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An interesting competition between 6π-electro- and Garratt–Braverman cyclization in bis-diene-allene sulfones: synergy between experiment and theory

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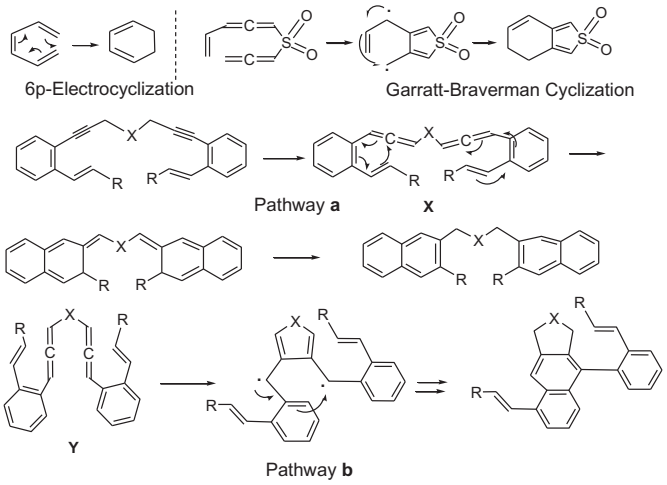
ABSTRACT

The reactivity of a series of bispropargyl sulfones with an *ortho* alkenyl moiety was studied. Under basic condition, these molecules isomerized to the bis-diene-allene system capable of undergoing 6π-electro- (EC) as well as Garratt–Braverman (GB) cyclization. The reaction generally favours the GB process but the balance can be tilted towards the 6π-EC pathway by suitable perturbation of structure and temperature. The findings are useful as the systems undergoing GB pathway can show DNA-damage activities.

1. Introduction

Substrates endowed with functionalities geared towards various reaction pathways are of interest, both from the standpoint of theory and experiment.[1] In many cases it is important to know, which pathway will be followed as one reaction may be biologically or synthetically more relevant than the other. Bis-*Z*-dienyl propargyl sulfones constitute one such system. Under basic condition, these isomerize to the corresponding bisallenic sulfones capable of undergoing two processes, namely a 6π-Electrocyclization (EC)[2] and the other a Garratt–Braverman (GB) cyclization.[3] The major difference between the two processes is the nature of reaction mechanism. The former, if a truly pericyclic process, is a thermally allowed one-step disrotatory ring closing process without the involvement of any intermediate and leads to formation of a new C–C bond. On the other hand, GB cyclization is a multistep process involving a diradical, which collapses to the final product via a self-quenching process and involves the formation of two C–C bonds (Scheme 1). It has been recently shown[1] that sulfones undergoing a slow GB rearrangement can show significant DNA cleavage. The slowing down of GB kinetics was achieved by suitable perturbation of the structure. We wanted to study the effect of attaching substituted vinyl groups at the 2-position of aromatic bispropargyl sulfones upon GB cyclization. Since the possibility of a 6π-EC exists for these molecules (Scheme 1), it is important to know the relative preference of the two processes. Towards that end, we have synthesized differently substituted dieneyl bispropargyl sulfones and studied their reactivity under basic conditions. The results have shown a general preference for GB cyclization over 6π-EC; however, the preference can be modulated by electronic, steric as well as by changing the alkene geometry and temperature. All these are discussed in this paper.



Scheme 1. Reaction pathways for bis-diene-allene sulfones (a) 6π-EC and (b) GBC.

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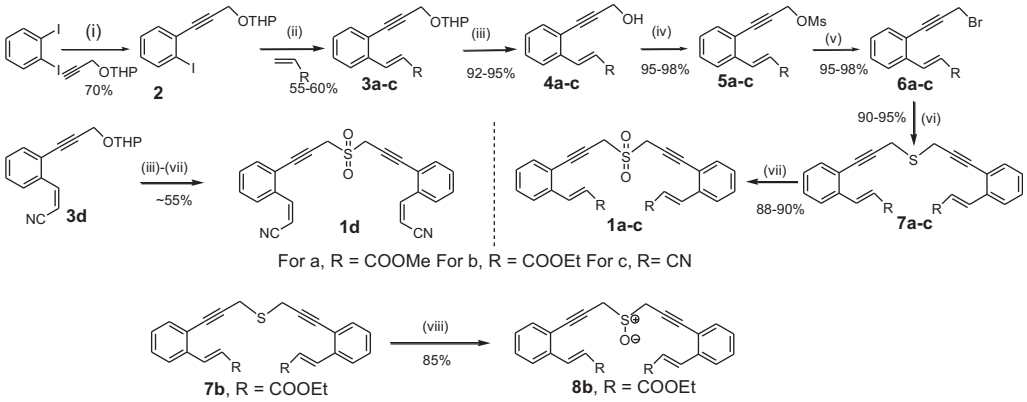
2. Results and discussion

The various sulfones were prepared following slightly different strategies. The sulfones **1a**–**d** were synthesized starting from 1,2-diiodo benzene (Scheme 2). The key steps involved Sonogashira[5] coupling with THP-protected propargyl alcohol followed by Heck coupling[6] with various α,β-unsaturated esters or acrylonitrile. Removal of THP produced the alcohols **4a**–**d**, which were converted to the corresponding bromides **6a**–**d**. The bromides were then transformed to the sulfides **7a**–**d** (Na_2S, MeOH).[1,9] Oxidation of sulfides with *m*-CPBA produced the desired sulfones **1a**–**d**.[1] The Heck coupling with acrylic esters produced only the *E*-isomers, which were converted to the *E*-sulfones. Only with acrylonitrile, the Heck coupling afforded a mixture of *E* and *Z* isomers, which were separated and converted similarly to the sulfones **1c** and **1d**, respectively. Sulfoxide **8b** was synthesized by the controlled oxidation of sulfide **7b** by *m*-CPBA.

Sufones **1i**–**k** were prepared from bromoaldehydes, respectively, using a Wittig reaction and a Sonogashira coupling (Scheme 5). The synthesis of sulfone **1l** from *o*-iodobenzaldehyde followed similar steps (Scheme 5). To avoid epoxidation of double bond, oxone was used for the oxidation of sulfides **7k**,**l** to the corresponding sulfone **1k**,**l**.[8]

Monopropargyl sulfones **1m**–**o** were prepared by the reaction of thiophenol with bromides **6e**, **6f** and **6h** followed by the oxidation (Scheme 6). All the sulfones were characterized by NMR and mass spectral data.

With the target sulfones in hand, we proceeded with checking their reactivity under basic conditions and at ambient temperature of 30 °C. In an initial experiment, sulfone **1a** (10 mg) dissolved in $CDCl_3$ was treated with a catalytic amount of triethylamine and ^1H NMR spectra were recorded at different time points. The concentration of the starting material decreased with time while new peaks corresponding to GB and 6π-electrocyclization started

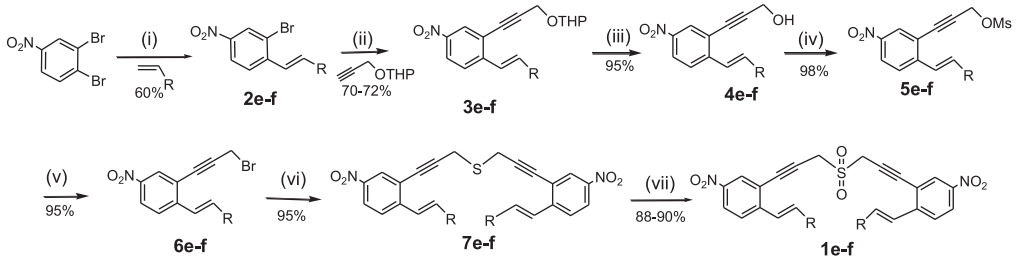


Reagents and Conditions: i) $Pd(PPh_3)_4$, CuI, Et_3N, 1.5 h; ii) $Pd(OAc)_2$, PPh_3, K_2CO_3, DMF, 110 °C, 5 h; iii) PPTS, EtOH, rt, 6 h; iv) MsCl, Et_3N, DCM, 0 °C, 10 min; v) LiBr, THF, rt, 20 min; vi) Na_2S, MeOH, rt, 15 min; vii) *m*-CPBA (2.2 eq.), DCM, 0 °C, 30 min; viii) *m*-CPBA (1 eq.), DCM, 0 °C, 10 min.

Scheme 2. Synthesis of sulfones **1a**–**d** and sulfoxide **8b**.

The nitro analogues **1e**,**f** were synthesized starting from 1,2-dibromo-4-nitro benzene (Scheme 3).[4] Here the Sonogashira and Heck coupling steps had to be interchanged as we wanted to position the alkene moiety *para* to the nitro group. Placing the propargyl arm *para* to the nitro caused problem in the sulfide formation step.

to appear. The transformation was complete within 72 h. The two products were separately isolated by Si-gel column chromatography in excellent combined yields (Scheme 7). The experiment was repeated with all the sulfones **1b**–**l** and sulfoxide **8b**. The results are compiled in Table 1. Except for the *Z*-alkene **1d**, which exclusively reacted in GB mode, all other sulfones produced a mixture of

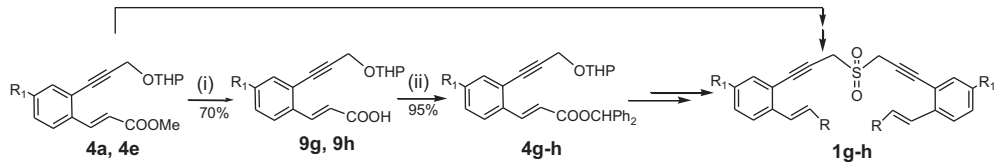


Reagents and Conditions: i) $Pd(OAc)_2$, PPh_3, Et_3N, CH_3CN, 90 °C, 5 h; ii) $Pd(PPh_3)_4$, CuI, Et_3N, 90 °C, 7 h; iii) PPTS, EtOH, rt, 6 h; iv) MsCl, Et_3N, DCM, 0 °C, 10 min; v) LiBr, THF, rt, 20 min; vi) Na_2S, TBAB, THF-H_2O, 0 °C, 15 min; vii) *m*-CPBA, DCM, 0 °C, 30 min.

Scheme 3. Synthesis of sulfones **1e**,**f**.

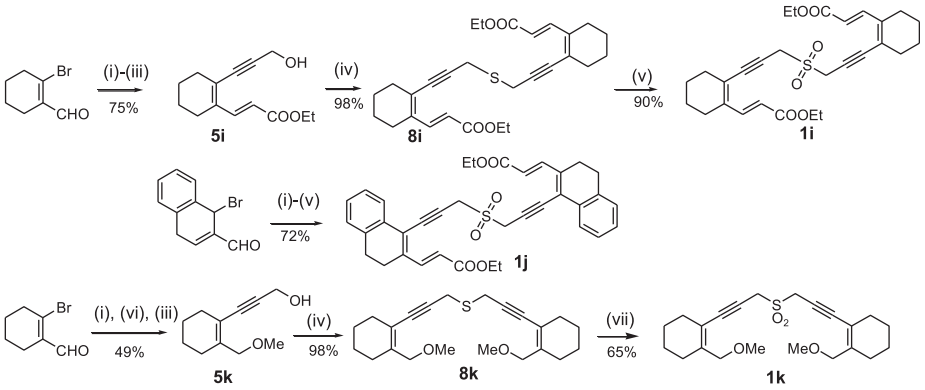
The benzhydryl analogues **1g**,**h** were prepared via hydrolysis of the methyl esters **3a** and **3e** followed by esterification with diphenyl diazomethane (Scheme 4).[7] The resulting benzhydryl esters were further elaborated to the target sulfones following the earlier procedure.

GB and 6π-electrocylization products in an overall yield of 80–98%. The reaction generally favours the GB pathway over 6π-EC. Increasing the steric bulk of the R group from hydrogen to benzhydryl ester[10] has minimal effect on the selectivity profile of the reaction (entries 1, 3, 5, 7, 9). It is only when electron withdrawing nitro

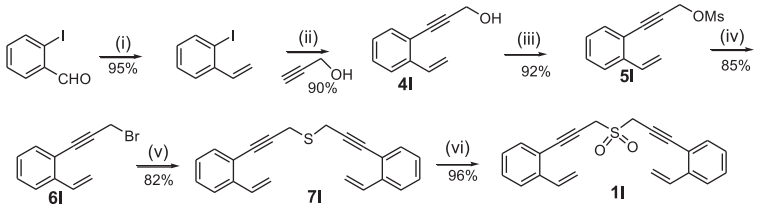


Reagents and Conditions: i) LiOH, THF-H_2O, rt, 6 h; ii) DPDM, EtOAc, rt, 12 h.

Scheme 4. Synthesis of sulfones **1g**,**h**.

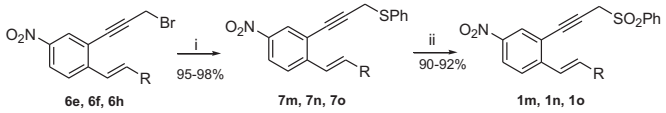


Reagents and Conditions:i) $Pd(PPh_3)_4$, CuI, Et_3N, 60 °C, 3h; ii) $(COOEt)CHPPh_3$, Benzene, Reflux, 4h; iii) PPTS, EtOH, rt, 6 h; iv) a. MsCl, Et_3N, DCM, 0 °C, 10 min; b. LiBr, THF, rt, 20 min; c. Na_2S, MeOH, rt, 15 min; v) *m*-CPBA, DCM, 0 °C, 30 min; vi) a.DIBAL-H, THF, 0 °C to rt, 6h; b. NaH, THF, MeI, rt, 6h; vii) OXONE , MeOH-H_2O (1: 1), 3h.



Reagents and conditions: i) CH_3PPh_3Br, BuLi, THF, -78 °C, 3h; ii) $Pd(PPh_3)_4$, CuI, Et_3N, 4h, rt; iii) MsCl, Et_3N, DCM, 0 °C, 5 min; iv) LiBr, THF, rt, 4h; v) Na_2S, TBAB, THF-H_2O, 0 °C-rt, 15 min ; vi) OXONE, MeOH-H_2O, rt, 5h.

Scheme 5. Synthesis of sulfones **1i**–**l**.

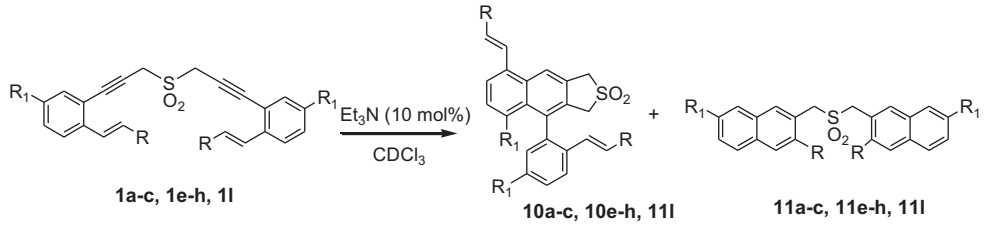


Reagents and conditions: i) PhSH, Et_3N, DCM, rt, 4h; ii) *m*-CPBA, DCM, 0 °C, 30 min.

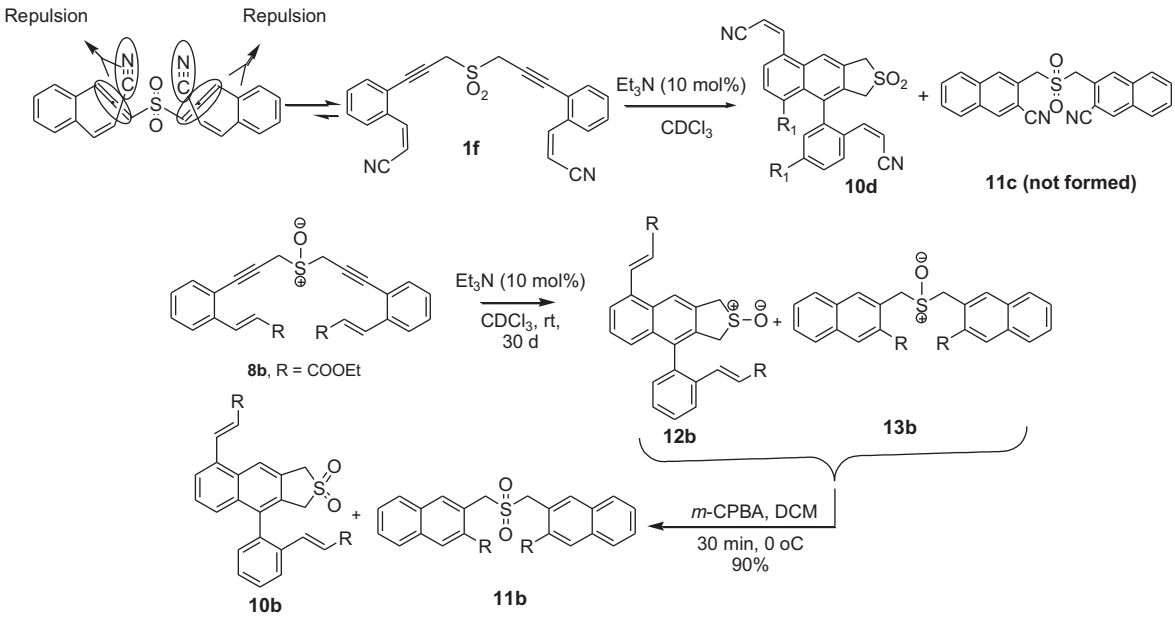
Scheme 6. Synthesis of sulfones **1m**–**o**.

group is present in the aromatic ring significant change in selectivity was observed and that too only for sterically demanding esters (entries 2, 4, 6). Thus, there is a cooperative effect of electron withdrawl and steric bulk. The complete GB-selectivity for *Z*-alkene (entry 8) was possibly due to the restriction in achieving the conformation suitable for undergoing 6π-EC (Scheme 7). Temperature has a profound influence on the product ratio. Lowering the temperature of the reaction favoured the GB process while higher temperature favoured the 6π-EC pathway (entries 1 and 3). This indicated that the GB product is kinetically controlled while the 6π-EC product is thermodynamically controlled. The reactivity of sulfone **1d**, however, remained unaffected by rise of temperature (up to 60 °C) thus pointing out high kinetic barrier for 6π-EC pathway for **1d**. In case of the sulfoxide **8b**, the base mediated rearrangement was found to be very slow and took 30 days for completion. In this case, the reaction was possibly thermodynamically driven to tilt the ratio in favour of 6π-EC (ratio of 6π-EC:GB=10:1, Table 1, entry 10).

When cyclohexene or benzcyclohexene is a part of the inner double bond of the dieneyne system, exclusive formation of 6π-EC product was observed and the reaction was much faster in comparison to the aromatic counterparts completing only within 10–40 min (Scheme 8). In this case, although the GB biradicals can self-quench, stabilization through the final aromatization is not possible. It may be mentioned that for the sulfones **1a**–**h**, two regiomeric *ortho* positions, one bearing the alkenyl moiety and the other having hydrogen can participate in self quenching of radicals. The reaction has chosen to self quench via the *ortho* position bearing hydrogen, which allowed aromatization in the last step.



For a R = COOMe R_1 = H; For b R = COOEt R_1 = H; For c R = CN R_1 = H; For e R = COOMe R_1 = NO_2;
For f R = COOEt R_1 = NO_2; For g R = $COOCHPh_2$ R_1 = H; For h R = $COOCHPh_2$ R_1 = NO_2; For I R = R_1 = H



Scheme 7. Reactivity of sulfones **1a**–**h, 1l** and sulfoxide **8b** with catalytic Et_3N.

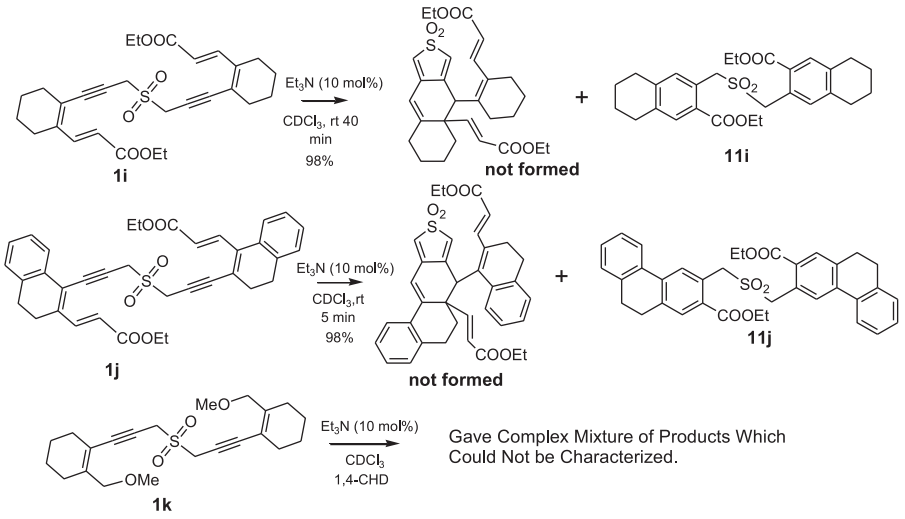
Table 1
Results of triethylamine (10 mol %) treatment of sulfones **1a**–**l** and sulfoxide **8b**

Entry	Sulfone/sulfoxide	Temperature (°C), time	GB product (%)	6π-EC product (%)	Combined yield (%)
1	**1a**, R=COOMe R_1=H	0, 15 d rt, 72 h 60, 4 h	**10a** (89) **10a** (74) **10a** (30)	**11a** (11) **11a** (26) **11a** (70)	80 80 82
2	**1e**, R=COOMe R_1=NO_2	Rt, 52 h	**10e** (74)	**11e** (26)	87
3	**1b**, R=COOEt R_1=H	0, 15 d rt, 72 h 60, 4 h	**10b** (89) **10b** (72) **10b** (29)	**11b** (11) **11b** (28) **11b** (71)	82 85 90
4	**1f**, R=COOEt R_1=NO_2	rt, 56 h	**10f** (56)	**11f** (44)	93
5	**1g**, R=$COOCHPh_2$ R_1=H	rt, 75 h	**10g** (70)	**11g** (30)	89
6	**1h**, R=$COOCHPh_2$ R_1=NO_2	rt, 60 h	**10h** (44)	**11h** (56)	95
7	**1c**, R=CN (*trans*) R_1=H	rt, 72 h	**10c** (78)	**11c** (22)	84
8	**1d**, R=CN (*cis*) R_1=H	rt, 35 h 60, 2 h	**10d** (>99) **10d** (>99)	Not detected Not detected	98 98
9	**1l**, R=R_1=H	rt, 8 h	**10l** (67)	**11l** (33)	82
10	**8b**, R=COOEt R_1=H	rt, 30 d	**12b** (9)	**13b** (91)	90

The grey shade signifies the effect of temperature on the reaction profile.

This possibility is not there for the sulfones **1i**–**k**. If we shut down the option of 6π-EC pathway as in **1k** (Scheme 8), no identifiable product could be isolated.

Structure elucidation of the various products was done on the basis of NMR and mass spectral data. For example, the compounds **11a**–**c**, **11e**–**h** and **11m**–**o** all showed the presence of new aromatic protons. At the same time, the absence of four vinylic protons in ^{1}H NMR and four acetylenic carbons in ^{13}C NMR indicated occurrence of aromatization through electrocyclization. The molecular ions as observed in the mass spectra were in conformity with the



Scheme 8. Reactivity of sulfones **1i**–**k** with Et_3N.

molecular formulae. The NMR spectra of the GB products compared well with similar compounds prepared earlier.[1] Final confirmation about the structure of the electrocyclization products was obtained from single crystal X-ray analysis[11] of products **11a** and **11f** (ORTEP diagram showed in Fig. 1).

The cooperative effect of steric bulk of the ester and the electron withdrawing group in the aryl ring as mentioned may affect the GB or 6π-EC or both reaction pathways in order to alter the product ratio. To address this point, monopropargyl sulfones **1m**–**o**, which can only undergo the 6π-EC reaction, were treated with triethylamine (Scheme 9). The rates of reaction, as shown in Table 2, remain almost the same even for **1o** having both electron withdrawing nitro as well as sterically bulky benzhydryl ester. Thus there is no cooperative effect for the 6π-EC pathway and the effect may be more pronounced for the GB process.

3. Computational study

The delicate balance between the two competing reactions, GB and 6π-EC, prompted us to explore the mechanism using computational methods. Systematic conformation search was carried out to identify few possible substrate orientations for **1a**. This was done by systematic choice of unique orientations as the starting geometries, which are then completely optimized using rather strict convergence criteria. The conformation **A** where the allenyl groups are opposite to each other with respect to the central S, is least stable among all the other conformations where allenyl groups are nearer. Through-space interaction between the π-electrons plays a crucial role in stabilizing the substrate geometry. While allenyl groups inherently repel each other, the π-stacking

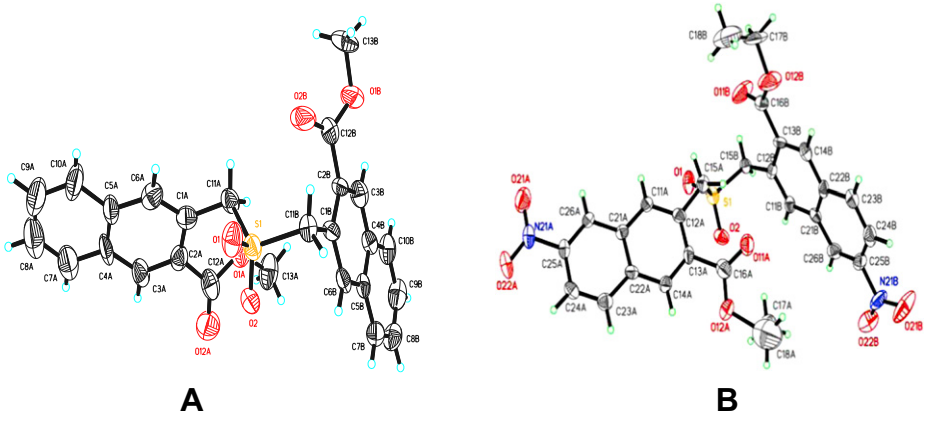
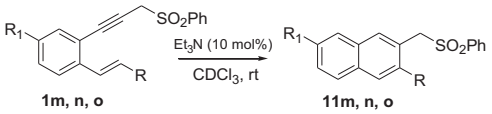


Fig. 1. X-ray structure of product **11a** (A) and **11f** (B).

Table 2
Results of triethylamine treatment of sulfones **1m**–**o**

Entry	Sulfones	Rate constant (min^{-1})
1	**1m**, R=COOMe R_1=NO_2	5.1×10^{-4}
2	**1n**, R=COOEt R_1=NO_2	4.9×10^{-4}
3	**1o**, R=$COOCHPh_2$ R_1=NO_2	5.0×10^{-4}



Scheme 9. Reactivity of sulfones **1m**–**o** with Et_3N.

interaction[12] between the aromatic groups brings them close. Comparison of the distance between the central carbon atoms of the allyl groups in the optimized geometries of phenyl substituted bisallenyl sulfones and the unsubstituted one, C's are closer in the former (3.193 Å) compared to the latter (3.754 Å). The other conformations, **B**–**E**, are differentiated by the chirality of allenyl groups, and the position of the vinyl groups with respect to their proximity to the central allenyl carbon.

We have computed the complete pathway for GBC and 6π-EC starting from the lowest energy structure (**B**) of the substrate. First step in GBC, the C–C bond formation, requires a free energy of activation (ΔG_{act}) of 13.9 kcal/mol. The self-quenching step of the biradical intermediate requires a reorientation of the aryl group, which has an activation free energy of 6.64 kcal/mol. This is followed by the quenching with a relatively low barrier (ΔG_{act}=2.04 kcal/mol). Hydride shift completes the reaction, with the overall exothermicity of 76.27 kcal/mol for GB cyclization. The alternative 6π-EC is initiated by a rotation of the vinyl group. The resulting geometry is 4.92 kcal/mol higher in energy than the starting conformation of **B**. This rotation is nearly barrierless. The overall ΔG_{act} from **B** for the electrocyclization step is 16.92 kcal/mol. Comparing the highest point in each of the pathways, the TS in the GB cyclization is lower in energy ($\Delta\Delta G_{act}$) compared to the corresponding TS for 6π-EC by 3.02 kcal/mol. From the reaction profile for **B**, it is clear that the TS for the first C–C bond formation is the highest point in the complete reaction profile. Therefore, we have computed the activation energy of the initial C–C bond formation for other conformations, **A**, **C**–**E**. Comparison of the energetics (Fig. 2) shows that the TS for GB has lowest barrier among all the TS's. It is to be mentioned that some of the isomers do not have the possibility to undergo both GBC and 6π-EC without undergoing a major conformational change, e.g., **A** can undergo only 6π-EC, and **C** and **E** can undergo only GBC. The overall energetics is in favour of GB cyclization, even though the energy differences are too high to give an experimental product ratio of 74:26. Some of the higher energy conformations have lower barriers for 6π-EC (e.g., ΔG_{act} for **E** is 9.09 kcal/mol) compared to the lowest GB barrier ΔG_{act} for **D** is 9.191 kcal/mol. Higher energy conformations can get more populated with rise in temperature, which can change the kinetics and therefore the product ratio, as seen in the experiment.

We have carried out similar conformational analysis for **1f** (R_1=NO_2, R=COOEt). The lowest energy conformation is found to have similar orientation as the one for **1a**. The ΔG_{act} for the first cyclization steps are 14.75 and 16.49 kcal/mol, respectively, for GBC and 6π-EC. The difference in TS energies ($\Delta\Delta G_{act}$) is 1.74 kcal/mol. Similarly, $\Delta\Delta G_{act}$ (in kcal/mol) for other compounds are, **1b**: 2.72 (R_1=H, R=COOEt), **1e**: 3.35 (R_1=NO_2, R=COOMe), **1c**: 3.55 (R_1=H, R=CN(*trans*)), **1d**: 4.76 (R_1=H, R=CN(*cis*)). **1f** has highest of $\Delta\Delta G_{act}$ where exclusive product is from GBC. While the overall trend in the barrier and product ratio is in agreement, firm conclusions with such small changes in energy may not be appropriate (Table 3).

Table 3
Activation free energy (ΔG_{act}) and activation energy (ΔE_{act}) of GB and 6π cyclizations and the experimental ratio of the products formed

Entry	Sulfones		ΔG_{act} (kcal/mol)		ΔE_{act} (kcal/mol)		% of Product (experimental data)	
	R	R_1	GB	6π	GB	6π	GB	6π
1	–COOMe	H	13.9	16.92	13.06	17.59	74	26
2	–COOMe	NO_2	14.21	17.55	13.62	17.70	74	26
3	–COOEt	H	13.75	16.47	13.33	17.12	73	27
4	–COOEt	NO_2	14.75	16.49	13.87	17.64	56	44
5	–CN (*trans*)	H	13.94	17.49	12.80	17.80	78	22
6	–CN (*cis*)	H	12.89	19.75	11.66	19.61	>99	ND

In conclusion, the competitive reactivity (GB vs 6π-EC) study of bispropargyl sulfones with various *o*-alkenyl moieties have indicated definite guidelines to make one reaction pathway to dominate over the other. These findings are important not only for synthesis but also in the development of artificial DNA-cleaving agents.

4. Experimental

4.1. General

All ^{1}H and ^{13}C NMR were, respectively, recorded at 400 MHz and 100 MHz in $CDCl_3$ unless mentioned otherwise. The X-ray crystal data was recorded on Bruker AXS Smart Apex-II. ESI-MS and HRMS were taken using a Waters LCT mass spectrometer; the solutions of the compounds were injected directly into the spectrometer via

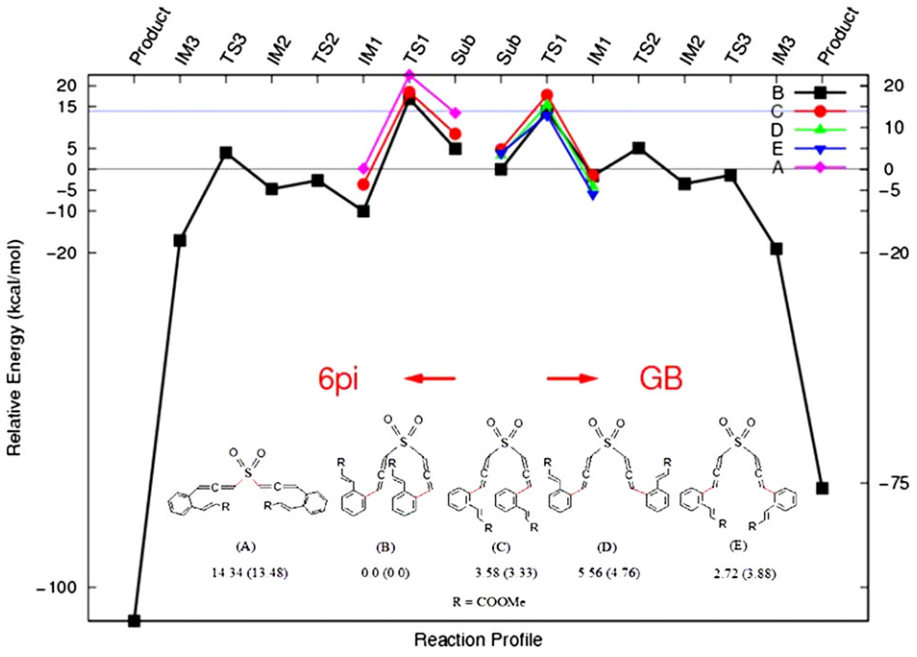


Fig. 2. The full reaction profile for the GBC and 6π-EC.

a Rheodyne injector equipped with 10 μL loop. A Phoenix 20 micro LC syringe pump delivered the solution to the vaporization nozzle of the electrospray ion source at a flow rate of 3 μL min^{-1}. Nitrogen was used both as a drying gas and for nebulisation with flow rates of approximately 3 L min^{-1} and 100 mL min^{-1}, respectively. Pressure in the analyzer region was usually about 3×10^{-5} torr.

4.2. General procedure for Garratt–Braverman and 6π-electrocyclization reaction and spectral data of the final compounds

Sulfone or sulfoxide (10–15 mg) was taken in NMR tube and dissolved in $CDCl_3$ (600 μL). Catalytic amount of Et_3N (10 mol %) was added and reaction was monitored by recording proton NMR in different time interval. Reaction mixture was worked up by chloroform/water and the final products were isolated in pure form by column chromatography (Si-gel, petroleum ether/ethyl acetate mixture as eluent).

*4.2.1. 3-{9-[2-(2-Methoxycarbonyl-vinyl)-phenyl]-2,2-dioxo-2,3-dihydro-1H-2λ^6-naphtho[2,3-c]thiophen-5-yl}-acrylic acid methyl ester (**10a**) state.* Brown solid; mp 110 °C; yield: 59%; R_f=0.4 (PE/EA=2:1); ν_{max} (KBr, cm^{-1}): 2924, 2365, 1718, 1636, 1437, 1320, 1173. δ_H 3.64 (3H, s), 3.89 (3H, s), 4.00, 4.06 (2× 1H, ABq, J=16.4 Hz), 4.61, 4.70 (2× 1H, ABq, J=16.0 Hz), 6.37 (1H, d, J=15.6 Hz), 6.55 (1H, d, J=15.6 Hz), 7.13 (1H, d, J=16.0 Hz), 7.21–7.26 (1H, m), 7.38–7.45 (2H, m), 7.54–7.56 (2H, m), 7.78 (1H, d, J=6.8 Hz), 7.83–7.85 (1H, m), 8.23 (1H, s), 8.50 (1H, d, J=15.6 Hz). δ_C 51.7, 51.9, 56.0, 57.3, 120.2, 121.2, 121.8, 126.1, 126.8, 127.0, 128.3, 129.2, 129.5, 130.6, 131.2, 132.2, 132.3, 133.4, 136.0, 137.7, 141.1, 141.2, 166.7, 167.0. MS: m/z=463.13 [MH^+]; HRMS: found 463.1221. $C_{26}H_{22}O_6S+H^+$ requires 463.1215.

*4.2.2. Dimethyl 3,3′-sulfonylbis(methylene)di-2-naphthoate (**11a**) state.* White solid; mp 158 °C; yield: 21%; R_f=0.6 (PE/EA=2:1); ν_{max} (KBr, cm^{-1}): 2924, 2361, 1718, 1217, 771. δ_H 3.80 (6H, s), 5.08 (4H, s), 7.54–7.61 (4H, m), 7.83 (2H, d, J=7.6 Hz), 7.91 (4H, d, J=6.4 Hz), 8.55 (2H, d, J=6.4 Hz). δ_C 52.3, 56.3, 123.9, 127.5, 127.7, 127.9, 128.7, 132.2, 132.7, 133.3, 134.3, 167.7. MS: m/z=463.12 [MH^+]; HRMS: found 463.1219. $C_{26}H_{22}O_6S+H^+$ requires 463.1215.

*4.2.3. 3-{9-[2-(2-Methoxycarbonyl-vinyl)-phenyl]-2,2-dioxo-2,3-dihydro-1H-2λ^6-naphtho[2,3-c]thiophen-5-yl}-acrylic acid ethyl ester (**10b**) state.* Yellow solid; mp 68 °C; yield: 62%; R_f=0.4 (PE/EA=2:1); ν_{max} (KBr, cm^{-1}): 2926, 2364, 1709, 1636, 1179. δ_H 1.21 (3H, t, J=7.2 Hz), 1.40 (3H, t, J=7.2 Hz), 4.00, 4.06 (2× 1H, ABq, J=16.4 Hz), 4.10 (2H, q, J=7.2 Hz), 4.34 (2H, q, J=7.2 Hz), 4.61, 4.70 (2× 1H, ABq, J=16.0 Hz), 6.38 (1H, d, J=16.0 Hz), 6.55 (1H, d, J=15.6 Hz), 7.13 (1H, d, J=16.0 Hz), 7.22–7.26 (1H, m), 7.38–7.44 (2H, m), 7.53–7.55 (2H, m), 7.77–7.79 (1H, m), 7.83–7.85 (1H, m), 8.23 (1H, s), 8.48 (1H, d, J=15.6 Hz). δ_C 14.4, 14.6, 56.3, 57.6, 60.8, 61.1, 121.0, 121.6, 122.6, 126.4, 127.1, 127.2, 128.6, 129.5, 129.7, 129.8, 130.8, 130.9, 131.5, 132.6, 132.7, 133.8, 136.4, 138.1, 141.2, 141.3, 166.5, 166.9. MS: m/z=491.24 [MH^+]; HRMS: found 491.1519. $C_{28}H_{26}O_6S+H^+$ requires 491.1528.

*4.2.4. Diethyl 3,3′-sulfonylbis(methylene)di-2-naphthoate (**11b**) state.* Gummy oil; yield: 23%; R_f=0.7 (PE/EA=2:1); ν_{max} (neat, cm^{-1}): 2294, 2363, 1718, 1560, 1219, 772. δ_H 1.38 (6H, d, J=7.2 Hz), 4.35 (4H, q, J=7.2 Hz), 5.09 (4H, s), 7.56–7.60 (4H, m), 7.82 (2H, d, J=7.6 Hz), 7.92 (4H, d, J=8.4 Hz), 8.55 (2H, s). δ_C 14.2, 56.4, 61.5, 124.1, 127.5, 128.3, 128.6, 128.8, 132.3, 132.6, 133.3, 134.3, 167.4. MS: m/z=491.08 [MH^+]; HRMS: found 491.1523. $C_{28}H_{26}O_6S+H^+$ requires 491.1528.

*4.2.5. 3-{9-[2-(2-Cyano-vinyl)-phenyl]-2,2-dioxo-2,3-dihydro-1H-2λ^6-naphtho[2,3-c]thiophen-5-yl}-acrylonitrile (**10c**) state.* White solid; mp above 270 °C; yield: 65%; R_f=0.4 (PE/EA=2:1); ν_{max} (KBr, cm^{-1}): 2925, 2345, 2218, 1654, 1560, 1315. δ_H (DMSO-d_6) 4.13 (2H, s), 4.74, 4.80 (2× ABq, J=16.0 Hz), 6.41 (1H, d, J=16.4 Hz), 6.58 (1H, d, J=16.4 Hz), 6.74 (1H, d, J=16.4 Hz), 7.22 (1H, d, J=8.8 Hz), 7.28 (1H, d, J=7.2 Hz), 7.52 (1H, t, J=8.0 Hz), 7.62–7.65 (2H, m), 7.97 (1H, d, J=7.2 Hz), 8.02 (1H, d, J=7.2 Hz), 8.54 (1H, s), 8.56 (1H, d, J=16.8 Hz). δ_C 29.6, 55.9, 57.2, 98.6, 100.8, 117.4, 117.5, 121.1, 126.1, 127.1, 128.8, 129.6, 129.9, 130.3, 130.5, 131.6, 131.7, 132.1, 132.4, 135.5, 137.3, 146.9, 147.1. MS: m/z=397.13 [MH^+]; HRMS: found 397.1013. $C_{24}H_{16}N_2O_2S+H^+$ requires 397.1011.

*4.2.6. 3,3′-Sulfonylbis(methylene)di-2-naphthonitrile (**11c**) state.* White solid; mp above 270 °C; yield: 19%; R_f=0.5 (PE/EA=2:1); ν_{max} (KBr, cm^{-1}): 2220. δ_H (DMSO-d_6): 5.00 (4H, s), 7.69–7.77 (4H, m), 8.04–8.09 (4H, m), 8.23 (2H, s), 8.67 (2H, s). MS: m/z=397.16 [MH^+]; HRMS: found 365.1022. $C_{24}H_{16}N_2O_2S+H^+$ requires 397.1011.

*4.2.7. 3-{9-[2-(2-Cyano-vinyl)-phenyl]-2,2-dioxo-2,3-dihydro-1H-2λ^6-naphtho[2,3-c]thiophen-5-yl}-acrylonitrile (**10d**) state.* White gummy liquid; yield: 99%; R_f=0.2 (PE/EA=4:1); ν_{max} (neat, cm^{-1}): 2365, 2219, 1636, 1220, 772. δ_H 3.98 (1H, d, J=16.4 Hz), 4.17 (1H, d, J=16.4 Hz), 4.66 (2H, s), 5.28 (1H, d, J=12.0 Hz), 5.83 (1H, d, J=11.6 Hz), 6.58 (1H, d, J=12.0 Hz), 7.29 (1H, d, J=7.2 Hz), 7.31 (1H, d, J=8.4 Hz), 7.53 (1H, t, J=7.8 Hz), 7.61–7.68 (2H, m), 7.91 (1H, d, J=11.6 Hz), 7.97 (1H, s), 8.02 (1H, d, J=7.2 Hz), 8.35 (1H, d, J=7.6 Hz). δ_C 55.9, 57.1, 98.0, 100.7, 116.3, 116.6, 121.1, 127.2, 128.0, 128.3, 128.6, 129.6, 129.7, 129.9, 130.1, 130.7, 131.0, 131.3, 132.0, 132.5, 136.0, 137.3, 145.7, 146.7. MS: m/z=419.11 [MNa^+], 397.14 [MH^+]; HRMS: found 397.1018. $C_{24}H_{16}N_2O_2S+H^+$ requires 397.1011.

*4.2.8. 3-{9-[2-(2-Methoxycarbonyl-vinyl)-5-nitro-phenyl]-8-nitro-2,2-dioxo-2,3-dihydro-1H-2λ^6-naphtho[2,3-c]thiophen-5-yl}-acrylic acid methyl ester (**10e**) state.* Brown viscous oil; yield: 64%; R_f=0.3 (PE/EA=2:1); ν_{max} (neat, cm^{-1}): 2927, 2364, 1718, 1527, 1322, 1186. δ_H 3.77 (4H, d, 13.6 Hz), 3.88 (3H, s), 4.09 (1H, d, J=16.4 Hz), 4.64, 4.72 (2× 1H, ABq, J=16.0 Hz), 6.60–6.64 (2H, m), 7.44 (1H, d, J=16.0 Hz), 7.80 (1H, d, J=8.0 Hz), 7.82–7.87 (2H, m), 7.93 (1H, d, J=8.4 Hz), 8.31–8.37 (2H, m), 8.43 (1H, d, J=16.0 Hz). δ_C 52.1, 52.3, 56.0, 57.0, 123.2, 124.1, 124.5, 124.6, 124.8, 125.4, 125.5, 128.0, 131.1, 131.7, 132.6, 134.3, 137.3, 139.1, 139.4, 139.7, 147.6, 148.9, 165.9, 166.1. MS: m/z=575.16 [MNa^+]; HRMS: found 575.0728. $C_{26}H_{20}N_2O_{10}S+Na^+$ requires 575.0736.

*4.2.9. Dimethyl 3,3′-sulfonylbis(methylene)bis(6-nitro-2-naphthoate) (**11e**) state.* Greenish yellow solid; yield: 23%. R_f=0.4 (PE/EA=2:1)δ_H (DMSO-d_6) δ 3.75 (6H, s), 5.17 (4H, s), 8.27–8.34 (4H, m), 8.40 (2H, s), 8.62 (2H, s) 8.97 (2H, s). MS: m/z=553.10 [MH^+]; HRMS: found 553.0927. $C_{26}H_{20}N_2O_{10}S+H^+$ requires 553.0917.

*4.2.10. 3-{9-[2-(2-Methoxycarbonyl-vinyl)-5-nitro-phenyl]-8-nitro-2,2-dioxo-2,3-dihydro-1H-2λ^6-naphtho[2,3-c]thiophen-5-yl}-acrylic acid ethyl ester (**10f**) state.* Yellow solid; mp 130 °C; yield: 52%; R_f=0.4 (PE/EA=2:1); ν_{max} (KBr, cm^{-1}): 2928, 2365, 1718, 1528, 1321, 1186. δ_H 1.29 (3H, t, J=7.2 Hz), 1.41 (3H, t, J=7.2 Hz), 3.76 (1H, d, J=16.4 Hz), 4.10 (1H, d, J=16.4 Hz), 4.21 (2H, q, J=7.2 Hz), 4.37 (2H, q, J=7.2 Hz), 4.64, 4.72 (2× 1H, ABq, J=16.0 Hz), 6.61 (1H, d, J=15.6 Hz), 6.63 (1H, d, J=16.0 Hz), 7.43 (1H, d, J=16.0 Hz), 7.81 (1H, d, J=8.0 Hz), 7.83 (1H, d, J=8.0 Hz), 7.87 (1H, d, J=2.4 Hz), 7.49 (1H, d, J=8.8 Hz), 8.33–8.37 (2H, m), 8.42 (1H, d, J=16.0 Hz). δ_C 14.2, 14.3, 56.1, 57.0, 61.2, 61.4, 123.0, 123.3, 124.2, 124.6, 124.9, 125.1, 125.4, 126.0, 128.0, 131.2, 131.7, 132.6, 134.4, 137.4, 137.5, 138.9, 139.2, 139.9, 147.6, 149.0, 165.6, 165.8. MS: m/z=581.19 [MH^+]; HRMS: found 581.1233. $C_{28}H_{24}N_2O_{10}S+H^+$ requires 581.1230.

*4.2.11. Diethyl 3,3′-sulfonylbis(methylene)bis(6-nitro-2-naphthoate) (**11f**) state.* Yellow solid; mp 114 °C; yield: 41%; R_f=0.5 (PE/EA=2:1); ν_{max} (KBr, cm^{-1}): 2923, 2365, 1718, 1560, 1220. δ_H 1.44

(6H, t, J=7.2 Hz), 4.39 (4H, q, J=7.2 Hz), 5.16 (4H, s), 8.07 (2H, d, J=8.8 Hz), 8.11 (2H, s), 8.32 (2H, d, J=8.8 Hz), 8.62 (2H, s), 8.76 (2H, s). δ_C 14.1, 56.3, 62.0, 120.9, 124.0, 126.4, 130.5, 131.7, 132.0, 132.9, 134.6, 134.9, 147.1, 166.4. MS: m/z=581.14 [MH^+]; HRMS: found 581.1219. $C_{28}H_{24}N_2O_{10}S+H^+$ requires 581.1230.

*4.2.12. 3-{9-[2-(2-Benzhydryloxycarbonyl-vinyl)-phenyl]-2,2-dioxo-2,3-dihydro-1H-2λ⁶-naphtho[2,3-c]thiophen-5-yl}-acrylic acid benzhydryl ester (**10g**) state.* Yellow solid; mp 74 °C; yield: 62%; R_f=0.4 (PE/EA=3:1); ν_{max} (KBr, cm^{-1}): 2926, 2364, 1718, 1641. δ_H 4.03 (2H, s), 4.57, 4.63 (2× 1H, ABq, J=16.0 Hz), 6.52 (1H, d, J=16.0 Hz), 6.68 (1H, d, J=16.0 Hz), 6.65 (1H, s), 6.97 (1H, s), 7.05, 7.46 (24H, m), 7.55–7.57 (2H, m), 7.80 (1H, d, J=6.4 Hz), 7.87–7.89 (1H, m), 8.20 (1H, s), 8.54 (1H, d, J=15.6 Hz). MS: m/z=767.24 [MH^+]; HRMS: found 767.2479. $C_{50}H_{38}O_6S+H^+$ requires 767.2467.

*4.2.13. Dibenzhydryl 3,3′-sulfonylbis(methylene)di-2-naphthoate (**11g**) state.* White solid; mp 144 °C; yield: 27%; R_f=0.6 (PE/EA=3:1); ν_{max} (KBr, cm^{-1}): 2927, 2365, 1718, 1560, 1275. δ_H 4.94 (4H, s), 6.91 (2H, s), 7.20–7.45 (20H, m), 7.57 (4H, q, J=3.2 Hz), 7.73–7.75 (2H, m), 7.83 (2H, s), 7.93–7.95 (2H, m), 8.62 (2H, s). δ_C 56.0, 77.9, 124.3, 127.2, 127.7, 127.8, 128.1, 128.6, 128.7, 128.9, 132.2, 132.6, 133.6, 134.5, 140.0, 166.1. MS: m/z=767.27 [MH^+]; HRMS: found 767.2458. $C_{50}H_{38}O_6S+H^+$ requires 767.2467.

*4.2.14. 3-{9-[2-(2-Benzhydryloxycarbonyl-vinyl)-5-nitro-phenyl]-8-nitro-2,2-dioxo-2,3-dihydro-1H-2λ⁶-naphtho[2,3-c]thiophen-5-yl}-acrylic acid benzhydryl ester (**10h**).* State: yellow solid; mp 110 °C; yield: 42%; R_f=0.4 (PE/EA=2:1); ν_{max} (KBr, cm^{-1}): 2924, 1718, 1527, 1347, 1168. δ_H 3.78 (1H, d, J=16.4 Hz), 4.04 (1H, d, J=16.4 Hz), 4.58, 4.64 (2× 1H, ABq, J=16.0 Hz), 6.72 (1H, d, J=15.6 Hz), 6.75 (1H, d, J=16.0 Hz), 6.85 (1H, s), 6.97 (1H, s), 7.22–7.45 (21H, m), 7.75 (1H, d, J=8.0), 7.81 (1H, d, J=8.0 Hz), 8.09 (1H, d, J=7.2 Hz), 7.90 (1H, d, J=2.0 Hz), 8.31 (1H, s), 8.35 (1H, dd, J=8.8, 2.0 Hz), 8.44 (1H, d, J=15.6 Hz). MS: m/z=857.25 [MH^+]; HRMS: found 857.2166. $C_{50}H_{36}N_2O_{10}S+H^+$ requires 857.2169.

*4.2.15. Dibenzhydryl 3,3′-sulfonylbis(methylene)bis(6-nitro-2-naphthoate) (**11h**) state.* White solid; mp 194 °C; yield: 53%; R_f=0.6 (PE/EA=2:1); ν_{max} (KBr, cm^{-1}): 2926, 2366, 1718, 1527, 1345, 1273. δ_H 4.98 (4H, s), 6.92 (2H, s), 7.19–7.49 (20H, m), 8.00 (2H, s), 8.08 (2H, d, J=9.2 Hz), 8.31 (2H, d, J=8.8 Hz), 8.67 (4H, s). δ_C 56.0, 78.5, 120.8, 124.1, 126.5, 127.3, 128.2, 128.7, 130.6, 131.2, 132.0, 133.0, 134.5, 135.3, 139.3, 141.2, 165.4. MS: m/z=857.28 [MH^+]; HRMS: found 857.2180. $C_{50}H_{36}N_2O_{10}S+H^+$ requires 857.2169.

*4.2.16. Diethyl 3,3′-sulfonylbis(methylene)bis(5,6,7,8-tetrahydronaphthalene-2-carboxylate) (**11i**) state.* Viscous liquid; yield: 98%; R_f=0.5 (PE/EA=2:1); ν_{max} (neat, cm^{-1}): 2927, 1712, 1274, 1118. δ_H 1.35 (6H, t, J=7.0 Hz), 1.79 (8H, br s), 2.76–2.77 (8H, m), 4.31 (4H, q, J=7.0 Hz), 4.83 (4H, s), 7.12 (2H, s), 7.70 (2H, s). δ_C 14.4, 22.8, 23.0, 29.2, 29.4, 56.1, 61.2, 125.3, 128.4, 132.2, 134.3, 138.2, 142.1, 167.5. MS: m/z=499.16 [MH^+]; HRMS: found 499.2138. $C_{28}H_{34}O_6S+H^+$ requires 499.2154.

*4.2.17. Diethyl 3,3′-sulfonylbis(methylene)bis(9,10-dihydrophenanthrene-2-carboxylate) (**11j**) state.* Brown viscous liquid; yield: 98%; R_f=0.6 (PE/EA=2:1); ν_{max} (neat, cm^{-1}): 2935, 1706, 1296, 1187. δ_H 1.37 (6H, t, J=7.0 Hz), 2.85 (8H, s), 4.34 (4H, q, J=7.0 Hz), 5.01 (4H, s), 7.22–7.29 (6H, m), 7.74–7.67 (2H, m), 7.80 (2H, s), 7.86 (2H, s). δ_C 14.4, 28.6, 28.7, 56.5, 61.5, 124.7, 127.3, 127.4, 128.4, 128.7, 128.8, 129.7, 131.1, 133.0, 137.9, 138.0, 138.3, 167.2. MS: m/z=617.27 [MNa^+], 595.19 [MH^+]; HRMS: for $C_{36}H_{34}O_6S+H^+$ 595.2154 found 595.2137.

*4.2.18. 2-Naphthylmethanesulfonylmethyl-naphthalene (**11l**) state.* Viscous liquid; yield: 27.34%; R_f=0.5 (PE/EA=7:1); ν_{max} (neat, cm^{-1}): 1345. δ_H 4.32 (4H, s), 7.50–7.55 (6H, m), 7.81–7.90 (8H, m). δ_C 58.3, 124.9, 126.6, 126.8, 127.7, 127.9, 128.8, 130.6, 133.1, 133.2. MS: m/z=347.11 [MH^+]; HRMS: calcd for $C_{22}H_{18}O_2S+H^+$ 347.1106 found 347.1115.

*4.2.19. 3-Benzenesulfonylmethyl-6-nitro-naphthalene-2-carboxylic acid ethyl ester (**11m**).* State: brown solid; mp 133 °C; yield: 89%; R_f=0.5 (PE/EA=3:1); ν_{max} (KBr, cm^{-1}): 2365, 1718, 1557, 1347. δ_H 3.91 (3H, s), 5.21 (2H, s), 7.47 (2H, t, J=7.6 Hz), 7.63 (1H, t, J=7.6 Hz), 7.69 (2H, d, J=7.6 Hz), 7.91 (1H, s), 8.06 (1H, d, J=9.2 Hz), 8.33 (1H, d, J=9.2 Hz), 8.56 (1H, s), 8.73 (1H, s). δ_C 52.7, 59.2, 120.9, 124.1, 127.2, 128.5, 129.1, 130.6, 131.8, 131.9, 132.9, 133.9, 134.6, 135.0, 138.4, 147.2, 166.3. MS: m/z=386.08 [MH^+]; HRMS: calcd for $C_{19}H_{15}NO_6S+H^+$ 386.0693 found 386.0706.

*4.2.20. 3-Benzenesulfonylmethyl-6-nitro-naphthalene-2-carboxylic acid ethyl ester (**11n**) state.* Dark brown solid; mp 170 °C; yield: 98%; R_f=0.6 (PE/EA=3:1); ν_{max} (KBr, cm^{-1}): 2363, 1718, 1560, 1340. δ_H 1.44 (3H, t, J=7.0 Hz), 4.37 (2H, q, J=7.0 Hz), 5.21 (2H, s), 7.47 (2H, t, J=7.8 Hz), 7.63 (1H, t, J=7.8 Hz), 7.69 (2H, d, J=7.2 Hz), 7.89 (1H, s), 8.07 (1H, d, J=8.8 Hz), 8.32 (1H, dd, J=8.8, 2.2 Hz), 8.55 (1H, s), 8.72 (1H, s). δ_C 14.2, 59.2, 62.0, 120.9, 124.1, 127.2, 128.5, 129.1, 130.6, 131.8, 131.9, 132.9, 133.9, 134.6, 135.0, 138.4, 147.2, 166.3. MS: m/z=422.03 [MNa^+]; HRMS: calcd for $C_{20}H_{17}NO_6S+Na^+$ 422.0674 found 422.0683.

*4.2.21. 3-Benzenesulfonylmethyl-6-nitro-naphthalene-2-carboxylic acid benzhydryl ester (**11o**) state.* Yellow solid; mp 156 °C; yield: 95%; R_f=0.5 (PE/EA=4:1); ν_{max} (KBr, cm^{-1}): 2368, 1719, 1654, 1560, 1347. δ_H 5.19 (2H, s), 7.04 (1H, s), 7.33–7.47 (13H, m), 7.58 (2 h, d, J=7.6 Hz), 8.00 (1H, s), 8.11 (1H, d, J=9.0 Hz), 8.34 (1H, dd, J=9.0, 2.0 Hz), 8.65 (1H, s), 8.77 (1H, d, J=1.6 Hz). δ_C 59.1, 78.8, 121.1, 124.3, 127.4, 127.5, 128.4, 128.6, 128.8, 129.1, 130.9, 131.6, 132.2, 133.2, 134.0, 134.7, 135.3, 138.6, 139.7, 147.5, 165.4. MS: m/z=538.11 [MH^+]; HRMS: calcd for $C_{31}H_{23}NO_6S+H^+$ 538.1324 found 538.1342.

4.2.22. Computational details. All the computations were performed with Orca 2.8.0[13] software package. All optimizations of the ground state geometries were done using the Density Functional Theory (DFT) method BP86[14] with Resolution of the Identity (RI) approximation[15] and the corresponding auxiliary basis set. Empirical dispersion correction[16] was included in all calculations. The def2-SVP basis set[17] was used for all of calculations. Restricted approach was used in the computational analysis for the closed shell structures, whereas unrestricted approach for the open shell singlet states and intermediates. The nature of the stationary point was characterized by vibrational frequency calculation.

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Supplementary data

Synthesis of starting sulfones along with their spectral data, total energies, the optimized Cartesian coordinates and the various ^1H, ^{13}C and ^1H NMR kinetics spectra. Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2012.06.001.

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