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Electronic Supplementary Information (ESI)

Sterically hindered diarylethenes with a benzobis(thiadiazole) bridge: photochemical and kinetic studies

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1. Computational Details

We employed density functional theory (DFT) calculations to investigate the photochromic DAE compounds. The hybrid B3LYP functional[1,2] and the triple-zeta 6-311G(d,p) basis set[3] were employed in all calculations, with solvent effects taken into account by the polarizable continuum model (PCM).[4] The dispersion corrections are included by the D3 version of Grimme's dispersion with Becke-Johnson damping.[5] For the transition state searching of the ring-opening process, the biradical character of the transition state is described as an open-shell singlet state[6], generated by the Guess (Mix, Always) keyword in the Gaussian 09 program package. In addition, time-dependent (TD) DFT calculations were conducted for **3c** and **4c** in THF, using the 6-311+G(d,p) basis set in which diffuse functions are included.

References

(1) A. D. Becke, Density‐functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.*, 1993, **98**, 5648-5652.

(2) C. Lee, W. Yang and R. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*, 1988, **37**, 785-789.

(3) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, Self‐consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.*, 1980, **72**, 650-654.

(4) J. Tomasi, B. Mennucci and R. Cammi, Quantum Mechanical Continuum Solvation Models. *Chem. Rev.*, 2005, **105**, 2999-3094.

(5) S. Grimme, S. Ehrlich and L. Goerigk, Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.*, 2011, **32**, 1456-1465.

(6) M. Ohsumi, T. Fukaminato and M. Irie, Chemical control of the photochromic reactivity of diarylethene derivatives. *Chem. Commun.*, 2005, 3921-3923.

2. Supplementary spectra

Table S1 Spectroscopic data of *o*-DAEs 2 and 3 in THF.

DAE	λ_{max}[a] [nm]	ε_{max} [10^3 M^{-1} cm^{-1}]	λ_{em}[a] [nm]	Φ_F[b] [%]
2a	282	40.6	514	3.36
2p	283	39.5	492	2.74
3a	288	53.7	600	0.78
3p	287	57.2	590	0.33

[a] Typical absorption (λ_{max}) and emission maxima (λ_{em}), respectively. [b] Fluorescence quantum yield (Φ_F).

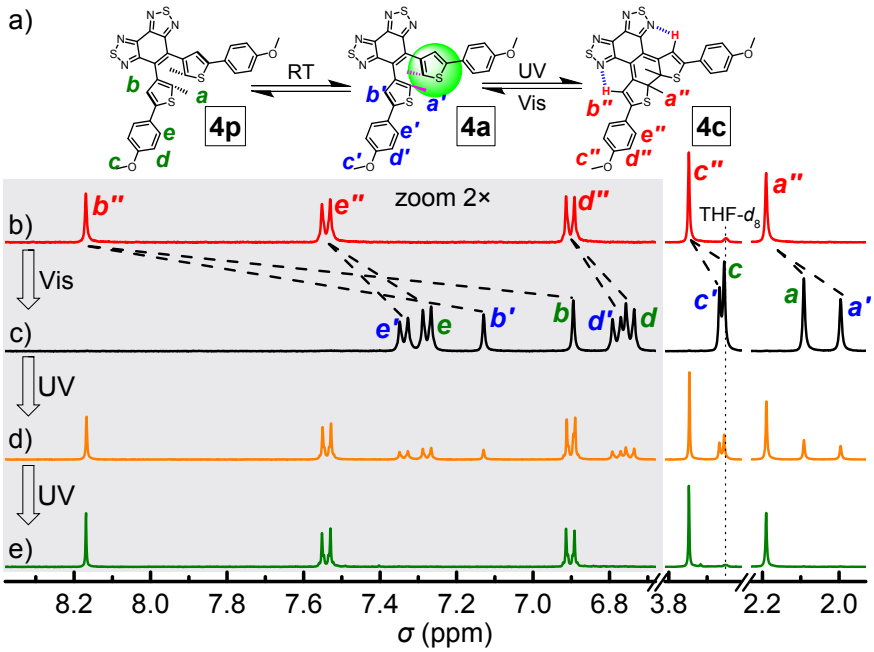


Fig. S1 a) Conversion relationship of **4a**, **4p**, and **4c**. ^{1}H NMR spectroscopic changes of **DAE 4** in THF-d_8: b) **4c**; c) **4o** generated from **4c** by visible irradiation (λ > 470 nm); d) **4o** upon irradiation at 302±20 nm for 1 h; e) **4o** upon irradiation at 302±20 nm for 4 h (PSS). Note: **4o** means the unity of **4a** and **4p**. From integrations, the ratios of **4a** and **4p** always keep 44:56 during the photochromic reactions. ^{1}H NMR spectra in the low-field (marked with shadow) are magnified twice for better presentation. Note: the marked deuterated solvent residues belong to the satellite peaks of residual THF.

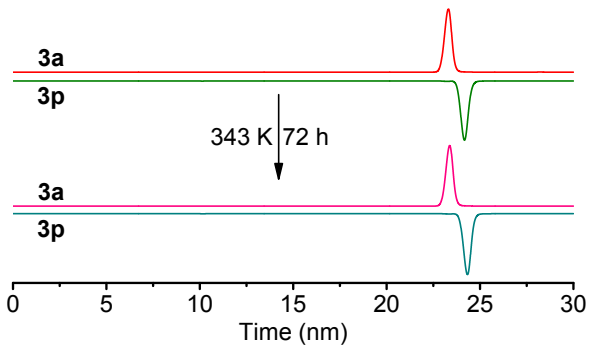


Fig. S2 HPLC chromatograms (C18 column, 250 × 4.6 mm) of **3a** and **3p** (vertically flipped) kept in CH_3CN at 343 K for 72 h, eluted with CH_3CN:H_2O = 85:15 at a flow rate of 0.8 mL / min, detected at 288 nm. No obvious interconversion between **3a** and **3p** was observed.

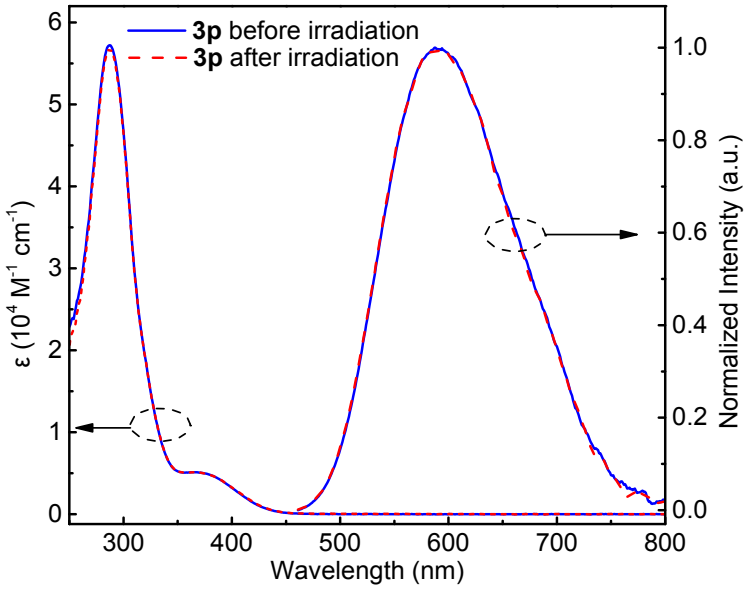
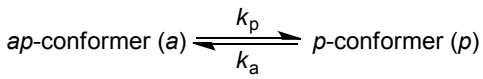


Fig. S3 Spectral changes of UV–Vis absorption and fluorescence of **3p** (2.14×10^{-5} M) in THF upon irradiation at 313 nm (0.21 mW cm^{-2}) for 6 min. No color changes can be observed.

3. Isomeric kinetics of 1a and 1p



Scheme S1

The concentration change of *p*-conformer [*p*] has two contributions: the decay to *ap*-conformer $v = k_a[p]$, and the increase from *ap*-conformer $v = k_p[a]$, where k_a and k_p are first-order rate constants.

$$\frac{d[p]}{dt} = k_p[a] - k_a[p] \qquad \textbf{Eq. 1}$$

Due to the total concentration is constant ($c_0 = [a] + [p]$), Eq.1 can be simplified as Eq.2:

$$\frac{d[p]}{dt} = k_p c_0 - (k_a + k_p)[p] \qquad \textbf{Eq. 2}$$

Replacing the concentration of *p*-conformer [*p*] with its ratio $\alpha_p = [p]/c_0$, Eq. 2 can be further written as Eq. 3:

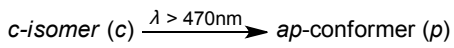
$$\frac{d\alpha_p}{dt} = k_p - (k_a + k_p)\alpha_p \qquad \textbf{Eq.3}$$

After integration (Eq. 4), we get Eq. 5, which reveals the relationship between α_p and *t*.

$$\int \frac{d\alpha_p}{k_p - (k_a + k_p)\alpha_p} = \int dt + constant \qquad \textbf{Eq. 4}$$

$$\alpha_p = \frac{k_p}{k_a + k_p}(1 - e^{-(k_a + k_p)t}) \qquad \textbf{Eq. 5}$$

In order to get the experimental change of α_p, we *in situ* photogenerated the pure *ap*-conformer from the *c*-isomer by visible irradiation ($\lambda > 470$ nm, Scheme S2).



Scheme S2

However, the full conversion inevitably needs certain time (*ca*. 15 min, Fig. 2d). When the *c*-isomer is completely convert to *ap*-conformer, partial *ap*-conformer has already started the exchanging to *p*-conformer. To fix this problem, a time-correction (t_0) should be added to *t*, setting an extrapolated zero time (Eq. 6).

$$\alpha_p = \frac{k_p}{k_a + k_p}(1 - e^{-(k_a + k_p)(t - t_0)}) \qquad \textbf{Eq. 6}$$

α_p was determined by integrating the methyl peaks of *ap*- and *p*-conformers in ^{1}H NMR spectra. Fitting the experimental data with Eq. 6 (Fig. 2e), gave $k_p = 1.21 \times 10^{-5}$ (±0.2%) s^{-1} and $k_a = 9.89 \times 10^{-6}$ (±0.2%) s^{-1}.

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G}{RT}} \qquad \textbf{Eq. 7}$$

We further got thermodynamic data, utilizing Eyring–Polanyi Equation (Eq. 7), where ΔG is the Gibbs energy of activation, k_B is Boltzmann's constant, and h is Planck's constant. At 293 K, the activation energy of *ap*- and *p*-conformer was calculated as ΔG_a = 99.34 kJ mol^{-1} and ΔG_p = 99.84 kJ mol^{-1}. Apparently, *p*-conformer is more stable than *ap*-conformer, leading to a final equilibrium ratio of 45:55 ([*a*]/[*p*]).

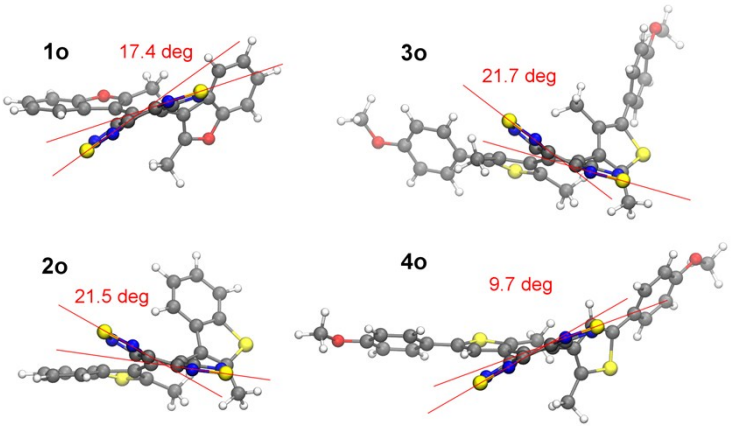


Fig. S4. Optimized *ap*-to-*p* transition states for the ring-open isomers of the photochromic compounds. The bent angles of the BBT bridges are shown.

Table S2. Non-planarity of the furan/thiophene rings and BBT bridges of the photochromic compounds at their *ap*-to-*p* transition states.

	1o	**2o**	**3o**	**4o**
Aryl ring	0.063	0.120	0.112	0.013
BBT bridge	0.177	0.211	0.218	0.117

4. Ring-opening kinetics

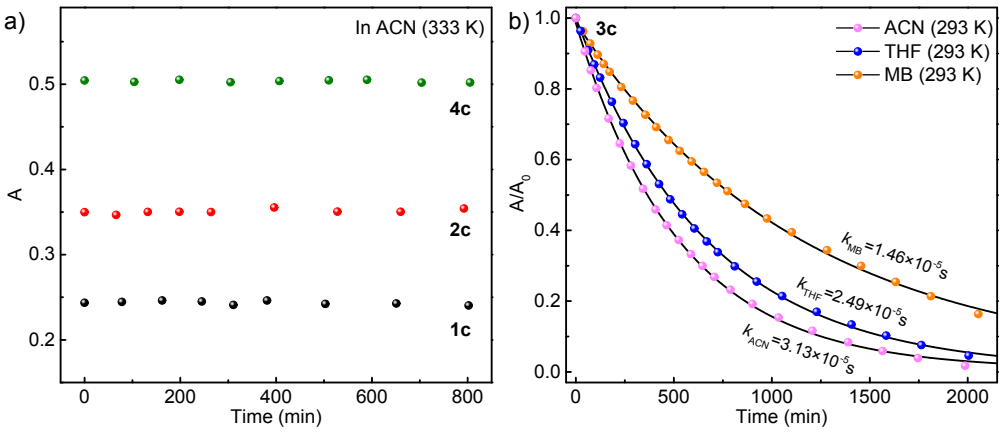


Fig. S5 a) Decay curves (333 K) of **1a** (2.92 × 10^{-5} M), **2a** (5.3 × 10^{-5} M), and **4o** (4.4 × 10^{-5} M) at PSS in acetonitrile (ACN). b) Normalized decay curves (293 K) of **3a** (5.7 × 10^{-5} M) at PSS in toluene (MB), tetrahydrofuran (THF), and acetonitrile (ACN).

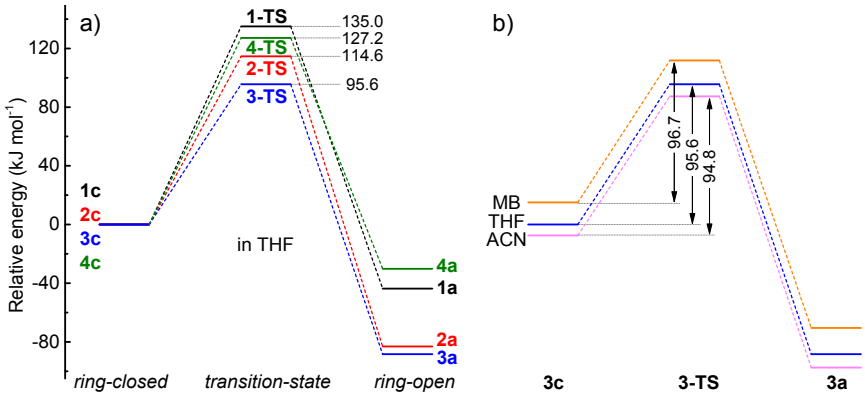


Fig. S6 a) Computed thermal ring-opening processes of *c*-DAEs **1**-**4** in THF. b) Energy level changes of DAE **3** in different solvents. Note: MB = toluene, THF = tetrahydrofuran, ACN = acetonitrile.

Table S3. Kinetic data (first-order) of thermal fading for 3c in various solvents at 293 K.

Solvents	ε_r[a]	λ_{max}[b] [nm]	$\tau_{1/2}$ [h]	k [10^{-5} s^{-1}]
toluene	2.37	575	14.1	1.46
THF	7.85	566	7.84	2.49
acetonitrile	37.5	559	6.21	3.13

[a] solvent dielectric constant. [b] Absorption maxima (λ_{max}) in visible region.

5. Crystal data

Table S4 Crystal data of 1a, 1p, and 1c.

Compounds	**1c**	**3a**	**3p**
CCDC Number	1044913	1044914	1044915
Empirical formula	$C_{24}H_{14}N_4O_2S_2$	$C_{32}H_{26}N_4O_2S_4$	$C_{32}H_{26}N_4O_2S_4$
Formula weight	454.51	626.81	626.81
Temperature / K	140(2)	140(2)	140(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	12.725(4)	16.1783(17)	9.770(2)
b / Å	19.714(6)	11.4535(13)	16.009(4)
c / Å	15.431(5)	15.8616(17)	18.723(4)
α / deg	90.00	90.00	90.00
β / deg	90.046(5)	103.364(2)	97.167(4)
γ / deg	90.00	90.00	90.00
Volume / $Å^3$	3871(2)	2859.5(5)	2905.6(12)
Z	8	4	4
ρ_{calc} / mg/mm^3	1.560	1.456	1.433
F (000)	1872.0	1304.0	1304.0
Crystal size / mm^3	0.15 × 0.12 × 0.08	0.32 × 0.28 × 0.25	0.08 × 0.06 × 0.05
2Θ range for data collection / deg	2.066 - 54	2.588 - 61.68	3.36 - 52
index ranges	$-16 \le h \le 16$,	$-23 \le h \le 21$,	$-11 \le h \le 12$,
	$-25 \le k \le 21$,	$-16 \le k \le 16$,	$-18 \le k \le 19$,
	$-19 \le l \le 19$	$-22 \le l \le 21$	$-22 \le l \le 23$
reflections collected	30337	28671	20574
Independent reflections [R(int)]	8440	8877	5697
	0.0961	0.0555	0.1423
GOF on F^2	0.951	1.031	1.007
Final R indexes [$I \ge 2\sigma$ (I)]	$R_1 = 0.0677$, $wR_2 = 0.1682$	$R_1 = 0.0456$, $wR_2 = 0.1129$	$R_1 = 0.0727$, $wR_2 = 0.1637$
Final R indexes [all data]	$R_1 = 0.1277$, $wR_2 = 0.2090$	$R_1 = 0.0665$, $wR_2 = 0.1287$	$R_1 = 0.1676$, $wR_2 = 0.2165$
Largest diff. peak / hole / e $Å^{-3}$	0.74 / -0.54	0.49 / -0.51	0.44 / -0.31

6. Characterization

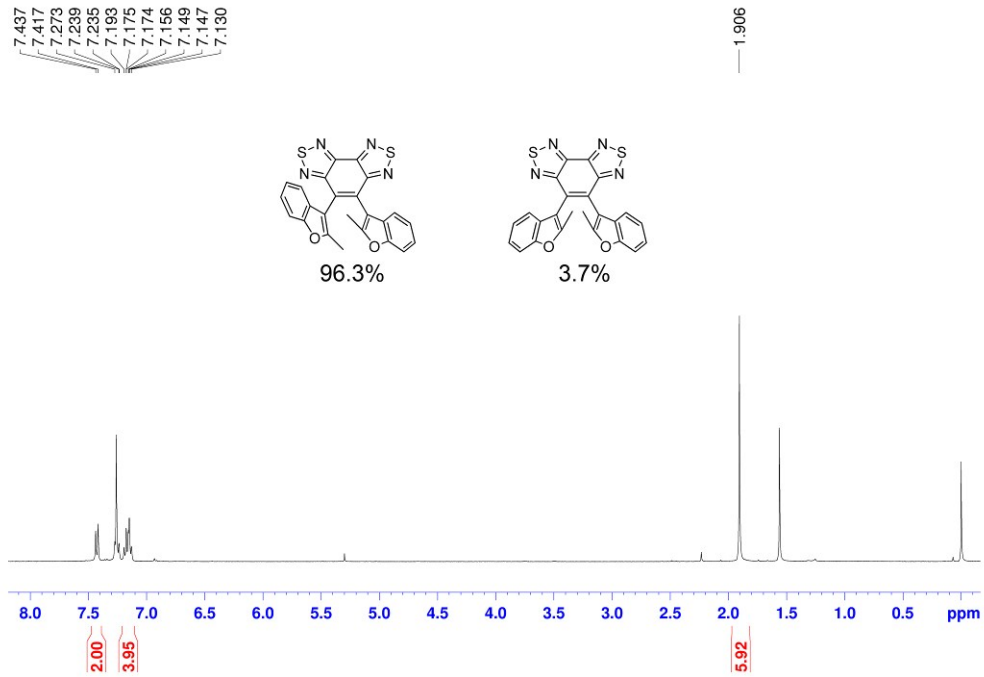


Fig. S7 ^{1}H NMR spectrum of **1a** (96.3%) in $CDCl_3$.

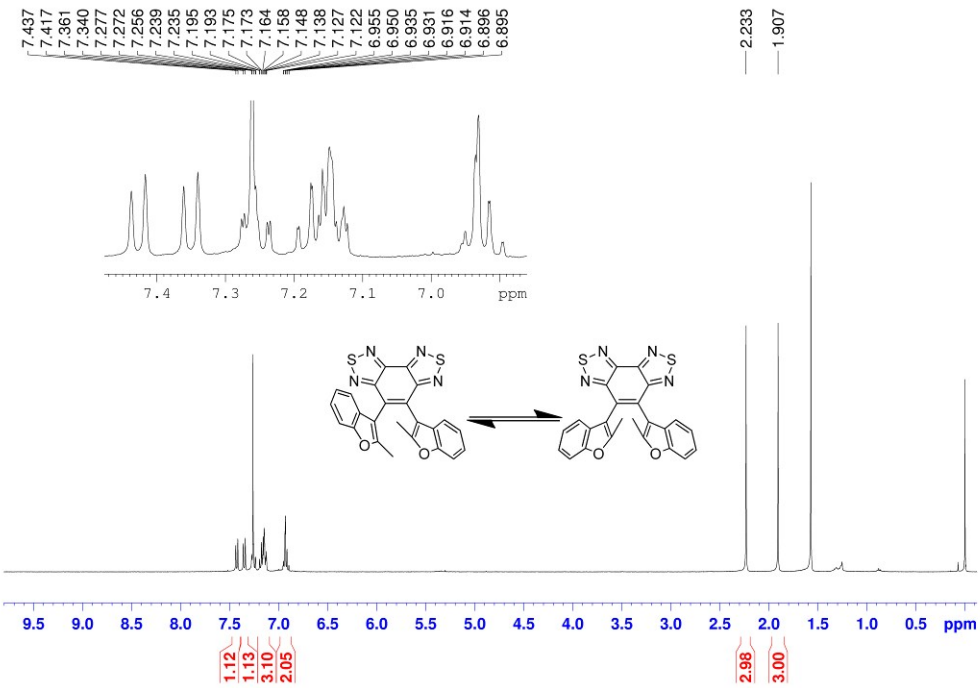


Fig. S8 ^{1}H NMR spectrum of **1a** and **1p** in $CDCl_3$.

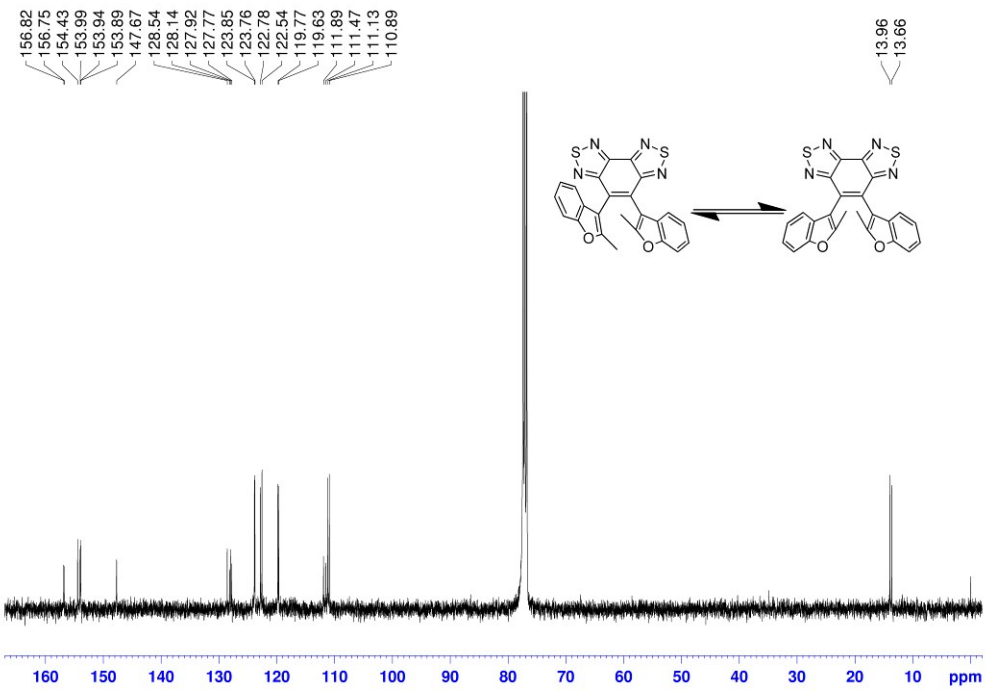


Fig. S9 ^{13}C NMR spectrum of **1a** and **1p** in $CDCl_3$.

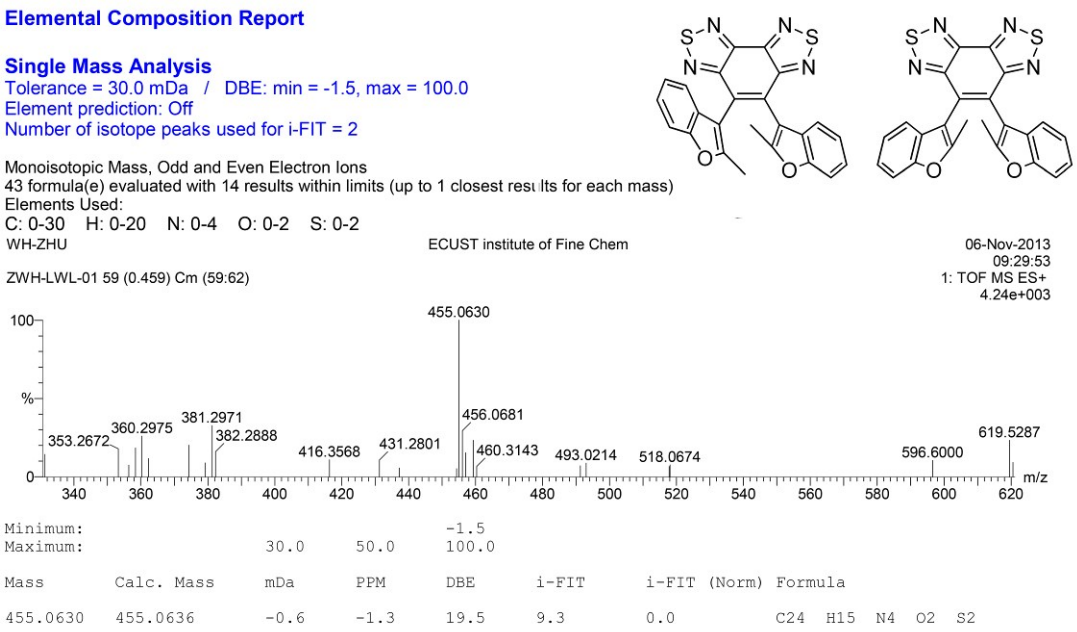


Fig. S10 HRMS spectrum of **1a** and **1p**.

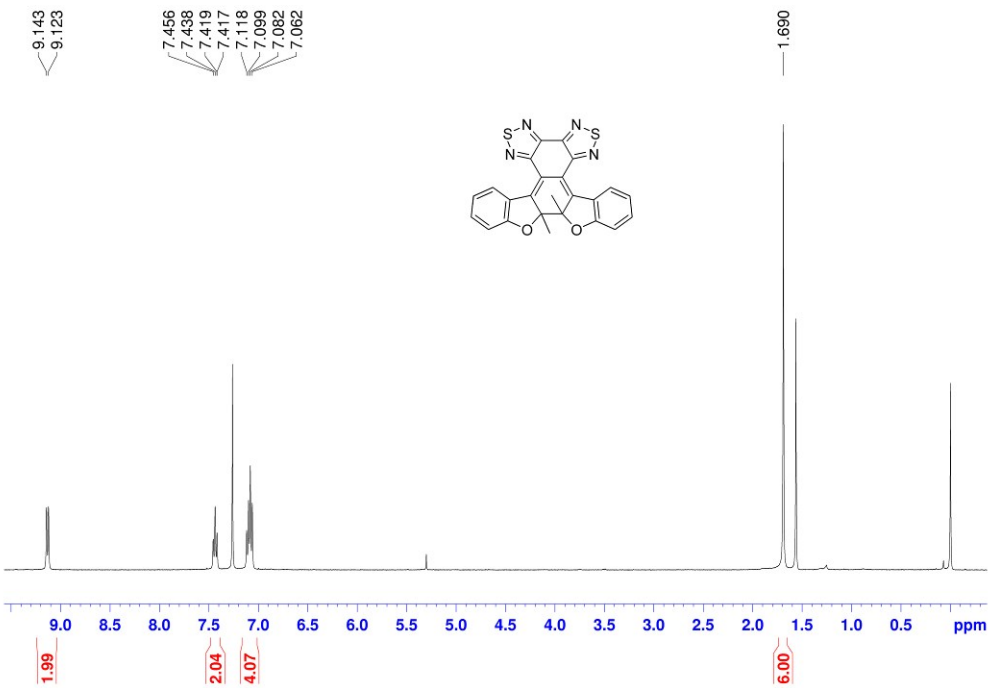


Fig. S11 ^{1}H NMR spectrum of **1c** in $CDCl_3$.

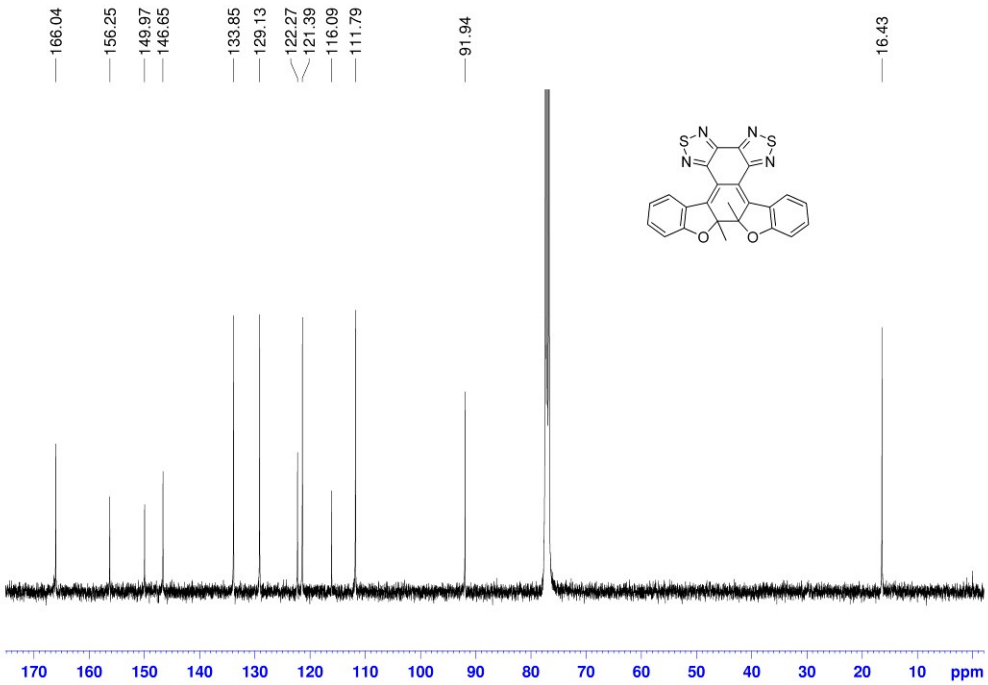


Fig. S12 ^{13}C NMR spectrum of 1c in $CDCl_3$.

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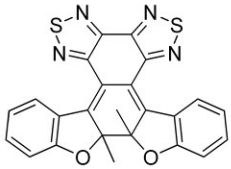

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Number of isotope peaks used for i-FIT = 2

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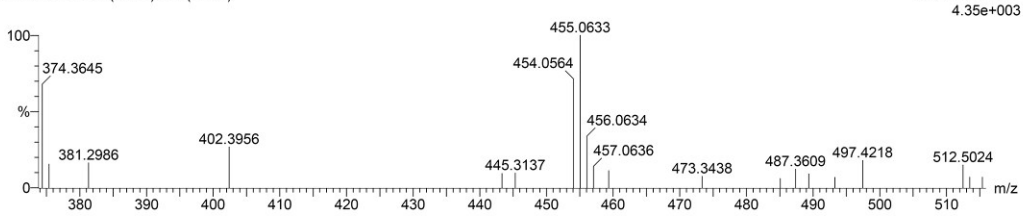

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Fig. S13 HRMS spectrum of **1c**.

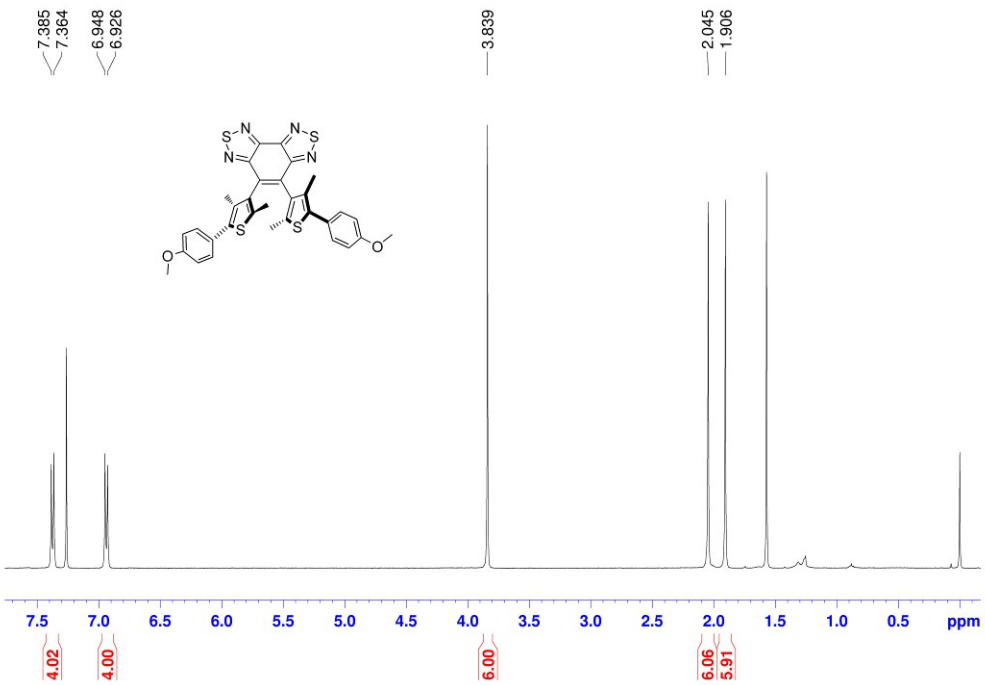

Fig. S14 ^{1}H NMR spectrum of **3a** in $CDCl_3$.

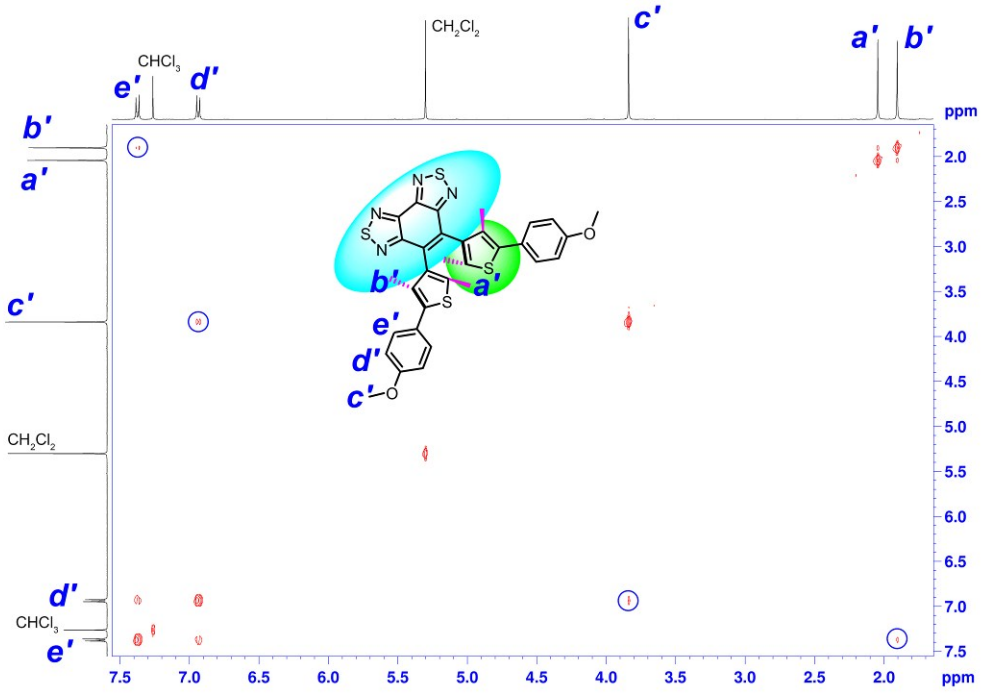

Fig. S15 NOESY NMR spectrum of **3a** in $CDCl_3$.

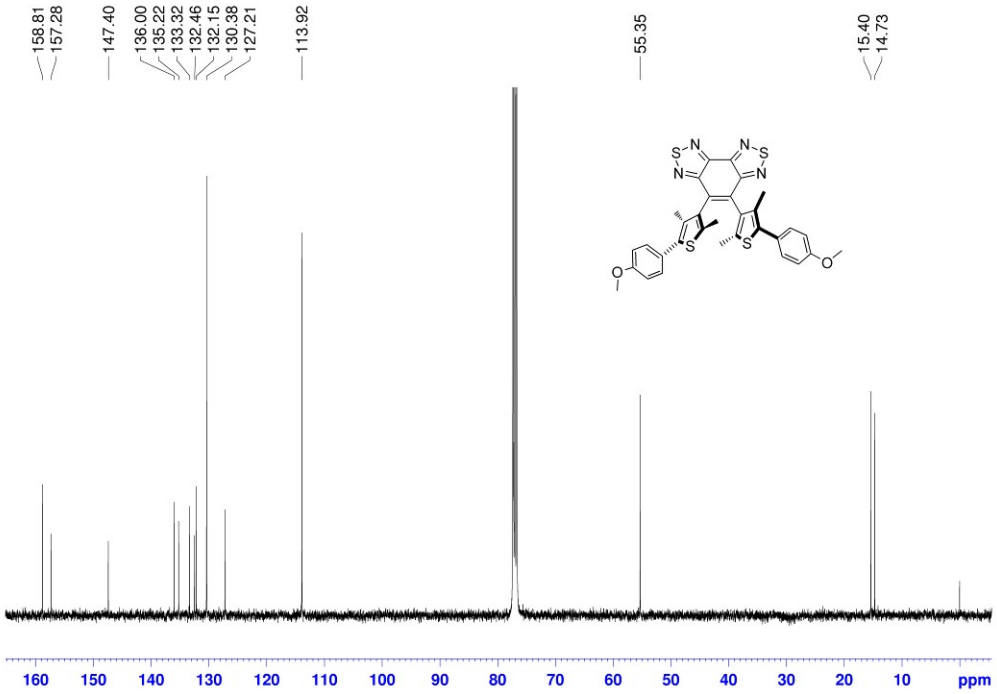

Fig. S16 ^{13}C NMR spectrum of **3a** in $CDCl_3$.

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Monoisotopic Mass, Even Electron Ions
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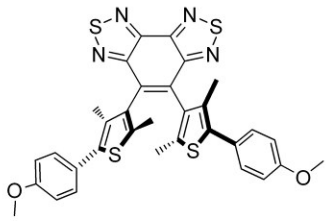

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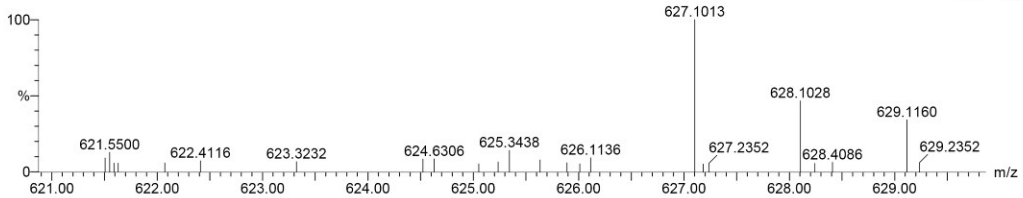

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Fig. S17 HRMS spectrum of **3a**.

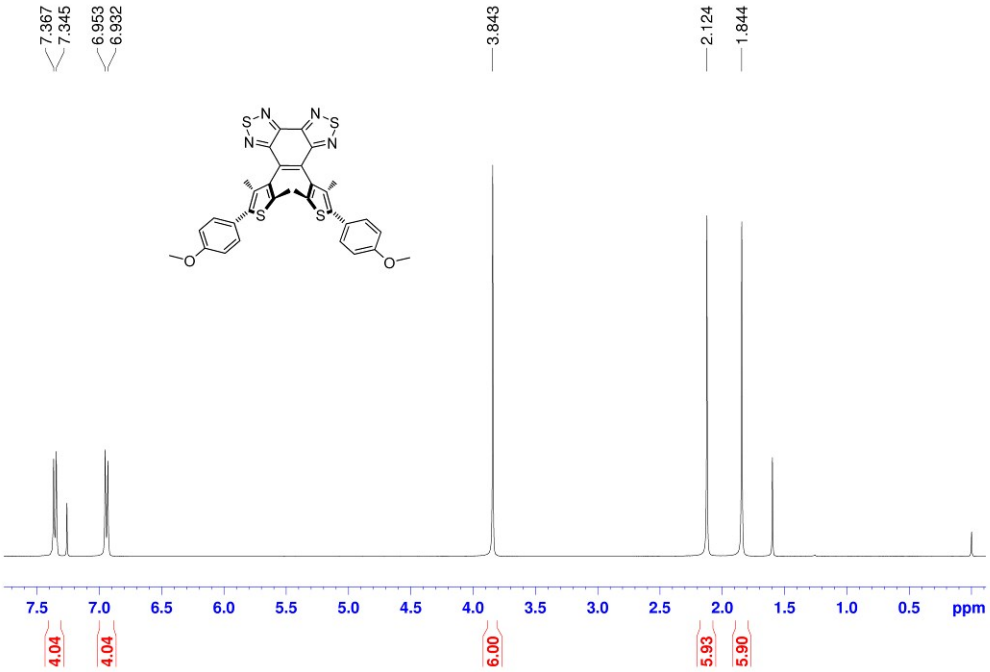

Fig. S18 ^{1}H NMR spectrum of **3p** in $CDCl_3$.

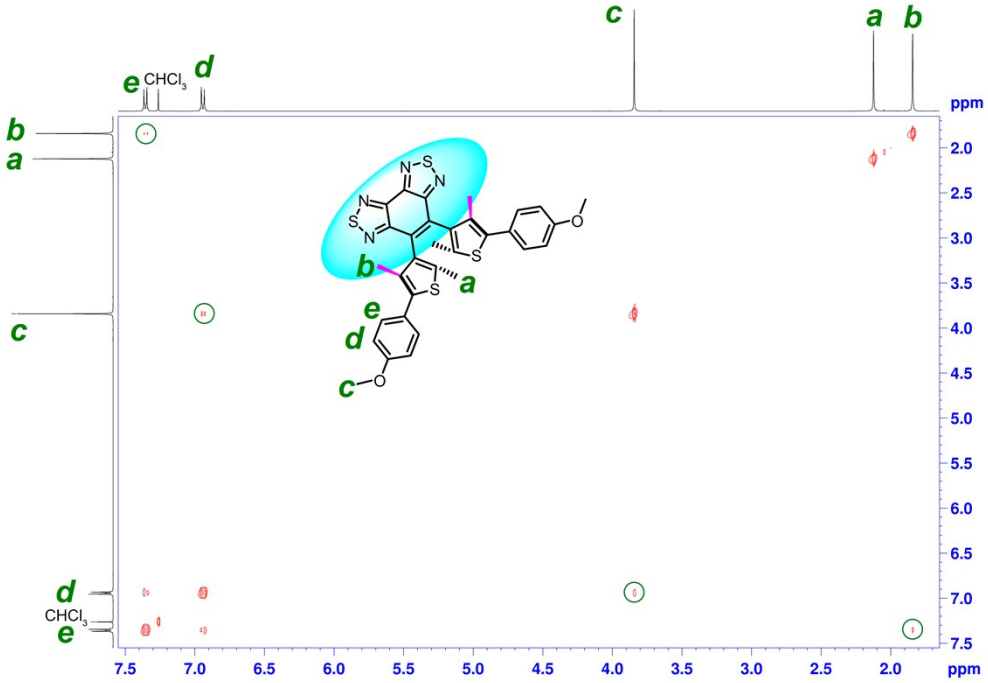

Fig. S19 NOESY NMR spectrum of **3p** in $CDCl_3$.

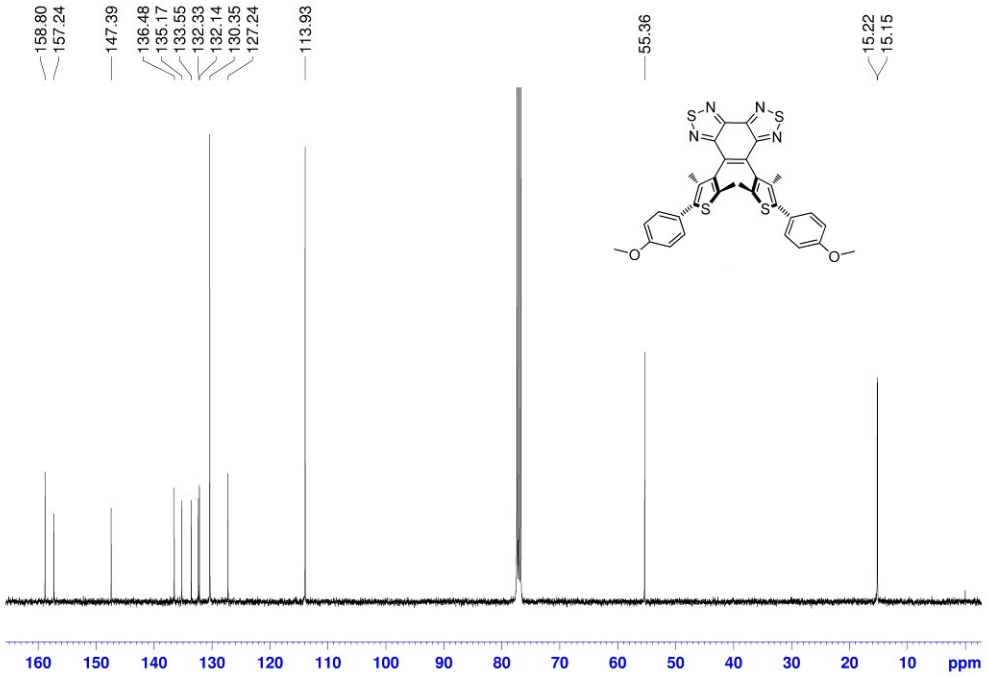

Fig. S20 ^{13}C NMR spectrum of **3p** in $CDCl_3$.

Elemental Composition Report

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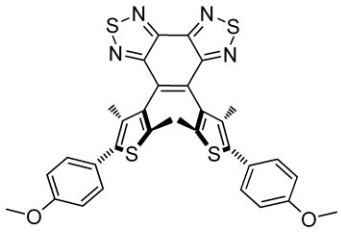
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
83 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-32 H: 0-30 N: 0-4 O: 0-3 S: 0-4



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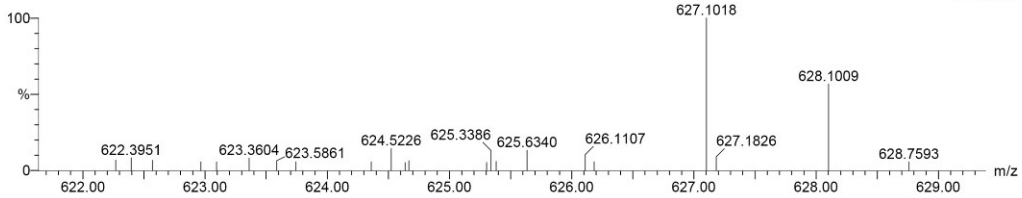
ZWH-LWL-10 11 (0.422) Cm (10:12) 1: TOF MS ES+ 9.11e+001



Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
627.1018	627.1017	0.1	0.2	21.5	12.8	0.0	C32 H27 N4 O2 S4

Fig. S21 HRMS spectrum of **3p**.

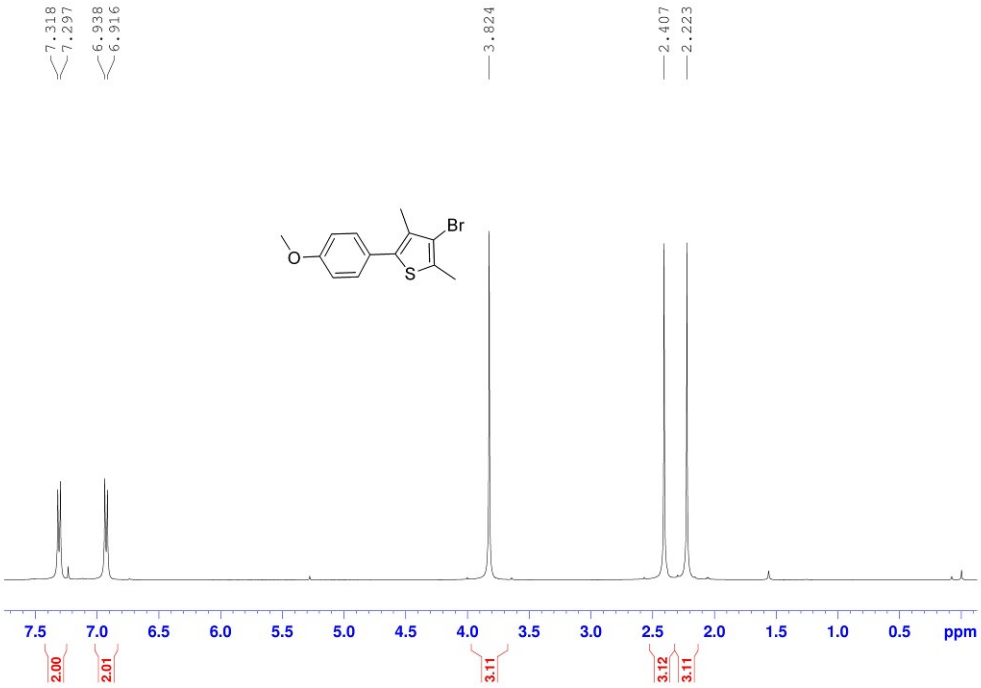


Fig. S22 ^{1}H NMR spectrum of **5** in $CDCl_3$.

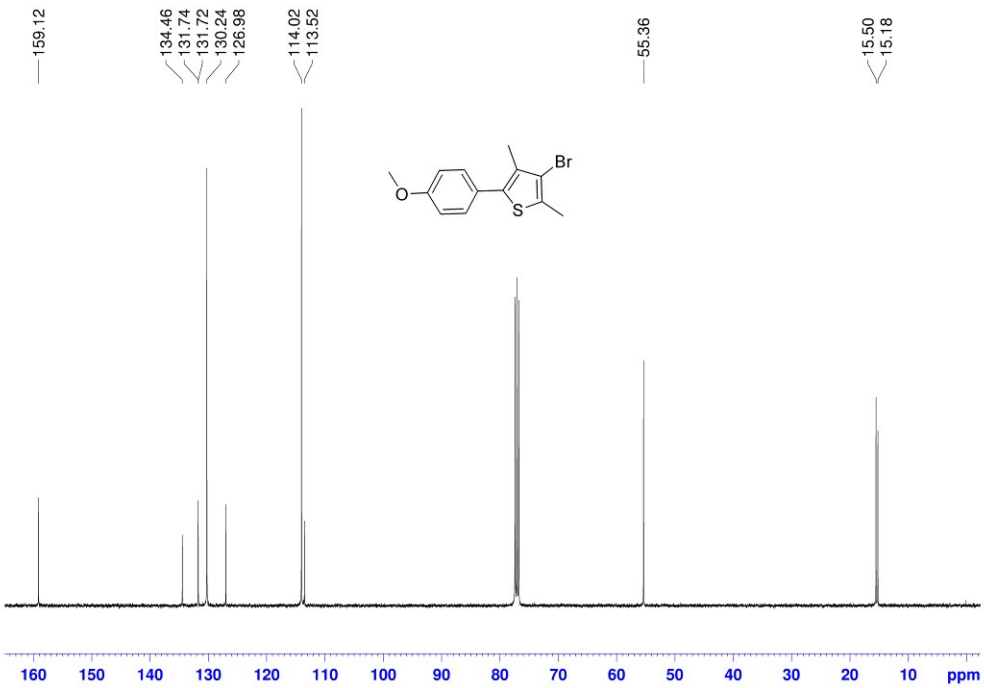
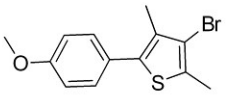


Fig. S23 ^{13}C NMR spectrum of **5** in $CDCl_3$.

Elemental Composition Report

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2



Monoisotopic Mass, Even Electron Ions
215 formula(e) evaluated with 31 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-33 H: 0-26 O: 0-6 S: 0-6 Br: 0-2

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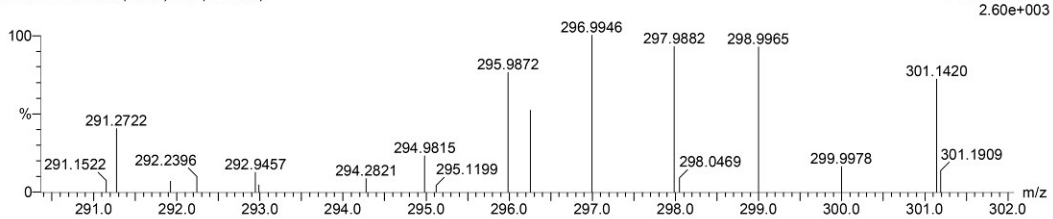
15:33:03
ZWH-LWL-3 199 (1.328) Cm (181:207) 1: TOF MS ES+
2.60e+003



Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
296.9946	296.9949	-0.3	-1.0	6.5	292.4	0.0	C13 H14 O S Br

Fig. S24 HRMS spectrum of **5**.