Supporting Information for

Electron Donor-Acceptor Complex-Driven Strategy Enables Initiation of Photoiniferter RAFT Polymerization from Amines, Carboxylic Acids and Alcohols

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1. General information

Materials

All solvents and commercial reagents were purchased from Sigma-Aldrich and TCI Chemicals and used without further purification, unless otherwise noted. For organic synthesis, solvents were distilled and dried before use by standard methods.[1] For polymerization procedures, N,N-dimethylacetamide was distilled over CaH_2 and stored over MS 3 Å under Ar atmosphere. Methyl methacrylate, methyl acrylate, n-butyl acrylate and 2-vinyl pyridine were distilled over CaH_2 under reduced pressure and stored under Ar atmosphere at -30°C.

Methods

Flash column chromatography was performed on Merck silica gel (40-63 mesh) using standard techniques. Thin layer chromatography (TLC) was accomplished by using Silica gel 60 F254 plates and visualized using UV light, aqueous $KMnO_4$, ninhydrin stain and phosphoromolybdic acid.

Size exclusion chromatography (SEC) analysis was undertaken on Ultimate 3000 Thermo Scientific apparatus equipped with Agilent PLgel 5 μm MIXED-C (300 × 7.5 mm) column, one precolumn (PLgel 5 μm guard 50 × 7.5 mm) and differential refractometer (RI) detector. THF was eluted at a flow rate of 1.0 mL/ min at 30 °C. The determination of molecular weight and polydispersity values was carried out using a set of polystyrene standards with extremely low polydispersity (Polymer Labs, Germany).

NMR spectra were recorded on Bruker Avance 500 MHz spectrometer at ambient temperature. Chemicals shifts (δ) are reported in parts per million (ppm) downfield of tetramethylsilane with multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, bs = broad singlet, or combinations thereof). The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). ^{19}F NMR spectra are not calibrated by an internal reference. Coupling constants (J) are quoted in Hertz (Hz).

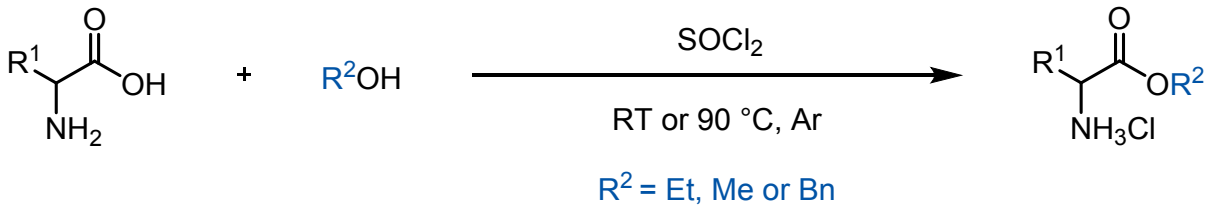
The UV-visible measurement was performed using HR2000+ spectrophotometer with a DH-2000 light source (Ocean Optics).

Photoluminescence spectra were recorded using Agilent Cary Eclipse spectrofluorimeter.

Gas chromatography – mass spectrometry (GC-MS) analysis was performed on an Agilent 8860 GC instrument using Astec CHIRALDEX B-DM (30 m × 0.25 mm) column and mass selective detector Agilent 5977B.

2. Synthesis of Starting Materials

General Procedure A: Esterification of Amino Acids



Ethyl and methyl esters:

A 50 mL round-bottom flask with a magnetic stirring bar was charged with amino acid (1.00 eq., 3.00 mmol) and filled with Ar. Dry EtOH or MeOH (25 mL) was added and the resulting suspension was cooled to 0 °C in an ice bath. Then, $SOCl_2$ (5.00 eq., 15.00 mmol, 1.09 mL) was added in portions over 15 min. The resulting solution was allowed to warm up to room temperature and stirred overnight. After this, Et_2O (150 mL) was added until turbidity appeared and the resulting suspension was kept in a refrigerator at -20°C for a few hours to crystallize the product. The precipitated product was filtered, washed with Et_2O (3 x 10 mL) and dried under vacuum.

Benzyl esters:

A 50 mL round-bottom flask with a magnetic stirring bar was charged with amino acid (1.00 eq., 3.00 mmol) and filled with Ar. Dry BnOH (25 mL) was added and the resulting suspension was cooled to 0°C in an ice bath. Then, $SOCl_2$ (5.00 eq., 15.00 mmol, 1.09 mL) was added in portions over 15 min. The resulting solution was allowed to warm up to room temperature and heated at 90 °C for 7 h. After this, the reaction mixture was cooled down to room temperature and Et_2O (150 mL) was added until turbidity appeared. The resulting suspension was kept in a refrigerator at -20°C for a few hours to crystallize the product. The precipitated product was filtered, washed with Et_2O (3 x 10 mL) and dried under vacuum.

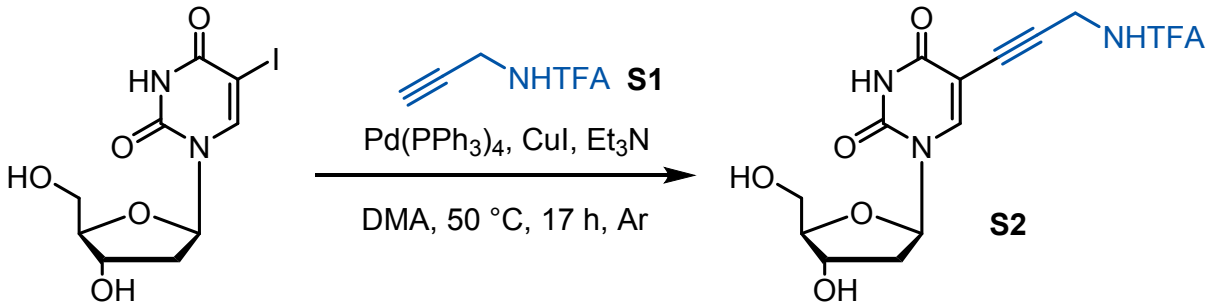
$Cu(PPh_3)_3Br$

This procedure was adapted from the literature.[2]

A 250 mL Erlenmeyer flask with a magnetic stirring bar was charged with MeOH (100 mL) and heated to boiling. PPh_3 (4.25 eq., 22.40 mmol, 5.88 g) was slowly added to the stirring MeOH. After the complete dissolution of PPh_3, $CuBr_2$ (1.00 eq., 5.27 mmol, 1.88 g) was added in portions. No special precautions were taken for the exclusion of air. Upon addition of the copper bromide, a white precipitate was formed. After the completion of the addition, the contents were stirred for 10 min and the flask was allowed to cool to ambient temperature. The precipitated product

was filtered, washed with EtOH (3 x 25 mL), Et_2O (3 x 25 mL) and dried under vacuum. The resulting white solid was dried under vacuum to give $Cu(PPh_3)_3Br$ (4.26 g, 87 % yield, m.p. 162-164 °C).

5-(3''-Trifluoroacetamidopropynyl) -2'-deoxyuridine S2



2,2,2-trifluoro-N-(prop-2-yn-1-yl)acetamide **S1**

This procedure was adapted from the literature.[3]

A 25 mL round-bottom flask with a magnetic stirring bar was charged with propargylamine (1.00 eq., 5.00 mmol, 320 µL) and filled with Ar. Dry DCM (10 mL) was added and the solution was cooled to 0°C. A solution of trifluoroacetic anhydride (1.00 eq., 5.00 mmol, 700 µL) in dry DCM (5 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The mixture was poured into 15 mL H_2O, the organic phase was separated, and the aqueous phase was extracted with DCM (5 mL). The combine organic phases were washed with 5 wt. % $NaHCO_3$ (3 x 10 mL), H_2O (2 x 10 mL) and brine (1 x 10 mL), dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography on silica gel with dichloromethane to give product **S1** (430 mg, 57 % yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (bs, 1H), 4.15 (dd, J = 5.4, 2.6 Hz, 2H), 2.34 (t, J = 2.6 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.87 (s).

^{1}H and ^{19}F NMR spectra are in agreement with those reported in the literature.[3]

5-(3''-Trifluoroacetamidopropynyl)-2'-deoxyuridine **S2**

This procedure was adapted from the literature with some deviations.[4]

A 10 mL Schlenk tube with a magnetic stirring bar was heated under vacuum with a heat gun and backfilled with Ar. After this, 5-iodo-2'-deoxyuridine (1.00 eq., 0.565 mmol, 200.0 mg) was dissolved in dry DMA (5.00 mL). $Pd(PPh_3)_4$ (0.10 eq., 56.5□10^{-3} mmol, 65.3 mg), Et_3N (2.00 eq., 1.129 mmol, 157.4 µL), **S1** (2.50 eq., 1.411 mmol, 213.3 mg) and CuI (0.20 eq., 0.113 mmol, 21.5 mg) were added

sequentially. The mixture was stirred at 50 °C for 17 h, the solvent was evaporated, and the residue was dissolved in mixture of DCM : EtOH = 9 : 1 v/v (10 mL). K_2CO_3 (156 mg) was added and the reaction mixture was stirred at room temperature for 60 min. The resulting mixture was filtered through Celite pad, the solid was washed with DCM : EtOH = 1 : 1 v/v (10 mL), and the combined filtrates were evaporated. The residue was purified by silica column chromatography (DCM : EtOH = 9 : 1) to give product **S2** (131.0 mg, 59 % yield) as a yellow foam.

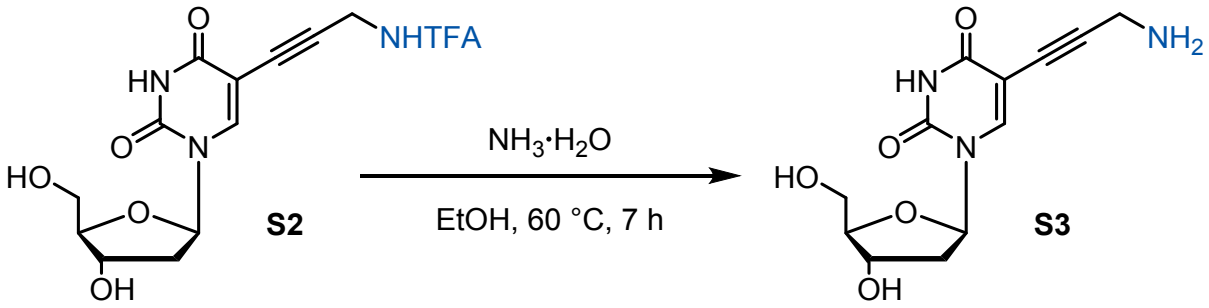
Note: DMA and Et_3N used for this reaction were distilled and stored under Ar.

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.65 (bs, 1H), 10.06 (t, J = 5.6 Hz, 1H), 8.17 (s, 1H), 6.07 (t, J = 6.7 Hz, 1H), 5.23 (d, J = 4.2 Hz, 1H), 5.08 (t, J = 5.1 Hz, 1H), 4.23 – 4.17 (m, 3H), 3.78 – 3.75 (m, 1H), 3.60 – 3.50 (m, 2H), 2.11 – 2.07 (m, 2H).

^{19}F NMR (470 MHz, DMSO-d_6) δ -74.27 (s).

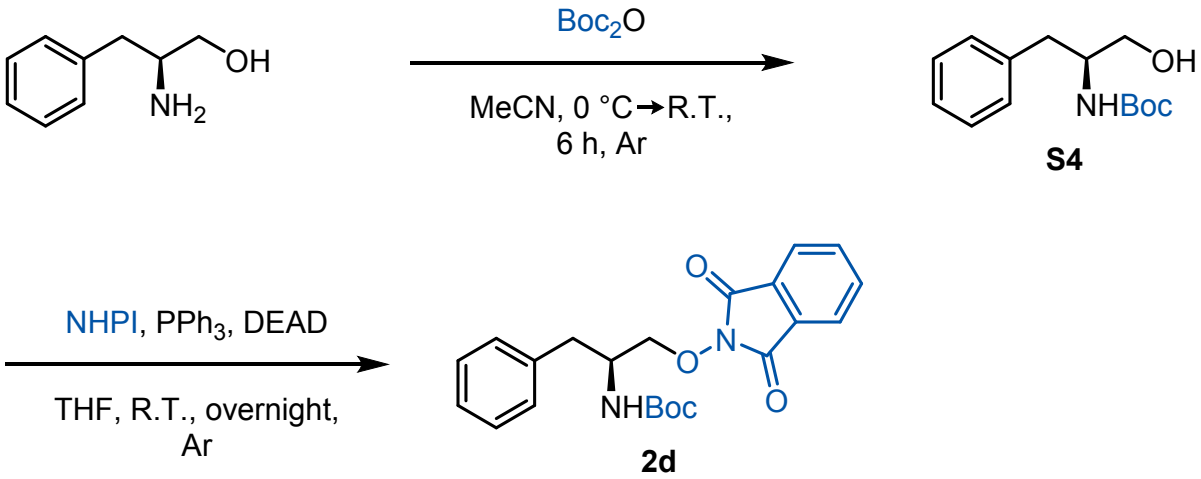
^{1}H and ^{19}F NMR spectra are in agreement with those reported in the literature.[4]

5-(3''-aminopropynyl)-2'-deoxyuridine S3



A 25 mL round-bottom flask with a magnetic stirring bar was charged with **S2** (1.000 mmol, 377.3 mg), EtOH (7 mL) and 25 wt. % aq. NH_3 (3 mL). The resulting mixture was stirred at 60 °C for 7 h. The solvent was evaporated. The residue was extracted (CH_2Cl_2 / H_2O, 4 mL / 1.5 mL), the organic layer was washed with brine (1.5 mL), dried over Na_2SO_4 and concentrated under vacuum to obtain the desired product as a yellowish oil (quantitative yield), which was used without further purification.

tert-butyl (_S_)-(1-((1,3-dioxoisoindolin-2-yl)oxy)-3-phenylpropan-2-yl) carbamate 2d



tert-butyl (S)-(1-hydroxy-3-phenylpropan-2-yl)carbamate **S4**

This procedure was adapted from the literature.[5]

A 25 mL round-bottom flask with a magnetic stirring bar was charged with (*S*)-2-amino-3-phenylpropan-1-ol (1.00 eq., 6.61 mmol, 1.000 g) and filled with Ar. Dry MeCN (10 mL) was added and the resulting solution was cooled to 0°C. Then, Boc_2O (1.20 eq., 7.93 mmol, 1.731 g) in MeCN (5 mL) was added in portions via syringe. The mixture was allowed to warm up to room temperature and stirred at room temperature for 6 h. The solvent was evaporated and the residue was extracted (Et_2O / 10 wt. % aq. NaOH solution, 25 mL x 2 / 10 mL), the combined organic layers was dried over Na_2SO_4 and concentrated under vacuum to give product **S4** (1.639 g, 99 % yield) as a white waxy solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 4.74 (bs, 1H), 3.87 (bs, 1H), 3.67 (dd, J = 11.0, 3.7 Hz, 1H), 3.55 (dd, J = 11.0, 3.7 Hz, 1H), 2.84 (d, J = 7.2 Hz, 2H), 1.41 (s, 9H).

^{1}H spectrum is consistent with those reported in the literature.[5]

tert-butyl (S)-(1-((1,3-dioxoisoindolin-2-yl)oxy)-3-phenylpropan-2-yl) carbamate **2d**

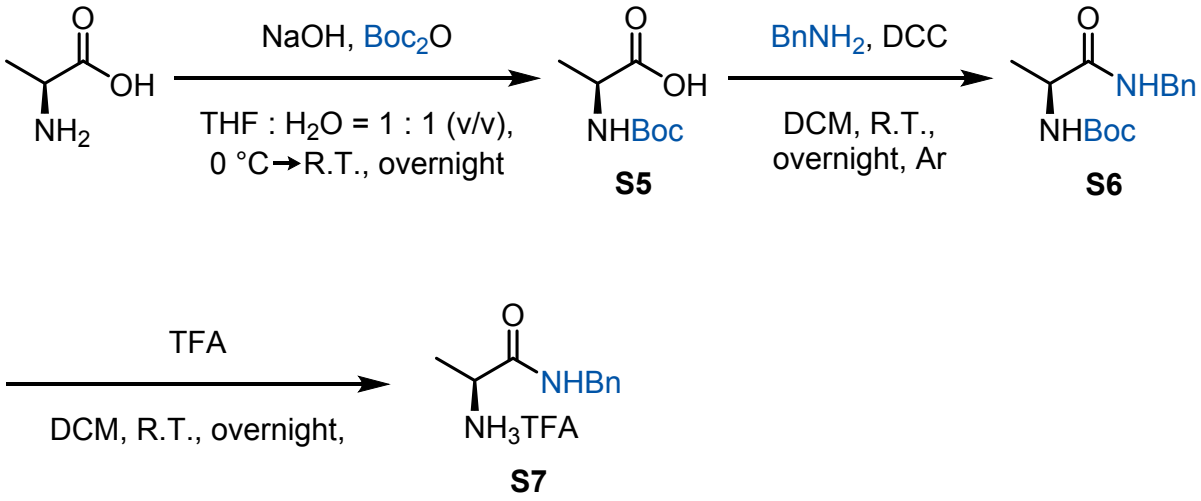
This procedure was adapted from the literature.[6]

A 25 mL round-bottom flask with a magnetic stirring bar was charged with **S4** (1.00 eq., 5.97 mmol, 1.500 g), PPh_3 (1.00 eq., 5.97 mmol, 1.565 g), N-hydroxyphthalimide (1.00 eq., 5.97 mmol, 0.974 g) and filled with Ar. Dry THF (10 mL) was added and the resulting solution was stirred at room temperature for 5 min. Then, DEAD (40 wt. % in toluene, 1.00 eq., 5.97 mmol, 2.72 mL) was added in portions over 10 min. The mixture was stirred at room temperature overnight,

taken up in EtOAc (20 mL), washed with saturated aq. $NaHCO_3$ solution (3 x 15 mL), brine (2 x 15 mL). The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography (hexane : EtOAc = 100 : 0 → 60 : 40) to give product **2d** (1.437 g, 61 % yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, J = 5.5, 3.1 Hz, 2H), 7.76 (dd, J = 5.5, 3.1 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H + $CHCl_3$ residual peak), 4.24 (dd, J = 9.7, 4.1 Hz, 1H), 4.13 (dd, J = 9.7, 4.1 Hz, 1H), 4.05 (bs, 1H), 3.14 – 3.00 (m, 2H), 1.41 (s, 9H).

(*S*)-1-(benzylamino)-1-oxopropan-2-aminium trifluoroacetate S7



(tert-butoxycarbonyl)-L-alanine **S5**

This procedure was adapted from the literature.[27]

A 25 mL round-bottom flask with a magnetic stirring bar was charged with *L*-alanine (1.00 eq., 4.49 mmol, 400 mg), THF (7 mL) and H_2O (7 mL). Next, NaOH (2.00 eq., 3.37 mmol, 359 mg) in H_2O (1.4 mL) was added in portions, followed by Boc_2O (0.75 eq., 7.93 mmol, 735 mg) in THF (2 mL) at 0 °C. The mixture was allowed to warm up to room temperature and stirred at room temperature overnight. The solvent was evaporated and the residue was dissolved in H_2O (2 mL). Then 1.0 M aqueous HCl was added dropwise to the reaction mixture until pH ~ 2-3 and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to give product **S5** (688 mg, 73 % yield) as a colorless oil, which was used in the next step without further purification.

tert-butyl (S)-(1-(benzylamino)-1-oxopropan-2-yl)carbamate **S6**

This procedure was adapted from the literature.[28]

A 5 mL round-bottom flask with a magnetic stirring bar was charged with (*tert*-butoxycarbonyl)-*L*-alanine **S5** (1.00 eq., 2.000 mmol, 556.7 mg), dry DCM (7.5 mL) and filled with Ar. DCC (1.20 eq., 2.400 mmol, 495.2 mg) in DCM (1.0 mL) was added in portions via syringe and the resulting mixture was stirred for 10 min. Next, benzylamine (1.00 eq., 2.000 mmol, 218.5 μL) was added in portions via syringe and the resulting mixture was stirred overnight. The resulting suspension was filtered from DCU precipitate through cotton and concentrated under reduced pressure. The residue was purified by column chromatography (DCM 100 %) to give the desired product **S6** (503.0 mg, 96 % yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.27 – 7.21 (m, 3H + $CHCl_3$ residual peak), 6.64 (bs, 1H), 5.07 (bs, 1H), 4.43 (bs, 2H), 4.16 (bs, 1H), 1.44 – 1.33 (m, 12H).

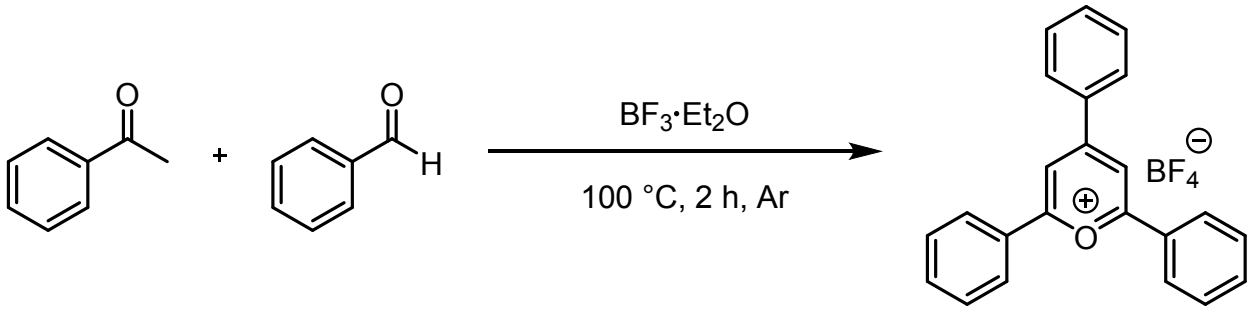
^{1}H spectrum is consistent with those reported in the literature.[28]

(S)-1-(benzylamino)-1-oxopropan-2-aminium trifluoroacetate **S7**

This procedure was adapted from the literature.[28]

A 10 mL round-bottom flask with a magnetic stirring bar was charged with *tert*-butyl (*S*)-(1-(benzylamino)-1-oxopropan-2-yl)carbamate **S6** (1.00 eq., 1.100 mmol, 290.7 mg), DCM (2 mL) and trifluoroacetic acid (2 mL). The solution was stirred at room temperature overnight. The mixture was concentrated under vacuum to give product **S7** (quantitative yield) as a yellowish solid, which was used without further purification.

2,4,6-Triphenylpyrylium tetrafluoroborate



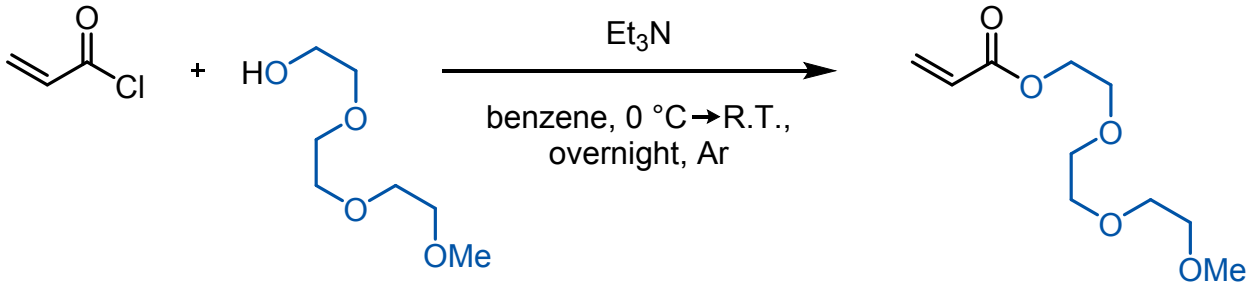
This procedure was adapted from the literature.[7]

A 500 mL round-bottom flask with a magnetic stirring bar and a reflux condenser was charged with benzaldehyde (1.00 eq., 0.30 mol, 30.5 mL), acetophenone (2.00 eq., 0.60 mol, 70.0 mL) and filled with Ar. $BF_3 \cdot Et_2O$ (2.40 eq., 0.72 mol, 88.9 mL)

was added portionwise via syringe. The mixture turned a red-brown color and was vigorously stirred for 2 h at 100°C. 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 (2 x 10 mL), and dried in vacuum. Triple recrystallization in MeCN afforded the pure 2,4,6-triphenylpyrylium tetrafluoroborate (43.2 g, 36 % yield) as a bright yellow powder.

^{1}H and ^{19}F NMR spectra are in agreement with those reported in the literature.[7]

2-[2-(2-Methoxyethoxy)ethoxy]ethyl acrylate



A 100 mL round-bottom flask with a magnetic stirring bar was charged with dry benzene (30 mL), triethylene glycol monomethyl ether (1.00 eq., 35.90 mmol, 5.61 mL), Et_3N (2.40 eq., 86.16 mmol, 12.00 mL) and filled with Ar. The resulting solution was cooled to 0 °C in an ice bath. Then, acryloyl chloride (1.20 eq., 43.08 mmol, 3.50 mL) was added in portions over 15 min. The resulting suspension was allowed to warm up to room temperature and stirred overnight. After this, The mixture was filtered through cotton pad, the solid was washed with EtOAc (2 x 10 mL), and the combined filtrates were evaporated. The residue was dissolved in EtOAc (100 mL), washed with saturated aq. $NaHCO_3$ solution (1 x 50 mL). The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography (hexane : EtOAc = 1 : 2) to give the product (4.67 g, 60 % yield) as a yellowish oil.

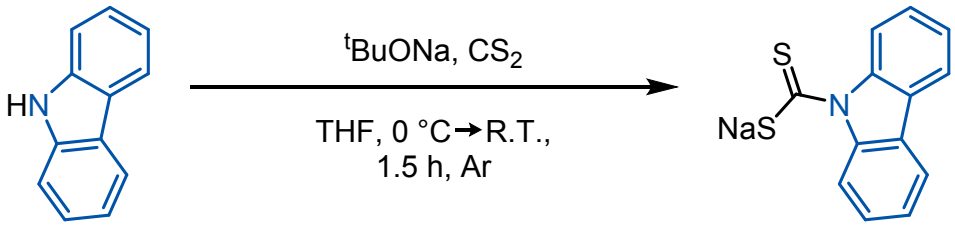
Note: Once isolated, 2-[2-(2-methoxyethoxy)ethoxy]ethyl acrylate should be stored at -30 °C under Ar in the presence of small amounts of BHT stabilizer. Prior to the polymerization, the monomer was filtered through a plug of aluminum oxide to remove inhibitor.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.42 (dd, J = 17.3, 1.4 Hz, 1H), 6.15 (dd, J = 17.3, 10.4 Hz, 1H), 5.83 (dd, J = 10.4, 1.4 Hz, 1H), 4.33 – 4.29 (m, 2H), 3.76 – 3.72 (m, 2H), 3.69 – 3.62 (m, 6H), 3.57 – 3.51 (m, 2H), 3.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.30, 131.14, 128.40, 72.05, 70.74, 69.24, 63.83, 59.18 (two carbon signals are missing due to signal broadening).

3. Synthesis of Chain-Transfer Agents Precursors

Sodium 9H-carbazole-9-carbodithioate (pCTA-1)



This procedure was adapted from the literature.[8]

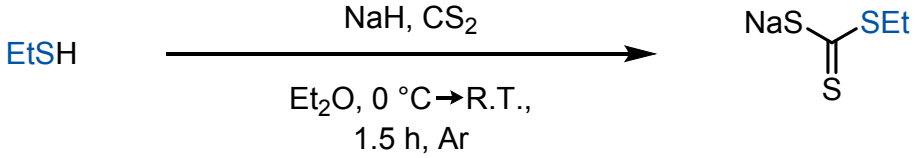
A 25 mL round-bottom flask with a magnetic stirring bar was charged with carbazole (1.00 eq., 5.981 mmol, 1.000 g) and filled with Ar. Dry THF (10 mL) was added and the solution was cooled to 0 °C. Sodium tert-butoxide (1.10 eq., 6.579 mmol, 0.632 g) was added portionwise. The mixture turned a slight yellow/ orange color and was left to stir for 30 minutes. Still at 0 ºC, CS_2 (1.50 eq., 8.972 mmol, 0.54 mL) was added dropwise via syringe. The mixture immediately turned a bright orange color and was left to stir for one hour at 0 ºC. After warming up to ambient temperature, THF was evaporated carefully on a rotary evaporator to a thick syrupy consistency. Diethyl ether (25 mL) was added and the resulting suspension stirred vigorously to free the solid. The yellow solid was then filtered under a flow of Ar, washed twice with a small amount of Et_2O and further dried under high vacuum to obtain the desired product (1.530 g, 96 % yield) as a bright yellow free-flowing powder.

Note: Once isolated, **pCTA-1** is slightly hygroscopic and should therefore be protected from ambient humidity. **pCTA-1** was stored in brown glass bottles at -30 °C under Ar. Only minor degradation to the parent carbazole was observed over a 1.5-month period, as indicated by NMR analysis. **pCTA-1** could be readily purified again by washing the solid with diethyl ether to remove the carbazole from the yellow solid.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.47 (d, J=8.3 Hz, 2H); 8.07 (d, J=7.6 Hz, 2H); 7.36 (t, J=7.9 Hz, 2H); 7.18 (t, J=7.9 Hz, 2H).

^{1}H spectrum is consistent with those reported in the literature.[8]

Sodium Ethyl Carbonotrithioate (pCTA-2)



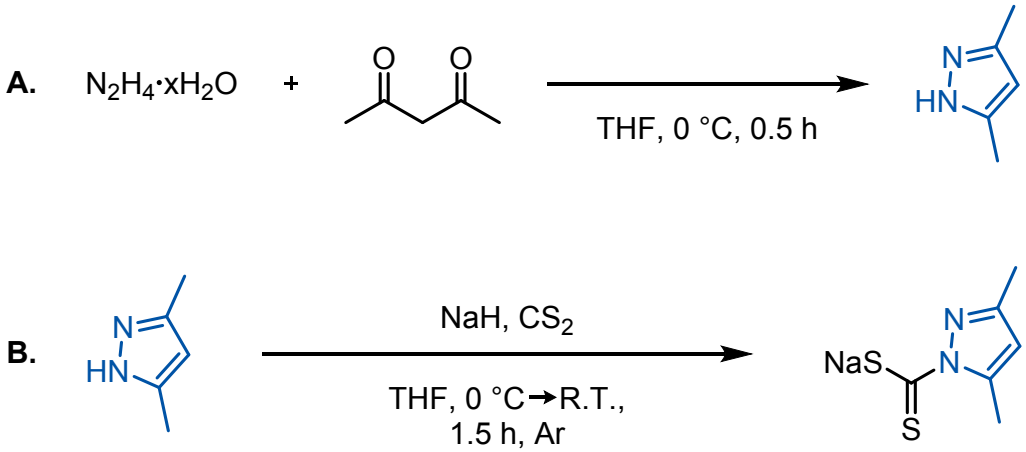
A 50 mL round-bottom flask with a magnetic stirring bar was charged with NaH (60 wt. % suspension in mineral oil, 1.05 eq., 25.00 mmol, 1.000 g) and filled with Ar. Dry Et_2O (20 mL) was added and the mixture was cooled to 0°C. EtSH (1.00 eq., 23.81 mmol, 1.72 mL) was added dropwise via syringe and the mixture was left to stir for 45 min at 0 ºC. Still at 0 ºC, CS_2 (1.50 eq., 35.72 mmol, 2.16 mL) was added dropwise via syringe addition. A yellow solid precipitated. The resulting suspension was allowed to warm to room temperature and stirred for another 3 hours at room temperature. Hexane (20 mL) was added to the reaction mixture and the yellow solid was then filtered, washed with Et_2O (3 x 5 mL), hexane (3 x 10 mL) and further dried under high vacuum to obtain the desired product (3.636 g, 95 % yield) as a yellow free-flowing powder.

Note: Once isolated, **pCTA-2** is slightly hygroscopic and should therefore be protected from ambient humidity. **pCTA-2** was stored in brown glass bottles at 0 °C under Ar. No degradation was observed over a 6-month period, as indicated by NMR analysis.

^{1}H NMR (500 MHz, DMSO-d_6) δ 2.95 (q, J = 7.4 Hz, 2H), 1.12 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 215.68, 33.90, 14.06.

Sodium 3,5-dimethyl-1H-pyrazole-1-carbodithioate (pCTA-3)



A. *3,5-dimethyl-1H-pyrazole*

This procedure was adapted from the literature [ref. 12 of the manuscript].

A 50 mL round-bottom flask with a magnetic stirring bar was charged with acetylacetone (1.00 eq., 30.00 mmol, 3.08 mL) and THF (25 mL). The solution was cooled to 0°C. Hydrazine hydrate (1.10 eq., 33.00 mmol, 1.00 mL) was added dropwise and the mixture was left to stir for 30 min at 0 ºC. A white solid precipitated. The precipitate was then filtered, washed with Et_2O (3 x 5 mL), hexane (3 x 10 mL) and further dried under high vacuum to obtain the desired product (2.110 g, 73 % yield) as a white solid.

B. *3,5-dimethyl-1H-pyrazole-1-carbodithioate*

A 50 mL round-bottom flask with a magnetic stirring bar was charged with NaH (60 wt. % suspension in mineral oil, 1.05 eq., 21.00 mmol, 0.840 g) and filled with Ar. Dry THF (15 mL) was added and the mixture was cooled to 0 °C. 3,5-dimethyl-1H-pyrazole (1.00 eq., 20.00 mmol, 1.923 g) in THF (5 mL) was added dropwise via syringe and the mixture was left to stir for 45 min at 0 ºC. Still at 0 ºC, CS_2 (1.50 eq., 30.00 mmol, 1.81 mL) was added dropwise via syringe addition. An orange solid precipitated. The resulting suspension was allowed to warm to room temperature and stirred for another 3 hours at room temperature. Hexane (20 mL) was added to the reaction mixture and the orange solid was then filtered, washed with Et_2O (3 x 5 mL), hexane (3 x 10 mL) and further dried under high vacuum to obtain the desired product (3.511 g, 90 % yield) as a light orange free-flowing powder.

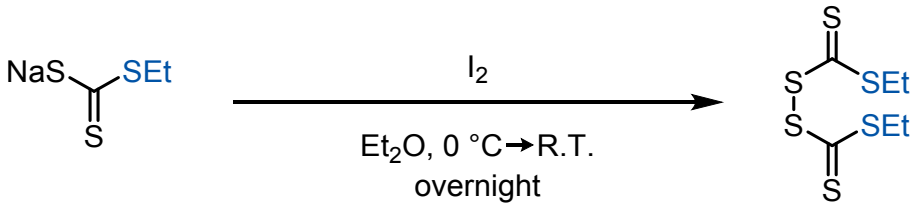
Note: Once isolated, **pCTA-3** is slightly hygroscopic and should therefore be protected from ambient humidity. **pCTA-3** was stored in brown glass bottles at 0 °C

under Ar. No degradation was observed over a 1-month period, as indicated by NMR analysis.

^{1}H NMR (500 MHz, DMSO-d_6) δ 5.79 (s, 1H), 2.44 (s, 3H), 2.05 (s, 3H).

^{1}H spectrum is consistent with those reported in the literature [ref. 12 of the manuscript].

Disulfide CTA-4



This procedure was adapted from the literature.[9]

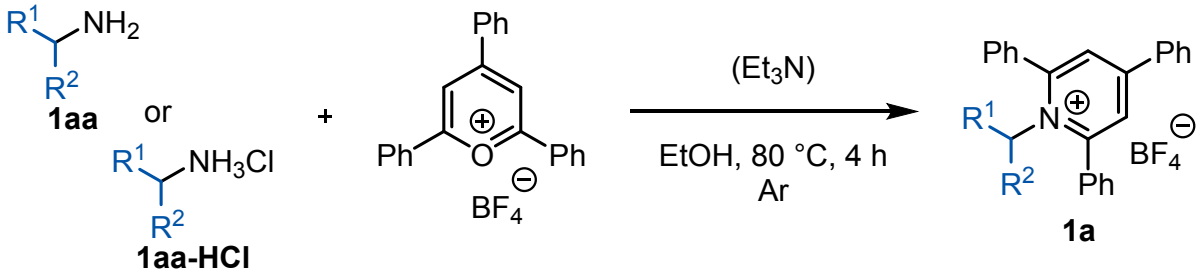
A 10 mL round-bottom flask with a magnetic stirring bar was charged with **pCTA-2** (1.00 eq., 6.24 mmol, 1.000 g) and Et_2O (10 mL) and the resulting suspension was cooled to 0°C. Solid I_2 (0.55 eq., 3.43 mmol, 0.871 g) was added in portions over 5 min. The mixture was allowed to warm to room temperature and stirred overnight. The precipitate was filtered off, the filtrate was washed with H_2O (2 x 5 mL) and saturated aq. $Na_2S_2O_3$ (3 x 5 mL, at this point the washings became colorless), dried over Na_2SO_4 and concentrated under vacuum. The residue was dried under high vacuum to obtain the desired product (0.720 g, 84 % yield) as an orange oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.31 (q, J = 7.5 Hz, 4H), 1.36 (t, J = 7.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 221.53, 32.75, 12.51.

4. Synthesis of Katritzky Salts

General Procedure B: Conversion of Primary Amines to Katritzky Salts



All pyridinium salts were synthesized following the procedure by Watson *et al.*[10] with minor deviations.

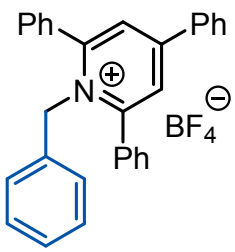
A 10 mL round-bottom flask with a reflux condenser was charged with 2,4,6-triphenylpyrylium tetrafluoroborate (1.00 eq., 1.00 mmol, C = 1.00 M in EtOH) and filled with Ar. Dry EtOH and primary amine **1aa** (1.10 eq., 1.10 mmol) were added sequentially. The resulting suspension was stirred and heated at 80 °C in an oil bath for 4 h. The mixture was allowed to cool to room temperature. The precipitated product was filtered, washed with EtOH (1 x 2 ml), Et_2O (3 x 2 ml) and dried under vacuum.

At this point most of the products were sufficiently pure for polymerization procedures. To obtain analytically pure pyridinium salts, they were subjected to flash column chromatography on silica gel ($CHCl_3$ / MeOH as eluent).

Modified procedure for amine hydrochloride salts as starting materials:

Et_3N (1.20 eq., 1.20 mmol) was added to a solution of the corresponding alkyl ammonium hydrochloride **1aa-HCl** (1.10 eq., 1.10 mmol, C = 1.10 M in EtOH) in dry EtOH and the resulting mixture was stirred for 30 min at room temperature. After this 2,4,6-triphenylpyrylium tetrafluoroborate (1.00 eq., 1.00 mmol) was added. The following steps were analogous to the previous procedure. Prior to washing with EtOH, the crude product was washed with H_2O (3 x 2 ml) to remove Et_3N□HCl.

1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2a)



Obtained according to the General Procedure B using benzylamine **2aa** (131.1 µL), 2,4,6-triphenylpyrylium tetrafluoroborate (396.2 mg) and EtOH (1.00 mL). The product was purified by flash column chromatography on silica gel (100 % $CHCl_3$) to provide a pale green foam (364.0 mg, 0.750 mmol, 75 % yield).

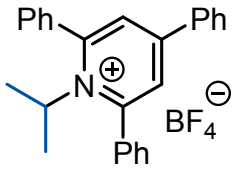
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.81 – 7.77 (m, 2H), 7.66 – 7.60 (m, 4H), 7.59 – 7.41 (m, 10H), 7.15 (t, J = 7.4 Hz, 1H), 7.09 (t, J = 7.4 Hz, 2H), 6.45 (d, J = 7.4 Hz, 2H), 5.76 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.68, 156.40, 134.20, 133.85, 132.85, 132.51, 131.08, 129.92, 129.28, 129.18, 128.94, 128.36, 128.28, 126.66, 126.34, 58.35.

^{19}F NMR (470 MHz, $CDCl_3$) δ -152.97 (s), -153.00 – -153.06 (m).

^{1}H spectrum is consistent with those reported in the literature.[11]

1-isopropyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (3a)



Obtained according to the General Procedure B using isopropylamine **3aa** (94.5 µL), 2,4,6-triphenylpyrylium tetrafluoroborate (396.2 mg) and EtOH (1.00 mL). The product was purified by flash column chromatography on silica gel (100 % $CHCl_3$) to provide a pale green foam (310.9 mg, 0.711 mmol, 71 % yield).

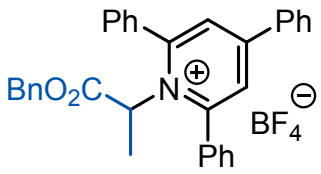
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 6H), 7.72 – 7.69 (m, 2H), 7.61 – 7.54 (m, 6H), 7.52 – 7.48 (m, 1H), 7.47 – 7.42 (m, 2H), 5.10 (hept, J = 7.0 Hz, 1H), 1.34 (d, J = 7.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.13, 155.22, 134.16, 133.99, 131.97, 130.93, 129.67, 129.61, 128.95, 128.76, 128.69, 128.38, 62.78, 23.47.

^{19}F NMR (470 MHz, $CDCl_3$) δ -153.26 (s), -153.31 (s).

^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[12]

1-(1-(benzyloxy)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (4a)



Obtained according to the General Procedure B using *L*-alanine benzyl ester hydrochloride **4aa** (237.2 mg), Et_3N (167.3 µL), 2,4,6-triphenylpyrylium tetrafluoroborate (396.2 mg) and EtOH (1.00 mL). The product was purified by flash column chromatography on silica gel ($CHCl_3$: MeOH = 100 : 0 → 95 : 5) to provide a pale yellow solid (304.9 mg, 0.547 mmol, 55 % yield).

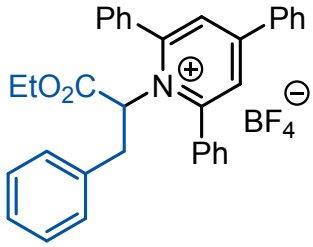
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.84 – 7.66 (m, 4H), 7.58 – 7.43 (m, 9H), 7.41 – 7.35 (m, 4H), 7.24 – 7.20 (m, 2H), 5.59 (q, J = 7.2 Hz, 1H), 5.14 (d, J = 12.0 Hz, 1H), 5.06 (d, J = 12.0 Hz, 1H), 1.44 (d, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.18, 157.10, 156.89, 134.13, 134.04, 133.06, 132.99, 132.33, 131.33, 129.78, 129.23, 129.14, 128.94, 128.58, 68.81, 65.07, 17.06 (one carbon signal is missing due to signal broadening).

^{19}F NMR (470 MHz, $CDCl_3$) δ -153.05 (s), -153.10 (s).

^{1}H, ^{19}F and ^{13}C NMR spectra are in agreement with those reported in the literature.[13]

1-(1-ethoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (5a)



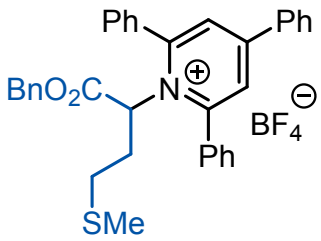
Obtained according to the General Procedure B using *L*-phenylalanine ethyl ester hydrochloride **5aa** (252.7 mg), Et_3N (167.3 µL), 2,4,6-triphenylpyrylium tetrafluoroborate (396.2 mg) and EtOH (1.00 mL). The product was purified by flash column chromatography on silica gel ($CHCl_3$: MeOH = 100 : 0 → 95 : 5) to provide a green solid (370.6 mg, 0.649 mmol, 65 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.89 – 7.75 (m, 4H), 7.64 – 7.51 (m, 11H), 7.11 – 7.05 (m, 3H), 6.81 – 6.76 (m, 2H), 5.64 (dd, J = 8.7, 3.2 Hz, 1H), 4.17 – 4.02 (m, 2H), 3.55 (dd, J = 14.3, 3.2 Hz, 1H), 2.80 (dd, J = 14.3, 8.7 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.27, 157.21, 156.88, 136.90, 134.07, 132.68, 132.45, 131.54, 129.83, 129.24, 128.94, 128.72, 128.61, 128.12, 127.22, 70.65, 63.48, 37.89, 13.80.

^{19}F NMR (470 MHz, $CDCl_3$) δ -152.74 (s), -152.80 (s).

1-(1-(benzyloxy)-4-(methylthio)-1-oxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (6a)



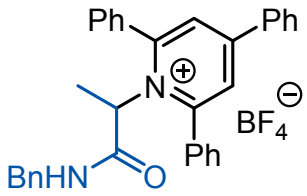
Obtained according to the General Procedure B using *L*-methionine benzyl ester hydrochloride **6aa** (303.4 mg), Et_3N (167.3 µL), 2,4,6-triphenylpyrylium tetrafluoroborate (396.2 mg) and EtOH (1.00 mL). The product was purified by flash column chromatography on silica gel ($CHCl_3$: MeOH = 100 : 0 → 95 : 5) to provide a yellowish solid (412.4 mg, 0.668 mmol, 67 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.85 – 7.82 (m, 2H), 7.64 – 7.45 (m, 9H), 7.43 – 7.30 (m, 5H), 7.25 – 7.19 (m, 3H), 6.08 (dd, J = 9.0, 2.2 Hz, 1H), 5.20 (d, J = 11.9 Hz, 1H), 5.11 (d, J = 11.9 Hz, 1H), 2.41 – 2.20 (m, 4H), 1.84 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.89, 157.21, 134.22, 133.85, 132.88, 132.28, 131.41, 129.75, 129.35, 129.23, 129.05, 128.98, 128.91, 128.78, 128.66, 128.48, 69.03, 67.00, 31.74, 30.50, 14.70.

^{19}F NMR (470 MHz, $CDCl_3$) δ -152.74 (s), -152.80 (s).

1-(1-(benzylamino)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (7a)

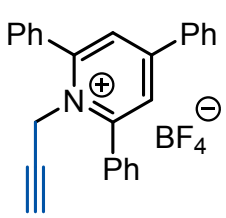


Obtained according to the General Procedure B using (*S*)-1-(benzylamino)-1-oxopropan-2-aminium trifluoroacetate **S7** (1.100 mmol), Et_3N (167.3 µL), 2,4,6-triphenylpyrylium tetrafluoroborate (396.2 mg) and EtOH (1.00 mL). The product was purified by flash column chromatography on silica gel ($CHCl_3$: MeOH = 100 : 0 → 95 : 5) to provide a yellow solid (402.5 mg, 0.704 mmol, 70 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.80 – 7.74 (m, 2H), 7.70 – 7.37 (m, 11H), 7.37 – 7.27 (m, 5H), 7.04 (t, J = 6.1 Hz, 1H), 5.53 (q, J = 7.1 Hz, 1H), 4.33 (dd, J = 14.1, 6.1 Hz, 1H), 4.28 – 4.22 (dd, J = 14.1, 6.1 Hz, 1H), 1.35 (d, J = 7.1 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -152.06 (s), -152.11 (s).

1-(prop-2-yn-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (10a)



Obtained according to the General Procedure B using propargylamine **10aa** (64.0 µL), 2,4,6-triphenylpyrylium tetrafluoroborate (396.2 mg) and EtOH (1.00 mL). The product was purified by flash column chromatography on silica gel (100 % $CHCl_3$) to provide a pale green foam (148.5 mg, 0.343 mmol, 34 % yield).

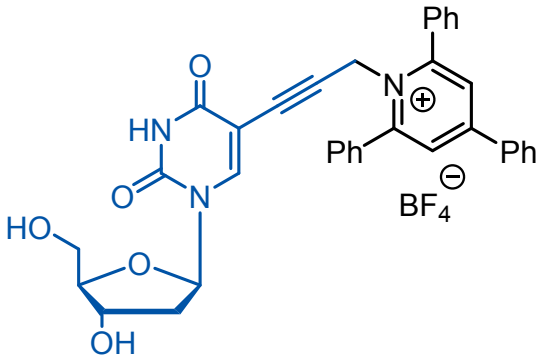
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.87 (d, J = 6.6 Hz, 4H), 7.80 (d, J = 7.2 Hz, 2H), 7.64 – 7.52 (m, 9H), 5.01 (d, J = 1.9 Hz, 2H), 2.47 (t, J = 1.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.34, 156.81, 133.97, 132.52, 132.17, 131.48, 129.93, 129.49, 129.33, 128.33, 126.73, 115.17, 46.32, 29.83.

^{19}F NMR (470 MHz, $CDCl_3$) δ -153.42 (s), -153.47 (s).

^{1}H spectrum is consistent with those reported in the literature.[14]

1-(3-(1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)prop-2-yn-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (S8)



Obtained according to the General Procedure B with minor deviations using 5-(3''-aminopropynyl)-2'-deoxyuridine **S3** (1.000 mmol), 2,4,6-triphenylpyrylium tetrafluoroborate (396.2 mg, C = 0.75 M) and EtOH (1.34 mL). The product was purified by flash column chromatography on silica gel ($CHCl_3$: MeOH = 100 : 0 → 80 : 20) to provide a yellowish solid (159.6 mg, 0.242 mmol, 24 % yield).

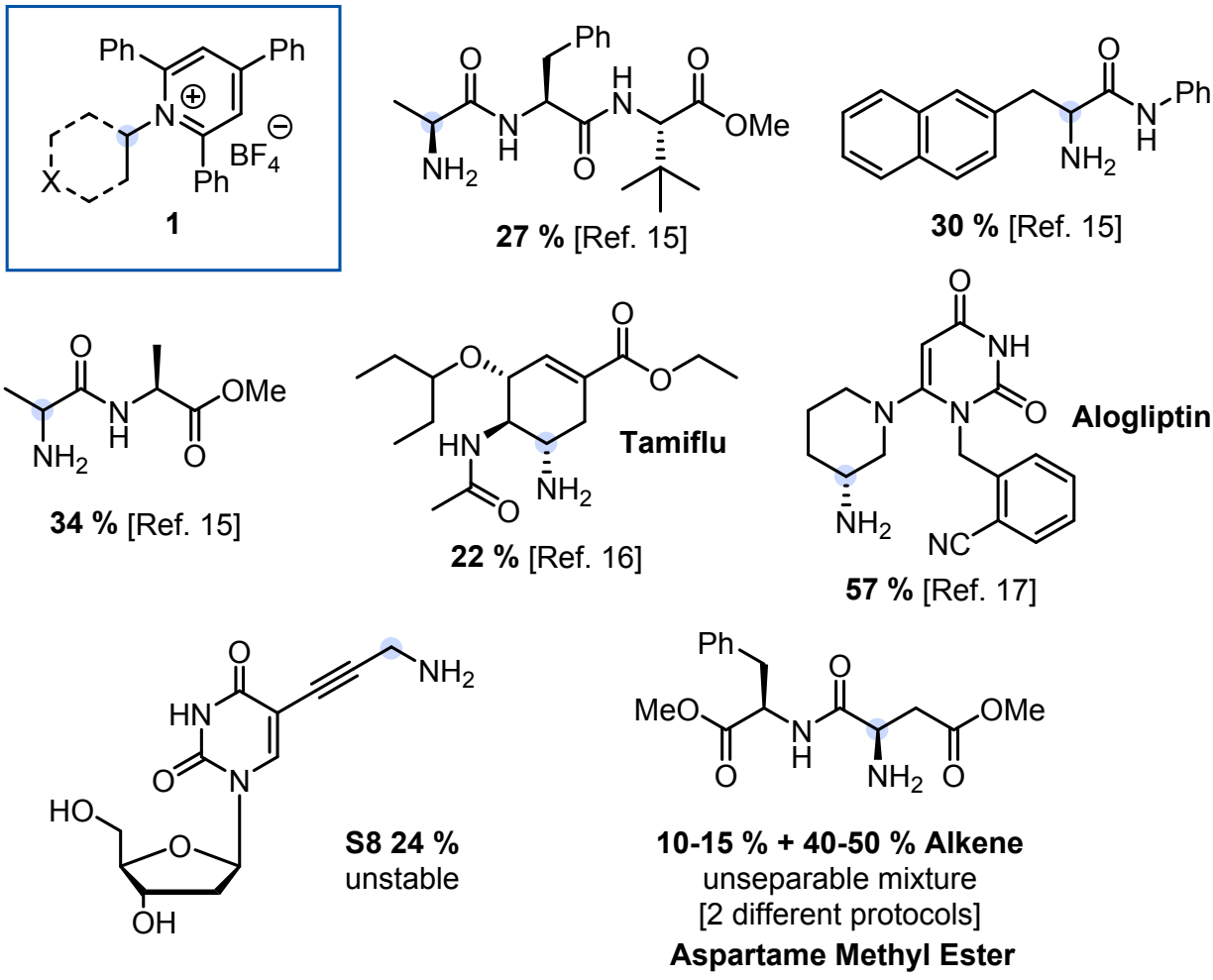
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.54 (s, 2H), 8.29 – 8.24 (m, 2H), 8.15 (s, 1H), 7.95 – 7.88 (m, 4H), 7.74 – 7.59 (m, 10H), 6.10 (t, J = 6.5 Hz, 1H), 5.30 (d, J = 4.2 Hz, 1H), 5.14 (t, J = 5.5 Hz, 1H), 5.01 (s, 2H), 4.29 – 4.24 (m, 1H), 4.22 – 4.09 (m, 2H), 3.87 – 3.83 (m, 1H), 3.67 – 3.60 (m, 2H), 2.21 – 2.12 (m, 2H).

^{19}F NMR (470 MHz, DMSO-d_6) δ -148.15 (s), -148.20 (s).

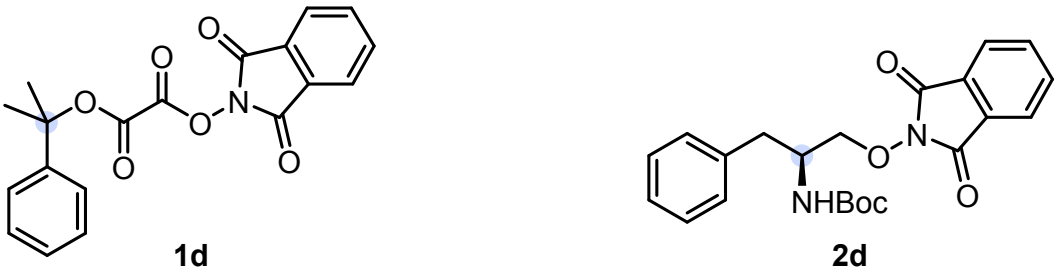
This compound was found to be unstable as a solution in DMSO-d_6.

5. Synthesis of Gly-Gly KS Reagent for Complex Amines and Alcohols Polymerization

Yields of Katritzky Salts **1** for Some Complex Amines:



Alcohol Derivates Tested in Polymerization Processes:



Low I_{eff} & Control Over Polymerization Process

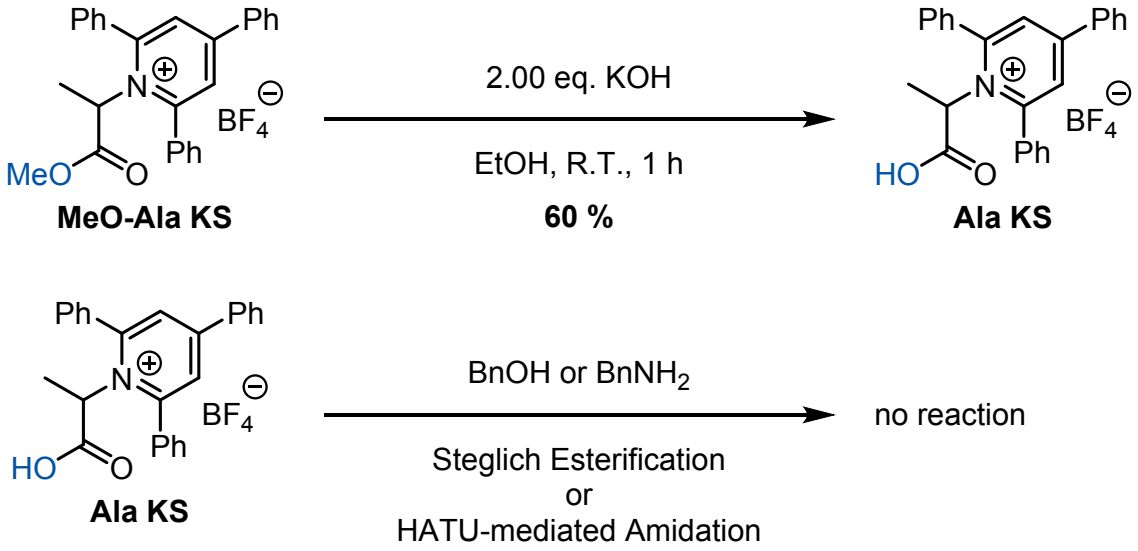
Figure S1. Yields of Katritzky salts **1** for some complex amines (top). Alcohol derivates tested in polymerization processes (bottom).

Literature search on the yields of Katritzky salts **1** from complex amines together with our results (nucleoside derivate **S8** and Aspartame methyl ester) and the unsatisfactory performance of the alcohols derivates **1d** and **2d** in polymerization

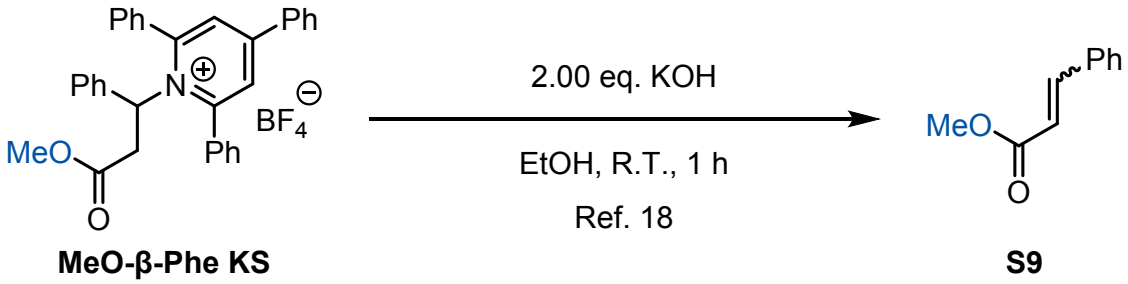
processes motivated us to design a reagent that would allow the polymerization of these classes of substrates.

Generation I: We started our investigation with synthesis of **Ala KS**. However, it appeared to be ineffective in coupling reactions with BnOH or $BnNH_2$, presumably, due to the combination of steric hindrance and EWG effect of pyridinium core.

Generation I:



Generation II:



Generation III:

-long linker (no steric / electronic influence from pyrydinium core)
-no possible elimination side reactions
-mild procedure for methyl group removal from the ester
-still stable radical to enable photoinduced deaminative fragmentation

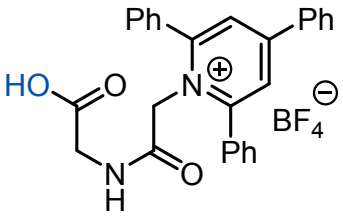


Figure S2. Optimization of universal reagent structure.

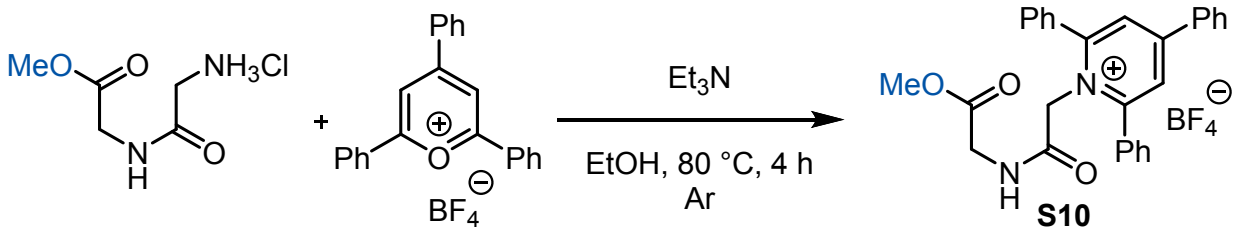
It should also be noted that two-step procedure from the corresponding methyl ester is required as no **Ala KS** formation was observed with free amino acid (*rac*-alanine) as a starting material.

Generation II: Next, we switch our attention to **MeO-β-Phe KS**. 1 methylene unit between carboxyl FG and pyridinium fragment should be sufficient to eliminate the influence of the latter. But the attempt for methyl group removal failed: only alkene **S9** was observed in the reaction mixture.

Generation III: Finally, **Gly-Gly KS** was designed. Its structure reflects our previous attempts (see figure for details).

1-(2-((carboxymethyl)amino)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (Gly-Gly KS)

1-(2-((2-methoxy-2-oxoethyl)amino)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **S10**



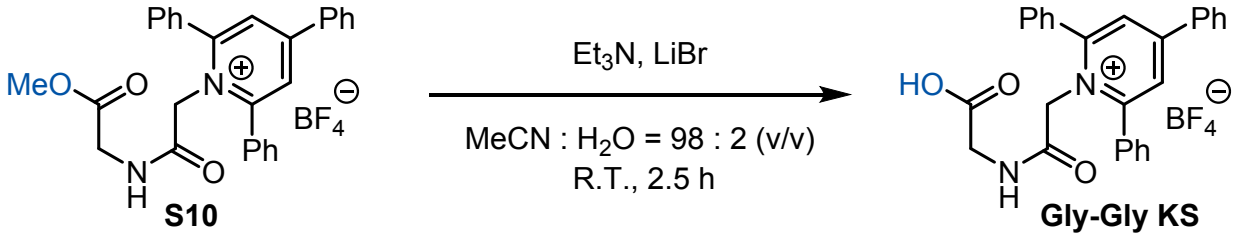
Obtained according to the General Procedure B with minor deviations using methyl glycylglycinate hydrochloride (1.10 eq., 5.476 mmol, 1.000 g), Et_3N (1.20 eq., 5.974 mmol, 832.7 µL), 2,4,6-triphenylpyrylium tetrafluoroborate (1.00 eq., 4.979 mmol, 1.972 g, C = 0.75 M) and EtOH (6.64 mL). The product was purified by flash column chromatography on silica gel ($CHCl_3$: MeOH = 100 : 0 → 95 : 5) to provide **S10** as an off-white foam (1.423 g, 2.714 mmol, 55 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.81 – 7.78 (m, 2H), 7.66 – 7.54 (m, 13H), 6.93 (t, J = 5.7 Hz, 1H), 5.19 (s, 2H), 3.76 (d, J = 5.7 Hz, 2H), 3.68 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.91, 165.68, 157.88, 156.56, 133.91, 132.60, 131.95, 131.63, 130.00, 129.57, 129.05, 128.22, 126.13, 57.39, 52.34, 41.47.

^{19}F NMR (470 MHz, $CDCl_3$) δ -152.17 (s), -152.23 (s).

Gly-Gly KS



This procedure was adapted from the literature with minor deviations.[19]

A 10 mL round-bottom flask was charged with the product **S10 (**1.00 eq., 0.477 mmol, 250.0 mg) and dry MeCN (3.18 mL). After this H_2O (2.0 vol. %, 5.362□10^{-3} mmol, 63.5 µL), LiBr (10.00 eq., 4.765 mmol, 413.8 mg) and Et_3N (3.00 eq., 1.430 mmol, 199.3 µL) were added sequentially. The resulting yellowish solution was stirred for 5 h at room temperature. Then 1.0 M aqueous HCl was added dropwise to the reaction mixture until pH ~ 2 and extracted with EtOAc (15 mL). The organic phase was washed with H_2O (2 x 5 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum to provide the product as a yellowish foam (230.9 mg, 0.452 mmol, 95 % yield).

Note: After isolation, **Gly-Gly KS** was stored in brown glass bottles at -20 °C under Ar. No degradation was observed over a 2-month period, as indicated by NMR analysis.

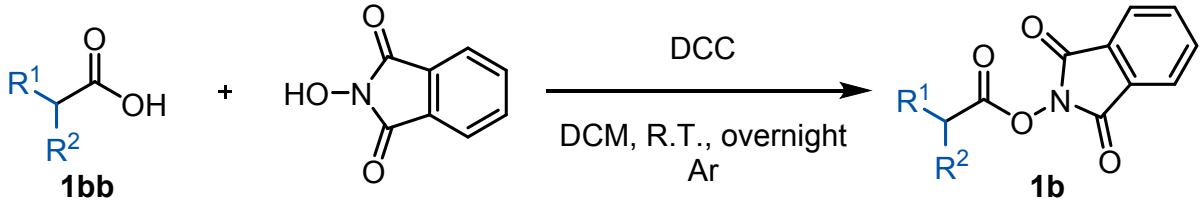
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.81 – 7.67 (m, 5H), 7.63 – 7.54 (m, 4H), 7.53 – 7.45 (m, 6H), 7.18 (t, J = 4.3 Hz, 1H), 5.31 (s, 2H), 3.65 (d, J = 4.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.05, 165.22, 157.77, 156.13, 133.83, 132.58, 132.31, 131.25, 130.00, 129.35, 129.17, 128.17, 125.91, 58.57, 42.18.

^{19}F NMR (470 MHz, $CDCl_3$) δ -151.62 (s), -151.67 (s).

6. Synthesis of N-Hydroxyphthalimide esters (NHPI esters)

General Procedure C: Conversion of Carboxylic Acids to NHPI esters



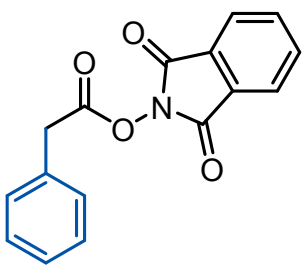
All NHPI esters were synthesized following the modified procedure by Baran *et al*.[20]

A 10 mL round-bottom flask was charged with carboxylic acid (1.00 eq., 1.00 mmol, final C = 0.4 M in DCM) and N-hydroxyphthalimide (1.00 eq., 1.00 mmol) and filled with Ar. Dry DCM (C = 0.8 M) was added and the resulting suspension was stirred for 5 min at 0 °C. In separate vessel DCC (1.10 eq., 1.00 mmol) was dissolved in dry DCM (C = 0.9 M) under Ar atmosphere and added dropwise via syringe addition to the reaction mixture. The resulting mixture was allowed to warm up to room temperature and stirred overnight. The precipitate was filtered, washed with DCM and filtrate was dried under vacuum.

At this point most of the products were sufficiently pure for polymerization procedures. To obtain analytically pure NHPI esters, they were subjected to flash column chromatography on silica gel (hexane / EtOAc as eluent).

Note: Some esters are prone to hydrolysis on silica gel during column chromatography and should be purified as quickly as possible to obtain reasonable separation.

1,3-dioxoisoindolin-2-yl 2-phenylacetate (2b)



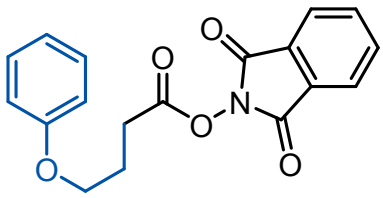
Obtained according to the General procedure C using phenylacetic acid **2bb** (136.2 mg), N-hydroxyphthalimide (163.1 mg.), DCC (227.0 mg), and DCM (2.50 mL). The product was purified by filtration to provide a white solid (279.0 mg, 0.992 mmol, 99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, J = 5.5, 3.1 Hz, 2H), 7.79 (dd, J = 5.5, 3.1 Hz, 2H), 7.42 – 7.36 (m, 4H), 7.35 – 7.31 (m, 1H), 4.00 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.84, 161.99, 134.95, 131.65, 129.44, 129.01, 127.95, 124.15, 37.83.

^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[21]

1,3-dioxoisoindolin-2-yl 4-phenoxybutanoate (3b):



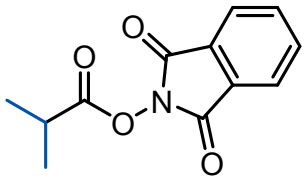
Obtained according to the General procedure C using 4-phenoxybutanoic acid **3bb** (180.2 mg), N-hydroxyphthalimide (163.1 mg.), DCC (227.0 mg), and DCM (2.50 mL). The product was purified by flash column chromatography on silica gel (hexane : EtOAc = 100 : 0 → 70 : 30) to provide a white solid (205.0 mg, 0.630 mmol, 63 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, J = 5.5, 3.1 Hz, 2H), 7.79 (dd, J = 5.5, 3.1 Hz, 2H), 7.34 – 7.27 (m, 2H), 6.94 (dd, J = 10.9, 7.9 Hz, 3H), 4.09 (t, J = 5.9 Hz, 2H), 2.93 (t, J = 7.4 Hz, 2H), 2.27 (tt, J = 7.4, 5.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.50, 162.06, 158.73, 134.92, 129.63, 129.02, 124.14, 121.06, 114.63, 65.96, 27.97, 24.67.

^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[22]

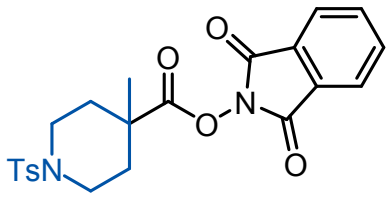
1,3-dioxoisoindolin-2-yl 4-phenoxybutanoate (4b):



Obtained according to the General procedure C using commercially available 4-phenoxybutanoic acid **3bb** (88.1 mg), N-hydroxyphthalimide (163.1 mg.), DCC (227.0 mg), and DCM (2.50 mL). The product was purified by flash column chromatography on silica gel (hexane : EtOAc = 100 : 0 → 70 : 30) to provide a white solid (202.0 mg, 0.866 mmol, 87 % yield).

^{1}H NMR spectrum is in agreement with those reported in the literature.[21]

1,3-dioxoisoindolin-2-yl 4-methyl-1-tosylpiperidine-4-carboxylate (5b):

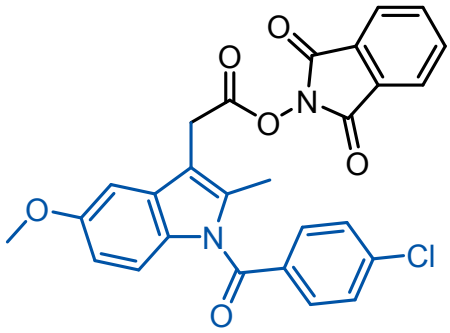


Obtained according to the General procedure C using 4-methyl-1-tosylpiperidine-4-carboxylic acid **5bb** (297.4 mg), N-hydroxyphthalimide (163.1 mg.), DCC (227.0 mg), and DCM (2.50 mL). The product was purified by flash column chromatography on silica gel (100 % EtOAc) to provide a white solid (303.9 mg, 0.687 mmol, 69 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, J = 5.5, 3.1 Hz, 2H), 7.80 (dd, J = 5.5, 3.1 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 3.46 (d, J = 11.8 Hz, 1H), 3.09 – 2.94 (m, 3H), 2.09 (dt, J = 13.0, 6.1 Hz, 1H), 1.84 (p, J = 5.9 Hz, 2H), 1.62 (dt, J = 13.0, 6.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.69, 170.69, 143.79, 134.92, 129.85, 129.12, 127.92, 124.12, 52.51, 46.29, 42.51, 32.76, 22.17, 21.73.

1,3-dioxoisoindolin-2-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (8b):



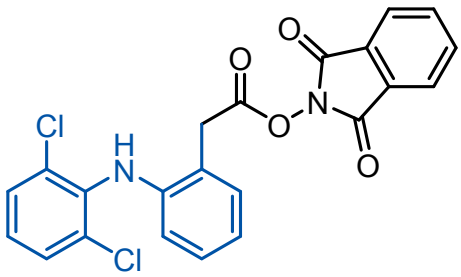
Obtained according to the General procedure B using commercially available Indometacin **8bb** in the free acid form (357.8 mg), N-hydroxyphthalimide (163.1 mg.), DCC (227.0 mg), and DCM (2.50 mL). The product was purified by flash column chromatography on silica gel (100 % EtOAc) to provide a white solid (403.8 mg, 0.803 mmol, 80 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, J = 5.4, 3.1 Hz, 2H), 7.79 (dd, J = 5.4, 3.1 Hz, 2H), 7.71 – 7.66 (m, 2H), 7.50 – 7.46 (m, 2H), 7.03 (d, J = 2.5 Hz, 1H), 6.93 (d, J = 9.0 Hz, 1H), 6.70 (dd, J = 9.0, 2.5 Hz, 1H), 4.04 (s, 2H), 3.89 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.46, 167.18, 161.94, 156.35, 139.57, 136.60, 134.99, 133.80, 131.45, 130.87, 130.08, 129.32, 128.99, 124.17, 115.18, 112.61, 110.32, 100.74, 55.89, 27.27, 13.61.

^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[24]

1,3-dioxoisoindolin-2-yl 2-(2-((2,6-dichlorophenyl)amino)phenyl)acetate (9b):



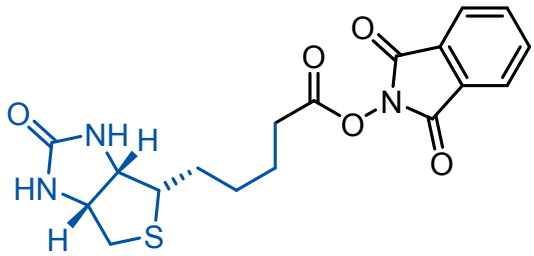
Obtained according to the General procedure B using commercially available Diclofenac in the free acid form **9bb** (296.1 mg), N-hydroxyphthalimide (163.1 mg.), DCC (227.0 mg), and DCM (2.50 mL). The product was purified by flash column chromatography on silica gel (hexane : EtOAc = 100 : 0 → 70 : 30) to provide a white solid (357.5 mg, 0.810 mmol, 81 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, J = 5.4, 3.1 Hz, 2H), 7.79 (dd, J = 5.4, 3.1 Hz, 2H), 7.37 (dd, J = 7.6, 1.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.19 (td, J = 7.6, 1.6 Hz, 1H), 7.06 (td, J = 7.4, 1.3 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.29 (s, 1H), 4.20 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.44, 161.80, 142.95, 138.22, 134.96, 131.21, 129.38, 129.13, 128.98, 128.92, 124.21, 123.48, 123.22, 119.93, 35.11.

^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[24]

1,3-dioxoisoindolin-2-yl 5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d] imidazol-4-yl)pentanoate (10b):

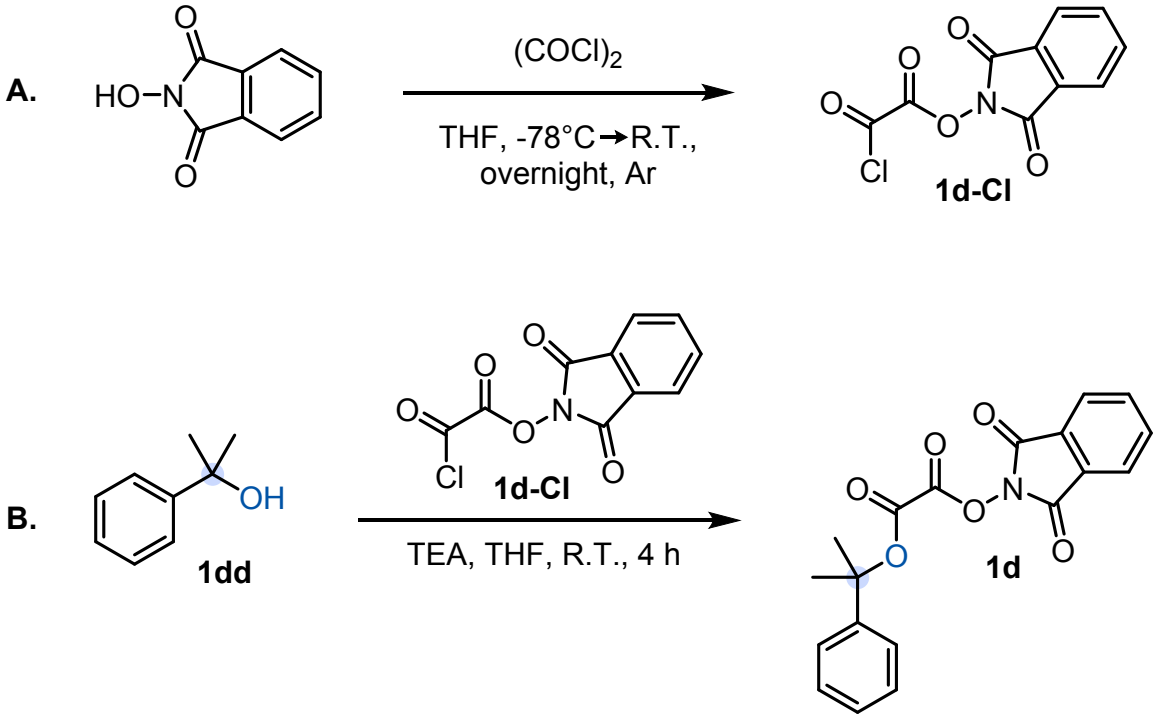


Obtained according to the General procedure C with minor deviations using 5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno [3,4-d]imidazol-4-yl)pentanoic acid [biotin] **10bb** (244.3 mg), N-hydroxyphthalimide (163.1 mg.), DCC (227.0 mg), and DCM (2.50 mL). After the completion of the reaction, the precipitate was filtered, washed with DCM and the filtrate was dried under vacuum. Next, the residue was dissolved in a minimal amount of DCM and poured into the excess of Et_2O. The precipitate was filtered off and dried under vacuum to provide a white solid (167.8 mg, 0.431 mmol, 43 % yield).

Note: Purification of this compound on SiO_2 was unsuccessful due to rapid hydrolysis.

^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[25]

Synthesis of 1,3-dioxoisoindolin-2-yl (2-phenylpropan-2-yl) oxalate (1d):



Compound **1d** was synthesized following the modified procedure by Overman *et al.* [ref. 28 of the manuscript]

A. A 25 mL Schlenk tube with a magnetic stirring bar was heated under vacuum with a heat gun, allowed to cool down to room temperature and backfilled with Ar. The reaction vessel was then evacuated and backfilled with Ar (x 2). N-hydroxyphthalimide (1.00 eq., 0.613 mmol, 100.0 mg) and THF (10 mL, C_{NHPI} = 0.06 M) were added sequentially under Ar and the resulting solution was stirred for 10 min at -78 °C. Next, oxalyl chloride (5.00 eq., 3.065 mmol, 263 µL) was added portionwise via syringe addition to the reaction mixture. The solution was allowed to warm up to room temperature and stirred overnight. The solvent was evaporated and the residue was dried under high vacuum at 30 °C for 3 h to yield chloro N-phthalimidoyl oxalate **1d-Cl** as a colorless solid. The crude product was redissolved in THF (10 mL, C_{NHPI} = 0.06 M) and used as a soltion in the next step.

B. A 10 mL Schlenk tube with a magnetic stirring bar was heated under vacuum with a heat gun, allowed to cool down to room temperature and backfilled with Ar. The reaction vessel was then evacuated and backfilled with Ar (x 2).
Cumyl alcohol **1dd** (1.25 eq., $9.30 \cdot 10^{-2}$ mmol, 12.7 mg) in 300 µL of THF and Et_3N (2.25 eq., 0.167 mmol, 23.3 µL) were added sequentially under Ar. Next, 0.06 M solution of chloro N-phthalimidoyl oxalate **1d-Cl** (1.00 eq., $7.44 \cdot 10^{-2}$ mmol) in THF (1.24 mL) was added. The resulting heterogeneous mixture was allowed to stir at room temperature for 4 h. The volatiles were removed under reduced pressure and the residue was dried under high vacuum at 30 °C for 3 h to yield compound **1d** as a beige solid. 1,3-dioxoisoindolin-2-yl (2-phenylpropan-2-yl) oxalate **1d** was then used in further polymerizations without additional purification.

7. Polymerization Procedures

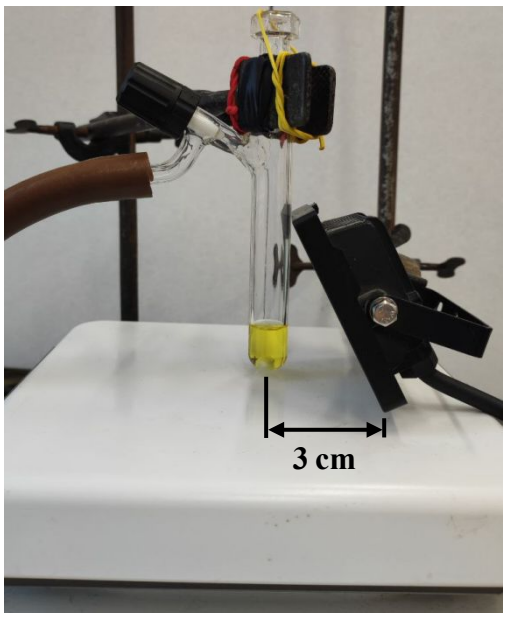
General Considerations and Experimental Setup for Photopolymerizations

Katritzky salts, NHPI esters, primary amines (their hydrochlorides), carboxylic acids, **pCTA's** and **CTA-4** were dried under high vacuum at 35 °C for 3 h and stored under Ar at 0 °C as solutions in DMA. For labile compounds, drying at room temperature was used instead. Liquid compounds with low boiling point were dried with 3 Å MS. **pCTA-1**, **pCTA-2** and **pCTA-3** as solutions were protected from the ambient light with aluminum foil and used for no longer, than 2 weeks.

For all photopolymerizations a 10 mL Schlenk reactor equipped with a PTFE-coated stirring bar and the appropriate light source was used. The reaction temperature was measured to be between 38-40 ºC without external cooling.

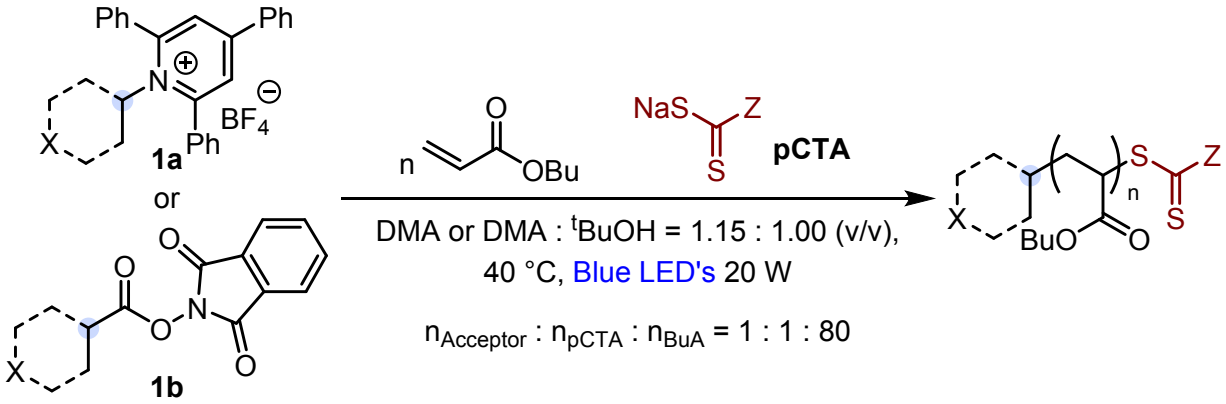
#	Name	λ^{max}, nm	Output Power, W	Measured Light Intensity, mW / cm^2
1	Feron LL-902 41521	435	20	145
2	HAUTY DC24V-2835-120D-8MM-B	435	10	60
3	Feron LL-903 32211	530	30	155
4	Svetotron SV-20W-UV	395	20	130

Typical polymerization setup (left), color change during the polymerization (right):



From left to right: before **pCTA-2** addition, + **pCTA-2**, 15 min under Blue LED's irradiation

General Procedure D: EDA-RAFT Polymerization of Butyl Acrylate



*Katritzky Salt **1a** as Acceptor*

A 10 mL Schlenk tube with a magnetic stirring bar was heated under vacuum with a heat gun, allowed to cool down to room temperature and backfilled with Ar. The reaction vessel was then evacuated and backfilled with Ar (x 2). DMA (475 µL), butyl acrylate (80.00 eq., 5.952 mmol, 853 µL, C_{mix} = 3.50 M), Katritzky salt **1a** (1.00 eq., 7.44□10^{-2} mmol, 186 µL 0.40 M in DMA) and **pCTA** (1.00 eq., 7.44□10^{-2} mmol, 186 µL 0.40 M in DMA) were added sequentially under Ar. The reaction mixture was degassed by a freeze-pump-thaw cycle (x 3) and placed under 20 W blue LED projector. After a predetermined time, aliquots of approximately 150 µL were taken out from the reaction mixture and quenched in an excess of MeOH : H_2O = 9 : 1 (v/v) mixture. Monomer conversions were determined gravimetrically. The obtained samples were reprecipitated one more time for ^{1}H NMR analysis.

Note: After the addition of **pCTA** the reaction mixture should be protected from ambient light as it may induce the polymerization process.

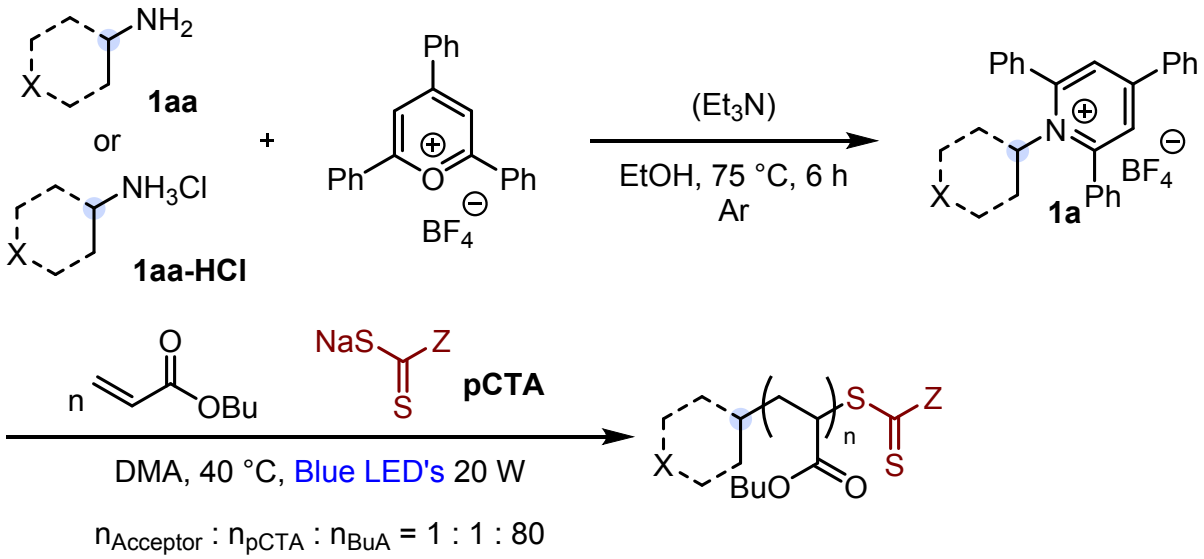
*NHPI Ester **1b** as Acceptor*

A 10 mL Schlenk tube with a magnetic stirring bar was heated under vacuum with a heat gun, allowed to cool down to room temperature and backfilled with Ar. The reaction vessel was then evacuated and backfilled with Ar (x 2). DMA (310 µL), ^{t}BuOH (510 µL), butyl acrylate (80.00 eq., 4.255 mmol, 610 µL, C_{mix} = 2.50 M), NHPI ester **1b** (1.00 eq., 5.32□10^{-2} mmol, 133 µL 0.40 M in DMA) and **pCTA** (1.00 eq., 5.32□10^{-2} mmol, 133 µL 0.40 M in DMA) were added sequentially under Ar. The reaction mixture was degassed by a freeze-pump-thaw cycle (x 3) and placed under 20 W blue LED projector. After a predetermined time, aliquots of approximately 150 µL were taken out from the reaction mixture and quenched in an excess of MeOH : H_2O = 9 : 1 (v/v) mixture. Monomer conversions were determined gravimetrically. The obtained samples were reprecipitated one more time for ^{1}H NMR analysis.

Note: After the addition of **pCTA** the reaction mixture should be protected from ambient light as it may induce the polymerization process.

General Procedure E: 'One-Pot' EDA-RAFT Polymerization of Butyl Acrylate

*Procedure for Katritzky Salt **1a***



Note: We did not observe any significant changes in IE and PDI of the products after scaling up polymerizations from General Procedure D to scale in this procedure (x 2.5, see Characterization Data of Synthesized Polymers).

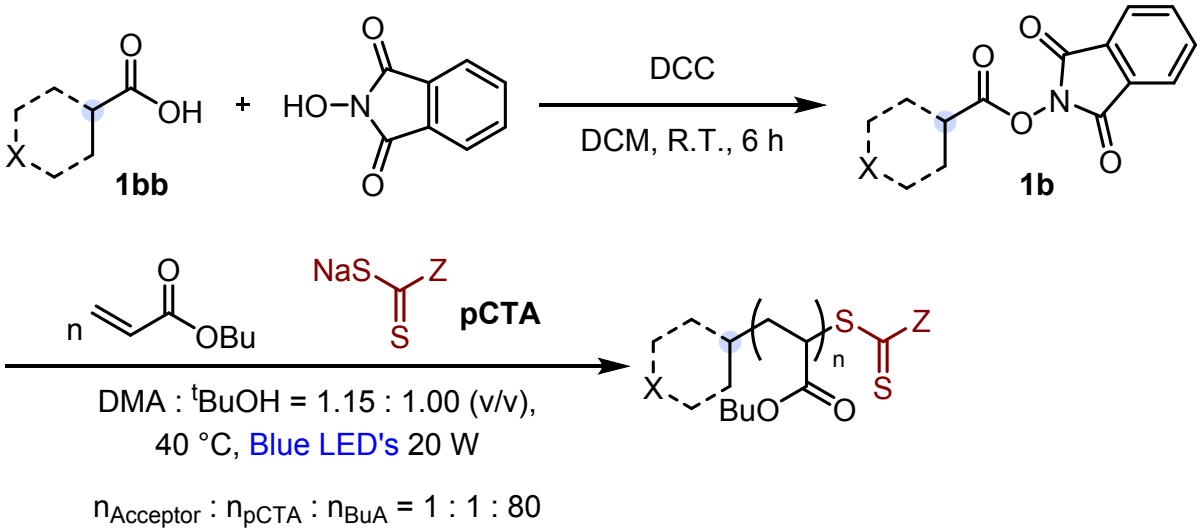
A 10 mL Schlenk tube with a magnetic stirring bar was heated under vacuum with a heat gun, allowed to cool down to room temperature and backfilled with Ar. The reactor was charged with 2,4,6-triphenylpyrylium tetrafluoroborate (1.00 eq., 0.186 mmol, 73.7 mg, C = 0.50 M in EtOH), dry EtOH (373 µL) and primary amine **1aa** (1.10 eq., 0.205 mmol) were added sequentially. The resulting suspension was stirred and heated at 75 °C in an oil bath for 6 h. The mixture was allowed to cool down to room temperature and dried under high vacuum at 45 °C for 3 h. After this, DMA (1.65 mL), butyl acrylate (80.00 eq., 14.880 mmol, 2.13 mL, C_{mix} = 3.50 M) and **pCTA** (1.00 eq., 0.186 mmol, 465 µL 0.4 M in DMA) were added sequentially under Ar. The reaction mixture was degassed by a freeze-pump-thaw cycle (x 3) and placed under 20 W blue LED projector. After a predetermined time, aliquots of approximately 200 µL were taken out from the reaction mixture and quenched in an excess of MeOH : H_2O = 9 : 1 (v/v) mixture. Monomer conversions were determined gravimetrically. The obtained samples were reprecipitated one more time for ^{1}H NMR analysis.

Note: After the addition of **pCTA** the reaction mixture should be protected from ambient light as it may induce the polymerization process.

Modified procedure for amine hydrochloride salt as a starting material:

Et_3N (1.20 eq., 0.223 mmol, 31.0 µL) was added to a solution of the corresponding alkyl ammonium hydrochloride **1aa-HCl** (1.10 eq., 0.205 mmol, C = 0.55 M in EtOH) in dry EtOH (373 µL) and the resulting mixture was stirred for 30 min at room temperature. After this 2,4,6-triphenylpyrylium tetrafluoroborate (1.00 eq., 0.186 mmol, 73.8 mg, C = 0.50 M in EtOH) was added. The following steps were analogous to the procedure for free amines.

*Procedure for NHPI Ester **1b***

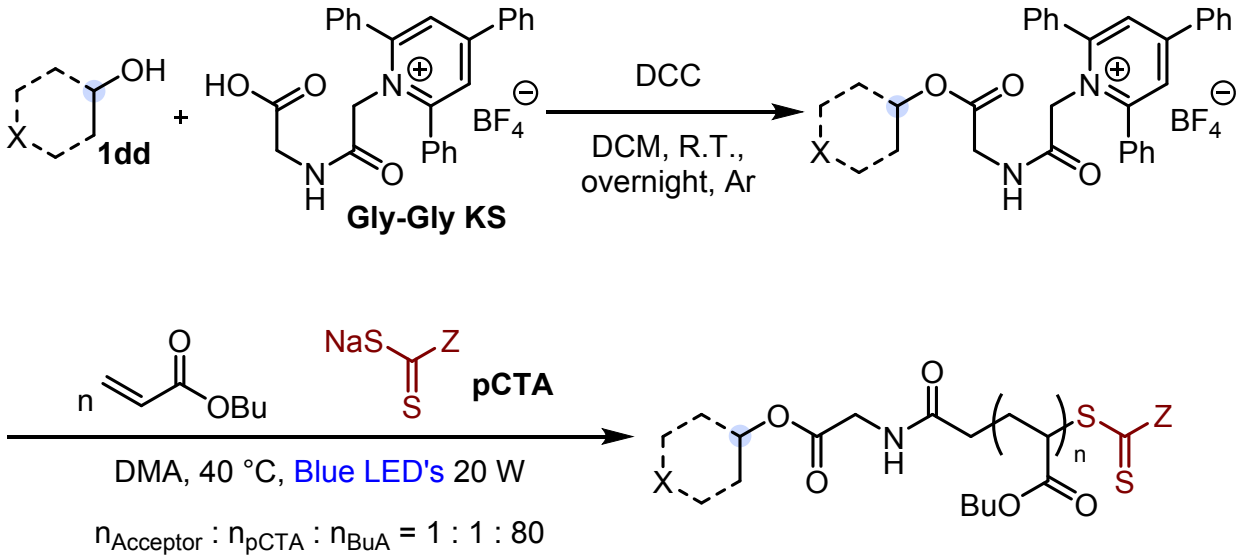


A 10 mL Schlenk tube with a magnetic stirring bar was heated under vacuum with a heat gun, allowed to cool down to room temperature and backfilled with Ar. The reactor was charged with carboxylic acid **1bb** (1.00 eq., $5.32\square10^{-2}$ mmol) and N-hydroxyphthalimide (1.00 eq., $5.32\square10^{-2}$ mmol, 105 µL 0.51 M in DCM) and the resulting suspension was stirred for 5 min at 0 °C. After this, DCC (1.00 eq., $5.32\square10^{-2}$ mmol, 60 µL 0.89 M in DCM) added in 3 portions to the reaction mixture. The resulting mixture was allowed to warm up to room temperature and stirred for 6 h. The solvent was evaporated and the residue was dried under high vacuum at 35 °C for 3 h. The following steps were analogous to the General Procedure D for NHPI esters.

Note: After the addition of **pCTA** the reaction mixture should be protected from ambient light as it may induce the polymerization process

General Procedure F: EDA-RAFT Polymerization of Butyl Acrylate with Gly-Gly KS reagent

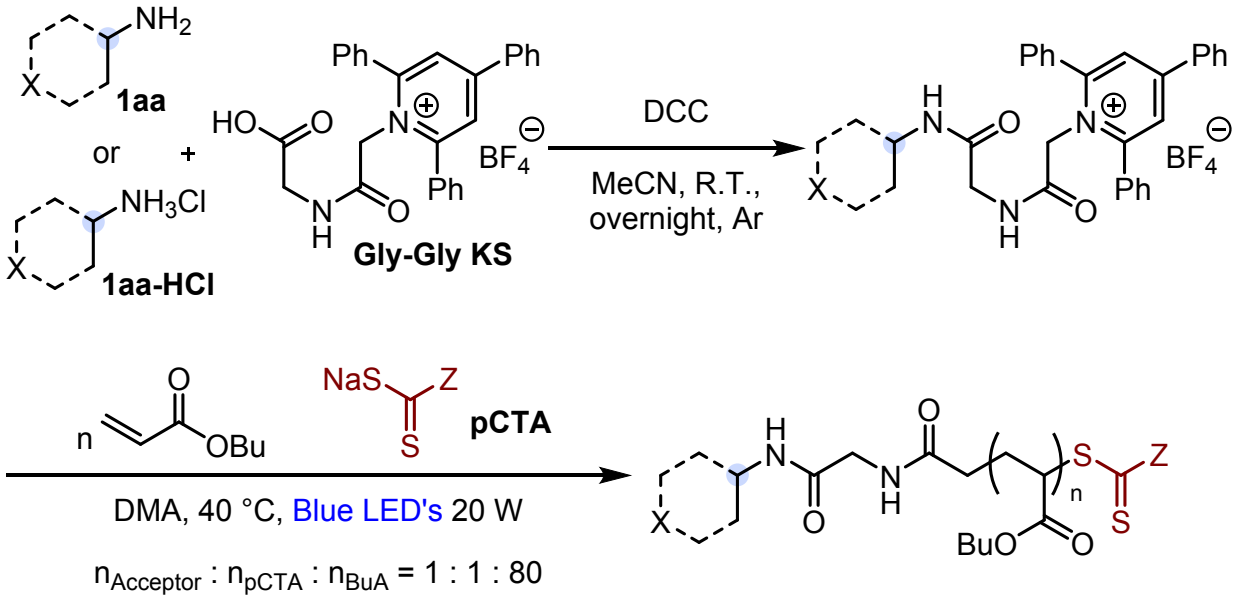
*Procedure for **Gly-Gly KS** coupling with alcohols*



A 10 mL Schlenk tube with a magnetic stirring bar was heated under vacuum with a heat gun, allowed to cool down to room temperature and backfilled with Ar. The reactor was charged with **Gly-Gly KS** (1.00 eq., $7.44 \square 10^{-2}$ mmol, 38.0 mg), dry DCM (180 µL) and alcohol **1dd** (1.05 eq., $7.81 \square 10^{-2}$ mmol). After this, DCC (1.00 eq., $7.44 \square 10^{-2}$ mmol, 68 µL 1.10 M in DCM) added in 2 portions to the reaction mixture at 0 °C. The resulting mixture was allowed to warm up to room temperature and stirred overnight (full conversion was confirmed by TLC). The suspension was filtered into another Schlenk tube through cotton, which was then washed with DCM x 5 (c.a. 700-800 µL in total). The solvent was evaporated (0 °C → 35 °C) and the residue was dried under high vacuum at 35 °C for 3 h. The following steps were analogous to the General Procedure D for Katritzky salts.

Note: For some substrates, the addition of catalytic amounts of DMAP may be necessary. We tested the effect of 5 mol % DMAP on the polymerization process and observed no significant changes.

*Procedure for **Gly-Gly KS** coupling with amines and their hydrochlorides*

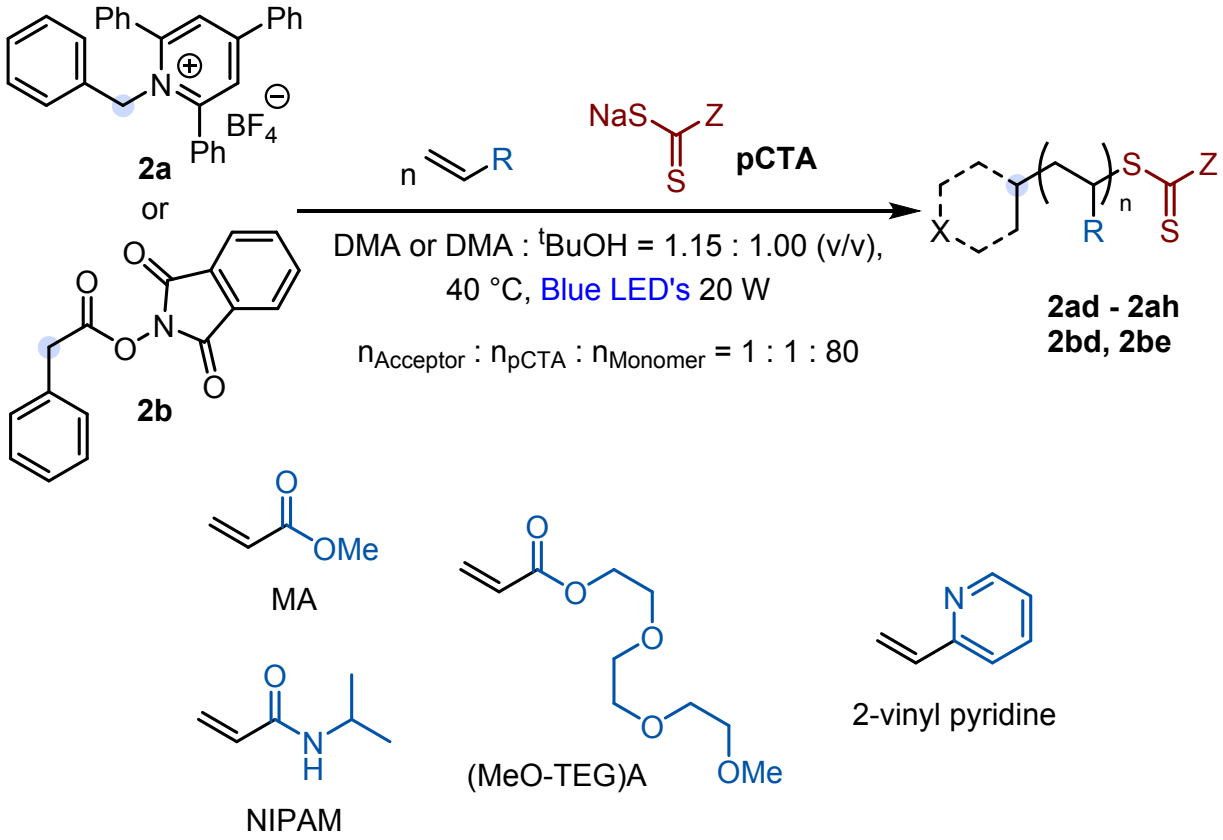


A 10 mL Schlenk tube with a magnetic stirring bar was heated under vacuum with a heat gun, allowed to cool down to room temperature and backfilled with Ar. The reaction vessel was then evacuated and backfilled with Ar (x 2). The reactor was charged with **Gly-Gly KS** (1.00 eq., $7.44\square10^{-2}$ mmol, 38.0 mg), dry MeCN (200 µL). DCC (1.00 eq., $7.44\square10^{-2}$ mmol, 68 µL 1.10 M in MeCN) was added in 2 portions to the reaction mixture and the mixture was left to stir for 10 min. After this, amine **1aa** (1.05 eq., $7.81\square10^{-2}$ mmol, 200 µL MeCN) was added and the resulting mixture stirred overnight (full conversion was confirmed by TLC). The suspension was filtered into another Schlenk tube through cotton, which was then washed with MeCN x 3 (c.a. 400-500 µL in total). The solvent was evaporated (0 °C → 35 °C) and the residue was dried under high vacuum at 35 °C for 4 h. The following steps were analogous to the General Procedure D for Katritzky salts.

<u>Modified procedure for amine hydrochloride salt as a starting material:</u>

Et_3N (1.05 eq., $7.81\square10^{-2}$ mmol, 10.9 µL) was added to a solution of the corresponding alkyl ammonium hydrochloride **1aa-HCl** (1.05 eq., $7.81\square10^{-2}$ mmol) in dry MeCN (200 µL) and the resulting mixture was stirred for 30 min at room temperature. The following steps were analogous to the procedure for free amines.

General Procedure G: EDA-RAFT Polymerization of Various Monomers



All polymerizations were performed according to the General Procedure D with $n_{Acceptor} : n_{\mathbf{pCTA\text{-}2}} : n_{Monomer} = 1 : 1 : 80$; [**2a**] = [**pCTA**] = 4.38□10^{-2} M or [**2b**] = [**pCTA**] = 3.13□10^{-2} M; and total V_{mix} = 1.70 mL.

#	Monomer	Solvent for precipitation
1	MA	Cold MeOH*
2	NIPAM	Hexane**
3	(MeO-TEG)A	-***
4	2-vinyl pyridine	Et_2O*

* The obtained samples were reprecipitated one more time for ^{1}H NMR analysis.
** poly(N-isopropyl acrylamide) samples were reprecipitated two more times from hexane to remove most of the monomer.
*** poly(methoxy triethylene glycol acrylate) samples were quenched with 300 µL of MeOH and evaporated. Conversions were determined by ^{1}H NMR (see Characterization Data of Synthesized Polymers for details).

8. Characterization Data of Synthesized Polymers

General Considerations:

- Theoretical molecular weight, M_n(theor) [a] was calculated as: M_n(theor) = [BuA] × Conv. × 128.17 + M_r(pCTA) – 23 + M_r(Head Group).
- M_n(SEC) [b] was determined by SEC against polystyrene standards (BuA, MA, (MeO-TEG)A, 2-VP) or poly(methyl methacrylate) standards (NIPAM).
- M_n(NMR) was determined by ^{1}H NMR and calculated as:

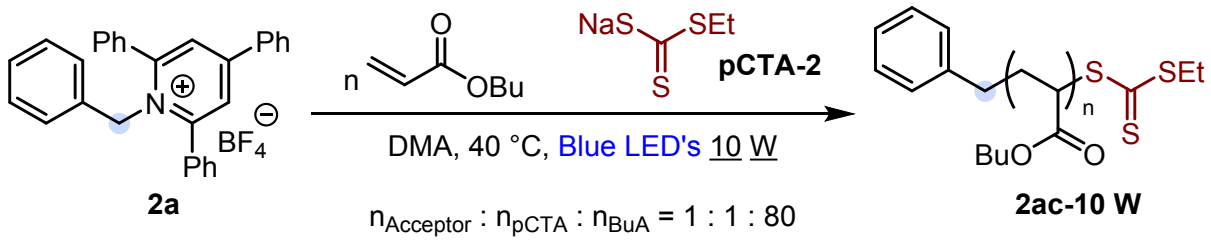
  M_n(NMR, Head) = (∫(f*) / 2 × 128.17) / (∫(Head) / N) + M_r(pCTA) – 23 + + M_r(Head Group), where ∫(Head) – integral intensity of the selected group of protons from the 'head' of the polymer chain; N – number of protons in the selected group. * – assigned for PBuA.

  M_n(NMR, Tail) = (∫(f*) / 2 × 128.17) / (∫(c*)) + M_r(pCTA) – 23 + + M_r(Head Group). * – assigned for PBuA.
- Initiation Efficiency, I_{eff} [e] was calculated as: I_{eff} = M_n(theor) / M_n(NMR, Head).
- α-end group incorporation, φ [f] was determined by ^{1}H NMR and calculated as: φ = (∫(Head) / N - ∫(PI)) / (∫(Head) / N) × 100 %, where ∫(Head) – integral intensity of the selected group of protons from the 'head' of the polymer chain; N – number of protons in the selected group; PI = multiplet at 2.70 ppm for **pCTA-2** (see Mechanistic Studies for details) and PI = singlet at ~ 5.75 ppm for **pCTA-3** [ref. 12 of the manuscript]. In some cases, φ was additionally confirmed by MALDI TOF MS analysis.
- * - degradation product of ω-end CTA (see Mechanistic Studies for details).
- The head group protons were assigned based on the ^{1}H NMR of the starting Katritzky salts / NHPI esters. In some cases, additional literature search was performed, focusing on the corresponding Giese addition products to acrylates.

Optimization of EDA-RAFT Polymerization Conditions (Selected Data)

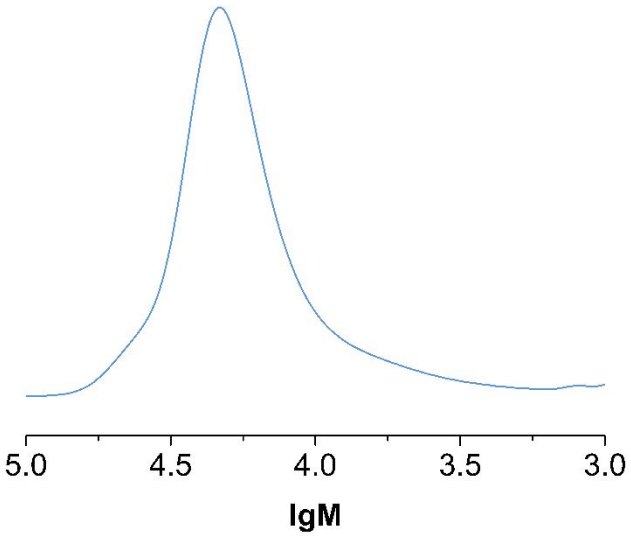
10 W Blue LED's instead of 20 W Blue LED's

Poly(butyl acrylate) **2ac-10W** was synthesized according to the General Procedure D, but using 10 W LED strip instead.



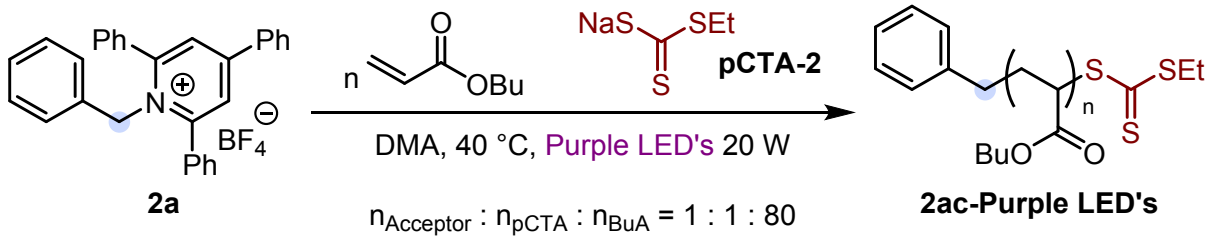
Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR, Head) [c] (g mol^{-1})	I_{eff} [e]	Đ
94.0	9850	14600	14700	0.67	1.40

GPC traces for poly(butyl acrylate) **2ac-10W** (**Figure S3**):



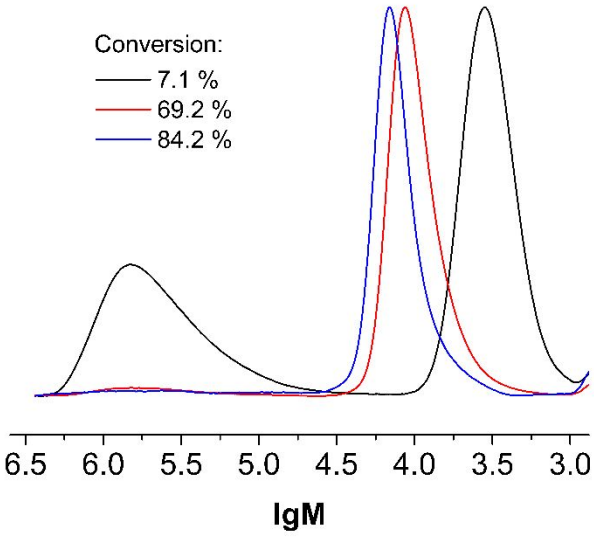
20 W Purple LED's instead of 20 W Blue LED's

Poly(butyl acrylate) **2ac-Purple LED's** was synthesized according to the General Procedure D, but using 20 W purple (395 nm) LED's.

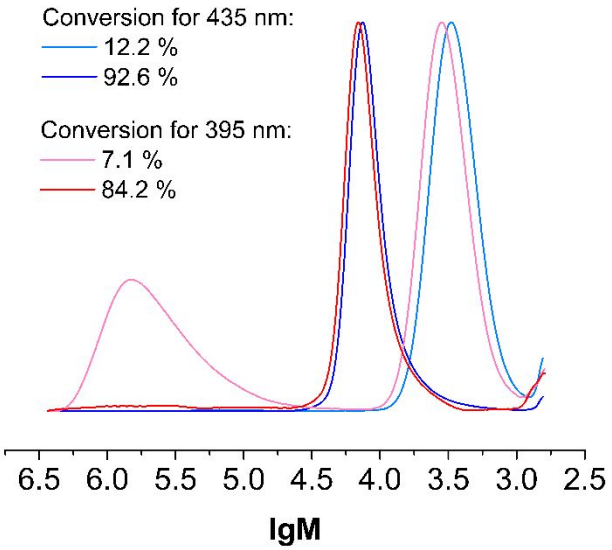


Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR, Head) [c] (g mol^{-1})	I_{eff} [e]	Đ
84.2	8850	11800	11200	0.79	1.15

GPC traces for poly(butyl acrylate) **2ac-Purple LED's** at various conversions (**Figure S4**):

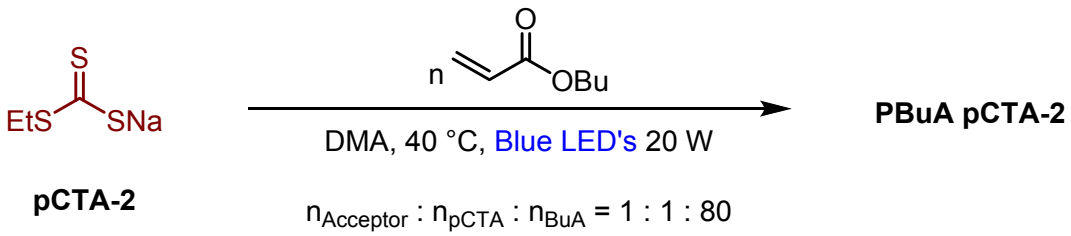


Overlaid GPC traces for poly(butyl acrylate) **2ac-Purple LED's** and poly(butyl acrylate) **2ac** at various conversions (**Figure S5**):



pCTA-2 as the sole initiator of polymerization

Poly(butyl acrylate) **PBuA pCTA-2** was synthesized according to the General Procedure D, but instead of Katritzky salt **1a** and **pCTA-2**, **pCTA-2** was used as the sole initiator.

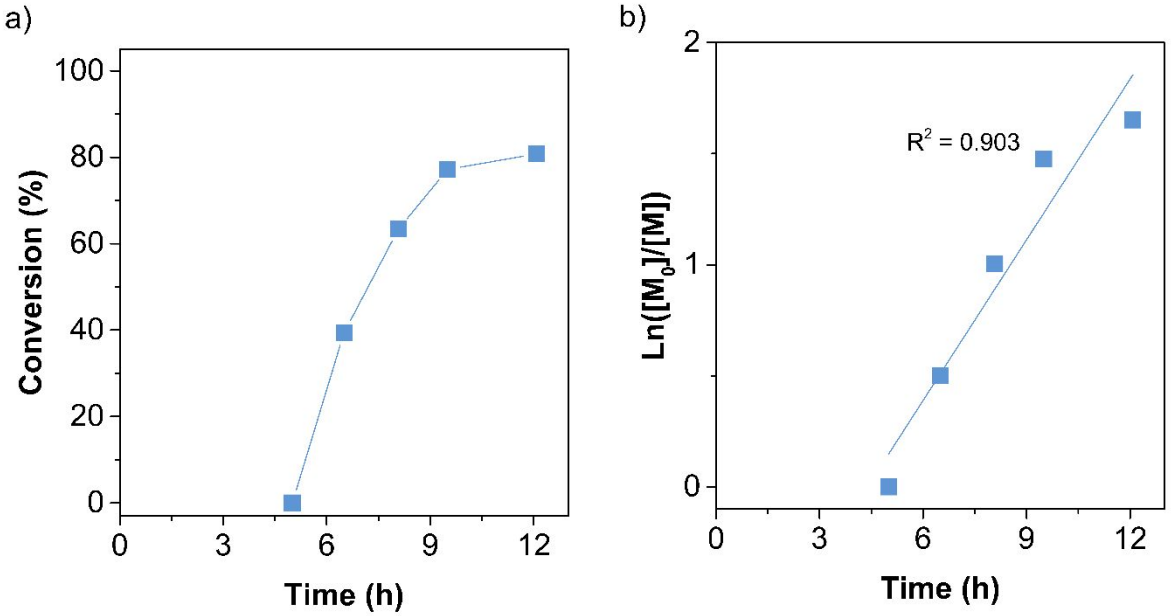


pCTA-2

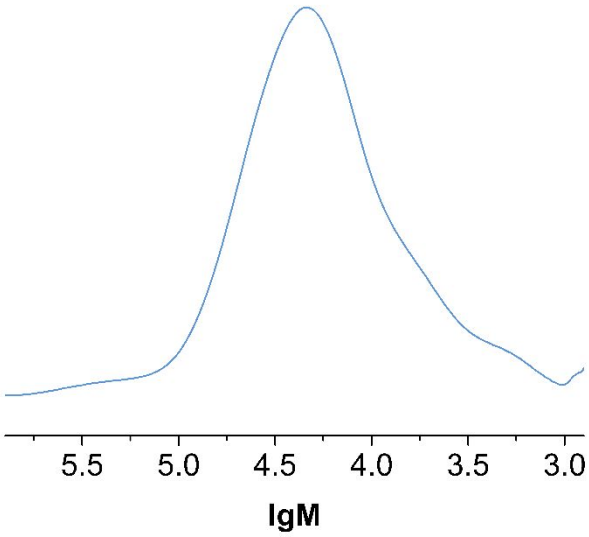
$n_{Acceptor} : n_{pCTA} : n_{BuA} = 1 : 1 : 80$

Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	Đ
80.8	8400	11000	2.82

Additional kinetic data for poly(butyl acrylate) **PBuA pCTA-2** (**Figure S6**):



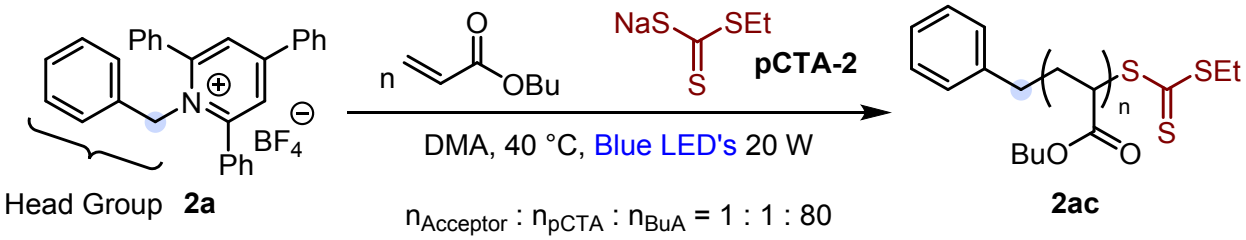
GPC traces for poly(butyl acrylate) **PBuA pCTA-2** (**Figure S7**):



Katritzky Salts / Amines:

Poly(butyl acrylate) 2ac

Poly(butyl acrylate) **2ac** was synthesized according to the General Procedure D.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**k+m**) [c]	Tail (**c**) [d]			
92.6	9700	10200	10400	12600	0.93	> 99	1.22

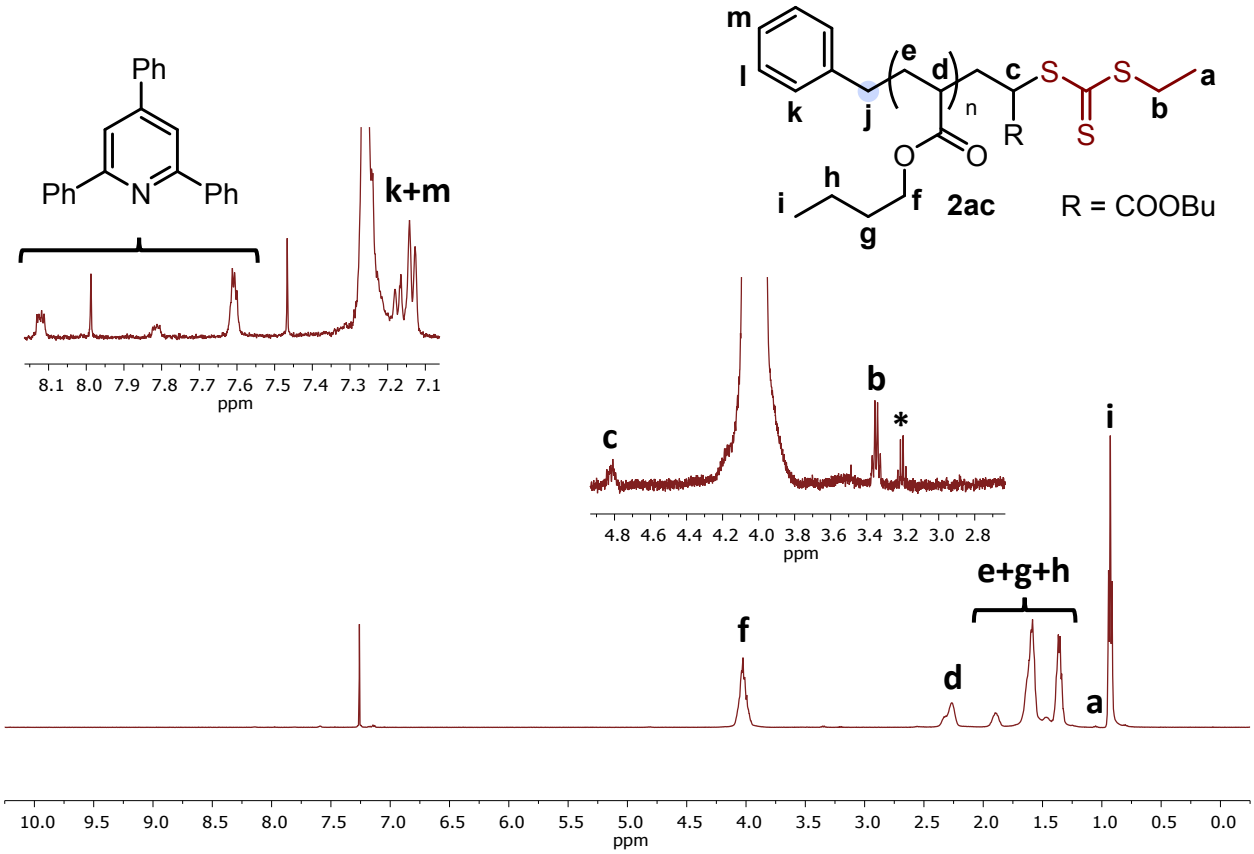
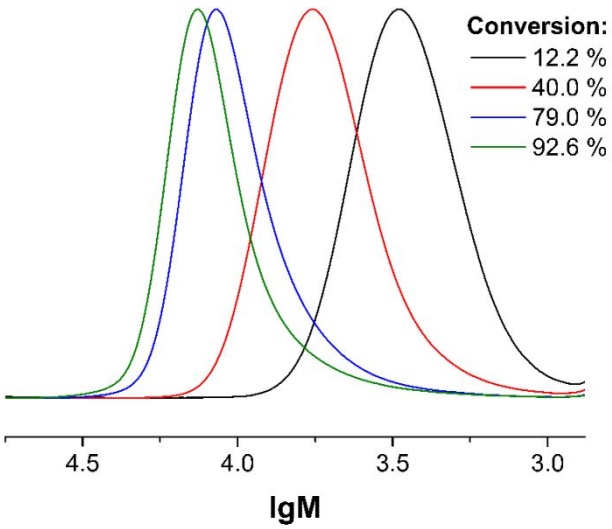
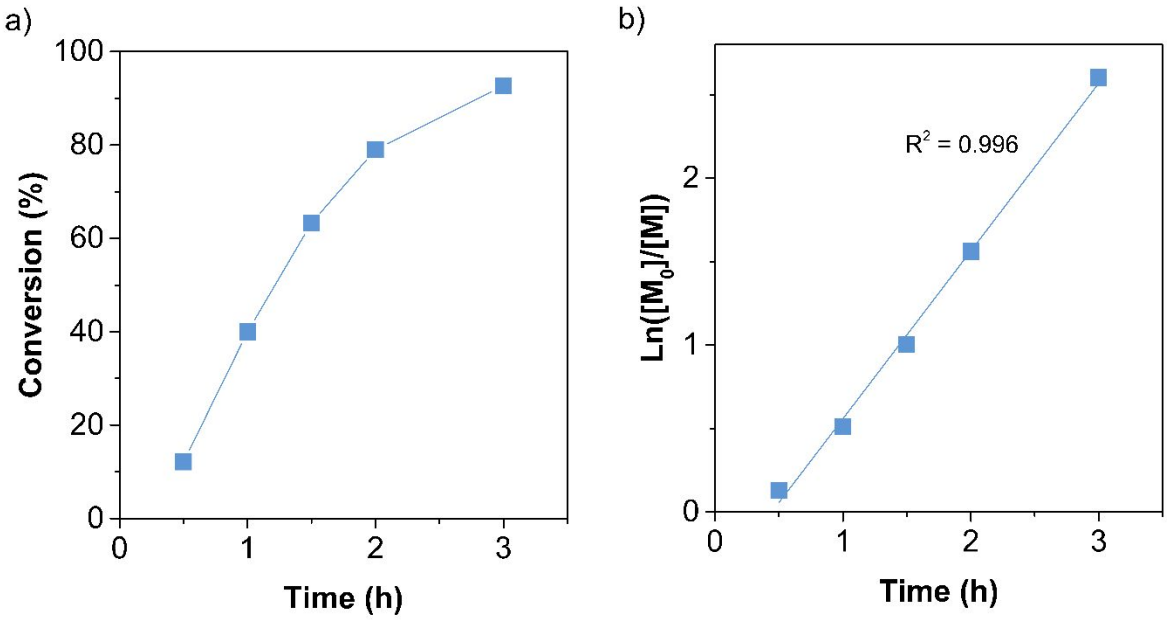


Figure S8. ^{1}H NMR spectrum of poly(butyl acrylate) **2ac**. *degradation product of ω-end CTA.

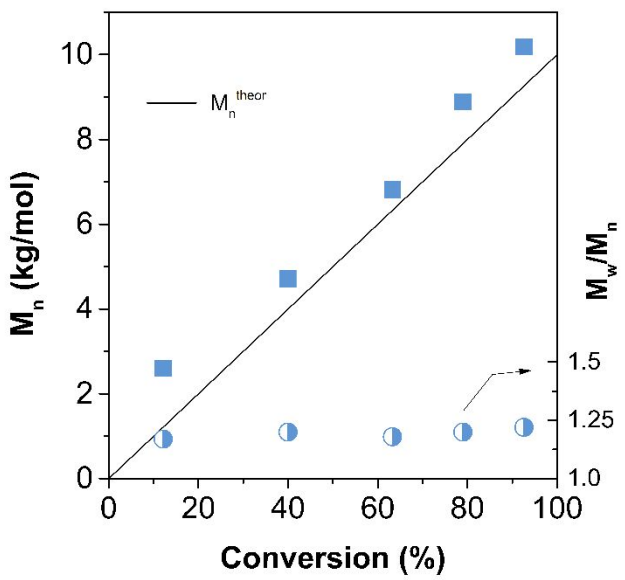
GPC traces for poly(butyl acrylate) **2ac** at various conversions:



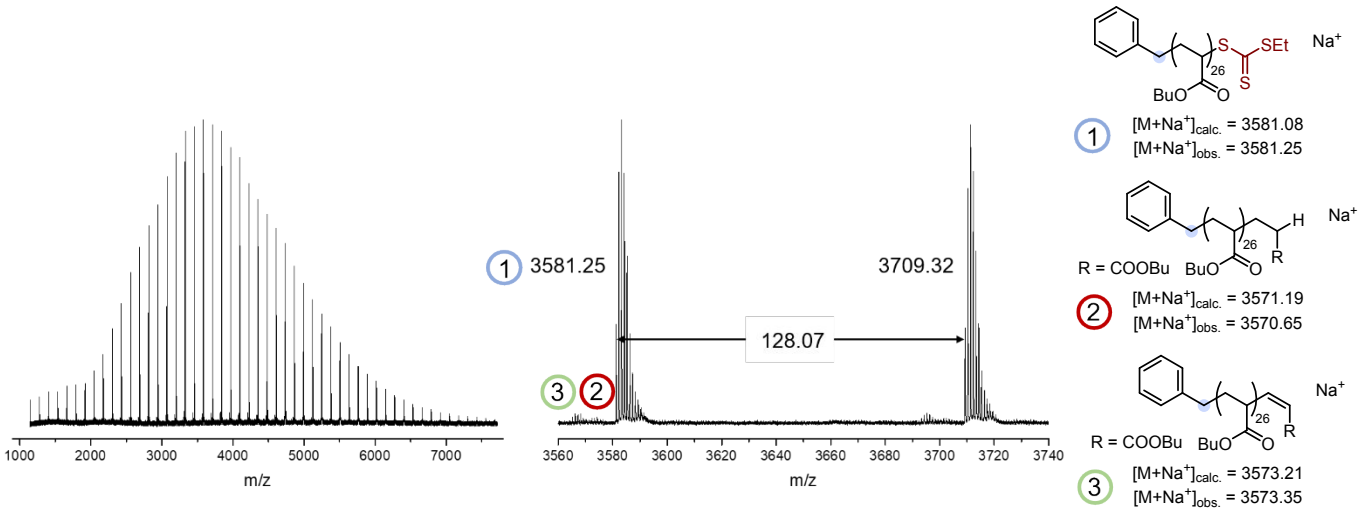
Additional kinetic data for poly(butyl acrylate) **2ac**:



c)



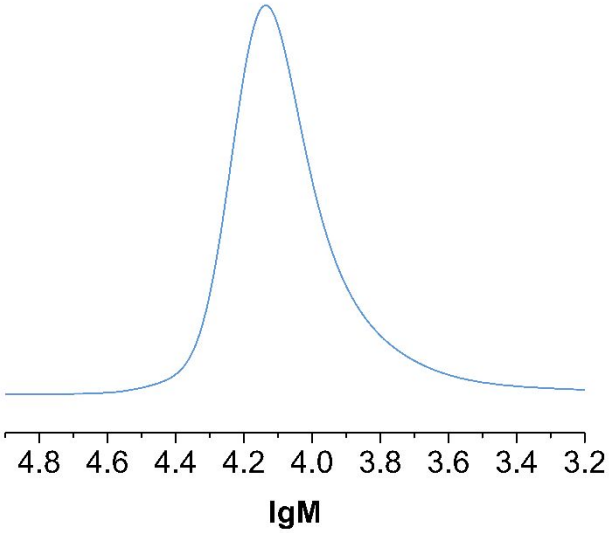
MALDI-TOF MS spectrum of PBuA **2ac** with Conv. = 19.6 %, M_n = 3500, Đ = 1.20 (left); possible peaks assignment (right):



Poly(butyl acrylate) 2ac' – 2.5x scale:

Conv., %	Time, h	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR, Head) [c] (g mol^{-1})	IE [e]	Đ
95.9	3.0	10050	10900	11000	0.91	1.21

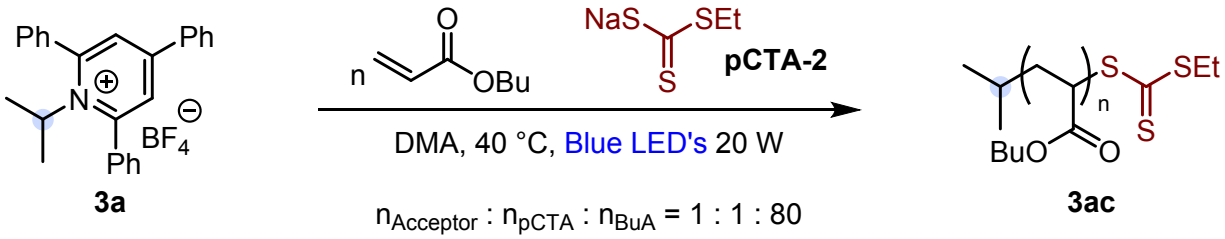
GPC traces for poly(butyl acrylate) **2ac'**:



This data clearly shows, that there are no significant changes in M_n, IE and Đ of the product after scaling up polymerization from the General Procedure D.

Poly(butyl acrylate) 3ac

Poly(butyl acrylate) **3ac** was synthesized according to the General Procedure D.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head [c]	Tail (c) [d]			
83.0	8700	20200	-	20200	-	> 99	1.31

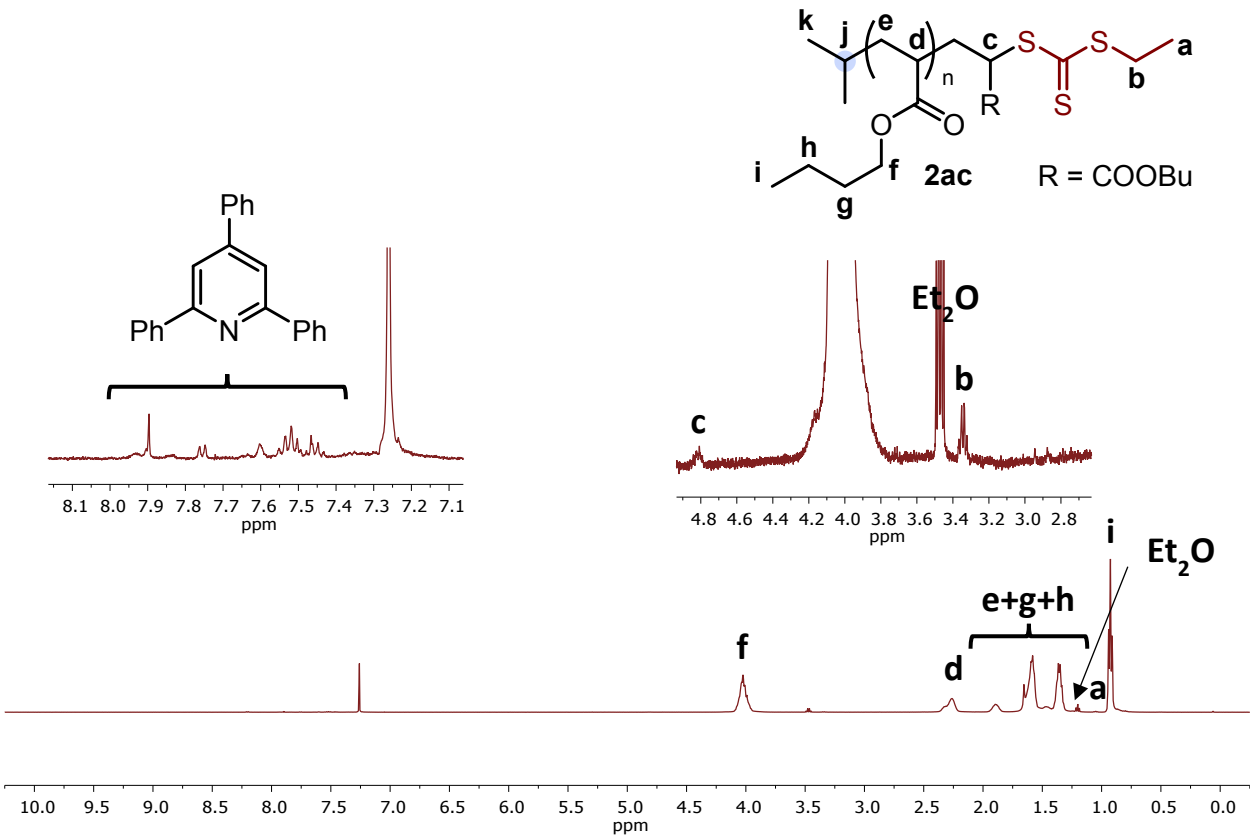
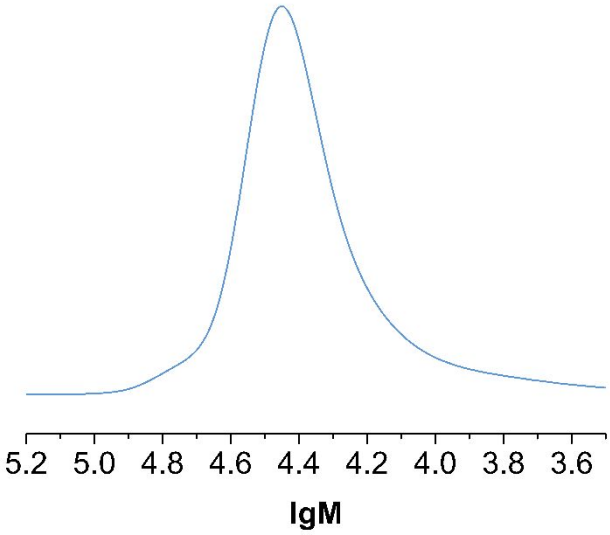
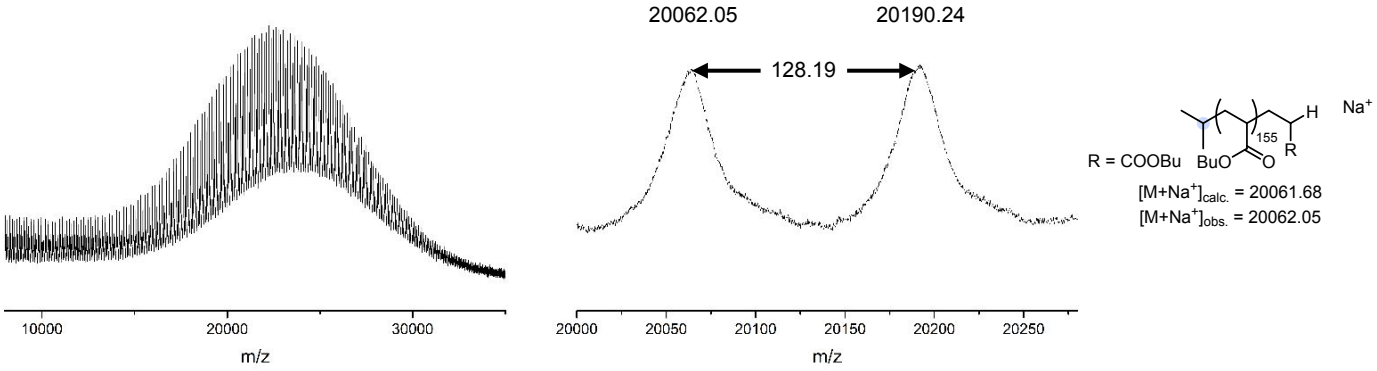


Figure S9. ^{1}H NMR spectrum of poly(butyl acrylate) **3ac**.

GPC traces for poly(butyl acrylate) **3ac** (**Figure S10**):



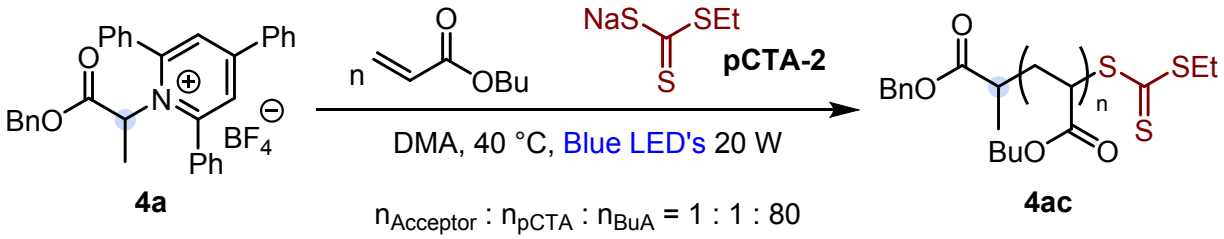
MALDI-TOF MS spectrum of PBuA **3ac** with Conv. = 74.7 %, M_n = 16000, Đ = 1.23 (left); possible peaks assignment (right) (**Figure S11**):



Unlike other MALDI-TOF MS spectra, the main product observed here was hydride-capped polymer chains at ω-end. This may be due to the lower percentage of CTA at ω-end of the initial sample.

Poly(butyl acrylate) 4ac

Poly(butyl acrylate) **4ac** was synthesized according to the General Procedure D.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**l**) [c]	Tail (**c**) [d]			
> 99	10550	10100	10700	12400	0.99	> 99	1.25

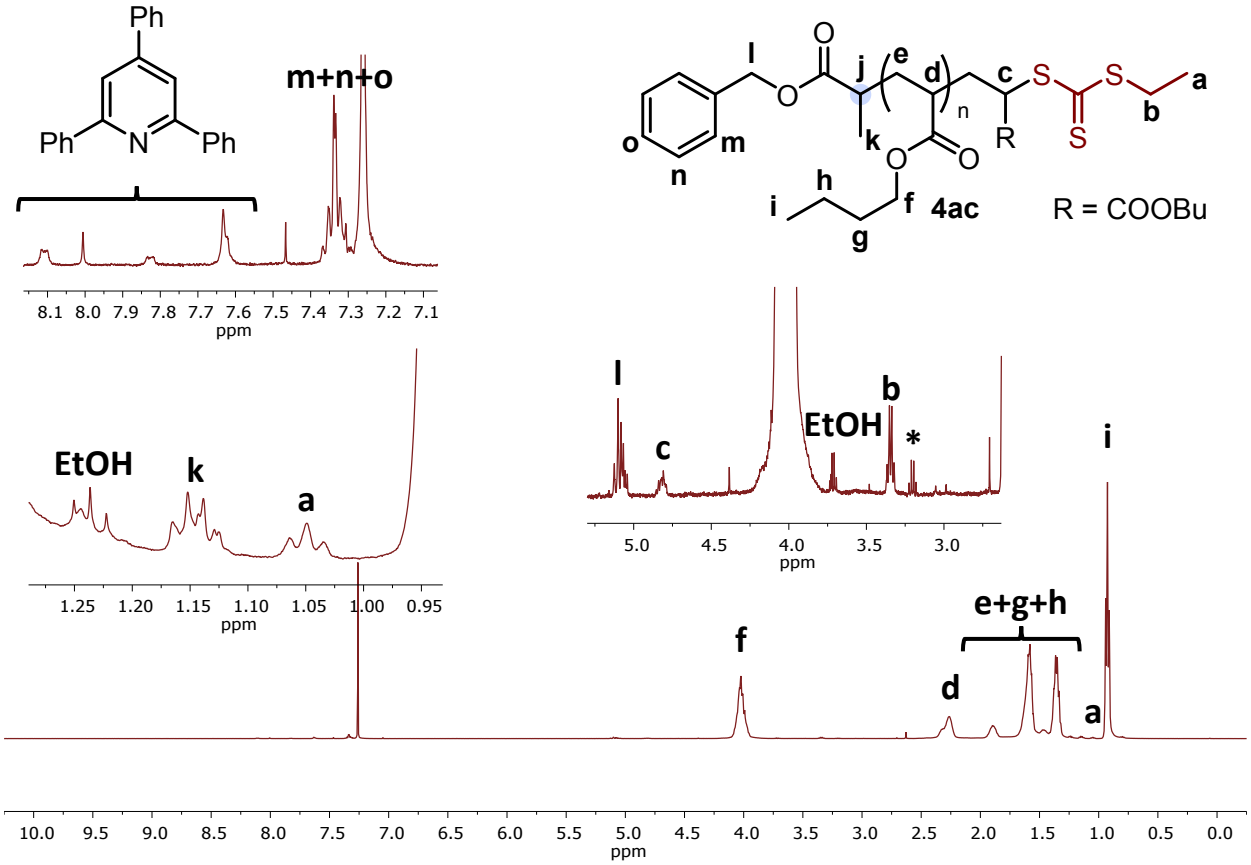
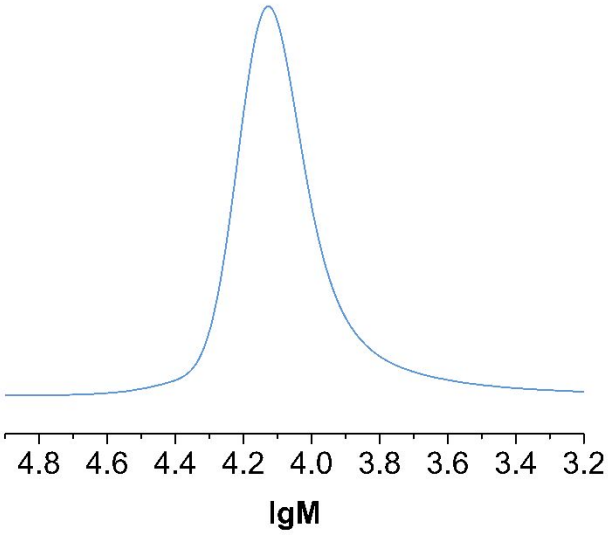


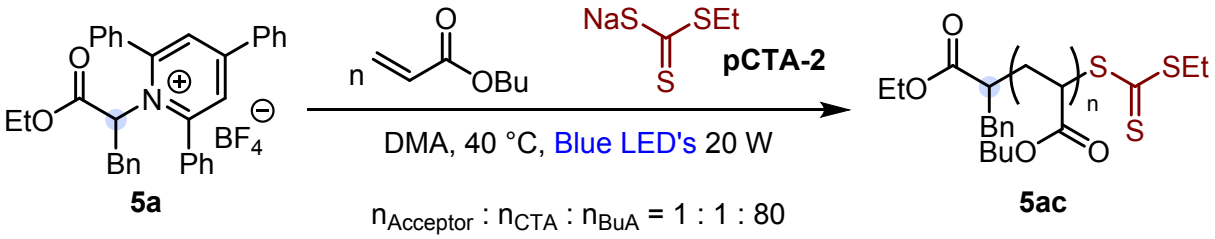
Figure S12. ^{1}H NMR spectrum of poly(butyl acrylate) **4ac**. *degradation product of ω-end CTA.

GPC traces for poly(butyl acrylate) **4ac** (**Figure S13**):



Poly(butyl acrylate) 5ac

Poly(butyl acrylate) **5ac** was synthesized according to the General Procedure D.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**l**) [c]	Tail (**c**) [d]			
84.9	9000	9000	9500	13100	0.95	> 99	1.24

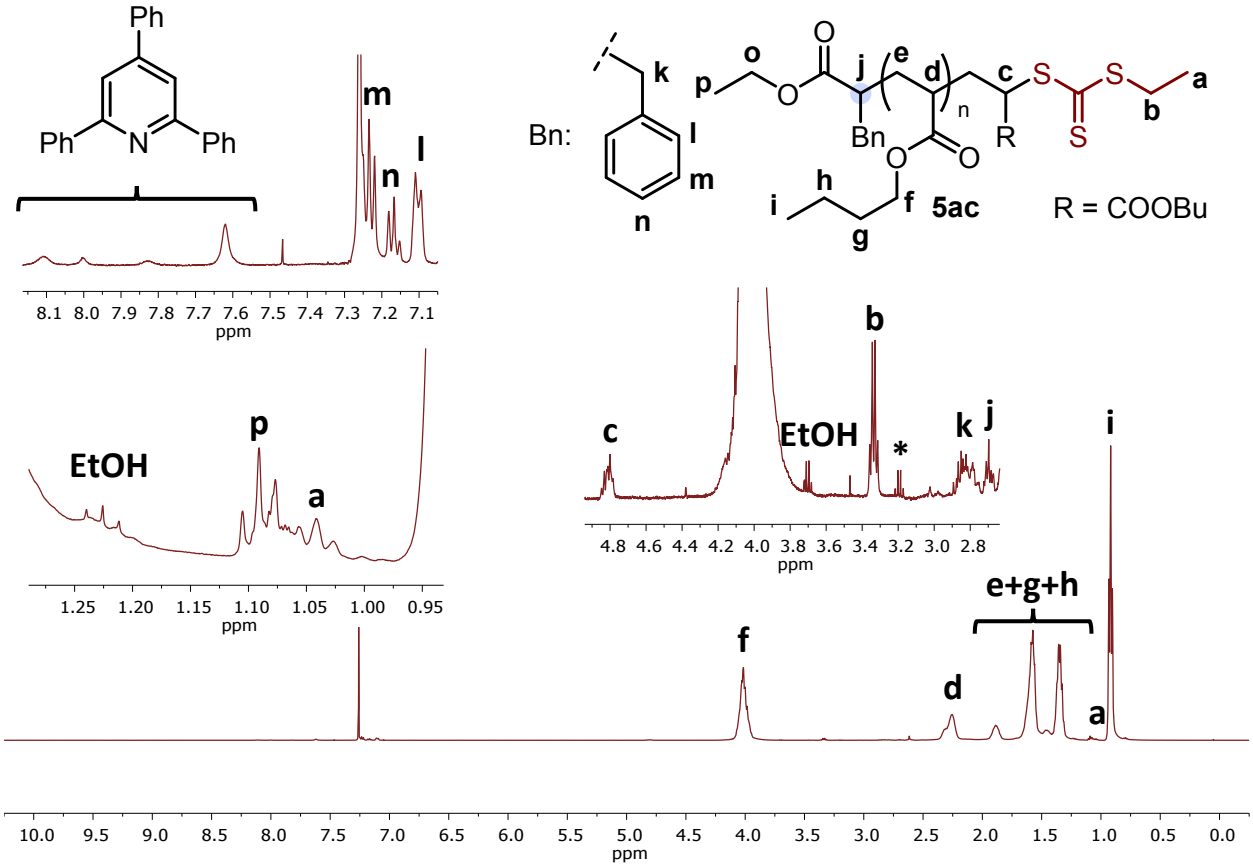
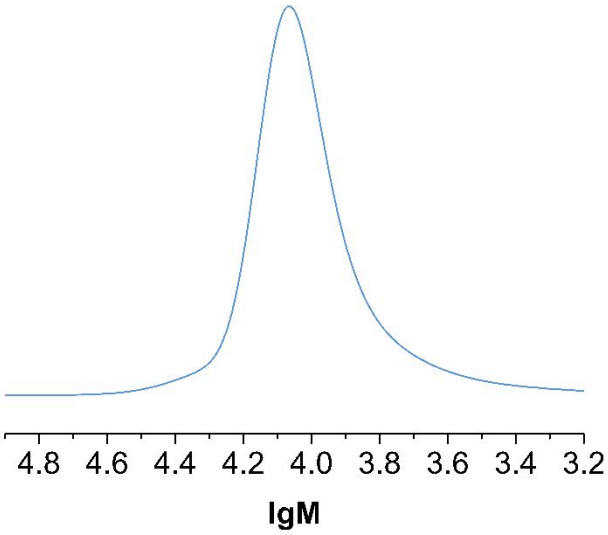


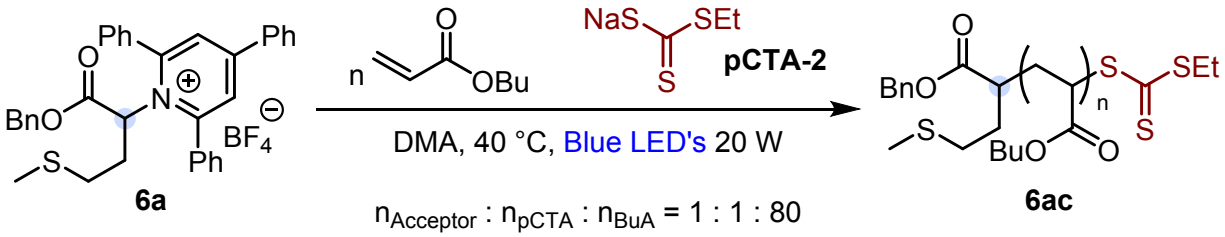
Figure S14. ^{1}H NMR spectrum of poly(butyl acrylate) **5ac**. *degradation product of ω-end CTA.

GPC traces for poly(butyl acrylate) **5ac** (**Figure S15**):



Poly(butyl acrylate) 6ac

Poly(butyl acrylate) **6ac** was synthesized according to the General Procedure D.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**n**) [c]	Tail (**c**) [d]			
88.7	9450	10400	12000	13200	0.79	> 99	1.26

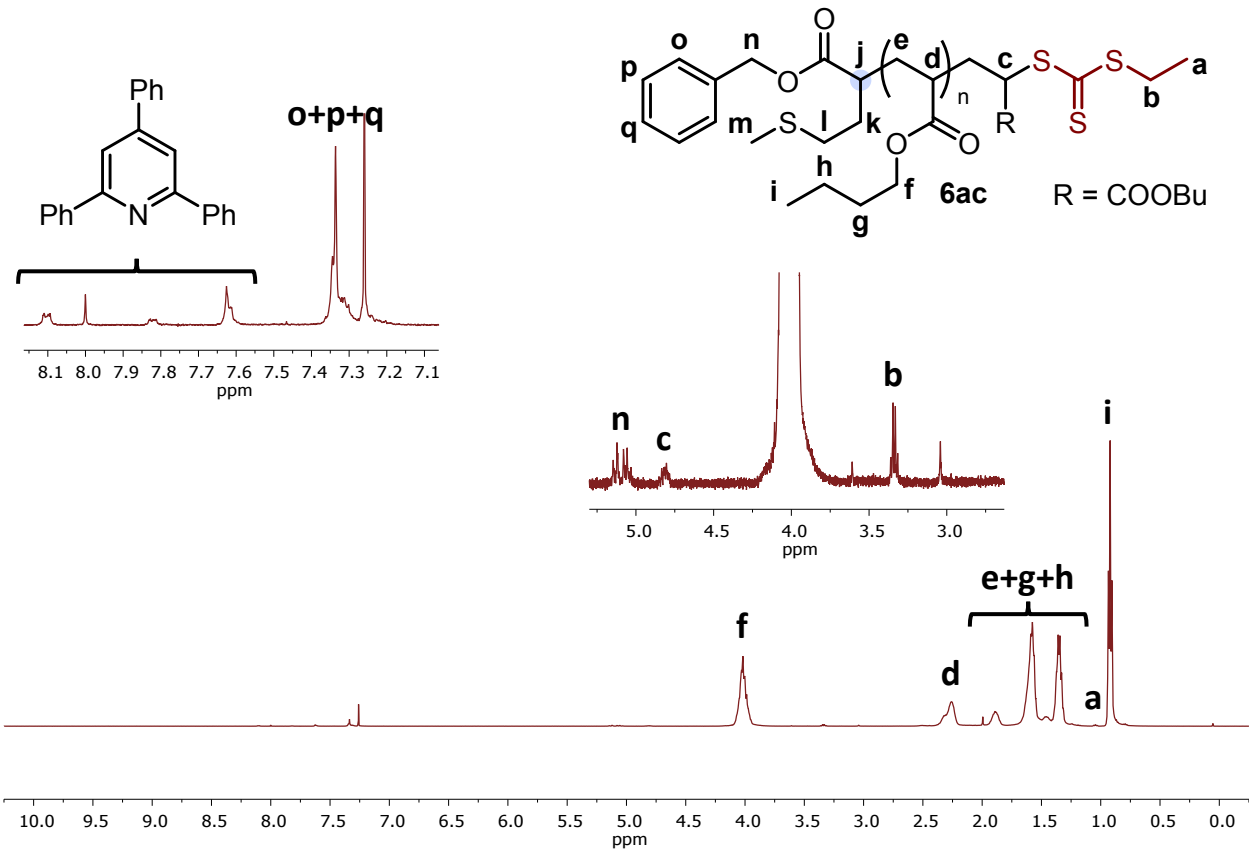
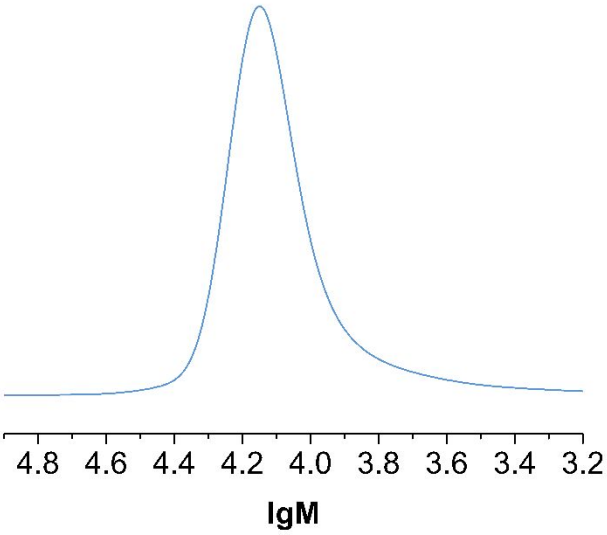


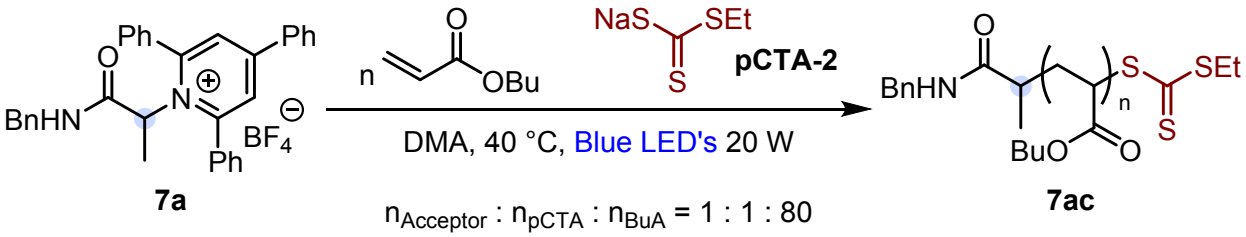
Figure S16. ^{1}H NMR spectrum of poly(butyl acrylate) **6ac**.

GPC traces for poly(butyl acrylate) **6ac** (**Figure S17**):



Poly(butyl acrylate) 7ac

Poly(butyl acrylate) **7ac** was synthesized according to the General Procedure D.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**m**) [c]	Tail (**c**) [d]			
44.5	4850	15400	15800	-*	0.31	> 99	1.62

*Only trace amounts of ω-end CTA were found. Large quantities of the degradation product of ω-end CTA were observed.

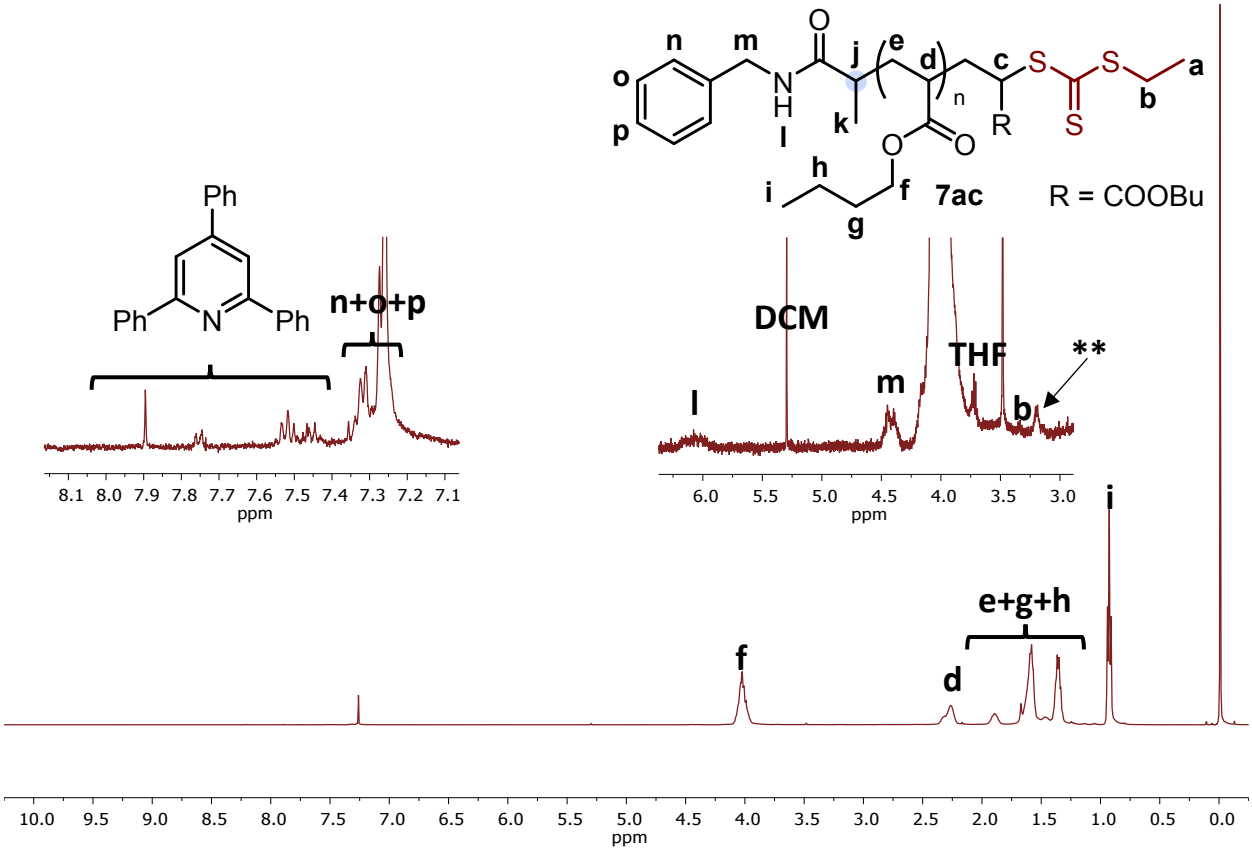
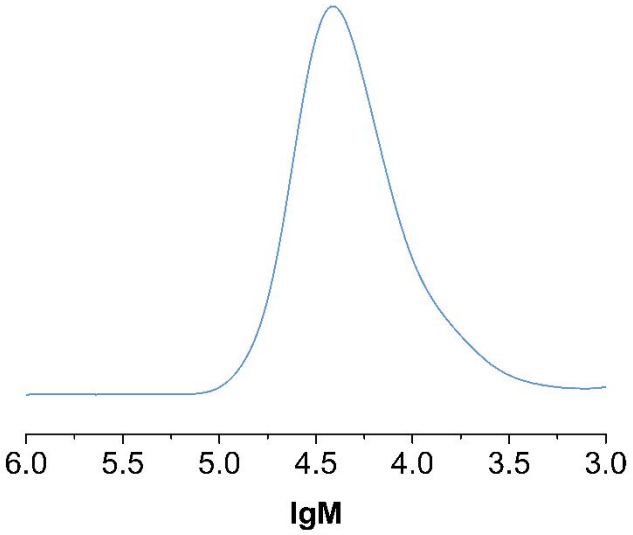


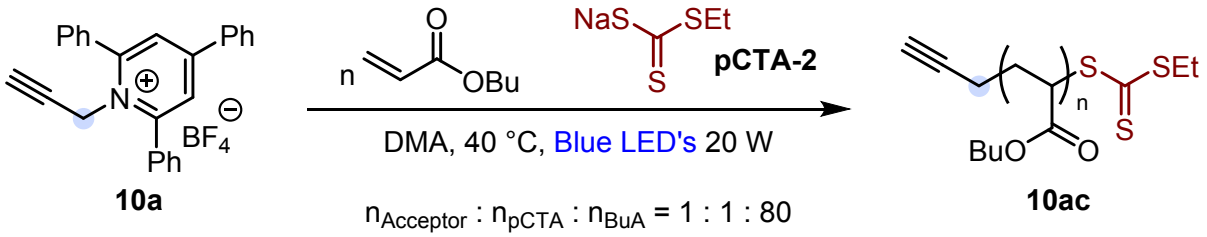
Figure S18. ^{1}H NMR spectrum of poly(butyl acrylate) **7ac**. **degradation product of ω-end CTA.

GPC traces for poly(butyl acrylate) **7ac** (**Figure S19**):



Poly(butyl acrylate) 10ac

Poly(butyl acrylate) **10ac** was synthesized according to the General Procedure D.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head [c]	Tail (c) [d]			
99.9	10400	14200	-	16100	-	> 99	1.26

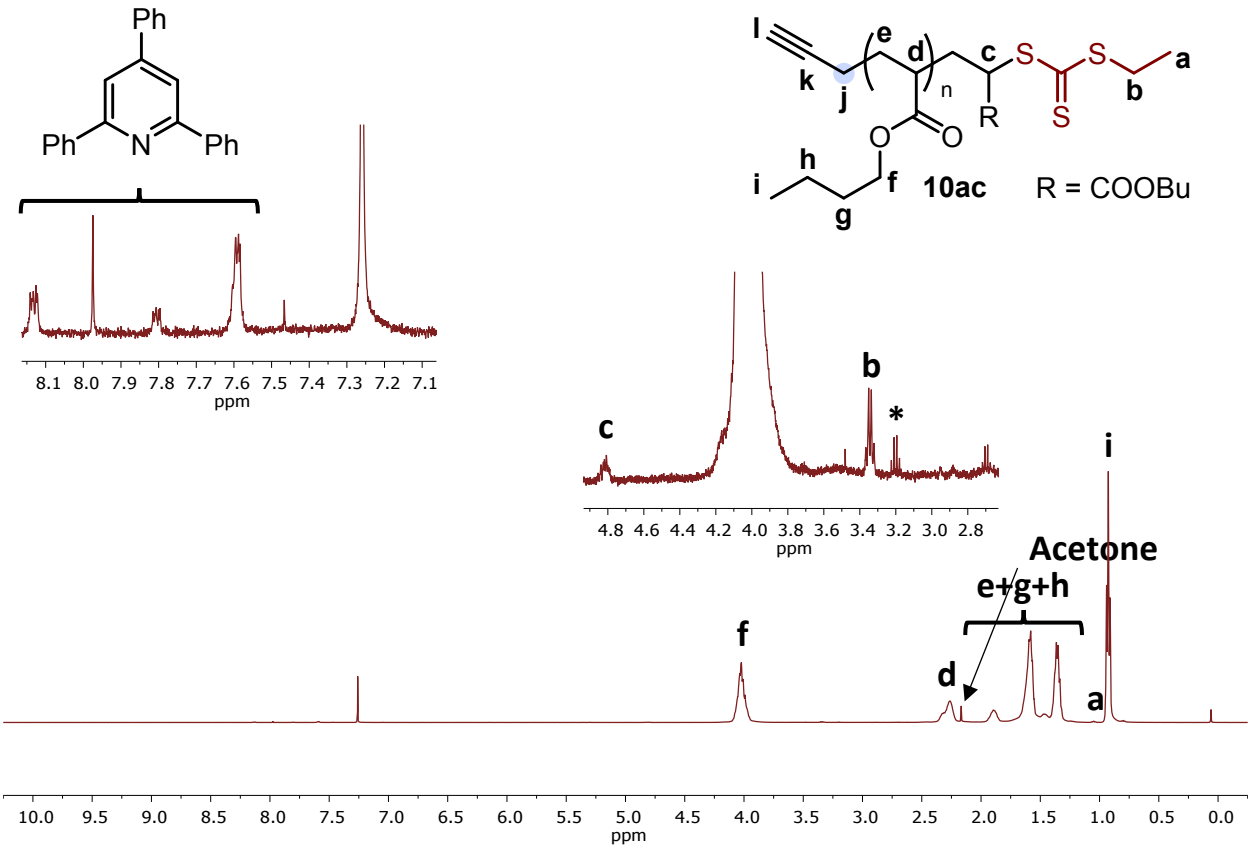
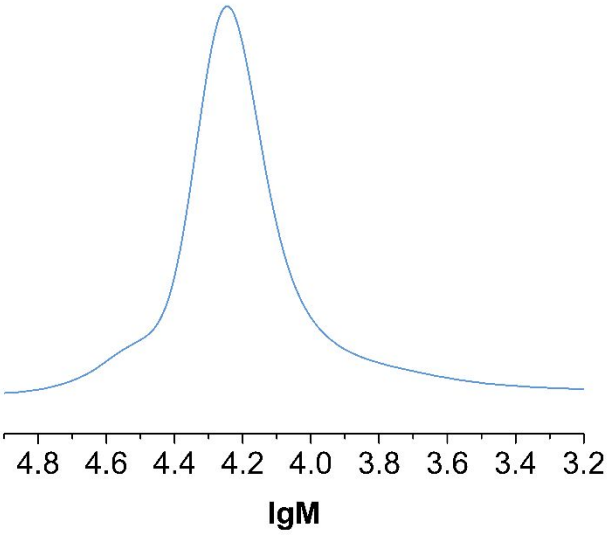
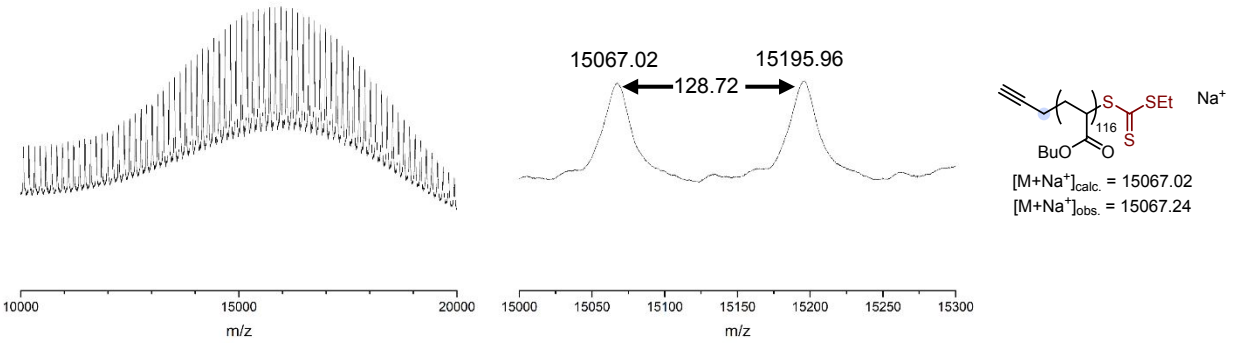


Figure S20. ^{1}H NMR spectrum of poly(butyl acrylate) **10ac**. *degradation product of ω-end CTA.

GPC traces for poly(butyl acrylate) **10ac** (**Figure S21**):



MALDI-TOF MS spectrum of PBuA **10ac** with Conv. = 99.9 %, M_n = 14200, Đ = 1.26 (left); possible peaks assignment (right) (**Figure S22**):

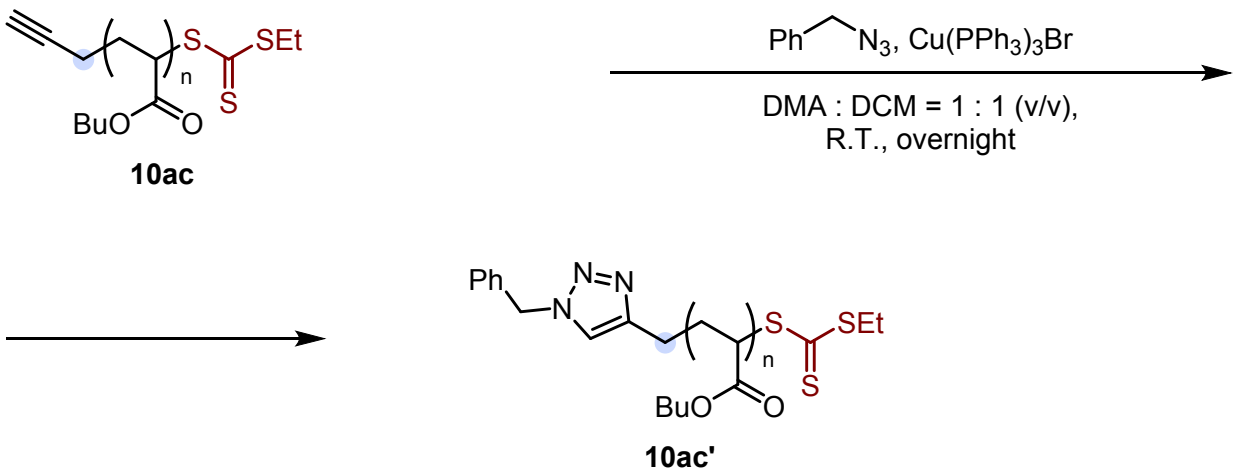


Poly(butyl acrylate) 10ac'

Poly(butyl acrylate) **10ac'** was synthesized from poly(butyl acrylate) **10ac** as follows:

A 10 mL Schlenk tube with a magnetic stirring bar was heated under vacuum with a heat gun, allowed to cool down to room temperature and backfilled with Ar. The reaction vessel was then evacuated and backfilled with Ar (x 2). Poly(butyl acrylate) **10ac** (1.00 eq. with respect to "alkyne" moiety, 4.930×10^{-3} mmol, 70.0 mg of polymer in 247 µL of DMA), benzyl azide (3.00 eq., 1.479×10^{-2} mmol, 59.1 µL 0.25 M in DCM) and $Cu(PPh_3)_3Br$ (0.50 eq., 2.465×10^{-3} mmol, 187 µL 0.013 M in DCM). The resulting solution was stirred at room temperature for 24 h. Then the reaction mixture was poured into an excess of MeOH : H_2O = 9 : 1 (v/v) mixture and centrifuged, the precipitated polymer was dried under high vacuum at 35 °C for 6 h.

Note: In this protocol we used $Cu(PPh_3)_3Br$, which was shown to be effective for CuAAC by Díez-González *et al*.[26]



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**k**) [c]	Tail (**c**) [d]			
-	-	14200	14500	30100	-	-	1.26

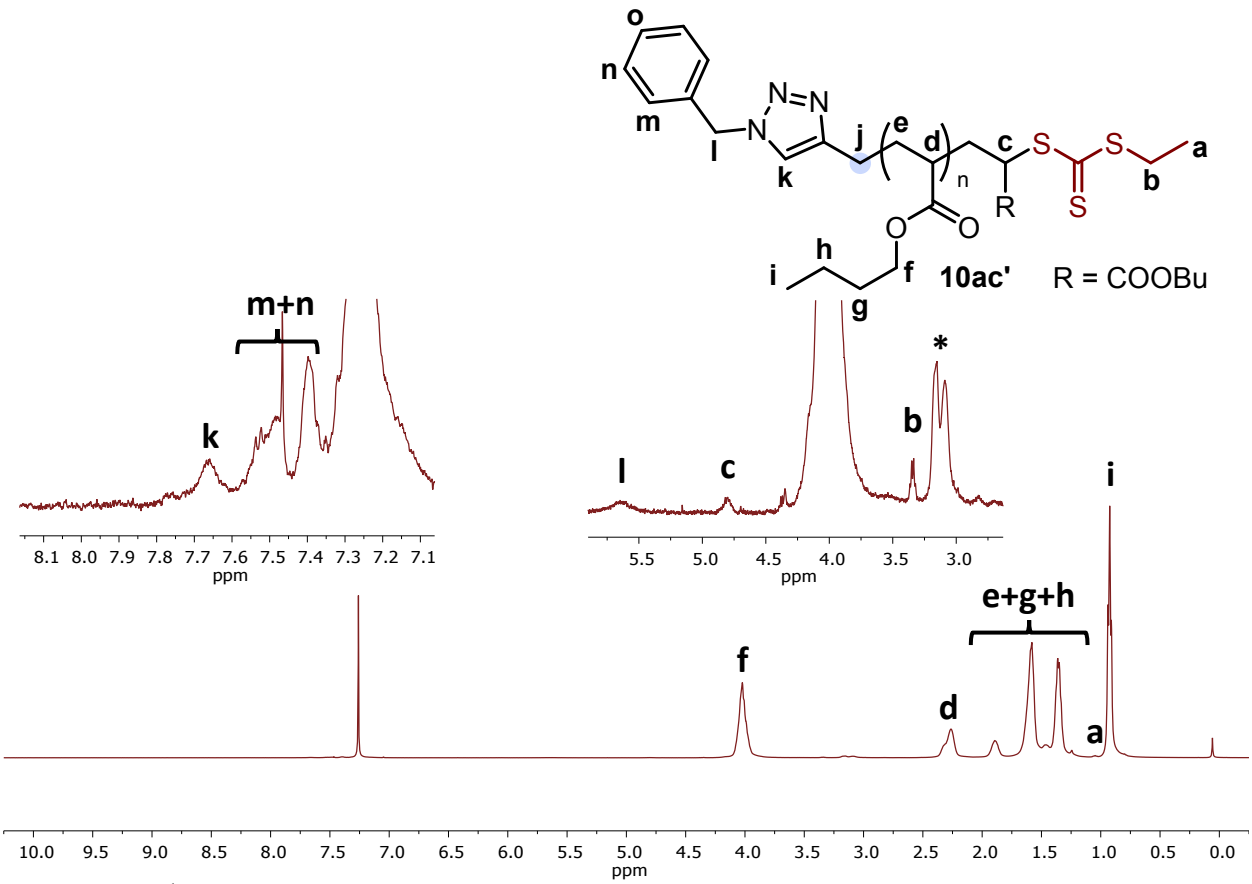
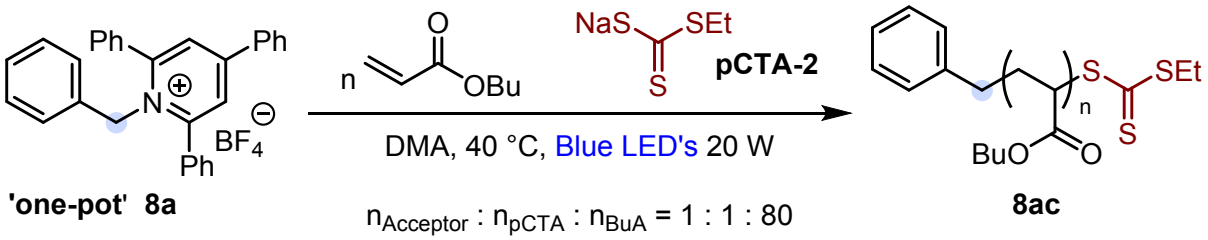


Figure S23. ^{1}H NMR spectrum of poly(butyl acrylate) **10ac'**. *Signals from the polymer backbone shifted upfield, possibly, due to the coordination with trace amounts of copper catalyst in the polymer.

Poly(butyl acrylate) 8ac

Poly(butyl acrylate) **8ac** was synthesized according to the General Procedure E.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**k+m**) [c]	Tail (**c**) [d]			
91.0	9550	10600	10900	13000	0.88	> 99	1.25

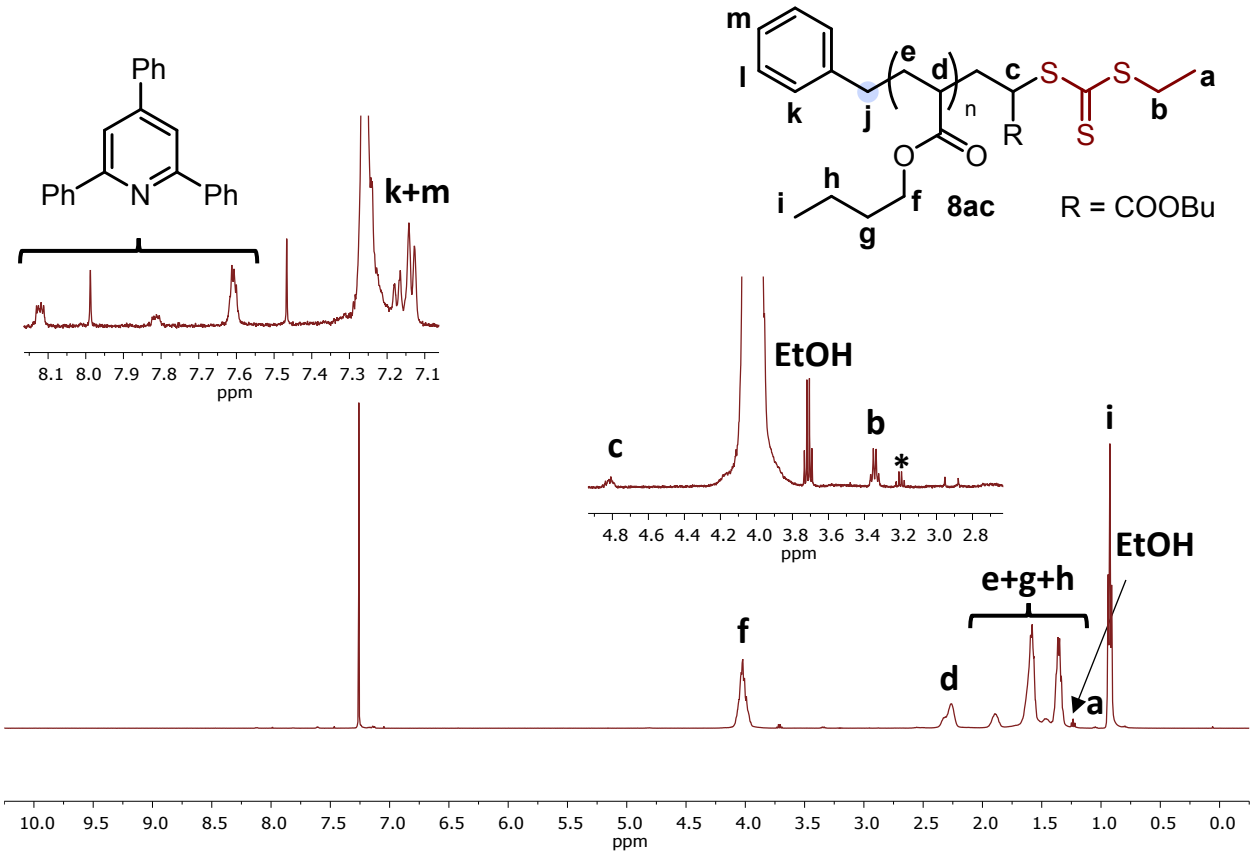
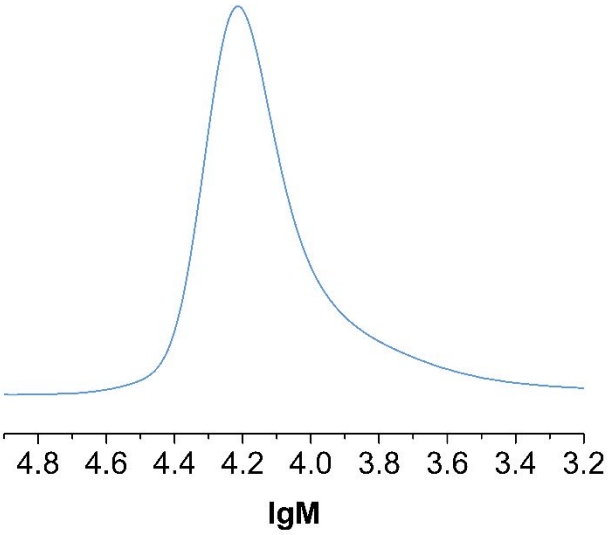


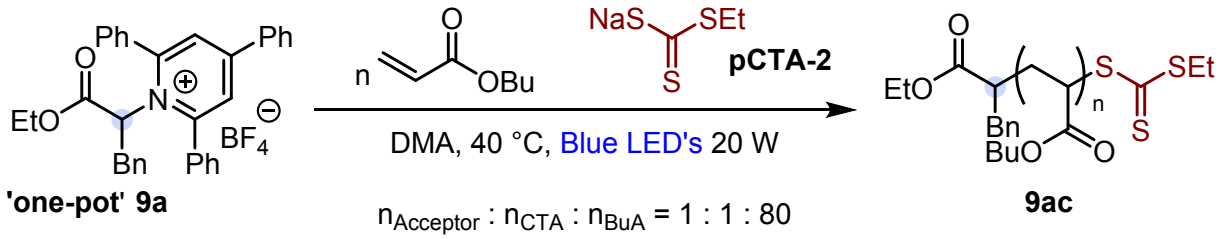
Figure S24. ^{1}H NMR spectrum of poly(butyl acrylate) **8ac**. *degradation product of ω-end CTA.

GPC traces for poly(butyl acrylate) **8ac** (**Figure S25**):



Poly(butyl acrylate) 9ac

Poly(butyl acrylate) **9ac** was synthesized according to the General Procedure E.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**l**) [c]	Tail (**c**) [d]			
67.9	7300	8000	8000	8600	0.91	> 99	1.20

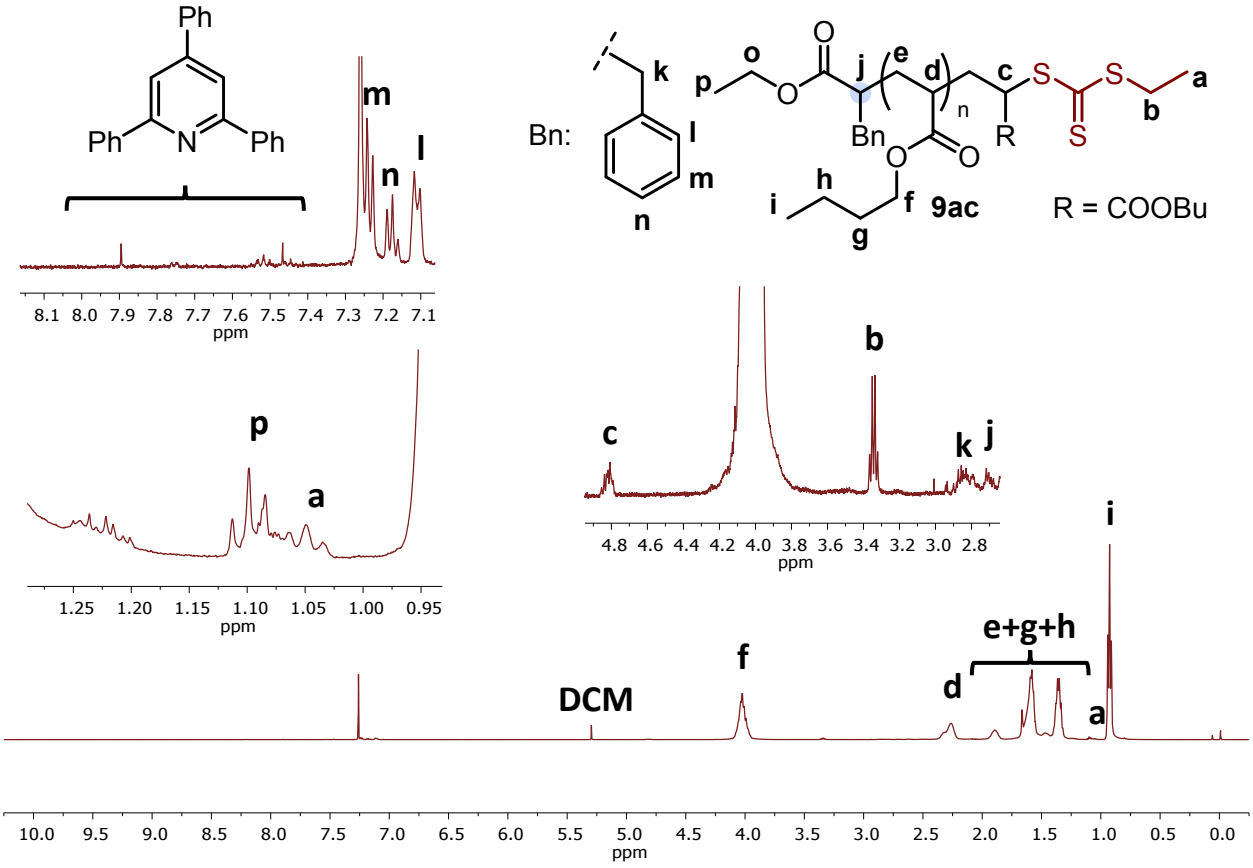
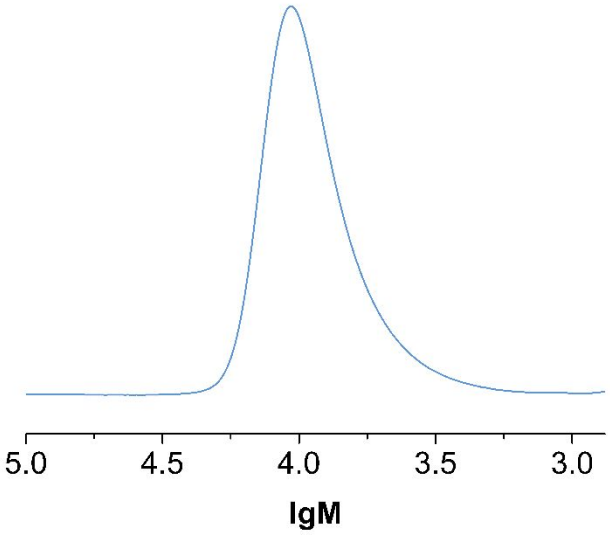


Figure S26. ^{1}H NMR spectrum of poly(butyl acrylate) **9ac**.

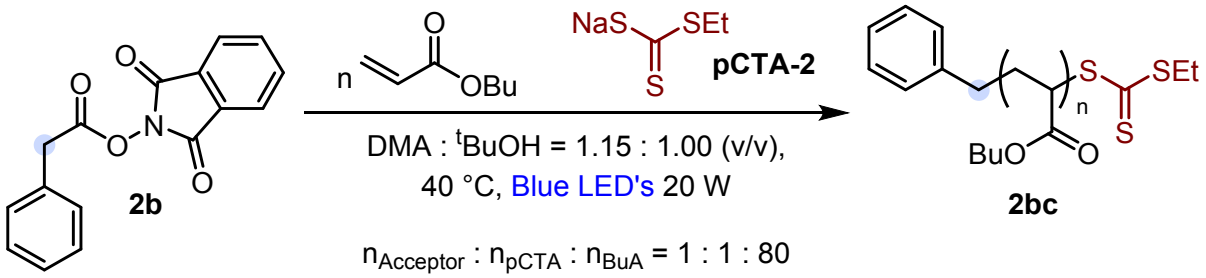
GPC traces for poly(butyl acrylate) **9ac** (**Figure S27**):



NHPI Esters / Carboxylic Acids:

Poly(butyl acrylate) 2bc

Poly(butyl acrylate) **2bc** was synthesized according to the General Procedure D.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**k+m**) [c]	Tail (**c**) [d]			
89.0	9350	14900	15300	22900	0.61	> 99	1.34

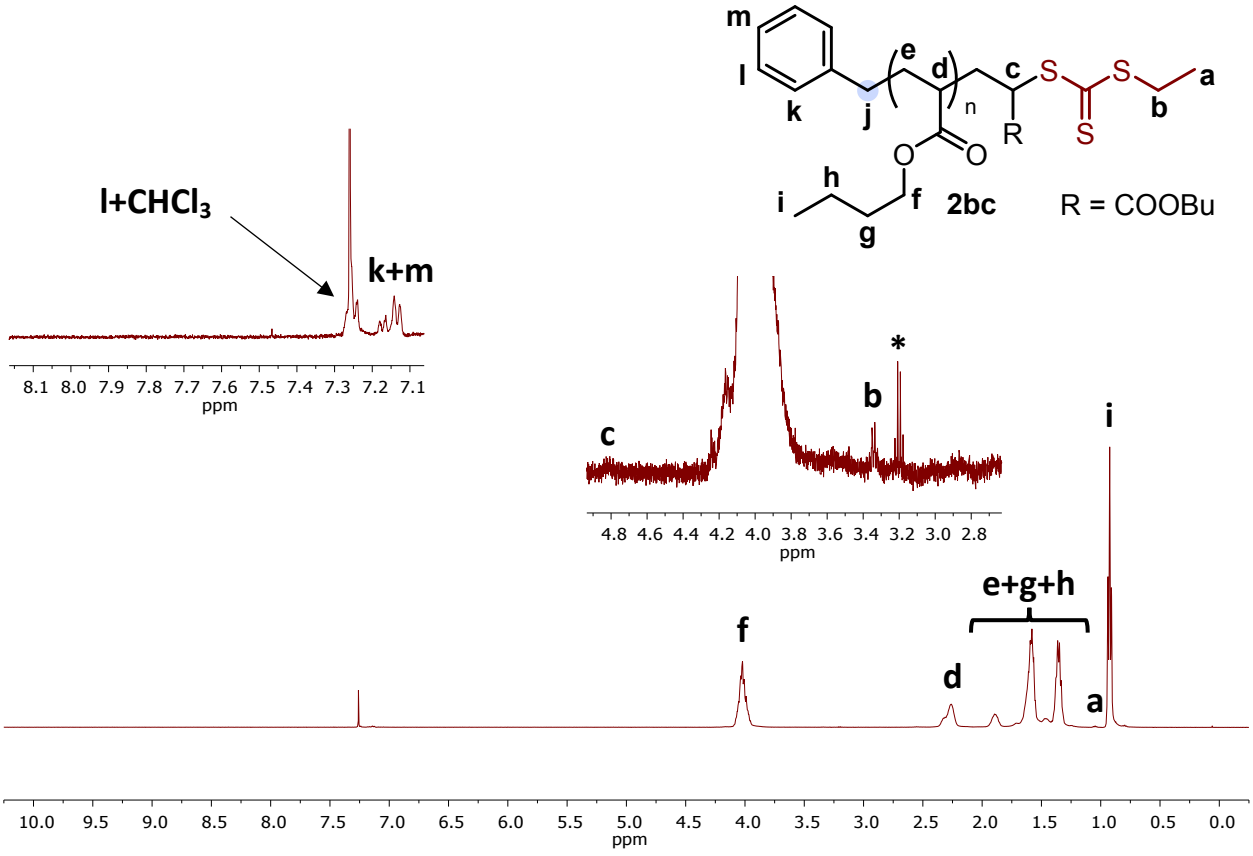
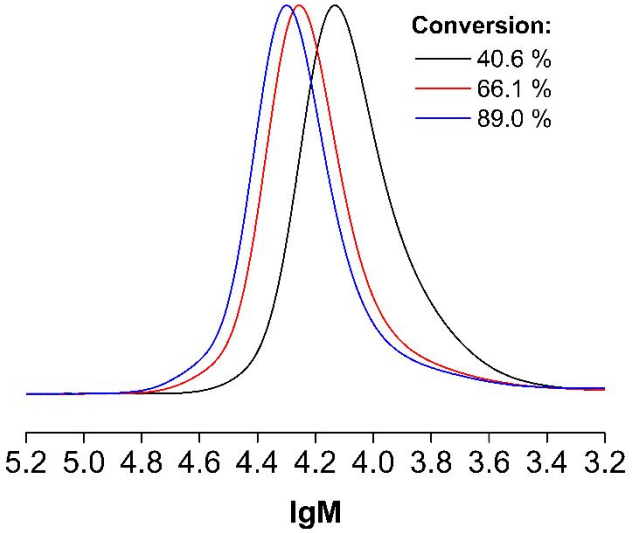
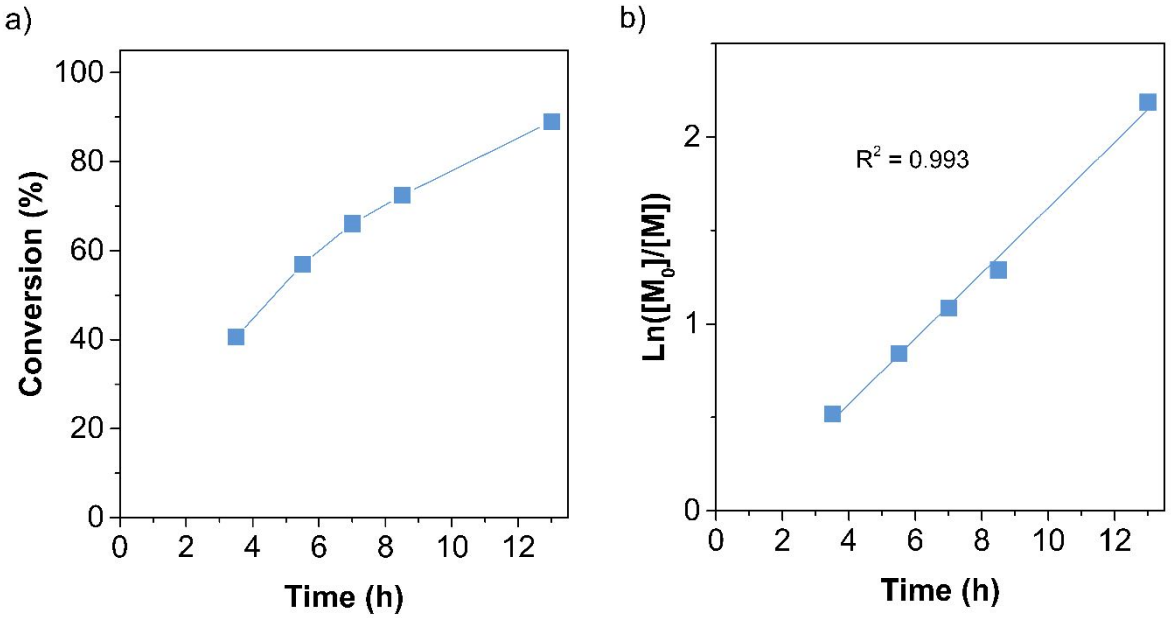


Figure S28. ^{1}H NMR spectrum of poly(butyl acrylate) **2bc**. *degradation product of ω-end CTA.

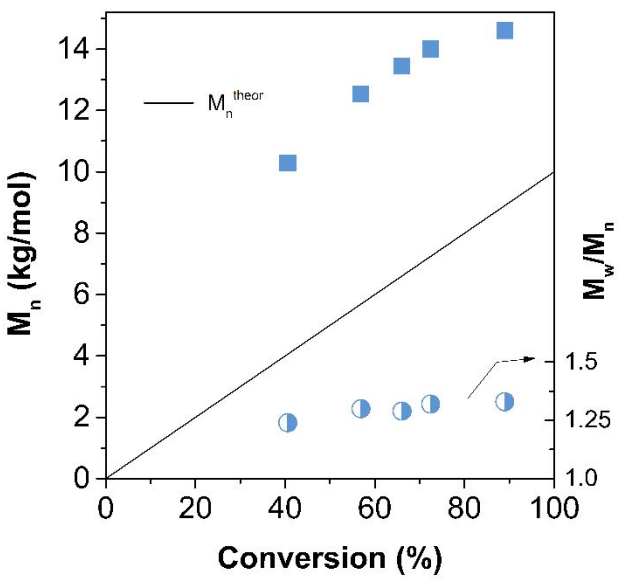
GPC traces for poly(butyl acrylate) **2bc** at various conversions (**Figure S29**):



Additional kinetic data for poly(butyl acrylate) **2bc**:

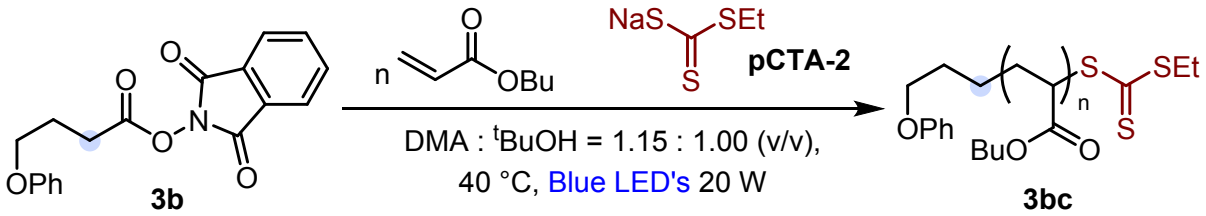


c)


M_n theor
M_n (kg/mol)
M_w/M_n
Conversion (%)
0
2
4
6
8
10
12
14
0
20
40
60
80
100
1.0
1.25
1.5

Poly(butyl acrylate) 3bc

Poly(butyl acrylate) **3bc** was synthesized according to the General Procedure D.



$n_{Acceptor} : n_{pCTA} : n_{BuA} = 1 : 1 : 80$

Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (k+m) [c]	Tail (c) [d]			
69.0	7350	25900	26000	37200	0.28	> 99	1.38

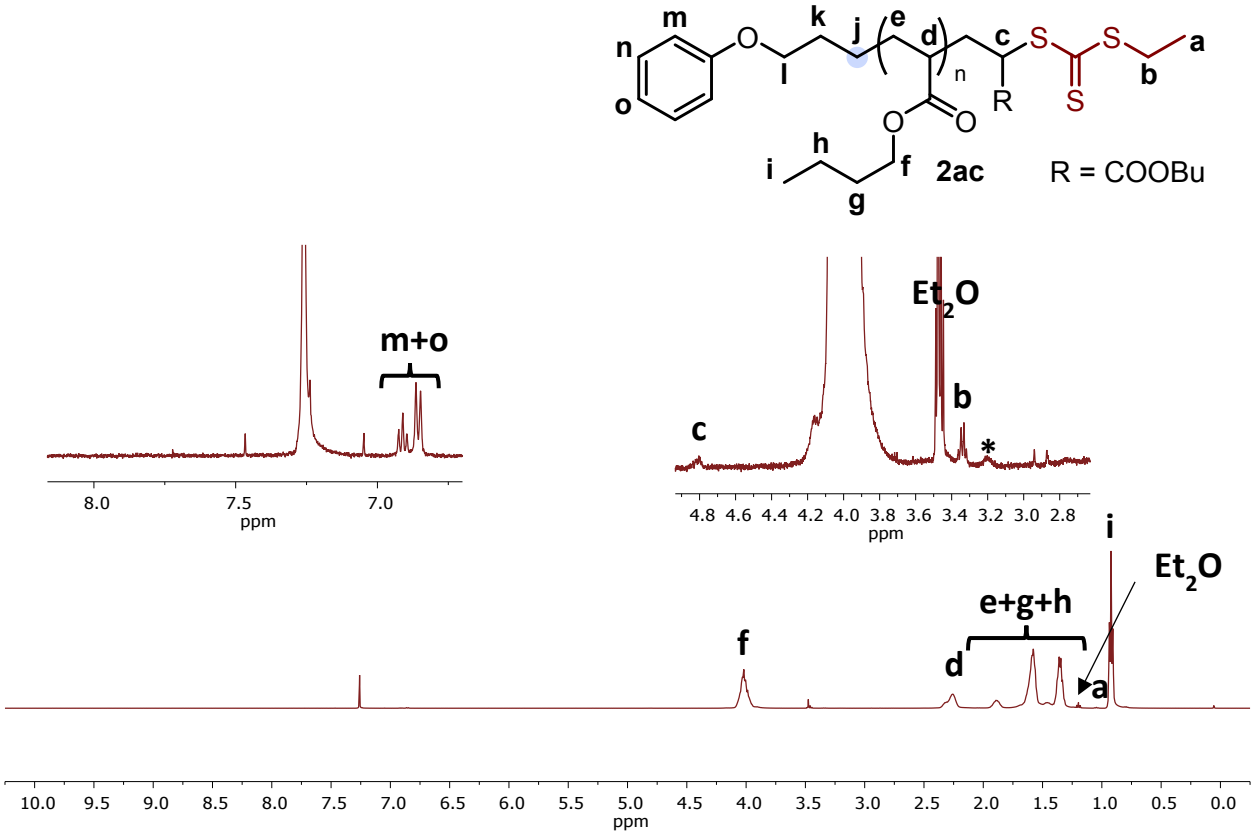
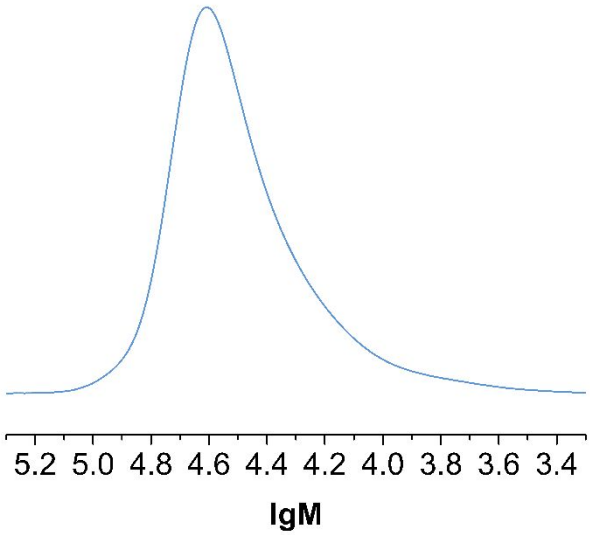


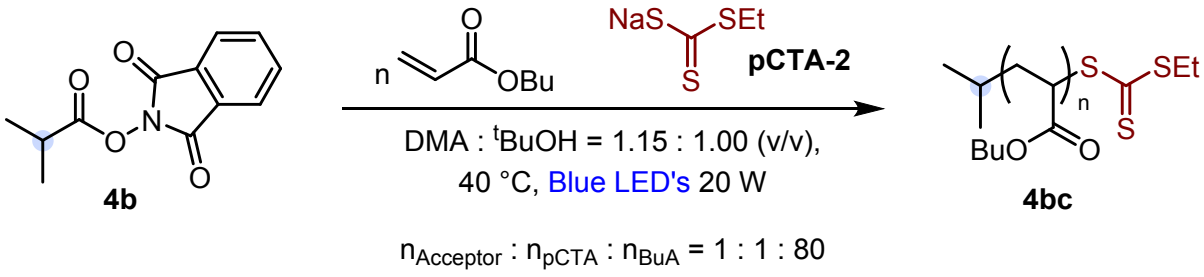
Figure S30. ^{1}H NMR spectrum of poly(butyl acrylate) **3bc**.*degradation product of ω-end CTA.

GPC traces for poly(butyl acrylate) **3bc** (**Figure S31**):



Poly(butyl acrylate) 4bc

Poly(butyl acrylate) **4bc** was synthesized according to the General Procedure D.



$n_{Acceptor} : n_{pCTA} : n_{BuA} = 1 : 1 : 80$

Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head [c]	Tail (**c**) [d]			
42.8	4600	20900	-	20900	-	-	1.27

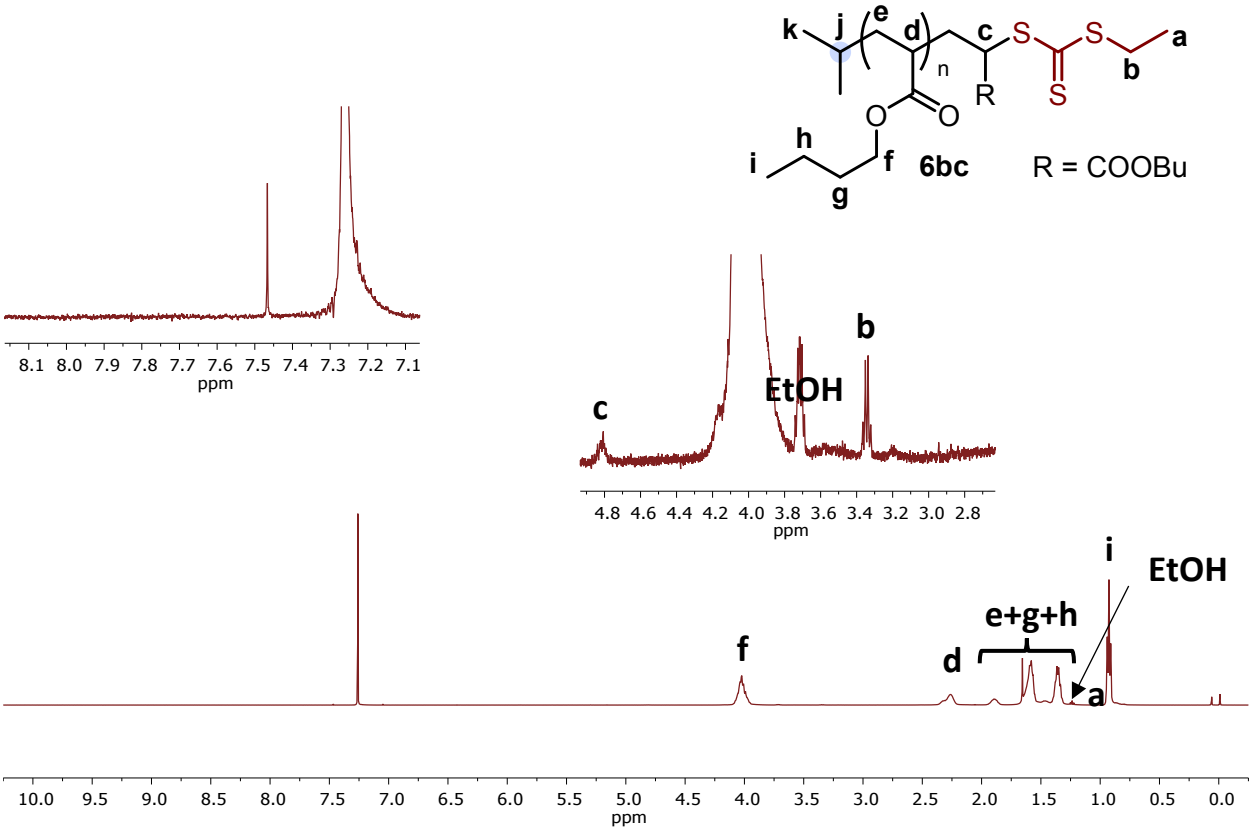
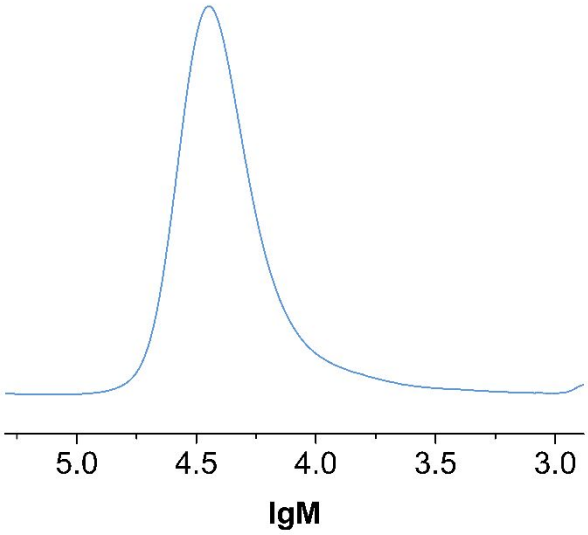


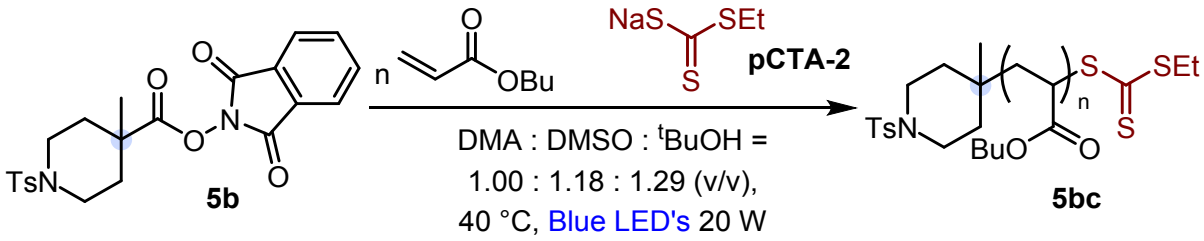
Figure S32. ^{1}H NMR spectrum of poly(butyl acrylate) **4bc**.

GPC traces for poly(butyl acrylate) **4bc** (**Figure S33**):



Poly(butyl acrylate) 5bc

Poly(butyl acrylate) **5bc** was synthesized according to the General Procedure D with some deviations. The reaction vessel was prepared as described in the standard protocol. Next, NHPI ester **5b** (1.00 eq., $4.69 \cdot 10^{-2}$ mmol, 20.8 mg), DMA (233 µL), DMSO (380 µL), ^{t}BuOH (510 µL), butyl acrylate (80.00 eq., 3.750 mmol, 540 µL, C_{mix} = 2.18 M) and **pCTA-2** (1.00 eq., $4.69 \cdot 10^{-2}$ mmol, 117 µL 0.40 M in DMA) were added sequentially under Ar. The following steps were analogous to the General Procedure D.



$n_{Acceptor} : n_{pCTA} : n_{BuA} = 1 : 1 : 80$

Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**m**) [c]	Tail (**c**) [d]			
52.1	5750	14100	14200	14200	0.40	> 99	1.27

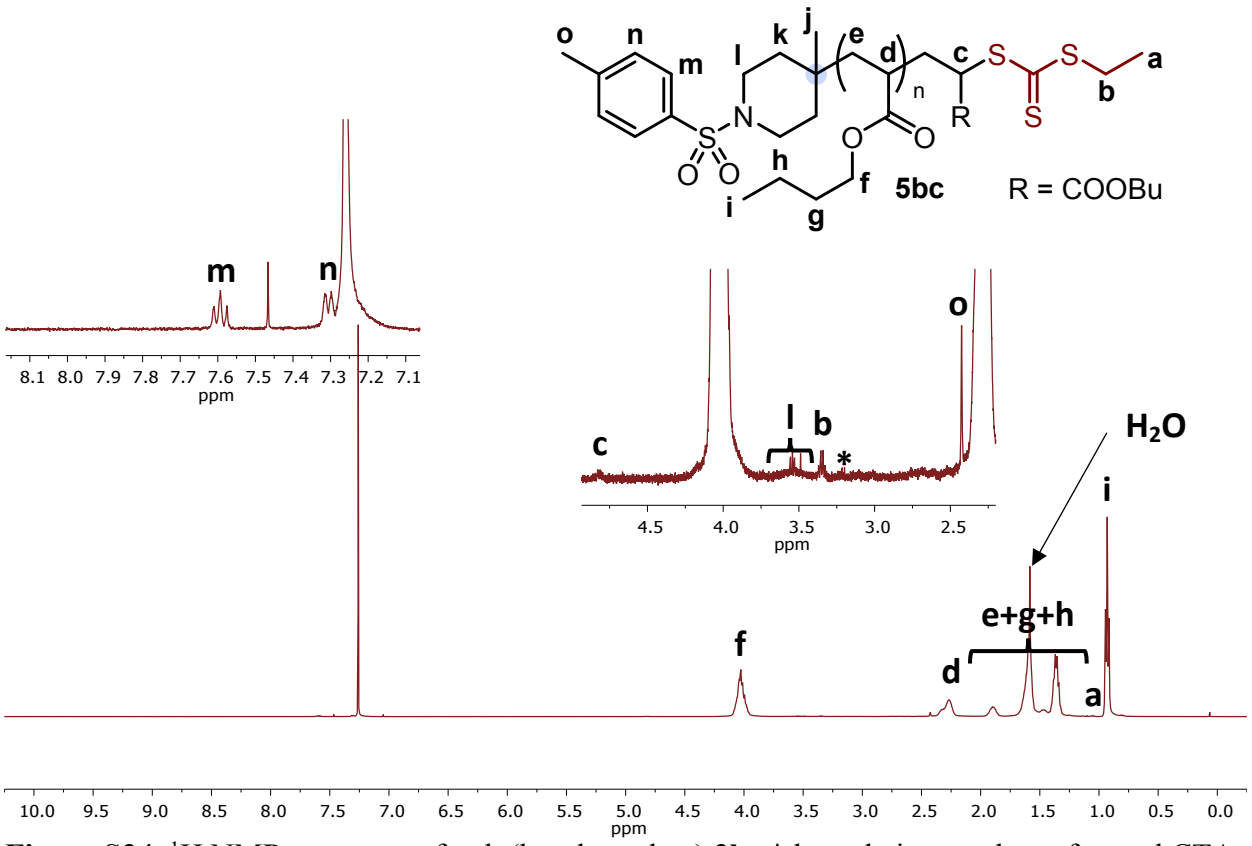
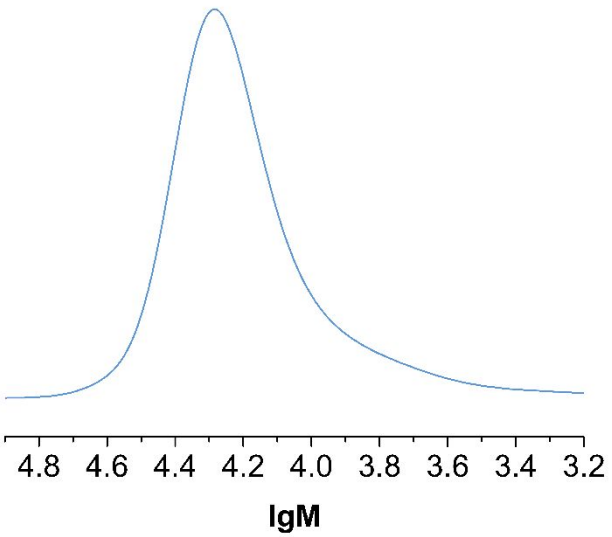


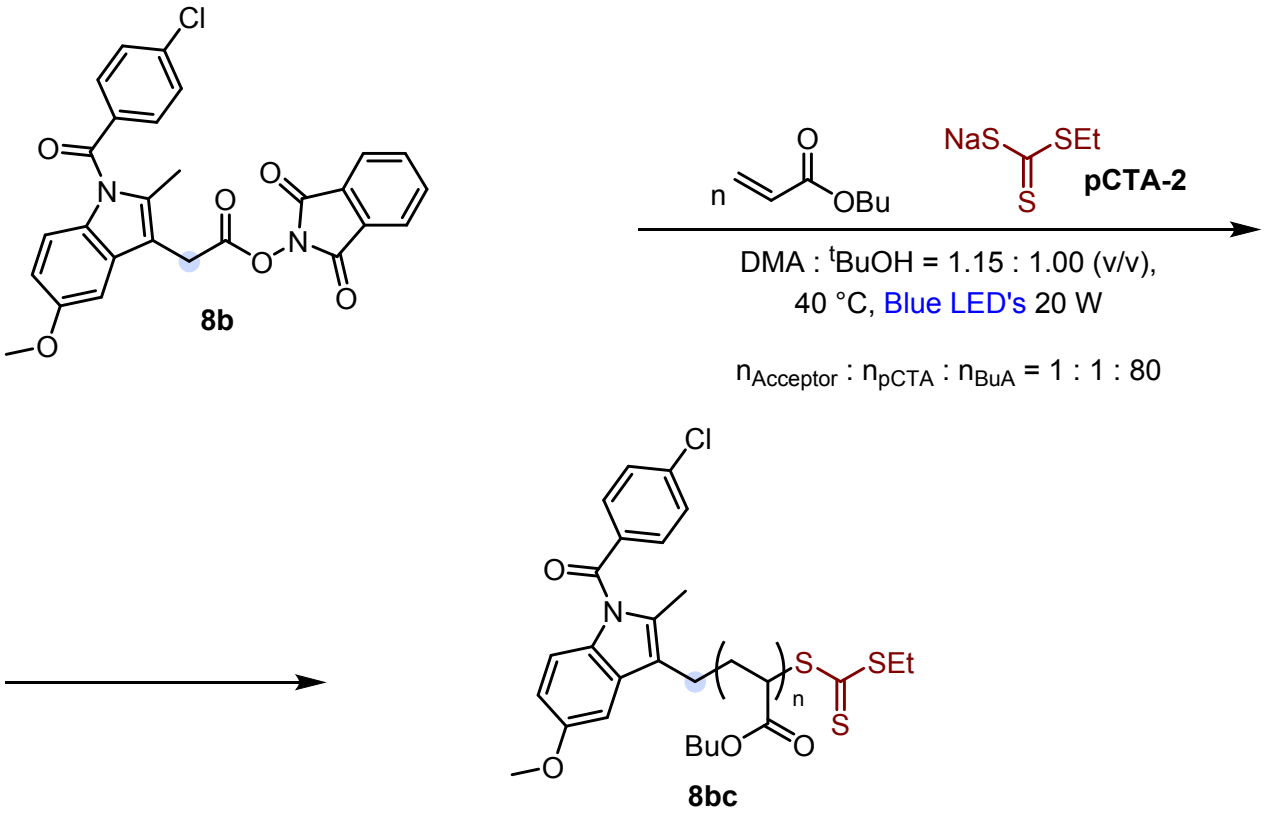
Figure S34. ^{1}H NMR spectrum of poly(butyl acrylate) **3bc**.*degradation product of ω-end CTA. **Integral intensity of the protons ∫(**m**) : ∫(**n**) : ∫(**c**) : ∫(**o**) = 2 : 2 : 1 : 3 as well as their characteristic δ (see ^{1}H spectrum of NHPI ester **5b**), confirm the identity of the head group, while the nature of the unusual splitting pattern of proton **m** remains unclear.

GPC traces for poly(butyl acrylate) **5bc** (**Figure S35**):



Poly(butyl acrylate) 8bc

Poly(butyl acrylate) **8bc** was synthesized according to the General Procedure D.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**p**) [c]	Tail (**c**) [d]			
91.0	9800	24200	27100	37600	0.36	> 99	1.29

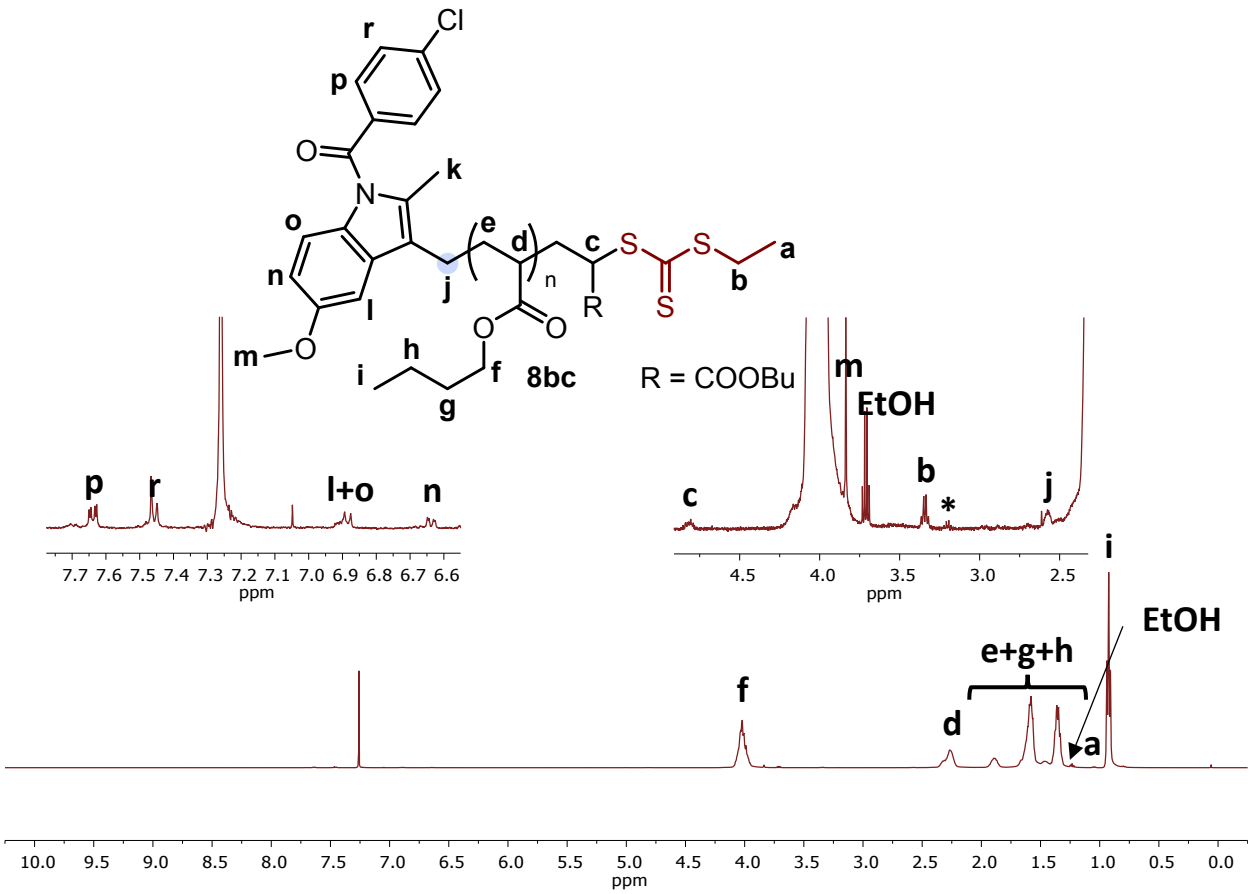
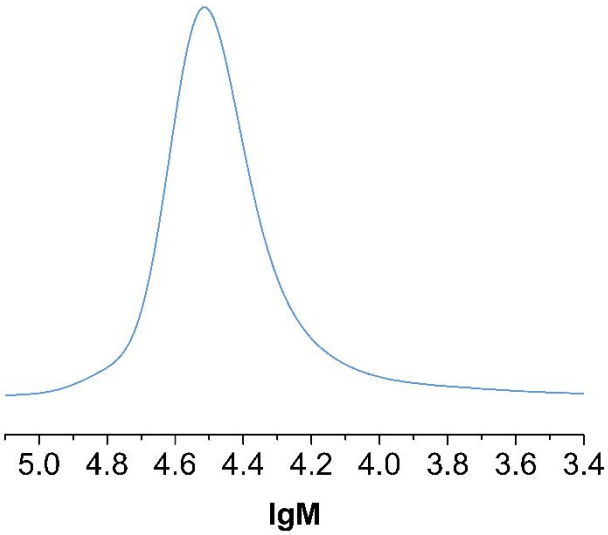
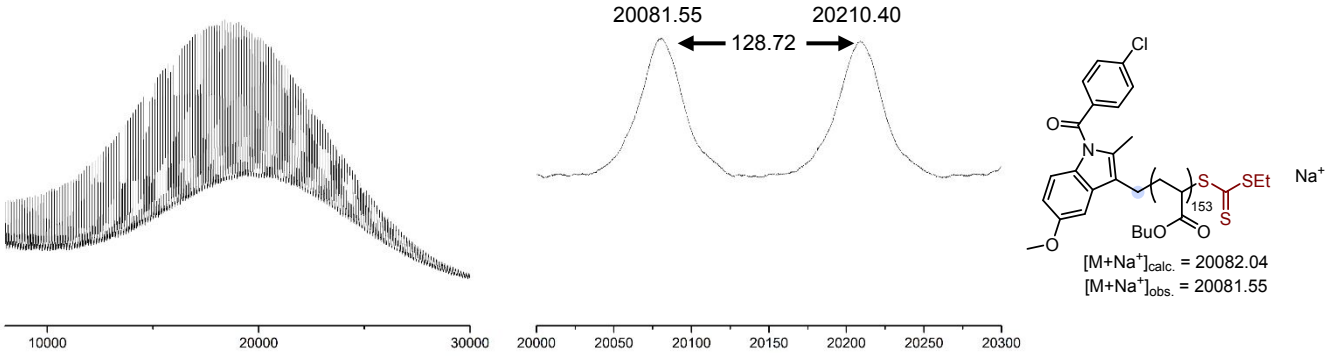


Figure S36. ^{1}H NMR spectrum of poly(butyl acrylate) **8bc**. *degradation product of ω-end CTA.

GPC traces for poly(butyl acrylate) **8bc** (**Figure S37**):

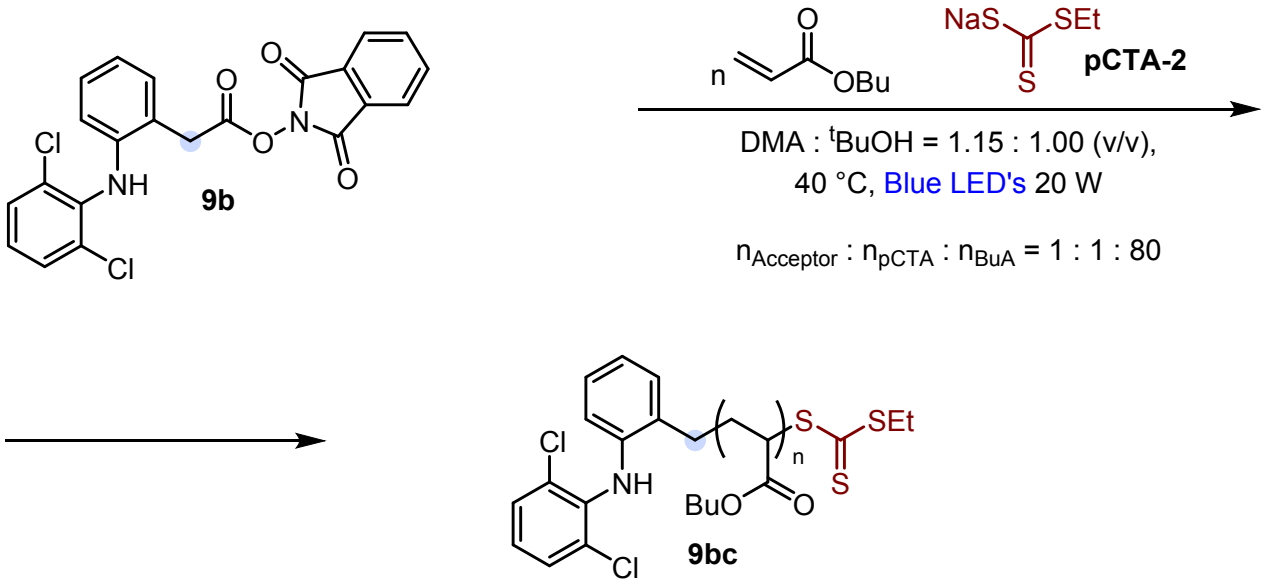


MALDI-TOF MS spectrum of PBuA **8bc** with Conv. = 52.1 %, Mn = 16400, Đ = 1.21 (left); possible peaks assignment (right) **(Figure S38)**:



Poly(butyl acrylate) 9bc

Poly(butyl acrylate) **9bc** was synthesized according to the General Procedure D.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**p**) [c]	Tail (**c**) [d]			
65.0	7050	35700	36200	36200	0.19	> 99	1.40

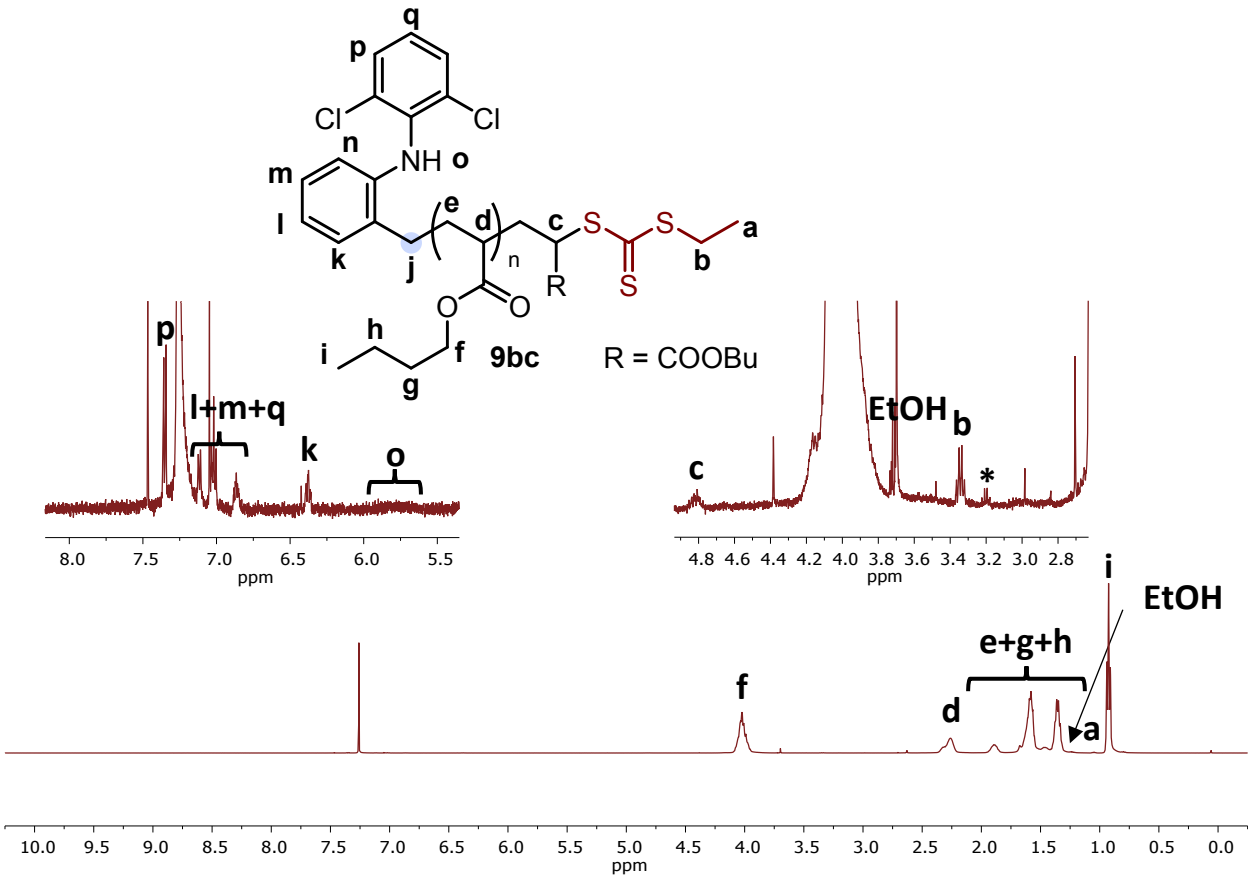
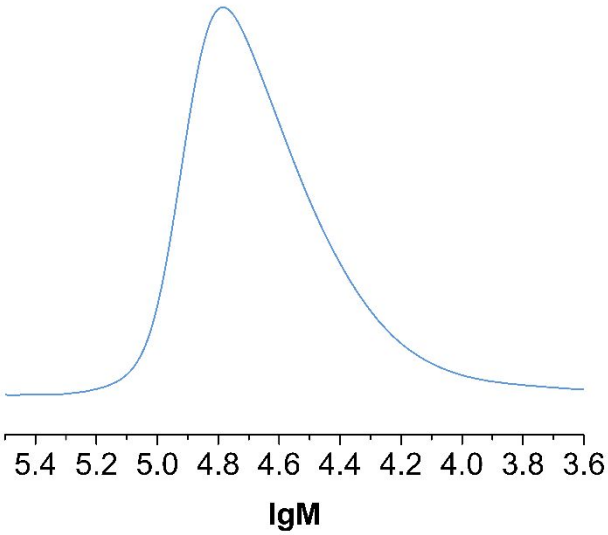


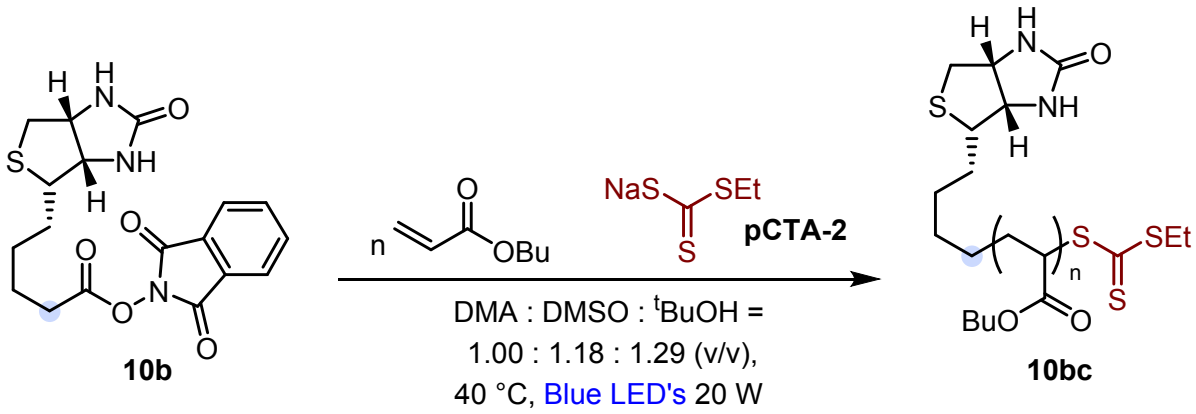
Figure S39. ^{1}H NMR spectrum of poly(butyl acrylate) **9bc**. *degradation product of ω-end CTA.

GPC traces for poly(butyl acrylate) **9bc** (**Figure S40**):



Poly(butyl acrylate) 10bc

Poly(butyl acrylate) **10bc** was synthesized according to the General Procedure D with some deviations. The reaction vessel was prepared as described in the standard protocol. Next, NHPI ester **10b** (1.00 eq., $4.69 \cdot 10^{-2}$ mmol, 18.3 mg), DMA (233 µL), DMSO (380 µL), ^{t}BuOH (510 µL), butyl acrylate (80.00 eq., 3.750 mmol, 540 µL, C_{mix} = 2.18 M) and **pCTA-2** (1.00 eq., $4.69 \cdot 10^{-2}$ mmol, 117 µL 0.40 M in DMA) were added sequentially under Ar. The following steps were analogous to the General Procedure D.



$n_{Acceptor} : n_{pCTA} : n_{BuA} = 1 : 1 : 80$

Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**t**) [c]	Tail (**c**) [d]			
37.3	4150	16100	16800	26200	0.25	> 99	1.46

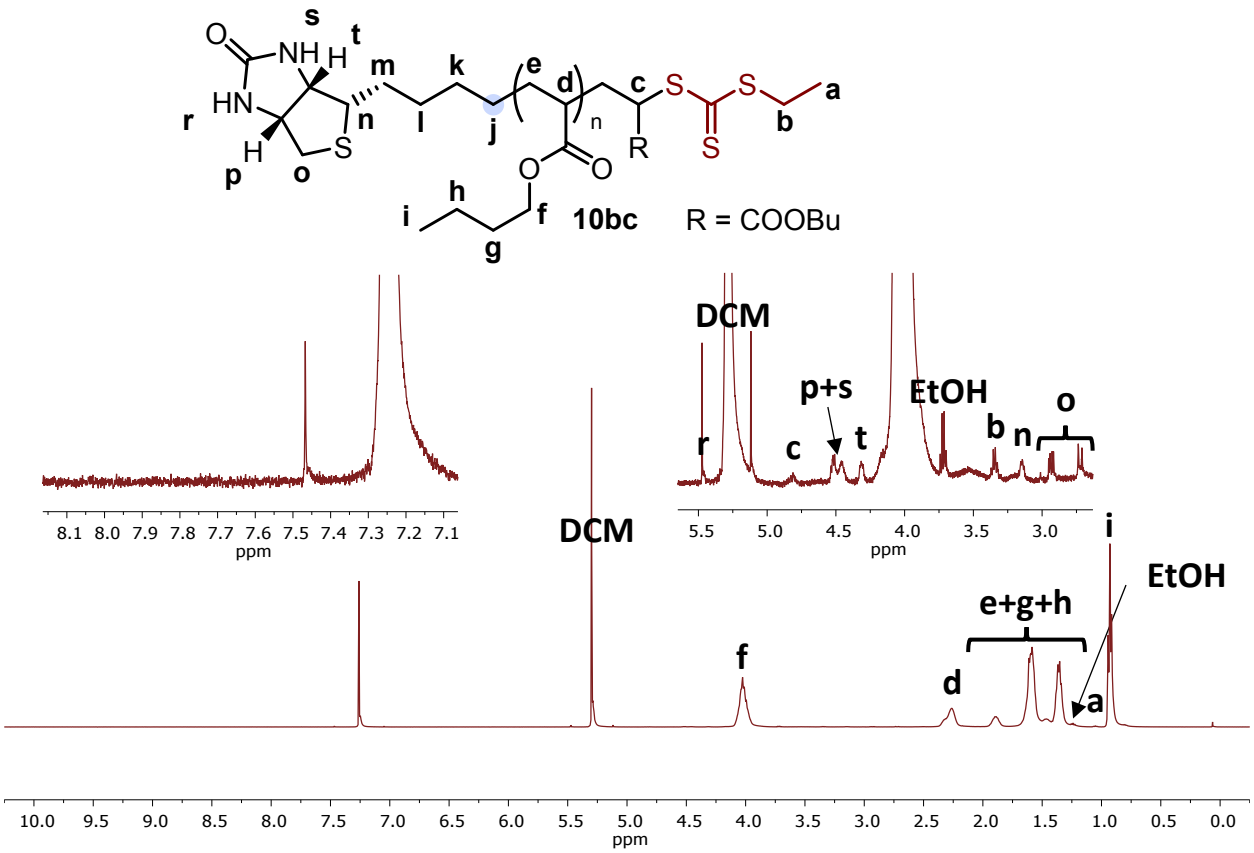
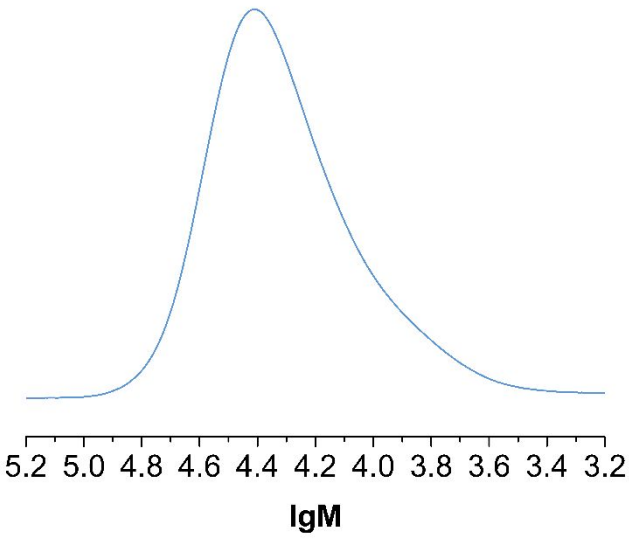


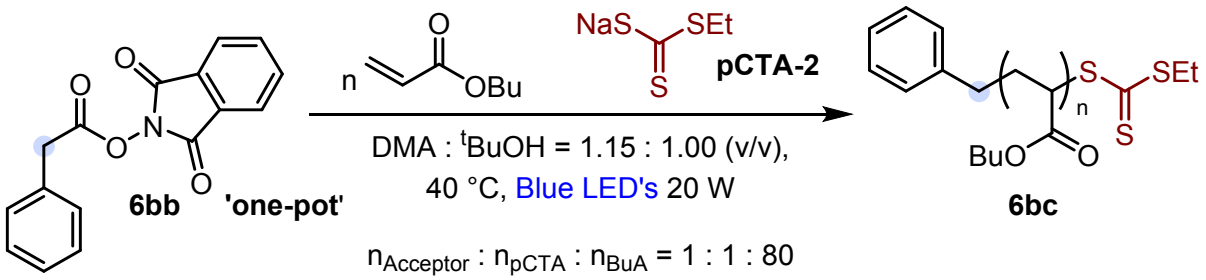
Figure S41. ^{1}H NMR spectrum of poly(butyl acrylate) **10bc**.

GPC traces for poly(butyl acrylate) **10bc** (**Figure S42**):



Poly(butyl acrylate) 6bc

Poly(butyl acrylate) **6bc** was synthesized according to the General Procedure E.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (k+m) [c]	Tail (c) [d]			
91.1	9550	29200	32800	37700	0.29	> 99	1.39

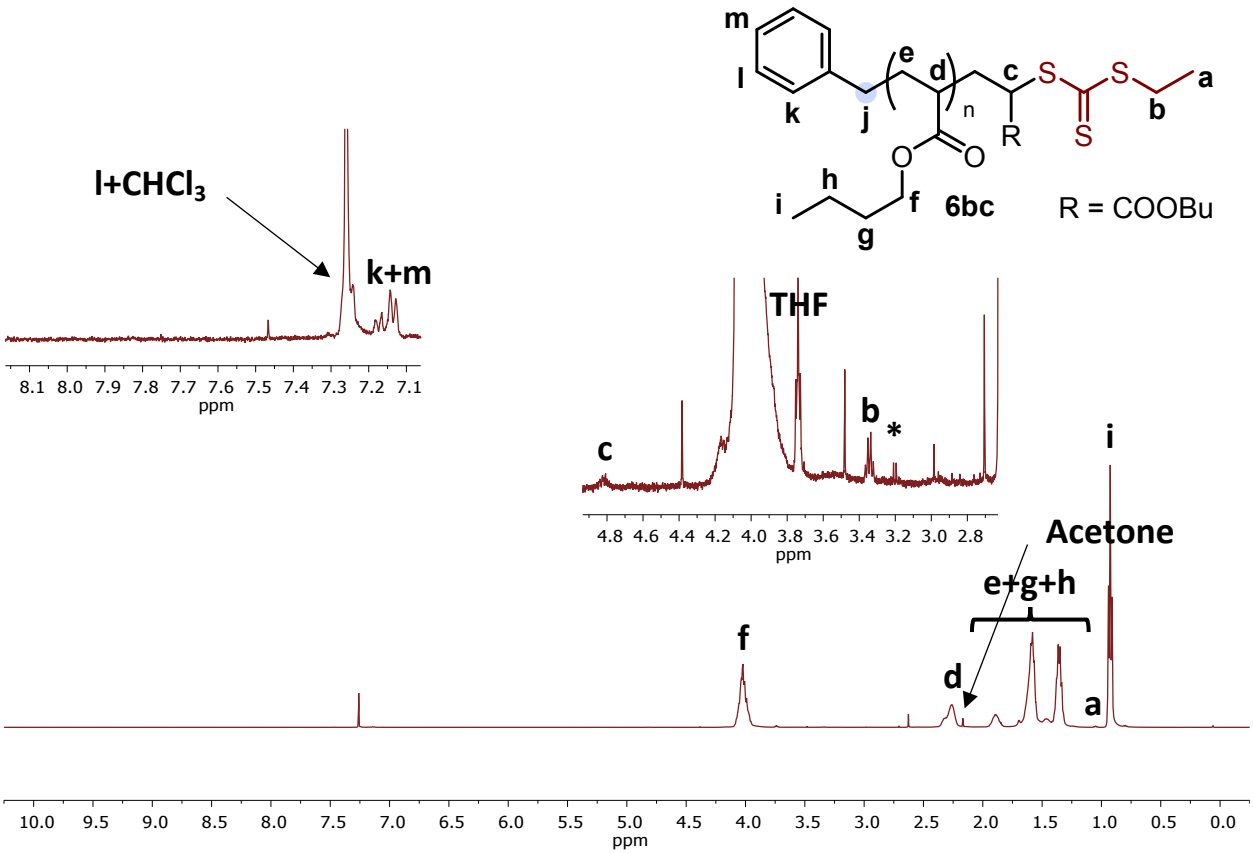
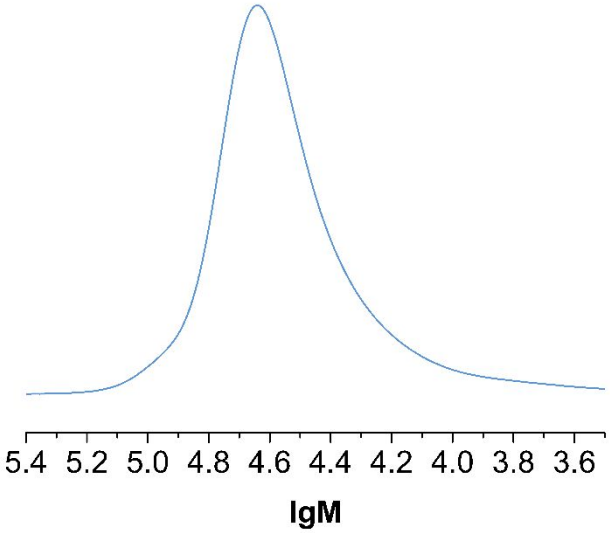


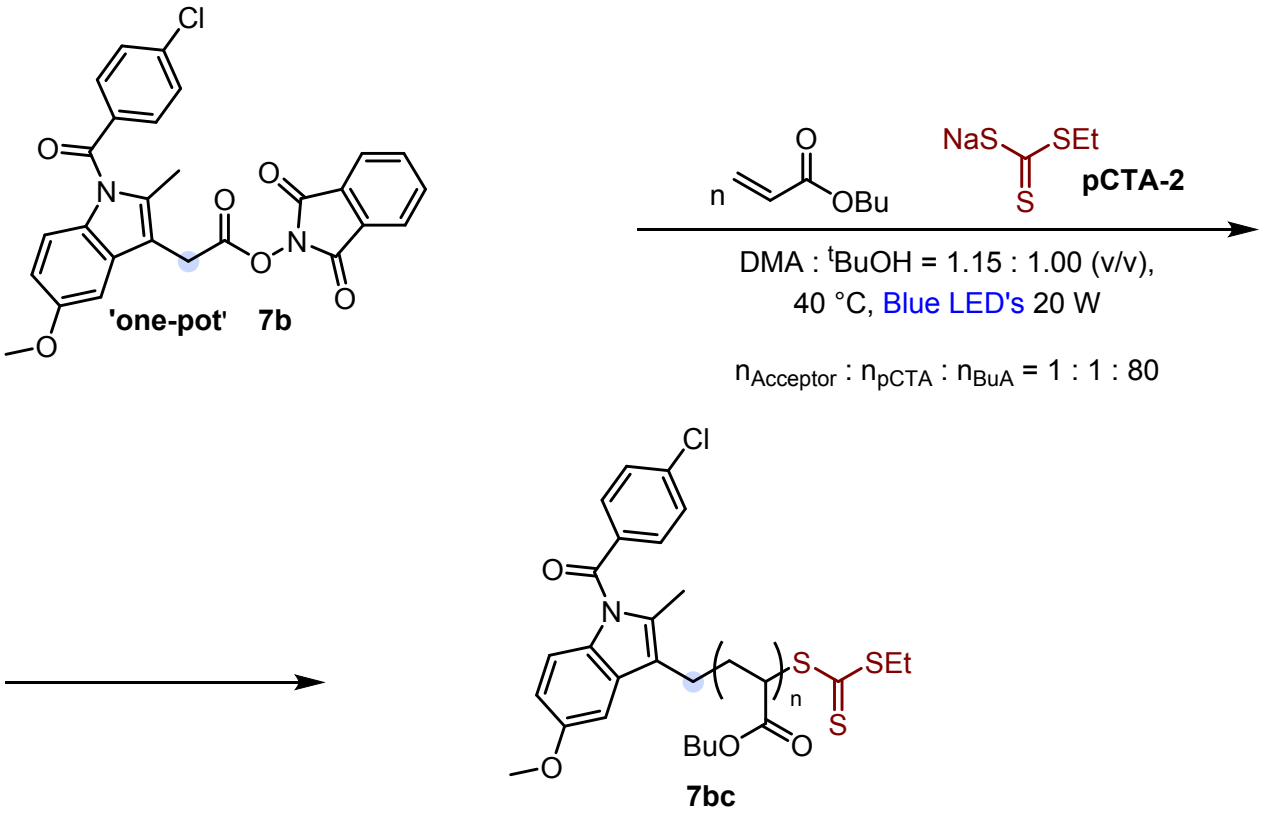
Figure S43. ^{1}H NMR spectrum of poly(butyl acrylate) **6bc**.*degradation product of ω-end CTA.

GPC traces for poly(butyl acrylate) **6bc** (**Figure S44**):


5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6
IgM

Poly(butyl acrylate) 7bc

Poly(butyl acrylate) **7bc** was synthesized according to the General Procedure E.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**p**) [c]	Tail (**c**) [d]			
78.0	8450	26000	33800	35200	0.25	> 99	1.39

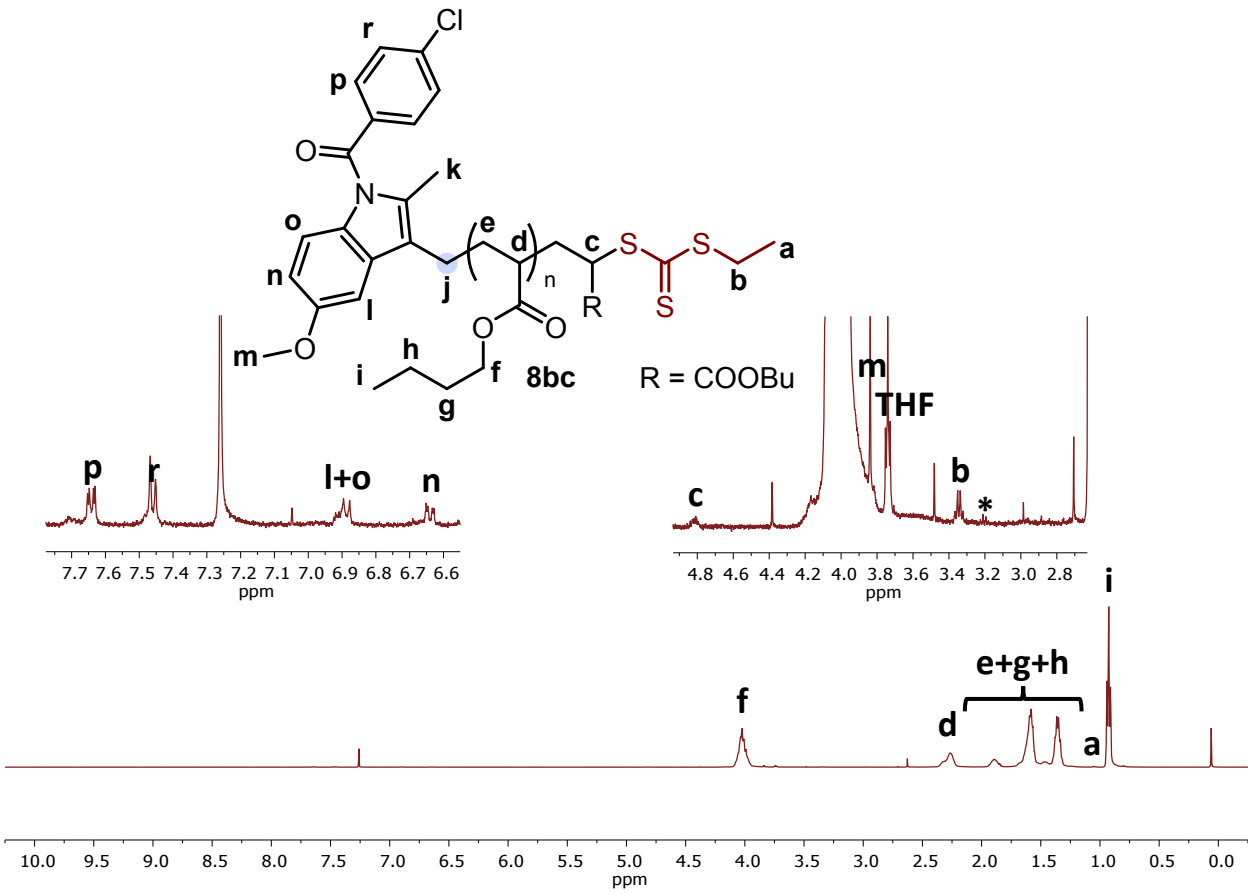
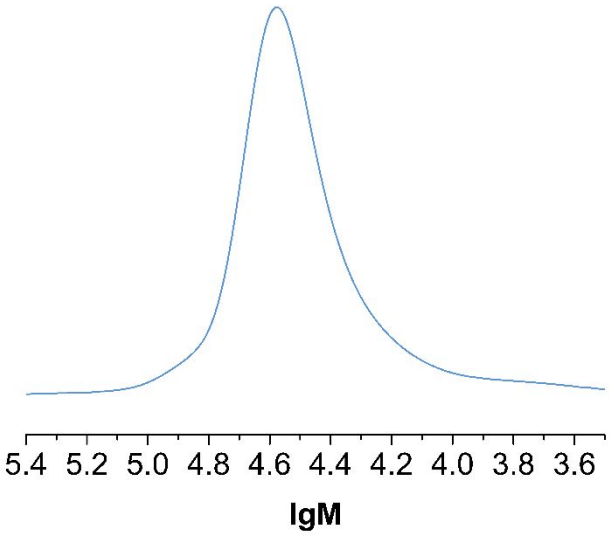


Figure S45. ^{1}H NMR spectrum of poly(butyl acrylate) **7bc**.*degradation product of ω-end CTA.

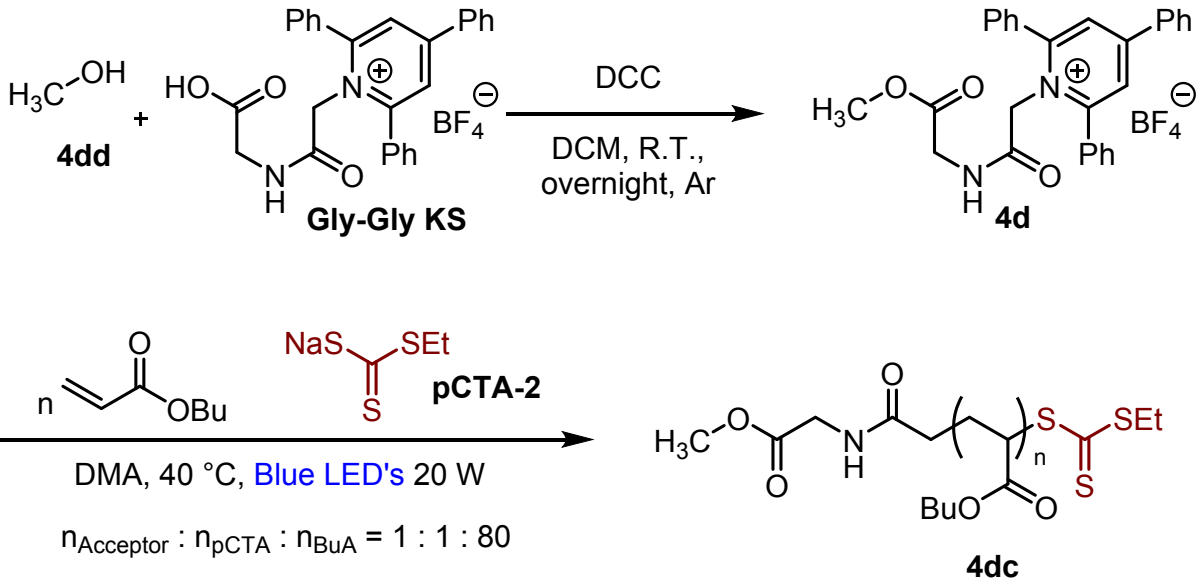
GPC traces for poly(butyl acrylate) **7bc** (**Figure S46**):



Alcohols and amines with Gly-Gly KS:

Poly(butyl acrylate) 4dc

Poly(butyl acrylate) **4dc** was synthesized according to the General Procedure F.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**m**) [c]	Tail (**c**) [d]			
44.0	4800	14700	16800	16100	0.29	> 99	1.51

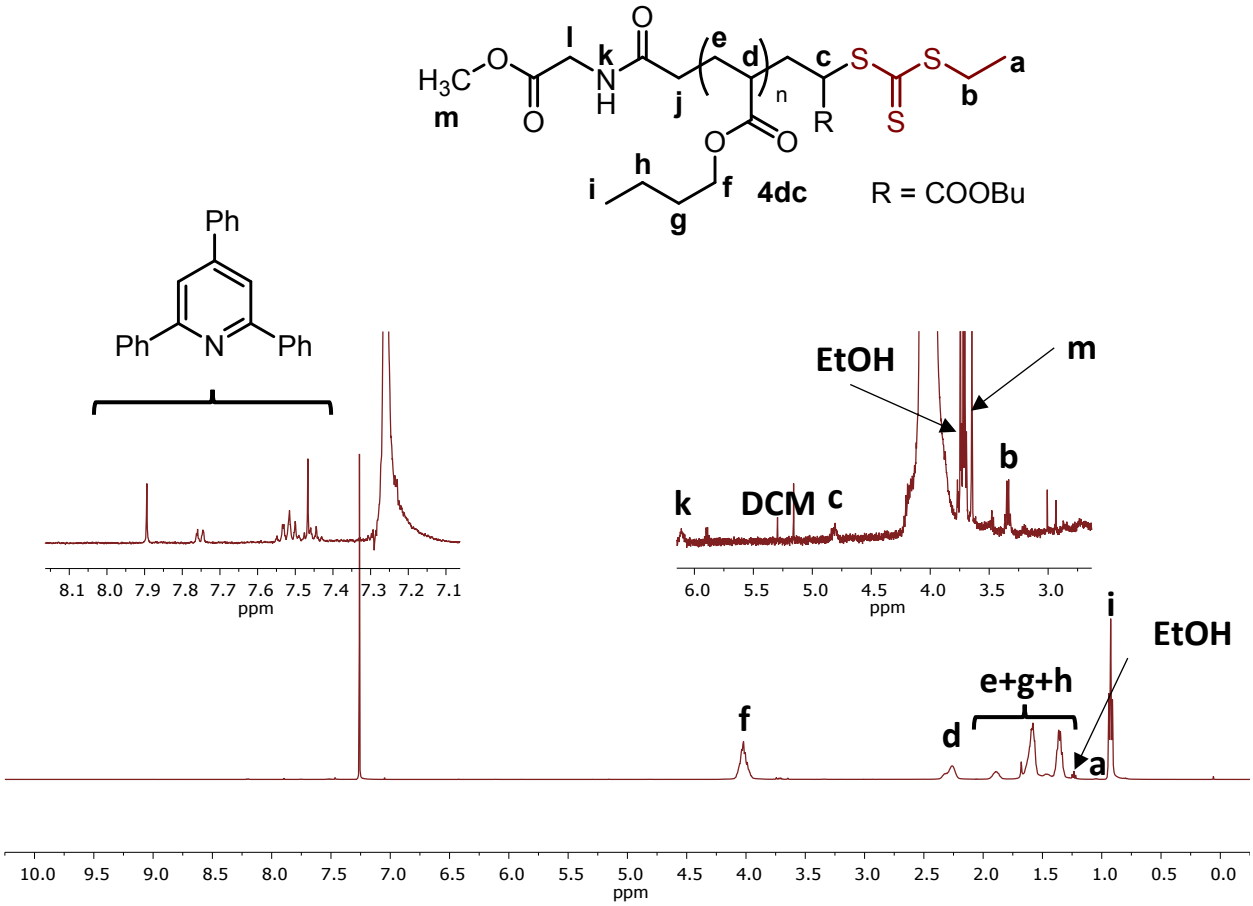
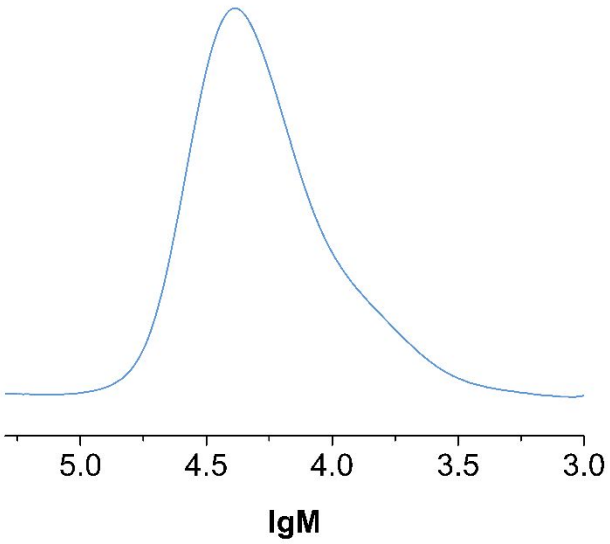


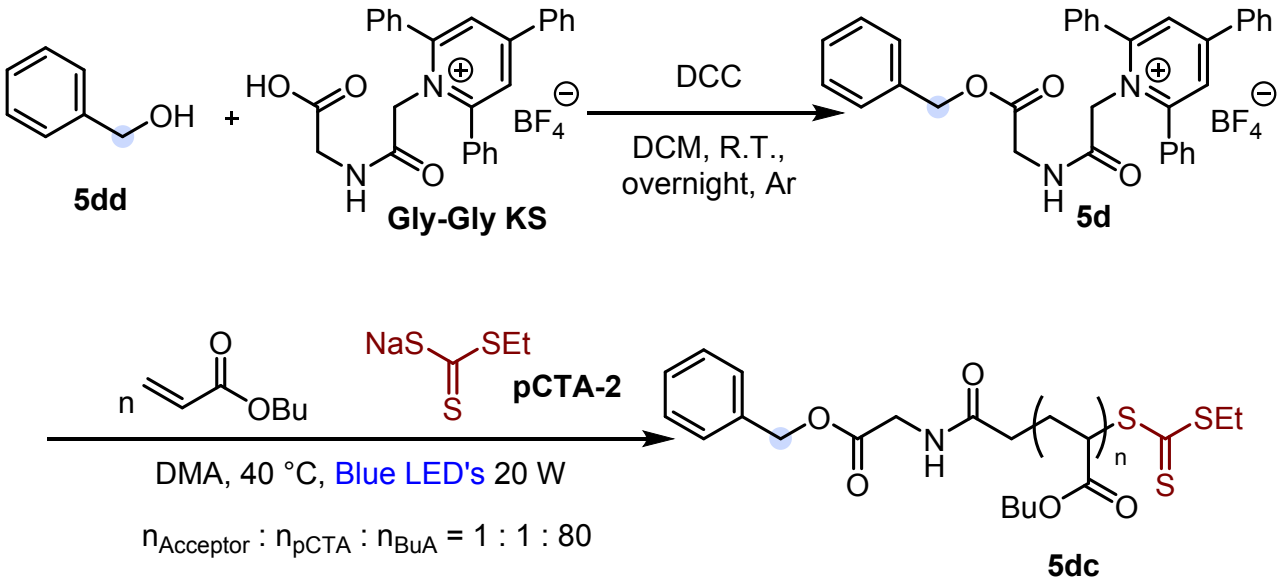
Figure S47. ^{1}H NMR spectrum of poly(butyl acrylate) **4dc**.

GPC traces for poly(butyl acrylate) **4dc** (**Figure S48**):



Poly(butyl acrylate) 5dc

Poly(butyl acrylate) **5dc** was synthesized according to the General Procedure F.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**m**) [c]	Tail (**c**) [d]			
65.6	7100	16350	16400	17000	0.43	> 99	1.48

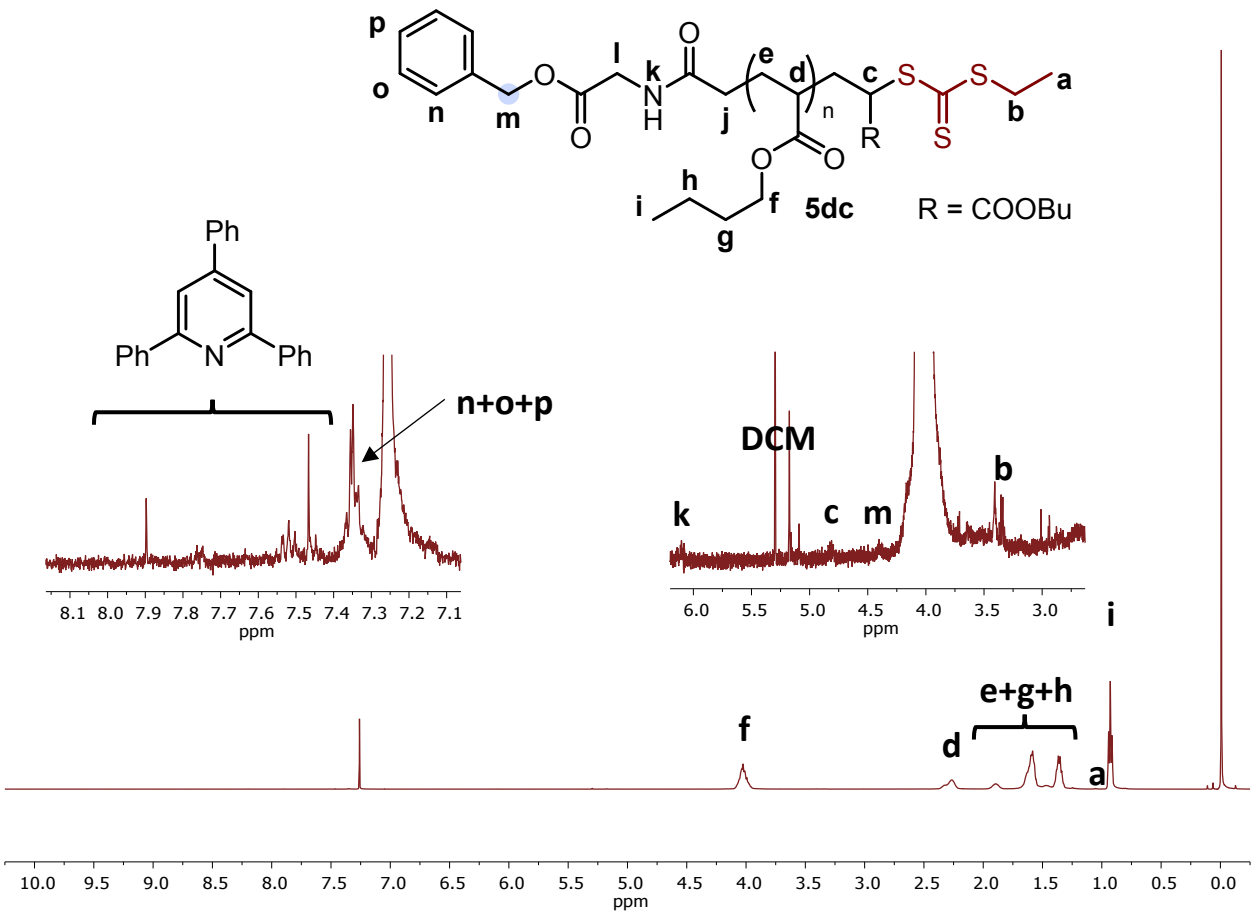
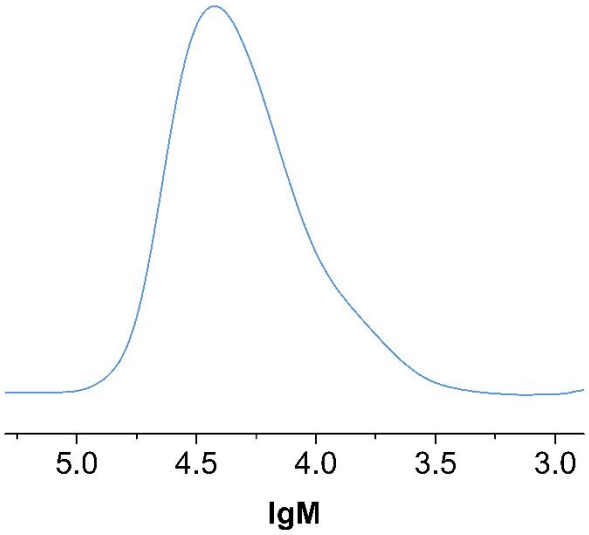


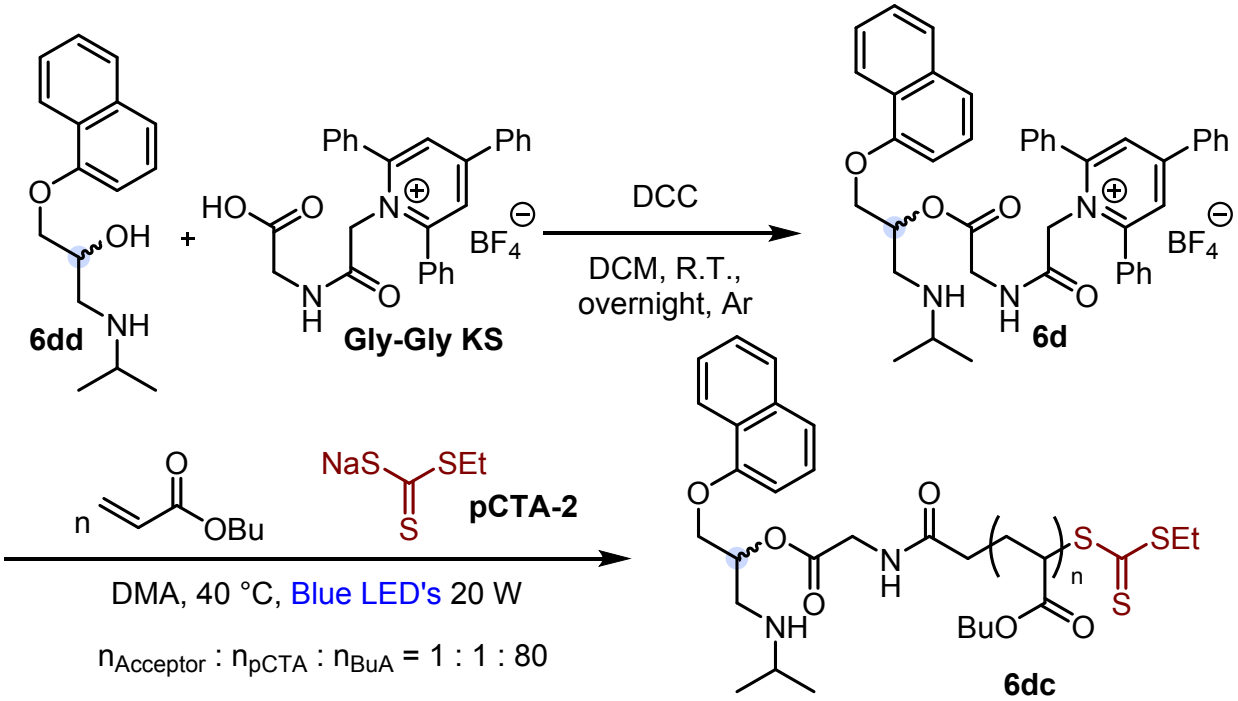
Figure S49. ^{1}H NMR spectrum of poly(butyl acrylate) **5dc**.

GPC traces for poly(butyl acrylate) **5dc** (**Figure S50**):



Poly(butyl acrylate) 6dc

Poly(butyl acrylate) **6dc** was synthesized according to the General Procedure F.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**o**) [c]	Tail (**c**) [d]			
61.5	6700	25500	26500	27300	0.25	> 99	1.32

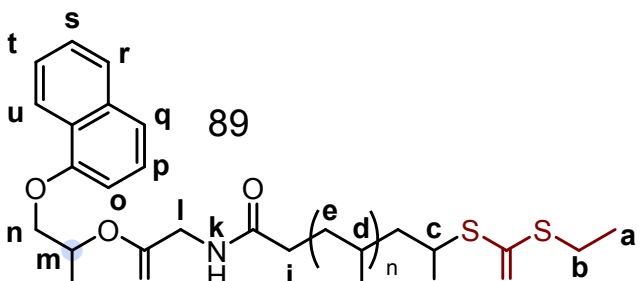


Figure S51. ^{1}H NMR spectrum of poly(butyl acrylate) **6dc**.

We compared the resulting PBuA **6dc** spectrum with that of Propranolol. The stacked aromatic parts of the two spectra clearly show that the coupling reaction and subsequent polymerization were successful.

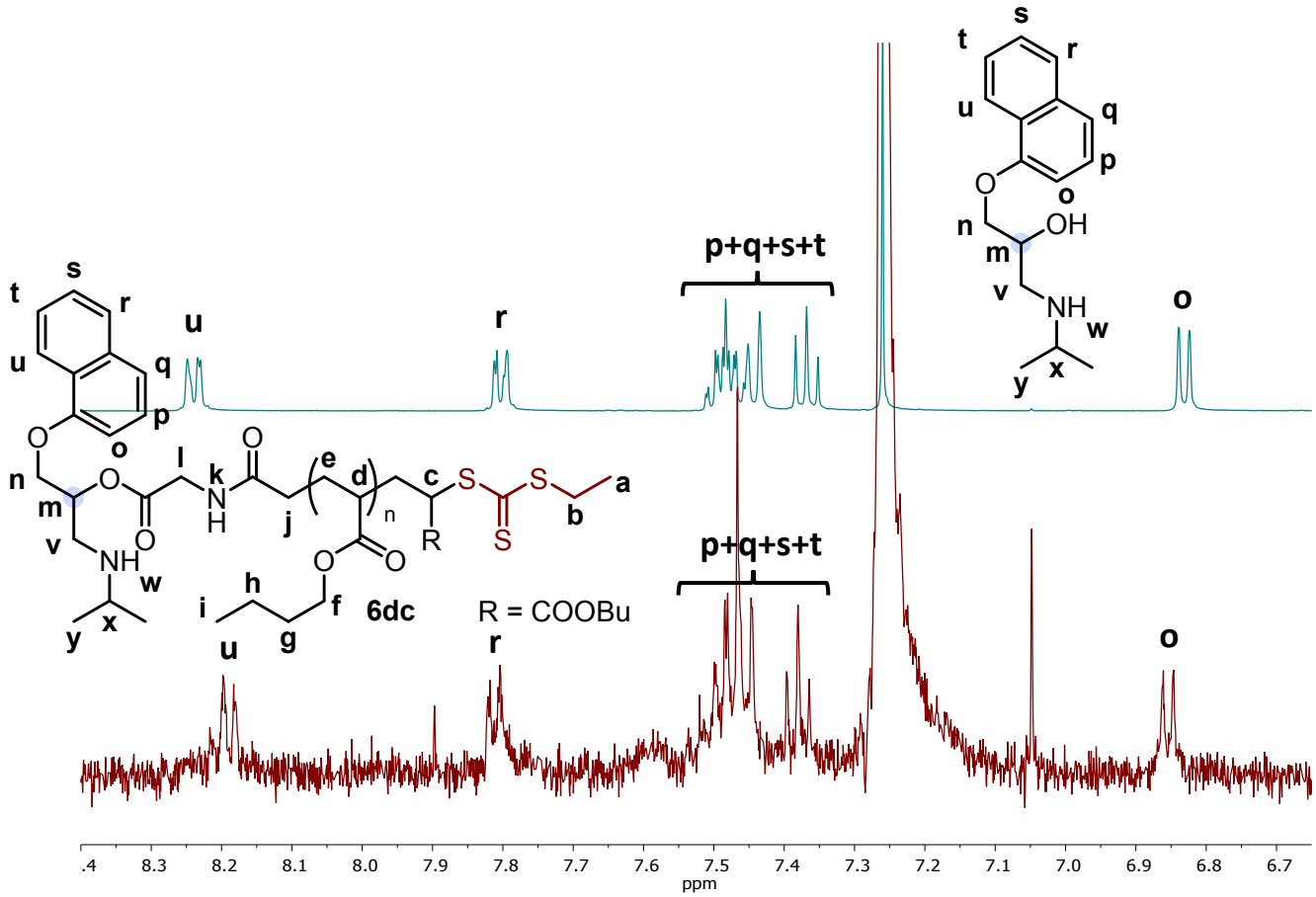
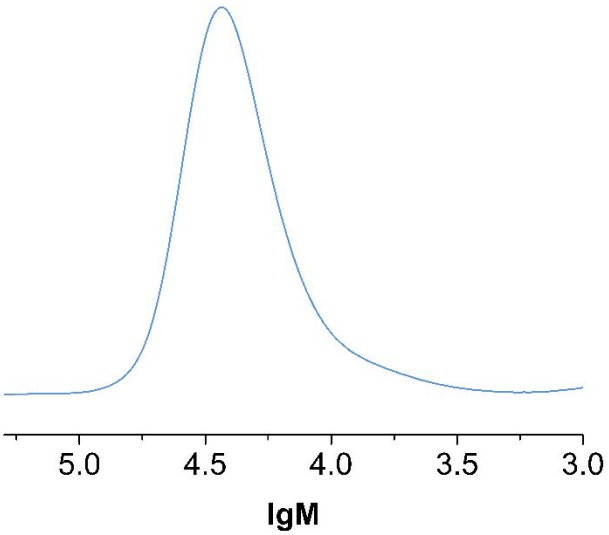


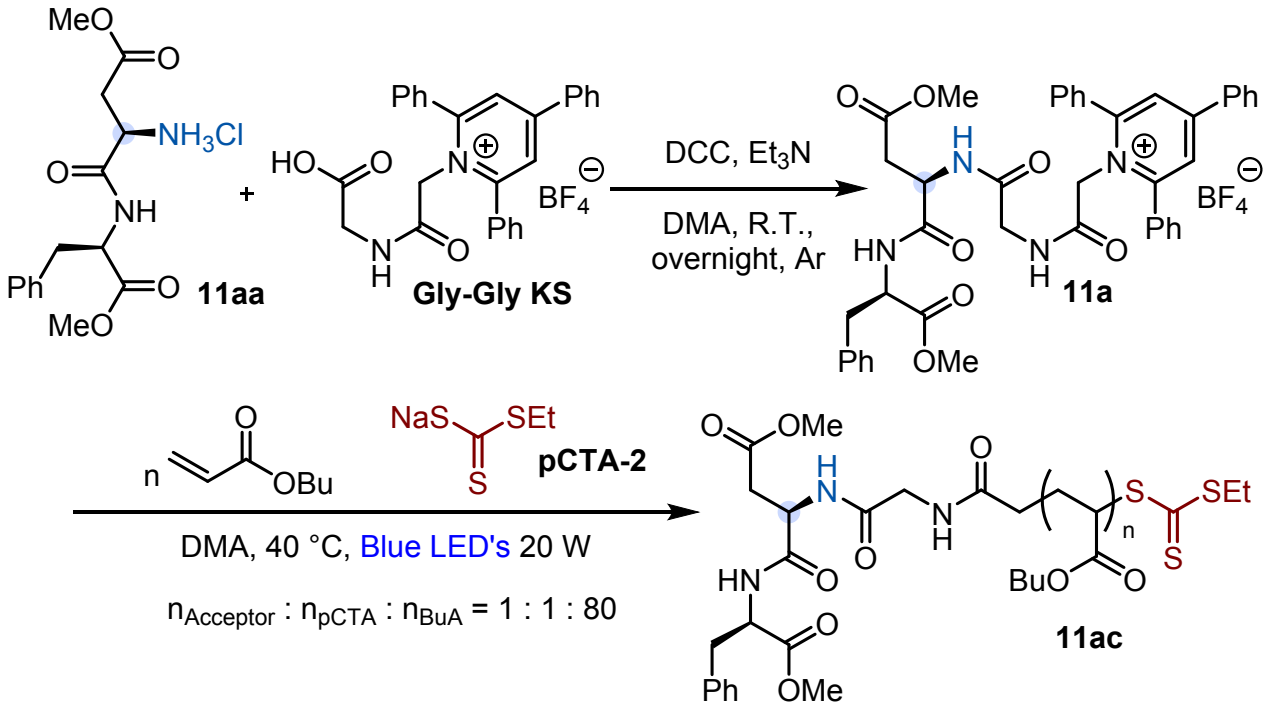
Figure S52. Stacked ^{1}H NMR spectra of Propranolol and poly(butyl acrylate) **6dc**.

GPC traces for poly(butyl acrylate) **6dc** (**Figure S53**):



Poly(butyl acrylate) 11ac

Poly(butyl acrylate) **11ac** was synthesized according to the General Procedure F.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**s**) [c]	Tail (**b**) [d]			
56.3	6300	15900	16100	16700	0.39	> 99	1.33

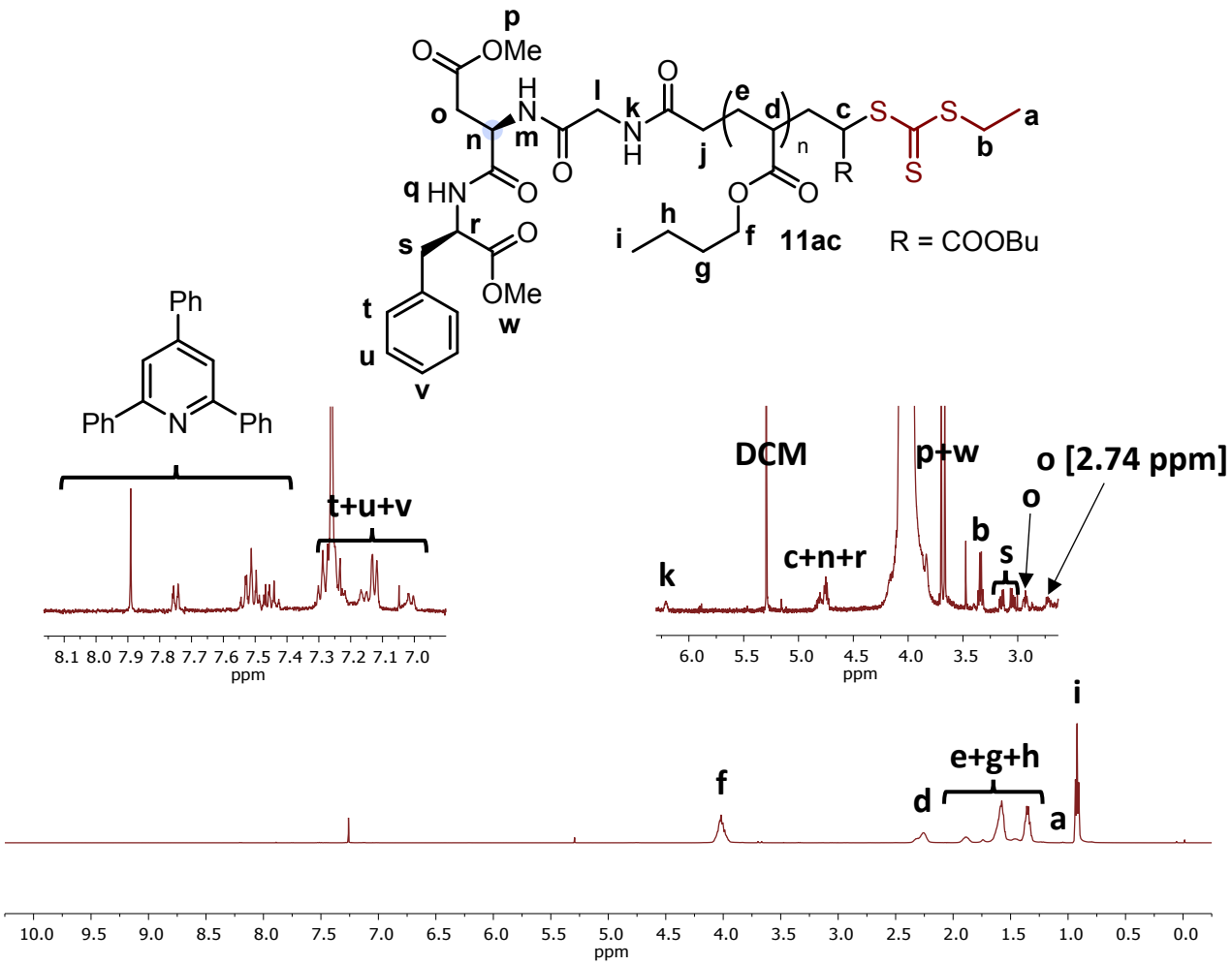


Figure S54. ^{1}H NMR spectrum of poly(butyl acrylate) **11ac**.

We compared the resulting spectrum of PBuA **11ac** with that of Aspartame methyl ester hydrochloride. Due to the use of different solvents ($CDCl_3$ and DMSO-d_6), as well as the coupling reaction with **Gly-Gly KS**, most of the signals changed their chemical shifts. However, the presence of two methyl groups and the specific splitting pattern of protons **s** and **o** proved that the complete structure of Aspartame methyl ester is present in PBuA **11ac**.

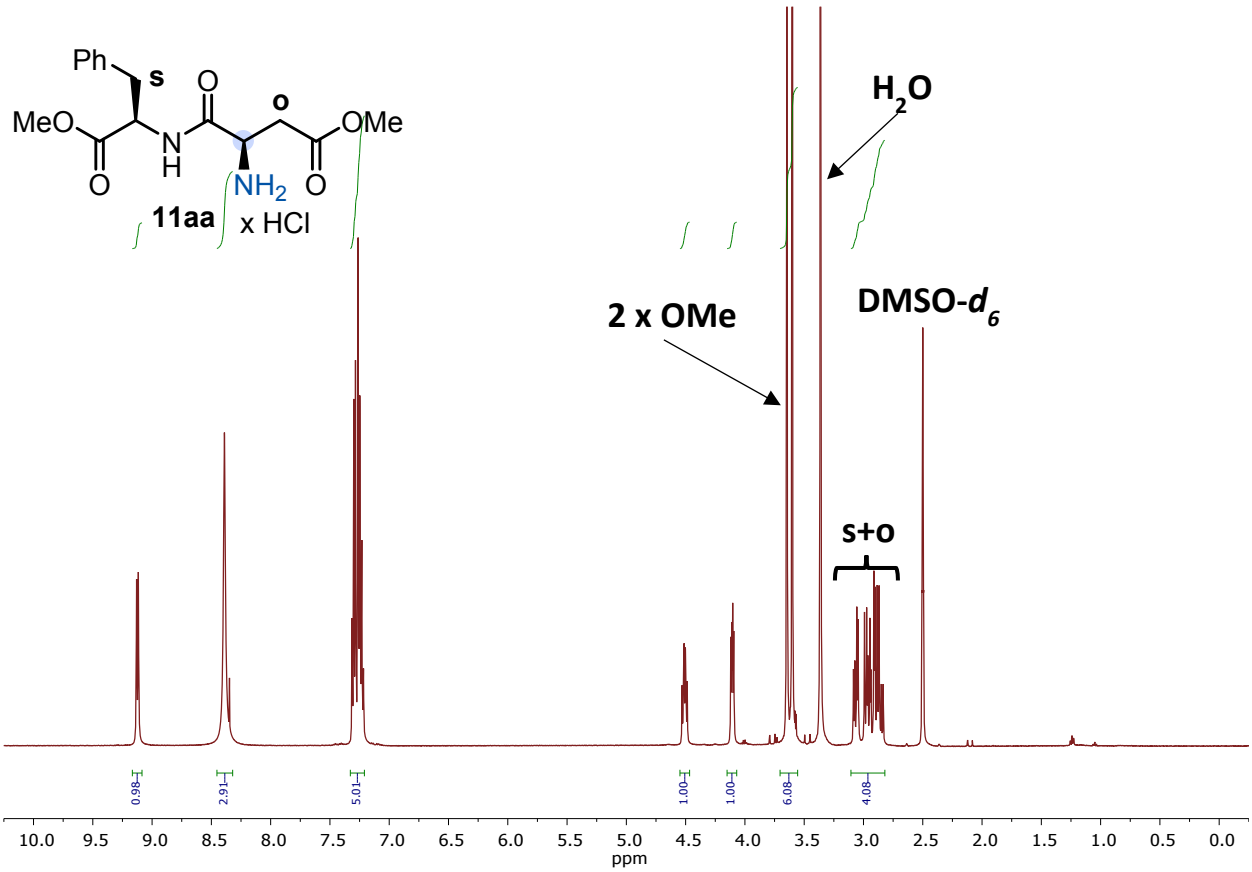
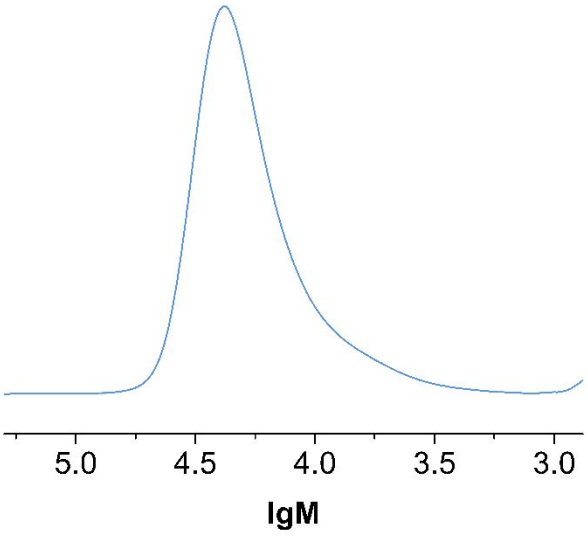


Figure S55. ^{1}H NMR spectrum of Aspartame methyl ester hydrochloride **11a**.

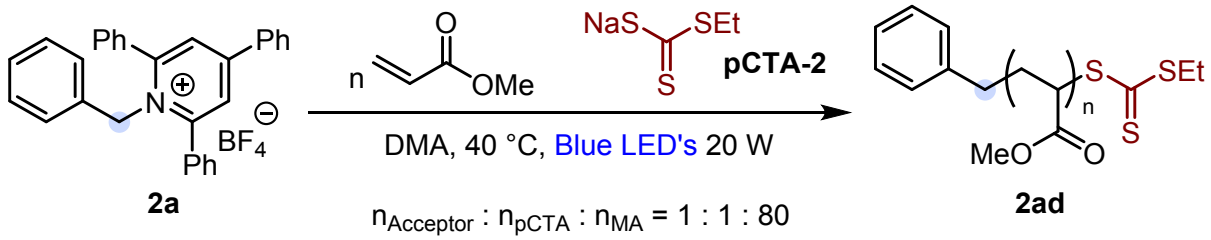
GPC traces for poly(butyl acrylate) **11ac** (**Figure S56**):



Monomers screening:

Poly(methyl acrylate) 2ad

Poly(methyl acrylate) **2ad** was synthesized according to the General Procedure G.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**h+j**) [c]	Tail (**c**) [d]			
99.1	7050	11600	11400	12500	0.62	> 99	1.22

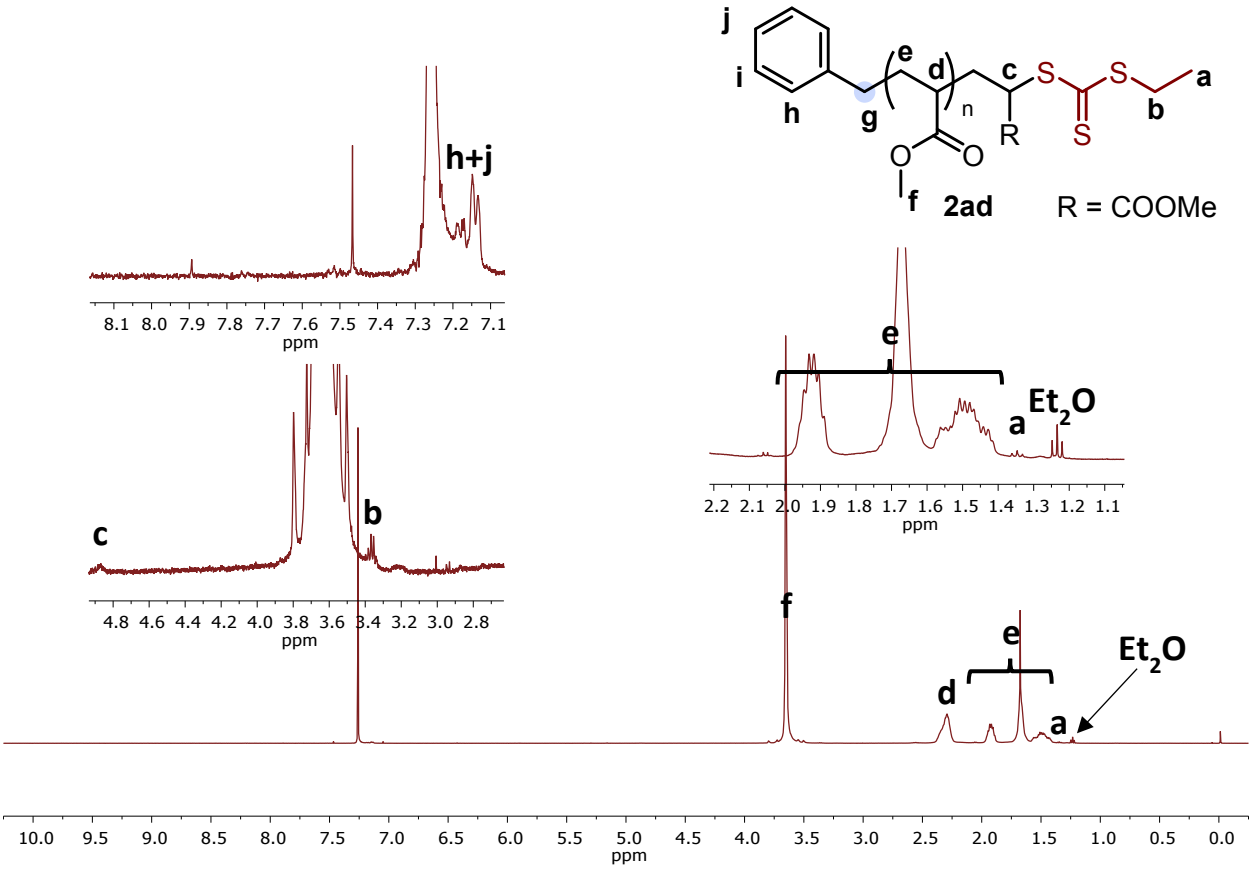
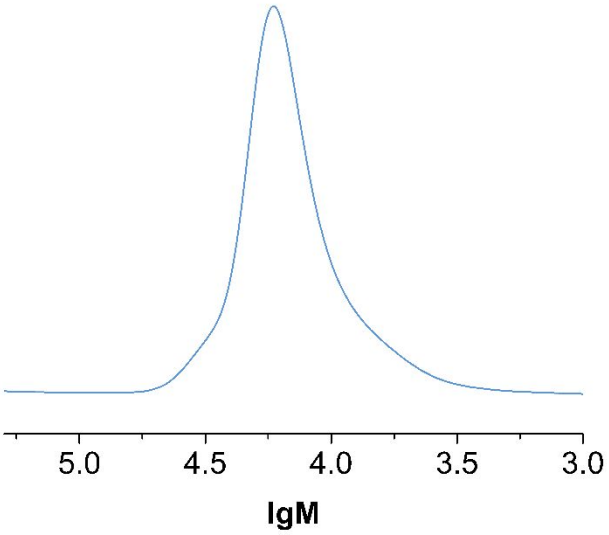


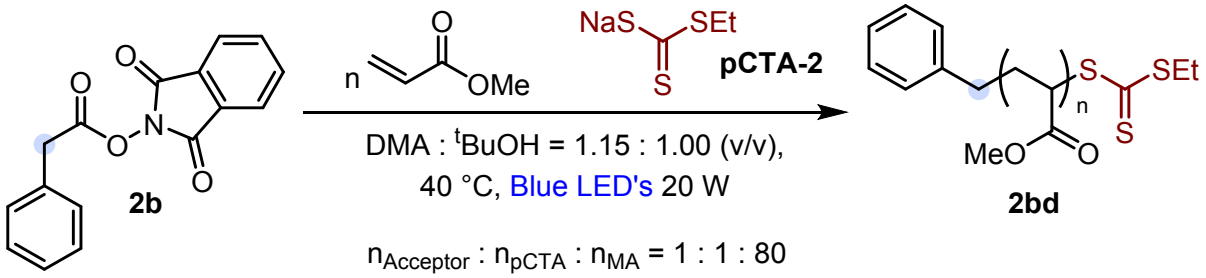
Figure S57. ^{1}H NMR spectrum of poly(butyl acrylate) **2ad**.

GPC traces for poly(butyl acrylate) **2ad** (**Figure S58**):



Poly(methyl acrylate) 2bd

Poly(methyl acrylate) **2bd** was synthesized according to the General Procedure G.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**h+j**) [c]	Tail (**c**) [d]			
65.3	4750	11200	11500	11850	0.41	> 99	1.23

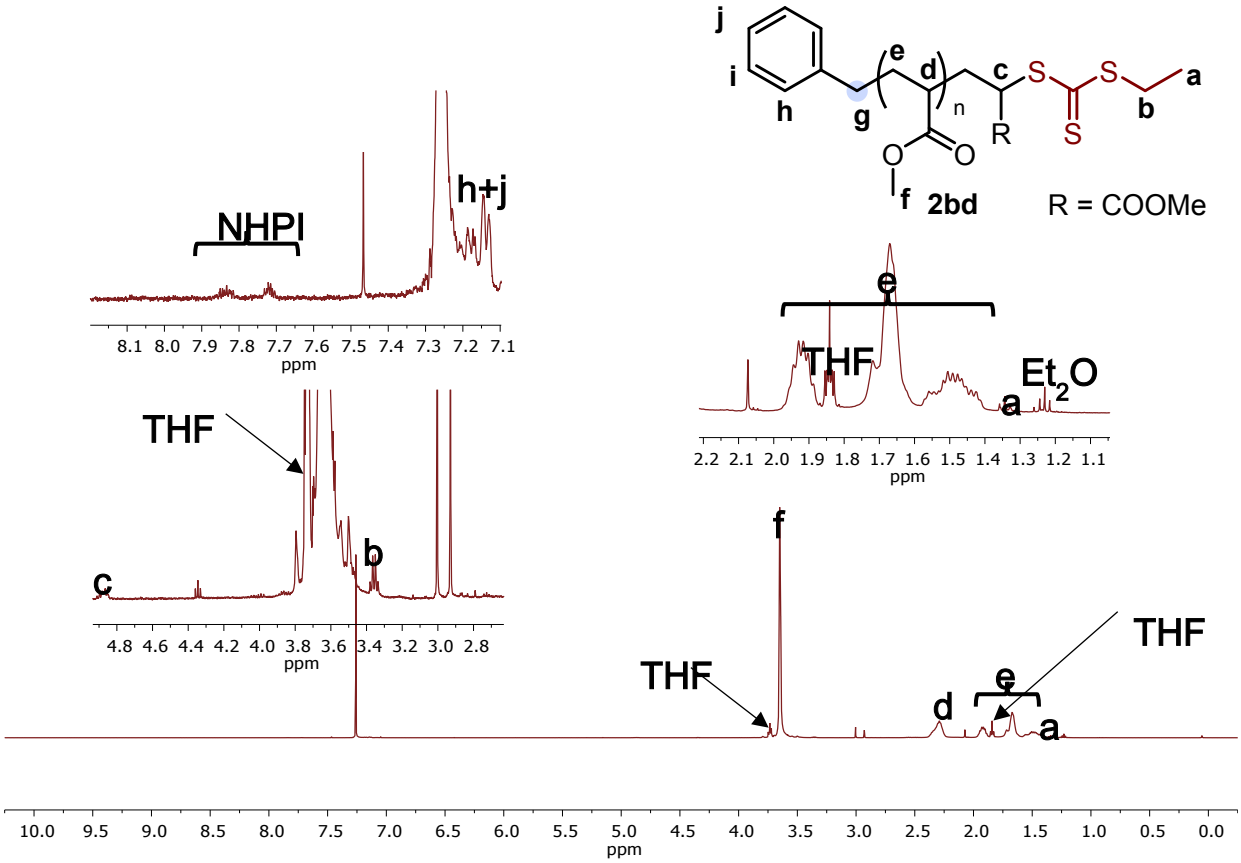
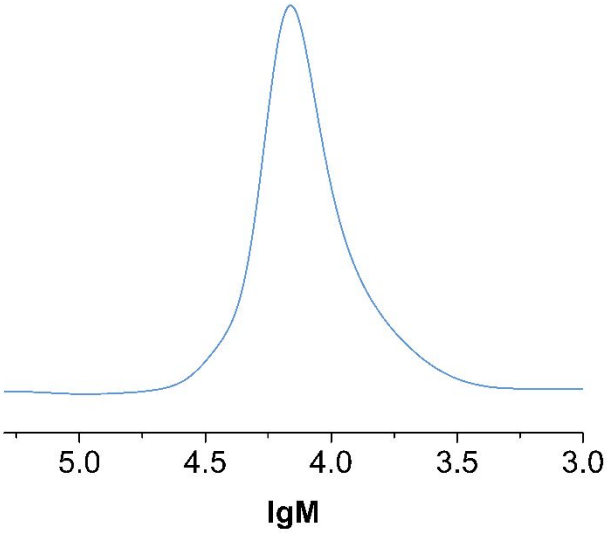


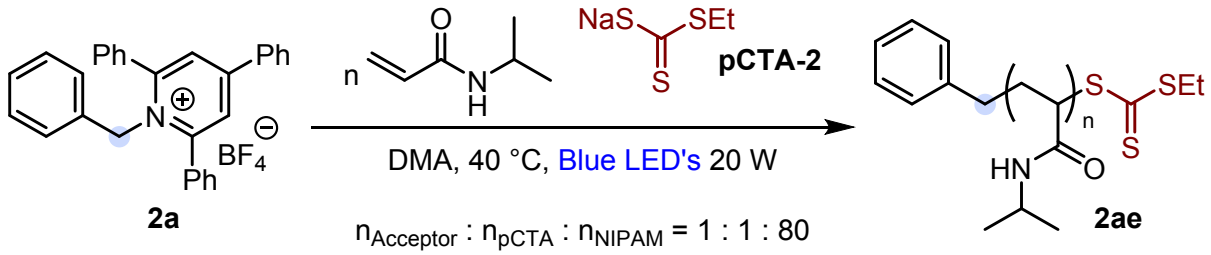
Figure S59. ^{1}H NMR spectrum of poly(methyl acrylate) **2bd**.

GPC traces for poly(butyl acrylate) **2bd** (**Figure S60**):



Poly(N-isopropyl acrylamide) 2ae

Poly(N-isopropyl acrylamide) **2ae** was synthesized according to the General Procedure G.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (g+l) [c]	Tail (b) [d]			
40.1	3850	8200	8000	8700	0.48	> 99	1.52
99.5	9250	22400	-	-	-	-	1.32

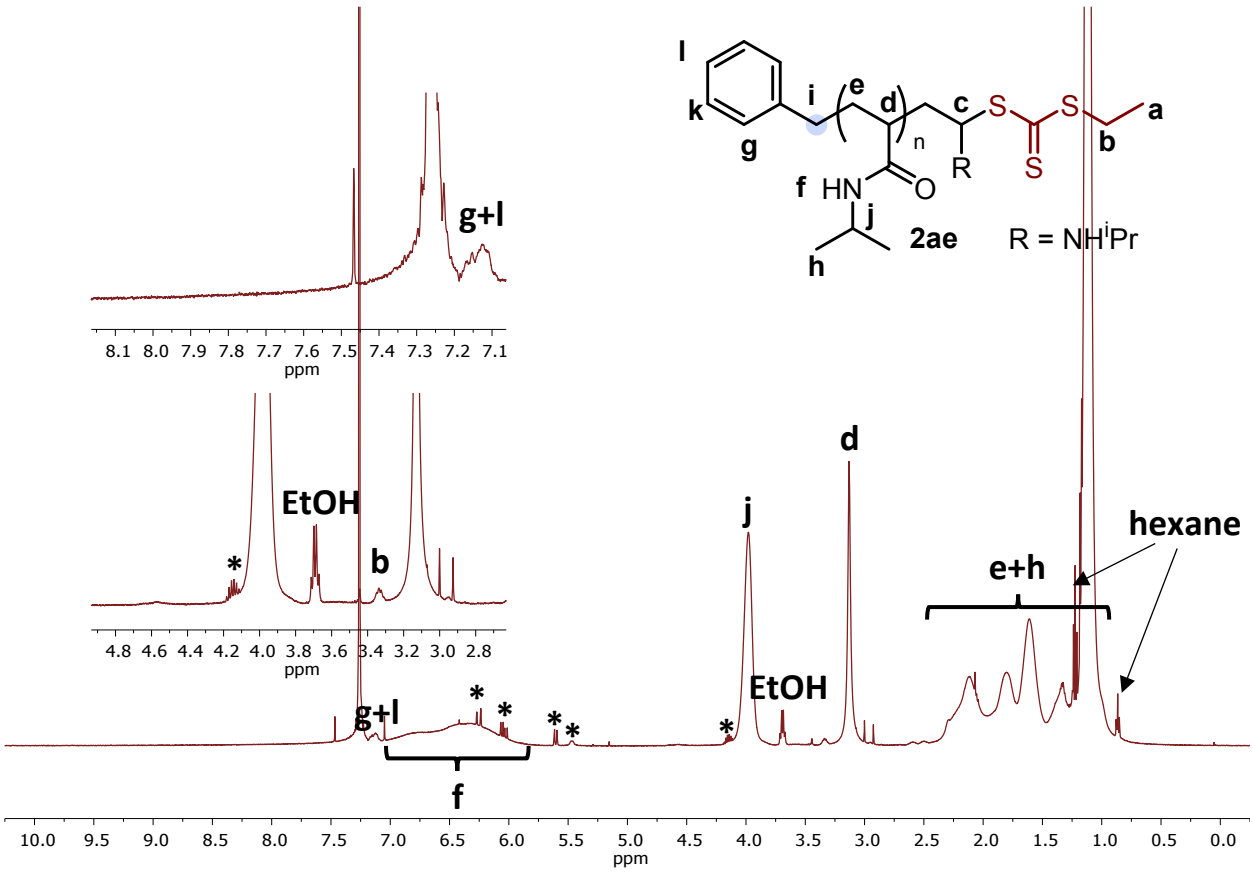
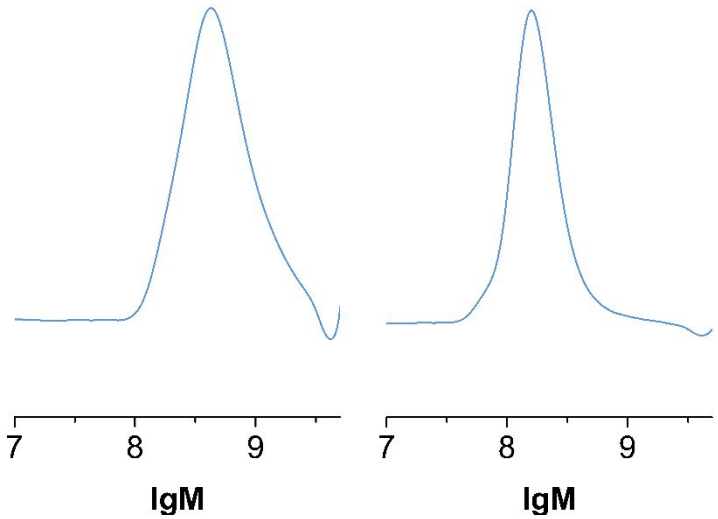


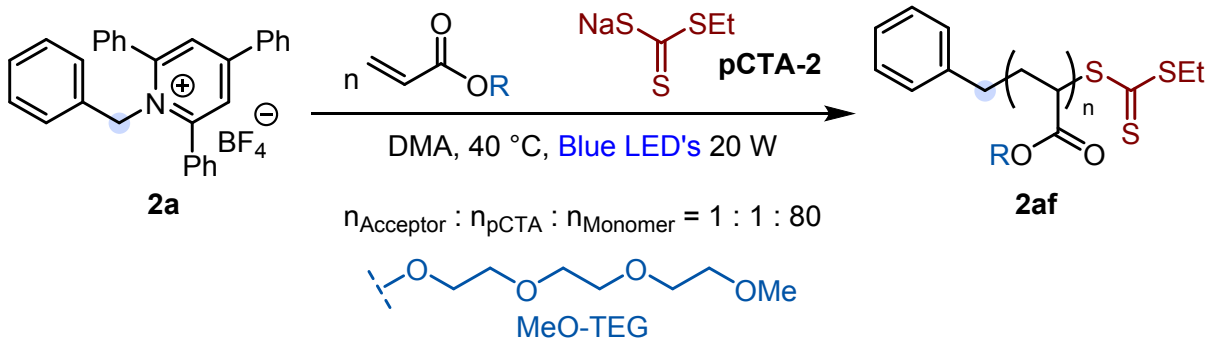
Figure S61. ^{1}H NMR spectrum of poly(N-isopropyl acrylamide) **2ae** (Conv. = 40.1 %). * Trace signals of protons from N-isopropyl acrylamide monomer.

GPC traces for poly(butyl acrylate) **2ae** with Conv. = 40.1 % (left) and Conv. = 99.5 % (right) (**Figure S62**):



Poly(methoxy triethylene glycol acrylate) 2af

Poly(methoxy triethylene glycol acrylate) **2af** was synthesized according to the General Procedure G.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (n+p) [c]	Tail [d]			
64.2**	11450	17300	15300	-	0.75	> 99	1.43

Conversion was determined from ^{1}H NMR spectrum (Figure S64**).

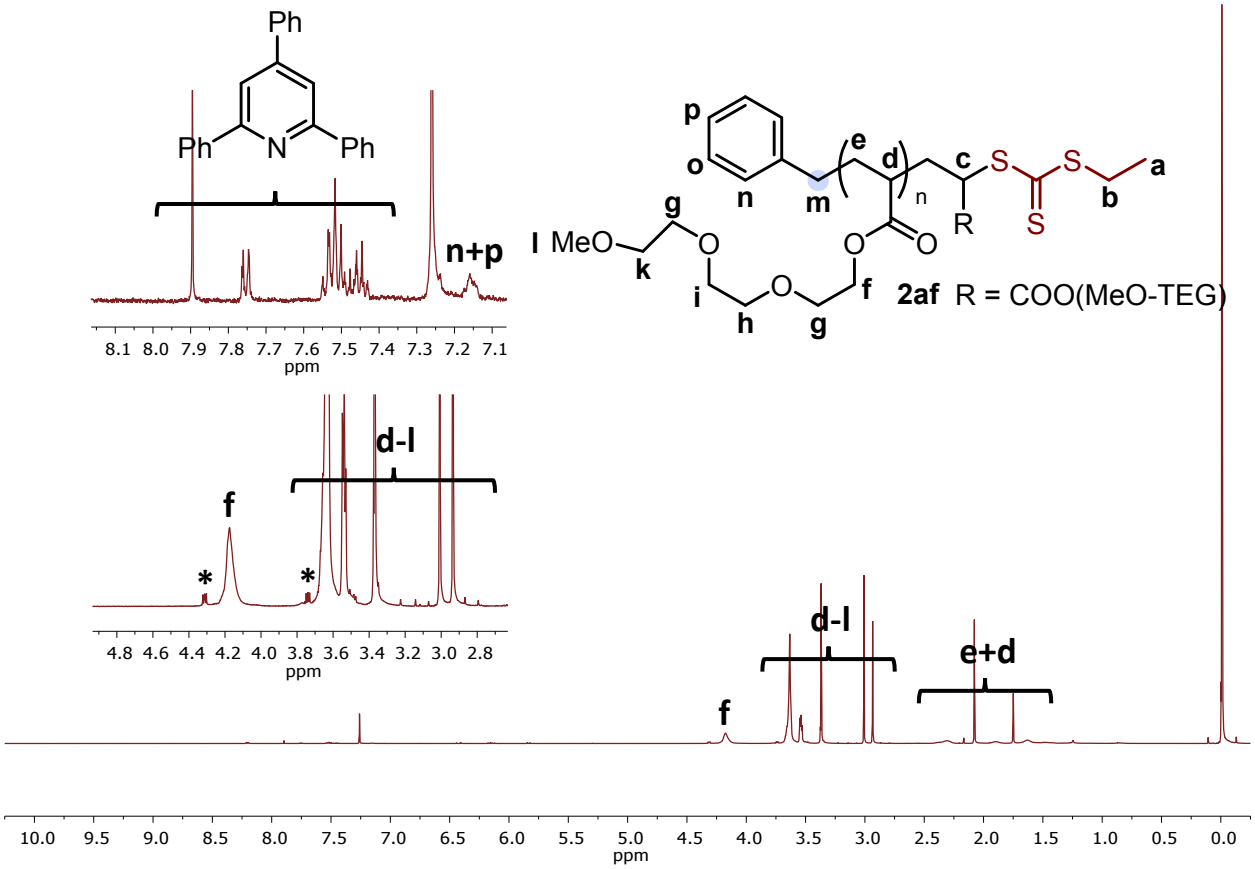


Figure S63. ^{1}H NMR spectra of poly(methoxy triethylene glycol acrylate) **2af**. * Signals of protons from poly(methoxy triethylene glycol acrylate) monomer.

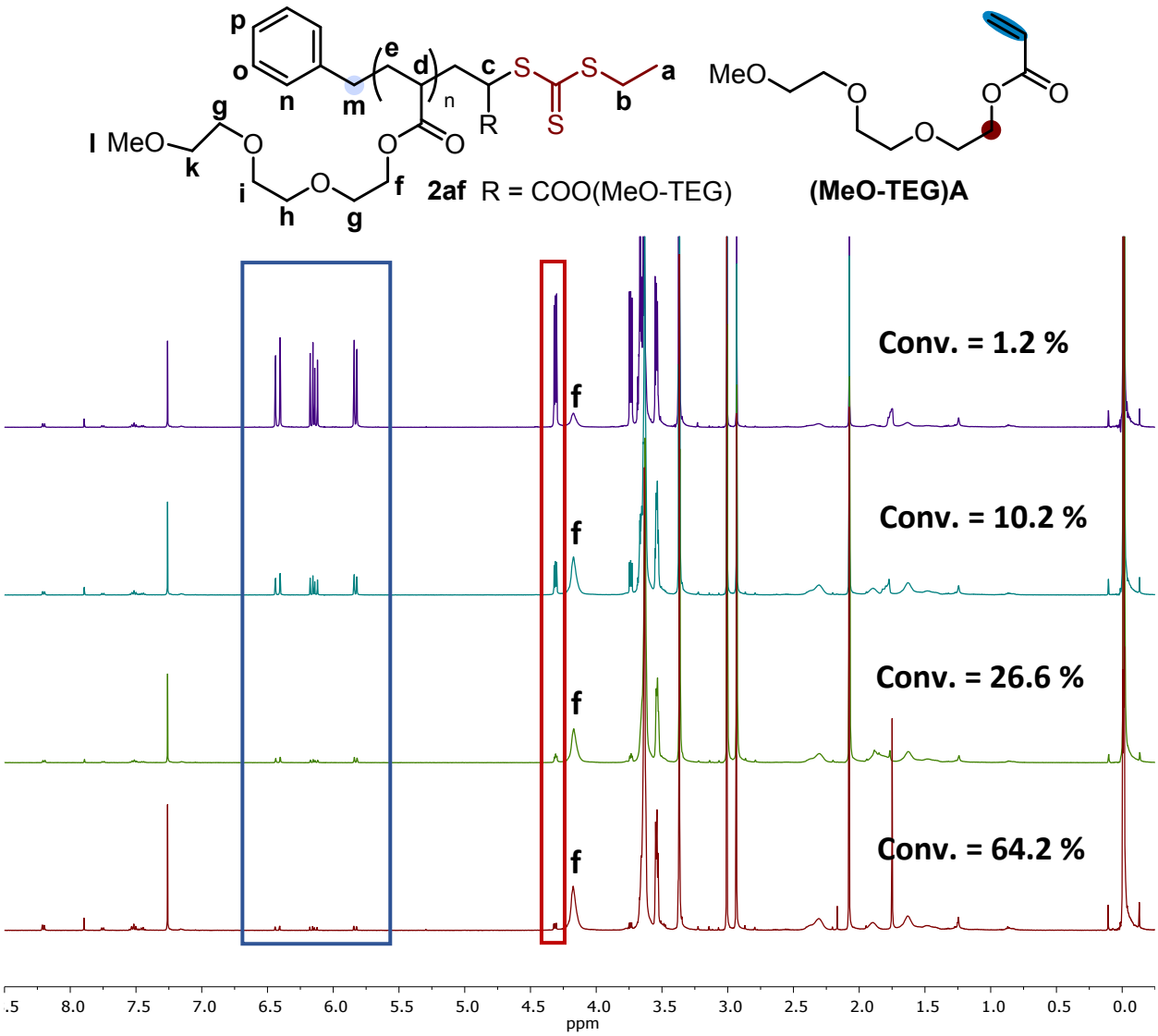
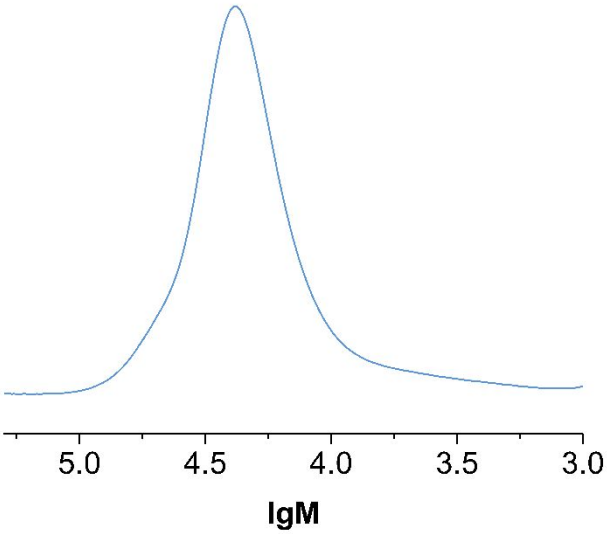


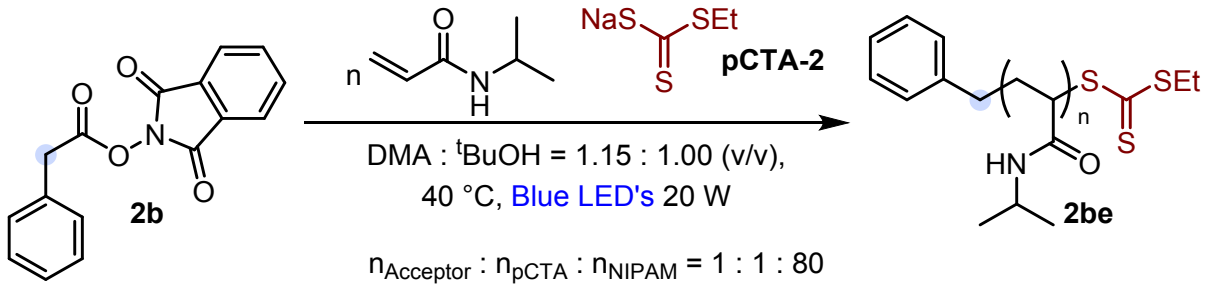
Figure S64. ^{1}H NMR spectra of poly(methoxy triethylene glycol acrylate) **2af** at various conversions.

GPC traces for poly(methoxy triethylene glycol acrylate) **2af** (**Figure S65**):



Poly(N-isopropyl acrylamide) 2be

Poly(N-isopropyl acrylamide) **2be** was synthesized according to the General Procedure G.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**h+j**) [c]	Tail (**c**) [d]			
23.5	2350	6000	6000	7600	0.39	> 99	1.74
60.5	5700	15300	-	-	-	-	1.50

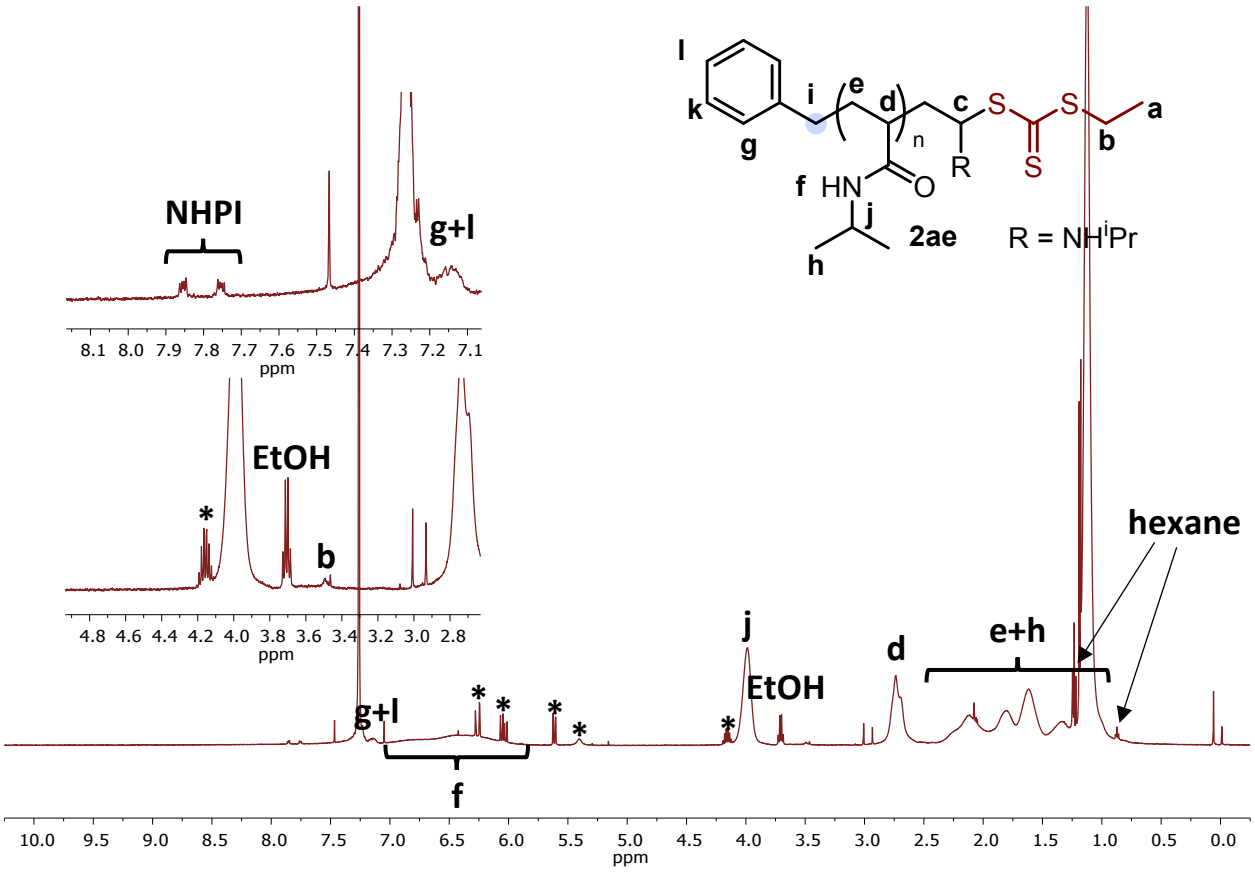
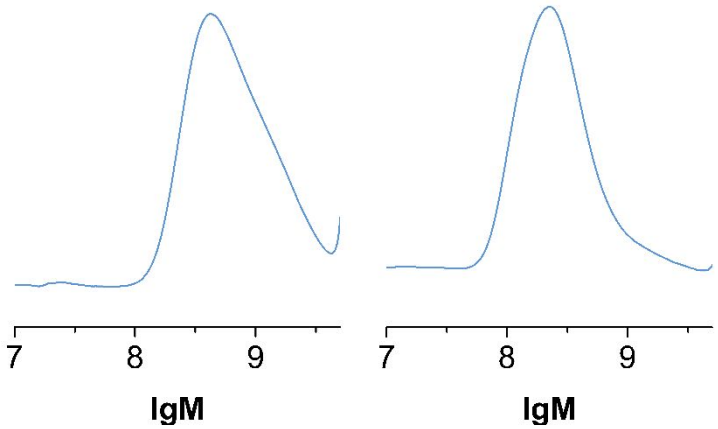


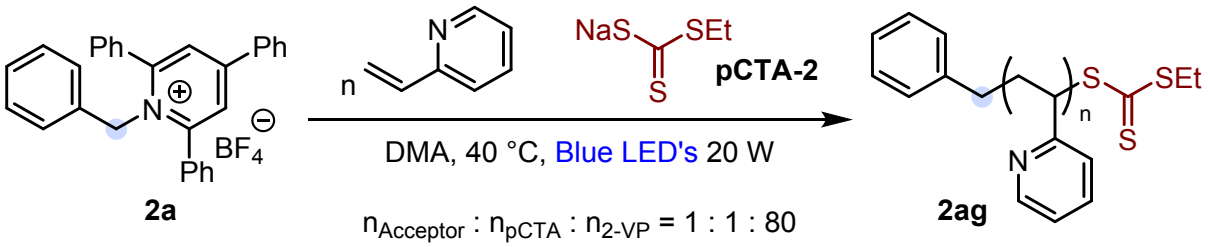
Figure S66. ^{1}H NMR spectrum of poly(N-isopropyl acrylamide) **2be** (Conv. = 23.5 %). * Trace signals of protons from N-isopropyl acrylamide monomer.

GPC traces for poly(butyl acrylate) **2be** with Conv. = 23.5 % (left) and Conv. = 60.5 % (right) (**Figure S67**):



Poly(2-vinylpyridine) 2ag

Poly(2-vinylpyridine) **2ag** was synthesized according to the General Procedure G.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head	Tail (**c**) [d]			
50.4	4200	5600	-	5600	-	> 99	1.67

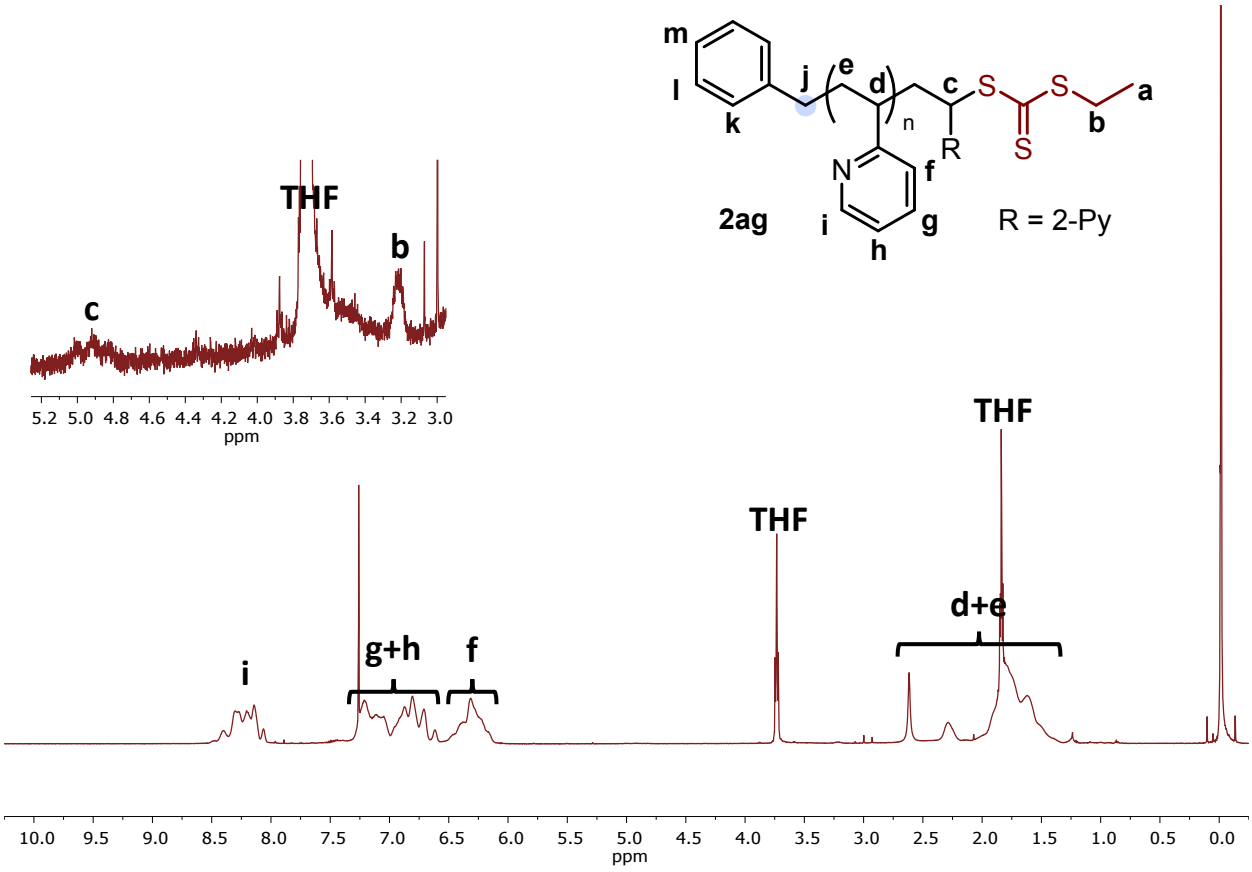
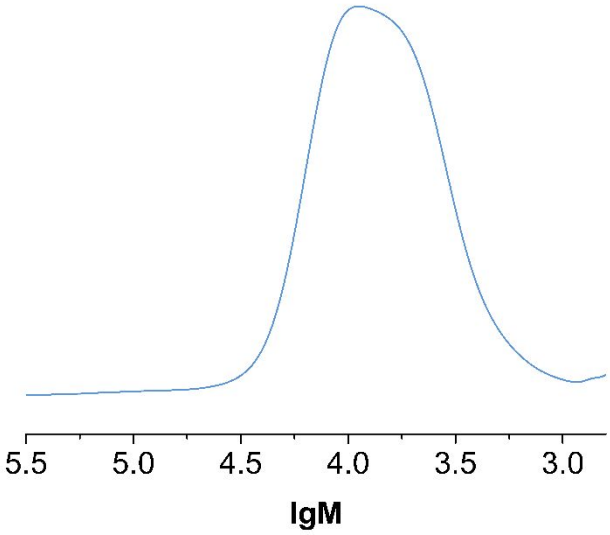


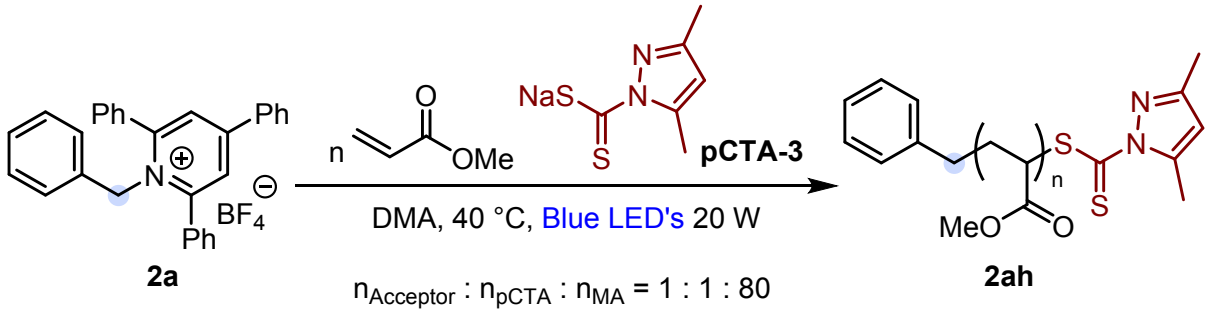
Figure S68. ^{1}H NMR spectrum of poly(butyl acrylate) **2ag**.

GPC traces for poly(butyl acrylate) **2ag** (**Figure S69**):



Poly(methyl acrylate) 2ah

Poly(methyl acrylate) **2ah** was synthesized according to the General Procedure G.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**i+k**) [c]	Tail (**d**) [d]			
99.9	7150	9100	9300	9700	0.77	> 99	1.28

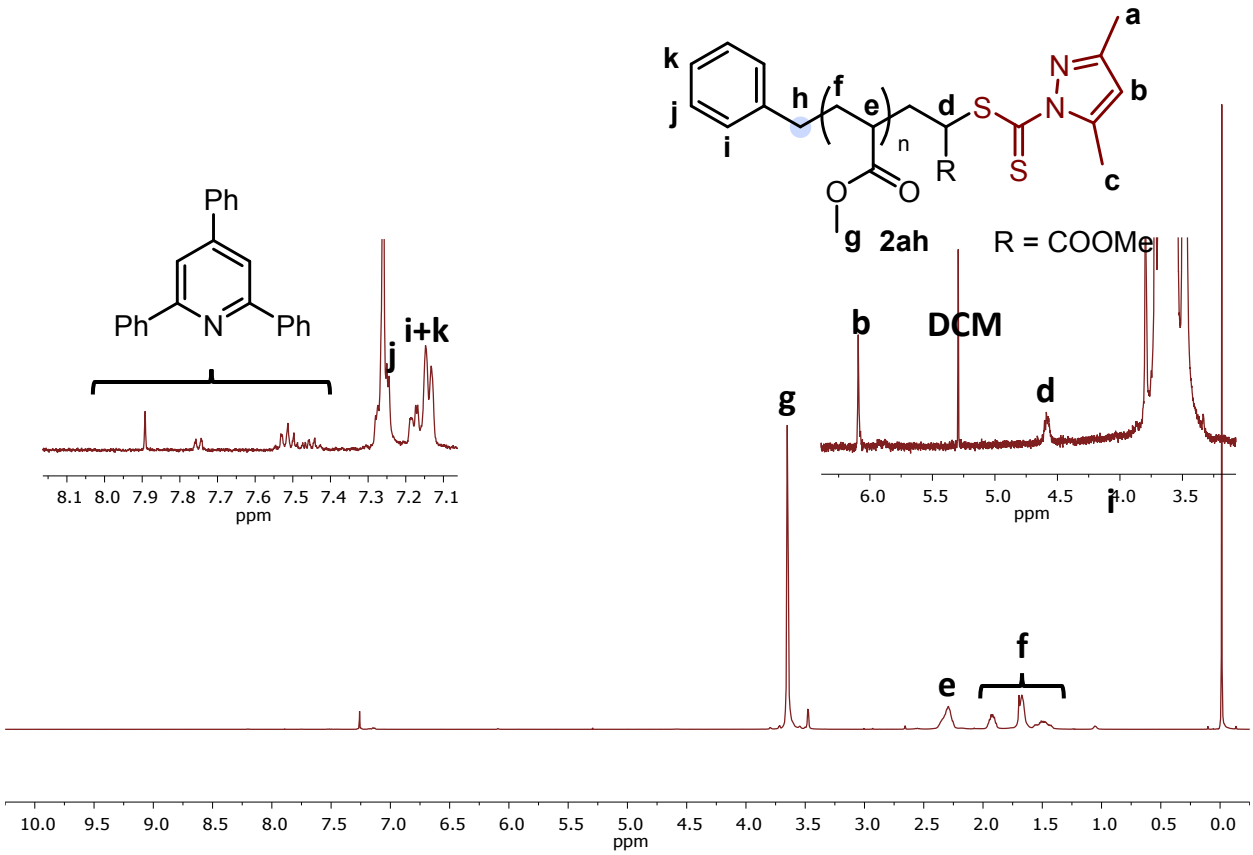
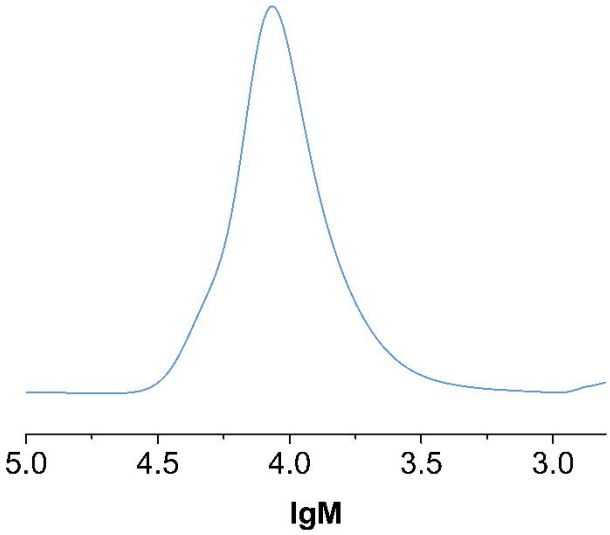


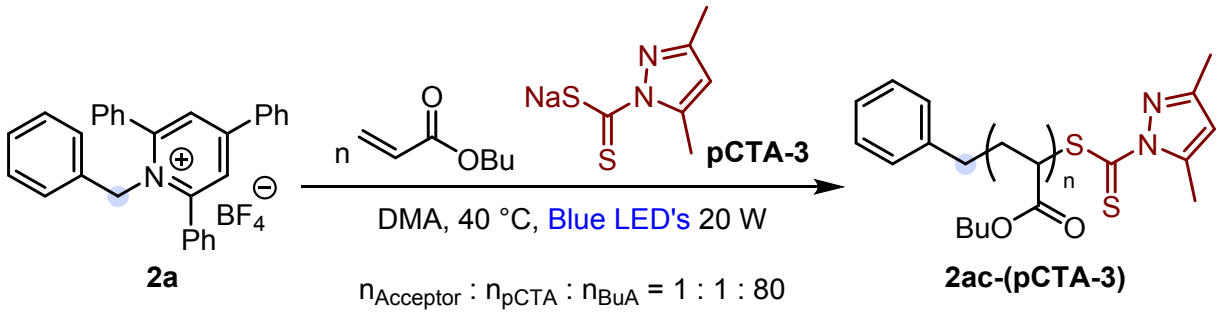
Figure S70. ^{1}H NMR spectrum of poly(butyl acrylate) **2ah**.

GPC traces for poly(butyl acrylate) **2ah** (**Figure S71**):



Poly(butyl acrylate) 2ac-(pCTA-3)

Poly(butyl acrylate) **2ac-(pCTA-3)** was synthesized according to the General Procedure G.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		I_{eff} [e]	φ, [f] %	Đ
			Head (**l+n**) [c]	Tail (**d**) [d]			
81.6	8650	8900	9600	9600	0.90	> 99	1.28

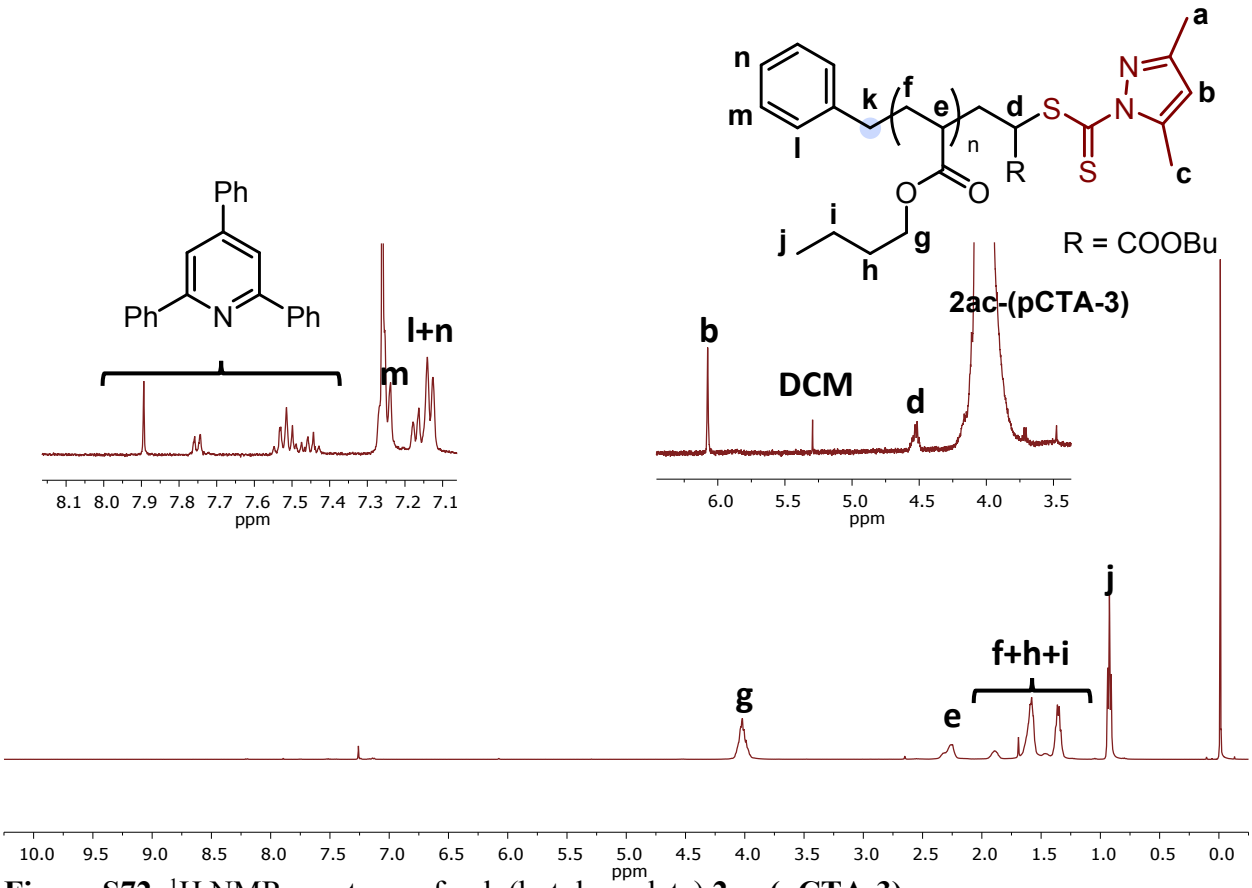


Figure S72. ^{1}H NMR spectrum of poly(butyl acrylate) **2ac-(pCTA-3)**.

GPC traces for poly(butyl acrylate) **2ac-(pCTA-3)** (**Figure S73**):

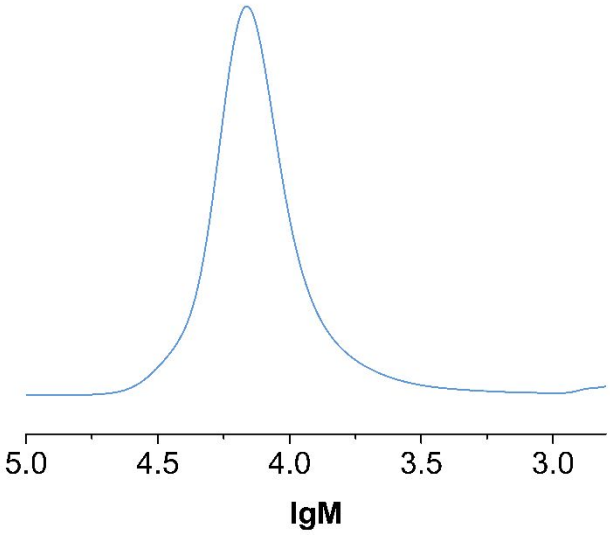
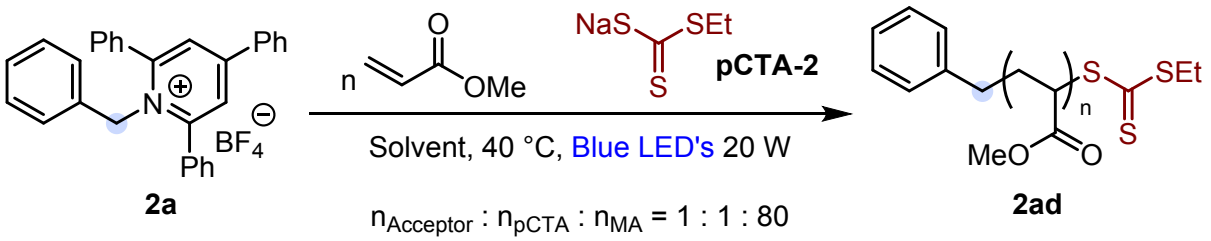


Table S1. Additional Solvents Screening for MA:



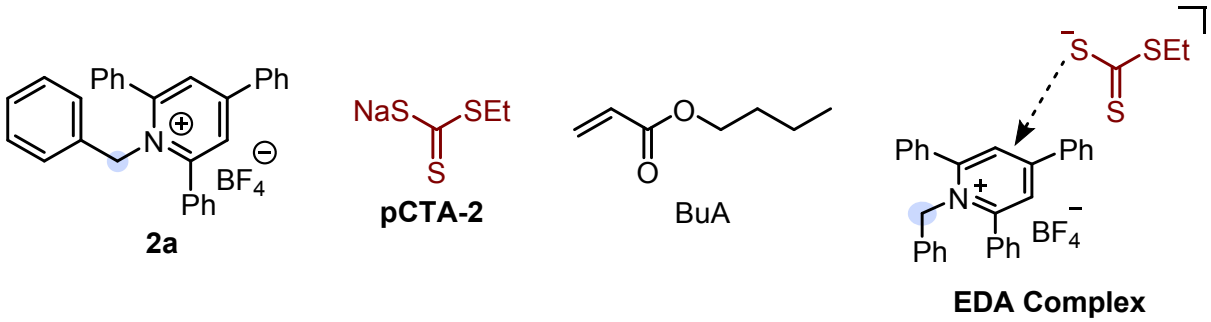
Solvent	Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR, Head) [c] (g mol^{-1})	I_{eff} [e]	Đ
NMP	96.2	6850	7900	7400	0.93	1.22
DMSO	88.8	6350	8600	8500	0.75	1.21

9. Mechanistic Studies

Uv-Vis Absorption Spectra

*Katritzky salt **2a** as acceptor*

The UV-Vis absorption spectra of Katritzky salt **2a**, **pCTA-2**, BuA and their mixtures in DMA (0.01 M) are shown below. The bathochromic shift is indicative of EDA complex formation between Katritzky salt **2a** and **pCTA-2**.



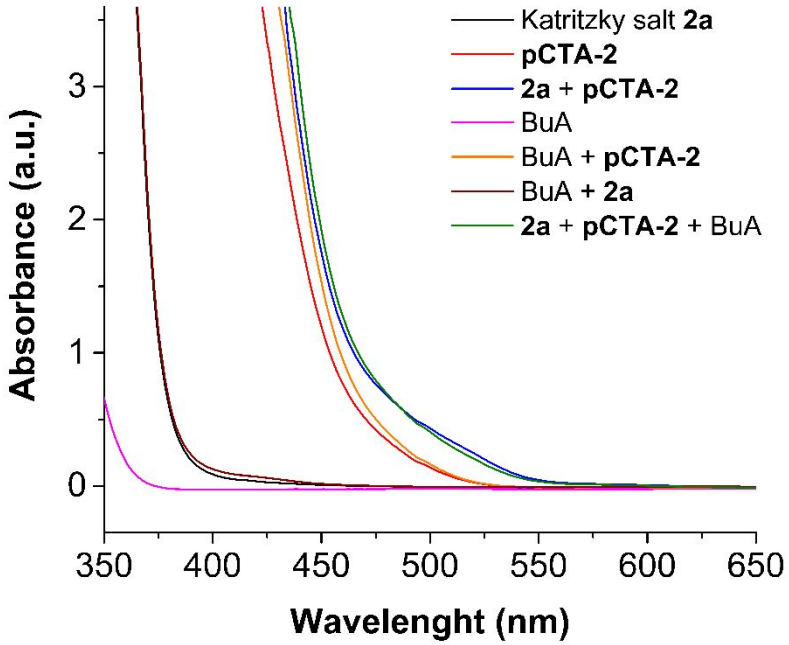
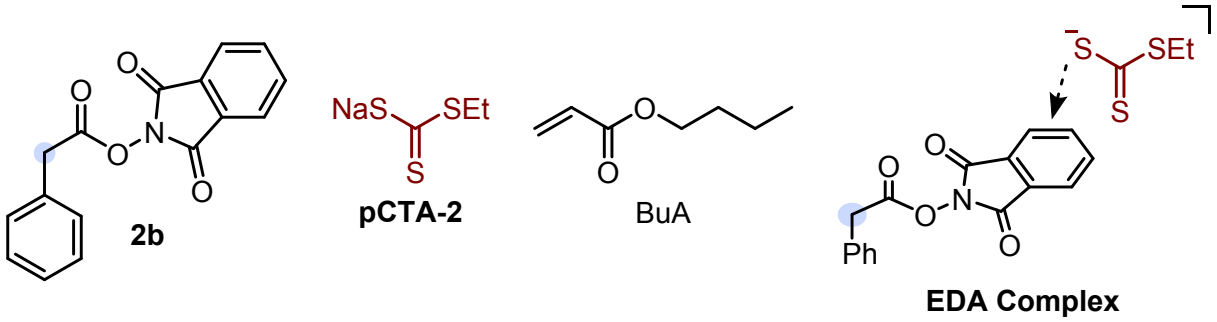


Figure S74. The UV-Vis absorption spectra of Katritzky salt **2a**, **pCTA-2**, **BuA** and their mixtures in DMA (0.01 M).
*All absorption spectra were recorded in quartz cuvettes with a path length of 1.0 cm.

*NHPI ester **2b** as acceptor*

The UV-Vis absorption spectra of NHPI ester **2b**, **pCTA-2**, BuA and their mixtures in DMA (0.01 M) are shown below. The bathochromic shift is indicative of EDA complex formation between NHPI ester **2b** and **pCTA-2**.



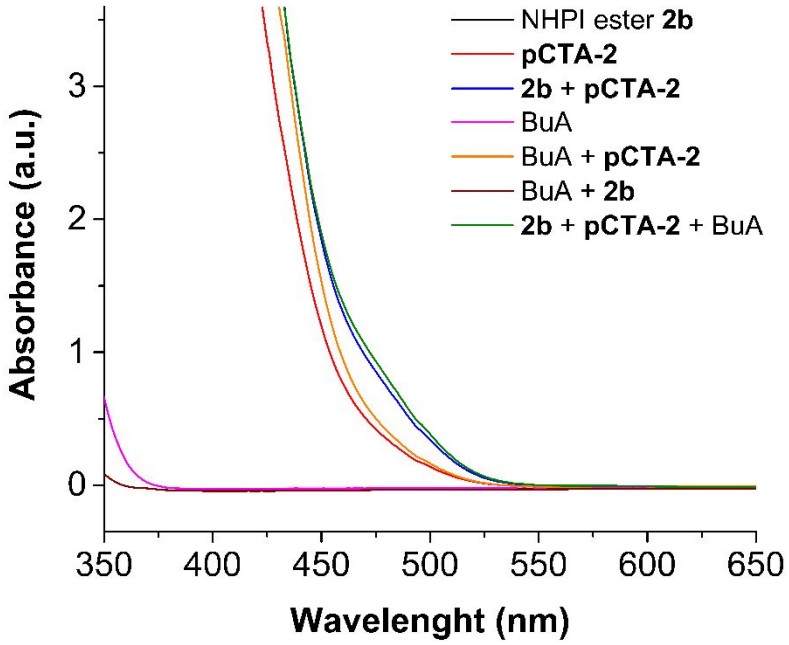
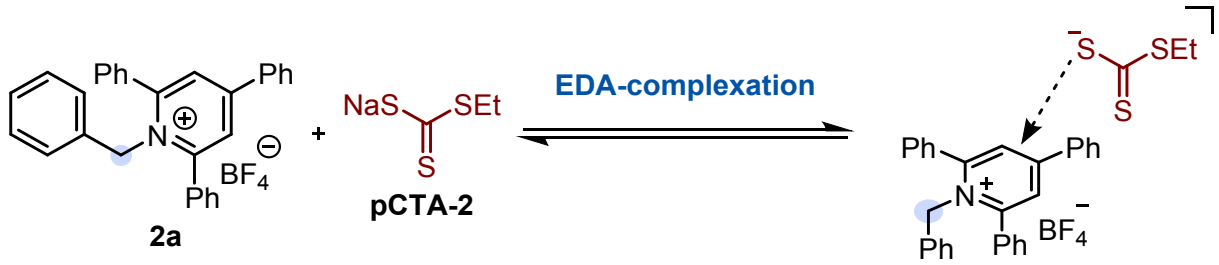


Figure S75. The UV-Vis absorption spectra of NHPI ester **2b**, **pCTA-2**, **BuA** and their mixtures in DMA (0.01 M).
*All absorption spectra were recorded in quartz cuvettes with a path length of 1.0 cm.

Determination of the Stoichiometry of the EDA-Complex

*Katritzky salt **2a** as acceptor*

The stoichiometry of the EDA complex was determined using Job's method with varying ratios of Katritzky salt **2a** and **pCTA-2** in DMA at 520 nm, where the total concentration of the two components remained constant at 0.02 M. The absorbance values were corrected with respect to the molar fraction of **pCTA-2** and plotted against the molar fraction (%) of **pCTA-2**. The maximum absorbance at 50 % molar fraction of **pCTA-2** indicated the 1:1 stoichiometry of the EDA complex in solution.



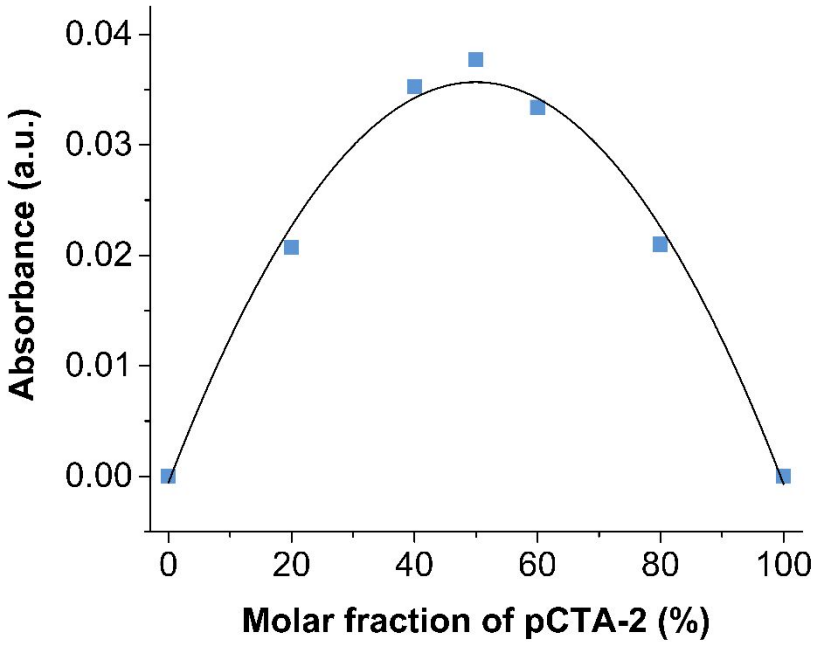


Figure S76. Job's plot of Katritzky salt **2a** and **pCTA-2** in DMA at 520 nm.
*All absorption spectra were recorded in quartz cuvettes with a path length of 1.0 cm.

*NHPI ester **2b** as acceptor*

The stoichiometry of the EDA complex was determined using Job's method with varying ratios of NHPI ester **2b** and **pCTA-2** in DMA at 500 nm, where the total concentration of the two components remained constant at 0.02 M. The absorbance values were corrected with respect to the molar fraction of **pCTA-2** and plotted against the molar fraction (%) of **pCTA-2**. The maximum absorbance at 50 % molar fraction of **pCTA-2** indicated the 1:1 stoichiometry of the EDA complex in solution.

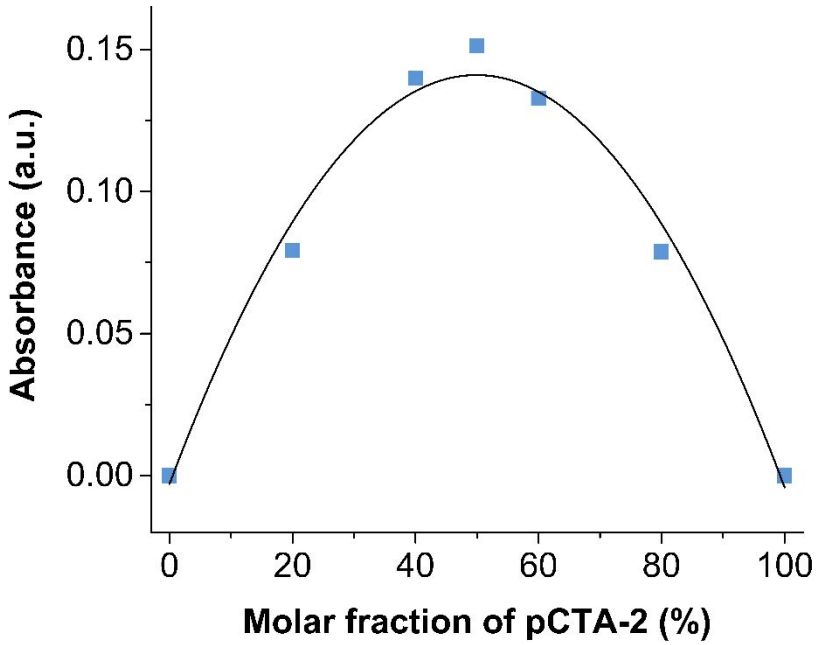


Figure S77. Job's plot of NHPI ester **2b** and **pCTA-2** in DMA at 500 nm.
*All absorption spectra were recorded in quartz cuvettes with a path length of 1.0 cm.

Stern-Volmer Quenching Studies

The emission spectra were recorded by Agilent Cary Eclipse spectrofluorimeter. Samples for the luminescence quenching experiment were prepared mixing Katritzky salt **2a** (C = 0.10 mM) with the required amount of **pCTA-2** in a total volume of 2.0 mL of dry DMA in quartz cuvettes with a path length of 1.0 cm under Ar atmosphere. The excitation wavelength was fixed at 350 nm (incident light slit regulated to 1.5 nm), while the emission light was acquired from 370 nm to 670 nm (emission light slit regulated to 20 nm).

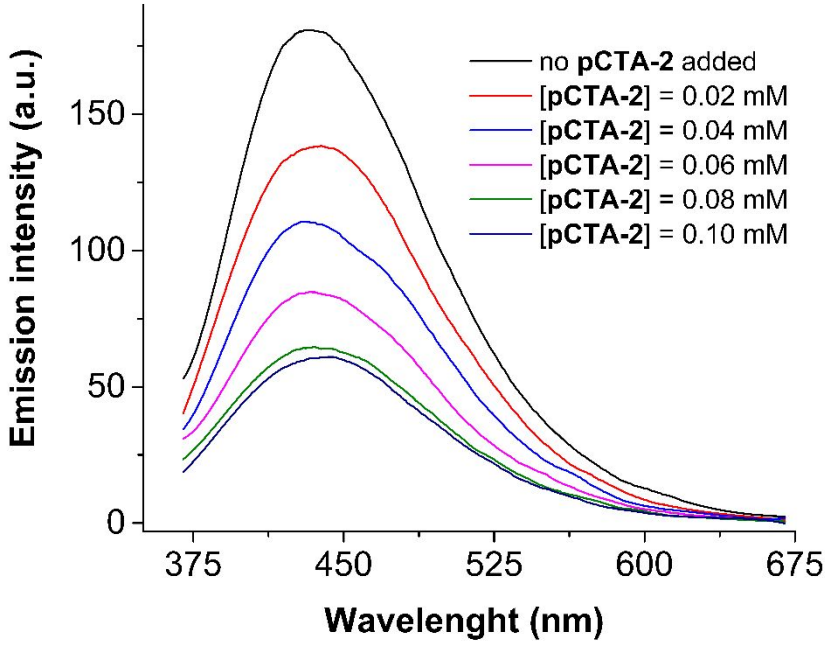


Figure S78. Quenching of Katritzky salt **2a** emission (0.10 M in DMA) in the presence of increasing amounts of **pCTA-2**.

The Stern-Volmer plot shows a linear correlation between the amounts of **pCTA-2** and the ratio I_0/I. On the basis of the following equation (1), the Stern-Volmer quenching constant (K_{SV}) was calculated to be 19.6□10^3 M^{-1}.

(1) $I_0/I = 1 + K_{SV}[Q]$

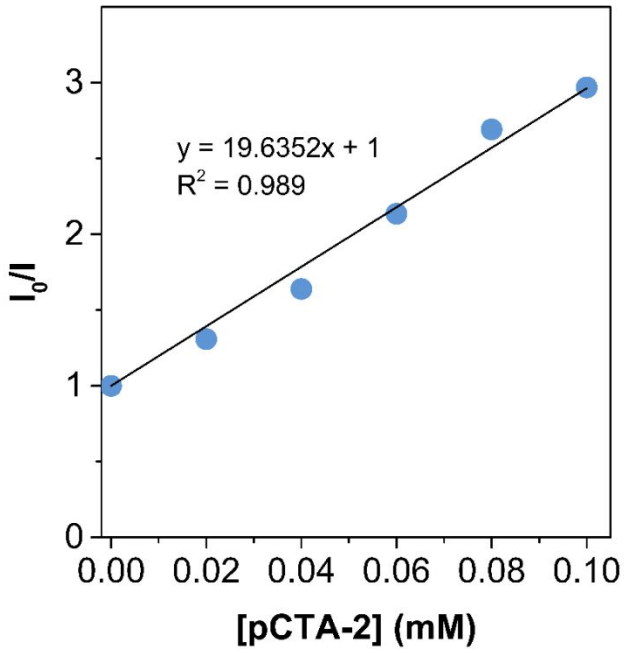
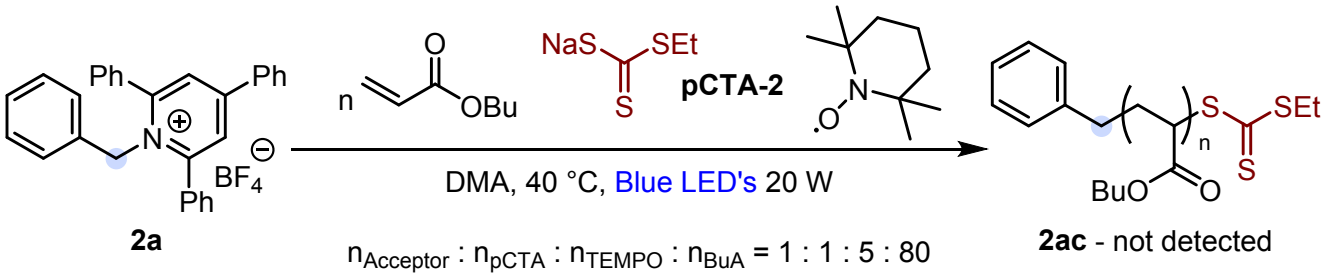


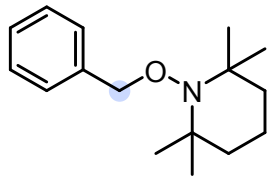
Figure S79. Stern-Volmer quenching plot.

Radical Trapping Experiment

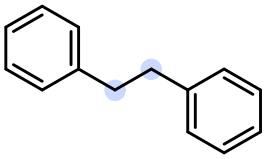
The experiment was carried out to further support radical mechanism of the photoinduced transformation of Katritzky salts. It was performed according to the General Procedure D, but with the addition of 5 eq. of TEMPO relative to **pCTA-2** and Katritzky salt **2a**. After 3 hours of irradiation, no polymer was precipitated, indicating complete inhibition of the polymerization process. Next, an aliquot of the reaction mixture was taken, evaporated, and subjected to GC-MS analysis.



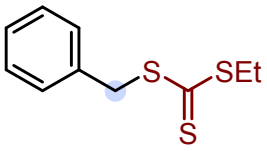
Products (detected by GC-MS):



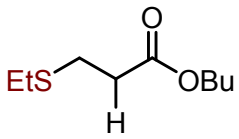
Bn-TEMPO (247.16)



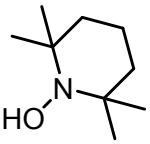
Bn-Bn (182.03)



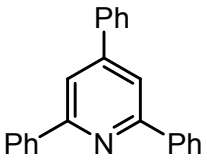
Bn-CTA (228.00)



EtS-BuA (190.09)



TEMPO-H (156.15)



Pyr (307.11)

Figure S80. Radical trapping experiment design (top) and detected products (bottom; the observed m/z for each structure is shown in parentheses.).

This result is in accordance with the proposed radical nature of the process.

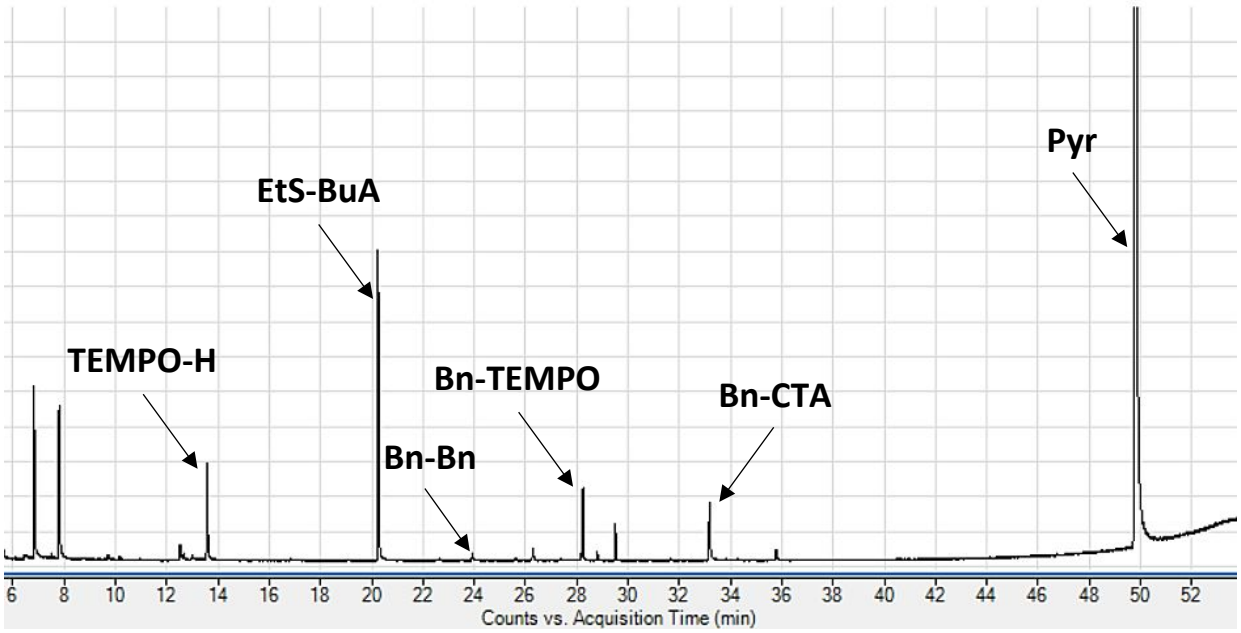


Figure S81. GC-MS analysis of the reaction mixture.

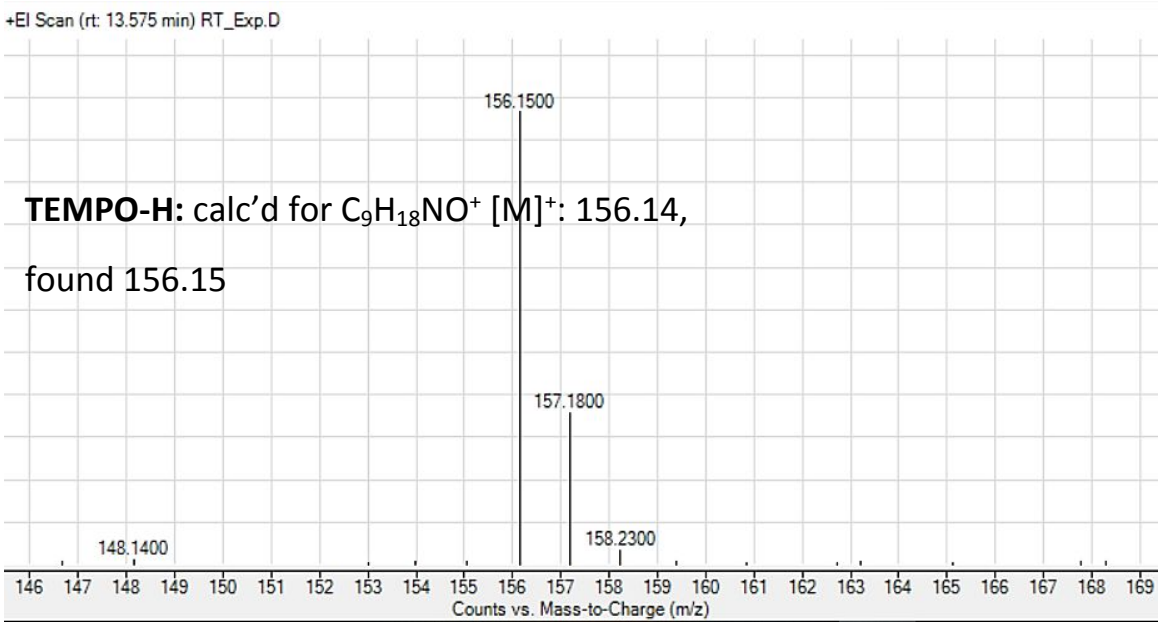


Figure S82. GC-MS analysis of the radical-trapping product **TEMPO-H**.

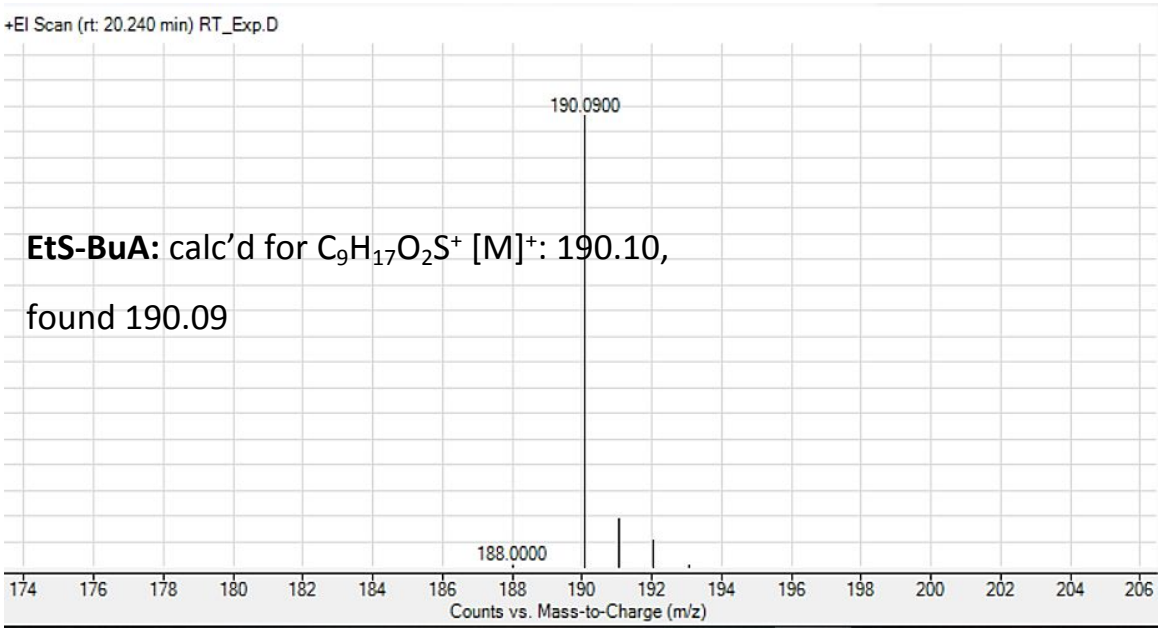


Figure S83. GC-MS analysis of the radical-trapping product **EtS-BuA**.

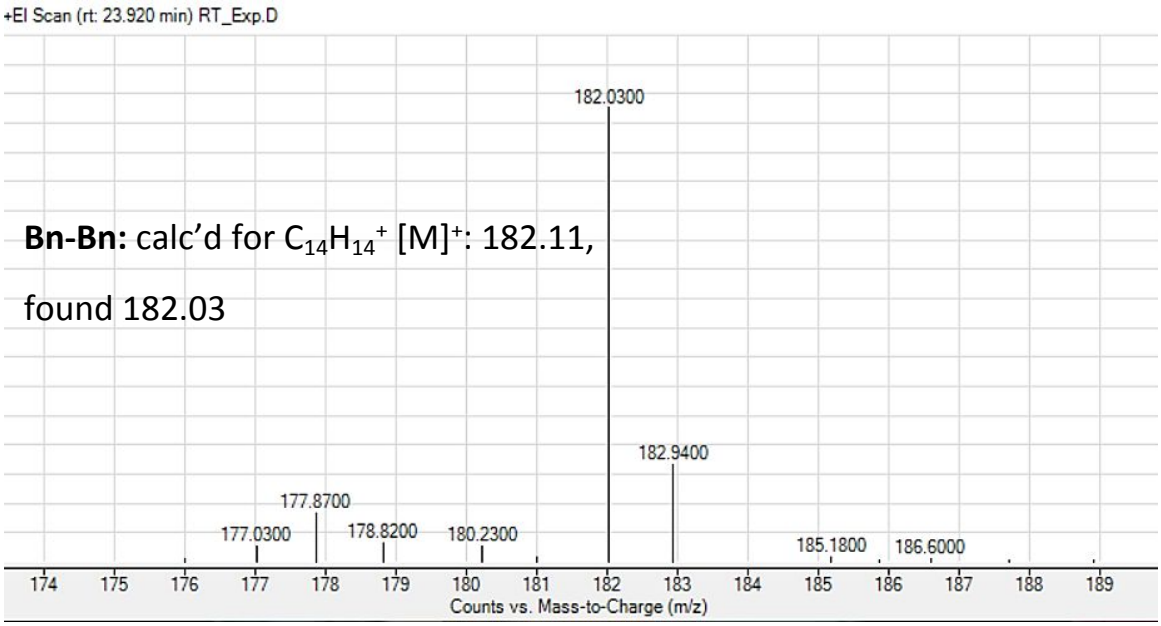


Figure S84. GC-MS analysis of the radical-trapping product **Bn-Bn**.

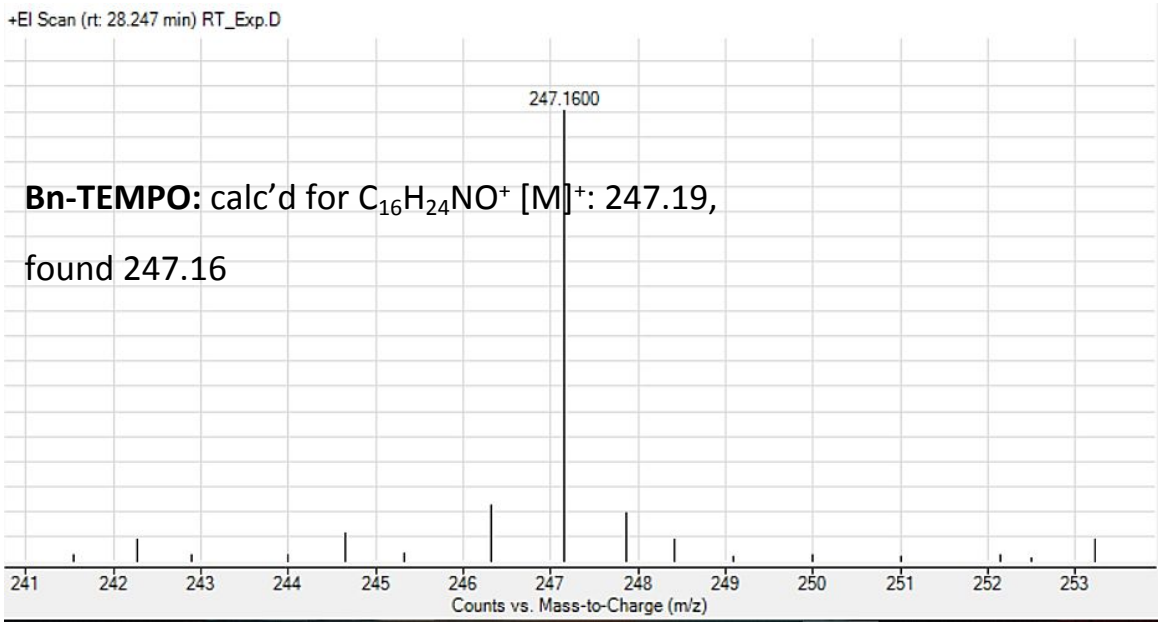


Figure S85. GC-MS analysis of the radical-trapping product **Bn-TEMPO**.

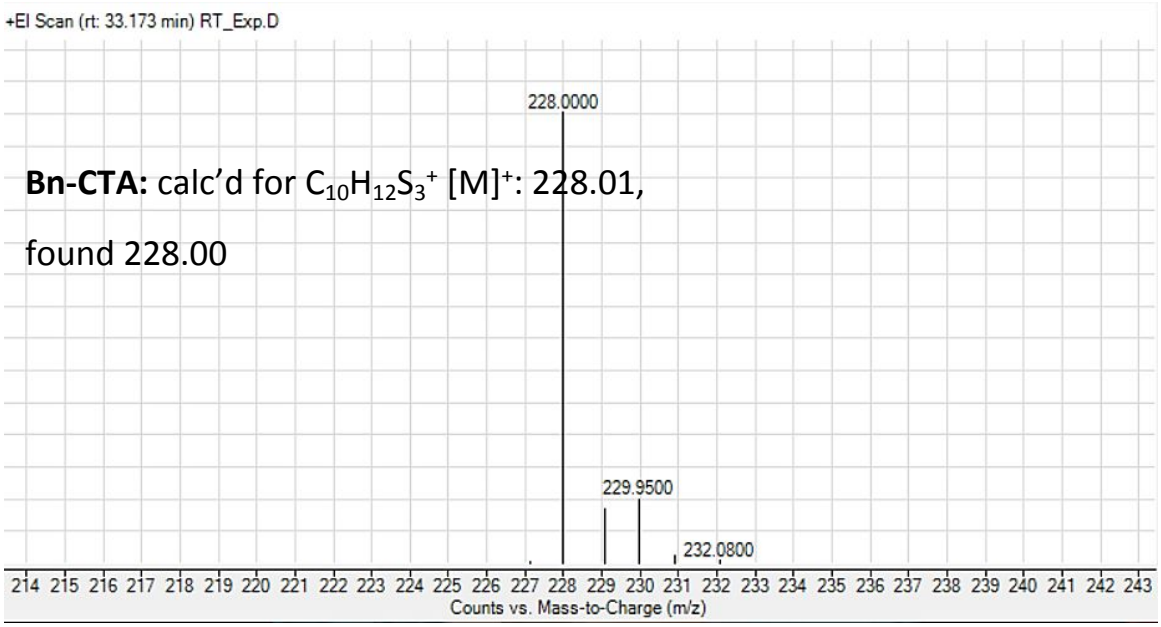


Figure S86. GC-MS analysis of the radical-trapping product **Bn-CTA**.

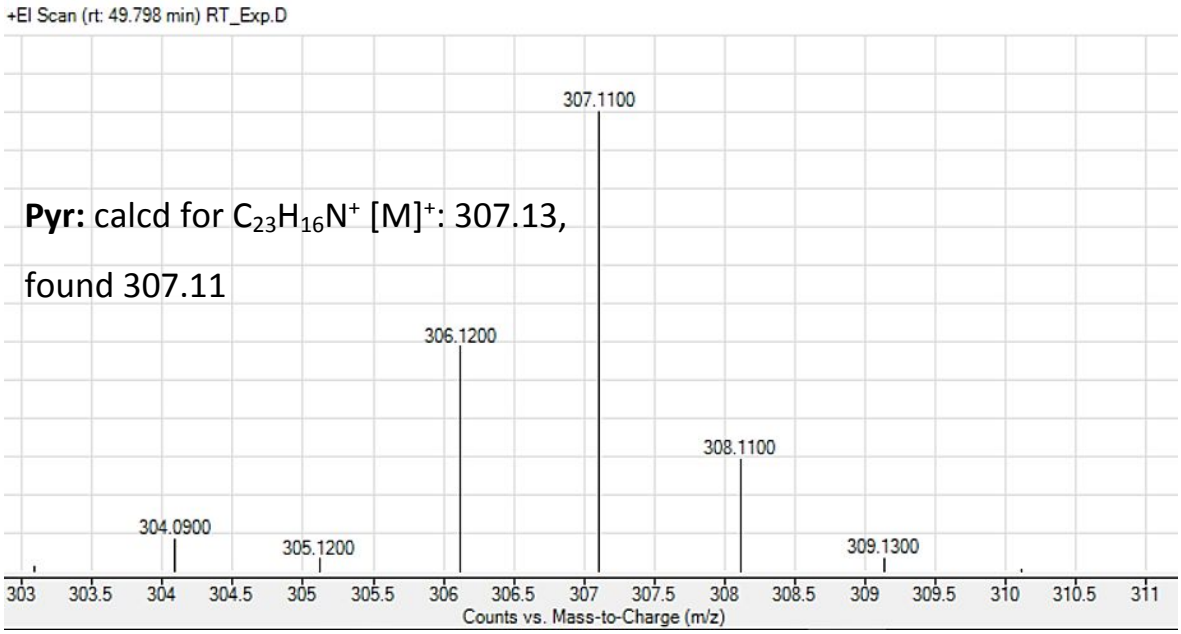
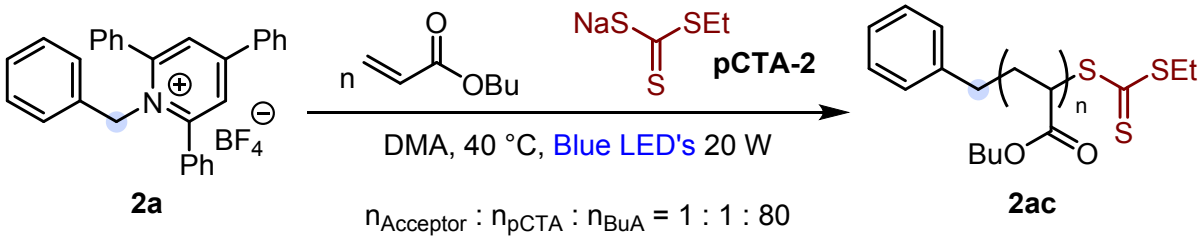


Figure S87. GC-MS analysis of the radical-trapping product **Pyr**.

On / Off Experiment

We tested our catalytic system under two "off" periods (3 h and 20 h), during which no increasing of conversion was observed. After the second "off" period, full conversion of PBuA was reached under light irradiation. The resulting characteristics of polymer were almost similar to standard conditions and no increasing conversion was observed during "off" periods which is in accordance with the intended photocontrolled nature of the process.



#	Conv., %	Time, h	M_n(theor) [a] (g mol^{-1})	M_n [b] (g mol^{-1})	Đ	Light
1	10.8	0.5	1350	3500	1.17	ON
2	36.9	1.0	4000	5300	1.20	ON
3	37.0	4.0	4000	5300	1.19	OFF
4	59.6	4.5	5950	6800	1.19	ON
5	59.6	24.5	5950	6800	1.20	OFF
6	78.0	25.0	8250	9400	1.22	ON
7	98.0	26.0	10400	11400	1.23	ON

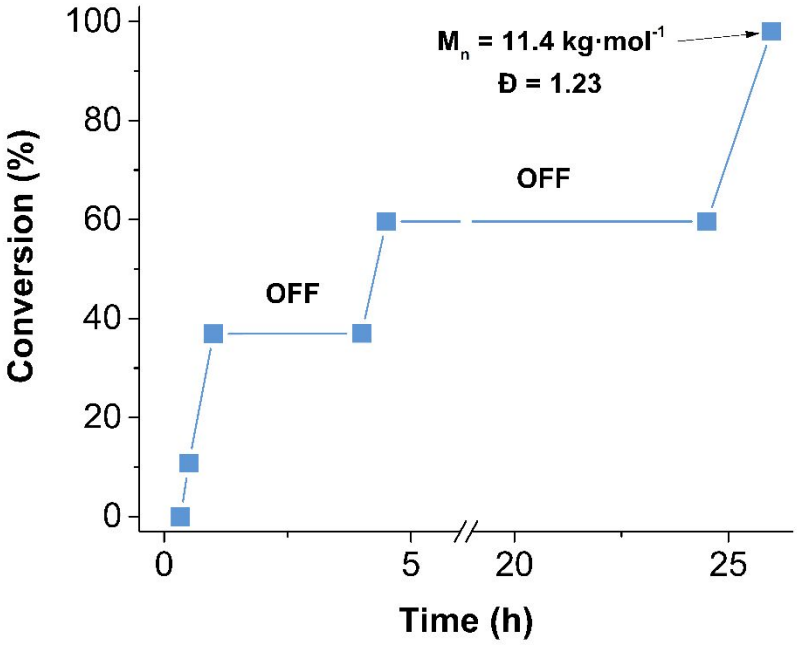
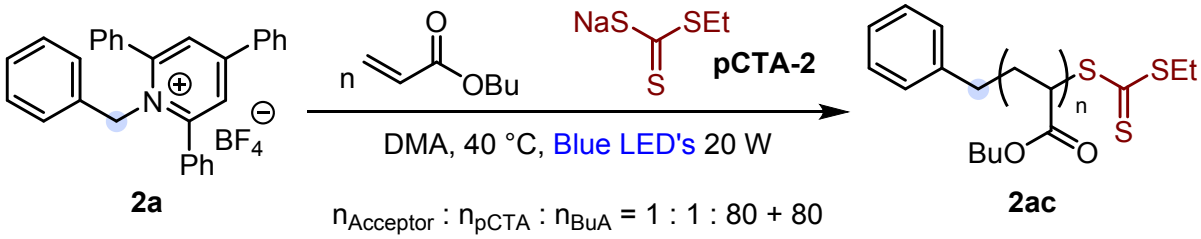


Figure S88. Conversion vs Time plot for on / off experiment.

Chain Extension Experiment

Chain extension was carried out to test the trithiocarbonate chain-end fidelity: a new portion of monomer was added at 98 % conversion of PBuA under standard conditions. We observed efficient chain extension, obtaining PBuA in 175 % conversion with good matching of M_n(theor) and M_n and narrow Đ.



Conv., %	Time, h	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	Đ
98.4	3.1	10300	11700	1.23
175.2	5.0	18200	22000	1.28

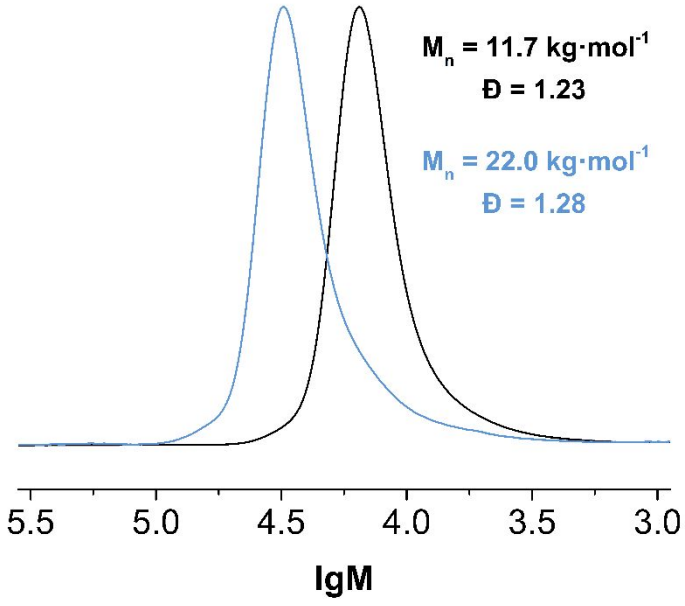


Figure S89. GPC traces of PBuA **2ac**.

Uv-Vis Kinetics Experiment

We performed the experiment, demonstrating the kinetics of consumption of EDA complex and formation of macroRAFT species during the course of the polymerization. The experiment was conducted according to General Procedure D, and aliquots were taken at predetermined time intervals. It is clearly visible that after 30 min of the irradiation almost all EDA complex was transformed into the macro-CTA agent with lower absorption.

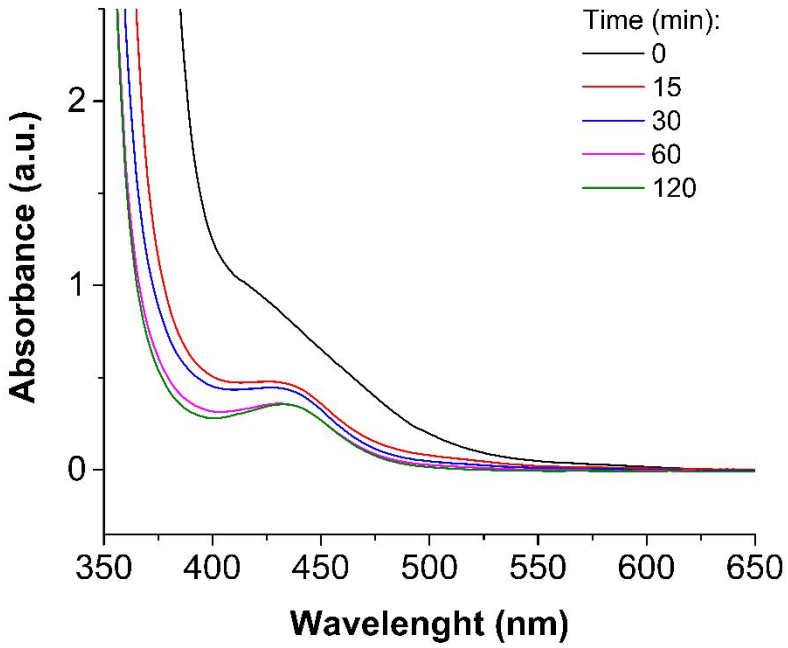
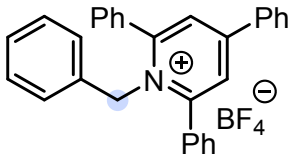


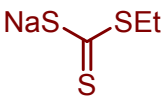
Figure S90. The UV-Vis absorption spectra of aliquots taken from the reaction mixture (DMA, 0.01 M).
*All absorption spectra were recorded in quartz cuvettes with a path length of 1.0 cm.

Extinction Coefficient Determination for Katritzky Salt 2a, pCTA-2 and their EDA Complex

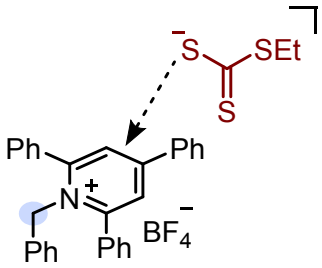
The UV-Vis absorption spectra of Katritzky salt **2a**, **pCTA-2** and their EDA complex in DMA at various concentrations are shown below. Extinction coefficients were calculated at the standard for the most experiments wavelength – 435 nm.



2a



pCTA-2



EDA Complex

Katritzky salt **2a**:

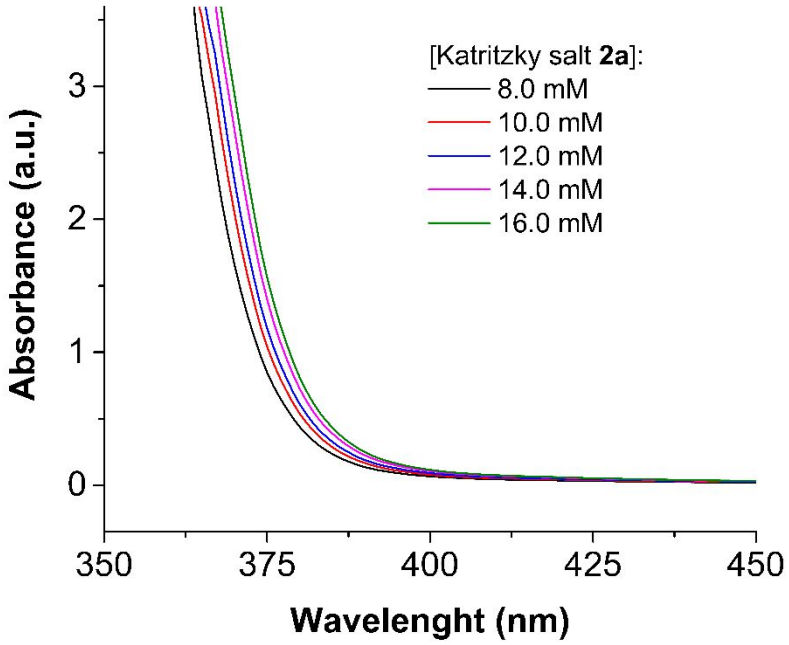


Figure S91. The UV-Vis absorption spectra of Katritzky salt **2a** in DMA at various concentrations. *All absorption spectra were recorded in quartz cuvettes with a path length of 1.0 cm.

The absorbance shows a Lambert-Beer linear correlation with the concentration of Katritzky salt **2a** at 435 nm. On the basis of the following equation (2), the extinction coefficient (ε) was calculated to be 2.8 M^{-1}□cm^{-1}.

(2) $A = \varepsilon lc$

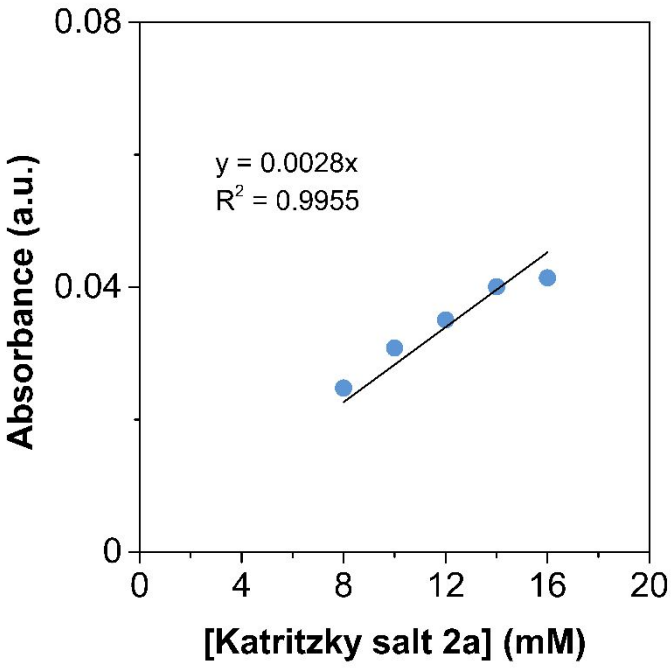


Figure S92. Absorbance vs concentration of Katritzky salt **2a** plot at 435 nm.

pCTA-2:

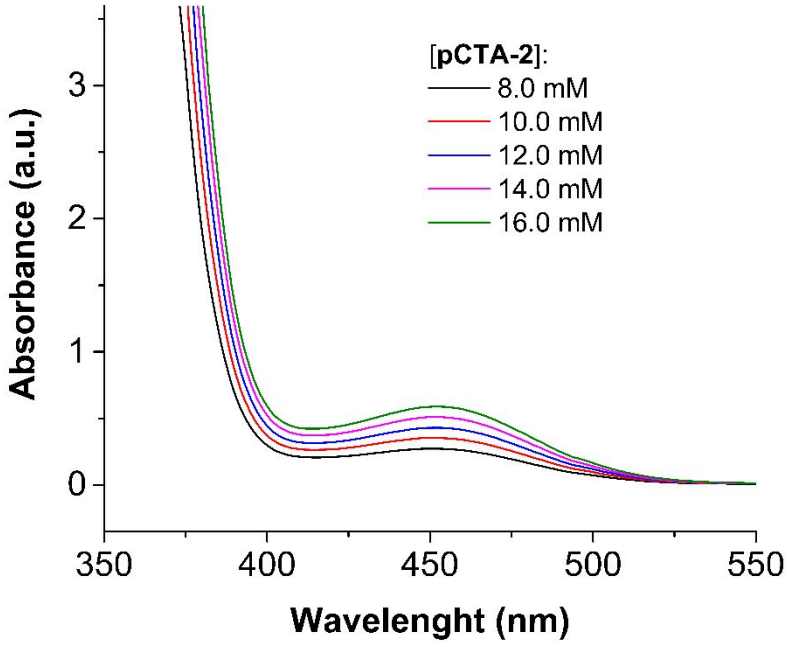


Figure S93. The UV-Vis absorption spectra of **pCTA-2** in DMA at various concentrations.
*All absorption spectra were recorded in quartz cuvettes with a path length of 1.0 cm.

The absorbance shows a Lambert-Beer linear correlation with the concentration of **pCTA-2** at 435 nm. On the basis of the following equation (2), the extinction coefficient (ε) was calculated to be 31.9 M^{-1}□cm^{-1}.

(2) $A = \varepsilon lc$

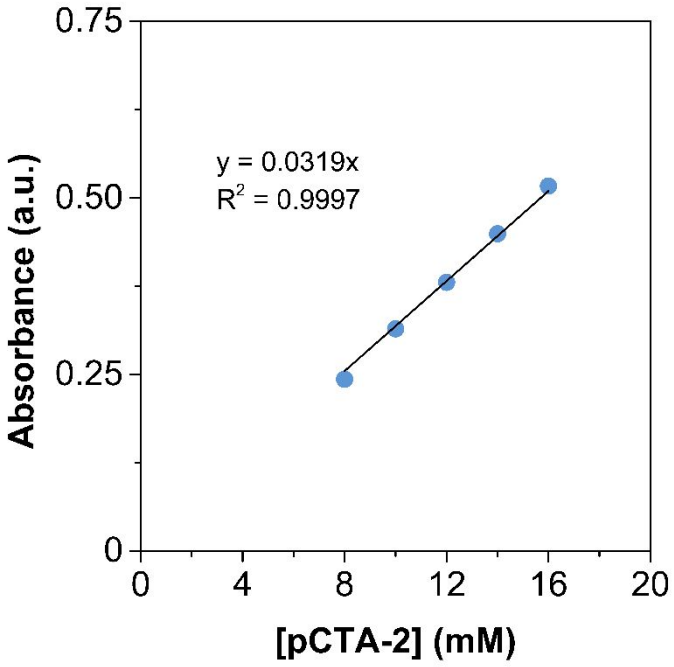


Figure S94. Absorbance vs concentration of **pCTA-2** plot at 435 nm.

EDA complex:

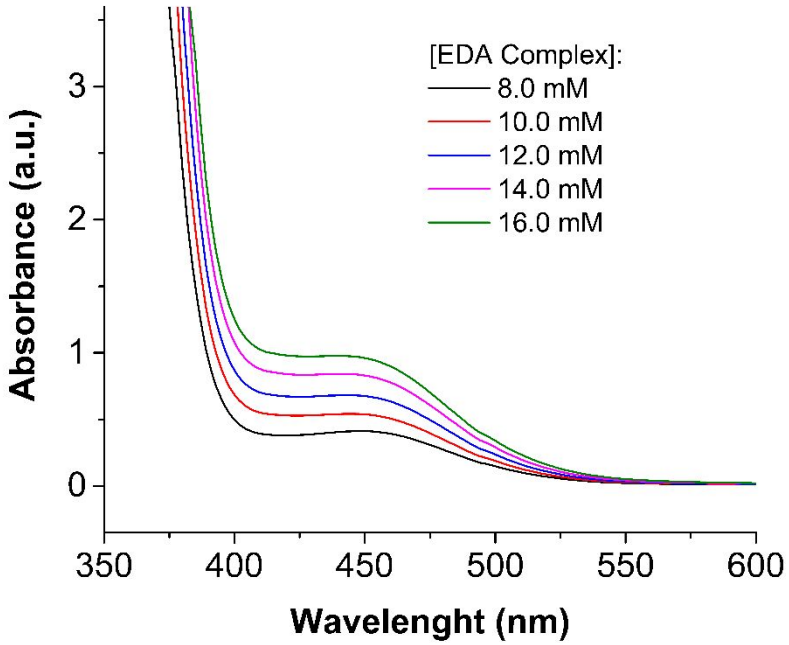


Figure S95. The UV-Vis absorption spectra of EDA complex in DMA at various concentrations. *All absorption spectra were recorded in quartz cuvettes with a path length of 1.0 cm.

The absorbance shows a Lambert-Beer linear correlation with the concentration of EDA complex at 435 nm. On the basis of the following equation (2), the extinction coefficient (ε) was calculated to be 57.9 M^{-1}□cm^{-1}.

(2) $A = \varepsilon lc$

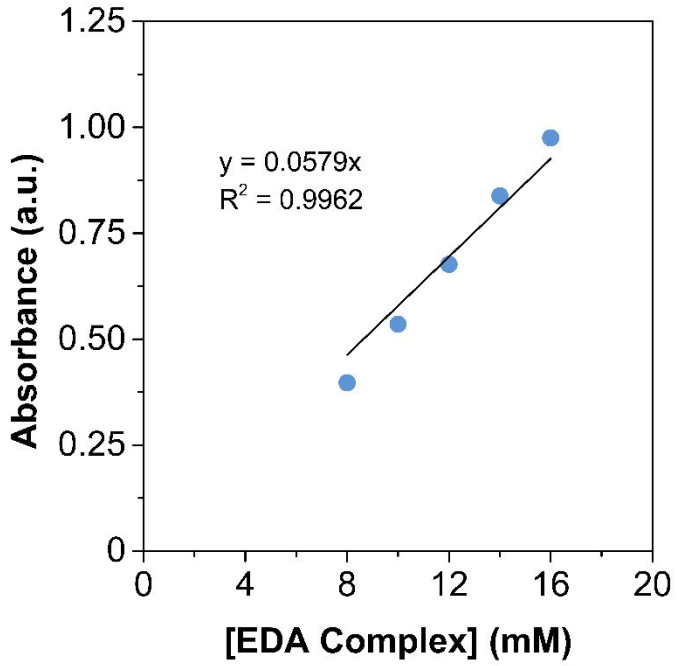
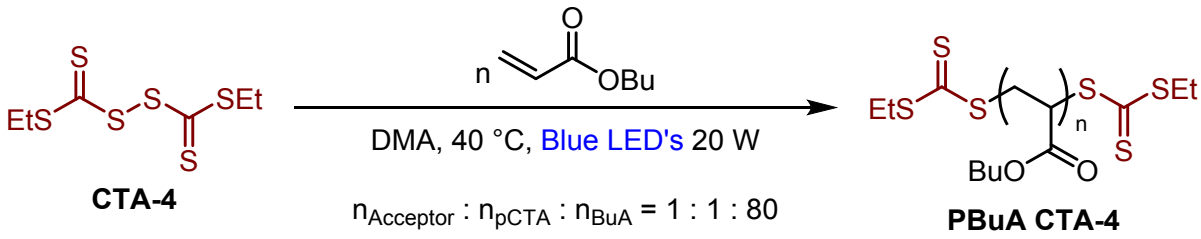
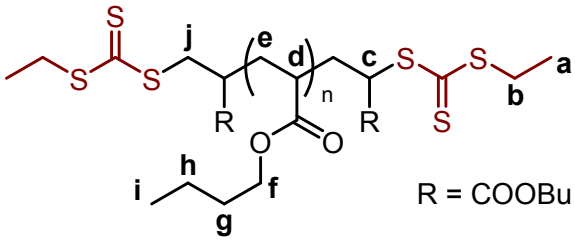


Figure S96. Absorbance vs concentration of EDA complex plot at 435 nm.

(CTA-4)-initiated Photoiniferter Polymerization of Butyl Acrylate

Poly(butyl acrylate) **PBuA CTA-4** was synthesized according to the General Procedure D, but instead of Katritzky salt **1a** and **pCTA-2**, **CTA-4** was used as initiator. We were able to detect protons **j** from the initiation by thiocarbonylthio radical (see ^{1}H NMR spectrum below). Possible parasitic initiation in our EDA-RAFT polymerization, lowering α-end functionality, would have the same nature. Therefore, we used protons **j** as a reference to detect if we had parasitic initiation in polymerizations.





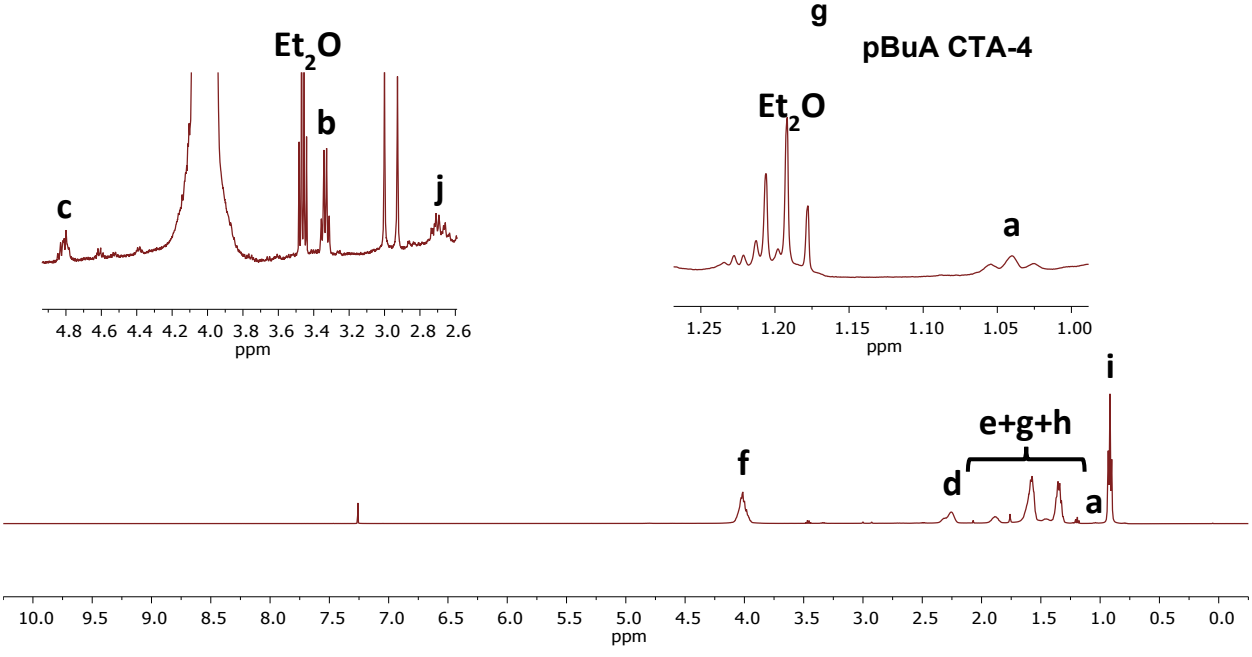


Figure S97. ^{1}H NMR spectrum of poly(butyl acrylate) **PBuA CTA-4**. *degradation product of ω-end CTA.

Stacked ^{1}H NMR spectra of poly(butyl acrylate) **2ac** [top] and poly(butyl acrylate) **PBuA CTA-4** [bottom], that demonstrate complete α-end functionality of poly(butyl acrylate) **2ac**:

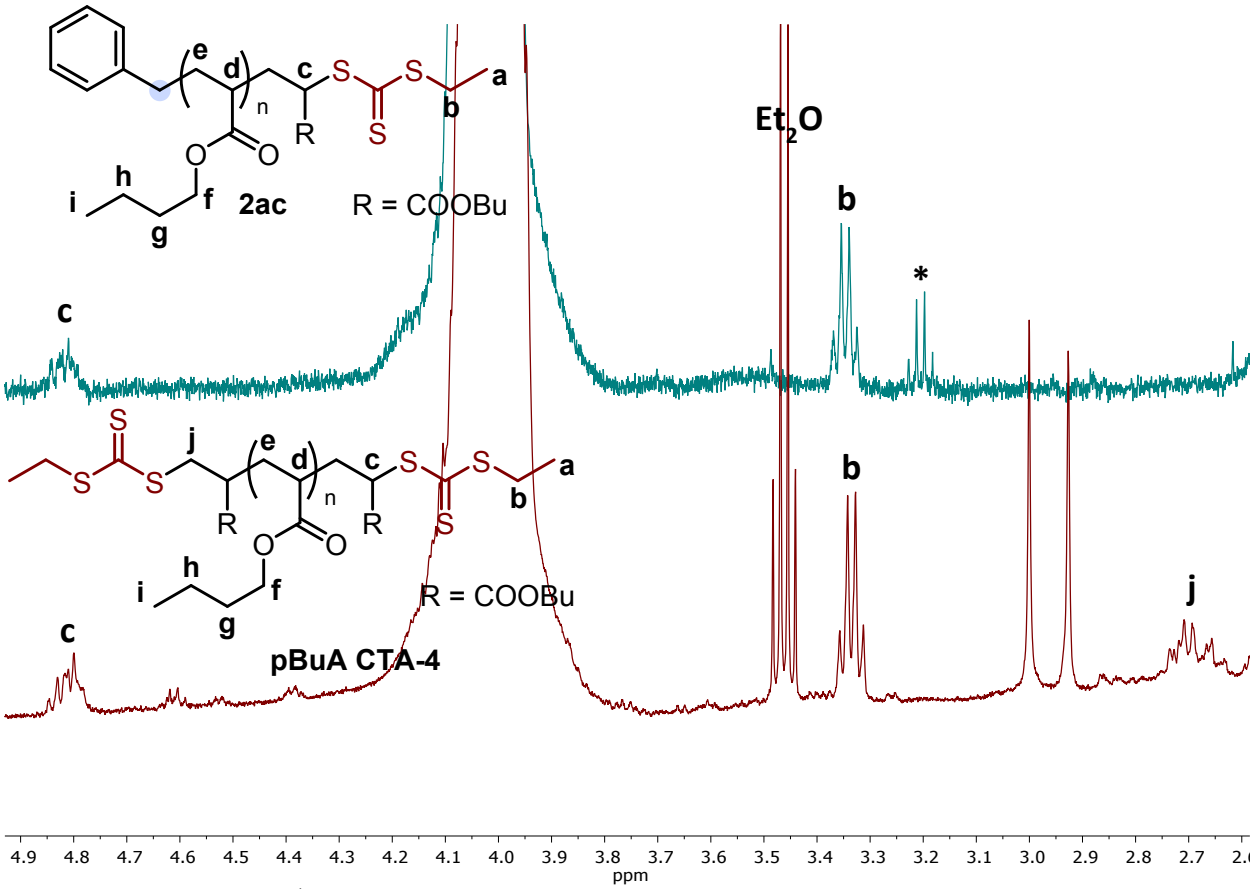
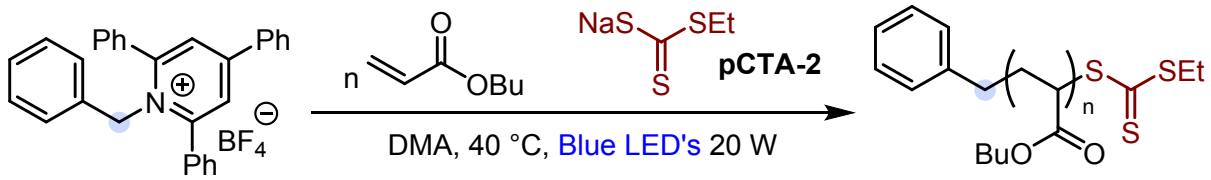


Figure S98. Stacked ^{1}H NMR spectra of poly(butyl acrylate) PBuA **2ac** and **PBuA CTA-4**. *degradation product of ω-end CTA.

Evaluation of ω-end Thiocarbonylthio Group Stability

Poly(butyl acrylate) **2ac** was synthesized according to the General Procedure D. The polymer was precipitated in an excess of MeOH : H_2O = 9 : 1 (v/v) mixture.



Conv., %	M_n(theor) [a] (g mol^{-1})	M_n(SEC) [b] (g mol^{-1})	M_n(NMR) (g mol^{-1})		IE [e]	φ, [f] %	Đ
			Head (**k+m**) [c]	Tail (**c**) [d]			
92.6	9700	10200	10400	12600	0.93	> 99	1.22

Dried polymer (35 °C) was then reprecipitated and three samples of *ca.* 25 mg were taken:

- **#1** was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy.
- **#2** was dissolved in $CHCl_3$ (2 mL) and heated to 48 °C for 8 h in a closed vial. The solvent was removed under high vacuum, the residue was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy.
- **#3** was dissolved in $CHCl_3$ (2 mL) and heated to 65 °C for 8 h in a closed vial. The solvent was removed under high vacuum, the residue was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy.

The resulting stacked ^{1}H NMR spectra of samples **#1**, **#2** and **#3** are shown below. This result clearly demonstrates the thermal lability of ω-end thiocarbonylthio group and that protons * are associated wih the degradation product of ω-end CTA.

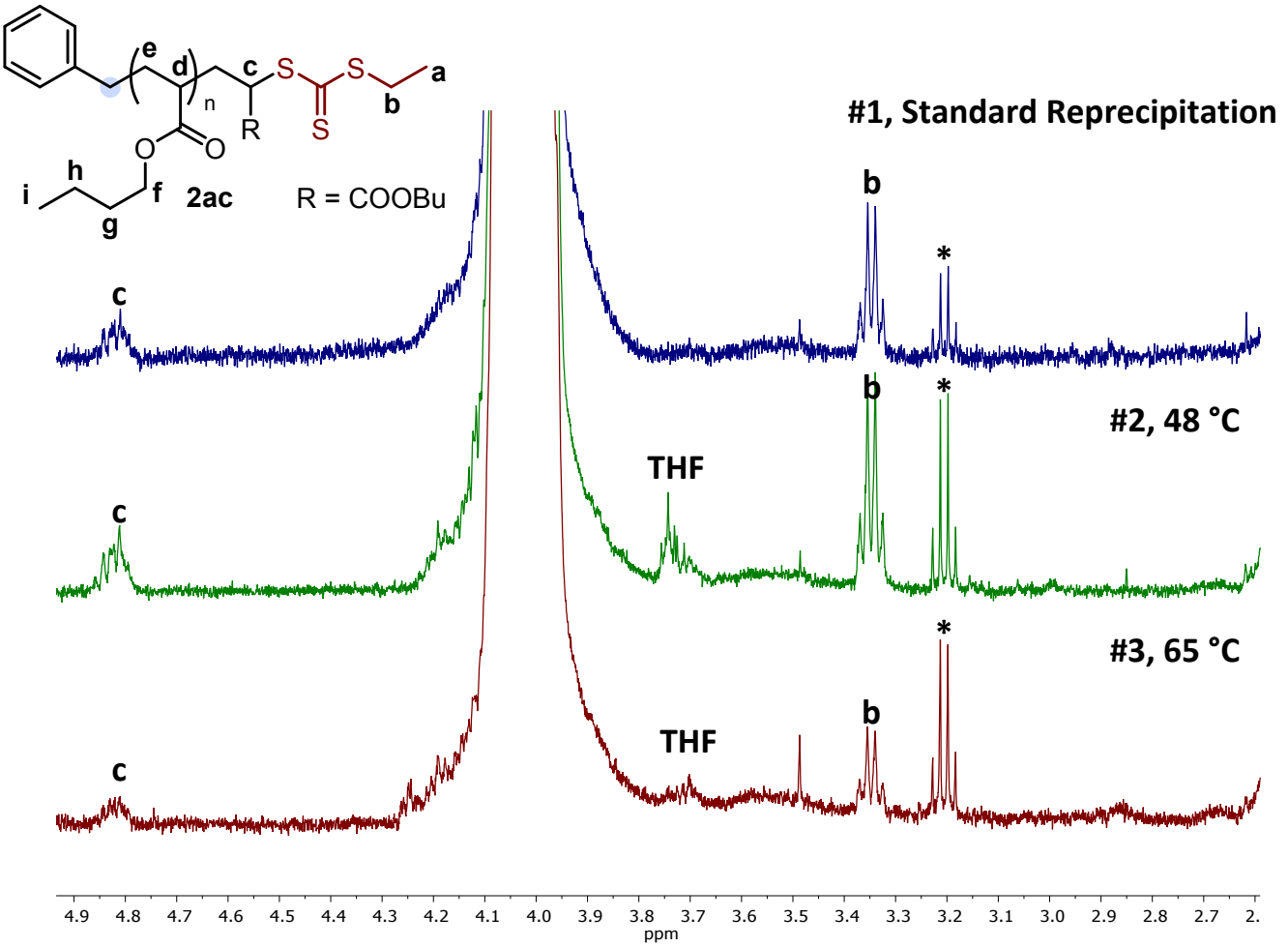
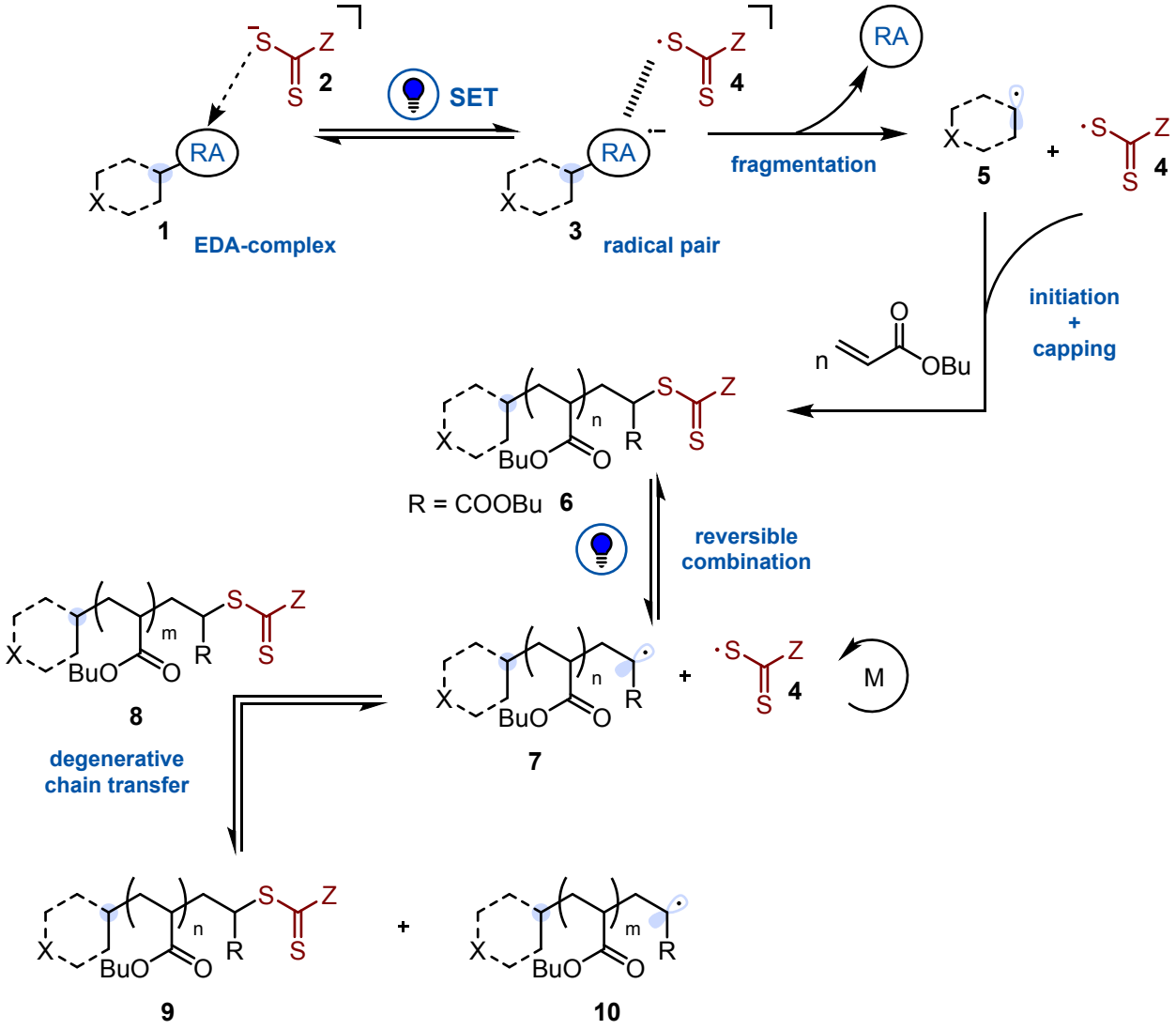


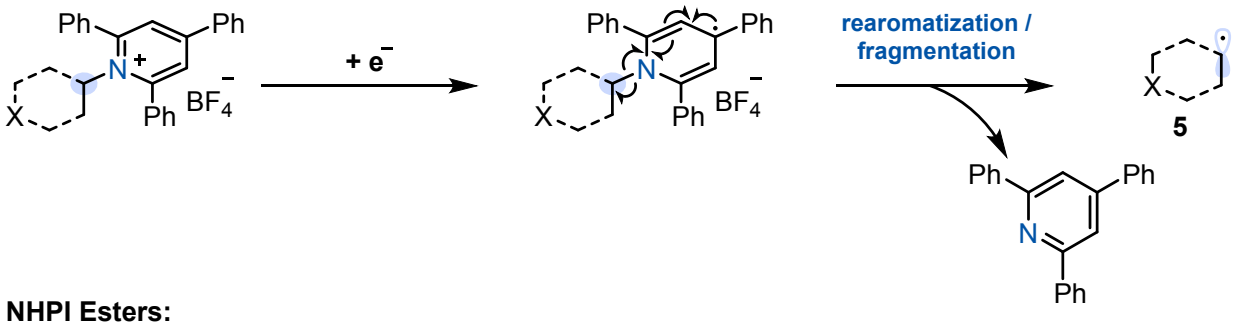
Figure S99. Stacked ^{1}H NMR spectra of poly(butyl acrylate) samples #**1**, #**2** and #**3**. *degradation product of ω-end CTA.

10. Full Mechanistic Proposal

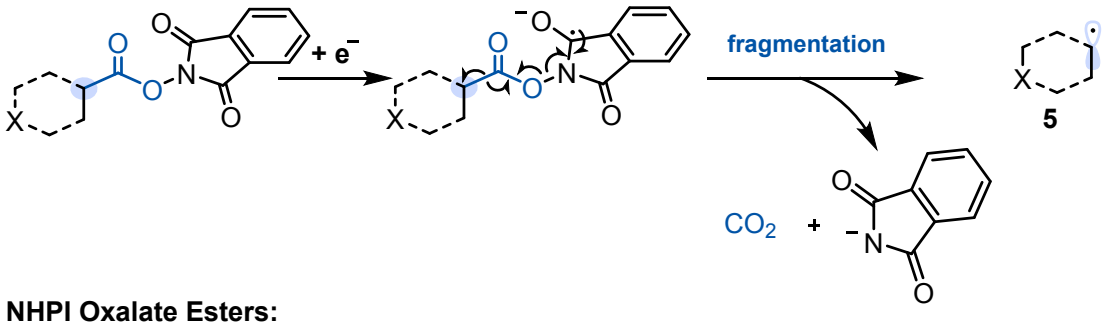


Mechanism of Fragmentation

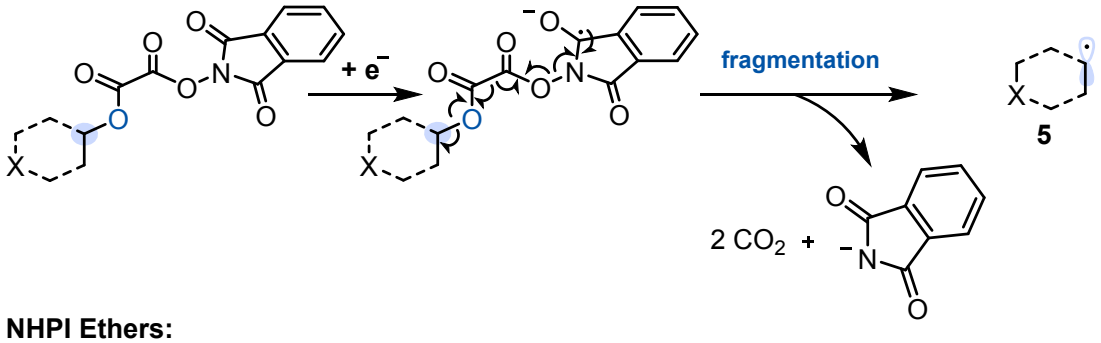
Katritzky Salts:



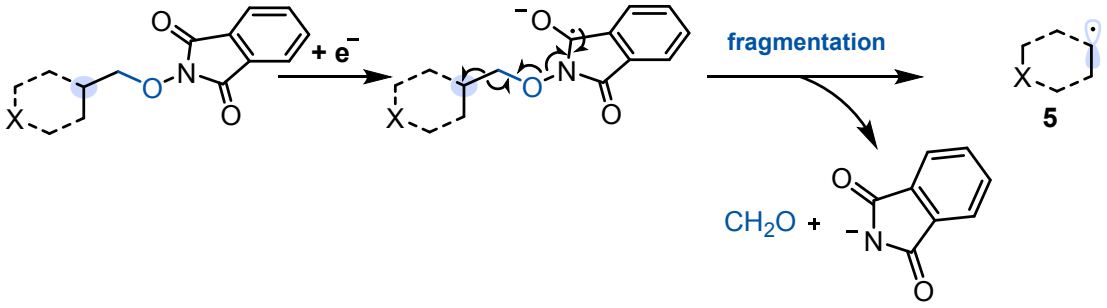
NHPI Esters:



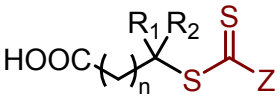
NHPI Oxalate Esters:



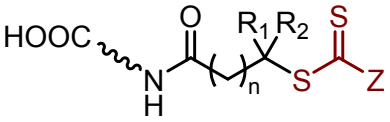
NHPI Ethers:



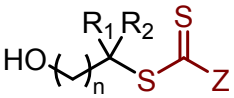
11. Comparison of Conventional Conjugation with CTA and EDA Complex-Driven RAFT Polymerization



RAFT-COOH

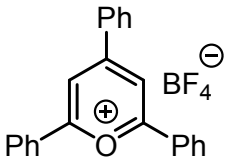


RAFT-oligopeptide

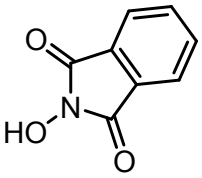


RAFT-OH

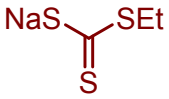
pRA:



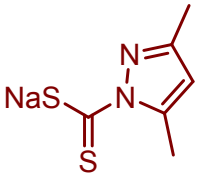
2,4,6-triphenylpyrylium tetrafluoroborate



NHPI



pCTA-2

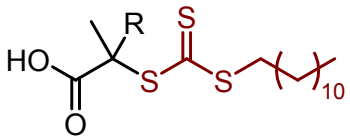


pCTA-3

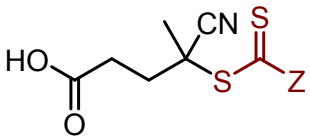
	CTA conjugation			**Our approach**		
	COOH	oligopeptide	OH	Katritzky Salt **2a** + pCTA	NHPI ester **2b** + pCTA	**Gly-Gly KS** + pCTA
Coupling between CTA (pRA) and [substrate]	1 step* [amines, alcohols]	1 step* [amines, alcohols]	1 step* [carboxylic acids]	1 step** [amines]	1 step** [carboxylic acids]	1 step** [amines, alcohols]
* Filtration procedure may be required for DCC-mediated coupling in case of PI polymerization (I_{eff} ↓). DCU filtration may be complex in case of polar solvents / low quantities of substrates. The efficiency of DCC-mediated coupling may vary depending on the substrate (especially alcohols). Some optimization of the reaction conditions may be required. ** "one-pot" procedure without filtration is available. There are some limitations regarding amine complexity (decrease in yield or inapplicable) [see SI].						
Commercial availability of CTA or pRA and pCTA / # of steps for synthesis	+* / 2-4 steps** 1-2 column chromatogr. [CC]	- / 5SD or 7SN steps*** 1 CC [29, 30]	+ / 3 steps 1 CC [31]	+ / 2 steps**** No CC	+ / 2 steps**** No CC	- / 1SD or 3SN steps 1 CC
* 3 Options for trithiocarbonate- and 2 options for dithiocarbonate-based RAFT-agents with variable linkers are available at Sigma Aldrich. Another 2 options were NHS-esters, which also proved to be effective in coupling reactions. ** The exact number of steps required depends on the desired head group and linker. For the most purposes, 2-step synthesis with 1 column chromatography will be required. *** Estimated for 5-amino-4-methyl-4-(propylthiocarbonothioylthio)-5-oxopentanoic acid as CTA. Commercially available CTA would potentially deliver the product in 1 step (solid phase, SD) or 3 steps (solution phase, SN). The latter could be associated with degradation of the product, as the consequence of instability of RAFT agents in the presence of free amines [32, 33, 34, 35]. **** Estimated for **pCTA-2**. **pCTA-3** would require 3 steps synthesis with 1 CC.						
Modularity	Substrate should be conjugated with CTA when varying Z-group			pCTA could be chosen independently		
Efficiency of initiation (I_{eff})	High*			from moderate to high**		

* Head group predesigned for high I_{eff}. ** The I_{eff} of polymerization depends on the stability of generated radical from the substrate.						
Available substrates	benzylic, 1°, 2°, 3°			benzylic, 2°, 3°	benzylic, 1°, 2°, 3°	benzylic, 1°, 2°, 3°
Preservation of natural functionality of the substrate	+	+	+	-	-	+

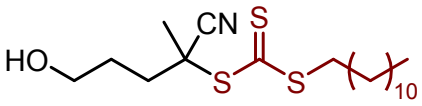
Cost-efficiency:



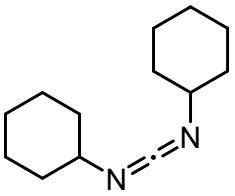
R = CH_3
€526.00 for 5 g; 38.36 €/mmol
R = H
€511.00 for 5 g; 35.83 €/mmol



Z = $S(CH_2)_{11}CH_3$
€621.00 for 5 g; 50.14 €/mmol
Z = Ph
€555.00 for 5 g; 31.01 €/mmol

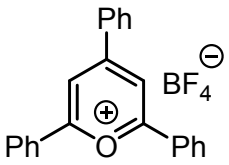


€706.00 for 5 g; 55.02 €/mmol

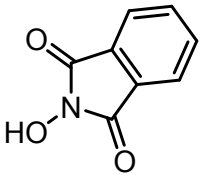


N,N′-Dicyclohexylcarbodiimide
€208.00 for 1000 g; 0.04 €/mmol

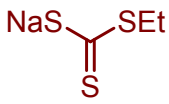
pRA:



2,4,6-triphenylpyrylium tetrafluoroborate
€67.80 for 5 g; 5.37 €/mmol



NHPI
€23.30 for 5 g; 0.76 €/mmol
€167.00 for 500 g; 0.05 €/mmol



pCTA-2
EtSH, CS_2, NaH:
~0.05 €/mmol of **pCTA-2**

Summary:

*RAFT-COOH vs Katritzky salt **2a** + pCTA [Amines as substrates]:*

A higher efficiency of polymerization is expected for EDA-driven RAFT polymerization for stabilized radicals. Conventional coupling with CTA would deliver a product with diminished yields due to the low stability of thiocarbonyl group in the presence of free amines [32, 33, 34, 35].

*RAFT-OH vs NHPI ester **2b** + pCTA [Carboxylic acids as substrates]:*

In this case, a well-designed CTA will generally be more efficient, than EDA-driven RAFT polymerization. We believe that, for stabilized radicals and with further

optimization (sodium phthalimide precipitation issue) of reaction conditions, our catalytic system could achieve a similar level of initiation efficiency.

*RAFT-oligopeptide vs **Gly-Gly KS** + pCTA [Amines and alcohols as substrates]:*

Solution-phase chemistry. This is preferable for short di-/tripeptides due to the simplicity and affordability of their synthesis in solution. Conventional coupling with CTA would result in a product with lower yields due to the instability of thiocarbonyl group in the presence of free amines. Additionally, the stability issue of CTA rises on the deprotection step of ester group from the CTA-oligopeptide C-terminus. In this case, our method would be superior, however, further optimization of the conditions is required to increase I_{eff} of polymerization.

Solid-phase chemistry. This is preferable for relatively long oligopeptides as the synthesis is often multistep, and further coupling with CTA could be performed prior to removal from the resin. The resulting product could then be purified by HPLC and repricipation, coupled with the target amine and purified one more time. Here, predesigned CTA outperform our method in most cases.

General considerations:

- EDA complex-driven RAFT polymerization is more cost-effective than conventional coupling with CTA, when the latter are purchased (see above), and significantly easier / faster if synthesis of CTA's is required.
- Our method grants several possibilities for advanced macromolecular design including selective grafting from amino group near 2° and 3° center, while preserving redox tag at 1° for further redox transformation. It also allows two donors to be used simultaneously, enabling the most effective mixture to be devised for a particular monomer group while preserving close to complete α-end functionalization [36].

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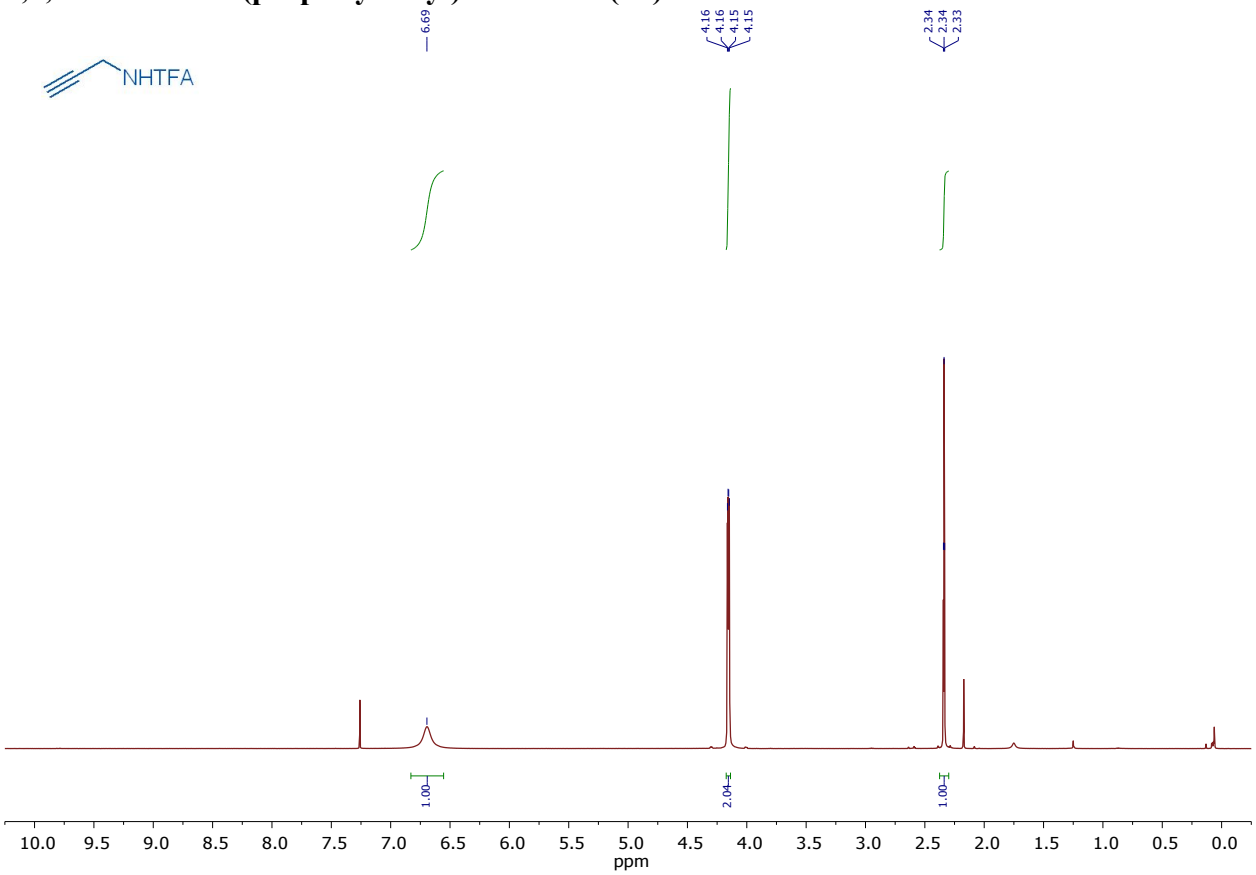
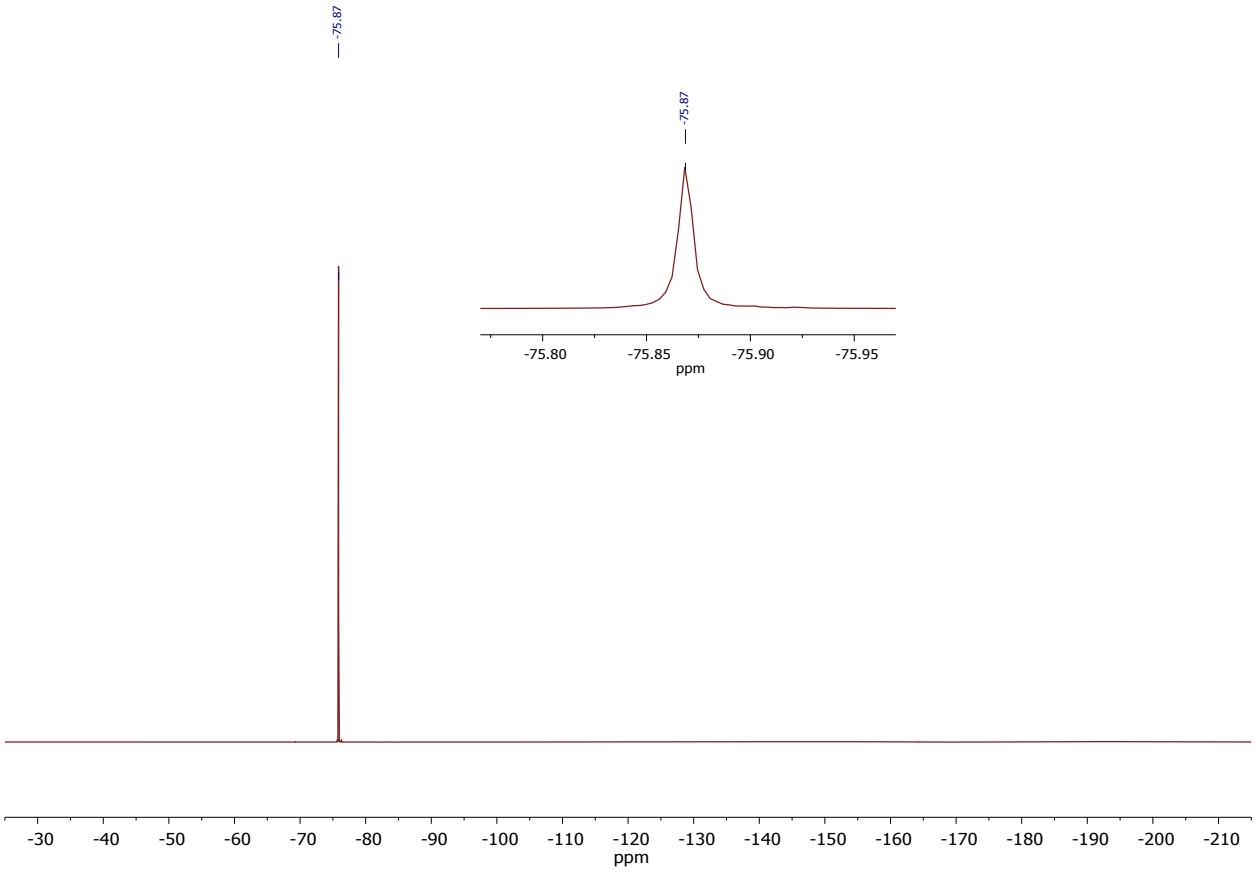
13. Spectral Data for Low-Molecular Weight Compounds

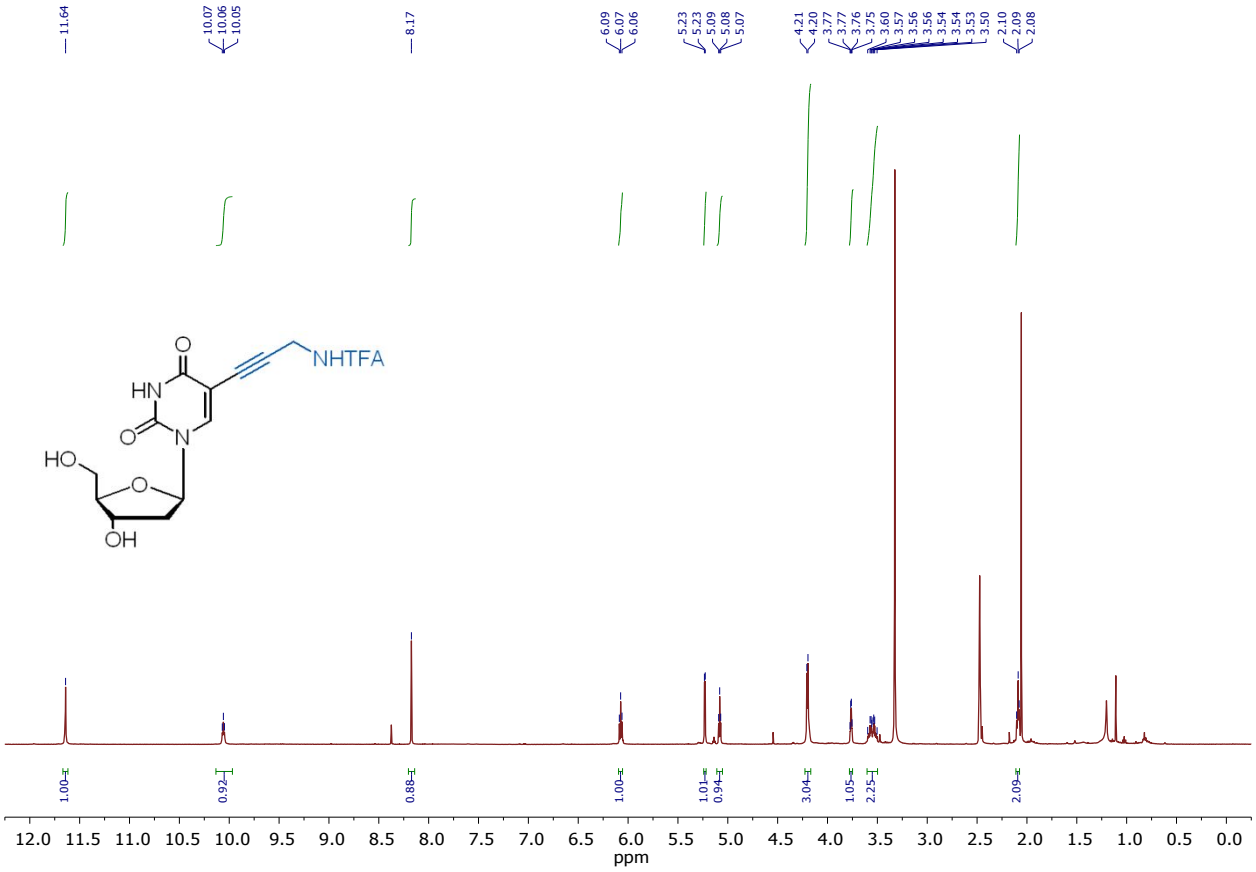
Starting Materials

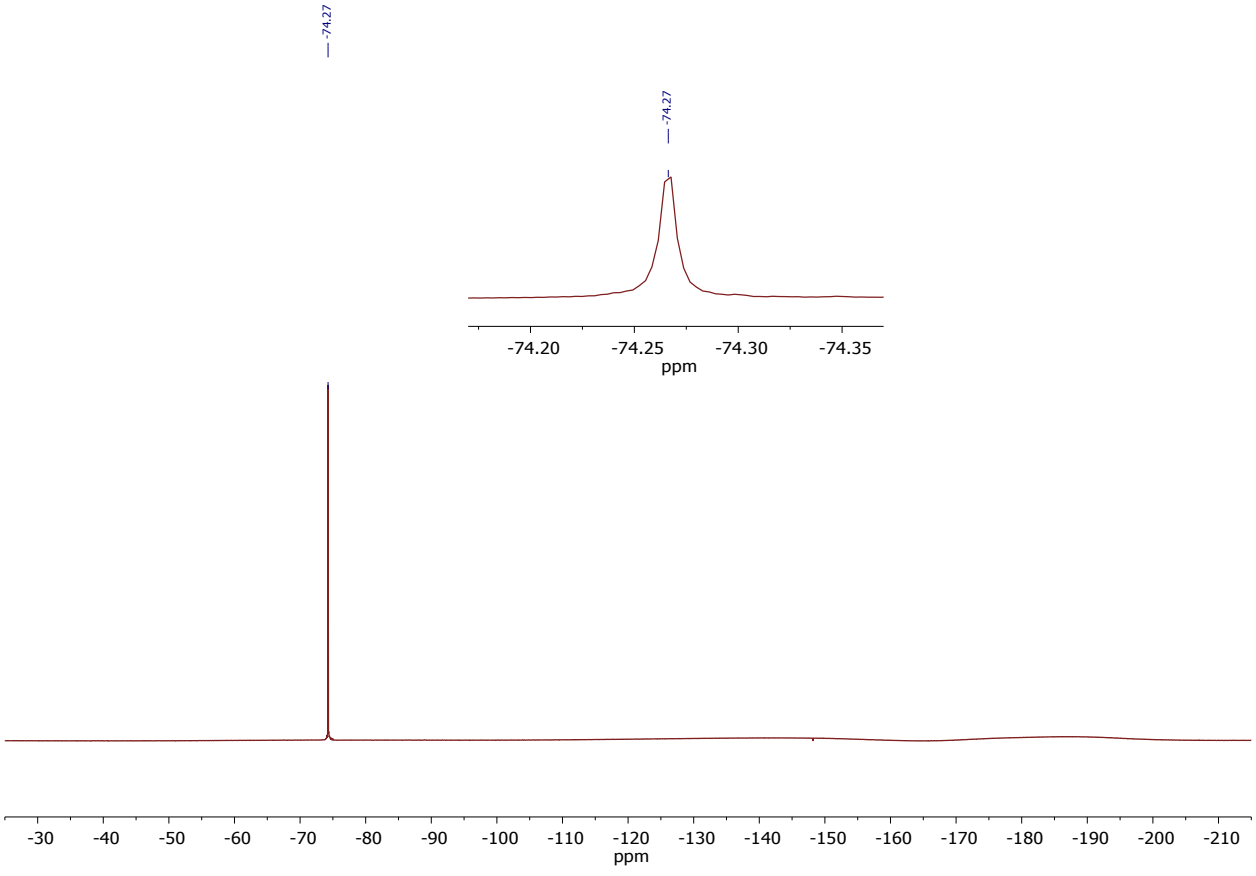
2,2,2-trifluoro-N-(prop-2-yn-1-yl)acetamide (S1)



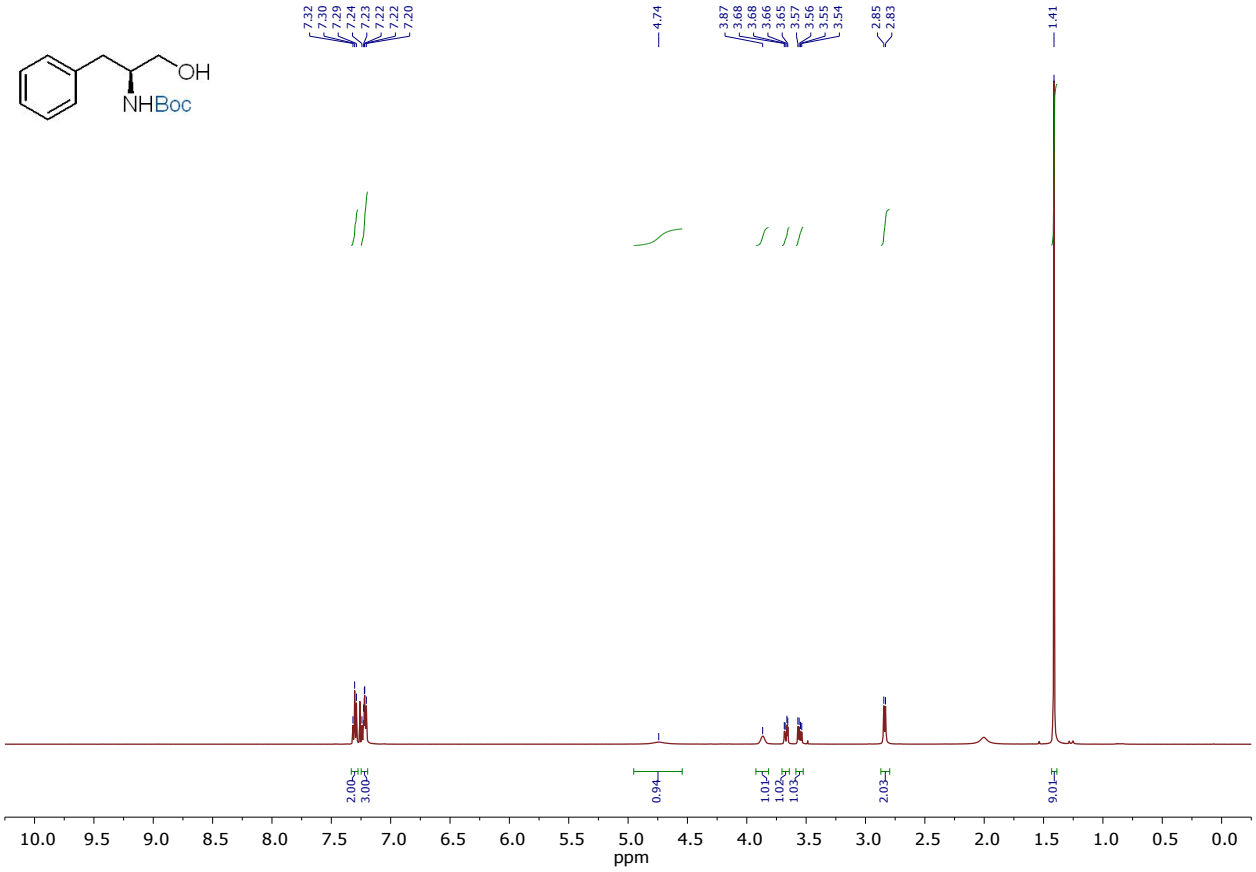


5-(3’’-Trifluoroacetamidopropynyl)-2’-deoxyuridine (S2)

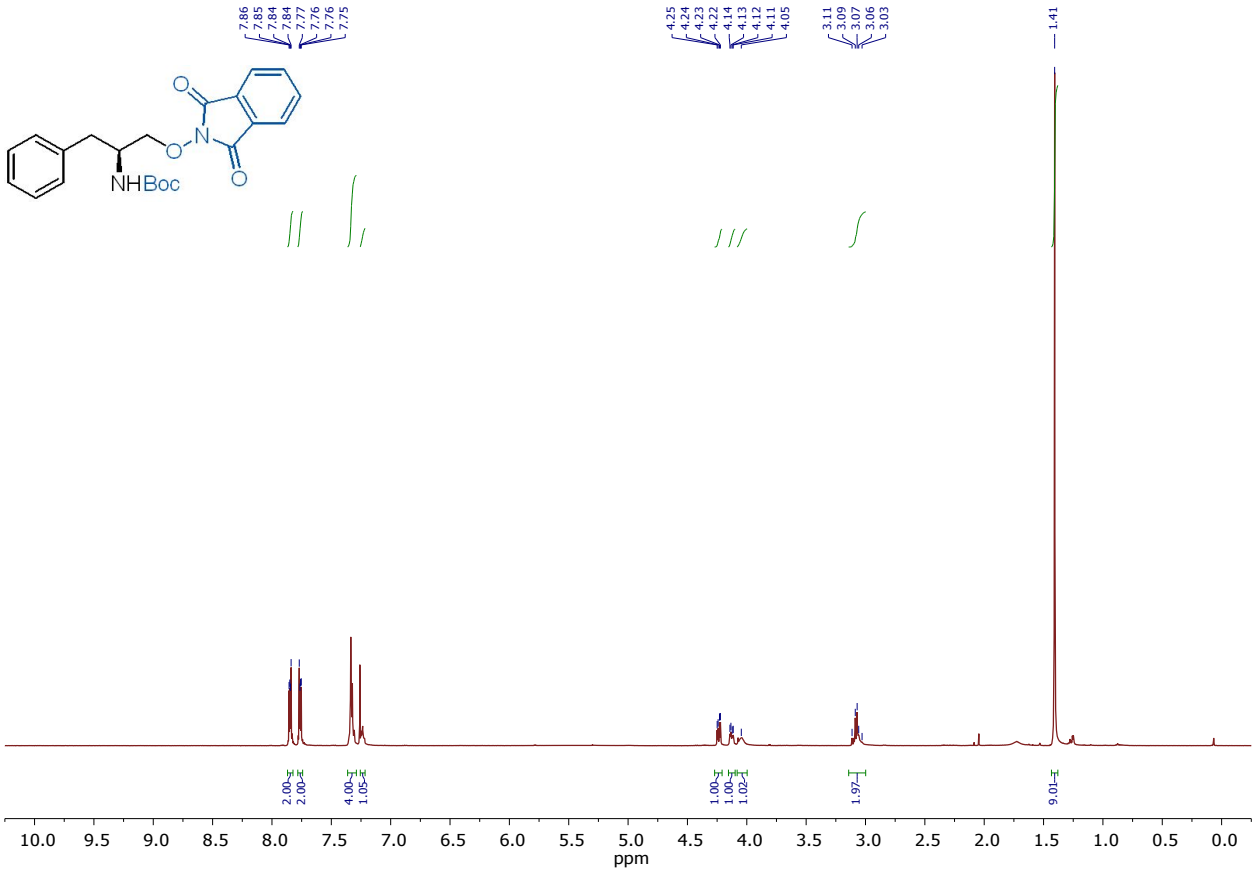




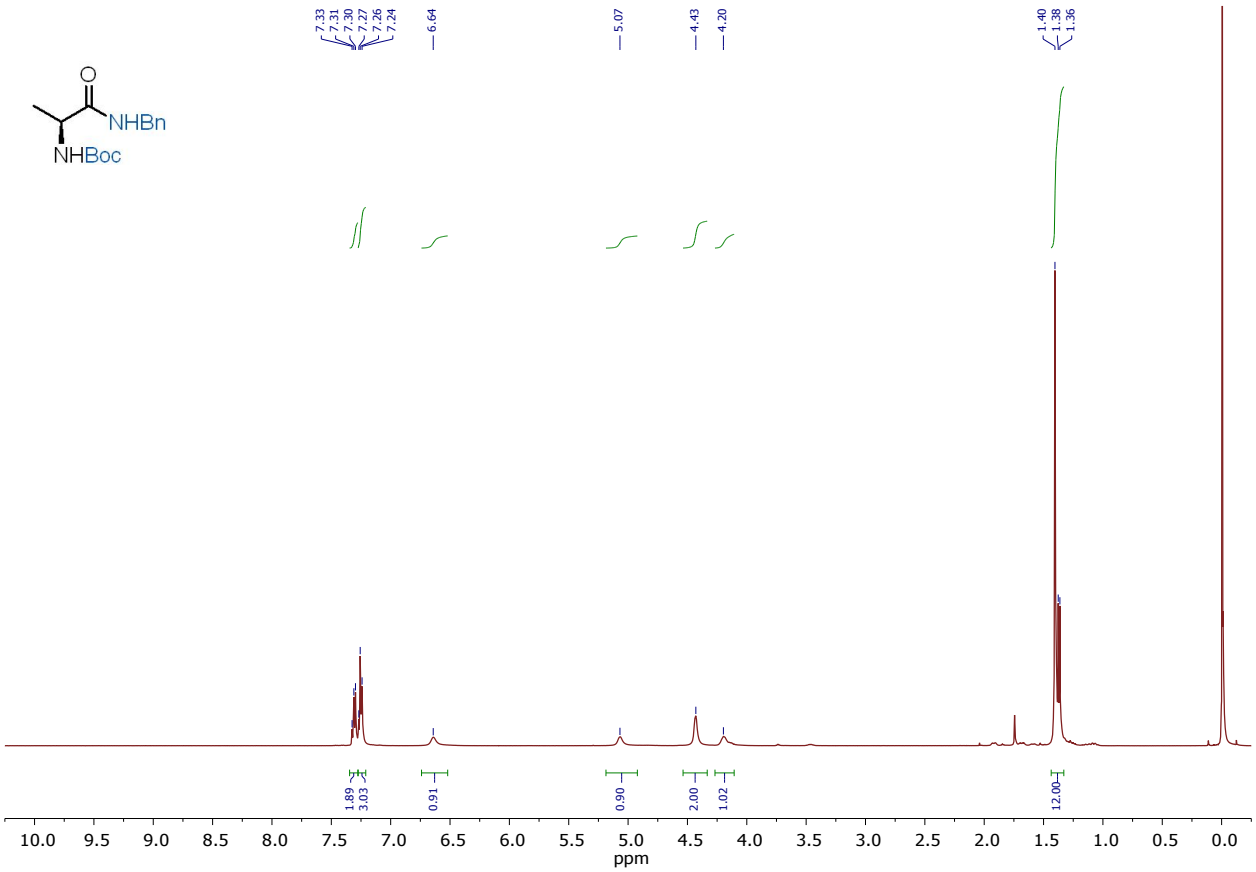
***tert*-butyl (*S*)-(1-hydroxy-3-phenylpropan-2-yl)carbamate (S4)**



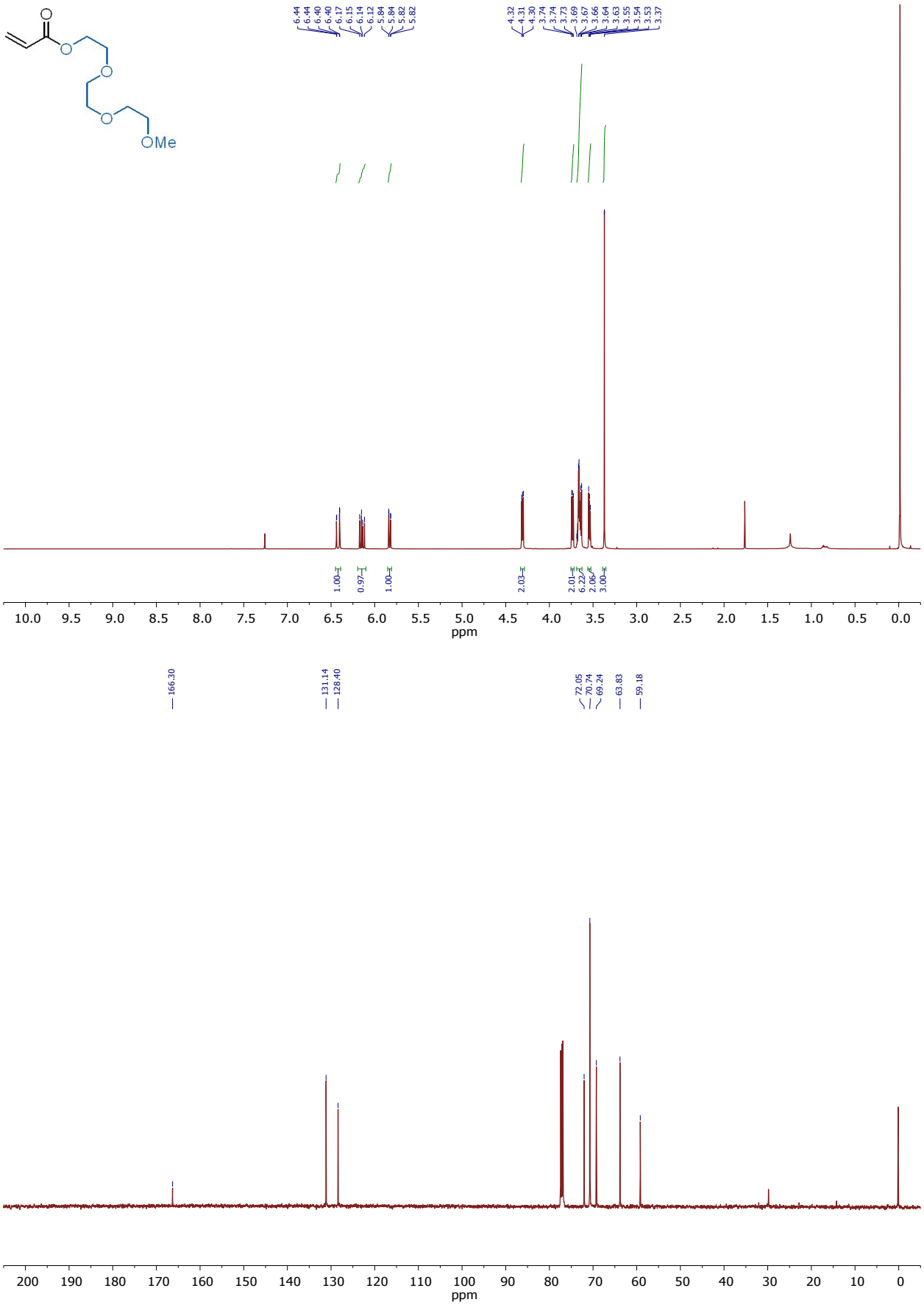
***tert*-butyl (*S*)-(1-((1,3-dioxoisoindolin-2-yl)oxy)-3-phenylpropan-2-yl) carbamate (2d)**



***tert*-butyl (*S*)-(1-(benzylamino)-1-oxopropan-2-yl)carbamate S6**

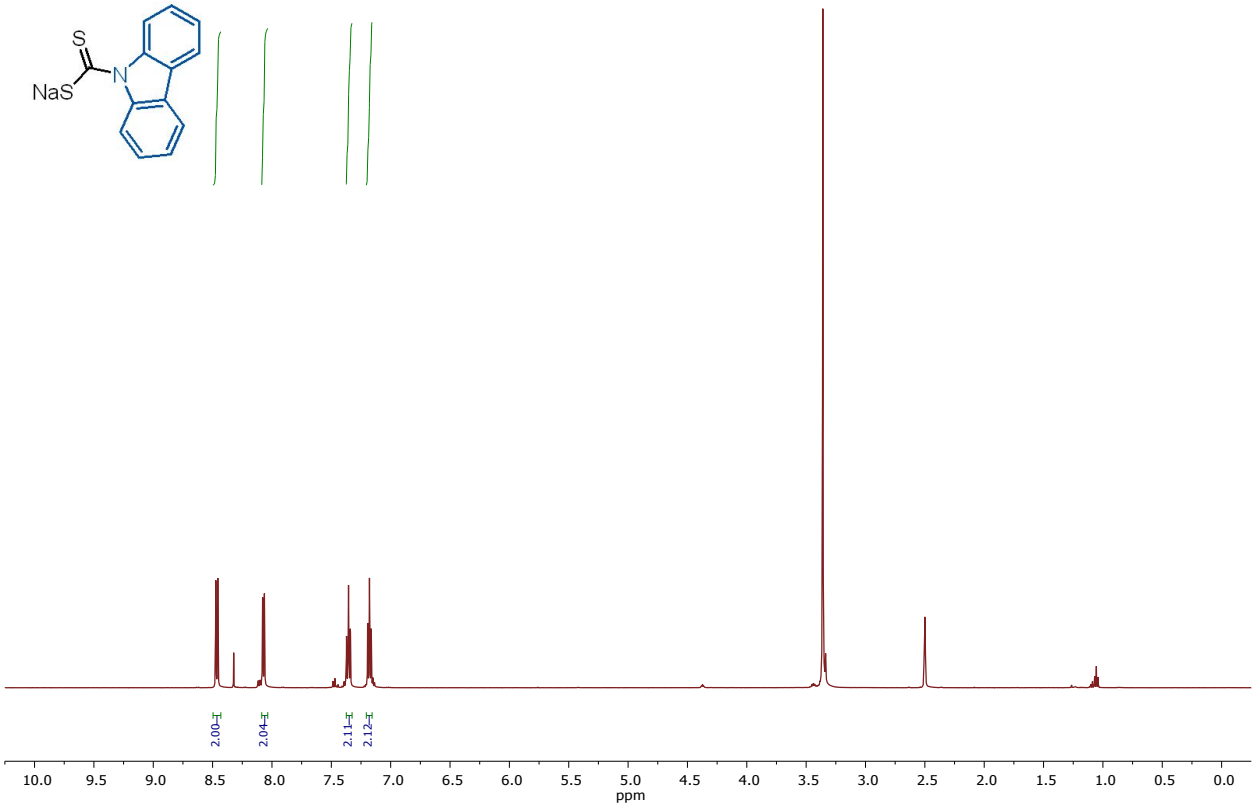


2-[2-(2-Methoxyethoxy)ethoxy]ethyl acrylate

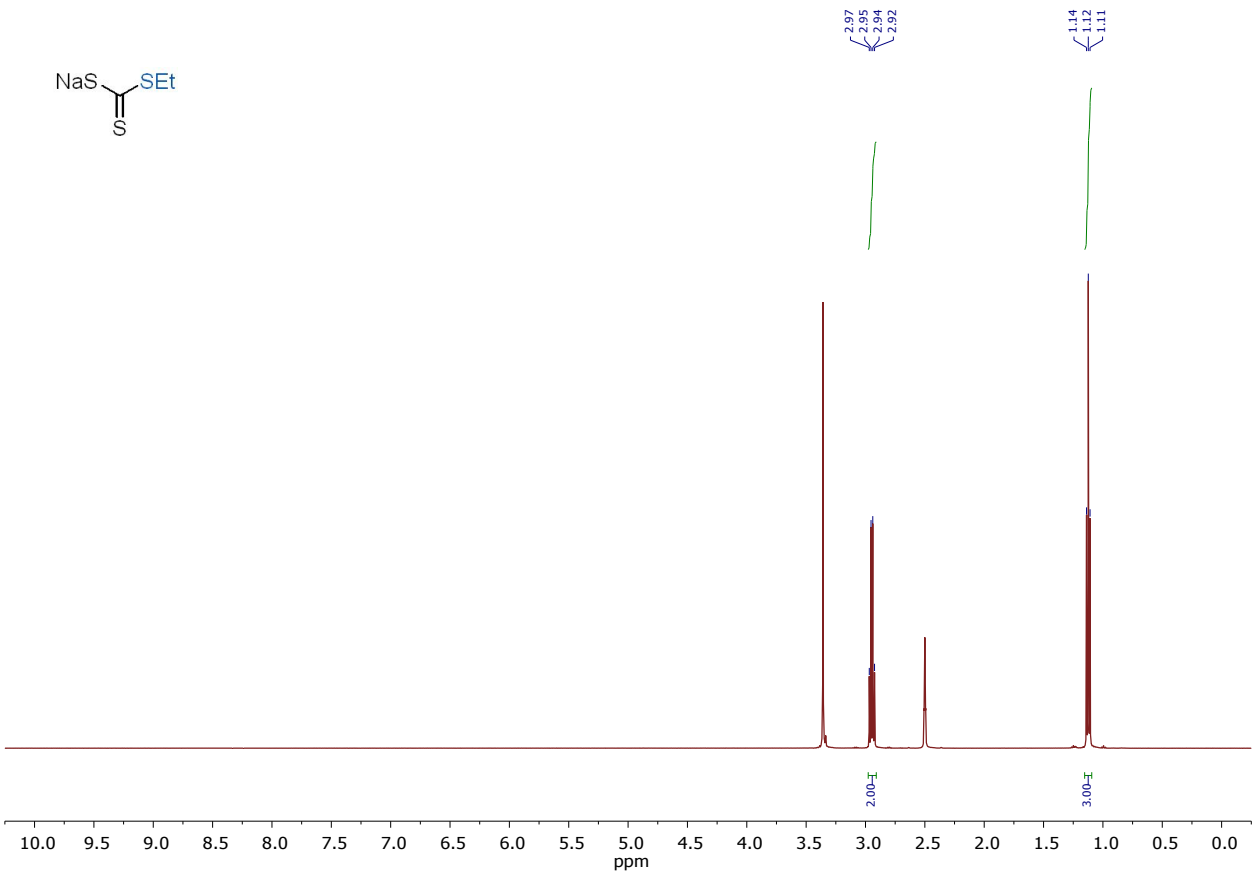


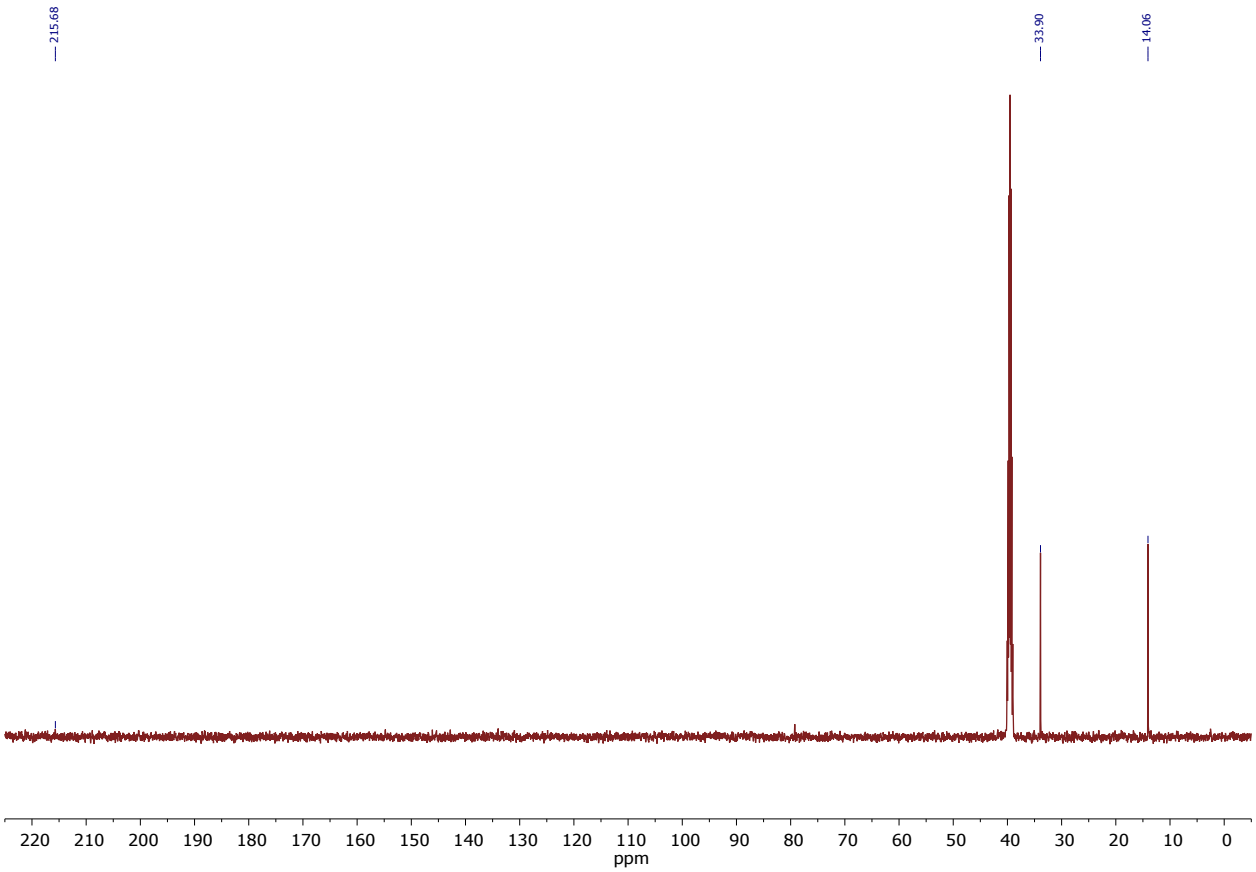
Chain-Transfer Agents Precursors

Sodium 9H-carbazole-9-carbodithioate (CTA-1)Sodium 9H-carbazole-9-carbodithioate (pCTA-1)

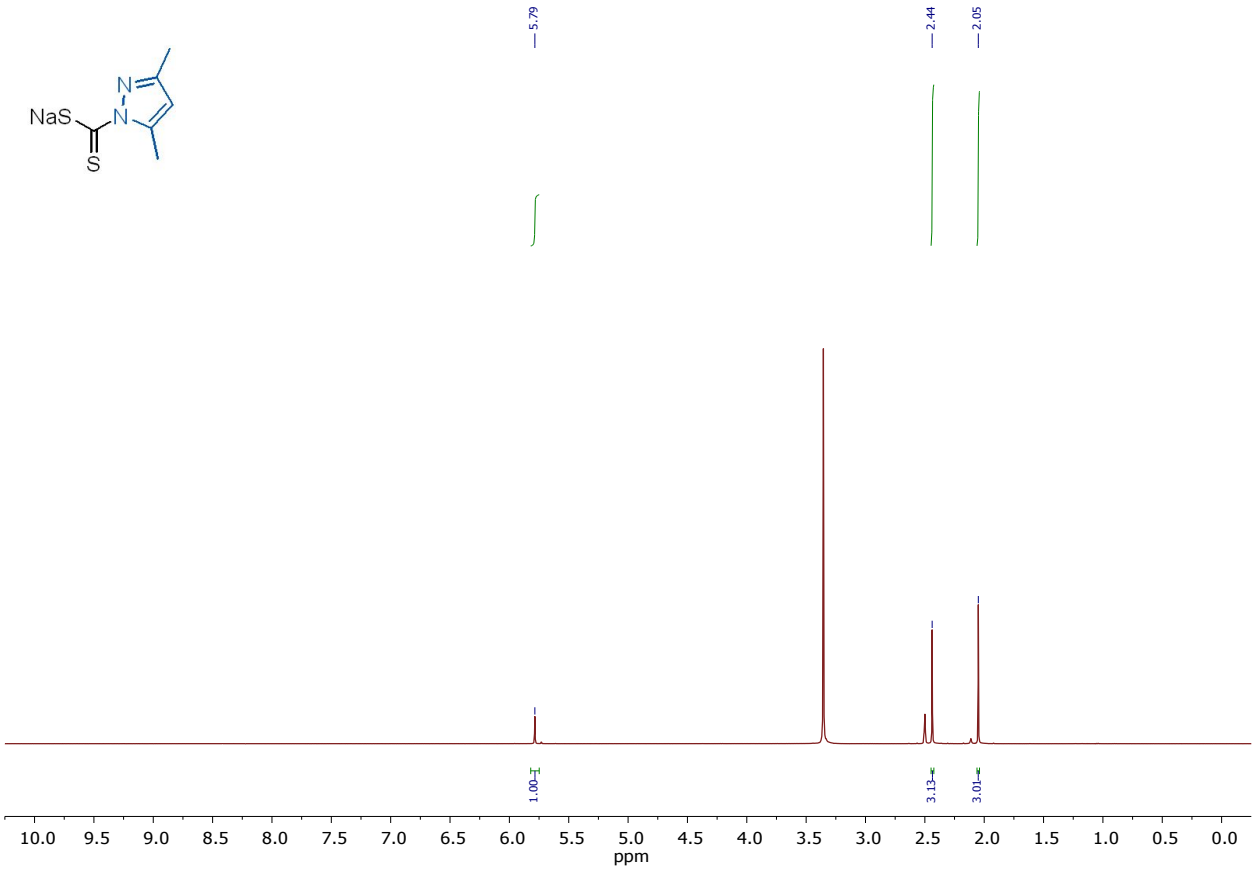


Sodium Ethyl Carbonotrithioate (pCTA-2)

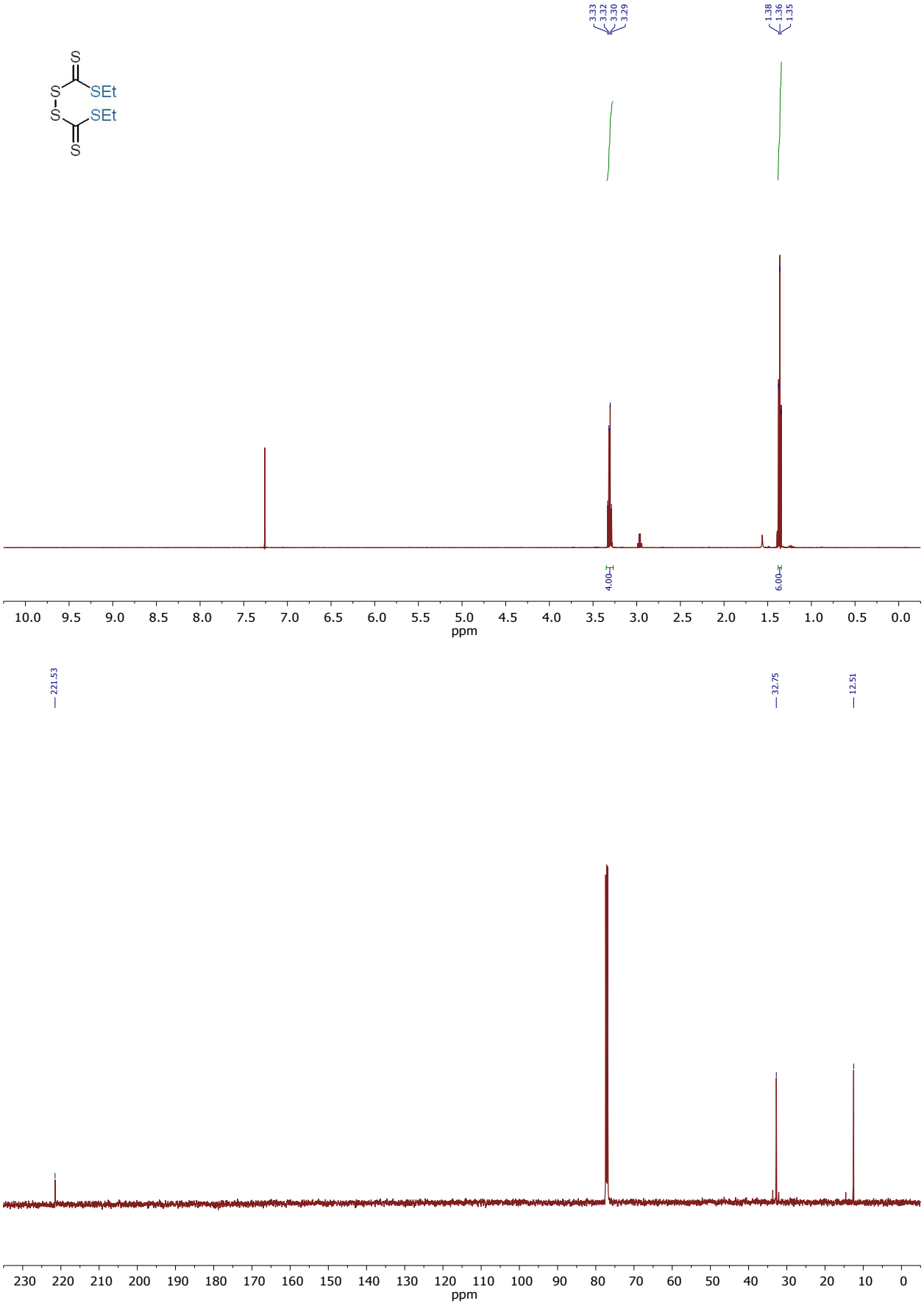




Sodium 3,5-dimethyl-1H-pyrazole-1-carbodithioate (pCTA-3)

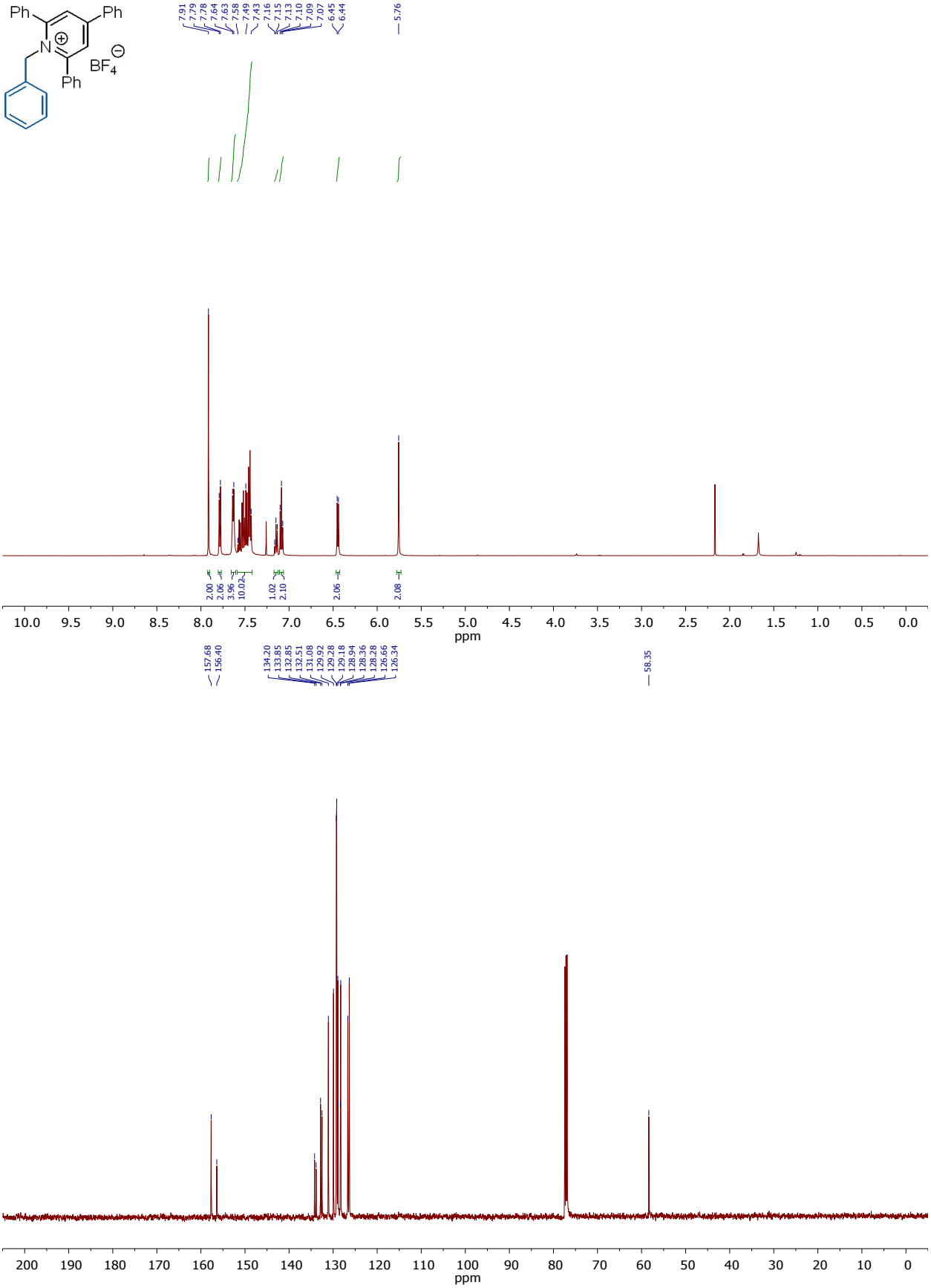


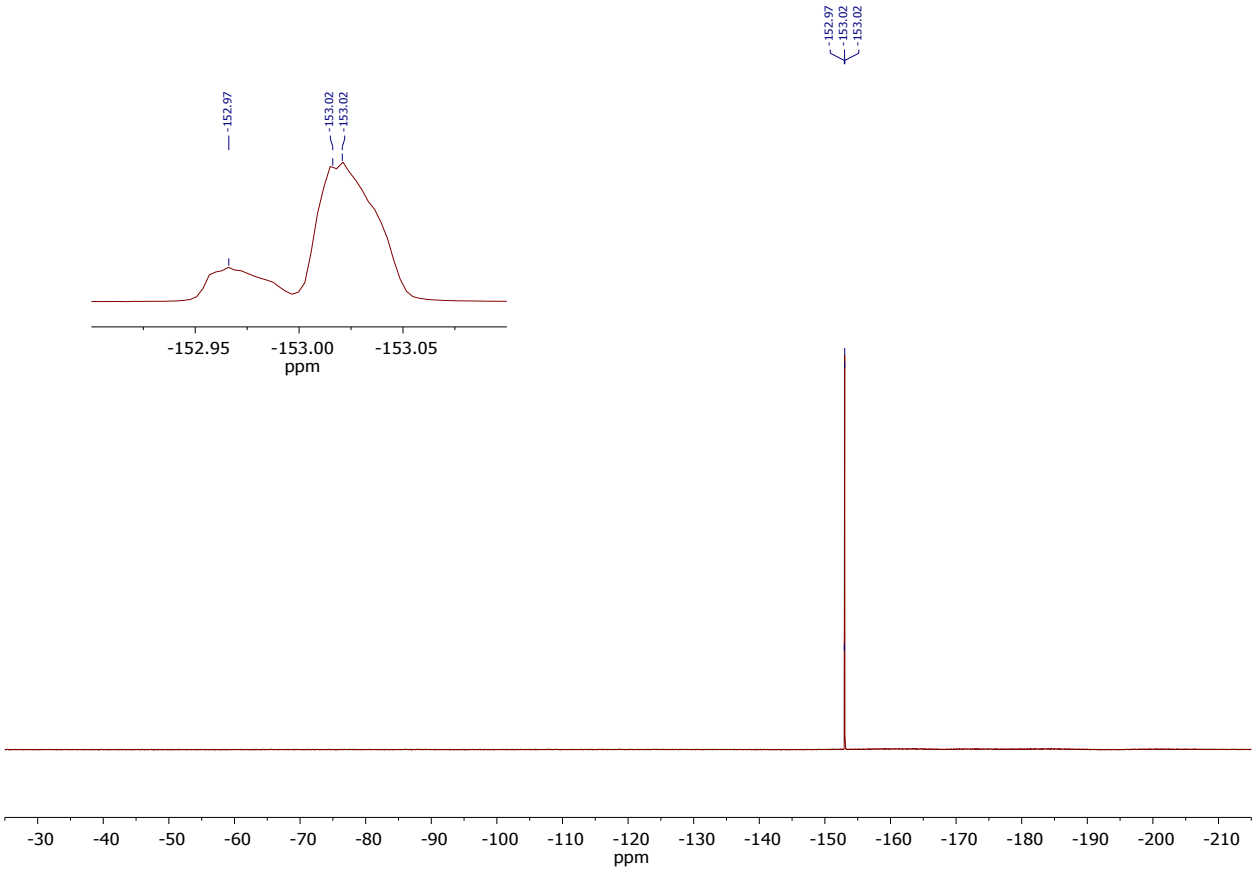
Disulfide CTA-4



Pyridinium Salts

1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2a)




-152.97
-153.02
-153.02
-152.95
-153.00
-153.05
ppm
-152.97
-153.02
-153.02
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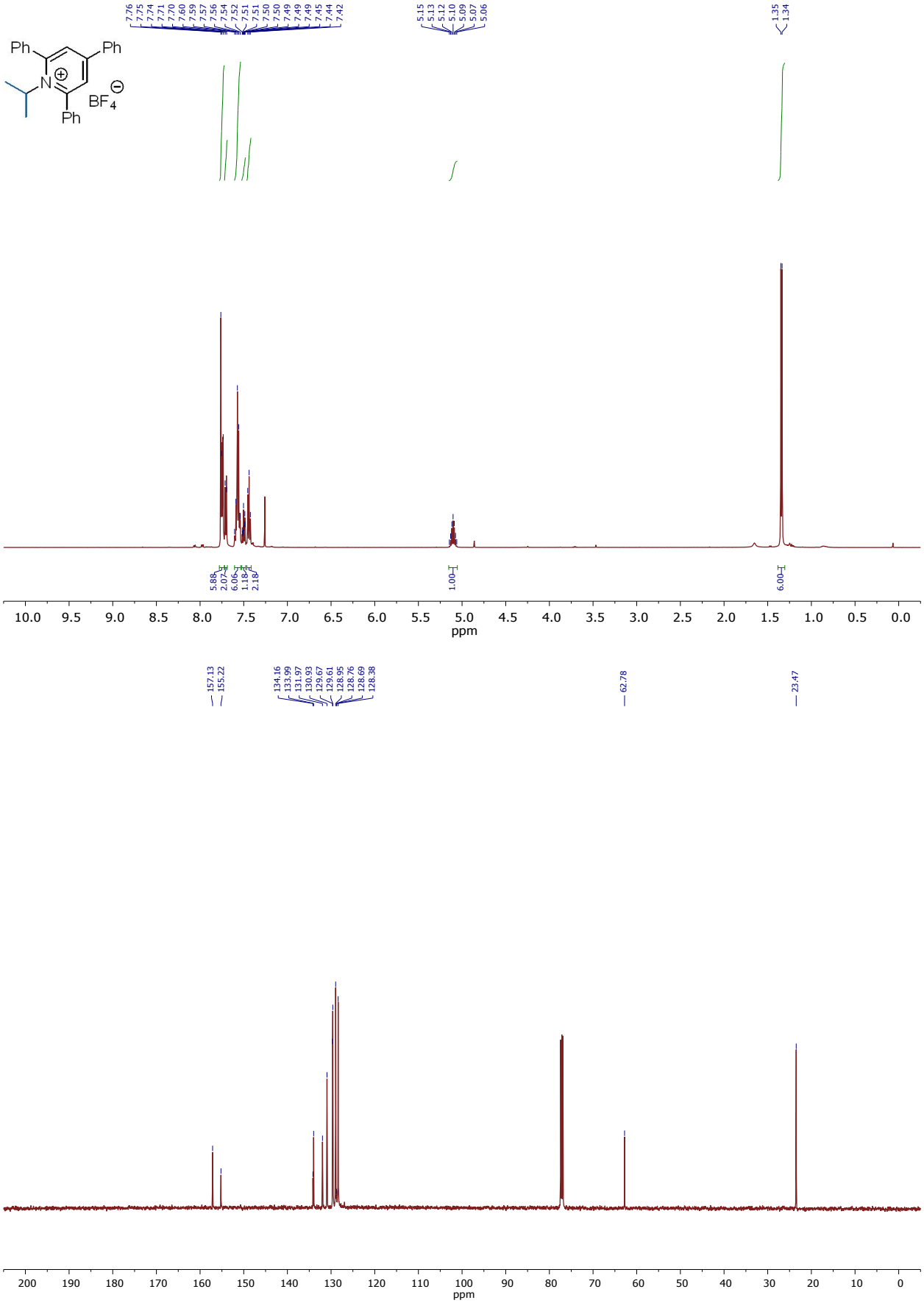
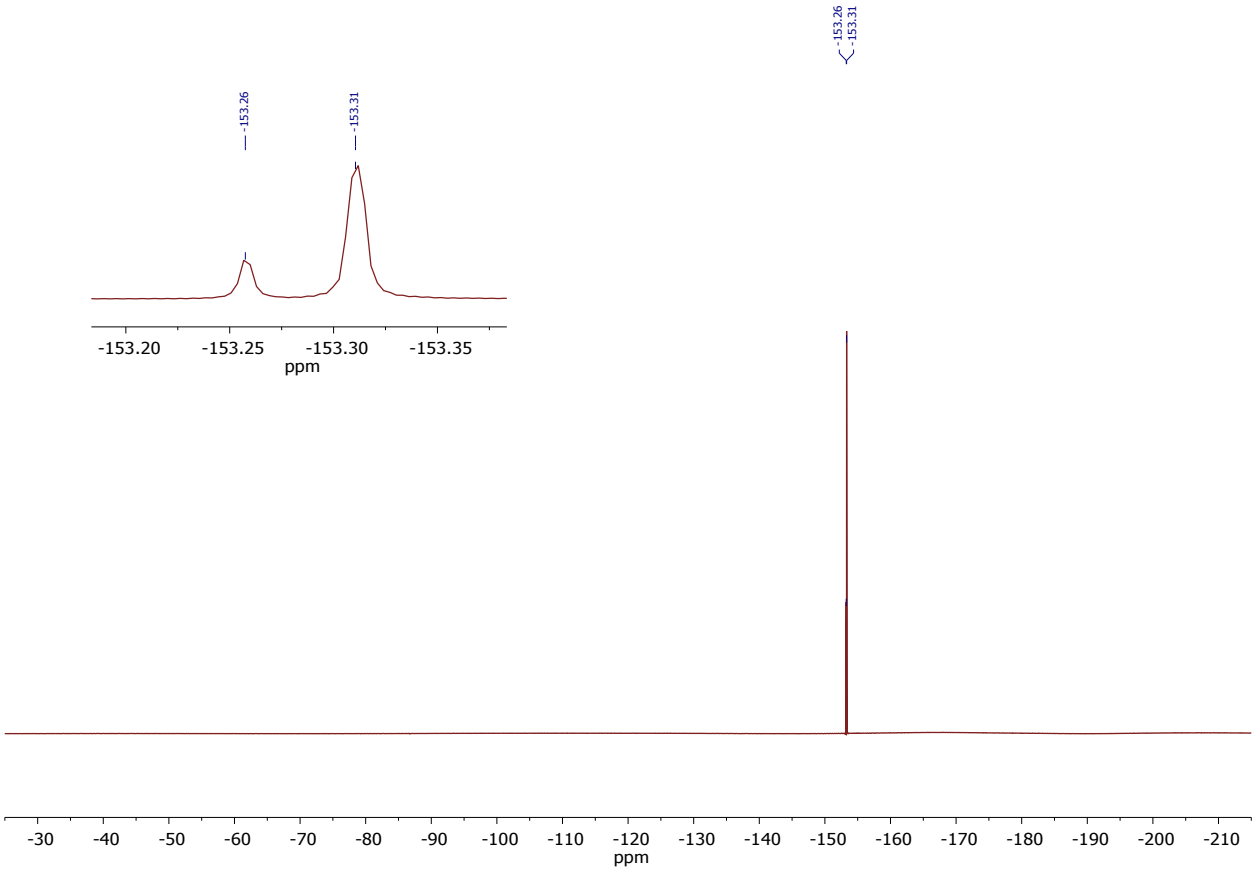
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

1-isopropyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (3a)

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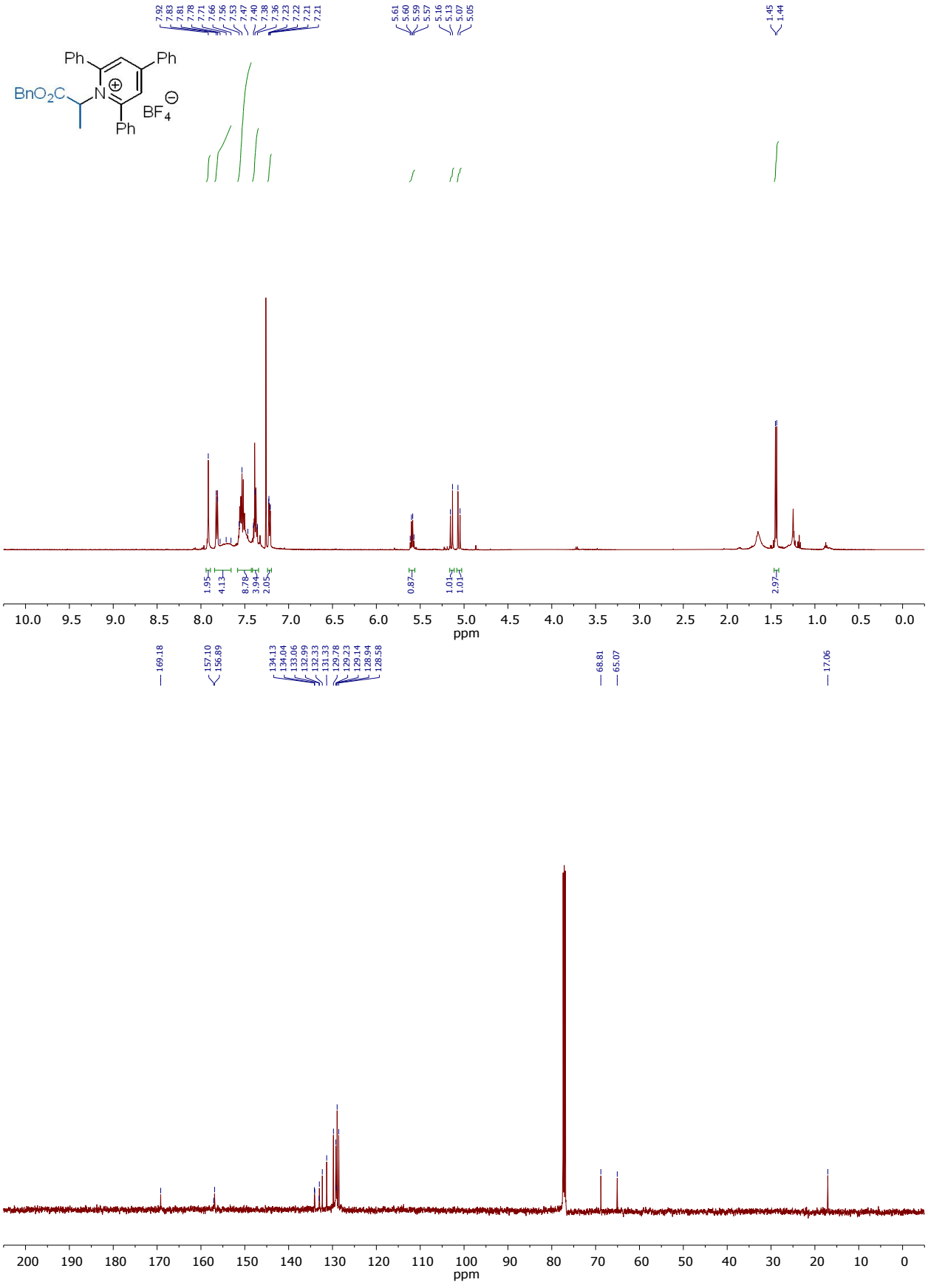
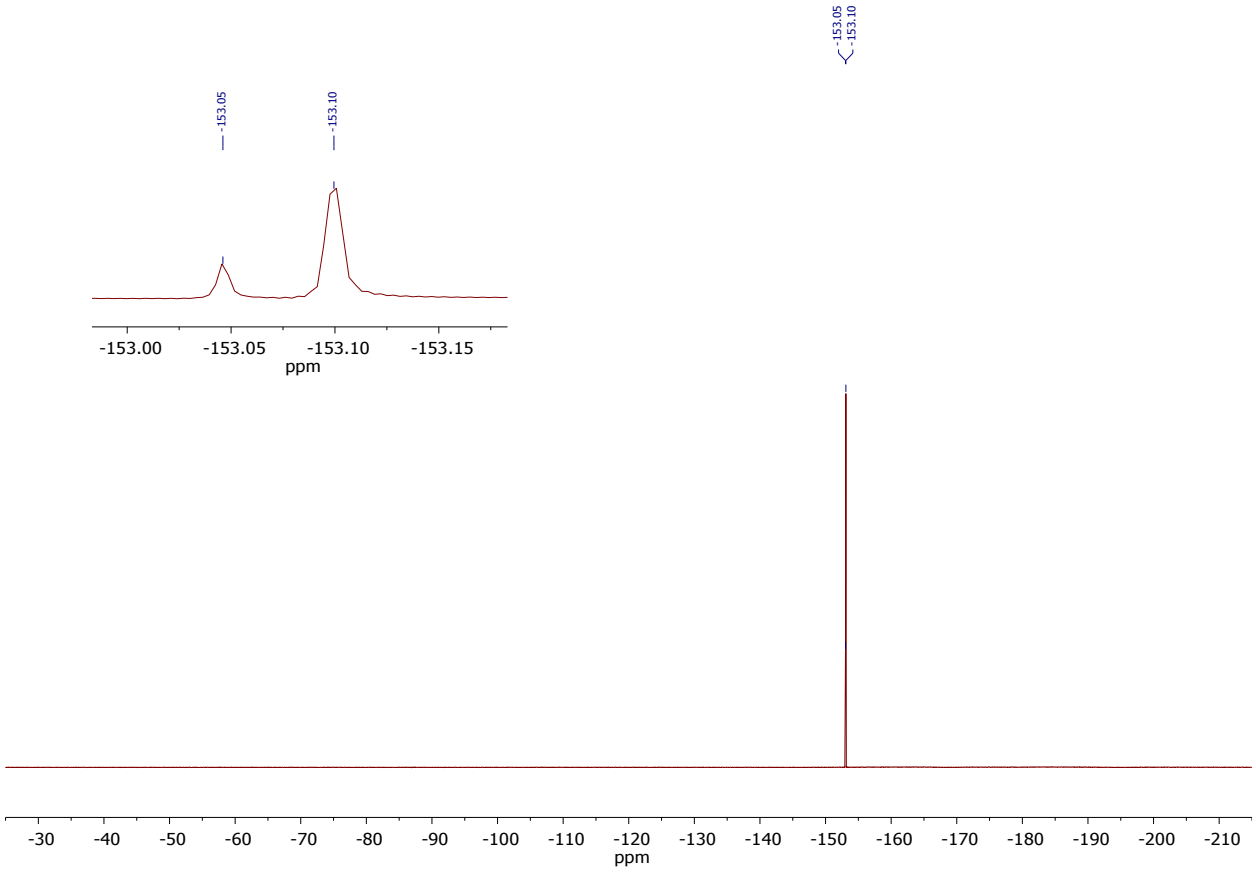
-153.31
-153.26
-153.31
-153.20
-153.25
-153.30
-153.35
ppm
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

1-(1-(benzyloxy)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (4a)




-153.05
-153.10
-153.05
-153.10
-153.00
-153.05
-153.10
-153.15
ppm
-30
-40
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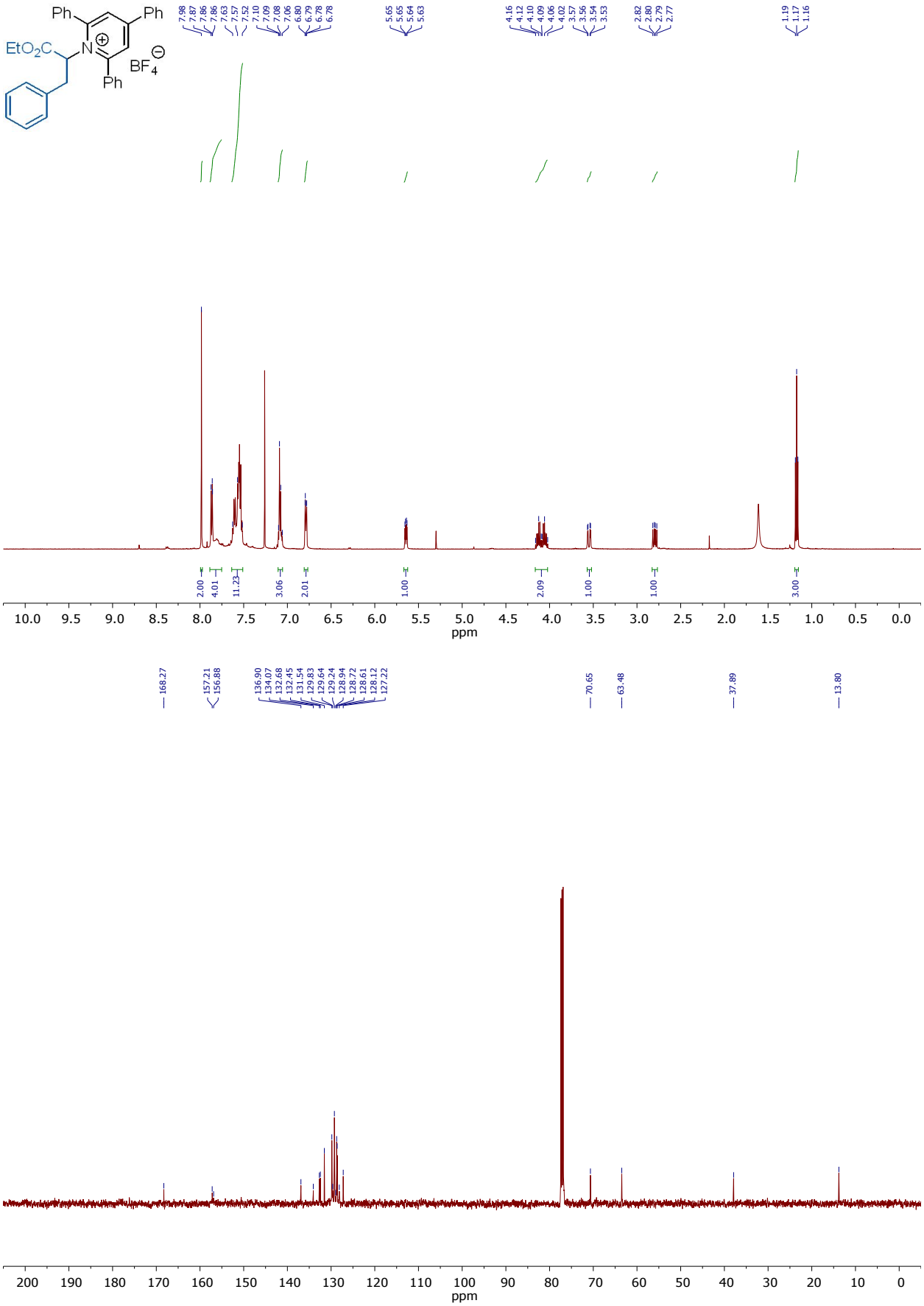
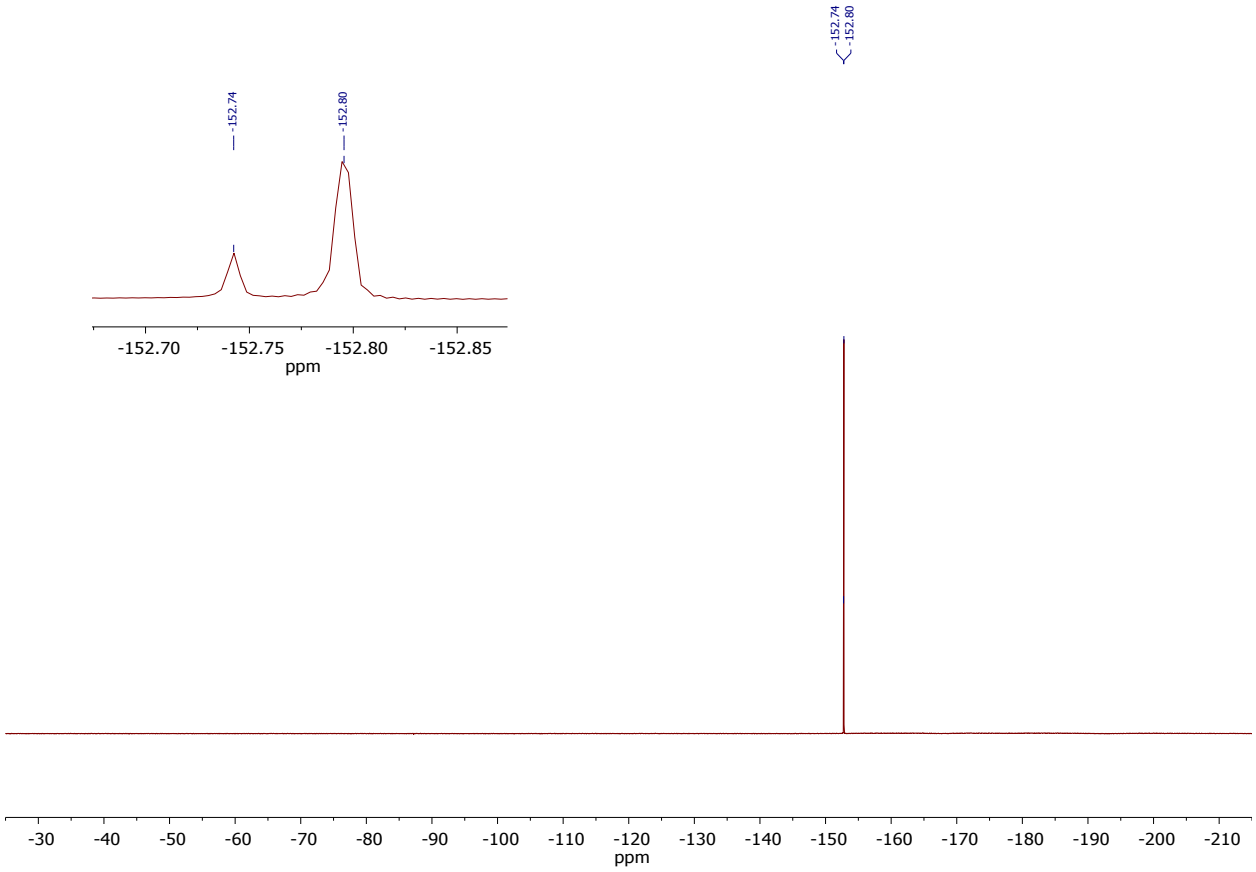
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

1-(1-ethoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (5a)




-152.74
-152.80
-152.74
-152.80
-152.70
-152.75
-152.80
-152.85
ppm
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-40
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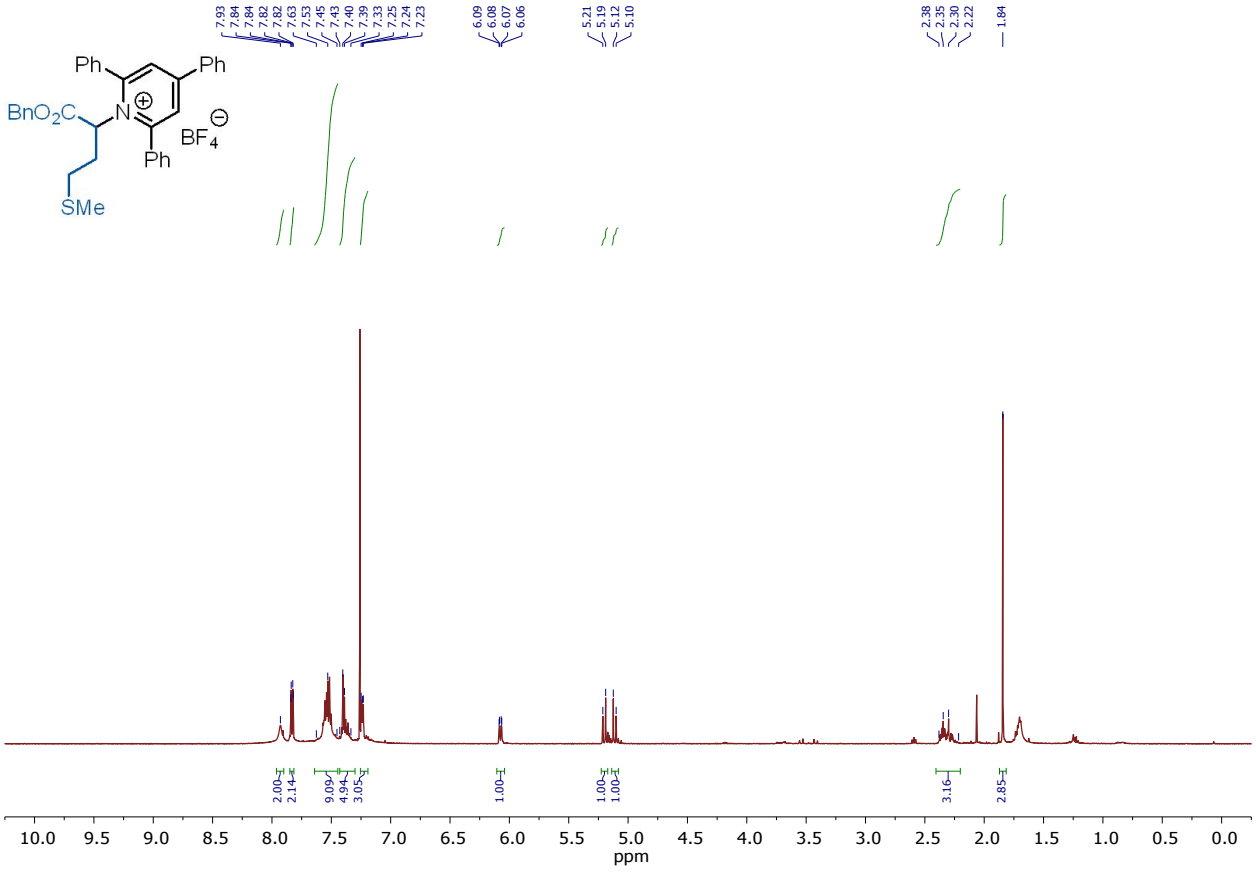
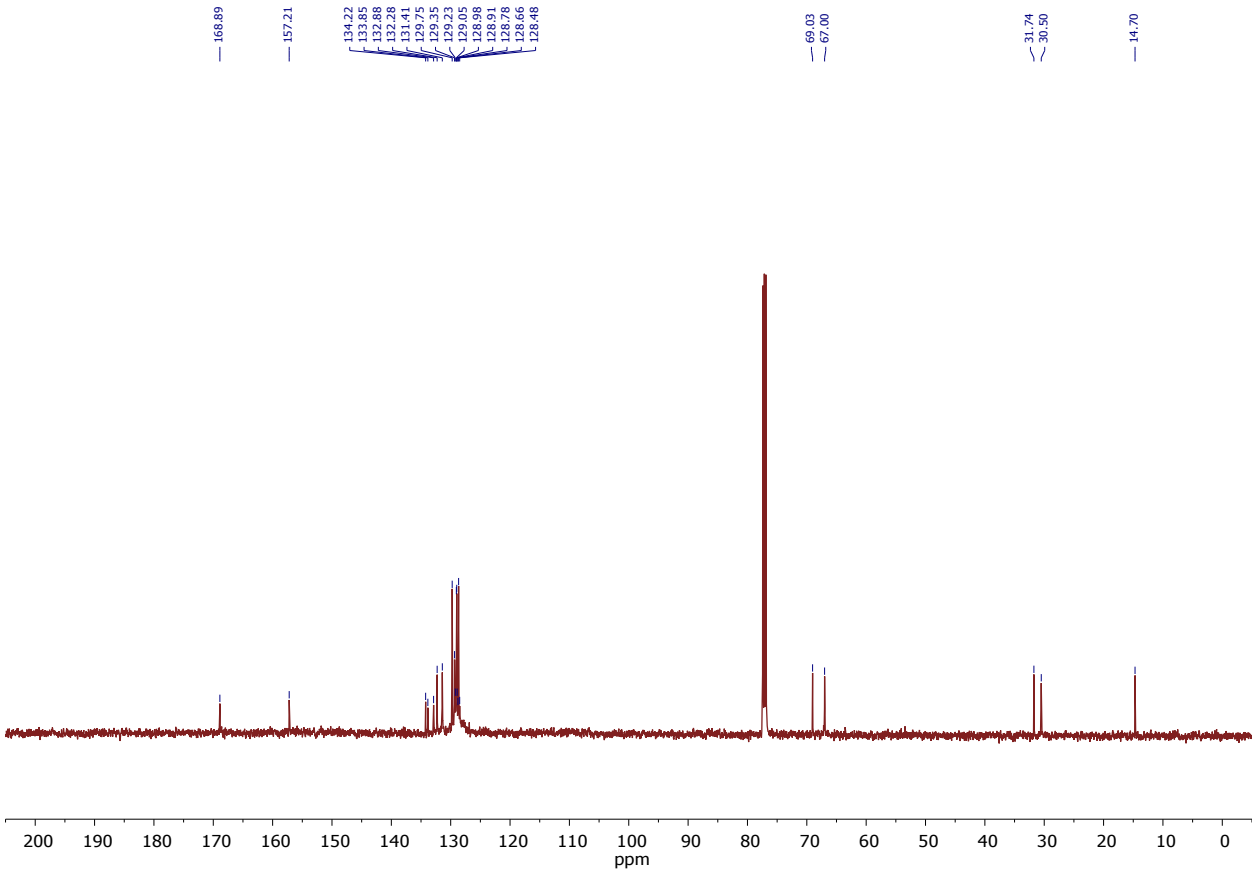
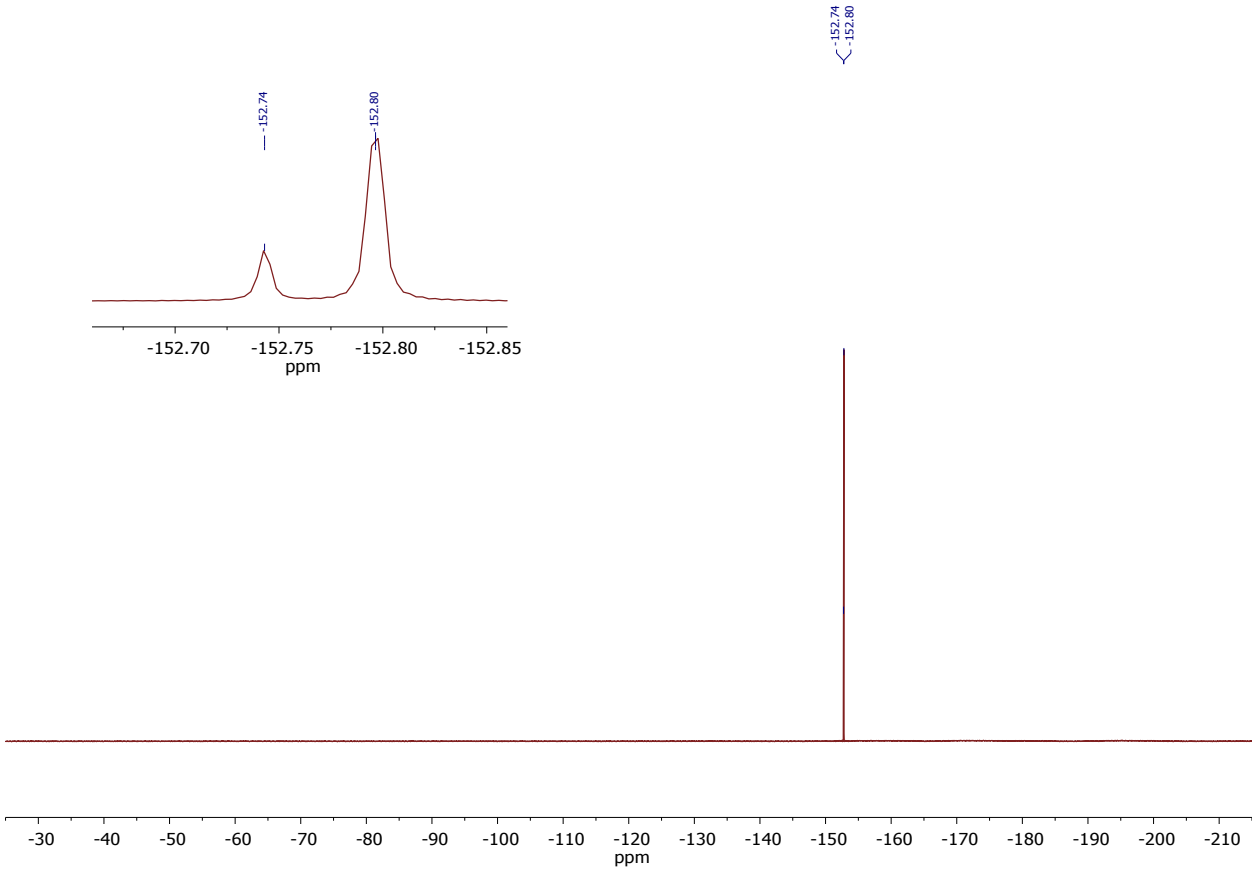
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

1-(1-(benzyloxy)-4-(methylthio)-1-oxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (6a)






-152.74
-152.80
-152.74
-152.80
-152.70
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-152.80
-152.85
ppm
-30
-40
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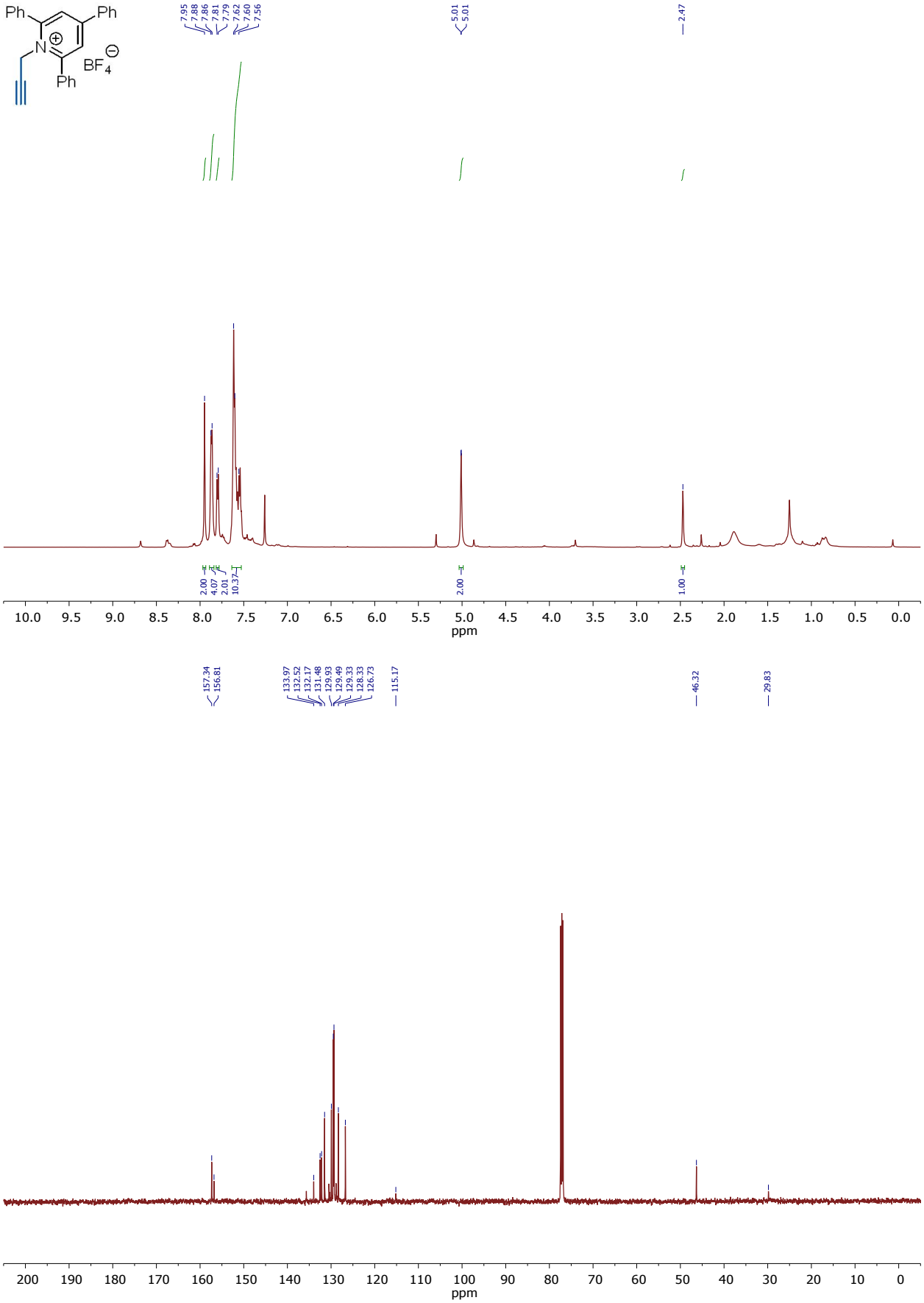
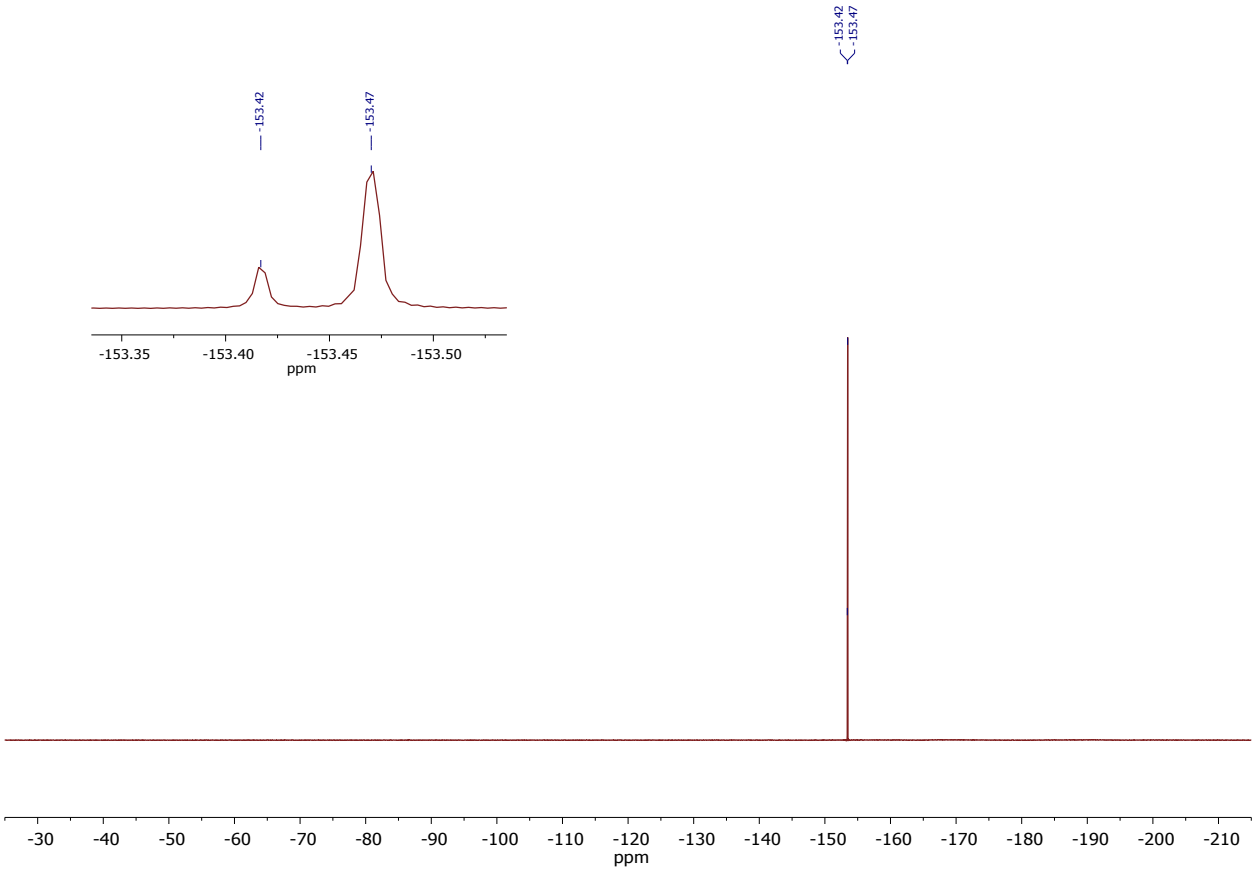
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

1-(prop-2-yn-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (9a)




-153.42
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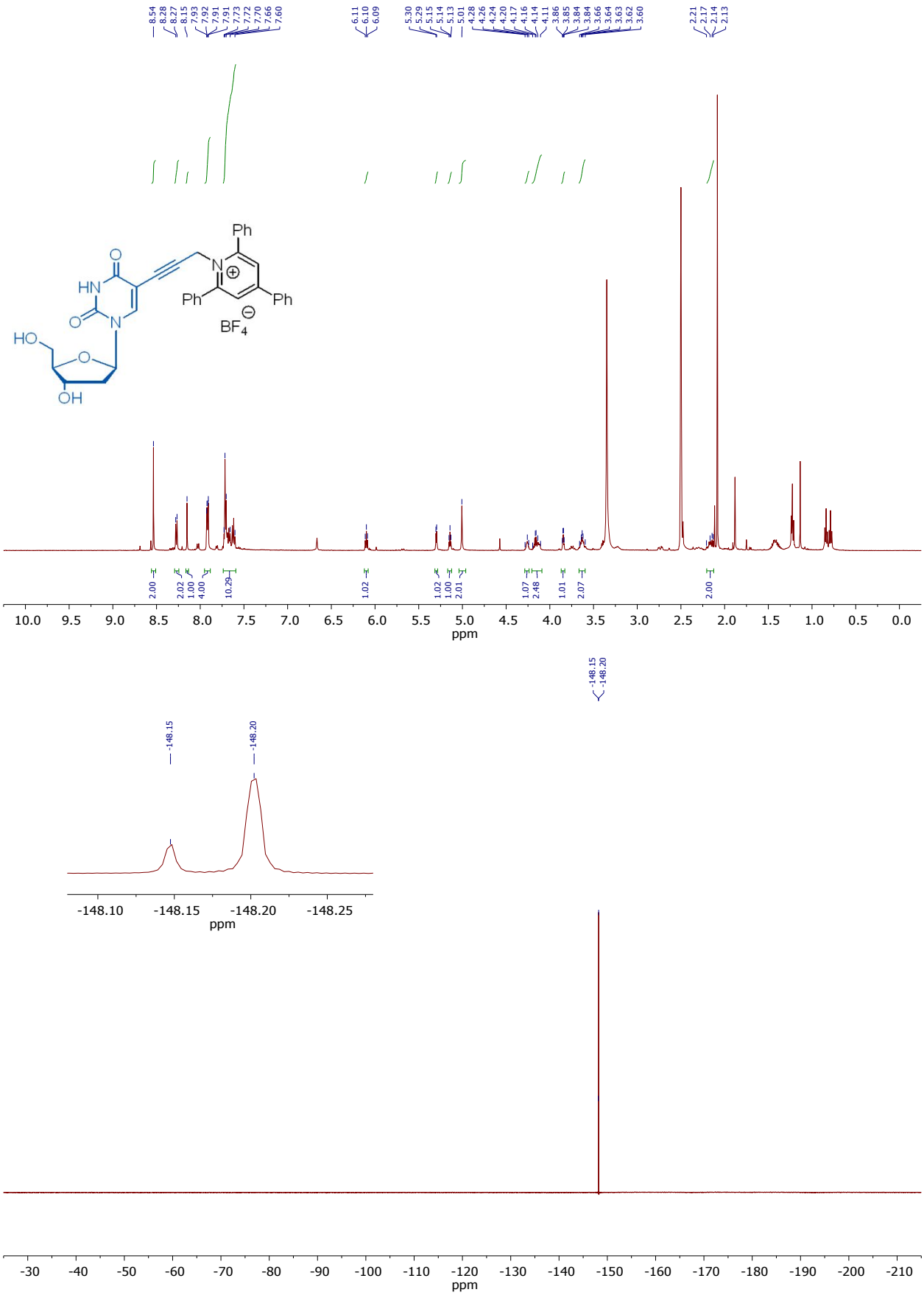
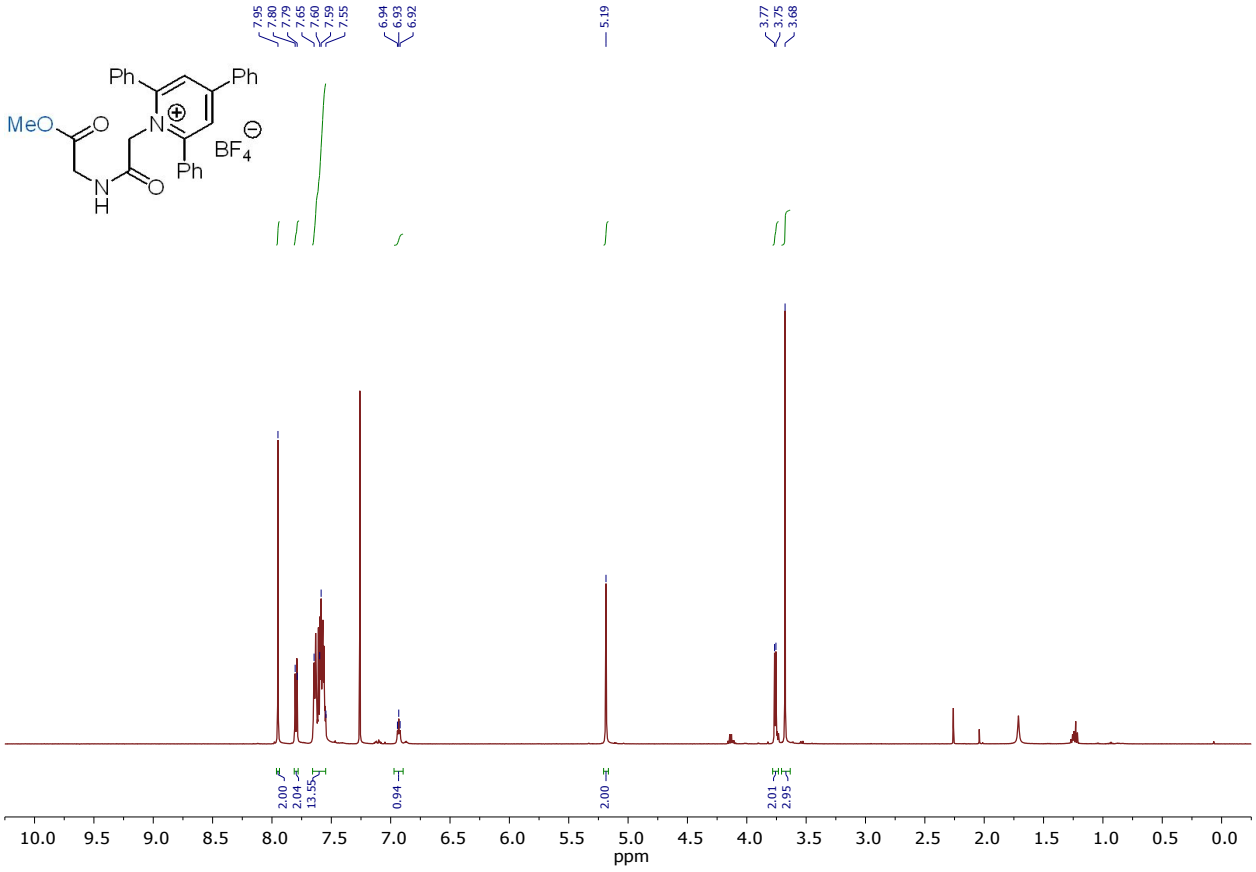
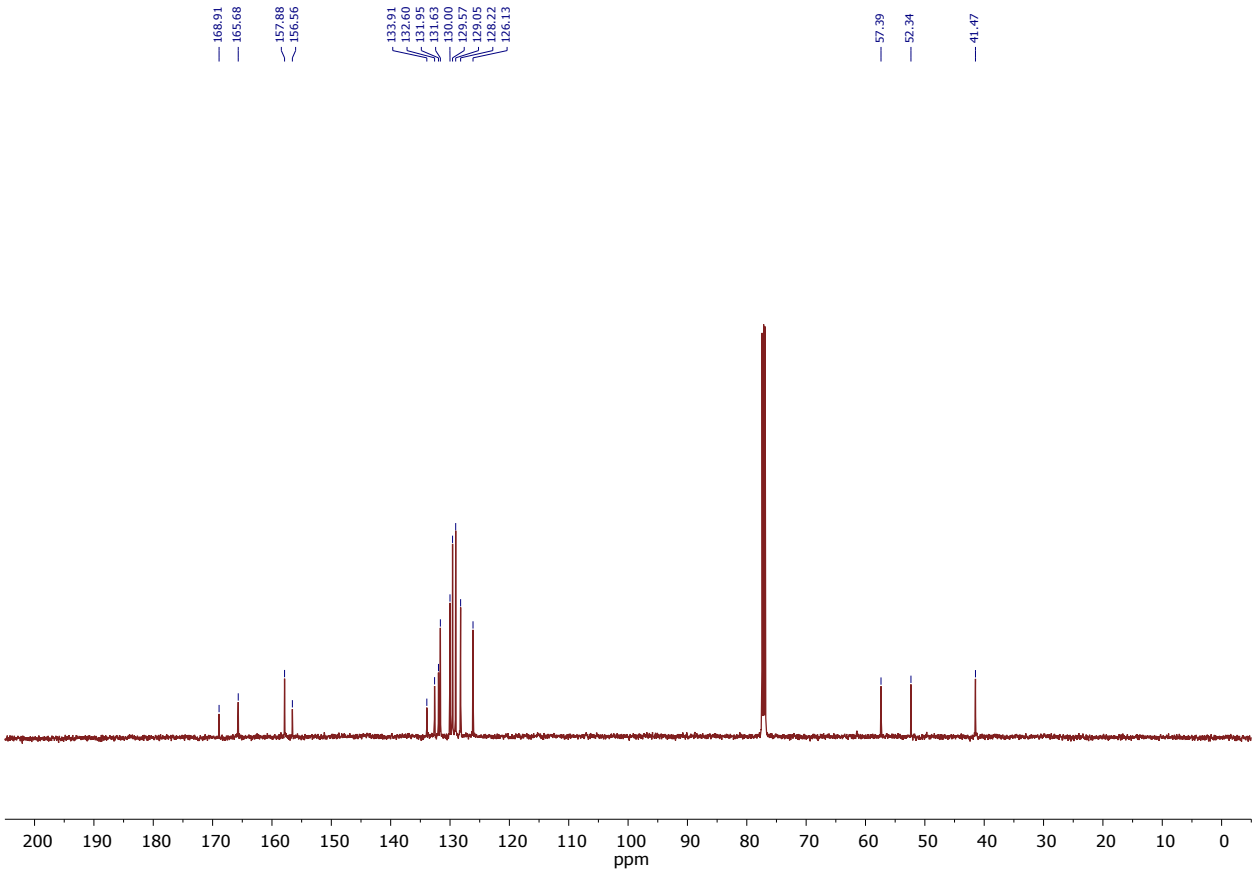
-153.42
-153.47
-153.35
-153.40
-153.45
-153.50
ppm
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

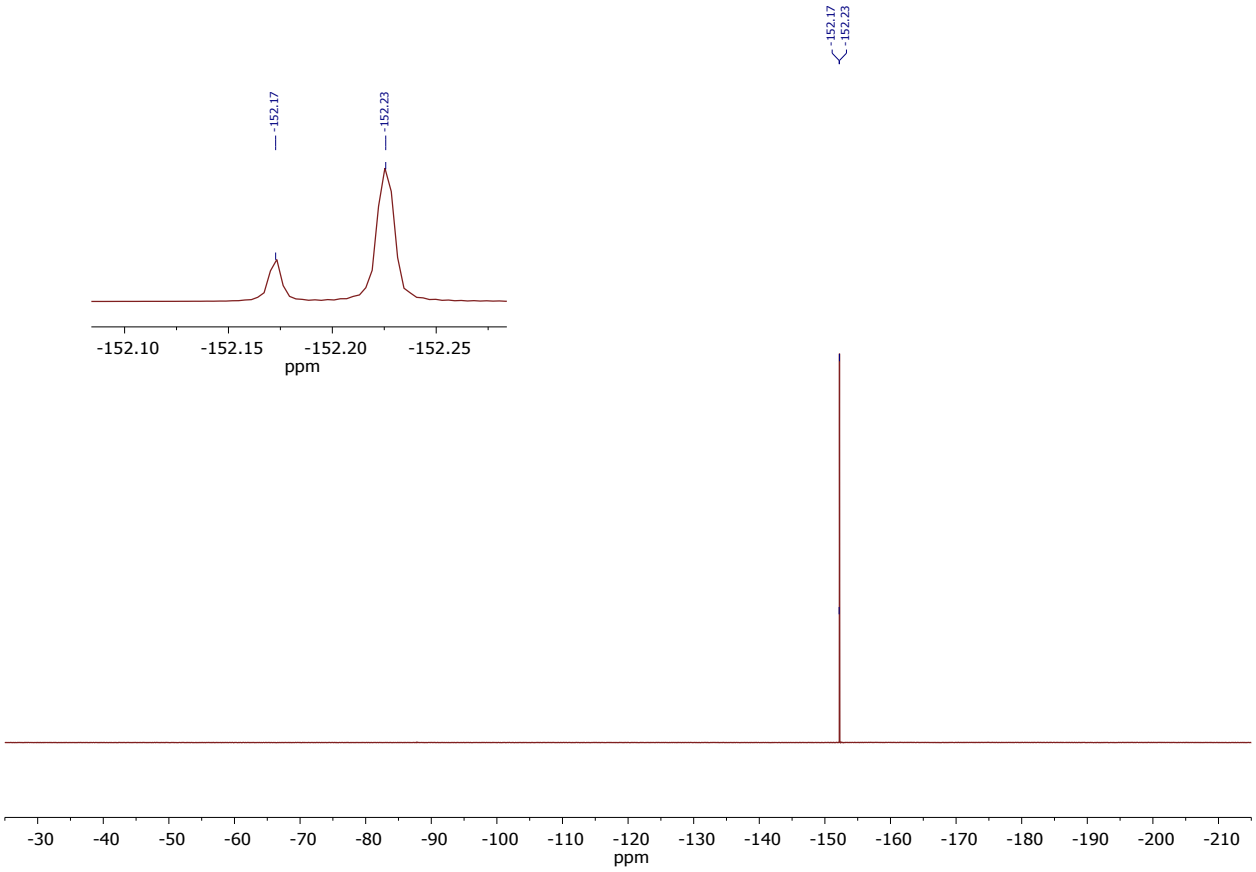
1-(3-(1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)prop-2-yn-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (S8)



1-(2-((2-methoxy-2-oxoethyl)amino)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (S10)



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ppm
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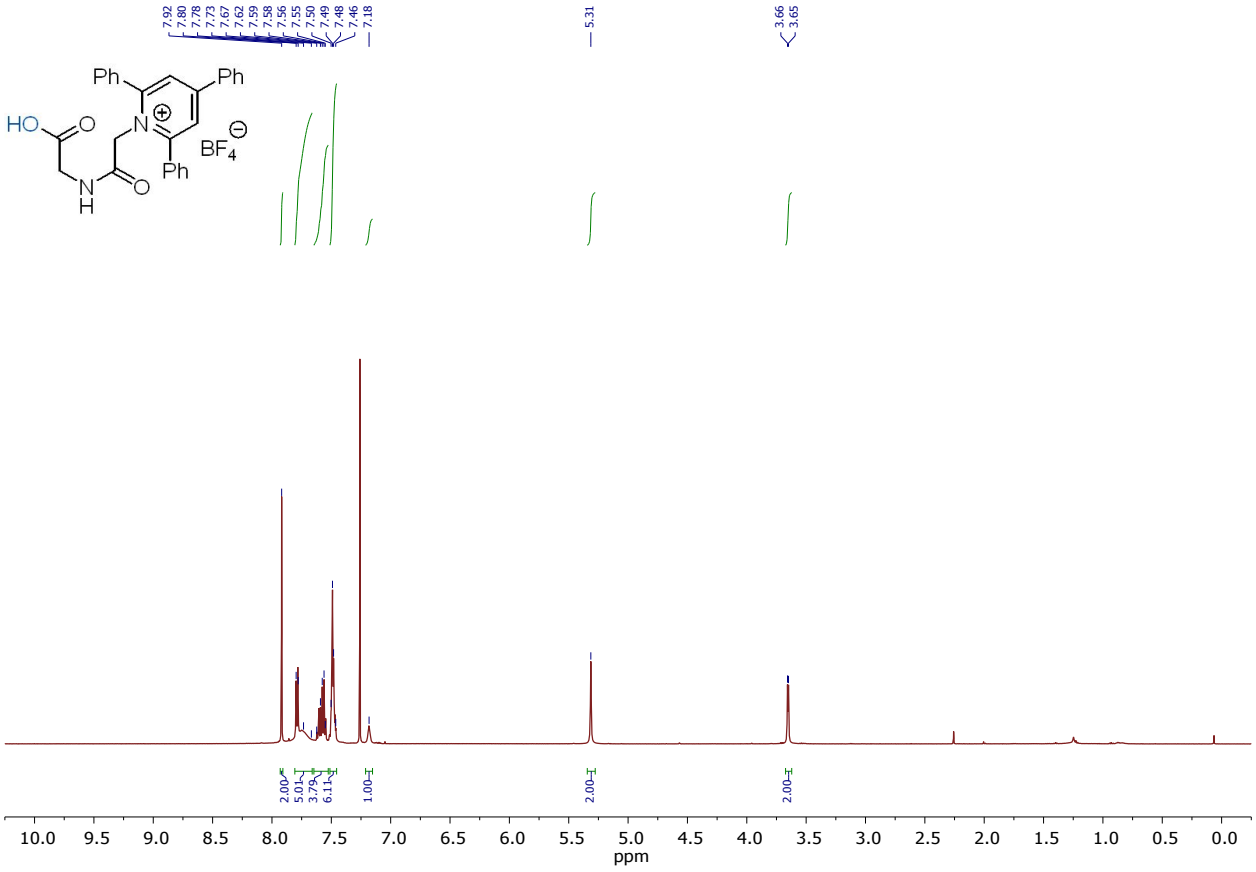
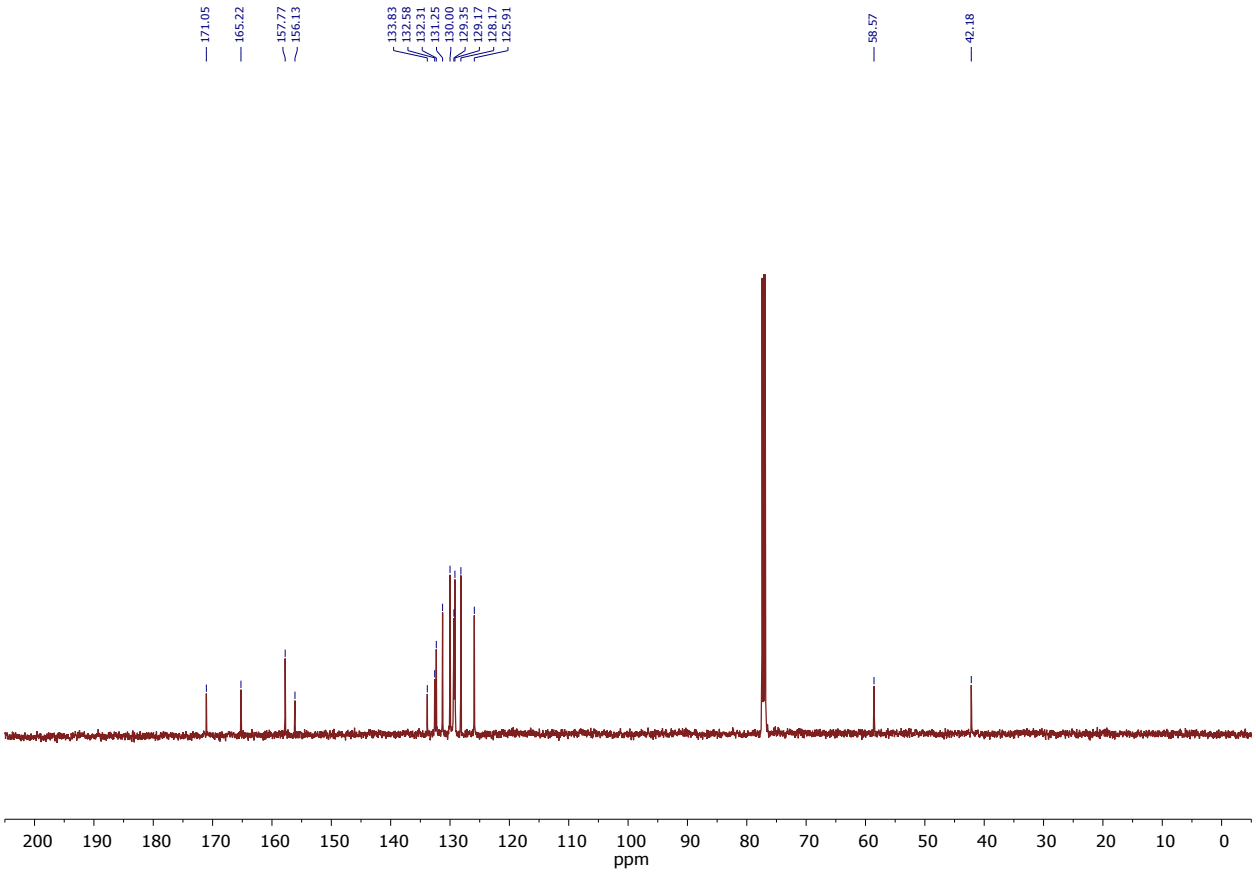
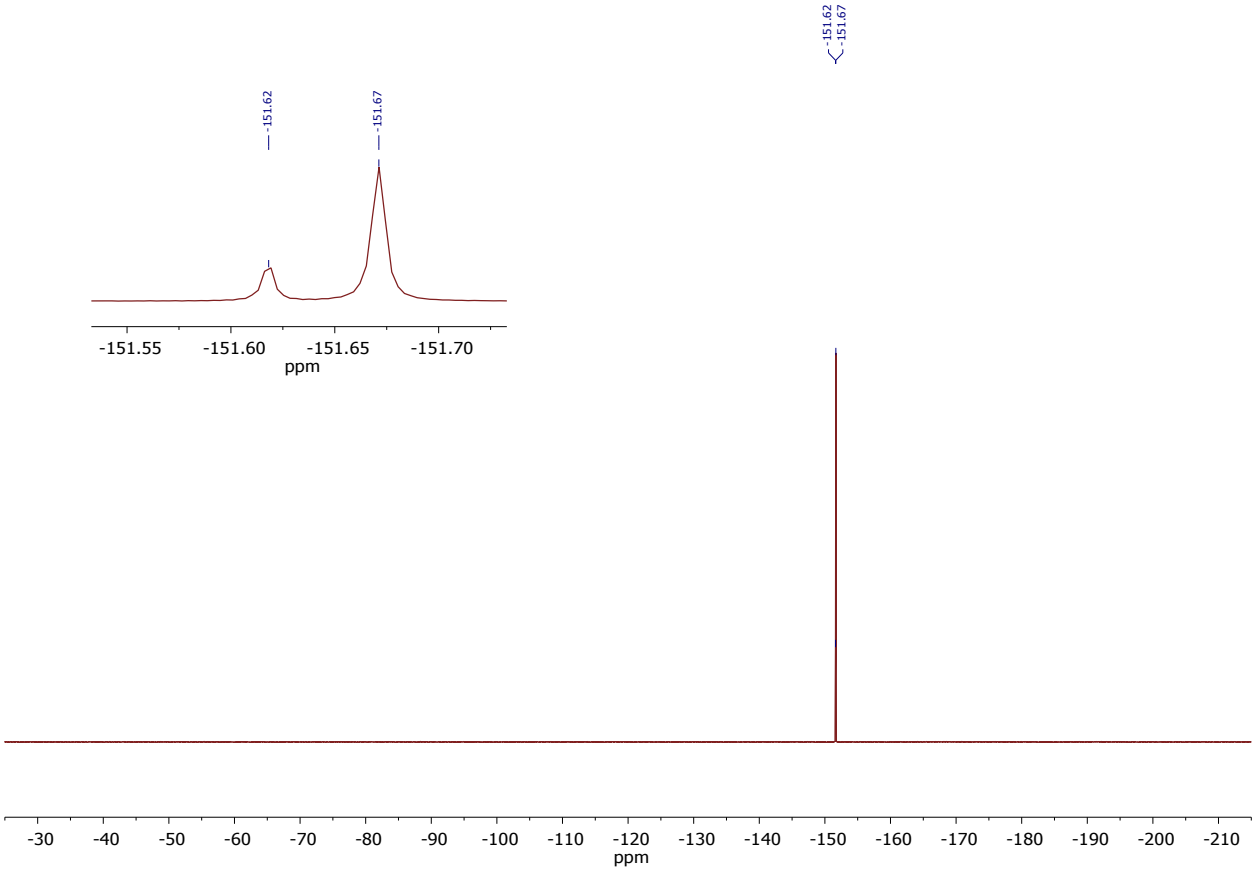
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

1-(2-((carboxymethyl)amino)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (Gly-Gly KS)






-151.62
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-151.55
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-151.65
-151.70
ppm
-151.62
-151.67
-30
-40
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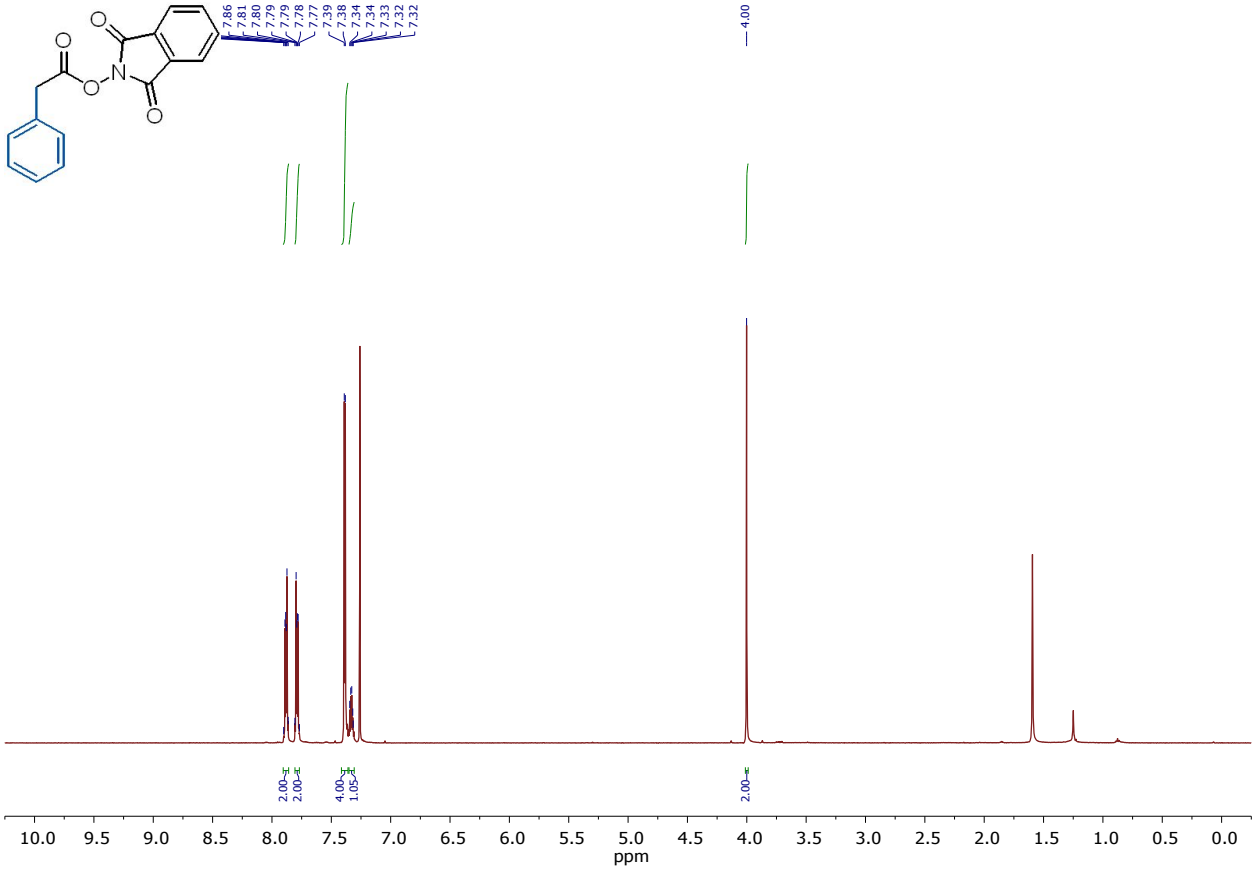
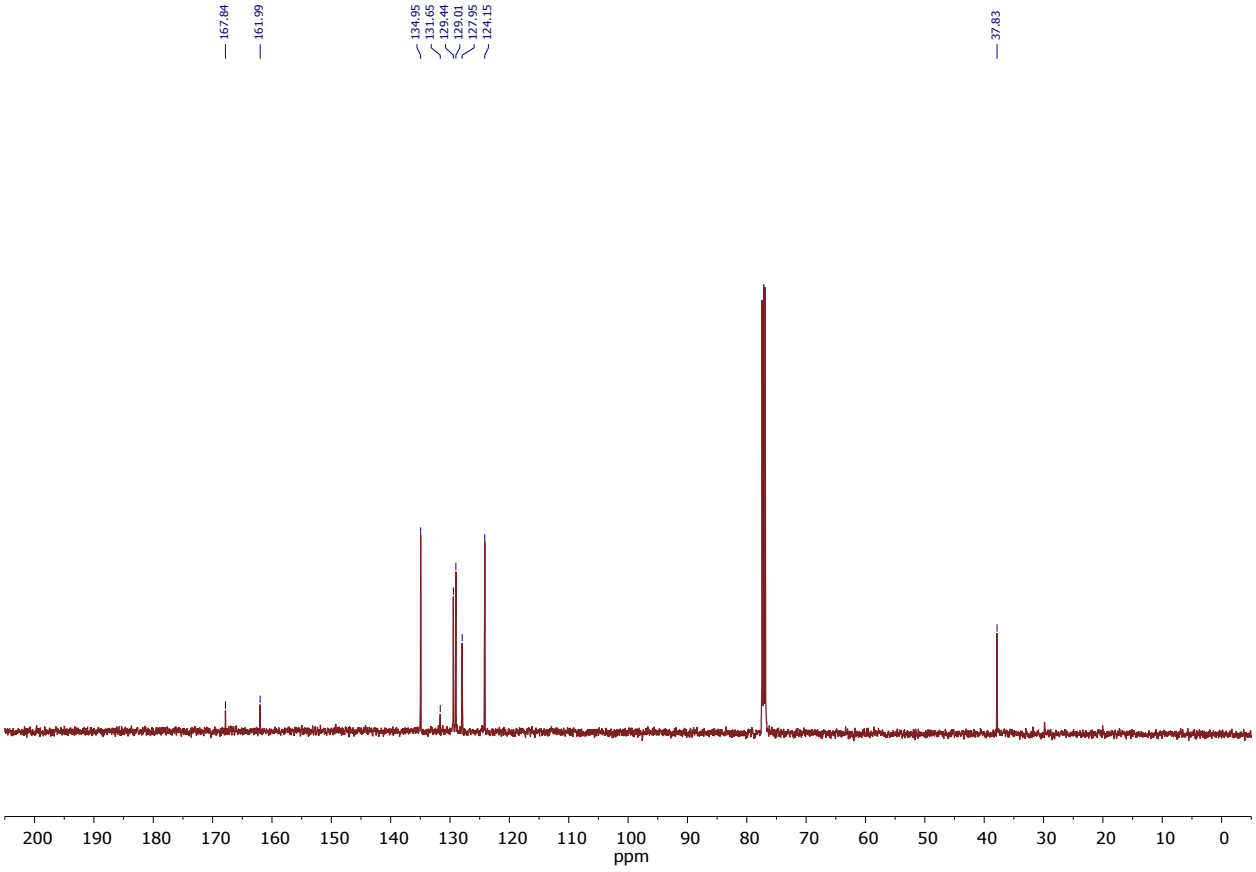
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

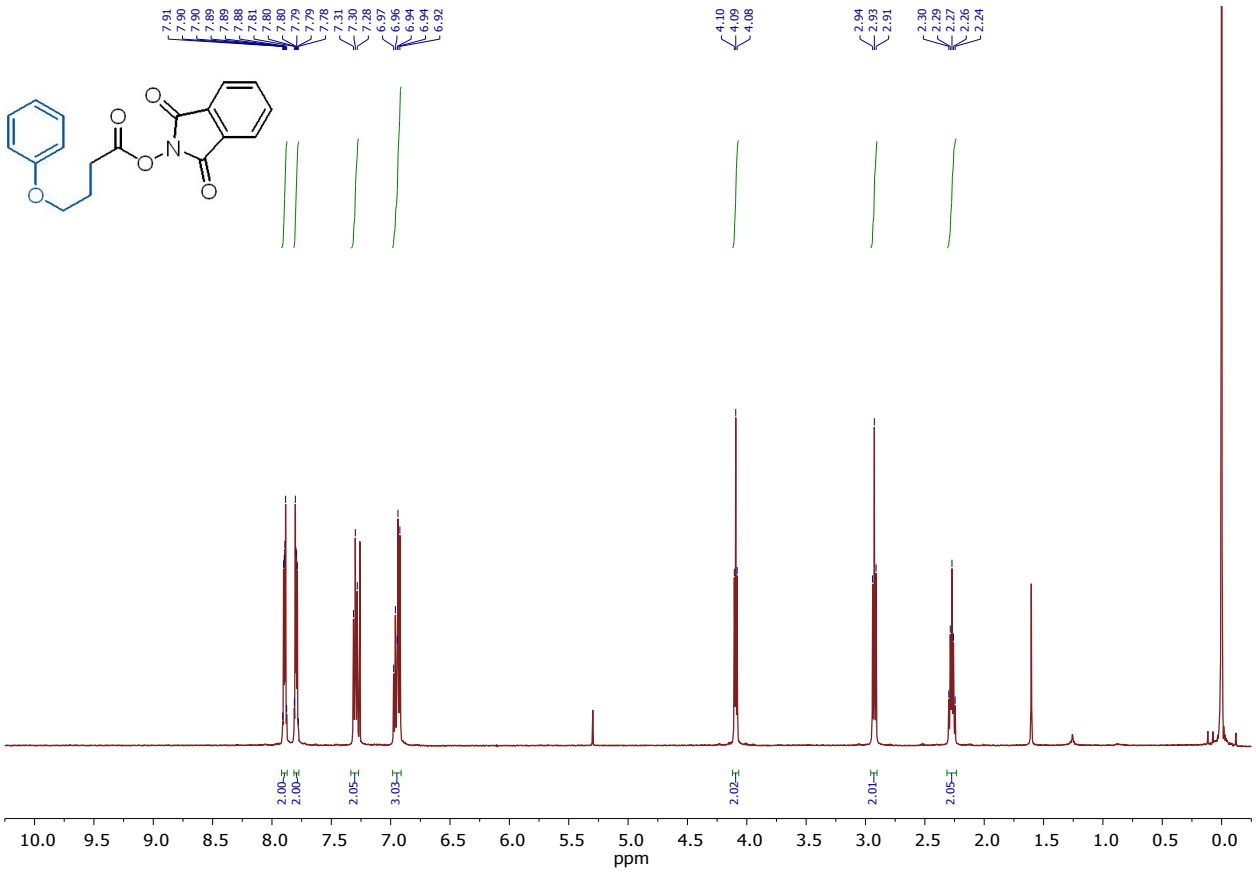
NHPI Esters

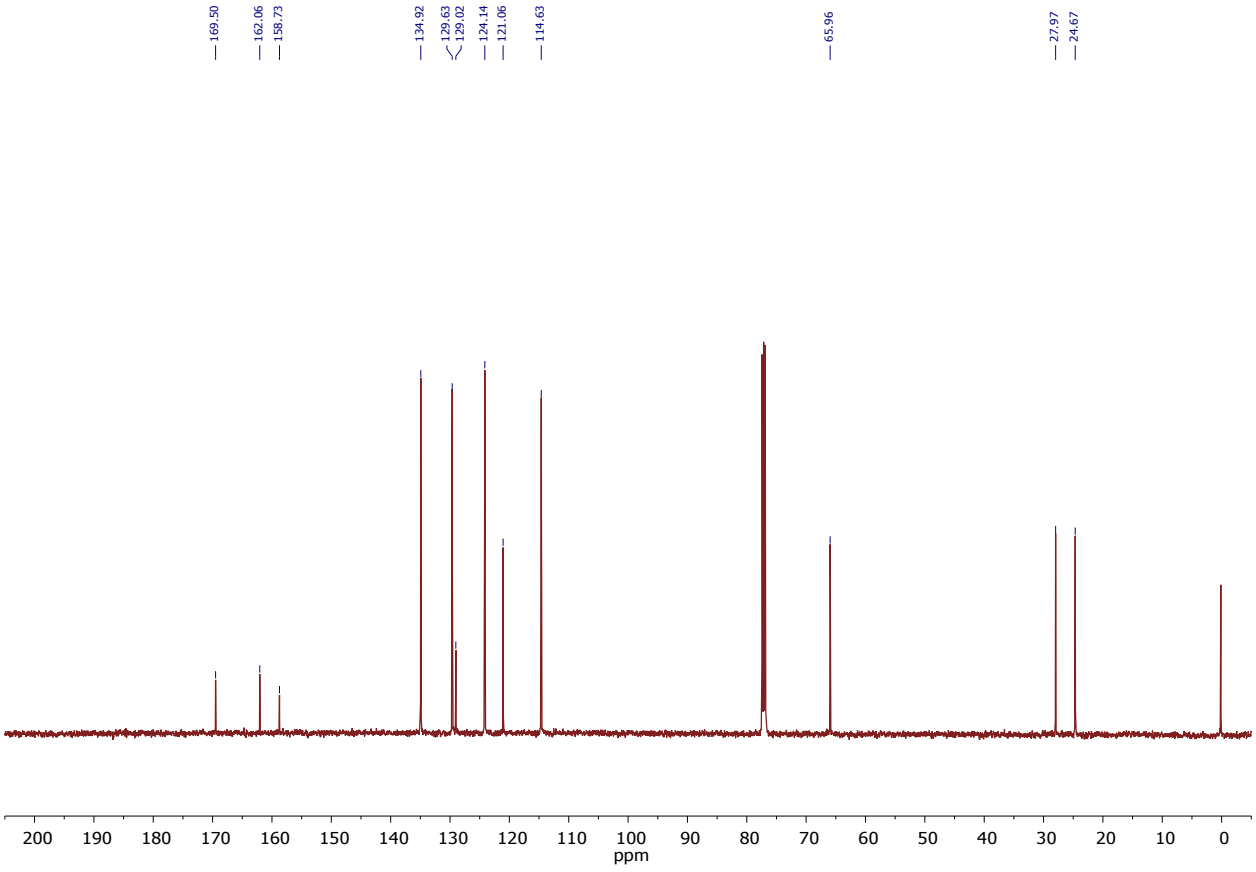
1,3-dioxoisoindolin-2-yl 2-phenylacetate (2b)



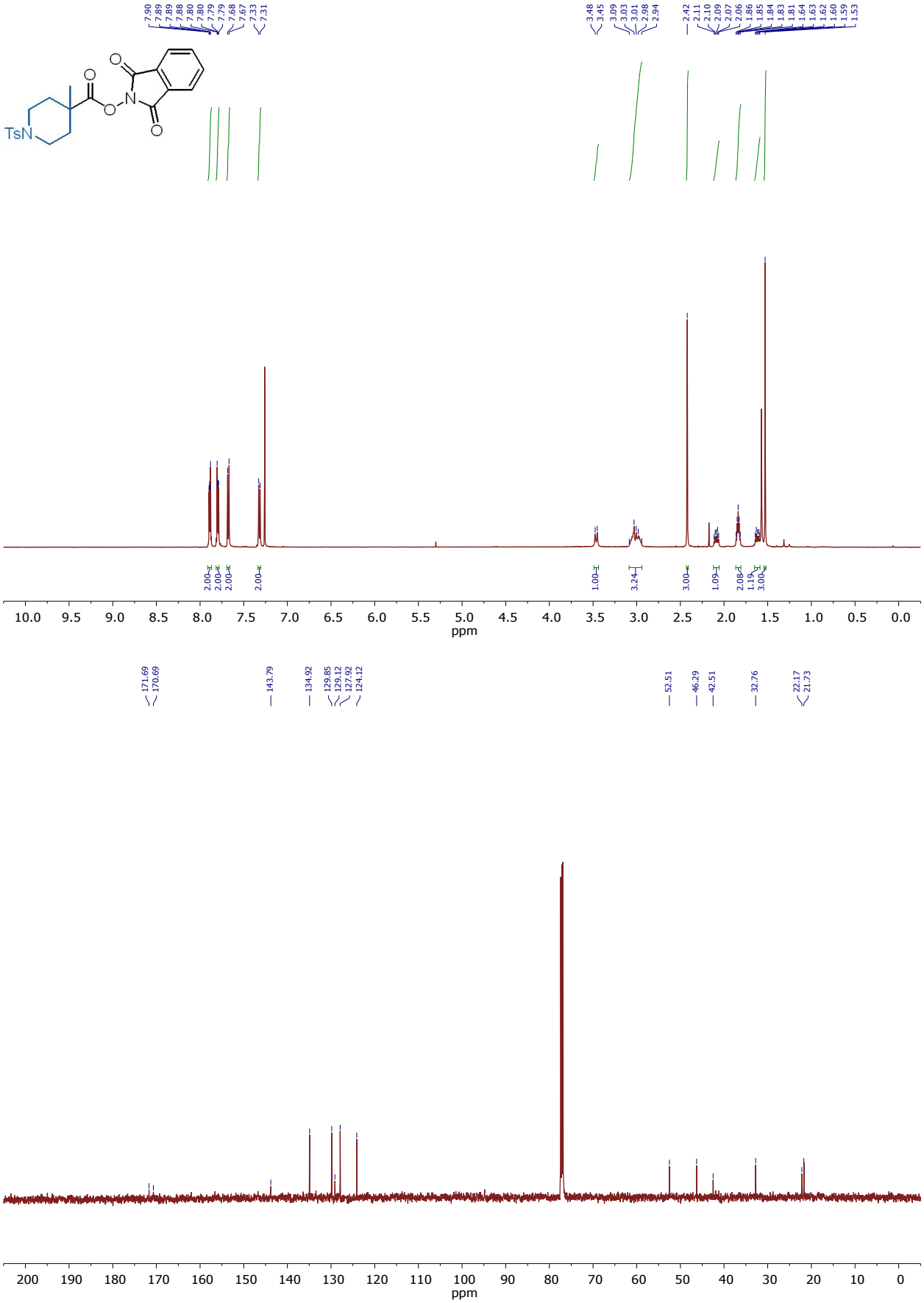


1,3-dioxoisoindolin-2-yl 4-phenoxybutanoate (3b)

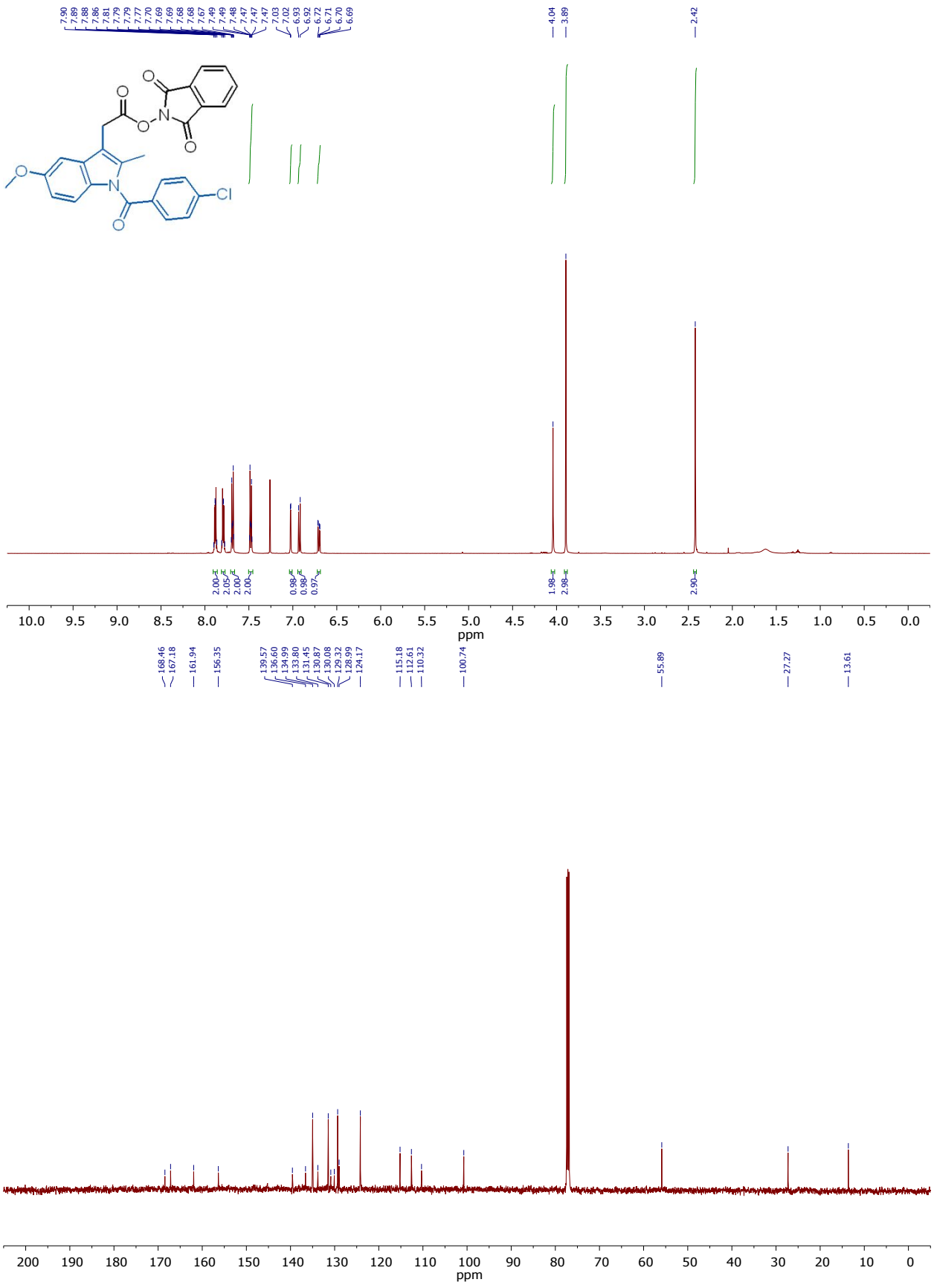




1,3-dioxoisoindolin-2-yl 4-methyl-1-tosylpiperidine-4-carboxylate (5b)



1,3-dioxoisoindolin-2-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (8b)



1,3-dioxoisoindolin-2-yl 2-(2-((2,6-dichlorophenyl)amino)phenyl)acetate (9b)