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Dearomatizing and Derivatizing a Mesityl on Boron *via* One-pot Photoisomerization and [4 + 2] Diels-Alder Addition

Billy Deng^[a], Xiang Wang^[a] and Suning Wang^{*[a]}

Abstract: Boron compounds that have a conjugated chelate backbone (N,C-chelate or C,C-chelate) and two mesityl substituents on boron have been found to undergo one-pot facile transformation/reaction with dienophiles, which leads to the dearomatization of one mesityl ring and its [4+2] Diels-Alder addition with the dienophiles. Photochemical activation is the key in this facile one-pot transformation of the aryl ring.

Introduction

Arene dearomatization is a powerful approach for generating structurally-complex alicyclic building blocks in total synthesis.^[1a] Amongst the myriad of dearomatization strategies,^[1c,2c] dearomatization by cycloaddition reaction has the advantage of high atom efficiency and significantly increasing the structural complexity in a single step by forming bridged or bicyclic products from simple arenes.^[1] The Diels-Alder (D-A) [4+2] reaction is perhaps the most widely-used and versatile mode of cycloaddition in synthetic chemistry.^[2a,b] However, despite its importance, D-A reactions of non-activated monocyclic arenes (e.g. benzene, toluene, mesitylene) continue to be a synthetic challenge due to their exceptional stability conferred by the aromaticity.^[1b] Typical D-A reactions of non-activated monocyclic arenes require high temperatures/pressures or transition metal catalysts,^[3] or activated dienophiles.^[4] Transition metal mediated dearomatization has been extensively explored in recent decades, wherein simple arenes are either η^6 - or η^2 -coordinated to transition metals, enabling their reactivity towards D-A reactions with electrophiles under relatively mild conditions.^[3]

Recently, certain chelate boron compounds bearing two aryl substituents on boron were found to readily undergo quantitative photoisomerization, dearomatizing one aryl group to a cyclohexadienyl unit that is η^2 -coordinated to the boron atom, which could be described as a boratanorcaradiene (BNCD) or a 7-

borabicyclo[4.1.0]hepta-2,4-diene or a borirane-fused cyclohexadiene, (e.g. **1a-3a** in Scheme 1).^[5] Compared to the chelate starting materials (e.g. **1-3** in Scheme 1), which are thermally and chemically inert, the species **1a-3a** are much higher in energy (~30 kcal mol⁻¹ higher) and their borirane-cyclohexadienyl unit is highly electron-rich and reactive toward oxygen.^[5a] We therefore considered the possibility of taking advantage of the photoisomerization to derivatize the aryl substituents in molecules such as **1-3**. This could be achieved by a one-pot process that involves first the generation of the BNCD unit via photoisomerization, followed by a [4+2] D-A reaction with an appropriate alkyne or alkene, as illustrated in Scheme 1. To our delight, we have found that the photochemically generated species **1a-3a** react readily with electrophilic alkynes/alkenes in a highly stereoselective manner at mild conditions, generating the corresponding [4+2] D-A cycloadduct quantitatively. The unique features of this approach include the absence of transition metal catalysts as well as mild reaction conditions. The key activation step of this reaction is driven by light, a form of renewable energies. Furthermore, while examples of [4+2] cycloaddition of alkynes^[6] and azides^[7] to boracyclopolyenes were reported previously, they involved highly reactive boroles. To our best knowledge, cycloaddition reactions involving species such as BNCDs are previously unknown.

Herein we demonstrate a series of stepwise, light-assisted, catalyst-free [4+2] cycloaddition of BNCDs with dienophiles under ambient conditions to produce a series of air-stable borirane-fused D-A adducts. The new light-driven dearomatization and functionalization of arenes facilitated by boron further enriches the metal-free bond activation chemistry enabled by boron.^[8]

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Scheme 1. Sequential photoisomerization and [4+2] D-A reaction of compounds **1-3**.

Results and Discussion

Scheme 2. Synthetic routes for compounds **1b-3b** and their isolated yields.

Scheme 3. Dienophiles that failed to react with compounds **1-3**.

One-pot syntheses of 1b-3b, and 1c. Boranes **1-3** were obtained by previously reported procedures.^[5a-c] They are air stable and thermally stable. Upon photoirradiation, they can be quantitatively converted to their corresponding dark coloured isomers quantitatively. The one-pot procedure used in our investigation (Scheme 2) involves first photochemically converting **1-3** to their respective dark borirane isomers **1a-3a** in a J-young NMR tube with benzene or toluene as the solvent per our previous procedures.^[5] This photochemical conversion can be tracked readily by NMR spectroscopy. Upon full conversion to **1a-3a**, various dienophiles were examined for their reactivity with the cyclohexadienyl unit in **1a-3a**. Among the alkyne dienophiles we examined, dimethyl acetylenedicarboxylate (DMAD) is the most reactive toward **1a-3a**, showing appreciable reactions with **1a-3a** at ambient temperature, which can be attributed to its relatively high electrophilicity toward the electron-rich dienyl unit. Other alkyne dienophiles such as those shown in Scheme 3 do not show any appreciable reactivity with **1a-3a** at ambient temperature. Because **1a** and **2a** either thermally revert back rapidly to **1** and **2**, respectively, or transform to other species at high temperatures,^[5a-b] we restricted the reaction temperature with dienophiles to ambient temperature or 30 °C. Compound **3a** has a high thermal stability and does not thermally revert back to **3**.^[5c] Nonetheless, besides DMAD, none of the dienophiles in Scheme 3 react with **3** even at elevated temperature (e.g. 100 °C).

Figure 1. ¹H NMR spectra showing the clean photochemical conversion of **1** to **1a** (the green highlighted peaks) and the quantitative formation of **1b** (the blue highlighted peaks) after the addition of ~40 eq. DMAD (the yellow highlighted peak at $\delta = 3.06$ ppm along with the impurity peaks from DMAD) to the C₆D₆ solution of **1a** (0.04 M).

The ^1H NMR spectra in Figure 1 demonstrate the quantitative one-pot transformation of **1** to **1b**. Irradiating the benzene solution (0.04 M) of **1** at 365 nm for about 12 hr converts it quantitatively to **1a**. After the addition of excess DMAD to the solution of **1a**, and heating the mixture at 30 °C overnight, the D-A product **1b** forms quantitatively. The DMAD starting material (99%, Aldrich) contains unidentified impurities, which can be readily separated from the product by neutral activated alumina column chromatography. The one-pot conversion of **2** to **2b** and **3** to **3b** proceeds in a similar manner (see SI) except that for **3** the excitation energy of 300 nm is necessary owing to the much blue shifted absorption spectrum of **3**, compared to that of **1** and **2**. Interestingly, the D-A reaction of **3a** with DMAD to produce **3b** appears to be much faster, complete within a few hours at 30 °C, than that of **1a** and **2a**. Considering the strong σ -donating NHC-chelate and the high electron density on the borirane ring in **3a**, the strong electron-donating substituent on boron accelerates the D-A reactions. Compounds **1b-3b** are unstable on silica and basic alumina columns but are easily purified/isolated *via* neutral alumina with a small amount of decomposition. **1b-2b** yield orange crystals while **3b**, light-yellow crystals from the solvent mixture of hexanes-ethyl acetate. **1b-3b** are air-stable and can be heated up in solution to 90°C overnight under inert conditions without change.

Out of the various alkene dienophiles (Scheme 3) we examined, only maleic anhydride (MA) shows the D-A reactivity with the borirane molecule **1a**. The reaction of **1a** with 5 eq. MA reaches completion at room temperature in about 20 min., yielding the D-A product **1c** quantitatively as shown in Figure 2. **1c** could not be purified by column chromatography. When the reaction of **1a** with MA is repeated at a 1:1.05 ratio under the same conditions, it reaches completion in about two hours, and without further purification, compound **1c** can be isolated as orange crystals by recrystallization in 42% yield. Compounds **1b-3b** and **1c** were fully characterized by ^1H , ^{13}C and ^{11}B NMR, HRMS spectroscopy, and single-crystal X-ray diffraction analysis (see Experimental Section and SI for details).

We also examined unsymmetrical molecules^[9] such as BMes(Ar) chelate compounds for possible selective aryl activation via the same approach. However, the borirane-cyclohexadienyl unit generated from the Ar ring of the unsymmetrical molecules undergoes efficient thermal isomerization that competes effectively with the intermolecular Diels-Alder addition reactions. We performed low temperature photoisomerization on the

unsymmetrical boron compounds in order to slow down the undesired thermal isomerization and achieve effective Diels-Alder additions. Nonetheless, only thermal isomerization products were observed and no [4+2] D-A reactivity was detected for the unsymmetrical boron molecules.

Structures of **1b – 3b** and **1c**

Compounds **1b – 3b** have a distinct ^{11}B NMR peak at -5.7, -6.3, and -16.0 ppm, respectively (recorded in C_6D_6) ppm, which are downfield shifted by a few ppm, relative to those of **1a – 3a**, and in agreement with the saturated borirane structures.^[5, 10] Similarly, compound **1c** has a ^{11}B NMR peak at -8.5 ppm.

Figure 2. ^1H NMR spectra showing the quantitative formation of **1c** (the blue highlighted peaks) from the reaction of **1a** with 5 eq. maleic anhydride (MA, the yellow highlighted peaks) in C_6D_6 (0.03 M) at room temperature.

The structures of **1b – 3b** and **1c** were determined first by comprehensive 2D NMR spectroscopic analysis, which established that the addition of the dienophile to the cyclohexadienyl ring proceeds exclusively from the exposed face of the cyclohexadienyl ring, instead of the cavity between the mesityl and the cyclohexadienyl, owing to the much less steric hindrance. The resulting 3-boratricyclo[3.2.2.0^{2,4}]nona-6,8-diene has the *endo* stereochemistry, following the typical [4+2] D-A reaction pathway.^[2] The Me^d, Me^e and H_a groups on the D-A addition unit of **1b** have a long range coupling to one of the methyls (Me^f) of the mesityl as shown by the 2D NOESY spectrum in Figure 3. Similar coupling patterns were also observed in the 2D NOESY spectra of **1c** and **2b** (see SI). The *ortho*-H₁ atom in the phenyl ring of **1b** is unusually downfield shifted, appearing as a doublet at about 9.2 ppm (Figure 1). The H₁ atom in compounds **2b** and **3b** has a similar chemical shift

(see SI). One possible explanation for this is the formation of an H bond between the H₁ atom and one of the carbonyl oxygen atoms. This is indeed confirmed by crystal structures of **1b** – **3b**. The borirane species **1a** is known to undergo slow enantiomer interconversion in solution via a 1,3-sigmatropic B-C bond migration, based on a chemical exchange peak observed in NOESY spectra between the two methyl groups on the *sp*³ carbon atoms of the borirane unit.^[5a] Interestingly, similar enantiomer interconversion was not observed for **1b**, peraps because of its highly congested nature.

Figure 3. 2D HH NOESY of **1b** showing the long range coupling of the Me¹ of the mesityl with the bridged ring (mixing time = 0.4 s, recorded in C₆D₆).

Table 1. Selected bond lengths (Å) and angles (°) for **1b-3b** and **1c**

1b	B1-C1	1.664(3)	C3-C11	1.521(3)
	B1-C2	1.582(3)	C6-C10	1.550(3)
	B1-N1	1.600(3)	C10-C11	1.341(3)
	B1-C27	1.605(3)	C2-B1-C1	57.09(14)
	C1-C2	1.553(3)	C2-C1-B1	58.80(14)
	C2-C3	1.562(3)	C1-C2-B1	64.11(15)
	C3-C4	1.529(3)	C2-B1-N1	116.28(19)
	C4-C5	1.322(3)	C27-B1-C1	132.04(19)
	C1-C6	1.590(3)	N1-B1-C27	107.77(19)
	C5-C6	1.513(3)	B1-C1-C6	128.09(18)
1c	B1-C1	1.636(3)	C4-C10	1.581(3)
	B1-C2	1.602(3)	C5-C6	1.324(3)
	B1-N1	1.574(3)	C10-C11	1.539(3)
	B1-C25	1.607(3)	C2-B1-C1	57.89(12)

	C1-C2	1.567(3)	C2-C1-B1	59.99(12)
	C1-C4	1.563(3)	C1-C2-B1	62.12(12)
	C2-C3	1.543(3)	N1-B1-C25	109.84(16)
	C2-C7	1.525(3)	N1-B1-C1	112.05(15)
	C3-C11	1.558(3)	C4-C1-B1	120.44(14)
	C3-C6	1.508(3)	C3-C2-B1	124.29(16)
	C4-C5	1.518(3)		
2b	B1-C1	1.695(3)	C6-C11	1.546(3)
	B1-C2	1.578(3)	C10-C11	1.341(3)
	B1-C26	1.597(3)	C2-C1-B1	57.99(12)
	B1-N1	1.568(3)	C1-C2-B1	65.57(13)
	C1-C2	1.551(3)	N1-B1-C26	106.93(16)
	C2-C3	1.570(3)	N1-B1-C1	109.31(16)
	C3-C4	1.519(3)	C16-C1-B1	117.63(16)
	C1-C6	1.592(3)	C6-C1-B1	122.80(16)
	C5-C6	1.508(3)	B1-C2-C3	120.33(16)
	C4-C5	1.324(3)		
3b	B1-C1	1.6976(17)	C4-C5	1.3265(18)
	B1-C2	1.5941(17)	C6-C10	1.5517(17)
	B1-C23	1.5969(17)	C10-C11	1.3353(19)
	B1-C31	1.6092(18)	C10-C11	1.3353(19)
	C1-C2	1.5316(16)	C2-B1-C1	55.35(7)
	C1-C6	1.5813(16)	C2-C1-B1	58.89(7)
	C2-C3	1.5705(17)	C1-C2-B1	65.76(8)
	C3-C4	1.5268(17)	C2-B1-C23	121.35(10)
	C4-C5	1.3265(18)	C2-B1-C31	124.08(10)
	C5-C6	1.5138(17)	C3-C2-B1	119.53(10)
	C3-C11	1.5195(17)	C23-B1-C31	108.33(10)
	C6-C10	1.5517(17)

Figure 4. Crystal structures of **1b** and **1c**, with a partial labelling scheme and 35% thermal ellipsoids. H atoms are omitted for clarity. The mesityl and part of the dienophile are shown as sticks.

Figure 5. Crystal structures of **2b** and **3b** with a partial labelling scheme and 35% thermal ellipsoids. H atoms are omitted for clarity. The mesityl and part of the dienophile are shown as sticks.

Formation of four new stereogenic centers is evident for **1c** based on its ^1H -COSY NMR spectrum (see SI). The clean formation of one stereoisomer shown by NMR for **1b-3b** and **1c** also supports the high stereoselectivity of the adduct formation. The absence of the highly deshielded doublet for the *ortho*-H atom of the phenyl ring in **1c** indicates that the carbonyl groups in the anhydride unit are oriented away from the phenyl ring, with the exclusive formation of the *endo* adduct.^[11]

The crystal structures of **1b-3b** and **1c** are shown in Figure 4 and 5, respectively. Selected bond lengths and angles are shown in Table 1. The two C=C double bonds in the cycloaddition unit (C4-C5, 1.322 – 1.326 Å; and C10-C11, 1.341 – 1.345 Å) of **1b-3b** have the typical olefinic bond lengths. The double bond of C5-C6 in the cycloaddition unit of **1c** also has a typical C=C bond length of 1.324(3) Å. The crystal structures show that one of the CO₂Me groups (C14 in **1b**, C12 in **2b** and **3b**) is close to the phenyl ring and oriented approximately perpendicular with respect to the C=C bond. The carbonyl oxygen atom in this group, in fact, forms an H bond with the H atom of the phenyl ring (bound to C17 in **1b** and **2b**, and C18 in **3b**), as evidenced by the separation distance of 2.18 – 2.20 Å between the oxygen atom and the H atom. This observation is consistent with the deshielded chemical shift of the H₁ atom of **1b** shown in Figure 1. The crystal structures confirmed the stereochemistry established by NMR data. The borirane ring remains intact in all four structures. **1b-3b** all have a relatively long B-C bond in the borirane ring (B1-C1 = 1.664(3) Å, 1.695(3) Å, 1.6976(17) Å for **1b-3b**, respectively). Comparing to

the previously characterized borirane ring in **3a**, the D-A adduct formation increase the B-C_{ph} bond length in **3b** by about 0.013 Å, which could be ascribed to the increased steric congestion around the B atom in **3b**. In the adducts **1b-3b**, the bicyclo[2.2.2]octa-2,5-diene is approximately perpendicular to the borirane ring. The cyclohexene bridge (pink) (e.g. in **1b**, C3-C4-C5-C6) is bent away from the bridgehead (C3-C11-C10-C6 in **1b**) towards the mesityl.

The structure of **1c** (Figure 4) shows that the MA anhydride unit in the adduct is indeed oriented away from the phenyl ring without any intramolecular H-bond interactions. This preferred orientation is likely dictated by the need to minimize steric interactions between the phenyl ring and the anhydride unit.

Figure 6. Absorption spectra of **1a-3a**, **1b-3b** and **1c** recorded in benzene (normalized with respect to the first low energy band). Inset: photographs showing the solution colours of the same molecules in benzene.

Absorption spectra of 1b-3b and 1c. The absorption spectra of **1b-3b** and **1c** along with those of **1a-3a** are shown in Figure 6. For **1b**, **1c**, and **2b**, the first low energy absorption band appears at $\lambda_{\text{max}} = \sim 420$ nm, which is responsible for the yellow-orange colour of these three compounds. In contrast, the first low energy absorption band of **3b** is about 60 nm hypsochromically shifted, relative to **1b** and **2b**, making it pale yellow. Compared to the cyclohexadienyl borirane parent molecules **1a**, **2a**, and **3a**, which are much more intensely coloured, with the first absorption band appearing at ~ 600 nm for **1a** and **2a**, and 454 nm for **3a**, the first absorption band of the D-A borirane species **1b-3b** and **1c** is sharply hypsochromically shifted. This difference is caused by the unsaturated dienyl unit attached directly to the borirane ring in **1a-**

3a that contributes significantly to the HOMO level along with the borirane ring, raising the HOMO energy level such that they display reactivity toward oxygen.^[5] In **1b-3b/1c**, D-A addition converts the unstaturated sp^2 carbon atoms attached to the borirane ring to sp^3 carbon atoms, which likely greatly reduces the contribution of the D-A unit to the HOMO level and the electron density on the borirane unit, leading to a stabilized HOMO and an increased HOMO-LUMO gap. To further understand the electronic properties of **1b-3b/1c**, TD-DFT computational studies were performed at the B3LYP/6-311G(d) level of theory.^[12] The HOMO-LUMO diagrams for **1b-3b/1c** are shown in Figure 7.

Figure 7. HOMO and LUMO orbitals of **1c**, **1b-3b** with an iso-contour of 0.03 for all surfaces.

Consistent with the absorption spectra, the calculated HOMO-LUMO gaps of **1b** and **1c** are significantly higher (3.47 eV and 3.43 eV respectively) than their precursor **1a** (2.32 eV).^[5a] TD-DFT data indicate that the vertical excitation to the S_1 state for **1b** and **1c** is dominated by the HOMO to LUMO transition with an energy of ~2.85 eV, approximately 0.90 eV higher than that of **1a**. The same trend is also found for **2b** vs **2a** and **3a** vs **3b** (see SI). As shown in Figure 7, the LUMO level for **1b-3b** and **1c** is mainly localized on the chelate backbone. Unlike **1a-3a**, where the HOMO is dominated by the borirane and the cyclohexadienyl ring,^[5a] the key contributions to the HOMO of **1b/1c** are from the mesityl ring and the C=C bonds in the D-A adduct, which clearly is responsible for their widening of the HOMO-LUMO gap. For **2b** and **3b**, although there are significant contributions from the borirane ring to the HOMO, the contributions from the D-A adduct unit to the HOMO are very small, leading to the widening of the HOMO-LUMO gap relative to that of **2a** and **3a**. In contrast to the

instability of **1a-3a** toward oxygen, the relatively deeper HOMO of **1b-3b** and **1c** (stabilized by ~ 1 eV), compared to that of **1a-3a**, makes **1b-3b** and **1c** stable to air. Furthermore, unlike their precursor compounds **1a-3a**, which are either thermally or photochemically active, molecules **1b-3b** and **1c** do not show any thermal or photoreactivities upon heating up to 100°C or irradiation near λ_{max} of their first low energy absorption band.

Conclusions

Photochemical transformation of an aromatic mesityl group on boron has been established to be an effective method to activate the mesityl on boron toward facile Diels-Alder addition reactions with dienophiles in a one-pot manner. This type of photo-initiated aryl activation has been found to be a general reactivity for a BMes₂ unit with different diaryl chelate backbones. The clean photochemical conversion of the BMes₂ chelate compounds to the corresponding cyclohexadienyl fused boriranes is the key step in this type of aryl activation.

Experimental Section

Unless stated otherwise, all reactions were carried out under an inert atmosphere of dry nitrogen in sealed J-Young NMR tubes (conventional DURAN®glass). Starting reagents were purchased from chemical suppliers and used without further purification. Deuterated benzene (C₆D₆) was purchased from Cambridge Isotope Laboratories and purged with dry nitrogen and stored over molecular sieves prior to use. NMR spectra were recorded at 298 K using the following spectrometers: Bruker Avance-400, Neo-500, Avance-600, or Neo-700. Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, m = multiplet. High resolution mass spectra were recorded on a Thermo Fischer Scientific MALDI LTQ Orbitrap XL mass spectrometer. Exact masses were calculated based on the predominant combination of natural isotopes. Photoisomerization reactions of all compounds were done in sealed J-Young NMR tubes using a Rayonet Photochemical Reactor at 298 K. UV-vis spectra were recorded on a Varian Cary 50 spectrometer.

Synthesis of 1b. Compound **1** was synthesized according to previous literature.^[5a] **1** (15 mg, 37 μ mol) was dissolved in C₆D₆

(0.90 mL, $c = 0.04$ M) and irradiated at ambient temperature with UV lamps at 365 nm for 8 hours to fully convert colourless **1** to dark blue **1a**, as monitored by ^1H NMR spectra. DMAD (0.1 mL, 0.82 mmol) was then added in a single portion to the solution of **1a**. After heating in a 30°C oil bath for overnight, the solution colour became yellow and NMR spectra indicated nearly quantitative formation of **1b**. The clear yellow solution containing the product was concentrated *in vacuo* and purified by column chromatography on neutral alumina using a hexanes/ethyl acetate (9:1) mixture, affording a yellow-orange residue. Crystals of **1b** were grown by the slow evaporation of a concentrated hexanes:ethyl acetate (5:1) solution and subsequently washed with hexanes to afford the pure product. (19 mg, 93%). ^1H NMR (400 MHz, C_6D_6): δ 9.19 (d, $J = 8.3$ Hz, 1H, *o*-Cbz-H), 8.18 (dd, $J = 6.5, 1.7$ Hz, 1H, *o*-Py-H), 7.64 (t, $J = 7.5$ Hz, 1H, *m*-3-Cbz-H), 7.58 (d, $J = 8.2$ Hz, 1H, *m*-5-Cbz-H), 7.39 (d, $J = 8.5$ Hz, 1H, *m*-5-Py-H), 6.99 (t, $J = 7.6$ Hz, 1H, *p*-Cbz-H, ov. with Mes-H), 6.95 (s, 1H, Mes-H, ov. with *p*-Cbz-H), 6.82 (s, 1H, Mes-H), 6.56 (td, $J = 8.3$ Hz, 1.6 Hz, 1H, *p*-Py-H), 5.88 (t, $J = 6.8$ Hz, 1H, *m*-3-Py-H), 5.18 (s, 1H, cyclohexene- sp^2 -C-H), 4.42 (d, $^4J = 2.0$ Hz, 1H, cyclohexene- sp^3 -C-H), 3.60 (s, 3H, -OCH₃), 3.38 (s, 3H, -OCH₃), 2.66 (s, 3H, *o*-Mes-2-CH₃, prox. to *o*-Py-H), 2.27 (s, 3H, *p*-Mes-CH₃), 2.10 (s, 3H, *o*-Mes-6-CH₃), 2.07 (s, 3H, cyclohexene-CH₃), 1.52 (d, $^4J = 1.06$ Hz, 3H, allylic CH₃), 0.62 (s, 3H, BCC-CH₃). ^{13}C NMR (126 MHz, C_6D_6): δ 169.49, 165.57, 160.24, 151.70, 148.61, 147.82, 147.61, 145.80, 145.64, 141.40, 140.24, 137.12, 136.20, 134.33, 131.61, 130.39, 127.98, 127.88, 127.69, 127.49, 126.28, 125.78, 122.94, 120.95, 119.93, 54.80, 52.52, 51.47, 51.04, 29.88, 23.68, 23.16, 20.92, 20.56, 20.05, 16.58. ^{11}B NMR (128 MHz, C_6D_6): δ -5.77. HREI-MS Calcd for $\text{C}_{35}\text{H}_{36}\text{BNO}_4$ [M]⁺: 545.2737. Found: 545.2738.

Synthesis of 2b. Compound **2** was synthesized according to previous literature.^[5b] **2** (22 mg, 51 μmol) was dissolved in C_6D_6 (2 mL, $c = 0.025$ M) and irradiated with UV at 365 nm for 7 days to fully convert to **2a**. DMAD (0.1 mL, 0.82 mmol) was then added in a single portion to the solution of **2a**. After heating in a 30°C oil bath for overnight, the clear yellow solution containing the product was concentrated *in vacuo* and purified by column chromatography on neutral alumina using a hexanes/ethyl acetate (9:1) mixture, affording a yellow residue of **2b**. Crystals of **2b** were grown by the slow evaporation of a concentrated hexanes:ethyl acetate (5:1) solution and washed with hexanes

to afford the pure compound **2b** (28 mg, 94%). ^1H NMR (700 MHz, C_6D_6): δ 9.23 (d, $J = 8.5$ Hz, 1H, *o*-Cbz-H), 7.56 (td, $J = 7.8, 7.2, 1.3$ Hz, 1H, *m*-3-Cbz-H), 7.49 (dd, $J = 7.8, 1.1$ Hz, 1H, *m*-5-Cbz-H), 6.95 (s, 1H, Mes-H), 6.86 (t, $J = 7.5$ Hz, 1H, *p*-Cbz-H), 6.84 (s, 1H, Mes-H), 6.75 (d, $J = 1.4$ Hz, 1H, thiazole-H), 5.28 (t, $J = 2.0$ Hz, 1H, cyclohexene- sp^2 -C-H), 4.45 (d, $J = 2.2$ Hz, 1H, cyclohexene- sp^3 -C-H), 3.62 (s, 3H, -OCH₃), 3.38 (s, 3H, -OCH₃), 2.66 (s, 3H, *o*-Mes-2-CH₃, prox. to thiazole-H), 2.27 (s, 3H, *p*-Mes-CH₃), 2.16 (s, 3H, *o*-Mes-6-CH₃), 2.08 (s, 3H, cyclohexene-CH₃), 1.42 (d, $^4J = 1.7$ Hz, 3H, allylic CH₃), 1.16 (d, $^4J = 1.2$ Hz, 3H, thiazole-CH₃), 0.59 (s, 3H, BCC-CH₃). ^{13}C NMR (176 MHz, C_6D_6): δ 169.90, 165.83, 162.79, 159.64, 148.53, 147.59, 141.03, 140.90, 137.40, 136.92, 134.74, 134.31, 132.22, 131.16, 129.04, 128.20, 128.06, 127.92, 127.10, 123.90, 123.17, 54.65, 52.50, 51.87, 51.44, 23.90, 23.89, 21.30, 20.32, 20.27, 16.33, 11.15. ^{11}B NMR (128 MHz, C_6D_6): δ -6.32. HREI-MS Calcd for $\text{C}_{34}\text{H}_{36}\text{BNO}_4\text{S}$ [M]⁺: 565.2458. Found: 565.2473.

Synthesis of 3b. Compound **3** was synthesized according to the previous literature.^[5c] **3** (4.0 mg, 9 μmol) was solubilized in C_6D_6 (0.51 mL, $c = 0.017$ M) and irradiated with UV at 300 nm for 3 hours to fully convert to **3a**. DMAD (0.1 mL, 0.82 mmol) was then added in a single portion to the reaction mixture. After heating in a 30°C oil bath for 2 hours, the clear light-yellow solution containing the product was concentrated *in vacuo* and purified by column chromatography on neutral alumina using a hexanes/ethyl acetate (9:1) mixture, affording a light-yellow residue of **3b**. Crystals of **3b** were grown by the slow evaporation of a concentrated hexanes:dichloromethane (9:1) solution and washed with hexanes to afford the pure compound (4.4 mg, 84%). ^1H NMR (700 MHz, C_6D_6): δ 9.39 (d, $J = 8.0$ Hz, 1H, *o*-Cbz-H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.65 – 7.61 (m, 1H, CBz-N(Ph)C=C-H), 7.61 (t, $J = 8.0$ Hz, 1H, *m*-3-Cbz-H), 7.05 (t, $J = 8.5$ Hz, 1H, *p*-CBz-H, overlap with a C_6D_6 satellite peak), 6.85 (s, 1H, Mes-H), 6.84 – 6.80 (m, 2H, BzIm-H), 6.73 (s, 1H, Mes-H), 6.44 – 6.40 (m, 1H, (CH₃-N(Ph)C=C-H), 5.27 (t, $J = 2.0$ Hz, 1H, cyclohexene- sp^2 -C-H), 4.43 (d, $J = 2.2$ Hz, 1H, cyclohexene- sp^3 -C-H), 3.60 (s, 3H, -OCH₃), 3.41 (s, 3H, -OCH₃), 2.75 (s, 3H, *o*-Mes-CH₃, prox. to N-CH₃), 2.49 (s, 3H, N-CH₃), 2.29 (s, 3H, *p*-Mes-CH₃), 2.00 (s, 3H, cyclohexene-CH₃), 1.86 (s, 3H, *o*-Mes-6-CH₃), 1.49 (d, $^4J = 1.59$, 3H, allylic CH₃), 0.88 (s, 3H, BCC-CH₃). ^{13}C NMR (176 MHz, C_6D_6): δ 170.01, 165.91, 162.37, 150.67, 145.78, 142.71, 141.30, 137.18, 136.60, 136.60, 135.58, 133.70, 132.71, 132.37, 130.18, 128.45, 128.20, 128.06, 127.92, 126.13,

124.14, 123.74, 123.09, 118.67, 114.45, 110.28, 56.46, 53.63, 51.87, 51.44, 31.50, 30.23, 24.86, 23.75, 21.91, 21.31, 20.70, 19.76. ^{11}B NMR (225 MHz, C_6D_6) δ -15.96. HREI-MS Calcd for $\text{C}_{38}\text{H}_{39}\text{BN}_2\text{O}_4$ [M] $^{+}$: 598.3003. Found: 598.3001.

Synthesis of 1c. Compound **1a** (8.8 mg, 21.8 μmol , 30 mM, 0.5 mL of C_6D_6) was generated in the same manner as described for the synthesis of **1b**. Maleic anhydride (2.20 mg, 22 μmol) was added in a single portion to the reaction mixture. After 24 hours under room temperature, the clear yellow solution was concentrated *in vacuo*, followed by extraction with hexanes to afford the yellow residue of **1c**. Crystals of **1c** were grown by the slow evaporation of a concentrated hexanes solution and washed with cold hexanes to afford the pure compound (42%). ^1H NMR (700 MHz, C_6D_6) δ 8.10 (d, J = 6.4 Hz, 1H, *o*-Py-H), 7.96 (d, J = 8.4 Hz, 1H, *o*-Cbz-H), 7.67 (d, J = 8.2 Hz, 1H, *m*-5-Cbz-H), 7.43 (d, J = 8.6 Hz, 1H, *m*-5-Py-H), 7.29 – 7.26 (m, 1H, *m*-2-Cbz-H), 7.01 (t, J = 7.6 Hz, 1H, *p*-Cbz-H), 6.88 (s, 1H, Mes-H), 6.75 (s, 1H, Mes-H), 6.57 (t, J = 7.8 Hz, 1H *p*-Py-H), 5.89 (t, J = 6.8 Hz, 1H, *m*-2-Py-H), 4.82 (t, J = 1.9 Hz, 1H, cyclohexene- sp^2 -C-H), 3.63 (d, J = 8.1 Hz, 1H, *exo*-H, prox. to *o*-Cbz-H), 3.23 (t, J = 2.6 Hz, 1H, Cyclohexene- sp^3 -C-H), 2.81 (dd, J = 8.1, 3.2 Hz, 1H, *exo*-H), 2.37 (s, 3H, *o*-Mes-CH $_3$, prox. to *o*-py-H), 2.24 (s, 3H, *p*-Mes-CH $_3$), 2.16 (s, 3H, cyclohexene-CH $_3$), 1.87 (s, 3H, *o*-Mes-CH $_3$), 1.46 (d, J = 1.6 Hz, 3H, allylic CH $_3$), 0.05 (s, 3H, BCC-CH $_3$). ^{13}C NMR (176 MHz, C_6D_6) δ 173.95, 173.09, 146.02, 145.51, 141.75, 140.21, 139.54, 136.07, 136.01, 135.14, 130.17, 129.96, 128.59, 128.20, 128.06, 127.92, 127.41, 122.62, 121.16, 120.45, 49.92, 49.09, 44.32, 43.36, 23.64, 23.56, 23.30, 21.83, 21.23, 13.97. ^{11}B NMR (225 MHz, C_6D_6) δ -8.70. HRESI-MS Calcd for $\text{C}_{33}\text{H}_{32}\text{BNO}_3$ [M+1]: 502.2548. Found: 502.2536.

X-ray crystallographic analysis. The crystal data of **1b-3b** and **1c** were collected on a Bruker D8-Venture diffractometer with Mo-target (λ = 0.71073 Å) at 180 K. Data were processed on a PC with the aid of the Bruker SHELXTL software package^[13] and corrected for absorption effects. The crystals of **1b**, **1c**, and **2b** belong to the triclinic space group *P*-1 while that of **3b** belongs to the monoclinic space group *P*2 $_1$ /n. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and their contributions in structural factors were included. The details of crystal data, collection parameters and results of analyses are provided in the supporting materials. The crystal data of **1b-3b** and **1c** were deposited to the Cambridge Crystallographic Data Center with deposition numbers of CCDC

1943914-1943917 for **1b**, **2b**, **3b**, and **1c**, respectively. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational study. DFT and TD-DFT calculations were performed using the Gaussian 09 suite of programs^[12] and computational facilities provided by Compute Canada. Geometry optimizations and vertical excitations of all compounds were obtained at the B3LYP/6-31g(d) level of theory, using crystal structural data as the initial geometrical parameters, followed by geometry optimization.

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Keywords: borirane • dearomatisation • photoisomerization • Diels-Alder addition • structures

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Dearomatising and Derivatising a
Mesityl on Boron via One-pot
Photoisomerization and [4 + 2] Diels-
Alder Addition

One-pot photochemical activation of an aryl ring on boron and the subsequent [4 + 2] Diels-Alder addition with dienophiles leads to clean conversion of the aryl ring to a 3-boratricyclo[3.2.2.0^{2,4}]nona-6,8-diene.