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Article

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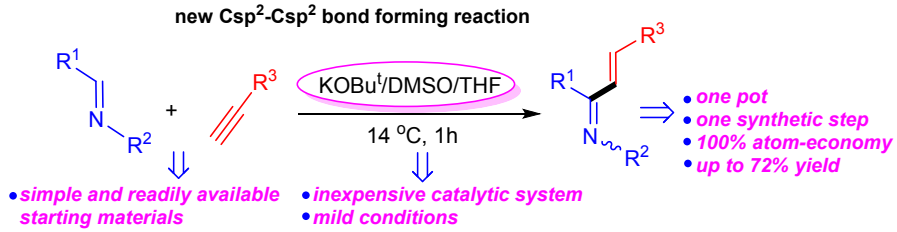
Graphical abstract



ABSTRACT: Aldimines react with aryl- and hetarylacetylenes in the presence of KOBu^t/DMSO or NaOBu^t/DMSO systems under exceptionally mild conditions (14 °C, 1 h) to afford the C-H-vinylated products, 1-azadienes of *E* configuration relative to the C-C bond, in up to 72% yield. The vinylation involves the unprecedentedly fast multi-position proton transfer in the intermediate adducts of acetylene to the C=N bond. This new Csp^2-Csp^2 bond forming reaction opens a straightforward pot-, atom-, step-, and energy-economic access to synthetically valuable 1-azadienes.

INTRODUCTION

In modern organic synthesis, the criteria of efficiency, versatility, pot-atom-step-economy are of paramount importance. Therefore, nowadays there is an increasing demand for the development of strategies that allow the transformation of readily available precursors into the target products in a rapid, economical and efficient manner.[1] In this context, the application of acetylenes is one of the mainstreams[2] due to exceptionally high reactivity of the triple bond and the possibility of rendering atom-economic and energy-saving processes via diverse addition and cycloaddition reactions. Acetylenes as reactants especially fit the construction of unsaturated heteroatomic compounds, among which α,β-unsaturated imines, also called 1-azadienes, attract great attention as versatile building blocks in organic chemistry[3] and privileged intermediates in total syntheses of natural molecules.[4] They serve as useful platform to create molecular complexity and diversity because of their multi-faceted reactivity acting as nucleophiles (due to the presence of the electron-rich nitrogen atom), electrophiles (addition reactions), dienes (cycloaddition reactions) and dienophiles (both the alkene and the imine functionality).[3]

The most popular synthesis of 1-azadienes is the condensation of α,β-unsaturated carbonyl compounds with primary amines.[3a,b] However, this reaction is often complicated by the competing

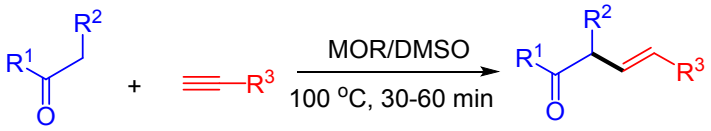
Michael addition.[5] To overcome this problem, various combinations of the Wittig reaction are used, e.g. interaction of α-imino phosphonium ylides with aldehydes[6] or α,β-unsaturated carbonyl compounds with phosphazenes.[7] Also, the olefination of β-phosphorated imines or enamines with aldehydes is an alternative.[8] A shortcoming of these approaches is the formation of equimolar amount of phosphorus-containing by-product. Other syntheses are based on transition metal-catalyzed enyne hydroamination,[9] hydroamination/hydroalkylation of terminal alkynes,[10] carboamination of diarylalkynes with aldimines,[11] cross-coupling of arylhalides with propargylamines[12] and imidoyl halides with alkenes.[13] In a one special case, a similar 1-azadiene was obtained by acid-catalyzed reaction of N-(2,6-dimethylphenyl)-1-phenylmethanimine and phenylacetylene.[14]

Owing to immense synthetic potential of 1-azadienes, efficient pot-atom-step-economic approaches to their synthesis from the available starting materials under transition metal-free conditions are highly sought.

In 2012, the transition metal-free α-C-H vinylation of ketones with acetylenes, i.e. a new Csp^3-Csp^2 bond constructing reaction, catalyzed by the superbase systems, such as alkali metal hydroxide (alkoxide)/DMSO was discovered (Scheme 1, **A**)[15] and since then it has been actively exploited. Recently, we have disclosed the superbase-catalyzed (KOBu^t/DMSO) ethynylation of the C=N bond of ketimines (Scheme 1, **B**), i.e. another new Csp^3-Csp bond constructing reaction.[16] In a degree, this reaction represents an analogue of Favorsky ethynylation of ketones and was referred by us as the "aza-Favorsky" reaction.

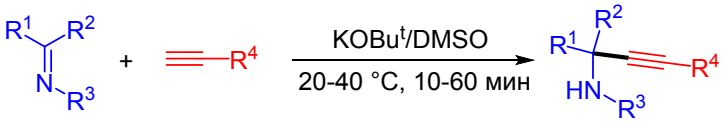
Scheme 1. Previous and Present Works

A. C-H Vinylation of ketones with acetylenes[15]



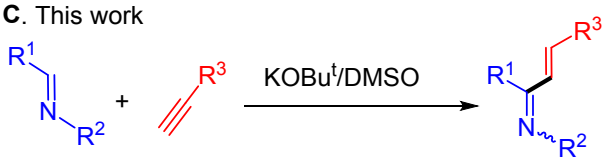
R^1,R^2=H, alkyl, (het)aryl; R^3=(het)aryl; M=Na, K, Cs; R=H, Bu^t

B. Ethynylation of ketimines with acetylenes[16]



R^1,R^2=alkyl, (het)aryl; R^3=(het)aryl; R^4=H, (het)aryl

C. This work

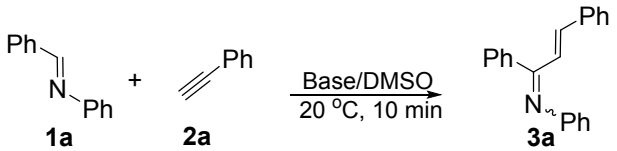


Since the latter reaction (Scheme 1, **B**)[16] was implemented using ketimines as a source of widespread C=N bond, it was logical to evaluate generality of the process, i.e. to determine its substrate scope relative to another family of ubiquitous C=N electrophiles like aldimines (aldehyde/amine Schiff adducts). Surprisingly, our preliminary experiments have shown that aldimines react with acetylenes under mild conditions to form, instead of the expected propargylamines, 1-azadienes (Scheme 1, **C**). Virtually, we have encountered with a new Csp^2-Csp^2 bond building process, a kind of benzoin condensation.

RESULTS AND DISCUSSION

For optimization of the synthesis, we have chosen, as a reference, the reaction of aldimine **1a** (benzaldehyde/aniline adduct) and phenylacetylene **2a**. In order to determine the provisionally optimum conditions, we have first evaluated the effect of the base nature and its content in DMSO on the yield of 1-azadiene **3a** (Table 1).

Table 1. Effect of base nature and its content on the yield of 3a[a]



1a **2a** **3a**

entry	base	**1a**:base[b]	conversion of **1a** (%)[c]	yield of **3a** (%)[d]
1	$KOBu^t$	1:1	100	7
2	$KOBu^t$	1:0.5	100	15
3	$KOBu^t$	1:0.2	100	52
4	$KOBu^t$	1:0.1	90	49
5	$KOBu^t$	1:0.05	20	17
6	$NaOBu^t$	1:0.2	91	46
7	$LiOBu^t$	1:0.2	57	31
8	KOH	1:0.2	43	23
9	NaOH	1:0.2	15	10
10	K_2CO_3	1:0.2	0	0
11	Et_3N	1:0.2	0	0

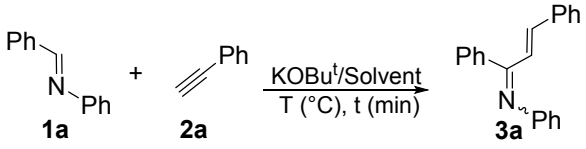
[a]Conditions: **1a** (1 mmol), **2a** (1 mmol), base (0.05-1 mmol), DMSO (3 mL), 20 °C, 10 min. [b]Molar ratio. [c]According to ^1H NMR data of the crude product (*n*-dodecane was used as an internal standard). [d]Isolated yield after column chromatography (SiO_2, *n*-hexane/diethyl ether, 50:1).

The selected results (Table 1) show that the reaction proceeds with both hydroxides and alkoxides of alkali metals, however, the best yields of **3a** were reached in the $KOBu^t$/DMSO (52%) and $NaOBu^t$/DMSO (46%) systems (**1a**:$MOBu^t$ molar ratio = 1:0.2, entries 3,6).

Next, using the $KOBu^t$ as a major component of the superbase system, we have examined the effects of the second component of the superbase (polar nonhydroxylic solvent acting as a ligand relative to K^+), reaction temperature and time on the process efficiency.

As can be seen from the representative results (Table 2), the KOBu^t/DMSO superbase pair turned out to be the best catalytic system (entry 5). The KOBu^t/DMF pair showed low activity (entry 2), and other KOBu^t/ligand combinations were inactive at all. Then, we tried to increase the yield of **3a** by temperature and time variation. Indeed, carrying out the reaction at 17 °C (further cooling led to the crystallization of the reaction mixture) increased the yield of **3a** to 60% for 1 h (entry 7). As follows from Table 2 data, the final product **3a** is able to undergo secondary transformations under the reaction conditions. In fact, when the reaction time increased to 2 h (entry 8), the yield of **3a** dropped to 39%. Certain instability of azadiene **3a** under the reaction conditions is evidenced by the formation of noticeable amounts of polymeric products, which maybe resulted from its further condensation. Additionally, chemical evolution of the final product during the synthesis was confirmed by the special experiment, when pure **3a** was kept in the KOBu^t/DMSO system (17 °C, 1 h), its content decreased by ~30%. All this urged us to implement the synthesis at a lower temperature. To further decrease the reaction temperature, 10 vol.% THF was added to DMSO that permitted the process to be conducted at 14 °C without freezing the catalytic solution. This enabled to increase the yield of **3a** up to 72% (entry 14).

Table 2. Effect of ligand, temperature, and time on the yield of azadiene 3a[a]



entry	ligand	T (°C)	t (min)	conversion of **1a** (%)[b]	yield of **3a** (%)[c]
1	THF	20	10	0	0
2	DMF	20	10	47	27
3	NMP	20	10	0	0
4	dioxane	20	10	0	0
5	DMSO	20	10	100	52
6	DMSO	17	10	86	46
7	DMSO	17	60	96	60
8	DMSO	17	120	100	39
9	DMSO/H_2O (100:1)[d]	16	10	77	34
10	DMSO/HOBu^t (20:1)[d]	16	10	100	53
11	DMSO/NMP (10:1)[d]	16	60	100	0
12	DMSO/THF (10:1)[d]	14	15	96	60
13	DMSO/THF (10:1)[d]	14	30	98	62
14	DMSO/THF (10:1)[d]	14	60	100	72
15[e]	DMSO/THF (10:1)[d]	14	60	100	70

[a]Conditions: **1a** (1 mmol), **2a** (1 mmol), KOBu^t (0.2 mmol), solvent (3 mL). [b]According to ^{1}H NMR data of the crude product. [c]Isolated yield (SiO_2, *n*-hexane/diethyl ether, 50:1). [d]Volume ratio. [e]**2a** (2 mmol).

The structure and stereochemistry of compound **3a** (1*E*,2*E*-isomer) was determined by X-ray analysis (See the Supporting Information). NMR spectra analysis (COSY, NOESY, ^{1}H-^{13}C,

and ^{1}H-^{15}N HMBC experiments) shows that azadiene **3a** in $CDCl_3$ presents as a mixture of 1*E*,2*E*- and 1*Z*,2*E*-isomers in 3:1 ratio, respectively (Fig. 1).

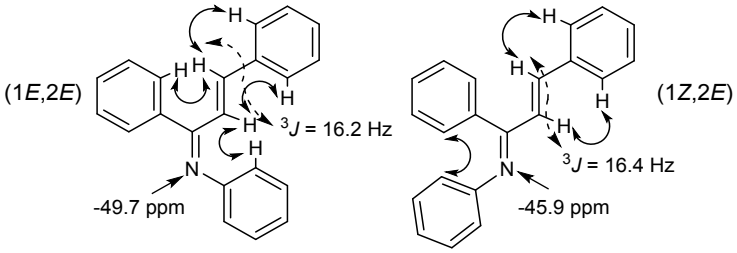
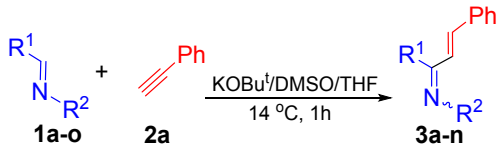
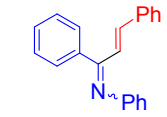


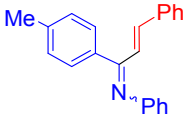
Figure 1. Main NOESY correlations for azadiene **3a**

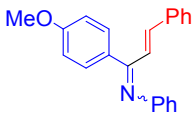
With the provisionally optimum conditions established, we have investigated the substrate scope of the reaction. First, we have changed aldimine **1** structure, while retaining phenylacetylene **2a** as a reference (Table 3).

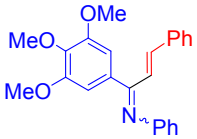
Table 3. Scope of aldimines[a]

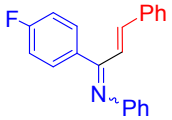


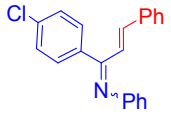

3a, 72%

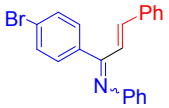

3b, 61% (93%)

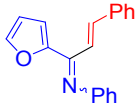

3c, 70%

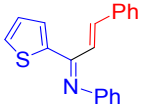

3d, 39%

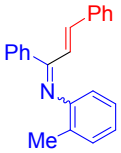

3e, 61%

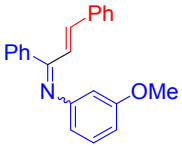

3f, 50% (85%)

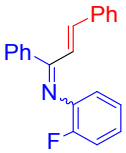

3g, 42% (74%)

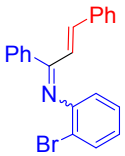

3h, 56%

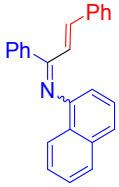

3i, 58% (75%)

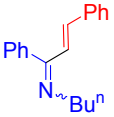

3j, 59% (96%)


3k, 58%


3l, 64%


3m, 33% (68%)


3n, 43%


3o, 0% (0%)

[a]Conditions: **1** (1 mmol) in DMSO (0.5 mL) was added dropwise to a mixture of **2a** (1 mmol), $KOBu^t$ (0.2 mmol), THF (0.3 mL) in DMSO (3 mL) at 14 °C for 1 min. The resulting mixture was stirred at 14 °C for 1 h. Isolated yields after column chromatography (SiO_2, *n*-hexane/diethyl ether) are given. In

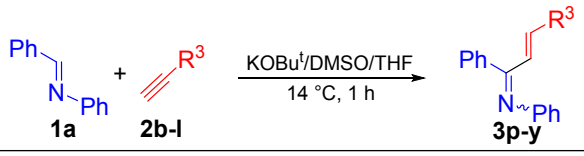
parentheses, conversion of aldimine **1** (determined by ^{1}H NMR data of the crude reaction mixtures) is given; in all other cases the conversion is complete.

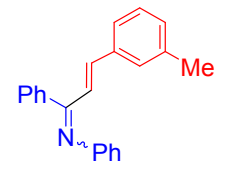
As follows from Table 3, the synthesis was successfully extended over aldimines derived from aryl and hetaryl substituted aldehydes and arylamines, the yields of azadienes **3a–n** being 33-72%. In the aldehyde counterpart, along with unsubstituted phenyl, the benzene ring is substituted by alkyl, alkoxy, fluorine, bromine, chlorine groups, and the hetaryls are furyl and thienyl. The aldimines derived from aliphatic aldehydes and aromatic amines are much less accessible compounds. To our knowledge, no synthetically acceptable protocols exist in literature. The amine counterpart contains phenyl, 2-methyl-, 4-methoxy-, 2-fluoro-, 2-bromophenyl, and condensed aromatic substituent (2-naphthyl).

In some cases, the reaction proceeded with incomplete conversion of the starting aldimine. As to the influence of aldimine **1** structure on azadiene **3** yield, the results obtained show no clear regularity in the substituents effect on the process efficiency. As exemplified by imine **1o** (R^2 = Bu^n), donor effect of the alkyl substituent completely suppresses the reaction probably due to depolarization of the C=N bond, i.e. decreasing its electrophilicity.

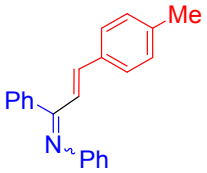
The scope of acetylene substrates has been examined for the reference aldimine **1a** (Table 4).

Table 4. Scope of acetylenes[a]

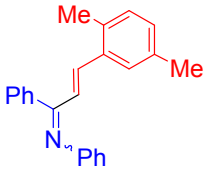




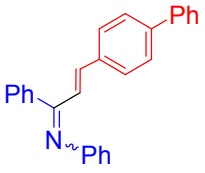
3p, 64%



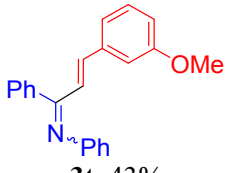
3q, 53%



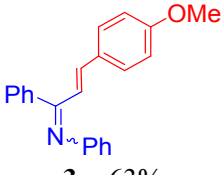
3r, 31%



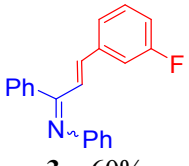
3s, 43%



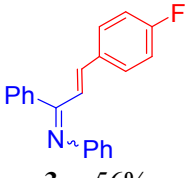
3t, 43%



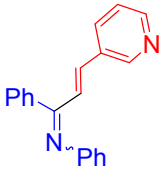
3u, 63%



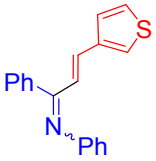
3v, 60%



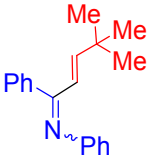
3w, 56%



3x, 31%



3y, 52%



3z, 0%

[a]Reactions were carried out under conditions as in Table 3. Isolated yields after column chromatography are given.

The experiments have shown that the reaction tolerates a series of aryl- and hetarylacetylenes with donor and acceptor substituents in the benzene ring, the yields of the corresponding azadienes **3p–y** being 31-64% (Table 4). As seen, arylacetylenes are decorated with a variety of different in chemical nature substituents such as methyl, phenyl, methoxy, and fluoro. Hetarylacetylenes are 3-ethynylpyridine and 3-ethynylthiophene. It is important that most of the above substrates (Tables 3, 4) contains substituents capable of feasible further transformations (halogens, heterocycles) that allows to easily multiply the real substrate scope.

In this case, the more pronounced is steric effect, which is likely the major cause of a lower yield of acetylene **2d** (R^3 = 2,5-diMeC_6H_4). The reaction of aldimine **1a** with *tert*-butylacetylene **2l** does not give the expected product **3z** both under the same conditions and at higher temperature (30 °C): only the starting compounds were almost completely recovered. Since acidity of *tert*-butylacetylene is much lower than that of phenylacetylene (pK_a=25.5 and 23.2, respectively),[17] the negative result here can be attributed to a small concentration of *tert*-butylethenyl anions in the reaction mixture. Acetylenes with normal or secondary aliphatic substituents under the reaction conditions are rapidly prototropically isomerized to allenes and internal acetylenes.

The irregularly variable yields of azadienes **3** (Tables 3, 4) appear to be indicative of the fact that the overall process is a complex function of a number of parameters: electronic and steric effects of the substituents in aldimine (both aldehyde and amine moieties) and acetylene, stability of the starting aldimines **1** and the target azadienes **3** under the reaction conditions, particularly propensity to condensation and addition reactions. Certainly, to reach a higher yield for each aldimine/acetylene pair, an additional tuning of the reaction conditions is required.

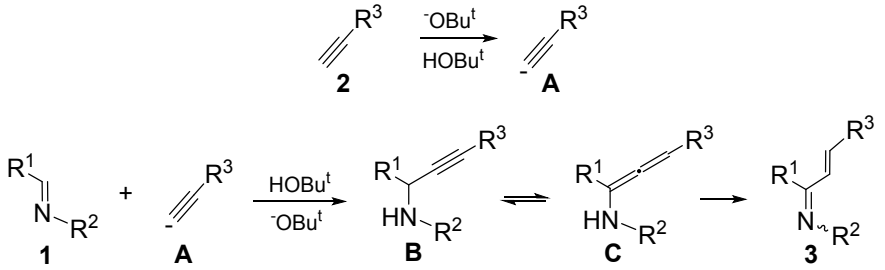
According to the NMR data, in $CDCl_3$ azadienes **3** are present as a mixture of 1*E*,2*E*- and 1*Z*,2*E*-isomers in ~ 3:1 ratio, except for **3i**, which was obtained exclusively as 1*E*,2*E*-isomer (Table 3).

To verify scalability of the developed strategy, a gram-scale synthesis of azadiene **3l** has been implemented. Under the optimized conditions, aldimine **1l** (5 mmol, 1 g) and acetylene **2a** (5 mmol, 0.51 g) reacted smoothly to give **3l** in 69% (1.04 g) isolated yield. This demonstrates a high potential of this synthesis for large-scale application.

Apparently, the reaction represents an ordinary nucleophilic addition of the aldimine C-H moiety to the triple bond, somewhat like the aldehyde C-H bond addition to the C=O bond, i.e. benzoin condensation.

Alternatively, the reaction might be assumed to start (Scheme 2) with the deprotonation of acetylene **2** under the action of superbase, and addition of acetylenic anion **A** to the C=N bond of aldimine **1**. Propargylamine **B** thus formed might undergo further prototropic isomerization to 1-azadiene **3** via allenic intermediate **C**.

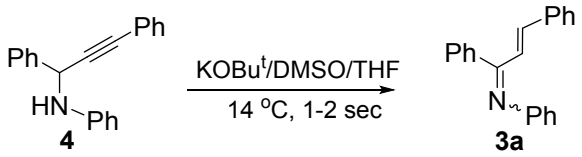
Scheme 2. Tentative Scheme for 1-Azadienes **3** Formation



However, it is highly astonishing that none of the both intermediates (**B** and **C**) is detected (^{1}H NMR) in the reaction mixture though in trace amounts, even after a few minutes the reaction started. Such extremely fast double prototropic isomerization of propargylamine **B** to allene **C** and, further, to azadiene **3** under so low temperature (14 ^{o}C) looks very extraordinary.

To discriminate the two options, we have subjected separately synthesized intermediate **B** (from benzaldehyde, aniline and phenylacetylene in the presence of $CuCl_2$)[18] to the reaction conditions. What we have observed was lighting-like (just after the reactants mixing) quantitative transformation of this propargylamine **4** to azadiene **3a** (Scheme 3).

Scheme 3. Fast Isomerization of Propargylamine **4** to 1-Azadiene **3a**



The result obtained is unambiguous evidence for the fast prototropic isomerization of secondary propargylamines to 1-azadienes. Consequently, the synthesis here developed proceeds via ethynylation of the C=N bond followed by the above rapid isomerization of the intermediates **B** and **C** (Scheme 3). This unprecedented chemical transformation represents a self-standing value both for synthetic and theoretical chemistry.

CONCLUSION

In summary, we have found and developed base-catalyzed transition metal-free C-H vinylation of aldimines with aryl- and hetarylacetylenes opening a simple straightforward access to synthetically valuable 1-azadienes of *E* configuration relative to the C-C bond in good yields.

The reaction mechanism of this new Csp^2-Csp^2 bond forming reaction includes a nucleophilic addition of acetylenes to the C=N bond with further unprecedentedly fast quantitative acetylene-allene-azadiene isomerization. The reaction meets PASE[19] requirements as being one-pot and atom-economic in a one operation step. This together with availability of the starting materials and catalytic system (without transition metals), mild reaction conditions, good scalability renders the process technologically feasible. Despite a number of synthetic approaches to 1-azadienes, the reaction allows synthesizing a novel family of these important intermediates.

EXPERIMENTAL SECTION

1. General Remarks. ^{1}H (400.1 MHz), ^{13}C (100.6 MHz), and ^{15}N (40.5 MHz) NMR spectra were recorded on a Bruker AV400 instrument in $CDCl_3$. The assignment of signals in the ^{1}H NMR spectra was made using COSY and NOESY experiments. Resonance signals of carbon atoms were assigned based on ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC experiments. The ^{1}H and ^{13}C chemical shifts (δ) were referenced to hexamethyldisiloxane (0.05 ppm and 2.0 respectively). The chemical shifts were recorded in ppm. Coupling constants (*J*) in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: s (singlet), d (doublet), dd (doublet of doublets), m (multiplet). The values of the δ ^{15}N were measured through the 2D ^{1}H-^{15}N HMBC experiment. The ^{15}N chemical shifts were referenced to CH_3NO_2. IR spectra were taken with FT-IR. Melting points (uncorrected) were measured on a Kofler micro hot-stage apparatus. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer. Thin layer chromatography was carried out on Merck silica gel 60 F_{254} pre-coated aluminium foil sheets (eluent: hexane/diethyl ether = 1:3) and were visualized using UV light (254 nm). Column chromatography was carried out using slurry packed Sigma Aldrich silica gel, 70-230 mesh, pore size 60 Å (eluent: hexane/diethyl ether). Aldehydes, amines and all other chemicals and solvents are commercially available and were used without further purification.

2. Starting Materials. Aldimines **1** were synthesized by published procedure from aldehydes and amines.[20] Propargylamine **4** was synthesized by A^3 condensation from benzaldehyde, phenylacetylene and aniline in the presence of $CuCl_2$.[18]

3. Synthesis of 1-Azadienes 3 (*general procedure*). A mixture of aldimine **1** (1 mmol) in DMSO (0.5 mL) was added dropwise to a mixture of acetylene **2** (1 mmol), $KOBu^t$ (0.2 mmol, 22 mg), THF (0.3 mL) in DMSO (3 mL) at 14 °C for 1 min. The resulting mixture was stirred at 14 °C for 1 h. Then, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (1 mL × 7). The organic extract was washed with H_2O (1 mL × 3) and dried over $MgSO_4$. Et_2O was evaporated under reduced pressure, and the residue was purified by column chromatography [SiO_2, eluent:

hexane/Et_2O = 50 : 1 or 10 : 1 (for **3d**,**v**), 1 : 1 (for **3x**)]. Physical-chemical characteristics of 1-azadiene **3a** were identical to the literature data.[6]

4. Rearrangement of Propargylamine 4 to 1-Azadiene 3a. A mixture of propargylamine **4** (1 mmol, 0.283 g) in DMSO (0.5 mL) was added in a mixture of $KOBu^t$ (0.2 mmol, 22 mg), THF (0.3 mL) in DMSO (3 mL) at 14 °C. Almost immediately (after 1-2 sec), the resulting mixture was diluted with H_2O (5 mL) and extracted with Et_2O (1 mL × 7). The organic extract was washed with H_2O (1 mL × 3) and dried over $MgSO_4$. Et_2O was evaporated under reduced pressure. The crude product is 1-azadiene **3a** (0.271 mg, yield 96%).

*(2E)-N,1,3-Triphenylprop-2-en-1-imine (**3a**)*. Following the general procedure, **3a** was prepared from **1a** (1 mmol, 0.181 g) and **2a** (1 mmol, 0.102 g). **3a** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 3:1 molar ratio (0.204 g, 72% yield). Yellow solid; m.p.: 103-106 °C. Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 88.97; H, 6.11; N, 4.79. IR (film): ν_{max} 3057, 3029, 2924, 2856, 1619, 1583, 1485, 1446, 1313, 1205, 1173, 1073, 1024, 975, 907, 862, 825, 754, 695. 1*E*,2*E*-**3a**. ^{1}H NMR: δ 7.79-7.68 (m, 2H, Ho^2), 7.52-7.47 (m, 3H, Hm^2,p^2), 7.41-7.38 (m, 2H, Hm^1), 7.36-7.32 (m, 2H, Ho^3), 7.32-7.30 (m, 3H, Hm^3,p^3), 7.18-7.13 (m, 1H, Hp^1), 7.00-6.96 (m, 2H, Ho^1), 6.95 (d, ^3J = 16.2 Hz, 1H, H3), 6.90 (d, ^3J = 16.2 Hz, 1H, H2). ^{13}C {^{1}H} NMR: δ 167.2 (C1), 151.1 (Ci^1), 141.7 (C3), 139.5 (Ci^2), 135.8 (Ci^3), 130.0 (Cp^2), 129.5 (Cp^3), 129.4 (Co^2), 129.0 (Cm^1), 128.9 (Cm^3), 128.4 (Cm^2), 127.6 (Co^3), 124.0 (Cp^1), 122.0 (C2), 120.9 (Co^1). ^{15}N NMR: δ -49.7. 1*Z*,2*E*-**3a**. ^{1}H NMR: δ 7.45-7.36 (m, 2H, Ho^3), 7.32-7.29 (m, 6H, Hm^2,p^2,m^3,p^3), 7.30 (d, ^3J = 16.4 Hz, 1H, H2), 7.18-7.14 (m, 2H, Ho^2), 7.14-7.09 (m, 2H, Hm^1), 6.94-6.88 (m, 2H, Hp^1), 6.85 (d, ^3J = 16.4 Hz, 1H, H3), 6.71-6.67 (m, 2H, Ho^1). ^{13}C {^{1}H} NMR: δ 169.0 (C1), 150.8 (Ci^1), 141.4 (C3), 135.9 (Ci^3), 135.6 (Ci^2), 131.8 (C2), 129.3 (Cp^3), 129.1 (Co^2), 128.9 (Cm^3), 128.5 (Cp^2), 128.4 (Cm^1), 128.1 (Cm^2), 127.6 (Co^3), 123.4 (Cp^1), 121.1 (Co^1). ^{15}N NMR: δ -45.9.

*(2E)-N,3-Diphenyl-1-(p-tolyl)prop-2-en-1-imine (**3b**)*. Following the general procedure, **3b** was prepared from **1b** (1 mmol, 0.195 g) and **2a** (1 mmol, 0.102 g). **3b** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 3:1 molar ratio (0.181 g, 61% yield). Yellow solid; m.p.: 92-93 °C. Anal. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.93; H, 6.35; N, 4.68. IR (film): ν_{max} 3055, 3029, 2947, 2921, 2862, 1741, 1616, 1584, 1499, 1484, 1402, 1313, 1205, 1178, 1104, 1075, 1024, 976, 907, 856, 814, 759, 694. 1*E*,2*E*-**3b**. ^{1}H NMR: δ 7.66-7.58 (m, 2H, Ho^2), 7.37-7.29 (m, 2H, Hm^1), 7.30-7.22 (m), 7.13-6.98 (m), 6.96-6.81 (m) [12H, H2,3,*Ar*], 2.42 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 167.0 (C1), 151.3 (Ci^1), 141.4 (C3), 140.2 (Cp^2), 136.8, 136.0 (Ci^2,i^3), 129.5 (Cm^2), 129.4 (Cp^3), 129.2, 129.0, 128.9, (Co^2,m^1,m^3), 127.6 (Co^3), 123.9 (Cp^1), 122.4 (C2), 121.0 (Co^1), 21.5 (Me). ^{15}N NMR: δ -53.2. 1*Z*,2*E*-**3b**. ^{1}H NMR: δ 7.49-7.43 (m, 2H, Ho^3), 7.37-7.21 (m), 7.13-6.98 (m), 6.96-6.81 (m) [12H, H2,3, *Ar*], 6.68-6.64 (m, 2H, Ho^1), 2.29 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 169.0 (C1), 151.1 (Ci^1), 141.2 (C3), 138.4 (Cp^2), 136.1 (Ci^3), 132.7 (Ci^2), 132.1 (C2), 129.3 (Cp^3),

129.1, 128.9, 128.5 (Cm^1,m^2,m^3,o^2), 127.7 (Co^3), 123.3 (Cp^1), 121.2 (Co^1), 21.5 (Me). ^{15}N NMR: δ -47.4.

*(2E)-1-(4-Methoxyphenyl)-N,3-diphenylprop-2-en-1-imine (**3c**)*. Following the general procedure, **3c** was prepared from **1c** (1 mmol, 0.211 g) and **2a** (1 mmol, 0.102 g). **3c** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 7:2 molar ratio (0.219 g, 70% yield). Yellow solid; m.p.: 112-114 ^{o}C. Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.42; H, 6.07; N, 4.24. IR (film): ν_{max} 3056, 3033, 2924, 2857, 1662, 1585, 1508, 1486, 1449, 1416, 1311, 1251, 1206, 1174, 1107, 1077, 1029, 977, 833, 761, 695. 1*E*,2*E*-**3c**. ^{1}H NMR: δ 7.79-7.75 (m, 2H, Ho^2), 7.41-7.36 (m, 2H, Hm^1), 7.38-7.36 (m, 2H, Hm^1), 7.35-7.32 (m, 5H, Ho^3,m^3,p^3), 7.15-7.13 (m, 1H, Hp^1), 7.05-7.01 (m, 2H, Hm^2), 7.01-6.97 (m, 2H, Ho^1), 6.98 (d, ^3J = 16.4 Hz, 1H, H3), 6.90 (d, ^3J = 16.4 Hz, 1H, H2), 3.91 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 166.4 (C1), 161.3 (Cp^2), 151.3 (Ci^1), 141.2 (C3), 135.9 (Ci^3), 132.0 (Ci^2), 131.1 (Co^2), 129.4 (Cp^3), 128.9 (Cm^1,m^3), 127.5 (Co^3), 123.9 (Cp^1), 122.5 (C2), 121.1 (Co^1), 113.8 (Cm^2), 55.5 (Me). ^{15}N NMR: δ -55.8. 1*Z*,2*E*-**3c**. ^{1}H NMR: δ 7.54-7.51 (m, 2H, Ho^3), 7.38-7.36 (m, 2H, Hm^3), 7.35-7.32 (m, 1H, Hp^3), 7.31 (d, ^3J = 16.7 Hz, 1H, H2), 7.20-7.15 (m, 2H, Hm^1), 7.12-7.08 (m, 2H, Ho^2), 6.94 (d, ^3J = 16.7 Hz, 1H, H3), 6.95-6.93 (m, 1H, Hp^1), 6.85-6.81 (m, 2H, Hm^2), 6.74-6.70 (m, 2H, Ho^1), 3.81 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 168.5 (C1), 159.64 (Cp^2), 151.1 (Ci^1), 141.1 (C3), 136.0 (Ci^3), 132.0 (C2), 130.7 (Co^2), 129.3 (Cp^3), 128.9, 128.5 (Cm^3,m^1), 127.8 (Ci^2), 127.6 (Co^3), 123.3 (Cp^1), 121.2 (Co^1), 113.6 (Cm^2), 55.3 (Me). ^{15}N NMR: δ -49.0.

*(2E)-N,3-Diphenyl-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-imine (**3d**)*. Following the general procedure, **3d** was prepared from **1d** (1 mmol, 0.271 g) and **2a** (1 mmol, 0.102 g). **3d** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 5:1 molar ratio (0.146 g, 39 % yield). Yellow oil. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.36; H, 6.05; N, 3.28. IR (film): ν_{max} 3076, 3058, 2999, 2958, 2937, 2904, 2836, 1661, 1623, 1588, 1577, 1504, 1482, 1463, 1450, 1411, 1345, 1233, 1204, 1128, 1107, 1006, 786, 760, 699. 1*E*,2*E*-**3d**. ^{1}H NMR: δ 7.39-7.27 (m), 7.16-7.09 (m), 7.01-6.92 (m) [13H, H3,*Ar*], 6.85 (d, ^3J = 16.4 Hz, 1H, H2), 3.91 (s, 3H, p^2-OMe), 3.89 (s, 6H, m^2-OMe). ^{13}C {^{1}H} NMR: δ 166.8 (C1), 153.2 (Cm^2), 151.0 (Ci^1), 141.7 (C1), 141.2, 135.8, 134.9, 129.6 (4C, Ci^2,p^2,i^3,p^3), 129.0, 129.0, 127.6 (6C, Cm^1,o^3,m^3), 124.1 (Cp^1), 122.1 (C2), 121.0 (Co^1), 106.9 (Co^2), 61.1 (p^2-OMe), 56.4 (m^2-OMe). 1*Z*,2*E*-**3d**. ^{1}H NMR: δ 7.53-7.48 (m), 7.39-7.19 (m), 7.15-7.10 (m), 7.04-6.90 (m), 6.70-6.65 (m) [12H, H2,3,*Ar*], 6.32 (s, 2H, Ho^2), 3.83 (s, 3H, p^2-OMe), 3.65 (s, 6H, m^2-OMe).

*(2E)-1-(4-Fluorophenyl)-N,3-diphenylprop-2-en-1-imine (**3e**)*. Following the general procedure, **3e** was prepared from **1e** (1 mmol, 0.199 g) and **2a** (1 mmol, 0.102 g). **3e** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 2:1 molar ratio (0.184 g, 61% yield). Yellow solid; m.p.: 87-89 ^{o}C. Anal. Calcd for $C_{21}H_{16}FN$: C, 83.70; H, 5.35; F, 6.30; N, 4.65. Found: C, 83.86; H, 5.21; F, 6.15;

N, 4.32. IR (film): ν_{max} 3060, 3033, 2955, 2923, 2855, 1741, 1581, 1505, 1485, 1450, 1401, 1311, 1225, 1157, 1087, 1074, 1020, 976, 837, 759, 694. 1*E*,2*E*-**3e**. ^{1}H NMR: δ 7.78-7.73 (m, 2H, Ho^2), 7.40-7.34 (m, 2H, Hm^1), 7.33-7.30 (m, 5H, Ho^3,m^3,p^3), 7.19-7.14 (m, 1H, Hp^1), 7.01-6.89 (m, 5H, H3,o^1,m^2), 6.83 (d, ^3J = 16.4 Hz, 1H, H2). ^{13}C {^{1}H} NMR: δ 166.1 (C1), 164.1 (d, $^1J_{CF}$ = 249.6 Hz, Cp^2), 151.0 (Hi^1), 141.7 (H3), 135.7 (Hi^3), 135.6 (d, $^4J_{CF}$ = 3.3 Hz, Ci^2), 131.5 (d, $^3J_{CF}$ = 8.6 Hz, Co^2), 129.7 (Cp^3), 129.1 (Cm^1), 129.0 (Cm^3), 127.7 (Co^3), 124.2 (Cp^1), 122.1 (C2), 120.9 (Co^1), 115.5 (d, $^2J_{CF}$ = 21.6 Hz, Cm^2). ^{15}N NMR: δ -51.0. 1*Z*,2*E*-**3e**. ^{1}H NMR: δ 7.51-7.47 (m, 2H, Ho^3), 7.40-7.29 (m), 7.20-7.10 (m), 7.06-6.85 (m) [12H, H2,3,*Ar*], 6.68-6.64 (m, 2H, Ho^1). ^{13}C {^{1}H} NMR: δ 168.0 (C1), 162.6 (d, $^1J_{CF}$ = 248.6 Hz, Cp^2), 150.8 (Ci^1), 141.5 (C3), 135.8 (Ci^3), 135.6 (d, $^4J_{CF}$ = 3.3 Hz, Ci^2), 131.7 (C2), 131.1 (d, $^3J_{CF}$ = 8.1 Hz, Co^2), 129.5 (Cp^3), 129.0, 128.6, 127.7 (Cm^3,m^1,o^3), 123.6 (Cp^1), 121.1 (Co^1), 115.4 (d, $^2J_{CF}$ = 21.6 Hz, Cm^2). ^{15}N NMR: δ -45.2.

*(2E)-1-(4-Chlorophenyl)-N,3-diphenylprop-2-en-1-imine (**3f**)*. Following the general procedure, **3f** was prepared from **1f** (1 mmol, 0.216 g) and **2a** (1 mmol, 0.102 g). **3f** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 3:1 molar ratio (0.159 g, 50% yield). Brown oil. Anal. Calcd for $C_{21}H_{16}ClN$: C, 79.36; H, 5.07; Cl, 11.15; N, 4.41. Found: C, 79.43; H, 4.95; Cl, 11.02; N, 4.36. IR (film): ν_{max} 3086, 3056, 3035, 2980, 2925, 2856, 1618, 1588, 1494, 1437, 1370, 1313, 1208, 1161, 1076, 1025, 977, 909, 825, 781, 750, 693. 1*E*,2*E*-**3f**. ^{1}H NMR: δ 7.70-7.64 (m, 2H, Ho^2), 7.48-6.82 (m, 13H, H3,*Ar*), 6.78 (d, ^3J = 16.6 Hz, 1H, H2). ^{13}C {^{1}H} NMR: δ 166.1 (C1), 150.8 (Ci^1), 141.8 (C3), 137.9 (Ci^2), 136.2 (Cp^2), 135.6 (Ci^3), 130.9 (Co^2), 129.7 (Cp^3), 129.0, 128.7 (Cm^1,m^2,m^3), 127.6 (Co^3), 124.3 (Cp^1), 121.8 (C2), 120.8 (Co^1). ^{15}N NMR: δ -50.3. 1*Z*,2*E*-**3f**. ^{1}H NMR: δ 7.48-6.75 (m, 14H, H2,3,*Ar*), 6.65-6.60 (m, 2H, Ho^1). ^{13}C {^{1}H} NMR: δ 167.8 (C1), 150.6 (Ci^1), 141.6 (C3), 135.7 (Ci^3), 134.6 (Ci^2), 134.0 (Cp^2), 131.5 (C2), 130.5 (Co^2), 129.6 (Cp^3), 129.0, 128.7, 128.6, 127.7 (Cm^1,m^2,m^3,o^3), 123.7 (Cp^1), 121.0 (Co^1). ^{15}N NMR: δ -45.2.

*(2E)-1-(4-Bromophenyl)-N,3-diphenylprop-2-en-1-imine (**3g**)*. Following the general procedure, **3g** was prepared from **1g** (1 mmol, 0.260 g) and **2a** (1 mmol, 0.102 g). **3g** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 5:1 molar ratio (0.152 g, 42% yield). Brown oil. Anal. Calcd for $C_{21}H_{16}BrN$: C, 69.63; H, 4.45; Br, 22.06; N, 3.87. Found: C, 69.76; H, 4.25; Br, 21.88; N, 3.54. IR (film): ν_{max} 3053, 3033, 3024, 2925, 2860, 1676, 1584, 1506, 1495, 1456, 1437, 1370, 1314, 1259, 1208, 1176, 1094, 1076, 976, 751, 697. 1*E*,2*E*-**3g**. ^{1}H NMR: δ 7.61-7.58 (m, 2H, Ho^2), 7.47-6.87 (m, 13H, H3,*Ar*), 6.78 (d, ^3J = 16.4 Hz, 1H, H2). ^{13}C {^{1}H} NMR: δ 166.1 (C1), 150.8 (Ci^1), 141.8 (C3), 138.4 (Ci^2), 135.6 (Ci^3), 131.7, 131.1 (Co^2,m^2), 129.7 (Cp^3), 129.0 (Cm^1,m^3), 127.6 (Co^3), 124.5, 124.3 (Cp^1,p^2), 121.7 (C2), 120.8 (Co^1). 1*Z*,2*E*-**3g**. ^{1}H NMR: δ 7.47-6.81 (m, 14H, H2,3*Ar*), 6.65-6.61 (m, 2H, Ho^1). ^{13}C {^{1}H} NMR: δ 167.7 (C1), 150.5 (Ci^1), 141.6 (C3), 135.7, 134.5 (Ci^2,i^3), 132.0 (C2), 131.5, 130.7 (Co^2,m^2), 129.6 (Cp^3), 129.0, 128.7, 127.7 (Cm^1,m^3,o^3), 123.7, 122.9 (Cp^1,p^2), 121.0 (Co^1).

*(2E)-1-(Furan-2-yl)-N,3-diphenylprop-2-en-1-imine (**3h**)*. Following the general procedure, **3h** was prepared from **1h** (1 mmol, 0.171 g) and **2a** (1 mmol, 0.102 g). **3h** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 4:1 molar ratio (0.153 g, 56% yield). Yellow oil. Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.61; H, 5.38; N, 4.95. IR (film): ν_{max} 3134, 3109, 3059, 3027, 2958, 2926, 2857, 1629, 1581, 1478, 1453, 1389, 1313, 1233, 1204, 1162, 1094, 1069, 1019, 975, 913, 882, 821, 754, 695. 1*E*,2*E*-**3h**. ^{1}H NMR: δ 7.61-7.58 (m, 1H, H5′), 7.48-6.77 (m, 12H, H3,*Ph*,3′), 6.74 (d, ^3J = 16.4 Hz, 1H, H2), 6.57-6.53 (m, 1H, H4′). ^{13}C {^{1}H} NMR: δ 155.5 (C1), 152.5 (C2′), 150.2 (Ci^1), 145.0 (C5′), 140.0 (C3), 135.7 (Ci^3), 129.4 (Cp^3), 128.9, 128.8, 127.4 (Cm^1,m^3,o^3), 124.2 (Cp^1), 121.3 (Co^1), 118.7 (C2), 114.9 (C4′), 111.7 (C3′). ^{15}N NMR: δ -63.5. 1*Z*,2*E*-**3h**. ^{1}H NMR: δ 7.61-7.58 (m, 1H, H5′), 7.2-7.58 (m, 2H, Ho^3), 7.47-6.54 (m, 12H, H3,*Ph*,3′,4′). ^{13}C {^{1}H} NMR: δ 153.5 (C1), 152.6 (C2′), 148.2 (Ci^1), 143.0 (C5′), 138.2 (C3), 136.2 (Ci^3), 130.6 (C2), 129.3 (Cp^3), 128.8, 128.6, 127.7 (Cm^1,m^3,o^3), 123.4 (Cp^1), 121.2 (Co^1), 115.8 (C4′), 112.6 (C3′). ^{15}N NMR: δ -61.3.

*(1E,2E)-N,3-Diphenyl-1-(thiophen-2-yl)prop-2-en-1-imine (**3i**)*. Following the general procedure, **3i** was prepared from **1i** (1 mmol, 0.187 g) and **2a** (1 mmol, 0.102 g). **3i** was isolated as a yellow solid (0.168 g, 58% yield). M.p.: 102-103 ^{o}C. Anal. Calcd for $C_{19}H_{15}NS$: C, 78.86; H, 5.22; N, 4.84; S, 11.08. Found: C, 78.92; H, 5.17; N, 4.72; S, 11.13. IR (film): ν_{max} 3064, 3027, 2955, 2922, 2851, 1625, 1568, 1483, 1425, 1357, 1326, 1297, 1200, 1166, 1063, 1014, 975, 907, 849, 818, 781, 757, 696. ^{1}H NMR: δ 7.60 (dd, ^3J = 3.7 Hz, ^4J = 1.2 Hz, 1H, H3′), 7.56 (dd, ^3J = 5.1 Hz, ^4J = 1.2 Hz, 1H, H5′), 7.41-7.37 (m, 2H, Ho^2), 7.39-7.35 (m, 2H, Hm^1), 7.35-7.33 (m, 3H, Hm^2,p^2), 7.29 (d, ^3J = 16.5 Hz, 1H, H3), 7.56 (dd, ^3J = 5.1 Hz, ^3J = 3.7 Hz, 1H, H4′), 7.17-7.10 (m, 1H, Hp^1), 7.01-6.95 (m, 2H, Ho^1), 6.86 (d, ^3J = 16.5 Hz, 1H, H2). ^{13}C {^{1}H} NMR: δ 159.9 (C1), 150.3 (Ci^1), 144.5 (C2′), 140.2 (C3), 135.7 (C3′), 130.0 (Ci^3), 129.7 (C3′), 129.4 (C5′), 128.9, 127.4 (Cp^3,m^1,m^3,4′), 124.2 (Cp^1), 122.1 (C2), 121.3 (Co^1). ^{15}N NMR: δ -59.8.

*(2E)-1,3-Diphenyl-N-(o-tolyl)prop-2-en-1-imine (**3j**)*. Following the general procedure, **3j** was prepared from **1j** (1 mmol, 0.195 g) and **2a** (1 mmol, 0.102 g). **3j** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 4:1 molar ratio (0.175 g, 59% yield). Yellow oil. Anal. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.76; H, 6.39; N, 4.78. IR (film): ν_{max} 3059, 3028, 2973, 2923, 2856, 1617, 1588, 1485, 1449, 1379, 1313, 1213, 1185, 1108, 1077, 1032, 977, 911, 863, 839, 797, 750, 696. 1*E*,2*E*-**3j**. ^{1}H NMR: δ 7.81-7.72 (m, 2H, Ho^2), 7.57-7.45 (m), 7.42-7.18 (m), 7.16-7.04 (m) [11H, H2,*Ar*], 6.97 (d, ^3J = 16.5 Hz, 1H, H3), 6.99-6.75 (m, 2H, *Ar*), 2.19 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 166.8 (C1), 149.9 (C1′), 141.6 (C3), 139.3 (Ci^2), 135.8 (Ci^3), 130.5, 129.9, 129.5, 129.3, 128.9, 128.4, 127.6, 126.4, 123.8 [14C, *Ar*], 121.7 (C2), 119.3 (C6′), 18.1 (Me). ^{15}N NMR: δ -48.1. 1*Z*,2*E*-**3j**. ^{1}H NMR: δ 7.57-7.45 (m), 7.42-7.18 (m), 7.16-7.04 (m), 6.99-6.75 (m) [16H, H2,3,*Ar*], 2.23 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 168.3 (C1), 149.9 (C1′), 141.1 (C3),

136.0, 135.9 (Ci^2,i^3), 131.6 (C2), 130.0, 129.3, 128.9, 128.5, 128.1, 125.8, 123.3, 119.7 [15C, C*Ar*], 18.3 (Me). ^{15}N NMR: δ -44.4.

*(2E)-N-(3-Methoxyphenyl)-1,3-diphenylprop-2-en-1-imine (**3k**)*. Following the general procedure, **3k** was prepared from **1k** (1 mmol, 0.211 g) and **2a** (1 mmol, 0.102 g). **3k** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 3:1 molar ratio (0.182 g, 58 % yield). Yellow oil. Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.19; H, 6.23; N, 4.26. IR (film): ν_{max} 3099, 3079, 3058, 3025, 3001, 2955, 2937, 2913, 2833, 1613, 1589, 1482, 1447, 1316, 1281, 1259, 1146, 1074, 1043, 974, 939, 870, 853, 762, 754, 697. 1*E*,2*E*-**3k**. ^{1}H NMR: δ 7.75-7.67 (m, 2H, Ho^2), 7.51-7.41 (m), 7.35-7.22 (m), 6.93-6.88 (m), 6.55-6.49 (m) [14H, H2,3,*Ar*], 3.79 (s, 3H, OMe). ^{13}C {^{1}H} NMR: δ 167.3 (C1), 160.4 (C*3′*), 152.4 (Ci^1), 141.8 (C3), 139.4 (Ci^2), 135.8 (Ci^3), 130.0, 129.8, 129.5, 128.9, 128.5, 127.7 (11C, C*Ar*), 122.1 (C3), 113.1, 110.1, 106.3 (3C, C*2′*,*4′*,*6′*), 55.4 (OMe). 1*Z*,2*E*-**3k**. ^{1}H NMR: δ 7.49-7.44 (m), 7.33-7.21 (m), 7.18-7.09 (m) [12H, H2,*Ar*], 6.98 (d, ^3J = 16.4 Hz, H3), 6.47-6.43 (m), 6.26-6.20 (m) [3H, H*Ar*], 3.63 (s, 3H, OMe). ^{13}C {^{1}H} NMR: δ 169.1 (C1), 159.8 (C*3′*), 153.3 (Ci^1), 141.6 (C3), 131.7, 129.2, 129.0, 128.9, 128.6, 128.2, 127.7, 113.8, 109.6, 106.7 (17C, C2,*Ar*), 55.2 (OMe).

*(2E)-N-(2-Fluorophenyl)-1,3-diphenylprop-2-en-1-imine (**3l**)*. Following the general procedure, **3l** was prepared from **1l** (1 mmol, 0.199 g) and **2a** (1 mmol, 0.102 g). **3l** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 2:1 molar ratio (0.193 g, 64% yield). Yellow oil. Anal. Calcd for $C_{21}H_{16}FN$: C, 83.70; H, 5.35; F, 6.30; N, 4.65. Found: C, 83.96; H, 5.21; F, 6.19; N, 4.59. IR (film): ν_{max} 3146, 3059, 3032, 2958, 2924, 2855, 1662, 1595, 1487, 1448, 1317, 1233, 1186, 1100, 1080, 1027, 976, 911, 865, 842, 752, 697. 1*E*,2*E*-**3l**. ^{1}H NMR: 7.79-7.72 (m, 2H, Ho^2), 7.51-7.42 (m, 3H, Hm^2,p^2), 7.36-7.22 (m), 7.17-7.05 (m), 7.01-6.92 (m), 6.88-6.980 (m), 6.67-6.58 (m) [11H, H2,3,*Ar*]. ^{13}C {^{1}H} NMR: δ 169.4 (C1), 152.7 (d, $^1J_{CF}$ = 245.7 Hz, C*2′*), 142.4 (C3), 138.9 (Ci^2), 138.7 (d, $^2J_{CF}$ = 12.5 Hz, C*1′*), 135.6 (Ci^3), 130.2, 129.7 (Cp^2,p^3), 129.5, 128.6, 128.4, 127.6 (Co^2,o^3,m^2,m^3), 125.0 (d, $^3J_{CF}$ = 7.2 Hz, C*4′*), 124.3 (d, $^3J_{CF}$ = 3.8 Hz, C*6′*), 122.8 (d, $^4J_{CF}$ = 2.3 Hz, C*5′*), 121.6 (C2), 116.1 (d, $^2J_{CF}$ = 19.8 Hz, C*3′*). 1*Z*,2*E*-**3l**. ^{1}H NMR: 7.851-7.24 (m), 7.16-7.04 (m), 7.00-6.78 (m) [11H, H2,3,*Ar*], 6.67-6.00 (m, 1H, C*3′*). ^{13}C {^{1}H} NMR: δ 171.8 (C1), 152.5 (d, $^1J_{CF}$ = 244.3 Hz, C*2′*), 142.3 (C3), 139.1 (d, $^2J_{CF}$ = 12.4 Hz, C*1′*), 135.7 (Ci^2,i^3), 131.12 (C2), 129.5 (Cp^3), 128.9 (Cm^3), 128.8 (Cp^2), 128.3, 128.1, 127.7 (Co^2,m^2,o^3), 124.4 (d, $^3J_{CF}$ = 7.3 Hz, C*4′*), 123.8 (d, $^3J_{CF}$ = 3.6 Hz, C*6′*), 122.6 (d, $^4J_{CF}$ = 2.3 Hz, C*5′*), 115.6 (d, $^2J_{CF}$ = 20.2 Hz, C*3′*).

*(2E)-N-(2-Bromophenyl)-1,3-diphenylprop-2-en-1-imine (**3m**)*. Following the general procedure, **3m** was prepared from **1m** (1 mmol, 0.260 g) and **2a** (1 mmol, 0.102 g). **3m** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 2:1 molar ratio (0.120 g, 33% yield). Yellow oil. Anal. Calcd for $C_{21}H_{16}BrN$: C, 69.63; H, 4.45; Br, 22.06; N, 3.87. Found: C, 69.89; H, 4.31; Br, 22.12; N, 3.64.

IR (film): ν_{max} 3058, 3033, 2954, 2923, 2854, 1676, 1586, 14519, 1797, 1455, 1443, 1314, 1258, 1210, 1180, 10941075, 1026, 976, 912, 859, 752, 696. 1*E*,2*E*-**3m**. ^{1}H NMR: 7.82-7.74 (m, 2H, H*o*^{2}), 7.65-7.07 (m), 7.01-6.81 (m), 6.78-6.65 (m) [14H, H2,3,*Ar*]. ^{13}C {^{1}H} NMR: δ 168.5 (C1), 149.6 (C*2′*), 142.7 (C3), 138.7, 135.7 (C*i*^{2},C*i*^{3}), 133.1 (C*Ar*), 130.2 (C*p*^{2}), 129.8 (C*p*^{3}), 129.5, 128.9, 128.5 (C*o*^{2},*m*^{2},*m*^{3}), 128.1 (C*Ar*), 127.8 (C*o*^{3}), 124.9 (C*Ar*), 121.5 (C2), 121.1, 114.6 (2C, C*Ar*). 1*Z*,2*E*-**3m**. ^{1}H NMR: 8.03-7.96 (m), 7.94-7.87 (m), 7.65-7.07 (m), 7.01-6.81 (m), 6.78-6.65 (m), 6.45-6.40 (m) [16H, H2,3,*Ar*]. ^{13}C {^{1}H} NMR: δ 170.2 (C1), 150.0 (C*2′*), 142.6 (C3), 135.8, 135.4 (C*i*^{2},*i*^{3}), 132.4 (C*Ar*), 131.0 (C2), 129.6 (C*p*^{3}), 128.9 (C*m*^{3}), 128.9 (C*p*^{2}), 128.4, 128.1, 127.8 (C*o*^{2},*m*^{2},*o*^{3}), 127.5, 124.4, 121.4, 115.5 (4C, C*Ar*).

*(2E)-N-(Naphthalen-1-yl)-1,3-diphenylprop-2-en-1-imine (**3n**).* Following the general procedure, **3n** was prepared from **1n** (1 mmol, 0.231 g) and **2a** (1 mmol, 0.102 g). **3n** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 3:1 molar ratio (0.143 g, 43% yield). Yellow oil. Anal. Calcd for $C_{25}H_{19}N$: C, 90.06; H, 5.74; N, 4.20. Found: C, 90.32; H, 5.51; N, 4.15. IR (film): ν_{max} 3053, 2922, 2854, 2257, 1615, 1571, 1498, 1446, 1389, 1311, 1266, 1218, 1175, 1155, 1097, 1073, 1019, 974, 908, 871, 778, 732, 695. 1*E*,2*E*-**3n**. ^{1}H NMR: δ 7.94-7.88 (m, 1H, H*Naphth*), 7.87-7.80 (m, 2H, H*o*^{2}), 7.64-7.58 (m, 1H, H*Naphth*), 7.54-7.27 (m), 7.24-7.02 (m), 6.99-6.75 (m) [15H, H2,3,*Ar*]. ^{13}C {^{1}H} NMR: δ 167.9 (C1), 147.7 (C*1′*), 142.0 (C3), 139.4, 135.7 (C*i*^{2},*i*^{3}), 134.3, 130.1, 129.6, 129.5, 128.8, 128.5, 128.0, 127.6, 126.4, 125.9, 125.6, 124.2, 124.0 (18C, C*Ar*), 122.1 (C2), 114.6 (C*Naphth*). 1*Z*,2*E*-**3n**. ^{1}H NMR: δ 8.07-8.03 (m), 7.76-7.71 (m) [2H, H*Naphth*], 7.54-7.27 (m), 7.24-7.02 (m), 6.99-6.75 (m) [16H, H2,3,*Ar*], 6.40-6.36 (m, 1H, H*Naphth*). ^{13}C {^{1}H} NMR: δ 169.7 (C1), 141.6 (C3), 136.0, 135.7 (C*i*^{2},*i*^{3}), 133.9, 131.7, 130.1, 129.5, 129.0, 128.6, 128.5, 128.4, 128.0, 127.9, 127.7, 126.9, 126.1, 125.6, 123.4, 114.7 (21C, C2, C*Ar*).

*(2E)-N,1-Diphenyl-3-(m-tolyl)prop-2-en-1-imine (**3p**).* Following the general procedure, **3p** was prepared from **1a** (1 mmol, 0.181 g) and **2b** (1 mmol, 0.116 g). **3p** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 5:2 molar ratio (0.191 g, 64 % yield). Yellow oil. Anal. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.72; H, 6.88; N, 4.56. IR (film): ν_{max} 3057, 3027, 2950, 2920, 2860, 1622, 1602, 1587, 1573, 1482, 1445, 1318, 1305, 1278, 1233, 1207, 1168, 1085, 1073, 1026, 978, 907, 835, 781, 770, 739, 697, 660. 1*E*,2*E*-**3p**. ^{1}H NMR: δ 7.76-7.68 (m, 2H, H*o*^{2}), 7.49-7.41 (m), 7.37-7.32 (m), 7.29-7.05 (m), 6.96-6.92 (m), 6.90-6.86 (m) [14H, H2,3,*Ar*], 2.28 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 167.3 (C1), 151.1 (C*i*^{1}), 142.0 (C3), 139.6, 138.6, 135.8, 130.4, 130.0, 129.5, 129.0, 128.8, 128.4, 124.6, 124.0 (15C, C*Ar*), 121.9 (C2), 120.9 (C*o*^{1}), 21.4 (Me). 1*Z*,2*E*-**3p**. ^{1}H NMR: δ 7.49-7.41 (m), 7.30-7.05 (m), 6.90-6.84 (m) [13H, H2, *Ar*], 6.79 (d, ^{3}J = 16.3 Hz, 1H, H3), 6.67-6.62 (m, 2H, H*o*^{1}), 2.32 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 169.1 (C1), 150.9 (C*i*^{1}), 141.6 (C3), 138.45, 135.9, 135.7, 131.7, 130.2, 129.1, 128.5, 128.4, 128.1, 124.7, 123.4 (16C, C2,*Ar*) 121.2 (C*o*^{1}), 21.5 (Me).

*(2E)-N,1-Diphenyl-3-(p-tolyl)prop-2-en-1-imine (**3q**)*. Following the general procedure, **3q** was prepared from **1a** (1 mmol, 0.181 g) and **2c** (1 mmol, 0.116 g). **3q** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 3:1 molar ratio (0.158 g, 53% yield). Light yellow solid; m.p.: 87-89 °C. Anal. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.77; H, 6.48; N, 4.63. IR (film): ν_{max} 3052, 3028, 2921, 2866, 1583, 1508, 1484, 1446, 1315, 1206, 1180, 1076, 1025, 977, 909, 812, 767, 736, 699. 1*E*,2*E*-**3q**. ^{1}H NMR: δ 7.81-7.75 (m, 2H, Ho^2), 7.55-7.47 (m, 3H, Hm^2,p^2), 7.44-7.37 (m), 7.25-7.22 (m) [4H, Ho^3,m^1), 7.18-7.14 (m, 1H, Hp^1), 7.16-7.11 (m), 7.03-7.99 (m) [4H, Hm^3,o^1), 6.94 (d, ^3J = 18.3 Hz, 1H, H3), 6.89 (d, ^3J = 18.3 Hz, 1H, H2), 2.36 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 167.4 (C1), 151.2 (Ci^1), 141.8 (C3), 139.8 (Ci^2), 139.6 (Cp^3), 133.1 (Ci^3), 129.9 (Cp^2), 129.6, 129.5, 128.9, 128.4, 127.6 (Cm^1,m^2,m^3,o^2,o^3), 123.9 (Cp^1), 121.1 (C2), 120.9 (Co^1), 21.5 (Me). ^{15}N NMR: δ -52.8. 1*Z*,2*E*-**3q**. ^{1}H NMR: δ 7.44-7.37 (m, 2H, Ho^3), 7.33-7.28 (m, 3H, Hm^2,p^2), 7.29 (d, ^3J = 16.2 Hz, 1H, H2), 7.21-7.12 (m, 6H, Hm^1,m^3,o^2), 6.94-6.92 (m, 1H, Hp^1), 6.85 (d, ^3J = 16.2 Hz, 1H, H3), 6.74-6.69 (m, 2H, Ho^1), 2.39 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 169.12 (C1), 150.9 (Ci^1), 141.5 (C3), 139.6 (Cp^3), 135.7, 133.2 (Ci^2,Ci^3), 130.8 (C2), 129.6, 129.1 (Cm^3,o^2), 128.5 (Cp^2), 128.4, 128.1, 127.6 (Cm^1,m^2,o^3), 123.3 (Cp^1), 121.2 (Co^1), 21.5 (Me). ^{15}N NMR: δ -49.0.

*(2E)-3-(2,5-Dimethylphenyl)-N,1-diphenylprop-2-en-1-imine (**3r**)*. Following the general procedure, **3r** was prepared from **1a** (1 mmol, 0.181 g) and **2d** (1 mmol, 0.130 g). **3r** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 3:1 molar ratio (0.097 g, 31% yield). Yellow oil. Anal. Calcd for $C_{23}H_{21}N$: C, 88.71; H, 6.80; N, 4.50. Found: C, 88.84; H, 6.71; N, 4.44. IR (film): ν_{max} 3056, 3025, 2957, 2922, 2864, 1658, 1587, 1489, 1447, 1381, 1312, 1255, 1208, 1165, 1129, 1064, 977, 844, 812, 763, 697. 1*E*,2*E*-**3r**. ^{1}H NMR: δ 7.79-7.73 (m, 2H, Ho^2), 7.49-7.43 (m, 3H, Hm^2,p^2), 7.38-7.31 (m, 2H, Hm^1), 7.28-7.22 (m), 7.19-7.05 (m), 7.04-6.85 (m), 6.79-6.71 (m) [8H, H2,3,*Ar*], 2.24 (s, 3H, Me), 2.15 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 167.4 (C1), 151.2 (Ci^1), 140.0 (Ci^2), 139.7 (C3), 135.8, 134.7, 133.9, 130.6, 130.1, 130.0 [6C, Cp^2,*Ar*], 129.5, 129.0, 128.4 (Co^2,m^1,m^2), 124.0 (Cp^1), 126.7 (C*Ar*), 123.1 (C2), 120.9 (Co^1), 21.1 (Me), 19.3 (Me). 1*Z*,2*E*-**3r**. ^{1}H NMR: δ 7.38-7.31 (m), 7.28-7.22 (m), 7.19-7.05 (m), 7.04-6.85 (m), 6.79-6.71 (m) [13H, H2,3,*Ar*], 6.68-6.64 (m, 2H, Ho^1), 2.32 (s, 3H, Me), 2.15 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 169.2 (C1), 150.9 (Ci^1), 139.5 (C3), 135.8, 134.7, 133.9 (4C, Ci^2,*Ar*), 132.6 (C2), 130.6, 130.0 (2C, C*Ar*), 129.1 (Co^2), 128.5, 128.1 (Cp^2,m^1,m^2), 126.8 (C*Ar*), 123.4 (Cp^1), 121.2 (Co^1), 21.1 (Me), 19.2 (Me).

*(2E)-3-([1,1'-Biphenyl]-4-yl)-N,1-diphenylprop-2-en-1-imine (**3s**)*. Following the general procedure, **3s** was prepared from **1a** (1 mmol, 0.181 g) and **2e** (1 mmol, 0.178 g). **3s** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 5:2 molar ratio (0.155 g, 43% yield). Brown oil. Anal. Calcd for $C_{27}H_{21}N$: C, 90.21; H, 5.89; N, 3.90. Found: C, 90.58; H, 5.75; N, 3.62. IR (film): ν_{max} 3056, 3029, 2958, 2924, 2857, 1658, 1618, 1584, 1483, 1447, 1405, 1316, 1208, 1177, 1102, 1075,

1016, 977, 908, 831, 762, 696. 1*E*,2*E*-**3s**. ^{1}H NMR: δ 7.77-7.72 (m, 2H, H*o*^{2}), 7.66-7.31 (m), 7.29-7.21 (m), 7.15-7.06 (m), 6.99-6.82 (m) [19H, H2,3,*Ar*]. ^{13}C {^{1}H} NMR: δ 167.1 (C1), 151.2 (C*i*^{1}), 142.2 (C*Ar*), 141.2 (C3), 140.3, 139.5 [2C, C*Ar*], 135.7 (C*i*^{2}), 134.8 (C*Ar*), 130.0 (C*p*^{2}), 129.5, 129.0, 128.9, 128.4, 128.0, 127.5, 127.0 [14C, C*Ar*], 124.0 (C*p*^{1}), 122.0 (C2), 120.9 (C*o*^{1}). 1*Z*,2*E*-**3s**. ^{1}H NMR: δ 7.66-7.31 (m), 7.29-7.21 (m), 7.15-7.06 (m), 6.99-6.82 (m) [19H, H2,3,*Ar*], 6.68-6.63 (m, 2H, H*o*^{1}). ^{13}C {^{1}H} NMR: δ 168.9 (C1), 150.9 (C*i*^{1}), 142.0 (C*Ar*), 140.8 (C3), 140.4, 135.0 [2C, C*Ar*], 131.8 (C2), 129.0, 128.7, 128.6, 128.5, 128.1, 127.8, 127.7, 127.7, 127.1 [17C, C*Ar*], 123.4 (C*p*^{1}), 121.2 (C*o*^{1}).

*(2E)-3-(3-Methoxyphenyl)-N,1-diphenylprop-2-en-1-imine (**3t**)*. Following the general procedure, **3t** was prepared from **1a** (1 mmol, 0.181 g) and **2f** (1 mmol, 0.132 g). **3t** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 5:2 molar ratio (0.135 g, 43% yield). Yellow oil. Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.42; H, 6.25; N, 4.23. IR (film): ν_{max} 3057, 3027, 2950, 2933, 2837, 1662, 1587, 1485, 1452, 1313, 1282, 1247, 1210, 1162, 1076, 1044, 976, 908, 842, 773, 696. 1*E*,2*E*-**3t**. ^{1}H NMR: δ 7.74-7.69 (m, 2H, H*o*^{2}), 7.49-7.42 (m, 3H, H*m*^{2},*p*^{2}), 7.37-7.30 (m, 2H, H*m*^{1}), 7.28-6.98 (m), 6.97-6.74 (m) [9H, H2,3,*Ar*], 3.73 (s, 3H, OMe). ^{13}C {^{1}H} NMR: δ 167.0 (C1), 160.0 (C*i*^{1}), 151.1 (C*3′*), 141.5 (C3), 139.5, 137.2 (C*i*^{2},*1′*), 130.0 (C*p*^{2}), 129.9 (C*5′*), 129.4, 128.9, 128.4 (C*o*^{2},*m*^{1},*m*^{2}), 124.0 (C*p*^{1}), 122.4 (C2), 120.8 (C*o*^{1}), 120.1 (C*6′*), 115.6, 113.0 (2C, C*2′*,*4′*), 55.3 (OMe). 1*Z*,2*E*-**3t**. ^{1}H NMR: δ 7.28-6.98 (m), 6.97-6.74 (m) [14H, H2,3,*Ar*], 7.67-7.62 (m, 2H, H*o*^{1}), 3.78 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 168.9 (C1), 160.0 (C*i*^{1}), 150.8 (C*3′*), 141.3 (C3), 137.3, 135.6 (C*1′*,*i*^{2}), 132.1 (C2), 129.8 (C*5′*), 129.0 (C*o*^{2}), 128.5 (C*p*^{2}), 128.4, 128.1 (C*m*^{1},*m*^{2}), 123.4 (C*p*^{1}), 121.1 (C*o*^{1}), 120.5 (C*6′*), 115.0, 112.1 (2C, C*2′*,*4′*), 55.3 (OMe).

*(2E)-3-(4-Methoxyphenyl)-N,1-diphenylprop-2-en-1-imine (**3u**)*. Following the general procedure, **3u** was prepared from **1a** (1 mmol, 0.181 g) and **2g** (1 mmol, 0.132 g). **3u** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 3:1 molar ratio (0.197 g, 63 % yield). Yellow solid; m.p.: 88-90 ^{o}C. Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.41; H, 6.18; N, 4.32. IR (film): ν_{max} 3058, 3030, 3013, 2957, 2934, 2909, 2836, 1603, 1586, 1573, 1511, 1482, 1443, 1421, 1319, 1307, 1253, 1207, 1174, 1085, 1073, 1028, 976, 908, 827, 793, 762, 732, 698. 1*E*,2*E*-**3u**. ^{1}H NMR: δ 7.74-7.67 (m, 2H, H*o*^{2}), 7.50-7.30 (m), 7.27-7.20 (m), 7.14-7.05 (m), 6.97-6.92 (m), 6.89-6.71 (m) [14H, H2,3,*Ar*], 3.78 (s, 3H, OMe). ^{13}C {^{1}H} NMR: δ 167.5 (C1), 160.8 (C*i*^{1}), 151.3 (C*p*^{3}), 141.5 (C3), 139.7, 129.8, 129.4, 129.1, 128.9, 128.4, 123.8, 120.9 (15C, C2,*Ar*), 114.3 (C*m*^{3}), 55.4 (OMe). 1*Z*,2*E*-**3u**. ^{1}H NMR: δ 7.50-7.38 (m), 7.27-7.20 (m), 7.14-7.05 (m), 6.89-6.71 (m) [14H, H2,3,*Ar*], 6.67-6.61 (m, 2H, H*o*^{1}), 3.81 (s, 3H, Me). ^{13}C {^{1}H} NMR: δ 169.2 (C1), 160.7 (C*i*^{1}), 151.0 (C*p*^{3}), 141.1 (C3), 135.8, 129.7, 129.1, 128.7, 128.5, 128.4, 128.1, 123.2, 121.2, 119.9 (17C, C2,*Ar*), 55.4 (OMe).

*(2E)-3-(3-Fluorophenyl)-N,1-diphenylprop-2-en-1-imine (**3v**).* Following the general procedure, **3v** was prepared from **1a** (1 mmol, 0.181 g) and **2h** (1 mmol, 0.120 g). **3v** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 2:1 molar ratio (0.181 g, 60% yield). Yellow solid; m.p.: 81-83 °C. Anal. Calcd for $C_{21}H_{16}FN$: C, 83.70; H, 5.35; F, 6.36; N, 4.65. Found: C, 83.77; H, 5.42; F, 6.23; N, 4.57. IR (film): ν_{max} 3061, 3033, 2924, 2875, 1665, 1585, 1486, 1444, 1312, 1274, 1234, 1214, 1146, 1076, 1023, 973, 908, 856, 778, 735, 697. 1*E*,2*E*-**3v**. ^{1}H NMR: δ 7.74-7.68 (m, 2H, Ho^2), 7.50-7.43 (m, 3H, Hm^2,p^2), 7.39-7.21 (m), 7.18-6.85 (m) [11H, H2,3,*Ar*]. ^{13}C {^{1}H} NMR: δ 166.7 (C1), 163.1 (d, $^1J_{CF}$ = 246.6 Hz, C3′), 150.9 (Ci^1), 140.2 (d, $^4J_{CF}$ = 2.1 Hz, C3), 139.3 (Ci^2), 138.1 (d, $^3J_{CF}$ = 7.7 Hz, C1′), 130.4 (d, $^3J_{CF}$ = 8.1 Hz, C5′), 130.1 (Cp^2), 129.4, 129.0, 128.5 (Co^2,m^1,m^2), 124.2 (Cp^1), 123.4 (d, $^4J_{CF}$ = 2.8 Hz, C6′), 123.2 (C2), 120.8 (Co^1), 116.3 (d, $^2J_{CF}$ = 21.3 Hz), 113.9 (d, $^2J_{CF}$ = 21.8 Hz) [2C, C2′,4′]. 1*Z*,2*E*-**3v**. ^{1}H NMR: δ 7.52-7.42 (m), 7.39-7.21 (m), 7.18-6.85 (m) [14H, H2,3,*Ar*], 6.78 (d, 1H, ^3J = 16.3 Hz, H3), 6.61-6.62 (m, 2H, Ho^1). ^{13}C {^{1}H} NMR: δ 168.5 (C1), 164.4 (d, $^1J_{CF}$ = 246.6 Hz, C3′), 150.7 (Ci^1), 139.8 (d, $^4J_{CF}$ = 1.0 Hz, C3), 138.3 (d, $^3J_{CF}$ = 7.7 Hz, C1′), 135.5 (Ci^2), 133.1 (C2), 130.3 (d, $^3J_{CF}$ = 7.9 Hz, C5′), 129.0 (Co^2), 128.6 (Cp^2), 128.5, 128.2 (Cm^1,m^2), 123.6 (Cp^1), 123.3 (d, $^4J_{CF}$ = 1.2 Hz, C6′), 121.1 (Co^1), 116.1 (d, $^2J_{CF}$ = 21.2 Hz), 114.0 (d, $^2J_{CF}$ = 21.8 Hz) [C2′,4′].

*(2E)-3-(4-Fluorophenyl)-N,1-diphenylprop-2-en-1-imine (**3w**).* Following the general procedure, **3w** was prepared from **1a** (1 mmol, 0.181 g) and **2i** (1 mmol, 0.120 g). **3w** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 5:2 molar ratio (0.169 g, 56% yield). Yellow solid; m.p.: 76-79 °C. Anal. Calcd for $C_{21}H_{16}FN$: C, 83.70; H, 5.35; F, 6.36; N, 4.65. Found: C, 83.86; H, 5.48; F, 6.12; N, 4.49. IR (film): ν_{max} 3058, 2925, 2871, 1662, 1591, 1506, 1483, 1446, 1413, 1314, 1230, 1160, 1093, 1076, 1020, 977, 908, 830, 765, 697. 1*E*,2*E*-**3w**. ^{1}H NMR: δ 7.72-7.68 (m, 2H, Ho^2), 7.52-7.39 (m, 3H, Hm^2,p^2), 7.39-7.32 (m, 2H, Hm^1), 7.29-7.21 (m), 7.15-6.80 (m) [9H, H2,3,*Ar*]. ^{13}C {^{1}H} NMR: δ 167.0 (C1), 163.5 (d, $^1J_{CF}$ = 250.3 Hz, Cp^3), 151.1 (Ci^1), 140.4 (d, $^5J_{CF}$ = 1.0 Hz, C3), 139.4 (Ci^2), 132.0 (d, $^4J_{CF}$ = 3.4 Hz, Ci^3), 130.0 (Cp^2), 129.4 (Co^2), 129.3 (d, $^3J_{CF}$ = 8.3 Hz, Co^3), 129.0, 128.5 (Cm^1,m^2), 124.1 (Cp^1), 120.8 (C2,o^1), 116.0 (d, $^2J_{CF}$ = 21.9 Hz, Cm^3). ^{15}N NMR: δ -50.3. 1*Z*,2*E*-**3w**. ^{1}H NMR: δ 7.65-7.39 (m), 7.21-6.74 (m) [14H, H2,3,*Ar*], 6.61-6.62 (m, 2H, Ho^1). ^{13}C {^{1}H} NMR: δ 168.8 (C1), 163.4 (d, $^1J_{CF}$ = 249.9 Hz, Cp^3), 150.8 (Ci^1), 140.0 (d, $^5J_{CF}$ = 1.0 Hz, C3), 135.6 (Ci^2), 132.9 (C2), 132.2 (d, $^4J_{CF}$ = 3.4 Hz, Ci^3), 129.3 (d, $^3J_{CF}$ = 8.3 Hz, Co^3), 129.0 (Co^2), 128.6 (Cp^2), 128.5, 128.2 (Cm^1,m^2), 123.5 (Cp^1), 121.1 (Co^1), 116.2 (d, $^2J_{CF}$ = 21.9 Hz, Cm^3). ^{15}N NMR: δ -46.6.

*(2E)-N,1-Diphenyl-3-(pyridin-3-yl)prop-2-en-1-imine (**3x**).* Following the general procedure, **3x** was prepared from **1a** (1 mmol, 0.181 g) and **2j** (1 mmol, 0.103 g). **3x** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 2:1 molar ratio (0.088 g, 31% yield). Light yellow solid; m.p.: 116-119 °C. Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.61; H, 5.57; N, 9.78.

IR (film): ν_{max} 3055, 3029, 2967, 2924, 2856, 1617, 1583, 1568, 1516, 1482, 1446, 1415, 1313, 1280, 1209, 1175, 1124, 1098, 1074, 1023, 977, 910, 827, 770, 735, 700. 1*E*,2*E*-**3x**. ^{1}H NMR: δ 8.49-8.42 (m, 2H, H*2′*,*6′*), 7.72-7.65 (m, 2H, H*o*^{2}), 7.59-7.52 (m, 1H, H*4′*), 7.49-7.39 (m, 3H, H*m*^{2},*p*^{2}), 7.36-7.27 (m, 2H, H*m*^{1}), 7.29-7.02 (m, 1H, H*5′*), 7.22-7.02 (m, 1H, H*p*^{1}), 6.95-6.80 (m, 4H, H2,3,*o*^{1}). ^{13}C {^{1}H} NMR: δ 166.4 (C1), 150.8 (C*i*^{1}), 150.2 (C*6′*), 149.4 (C*2′*), 139.0 (C*i*^{2}), 137.7 (C3), 133.5 (C*4′*), 133.5 (C*3′*), 130.1 (C*p*^{2}), 129.3, 129.0, 128.5 (C*o*^{2},*m*^{1},*m*^{2}), 124.2, 123.9, 123.6 (C2,*5′*,*p*^{1}), 120.6 (C*o*^{1}). 1*Z*,2*E*-**3x**. ^{1}H NMR: δ 8.62-8.42 (m, 2H, H*2′*,*6′*), 7.82-7.74 (m, 1H, H*4′*), 7.28-7.02 (m, 9H, H2,*5′*,*Ar*), 6.90-6.85 (m, 1H, H*p*^{1}), 6.77 (d, ^3J = 16.4 Hz, 1H, H3), 6.63-6.58 (m, 2H, H*o*^{1}). ^{13}C {^{1}H} NMR: δ 168.3 (C1), 150.5 (C*i*^{1}), 150.1 (C*6′*), 149.3 (C*2′*), 137.3 (C3), 135.1 (C*i*^{2}), 133.7 (C*4′*), 131.6 (C*3′*), 131.4 (C2), 128.9 (C*o*^{2}), 128.7 (C*p*^{2}), 128.4, 128.2 (C*m*^{1},*m*^{2}), 123.7, 123.6 (C*5′*,*p*^{1}), 121.0 (C*o*^{1}).

*(2E)-N,1-Diphenyl-3-(thiophen-3-yl)prop-2-en-1-imine (**3y**)*. Following the general procedure, **3y** was prepared from **1a** (1 mmol, 0.181 g) and **2k** (1 mmol, 0.108 g). **3y** was isolated as a mixture of 1*E*,2*E*/1*Z*,2*E*-isomers in a 2:1 molar ratio (0.150 g, 52% yield). Light yellow oil. Anal. Calcd for $C_{19}H_{15}NS$: C, 78.86; H, 5.22; N, 4.84; S, 11.08. Found: C, 78.99; H, 5.34; N, 4.75; S, 10.91. IR (film): ν_{max} 3092, 3059, 3028, 2958, 2924, 2859, 1615, 1584, 1515, 1483, 1445, 1312, 1256, 1206, 1163, 1077, 1023, 972, 908, 866, 833, 772, 697. 1*E*,2*E*-**3y**. ^{1}H NMR: δ 7.73-7.64 (m, 2H, H*o*^{2}), 7.51-7.42 (m, 3H, H*m*^{2},*p*^{2}), 7.38-7.29 (m), 7.29-7.20 (m), 7.14-7.04 (m) [6H, H*2′*,*4′*,*5′*,*Ar*], 6.96-6.93 (m, 2H, H*o*^{1}), 6.90 (d, ^3J = 16.3 Hz, 1H, H3), 6.71 (d, ^3J = 16.3 Hz, 1H, H2). ^{13}C {^{1}H} NMR: δ 167.4 (C1), 151.1 (C*i*^{1}), 139.5 (C*i*^{2}), 138.9 (C3), 135.6 (C*3′*), 129.9 (C*p*^{2}), 129.4, 129.0, 128.5 (C*o*^{2},*m*^{1},*m*^{2}), 126.8, 126.2, 125.2 (C*2′*,*4′*,*5′*), 124.0 (C*p*^{1}), 121.9 (C2), 120.8 (C*o*^{1}). ^{15}N NMR: δ -51.8. 1*Z*,2*E*-**3y**. ^{1}H NMR: δ 7.38-7.29 (m), 7.29-7.20 (m), 7.14-7.04 (m) [11H, H2,*2′*,*4′*,*5′*,*Ar*], 6.90-6.84 (m, 1H, H*p*^{1}), 6.80 (d, ^3J = 16.2 Hz, 1H, H3), 6.66-6.59 (m, 2H, H*o*^{1}). ^{13}C {^{1}H} NMR: δ 169.2 (C1), 150.9 (C*i*^{1}), 139.0 (C3), 135.6 (C*i*^{2}), 135.2 (C*3′*), 131.8 (C2), 129.1 (C*o*^{2}), 128.5 (C*p*^{2}), 128.4, 128.2 (C*m*^{1},*m*^{2}), 126.8, 126.0, 125.3 (C*2′*,*4′*,*5′*), 123.34 (C*p*^{1}), 121.2 (C*o*^{1}). ^{15}N NMR: δ -48.1.

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The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc. Copies of ^{1}H and ^{13}C NMR spectra of all compounds, and crystallographic data (PDF).

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