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PET-RAFT single unit monomer insertion of *β*-methylstyrene derivatives: RAFT degradation and reaction selectivity

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1. Materials and instrumentation

1.1. Materials

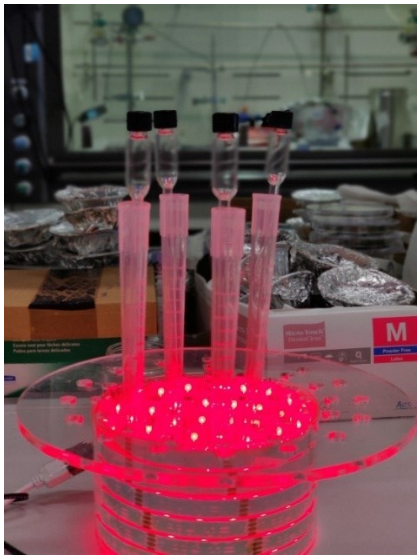
N-phenylmaleimide (PMI, 97%), *trans*-anethole (Ane, 99%) and 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine zinc (ZnTPP, 98%) were purchased from Sigma-Aldrich and used as received. Acrylonitrile (ACN, 99%) and trans-*β*-methyl styrene (MeSt) were purchased from Sigma-Aldrich and purified with a column of basic alumina before use. (2-Cyanopropan-2-yl) butyl trithiocarbonate (CPBTC) and *n*-butyl benzyl trithiocarbonate (BBTC) were synthesized according to previous procedures.[1-2] Dimethyl sulfoxide (DMSO), DMSO-d_6, chloroform, chloroform-*d*, *n*-hexane, ethyl acetate, were purchased from Ajax Chemical and used as received.

1.2. Instrumentation

Nuclear magnetic resonance (NMR) spectroscopy was carried out on a Bruker Advance III (400 MHz) with SampleXpress operating at 400 MHz for ^{1}H, ^{13}C, ^{1}H-^{13}C HMBC and ^{1}H-^{13}C HSQC using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as a reference. The data obtained was reported as chemical shift (δ) measured in ppm downfield from TMS.

Biotage® (Isolera One) **automated flash chromatography** with SNAP Ultra cartridges and ZIP Sphere cartridges was used for the purification and separation of desired SUMI products.

Photo reactors were irradiated by LED RGB strip light rearranged in a glass bath with a diameter of 12 cm (red light: λ_{max} = 635 nm, 0.23 mW cm^{-2}) as shown below.



2. Synthesis of RAFT agents

Synthesis of CPBTC-PMI: CPBTC (260 mg, 1.11 mmol), PMI (231 mg, 1.33 mmol) and ZnTPP (6 mg, 0.009 mol) was dissolved in 10 mL DMSO in a 21 mL glass vial. The vial was sealed with a rubber septum and the reaction solution was degassed with nitrogen for 20 min. Then the reaction mixture was irradiated under red LED light (0.23 mW cm^{-2}) at room temperature. After 30 h, 30 mL $CHCl_3$ was added to the reaction solution and 30 mL deionized water was also added to extract DMSO from $CHCl_3$. The extraction step was repeated three times and the organic phase was collected. The solvent $CHCl_3$ was removed, and the crude mixture was purified by column chromatography using *n*-hexane/ethyl acetate (50/1 to 10/1, v/v) as gradient eluent. The final product was yellow oil (yield: 90%).

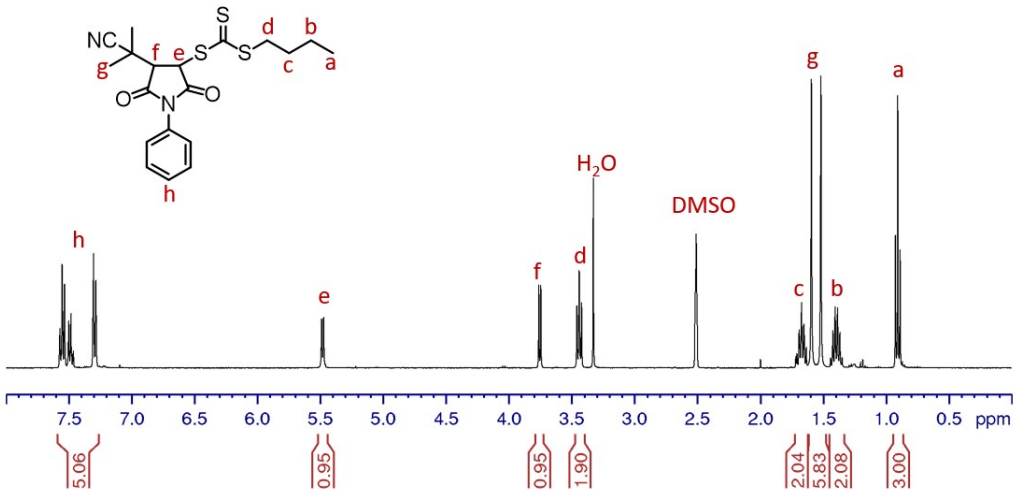
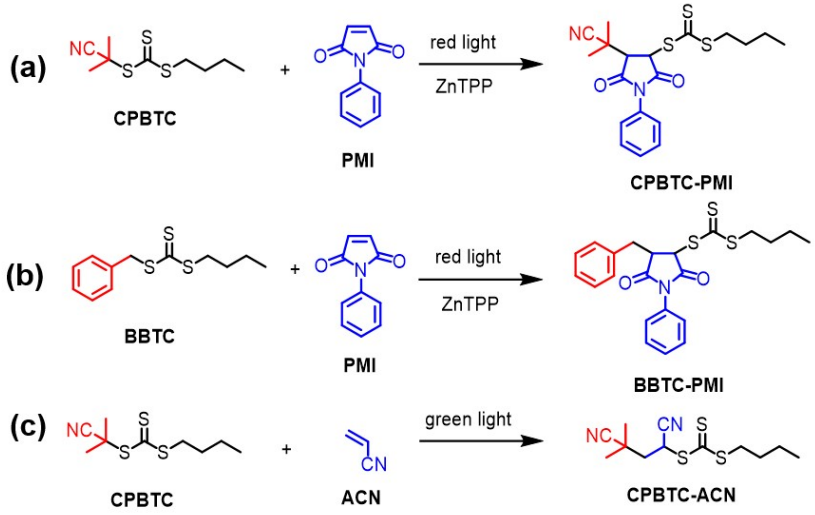


Fig. S1 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of purified CPBTC-PMI.

The synthetic procedure of BBTC-PMI and CPBTC-ACN refers to our previous report.[3]

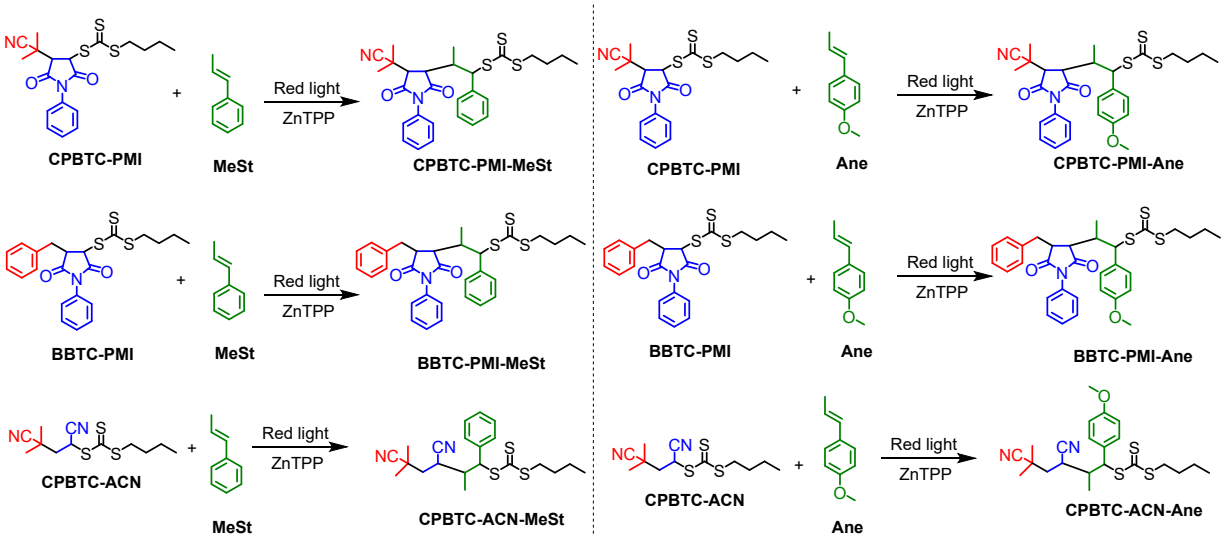


Scheme S1. Synthetic routes of CPBTC-PMI, BBTC-PMI, and CPBTC-ACN.

3. Kinetic investigation of MeSt and Ane into different RAFT agents

3.1. Kinetic experiment

The kinetic experiment was carried out in DMSO-d_6 by monitoring RAFT agent consumption using online ^{1}H NMR spectroscopy. Different RAFT agents, β-methylstyrene derivatives (MeSt or Ane), ZnTPP was dissolved in 600 μL DMSO-d_6 with the molar ratio of [RAFT]:[MeSt or Ane]:[ZnTPP] = 1:10:0.01 and [RAFT] = 0.05 mol L^{-1}. Then the solution was transferred into a screw-cap NMR tube, which was sealed and degassed by nitrogen for 10 min. The reaction mixture was then irradiated under red LED strip (0.23 mW cm^{-2}) at room temperature. At different time intervals, the NMR spectrum was collected, which are used for the analysis and quantification of RAFT agents consumption and products formation.



Scheme S2. Summary of six reactions for SUMI of MeSt or Ane into three different macro-RAFT agents for kinetic investigations.

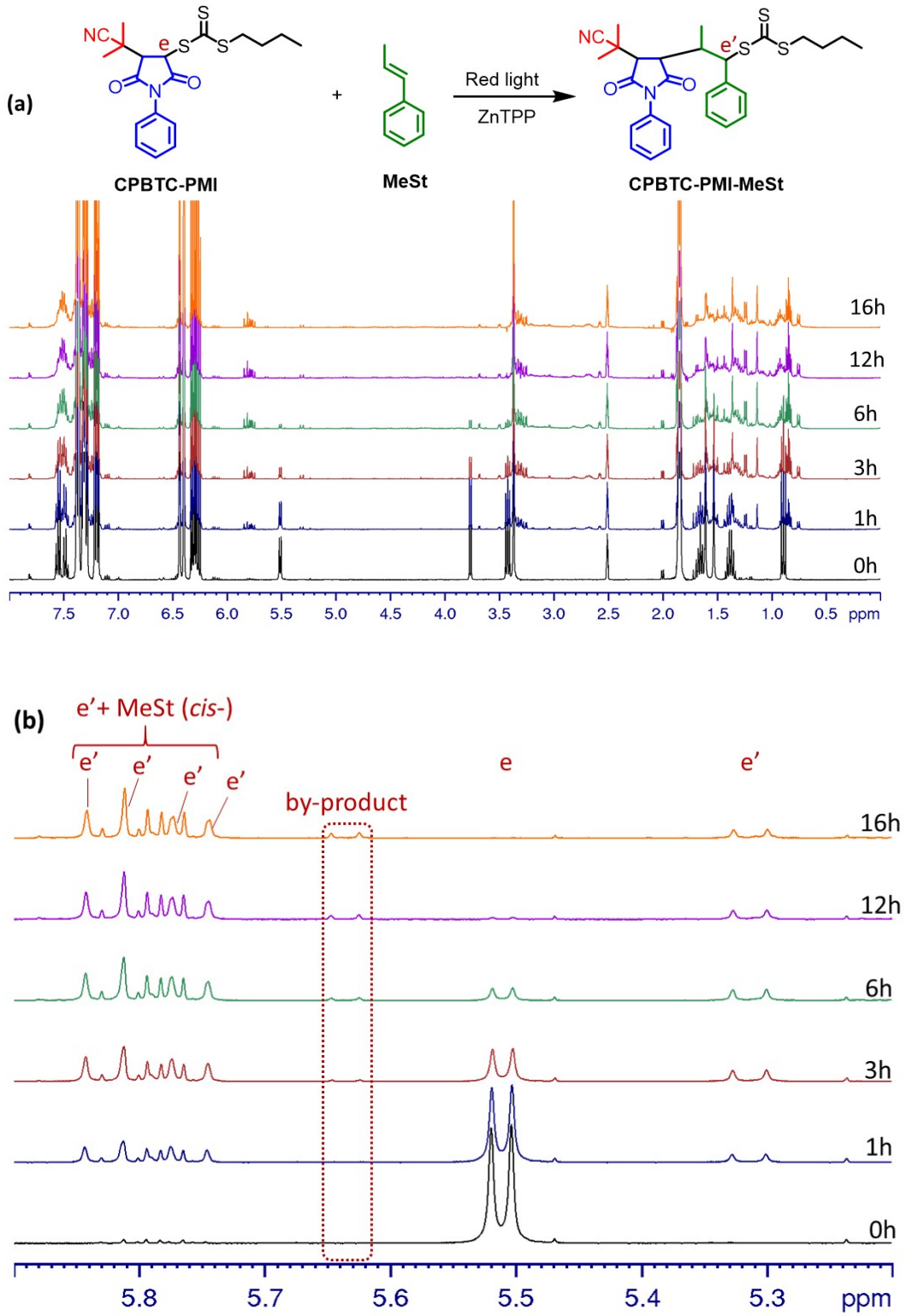


Fig. S2 Stacked ^{1}H NMR (DMSO-d_6, 400 MHz) spectra: (a) full and (b) enlarged spectra at different irradiation time for investigating SUMI kinetics of MeSt insertion into CPBTC-PMI. *Note:* There are four doublet peaks for the proton e' in the terminal unit adjacent to thiocarbonylthio group that correspond to four diastereomers. However, two doublet peaks are overlapped at 5.85~5.80 ppm with the *cis*-isomer of MeSt (refer to **Fig. S14** for the peaks of MeSt *cis*-isomer in the area).

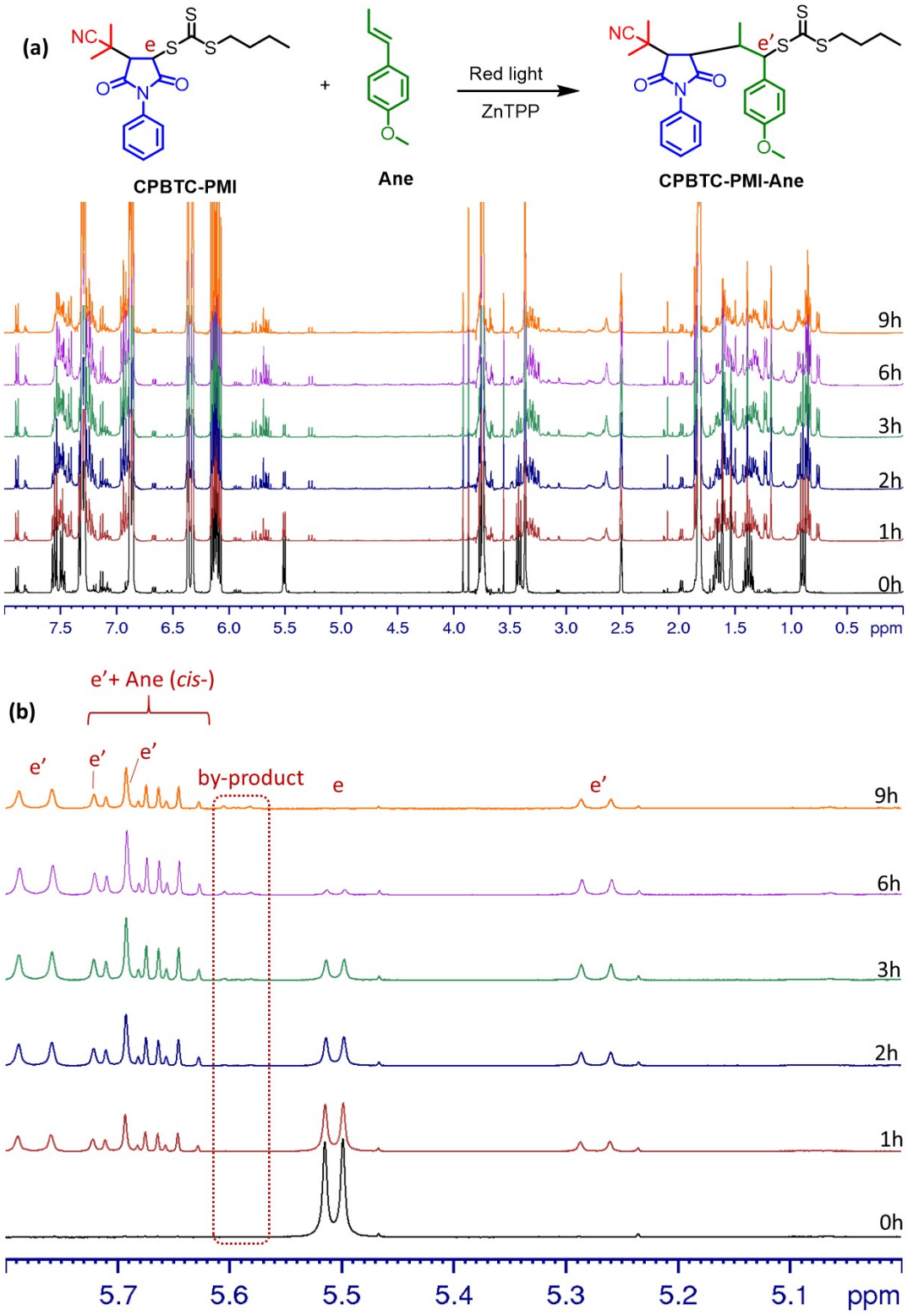


Fig. S3 Stacked ^{1}H NMR (DMSO-d_6, 400 MHz) spectra: (a) full and (b) enlarged spectra at different irradiation time intervals for investigating SUMI kinetics of Ane insertion into CPBTC-PMI. *Note:* There are four doublet peaks for the proton e' in the terminal unit adjacent to thiocarbonylthio group that correspond to four diastereomers. However, two doublet peaks are overlapped at 5.70 ppm with the *cis*-isomer of Ane (refer to **Fig. S15** for the peaks of Ane *cis*-isomer in the area).

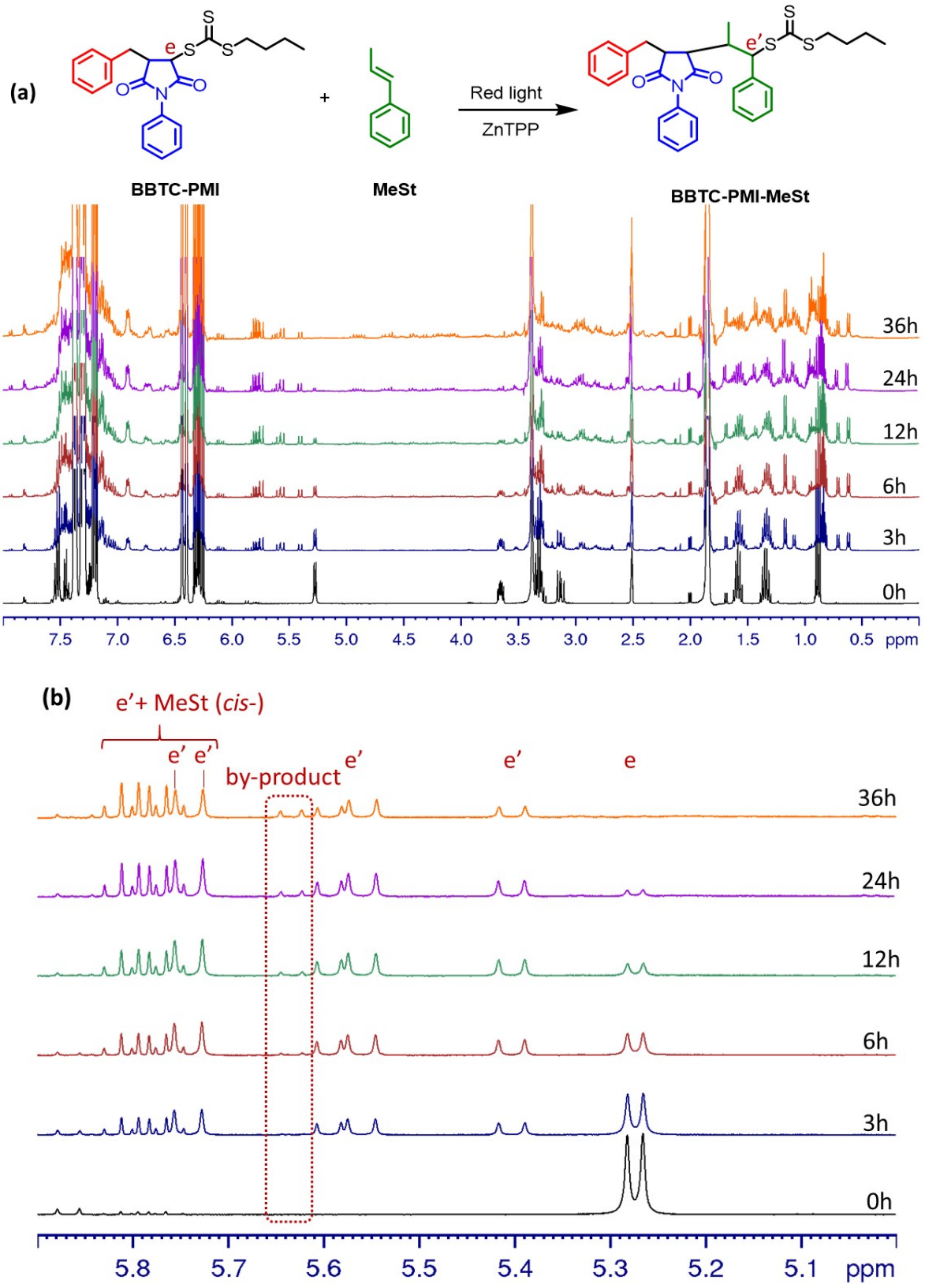


Fig. S4 ^{1}H NMR (DMSO-d_6, 400 MHz) stacked (a) full and (b) enlarged spectra at different irradiation time intervals for investigating SUMI kinetics of MeSt insertion into BBTC-PMI.

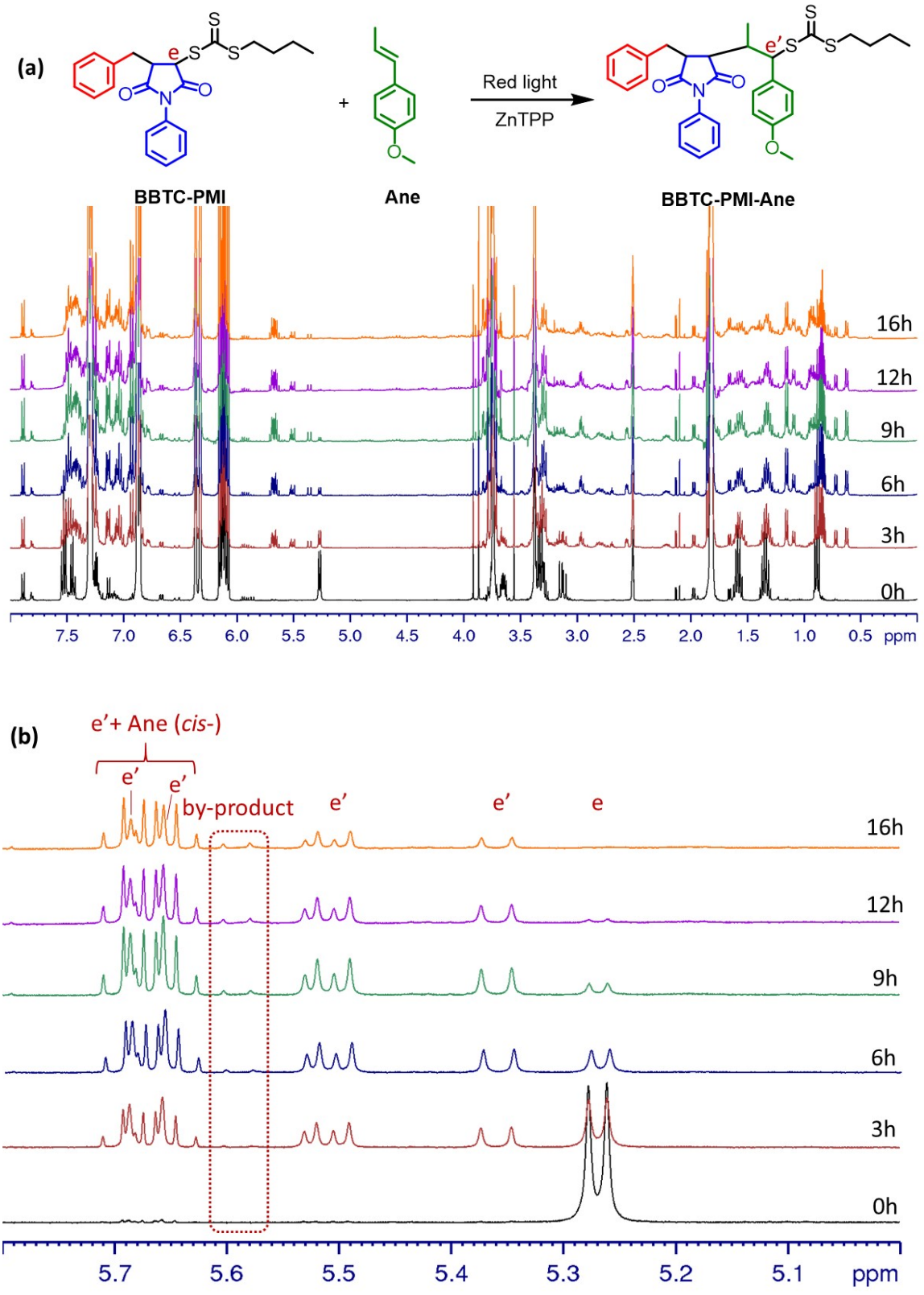


Fig. S5 ^{1}H NMR (DMSO-d_6, 400 MHz) stacked (a) full and (b) enlarged spectra at different irradiation time intervals for investigating SUMI kinetics of Ane insertion into BBTC-PMI.

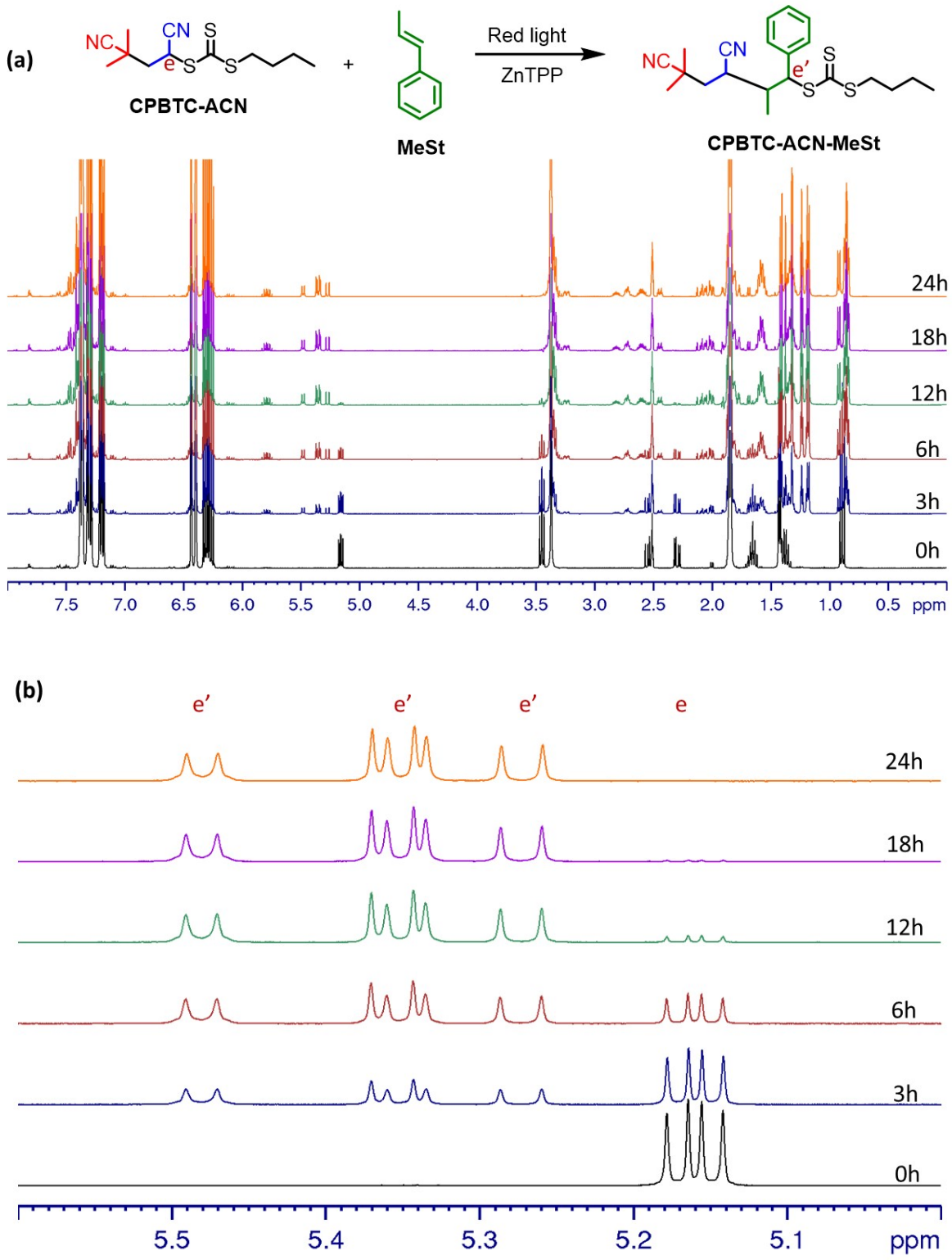


Fig. S6 ^{1}H NMR (DMSO-d_6, 400 MHz) stacked (a) full and (b) enlarged spectra at different irradiation time intervals for investigating SUMI kinetics of MeSt insertion into CPBTC-ACN.

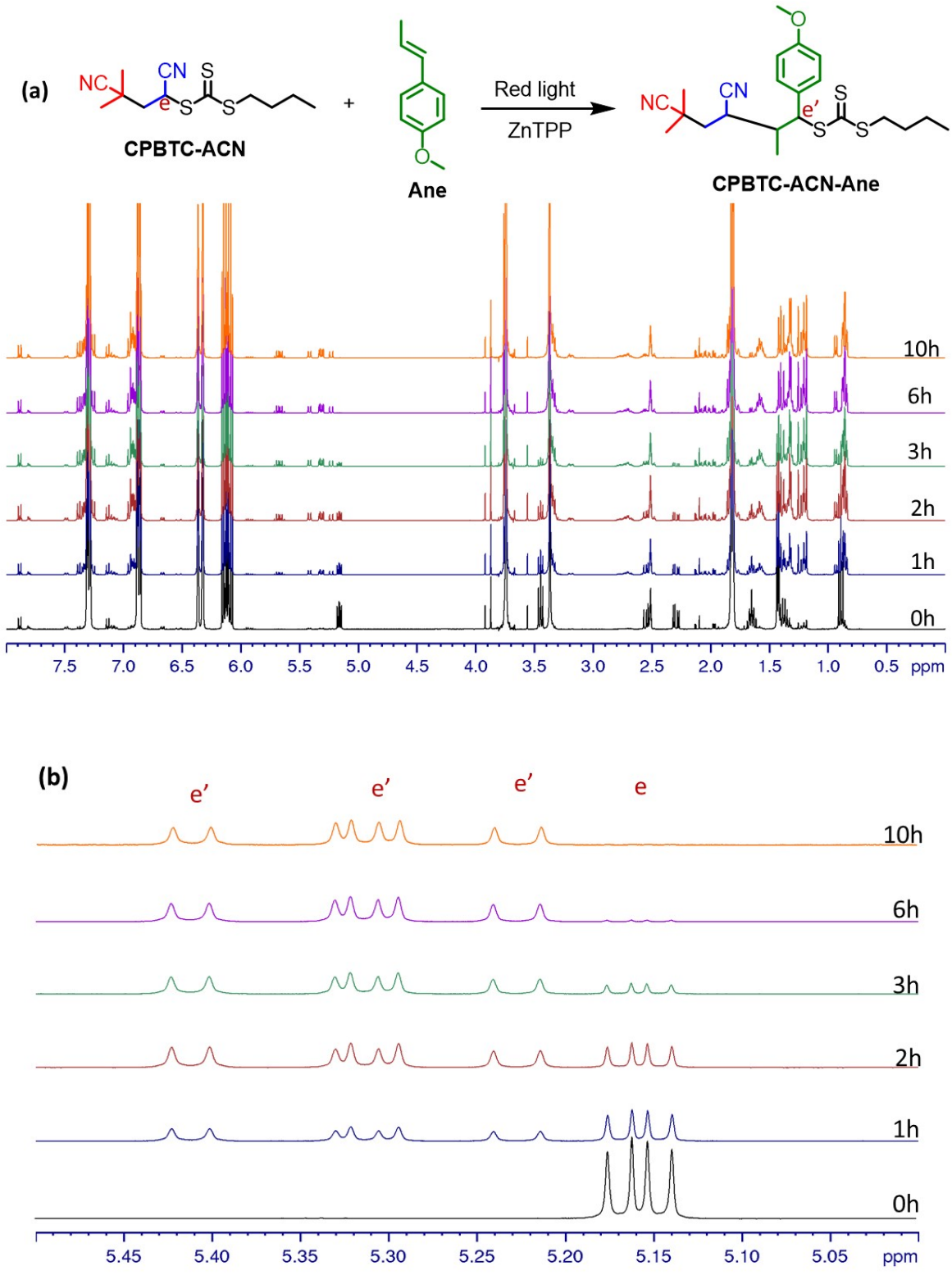


Fig. S7 ^{1}H NMR (DMSO-d_6, 400 MHz) stacked (a) full and (b) enlarged spectra at different irradiation time intervals for investigating SUMI kinetics of Ane insertion into CPBTC-ACN.

3.2. Purification of SUMI products

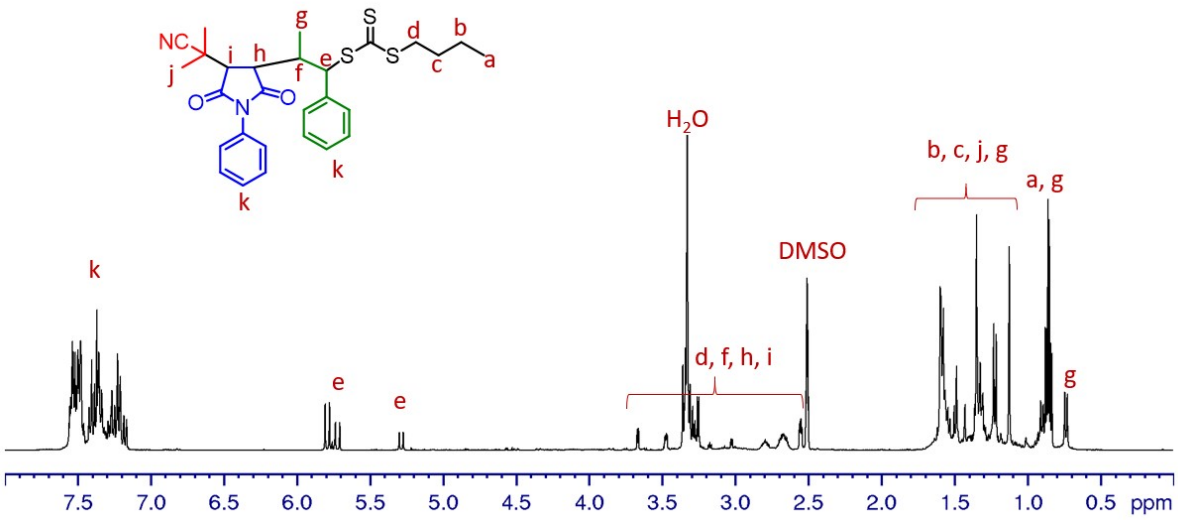


Fig. S8 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of purified CPBTC-PMI-MeSt.

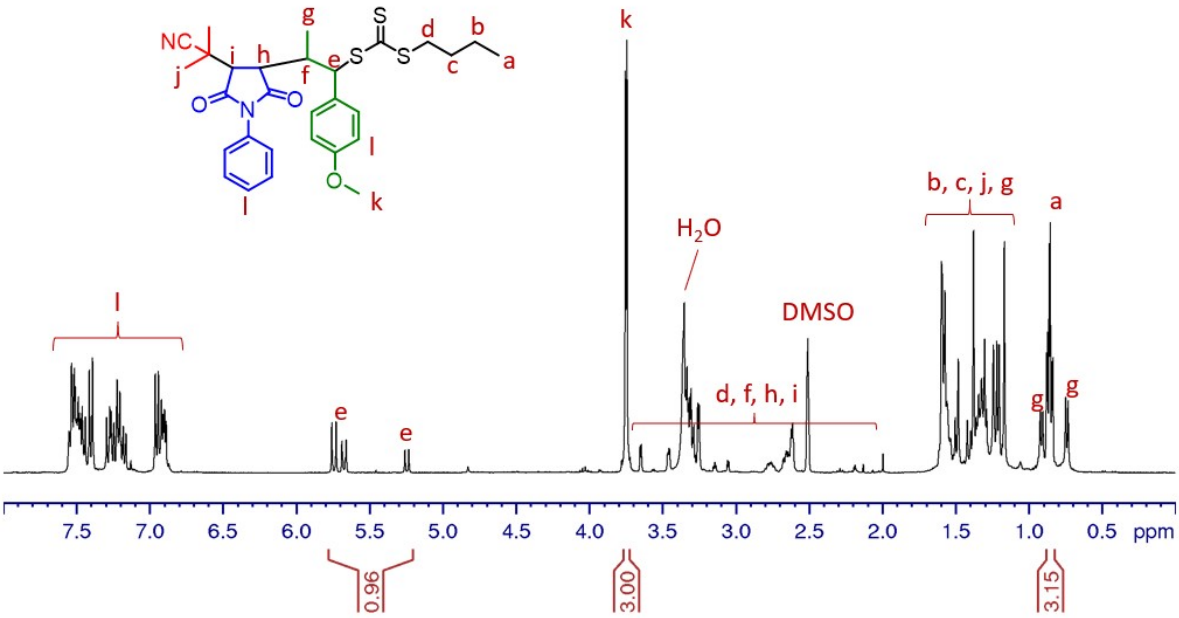


Fig. S9 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of purified CPBTC-PMI-Ane.

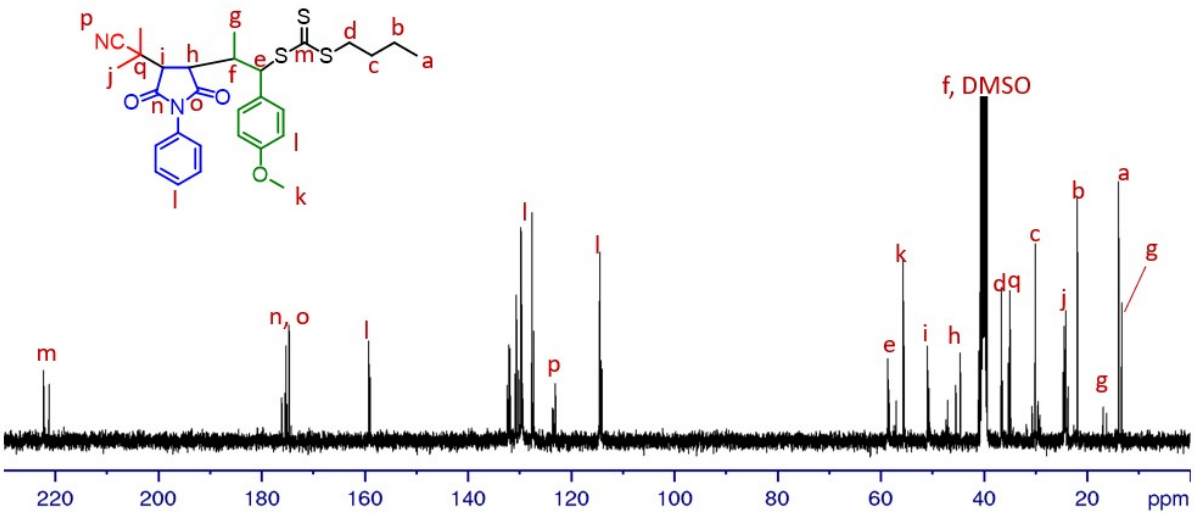


Fig. S10 ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of purified CPBTC-PMI-Ane.

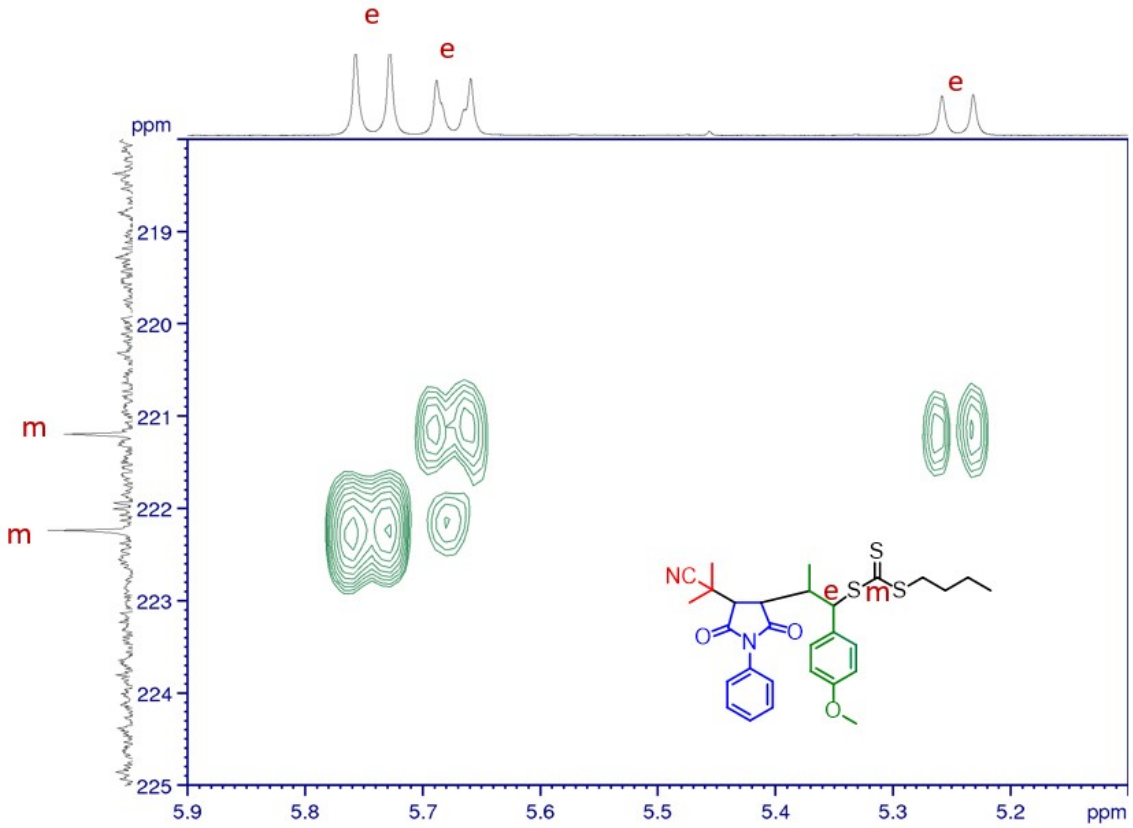


Fig. S11 Enlarged ^{1}H-^{13}C HMBC NMR (DMSO-d_6) spectrum of purified CPBTC-PMI-Ane.

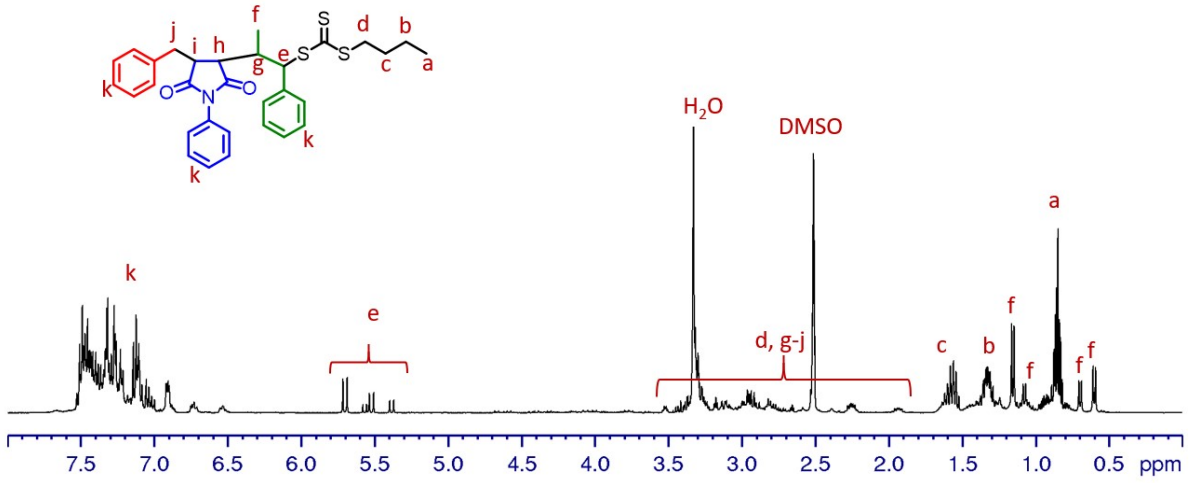


Fig. S12 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of purified BBTC-PMI-MeSt.

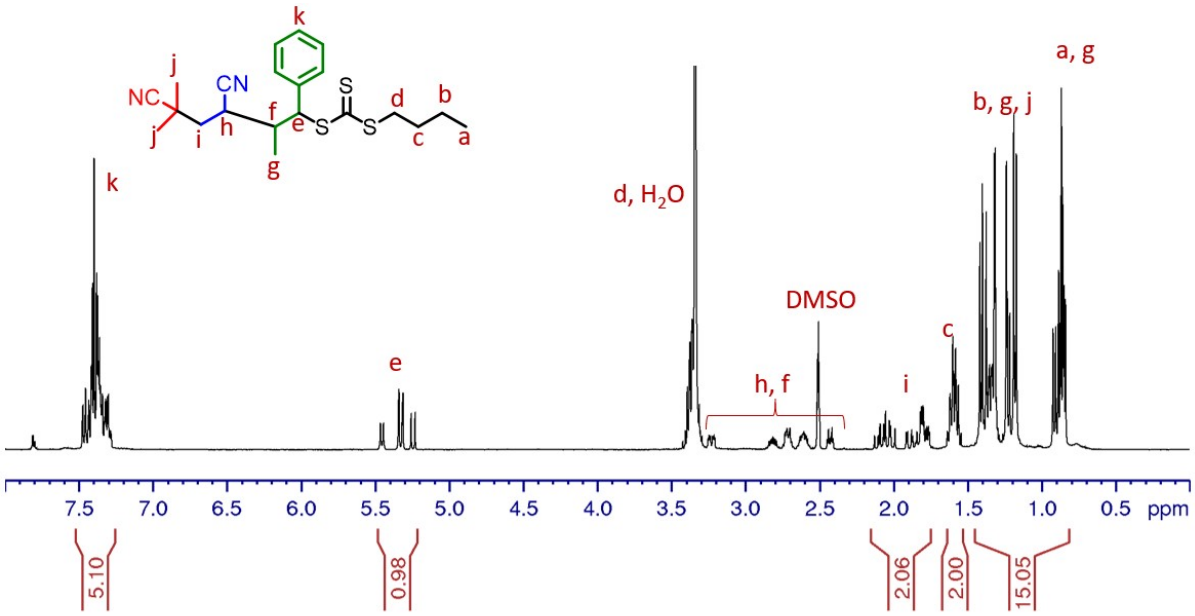


Fig. S13 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of purified CPBTC-ACN-MeSt.

3.3. Photoirradiation of MeSt and Ane

The monomers of MeSt and Ane were irradiated under red light in DMSO-d_6 in the presence of photo-catalyst ZnTPP without any RAFT agents. NMR spectra were collected at different irradiation time to investigate the isomerization under light.

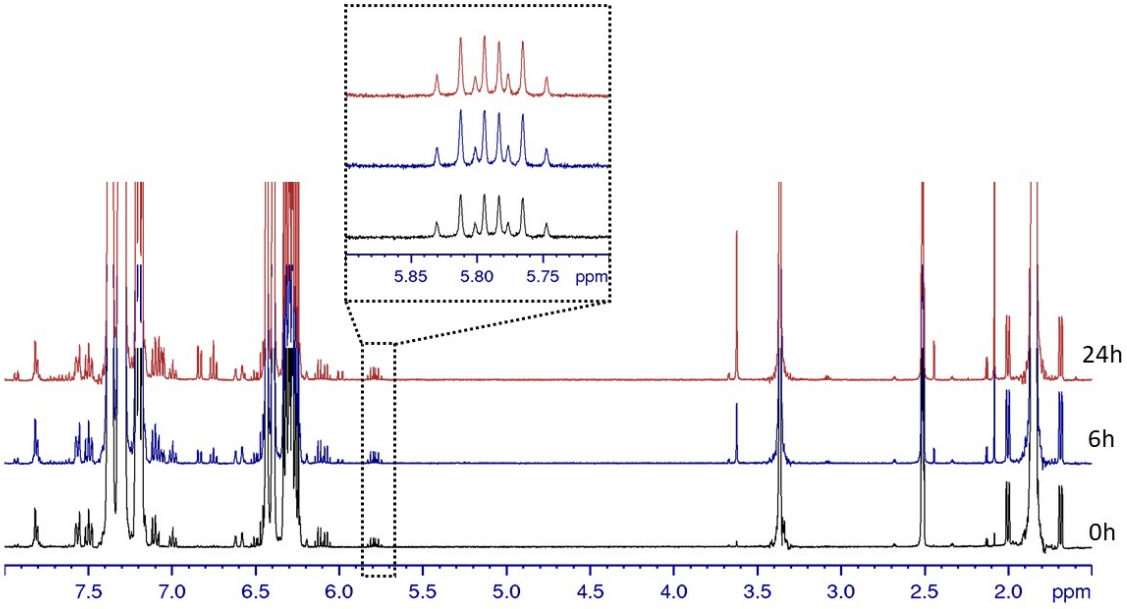


Fig. S14 Stacked NMR spectra of MeSt at different irradiation time, indicating very slight isomerization of *trans*-isomer to *cis*-isomer.

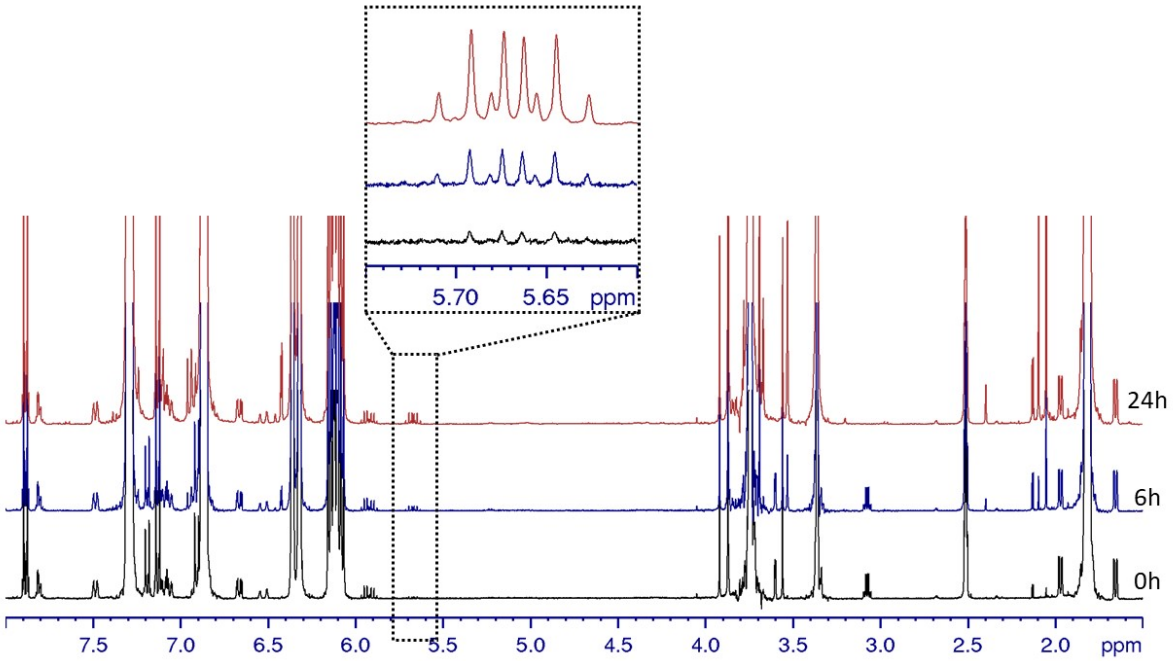


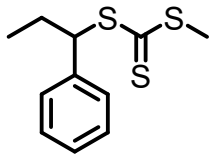
Fig. S15 Stacked NMR spectra of Ane at different irradiation time, indicating slight isomerization of *trans*-

isomer to *cis*-isomer..

4. Quantum chemical calculation

Quantum chemical calculations were carried out using Gaussian 09[4] software. Geometry optimization and frequency analysis of molecules and radicals were performed using density functional theory (DFT) at M06-2X[5]/6-31+G(d,p)[6-12] level using SMD solvent model[13] (DMSO as solvent) at 298.15K.

Cartesian coordinates



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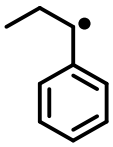

MeSt radical

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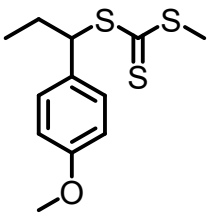

Ane-SCSZ

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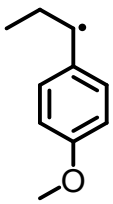

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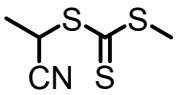

ACN-SCSZ

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ACN radical

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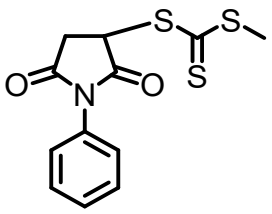

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C, 0, 2. 933630529, -0. 9084994811, 2. 0100760931
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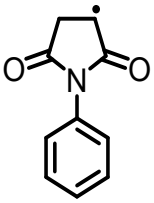

PMI radical \

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C, 0, 1.7476293194, 1.6125531536, 1.4698614017
C, 0, 1.1421485116, 0.4612295655, 0.9698410609
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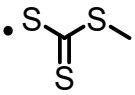

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H, 0, 1.795135681, -0.2514133851, -0.9007211569

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