

## INTRODUCTION

The Diels-Alder reaction is a prominent pericyclic reaction in organic chemistry that is able to reliably form cyclohexene rings with predictable regio- and stereochemistry under relatively simple conditions.<sup>1</sup> The reaction occurs between a conjugated diene, and dienophile and proceeds via a concerted [4+2] cycloaddition, the simplicity of which allows for a considerable amount of synthetically useful reactions.<sup>2</sup> In addition to the classic Diels-Alder reaction, there are a number of related variants including the intramolecular Diels-Alder reaction, capable of forming bridged and fused polycyclic adducts, the hetero-Diels-Alder reaction which can form a variety of heterocycles, and the hexadehydro Diels-Alder reaction, an analogous alkyne reaction which able to form substituted benzene compounds.<sup>3,4</sup> There is even evidence of enzymes capable of mediating Diels-Alder reactions in biosynthetic pathways.<sup>5</sup> As such it has applications in a wide range of disciplines including the industrial production of pharmaceuticals and agrochemicals, the total synthesis of natural products, and polymer chemistry among others.<sup>2,6,7</sup> Of the many diene/dienophile pairs that have been investigated, the reaction between furan and maleimide has been the most studied due to its application in polymer chemistry.<sup>7</sup> This popularity is in large part due to the convenient temperature range of Diels-Alder/retro-Diels-Alder equilibrium of the reaction, and low possibility of side reactions or thermal degradation.<sup>8</sup> These properties have been exploited to produce cross-linked polymeric material capable of re-mending under mild conditions.<sup>9</sup> A sizeable amount of research has also been put into the application of furan/maleimide polymers with epoxy functionalities in order to develop thermally removable epoxy adhesives.<sup>10</sup> Another opposite approach involves the transformation of the Diels-Alder adduct by an aromatization reaction to produce highly thermostable polymers.<sup>8</sup> This process is irreversible and produces polymers that are stable at temperatures well above those which favor retro-Diels-Alder reactions in the original adducts.<sup>11</sup> The furan/maleimide combination is also advantageous in terms of green chemistry as there is some interests in the use of furan compounds derived from renewable sources.<sup>12</sup> The maleimide component can be obtained in a relatively simple two-step synthesis involving the reaction of maleic anhydride and amines followed by dehydration.<sup>7</sup> In this paper, we present a green synthesis of *N*-phenylmaleimide precursors by utilizing a solvent free room temperature reaction in the formation of the maleimide, and demonstrate its use as a dienophile in furan/maleimide Diels-Alder reactions. This contributes to the already sizeable body of knowledge on furan/maleimide Diels-Alder reactions, and presents a greener alternative to more traditional synthetic methods.

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