有机化学 DOI: 10.6023/cjoc202110042 研究论文
Chinese Journal of Organic Chemistry ARTICLE

镍催化丁二烯、亚胺和烯基硼酸的三组分偶联反应

张玉荣[a,b] 王 晗*[,a] 茆勇军[a] 施世良*[,a,b]
([a]上海工程技术大学化学化工学院 上海 201620)
([b]中国科学院上海有机化学研究所 金属有机化学国家重点实验室 上海 200032)

摘要 发展了一种镍催化的烯基硼酸、亚胺和1,3-丁二烯的三组分偶联反应, 用于高效合成含有1,4-二烯结构的高烯丙基胺类化合物. 该反应的原料均简单易得, 其中 1,3-丁二烯是大宗化工产品. 该过程实现了少有报道的 1,3-丁二烯的1,4-双碳化反应. 反应以优秀的区域选择性和立体选择性, 高收率地合成了一系列(*E*)-高烯丙基胺产物, 简单温和、无外加碱的反应条件使该方法具有广泛的底物范围和优秀的官能团兼容性.

关键词 1,4-二烯; 镍催化; 丁二烯; 多组分反应; 偶联; 高烯丙基胺

Ni-Catalyzed Three-Component Coupling Reaction of Butadiene, Aldimines and Alkenylboronic Acids

Zhang, Yurong[a,b] Wang, Han*[,a] Mao, Yongjun[a] Shi, Shiliang*[,a,b]
([a] *College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai 201620*)
([b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032*)

Abstract A Ni-catalyzed three-component coupling reaction of alkenylboronic acids, aldimines, and 1,3-butadiene for rapid synthesis of homoallylic amines bearing a skipped diene moiety is disclosed. This reaction represents a rare example for modular 1,4-dicarbofunctionalization of 1,3-butadiene, an abundant feedstock chemical. This protocol furnishes a diverse variety of (*E*)-homoallylic amines in high yields with excellent regio- and stereo-selectivity. The mild and base-free reaction condition enables excellent functional group tolerance and broad scope for aldimine and alkenylboronic acid coupling partners.

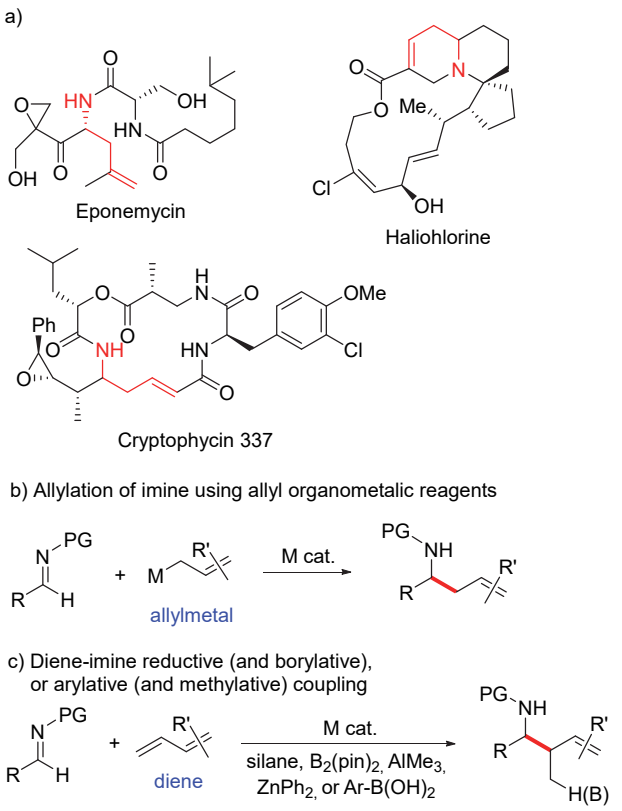
Keywords skipped diene; nickel catalysis; butadiene; multicomponent reaction; coupling; homoallylic amine

1 Introduction

Homoallylic amines not only are important structural units in bioactive molecules but also serve as useful synthetic intermediates in organic chemistry (Scheme 1a).[1] A typical approach to synthesize homoallylic amines is the nucleophilic addition of aldimines using allyl metal reagents (Scheme 1b).[2] Although substantial progress has been made in this field, and it is more desirable to synthesize homoallylic amines using easily accessible and stable allyl surrogates, such as butadiene (production of ~13×10^6 tons/year) and isoprene,[3] instead of allyl metal reagents because the preparation of allyl metal reagents is generally complicated.[4] As a result, various metal-catalyzed borylative (or reductive) butadiene−aldimine coupling[5-7] as well as multi-component arylative (or methylative) coupling of aldimine and butadiene with $AlMe_3$, $ZnPh_2$,[8] or arylboronic acids,[9] have been developed to prepare homoallylic amines in a single operation (Scheme 1c). However, general and practical methods on dicarbofunctionalization of butadiene[10] to construct substituted homoallylic amines remain underdeveloped.

On the other hand, skipped dienes (or 1,4-dienes) serve as versatile synthetic intermediates for organic synthesis,[11] whose structures are found in many bioactive molecules and natural products (Scheme 2a).[12] The importance of skipped dienes has spurred the development of many effective methods to this building block, including metal-catalyzed coupling reactions of 1,3-diene with alkenes,[13] alkynes,[8b,14] or vinyl components.[15-16] For instance, the Sigman group developed a Pd-catalyzed coupling of 1,3-diene, vinyl triflate, and arylboronic acid for the modu-

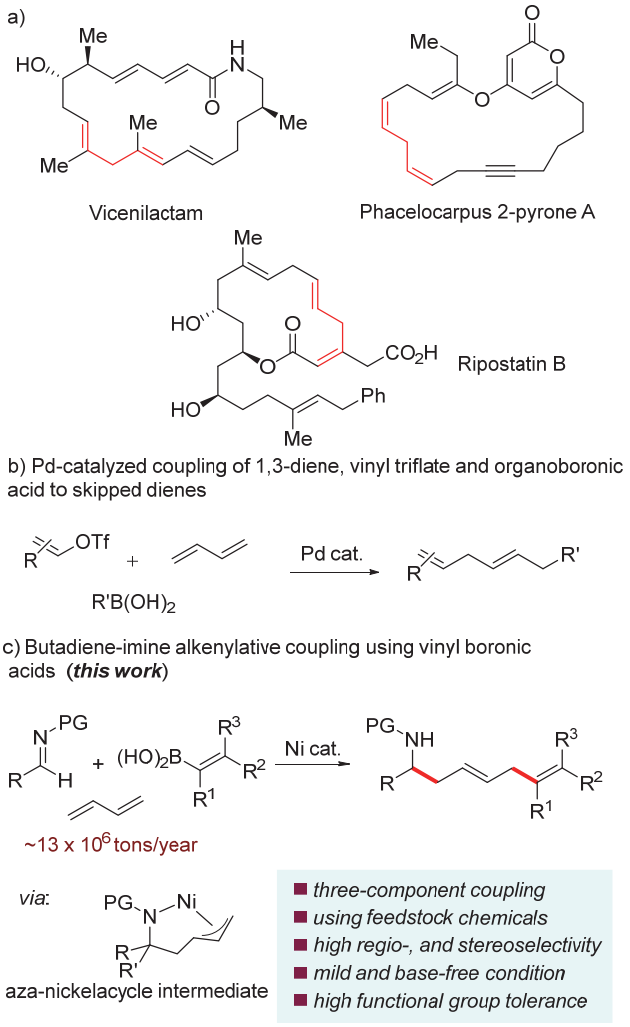
* Corresponding authors. E-mail: wanghan@sues.edu.cn; shiliangshi@sioc.ac.cn
Received October 29, 2021; revised November 28, 2021; published online December 2, 2021.
Project supported by the National Natural Science Foundation of China (Nos. 21690074, 21871288, 91856111, 21821002, 22171280) and the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDB20000000).
国家自然科学基金(Nos. 21690074, 21871288, 91856111, 21821002, 22171280)和中国科学院战略性先导科技专项(No. XDB20000000)资助项目.



Scheme 1 Examples of natural products containing homoallylic amines and approaches to homoallylic amines

lar synthesis of 1,4-diene products (Scheme 2b).[15a] The Shu group recently reported a reductive approach for a 1,2-hydrovinylation of aliphatic 1,3-dienes with vinyl triflates furnishing branch- selective skipped dienes.[15d] Despite significant progress, the development of efficient methods for preparing functionalized skipped dienes is still highly desirable.

We aimed to develop a practical and general synthetic method to homoallylic amines containing a skipped diene moiety via selective dicarbofunctionalization of feedstock butadiene (Scheme 2c). We have recently developed a Ni-catalyzed three-component butadiene-aldimine arylative coupling using arylboronic acids to form homoallylic amines.[9] The reaction is suggested to proceed via an aza-nickelacycle intermediate generated by the oxidative cyclization of diene, imine, and nickel(0).[17] The resulting Ni(II)—N bond could promote the transmetalation of arylboronic acids without an external base, thus allowing for excellent functional group compatibility and broad substrate scope. Consequently, we envisaged that a three-component coupling of readily available alkenylboronic acids with aldimines and 1,3-butadiene would afford homoallylic amines containing skipped dienes. However, several challenges remain: (1) the weak nucleophile alkenylboronic acids need to undergo transmetalation via the aza-nickelacycle intermediate without the help of exogenous base, which is generally a complicated process for Suzuki-type couplings;[18] (2) the controls over regio- and stereo- selectivity are typically tricky; (3) side reactions such as direct addition of imines or possible four-component reaction[14a,19] requires to be avoided. As our ongoing research interests in nickel catalysis,[20] we herein report a highly regio- and stereo-selective nickel-catalyzed coupling of 1,3-butadiene, aldimines, and alkenylboronic acids to afford homoallylic amines containing skipped dienes under the mild conditions (Scheme 2c).



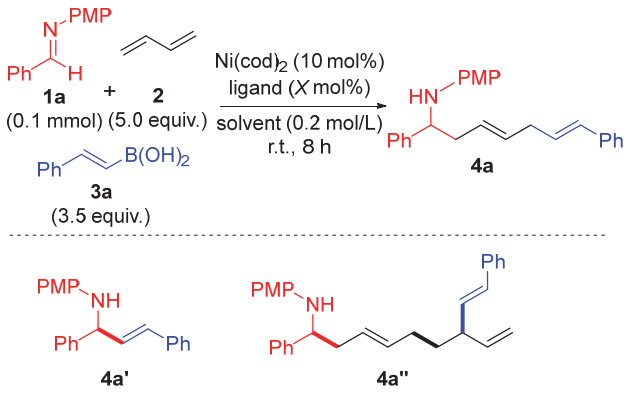
Scheme 2 Examples of skipped dienes in natural products, and synthetic method to skipped dienes

2 Results and discussion

The reaction optimization using *N*-PMP-phenylmethanimine (**1a**), butadiene (**2**), and alkenylboronic acid (**3a**) as model substrates, $Ni(cod)_2$ as the catalyst in the presence or absence of a ligand was started (Table 1). It was found that the three-component coupling did occur at room temperature without adding a ligand through the desired 1,4-dicarbofunctionalization of butadiene, giving the homoallylic amine containing a skipped diene (**4a**) in 21% yield (Entry 1). Interestingly, the use of a typical phosphine ligand (PCy_3) and N-heterocyclic carbene ligand (IPr) inhibited the reaction (Entries 2～3). Although 1-phenyl-1-hexyne or

1-hexyne ligands decreased the yield (Entries 4～5), using 1 equiv. of 3-hexyne significantly improved the yield of **4a** to 79% (Entry 10). It is noteworthy that 3-hexyne was not incorporated in the coupling product but acted as a ligand.[8c] A considerable amount of byproduct derived from the direct addition of imines was observed (**4a'**) and a four-component reaction in which 2 equiv. of butadiene was coupled when the amount of 3-hexyne ligand was not sufficient (**4a''**) (Entries 6～9). An extensive examination of solvent effect suggested that cyclohexane was the optimal solvent, affording product in 72% isolated yield using 5 equiv. of 1,3-butadiene (Entries 10～19). The isolated yield of **4a** was further improved to 84% when using 8 equiv. of the feedstock butadiene (Entry 20). Notably, under the optimized condition, the skipped diene was obtained in a complete linear selectivity and *E*-form for both alkene double bonds.

Table 1 Optimization of the reaction conditions



Entry	Ligand	*x*/mol%	Solvent	Yield[a]/%
1	None		*c*-Hexane	21
2	PCy_3	20	*c*-Hexane	<5
3	IPr	20	*c*-Hexane	11
4	1-Phenyl-1-hexyne	20	*c*-Hexane	19
5	1-Heptyne	20	*c*-Hexane	<5
6	3-Hexyne	20	*c*-Hexane	26
7	3-Hexyne	40	*c*-Hexane	37
8	3-Hexyne	60	*c*-Hexane	54
9	3-Hexyne	80	*c*-Hexane	67
10	3-Hexyne	100	*c*-Hhexane	79 (72)[b]
11	3-Hexyne	100	*c*-Pentane	37
12	3-Hexyne	100	THF	56
13	3-Hexyne	100	DMF	55
14	3-Hexyne	100	DCM	11
15	3-Hexyne	100	Toluene	55
16	3-Hexyne	100	Dioxane	30
17	3-Hexyne	100	*n*-Hexane	54
18	3-Hexyne	100	*n*-Heptane	28
19	3-Hexyne	100	MeCN	<5
20	3-Hexyne	100	*c*-Hexane	84[b,c]

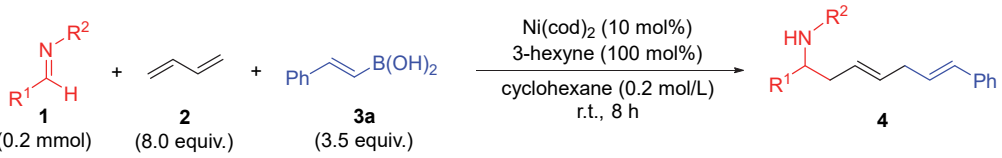
[a] Determined by ^{1}H NMR analysis using an internal standard. [b] Isolated yield shown in the paratheses. [c] Using 8.0 equiv of butadiene.

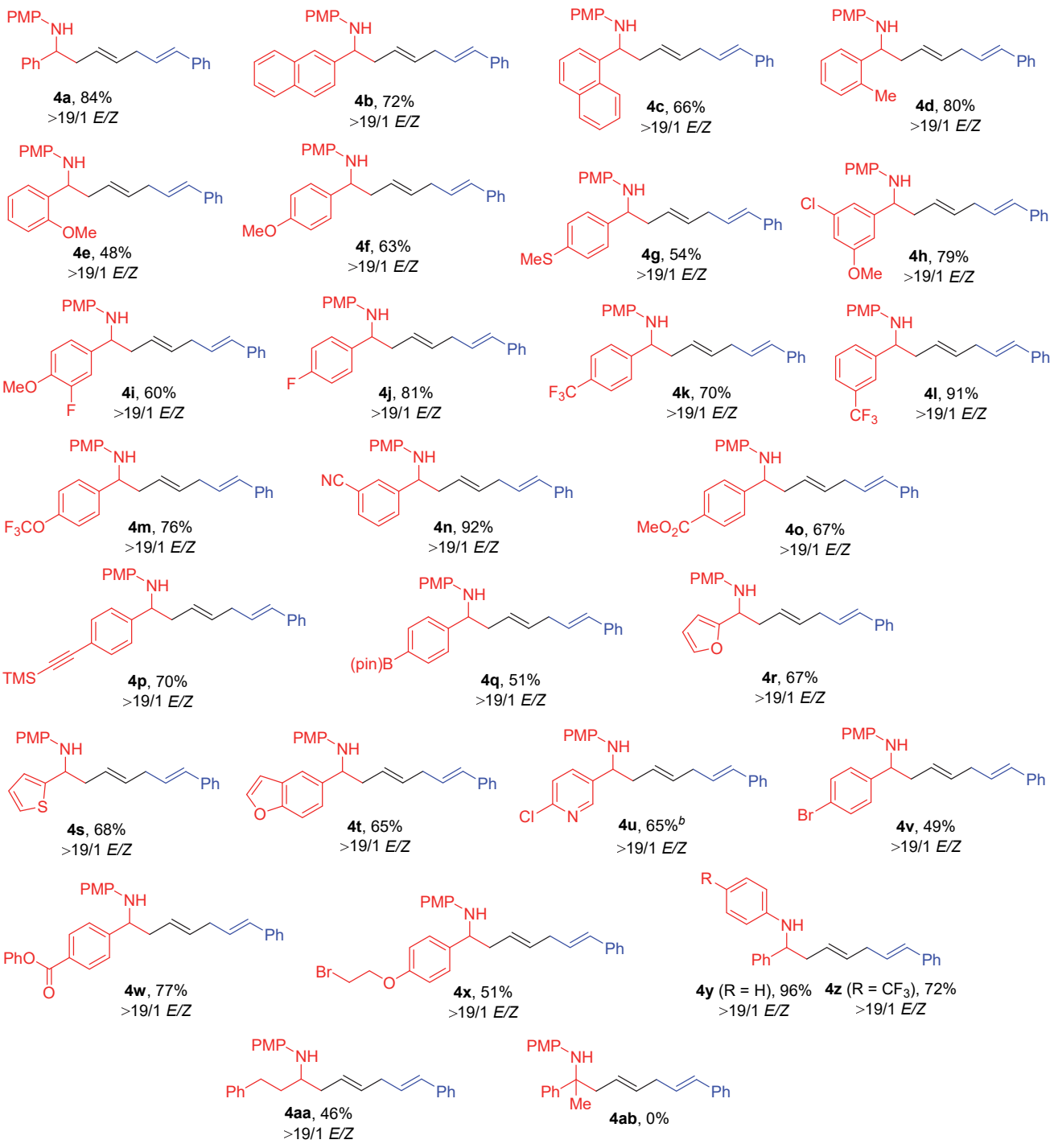
With the optimized reaction conditions in hand, the substrate scope of this three-component coupling reaction using various aldimines was next surveyed (Table 2). It was found that a wide variety of homoallylic amines were obtained in good to high yields with excellent regio- and stereo-selectivity. The reaction was not very sensitive to the steric effect of the aldimine, as bulky 2- or 1-naphthaldimines (**4b**～**4c**) and 2-methyl or 2-methoxyl benzaldimines (**4d**～**4e**) were applicable. Aromatic aldimines with ether electron-donating substituents (such as methoxy, methylthio, and methyl, **4d**～**4h**) or electron-withdrawing groups (such as trifluoromethyl, trifluoromethoxy, fluoro, cyano, and ester group, **4j**～**4o** and **4w**) were all competent substrates. Moreover, substrates bearing TMS-alkynyl group (**4p**), arylboronic ester (Bpin, **4q**), or aryl chloride (**4v**) and bromide (**4x**) were well tolerated, allowing for further manipulation via modern cross-coupling techniques. Additionally, various heteroaromatic aldimines, including furan (**4r**), thiophene (**4s**), benzofuran (**4t**), pyridine derivatives (**4u**), were also effective substrates. Notably, functional groups that are generally labile under alkaline conditions such as a phenyl ester (**4w**), an alkyl bromide (**4x**), TMS-alkynyl (**4p**) and Bpin (**4q**) groups were all compatible, highlighting the mildness of the base-free reaction condition. In addition, an aliphatic aldimine gave moderated yield of the product (**4aa**). The scope of *N*-substituent on the aldimine was next investigated and it was found that electron-rich (**4a**～**4x**), electron-neutral (**4y**), and electron-deficient aryl groups (**4z**) were all feasible. However, the use of a ketimine (**4ab**) derived from acetophenone gave no conversions, probably due to the challenging formation of the corresponding azanickelacycle intermediate.

Subsequently, the generality of the organoboronic acid coupling partners for this method was investigated, as shown in Table 3. Various stable and inexpensive alkenyl boronic acids efficiently participated in the coupling reaction, furnishing homoallylic amine products bearing a skipped diene moiety in good to high yields. It was found that both electron-rich and electron-poor phenyl-ethenyl boronic acids underwent the desired coupling giving products in good yields and stereoselectivities (**4a**, **5a**～**5c**). In addition to aryl-substituted alkenyl boronic acids, alkyl-, or dialkyl-substituted substrates (**5d**～**5e**) and cyclic alkenyl boronic acids (**5f**～**5g**) performed well, affording multi-substituted skipped dienes in high yields. Although the *E*/*Z* ratios for acyclic substrates decreased to some extent, cyclic substrates provided the related products as a single isomer. The erosion of *E*/*Z* ratio might due to the more challenging transmetalation step when bulky or electron-deficient organoboronic acid substrates were used (**5b**～**5e**).

Importantly, it was found this butadiene-imine vinylative coupling reaction could be easily performed in a gram scale (5 mmol) using even lower catalyst loading; homoallylic amine product **4a** was provided in 87% yield with complete regio- and *trans*-selectivity, demonstrating the practicality and scalability of our protocol (Scheme 3a). Moreover, a complicated isoindolinone **7**, could be obtained in a single

Table 2 Scope of aldimines[a]

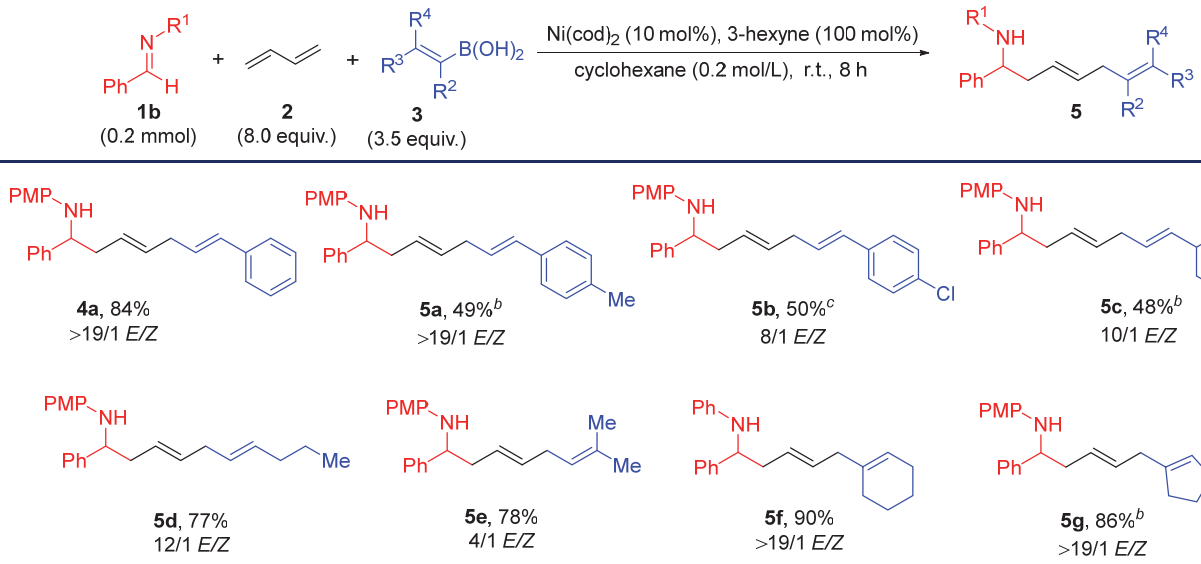




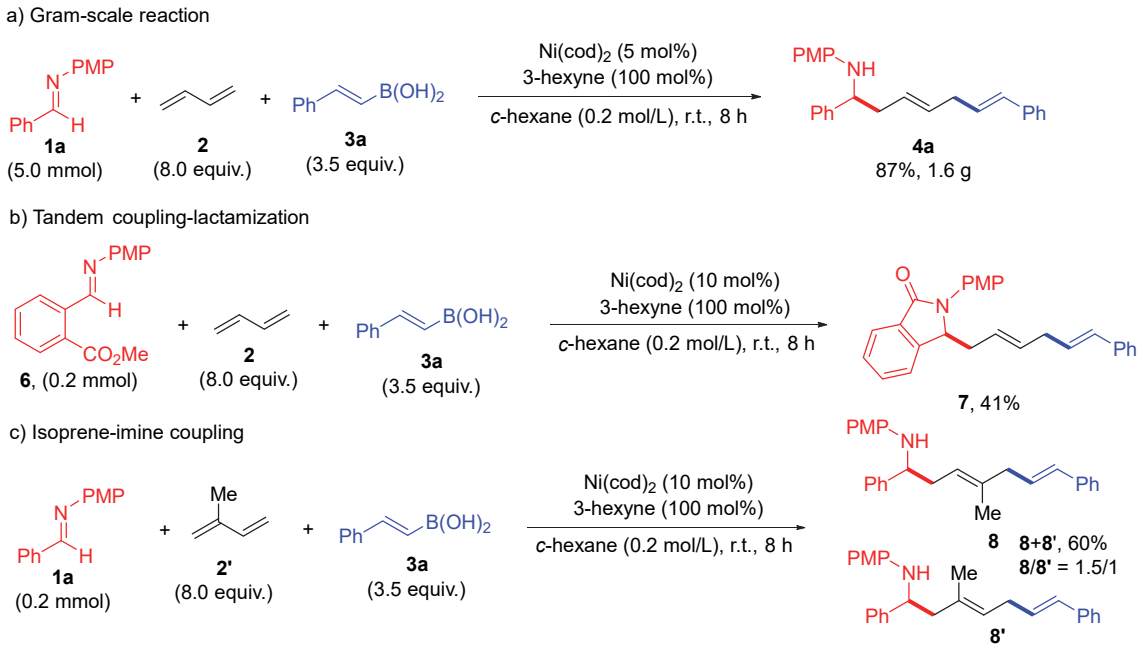
[a] Yields of isolated products on a 0.2 mmol scale; *E*/*Z* ratios were determined by ^{1}H NMR analysis of the crude product. [b] Using 0.2 equiv of Ni(cod)$_2$.

operation through a sequential three-component coupling-lactamization process (Scheme 3b). In addition, a 1,4-dicarbofunctionalization of isoprene (production of *ca.* 8×10^5 tons/year) using imine and alkenylboronic acid was successfully conducted to deliver the corresponding homoallylic amines **8** in good yield, albeit with low regio-selectivity (Scheme 3c).

Table 3 Scope of organoboronic acids



[a] Isolated yields are given; *E*/*Z* ratios were determined by ^{1}H NMR analysis of the crude product. [b] Using 0.2 equiv. of Ni(cod)$_2$. [c] Using 0.4 equiv. of Ni(cod)$_2$.

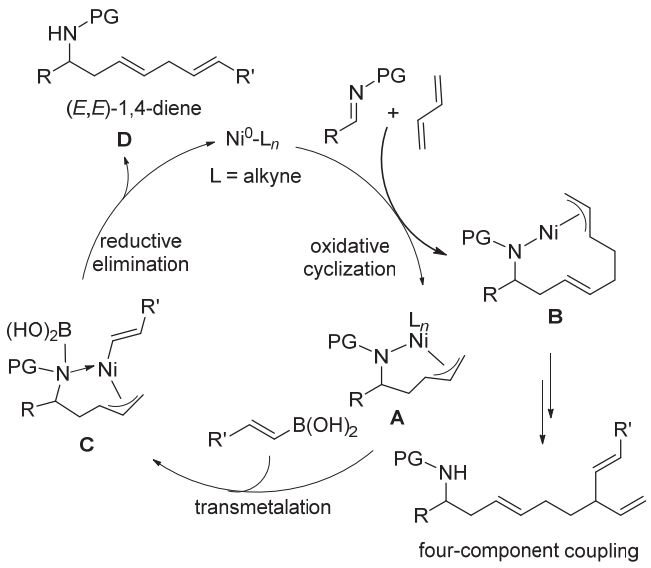


Scheme 3 Gram-scale reaction, tandem coupling-lactamization, and isoprene-imine coupling

A possible catalytic cycle for the three-component reaction based on previous reports is proposed (Figure 3).[5,8] First, the oxidative cyclization of Ni(0) with butadiene and aldimine affords aza-nickelacycle intermediate **A**. In the absence of an alkyne ligand, aza-nickelacycle intermediate **B**, which accounts for a competitive four-component coupling reaction involved with 2 equiv. of butadiene, would be formed. The use of 1 equiv. of 3-hexyne ligand avoids the undesired coordination and insertion of the second butadiene. The subsequent transmetalation of **A** with alkenylboronic acid gives a π-allyl nickel complex **C**. Finally, complex **C** undergoes reductive elimination to furnish the (*E*,*E*)-1,4-diene product **D**, and Ni(0) is regenerated. The regio- and stereo-selectivities in this coupling are likely controlled by the reductive elimination step.

3 Conclusions

In summary, we have described a highly regio- and *trans*-selective nickel-catalyzed three-component coupling reaction of alkenylboronic acids, aldimines, and feedstock butadiene for an efficient 1,4-dicarbofunctionalization of butadiene. A wide variety of substituted homoallylic amines bearing a 1,4-diene fragment were prepared from stable and readily available substrates in a single operation. The use of an alkyne ligand is essential to avoid several side reactions. The mild and base-free reaction conditions permit high functional group compatibility and broad substrate scope, rendering this coupling a practical and valuable method.



Scheme 4 Proposed catalytic cycle

4 Experimental section

4.1 General information

All reactions were conducted under a nitrogen atmosphere in oven-dried glassware with a standard drybox or vacuum-line techniques unless otherwise indicated. Reaction solvents, including *N*,*N*-dimethylformamide (DMF), dichloromethane (DCM), MeCN, tetrahydrofuran (THF), *n*-hexane, *n*-pentane, toluene, cyclohexane and cyclopentane were purchased from Energy Chemical Co. Ltd. or J&K Chemical Co. Ltd. and used as received. Bis(1,5-cyclooctadiene)-nickel was purchased from Strem Chemicals Inc. and stored in the fridge (−20 ℃) of the glovebox. Chemicals were used as received from the suppliers. All new compounds were characterized by NMR spectroscopy and high-resolution mass spectroscopy. NMR spectra were recorded on a Bruker 400 MHz spectrometer and were calibrated using residual solvent as an internal reference ($CDCl_3$ δ: 7.26 for ^1H NMR and 77.16 for ^{13}C NMR). EI-HRMS spectra were obtained on a Waters Micromass G1540N/GCT Premier. ESIHRMS spectra were obtained on a Thermo Fisher Scientific LTQ FT Ultra or an Agilent Technologies 6224 TOF LC/MS. FI-HRMS spectra were obtained on a JEOL-AccuTOF-GCv4G-GTC MS.

4.2 General procedure for Ni-catalyzed coupling reaction of 1,3-butadiene, aldimine, and alkenylboronic acids

In a nitrogen-filled glovebox, aldimine (0.2 mmol), $Ni(cod)_2$ (5.5 mg, 0.02 mmol), and alkenylboronic acids (103.6 mg, 0.7 mmol, 3.5 equiv.) were dissolved in cyclohexane (1.0 mL) in a vial equipped with a magnetic stir bar. Then 1,3-butadiene (3.0 mol/L in toluene, 533 μL, 1.6 mmol, 8.0 equiv.), 3-hexyne (23 μL, 0.2 mmol) were added successively. The vial was sealed, taken out of the glovebox, and stirred at room temperature for 8 h. The resulting mixture was then filtered through a silica gel pad, eluting with EtOAc and concentrated *in vacuo* to give the crude product. *E*/*Z* of the crude samples were determined by ^1H NMR analysis. The crude product was purified by flash column chromatography (hexanes/EtOAc, V∶V=10/1) on silica gel to give the corresponding homoallylic amines.

N-(3*E*,6*E*)-1,7-Diphenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4a**): Reddish-brown oil, 84% yield (62.0 mg). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.35～7.25 (m, 8H), 7.21～7.15 (m, 2H), 6.66～6.62 (m, 2H), 6.44～6.41 (m, 2H), 6.35 (d, J=15.8 Hz, 1H), 6.21～6.12 (m, 1H), 5.66～5.58 (m, 1H), 5.51～5.41 (m, 1H), 4.24 (dd, J=8.0, 4.0 Hz, 1H), 3.63 (s, 3H), 2.89 (t, J=8.0 Hz, 2H), 2.58～2.50 (m, 1H), 2.46～2.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.0, 144.1, 141.8, 137.6, 131.9, 130.7, 128.6, 128.6, 128.6, 127.7, 127.1, 127.0, 126.4, 126.1, 114.8, 114.7, 58.4, 55.7, 42.3, 35.9; IR (neat) ν: 1509, 1235, 1037, 965, 817, 744, 693 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{28}NO$ $[M+H]^+$ 370.2165, found 370.2159.

N-((3*E*,6*E*)-1-(Naphthalen-2-yl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4b**): Reddish-brown oil, 72% yield (60.2 mg). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.80～7.76 (m, 4H), 7.49～7.47 (m, 1H), 7.43～7.40 (m, 2H), 7.30～7.26 (m, 4H), 7.21～7.16 (m, 1H), 6.64～6.61 (m, 2H), 6.50～6.45 (m, 2H), 6.34 (d, J=15.8 Hz, 1H), 6.19～6.12 (m, 1H), 5.69～5.61 (m, 1H), 5.54～5.46 (m, 1H), 4.41 (dd, J=12.0, 8.0 Hz, 1H), 4.01 (br, 1H), 3.63 (s, 3H), 2.90 (t, J=8.0 Hz, 2H), 2.65～2.59 (m, 1H), 2.54～2.46 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.1, 141.9, 141.7, 137.7, 133.7, 132.9, 132.1, 130. 8, 128.6, 128.5, 128.0, 127.8, 127.1, 127.2, 126.2, 126.1, 125.6, 125.1, 124.9, 114.9, 58.7, 55.8, 42.3, 36.0; IR (neat) ν: 1509, 1235, 1038, 965, 816, 744, 692 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{29}NONa$ $[M+Na]^+$ 442.2141, found 442.2152.

N-((3*E*,6*E*)-1-(Naphthalen-1-yl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4c**): Brown oil, 66% yield (55.0 mg). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, J=8.0 Hz, 1H), 7.90 (d, J=8.0 Hz, 1H), 7.73 (d, J=8.0 Hz, 1H), 7.66 (d, J=8.0 Hz, 1H), 7.57～7.49 (m, 2H), 7.39 (t, J=8.0 Hz, 1H), 7.34～7.27 (m, 4H), 7.22～7.18 (m, 1H), 6.63～6.59 (m, 2H), 6.40～6.38 (m, 2H), 6.38～6.36 (d, J=8.0 Hz, 1H), 6.21～6.14 (m, 1H), 5.74～5.66 (m, 1H), 5.61～5.52 (m, 1H), 5.10 (dd, J=8.0, 4.0 Hz, 1H), 3.63 (s, 3H), 2.93 (t, J=8.0 Hz, 2H), 2.82～2.76 (m, 1H), 2.53～2.44 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.0, 141.7, 138.7, 137.6, 134.3, 132.0, 130.8, 129.3, 128.6, 128.0, 127.5, 127.2, 126.2, 126.1, 126.0, 125.5, 123.3, 122.6, 114.9, 114.6, 55.8, 54.2, 40.9, 36.0; IR (neat) ν: 1509, 1236, 1036, 965, 777, 729, 692 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{30}NO$ $[M+H]^+$ 420.2321, found 420.2312.

N-((3*E*,6*E*)-7-Phenyl-1-(o-tolyl)hepta-3,6-dien-1-yl)-4-methoxyaniline (**4d**): Purple liquid, 80% yield (61.5 mg). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.43～7.40 (m, 1H), 7.35～7.27 (m, 4H), 7.22～7.20 (m, 1H), 7.16～7.11 (m, 3H), 6.68～6.63 (m, 2H), 6.40～6.34 (m, 3H), 6.22～6.14 (m, 1H), 5.71～5.62 (m, 1H), 5.54～5.46 (m, 1H), 4.48～4.45 (dd, J=4.0, 2.0 Hz, 1H), 3.66 (s, 3H), 2.92 (t, J=8.0 Hz,

2H), 2.56～2.49 (m, 1H), 2.42 (s, 3H), 2.39～2.31 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.2, 141. 6, 141.5, 137.7, 131.9, 130.8, 130.7, 128.6, 127.9, 127.2, 126.8, 126.6, 126.3, 126.2, 125.6, 114.9, 114.7, 55.8, 54.8, 40.4, 36.0, 19.3; IR (neat) ν: 1510, 1235, 1037, 965, 817, 727, 692 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{30}NO$ $[M+H]^+$ 384.2321, found 384.2327.

N-((3*E*,6*E*)-1-(2-Methoxyphenyl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4e**): Reddish-brown oil, 48% yield (38.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.27 (m, 5H), 7.22～7.17 (m, 2H), 6.89～6.85 (m, 2H), 6.68～6.64 (m, 2H), 6.47～6.43 (m, 2H), 6.36 (d, J=12 Hz, 1H), 6.21～6.14 (m, 1H), 5.65～5.58 (m, 1H), 5.52～5.45 (m, 1H), 4.68 (dd, J=8.0, 4.0 Hz, 1H), 3.87 (s, 3H), 3.67 (s, 3H), 2.91 (t, J=4.0 Hz, 2H), 2.65～2.59 (m, 1H), 2.43～2.36 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.9, 152.0, 141.7, 137.7, 131.2, 130.6, 129.0, 128.6, 128.5, 127.8, 127.3, 127.1, 126.2, 120.8, 114.8, 110.5, 55.9, 55.4, 52.9, 39.6, 36.0; IR (neat) ν: 1059, 1232, 1028, 965, 817, 751, 692 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{30}NO_2$ $[M+H]^+$ 400.2271, found 400.2278.

N-((3*E*,6*E*)-1-(4-Methoxyphenyl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4f**): a yellow oil, 63% yield (50.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35～7.25 (m, 6H), 7.22～7.18 (m, 1H), 6.86～6.83 (m, 2H), 6.68～6.64 (m, 2H), 6.46～6.42 (m, 2H), 6.36 (d, J=16 Hz, 1H), 6.22～6.15 (m, 1H), 5.65～5.60 (m, 1H), 5.51～5.45 (m, 1H), 4.22 (dd, J=8.0, 4.0 Hz, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 2.92 (t, J=4.0 Hz, 2H), 2.57～2.48 (m, 1H), 2.48～2.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.6, 152.1, 141.9, 137.7, 136.1, 131.8, 130.7, 128.8, 128.6, 127.9, 127.5, 127.2, 126.2, 114.9, 114.0, 57.9, 55.9, 55.3, 42.5, 36.0; IR (neat) ν: 1058, 1236, 1033, 965, 817, 730, 692 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{30}NO_2$ $[M+H]^+$ 400.2271, found 400.2278.

N-((3*E*,6*E*)-1-(4-(Methylthio)phenyl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4g**): Reddish-brown oil, 54% yield (44.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.25 (m, 6H), 7.22～7.17 (m, 3H), 6.67～6.64 (m, 2H), 6.43～6.42 (m, 2H), 6.38～6.34 (d, J=16.0 Hz, 1H), 6.21～6.13 (m, 1H), 5.67～5.59 (m, 1H), 5.50～5.42 (m, 1H), 4.22 (dd, J=8.0, 4.0 Hz, 1H), 3.67 (s, 3H), 2.91 (t, J=8.0 Hz, 2H), 2.54～2.49 (m, 1H), 2.43 (s, 3H), 2.41～2.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.1, 141.6, 141.0, 137.6, 136.7, 132.0, 130.8, 128.6, 127.6, 127.2, 127.1, 127.0, 126.1, 114.9, 114.8, 58.1, 55.8, 42.3, 36.0, 16.0. HRMS (FI) calcd for $C_{27}H_{29}NOS$ $[M+H]^+$ 415.1964, found 415.1961.

N-((3*E*,6*E*)-1-(3-Chloro-5-methoxyphenyl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4h**): Yellow oil, 79% yield (68.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35～7.27 (m, 4H), 7.22～7.18 (m, 1H), 6.96 (t, J=4.0 Hz, 1H), 6.81 (t, J=4.0 Hz, 1H), 6.74 (t, J=4.0 Hz, 1H), 6.68～6.66 (m, 2H), 6.43～6.39 (m, 2H), 6.37 (d, J=16 Hz, 1H), 6.22～6.14 (m, 1H), 5.69～5.61 (m, 1H), 5.50～5.41 (m, 1H), 4.16 (dd, J=8.0, 4.0 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 2.92 (d, J=8.0 Hz, 2H), 2.53～2.49 (m, 1H), 2.43～2.35 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.6, 152.3, 147.7, 141.5, 137.6, 135.1, 132.4, 130.9, 128.6, 128.5, 127.3, 127.2, 126.2, 119.0, 114.9, 114.8, 112.6, 111.0, 58.3, 55.9, 55.6, 42.2, 36.0; IR (neat) ν: 1511, 1237, 1040, 966, 813, 749, 677 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{29}NO_2Cl$ $[M+H]^+$ 434.1881, found 434.1884.

N-((3*E*,6*E*)-1-(3-Fluoro-4-methoxyphenyl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4i**): Reddish-brown oil, 60% yield (50.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.27 (m, 4H), 7.22～7.18 (m, 1H), 7.11～7.03 (m, 2H), 6.87 (t, J=8.4 Hz, 1H), 6.69～6.65 (m, 2H), 6.44～6.40 (m, 2H), 6.36 (d, J=15.8 Hz, 1H), 6.22～6.13 (m, 1H), 5.67～5.59 (m, 1H), 5.48～5.41 (m, 1H), 4.18 (dd, J=8.1, 4.0 Hz, 1H), 3.89 (br, 1H), 3.82 (s, 3H), 3.67 (s, 3H), 2.91 (t, J=6.5 Hz, 2H), 2.53～2.46 (m, 1H), 2.44～2.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.6 (d, J=246.5 Hz), 152.1, 146.4 (d, J=10.9 Hz), 141.5, 137.6, 137.3 (d, J=5.0 Hz), 132.1, 130.7, 128.6, 128.5, 127.4, 127.1, 126.1, 121.9 (d, J=3.4 Hz), 114.8, 114.7, 114.1 (d, J=18.7 Hz), 113.4, 57.6, 56.3, 55.8, 42.3, 35.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −134.84; IR (neat) ν: 1510, 1235, 1029, 966, 816, 729, 692 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{29}NO_2F$ $[M+H]^+$ 418.2176, found 418.2183.

N-((3*E*,6*E*)-1-(4-Fluorophenyl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4j**): Yellow oil, 81% yield (62.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33～7.27 (m, 6H), 7.21～7.17 (m, 1H), 7.01～6.95 (m, 2H), 6.68～6.64 (m, 2H), 6.43～6.39 (m, 2H), 6.36 (d, J=8.0 Hz, 1H), 6.21～6.13 (m, 1H), 5.66～5.59 (m, 1H), 5.48～5.40 (m, 1H), 4.23 (dd, J=8.2, 5.1 Hz, 1H), 3.91 (br, 1H), 3.66 (s, 3H), 2.91 (t, J=6.6 Hz, 2H), 2.54～2.47 (m, 1H), 2.44～2.35 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 161.9 (d, J=242.8 Hz), 152.2, 141.6, 139.7 (d, J=3.0 Hz), 137.6, 132.2, 130.8, 128.6, 128.0, 127.9 (d, J=7.9 Hz), 127.5, 127.2, 126.1, 115.4 (d, J=21.2 Hz), 114.8, 57.8, 55.8, 42.5, 36.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −116.11; IR (neat) ν: 1507, 1235, 1036, 965, 818, 731, 692 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{27}NOF$ $[M+H]^+$ 388.2071, found 388.2075.

N-((3*E*,6*E*)-7-Phenyl-1-(4-(trifluoromethyl)phenyl)hepta-3,6-dien-1-yl)-4-methoxyaniline (**4k**): Yellow oil, 70% yield (61.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, J=8.2 Hz, 2H), 7.48 (d, J=8.1 Hz, 2H), 7.35～7.28 (m, 4H), 7.24～7.19 (m, 1H), 6.69～6.65 (m, 2H), 6.42～6.35 (m, 3H), 6.22～6.14 (m, 1H), 5.71～5.63 (m, 1H), 5.51～5.42 (m, 1H), 4.31 (dd, J=8.3, 4.9 Hz, 1H), 3.68 (s, 3H), 2.93 (t, J=6.6 Hz, 2H), 2.59～2.53 (m, 1H), 2.46～2.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.3, 148.4, 141.3, 137.6, 132.6, 130.9, 129.3 (q, J=32.4 Hz), 128.7, 128.4, 127.2, 127.1, 126.8, 126.1, 125.7 (q, J=3.8 Hz), 124.4 (q, J=273.7 Hz), 115.0, 114.9, 114.8, 114.7, 58.1, 55.8, 42.2, 36.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −62.28; IR (neat) ν: 1510, 1237,1016, 965, 817, 733, 692 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{27}NOF_3$ $[M+H]^+$ 438.2039, found 438.2043.

N-((3*E*,6*E*)-7-Phenyl-1-(3-(trifluoromethyl)phenyl)hepta-3,6-dien-1-yl)-4-methoxyaniline (**4l**): Reddish-brown oil, 91% yield (79.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (s, 1H), 7.55 (d, J=7.6 Hz, 1H), 7.48 (d, J=7.7 Hz, 1H),

7.41 (t, J=7.7 Hz, 1H), 7.35～7.28 (m, 4H), 7.21～7.18 (m, 1H), 6.69～6.65 (m, 2H), 6.42～6.35 (m, 3H), 6.22～6.13 (m, 1H), 5.70～5.60 (m, 1H), 5.51～5.41 (m, 1H), 4.30 (dd, J=8.3, 5.0 Hz, 1H), 3.68 (s, 3H), 2.93 (t, J=6.5 Hz, 2H), 2.58～2.51 (m, 1H), 2.46～2.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.3, 145.4, 141.4, 137.6, 132.7, 131.0 (q, J=32.4 Hz), 130.9, 129.9, 129.1, 128.6, 128.4, 127.2, 127.0, 126.2, 124.4 (q, J=273.7 Hz), 124.0 (q, J=4.0 Hz), 123.3 (q, J=3.9 Hz), 114.9, 114.8, 58.3, 55.8, 42.3, 36.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −62.43; IR (neat) ν: 1510, 1236, 1036, 965, 817, 734, 693 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{27}NOF_3$ $[M+H]^+$ 438.2039, found 438.2041.

N-((3*E*,6*E*)-7-Phenyl-1-(4-(trifluoromethoxy)phenyl)hepta-3,6-dien-1-yl)-4-methoxyaniline (**4m**): Yellow oil, 76% yield (67.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45～7.33 (m, 6H), 7.28 (d, J=7.1 Hz, 1H), 7.21 (d, J=8.1 Hz, 2H), 6.76～6.71 (m, 2H), 6.49～6.41 (m, 3H), 6.29～6.20 (m, 1H), 5.75～5.67 (m, 1H), 5.56～5.48 (m, 1H), 4.32 (dd, J=8.3, 4.9 Hz, 1H), 4.00 (br, 1H), 3.74 (s, 3H), 2.99 (t, J=6.7 Hz, 2H), 2.63～2.56 (m, 1H), 2.51～2.42 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.3, 148.2, 142.9, 141.5, 137.6, 132.5, 130.9, 128.7, 128.5, 127.8, 127.3, 127.2, 121.2, 120.5 (q, J=258.0 Hz), 114.9, 114.8, 57.8, 55.8, 42.4, 36.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −57.80; IR (neat) ν: 1509, 1252, 1036, 965, 817, 735, 692 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{27}NO_2F_3$ $[M+H]^+$ 454.1988, found 454.1994.

3-((3*E*,6*E*)-1-((4-Methoxyphenyl)amino)-7-phenylhepta-3,6-dien-1-yl)benzonitrile (**4n**): Reddish-brown oil, 92% yield (72.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 1H), 7.60 (d, J=7.8 Hz, 1H), 7.51 (d, J=7.6 Hz, 1H), 7.40 (t, J=7.7 Hz, 1H), 7.35～7.28 (m, 4H), 7.21 (t, J=6.9 Hz, 1H), 6.67 (d, J=8.9 Hz, 2H), 6.40～6.35 (m, 3H), 6.22～6.13 (m, 1H), 5.66 (d, J=15.3 Hz, 1H), 5.49～5.40 (m, 1H), 4.28 (dd, J=8.3, 5.0 Hz, 1H), 3.69 (s, 3H), 2.93 (t, J=6.5 Hz, 2H), 2.54 (d, J=14.4 Hz, 1H), 2.45～2.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.5, 145.9, 141.0, 137.5, 133.0, 131.1, 131.0, 130.9, 130.2, 129.5, 128.7, 128.3, 127.3, 126.7, 126.2, 119.1, 114.9, 114.8, 112.7, 57.9, 55.8, 42.2, 36.0; IR (neat) ν: 1511, 1236, 1035, 967, 818, 799, 692 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{27}N_2O$ $[M+H]^+$ 395.2117, found 395.2121.

Methyl-4-((3*E*,6*E*)-1-((4-methoxyphenyl)amino)-7-phenylhepta-3,6-dien-1-yl)benzoate (**4o**): Reddish-brown oil, 67% yield (57.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.27 (m, 6H), 7.22～7.18 (m, 1H), 7.05～7.01 (m, 2H), 6.68～6.64 (m, 2H), 6.44～6.41 (m, 2H), 6.40～6.35 (d, J=20 Hz, 1H), 6.22～6.14 (m, 1H), 5.68～5.61 (m, 1H), 5.51～5.43 (m, 1H) 4.25 (dd, J=8.3, 4.9 Hz, 1H), 3.67 (s, 3H), 2.92 (t, J=6.4 Hz, 2H), 2.57～2.51 (m, 1H), 2.44～2.36 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.5, 152.1, 149.5, 141.6, 137.6, 132.1, 130.7, 128.6, 128.5, 127.5, 127.3, 127.1, 126.1, 121.6, 114.7, 57.9, 55.8, 42.3, 35.9, 21.2; IR (neat) ν: 1511, 1235, 1036, 966, 818, 732, 693 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{29}NO_3$ $[M+Na]^+$ 450.2039, found 450.2037.

N-((3*E*,6*E*)-7-Phenyl-1-(4-((trimethylsilyl)ethynyl)phenyl)hepta-3,6-dien-1-yl)-4-methoxyaniline (**4p**): Yellow oil, 70% yield (65.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, J=7.9 Hz, 2H), 7.31～7.24 (m, 6H), 7.19～7.15 (m, 1H), 6.63～6.59 (m, 2H), 6.38～6.31 (m, 3H), 6.19～6.10 (m, 1H), 5.63～5.55 (m, 1H), 5.46～5.37 (m, 1H), 4.20 (dd, J=8.1, 5.1 Hz, 1H), 3.64 (s, 3H), 2.88 (t, J=8.0 Hz, 2H), 2.52～2.46 (m, 1H), 2.42～2.33 (m, 1H), 0.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.1, 144.7, 141.5, 137.5, 132.3, 132.2, 130.7, 128.6, 128.5, 127.3, 127.1, 126.4, 126.1, 121.6, 114.8, 114.7, 105.2, 93.8, 58.3, 55.8, 42.1, 35.9, 0.1; IR (neat) ν: 1510, 1237, 1037, 966, 862, 730, 692 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{36}NOSi$ $[M+H]^+$ 466.2560, found 466.2558.

N-((3*E*,6*E*)-7-Phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)hepta-3,6-dien-1-yl)-4-methoxyaniline (**4q**): Reddish-brown oil, 51% yield (50.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, J=8.0 Hz, 2H), 7.38～7.27 (m, 6H), 7.22～7.18 (m, 1H), 6.66～6.62 (m, 2H), 6.44～6.41 (m, 2H), 6.48 (d, J=16 Hz, 1H), 6.22～6.15 (m, 1H), 5.69～5.61 (m, 1H), 5.50～5.43 (m, 1H), 4.27 (dd, J=8.3, 4.9 Hz, 1H), 3.94 (br, 1H), 3.67 (s, 3H), 2.92 (t, J=6.2 Hz, 2H), 2.59～2.52 (m, 1H), 2.46～2.38 (m, 1H), 1.33 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.1, 147.6, 141.8, 137.7, 135.2, 132.1, 130.8, 129.9, 129.1, 128.7, 128.6, 127.7, 127.2, 126.2, 125.9, 114.8, 58.6, 55.9, 42.3, 36.0, 25.0; IR (neat) ν: 1511, 1236, 1037, 963, 818, 729, 659 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{39}BNO_3$ $[M+H]^+$ 496.3017, found 496.3021.

N-((3*E*,6*E*)-1-(Furan-2-yl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4r**): Reddish-brown oil, 67% yield (48.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (m, 5H), 7.22～7.17 (m, 1H), 6.74～6.70 (m, 2H), 6.58～6.54 (m, 2H), 6.35 (d, J=15.8 Hz, 1H), 6.27 (dd, J=4.0, 4.0 Hz, 1H), 6.21～6.13 (m, 2H), 5.67～5.58 (m, 1H), 5.50～5.41 (m, 1H), 4.43 (t, J=6.4 Hz, 1H), 3.71 (s, 3H), 2.91 (t, J=6.5 Hz, 2H), 2.66～2.57 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.3, 152.5, 141.5, 141.4, 137.7, 132.0, 130.7, 128.8, 128.6, 127.1, 126.1, 115.3, 114.9, 110.2, 106.2, 55.8, 52.9, 38.3, 36.0; IR (neat) ν: 1511, 1242, 1034, 986, 807, 732, 693 cm^{-1}. HRMS (DART) calcd for $C_{24}H_{26}NO_2$ $[M+H]^+$ 360.1958, found 360.1954.

N-((3*E*,6*E*)-7-Phenyl-1-(thiophen-2-yl)hepta-3,6-dien-1-yl)-4-methoxyaniline (**4s**): Yellow oil, 68% yield (50.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.27 (m, 4H), 7.22～7.18 (m, 1H), 7.16～7.15 (m, 1H), 6.96～6.92 (m, 2H), 6.73～6.69 (m, 2H), 6.57～6.53 (m, 2H), 6.36 (d, J=15.7 Hz, 1H), 6.22～6.14 (m, 1H), 5.70～5.62 (m, 1H), 5.56～5.47 (m, 1H), 4.60～4.57 (m, 1H), 3.70 (s, 3H), 2.92 (t, J=6.4 Hz, 2H), 2.67～2.55 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.5, 149.5, 141.5, 137.7, 132.4, 130.8, 128.6, 127.2, 126.9, 126.2, 123.8, 123.4, 115.2, 114.9, 55.8, 54.9, 42.3, 36.0; IR (neat) ν: 1512, 1245, 1035, 974, 705, 695, 671 cm^{-1}. HRMS (FI) calcd for $C_{24}H_{25}NOS$ $[M+H]^+$ 375.1651, found 375.1658.

N-((3*E*,6*E*)-1-(Benzofuran-5-yl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4t**): Reddish-brown oil, 65% yield (52.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59～7.56 (m,

2H), 7.43 (d, J=8.5 Hz, 1H), 7.33～7.26 (m, 5H), 7.21～7.17 (m, 1H), 6.68～6.63 (m, 3H), 6.47～6.44 (m, 2H), 6.35 (d, J=15.9 Hz, 1H), 6.21～6.13 (m, 1H), 5.68～5.61 (m, 1H), 5.53～5.45 (m, 1H), 4.35 (dd, J=8.2, 5.0 Hz, 1H), 3.65 (s, 3H), 2.91 (t, J=6.4 Hz, 2H), 2.61～2.55 (m, 1H), 2.50～2.42 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.3, 152.0, 145.3, 141.9, 138.7, 137.6, 131.9, 130.7, 128.7, 128.6, 127.9, 127.7, 127.2, 126.1, 122.9, 118.8, 114.8, 111.4, 106.8, 58.5, 55.8, 42.9, 36.0; IR (neat) ν: 1509, 1234, 1031, 966, 816, 734, 693 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{28}NO_2$ $[M+H]^+$ 410.2114, found 410.2119.

N-((3*E*,6*E*)-1-(6-Chloropyridin-3-yl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4u**): Yellow oil, 65% yield (53.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (d, J=2.4 Hz, 1H), 7.64 (dd, J=8.2, 2.5 Hz, 1H), 7.36～7.27 (m, 4H), 7.26～7.24 (m, 1H), 7.23～7.19 (m, 1H), 6.70～6.66 (m, 2H), 6.42～6.34 (m, 3H), 6.22～6.12 (m, 1H), 5.71～5.61 (m, 1H), 5.50～5.40 (m, 1H), 4.30 (dd, J=8.0, 5.2 Hz, 1H), 3.69 (s, 3H), 2.93 (t, J=8.0 Hz, 2H), 2.58～2.51 (m, 1H), 2.49～2.40 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.6, 150.1, 148.6, 140.8, 138.6, 137.5, 137.2, 133.3, 131.0, 128.7, 128.2, 127.3, 126.4, 126.2, 124.4, 115.0, 55.9, 55.7, 42.1, 36.0; IR (neat) ν: 1509, 1236, 1034, 965, 817, 731, 692. HRMS (ESI) calcd for $C_{25}H_{26}N_2OCl$ $[M+H]^+$ 405.1728, found 405.1724.

N-((3*E*,6*E*)-1-(4-Bromophenyl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4v**): Yellow oil, 49% yield (43.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44～7.40 (m, 2H), 7.34～7.28 (m, 4H), 7.25～7.19 (m, 3H), 6.68～6.64 (m, 2H), 6.42～6.34(m, 1H), 6.22～6.13 (m, 1H), 5.67～5.59 (m, 1H), 5.49～5.40 (m, 1H), 4.21 (dd, J=8.1, 5.0 Hz, 1H), 3.67 (s, 3H), 2.92 (t, J=6.5 Hz, 2H), 2.54～2.47 (m, 1H), 2.43～2.35 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.2, 143.2, 141.5, 137.6, 132.4, 131.8, 130.8, 128.7, 128.5, 128.3, 127.3, 127.2, 126.2, 120.6, 114.9, 114.8, 58.0, 55.8, 42.3, 36.0; IR (neat) ν: 1510, 1236, 1036, 965, 816, 730, 692 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{27}NOBr$ $[M+H]^+$ 448.1270, found 448.1261.

Phenyl-4-((3*E*,6*E*)-1-((4-methoxyphenyl)amino)-7-phenylhepta-3,6-dien-1-yl)benzoate (**4w**): Reddish-brown oil, 77% yield (75.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, J=8.2 Hz, 2H), 7.50 (d, J=8.2 Hz, 2H), 7.41 (t, J=7.9 Hz, 2H), 7.35～7.25 (m, 5H), 7.23～7.17 (m, 3H), 6.67 (d, J=8.9 Hz, 2H), 6.42 (d, J=8.9 Hz, 2H), 6.36 (d, J=15.9 Hz, 1H), 6.23～6.14 (m, 1H), 5.71～5.62 (m, 1H), 5.52～5.43 (m, 1H), 4.35 (dd, J=8.2, 4.9 Hz, 1H), 3.68 (s, 3H), 2.93 (t, J=6.4 Hz, 2H), 2.62～2.54 (m, 1H), 2.50～2.41 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.1, 152.3, 151.0, 150.5, 141.3, 137.5, 132.5, 130.9, 130.7, 129.6, 128.6, 128.4, 127.2, 127.1, 126.8, 126.1, 126.0, 121.8, 114.8, 58.3, 55.8, 42.1, 35.9; IR (neat) ν: 1510, 1233, 1038, 974, 855, 704, 691 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{32}NO_3$ $[M+H]^+$ 490.2376, found 490.2389.

N-((3*E*,6*E*)-1-(4-(2-Bromoethoxy)phenyl)-7-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**4x**): Yellow oil, 51% yield (49.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.25 (m, 6H), 7.23～7.18 (m, 1H), 6.85 (d, J=8.7 Hz, 2H), 6.66 (d, J=8.9 Hz, 2H), 6.44 (d, J=8.9 Hz, 2H), 6.36 (d, J=15.8 Hz, 1H), 6.22～6.13 (m, 1H), 5.67～5.58 (m, 1H), 5.51～5.42 (m, 1H), 4.24～4.19 (m, 3H), 3.68 (s, 3H), 3.60 (t, J=6.3 Hz, 2H), 2.92 (t, J=6.4 Hz, 2H), 2.54～2.50 (m, 1H), 2.43～2.40 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.1, 152.1, 141.8, 137.7, 136.9, 131.9, 130.7, 128.7, 128.6, 127.2, 126.2, 114.9, 114.8, 68.0, 57.9, 55.9, 42.4, 36.0, 29.4; IR (neat) ν: 1508, 1235, 1033, 965, 878, 730, 692 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{30}NO_2NaBr$ $[M+Na]^+$ 514.1352, found 514.1354.

N-((3*E*,6*E*)-1,7-Diphenylhepta-3,6-dien-1-yl)aniline (**4y**): Reddish-brown oil, 96% yield (65.4 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.27 (m, 9H), 7.23～7.18 (m, 1H), 7.06 (dd, J=8.5, 7.3 Hz, 2H), 6.63 (t, J=7.2 Hz, 1H), 6.48 (d, J=7.9 Hz, 2H), 6.37 (d, J=15.9 Hz, 1H), 6.21～6.14 (m, 1H), 5.70～5.60 (m, 1H), 5.51～5.44 (m, 1H), 4.34 (dd, J=8.2, 5.0 Hz, 1H), 2.92 (t, J=6.6 Hz, 2H), 2.61～2.54 (m, 1H), 2.49～2.41 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.5, 143.8, 137.7, 132.0, 130.8, 129.2, 128.7, 128.6, 127.7, 127.2, 127.0, 126.4, 126.2, 117.4, 113.6, 57.6, 42.3, 36.0; IR (neat) ν: 1503, 1264, 1028, 964, 869, 745, 690 cm^{-1}. HRMS (FI) calcd for $C_{25}H_{25}N$ $[M+H]^+$ 339.1982, found 339.1986.

N-((3*E*,6*E*)-1,7-Diphenylhepta-3,6-dien-1-yl)-4-(trifluoromethyl)aniline (**4z**): Reddish-brown oil, 72% yield (58.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.32 (m, 7H), 7.30～7.29 (m, 2H), 7.28～7.26 (m, 1H), 7.25～7.21 (m, 2H), 6.48 (d, J=8.5 Hz, 2H), 6.37 (d, J=16.0 Hz, 1H), 6.22～6.13 (m, 1H), 5.72～5.63 (m, 1H), 5.52～5.42 (m, 1H), 4.48 (s, 1H), 4.38 (dd, J=8.1, 5.1 Hz, 1H), 2.93 (t, J=6.5 Hz, 2H), 2.64～2.57 (m, 1H), 2.53～2.42 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.9, 142.8, 137.6, 132.5, 130.9, 128.8, 128.7, 128.5, 127.4, 127.3, 127.1, 126.6 (q, J=3.9 Hz), 126.2, 125.1 (q, J=270.7 Hz), 119.0 (q, J=32.7 Hz), 112.8, 57.3, 42.1, 36.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −61.10; IR (neat) ν: 1529, 1276, 1028, 965, 823, 743, 697 cm^{-1}. HRMS (DART)calcd for $C_{26}H_{25}NF_3$ $[M+H]^+$ 408.1934, found 408.1929.

N-((5*E*,8*E*)-1,9-Diphenylnona-5,8-dien-3-yl)-4-methoxyaniline (**4aa**): Yellow oil, 46% yield (36.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.30 (m, 6H), 7.24～7.19 (m, 4H), 6.81～6.77 (m, 2H), 6.57～6.53 (m, 2H), 6.45 (d, J=16.0 Hz, 1H), 6.25～6.18 (m, 1H), 5.63～5.50 (m, 2H), 3.78 (s, 3H), 3.41～3.36 (m, 1H), 2.96～2.93 (t, J=4.0 Hz, 2H), 2.79～2.76 (m, 2H). 2.35～2.31 (m, 2H), 1.96～1.87 (m, 1H), 1.85～1.76 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.0, 142.3, 142.1, 137.8, 131.3, 130.6, 128.9, 128.6, 128.5, 127.6, 127.1, 126.2, 126.0, 115.1, 115.0, 56.0, 53.3, 37.5, 36.3, 36.1, 32.5; IR (neat) ν: 1509, 1233, 1037, 965, 817, 742, 695 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{32}NO$ $[M+H]^+$ 398.2478, found 398.2480.

N-((3*E*,6*E*)-1-Phenyl-7-(p-tolyl)hepta-3,6-dien-1-yl)-4-methoxyaniline (**5a**): Reddish-brown oil, 49% yield (37.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.29 (m, 4H), 7.24～7.22 (m, 3H), 7.10 (d, J=7.8 Hz, 2H), 6.66 (d, J=8.7 Hz, 2H), 6.43 (d, J=8.9 Hz, 2H), 6.34 (d, J=15.8 Hz, 1H), 6.17～6.09 (m, 1H), 5.68～5.61 (m, 1H), 5.51～5.43

(m, 1H), 4.25 (dd, J=8.3, 5.0 Hz, 1H), 3.67 (s, 3H), 2.91 (t, J=6.3 Hz, 2H), 2.58～2.52 (m, 1H), 2.46～2.41 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.1, 144.2, 141.9, 136.9, 134.9, 132.2, 130.6, 129.3, 128.7, 127.6, 127.0, 126.5, 126.1, 114.8, 58.5, 55.9, 42.4, 36.0, 21.3; IR (neat) v: 1509, 1235, 1036, 966, 817, 754, 700 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{30}NO$ $[M+H]^+$ 384.2321, found 384.2327.

N-((3*E*,6*E*)-7-(4-Chlorophenyl)-1-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**5b**): Reddish-brown oil, 50% yield (40.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.28 (m, 4H), 7.23～7.19 (m, 5H), 6.66 (d, J=8.8 Hz, 2H), 6.43 (d, J=8.9 Hz, 2H), 6.30 (d, J=15.9 Hz, 1H), 6.20～6.10 (m, 1H), 5.66～5.58 (m, 1H), 5.51～5.43 (m, 1H), 4.26 (dd, J=8.2, 5.0 Hz, 1H), 3.67 (s, 3H), 2.90 (t, J=6.5 Hz, 2H), 2.59～2.52 (m, 1H), 2.48～2.39 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.1, 144.0, 141.8, 136.2, 132.7, 131.6, 129.5, 129.4, 128.7, 128.0, 127.4, 127.0, 126.5, 114.8, 58.5, 55.8, 42.4, 35.9; IR (neat) v: 1509, 1236, 1032, 974, 819, 733, 680 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{27}NOCl$ $[M+H]^+$ 404.1775, found 404.1769.

N-((3*E*,6*E*)-7-(4-Fluorophenyl)-1-phenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**5c**): Reddish-brown oil, 48% yield (37.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.32 (m, 3H), 7.3～7.26 (m, 4H), 7.23～7.19 (m, 1H), 6.98 (t, J=8.7 Hz, 2H), 6.66 (d, J=8.9 Hz, 2H), 6.43 (d, J=8.9 Hz, 2H), 6.32 (d, J=15.8 Hz, 1H), 6.13～6.04 (m, 1H), 5.67～5.59 (m, 1H), 5.51～5.43 (m, 1H), 4.26 (dd, J=8.2, 5.0 Hz, 1H), 3.67 (s, 3H), 2.91 (t, J=6.3 Hz, 2H), 2.59～2.52 (m, 1H), 2.47～2.39 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.1 (d, J=246.7 Hz), 152.1, 144.1, 141.8, 133.8 (d, J=3.3 Hz), 131.8, 129.6, 128.7, 128.4 (d, J=2.2 Hz), 127.9, 127.6 (d, J=7.9 Hz), 127.0, 126.5, 115.5 (d, J=21.6 Hz), 114.8, 58.5, 55.9, 42.4, 35.9; IR (neat) v: 1506, 1229, 1035, 966, 843, 731, 668 cm^{-1}; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −115.37. HRMS (ESI) calcd for $C_{26}H_{27}NOF$ $[M+H]^+$ 388.2071, found 388.2079.

N-((3*E*,6*E*)-1-Phenyldeca-3,6-dien-1-yl)-4-methoxyaniline (**5d**): Reddish-brown oil, 77% yield (51.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40～7.27 (m, 5H), 7.24～7.19 (m, 1H), 6.67 (d, J=8.8 Hz, 2H), 6.43 (d, J=8.6 Hz, 2H), 5.62～5.54 (m, 1H), 5.40 (m, 3H), 4.23 (dd, J=8.3, 4.9 Hz, 1H), 3.67 (s, 3H), 2.72～2.69 (m, 2H), 2.56～2.50 (m, 1H), 2.44～2.35 (m, 1H), 2.00～1.95 (m, 2H), 1.40～1.34 (m, 2H), 0.88 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.1, 144.2, 141.9, 133.1, 131.5, 128.6, 128.2, 127.0, 126.7, 126.5, 114.8, 58.5, 55.9, 42.4, 35.7, 34.8, 22.8, 13.8, 1.2; IR (neat) v: 1509, 1236, 1037, 968, 817, 752, 699 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{30}NO$ $[M+H]^+$ 336.2321, found 336.2312.

(*E*)-4-Methoxy-*N*-(7-methyl-1-phenylocta-3,6-dien-1-yl)aniline (**5e**): Yellow oil, 78% yield (50.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40～7.27 (m, 4H), 7.24～7.19 (m, 1H), 6.67 (d, J=8.9 Hz, 2H), 6.46～6.36 (m, 2H), 5.57～5.51 (m, 1H), 5.43～5.32 (m, 1H), 5.14～5.10 (m, 1H), 4.28～4.19 (m, 1H), 3.67 (s, 3H), 2.70 (t, J=6.9 Hz, 2H), 2.57～2.48 (m, 1H), 2.37 (m, 1H), 1.71 (s, 3H), 1.64 (s, 1H), 1.60 (s,2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.0, 144.3, 142.0, 133.3, 128.6, 126.9, 126.5, 126.1, 125.3, 122.1, 114.8, 58.5, 55.9, 42.5, 31.4, 25.8, 17.8; IR (neat) v: 1509, 1236, 1037, 970, 818, 754, 700 cm^{-1}. HRMS (FI) calcd for $C_{22}H_{27}NO$ $[M+H]^+$ 321.2087, found 321.2085.

(*E*)-*N*-(5-(Cyclohex-1-en-1-yl)-1-phenylpent-3-en-1-yl)-aniline (**5f**): Reddish-brown oil, 90% yield (57.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.28 (m, 4H), 7.23～7.19 (m, 1H), 7.06 (t, J=7.8 Hz, 2H), 6.63 (t, J=7.3 Hz, 1H), 6.47 (d, J=8.1 Hz, 2H), 5.59～5.52 (m, 1H), 5.41～5.33 (m, 2H), 4.31 (dd, J=8.0, 5.2 Hz, 1H), 2.68～2.48 (m, 3H), 2.46～2.38 (m, 1H), 2.01～1.96 (m, 2H), 1.88～1.87 (m, 2H), 1.63～1.52 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.6, 143.9, 136.6, 132.8, 129.2, 128.7, 127.3, 127.0, 126.4, 122.0, 117.4, 113.6, 57.6, 42.3, 41.4, 28.5, 25.4, 23.1, 22.6; IR (neat) v: 1503, 1265, 1028, 992, 746, 699, 691 cm^{-1}. HRMS (DART) calcd for $C_{23}H_{28}N$ $[M+H]^+$ 318.2216, found 318.2213.

(*E*)-*N*-(5-(Cyclopent-1-en-1-yl)-1-phenylpent-3-en-1-yl)-4-methoxyaniline (5g): Yellow oil, 86% yield (57.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.29 (m, 4H), 7.25～7.19 (m, 1H), 6.67 (d, J=8.7 Hz, 2H), 6.43 (d, J=8.6 Hz, 2H), 5.71～5.57 (m, 1H), 5.47～5.28 (m, 2H), 4.24 (dd, J=8.2, 5.0 Hz, 1H), 3.68 (s, 3H), 2.77 (d, J=6.8 Hz, 2H), 2.58～2.51 (m, 1H), 2.45～2.37 (m, 1H), 2.33～2.28 (m, 2H), 2.22 (t, J=7.4Hz, 2H), 1.91～1.81 (m, 2H). 1.60 (dr, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.0, 144.2, 143.4, 141.9, 132.1, 128.7, 127.3, 127.0, 126.5, 124.4, 114.9, 114.7, 58.4, 55.9, 42.4, 35.2, 34.7, 32.6, 23.6; IR (neat) v: 1509, 1235, 1036, 971, 816, 751, 700 cm^{-1}. HRMS (FI) calcd for $C_{23}H_{27}NO$ $[M+H]^+$ 333.2087, found 333.2092.

2-(4-Methoxyphenyl)-3-((2*E*,5*E*)-6-phenylhexa-2,5-dien-1-yl)isoindolin-1-one (**7**): Reddish-brown oil, 41% yield (32.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J=7.4 Hz, 1H), 7.56 (d, J=7.1 Hz, 1H), 7.49 (d, J=10.3 Hz, 2H), 7.43 (d, J=8.9 Hz, 2H), 7.29～7.25 (m, 4H), 7.21～7.18 (m, 1H), 6.96 (d, J=9.0 Hz, 2H), 6.20 (d, J=15.7 Hz, 1H), 6.02～5.94 (m, 1H), 5.33～5.26 (m, 1H), 5.16～5.14 (dd, J=6.2, 3.4 Hz, 1H), 5.08～5.00 (m, 1H), 3.81 (s, 3H), 2.74～2.66 (m, 3H), 2.58～2.50 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.43, 157.54, 144.41, 137.63, 133.15, 132.71, 131.78, 130.60, 130.00, 128.68 ～ 128.26 (m), 127.11, 126.09, 125.73, 124.12, 123.74, 122.52, 114.49, 61.04, 55.58, 35.83, 34.65; IR (neat) v: 1510, 1244, 1029, 967, 828, 728, 691 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{26}NO_2$ $[M+H]^+$ 396.1958, found 396.1963.

N-((3*E*,6*E*)-4-Methyl-1,7-diphenylhepta-3,6-dien-1-yl)-4-methoxyaniline (**8**): Reddish-brown oil, 60% yield (45.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.37 (m, 2H), 7.34～7.26 (m, 6H), 7.22～7.18 (m, 2H), 6.63～6.58 (m, 2H), 6.41～6.34 (m, 3H), 6.23～6.12 (m, 1H), 5.40 (t, J=7.2 Hz, 1H), 4.28 (dd, J=10.1, 4.4 Hz, 1H), 3.64 (s, 3H), 2.97～2.91 (m, 2H), 2.69～2.63 (m, 1H), 2.34～2.30 (m, 1H), 1.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.0, 144.9, 142.2, 137.7, 133.7, 133.2, 130.2, 129.2, 128.7, 128.6, 127.1, 126.9, 126.3, 126.1, 126.0, 114.7, 56.6, 55.8, 50.2, 31.6, 15.8. HRMS (ESI) calcd for $C_{27}H_{30}NO$ [M+

H]$^+$ 384.2321, found 384.2336.

辅助材料(Supporting Information) 化合物 **4a**～**4aa**、**5a**～**5g**、**7** 和 **8** 的 ^{1}H NMR 和 ^{13}C NMR 图谱. 这些材料可以免费从本刊网站(http://sioc-journal.cn/)上下载.

References

[1] (a) Nugent, T. C. *Chiral Amine Synthesis*: *Methods, Developments and Applications*, Wiley-VCH, Weinheim, **2010**.
(b) Lawrence, S. A. *Amines: Synthesis*, *Properties and Applications*, Cambridge University Press, Cambridge, U. K., **2004**.
(c) Puentes, C. O.; Kouznetsov, V. J. *J. Heterocycl. Chem*. **2002**, *39*, 595.

[2] (a) Yus, M.; Gonzalez-Gomez, J. C.; Foubelo, F. *Chem. Rev*. **2011**, *111*, 7774.
(b) Yus, M.; González-Gómez, J. C.; Foubelo, F. *Chem. Rev*. **2013**, *113*, 5595.
(c) Huo, H.-X.; Duvall, J. R.; Huang, M.-Y.; Hong, R. *Org. Chem. Front*. **2014**, *1*, 303.

[3] (a) Dahlmann, M.; Grub, J.; Löser, E. *Butadiene*, Wiley-VCH, Weinheim, Germany, **2011**.
(b) Weitz, H. M.; Löser, E. *Isoprene*, Wiley-VCH, Weinheim, Germany, **2000**.

[4] (a) Wu, Z.; Zhang, W. *Chin. J. Org. Chem*. **2017**, *37*, 2250 (in Chinese).
(吴正兴, 张万斌, 有机化学, **2017**, *37*, 2250.)
(b) Xiong, Y.; Sun, Y.-W.; Zhang, G.-Z. *Tetrahedron Lett*. **2018**, *59*, 347.
(c) Holmes, M.; Schwartz, L. A.; Krische, M. J. *Chem. Rev*. **2018**, *118*, 6026.
(d) Wang, P.-S.; Shen, M.-L.; Gong, L.-Z. *Synthesis* **2018**, *50*, 956.
(e) Perry, G. J. P.; Jia, T.; Procter, D. J. *ACS Catal*. **2020**, *10*, 1485.
(f) Wang, X.-X.; Lu, X.; Li, Y.; Wang J.-W.; Fu, Y. *Sci. China Chem*. **2020**, *63*, 1586.
(g) Zhang, H.; Gu, Q.; You, S.; *Chin. J. Org. Chem*. **2019**, *39*, 15 (in Chinese).
(张慧君, 顾庆, 游书力, 有机化学, **2019**, *39*, 15.)

[5] Kimura, M.; Miyachi, A.; Kojima, K.; Tanaka, S.; Tamaru, Y. *J. Am. Chem. Soc*. **2004**, *126*, 14360.

[6] (a) Chen, T.-Y.; Tsutsumi, R.; Montgomery, T. P.; Volchkov, I.; Krische, M. J. *J. Am. Chem. Soc*. **2015**, *137*, 1798.
(b) Schmitt, D. C.; Lee, J.; Dechert-Schmitt, A.-M. R.; Yamaguchi, E.; Krische, M. J. *Chem. Commun*. **2013**, *49*, 6096.
(c) Zhu, S.; Lu, X.; Luo, Y.; Zhang, W.; Jiang, H.; Yan, M.; Zeng, W. *Org. Lett*. **2013**, *15*, 1440.

[7] (a) Li, C.; Liu, R.-Y.; Jesikiewicz, L. T.; Yang, Y.; Liu, P.; Buchwald, S. L. *J. Am. Chem. Soc*. **2019**, *141*, 5062.
(b) Jiang, L.; Cao, P.; Wang, M.; Chen, B.; Wang, B.; Liao, J. *Angew. Chem., Int. Ed*. **2016**, *55*, 13854.
(c) Li, M.; Wang, J.; Meng, F. *Org. Lett*. **2018**, *20*, 7288.
(d) Fu, B.; Yuan, X.; Li, Y.; Wang, Y.; Zhang, Q.; Xiong, T.; Zhang, Q. *Org. Lett*. **2019**, *21*, 3576.
(e) Gui, Y.-Y.; Hu, N.; Chen, X.-W.; Liao, L.-L.; Ju, T.; Ye, J.-H.; Zhang, Z.; Li, J.; Yu, D.-G. *J. Am. Chem. Soc*. **2017**, *139*, 17011.

[8] (a) Kojima, K.; Kimura, M.; Tamaru, Y. *Chem. Commun*. **2005**, 4717.
(b) Kimura, M.; Kojima, K.; Tatsuyama, Y.; Tamaru, Y. *J. Am. Chem. Soc*. **2006**, *128*, 6332.
(c) Kimura, M.; Tatsuyama, Y.; Kojima, K.; Tamaru, Y. *Org. Lett*. **2007**, *9*, 1871.

[9] Li, Y.-Q.; Shi, S.-L. *Organometallics* **2021**, *40*, 2345.

[10] (a) McCammant, M. S.; Liao, L.; Sigman, M. S. *J. Am. Chem. Soc*. **2013**, *135*, 4167.
(b) Tao, Z.-L.; Adili, A.; Shen, H.-C.; Han, Z.-Y.; Gong, L.-Z. *Angew. Chem. Int. Ed*. **2016**, *55*, 4322.
(c) Tortajada, A.; Ninokata, R.; Martin, R. *J. Am. Chem. Soc*. **2018**, *140*, 2050.
(d) Boerth, J. A.; Maity, S.; Williams, S. K.; Mercado, B. Q.; Ellman, J. A. *Nat. Catal*. **2018**, *1*, 673.
(e) Xiong, Y.; Zhang, G. *J. Am. Chem. Soc*. **2018**, *140*, 2735.
(f) Yang, J.; Ji, D.-W.; Hu, Y.-C.; Min, X.-T.; Zhou, X.; Chen, Q.-A. *Chem. Sci*. **2019**, *10*, 9560.
(g) Yang, J.; Liu, J.; Neumann, H.; Franke, R.; Jackstell, R.; Beller, M. *Science* **2019**, *366*, 1514.
(h) Li, Y.-Q.; Chen, G.; Shi, S.-L. *Org. Lett*. **2021**, *23*, 2571.

[11] (a) Denmark, S. E.; Guagnano, V.; Dixon, J. A.; Stolle, A. *J. Org. Chem*. **1997**, *62*, 4610.
(b) Lin, H.-C.; Wang, P.-S.; Tao, Z.-L.; Chen, Y.-G.; Han, Z.-Y.; Gong, L.-Z. *J. Am. Chem. Soc*. **2016**, *138*, 14354.
(c) Fan, L.-F.; Luo, S.-W.; Chen, S.-S.; Wang, T.-C.; Wang, P.-S.; Gong, L.-Z. *Angew. Chem., Int. Ed*. **2019**, *58*, 16806.

[12] (a) Shinohara, Y.; Kudo, F.; Eguchit, T. *J. Am. Chem. Soc*. **2011**, *133*, 18134.
(b) Tang, W.; Prusov, E. V. *Angew. Chem., Int. Ed*. **2012**, *51*, 3401.
(c) Winter, P.; Hiller, W.; Christmann, M. *Angew. Chem., Int. Ed*. **2012**, *51*, 3396.

[13] (a) Lian, X.; Chen, W.; Dang, L.; Li, Y.; Ho, C.-Y. *Angew. Chem., Int. Ed*. **2017**, *56*, 9048.
(b) Jing, S.-M.; Balasanthiran, V.; Pagar, V.; Gallucci, J. C.; RajanBabu, T.-V. *J. Am. Chem. Soc*. **2017**, *139*, 18034.
(c) Schmidt, V.-A.; Kennedy, C.-R.; Bezdek, M.-J.; Chirik, P.-J. *J. Am. Chem. Soc*. **2018**, *140*, 3443.
(d) Bohn, M.-A.; Schmidt, A.; Hilt, G.; Dindaroğlu, M.; Schmalz, H.-G. *Angew. Chem., Int. Ed*. **2011**, *50*, 9689.

[14] (a) Kimura, M.; Ezoe, A.; Mori, M.; Tamaru, Y. *J. Am. Chem. Soc*. **2005**, *127*, 201.
(b) Li, Y.-Q.; Shi, S.-L. *Chin. J. Org. Chem*. **2021**, *41*, 1939 (in Chinese).
(李雨青, 施世良, 有机化学, **2021**, *41*, 1939.)

[15] (a) McCammant, M.-S.; Liao, L.; Sigman, M.-S. *J. Am. Chem. Soc*. **2013**, *135*, 4167.
(b) McCammant, M.-S.; Sigman, M.-S. *Chem. Sci*. **2015**, *6*, 1355.
(c) Wang, C.-G.; Zhang, Y.; Wang, S.; Chen, B.; Li, Y.; Gao, Y.; Hu, P.; Wang, B.-Q.; Cao, P. *Org. Lett*. **2021**, *23*, 535.
(d) Pang, X.; Zhao, Z.-Z.; Wei, X.-X.; Qi, L.; Xu, G.-L.; Duan, J.; Liu, X.-Y.; Shu, X.-Z. *J. Am. Chem. Soc*. **2021**, *143*, 4536.

[16] (a) Bin, H.-Y.; Wei, X.; Zi, J.; Zuo, Y.-J.; Wang, T.-C.; Zhong, C.-M. *ACS Catal*. **2015**, *5*, 6670.
(b) Xu, G.; Zhao, H.; Fu, B.; Cang, A.; Zhang, G.; Zhang, Q.; Xiong, T.; Zhang, Q. *Angew. Chem., Int. Ed*. **2017**, *56*, 13130.
(c) Song, F.; Wang, F.; Guo, L. Feng, X.; Zhang, Y.; Chu, L. *Angew. Chem., Int. Ed*. **2020**, *59*, 177.
(d) Ma, W.-Y.; Han, G.-Y.; Kang, S.-l.; Pang, X.-B.; Liu, X.-Y.; Shu, X.-Z. *J. Am. Chem. Soc*. **2021**, *143*, 15930.

[17] (a) Montgomery, L. *Angew. Chem., Int. Ed*. **2004**, *43*, 3890.
(b) Standley, E.-A.; Tasker, S.-Z.; Jensen, K.-L.; Jamison, T.-F. *Acc. Chem. Res*. **2015**, *48*, 1503.
(c) Hoshimoto, Y.; Ohashi, M.; Ogoshi S. *Acc. Chem. Res*. **2015**, *48*, 1746.

[18] (a) Lennox, A.-J.; Lloyd-Jones, G.-C. *Angew. Chem., Int. Ed*. **2013**, *52*, 7362.
(b) Carrow, B.-P.; Hartwig, J.-F. *J. Am. Chem. Soc*. **2011**, *133*, 2116.
(c) Thomas, A.-A.; Denmark, S.-E. *Science* **2016**, *352*, 329.

(d) Malapit, C. A.; Bour, J. R.; Brigham, C. E.; Sanford, M. S. *Nature* **2018**, *563*, 100.

[19] Kimura, M.; Matsuo, S.; Shibata, K.; Tamaru, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3386.

[20] (a) Zhang, W.-B.; Yang, X.-T.; Ma, J.-B.; Su, Z.-M.; Shi, S.-L. *J. Am. Chem. Soc.* **2019**, *141*, 5628.
(b) Cai, Y.; Zhang, J.-W.; Li, F.; Liu, J.-M.; Shi, S.-L. *ACS Catal.* **2019**, *9*, 1.
(c) Cai, Y.; Ye, X.; Liu, S.; Shi, S.-L. *Angew. Chem., Int. Ed.* **2019**, *58*, 13433.
(d) Shen, D.; Zhang, W.-B.; Li, Z.; Shi, S.-L.; Xu, Y. *Adv. Synth. Catal.* **2020**, *362*, 1125.
(e) Li, Y.-Q.; Li, F.; Shi, S.-L. *Chin. J. Chem.* **2020**, *38*, 1035.
(f) Cai, Y.; Ruan, L.-X.; A. Rahman; Shi, S.-L. *Angew. Chem., Int. Ed.* **2021**, *60*, 5262.
(g) Wang, Z.-C.; Gao, J.; Cai, Y.; Ye, X.; Shi, S.-L. *CCS Chem.* **2021**, *3*, 1445.
(h) Wang, Z.-C.; Xie, P.-P.; Xu, Y.; Hong, X.; Shi, S.-L. *Angew. Chem., Int. Ed.* **2021**, *60*, 16077.
(i) Cai, Y.; Shi, S.-L. *J. Am. Chem. Soc.* **2021**, *143*, 11963.
(j) Zhang, W.-B.; Chen, G.; Shi, S.-L. *J. Am. Chem. Soc.* **2021**, **2022**, *144*, 130.

(Fan, Y.)

