

Electronic Supporting Information

***Cis* alkenes stabilized by intramolecular sulphur $\cdots\pi$ interactions**

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1. General

Analytical grade reagents were purchased from commercial suppliers Aladdin (AR) and Sigma-Aldrich (AR) and used without any further purification unless otherwise stated. Compounds **1a** and **2a–2c** were prepared according to the reported procedure.^{S1} Column chromatography was carried out on silica gel (200–300 mesh). All melting points were measured without corrections. Ultraviolet-Visible (UV–Vis) spectra were recorded with a Shimadzu UV–3150 double-beam spectrophotometer using a quartz cell with a path length of 10 mm at room temperature (25 °C). Irradiation experiments were conducted using a portable LED light source (HXGY-II, Beijing Huaxing science&technology CO.LTD) equipped with ten light intensities (white light/365 nm/415 nm/450 nm/CSS/490 nm/530 nm/ 555 nm/ 570 nm/610 nm). NMR spectroscopic measurements were performed on a Bruker X400 MHz, using chloroform-*d* (CDCl₃), dichloromethane-*d*₂ (CD₂Cl₂) and tetrahydrofuran-*d*₈

(THF- d_8) as the solvents at room temperature (25 °C). Mass spectrometric data were obtained from SHIMADZU LCMS-2020.

2.1. Preparation of compound **1b**

2-Amino-4-chloro-5-formylthiophene-3-carbonitrile (0.94 g, 5.00 mmol) was dissolved in a mixture of concentrated sulfuric acid (3 mL) and phosphoric acid (2.5 mL) at -5 °C in an ice-salt bath. Nitrosylsulphuric acid (5 mL) was added dropwise to the reaction mixture within 15 min and the mixture was stirred for additional 0.5 h. The diazonium salt was obtained and used for the next coupling reaction. *N,N*-diethylaniline (0.75 g, 5.00 mmol) was dissolved in a mixture of methanol and water (30 mL, v:v = 2:1) in a three-necked flask immersed in an ice-salt bath. The freshly prepared diazonium salt was added dropwise to the reaction mixture under vigorous mechanical stirring (0–5 °C). After additional stirring for 2 h, the precipitate was filtered and dried after thorough washing with distilled water. The crude solid was subjected to column chromatography on silica gel (dichloromethane:petroleum ether = 2:1), and compound **1b** was obtained as the purple powder in a yield of 1.21 g (70 %). Mp: 251–253 °C. UV–Vis in CHCl₃, λ_{\max} (nm)/ ϵ ($\times 10^4$ L·mol⁻¹·cm⁻¹) = 591/3.94. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 10.02 (s, 1H), 7.92 (s, 2H), 6.75 (d, J = 8.6 Hz, 2H), 3.55 (m, 4H), 1.30 (t, J = 6.5 Hz, 6H). ¹³C NMR (400 MHz, CDCl₃, ppm): δ = 181.25, 153.63, 142.98, 134.67, 131.36, 129.90, 112.18, 111.85, 107.20, 105.97, 45.51, 12.78. MS (positive mode, m/z) calcd for C₁₆H₁₅ClN₄OS [M + H]⁺: 347.1, found: 347.0.

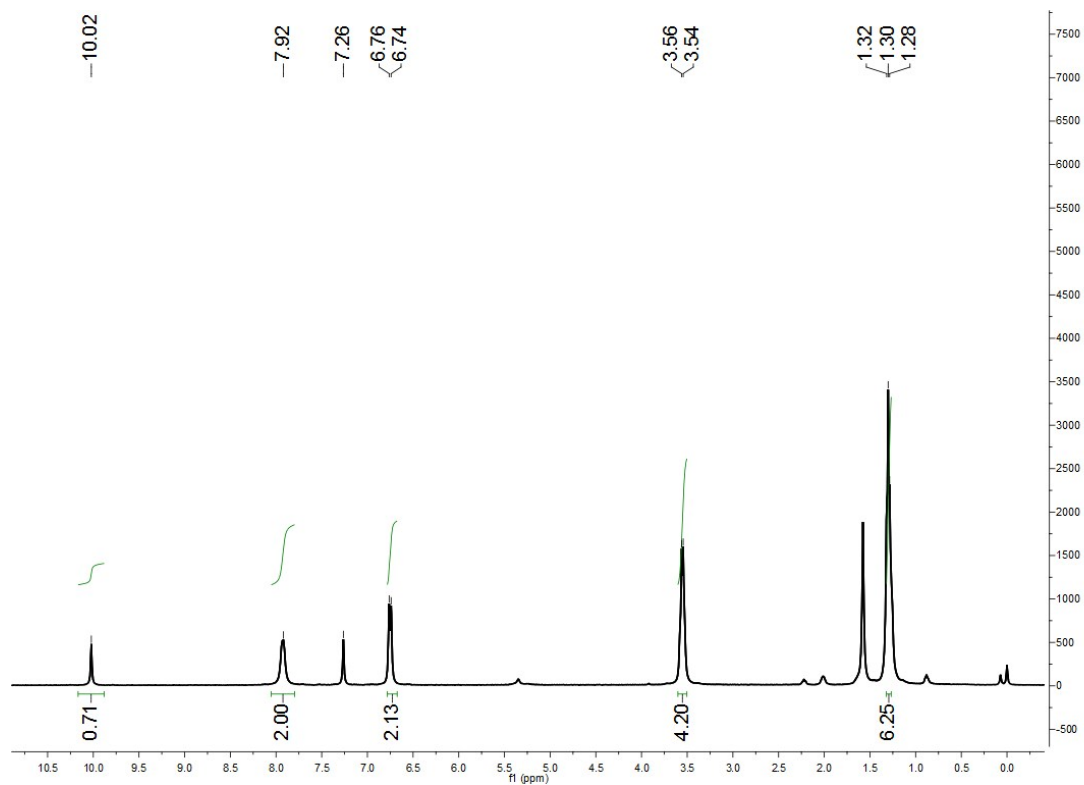


Fig. S1 ^1H NMR spectrum of compound **1b** in CDCl_3 .

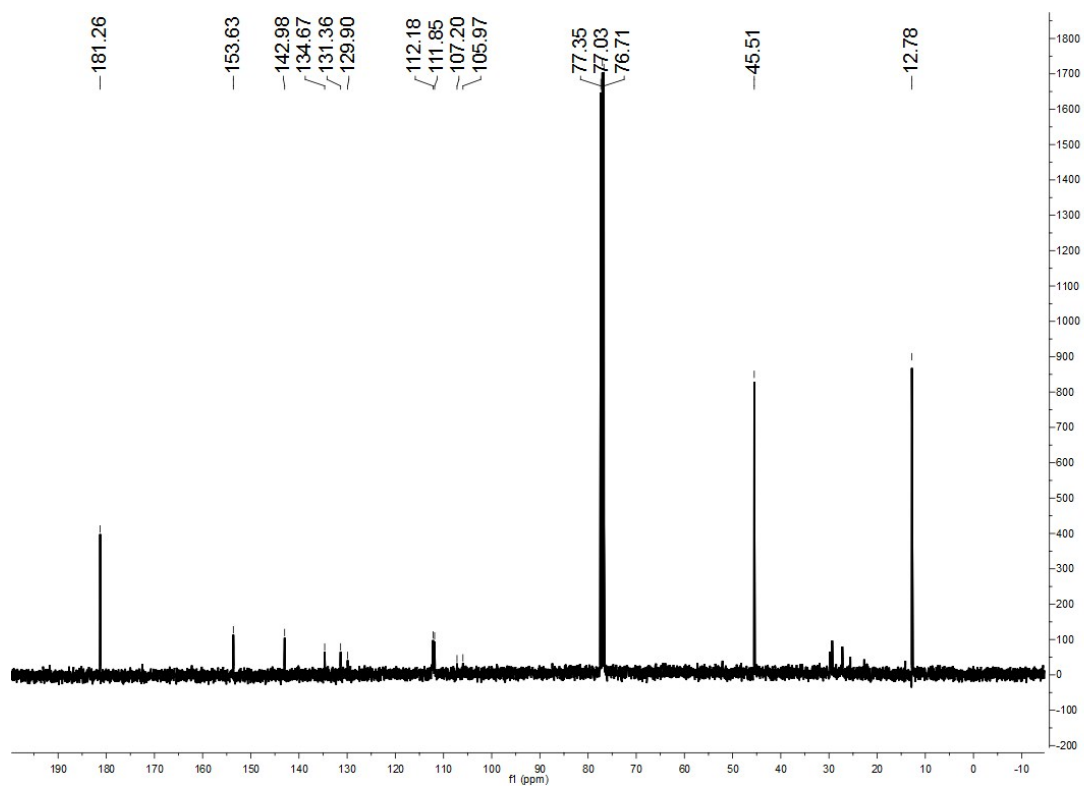


Fig. S2 ^{13}C NMR spectrum of compound **1b** in CDCl_3 .

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BG Mode:Averaged 0.033-0.700(3-43) Segment 1 - Event 1

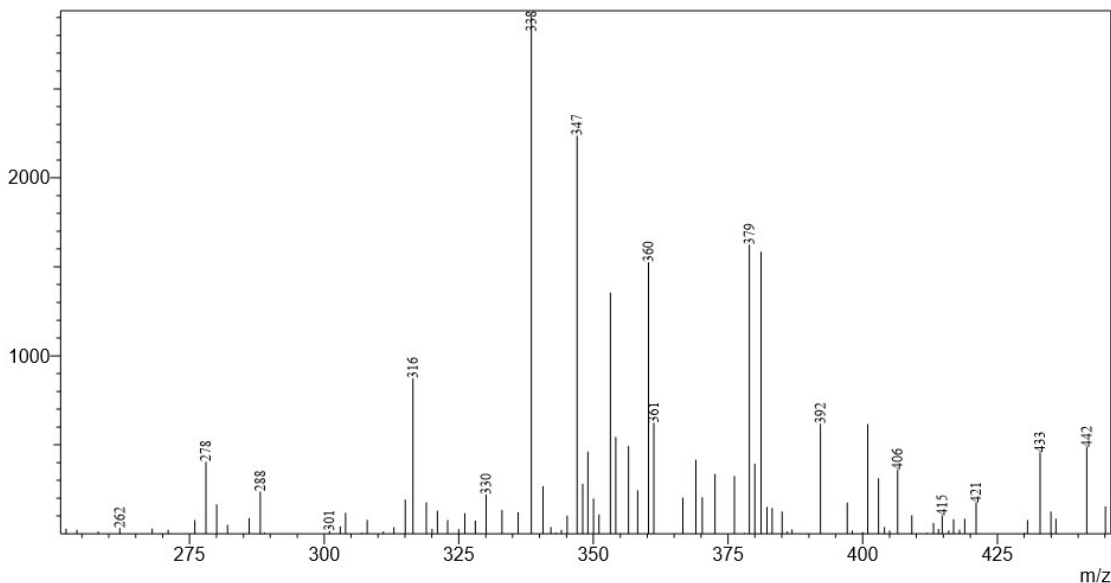


Fig. S3 ESI-MS spectrum of the compound **1b**.

2.2. Preparation of *cis*-**3**

Under dry and inert atmosphere, *t*-BuONa (0.29 g, 3.00 mmol) was quickly added to a mixture of compound **2a** (0.95 g, 2.00 mmol) in anhydrous THF (40 mL) at 0 °C. After stirring for 0.5 h at 0 °C, a solution of compound **1a** (0.32 g, 1.00 mmol) in anhydrous THF (10 mL) was added dropwise into the reaction mixture. While the addition was completed, the reaction mixture was then refluxed for 5 h at 70 °C. Following, the mixture was cooled to RT and the solvent was removed under reduced pressure. The crude solid was subjected to column chromatography on silica gel (dichloromethane:petroleum ether = 1:1), and *cis*-**3** was obtained as the purple powder in a yield of 0.23 g (53 %). Mp: 213–215 °C. UV–Vis in CHCl₃, λ_{\max} (nm)/ ϵ ($\times 10^4$ L·mol⁻¹·cm⁻¹) = 580/2.57. ¹H NMR (400 MHz, CDCl₃, ppm) : δ = 8.24 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 9.3 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 12.2 Hz, 1H), 6.81 (d, *J* = 12.2 Hz, 1H), 6.69 (d, *J* = 9.4 Hz, 2H), 3.15 (s, 6H). ¹³C NMR (400 MHz, CDCl₃, ppm): δ = 165.10, 154.20, 147.54, 142.92, 142.84, 130.77, 129.74, 129.67, 126.98, 124.13, 122.16, 112.58, 111.83, 107.77, 96.00, 40.37. MS (positive mode, *m/z*) calcd for C₂₁H₁₆ClN₅O₂S [M + H]⁺: 438.1, found: 438.0.

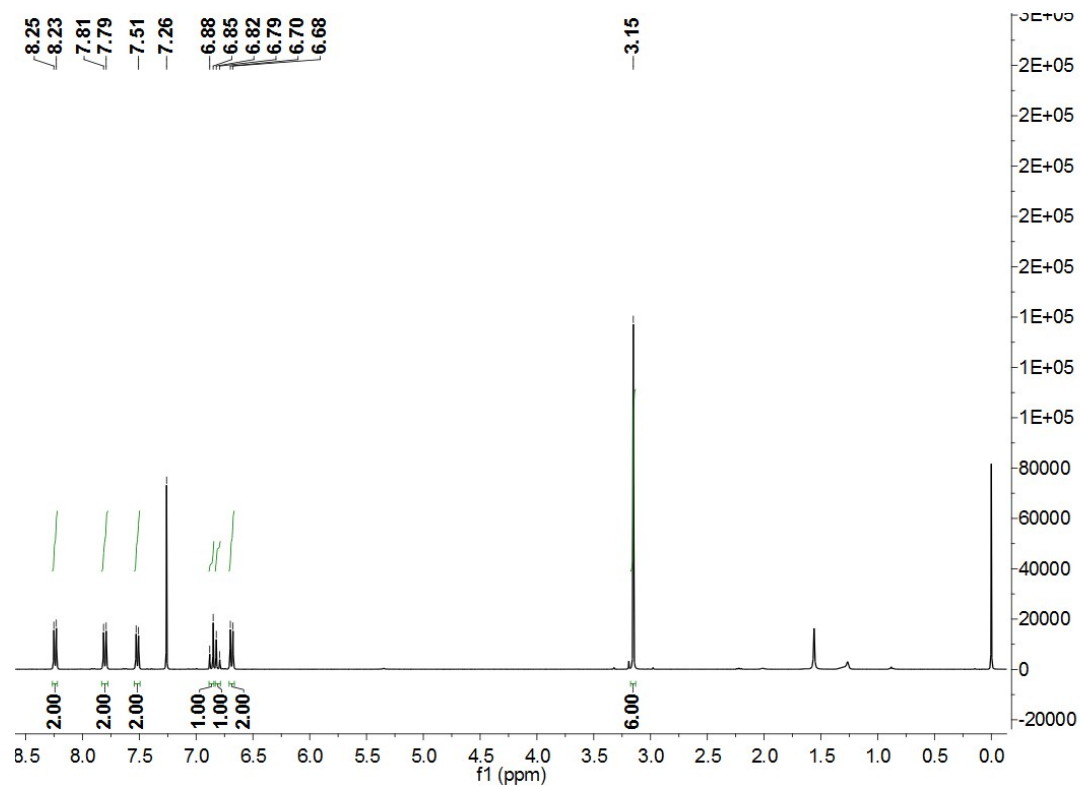


Fig. S4 ^1H NMR spectrum of *cis-3* in CDCl_3 .

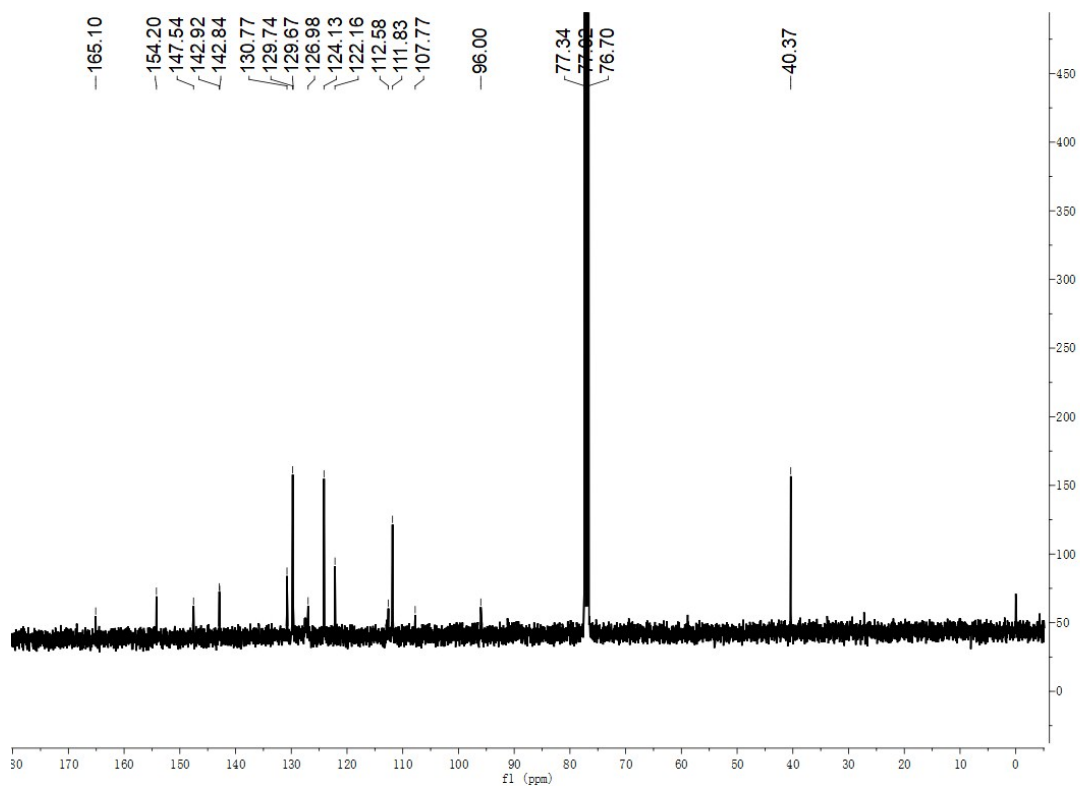


Fig. S5 ^{13}C NMR spectrum of *cis-3* in CDCl_3 .

Line# 1 R.Time:----(Scan#:----)
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RawMode:Averaged 0.300-0.367(19-23) BasePeak:438(2954)
BG Mode:Averaged 0.033-0.733(3-45) Segment 1 - Event 1

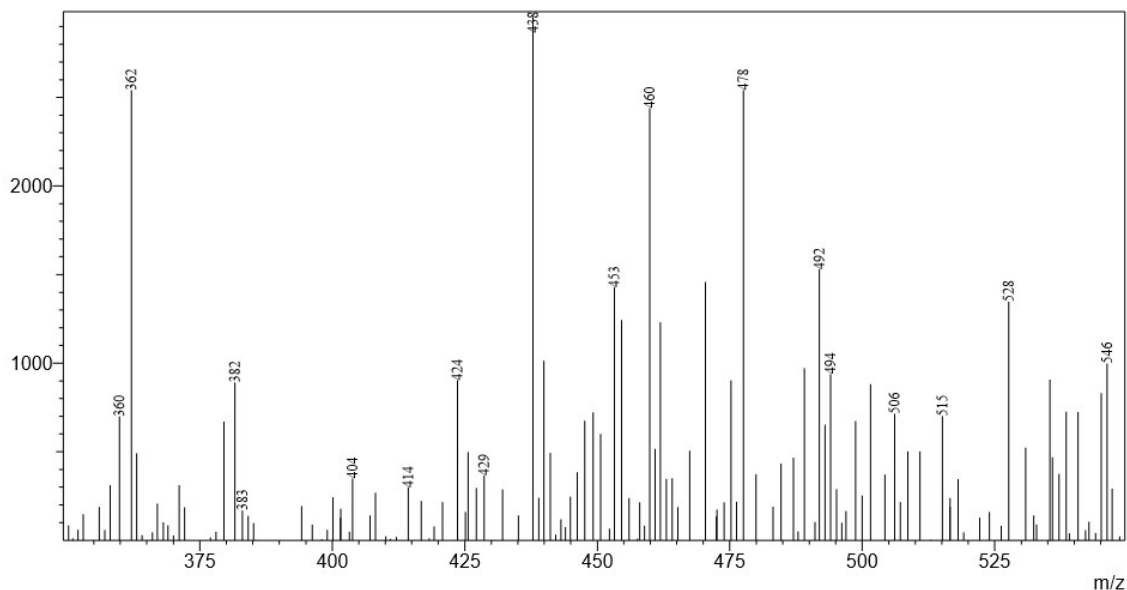


Fig. S6 ESI-MS spectrum of the compound *cis-3*.

2.3. Preparation of *cis-4*

The synthetic procedure for *cis-4* was analogous to that described for *cis-3* except that compound **1b** (0.35 g, 1.00 mmol) was used as the starting material to replace compound **1a**. Yield: 0.32 g (68 %). Mp: 208–211 °C. UV–Vis in CHCl₃, λ_{\max} (nm)/ ϵ ($\times 10^4$ L·mol⁻¹·cm⁻¹) = 582/2.77. ¹H NMR (400 MHz, CDCl₃, ppm) : δ = 8.27–8.21 (m, 2H), 7.78 (d, *J* = 9.2 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 12.2 Hz, 1H), 6.79 (d, *J* = 12.2 Hz, 1H), 6.67 (d, *J* = 9.4 Hz, 2H), 3.49 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (400 MHz, CDCl₃, ppm): δ = 154.11, 152.38, 147.54, 142.97, 142.65, 130.53, 129.76, 129.38, 129.06, 127.34, 126.90, 124.12, 122.21, 112.76, 111.61, 45.16, 12.71. Single crystals of *cis-4* suitable for X-ray diffraction measurement were obtained by slow evaporation of a mixture of CHCl₃ and MeOH (v:v = 1:1) in air for one week. MS (positive mode, m/z) calcd for C₂₃H₂₀ClN₅O₂S [M + H]⁺: 466.1, found: 466.0.

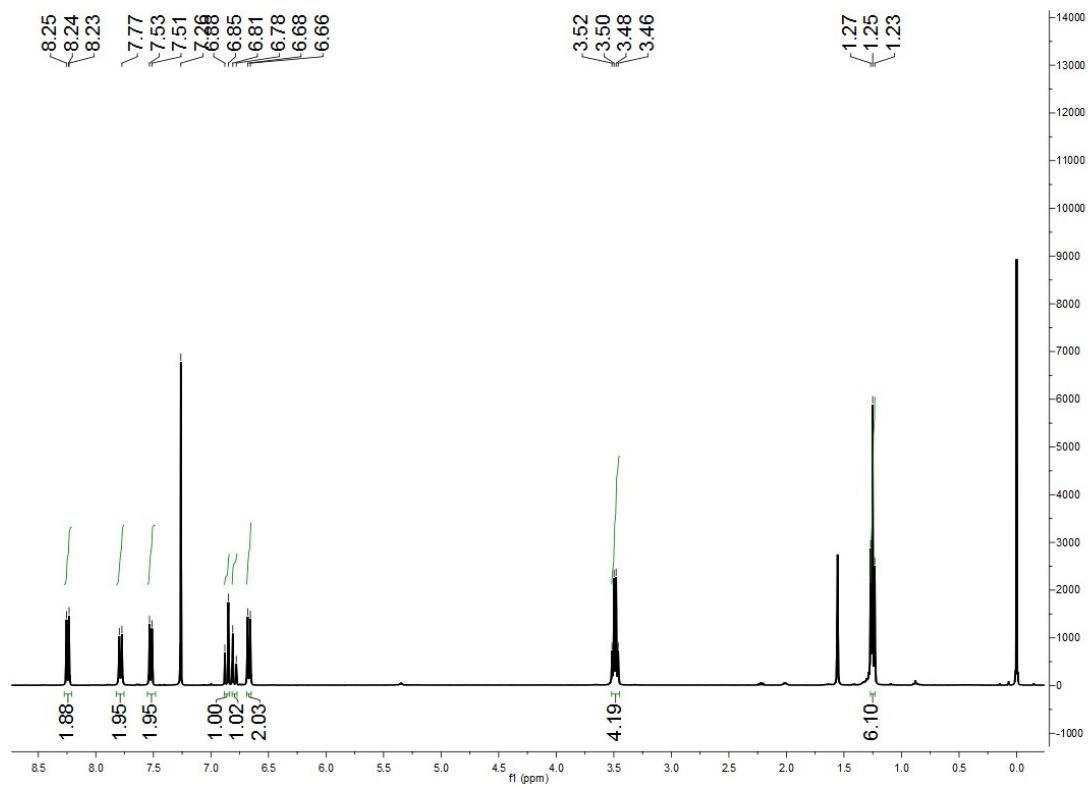


Fig. S7 ¹H NMR spectrum of *cis-4* in CDCl₃.

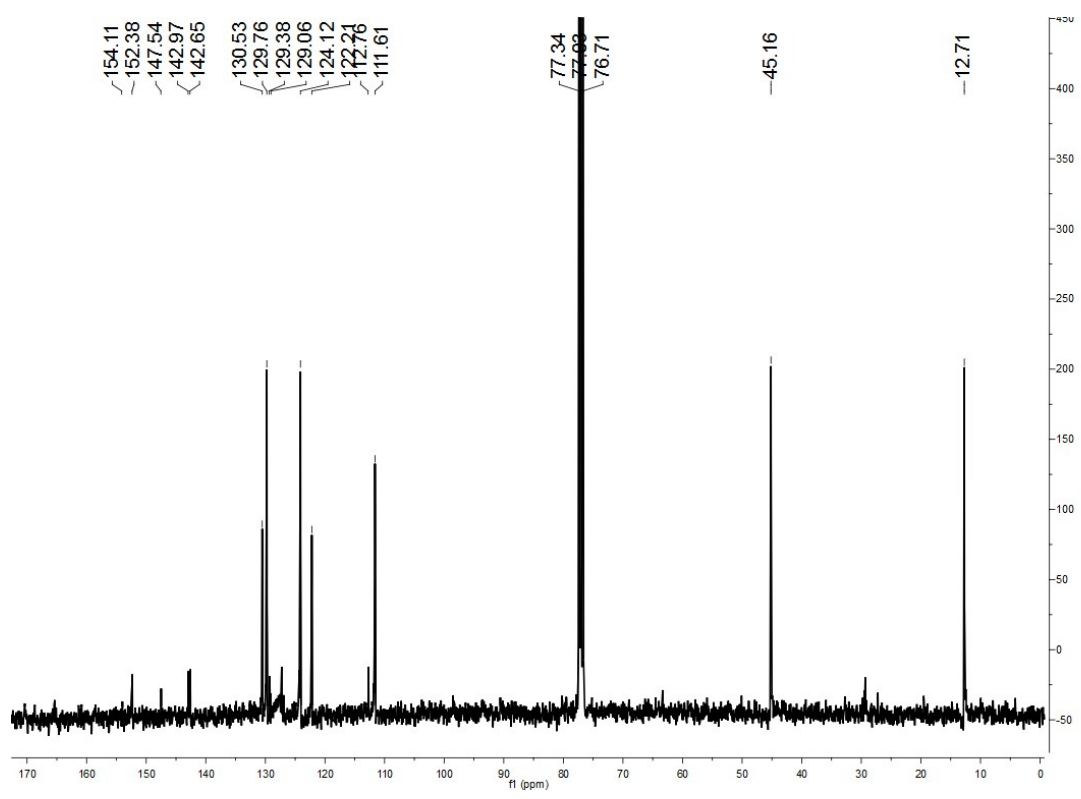


Fig. S8 ¹³C NMR spectrum of *cis-4* in CDCl₃.

Line# 1 R.Time:----(Scan#:----)
MassPeaks:44
RawMode:Averaged 0.333-0.400(21-25) BasePeak:466(4165)
BG Mode:Averaged 0.067-0.800(5-49) Segment 1 - Event 1

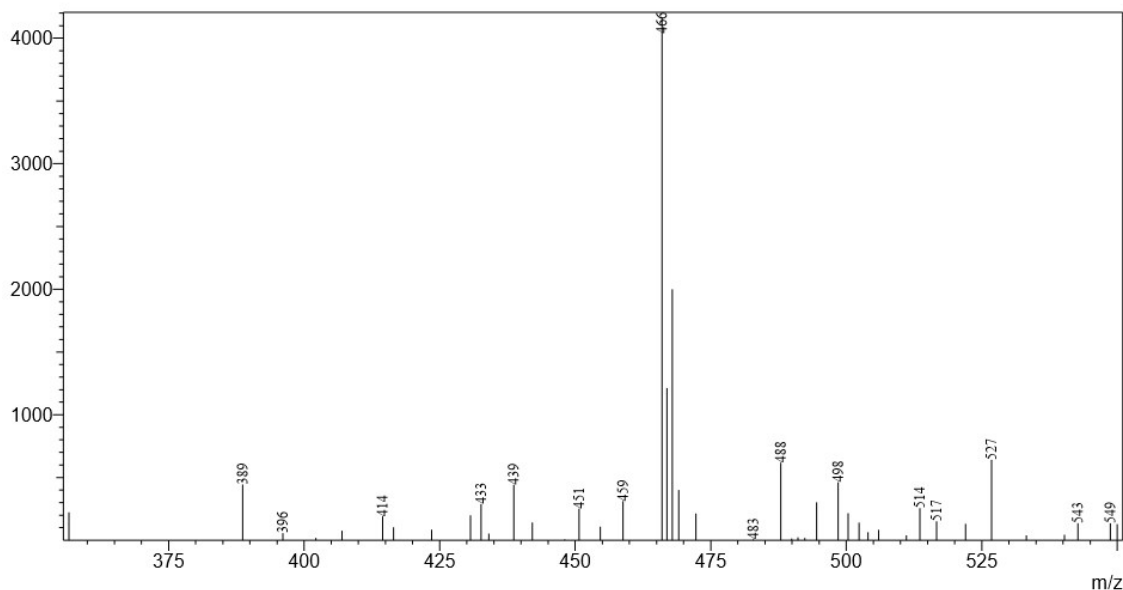


Fig. S9 ESI-MS spectrum of the compound *cis-4*.

2.4. Preparation of *cis-/trans-5*

The synthetic procedure for *cis-/trans-5* was analogous to that described for *cis-3* except that compound **2b** (0.86 g, 2.00 mmol) was used as the starting material to replace compound **2a**. A mixture of *cis-5* and *trans-5* was obtained in a ratio of 3:2 in a yield of 0.20 g (51 %). Mp: 121–123 °C. UV–Vis of *cis-/trans-5* in CHCl₃, λ_{\max} (nm)/ ϵ ($\times 10^4$ L·mol⁻¹·cm⁻¹) = 565/2.62. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.80 (d, *J* = 9.3 Hz, 0.66H, *trans-*), 7.69 (d, *J* = 9.3 Hz, 1.01H, *cis-*), 7.47 (d, *J* = 7.3 Hz, 0.82H), 7.34–7.19 (m, 3.82H), 7.03 (d, *J* = 16.1 Hz, 0.39H, *trans-*), 6.81 (d, *J* = 12.0 Hz, 0.60H, *cis-*), 6.70 (d, *J* = 9.3 Hz, 0.78H), 6.64 (dd, *J* = 10.7, 2.4 Hz, 1.80H), 3.09 (s, 2.38H), 3.05 (s, 3.63H). ¹³C NMR (400 MHz, CDCl₃, ppm): δ = 164.31 (*cis-*), 163.71 (*tran-*), 153.93 (*trans-*), 153.84 (*cis-*), 143.01 (*trans-*), 142.93 (*cis-*), 135.94, 134.80, 134.05, 132.61, 131.59, 128.93 (*trans-*), 128.88 (*cis-*), 128.67 (*cis-*), 128.50 (*trans-*), 126.98, 125.7, 123.87, 119.55, 117.90, 112.86 (*cis-*), 112.71 (*trans-*), 111.89 (*trans-*), 111.70 (*cis-*), 108.82, 107.95, 40.38 (*trans-*), 40.33 (*cis-*). MS (positive mode, m/z) calcd for C₂₁H₁₇ClN₄S [M + H]⁺: 393.1, found: 393.0.

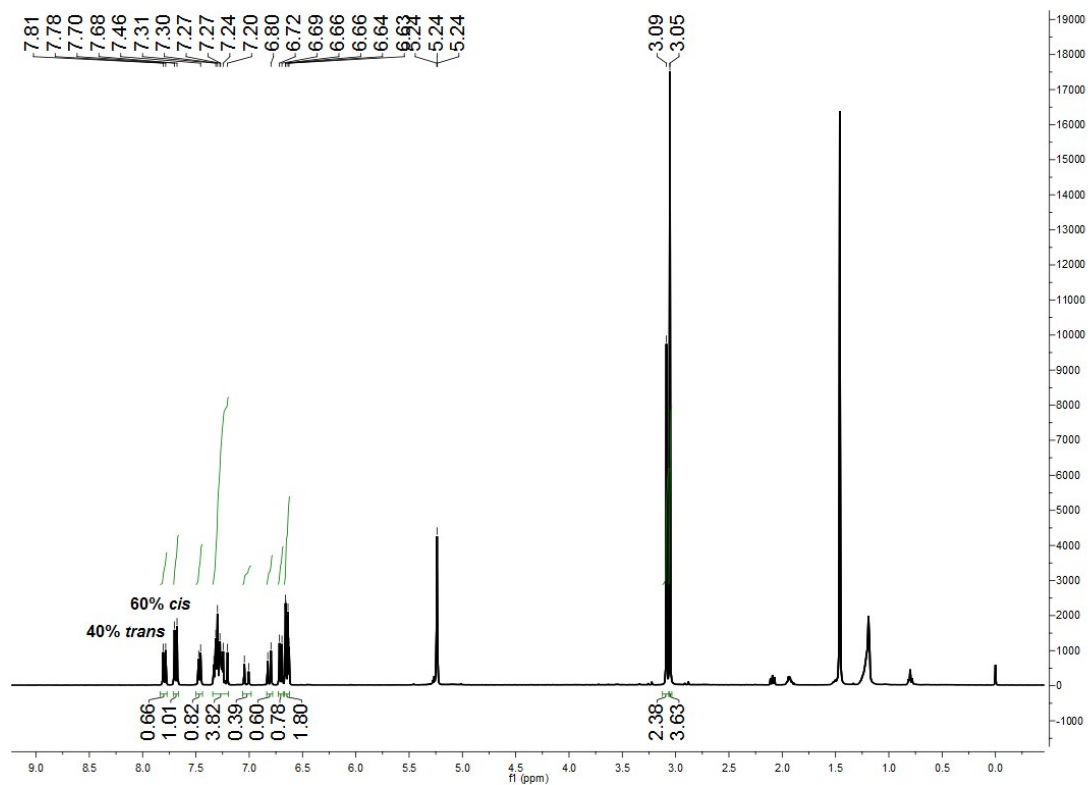


Fig. S10 ^1H NMR spectrum of *cis-/trans-5* in CD_2Cl_2 .

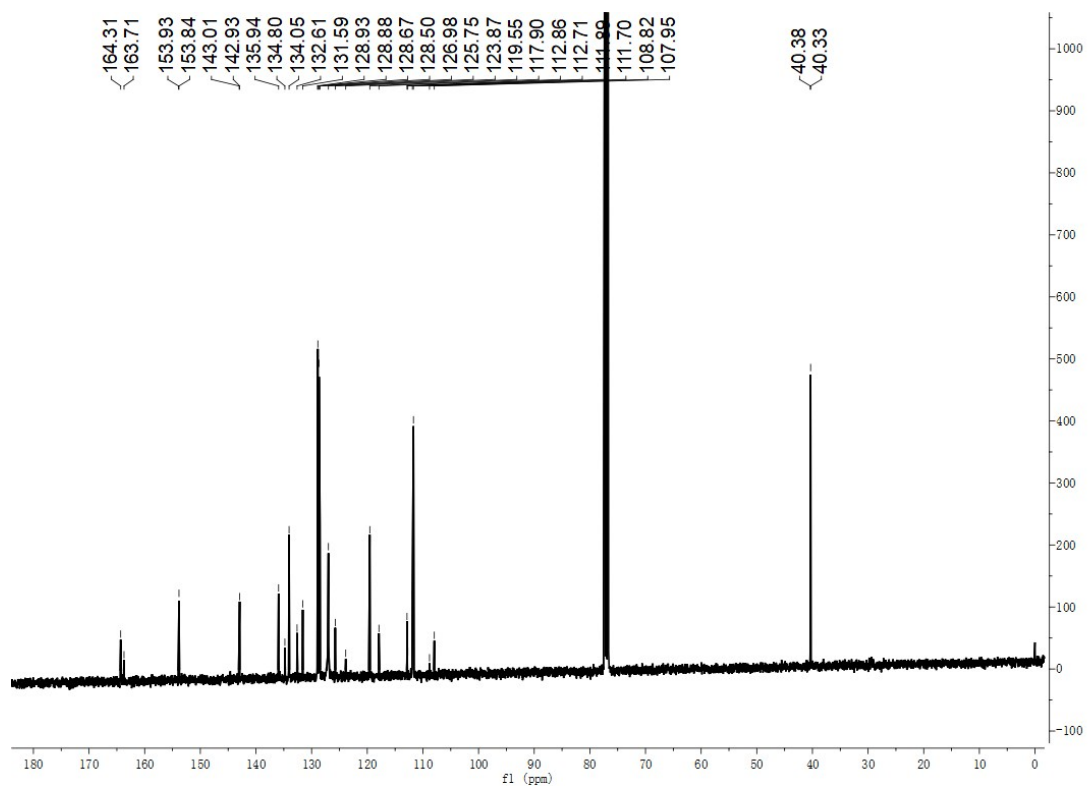


Fig. S11 ^{13}C NMR spectrum of *cis-/trans-5* in CDCl_3 .

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RawMode:Averaged 0.333-0.367(21-23) BasePeak:393(4154)
BG Mode:Averaged 0.067-0.733(5-45) Segment 1 - Event 1

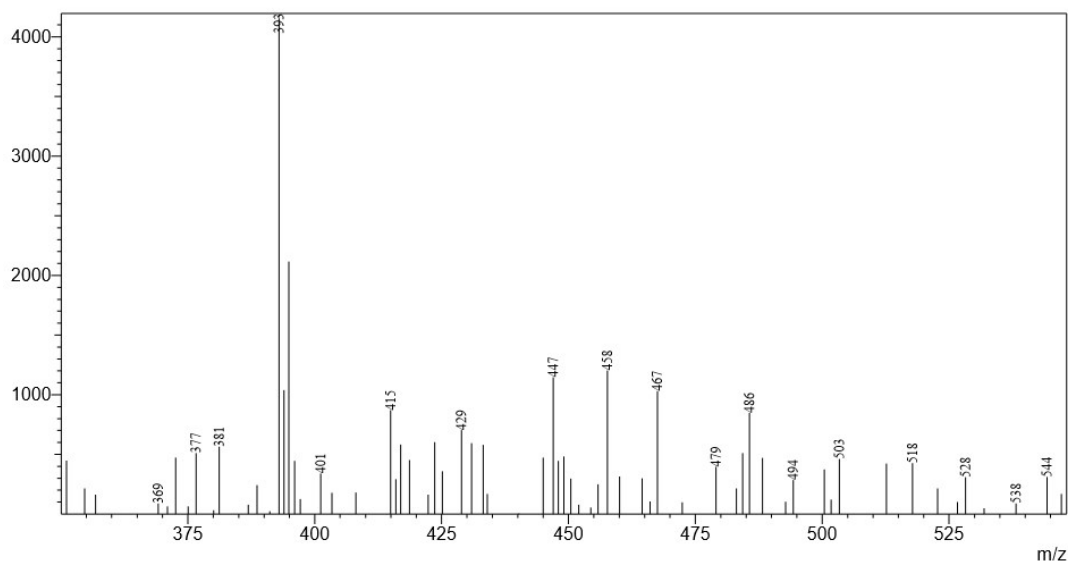


Fig. S12 ESI-MS spectrum of the compound *cis-/trans-5*.

2.5. Preparation of *cis-/trans-6*

The synthetic procedure for *cis-/trans-6* was analogous to that described for *cis-4* except that compound **2b** (0.86 g, 2.00 mmol) was used as the starting material to replace compound **2a**. A mixture of *cis-6* and *trans-6* was obtained in a ratio of 3:2 in a yield of 0.23 g (55 %). Mp: 125–127 °C. UV–Vis of *cis-/trans-6* in CHCl₃, λ_{\max} (nm)/ ϵ ($\times 10^4$ L·mol⁻¹·cm⁻¹) = 565/2.85. ¹H NMR (400 MHz, CDCl₃, ppm) : δ = 7.88 (d, *J* = 9.3 Hz, 0.74H, *trans-*), 7.77 (d, *J* = 9.3 Hz, 1.09H, *cis-*), 7.51 (d, *J* = 7.4 Hz, 0.82H, *trans-*), 7.41–7.30 (m, 3.60H), 7.27 (d, *J* = 16.1 Hz, 0.19H, *trans-*), 7.05 (d, *J* = 16.1 Hz, 0.21H, *trans-*), 6.84 (d, *J* = 12.0 Hz, 0.37H, *cis-*), 6.74–6.71 (m, 0.56H, *trans-*), 6.69–6.65 (m, 2.53H, *cis-*), 3.48 (m, *J* = 14.2, 7.1 Hz, 4H), 1.32–1.23 (m, 6H). ¹³C NMR (400 MHz, CDCl₃, ppm): δ = 152.03 (*trans-*), 151.91 (*cis-*), 142.68 (*trans-*), 142.57 (*cis-*), 136.00 (*trans-*), 135.96 (*cis-*), 134.41, 133.82, 132.41, 128.92 (*trans-*), 128.86 (*cis-*), 128.69, 128.45, 126.96, 119.58, 118.76, 117.98, 112.97 (*trans-*), 112.82 (*cis-*), 111.64 (*trans-*), 111.43 (*cis-*), 45.14 (*trans-*), 45.06 (*cis-*), 12.75 (*trans-*), 12.71 (*cis-*). Single crystals of compounds *cis-6* and *trans-6* suitable for X–ray diffraction measurement were obtained separately by slow evaporation of a mixture of CHCl₃ and MeOH (v:v = 1:1) in air for one week. MS (positive mode, m/z) calcd for C₂₃H₂₁ClN₄S [M + H]⁺: 421.1,

found: 421.0.

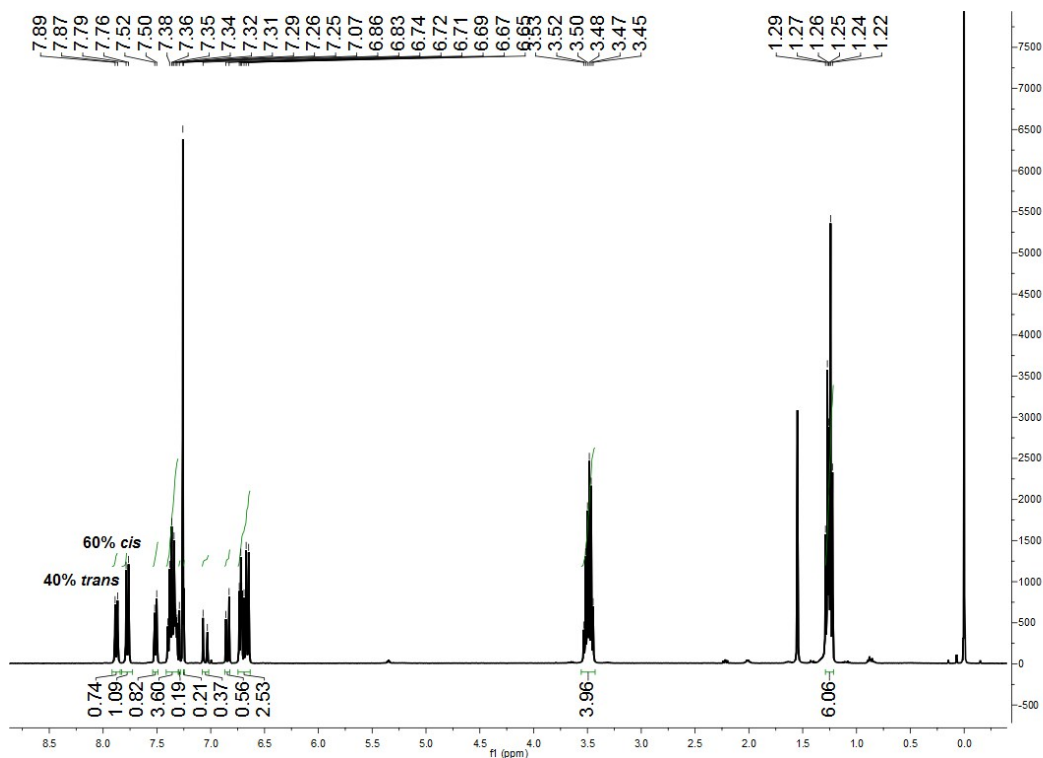


Fig. S13 ¹H NMR spectrum of *cis*-/*trans*-6 in CDCl₃.

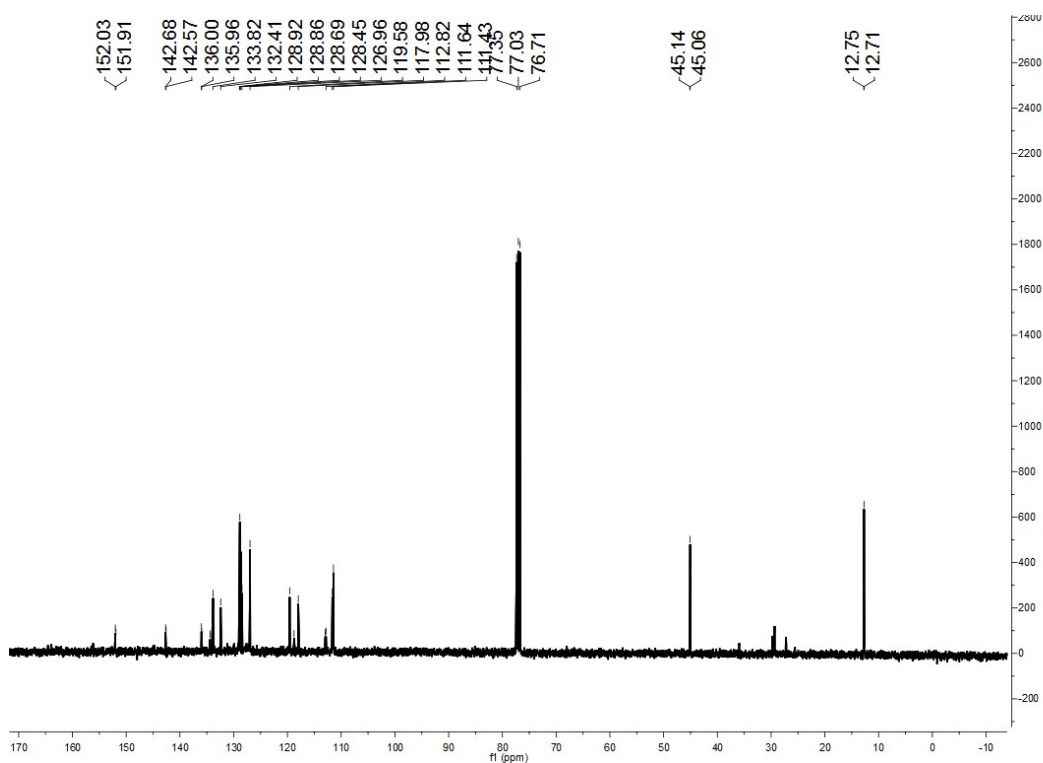


Fig. S14 ¹³C NMR spectrum of *cis*-/*trans*-6 in CDCl₃.

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RawMode:Averaged 0.400-0.467(25-29) BasePeak:421(3802)
BG Mode:Averaged 0.000-0.833(1-51) Segment 1 - Event 1

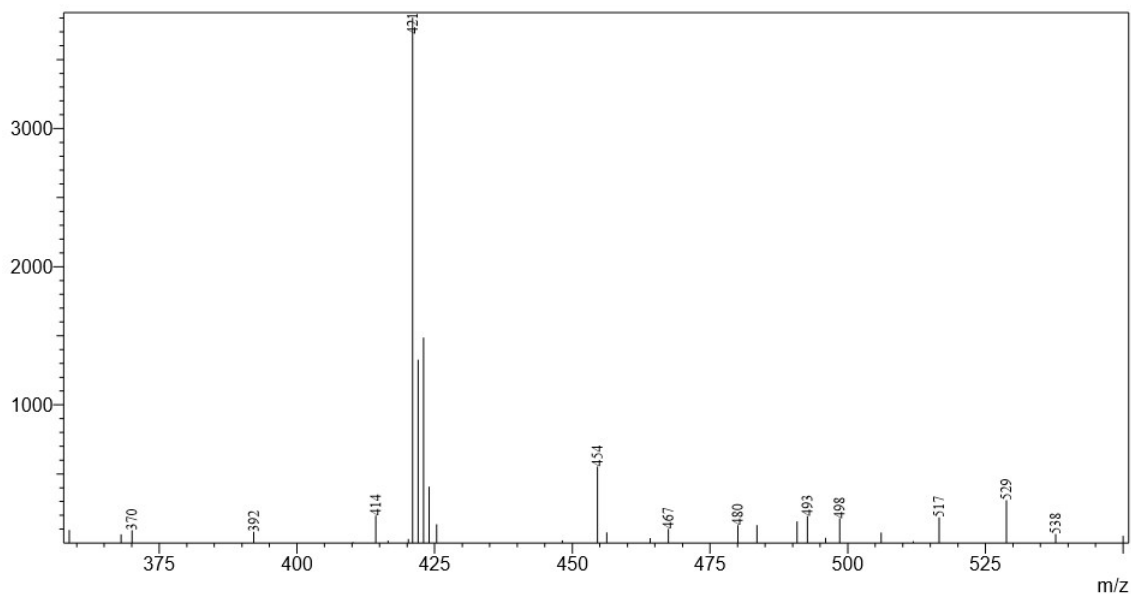


Fig. S15 ESI-MS spectrum of the compound *cis-/trans-6*.

2.6. Preparation of *trans-7*

The synthetic procedure for *trans-7* was analogous to that described for *cis-4* except that compound **2c** (0.89 g, 2.00 mmol) was used as the starting material to replace compound **2a**. Yield: 0.30 g (70 %). Mp: 122–124 °C. UV–Vis in CHCl₃, λ_{\max} (nm)/ ϵ ($\times 10^4$ L·mol⁻¹·cm⁻¹) = 567/5.90. ¹H NMR (400 MHz, CDCl₃, ppm) : δ = 7.87 (d, *J* = 9.1 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 12.6 Hz, 3H), 7.03 (d, *J* = 16.1 Hz, 1H), 6.72 (d, *J* = 9.2 Hz, 2H), 3.51 (q, *J* = 7.1 Hz, 4H), 2.37 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 6H). ¹³C NMR (400 MHz, CDCl₃, ppm): δ = 163.62, 152.02, 142.64, 139.17, 134.85, 134.18, 133.16, 132.50, 129.65, 128.48, 126.91, 118.87, 117.00, 112.81, 111.62, 45.12, 21.42, 12.75. Single crystals of *trans-7* suitable for X-ray diffraction measurement were obtained by slow evaporation of a mixture of CHCl₃ and MeOH (v:v = 1:1) in air for one week. MS (positive mode, m/z) calcd for C₂₄H₂₃ClN₄S [M + H]⁺: 435.1, found: 435.0.

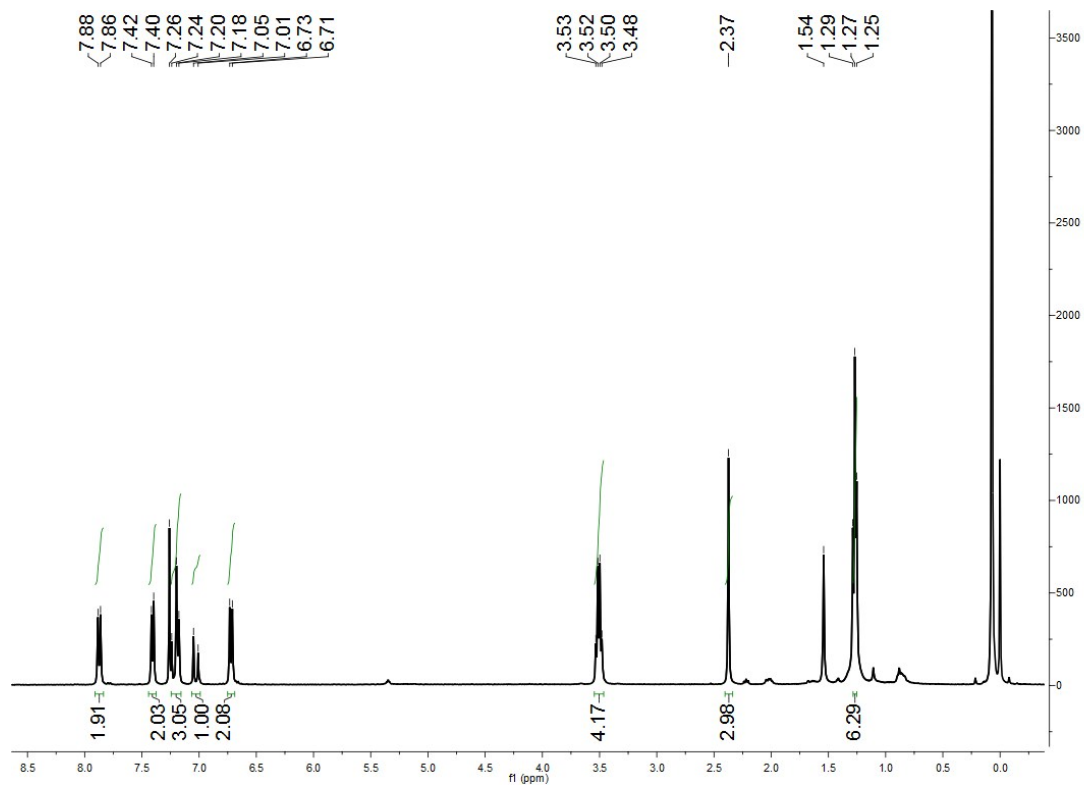


Fig. S16 ^1H NMR spectrum of *trans*-7 in CDCl_3 .

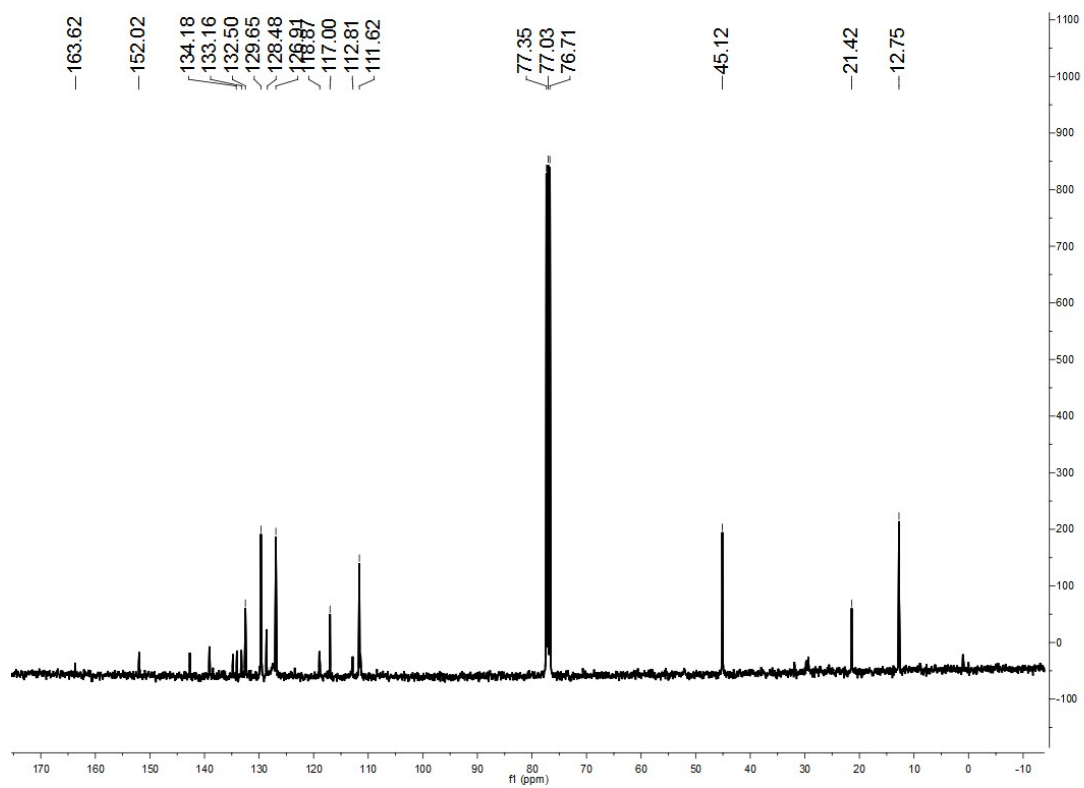


Fig. S17 ^{13}C NMR spectrum of *trans*-7 in CDCl_3 .

Line#:1 R.Time:----(Scan#:----)
MassPeaks:36
RawMode:Averaged 0.367-0.433(23-27) BasePeak:435(4553)
BG Mode:Averaged 0.033-0.800(3-49) Segment 1 - Event 1

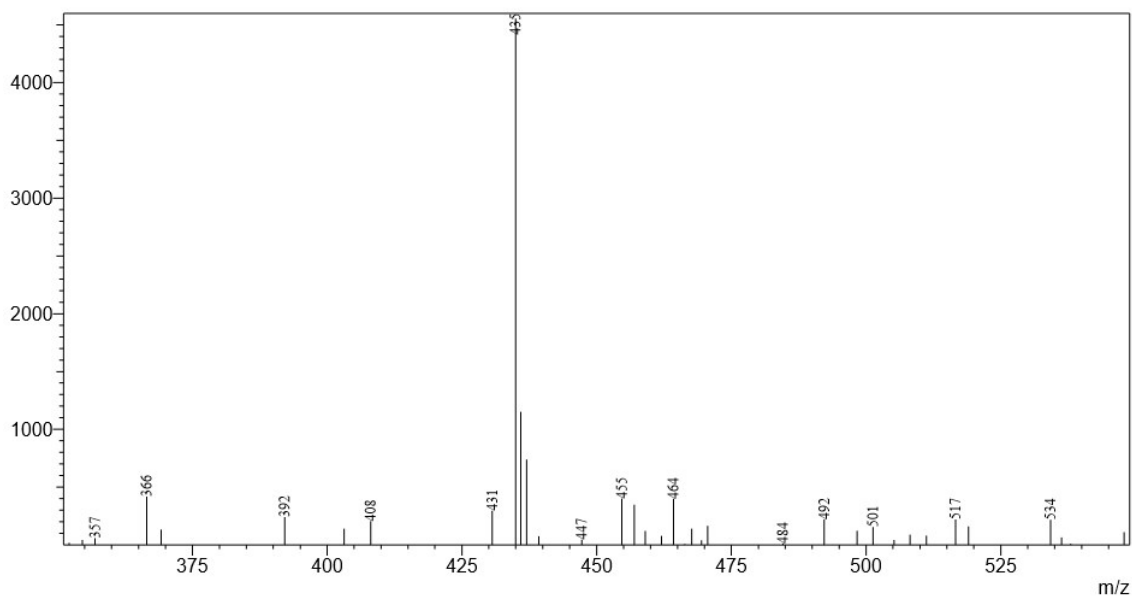


Fig. S18 ESI-MS spectrum of the compound *trans-7*.

2.7. Preparation of *trans-8*

The synthetic procedure for *trans-8* was analogous to that described for *cis-3* except that 2-amino-4-chloro-5-formylthiophene-3-carbonitrile (0.19 g, 1.00 mmol) was used as the starting material to replace compound **1a**. Yield: 0.16 g (52 %). Mp: >300 °C. ^1H NMR (400 MHz, THF- d_8 , ppm) : δ = 8.10 – 8.02 (m, 2H), 7.58 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 16.1 Hz, 1H), 7.26 (s, 2H), 6.53 (d, J = 16.1 Hz, 1H). ^{13}C NMR (400 MHz, THF- d_8 , ppm): δ = 162.81, 146.66, 143.47, 126.47, 124.11, 123.76, 123.02, 122.98, 121.93, 116.93, 112.48, 87.02. MS (negative mode, m/z) calcd for $\text{C}_{13}\text{H}_8\text{ClN}_3\text{O}_2\text{S} [\text{M} - \text{H}]^-$: 304.0, found: 304.0.

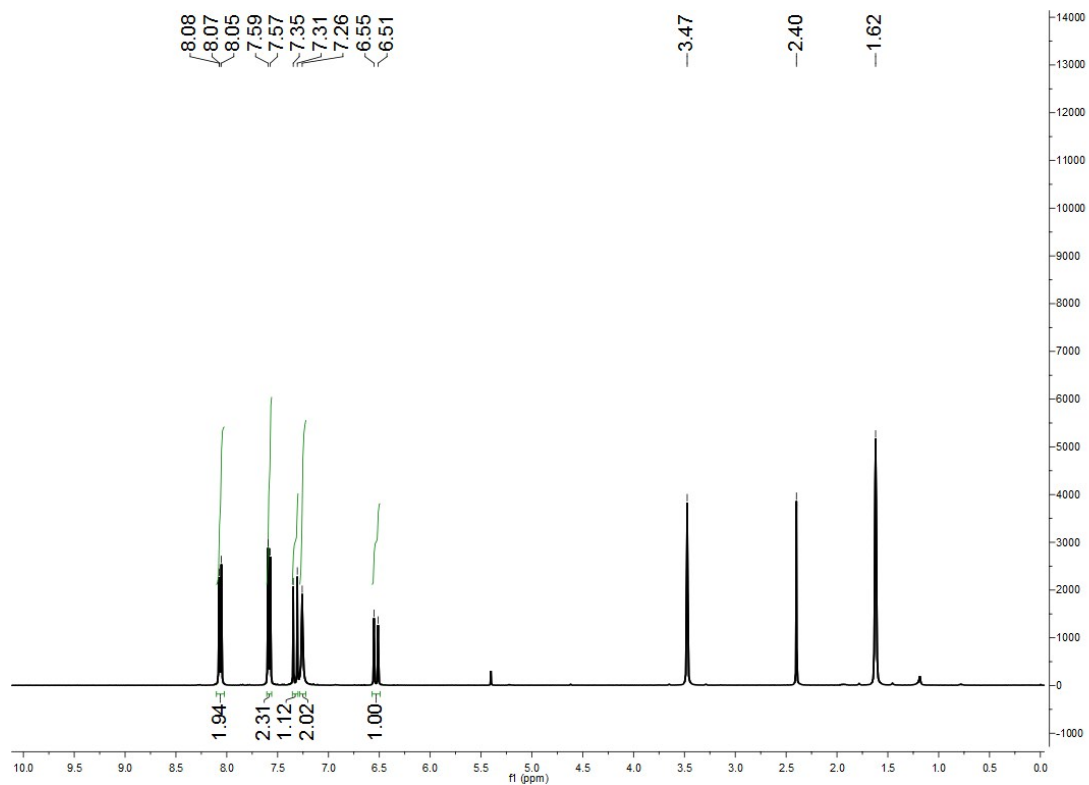


Fig. S19 ^1H NMR spectrum of *trans*-8 in $\text{THF-}d_8$.

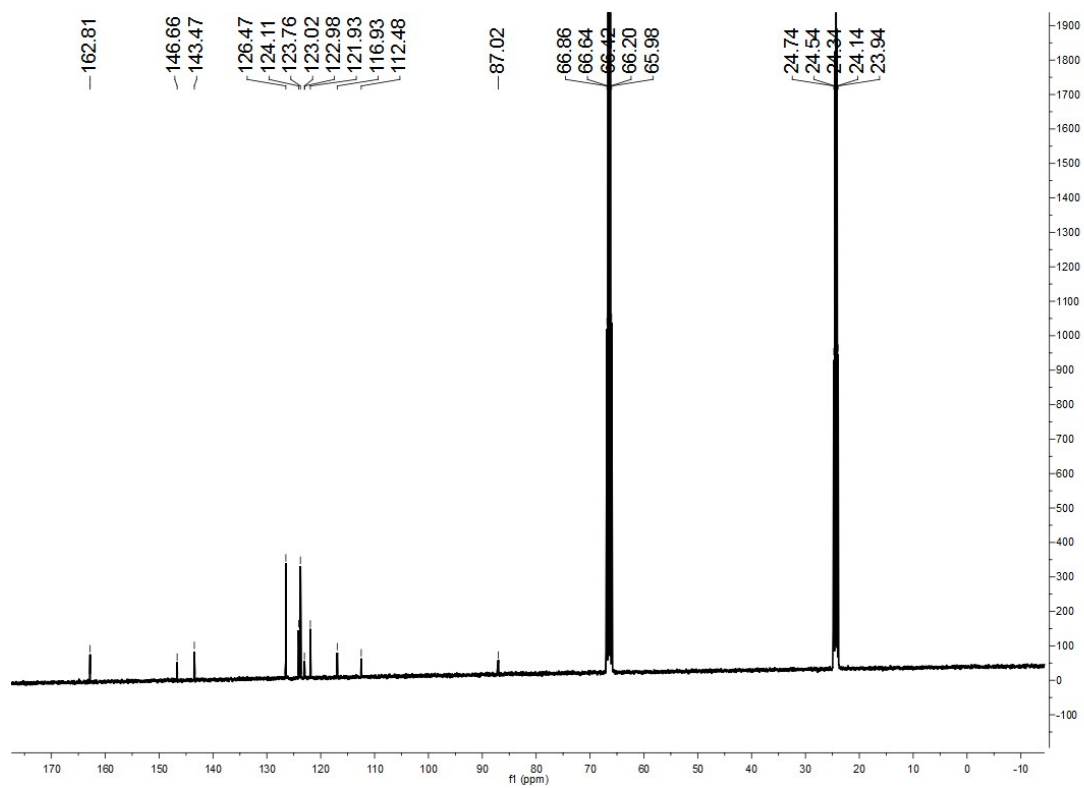


Fig. S20 ^{13}C NMR spectrum of *trans*-8 in $\text{THF-}d_8$.

Line#:2 R.Time:----(Scan#:----)
MassPeaks:144
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BG Mode:Averaged 0.050-0.883(4-54) Segment 1 - Event 2

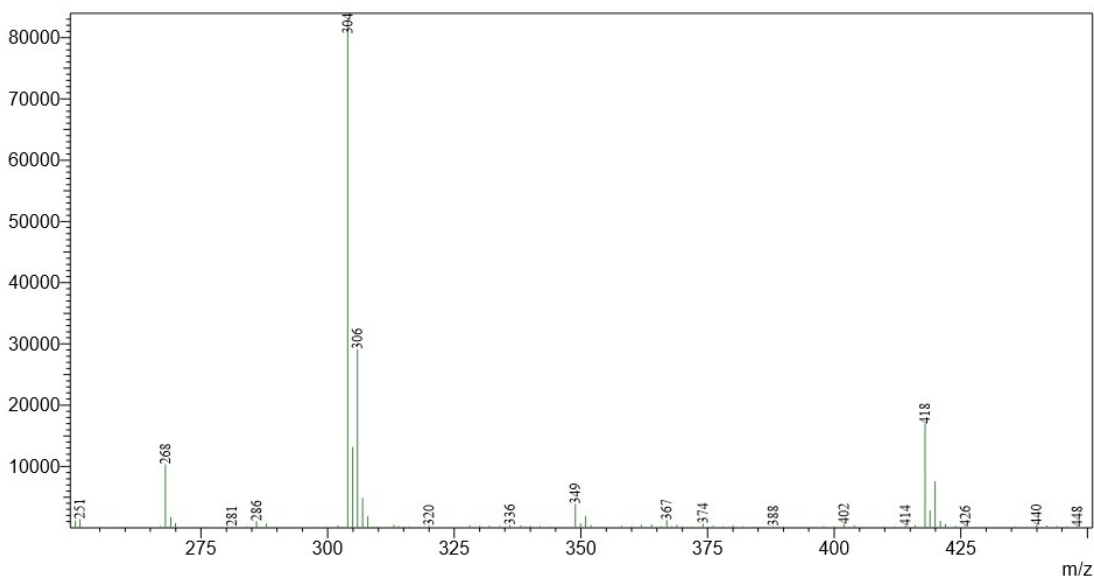


Fig. S21 ESI-MS spectrum of the *trans*-**8**.

3. X-ray data collection and solution

Single-crystal samples of *cis*-**4**, *trans*-**4**, *cis*-**6**, *trans*-**6** and *trans*-**7** were covered with glue and were mounted on glass fibers for data collection on a Bruker SMART 1K CCD area detector at 291(2) K, using graphite mono-chromated Mo K α radiation ($\lambda = 0.71073$ Å). The collected data were reduced by using the program SAINT^{S2} and empirical absorption corrections were done by SADABS^{S3} program. The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences by using XPREP. The structures were solved by direct method and refined by least-squares method. All the non-hydrogen atoms were refined on F^2 by full-matrix least-squares procedure using anisotropic displacement parameters. All the other hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters at 1.2 times of the equivalent isotropic U of the atoms to which they are attached (1.5 times for the methyl groups) and allowed to ride on their respective parent atoms. The carbon atoms (C22, C23 in compound *cis*-**6** and C21, C22 in *trans*-**7**) were refined as the disordered mode with the site occupancy factors as 0.62(2):0.38(2) and 0.70(1):0.30(1), respectively. All calculations were carried out on a PC with the

SHELXTL^{S4} PC program package and molecular graphics were drawn by using XSELL, Diamond and ChemBioDraw software. Details of the data collection and refinement results for *cis-4*, *trans-4*, *cis-6*, *trans-6* and *trans-7* are listed in Table S1. Selected bond distances and bond angles are given in Table S2.

Table S1 Crystal data and structural refinements for *cis-4*, *trans-4*, *cis-6*, *trans-6* and *trans-7*.

Compound	<i>cis-4</i>	<i>trans-4</i>	<i>cis-6</i>	<i>trans-6</i>	<i>trans-7</i>
Empirical formula	C ₂₃ H ₂ OCIN ₅ O ₂ S	C ₂₃ H ₂ OCIN ₅ O ₂ S	C ₂₃ H ₂₁ ClN ₄ S	C ₂₃ H ₂₁ ClN ₄ S	C ₂₄ H ₂₃ ClN ₄ S
Formula weight	465.95	465.95	420.95	420.95	434.97
Temperature / K	291(2)	291(2)	291(2)	291(2)	291(2)
Wavelength / Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal Size (mm)	0.12×0.12×0.10	0.10×0.10×0.08	0.12×0.12×0.10	0.12×0.10×0.10	0.12×0.10×0.10
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> / Å	5.093(4)	10.936(1)	12.225(4)	14.773(2)	7.902(2)
<i>b</i> / Å	18.689(15)	10.859(1)	12.945(4)	7.626(1)	9.496(2)
<i>c</i> / Å	24.05(2)	38.833(4)	15.227(5)	19.442(2)	15.018(3)
α / °	90	90	114.539(5)	90	78.986(4)
β / °	93.684(10)	91.052(2)	95.090(6)	95.253(2)	87.800(5)
γ / °	90	90	93.604(5)	90	85.372(5)
<i>V</i> / Å ³	2284(3)	4610.9(8)	2170.2(11)	2181.1(4)	1102.3(3)
<i>Z</i> / <i>D</i> _{calcd} (g / cm ³)	4 / 1.355	8 / 1.342	4 / 1.288	4 / 1.282	2 / 1.311
<i>F</i> (000)	968	1936	880	880	456
μ / mm ⁻¹	0.289	0.286	0.289	0.287	0.286
<i>h</i> _{min} / <i>h</i> _{max}	-6 / 4	-12 / 13	-11 / 14	-17 / 17	-10 / 10
<i>k</i> _{min} / <i>k</i> _{max}	-22 / 22	-12 / 12	-15 / 15	-7 / 9	-12 / 11
<i>l</i> _{min} / <i>l</i> _{max}	-28 / 28	-46 / 46	-18 / 18	-23 / 23	-19 / 19
Data / parameters	3995 / 291	8049 / 581	7575 / 546	3811 / 264	5033 / 294
Final <i>R</i> indices	<i>R</i> ₁ = 0.0988	<i>R</i> ₁ = 0.0892	<i>R</i> ₁ = 0.0825	<i>R</i> ₁ = 0.0662	<i>R</i> ₁ = 0.0525
	<i>wR</i> ₂ = 0.2219	<i>wR</i> ₂ = 0.2135	<i>wR</i> ₂ = 0.2026	<i>wR</i> ₂ = 0.1768	<i>wR</i> ₂ = 0.1076
<i>R</i> indices	<i>R</i> ₁ = 0.2352	<i>R</i> ₁ = 0.1599	<i>R</i> ₁ = 0.1638	<i>R</i> ₁ = 0.0894	<i>R</i> ₁ = 0.0998
	<i>wR</i> ₂ = 0.2838	<i>wR</i> ₂ = 0.2444	<i>wR</i> ₂ = 0.2456	<i>wR</i> ₂ = 0.1920	<i>wR</i> ₂ = 0.1248
<i>S</i>	0.907	1.010	0.945	1.100	1.014
Max. / min. $\Delta\rho$ /e·Å ⁻³	0.421 / -0.487	0.861 / -0.773	0.534 / -0.415	1.158 / -0.683	0.340 / -0.312

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2} \right]^{1/2}$$

Table S2 Selected bond distances (Å) and angles (°) for *cis-4*, *trans-4*, *cis-6*, *trans-6* and *trans-7*.

<i>cis-4</i>		<i>trans-4</i>		<i>cis-6</i>	
Bond distances					
Cl1-C2	1.726(7)	Cl1-C3	1.717(6)	S1-C1	1.738(5)
S1-C1	1.736(6)	Cl2-C26	1.709(6)	S1-C4	1.744(6)
S1-C4	1.733(6)	S1-C4	1.745(6)	S2-C24	1.734(5)
O1-N5	1.263(18)	S1-C1	1.725(6)	S2-C27	1.719(5)
O2-N5	1.17(2)	S2-C27	1.736(6)	N1-N2	1.284(6)
N1-N2	1.292(8)	S2-C24	1.733(6)	N1-C4	1.362(6)
N1-C4	1.351(8)	O1-N5	1.227(9)	N2-C14	1.389(6)
N2-C14	1.363(8)	O2-N5	1.211(9)	N3-C13	1.142(9)
N3-C13	1.144(12)	O3-N10	1.082(15)	N4-C22	1.479(13)
N4-C17	1.347(10)	O4-N10	1.265(15)	N4-C17	1.364(7)
N4-C20	1.468(12)	N1-C1	1.370(7)	N4-C20	1.471(8)
N4-C22	1.474(11)	N1-N2	1.289(6)	N4-C22'	1.585(19)
N5-C10	1.484(19)	N2-C14	1.380(7)	N5-C27	1.382(6)
		N3-C13	1.156(10)	N5-N6	1.292(6)
		N4-C17	1.377(11)	N6-C37	1.388(6)
		N4-C20	1.524(14)	N7-C36	1.145(10)
		N4-C22	1.539(15)	N8-C43	1.463(7)
		N5-C10	1.461(9)	N8-C45	1.446(8)
		N6-C24	1.374(7)	N8-C40	1.367(7)
		N6-N7	1.287(6)		
		N7-C37	1.391(7)		
		N8-C36	1.143(9)		
		N9-C40	1.364(9)		
		N9-C43	1.504(11)		
		N9-C45	1.555(10)		

		N10-C33	1.448(16)		
Bond angles					
C1-S1-C4	92.6(3)	C1-S1-C4	91.7(3)	C1-S1-C4	92.0(3)
N2-N1-C4	113.1(5)	C24-S2-C27	91.5(3)	C24-S2-C27	91.7(2)
N1-N2-C14	116.1(6)	N2-N1-C1	112.5(4)	N2-N1-C4	114.9(4)
C17-N4-C20	122.9(7)	N1-N2-C14	115.0(5)	N1-N2-C14	114.7(4)
C17-N4-C22	120.5(7)	C17-N4-C22	119.4(8)	C17-N4-C20	121.7(5)
C20-N4-C22	116.6(7)	C20-N4-C22	116.7(8)	C17-N4-C22	119.6(6)
O1-N5-O2	125.2(14)	C17-N4-C20	123.6(9)	C20-N4-C22	116.0(6)
O1-N5-C10	112.3(12)	O1-N5-O2	124.2(7)	C20-N4-C22'	110.9(7)
O2-N5-C10	122.5(14)	O2-N5-C10	118.6(6)	C17-N4-C22'	120.9(8)
S1-C1-C2	108.3(5)	O1-N5-C10	117.2(6)	N6-N5-C27	112.9(4)
S1-C1-C5	125.5(6)	N7-N6-C24	110.9(4)	N5-N6-C37	114.8(4)
Cl1-C2-C1	123.3(5)	N6-N7-C37	116.2(4)	C43-N8-C45	117.4(5)
Cl1-C2-C3	120.7(7)	C43-N9-C45	114.4(6)	C40-N8-C45	121.5(5)
S1-C4-N1	124.2(5)	C40-N9-C43	121.1(6)	C40-N8-C43	120.9(4)
S1-C4-C3	110.9(5)	C40-N9-C45	123.3(6)	S1-C1-C5	125.6(5)
N1-C4-C3	124.9(6)	O3-N10-O4	114.0(9)	S1-C1-C2	108.9(4)
N5-C10-C9	123.1(11)	O3-N10-C33	124.6(12)	Cl1-C2-C3	121.6(4)
N5-C10-C11	116.0(11)	O4-N10-C33	121.1(11)	Cl1-C2-C1	122.6(4)
N3-C13-C3	177.6(8)	S1-C1-N1	124.6(4)	N1-C4-C3	124.2(5)
N2-C14-C15	125.9(6)	N1-C1-C2	123.9(5)	S1-C4-N1	124.8(4)
N2-C14-C19	116.9(6)	S1-C1-C2	111.5(4)	S1-C4-C3	111.0(4)
N4-C17-C16	122.1(7)	Cl1-C3-C2	122.0(4)	N2-C14-C15	117.7(5)
N4-C17-C18	122.7(7)	Cl1-C3-C4	123.2(4)	N2-C14-C19	124.7(5)
N4-C20-C21	112.9(8)	S1-C4-C5	121.5(4)	N4-C17-C16	122.0(5)
N4-C22-C23	112.6(7)	S1-C4-C3	110.1(4)	N4-C17-C18	121.9(5)
		N5-C10-C9	119.3(5)	N4-C20-C21	114.5(5)
		N5-C10-C11	119.8(6)	N4-C22-C23	110.1(9)

	N3-C13-C2	178.3(7)	N4-C22'-C23'	105.0(16)
	N2-C14-C15	125.2(5)		
	N2-C14-C19	116.4(5)		
	N4-C17-C16	120.9(7)		
	N4-C17-C18	121.5(7)		
	N4-C20-C21	101.9(9)		
	N4-C22-C23	107.1(10)		

trans-6

trans-7

Bond distances

Cl1-C2	1.715(4)	Cl1-C2	1.726(2)
S1-C1	1.741(3)	S1-C1	1.744(3)
S1-C4	1.731(3)	S1-C4	1.746(3)
N1-N2	1.285(4)	N1-C14	1.142(4)
N1-C4	1.376(5)	N2-N3	1.291(3)
N2-C14	1.382(4)	N2-C4	1.379(3)
N3-C13	1.127(7)	N3-C15	1.391(3)
N4-C17	1.357(6)	N4-C18	1.363(3)
N4-C20	1.566(7)	N4-C21	1.491(5)
N4-C22	1.472(5)	N4-C23	1.462(4)
		N4-C21'	1.609(12)

Bond angles

C1-S1-C4	91.7(2)	C1-S1-C4	91.6(1)
N2-N1-C4	113.0(3)	N3-N2-C4	113.0(2)
N1-N2-C14	115.5(3)	N2-N3-C15	115.2(2)
C17-N4-C20	120.2(4)	C18-N4-C21	121.7(3)
C17-N4-C22	121.9(4)	C18-N4-C23	121.7(2)
C20-N4-C22	117.0(4)	C18-N4-C21'	115.4(5)
S1-C1-C2	110.3(2)	C21-N4-C23	116.0(3)
S1-C1-C5	122.4(3)	C21'-N4-C23	114.8(4)

CI1-C2-C1	123.7(3)	S1-C1-C2	110.4 (2)
CI1-C2-C3	121.8(3)	S1-C1-C5	122.8(2)
S1-C4-N1	124.6(3)	CI1-C2-C1	123.7(2)
S1-C4-C3	111.5(3)	CI1-C2-C3	121.8(2)
N1-C4-C3	123.8(3)	S1-C4-N2	124.3(2)
N3-C13-C3	179.4(5)	S1-C4-C3	111.6(2)
N2-C14-C15	125.4(3)	N2-C4-C3	124.0(2)
N2-C14-C19	116.7(3)	N4-C18-C17	122.0(2)
N4-C17-C16	122.0(4)	N4-C18-C19	120.7(3)
N4-C17-C18	121.4(4)	N4-C21-C22	108.5(3)
N4-C20-C21	100.4(5)	N4-C21'-C22'	100.8(8)
N4-C22-C23	112.0(4)	N4-C23-C24	113.9(2)

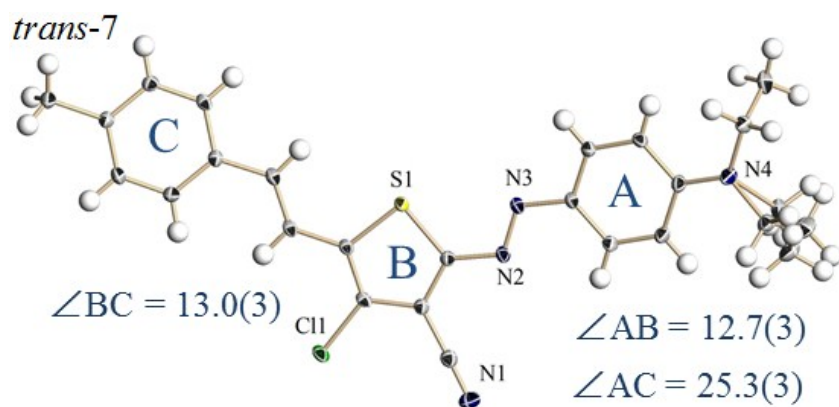
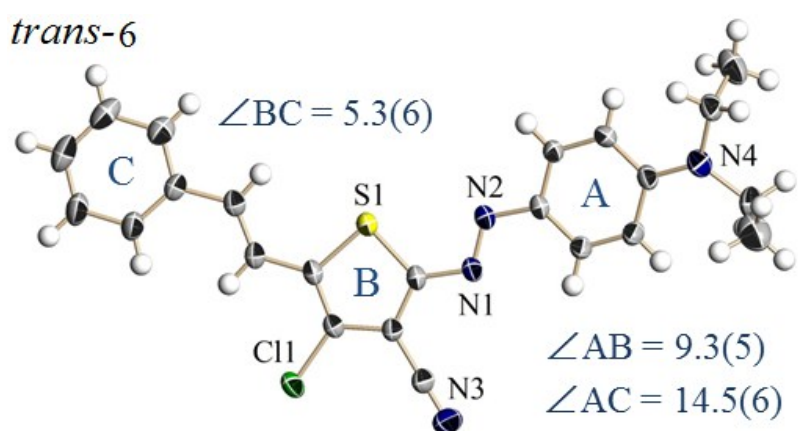
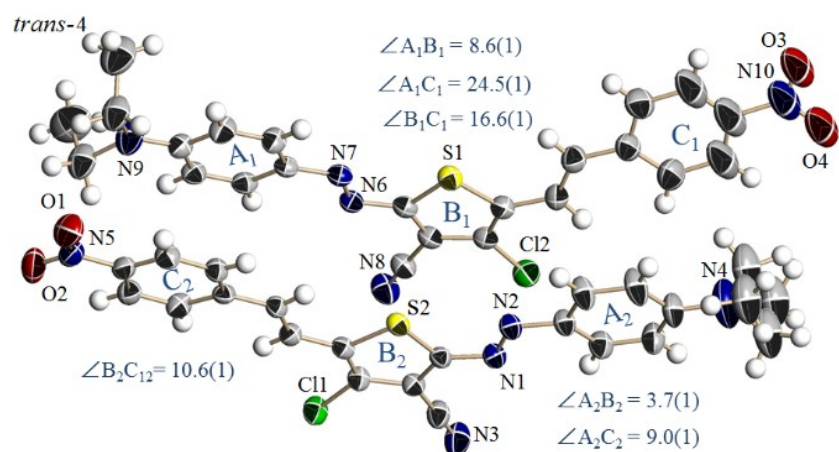
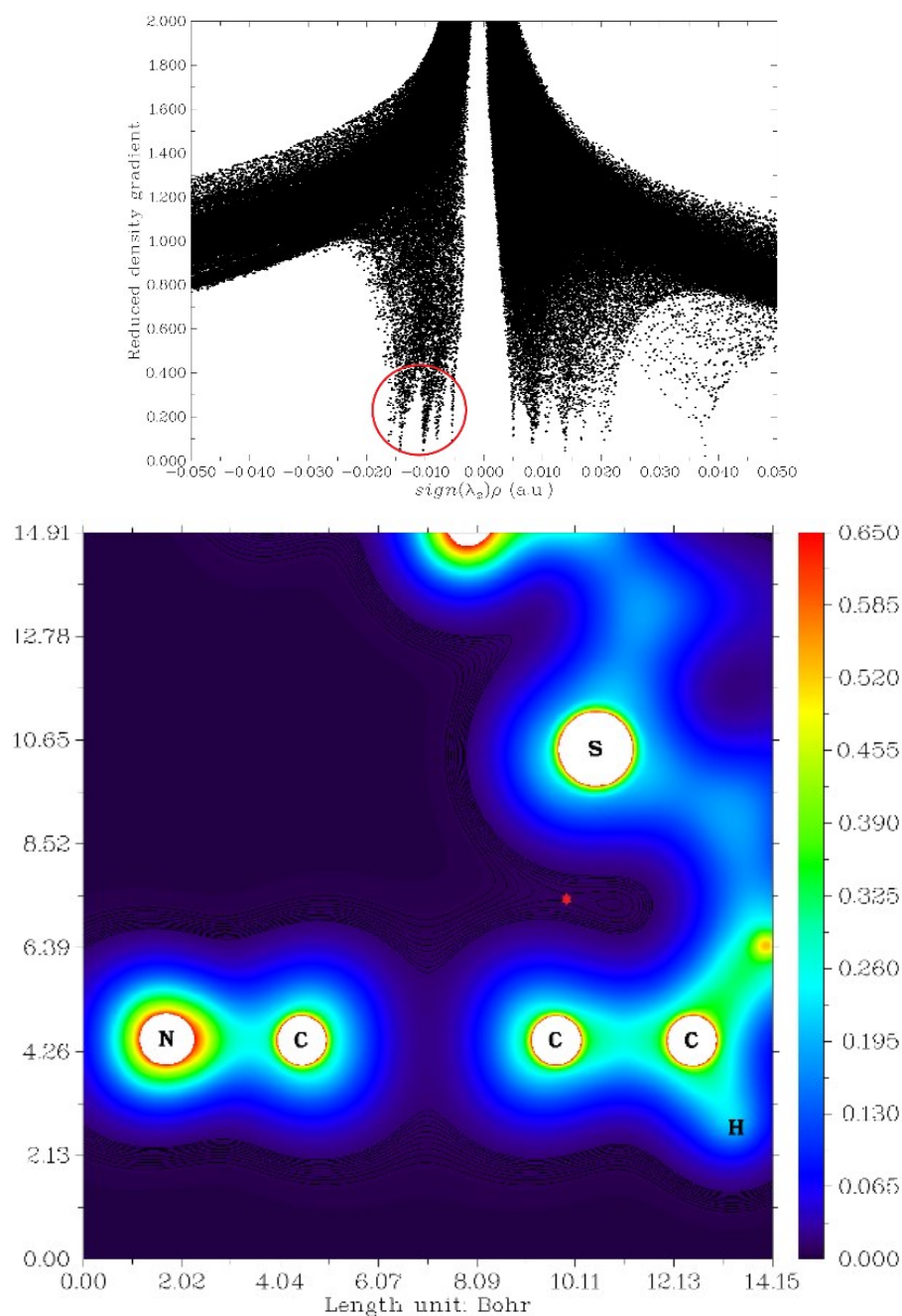


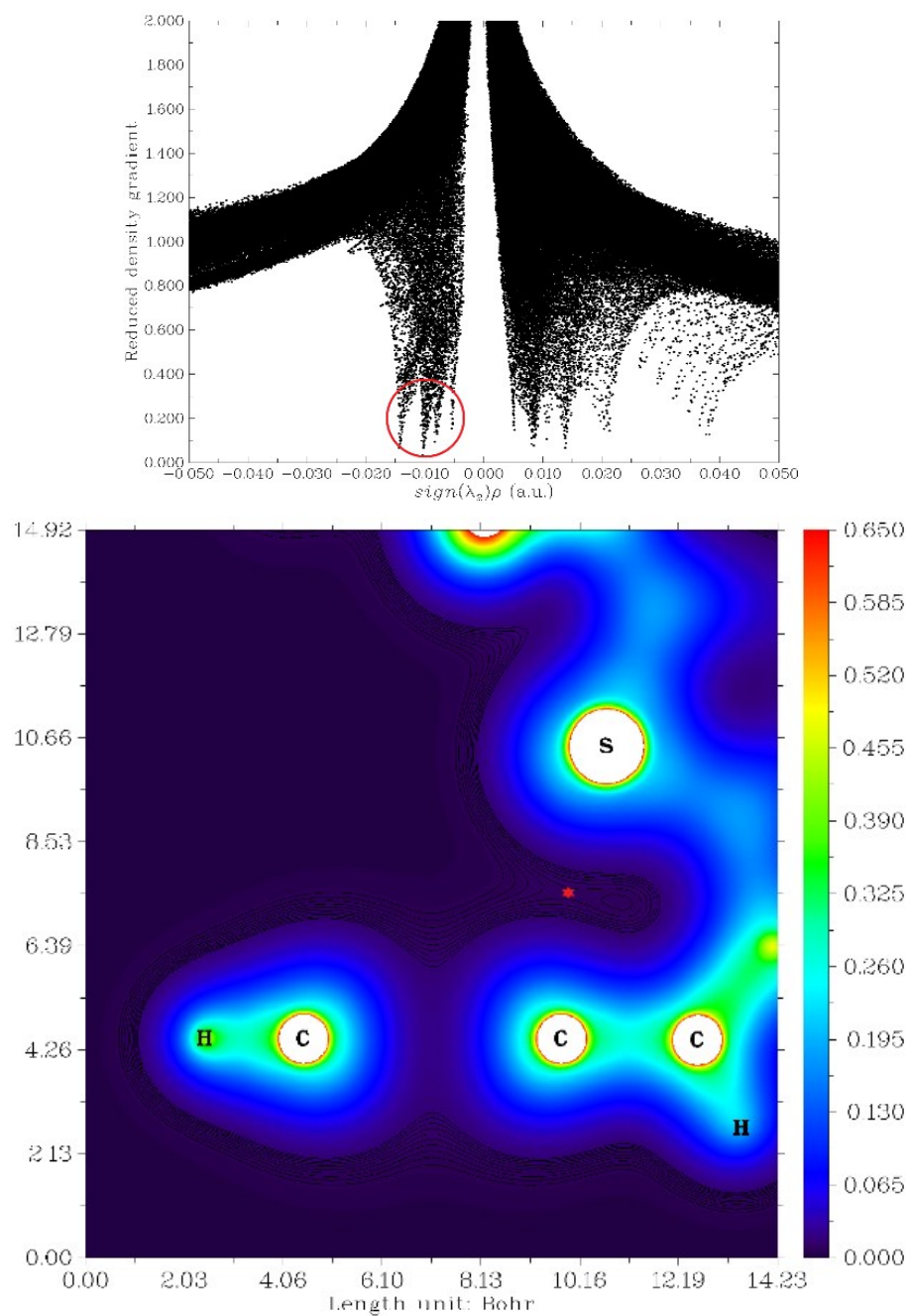
Fig. S22 ORTEP drawing of *trans-4*, *trans-6* and *trans-7* with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level and the hydrogen atoms are shown as small spheres of arbitrary radii. The dihedral angles between adjacent aromatic rings are given (°).

4. Calculation Details

Theoretical calculations were performed using the Gaussian 09 (revision D01) suite of programs.⁵⁵ Both the *cis* conformers for alkenes were fully optimized by using the M062X method including the Grimme's dispersion correction in its version (DFT-D3)⁵⁶ and the 6-31+G** basis. Analyses of the noncovalent interactions and electron density difference were carried out by analyzing the wave functions for the optimized structures using the multiwfn software package.⁵⁷



(a)



(b)

Fig. S23 Plots of reduced density gradient (RDG) versus $\text{sign}(\lambda_2)\rho$, and electron density color-filled maps for *cis-4* (a) and *cis-6* (b). The data was obtained by evaluating M062X /6-31+G** density and gradient values on cuboid grids.

Table S3 Electron densities (ρ) and Laplacians of electron density ($\nabla^2\rho$) of BCP in *cis-4* and *cis-6*

	<i>cis-4</i> ($S\cdots\pi$ interaction)	<i>cis-6</i> ($S\cdots\pi$ interaction)
ρ (a.u.)	0.1043E-01	0.1033E-01
$\nabla^2\rho$ (a.u.)	0.3493E-01	0.3443E-01

5. UV-Vis spectra of compounds 4 and 6

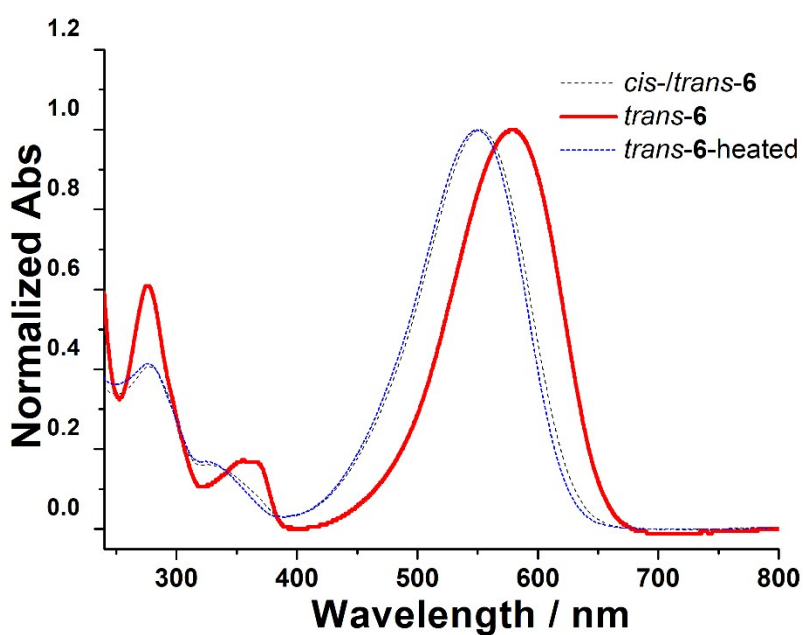


Fig. S24 Normalized UV-Vis spectra of the photoisomerization of *cis-/trans-6* (black dotted line) in CHCl_3 at 25 °C, and *trans-6* (red line) obtained upon irradiation of the sample at 570 nm (59 % *cis*-isomer; irradiation time 1 h). The reverse isomerization of *trans-6* back to *cis-/trans-6* (blue dotted line) triggered by heating under 60 °C for 1 h.

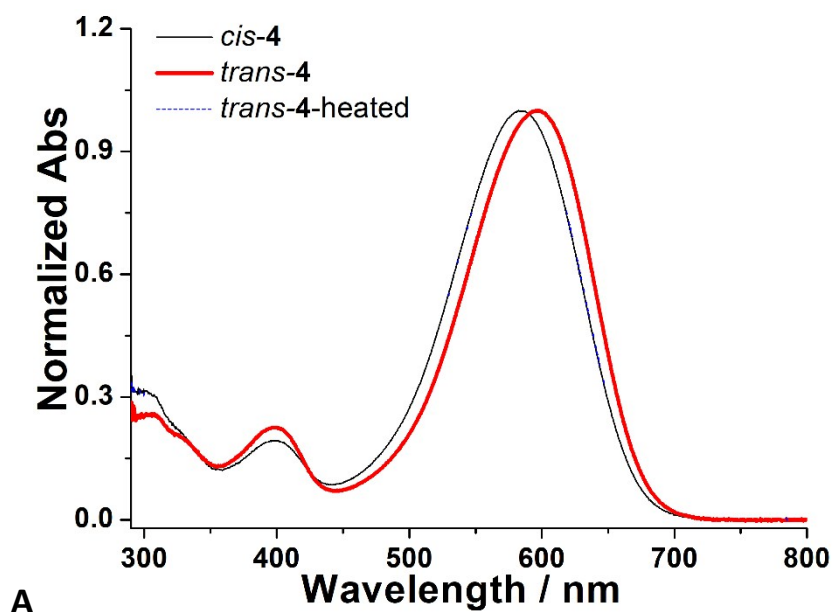


Fig. S25 The reverse isomerization of *trans*-4 (red line) back to *cis*-4 (blue dotted line) triggered by heating under 60 °C for 1 h.

Note

We first prepared a solution with a concentration of 8×10^{-3} mol/L for *cis*-4 and *cis*-/*trans*-6, respectively, for irradiation with a 570 nm laser light at 25 °C. In the case of *cis*-4, the changes of the molecular structure were monitored by ^1H NMR spectroscopy every 20 minutes until the spectrum keeps unchangeable (about illumination for 80 min). Meanwhile, the corresponding solutions before and after complete irradiation were diluted to 8×10^{-5} mol/L and tested using UV-Vis spectroscopy method. Thus, the UV-Vis absorption spectra of *cis* and *trans* isomers for compound 4 were obtained. Then, the diluted solution of *trans*-4 was heated for about 1 h to obtain the *cis* isomer, in which the UV-Vis spectrum coincided with that of original *cis* isomer. As for *cis*-/*trans*-6, similar procedures were performed and the complete isomerization of *cis*-*trans* took about 1h via irradiation and heating, respectively.

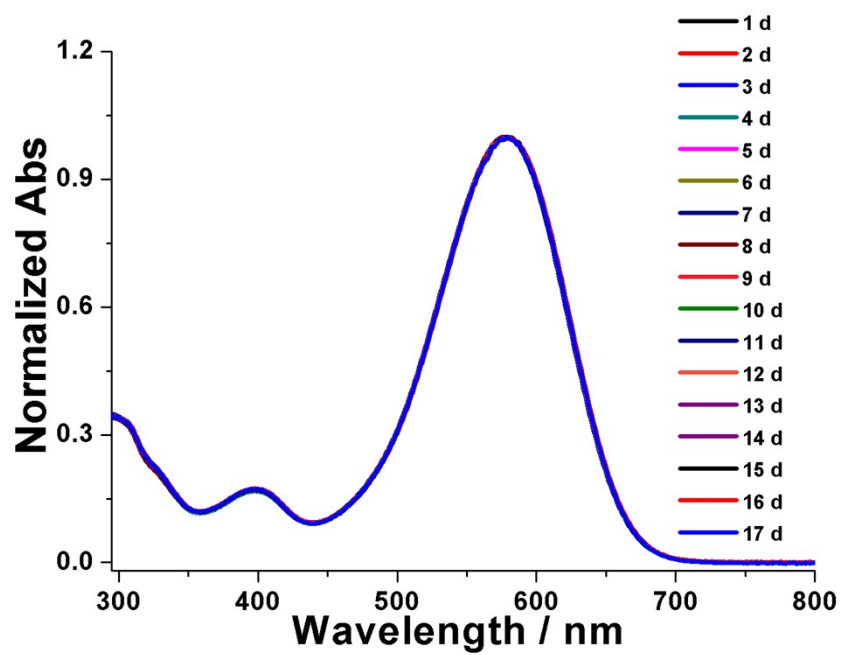


Fig. S26 Normalized UV-Vis spectra of *cis*-4 in CHCl_3 at 25 °C (d: days).

6. ¹H NMR spectra of compounds 4 and 6

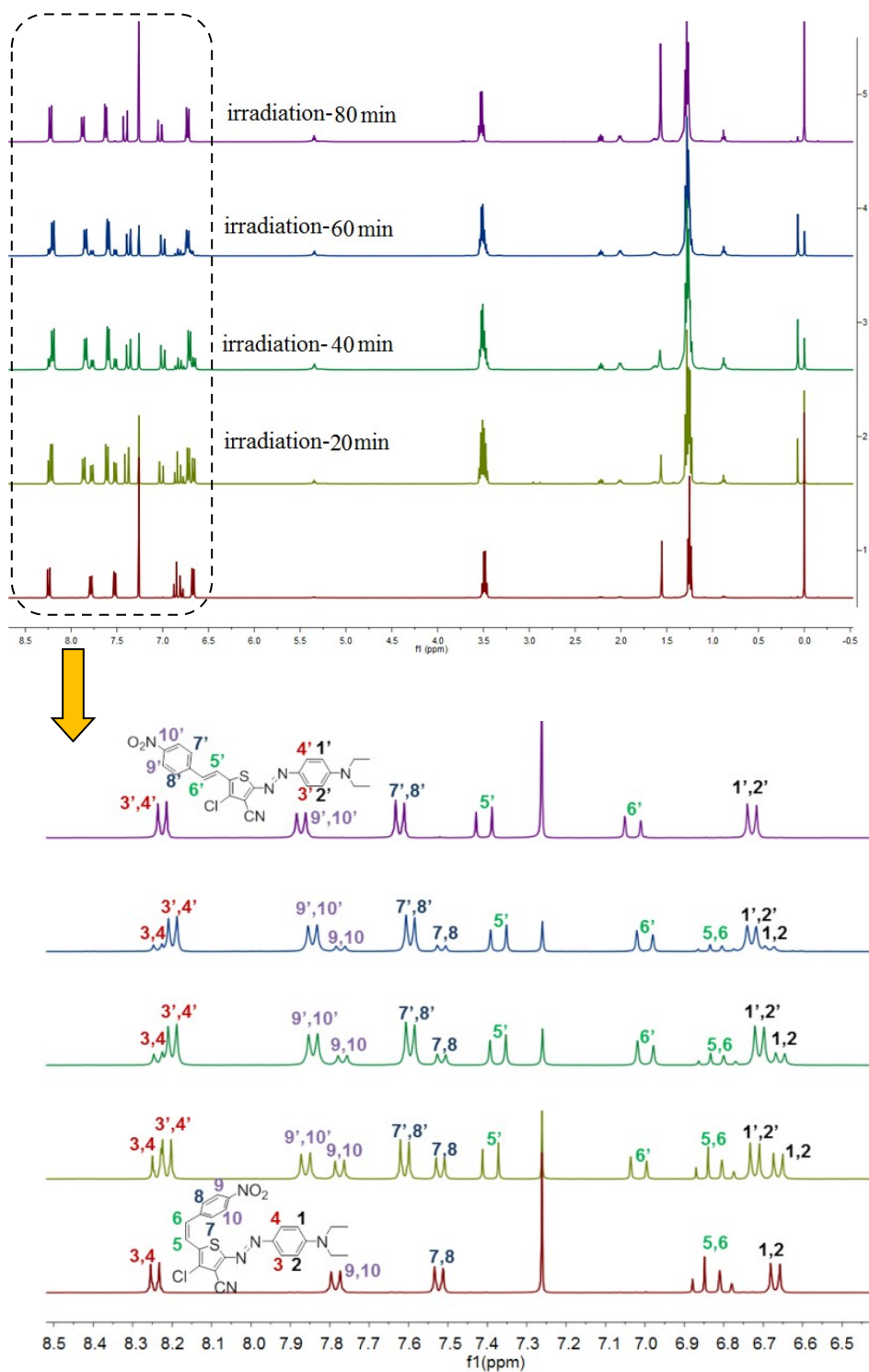


Fig. S27 ¹H NMR spectra of *cis*-4 (red line), photostationary states (*cis*→*trans*) and *trans*-4 (purple line) recorded in CDCl₃ (up: full spectra; below: partial enlarged detail).

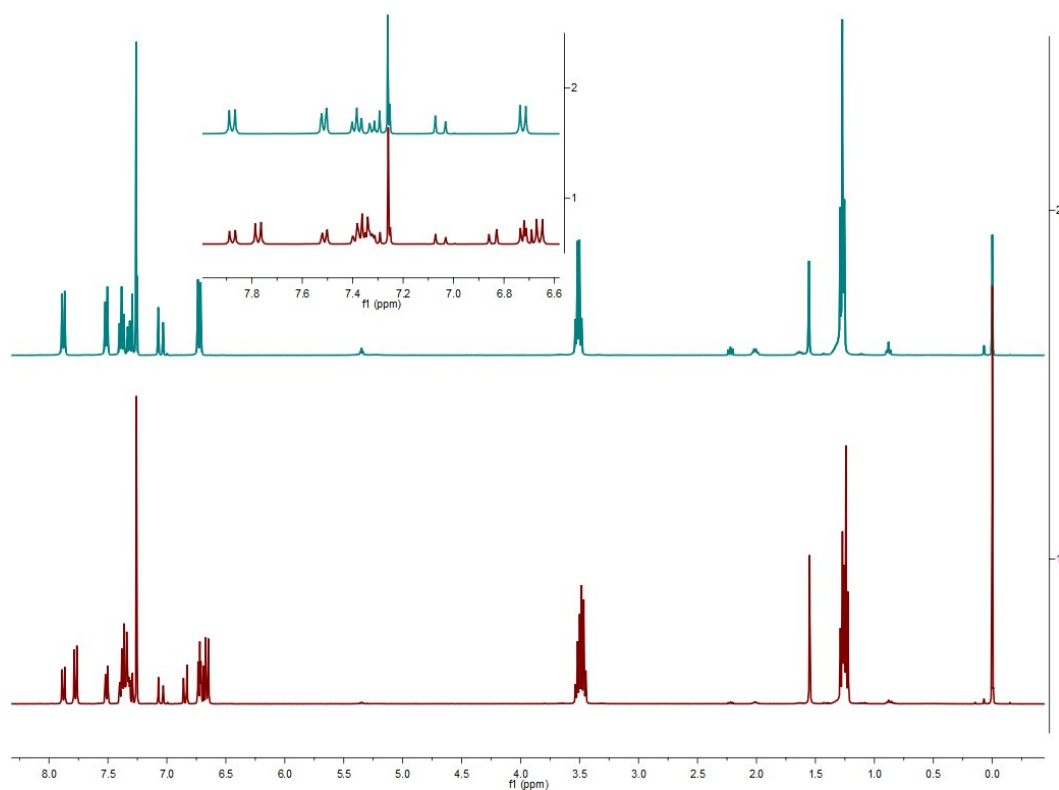
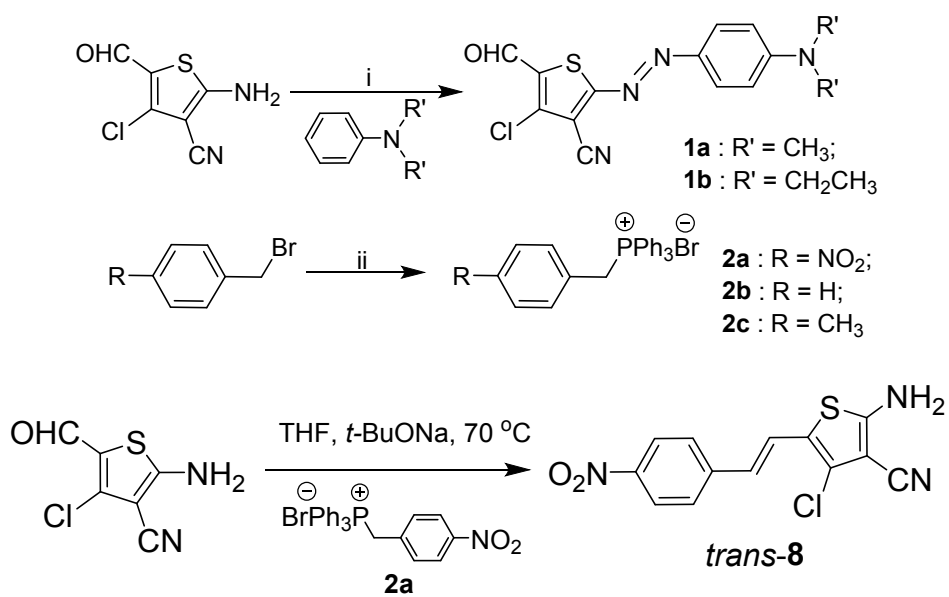


Fig. S28 ^1H NMR spectra of *cis/trans*-**6** (red line) and *trans*-**6** (blue line) recorded in CDCl_3 .

7. Scheme



i): $\text{NaNO}_2 / \text{H}_2\text{SO}_4 / \text{H}_3\text{PO}_4$; ii): PPh_3 , toluene, 90°C

Scheme S1 Synthesis of compounds **1a-1b**, **2a-2b** and *trans*-**8**.

8. References:

- S1 (a) J. Geng, Y. Dai, H. F. Qian, N. Wang and W. Huang, *Dyes Pigm.*, 2015, **117**, 133-140; (b) M. C. Cui, Z. J. Li, R. K. Tang, H. M. Jia and B. L. Liu, *Eur. J. Med. Chem.*, 2011, **46**, 2908-2916.
- S2 Siemens. SAINT v4 software reference manual. Madison, Wisconsin, USA: Siemens Analytical X-ray Systems, Inc.; 2000.
- S3 Sheldrick GM. SADABS, program for empirical absorption correction of area detector data. Germany: Univ. of Gottingen; 2000.
- S4 Siemens. SHELXTL, Version 6.10 reference manual. Madison, Wisconsin, USA: Siemens Analytical X-Ray Systems, Inc.; 2000.
- S5 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
- S6 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- S7 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.