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Iron-Catalyzed Allylic C–H Amination of Substituted 1,3-Dienes

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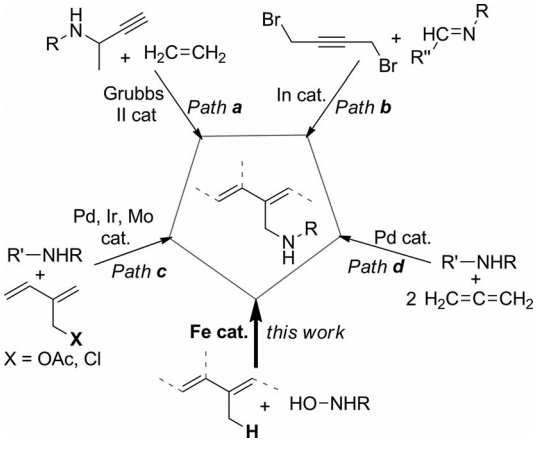
A catalytic method for the selective allylic C–H amination of dienes and trienes using arylhydroxylamines has been developed. This iron-catalyzed approach involves the in situ generation of activated nitrosoarenes, which in turn react with dienes or trienes to give the corresponding aminomethyl dienes or trienes as the major products, and hetero-Diels–Alder adducts as minor products. The selectivity depends on the structures of both the catalyst and the substrate. We have also studied substituent effects using *p*-substituted phenylhydroxylamines.

Introduction

The construction of C–N bonds by C–H amination is one of the most exciting and important developments in organic synthesis.[1] The practical utility of such reactions for the synthesis of complex molecules comes from their ability to operate with predictable chemo-, stereo-, regio-, and site selectivity.[2] Classical amination methods range from nucleophilic displacement of leaving groups to reductive amination of carbonyl compounds.[3] Modern methods have taken advantage of transition-metal-catalyzed C–H amination.[4] The main approaches include oxidative C(sp^2)–N coupling,[1a–1e] and benzylic[5] and allylic[1f,6] C–H amination.

Allylic C–H amination is a very useful process, and it replaces the classical nucleophilic allylic substitution method to access allylamines, which are fundamental building blocks in organic synthesis.[1a] Transition-metal-catalyzed allylic C–H amination occurs via metal–nitrene species,[7] via π-allyl species,[8] by dehydrogenative diamination,[9] or by ene-like reactions.[10–12] Recently, Muniz et al. reported a metal-free hypervalent-iodine-mediated allylic amination approach.[13] However, all these methods focused on the allylic amination of olefins. No method has been reported for the allylic C–H amination of 1,3-dienes to prepare aminomethyl-1,3-dienes, which are also useful intermediates in organic synthesis.[14]

A few methods have been reported for the preparation[15] of aminomethyl-1,3-dienes using prefunctionalized substrates (Scheme 1). These include ene–yne cross metathesis using the expensive Grubbs II catalyst (path a),[15a] the addition of highly reactive organometallic reagents to imines using 1,4-dibromo-2-butyne (path b),[15b] Pd- or Ir-catalyzed allylic amination using prefunctionalized dienes, such as dienyl acetates or halomethyl-1,3-dienes (path c),[15c,15d,15e] and the reaction of allenes (2 equiv.) with amines in the presence of Pd catalysts (path d).[15h] Although the reaction of allenes with amines is effective, bis(dienyl)amines were observed as by-products. Other methods include the reaction of 2-halomethyl-1,3-dienes with secondary amines, but this requires the tedious preparation of 2-halomethyl-1,3-dienes.[15f,15g] The Grignard cross-coupling reaction of 2-bromo-3-aminopropene and vinyl bromides is reported to proceed with poor chemoselectivity.[15h,15i] In general, all of these methods rely on leaving-group chemistry and multi-step transformations, and require prefunctionalized substrates.



Scheme 1. Comparative chart of existing routes and our approach to aminomethyl 1,3-dienes.

Results and Discussion

In a continuation of our efforts on the development of transition-metal-catalyzed allylic C–H amination[11] of alkenes by nitroso-ene reactions,[10] we were interested in de-

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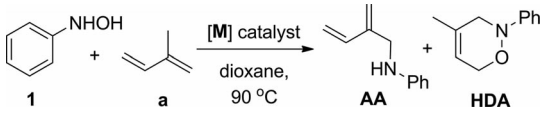
veloping a method for the allylic C–H amination of 1,3-dienes. Although significant progress has been made in the area of metal-catalyzed allylic amination by nitroso-ene reactions using simple olefins,[10–12] no method has been reported for the allylic amination of polyenes such as dienes or trienes that yields aminomethyl polyenes selectively. This is mainly due to the propensity of dienes and trienes to react with dienophiles to give hetero-Diels–Alder (HDA) adducts[16] instead of allylamines. Rarely has any effort been made to develop selective allylic amination by a nitroso-ene reaction for the synthesis of useful aminomethyl-1,3-dienes (Scheme 2).



Scheme 2. Formation of allylic amine and HDA adduct of isoprene.

Our interest in allylic amination using arylhydroxylamines and our experience in this area led us to consider a metal-catalyzed approach for the selective allylic C–H amination of simple 1,3-dienes. In our previous study, we have used 2,3-dimethyl-1,3-butadiene to probe whether the reaction is an "on-metal" or "off-metal" process, i.e., whether free nitrosoarene is absent or present in the reaction mixture. The facts that the allylic amine was formed as the major product, and that a negligible amount of the HDA adduct was formed ruled out the presence of free nitrosoarene in our reactions. In contrast to our observations, Lau et al. (using a $CuCl_2$ catalyst)[12j] and Ragaini et al. [using a Ru(Ar-BIAN) catalyst; BIAN = 1,2-bis(arylimino)acenaphthene][12k] detected the formation of HDA adducts as major products along with the allylic amines (minor product), which confirms the presence of a free nitrosoarene intermediate.

Furthermore, based on our mechanistic insights into allylic amination, we envisaged that the use of a suitable metal catalyst that operates in an "on-metal" fashion would result in the selective allylic amination of 1,3-dienes. Accordingly, we started our study with a set of copper and iron catalysts (Table 1) for the reaction of isoprene (**a**; an allylic 1,3-diene) and phenylhydroxylamine (**1**). For our initial experimentation we used our standard allylic amination procedure,[11b,11c] in which a phenylhydroxylamine (0.25 mmol) solution in dioxane (4 mL) is added slowly using a syringe pump to the solution of metal catalyst (0.025 mmol) and isoprene (1 mmol) in dioxane (3 mL) over 4 h at 90 °C (Scheme 2). To find an efficient catalyst for the selective amination reaction, we screened some known allylic amination catalysts, as shown in Table 1.

Copper-based catalysts (Table 1, entries 1 and 2) did not work well. However, good conversions were observed with most iron catalysts. The iron azobenzene dioxide complex $[Fe\{PhN(O)N(O)Ph\}_3][FeCl_4]_2$[11b,11c] (Table 1, entries 8, 10, and 11) was found to be the most efficient catalyst to yield the allylic amine selectively in good to high yield. We also examined the reaction with 30 mol-% of $FeCl_2$ (Table 1, entry 5) and $FeCl_3$ (Table 1, entry 7) to compare their reactivities with that of the Fe azobenzene dioxide complex (10 mol-%), but poor selectivity for the allylic amine was observed. In these reactions, both possible isomeric HDA adducts were observed, along with varying amounts of aniline and azoxybenzene, which are common by-products in amination reactions. The yield improved slightly when the reaction temperature was lowered to 60 °C, but the selectivity remained almost the same (Table 1, entry 10). Lowering the temperature further led to a decrease in the yield and selectivity of formation of the allylic amine (Table 1, entry 11). Based on these results, we chose to use Fe azobenzene dioxide as a catalyst at 60 °C to test the selective allylic amination of other substituted 1,3-dienes.

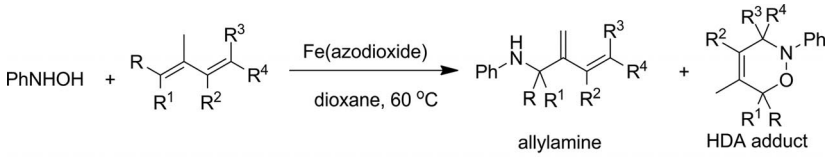
Next, we evaluated a set of 1,3-dienes with allylic C–H groups at the 1, 2, 3, and 4 positions of the diene moiety (Table 2). We observed an intriguing dependence of the product selectivity on the structure of the substrate. 2,3-Dimethyl-1,3-butadiene (**b**) was relatively less selective than isoprene (**a**), but nevertheless, it reacted well to give allylic amine **1b** in 56% yield. Similar dienes with different substitution patterns, i.e., 2,4-dimethyl-1,3-pentadiene (**c**) and 3-methyl-1,3-pentadiene (**d**) were converted into the corresponding allylic amines (i.e., **1c** and **1d**) in good yields (68 and 70%, respectively) with high selectivity; <5% of the

Table 1. Catalyst optimization for the selective allylic amination (AA)of dienes.[a,b]

Entry	Catalyst	Yield [%] [AA + HDA]	AA selectivity [%]
1	$CuCl_2{\cdot}4H_2O$	35	31.4
2	$Cu(MeCN)_4PF_6$	51	41.2
3	Fe(Pc)	47	63.8
4	$FeCl_2{\cdot}4H_2O$	69	37.6
5	$FeCl_2{\cdot}4H_2O$ (30 mol-%)	73	29.8
6	$FeCl_3$	39	64.1
7	$FeCl_3$ (30 mol-%)	45	52.3
8	$[Fe\{Ph(O)NN(O)Ph\}_3][FeCl_4]_2$	64	86.1
9	$FeCl_2{\cdot}4H_2O/FeCl_3$ (9:1)	67	67.2
10	$[Fe\{Ph(O)NN(O)Ph\}_3][FeCl_4]_2$	71	84.5[c]
11	$[Fe\{Ph(O)NN(O)Ph\}_3][FeCl_4]_2$	56	73.2[d]

[a] All reactions were performed at 90 °C with 1:4 substrate ratio (PhNHOH: isoprene). [b] Yield and Selectivity calculated based on GC yields of AA and HDA products. [c] Reaction carried out at 60 °C. [d] Reactions carried out at 40 °C.

Table 2. Substrate dependence of selective allylic amination.[a]



1,3-Diene	Allylamine	HDA adduct	Yield (%)[b] AA (HDA)
(**a**)	(**1a**)	(**1a'**)	60 (11)[c]
(**b**)	(**1b**)	(**1b'**)	56 (16)
(**c**)	(**1c**)		68[d]
(**d**)	(**1d**)		70[d]
(**e**)	(**1e**)	(**1e'**)	6 (52)
(**f**)	(**1f**)	(**1f'**)	8 (38)
(**g**)	(**1g**), (**1g'**)		58[d,e]
(**h**)	(**1h**)		73

[a] All reactions were performed at 60 °C with 1:4 substrate ratio (PhNHOH: diene/triene). [b] GC yields. [c] Both possible isomers detected. [d] <5% HDA adduct observed. [e] Combined yield of both isomeric amines.

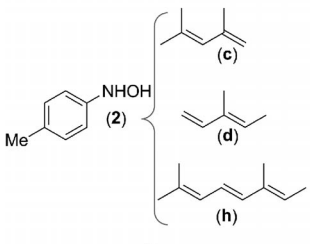
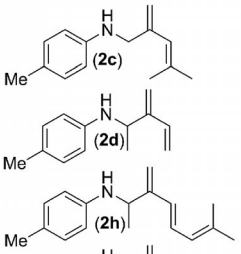
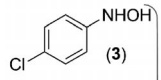
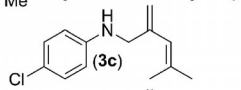
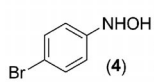
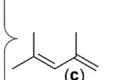
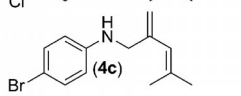
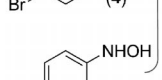
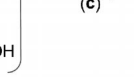
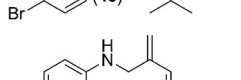
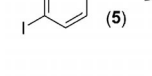
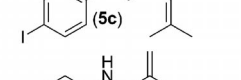
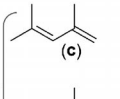
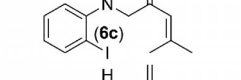
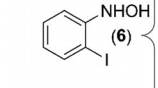
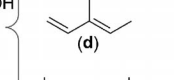
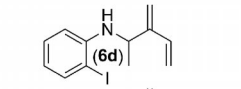
HDA adducts were observed. Another set of 1,3-dienes with methyl substituents at the 1 and 4 positions, i.e., 2,4-hexadiene (**e**) and 2,5-dimethyl-2,4-hexadiene (**f**) gave the HDA adducts (i.e., **1e′** and **1f′**) as the major products. It seems that the presence of methyl substituents on either the 2 or 3 position of the 1,3-diene is a prerequisite for a selective allylic amination that gives a product in which the conjugation of the diene is retained.

Based on the observed selectivity for allylic amine formation, we classified the 1,3-dienes into two categories: i) 1,3-dienes with at least one methyl substitution at either the 2 or 3 position (**a**, **b**, **c**, and **d**); and ii) 1,3-dienes without methyl substitution (allylic position) at either the 2 or 3 position (**e** and **f**). To further investigate the influence of the substrate structure on the outcome of the reaction, we tested two substituted octatrienes (i.e., **g** and **h**) that satisfy the requirement for selective allylic amination of methyl substitution on the 2 or 3 position. Allylic amination of myrcene (**g**) led to two different allylic amine products (**1g** and **1g′**), as shown in Table 2. To our surprise, 2,6-dimethyl-2,4,6-octatriene (**h**) gave an allylic amination product (**1h**, 73%) with exceptional selectivity, with retention of conjugation.

We then further extended this method to *ortho*- and *para*-substituted arylhydroxylamines. For these reactions, we chose a set of the most selective as well as efficient diene and triene substrates, i.e., 2,4-dimethyl-1,3-pentadiene (**c**), 3-methyl-1,3-pentadiene (**d**), and 2,6-dimethyl-2,4,6-octatriene (**h**) (Table 3). As expected, *p*-tolylhydroxylamine (**2**) reacted well with both dienes **c** and **d** and triene **h** to produce the corresponding allylic amines (i.e., **2c**, **2d**, and **2h**). The halogenated polyene products generated from halo-substituted phenylhydroxylamines **3**–**6**, allow further transformations to access complex compounds by metal-catalyzed cou-

pling reactions.[14c] 4-halo phenylhydroxylamines **3**–**5** reacted well with 2,4-dimethyl-1,3-pentadiene (**c**) to give the corresponding dienyl allylic amines (i.e., **3c**, **4c**, and **5c**) in excellent yields. Despite the sterically bulky nature of its *ortho* substituent, the reaction of 2-iodophenyl hydroxylamine (**6**) with the dienes and triene gave the corresponding allylic amines (i.e., **6c**, **6d**, and **6h**) with very good selectivities in high yields up to 76%.

Table 3. Selective allylic amination of dienes and triene.[a,b]

Hydroxylamine	Diene/Triene	Allylamine	Yield (%)
			65[c]
			63[c]
			71
			80[c]
			83[c]
			78[c]
			67[c]
			72[c]
			76

[a] All reactions were performed at 60 °C with a 1:4 substrate ratio (PhNHOH: diene/triene). [b] Isolated yields. [c] <5% HDA adduct observed in GC–MS.

The selectivity for the allylic amination over the HDA reaction can be attributed to steric and electronic properties of both the catalyst and the substrates. Two findings were observed from the results shown in Tables 1–3: i) the selective formation of the allylic amines from dienes is catalyst dependent, and the Fe azobenzene dioxide catalyst is the best catalyst for this reaction; and ii) the selectivity also depends on the structure of the substrate – there is a requirement for at least one methyl group at either the 2 or 3 position of the 1,3-diene for the product of selective allylic amination to be formed. The presence of a methyl group at the 2 or 3 position is necessary if the conjugation of the diene is to be retained after the formation of the allylic amine (see Tables 2 and 3). This behavior is consistent with the skew effect, which says that the abstraction of a hydrogen in nitroso-ene reactions is mainly due to the twix (*cis* and *gem*) orientation of double bond.[9]

To understand the electronic nature of the transition state, rate constants were determined for the reaction of 2,4-dimethyl-1,3-pentadiene (**c**) with a set of *para*-substituted phenylhydroxylamines, as shown in Figure 1. Electron-withdrawing groups (R = Cl, Br) gave increased reaction rates compared to the unsubstituted compound (R = H), whereas an electron-rich substituent (R = Me) led to a decrease in rate. The Hammett plot indicates the development of a small negative charge on the nitrogen of the nitroso intermediate. This observation is consistent with our previous study on allylic amination using *para*-substituted nitrobenzenes.[11g]

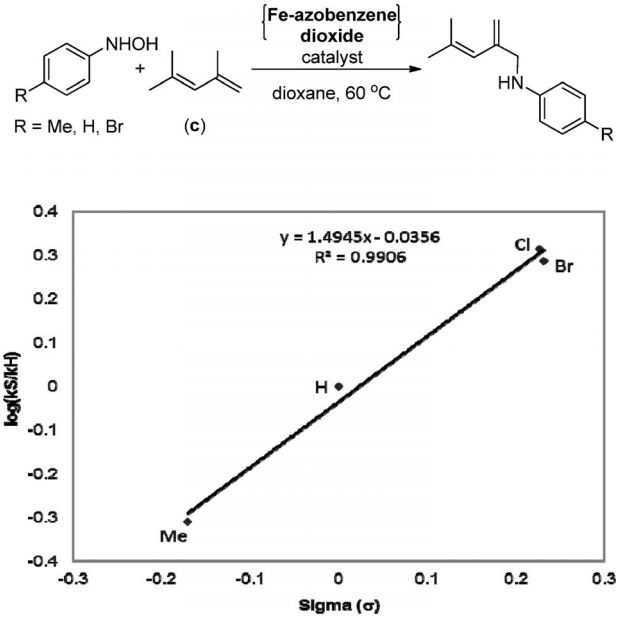
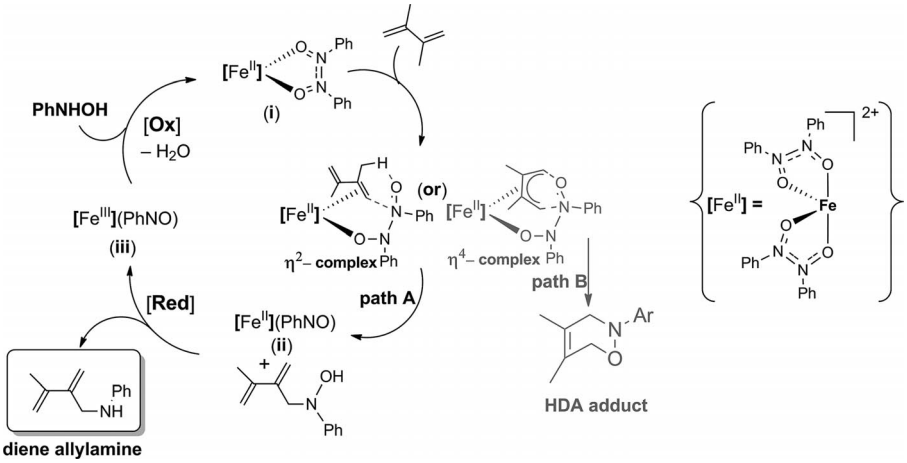


Figure 1. Hammett plot (k_{rel} vs. σ) for the reaction of diene **c** with *p*-substituted phenylhydroxylamines.

In our previous reports, involvement of the Fe azobenzene dioxide complex and its olefin adducts (on-metal process) in allylic amination has been strongly implicated on the basis of kinetic and isolation studies of reactions with different olefins.[11c,11i] For instance, acyclic and cyclic diene–iron complexes are stable compounds that have found a wide range of applications in organic synthesis.[17,18] The reactivity of the 1,3-diene system is altered drastically by coordination to the iron complexes. For acyclic 1,3-dienes, the diene adopts an *s-cis* conformation to form stable η^4 complexes, which requires C–C single-bond rotation.

Considering these facts, we believe that the selective allylic amination approach described in this paper involve the formation of intermediate iron η^2 complexes with 2,3-substituted dienes. Our observations show that 2,3-unsubsti-



Scheme 3. Plausible reaction pathway for the selective allylic amination of dienes.

tuted dienes preferentially give HDA reaction products, whereas 2,3-substituted 1,3-dienes prefer allylic amination. The formation of HDA products might involve formation of η^4 diene complexes by attaining an *s-cis* conformation. However, for 2,3-substituted 1,3-dienes, it is difficult to attain an *s-cis* conformation, due to possible steric factors and restricted C–C single bond rotation, so the dienes would form η^2 complexes. In this case, only one double bond is activated by the metal, and this might be the origin of the selectivity for allylic amination over HDA reaction. Based on these considerations and our previous reports,[11] we propose a pathway for the selective allylic amination of 1,3-dienes, as shown in Scheme 3. This pathway involves the Fe-catalyzed oxidation of arylhydroxylamine to activated azo complex **i** followed by diene coordination to form either an η^2 or an η^4 complex, depending on the structure of the diene (vide supra). The η^2 diene complex would lead to the formation of dienyl allyl *N*-hydroxylamine and Fe nitroso complex **ii** by path A, whereas the η^4 diene complex would lead to the HDA adduct (path B). Further reduction (deoxygenation) of dienyl *N*-hydroxyallylamine gives the desired dienyl allylamine with concomitant oxidation of Fe^{II} to Fe^{III} catalytic species **iii**, and the catalytic cycle continues in the same way.

Conclusions

In conclusion, we have developed the first method for the selective allylic amination of substituted 1,3-dienes. The selectivity depends on the electronic and steric properties of both the catalyst and the substrate. We conclude that the catalyst also plays a key role in accelerating the ene reaction by hindering the HDA reaction by selective activation of the diene and the nitrosoarene. A variety of 1,3-dienes and trienes with an allylic C–H (methyl) group at the 2 or 3 position of the diene moiety were selectively converted into the respective allylic amines. This is a simple and useful method for the preparation of functionalized polyenes, and it may find applications in the polymer and/or related industries.

Experimental Section

General Information: All the reagents were commercial grade, and were purified according to established procedures. The $[Fe\{PhN(O)N(O)Ph\}_3][FeCl_4]_2$ catalyst, a dark brown crystalline compound, was prepared following our reported procedure.[11b,11c] The purity of the recrystallized catalyst was confirmed by comparing its IR spectrum with that of the original product. Organic extracts were dried with anhydrous sodium sulfate. Solvents were removed using a rotary evaporator under reduced pressure. Silica gel (60–120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25 mm). GC–MS analysis was carried out using an Agilent GC–MS (7890A-5975C VL MSD) system. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard for ^1H (400 MHz) and for ^{13}C (100 MHz) spectra.

General Procedure for the Selective Allylic Amination of Dienes and Trienes: A solution of arylhydroxylamine (0.25 mmol) in dioxane (4 mL) was slowly added by syringe pump over 4 h to a solution of $[Fe\{PhN(O)N(O)Ph\}_3][FeCl_4]_2$ (28 mg, 0.025 mmol) and olefin (1 mmol) in dioxane (3 mL) at 60 °C. Reactions were allowed to continue for a further 2 h to ensure complete consumption of the arylhydroxylamine. After that, the mixture was filtered through Celite, and the filtrate was concentrated to dryness. The crude product was purified over a short column of silica gel (hexane/ethyl acetate eluents) to give the corresponding *N*-aryl- and aminomethyl-substituted 1,3-diene/triene, which was analyzed directly by GC–MS and NMR spectroscopy.

***N*-(4-Methyl-2-methylenepent-3-enyl)benzeneamine (1c):** Yield 67%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.80 (s, 3 H), 1.81 (s, 3 H), 3.71 (s, 2 H), 3.82 (br. s, 1 H), 4.94 (s, 1 H), 5.22 (s, 1 H), 5.64 (s, 1 H), 6.60 (d, J = 6.0 Hz, 2 H), 6.69 (t, J = 6.8 Hz, 1 H), 7.16 (t, J = 6.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 27.0, 50.0, 113.1, 113.8, 117.5, 123.9, 129.3, 137.3, 143.2, 148.4 ppm. IR (KBr): $\tilde{\nu}$ = 691, 748, 898, 1061, 1179, 1267, 1316, 1375, 1453, 1504,

1600, 1727, 2871, 2929, 2967, 3406 cm^{-1}. GC–MS: *m*/*z* = 159.0 $[M]^+$.

***N*-(3-Methylenepent-4-en-2-yl)benzeneamine (1d):** Yield 69%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.39 (d, *J* = 6.8 Hz, 3 H), 3.81 (br. s, 1 H), 4.20 (q, *J* = 6.8 Hz, 1 H), 5.09 (s, 1 H), 5.13 (d, *J* = 11.2 Hz, 1 H), 5.26 (s, 1 H), 5.37 (d, *J* = 18.0 Hz, 1 H), 6.42 (dd, *J* = 11.2, *J* = 18.0 Hz, 1 H), 6.51 (d, *J* = 6.4 Hz, 2 H), 6.67 (t, *J* = 7.2 Hz, 1 H), 7.13 (t, *J* = 6.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.0, 49.4, 113.0, 114.3, 122.3, 125.5, 129.1, 137.0, 144.0, 147.9 ppm. IR (KBr): $\tilde{\nu}$ = 684, 763, 906, 1024, 1071, 1162, 1275, 1299, 1437, 1482, 1602, 1729, 2853, 2924, 3066, 3407 cm^{-1}. GC–MS: *m*/*z* = 173.1 $[M]^+$.

3,6-Dihydro-3,6-dimethyl-2-phenyl-2*H*-1,2-oxazine (1e′): Yield 52%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 6.4 Hz, 3 H), 1.30 (d, *J* = 6.8 Hz, 3 H), 4.14 (q, *J* = 6.4 Hz, 1 H), 4.67 (q, *J* = 6.8 Hz, 1 H), 5.77 (d, *J* = 10.0 Hz, 1 H), 5.92 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.6, 19.1, 54.5, 73.7, 115.7, 121.2, 129.0, 129.2, 130.2, 148.9 ppm. IR (KBr): $\tilde{\nu}$ = 687, 751, 906, 1025, 1082, 1215, 1275, 1328, 1437, 1490, 1506, 1602, 2839, 2928, 3057 cm^{-1}. GC–MS: *m*/*z* = 189.0 $[M]^+$.

***N*-[(*E*)-7-Methyl-3-methyleneocta-4,6-dien-2-yl]benzeneamine (1h):** Yield 73%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.41 (d, *J* = 6.4 Hz, 3 H), 1.78 (s, 3 H), 1.82 (s, 3 H), 3.81 (br. s, 1 H), 4.20 (q, *J* = 6.4 Hz, 1 H), 5.05 (s, 1 H), 5.17 (s, 1 H), 5.90 (d, *J* = 11.2 Hz, 1 H), 6.18 (d, *J* = 15.6 Hz, 1 H), 6.52 (d, *J* = 7.6 Hz, 2 H), 6.60 (dd, *J* = 16.0 Hz, *J* = 11.2 Hz, 1 H), 6.66 (t, *J* = 6.8 Hz, 1 H), 7.13 (t, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.7, 22.4, 26.4, 50.3, 112.8, 113.2, 117.3, 125.3, 125.8, 129.3, 130.1, 136.8, 147.4, 148.3 ppm. IR (KBr): $\tilde{\nu}$ = 692, 750, 957, 1030, 1076, 1257, 1316, 1375, 1453, 1504, 1600, 1727, 2871, 2929, 2967, 3406 cm^{-1}. GC–MS: *m*/*z* = 227.3 $[M]^+$.

4-Methyl-*N*-(4-methyl-2-methylenepent-3-enyl)benzeneamine (2c): Yield 65%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.81 (s, 6 H), 2.43 (s, 3 H), 3.86 (s, 2 H), 4.94 (s, 1 H), 5.30 (s, 1 H), 5.65 (s, 1 H), 6.63 (d, *J* = 8.0 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 20.5, 26.9, 50.2, 113.2, 122.3, 124.0, 126.6, 129.8, 137.0, 143.3, 146.1 ppm. IR (KBr): $\tilde{\nu}$ = 806, 1018, 1261, 1518, 1616, 1681, 1752, 2923, 2965, 3349 cm^{-1}. GC–MS: *m*/*z* = 200.9 $[M]^+$.

4-Methyl-*N*-(3-methylenepent-4-en-2-yl)benzeneamine (2d): Yield 63%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.38 (d, *J* = 6.4 Hz, 3 H), 2.21 (s, 3 H), 3.68 (br. s, 1 H), 4.17 (q, *J* = 6.4 Hz, 1 H), 5.07 (s, 1 H), 5.13 (d, *J* = 11.2 Hz, 1 H), 5.22 (s, 1 H), 5.37 (d, *J* = 17.6 Hz, 1 H), 6.43 (d, *J* = 8.0 Hz, 2 H), 6.95 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.5, 22.2, 49.7, 113.3, 114.4, 122.3, 126.4, 129.8, 137.3, 145.0, 148.3 ppm. IR (KBr): $\tilde{\nu}$ = 759, 902, 1068, 1165, 1206, 1274, 1302, 1439, 1598, 2847, 2933, 3057, 3402 cm^{-1}. GC–MS: *m*/*z* = 187.0 $[M]^+$.

4-Methyl-*N*-[(*E*)-7-methyl-3-methyleneocta-4,6-dien-2-yl]benzeneamine (2h): Yield 71%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.39 (d, *J* = 6.8 Hz, 3 H), 1.77 (s, 3 H), 1.81 (s, 3 H), 2.20 (s, 3 H), 3.68 (br. s, 1 H), 4.16 (q, *J* = 6.8 Hz, 1 H), 5.04 (s, 1 H), 5.15 (s, 1 H), 5.89 (d, *J* = 10.8 Hz, 1 H), 6.16 (d, *J* = 15.6 Hz, 1 H), 6.43 (d, *J* = 8.0 Hz, 2 H), 6.60 (dd, *J* = 15.6 Hz, *J* = 10.8 Hz, 1 H), 6.93 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.7, 20.6, 22.5, 26.4, 50.5, 112.7, 113.4, 115.9, 125.2, 125.8, 129.8, 130.2, 136.7, 145.1, 148.5 ppm. IR (KBr): $\tilde{\nu}$ = 705, 807, 890, 1038, 1095, 1259, 1298, 1375, 1447, 1518, 1617, 2868, 2914, 2965, 3409 cm^{-1}. GC–MS: *m*/*z* = 241.3 $[M]^+$.

4-Chloro-*N*-(4-methyl-2-methylenepent-3-enyl)benzeneamine (3c): Yield 80%, colorless gum. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.78 (s, 3 H), 1.80 (s, 3 H), 3.68 (s, 2 H), 3.84 (br. s, 1 H), 4.94 (s, 1 H), 5.19 (s, 1 H), 5.61 (s, 1 H), 6.51 (d, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.8, 26.9, 49.9, 113.8, 114.1, 121.9, 123.6, 129.0, 137.4, 142.7, 146.8 ppm. IR (KBr): $\tilde{\nu}$ = 811, 901, 1071, 1122, 1178, 1318, 1497, 1595, 2855, 2911, 2928, 2968, 3426 cm^{-1}. GC–MS: *m*/*z* = 221.0 $[M]^+$.

4-Bromo-*N*-(4-methyl-2-methylenepent-3-enyl)benzeneamine (4c): Yield 83%, colorless gum. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (s, 3 H), 1.82 (s, 3 H), 3.69 (s, 2 H), 3.89 (br. s, 1 H), 4.95 (s, 1 H), 5.19 (d, *J* = 1.6 Hz, 1 H), 5.62 (s, 1 H), 6.47 (d, *J* = 8.8 Hz, 2 H), 7.23 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 26.8, 49.7, 108.8, 113.7, 114.4, 123.4, 131.8, 137.4, 142.5, 147.1 ppm. IR (KBr): $\tilde{\nu}$ = 811, 901, 1000, 1071, 1122, 1178, 1268, 1318, 1446, 1497, 1595, 2856, 2911, 2968, 3426 cm^{-1}. GC–MS: *m*/*z* = 265.1 $[M]^+$.

4-Iodo-*N*-(4-methyl-2-methylenepent-3-enyl)benzeneamine (5c): Yield 78%, colorless gum. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.78 (s, 3 H), 1.80 (s, 3 H), 3.68 (d, *J* = 4.8 Hz, 2 H), 3.87 (br. s, 1 H), 4.94 (s, 1 H), 5.18 (d, *J* = 1.2 Hz, 1 H), 5.61 (s, 1 H), 6.38 (d, *J* = 8.8 Hz, 2 H), 7.39 (d, *J* = 9.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 27.0, 49.7, 78.0, 113.9, 115.3, 123.6, 137.6, 137.8, 142.6, 147.8 ppm. IR (KBr): $\tilde{\nu}$ = 809, 899, 1059, 1122, 1181, 1268, 1293, 1318, 1446, 1495, 1591, 2926, 2965, 3424 cm^{-1}. GC–MS: *m*/*z* = 312.9 $[M]^+$.

2-Iodo-*N*-(4-methyl-2-methylenepent-3-enyl)benzeneamine (6c): Yield 67%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (s, 3 H), 1.82 (s, 3 H), 3.77 (s, 2 H), 4.41 (br. s, 1 H), 4.96 (s, 1 H), 5.21 (s, 1 H), 5.65 (s, 1 H), 6.43 (t, *J* = 7.6 Hz, 1 H), 6.51 (d, *J* = 8.0 Hz, 1 H), 7.17 (t, *J* = 8.0 Hz, 1 H), 7.65 (d, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.8, 26.9, 49.9, 85.5, 111.3, 113.8, 118.8, 123.6, 129.5, 137.7, 139.1, 142.4, 147.3 ppm. IR (KBr): $\tilde{\nu}$ = 754, 1016, 1074, 1289, 1378, 1434, 1465, 1511, 1586, 1721, 2929, 2982, 3365 cm^{-1}. GC–MS: *m*/*z* = 313.0 $[M]^+$.

2-Iodo-*N*-(3-methylenepent-4-en-2-yl)benzeneamine (6d): Yield 72%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 6.8 Hz, 3 H), 4.22 (t, *J* = 6.8 Hz, 1 H), 4.34 (br. s, 1 H), 5.07 (s, 1 H), 5.15 (d, *J* = 11.6 Hz, 1 H), 5.17 (s, 1 H), 5.36 (d, *J* = 18.0 Hz, 1 H), 6.33 (d, *J* = 8.0 Hz, 1 H), 6.38–6.46 (m, 2 H), 7.12 (t, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3, 50.1, 85.5, 111.8, 113.8, 114.8, 118.7, 129.4, 137.1, 139.0, 146.2, 147.4 ppm. IR (KBr): $\tilde{\nu}$ = 739, 902, 1004, 1171, 1279, 1319, 1375, 1425, 1450, 1506, 1590, 2927, 2965, 3073, 3396 cm^{-1}. GC–MS: *m*/*z* = 299.1 $[M]^+$.

2-Iodo-*N*-[(*E*)-7-methyl-3-methyleneocta-4,6-dien-2-yl]benzeneamine (6h): Yield 76%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.49 (d, *J* = 6.4 Hz, 3 H), 1.80 (s, 3 H), 1.83 (s, 3 H), 4.22 (br. s, 1 H), 4.35 (br. s, 1 H), 5.03 (s, 1 H), 5.08 (s, 1 H), 5.88 (d, *J* = 10.8 Hz, 1 H), 6.16 (d, *J* = 15.6 Hz, 1 H), 6.34–6.41 (m, 2 H), 6.60 (dd, *J* = 15.6, *J* = 10.8 Hz, 1 H), 7.11 (t, *J* = 7.6 Hz, 1 H), 7.62 (d, *J* = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8, 22.6, 26.4, 50.9, 85.5, 112.0, 113.1, 118.7, 125.4, 125.8, 129.5, 129.9, 137.0, 139.0, 146.3, 147.6 ppm. IR (KBr): $\tilde{\nu}$ = 742, 799, 870, 1018, 1260, 1314, 1376, 1454, 1505, 1588, 2964, 3395 cm^{-1}. GC–MS: *m*/*z* = 352.9 $[M]^+$.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H and ^{13}C NMR spectra are provided.

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