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Generating Skeletal Diversity and Complexity from Boron-Substituted 1,3-Dienes and Enophiles

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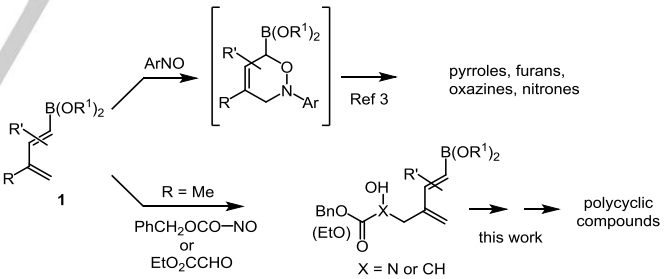
Abstract: Boron-substituted 1,3-dienes participate in ene reactions to afford new functionalized synthetic intermediates. After evaluating several enophiles as partners, the resulting products have been engaged in multistep sequences involving first a Diels Alder/allylboration process. A variety of skeletally diverse and complex polycyclic heterocycles were thus synthesized, such as tetrahydro-*1H*-isoindole-1,3(*2H*)-diones, eight-membered lactones or tricyclic spiro compounds.

Introduction

Advances in high-throughput and high-content screenings have greatly accelerated the investigation of biological systems, providing a major opportunity for the development of improved therapeutic approaches. In this interdisciplinary research area, diversity-oriented synthesis (DOS) is now an essential tool to explore chemical space with original potentially bioactive small molecules.[1] This strategy implies *inter alia* to have access to libraries of high-quality compounds, particularly through the efficient creation of skeletal and stereochemical diversity.
Boron-substituted 1,3-dienes **1** have already been successfully used as key elements to synthesize a large variety of organic compounds due to the presence within the same core of a boryl group and a conjugated unsaturated system.[2] For example, we previously reported the reactivity of these versatile building blocks as dienes towards aryl nitroso compounds and showed that they are valuable precursors of important heterocycles such as pyrroles, furans, nitrones and oxazines (Scheme 1).[3] The polarization of the nitrogen-oxygen bond of nitroso derivatives confers them with high reactivity.[4] For this reason, besides [4+2] cycloadditions, they can also be involved in a large number of other processes, whether metal-catalysed or not, with enolizable carbonyl compounds,[4a-b,4e-f,4h,5] Grignard reagents,[6] amines [4b,7] or can be used for scavenging radicals.[4b,4f,8] Activated by an electron-withdrawing group, they are also excellent partners for participating in ene reactions.[4b-c, 4j,9] Unlike nitroso arenes, acyl nitroso species have not been isolated, except in exceptional cases, and have mostly been generated *in situ* by oxidation of hydroxamic acid derivatives.[10] Through reaction with 1,3 dienes, they mainly provide the corresponding 3,6-dihydro-2*H*-1,2-oxazines *via* a Diels Alder [4+2]-cycloaddition. However, when an allylic σ-bond is present, a competitive ene reaction can also occur. In this context, we hypothesized that the pre-functionalization of the dienyl system of **1** *via* this latter process can greatly increase the synthetic potential of these versatile building blocks, thus opening the way for the synthesis of more complex structures. Herein, we investigate the reactivity of diene **1** towards activated nitroso compounds, extend this study to other enophiles, and describe further explorations of the use of the resulting products as precursors to access diverse polycyclic architectures (Scheme 1).

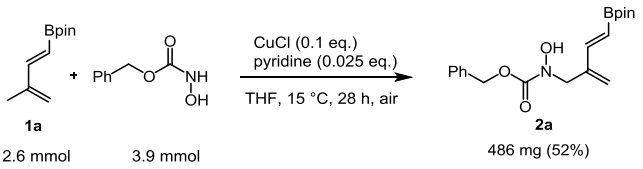


Scheme 1. Reactivity of dienyl boronic esters towards nitroso compounds.

Results and Discussion

Although unsaturated boronic esters are widely used synthetic intermediates, their ene-reactions have only been rarely reported,[11] and never in the case of boron-substituted 1,3-dienes. In general, for all-carbon dienes, the ratio of cyclo-/ene adducts is not always predictable and difficult to control. For example, for 2,3-dimethyl-1,3-butadiene, several main parameters can impact the reaction outcome, i.e.; solvent,[10i] diene conformation,[12] methods for the oxidation of hydroxamic derivatives [13] and the nature of the starting nitroso compound.[14] We started our research by investigating suitable oxidation systems which could be used in the presence of the boronated group of **1a**, as a

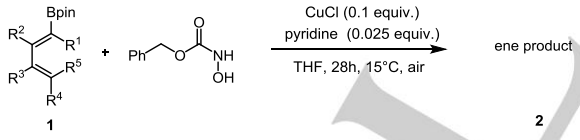
model substrate. Various solvents (THF, acetonitrile, acetone, methanol, toluene methylene chloride), catalyst (CuCl: 5, 10 or 20 mol%, $CuCl_2$ 20 mol%) and co-catalysts (pyridine, 2-ethyl oxazoline) were examined. Finally, the reaction was scaled up under the conditions [CuCl (0.1 eq.), pyridine (0.025 eq.) in THF at 15 °C in the presence of air. **2a** was obtained in 52% yield, an average over three runs carried out on a 2.6 mmol scale (Scheme 2). The control of the temperature was crucial since significant degradation occurred when the temperature exceeded 20 °C. It is also worth noting that only traces of pyrrole **3** were produced (detected in the crude reaction mixture), if any, which results from the competitive Diels Alder route (see Scheme 1).[3]

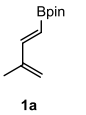
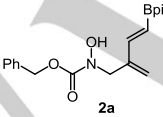
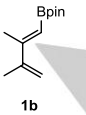
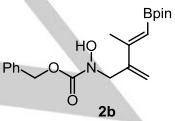
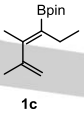
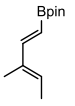
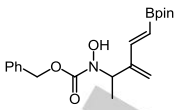
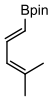
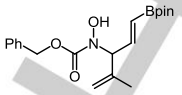
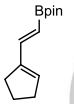
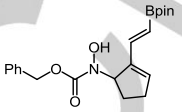
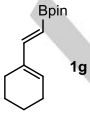
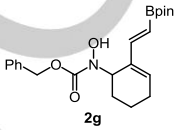


Scheme 2. Half-gram scale synthesis of **2a**.

We then explored other parameters that could influence the behavior of the boron-substituted 1,3-dienes towards benzyl nitrosoformate under our optimized conditions (Table 1). A series of diversely substituted boronates **1** was first synthetized using: i) carboboration of 2-methylbut-1-en-3-yne and 2-methylhex-1-en-3-yne with bis(pinacolato)diboron and methyl iodide in the presence of CuCl and sodium *tert*-butoxide, respectively for **1b** and **1c**;[15] ii) boron-Wittig reaction between bis((pinacolato)boryl)methane and (*E*)-2-methyl-2-butenal or 3,3-dimethylacrolein, respectively for **1d** and **1e**;[16] iii) hydroboration of 1-ethynylcyclopentene and cyclohexene with pinacolborane in the presence of Cp_2ZrHCl, respectively for **1f** and **1g**.[17]

Table 1. Nitroso ene reaction of **1a-g** with *in situ*-generated benzyl nitrosoformate.

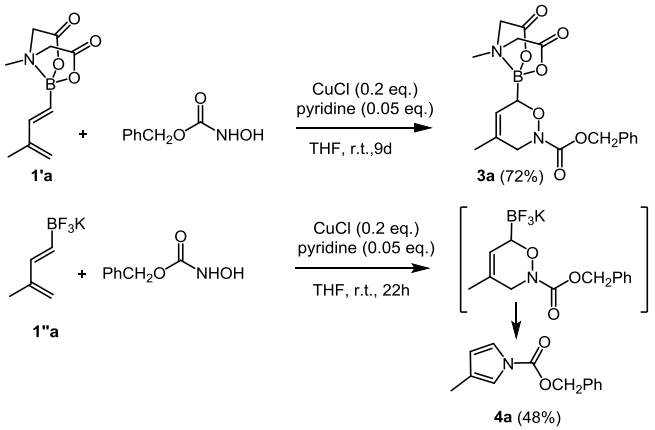


Entry	Diene	Product	Yield (%)[a]
1			53
2			30
3		-	0
4			88
5			26
6			35
7			23

[a] Yield of isolated product after purification by column chromatography, the reactions being carried out on a 0.5 mmol scale.

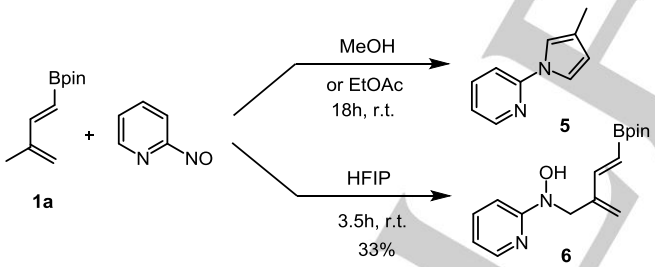
As we can see from Table 1, yields varied from low to moderate and varied on the diene used. With one exception, **1f**, it was not possible to achieve the total consumption of the diene after 28h at 15°C. For longer reaction times (> 36h) or higher temperature, significant degradation of the final product was observed, which resulted in a tedious purification step and a decrease in isolated yield. The introduction of a methyl group at the 2-position also proved detrimental and led to a substantial decrease in yield (Entry 2). No transformation occurred when an additional substituent was present at the α-position to the boron atom (Entry 3). In contrast, if a methyl group was located at position 4, the reaction became much more efficient exemplified by a 88% yield obtained for **2d** (Entry 4). Unfortunately, poor yields were obtained with the cyclic analogues **1f** and **1g** (Entries 6 and 7). In the absence of an allylic hydrogen at position 3, the ene reaction still occurred with **1e** which possesses a gem-dimethyl unit at the terminal position, then giving the 1,4-diene **2e** in a modest 26% yield (Entry 5).

Changing the boron hybridisation from sp^2 to sp^3 substantially modified the course of the reaction as can be seen for **1'a** and **1''a**. The nitroso Diels Alder reaction then became the only observed process, giving respectively, either the stable oxazine **3a** or the rearranged pyrrole **4a** respectively, as previously observed with nitrosobenzene (Scheme 3).[3]



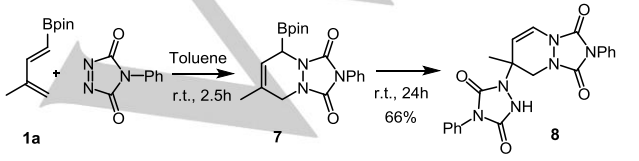
Scheme 3. Reactions of dienes **1'a** and **1''a** with *in situ*-generated benzyl nitrosoformate.

To extend the scope of the ene-reactions of dienyl boronates, we then examined the reactivity of **1a** towards other enophiles. 2-Nitrosopyridine, prepared according to the method of Taylor *et al*.,[18] has already been used to react with a variety of substituted alkenes to give the corresponding ene products,[19] while 1,3-dienes afforded the corresponding 3,6-dihydro-*2H*-1,2-oxazines.[20] In our case, we also observed a unique [4+2] cycloaddition/ring contraction sequence in methanol or ethyl acetate and 3-methyl-1-(2-pyridyl)-pyrrole **5** was only detected by ^{1}H NMR with respective conversions of 43 and 14% after 16h. With 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), the reaction is much faster, with 78% conversion after 2h, and the formation of the ene product **6** was mainly observed (Scheme 4). Such a dramatic improvement in reactivity has already been observed for α-methylstyrene using HFIP as solvent, probably due to the activation of the nitroso group through hydrogen bonding.[21]



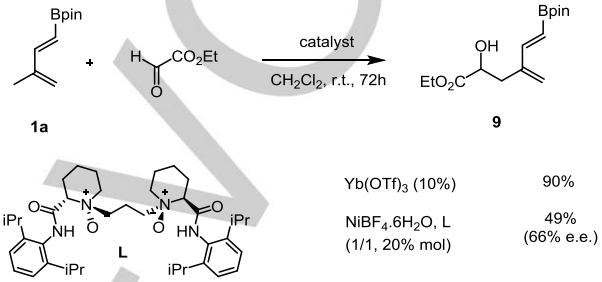
Scheme 4. Reaction of diene **1a** with 2-nitrosopyridine.

With regards to 4-phenyl-1,2,4-triazoline-3,5-dione, its reaction with **1a** exclusively afforded the Diels Alder cycloadduct **7** which was identified by its ^{1}H and ^{13}C NMR data. Its low stability prevented direct isolation or purification by chromatography. However, upon using extended times and in the presence of an excess of enophile, an allylboration on the activated N=N bond occurred to afford the stable bis adduct **8,** as previously reported for a similar diene (Scheme 5).[22]



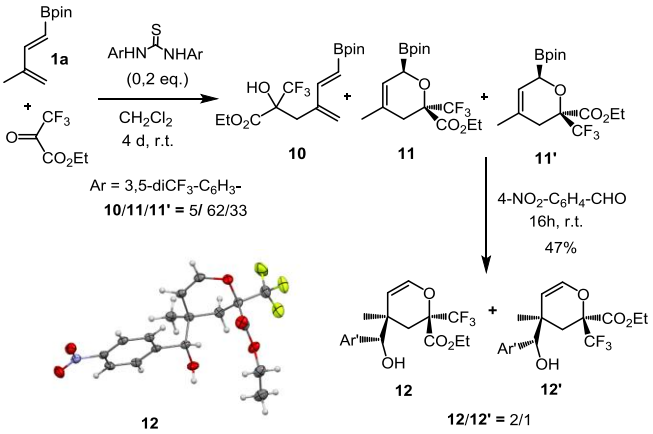
Scheme 5. Reaction of diene **1a** with 4-phenyl-1,2,4-triazoline-3,5-dione.

Among the most impressive results reported in the field of ene reactions are those achieved with glyoxylate derivatives.[23] The diene **1a** has proven to be a very good partner for this type of transformation since the boronate **9** was obtained in the presence of ytterbium (III) trifluoromethanesulfonate in 90% yield after 3 days at room temperature (two mmoles scale) (Scheme 6). Unfortunately, the asymmetric version using a *N,N'*-dioxide/nickel(II)complex (one of the numerous possible chiral catalysts) was unsatisfactory.[24] After 72 h at r. t. in 1,2-dichloroethane, the expected product was obtained in 49% yield with a modest 66% enantiomeric excess (determined by Mosher's method). Heating at 40°C, despite a complete conversion, resulted in reduced yield and e.e.



Scheme 6. Reaction of diene **1a** with ethyl glyoxylate.

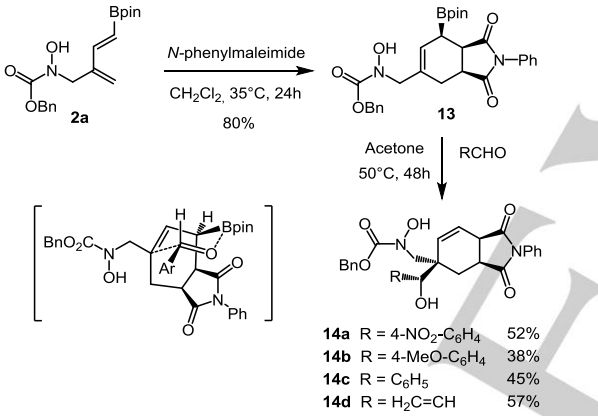
With ethyl 3,3,3-trifluoropyruvate (an activated ketone due to the presence of a strong electron withdrawing group), catalysis was, however, necessary to carry out the reaction with **1a**. Under organocatalytic conditions, a system which is prone to undergo carbonyl ene reactions,[25] the Diels Alder cycloadducts (mixture of diastereomers **11** and **11'**) were by far the major products (**10**/**11**+**11'** = 5/62 +33) (Scheme 7). These compounds show a poor stability on silica gel which prevented their isolation and their structures were established by ^{1}H NMR in comparison with similar derivatives.[26] Fortunately, treatment of the crude mixture with 4-nitrobenzaldehyde afforded the corresponding homoallylic alcohols in 47% yield (two steps). X-ray crystallographic analysis of the major isomer **12** confirmed the regiochemical course of the initial [4+2] cycloaddition.[27]



Scheme 7. Reaction of diene **1a** with ethyl 3,3,3-trifluoropyruvate and X-ray structure of **12**.

Having access to new functionalized dienes, we then turned our attention to their use as precursors of various polycyclic heterocycles. Compounds **2a** and **9**, selected as model substrates, were therefore engaged in several synthetic sequences mainly combining Diels Alder cycloaddition and allylboration as key steps.[28]

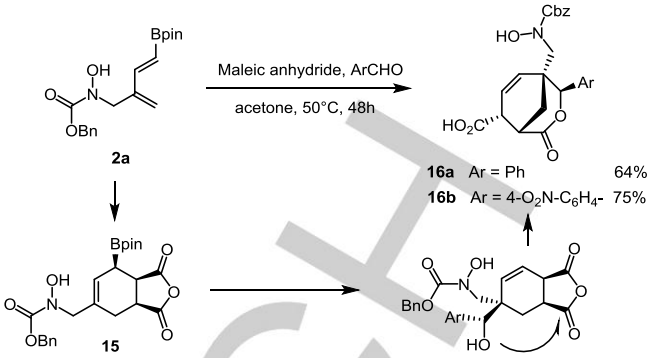
Stereocontrolled access to functionalized tetrahydro-*1H*-isoindole-1,3(*2H*)-diones possessing a quaternary center was first envisaged. Hence, the reaction of **2a** with *N*-phenyl maleimide was carried out and found to be complete after 24 h in CH_2Cl_2 at 35°C affording **13** in 80% isolated yield after silica gel chromatography (Scheme 8). The *endo*-stereochemistry of this cycloadduct was established from its ^{1}H NMR spectrum in comparison with the literature.[29] Subsequent allylboration of **13** with various aldehydes afforded the corresponding bicycles **14** in moderate yields, varying from 38% (when an electron donor substituent is located on the aromatic nucleus) to 52% and 57% (when an electron withdrawing NO_2 group or a vinyl moiety was present, respectively). The relative configuration of the two new stereogenic centers created during this step was consistent with a Zimmerman–Traxler transition state model involving the coordination of the aldehyde to the boronyl group positioned in a *pseudo*-axial orientation.



Scheme 8. Reaction of diene **2a** with *N*-phenylmaleimide and subsequent addition to various aldehydes.

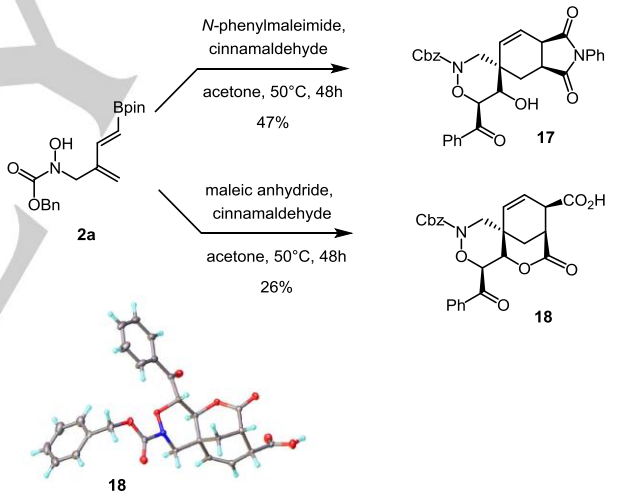
These reactions can also be valuably conducted in a one-pot process. Hence, after optimization of the experimental conditions (solvent, temperature, concentration, and time), **14c**, selected as test compound, was obtained in 52% yield (instead of 0.8 x 0.45 = 36% for the two steps sequence) after heating in acetone for 48h at 50°C.

Alternatively, the use of maleic anhydride as dienophile allowed a supplementary intramolecular cyclisation process to afford, *via* the cycloadduct **15**,[30] the bicyclic eight-membered lactones **16a** and **16b** in good overall yields (3 steps) with the control of the relative stereochemistry of the four stereogenic centers of the bicyclo[3.2.1]octane moiety (Scheme 9).[29,31,32]



Scheme 9. Access to eight-membered lactones **16a** and **16b** *via* a Diels Alder/allylboration/lactonisation sequence.

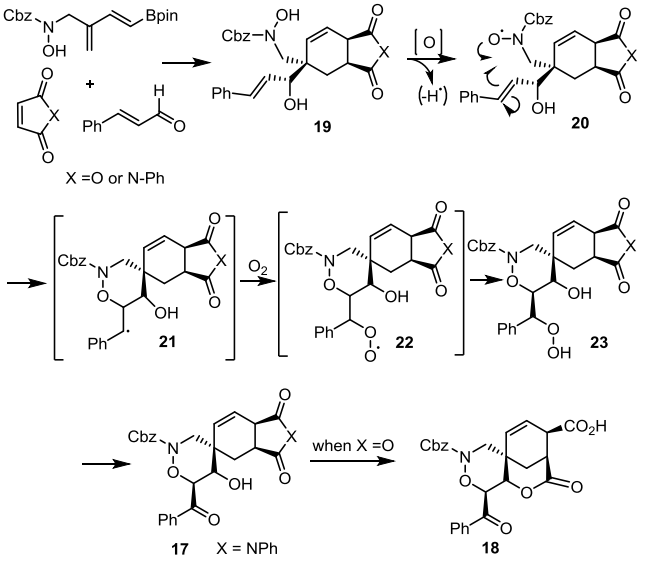
With cinnamaldehyde, surprisingly instead of the expected products **14** (R=PhCH=CH, Scheme8), new tricyclic heterocycles **17** and **18** were produced, whether with *N*-phenyl maleimide or maleic anhydride (Scheme 10). For this latter dienophile, a single crystal of **18** suitable for X-Ray analysis enabled the determination of its exact structure, which were also confirmed by ^{1}H and ^{13}C NMR.[27] Five stereogenic centers, including a quaternary one, were all controlled in this single-pot operation.



Scheme 10. One-pot synthesis of polycyclic heterocycles **17** and **18** from **2a** and X-ray structure of **18**.

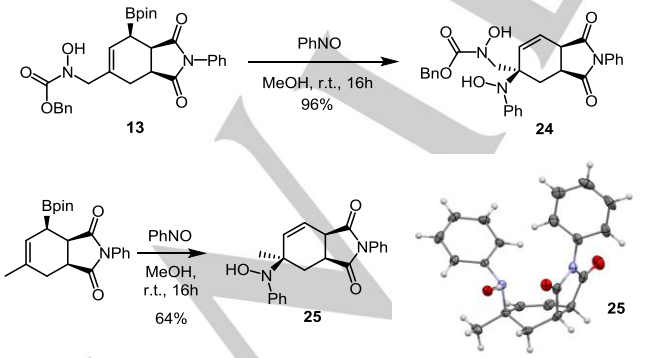
Mainly based on the observations of Alexanian and co-workers,[33] these experimental results can be rationalized by the following mechanistic hypotheses, mainly based on the observations of Alexanian and co-workers. After the formation of **19** *via* the classical Diels Alder/allylboration sequence as described previously, an aerobic ketooxygenation reaction occurred (Scheme 11). Initiation of this process is likely initiated by autoxidation of **19** to generate the amidoxyl radical **20**. Cyclisation would then give the oxazine **21** *via* a 6-*exo*-trig process with creation of a new carbon-centered radical stabilised due to its benzylic position. Addition of O_2 would afford **22** which, after H-abstraction from the starting substrate **19**, would provide the alkyl hydroperoxide **23**. Whereas acylation of such compound is usually required in order to observe the formation of the benzoyl group,[33a] in our case, no external

reagent was necessary to observe the same reactivity. The origin of this unexpected behaviour still remains unclear. When maleic anhydride was used as dienophile, an intramolecular lactonisation ended the sequence to afford **18**.



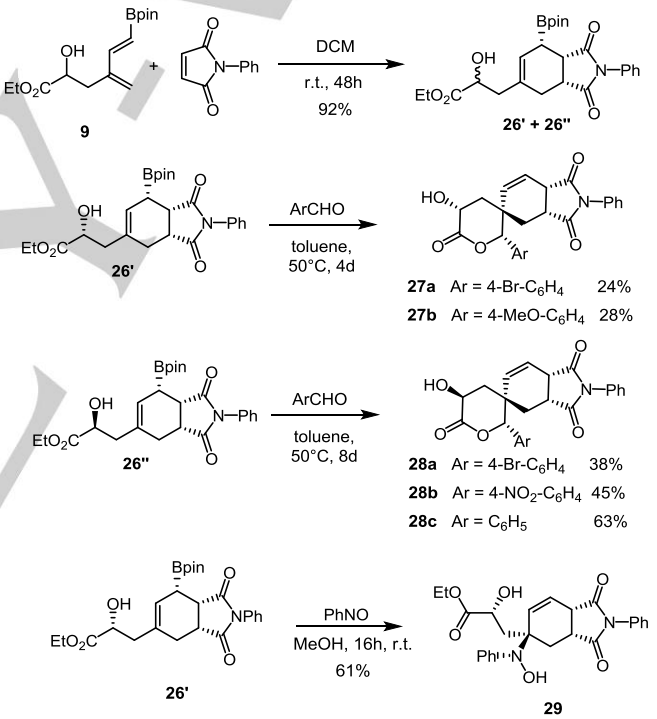
Scheme 11. Suggested mechanism for the formation of **17** and **18**.

In parallel to these sequences involving aldehydes, nitrosobenzene has been also employed as allylboration partner with **2a**, with improved efficiency compared to those observed with previously used carbonyl derivatives. For example, the adduct **24** was obtained in 96% isolated yield after 16 h at r. t. in methanol (Scheme 12). It is noteworthy that the addition only occurred on the nitrogen atom, contrary to that which was usually observed for other allyl boronates.[34] Unfortunately, it was not possible to obtain a single crystal of **24**. However, its structure, and therefore the regioselectivity of the allylation, was established by comparison of its ^{1}H and ^{13}C NMR data with those of its analog **25**, (itself prepared from **1a**,[29] *N*-phenylmaleimide and nitrosobenzene). In particular, signals at δ = 62.9 ppm and 60.9 ppm for the quaternary carbon of the cyclohexene ring, respectively for **24** and **25** confirmed structural assignment.[35] The structure of **25** was also secured by X-ray crystallography.[27]

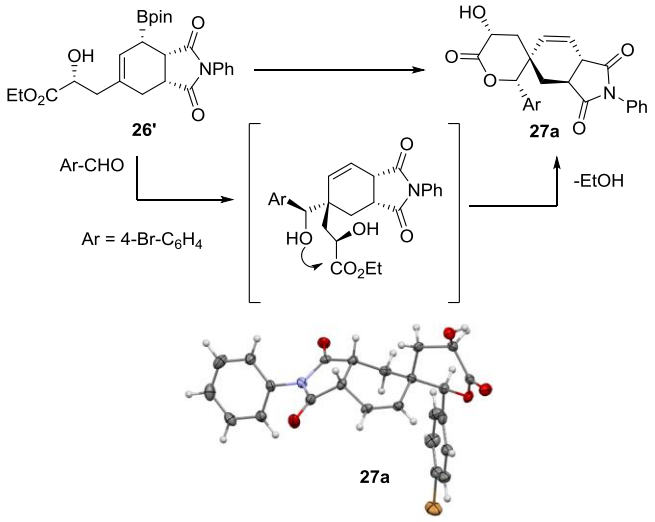


Scheme 12. Reaction of the cycloadduct **13** with nitrosobenzene and X-ray structure of **25**.

Similarly, to the carbamate **2a**, the diene **9** derived from ethyl glyoxylate can be engaged in Diels Alder reactions. Hence, reaction of *N*-phenylmaleimide in dichloromethane at r. t. for 48 h led to the corresponding cyclohexene as a mixture of two diastereoisomers **26'** and **26''** in a ratio of 1/1, separable by chromatography on silica gel (Scheme 13). These isomers were engaged independently in allylboration reactions in toluene at 50 °C with aryl aldehydes. In both cases, complete conversions of the starting material were observed at 50°C in toluene after 4 days for **26**', and double time for the isomer **26''** (Scheme 13). However, the expected homoallyl alcohols were not obtained, the isolated products being spirolactones **27a-b** and **28a-c** resulting from the ring-closure between the ester group and the hydroxyl group in benzylic position (Scheme 13 and 14). The ^{1}H and ^{13}C NMR data were in full agreement with the proposed structures, particularly the absence of the ethyl ester. Moreover, it was confirmed by X-ray crystallographic analysis of **27a**,[27] showing that five stereocenters had been controlled during the assembly process that allows a rapid access to new spirocyclic scaffolds. As previously described for the nitrogen analogue **13**, the hydroxylamine **29** can be prepared from nitrosobenzene and **26'**, with no cyclization being observed in this case (Scheme 13).



Scheme 13. Diels Alder/allyboration/lactonisation sequence from diene **9**



Scheme 14. Proposed mechanism of formation of spirolactones and X-ray structure of **27a**.

Conclusion

In summary, the ene reaction of 1,3-dienylboronates gives operationally simple access to a variety of new functionalized dienes. In particular, in the case of benzyl nitrosoformate and ethyl glyoxylate, these products can be engaged in multistep sequences based on a first key Diels Alder/allyboration process. This methodology provides, in a stereocontrolled manner, various skeletally diverse and complex polycyclic heterocycles, such as tetrahydro-*1H*-isoindole-1,3(*2H*)-diones, eight-membered lactones or tricyclic spiro compounds.

Experimental Section

General. Air- and water-sensitive reactions were performed in flame-dried glasswares under argon atmosphere. Anhydrous dichloromethane was obtained after distillation over P_2O_5 and tetrahydrofuran over sodium/benzophenone. For oxygen sensitive reaction, when specified, solvent was degassed prior to use by slow bubbling of argon. Unless otherwise noted, all solvents and all commercially available chemicals were used without further purification. ^{1}H NMR spectra (300 MHz, 400 MHz), ^{13}C NMR (75 MHz, 101 MHz), ^{11}B (96 MHz, 128 MHz) and ^{19}F (282 MHz, 376 MHz) were recorded on Bruker AC 300 and AC 400 spectrometers. Chemical shifts δ are given in ppm and coupling constants *J* in Hz. Multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The carbon bearing the boron atom was not always observed due to the quadrupolar relaxation of ^{11}B nucleus. High-resolution mass spectra (HRMS) were recorded, either on a Bruker MaXis 4G, an Agilent 6510, or a Thermo Fisher Q-Exactive spectrometer (Centre Régional de Mesures Physiques de l'Ouest, Rennes) using positive or negative ion Electron-Spray ionization techniques (respectively ESI+, ESI-). Purifications by silica gel chromatography were carried out on silica 0.060-0.200 mm, 60 A. Flash chromatography purifications were performed on a Grace Reveleris™ apparatus. Analytical thin layer chromatography was performed on Merck Silica Gel 60 F254 plates. Compounds were visualized by exposure to UV-light (254 nm) or by dipping the plates in a 2.5% solution of *p*-anisaldehyde in a mixture AcOH/H_2SO_4/EtOH (1/4/95) or in a potassium permanganate solution in a mixture K_2CO_3/(5%) NaOH/Water (20/5/300). Melting points were measured on a Kofler bench Reichert-Jung Heizbank or a melting point apparatus Stuart SMP10 and are uncorrected. Boron substituted 1,3-dienes **1a**,[36] **1b**,[15] **1c**,[15] **1d**,[37] **1e**,[16] **1f**,[38] **1g**,[38] **1'a**,[3b] **1''a**,[39] benzylhydroxycarbamate,[40] 2-nitrosopyridine,[18] were prepared as previously reported.

General procedure for the ene reactions of pinacol boronates 1 with benzylnitrosoformate. To a solution of pyridine (0.125 mmol, 125 µL of a 0.1 mol.L^{-1} THF solution) in THF (2 mL) was added CuCl (5 mg, 0.05 mmol). The reaction mixture was stirred at 15°C (cryostat) for 5 min. Diene 1 (0.50 mmol), benzyl hydroxycarbamate (125 mg, 0.75 mmol) were then added and the mixture was stirred at the same temperature for 28 h. The solvent was evaporated, and the crude reaction product was purified by silica gel chromatography.

Benzyl (*E*)-hydroxy(2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)carbamate (2a). 95 mg (53%). The reaction was also carried out at a half-gram scale in a similar isolated yield. mp = 98-99 °C. R_f = 0.32 (Cyclohexane/EtOAc: 70/30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 5H), 7.08 (d, *J* = 18.6 Hz, 1H), 6.79 (brs, 1H), 5.66 (d, *J* = 18.6 Hz, 1H), 5.38 (s, 1H), 5.34 (S, 1H), 5.20 (s, 2H), 4.36 (s, 2H), 1.29 (s, 12H). ^{13}C NMR (101 MHz $CDCl_3$) δ 157.1, 148.9, 140.6, 135.8, 128.5, 128.3, 128.2, 120.9, 117.4 (br), 83.4, 68.2, 51.4, 24.8. ^{11}B NMR (96 MHz, $CDCl_3$) δ 30.1. HRMS (ESI+): *m/z* $(M+H)^+$ calc. for $C_{19}H_{27}NO_5{}^{11}B$ 360.1982, found 360.1992.

Benzyl (*E*)-hydroxy(3-methyl-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)carbamate (2b). 56 mg (30%). Colorless oil. R_f = 0.44 (Cyclohexane/EtOAc: 70/30). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.32 (m, 5H), 6.29 (brs, 1H), 5.44 (brs, 1H), 5.42 (brs, 1H), 5.21 (brs, 1H), 5.19 (s, 2H), 4.40 (s, 2H), 2.17 (s, 3H), 1.28 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 154.6, 143.7, 136.0, 128.7, 128.4, 128.3, 115.9, 83.2, 68.3, 53.2, 25.0, 19.1. The carbon α to boron was not observed. ^{11}B NMR (96 MHz, $CDCl_3$) δ 30.0. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{20}H_{28}NO_5{}^{11}BNa$ 396.19527, found 396.1958.

Benzyl (*E*)-hydroxy(3-methylene-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)carbamate (2d). 164 mg (88%). Colorless oil. R_f = 0.30 (Cyclohexane/EtOAc: 70/30). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.28 (m, 5H), 7.00 (d, *J* = 18.6 Hz, 1H), 5.72 (d, *J* = 18.6 Hz, 1H), 5.44 (brs, 1H), 5.40 (brs, 1H), 5.23-5.10 (m, 2H), 5.04 (q, *J* = 6.9 Hz, 1H), 1.38 (d, *J* = 6.9 Hz, 3H), 1.26 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 149.7, 145.7, 136.1, 128.6, 128.25, 128.16, 120.3, 117.1(br), 83.4, 68.1, 53.9, 24.9, 15.7. ^{11}B NMR (96 MHz, $CDCl_3$) δ 30.1. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{20}H_{28}NO_5{}^{11}BNa$ 396.19527, found 396.1949.

Benzyl (*E*)-hydroxy(4-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,4-dien-3-yl)carbamate (2e). 48 mg (26%). Colorless oil. R_f = 0.46 (pentane/Et_2O : 6/4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.32 (m, 5H), 6.72 (dd, *J* = 18.2, 6.2 Hz, 1H), 5.94 (brs, 1H), 5.64 (dd, *J* = 18.2, 1.4 Hz, 1H), 5.20 (s, 2H), 5.07 (d, *J* = 6.2 Hz, 1H), 5.04-5.01 (m, 1H), 4.97 (brs, 1H), 1.77 (s, 3H), 1.26 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 146.9, 141.6, 136.0, 128.7, 128.4, 128.2, 115.2, 83.6, 68.3, 67.1,

25.0, 24.9, 21.0. The carbon α to boron was not observed. ^{11}B NMR (96 MHz, $CDCl_3$) δ 29.5. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{20}H_{28}NO_5{}^{11}BNa$ 396.19527, found 396.1956.

Benzyl (*E*)-hydroxy(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclopent-2-en-1-yl)carbamate (2f). 67 mg (35%). Colorless oil. R_f = 0.35 (Cyclohexane/EtOAc : 75/25). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.29 (m, 5H), 7.14 (d, *J* = 18.5 Hz, 1H), 6.18-6.14 (m, 1H), 6.12 (brs, 1H), 5.66 (d, *J* = 18.5 Hz, 1H), 5.49-5.37 (m, 1H), 5.25 (d, *J* = 12.3 Hz, 1H), 5.15 (d, *J* = 12.3 Hz, 1H), 2.68-2.54 (m, 1H), 2.41-2.15 (m, 2H), 2.07-1.95 (m, 1H), 1.26 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.9, 144.0, 140.2, 139.9, 136.2, 128.6, 128.3, 128.2, 83.4, 68.1, 63.6, 31.5, 28.1, 24.9, 24.8. The carbon α to boron was not observed. ^{11}B NMR (96 MHz, $CDCl_3$): δ 30.3. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{21}H_{28}NO_5{}^{11}BNa$ 408.19527, found 408.1955.

Benzyl (*E*)-hydroxy(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclohex-2-en-1-yl)carbamate (2g). 46 mg (23%). Colorless oil. R_f = 0.35 (Cyclohexane/EtOAc : 70/30). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.28 (m, 5H), 6.95 (d, *J* = 18.6 Hz, 1H), 6.28 (t, *J* = 4.2 Hz, 1H), 5.78 (brs, 1H), 5.57 (d, *J* = 18.5 Hz, 1H), 5.27 (d, *J* = 12.3 Hz, 1H), 5.16 (d, *J* = 12.3 Hz, 1H), 4.92 (brs, 1H), 2.33-2.04 (m, 2H), 2.03-1.74 (m, 3H), 1.65-1.50 (m, 1H), 1.26 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 150.4, 139.3, 136.3, 133.7, 128.6, 128.2, 128.2, 83.3, 68.0, 53.2, 27.8, 26.0, 24.9, 24.9, 19.4. The carbon α to boron was not observed. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{22}H_{30}NO_5{}^{11}BNa$ 422. 2115, found 422.2110.

Ene reaction of diethanolamine ester 1'a with benzylnitrosoformate. To a solution of pyridine (0.25 mmol, 250 µL of a 0.1 mol.L^{-1} THF solution) in THF (2 mL) was added CuCl (10 mg, 0.05 mmol). The reaction mixture was stirred at r.t. for 5 min. Diene **1'a** (100 mg, 0.45 mmol), benzyl hydroxycarbamate (113.5 mg, 0.67 mmol) were then added and the mixture was stirred at r.t. for 9 days. The solvent was evaporated, and the crude reaction product was purified by silica gel chromatography.

Benzyl 4-methyl-6-(4-methyl-2,6-dioxotetrahydro-2*H*-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-8-yl)-3,6-dihydro-2*H*-1,2-oxazine-2-carboxylate (3a). 125 mg (72%). White solid, mp = 185-186 °C. R_f = 0.55 (Et_2O/MeCN: 80/20). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.45-7.31 (m, 5H), 5.66 (dt, *J* = 3.2, 1.5 Hz, 1H), 5.20 (d, *J* = 12.2 Hz, 1H), 5.15 (d, *J* = 12.1 Hz, 1H). 4.40 (br s, 1H), 4.30 (d, *J* = 17.2 Hz, 1H), 4.16 (d, *J* = 16.4 Hz, 1H), 4.19-4.11 (m, 1H), 4.03 (d, *J* = 17.2 Hz, 1H) 3.86 (d, *J* = 16.4 Hz, 1H), 3.89-3.83 (m, 1H), 3.20 (s, 3H), 1.77-1.75 (m, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 169.1, 168.0, 156.3, 137.4, 129.4, 129.2, 129.1, 128.8, 120.9, 68.2, 63.1, 63.0, 49.1, 46.5, 20.1. The carbon α to boron was not observed. ^{11}B NMR (96 MHz, Acetone-d_6) δ 9.8. HRMS (ESI+): calcd. for $[M+H]^+$ $C_{18}H_{22}N_2O_7{}^{10}B$ 388.1556, found: 388.1535.

Ene reaction of trifluoroborate 1''a with benzylnitrosoformate. To a solution of pyridine (0.25 mmol, 250 µL of a 0.1 mol.L^{-1} THF solution) in THF (2 mL) was added CuCl (10 mg, 0.05 mmol). The reaction mixture was stirred at r.t. for 5 min. Diene **1''a** (80 mg, 0.46 mmol), benzyl hydroxycarbamate (115 mg, 0.69 mmol) were then added and the mixture was stirred at r.t. for 22h. The crude reaction mixture was filtered over a pad of celite and washed with acetone (50 mL). The solvent was evaporated and the crude product was purified by silica gel chromatography.

Benzyl 3-methyl-1H-pyrrole-1-carboxylate (4a).[41] 48 mg (48%). Yellow oil. R_f = 0.85 (Hexane/AcOEt: 70/30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 5H), 7.23 (t, *J* = 2.8 Hz, 1H), 7.06 (br s, 1H), 6.11 (ddd, *J* = 3.1, 1.6 Hz, 1H), 5.37 (s, 2H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 135.2, 128.8, 128.8, 128.5, 123.4, 120.3, 117.4, 114.9, 68.8, 12.0. HRMS (ESI+): calcd. for $[M+H]^+$ $C_{13}H_{14}NO_2$ 216.1025, found 216.1021.

Ene reaction of pinacol boronate 1a with other enophiles

With 2-nitrosopyridin. To a solution of **1a** (50 mg, 0.26 mmol) in HFIP (0.5 mL), was added under air 2-nitrosopyridine [18] (28 mg, 0.26 mmol). After stirring 1.5 h at r. t., 2-nitrosopyridine (14 mg, 0.13 mmol) was added again. The reaction was further stirred for 2 h at r. t.. The mixture was extracted with pentane. The pentane phase was evaporated and the product was purified by silica gel chromatography. When the reaction was carried in methanol or ethyl acetate, 3-methyl-1-(2-pyridyl)-pyrrole **5** was only detected by ^{1}H NMR by comparison with the reported data.[42]

(*E*)-*N*-(2-Methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)-*N*-(pyridin-2-yl)hydroxylamine (6). 26 mg (33 %). Colorless oil. R_f = 0.48 (Cyclohexane/EtOAc: 70/30). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26-8.17 (m, 1H), 7.61-7.49 (m, 1H), 7.13 (d, *J* = 18.6 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.84-6.73 (m, 1H), 5.84 (d, *J* = 18.4 Hz, 1H), 5.45-5.43 (m, 2H), 4.47 (s, 2H), 1.27 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 149.4, 147.0, 142.4, 137.7, 121.5, 115.8, 109.0, 83.2, 55.8, 24.6. The carbon α to boron was not observed. ^{11}B NMR (96 MHz, $CDCl_3$) δ 29.7. HRMS (ESI+): *m/z* $(M+H)^+$ calc. for $C_{16}H_{24}N_2O_3{}^{11}B$ 303.1880, found 303.1874.

With 4-phenyl-1,2,4-triazoline-3,5-dione. Under an argon atmosphere, was added 4-phenyl-1,2,4-triazoline-3,5-dione (9 mg, 0.05 mmol) to a solution of **1a** (10 mg, 0.05 mmol) in toluene d^8 (0.65 mL). After 2.5h at room temperature, the reaction was analysed by ^{1}H NMR spectroscopy.

7-Methyl-2-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,8-dihydro-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (7). The spectroscopic data were extracted from the reaction mixture and are in agreement with the similar pinanediol derivative.[22] ^{1}H NMR (400 MHz, Toluene-d_8) δ 7.81-7.78 (m, 2H), 7.12-7.17 (m, 2H), 6.97-6.99 (m, 1H), 5.31-5.27 (m, 1H), 3.96-3.92 (m, 1H), 3.56-3.44 (m, 2H), 1.28 (s, 3H), 1.08 (s, 6H), 1.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 152.0, 131.5, 129.1, 128.0, 127.3, 125.6, 115.6, 84.8, 46.2, 43.4(br), 24.8, 24.4, 20.4.

The same experimental conditions as those described above were implemented with three equivalents of 4-phenyl-1,2,4-triazoline-3,5-dione. After 24 hours of stirring at room temperature, the sample was analyzed by ^{1}H NMR spectroscopy.

6-(3,5-Dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-6-methyl-2-phenyl-5,6-dihydro-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (8). ^{1}H NMR (300 MHz, Toluene-d_8) δ 7.27-7.10 (m, 10H), 6.71 (d, *J* = 8.2 Hz, 1H), 4.72 (d, *J* = 8.2 Hz, 1H), 4.62 (d, *J* = 12.8 Hz, 1H), 2.89 (d, *J* = 12.8 Hz, 1H), 1.23 (s, 3H). The spectroscopic data agree with those reported in the literature.[22]

***With ethyl glyoxylate*:** In a flame dried Schlenk under an argon atmosphere was introduced diene **1a** (300 mg, 1.55 mmol), a solution of 50% ethyl glyoxylate in toluene (0.6 mL, 3.09 mmol) and anhydrous dichloromethane (6 mL). To this solution was added ytterbium triflate (96 mg, 0.16 mmol) (previously dried at 140°C under 0.1 mbar for 48 h). The flask was closed with a glass stopper and the reaction mixture was stirred 3 days at room temperature. The solvent was evaporated and the product was purified by silica gel chromatography.

Ethyl (*E*)-2-hydroxy-4-methylene-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (9). 412 mg (90%). Colorless oil. R_f = 0.26 (Cyclohexane/EtOAc : 80/20). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, *J* = 18.5 Hz, 1H), 5.64 (d, *J* = 18.5 Hz, 1H), 5.34 (brs, 1H), 5.29 (brs, 1H), 4.31 (dd, *J* = 8.5, 3.9 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.80 (dd, *J* = 14.3, 3.9 Hz, 1H), 2.71 (brs, 1H), 2.48 (dd, *J* = 14.3, 8.5 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.26 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 150.9, 142.0, 122.5, 117.1 (br), 83.4, 69.2, 61.8, 36.6, 25.0, 14.3. ^{11}B NMR (96 MHz, $CDCl_3$) δ 30.0. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{15}H_{25}O_5{}^{11}BNa$ 319.16872, found 319.1689.

***With ethyl 3,3,3-trifluoropyruvate*:** In a flame dried Schlenk under an argon atmosphere was introduced diene **1a** (116 mg, 0.60 mmol), 1,3-bis[3,5-bis(trifluoromethyl)phenyl]thiourea (50 mg, 0.10 mmol) and dichloromethane (2 mL). To this solution was added ethyl 3,3,3-trifluoropyruvate (66 µL, 0.50 mmol). The flask was closed with a glass stopper and the reaction mixture was stirred 4 days at room temperature. The sample was analysed by ^{1}H NMR spectroscopy that revealed the presence a mixture of **1a**/**10**/**11**+**11'** in a 1/0.1/1 ratio. Their NMR data were extracted from the spectrum of the crude mixture.

Ethyl (*E*)-2-hydroxy-4-methylene-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trifluoromethyl)hex-5-enoate (10). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98 (d, *J* = 18.4 Hz, 1H), 5.70 (d, *J* = 18.4 Hz, 1H), 5.40 (brs, 1H), 5.33 (brs, 1H), 4.37-4.13 (m, 2H), 3.79 (s, 1H), 3.01 (d, *J* = 14.4 Hz, 1H), 2.77 (d, *J* = 14.4 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H),1.27 (s, 12H).

Ethyl 4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trifluoromethyl)-3,6-dihydro-2H-pyran-2-carboxylates (11+**11')**. The NMR data were extracted from the spectrum of the crude mixture. Two diastereomers (ratio 65/35) with the following characteristic signals : ^{1}H NMR (300 MHz, CD_2Cl_2) δ 5.66 (s, 0.65H), 5.49 (s, 0.35H), 2.63 (dd, *J* = 16.5, 2.9 Hz, 0.35H), 2.60 (d, *J* = 16.4 Hz, 0.65H), 2.51-2.40 (m, 0.65H+0.35H), 1.80 (s, 3x0.65H), 1.77 (s, 3x0.35H). ^{13}C NMR (75 MHz, CD_2Cl_2): major diastereomer δ 167.0, 84.3, 62.6, 30.7, 24.2, 22.7, 13.6 ; minor diastereomer δ 166.5, 84.4, 62.6, 30.2, 24.2, 22.8, 13.5.

To the crude mixture of the ene reaction was added 4-nitrobenzaldehyde (75 mg, 0.5 mmol). After 16h at r.t., the solvent was evaporated and the residue was purified by silica gel chromatography to give the 2 diastereomers **12** and **12'** (ratio 2/1).

Ethyl (2*R*,4*R*)-4-((*S*)-hydroxy(4-nitrophenyl)methyl)-4-methyl-2-(trifluoromethyl)-3,4-dihydro-2H-pyran-2-carboxylate (12). Major diastereomer : 60 mg (31%). white solid, mp = 145-147 °C. R_f = 0.40 (Cyclohexane/EtOAc : 80/20). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 6.4 Hz, 1H), 4.45-4.38 (m, 4H), 3.08 (d, *J* = 14.6 Hz, 1H), 2.56 (d, *J* = 4.0 Hz, 1H), 1.78 (d, *J* = 14.6 Hz, 1H), 1.41 (t, *J* = 7.1 Hz, 3H), 0.93 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 147.4, 147.1, 141.5, 128.5, 122.8, 122.7 (q, *J* = 285.4 Hz), 107.4, 78.5 (q, *J* = 29.2 Hz), 76.6, 63.5, 35.2, 31.2, 22.5, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -78.6. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{17}H_{18}NO_6F_3Na$ 412.0984, found 412.0980.

Ethyl (2*S*,4*R*)-4-((*S*)-hydroxy(4-nitrophenyl)methyl)-4-methyl-2-(trifluoromethyl)-3,4-dihydro-2H-pyran-2-carboxylate (12'). Minor diastereomer : 30 mg (16%). Colorless oil. R_f = 0.29 (Cyclohexane/EtOAc : 80/20). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 6.3 Hz, 1H), 4.70 (dd, *J* = 6.3, 1.8 Hz, 1H), 4.52 (s, 1H), 4.43-4.09 (m, 2H), 2.48 (d, *J* = 13.8 Hz, 1H), 2.31 (brs, 1H), 2.13 (d, *J* = 13.8 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 147.8, 146.3, 143.3, 128.6, 123.1, 122.7 (q, *J* = 284.7 Hz), 106.9, 80.1, 78.6 (q, *J* = 29.4 Hz), 63.0, 36.0, 30.3, 23.8, 13.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ -78.4. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{17}H_{18}NO_6F_3Na$ 412.0984, found 412.0979.

Diels-Alder cycloadditions of 2a with N-phenylmaleimide and maleic anhydride. To a solution of **2a** (200 mg, 0.56 mmol) in DCM (7 mL) in a Schlenk flask was added N-phenylmaleimide (96 mg, 0.56 mmol) (or maleic anhydride: 56 mg, 0.56 mmol) under an argon atmosphere. The reaction was stirred at 35°C for 25h (or at r. t. for 3 days for maleic anhydride). The solvent was evaporated and the product was purified by silica gel chromatography.

Benzyl (((3aS*,7R*,7aR*)-1,3-dioxo-2-phenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,3a,4,7,7a-hexahydro-1H-isoindol-5-yl)methyl)(hydroxy)carbamate (13). 240 mg (80%). White solid, mp = 89-91°C. Rf = 0.72 (Cyclohexane/EtOAc: 1/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.31 (m, 8H), 7.22-7.19 (m, 2H), 6.63 (br s, 1H), 6.09-6.07 (m, 1H), 5.16 (s, 2H), 4.24 (d, J = 15.5 Hz, 1H), 4.07 (d, J = 15.5 Hz, 1H), 3.44 (dd, J = 9.4, 6.3 Hz, 1H), 3.26 (ddd, J = 9.4, 7.6, 3.9 Hz, 1H), 2.69 (dd, J = 15.3, 3.9 Hz, 1H), 2.30 (dd, J = 15.3, 7.6, 1H), 2.13-2.04 (m, 1H), 1.27 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.1, 179.0, 157.5, 136.0, 135.3, 132.1, 129.2, 128.8, 128.7, 128.4, 128.3, 127.1, 126.7, 84.3, 68.2, 55.1, 42.1, 40.5, 25.9, 25.1, 24.8, 21.8 (br). ^{11}B NMR (96 MHz, $CDCl_3$) δ 31.1. HRMS (ESI+): m/z (M+H)+ calc. for $C_{29}H_{34}{}^{10}BN_2O_7$ 532.2495, found 532.2505.

Benzyl (((3aS*,7R*,7aR*)-1,3-dioxo-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,3a,4,7,7a-hexahydroisobenzofuran-5-yl)methyl)(hydroxy)carbamate (15). Colorless oil, 59 mg (93%). ^{1}H NMR (300 MHz, Acetone-d_6)

δ 8.46 (brs, 1H), 7.43-7.32 (m, 5H), 6.00 (d, J = 5.3 Hz, 1H), 5.15 (s, 2H), 4.18 (d, J = 15.4 Hz, 1H), 4.10 (d, J = 15.4 Hz, 1H), 3.67-3.54 (m, 2H), 2.56-2.40 (m, 2H), 2.17 (t, J = 5.3 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 176.2, 175.8, 158.0, 138.0, 136.3, 129.4, 128.88, 128.85, 126.5, 85.0, 67.9, 56.7, 43.0, 41.2, 26.4, 25.14, 25.08, 21.9 (br). ^{11}B NMR (96 MHz, Acetone-d_6) δ 31.5. HRMS (ESI+): m/z (M+Na)+ calc. for $C_{23}H_{28}{}^{10}BNO_8$ 480.1800, found 480.1793.

Allyboration reactions with 13. In a flame dried Schlenk tube were added, under an argon atmosphere, **13** (79 mg, 0.15 mmol), aldehyde (0.31 mmol) and acetone (1 mL). The reaction mixture was stirred at 50°C for 48 hours. The solvent was evaporated and the product was purified by silica gel chromatography.

Benzyl hydroxy(((3*aS,5*R**,7*aR**)-5-((*S**)-hydroxy(4-nitrophenyl)methyl)-1,3-dioxo-2-phenyl-2,3,3*a*,4,5,7*a*-hexahydro-1*H*-isoindol-5-yl)methyl)carbamate (14a).** 43 mg (52 %). White solid, mp = 157-159°C. R_f = 0.40 (Cyclohexane/EtOAc: 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.43-7.38 (m, 10H), 7.15 (d, *J* = 7.3 Hz, 2H), 6.14 (d, *J* = 10.7 Hz, 1H), 6.09 (dd, *J* = 10.1, 2.7 Hz, 1H), 5.23 (s, 2H), 4.65 (s, 1H), 4.04 (d, *J* = 15.6 Hz, 1H), 3.49-3.39 (m, 2H), 3.37 (d, *J* = 15.5 Hz, 1H), 2.28 (dd, *J* = 13.7, 5.7 Hz, 1H), 1.45-1.33 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 175.0, 158.4, 147.7, 146.5, 135.3, 131.6, 131.4, 129.4, 129.04, 128.96, 128.9, 128.8, 128.6, 126.3, 124.2, 123.2, 75.3, 69.1, 53.7, 45.1, 40.9, 36.7, 28.3. HRMS (ESI+): *m/z* (M+H)$^+$ calc. for $C_{30}H_{28}N_3O_8$ 558.1876, found 558.1900.

Benzyl hydroxy(((3*aS,5*R**,7*aR**)-5-((*S**)-hydroxy(4-methoxyphenyl)methyl)-1,3-dioxo-2-phenyl-2,3,3*a*,4,5,7*a*-hexahydro-1*H*-isoindol-5-yl)methyl)carbamate (14b).** 31 mg (38 %). White solid, mp = 131-133°C. R_f = 0.30 (Cyclohexane/EtOAc: 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (brs, 1H), 7.45-7.34 (m, 8H), 7.17 (d, *J* = 8.2 Hz, 4H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.05 (s, 2H), 5.21 (s, 2H), 4.51 (d, *J* = 3.8 Hz, 1H), 3.92 (d, *J* = 15.5 Hz, 1H), 3.78 (s, 3H), 3.48 (d, *J* = 15.5 Hz, 1H), 3.47-3.38 (m, 2H), 2.17 (dd, *J* = 13.8, 6.5 Hz, 1H), 1.59 (dd, *J* = 13.8, 9.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 175.5, 159.4, 157.7, 135.7, 132.8, 131.7, 131.1, 129.3, 129.1, 128.9, 128.8, 128.7, 128.5, 126.4, 123.2, 113.6, 76.7, 68.7, 55.4, 53.9, 44.8, 40.9, 36.8, 28.1. HRMS (ESI+): *m/z* (M+H)$^+$ calc. for $C_{31}H_{31}N_2O_7$ 543.2131, found 543.2109.

Benzyl hydroxy(((3*aS,5*R**,7*aR**)-5-((*S**)-hydroxy(phenyl)methyl)-1,3-dioxo-2-phenyl-2,3,3*a*,4,5,7*a*-hexahydro-1*H*-isoindol-5-yl)methyl)carbamate (14c).** 34 mg (45%). White solid, mp = 115-117°C. R_f = 0.40 (Cyclohexane/EtOAc: 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.45-7.32 (m, 8H), 7.29-7.21 (m, 5H), 7.15 (d, *J* = 7.3 Hz, 2H), 6.09 (dd, *J* = 10.4, 1.4 Hz, 1H), 6.03 (dd, *J* = 10.2, 2.8 Hz, 1H), 5.20 (s, 2H), 4.55 (d, *J* = 3.7 Hz, 1H), 3.96 (d, *J* = 15.5 Hz, 1H), 3.70 (brs, 1H), 3.46-3.41 (m, 3H), 2.20 (dd, *J* = 13.9, 6.5 Hz, 1H), 1.54 (dd, *J* = 13.9, 8.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 175.5, 157.9, 139.0, 135.7, 132.7, 131.6, 129.3, 128.9, 128.8, 128.7, 128.5, 128.20, 128.16, 128.0, 126.4, 123.2, 76.9, 68.7, 53.9, 44.7, 40.9, 36.8, 28.1 . HRMS (ESI+): *m/z* (M+H)$^+$ calc. $C_{30}H_{29}N_2O_6$ 513.2026, found 513.2028.

Benzyl hydroxy(((3*aS,5*R**,7*aR**)-5-((*S**)-1-hydroxyallyl)-1,3-dioxo-2-phenyl-2,3,3*a*,4,5,7*a*-hexahydro-1*H*-isoindol-5-yl)methyl)carbamate (14d).** 39 mg (57%). White solid, mp = 104-106°C. R_f = 0.35 (Cyclohexane/EtOAc : 1/1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (brs, 1H), 7.49-7.32 (m, 8H), 7.25-7.22 (m, 2H), 6.09 (dd, *J* = 10.2, 3.8 Hz, 1H), 5.96 (dd, *J* = 10.2, 2.6 Hz, 1H), 5.83 (ddd, *J* = 16.5, 10.9, 7.1 Hz, 1H), 5.26 (s, 1H), 5.21 (d, *J* = 8.5 Hz, 1H), 5.20 (s, 2H), 3.88 (d, *J* = 7.1 Hz, 1H), 3.79 (d, *J* = 15.5 Hz, 1H), 3.52 (d, *J* = 15.5 Hz, 2H), 3.43-3.38 (m, 1H), 2.13 (dd, *J* = 14.0, 6.6 Hz, 1H), 1.78 (dd, J = 14.0, 9.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 175.5, 157.5, 135.8, 135.0, 132.5, 131.7, 129.4, 128.9, 128.8, 128.6, 128.5, 126.4, 123.5, 119.4, 76.4, 68.5, 53.6, 43.7, 41.0, 36.7, 27.7. HRMS (ESI+): *m/z* (M+H)$^+$ calc. for $C_{26}H_{27}N_2O_6$ 463.1869, found 463.1874.

Diels Alder/Allyboration/cyclisation reactions with maleic anhydride (one pot sequence). Diene **2a** (84 mg, 0.23 mmol), maleic anhydride (25 mg, 0.25 mmol) and benzaldehyde (51 mg, 0.48 mmol) or 4-nitrobenzaldehyde **(**73 mg, 0.48 mmol) were stirred in acetone (1 mL) at 50 °C for 48 h. Acetone was evaporated and the crude product was dissolved in a minimum of $CHCl_3$ and stored 24 h at + 4 °C. The precipitate was filtered and washed with Et_2O (2x5mL) to afford compound **16a** or **16b.**

(1*R*,2*R*,5*R*,6*R*)-1-((((Benzyloxy)carbonyl)(hydroxy)amino)methyl)-4-oxo-2-phenyl-3-oxabicyclo[3.3.1]non-7-ene-6-carboxylic acid (16a). 64 mg (64%). White solid, Mp = 120-122 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.46-7.30 (m, 10H), 6.11-6.06 (m, 2H), 5.39 (d, *J* = 1.7 Hz, 1H), 5.09 (d, *J* = 12.5 Hz, 1H), 5.06 (d, *J* = 12.5 Hz, 1H), 3.86 (d, *J* = 14.5 Hz, 1H), 3.55-3.52 (m, 2H), 2.90 (d, *J* = 14.5 Hz, 1H), 2.43-2.36 (m, 1H), 2.09-2.04 (m, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 172.3, 170.1, 158.2, 137.9, 137.6, 134.0, 129.4, 129.3, 129.2, 128.8, 128.7, 128.6, 128.3, 86.2, 67.9, 57.4, 46.7, 40.3, 40.1, 26.8. HRMS (ESI+): *m/z* (M+H)$^+$ calc. for $C_{24}H_{24}NO_7$ 438.1553, found 438.1544.

(1*R*,2*R*,5*R*,6*R*)-1-((((Benzyloxy)carbonyl)(hydroxy)amino)methyl)-2-(4-nitrophenyl)-4-oxo-3-oxabicyclo[3.3.1]non-7-ene-6-carboxylic acid (16b). 64 mg (75%). White solid, mp = 188-190 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.65 (brs, 1H), 8.29 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.34-7.30 (m, 5H), 6.15 (d, *J* = 10.1 Hz, 1H), 6.09 (d, *J* = 10.3 Hz, 1H), 5.61 (brs, 1H), 5.09 (d, *J* = 12.5 Hz, 1H), 5.05 (d, *J* = 12.3 Hz, 1H), 3.90 (d, *J* = 14.5 Hz, 1H), 3.57 (s, 2H), 2.95 (d, *J* = 14.5 Hz, 1H), 2.38-2.34 (m, 1H), 2.11 (d, *J* = 13.9 Hz, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 172.2, 169.8, 158.2, 148.9, 145.2, 137.5, 133.5, 130.0, 129.2, 128.9, 128.8, 128.7, 124.2, 85.2, 68.0, 57.1, 46.5, 40.2, 39.9, 26.7. HRMS (ESI+): *m/z* (M+H)$^+$ calc. for $C_{24}H_{23}N_2O_9$ 483.1404, found: 483.1414.

Diels Alder/allyboration/ketooxygenation sequence. Diene **2a** (85 mg, 0.24 mmol), *N*-phenyl maleimide (45 mg, 0.26 mmol) or maleic anhydride (25 mg, 0.25 mmol) and *trans*-cinnamaldehyde (61mg, 63 µL, 0.50 mmol) were stirred in acetone (1 mL) at 50 °C for 48 h. After evaporation of the solvent, the residue was purified by silica gel chromatography to afford compound **17** or **18.**

Benzyl (3*aS*,5*R*,5'S,6'S,7*aR*)-6'-benzoyl-5'-hydroxy-1,3-dioxo-2-phenyl-1,2,3,3*a*,4,7*a*-hexahydrospiro[isoindole-5,4'-[1,2]oxazinane]-2'-carboxylate (17). 62 mg (47%). White solid,

mp = 204-206 °C. R_f = 0.60 (Hexane/EtOAc: 1/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.7 Hz, 2H). 7.54 (t, *J* = 7.4 Hz, 1H), 7.49-7.38 (m, 8H), 7.29-7.23 (m, 4H), 6.28 (dd, *J* = 10.0, 4.0 Hz, 1H), 5.83 (dd, *J* = 10.1, 2.7 Hz, 1H), 5.41 (d, *J* = 11.8 Hz, 1H), 5.25 (d, *J* = 11.8 Hz, 1H), 5.02 (d, *J* = 9.3 Hz, 1H), 4.21 (dd, *J* = 9.3, 3.5 Hz, 1H), 4.05 (d, *J* = 14.3 Hz, 1H), 3.64-3.54 (m, 1H), 3.40-3.30 (m, 1H), 3.29 (d, *J* = 14.3 Hz, 1H), 3.09 (d, *J* = 3.6 Hz, 1H), 2.30-2.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 178.2, 175.3, 155.4, 135.3, 134.7, 134.6, 133.5, 132.0, 130.2, 129.3, 129.2, 129.05, 128.99, 128.72,128.69, 126.5, 125.4, 79.1, 72.0, 69.1, 51.9, 40.5, 39.6, 36.3, 24.5. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{32}H_{28}N_2O_7Na$ 575.1794, found 575.1791.

(3*S*,4*R*,6a*R*,10*S*,10a*S*)-10-Benzoyl-8-((benzyloxy)carbonyl)-2-oxo-3,4,7,8,10,10a-hexahydro-2*H*-3,6a-methanooxocino[3,2-*d*][1,2]oxazine-4-carboxylic acid (18). 30 mg (26 %). White solid, mp = 194-196 °C. R_f = 0.60 (Hexane/EtOAc: 1/1). ^{1}H NMR (700 MHz, Acetone-d_6) δ 8.27 (d, *J* = 7.7 Hz, 2H), 7.68-7.62 (m, 1H), 7.51 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.45-7.38 (m, 5H), 6.21 (ddd, *J* = 10.1, 1.9, 0.9 Hz, 1H), 5.80 (dt, *J* = 10.1, 2.4 Hz, 1H), 5.65 (d, *J* = 9.7 Hz, 1H), 5.34 (d, *J* = 12 Hz, 1H), 5.31 (d, *J* = 12.1 Hz, 1H), 4.84 (dd, *J* = 9.7, 1.7 Hz, 1H), 4.19 (d, *J* = 14.3 Hz, 1H), 3.74 (d, *J* = 14.3 Hz, 1H), 3.63 (ddd, *J* = 4.9, 2.8, 1.9 Hz, 1H), 3.35 (t, *J* = 4.6 Hz, 1H), 2.81 (ddd, *J* = 13.4, 5.2, 1.9 Hz, 1H), 2.09-2.04 (m, 1H), 1.87 (dt, *J* = 13.4, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 191.3, 172.1, 168.8, 156.3, 137.0, 136.6, 135.1, 130.7, 130.5, 130.3, 129.73, 129.73, 129.67, 129.5, 77.14, 77.07, 69.3, 53.8, 46.7, 39.7, 34.7, 28.4. HRMS (ESI+): *m/z* $(M+H)^+$ calc. for $C_{26}H_{24}NO_8$ 478.1502, found 478.1497.

Diels-Alder/allylboration sequence with nitrosobenzene To a solution of **13** (21 mg, 0.04 mmol) in MeOH (0.5 mL) was added nitrosobenzene (4.3 mg, 0.04 mmol). The reaction was stirred at room temperature for 16h. Solvent was evaporated and the product was purified by silica gel chromatography.

Benzyl hydroxy(((3a*S,5*S**,7a*R**)-5-(hydroxy(phenyl)amino)-1,3-dioxo-2-phenyl-2,3,3a,4,5,7a-hexahydro-1*H*-isoindol-5-yl)methyl)carbamate (24).** 18 mg (96%). White solid, mp = 83-84°C. R_f = 0.36 (Cyclohexane/EtOAc: 1/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.32 (m, 8H), 7.25-7.11 (m, 7H), 6.34 (brs, 1H), 6.12 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.44 (d, *J* = 9.8, 1.7 Hz, 1H), 5.23 (d, *J* = 12.3 Hz, 1H), 5.18 (d, *J* = 12.3 Hz, 1H), 3.99-3.81 (m, 3H), 3.31 (ddd, *J* = 8.5, 6.0, 2.3 Hz, 1H), 3.03 (dt, *J* = 14.6, 1.7 Hz, 1H), 1.85 (dd, *J* = 14.6, 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.8, 175.4, 156.6, 147.0, 136.0, 133.7, 131.8, 129.4, 129.0, 128.8, 128.5, 128.4, 128.3, 126.6, 126.1, 125.7, 125.0, 68.3, 62.9, 52.0, 42.0, 37.4, 27.9. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{29}H_{27}N_3O_6Na$ 536.1792, found 536.1789.

The same experimental procedure was carried out with the cycloadduct of **1a** with *N*-phenylmaleimide [29] (38 mg, 0.1 mmol) and nitrosobenzene (11 mg, 0.1 mmol) to afford the tetrahydro-*1H*-isoindole-1,3(*2H*)-dione **25**.

(3a*S,5*S**,7a*R**)-5-(Hydroxy(phenyl)amino)-5-methyl-2-phenyl-3a,4,5,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (25).** 23 mg (64%). White solid, mp = 143-145°C. R_f = 0.22 (Cyclohexane/EtOAc: 8/2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.33 (m, 3H), 7.23-7.17 (m, 4H), 7.12-7.06 (m, 3H), 6.07 (dd, *J* = 9.7, 5.3 Hz, 1H), 5.72 (s, 1H), 5.41 (dt, *J* = 9.7, 1.5 Hz, 1H), 3.81 (ddd, *J* = 8.6, 5.3, 1.7 Hz, 1H), 3.28 (ddd, *J* = 8.6, 5.0, 2.1 Hz, 1H), 3.07 (dt, *J* = 14.2, 1.7 Hz, 1H), 1.58 (dd, *J* = 14.2, 6.0 Hz, 1H), 1.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.5, 175.9, 148.8, 137.6, 132.0, 129.3, 128.8, 127.9, 126.7, 125.3, 124.7, 124.5, 60.4, 41.7, 38.0, 32.6, 18.1. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{21}H_{20}N_2O_3Na$ 371.13661, found 371.1366.

Diels-Alder reaction of 9 and *N*-phenylmaleimide. In a flame dried round bottom flask under an argon atmosphere, to a solution of **9** (40 mg, 0.13 mmol) in anhydrous DCM (1 mL) was added *N*-phenylmaleimide (26 mg, 0.15 mmol). The reaction mixture was stirred at room temperature for 48 hours. The solvent was evaporated and the two diastereomers were separated by silica gel chromatography.

Ethyl (*R)-3-((3a*R**,7*S**,7a*S**)-1,3-dioxo-2-phenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-5-yl)-2-hydroxypropanoate (26').** 28 mg (46%). Colorless oil, R_f = 0.07 (Cyclohexane/EtOAc: 70/30). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.39 (m, 2H), 7.38-7.31 (m, 1H), 7.26-7.20 (m, 2H), 5.96 (d, *J* = 5.0 Hz, 1H), 4.27-4.17 (m, 3H), 3.42 (dd, *J* = 9.4, 6.2 Hz, 1H), 3.25 (ddd, *J* = 9.4, 8.0, 4.3 Hz, 1H), 2.66 (dd, *J* = 15.3, 4.3 Hz, 1H), 2.60-2.52 (m, 1H), 2.49-2.34 (m, 2H), 2.12 (t, *J* = 5.6 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.20 (s, 6H), 1.19 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.4, 179.1, 174.7, 135.8, 132.4, 129.1, 128.5, 126.8, 126.6, 84.2, 70.0, 62.0, 42.2, 42.0, 40.6, 28.7, 25.1, 24.8, 14.4. The carbon α to boron was not observed. ^{11}B NMR (96 MHz, $CDCl_3$) δ 32.3. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{25}H_{32}NO_7{}^{11}BNa$ 492.21695, found 492.2172.

Ethyl (*S)-3-((3a*R**,7*S**,7a*S**)-1,3-dioxo-2-phenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-5-yl)-2-hydroxypropanoate (26'').** 28 mg (46%). Colorless oil. R_f = 0.17 (Cyclohexane/EtOAc: 70/30). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.26 (m, 5H), 5.96 (d, *J* = 4.8 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.24-4.17 (m, 1H), 3.43 (dd, *J* = 9.5, 6.1 Hz, 1H), 3.25 (ddd, *J* = 9.5, 8.6, 3.8 Hz, 1H), 2.64 (dd, *J* = 15.4, 4.0 Hz, 1H), 2.58-2.55 (m, 2H), 2.41-2.31 (m, 2H), 2.08 (t, *J* = 5.6 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.28 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.4, 179.1, 174.8, 135.6, 132.5, 129.1, 128.5, 126.9, 126.8, 84.2, 69.1, 61.9, 42.2, 42.1, 40.6, 28.3, 25.1, 24.9, 14.4. The carbon α to boron was not observed. ^{11}B NMR (96 MHz, $CDCl_3$) δ 31.5. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{25}H_{32}NO_7{}^{11}BNa$ 492.21695, found 492.2170.

Allyboration/lactonisation from 26' or 26''. Under an argon atmosphere in a flame dried Schlenk tube, a solution **26'** or **26''** (92 mg, 0.20 mmol) in toluene (1 mL) and arylaldehyde (0.22 mmol) was stirred at 50°C for 4 or 8 days respectively. The solvent was evaporated and the product was purified by silica gel chromatography.

(2'*R,3a*S*,5*R**,5'*R**,7a*S**)-2'-(4-Bromophenyl)-5'-hydroxy-2-phenyl-3a,4',5',7a-tetrahydro-2'*H*,6'*H*-spiro[isoindole-5,3'-pyran]-1,3,6'(2*H*,4*H*)-trione (27a).** 24 mg (24%). White solid, mp = 252-254°C. R_f = 0.13 (Cyclohexane/EtOAc: 40/60). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.29 (dd, *J* = 10.3, 2.8 Hz, 1H), 6.05 (dd, *J* = 10.3, 3.4 Hz, 1H), 5.20 (s, 1H), 4.67 (td, *J* = 9.5, 2.8 Hz, 1H),

3.51 (dt, *J* = 8.8, 3.4 Hz, 1H), 3.35 (ddd, *J* = 12.7, 8.8, 6.0 Hz, 1H), 3.22 (d, *J* = 2.8 Hz, 1H), 2.69 (dd, *J* = 13.7, 9.5 Hz, 1H), 2.23 (dd, *J* = 12.7, 6.0 Hz, 1H), 1.84 (dd, *J* = 13.7, 9.5 Hz, 1H), 1.19 (t, *J* = 12.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 174.6, 174.4, 132.7, 132.3, 131.9, 131.5, 129.5, 129.4, 129.0, 126.4, 123.8, 122.5, 83.7, 64.2, 40.5, 40.0, 39.7, 36.3, 34.0. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{24}H_{20}NO_5{}^{79}BrNa$ 504.0417, found 504.0418.

(2'*R,3*aS**,5*R**,5'*R**,7*aS**)-2'-(4-Methoxyphenyl)-5'-hydroxy-2-phenyl-3*a*,4',5',7*a*-tetrahydro-2'*H*,6'*H*-spiro[isoindole-5,3'-pyran]-1,3,6'(2*H*,4*H*)-trione (27b).** 24 mg (28%). Colorless oil, R_f = 0.3 (Cyclohexane/EtOAc: 20/80). ^{1}H NMR (300 MHz, CD_3CN) δ 7.54-7.40 (m, 3H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.23-7.13 (m, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.44-6.33 (m, 1H), 5.90 (dd, *J* = 10.2, 3.7 Hz, 1H), 5.34 (s, 1H), 4.71 (td, *J* = 9.7, 4.6 Hz, 1H), 3.80 (s, 3H), 3.71 (d, *J* = 4.6 Hz, 1H), 3.66-3.56 (m, 1H), 3.47-3.32 (m, 1H), 2.71 (dd, *J* = 13.6, 9.2 Hz, 1H), 2.23 (dd, *J* = 12.7, 6.0 Hz, 1H), 1.67 (dd, *J* = 13.6, 10.2 Hz, 1H), 1.15 (t, *J* = 12.9 Hz, 1H). ^{13}C NMR (75 MHz, CD_3CN) δ 179.1, 176.5, 175.6, 160.9, 134.2, 133.4, 130.3, 130.0, 129.5, 128.0, 127.9, 122.2, 114.4, 83.7, 65.2, 55.9, 41.4, 41.0, 40.5, 37.2, 34.2. HRMS (ESI+): *m/z* $(M-H)^-$ calc. for $C_{25}H_{22}NO_6$ 432.1447, found 432.1456.

(2'*R,3*aS**,5*R**,5'*S**,7*aS**)-2'-(4-Bromophenyl)-5'-hydroxy-2-phenyl-3*a*,4',5',7*a*-tetrahydro-2'*H*,6'*H*-spiro[isoindole-5,3'-pyran]-1,3,6'(2*H*,4*H*)-trione (28a).** 36 mg (38%). White solid, mp = 174-175°C. R_f = 0.17 (Cyclohexane/EtOAc: 40/60). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.38 (m, 5H), 7.25-7.20 (m, 2H), 7.15-7.12 (m, 2H), 6.36 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.19 (dd, *J* = 10.2, 3.2 Hz, 1H), 5.24 (s, 1H), 4.40 (dd, *J* = 12.2, 6.7 Hz, 1H), 3.57 (dt, *J* = 8.8, 3.1 Hz, 1H), 3.40 (ddd, *J* = 12.6, 9.0, 6.1 Hz, 1H), 3.22 (d, *J* = 1.6 Hz, 1H), 2.49 (dd, *J* = 12.3, 6.7 Hz, 1H), 2.20 (dd, *J* = 12.5, 6.1 Hz, 1H), 2.10 (t, *J* = 12.2 Hz, 1H), 1.18 (t, *J* = 12.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 174.4, 173.3, 133.2, 131.8, 131.4, 129.4, 129.3, 129.2, 129.0, 126.4, 124.9, 123.6, 88.8, 65.7, 40.5, 40.45, 40.4, 36.1, 33.3. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{24}H_{20}NO_5{}^{79}BrNa$ 504.0417, found 504.0417.

(2'*R,3*aS**,5*R**,5'*S**,7*aS**)-2'-(4-Nitrophenyl)-5'-hydroxy-2-phenyl-3*a*,4',5',7*a*-tetrahydro-2'*H*,6'*H*-spiro[isoindole-5,3'-pyran]-1,3,6'(2*H*,4*H*)-trione (28b).** 40 mg (45%). White solid, mp = decomposition at 235-237°C. R_f = 0.10 (Cyclohexane/EtOAc: 40/60). ^{1}H NMR (300 MHz, CD_3CN) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.50-7.37 (m, 3H), 7.16 (dd, *J* = 8.3, 1.6 Hz, 2H), 6.47 (ddd, *J* = 10.2, 3.1, 1.4 Hz, 1H), 6.04 (dd, *J* = 10.2, 3.4 Hz, 1H), 5.53 (s, 1H), 4.36 (ddd, *J* = 12.3, 6.6, 4.2 Hz, 1H), 3.96 (d, *J* = 4.2 Hz, 1H), 3.65 (dt, *J* = 8.8, 3.2 Hz, 1H), 3.42 (ddd, *J* = 13.2, 8.8, 6.2 Hz, 1H), 2.46 (dd, *J* = 12.5, 6.6 Hz, 1H), 2.20 (dd, *J* = 12.5, 6.1 Hz, 1H), 1.18 (t, *J* = 12.9 Hz, 1H) (The signals of two hydrogens are found to be masked by the peak of water at 2.10 ppm by comparison with the spectrum of **28a**). ^{13}C NMR (75 MHz, CD_3CN) δ 178.9, 176.3, 173.4, 149.1, 143.6, 133.4, 130.1, 129.9, 129.9, 128a)9.5, 128.0, 125.3, 124.2, 87.8, 66.3, 41.6, 41.4 (2C), 36.9, 33.2. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{24}H_{20}N_2O_7Na$ 471.1168, found 471.1165.

(2'*R,3*aS**,5*R**,5'*S**,7*aS**)-2'-(Phenyl)-5'-hydroxy-2-phenyl-3*a*,4',5',7*a*-tetrahydro-2'*H*,6'*H*-spiro[isoindole-5,3'-pyran]-1,3,6'(2*H*,4*H*)-trione (28c).** 52 mg (63%). White solid, mp = 262-264°C. R_f = 0.33 (Cyclohexane/EtOAc: 40/60). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.32 (m, 6H), 7.27-7.22 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.43 (d, *J* = 10.1 Hz, 1H), 6.17 (dd, *J* = 10.2, 3.2 Hz, 1H), 5.28 (s, 1H), 4.42 (dd, *J* = 12.3, 6.7 Hz, 1H), 3.56 (dd, *J* = 7.7, 4.4 Hz, 1H), 3.50-3.29 (m, 1H), 3.18 (s, 1H), 2.50 (dd, *J* = 12.4, 6.7 Hz, 1H), 2.21 (dd, *J* = 12.8, 6.3 Hz, 1H), 2.11 (t, *J* = 12.3 Hz, 1H), 1.26 (t, *J* = 12.9 Hz, 1H). ^{13}C NMR (75 MHz, CD_3CN) δ 179.1, 176.5, 173.9, 136.6, 133.4, 131.0, 130.0, 129.7, 129.5, 129.1, 128.7, 127.9, 124.6, 89.1, 66.3, 41.6, 41.4, 41.3, 37.0, 33.6. HRMS (ESI+): *m/z* $(M-H)^-$ calc. for $C_{24}H_{20}NO_5$ 402.1342, found 402.1349.

Allyboration of 26' with nitrosobenzene. To a solution of **26'** (44 mg, 0.094 mmol) in MeOH (1 mL) was added nitrosobenzene (12 mg, 0.1 mmol). The reaction was stirred at room temperature for 16h. Solvent was evaporated and the product was purified by silica gel chromatography.

Ethyl (*R*)-2-hydroxy-3-((3aR,5S,7aS)-5-(hydroxy(phenyl)amino)-1,3-dioxo-2-phenyl-2,3,3a,4,5,7a-hexahydro-1H-isoindol-5-yl)propanoate (29). 26 mg (61%). Brownish oil, R_f = 0.5 (Cyclohexane/EtOAc: 50/50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.31 (m, 3H), 7.28-7.16 (m, 4H), 7.16-7.10 (m, 3H), 6.12 (dd, *J* = 9.8, 5.1 Hz, 1H), 5.98 (s, 1H), 5.62 (dt, *J* = 9.8, 1.5 Hz, 1H), 4.45-4.37 (m, 1H), 4.35-4.26 (m, 2H), 3.88 (ddd, *J* = 8.7, 5.2, 1.8 Hz, 1H), 3.39 (ddd, *J* = 8.4, 5.9, 2.1 Hz, 1H), 3.09 (d, *J* = 14.5 Hz, 1H), 2.79 (brs, 1H), 2.71 (dd, *J* = 14.3, 2.5 Hz, 1H), 2.03 (dd, *J* = 14.2, 6.0 Hz, 1H), 1.72 (dd, *J* = 14.3, 10.3 Hz, 1H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.7, 175.8, 175.4, 148.1, 137.1, 131.9, 129.4, 1, 128.9, 128.0, 126.7, 125.5, 124.9, 124.0, 68.4, 62.4, 62.3, 41.7, 37.7, 36.7, 28.9, 14.4. HRMS (ESI+): *m/z* $(M+Na)^+$ calc. for $C_{25}H_{26}N2O_6Na$ 473.1689, found 473.1683.

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Conflict of interest

The authors declare no conflict of interest.

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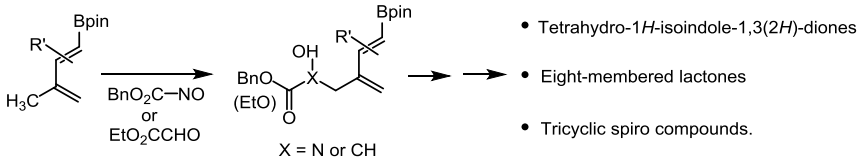
Entry for the Table of Contents



Ene reactions of boron-substituted 1,3-dienes afford new functionalized privileged precursors of skeletally diverse and complex polycyclic heterocycles. Multistep sequences based on a key Diels Alder/allyboration process are thus used to access tetrahydro-*1H*-isoindole-1,3(*2H*)-diones, eight-membered lactones or tricyclic spiro compounds.