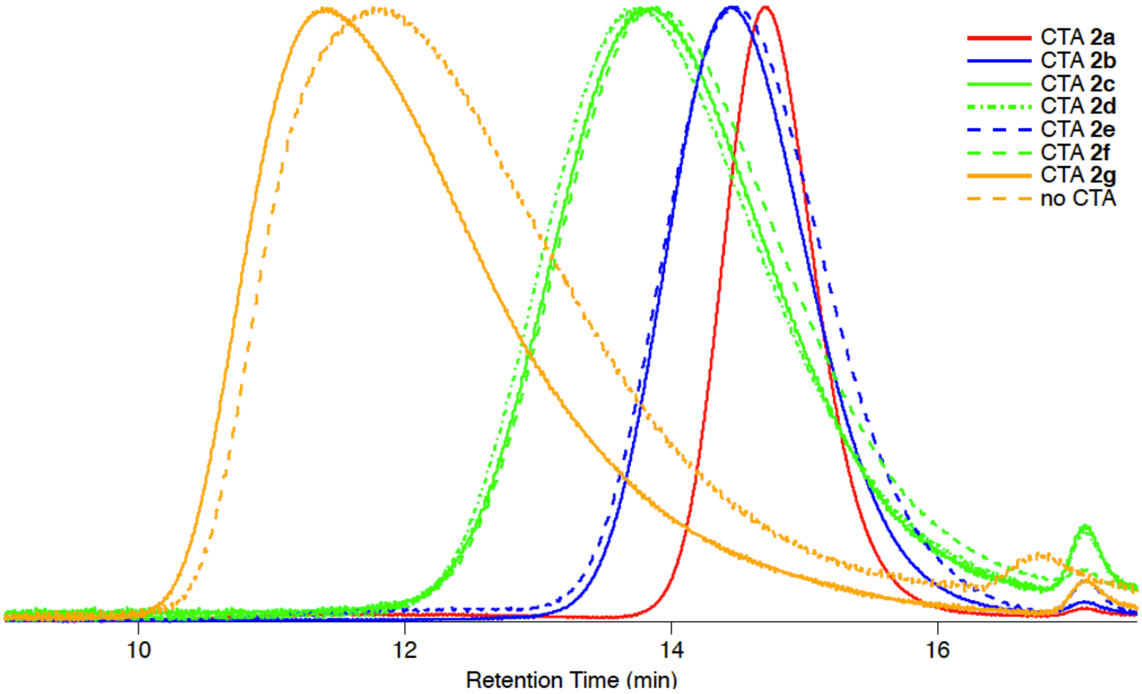


Figure S10. GPC traces of poly(isobutyl vinyl ether)s synthesized with various CTAs (Table 3, entries 1,3,5,7,9,11,13,15).

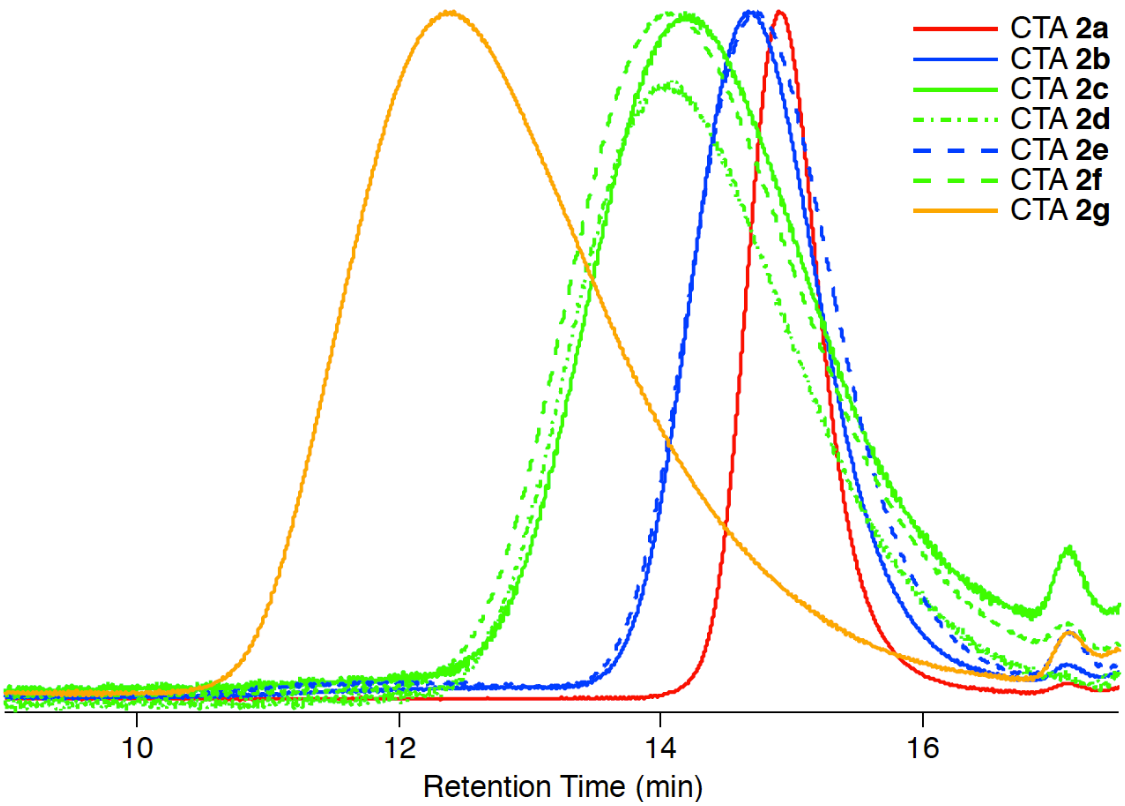


Figure S11. GPC traces of poly(ethyl vinyl ether)s synthesized with various CTAs (Table 3, entries 2,4,6,8,10,12,14).

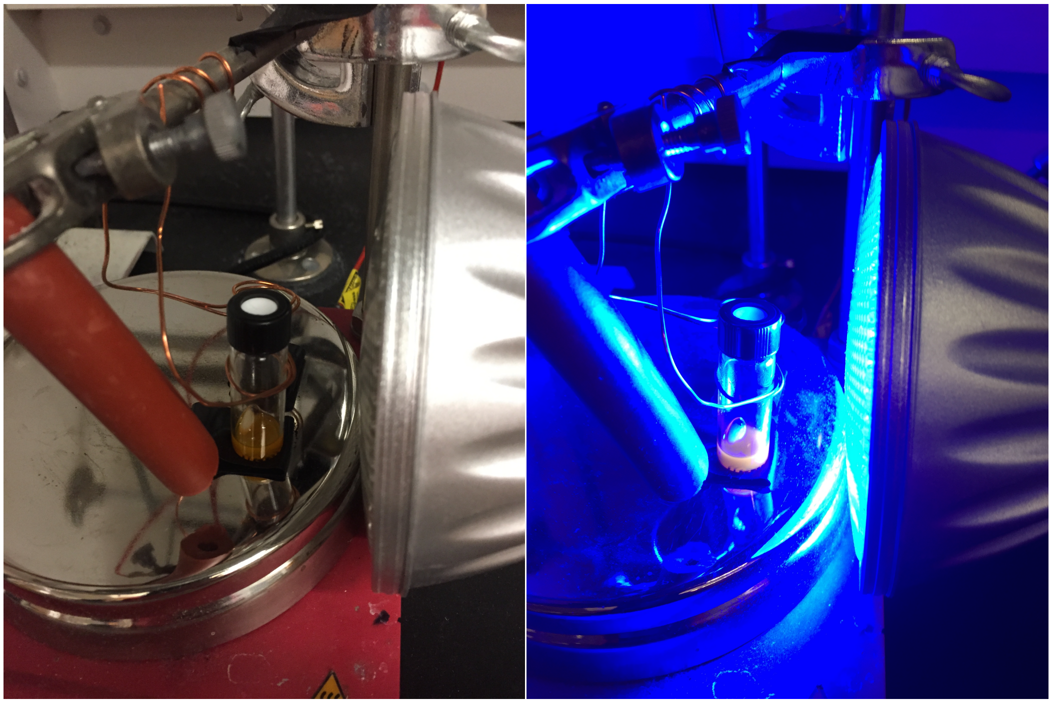


Figure S12. Polymerization setup.

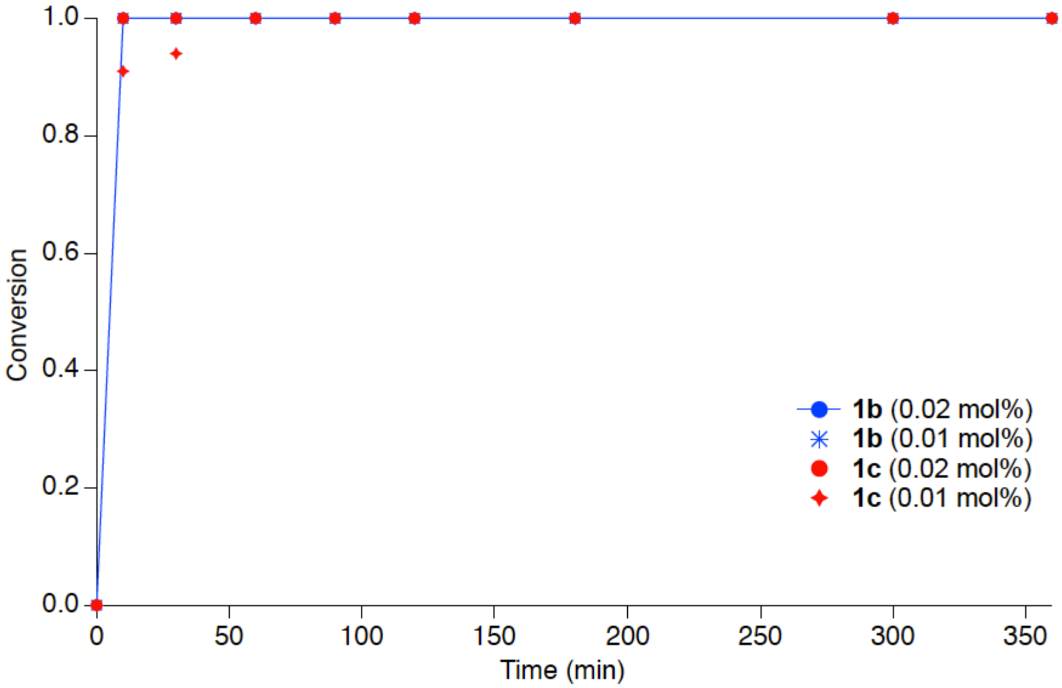


Figure S13. Polymerization of IBVE: Conversion vs time for pyrylium photocatalysts 1b and 1c.

Table S1. Cationic Polymerization of Various Monomers with Photocatalyst 1a and CTA 2a

Monomer (0.02 mol%)	Conv. (%)	time	M_n(exp)	M_n(theo)	$Đ$
EVE	97	5.3 h	6.3	7.0	1.16
PVE	>99	5.3 h	6.0	8.6	1.17
BVE	>99	8 h	8.1	10.0	1.21
2-ClEt	4	71 h	–	10.6	–

Time-Resolved Fluorescence Quenching Experiments

All data were taken using 440 nm pulsed excitation (Becker&Hickl BDL-SMN-440 pulsed diode laser with ~100 ps FWHM pulsewidth) and a Becker & Hickl SPC-830 Time-Correlated Single Photon Counting (TCSPC) card (Becker & Hickl GmbH, Berlin, Germany). Fluorescence was detected by a R3809U-50 microchannel plate photomultiplier tube with a 25 ps transit time spread (Hamamatsu, Bridgewater, NJ). Fluorescence decay curves were collected from samples in 1 cm path-length quartz cuvettes at 90 degrees through Glan-Thompson polarizer set at the magic angle (54.7 degrees) relative to the excitation beam and a 480/50 bandpass filter (Chroma Technology, Bellows Falls, VT). All samples were prepared in a nitrogen-filled glove box by adding 0.3 mL of a solution of photocatalyst **1a** (2.0 mM), CTA **2a** or IBVE (**3a**) (various concentrations, see tables S2 and S3), and DCM (volume of cuvette completed to 3.0 mL), then sealed before being taken out of the box. Figure 7 in the article shows the fits for each concentration of quencher **2a** or **3a**. An example of the collected data, fit and residuals is shown in figure S5 (X^2 = 1.11, τ_0 = 6.07 ns).

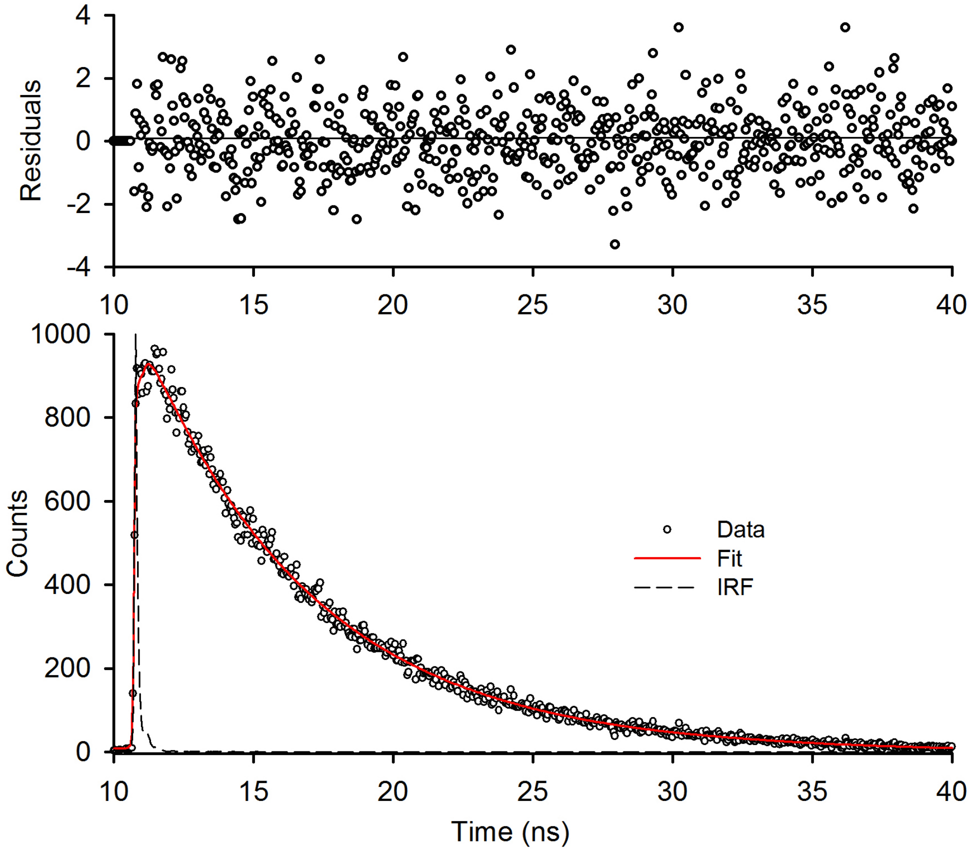


Figure S14. Time-resolved fluorescence data, fit and residuals for 2,4,6-tris(*p*-methoxyphenyl)pyrylium tetrafluoroborate (1a) in DCM with no quencher (X^2 = 1.11, τ_0 = 6.07 ns). IRF = impulse response function.

Table S2. τ_0/τ vs Concentration of 2a

[CTA **2a**] (M)	τ_0/τ
0	1
0.0054	1.2
0.012	1.5
0.046	2.8
0.13	5.6

Table S3. τ_0/τ vs Concentration of IBVE (3a)

[**3a**] (M)	τ_0/τ
0	1
0.26	1.1
0.51	1.3
0.77	1.5
1.02	1.8

Cyclic Voltammetry With CTA 2a and/or IBVE (3a) (Figure 9)

Measurements were performed in MeCN with tetrabutylammonium perchlorate as the electrolyte. The cyclic voltammograms were obtained using a platinum working microelectrode (d = 15 μm), a platinum counter electrode, and a Ag/Ag$^+$ reference electrode (+260 mV vs. SCE). A scan rate of 50 mV•s^{-1} was used. Oxidation potentials for **2a** and **3a** were determined at the onset of the oxidation wave.

A CV was collected for the three following solutions:

1) IBVE (0.26 mL), MeCN (0.4 mL), TBAP (1.0 g), and DCM (20 μL)
2) IBVE (0.26 mL), MeCN (0.4 mL), TBAP (1.0 g), and CTA **2a** in DCM (1 M, 20 μL)
3) TBAP (0.1 M) and CTA **2a** in MeCN (1 mM)

Electropolymerization of IBVE (3a) at Set Potential

A chronoamperometry setup was used to electropolymerize IBVE (**3a**) at a set potential. A clean glassy carbon electrode was immersed in a three-chambered electrochemical cell separated by a glass frit. The working electrode was placed in a solution containing

3a (0.26 mL), MeCN (0.4 mL), TBAP (1.0 g), and DCM (20 µL) or CTA **2a** in DCM (1 M, 20 µL), while Ag/Ag$^+$ reference and platinum counter electrodes were in the other two chambers containing only the electrolyte. Potential was held at 0.80 V for 5 min, and then the electrode was rinsed with (in the following order) water, acetone (only for a few seconds), then water. Any polymer potentially deposited at the surface of the electrode was subsequently dissolved in $CDCl_3$ and analyzed by ^{1}H NMR and SEC.

When no CTA was added, no polymer was isolated after 5 min, as determined by NMR and SEC analysis.

When CTA 2a was added, a polymer (< 5 mg, $Đ$ = 2.34, M_n = 10.1 kg/mol) was isolated and characterized by NMR and SEC analysis.

Study of Electron Transfers via ESR Spectroscopy

All samples were prepared in a nitrogen-filled glove box. Samples in DCM (100 µl) were analyzed using standard 4 mm o.d. ESR quartz tubes equipped with a J. Young valve. Samples in MeCN (20 µl) were transferred into quartz capillaries of 1.0 mm i.d. and 2.0 mm o.d. Capillaries were then centered in standard 4 mm o.d. ESR quartz tubes equipped with a J. Young valve. Irradiation during the ESR experiments was done using a Royal-Blue (447.5nm) LUXEON Rebel ES LED (1W luminous power). ESR spectra were recorded using a continuous wave X-band Brüker ElexSys E500 EPR spectrometer. The acquisition parameters were fixed to 20dB (2mW) microwave power, 60dB receiver gain, and 100 kHz modulation frequency. The amplitude modulation was varied to resolve the hyperfine coupling constants during irradiation. All ESR spectra were recorded at 298K using a Varian Temperature controller. The signal intensity was determined by double integration after linear baseline correction. The evaluation of the total spin concentration for each scan was done by comparison to a TEMPO concentration calibration scale in MeCN.[5]

*ESR spectroscopic analysis of **1a** or **1b** in presence of CTA **2a** under blue light irradiation (Figure 10)*

A mixture of **1a** (20 mM) and **2a** (200 mM) or **1b** (1 mM) and **2a** (1 mM) was irradiated and monitored by ESR following the general setup described above.

ESR signals were recorded through *in situ* steady-state blue LED irradiation with a 60 scan accumulation, a 2mW power, and a modulation of amplitude M = 0.08 G.

Determination of the g-factor and the hyperfine coupling constant of pyranyl radicals **1a•** *and* **1b•** *by ESR acquisition and simulation*

The determination of the g-factor and the hyperfine coupling constant of the pyranyl radicals (**1a•** and **1b•**) was achieved in DCM under steady state irradiation (blue LEDs) at 298K by using THF as a sacrificial electron donor. The samples (100 µL, 1:1 DCM:THF) containing **1a** or **1b** (10 mM) were loaded in standard 4 mm o.d. ESR sample tubes for spectral recordings according to the general setup. The resulting spectra are depicted in Figure S15 (black curves).

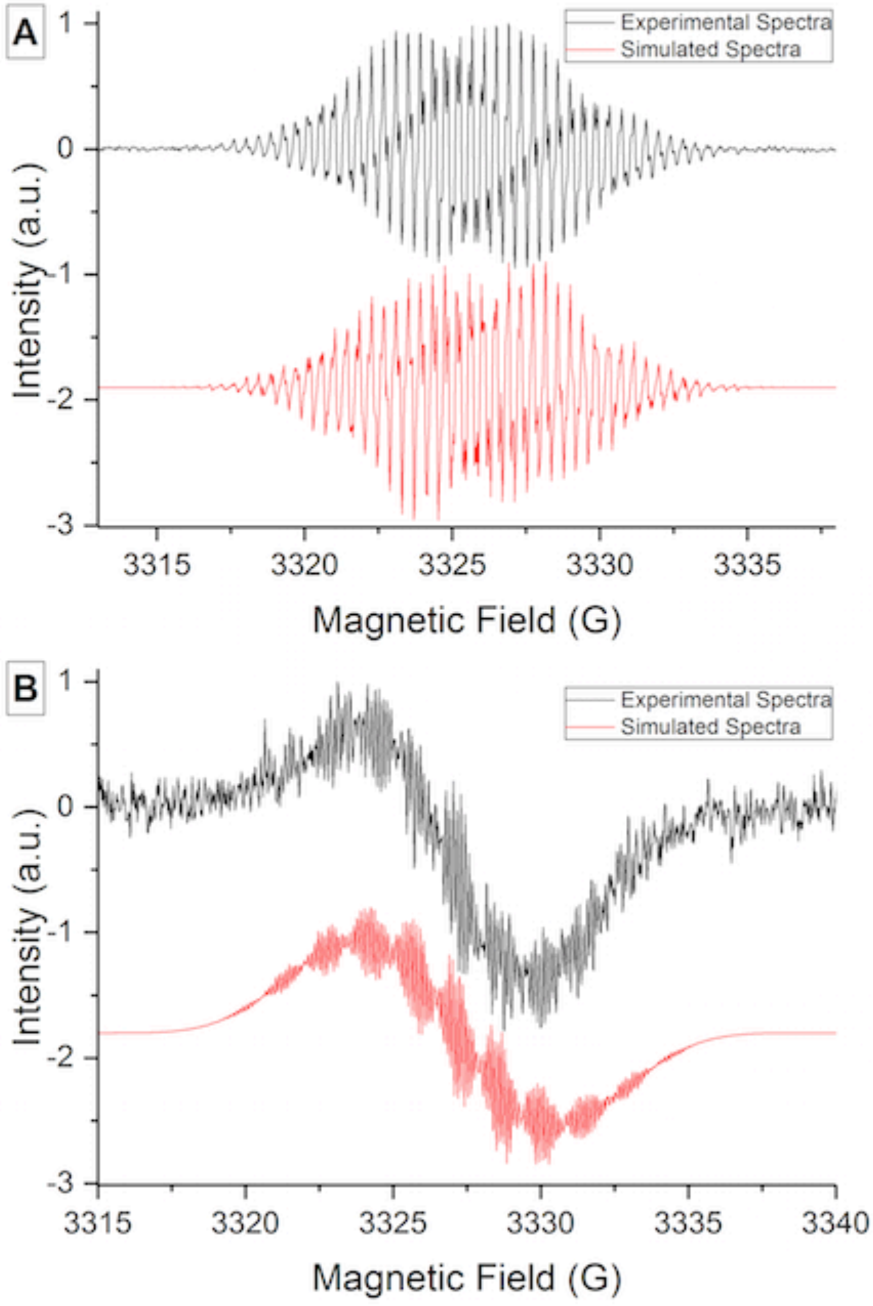
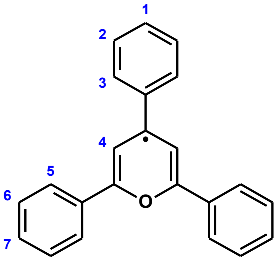
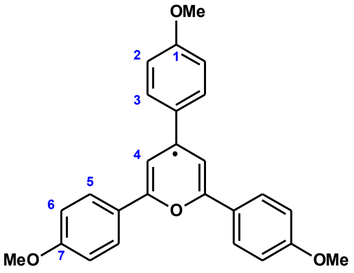


Figure S15. Experimental and simulated ESR spectra of the systems A) “1b + THF” in DCM under blue light irradiation, B) “1a + THF” in DCM under blue light irradiation. The experimental spectra were recorded at room temperature at 298 K with 2 mW power (20 dB), and an amplitude modulation of A) M = 0.02 G and B) M = 0.2 G. A simulation was generated for each species (red curve) by using the parameters described in Table S4.

The Bruker Strong Pitch was used as a g-factor standard reference (g = 2.0028).[6] The hyperfine coupling constant (hfc) values of the pyrylium-based radical was determined by simulation using the easyspin toolbox developed by Stoll et al.[7] The values obtained are presented in Table 1 and compared to literature values.

Table S4. Summaries of the hfc Values and g-Factor Obtained for 1a and 1b

Chemical structure	g_{factor} and ^{1}H proton position	Number of proton	Cw-ESR Simulation	Reference	
	g	-	2.0031±0.0003 (DCM/THF)	-	2.0030[b] (acetone)
	1	1	2.43	2.52[a]	2.52[b]
	2	2	0.85	0.80[a]	0.80[b]
	3	2	2.18	2.10[a]	2.25[b]
	4	2	1.72	1.68[a]	1.62[b]
	5	4	1.29	1.38[a]	1.25[b]
	6	4	0.37	0.42[a]	0.41[b]
	7	2	1.24	1.26[a]	1.38[b]
	g	-	2.0042±0.0003 (DCM/THF)	2.0031[c]	
	1	3	0.33	0.34[c]	
	2	2	0.98	1.03[c]	
	3	2	2.87	2.92[c]	
	4	2	1.44	1.33[c]	
	5	4	1.56	-	
	6	4	0.35	-	
	7	6	0.13	-	

[a]Values obtained by Niizuma *et al.* at room temperature.[8] [b]Values obtained in acetone and THF at 250 K.[9] [c]hfc and g-factor obtained for the radical species arising from the reduction of the analogous 2,6-di-tert-butyl-4-(4-methoxyphenyl)pyrylium.[10]

The ESR spectrum of **1b•** is well reproduced by the simulation (see Figure S15A) and the hfc constants of the different protons are in agreement with literature reports and simulations.[8,9] The slight difference in the hfc values is likely explained by the fact that these spectra were recorded in a mixture of MeCN and THF, more relevant to the polymerization conditions, rather than just THF as in the cited publications.

The ESR spectrum of **1a•** obtained in DCM:THF was more difficult to simulate due to both the poor signal-to-noise ratio obtained and the high number of hyperfine splitting patterns observed (see Figure S15B). Nevertheless, we successfully fitted the experimental spectrum with a simulated spectrum by increasing the hfc constant of the two H3 protons to 2.87 G and by adding small hfc constants (0.33G for H1 and 0.13G for H7) due to the 9 protons of the three methoxy groups. This set of parameters was analogous to the reported spectrum of the radical arising from the reduction of 2,6-di-tert-butyl-4-(4-methoxyphenyl)pyrylium[10] and closely related to the hfc structure of **1b$^\bullet$**, which strongly supports the proposed formation of **1a$^\bullet$**.

*ESR spectral comparison of photoinduced **1a$^\bullet$** in presence of THF or CTA **2a***

The ESR spectra obtained by irradiation of photocatalyst **1a** in presence of THF in DCM or in presence of CTA **2a** in MeCN are depicted in Figure S16. A 15 G large ESR signal was observed for the two samples, which supports our conclusion that the radicals are identical in nature. In the case of **1a** and THF in DCM, a hyperfine splitting structure was resolved, while none could be observed with **1a** combined with **2a** in MeCN. The broadening observed in the latter case may be attributed to the Heisenberg exchange effect, as has previously been observed in the case of nitroxide radicals.[11,12]

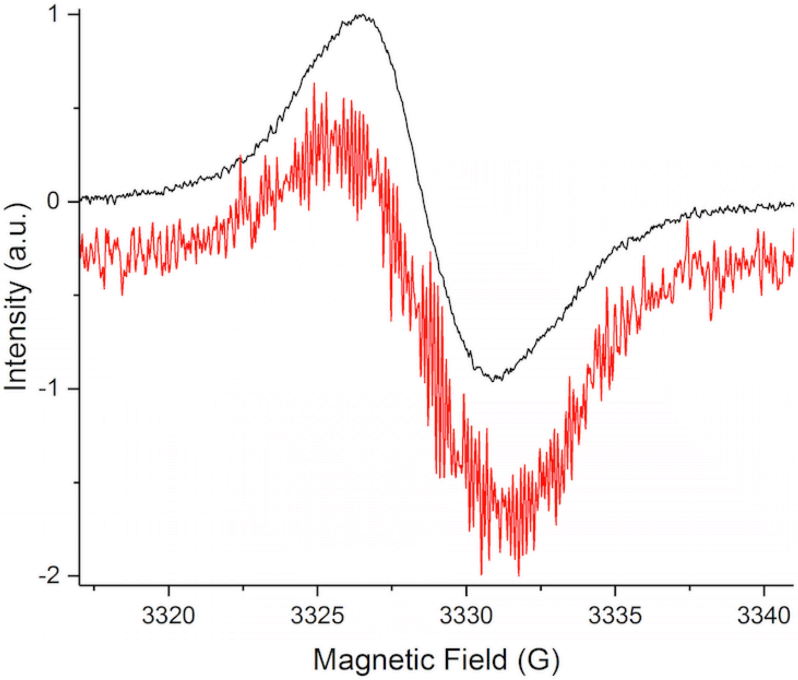


Figure S16. Experimental ESR spectra obtained with 1) 1a (20 mM) and CTA 2a (200 mM) in MeCN (20 µL) (black curve), and 2) 1a (10 mM) and THF in DCM (100 µL, 1:1 DCM:THF) (red curve). The experimental ESR parameters were identical for both spectra: accumulation (10 scans), power (2 mW), and amplitude modulation (M = 0.2 G).

*ESR spectroscopic analysis of **1a** or **1b** in presence of IBVE (**3a**) under blue light irradiation (Figure 11)*

A mixture of **1a** (10 mM) and **3a** (4 M) or **1b** (1 mM) and **3a** (1 mM) was irradiated and monitored by ESR following the general set-up described above.

ESR signals were recorded through *in situ* steady-state Blue-LED light irradiation with a 10 scan accumulation for **1a** (80 scan accumulation for **1b)**, a 2mW power, and a modulation of amplitude M = 0.2 G. A broadening of the line width was observed after 10 scans in the case of **1a**. This broadening is likely due to the increase of viscosity caused by polymerization of **3a** (similar to the broadening depicted in figure S8).

*ESR spectra of the system "**1a** + CTA **2a** + IBVE (**3a**)" under blue light irradiation*

A mixture of **1a** (10 mM), **2a** (100 mM), and **3a** (4 M) in MeCN was irradiated and monitored by ESR. The recorded ESR signal (see Figure S17) was similar to the signals obtained with the combination **1a**/**3a**. The linewidth broadened with increased irradiation time, resulting in the formation of an ESR signal with 8 apparent peaks separated by a 2.7G average hyperfine coupling constant (see Figure S17) after 15 min of irradiation. This broadening may be caused by an increase in viscosity during the acquisition due to the formation of poly(IBVE).

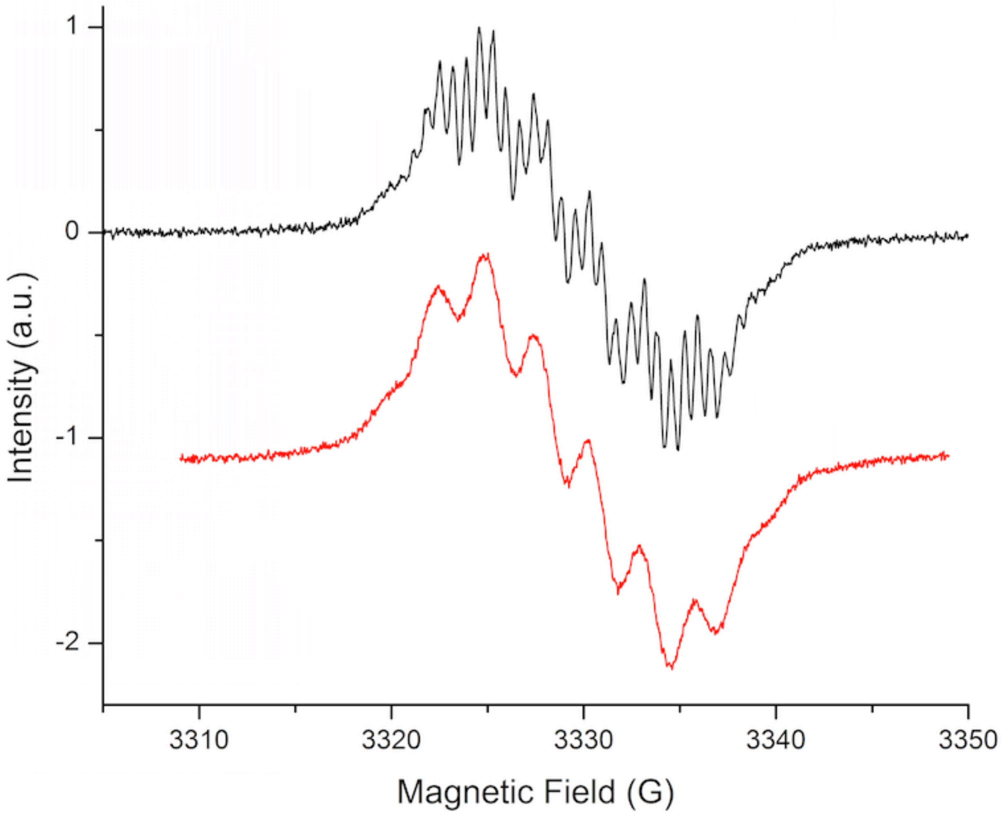


Figure S17. ESR spectra of the system "1a + CTA 2a + IBVE (3a)" in MeCN obtained after 10 s irradiation (black upper curve) and after 15 min irradiation (red lower curve). Both spectra were recorded using the same power (2 mW) and amplitude modulation (M = 0.2 G), but the accumulation was different for the black curve (10 scans) and the red curve (40 scans).

*ESR spectrum of the system “**1b** + **2a** + **3a**” under blue light irradiation*

A mixture of **1b** (1 mM), **2a** (1 mM), and **3a** (1 mM) in MeCN was irradiated and monitored by ESR. A very weak, broad signal was recorded, consisting of 7 distinct peaks separated by a 2.8G average hyperfine coupling (see Figure S18). This weak signal may be the result of a rapid radical recombination rate.

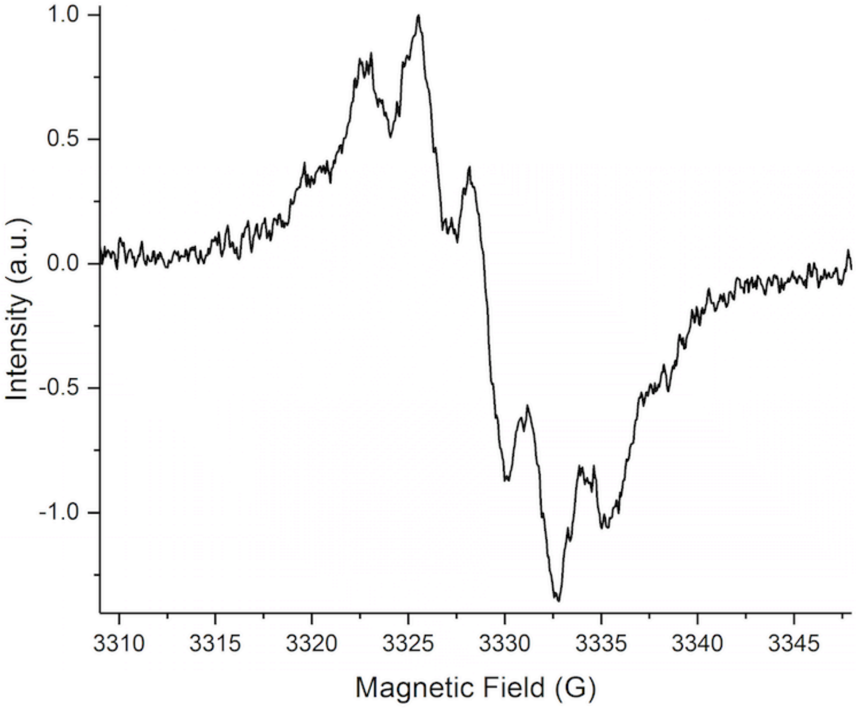


Figure S18. ESR spectra of the system “1b + CTA 2a + IBVE (3a)” in MeCN

*ESR Simulation of the radical generated by irradiation of **1a** in presence of IBVE (**3a**)* with and without CTA **2a**

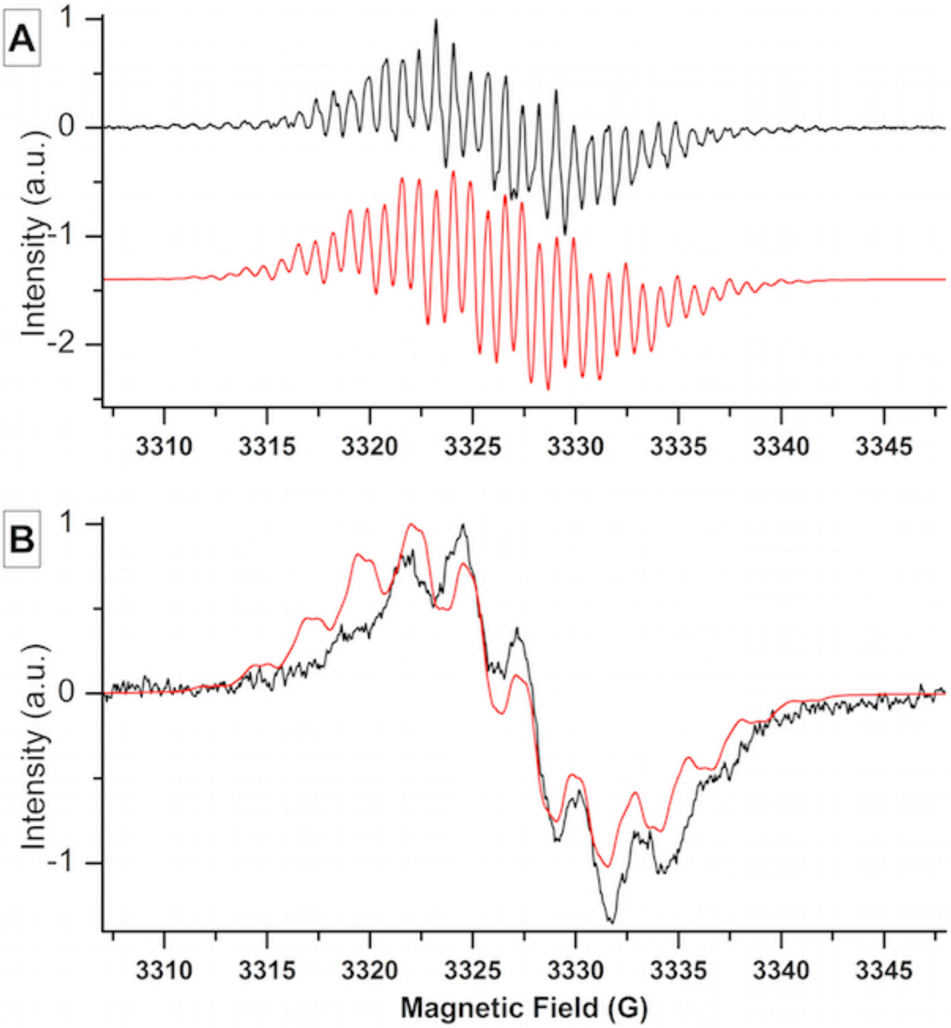


Figure S19. Experimental (black curve) and simulated (red curve) ESR spectra recorded during the polymerization of IBVE (3a) catalyzed by photocatalyst 1b without (A) or with CTA 2a (B). A) Mixture of **1b** and **3a** in MeCN irradiated with blue LEDs; ESR spectrum acquisition: 80 scans accumulation, 2 mW power and M = 0.2 G amplitude modulation. B) Mixture of **1b**, **2a**, and **3a** in MeCN irradiated with blue LEDs; ESR spectrum acquisition: 200 scans accumulation, 2 mW power and M = 1 G amplitude modulation. The simulated (red) curves were generated with the same set of parameters: a1(H) (1x) = 2.57 G, a2(H) (2x) = 0.82 G, a3(H) (2x) = 2.3 G, a4(H) (2x) = 2.6 G, a5(H) (2x) = 2.55 G, a6(H) (4x) = 0.20 G, a7(H) (4x) = 1.75 G, a8(H) (2x) = 3.35 G with a Lorentzian linewidth of 0.27 G. The experimental amplitude modulation was modeled using the Easyspin toolbox.

*Evolution of **1b$^\bullet$** after adding IBVE monomer monitored by ESR spectroscopy*

Radical **1b$^\bullet$** was generated by irradiating a solution of **1b** (2mM) in a mixture of DCM:THF (1:1) with blue LEDs. After 80s of irradiation, a spin concentration of 220 μM was measured by double integration. An excess of IBVE (**3a**) was then added under nitrogen with an air-tight syringe. No major change in the structure of ESR signal was observed (see Figure S20), aside from a decrease of the line width (possibly due to the Heisenberg effect), and no increase of the spin concentration was noted (see inset).

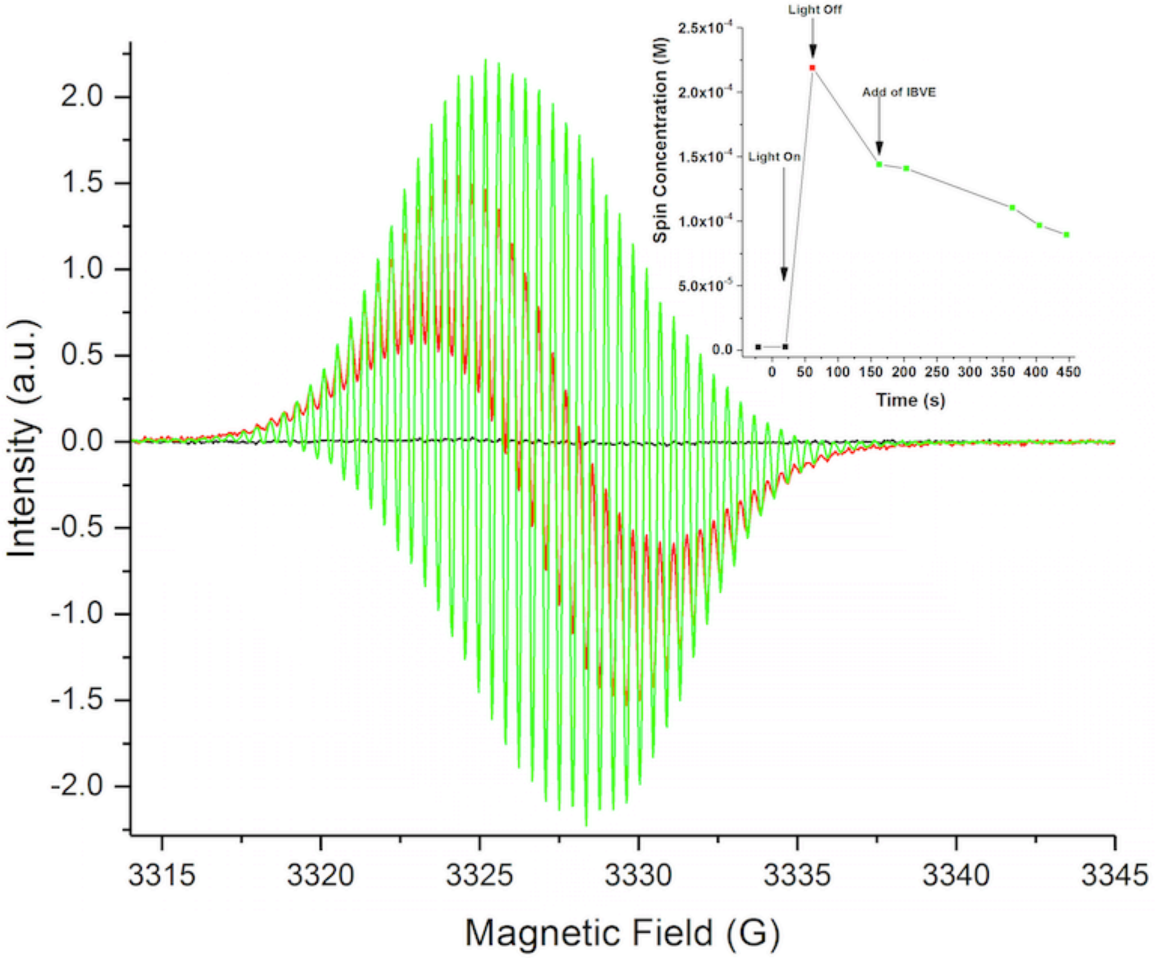


Figure S20. ESR spectrum of 1b and THF before irradiation (black curve), after irradiation (red curve) showing the formation of radical 1b$^\bullet$, and after addition of IBVE (3a) (green curve). The inset shows the evolution of the spin concentration vs time. The arrows indicate when the light was switched on, switched off, and when 3a was added to the ESR tube.

Study of Electron Transfers via UV-Vis Spectroscopy

A solution of **1b** (0.06 mM) and CTA **2a** (30 mM) in DCM (2.0 mL) was prepared and sealed in a nitrogen-filled glove box. The resulting solution was irradiated with blue LEDs for 10 s and a UV-visible spectrum was recorded. This spectrum revealed the apparition of new absorption bands at λ = 515 nm and λ = 550 nm characteristic of **1b**$^\bullet$ radical based on previous reports;[8] the obtained values were compared to the UV-visible spectrum recorded after irradiation of **1b** (0.06 mM) in DCM:THF (2.0 mL, 1:1) (see Table S5 and Figure S21A).

Interestingly, when **1a** was substituted for **1b** in combination with **2a**, no novel absorption bands were recorded, suggesting that **1a**$^\bullet$ is not stable enough under these conditions to be observed by UV-visible spectroscopy. However, bands characteristic of **1a**$^\bullet$ (λ = 358nm and λ = 562 nm) were detected after irradiation of **1a** (0.06 mM) in DCM:THF (1:1), or after single electron reduction with cobaltocene (0.03 mM) (see Table S5 and Figure S21B).[13]

Table S5. Experimental UV-Visible Characteristics for Radicals 1a$^\bullet$ and 1b$^\bullet$

Characterized systems	Solvent	A_{max} (1) (nm)	A_{max} (2) (nm)
1b + CTa **2a**[a]	DCM	515	552
1b + THF[a]	DCM/THF (1:1)	515	552
1a + THF[a]	DCM/THF (1:1)	358	562
1a + Cobaltocene[b]	DCM	355	558

[a] Cuvettes were irradiated with blue LEDs. [b] Reduction of **1a** in the ground state by cobaltocene (E_{red} = –0.91 V vs SCE in DMF).[14]

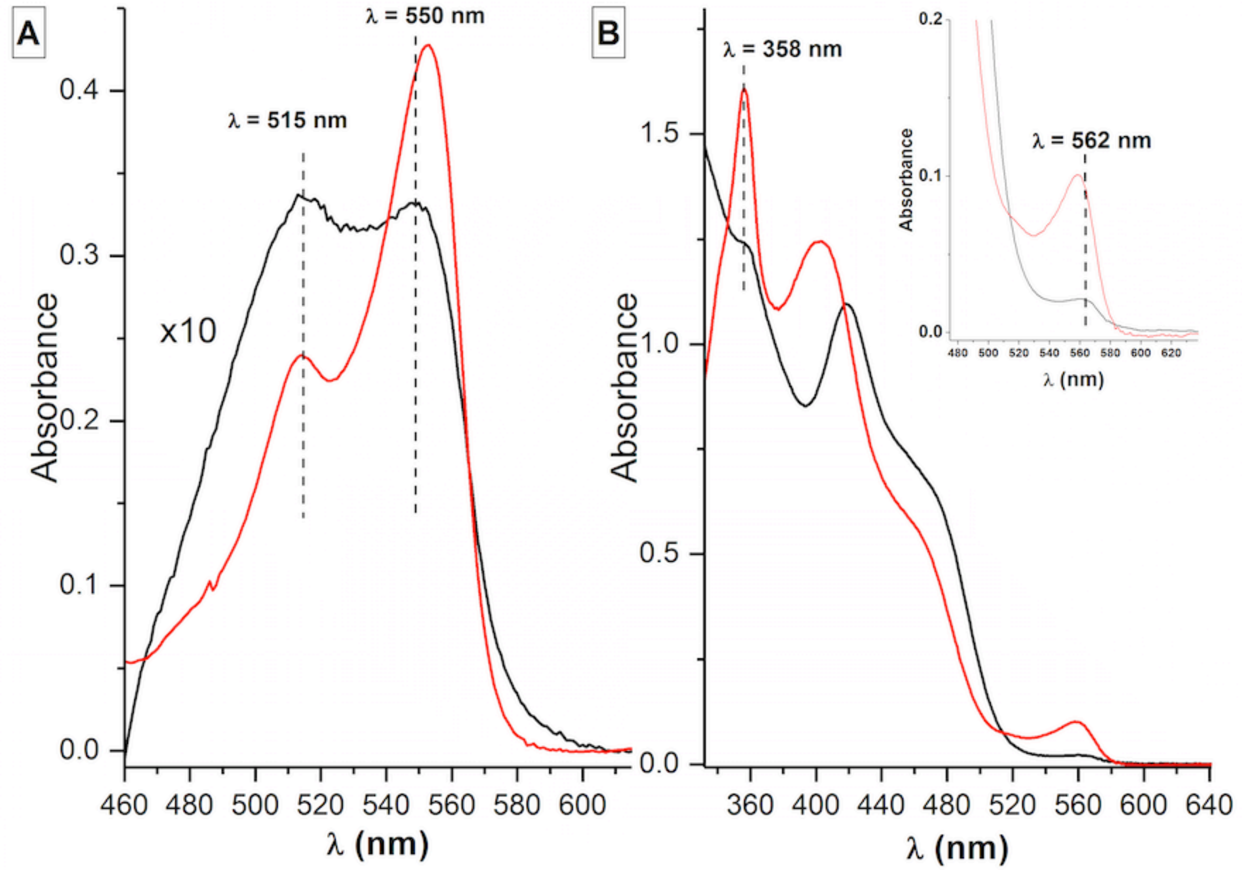


Figure S21. A) UV-Visible absorption spectra obtained for the system: "1b (0.06 mM) + CTA 2a (30 mM)" in DCM (black curve) and the system "1b (0.06 mM) + THF" in DCM (red curve). B) UV-Visible absorption spectra obtained for the system: "1a (0.06 mM) + THF" in DCM (black curve) and comparison with the system "1a + cobaltocene (0.03 mM)" in DCM (red curve).

*Investigation of the formation of a donor-acceptor complex between photocatalysts **1a,b** and monomer **3a** (Figure 12)*

UV-VIS absorption spectra were collected for dilute solutions of **1a** and **1b** in MeCN. Based on known extinction coefficients[15] (ε_{450} = 33000 L•mol^{-1}•cm^{-1} for **1a** and ε_{450} = 26000 L•mol^{-1}•cm^{-1} for **1b** in MeCN) concentrations were calculated to be 58.6 µM for **1a** and 58.4 µM for **1b**. In each cuvette, the concentration of monomer **3a** was gradually increased from 0 M to 1.92 M (see inset of figure S13A,C). A slight bathochromic shift in the band above 400 nm was observed (see Figure S22A,C) revealing a weak new feature present in the absorption spectra of both photocatalysts. This new feature centered at λ = 483 nm for **1a** and at λ = 429 nm for **1b** was attributed to the formation of a donor-acceptor complex between the pyrylium photocatalysts and IBVE (**3a**).[16] The equilibrium constant K_{DA} is defined as K_{DA} = [**DA**]/[**3a**][**1**], where **DA** is assumed to be a binary complex between **3a** and **1**.

According to the method of Benesi-Hildebrand,[17] we determined the value of K_{DA} by linear fitting according to equation S1:

$$\frac{[\mathbf{1}]}{\Delta_{abs}} = \frac{1}{\varepsilon_{\mathrm{DA}} \times K_{\mathrm{DA}}} \times \frac{1}{[\mathbf{3a}]} + \frac{1}{\varepsilon_{\mathrm{DA}}} \quad \text{(eq. S1)}$$

Where ε_{DA} is the molar extinction of the donor-acceptor complex and Δ_{abs} the difference of absorptions with and without **3a**. It should be noted that the Benesi-Hildebrand method is not typically calculated with difference of absorptions, but this slight modification method has been previously used by Romero *et al.* for similar systems.[16] The Benesi-Hildebrand plots are presented in figure S22B,D for **1b** and **1a.** As expected, a linear relation was observed and the parameters used for the fit are reported in Table S6. A value of K_{DA} = 0.06 for **1a** and K_{DA} = 0.19 for **1b** was determined.

Table S6. Linear Fit Data for the Benesi-Hildebrand Plots (Figure S22B and S22D)

Photocatalyst	**Intercept (M)**	**Slope (M^2)**	**AdjRsquare**	**ε_{DA} ($L \cdot mol^{-1} \cdot cm^{-1}$)**	**K_{DA}**
1a	7×10^{-5}	1.2×10^{-3}	0.996	15110	0.06
1b	2.1×10^{-4}	1.1×10^{-3}	0.973	4890	0.19

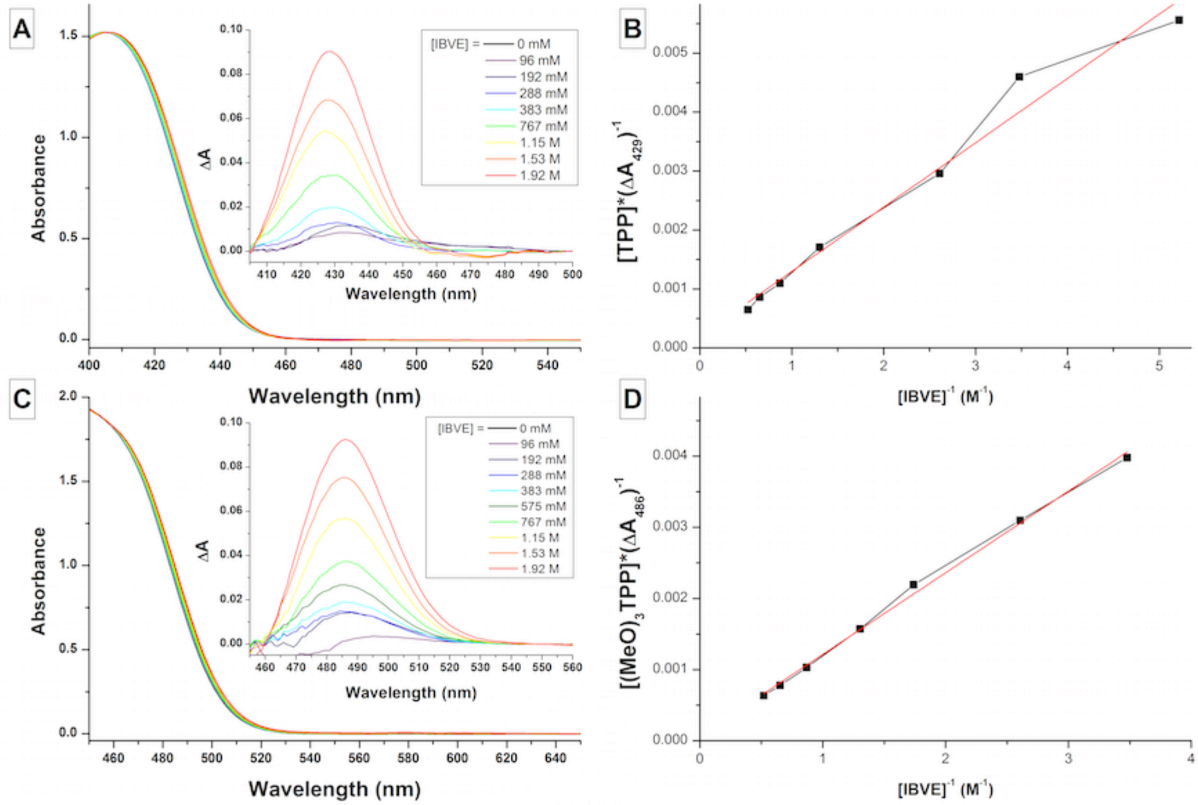
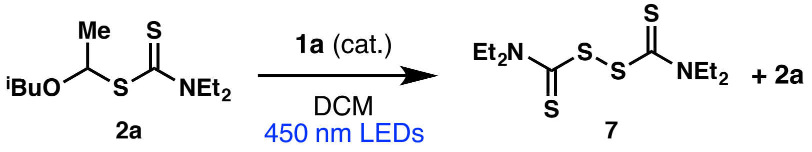


Figure S22. UV-Vis Absorption spectra recorded under air atmosphere in MeCN for (A) 1b with different concentrations of IBVE (3a) and (C) 1a with different concentrations of IBVE (3a). The inset shows Δ_{abs}. Benesi-Hildebrand plots for 1b and 1a are shown in Figure S22B and D, respectively. Slope and intercept values are reported in Table S6.

In parallel, we applied the method of Nash, which accounts for the absorbance of **1**.[18] We calculated K_{DA} = 0.14 for both **1a** and **1b** with this other method, which is in in the same order of magnitude as the constants calculated with the Benesi-Hildebrand method.

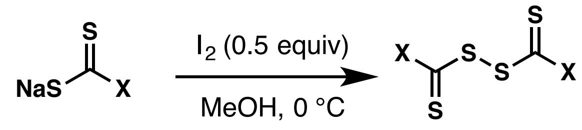
Isolation and Synthesis of Disulfides 7, 8 and Crossover Experiment

<u>*Isolation of thiuram disulfide **7** with the typical conditions of polymerization*</u>



In a nitrogen-filled glove box, an oven-dried one-dram vial was equipped with a stir bar and charged with CTA **2a** (5.0 mg, 0.02 mmol, 1 equiv), and 0.2 mL of a stock solution of photocatalyst **1a** in DCM (2.0 mM, 0.40 µmol, 2 mol%). The vial was sealed with a containing a teflon septum under an atmosphere of nitrogen, placed next to blue LED strips (~450 nm), and stirred while cooling by blowing compressed air over the reaction vial for 12 h. The solvent was then evaporated to dryness *in vacuo* and purification by preparative TLC (1.5:8.5 EtOAc:hexanes) afforded **7**, as well as some recovered **2a**. The spectroscopic data for **7** were consistent with those reported in the literature[19] and to those obtained for a synthetic sample of **7** (see below).

__Preparation of thiuram disulfide 7 and bis(ethylsulfanylthiocarbonyl) disulfide 8__



X = NEt_2 or SEt

7: X = NEt_2
8: X = SEt

Sodium diethyldithiocarbamate (500 mg, 2.22 mmol, 1.0 equiv) was dissolved in methanol (40 mL) and cooled to 0 °C. A solution of iodine (282 mg, 1.11 mmol, 0.5 equiv) in MeOH (10 mL) was added dropwise. The solution should remain pale purple over the course of addition. The solvent was concentrated *in vacuo*, the residue was dissolved in Et_2O (30 mL), and saturated aqueous sodium thiosulfate (30 mL) was added. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic phases were dried over $MgSO_4$, and evaporated to dryness *in vacuo*. The yellow oil was further purified by column chromatography (SiO_2, gradient from 10:0 to 8:2 hexanes:ethyl ether) to yield **7** as an off-white solid (314 mg, 95%). The spectroscopic data for **7** were consistent with those reported in the literature.[19] ^1H NMR ($CDCl_3$, 500 MHz) δ 4.10–3.93 (m, 8 H), 1.52–1.43 (m, 6 H), 1.36–1.27 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ 192.9, 52.2, 47.8, 13.6, 11.6 ppm.

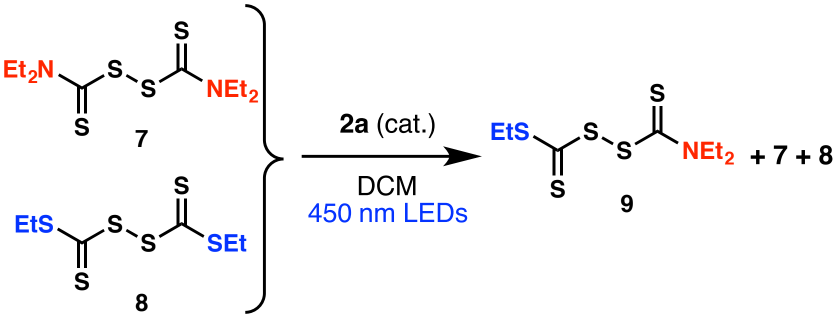
Sodium ethyltrithiocarbonate (400 mg, 2.50 mmol, 1.0 equiv) was dissolved in methanol (15 mL) and cooled to 0 °C. A solution of iodine (317 mg, 1.25 mmol, 0.5 equiv) in MeOH (5 mL) was added dropwise. The solution should remain pale purple over the course of addition. The solvent was concentrated *in vacuo*, the residues were dissolved in Et_2O (30 mL), and saturated aqueous sodium thiosulfate (30 mL) was added. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic phases were dried over $MgSO_4$, and evaporated to dryness *in vacuo*. The dark yellow oil was further purified by column chromatography (SiO_2, hexanes) to yield **8** as a yellow oil (297 mg, 87%). The spectroscopic data for **7** were consistent with those reported in the literature.[20] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.31 (q, J = 9.5 Hz, 4 H), 1.36 (t, J = 9.0 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 221.5, 32.8, 12.5 ppm.

Table S7. Cationic Polymerization with Disulfide 7

Conditions	Conv. (%)	Time	M_n(exp) (kg/mol)	M_n(theo) (kg/mol)	$Đ$
7 (1 equiv), **3a** (100 equiv)	20	2 h	31.5	2.0[a]	1.77
CTA **2a** (1 equiv), **7** (1 equiv), **3a** (100 equiv)	13	2 h	2.67	1.3[b]	1.28

[a]Based on **7**. [b]Based on CTA **2a**.

*Crossover experiment with disulfides **7** and **8***



A flame-dried one-dram vial was equipped with a stir bar and charged with **7** (5.0 mg, 0.017 mmol, 1 equiv), **8** (4.6 mg, 0.017 mmol, 1 equiv), 0.2 mL of a stock solution of photocatalyst **1a** in DCM (2.0 mM, 0.40 µmol, 2 mol%), and DCM (0.3 mL) under nitrogen. The solution was degassed by three freeze-pump-thaw cycles, placed 2 cm away from the 9W Kobi Electric (460–470 nm) bulb outside, and stirred while cooling by blowing compressed air over the reaction vial for 12 h. The solvent was then evaporated to dryness *in vacuo*. NMR analysis of the crude mixture the revealed characteristics peaks of mixed disulfide **9** in addition to those of **7** and **8**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.03–3.94 (m, 2 H, N–CH_2CH$_3$), 3.87–3.81 (m, 2 H, N–CH'_2CH'$_3$), 3.21 (q, *J* = 9.5 Hz, 2 H, S–CH_2CH$_3$), 1.27 (t, *J* = 9.0 Hz, 3 H, S-CH$_2$CH_3).

Determination of the Quantum Yields of Polymerization for 1a and 1b Using Ferrioxalate Actinometry

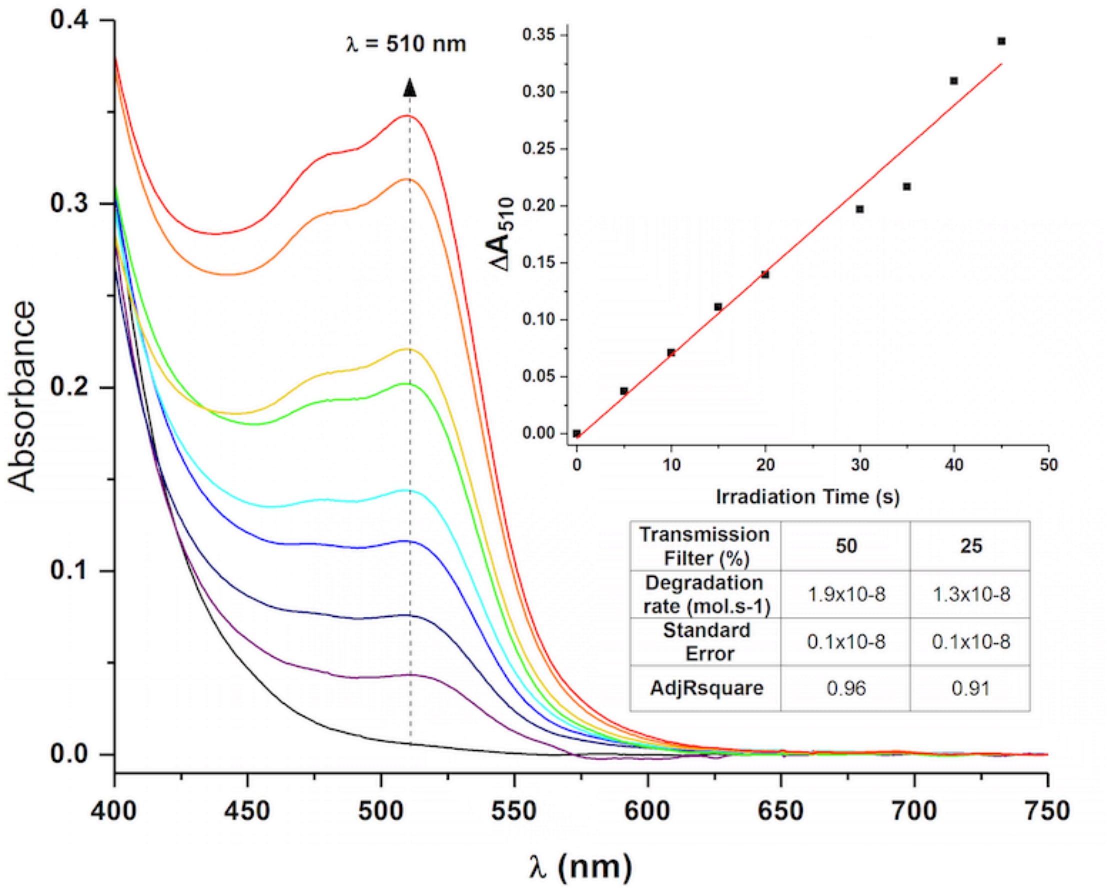
The quantum yield of polymerization for **1a** and **1b** was deduced by comparison of the early rate of IBVE (**3a**) polymerization and the rates of photodegradation of potassium ferrioxalate ([Fe(III)]), according to equation S2:

$$\Phi_{\mathbf{1}} = \Phi_{[\mathrm{Fe(III)}]} * \frac{q(\mathbf{1})}{q([\mathrm{Fe(III)}])} * \frac{\left(1-10^{-A_{[\mathrm{Fe(III)}]}}\right)}{\left(1-10^{-A_1}\right)} \quad (\mathrm{eq.\,S2})$$

where q(**1**) and q([Fe(III)]) are the conversion rate (in mol•s^{-1}) of **3a** during polymerization and of [Fe(III)] during photodegradation, respectively. The corrective factor accounts for the real flux of absorbed photon by the actinometer and photocatalysts **1** and therefore depends on the absorbance of both species at 455 nm. $\Phi_{[\mathrm{Fe(III)}]}$ is the known quantum yield of potassium ferrioxalate decomposition. A reported value of $\Phi_{[\mathrm{Fe(III)}]}$ of 0.86 at 457 nm was used in the calculations.[21]

The degradation rate q([Fe(III)]) was determined according to the protocol described by Kuhn *et al.*[22] A solution of potassium ferrioxalate (300 μl, 0.15 M) in aq. H_2SO_4 (0.05 M) in a 1 dram vial was irradiated with a 9W Kobi Electric (460–470 nm) bulb placed 2 cm away from the vial, with a 25% or 50% transmission neutral density filter placed in between the vial and the bulb. Aliquots (24 μl) were taken every 5 seconds and added to vials containing a solution of phenanthroline (96 μl, 0.01 % weight), sodium propionate buffer (12 μl, 0.6 M in aq. H_2SO_4 (0.19 M), and water (54 μl). After 1 h in the dark, the concentration of the resulting Fe(II) phenantroline complex present in each solution was measured by UV-visible spectroscopy (absorption at 510 nm, ε_{510} = 11100 L.mol^{-1}.cm^{-1}) (see Figure S23 for 50% transmission). The degradation rate q([Fe(III)]) was then determined by linear fitting (see the inset of Figure S23).

The quantum yields of polymerization were estimated to be about six monomer additions per photon absorbed for photocatalyst **1a** and about 35 monomer additions/photon for **1b**.



Transmission Filter (%)	50	25
Degradation rate (mol.s-1)	1.9x10-8	1.3x10-8
Standard Error	0.1x10-8	0.1x10-8
AdjRsquare	0.96	0.91

Figure S23. Ferrioxalate actinometry experiments using a 50% transmission filter. UV-visible absorption spectra of the phenanthroline/[Fe^{II}] complex recorded during the photodegradation of the [Fe^{III}] complex were recorded from aliquots taken every 5 s. In the inset, the difference $\Delta A_{510}=A_{510}(t)–A_{510}(t = 0\ s)$ is plotted vs irradiation time and the linear fit is depicted. Resulting fit data for both 25% and 50% filters are shown in the inset table.

Procedure for On/Off Photocontrolled Cationic Polymerization of Isobutyl Vinyl Ether (Figure 14)

In a nitrogen-filled glove box, an oven-dried 20 mL scintillation vial was equipped with a stir bar and charged with isobutyl vinyl ether (0.26 mL, 2.0 mmol, 50 equiv), 0.2 mL of a stock solution of **1a** or **1b** in DCM (2.0 mM, 4.0 μmol, 0.02 mol% relative to IBVE), 0.04 mL of a stock solution of **2a** in DCM (1 M, 0.04 mmol, 1.0 equiv), and benzene (15 μL, 0.17 mmol, 4.25 equiv) as an internal standard for NMR. The vial was sealed with a cap containing a teflon septum under an atmosphere of nitrogen, placed 2 cm away from the 9W Kobi Electric (460–470 nm) bulb outside of the glove box, and stirred while cooling by blowing compressed air over the reaction vial. Following the appropriate amount of reaction time, aliquots for NMR and GPC analysis were taken under positive pressure of nitrogen. Aliquots were taken after 30 min (5 min respectively) intervals under positive nitrogen pressure and subjected to ^{1}H NMR and GPC analysis. The vial was covered in aluminum foil during “off” periods. The GPC traces of all aliquots and the development of M_n vs. time are depicted in Figures S15 and S16.

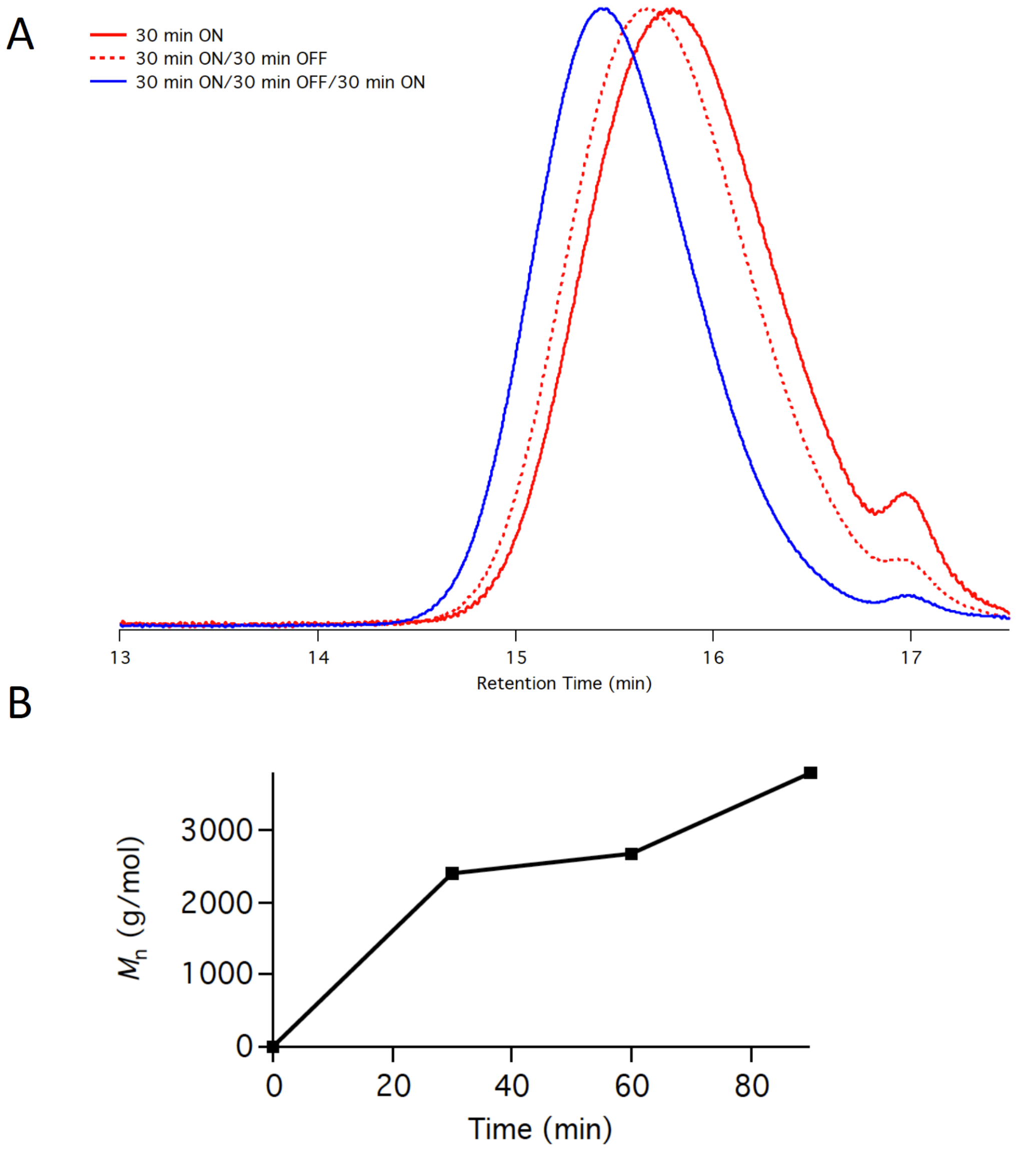


Figure S24. (A) GPC traces of aliquots and (B) M_n vs. time development of On/Off-Experiment (Figure 14a).

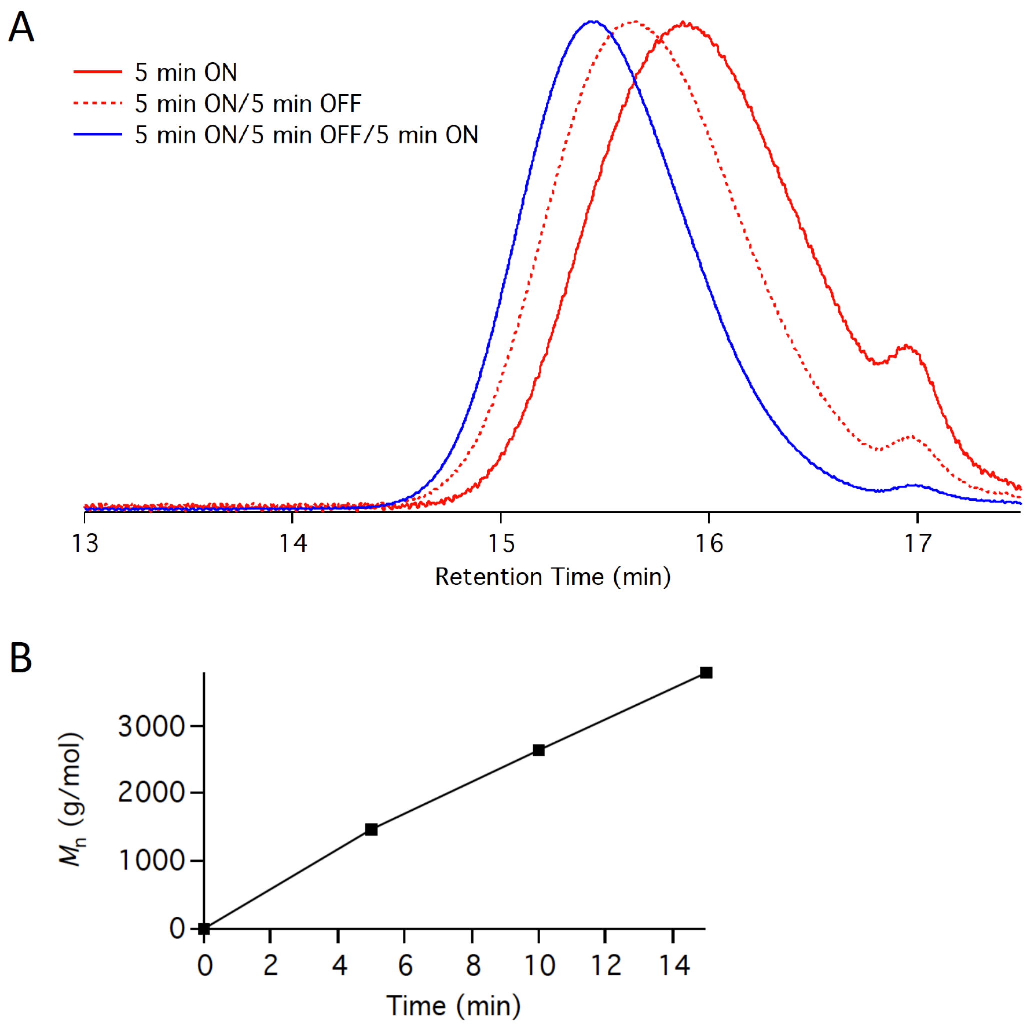


Figure S25. (a) GPC traces of aliquots and (b) M_n vs. time development of On/Off-Experiment (Figure 14b).

Study of the Catalyst Turnover and Chain-End Capping

*Investigation of the catalyst turnover through oxidation by thiuram disulfide **7** (Figure 15)*

In a nitrogen-filled glove box, **1a** (10.0 mg, 0.02 mmol, 1 equiv) was dissolved in MeCN (1 mL) in an oven-dried vial. A solution of cobaltocene in MeCN (0.9 mL, 0.02 M, 0.018 mmol, 0.9 equiv) was added to the solution of **1a**. A small excess of **1a** compared to cobaltocene was used to ensure full oxidation of cobaltocene. Aliquots of this solution were taken for ESR and UV-visible analysis (Figure 15a,b, red curves). Then, 0.1 mL of the solution were added to disulfide **7** (6.0 mg, 0.02 mmol, ~20 equiv) and aliquots of the mixture were taken after 5 min for ESR and UV-visible analysis (Figure 15a,b, green curves).

This study clearly demonstrates that **1a**$^{\bullet}$ is oxidized by thiuram disulfide **7,** which regenerates **1a**.

Investigation of a potential electron transfer between ***1a***$^{\bullet}$ *and CTA* ***2a***

In a nitrogen-filled glove box, **1a** (10.0 mg, 0.02 mmol, 1 equiv) was dissolved in MeCN (1 mL) in an oven-dried vial. A solution of cobaltocene in MeCN (0.9 mL, 0.02 M, 0.018 mmol, 0.9 equiv) was added to the solution of **1a**. A small excess of **1a** compared to cobaltocene was used to ensure full oxidation of cobaltocene. Aliquots of this solution were taken for ESR and UV-visible analysis (Figure S26a,b, red curves). Then, 0.1 mL of the solution were added to CTA **2a** (5.0 mg, 0.02 mmol, ~20 equiv) and aliquots of the mixture were taken after 5 min for ESR and UV-visible analysis (Figure S26a,b, green curves).

This study clearly demonstrates that **1a**$^{\bullet}$ does not react with CTA **2a**.

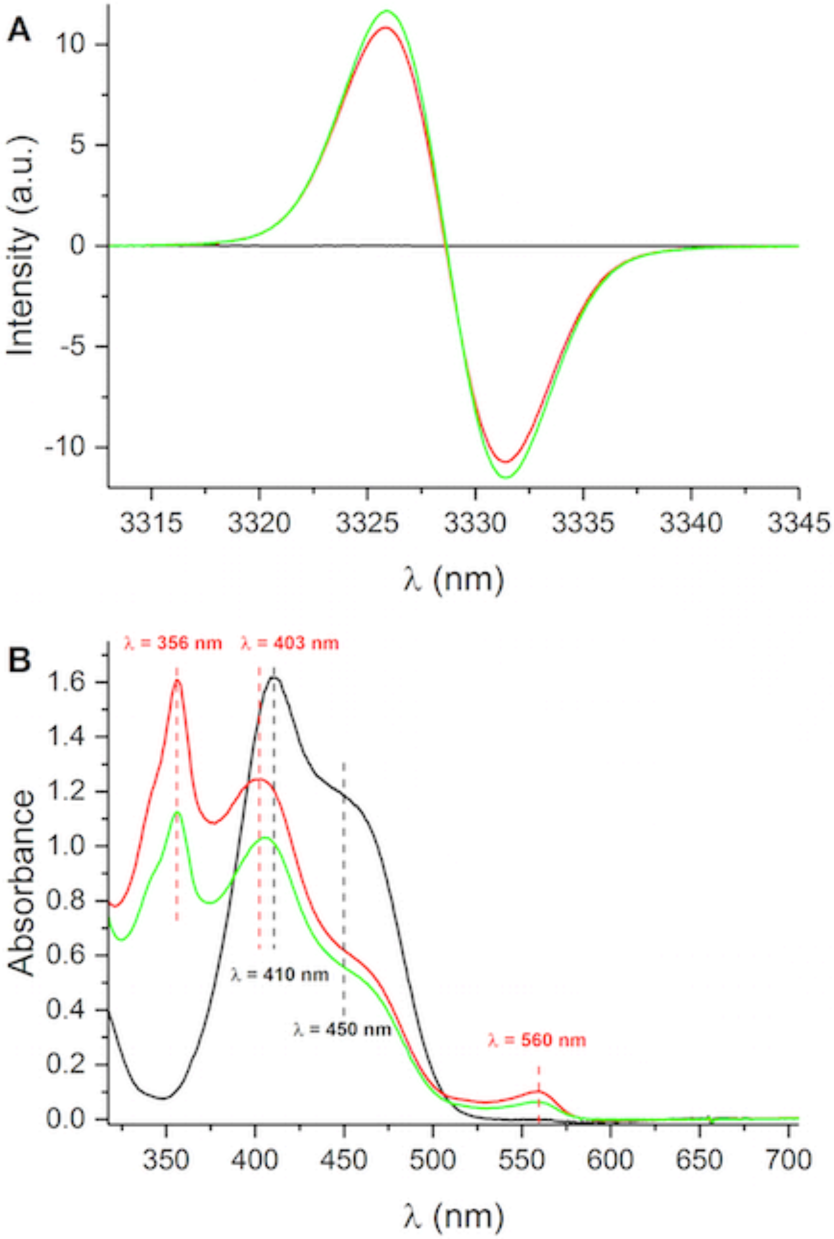


Figure S26. Reduction of 1a to $1a^{\bullet}$ with $Co(C_5H_5)_2$, followed by addition of CTA 2a: (a) ESR spectra of 1a (in black), $1a^{\bullet}$ after addition of $CoCp_2$ (in red), and $1a^{\bullet}$ after addition of CTA 2a (in green) (No changes observed). (b) UV-visible spectra of 1a (in black), $1a^{\bullet}$ after addition of $Co(C_5H_5)_2$ (in red), and $1a^{\bullet}$ after addition of 2a (in green) (No changes observed).

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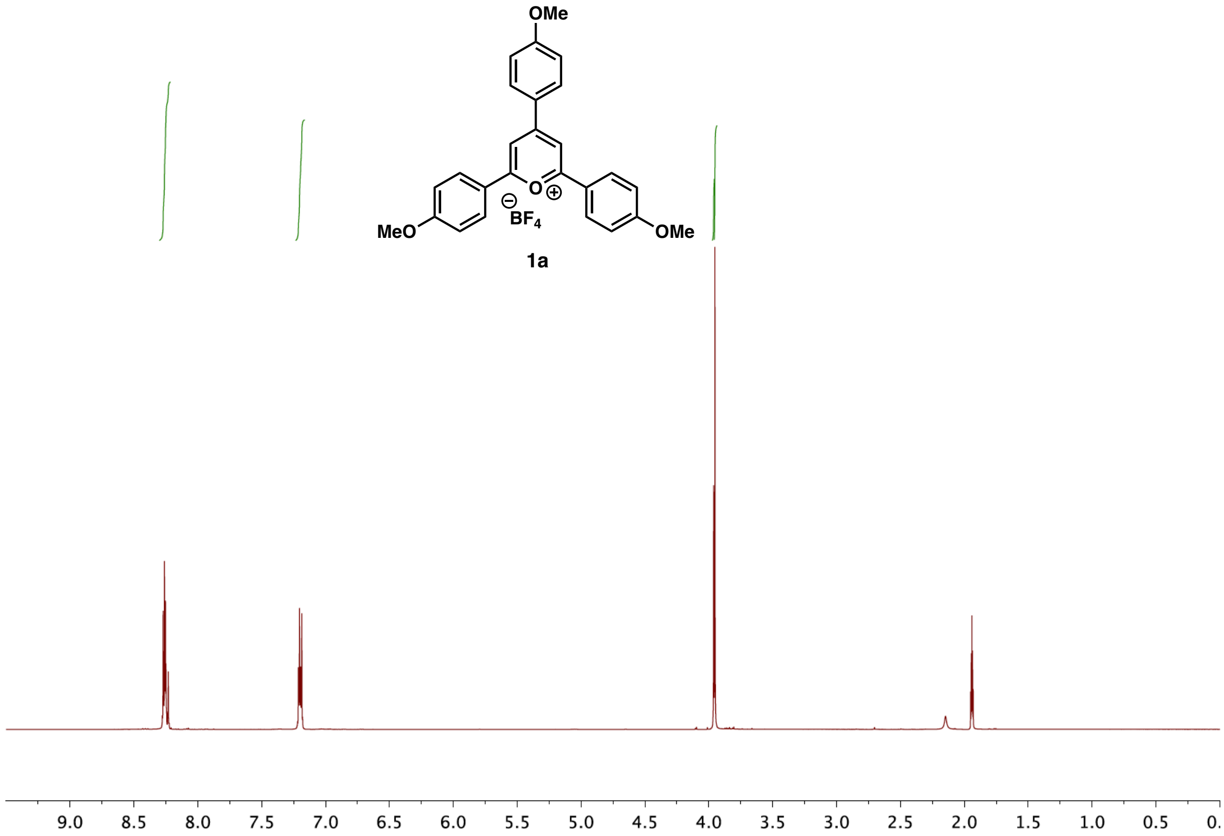

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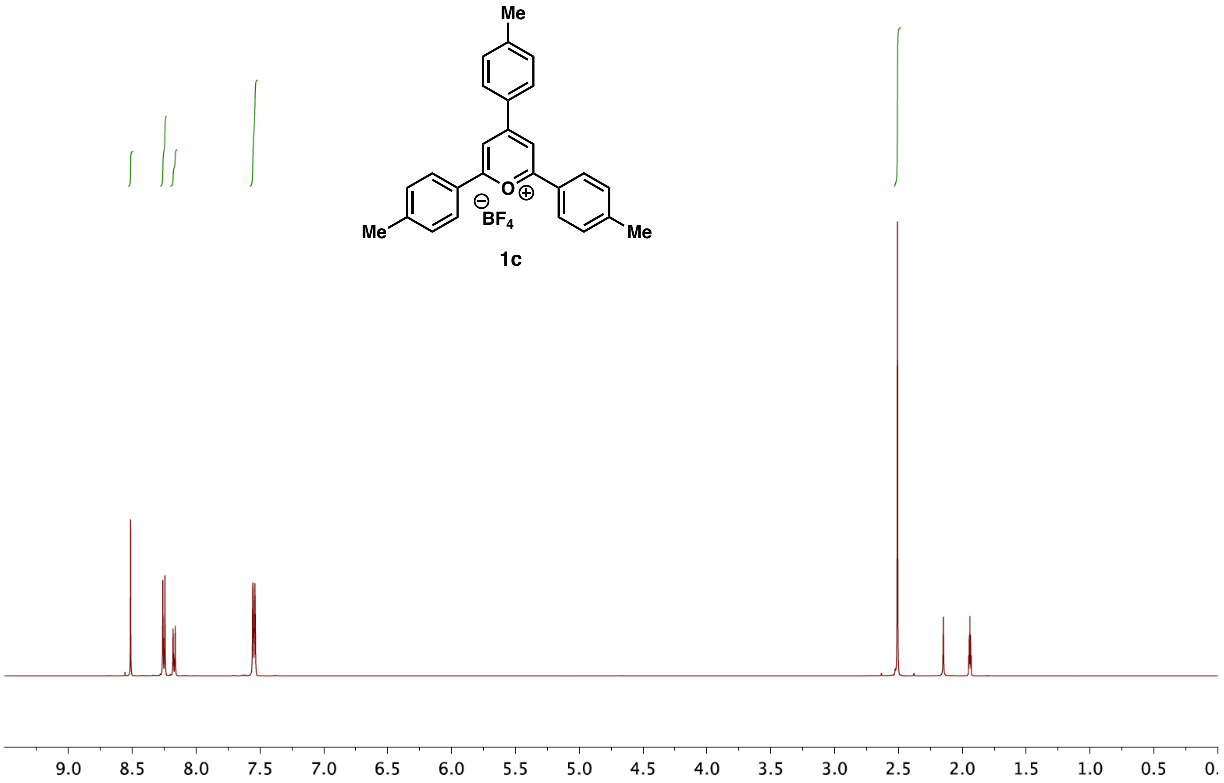

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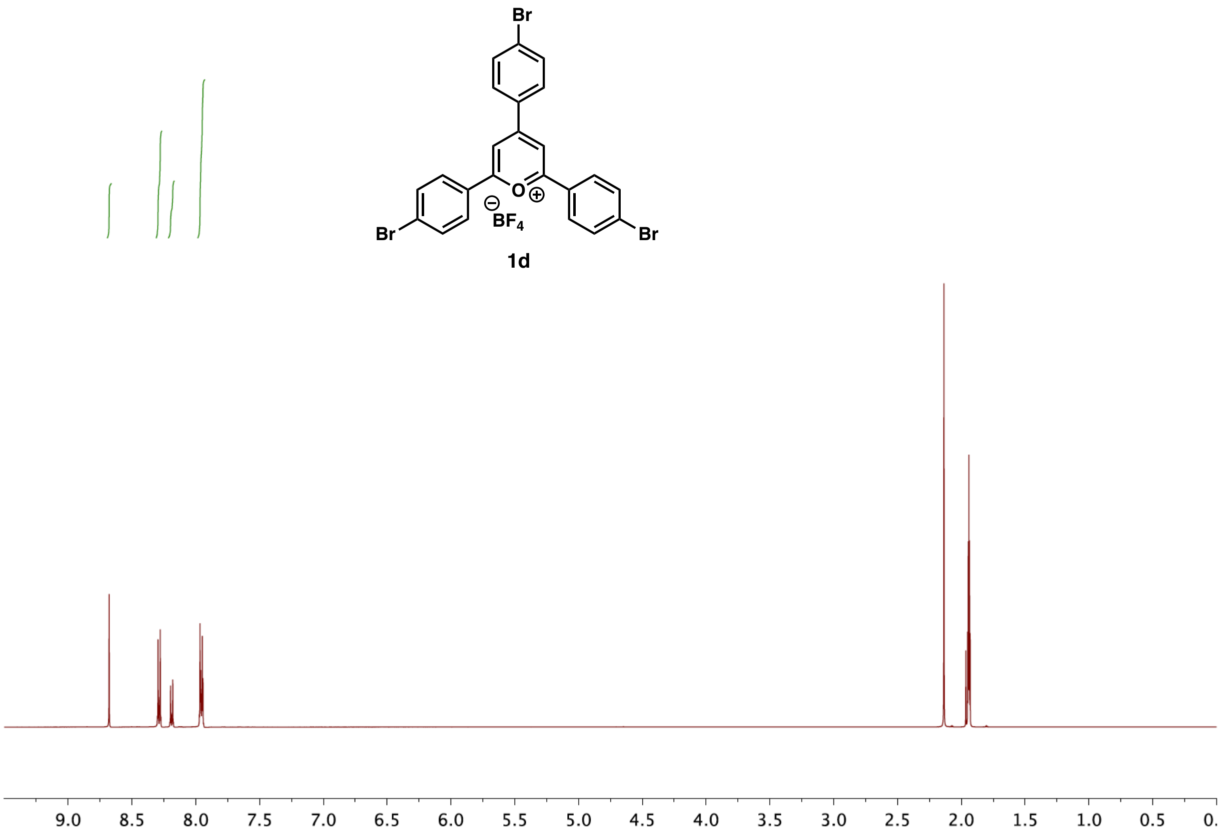
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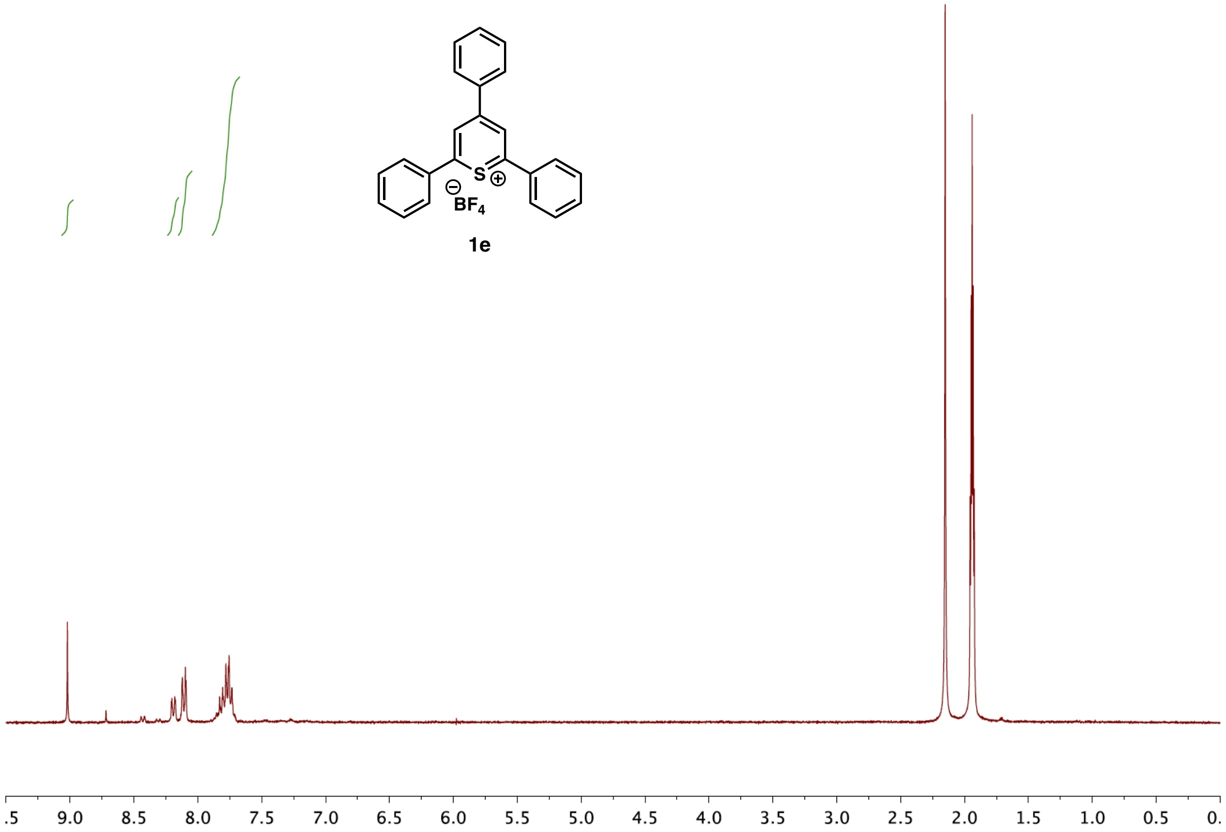
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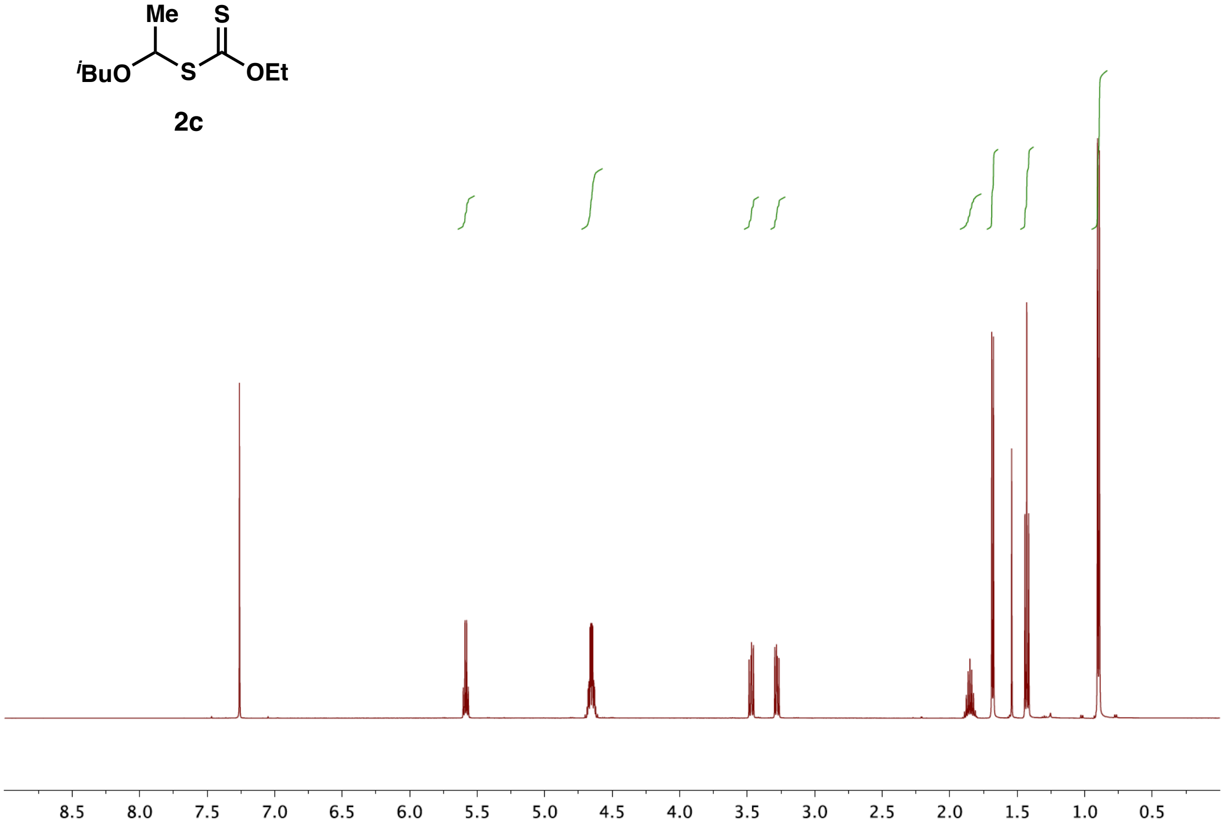
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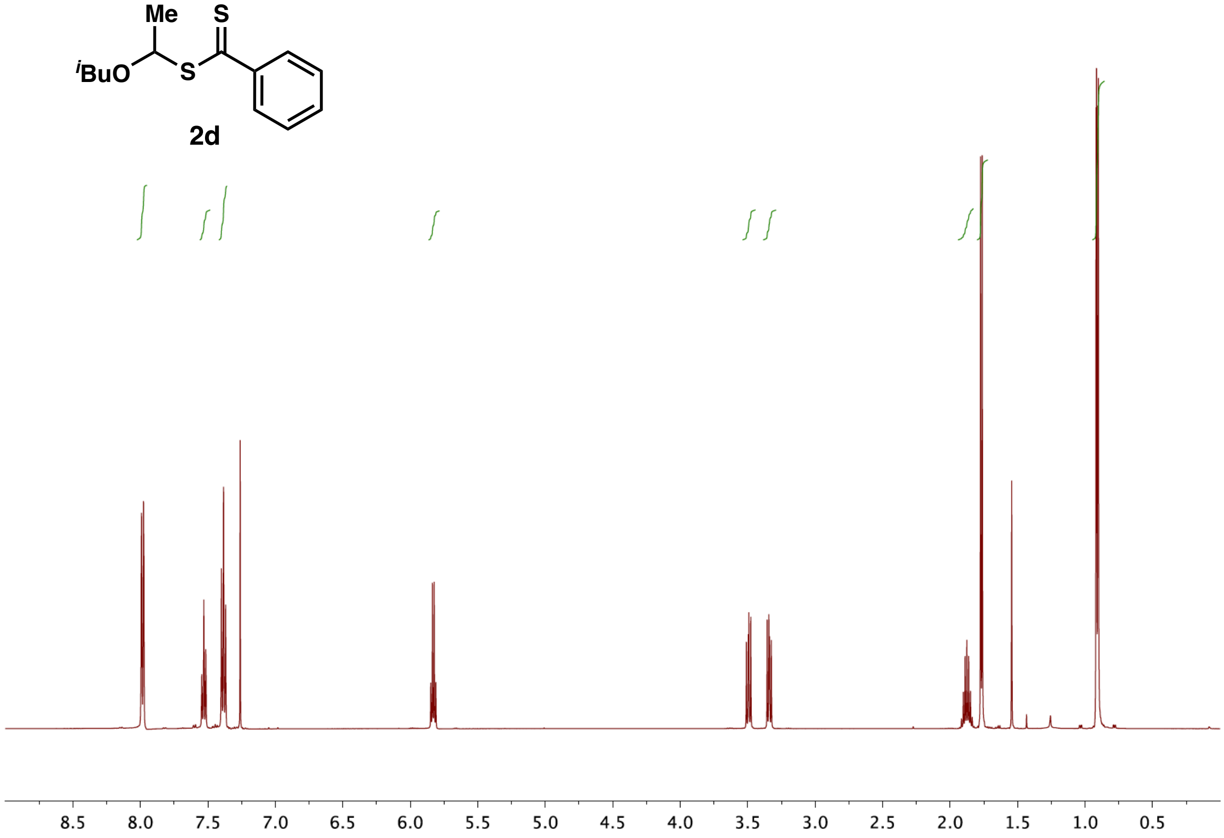
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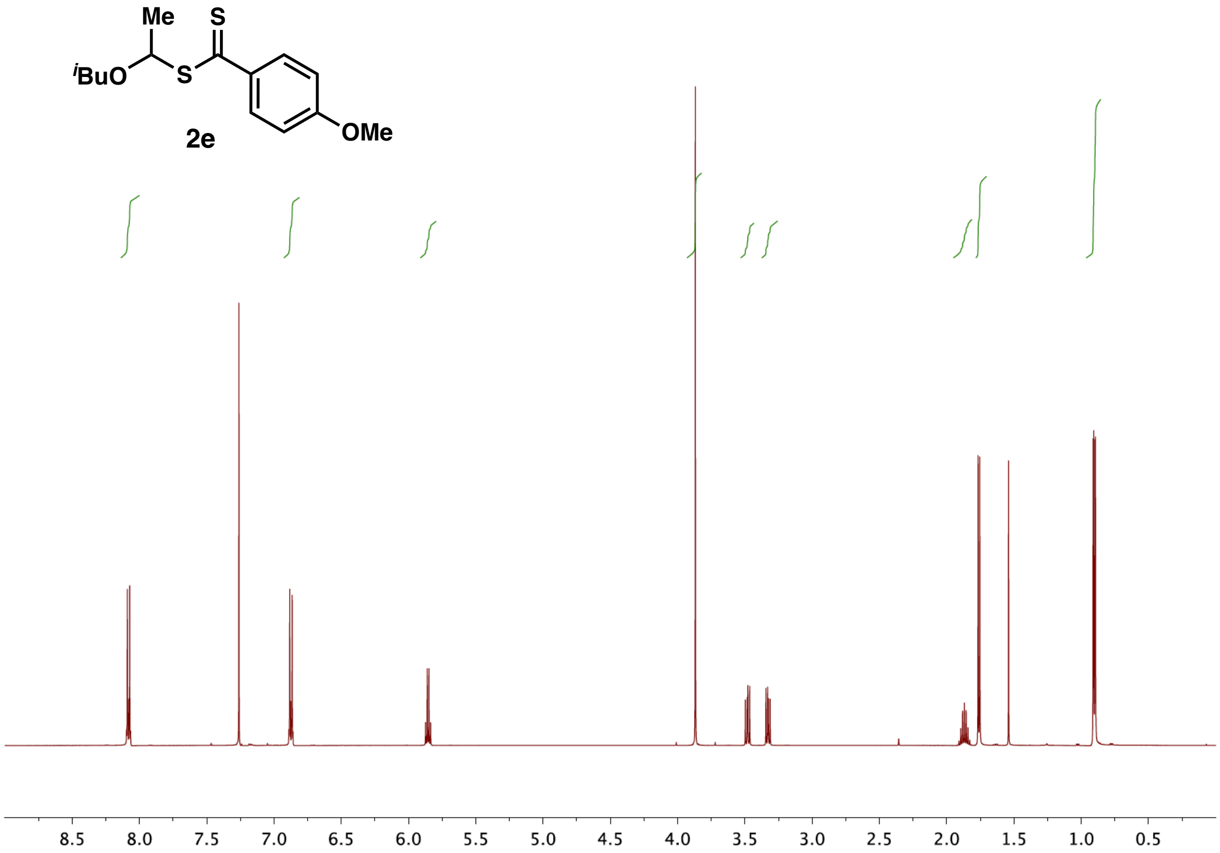
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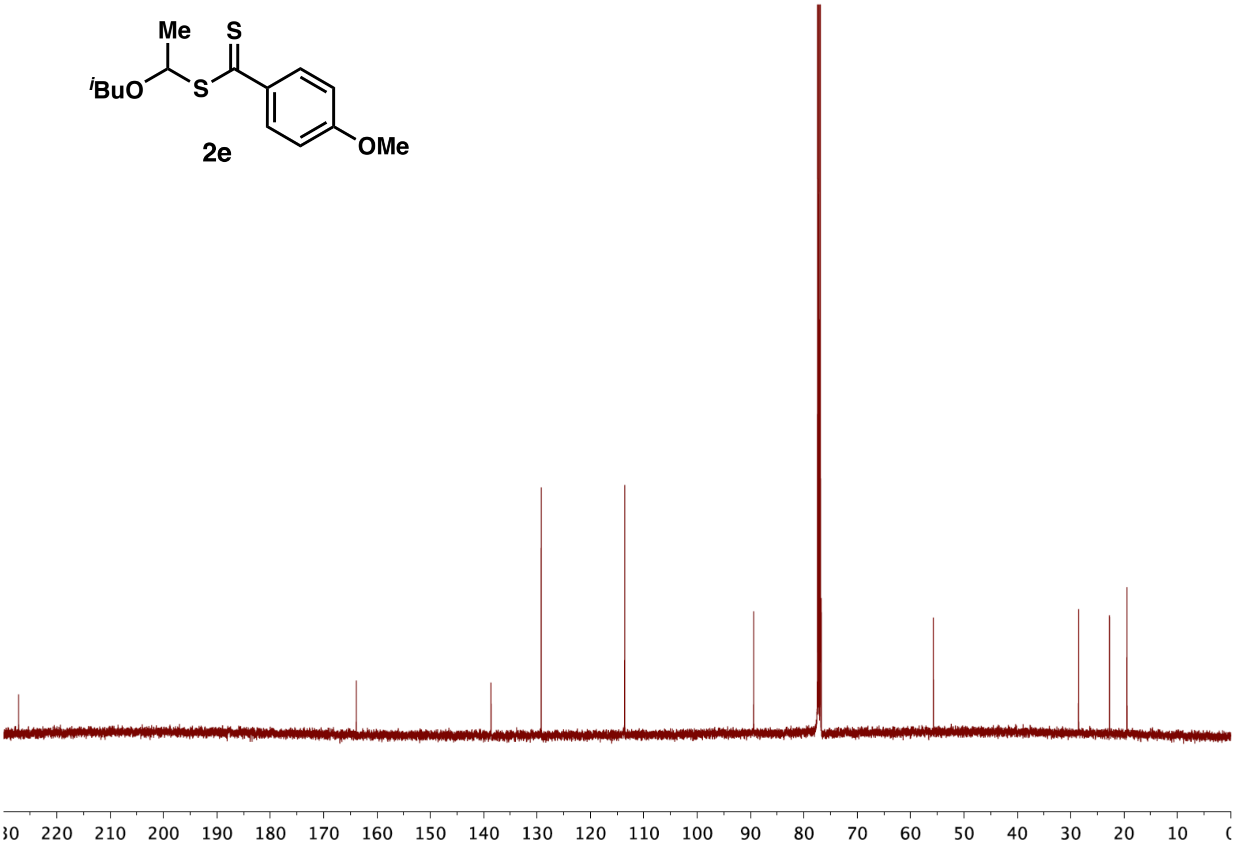
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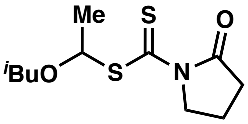

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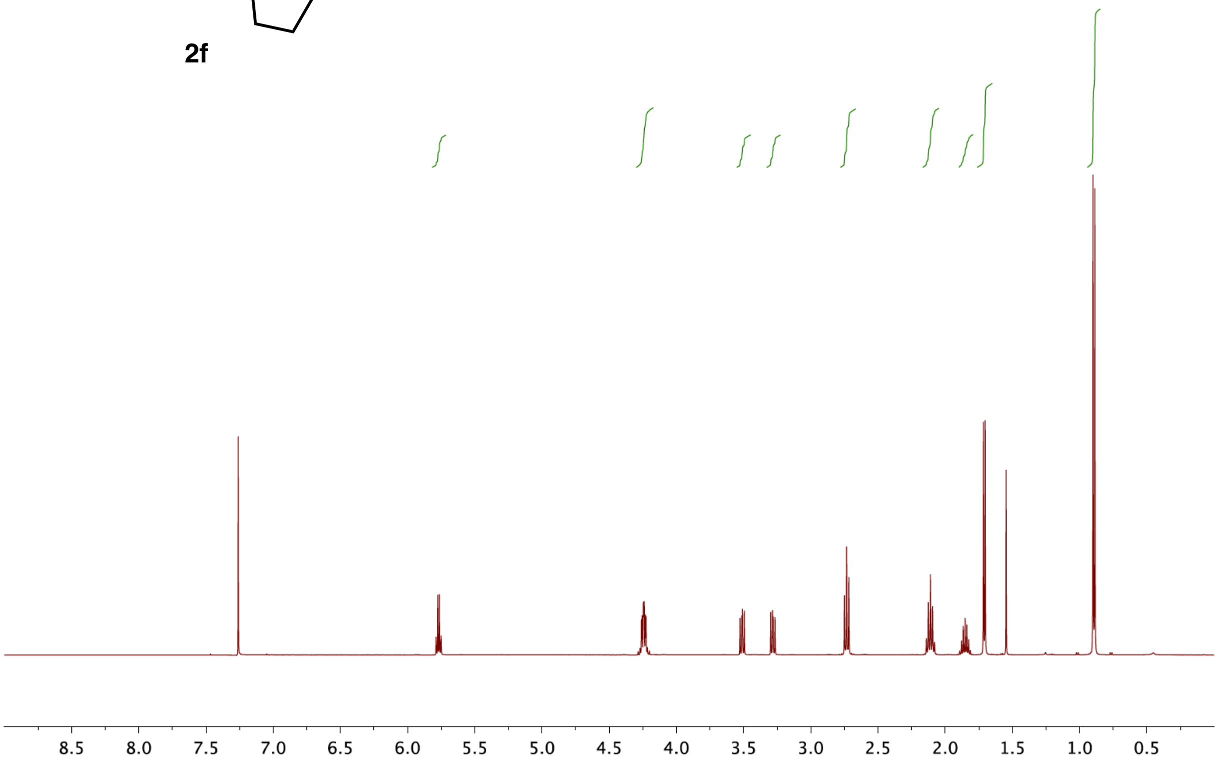

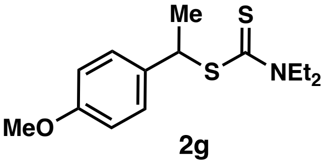
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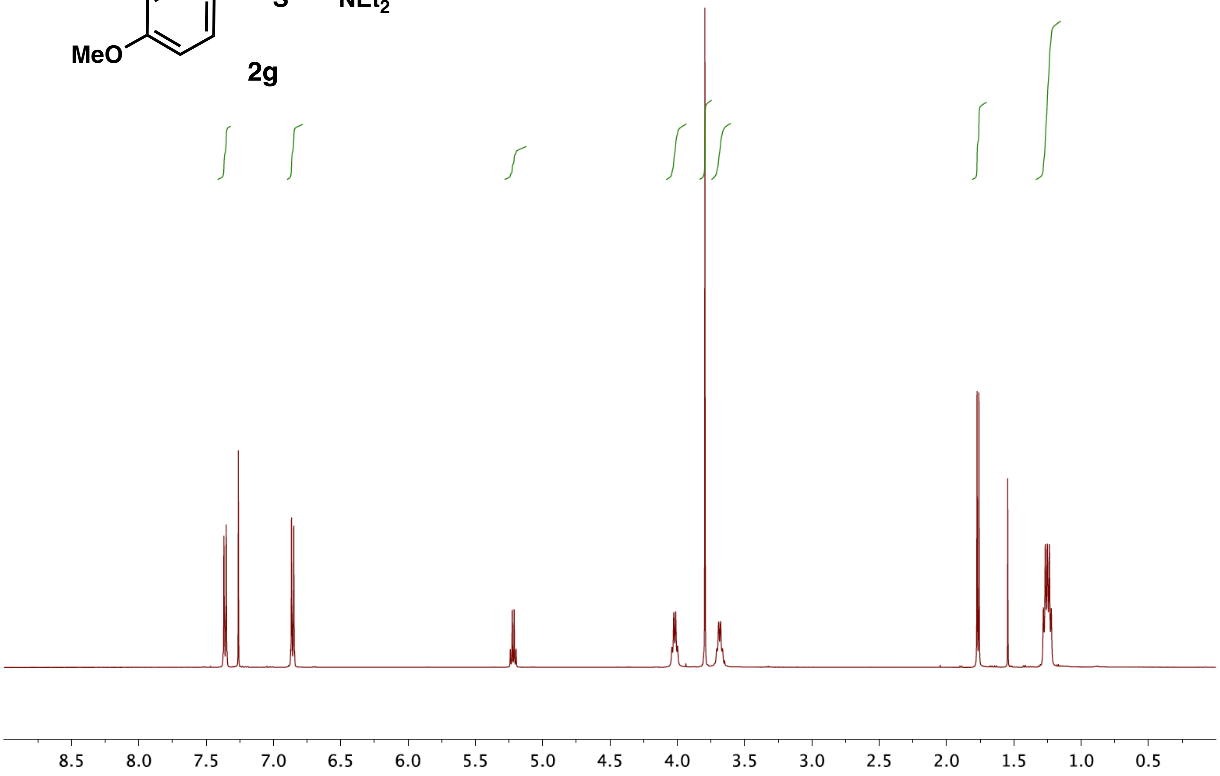
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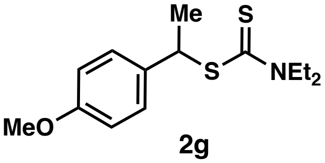
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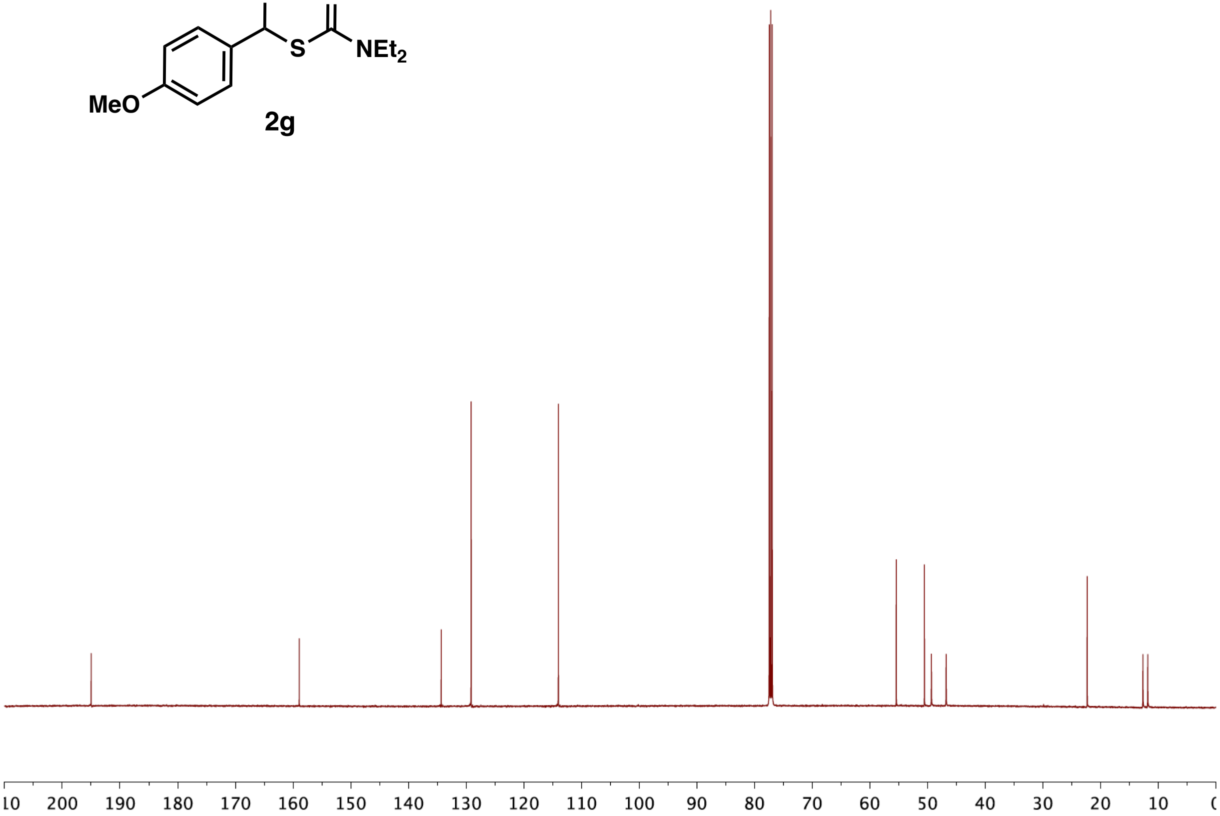
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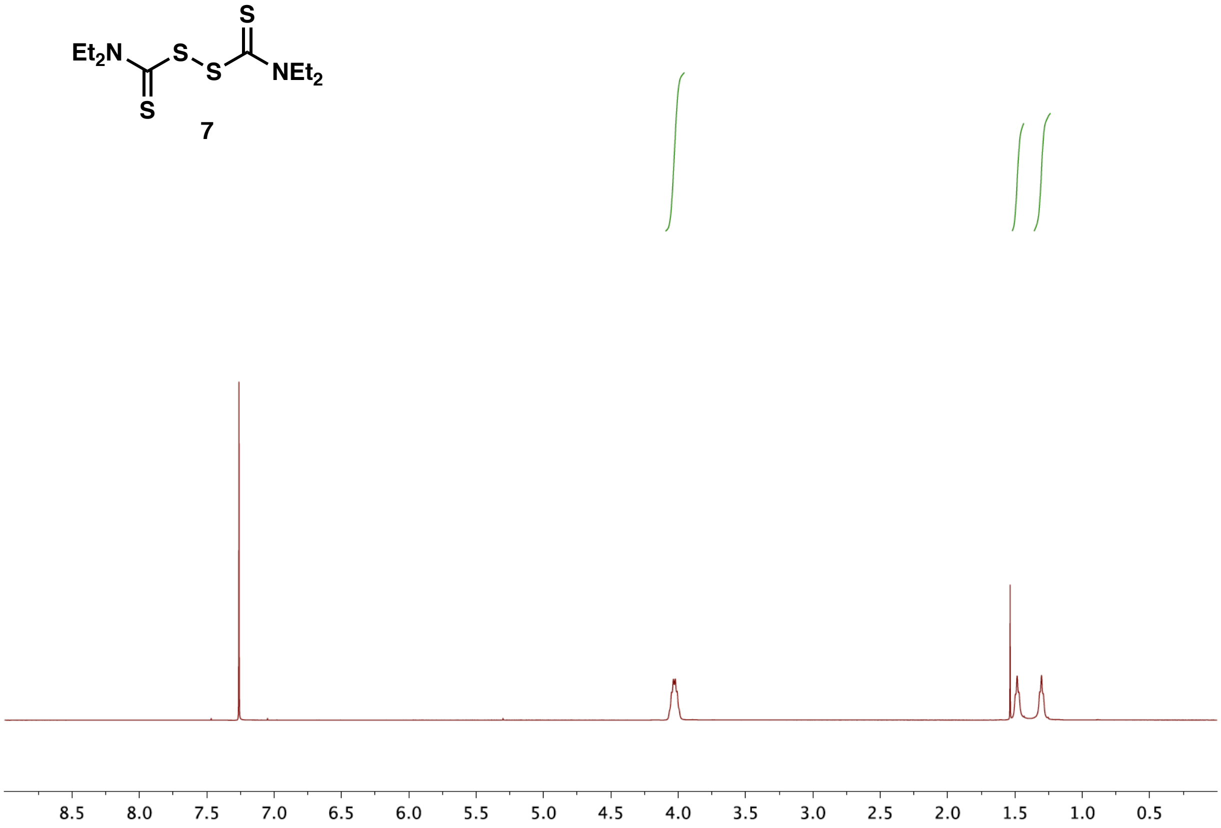
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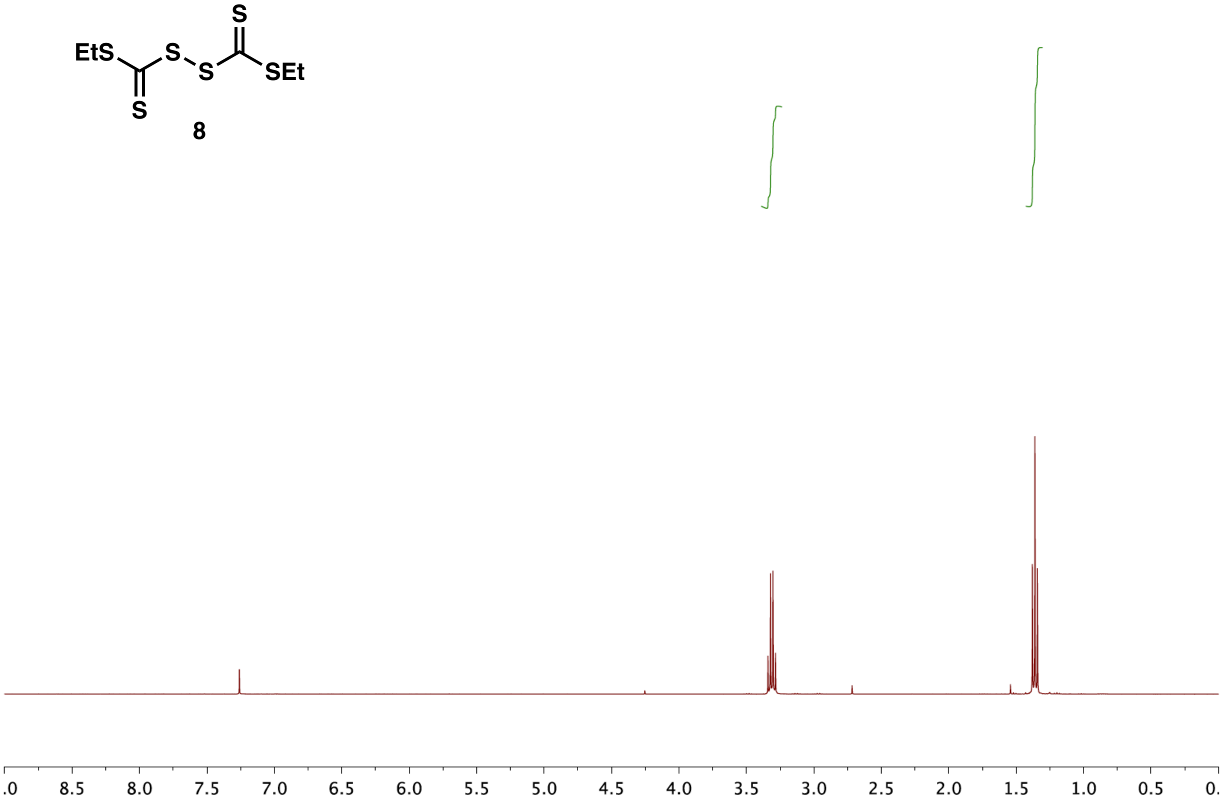
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