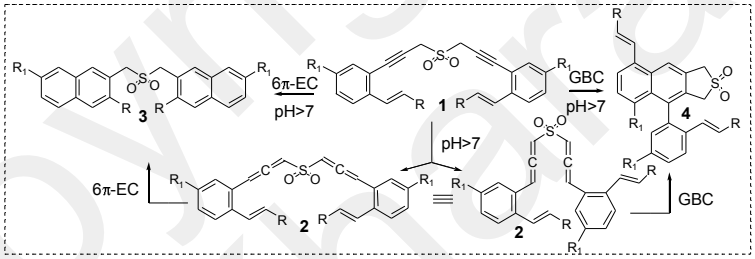
## *Abstract*

### Eneynes and Dieneynes: Reactivity and Synthetic Utility

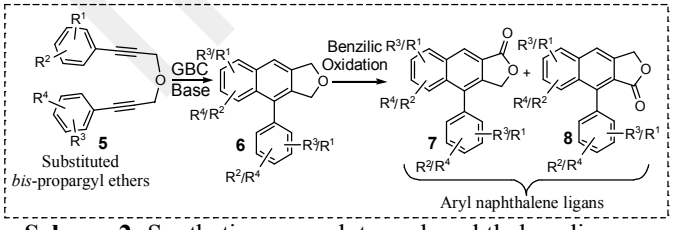
The usefulness of biradicals in biology has been well-exploited in the development of anticancer agents and continues to be an important topic of interest. Bergman, Myers-Saito, Moore and Schmittel Cyclization give rise to such biradicals which need external sources like hydrogen atom donor for quenching. The Garratt-Braverman Cyclization (GBC) and Hopf Cyclization (HC) belong to the self-quenching category and are the topic of interest of the present thesis. The first chapter contains a critical survey of biradical generating processes. We have reported the synthesis and reactivity of differently substituted *bis*-dieneyl propargyl sulfones **1** in the second chapter. These sulfones under basic condition isomerise to the corresponding *bis*-*Z*-dienylallenic sulfones **2** capable of undergoing two parallel processes, namely, GBC and 6π-Electrocyclization (6π-EC) (**Scheme 1**). The results have shown a general preference for GBC over 6π-EC; the preference can be modulated or even reversed by temperature, electronic, steric effect of substituents as well as by changing the alkene geometry (**Table 1**). An explanation based on reacting conformations has been put forward to explain the cooperative effect comprising electronic and steric parameters. Third chapter describes a short synthesis of a wide array of Justicidin analogues involving GB Cyclization of various substituted aryl *bis*-propargyl ethers **5** as a key step followed by benzylic oxidation of the resultant dihydroisofuran derivatives **6** to the aryl naphthalene lignans (**7, 8**) (**Scheme 2**). The selectivity issues in both the reactions have been judiciously addressed by suitable perturbation of the electronic character of the two aryl rings (for GBC) and introducing steric factor (for lactone formation). In the final chapter 4, we have attempted the synthesis of cyclic dieneynes having oxygen or nitrogen atom in cyclic framework. We are successful in synthesizing 9- and 10-membered aza-dieneynes (**9**, **10**) for the first time. The compounds showed spontaneous Hopf Cyclization (HC) to dihydroisoquinoline derivatives (**11**, **12**) (**Scheme 3**). Compound **9** which can also be regarded as an ene-yne-imine has exhibited DNA cleaving activity at micromolar concentrations *via* a possible alkylation process.

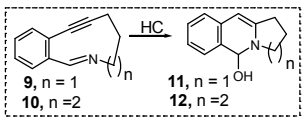

**Scheme 1:** *Bis*-dieneallene sulfones capable of undergoing both GBC and 6π-EC

**Table 1:** Results of triethylamine treatment of sulfones

| Entry | Sulfone | Temperature (°C) | Time | % of GB Product | % of 6π–EC Product | Combined yield (%) |
|---|---|---|---|---|---|---|
| 1 | R = COOMe $R_1$ = H | 0 | 15d | 89 | 11 | 80 |
| | | 30 | 72h | 74 | 26 | 80 |
| | | 60 | 4h | 30 | 70 | 82 |
| 2 | R = $COOCHPh_2$ $R_1$ = $NO_2$ | 30 | 60h | 40 | 60 | 95 |
| 3 | R = CN (*cis*) $R_1$ = H | 30 | 35h | >99 | Not Detected | 98 |




**Scheme 2:** Synthetic approach to aryl naphthalene lignan




**Scheme 3:** Hopf Cyclization of **9**- and **10**-membered aza-dieneynes


**Keywords:** Garratt-Braverman, Hopf, self-quenching, biradical, eneynes, dieneallenes, dieneynes