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钴催化烯胺远程硼氢化

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摘要 报道了一例钴催化烯胺的远程硼氢化反应. 此方法使用含量丰富的金属和商业化配体, 通过链行走和硼氢化过程可以快速地构建硼基胺类化合物. 该方法具有反应条件温和、底物普适性广、官能团相容性好等优点. 此外, 通过克级反应和硼胺产物的多样合成转化, 证明了该反应在合成中的实用性和潜在的应用价值.
关键词 钴; 烯胺; 远程硼氢化; 硼酸酯

Cobalt-Catalyzed Remote Hydroboration of Enamines

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Abstract A cobalt-catalyzed remote hydroboration of enamines via a sequence of chain walking and hydroboration in the presence of an earth abundant catalyst and a commercially available ligand is reported, providing a rapid access to borylamines. This protocol exhibites mild reaction conditions, broad substrate scope and good functional group compatibility. In addition, the practicability and the potential synthesis value of this reaction were demonstrated by a gram reaction and a variety of synthetic transformations of the borylamine products.
Keywords cobalt; enamines; remote hydroboration; bornic esters

1 Introduction

Alkene remote functionalization is an attractive method for constructing carbon-carbon bonds and carbon-heteroatom bonds.[1] This strategy allows for carbon-carbon bond formation on remote and unfunctionalized sites by a "metal-walk" or "chain-walk" process, providing complex structures that are challenging to be prepared by conventional methods.[2] To this end, transition-metal-catalyzed alkene remote functionalization reactions have been a hot topic and of great interest in organic synthesis. In recent years, significant progress has been made to enable remote functionalization in the presence of precious-metal catalysts such as Pd,[3] Ni,[4] Ir[5] *etc.* (Scheme 1a). The alkene distal functionalization catalyzed by earth abundant metals is rarely explored and highly desirable. Additionally, the existing methods typically require the use of directing groups such as heteroatoms or aromatic groups as a thermaldynamically driving force in close proximity to the reaction site to govern site selectivity. Therefore, the development of earth abundant metal-catalyzed alkene remote functionalization is in great demand.

The first-row transition-metal catalyzed remote borylation has attracted more and more attention in recent years not only for the potential cost and environmental advantages of first-row transition-metals but also for the wide applications of organoboron compounds in synthetic chemistry, natural product synthesis and materials science,[6] and has made significant advances (Scheme 1b).[7] For instance, the Chirk group reported a bis(imino)pyridine-cobalt catalyzed remote hydroboration of alkenes, which represents the first example of cobalt-catalyzed remote hydroboration of internal alkenes with HBpin for the synthesis of primary alkylboronate esters.[7] Subsequently, the same group disclosed an isomerization-hydroboration of alkenes with phosphine-ligated cobalt catalysts, providing benzylic organoboronates.[7] In 2018, the Lu group[7] demonstrated a highly regio- and enantio-selective cobalt-catalyzed remote C—H bond borylation of aryl group-terminated internal alkenes. In 2019, the Ge group[7] developed a cobalt-catalyzed remote hydroboration of 1,*n*-dienes for the synthesis of *gem*-bis(boryl)alkanes. These methods are undoubtedly

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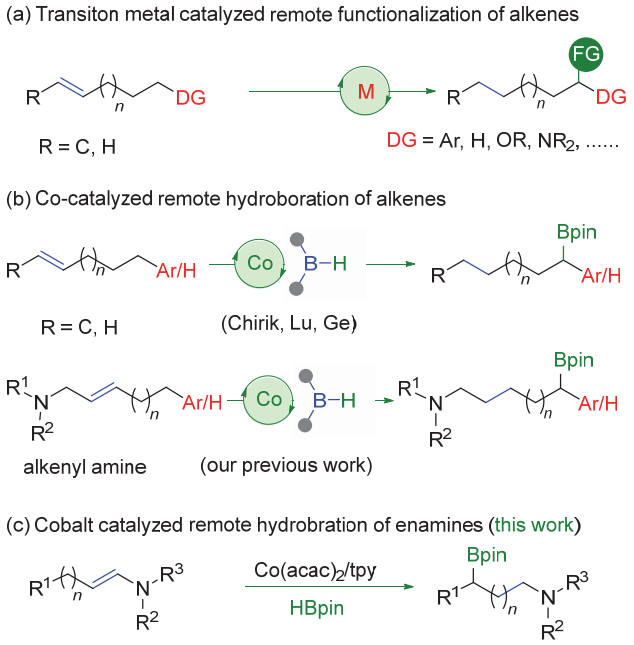
effective, but suffer from some limitations. For instance, the alkenes are largely limited to *C*-substituted alkenes. Heteroatom-substituted alkenes are not tolerated. Recently, we have developed a cobalt-catalyzed remote hydroboration of alkenyl amines for the preparation borylamines and aminoalcohols,[8] in which the chain walking occurs along the direction of carbon rather than the nitrogen, realizing the compatibility of nitrogen atoms. Given that nitrogen-containing compounds play an important role in pharmaceutical, agrochemical and natural products as well as chemical industries, the development of facile and novel catalytic approaches for the remote hydroboration of heteroatom-substituted alkenes with readily accessible catalysts remains to be an important scientific pursuit in chemistry.[9] As a continuation of our interest in remote hydroboration reactions of heteroatom-substituted alkenes, herein, we reported a cobalt-catalyzed remote hydroboration of enamines, which provides an effective method for the synthesis of aminoboronic esters (Scheme 1c).

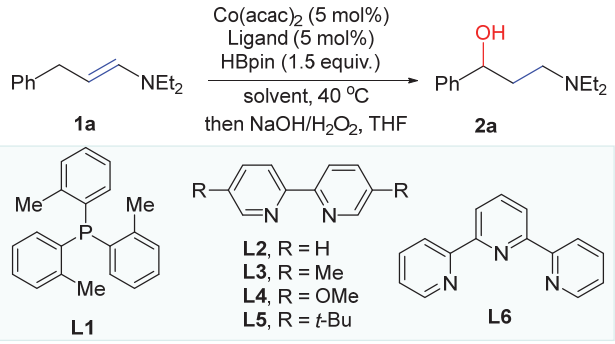


Scheme 1 Remote functionalization of alkenes

2 Results and discussion

Inspired by our previous studies,[8] the remote hydroboration reaction of enamines with the cobalt catalytic system was examined. Initial investigations were carried out using enamine **1a** as the model substrate in the presence of 5 mol% $Co(acac)_2$, 5 mol% ligand, 1.5 equiv. HBpin in 0.5 mL of tetrahydrofuran (THF), and the reaction was conducted at 40 ℃. Phosphine ligands including Ph_2PCy, PPh_3 and **L1** resulted in no reaction (Entries 1～3). Subsequently, dipyridyl ligands were examined, and no desired product was observed (Entries 4～7). Based on our previous research,[8] then terpyridine was used as the ligand. To our delight, the desired product **2a** was obtained in 31% yield (Entry 8). The effect of solvents was then evaluated. While *N*,*N*-dimethylformamide (DMF) gave no reaction (Entry 9), nonpolar solvents such as cyclohexane, octane and toluene improved the yields dramatically (Entries 10～12). In addition, the product **2a** were obtained in moderate yields in other etheric solvents such as cyclopentyl methyl ether (CPME) and dimethoxyethane (DME) (Entries 13, 14). Finally, it was pleased to find that the employment of ethyl acetate (EA) as the solvent gave the best yield (Entry 15).

Table 1 Optimization of the reaction conditions[a,b]



Entry	Ligand	Solvent	Yield/%
1	Ph_2PCy	THF	ND
2	PPh_3	THF	ND
3	**L1**	THF	ND
4	**L2**	THF	ND
5	**L3**	THF	ND
6	**L4**	THF	ND
7	**L5**	THF	ND
8	**L6** (tpy)	THF	31
9	**L6**	DMF	ND
10	**L6**	Cyclohexane	57
11	**L6**	Octane	74
12	**L6**	Toluene	43
13	**L6**	CPME	60
14	**L6**	DME	54
15	**L6**	EA	89

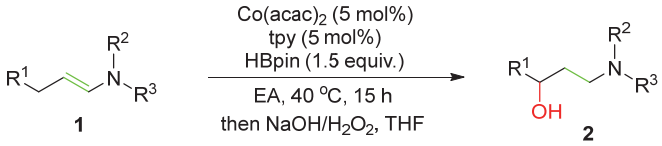
[a] Unless otherwise noted, the reactions were carried out with **1a** (0.10 mmol), $Co(acac)_2$ (5 mol%), ligand (5 mol%), and HBpin (1.5 equiv.) in 0.5 mL of solvent at 40 ℃ for 15 h. The crude borylated product was oxidized by $NaOH/H_2O_2$ in THF. [b] Yields measured by ^1H NMR with nitromethane as an internal standard.

With the optimal conditions in hand (Table 1, Entry 15), the substrate scope of enamines in this remote hydroboration reaction was next explored. As demonstrated in Table 2, a range of enamines successfully participated in this remote C—H bond borylation reaction to afford the corresponding aminoalcohol products in moderate to excellent yields. With regard to the amine moiety of the substrate, a variety of amine-derived enamines **2a**～**2o** were successfully converted to the desired products under the standard conditions. Alkyl amines with different chain lengths (Et, Me, *n*-Bu, **2a**～**2c**) performed well. In addition to the linear

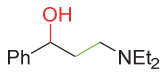
substituted amines, isopropyl, *t*-butyl and cyclohexyl substituted ones also proceeded smoothly to give the desired remote functionalization products **2d**～**2f** in good yields. Gratifyingly, saturated nitrogen heterocycles such as pyrrole, azepane and morpholine were all well-tolerated, furnishing products **2g**～**2i** in moderate to excellent yields, respectively. Meanwhile, OMe and NMe_2 terminally substituted amines were also compatible, leading to the functionalized products **2j** and **2k** in 65% and 55% yields, respectively. In addition, the reaction of benzylic substrates also occurred efficiently, providing corresponding products **2l**～**2n** in 70%～83% isolated yields. Of note, the amine bearing terminal an NMe_2 and a benzyl group could give the corresponding product **2o** in 85% yield.

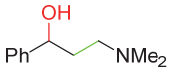
Next, our attention to the alkene moiety was turned. It was found that substrate **1p** with a longer chain length was amenable, albeit with diminished reaction efficiency (**2p**). Enamines that contain a Me substituent at the *ortho*-, *meta*- or *para*-position of the phenyl ring were all successfully transformed to the borylation products under the standard conditions, giving the desired products **2q**～**2s** in moderate to excellent yields. In addition, the mild reaction conditions tolerated a variety of functional groups, including electron-donating groups such as OMe and NMe_2 (**2t** and **2u**), and electron-withdrawing groups such as F, and CF_3 (**2v** and **2w**), affording the corresponding aminoalcohol in good yields. It was found that this remote borylation reaction tolerated the alkyl chains (**2x** and **2y**). Secondary amide was also tested. The use of (*E*)-enamide resulted in the formation of *α*-borylamide product **2z**.

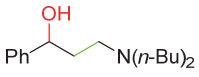
Table 2 Substrate scope of enamines[a,b]

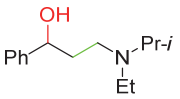


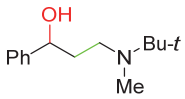
Scope of amine moiety

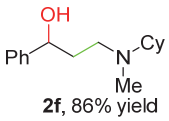

2a, 83% yield

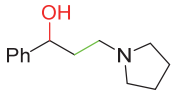

2b, 55% yield

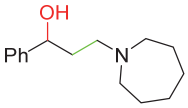

2c, 77% yield

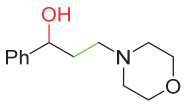

2d, 53% yield

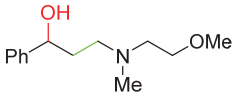

2e, 76% yield

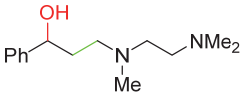

2f, 86% yield

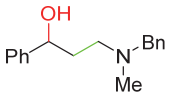

2g, 48% yield

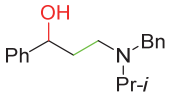

2h, 80% yield

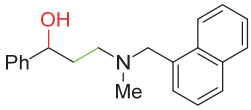

2i, 72% yield

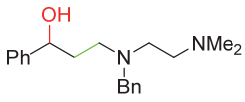

2j, 65% yield


2k, 55% yield

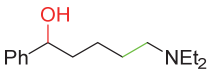

2l, 70% yield

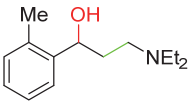

2m, 83% yield

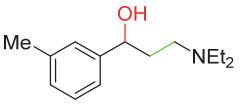

2n, 83% yield

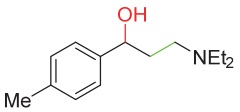

2o, 85% yield

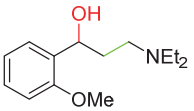
Scope of alkene moiety

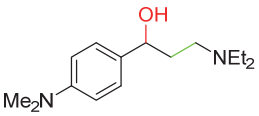

2p, 40% yield

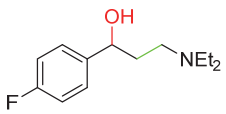

2q, 43% yield

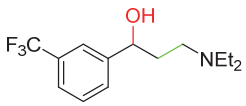

2r, 55% yield

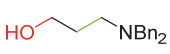

2s, 74% yield

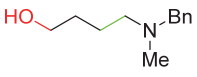

2t, 77% yield


2u, 51% yield

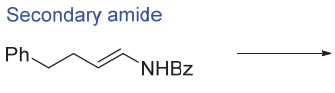

2v, 60% yield


2w, 54% yield


2x, 38% yield

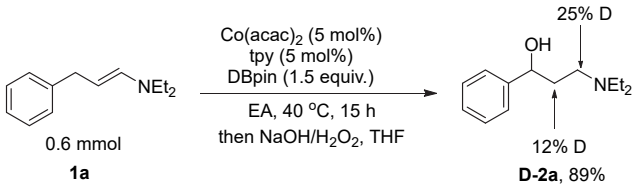

2y, 57% yield

Secondary amide


2z[c], 67% yield

[a] Unless otherwise noted, all reactions were carried out with **1** (0.6 mmol), HBpin (1.5 equiv.), $Co(acac)_2$ (5 mol%), tpy (5 mol%), EA (3 mL), 40 ℃ for 15 h in N_2 atmosphere. The crude borylated product was oxidized by H_2O_2 (4.5 equiv. 30%) at room temperature for 0.5 h. [b] Yields are based on isolated products. [c] 0.2 mmol.

To gain further insight into the reaction mechanism, a deuterated reaction with enamine **1a** and DBpin was carried out (Scheme 2). The deuterium incorporation at the *β*-position of **D-2a** is consistent with the chain walking mechanism (*β*-hydride elimination and reinsertion). To demonstrate the practical applicability of this transformation, a 6.0 mmol scale reaction of **1m** was carried out with the standard conditions, and 1.74 g (74% yield) of **3m** was isolated, indicating the possibility of scale-up for this procedure (Scheme 3). To demonstrate the synthetic applications of this protocol, a couple of transformations of **3m** were conducted, and were shown in Scheme 3. First, the treatment of **3m** with vinylmagnesium bromide and I_2 leads to the formation of vinyl amine **4** in 66% yield, which can proceed further with carbon-carbon double bond functionalization to give more complex fragments. Furthermore, the sp^2-sp^3 coupling of furan with **3m** leads to the formation of **5** in 63% yield. In addition, amination of **3m** with $MeONH_2$ is carried out, providing the desired amination product **6** in 74% yield. Finally, it was demonstrated that **3m** could undergo the Suzuki-Miyaura coupling reaction to give the corresponding functionalized product **7** in 42% yield.



Scheme 2 Deuterium-labeling experiment

3 Conclusions

In summary, we have developed the first Co-catalyzed remote hydroboration of enamines. This hydroboration proceeds under mild conditions, and the reaction shows broad substrate scope, good functional group compatibility and operational simplicity. We also demonstrated that the amino boronic esters product could undergo a variety of transformations, including C—N and C—C bond forming reactions to deliver a variety of valuable synthetic building blocks. Further application of the obtained products and the development of asymmetric Co-catalyzed remote hydroboration reactions are currently underway in our laboratory.

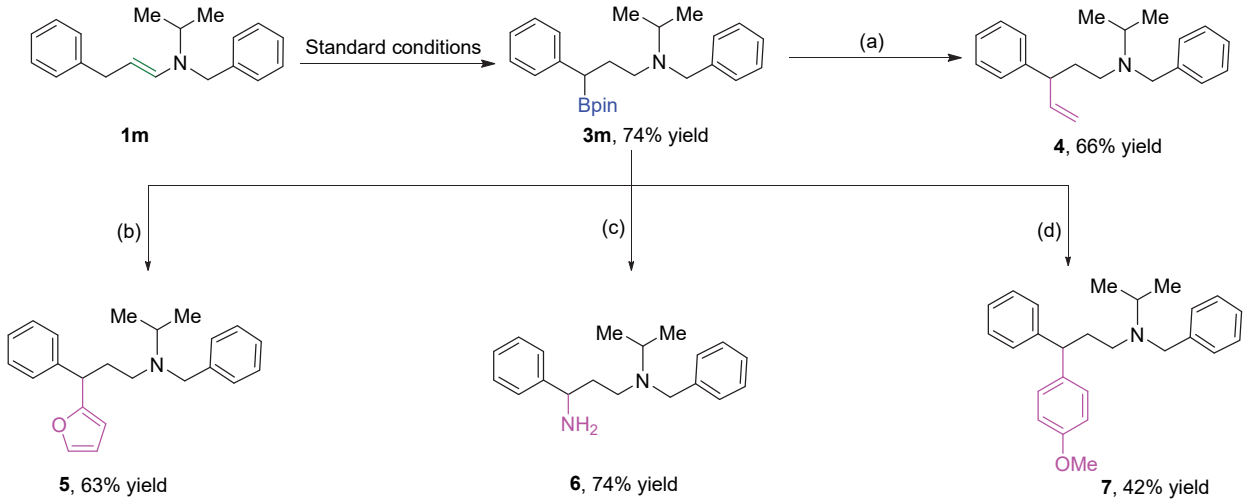
4 Experimental section

4.1 General information

All reactions were conducted in oven-dried vials with a magnetic stir bar under nitrogen atmosphere. Solvents were purified under nitrogen using a solvent purification system. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Analytical thin layer chromatography (TLC) was performed using silica gel plates. Visualization was by ultraviolet fluorescence, phosphomolybdic acid, and/or $KMnO_4$. Flash column chromatography was performed using EM Science (200～300 mesh) silica gel. ^1H NMR, and ^{13}C NMR spectra were recorded on Bruker 400 MHz at 20 ℃ using $CDCl_3$ or acetone-d_6 as solvent, and were referenced to TMS (δ=0 for ^1H NMR) and $CDCl_3$ (δ=77.16 for ^{13}C NMR). High resolution mass spectra (HRMS) were recorded on a Bruker Maxis System using Electron Spray Ionization (ESI).

4.2 Preparation of enamines

Enamine substrates were prepared according to a modified procedure.[10] The secondary amine (1.05 equiv.) was added to a solution of K_2CO_3 (1.0 equiv.) and molecular sieves (4 Å) in Et_2O at room temperature. The solution was cooled to 0 ℃, then the aldehyde (1.0 equiv.) was added



Reaction conditions: (a) vinylmagnesium bromide (8.0 equiv.), THF, −78 ℃, 0.5 h, then I_2 (8.0 equiv.), −78 ℃, 0.5 h; (b) furan, *n*-BuLi (1.5 equiv.), THF, −78 ℃, 1 h, then *N*-bromosuccinimide (NBS) (1.5 equiv.), −78 ℃～r.t., 10 h; (c) $MeONH_2$ (3.0 equiv.), *n*-BuLi (3.0 equiv.), −78 ℃ to 60 ℃, 15 h; (d) $Pd_2(dba)_3$ (5 mol%), PPh_3 (40 mol%), Ag_2O (1.5 equiv.), (4-$MeOC_6H_4$)I (2.0 equiv.), THF, 80 ℃, 24 h.

Scheme 3 Gram-scale reaction and synthetic applications

and the reaction mixture was stirred for 16 h at room temperature. Then the mixture was filtered through a pad of celite and washed with Et_2O. Compound **1** was obtained after removal of the solvent. If necessary, purified compound **1** by distillation.

Compound **1z** were synthesized according to a reported method.[11] To a Schlenk tube equipped with a stirrer bar was charged with CuI (95.2 mg, 0.5 mmol), K_2CO_3 (1.27 g, 9.2 mmol), and benzamide (666.3 mg, 5.5 mmol). *N*,*N*′-Dimethylethylenediamine (0.2 mL, 1.8 mmol), (*E*)-(4-bromobut-3-en-1-yl)benzene (979.2 mg, 4.6 mmol), and THF (9.0 mL) were then added under nitrogen. The reaction mixture was stirred at 80 ℃ for 12 h. The mixture was cooled to room temperature, filtered through a celite pad with EtOAc and concentrated in vacuo. The residue was purified by column chromatography on silica gel to provide **1z**.

(*E*)-*N*,*N*-Diethyl-3-phenylprop-1-en-1-amine (**1a**):[10] 2.56 g, 68% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.27～7.18 (m, 5H), 6.00 (d, J=13.7 Hz, 1H), 4.23 (dt, J=13.9, 7.1 Hz, 1H), 3.27 (d, J=7.0 Hz, 2H), 2.98 (q, J=7.2 Hz, 4H), 1.03 (t, J=7.0 Hz, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.7, 139.3, 129.1 (2C), 126.4, 96.2, 45.3, 37.9, 13.0.

(*E*)-*N*,*N*-Dimethyl-3-phenylprop-1-en-1-amine (**1b**):[12] 3.36 g, 69% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.27～7.20 (m, 5H), 6.05 (dd, J=13.5, 1.4 Hz, 1H), 4.30 (dt, J=13.9, 7.1 Hz, 1H), 3.30 (d, J=7.1 Hz, 2H), 2.56 (s, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.3, 142.2, 129.2 (2C), 126.5, 98.8, 41.2, 37.5.

(*E*)-*N*,*N*-Dibutyl-3-phenylprop-1-en-1-amine (**1c**):[13] 3.70 g, 75% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.30～7.10 (m, 5H), 6.03 (d, J=13.6 Hz, 1H), 4.26～4.14 (m, 1H), 3.28 (q, J=7.7, 7.2 Hz, 2H), 2.97～2.91 (m, 4H), 1.54～1.44 (m, 4H), 1.36～1.27 (m, 4H), 0.92 (t, J=8.0 Hz, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.9, 140.2, 129.14, 129.10, 126.4, 95.0, 51.9, 37.9, 30.7, 21.1, 14.4.

(*E*)-*N*-Ethyl-*N*-isopropyl-3-phenylprop-1-en-1-amine (**1d**): 3.56 g, 88% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.26～7.17 (m, 5H), 6.06 (d, J=13.6 Hz, 1H), 4.22 (dt, J=13.9, 7.1 Hz, 1H), 3.37～3.30 (m, 1H), 3.28 (d, J=7.1 Hz, 2H), 2.92 (t, J=7.1 Hz, 2H), 1.08 (d, J=6.6 Hz, 6H), 1.04 (t, J=7.0 Hz, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.9, 137.4, 129.10, 129.08, 126.4, 95.8, 53.5, 40.8, 38.1, 21.2, 14.4; IR (neat) ν: 2972, 1452, 1382, 1088, 1051, 884, 701 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{22}N$ $[M+H]^+$ 204.1752, found 204.1751.

(*E*)-*N*-(*tert*-Butyl)-*N*-methyl-3-phenylprop-1-en-1-amine (**1e**): 351.3 mg, 86% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.27～7.22 (m, 4H), 7.17～7.13 (m, 1H), 6.49 (dt, J=13.3, 1.2 Hz, 1H), 4.32 (dt, J=13.7, 7.0 Hz, 1H), 3.32 (d, J=6.9 Hz, 2H), 2.49 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.6, 137.1, 129.15, 129.08, 126.4, 99.5, 55.4, 38.1, 31.7, 28.1; IR (neat) ν: 2966, 1647, 1395, 1099, 1023, 939, 736, 698 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{22}N$ $[M+H]^+$ 204.1752, found 204.1750.

(*E*)-*N*-Methyl-*N*-(3-phenylprop-1-en-1-yl)cyclohexanamine (**1f**): 1.95 g, 42% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.28～7.11 (m, 5H), 6.19 (d, J=13.4 Hz, 1H), 4.28～4.16 (m, 1H), 3.30 (dd, J=7.4, 4.3 Hz, 2H), 2.85～2.78 (m, 1H), 2.49 (s, 3H), 1.81～1.75 (m, 2H), 1.75～1.69 (m, 2H), 1.65～1.59 (m, 1H), 1.40～1.26 (m, 4H), 1.16～1.06 (m, 1H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.8, 140.0, 129.2, 129.1, 126.4, 97.0, 63.8, 37.9, 33.3, 31.3, 26.9, 26.8; IR (neat) ν: 2928, 1646, 1448, 1397, 1066, 937, 737, 697 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{16}H_{24}N$ $[M+H]^+$ 230.1909, found 230.1907.

(*E*)-1-(3-Phenylprop-1-en-1-yl)pyrrolidine (**1g**):[14] 362.4 mg, 97% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.27～7.16 (m, 5H), 6.26 (d, J=13.4 Hz, 1H), 4.16 (dt, J=13.8, 7.1 Hz, 1H), 3.27 (d, J=7.0 Hz, 2H), 2.96 (t, J=6.4 Hz, 4H), 1.83～1.79 (m, 4H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.6, 137.8, 129.11, 129.07, 126.4, 97.3, 49.7, 37.7, 25.7.

(*E*)-1-(3-Phenylprop-1-en-1-yl)azepane (**1h**): 2.73 g, 63% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.27～7.10 (m, 5H), 6.10 (d, J=13.3 Hz, 1H), 4.19～4.06 (m, 1H), 3.27 (dd, J=6.8, 3.8 Hz, 2H), 3.12～3.08 (m, 4H), 1.68～1.62 (m, 4H), 1.56～1.52 (m, 4H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 145.1, 140.7, 129.12, 129.09, 126.4, 93.7, 51.8, 37.9, 29.6, 28.7; IR (neat) ν: 2921, 1647, 1449, 1395, 1146, 935, 732, 697 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{15}H_{22}N$ $[M+H]^+$ 216.1752, found 216.1751.

(*E*)-4-(3-Phenylprop-1-en-1-yl)morpholine (**1i**):[10] 4.65 g, 76% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.28～7.16 (m, 5H), 5.97 (d, J=13.7 Hz, 1H), 4.55 (dt, J=14.0, 7.2 Hz, 1H), 3.64～3.61 (m, 4H), 3.28 (d, J=7.1 Hz, 2H), 2.78～2.74 (m, 4H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 143.7, 141.9, 129.19, 129.17, 126.6, 101.2, 67.1, 50.3, 37.4.

(*E*)-*N*-(2-Methoxyethyl)-*N*-methyl-3-phenylprop-1-en-1-amine (**1j**): 283.1 mg, 69% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.25～7.14 (m, 5H), 6.11 (dt, J=13.5, 1.1 Hz, 1H), 4.19 (dt, J=13.8, 7.1 Hz, 1H), 3.43 (t, J=5.7 Hz, 2H), 3.28 (s, 3H), 3.26 (d, J=2.8 Hz, 2H), 3.09 (t, J=5.7 Hz, 2H), 2.61 (s, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.6, 141.2, 129.12, 129.08 126.4, 96.6, 71.7, 58.9 (2C), 55.3, 37.6; IR (neat) ν: 3026, 1650, 1451, 1117, 1021, 943, 737, 700 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1545, found 206.1543.

(*E*)-N^1,N^1,N^2-Trimethyl-N^2-(3-phenylprop-1-en-1-yl)-ethane-1,2-diamine (**1k**): 302.4 mg, 69% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.26～7.21 (m, 4H), 7.15～7.10 (m, 1H), 6.10 (dt, J=13.5, 1.1 Hz, 1H), 4.19 (dt, J=13.9, 7.1 Hz, 1H), 3.27 (d, J=7.1 Hz, 2H), 3.06～2.98 (m, 2H), 2.59 (s, 3H), 2.36～2.32 (m, 2H), 2.17 (s, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.6, 141.2, 129.10, 129.06, 126.4, 96.6, 58.1, 53.9, 46.2, 37.6, 37.4; IR (neat) ν: 2943, 1650, 1454, 1123, 1029, 944, 736, 700 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{23}N_2$ $[M+H]^+$ 219.1861, found 219.1857.

(*E*)-*N*-Benzyl-*N*-methyl-3-phenylprop-1-en-1-amine

(**1l**):[15] 2.07g, 44% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.34～7.18 (m, 10H), 6.28 (dd, J=13.5, 1.3 Hz, 1H), 4.39～4.24 (m, 1H), 4.08 (s, 2H), 3.35～3.28 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.5, 141.5, 140.0, 129.3, 129.19, 129.15, 128.9, 128.0, 126.5, 98.1, 59.8, 37.6, 37.0.

(*E*)-*N*-Benzyl-*N*-isopropyl-3-phenylprop-1-en-1-amine (**1m**): 5.47g, 68% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.35～7.27 (m, 4H), 7.24～7.17 (m, 3H), 7.16～7.06 (m, 3H), 6.23 (dd, J=13.6, 1.4 Hz, 1H), 4.27～4.14 (m, 1H), 4.08 (s, 2H), 3.49～3.40 (m, 1H), 3.29～3.21 (m, 2H), 1.16 (d, J=6.7 Hz, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.5, 141.4, 138.0, 129.2, 129.1 (2C), 128.0, 127.4, 126.4, 98.7, 54.2, 51.0, 37.8, 20.8; IR (neat) v: 2967, 1648, 1452, 1173, 938, 728, 696 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{19}H_{24}N$ $[M+H]^+$ 266.1909, found 266.1906.

(*E*)-*N*-Methyl-*N*-(naphthalen-1-ylmethyl)-3-phenylprop-1-en-1-amine (**1n**): 4.57 g, 80% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 8.15～8.10 (m, 1H), 7.94～7.90 (m, 1H), 7.86～7.82 (m, 1H), 7.55～7.42 (m, 5H), 7.27～7.22 (m, 4H), 6.36 (d, J=13.5 Hz, 1H), 4.51 (s, 2H), 4.47～4.39 (m, 1H), 3.33 (d, J=7.1 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.4, 141.3, 135.3, 135.1, 133.0 129.6, 129.2, 129.1, 128.8, 127.2, 126.9, 126.7, 126.5, 126.3, 124.9, 98.3, 57.2, 37.6, 37.4; IR (neat) v: 2859, 1649, 1451, 1377, 1055, 776, 737, 698 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{21}H_{22}N$ $[M+H]^+$ 288.1752, found 288.1754.

(*E*)-N^1-Benzyl-N^2,N^2-dimethyl-N^1-(3-phenylprop-1-en-1-yl)ethane-1,2-diamine (**1o**): 486.5 mg, 83% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.31～7.29 (m, 4H), 7.24～7.15 (m, 6H), 6.21 (d, J=14.4 Hz, 1H), 4.25 (dt, J=14.0, 7.2 Hz, 1H), 4.20 (s, 2H), 3.26 (d, J=7.1 Hz, 2H), 3.09 (t, J=7.0 Hz, 2H), 2.38 (t, J=7.0 Hz, 2H), 2.13 (s, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.6, 140.7, 140.3, 129.3, 129.11, 129.07, 128.5, 127.7, 126.4, 96.6, 57.9, 56.3, 50.5, 46.2, 37.6; IR (neat) v: 2960, 1493, 1453, 1127, 1028, 945, 734, 697 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{20}H_{27}N_2$ $[M+H]^+$ 295.2174, found 295.2175.

(*E*)-*N*,*N*-Diethyl-5-phenylpent-1-en-1-amine (**1p**): 763,1 mg, 75% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.26～7.16 (m, 5H), 5.86 (d, J=13.6 Hz, 1H), 4.12 (dt, J=13.9, 6.5 Hz, 1H), 2.95 (q, J=7.0 Hz, 4H), 2.61 (t, J=7.9 Hz, 2H), 1.99 (q, J=7.1 Hz, 2H), 1.65～1.61 (m, 2H), 1.02 (t, J=7.1 Hz, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.0, 138.6, 129.4, 129.2, 126.5, 97.2, 45.2, 36.1, 34.8, 31.4, 12.9; IR (neat) v: 2970, 2929, 1650, 1452, 1380, 1089, 743, 698 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{15}H_{24}N$ $[M+H]^+$ 218.1909, found 218.1910.

(*E*)-*N*,*N*-Diethyl-3-(*o*-tolyl)prop-1-en-1-amine (**1q**): 2.17 g, 63% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.19～7.06 (m, 4H), 5.94 (d, J=13.6 Hz, 1H), 4.20 (dt, J=13.7, 6.8 Hz, 1H), 3.26 (d, J=6.8 Hz, 2H), 2.97 (q, J=7.1 Hz, 4H), 2.29 (s, 3H), 1.03 (t, J=7.1 Hz, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 142.5, 139.3, 136.8, 130.9, 129.5, 126.8, 126.6, 95.3, 45.4, 35.5, 19.7, 13.1; IR (neat) v: 2969, 2931, 1649, 1455, 1380, 1097, 940, 742 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{22}N$ $[M+H]^+$ 204.1752, found 204.1750.

(*E*)-*N*,*N*-Diethyl-3-(*m*-tolyl)prop-1-en-1-amine (**1r**): 2.30 g, 84% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.12 (t, J=7.5 Hz, 1H), 7.02～6.93 (m, 3H), 5.99 (d, J=13.7 Hz, 1H), 4.23 (dt, J=13.9, 7.1 Hz, 1H), 3.23 (d, J=7.0 Hz, 2H), 2.98 (q, J=7.1 Hz, 4H), 2.28 (s, 3H), 1.04 (t, J=7.1 Hz, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 144.7, 139.2, 138.4, 129.9, 129.1, 127.1, 126.2, 96.5, 45.4, 37.9, 21.7, 13.1; IR (neat) v: 2969, 2929, 1649, 1453, 1383, 1098, 770, 698 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{22}N$ $[M+H]^+$ 204.1752, found 204.1750.

(*E*)-*N*,*N*-Diethyl-3-(*p*-tolyl)prop-1-en-1-amine (**1s**): 2.63 g, 81% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.10～7.04 (m, 4H), 5.98 (dd, J=13.6, 1.1 Hz, 1H), 4.22 (dt, J=13.9, 7.1 Hz, 1H), 3.23 (d, J=7.0 Hz, 2H), 2.98 (q, J=7.1 Hz, 4H), 2.27 (s, 3H), 1.03 (t, J=7.1 Hz, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 141.7, 139.1, 135.5, 129.8, 129.1, 96.6, 45.3, 37.5, 21.2, 13.1; IR (neat) v: 2967, 2873, 1650, 1371, 1104, 939, 802, 702 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{22}N$ $[M+H]^+$ 204.1752, found 204.1750.

(*E*)-*N*,*N*-Diethyl-3-(2-methoxyphenyl)prop-1-en-1-amine (**1t**): 2.90 g, 60% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.19～7.10 (m, 2H), 6.90～6.82 (m, 2H), 5.96 (d, J=13.7 Hz, 1H), 4.25 (dt, J=14.0, 7.1 Hz, 1H), 3.81 (s, 3H), 3.24 (d, J=6.7 Hz, 2H), 2.97 (q, J=7.1 Hz, 4H), 1.03 (t, J=7.1 Hz, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 158.3, 139.4, 132.9, 130.0, 127.6, 121.3, 111.2, 95.4, 55.8, 45.3, 31.6, 13.1; IR (neat) v: 2969, 2931, 2863, 1519, 1342, 1123, 1055, 804 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{22}NO$ $[M+H]^+$ 220.1701, found 220.1697.

(*E*)-4-(3-(Diethylamino)allyl)-*N*,*N*-dimethylaniline (**1u**): 200.1 mg, 78% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.02 (d, J=8.4 Hz, 2H), 6.67 (d, J=8.6 Hz, 2H), 5.94 (d, J=13.6 Hz, 1H), 4.22 (dt, J=13.9, 7.0 Hz, 1H), 3.16 (d, J=6.9 Hz, 2H), 2.96 (q, J=7.1 Hz, 4H), 2.86 (s, 6H), 1.03 (t, J=6.9 Hz, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 150.1, 138.7, 132.5, 129.5, 113.8, 97.5, 45.3, 41.2, 36.9, 13.0; IR (neat) v: 2971, 2932, 1649, 1491, 1458, 1238, 1104, 749 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{15}H_{25}N_2$ $[M+H]^+$ 233.2018, found 233.2015.

(*E*)-*N*,*N*-Diethyl-3-(4-fluorophenyl)prop-1-en-1-amine (**1v**): 248.4 mg, 60% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.22 (dd, J=8.4, 5.6 Hz, 2H), 7.00 (t, J=8.8 Hz, 2H), 6.01 (d, J=14.8 Hz, 1H), 4.21 (dt, J=13.9, 7.1 Hz, 1H), 3.26 (d, J=6.9 Hz, 2H), 2.99 (q, J=7.1 Hz, 4H), 1.04 (t, J=7.0 Hz, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 162.1 (d, J=241.6 Hz), 140.8 (d, J=3.0 Hz), 139.4, 130.6 (d, J=7.8 Hz), 115.5(d, J=21.1 Hz), 95.9, 45.3, 37.0, 13.0; ^{19}F NMR (376 MHz, Acetone-d_6) δ: −120.0; IR (neat) v: 2972, 2932, 2864, 1507, 1383, 1223, 1118, 820 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{13}H_{19}FN$ $[M+H]^+$ 208.1502, found 208.1497.

(*E*)-*N*,*N*-Diethyl-3-(3-(trifluoromethyl)phenyl)prop-1-en-1-amine (**1w**): 291.0 mg, 81% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.55～7.48 (m, 4H), 6.08 (d, J=13.5

Hz, 1H), 4.24 (dt, J=14.0, 7.2 Hz, 1H), 3.38 (d, J=7.1 Hz, 2H), 3.00 (q, J=7.1 Hz, 4H), 1.04 (t, J=7.1 Hz, 6H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 146.5, 140.0, 133.1, 130.9 (d, J=31.6 Hz), 130.0, 125.8 (d, J=272.4 Hz), 125.6 (q, J=3.9 Hz), 123.2 (q, J=3.9 Hz), 94.8, 45.4, 37.6, 13.1; ^{19}F NMR (376 MHz, Acetone-d_6) δ: −63.0; IR (neat) ν: 2972, 2930, 1650, 1327, 1161, 1119, 1071, 702 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{19}F_3N$ $[M+H]^+$ 258.1470, found 258.1467.

(*E*)-*N*,*N*-Dibenzylprop-1-en-1-amine (**1x**):[16] 2.65 g, 82% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.33～7.21 (m, 10H), 6.21 (d, J=13.9 Hz, 1H), 4.15 (dt, J=13.4, 6.5 Hz, 1H), 4.09 (s, 4H), 1.58～1.53 (m, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 140.2, 139.9, 129.3, 128.7, 127.8, 93.6, 55.9, 15.9.

(*E*)-*N*-Benzyl-*N*-methylbut-1-en-1-amine (**1y**): 2.30 g, 66% yield. ^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.33～7.23 (m, 5H), 6.13 (d, J=13.7 Hz, 1H), 4.19 (dt, J=13.5, 6.8 Hz, 1H), 4.02 (s, 2H), 2.44 (s, 3H), 2.01～1.93 (m, 2H), 0.94 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ: 140.1, 139.9, 129.2, 128.9, 127.9, 101.3, 59.8, 36.9, 24.6, 16.9; IR (neat) ν: 2966, 2931, 2866, 1651, 1453, 1059, 736, 698 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{12}H_{18}N$ $[M+H]^+$ 176.1439, found 176.1433.

4.3 General procedure for remote hydroboration of enamines

In a N_2-filled glove box, to an oven-dried 10-mL vial were added $Co(acac)_2$ (7.7 mg, 0.03 mmol), tpy (7.0 mg, 0.03 mmol) and anhydrous EtOAc (3.0 mL). The resulting solution was stirred for 20 min at room temperature, at which time HBpin (115.2 mg, 0.9 mmol) was added. After the resulting mixture was stirred for an additional 5 min, enamine **1** (0.6 mmol) was added and stirred for 15 h at 40 ℃. The resulting suspension was cooled to room temperature, filtered through a celite pad with EtOAc, and concentrated in vacuo. The residue was dissolved in THF (3.0 mL) and cooled to 0 ℃. NaOH (4.5 equiv., 3.0 mol/L) and H_2O_2 (4.5 equiv., 30%) were then added. The resulting mixture was stirred for 0.5 h, and extracted with EtOAc. The combined organic phase was then dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel chromatography using dichloromethane (DCM)/MeOH as the eluent to afford the desired product **2**.

3-(Diethylamino)-1-phenylpropan-1-ol (**2a**):[17] 103.6 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.37 (m, 2H), 7.36～7.30 (m, 2H), 7.26～7.21 (m, 1H), 4.93 (dd, J=7.7, 4.0 Hz, 1H), 2.82～2.75 (m, 1H), 2.74～2.66 (m, 2H), 2.65～2.60 (m, 1H), 2.54～2.44 (m, 2H), 1.85～1.76 (m, 2H), 1.09 (t, J=7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.4, 128.3, 126.9, 125.7, 75.8, 52.7, 46.8, 34.6, 11.6.

3-(Dimethylamino)-1-phenylpropan-1-ol (**2b**):[18] 62.1 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.31 (m, 4H), 7.27～7.22 (m, 1H), 4.94 (dd, J=7.8, 3.9 Hz, 1H), 2.71～2.63 (m, 1H), 2.53～2.44 (m, 1H), 2.31 (s, 6H), 1.90～1.78 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.2, 128.3, 127.0, 125.7, 75.9, 58.5, 45.4, 34.6.

3-(Dibutylamino)-1-phenylpropan-1-ol (**2c**):[19] 122.1 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.37 (m, 2H), 7.33 (dd, J=8.5, 6.7 Hz, 2H), 7.25～7.20 (m, 1H), 4.92 (dd, J=8.6, 3.2 Hz, 1H), 2.84～2.76 (m, 1H), 2.63～2.54 (m, 3H), 2.39～2.30 (m, 2H), 1.89～1.74 (m, 2H), 1.54～1.45 (m, 4H), 1.40～1.29 (m, 4H), 0.94 (t, J=7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.4, 128.3, 126.9, 125.7, 75.9, 54.1, 53.9, 34.8, 28.9, 20.9, 14.2.

3-(Ethyl(isopropyl)amino)-1-phenylpropan-1-ol (**2d**): 70.7 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.37 (m, 2H), 7.32 (t, J=7.6 Hz, 2H), 7.25～7.20 (m, 1H), 4.90 (dd, J=9.4, 2.6 Hz, 1H), 3.17～3.08 (m, 1H), 2.86～2.78 (m, 1H), 2.67～2.57 (m, 2H), 2.45～2.36 (m, 1H), 1.88～1.68 (m, 2H), 1.16～1.11 (m, 6H), 0.96 (d, J=6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.4, 128.2, 126.9, 125.7, 76.0, 49.2, 48.8, 43.2, 35.0, 19.7, 15.3, 13.9; IR (neat) ν: 2970, 2832, 1462, 1269, 1063, 742, 703 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{24}NO$ $[M+H]^+$ 222.1858, found 222.1855.

3-(*tert*-Butyl(methyl)amino)-1-phenylpropan-1-ol (**2e**): 100.6 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.37 (m, 2H), 7.33 (dd, J=8.5, 6.8 Hz, 2H), 7.25～7.20 (m, 1H), 4.90 (dd, J=9.8, 2.3 Hz, 1H), 3.12～3.04 (m, 1H), 2.47～2.40 (m, 1H), 2.30 (s, 3H), 1.93～1.83 (m, 1H), 1.74～1.68 (m, 1H), 1.13 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.4, 128.3, 126.9, 125.7, 76.2, 54.8, 50.6, 35.2, 34.5, 26.0; IR (neat) ν: 2974, 2835, 1469, 1267, 740, 704 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{24}NO$ $[M+H]^+$ 222.1858, found 222.1854.

3-(Cyclohexyl(methyl)amino)-1-phenylpropan-1-ol (**2f**): 127.4 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40～7.31 (m, 4H), 7.26～7.20 (m, 1H), 4.92 (dd, J=8.1, 3.7 Hz, 1H), 2.90～2.82 (m, 1H), 2.71～2.64 (m, 1H), 2.54～2.46 (m, 1H), 2.31 (s, 3H), 1.86～1.76 (m, 6H), 1.31～1.05 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.4, 128.3, 126.9, 125.7, 76.0, 63.5, 53.5, 36.7, 34.5, 28.3, 28.1, 26.4, 26.1, 26.0; IR (neat) ν: 2933, 1460, 1268, 1051, 739, 705 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{16}H_{26}NO$ $[M+H]^+$ 248.2014, found 248.2013.

1-Phenyl-3-(pyrrolidin-1-yl)propan-1-ol (**2g**):[20] 58.6 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.31 (m, 4H), 7.26～7.21 (m, 1H), 4.94 (dd, J=8.3, 3.5 Hz, 1H), 2.96～2.87 (m, 1H), 2.73～2.62 (m, 3H), 2.60～2.53 (m, 2H), 1.93～1.83 (m, 2H), 1.83～1.78 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.3, 128.3, 127.0, 125.7, 75.9, 54.9, 54.2, 35.8, 23.6.

3-(Azepan-1-yl)-1-phenylpropan-1-ol (**2h**):[21] 112.3 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40～7.31 (m, 4H), 7.26～7.21 (m, 1H), 4.97 (dd, J=7.8, 3.8 Hz, 1H), 2.76～2.69 (m, 4H), 2.68～2.62 (m, 2H), 1.85～1.76 (m, 2H), 1.75～1.69 (m, 4H), 1.64～1.59 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.5, 128.3, 126.9, 125.7, 76.0, 57.9, 56.1, 34.7, 28.2, 26.9.

3-Morpholino-1-phenylpropan-1-ol (**2i**):[22] 95.9 mg,

72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.32 (m, 4H), 7.27～7.23 (m, 1H), 4.95 (t, J=5.8 Hz, 1H), 3.76 (t, J=4.7 Hz, 4H), 2.73～2.46 (m, 6H), 1.90～1.84 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.8, 128.4, 127.1, 125.6, 75.7, 67.1, 57.7, 53.8, 33.5.

3-((2-Methoxyethyl)(methyl)amino)-1-phenylpropan-1-ol (**2j**): 43.8 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40～7.36 (m, 2H), 7.35～7.30 (m, 2H), 7.26～7.20 (m, 1H), 4.93 (t, J=5.8 Hz, 1H), 3.53 (t, J=5.7 Hz, 2H), 3.36 (s, 3H), 2.77～2.58 (m, 4H), 2.35 (s, 3H), 1.86～1.81 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.2, 128.3, 126.9, 125.7, 75.6, 70.6, 58.9 (2C), 57.1, 42.6, 34.7; IR (neat) v: 2979, 1461, 1268, 1118, 1052, 739, 705 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{13}H_{22}NO_2$ $[M+H]^+$ 224.1651, found 224.1644.

3-((2-(Dimethylamino)ethyl)(methyl)amino)-1-phenylpropan-1-ol (**2k**): 77.9 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40～7.30 (m, 4H), 7.25～7.20 (m, 1H), 4.92 (dd, J=9.0, 3.2 Hz, 1H), 2.72～2.65 (m, 1H), 2.60～2.50 (m, 4H), 2.40～2.34 (m, 1H), 2.31 (s, 3H), 2.26 (s, 6H), 1.88～1.71 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.4, 128.3, 126.9, 125.7, 74.2, 57.1, 55.5, 55.1, 45.6, 42.6, 35.4; IR (neat) v: 2978, 1463, 1268, 1046, 739, 706 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{25}N_2O$ $[M+H]^+$ 237.1967, found 237.1962.

3-(Benzyl(methyl)amino)-1-phenylpropan-1-ol (**2l**):[23] 106.9 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.28 (m, 9H), 7.25～7.20 (m, 1H), 4.91 (dd, J=7.8, 3.9 Hz, 1H), 3.65 (d, J=12.8 Hz, 1H), 3.48 (d, J=12.8 Hz, 1H), 2.86～2.78 (m, 1H), 2.63～2.57 (m, 1H), 2.27 (s, 3H), 1.93～1.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.1, 137.9, 129.4, 128.7, 128.3, 127.6, 127.0, 125.7, 75.9, 63.0, 56.7, 41.9, 34.7.

3-(Benzyl(isopropyl)amino)-1-phenylpropan-1-ol (**2m**):[24] 141.5 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40～7.28 (m, 9H), 7.24～7.18 (m, 1H), 4.78 (dd, J=9.3, 2.6 Hz, 1H), 3.81 (d, J=13.3 Hz, 1H), 3.39 (d, J=13.3 Hz, 1H), 3.16～3.05 (m, 1H), 2.91～2.81 (m, 1H), 2.69～2.61 (m, 1H), 1.92～1.81 (m, 1H), 1.77～1.69 (m, 1H), 1.15 (d, J=6.7 Hz, 3H), 1.01 (d, J=6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.2, 139.0, 129.3, 128.7, 128.2, 127.4, 126.9, 125.7, 75.8, 54.2, 48.6, 48.1, 34.9, 19.4, 14.8.

3-(Methyl(naphthalen-1-ylmethyl)amino)-1-phenylpropan-1-ol (**2n**):[25] 152.8 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (dd, J=8.5, 1.1 Hz, 1H), 7.91～7.79 (m, 2H), 7.61～7.56 (m, 1H), 7.53～7.48 (m, 1H), 7.42 (d, J=5.2 Hz, 2H), 7.25～7.13 (m, 5H), 4.79 (dd, J=7.4, 4.1 Hz, 1H), 4.02～3.89 (m, 2H), 2.85～2.78 (m, 1H), 2.70～2.63 (m, 1H), 2.37 (s, 3H), 1.94～1.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.9, 134.1, 133.6, 132.5, 128.8, 128.6, 128.2, 128.2, 126.9, 126.5, 126.0, 125.6, 125.3, 124.1, 75.4, 61.3, 56.4, 42.3, 34.8.

3-(Benzyl(2-(dimethylamino)ethyl)amino)-1-phenylpropan-1-ol (**2o**): 159.5 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.26 (m, 9H), 7.23～7.18 (m, 1H), 4.99 (dd, J=9.9, 2.9 Hz, 1H), 3.66 (d, J=13.2 Hz, 1H), 3.55 (d, J=13.2 Hz, 1H), 2.91～2.83 (m, 1H), 2.65～2.53 (m, 3H), 2.52～2.44 (m, 1H), 2.31～2.24 (m, 1H), 2.17 (s, 6H), 1.95～1.86 (m, 1H), 1.82～1.72 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.5, 138.6, 129.4, 128.5, 128.3, 127.3, 126.8, 125.8, 72.9, 59.5, 56.9, 50.9, 50.5, 45.2, 36.3; IR (neat) v: 2817, 1455, 1268, 1054, 739, 701 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{20}H_{29}N_2O$ $[M+H]^+$ 313.2280, found 313.2277.

5-(Diethylamino)-1-phenylpentan-1-ol (**2p**): 56.0 mg, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.31 (m, 4H), 7.28～7.25 (m, 1H), 4.67 (dd, J=7.8, 5.4 Hz, 1H), 2.54 (dd, J=7.2, 1.4 Hz, 4H), 2.43 (m, 2H), 1.85～1.69 (m, 2H), 1.54～1.47 (m, 2H), 1.46～1.30 (m, 2H), 1.02 (t, J=7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.3, 128.5, 127.5, 126.0, 74.4, 52.7, 46.8, 38.9, 26.4, 23.8, 11.4; IR (neat) v: 2976, 1458, 1421, 1381, 1269, 1050, 739, 705 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{15}H_{26}NO$ $[M+H]^+$ 236.2014, found 236.2010.

3-(Diethylamino)-1-(*o*-tolyl)propan-1-ol (**2q**): 57.9 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, J=7.7 Hz, 1H), 7.26～7.20 (m, 1H), 7.16～7.08 (m, 2H), 5.10 (dd, J=8.0, 3.7 Hz, 1H), 2.84～2.61 (m, 4H), 2.54～2.44 (m, 2H), 2.31 (s, 3H), 1.78～1.69 (m, 2H), 1.11 (t, J=7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.2, 133.9, 130.2, 126.7, 126.1, 125.6, 72.7, 53.0, 46.7, 33.1, 19.1, 11.6; IR (neat) v: 2975, 1421, 1378, 1268, 1050, 740, 706 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{24}NO$ $[M+H]^+$ 222.1858, found 222.1850.

3-(Diethylamino)-1-(*m*-tolyl)propan-1-ol (**2r**): 72.6 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24～7.19 (m, 2H), 7.18～7.14 (m, 1H), 7.05 (d, J=7.4 Hz, 1H), 4.88 (dd, J=8.1, 3.6 Hz, 1H), 2.79～2.60 (m, 4H), 2.54～2.45 (m, 2H), 2.35 (s, 3H), 1.86～1.76 (m, 2H), 1.09 (t, J=7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.3, 137.8, 128.2, 127.7, 126.4, 122.8, 75.8, 52.7, 46.8, 34.6, 21.6, 11.6; IR (neat) v: 2980, 1421, 1269, 1090, 1051, 740 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{24}NO$ $[M+H]^+$ 222.1858, found 222.1850.

3-(Diethylamino)-1-(*p*-tolyl)propan-1-ol (**2s**):[26] 98.4 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, J=7.8 Hz, 2H), 7.14 (d, J=7.8 Hz, 2H), 4.89 (dd, J=8.3, 3.5 Hz, 1H), 2.81～2.58 (m, 4H), 2.53～2.43 (m, 2H), 2.33 (s, 3H), 1.85～1.74 (m, 2H), 1.08 (t, J=7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.4, 136.4, 128.9, 125.6, 75.6, 52.7, 46.7, 34.6, 21.2, 11.6.

3-(Diethylamino)-1-(2-methoxyphenyl)propan-1-ol (**2t**): 109.6 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (dd, J=7.5, 1.7 Hz, 1H), 7.21 (td, J=7.8, 1.8 Hz, 1H), 6.99 (td, J=7.5, 1.0 Hz, 1H), 6.83 (dd, J=8.2, 1.1 Hz, 1H), 5.20 (dd, J=8.2, 2.9 Hz, 1H), 3.81 (s, 3H), 2.76～2.45 (m, 6H), 1.95～1.87 (m, 1H), 1.78～1.68 (m, 1H), 1.09 (t, J=7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.9, 133.6, 127.6, 126.6, 120.6, 110.1, 70.5, 55.3, 52.7, 46.7, 32.5, 11.6; IR (neat) v: 2964, 2927, 1463, 1269, 1239, 1060, 744 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{24}NO_2$ $[M+H]^+$ 238.1807, found 238.1805.

3-(Diethylamino)-1-(4-(dimethylamino)phenyl)propan-1-ol (**2u**): 77.1 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (d, J=7.9 Hz, 2H), 6.73 (d, J=8.5 Hz, 2H), 4.83 (dd, J=9.0, 2.8 Hz, 1H), 2.93 (s, 6H), 2.77～2.58 (m, 4H), 2.51～2.43 (m, 2H), 1.87～1.71 (m, 2H), 1.08 (t, J=7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.9, 133.7, 126.6, 112.7, 75.6, 52.8, 46.8, 41.0, 34.7, 11.6; IR (neat) v: 2974, 1421, 1345, 1268, 1053, 740,706 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{15}H_{27}N_2O$ $[M+H]^+$ 251.2123, found 251.2113.

3-(Diethylamino)-1-(4-fluorophenyl)propan-1-ol (**2v**): 80.5 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (dd, J=8.3, 5.5 Hz, 2H), 7.01 (td, J=8.6, 1.2 Hz, 2H), 4.89 (dd, J=8.4, 3.3 Hz, 1H), 2.82～2.58 (m, 4H), 2.51～2.42 (m, 2H), 1.85～1.70 (m, 2H), 1.09 (t, J=7.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 161.9 (d, J=244.8 Hz), 141.1 (d, J=3.0 Hz), 127.2 (d, J=7.9 Hz), 115.0 (d, J=21.3 Hz), 75.3, 52.7, 46.8, 34.7, 11.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −116.6; IR (neat) v: 2976, 1510, 1269, 1220, 1058, 839, 740 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{13}H_{21}FNO$ $[M+H]^+$ 226.1607, found 226.1601.

3-(Diethylamino)-1-(3-(trifluoromethyl)phenyl)propan-1-ol (**2w**): 88.4 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (s, 1H), 7.56 (d, J=7.6 Hz, 1H), 7.51～7.41 (m, 2H), 5.01～4.95 (m, 1H), 2.84～2.76 (m, 1H), 2.73～2.59 (m, 3H), 2.53～2.44 (m, 2H), 1.85～1.77 (m, 2H), 1.09 (t, J=7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 146.4, 130.5 (d, J=32.0 Hz), 129.1, 128.7, 124.5 (d, J=273.3 Hz), 123.7(q, J=4.0 Hz), 122.6 (q, J=3.8 Hz), 75.4, 52.6, 46.8, 34.4, 11.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.5; IR (neat) v: 2977, 1329, 1269, 1165, 1123, 1069, 801, 740 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{21}F_3NO$ $[M+H]^+$: 276.1575, found 276.1572.

3-(Dibenzylamino)propan-1-ol (**2x**):[23] 58.1 mg, 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.24 (m, 10H), 3.67～3.62 (m, 2H), 3.57 (s, 4H), 2.66～2.61 (m, 2H), 1.79～1.72 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.4, 129.3, 128.6, 127.4, 64.0, 58.8, 53.3, 28.2.

4-(Benzyl(methyl)amino)butan-1-ol (**2y**):[27] 66.4 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.25 (m, 5H), 3.63～3.59 (m, 2H), 3.55 (s, 2H), 2.49～2.44 (m, 2H), 2.17 (s, 3H), 1.73～1.66 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 137.5, 129.6, 128.6, 127.5, 62.9, 62.8, 58.1, 41.3, 32.5, 26.1.

α-Aminoboronic ester **2z**:[28] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80～7.71 (m, 3H), 7.54～7.48 (m, 1H), 7.38 (t, J=7.8 Hz, 2H), 7.19～7.14 (m, 3H), 2.82 (broad, 1H), 2.71～2.56 (m, 2H), 1.77～1.72 (m, 2H), 1.64～1.56 (m, 1H), 1.24 (s, 13H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.9, 142.6, 133.2, 128.8, 128.6, 128.4, 128.1, 125.8, 81.2, 36.1, 31.2, 29.8, 25.5, 25.2, 25.0.

4.4 Deuterium-labeling experiment

In a glove box, to an oven-dried 10-mL vial were added $Co(acac)_2$ (7.7 mg, 0.03 mmol), tpy (7.0 mg, 0.03 mmol) and anhydrous EtOAc (2.0 mL). The resulting solution was stirred for 20 min at room temperature, at which time DBpin (116.1 mg, 0.9 mmol) was added. After the resulting mixture was stirred for an additional 5 min, the mixture of (*E*)-*N*,*N*-diethyl-3-phenylprop-1-en-1-amine (**1a**) (113.6 mg, 0.60 mmol) was added and stirred for 15 h at 40 ℃. The resulting suspension was cooled to room temperature, filtered through a celite pad with EtOAc and concentrated in vacuo. The residue was dissolved in THF (3.0 mL) and cooled to 0 ℃. NaOH (4.5 equiv., 3.0 mol/L) and H_2O_2 (4.5 equiv., 30%) were then added. The resulting mixture was stirred for 0.5 h, extracted with EtOAc, dried with Na_2SO_4, filtered and concentrated. The residue was purified by silica gel chromatography using DCM/MeOH (V∶V=10∶1) as eluent to afford 3-(diethylamino)-1-phenylpropan-1-ol (**D-2a**) (111.1 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.30 (m, 4H), 7.26～7.21 (m, 1H), 4.94～4.89 (m, 1H), 2.87～2.65 (m, 3.50H), 2.63～2.52 (m, 2H), 1.89～1.80 (m, 1.76H), 1.12 (t, J=7.2 Hz, 6H).

4.5 Gram-scale reaction

In a N_2-filled glove box, an oven-dried 75-mL sealed tube equipped with a stirrer bar was charged with $Co(acac)_2$ (77.1 mg, 0.3 mmol), tpy (70.0 mg, 0.3 mmol) and anhydrous EtOAc (30.0 mL). The resulting solution was stirred for 20 min at room temperature, at which time HBpin (1.2 g, 9.0 mmol) was added. After the resulting mixture was stirred for an additional 5 min, (*E*)-*N*-benzyl-*N*-isopropyl-3-phenylprop-1-en-1-amine (**1m**) (1.6 g, 6.0 mmol) was added and stirred for 15 h at 40 ℃. The resulting suspension was cooled to room temperature, filtered through a celite pad with EtOAc and concentrated in vacuo. The residue was purified by Kugelrohr short path distillation to afford *N*-benzyl-*N*-isopropyl-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (**3m**) (1.74 g, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.33 (m, 2H), 7.29～7.24 (m, 2H), 7.22～7.14 (m, 5H), 7.12～7.07 (m, 1H), 3.53 (s, 2H), 2.92 (q, J=6.6 Hz, 1H), 2.42～2.35 (m, 3H), 2.03～1.93 (m, 1H), 1.83～1.73 (m, 1H), 1.13 (d, J=15.8 Hz, 12H), 0.96 (t, J=6.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.4, 128.6, 128.4, 128.3, 128.2, 126.5, 125.2, 83.3, 54.1, 49.5, 49.0, 24.8, 24.6, 18.2, 18.0 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR (128 MHz, $CDCl_3$) δ: 33.2; IR (neat) v: 2976, 1361, 1323, 1268, 1142, 738, 701 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{25}H_{37}BNO_2$ $[M+H]^+$ 394.2917, found 394.2924.

4.6 Synthetic applications

4.6.1 Procedure for the synthesis of compound **4**

Following a modified procedure,[29] to a 25-mL flame-dried Schlenk tube charged with **3m** (78.7 mg, 0.20 mmol) and THF (1.0 mL) was slowly added vinylmagnesium bromide (0.8 mL, 1.0 mol/L in THF, 8.0 equiv.). After stirring for 0.5 h at −78 ℃, a solution of I_2 (203.1 mg, 0.8 mmol) in THF was added and stirred for 0.5 h, then allowed to warm to 0 ℃. The resulting mixture was quenched with saturated aqueous solution of $Na_2S_2O_3$, extracted with

EtOAc, dried with Na_2SO_4, filtered and concentrated. The residue was purified by silica gel flash chromatography using petroleum ether/EtOAc (V∶V=20∶1) as the eluent to afford *N*-Benzyl-*N*-isopropyl-3-phenylpent-4-en-1-amine (**4**) (38.8 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.26 (m, 5H), 7.25～7.09 (m, 5H), 5.92～5.82 (m, 1H), 4.97～4.89 (m, 2H), 3.53 (s, 2H), 3.37～3.30 (m, 1H), 2.95～2.84 (m, 1H), 2.46～2.31 (m, 2H), 1.85～1.76 (m, 2H), 0.95 (d, J=6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.6, 142.5, 141.7, 128.6, 128.5, 128.2, 127.8, 126.6, 126.2, 114.1, 54.3, 50.0, 47.6, 47.5, 34.4, 18.12, 18.07; IR (neat) ν: 2977, 1423, 1268, 1090, 1052, 739, 708 cm^{-1}. HRMS (ESI- TOF) calcd for $C_{21}H_{28}N$ $[M+H]^+$ 294.2222, found 294.2214.

4.6.2 Procedure for the synthesis of compound **5**

Following a modified procedure,[30] to a 25 mL flame-dried Schlenk tube charged with furan (20.4 mg, 0.3 mmol) and THF (1 mL) was added *n*-BuLi (0.12 mL, 2.5 mol/L in hexane, 0.3 mmol) at −78 ℃ under N_2 atmosphere. After stirring for 1 h at room temperature, the reaction mixture was cooled back to −78 ℃ and a solution of **3m** (78.7 mg, 0.20 mmol) in THF (1 mL) was added. The resulting mixture was then allowed to stir at −78 ℃ for 5 h and a THF (1 mL) solution of *N*-bromosuccinimide (NBS) (53.4 mg, 0.3 mmol) was then added. The reaction was vigorously stirred at the same temperature. The resulting mixture was then warmed up to room temperature and stirred for 10 h, then quenched with saturated NH_4Cl, extracted with EtOAc, dried with Na_2SO_4, filtered and concentrated. The residue was purified by silica gel flash chromatography using petroleum ether/EtOAc (V∶V=20∶1) as the eluent to afford *N*-benzyl-3-(furan-2-yl)-*N*-isopropyl-3-phenylpropan-1-amine (**5**) (42.3 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35～7.25 (m, 6H), 7.23～7.12 (m, 5H), 6.23 (dd, J=3.2, 1.8 Hz, 1H), 5.96～5.91 (m, 1H), 4.07 (t, J=7.5 Hz, 1H), 3.54 (d, J=3.2 Hz, 2H), 2.94～2.86 (m, 1H), 2.39 (t, J=6.9 Hz, 2H), 2.23～2.14 (m, 1H), 2.01～1.91 (m, 1H), 0.93 (dd, J=8.4, 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.1, 143.1, 141.3, 128.6, 128.5, 128.2, 127.9, 126.6, 126.5, 110.0, 105.3, 54.3, 49.9, 47.3, 42.7, 33.9, 18.04, 17.98; IR (neat) ν: 2962, 1497, 1460, 1024, 943, 740, 703 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{23}H_{28}NO$ $[M+H]^+$ 334.2171, found 334.2167.

4.6.3 Procedure for the synthesis of compound **6**

Following a modified procedure,[31] to a solution of $MeONH_2$ (1.39 mol/L in THF, 3.0 equiv.) in THF was added *n*-BuLi (0.72 mL, 2.5 mol/L in hexane, 1.8 mmol) at −78 ℃. After stirring for 0.5 h at room temperature, **3m** (236.0 mg, 0.60 mmol) was added. The resulting mixture was then heated to 60 ℃ and stirred for 15 h, then quenched with H_2O, extracted with EtOAc, dried with Na_2SO_4, filtered and concentrated. The residue was purified by silica gel chromatography using DCM/MeOH (V∶V=10∶1) as eluent to afford N^1-Benzyl-N^1-isopropyl-3-phenylpropane-1,3-diamine (**6**) (124.7 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40～7.27 (m, 7H), 7.26～7.20 (m, 3H), 3.96 (t, J=6.7 Hz, 1H), 3.56 (s, 2H), 3.06～2.98 (m, 1H), 2.55～2.47 (m, 2H), 1.88 (brs, 2H), 1.82～1.69 (m, 2H), 1.06～1.02 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 146.6, 141.2, 128.8, 128.5, 128.3, 126.9, 126.8, 126.4, 54.5, 53.9, 49.5, 46.9, 37.8, 18.0, 17.7; IR (neat) ν: 2973, 1366, 1330, 1269, 1170, 739, 703 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{19}H_{27}N_2$ $[M+H]^+$ 283.2174, found 283.2171.

4.6.4 Procedure for the synthesis of compound **7**

Following a modified procedure,[32] in a glove box, to a Schlenk tube equipped with a magnetic stir bar were added Ag_2O (208.6 mg, 0.9 mmol), $Pd_2(dba)_3$ (27.5 mg, 0.03 mmol), PPh_3 (63.8 mg, 0.24 mmol), **3m** (236.0 mg, 0.6 mmol), and 1-iodo-4-methoxybenzene (280.8 mg, 1.2 mmol,). THF (6.0 mL, 0.1 mol/L) was then added and the tube was sealed. The mixture was stirred at 80 ℃ for 24 h. After cooling to room temperature, water was added and the mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried with Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography using petroleum ether/EtOAc (V∶V=40∶1) as eluent to afford *N*-Benzyl-*N*-isopropyl-3-(4-methoxyphenyl)-3-phenyl-propan-1-amine (**7**) (94.7 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.27 (m, 4H), 7.24～7.18 (m, 3H), 7.14～7.04 (m, 5H), 6.79～6.74 (m, 2H), 3.94 (t, J=7.6 Hz, 1H), 3.75 (s, 3H), 3.53 (s, 2H), 2.93～2.85 (m, 1H), 2.37 (t, J=7.0 Hz, 2H), 2.13～2.07 (m, 2H), 0.91 (d, J=6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.9, 145.7, 141.6, 137.4, 128.9, 128.6, 128.4, 128.2, 127.9, 126.6, 126.0, 113.8, 55.3, 54.4, 50.0, 48.0, 47.9, 35.2, 29.9, 18.2, 18.0; IR (neat) ν: 2973, 1511, 1267, 1173, 1046, 739, 704 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{26}H_{32}NO$ $[M+H]^+$ 374.2484, found 374.2479.

Supporting Information ^{1}H NMR and ^{13}C NMR spectra of compounds **1** and **2**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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