**Electronic Supplementary Information**

# Sequential and alternating RAFT single unit monomer insertion: model trimers as the guide for discrete oligomer synthesis

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## 1. Experimental Section

**Materials.** dimethyl fumarate (DMF, 97%), fumaronitrile (FCN, 98%), *N*-phenylmaleimide (PMI, 97%), indene (Ind, 98%) and 5,10,15,20-tetraphenyl-21H,23H-porphine zinc (ZnTPP, 98%) were all purchased from Sigma-Aldrich and used as received. *n*-Butyl-1-phenylethyl trithiocarbonate (BETC) was synthesized according to the reported literature[1]. dimethyl sulfoxide (DMSO), dichloromethane, *n*-hexane and silica gel (40~63 micron) were purchased from Ajax Chemical and used as received.

**Instrumentation.** Nuclear magnetic resonance (NMR) spectroscopy was carried out on a Bruker Advance III with SampleXpress operating at 300 MHz, 400 MHz and high-resolution Bruker Advance III HD 600 MHz Cryoprobe for $^{1}$H, $^{13}$C, $^{1}$H-$^{13}$C HMBC, $^{1}$H-$^{13}$C HSQC and online kinetics using $CDCl_3$ or DMSO-$d_6$ as solvent. Data obtained was reported as chemical shift ($\delta$) measured in ppm.

Electrospray ionization mass spectroscopy (ESI-MS) was attained using a Finnigan LCQ Deca mass spectrometer (Thermo Finnigan, San Jose, CA) equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray voltage of 5 kV, with nitrogen as sheath gas. Xcalibur ver. 1.3 (Finnigan) was used for spectral processing.

**Photopolymerization reactions.** The SUMI reactions were carried out in the reaction vessel where the reaction mixtures are irradiated by RS Component PACK LAMP RGB red LED lights (5W, $\lambda_{max}$ = 635 nm). The distance of the sample to the light bulb was around 6 cm (0.4 mW cm$^{-2}$ for red light). Online kinetic studies for SUMI process were conducted in the screw-cap NMR tubes irradiated by a 5050 SMD RGB red LED strip light (3 meters with 180 LEDs, $\lambda_{max}$ = 635 nm). The samples were placed in the centre of round bath reactor (a

diameter of 9 cm, 0.46 mW $cm^{-2}$ with the red LED strip). The red LED strip light with remote control were purchased from RS Components Australia (**Figure S1**).

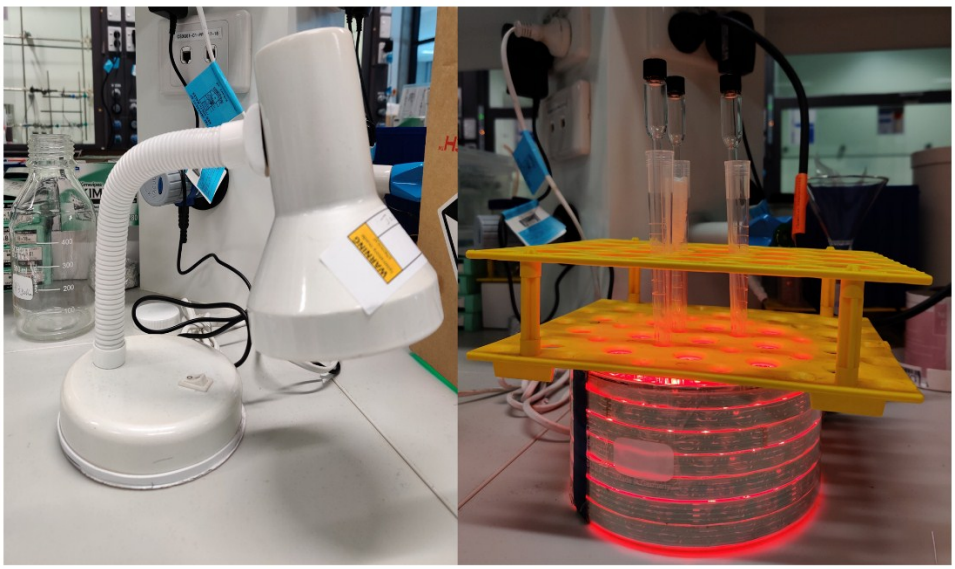


**Figure S1.** LED lamp (left) and LED strip (right) utilized for SUMI reactions and online kinetic studies.

**General Synthetic Procedure of SUMI reaction.** Taking the SUMI reaction of BETC-F as an example. A solution containing RAFT agent (BETC, 120 mg, 0.44 mmol), monomer (FCN, 173 mg, 2.22 mmol), photocatalyst (ZnTPP, 1.5 mg, 0.0022 mmol) and DMSO (1 mL) was prepared in a 4 mL glass vial, using the molar ratio [FCN]/[BETC]/[ZnTPP] = 5/1/0.005. The glass vial was sealed with a rubber septum and the reaction solution was degassed with nitrogen for 20 min. The reaction mixture was irradiated under red LED lamp ($\lambda_{max}$ = 635 nm, 0.46 mW $cm^{-2}$) at room temperature. After 24 h light irradiation, DMSO was removed by water extraction. The crude product was then subject to flash chromatography using Biotage® flash chromatography. The final product (136 mg, isolated yield 88%) was subjected for $^{1}H$, $^{13}C$, $^{1}H$-$^{13}C$ HMBC, and $^{1}H$-$^{13}C$ HSQC NMR analysis.

**Kinetics of SUMI by online $^{1}H$ NMR spectroscopy.**

***First monomer unit insertion:*** The kinetic study of PMI, FCN and DMF monomer insertions was performed in DMSO-$d_6$ by monitoring RAFT conversion using online $^{1}H$ NMR spectroscopy. For the SUMI reaction of FCN monomers into initial RAFT agent BETC, a stock solution containing initial RAFT agent (BETC, 15.0 mg, 0.05 mmol), monomer (FCN, 21.6 mg, 0.27 mmol); photocatalyst (ZnTPP, 0.18 mg, $2.7\times10^{-4}$ mmol) and DMSO-$d_6$ (360

μL) was prepared in a 4 mL glass vial, using the molar ratio [FCN]/[BETC]/[ZnTPP] = 5/1/ 0.005. Next, the reaction solution was transferred into a screw-cap NMR tube, which was then sealed and degassed with nitrogen for 20 min. For SUMI reactions of PMI and DMF monomers into BETC, the preparation procedures were similar with FCN SUMI reaction except different molar ratios, in which [PMI]/[BETC]/[ZnTPP] = 1/1/ 0.005, and [DMF]/[BETC]/[ZnTPP] = 5/1/ 0.005 were used, respectively. After deoxygenation, these three screw-cap NMR tubes containing different reaction mixtures were irradiated under red LED strip ($\lambda_{max}$ = 635 nm, 0.46 mW cm$^{-2}$) at room temperature. To analyse the RAFT agent conversion, these NMR tubes were transferred into the sample holder manually for NMR analysis at predetermined time intervals. After 3 min scanning, the NMR tubes were moved back into light.

***Second monomer unit insertion:*** The kinetic study of SUMI of indene (Ind) into BETC-M, BETC-F and BETC-Q was performed in DMSO-$d_6$ by monitoring macro-RAFT conversions using online $^1$H NMR spectroscopy. For the SUMI reaction of Ind monomers into macro-RAFT agent BETC-F, a stock solution containing synthesized macro-RAFT (BETC-F, 21 mg, 0.06 mmol), monomer (Ind, 7.03 μL 0.06 mmol), photocatalyst (ZnTPP, 0.2 mg, 2.9×10$^{-4}$ mmol) and DMSO-$d_6$ (514 μL) was prepared in a 4 mL glass vial, using the molar ratio [Ind]/[BETC-F]/[ZnTPP] = 1/1/ 0.005. Afterwards, the reaction solution was transferred into a screw-cap NMR tube, which was then sealed and degassed with nitrogen for 20 min. For SUMI reaction of Ind monomers into macro-RAFT agent BETC-M and BETC-Q, the preparation procedures were similar with that in BETC-F reaction using different molar ratio, in which [Ind]/[BETC-M or BETC-Q]/[ZnTPP] = 5/1/ 0.005 was used. After deoxygenation, these three screw-cap NMR tubes containing different second step reaction mixtures were irradiated under red LED strip ($\lambda_{max}$ = 635 nm, 0.46 mW cm$^{-2}$) at room temperature. To analyse the RAFT agent conversion, these NMR tubes were transferred into the sample holder manually for NMR analysis at predetermined time intervals. After 3 min scanning, the NMR tubes were moved back into light.

***Third monomer unit insertion:*** The kinetic study of nine SUMI reactions was performed in DMSO-$d_6$ by monitoring macro-RAFT conversions using online $^1$H NMR spectroscopy. For the SUMI of PMI into BETC-F-I, a stock solution containing synthesized macro-RAFT (BETC-F-I, 12 mg, 0.02 mmol), monomer (PMI, 4.47 mg, 0.02 mmol), photocatalyst (ZnTPP, 0.07 mg, 1×10$^{-4}$ mmol) and DMSO-$d_6$ (360 μL) was prepared in a 4 mL glass vial, using the molar ratio [PMI]/[BETC-F-I]/[ZnTPP] = 1/1/ 0.005. Afterwards, the reaction solution was

transferred into a screw-cap NMR tube, which was then sealed and degassed with nitrogen for 20 min. The molar ratios for the other eight monomer insertions were shown in **Table 1** (#8 ~ #15). After deoxygenation, those screw-cap NMR tubes containing different third step reaction mixtures were irradiated under red LED strip ($\lambda_{max}$ = 635 nm, 0.46 mW $cm^{-2}$) at room temperature. These NMR tubes were transferred into the sample holder manually for NMR analysis at predetermined time intervals. After 3~8 min scanning, the NMR tubes were moved back into light.

**General procedure for the purification of SUMI products.** The SUMI products were purified by Biotage® (Isolera One) automated flash chromatography **(Figure S2)**. Again, taking the purification of BETC-F as an example, after the removal of DMSO from the reaction mixture the organic phase was collected and concentrated under vacuum. It was then subjected to Biotage® flash chromatography using Biotage® Sfär Silica HC (High capacity 5g 20 $\mu$m silica) as colum 20/1, v/v) as the gradient eluent. The collected fractio reduced pressure.


**Figure S2.** Biotage® (Isolera One) automated flash chromatography system with a Biotage® Sfär Silica HC 5g.

## 2. Supporting Documents for Results and Discussion Section

### 2.1. Synthesis and SUMI kinetics of nine model trimers

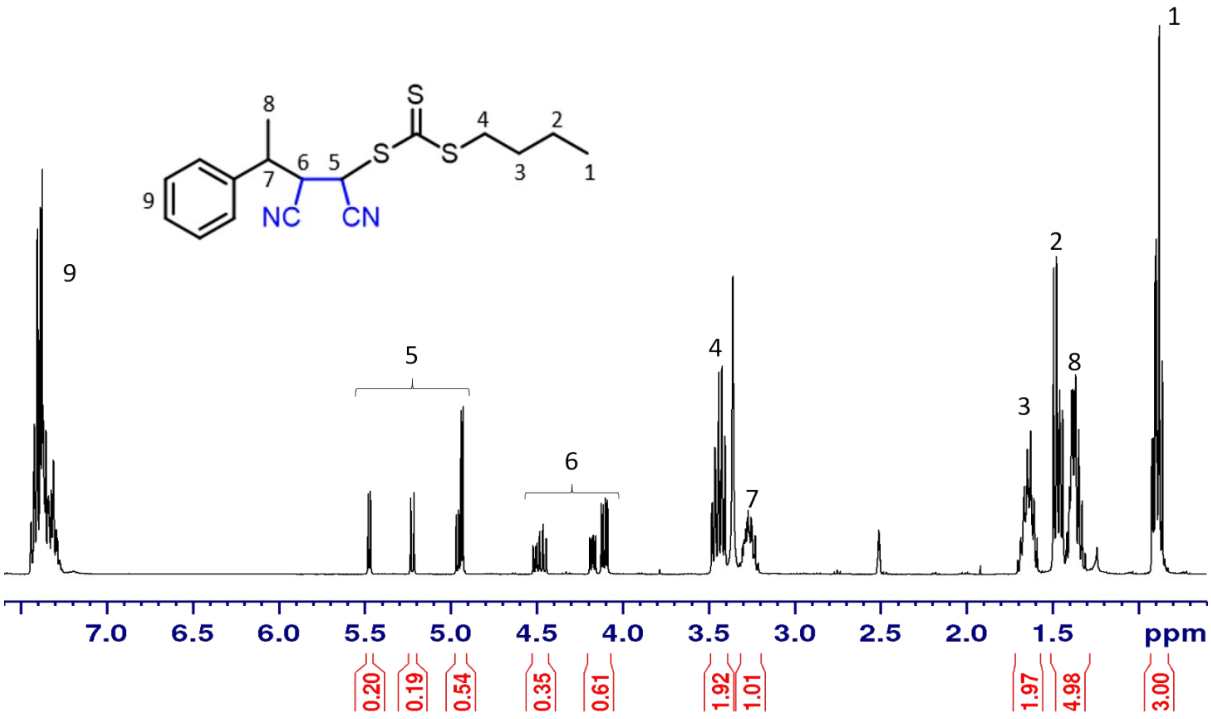



**Figure S3.** $^{1}$H NMR (DMSO-$d_6$, 400 MHz) spectrum of purified SUMI product, BETC-F.

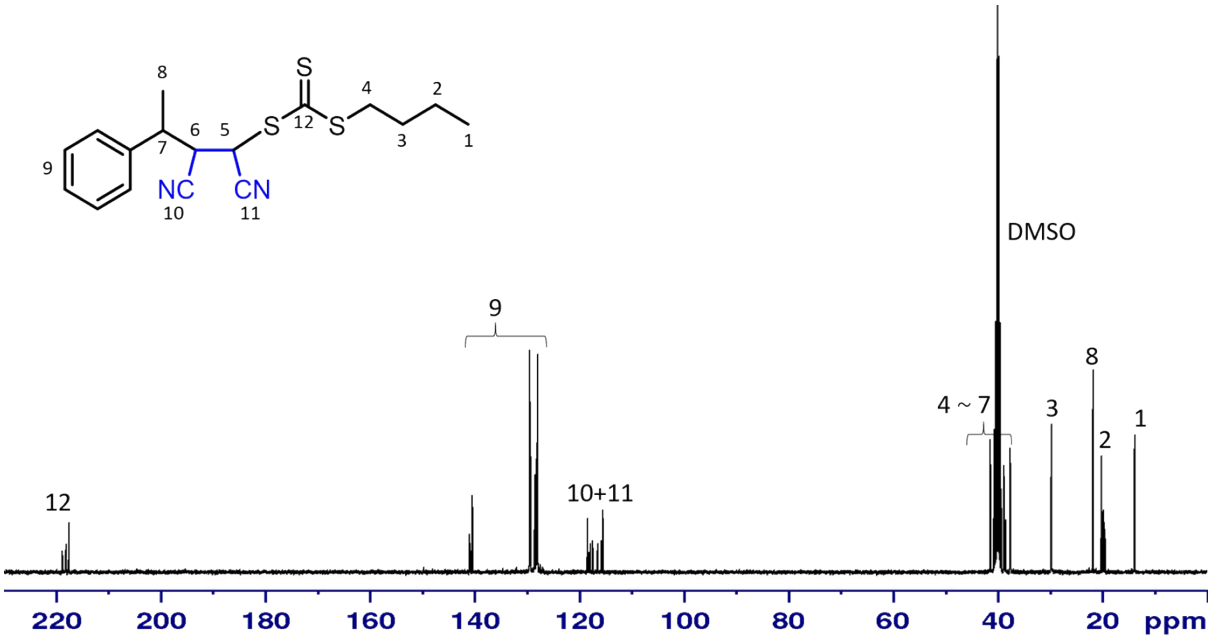



**Figure S4.** $^{13}$C NMR (DMSO-$d_6$, 100 MHz) spectrum of purified SUMI product, BETC-F.

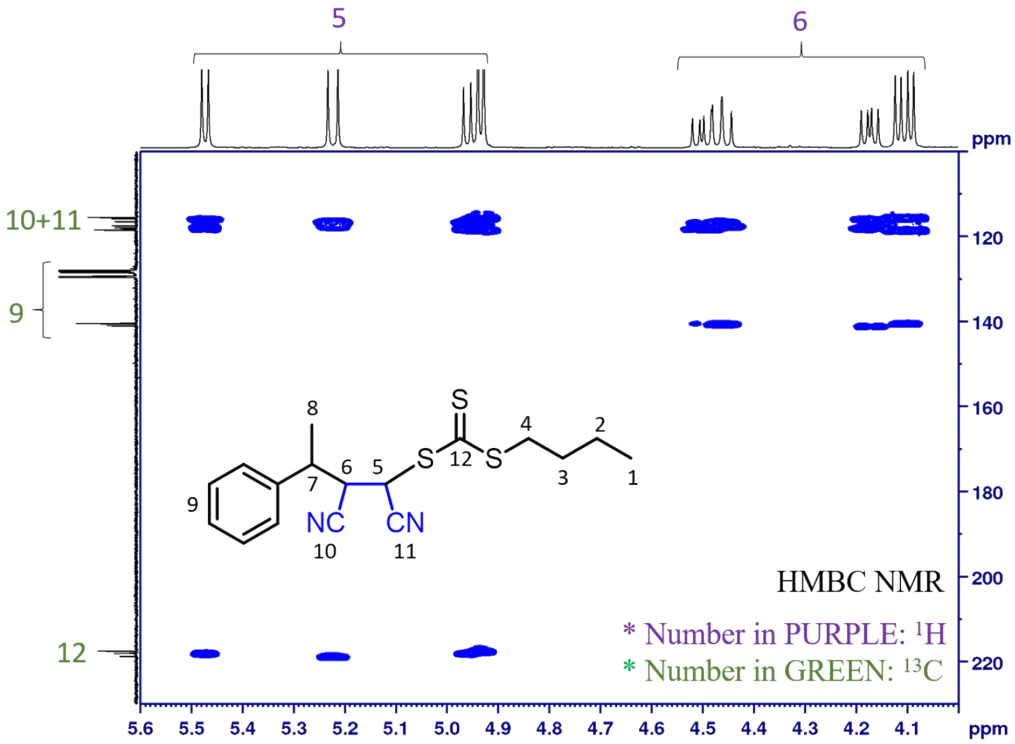



**Figure S5.** Enlarged $^{1}$H-$^{13}$C HMBC NMR (DMSO-$d_6$, $^{1}$H: $\delta$ 4.0~5.6ppm; $^{13}$C: $\delta$ 100~230ppm) spectrum of purified SUMI product, BETC-F.

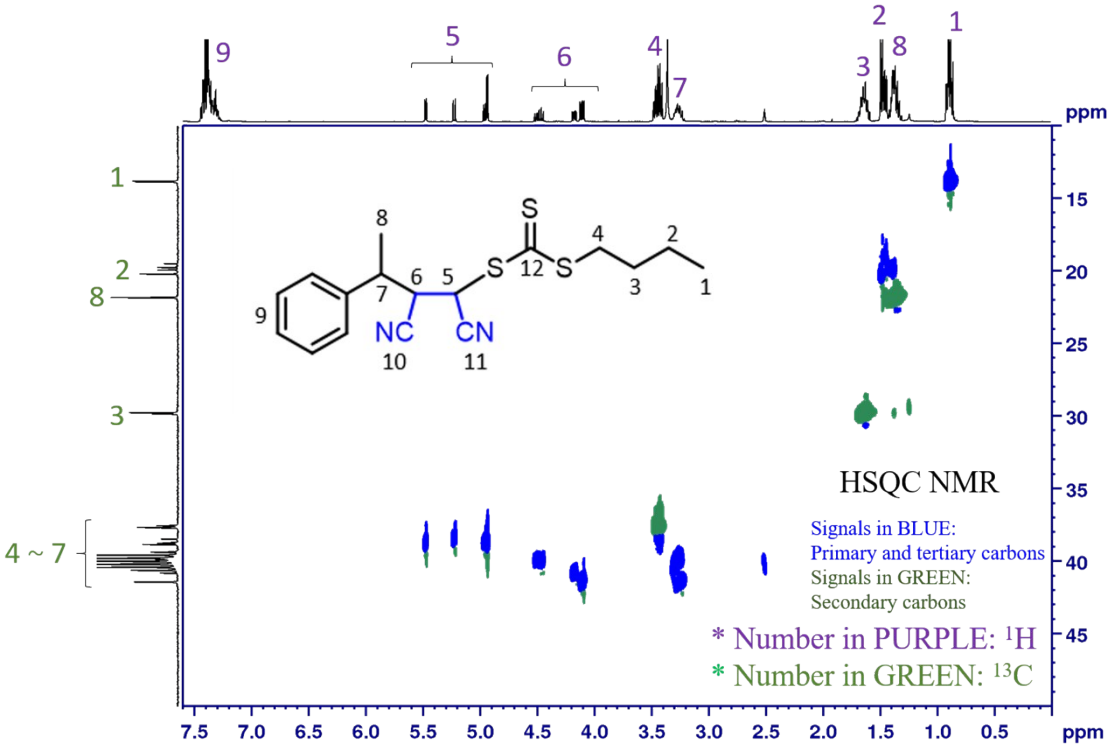



**Figure S6.** Enlarged $^{1}$H-$^{13}$C HSQC NMR (DMSO-$d_6$, $^{1}$H: $\delta$ 0~7.6 ppm; $^{13}$C: $\delta$ 10~55 ppm) spectrum of purified SUMI product, BETC-F.

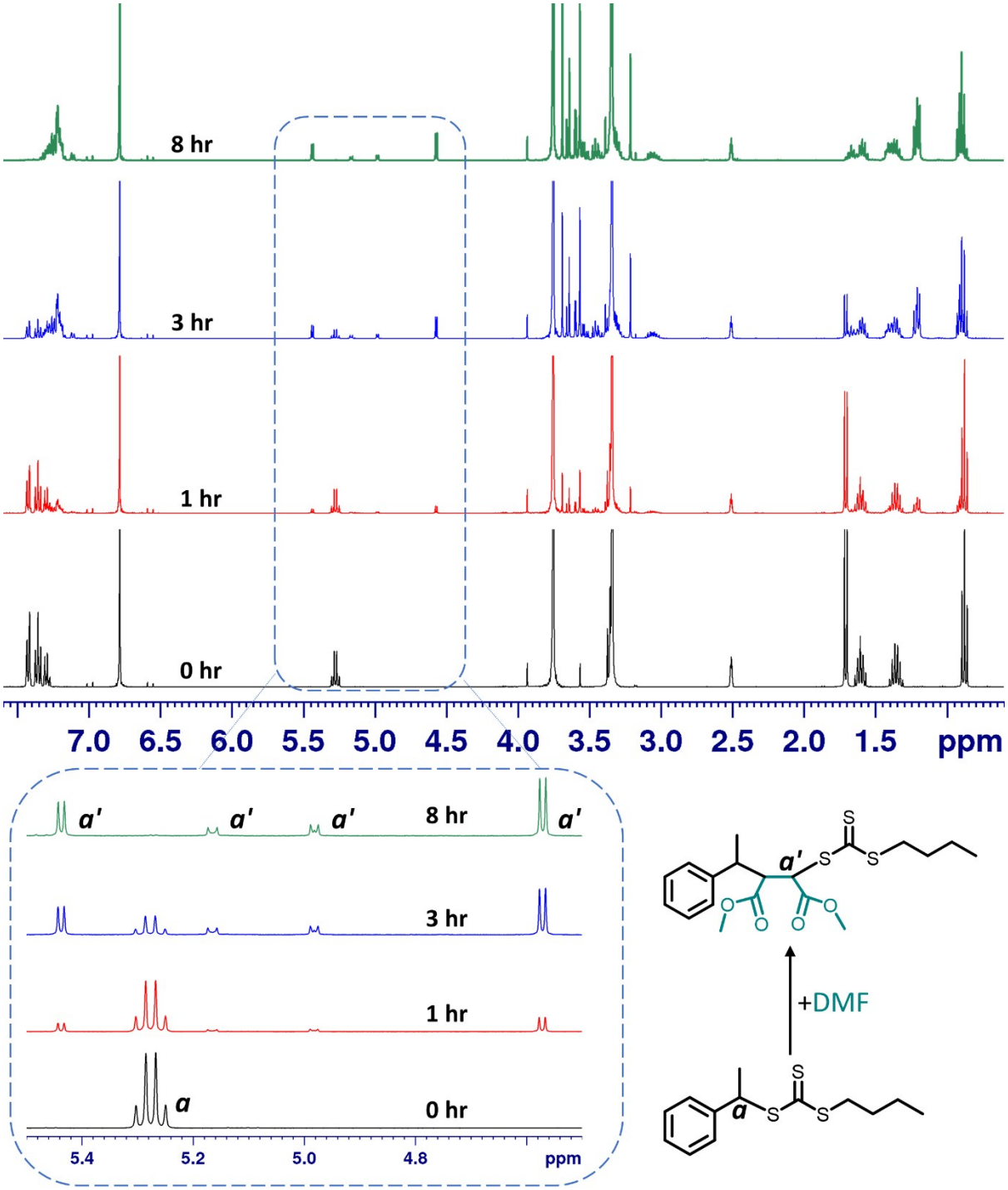



**Figure S7.** The reaction kinetics of SUMI of DMF into BETC. Stacked $^{1}$H NMR (DMSO-$d_6$, 400 MHz) spectra of SUMI of DMF into BETC at different time points.

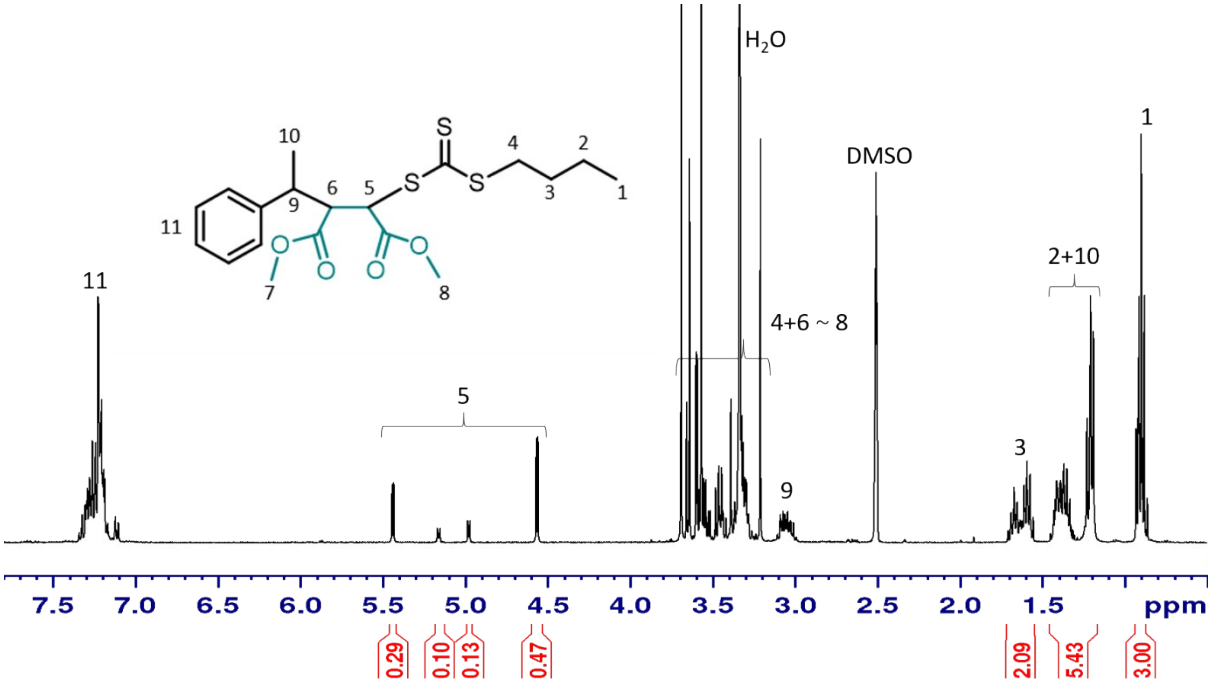



**Figure S8.** $^{1}$H NMR (DMSO-$d_6$, 400 MHz) spectrum of the SUMI product BETC-Q.

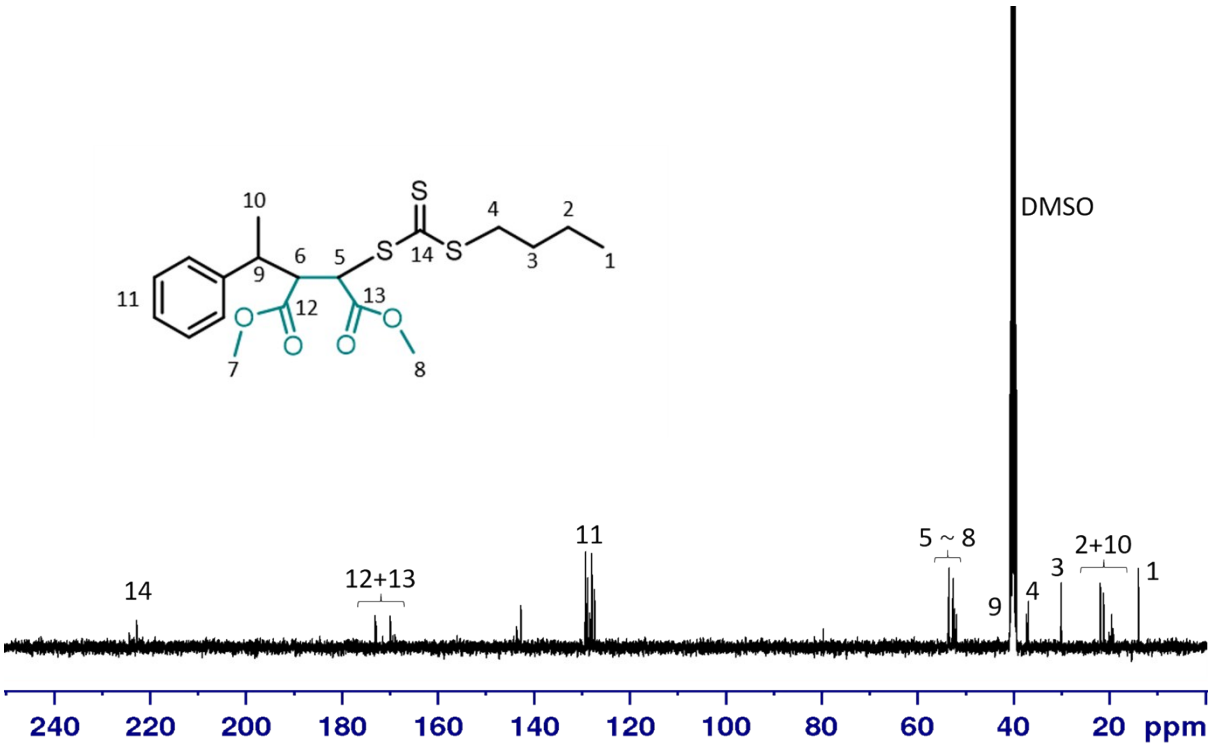



**Figure S9.** $^{13}$C NMR (DMSO-$d_6$, 100 MHz) spectrum of the SUMI product BETC-Q.

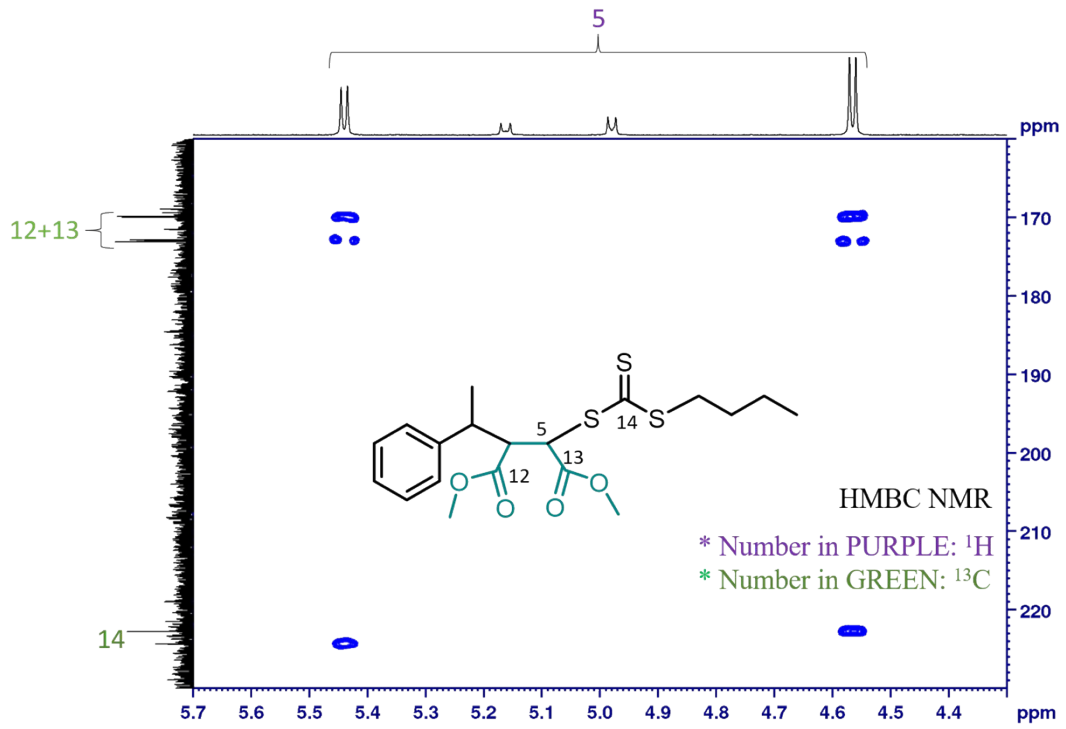



**Figure S10.** Enlarged $^{1}$H-$^{13}$C HMBC NMR (DMSO-$d_6$, $^{1}$H: $\delta$ 4.0~5.7ppm; $^{13}$C: $\delta$ 160~230ppm) spectrum of SUMI product BETC-Q.

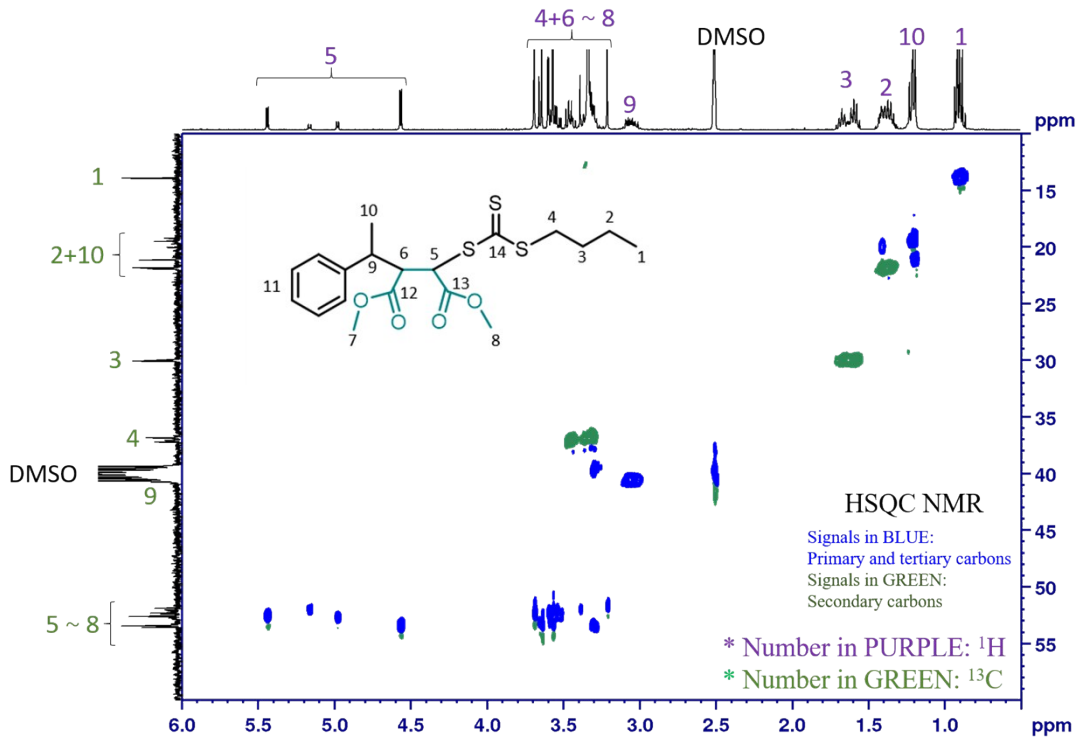



**Figure S11.** Enlarged $^{1}$H-$^{13}$C HSQC NMR (DMSO-$d_6$, $^{1}$H: $\delta$ 0~6.0 ppm; $^{13}$C: $\delta$ 10~60 ppm) spectrum of SUMI product BETC-Q.

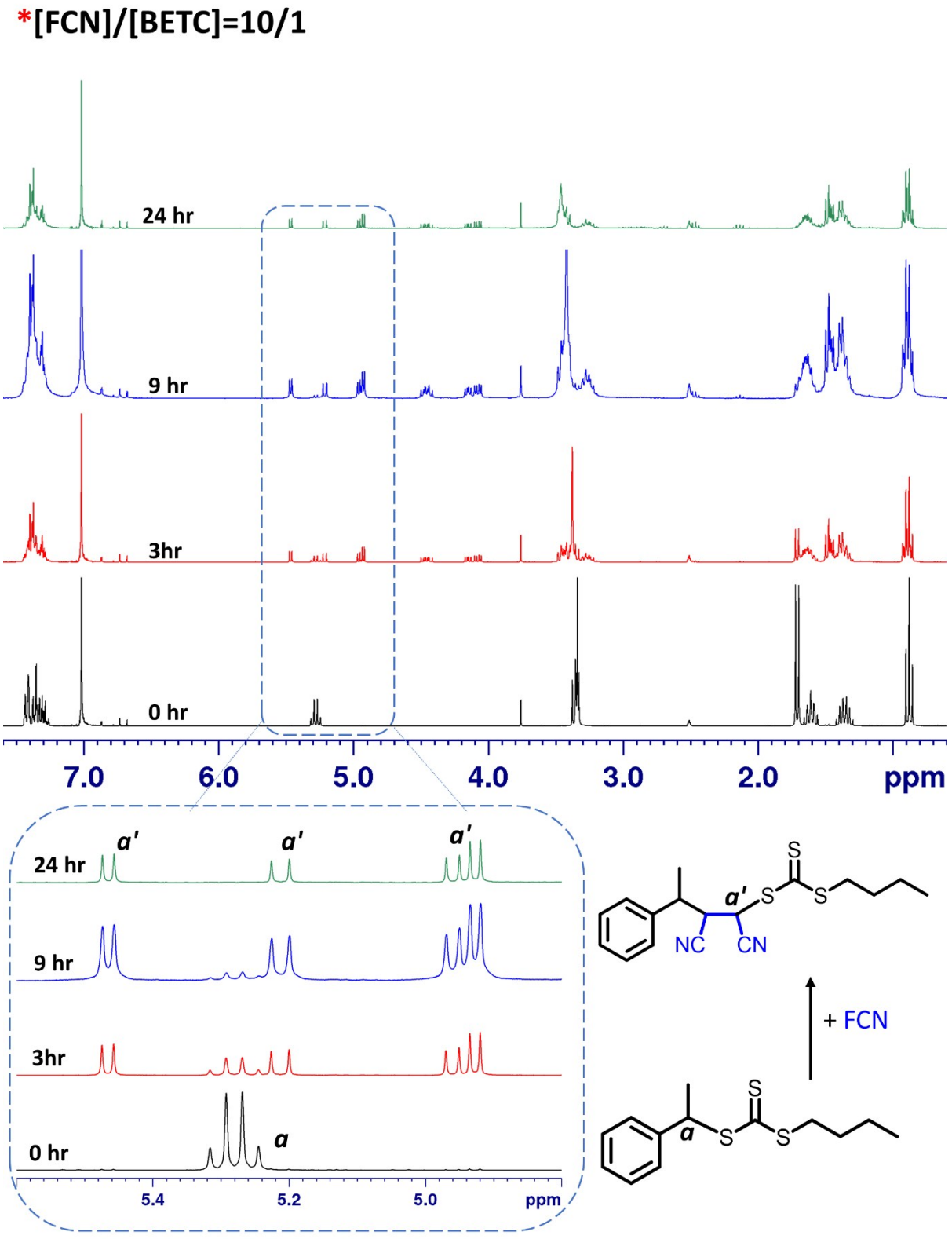
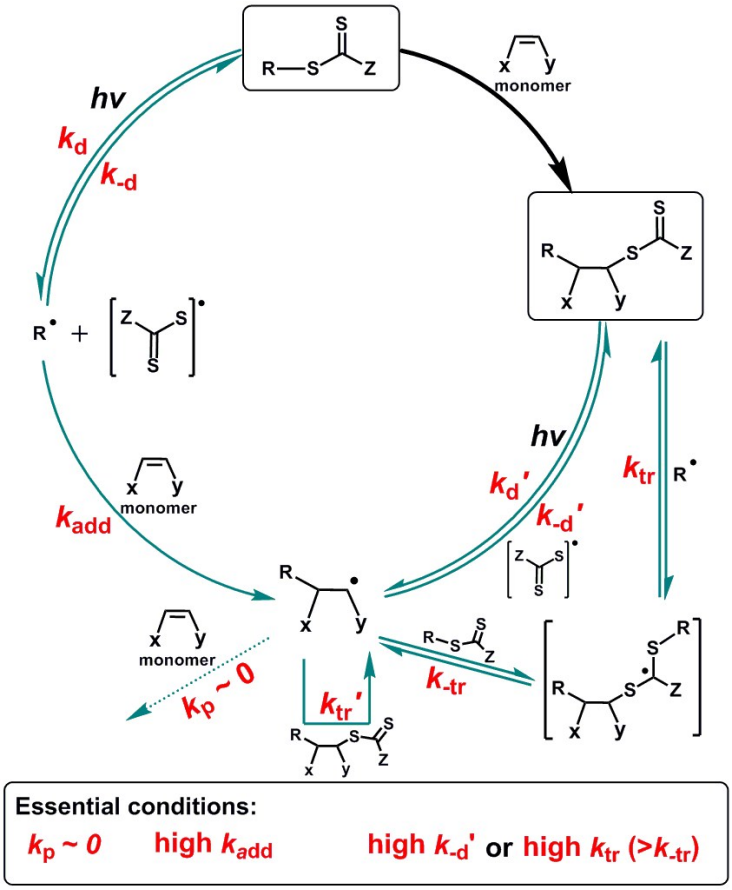



**Figure S12.** $^{1}$H NMR (DMSO-$d_6$, 300 MHz) spectra of reaction mixture at different time points for investigating the SUMI kinetics of BETC and FCN with the molar ratio of [FCN]/[BETC]/[ZnTPP] =10/1/0.005. *Note:* the peak at 3.8 ppm has been verified to be the signal of impurity in FCN monomer.




**Scheme S1.** Mechanism for photo-RAFT SUMI process and essential conditions for effective SUMI. $k_d$: decomposition rate constant of initial RAFT agent under light; $k_{-d}$: recombination rate constant of initial RAFT agent; $k_{add}$: addition rate constant of monomer to radical; $k_p$: propagation rate constant of monomer to its SUMI adduct radical; $k_{tr}$: chain transfer rate constant of SUMI adduct radical to initial RAFT agent; $k_{-tr}$: chain transfer rate constant of R group radical (R·) from initial RAFT agent to SUMI adduct macro-RAFT agent; $k_{tr}'$: chain transfer rate constant of SUMI adduct radical to SUMI adduct macro-RAFT agent; $k_d'$: decomposition rate constant of SUMI adduct macro-RAFT agent under light; $k_{-d}'$: recombination rate constant of SUMI adduct macro-RAFT agent. For clarity, the PET-RAFT technique, which involves electron transfer in the presence of a photoredox catalyst, was not depicted in the scheme. (This Scheme is adapted from our published paper[1].)

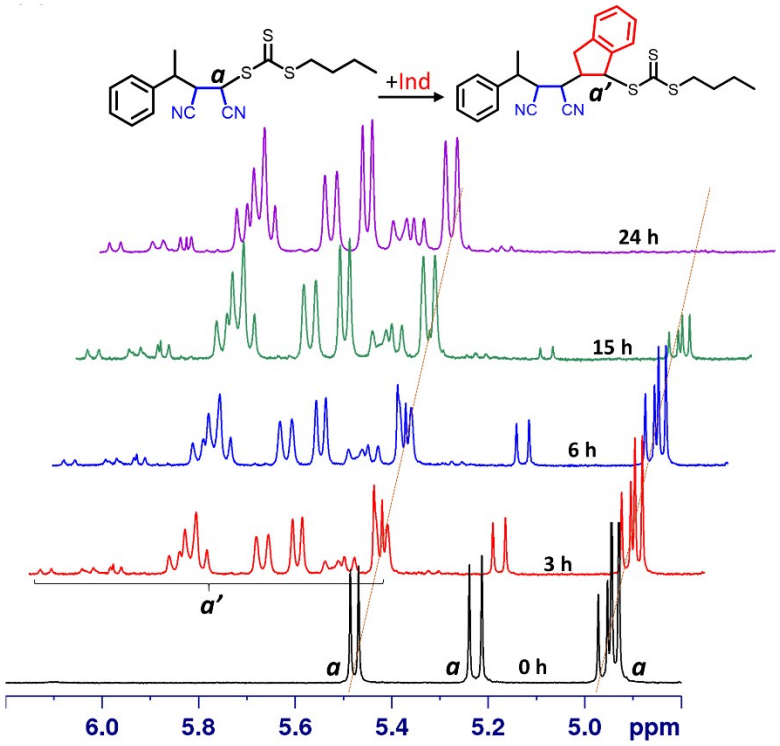



**Figure S13**. Stacked $^{1}$H NMR (DMSO-$d_6$, 300 MHz) spectra of SUMI of Ind into BETC-F at different time points (0, 3, 6, 15 and 24 h).

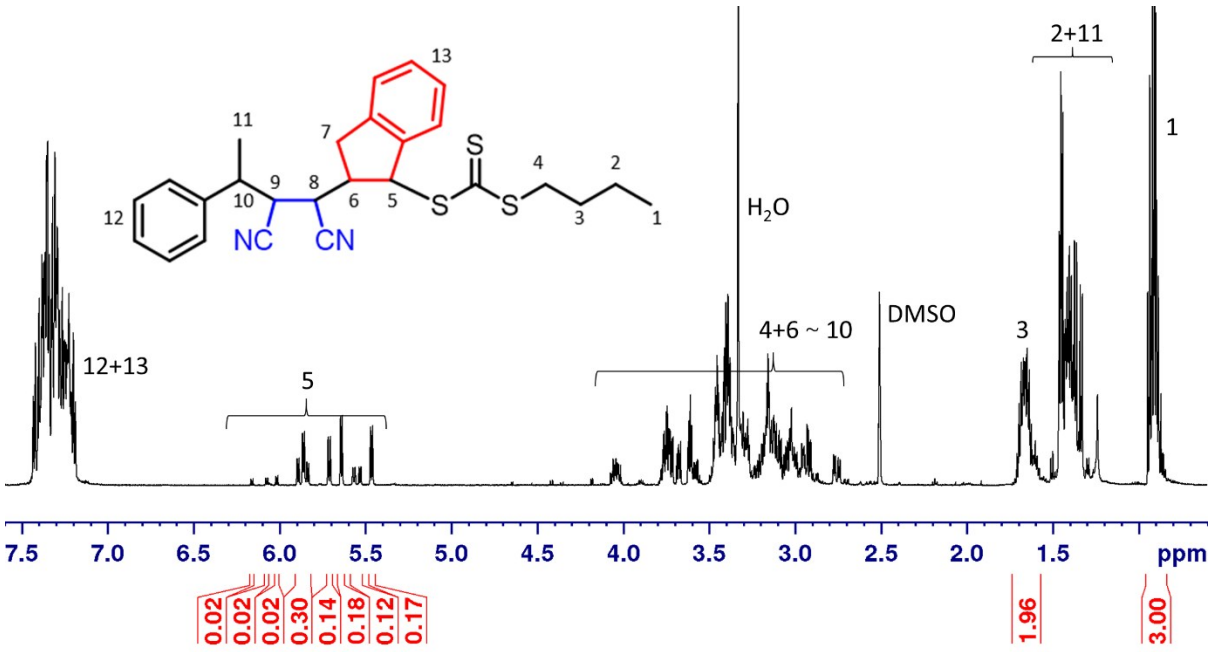



**Figure S14.** $^{1}$H NMR (DMSO-$d_6$, 600 MHz) spectrum of the crude SUMI product, BETC-F-I.

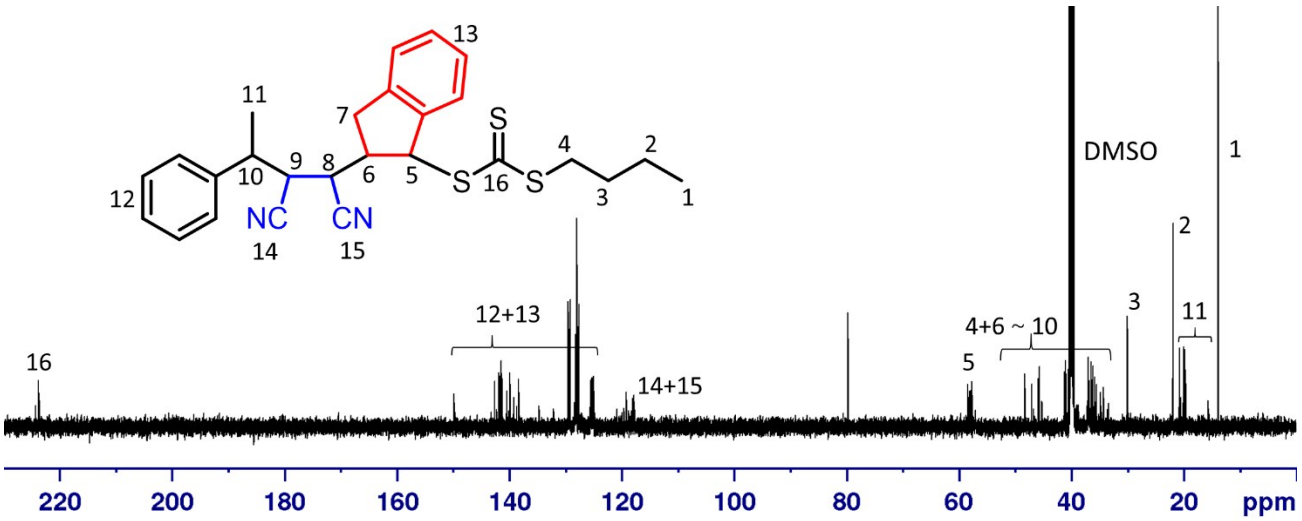



**Figure S15.** $^{13}$C NMR (DMSO-$d_6$, 150 MHz) spectrum of the SUMI product BETC-F-I

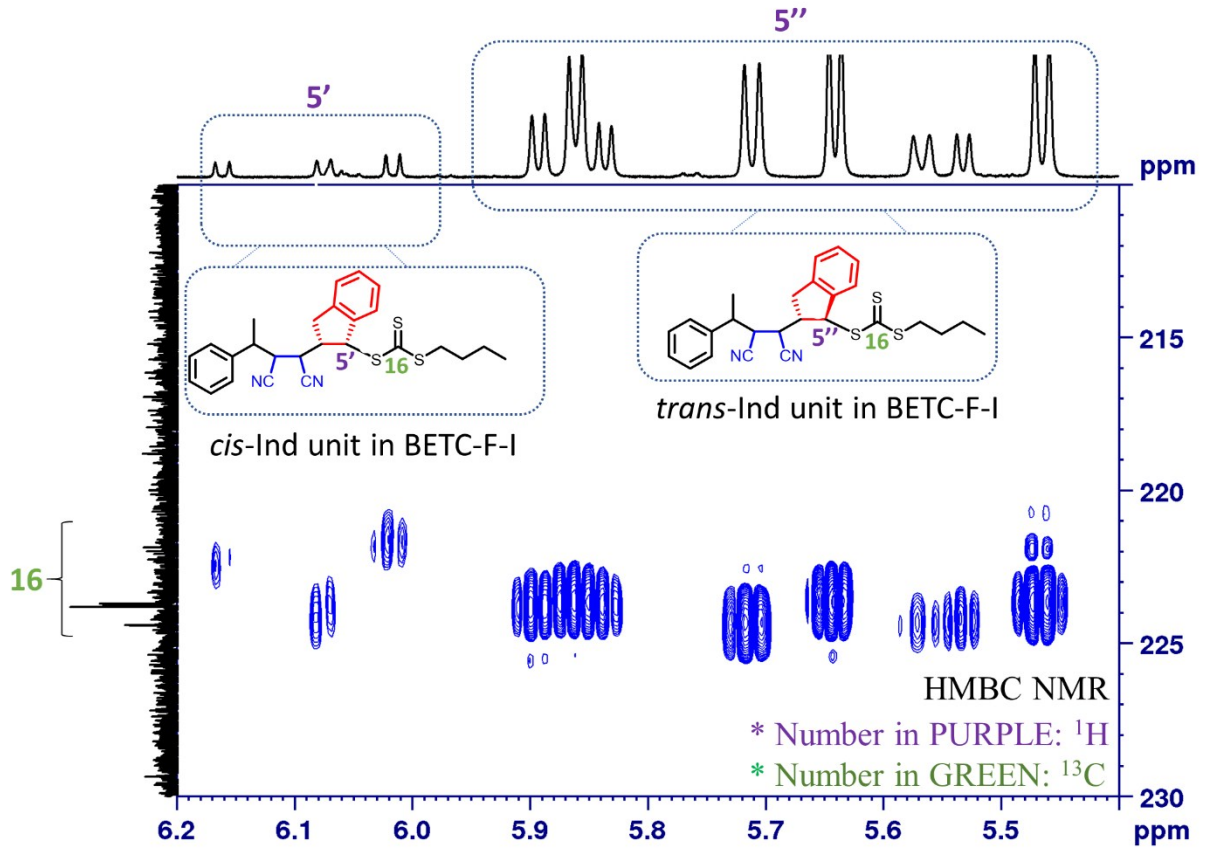



**Figure S16.** Enlarged $^{1}$H-$^{13}$C HMBC NMR (DMSO-$d_6$, $^{1}$H: $\delta$ 5.5~6.2ppm; $^{13}$C: $\delta$ 200~240ppm) spectrum of SUMI product BETC-F-I.

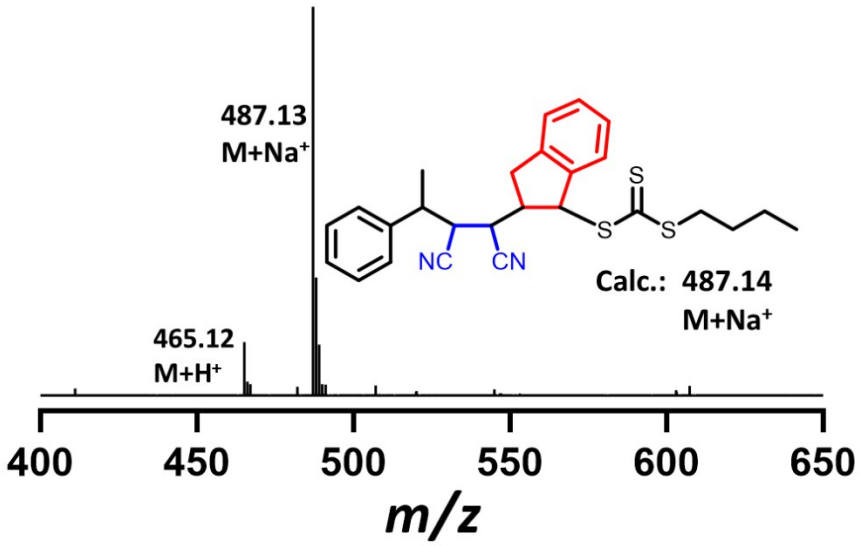



**Figure S17.** ESI-MS spectra for BETC-F-I. Note: the small peaks from the SUMI products have not been assigned.

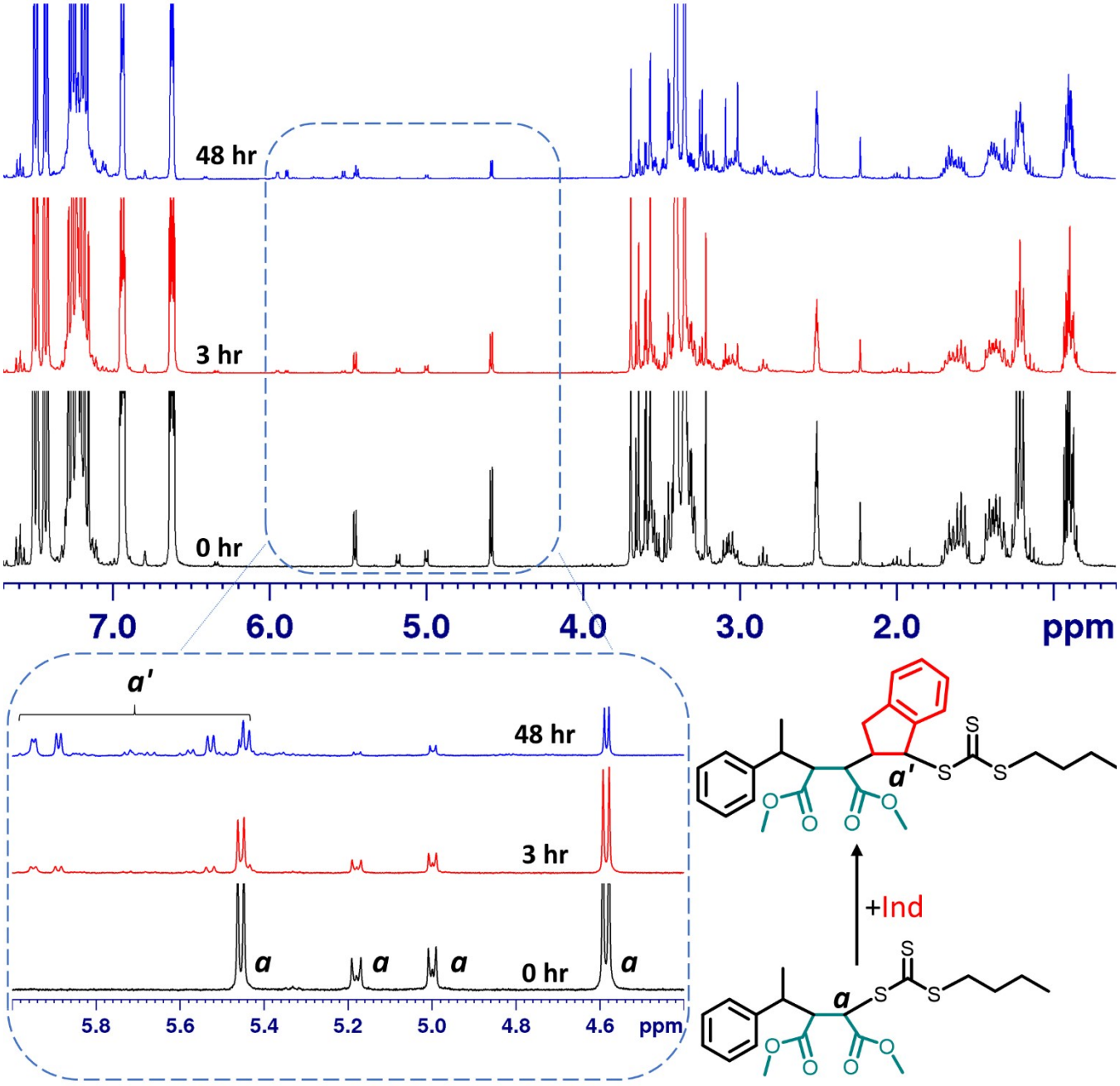



**Figure S18.** Stacked $^{1}$H NMR (DMSO-$d_6$, 300 MHz) spectra of reaction of Ind SUMI into BETC-Q with the molar ratio of [Ind]/[BETC-Q] /[ZnTPP] = 5/1/0.005 at different time points (0, 3 and 48 h).

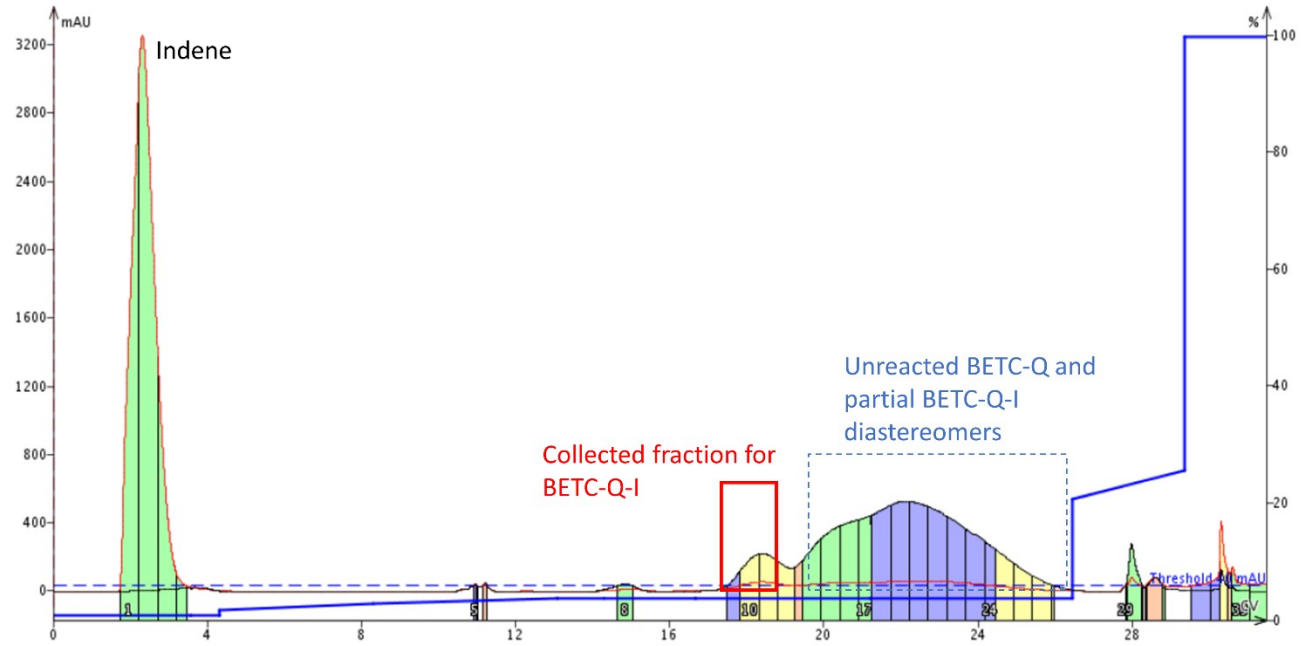



**Figure S19.** Chromatogram of the purification of crude product, BETC-Q-I, in Biotage® automated flash chromatography. The product with multiple diastereoisomers is substaintially overlapped with unreacted BETC-Q at the elution from 17 column volume (CV) to 27 CV. The collected fraction is only the elution of 17-19 CV which is part of the diastereomers of BETC-Q-I.

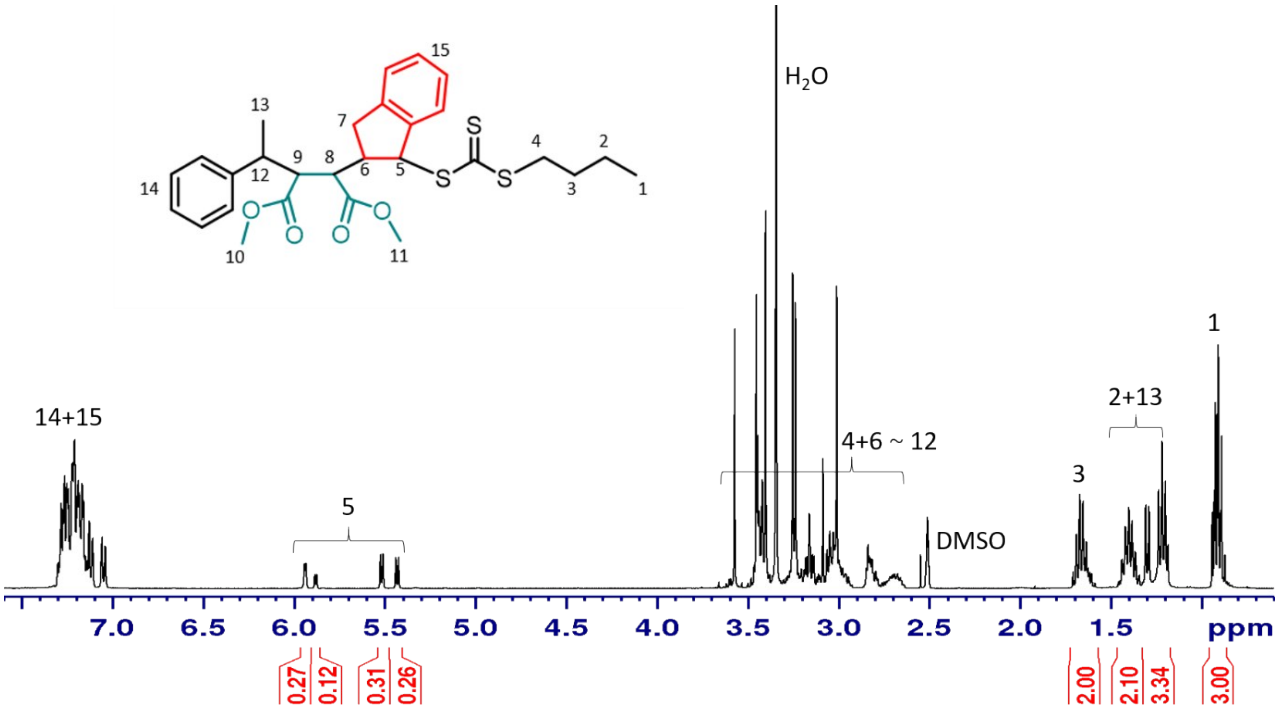



**Figure S20.** $^{1}$H NMR (DMSO-$d_6$, 400 MHz) spectrum of the purified SUMI product BETC-Q-I.

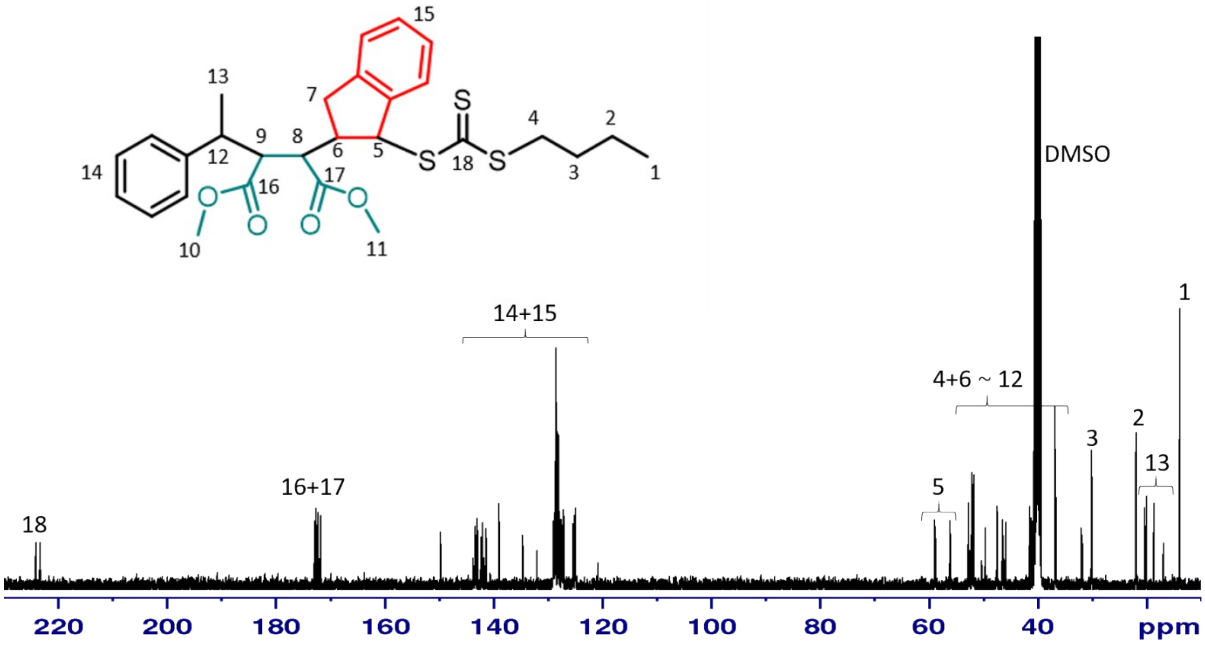



**Figure S21.** $^{13}$C NMR (DMSO-$d_6$, 100 MHz) spectrum of the purified SUMI product BETC-Q-I.

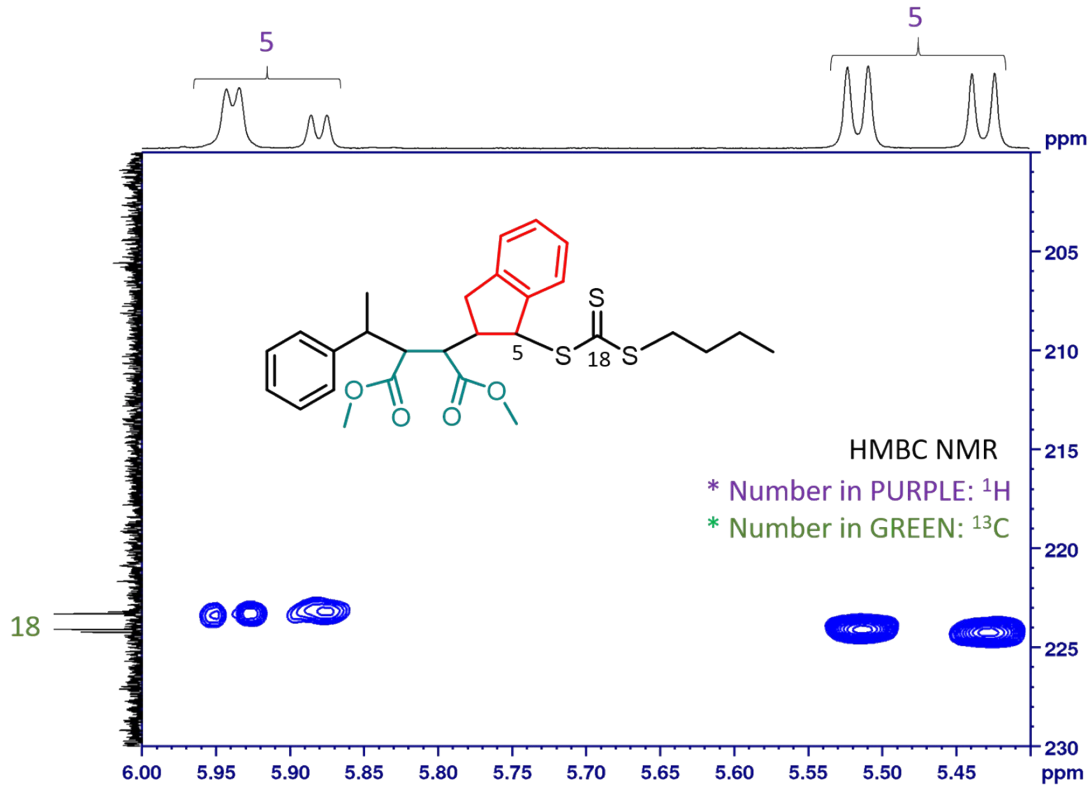



**Figure S22.** Enlarged $^{1}$H-$^{13}$C HMBC NMR (DMSO-$d_6$, $^{1}$H: $\delta$ 4.0~6.0ppm; $^{13}$C: $\delta$ 200~230 ppm) spectrum of purified SUMI product BETC-Q-I.

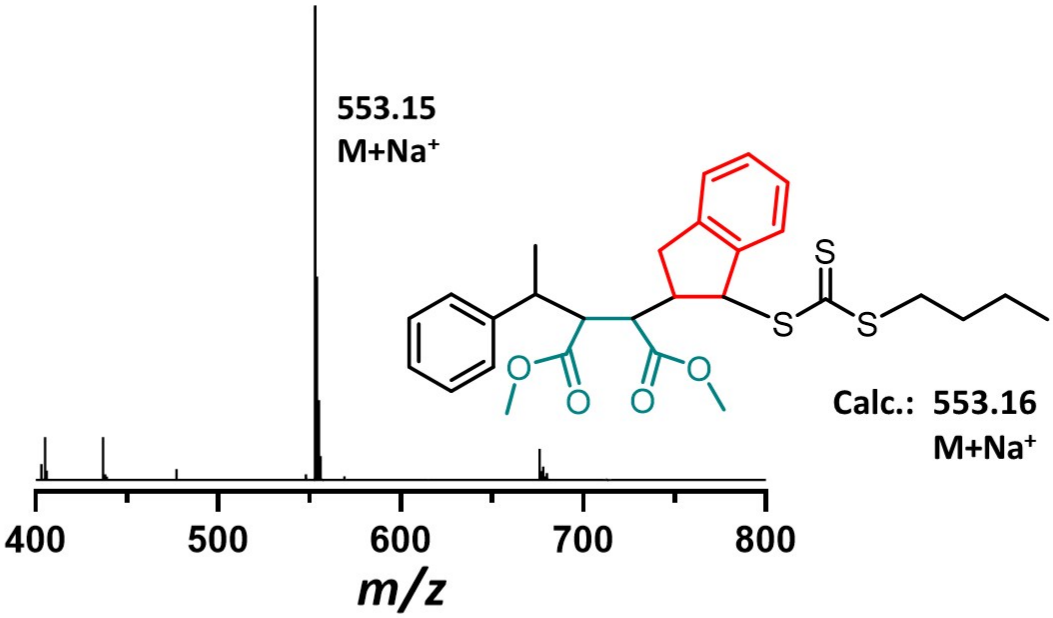



**Figure S23.** ESI-MS spectra for the purified BETC-Q-I.

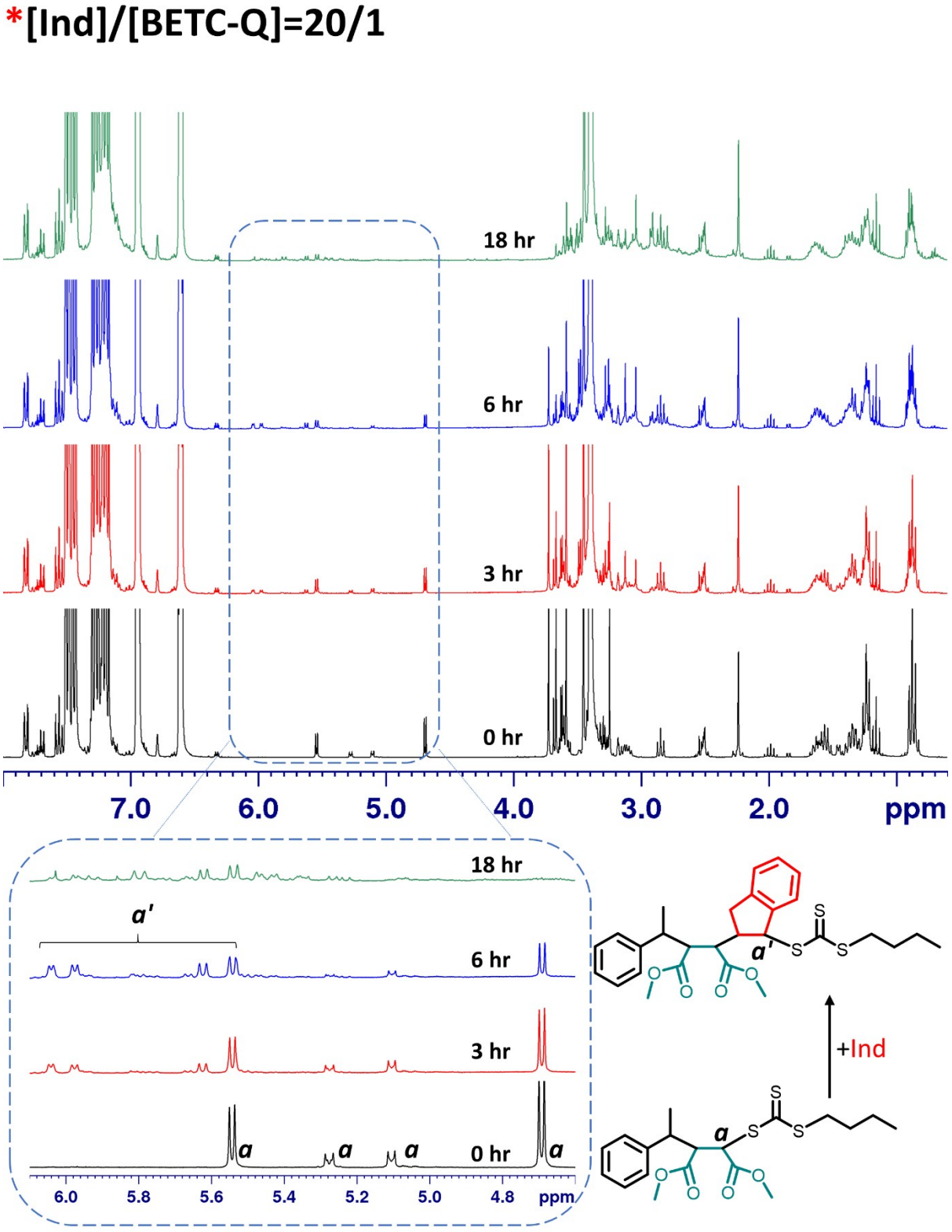



**Figure S24.** $^{1}$H NMR (DMSO-$d_6$, 300 MHz) spectra of reaction mixture at different time points for the kinetic reaction of high Ind molar ratio: [Ind]/[BETC-Q]/[ZnTPP] = 20/1/0.005.

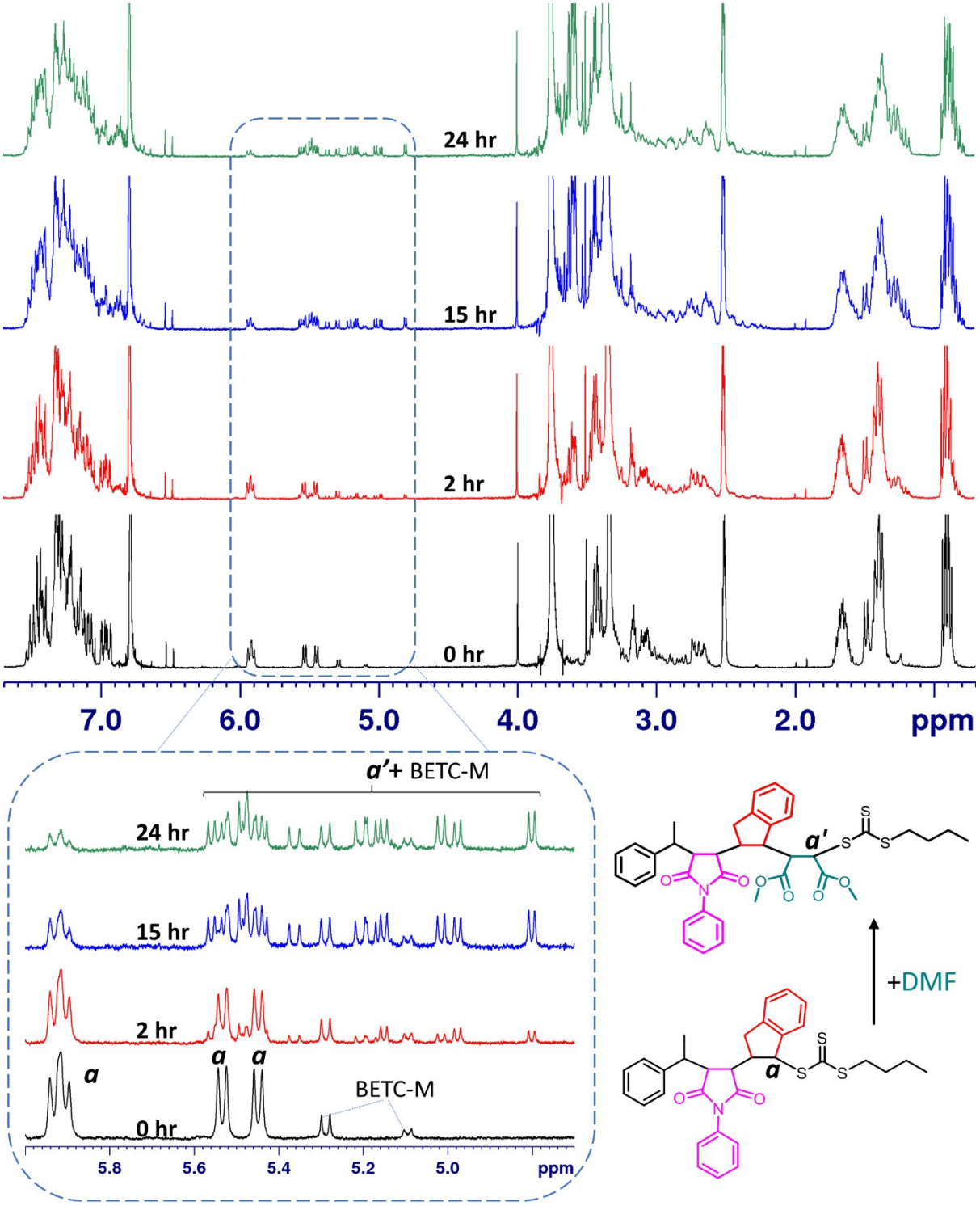



**Figure S25.** Stacked $^{1}$H NMR (DMSO-$d_6$, 300 MHz) spectra of DMF SUMI into BETC-M-I at different time points.

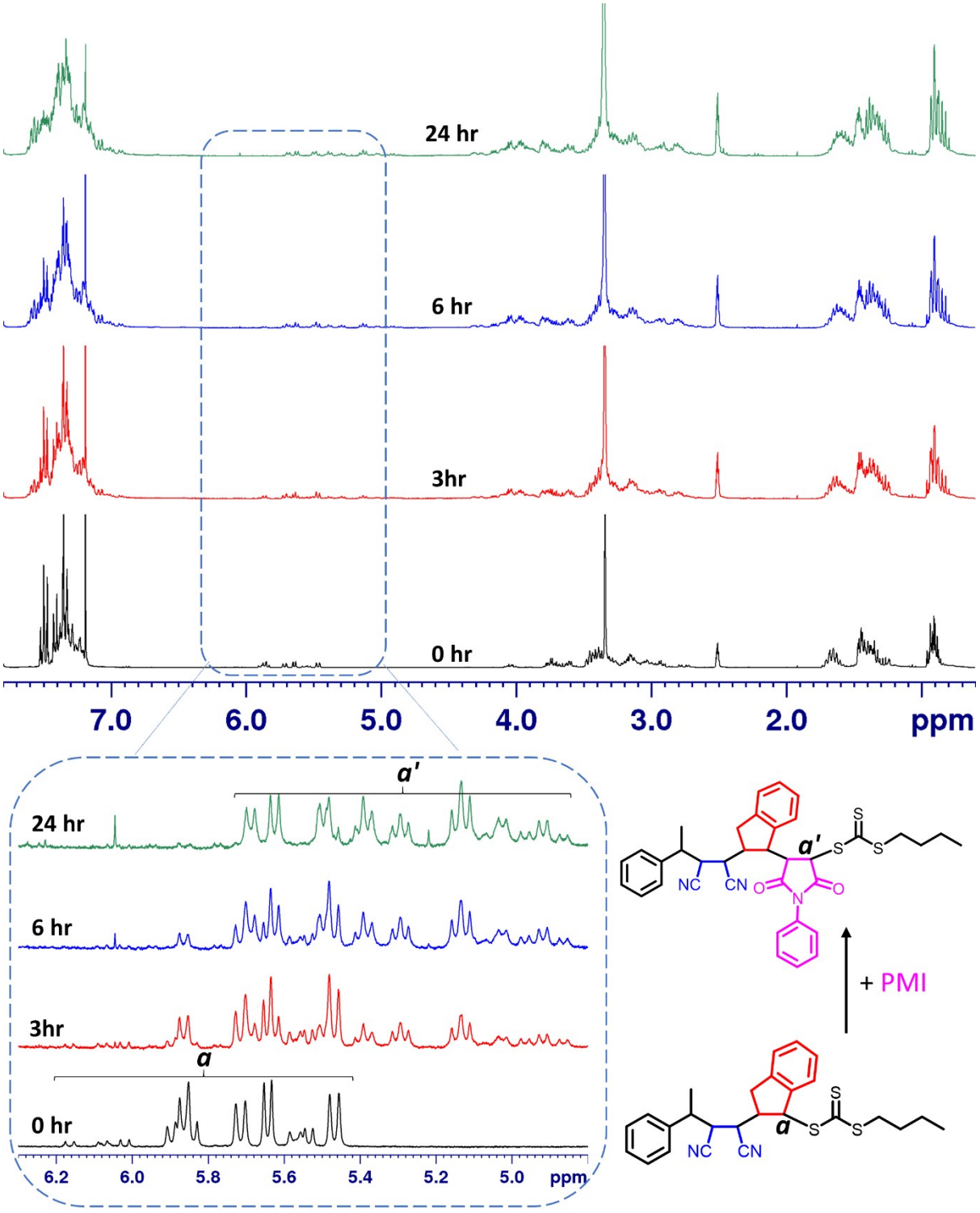



**Figure S26.** Stacked $^{1}$H NMR (DMSO-$d_6$, 300 MHz) spectra of SUMI of PMI into BETC-F-I at different time points.

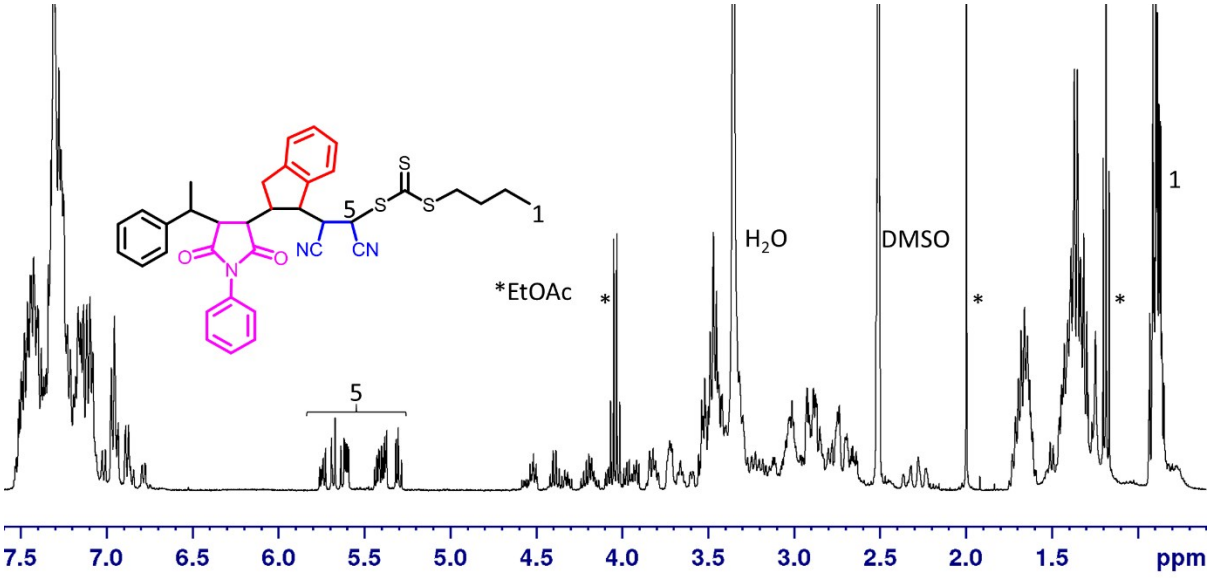



**Figure S27.** [1]H NMR (DMSO-$d_6$, 400 MHz) spectrum of the purified SUMI product BETC-M-I-F (#8 in **Table 1**).

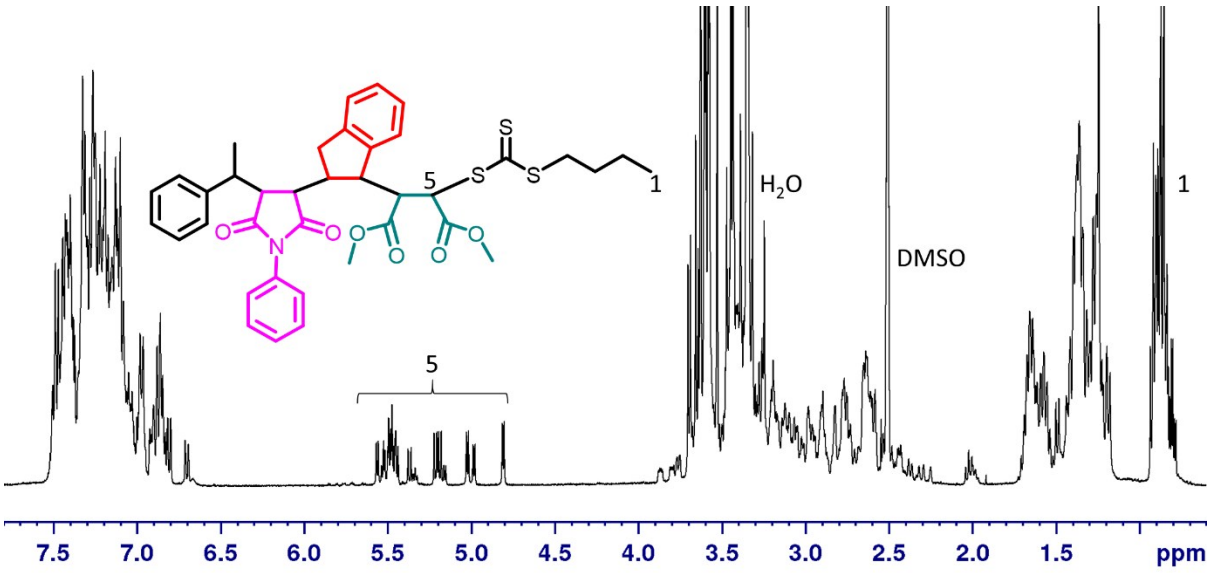



**Figure S28.** [1]H NMR (DMSO-$d_6$, 400 MHz) spectrum of the purified SUMI product BETC-M-I-Q (#9 in **Table 1**).

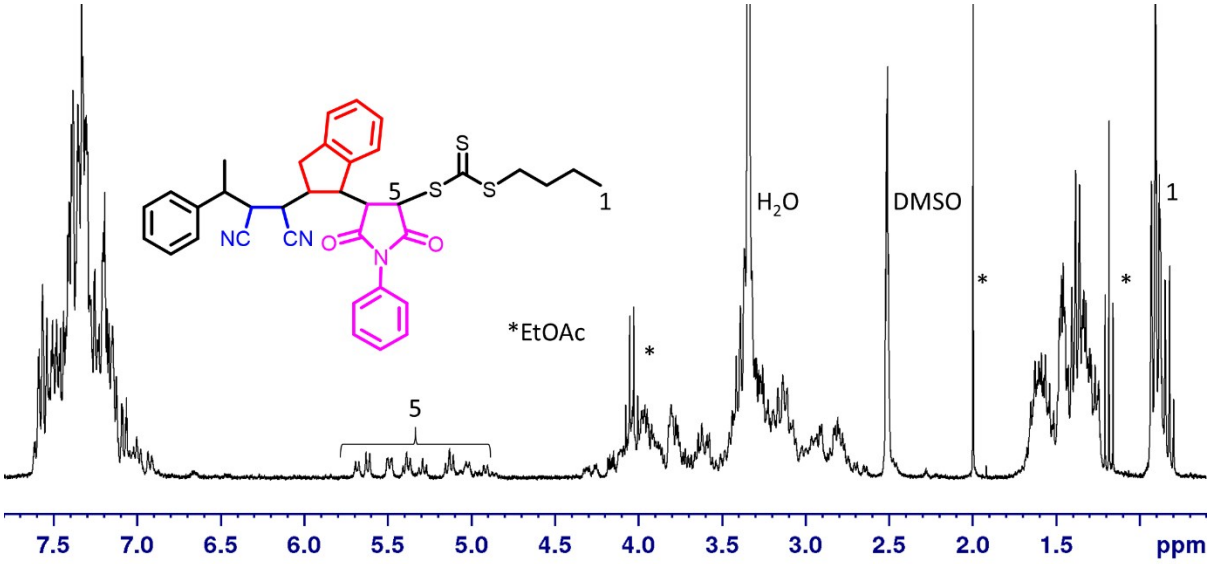



**Figure S29.** [1]H NMR (DMSO-$d_6$, 300 MHz) spectrum of the purified SUMI product BETC-F-I-M (#10 in **Table 1**).

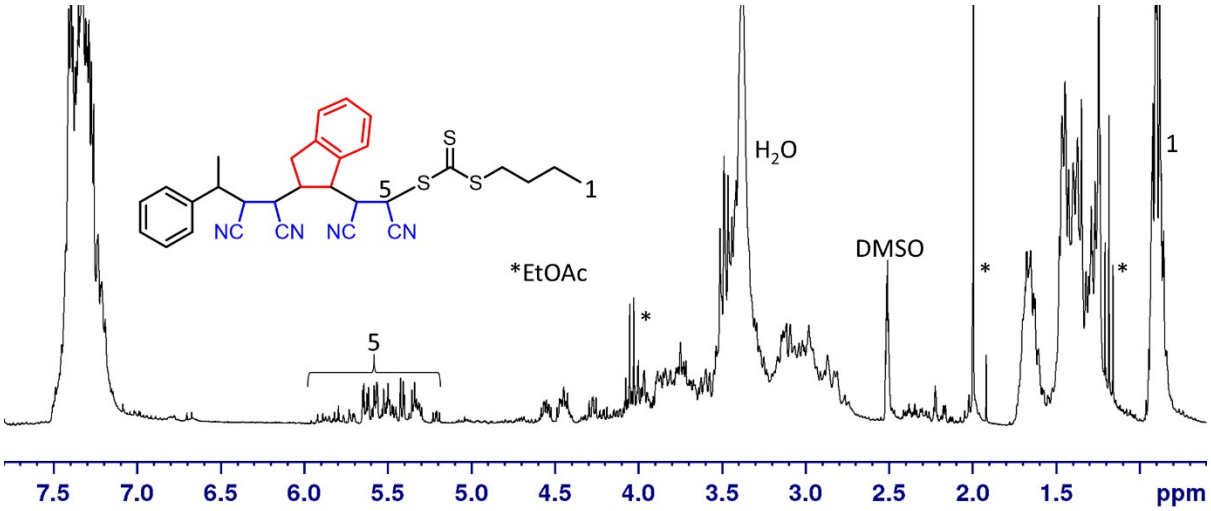



**Figure S30.** [1]H NMR (DMSO-$d_6$, 300 MHz) spectrum of the purified SUMI product BETC-F-I-F (#11 in **Table 1**).

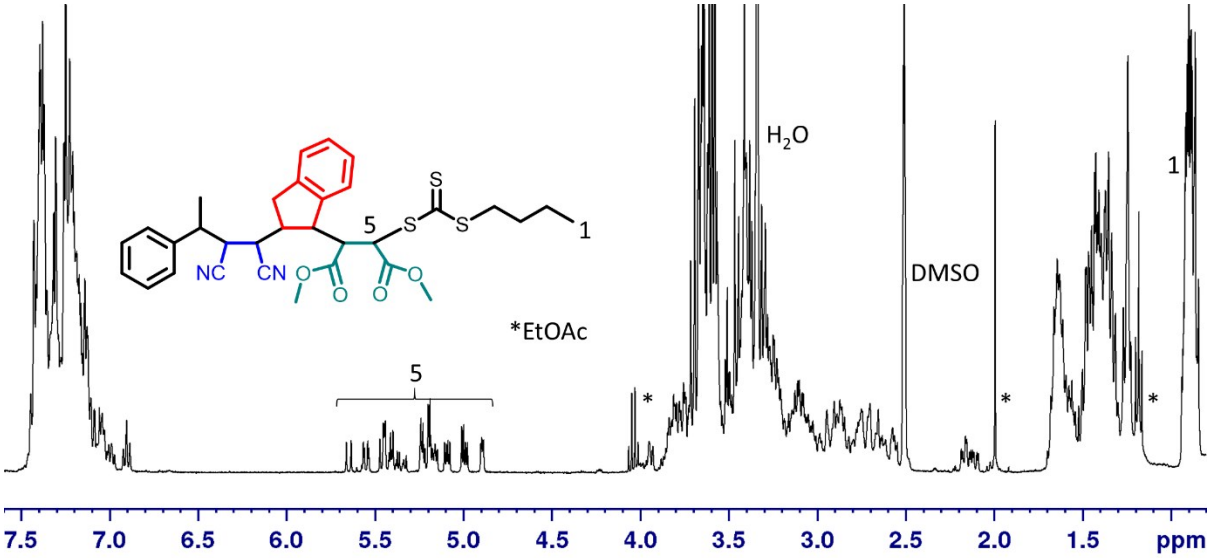



**Figure S31.** [1]H NMR (DMSO-$d_6$, 400 MHz) spectrum of the purified SUMI product BETC-F-I-Q (#12 in **Table 1**).

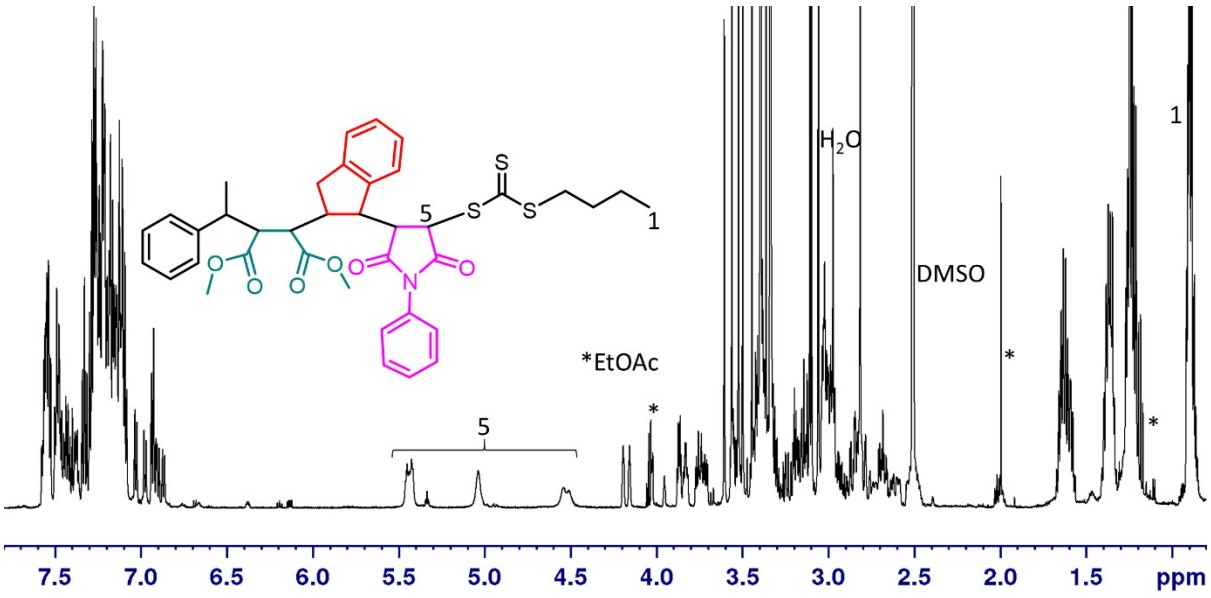



**Figure S32.** [1]H NMR (DMSO-$d_6$, 600 MHz) spectrum of the purified SUMI product BETC-Q-I-M (#13 in **Table 1**).

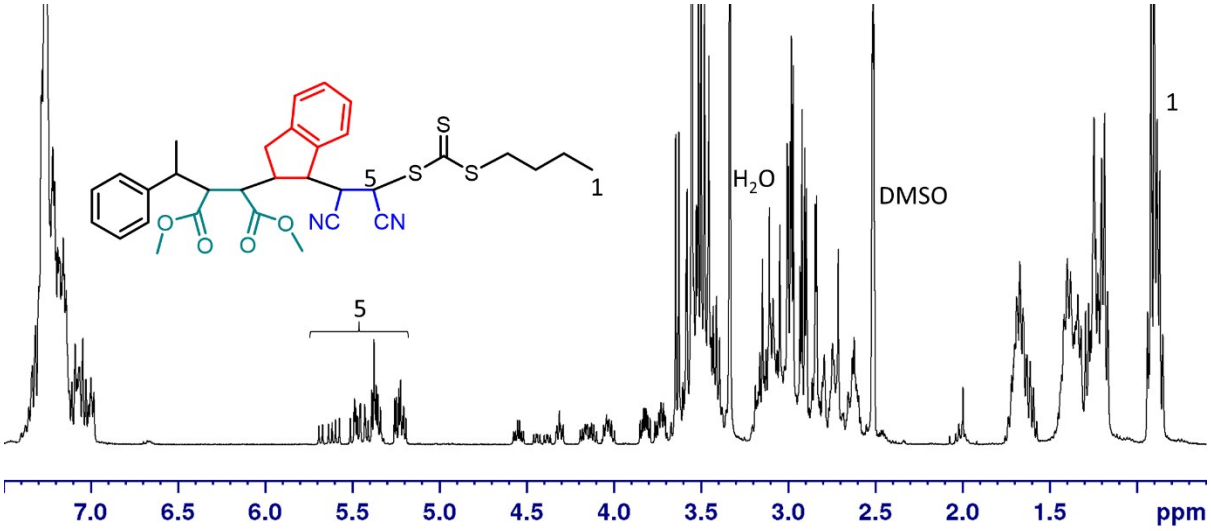



**Figure S33.** [1]H NMR (DMSO-$d_6$, 400 MHz) spectrum of the purified SUMI product BETC-Q-I-F (#14 in **Table 1**).

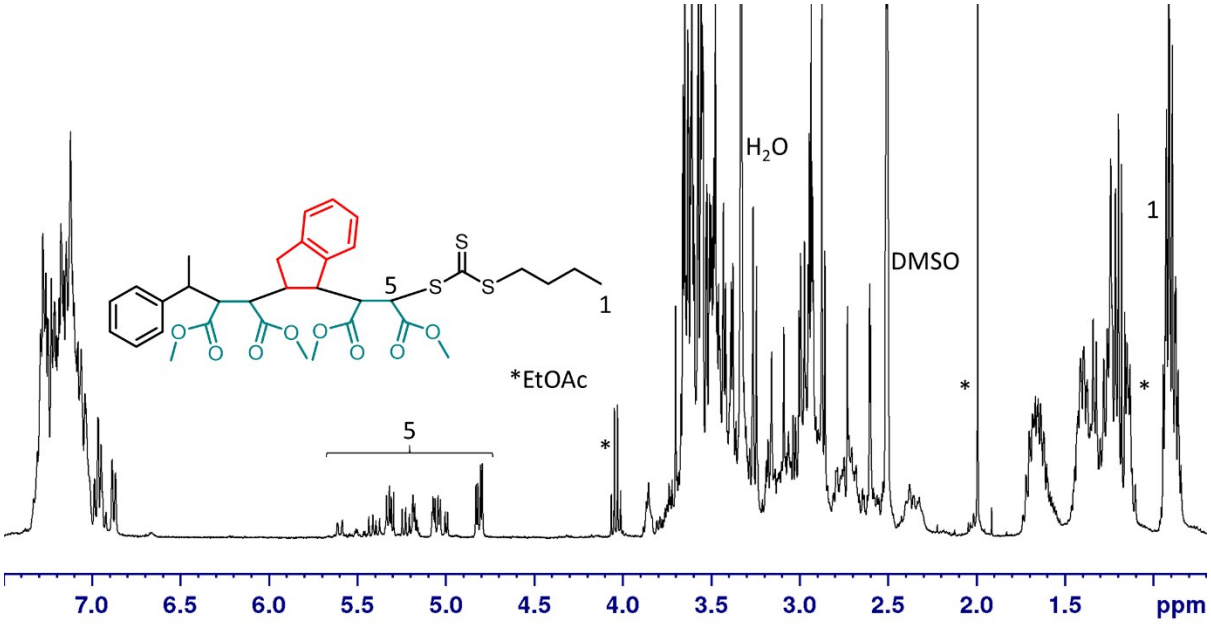



**Figure S34.** [1]H NMR (DMSO-$d_6$, 400 MHz) spectrum of the purified SUMI product BETC-Q-I-Q (#15 in **Table 1**).

## 2.2 Effective synthesis of long chain discrete oligomers

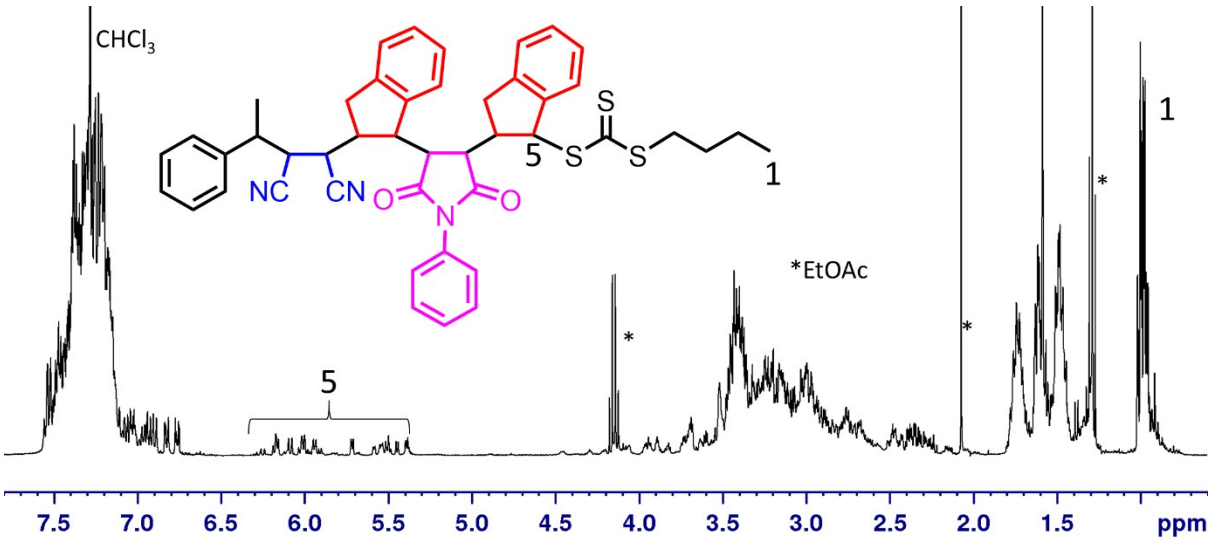



**Figure S35.** $^{1}$H NMR ($CDCl_3$, 600 MHz) spectrum of the purified SUMI product BETC-F-I-P-I (#16 in **Table 1**).

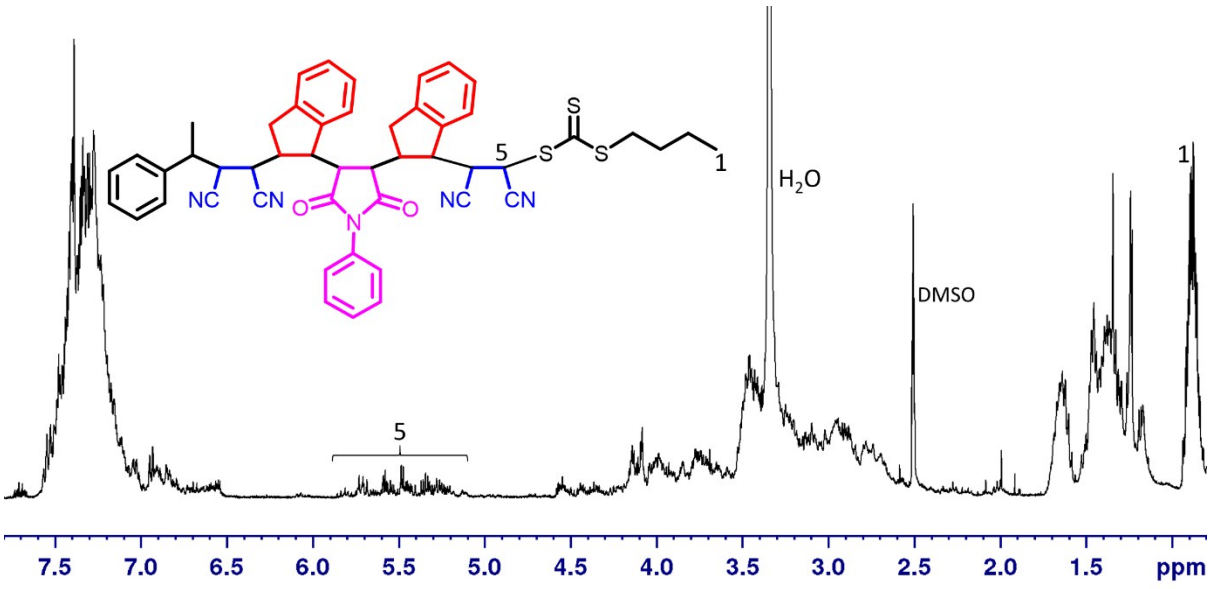



**Figure S36.** $^{1}$H NMR (DMSO-$d_6$, 400 MHz) spectrum of the purified SUMI product BETC-F-I-M-I-F (#17 in **Table 1**).

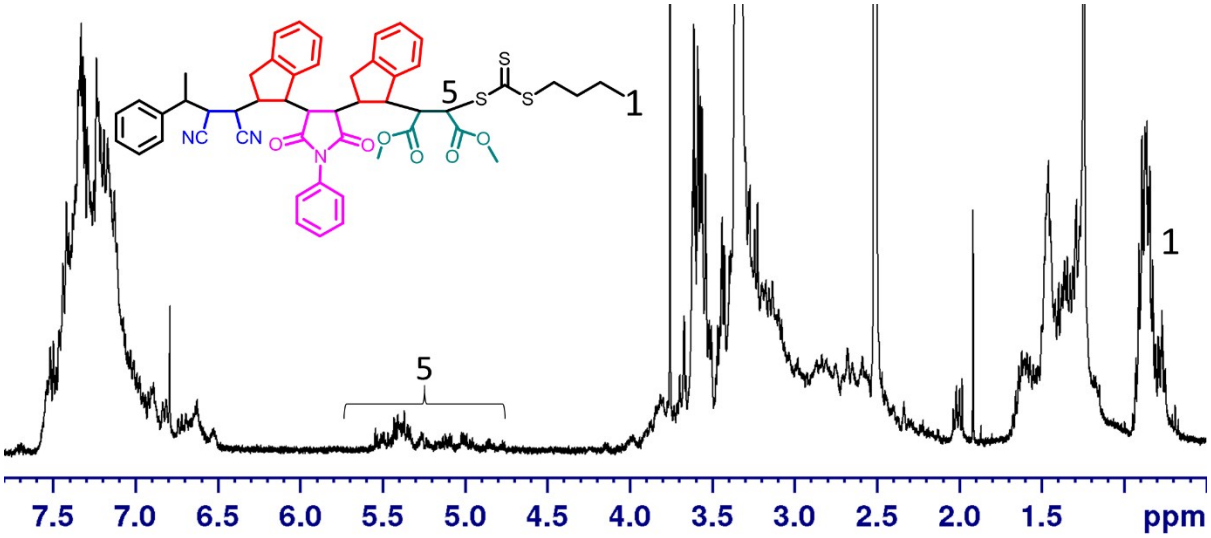



**Figure S37.** $^{1}$H NMR (DMSO-$d_6$, 400 MHz) spectrum of the purified SUMI product BETC-F-I-M-I-Q (#18 in **Table 1**).

## References

1. Huang, Z.; Noble, B. B.; Corrigan, N.; Chu, Y.; Satoh, K.; Thomas, D. S.; Hawker, C. J.; Moad, G.; Kamigaito, M.; Coote, M. L.; Boyer, C.; Xu, J. *J. Am. Chem.Soc.* 2018, **140**, 13392-13406.