Electronic Supplementary Material (ESI) for ChemComm.

# Supporting Information

to

# Pyrazole Carbodithiolate-Driven Iterative RAFT Single-Additions

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# Materials

Fumaronitrile (FCN, 98%), diethyl fumarate (DiEtFum, 98%), isobutyl vinyl ether (IBVE, 99%, 0.1% KOH added), styrene (St, ≥99%, 50 ppm BHT added) cinnamonitrile (CCN, 97%), 3,5-dimethylimidazole (99%), carbon disulphide ($CS_2$, anhydrous, ≥99%), 1-butanethiol (99%) and 2-cyanobutan-2-yl dodecyl carbonotrithioate (IBN-($C_{12}$)TTC, 98%) were sourced from Sigma–Aldrich Pty Ltd.

2-Cyanobutanyl-2-yl 3,5-dimethyl-1H-pyrazole-1-carbodithioate (IBN-PCDT, 98%) and 2-cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate (IBN-(Cl)PCDT, 98%), were sourced from Boron Molecular.

*N,N*-Dimethylformamide (99.9%, DMF), dimethylsulphoxide (99%, DMSO), ethyl acetate (EtOAc, analytical grade) and ascorbic acid (99%) were sourced from Chem-Supply Ltd.

deuterodimethylsulphoxide (DMSO-$d_6$, 99.5% atom D) and Deuterochloroform ($CDCl_3$, 99.8% atom D) were sourced from Cambridge Isotope Laboratories, Inc.

Acetonitrile (ACS/HPLC), diethyl ether (ACS/HPLC) and hexanes (ACS/HPLC) were sourced from Honeywell.

Zinc tetraphenylporphyrin (ZnTPP) was sourced from Frontier Scientific.

Indene (93–98%, Ind) was sourced from Combi-Blocks, Inc. Prior to use, indene was purified by column chromatography in 10% v/v diethyl ether in hexanes and then stored at −20 °C (under which temperatures it freezes).

# Purification/Characterisation Methods

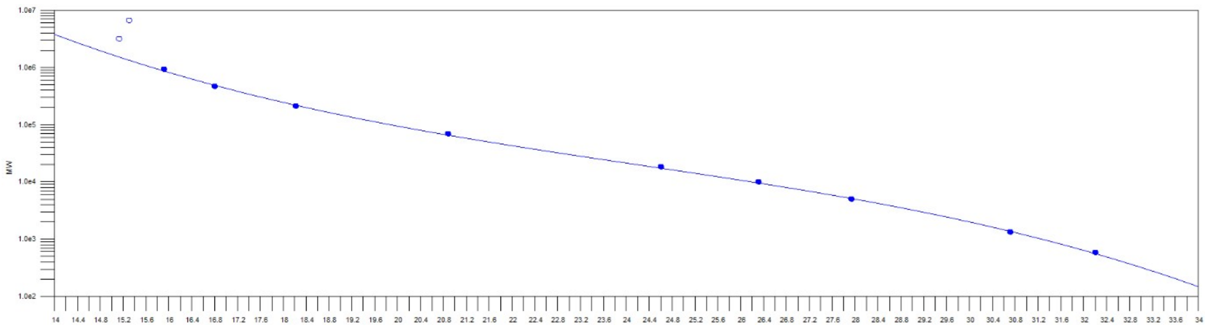
*Flash chromatography* was performed on a Biotage Isolera One system, equipped with a UV detection system set to 254 nm and 300 nm. (collection cutoff adjusted accordingly) Purification runs were performed under gradient elution of ethyl acetate and hexanes, through either a Biotage Sfär Silica HC 10g column or a Biotage ZIP KP-SIL 5g column, depending on the amount of crude material obtained.

*Nuclear magnetic resonance spectroscopy (NMR)* was performed on either a Bruker Avance 400 (400.17 MHz field strength) or a Bruker Avance 500 (500.13 MHz field strength) at a sample temperature of 300 K.

*High resolution mass spectrometry (HRMS)* was performed on a Thermo LTQ Orbitrap XL equipped with an atmospheric-pressure chemical ionisation (APCI) source. The *m/z* axis was calibrated to within 2 ppm of accuracy using a solution of Ultramark 1621. Samples were injected into the source by flow injection. Runs were performed on a Dionex UltiMate 3000 system without a column equipped, and the diversion line running through the Orbitrab mass spectrometer in positive ion mode which operated with the following ionisation parameters: capillary temperature 200 °C, vaporiser temperature 350 °C, source potential 6 kV, source current 5 μA, capillary potential 10 V, tube lens potential 90 V. Samples were injected into the system in 5 μL injections from 0.01 mg mL$^{-1}$ solutions in acetonitrile at an overall acetonitrile flow rate of 0.4 mL min$^{-1}$.

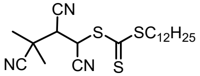
*Gel permeation chromatography (GPC)* was performed on a Shimadzu UFLC system with PhenogelTM columns (5 μm, 10$^3$ Å, 10$^4$ Å and 10$^5$ Å) in DMAc (BHT – 0.05 wt%, LiBr – 0.03 wt%) as an eluent at a flow rate of 1 mL min$^{-1}$ at 50 °C. SEC samples were dissolved and passed through a 450 nm PTFE filter prior to injection. Apparent molecular weights were determined using a calibration with near-monodispersed polystyrene (PSt) standards from Polymer Standards Service (PSS). For calibration curve, see below.

| Peak retention time (min) | $M_p$ (g mol$^{-1}$) | Log($M_p$) | Error (%) |
|---|---|---|---|
| 15.9167 | 920000 | 5.9638 | 5.9752 |
| 16.8000 | 466300 | 5.6687 | -4.5799 |
| 18.2167 | 206000 | 5.3139 | -6.2085 |
| 20.8833 | 67600 | 4.8299 | 3.0466 |
| 24.6000 | 17970 | 4.2545 | 3.3053 |
| 26.3167 | 9820 | 3.9921 | 2.9336 |
| 27.9333 | 4910 | 3.6911 | -4.2874 |
| 30.7167 | 1300 | 3.1139 | -5.0434 |
| 32.2000 | 580 | 2.7634 | 3.9462 |



# Nomenclature

TRITHIOCARBONATES



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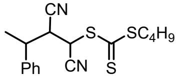

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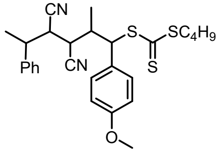

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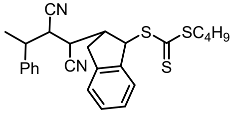

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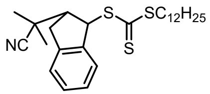

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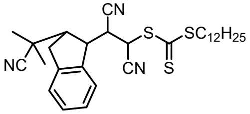

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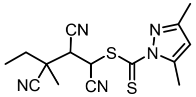
FUMARONITRILE TERMINAL UNIT



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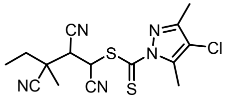

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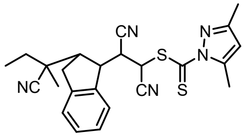

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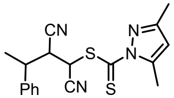

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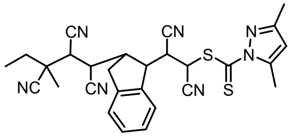

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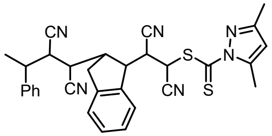

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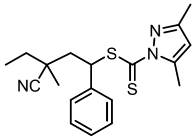

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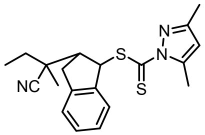

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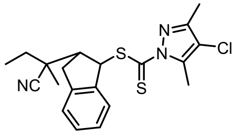

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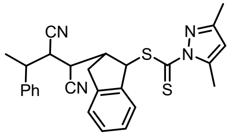

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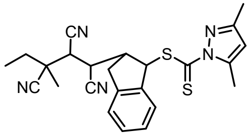

IPN-FCN-Ind-PCDT

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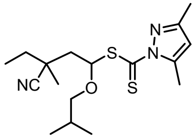

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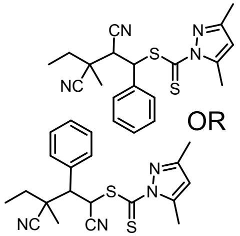

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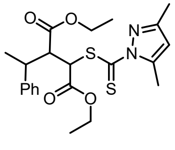

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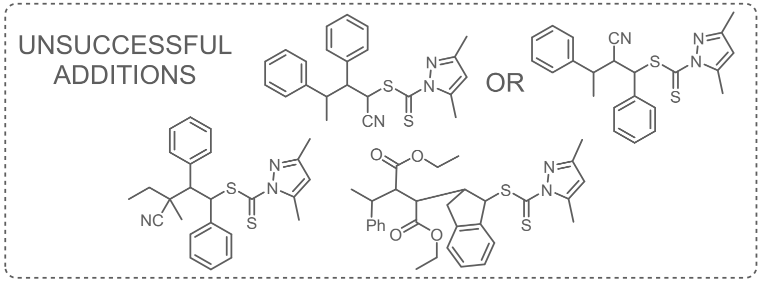

# S1. Solution-phase SUMI kinetics

Reactions noted as performed at "ambient temperature" refer more specifically to 23 °C (50% humidity). Photoreactions were irradiated inside a crystallisation dish lined with a blue LED strip (0.42 mW cm$^{-2}$). While referred to as "ambient temperature", the reactions heated to ~30 $^{o}$C.

Kinetics experiments were performed in Wilmad NMR tubes and monitored by $^{1}$H NMR (500.13 MHz, DMSO) (for further details of procedures, please refer to Appendix A2). Conversion was determined by the relative amount of product with respect to the starting RAFT agent.

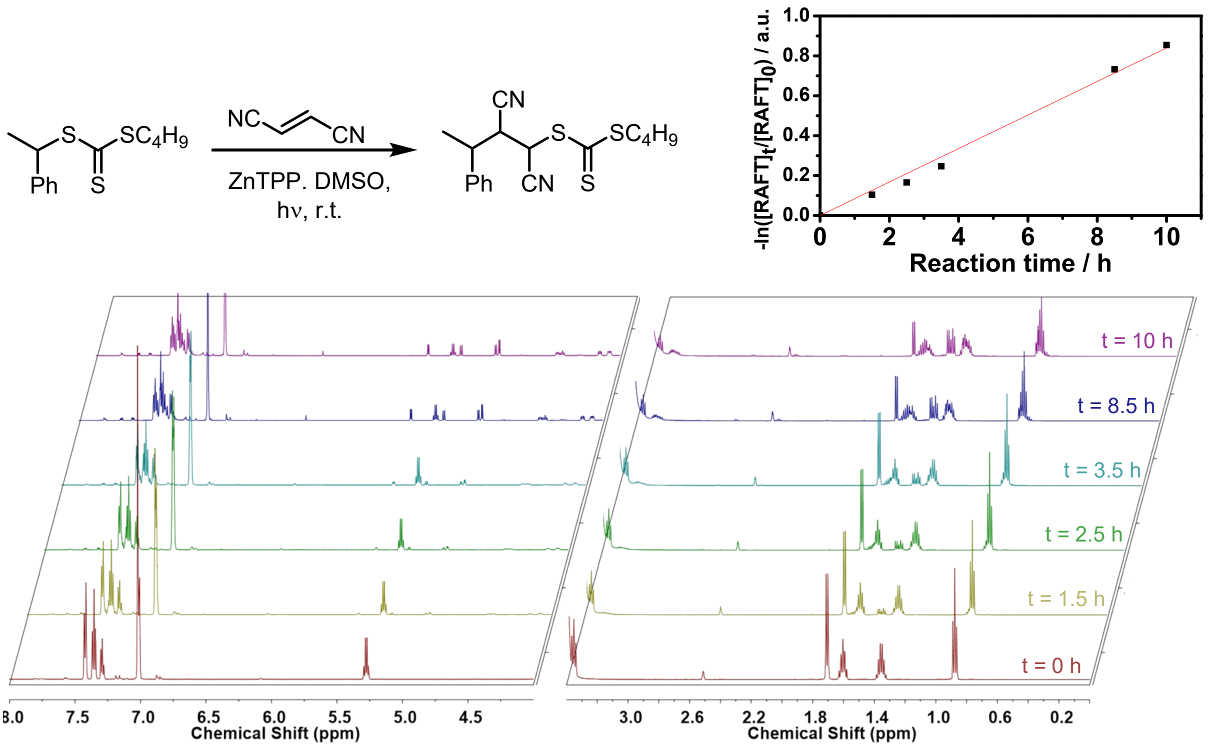

Fig. S1-1 Kinetics of PhMeCH-FCN-($C_4$)TTC synthesis by $^{1}$H NMR (500.13 MHz, DMSO-$d_6$).

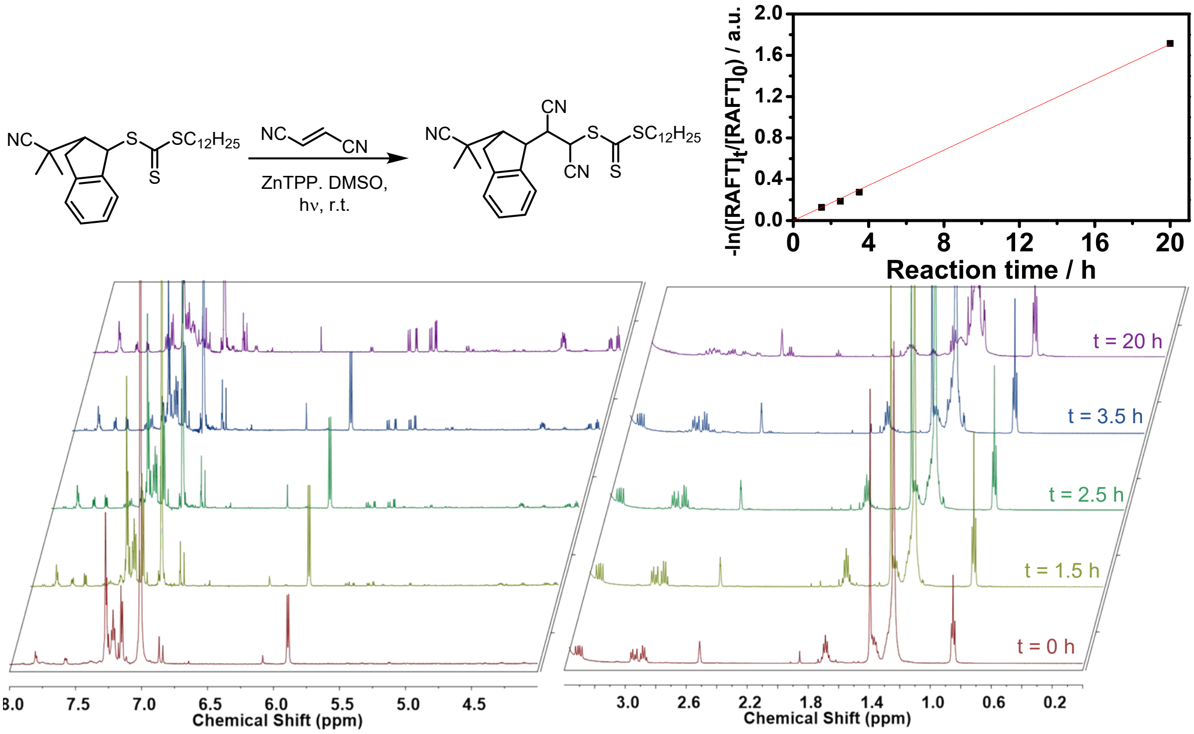

Fig. S1-2 Kinetics of IBN-Ind-FCN-($C_{12}$)TTC synthesis by $^1$H NMR (500.13 MHz, DMSO-$d_6$).

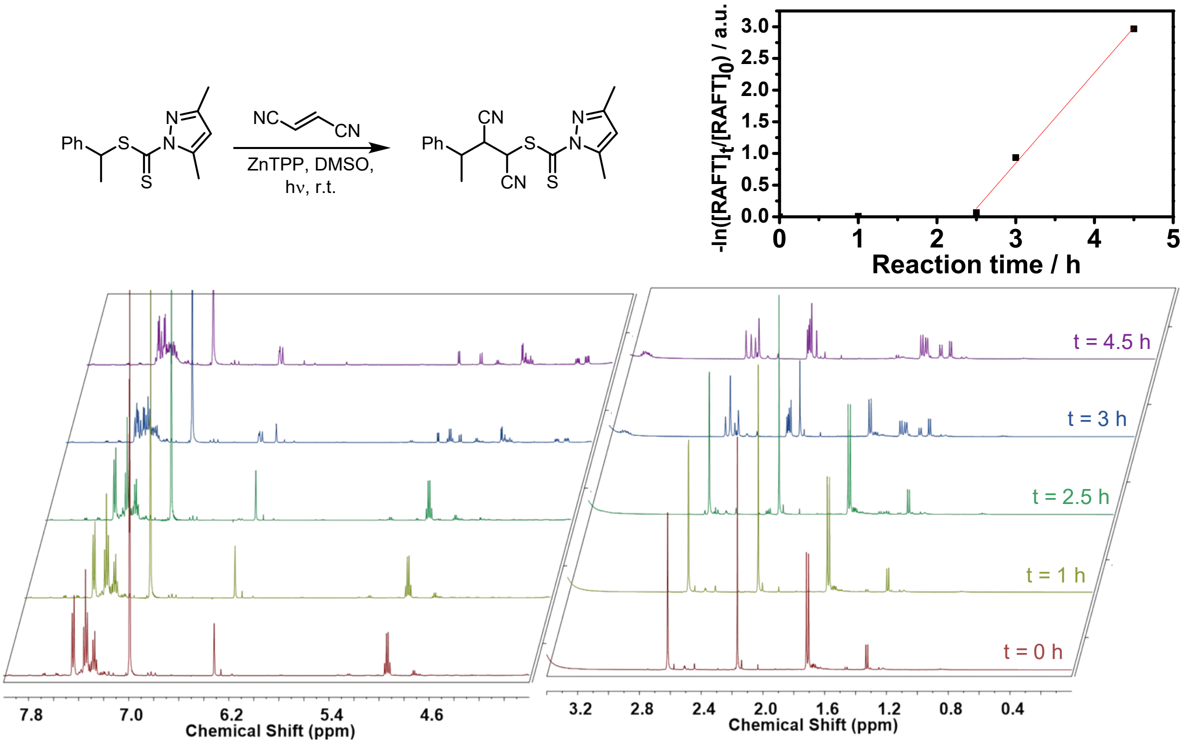

Fig. S1-3 Kinetics of PhMeCH-FCN-PCDT synthesis by $^1$H NMR (500.13 MHz, DMSO-$d_6$).

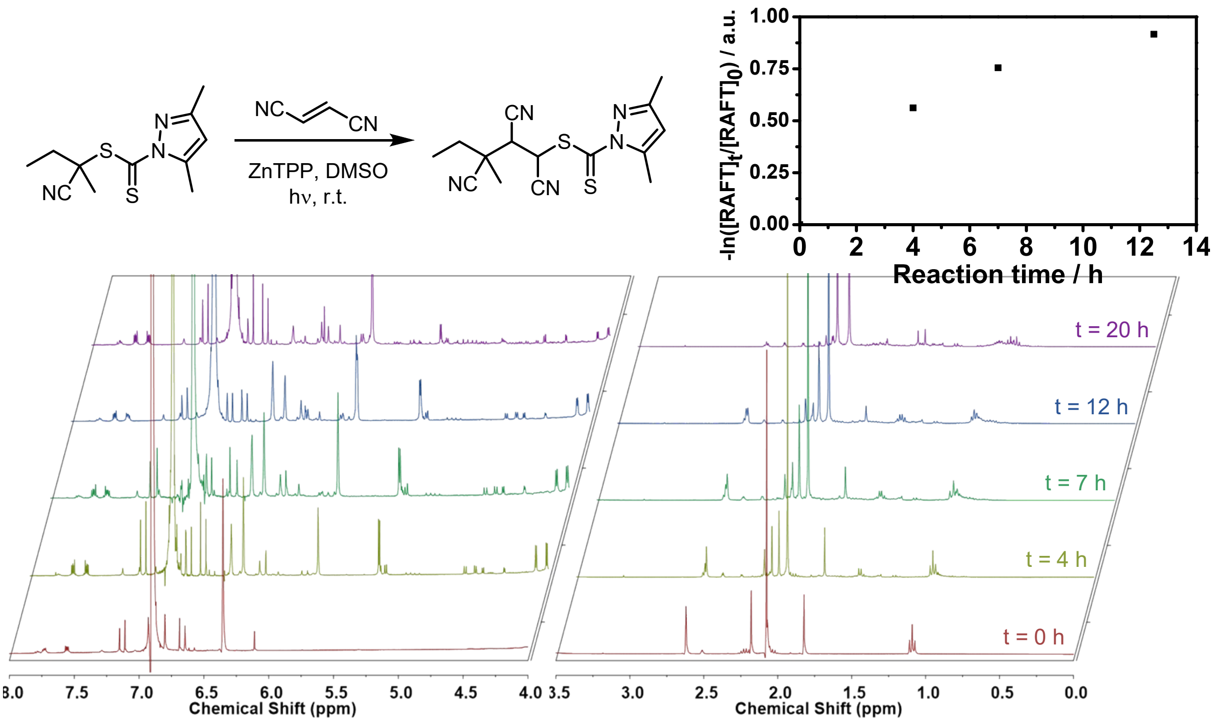

Fig. S1-4 Kinetics of IPN-FCN-PCDT synthesis by $^1$H NMR (500.13 MHz, DMSO-$d_6$).

Since the IPN-FCN-PCDT undergoes further reaction *in situ,* kinetics were not strictly pseudo first-order. Therefore, to calculate an approximate $k_{app}$, data points within 8 h of reaction and approximately in a linear regime were used.

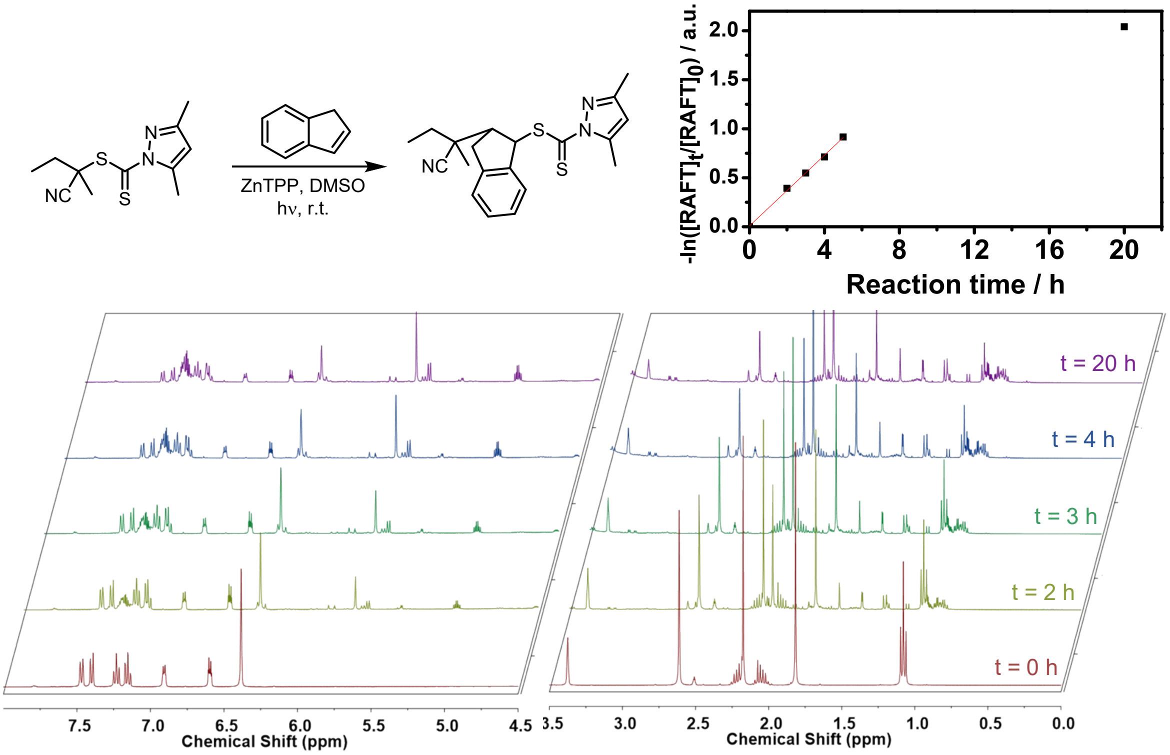

Fig. S1-5 Kinetics of IPN-Ind-PCDT synthesis by $^1$H NMR (500.13 MHz, DMSO-$d_6$).

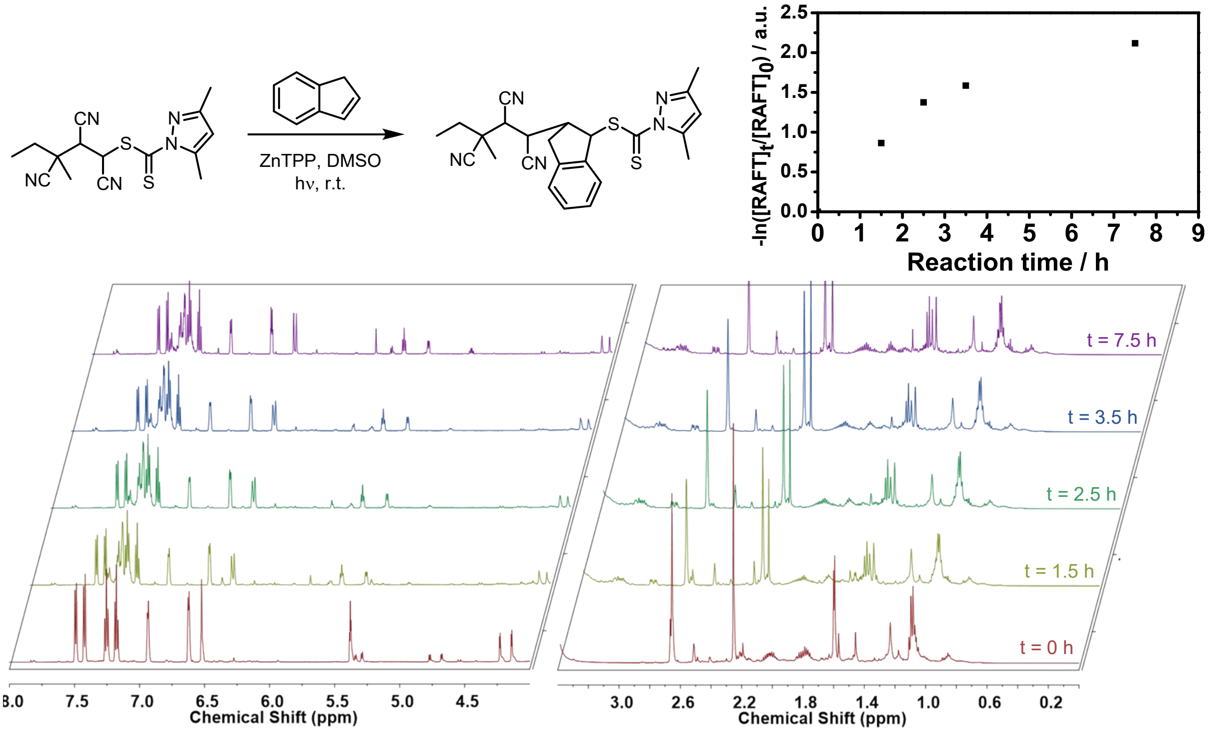

Fig. S1-6 Kinetics of IPN-FCN-Ind-PCDT synthesis by $^1$H NMR (500.13 MHz, DMSO-*d*$_6$).

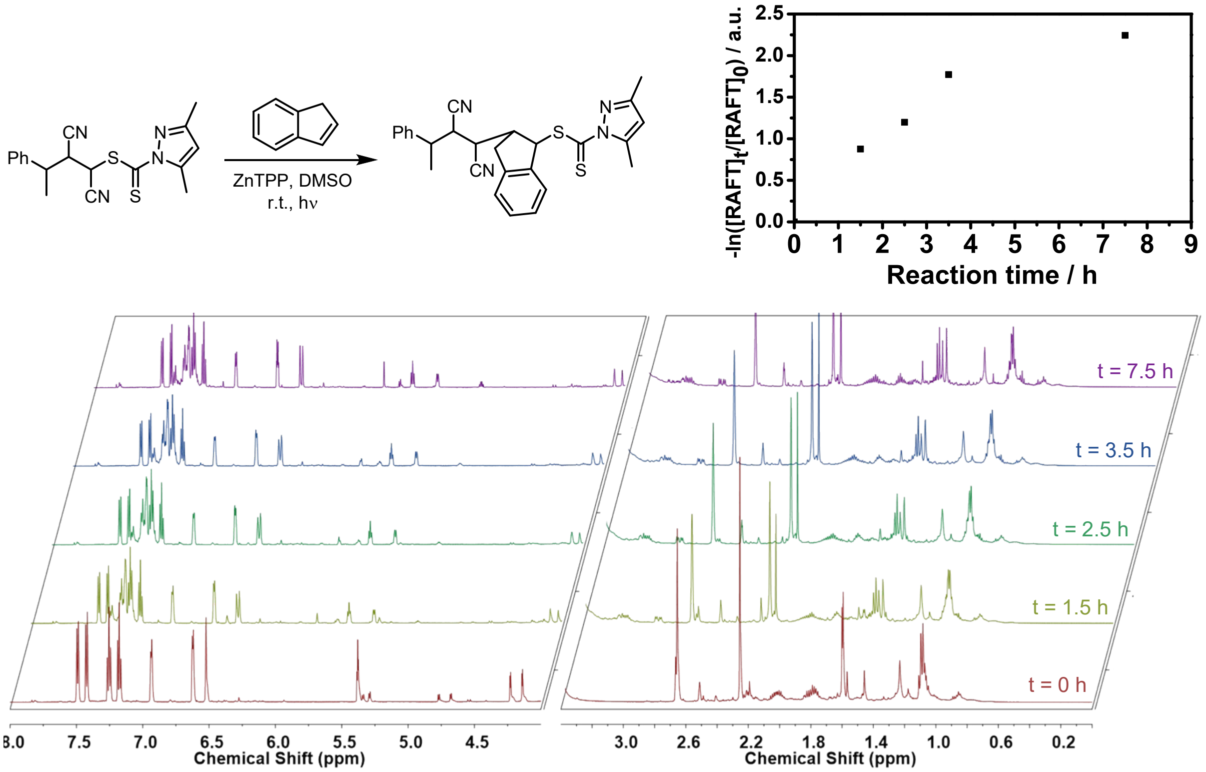

Fig. S1-7 Kinetics of PhMeCH-FCN-Ind-PCDT synthesis by $^1$H NMR (500.13 MHz, DMSO-*d*$_6$).

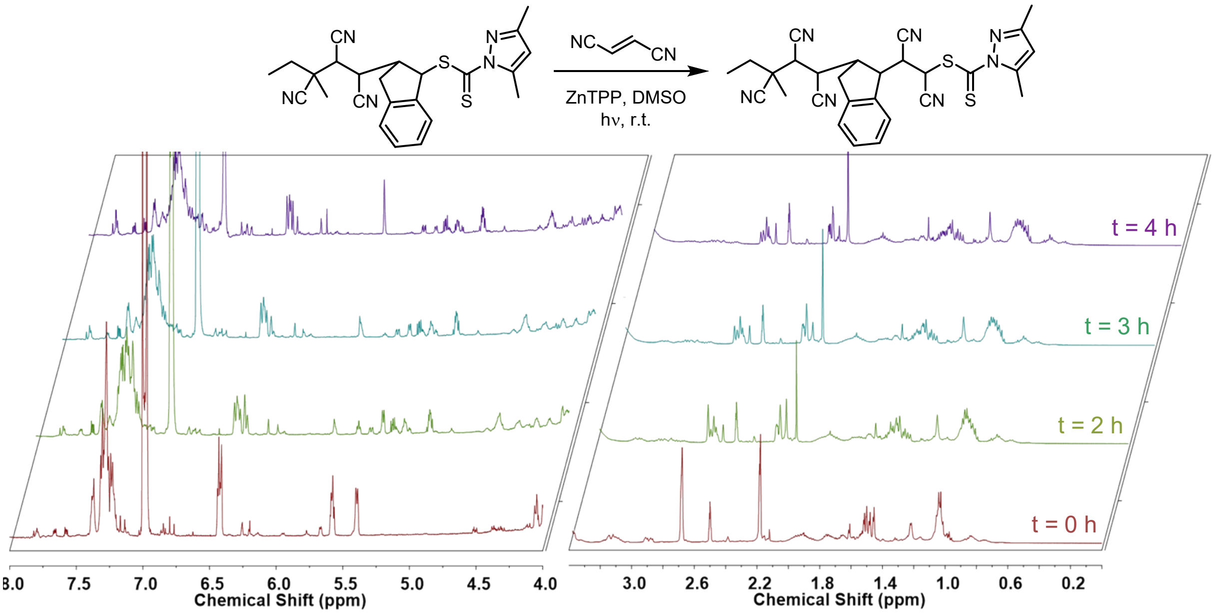

Fig. S1-8 Kinetics of IPN-FCN-Ind-FCN-PCDT synthesis by $^1H$ NMR (500.13 MHz, DMSO-$d_6$). *N.B.,* Reaction reached completion after 2 h and didn't change with subsequent time points.

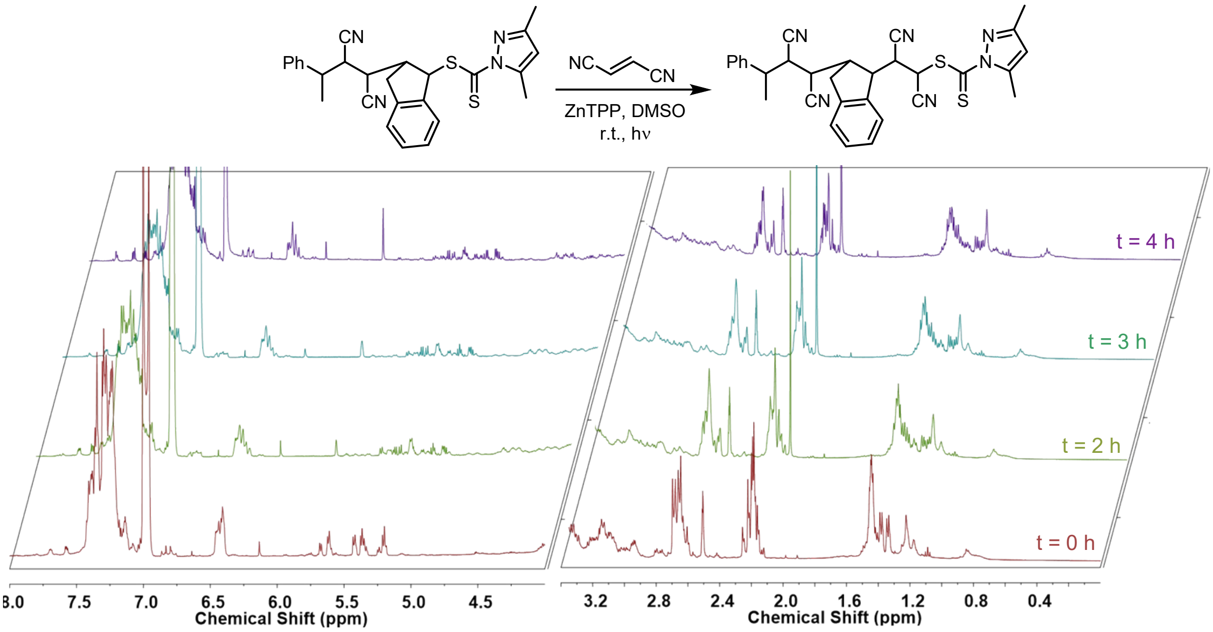

Fig. S1-9 Kinetics of PhMeCH-FCN-Ind-FCN-PCDT synthesis by $^1H$ NMR (500.13 MHz, DMSO-$d_6$). *N.B.,* Reaction reached completion after 2 h and didn't change with subsequent time points.

# S2. Supplementary Computational Data

## Detailed Quantum Mechanical Methodology

All density functional theory (DFT) and wavefunction calculations were performed in ORCA 5.0.4.[1] Geometry optimisations were performed using the B97M-V functional[2] and def2-TZVP basis set,[3] using the resolution of the identity (RI) approximation and a def2/J auxiliary basis set.[4] These optimisations were performed directly in a conductor-like polarisable continuum model (CPCM) solvent field,[5] with dimethyl sulfoxide (DMSO) chosen as the solvent. A full-tree search was conducted on all species using a resolution of 120° and 180° for $sp^3$-$sp^3$ and $sp^3$-$sp^2$ bonds, respectively. We also considered all possible diastereoisomers for the 4 SUMI adducts (see below). Having optimised the structures, (numerical) frequencies were calculated in CPCM solution to confirm structures were true minima (possessing no imaginary frequencies) or transition states (possessing a single imaginary frequency). Global minimum conformations were selected based on their respective B97M-V/def2-TZVP Gibbs Free Energy values.

Improved energies were calculated with DLPNO-CCSD(T)[6-8] and the cc-pVTZ basis set,[9, 10] using the RIJCOSX approximation and the cc-pVTZ/C and def2/J auxiliary basis sets, with Tight PNO cut-offs.[4, 11, 12] These DLPNO-CCSD(T) single point calculations were also performed in a CPCM solvent field. All DFT and DLPNO-CCSD(T) calculations were performed using ‘Tight’ Self-Consistent Field (SCF) cut-offs. Solution-phase Gibbs free energy values were then calculated using the “direct method”.[13] The default standard state used within ORCA 5.0.4. for entropic components (even in a CPCM solvent field) is based on the statistical mechanics for an ideal gas (evaluated at 1 atm of pressure and 25 °C). Thus, a standard state correction was applied to ensure all Gibbs Free Energy values were calculated at a standard state for solution (of 1 mol/L and 25 °C).

## Gibbs Free Energy Data

Table S2-1. Summary of key Gibbs Free Energy data for SUMI processes

| **System** | | **Gibbs Free Energy (kJ/mol)** | | | |
|---|---|---|---|---|---|
| **Z group** | **R group** | $\Delta G_{Frag}$ | $\Delta G_{Add}$ | $\Delta G_{Reform}$ | $\Delta G_{SUMI}$ |
| $(C_1)$TTC | IBN | 160.6 | −21.1 | −169.2 | −29.7 |
| PCDT | IBN | 152.3 | −21.1 | −162.8 | −31.6 |
| $(C_1)$TTC | PhMeCH | 172.2 | −26.0 | −178.4 | −32.2 |
| PCDT | PhMeCH | 165.3 | −26.0 | −172.4 | −33.1 |

Table S2-2. Raw energy values for all relevant species/intermediates involved in RAFT SUMI processes studied. All energy values are given in Hartree's.

| **Species** | **$E_0$ DLPNO-CCSD(T)** | **G B97M-V** | **$G{-}E_0$ B97M-V** | **$G_{sol}$ B97M-V** | **$G_{sol}$ High** |
|---|---|---|---|---|---|
| FCN | -262.631057 | -263.151062 | 0.022068 | -263.148043 | -262.605970 |
| PCDT-rad | -1137.175391 | -1138.563785 | 0.088469 | -1138.560766 | -1137.083903 |
| TTC-rad | -1271.042497 | -1272.319354 | 0.014432 | -1272.316336 | -1271.025047 |
| IBN-rad | -210.361289 | -210.758132 | 0.060110 | -210.755114 | -210.298161 |
| Sty-rad | -309.639197 | -310.251600 | 0.111836 | -310.248582 | -309.524342 |
| IBN-FCN-rad | -473.021374 | -473.904252 | 0.106192 | -473.901234 | -472.912163 |
| Sty-FCN-rad | -572.302301 | -573.404813 | 0.159077 | -573.401794 | -572.140206 |
| IBN-PCDT | -1347.619780 | -1349.361721 | 0.176680 | -1349.358703 | -1347.440081 |
| IBN-TTC | -1481.489352 | -1483.119649 | 0.101951 | -1483.116631 | -1481.384382 |
| Sty-PCDT | -1446.904290 | -1448.864082 | 0.230072 | -1448.861063 | -1446.671199 |
| Sty-TTC | -1580.773100 | -1582.622855 | 0.155106 | -1582.619836 | -1580.614975 |
| (*1R*,*2S*)-IBN-FCN-PCDT | -1610.286120 | -1612.515145 | 0.225028 | -1612.512127 | -1610.058073 |
| (*1S*,*2S*)-IBN-FCN-PCDT | -1610.283372 | -1612.513020 | 0.224724 | -1612.510001 | -1610.055629 |
| (*1R*,*2S*)-IBN-FCN-TTC | -1744.154086 | -1746.271854 | 0.149423 | -1746.268835 | -1744.001644 |
| (*1S*,*2S*)-IBN-FCN-TTC | -1744.153056 | -1746.271214 | 0.148894 | -1746.268195 | -1744.001143 |
| (*1R*,*2S*,*3R*)-PhMeCH-FCN-PCDT | -1709.570490 | -1712.018824 | 0.277715 | -1712.015805 | -1709.289757 |
| (*1S*,*2S*,*3R*)-PhMeCH-FCN-PCDT | -1709.570870 | -1712.018812 | 0.278315 | -1712.015793 | -1709.289536 |
| (*1S*,*2R*,*3R*)-PhMeCH-FCN-PCDT | -1709.569050 | -1712.017680 | 0.277126 | -1712.014661 | -1709.288905 |
| (*1R*,*2R*,*3R*)-PhMeCH-FCN-PCDT | -1709.569141 | -1712.017387 | 0.278083 | -1712.014369 | -1709.288039 |
| (*1R*,*2S*,*3R*)-PhMeCH-FCN-TTC | -1843.438580 | -1845.775630 | 0.202349 | -1845.772611 | -1843.233212 |
| (*1S*,*2S*,*3R*)-PhMeCH-FCN-TTC | -1843.438814 | -1845.775146 | 0.203265 | -1845.772127 | -1843.232530 |
| (*1S*,*2R*,*3R*)-PhMeCH-FCN-TTC | -1843.437042 | -1845.773468 | 0.202750 | -1845.770449 | -1843.231273 |
| (*1R*,*2R*,*3R*)-PhMeCH-FCN-TTC | -1843.437220 | -1845.773382 | 0.203682 | -1845.770363 | -1843.230520 |

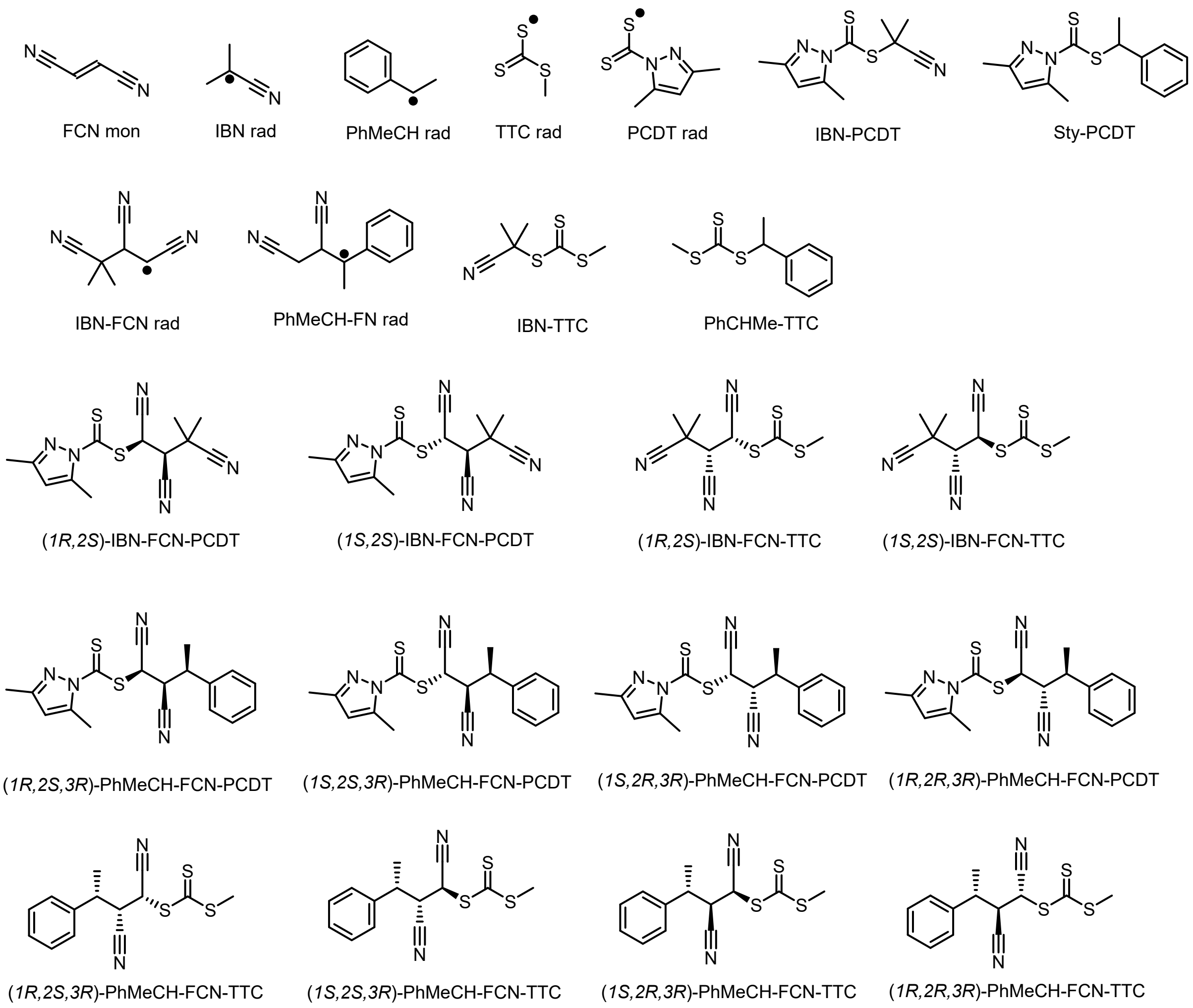

Fig. S2-1 Chemical structures of all relevant species/intermediates and their associated abbreviations.

# S3. Alternating copolymerisation methods and data

The alternating copolymerisations were performed with the following general conditions:

ZnTPP (~0.5 mg, 1 mol%) was dissolved in a solution of indene (1.16 g, 100 equiv) or styrene (1.02 g, 100 equiv), fumaronitrile (781 mg, 100 equiv) and chain transfer agent (~25.2 mg for IPN-PCDT, ~34.5 mg for IBN-($C_{12}$)TTC, 0.1 mmol, 1 equiv) in DMSO (7 mL). The mixture was then degassed by sparging under argon (*N.B.,* sparging with nitrogen was insufficient for this reaction) for 15 min, then irradiated under blue LED (0.42 mW $cm^{-2}$) for the allotted time.

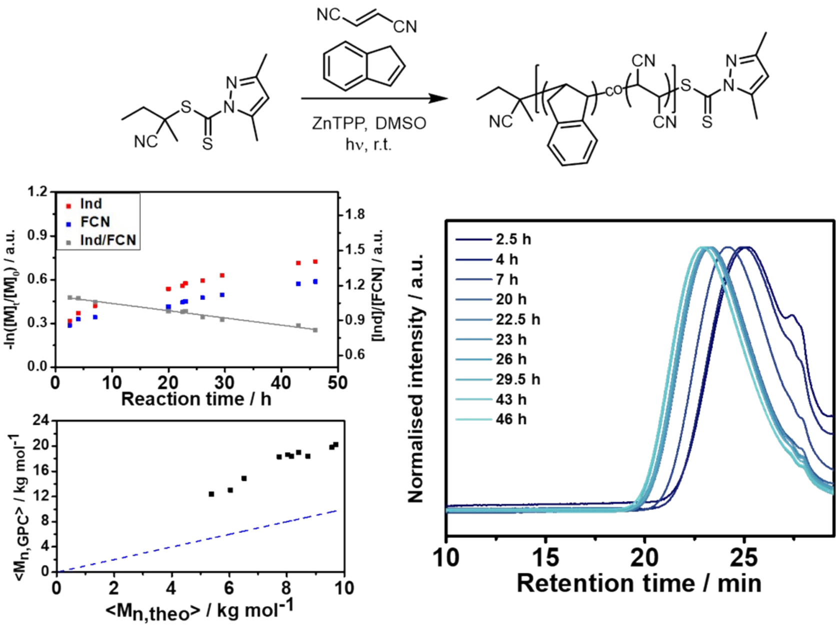

Fig. S3-1 Kinetics of each individual monomer conversion ([Ind]:[FCN]:[PCDT] = 100:100:1), their expected stoichiometry compared and the expected molecular weight (NMR) compared with the apparent molecular weight (GPC), along with GPC elugrams (DMAc, 1 mL $min^{-1}$, 50 $^{o}$C).

Indeed, similar kinetic features were observed with the “Z-group” changed to a trithiocarbontate. (see below)

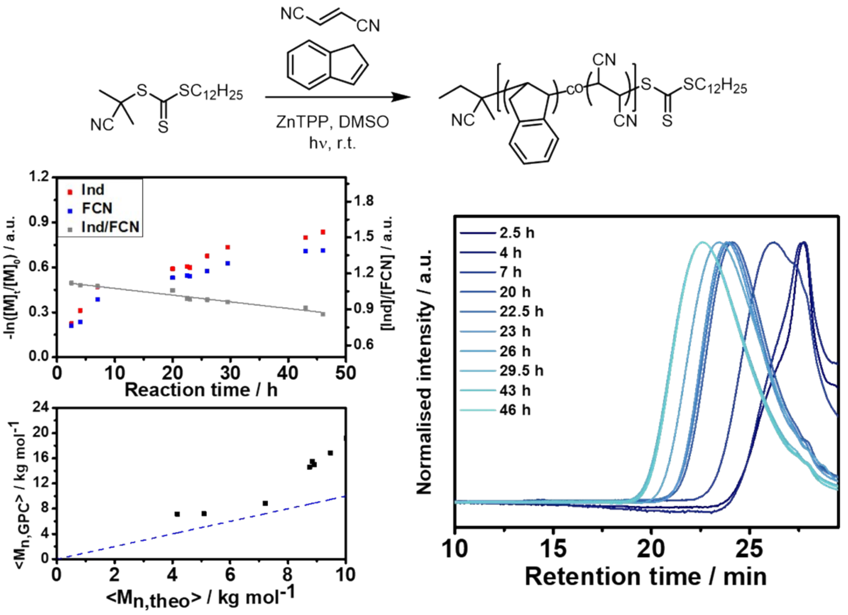

Fig. S3-2 Kinetics of each individual monomer conversion ([Ind]:[FCN]:[TTC] = 100:100:1), their expected stoichiometry compared and the expected molecular weight (NMR) compared with the apparent molecular weight (GPC), along with GPC elugrams (DMAc, 1 mL min$^{-1}$, 50 $^{o}$C).

When the alternating copolymerisation was run with [FCN]:[IND]:[PCDT] = 500:500:1, the apparent molecular weight (from GPC) over conversion appeared to converge more quickly than with a lower [FCN]:[IND]:[PCDT] stoichiometry, potentially indicating a limited kinetic chain length of polymerisation. (see below)

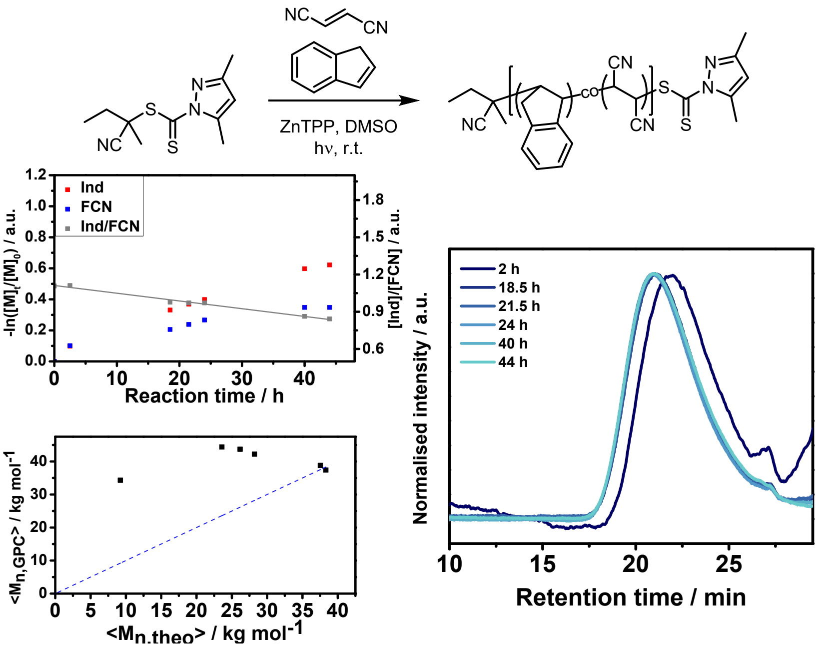

Fig. S3-3 Kinetics of each individual monomer conversion ([Ind]:[FCN]:[PCDT] = 500:500:1), their expected stoichiometry compared and the expected molecular weight (NMR) compared with the apparent molecular weight (GPC), along with GPC elugrams (DMAc, 1 mL min$^{-1}$, 50 $^{o}$C).

This behaviour was also observed when the indene was swapped for styrene (a higher $k_p$ monomer individually), albeit, converging to a higher molecular weight, possibly attributed to less backbone strain imparted from the styrene monomer unit. (see below)

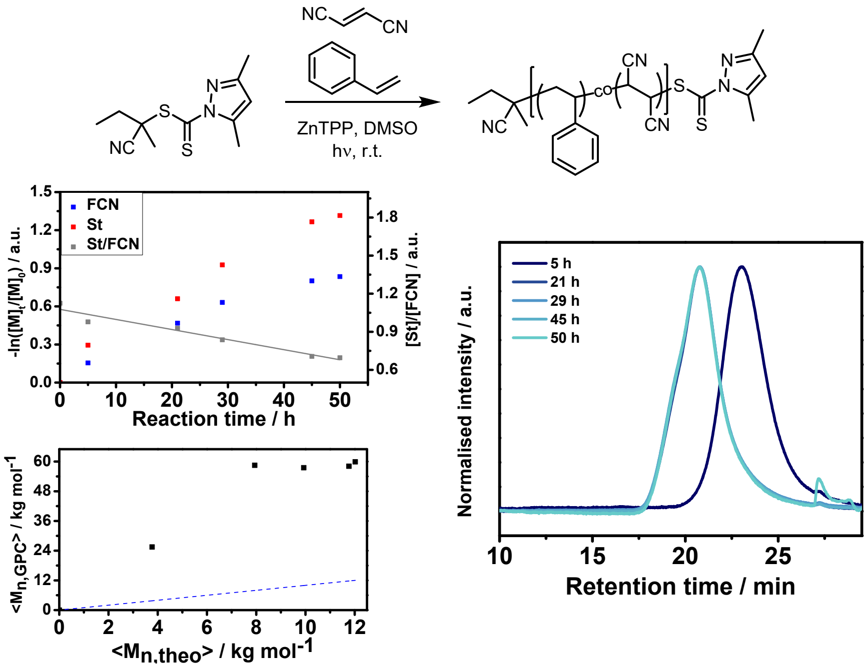

Fig. S3-4 Kinetics of each individual monomer conversion ([St]:[FCN]:[PCD] = 100:100:1), their expected stoichiometry compared and the expected molecular weight (NMR) compared with the apparent molecular weight (GPC), along with GPC elugrams (DMAc, 1 mL min$^{-1}$, 50 $^{o}$C).

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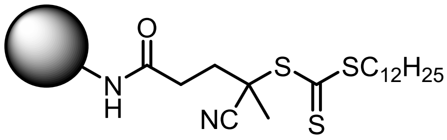
# APPENDIX

## A1. Solid-phase SUMI methods and characterisation

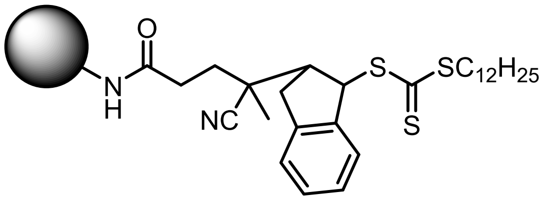
Reactions noted as performed at "ambient temperature" refer more specifically to 23 °C (50% humidity). Reactions were performed in fritted syringes, with photochemical reactions irradiated with two blue LED lamps ($\lambda_{max}$ = 450 nm, 1.05 mW cm$^{-2}$). See previous publication from our group for a photograph of the reaction setup.[14]

Reaction conversion measurements were performed by obtaining aliquots from the reaction solution under an atmosphere of nitrogen and minimal exposure to air. These were then analysed by $^1$H NMR. The integral of the resonances corresponding to the monomer (for indene: δ 7.44 ppm, d, 7.3 Hz; for fumaronitrile: δ 6.31 ppm, s) relative to resonance corresponding to DMF (δ 8.02 ppm, s) was used to determine the concentration of the monomer at the start of the reaction and at the end.



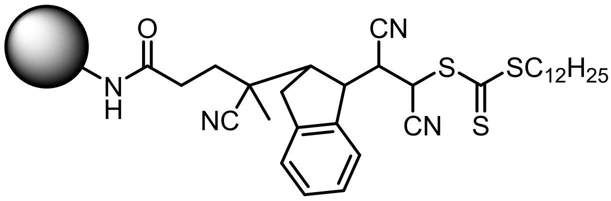
**Rink@CVA-($C_{12}$)TTC** The following procedure was performed according to our previous work.[14]

The functional Rink amide resin (105 mg) was first pre-swelled by agitating in DMF (3 mL) by shaking (900 rpm) at ambient temperature for 30 min. DMF was then ejected from the syringe, with the aid of vacuum (without fully drying the resin). A solution of piperidine in DMF (20% v/v, 2 mL) was then taken up and the resin left to agitate by shaking (900 rpm) at ambient temperature for 30 min. The reaction solution was then ejected, and the resin was washed with DMF (10 x 5 mL), DCM (4 x 5 mL) and finally, DMF again (4 x 5 mL). A solution of CVA-($C_{12}$)TTC (101 mg, 0.25 mmol), DIC (32 mg, 0.25 mmol) and Oxymapure (36 mg, 0.25 mmol) in DMF (1.25 mL) was then taken up and the resin agitated by shaking (900 rpm) at ambient temperature for 4 h. The reaction solution was then ejected, and the resin was washed with DMF (10 x 5 mL), DCM (4 x 5 mL) and finally, DMF again (4 x 5 mL). A solution of acetic anhydride in DMF (3 mL, 10% v/v) was then taken up and the resin agitated by shaking (900 rpm) at ambient temperature for 15 min. The solution was then ejected, and the resin was washed with DMF (7 x 3 mL).



**Rink@CVA-Ind-($C_{12}$)TTC** The following procedure was performed according to our previous work.[14]

Prior to starting the reaction, the Rink@CVA-($C_{12}$)TTC (100 mg) was pre-swelled by agitating in DMF (1.5 mL) by shaking (900 rpm) at ambient temperature for 15 min. DMF was then ejected from the syringe, with the aid of vacuum (without fully drying the resin). A solution of ascorbic acid (10 mg), indene (68.5 mg, 0.59 mmol) and ZnTPP (~1.4 mg, 1 mol% relative to CDTPA) in DMF (0.3 mL) was prepared by first dissolving the ascorbic acid and then the rest of the components in the order written. After this, the fritted syringe was capped and the resin left to agitate by shaking (900 rpm) at ambient temperature under blue LED irradiation ($\lambda_{max}$ = 450 nm, 1.05 mW $cm^{-2}$) for 15 h. The reaction solution was then ejected from the syringe, and an aliquot was taken for NMR analysis and a conversion of 36% was recorded.



**Rink@CVA-Ind-FCN-($C_{12}$)TTC** Prior to starting the reaction, the Rink@CVA-Ind-($C_{12}$)TTC (~110 mg) was pre-swelled by agitating in DMF (1.5 mL) by shaking (900 rpm) at ambient temperature for 15 min. DMF was then ejected from the syringe, with the aid of vacuum (without fully drying the resin). A solution of ascorbic acid (10 mg), fumaronitrile (32.5 mg, 0.42 mmol) and ZnTPP (~1.4 mg, 1 mol% relative to CDTPA) in DMF (0.3 mL) was prepared by first dissolving the ascorbic acid and then the rest of the components in the order written. After this, the fritted syringe was capped and the resin left to agitate by shaking (900 rpm) at ambient temperature under blue LED irradiation ($\lambda_{max}$ = 450 nm, 1.05 mW $cm^{-2}$) for 24 h. The reaction solution was then ejected from the syringe, and an aliquot was taken for NMR analysis and a conversion of 51% was recorded.

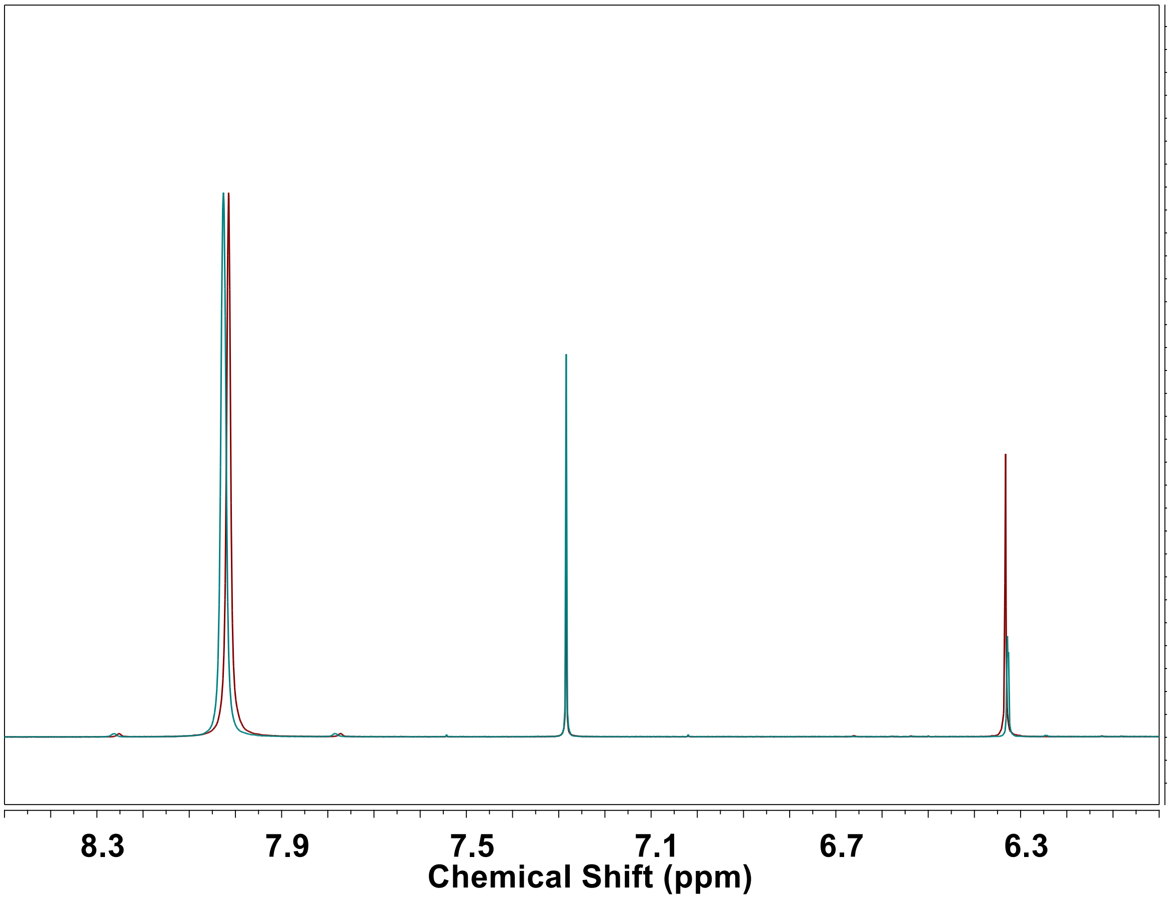
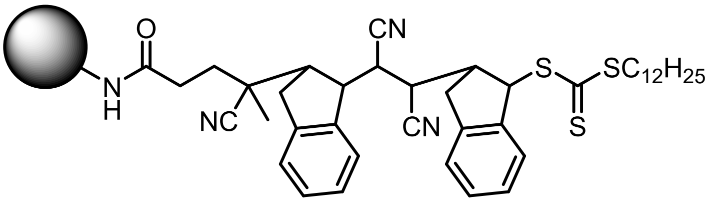
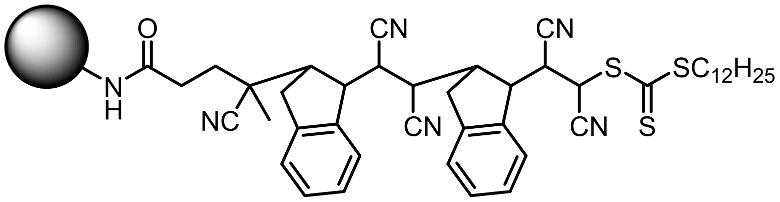


Fig. A1-1 $^1H$ NMR spectrum (400.17 MHz, $CDCl_3$) of the reaction mixture for the synthesis of Rink@CVA-Ind-FCN-($C_{12}$)TTC after 0 h irradiation (red) and 24 h irradiation (cyan).



**AND**



### Rink@CVA-Ind-FCN-Ind-($C_{12}$)TTC AND Rink@CVA-Ind-FCN-Ind-FCN-($C_{12}$)TTC

The procedure for synthesising Rink@CVA-Ind-($C_{12}$)TTC was repeated on this resin but with a smaller proportion of indene (48.3 mg, 0.42 mmol), and for 24 h irradiation, translating in a conversion of 57% by NMR.

After washing the resin with DMF, a similar procedure to the one used for synthesising Rink@CVA-Ind-FCN-($C_{12}$)TTC was repeated with 72 h irradiation, translating to nearly no conversion by NMR.

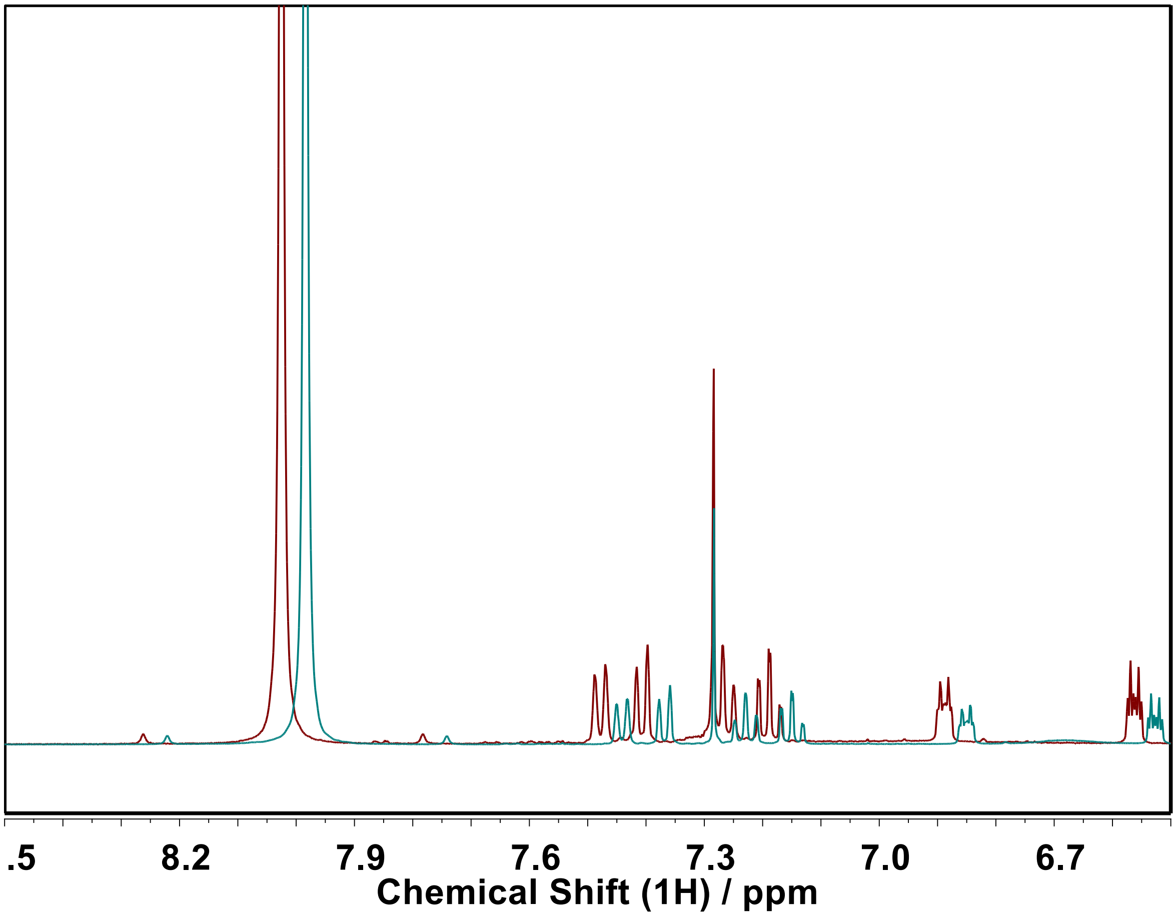


Fig. A1-2 $^1H$ NMR spectrum (400.17 MHz, $CDCl_3$) of the reaction mixture for the synthesis of Rink@CVA-Ind-FCN-Ind-($C_{12}$)TTC after 0 h irradiation (red) and 24 h irradiation (cyan).

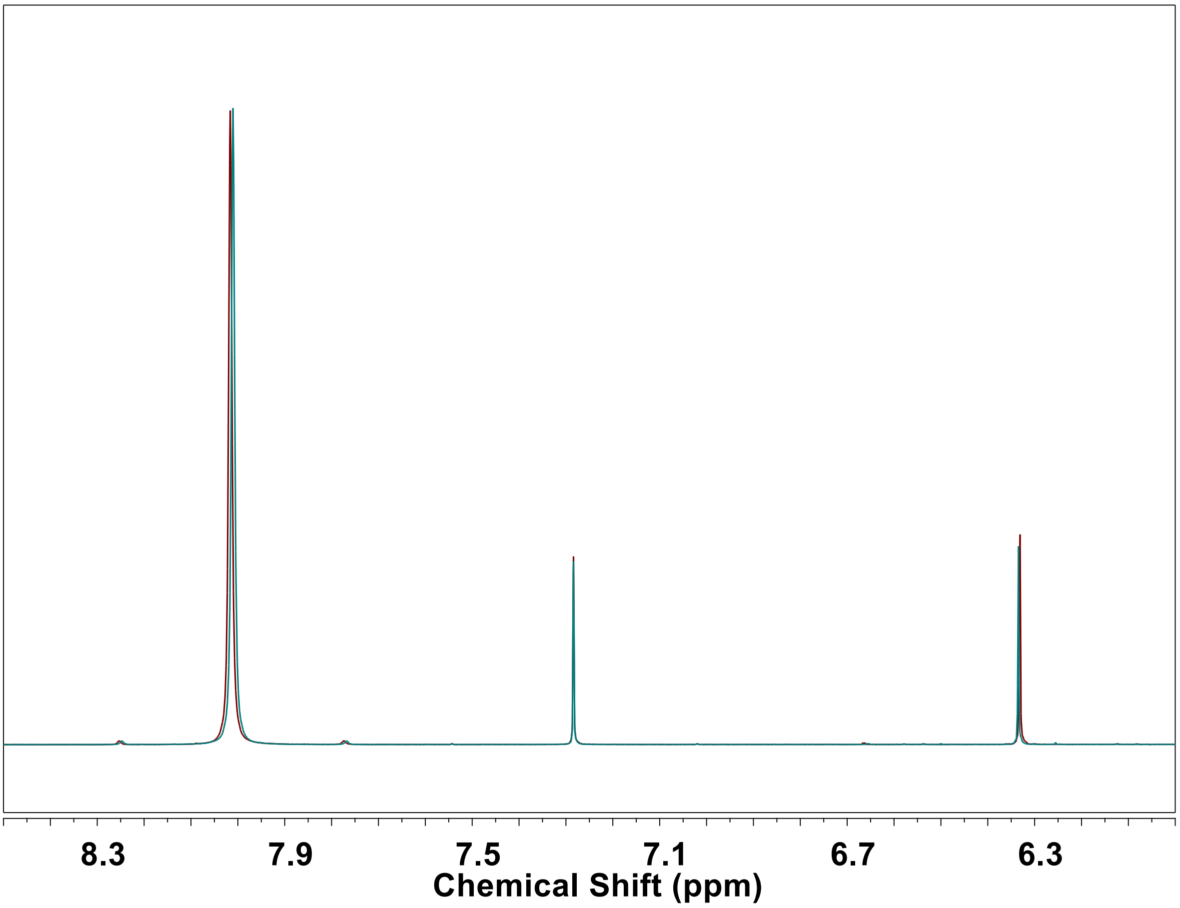
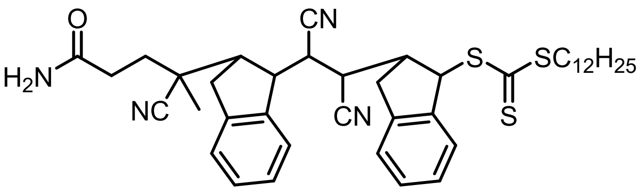
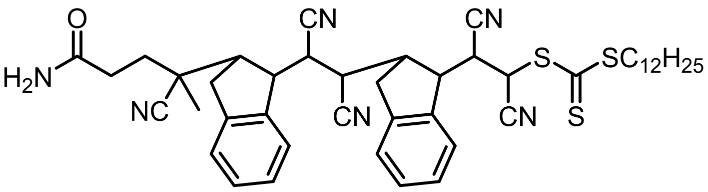


Fig. A1-3 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of the reaction mixture for the synthesis of Rink@CVA-Ind-FCN-Ind-($C_{12}$)TTC after 0 h irradiation (red) and 72 h irradiation (cyan).

The latter procedure was repeated again twice but with no change in reaction outcome.



**AND**



**CVAAm-Ind-FCN-Ind-($C_{12}$)TTC AND CVAAm-Ind-FCN-Ind-FCN-($C_{12}$)TTC** After washing the resin with DMF (5 x 3 mL) and DCM (5 x 3 mL), the product was then cleaved off by swelling the resin in a solution of TFA in DCM (50:50 v/v) and then agitated for 1 h at ambient temperature. The filtrate was then collected and dried under a stream of nitrogen, then under high vacuum and the product was isolated as a green solid.

HRMS (APCI) 791.36, 792.36, 793.36, 794.35 [CVAAm-Ind-FCN-Ind-FCN-($C_{12}$)TTC–H]$^+$; 713.34, 714.34, 715.33, 716.33 [CVAAm-Ind-FCN-Ind -($C_{12}$)TTC–H]$^+$; 597.27, 598.28, 599.27, 600.27 [CVAAm-Ind-FCN -($C_{12}$)TTC–H]$^+$; 513.24, 514.24, 515.25, 516.25 [CVAAm-Ind-($C_{12}$)TTC–H]$^+$

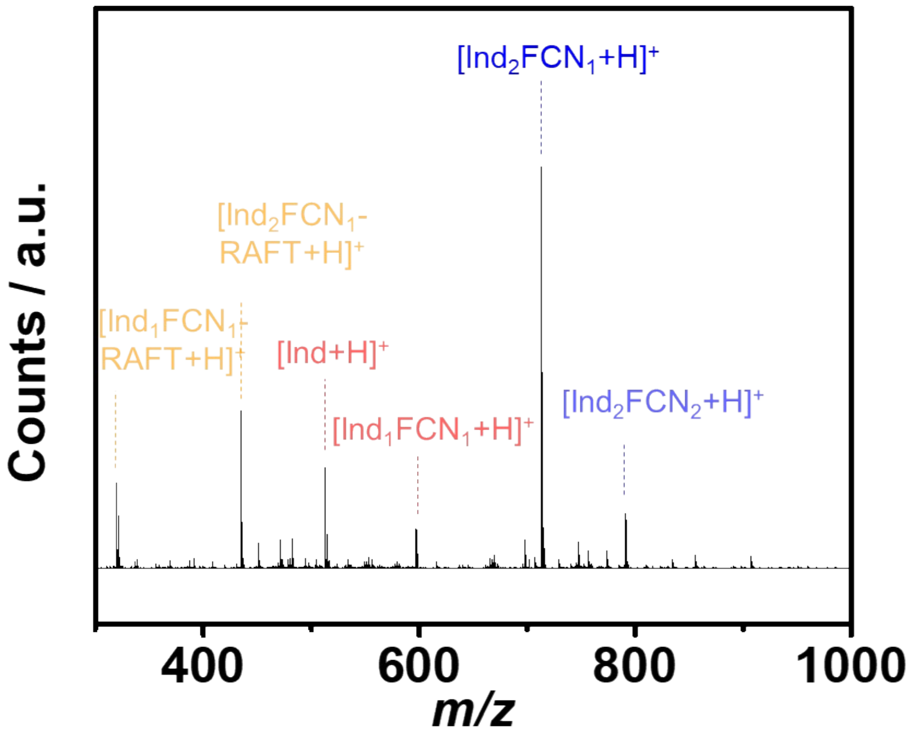
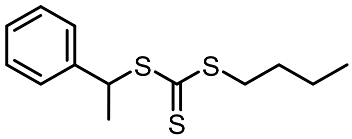


Fig. A1-4 APCI mass spectrum ($CH_3CN$) of CVAAm-Ind-FCN-Ind-($C_{12}$)TTC AND CVAAm-Ind-FCN-Ind-FCN-($C_{12}$)TTC.

## A2. Solution-phase SUMI methods and characterisation

For assignments of $^1$H NMR resonances annotated in the experimental, refer to spectra.



**PhMeCH-($C_4$)TTC** A solution of butanethiol (1.60 g, 17.7 mmol) and triethylamine (5.40 g, 31.6 mmol) in chloroform (15 mL) was stirred at ambient temperature for 30 min. Carbon disulphide (3.41 g, 44.8 mmol) was then added dropwise over the course of 30 min and the mixture was then left to stir at ambient temperature for 1 h. 1-Bromoethyl benzene (2.98 g, 15.5 mmol) was then added and the solution was left to stir at ambient temperature for 16 h. The reaction mixture was then washed with water (4 x 50 mL), dried under magnesium sulphate and then concentrated under vacuum. The residue was then purified under flash chromatography (ethyl acetate–hexanes gradient elution) and the product was obtained as a yellow oil (3.54 g, 80% yield).

TLC (hexanes) $R_f = 0.50$

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.41-7.35 (m, 2H), 7.35-7.30 (m, 2H), 7.29-7.23 (m, 1H), 5.34 (q, *J*= 7.1 Hz, 1H), 3.35 (d, *J*= 7.4 Hz, 2H), 1.76 (d, *J*= 7.1 Hz, 3H), 1.72-1.62 (m, 2H), 1.49-1.36 (m, 2H), 0.93 (t, *J*= 7.3 Hz, 3H).

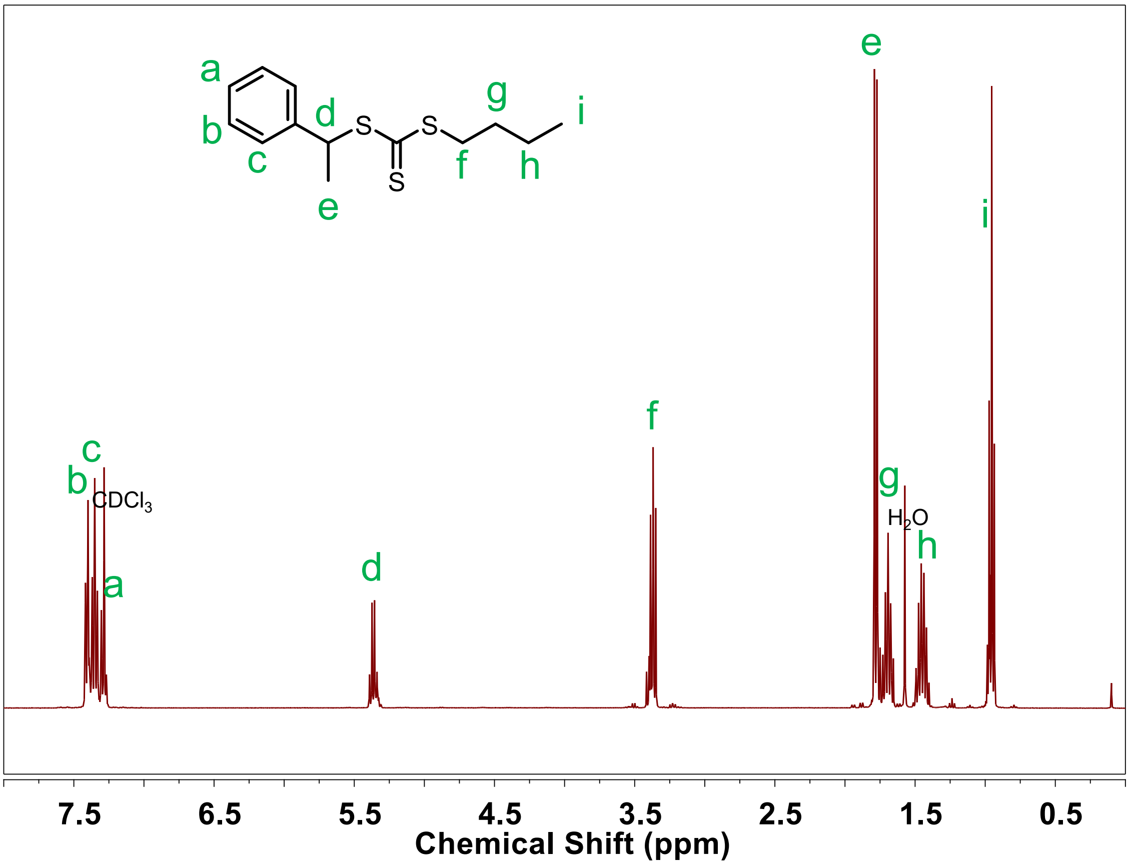
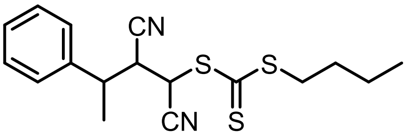


Fig. A2-1 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-($C_4$)TTC.



**PhMeCH-FCN-($C_4$)TTC** ZnTPP (~1.5 mg, 0.5 mol%) was added to a solution of PhMeCH-($C_4$)TTC (119 mg, 0.44 mmol) and fumaronitrile (344 mg, 10 eq) in DMSO (2 mL) in a 2 mL vial and sealed with a rubber septum. The reaction mixture was then irradiated under blue LED (0.42 mW $cm^{-2}$) for 16 h. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a green oil (89 mg, 58% yield).

A separate kinetic experiment was performed on an analogous solution in $d_6$-DMSO (0.5 mL – with all other components scaled equally) prepared in a Wilmad NMR tube (without a stirring bar) which was degassed by sparging under argon for 15 min prior to irradiation under the same blue LED. A similar workup and purification procedure was then performed to obtain the product in smaller yield (due to reaction scale).

TLC (20% v/v ethyl acetate in hexanes) $R_f = 0.52$

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.53-7.17 (m, 5H), 5.40 (d, *J*= 4.7 Hz), 5.10 (d, *J*= 5.9 Hz), 4.94 (d, *J*= 10.4 Hz), 4.83 (d, J = 4.4 Hz), 3.54 (dd, *J*= 10.4, 5.1 Hz), 3.47-3.25 (m), 3.20 (t, *J*= 7.4 Hz), 3.17 (dd, *J*= 10.9, 4.4 Hz), 1.76-1.62 (m, 2H), 1.61 (d, *J*= 6.8 Hz), 1.60 (d, *J*= 6.9 Hz), 1.59 (d, *J*= 7.0 Hz), 1.50-1.35 (m, 2H), 0.95 (td, J = 7.4, 1.4 Hz), 0.92 (t, *J*= 7.3 Hz).

HRMS (APCI) 349.09, 350.09, 351.08, 352.08 $[M–H]^+$. Calculated: 349.09, 350.09, 351.08, 352.09. N.B., No peaks from double addition (+78), from starting material (-78) or from β-elimination (-166) were found.

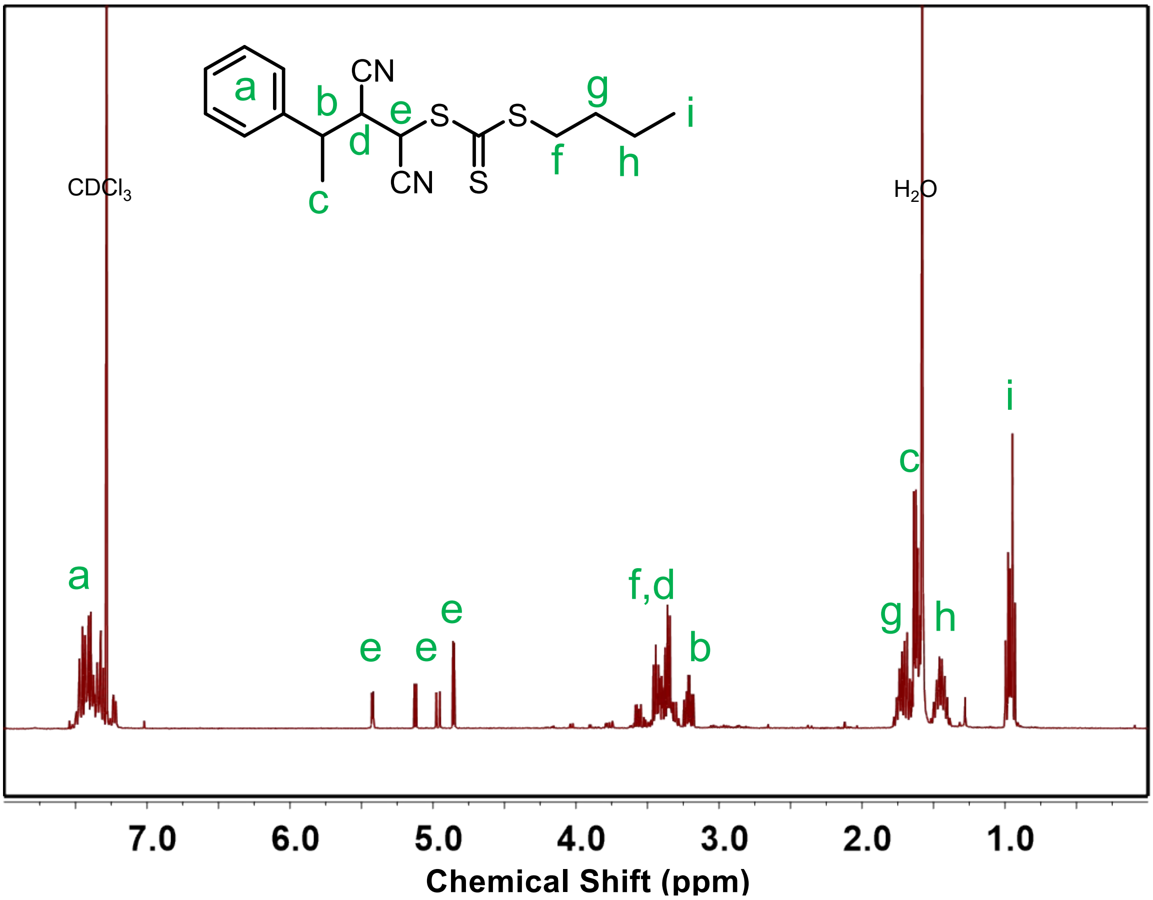


Fig. A2-2 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-FCN-($C_4$)TTC.

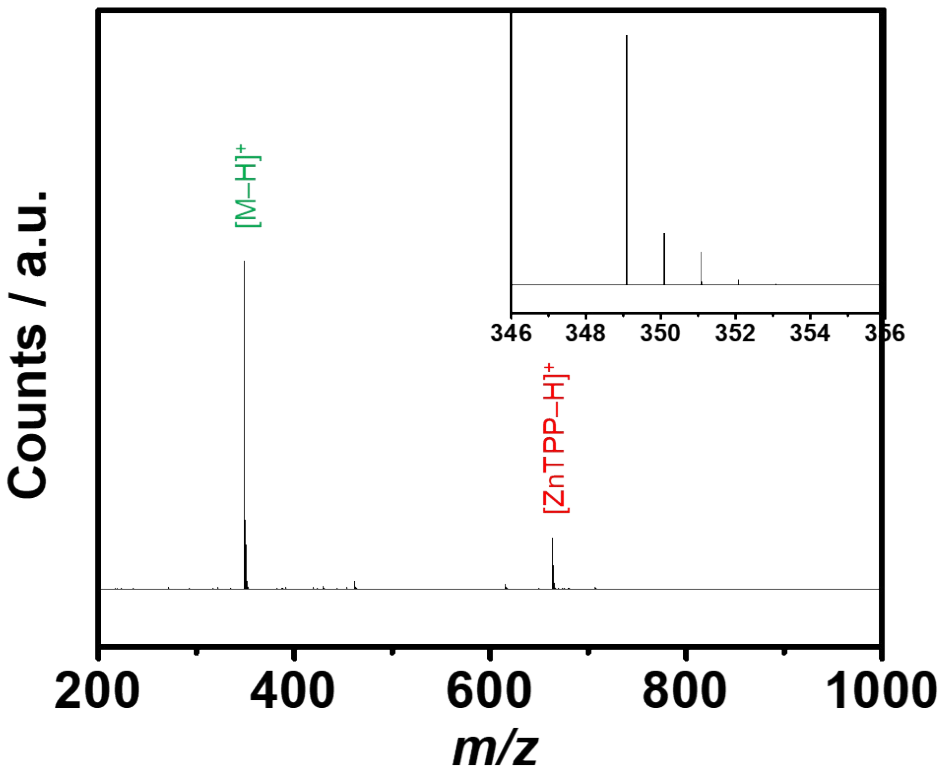


Fig. A2-3 APCI mass spectrum ($CH_3CN$) of PhMeCH-FCN-($C_4$)TTC.

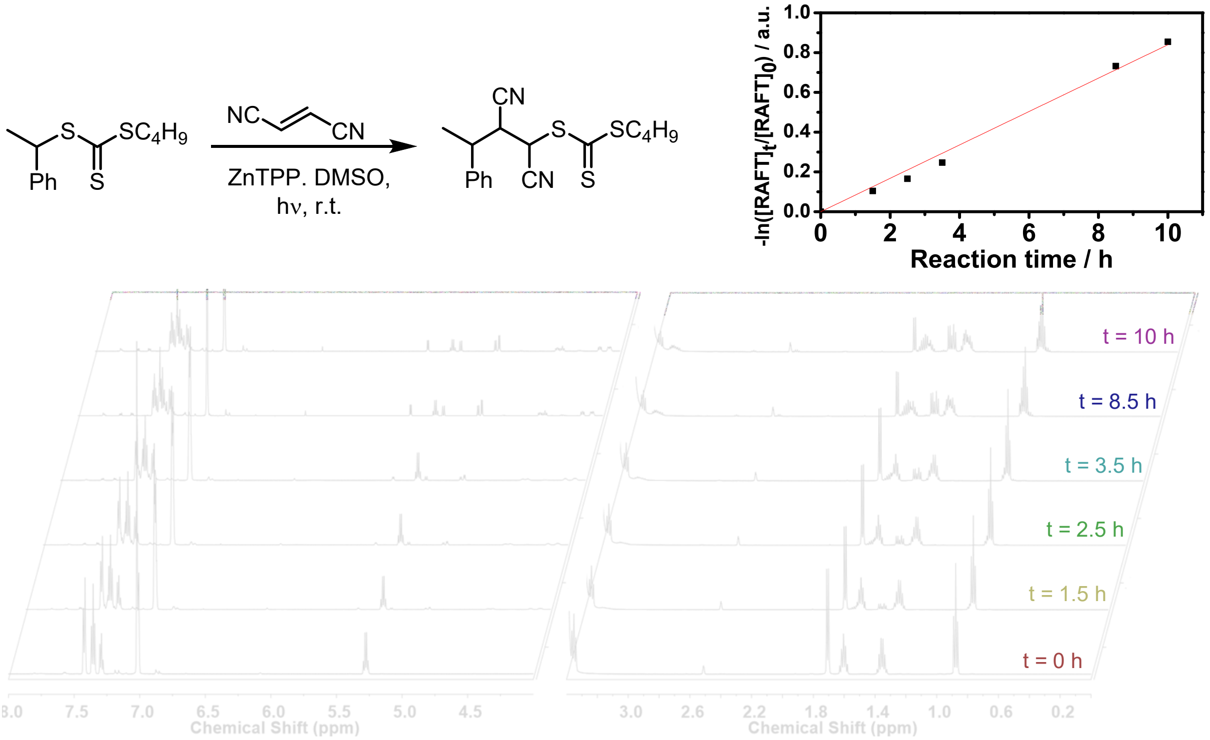
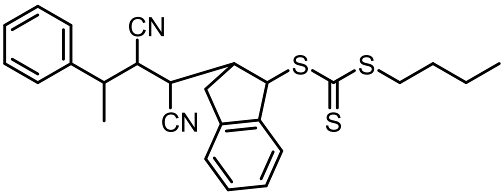


Fig. A2-4 Kinetics of PhMeCH-FCN-($C_4$)TTC synthesis by $^1H$ NMR (500.13 MHz, DMSO).



**PhMeCH-FCN-Ind-($C_4$)TTC** ZnTPP (~0.3 mg, 0.5 mol%) was added to a solution of PhMeCH-($C_4$)TTC (35 mg, 0.1 mmol) and indene (116 mg, 10 equiv) in DMSO (0.22 mL) in a 250 µL insert (without a stirring bar) and sealed with a septum. The reaction mixture was then irradiated under blue LED (0.42 mW $cm^{-2}$) for 16 h. The reaction mixture was then dissolved diethyl ether (30 mL) and then washed with water (3 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified by flash chromatography (ethyl acetate–hexanes gradient elution) and the product was obtained as two diastereomer fractions of yellow-to-green solids (40 mg, 85% total yield).

TLC (20% v/v ethyl acetate in hexanes) $R_f$ = 0.39 (diastereomer fraction 1); $R_f$ = 0.28 (diastereomer fraction 2)

$^1$H NMR (400.17 MHz, $CDCl_3$) 7.59-7.10 (m, 9H), 6.26 (d, *J*= 6.9 Hz), 6.16-6.06 (m), 5.79 (d, *J*= 8.2 Hz), 5.69 (d, *J*= 6.8 Hz), 5.68 (d, *J*= 5.5 Hz), 5.62 (d, *J*= 6.9 Hz), 5.39 (d, *J*= 4.8 Hz), 3.56-2.93 (m, 7H)  2.92-2.76 (m, 1H), 1.82-1.68 (m, 2H), 1.64 (d, *J*= 7.0 Hz), 1.60 (d, *J*= 6.5 Hz), 1.57-1.40 (m, 2H), 1.55 (d, *J*= 6.9 Hz), 1.50 (d, *J*= 6.9), 1.49 (d, *J*= 6.9), 1.04-0.94 (m, 3H). *N.B.,* Full list of resonances generated from both diastereomer fractions isolated.

HRMS (APCI) 465.15, 466.15, 467.16, 468.16 $[M–H]^+$. Calculated: 465.15, 466.15, 467.14, 468.15. N.B., No peaks from starting material (-116) or from Ind double-insertion (+116) were found.

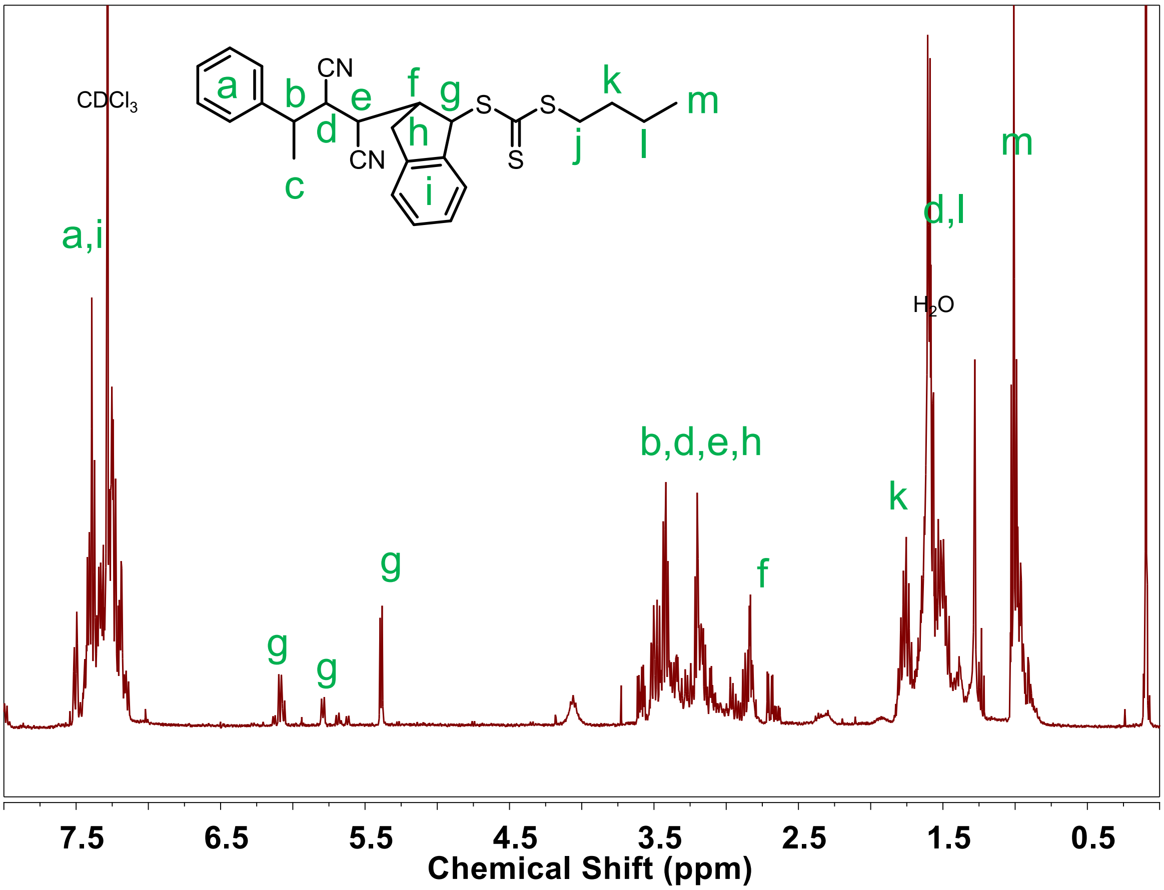


Fig. A2-5 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-FCN-Ind-($C_4$)TTC (fraction 1).

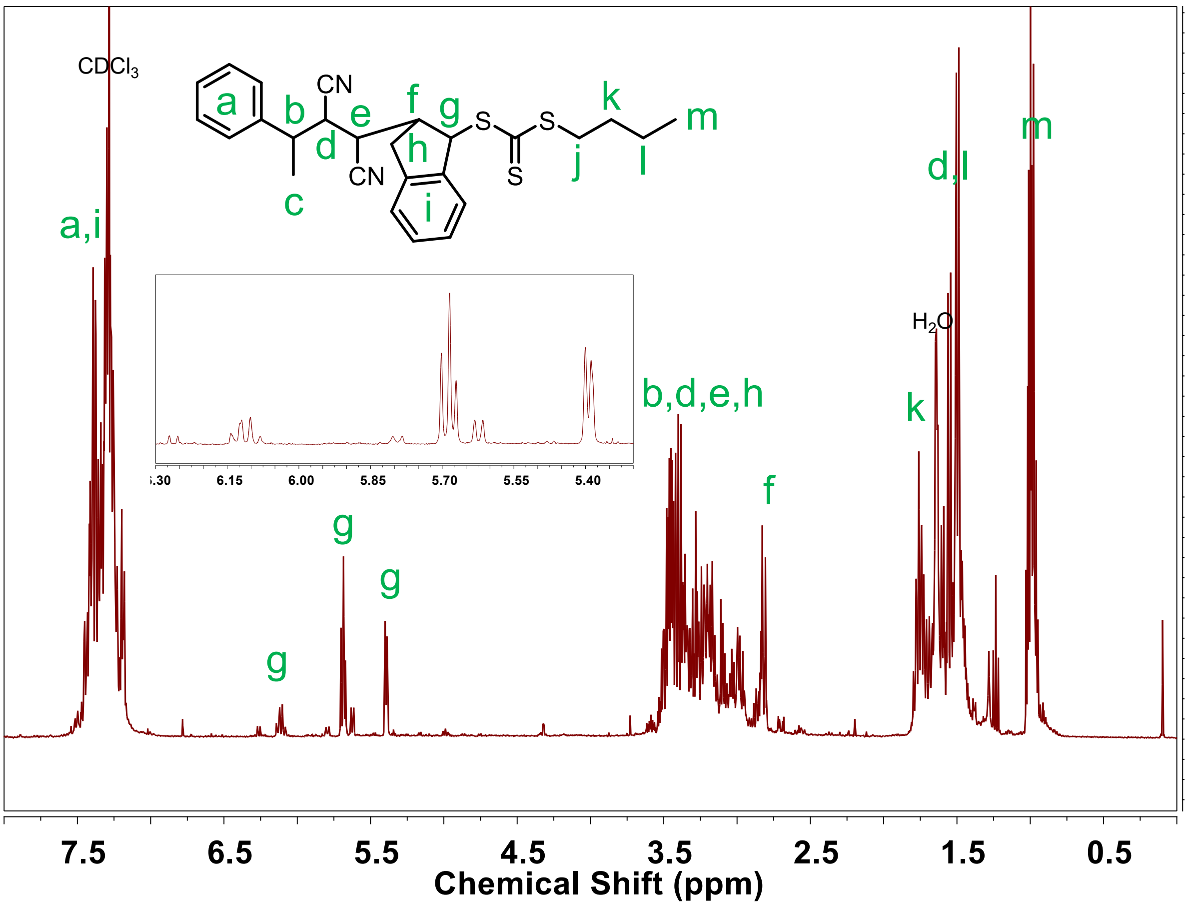


Fig. A2-6 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-FCN-Ind-($C_4$)TTC (fraction 2).

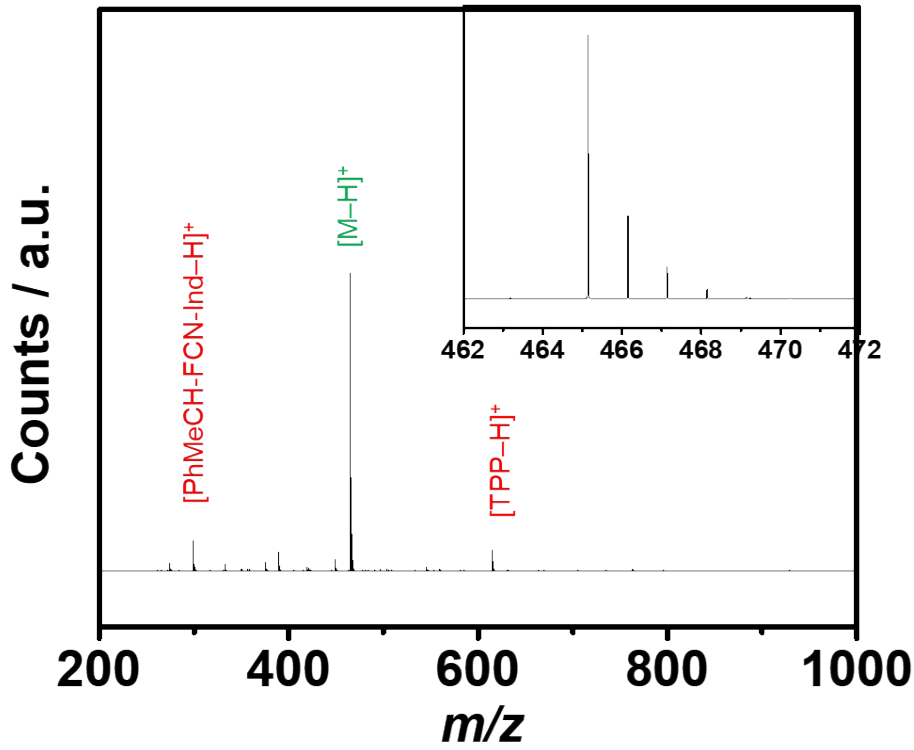
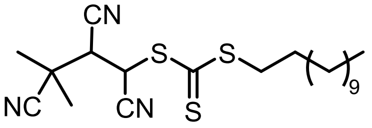


Fig. A2-7 APCI mass spectrum ($CH_3CN$) of PhMeCH-FCN-Ind-($C_{12}$)TTC.



**IBN-FCN-($C_{12}$)TTC** ZnTPP (~1.5 mg, 0.5 mol%) was added to a solution of IBN-($C_{12}$)TTC (152 mg, 0.44 mmol) and fumaronitrile (344 mg, 10 equiv) in DMSO (2 mL) in a 2 mL vial and sealed with a rubber septum. The reaction mixture was then irradiated under blue LED (0.42 mW cm$^{-2}$) for 48 h. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (3 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography (ethyl acetate–hexanes gradient elution) and the product was obtained as a yellow-to-green oil (7 mg, ~9% yield).

TLC (10% v/v ethyl acetate in hexanes) Rf = 0.15

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 5.72 (d, *J*= 5.9 Hz), 5.59 (d, *J*= 3.5 Hz), 3.53 (d, *J*= 6.0 Hz) 3.44 (t, *J*= 7.4 Hz), 3.32 (d, *J*= 3.5 Hz), 3.20 (t, J = 7.4 Hz), 1.77 (s, 3H), 1.77-1.70 (m, 2H), 1.68 (s, 3H), 1.47-1.16 (m, 18H) 0.88 (t, *J*= 6.8 Hz).

HRMS (APCI) 424.19. 425.19, 426.19, 427.19 [M–H]$^+$. Calculated: 424.19, 425.19, 426.19, 427.19. *N.B.,* No peaks from FCN double-insertion (+78) were found.

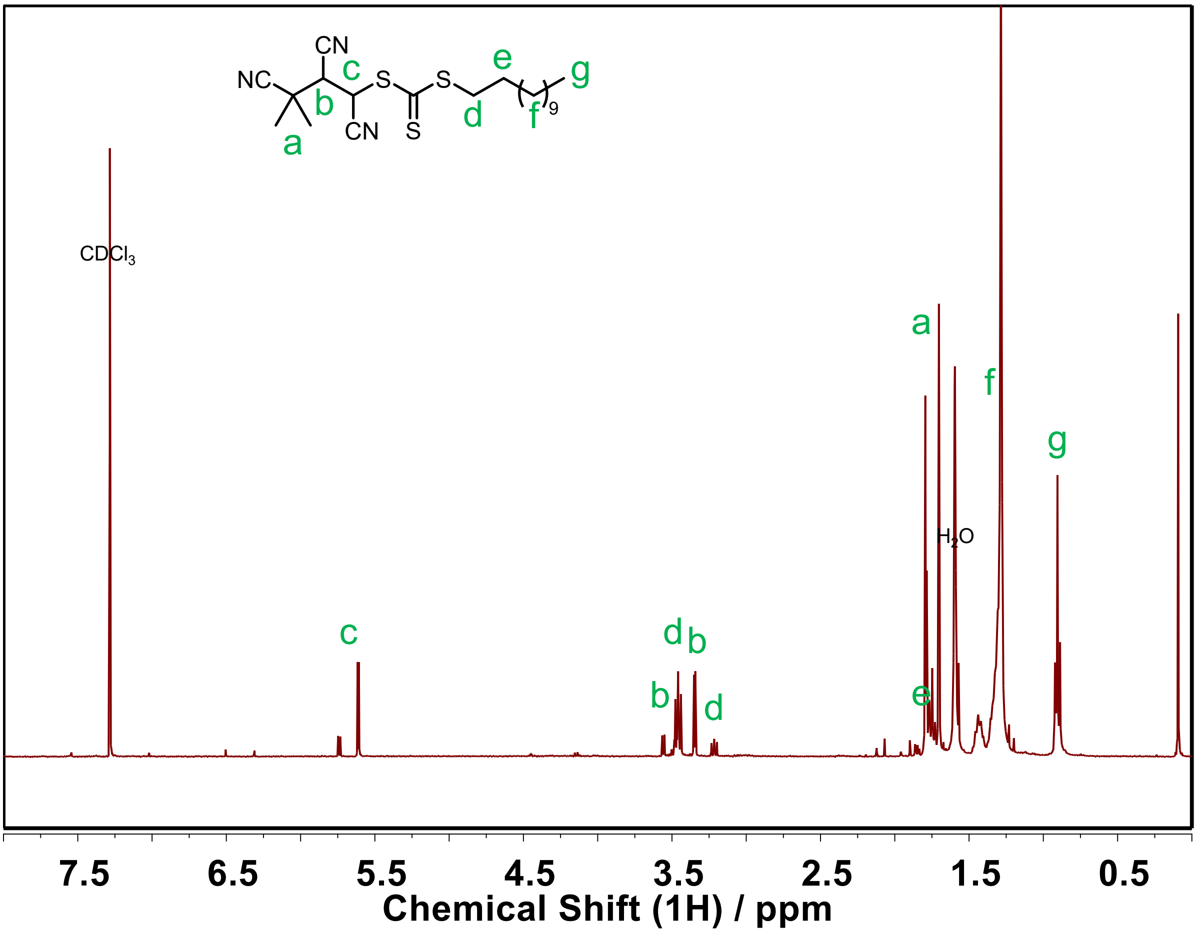


Fig. A2-8 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IBN-FCN-($C_{12}$)TTC.

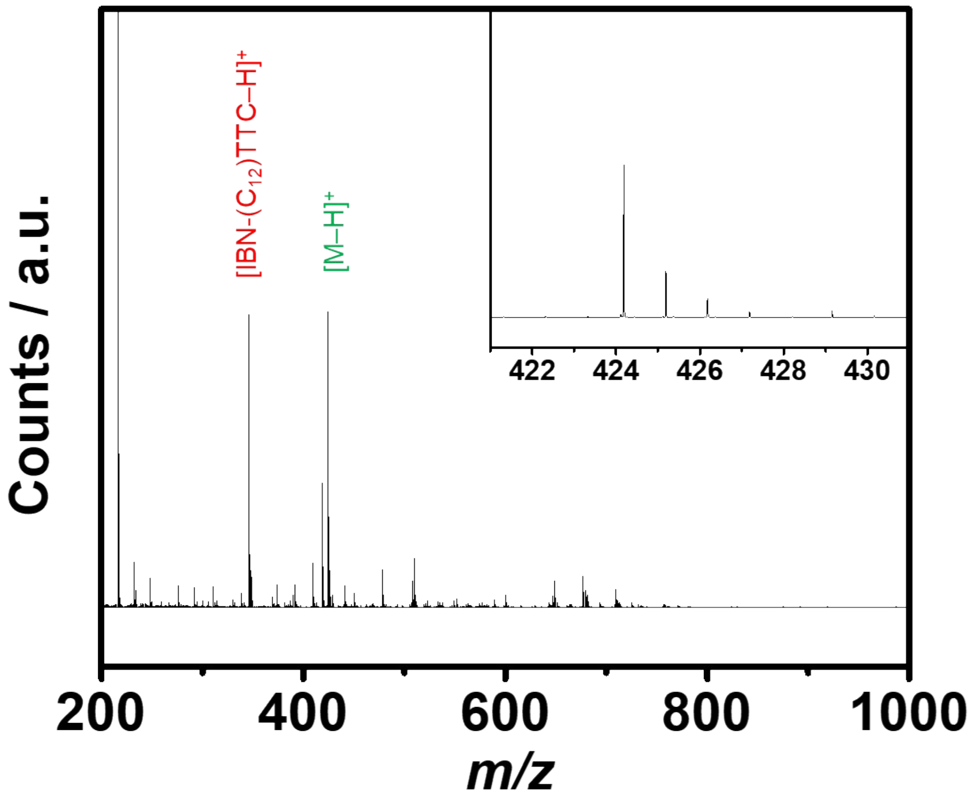
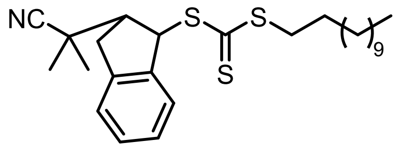


Fig. A2-9 APCI mass spectrum ($CH_3CN$) of IBN-FCN-($C_{12}$)TTC.



**IBN-Ind-($C_{12}$)TTC** ZnTPP (~1.5 mg, 0.5 mol%) was added to a solution of IBN-($C_{12}$)TTC (152 mg, 0.44 mmol) and indene (512 mg, 10 equiv) in DMSO (2 mL) in a 2 mL vial and sealed with a rubber septum. The reaction mixture was then irradiated under blue LED (0.42 mW $cm^{-2}$) for 16 h. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (3 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography (ethyl acetate–hexanes gradient elution) and the product was obtained as a yellow-to-green solid (162 mg, 80% yield).

TLC (4% v/v ethyl acetate in hexanes) $R_f = 0.27$.

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.36-7.10 (m, 4H), 5.98 (d, *J*= 7.2 Hz, 1H), 3.42 (td, *J*= 7.3, 3.5 Hz, 2H), 3.20 (ddd, *J*= 23.8, 16.4, 8.3 Hz, 2H), 2.72 (dt, *J*= 9.0, 7.3 Hz, 1H), 1.80-1.68 (m, 2H), 1.46 (d, *J*= 13.8 Hz, 6H), 1.41-1.23 (m, 18H), 0.88 (t, *J*= 6.9 Hz, 3H).

HRMS (APCI) 462.23, 463.23, 463.23, 464.23 $[M–H]^+$. Calculated: 462.23, 463.24, 464.23, 465.23. *N.B.,* No peaks from Ind double-insertion (+116) were found.

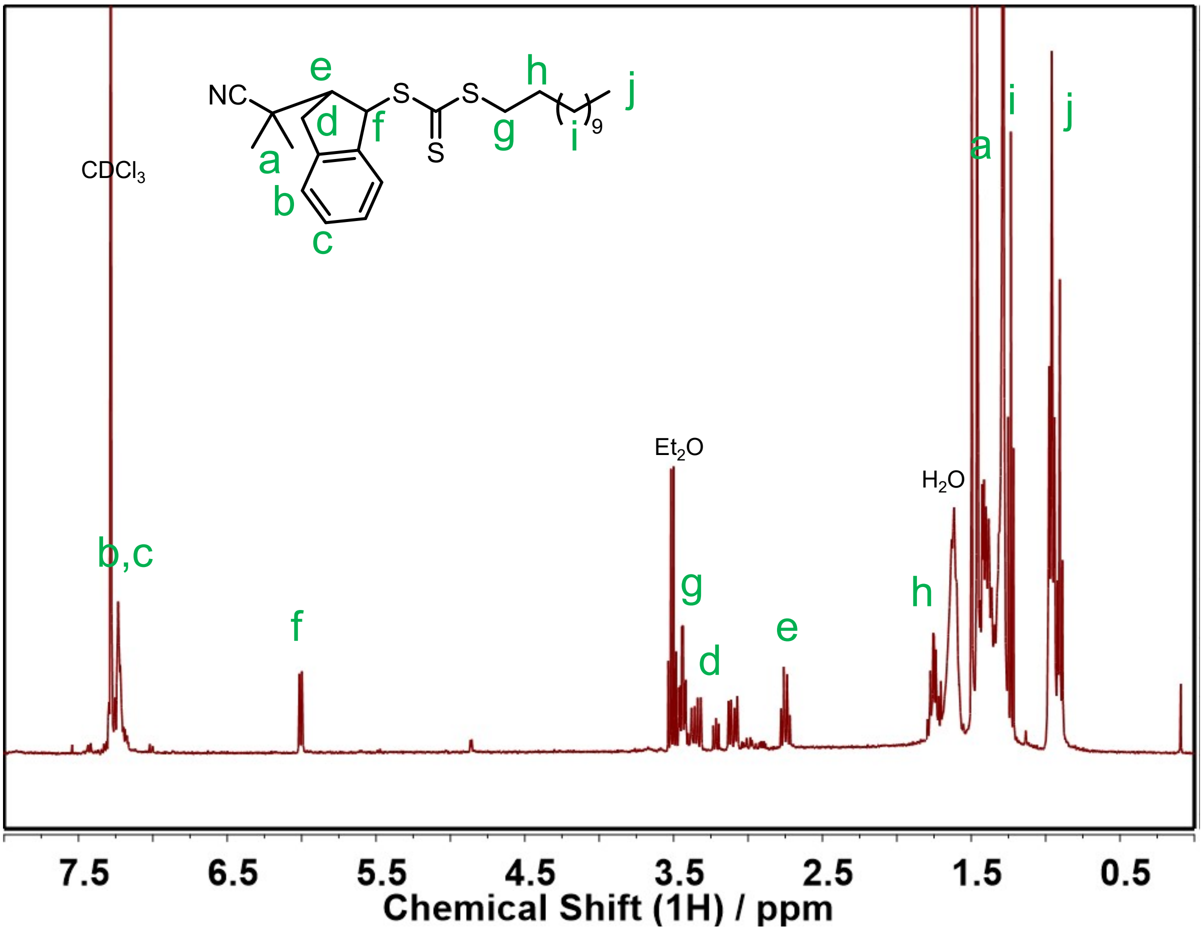


Fig. A2-10 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IBN-Ind-($C_{12}$)TTC.

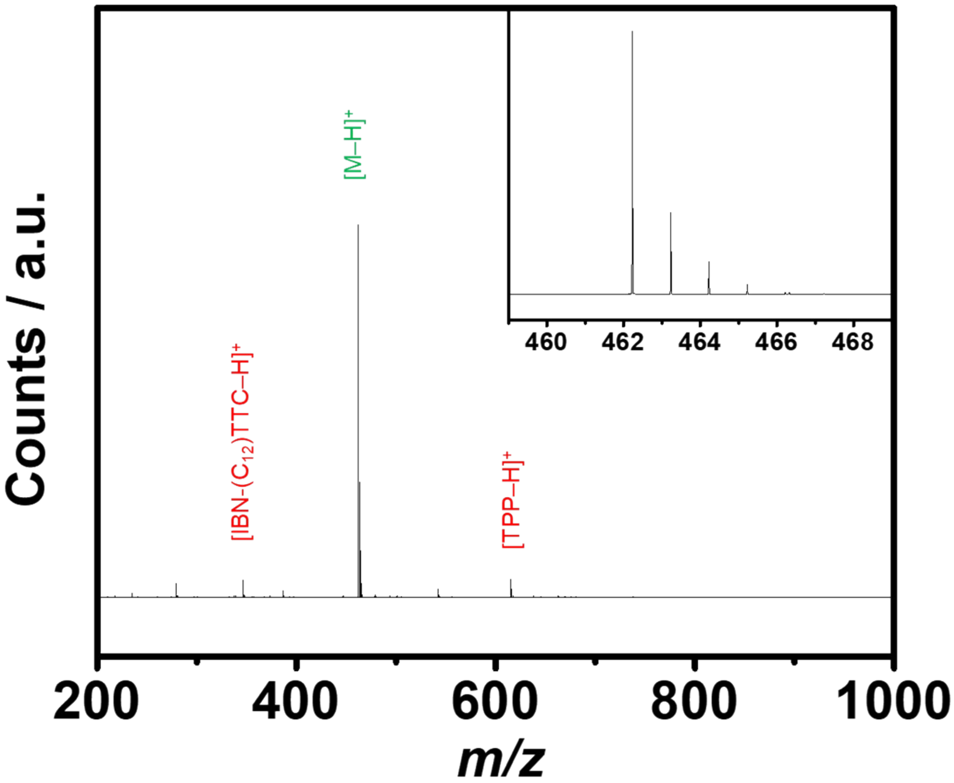
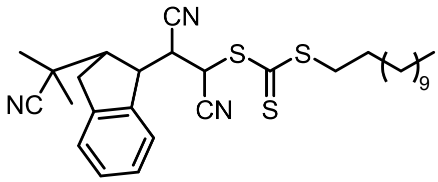


Fig. A2-11 APCI mass spectrum ($CH_3CN$) of IBN-Ind-($C_{12}$)TTC.



**IBN-Ind-FCN-($C_{12}$)TTC** ZnTPP (~1.5 mg, 0.5 mol%) was added to a solution of IBN-Ind-($C_{12}$)TTC (203 mg, 0.44 mmol) and fumaronitrile (344 mg, 10 equiv) in DMSO (2 mL) in a 2 mL vial and sealed with a rubber septum. The reaction mixture was then irradiated under blue LED (0.42 mW cm$^{-2}$) for 48 h. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (3 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography (ethyl acetate–hexanes gradient elution) and the product was obtained as a yellow-to-green oil (213 mg, 90% yield).

A separate kinetic experiment was performed on an analogous solution in $d_6$-DMSO (0.5 mL – with all other components scaled equally) prepared in a Wilmad NMR tube (without a stirring bar) which was degassed by sparging under argon for 15 min prior to irradiation under the same blue LED. A similar workup and purification procedure was then performed to obtain the product in smaller yield (due to reaction scale).

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.55-7.06 (m, 4H), 5.51 (dd, *J*= 9.8, 8.0 Hz), 5.38 (dd, *J*= 4.3, 1.3 Hz), 3.91-3.52 (m), 3.51-3.31 (m, 2H), 3.20 (ddd, *J*= 12.2, 8.5, 4.3 Hz), 3.10-2.88 (m), 2.86-2.80 (m), 1.81-1.65 (m, 2H), 1.48-1.18 (m, 24H), 0.88 (t, *J*= 6.8 Hz, 3H).

HRMS (APCI) 450.25, 451.25, 452.25, 453.25 [M–H]$^+$. Calculated: 540.25, 541.26, 542.25, 542.26. *N.B.,* No peaks from FCN double-insertion (+78), from starting material (-78) or from β-elimination (-188) were found.

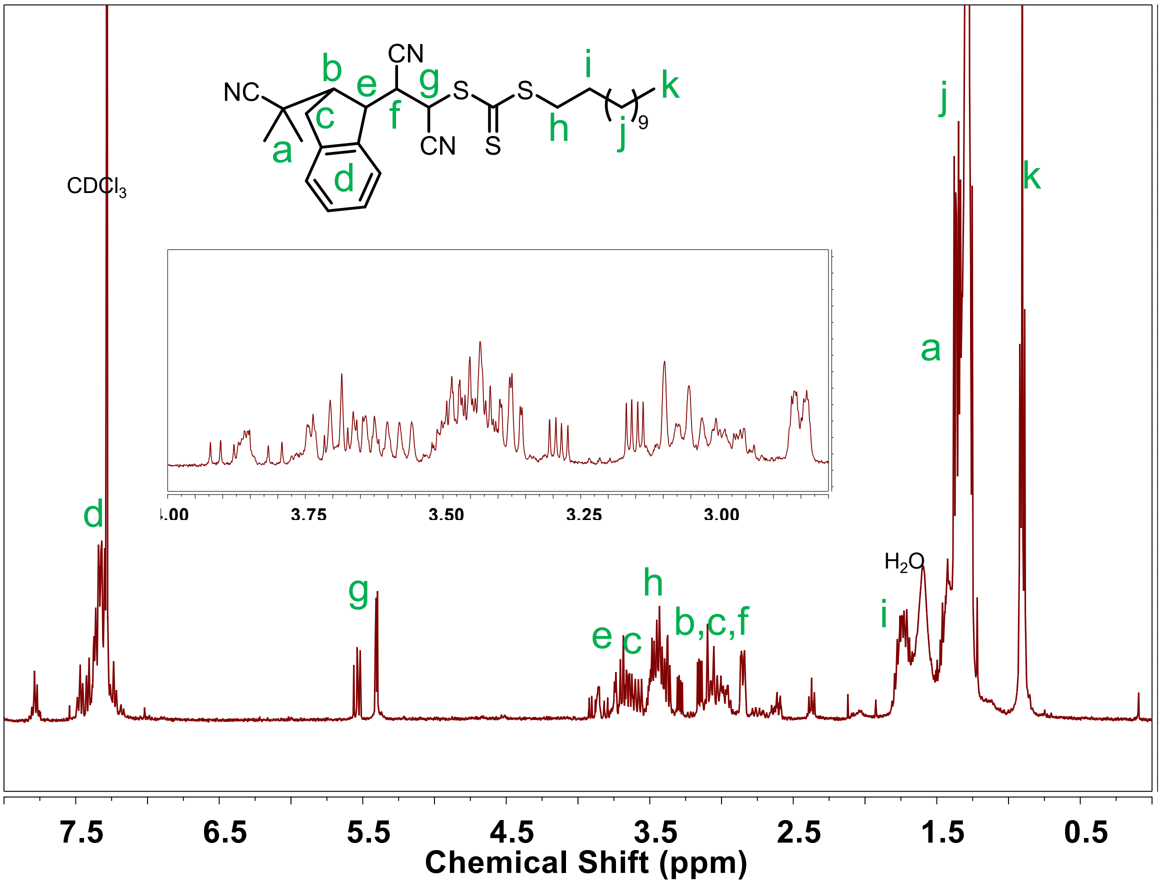


Fig. A2-12 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IBN-Ind-FCN-($C_{12}$)TTC.

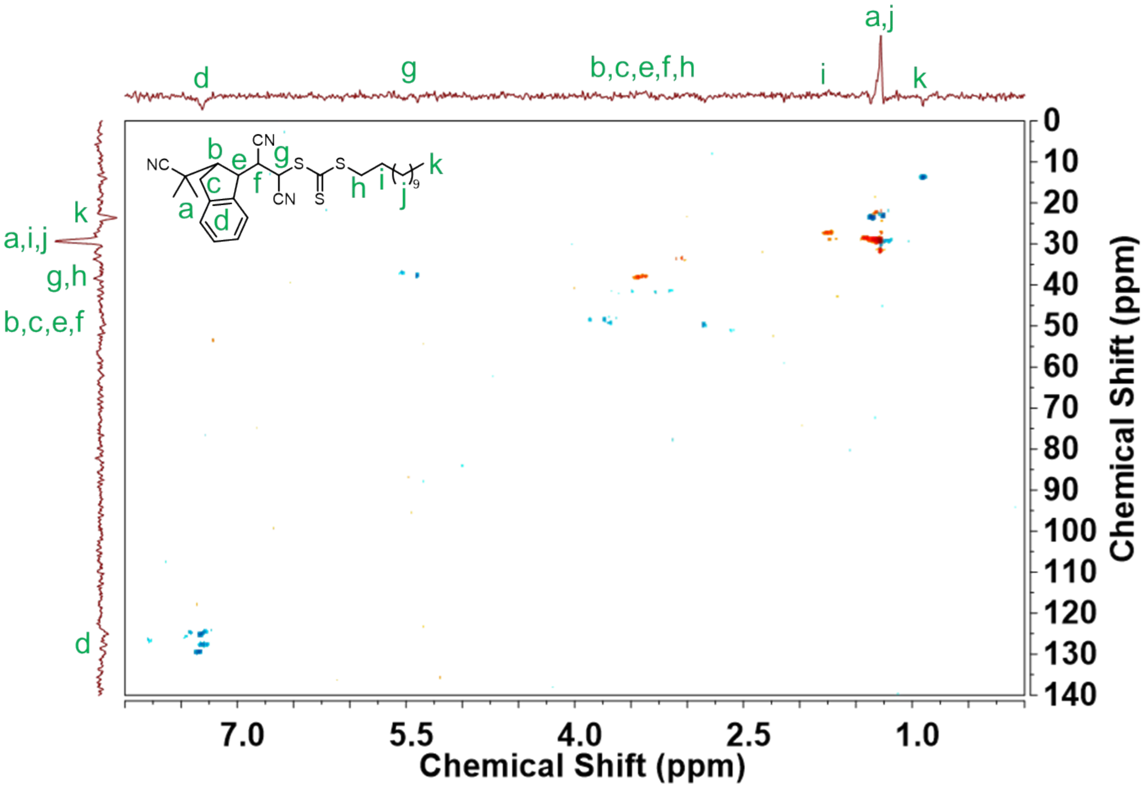


Fig. A2-13 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of IBN-Ind-FCN-$(C_{12})$TTC.

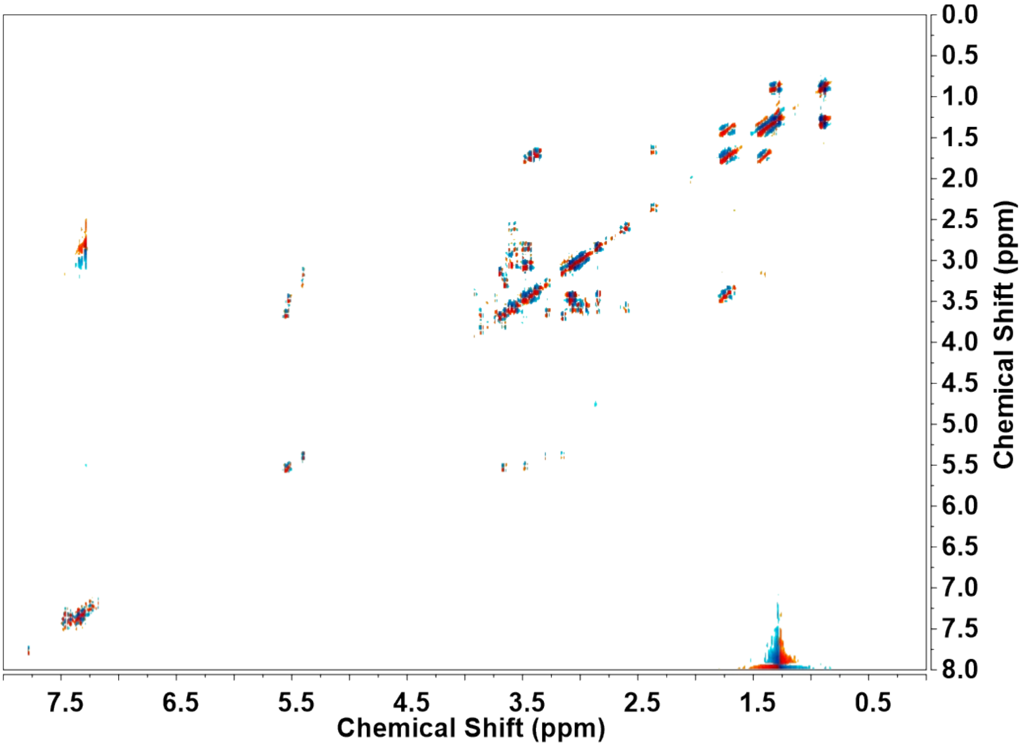


Fig. A2-14 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of IBN-Ind-FCN-$(C_{12})$TTC.

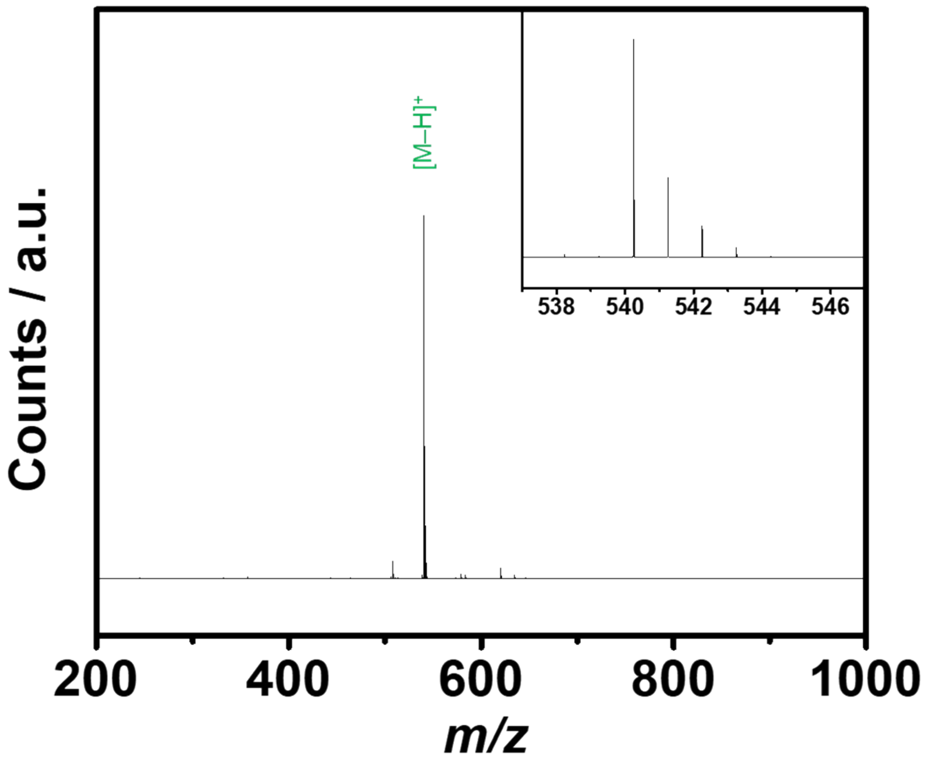


Fig. A2-15 APCI mass spectrum ($CH_3CN$) of IBN-Ind-FCN-($C_{12}$)TTC.

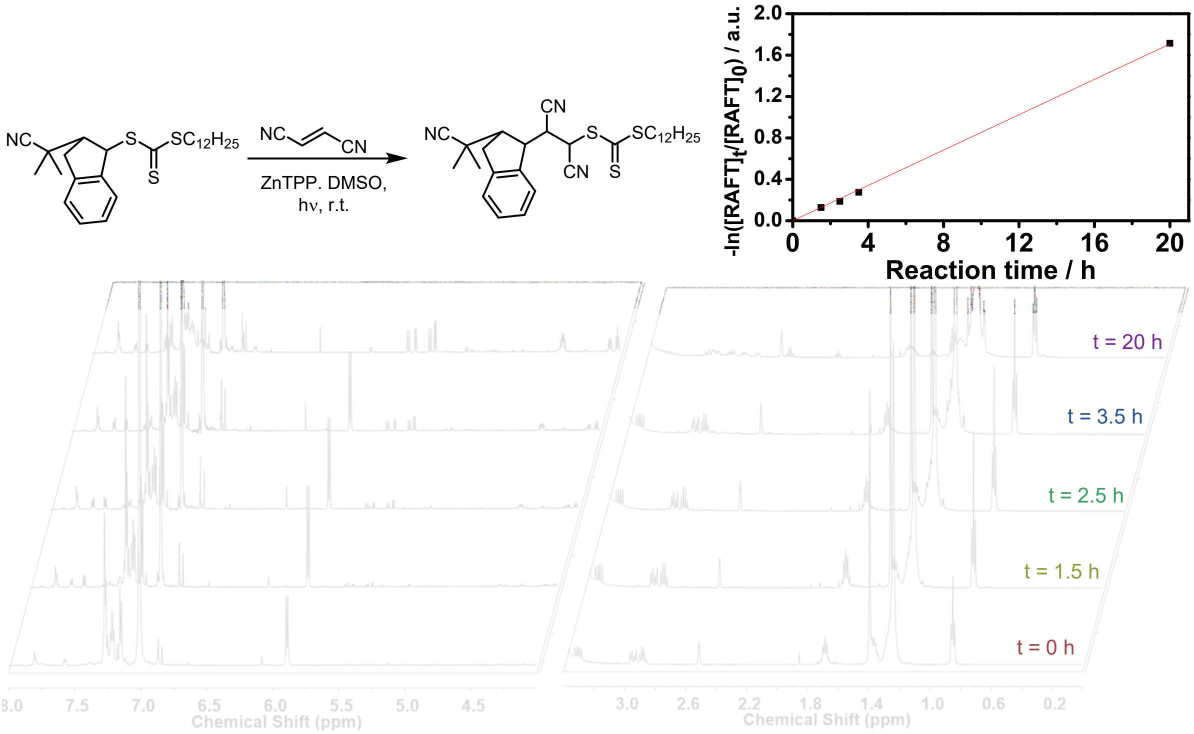
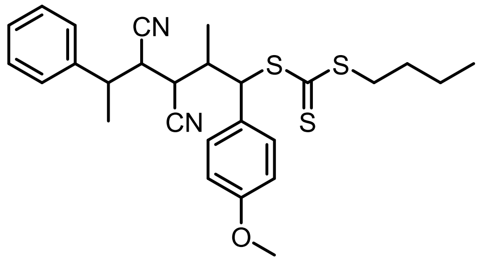


Fig. A2-16 Kinetics of IBN-Ind-FCN-($C_{12}$)TTC synthesis by $^1H$ NMR (500.13 MHz, DMSO).



**PhMeCH-TransAn-($C_4$)TTC** ZnTPP (~0.3 mg, 0.5 mol%) was added to a solution of PhMeCH-($C_4$)TTC (35 mg, 0.1 mmol) and *trans*-anethole (103 mg, 7 equiv) in DMSO (0.22 mL) in a 250 µL insert (without a stirring bar) and sealed with a septum. The reaction mixture was then irradiated under blue LED (0.42 mW cm$^{-2}$) for 16 h. The reaction mixture was then dissolved diethyl ether (30 mL) and then washed with water (3 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified by flash chromatography (ethyl acetate–hexanes gradient elution) and the product was obtained as two diastereomer fractions of yellow-to-green oils (37 mg, 74% total yield).

TLC (20% v/v ethyl acetate in hexanes) $R_f$ = 0.41 (diastereomer fraction 1), $R_f$ = 0.26 (diastereomer fraction 2).

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.49-6.97 (m), 6.96-6.57 (m, 2H), 5.70 (d, *J*= 5.7 Hz), 5.63 (d, *J*= 9.0 Hz), 5.60 (t, *J*= 6.3 Hz), 5.59 (d, *J*= 5.1 Hz), 5.51 (d, *J*= 4.8 Hz), 5.51 (d, *J*= 6.6 Hz), 5.41 (d, *J*= 7.1 Hz), 5.32 (d, *J*= 10.8 Hz), 5.25 (d, *J*= 8.5 Hz), 5.10 (d, *J*= 5.9 Hz), 5.04 (d, *J*= 6.3 Hz), 3.91-3.70 (m, 3H), 3.48-3.25 (m, 2H), 3.22-2.18 (m, 4H), 1.78-1.59 (m, 2H), 1.55 (dd, J = 9.0, 6.9 Hz), 1.51 (d, *J*= 6.9 Hz), 1.49-1.30 (m, 2H), 1.21 (d, *J*= 7.0 Hz), 1.19 (d, *J*= 7.1 Hz), 1.15 (d, *J*= 6.8 Hz), 1.11 (d, *J*= 6.9 Hz), 1.05 (d, *J*= 7.0 Hz) 1.01 (dd, *J*= 6.9, 4.4 Hz), 0.98-0.84 (m, 3H). *N.B.,* Full list of resonances generated from both diastereomer fractions isolated.

HRMS (APCI) 497.17, 498.17, 499.16, 500.17 $[M–H]^+$, 349.09, 350.09, 351.08, 352.08 $[\text{PhMeCH-FCN-(}C_4\text{)TTC–H}]^+$. Calculated: 497.17, 498.18, 499.17 (13.6%), 500.17 (4.0%). No peaks from TransAn double-insertion (+148) or β-elimination (-166) found.

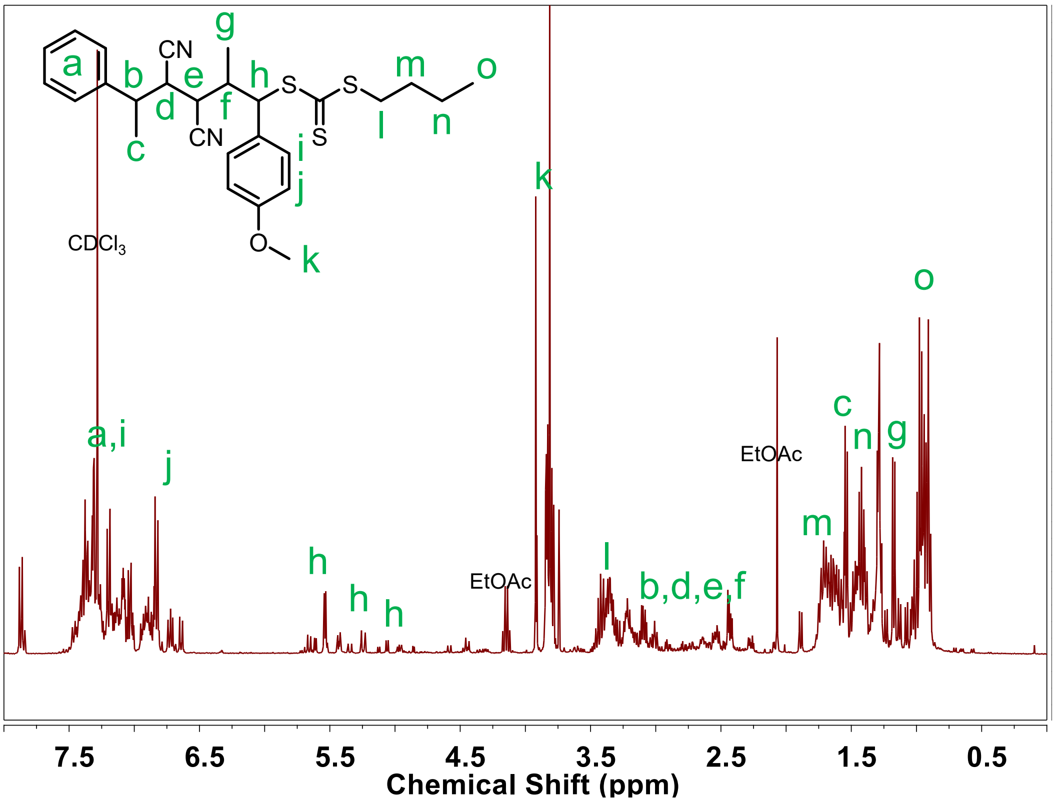


Fig. A2-17 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-FCN-TranAn-($C_4$)TTC (fraction 1).

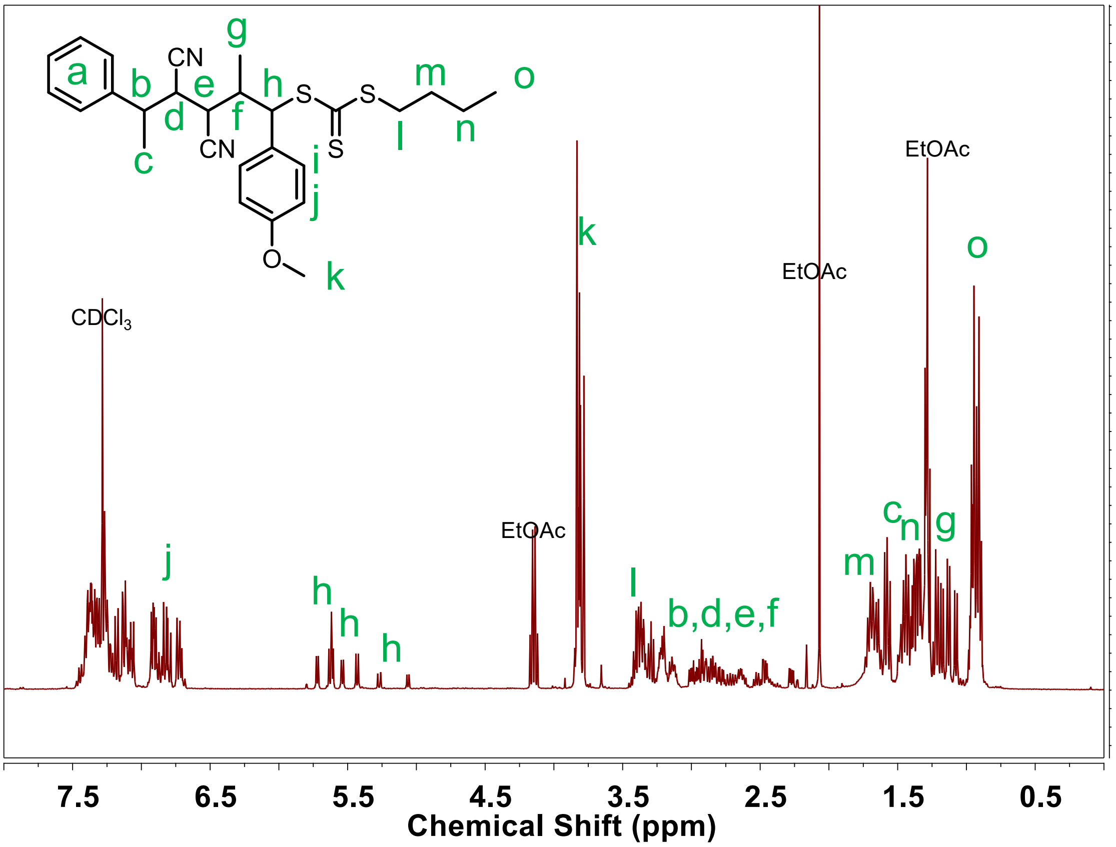


Fig. A2-18 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-FCN-TranAn-($C_4$)TTC (fraction 2).

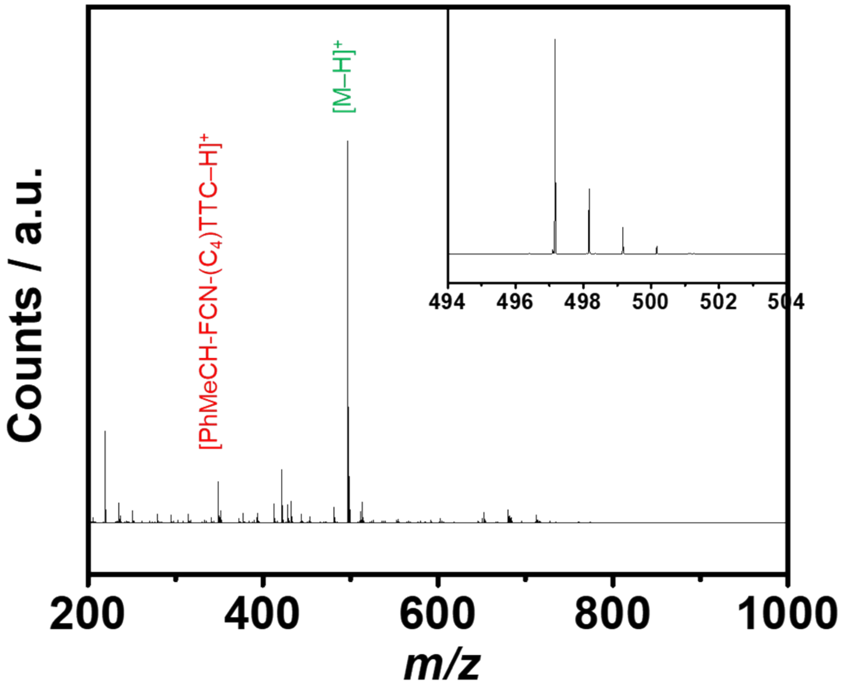
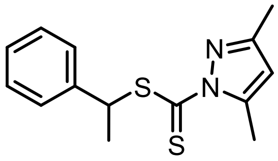


Fig. A2-19 APCI mass spectrum ($CH_3CN$) of IBN-Ind-FCN-($C_{12}$)TTC PhMeCH-FCN-TranAn-($C_4$)TTC (fraction 2).



**PhMeCH-PCDT** Potassium hydroxide (0.29 g, 1 equiv) pellets were added to a solution of 3,5-dimethyl pyrazole (0.50 g, 5.2 mmol) in THF (20 mL) and left at ambient temperature for 2 h to dissolve and react. Carbon disulphide (435 mg, 1.1 equiv) was then added dropwise over the time scale of 10 min and then left to stir at ambient temperature for 2 h. 1-Bromoethyl benzene (1 g, 1 equiv) was then added to the solution which was then left to stir at ambient temperature for 16 h. The reaction mixture was then concentrated under vacuum and the residue was purified under flash chromatography (ethyl acetate–hexanes gradient elution) to yield the product as a yellow oil (640 mg, 44% yield).

TLC (5% v/v ethyl acetate in hexanes) $R_f$ = 0.21.

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.48-7.41 (m, 2H), 7.40-7.21 (m, 3H), 6.06 (d, *J*= 0.5 Hz), 5.96 (s), 5.04 (q, *J*= 7.2 Hz), 4.91 (q, *J*= 6.4 Hz), 2.68 (d, *J*= 0.9 Hz, 3H), 2.25 (s, 3H), 1.78 (d, *J*= 7.1 Hz), 1.51 (d, *J*= 6.5 Hz).

HRMS (APCI) 277.08, 278.09, 279.09, 280.09 [M–H]$^+$. Calculated: 277.08, 278.09, 279.08, 280.08. *N.B.,* No peaks from the thiocarbonyl dipyrazole product (~235) were found.

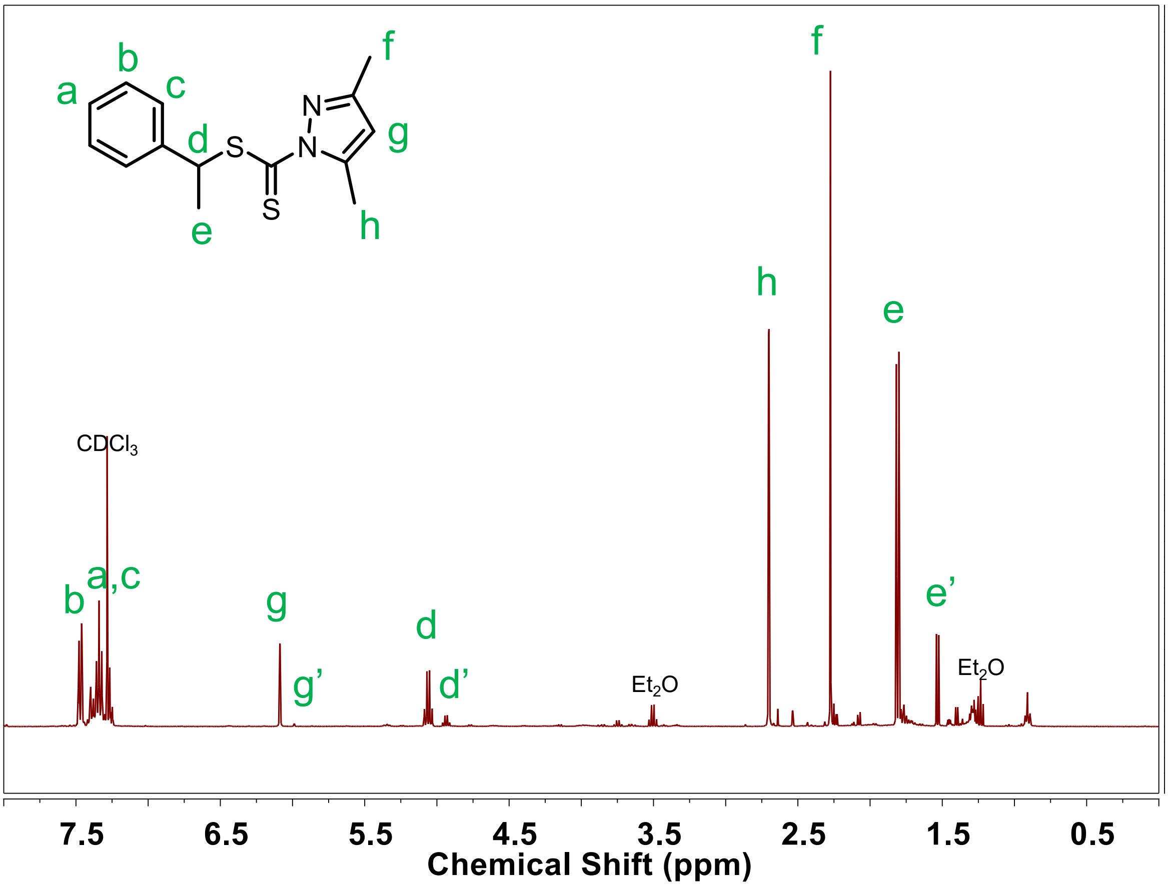


Fig. A2-20 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-PCDT.

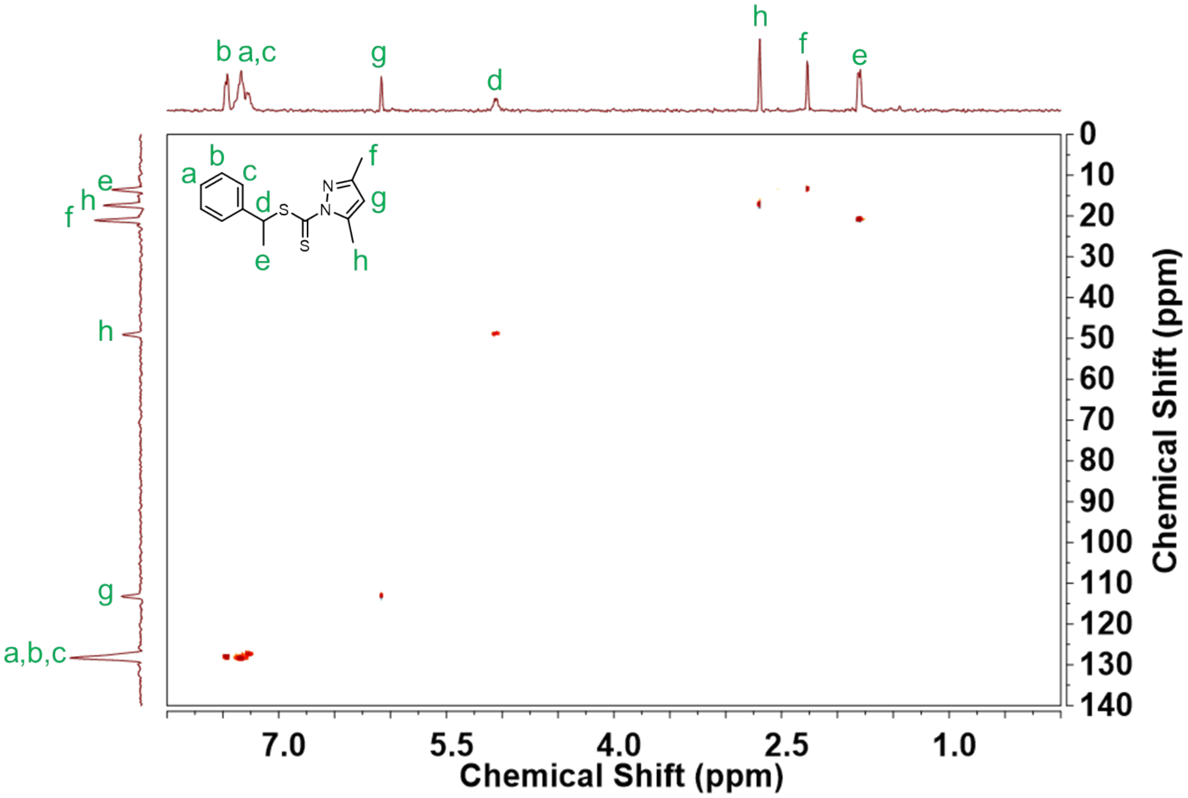


Fig. A2-21 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of PhMeCH-PCDT.

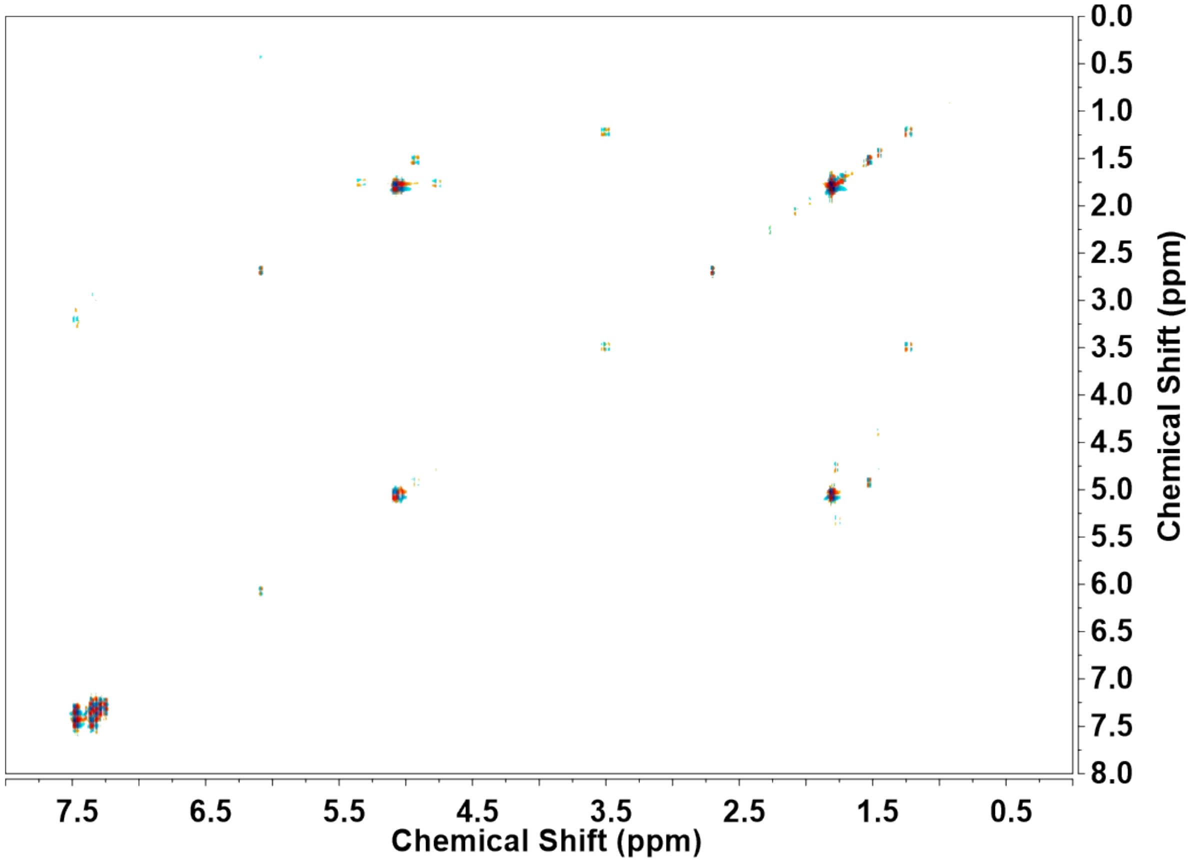


Fig. A2-22 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-PCDT.

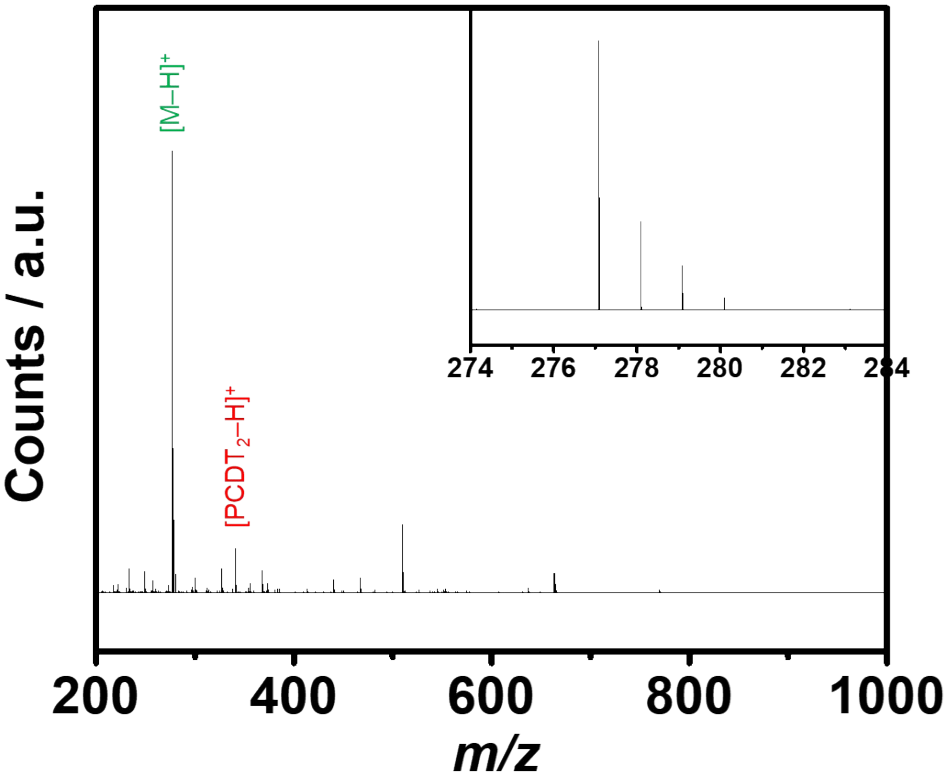
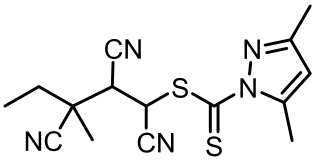


Fig. A2-23 APCI mass spectrum ($CH_3CN$) of PhMeCH-PCDT.



**IPN-FCN-PCDT** A solution of fumaronitrile (344 mg, 10 eq) in DMSO (2 mL) was added to IPN-PCDT (111 mg, 0.44 mmol) and ZnTPP (~1.5 mg, 0.5 mol%) in a 2 mL vial and sealed with a rubber septum. The heterogeneous reaction mixture was then irradiated under blue LED (0.42 mW $cm^{-2}$) for 5 h upon which, the solution became homogeneous. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as two diastereomer fractions of yellow oils (58 mg, 40% yield).

A separate kinetic experiment was performed on an analogous solution in $d_6$-DMSO (0.5 mL – with all other components scaled equally) prepared in a Wilmad NMR tube (without a stirring bar) which was degassed by sparging under argon for 15 min prior to irradiation under the same blue LED. A similar workup and purification procedure was then performed to obtain the product in smaller yield (due to reaction scale).

TLC (20% v/v ethyl acetate in hexanes) $R_f$ = ~0.28 (diastereomer fraction 1), $R_f$ = ~0.23 (diastereomer fraction 2)

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 6.20-6.16 (m, 1H), 5.29 (d, *J*= 3.3 Hz), 5.26 (d, *J*= 3.4 Hz), 3.44 (d, *J*= 3.3 Hz), 3.35 (d, *J*= 3.4 Hz), 2.70-2.67 (m, 3H), 2.30-2.24 (m, 3H), 1.95-1.81 (m, 2H), 1.80-1.62 (m, 3H), 1.20 (ddd, *J*= 14.9, 11.1, 4.9 Hz, 3H).

HRMS (APCI) 332.10, 333.10, 334.09, 335.09 $[M–H]^+$. Calculated: 332.10, 333.10, 334.10, 335.10. *N.B.,* No peaks detected for FCN double-insertion (+78) or for starting material (-78).

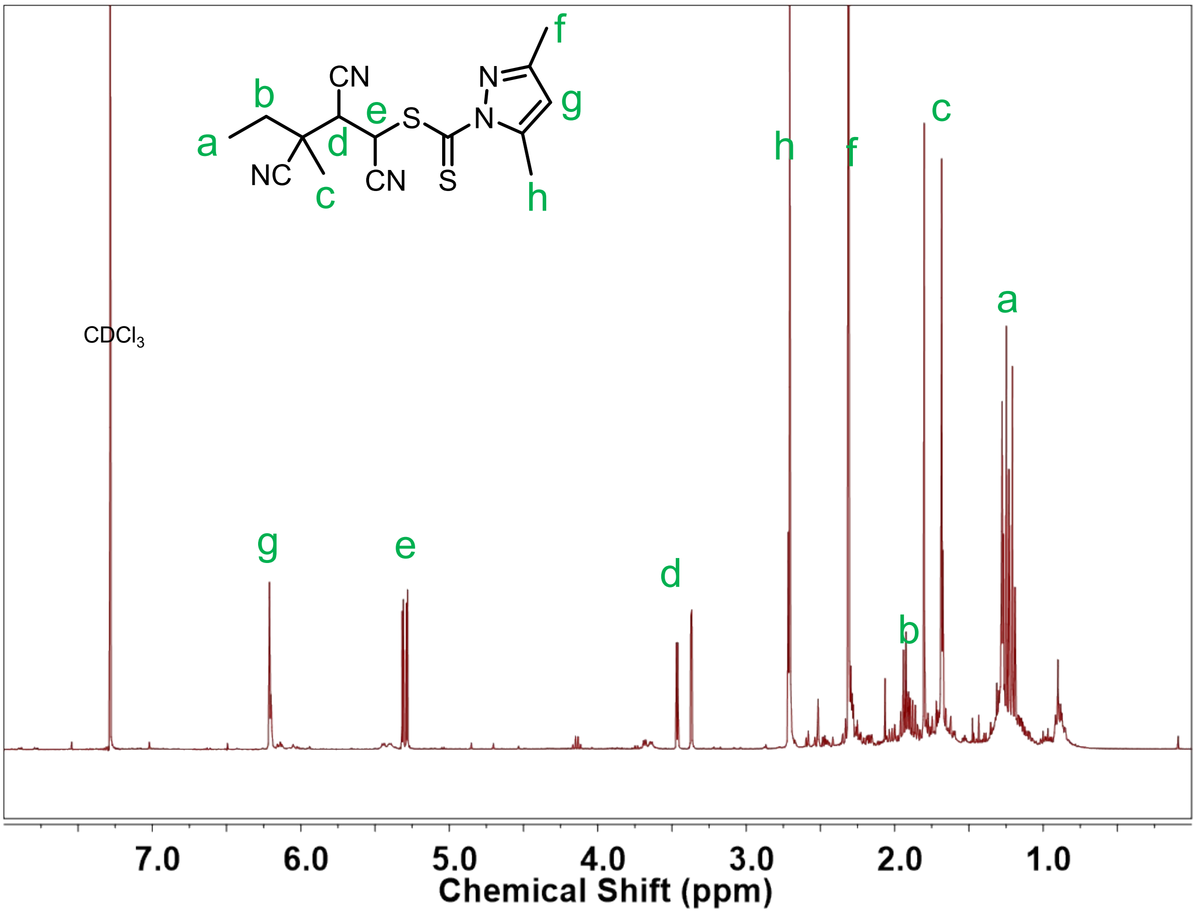


Fig. A2-24 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-FCN-PCDT (combined fraction).

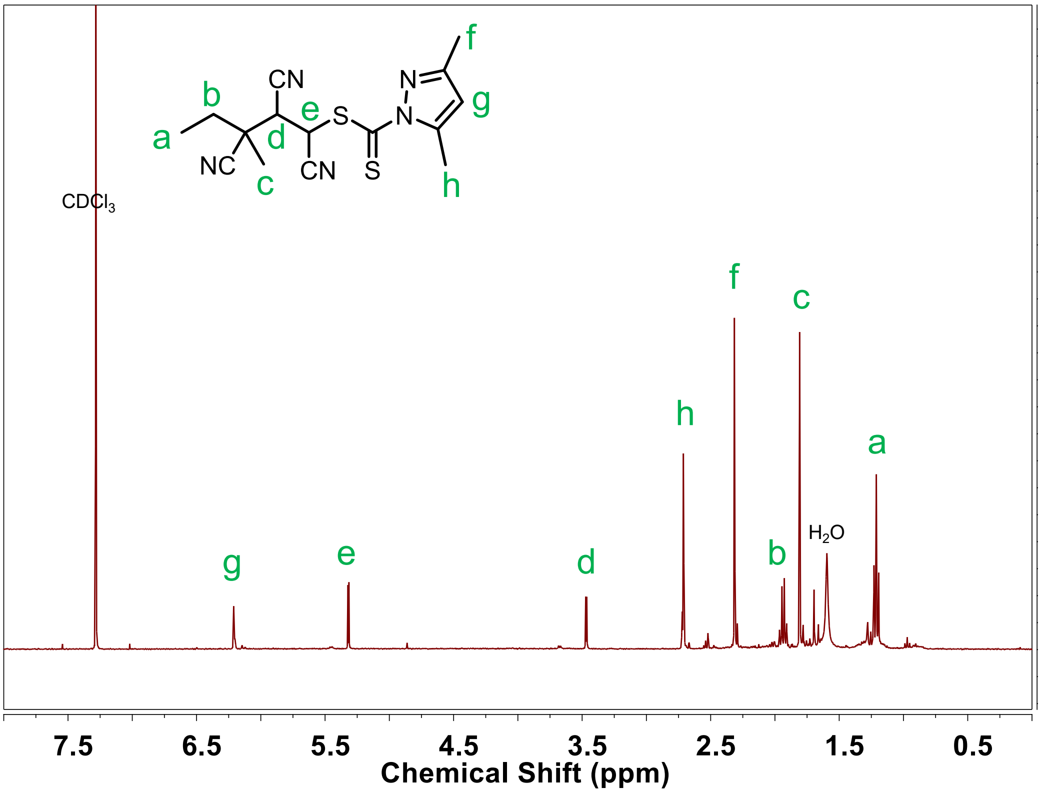


Fig. A2-25 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-FCN-PCDT (fraction 1).

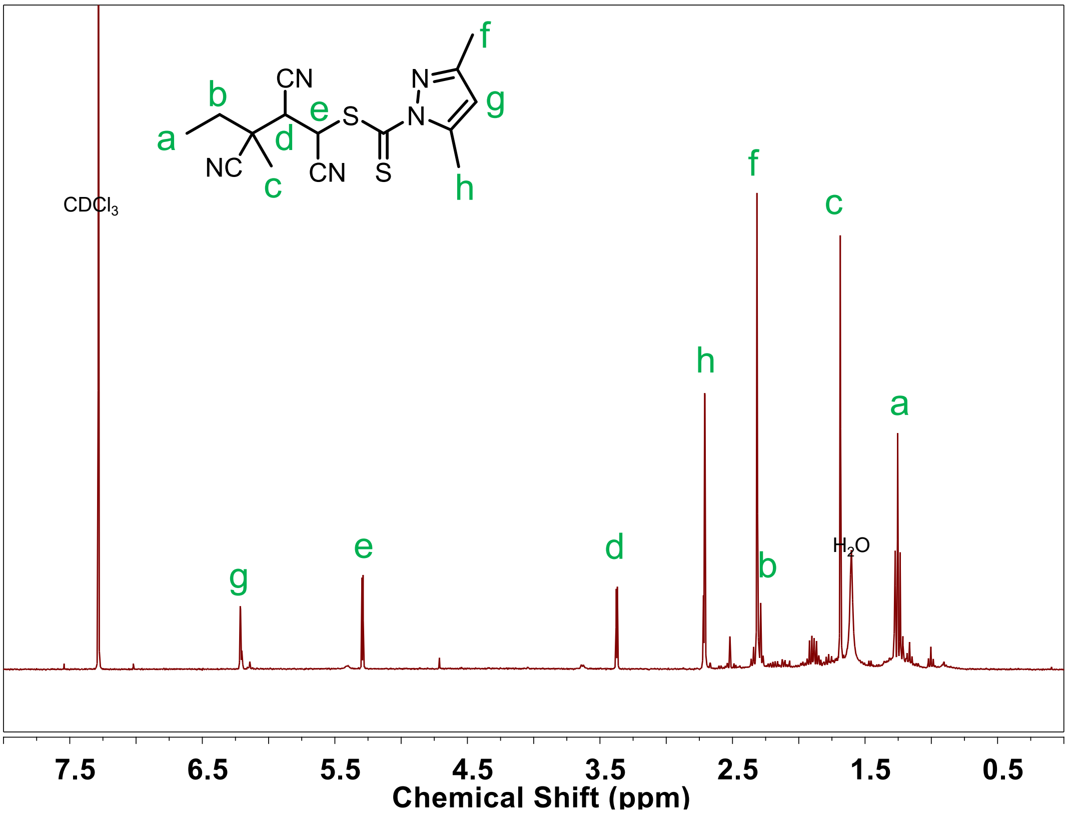


Fig. A2-26 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-FCN-PCDT (fraction 2).

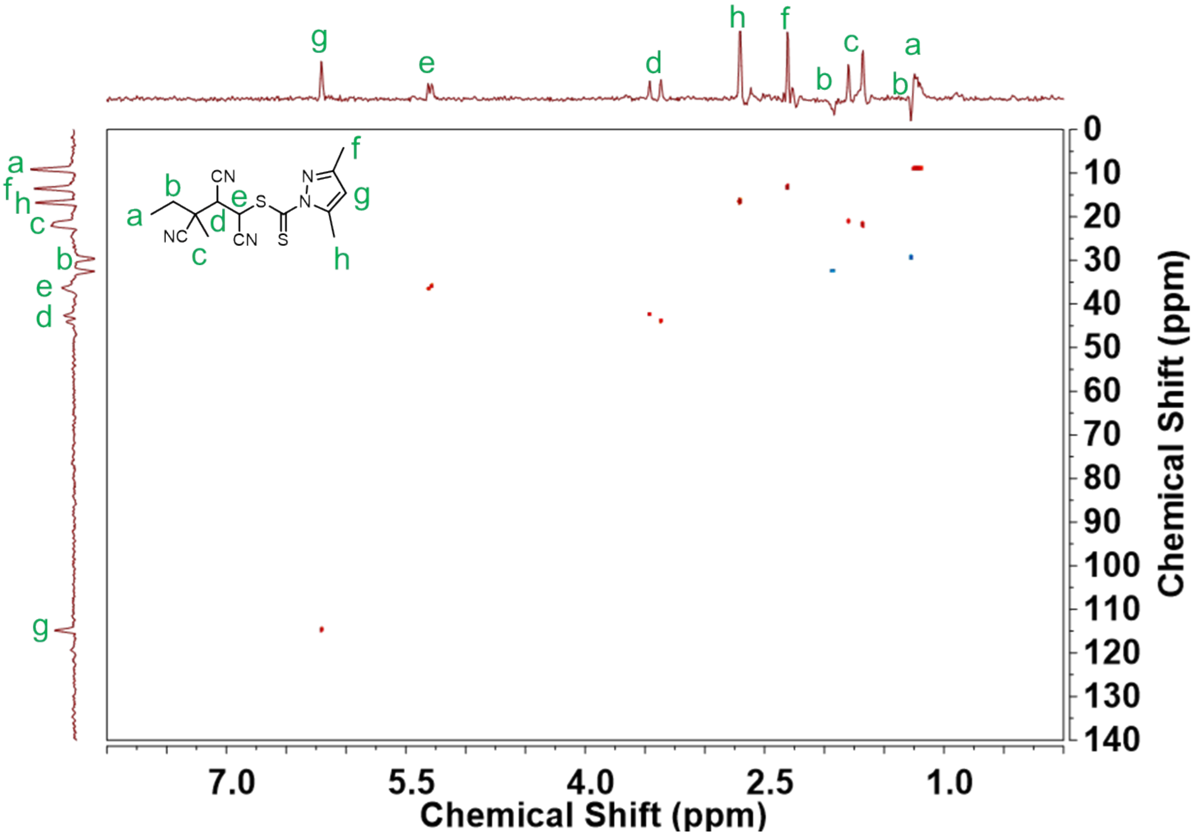


Fig. A2-27 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of IPN-FCN-PCDT (mixed fraction).

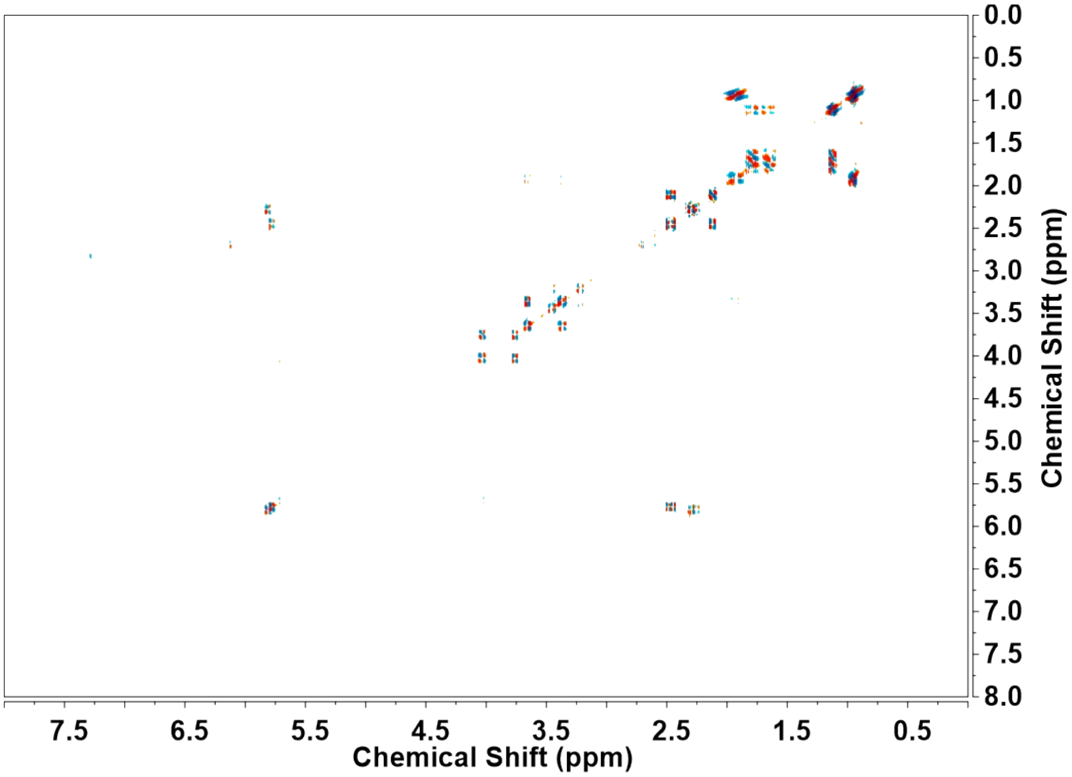


Fig. A2-28 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-FCN-PCDT (mixed fraction).

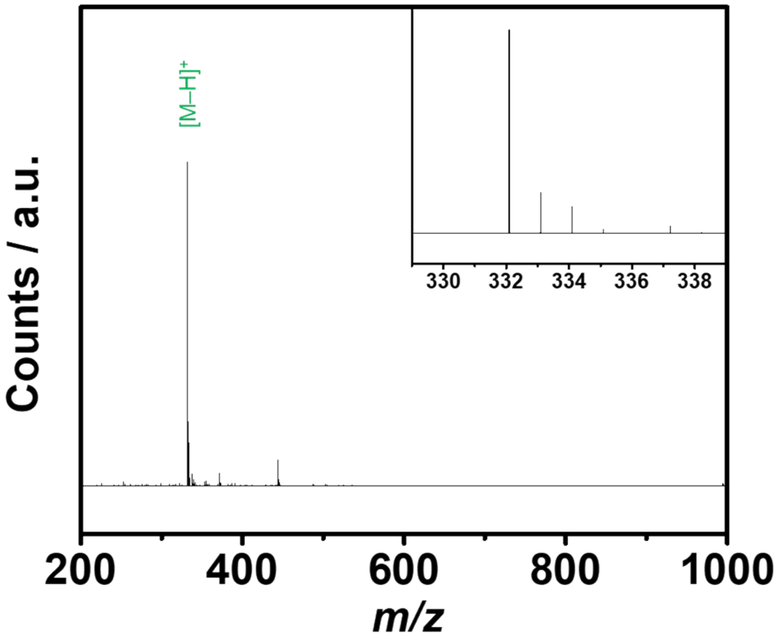


Fig. A2-29 APCI mass spectrum ($CH_3CN$) of IPN-FCN-PCDT.

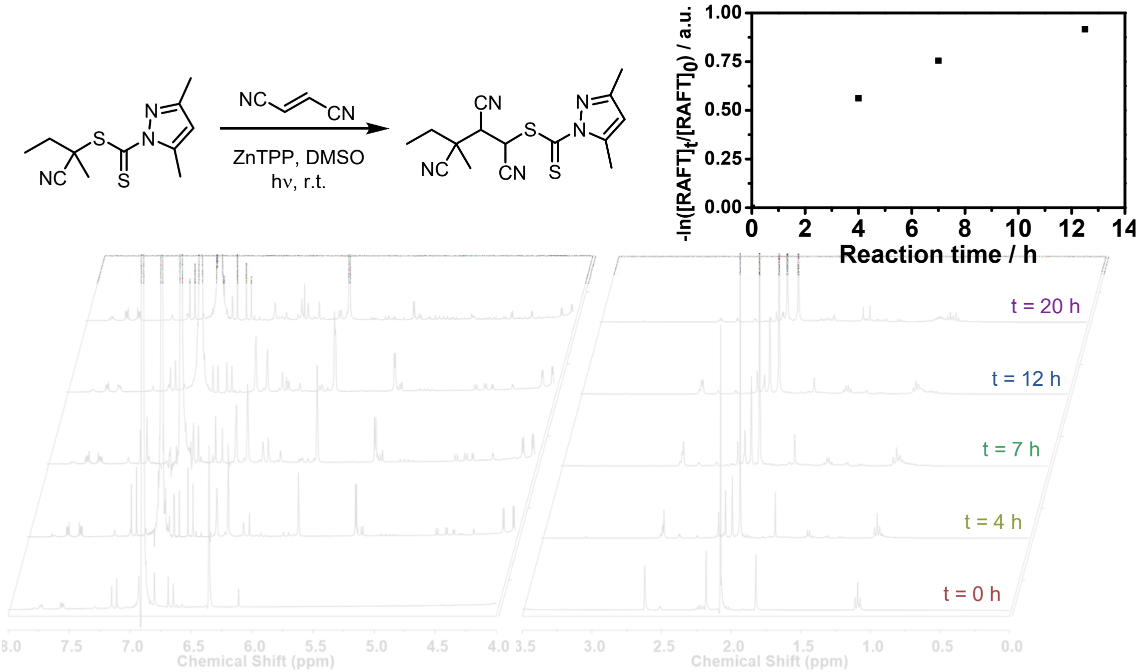
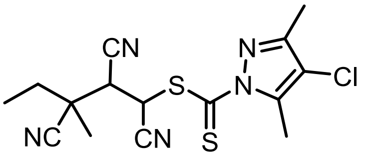


Fig. A2-30 Kinetics of IPN-FCN-PCDT synthesis by $^1$H NMR (500.13 MHz, DMSO).

IBN-PCDT was found to decompose which is explained by its low $\Delta G_{Reform}$ (Figure 4B, Supplementary Information S3).



**IPN-FCN-(Cl)PCDT** A solution of fumaronitrile (34 mg, 10 eq) in DMSO (0.2 mL) was added to IPN-(Cl)PCDT (12.1 mg, 0.044 mmol) and ZnTPP (~0.2 mg, 0.5 mol%) in a 250 µL insert (without a stirring bar) and sealed with a rubber septum. The heterogeneous reaction mixture was then irradiated under blue LED (0.42 mW $cm^{-2}$) for 5 h upon which, the solution became homogeneous. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a yellow oil (33 mg, 42% yield).

TLC (20% v/v ethyl acetate in hexanes) $R_f$ = 0.34 (diastereomer fraction 1), $R_f$ = 0.28 (diastereomer fraction 2)

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 5.28 (d, *J*= 3.3 Hz), 5.25 (d, *J*= 3.3 Hz), 3.42 (d, J = 3.3 Hz), 3.34 (d, *J*= 3.3 Hz), 2.73-2.67 (m, 3H), 2.34-2.24 (m, 3H), 1.95-1.81 (m, 2H), 1.80-1.62 (m, 3H), 1.21 (ddd, *J*= 14.9, 11.1, 4.9 Hz, 3H).

HRMS (APCI) 366.06, 367.06, 368.06, 369.05, 370.05 $[M–H]^+$. Calculated: 366.06, 367.06, 368.06, 369.06, 370.05. *N.B.,* No peaks from double addition (+78) or starting material (-78) were found.

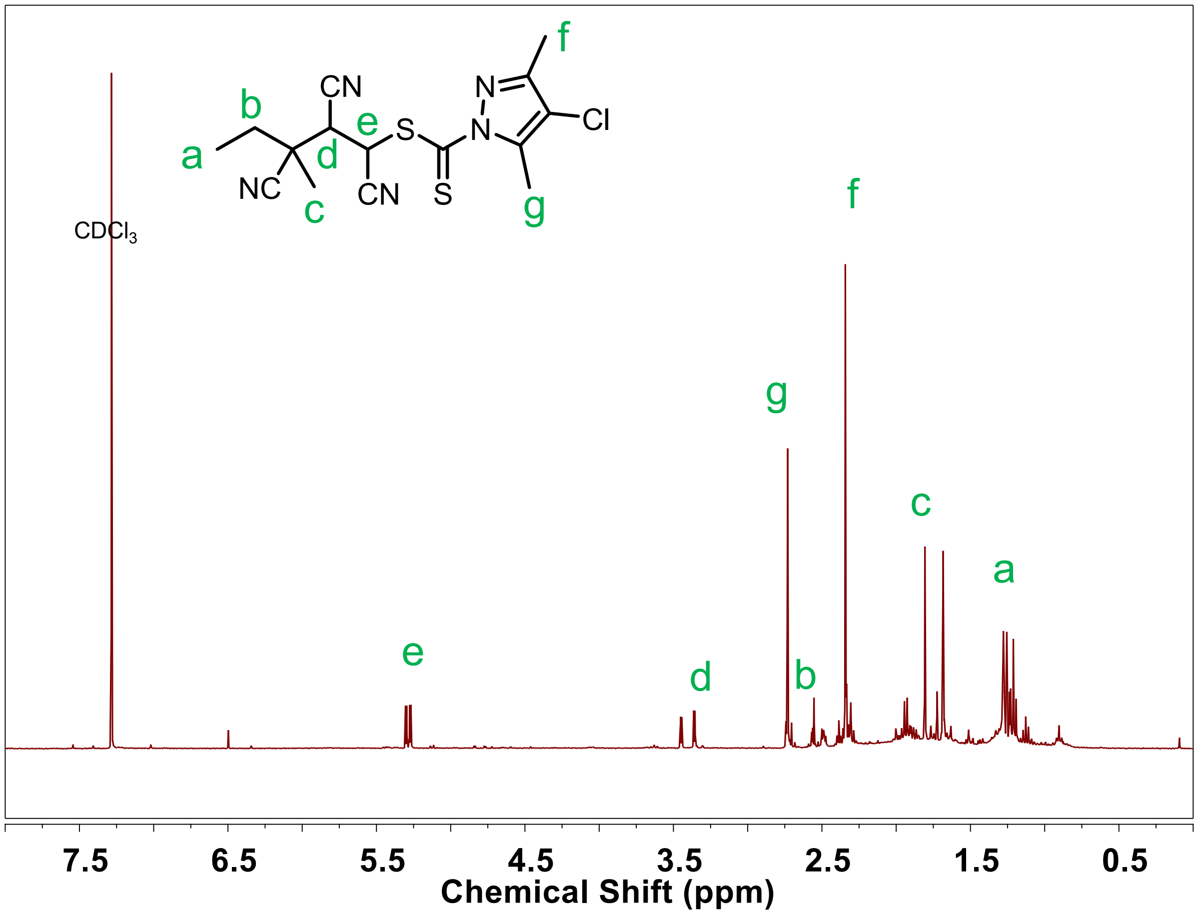


Fig. A2-31 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-FCN-(Cl)PCDT.

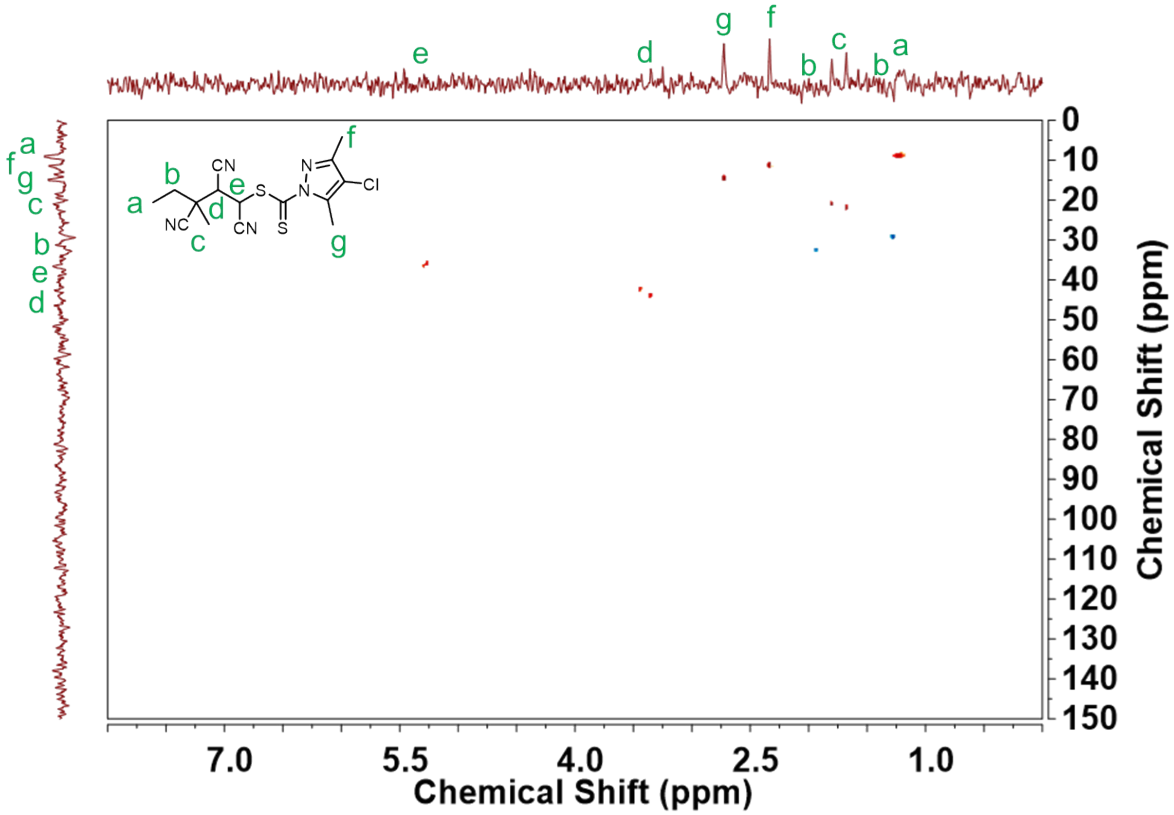


Fig. A2-32 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of IPN-FCN-(Cl)PCDT.

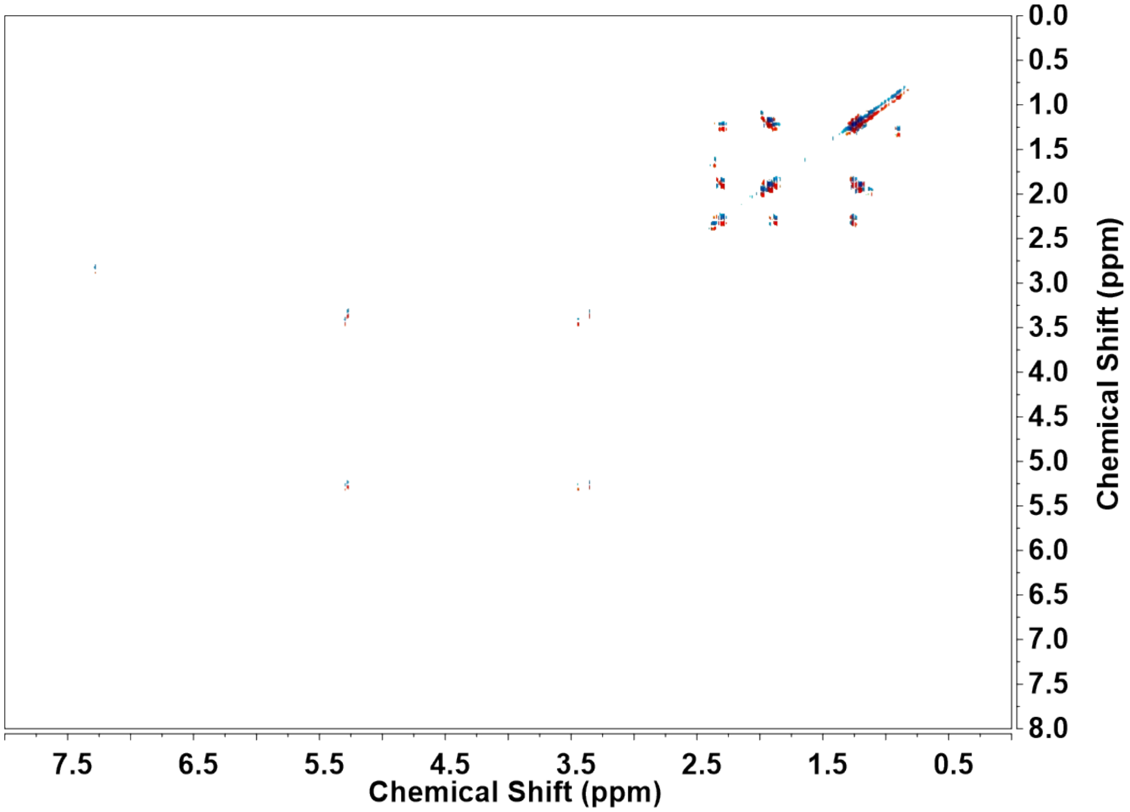


Fig. A2-33 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-FCN-(Cl)PCDT.

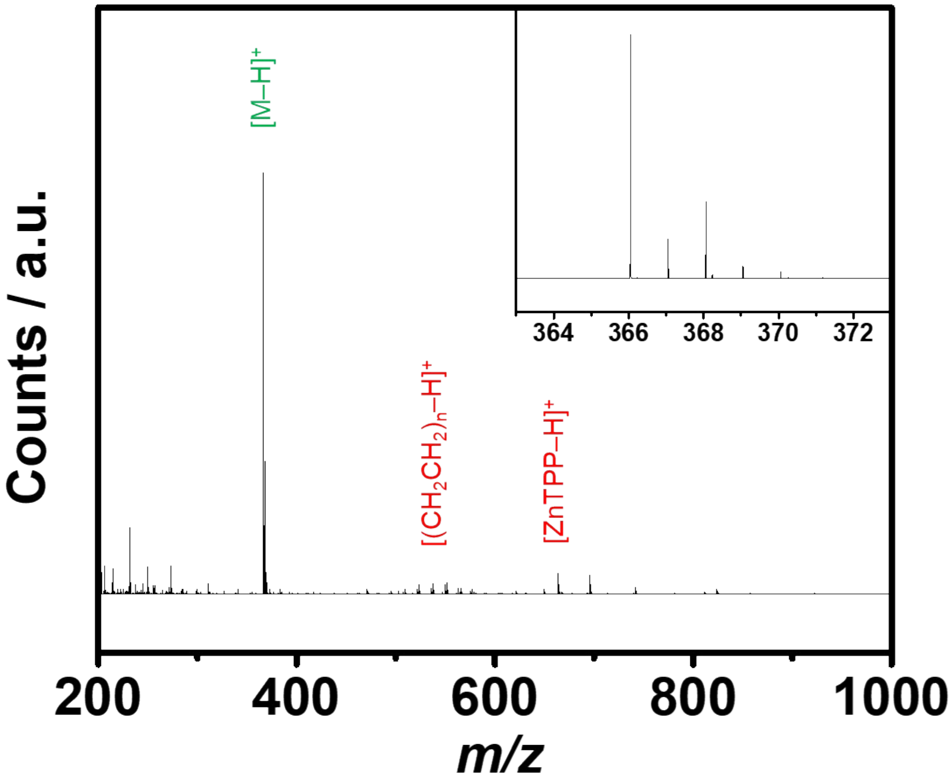
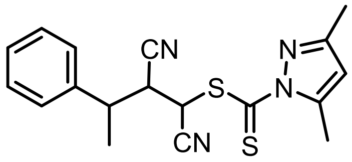


Fig. A2-34 APCI mass spectrum ($CH_3CN$) of IPN-FCN-(Cl)PCDT.



**PhMeCH-FCN-PCDT** ZnTPP (~1.5 mg, 0.5 mol%) was added to a solution of PhMeCH-PCDT (121 mg, 0.44 mmol) and fumaronitrile (344 mg, 10 eq) in DMSO (2 mL) in a 2 mL vial and sealed with a rubber septum. The reaction mixture was then irradiated under blue LED (0.42 mW cm$^{-2}$) for 4 h. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a yellow oil (138 mg, 89% yield).

A separate kinetic experiment was performed on an analogous solution in d$_6$-DMSO (0.5 mL – with all other components scaled equally) prepared in a Wilmad NMR tube (without a stirring bar) which was degassed by sparging under argon for 15 min prior to irradiation under the same blue LED. A similar workup and purification procedure was then performed to obtain the product in smaller yield (due to reaction scale).

TLC (20% v/v ethyl acetate in hexanes) $R_f = 0.32$

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.56-7.22 (m, 5H), 6.21-6.12 (m, 1H) 5.02 (d, *J*= 5.3 Hz), 4.75 (d, *J*= 9.6 Hz), 4.73 (d, *J*= 5.9 Hz), 4.57 (d, *J*= 4.4 Hz) 3.60-3.31 (m), 3.21 (d, *J*= 4.4 Hz), 3.19 (d, *J*= 4.4 Hz), 2.71 (d, *J*= 1.0 Hz), 2.68 (d, *J*= 0.9 Hz), 2.64 (d, *J*= 0.9 Hz), 2.62 (d, *J*= 0.9 Hz), 2.33-2.26 (m, 3H), 1.67-1.60 (m, 3H).

HRMS (APCI) 355.10, 356.11, 357.11, 358.10 [M–H]$^+$. Calculated: 355.10, 356.11, 357.10, 358.10. *N.B.,* No peaks from FCN double-insertion (+78) or from starting material (-78) were found.

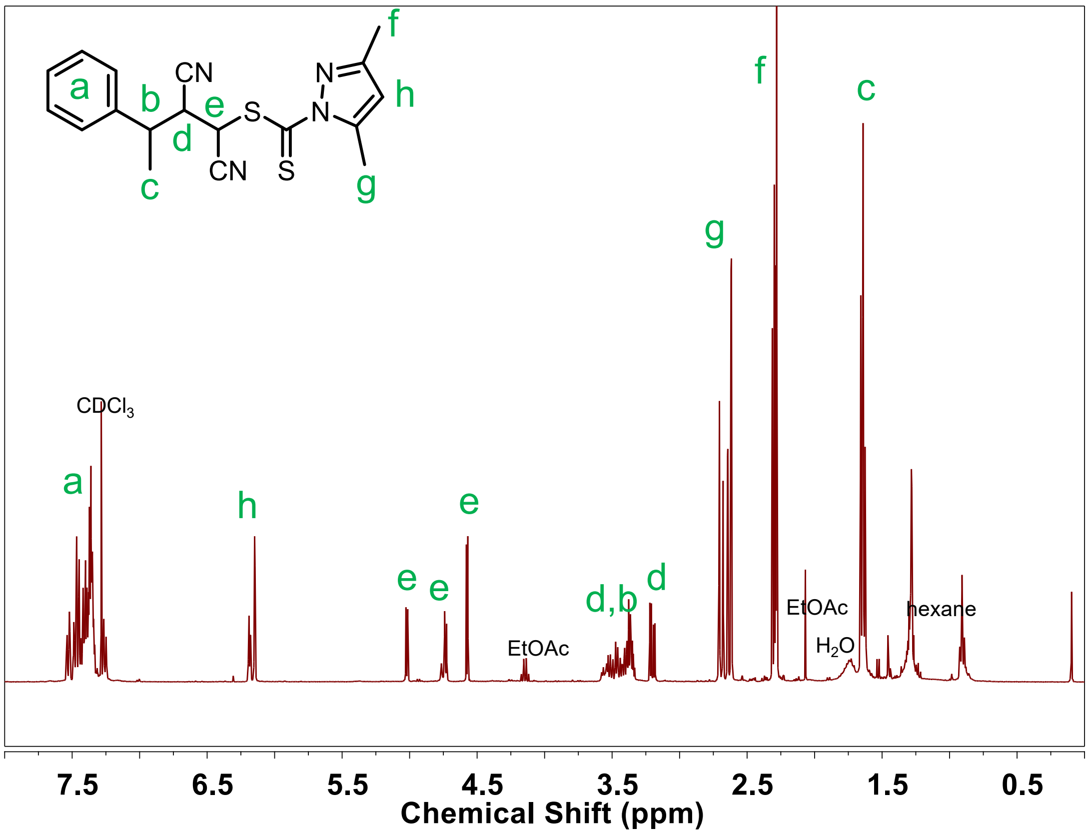


Fig. A2-35 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-FCN-PCDT.

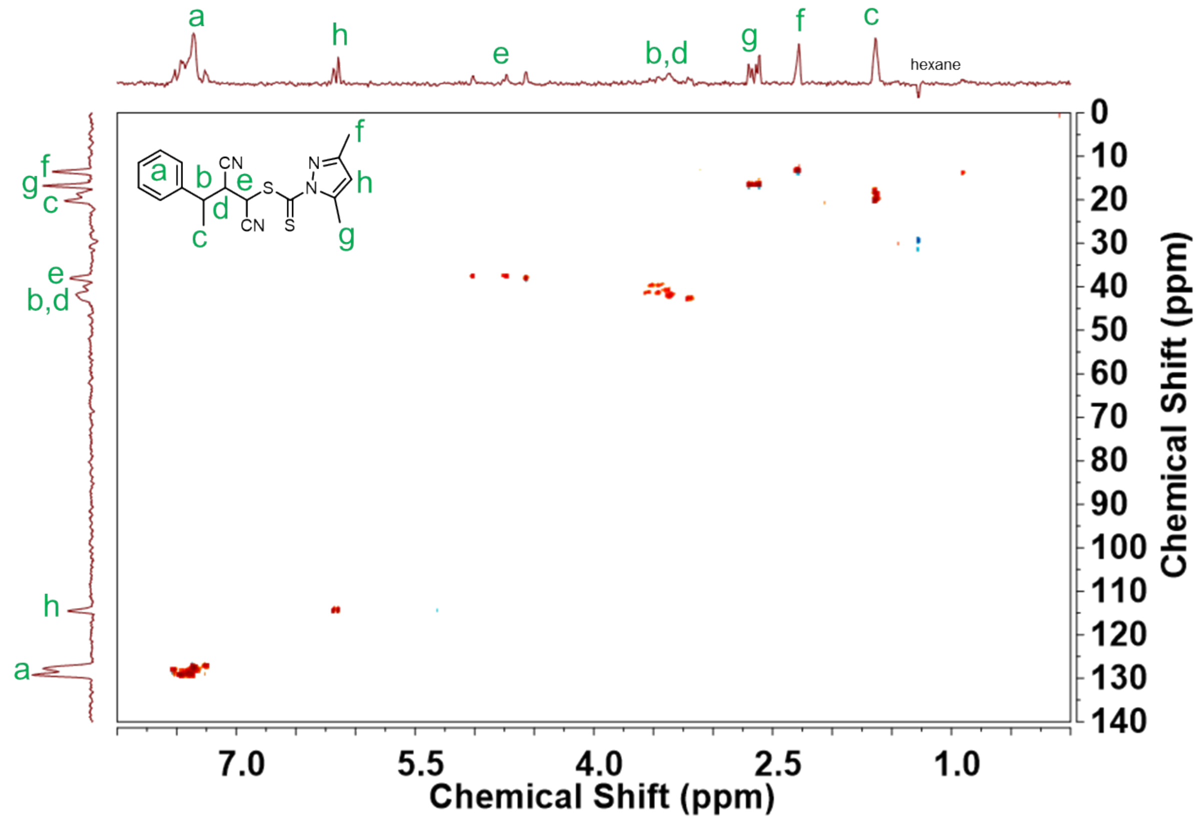


Fig. A2-36 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of PhMeCH-FCN-PCDT.

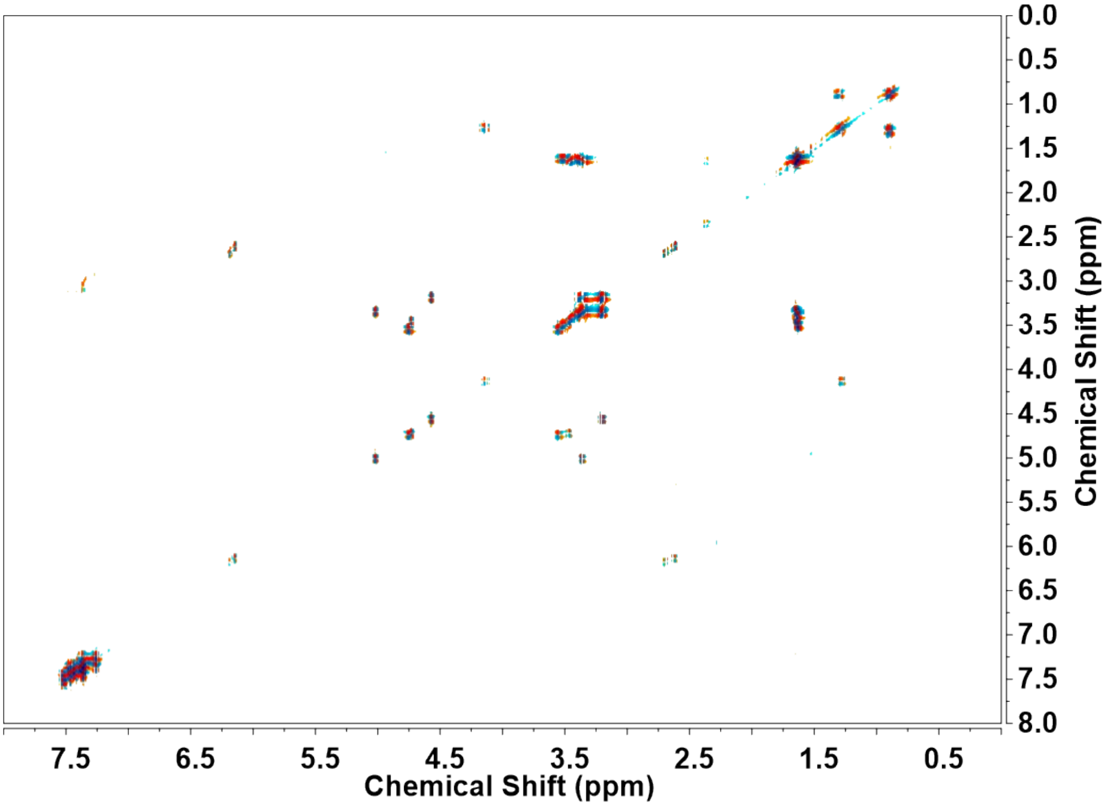


Fig. A2-37 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-FCN-PCDT.

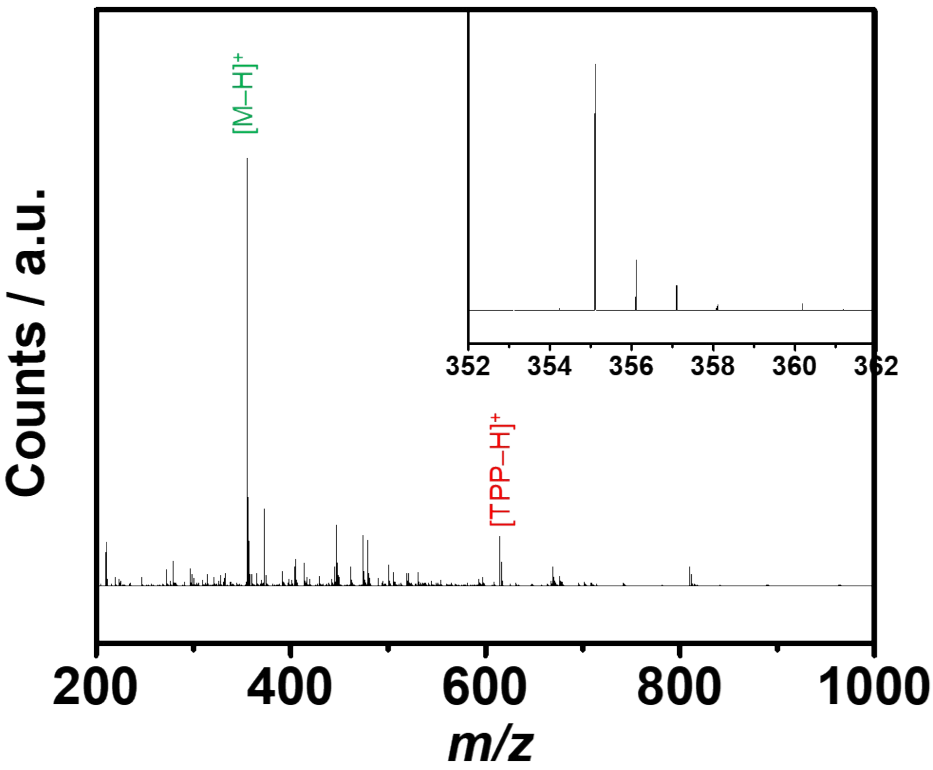


Fig. A2-38 APCI mass spectrum ($CH_3CN$) of PhMeCH-FCN-PCDT.

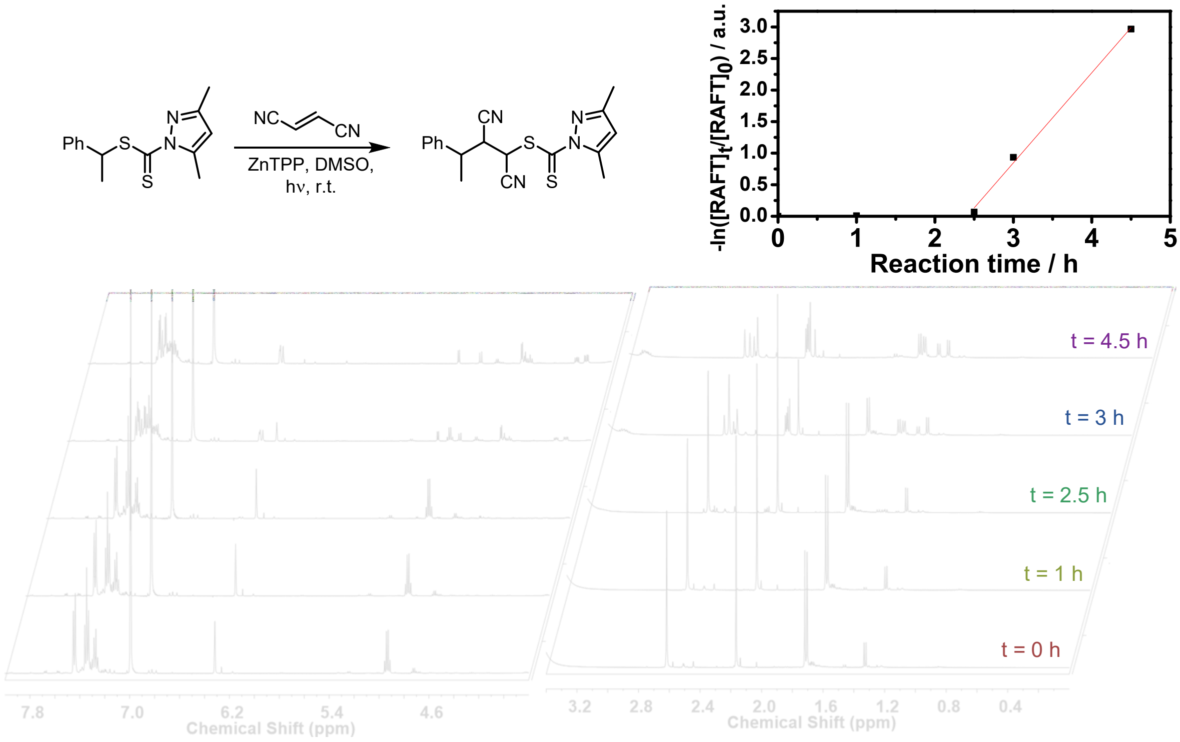
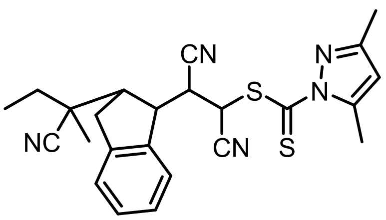


Fig. A2-39 Kinetics of PhMeCH-FCN-PCDT synthesis by $^1$H NMR (500.13 MHz, DMSO).



**IPN-Ind-FCN-PCDT** A solution of IPN-Ind-PCDT (16.1 mg, 0.044 mmol) and fumaronitrile (34.4 mg, 10 eq) in DMSO (0.2 mL) was added to ZnTPP (~0.2 mg, 0.5 mol%) in a 250 µL insert (without a stirring bar) and sealed with a rubber septum. The reaction mixture was then irradiated under blue LED (0.42 mW cm$^{-2}$) for 5 h. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a yellow oil (16 mg, 84% yield).

TLC (20% v/v ethyl acetate in hexanes) R$_f$ = 0.19

$^1$H NMR (400.17 MHz, CDCl$_3$) δ 7.60-7.10 (m, 4H), 6.20-6.10 (m, 1H), 5.13 (d, J = 8.5 Hz), 5.11 (d, *J*= 5.2 Hz), 5.10 (d, *J*= 3.8 Hz), 5.08 (d, *J*= 4.7 Hz), 5.06 (d, *J*= 4.0 Hz), 4.97 (d, *J*= 4.6 Hz), 3.98-3.39 (m), 3.18-3.09 (m), 3.09 (dd, *J*= 8.9, 4.0 Hz), 3.07-2.85 (m), 2.71 (d, *J*= 0.9 Hz) 2.71 (d, *J*= 1.0 Hz), 2.69 (d, *J*= 1.1 Hz), 2.69 (d, *J*= 1.0 Hz), 2.67 (d, *J*= 0.9 Hz), 2.66 (d, *J*= 0.9 Hz), 2.63 (d, *J*= 0.9 Hz), 2.60 (d, *J*= 0.9 Hz), 2.31-2.25 (m, 3H), 1.85-1.52 (m, 2H), 1.43 (d, *J*= 5.5 Hz), 1.24-1.07 (m).

HRMS (APCI) 448.16, 449.17, 450.17, 451.17 [M–H]$^+$. Calculated: 448.16, 449.17, 450.16, 451.16. N.B., No peaks from FCN double-insertion (+78) or starting material (-78) were found.

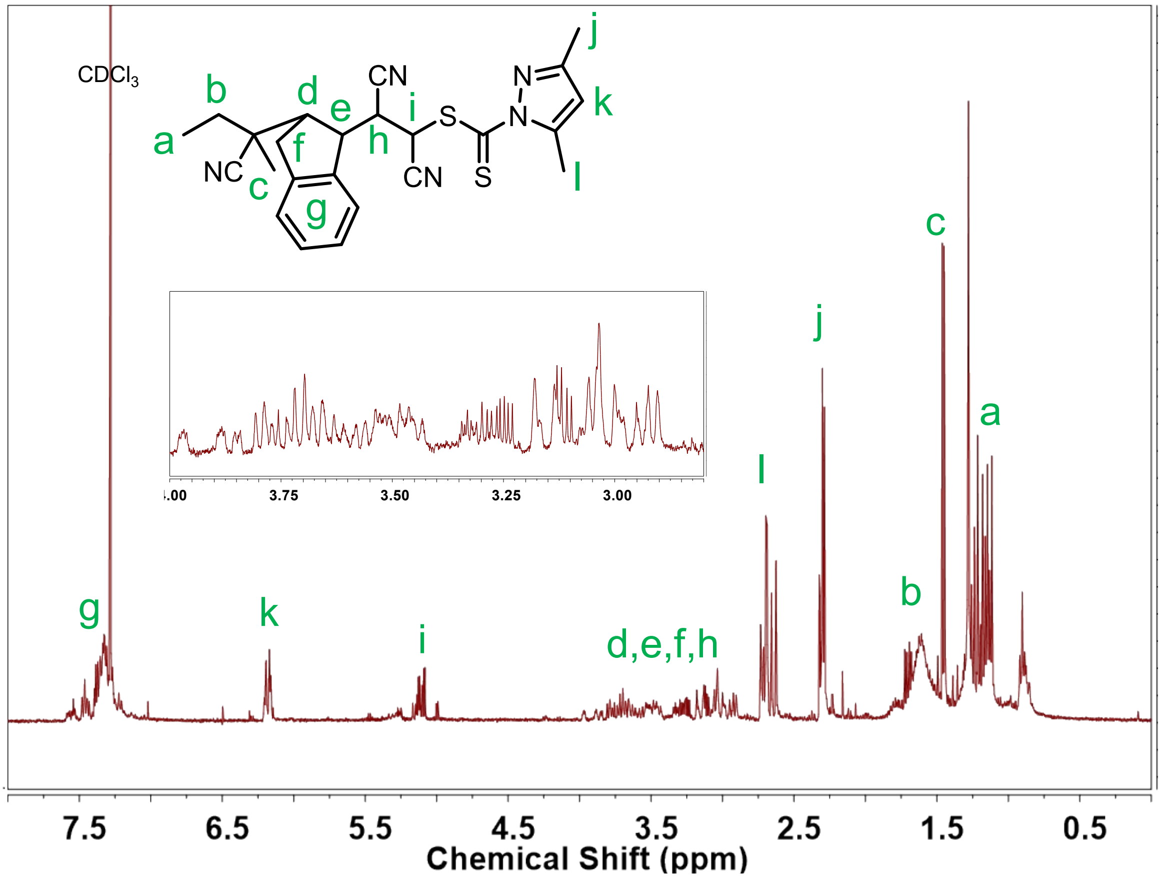


Fig. A2-40 $^1$H NMR spectrum (400.17 MHz, CDCl$_3$) of IPN-Ind-FCN-PCDT.

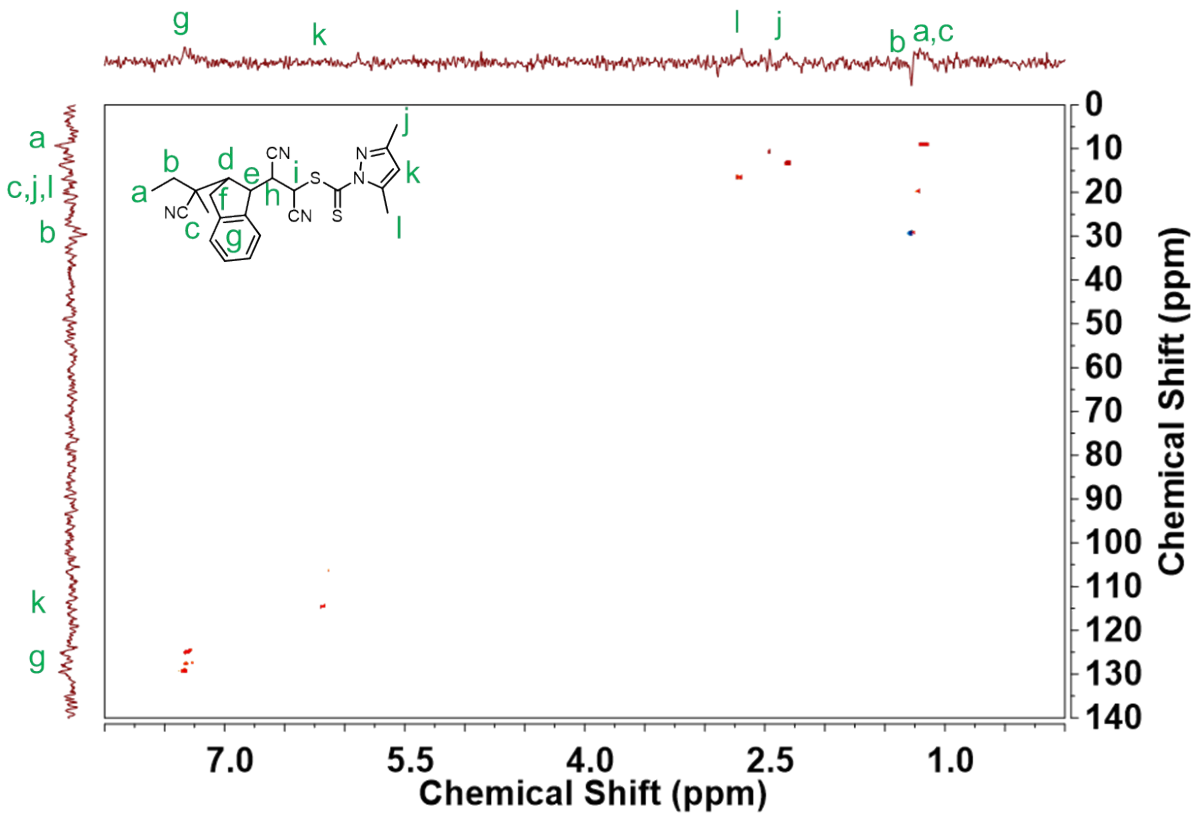


Fig. A2-41 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of IPN-Ind-FCN-PCDT.

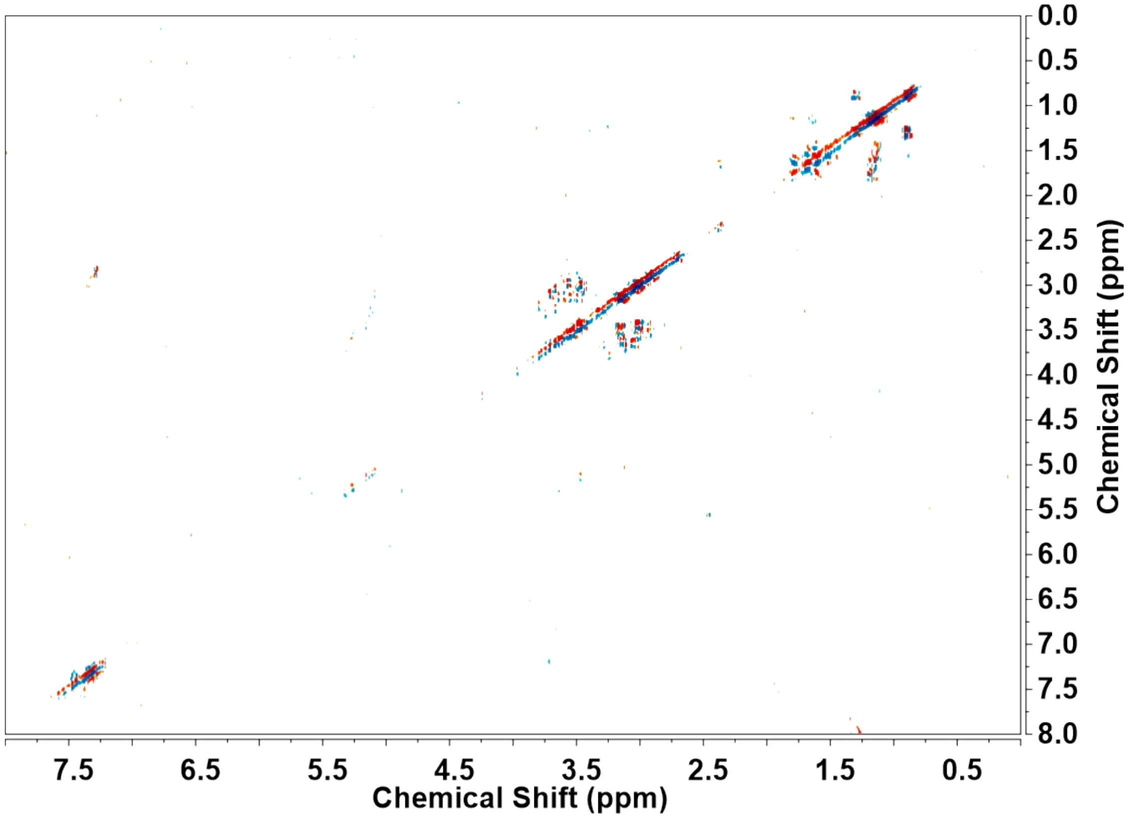


Fig. A2-42 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-Ind-FCN-PCDT.

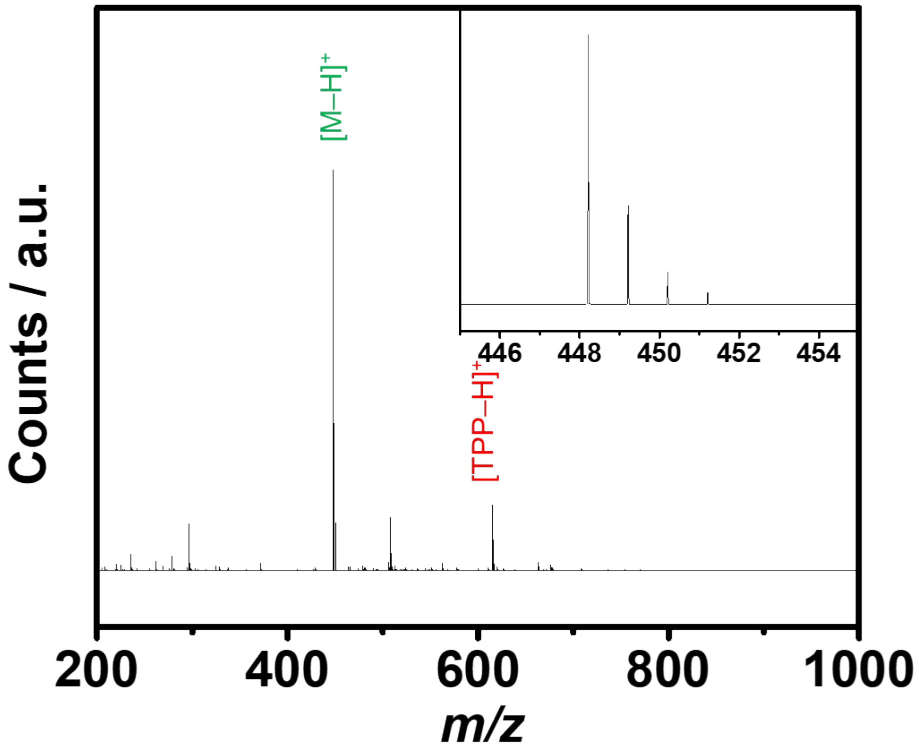
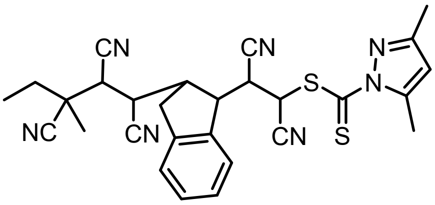


Fig. A2-43 APCI mass spectrum ($CH_3CN$) of IPN-Ind-FCN-PCDT.



**IPN-FCN-Ind-FCN-PCDT** A solution of IPN-FCN-Ind-PCDT (49 mg, 0.11 mmol) and fumaronitrile (86 mg, 10 eq) in $d_6$-DMSO (0.5 mL) was added to ZnTPP (~0.3 mg, 0.5 mol%) in a Wilmad NMR tube. The reaction mixture was then degassed by sparging under argon for 15 min and then irradiated under blue LED (0.42 mW cm$^{-2}$) and monitored by $^1$H NMR. After a suitable reaction time, the reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a yellow solid (48 mg, 85% yield).

TLC (40% v/v ethyl acetate in hexanes) $R_f = 0.3$

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.50-7.19 (m, 4H), 6.19-6.10 (m, 1H), 5.26 (dd, *J*= 12.3, 3.4 Hz), 5.19 (d, *J*= 4.5 Hz), 5.17 (d, *J*= 4.3 Hz), 5.16 (d, *J*= 4.4 Hz), 5.15 (d, *J*= 4.4 Hz), 5.15 (d, *J*= 4.4 Hz), 5.09 (d, *J*= 1.9 Hz), 5.07 (d, *J*= 1.8 Hz), 5.05 (d, *J*= 4.6 Hz), 5.02 (d, *J*= 4.7 Hz), 3.80-2.80 (m, 7H), 2.71-2.60 (m, 3H), 2.32-2.25 (m, 3H), 1.75-1.51 (m, 2H), 1.34-1.06 (m, 6H).

HRMS (APCI) 526.18, 527.19, 528.19, 529.19 $[M–H]^+$. Calculated: 526.18, 527.19, 528.18, 529.18. No peaks from FCN double-insertion (+78) or from starting material (-78) were found.

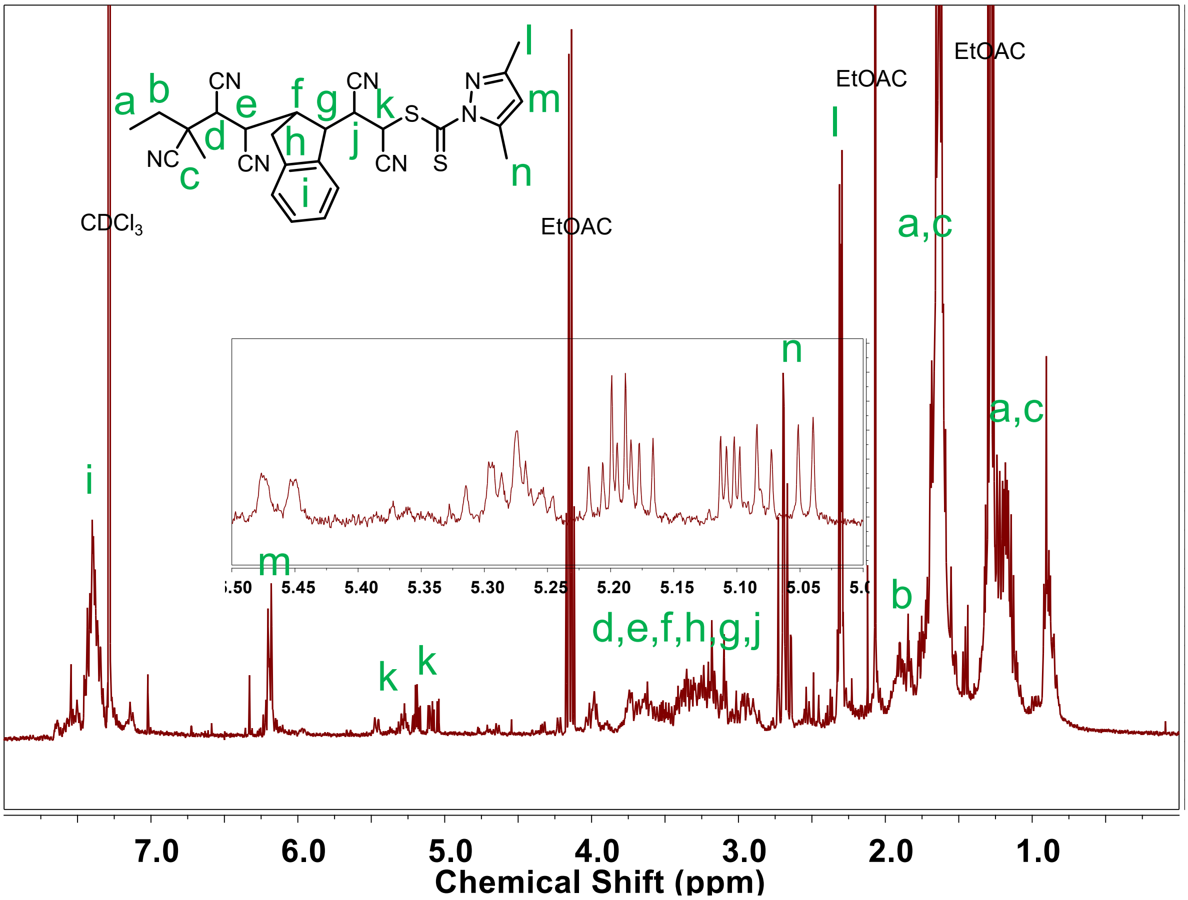


Fig. A2-44 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-FCN-Ind-FCN-PCDT.

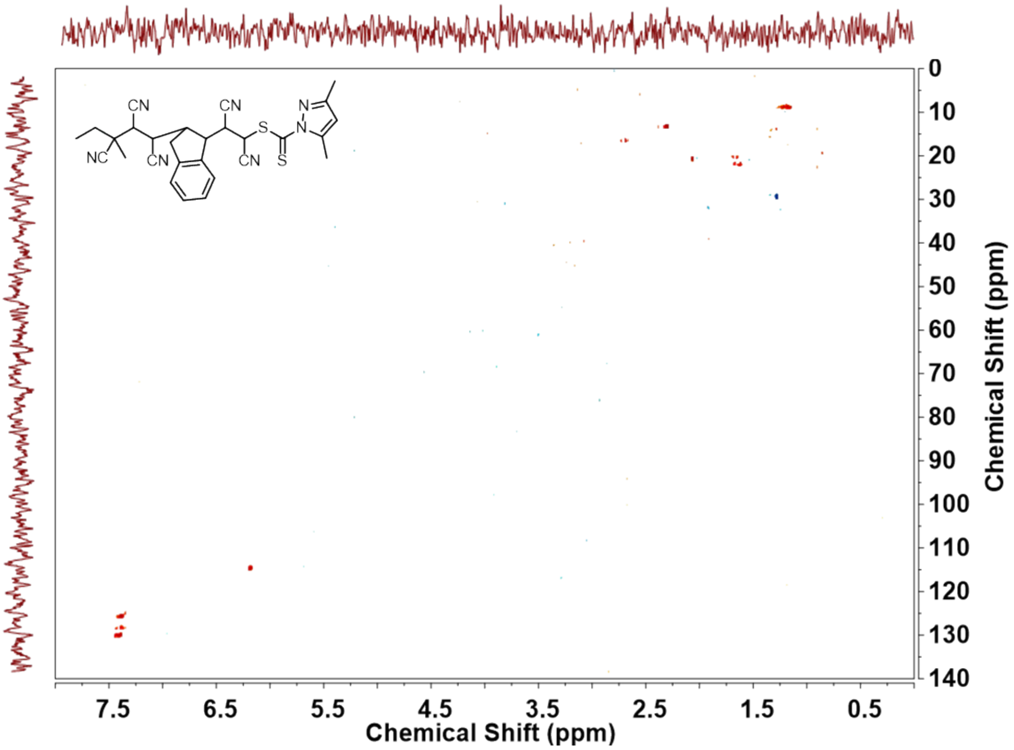


Fig. A2-45 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of IPN-FCN-Ind-FCN-PCDT.

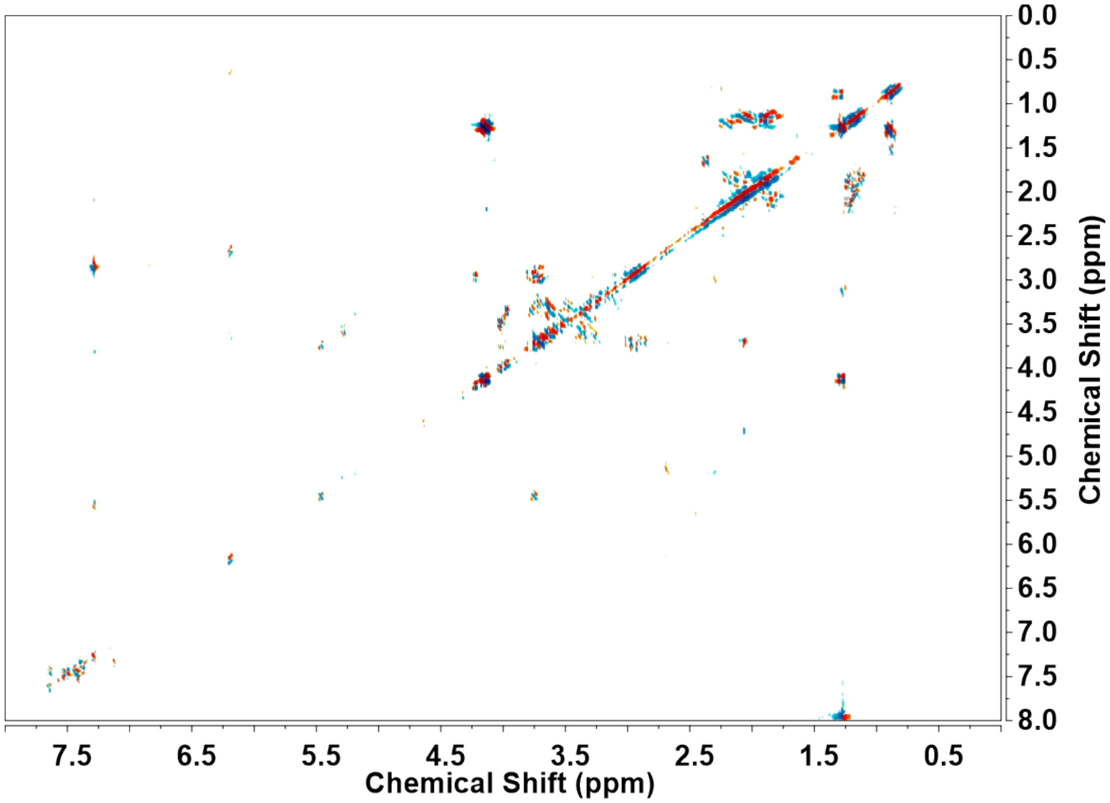


Fig. A2-46 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-FCN-Ind-FCN-PCDT.

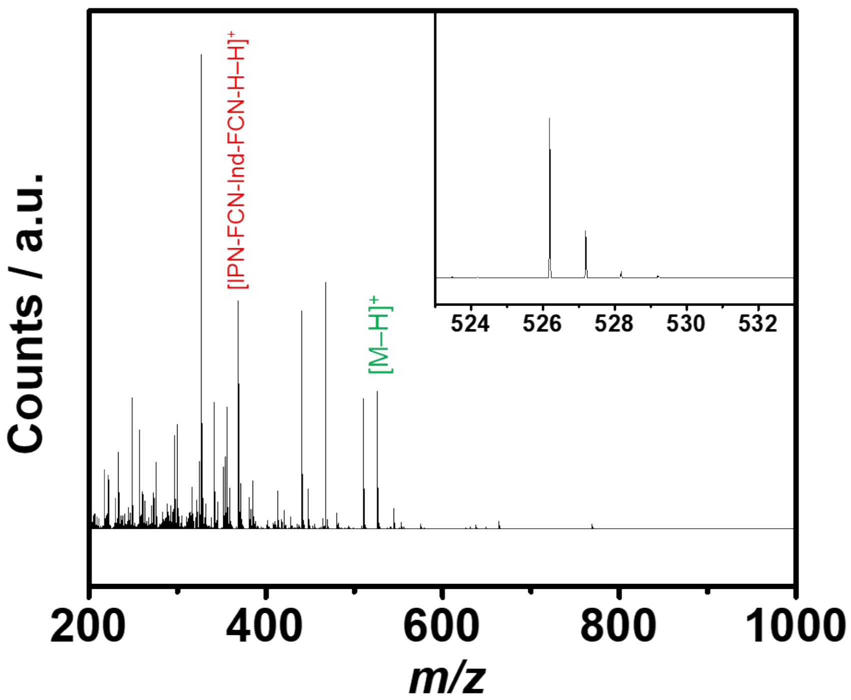


Fig. A2-47 APCI mass spectrum ($CH_3CN$) of IPN-FCN-Ind-FCN-PCDT.

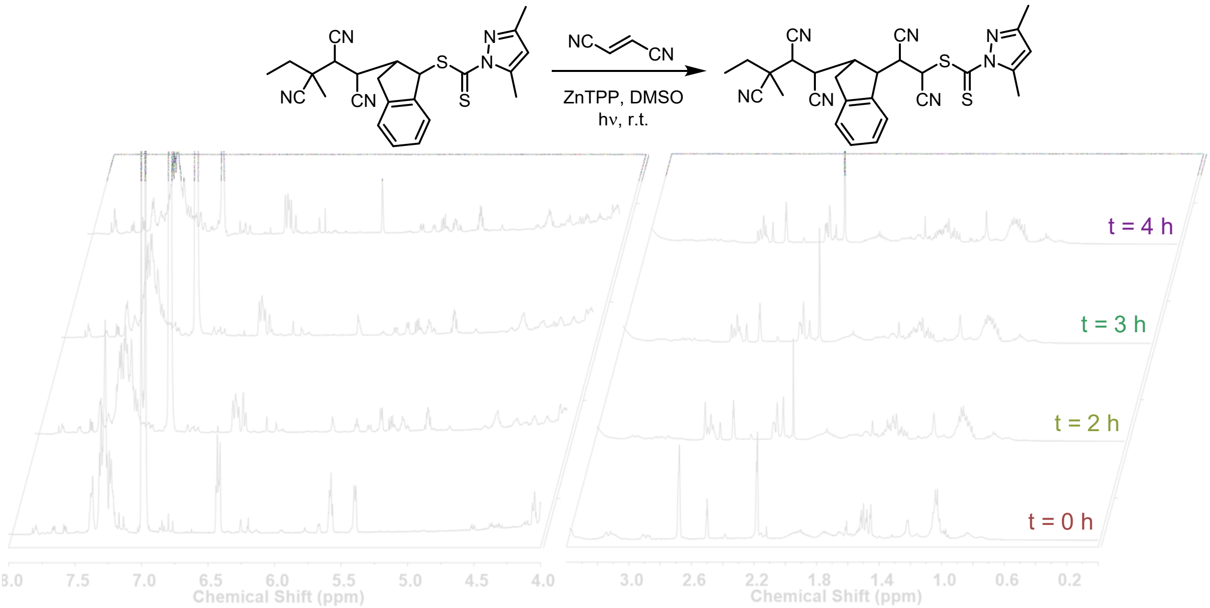
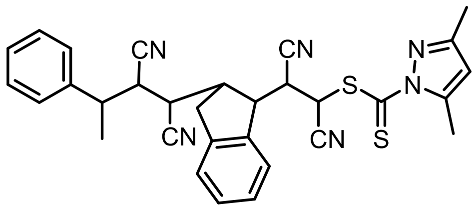


Fig. A2-48 Kinetics of IPN-FCN-Ind-FCN-PCDT synthesis by $^{1}H$ NMR (500.13 MHz, DMSO).

*N.B.,* Reaction reached completion after 2 h and didn't change with subsequent time points.



**PhMeCH-FCN-Ind-FCN-PCDT** A solution of PhCHMe-FCN-Ind-PCDT (51 mg, 0.11 mmol) and fumaronitrile (85 mg, 10 eq) in $d_6$-DMSO (0.5 mL) was added to ZnTPP (~0.3 mg, 0.5 mol%) in a Wilmad NMR tube. The reaction mixture was then degassed by sparging under argon for 15 min and then irradiated under blue LED (0.42 mW cm$^{-2}$) and monitored by $^1$H NMR. After a suitable reaction time, the reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as two diastereomer fractions of yellow oils (48 mg, 85% yield).

TLC (40% ethyl acetate in hexanes) $R_f$ = 0.41 (diastereomer fraction 1); $R_f$ = 0.55 (diastereomer fraction 2)

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.60-7.09 (m, 9H), 6.24-6.00 (m, 1H), 5.55 (d, *J*= 7.2 Hz), 5.43 (d, *J*= 6.7 Hz), 5.15 (d, *J*= 4.4 Hz), 5.11 (d, *J*= 4.7 Hz), 5.08 (d, *J*= 5.0 Hz), 5.07 (d, *J*= 4.2 Hz), 4.94 (d, *J*= 4.7 Hz), 4.89 (d, *J*= 4.4 Hz), 4.79 (dd, J = 13.5, 5.3 Hz), 4.79 (d, *J*= 5.3 Hz), 4.71 (d, *J*= 6.0 Hz), 4.55 (d, *J*= 4.4 Hz), 3.85-2.74 (m, 8H), 2.74-2.57 (m, 3H), 2.36-2.22 (m, 3H), 1.67-1.52 (m, 3H). *N.B.,* Full list of resonances generated from both diastereomer fractions isolated.

HRMS (APCI) 549.19, 550.20, 551.19, 552.18 $[M–H]^+$. Calculated: 549.19, 550.19, 551.18, 552.19. No peaks from FCN double-insertion (+78), from starting material (-78) or from β-elimination (-172 – of the product, however, β-elimination of the starting material was observed) were found.

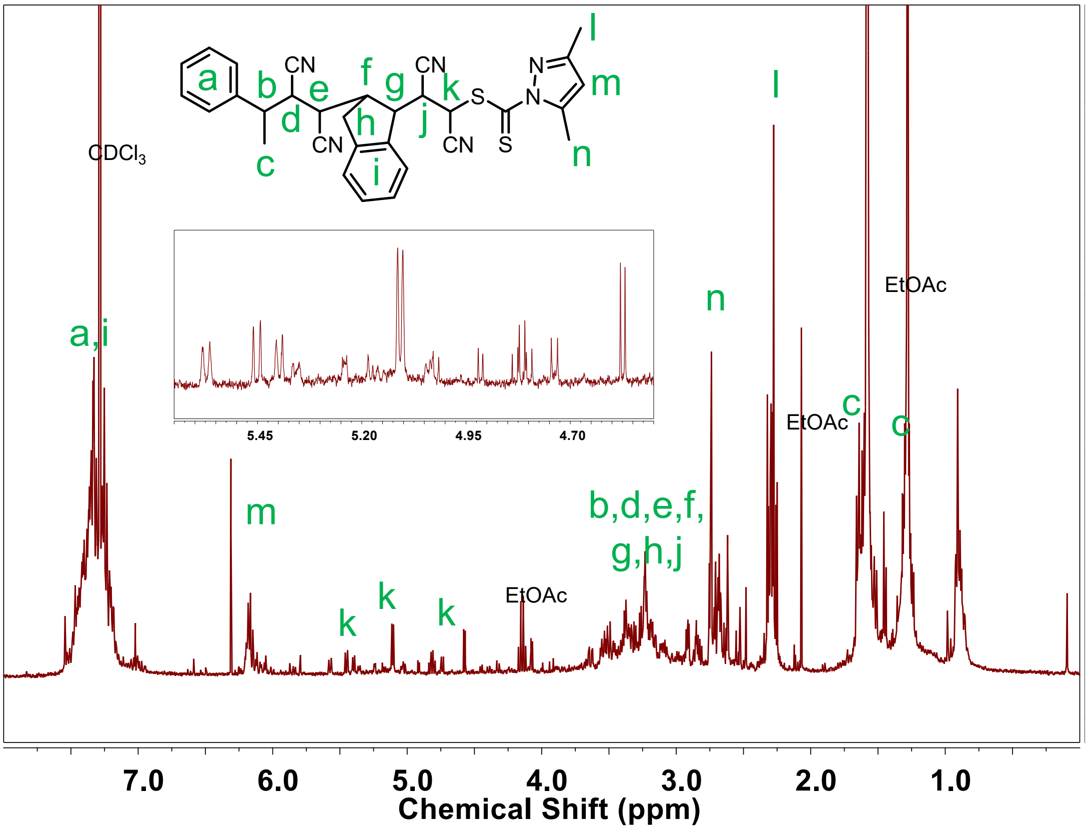


Fig. A2-49 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-FCN-Ind-FCN-PCDT (fraction 1).

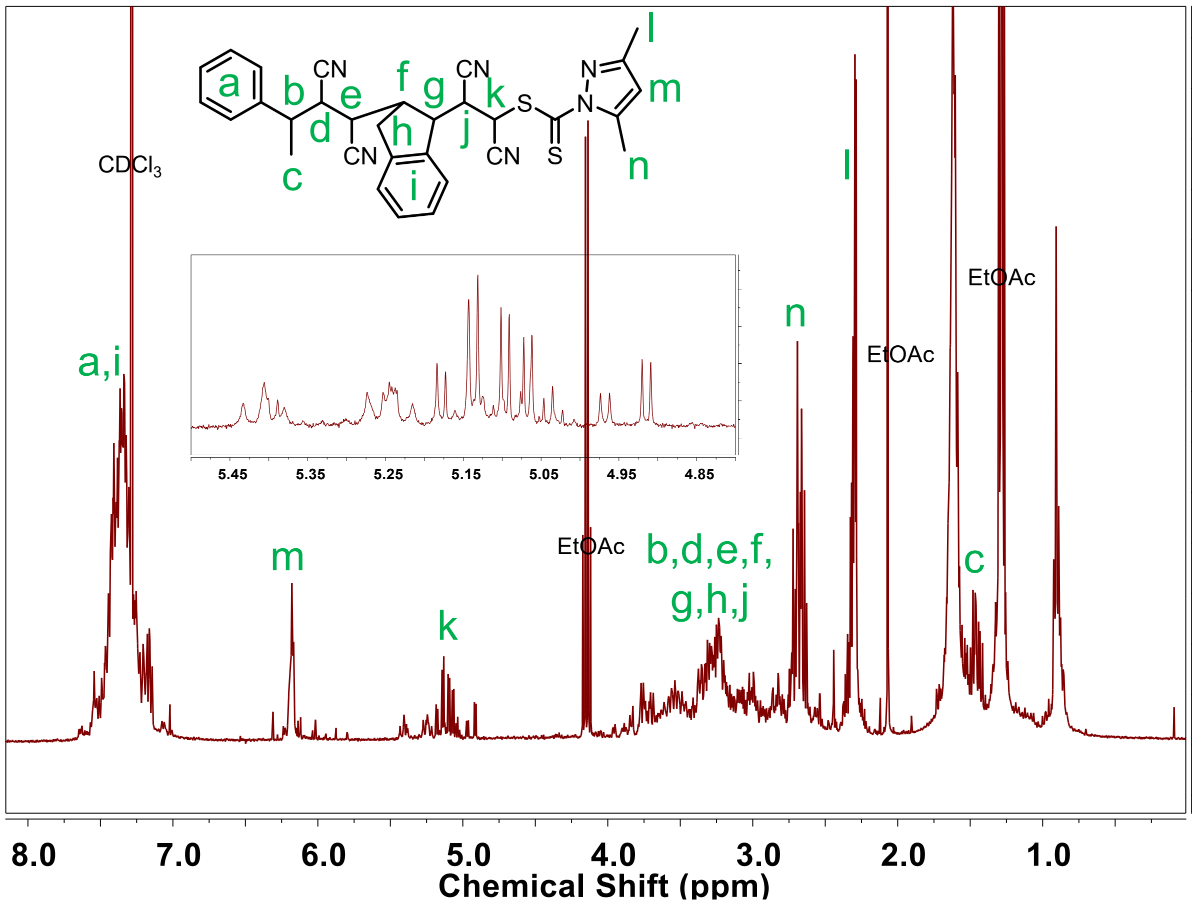


Fig. A2-50 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-FCN-Ind-FCN-PCDT (fraction 2).

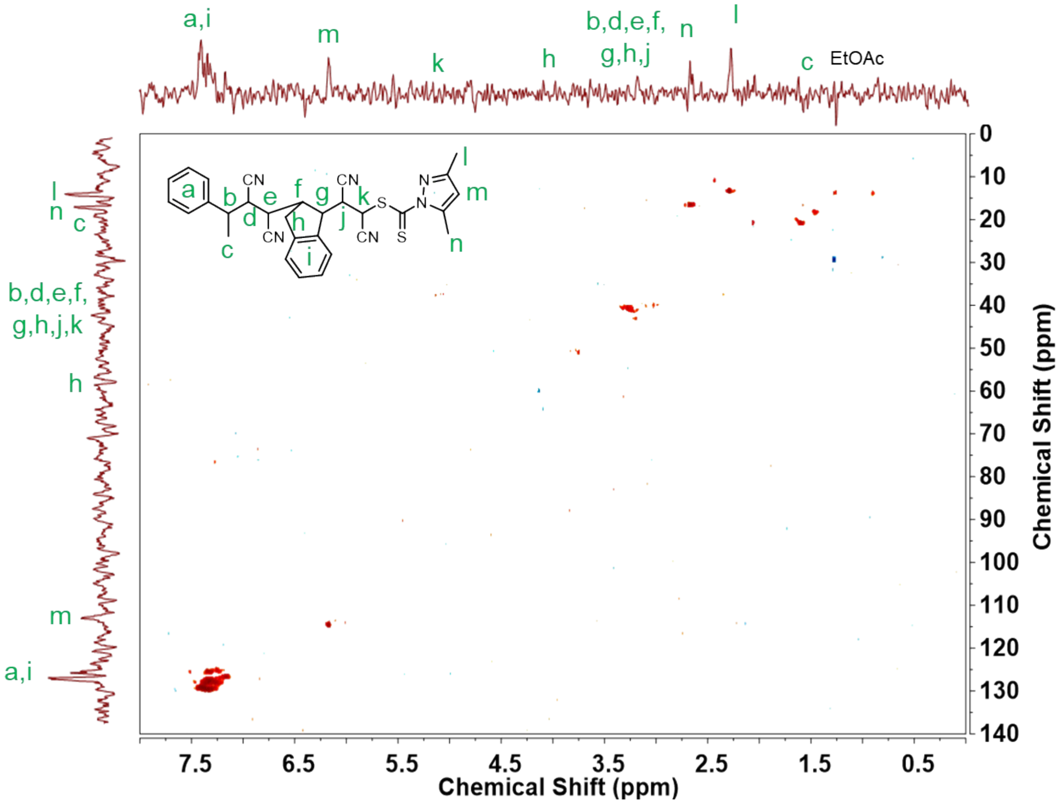


Fig. A2-51 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of PhMeCH-FCN-Ind-FCN-PCDT (fraction 2).

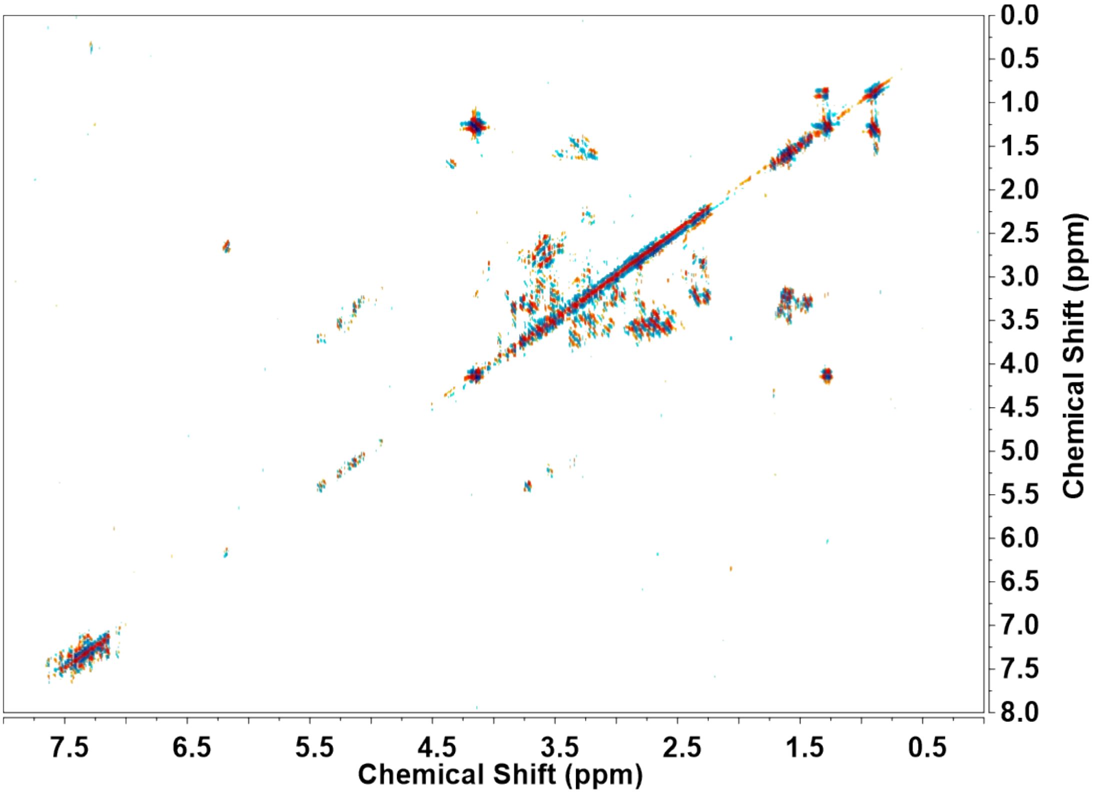


Fig. A2-52 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of PhMeCH-FCN-Ind-FCN-PCDT (fraction 2).

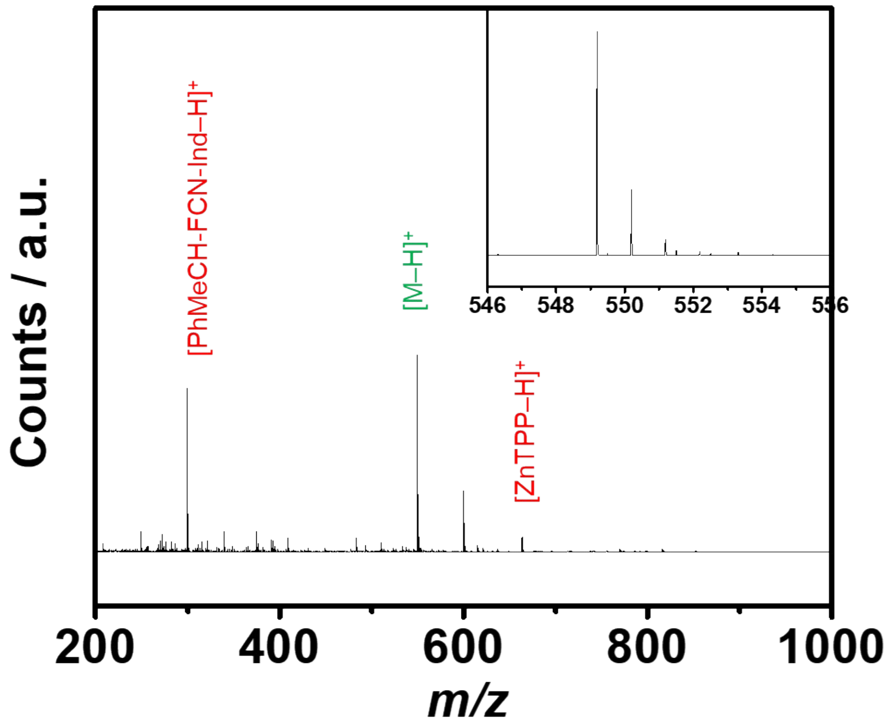


Fig. A2-53 APCI mass spectrum ($CH_3CN$) of PhMeCH-FCN-Ind-FCN-PCDT (fraction 2).

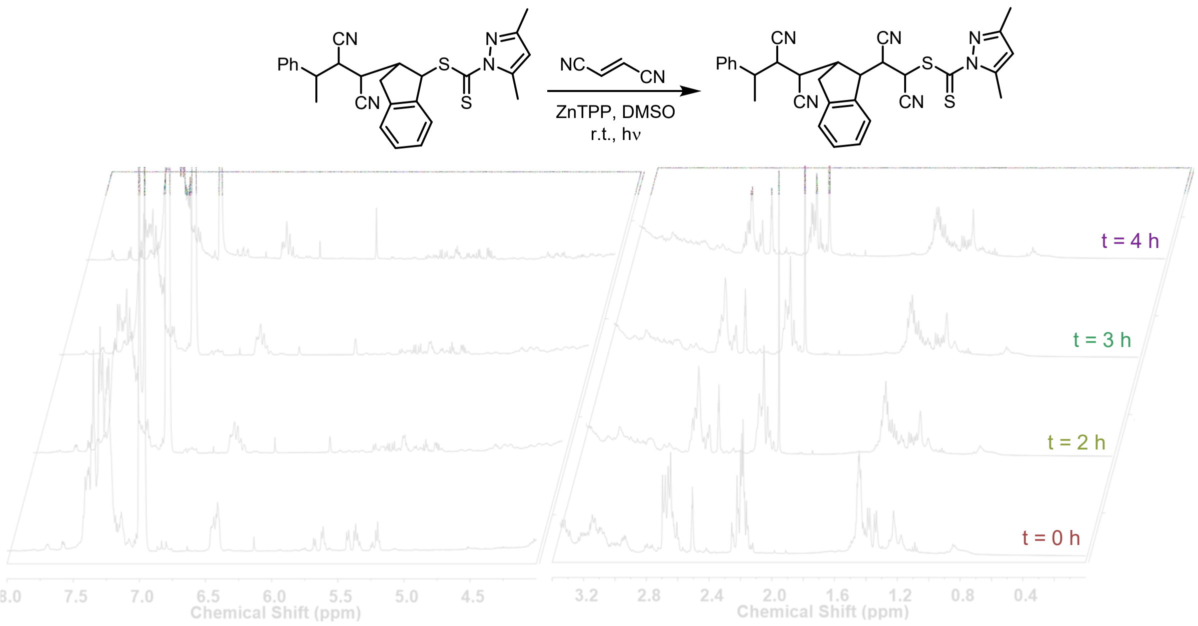
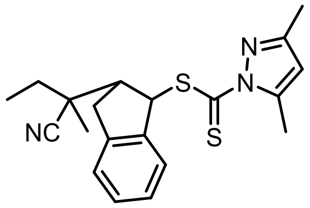


Fig. A2-54 Kinetics of PhMeCH-FCN-Ind-FCN-PCDT synthesis by $^1$H NMR (500.13 MHz, DMSO).

*N.B.,* Reaction reached completion after 2 h and didn't change with subsequent time points.



**IPN-Ind-PCDT** ZnTPP (~1.5 mg, 0.5 mol%) and IPN-PCDT (111 mg, 0.44 mmol) were added to a solution of indene (56 mg, 1.1 eq) in DMSO (2 mL) in a 2 mL vial and sealed with a rubber septum. The heterogeneous reaction mixture was then irradiated under blue LED (0.42 mW cm$^{-2}$) for 8 h upon which, the solution became homogeneous. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a yellow solid (117 mg, 73% yield).

A separate kinetic experiment was performed on an analogous solution in d$_6$-DMSO (0.5 mL – with all other components scaled equally) prepared in a Wilmad NMR tube (without a stirring bar) which was degassed by sparging under argon for 15 min prior to irradiation under the same blue LED. A similar workup and purification procedure was then performed to obtain the product in smaller yield (due to reaction scale).

TLC (20% v/v ethyl acetate in hexanes) R$_f$ = 0.45 (similar retention factor to starting material), R$_f$ = 0.25 (double-addition – observed if excess indene is used)

$^1$H NMR (400.17 MHz, CDCl$_3$) δ 7.38-7.11 (m, 4H), 6.20-6.03 (m), 5.87-5.79 (m), 5.43 (d, *J*= 6.7 Hz), 4.79 (td, *J*= 6.8, 5.3 Hz), 3.43 (ddd, *J*= 21.7, 16.3, 6.1 Hz, 1H), 3.47-3.32 (m), 3.18-3.05 (m), 2.99-2.91 (m), 2.80-2.43 (m), 2.37-2.18 (m), 1.50-1.34 (m), 1.18 (t, *J*= 7.4 Hz), 1.10 (td, *J*= 7.4, 4.2 Hz).

HRMS (APCI) 370.14, 371.14, 372.14, 373.14 [M–H]$^+$. Calculated: 370.14, 371.14, 372.14, 373.14. N.B., No peaks from starting material (-116) or double addition (+116) were found.

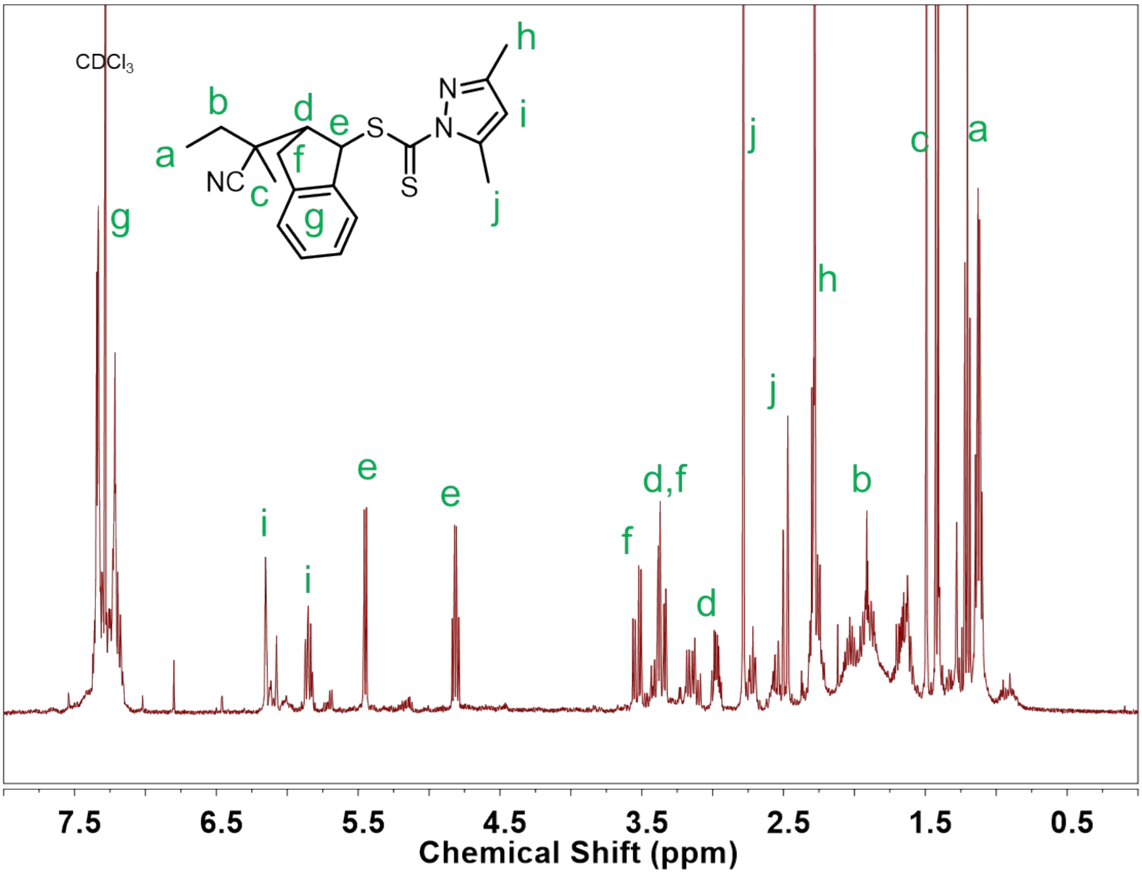


Fig. A2-55 $^1$H NMR spectrum (400.17 MHz, CDCl$_3$) of IPN-Ind-PCDT.

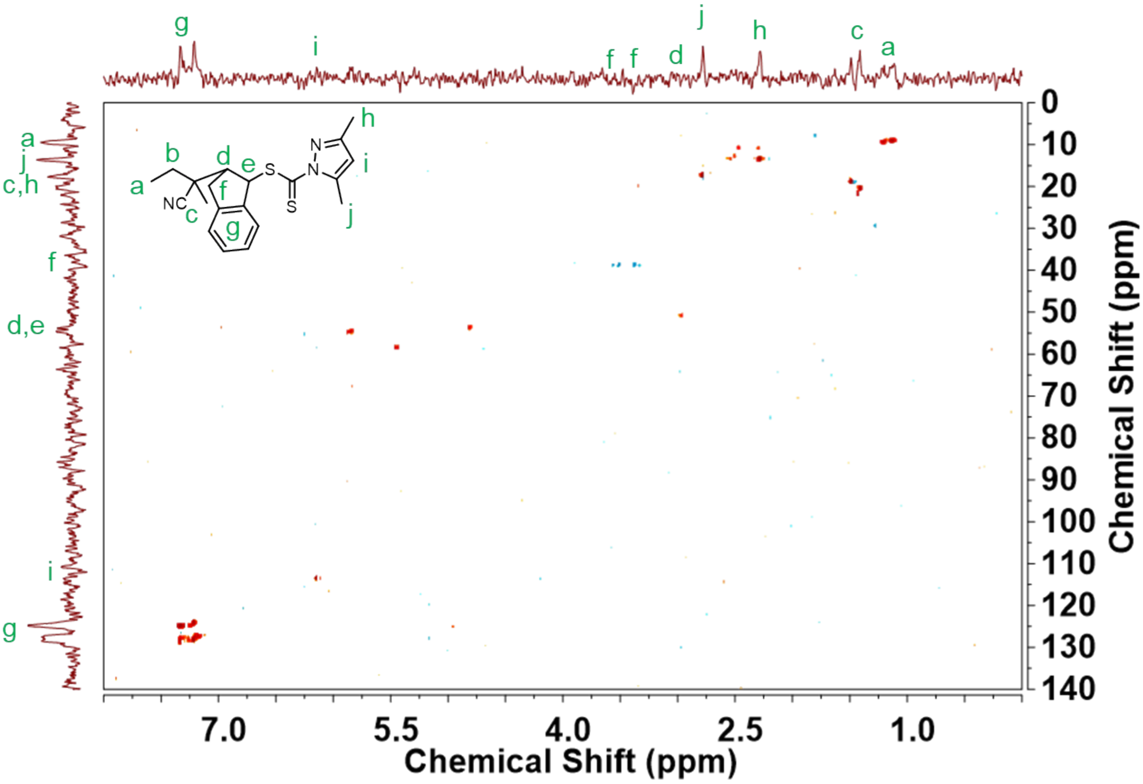


Fig. A2-56 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, CDCl$_3$) of IPN-Ind-PCDT.

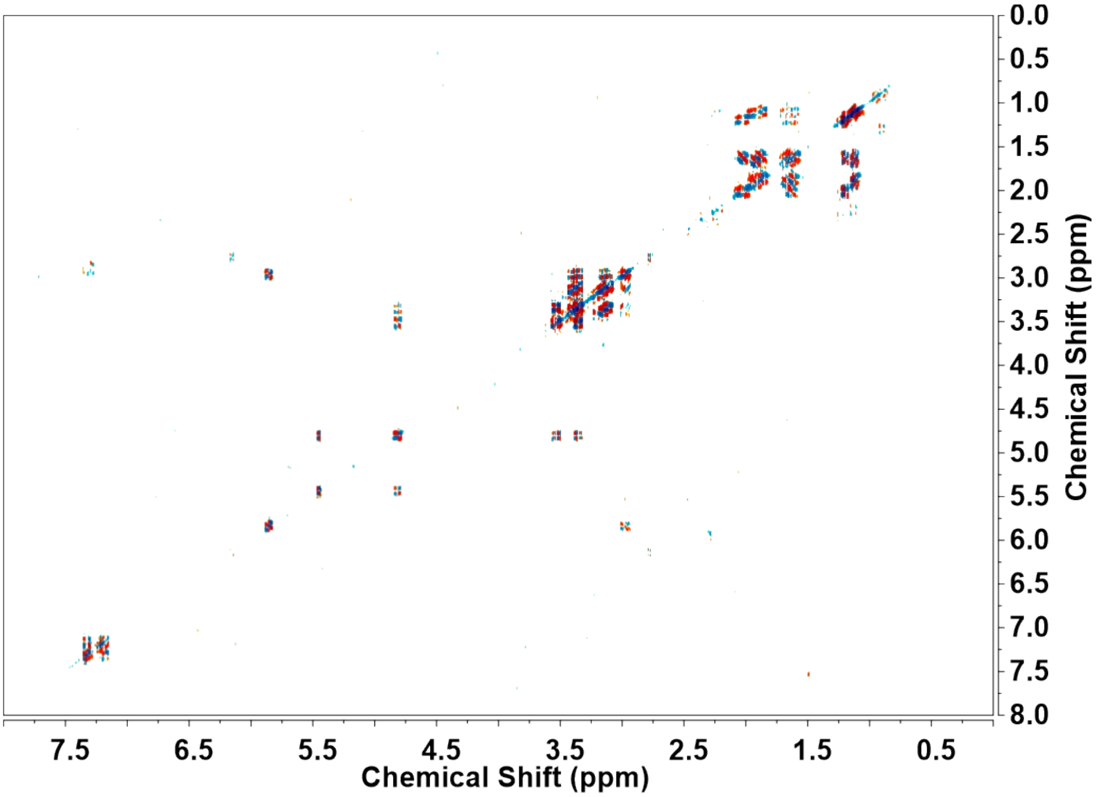


Fig. A2-57 COSY NMR spectrum (400.17 MHz, CDCl$_3$) of IPN-Ind-PCDT.

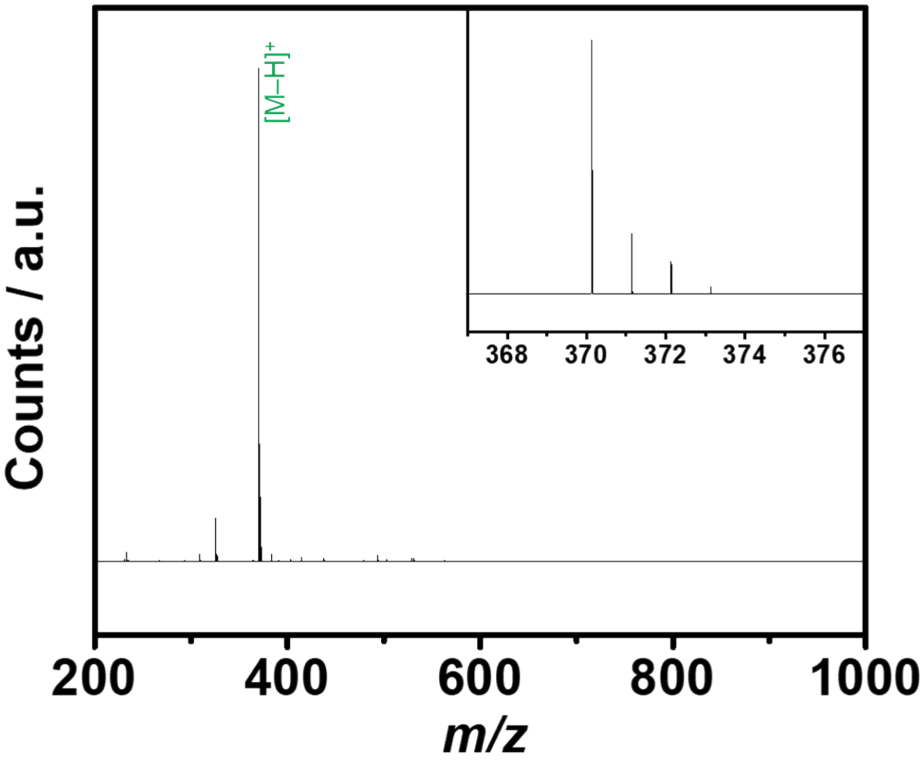


Fig. A2-58 APCI mass spectrum ($CH_3CN$) of IPN-Ind-PCDT.

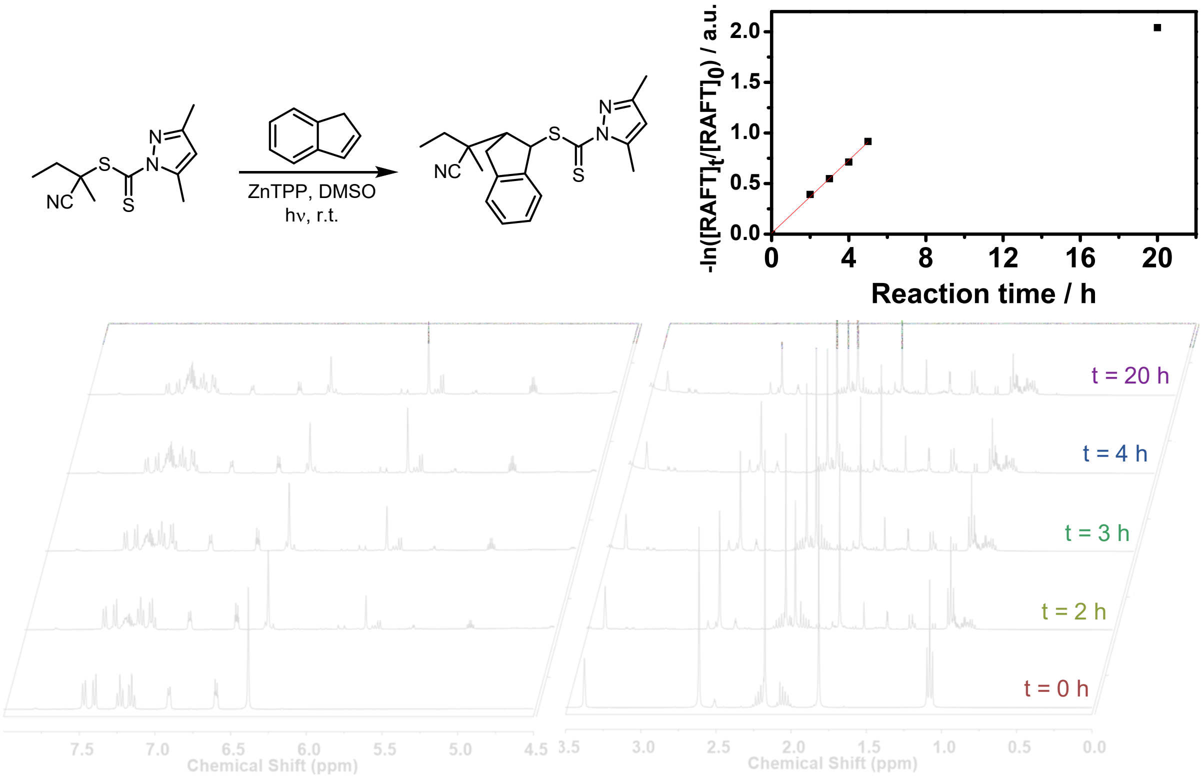
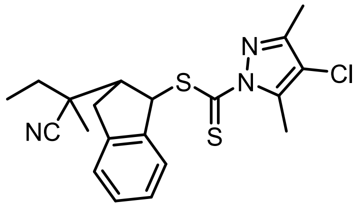


Fig. A2-59 Kinetics of IPN-Ind-PCDT synthesis by $^1$H NMR (500.13 MHz, DMSO).



**IPN-Ind-(Cl)PCDT** A solution of indene (~5.6 mg, 1.1 eq) in DMSO (0.2 mL) was added to IPN-PCDT (12.1 mg, 0.044 mmol) and ZnTPP (~0.2 mg, 0.5 mol%) were added to in a 250 µL insert (without a stirring bar) and sealed with a rubber septum. The heterogeneous reaction mixture was then irradiated under blue LED (0.42 mW cm$^{-2}$) for 8 h upon which, the solution became homogeneous. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a yellow solid (11 mg, 64% yield).

TLC (20% v/v ethyl acetate in hexanes) $R_f$ = 0.58 (similar retention factor to starting material)

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.31-7.12 (m, 4H), 5.87-5.78 (m, 1H), 45-3.30 (m), 3.20-3.06 (m) 3.01-2.92 (m), 2.80-2.73 (m, 3H), 2.33-2.24 (m, 3H), 1.98-1.52 (m, 2H), 1.41-1.36 (m, 3H), 1.14-1.06 (m, 3H).

HRMS (APCI) 404.10, 405.10, 406.10, 407.11, 408.11 $[M–H]^+$. Calculated: 404.10, 405.10, 406.10, 407.10, 408.09. *N.B.,* No peaks from Ind double-insertion (+116) or starting material (-116) were found.

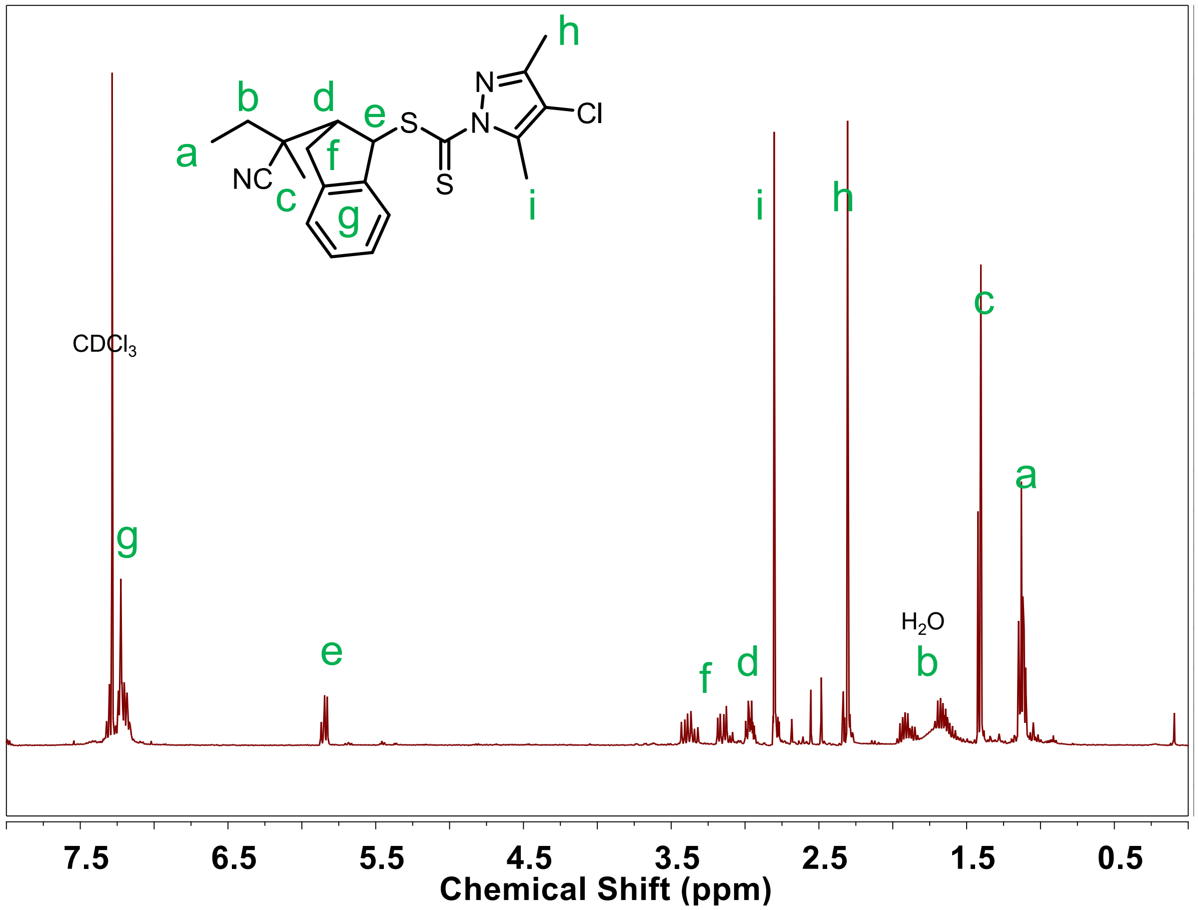


Fig. A2-60 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-Ind-(Cl)PCDT.

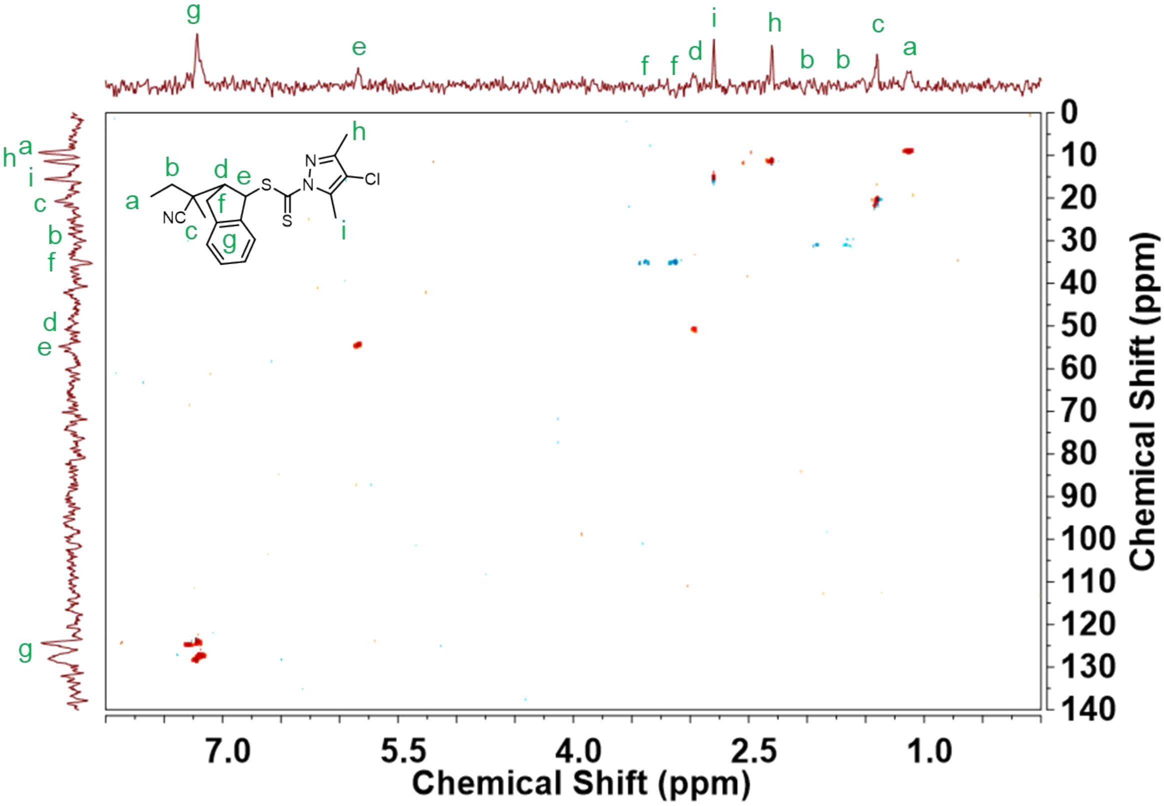


Fig. A2-61 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of IPN-Ind-(Cl)PCDT.

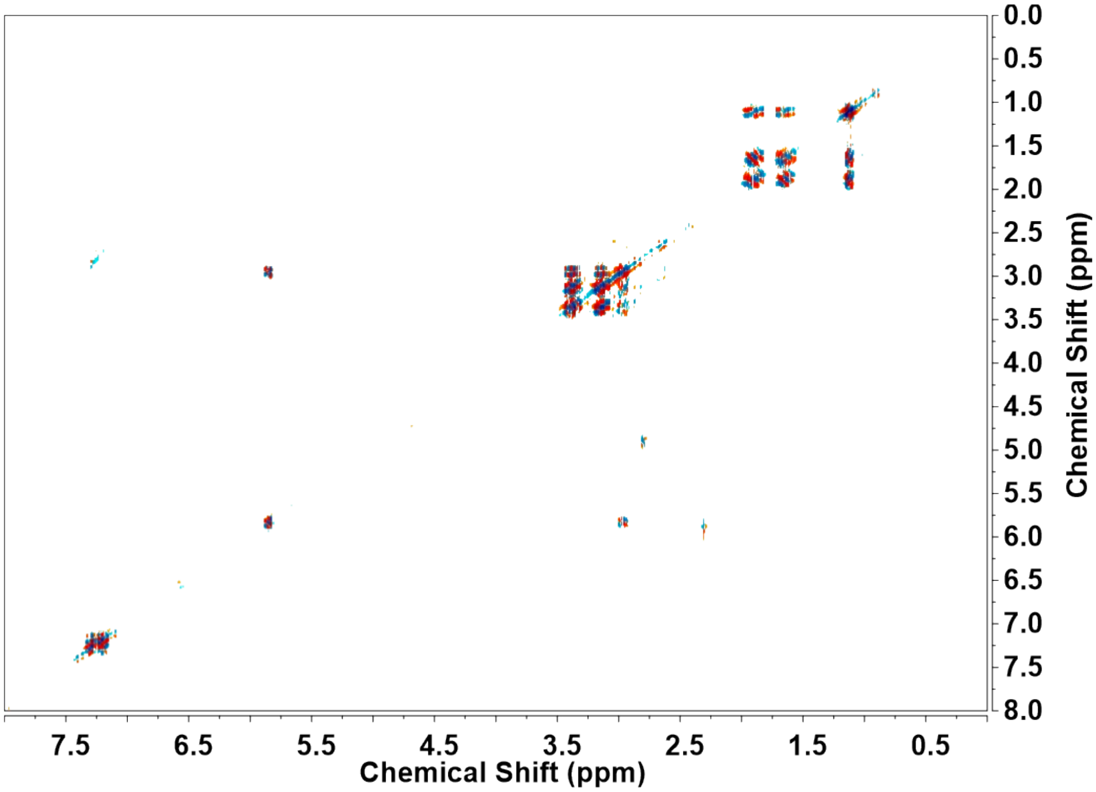


Fig. A2-62 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-Ind-(Cl)PCDT.

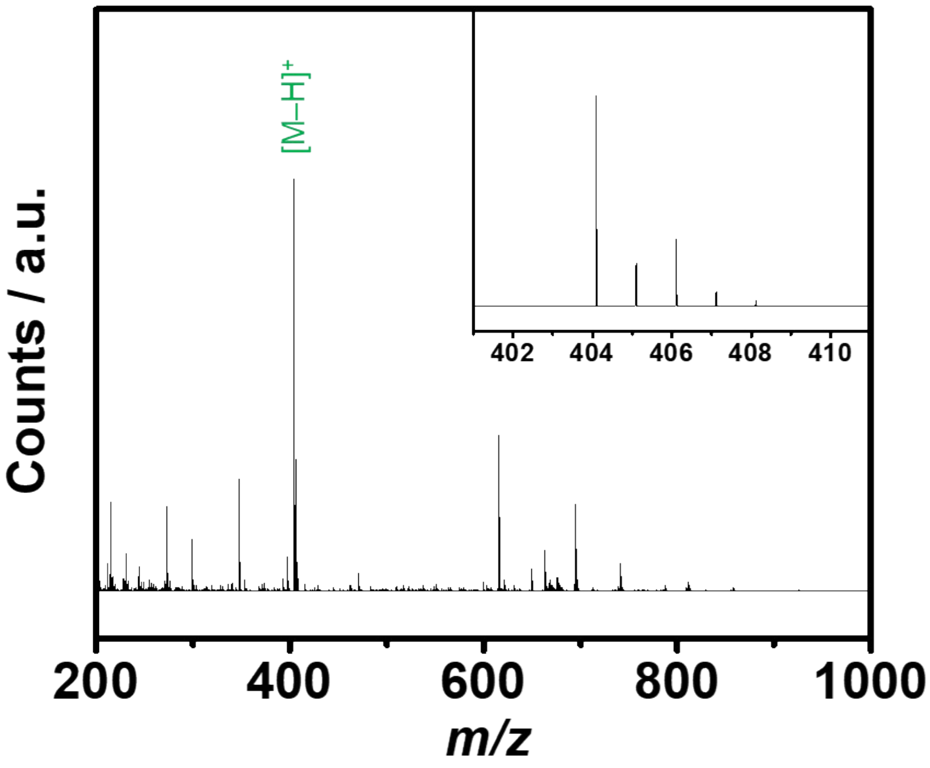
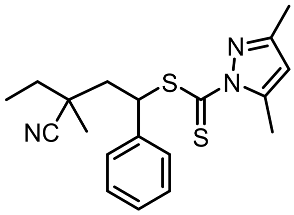


Fig. A2-63 APCI mass spectrum ($CH_3CN$) of IPN-Ind-(Cl)PCDT.



**IPN-St-PCDT** A solution of styrene (5.0 mg, 1.1 eq) in DMSO (0.2 mL) was added to IPN-PCDT (11.1 mg, 0.044 mmol) and ZnTPP (~0.2 mg, 0.5 mol%) in a 250 µL insert (without a stirring bar) and sealed with a rubber septum. The heterogeneous reaction mixture was then irradiated under blue LED (0.42 mW cm$^{-2}$) for 8 h upon which, the solution became homogeneous. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a yellow solid (9 mg, 59% yield).

TLC (20% v/v ethyl acetate in hexanes) $R_f$ = 0.28.

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.51-7.42 (m, 2H), 7.40-7.21 (m, 3H), 6.11-6.03 (m, 1H), 5.17 (ddd, *J*= 14.9, 10.3, 4.2 Hz, 1H), 2.68 (s, 3H), 2.58-2.27 (m, 2H), 2.24 (s, 3H), 1.77-1.45 (m, 2H) 1.41 (s), 1.09 (s), 1.02 (ddd, J = 20.5, 14.0, 6.5 Hz, 3H).

HRMS (APCI) 358.14, 359.14, 360.14, 361.15 [M–H]$^+$. Calculated: 358.14, 359.14, 360.14, 361.14. No peaks from St double-insertion (+104) or from starting material (-104) were found.

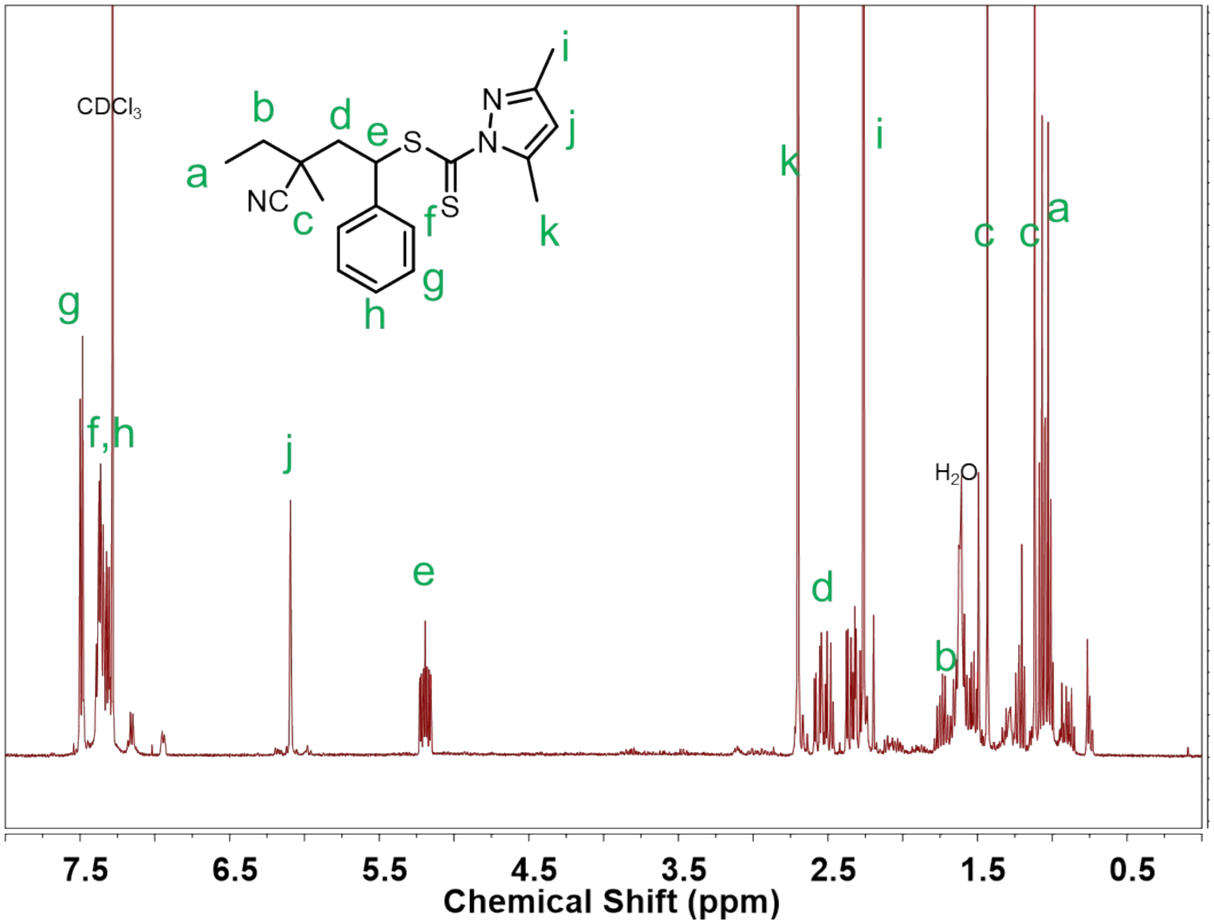


Fig. A2-64 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-St-PCDT.

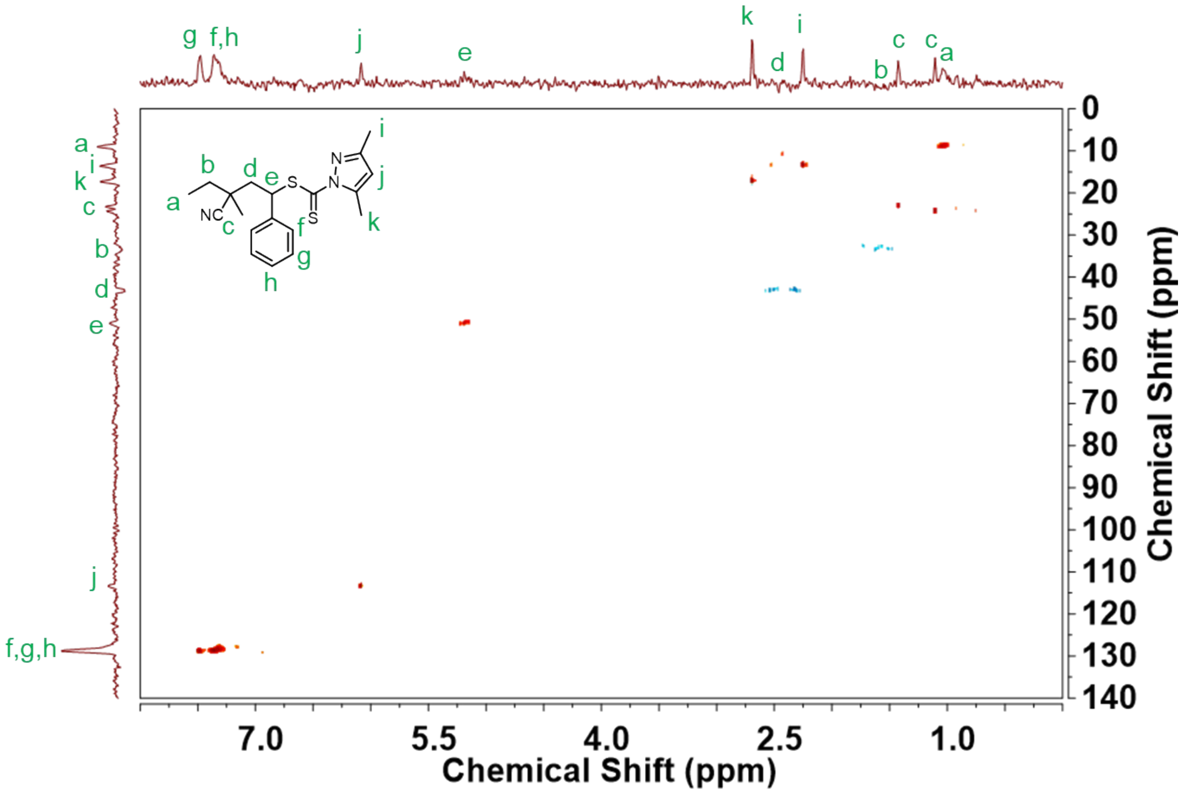


Fig. A2-65 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of IPN-St-PCDT.

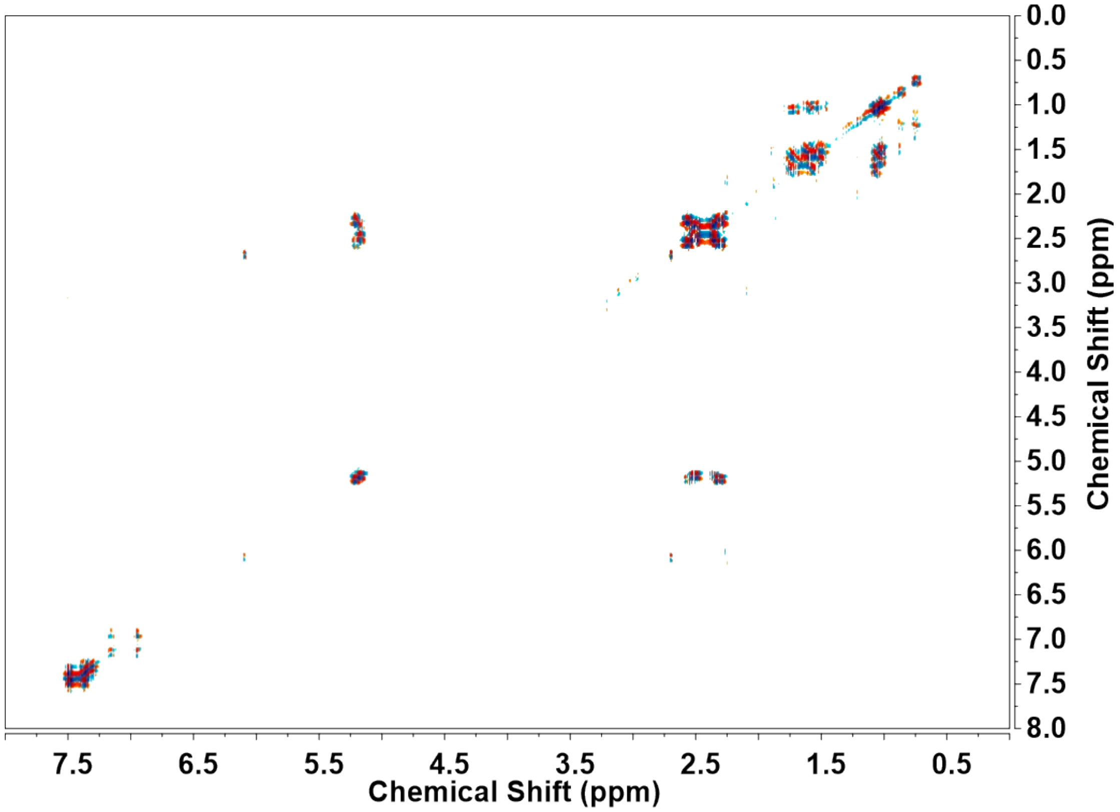


Fig. A2-66 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-St-PCDT.

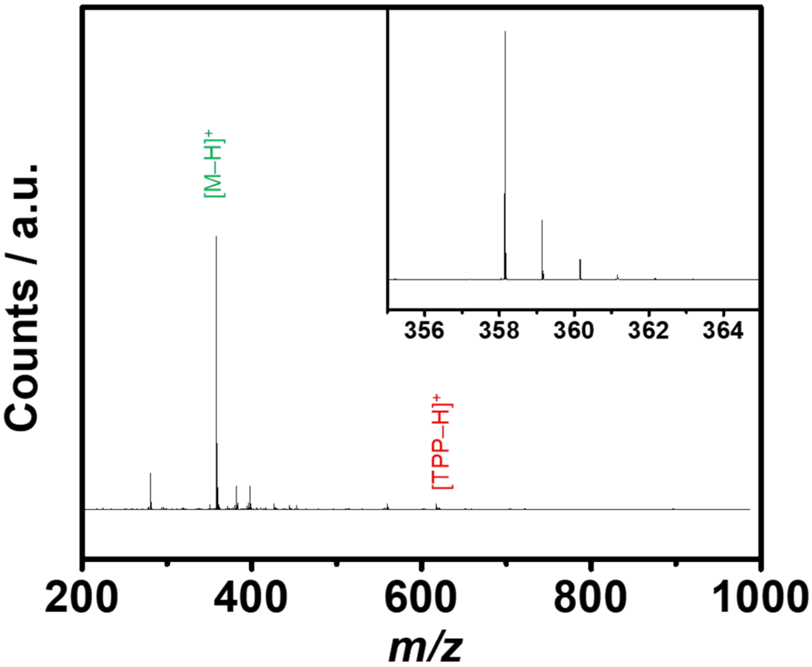
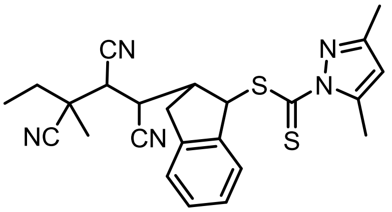


Fig. A2-67 APCI mass spectrum ($CH_3CN$) of IPN-St-PCDT.



**IPN-FCN-Ind-PCDT** ZnTPP (~0.3 mg, 0.5 mol%) was added to a solution of PhMeCH-FCN-PCDT (39 mg, 0.11 mmol) and indene (14 mg, 1.1 eq) in DMSO (0.5 mL) in a 4 mL vial and sealed with a rubber septum. The reaction mixture was then degassed by sparging under argon irradiated under blue LED (0.42 mW cm$^{-2}$) for 8 h. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a yellow-to-green solid (38 mg, 78% yield).

A separate kinetic experiment was performed on an analogous solution in d$_6$-DMSO (0.5 mL – at the same scale) prepared in a Wilmad NMR tube (without a stirring bar) which was degassed by sparging under argon for 15 min prior to irradiation under the same blue LED. A similar workup and purification procedure was then performed to obtain the product in smaller yield (due to reaction scale).

TLC (20% v/v ethyl acetate in hexanes) R$_f$ = 0.18

$^1$H NMR (400.17 MHz, CDCl$_3$) δ 7.44-7.20 (m, 4H), 6.17-6.09 (m, 1H), 5.28 (d, *J*= 3.6 Hz), 5.25 (d, *J*= 2.7 Hz), 5.21 (d, *J*= 1.9 Hz), 4.00 (d, *J*= 1.9 Hz), 3.89 (d, *J*= 1.9 Hz), 3.71 (ddd, *J*= 34.2, 5.2, 1.2 Hz), 3.62-3.47 (m), 3.41 (ddd, *J*= 7.3, 5.0, 1.9 Hz), 3.37-3.16 (m), 3.27-3.21 (m), 3.06-2.95 (m), 2.76-2.70 (m), 2.30-2.20 (m), 2.00-1.71 (m, 2H), 1.70 (s), 1.63 (d, *J*= 1.0), 1.60 (s), 1.50 (s), 1.31-1.03 (m, 3H).

HRMS (APCI) 448.16, 449.16, 450.16, 451.15 [M–H]$^+$. Calculated: 448.16, 449.17, 450.16, 451.16. *N.B.,* No peaks from starting material (-116) were found.

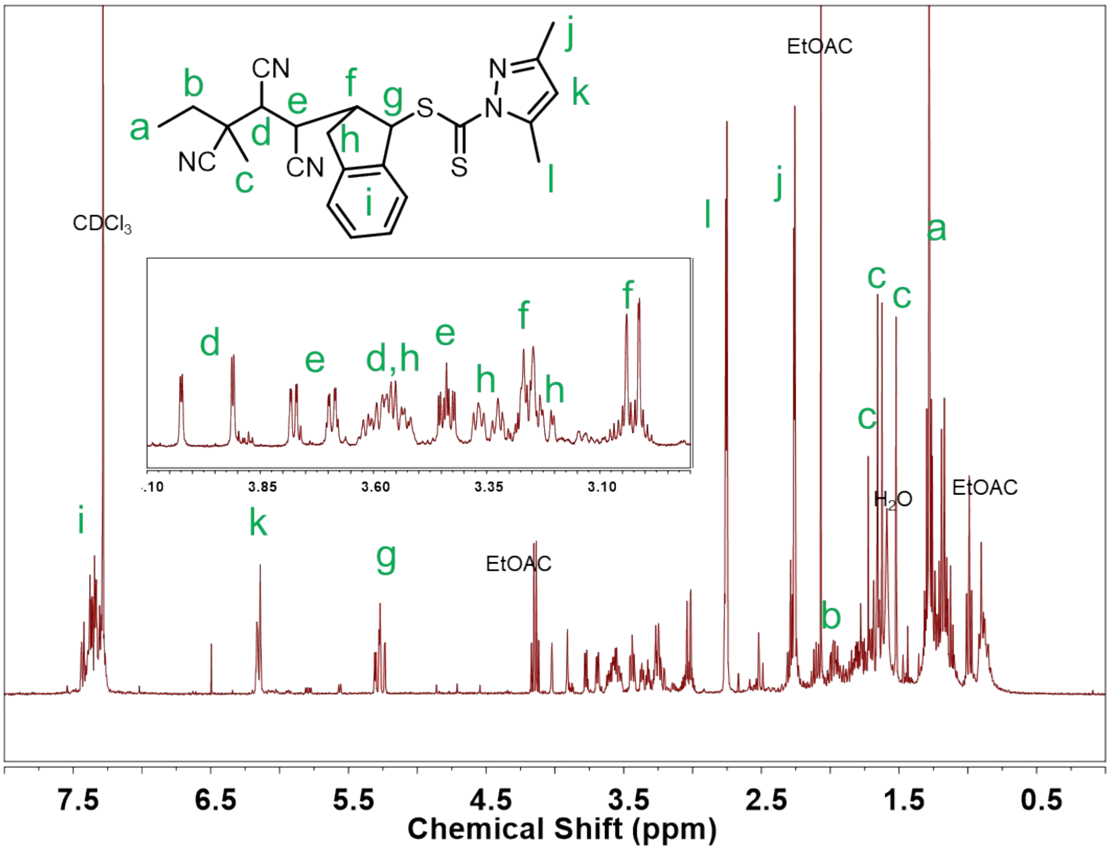


Fig. A2-68 $^1$H NMR spectrum (400.17 MHz, CDCl$_3$) of IPN-FCN-Ind-PCDT.

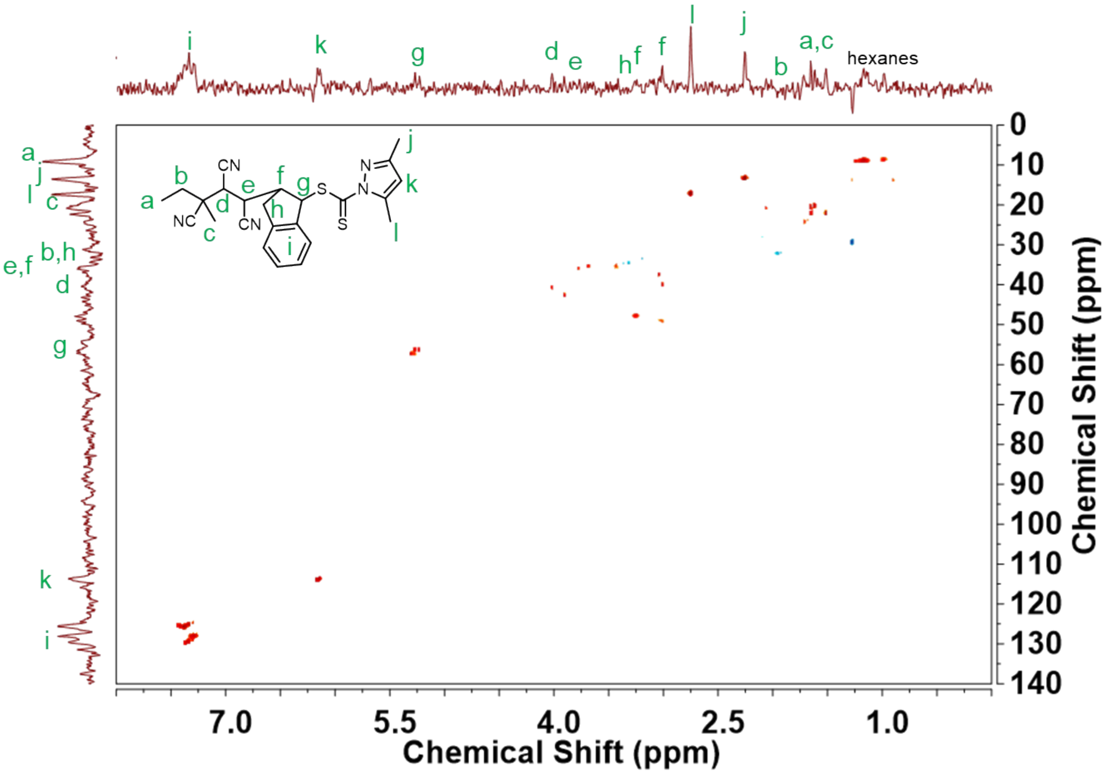


Fig. A2-69 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, CDCl$_3$) of IPN-FCN-Ind-PCDT.

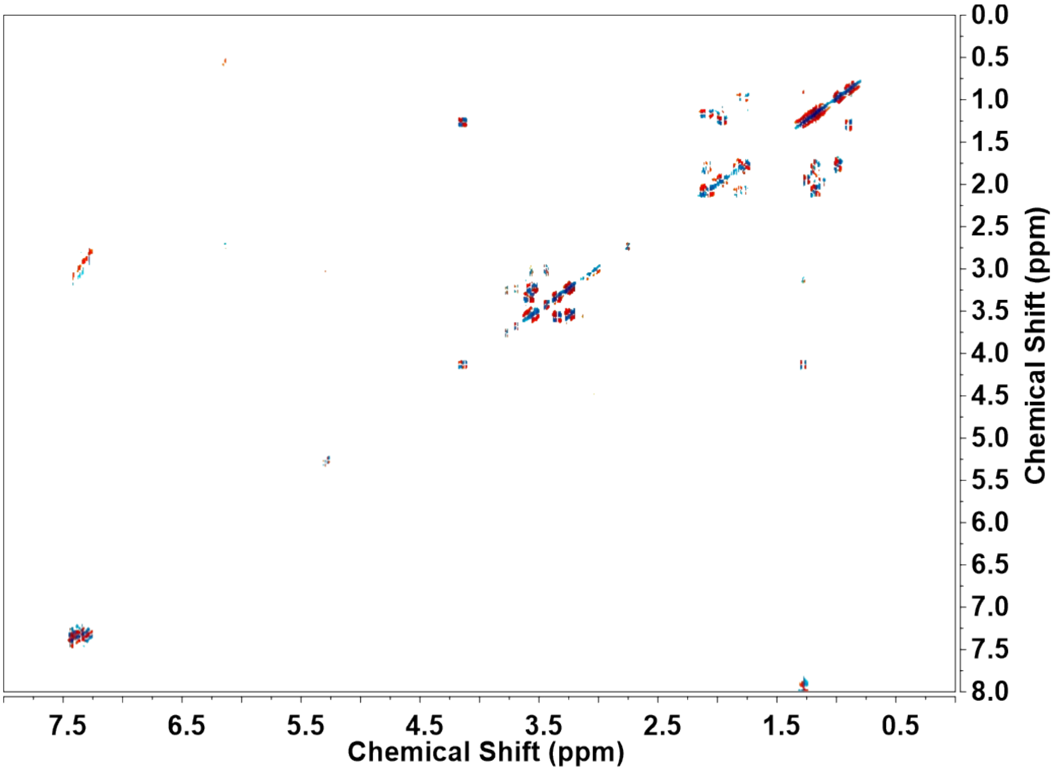


Fig. A2-70 COSY NMR spectrum (400.17 MHz, CDCl$_3$) of IPN-FCN-Ind-PCDT.

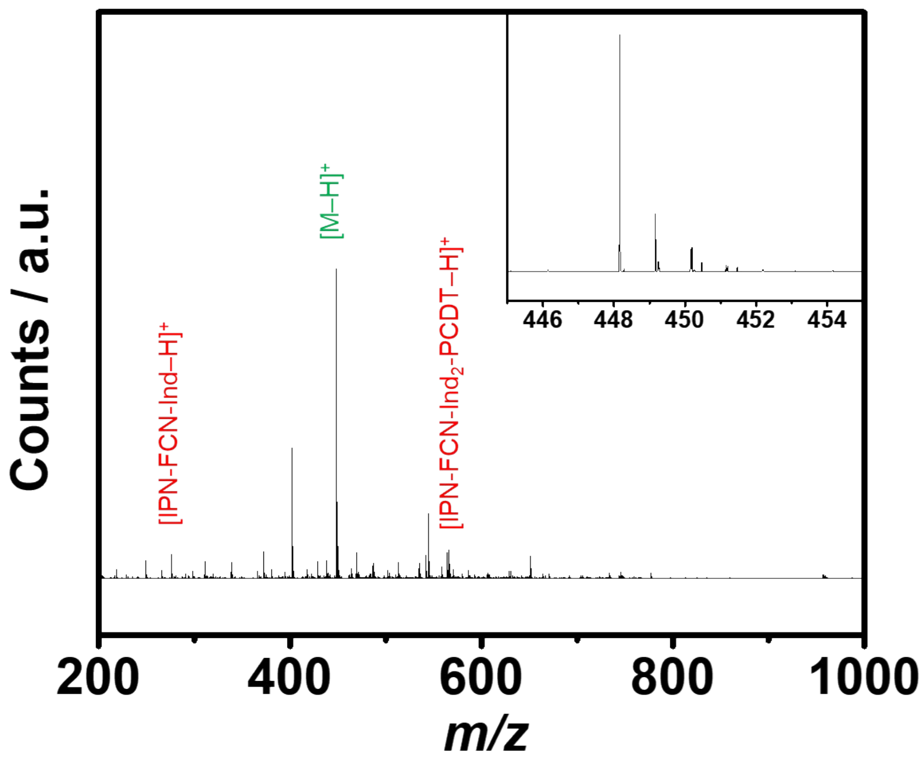


Fig. A2-71 APCI mass spectrum ($CH_3CN$) of IPN-FCN-Ind-PCDT.

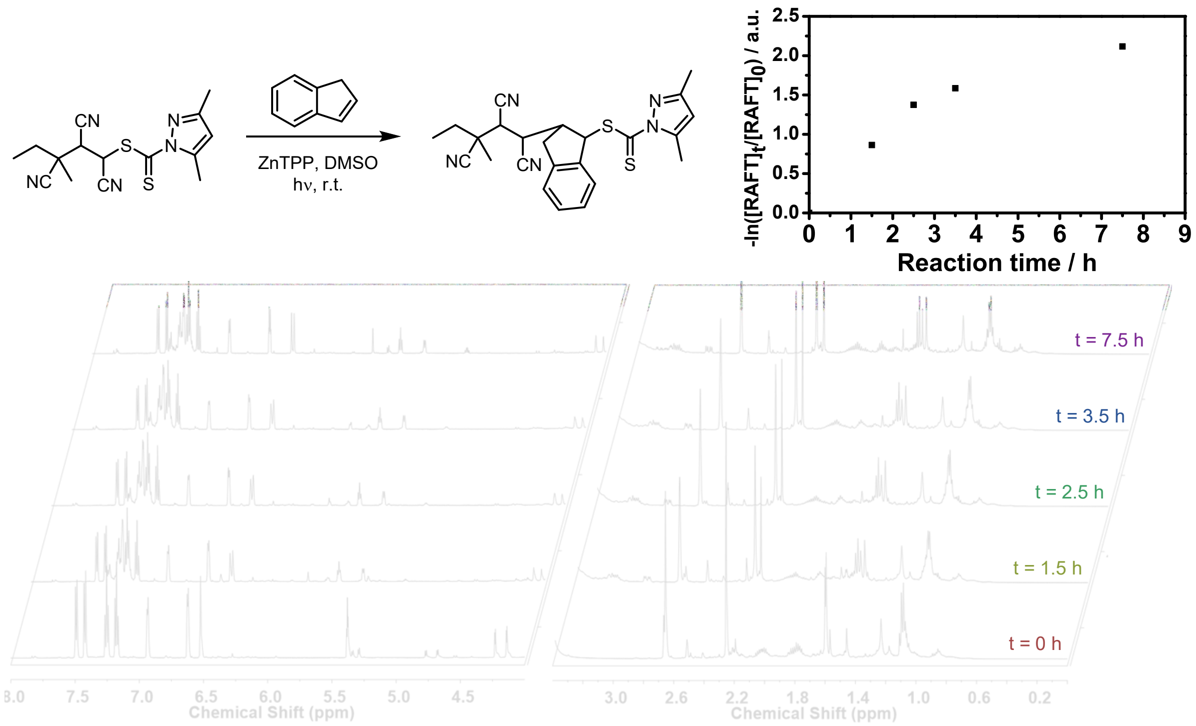
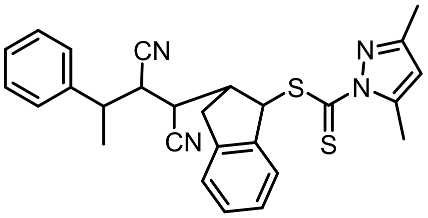


Fig. A2-72 Kinetics of IPN-FCN-Ind-PCDT synthesis by $^1H$ NMR (500.13 MHz, DMSO).



**PhMeCH-FCN-Ind-PCDT** ZnTPP (~0.3 mg, 0.5 mol%) was added to a solution of PhMeCH-FCN-PCDT (39 mg, 0.11 mmol) and indene (14 mg, 1.1 eq) in DMSO (0.5 mL) in a 4 mL vial and sealed with a rubber septum. The reaction mixture was then degassed by sparging under argon irradiated under blue LED (0.42 mW cm$^{-2}$) for 8 h. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a yellow-to-green solid (39 mg, 75% yield).

A separate kinetic experiment was performed on an analogous solution in d$_6$-DMSO (0.5 mL – at the same scale) prepared in a Wilmad NMR tube (without a stirring bar) which was degassed by sparging under argon for 15 min prior to irradiation under the same blue LED. A similar workup and purification procedure was then performed to obtain the product in smaller yield (due to reaction scale).

TLC (20% v/v ethyl acetate in hexanes) $R_f = 0.25$

$^1$H NMR (400.17 MHz, CDCl$_3$) δ 7.59-7.07 (m, 9H), 6.26-6.00 (m, 1H), 5.84 (dd, *J*= 22.8, 6.8 Hz), 5.75 (d, *J*= 4.7 Hz), 5.55 (d, *J*= 6.9 Hz), 5.42 (d, *J*= 6.6 Hz), 5.38 (d, *J*= 5.8 Hz), 5.34 (d, *J*= 6.1 Hz), 5.24 (d, *J*= 3.1 Hz), 5.09 (d, *J*= 5.0 Hz), 5.02 (d, *J*= 3.9 Hz), 3.72-2.72 (m, 5H), 2.77 (d, *J*= 0.9 Hz), 2.73 (dd, *J*= 2.1, 0.9 Hz), 2.72 (d, *J*= 0.7 Hz), 2.72 (d, *J*= 0.9 Hz), 2.69 (d, *J*= 0.9 Hz), 2.69 (d, J = 1.0 Hz), 2.65 (d, *J*= 0.8 Hz), 2.59 (d, *J*= 0.9 Hz), 2.53 (d, *J*= 1.0 Hz), 2.46 (d, *J*= 0.9 Hz), 2.31-2.19 (m, 3H), 1.64-1.44 (m, 3H).

HRMS (APCI) 471.17, 472.17, 473.17, 473.17 [M–H]$^+$.Calculated: 471.17, 472.17, 473.16, 474.17.

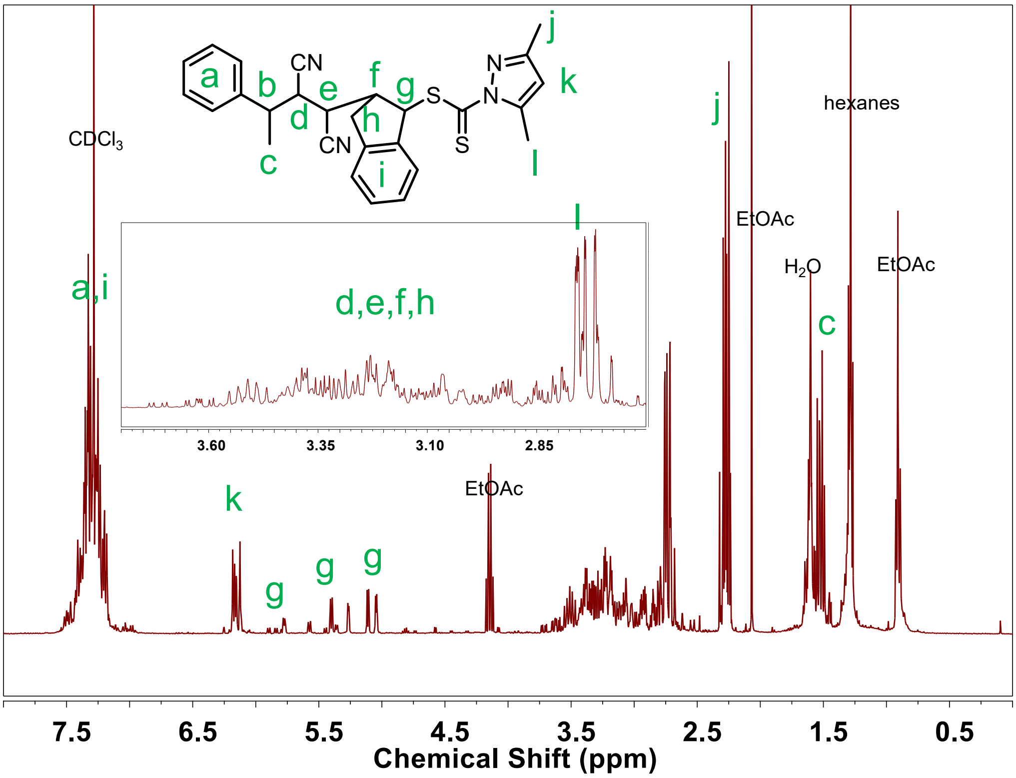


Fig. A2-73 $^1$H NMR spectrum (400.17 MHz, CDCl$_3$) of PhMeCH-FCN-Ind-PCDT.

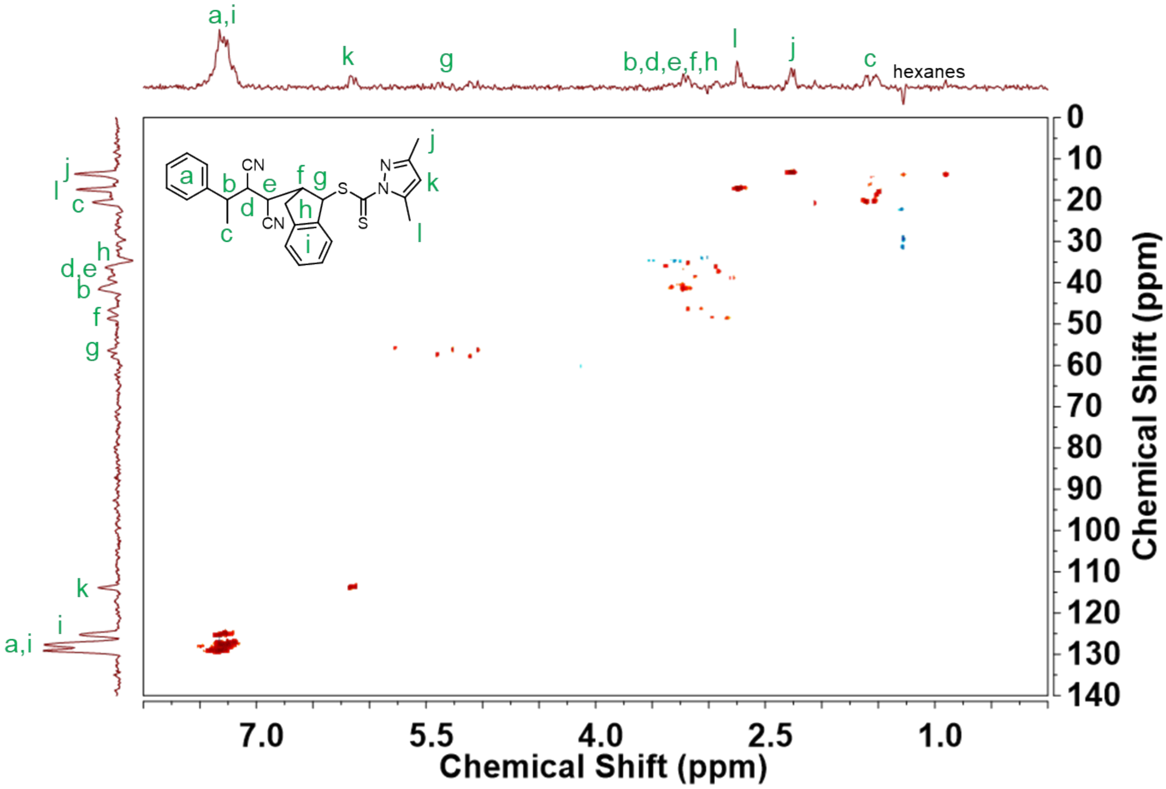


Fig. A2-74 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, CDCl$_3$) of PhMeCH-FCN-Ind-PCDT.

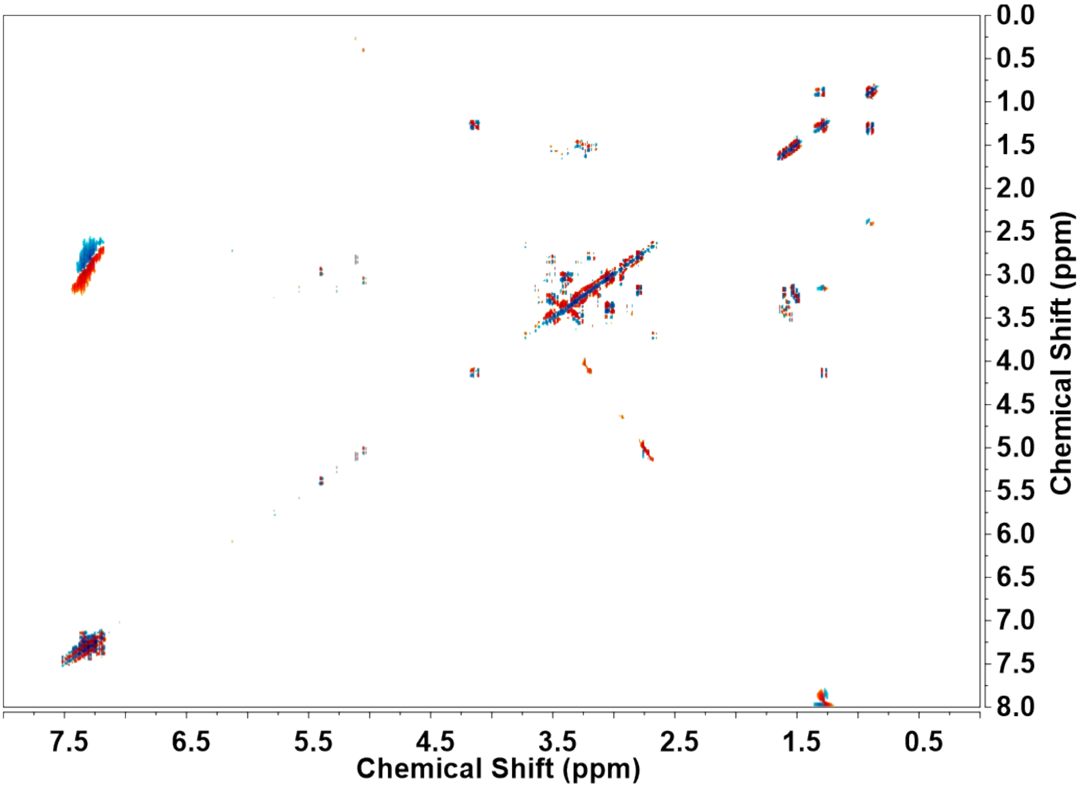


Fig. A2-75 COSY NMR spectrum (400.17 MHz, CDCl$_3$) of PhMeCH-FCN-Ind-PCDT.

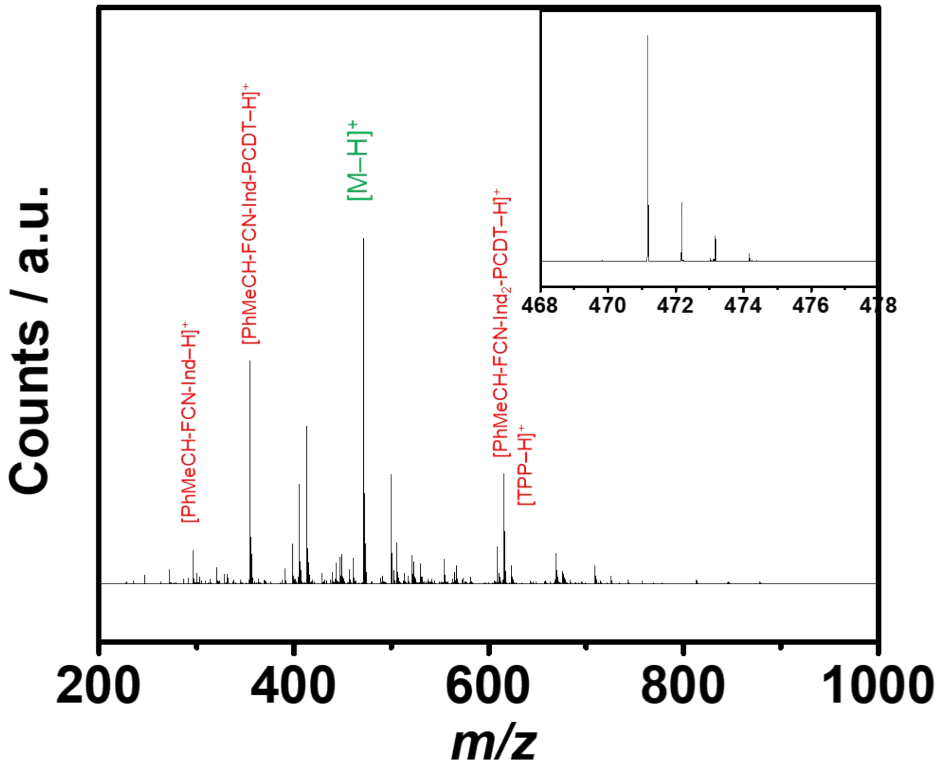


Fig. A2-76 APCI mass spectrum ($CH_3CN$) of PhMeCH-FCN-Ind-PCDT.

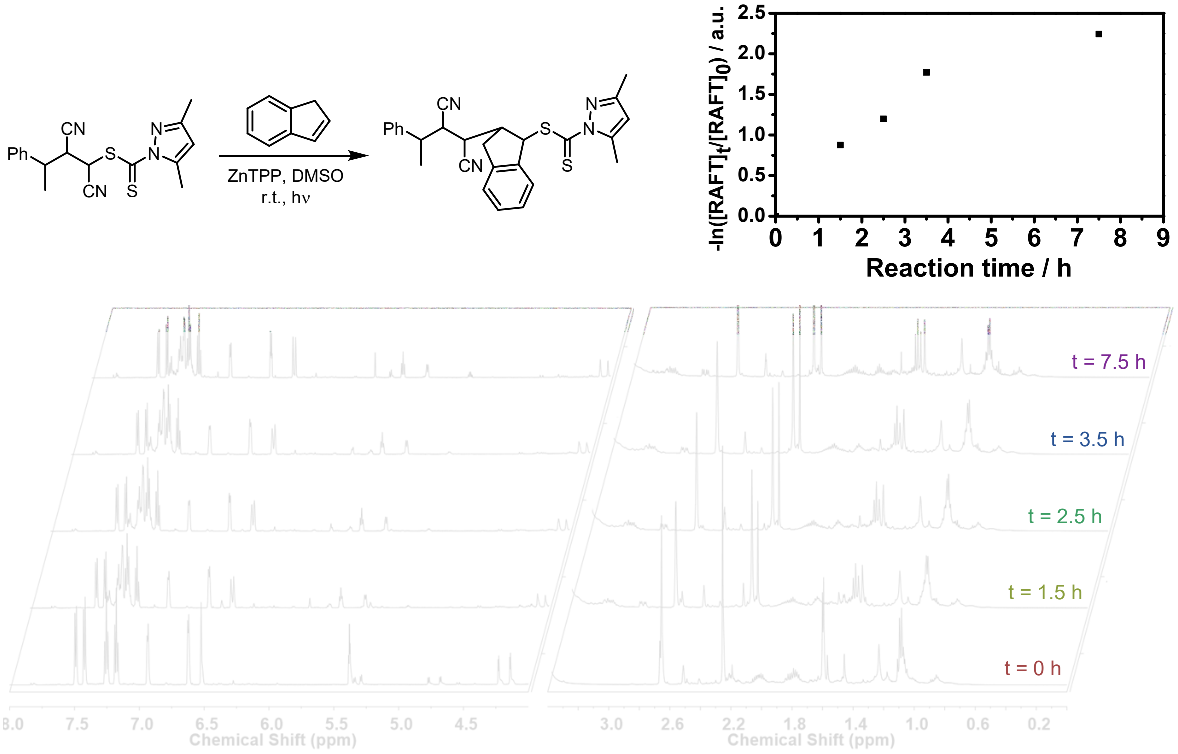
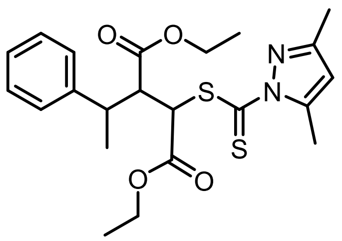


Fig. A2-77 Kinetics of PhMeCH-FCN-Ind-PCDT synthesis by $^1H$ NMR (500.13 MHz, DMSO).



**PhMeCH-DiEtFum-PCDT** ZnTPP (~1.5 mg, 0.5 mol%) was added to a solution of PhMeCH-PCDT (121 mg, 0.44 mmol) and diethyl fumarate (750 mg, 10 eq) in DMSO (2 mL) in a 2 mL vial and sealed with a rubber septum. The reaction mixture was then irradiated under blue LED (0.42 mW cm$^{-2}$) for 24 h. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a yellow oil (180 mg, 92% yield).

A separate kinetic experiment was performed on an analogous solution in d$_6$-DMSO (0.5 mL – with all other components scaled equally) prepared in a Wilmad NMR tube (without a stirring bar) which was degassed by sparging under argon for 15 min prior to irradiation under the same blue LED. A similar workup and purification procedure was then performed to obtain the product in smaller yield (due to reaction scale).

TLC (20% v/v ethyl acetate in hexanes) R$_f$ = 0.34

$^1$H NMR (400.17 MHz, CDCl$_3$) δ 7.33-7.14 (m, 5H), 6.11 (s), 6.08 (d, *J*= 0.8 Hz), 6.07 (d, *J*= 0.6 Hz), 5.18 (d, *J*= 4.6 Hz), 5.09 (d, *J*= 6.4 Hz), 4.84 (d, *J*= 6.7 Hz), 4.49 (d, *J*= 4.8 Hz), 4.30-4.00 (m), 3.80 (qd, J = 7.1, 0.4 Hz), 3.56-3.44 (m), 3.37-3.26 (m), 2.70 (d, *J*= 0.8 Hz), 2.69 (d, *J*= 0.8 Hz), 2.64 (d, *J*= 0.9 Hz), 2.63 (d, *J*= 0.8 Hz), 2.58 (d, *J*= 0.8 Hz), 2.32-3.26 (m), 1.35-1.14 (m, 9H).

HRMS (APCI) No ion peaks associated with the product were detected. Fragmentations such as C–N acyl imidazole cleavage, C–O ester cleavage and C–S PCDT cleavage were all considered.

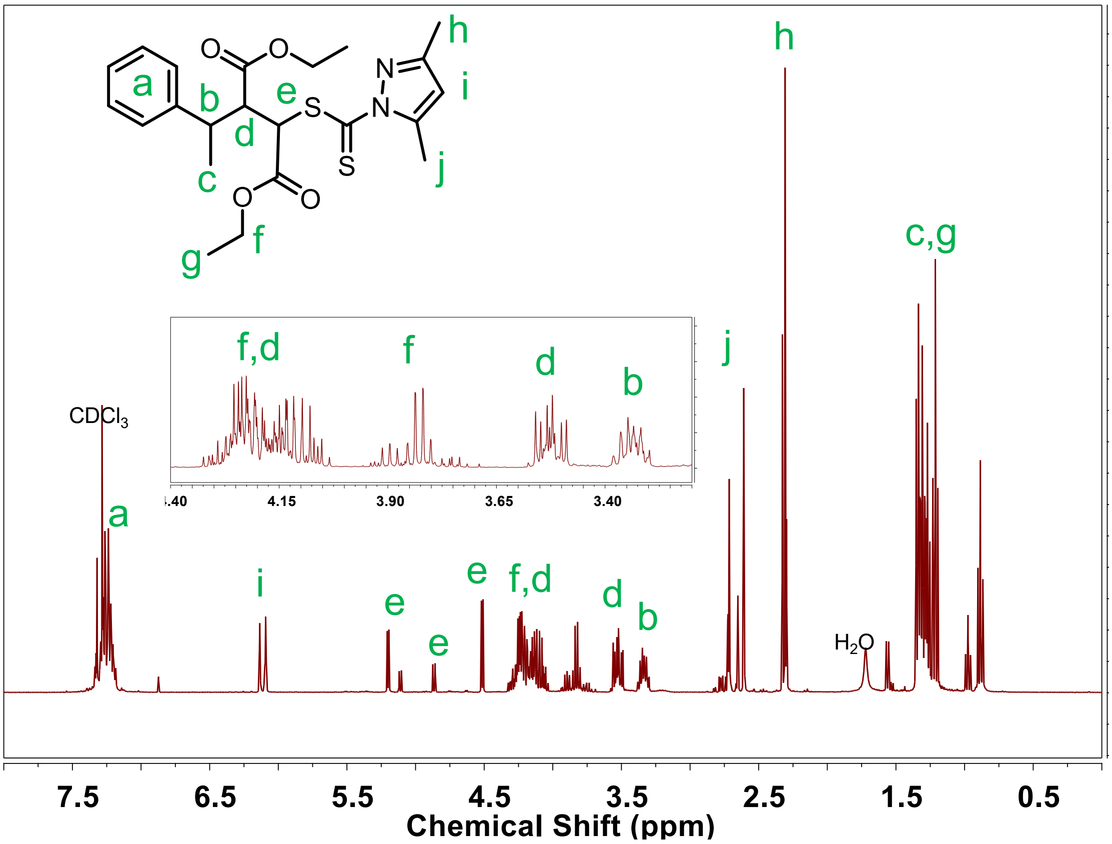


Fig. A2-78 $^1$H NMR spectrum (400.17 MHz, CDCl$_3$) of PhMeCH-DiEtFum-PCDT.

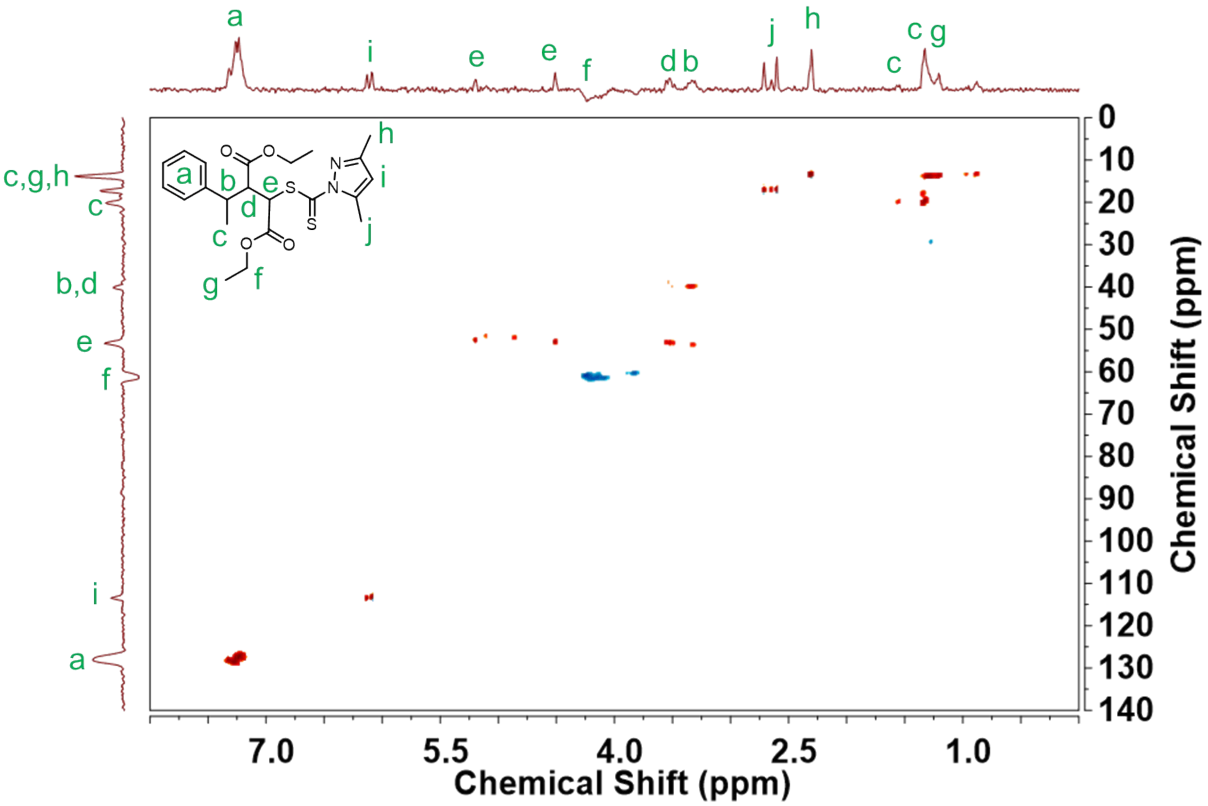


Fig. A2-79 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of IBN-DiEtFum-PCDT.

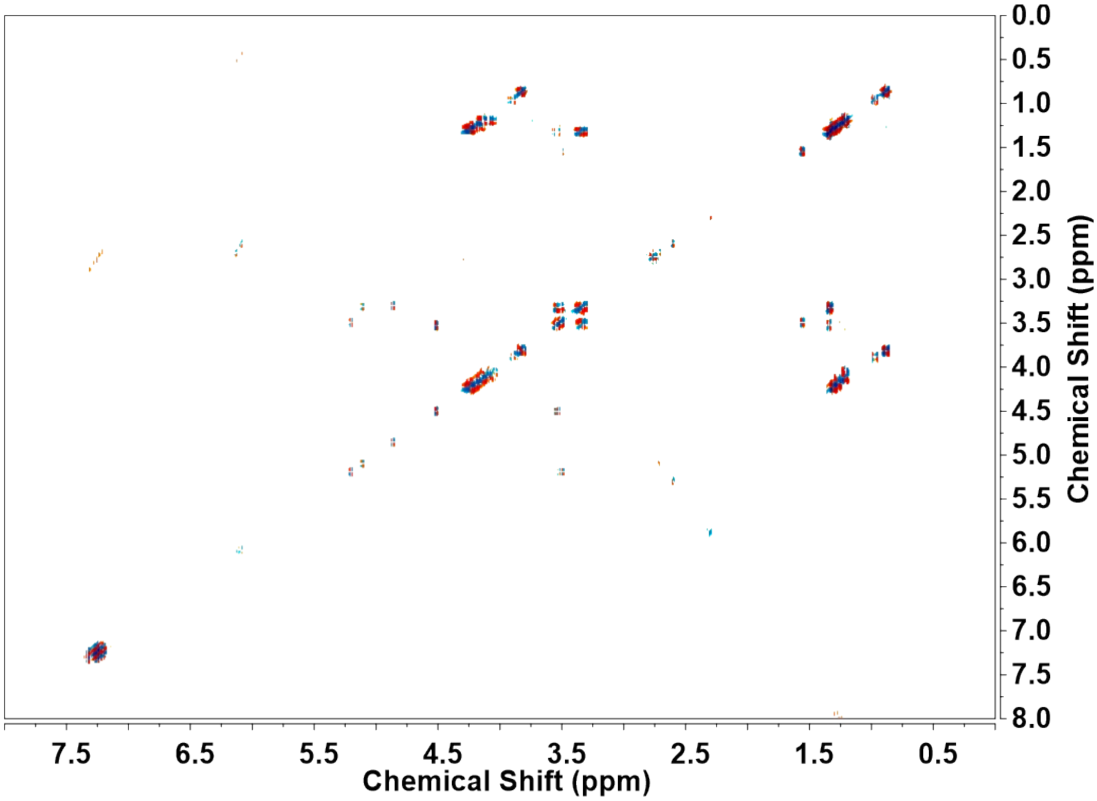


Fig. A2-80 COSY NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of IBN-DiEtFum-PCDT.

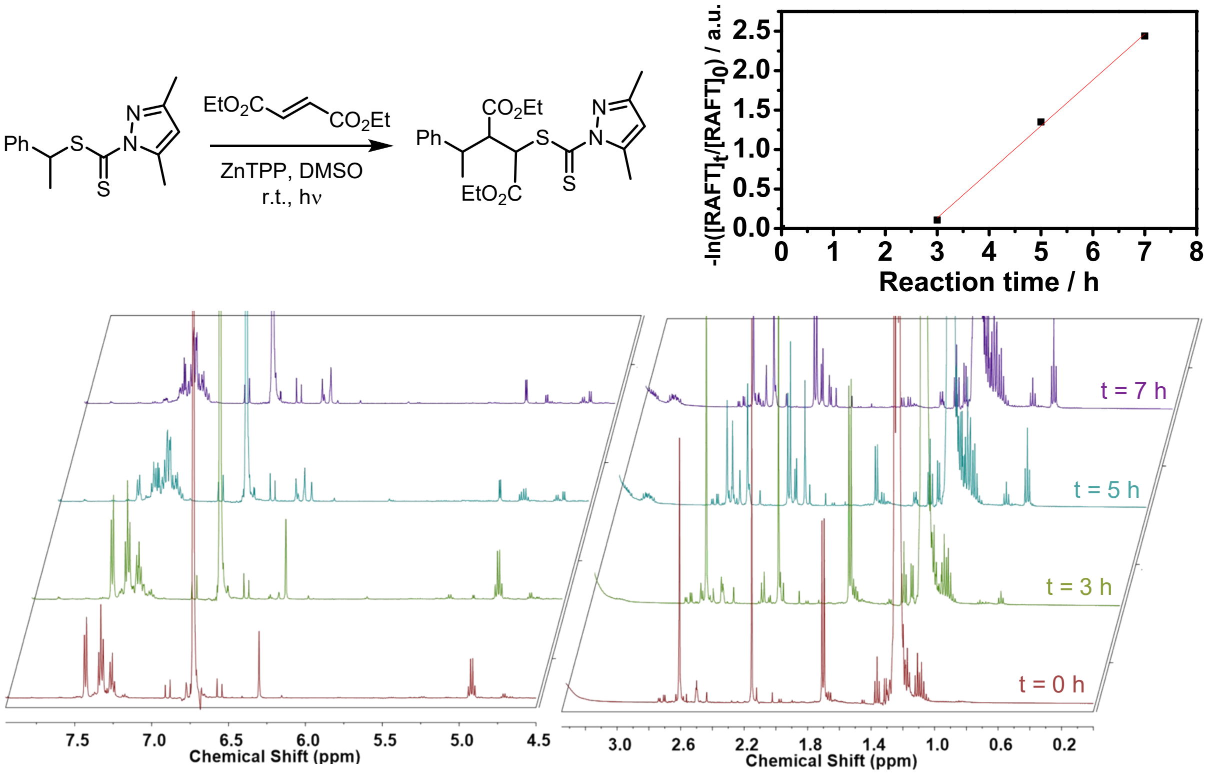
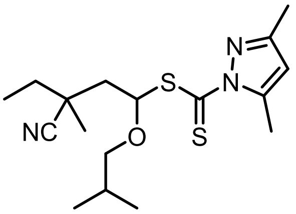


Fig. A2-81 Kinetics of IPN-DiMeFum-Ind-PCDT synthesis by $^1$H NMR (500.13 MHz, DMSO).



**IPN-IBVE-PCDT** ZnTPP (~0.2 mg, 0.5 mol%) and IPN-PCDT (11.1 mg, 0.044 mmol) were added to a solution of isobutyl vinyl ether (45 mg, 10 eq) in DMSO (0.2 mL) in a 250 µL insert (without a stirring bar) and sealed with a rubber septum. The heterogeneous reaction mixture was then irradiated under blue LED (0.42 mW cm$^{-2}$) for 5 h upon which, the solution became homogeneous. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the product was obtained as a yellow oil (11 mg, 71% yield).

TLC (5% v/v ethyl acetate in hexanes) $R_f$ = 0.07

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 6.09 (s, 1H), 5.78 (ddd, *J*= 12.3, 10.2, 2.9 Hz), 5.69 (dd, *J*= 4.1, 2.3 Hz), 4.02 (dd, *J*= 12.3, 4.2 Hz), 3.75 (dd, *J*= 12.3, 2.3 Hz), 3.64 (ddd, J = 8.7, 6.5, 1.6 Hz), 3.47 (d, *J*= 6.7 Hz), 3.45 (d, *J*= 6.7 Hz), 3.44 (d, *J*= 6.5 Hz), 3.38 (dt, *J*= 8.8, 6.7 Hz), 3.22 (dd, *J*= 8.7, 6.4 Hz), 2.01-1.87 (m), 1.86-1.52 (m, 2H), 1.45 (d, *J*= 4.8 Hz, 3H) 1.10 (td, J = 7.4, 5.6 Hz, 3H), 0.97-0.89 (m, 3H).

HRMS (APCI) No ion peaks associated with the product were detected. Fragmentations such as C–N acyl imidazole cleavage, hemithioacetal cleavage and C–S PCDT cleavage were all considered.

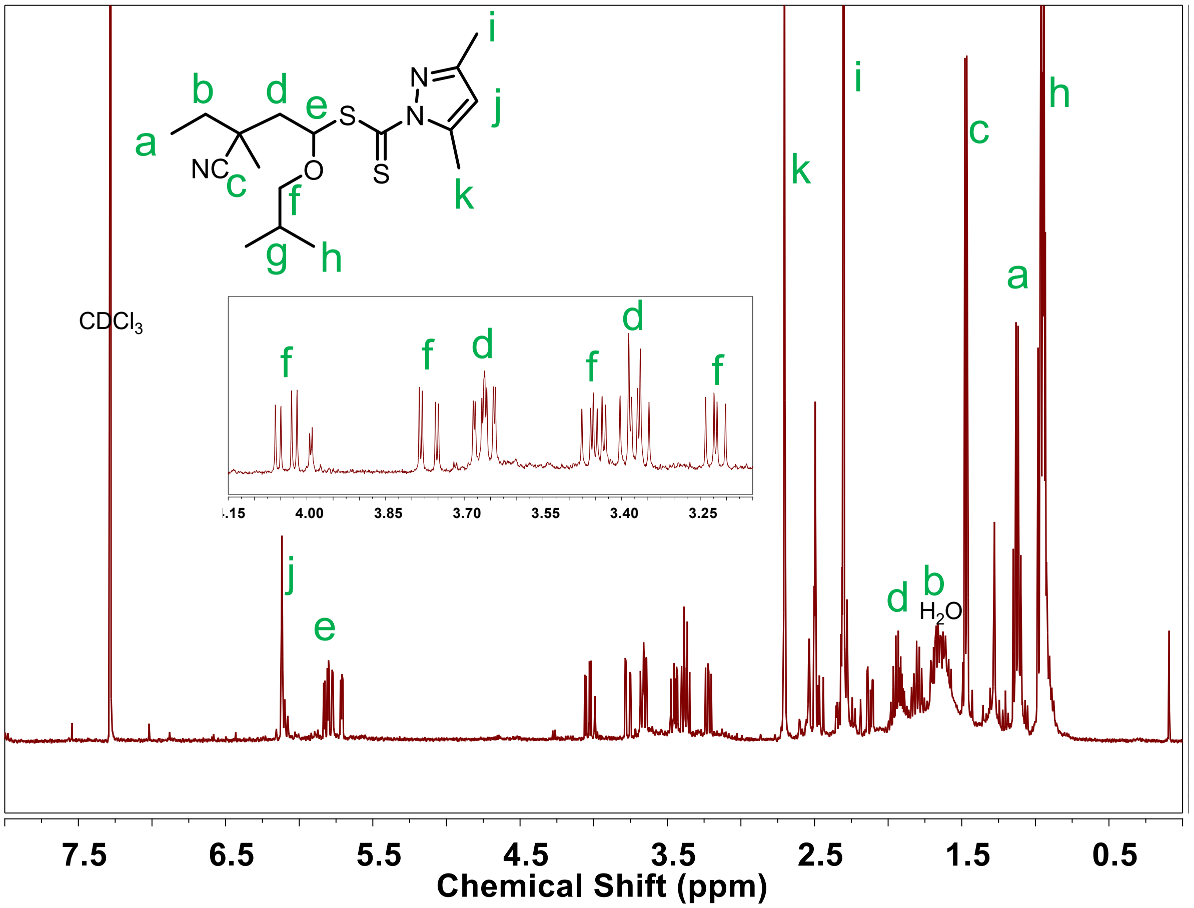


Fig. A2-82 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-IBVE-PCDT.

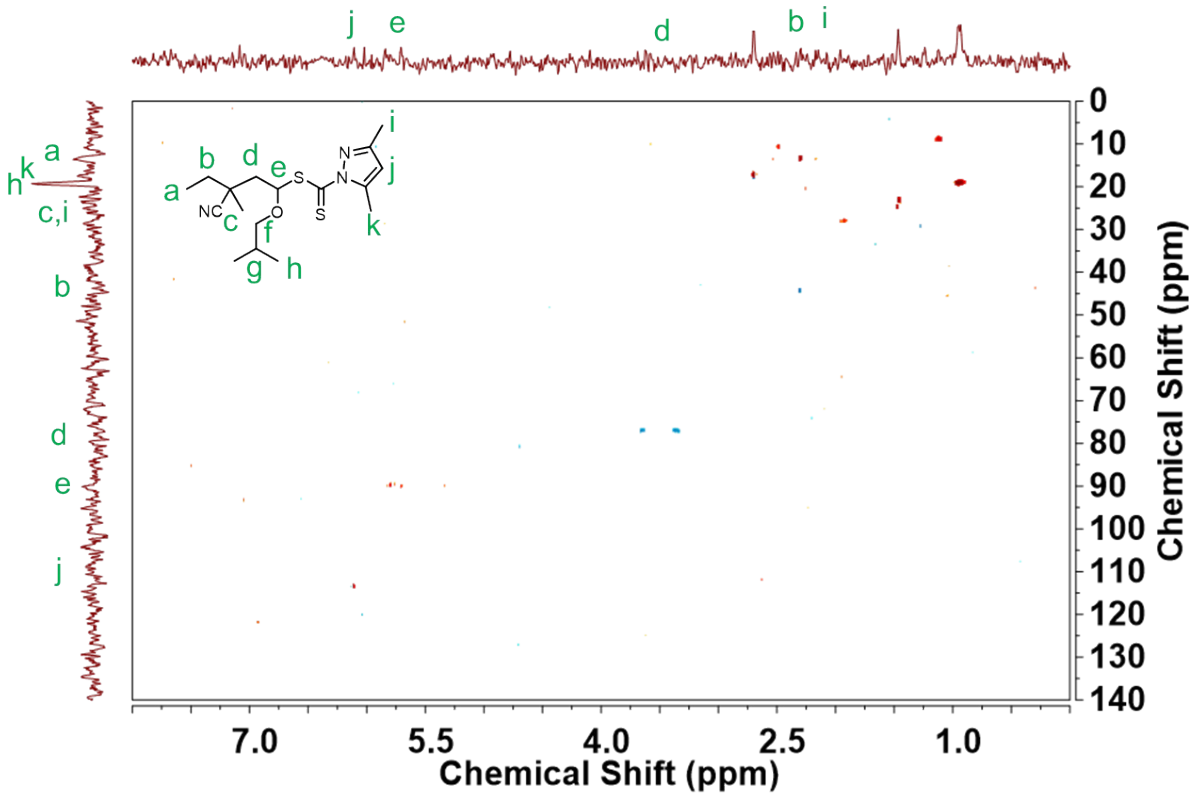


Fig. A2-83 HSQC NMR spectrum (400.17 MHz, 100.62 MHz, $CDCl_3$) of IBN-IBVE-PCDT.

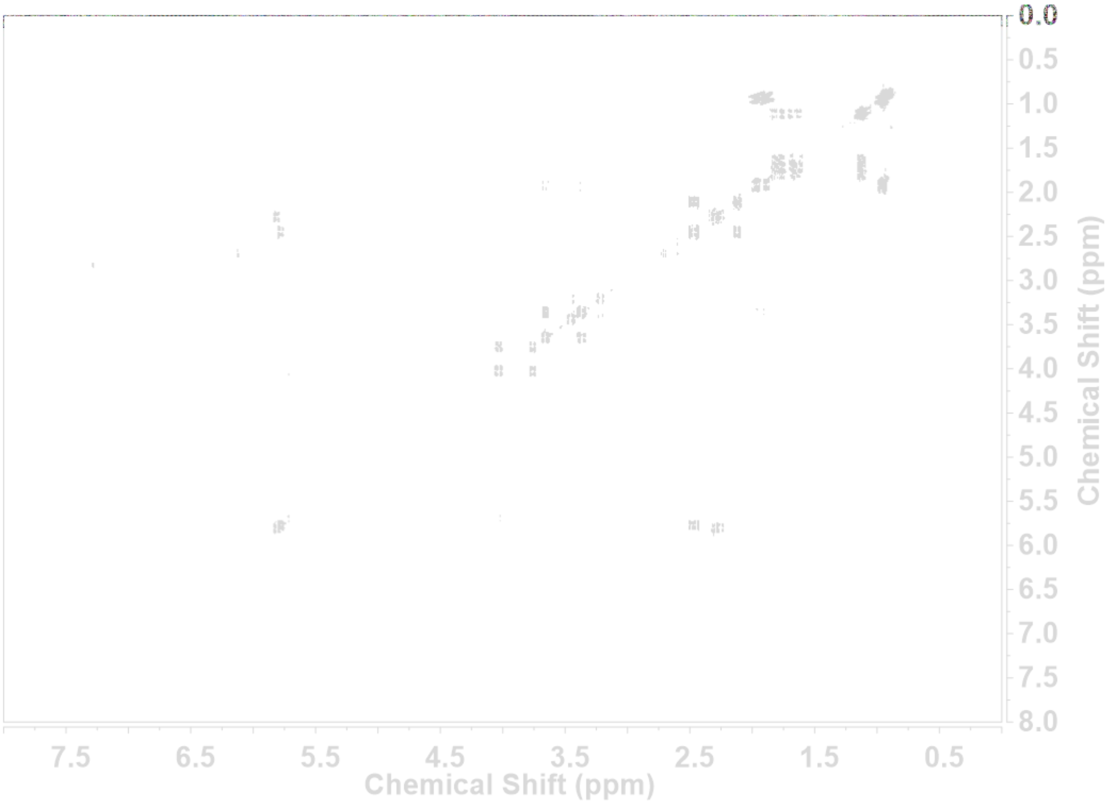
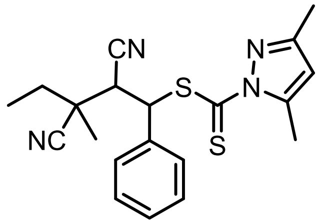


Fig. A2-84 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of IBN-IBVE-PCDT.



**IPN-CCN-PCDT (1)** ZnTPP (~0.2 mg, 0.5 mol%) and IPN-PCDT (11.1 mg, 0.044 mmol) were added to a solution of *trans*-cinnamonitrile (57 mg, 10 eq) in DMSO (0.2 mL) in a 250 μL insert (without a stirring bar) and sealed with a rubber septum. The heterogeneous reaction mixture was then irradiated under blue LED (0.42 mW cm$^{-2}$) for 5 h upon which, the solution became homogeneous. The reaction mixture was then dissolved in diethyl ether (30 mL) and washed with water (4 x 40 mL). The organic layer was then dried under magnesium sulphate and concentrated under vacuum. The residue was then purified under flash chromatography and the single regioisomer was obtained as a yellow oil (9 mg, 56% yield).

TLC (20% v/v ethyl acetate in hexanes) R$_f$ = 0.42

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 9.71 (d, *J*= 7.7 Hz), 8.02-7.32 (m, 5H), 7.13 (d, *J*= 12.1 Hz), 6.73 (dd, *J*= 16.0, 7.7 Hz), 6.67 (d, *J*= 1.7 Hz), 6.53 (d, *J*= 1.9 Hz) 6.19-6.00 (m, 1H), 5.89 (d, *J*= 16.7 Hz), 4.08 (d, *J*= 4.3 Hz), 2.75-2.44 (m, 3H), 2.36-2.22 (m, 3H), 2.04 (dd, *J*= 14.0, 7.4 Hz), 1.89 (s), 1.84-1.67 (m), 1.78 (s), 1.60 (s), 1.47 (s), 1.23 (d, *J*= 7.4 Hz), 1.21-1.09 (m)

HRMS (APCI) No ion peaks associated with the product were detected.

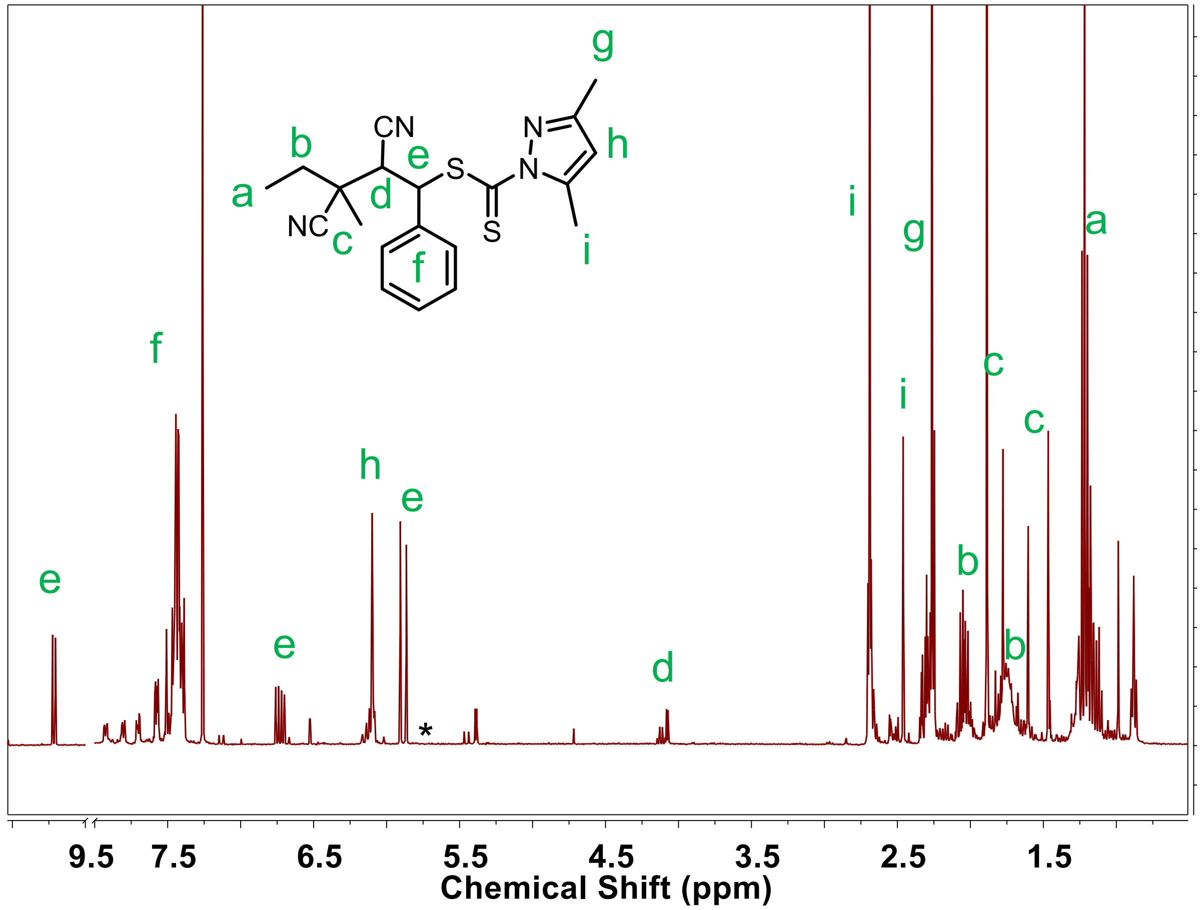


Fig. A2-85 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-CCN-PCDT (fraction 1).

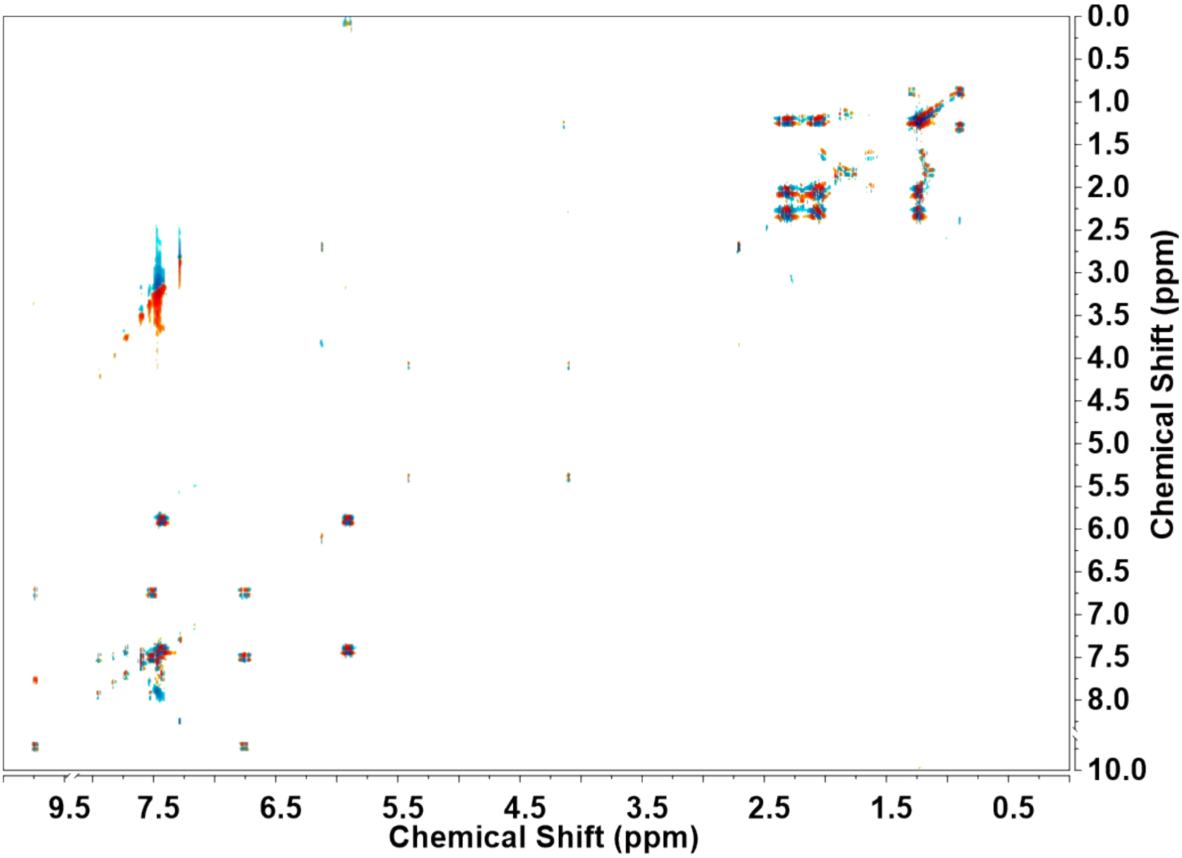
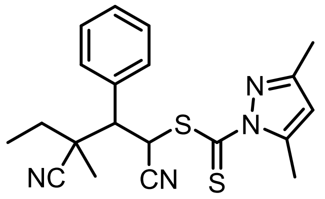


Fig. A2-86 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of IBN-CCN-PCDT (fraction 1).



**IPN-CCN-PCDT (2)** The following product was the second regioisomer fraction isolated as a yellow oil (3 mg, 19% yield) from the procedure referenced previously.

TLC (20% v/v ethyl acetate in hexanes) $R_f = 0.31$

$^1$H NMR (400.17 MHz, $CDCl_3$) δ 7.74-7.28 (m, 5H), 6.20-6.00 (m, 1H), 5.89 (d, *J*= 16.6 Hz), 5.70 (dd, *J*= 15.9, 4.9 Hz), 5.31 (d, *J*= 4.4 Hz), 3.90 (d, *J*= 4.4 Hz), 3.48 (dd, *J*= 14.8, 4.9 Hz), 2.72-2.62 (m, 3H), 2.32-2.18 (m, 3H), 1.95-1.77 (m, 2H), 1.63 (s), 1.60 (s), 1.54 (s), 1.51 (s), 1.13 (td, *J*= 7.4, 4.2 Hz), 1.01 (t, *J*= 7.4 Hz).

HRMS (APCI) No ion peaks associated with the product were detected.

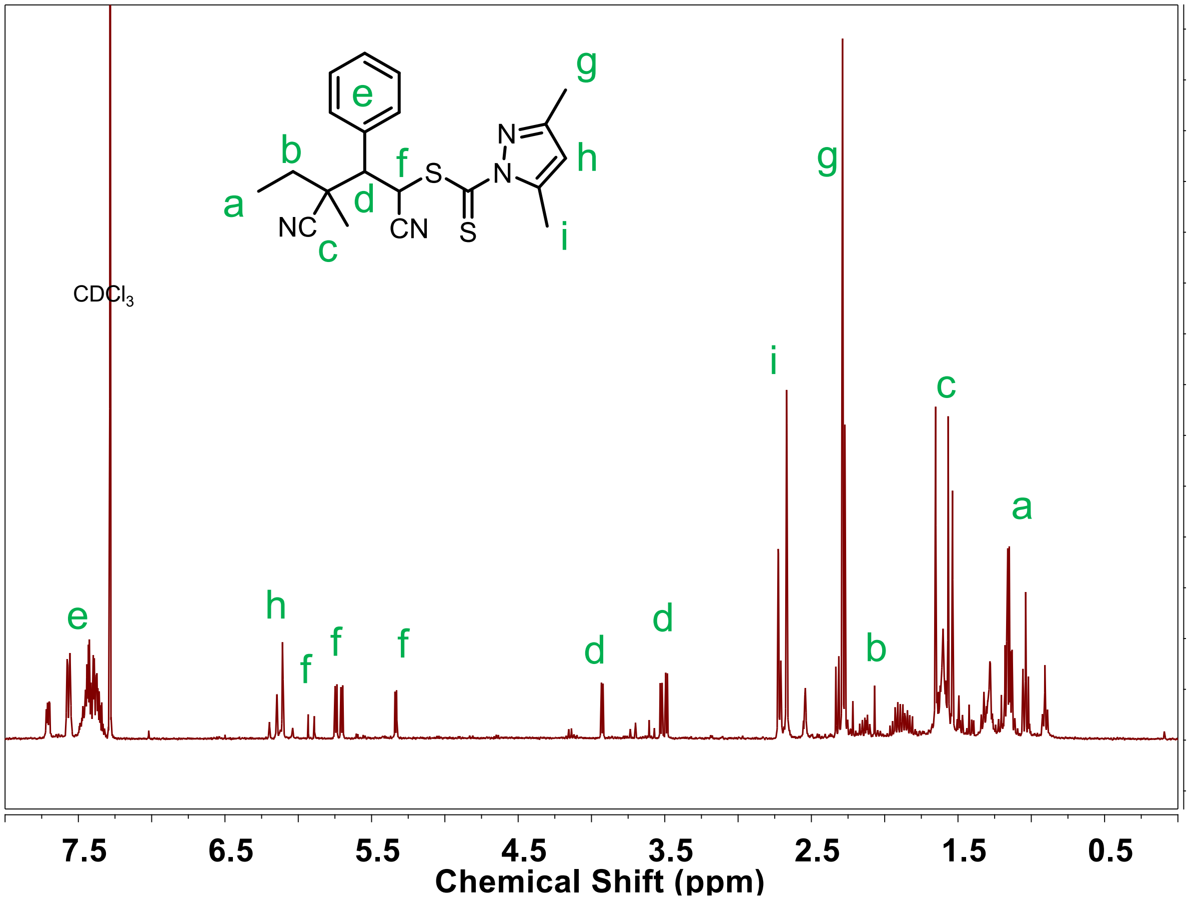


Fig. A2-87 $^1$H NMR spectrum (400.17 MHz, $CDCl_3$) of IPN-CCN-PCDT (fraction 2).

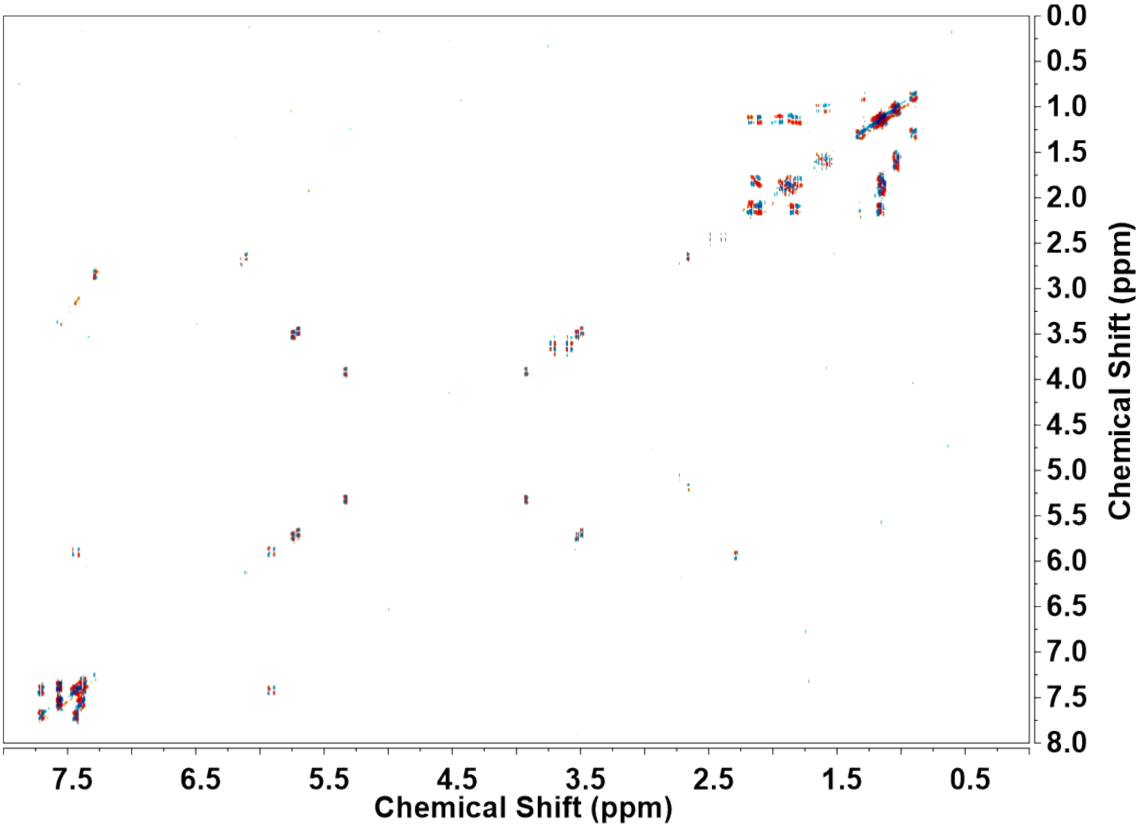


Fig. A2-88 COSY NMR spectrum (400.17 MHz, $CDCl_3$) of IBN-CCN-PCDT (fraction 2).

## A3 Chemical structures of computed species/intermediates in XYZ format

Table A3-1. xyz co-ordinates for the FCN monomer.

8

0 1

| | | | |
|---|---|---|---|
| C | 0.00000005363426 | -0.47633232813531 | -0.48671614362697 |
| C | 0.00000005575181 | 0.45203594045910 | 0.47700866036098 |
| C | -0.00000001134354 | -0.12664269408782 | -1.85251866083640 |
| H | 0.00000002442382 | -1.53125208011193 | -0.25877197090400 |
| H | 0.00000002245117 | 1.50696249271270 | 0.24909528007982 |
| C | -0.00000001178591 | 0.10234860697726 | 1.84281227309411 |
| N | -0.00000006653460 | 0.12782135233048 | -2.97691899534660 |
| N | -0.00000006659702 | -0.15204129014449 | 2.96722955717906 |

Table A3-2. xyz co-ordinates for the IBN radical.

11

0 2

| | | | |
|---|---|---|---|
| C | -0.00000005013597 | -0.00000000514515 | 0.44291916159767 |
| C | 0.00000000206840 | -0.00000000126238 | -0.93524406610199 |
| N | 0.00000004883336 | 0.00000004744178 | -2.10235114643095 |
| C | 0.11816653061410 | 1.27566668308605 | 1.18938339497178 |
| C | -0.11816655081802 | -1.27566669027589 | 1.18938341075123 |
| H | -0.77018743391894 | 1.43323588894447 | 1.80333571672434 |
| H | 0.24424848519048 | 2.13094198590736 | 0.53630185159704 |
| H | 0.96291927565975 | 1.22990710105833 | 1.87780702020078 |
| H | 0.77018745118854 | -1.43323585343092 | 1.80333569253740 |
| H | -0.24424849665699 | -2.13094200219994 | 0.53630187985857 |
| H | -0.96291926202472 | -1.22990715412370 | 1.87780708429413 |

Table A3-3. xyz co-ordinates for the PhMeCH radical.

17

0 2

| | | | |
|---|---|---|---|
| C | -2.45591826721043 | 1.56986781572128 | -0.13906809697622 |
| C | -3.35559140953480 | 0.49340360234857 | -0.08075587519402 |
| C | -2.92333254906923 | -0.85100992064152 | 0.01813345419506 |
| C | -3.83245688029076 | -1.88587526705858 | 0.07450325476778 |
| C | -5.20079549831244 | -1.63258021524310 | 0.03514151786780 |

| | | | |
|---|---|---|---|
| C | -5.65067551885459 | -0.31677989694658 | -0.06214860913862 |
| C | -4.75222536096059 | 0.72386647463540 | -0.11919514013457 |
| C | -0.98359217027296 | 1.42486709016546 | -0.10248764496470 |
| H | -2.87524290606700 | 2.56262852098305 | -0.21424985473968 |
| H | -1.86642733357281 | -1.06567896897711 | 0.05012702086880 |
| H | -3.47848894804759 | -2.90283471732023 | 0.15023882965584 |
| H | -5.90647270962068 | -2.44687686429294 | 0.07872872145521 |
| H | -6.71003506986168 | -0.11254072680384 | -0.09330289698089 |
| H | -5.10392644389937 | 1.74280639567658 | -0.19478437338212 |
| H | -0.64586922337199 | 0.91846925693319 | 0.80477258497678 |
| H | -0.48813606855924 | 2.38857015650068 | -0.14640821386246 |
| H | -0.61088264249385 | 0.82247726431968 | -0.93455467841401 |

Table A3-5. xyz co-ordinates for the TTC radical.

8

0 2

| | | | |
|---|---|---|---|
| C | 1.05172325598622 | 0.01936934098448 | 0.04042661673518 |
| S | 0.80347616038773 | 1.63724753477934 | -0.29498092111904 |
| S | -0.42552082686437 | -0.75557072920916 | 0.22421689902947 |
| S | 2.53298860513377 | -0.79975744142158 | 0.19088060399904 |
| C | 3.74454422800347 | 0.48774452330338 | -0.10442866651655 |
| H | 3.62109292849795 | 0.90292322233239 | -1.09781042294124 |
| H | 3.66756509690491 | 1.26298310848321 | 0.64887640456070 |
| H | 4.70859055195030 | -0.00274955925207 | -0.02908051374756 |

Table A3-6. xyz co-ordinates for the PCDT radical.

17

0 2

| | | | |
|---|---|---|---|
| C | -4.27649367482726 | 1.91008787916511 | -0.21394986576966 |
| C | -3.35431191277302 | 0.76189995791595 | -0.11198272936175 |
| N | -2.06585945111456 | 0.94198125650458 | 0.04007722104782 |
| N | -1.53348878585355 | -0.32466041898100 | 0.09355861690062 |
| C | -2.51815448103711 | -1.30123340774659 | -0.02813449260908 |
| C | -3.68302059849734 | -0.61951860034496 | -0.15992444310528 |
| C | -2.28385610841665 | -2.75568741761432 | -0.00776871970008 |
| C | -0.19355829320479 | -0.44179194976602 | 0.24980410556600 |

| | | | |
|---|---|---|---|
| S | 0.70350361984903 | -1.84536570373611 | 0.34179359323258 |
| S | 0.82444318508625 | 0.88191955426866 | 0.38200711509064 |
| H | -4.79969247105252 | 1.89619681598517 | -1.16760604037486 |
| H | -5.03491004388346 | 1.86263916562113 | 0.56427157675543 |
| H | -3.73716719505216 | 2.84615072605137 | -0.12277677975979 |
| H | -4.65795633603529 | -1.05328563155396 | -0.27625543352109 |
| H | -1.82595180191564 | -3.07931824094134 | 0.92369186518682 |
| H | -3.23890229879292 | -3.25841197821881 | -0.11701624013831 |
| H | -1.63092335247899 | -3.07369200660884 | -0.81692934943997 |

Table A3-7. xyz co-ordinates for the IBN-FCN radical.

19

0 2

| | | | |
|---|---|---|---|
| C | 1.74800507363132 | -0.44213413189088 | 0.29818111005428 |
| H | 1.44034108797175 | -0.87383542366600 | -0.64205097678517 |
| C | 2.76092738530192 | 0.66059909024223 | 0.30394443142369 |
| H | 2.93694101635544 | 1.00045753483712 | 1.32402976043195 |
| C | 4.15804640657038 | 0.21823858825496 | -0.24937497408277 |
| C | 5.12922809274597 | 1.39371660543279 | -0.17848922926402 |
| C | 4.67218646109527 | -0.95725564828688 | 0.57785148683109 |
| C | 4.00125934660759 | -0.19733977470835 | -1.63972204481062 |
| N | 3.87913441462221 | -0.52635205238431 | -2.73518741436777 |
| C | 2.23117480245742 | 1.78541323456560 | -0.45352922129853 |
| N | 1.80298856282441 | 2.65843117574568 | -1.06718244105829 |
| C | 1.18879496346162 | -0.91468956397818 | 1.45852028038198 |
| N | 0.71526355897281 | -1.31340050275596 | 2.44523847890318 |
| H | 5.22963011108056 | 1.70454088541866 | 0.85786066726540 |
| H | 6.10320693005411 | 1.08815477140138 | -0.54638899047858 |
| H | 4.78508113519817 | 2.23654637033034 | -0.76966345916484 |
| H | 4.01404178069464 | -1.81782300078730 | 0.50951932996273 |
| H | 5.65787740925997 | -1.24599174247252 | 0.22875239879647 |
| H | 4.74624146109436 | -0.65038641529839 | 1.61784080725982 |

Table A3-6. xyz co-ordinates for the PhMeCH-FCN radical.

25

0 2

| | | | |
|---|---|---|---|
| C | -0.82457550461101 | 0.62039182383668 | 0.37305485072545 |
| H | -0.64179976058225 | 0.79647565979402 | 1.42132819036464 |
| C | -1.75043628213813 | 1.52451554979765 | -0.37606718406324 |
| H | -1.62930050023693 | 1.37463210181173 | -1.44921994390319 |
| C | -3.24310131581883 | 1.23221129847797 | -0.01778038014353 |
| H | -3.34699105159755 | 1.40099920712160 | 1.05368225943148 |
| C | -4.16739080901355 | 2.17483018968619 | -0.76804399637385 |
| C | -3.53432218466564 | -0.21798033025423 | -0.29513461112475 |
| C | -3.79654534675678 | -1.09070604938588 | 0.75358004506645 |
| C | -4.04027203974151 | -2.43452664980158 | 0.51341958782261 |
| C | -4.01951535194537 | -2.92215852457728 | -0.78323836105447 |
| C | -3.75799427268220 | -2.05837783930222 | -1.83698687515970 |
| C | -3.51869263013616 | -0.71600585588208 | -1.59440401523456 |
| C | -1.41333176741848 | 2.90852343255982 | -0.08608374701395 |
| N | -1.15315496874828 | 4.00014602794759 | 0.16675905372804 |
| C | -0.26538127936298 | -0.48676655488127 | -0.21613439549697 |
| N | 0.21111492193209 | -1.42317685564722 | -0.71969728599702 |
| H | -3.97481546192019 | 3.21150009739753 | -0.50458503898990 |
| H | -4.04835235571114 | 2.06929429788104 | -1.84396162305964 |
| H | -5.20049108646780 | 1.95091263817447 | -0.51783908113507 |
| H | -3.80780934042183 | -0.71169152457072 | 1.76532832699414 |
| H | -4.24280127958084 | -3.09826982682986 | 1.33944492033116 |
| H | -4.20468107672505 | -3.96772608797591 | -0.97290757432848 |
| H | -3.73893009400203 | -2.43099577322687 | -2.84928566495531 |
| H | -3.31164916164749 | -0.05593045215120 | -2.42452745643033 |

Table A3-8. xyz co-ordinates for the IBN-TTC radical.

19

0 1

| | | | |
|---|---|---|---|
| C | -0.51622223993378 | -1.33432530264088 | 2.05276337594532 |
| S | -1.68187425660215 | -0.93864129794847 | 3.12739351305570 |
| S | -0.46046991054767 | -0.93765306165682 | 0.35131950377118 |
| C | -2.10109781278204 | -0.25160072003881 | -0.12401456070206 |
| C | -1.91041035048127 | 0.12205982608799 | -1.59746287497752 |
| C | -3.22613763383622 | -1.26221045575356 | 0.02999349847412 |
| C | -2.35553971639046 | 0.97222473682954 | 0.62098484666845 |

| | | | |
|---|---|---|---|
| N | -2.57751556987026 | 1.98616479938845 | 1.11881977170654 |
| S | 0.93983514760686 | -2.21128660095948 | 2.40953215895811 |
| C | 0.88835735792388 | -2.39315027869304 | 4.18525756675965 |
| H | -1.70001918425418 | -0.77564115035717 | -2.17065725837030 |
| H | -2.83108109356514 | 0.56467893404163 | -1.96526770870051 |
| H | -1.10006974645596 | 0.83162223631245 | -1.72872364960356 |
| H | -3.34690210912899 | -1.58012541879225 | 1.05718029744687 |
| H | -4.15488156408098 | -0.80943564778411 | -0.30920443395870 |
| H | -3.00845662897304 | -2.12279665752497 | -0.59465248718577 |
| H | 0.85403589934345 | -1.42184098326454 | 4.66481854240124 |
| H | 0.03346303127988 | -2.98854082329905 | 4.48242200222854 |
| H | 1.80931338074814 | -2.90549513394687 | 4.44260189608261 |

Table A3-9. xyz co-ordinates for the PhMeCH-TTC radical.

25

0 1

| | | | |
|---|---|---|---|
| S | -2.62382113279982 | -0.21492758950520 | 0.68590153744727 |
| C | -3.55653931228712 | -1.72552801893211 | 0.87746118639689 |
| C | -1.12248301592652 | -0.75762823421289 | 0.03923219831632 |
| S | -0.73111002024836 | -2.31992641324099 | -0.32367836537924 |
| S | 0.09061714582659 | 0.43882843465766 | -0.24473841431638 |
| C | -0.58643060740819 | 2.08291652114155 | 0.20255181024367 |
| H | -1.01243803887004 | 1.99522138131300 | 1.20000251542501 |
| C | 0.62793990792863 | 3.00091452511603 | 0.25447257368438 |
| C | -1.62869906606458 | 2.59170073962158 | -0.75108907960492 |
| C | -2.79808533092181 | 3.15028726737912 | -0.24986811165923 |
| C | -3.74539942872895 | 3.69118006804885 | -1.10495269721029 |
| C | -3.53345388220009 | 3.67603112521088 | -2.47450636057970 |
| C | -2.36785571341773 | 3.12049312049171 | -2.98251644245801 |
| C | -1.42120816045512 | 2.58397416083907 | -2.12611374363865 |
| H | 1.35051665776564 | 2.65992223398734 | 0.99039585750471 |
| H | 1.11570227991625 | 3.05487938283870 | -0.71619764467570 |
| H | 0.30286916180815 | 4.00241116801322 | 0.52294191547205 |
| H | -2.96664315784598 | 3.15483757600834 | 0.81744072921739 |
| H | -4.64945376115396 | 4.11961473999263 | -0.70106262419160 |
| H | -4.27179793685363 | 4.09196118647136 | -3.14193548641635 |

| | | | |
|---|---|---|---|
| H | -2.19558728931568 | 3.10525217396815 | -4.04749030506385 |
| H | -0.51814562187736 | 2.14857236793480 | -2.52825095545277 |
| H | -3.70910237555664 | -2.20234918070828 | -0.08357214296678 |
| H | -4.50865775293153 | -1.41939824859878 | 1.29837909787869 |
| H | -3.04880054838195 | -2.40332448783586 | 1.55344995202715 |

Table A3-10. xyz co-ordinates for the IBN-PCDT radical.

28

0 1

| | | | |
|---|---|---|---|
| C | -4.00671827642986 | 1.97187840545281 | -0.29216039444311 |
| C | -3.14828631150178 | 0.77839154991833 | -0.15049448130519 |
| N | -1.84540324958547 | 0.88830480984978 | -0.06071699789795 |
| N | -1.37274321967476 | -0.39473417862092 | 0.05662227123197 |
| C | -2.41276650496220 | -1.31871760738880 | 0.03842155873902 |
| C | -3.54624958082700 | -0.57879126912668 | -0.09331998811839 |
| C | -2.30344062252535 | -2.78555532860405 | 0.13870672805986 |
| C | -0.00974873709413 | -0.55848893284235 | 0.15895921702196 |
| S | 0.73967317890870 | -2.00154004625362 | 0.33110903598523 |
| S | 0.78467071820600 | 1.00745379432072 | 0.05376584567224 |
| C | 2.58531680081250 | 0.67798518301203 | 0.24863246911891 |
| C | 3.20315922652252 | 2.05110510354760 | -0.04971699949597 |
| C | 2.96363447363585 | 0.23533615067097 | 1.65454140503343 |
| C | 3.05824341114999 | -0.24189047500353 | -0.77365183249347 |
| N | 3.51237910971393 | -0.88248490714562 | -1.61599748181849 |
| H | -4.54172791359577 | 1.94889870225382 | -1.23923760829694 |
| H | -4.75644496453238 | 2.00096490450396 | 0.49504613028975 |
| H | -3.41456629901846 | 2.87918885899750 | -0.24791548313528 |
| H | -4.54539324765971 | -0.96811671853974 | -0.14142950093246 |
| H | -1.84279987167383 | -3.09565849804611 | 1.07197127471413 |
| H | -3.30500329117730 | -3.20010819988546 | 0.08282863723814 |
| H | -1.70066094589335 | -3.20431272265067 | -0.66182039880828 |
| H | 2.83475049363186 | 2.77491403298076 | 0.67127025912018 |
| H | 4.28158520517579 | 1.97776564175847 | 0.05127458977857 |
| H | 2.96280439921956 | 2.39010119690925 | -1.05211231763604 |
| H | 2.50544995369022 | -0.70724678293892 | 1.92131762560026 |
| H | 4.04454476584582 | 0.13271619970736 | 1.71644466579698 |

| | | | |
|---|---|---|---|
| H | 2.64703129963859 | 1.00344113316318 | 2.35346177098093 |

Table A3-11. xyz co-ordinates for the PhMeCH-PCDT radical

34

0 1

| | | | |
|---|---|---|---|
| C | -3.77830221730895 | 2.96254232750119 | 0.78079210717599 |
| C | -3.56140386532482 | 1.54857425434593 | 0.41077600013234 |
| N | -2.35275337203898 | 1.07857378076677 | 0.21773751945167 |
| N | -2.51796490432028 | -0.24245911264622 | -0.11570329560910 |
| C | -3.86255770296251 | -0.59431206166165 | -0.12162154548167 |
| C | -4.53393778555249 | 0.54112681478559 | 0.21348246678351 |
| C | -4.44034184676021 | -1.92115296024014 | -0.40619759575753 |
| C | -1.38155126504616 | -0.98282323308904 | -0.37474818780610 |
| S | -1.39613952342837 | -2.53343881688976 | -0.90854502366463 |
| S | 0.06042475554518 | -0.03809510447848 | -0.08153042044021 |
| C | 1.41212032092419 | -1.21816767517547 | -0.38990372307302 |
| H | 1.16678394478234 | -1.74940023566640 | -1.30532547729860 |
| C | 2.65340065526576 | -0.36011509918936 | -0.60168107306888 |
| C | 1.60698700961792 | -2.20647143120877 | 0.72425134425924 |
| C | 1.75571734384075 | -3.55585735035277 | 0.42784091991125 |
| C | 2.01097407573498 | -4.47722234862663 | 1.43161689696240 |
| C | 2.11616500065688 | -4.05833443914735 | 2.74864291232240 |
| C | 1.96995936429951 | -2.71263195519318 | 3.05345223144112 |
| C | 1.71931514338330 | -1.79396426370675 | 2.04767603325008 |
| H | -4.39192426272604 | 3.46542707833736 | 0.03644577960745 |
| H | -4.30665946332397 | 3.03608001866209 | 1.72878153698181 |
| H | -2.83303626752117 | 3.48718304957565 | 0.86614624539164 |
| H | -5.59921851730162 | 0.63177908316609 | 0.31012573977737 |
| H | -4.04093639331525 | -2.68912580954368 | 0.24977700832084 |
| H | -5.51439159213038 | -1.85527841059871 | -0.26197125961629 |
| H | -4.23896514677880 | -2.24540311420801 | -1.42271582856250 |
| H | 2.53019668838342 | 0.30917110497448 | -1.44866950881606 |
| H | 2.87783825312097 | 0.23418294704955 | 0.28122869492657 |
| H | 3.50413542573972 | -1.00921946720257 | -0.79114317481523 |
| H | 1.66457682219305 | -3.88236792873843 | -0.59749597785872 |
| H | 2.12044885569535 | -5.52191028208904 | 1.18465029763289 |

|  |  |  |  |
|---|---|---|---|
| H | 2.31003084979369 | -4.77318718246409 | 3.53297099320345 |
| H | 2.05307904460535 | -2.37760330249258 | 4.07581887806793 |
| H | 1.60572057225772 | -0.74798887455557 | 2.29339648626856 |

Table A3-12. xyz co-ordinates for the (*1R,2S*)-IBN-FCN-PCDT (*trans*) radical.

36

0 1

|  |  |  |  |
|---|---|---|---|
| C | -4.95191123193474 | 2.39649192068231 | 0.83221404603910 |
| C | -4.42627715432322 | 1.08895198374321 | 0.39369749390500 |
| N | -3.13808239990939 | 0.87483834116429 | 0.29274817913994 |
| N | -3.01257216571795 | -0.42360514103875 | -0.13559107982526 |
| C | -4.25809535451386 | -1.02554254990084 | -0.30104546378043 |
| C | -5.16194137729734 | -0.06832441013853 | 0.03344953261130 |
| C | -4.51632405412565 | -2.40750563674383 | -0.74093726319074 |
| C | -1.74380235264996 | -0.89858974236523 | -0.31838054442126 |
| S | -1.35862205532528 | -2.39607607711493 | -0.84746645476182 |
| S | -0.58263964091300 | 0.37453001561355 | 0.10625381397982 |
| C | 0.98142092175180 | -0.51404035337429 | -0.19334246253415 |
| H | 0.79052453788854 | -1.21389521460382 | -1.00727193041213 |
| C | 1.42737516687046 | -1.31834251057509 | 1.04541848123707 |
| H | 0.59824892684775 | -1.99233706160062 | 1.26679382300208 |
| C | 2.66744289826487 | -2.24482685556207 | 0.85456981108529 |
| C | 2.76920762685446 | -3.16579330788646 | 2.07392492218906 |
| C | 2.52404320888143 | -3.07958592281404 | -0.41754019206678 |
| C | 3.89431771520241 | -1.45598996116406 | 0.78121766882902 |
| N | 4.88186664474474 | -0.86768143972971 | 0.74060321621537 |
| C | 1.60542897875439 | -0.43845874562530 | 2.18679366268431 |
| N | 1.77516486233171 | 0.26690089172639 | 3.07864766998680 |
| C | 1.94015099056528 | 0.47594357129550 | -0.63097578780015 |
| N | 2.69303253712864 | 1.26959508865430 | -0.98586927561379 |
| H | -5.57856440119245 | 2.83513214922089 | 0.05876044000647 |
| H | -5.57438323000376 | 2.28050344444130 | 1.71652987471161 |
| H | -4.14246931454150 | 3.08134113236587 | 1.05848358036411 |
| H | -6.22892591843055 | -0.18381231978868 | 0.02312562086942 |
| H | -4.05593446565427 | -3.13632412043395 | -0.07999481843594 |
| H | -5.59013720219250 | -2.56334485853143 | -0.74599033834350 |

| | | | |
|---|---|---|---|
| H | -4.12710065318238 | -2.59650362522991 | -1.73735008434857 |
| H | 1.87212968542391 | -3.77691395517961 | 2.12788634835849 |
| H | 3.63068878355524 | -3.81710207670100 | 1.97141220326261 |
| H | 2.86941357338138 | -2.60081171866246 | 2.99564955929111 |
| H | 2.58523743342772 | -2.47767286323781 | -1.31852800233274 |
| H | 3.31841654650169 | -3.81785335257920 | -0.45006087741311 |
| H | 1.56802793353140 | -3.59547171832594 | -0.39756937248763 |

Table A3-13. xyz co-ordinates for the (*1S,2S*)-IBN-FCN-PCDT (*cis*) radical.

36

0 1

| | | | |
|---|---|---|---|
| C | -5.08726069083549 | 1.52552183439313 | 1.90375763565684 |
| C | -4.31038492342576 | 0.81082925961114 | 0.87248235461018 |
| N | -3.01593127781088 | 0.65083517027749 | 0.98844825035326 |
| N | -2.62833784480037 | -0.04627648527257 | -0.12996200205824 |
| C | -3.71632980491874 | -0.32146473635856 | -0.95688971206287 |
| C | -4.78879420027725 | 0.22162794838928 | -0.32519476063628 |
| C | -3.68796635526949 | -1.04413294150660 | -2.24027737020123 |
| C | -1.30091791786422 | -0.34761142089633 | -0.24969377352364 |
| S | -0.63146691862345 | -1.17061737647855 | -1.49207736496931 |
| S | -0.44054799872870 | 0.29502670963239 | 1.16681616396023 |
| C | 1.28444807137786 | -0.11310986330785 | 0.74855240286535 |
| H | 1.25449436133047 | -0.65224698830213 | -0.20311744131429 |
| C | 2.19463782329201 | 1.13586935554575 | 0.62370102549092 |
| H | 3.22560754958007 | 0.78409946260467 | 0.69576536915558 |
| C | 2.13667483435838 | 1.89036507414808 | -0.73579734775026 |
| C | 3.08294708066249 | 3.09405574012434 | -0.67049598007058 |
| C | 2.58281390176961 | 0.96083979312321 | -1.86568856578879 |
| C | 0.79438474765692 | 2.38932058215042 | -1.02438831093997 |
| N | -0.23266939367052 | 2.82323534934025 | -1.30827160137779 |
| C | 1.97353188112915 | 2.02633954340757 | 1.75118785435188 |
| N | 1.78787645573072 | 2.72288055670171 | 2.64682066764388 |
| C | 1.79904342480415 | -1.01132446377380 | 1.75838141272084 |
| N | 2.21255625165901 | -1.72159487820076 | 2.56341109417267 |
| H | -5.60624066726751 | 2.37744773086146 | 1.47017286291841 |
| H | -5.84827339562851 | 0.87465371560624 | 2.32867753520714 |

| | | | |
|---|---|---|---|
| H | -4.44065038784648 | 1.87617021671628 | 2.70027557887597 |
| H | -5.80105238565031 | 0.20168905004805 | -0.68136685174322 |
| H | -3.31994644652687 | -2.05991104960757 | -2.12675760474526 |
| H | -4.70073917192634 | -1.07715747661376 | -2.62827917202086 |
| H | -3.04596397903557 | -0.55527640497859 | -2.96745581549822 |
| H | 4.08656896264712 | 2.74063704755698 | -0.44881478937128 |
| H | 3.09521466547500 | 3.59626182027031 | -1.63169978854084 |
| H | 2.78044141486979 | 3.80623862300528 | 0.09004160804094 |
| H | 1.90503589470069 | 0.12788543002260 | -2.01371019457014 |
| H | 2.63574637556075 | 1.52342326827873 | -2.79191281760114 |
| H | 3.57402606350239 | 0.57926280348159 | -1.63484655123987 |

Table A3-14. xyz co-ordinates for the (*1R,2S*)-IBN-FCN-TTC (*trans*) radical.

27

0 1

| | | | |
|---|---|---|---|
| C | 1.97181140673891 | -0.21105065954252 | 0.02467357386568 |
| S | 1.61010008727982 | -1.06830785691095 | -1.31781918825249 |
| S | 3.46622303788740 | 0.57743813380261 | 0.37177040145411 |
| C | 4.49541399579324 | 0.14218682793463 | -1.02130047983252 |
| S | 0.90286754690667 | 0.07073833983421 | 1.39801672063262 |
| C | -0.65660122797272 | -0.65637593221894 | 0.80411064481715 |
| H | -0.36688488026098 | -1.51316608776034 | 0.19401659253347 |
| C | -1.44277345474923 | 0.33310669747137 | -0.08093980409937 |
| H | -0.75780864369575 | 0.61244823007073 | -0.88300222308015 |
| C | -2.70188366693985 | -0.24205109026106 | -0.79943145875846 |
| C | -3.17168004723409 | 0.78721424369680 | -1.83119894100286 |
| C | -2.36902870536727 | -1.56162982426463 | -1.49447274621287 |
| C | -3.78740279262467 | -0.45653011820310 | 0.15388502393217 |
| N | -4.67114460180647 | -0.62272280381434 | 0.87099293414184 |
| C | -1.77068897596592 | 1.53371669266816 | 0.66696530640142 |
| N | -2.05285129848639 | 2.46799932656758 | 1.27445443247774 |
| C | -1.37774086170331 | -1.11485248931291 | 1.97007745863340 |
| N | -1.94313763142200 | -1.47775743717738 | 2.90314955016881 |
| H | 4.62308245442815 | -0.93237164233181 | -1.07604817619108 |
| H | 4.06348915221852 | 0.51970554146743 | -1.94035562509471 |
| H | 5.44745374704079 | 0.62425483298173 | -0.82713841356912 |

| | | | |
|---|---|---|---|
| H | -2.38091874506232 | 0.93828666213640 | -2.56096955757556 |
| H | -4.05378728948020 | 0.41702504310132 | -2.34265034106480 |
| H | -3.41344042020587 | 1.73889103903868 | -1.36791213185159 |
| H | -2.16007683515263 | -2.36132046988580 | -0.79110905023874 |
| H | -3.21093286229325 | -1.86428092370485 | -2.10813023238939 |
| H | -1.50353848787047 | -1.41608427538303 | -2.13533426984461 |

Table A3-15. xyz co-ordinates for the (*1S,2S*)-IBN-FCN-TTC (*cis*) radical.

27

0 1

| | | | |
|---|---|---|---|
| C | -4.22154919371532 | -1.02882673937832 | 2.28174816938143 |
| S | -5.50327514207032 | -0.66129075352788 | 1.34078196606343 |
| S | -4.23005835413596 | -1.25964589624329 | 3.98829463256563 |
| C | -5.96335193707636 | -1.17313754769391 | 4.41067008557015 |
| S | -2.55787610357756 | -1.28849602676738 | 1.75048022143525 |
| C | -2.58347525407555 | -0.71563118755128 | 0.02466789487463 |
| H | -3.62857849032361 | -0.46905539530621 | -0.18641695208090 |
| C | -1.67490619282945 | 0.50977532819171 | -0.24555657541223 |
| H | -1.56297560326608 | 0.58136386911961 | -1.32955728652656 |
| C | -2.24061149599266 | 1.89438004642568 | 0.18152402108258 |
| C | -1.22024265453386 | 2.97306355488724 | -0.19961246803098 |
| C | -3.56002098572390 | 2.16903130384107 | -0.54030879474958 |
| C | -2.45741615235798 | 1.97321313707114 | 1.62409323088686 |
| N | -2.63821360157892 | 2.11381793696465 | 2.75161699282431 |
| C | -0.35061343435143 | 0.27250677790673 | 0.30474559571425 |
| N | 0.68929511949579 | 0.07178177055195 | 0.75179817638247 |
| C | -2.20149350211909 | -1.82213738717764 | -0.82559320076698 |
| N | -1.89055735352174 | -2.69768020409012 | -1.50338863610408 |
| H | -6.35719087122158 | -0.19091578555786 | 4.17886735998105 |
| H | -6.51966848693773 | -1.93842184513236 | 3.88228033339513 |
| H | -6.00163328611113 | -1.35036852051004 | 5.48009785960447 |
| H | -1.04386890189221 | 2.92820164206526 | -1.27097293026643 |
| H | -1.61877970363449 | 3.95107286754882 | 0.04744703428136 |
| H | -0.27810827478211 | 2.84027941758848 | 0.32212223339099 |
| H | -4.35208426952785 | 1.49398260272934 | -0.23549113016620 |
| H | -3.88073034391805 | 3.18254425914726 | -0.32266444811696 |

| | | | |
|---|---|---|---|
| H | -3.40269753022068 | 2.07782477489729 | -1.61172138521313 |

Table A3-16. xyz co-ordinates for the (*1R,2S,3R*)-PhMeCH-FCN-PCDT (*trans*-*trans*) radical.

42

0 1

| | | | |
|---|---|---|---|
| C | 5.45763890085511 | 0.82688226354345 | -2.44289252630749 |
| C | 4.86116763970343 | 0.13333398764891 | -1.28430871942186 |
| N | 3.60659615760771 | 0.31850547469598 | -0.95598378206958 |
| N | 3.39555023488950 | -0.46580557320732 | 0.15090990522108 |
| C | 4.55129811164404 | -1.15390764865126 | 0.51193083489264 |
| C | 5.48816166035663 | -0.77705326737471 | -0.39726358953453 |
| C | 4.70286493913825 | -2.09248624716812 | 1.63762878644985 |
| C | 2.14104248965353 | -0.45101991201283 | 0.69779196145202 |
| S | 1.67963416312255 | -1.26848973032886 | 2.03528234178850 |
| S | 1.09319071304216 | 0.59898793162494 | -0.27270804320371 |
| C | -0.47793583790361 | 0.40768520633113 | 0.62642865997594 |
| H | -0.23009921677446 | 0.24491283704427 | 1.67701204959196 |
| C | -1.31792468553516 | -0.79467139451143 | 0.14685488054476 |
| H | -0.71224305659232 | -1.68365367336513 | 0.33380331623859 |
| C | -2.65834267301224 | -0.92902395030517 | 0.91088922978642 |
| H | -3.24470244164485 | -0.03620384562588 | 0.69010883023810 |
| C | -3.42510994900124 | -2.14969389479553 | 0.42565603764641 |
| C | -2.41460026385875 | -0.96738996659932 | 2.39596719204498 |
| C | -2.87204593795666 | 0.06471738365912 | 3.20662451188752 |
| C | -2.65512947939431 | 0.03976425972595 | 4.57630671538637 |
| C | -1.97435424012058 | -1.02129451873929 | 5.15131364758558 |
| C | -1.51489339525782 | -2.05674510555891 | 4.35036046039526 |
| C | -1.73318840807370 | -2.02916025307175 | 2.98322263625293 |
| C | -1.54938337865109 | -0.70801716260234 | -1.28340062263022 |
| N | -1.75448249647984 | -0.62141821238814 | -2.41203727267653 |
| C | -1.19276596895159 | 1.65824411098644 | 0.49791322027246 |
| N | -1.77365268334423 | 2.64559586467144 | 0.39210895843893 |
| H | 6.30007686226560 | 1.43939244103504 | -2.12930430998470 |
| H | 5.83935156098555 | 0.10772252052097 | -3.16411065589183 |
| H | 4.72578213773165 | 1.46025293664654 | -2.93158469702921 |
| H | 6.50582799962631 | -1.11699536147988 | -0.42512087890382 |

| | | | |
|---|---|---|---|
| H | 4.01637361696903 | -2.93098941318585 | 1.56128601350888 |
| H | 5.72116449223368 | -2.46723518101450 | 1.62779066968264 |
| H | 4.50995508576605 | -1.61473628595101 | 2.59378297753464 |
| H | -3.66033536973910 | -2.07492890794557 | -0.63277218363957 |
| H | -2.84909357440475 | -3.05908427655319 | 0.58261423710630 |
| H | -4.35802857407422 | -2.24195950220952 | 0.97361828636220 |
| H | -3.40503775797611 | 0.89199282859860 | 2.76009573755673 |
| H | -3.01886249635077 | 0.84826602491169 | 5.19107903849648 |
| H | -1.80342160865410 | -1.04318011320955 | 6.21619720236725 |
| H | -0.98222408312103 | -2.88573951998708 | 4.78993457085986 |
| H | -1.36409518871824 | -2.83884715380229 | 2.37059637172763 |

Table A3-17. xyz co-ordinates for the (*1S,2S,3R*)-PhMeCH-FCN-PCDT (*cis-trans*) radical.

42

0 1

| | | | |
|---|---|---|---|
| C | 5.51240620730888 | 1.26457324039738 | -1.61662166131976 |
| C | 4.69354686935703 | 0.53526745733034 | -0.62818588026492 |
| N | 3.38603673627284 | 0.61931781059835 | -0.63622678007013 |
| N | 2.95950464892992 | -0.16611533784212 | 0.40580832521344 |
| C | 4.03332239052263 | -0.75254655031429 | 1.07015875420439 |
| C | 5.14027659584512 | -0.30910784511591 | 0.41841838026288 |
| C | 3.96495971312442 | -1.66253482510974 | 2.22694123478885 |
| C | 1.60873490336061 | -0.25003431741953 | 0.61376123725477 |
| S | 0.88953177912568 | -1.09302751822162 | 1.81532804751900 |
| S | 0.76772214825920 | 0.69596358479941 | -0.62455568609968 |
| C | -0.94957838648741 | 0.51422443520946 | -0.05554234861244 |
| H | -0.91433195428015 | 0.37453031616996 | 1.02500744625588 |
| C | -1.76140959967643 | 1.79352966896073 | -0.34395693347057 |
| H | -2.76929928366518 | 1.60590845261960 | 0.03312109729686 |
| C | -1.19157721732430 | 3.04614795960969 | 0.36972124589520 |
| H | -0.27023806544000 | 3.32095244290543 | -0.14136362766787 |
| C | -2.17930129953544 | 4.19678863817588 | 0.24963772493050 |
| C | -0.84780930382168 | 2.73667090834129 | 1.80111602087351 |
| C | 0.46434799250069 | 2.85719564291881 | 2.24265556386596 |
| C | 0.79932016769475 | 2.56695728459591 | 3.55658094960263 |
| C | -0.17698753756932 | 2.14339296386024 | 4.44406956382644 |

| | | | |
|---|---|---|---|
| C | -1.48996150041370 | 2.01958938830213 | 4.01298224196000 |
| C | -1.82327658876161 | 2.31725814250457 | 2.70179907063789 |
| C | -1.87664916456720 | 2.02897635191426 | -1.77224528670362 |
| N | -1.94729578432185 | 2.22288226102946 | -2.90403306497284 |
| C | -1.55906230287890 | -0.66120782862256 | -0.63551570381218 |
| N | -2.04605853829953 | -1.59203996867884 | -1.10505723158852 |
| H | 6.16070370135464 | 1.98311845016577 | -1.11955709880057 |
| H | 6.15781135917174 | 0.57800298241340 | -2.15943508096860 |
| H | 4.88314023663096 | 1.79202644720567 | -2.32469801702381 |
| H | 6.15407878493798 | -0.56293533659541 | 0.66288410865023 |
| H | 3.38165469053117 | -2.55275772120636 | 2.00964878649033 |
| H | 4.97756278935583 | -1.95752226592500 | 2.48243138976655 |
| H | 3.50557445469890 | -1.18919913646136 | 3.09002635965986 |
| H | -2.38453520086583 | 4.43384224222183 | -0.79170312150521 |
| H | -3.12177797594888 | 3.95227409929539 | 0.73515049631429 |
| H | -1.77343981938809 | 5.08505752283117 | 0.72415058500907 |
| H | 1.22783998681226 | 3.17684268558204 | 1.54817403755619 |
| H | 1.82272611765375 | 2.66691408406668 | 3.88355729352770 |
| H | 0.08218252221429 | 1.91041388109658 | 5.46490826578372 |
| H | -2.25597327559319 | 1.69144602305936 | 4.69815107532484 |
| H | -2.84974099682459 | 2.21708028333186 | 2.37791222040972 |

Table A3-18. xyz co-ordinates for the (*1S,2R,3R*)-PhMeCH-FCN-PCDT (*trans*-*cis*) radical.

42

0 1

| | | | |
|---|---|---|---|
| C | -5.25026279564174 | 2.89544800357564 | -1.17006788826810 |
| C | -4.98402990021120 | 1.53873064600531 | -0.65294605764291 |
| N | -3.76027738447231 | 1.11754726572644 | -0.45073164780070 |
| N | -3.88524601331431 | -0.16337332198133 | 0.02706756681088 |
| C | -5.22271495586594 | -0.54138650517551 | 0.11911377155936 |
| C | -5.92734852712574 | 0.53729460697254 | -0.31168556870458 |
| C | -5.74219237897209 | -1.83983147642900 | 0.58294179528399 |
| C | -2.72993469285355 | -0.83635376392111 | 0.31848429137612 |
| S | -2.64804212821907 | -2.35270391404522 | 0.92507481485442 |
| S | -1.34072084657577 | 0.19583395537623 | -0.06518651911646 |
| C | 0.01656639570193 | -0.94246256840783 | 0.35672618170748 |

| | | | |
|---|---|---|---|
| H | -0.32916866821832 | -1.53731075241804 | 1.20200697197439 |
| C | 0.37577311641536 | -1.90152906500180 | -0.79674846936386 |
| H | -0.53795272396983 | -2.45558908248736 | -1.01701464587540 |
| C | 1.49702949221245 | -2.90645170696627 | -0.44018527453660 |
| H | 2.39491570771640 | -2.32709402909834 | -0.22016999507627 |
| C | 1.12689936605207 | -3.73270743327075 | 0.78319404973307 |
| C | 1.79642375981113 | -3.78024931465983 | -1.62967333454591 |
| C | 3.05705821314043 | -3.76470233294743 | -2.21282827494505 |
| C | 3.34249531611369 | -4.57082054401140 | -3.30446277778931 |
| C | 2.36474243720788 | -5.40087134185205 | -3.82904429843631 |
| C | 1.10218761200669 | -5.42219503996482 | -3.25439383439520 |
| C | 0.82112200794442 | -4.61879935072397 | -2.16189784844262 |
| C | 0.73481654972012 | -1.14612998796408 | -1.98458005678197 |
| N | 1.04736013331932 | -0.54302776211482 | -2.91299857098736 |
| C | 1.14427201969626 | -0.13765638697132 | 0.76916993899451 |
| N | 2.05468602482084 | 0.48986037007147 | 1.08633486925190 |
| H | -5.82407964965459 | 2.84667043617970 | -2.09268821041397 |
| H | -5.84215646209883 | 3.46615030000729 | -0.45782256208681 |
| H | -4.32327671090448 | 3.42491136112906 | -1.35961952241032 |
| H | -6.99677484215587 | 0.60088834880305 | -0.37684457126880 |
| H | -5.45519048555764 | -2.04741442063741 | 1.60969327333844 |
| H | -6.82491510021648 | -1.81146275113825 | 0.51705319903860 |
| H | -5.37171946083356 | -2.66399393174563 | -0.01998628060863 |
| H | 1.03582154967272 | -3.12437082377007 | 1.67900205992359 |
| H | 0.18667646314994 | -4.25846445707193 | 0.63117038309960 |
| H | 1.90167341323753 | -4.47149637535798 | 0.96624920224569 |
| H | 3.81912731442181 | -3.11537674040751 | -1.80645257879739 |
| H | 4.32724144805618 | -4.54802720870929 | -3.74459078898562 |
| H | 2.58269351813607 | -6.02680628376146 | -4.68009615475830 |
| H | 0.33476881081475 | -6.06428869656565 | -3.65789723004053 |
| H | -0.16598094250658 | -4.64651992426905 | -1.72255240711297 |

Table A3-19. xyz co-ordinates for the (*1R,2R,3R*)-PhMeCH-FCN-PCDT (*cis*-*cis*) radical.

42

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| | | | |
|---|---|---|---|
| C | -5.44201526244635 | 1.44589101349948 | 1.87281191389016 |

| | | | |
|---|---|---|---|
| C | -4.79854754228865 | 0.52714162680233 | 0.91329719843496 |
| N | -3.52697071720081 | 0.63610046714297 | 0.61926709649242 |
| N | -3.27092859875408 | -0.36243074564316 | -0.28829231435517 |
| C | -4.41736113055160 | -1.10748277335747 | -0.55713358538609 |
| C | -5.39286017251124 | -0.54637257487811 | 0.20364519822879 |
| C | -4.52738766191155 | -2.25962459408505 | -1.46874591427286 |
| C | -1.98963174568164 | -0.47078460624113 | -0.75523681761069 |
| S | -1.48248172792761 | -1.56015858604393 | -1.86357488237921 |
| S | -0.98031669775919 | 0.76331892652900 | 0.03404940824220 |
| C | 0.64182107959937 | 0.35758446677975 | -0.67459483039762 |
| H | 0.44416643602213 | -0.29671174461461 | -1.52999921398692 |
| C | 1.57963453673575 | -0.36602120955901 | 0.31768017781366 |
| H | 1.82273040554322 | 0.32233599586730 | 1.12919313593896 |
| C | 2.91094829702112 | -0.80367542674512 | -0.35105836607935 |
| H | 3.35588414137990 | 0.12325355131321 | -0.71400117528446 |
| C | 3.84746857723117 | -1.39800050328332 | 0.68604151391503 |
| C | 2.67022148883433 | -1.69086510596883 | -1.54402227203177 |
| C | 2.68932307915805 | -1.14298442988205 | -2.82328439647284 |
| C | 2.41805520475691 | -1.92105035214436 | -3.93745020731597 |
| C | 2.12576524058058 | -3.26753765808049 | -3.78725142895200 |
| C | 2.11618546307287 | -3.82802348971599 | -2.51920196971628 |
| C | 2.38729081298326 | -3.04726152769168 | -1.40656504249297 |
| C | 0.89007377669568 | -1.48985357104354 | 0.92541750446199 |
| N | 0.37277048292541 | -2.38496808091303 | 1.42943835849239 |
| C | 1.24346766714934 | 1.57892972399642 | -1.15591137653191 |
| N | 1.72635735775386 | 2.54925917902992 | -1.54260499440256 |
| H | -6.25749590097967 | 1.98721144226340 | 1.39836446539852 |
| H | -5.87100166702781 | 0.88995304762877 | 2.70347456104814 |
| H | -4.72563195605019 | 2.16090847645460 | 2.26161330573102 |
| H | -6.41497888698912 | -0.87045606901251 | 0.25053053667667 |
| H | -3.85420122968964 | -3.06471162691100 | -1.18864461446285 |
| H | -5.54921289094610 | -2.62259205458977 | -1.42807883336155 |
| H | -4.28844086525958 | -1.99094378702993 | -2.49377663676418 |
| H | 4.02756441955703 | -0.68592941901987 | 1.48761122495141 |
| H | 3.44207210851115 | -2.30363648627340 | 1.13067453149560 |
| H | 4.80031170909841 | -1.64764648528486 | 0.22883703779745 |

| | | | |
|---|---|---|---|
| H | 2.92042521008309 | -0.09388723291200 | -2.94498843357333 |
| H | 2.43762509415309 | -1.47639511078290 | -4.92018142268849 |
| H | 1.91549228406666 | -3.87739330881805 | -4.65180074260911 |
| H | 1.89793207616277 | -4.87723562723408 | -2.39413164255314 |
| H | 2.37762970489983 | -3.50377972954777 | -0.42930305532786 |

Table A3-20. xyz co-ordinates for the (*1R,2S,3R*)-PhMeCH-FCN-TTC (*trans-trans*) radical.

33

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| | | | |
|---|---|---|---|
| C | -2.18293479986631 | -0.32928943611168 | -0.09713392254820 |
| S | -1.27014664692862 | -1.53117042812610 | 0.52594901612461 |
| S | -1.63910530827858 | 0.90721468516377 | -1.22798076867434 |
| C | 0.15668736587534 | 0.63604159451820 | -1.22952123016297 |
| H | 0.29792019910141 | -0.43725052815750 | -1.07972011304729 |
| C | 0.88449953212410 | 1.37472110384122 | -0.08712121726639 |
| H | 0.45180836607169 | 1.00178467444845 | 0.84358576523205 |
| C | 2.40766807209654 | 1.09502382954358 | -0.07858995740386 |
| H | 2.80975196211685 | 1.47306443375936 | -1.01949762361527 |
| C | 3.07716371582008 | 1.83680443848875 | 1.06767860399548 |
| C | 2.65995090322773 | -0.38865242681114 | -0.02822814724162 |
| C | 3.19218830921350 | -1.04526100636526 | -1.13173371653196 |
| C | 3.41679443467629 | -2.41344759196828 | -1.10176137912188 |
| C | 3.11166059984258 | -3.14152961759286 | 0.03712295009758 |
| C | 2.58266398603753 | -2.49458482326953 | 1.14432019178707 |
| C | 2.35666065659306 | -1.12874595057789 | 1.11067572543014 |
| C | 0.61788200357663 | 2.79959093120115 | -0.16189810506774 |
| N | 0.42621260690893 | 3.93074424172902 | -0.24459331055455 |
| C | 0.65809954475153 | 1.00304675160284 | -2.53434079406944 |
| N | 1.07254739839658 | 1.30108342152802 | -3.56507075462680 |
| S | -3.85550261427456 | -0.03596373952620 | 0.21187267003085 |
| C | -4.34441565710734 | -1.44269863412940 | 1.19788544082571 |
| H | 2.95530304133552 | 2.91184401860120 | 0.96599047903679 |
| H | 2.66008398770447 | 1.53879048092807 | 2.02692388630227 |
| H | 4.14058363143240 | 1.61731860802895 | 1.07767476805018 |
| H | 3.43110588584762 | -0.47842112173461 | -2.02036898939436 |
| H | 3.82900503784451 | -2.90854231454094 | -1.96710754228093 |

| | | | |
|---|---|---|---|
| H | 3.28570200006598 | -4.20579476772563 | 0.06329691290306 |
| H | 2.34296603970539 | -3.05432851521540 | 2.03502854088651 |
| H | 1.93813024945645 | -0.63806001840762 | 1.97719686448281 |
| H | -3.80089606495769 | -1.45356114876136 | 2.13494715858343 |
| H | -5.40450083760597 | -1.30467029829230 | 1.38142353854702 |
| H | -4.17502760080373 | -2.36327084606894 | 0.65190505929207 |

Table A3-21. xyz co-ordinates for the (*1S,2S,3R*)-PhMeCH-FCN-TTC (*cis-trans*) radical.

33

0 1

| | | | |
|---|---|---|---|
| C | -2.34123505419617 | -0.00334769214347 | -0.43783066268644 |
| S | -1.84573521512051 | -0.73651475365619 | -1.80955693092941 |
| S | -1.30915748001689 | 0.54955853929177 | 0.87812961078978 |
| C | 0.34079503981738 | 0.47720166862630 | 0.11883023035080 |
| H | 0.16991213482123 | 0.46465290902346 | -0.95903634081169 |
| C | 1.18861358185877 | 1.71774101526584 | 0.46583264764780 |
| H | 2.14397995010637 | 1.58581276123898 | -0.04744382791120 |
| C | 0.54792792109555 | 3.04505797642983 | -0.00889627356262 |
| H | -0.31299483748098 | 3.23712176137074 | 0.62963124556598 |
| C | 1.54497238217712 | 4.18240773529120 | 0.15588211657684 |
| C | 0.05250034025120 | 2.92726900251233 | -1.42412238398010 |
| C | -1.29133884175227 | 3.13716136508535 | -1.70956733493252 |
| C | -1.76514693802451 | 3.03294866628986 | -3.00832826350643 |
| C | -0.89771849016450 | 2.70753846757342 | -4.03861235259109 |
| C | 0.44569322081286 | 2.49429416044694 | -3.76397551560600 |
| C | 0.91797113300560 | 2.60663630003321 | -2.46676115686182 |
| C | 1.47156939558989 | 1.76647945712997 | 1.88934423318241 |
| N | 1.66973904436387 | 1.80871685690876 | 3.02165709638702 |
| C | 1.00575819872525 | -0.75604417777115 | 0.47636238715405 |
| N | 1.54225236338704 | -1.73246019144722 | 0.76305370967570 |
| S | -3.96664781119523 | 0.36687928721030 | 0.00593523866401 |
| C | -4.93462276576767 | -0.42232930067935 | -1.27123948857311 |
| H | 1.87479989221320 | 4.27340994350414 | 1.18815627058492 |
| H | 2.42105646918036 | 4.02342763290004 | -0.46937750381352 |
| H | 1.08542893982896 | 5.12213529722938 | -0.13493227694002 |
| H | -1.96964964266504 | 3.37945262830176 | -0.90391831517652 |

| | | | |
|---|---|---|---|
| H | -2.81181502767619 | 3.19816329456427 | -3.21184966945396 |
| H | -1.26396357313326 | 2.61843476793849 | -5.04929561397894 |
| H | 1.12651167999266 | 2.24046462780407 | -4.56140112011179 |
| H | 1.96721180781632 | 2.44010009589054 | -2.26765332585931 |
| H | -4.73255631491596 | -1.48692821245591 | -1.29319362597344 |
| H | -5.96810077949235 | -0.24203676249188 | -0.99573247221544 |
| H | -4.71936572344207 | 0.02298187278402 | -2.23499133110385 |

Table A3-22. xyz co-ordinates for the (*1S,2R,3R*)-PhMeCH-FCN-TTC (*trans-cis*) radical.

33

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| | | | |
|---|---|---|---|
| C | -2.71773453975582 | -0.09185646276444 | -0.10289125145690 |
| S | -2.22487488887533 | -0.66275568075988 | -1.55253804552206 |
| S | -1.93736786059751 | -0.38140282687399 | 1.44870412742237 |
| C | -0.47557292921694 | -1.33926740152114 | 0.94949683170248 |
| H | -0.79631664633869 | -1.94246631293633 | 0.09934689815919 |
| C | 0.70231925343553 | -0.44984558514108 | 0.50183000206518 |
| H | 0.32703176171133 | 0.15319459831905 | -0.32657337664243 |
| C | 1.92789345935105 | -1.26109965123962 | 0.01605753114973 |
| H | 2.25494265746589 | -1.88417945968606 | 0.84965524030843 |
| C | 1.55916297068472 | -2.15527495893076 | -1.15932054830999 |
| C | 3.05664499035985 | -0.32434507305583 | -0.32541323414662 |
| C | 4.24273614374176 | -0.36535454047932 | 0.39642428221548 |
| C | 5.28874689059965 | 0.49169177111779 | 0.09008010649513 |
| C | 5.15708073769995 | 1.40549951023104 | -0.94321308798295 |
| C | 3.97535306420962 | 1.45592855924813 | -1.66801499658399 |
| C | 2.93319535328261 | 0.59655362826727 | -1.36188730378273 |
| C | 1.08334299289234 | 0.45268574200322 | 1.57432529759945 |
| N | 1.39972422809618 | 1.14255247964232 | 2.43860608669033 |
| C | -0.12243579330090 | -2.20832994090177 | 2.04946294571984 |
| N | 0.17923294549995 | -2.89486225538618 | 2.92140653287878 |
| S | -4.09825741603348 | 0.90094572781634 | 0.19500181505442 |
| C | -4.82853210983755 | 1.08912878927065 | -1.42397807422551 |
| H | 0.84199524143271 | -2.92292361687860 | -0.88196605926054 |
| H | 1.13705829666944 | -1.57290965687604 | -1.97543181799438 |
| H | 2.45006097660386 | -2.65687768045661 | -1.52543800288269 |

|  |  |  |  |
|---|---|---|---|
| H | 4.34373089012847 | -1.07359095420180 | 1.20612984976232 |
| H | 6.20401851382634 | 0.44478387903078 | 0.65925971159063 |
| H | 5.96856417190939 | 2.07439171432339 | -1.18321514754224 |
| H | 3.86572049428563 | 2.16431303827483 | -2.47436084670439 |
| H | 2.01927276255463 | 0.64733694291163 | -1.93645375050364 |
| H | -5.11277165125767 | 0.12364434340834 | -1.82499200890149 |
| H | -5.70790979717757 | 1.70422990816746 | -1.26598600852188 |
| H | -4.13755516404961 | 1.58766142605732 | -2.09331369784922 |

Table A3-23. xyz co-ordinates for the (*1R,2R,3R*)-PhMeCH-FCN-TTC (*cis-cis*) radical.

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|  |  |  |  |
|---|---|---|---|
| C | -2.67124269953510 | 0.19423092539300 | 0.07012615814704 |
| S | -2.50565601180242 | 0.74316594744741 | 1.59923398442893 |
| S | -1.41713925202361 | -0.55746065469273 | -0.92228837124938 |
| C | 0.06724109845193 | -0.27338176784748 | 0.08141550065617 |
| H | -0.31368513577028 | -0.05423186942257 | 1.08539970030369 |
| C | 0.94090652716622 | 0.90114038629690 | -0.41174482505169 |
| H | 1.37308946006750 | 0.62924573028142 | -1.37643292893080 |
| C | 2.10692901005254 | 1.20279681606082 | 0.56837271763999 |
| H | 2.67197905132360 | 0.27183251455463 | 0.62031988358500 |
| C | 3.01317608121525 | 2.27460937170955 | -0.01060090787082 |
| C | 1.60502474997882 | 1.50703277182001 | 1.95568046998846 |
| C | 1.60673148239652 | 0.50618444300826 | 2.92280639643176 |
| C | 1.10172524373687 | 0.73940775390640 | 4.19212809274540 |
| C | 0.58922180007146 | 1.98592048961766 | 4.51522795568395 |
| C | 0.59456174557252 | 2.99525168463169 | 3.56467212077906 |
| C | 1.09889902015435 | 2.75886268433138 | 2.29558377127807 |
| C | 0.11677894310724 | 2.07332247211625 | -0.64489001824526 |
| N | -0.50947256442156 | 3.01726607178254 | -0.84349043613173 |
| C | 0.82847923209624 | -1.49940839862621 | 0.13194689927915 |
| N | 1.44281306826595 | -2.47112230120203 | 0.17473051014390 |
| S | -4.10851793537449 | 0.22766879957171 | -0.88125112561251 |
| C | -5.34269516302178 | 0.84573642962387 | 0.25233667312502 |
| H | 3.38111895283940 | 1.97618959419128 | -0.98913550008787 |
| H | 2.49699334122744 | 3.22477402370157 | -0.12276839039097 |

| | | | |
|---|---|---|---|
| H | 3.86630783588859 | 2.43228043263723 | 0.64246450306770 |
| H | 2.01097127553154 | -0.46605400440662 | 2.67669617849009 |
| H | 1.11169864916063 | -0.05050536839052 | 4.92686748328461 |
| H | 0.19590134518182 | 2.17264321681418 | 5.50213570453351 |
| H | 0.20520752049191 | 3.97104655545399 | 3.81023315816990 |
| H | 1.09755812516539 | 3.55802949252087 | 1.57122574020383 |
| H | -5.08370291346700 | 1.84479310759846 | 0.58176751671603 |
| H | -6.26516893999291 | 0.86575725091410 | -0.31787333016121 |
| H | -5.44137894373454 | 0.18124039860277 | 1.10256271505078 |