Alkenes

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Substrate-Assisted, Transition-Metal-Free Diboration of Alkynamides with Mixed Diboron: Regio- and Stereoselective Access to *trans*-1,2-Vinyldiboronates

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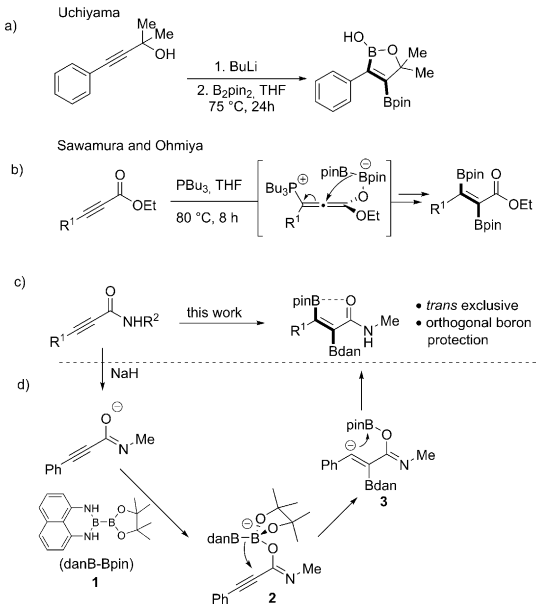
Abstract: *A substrate-assisted diboration of alkynamides using the unsymmetrical pinacolato-1,8-diaminonaphthalenato diboron (pinBBdan) is described. The transition-metal-free reaction proceeds in a regio- and stereoselective fashion to exclusively afford trans-vinyldiboronates in good to excellent yields. Notably, Bdan and Bpin are installed on the α- and β-carbon atoms, respectively.*

Vinylboronic acid derivatives play a pivotal role as key building blocks in the construction of polysubstituted alkenes, which are important structural motifs present in medicines, natural products, and materials science. Control of the stereo- and regiochemistry in these products is typically mediated by cross-coupling reactions such as the Suzuki–Miyaura reaction. As such, vinylboronic acid derivatives bearing multiple boron moieties with chemoselective reactivity are highly desirable. Diboration of alkynes with bis(pinacolato)diboron (B_2pin_2) has been intensely investigated and provides access to vinyldiboronates. However, synthetic approaches that employ transition-metal complexes, such as Pt,[1] Cu,[2] Au,[3] Co,[4] or Fe,[5] exclusively generate 1,2-*cis*-diborylalkenes.[6] Recently, metal-free conditions have been reported. For example, photocatalyzed diborations in the presence of a catalytic amount of diphenyl disulfide under light irradiation,[7] and diborations employing strongly Lewis acidic, unsymmetrical diborane ($pinBBMes_2$),[8] afford the 1,2-diborylalkenes as a mixture of *E*- and *Z*-configured products.

In contrast, diboration reactions of alkynes to generate the *trans*-configured products are scarce. Seminal work by Lin, Marder, Norman et al. reported the first example of cobalt-catalyzed alkyne diboration wherein the *trans* product was formed in a minor amount.[4] Uchiyama and co-workers elegantly utilized a pseudo-intramolecular activation of B_2pin_2, by treating propargylic alcohols with *n*-butyllithium at elevated temperature, to generate the *trans* product (Scheme 1 a).[9] Surprisingly, the pinacol group of one of the boron moieties was deprotected to feature a cyclic oxaborolole and vinyl pinacolboronate. While a lithium counterion is crucial for the reaction, the reaction is limited to secondary and tertiary alcohols. Subsequently, Sawamura, Ohmiya, and co-worker disclosed an organocatalytic protocol which employed tributylphosphine and a series of alkynoates as substrates (Scheme 1 b).[10] Interestingly, the mechanism of the reaction involves the formation of a phosphonium allenolate, which facilitates boryl transfer to afford the *trans* product exclusively. The limitation on the substrate scope as exemplified by these key contributions, and the paucity of protocols, highlight the necessity for the development of alternative strategies for the *trans*-diboration of alkynes. Our group has been interested in the installation of unsymmetrical diboron, pinacolato-1,8-diaminonaphthalenato diboron (pinBBdan; **1**),[11] to unsaturated carbon–carbon bonds.[12]



Scheme 1. Approaches to *trans* diboration of alkynes.

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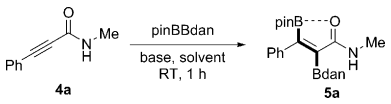
Therefore, we sought to develop a novel diboration protocol that not only provides *trans*-vinyldiboronates but also affords the opportunity for chemoselective functionalization, for example, in cross-coupling reactions (Scheme 1c). Inspired by studies on Lewis base intramolecular diboron activation and transfer,[13] we envisioned that the differential in Lewis acidity of the two boron atoms in pinBBdan could facilitate the selective complexation of a Lewis base to the Bpin moiety, thereby selectively transferring the Bdan group[12,14] to the α-carbon atom (Scheme 1d, **2**).[15] Intramolecular trapping of the resulting anion with Bpin affords the desired *trans*-diborated product.

We initiated our studies by investigating suitable bases to effect the diborylation of *N*-methyl-3-phenylpropiolamide (**4a**) with pinBBdan (Table 1). Organic bases such as pyridine, DBU, and TEA were inefficient (entries 1–3). We surmised that chelation of the metal counterion with a crown ether is key to generating a naked anion, thereby facilitating the formation of a Lewis acid/base complex with **1** to form **2** (Scheme 1d). Therefore, a crown ether was utilized in subsequent studies. Whereas weak bases were ineffective (Table 1, entries 4–7), strong bases such as KO*t*Bu, organolithium, and hydride sources promoted the reaction (entries 8–13). KO*t*Bu was sluggish but NaH was more efficient than BuLi (entries 13 and 14). A survey of solvents revealed THF as the optimal reaction medium (entries 13–17). The optimal reaction conditions afforded the product in 81% yield, as determined by NMR spectroscopy (entry 14), within 1 hour at room temperature. A control reaction without a crown ether as an additive showed diminished reaction yield (entry 18). Further, reaction conditions, which employed triethylphosphine and were developed by Sawamura and Ohmiya, were ineffective (entry 19).[10]

Table 1: Optimization of the reaction conditions using pinB-Bdan.[a]



Entry	Base	Solvent	Crown ether	Yield [%][b]
1	pyridine	THF	–	trace
2	DBU	THF	–	trace
3	TEA	THF	–	trace
4	NaOH	THF	15-crown-5	trace
5	NaOAc	THF	15-crown-5	trace
6	Cs_2CO_3	toluene	18-crown-6	16
7	CsOH	toluene	18-crown-6	27
8	KO*t*Bu	THF	18-crown-6	54
9	LiH	toluene	12-crown-4	14
10	MeLi	toluene	12-crown-4	21
11	BuLi	toluene	12-crown-4	44
12	NaH	toluene	15-crown-5	70
13	BuLi	THF	12-crown-4	71
14	NaH	THF	15-crown-5	81
15	NaH	1,4-dioxane	15-crown-5	74
16	NaH	CPME	15-crown-5	50
17	NaH	CH_3CN	15-crown-5	55
18	NaH	THF	–	50
19	PEt_3	THF	–	0

[a] General procedure: Base (1 equiv), alkynamide (1 equiv), and crown ether (1 equiv) were added in THF (0.29 M, 0 °C to RT) and stirred for 30 min. **1** (1.0 equiv) was added and the reaction was allowed to stir for 1 h. [b] Yields were determined by ^{1}H NMR analysis of the crude reaction mixture after aqueous workup.

Characterization of **5a** by X-ray crystallography unambiguously confirmed a stereoselective *trans* configuration of the two boron moieties and regioselective installation of Bdan on the α-carbon atom and Bpin on the β-carbon atom of the product (Figure 1). Interestingly, the amide oxygen atom is coordinated with Bpin to form a tetracoordinate boron adduct. Indeed, ^{11}B NMR spectroscopy supports the presence of a tricoordinate ($\delta = 27.6$ ppm) and tetracoordinate boron ($\delta = 14.1$ ppm; see the Supporting Information). Such an intramolecular complexation between the carbonyl oxygen atom and boron on the β-carbon atom is observed in solution by ^{11}B NMR studies of all vinyldiboronate products.

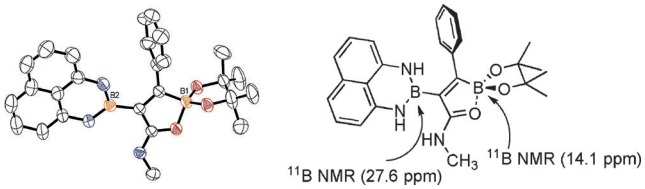
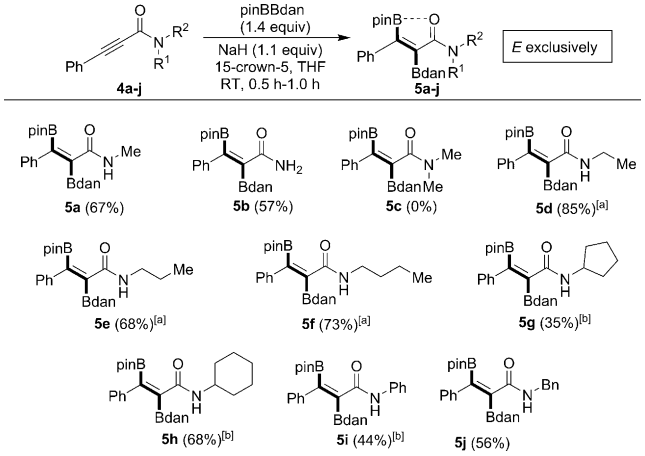


Figure 1. X-ray crystal structure[16] and ^{11}B NMR spectroscopy. Anisotropic displacement ellipsoid drawing (30%) of **5a**. Hydrogen atoms have been omitted for clarity.

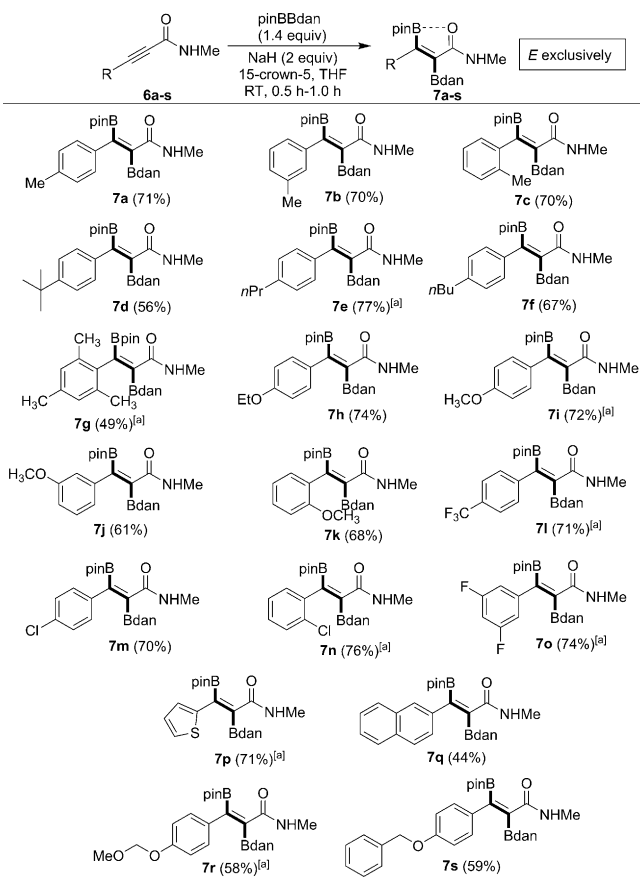
With the optimal reaction conditions in hand (Table 1, entry 14), we investigated the scope and limitations of the *trans*-diboration reaction by employing a variety of N-substituted phenylpropiolamides (Scheme 2). The model reaction with **4a** afforded **5a** in 67% yield upon isolation. While the primary amide **4b** yielded **5b** in good yield, the tertiary amide **4c** was not transformed into the desired product **5c**. This result further supports our prediction that activation of **1** by the alkynamide itself, enabled by increased Lewis basicity upon deprotonation, is required for efficient conversion into the diborylated product. Alkyl substitutions



Scheme 2. Substrate scope of the *trans* diborylation of N-substituted phenylpropiolamides. [a] 2 equiv NaH and 15-crown-5 was used. [b] 4 equiv NaH and 15-crown-5 was used. Heated to 60 °C for 3 h after addition of diboron.

ranging from a small ethyl group (**5d**) to a much larger butyl group (**5f**) provided the desired products in excellent yields. In general, bulkier substituents on the nitrogen atom had a slightly negative impact on the reaction yield and required higher temperatures for efficient conversion. While a cyclohexyl group (**5h**) was efficient (68% yield), cyclopentyl (**5g**), phenyl (**5i**), and benzyl (**5j**) groups were formed in moderate yields.

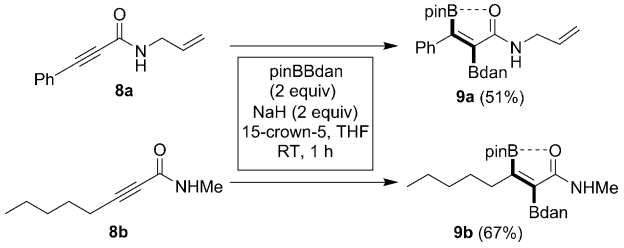
Having established the substrate scope with respect to the amide functionality, we investigated the effect of aryl ring substitution of the alkyne using the reaction conditions. As shown in Scheme 3, aryl rings with *para*-, *meta*-, and *ortho*-



Scheme 3. Substrate scope of *trans* diborylation of aryl-substituted amide substrates. [a] 1.1 equiv NaH and 15-crown-5 was used.

methyl groups were efficiently diborated to the corresponding *trans* products (**7a–c**) in excellent yields. While a 4-*tert*-butylphenyl group at the 4-position afforded **7d** in 56% yield, diborylation rings with alkyl substituents, such as *n*-propyl (**7e**) and *n*-butyl (**7f**), proceeded in excellent yields. A sterically encumbered mesityl group (**6g**) was also efficiently transformed into the vinyldiboronate **7g**. It is noteworthy that alkynamides containing strongly electron-donating groups, such as ethoxy and methoxy substituents, at various positions of the aryl ring (**7h–k**) underwent the *trans* diboration in high yields. Furthermore, phenyl rings with electron-withdrawing groups (trifluoromethyl, chlorine, and fluorine) also performed well under our reaction conditions. The nature of the aromatic ring could also be switched to a heteroatom-containing thiophene (**7p**) or naphthalene unit (**7q**). Alkynamides containing commonly employed protecting groups [methoxymethylether (**7r**) and benzyl ether (**7s**)] also served as efficient substrates. Overall, in all cases, the presence of the *cis* diastereomer was undetectable.

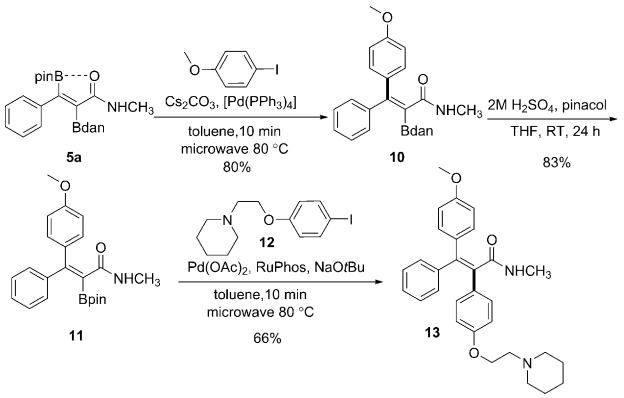
To further test the substrate scope of the developed reaction conditions, we reacted the alkynamide **8a**, bearing an allyl group, with pinBBdan (Scheme 4). The results demon-



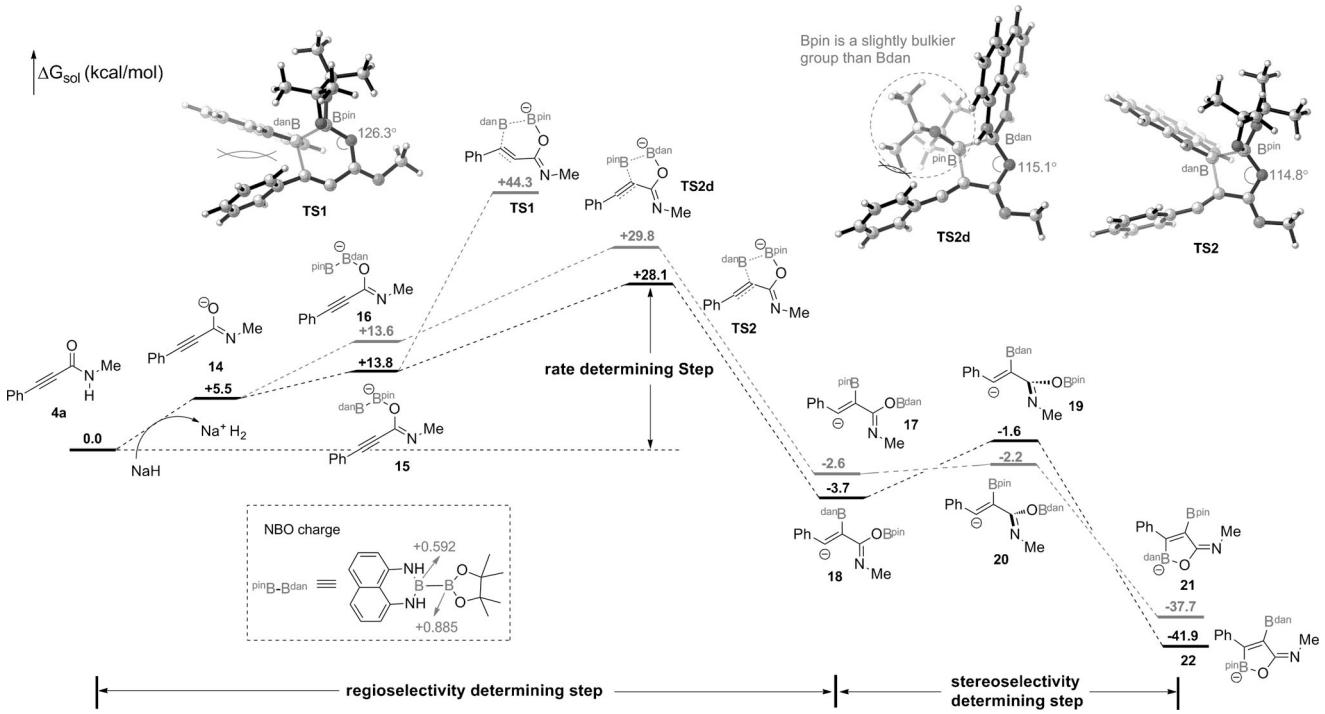
Scheme 4. Substrate scope of the diboration reaction.

strated a chemoselective diboration of the triple bond in the presence of an alkene, thus affording **9a** in 51% yield. To show that the reaction was not limited to alkynamides containing aryl rings, an alkynamide bearing a pentyl group (**8b**) was synthesized and subjected to the same reaction conditions. To our delight, **8b** was efficiently diborated in 67% yield to provide the vinyldiboronate **9b**. These investigations demonstrate the diverse functional-group tolerance of the reaction.

A key advantage of utilizing the unsymmetrical diboron pinBBdan is the orthogonal reactivity of the boron protecting groups. The carbon atom (sp^2) bearing Bpin is significantly more reactive than that of Bdan and can be used to strategically install various groups to generate exhaustively functionalized alkenes. For example, selective estrogen-receptor modulators which are structural derivatives of tamoxifen can be rapidly synthesized. To demonstrate this strategy, *trans* α,β-diborylacrylamide (**5a**) underwent facile Suzuki–Miyaura cross-coupling with 4-iodoanisole using tetrakis(triphenylphosphine)palladium and cesium carbonate under microwave irradiation to afford the 1,1-diarylvinylboronate **10** in 80% yield (Scheme 5). This reaction proceeded



Scheme 5. Chemoselective cross-coupling application.



Scheme 6. DFT calculations for the *trans* diboration of *N*-methyl-3-phenylpropiolamide at the M06/(6-311+G(d,p),SMD)//B3LYP/(6-31+G-(d),SMD) level of theory.

with excellent chemoselectivity. Subsequently, switching the dan protecting group for pinacol occurred smoothly under acidic conditions to generate **11**. To facilitate the second coupling reaction, we used a $Pd(OAc)_2$/RuPhos/NaO*t*Bu catalyst system with **11** and **12** as coupling partners, and installed the piperidinyl ethoxyphenyl group, thus providing the densely functionalized, tetrasubstituted tamoxifen analogue **13** in 66% yield.

To understand the regio- and stereoselectivity of the *trans*-diboration reaction, we performed a detailed DFT investigation as summarized in Scheme 6. Deprotonation with sodium hydride generates the charged Lewis base **14**, which can complex with pinBBdan. In agreement with the findings of Fernandez and co-workers,[14b] preferential activation of the more Lewis-acidic boron in Bpin (NBO charge +0.885) occurs in the presence of Bdan (NBO charge +0.592; compare **15** versus **16**). Although Lewis-base activation of diboron typically results in the addition of the boron moiety on the β-carbon atom,[15] a substrate-assisted, pseudo-intramolecular Bdan transfer in **TS1** has a high activation energy barrier of +44.3 kcal mol^{-1}. In contrast, α addition, such as in **TS2**, requires less energy (+28.1 kcal mol^{-1}) and therefore regioselectively installs Bdan on the α-carbon atom (**18**), and is thermodynamically favorable (**18** versus **17**). Carbon–carbon bond rotation (**19**/**20**) is associated with a small activation energy barrier, which is rapidly proceeded by an energetically favorable intramolecular trapping of Bpin to generate the boronate complex **22**, with a *trans* configuration. Herein, the intramolecular Bdan-transfer process in **TS2** is the rate- and regioselectivity-determining step of the overall transformation. The much higher energy barrier in **TS1** is probably a result of the ring strain of the six-membered ring (compare bond angles in Scheme 6) and steric hindrance between Bdan and phenyl ring. Because of the different electronic properties in Bpin and Bdan, and the slightly larger steric interaction, the energy barrier in **TS2d** is also slightly higher than that of **TS2**. Therefore, the more stable structure of **TS2** can account for the regioselectivity. The stereoselectivity for the *trans* product is due to a rapid carbon–carbon bond rotation process (**18**→**22**), which is highly thermodynamically favorable.

In summary, we have disclosed a transition-metal-free method for the diboration of alkynamides using an unsymmetrical diboron reagent, pinBBdan, which displays broad functional-group tolerance. The corresponding products are afforded in moderate to high yields and regioselectively install Bdan and Bpin on the α- and β-carbon atoms, respectively. Most notably, the diboration reaction proceeds with exclusive formation of the *trans*-configured product. An attractive feature of the orthogonally protected *trans*-1,2-vinyldiboronate is the demonstration of a chemoselective sequential Suzuki–Miyaura cross-coupling reaction to afford densely functionalized alkenes.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkenes · boron · chemoselectivity · cross-coupling · synthetic methods

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[16] CCDC 1523026 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Communications

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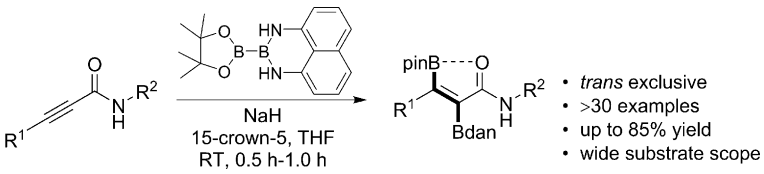

Substrate-Assisted, Transition-Metal-Free Diboration of Alkynamides with Mixed Diboron: Regio- and Stereoselective Access to *trans*-1,2-Vinyldiboronates

Who needs metals? Transition-metal-free diboron activation with alkynamides facilitates the intramolecular formation of differentially protected *trans*-vinyldiboronates. The reaction proceeds in a regio- and stereoselective fashion with Bdan and Bpin installed on the α- and β-carbon atoms, respectively. dan = 1,8-diaminonaphthalene, pin = pinacol.