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Copper-Catalyzed Asymmetric Conjugate Additions of Bis(pinacolato)diboron and Dimethylzinc to Acyl-*N*-methylimidazole Michael Acceptors: A Highly Stereoselective Unified Strategy for 1,3,5,...*n* (OH, Me) Motif Synthesis

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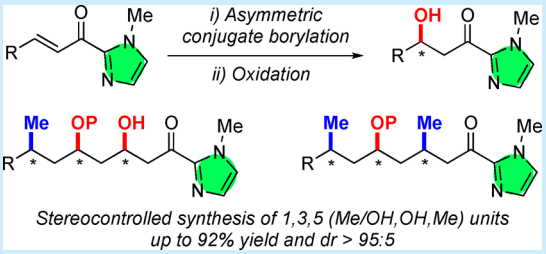
Supporting Information

ABSTRACT: A unified strategy for the construction of prevalent 1,3,5,...*n* (OH, Me) motifs based on consecutive copper-catalyzed asymmetric conjugate borylation (ACB) and methylation (ACA) reactions involving *α,β*-unsaturated 2-acyl-*N*-methylimidazoles is described. Good yields and high diastereoselectivities have been obtained in ACA and ACB reactions for both matched and mismatched pairs as illustrated in the synthesis of *syn*/*anti* and *anti*/*anti* (Me, OTBS, Me) and (OH, OTBS, Me) motifs.



Polyketides are a broad and structurally diverse class of secondary metabolites with various medicinal applications, as illustrated, for example, by the development of erythromycin, amphotericin, or eribulin.[1] Efficient strategies have been developed for the iterative construction of polyacetates, polypropionates, and poly-deoxypropionate motifs.[2,3] On the other hand, and despite the prevalence of 1,3,5,...*n* (OH, Me) motifs in biologically relevant molecules (Figure 1), no practical and broadly applicable unified strategy has been developed to date for the synthesis of these units with high stereocontrol.

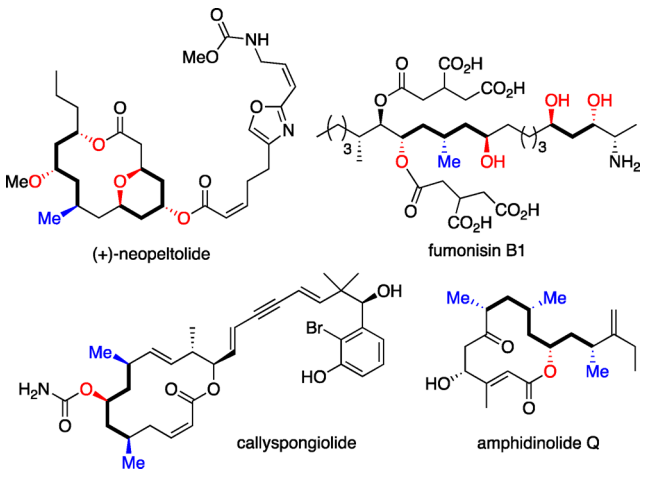


Figure 1. Natural products embedding the 1,3,5,...*n* (OH, Me) motifs.

The transition-metal-catalyzed asymmetric conjugate addition (ACA) of hard and soft nucleophiles to electron deficient alkenes has emerged as an efficient methodology for the selective formation of C−C and C−heteroatom bonds[4] and thus offers opportunities to tackle synthetic problems associated with the synthesis of such 1,3,5,...*n* (OH, Me) motifs. In the past decade, electron-deficient alkenes bearing the postfunctionalizable acylimidazole fragment have emerged as privileged substrates in ACA.[5] Recently, we efficiently engaged this family of substrates in the copper-catalyzed enantioselective conjugate addition of dimethylzinc to form all-carbon methyl-substituted chiral scaffolds (ACA, Scheme 1, eq a),[6] and highlighted the synthetic potential of this methodology in the iterative construction of chiral (poly)deoxypropionate motifs.[6b] In regard to the stereoselective introduction of the hydroxyl group, the asymmetric conjugate borylation (ACB) of boron reagents to *α,β*-unsaturated carbonyl compounds has attracted considerable interest in the recent years.[7−9] Nevertheless, and to the best of our knowledge, the construction of 1,3 diols through consecutive ACB reactions has only been scarcely described. Only two papers, both starting from unsaturated esters, have described such consecutive ACB reactions, albeit with moderate to good diastereoselectivities.[8] Whiting and co-workers have obtained low to moderate diastereoselectivities (from 58:42 to 92:8 for the match pairs and 58:42 to 87.5:12.5 for the mismatch pairs) starting from borylated starting material.[8a] In the second paper,[8b] Oestreich and co-workers described the enantioselec-

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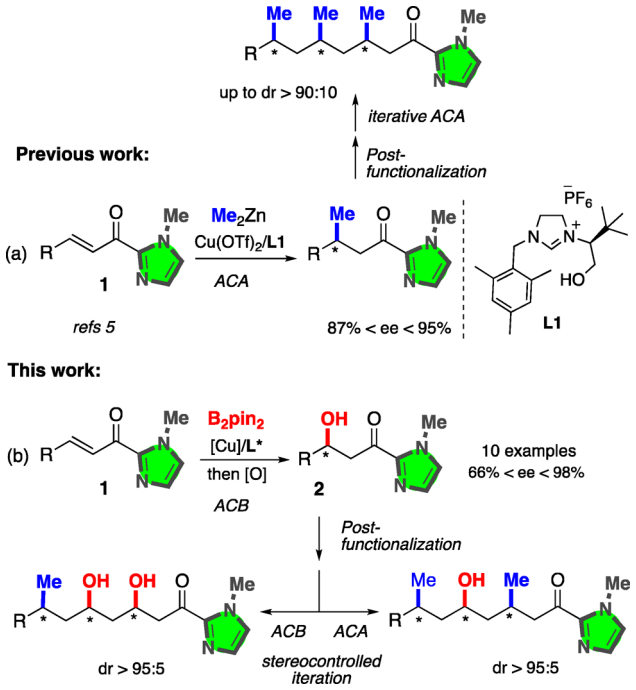
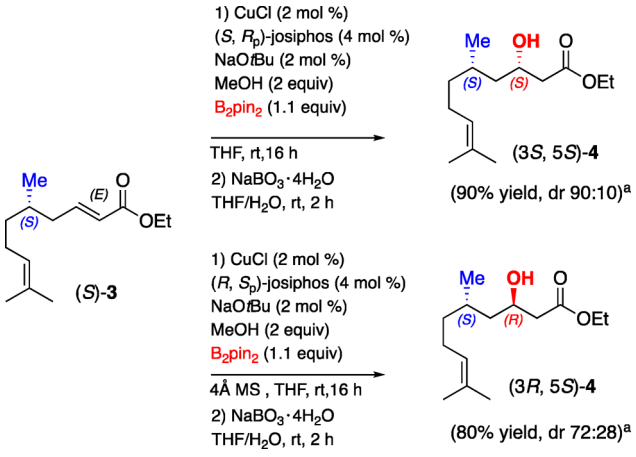
Scheme 1. Copper-Catalyzed ACA and ACB Involving α,β-Unsaturated 2-Acyl-*N*-methylimidazoles and Related Iterative Processes



Scheme 2. Diastereoselectivity Issues in the ACB from Unsaturated Ester 3



[a]Diastereomeric ratios were determined by ^{1}H NMR on the crude products.

tive borylation from TBSO derivatives, and in this case, a moderate 89:11 diastereoselectivity for both match and mismatch pairs was observed.

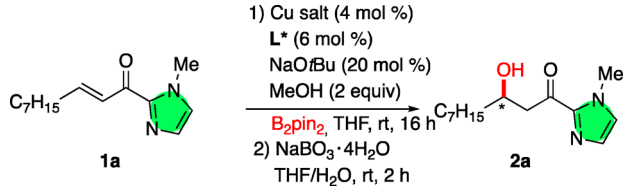
On the other hand, the construction of 1,3 OH/Me moieties through ACB reactions is to the best of our knowledge not yet described. We used the optimized ACB conditions developed for esters derivatives[7a,8b] on model compound (*S*)-**3** derived from citronellal with, however, disappointing diastereoselectivities (Scheme 2, see also the SI). There is thus room for improvement to develop a general system for consecutive ACA and ACB reactions. Thanks to the success obtained in ACA reactions with acylimidazole reactions (Scheme 1, eq b), we thus embarked on ACB reactions with such substrates to ideally develop a practical unified strategy for the stereoselective synthesis of 1,3,5,...*n* (OH, Me) motifs.

We report herein that Cu/Taniaphos efficiently catalyzes the addition of bis(pinacolato)diboron (B_2pin_2) to α,β-unsaturated 2-acyl-*N*-methylimidazoles with high enantioselectivies. Furthermore, thanks to the postfunctionalization of the acylimidazole fragment, we demonstrate that various 1,3,5-(OH, Me) motifs could be synthesized in good yields and excellent stereoselectivities through the consecutive Cu-catalyzed ACB/ACA.

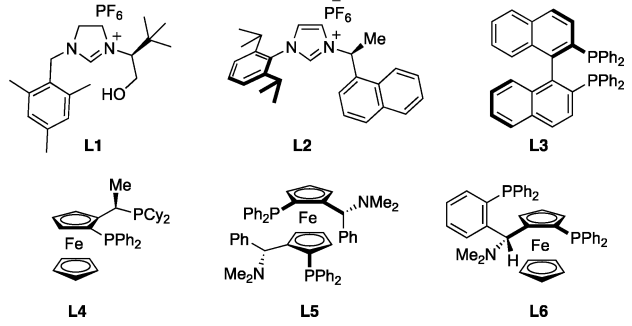
The copper-catalyzed conjugate addition of B_2pin_2 was initially investigated on the model compound **1a** (R = C_7H_{15}) bearing a nonsubstituted acyclic chain, and for the sake of simplicity, the enantiomeric excess was measured after oxidation on the corresponding hydroxyl compound **2a**. In the presence of a catalytic amount of $Cu(OTf)_2$ (4 mol %), NaO*t*Bu (20 mol %), and using B_2pin_2 (1.1 equiv), we could first demonstrate that the borylation reaction proceeded efficiently in the absence of ligand to afford the racemic product in 92% yield. This initial result highlighted the necessity of developing a stable and robust chiral catalytic system in order to prevent undesired racemic background catalysis (Table 1, entry 1).

On the basis of our recent success with the copper-catalyzed enantioselective transfer of methyl to α,β-unsaturated 2-acyl-*N*-

Table 1. Screening of Chiral Ligands L1−L6 for the Copper-Catalyzed ACB with Model Substrate 1a[a]



entry	Cu salt	ligand	NMR yield[b] (%)	ee[c] (%)
1	$Cu(OTf)_2$		92	0
2	$Cu(OTf)_2$	**L1**	86	0
3	$Cu(OTf)_2$	**L2**	84	49
4	$Cu(OTf)_2$	**L3**	73	76
5	$Cu(OTf)_2$	**L4**	61	85
6	$Cu(OTf)_2$	**L5**	82	16
7	$Cu(OTf)_2$	**L6**	67	98
8	$Cu(MeCN)_4PF_6$[d]	**L6**	84	98



[a]Reaction conditions: all reactions were carried out in a glovebox at 0.2 mmol scale: (1) Cu salt (4 mol %), **L** (6 mol %), NaO*t*Bu (20 mol %), THF 30 min, then B_2pin_2 (1.1 equiv), THF, 10 min, then **1a** (1 equiv), MeOH (2 equiv), THF, rt, 16 h; (2) $NaBO_3{\cdot}4H_2O$ (6 equiv), THF/H_2O (1/1), rt, 2 h. [b]Determined by ^{1}H NMR spectroscopy with mesitylene as internal standard. [c]Enantiomeric excesses were determined by HPLC on a chiral stationary phase. [d]Reaction carried out in the presence of 4 Å MS using the classical Schlenk technique.

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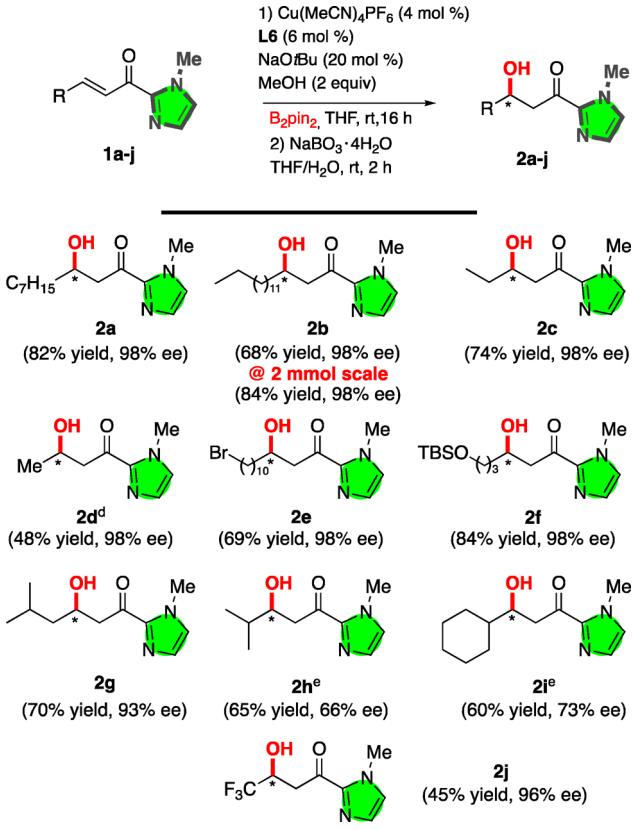
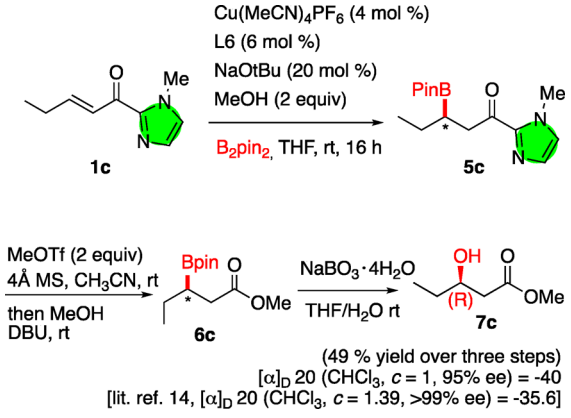
Scheme 3. Substrate Scope for the Copper-Catalyzed ACB with β-Substituted α,β-Unsaturated 2-Acyl-*N*-methylimidazoles 1a−j Catalyzed by L6/Cu(MeCN)$_4$PF$_6$[a−c]



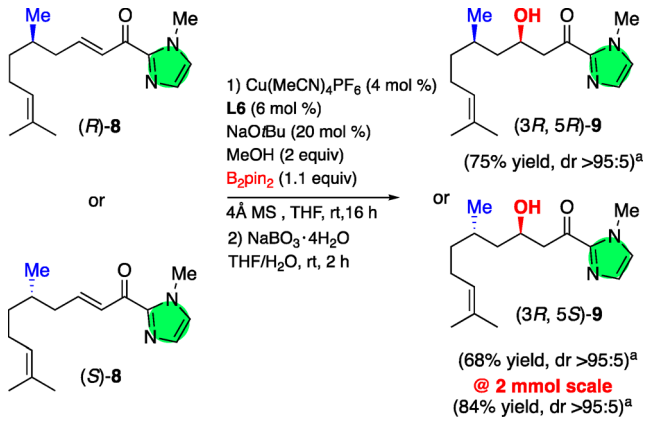
[a]Reaction conditions: all reactions have been carried out at a 0.2 mmol scale: (1) Cu salt (4 mol %), **L6** (6 mol %), NaO*t*Bu (20 mol %), 4 Å MS, THF 30 min, then B_2pin_2 (1.1 equiv), THF, 10 min, then **1a** (1 equiv), MeOH (2 equiv), THF, rt, 16 h; (2) $NaBO_3{\cdot}4H_2O$ (6 equiv), THF/H_2O (1/1), rt, 2 h. [b]Yield of isolated product. [c]Enantiomeric excesses were determined by HPLC on a chiral stationary phase. [d]Moderate yield due to the instability of the starting material. [e]The reaction was performed in Et_2O instead of THF.

Scheme 4. Determination of the Absolute Configuration of Compound 5c



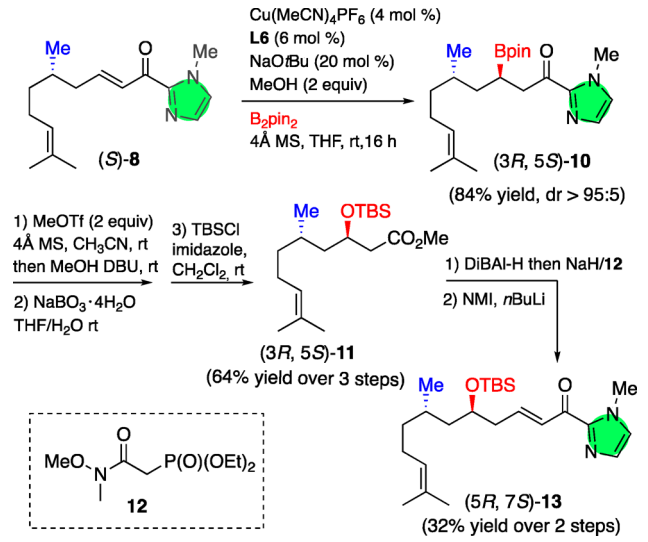
methylimidazoles, the ACB was first evaluated in the presence of the unsymmetrical chiral NHC ligands **L1** or **L2**.[10] Unfortunately, despite excellent conversions and isolated yields, the expected compound **2a** was obtained, respectively, in a racemic form and with moderate 49% ee (Table 1, entries 2 and 3). More

Scheme 5. Diastereoselectivity Issues in the Construction of 1,3 (Me,OH) Motifs

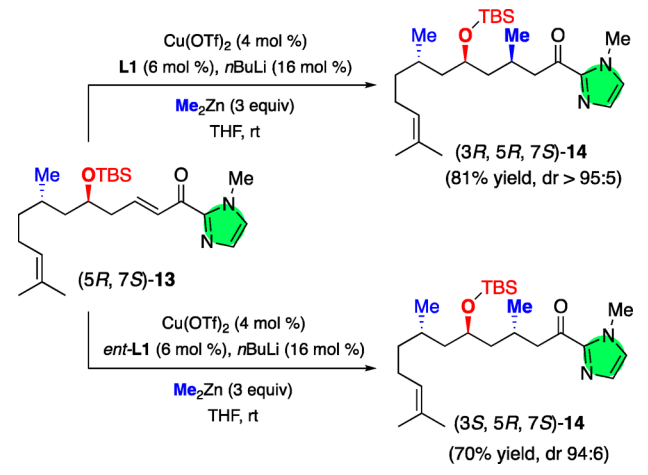


[a]Diastereomeric ratios were determined by ^{1}H NMR on the crude products.

Scheme 6. Synthesis of Homologated 2-Acyl-*N*-methylimidazole 13



Scheme 7. Stereocontrolled Synthesis of 1,3,5 (Me, OH, Me) Units



promising results were observed when moving to C_2-symmetric bisphosphines as illustrated with the 76% ee obtained using (*R*)-

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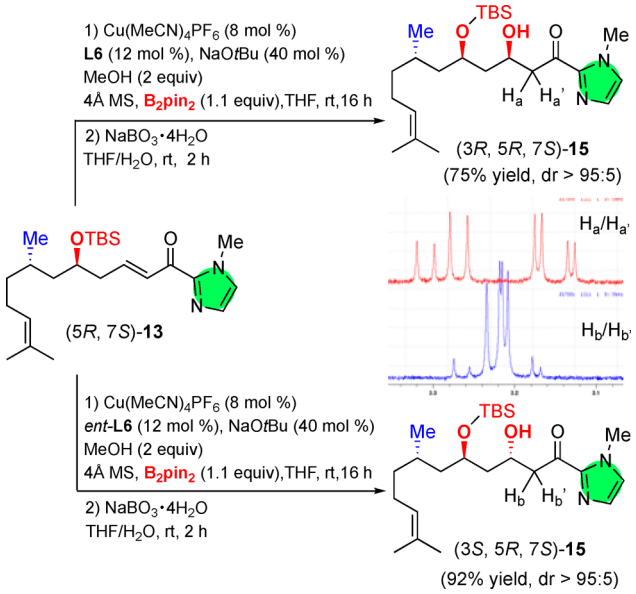
Scheme 8. Stereocontrolled Synthesis of 1,3,5 (OH, OH, Me) Units



Binap (Table 1, entry 4). Screening more elaborated bisphosphines such as (*R*),(S_P)-Josiphos **L4**, (*R*),(S_P),($S_{P'}$)-Mandyphos **L5**, and (*R*),(R_P)-Taniaphos **L6** led to enhanced enantioinduction with the identification of **L6** as the most efficient ligand affording **2a** in satisfactory 67% yield and excellent 98% ee (Table 1, entry 7).[11] Nevertheless, when the scale of the reaction was increased and the reaction was performed outside the glovebox, it was later evidenced that its efficiency could be impacted by water traces. Fortunately, replacement of $Cu(OTf)_2$ by the less hygroscopic $Cu(MeCN)_4PF_6$ (in the presence of 4 Å molecular sieves) provided a robust catalytic system allowing the formation of the desired product **2a** with both high 84% yield and excellent 98% enantiomeric excess (Table 1, entry 8).

With the optimized conditions in hand, the scope of the ACB reaction was next investigated with a variety of *α*,*β*-unsaturated 2-acyl-*N*-methylimidazole substrates (Scheme 3). As illustrated in Scheme 3, the reaction is very efficient with unsaturated acylimidazoles **1** bearing acyclic aliphatic chain substituents leading to the hydroxylated products **2a**−**d** in high yield and with very high enantioselectivity (98% ee). Interestingly, functionalized side chains are also well tolerated (see **2e**,**f**). On the other hand, the reaction appeared to be more sensitive to steric hindrance. In fact, while only a slight decrease of the enantioselectivity was observed for the isobutyl-substituted product **2g**, substrates **1h** and **1i** with bulkier *γ*-branched alkyl substituents resulted under the standard conditions, in reduced enantiocontrol (40 and 53% ee, respectively), which could be moderately improved using diethyl ether as the reaction solvent (66 and 73% ee's, respectively). Finally, the trifluoromethylated derivative **1j** was nicely hydrated, leading to compound **2j** in 45% yield and 96% ee.[12]

Having developed an efficient asymmetric borylation reaction with acylimidazole substrates, several key criteria needed to be addressed to ensure successful implementation in total synthesis strategies: (i) applicability of the catalytic system on larger scale; (ii) determination of the absolute configuration of the secondary alcohols; (iii) diastereoselectivity outcomes in the presence of 1,3 remote Me or (protected) OH; and (iv) practical homologation/ACB/ACA for the construction of 1,3,5 (Me, OH, Me) and 1,3,5 (OH, OH, Me) subunits.

The scale-up reaction was first attempted on acylimidazole **1b** (Scheme 3) bearing a long alkyl chain. Fruitfully, moving from a 0.2 to 2.0 mmol scale proved experimentally more practical and beneficial in terms of isolated yield (84% vs 68%) with no change in the enantiomeric excess (98%).

In order to determine the absolute configuration of the newly formed stereogenic carbon centers, the borylated acylimidazole **5c** was converted into the corresponding ester **6c** and subsequently oxidized in the presence of $NaBO_3$ to the hydroxyl derivative **7c** in 49% yield (over three steps, Scheme 4). The observed rotation (−40, *c* = 1, $CHCl_3$) compares favorably with the rotation described by Zhou for the (*R*) compound (−35.6, *c* = 1, $CHCl_3$).[13] Accordingly, the (*R*) absolute configuration was attributed to compounds **2a**−**g** obtained with (*R*),(R_P)-Taniaphos.[14]

Then, to evaluate the diastereoselectivity outcome in the presence of a remote methyl group, our asymmetric catalytic borylation system was attempted using compound **8** derived from (*R*)-citronellal (Scheme 5).[6] In the presence of (*R*),(R_P)-Taniaphos, the expected compound (3*R*,5*R*)-**9** was obtained in good 75% yield and an excellent >95:5 diastereomeric ratio. The diastereoselectivity for the mismatched pair could then be evaluated using the (*S*) enantiomer of **8** in the presence (*R*), (R_P)-Taniaphos. In this case, the (3*R*,5*S*)-**9** compound was obtained with an excellent >95:5 dr and in 68% yield, which could be improved to 84% at larger scale (2 mmol). Interestingly, the above results evidenced no significant match/mismatch effect and demonstrated that the control of the selectivity is mainly governed by the copper chiral catalyst and is the real benefit of acylimidazoles over esters in these diastereoselective ACB reactions (see Scheme 2).

With the aim of fulfilling the requirements for adequate methodology, the introduction of a third, either Me or OH, stereogenic center was next considered starting from compound (3*R*,5*S*)-**9**. However, the transformation of **9** to the corresponding homologated unsaturated acylimidazole **13** proved more challenging than initially expected. Indeed, after protection of the secondary alcohol of **9** with a TBS or a benzyl group, all attempts to transform the acylimidazole to an ester, aldehyde, or Weinreb amide failed in our hands. Fortunately, the borylated compound **10** (84% yield after ACB) could efficiently be converted to the TBS-protected ester **11**, which was further homologated to the desired functionalized *α*,*β*-unsaturated 2-acyl-*N*-methylimidazole (5*R*,7*S*)-**13** (Scheme 6).

From compound (5*R*,7*S*)-**13**, the ACA reaction was first attempted. As illustrated in Scheme 7, the matched reaction in the presence of **L1** proved efficient. Complete conversion, 81% isolated yield, and an excellent >95:5 diastereoselectivity could be observed. When the same reaction was carried out with *ent*-**L1** a small mismatch effect could be detected (90% conversion and 70% isolated yield) with, however, a very good 94:6 diastereoselectivity.

In related ACB reactions from (5*R*,7*S*)-**13**, the *syn,anti* (3*R*,5*R*,7*S*)-**15** and *anti,anti* (3*S*,5*R*,7*S*)-**15** have been obtained in good yields and excellent diastereoselectivities (>95:5 dr) with no marked differences between the match and mismatch pairs (Scheme 8). Interestingly, the diastereotopic signals of the CH_2 groups (C2 carbon) of the two diastereomers appear very differently in the ^1H NMR spectrum acquired in $CDCl_3$ (Scheme 8).

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In conclusion, Cu/Taniaphos catalyzed efficiently the β-borylation of α,β-unsaturated 2-acyl-*N*-methylimidazoles. After $NaBO_3$-mediated oxidation, the corresponding secondary alcohols were obtained in high yields and enantioselectivities (10 examples, 66−98%). Excellent enantioselectivities (93 to 98% ee) were obtained with aliphatic chains, including functionalized ones, with the exception of γ-branched substrates which gave moderate selectivity (up to 73% ee). Following the readily postfunctionalization of acylimidazole fragment, consecutive Cu-catalyzed ACB/ACA recations were successfully achieved, leading to 1,3,5-(Me, OH, Me) and 1,3,5-(OH, OH, Me) motifs in good yields and excellent stereoinductions (>95:5 dr). We have thus been able to propose a unified strategy for the construction of highly desirable 1,3,5,...*n* (OH, Me) motifs prevalent in biologically relevant molecules. Implementation of this methodology in the total synthesis of natural products is currently underway in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00479.

Spectral data (PDF)
Experimental procedures (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Hertweck, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 4688−4716. (b) Yu, M. J.; Zheng, W.; Seletsky, B. M. *Nat. Prod. Rep.* **2013**, *30*, 1158−1164.

(2) (a) Zheng, K.; Xie, C.; Hong, R. *Front. Chem.* **2015**, *3*, 32. (b) ter Horst, B.; Feringa, B.; Minnaard, A. *Chem. Commun.* **2010**, *46*, 2535−2547. (c) Che, W.; Wen, C. D.; Zhu, S.-F.; Zhou, Q.-L. *Org. Lett.* **2018**, *20*, 3305−3309. (d) Hassan, A.; Lu, Y.; Krische, M. J. *Org. Lett.* **2009**, *11*, 3112−3115. (e) Lu, Y.; Kim, I.; Hassan, A.; Del Valle, D.; Krische, M. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 5018−5021.

(3) (a) Ota, Y.; Murayama, T.; Nozaki, K. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 2857−2861. (b) Balieu, S.; Hallett, G.; Burns, M.; Bootwicha, T.; Studley, J.; Aggarwal, V. *J. Am. Chem. Soc.* **2015**, *137*, 4398−4403.

(4) (a) Mauduit, M.; Baslé, O.; Clavier, H.; Crévisy, C.; Denicourt-Nowicki, A. In *Comprehensive Organic Synthesis II*; Knochel, P., Molander, G. A., Eds.; Elsevier, 2014; Vol. *4*, p 186. (b) For a seminal review dealing with Cu-ACA in natural product synthesis, see: Calvo, B. C.; Buter, J.; Minnaard, A. J. Applications to the synthesis of natural products. In *Copper-Catalyzed Asymmetric Synthesis*; Alexakis, A., Krause, N., Woodward, S., Eds.; Wiley, 2014; Chapter 14, pp 373−447. (c) Cordova, A. *Catalytic Asymmetric Conjugate Reactions*; Wiley-VCH, 2010. (d) Alexakis, A.; Bäckvall, J. E.; Krause, N.; Pàmies, O.; Diéguez, M. *Chem. Rev.* **2008**, *108*, 2796−2823.

(5) For selected references on the use of acylimidazoles as ester surrogates in enantioselective reactions, see: (a) Evans, D. A.; Fandrick, K. R.; Song, H.-J.; Scheidt, K. A.; Xu, R. *J. Am. Chem. Soc.* **2007**, *129*, 10029−10041. (b) Zhang, L.; Meggers, E. *Acc. Chem. Res.* **2017**, *50*, 320−330. (c) Boersma, A. J.; Megens, R. P.; Feringa, B. L.; Roelfes, G. *Chem. Soc. Rev.* **2010**, *39*, 2083−2092.

(6) (a) Drissi-Amraoui, S.; Morin, M.; Crévisy, C.; Baslé, O.; de Figueiredo, R. M.; Mauduit, M.; Campagne, J. M. *Angew. Chem., Int. Ed.* **2015**, *54*, 11830−11834. (b) Drissi-Amraoui, S.; Schmid, T.; Lauberteaux, J.; Crévisy, C.; Baslé, O.; de Figueiredo, R. M.; Halbert, S.; Gérard, H.; Mauduit, M.; Campagne, J. M. *Adv. Synth. Catal.* **2016**, *358*, 2519−2540.

(7) For selected references, see: (a) Lee, J.; Yun, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 145−147. (b) Feng, X.; Yun, J. *Chem. Commun.* **2009**, 6577−6579. (c) O'Brien, J.; Lee, K.; Hoveyda, A. *J. Am. Chem. Soc.* **2010**, *132*, 10630−10633. (d) Park, J.; Lackey, H.; Rexford, M.; Kovnir, K.; Shatruk, M.; McQuade, D. *Org. Lett.* **2010**, *12*, 5008−5011. (e) Sim, H.-S.; Feng, X.; Yun, J. *Chem. - Eur. J.* **2009**, *15*, 1939−1943. (f) Chen, I.; Kanai, M.; Shibasaki, M. *Org. Lett.* **2010**, *12*, 4098−4101. (g) Ibrahem, I.; Breistein, P.; Córdova, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 12036−12041. (h) Moure, A.; Arrayás, R.; Carretero, J. *Chem. Commun.* **2011**, *47*, 6701−6703. (i) Solé, C.; Whiting, A.; Gulyás, H.; Fernández, E. *Adv. Synth. Catal.* **2011**, *353*, 376−384. (j) Kobayashi, S.; Xu, P.; Endo, T.; Ueno, M.; Kitanosono, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 12763−12766. (k) Wu, H.; Radomkit, S.; O'Brien, J. M.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2012**, *134*, 8277−8285. (l) Zhao, L.; Ma, Y.; He, F.; Duan, W.; Chen, J.; Song, C. *J. Org. Chem.* **2013**, *78*, 1677−1681. (m) Luo, Y.; Roy, I. D.; Madec, A. G. E.; Lam, H. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 4186−4190. (n) Xie, J.-B.; Lin, S.; Qiao, S.; Li, G. *Org. Lett.* **2016**, *18*, 3926−3929. (o) Jiang, Q.; Guo, T.; Gao, R.; Wang, Q.; Lou, J.; Yu, Z. *J. Org. Chem.* **2018**, *83*, 7981−7993.

(8) (a) Pujol, A.; Whiting, A. *J. Org. Chem.* **2017**, *82*, 7265−7279. (b) Hartmann, E.; Oestreich, M. *Org. Lett.* **2012**, *14*, 2406−2409.

(9) For selected reviews, see: (a) Westcott, S. A.; Fernandez, E. *Adv. Organomet. Chem.* **2015**, *63*, 39−130. (b) Hemming, D.; Westcott, S. A.; Santos, W. L.; Steel, P. G.; Fritzemeier, R. *Chem. Soc. Rev.* **2018**, *47*, 7477−7494. (c) Neeve, E.; Geier, S.; Mkhalid, I.; Westcott, S.; Marder, T. *Chem. Rev.* **2016**, *116*, 9091−9161.

(10) Tarrieu, R.; Dumas, A.; Thongpaen, J.; Vives, T.; Roisnel, T.; Dorcet, V.; Crévisy, C.; Baslé, O.; Mauduit, M. *J. Org. Chem.* **2017**, *82*, 1880−1887.

(11) For the seminal use of Taniaphos ligand in the ACB reactions of cyclic enones and lactones, see ref 7b.

(12) The relatively low (45%) yield obtained in this reaction is mainly due to the unoptimized oxidation reaction: 10% of the protodeborated compound could also be isolated. Moreover, compound **2j** and pinacol are unseparable by flash chromatography, thus requiring elimination of the pinacol byproduct by evaporation in vacuo. Under these purification conditions, undesired slow sublimation of **2j** could also be observed.

(13) Bao, D.; Wu, H.; Liu, C.; Xie, J.; Zhou, Q. *Angew. Chem., Int. Ed.* **2015**, *54*, 8791−8794.

(14) (*S*) configurations for compounds **2h**, **2i**, and **2j** due to inversed priorities in the CIP system.

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