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三苯基砷/铱催化的非活化一级碳氢键的双硼化反应合成 1,1-偕二硼烷

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摘要 报道了以吡唑作为导向基, 三苯基砷/铱催化的活化一级碳氢键的双硼化反应. 这一方法能够兼容多种官能团, 能够以中等到良好的收率实现一系列 1,1-偕二硼烷类化合物的合成. 同时, 这一方法也能够实现克级规模的反应, 所获得的硼化产物能够实现进一步的转化.

关键词 碳氢键活化; 有机硼; 合成方法; 铱

Synthesis of 1,1-Diboron Alkanes via Diborylation of Unactivated Primary C(sp^3)—H Bonds Enabled by $AsPh_3$/Iridium Catalysis

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Abstract The $AsPh_3$/iridium catalyzed diborylation of unactivated primary C(sp^3)—H bonds using pyrazoles as directing groups was disclosed. This method could tolerate a variety of functional groups, affording a vast array of 1,1-diboron alkanes in moderate to good yields. The synthetic utility of the current method on a gram-scale reaction for further functionalization was also demonstrated.

Keywords C—H borylation; organoboron; synthetic methods; iridium

1 Introduction

Organoboron compounds are a ubiquitous and critically important class of building blocks in synthetic chemistry.[1] In particular, 1,1-diboron alkanes have received intensive attention and they can serve as useful synthons in a vast array of transformations.[2-7] Accordingly, many methods have been developed to construct these frameworks. Besides diborylation of *gem*-haloalkanes,[8] 1,2-metallate shift involves substrates of diazoalkanes,[9] carbenes,[10] carbomates,[11] and carbonyl compounds[12] further expanded scope the 1,1-diboron alkanes. In addition, diborylation of alkenes[13] and alkynes,[14] borylation of alkenylboronates,[15] among others[16] have provided an attractive alternative to 1,1-diboron alkanes. On the other hand, the transition-metal-catalyzed C—H activation approach to 1,1-diboron alkanes has lagged far behind. In this vein, the group of Hartwig used a relay-directed strategy to accomplish iridium-catalyzed diborylation of benzylic primary C(sp^3)—H bonds (Scheme 1A).[17] Chirik and co-workers reported an elegant cobalt-catalyzed diborylation of benzylic primary C(sp^3)—H bonds and unactivated primary C(sp^3)—H bonds (Scheme 1B).[18] However, the reaction suffered from limitations such as high temperature and catalyst loading, low yields, and narrow substrate scope for the unactivated primary C(sp^3)—H bonds. The same group developed diborylation of benzylic secondary C(sp^3)—H bonds enabled by nickel catalysis.[19] Alternatively, the group of Suginome developed a boryl-directed iridium-catalyzed α-C(sp^3)—H borylation approach to 1,1-diboron alkanes (Scheme 1C).[20] Although this method could enable diborylation of unactivated primary C(sp^3)—H bonds, it was accompanied by tri- and tetra- borylation. Despite advances made, achieving highly selective diborylation of unactivated primary C(sp^3)—H bonds under mild reaction conditions remains a formidable challenge.

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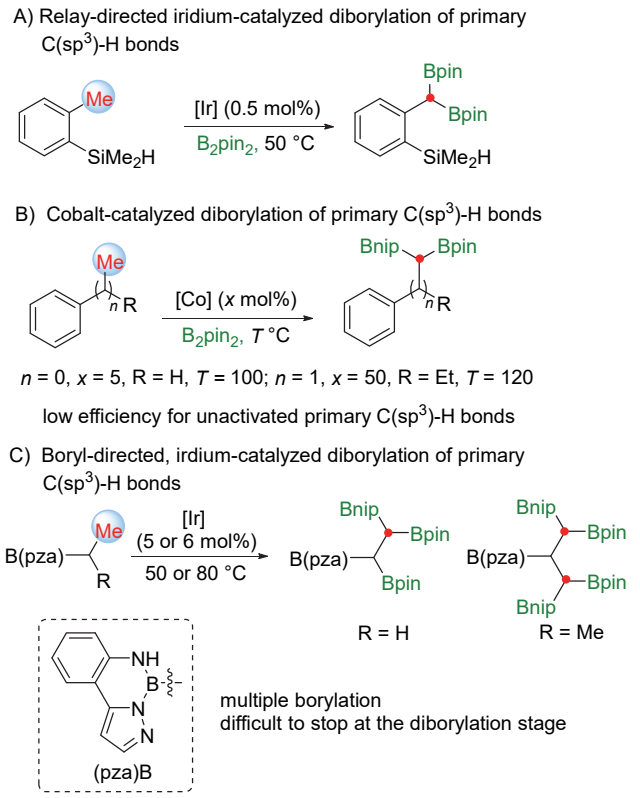
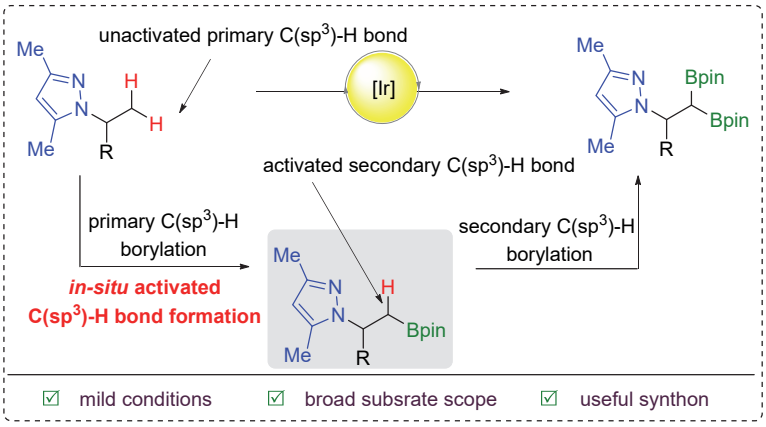


Scheme 1 Representative examples of primary C(sp^3)—H bonds

Recently, iridium- or rhodium-catalyzed functional group directed C—H borylation has emerged as an attractive tool to provide site-controllable organoboron compounds under mild reaction conditions.[21] However, only a few examples of C(sp^3)—H borylation of acyclic compounds are documented in this field.[22] In particular, diborylation of C(sp^3)—H bonds is largely underdeveloped.[17,20] The shortage of research is probably due to the increasing steric hindrance caused by first C(sp^3)—H borylation. It should be noted that the bond dissociation energy (BDE) of the boron-adjacent C(sp^3)—H bond is lower than that of its non-borylated C(sp^3)—H bond.[23] Thus, it is possible to find out a combination of suitable directing group and catalyst being capable of achieving diborylation of unactivated primary C(sp^3)—H bonds. Recently, we developed pyrazole-directed iridium-catalyzed borylation of secondary C(sp^3)—H bonds.[22i,22k] Interestingly, the pyrazole is a relatively strong directing group that is capable of borylating of benzylic secondary C(sp^3)—H bonds without an external ligand.[22k] Inspired by these results, we envisioned that a strategy that involves *in-situ* generated activated secondary C(sp^3)—H bonds from unactivated primary C(sp^3)—H bonds would be able to deliver 1,1-diboron alkanes (Scheme 2).

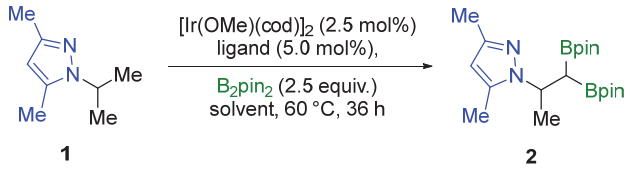
2 Results and discussion

With above considerations in mind, our studies commenced with optimizing reaction conditions for model substrate 1-isopropyl-3,5-dimethyl-1*H*-pyrazole (**1**). Gratifyingly, preliminary reaction of **1** with 2.5 equiv. of bis(pinacolato)diboron (B_2pin_2) in the presence of 2.5 mol% $[Ir(OMe)(cod)]_2$ (cod: 1,5-cyclooctadiene) in *n*-hexane (0.2 mol/L) at 60 ℃ for 36 h afforded desired 1,1-diboron alkane **2** in 63% isolated yield (Table 1, Entry 1). We then focused on other reaction conditions. Ligands such as electron-deficient triarylphosphines and triphenylarsine ($AsPh_3$) have been found to control site-selectivity of iridium-catalyzed functional group directed C—H borylation.[24] Our trials with 5 mol% $P(C_6F_5)_3$ or 5 mol% $P(4\text{-}CF_3\text{-}C_6H_4)_3$, however, met inferior isolated yield of **2** (Table 1, Entries 2 and 3). Pleasingly, the yield of **2** could be elevated to 79% when 5 mol% $AsPh_3$ was used (Table 1, Entry 4). To further improve the reaction performance, several more conditions were examined. Replacement of B_2pin_2 with 2.5 equiv. of HBpin resulted in a trace amount of **2** (Table 1, Entry 5**).** Decreasing catalyst loading (2.0 mol%) caused an obviously diminished yield (59%) (Table 1, Entry 6). A significantly decreased yield (57%) of **2** when the reaction was carried out 50 ℃ (Table, Entry 7). Unfortunately, inferior yield (51%) was also observed with elevated reaction temperature (70 ℃) (Table 1, Entry 8). It was probably caused



Scheme 2 Our strategy to 1,1-diboron alkanes

Table 1 Optimization of reaction conditions for **1**[a]



1 **2**

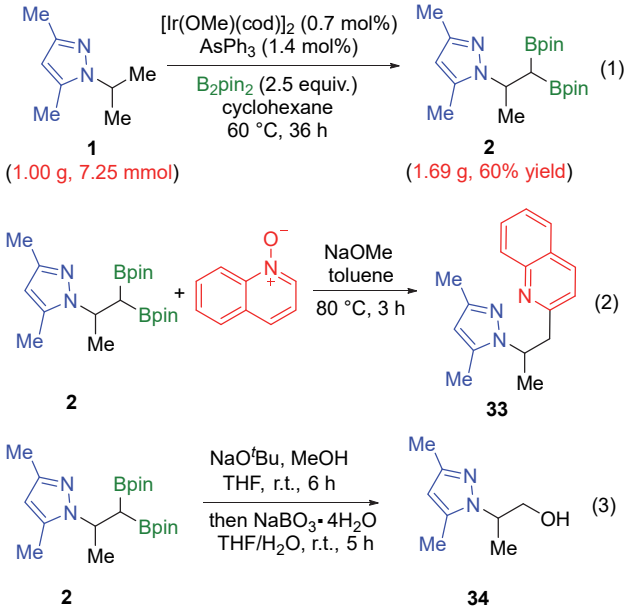
Entry	Ligand	Solvent	Yield[b]/%
1	None	*n*-Hexane	63
2	$P(C_6F_5)_3$	*n*-Hexane	51
3	$P(4\text{-}CF_3\text{-}C_6H_4)_3$	*n*-Hexane	51
4	$AsPh_3$	*n*-Hexane	79
5[c]	$AsPh_3$	*n*-Hexane	Trace
6[d]	$AsPh_3$	*n*-Hexane	59
7[e]	$AsPh_3$	*n*-Hexane	57
8[f]	$AsPh_3$	*n*-Hexane	51
9	$AsPh_3$	Cyclohexane	82
10	$AsPh_3$	THF	51
11	$AsPh_3$	1,4-Dioxane	51

[a] Unless otherwise noted, all the reactions were carried out with **1** (0.20 mmol), B_2pin_2 (0.20 mmol), $[Ir(OMe)(cod)]_2$ (0.005 mmol), and ligand (0.01 mmol) in solvent (1.0 mL) at 60 ℃ for 36 h. [b] Isolated yields. [c] 2.5 equiv. of HBpin was used instead of B_2pin_2. [d] 1.0 mol% $[Ir(OMe)(cod)]_2$ and 2.0 mol% $AsPh_3$ were used. [e] The reaction was carried out at 50 ℃. [f] The reaction was carried out at 70 ℃.

by side reactions because some unidentifiable byproducts were observed at this temperature. Finally, solvent effect revealed that cyclohexane was the optimal and **2** was obtained in 82% yield (Table 1, Entry 9).

With the optimized reaction conditions in hand, the substrate scope of the current reaction as illustrated in Table 2 was then determined. Firstly, the effect of substituent R' at 4 position of pyrazole was examined. Both the methyl and ester groups could be well-tolerated, delivering desired diborylated products **3** and **4** in 71% and 53% yields, respectively. We then move to survey the tolerance of R group. When R was an alkyl chain with length ranging from two to ten carbon units, the corresponding products **5**～**13** were obtained in 40%～74% yields. R of branched alkyl was also compatible. For example, **14** and **15** were obtained in 36% and 79% yields, respectively. The low yield of **14** is probably due to the steric hindrance near the reaction site. Although there is competing reactive benzylic secondary C(sp^3)—H bonds, the reaction of substrate bearing R of benzyl group could also furnish desired diborylated product **16** in 41% yield. The current reaction could also tolerate functional group such as ether and silyl ether, giving **19**～**28** in 30%～74% yields. For benzyl ethers, a *para*-, *meta*-, or *ortho*-substituent in the phenyl ring is compatible, affording **21**～**26** in 30%～70% yields. Pleasingly, the R groups bearing a nucleophile or base sensitive group such as ester and C(sp^3)—Br were well-tolerated. Accordingly, 1,1-diboron alkanes **29**～**32**, including a *Gemfibrozil* derivative, were obtained in 51%～74% yields. Obviously, these products provide promise of more opportunities for diverse downstream transformations. The structure and bond connections of 1,1-diboron alkane **18** (CCDC 2104779) were unambiguously confirmed by single crystal X-ray diffraction analysis.[25]

To further demonstrate the synthetic utility of the current method, a preparative-scale diborylation of **1** and several transformations of **2** were conducted, as shown in Scheme 3. The reaction of **1** (1.00 g, 7.25 mmol) with reduced catalyst loading (1.4 mol%) under concentrated conditions at 60 ℃ for 36 h afforded **2** (1.69 g, 4.35 mmol) in 60% yield (Scheme 3, Eq. 1). The reaction of **2** with quinoline *N*-oxide afforded **33** in 49% yield (Scheme 3, Eq. 2).[26] Treatment of **2** with NaO*t*Bu/MeOH followed by oxidation with $NaBO_3 \cdot 4H_2O$ could furnish **34** in 60% yield (Scheme 3, Eq. 3).



Scheme 3 Gram-scale diborylation of **1** and transformations of **2**

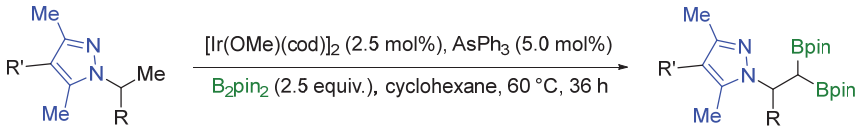
3 Conclusions

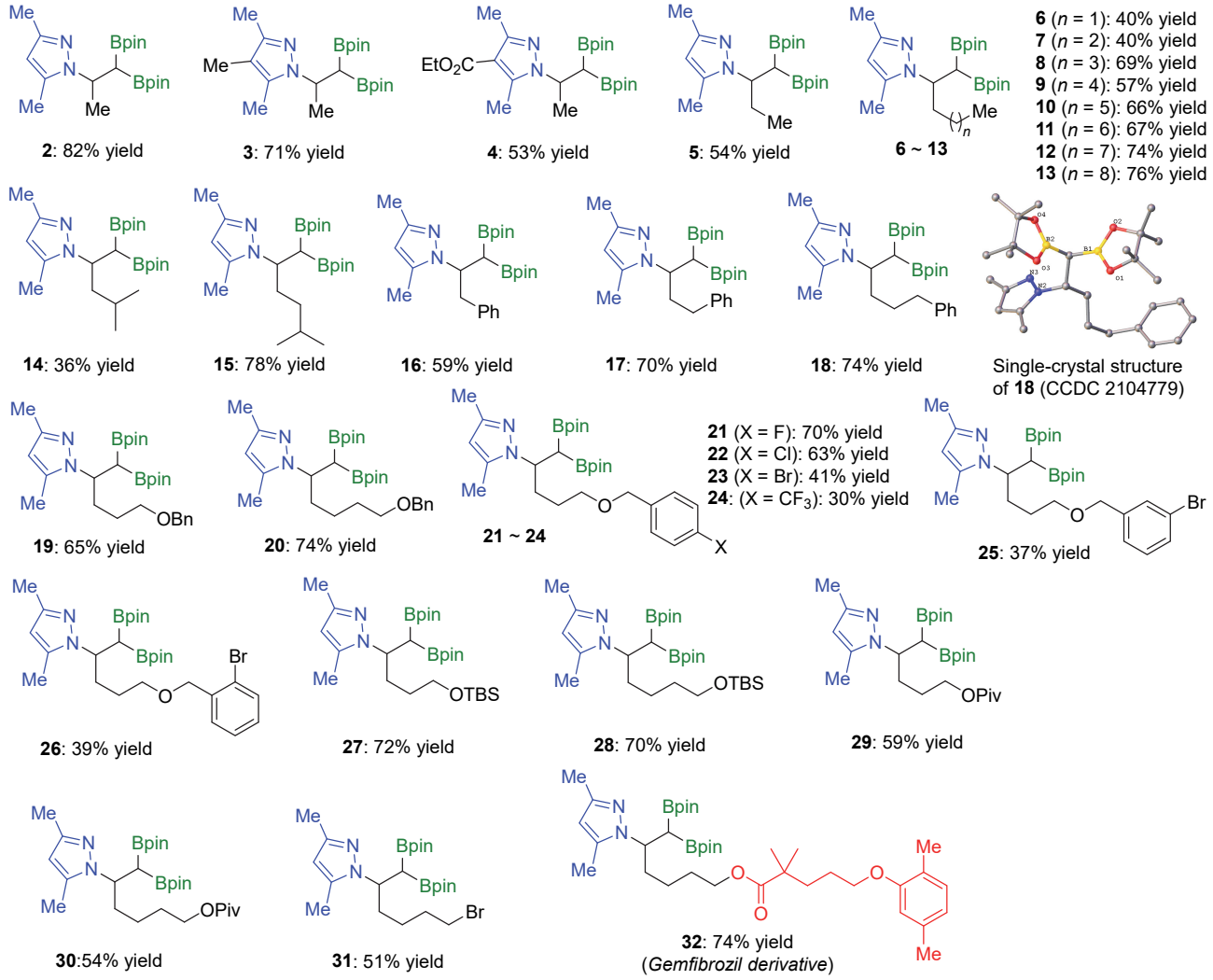
In summary, the $AsPh_3$/iridium catalyst system for the synthesis of 1,1-diboron alkanes via pyrazole-directed diborylation of unactivated primary C(sp^3)—H bonds for the first time has been developed. The current method features mild reactions conditions, wide substrate scope, and broad functional group compatibility. It is also demonstrated that the current method is amendable to preparative-scale diborylation and 1,1-diboron alkanes are useful synthetic intermediates.

4 Experimental section

The preparation of pyrazole substrate was adapted from the literature procedures.[27] B_2pin_2 was recrystallization from *n*-hexane prior to use. All other chemicals and solvents were purchased and used as received. ^1H NMR, ^{13}C NMR, ^{19}F NMR and ^{11}B NMR spectra were recorded on a Bruker DRX400 NMR spectrometer at ambient temperature with $CDCl_3$ as the solvent. High-resolution mass spectroscopy data were obtained on Agilent 6530, Agilent 6224 TOF

Table 2 Substrate scope[a]





[a] Unless otherwise noted, all the reactions were carried out with pyrazole (0.20 mmol), B_2pin_2 (0.50 mmol), $[Ir(OMe)(cod)]_2$ (0.005 mmol), and ligand (0.01 mmol) in cyclohexane (1.0 mL) at 60 ℃ for 36 h.

LC/MS spectrometer. Melting points were determined on an Electrothermal IA9000 Series Digital Melting Point Apparatus.

4.1 General procedures for the diborylation of unactivated primary C(sp^3)—H bonds

To a 25-mL flame-dried Schlenk tube in N_2-filled glovebox charged with substrate (0.2 mmol), $AsPh_3$ (3.1 mg, 0.01 mmol), $[Ir(OMe)(cod)]_2$ (3.3 mg, 0.005 mmol), and B_2pin_2 (127.0 mg, 0.50 mmol) was added cyclohexane (1.0 mL). The resulting mixture was allowed to stir at 60 ℃ for 36 h. After cooled to room temperature and concentrated, the residue was purified by column chromatography on silica gel using PE/EtOAc as the eluent to afford 1,1-diboron alkane.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**2**): R_f=0.3 (PE (petroleum ether)/EA (ethyl acetate), V∶V=7∶1), colorless oil, 64.0 mg, 82% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.63 (s, 1H), 4.58～4.49 (m, 1H), 2.25 (s, 3H), 2.17 (s, 3H), 1.81 (d, J=11.2 Hz, 1H), 1.41 (d, J=6.4 Hz, 3H), 1.25 (s, 6H), 1.23 (s, 6H), 1.04 (s, 6H), 0.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.09, 137.83, 103.80, 83.10, 82.67, 52.03, 24.85, 24.39, 23.97, 13.56, 11.10; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.1; HRMS (ESI-TOF) calcd for $C_{20}H_{36}B_2N_2NaO_4$ $[M+Na]^+$ 413.2761 , found 413.2757.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propan-2-yl)-3,4,5-trimethyl-1*H*-pyrazole (**3**): R_f = 0.2 (PE/EA, V∶V=7∶1), colorless oil, 57.4 mg, 71% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.58～4.49 (m, 1H), 2.16 (s, 3H), 2.13 (s, 3H), 1.84 (s, 3H), 1.72 (d, J=10.8 Hz, 1H), 1.40 (d, J=6.4 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H), 1.03 (s, 6H), 0.98 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 144.46, 134.80, 110.19, 83.06, 82.46, 52.41, 24.89, 24.52, 24.45, 23.96, 11.72, 9.60, 7.89; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 33.4; HRMS (ESI-TOF) calcd for $C_{21}H_{39}B_2N_2O_4$ $[M+H]^+$ 405.3098, found 405.3097.

Ethyl 1-(1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)-3,5-dimethyl-1*H*-pyrazole-4-carboxylate (**4**): R_f=0.2 (PE/EA, V∶V=7∶1), colorless oil, 49.0 mg, 53% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.65～4.56 (m, 1H), 4.29～4.20 (m, 2H), 2.53 (s, 3H), 2.35 (s, 3H), 1.83 (d, J=11.2 Hz, 1H), 1.39 (d, J=6.4 Hz, 3H), 1.32 (t, J=6.8 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H), 1.03 (s, 6H), 0.94 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 165.11, 149.78, 143.16, 108.23, 83.31, 82.96, 59.16, 52.20, 24.85, 24.41, 24.36, 24.19, 23.56, 14.45, 14.40, 11.01; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.1; HRMS (ESI-TOF) calcd for $C_{23}H_{41}B_2N_2O_6$ $[M+H]^+$ 463.3153, found 463.3152.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-butan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**5**): R_f = 0.2 (PE/EA, V∶V=7∶1), colorless oil, 43.6 mg, 54% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.61 (s, 1H), 4.26 (td, J=10.8, 4.0 Hz, 1H), 2.25 (s, 3H), 2.17 (s, 3H), 1.84～1.80 (m, 3H), 1.24 (s, 6H), 1.22 (s, 6H), 1.01 (s, 6H), 0.98 (s, 6H), 0.61 (t, J=7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.45, 139.45, 103.20, 83.08, 82.70, 57.55, 31.18, 24.82, 24.41, 24.31, 13.61, 11.33, 10.87; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.2; HRMS (ESI-TOF) calcd for $C_{21}H_{38}B_2N_2NaO_4$ $[M+Na]^+$ 427.2817, found 427.2912.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pentan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**6**): R_f = 0.2 (PE/EA, V∶V=7∶1), colorless oil, 33.5 mg, 40% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.59 (s, 1H), 4.34 (td, J=11.2, 2.8 Hz, 1H), 2.24 (s, 3H), 2.15 (s, 3H), 1.90～1.79 (m, 2H), 1.66～1.59 (m, 1H), 1.27～0.97 (m, 14H), 1.00 (s, 6H), 0.97 (s, 6H), 0.80 (d, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.38, 139.25, 103.21, 83.08, 82.69, 55.99, 40.52, 24.86, 24.40, 24.38, 24.31, 19.49, 13.79, 13.62, 11.32; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.2; HRMS (ESI-TOF) calcd for $C_{23}H_{40}B_2N_2NaO_4$ $[M+Na]^+$ 441.3074, found 441.3067.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-hexan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**7**): R_f = 0.2 (PE/EA, V∶V=7∶1), colorless oil, 34.6 mg, 40% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.60 (s, 1H), 4.37～4.30 (m, 1H), 2.25 (s, 3H), 2.16 (s, 3H), 1.92～1.80 (m, 2H), 1.24～1.21 (m, 16H), 1.00 (s, 6H), 0.98 (s, 6H), 0.81 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.45, 139.31, 102.27, 83.13, 82.75, 56.19, 37.95, 28.43, 24.88, 24.41, 24.37, 24.32, 22.31, 13.91, 13.58, 11.34; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.3; HRMS (ESI-TOF) calcd for $C_{23}H_{43}B_2N_2O_4$ $[M+H]^+$ 433.3412, found 433.3413.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-heptan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**8**): R_f=0.2 (PE/EA=8∶1), 61.5 mg, 69% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.60 (s, 1H), 4.36～4.31 (m, 1H), 2.25 (s, 3H), 2.16 (s, 3H), 1.90～1.80 (m, 2H), 1.69～1.64 (m, 1H), 1.28～1.21 (m, 18H), 1.01 (s, 6H), 0.98 (s, 6H), 0.81 (t, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.33, 139.23, 103.21, 83.06, 82.67, 56.15, 38.15, 31.12, 25.86, 24.86, 24.40, 24.37, 24.31, 22.41, 13.94, 13.62, 11.35; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.0; HRMS (ESI-TOF) calcd for $C_{24}H_{45}B_2N_2O_4$ $[M+H]^+$ 447.3568, found 447.3559.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-octan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**9**): R_f = 0.2 (PE/EA=8∶1), colorless oil, 52.4 mg, 57% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.60 (s, 1H), 4.37～4.30 (m, 1H), 2.25 (s, 3H), 2.17 (s, 3H), 1.94～1.80 (m, 2H), 1.72～1.64 (m, 1H), 1.25～1.18 (m, 20H), 1.01 (s, 6H), 0.98 (s, 6H), 0.83 (t, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.36, 139.25, 103.23, 83.08, 82.69, 56.15, 38.16, 31.64, 28.87, 26.14, 24.86, 24.39, 24.36, 24.30, 22.53, 14.00, 13.60, 11.34; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.1; HRMS (ESI-TOF) calcd for $C_{25}H_{47}B_2N_2O_4$ $[M+H]^+$ 461.3725, found 461.3717.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-nonan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**10**): R_f = 0.2 (PE/EA, V∶V=9∶1), colorless oil, 62.6 mg, 66% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.59 (s, 1H), 4.35～4.28 (m, 1H), 2.24 (s, 3H), 2.15 (s, 3H), 1.92～1.79 (m, 2H), 1.71～1.62 (m, 1H), 1.25～1.17 (m, 22H), 1.00 (s, 6H), 0.97 (s, 6H), 0.83 (t, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.33, 139.24, 103.21, 83.06, 82.66, 56.14, 38.13, 31.76, 29.17, 29.08, 26.18, 24.86, 24.39, 24.35, 24.30, 22.60, 14.02, 13.61, 11.35; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 31.9; HRMS (ESI-TOF) calcd for $C_{26}H_{49}B_2N_2O_4$ $[M+H]^+$ 475.3882, found 475.3874.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-decan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**11**): R_f = 0.2 (PE/EA, V∶V=9∶1), colorless oil, 65.4 mg, 67% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.60 (s, 1H), 4.36～4.29 (m, 1H), 2.24 (s, 3H), 2.16 (s, 3H), 1.92～1.79 (m, 2H), 1.72～1.63 (m, 1H), 1.25～1.18 (m, 24H), 1.00 (s, 6H), 0.97 (s, 6H), 0.84 (t, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.38, 139.28, 103.24, 83.09, 82.69, 56.16, 38.16, 31.83, 29.38, 29.22, 26.19, 24.88, 24.40, 24.36, 24.32, 22.61, 14.06, 13.61, 11.37; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.4; HRMS (ESI-TOF) calcd for $C_{27}H_{51}B_2N_2O_4$ $[M+H]^+$ 489.4039, found 489.4028.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-undecan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**12**): R_f = 0.2 (PE/EA, V∶V=9∶1), colorless oil, 74.3 mg, 74% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.59 (s, 1H), 4.36～4.29 (m, 1H), 2.24 (s, 3H), 2.15 (s, 3H), 1.89～1.79 (m, 2H), 1.69～1.66 (m, 1H), 1.25～1.17 (m, 26H), 1.00 (s, 6H), 0.97 (s, 6H), 0.85 (t, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.39, 139.26, 103.25, 83.09, 82.71, 56.17, 38.17, 31.84, 29.50, 29.41, 29.25, 29.21, 26.19, 24.87, 24.40, 24.37, 24.31, 22.62, 14.04, 13.59, 11.35; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 31.9; HRMS (ESI-TOF) calcd for $C_{28}H_{53}B_2N_2O_4$ $[M+H]^+$ 503.4196 , found 503.4188.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-

dodecan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**13**): R_f = 0.2 (PE/EA, *V*∶*V*=9∶1), colorless oil, 78.4 mg, 76% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 5.57 (s, 1H), 4.34～4.27 (m, 1H), 2.22 (s, 3H), 2.14 (s, 3H), 1.90～1.77 (m, 2H), 1.69～1.62 (m, 1H), 1.25～1.17 (m, 28H), 0.98 (s, 6H), 0.96 (s, 6H), 0.82 (t, *J*=6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 146.33, 139.20, 103.21, 83.04, 82.66, 56.14, 38.83, 31.82, 29.52, 29.37, 29.23, 29.18, 26.15, 24.83, 24.37, 24.34, 24.28, 22.58, 14.00, 13.56, 11.30; ^{11}B NMR ($CDCl_3$, 128 MHz) *δ*: 31.8; HRMS (ESI-TOF) calcd for $C_{29}H_{55}B_2N_2O_4$ $[M+H]^+$ 517.4352, found 517.4350.

3,5-Dimethyl-1-(4-methyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)-1*H*-pyrazole (**14**): R_f=0.2 (PE/EA, *V*∶*V*=7∶1), colorless oil, 31.1 mg, 36% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 5.59 (s, 1H), 4.46～4.38 (m, 1H), 2.27 (s, 3H), 2.15 (s, 3H), 2.01～1.95 (m, 1H), 1.76 (d, *J*=13.2 Hz, 1H), 1.42～1.37 (m, 1H), 1.23 (s, 6H), 1.21 (s, 6H), 1.16～1.07 (m, 1H), 1.00 (s, 6H), 0.98 (s, 6H), 0.89 (d, *J*=6.4 Hz, 3H), 0.74 (d, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 146.43, 139.21, 103.45, 83.11, 82.73, 54.53, 47.72, 24.97, 24.88, 24.44, 24.34, 24.31, 23.48, 22.00, 13.54, 11.37; ^{11}B NMR ($CDCl_3$, 128 MHz) *δ*: 31.9; HRMS (ESI-TOF) calcd for $C_{23}H_{43}B_2N_2O_4$ $[M+H]^+$ 433.3412, found 433.3407.

3,5-Dimethyl-1-(5-methyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)-1*H*-pyrazole (**15**): R_f=0.2 (PE/EA, *V*∶*V*=7∶1), colorless oil, 69.6 mg, 78% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 5.58 (s, 1H), 4.32～4.26 (m, 1H), 2.23 (s, 3H), 2.14 (s, 3H), 1.90～1.79 (m, 2H), 1.75～1.66 (m, 1H), 1.48～1.36 (m, 2H), 1.22 (s, 6H), 1.20 (s, 6H), 1.00～0.85 (m, 13H), 0.84～0.75 (m, 7H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 146.34, 139.24, 103.24, 83.08, 82.69, 56.37, 36.03, 35.35, 27.58, 24.86, 24.39, 24.34, 24.28, 22.58, 22.41, 13.53, 11.32; ^{11}B NMR ($CDCl_3$, 128 MHz) *δ*: 32.1; HRMS (ESI-TOF) calcd for $C_{24}H_{45}B_2N_2O_4$ $[M+H]^+$ 447.3568, found 447.3567.

3,5-Dimethyl-1-(3-phenyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)-1*H*-pyrazole (**16**): R_f=0.2 (PE/EA, *V*∶*V*=6∶1), colorless oil, 55.0 mg, 59% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.12～7.10 (m, 3H), 6.80～6.77 (m, 2H), 5.43 (s, 1H), 4.44～4.37 (m, 1H), 3.13～2.99 (m, 2H), 2.20 (s, 3H), 2.02 (d, *J*=11.6 Hz, 1H), 1.51 (s, 3H), 1.30 (s, 6H), 1.29 (s, 6H), 1.00 (s, 6H), 0.96 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 146.61, 140.11, 139.84, 129.13, 127.84, 125.97, 102.81, 83.30, 82.85, 58.74, 44.50, 25.07, 24.39, 24.26, 13.65, 10.28; ^{11}B NMR ($CDCl_3$, 128 MHz) *δ*: 32.7; HRMS (ESI-TOF) calcd for $C_{26}H_{41}B_2N_2O_4$ $[M+H]^+$ 467.3256, found 467.3246.

3,5-Dimethyl-1-(4-phenyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)-1*H*-pyrazole (**17**): R_f=0.2 (PE/EA, *V*∶*V*=6∶1), colorless oil, 67.2 mg, 70% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.19～7.13 (m, 2H), 7.08～7.04 (m, 3H), 5.55 (s, 1H), 4.36～4.30 (m, 1H), 2.22～2.16 (m, 4H), 2.13 (s, 3H), 2.06 (s, 3H), 1.78 (d, *J*=11.6 Hz, 1H), 1.17 (s, 6H), 1.16 (s, 6H), 0.94 (s, 6H), 0.92 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 146.76, 141.78, 139.56, 128.33, 128.12, 125.52, 103.43, 83.20, 82.80, 55.47, 38.81, 32.18, 24.94, 24.43, 24.29, 13.64, 11.23; ^{11}B NMR ($CDCl_3$, 128 MHz) *δ*: 33.3; HRMS (ESI-TOF) calcd for $C_{27}H_{43}B_2N_2O_4$ $[M+H]^+$ 481.3413, found 481.3409.

3,5-Dimethyl-1-(5-phenyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)-1*H*-pyrazole (**18**): R_f=0.2 (PE/EA, *V*∶*V*=7∶1), white solid, m.p.=112～114 ℃, 73.1 mg, 74% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.15 (t, *J*=7.2 Hz, 2H), 7.07～7.01 (m, 3H), 6.80～6.77 (m, 2H), 5.53 (s, 1H), 4.32～4.25 (m, 1H), 2.50～2.37 (m, 2H), 2.18 (s, 3H), 2.10 (s, 3H), 1.90～1.84 (m, 1H), 1.76 (d, *J*=11.2 Hz, 1H), 1.70～1.64 (m, 1H), 1.35～1.26 (m, 2H), 1.12 (s, 6H), 1.08 (s, 6H), 0.94 (s, 6H), 0.91 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 146.60, 142.50, 139.32, 128.41, 128.15, 125.52, 103.41, 83.15, 82.81, 55.16, 37.68, 35.43, 27.93, 24.81, 24.43, 24.34, 13.64, 11.42; ^{11}B NMR ($CDCl_3$, 128 MHz) *δ*: 32.2; HRMS (ESI-TOF) calcd for $C_{28}H_{45}B_2N_2O_4$ $[M+H]^+$ 495.3570, found 495.3570.

1-(5-(Benzyloxy)-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**19**): R_f=0.2 (PE/EA, *V*∶*V*=4∶1), colorless oil, colorless oil, 68.1 mg, 65% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.33～7.22 (m, 5H), 5.60 (s, 1H), 4.46 (s, 2H), 4.45～4.33 (m, 1H), 3.36 (t, *J*=6.4 Hz, 2H), 2.23 (s, 3H), 2.16 (s, 3H), 1.91～1.85 (m, 2H), 1.84 (d, *J*=11.6 Hz, 1H), 1.49～1.36 (m, 1H), 1.24～1.20 (m, 13H), 1.01 (s, 6H), 0.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 146.57, 139.33, 138.65, 128.20, 127.52, 127.31, 103.40, 83.14, 82.76, 72.68, 70.18, 56.03, 34.67, 26.59, 24.82, 24.38, 24.37, 24.29, 13.58, 11.29; ^{11}B NMR ($CDCl_3$, 128 MHz) *δ*: 31.7; HRMS (ESI-TOF) calcd for $C_{29}H_{47}B_2N_2O_5$ $[M+H]^+$ 525.3676, found 525.3668.

1-(6-(Benzyloxy)-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**20**): R_f=0.2 (PE/EA, *V*∶*V*=4∶1), colorless oil, 79.6 mg, 74% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.34～7.27 (m, 5H), 5.61 (s, 1H), 4.45 (s, 2H), 4.40～4.31 (m, 1H), 3.43～3.32 (m, 2H), 2.25 (s, 3H), 2.16 (s, 3H), 1.98～1.87 (m, 1H), 1.83 (d, *J*=11.6 Hz, 1H), 1.76～1.70 (m, 2H), 1.64～1.47 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H), 1.01 (s, 6H), 0.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 146.51, 139.34, 138.72, 128.28, 127.58, 127.39, 103.33, 83.14, 82.76, 72.81, 70.34, 56.11, 38.01, 26.69, 24.89, 24.44, 24.42, 24.33, 13.65, 11.36 ^{11}B NMR ($CDCl_3$, 128 MHz) *δ*: 33.1; HRMS (ESI-TOF) calcd for $C_{30}H_{49}B_2N_2O_5$ $[M+H]^+$ 539.3832, found 539.3829.

1-(5-((4-Fluorobenzyl)oxy)-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**21**): R_f=0.2 (PE/EA, *V*∶*V*=4∶1), colorless oil, 75.9 mg, 70% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.29～7.25 (m, 2H), 6.99 (t, *J*=8.4 Hz, 2H), 5.60 (s, 1H), 4.40～4.33 (m, 3H), 3.34 (t, *J*=6.8 Hz, 2H), 2.23 (s, 3H), 2.16 (s, 3H), 1.98～1.86 (m, 2H), 1.84 (d, *J*=11.2 Hz, 1H), 1.45～1.33 (m, 1H), 1.23 (s, 6H), 1.21 (s, 6H), 1.02 (s, 6H), 0.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 162.16 (d, *J*=243.4 Hz), 146.56, 139.29, 134.40, 129.21 (d, *J*=8.0 Hz), 114.99 (d, *J*=11.3 Hz), 103.38, 83.12, 82.75, 71.92, 70.17, 55.98, 34.62, 26.53, 24.81, 24.38, 24.36, 24.27, 13.59,

11.28; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −115.44; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 31.7; HRMS (ESI-TOF) calcd for $C_{29}H_{46}FB_2N_2O_5$ $[M+H]^+$ 543.3581, found 543.3571.

1-(5-((4-Chlorobenzyl)oxy)-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**22**): R_f=0.2 (PE/EA, *V*∶*V*=4∶1), colorless oil, 70.4 mg, 63% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.29～7.22 (m, 4H), 5.60 (s, 1H), 4.40～4.33 (m, 3H), 3.38～3.32 (m, 2H), 2.23 (s, 3H), 2.16 (s, 3H), 1.95～1.81 (m, 3H), 1.45～1.34 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H), 1.01 (s, 6H), 0.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.57, 139.29, 137.20, 133.00, 128.78, 128.31, 103.39, 83.12, 82.75, 71.82, 70.26, 55.98, 34.58, 26.51, 24.81, 24.37, 24.35, 24.26, 13.57, 11.27; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 31.4; HRMS (ESI-TOF) calcd for $C_{29}H_{46}ClB_2N_2O_5$ $[M+H]^+$ 559.3276, found 595.3285.

1-(5-((4-Bromobenzyl)oxy)-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**23**): R_f=0.2 (PE/EA, *V*∶*V*=4∶1), colorless oil, 48.2 mg, 41% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.43 (d, *J*=8.0 Hz, 2H), 7.17 (d, *J*=8.0 Hz, 2H), 5.60 (s, 1H), 4.40～4.33 (m, 3H), 3.36～3.32 (m, 2H), 2.23 (s, 3H), 2.16 (s, 3H), 1.92～1.81 (m, 3H), 1.44～1.38 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H), 1.01 (s, 6H), 0.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.62, 139.33, 137.77, 131.32, 129.15, 121.15, 103.43, 83.17, 82.80, 71.89, 70.32, 56.02, 34.62, 26.55, 24.85, 24.41, 24.40, 24.30, 13.61, 11.31; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 31.3; HRMS (ESI-TOF) calcd for $C_{29}H_{46}BrB_2N_2O_5$ $[M+H]^+$ 603.2783, found 603.2780.

1-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-((4-(trifluoromethyl)benzyl)oxy)pentan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**24**): R_f=0.2 (PE/EA, *V*∶*V*=4∶1), colorless oil, 35.5 mg, 30% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.55 (d, *J*=8.4 Hz, 2H), 7.40 (d, *J*=8.0 Hz, 2H), 5.59 (s, 1H), 4.46 (s, 2H), 4.40～4.33 (m, 1H), 3.38～3.34 (m, 2H), 2.22 (s, 3H), 2.15 (s, 3H), 1.98～1.81 (m, 3H), 1.45～1.35 (m, 2H), 1.22 (s, 6H), 1.20 (s, 6H), 1.01 (s, 6H), 0.98 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.63, 142.89, 138.32, 127.43, 125.16, 125.12, 103.42, 83.16, 82.80, 71.83, 70.52, 56.00, 34.58, 26.54, 24.82, 24.40, 24.37, 24.29, 13.60, 11.29; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 31.8; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −62.50; HRMS (ESI-TOF) calcd for $C_{30}H_{46}F_3B_2N_2O_5$ $[M+H]^+$ 593.3553, found 593.3548.

1-(5-((3-Bromobenzyl)oxy)-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**25**): R_f=0.2 (PE/EA, *V*∶*V*=4∶1), colorless oil, 44.5 mg, 37% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.46 (s, 1H), 7.39 (d, *J*=7.6 Hz, 1H), 7.23 (d, *J*=7.6 Hz, 1H), 7.17 (t, *J*=7.6 Hz, 1H), 5.61 (s, 1H), 4.44～4.33 (m, 3H), 3.35 (t, *J*=6.8 Hz, 2H), 2.24 (s, 3H), 2.16 (s, 3H), 1.97～1.82 (m, 3H), 1.47～1.38 (m, 2H), 1.24 (s, 6H), 1.21 (s, 6H), 1.02 (s, 6H), 0.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.64, 141.12, 139.39, 130.40, 129.80, 125.93, 122.41, 103.46, 83.19, 82.80, 71.85, 70.46, 56.05, 34.63, 26.55, 24.88, 24.41, 24.38, 24.31, 13.60, 11.33; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.0; HRMS (ESI-TOF) calcd for $C_{29}H_{46}BrB_2N_2O_5$ $[M+H]^+$ 603.2783, found 603.2784.

1-(5-((2-Bromobenzyl)oxy)-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**26**): R_f=0.2 (PE/EA, *V*∶*V*=4∶1), colorless oil, 47.0 mg, 39% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.49 (d, *J*=7.6 Hz, 1H), 7.45 (d, *J*=7.6 Hz, 1H), 7.30～7.25 (m, 1H), 7.13～7.09 (m, 1H), 5.61 (s, 1H), 4.48 (s, 2H), 4.42～4.35 (m, 1H), 3.46～3.41 (m, 2H), 2.26 (s, 3H), 2.17 (s, 3H), 1.97～1.89 (m, 2H), 1.85 (d, *J*=11.6 Hz, 1H), 1.51～1.41 (m, 1H), 1.25～1.20 (m, 13H), 1.02 (s, 6H), 0.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.58, 139.31, 138.06, 132.27, 128.70, 128.55, 127.22, 122.35, 103.42, 83.14, 82.76, 71.86, 70.68, 56.05, 34.66, 26.10, 24.83, 24.39, 24.30, 13.63, 11.35; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 31.4; HRMS (ESI-TOF) calcd for $C_{29}H_{46}BrB_2N_2O_5$ $[M+H]^+$ 603.2783, found 603.2780.

1-(5-((*tert*-Butyldimethylsilyl)oxy)-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**27**): R_f=0.2 (PE/EA, *V*∶*V*=6∶1), colorless oil, 78.9 mg, 72% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.59 (s, 1H), 4.37～4.30 (m, 1H), 3.49～3.44 (m, 2H), 2.24 (s, 3H), 2.15 (s, 3H), 1.85～1.80 (m, 3H), 1.34～1.27 (m, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.06～0.98 (m, 13H), 0.84 (s, 9H), −0.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.50, 139.26, 103.40, 83.14, 82.75, 63.12, 56.24, 34.66, 29.78, 25.97, 24.82, 24.47, 24.43, 24.32, 18.30, 13.58, 11.34, -5.34; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.3; HRMS (ESI-TOF) calcd for $C_{28}H_{55}B_2N_2O_5Si$ $[M+H]^+$ 549.4071, found 549.4064.

1-(6-((*tert*-Butyldimethylsilyl)oxy)-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**28**): R_f=0.2 (PE/EA, *V*∶*V*=6∶1), colorless oil, 78.7 mg, 70% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.60 (s, 1H), 4.38～4.30 (m, 1H), 3.55～3.48 (m, 2H), 2.25 (s, 3H), 2.17 (s, 3H), 1.95～1.81 (m, 2H), 1.72～1.68 (m, 1H), 1.48～1.38 (m, 4H), 1.25 (s, 6H), 1.23 (s, 6H), 1.01 (s, 6H), 0.99 (s, 6H), 0.85 (s, 9H), −0.01 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.47, 139.29, 103.28, 83.11, 82.73, 63.11, 56.18, 38.06, 32.60, 25.94, 24.88, 24.43, 24.41, 24.32, 22.59, 18.30, 13.64, 11.36, −5.32; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 33.6; HRMS (ESI-TOF) calcd for $C_{29}H_{57}B_2N_2O_5Si$ $[M+H]^+$ 563.4228, found 563.4226.

4-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl pivalate (**29**): R_f=0.2 (PE/EA, *V*∶*V*=4∶1), white solid, m.p. 89～90 ℃, 59.2 mg, 59% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.61 (s, 1H), 4.38～4.30 (m, 1H), 3.97～3.88 (m, 2H), 2.25 (s, 3H), 2.15 (s, 3H), 1.92～1.80 (m, 3H), 1.44～1.37 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H), 1.15 (s, 9H), 1.00 (s, 6H), 0.98 (s, 6H), 0.85 (s, 9H), −0.01 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.52, 146.73, 139.30, 103.50, 83.21, 82.84, 64.25, 55.88, 38.66, 34.51, 27.19, 25.65, 24.82, 24.50, 24.46, 24.30, 13.60, 11.33; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.1; HRMS (ESI-TOF) calcd for $C_{27}H_{49}B_2N_2O_6$ $[M+H]^+$ 518.3808, found 518.3809.

5-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-6,6-bis(4,4,5,5-tetra-

methyl-1,3,2-dioxaborolan-2-yl)hexyl pivalate (**30**): R_f=0.2 (PE/EA, V∶V=4∶1), colorless oil, 55.5 mg, 54% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.59 (s, 1H), 4.36～4.29 (m, 1H), 3.95 (t, J=6.4 Hz, 2H), 2.24 (s, 3H), 2.14 (s, 3H), 1.95～1.89 (m, 1H), 1.82 (d, J=11.6 Hz, 1H), 1.75～1.70 (m, 1H), 1.57～1.46 (m, 2H), 1.25～1.21 (m, 14H), 1.13 (s, 9H), 1.00 (s, 6H), 0.98 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.48, 146.58, 139.23, 103.38, 83.17, 82.79, 64.09, 55.95, 38.65, 37.64, 28.25, 27.13, 24.88, 24.40, 24.39, 24.29, 22.54, 13.60, 11.34; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 33.5; HRMS (ESI-TOF) calcd for $C_{28}H_{50}B_2N_2NaO_6$ $[M+Na]^+$ 539.3808 , found 539.3799.

1-(6-Bromo-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)-3,5-dimethyl-1*H*-pyrazole (**31**): R_f=0.2 (PE/EA, V∶V=6∶1), white solid, m.p. 116～118 ℃, 52.0 mg, 51% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.59 (s, 1H), 4.32 (td, J=10.8, 2.8 Hz, 1H), 3.56～3.24 (m, 2H), 2.24 (s, 3H), 2.14 (s, 3H), 1.95～1.86 (m, 1H), 1.81～1.68 (m, 4H), 1.24～1.20 (m, 14H), 0.99 (s, 6H), 0.97 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.63, 139.28, 103.39, 83.17, 82.78, 55.81, 36.91, 33.48, 32.31, 29.62, 24.85, 24.83, 24.38, 24.25, 13.57, 11.34; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.0; HRMS (ESI-TOF) calcd for $C_{23}H_{42}B_2BrN_2O_4$ $[M+Na]^+$ 511.2509, found 533.2515.

5-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-6,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**31**): R_f=0.2 (PE/EA, V∶V=4∶1), colorless oil, 100.6 mg, 74% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.99 (d, J=7.2 Hz, 1H), 6.64 (d, J=7.2 Hz, 1H), 6.60 (s, 1H), 5.60 (s, 1H), 4.33 (td, J=11.2, 3.2 Hz ,1H), 3.97 (t, J=6.8 Hz, 2H), 3.89 (t, J=5.2 Hz, 2H), 2.30 (s, 3H), 2.24 (s, 3H), 2.16 (s, 3H), 2.15 (s, 3H), 1.97～1.90 (m, 1H), 1.83 (d, J=11.2 Hz, 1H), 1.77～1.65 (m, 5H), 1.60～1.46 (m, 2H), 1.24 (s, 6H), 1.22 (s, 6H), 1.17 (s, 6H), 1.11～1.07 (m, 2H), 1.01 (s, 6H), 0.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 177.63, 156.89, 146.54, 139.18, 136.30, 130.18, 123.50, 120.58, 111.90, 103.35, 83.12, 82.75, 67.89, 64.13, 55.88, 44.94, 37.57, 36.99, 29.60, 28.20, 25.08, 25.05, 24.83, 24.36, 24.33, 24.23, 22.50, 21.30, 15.65, 13.54, 11.27; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 30.4; HRMS (ESI-TOF) calcd for $C_{38}H_{62}B_2N_2O_7$ $[M+H]^+$ 680.4853, found 680.4858.

4.2 Procedures for the synthesis of compound **33**

The reaction was adapted from the literature procedures.[26] To a 25 mL flame-dried Schlenk tube in N_2-filled glove-box charged with **2** (78.0 g, 0.20 mmol), NaOMe (16.0 mg, 0.30 mmol) and quinoline *N*-oxide (15.0 mg, 0.10 mmol), was added toluene (2.0 mL). The resulting mixture was allowed to stir at 80 ℃ for 3 h. After cooled to room temperature, the reaction mixture was filtrated through a pad of celite to remove solids. The filter was then concentrated, the residue was redissolved in THF/H_2O (V∶V=1∶1, 2 mL), followed by addition of $NaBO_3$•$4H_2O$ (47.0 mg, 0.30 mmol) at room temperature. The resulting mixture was allowed to stir at the same temperature for additional 3 h. The biphasic mixture was then diluted by H_2O (5 mL) and extracted with CH_2Cl_2 three times (10 mL×3). The combined organic phase was then dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (V∶V=1∶1) as the eluent to afford **33** as colorless oil (13.0 mg, 49% yield based on quinoline *N*-oxide). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.75 (d, J=8.8 Hz, 1H), 7.80～7.73 (m, 2H), 7.59 (t, J=7.6 Hz, 1H), 7.49 (d, J=8.4 Hz, 1H), 6.93 (d, J=8.4 Hz, 1H), 5.54 (s, 1H), 5.19～5.09 (m, 1H), 3.69 (dd, J=12.8, 4.8 Hz, 1H), 3.46 (dd, J=12.8, 5.2 Hz, 1H), 2.24 (s, 3H), 1.83 (s, 3H), 1.62 (d, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.67, 147.54, 146.13, 141.36, 139.13, 130.40, 129.48, 128.06, 125.23, 123.53, 119.48, 104.17, 49.15, 39.88, 29.69, 21.01, 10.33; HRMS (ESI-TOF) calcd for $C_{17}H_{20}N_3$ $[M+H]^+$ 266.1652 , found 266.1656.

4.2 Procedures for the synthesis of compound **34**

To a 25 mL flask with **2** (39.0 g, 0.10 mmol), NaO^{t}Bu (58.0 mg, 0.60 mmol), and MeOH (39.0 mg, 1.2 mmol) was added THF (1.0 mL). The resulting mixture was allowed to stir at for 6 h. The reaction mixture was added H_2O (1 mL) followed by addition of $NaBO_3$•$4H_2O$ (92.0 mg, 0.60 mmol) at room temperature. The resulting mixture was allowed to stir at the same temperature for additional 5 h. The biphasic mixture was then diluted by H_2O (10 mL) and extracted with CH_2Cl_2 (5 mL×3). The combined organic phase was then dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (V∶V=1∶1) as the eluent to afford **34** as colorless oil (20.0 mg, 60% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.78 (s, 1H), 4.28～4.20 (m, 1H), 3.92 (d, J=4.8 Hz, 2H), 2.90 (br, 1H), 2.23 (s, 3H), 2.21 (s, 3H), 1.41 (d, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.60, 138.83, 104.72, 65.91, 54.17, 17.25, 13.48, 10.84; HRMS (ESI-TOF) calcd for $C_8H_{15}N_2O$ $[M+H]^+$ 155.1179 , found 155.1178.

Supporting Information Experimental procedures and NMR spectra for all key and new compounds. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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