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Electronic Supporting Information

Photoisomerization of Dicyanorhodanine-Functionalized Thiophenes

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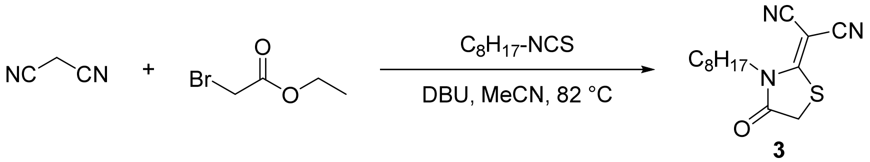
SYNTHESIS

General Information

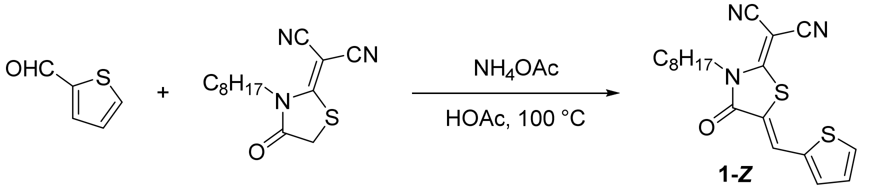
Reagents and solvents were purchased from commercial sources and used without further purification unless otherwise specified. THF was degassed in a 20 L drum and passed through activated alumina under a positive argon atmosphere. Thin layer chromatography (TLC) was performed on SiO_2-60 F_{254} aluminum plates with visualization by UV light. Column chromatography was performed using Silica gel technical grade, pore size 60 Å, 230 – 400 mesh particle size, 40 – 63 µm particle size from Sigma-Aldrich.

Note: Due to the photosensitivity of the RCN-functionalized products, the reaction vessels were covered with aluminum foil for the synthesis of both **1-*Z*** and **2-*Z***. Aluminum foil was used to cover all glassware during purification processes such that any source of excessive light exposure was eliminated while samples were dissolved in solution.

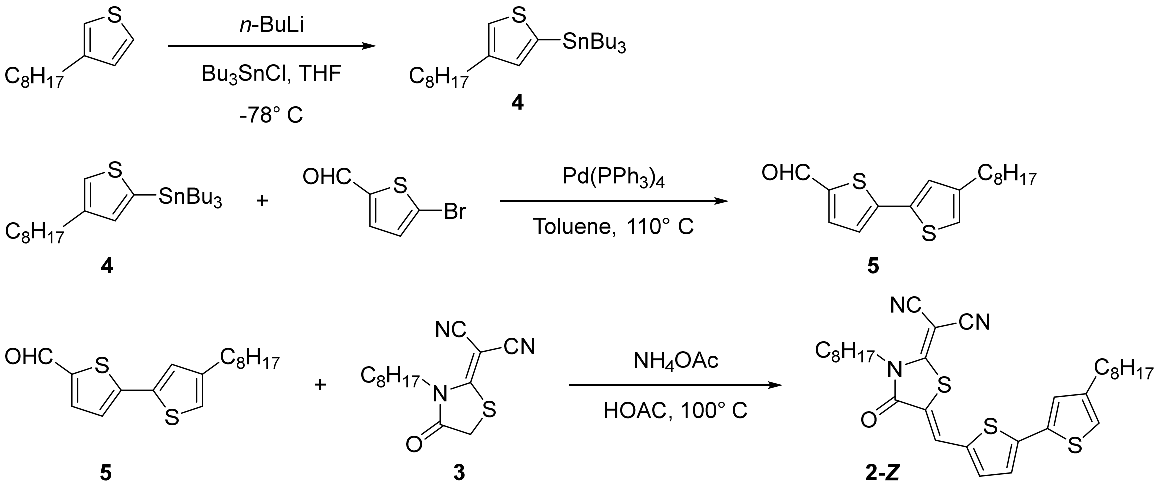
(a) Synthesis of 2-(1,1)-Dicyanomethylene rhodanine



(b) Synthesis of 1-*Z*



(c) Synthesis of 2-*Z*

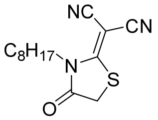


Scheme S1. (a) Synthesis of *N*-octyl-2-(1,1-dicyanomethylene)rhodanine. (b) Synthesis of **1-*Z***. (c) Synthesis of **2-*Z***.

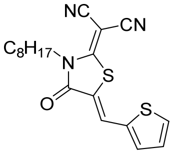
STRUCTURAL CHARACTERIZATION

General Information

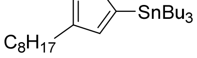
^{1}H (^{13}C) NMR were recorded on an INOVA-500 (^{1}H at 500 MHz; ^{13}C at 125 MHz) spectrometer and a Bruker 600 MHz spectrometer (^{1}H at 600 MHz; ^{13}C at 150 MHz). Chemical shifts (δ) are given in parts per million (ppm) referenced to residual deuterated solvent purchased from Cambridge Isotope Laboratories, Inc. ($CDCl_3$: δ H 7.26 ppm, δ C 77.16 ppm). Abbreviations used are s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), and m (multiplet). Electrospray ionization (ESI) high resolution mass spectra (HRMS) were recorded on an Agilent 6210 TOF spectrometer with MassHunter software.



2-(3-Octyl-4-oxothiazolidin-2-ylidene)malononitrile (3): A three-necked round-bottom flask containing malononitrile (0.53 g, 8.0 mmol) was equipped with a stir bar, two septa, and a reflux condenser. The flask was flushed with argon three times. Octyl isothiocyanate (1.5 g, 8.7 mmol) and acetonitrile (13 mL) were added to the flask. 1,8-Diazabicyclo[5.4.0]undec-7-ene (1.6 g, 11 mmol) was added dropwise to the mixture. The reaction mixture was stirred at 25 °C for 1 hour. Ethyl bromoacetate (2.3 g, 14 mmol) was added to the mixture. The reaction mixture was heated to reflux temperature (82 °C) and was allowed to stir overnight (12 h). The solvent was removed after cooling to room temperature. The resulting concentrate was purified by silica chromatography using 1:2:5 (EtOAc:DCM:hexanes) as the eluent to yield an off-white solid (1.6 g, 5.7 mmol, 71%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.08 (2H, t, J = 8.0 Hz), 3.99 (2H, s), 1.68 (2H, quin, J = 8.0 Hz), 1.39–1.27 (10H, m), 0.88 (3H, t, J = 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.69, 112.98, 111.80, 56.71, 45.45, 32.43, 31.79, 29.13, 28.66, 25.99, 22.70, 14.18 ppm. The NMR spectra match the literature.[1]

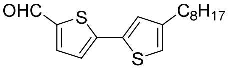


(*Z*)-2-(3-Octyl-4-oxo-5-(thiophen-2-ylmethylene)thiazolidin-2-ylidene) malononitrile (1-*Z*): A three-necked round-bottom flask containing 2-thiophenecarboxaldehyde (0.10 g, 0.82 mmol), 2-(3-octyl-4-oxothiazolidin-2-ylidene)malononitrile (0.27 g, 0.97 mmol), and ammonium acetate (90 mg, 1.2 mmol) was equipped with a stir bar, two septums, and a reflux condenser. The flask was flushed with argon three times. Glacial acetic acid (8 mL) was added to the flask. The reaction apparatus was covered in aluminum foil. The mixture was heated to reflux temperature (100 °C) and was allowed to reflux overnight (12 h) with stirring. After cooling to room temperature, the reaction mixture was neutralized with saturated $NaHCO_3$ solution. The aqueous phase was extracted three times with DCM and the combined organic extracts were dried over anhydrous Na_2SO_4. The solvent was removed and the resulting concentrate was purified by silica chromatography using 1:2:5 (EtOAc:DCM:hexanes) as the eluent to yield a bright yellow solid (0.27 g, 0.72 mmol, 88%). ^{1}H NMR ($CDCl_3$, 500 MHz): 8.10 (1H, s), 7.77 (1H, d, J = 5.0 Hz), 7.50 (1H, d, J = 3.5 Hz), 7.25 (1H, d, J = 5.0 Hz), 4.21 (2H, t, J = 8.0 Hz), 1.76 (2H, quin, J = 7.5 Hz), 1.42–1.28 (10H, m), 0.88 (3H, t, J = 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ 166.14, 165.68, 137.13, 134.94, 133.78, 129.39, 128.97, 114.80, 113.17, 112.23, 56.35, 45.46, 31.80, 29.17, 29.14, 28.89, 26.05, 22.70, 14.18 ppm; HRMS-DART: m/z $[M+NH_4]^+$ calc'd for $[C_{19}H_{25}N_4OS_2]^+$: 389.1464, found: 389.1478 (3.6 ppm).

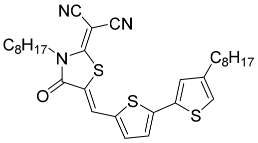


2-Tributylstannyl-4-octylthiophene (4): A three-necked round-bottom flask containing 3-*n*-octylthiophene (0.98 g, 5.0 mmol) was equipped with a stir bar and two septums. The flask was flushed with argon three times. Anhydrous tetrahydrofuran (15 mL) was added to the flask. The mixture was cooled to –78 °C. A *n*-BuLi solution in hexanes (2.7 mL, 6.7

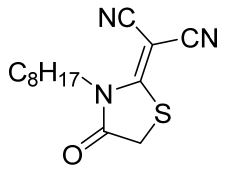
mmol, 2.5 M) was added dropwise to the mixture. The mixture was allowed to stir for two hours. Tributyltin chloride (0.19 g, 6.0 mmol) was added to the mixture. The mixture was allowed to warm to room temperature and stir overnight (12 h). The solvent was removed and the crude product was used for next step of synthesis without further purification according to the literature precedent.[2]



4'-Octyl-[2,2'-bithiophene]-5-carbaldehyde (5): A three-necked round-bottom flask containing 5-bromothiophene-2-carbaldehyde (0.38 g, 2.0 mmol), 2-tributylstannyl-4-octylthiophene (2.4 g, 5.0 mmol), and $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol) was flushed with argon three times. Toluene (15 mL) was added to the flask. The reaction mixture was heated to reflux temperature (110 °C) and was allowed to reflux overnight (12 h) with stirring. After cooling to room temperature, the solvent was evaporated, and the residue was purified by silica chromatography using 12:1 (hexanes:EtOAc) as the eluent to yield an amber colored oil (0.54 g, 1.8 mmol, 89%). ^1H NMR ($CDCl_3$, 500 MHz): δ 9.85 (1H, s), 7.66 (1H, d, J = 4.0 Hz), 7.22 (1H, d, J = 4.0 Hz), 7.19 (1H, s), 6.95 (1H, s), 2.60 (2H, t, J = 8.0 Hz), 1.63 (2H, quin, J = 7.5 Hz), 1.38–1.27 (10H, m), 0.88 (3H, t, J = 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 182.61, 147.78, 144.89, 141.55, 137.47, 135.73, 127.57, 124.02, 122.05, 32.00, 30.51, 29.52, 29.39, 22.80, 14.24 ppm. The NMR spectra match the literature.[3]



***Z*)-2-(3-Octyl-5-((4'-octyl-[2,2'-bithiophen]-5-yl)methylene)-4-oxothiazolidin-2-ylidene)malononitrile (2-*Z*)**: A three necked round-bottom flask containing 4'-octyl-[2,2'-bithiophene]-5-carbaldehyde (0.092 g, 0.30 mmol), 2-(3-octyl-4-oxothiazolidin-2-ylidene)malononitrile (0.13 g, 0.45 mmol), and ammonium acetate (35 mg, 0.45 mmol) was equipped with a stir bar, two septums, and a reflux condenser. The flask was flushed with argon three times. Glacial acetic acid (10 mL) was added to the flask, and the reaction apparatus was covered in aluminum foil. The mixture was heated to reflux temperature (100 °C) and was allowed to stir overnight (12 h). After cooling to room temperature, the reaction mixture was neutralized with saturated $NaHCO_3$ solution. The aqueous phase was extracted three times with DCM and the combined organic extracts were dried over anhydrous Na_2SO_4. The solvent was removed and the resulting concentrate was purified by silica chromatography using 1:2:5 (EtOAc:DCM:hexanes) as the eluent to yield a bright orange solid (0.14 g, 0.25 mmol, 82%). ^1H NMR ($CDCl_3$, 500 MHz): 8.03 (1H, s), 7.39 (1H, d, J = 4.0 Hz), 7.25 (1H, s), 7.23 (1H, d, J = 4.0 Hz), 6.97 (1H, s), 4.22 (2H, t, J = 8.0 Hz), 2.62 (2H, t, J = 8.0 Hz), 1.75 (2H, quin, J = 8.0 Hz), 1.66 (2H, quin, J = 8.0 Hz), 1.43–1.26 (20H, m), 0.88 (6H, t, J = 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.15, 165.68, 147.25, 145.24, 136.78, 135.37, 135.06, 128.95, 127.72, 124.94, 122.25, 113.48, 112.41, 55.90, 45.49, 32.01, 31.84, 30.60, 29.53, 29.47, 29.41, 29.22, 29.18, 28.95, 26.10, 22.81, 22.74, 14.25, 14.22 ppm; HRMS-DART: m/z $[M+H]^+$ calc'd for $[C_{31}H_{40}N_3OS_3]^+$: 566.2328, found: 566.2308 (3.5 ppm).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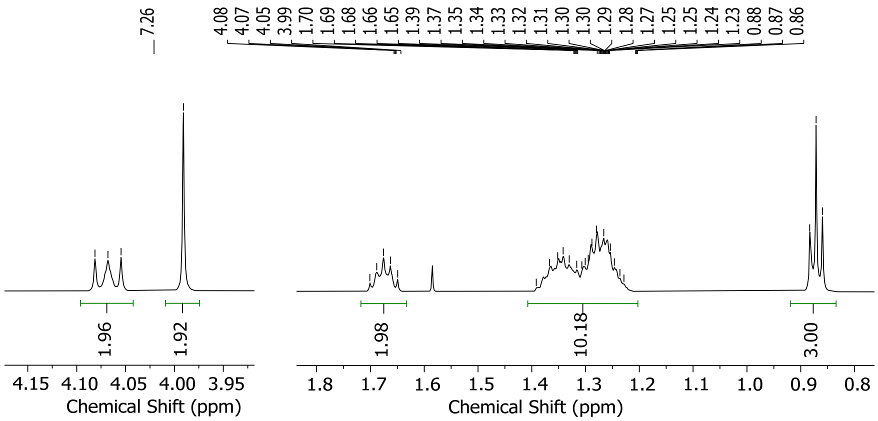
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4.00
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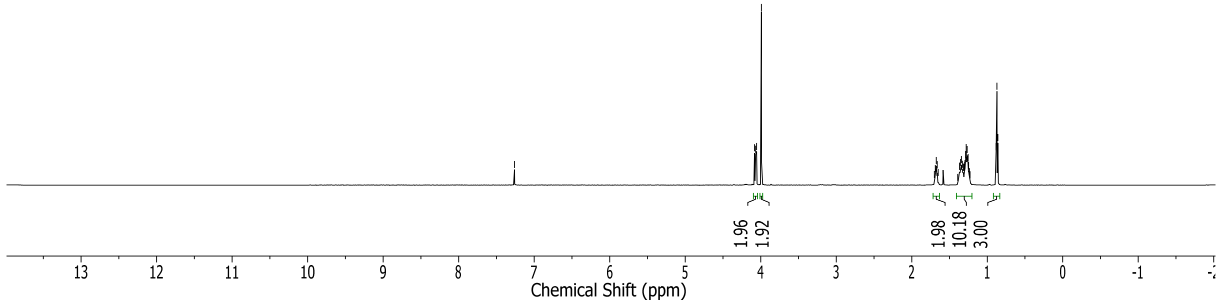
Chemical Shift (ppm)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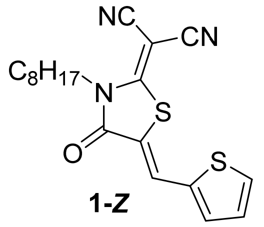
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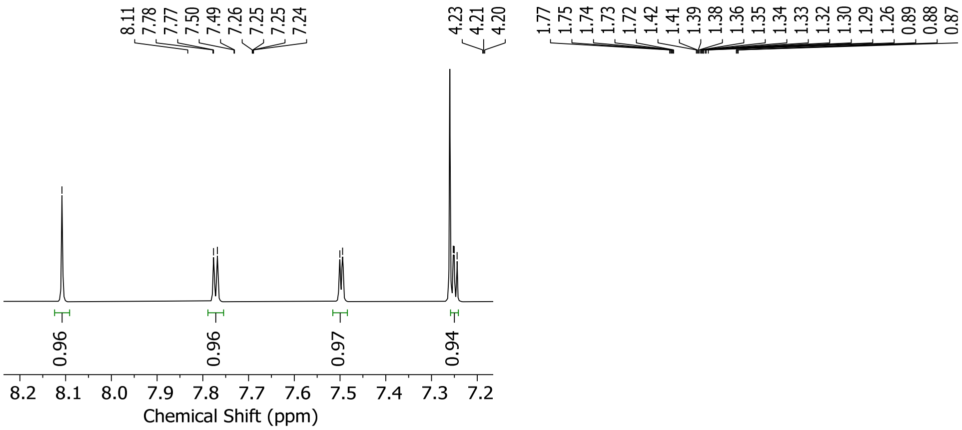
1-Z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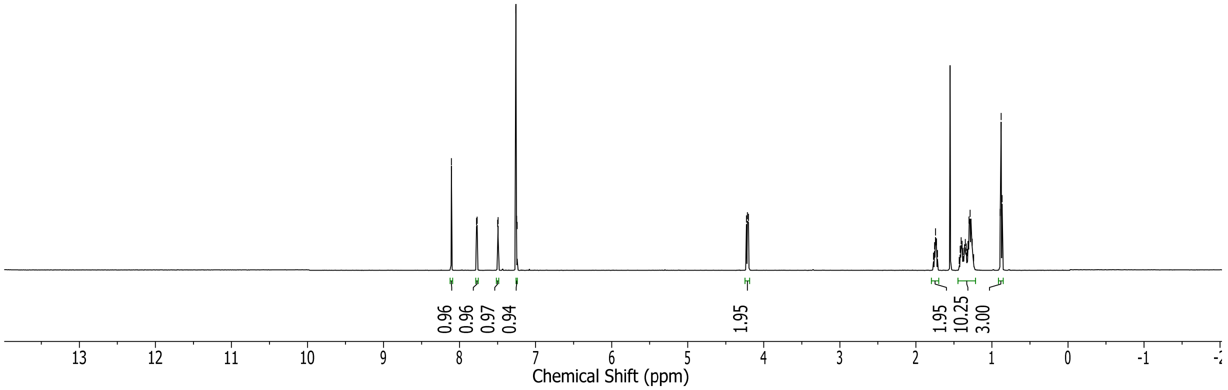
Chemical Shift (ppm)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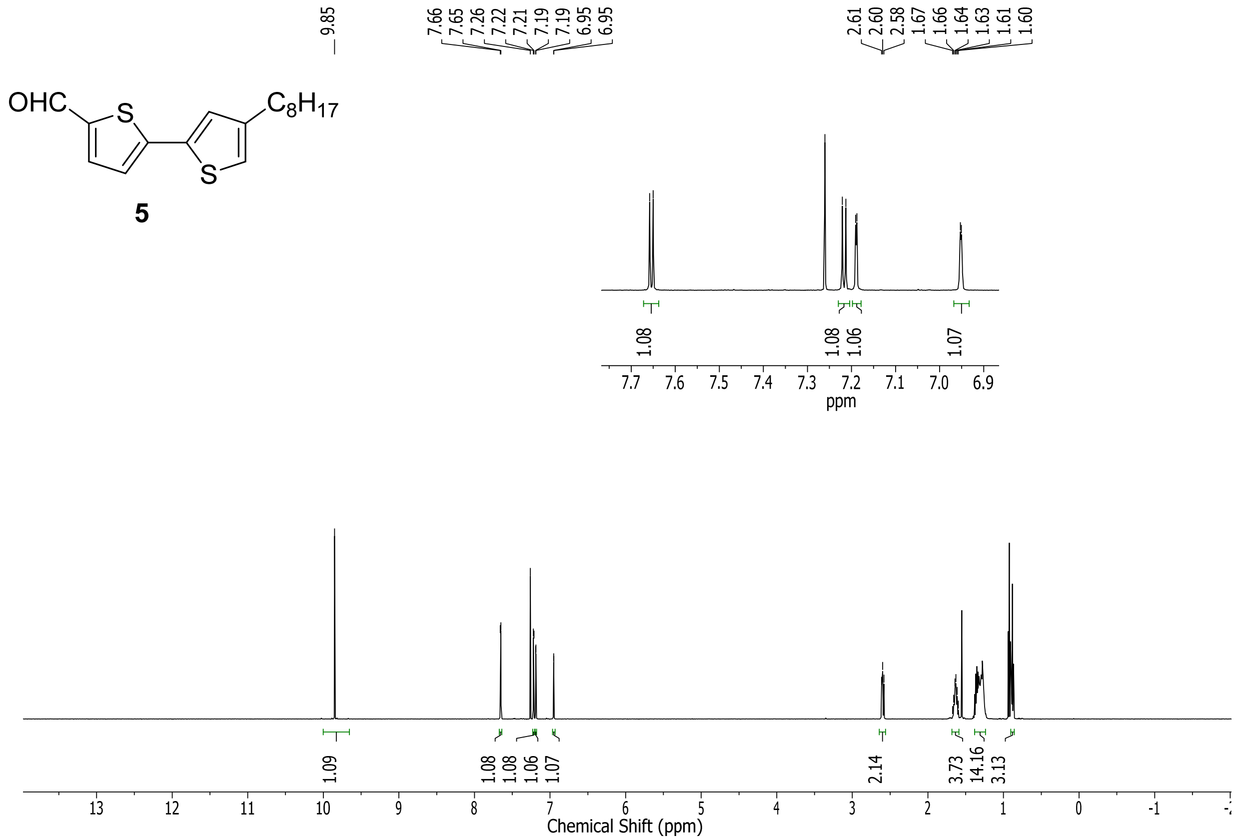
Chemical Shift (ppm)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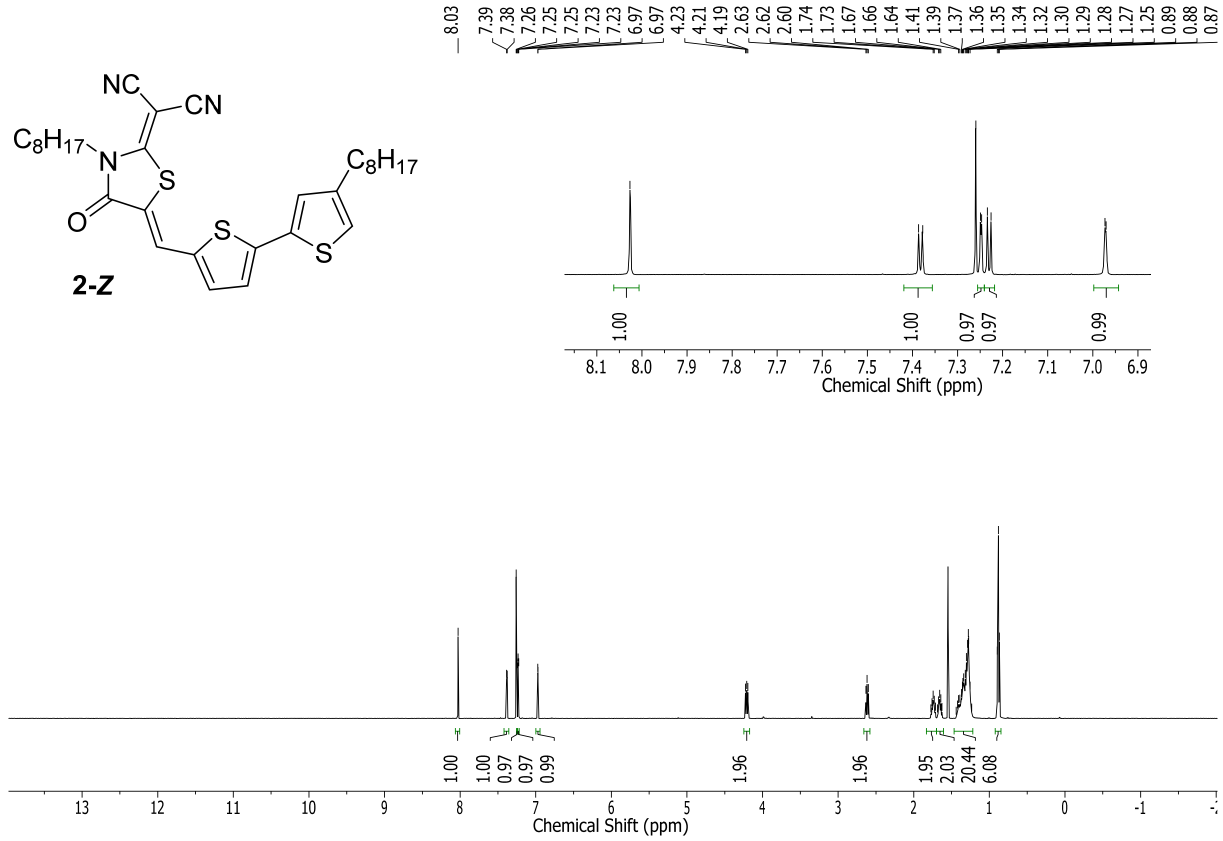
Chemical Shift (ppm)

5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C_8H_{17}
O
S
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Chemical Shift (ppm)
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0.97
0.99
1.96
1.96
1.95
2.03
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6.08
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3
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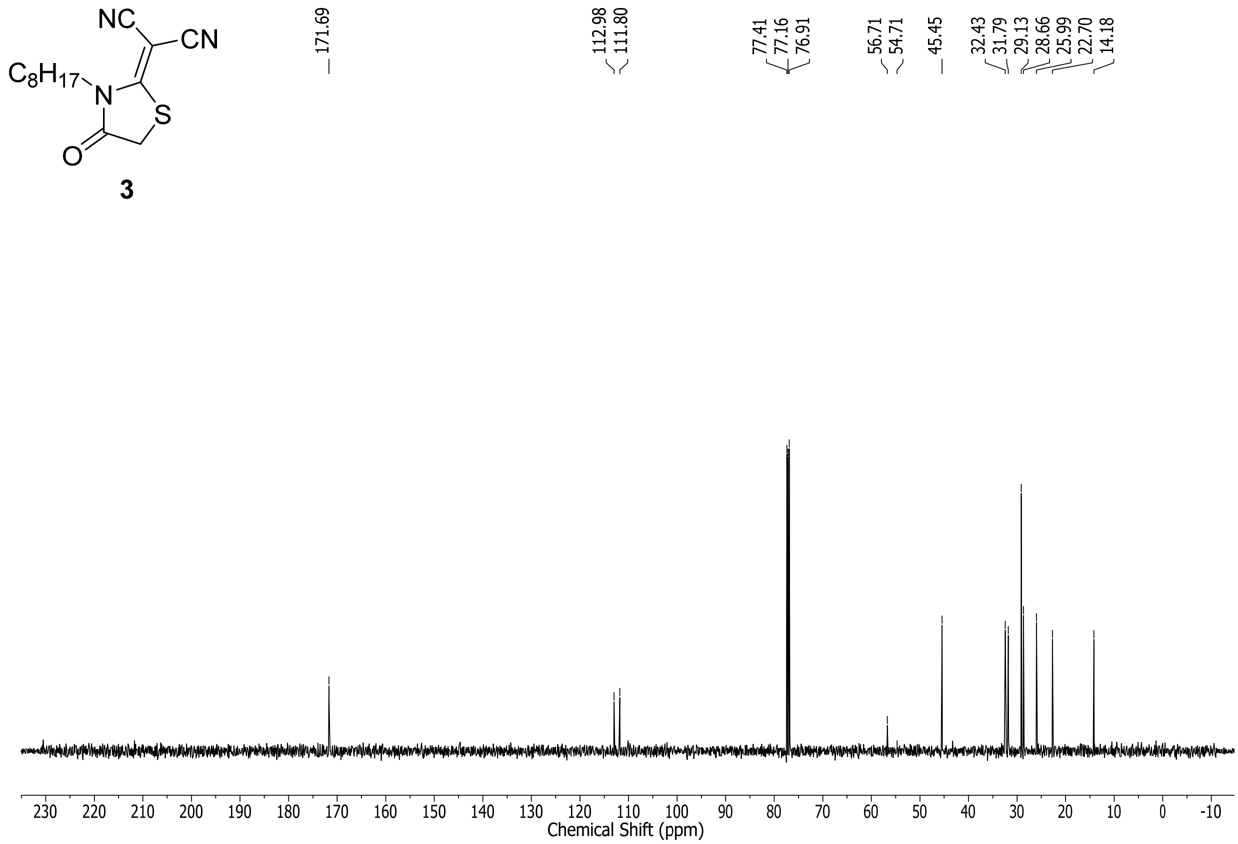
Chemical Shift (ppm)

2-*Z*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29.13
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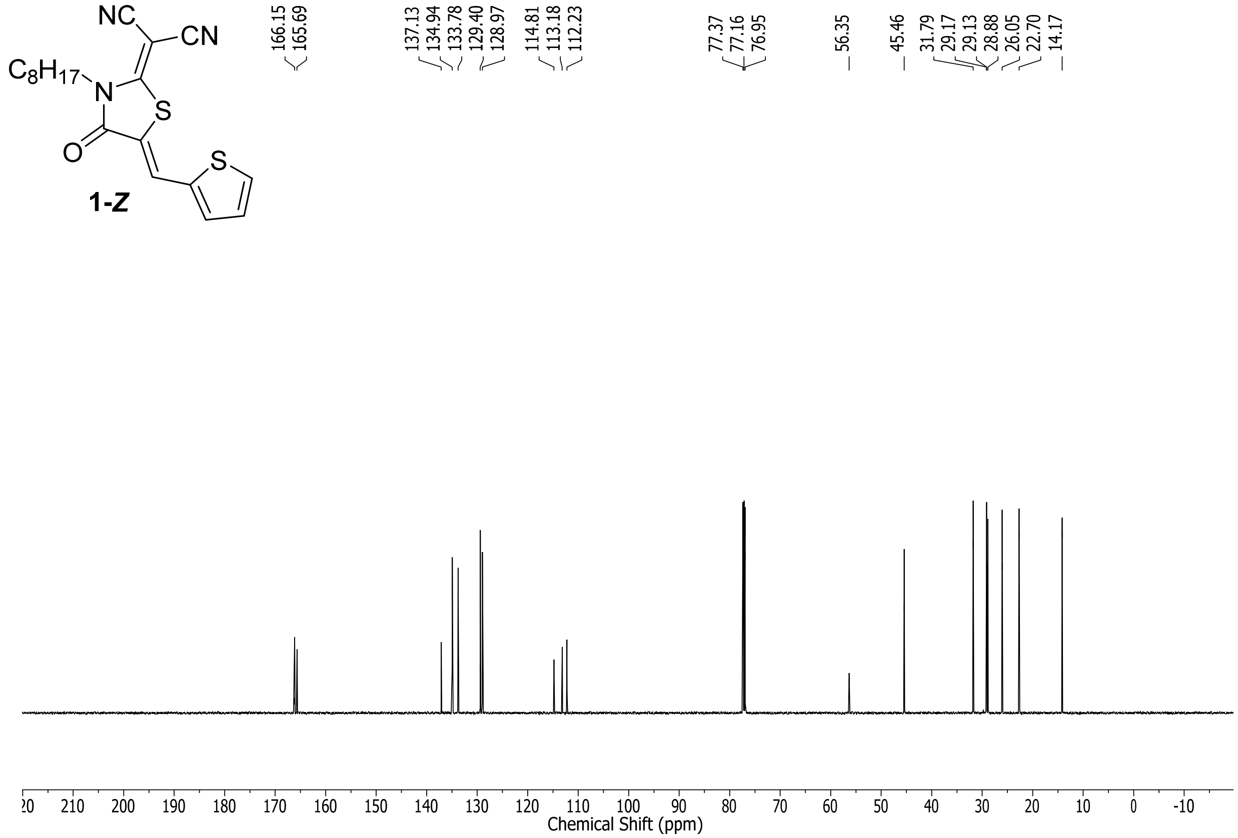
Chemical Shift (ppm)

3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29.17
29.13
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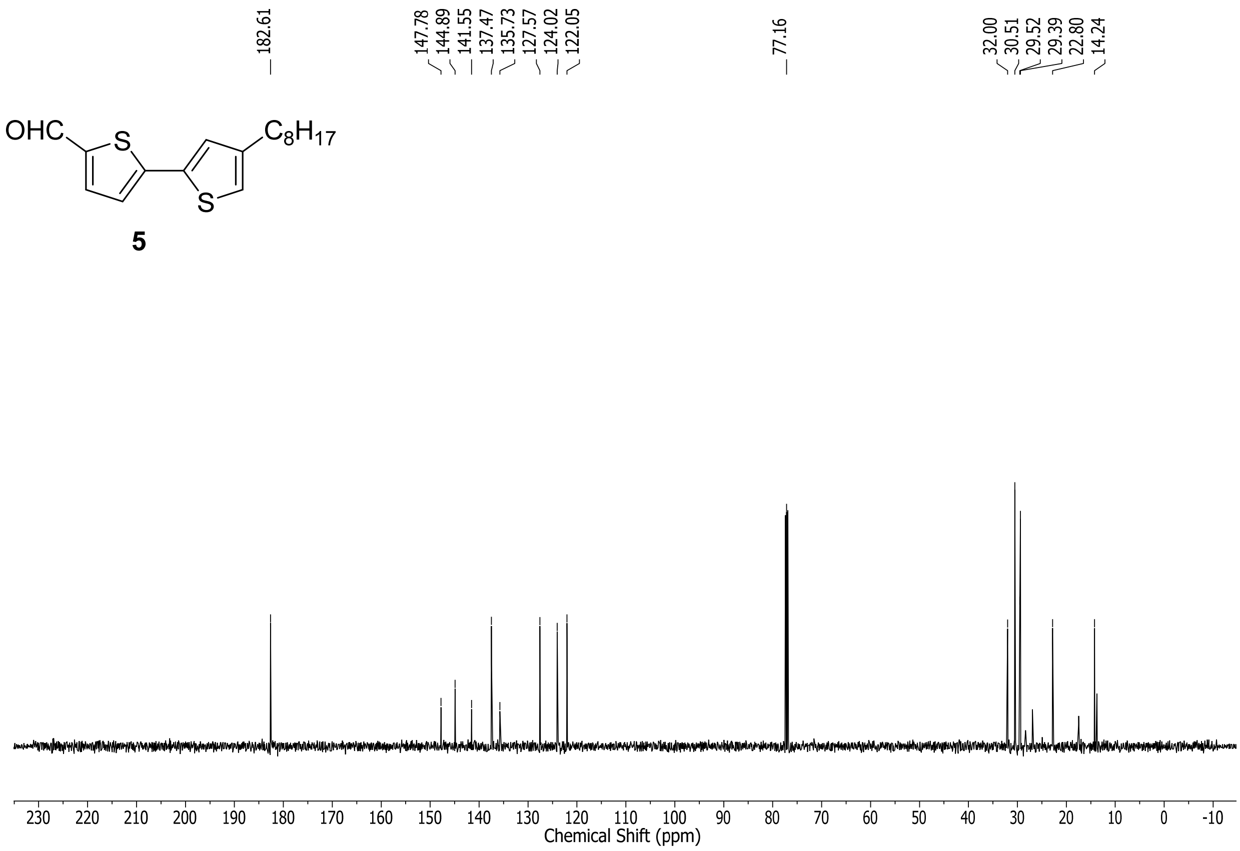
Chemical Shift (ppm)

1-*Z*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29.39
22.80
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C_8H_{17}
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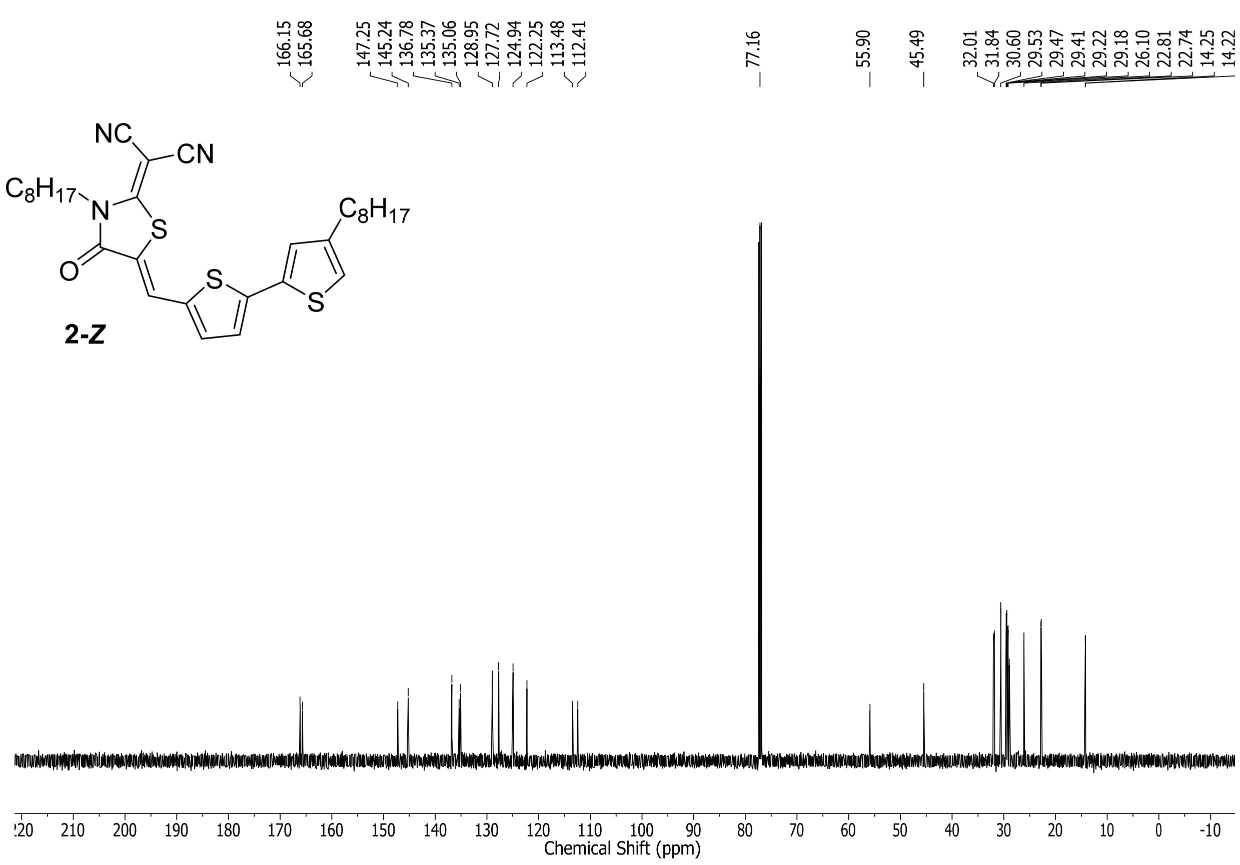
Chemical Shift (ppm)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30.60
29.53
29.47
29.41
29.22
29.18
26.10
22.81
22.74
14.25
14.22
NC
CN
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N
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2-Z
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Chemical Shift (ppm)

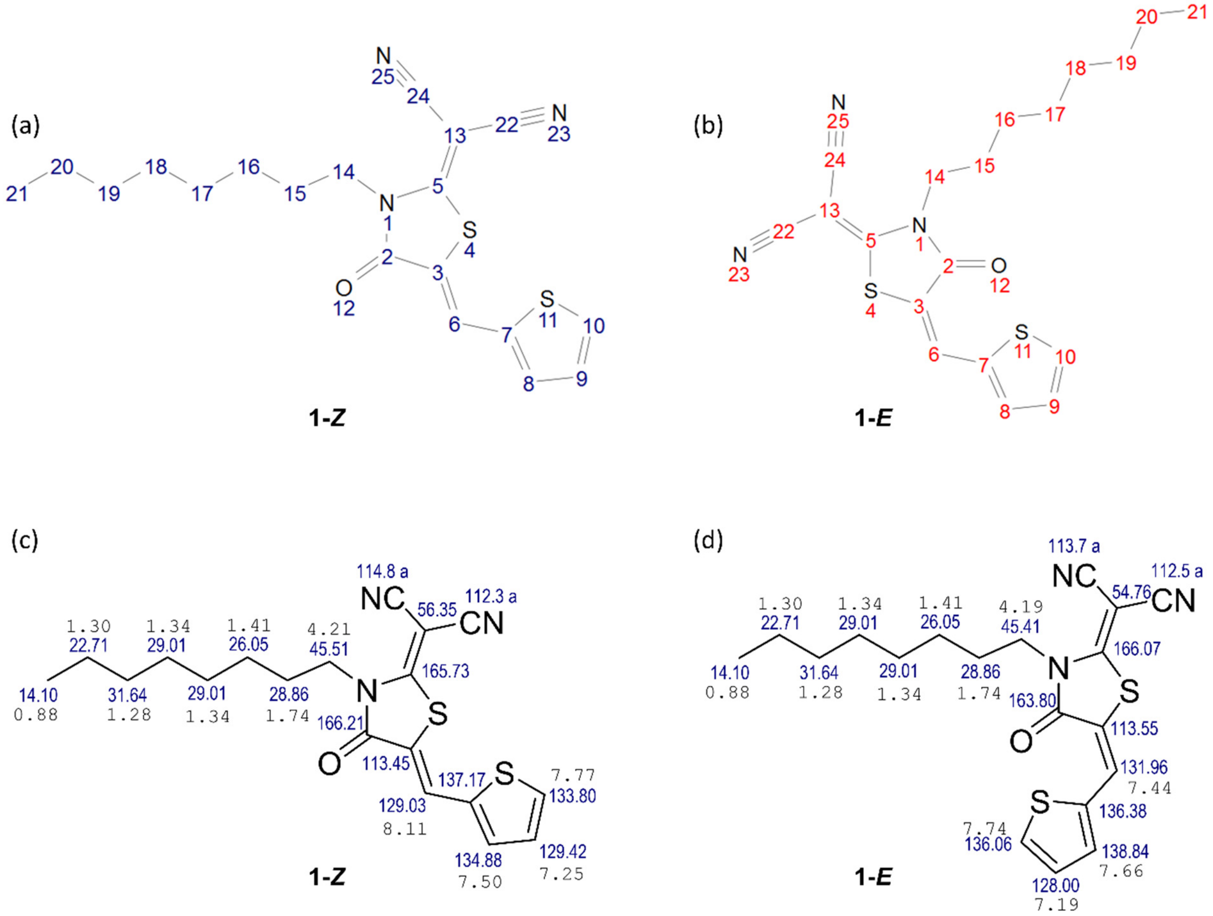


Figure S1. (a) ^{1}H and ^{13}C numbering system for **1-*Z*** (blue) used for gHSQC and gHMBC chemical shift assignments. (b) ^{1}H and ^{13}C numbering system for **1-*E*** (red) used for gHSQC and gHMBC chemical shift assignments. (c) Chemical shift assignments showing ^{1}H chemical shifts (black) and ^{13}C chemical shifts (blue) for **1-*Z***. (d) Assignments for **1-*E*** showing ^{1}H chemical shifts (black) and ^{13}C chemical shifts (blue).

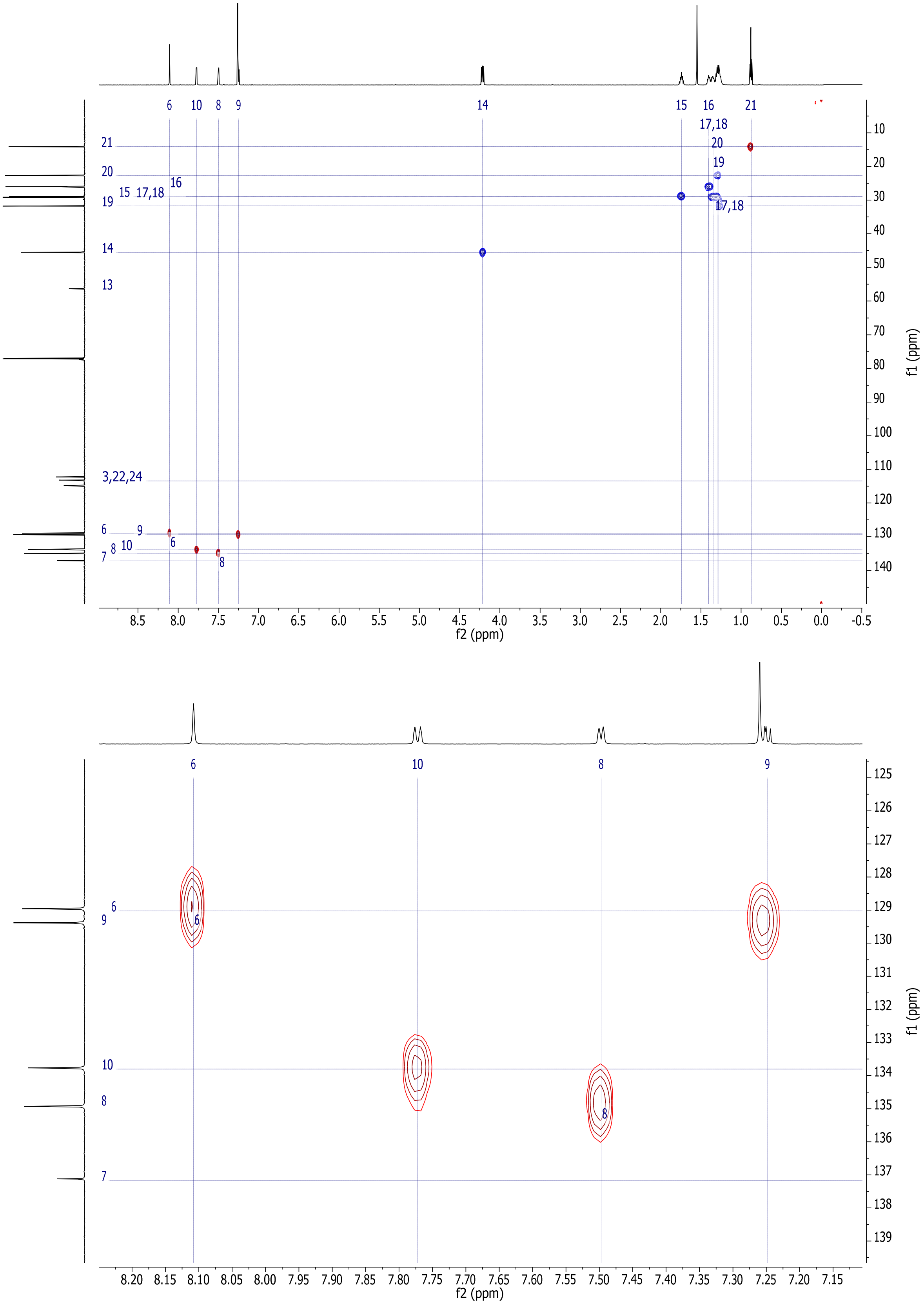
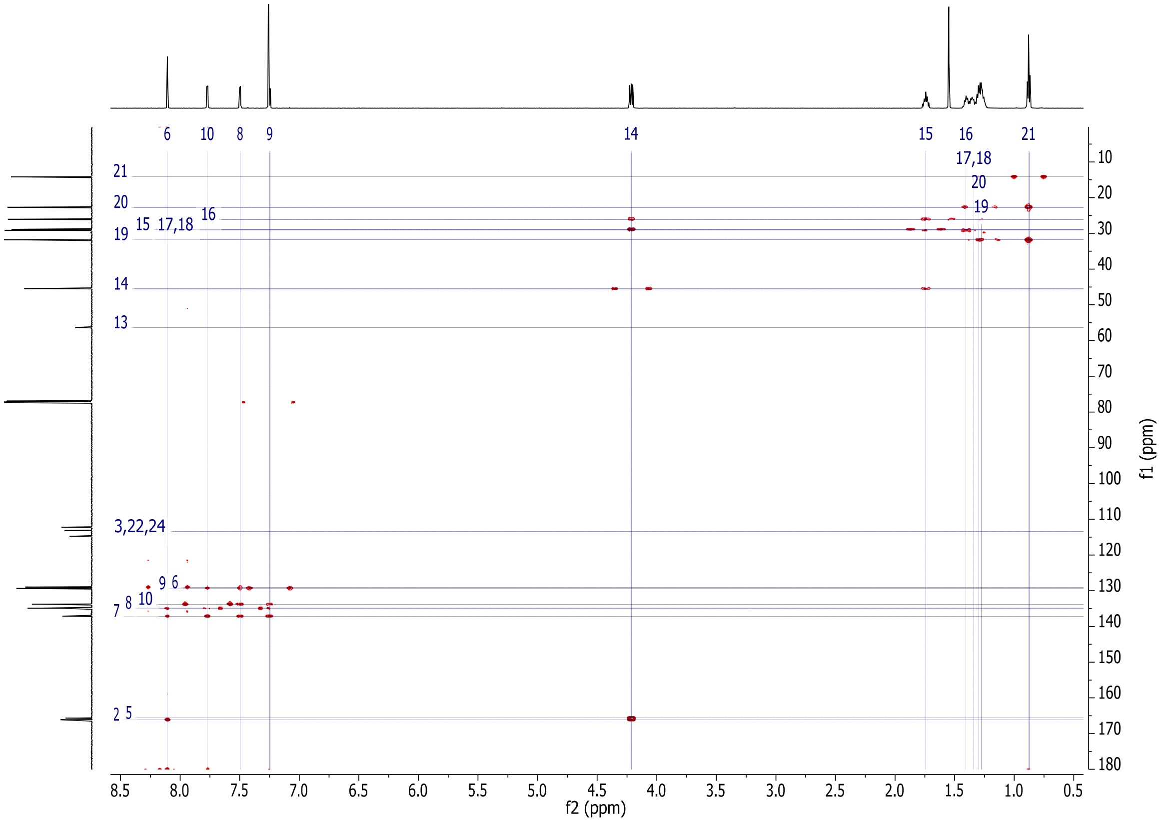


Figure S2. gHSQC spectrum of pure **1-*Z*** (top) and expanded gHSQC spectrum of pure **1-*Z*** (bottom).



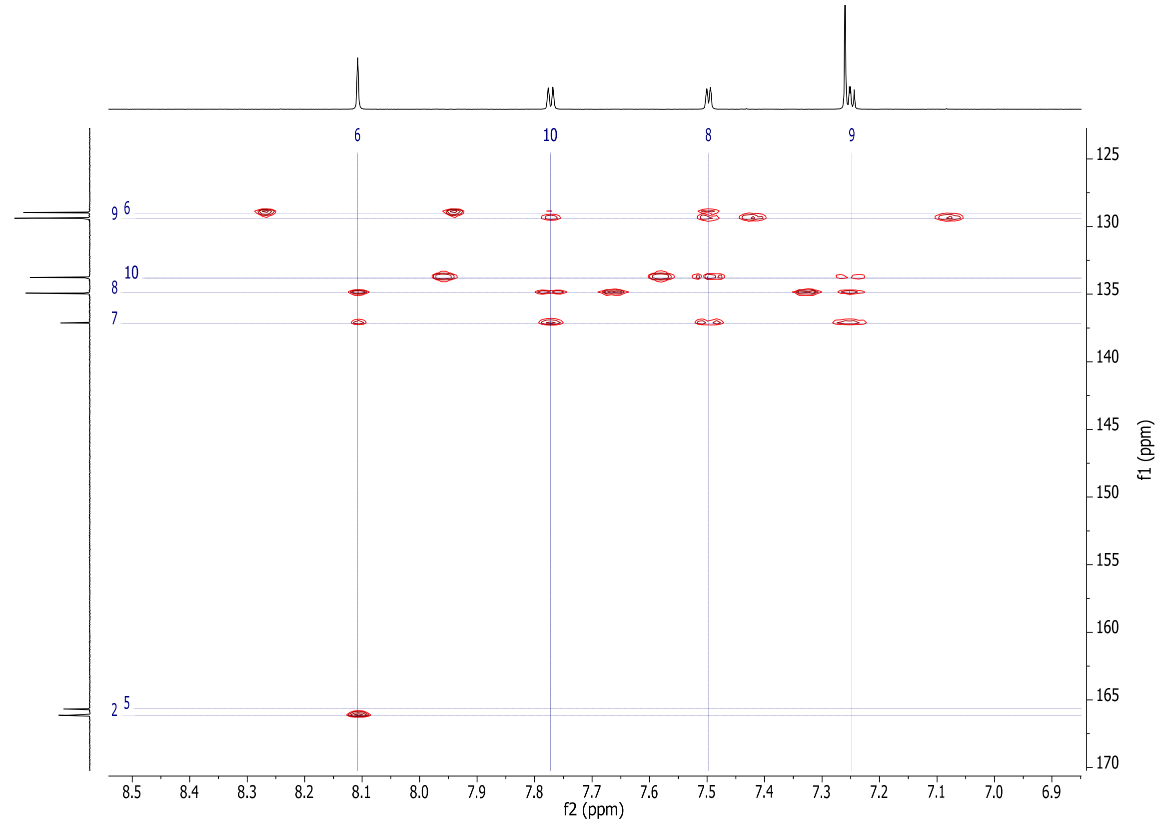
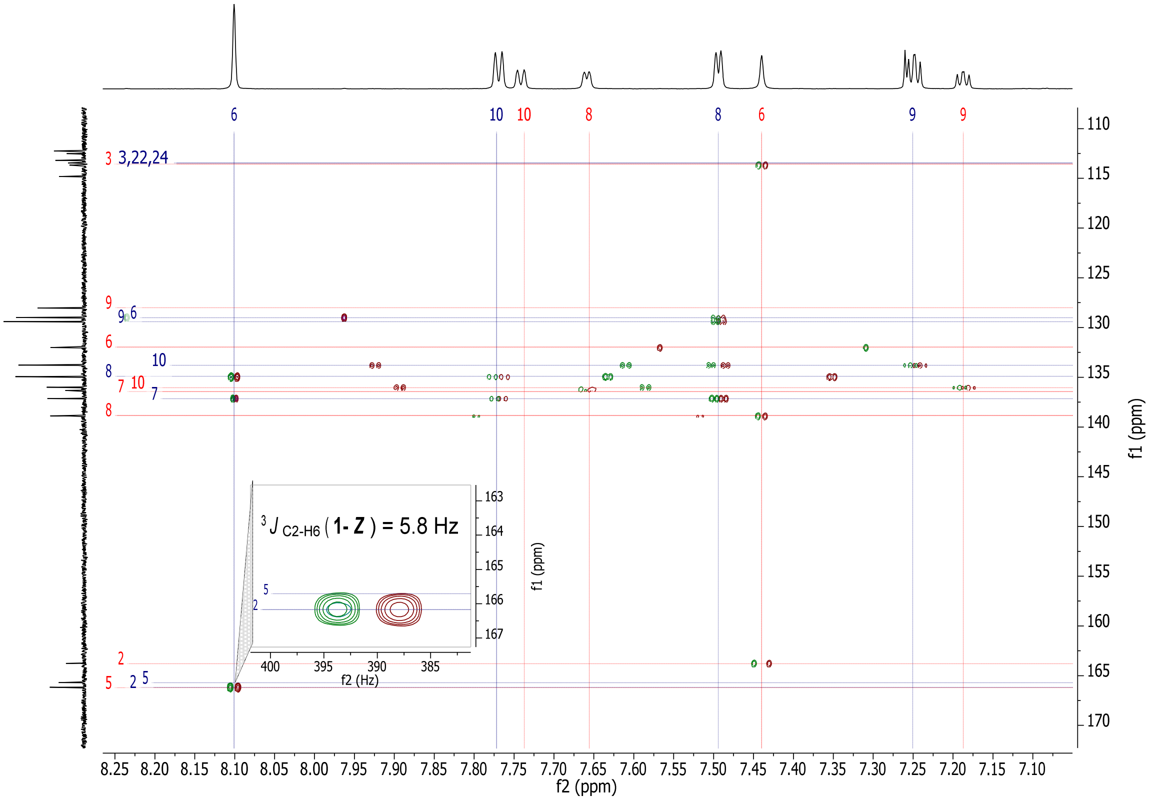


Figure S3. gHMBC spectrum of pure **1-*Z*** (top) and expanded gHMBC spectrum of pure **1-*Z*** (bottom).



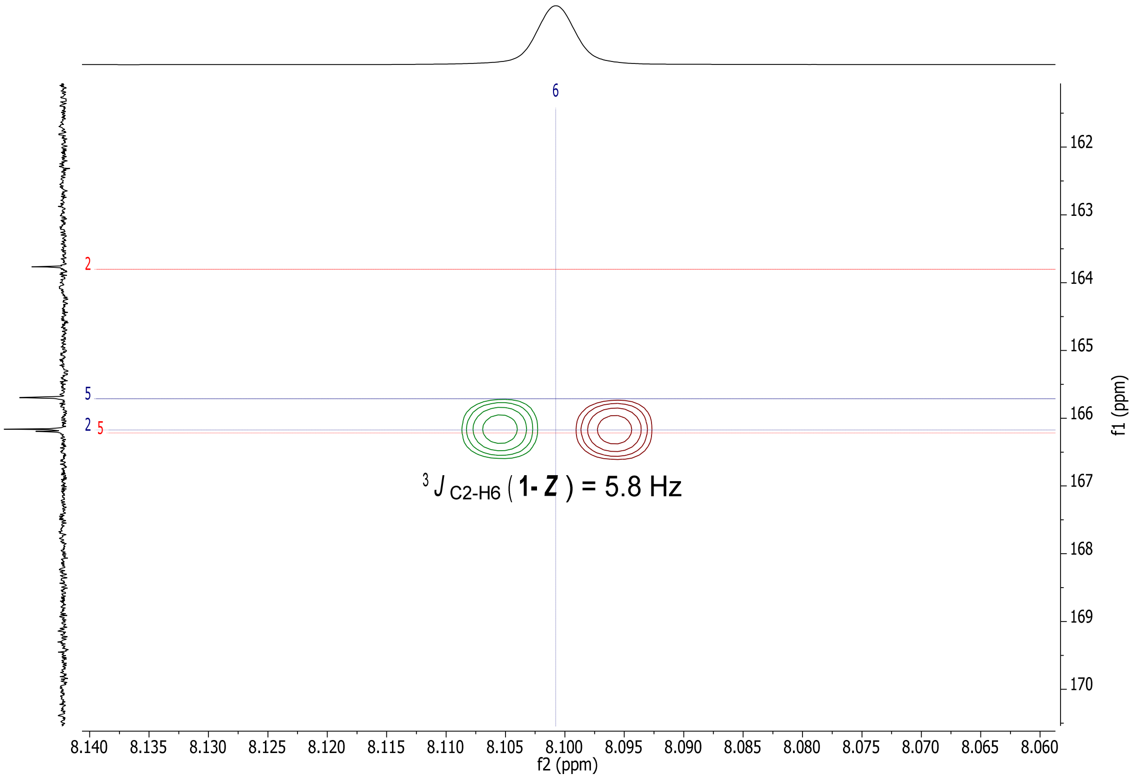
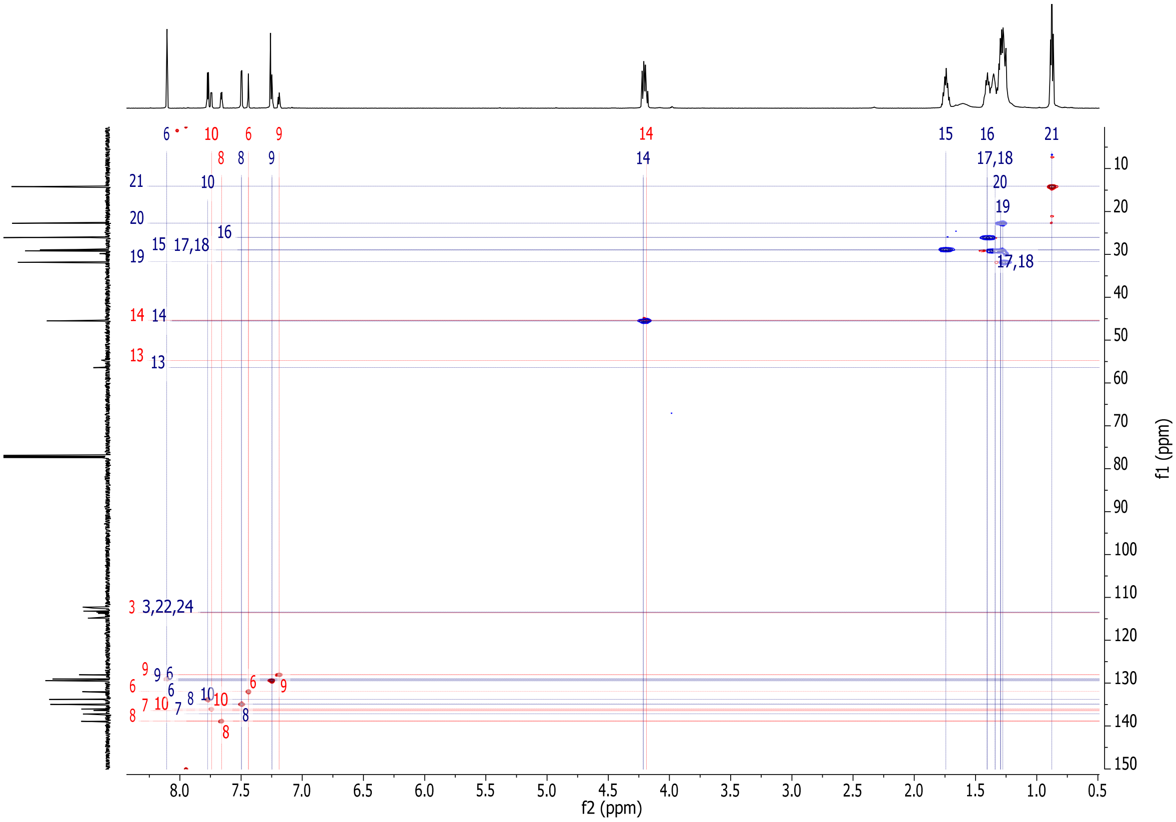


Figure S4. IPAP-HSMBC of **1-*Z/E*** mixture (top) and expanded region showing $^3J_{\text{C2-H6}}$ for **1-*Z*** (bottom).



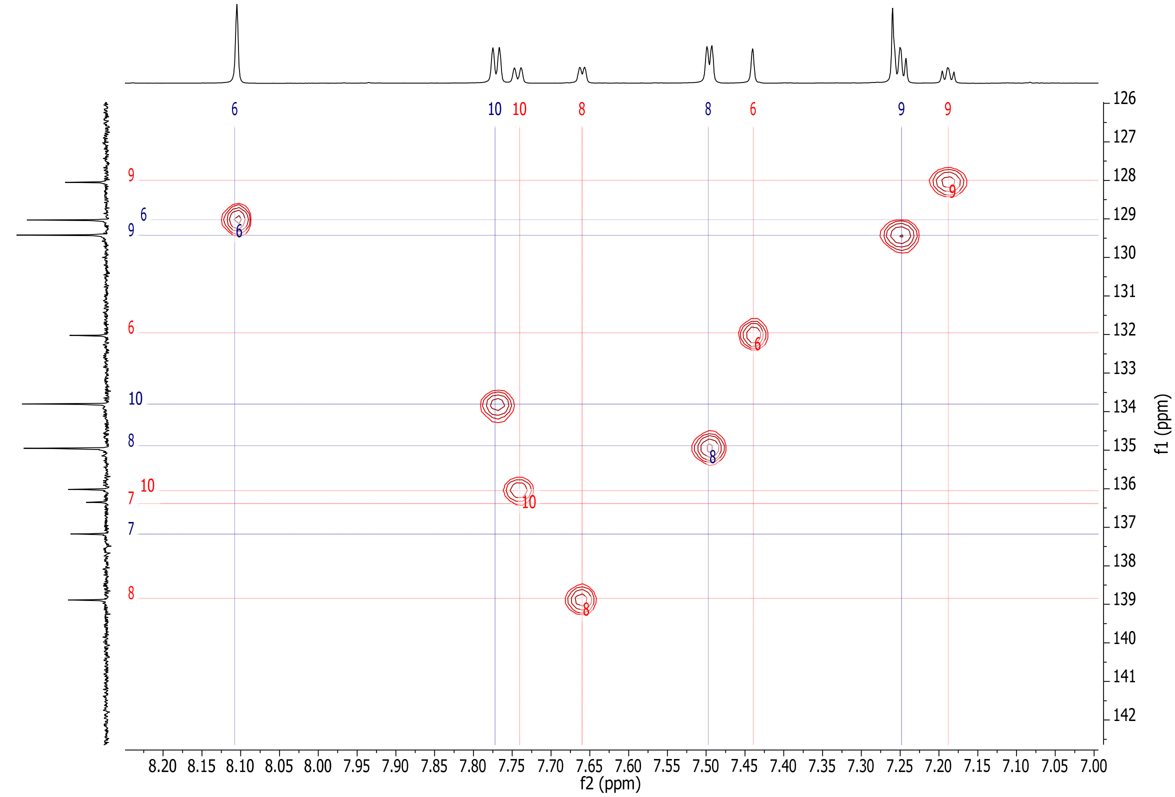


Figure S5. gHSQC of **1-*Z/E*** mixture (top) and expanded gHSQC spectrum of **1-*Z/E*** mixture (bottom).

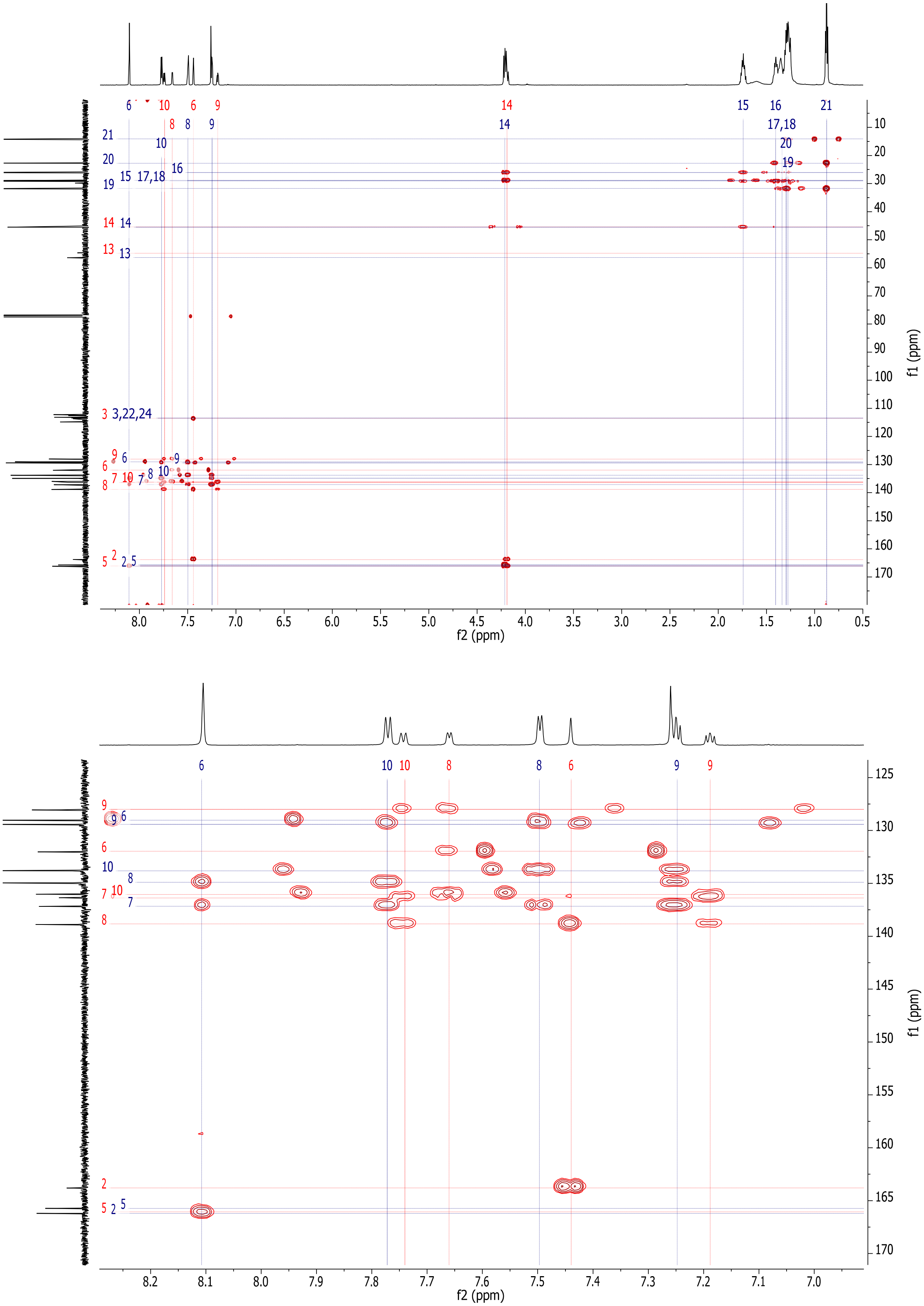


Figure S6. gHMBC of **1-*Z/E*** mixture (top) and expanded gHMBC spectrum of **1-*Z/E*** mixture (bottom).

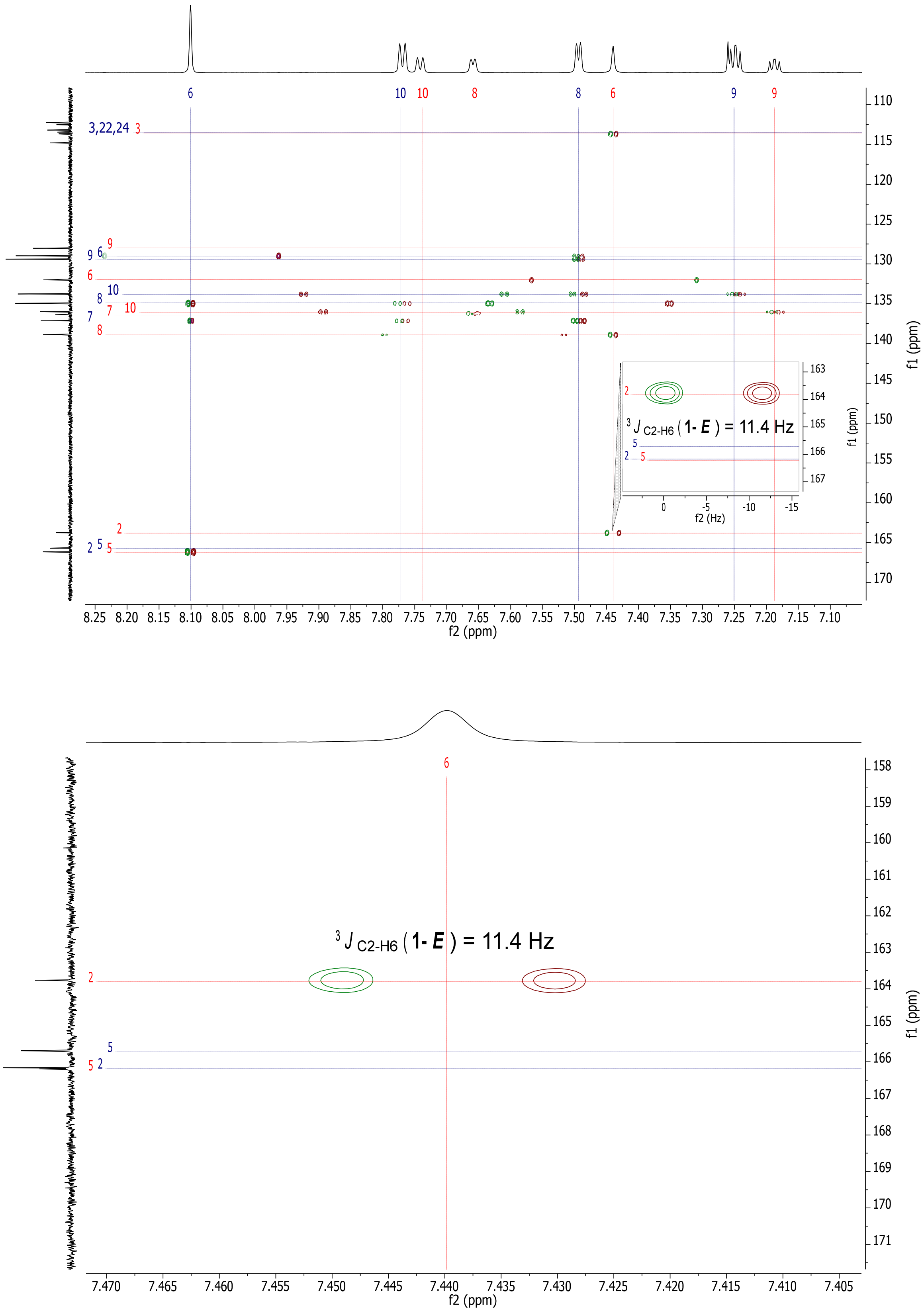


Figure S7. IPAP-HSMBC of **1-*Z/E*** mixture (top) and expanded region showing ${}^{3}J_{C2\text{-}H6}$ for **1-*E*** (bottom).

THIN LAYER CHROMATOGRAPHY

General Information

Reagents and solvents were purchased from commercial sources and used without further purification unless otherwise specified. Thin layer chromatography (TLC) was performed on SiO_2-60 F_{254} aluminum plates with visualization by UV light. Pure samples (*Z*-isomers) were spotted as solutions in dichloromethane. Samples of *Z*/*E* mixtures were obtained by irradiating a solution of pure target compound in dichloromethane with 254 nm light (**1-*Z***), 450 nm light (**2-*Z***), and ambient, laboratory light (***Z*-RCN-3T-Br**).

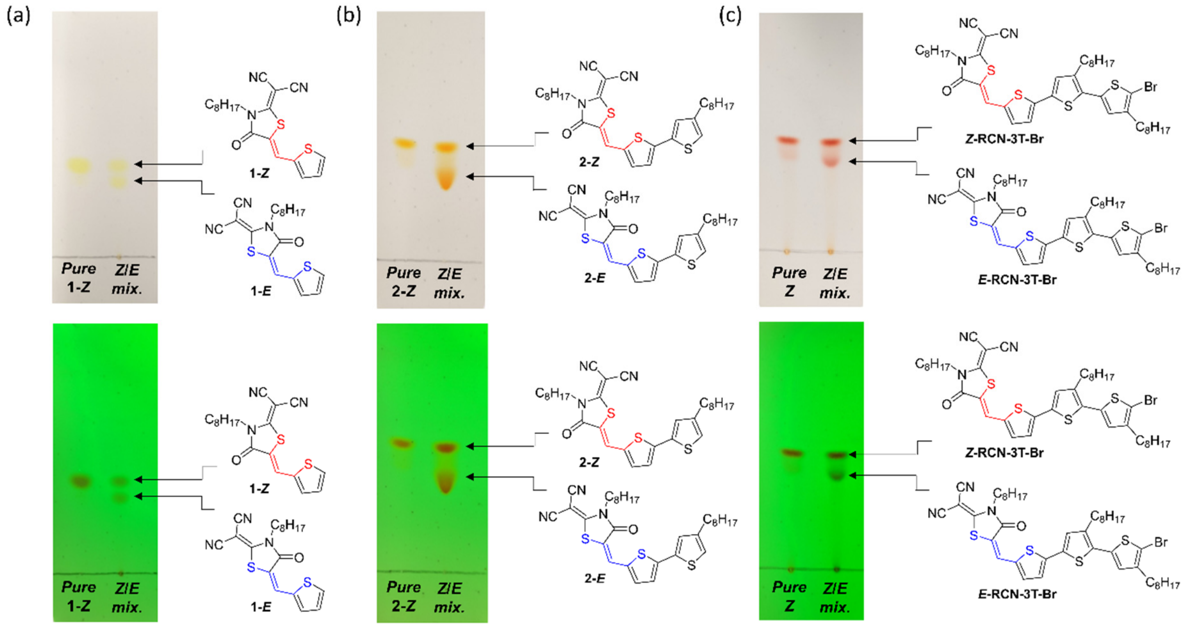


Figure S8. Thin layer chromatography (TLC) data showing pure *Z*-isomers compared to *Z*/*E* mixtures obtained after irradiation in dichloromethane of (a) compound **1**, (b) compound **2**, and (c) **RCN-3T-Br**.

NMR PHOTOISOMERIZATION STUDIES

General Information

^1H (^{13}C) NMR were recorded on an INOVA-500 (^1H at 500 MHz; ^{13}C at 125 MHz) spectrometer. In order to determine the photostationary state composition of each RCN-functionalized target molecule, a 15 mM stock solution in chloroform-*d* was prepared. Approximately 0.5 mL of the stock solution was placed in a conventional glass NMR tube unless otherwise specified. The samples were exposed to an appropriate irradiation wavelength and ^1H NMR spectra were recorded hourly. The integral ratios of signals corresponding to the *Z* isomer and the *E* isomer were compared to calculate a relative percentage of each species in solution. The samples were irradiated and ^1H NMR spectra were recorded until changes in the *Z*/*E* integral ratios were no longer observed, indicating that the photostationary state had been reached.

Irradiation Sources

Ultraviolet irradiation was achieved using a LSE Lighting (Model No. CFL15/UV/MED) compact fluorescent light bulb (15 Watt, 120 Volt) emitting a peak irradiation wavelength of 254 nm. Due to the heat given off from the UV bulb, a cooling fan was used for all irradiation experiments requiring 254 nm irradiation, resulting in a measured temperature at the hottest point near the bulb of 28 °C.

Blue LED irradiation was achieved using a Westinghouse Lighting (Model No. 3315100) 100-Watt Equivalent PAR38 Flood Blue Outdoor Weatherproof LED Light Bulb (15 Watt, 120 Volt) emitting a peak irradiation wavelength of 450 nm. No cooling fan was required for LED irradiation sources.

Green LED irradiation was achieved using Westinghouse Lighting (Model No. 3314900) 100-Watt Equivalent PAR38 Flood Green Outdoor Weatherproof LED Light Bulb (15 Watt, 120 Volt) emitting a peak irradiation wavelength of 525 nm. No cooling fan was required for LED irradiation sources.

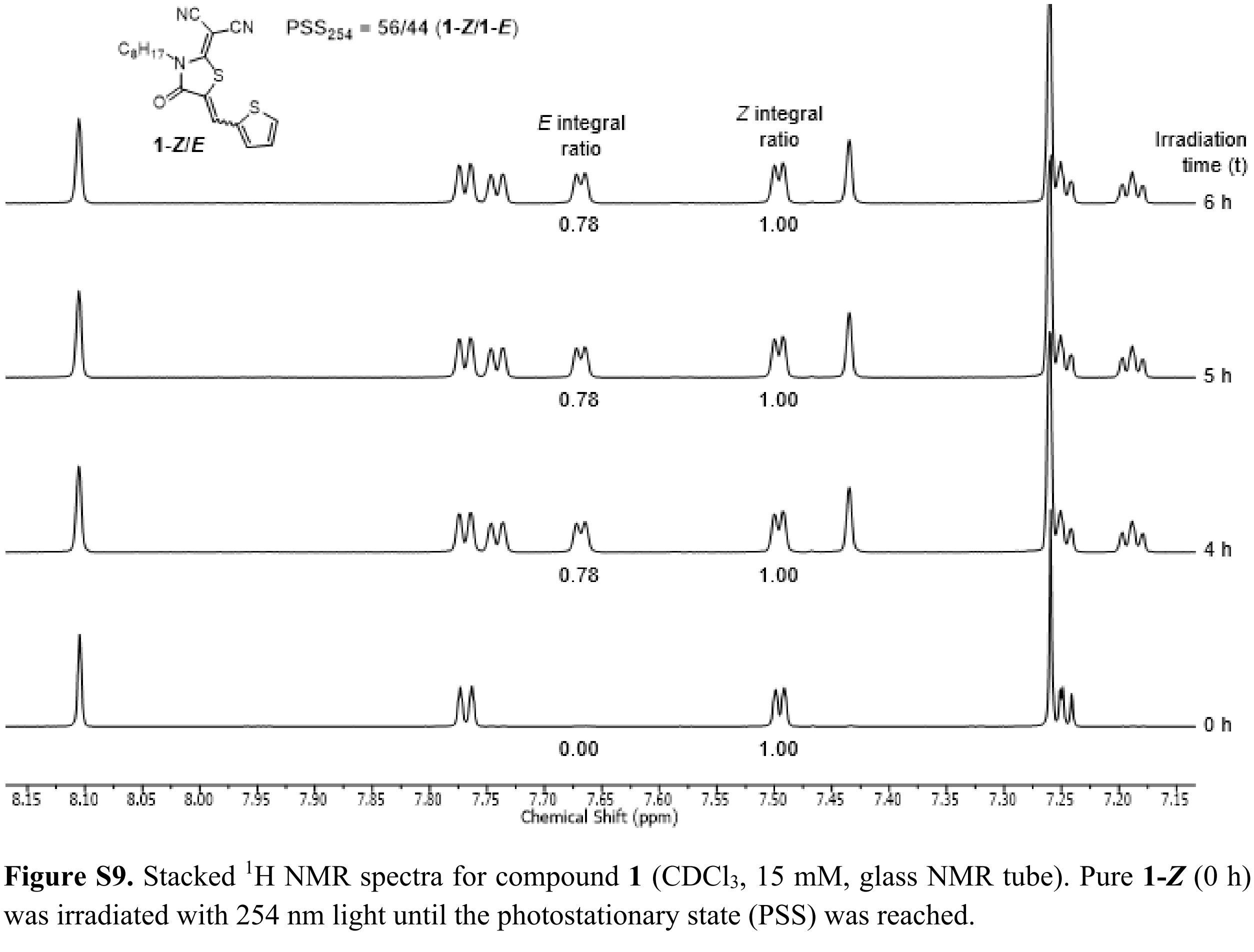


Figure S9. Stacked ^{1}H NMR spectra for compound **1** ($CDCl_3$, 15 mM, glass NMR tube). Pure **1-*Z*** (0 h) was irradiated with 254 nm light until the photostationary state (PSS) was reached.

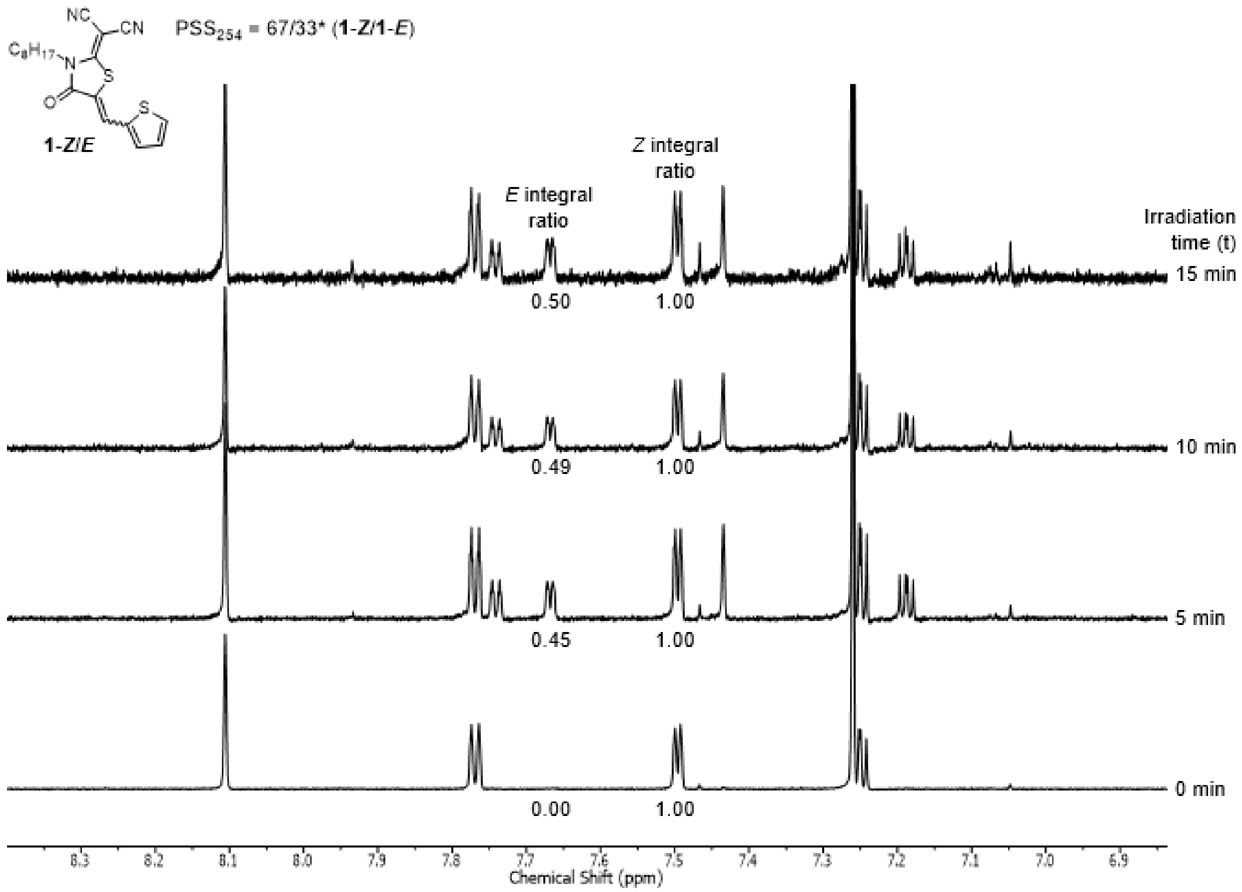


Figure S10. Stacked ^{1}H NMR spectra for compound **1** ($CDCl_3$, 15 mM, quartz NMR tube). Pure **1-*Z*** (0 h) was irradiated with 254 nm light until the photostationary state (PSS) was reached. *Significant photodegradation was observed after only 15 minutes of 254 nm irradiation of **1-*Z*** in a quartz NMR tube.

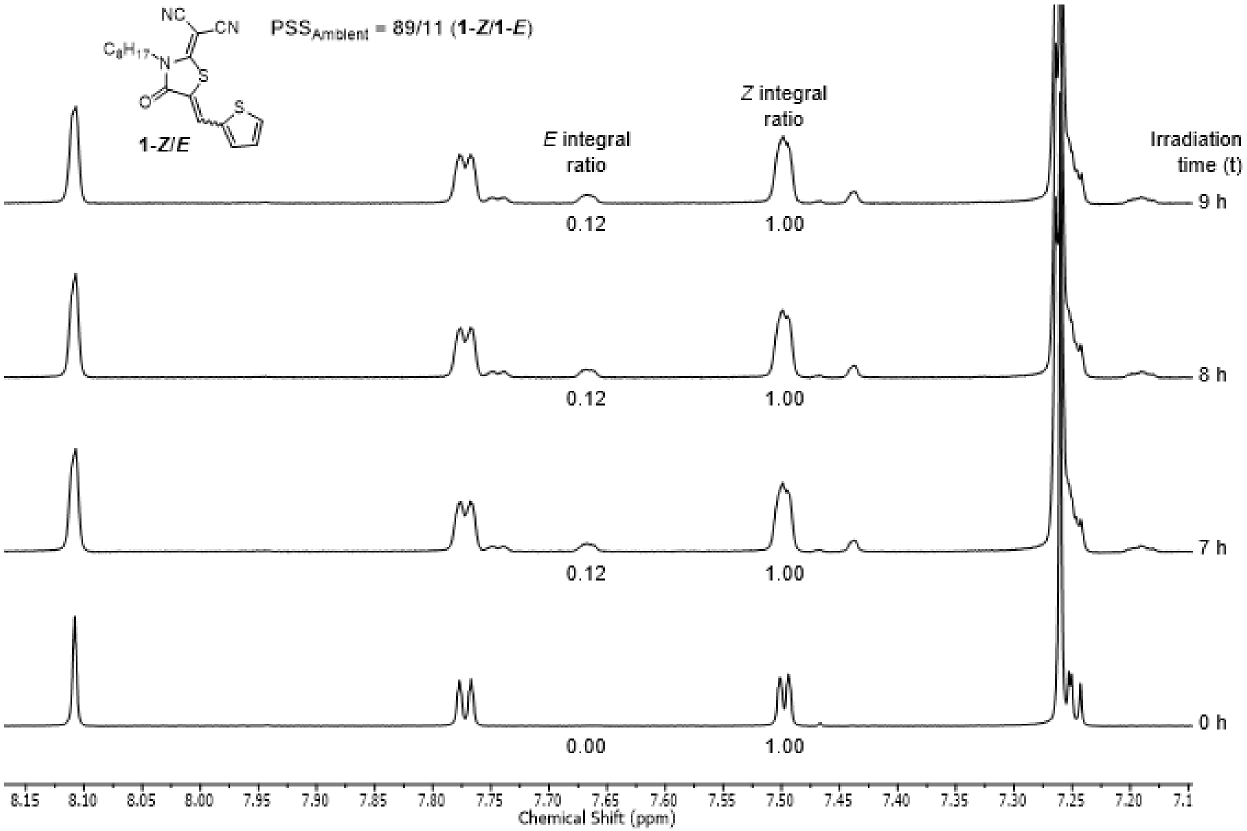


Figure S11. Stacked ^{1}H NMR spectra for compound **1** ($CDCl_3$, 15 mM, glass NMR tube). Pure **1-*Z*** (0 h) was irradiated with ambient light until the photostationary state (PSS) was reached.

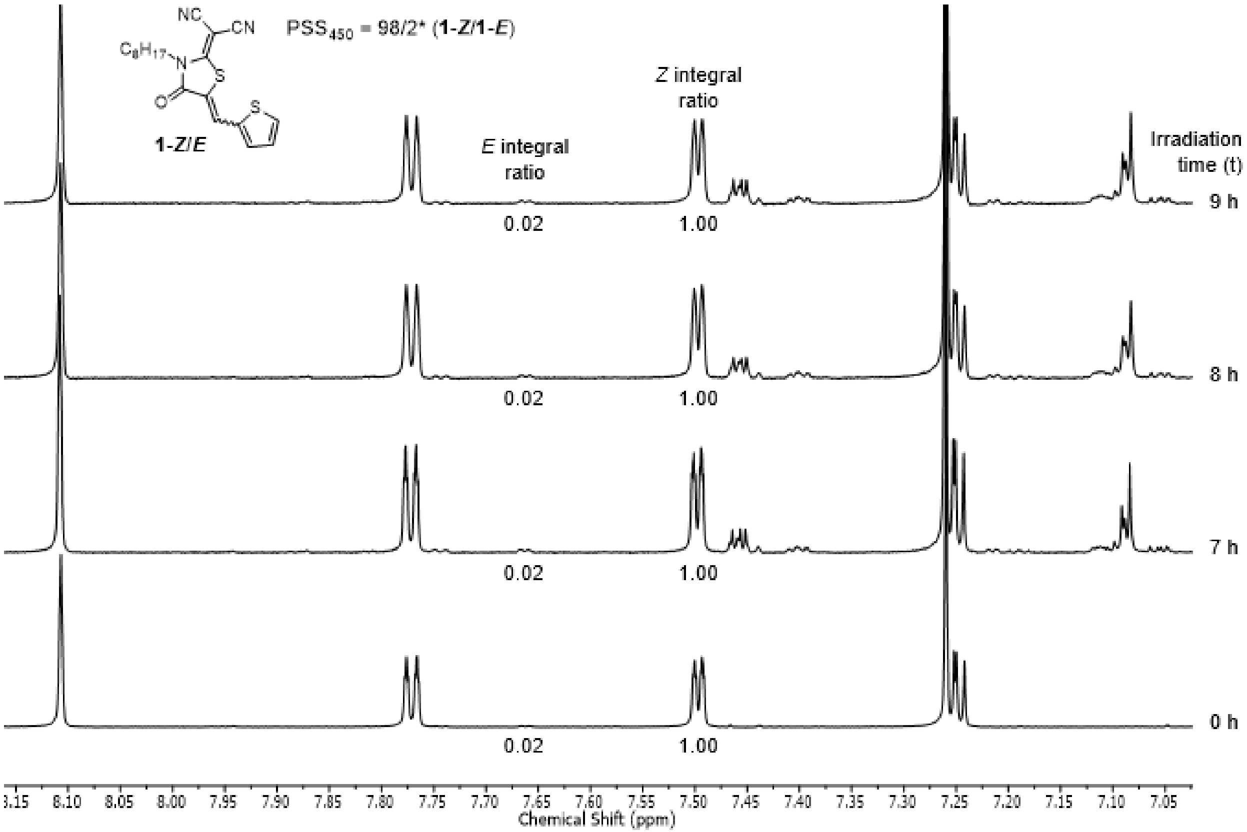


Figure S12. Stacked ^{1}H NMR spectra for compound **1** ($CDCl_3$, 15 mM, glass NMR tube). Pure **1-*Z*** (0 h) was irradiated with 450 nm light until the photostationary state (PSS) was reached.*450 nm irradiation of **1-*Z*** resulted in various photoproducts/photodegradation.

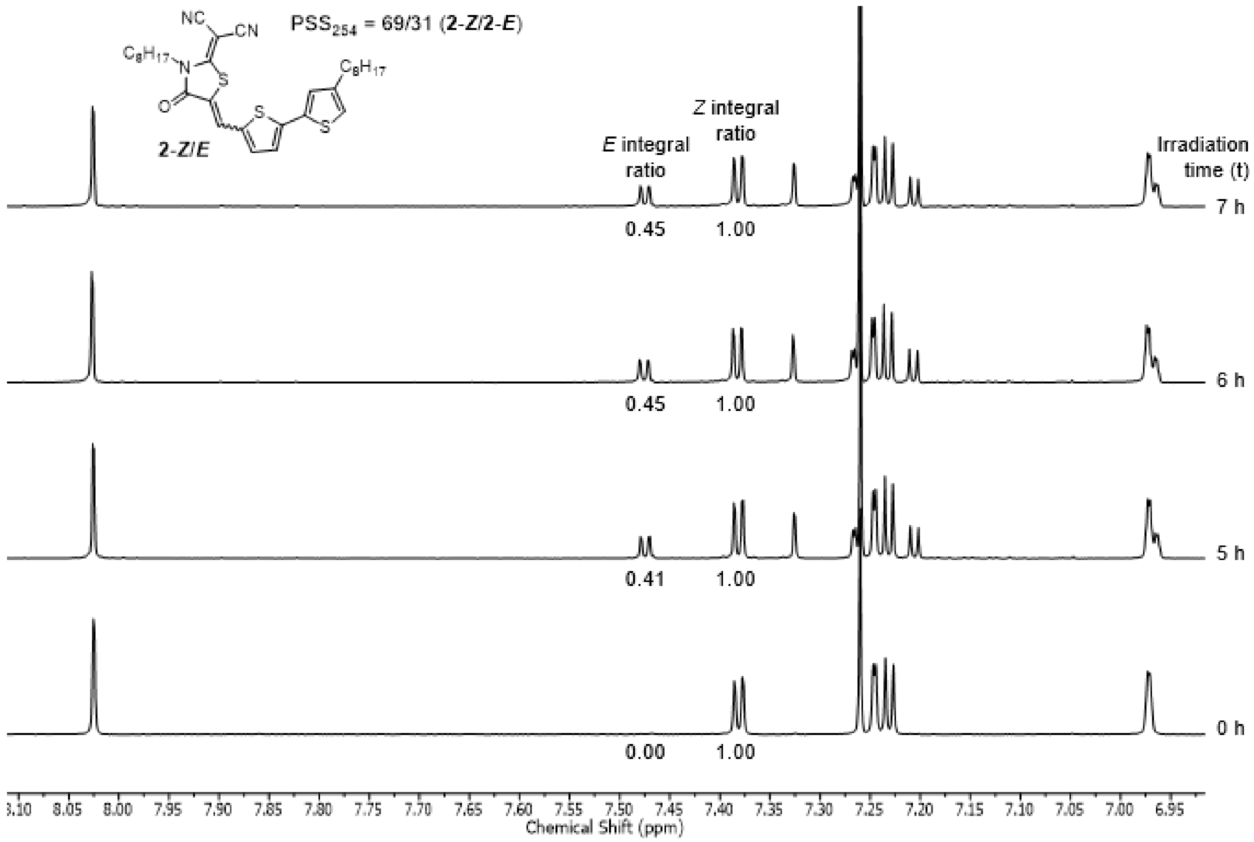


Figure S13. Stacked ^1H NMR spectra for compound **2** ($CDCl_3$, 15 mM, glass NMR tube). Pure **2-*Z*** (0 h) was irradiated with 254 nm light until the photostationary state (PSS) was reached.

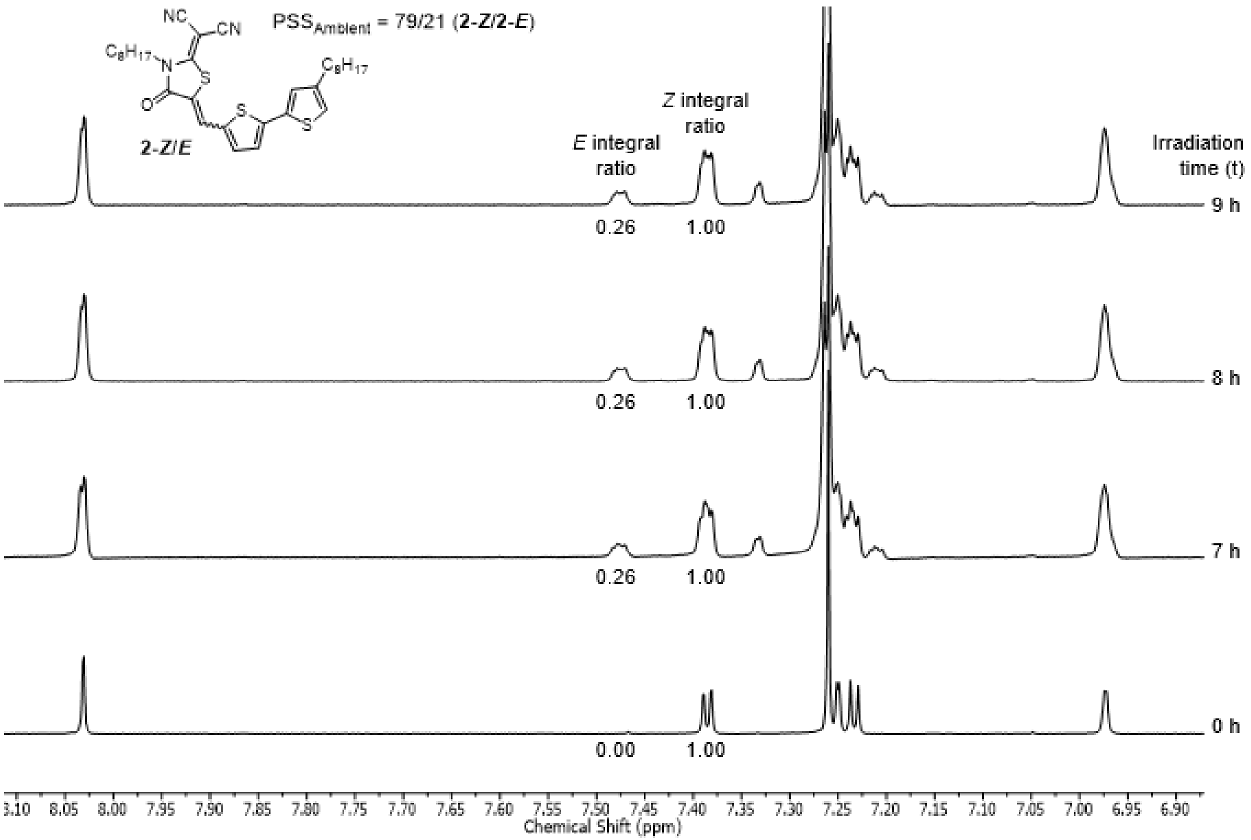


Figure S14. Stacked ^{1}H NMR spectra for compound **2** ($CDCl_3$, 15 mM, glass NMR tube). Pure **2-*Z*** (0 h) was irradiated with ambient light until the photostationary state (PSS) was reached.

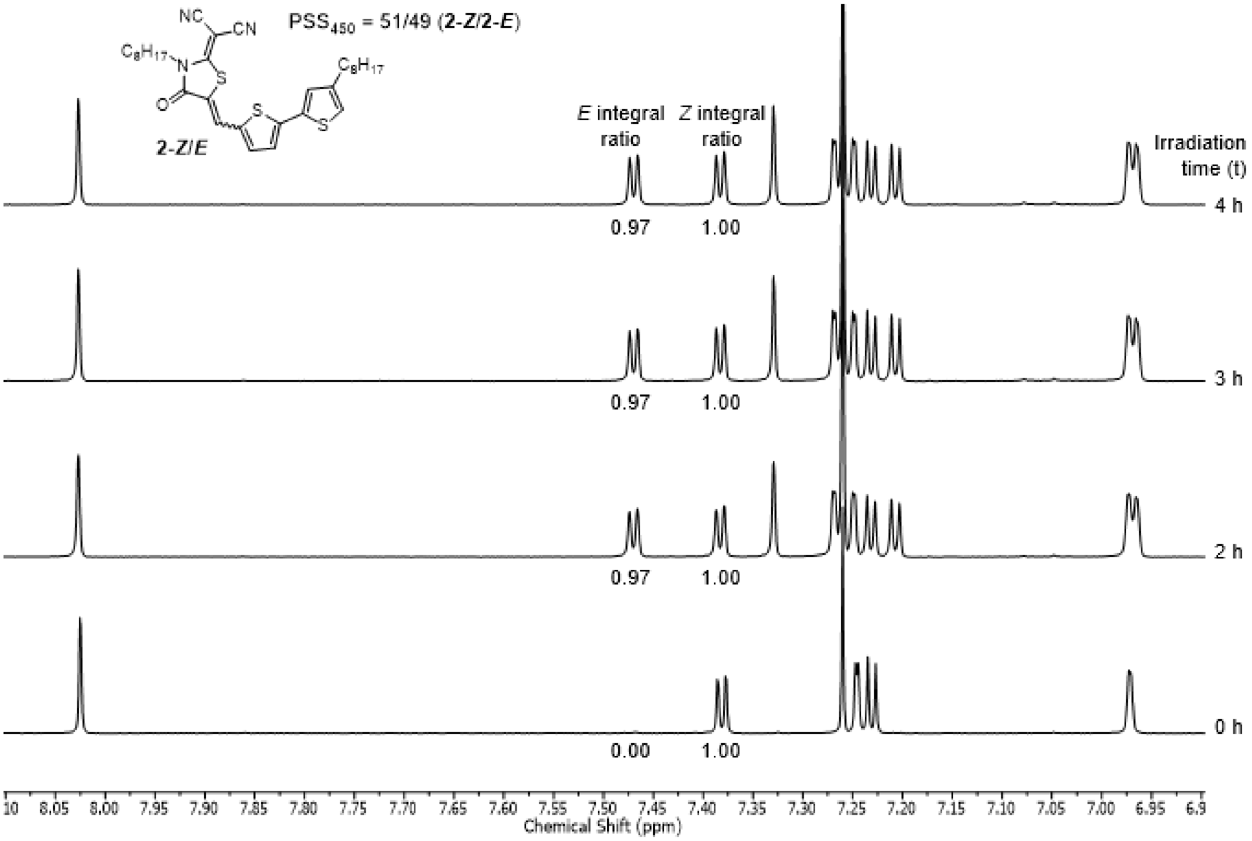


Figure S15. Stacked ^{1}H NMR spectra for compound **2** ($CDCl_3$, 15 mM, glass NMR tube). Pure **2-*Z*** (0 h) was irradiated with 450 nm light until the photostationary state (PSS) was reached.

UV-VIS PHOTOSTATIONARY STATE STUDIES

General Information

Solution absorption spectra were measured for 20 µM of the compounds in chloroform on a Perkin-Elmer Lambda 25 dual beam absorption spectrometer and a Cary 100 Bio spectrophotometer using 1 cm quartz cells. Spectrophotometric grade solvents were used for the absorption studies. Solutions of **1-*Z*** and **2-*Z*** (3.0 mL, 20 µM) in chloroform were prepared and transferred into a quartz cuvette for immediate UV/Vis absorption measurements. The solutions were then irradiated, and the UV-vis spectra were recorded to monitor the isomerization process. The photostationary states (PSS) were determined by continuous irradiation of the sample until no further changes in UV-vis spectra were observed.

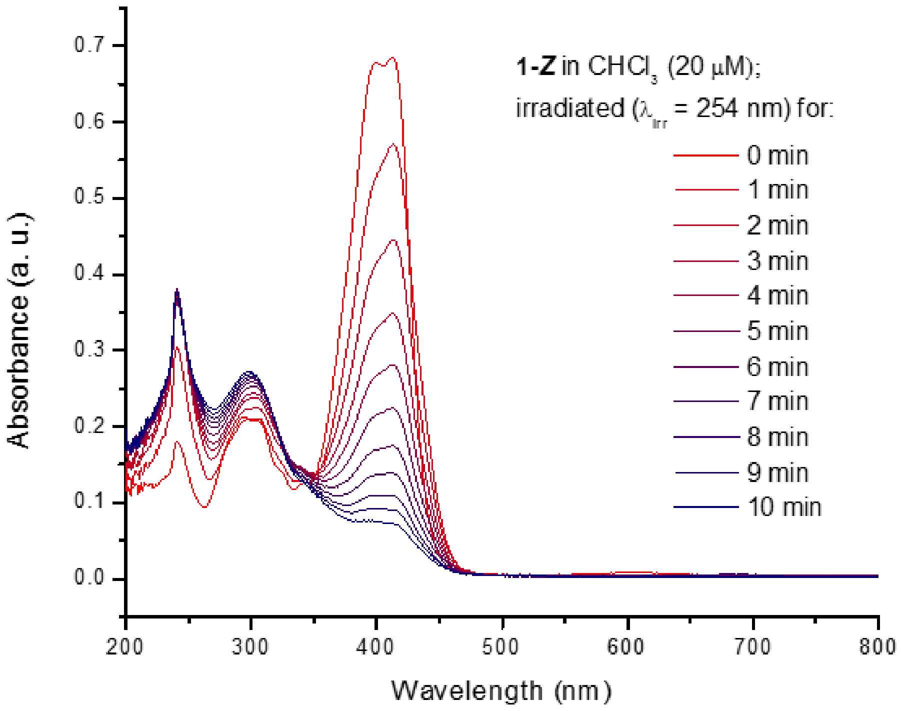


Figure S16. UV-vis spectra of **1-*Z*** in chloroform (0 min) upon irradiation with 254 nm light in a 1 cm quartz cuvette. *Significant photodegradation was observed for **1-*Z*** under 254 nm irradiation in quartz cuvette.

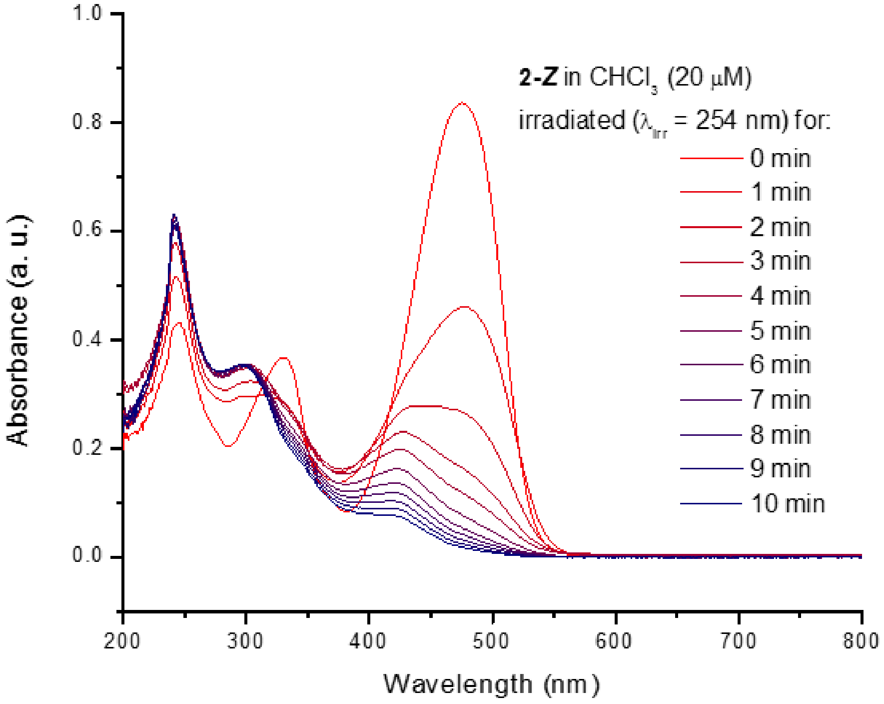


Figure S17. UV-vis spectra of **2-*Z*** in chloroform (0 min) upon irradiation with 254 nm light in a 1 cm quartz cuvette. *Significant photodegradation was observed for **2-*Z*** under 254 nm irradiation in quartz cuvette.

COMPUTATIONAL DETAILS

General Information

Ground state geometries and conformational analyses were conducted in the gas phase at the B3LYP/6-31+G(d) level as implemented in Gaussian 09. All octyl chains were truncated to methyl groups in order to reduce the computational cost. Excited state calculations were performed at the CAM-B3LYP/*aug*-cc-pVDZ level of theory using the coordinates from the previously optimized geometries. Molecular orbital plots were made using VMD from the Gaussian output files or using Avogadro visualization software. Frontier molecular orbital shapes were visualized using Avogadro molecular editor and visualization software.

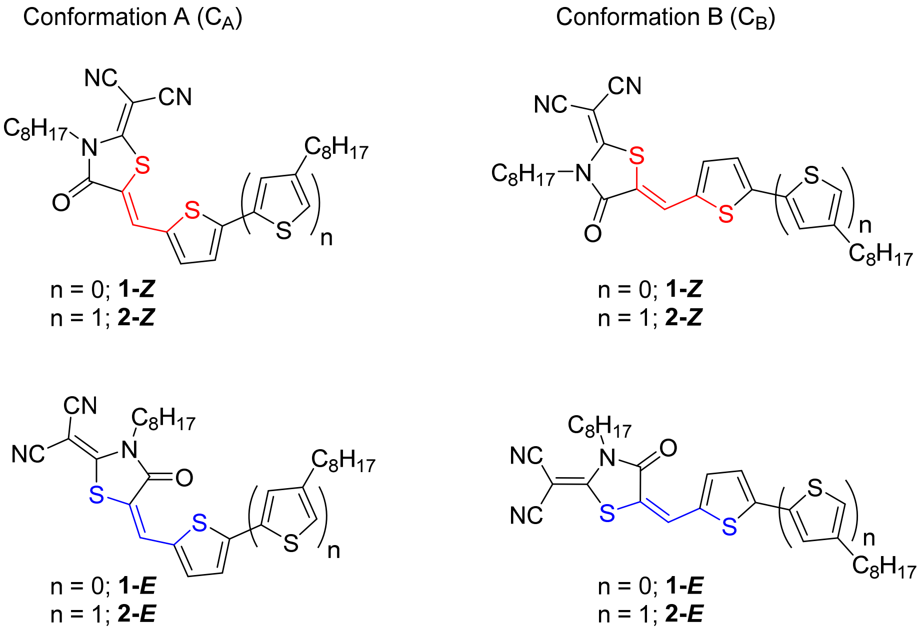
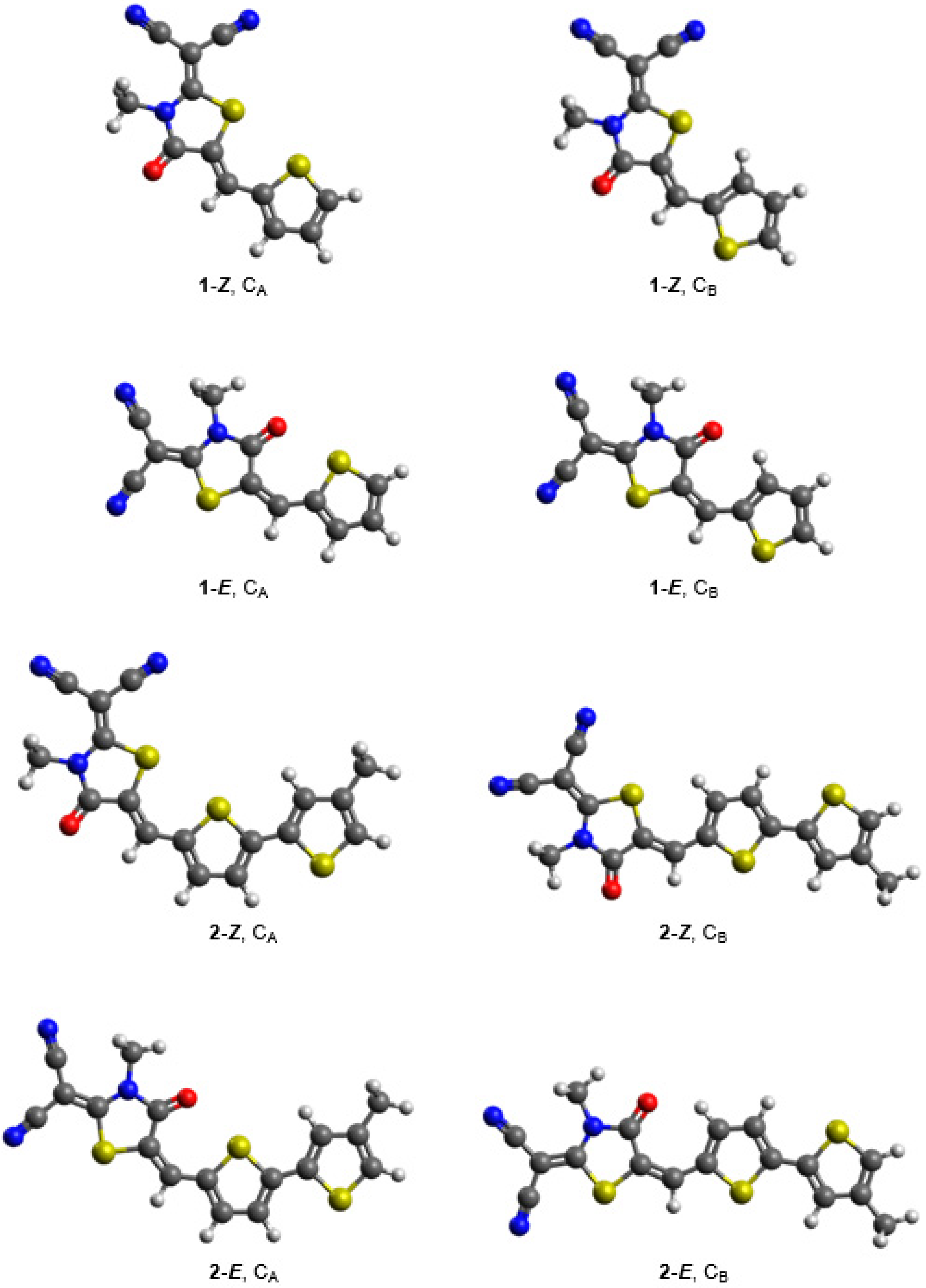


Figure S18. Line angle structures depicting optimized geometries used for conformational analysis of **1-*Z***, **1-*E***, **2-*Z***, and **2-*E*** in two lowest energy conformations.



1-*Z*, C_A

1-*Z*, C_B

1-*E*, C_A

1-*E*, C_B

2-*Z*, C_A

2-*Z*, C_B

2-*E*, C_A

2-*E*, C_B

Figure S19. DFT optimized geometries used for conformational analysis of **1-*Z***, **1-*E***, **2-*Z***, and **2-*E*** in the two modelled conformations.

	C_A (*Z*)	C_B (*Z*)	C_A (*E*)	C_B (*E*)
LUMO (eV) n = 0	-3.26	-3.30	-2.22	-3.30
n = 1	-3.28	-3.31	-3.24	-3.32
HOMO (eV) n = 0	-6.57	-6.61	-6.45	-6.48
n = 1	-6.06	-6.09	-5.98	-6.02
E_g (eV) n = 0	3.31	3.31	3.23	3.18
n = 1	2.78	2.78	2.74	2.70
Energy n = 0	0.00	0.44	3.39	3.95
(kcal/mol) n = 1	0.00	0.88	3.33	4.14
Dipole (D) n = 0	8.07	7.26	8.85	8.79
n = 1	8.52	9.81	10.53	11.09

Table S1. Gas phase DFT data summary for conformational analysis of **1-*Z***, **1-*E***, **2-*Z***, and **2-*E*** in two lowest energy conformations.

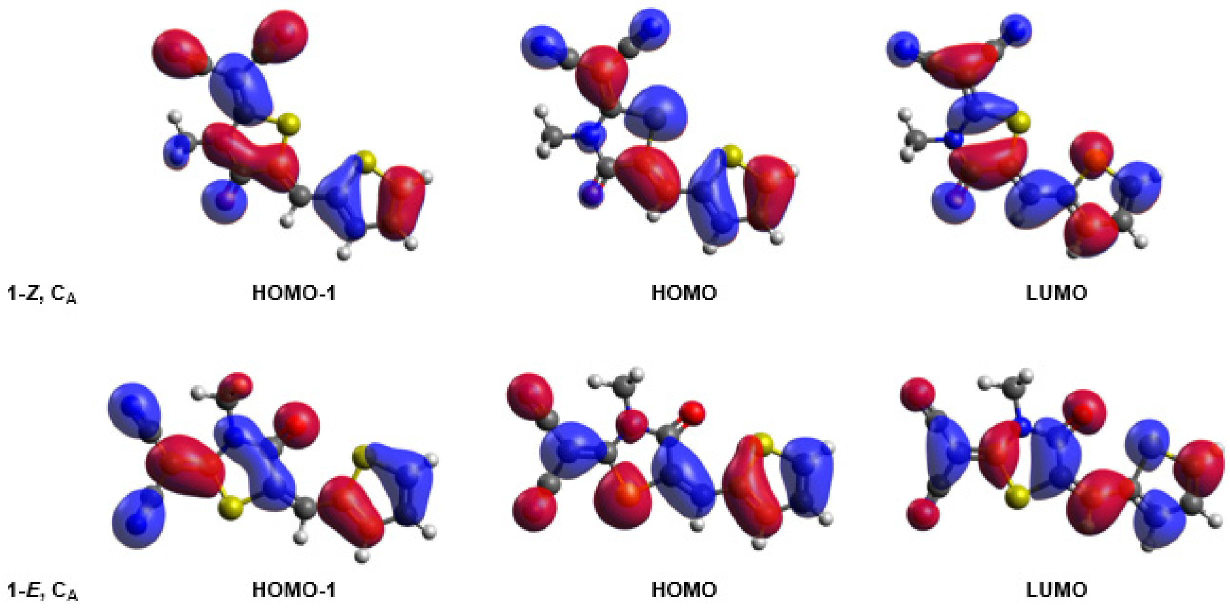


Figure S20. Frontier molecular orbital for **1-*Z*** and **1-*E*** (CAM-B3LYP/*aug*-cc-pVDZ).

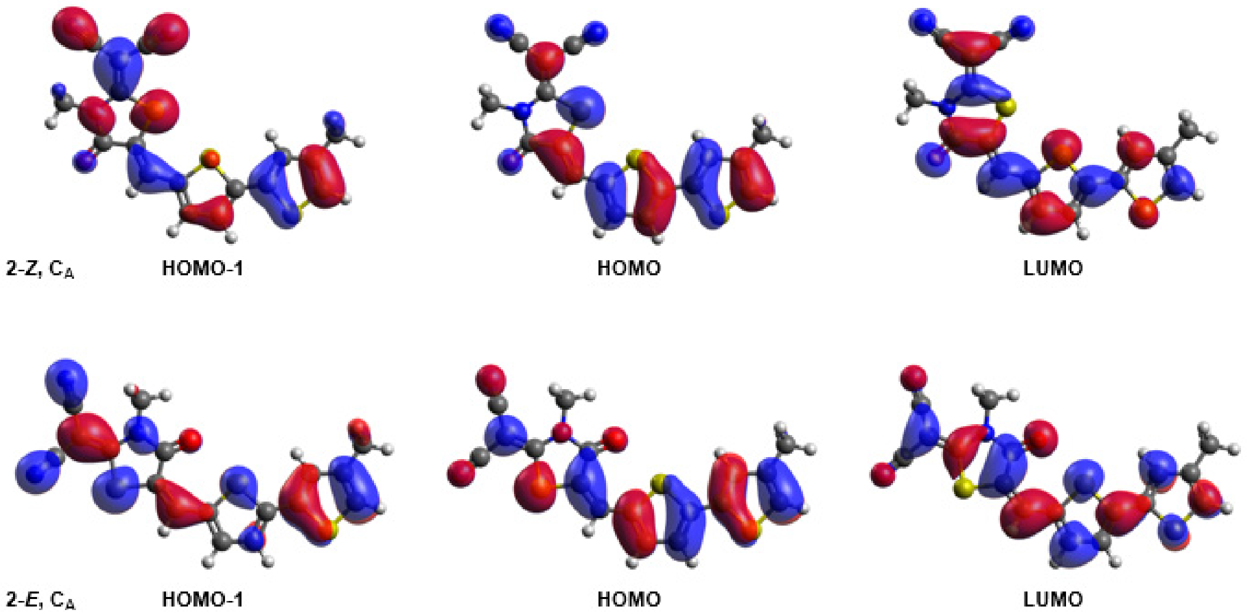


Figure S21. Frontier molecular orbital for **2-*Z*** and **2-*E*** (CAM-B3LYP/*aug*-cc-pVDZ).

Cartesian Coordinates: 1-*Z* (C_A), Total Energy = -1497.3221972 a. u.

0 1

C	-4.72385	-1.27709	-0.00045
C	-5.23946	-0.00189	-0.00043
C	-4.22967	0.99054	-0.00041
C	-2.93959	0.47296	-0.00042
S	-2.99695	-1.28400	-0.00046
C	-1.74300	1.26045	-0.00040
C	-0.43418	0.89676	-0.00042
S	0.25697	-0.72842	-0.00048
C	1.90037	-0.07074	0.00010
N	1.90411	1.29624	0.00011
C	0.63107	1.91615	-0.00047
O	0.48198	3.12585	0.00006
C	3.10550	2.13987	0.00066
C	2.98312	-0.93638	0.00055
C	4.35401	-0.54546	0.00111

N	5.48881	-0.27984	0.00156
C	2.73210	-2.34230	0.00044
N	2.51167	-3.48672	0.00039
H	-1.90123	2.33853	-0.00037
H	-4.42497	2.05813	-0.00039
H	-6.30268	0.21118	-0.00042
H	3.70567	1.95132	-0.89144
H	3.70485	1.95135	0.89331
H	2.75491	3.17216	0.00048
H	-5.26335	-2.21560	-0.00047

Cartesian Coordinates: 1-*Z* ($\mathrm{C_B}$), Total Energy = -1497.3214859 a. u.

0 1

C	5.17076	0.82965	0.00004
C	4.21882	1.82373	0.00013
C	2.89573	1.31685	0.00010
C	2.83726	-0.07216	-0.00004
S	4.46389	-0.74096	-0.00029
C	1.72656	-0.98088	-0.00005
H	1.95891	-2.04511	-0.00011
H	2.02302	1.95936	0.00022
H	4.45973	2.88108	0.00026
C	0.39354	-0.71798	-0.00000
C	-0.59440	-1.81232	-0.00000
O	-0.35851	-3.00778	0.00007
N	-1.91009	-1.28599	0.00014
C	-3.04719	-2.21442	0.00064
H	-3.65904	-2.06910	0.89291
H	-3.65880	-2.07047	-0.89204
H	-2.62278	-3.21861	0.00143
S	-0.41303	0.84962	0.00003

C	-2.00589	0.07709	0.00007
C	-3.14709	0.86383	-0.00001
C	-2.99326	2.28369	0.00016
N	-2.84721	3.43999	0.00031
C	-4.48707	0.37735	-0.00044
N	-5.59999	0.03151	-0.00084
H	6.24745	0.94124	0.00006

Cartesian Coordinates: 1-*E* (C_A), Total Energy = -1497.3167888 a. u.

0 1

C	5.15256	-0.53899	0.00043
C	5.29982	0.83080	0.00026
C	4.05299	1.49136	0.00013
C	2.95409	0.63032	0.00019
S	3.50422	-1.04228	0.00047
C	1.61265	1.13897	0.00005
C	0.37853	0.55800	0.00007
S	-1.10333	1.53959	-0.00016
C	-2.11521	0.09832	-0.00016
N	-1.36306	-1.04571	0.00006
C	0.04023	-0.86541	0.00027
O	0.82352	-1.80404	0.00033
C	-1.90278	-2.41062	0.00010
C	-3.49787	0.21933	-0.00038
C	-4.42385	-0.86358	-0.00042
N	-5.22216	-1.71301	-0.00046
C	-4.06205	1.53055	-0.00059
N	-4.50314	2.60955	-0.00077
H	1.60481	2.22951	-0.00010
H	3.93826	2.57098	-0.00003
H	6.25928	1.33605	0.00023

H	-2.50770	-2.58247	-0.89220
H	-2.50800	-2.58230	0.89223
H	-1.04327	-3.08110	0.00031
H	5.93794	-1.28524	0.00055

Cartesian Coordinates: 1-*E* (C_B), Total Energy = -1497.3159289 a. u.

0 1

C	-5.42914	0.01763	-0.00012
C	-4.78417	1.23469	-0.00005
C	-3.37359	1.11689	-0.00002
C	-2.93395	-0.20334	-0.00001
S	-4.32146	-1.29768	-0.00014
C	-1.63779	-0.82236	0.00006
H	-1.68408	-1.91195	0.00004
H	-2.68602	1.95083	0.00004
H	-5.30807	2.18441	-0.00004
C	-0.36679	-0.32096	0.00015
C	0.10013	1.07052	0.00023
O	-0.57940	2.08670	0.00007
N	1.51583	1.11817	0.00013
C	2.18062	2.42682	0.00009
H	2.79935	2.54090	0.89220
H	2.79902	2.54103	-0.89224
H	1.38822	3.17511	0.00028
S	1.02548	-1.42963	0.00017
C	2.16270	-0.08799	0.00009
C	3.52893	-0.33341	-0.00004
C	3.97127	-1.69059	-0.00003
N	4.31172	-2.80543	-0.00004
C	4.54989	0.66036	-0.00022
N	5.42235	1.43344	-0.00037

H	-6.49545	-0.16991	-0.00016

Cartesian Coordinates: 2-*Z* (C_A), Total Energy = -2088.4636562 a. u.

0 1

C	6.40496	0.85704	-0.00066
C	5.45316	1.84825	-0.00063
C	4.13413	1.30164	-0.00054
C	4.09150	-0.07934	-0.00050
S	5.72040	-0.73457	-0.00050
C	2.93850	-0.95004	-0.00043
C	2.89816	-2.33931	-0.00049
C	1.59354	-2.86412	-0.00039
C	0.59393	-1.89516	-0.00025
S	1.31748	-0.29114	-0.00025
C	-0.80629	-2.16385	-0.00013
C	-1.88060	-1.32655	0.00000
S	-1.89494	0.43952	0.00007
C	-3.66360	0.46437	0.00044
N	-4.19077	-0.79563	0.00043
C	-3.25133	-1.85829	0.00008
O	-3.58133	-3.03274	0.00025
C	-5.62325	-1.11438	0.00074
C	-4.33143	1.68081	0.00073
C	-5.74687	1.84639	0.00108
N	-6.89691	2.03658	0.00137
C	-3.55876	2.88135	0.00068
N	-2.91319	3.85193	0.00064
H	-1.07224	-3.22066	-0.00015
H	1.36867	-3.92594	-0.00041
H	3.79199	-2.95394	-0.00060
H	3.24070	1.91955	-0.00053

H	-6.10584	-0.71054	-0.89135
H	-6.10541	-0.71076	0.89315
H	-5.69440	-2.20228	0.00061
H	7.48148	0.97470	-0.00074
C	5.75161	3.32431	-0.00072
H	5.32534	3.81540	-0.88418
H	5.32546	3.81547	0.88277
H	6.82987	3.51110	-0.00080

Cartesian Coordinates: 2-*Z* (C_B) Total Energy = -2088.4622778 a. u.

0 1

C	6.88970	0.98658	-0.00158
C	6.75928	-0.38133	0.00110
C	5.38595	-0.77205	0.00170
C	4.49483	0.28341	-0.00048
S	5.36439	1.80818	-0.00334
C	3.04942	0.24891	-0.00047
C	2.15900	1.31676	0.00031
C	0.80566	0.93025	0.00023
C	0.61756	-0.44919	-0.00054
S	2.17924	-1.26310	-0.00165
C	-0.56631	-1.24925	-0.00067
H	-0.43354	-2.33051	-0.00127
H	-0.00474	1.64987	0.00094
H	2.48152	2.35255	0.00115
H	5.06862	-1.81098	0.00388
C	-1.87373	-0.86702	-0.00021
C	-2.95385	-1.86506	-0.00047
O	-2.83032	-3.07836	-0.00106
N	-4.21818	-1.22071	0.00011
C	-5.43418	-2.04251	0.00033

H	-6.03073	-1.84317	0.89260
H	-6.03073	-1.84375	-0.89208
H	-5.10182	-3.08085	0.00064
S	-2.53396	0.76753	0.00070
C	-4.19010	0.14451	0.00068
C	-5.25617	1.03200	0.00114
C	-4.97530	2.43193	0.00191
N	-4.72660	3.57070	0.00256
C	-6.63419	0.66818	0.00073
N	-7.77393	0.42417	0.00036
H	7.80635	1.56316	-0.00263
C	7.91046	-1.35244	0.00318
H	7.88215	-2.00013	0.88830
H	7.88228	-2.00377	-0.87926
H	8.87133	-0.82857	0.00217

Cartesian Coordinates: 2-*E* (C_A), Total Energy = -2088.4583502 a. u.

0 1

C	-6.76433	0.47480	0.00077
C	-5.94425	1.57777	0.00078
C	-4.56721	1.20158	0.00058
C	-4.35033	-0.16327	0.00043
S	-5.88493	-1.01751	0.00050
C	-3.09513	-0.88034	0.00023
C	-2.89520	-2.25783	0.00013
C	-1.53937	-2.61168	-0.00006
C	-0.66008	-1.52455	-0.00012
S	-1.57480	-0.01886	0.00006
C	0.75504	-1.71253	-0.00030
C	1.82681	-0.86215	-0.00041
S	3.49172	-1.48294	-0.00063

C	4.15173	0.14874	-0.00044
N	3.15989	1.09152	-0.00030
C	1.83252	0.59667	-0.00038
O	0.85743	1.33675	-0.00006
C	3.37555	2.54285	-0.00008
C	5.52708	0.34452	-0.00043
C	6.18307	1.60895	-0.00026
N	6.76736	2.61784	-0.00013
C	6.37364	-0.80434	-0.00059
N	7.04764	-1.75558	-0.00072
H	1.01224	-2.77238	-0.00037
H	-1.18405	-3.63767	-0.00014
H	-3.70583	-2.97867	0.00021
H	-3.75764	1.92572	0.00056
H	3.92570	2.84823	-0.89219
H	3.92569	2.84797	0.89212
H	2.38613	3.00058	-0.00003
H	-7.84710	0.45687	0.00090
C	-6.42625	3.00457	0.00102
H	-6.06542	3.54528	0.88478
H	-6.06517	3.54567	-0.88239
H	-7.51953	3.05451	0.00088

Cartesian Coordinates: 2-*E* (C_B), Total Energy = -2088.4571169 a. u.

0 1

C	7.10503	-0.49735	-0.00087
C	6.78792	0.83994	0.00111
C	5.37421	1.03791	0.00165
C	4.63633	-0.13042	0.00003
S	5.70768	-1.52100	-0.00230
C	3.20078	-0.29542	0.00014

C	2.46550	-1.47714	0.00067
C	1.07235	-1.29072	0.00061
C	0.69076	0.05006	-0.00003
S	2.13026	1.07867	-0.00028
C	-0.56977	0.72435	-0.00038
H	-0.47620	1.81098	-0.00073
H	0.34674	-2.09215	0.00097
H	2.93173	-2.45695	0.00118
H	4.91662	2.02311	0.00335
C	-1.86578	0.27941	-0.00035
C	-2.39453	-1.08515	0.00005
O	-1.76378	-2.13388	0.00069
N	-3.81292	-1.06751	0.00026
C	-4.53696	-2.34391	0.00094
H	-5.16017	-2.42954	0.89318
H	-5.16038	-2.43038	-0.89107
H	-3.77953	-3.12767	0.00122
S	-3.20385	1.45197	-0.00082
C	-4.40287	0.16636	-0.00018
C	-5.75732	0.47599	-0.00014
C	-6.13532	1.85213	-0.00063
N	-6.42249	2.98204	-0.00102
C	-6.82352	-0.46851	0.00034
N	-7.73133	-1.20005	0.00069
H	8.09247	-0.94197	-0.00164
C	7.79453	1.96027	0.00266
H	7.67709	2.60092	-0.88025
H	7.67713	2.59843	0.88736
H	8.81848	1.57393	0.00209

X-RAY CRYSTALLOGRAPHY

General Information

X-Ray intensity data were collected at 100 K on a Bruker DUO diffractometer using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector. Raw data frames were read by program SAINT1 and integrated using 3D profiling algorithms. The resulting data were reduced to produce *hkl* reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in *SHELXTL2014*, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The molecule has its end thiophene disordered and refined in two parts. Their geometries are kept similar using a number of SADI commands. Their SOF were fixed at 0.82 and 0.18 in the final cycles of refinements. In the final cycle of refinement, 4153 reflections (of which 3443 are observed with $I > 2\sigma(I)$) were used to refine 217 parameters and the resulting R1, wR2 and S (goodness of fit) were 5.19%, 10.03% and 1.084, respectively. The refinement was carried out by 23 minimizing the wR2 function using F2 rather than F values. R1 is calculated to provide a reference to the conventional R value but its function is not minimized.

Table 1. Crystal data and structure refinement for korn1.

Identification code	korn1	
CCDC	2022503	
Empirical formula	C19 H21 N3 O S2	
Formula weight	371.51	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.387(3) Å	α= 90°.
	b = 5.4878(11) Å	β= 90.130(6)°.
	c = 24.641(5) Å	γ = 90°.
Volume	1810.3(6) Å^3	
Z	4	
Density (calculated)	1.363 Mg/m^3	
Absorption coefficient	0.306 mm^{-1}	
F(000)	784	
Crystal size	0.189 x 0.144 x 0.052 mm^3	
Theta range for data collection	1.521 to 27.498°.	
Index ranges	$-17\leq h\leq 17$, $-7\leq k\leq 7$, $-32\leq l\leq 32$	

Reflections collected	35779
Independent reflections	4153 [R(int) = 0.0520]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Integration
Max. and min. transmission	0.9881 and 0.9578
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4153 / 17 / 217
Goodness-of-fit on F^2	1.084
Final R indices [I>2sigma(I)]	R1 = 0.0519, wR2 = 0.1003 [3443]
R indices (all data)	R1 = 0.0651, wR2 = 0.1043
Extinction coefficient	n/a
Largest diff. peak and hole	1.113 and -1.241 e.Å^{-3}

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

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