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Benzylic Boron Reagents Behaving as Allylic Boron Reagents towards Aldehydes: A New Asymmetric Reaction Leading to Homoallylic Alcohols with Concomitant Dearomatisation

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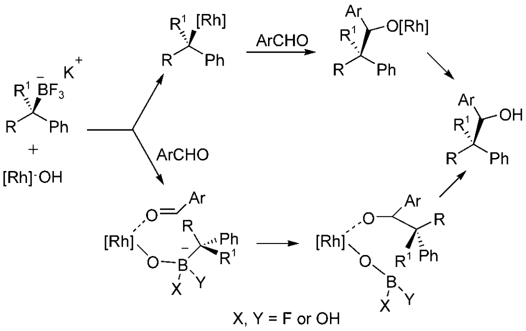
Dedicated to Professor José Barluenga on the occasion of his 70th birthday

The dearomatisation of an aromatic ring represents a powerful synthetic strategy as the aromatic ring can be easily carried through a number of synthetic manipulations and, following dearomatisation, a highly functionalised six-membered ring is created, primed for further transformations.[1] The Birch reduction is the best known example of this and has been used extensively.[2] Other methods for dearomatisation include metal-promoted nucleophilic and electrophilic addition to aromatic systems,[3] oxidation, reduction and radical cyclisation reactions.[4]

During the course of certain mechanistic studies (see later) we have discovered a new dearomatisation reaction in which benzylic boron substrates essentially behave as allylic boron reagents in reactions with aldehydes leading to cyclohexenones in high d.r. and e.r. In this paper we describe the optimisation of this novel process together with its asymmetric variant.

We recently reported the rhodium-catalysed 1,2-addition of chiral secondary and tertiary benzyl potassium trifluoroborate salts to aldehydes.[5] We proposed two possible mechanisms for this addition reaction: i) transmetallation of B→Rh followed by addition of the organometallic or ii) a cyclic mechanism in which [Rh–OH] activated both the boron and aldehyde substrates promoting the reaction (Scheme 1). In the latter mechanism Rh was essentially acting as a Lewis acid.[6] In order to distinguish between these two mechanisms we have now tested alternative, water-stable and more standard Lewis acids. Using $Sc(OTf)_3$ in the same solvent led to the same product, albeit in lower yield and with some erosion of e.r., nevertheless, implicating that the second mechanism was likely to be operating [Scheme 2, Eq. (1)].



Scheme 1. Possible mechanisms for Rh-catalysed 1,2-addition of benzylic trifluoroborate salts to aldehydes.

However, a minor change in the substrate (p-$MeOC_6H_4$ in place of Ph) led to a completely different product [Scheme 2, Eq. (2)]. Cyclohexenones (Z/E)-**2bA** (3:1, Z/E) were now obtained with complete diastereoselectivity at the new sp^3 centres.[7] A possible mechanism for the formation of the *Z* isomer is shown in Scheme 2. Conversion of the trifluoroborate salt to the difluoroborane would lead to a strongly electrophilic borane which could react with the aldehyde as if it was an allyl borane.[8] The high diastereoselectivity would arise from the closed six-membered ring TS which is often associated with allyl boron reactions with aldehydes.[8,9] Subsequent hydrolysis of the intermediate enol ether would give the product cyclohexenone. Presumably, the *E* isomer results from reaction through the alternate *ortho* position which places the substituents (Ar/Me) in slightly different steric environments.

Similar results were obtained using alternative water-stable Lewis acids such as $Gd(OTf)_3$, $In(OTf)_3$, $Y(OTf)_3$,

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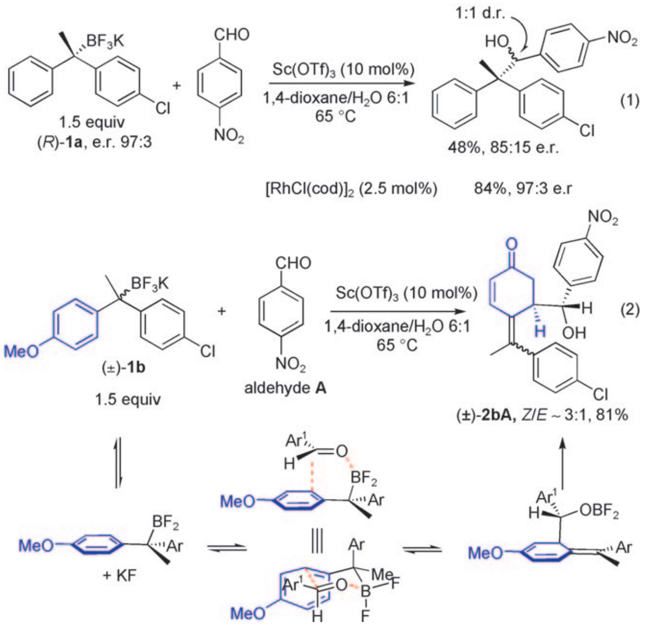
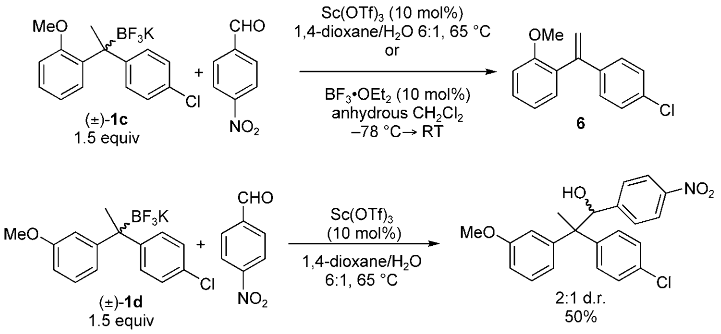


Scheme 2. Sc^{III}-catalysed addition of tertiary trifluoroborate salts to p-nitrobenzaldehyde.

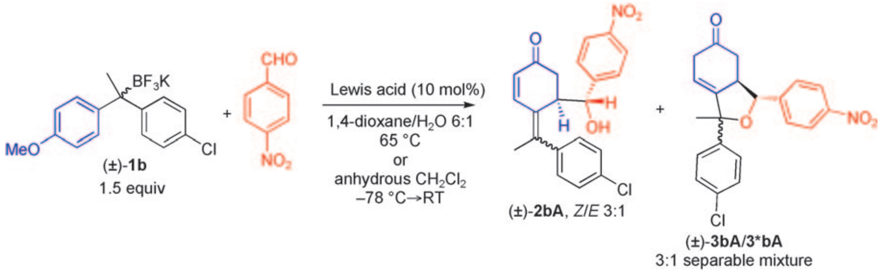
and $Yb(OTf)_3$. (Table 1, entries 2–6). Control experiments without Lewis acid (entry 1) or with TfOH (entry 7) showed that the lanthanide Lewis acids were critical to the success of the reaction. Using BF_3·OEt_2 or $SiCl_4$ in anhydrous CH_2Cl_2 at low temperature also led to adduct formation with dearomatisation, although with markedly different outcomes. $SiCl_4$ led to the *E* isomer (*E*)-**2bA** being the major product instead of the *Z* isomer (entry 8) whilst BF_3·OEt_2 led to formation of the furans **3bA/3*bA** (entry 9). Treatment of our isolated 3:1 *Z/E* olefin mixture of (±)-**2bA** with one equivalent of BF_3·OEt_2 in anhydrous CH_2Cl_2 at −78 °C led to the same mixture of furans **3bA/3*bA**. The reaction of the *ortho*- or *meta*-methoxy analogues of the trifluoroborate salts **1c**/**1d** did not show the same reactivity. The *ortho*-methoxy salt **1c** gave the alkene **6** as the major product as a result of dehydroboration, whilst the *meta*-methoxy salt **1d** showed similar reactivity to the phenyl substrate, resulting in predominantly 1,2-addition (Scheme 3).



Scheme 3. Reactivity of *o*- and *m*-analogues of salts (±)-**1c**, **1d**.

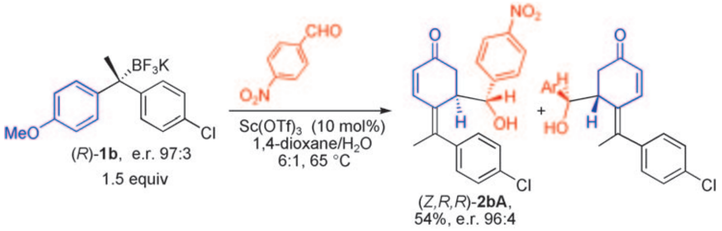
Further surprises emerged when we studied the reaction of enantioenriched **1b** (97:3 e.r.) with *p*-nitrobenzaldehyde in the presence of $Sc(OTf)_3$ (Scheme 4). The *E* and *Z* isomers of **2bA** were formed with markedly different e.r. values: the major *Z* isomer was formed with 96:4 e.r. (essentially complete stereoretention) whilst the minor *E* isomer was formed with only 36:64 e.r. Furthermore, from single crystal X-ray analyses of the major enantiomers of the *Z*- and *E*-cyclohexenones **2bA**[10] it was found that they both had *R,R* configuration at the newly created sp^3 centres. This implies that the *Z* isomer of **2bA** had been formed via a closed TS and that the *E* isomer of **2bA** had been formed via an open TS (Scheme 5).[11] The high e.r. observed in the formation of the *Z* isomer indicates that the closed TS **d** is strongly favoured over the open TS **b**. In contrast, the low e.r. observed for the *E* isomer indicates that the reaction

Table 1. Investigation of the effect of Lewis acid, solvent and temperature on course of reaction.



Entry	Catalyst (10 mol%)	Solvent	T [°C]	Yield [%] **2bA** (Z/E)[b]	Yield [%] **3bA/3*bA**[c]
1	none	1,4-dioxane/H_2O 6:1	65	–	–
2	$Sc(OTf)_3$	1,4-dioxane/H_2O 6:1	65	81 (3:1)	–
3	$Gd(OTf)_3$	1,4-dioxane/H_2O 6:1	65	34 (3:1)	–
4	$In(OTf)_3$	1,4-dioxane/H_2O 6:1	65	60 (3:1)	–
5	$Y(OTf)_3$	1,4-dioxane/H_2O 6:1	65	42 (3:1)	–
6	$Yb(OTf)_3$	1,4-dioxane/H_2O 6:1	65	68 (3:1)	–
7	TfOH	1,4-dioxane/H_2O 6:1	65	–	–
8	$SiCl_4$	anhydrous CH_2Cl_2	−78→ RT	52 (1:4)	–
9	BF_3·OEt_2	anhydrous CH_2Cl_2	−78→ RT	–	73 (3:1)

[a] A mixture of *p*-nitrobenzaldehyde (0.3 mmol), (±)-**1b** (0.45 mmol) and Lewis acid (10% mol) in deoxygenated 1,4-dioxane/H_2O 6:1 (1.65 mL) was stirred at 65 °C until consumption of aldehyde by TLC. With water-sensitive Lewis acids ($SiCl_4$ and BF_3·OEt_2), anhydrous CH_2Cl_2 (3 mL) was used and the Lewis acid addition was carried out at −78 °C→ RT. [b] Isolated yield. The *Z/E* ratio was determined by ^1H NMR of the crude. [c] Isolated yield. The **3** and **3*** refer to the two diastereomers at the quaternary centre. The ratio was determined by ^1H NMR of the crude.

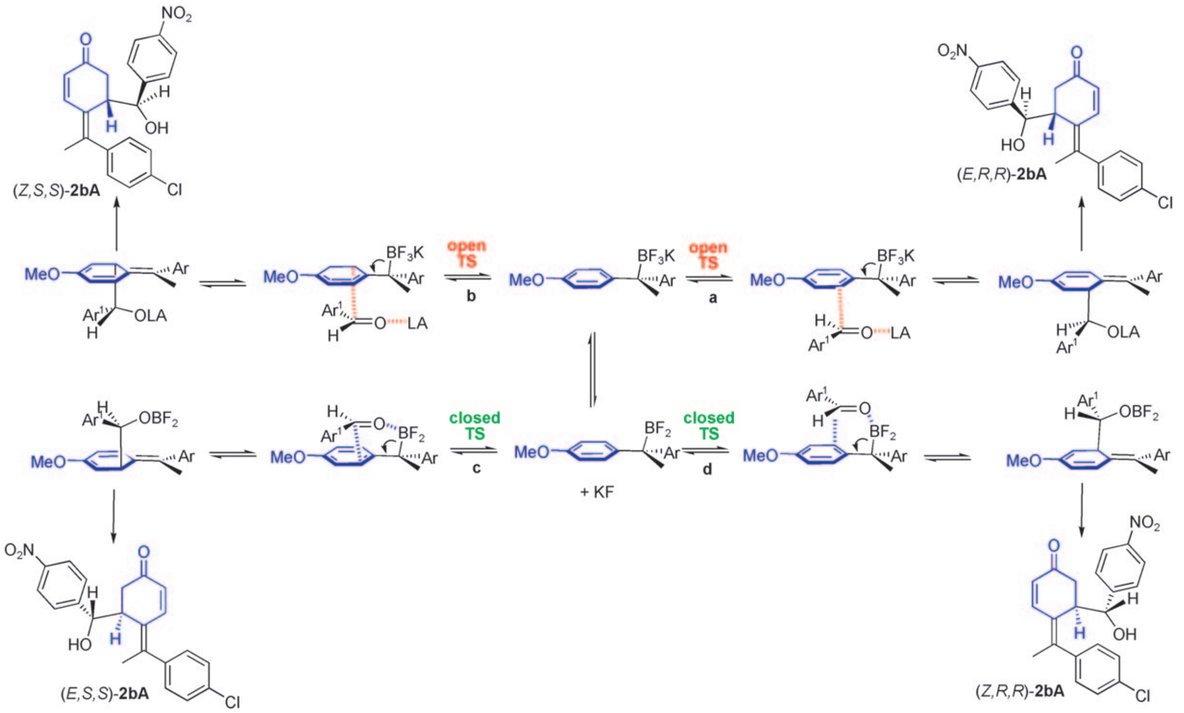


Scheme 4. Reaction of enantioenriched (*R*)-**1b** with *p*-nitrobenzaldehyde (major enantiomers drawn).

occurs via both open and closed TSs **a** and **c**, but now with the open TS **a** being marginally favoured over the closed TS **c** (~2:1).

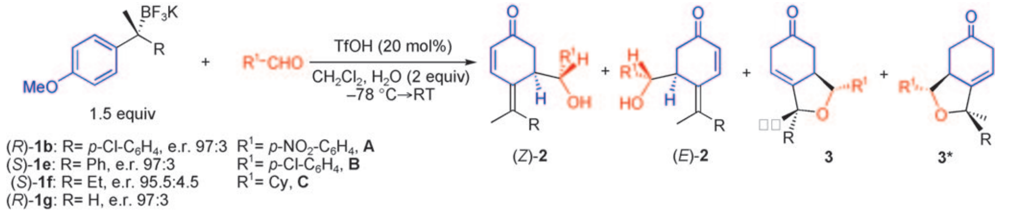
In order to enhance the e.r. of the *E* isomer of **2bA** we needed to shut down one of the two competing open and closed TSs **a** and **c** and sought to eliminate the open TS **a** as this would not impact negatively on the e.r. of the major *Z* isomer formed. We believed that this could be achieved by either i) converting more of the RBF$_3$K salt into the neutral difluoroborane to promote the closed TS or ii) using a weaker external LA to limit the extent of the open TS, or both. Brønsted acids were expected to fulfil both roles. We therefore tested triflic acid and were delighted to find that it was highly effective, leading to adducts in good yield and *without* significant erosion of e.r. in both *E* and *Z* isomers (Table 2, entry 1). These new conditions were general for a range of aldehydes and benzyl trifluoroborate substrates (Table 2). The reaction with the less activated aldehyde, PhCHO **B** (entry 2), gave cyclohexenones (*E*/*Z*)-**2bB** in good yield but with a small degree of erosion in e.r. (<5%) in the *E* isomer. Under the same conditions cyclohexanecarboxaldehyde **C** gave the furan derivatives **3/3*bC** by intramolecular 1,6-addition, rather than the free alcohol **2bC** (entry 3). Small amounts of the 1,6-addition adducts **3bA** and **3bB** were also observed with aromatic aldehydes with/when using longer reaction times (entries 1–2). A mixture of products **2/3eA** and **2/3eB** were obtained when the salt (*S*)-**1e** was used with aromatic aldehydes (**A** and **B**, entries 4 and 6), but treatment of the crude reaction mixtures with 20 mol% BF$_3$·OEt$_2$ in anhydrous CH$_2$Cl$_2$ (Method B, see Supporting Information) converted them into the furans **3/3*eA** and **3/3*eB** (entries 5 and 7). With cyclohexanecarboxaldehyde (entry 8) the furan derivatives **3/3*eC** were obtained exclusively and with complete stereoretention.

Having successfully demonstrated that the reactions of enantioenriched diarylalkyl trifluoroborate salts **1b** and **1e** with aromatic and aliphatic aldehydes occurred with almost complete transfer of stereochemical information, we considered the extension of the methodology to tertiary dialkylaryl and secondary arylalkyl trifluoroborate salts **1f–g**. The tertiary trifluoroborate salt **1f** reacted with aromatic and aliphatic aldehydes (**A**–**C**) giving the separable furan derivatives **3fA–fC** and **3*fA–fC** in good yields and again with almost complete retention of stereochemistry (entries 9–11). When similar conditions were applied to the secondary alkyl trifluoroborate salt **1g** (entry 12), considerable erosion of e.r. (71:29) was observed for the minor (*Z*)-**2gA** isomer. However, by decreasing the amount of TfOH to 5 mol% this erosion of e.r. was markedly improved (entry 13) to give 85:15 e.r. and 95:5 e.r. for (*Z*)-**2gA** and (*E*)-**2gA** (major isomer), respectively.



Scheme 5. Proposed reaction pathways leading to the observed isomers of adducts.

Table 2. TfOH-catalysed 1,2-addition of trifluoroborate salts **1b–1g** to aldehydes **A–C**.[a]



Entry	Salt (e.r.)	R	Aldehyde (R^1 =)	Yield (*Z*)-**2**,[b] e.r.[c]	Yield (*E*)-**2**,[b] e.r.[c]	Yield **3**,[b] e.r.[c]	Yield **3***,[b] e.r.[c]
1	(*R*)-**1b** (97:3)	*p*-Cl-C_6H_4	*p*-NO_2-C_6H_4 (A)	**2bA**, 70,[d] 96:4	**2bA**, 19, 95:5	–[e]	–
2	(*R*)-**1b** (97:3)	*p*-Cl-C_6H_4	Ph (B)	**2bB**, 51, 96:4	**2bB**, 26, 92:8	–[e]	–
3	(*R*)-**1b** (97:3)	*p*-Cl-C_6H_4	Cy (C)	–	–	**3bC**, 68, 97:3	**3*bC**, 19, 95:5
4	(*S*)-**1e** (97:3)	Ph	*p*-NO_2-C_6H_4 (A)	**2eA**, 33[f], 97:3	**2eA**, 16[f], 96:4	**3eA**, 21, 97:3	–
5[g]	(*S*)-**1e** (97:3)	Ph	*p*-NO_2-C_6H_4 (A)	–	**2eA**, 17, 95:5	**3eA**, 46, 97:3	–
6	(*S*)-**1e** (97:3)	Ph	Ph (B)	**2eB**, 16, 97:3	**2eB**, 13, 88:12	**3eB**, 33, 97:3	–
7[g]	(*S*)-**1e** (97:3)	Ph	Ph (B)	–	**2eB**, 13, 88:12	**3eB**, 42, 97:3	–
8	(*S*)-**1e** (97:3)	Ph	Cy (C)	–	–	**3eC**, 32, 96:4	**3*eC**, 20, 96:4
9	(*S*)-**1f** (95.5:4.5)	Et	*p*-NO_2-C_6H_4 (A)	–	–	**3fA**, 54, 95:5	**3*fA**, 30, 92:8
10	(*S*)-**1f** (95.5:4.5)	Et	Ph (B)	–	–	**3fB**, 40, 95:5	**3*fB**, 22, 93:7
11	(*S*)-**1f** (95.5:4.5)	Et	Cy (C)	–	–	**3fC**, 42[h]	**3*fC**, 19[h]
12	(*R*)-**1g** (97:3)	H	*p*-NO_2-C_6H_4 (A)	**2gA**, 40,[f] 71:29	**2gA**, 39,[f] 92:8	–	–
13[i]	(*R*)-**1g** (97:3)	H	*p*-NO_2-C_6H_4 (A)	**2gA**, 37,[f] 85:15	**2gA**, 48,[f] 95:5	–	–

[a] Method A: A mixture of aldehyde (0.3 mmol), (±)-**1b–g** (0.45 mmol), H_2O (0.6 mmol, 11 µL) and TfOH (20% mol, 5.4 µL) in deoxygenated and anhydrous CH_2Cl_2 (3 mL) was stirred at −78 °C→ RT until complete consumption of aldehyde was observed by TLC. [b] Isolated yield. [c] Determined by chiral HPLC or GC (see Supporting Information). [d] Isolated yield after partial recrystallisation. [e] The **3bA–3bB** adducts were formed in small amounts with longer reaction times. [f] Inseparable *Z*/*E* mixture. The yield was estimated by ^1H NMR on the isolated mixture. [g] Method A followed by work up and treatment with $BF_3{\cdot}OEt_2$ in anhydrous CH_2Cl_2 (see Supporting Information). Direct reaction of the salt and aldehyde with $BF_3{\cdot}OEt_2$ gave lower yields of furan adducts due to formation of side-products derived from dehydroboration. [h] The furan enantiomers were not separable by GC using α, β, or γ-DEX columns. See Supporting Information for further details. [i] The reaction was carried out with 5% mol of TfOH.

In summary, we have discovered a new reaction manifold for benzylic trifluoroborate salts which react with aldehydes in the presence of Lewis or Brønsted acids to give homoallylic alcohols.[12] The reactions are accompanied by dearomatisation of the aromatic ring which is especially synthetically useful since it leads to more functionalised products. The reactions show broad substrate scope in terms of both the benzylic trifluoroborate salts, which can be primary,[13] secondary or tertiary, and the aldehydes employed (aromatic/aliphatic). The use of enantioenriched benzylic trifluoroborate salts, which are easily accessible through the lithiation-borylation reaction,[5c–f] leads to adducts with almost complete retention of stereochemistry in most cases. This new reaction manifold extends the synthetic utility of benzylic boron reagents and the lithiation-borylation reactions that produce them.

Experimental Section

Typical procedure for (1*R*,3*S*,3a*S*)-3*fA and (1*R*,3*R*,3a*R*)-3fA (Table 2, entry 9): A dried Schlenk tube was charged with the potassium trifluoroborate salt (*S*)-**1f** (122 mg, 0.45 mmol) and the corresponding aldehyde (45 mg, 0.3 mmol). After cycles of vacuum/N_2 (three cycles), deoxygenated dry CH_2Cl_2 (3 mL) and H_2O (0.6 mmol, 11 µL) were added. The reaction mixture was cooled to −78 °C and TfOH (20% mol, 5.4 µL) was added. The dry ice/acetone bath was removed and the reaction mixture was stirred at room temperature until starting aldehyde is consumed by TLC (6 h). Saturated NH_4Cl solution was then added and the mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$ (anh.). Concentration and purification through silica gel column chromatography (petroleum ether 40–60/EtOAc 6:1→ 1:1) gave (1*R*,3*S*,3a*S*)-**3*fA** (first fraction, 27 mg, 30%) and (1*R*,3*R*,3a*R*)-**3fA** (second fraction, 49 mg, 54%) as yellow viscous oils. (1*R*,3*S*,3a*S*)-**3*fA**: $[\alpha]_D^{20} = +87$ (c = 0.7, $CHCl_3$) (e.r. 92:8); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, 2H, J=8.8 Hz, $CH_{Arom.}$), 7.54 (d, 2H, J=8.8 Hz, $CH_{Arom.}$), 5.62 (dt, 1H, J=4.4, 2.8 Hz, CH-*1*), 4.64 (d, 1H, J=9.5 Hz, CH-*5*), 3.02 (ddd, 1H, J=22.0, 4.4, 2.4 Hz, CH-*2a*), 2.91 (m, 1H, CH-*4*), 2.85 (dt, 1H, J=22.2, 2.8 Hz, CH-*2b*), 2.57 (dd, 1H, J=14.3, 5.5 Hz, CH-*3a*), 2.39 (dd, 1H, J=14.3, 12.1 Hz, CH-*3b*), 1.88–1.75 (m, 2H, CH_2CH$_3$), 1.47 (s, 3H, Me), 1.03 ppm (t, 3H, J=7.5 Hz, CH$_2$$CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.9 (C=O), 148.7 (C_{quat}), 147.9 (C_{quat}-Arom), 147.7 (C_{quat}-Arom), 126.6 (CH-Arom), 123.9 (CH-Arom), 113.4 (C1), 84.7 (C6), 84.4 (C5), 48.6 (C4), 41.0 (C3), 38.4 (C2), 33.0 (CH_2CH_3), 27.7 (Me), 8.6 ppm (CH$_2$$CH_3$); IR (neat): $\tilde{\nu}$ =2970, 2925, 1716, 1603, 1518, 1350 cm^{-1}; HRMS (CI): m/z: calcd for $C_{17}H_{20}NO_4$: 302.1392; found: 302.1396 $[M+H]^+$; HPLC: Chiralpak IA column with guard, 10% isopropanol in hexane, 0.35 mL min^{-1}, T=0 °C, t_R 37.3 min (major) and 41.1 min (minor). (1*R*,3*R*,3a*R*)-**3fA**: $[\alpha]_D^{20} = -34$ (c = 1.8, $CHCl_3$) (e.r. 95:5); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, 2H, J=8.8 Hz, $CH_{Arom.}$), 7.57 (d, 2H, J=8.8 Hz, $CH_{Arom.}$), 5.63 (dt, 1H, J=4.4, 2.7 Hz, CH-*1*), 4.66 (d, 1H, J=9.5 Hz, CH-*5*), 3.01 (ddd, 1H, J=22.5, 4.4, 2.5 Hz, CH-*2a*), 2.87 (dt, 1H, J=22.5, 2.9 Hz, CH-*2b*), 2.80 (m, 1H, CH-*4*), 2.56 (dd, 1H, J=14.2, 5.2 Hz, CH-*3a*), 2.40 (dd, 1H, J=14.2, 12.0 Hz, CH-*3b*), 1.84 (m, 1H, CH_2CH$_3$), 1.77 (m, 1H, CH_2CH$_3$), 1.45 (s, 3H, Me), 1.02 ppm (t, 3H, J=7.3 Hz, CH$_2$$CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.9 (C=O), 148.7 (C_{quat}), 147.8 (C_{quat}-Arom), 147.4 (C_{quat}-Arom), 126.6 (CH-Arom), 123.9 (CH-Arom), 114.0 (C1), 84.9 (C6), 83.1 (C5), 49.7 (C4), 41.3 (C3), 38.3 (C2), 34.7 (CH_2CH$_3$), 26.0 (Me), 8.8 ppm (CH$_2$$CH_3$); IR (neat): $\tilde{\nu}$= 2970, 2926, 1714, 1603, 1519, 1360 cm^{-1}; HRMS (CI): m/z: calcd for $C_{17}H_{20}NO_4$: 302.1392; found: 302.1394 $[M+H]^+$; HPLC: Chiralpak IA column with guard, 10% isopropanol in hexane, 0.5 mL min^{-1}, T=RT, t_R = 27.4 (minor) and 30.1 min (major).

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Keywords: allylboration · asymmetric catalysis · borylation · dearomatization · lithiation

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