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Transition Metal-Free Generation of *N*-Unsubstituted Imines from Benzyl Azides: Synthesis of *N*-Unsubstituted Homoallylic Amines

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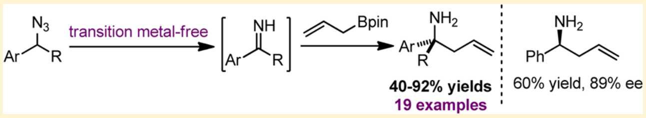
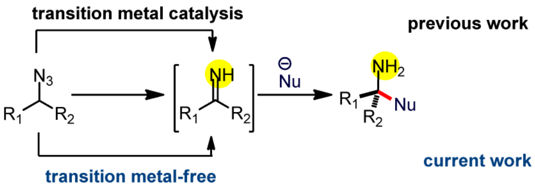
Supporting Information

ABSTRACT: An efficient transition metal-free approach for the generation of *N*-unsubstituted imines from azides followed by trapping with allyl nucleophile to provide *N*-unsubstituted homoallylic amines has been described. Although catalytic KO^{t}Bu in DMSO is sufficient to allow imine generation, stoichiometric KO^{t}Bu is essential in THF. Further, an enantio- and diastereoselective synthesis of homoallylic amines from benzyl azide has also been exemplified.



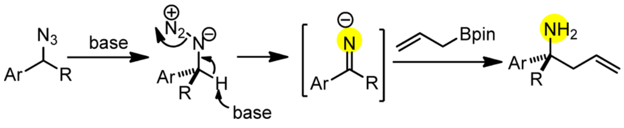
Imines are important intermediates for the synthesis of amines,[1] *N*-containing natural products,[2] and other transformations.[3] In general, imines are unstable in nature, and their synthesis and isolation have remained a continuing challenge in organic chemistry. The synthetic methods available in the literature are mostly for the synthesis of *N*-substituted imines.[4] These methods are mostly based on the condensation of carbonyls with an amine counterpart where the equilibrium favors imine with *N*-substitution. Nevertheless, acquiring an *N*-unprotected amine through an *N*-protected imine always requires an additional step for the removal of the corresponding *N*-protection.[5,6a] Therefore, the reactions through the *N*-unsubstituted imines would be highly important, leading to the shorter, atom-economical, and waste-free routes (Scheme 1).

Scheme 1. Synthesis of *N*-Unsubstituted Amine from Azides



In this context, an aminoallylation of aldehydes using ammonia has been developed by Kobayashi et al.;[5a] nevertheless, the imine intermediate has not been isolated or characterized. Further, excess ammonia is needed because of the reversibility of the reaction that limits the range of different nucleophiles that can be used for this method. Further, *N*-metalloketamines from alkyl nitrile have been developed and used for hydrogenation[5b] and allylation.[5c] In the past decade, many methods based on transition metal–imine complexes involving the transition metal or noble metals have been developed.[6] Recently, Rhee, Park, and co-workers[6a] reported a Ru-catalyzed synthesis of imines from azides and further utility for the synthesis of homoallylic amines. Synthesis of azaspirocyclohexadienes from α-azido-*N*-arylamides through the generation of *N*-unsubstituted imines has been reported by Chiba et al. using Cu catalyst.[6b] However, identification of transition metal-free methods is important to avoid metallic impurities in products.[7] Encouraged by the recent progress in the efficient synthesis of azides,[8] we became interested in developing a supplemental transition metal-free strategy for the synthesis of *N*-unsubstituted imines from alkyl azides. Further, the trapping of in situ-formed *N*-unsubstituted imines would provide the corresponding *N*-unsubstituted amines. Here, we developed a base-promoted decomposition of α-H-containing azides to generate imine followed by trapping with allylpinacol borane to provide the speculated homoallylic amines (see Scheme 2).

Scheme 2. Synthesis of Homoallylic Amines from Azides Promoted by Base



We started the initial screening for the conversion of benzyl azides to the corresponding homoallylic amines[9] using various bases such as Et_3N, ethylenediamine (en), TMEDA, pyridine, NaH, NaOMe, NaOEt, NaO^{t}Bu, and KO^{t}Bu in THF using allylpinacol borane as the allylating reagent. Interestingly, only KO^{t}Bu was found to be effective in providing homoallylic amine **3a** (Table 1, entries 1–9), whereas other bases failed to initiate the formation of imine itself. NaO^{t}Bu did not even react with azide **1a**, probably because of its weaker basicity compared to that of KO^{t}Bu. Among several solvents, only THF, DMSO,

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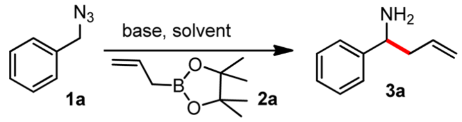
Table 1. Optimization of the Reaction Conditions[a]



entry	bases (equiv)	solvent	yield of **3a** (%)[b]
1	Et_3N (1.1)	THF	0
2	en (1.1)	THF	0
3	tmeda (1.1)	THF	0
4	pyridine (1.1)	THF	0
5	NaH (1.1)	THF	0
6	NaOMe (1.1)	THF	0
7	NaOEt (1.1)	THF	0
8	NaO^{t}Bu (1.1)	THF	0
9	KO^{t}Bu (1.1)	THF	72 (70)[c]
10	KO^{t}Bu (1.1)	DMF	5
11	KO^{t}Bu (1.1)	CH_2Cl_2	0
12[d]	KO^{t}Bu (1.1)	DMSO	52
13	KO^{t}Bu (1.1)	CH_3CN	13
14	KO^{t}Bu (1.1)	diethyl ether	0
15	KO^{t}Bu (1.1)	CH_3NO_2	0
16	KO^{t}Bu (1.1)	DME	60
17	KO^{t}Bu (1.1)	MeOH	0
18	KO^{t}Bu (1.1)	toluene	0
19	KO^{t}Bu (1.1)	EtOAc	0
20	KO^{t}Bu (1.1)	1,4-dioxane	0
21[d]	KO^{t}Bu (0.1)	DMSO	56
22	KO^{t}Bu (0.1)	THF	<5

[a] Reaction conditions: azide (0.2 mmol, 1.0 equiv), base (1.1 equiv) stirred at rt for 15 min, then allyl-Bpin (**2a**, 1.3 equiv) added at 0 °C, stirred for 1 h and then for 15 min at rt. [b] ^{1}H NMR yield of the reaction mixture using acetophenone as an internal standard. [c] Yields (in parentheses) after column chromatography. [d] Reaction conducted at rt.

and DME were found to be suitable for the current process (Table 1, entries 9−20). However, using catalytic KO^{t}Bu in DMSO, the formation of imine was substantial (entry 21) and provided desired product **3a**; on the other hand, a trace amount of amine was formed in THF (entry 22).

Although the catalytic KO^{t}Bu in DMSO provided the desired amine **3a** from benzyl azide, we decided to continue our studies using stoichiometric KO^{t}Bu in THF as the conversion was better to provide the homoallylic amine. Benzyl azides with different substituents like *p*-Cl, *p*-Ph, *p*-BnO (Table 2, entries 1−4), and electron-withdrawing benzyl azides (Table 2, entries 5 and 6) worked smoothly to provide the corresponding homoallylic amines with good yields. Alkyl azides derived from *α*- and *β*-naphthaldehydes as well as heteroaromatic rings reacted under optimized conditions to furnish amines **3g**−**3k** (entries 7−11, respectively). After successful synthesis of amines from benzyl azides containing aromatic and heteroaromatic rings, we tested our methodology for the cinnamyl azides (entries 12 and 13) that afforded the homoallylic amines (**3l** and **3m**) in good yields. The reactions of *α*-branched azides were also investigated, which provides the desired tertiary homoallylic amines **3n** and **3o** (entries 14 and 15, respectively). Interestingly, the cinnamyl-based tertiary amine **3p** was also synthesized from the corresponding azide (entry 16). Unfortunately, the aliphatic azide remained unreactive under current reaction conditions (entry 17).[10]

Later, a reagent-controlled allylation was performed at −40 °C, and excellent diastereoselectivities were obtained using *trans*- and *cis*-crotylboronic acid pinacol esters (**2b** and **2c**, respectively) to furnish *anti* and *syn* products, respectively (Scheme 3, **3q** and **3r**, respectively). Generally, *α*-aminoallylation of aldehyde was found to give poor enantioselectivity,[5a] but the stronger coordination of *in situ* formed benzylideneamine [**II** (Scheme 5)] with boron results in an increase in enantioselectivity via our approach. Reaction of (+)-(ipc)$_2$allylborane (**2d**) with the *in situ* formed imine at −78 °C followed by oxidation with H_2O_2 under basic conditions provided **3a-(+)-crl** in 60% yield and 89% ee (Scheme 3).

Further, we also focused on the isolation of *N*-unsubstituted imines, keeping in mind its immense synthetic application in organic synthesis[3a,e,f] as well as to establish the mechanistic relevance (Scheme 4). Notably, the *N*-unsubstituted ketimines are generally synthesized by the reactions of arylnitrile and Grignard reagents via a prolonged heating reaction.[3e,5b,11] However, the azides provided imines **4a** and **4b** in good yields in a shorter reaction time using catalytic KO^{t}Bu (10 mol %) in DMSO.

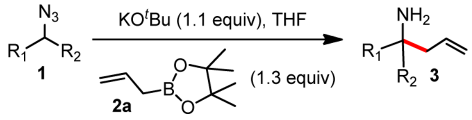
The exclusive formation of corresponding *N*-deuterated imine was observed during the ^{1}H NMR spectroscopy study of current decomposition of benzyl azide (**1a**) using 10 mol % KO^{t}Bu as a catalyst in d_6-DMSO as a solvent. Further, when this reaction was conducted in d_8-THF as a solvent, the corresponding *N*-protonated imine was not observed (see the Supporting Information).

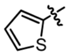
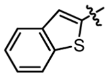
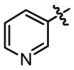
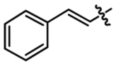
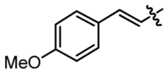
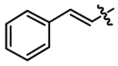
A plausible mechanism based on these results and studies mentioned above is proposed in Scheme 5. In THF, KO^{t}Bu promotes the direct deprotonation and denitrogenation, providing intermediate **II**. Presumably, the proton exchange of **II** with HO^{t}Bu is very slow, because of the relatively higher pK_a of HO^{t}Bu in THF,[12] which restricts the process to being catalytic. On the other hand in DMSO, KO^{t}Bu first generates potassium methylsulfinylmethylide (**III**),[13] which deprotonates the azide to provide intermediate **II**. The relatively lower pK_a of HO^{t}Bu in DMSO accelerates the proton exchange of **II** with HO^{t}Bu and thus regenerates KO^{t}Bu, providing imine **IV**. However, the 1,2-hydride shift of alkyl azide to give imine, which was observed in the case of the corresponding Ru-catalyzed process,[6a] is not occurring here.

To confirm the proton abstraction of methylsulfinylmethylide (**III**) by the *α*-deprotonation of the benzyl azide, the following competitive experiments were conducted as described in Table 3. When the current decomposition of benzyl azide (**1a**) was performed using 10 mol % KO^{t}Bu as a catalyst in d_6-DMSO as a solvent, the formation of partially protonated d_6-DMSO (HD_2CSOCD_3) was observed as shown in entries 2 and 3. Notably, the level of formation of HD_2CSOCD_3 was increased with an increase in the amount of benzyl azide (**1a**) (entry 2 vs entry 3).

In summary, we have developed an efficient transition metal-free, simple KO^{t}Bu-promoted approach for the synthesis of *N*-unsubstituted imines from azides. Further, the trapping of such imines *in situ* with allylpinacol borane as an allylating reagent provided *N*-unsubstituted homoallylic amines in good yields. This transition metal-free condition, obviously, offers significant advantages over the previous protocols for the synthesis of *N*-unsubstituted imines. The isolation of *N*-unsubstituted imines from corresponding azides has also been exemplified. Interestingly, a contrasting reactivity of KO^{t}Bu for the generation of imines from azides in DMSO and THF is

Table 2. Scope of Azides for Homoallylic Amination[a]



Entry	Cond^n	R^1	R^2	T (h)	**3**, (%)^b
1	A	C_6H_5-	H	1	**3a**, 70
2	B	p-Cl-C_6H_4-	H	0.2	**3b**, 65
3	B	p-Ph-C_6H_4-	H	1.5	**3c**, 90
4	B	m-BnO-C_6H_4-	H	0.25	**3d**, 70
5	B	m-NO_2-C_6H_4-	H	0.1	**3e**, 71
6	A	p- NO_2-C_6H_4-	H	0.5	**3f**, 43
7	B	α-naphthyl-	H	0.1	**3g**, 87
8	B	β-naphthyl-	H	0.25	**3h**, 92
9	B		H	3	**3i**, 67
10	C		H	0.1	**3j**, 81
11	A		H	1	**3k**, 40
12	B		H	0.1	**3l**, 81
13	B		H	0.1	**3m**, 87
14	D	p-F-C_6H_4-	Me	18	**3n**, 76
15	D	p-NO_2-C_6H_4-	Me	12	**3o**, 83
16	B		Me	0.1	**3p**, 51
17	B	n-C_6H_{13}-	H	1	-

[a]Reaction conditions: (A) azide (**1**,1.0 mmol, 1.0 equiv), KO^{t}Bu (1.1 equiv) stirred in THF at 0 °C for t hours and then rt for 15 min, then **2a** (1.3 equiv) added at 0 °C, stirred for 1 h and then 15 min at rt; (B) azide (**1**, 1.0 mmol, 1.0 equiv), KO^{t}Bu (1.1 equiv) stirred in THF at 0 °C for t h, then **2a** (1.3 equiv) added, stirred for 1 h and then 15 min at rt; (C) azide (**1**, 1.0 mmol, 1.0 equiv), KO^{t}Bu (0.1 equiv) stirred in DMSO at rt for time t, then **2a** (1.3 equiv) added and stirred for 15 min; (D) azide (**1**, 1.0 mmol, 1.0 equiv), KO^{t}Bu (0.1 equiv) stirred in DMSO at rt for 5 min, then **2a** (1.3 equiv) added and heated at 65 °C for t h. [b]Isolated yields.

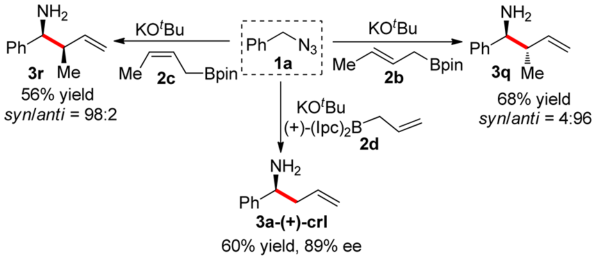
observed. Although catalytic KO^{t}Bu in DMSO is sufficient to allow imine generation, stoichiometric KO^{t}Bu is essential in THF. Hence, we anticipate that our methodology may draw significant attention of chemists working on the development of synthetic methodologies for better methods for the synthesis of N-unsubstituted imines and corresponding homoallylic amines.

■ EXPERIMENTAL SECTION

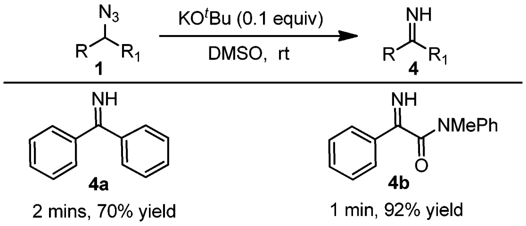
Safety Note. Although we have experienced no hazards during the course of this work, any preparative work with these azides should be conducted behind a blast shield in a fume hood with care and awareness of the potential for spontaneous and exothermic decomposition of azides.[14] Addition of KO^{t}Bu to the azides should be performed with care (e.g., the addition of KO^{t}Bu in 2–3 portions, conducting the reaction behind a blast shield) because it generates N_2 gas in an exothermic way.

General Methods. All reagents were used as supplied commercially unless otherwise stated. Dichloromethane (CH_2Cl_2) and dimethyl sulfoxide (DMSO) were distilled over CaH_2. Tetrahydrofuran (THF) was distilled immediately before use from sodium benzophenone ketyl. Reactions were conducted under an argon atmosphere. Analytical thin layer chromatography (TLC) was performed on 0.2 mm coated Science silica gel (EM 60-F254) plates

Scheme 3. Diastereoselective and Enantioselective Homoallylic Amination



Scheme 4. Synthesis of *N*-Unsubstituted Imines[a,b]



[a]Reaction conditions: azide (**1**, 1.0 mmol, 1.0 equiv), KO^{t}Bu (0.1 equiv) stirred for 1−2 min at rt. [b]Isolated yields.

Scheme 5. Proposed Mechanism for Imine Synthesis

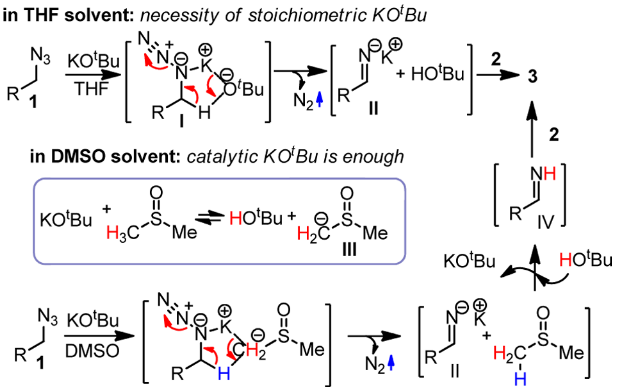
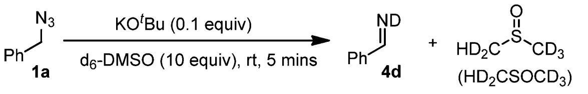


Table 3. Investigation of the Abstraction of H from Azide by DMSO[a]



entry	substrate (mmol)	d_6-DMSO (10 equiv)	HD_2SOCD_3[b] (mmol)	HD_2SOCD_3[c] (mmol)
1	–	2.25	0.09	–
2	0.225	2.25	0.25	0.16
3	0.45	4.50	0.62	0.44

[a]Reaction conditions: starting material **1a** (0.225 mmol for entry 2, 0.45 mmol for entry 3), d_6-DMSO (10 equiv, 2.25 mmol for entries 1 and 2 and 4.5 mmol for entry 3) stirred at rt for 5 min. ^{1}H NMR data were recorded in d_6-benzene using anisole as an internal standard. [b]Total amount of H content in d_6-DMSO observed in the ^{1}H NMR spectrum. [c]Amount of HD_2CSOCD_3 forming by the abstraction of H from azide **1a**.

purchased from Merck. Visualization was accomplished with UV light (254 nm) and exposure to either ethanolic phosphomolybdic acid (PMA), anisaldehyde, or a KMnO$_4$ solution followed by heating. Melting points are uncorrected. ^{1}H NMR spectra were acquired on a 400 MHz spectrometer, and chemical shifts are reported in parts per million relative to the residual solvent peak. ^{13}C NMR spectra were acquired on a 100 MHz spectrometer, and chemical shifts are reported in parts per million relative to the residual solvent peak. Unless noted, NMR spectra were acquired in CDCl$_3$; individual peaks are reported as multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), integration, and coupling constants in hertz. All IR spectra were obtained as neat films, and selected absorbances are reported in cm^{-1}. Low-resolution (LR) and high-resolution (HR) mass spectrometry data were acquired on a MicroTOF-Q-II mass spectrometer or a GC Q-TOF mass spectrometer or by GC−MS (EI 70 eV) using a DB-5 column.

Procedures for Substrate Preparation. Benzyl azides **1a**−**1g** were prepared in a single step according to the procedure described in ref 8e.

Other azides (e.g., **1h**−**1p**) were prepared according to the following procedure unless otherwise mentioned.

To a stirred solution of carbonyl (10 mmol) in MeOH was added NaBH$_4$ (1.3 equiv., 13 mmol) by portion at 0 °C (Luche reduction was performed to synthesize the alcohol of azide **1p** using 1.2 equiv of CeCl$_3$·7H$_2$O and 1.2 equiv of NaBH$_4$ in MeOH solvent). After being stirred for 15 min at that temperature, the reaction mixture was brought to room temperature and stirred for 1 h until the carbonyl was completely consumed. MeOH was evaporated from the reaction mixture by rotary evaporator. The reaction mixture was extracted with EtOAc and brine solution three times. The organic parts were combined and dried over Na$_2$SO$_4$, and the solvent was evaporated on a rotavapor. The crude alcohol was used for the next step without further purification.

The crude alcohol was dissolved in anhydrous CH$_2$Cl$_2$ and stirred at 0 °C. Mesyl chloride (1.2 equiv, 12 mmol) was added dropwise via syringe under a N$_2$ atmosphere at the same temperature followed by the addition of triethylamine (1.3 equiv, 13 mmol) dropwise. The reaction mixture was stirred for 30 min at the same temperature and then stirred at room temperature for 1−3 h until the alcohol was consumed. The reaction mixture was extracted with dichloromethane (3 × 50 mL) and water (50 mL). The organic parts were combined and dried over Na$_2$SO$_4$. The solvent was evaporated with a rotary evaporator, and the crude was used for the next step without further purification.

To a solution of the crude mesylated alcohol in DMF was added NaN$_3$ (2.0 equiv, 20 mmol), and the mixture was stirred at 60 °C for 1 h (for synthesizing compounds **1m** and **1p**) or at rt for 3 h (for synthesizing compounds **1n**, **1o**, and **1r**) until the mesylated alcohol was consumed. After the reaction had reached completion, the DMF was evaporated with a rotary evaporator and then extracted with EtOAc (3 × 50 mL) and brine solution (50 mL). The organic parts were combined and dried over MgSO$_4$, and the solvent was evaporated using a rotary evaporator. The crude was purified by column chromatography (EtOAc in *n*-hexane) on silica gel.

*(E)-1-(3-Azidoprop-1-en-1-yl)-4-methoxybenzene (**1m**).* Yield: 1.00 g, 53%, over three steps. R_f = 0.39 (2% EtOAc/*n*-hexane). Colorless liquid. IR (neat): 3338, 2960, 2100, 1513, 1253, 1176, 1034, 969, 841 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.58 (d, J = 15.5 Hz, 1H), 6.10 (td, J = 6.8, 15.7 Hz, 1H), 3.90 (d, J = 6.7 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.7, 134.2, 128.78, 127.94, 120.1, 114.1, 55.3, 53.3. HRMS (ESI): [M]$^+$ calcd for C$_{10}$H$_{11}$N$_3$O, *m/z* 189.0902; found, *m/z* 189.1028.

*1-(1-Azidoethyl)-4-fluorobenzene (**1n**).* Yield: 940 mg, 57%, over three steps. R_f = 0.35 (1% EtOAc/*n*-hexane). Colorless liquid. IR (neat): 3333, 2981, 2105, 1605, 1513, 1233, 836 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 (2H), 7.05 (2H), 4.59 (q, J = 6.8 Hz, 1H), 1.50 (d, J = 6.85 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 162.44 (d, J = 246.6 Hz), 136.69 (d, J = 3.2 Hz), 128.10 (d, J = Hz), 115.66 (d, J = Hz), 60.4, 21.6. HRMS (ESI): [MH-N$_2$]$^+$ calcd for C$_8$H$_9$FN, *m/z* 138.0719; found, *m/z* 138.0736.

*1-(1-Azidoethyl)-4-nitrobenzene (**1o**).*[15] Yield: 1.767 g, 92%, over three steps. R_f = 0.36 (5% EtOAc/*n*-hexane). Yellowish oil. IR (neat): 2105, 1520, 1346, 1111, 1064, 855, 790 cm^{-1}. ^{1}H NMR (400 MHz,

$CDCl_3$): δ 8.18 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 4.73 (q, J = 6.85 Hz, 1H), 1.53 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 147.6, 127.2, 124.0, 60.1, 21.7. LRMS (ESI): $[M - N_2 + H]^+$ calcd for $C_8H_8N_2O_2$, m/z 165.1; found, m/z 165.1.

*(E)-(3-Azidobut-1-en-1-yl)benzene (**1p**).*[16] Yield: 588 mg, 34%, over three steps. R_f = 0.35 (1% EtOAc/n-hexane). Colorless liquid. IR (neat): 2979, 2102, 1300, 1235, 1143, 1040, 967, 750, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47−7.26 (5H), 6.63 (d, J = 15.8 Hz, 1H), 6.18 (dd, J = 7.4, 15.8 Hz, 1H), 4.19 (1H), 1.40 (d, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1, 132.2, 128.7, 128.4, 128.1, 126.7, 59.7, 20.2. LRMS (ESI): $[M - N_2 + H]^+$ calcd for $C_{10}H_{12}N$, m/z 146.1; found, m/z 146.2.

*2-Azido-N-methyl-N,2-diphenylacetamide (**1r**).*[6b] Yield: 2.474 g, 93%, over three steps. R_f = 0.27 (10% EtOAc/n-hexane). Colorless solid. Mp: 75−77 °C. IR (neat): 3033, 2978, 2097, 1668, 1595, 1494, 1454, 1420, 1384, 1229, 1123, 771, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37−7.21 (6H), 7.14−7.05 (2H), 6.88 (2H), 4.59 (s, 1H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 142.2, 134.3, 129.8, 129.0, 128.9, 128.5, 128.1, 127.6, 62.8, 37.8. LRMS (ESI): $[M - N_2 + H]^+$ calcd for $C_{15}H_{15}N_2O$, m/z 239.1; found, m/z 239.1.

*Synthesis of (Azidomethylene)dibenzene (**1q**).* To a stirring solution of benzhydryl alcohol (8.77 mmol, 1.613 g) in CH_2Cl_2 was added azidotrimethylsilane (2.0 equiv, 17.5 mmol, 2.3 mL) at 0 °C followed by the addition of $FeCl_3$ (30 mol %, 0.3 equiv, 426 mg) in 2 portions. After the mixture had been stirred for 10 min at the same temperature, the reaction was quenched by the addition of brine solution (10 mL). It was extracted with water and dichloromethane. The organic portion was dried over Na_2SO_4, and solvent was evaporated on a rotavapor. The crude was purified by flash column chromatography (EtOAc/n-hexane) on silica gel.

*(Azidomethylene)dibenzene (**1q**).*[16] Yield: 1.467 g, 80%. R_f = 0.37 (1% EtOAc/n-hexane). Colorless liquid. IR (neat): 3065, 3037, 2103, 1453, 1259, 1240, 870, 743, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.45−7.28 (10H), 5.74 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 128.7, 128.1, 127.5, 68.6. LRMS (ESI): $[M - N_2 + H]^+$ calcd for $C_{13}H_{12}N$, m/z 182.1; found, m/z 182.1.

Homoallylic Amine Synthesis. *Standard Procedure for Synthesis of Homoallylic Amine from Azides Using Condition A.* To a stirred solution of azide (**1**, 1.00 mmol) in anhydrous THF (3.0 mL) at 0 °C was added potassium *tert*-butoxide (1.10 equiv, 1.10 mmol) under an Ar atmosphere, and the mixture was stirred at that temperature. After being stirred for t hours (the time listed in column 5 of Table 2), the mixture was brought to room temperature and stirred for 15 min to completely consume the starting material to imine. The reaction mixture was brought to 0 °C, and allylboronic acid pinacol ester (**2a**, 1.3 equiv, 1.3 mmol) was added dropwise via a syringe. After being stirred at that temperature for 1 h, the mixture was stirred at room temperature for 15 min. It was extracted with 1 N HCl (10 mL) and diethyl ether (4 mL). The aqueous part was washed with diethyl ether (4 mL). The aqueous layer was further basified to pH 10 using a 6 N KOH solution. Thereafter, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was dried over sodium carbonate, and the solvent was removed by a rotary evaporator and the crude purified by flash column chromatography (1% aqueous NH_4OH and MeOH in $CHCl_3$) on silica gel.

Standard Procedure for Homoallylic Amine Synthesis from Azides Using Condition B. To a stirred solution of azide (**1**, 1.00 mmol) in anhydrous THF (3.0 mL) at 0 °C was added potassium *tert*-butoxide (1.10 equiv, 1.10 mmol) under an Ar atmosphere, and the mixture was stirred at that temperature. After the mixture had been stirred for t hours (listed in column 5 of Table 2) to completely consume the starting material to imine, allylboronic acid pinacol ester (**2a**, 1.3 equiv, 1.3 mmol) was added dropwise via syringe. After being stirred at that temperature for 1 h, the mixture was stirred at room temperature for 15 min. It was extracted with 1 N HCl (10 mL) and diethyl ether (4 mL). The aqueous part was washed with diethyl ether (4 mL). The aqueous layer was further basified to pH 10 using a 6 N KOH solution. Thereafter, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was dried over sodium carbonate, and the solvent was removed with a rotary evaporator and the crude purified by flash column chromatography (1% aqueous NH_4OH and MeOH in $CHCl_3$) on silica gel.

Standard Procedure for Homoallylic Amine Synthesis from Azides Using Condition C. To a stirred solution of azide (**1**, 1.00 mmol) in anhydrous DMSO (3.0 mL) at room temperature was added potassium *tert*-butoxide (0.1 equiv, 0.1 mmol) under an argon atmosphere, and the mixture was stirred for time t (see Table 2, column 5) at that temperature to completely consume the starting material to imine. Allylboronic acid pinacol ester (**2a**, 1.3 equiv, 1.3 mmol) was added dropwise via syringe, and the reaction mixture was stirred at room temperature for 15 min. It was extracted with 0.5 M NaOH (10 mL) and EtOAc (3 × 15 mL). The organic layers were combined and dried over sodium carbonate. The solvent was evaporated on a rotary evaporator and further extracted with 1 N HCl (10 mL) and diethyl ether (4 mL). The aqueous part was washed with diethyl ether (4 mL). The aqueous layer was further basified to pH 10 using a 6 N KOH solution. Thereafter, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was dried over sodium carbonate, and the solvent was removed with a rotary evaporator and the crude purified by flash column chromatography (1% aqueous NH_4OH and MeOH in $CHCl_3$) on silica gel.

Standard Procedure for Homoallylic Amine Synthesis from Azides Using Condition D. To a stirred solution of azide (**1**, 1.00 mmol) in anhydrous DMSO (3.0 mL) at room temperature was added potassium *tert*-butoxide (0.1 equiv, 0.1 mmol) under an argon atmosphere, and the mixture was stirred for 5 min at that temperature to completely consume the starting material to imine. Allylboronic acid pinacol ester (**2a**, 1.3 equiv, 1.3 mmol) was added dropwise via a syringe, and the reaction mixture was stirred at 65 °C for t hours (see Table 2, column 5). It was extracted with 0.5 M NaOH (10 mL) and EtOAc (3 × 15 mL). The organic layers were combined and dried over sodium carbonate. The solvent was evaporated on a rotary evaporator and further extracted with 1 N HCl (10 mL) and diethyl ether (4 mL). The aqueous part was washed with diethyl ether (4 mL). The aqueous layer was further basified to pH 10 using a 6 N KOH solution. Thereafter, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was dried over sodium carbonate, and the solvent was removed witha rotary evaporator and the crude purified by flash column chromatography (1% NEt_3 and EtOAc in n-hexane) on silica gel.

*1-Phenylbut-3-en-1-amine (**3a**).*[5a] Yield: 109 mg, 74%. R_f = 0.18 (100% EtOAc). Colorless oil. IR (neat): 3371, 3076, 3028, 2925, 2854, 2360, 1640, 1603, 1493, 1453, 998, 916 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46−7.18 (5H), 5.92−5.64 (1H), 5.26−4.96 (2H), 4.02 (t, J = 5.6 Hz, 1H), 2.59−2.25 (2H), 1.68 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 135.4, 128.4, 126.9, 126.3, 117.6, 55.3, 44.2. HRMS (ESI): $[M + H]^+$ calcd for $C_{10}H_{14}N$, m/z 148.1126; found, m/z 148.1132.

*1-(4-Chlorophenyl)but-3-en-1-amine (**3b**).*[17] Yield: 117.6 mg, 65%. R_f = 0.40 (5% MeOH/$CHCl_3$). Colorless oil. IR (neat): 3373, 3077, 2978, 2910, 2854, 2361, 1901, 1640, 1594, 1435, 1411, 1091, 1014, 918, 826, 537 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.29−7.22 (4H), 5.76−5.62 (1H), 5.13−4.02 (2H), 3.99−3.92 (dd, J = 5.2, 7.6 Hz, 1H), 2.44−2.24 (2H), 1.58 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 134.99, 132.5, 128.5, 127.7, 117.98, 54.8, 44.2. LRMS (ESI): $[M + H]^+$ calcd for $C_{10}H_{13}ClN$, m/z 182.1; found, m/z 182.1.

*1-[(1,1′-Biphenyl)-4-yl]but-3-en-1-amine (**3c**).*[17] Yield: 201 mg, 90% yield. R_f = 0.25 (3:97 MeOH/$CHCl_3$). Colorless liquid. IR (neat): 3371, 3076, 3029, 2908, 1639, 1601, 1487, 1435, 1410, 1075, 1008, 916, 838, 766, 734, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.65−7.28 (9H), 5.86−5.71 (1H), 5.20−5.06 (2H), 4.04 (dd, J = 5.6, 8.0 Hz, 1H), 2.56−2.34 (2H), 1.70 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 140.9, 139.9, 135.4, 128.8, 127.2, 127.1, 126.8, 117.8, 55.1, 44.1. HRMS (ESI): $[M + H]^+$ calcd for $C_{16}H_{18}N$, m/z 224.1; found, m/z 224.1.

*1-[3-(Benzyloxy)phenyl]but-3-en-1-amine (**3d**).* Yield: 177 mg, 70% yield. R_f = 0.44 (5:95 MeOH/$CHCl_3$). Colorless liquid. IR (neat): 3374, 3067, 2916, 1600, 1455, 1381, 1260, 1152, 1027, 917, 781, 740, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48−7.20 (6H), 7.80–7.03 (3H), 5.80–5.67 (1H), 5.15–5.03 (4H), 3.99–3.92 (dd, J = 5.2, 7.6 Hz, 1H), 2.50–2.29 (2H), 1.69 (bs, 2H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 158.99, 147.6, 137.1, 135.4, 129.5, 128.6, 127.9, 127.5, 119.0, 117.7, 113.3, 112.9, 69.99, 55.4, 44.1. HRMS (ESI): $[\mathrm{M + H}]^+$ calcd for $\mathrm{C_{17}H_{20}NO}$, m/z 254.1545; found, m/z 254.1509.

1-(3-Nitrophenyl)but-3-en-1-amine (***3e***). Yield: 136 mg, 71% yield. R_f = 0.38 (5:95 MeOH/$\mathrm{CHCl_3}$). Yellow oil. IR (neat): 3379, 3078, 2926, 1532, 1438, 1351, 1097, 1000, 921, 808, 740, 690 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 8.19 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 5.80–5.60 (1H), 5.14–5.02 (2H), 4.15–4.05 (dd, J = 5.6, 8.0 Hz, 1H), 2.49–2.25 (2H), 1.60 (bs, 2H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 148.4, 147.99, 134.4, 132.8, 129.3, 122.0, 121.5, 118.6, 54.7, 44.1. HRMS (ESI): $[\mathrm{M + H}]^+$ calcd for $\mathrm{C_{10}H_{13}N_2O_2}$, m/z 193.0977; found, m/z 193.0933.

1-(4-Nitrophenyl)but-3-en-1-amine (***3f***).[5a] Yield: 82 mg, 43%. R_f = 0.40 (5:95 MeOH/$\mathrm{CHCl_3}$). Yellow oil. IR (neat): 3379, 3078, 2979, 2917, 2852, 1600, 1520, 1436, 1347, 1109, 999, 920, 855, 754, 701 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 8.15 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 5.76–5.62 (1H), 5.16–5.02 (2H), 4.11 (dd, J = 5.2, 7.6 Hz, 1H), 2.48–2.25 (2H), 1.61 (bs, 2H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 153.3, 147.0, 134.2, 127.3, 123.7, 118.6, 54.9, 44.0. LRMS (ESI): $[\mathrm{M + H}]^+$ calcd for $\mathrm{C_{10}H_{13}N_2O_2}$, m/z 193.1; found, m/z 193.1.

1-(Naphthalen-1-yl)but-3-en-1-amine (***3g***).[9d] Yield: 171 mg, 87% yield. R_f = 0.32 (5:95 MeOH/$\mathrm{CHCl_3}$). Colorless solid. Mp: 74–76 °C. IR (neat): 3377, 3070, 2976, 2924, 1638, 1597, 1510, 1436, 1396, 1340, 1258, 1166, 1065, 997, 916, 799, 778, 736, 611, 567 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 8.14 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 7.2 Hz, 1H), 7.58–7.42 (3H), 5.94–5.78 (1H), 5.26–5.06 (2H), 4.85 (dd, J = 4.0, 8.4 Hz, 1H), 2.77–2.40 (2H), 1.72 (bs, 2H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 141.4, 135.6, 133.9, 130.8, 129.0, 127.4, 126.0, 125.6, 125.5, 122.8, 122.5, 117.8, 50.3, 43.2. HRMS (APCI): $[\mathrm{M + H}]^+$ calcd for $\mathrm{C_{14}H_{16}N}$, m/z 198.1; found, m/z 198.1.

1-(Naphthalen-2-yl)but-3-en-1-amine (***3h***).[9d] Yield: 181 mg, 92%. R_f = 0.32 (5:95 MeOH/$\mathrm{CHCl_3}$). Colorless solid. Mp: 68–69 °C. IR (neat): 3373, 3056, 2926, 2361, 1602, 1506, 1436, 1374, 1272, 1125, 997, 916, 856, 819, 748, 480 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.87–7.71 (4H), 7.54–7.36 (3H), 5.895.65 (1H), 5.20–5.02 (2H), 4.20–4.10 (dd, J = 5.6, 8.0 Hz, 1H), 2.61–2.37 (2H), 1.75 (bs, 2H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 143.2, 135.4, 133.5, 132.8, 128.2, 127.8, 127.7, 126.0, 125.6, 124.9, 124.7, 117.8, 55.5, 44.0. LRMS (ESI): $[\mathrm{M + H}]^+$ calcd for $\mathrm{C_{14}H_{16}N}$, m/z 198.1; found, m/z 198.1.

1-(Thiophen-2-yl)but-3-en-1-amine (***3i***).[5a] Yield: 102 mg, 67%. R_f = 0.33 (2:98 MeOH/$\mathrm{CHCl_3}$). Light yellow liquid. IR (neat): 3371, 3075, 2977, 2924, 2853, 2361, 1640, 1591, 1436, 1416, 1374, 1321, 1239, 998, 918, 850, 827, 698, 424, 416 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.17 (dd, J = 1.2, 4.8 Hz, 1H), 6.98–6.82 (2H), 5.86–5.66 (1H), 5.19–5.04 (2H), 4.25 (dd, J = 5.6, 8.0 Hz, 1H); 2.60–2.33 (2H), 1.70 (bs, 2H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 150.7, 134.8, 126.6, 123.6, 122.8, 118.2, 51.3, 44.7. LRMS (ESI): $[\mathrm{M + H}]^+$ calcd for $\mathrm{C_8H_{12}NS}$, m/z 154.1; found, m/z 154.1.

1-(Benzo[b]thiophen-2-yl)but-3-en-1-amine (***3j***). Yield: 164 mg, 81%. R_f = 0.46 (5:95 MeOH/$\mathrm{CHCl_3}$). Yellow liquid. IR (neat): 3060, 2909, 2848, 1623, 1434, 1362, 1303, 1248, 995, 919, 855, 826, 748 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.79 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 7.2 Hz, 1H), 7.35–7.22 (2H), 7.14 (s, 1H), 5.88–5.71 (1H), 5.22–5.07 (2H), 4.36–4.28 (dd, J = 5.6, 7.6 Hz, 1H), 2.69–2.39 (2H), 1.79 (s, 2H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 151.4, 139.7, 139.1, 134.5, 124.2, 123.8, 123.2, 122.4, 119.4, 118.4, 51.9, 44.2. HRMS (ESI): $[\mathrm{MH - NH_3}]^+$ calcd for $\mathrm{C_{12}H_{11}S}$, m/z 187.0581; found, m/z 187.0598.

1-(Pyridin-3-yl)but-3-en-1-amine (***3k***).[9b] Yield: 59 mg, 40%. R_f = 0.26 (5:95 MeOH/$\mathrm{CHCl_3}$). Yellow oil. IR (neat): 3360, 1594, 1481, 1430, 1028, 998, 921, 814, 716 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 8.50 (s, 1H), 8.41 (d, J = 4.4 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.23–7.14 (dd, J = 4.8, 8.0 Hz, 1H), 5.72–5.57 (1H), 5.10–4.98 (2H), 4.04–3.94 (dd, J = 5.6, 7.2 Hz, 1H), 2.50–2.28 (4H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 148.50, 148.47, 140.38, 134.3, 134.1, 123.4, 118.5, 53.0, 43.7. LRMS (ESI): $[\mathrm{M + H}]^+$ calcd for $\mathrm{C_9H_{13}N_2}$, m/z 149.1; found, m/z 149.2.

1-Phenylhexa-1,5-dien-3-amine (***3l***).[5a] Yield: 140 mg, 81% yield. R_f = 0.33 (5:95 MeOH/$\mathrm{CHCl_3}$). Yellow oil. IR (neat): 3367, 3078, 3026, 2977, 2908, 1649, 1599, 1494, 1449, 1374, 967, 916, 749, 694 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.40–7.16 (5H), 6.55–6.44 (1H), 6.24–6.12 (1H), 5.88–5.73 (1H), 5.18–5.03 (2H), 3.63–3.45 (1H), 2.39–2.16 (2H), 1.48 (bs, 2H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 137.1, 135.1, 134.2, 129.0, 128.6, 127.3, 126.3, 117.8, 53.2, 42.5. LRMS (ESI): $[\mathrm{M - H}]^+$ calcd for $\mathrm{C_{12}H_{14}N}$, m/z 172.1; found, m/z 172.1.

1-(4-Methoxyphenyl)hexa-1,5-dien-3-amine (***3m***). Yield: 177 mg, 87%. R_f = 0.38 (5:95 MeOH/$\mathrm{CHCl_3}$). Yellow oil. IR (neat): 3364, 3074, 2933, 2837, 1607, 1513, 1464, 1301, 1249, 1175, 1035, 968, 916, 846, 815 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.28 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.46–6.38 (1H), 6.09–5.98 (1H), 5.87–5.71 (1H), 5.16–5.04 (2H), 3.77 (s, 3H), 3.56–3.48 (1H), 2.37–2.15 (2H), 1.57 (bs, 2H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 159.0, 135.1, 131.99, 129.9, 128.5, 127.4, 117.7, 113.98, 55.3, 53.3, 42.6. HRMS (ESI): $[\mathrm{M - H}]^+$ calcd for $\mathrm{C_{13}H_{16}NO}$, m/z 202.1232; found, m/z 202.1200.

2-(4-Fluorophenyl)pent-4-en-2-amine (***3n***). Yield: 136 mg, 76%. R_f = 0.26 (70:30 EtOAc/*n*-hexane). Colorless liquid. IR (neat): 3369, 2976, 2926, 1600, 1509, 1233, 1163, 918, 835, 729, 622 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.41 (2H), 6.98 (2H), 5.60–5.46 (1H), 5.09–5.00 (2H), 2.44 (2H), 1.54 (s, 2H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 161.35 (d, J = 244.4 Hz), 144.34 (d, J = 3.1 Hz), 134.07, 126.92 (d, J = 7.8 Hz), 118.7, 114.73 (d, J = 21.0 Hz), 54.3, 49.8, 31.1. HRMS (ESI): $[\mathrm{MH - NH_3}]^+$ calcd for $\mathrm{C_{11}H_{12}F}$, m/z 163.0923; found, m/z 163.0942.

2-(4-Nitrophenyl)pent-4-en-2-amine (***3o***).[18] Yield: 171 mg, 83%. R_f = 0.25 (70:30 EtOAc/*n*-hexane). Yellow liquid. IR (neat): 2260, 3077, 2977, 2910, 2338, 1525, 1339, 1110, 921, 857 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 8.14 (d, J = 8.9 Hz, 2H), 7.63 (d, J = 8.9 Hz, 2H), 5.57–5.41 (1H), 5.09–5.00 (2H), 2.60–2.34 (2H), 1.63 (s, 2H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 156.3, 146.4, 133.1, 126.5, 123.3, 119.5, 55.0, 49.5, 30.9. LRMS (ESI): $[\mathrm{M + H}]^+$ calcd for $\mathrm{C_{11}H_{15}N_2O_2}$, m/z 207.1; found, m/z 207.2.

3-Methyl-1-phenylhexa-1,5-dien-3-amine (***3p***).[18] Yield: 95 mg, 51%. R_f = 0.29 (5:95 MeOH/$\mathrm{CHCl_3}$). Colorless oil. IR (neat): 3354, 3026, 2964, 2925, 1640, 1599, 1494, 1448, 1373, 1282, 1183, 1073, 971, 917, 749, 694 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.33–7.11 (5H), 6.49–6.35 (1H), 6.29–6.15 (1H), 5.82–5.64 (1H), 5.12–4.98 (2H), 2.33–2.15 (2H), 1.93 (bs, 2H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 137.9, 137.1, 133.9, 128.5, 127.3, 126.9, 126.3, 118.8, 53.5, 47.9, 28.4. HRMS (APCI): $[\mathrm{M + H}]^+$ calcd for $\mathrm{C_{13}H_{18}N}$, m/z 188.1; found, m/z 188.1.

Diastereoselective Homoallylic Amination of Azides. To a stirred solution of benzyl azide (**1a**, 1.00 mmol) in anhydrous THF (3.0 mL) at 0 °C was added potassium *tert*-butoxide (1.10 equiv, 1.10 mmol) under an Ar atmosphere, and the mixture was stirred at that temperature. After being stirred for 1 h, the mixture was brought to room temperature and stirred for 15 min to completely consume the starting material to imine. The reaction mixture was brought to −40 °C and *trans*- or *cis*-crotylboronic acid pinacol ester (**2b** or **2c**, respectively, 1.3 equiv, 1.3 mmol) was added dropwise via syringe. The temperature of the reaction was slowly increased to room temperature over 4 h. It was extracted with 1 N HCl (10 mL) and diethyl ether (4 mL). The aqueous part was washed with diethyl ether (4 mL). The aqueous layer was further basified to pH 10 using a 6 N KOH solution. Thereafter, the aqueous layer was extracted with $\mathrm{CH_2Cl_2}$ (3 × 20 mL). The organic layer was dried over sodium carbonate, and the solvent was removed with a rotary evaporator and the crude purified by flash column chromatography (1% aqueous $\mathrm{NH_4OH}$ and MeOH in $\mathrm{CHCl_3}$) on silica gel.

anti-2-Methyl-1-phenylbut-3-en-1-amine (***3q***).[5a] Yield: 109 mg, 68%. R_f = 0.36 (5:95 MeOH/$\mathrm{CHCl_3}$). Colorless liquid. IR (neat): 3380, 3064, 3029, 2973, 2929, 1638, 1603, 1494, 1455, 1418, 1374, 998, 916, 760, 702, 679 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.35–7.18 (5H), 5.80–5.65 (1H), 5.20–5.05 (2H), 3.65–3.57 (d, J = 8.4

Hz, 1H), 2.43−2.28 (1H), 1.73 (s, 2H), 0.84−0.74 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 141.7, 128.3, 127.3, 127.1, 115.9, 60.7, 46.3, 17.7; LRMS (APCI, m/z): $[M + H]^+$ calcd for $C_{11}H_{16}N$, 162.1; found, 162.1.

syn-2-Methyl-1-phenylbut-3-en-1-amine ***(3r)***.[5a] Yield: 90 mg, 56%. R_f = 0.35 (5:95 MeOH/$CHCl_3$). Colorless liquid. IR (neat): 3375, 3064, 3029, 2970, 2930, 1603, 1494, 1454, 1373, 1002, 914, 762, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.16 (5H), 5.73−5.59 (1H), 5.06−4.95 (2H), 3.90−3.80 (d, J = 5.6 Hz, 1H), 2.56−2.40 (1H), 1.75 (s, 2H), 1.01−0.92 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 140.9, 128.0, 127.2, 126.8, 115.1, 59.99, 44.6, 15.1. LRMS (APCI): $[M + H]^+$ calcd for $C_{11}H_{16}N$, m/z 162.1; found, m/z 162.1.

Procedure for Enantioselective Homoallylic Allylation of Benzyl Azide. To a stirred solution of benzyl azide (**1a**, 0.5 mmol) in anhydrous THF (1.5 mL) at 0 °C potassium was added *tert*-butoxide (1.10 equiv, 0.55 mmol) under an Ar atmosphere, and the mixture was stirred at that temperature. After being stirred for 1 h, the mixture brought to room temperature and stirred for 15 min to completely consume the starting material to imine. The reaction mixture was brought to −78 °C, and a (+)-Ipc_2B(allyl)borane solution (**2d**, 1.3 equiv, 0.65 mmol) was added dropwise via syringe. After the mixture had been stirred at that temperature for 12 h, the temperature was increased slowly to room temperature over 6 h. Then, 0.15 mL of 3 N NaOH and 0.15 mL of 30% H_2O_2 were added to the reaction mixture and further stirred for 12 h at 25 °C. It was extracted with 1 N HCl (6 mL) and diethyl ether (3 mL). The aqueous part was washed with diethyl ether (3 mL). The aqueous layer was further basified to pH 10 using a 6 N KOH solution. Thereafter, the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The organic layer was dried over sodium carbonate, and the solvent was removed with a rotary evaporator and the crude purified by flash column chromatography (1% aqueous NH_4OH and MeOH in $CHCl_3$) on silica gel.

*(S)-1-Phenylbut-3-en-1-amine [**3a-crl-(+)**].* Yield: 44 mg, 60%. 89% ee. $[\alpha]^{25}_D$ = +35.5° (c 1.2, $CHCl_3$). HPLC conditions: Diacel Chiralpak OD-3 column, 4% ^{i}PrOH, 0.5% DEA in n-hexane, flow rate of 0.8 mL min^{-1}, t_R = 16.64 min for the major enantiomer, t_R = 24.08 min for the minor enantiomer.

Procedure for the Synthesis of N-Unsubstituted Imines. To a stirred solution of azide (**1**, 1.00 mmol) in anhydrous DMSO (3.0 mL) at room temperature was added potassium *tert*-butoxide (0.1 equiv, 0.1 mmol) under an argon atmosphere, and the mixture was stirred for 2 min for azide **1q** or 1 min for azide **1r** at that temperature to completely consume the starting material to imine. It was extracted with 1 M NaOH (10 mL) and EtOAc (2 × 15 mL). The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed with a rotary evaporator, and the crude was purified by flash column chromatography (1% NEt_3 and EtOAc in n-hexane) on silica gel.

Diphenylmethanimine ***(4a)***.[3e] Yield: 127 mg, 70%. R_f = 0.18 (10:90 EtOAc/n-hexane). Colorless liquid. IR (neat): 3258, 3060, 3029, 2926, 1961, 1660, 1601, 1570, 1446, 1363, 1319, 1278, 1196, 1151, 929, 892, 761, 703 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.43 (bs, 1H), 7.65−7.51 (4H), 7.48−7.32 (6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3, 139.4, 130.3, 128.4, 128.3. LRMS (ESI): $[M + H]^+$ calcd for $C_{13}H_{12}N$, m/z 182.1; found, m/z 182.1.

2-Imino-N-methyl-N,2-diphenylacetamide ***(4b)***. Yield: 219 mg, 92%. Z:E isomer ratio: 1:3.3. R_f = 0.32 (25:75 = EtOAc/n-hexane). Crystalline yellow solid. Mp: 147−149 °C. IR (neat): 3259 (br), 1634, 1608, 1588, 1325, 1154, 689 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.2 Hz, 0.71H), 7.64 (bs, 0.65H), 7.49−6.97 (8H), 6.67 (d, J = 7.4 Hz, 1.29H), 5.66 (bs, 0.35H), 2.95 (d, J = 5.1 Hz, 1.97H), 2.60 (d, J = 4.9 Hz, 1.03H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 164.5, 163.3, 161.6, 149.7, 148.3, 134.6, 131.7, 131.6, 129.74, 129.40, 129.02, 128.79, 128.63, 128.33, 127.76, 124.96, 124.86, 120.8, 119.9, 26.3, 25.7. HRMS (ESI): $[M + H]^+$ calcd for $C_{15}H_{15}N_2O$, m/z 239.1184; found, m/z 239.1179.

Mechanistic Investigation of the Synthesis of *N*-Unsubstituted Imines. To a stirred solution of benzyl azide (**1a**, 0.19 mmol) in d_6-DMSO (0.6 mL) at rt was added potassium *tert*-butoxide (0.1 equiv, 0.019 mmol) under an Ar atmosphere, and the mixture was stirred at that temperature. After being stirred for 15 min [complete consumption of benzyl azide (**1a**) observed by TLC], the crude reaction mixture was transferred to a NMR tube after anisole had been added as an internal standard, and ^{1}H NMR data were recorded via 500 MHz NMR.

Mechanistic Investigation for the Abstraction of a Proton by DMSO. A blank reaction was conducted in the absence of substrate to observe the H content d_6-DMSO (entry 1, Table 3). To d_6-DMSO (2.25 mmol, 160 μL) at rt was added potassium *tert*-butoxide (0.1 equiv, 0.0225 mmol, 2.5 mg) under an Ar atmosphere, and the mixture was stirred at that temperature. After being stirred for 5 min, the crude reaction mixture was transferred to a NMR tube after 18 μL of anisole had been added as an internal standard with d_6-benzene. ^{1}H NMR data were recorded via 500 MHz NMR.

Then, another reaction was conducted to observe the amount of abstraction of H by d_6-DMSO from azide as mentioned in entry 2 of Table 3. To a stirred solution of benzyl azide (**1a**, 0.225 mmol) in d_6-DMSO (2.25 mmol, 160 μL) at rt was added potassium *tert*-butoxide (2.5 mg, 0.0225 mmol, 0.1 equiv) under an Ar atmosphere, and the mixture was stirred at that temperature. After being stirred for 5 min, the crude reaction mixture was transferred to a NMR tube after 18 μL of anisole had been added as an internal standard with d_6-benzene. ^{1}H NMR data were recorded via 500 MHz NMR.

A similar reaction was conducted using 0.45 mmol of substrate, 4.5 mmol of d_6-DMSO, and 0.045 mmol of KO^{t}Bu (10 mol %) as mentioned in entry 3 of Table 3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of NMR spectra for all products and a HPLC chromatogram. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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