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Synthesis of α,β-Unsaturated *N*-Aryl Ketonitrones from Oximes and Diaryliodonium Salts: Observation of a Metal-Free *N*-Arylation Process

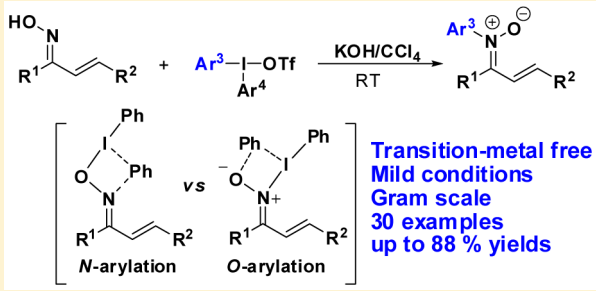
Xiao-Pan Ma,[†] Wei-Min Shi,[†] Xue-Ling Mo,[†] Xiao-Hua Li,[†] Liang-Gui Li,[†] Cheng-Xue Pan,[†] Bo Chen,*[,‡] Gui-Fa Su,*[,†] and Dong-Liang Mo*[,†]

[†]Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources, Ministry of Education of China, School of Chemistry & Pharmaceutical Sciences, Guangxi Normal University, 15 Yu Cai Road, Guilin 541004, People's Republic of China

[‡]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States

Supporting Information

ABSTRACT: An efficient transition-metal-free method for the preparation of α,β-unsaturated *N*-aryl ketonitrones under mild conditions has been developed. This reaction shows good functional group tolerance for both electron-rich and electron-deficient substituents on both oximes and diaryliodonium salts. Two examples of gram-scale preparations have been realized in good yields. Further transformations of these nitrones to different *N*-heterocycles have been demonstrated. DFT calculations suggest that *N*-arylation products are formed by [1,3]-phenyl migration of an *O*-coordinated oximate complex via a four-centered transition state, while the *O*-arylation products are formed by [1,3]-phenyl migration of a *N*-coordinated oximate complex.



INTRODUCTION

Oximes, owing to their ability to act as ambident nucleophiles (*O*- or *N*-nucleophiles), have been extensively utilized as important starting materials to construct key building blocks in organic synthesis.[1,2] Arylation of the N−O bond is one of the most important transformations of oximes. *O*-Arylations have been used to build aryloxyamines, which are important precursors of *O*-aryloximes or benzofurans, while *N*-arylations have been employed to prepare oxyarylamines.[3] In the past, efficient *O*-arylations of oximes have been achieved by transition-metal-catalyzed cross-coupling reactions of oximes with aryl halides or arylboronic acids.[4,5] For example, Maitra and Wailes reported the coupling of oximes with aryl iodides catalyzed by a CuI/1,10-phenanthroline catalyst system.[4a] In 2010, Buchwald developed an efficient Pd catalyst for the *O*-arylation of ethyl acetohydroximate with aryl chlorides, bromides, and iodides to prepare *O*-arylhydroxyamines and substituted benzofurans (Scheme 1A).[4b] In addition, both Huang and Meyer have reported the copper-mediated coupling of oximes with arylboronic acids to form *O*-arylation products (Scheme 1A).[5] More recently, Anderson and co-workers found that α,β-unsaturated *N*-aryl ketonitrones can be generated by copper-mediated *N*-arylation of chalcone oximes with arylboronic acids in good yields (Scheme 1B).[6] Despite the efficiencies of these metal-catalyzed or -mediated arylations of oximes, these methods suffer from several drawbacks such as harsh conditions, prolonged reaction times, the requirement of complex ligands, and trace-metal impurities remaining in the products.

To overcome the aforementioned drawbacks, recent emphasis has been placed on the development of metal-free methods for *O*-arylation or *N*-arylation of oximes using diaryliodonium salts as arylation reagents.[7] Diaryliodonium salts are readily available reagents that exhibit high reactivity and selectivity and good tolerance of a wide range of functional groups and are considered to be nontoxic in many areas of organic synthesis.[8] Very recently, Kürti and Olofsson independently developed metal-free methods for the *O*-arylation of oximes with diaryliodonium salts to access *O*-arylhydroxylamines for synthesis of benzofuran scaffolds (Scheme 1C).[7b,c]

In contrast to the work of Kürti and Olofsson, herein we report a metal-free *N*-arylation of oximes with diaryliodonium salts to produce α,β-unsaturated *N*-aryl ketonitrones (Scheme 1D). Due to their rich chemistry resulting from the inclusion of the conjugated double bond moiety in nitrone, α,β-unsaturated *N*-aryl ketonitrones have recently gained much attention as key building blocks in the synthesis of highly complex molecules.[9] Traditional methods for the preparation of nitrones, such as the condensation of a hydroxylamine with a carbonyl compound[10] or oxidation of a secondary hydroxylamine,[11] are inefficient in making α,β-unsaturated *N*-aryl ketonitrones because of the low

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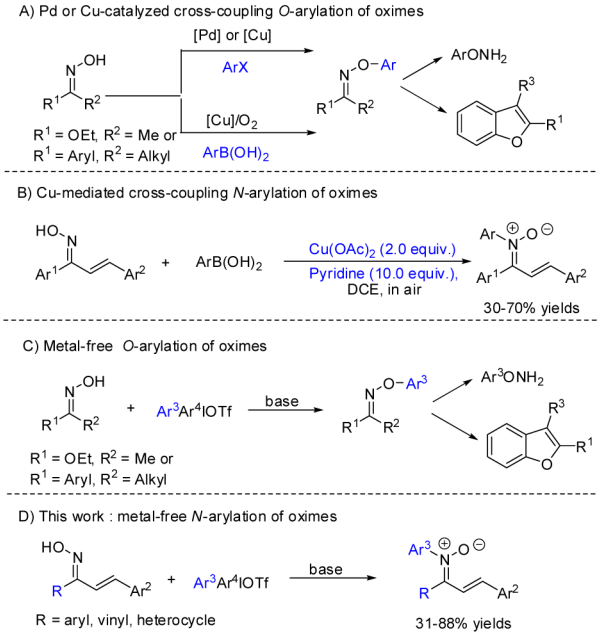
Scheme 1. Arylation Strategies of Oximes

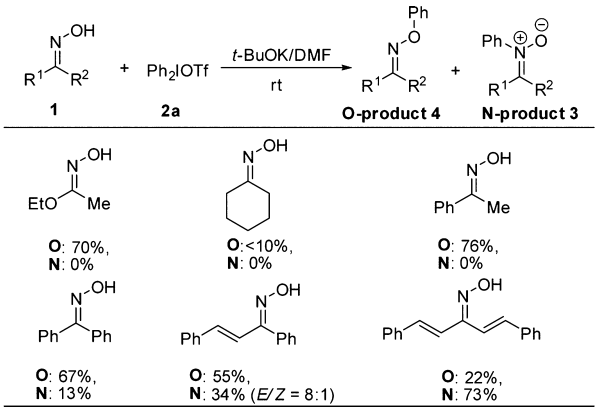


nucleophilicity of *N*-aryl hydroxylamines and side reactions such as oxidation of the double bond. The reported method in this article represents an advance in synthesizing α,β-unsaturated *N*-aryl ketonitrones.[12]

RESULTS AND DISCUSSION

Our investigation began with the reaction of different types of oximes **1** with diphenyliodonium triflate **2a**. These transformations were carried out with potassium *tert*-butoxide in DMF at ambient temperature (Scheme 2). When ethyl

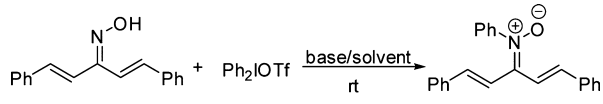
Scheme 2. Selective *O*-Arylation and *N*-Arylation for Oximes



acetohydroximate and acetophenone oxime were combined under the reaction conditions, only *O*-arylation products were isolated in good yields, and <5% yields of *N*-arylation products were observed in the crude reaction mixture. The isolated yields of the *O*-arylation products were in agreement with those in the literature.[8b] In contrast, when cyclohexanone oxime was treated with diaryliodonium salt **2a**, the reaction mixture was complex and only a <10% yield of the *O*-arylation product was observed. To our surprise, in the case of benzophenone oxime, chalcone oxime, and dibenzylideneacetone oxime, a mixture of *O*- and *N*-arylation products were observed. For dibenzylideneacetone oxime, the *N*-arylation product was isolated in 73% yield as the major product. Encouraged by the observed switch in selectivity from *O*-arylation to *N*-arylation, we decided to optimize the reaction conditions of this *N*-arylation process.

Dibenzylideneacetone oxime **1a** was initially chosen as the model substrate for screening conditions for oxime *N*-arylation. As illustrated in Table 1, a screen of various solvents showed

Table 1. Optimization of Reaction[a]



entry	base	solvent	time (h)	yield of **3a** (%)[b]
1	KOH	DMF	13	69
2	KOH	DMSO	13	45[c]
3	KOH	MeCN	1.5	60
4	KOH	THF	0.5	67
5	KOH	PhMe	1.6	70
6	KOH	DCE	2.5	64
7	KOH	CCl_4	2.5	75[d]
8	KOH	CCl_4	5	74[e]
9	*t*-BuOK	CCl_4	4	74
10	Cs_2CO_3	CCl_4	7.5	71
11	pyridine	CCl_4	24	0
12		CCl_4	24	0

[a]Reaction conditions unless noted otherwise: oxime **1a** (0.5 mmol), Ph_2IOTf (1.5 equiv), KOH (1.5 equiv), CCl_4 (5 mL), room temperature. [b]Isolated yields. [c]*O*-arylation product **4a** was also isolated with 40% yield. [d]*O*-arylation product **4a** was also isolated with 10% yield. [e]H_2O (0.5 mL) was added in CCl_4.

that CCl_4 was the best solvent for this transformation (entries 1−7). The choice of base had little effect on the yield of nitrone **3a**, except for pyridine, which prevented the desired transformation (entries 7, 9, and 10 vs entry 11). The *N*-arylation reaction proceeded smoothly and provided analogous yields in either the presence or absence of water (entry 8). No desired product was observed, and only oxime **1a** was recovered in the absence of base (entry 12).

To examine the scope of the *N*-arylation of oximes with diaryliodonium reagents, the most general conditions identified in Table 1 (entry 7) were applied to various substrates. As shown in Table 2, oximes with both electron-rich and electron-deficient styrenyl functional groups having ortho, meta, and para substitution patterns were tolerated under the reaction conditions and provided the desired nitrones in moderate to good yields (Table 2, entries 1−8). However, when oxime **1e** was tested, the yield of *N*-arylation decreased sharply in either toluene or THF, perhaps due to the poor solubility of the substrate (Table 2, entry 5). Interestingly, the unsymmetrically substituted oximes **1i−n** (*E*/*Z* = 1/1) were also smoothly converted to 1/1 mixtures of *E*/*Z* isomers of nitrones **3** (Table 2, entries 9−14). When oxime **1i** was used as substrate, product **3i** was obtained in 78% yield in THF while only a 46% yield was obtained in CCl_4 (Table 2, entry 9). To our delight, the reaction tolerated heterocyclic substitutents such as 2-furanyl and 2-thienyl groups, and good yields of the corresponding nitrones were achieved (Table 2, entries 7 and 8). When an oxime containing two conjugated double bonds was used as substrate, the desired nitrone **3n** was obtained with 67% yield (Table 2, entry 14). The conjugated system in **3n** further

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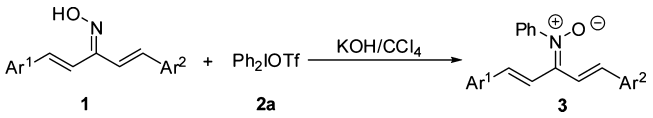
Table 2. Scope of Oximes[a]



1 2a 3

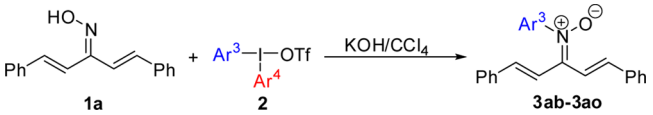
entry	1	Ar^1	Ar^2	3	yield (%)[b]
1	**1a**	Ph	Ph	**3a**	75
2	**1b**	4-MeO-C_6H_4	4-MeO-C_6H_4	**3b**	65 (39,[c] 56[d])
3	**1c**	4-Me-C_6H_4	4-Me-C_6H_4	**3c**	81 (41[d])
4	**1d**	4-CF_3-C_6H_4	4-CF_3-C_6H_4	**3d**	76 (61[d])
5	**1e**	3-Br-C_6H_4	3-Br-C_6H_4	**3e**	46 (52[c], 50[d])
6	**1f**	2-Br-C_6H_4	2-Br-C_6H_4	**3f**	68
7	**1g**	2-furanyl	2-furanyl	**3g**	74
8	**1h**	2-thienyl	2-thienyl	**3h**	75
9	**1i**	Ph	4-MeO-C_6H_4	**3i**	46, 78[d] (1/1)[e]
10	**1j**	Ph	4-CF_3-C_6H_4	**3j**	75 (1/1)[e]
11	**1k**	Ph	4-Br-C_6H_4	**3k**	75 (1/1)[e]
12	**1l**	Ph	3-Br-C_6H_4	**3l**	77 (1/1)[e]
13	**1m**	Ph	2-Br-C_6H_4	**3m**	60 (1/1)[e]
14	**1n**	Ph	PhCH=CH	**3n**	67 (1/1)[e]

[a]Reaction conditions unless noted otherwise: oxime **1** (0.5 mmol), Ph_2IOTf (1.5 equiv), KOH (1.5 equiv), CCl_4 (5 mL), room temperature, 0.5–24 h. [b]Isolated yields. [c]Run in toluene. [d]Run in THF. [e]The C=N geometry ratio of *E*/*Z* in nitrones.

enhances the potential synthetic applications of the nitrone products.

In addition to screening oxime substrates, a variety of diaryliodonium salts **2** were tested to examine its effect on the formation of *N*-aryl nitrones. These reagents were easily prepared in one step from commercially available starting materials such as arylboronic acids.[13] As shown in Table 3, both electron-rich and electron-deficient diaryliodonium salts **2**, with para, meta, or ortho substituents provided the corresponding nitrones in good yields. It is worth noting that iodonium reagents with *o*-methyl or *o*-bromo and heterocyclic substituents also gave the desired nitrones (Table 3, entries 9, 14, and 15). Analogous challenging nitrones were obtained in lower yields by Yang's method[12] and were not discussed in the copper-mediated cross-coupling reaction of oximes with arylboronic acids developed by Anderson and co-workers in 2013.[6] To our delight, when unsymmetrical diaryliodonium salts were tested, the *N*-arylation reaction proceeded with high chemoselectivity and electron-deficient aryl moieties were preferentially transferred to the nitrones (Table 3, entries 10–14).[14] The bromo, chloro, thienyl, nitro, and ester functional groups were all tolerated as substituents of the iodonium reagents in this transformation.

Table 3. Scope of Diaryliodonium Salts[a]



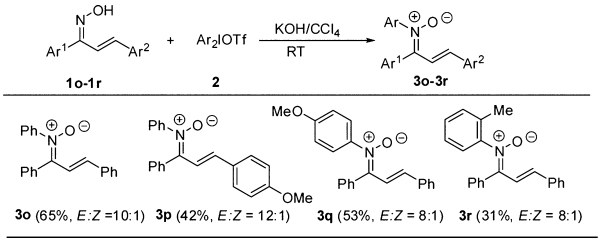
1a 2 3ab-3ao

Entry	2	Ar^3	Ar^4	3	Yield %[b]
1	**2a**	Ph	Ph	**3a**	75
2	**2b**	4-MeO(C_6H_4)	4-MeO(C_6H_4)	**3ab**	74
3	**2c**	4-Me(C_6H_4)	4-Me(C_6H_4)	**3ac**	71
4	**2d**	4-*t*-Bu(C_6H_4)	4-*t*-Bu(C_6H_4)	**3ad**	78
5	**2e**	4-Cl(C_6H_4)	4-Cl(C_6H_4)	**3ae**	71
6	**2f**	4-F(C_6H_4)	4-F(C_6H_4)	**3af**	73
7	**2g**	3-NO_2(C_6H_4)	3-NO_2(C_6H_4)	**3ag**	65
8	**2h**	3,5-Me_2(C_6H_4)	3,5-Me_2(C_6H_4)	**3ah**	70
9	**2i**	2-Me(C_6H_4)	2-Me(C_6H_4)	**3ai**	65
10	**2aa**	Ph	4-MeO(C_6H_4)	**3a**	69
11	**2j**	4-CF_3(C_6H_4)	4-MeO(C_6H_4)	**3aj**	58
12	**2k**	4-Br(C_6H_4)	4-MeO(C_6H_4)	**3ak**	68
13	**2l**	3-Br(C_6H_4)	4-MeO(C_6H_4)	**3al**	72
14	**2m**	2-Br(C_6H_4)	4-MeO(C_6H_4)	**3am**	88
15	**2n**	3-(thienyl)	4-MeO(C_6H_4)	**3an**	44[c]
16	**2o**	4-CO_2Me(C_6H_4)	Ph	**3ao**	81

[a]Reaction conditions: oxime **1a** (0.5 mmol), Ar^3Ar^4IOTf (1.5 equiv), KOH (1.5 equiv), CCl_4 (5 mL), room temperature, 0.5–24 h. [b]Isolated yields. [c]**3ab** was also obtained with 40% yield.

When chalcone oximes (**1o–r**) were subjected to the optimal oxime *N*-arylation conditions described above, the desired products were obtained in moderate yields with the *E* isomers as the major products (Scheme 3).[12] Interestingly, the *E*/*Z* geometry ratio of the C=N bond in nitrones **3** ranged from 8/1 to 12/1 (**3o–r**). To our delight, the sterically hindered ortho-substituted *N*-aryl nitrone **3r** was obtained in 31% yield.[12]

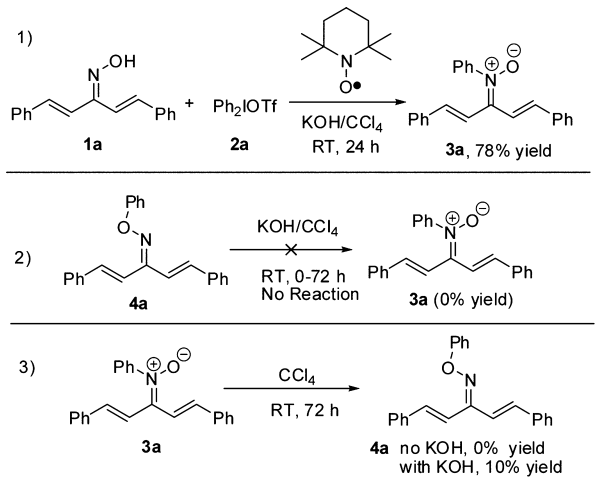
Scheme 3. Synthesis of *N*-Aryl Nitrones from Chalcone Oximes 1o–r



3o (65%, *E*:*Z* =10:1) **3p** (42%, *E*:*Z* = 12:1) **3q** (53%, *E*:*Z* = 8:1) **3r** (31%, *E*:*Z* = 8:1)

When the radical trap TEMPO (2.0 equiv) was added to the reaction mixture of oxime **1a** and iodonium salt **2a**, nitrone **3a** was still obtained in 78% yield after 24 h (Scheme 4-1), which suggests that a radical mechanism is unlikely. The synthesis of nitrones by the *N*-arylation of oximes with diaryliodonium salts could occur via a direct C–N bond forming pathway or an initial C–O bond forming step followed by a rearrangement. When *O*-arylation product **4a** was subjected to the optimal *N*-arylation reaction conditions for 72 h, nitrone **3a** was not observed and only starting material was recovered (Scheme 4-2). This experiment revealed that nitrone **3a** cannot be formed from a rearrangement of *O*-arylation product **4a**. However,

Scheme 4. Mechanism Studies



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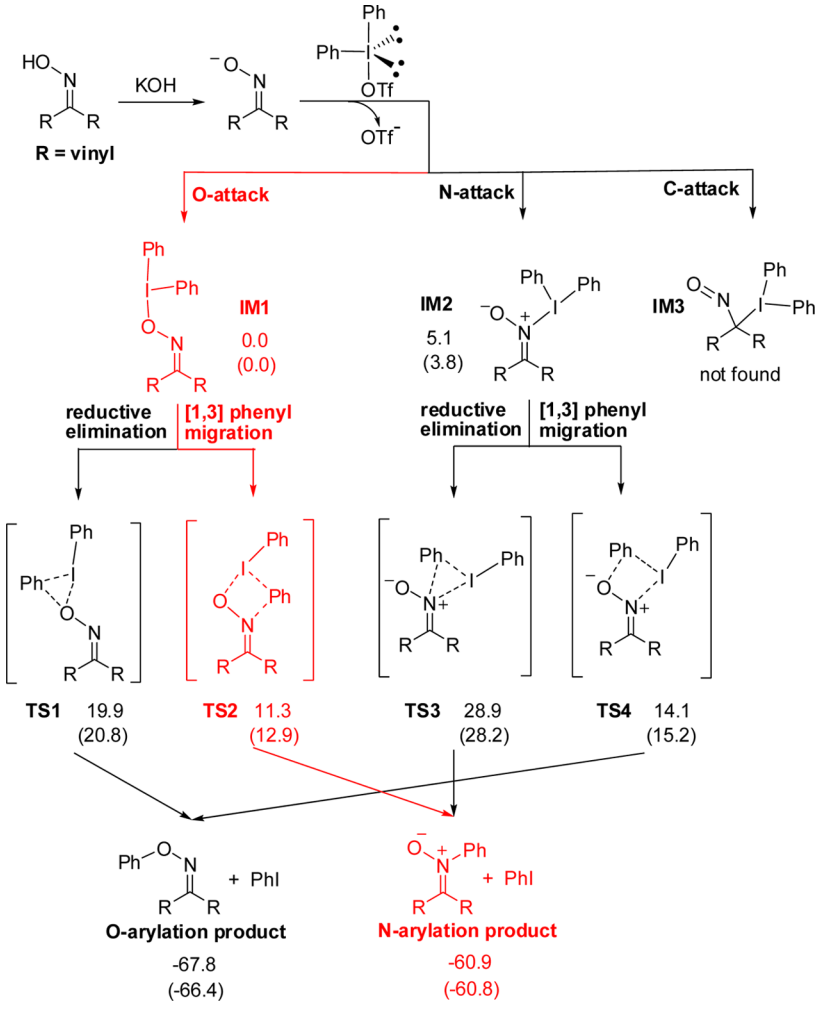
Scheme 5. Possible Reaction Pathways (R = Vinyl), with Calculated Energies for Intermediates, Transition States, and Products[a]



[a]Free energies both in the gas phase (ΔG_{gas}) and in solvent (ΔG_{sol} in parentheses) are given in units of kcal/mol. The most favorable pathway that gives the *N*-arylation product is highlighted in red.

when nitrone **3a** was subjected to the optimal condition, *O*-arylation product was observed in 10% yield for 72 h (Scheme 4-3).[15] This experiment suggests that the *O*-arylation product might be the thermodynamic product, while nitrone was the kinetic product.

To further study the oxime *N*-arylation reaction mechanism, DFT calculations were carried out on a model system of divinyl oxime with diphenyliodonium triflate (Scheme 5).[16] It is proposed that this reaction begins with the deprotonation of oxime by KOH;[2a] the resultant oximate anion, as an ambident nucleophile, could attack diphenyliodonium triflate as either the *O*-nucleophile or the *N*-nucleophile, leading to the two distinct intermediates **IM1** and **IM2**, respectively. **IM1** is calculated to be lower in energy than **IM2** by 3.8 kcal/mol. We surmise that this difference may be due to the fact that the **IM1** can be represented by a non-charge-separated Lewis structure while the **IM2** cannot. We also explored theoretically the possibility of another resonance structure of oximate anion (nitroso carbanion) as a potential C-nucleophile to attack diphenyliodonium triflate. However, no intermediate structure with a C−I bond was located in our calculations.

Starting from either **IM1** or **IM2**, there are two potential arylation pathways: (1) direct reductive elimination at iodine center via a three-membered-ring transition state (**TS1** and **TS3**) and (2) a [1,3]-phenyl migration via a four-membered ring transition state (**TS2** and **TS4**). **TS1** and **TS4** lead to the *O*-arylation product, while **TS2** and **TS3** lead to the *N*-arylation product. Calculations show that **TS2** is 15.3 kcal/mol lower than **TS3**, 2.3 kcal/mol lower than **TS4**, and represents the lowest overall activation barrier. These transition state energy differences suggest that the most favorable pathway is the initial formation of *O*-coordinated diphenyliodonium oximate complex **IM1** followed by [1,3]-phenyl migration, as highlighted in Scheme 5.[17] This predicted pathway gives the *N*-arylation product, in agreement with experiments. DFT calculations also show that the most favorable *O*-arylation pathway is the formation of *N*-coordinated diphenyliodonium oximate complex **IM2** followed by [1,3]-phenyl migration via **TS4**.[18] The *O*-arylation product is computed to be 5.6 kcal/mol lower in energy than the *N*-arylation product, in agreement with the experiments that the *O*-arylation product is the thermodynamic product and the *N*-arylation product is the kinetic product (Scheme 4-2,3).

In order to show the superiority of this new transformation, gram-scale reactions were performed using the optimal condition for oxime *N*-arylation. When 2.2 g (8.8 mmol) of

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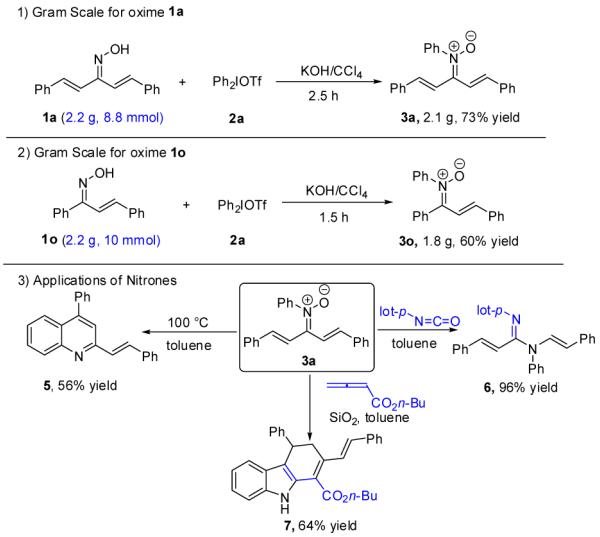
oxime **1a** was treated with **2a** for 2.5 h, 2.1 g of the desired nitrone **3a** was obtained in 73% yield (Scheme 6-1). Treatment of oxime **1o** (2.2 g, 10 mmol) with **2a** gave nitrones **3o** in 60% yield (Scheme 6-2).

Scheme 6. Gram Scales and Synthetic Applications of Nitrone 3a



With *N*-aryl nitrones in hand, we studied their synthetic applications (Scheme 6-3). When nitrone **3a** was heated at 100 °C for 18 h, the quinoline product **5** was afforded in 56% yield. When nitrone **3a** was treated with *p*-tolyl isocyanate, *N*-vinyl amidine **6** was isolated in excellent yield. When **3a** was treated with monosubstituted allenoate, dihydrocarbazole **7** was isolated with 64% yield. These quinoline, amidine, and dihydrocarbazole products are important and useful intermediates in organic synthesis.[19] The facile method that we have developed for the synthesis of *N*-aryl nitrones will allow these important scaffolds to be studied more frequently.

CONCLUSIONS

In summary, we have shown that the α,β-unsaturated *N*-aryl ketonitrones can be prepared in one step from the corresponding oximes through a metal-free *N*-arylation reaction with diaryliodonium salts under mild conditions. The reaction tolerates electron-rich or electron-deficient substituents on both the oximes and the diaryliodonium reagents. In particular, *N*-ortho-substituted aryl ketonitrones and *N*-heterocycle-substituted nitrones are easily obtained by this method. The salient features of this transformation include simple conditions, short reaction times, good yields, high selectivity for diaryliodonium salts, the ability to scale up to gram scale, and the ability to facilitate further investigation of nitrone chemistry. Applications of the *N*-arylated nitrone products to the synthesis of different *N*-heterocycles have also been demonstrated. DFT calculations suggest that *N*-aryl nitrones are formed via a four-membered-ring transition state after the formation of *O*-coordinated diaryliodonium oximate.

EXPERIMENTAL SECTION

General Methods. All reactions were performed under an atmosphere of air. Commercially available reagents were used without further purification. The NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on 400, 500, and 600 MHz instruments with TMS as the internal standard. NMR data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in hertz (Hz), and integration. IR spectra were recorded on an FT-IR spectrometer, and only major peaks are reported in cm^{-1}. HRMS were measured in EI or ESI mode, and the mass analyzer of the HRMS was TOF. Flash column chromatography was performed on silica gel (300−400 mesh). The oximes **1a,i,j,o,p**,[6,20] **1b**,[21] **1c**,[22] **1g,h**,[23] diaryliodonium salts **2a,aa,c,o**,[13a,24] **2b,d−f,i**,[25] **2g**,[26] **2h**,[27] **2j**,[28] **2k**,[29] and **2l**[30] were prepared according to literature methods and their spectral data matched literature values.

***N*-Arylation of Oximes To Prepare Nitrones 3.** A round-bottle flask, open to the air, was charged with oxime **1** (0.5 mmol), CCl_4 (5 mL) and KOH (0.75 mmol, 1.5 equiv). The mixture was stirred vigorously at room temperature for 5 min. Then diaryliodonium salt **2** (0.75 mmol, 1.5 equiv) was added in one portion. The reaction was monitored by TLC until the oxime was consumed completely. At this time, the CCl_4 was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded on silica gel; 1/10−1/1 ethyl acetate/petroleum ether) to provide nitrones **3** as solid.

*N-((1E,4E)-1,5-Diphenylpenta-1,4-dien-3-ylidene)aniline oxide (**3a**):* 0.122 g, 75% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65−7.61 (m, 3H), 7.59 (d, J = 17.5 Hz, 1H), 7.51−7.45 (m, 5H), 7.41 (t, J = 7.5 Hz, 2H), 7.36 (d, J = 7.0 Hz, 1H), 7.32−7.28 (m, 5H), 7.00 (d, J = 16.0 Hz, 1H), 6.67 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 139.6, 136.5, 136.1, 134.8, 129.6, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 127.4, 126.8, 124.7, 120.5, 119.5; IR (thin film) 3055, 1593, 1487, 1229, 965, 769, 690 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{20}NO$ $(M + H)^+$ 326.1545, found 326.1542; mp 163−164 °C.

*N-((1E,4E)-1,5-Bis(4-methoxyphenyl)penta-1,4-dien-3-ylidene)-aniline oxide (**3b**):* 0.125 g, 65% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 8.5 Hz, 2H), 7.51−7.49 (m, 4H), 7.46−7.42 (m, 3H), 7.23 (d, J = 8.5 Hz, 2H), 6.94−6.91 (m, 3H), 6.84 (d, J = 8.5 Hz, 2H), 6.50 (d, J = 16.5 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 160.2, 147.2, 146.4, 139.4, 134.7, 129.4, 129.3, 129.1, 128.9, 128.8, 128.2, 124.7, 118.5, 117.5, 114.3, 114.2, 55.4, 55.3; IR (thin film) 3034, 2836, 1598, 1509, 1252, 962, 821, 769, 692 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{24}NO_3$ $(M + H)^+$ 386.1756, found 386.1752; mp 150−152 °C.

*N-((1E,4E)-1,5-Di-p-tolylpenta-1,4-dien-3-ylidene)aniline oxide (**3c**):* 0.143 g, 81% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 16.5 Hz, 1H), 7.55−7.49 (m, 5H), 7.46−7.42 (m, 3H), 7.20−7.16 (m, 4H), 7.11 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 16.5 Hz, 1H), 6.60 (d, J = 16.5 Hz, 1H), 2.37 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 146.6, 139.6, 139.4, 139.0, 134.9, 133.8, 133.4, 129.6, 129.5, 129.4, 129.2, 127.5, 126.8, 124.8, 119.7, 118.6, 21.4, 21.3; IR (thin film) 3019, 2860, 1599, 1509, 1229, 964, 774, 696 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{24}NO$ $(M + H)^+$ 354.1858, found 354.1856; mp 146−147 °C.

*N-((1E,4E)-1,5-Bis(4-(trifluoromethyl)phenyl)penta-1,4-dien-3-ylidene)aniline oxide (**3d**):* 0.176 g, 76% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.66−7.65 (m, 4H), 7.57 (d, J = 8.0 Hz, 2H), 7.50 (s, 5H), 7.39 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 16.5 Hz, 1H), 6.77 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 145.4, 139.8, 139.3, 137.6, 132.6, 130.6 (q, J = 31.8 Hz), 130.1, 129.3, 127.5, 126.9, 125.8 (q, J = 3.6 Hz), 125.0 (q, J = 274 Hz), 124.9, 124.6, 122.9, 122.7, 121.3; IR (thin film) 3051, 1612, 1486, 1279, 981, 776, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{18}F_6NO$ $(M + H)^+$ 462.1293, found 462.1268; mp 148−149 °C.

*N-((1E,4E)-1,5-Bis(3-bromophenyl)penta-1,4-dien-3-ylidene)-aniline oxide (**3e**):* 0.110 g, 46% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.57−7.53 (m, 3H), 7.50−7.46 (m, 5H), 7.41−7.39 (m, 2H), 7.29−7.25 (m, 2H), 7.20−7.17 (m, 2H), 6.89 (d, J = 16.0 Hz, 1H), 6.65 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 145.5, 138.6, 138.1, 137.7, 132.9, 131.9, 131.7, 130.4, 130.3, 130.2, 130.0, 129.8, 129.3, 125.9, 125.2, 124.6, 123.1, 123.0, 121.8, 120.6; IR (thin film) 3054, 1588, 1463, 1229, 960, 773, 690

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cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{18}Br_2NO$ $(M + H)^+$ 481.9755, found 481.9761; mp 51−52 °C.

*N-((1E,4E)-1,5-Bis(2-bromophenyl)penta-1,4-dien-3-ylidene)-aniline oxide (**3f**):* 0.164 g, 68% yield, yellow solid; ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 16.5 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.65 (d, J = 16.5 Hz, 1H), 7.60−7.42 (m, 8H), 7.38 (d, J = 7.5 Hz, 1H), 7.25−7.17 (m, 3H), 7.13 (t, J = 7.0 Hz, 1H), 6.64 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 146.2, 137.8, 136.3, 136.0, 133.4, 133.2, 133.1, 130.1, 129.8, 129.7, 129.2, 127.6, 127.5, 127.4, 126.5, 124.9, 124.8, 124.7, 122.7, 121.8; IR (thin film) 3055, 1587, 1459, 1229, 958, 752, 692 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{18}Br_2NO$ $(M + H)^+$ 481.9755, found 481.9761; mp 118−119 °C.

*N-((1E,4E)-1,5-Bis(furan-2-yl)penta-1,4-dien-3-ylidene)aniline oxide (**3g**):* 0.113 g, 74% yield, yellow solid; ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 15.5 Hz, 1H), 7.50−7.46 (m, 6H), 7.32−7.29 (m, 2H), 6.76 (d, J = 16.0 Hz, 1H), 6.58−6.55 (m, 2H), 6.47 (s, 1H), 6.38 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 152.2, 146.6, 144.9, 143.9, 143.3, 129.5, 129.2, 126.1, 124.6, 120.4, 119.1, 116.3, 112.4, 112.2, 112.0, 111.3; IR (thin film) 3080, 1606, 1552, 1222, 964, 739, 691 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{16}NO_3$ $(M + H)^+$ 306.1130, found 306.1127; mp 144−145 °C.

*N-((1E,4E)-1,5-Bis(thiophen-2-yl)penta-1,4-dien-3-ylidene)aniline oxide (**3h**):* 0.126 g, 75% yield, yellow solid; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 16.5 Hz, 1H), 7.47−7.42 (m, 5H), 7.35−7.32 (m, 2H), 7.22−7.21 (m,2H), 7.09 (d, J = 16.5 Hz, 1H), 7.04 (s, 2H), 6.98 (t, J = 4.0 Hz, 1H), 6.43 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 145.4, 142.1, 141.4, 132.3, 129.6, 129.2, 129.1, 128.8, 128.0, 127.9, 127.1, 126.3, 124.6, 124.5, 119.8, 118.1; IR (thin film) 3069, 1589, 1486, 1242, 957, 769, 691 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{16}NOS_2$ $(M + H)^+$ 338.0673, found 338.0671; mp 140−141 °C

*N-((1E,4E)-1-(4-Methoxyphenyl)-5-phenylpenta-1,4-dien-3-ylidene)aniline oxide (**3i**):* 0.087 g, 46% yield (E/Z = 1:1), yellow solid; isomer 1, ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 16.5 Hz, 1H), 7.53−7.49 (m, 5H), 7.47−7.44 (m, 4H), 7.41 (t, J = 7.5 Hz, 1H), 7.30−7.28 (m, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.64 (d, J = 16.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 146.9, 146.5, 139.5, 136.1, 135.0, 129.5, 129.2, 129.1, 129.0, 128.9, 128.8, 128.3, 127.5, 126.9, 124.8, 114.3, 55.3; *isomer 2*: ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 16.5 Hz, 1H), 7.53−7.49 (m, 5H), 7.47−7.44 (m, 4H), 7.35 (t, J = 7.5 Hz, 1H), 7.30−7.28 (m, 2H), 7.23 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 6.52 (d, J = 16.0 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 147.0, 146.5, 139.7, 136.6, 134.7, 129.5, 129.2, 129.1, 129.0, 128.9, 128.8, 120.7, 119.7, 118.4, 117.4, 114.4, 55.4; IR (thin film) 3030, 2850, 1599, 1508, 1251, 964, 753, 692 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{22}NO_2$ $(M + H)^+$ 356.1651, found 356.1649; mp 54−55 °C.

*N-((1E,4E)-1-Phenyl-5-(4-(trifluoromethyl)phenyl)penta-1,4-dien-3-ylidene)aniline oxide (**3j**):* 0.147 g, 75% yield (E/Z = 1/1), yellow solid; isomer 1, ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.5 Hz, 2H), 7.68−7.62 (m, 4H), 7.58 (d, J = 8.0 Hz, 1H), 7.52−7.49 (m, 4H), 7.44 (t, J = 7.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.35−7.32 (m, 2H), 7.01 (d, J = 15.5 Hz, 1H), 6.71 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 139.6, 137.5, 134.7, 132.6, 130.7 (q, J = 31.5 Hz), 129.8, 129.3, 128.9, 127.5, 126.8, 125.8 (q, J = 3.6 Hz), 125.1 (d, J = 271.1 Hz), 124.6, 122.8, 121.7, 120.3, 119.1; isomer 2, ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.5 Hz, 2H), 7.68−7.62 (m, 4H), 7.58 (d, J = 8.0 Hz, 1H), 7.52−7.49 (m, 4H), 7.44 (t, J = 7.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.35−7.32 (m, 2H), 7.04 (d, J = 15.5 Hz, 1H), 6.78 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 140.0, 136.4, 135.9, 132.6, 130.7 (q, J = 31.5 Hz), 129.9, 129.2, 128.8, 127.4, 126.9, 125.8 (q, J = 3.6 Hz), 124.9 (d, J = 271.1 Hz), 124.6, 122.9, 121.7, 120.3, 119.1; IR (thin film) 3057, 1613, 1461, 1277, 965, 752, 692 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{19}F_3NO$ $(M + H)^+$ 394.1419, found 394.1419; mp 55−57 °C

*N-((1E,4E)-1-(4-Bromophenyl)-5-phenylpenta-1,4-dien-3-ylidene)aniline oxide (**3k**):* 0.151 g, 75% yield (E/Z = 1/1), yellow solid; isomer 1, ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 7.0 Hz, 1H), 7.58−7.56 (m, 2H), 7.52−7.46 (m, 6H), 7.42−7.38 (m, 2H), 7.30−7.28 (m, 3H), 7.14 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 16.0 Hz, 1H), 6.66 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 139.5, 138.0, 135.9, 135.0, 131.9, 129.7, 129.2, 128.9, 128.8, 128.1, 127.4, 126.8, 124.6, 121.2, 120.4, 120.0; isomer 2, ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 7.0 Hz, 1H), 7.58−7.56 (m, 2H), 7.52−7.46 (m, 6H), 7.42−7.38 (m, 2H), 7.30−7.28 (m, 3H), 7.14 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 16.5 Hz, 1H), 6.65 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0, 139.5, 136.4, 135.5, 134.7, 133.1, 132.0, 129.2, 128.9, 128.8, 128.1, 127.4, 126.8, 123.1, 122.7, 121.4, 119.2; IR (thin film) 3055, 1589, 1484, 1228, 962, 811, 769, 689 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{19}BrNO$ $(M + H)^+$ 404.0650, found 404.0648; mp 144−146 °C.

*N-((1E,4E)-1-(3-Bromophenyl)-5-phenylpenta-1,4-dien-3-ylidene)aniline oxide (**3l**):* 0.155 g, 77% yield (E/Z = 1/1), yellow solid; isomer 1, ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.62 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.49−7.45 (m, 5H), 7.40 (d, J = 7.5 Hz, 2H), 7.32−7.26 (m, 3H), 7.20 (d, J = 7.5 Hz, 1H), 6.97 (d, J = 16.0 Hz, 1H), 6.67 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 139.6, 137.7, 135.9, 134.6, 132.9, 131.8, 130.3, 130.2, 129.7, 129.2, 128.9, 128.8, 127.4, 126.8, 124.6, 121.9, 120.7, 119.3; isomer 2, ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 7.0 Hz, 2H), 7.49−7.45 (m, 5H), 7.41 (s, 1H), 7.36 (d, J = 7.0 Hz, 2H), 7.32−7.26 (m, 3H), 7.18 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 16.0 Hz, 1H), 6.66 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0, 138.7, 138.2, 136.4, 134.6, 132.9, 131.9, 130.3, 130.2, 129.8, 129.3, 128.9, 128.8, 125.9, 125.2, 123.0, 122.9, 120.7, 120.4; IR (thin film) 3052, 1587, 1462, 1229, 963, 778, 691 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{19}BrNO$ $(M + H)^+$ 404.0650, found 404.0648; mp 147−149 °C.

*N-((1E,4E)-1-(2-Bromophenyl)-5-phenylpenta-1,4-dien-3-ylidene)aniline oxide (**3m**):* 0.121 g, 60% yield (E/Z = 1/1), yellow solid; isomer 1, ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 16.0 Hz, 1H), 7.68−7.55 (m, 3H), 7.52−7.47 (m, 6H), 7.43−7.32 (m, 3H), 7.30−7.28 (m, 2H), 7.23−7.17 (m, 2H), 6.70 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 146.5, 139.9, 138.1, 136.5, 136.2, 135.3, 133.2, 129.8, 129.3, 128.9, 127.8, 127.7, 127.6, 127.5, 126.9, 124.8, 123.0, 120.1; isomer 2, ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 16.0 Hz, 1H), 7.68−7.55 (m, 3H), 7.52−7.47 (m, 6H), 7.43−7.32 (m, 3H), 7.30−7.28 (m, 2H), 7.14−7.11 (m, 2H), 6.57 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 146.4, 139.9, 138.1, 136.4, 136.1, 135.3, 133.1, 130.1, 129.2, 128.8, 127.8, 127.7, 127.6, 127.5, 126.6, 124.7, 122.1, 119.2; IR (thin film) 3058, 1599, 1458, 1230, 961, 750, 691 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{19}BrNO$ $(M + H)^+$ 404.0650, found 404.0641; mp125−126 °C.

*N-((1E,4E,6E)-1,7-Diphenylhepta-1,4,6-trien-3-ylidene)aniline oxide (**3n**):* 0.118 g, 67% yield (E/Z = 1/1), yellow solid; isomer 1, ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.51−7.44 (m, 6H), 7.41−7.31 (m, 4H), 7.30−7.28 (m, 2H), 7.18 (d, J = 15.5 Hz, 1H), 6.95 (d, J = 16.5 Hz, 1H), 6.83−6.80 (m, 2H), 6.61 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 146.4, 139.4, 137.1, 136.6, 136.3, 134.4, 129.6, 129.3, 129.2, 128.9, 128.8, 128.4, 128.3, 127.5, 126.8, 124.7, 122.9, 119.3; isomer 2, ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.51−7.44 (m, 6H), 7.41−7.31 (m, 4H), 7.30−7.28 (m, 2H), 7.14 (d, J = 16.0 Hz, 1H), 7.12 (d, J = 16.0 Hz, 1H), 6.72−6.58 (m, 2H), 6.25 (d, J = 15.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 146.1, 140.1, 136.7, 136.6, 136.1, 135.2, 129.7, 129.3, 129.1, 128.9, 128.8, 128.4, 128.3, 126.9, 126.7, 124.8, 124.1, 120.7; IR (thin film) 3023, 1591, 1487, 1228, 971, 747, 690 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}NO$ $(M + H)^+$ 352.1701, found 352.1699; mp 62−63 °C.

*N-((1E,4E)-1,5-Diphenylpenta-1,4-dien-3-ylidene)-4-methoxyaniline oxide (**3ab**):* 0.133 g, 74% yield, yellow solid; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63−7.60 (m, 3H), 7.53 (d, J = 16.0 Hz, 1H), 7.47 (d, J = 9.0 Hz, 2H), 7.40−7.37 (m, 2H), 7.35−7.28 (m, 6H), 6.99 (d, J = 16.0 Hz, 1H), 6.95 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 16.0 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 146.3, 139.8, 139.3, 136.6, 136.2, 124.5, 129.1, 129.0, 128.9, 128.8, 127.4, 126.8, 126.2, 120.9, 119.9, 114.1, 55.6; IR (thin film) 3056, 2835, 1599, 1503, 1251, 963, 837, 762, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{22}NO_2$ $(M + H)^+$ 356.1651, found 356.1646; mp 151−153 °C.

*N-((1E,4E)-1,5-Diphenylpenta-1,4-dien-3-ylidene)-4-methylaniline oxide (**3ac**):* 0.120 g, 71% yield, yellow solid; ^1H NMR (500 MHz,

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$CDCl_3$) δ 7.64−7.60 (m, 3H), 7.56 (d, J = 16.5 Hz, 1H), 7.40−7.38 (m, 4H), 7.35−7.28 (m, 6H), 7.25−7.24 (m, 2H), 6.99 (d, J = 16.0 Hz, 1H), 6.70 (d, J = 16.0 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 144.2, 139.9, 139.4, 136.6, 136.2, 134.5, 129.7, 129.1, 129.0, 128.9, 128.8, 127.4, 126.9, 124.5, 120.8, 119.7, 21.3; IR (thin film) 3057, 2950, 1602, 1499, 1230, 964, 762, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{22}NO$ (M + H)$^+$ 340.1701, found 340.1697; mp 170−171 °C.

*4-tert-Butyl-N-((1E,4E)-1,5-diphenylpenta-1,4-dien-3-ylidene)-aniline oxide (**3ad**):* 0.148 g, 78% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65−7.61 (m, 3H), 7.54 (d, J = 16.5 Hz, 1H), 7.47−7.43 (m, 4H), 7.41−7.38 (m, 2H), 7.35−7.28 (m, 7H), 7.01 (d, J = 16.0 Hz, 1H), 6.72 (d, J = 16.5 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 146.6, 144.0, 139.5, 136.5, 136.2, 134.8, 129.7, 129.1, 128.9, 128.8, 127.5, 126.9, 126.1, 124.3, 120.8, 119.8, 31.2; IR (thin film) 3053, 2867, 1604, 1499, 1381, 1235, 966, 752, 691 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{28}NO$ (M + H)$^+$ 382.2171, found 382.2149; mp 150−152 °C.

*4-Chloro-N-((1E,4E)-1,5-diphenylpenta-1,4-dien-3-ylidene)aniline oxide (**3ae**):* 0.127 g, 71% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62−7.57 (m, 4H), 7.48−7.31 (m, 12H), 7.02 (d, J = 16.5 Hz, 1H), 6.65 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 144.8, 140.1, 136.3, 135.8, 135.6, 135.5, 129.4, 129.3, 129.1, 128.9, 128.8, 127.5, 126.9, 126.1, 120.1, 119.4; IR (thin film) 3059, 1614, 1448, 1229, 967, 757, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{19}ClNO$ (M + H)$^+$ 360.1155, found 360.1149; mp 169−170 °C.

*N-((1E,4E)-1,5-Diphenylpenta-1,4-dien-3-ylidene)-4-fluoroaniline oxide (**3af**):* 0.125 g, 73% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.60 (m, 3H), 7.56 (d, J = 16.5 Hz, 1H), 7.53−7.51 (m, 2H), 7.41−7.38 (m, 2H), 7.36−7.30 (m, 6H), 7.17 (t, J = 8.5 Hz, 2H), 7.01 (d, J = 16.0 Hz, 1H), 6.65 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6 (d, J = 249.6 Hz), 146.8, 142.6 (d, J = 3.6 Hz), 139.9, 136.3, 135.8, 135.3, 129.2 (d, J = 31 Hz), 128.9, 128.8, 127.5, 126.9, 126.8, 126.7, 120.2, 119.4, 116.2 (d, J = 23 Hz); IR (thin film) 3061, 1598, 1498, 1228, 967, 760, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{19}FNO$ (M + H)$^+$ 344.1451, found 344.1436; mp 180−182 °C.

*N-((1E,4E)-1,5-Diphenylpenta-1,4-dien-3-ylidene)-3-nitroaniline oxide (**3ag**):* 0.120 g, 65% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.33 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 7.5 Hz, 1H), 7.65−7.62 (m, 4H), 7.43−7.36 (m, 4H), 7.32−7.31 (m, 5H), 7.07 (d, J = 16.5 Hz, 1H), 6.60 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 147.7, 147.0, 141.0, 137.0, 136.1, 135.5, 130.6, 130.2, 129.6, 129.4, 129.0, 128.9, 127.7, 127.0, 124.3, 120.4, 119.3, 119.1; IR (thin film) 3058, 1651, 1576, 1228, 967, 753, 692 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{19}N_2O_3$ (M + H)$^+$ 371.1396, found 371.1376; mp 135−136 °C.

*N-((1E,4E)-1,5-Diphenylpenta-1,4-dien-3-ylidene)-3,5-dimethylaniline oxide (**3ah**):* 0.123 g, 70% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 7.41−7.38 (m, 2H), 7.35−7.29 (m, 6H), 7.09 (s, 2H), 7.07 (s, 1H), 6.99 (d, J = 16.0 Hz, 1H), 6.69 (d, J = 16.5 Hz, 1H), 2.34 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 139.5, 139.2, 136.6, 136.2, 134.4, 131.3, 129.1, 128.9, 128.8, 128.7, 127.5, 126.9, 122.2, 120.7, 119.4, 21.2; IR (thin film) 3018, 2919, 2863, 1594, 1472, 1272, 960, 756, 692 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{24}NO$ (M + H)$^+$ 354.1858, found 354.1837; mp 138−139 °C.

*N-((1E,4E)-1,5-Diphenylpenta-1,4-dien-3-ylidene)-2-methylaniline oxide (**3ai**):* 0.110 g, 65% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 16.5 Hz, 1H), 7.64−7.61 (m, 3H), 7.41−7.38 (m, 2H), 7.36−7.34 (m, 2H), 7.32−7.31 (m, 3H), 7.28−7.25 (m, 3H), 7.23 (d, J = 7.5 Hz, 2H), 7.00 (d, J = 16.0 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 145.2, 139.6, 136.4, 136.0, 134.8, 131.9, 131.4, 129.4, 129.1, 128.9, 128.8, 127.9, 127.4, 127.1, 126.8, 124.3, 119.4, 118.3, 16.9; IR (thin film) 3058, 2926, 1609, 1576, 1449, 1229, 965, 759, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{22}NO$ (M + H)$^+$ 340.1701, found 340.1683; mp 169−170 °C.

*N-((1E,4E)-1,5-Diphenylpenta-1,4-dien-3-ylidene)-4-(trifluoromethyl)aniline oxide (**3aj**):* 0.114 g, 58% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.5 Hz, 2H), 7.66−7.60 (m, 5H), 7.45−7.31 (m, 9H), 7.05 (d, J = 16.0 Hz, 1H), 6.62 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 147.4, 140.6, 136.3, 136.2, 135.6, 132.0 (q, J = 32 Hz), 129.5, 129.2, 128.9, 128.8, 127.6, 126.9, 126.5 (q, J = 3.6 Hz), 125.3, 124.5 (q, J = 270.6 Hz), 119.6, 119.1; IR (thin film) 3018, 1619, 1574, 1487, 1229, 951, 766, 694 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{19}F_3NO$ (M + H)$^+$ 394.1419, found 394.1398; mp 147−148 °C.

*4-Bromo-N-((1E,4E)-1,5-diphenylpenta-1,4-dien-3-ylidene)aniline oxide (**3ak**):* 0.137 g, 68% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62−7.57 (m, 6H), 7.42−7.38 (m, 4H), 7.36−7.32 (m, 6H), 7.02 (d, J = 16.0 Hz, 1H), 6.65 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 145.3, 140.1, 136.3, 135.8, 135.6, 132.4, 129.3, 129.1, 128.9, 128.8, 127.5, 126.9, 126.4, 123.6, 120.1, 119.4; IR (thin film) 3057, 1579, 1481, 1228, 965, 756, 694 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{19}BrNO$ (M + H)$^+$ 404.0650, found 404.0648; mp 173−174 °C.

*3-Bromo-N-((1E,4E)-1,5-diphenylpenta-1,4-dien-3-ylidene)aniline oxide (**3al**):* 0.145 g, 72% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.63 (d, J = 7.0 Hz, 2H), 7.59−7.58 (m, 3H), 7.42−7.31 (m, 10H), 7.02 (d, J = 16.0 Hz, 1H), 6.64 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 147.0, 140.2, 136.2, 135.8, 135.7, 132.8, 130.3, 129.3, 129.1, 128.9, 128.8, 128.0, 127.5, 126.9, 123.3, 122.7, 119.9, 119.1; IR (thin film) 3042, 1577, 1452, 1226, 964, 755, 692 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{19}BrNO$ (M + H)$^+$ 404.0650, found 404.0628; mp 149−151 °C.

*2-Bromo-N-((1E,4E)-1,5-diphenylpenta-1,4-dien-3-ylidene)aniline oxide (**3am**):* 0.177 g, 88% yield, yellow solid; ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.74 (d, J = 17.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.64−7.61 (m, 3H), 7.48−7.45 (m, 2H), 7.41−7.25 (m, 9H), 7.03 (d, J = 16.0 Hz, 1H), 6.45 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 145.2, 140.3, 136.4, 135.9, 133.9, 130.5, 129.3, 129.0, 128.9, 128.8, 128.4, 128.3, 127.6, 126.9, 126.3, 119.0, 118.1, 117.4; IR (thin film) 3045, 3001, 1604, 1574, 1477, 1238, 973, 754, 689 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{19}BrNO$ (M + H)$^+$ 404.0650, found 404.0625; mp 126−128 °C.

*N-((1E,4E)-1,5-Diphenylpenta-1,4-dien-3-ylidene)thiophen-3-amine oxide (**3an**):* 0.073 g, 44% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 17.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.53−7.48 (m, 2H), 7.40−7.31 (m, 10H), 7.03 (d, J = 16.0 Hz, 1H), 6.87 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 144.8, 139.9, 136.4, 135.9, 135.4, 129.2, 129.0, 128.9, 128.8, 127.5, 126.9, 125.8, 124.4, 121.4, 120.3, 119.7; IR (thin film) 3040, 1614, 1574, 1448, 1232, 966, 760, 693 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{18}SNO$ (M + H)$^+$ 332.1109, found 332.1092; mp 154−156 °C.

*N-((1E,4E)-1,5-Diphenylpenta-1,4-dien-3-ylidene)-4-(methoxycarbonyl)aniline oxide (**3ao**):* 0.155 g, 81% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.5 Hz, 2H), 7.63−7.57 (m, 6H), 7.42−7.34 (m, 4H), 7.33−7.27 (m, 5H), 7.03 (d, J = 16.0 Hz, 1H), 6.62 (d, J = 16.0 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 149.5, 147.1, 140.3, 136.2, 135.8, 135.7, 131.1, 130.7, 129.4, 129.1, 128.9, 128.8, 127.5, 126.9, 124.9, 119.9, 119.2, 52.4; IR (thin film) 3054, 2949, 1721, 1601, 1279, 964, 757, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}NO_3$ (M + H)$^+$ 384.1600, found 384.1593; mp 101−102 °C.

*N-((E)-1,3-Diphenylallylidene)aniline oxide (**3o**):* 0.097 g, 65% yield (E/Z = 10:1), yellow solid; E isomer (major), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 16.5 Hz, 1H), 7.56−7.52 (m, 3H), 7.35−7.27 (m, 7H), 7.22−7.16 (m, 5H), 6.72 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 147.0, 140.6, 136.2, 132.7, 130.7, 129.2, 128.8, 128.7, 128.6, 128.5, 128.3, 127.6, 124.8, 121.9; Z isomer (minor), ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (d, J = 16.0 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H); IR (thin film) 3051, 1592, 1497, 1235, 971, 768, 693 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{18}NO$ (M + H)$^+$ 300.1388, found 300.1368; mp 104−105 °C.

*N-((E)-3-(4-Methoxyphenyl)-1-phenylallylidene)aniline oxide (**3p**):* 0.069 g, 42% yield (E/Z = 12/1), yellow solid; E isomer (major) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 16.0 Hz, 1H), 7.49 (d, J = 9.0 Hz, 2H), 7.27−7.26 (m, 5H), 7.19−7.16 (m, 5H), 6.88 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 16.5 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR

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(125 MHz, $CDCl_3$) δ 160.7, 150.1, 147.0, 140.6, 132.9, 130.8, 130.0, 129.2, 129.1, 128.8, 128.5, 128.3, 124.9, 119.9, 114.2, 55.3; *Z* isomer (minor), ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.36 (d, J = 15.5 Hz, 1H), 3.76 (s, 3H); IR (thin film) 3053, 2836, 1590, 1509, 1239, 974, 760, 696 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{20}NO_2$ (M + H)$^+$ 330.1494, found 330.1490; mp 112−113 °C.

*N-((E)-1,3-Diphenylallylidene)-4-methoxyaniline oxide (**3q**):* 0.087 g, 53% yield (*E*/*Z* = 8/1), yellow solid; *E* isomer (major), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 16.5 Hz, 1H), 7.53 (d, J = 7.0 Hz, 2H), 7.35−7.28 (m, 8H), 7.21−7.17 (m, 4H), 6.70−6.67 (m, 3H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 149.2, 140.2, 136.3, 133.1, 130.7, 129.1, 128.8, 128.7, 128.4, 127.5, 126.1, 122.3, 114.3, 113.5, 55.3; *Z* isomer (minor), ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.40 (d, J = 16.0 Hz, 1H), 3.89 (s, 3H); IR (thin film) 3034, 2836, 1603, 1501, 1238, 971, 752, 693 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{20}NO_2$ (M + H)$^+$ 330.1494, found 330.1487; mp 155−157 °C.

*N-((E)-1,3-Diphenylallylidene)-2-methylaniline oxide (**3r**):* 0.049 g, 31% yield (*E*/*Z* = 8:1), yellow solid; *E* isomer (major), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 16.5 Hz, 1H), 7.53 (d, J = 7.0 Hz, 2H), 7.34−7.27 (m, 3H), 7.24−7.23 (m, 3H), 7.17−7.16 (m, 2H), 7.09−7.08 (m, 3H), 7.01−6.98 (m, 1H), 6.69 (d, J = 16.5 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 145.7, 140.7, 136.0, 132.0, 131.6, 130.9, 129.9, 129.2, 128.9, 128.6, 128.5, 128.1, 127.5, 126.0, 125.0, 121.1, 17.2; IR (thin film) 3058, 2933, 2858, 1599, 1496, 1271, 968, 772, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{20}NO$ (M + H)$^+$ 314.1545, found 314.1534; mp 62−63 °C.

(1*E*,2*E*)-Chalcone *O*-phenyl Oxime (4a). This compound was prepared as detailed in Table 1, entry 2, in 40% yield as a yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.49 (d, J = 17.0 Hz, 1H), 7.42−7.30 (m, 10H), 7.27−7.24 (m, 1H), 7.18 (d, J = 16.5 Hz, 1H), 7.06 (t, J = 7.0 Hz, 1H), 7.02 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 156.6, 138.3, 136.4, 136.3, 136.0, 129.2, 128.9, 128.8, 128.7, 127.5, 127.4, 127.1, 122.4, 121.6, 117.4, 115.0; IR (thin film) 3033, 1588, 1485, 1212, 969, 753, 690 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{20}NO$ (M + H)$^+$ 326.1545, found 326.1536; mp 88−89 °C.

(*E*)-4-Phenyl-2-styrylquinoline (5).[31] This compound was prepared as follows. Nitrone **3a** (0.065 g, 0.20 mmol) was dissolved in toluene (2 mL), and the mixture was stirred at 100 °C. The reaction was monitored by TLC until the nitrone was consumed completely. At this time, the toluene was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded on silica gel; 1/20 ethyl acetate/petroleum ether) to afford **5** as a yellow oil (0.033 g, 56%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 7.5 Hz, 2H), 7.52 (s, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.35−7.30 (m, 7H), 7.21 (d, J = 16.5 Hz, 1H), 7.13−7.10 (m, 1H), 6.93 (d, J = 7.5 Hz, 2H), 6.78 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 150.7, 138.4, 138.0, 136.1, 135.7, 129.7, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 127.5, 127.3, 125.9, 123.8, 122.3, 120.9; IR (thin film) 3055, 1620, 1591, 1493, 1284, 974, 757, 694 cm^{-1}.

(*E*)-*N*-Phenyl-*N*-styryl-*N*′-*p*-tolylcinnamimidamide (6). This compound was prepared as follows. Nitrone **3a** (0.065 g, 0.20 mmol) and isocyanate (0.079 mg, 0.6 mmol) were dissolved in toluene (2 mL). The mixture was stirred at 80 °C. The reaction was monitored by TLC until the nitrone was consumed completely. At this time, the toluene was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded on silica gel; 1/20 ethyl acetate/petroleum ether) to afford **6** as a yellow oil (0.079g, 96%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 14.5 Hz, 1H), 7.41−7.38 (m, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.27−7.18 (m, 8H), 7.09−7.05 (m, 3H), 6.98−6.97 (m, 2H), 6.85 (d, J = 7.5 Hz, 2H), 6.58 (d, J = 16.0 Hz, 1H), 6.18 (d, J = 16.5 Hz, 1H), 5.66 (d, J = 14.5 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 147.3, 141.6, 140.4, 137.4, 135.6, 132.4, 131.9, 129.4, 129.3, 128.8, 128.6, 128.5, 128.4, 126.9, 126.8, 125.6, 125.3, 121.9, 119.1, 112.1, 20.8; IR (thin film) 3027, 2924, 2858, 1638, 1495, 1327, 746 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{27}N_2$ (M + H)$^+$ 415.2174, found 415.2160.

(*E*)-Butyl 4-Phenyl-2-styryl-4,9-dihydro-3*H*-carbazole-1-carboxylate (7). This compound was prepared as follows. Nitrone **3a** (0.065 g, 0.20 mmol), SiO_2 (200 mg), and allene (0.056 mg, 0.4 mmol) were placed in a round-bottle flask. Toluene (2 mL) was added, and the mixture was stirred at 80 °C. The reaction was monitored by TLC until the nitrone was consumed completely. At this time, the toluene was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded on silica gel; 1/10 ethyl acetate/petroleum ether) to afford **7** as a red-brown oil (0.057 g, 64%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.07 (d, J = 16.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.37−7.31 (m, 7H), 7.28−7.24 (m, 2H), 7.10−7.07 (m, 1H), 6.98 (d, J = 16.5 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 4.46 (t, J = 6.0 Hz, 2H), 4.41 (dd, J = 10.5 Hz, 7.5 Hz, 1H), 3.31 (dd, J = 16.5 Hz, 7.5 Hz, 1H), 3.11 (dd, J = 16.5 Hz, 6.0 Hz, 1H), 1.87−1.84 (m, 2H), 1.56−1.52 (m, 2H), 1.02 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 144.3, 141.6, 137.2, 136.6, 133.3, 132.3, 128.7, 128.6, 128.3, 128.0, 127.1, 127.0, 126.7, 125.8, 122.2, 119.6, 119.5, 119.4, 113.8, 111.1, 65.4, 38.4, 36.4, 30.8, 19.5, 13.7; IR (thin film) 3427, 3055, 2956, 2871, 1670, 1599, 1270, 740, 690 cm^{-1}; HRMS (ESI) m/z calcd for $C_{31}H_{30}NO_2$ (M + H)$^+$ 448.2277, found 448.2268.

General Procedure for the Preparation of Oximes 1.[20] A solution of synthesized ketones (10.0 mmol), NH_2OH·HCl (1.42 g, 20.0 mmol), and pyridine (2.4 mL, 30.0 mmol) in MeOH (30 mL) was stirred at room temperature for about 18−24 h. The reaction mixture was evaporated to remove MeOH in vacuo, and to the residue was then added water (50 mL). After extraction with DCM (50 mL × 2), the combined organic layers were washed with brine, dried over $MgSO_4$, and filtered. Volatiles were then removed under vacuum, and the crude product mixture was purified by medium-pressure chromatography (1/20−1/3; ethyl acetate/petroleum ether) to give oxime **1** as a white solid or yellow solid.

*(1E,4E)-1,5-Bis(4-(trifluoromethyl)phenyl)penta-1,4-dien-3-one oxime (**1d**):* 1.47 g, 38% yield, white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 4H), 7.61−7.59 (m, 4H), 7.45 (d, J = 16.5 Hz,1H), 7.17 (d, J = 16.5 Hz, 1H), 7.15 (d, J = 16.5 Hz, 1H), 6.99 (d, J = 16.5 Hz, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 139.5, 139.3, 136.0, 133.8, 131.0 (q, J = 32 Hz), 127.4, 127.1, 125.8 (q, J = 3.6 Hz), 125.1, 125.0 (q, J = 276 Hz), 124.2, 122.9, 122.8, 118.8; IR (thin film) 3320, 3060, 1616, 1447, 1329, 1168, 970, 826 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{14}F_6NO$ (M + H)$^+$ 386.0980, found 386.0976; mp 164−165 °C.

*(1E,4E)-1,5-Bis(3-bromophenyl)penta-1,4-dien-3-one oxime (**1e**):* 1.1 g, 27% yield, white solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.7 (s, 1H), 7.87 (d, J = 16.5 Hz, 2H), 7.66 (t, J = 9.5 Hz, 2H), 7.52 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.38−7.31 (m, 3H), 7.28 (d, J = 16.5 Hz, 1H), 7.11 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 151.7, 139.0, 138.9, 134.1, 131.2, 130.8, 130.7, 130.6, 129.8, 129.4, 125.9, 125.8, 124.4, 122.2, 118.1; IR (thin film) 3184, 3070 1589, 1564, 1255, 969, 777, 684 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{14}Br_2NO$ (M + H)$^+$ 405.9442, found 405.9442; mp 131−132 °C.

*(1E,4E)-1,5-Bis(2-bromophenyl)penta-1,4-dien-3-one oxime (**1f**):* 1.15 g, 29% yield, white solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.8 (s, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 6.5 Hz, 1H), 7.68−7.64 (m, 2H), 7.46−7.39 (m, 4H), 7.32−7.24 (m, 3H), 7.07 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 152.1, 135.7, 135.6, 133.7, 133.0, 132.9, 130.6, 130.5, 130.0, 128.2, 128.1, 127.5, 127.3, 126.1, 123.7, 123.5, 120.0; IR (thin film) 3260, 3056, 1626, 1586, 1463, 1252, 965, 745 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{14}Br_2NO$ (M + H)$^+$ 405.9442, found 405.9433; mp 148−149 °C.

*(1E,4E)-1-(4-Bromophenyl)-5-phenylpenta-1,4-dien-3-one oxime (**1k**):* 1.20 g, 37% yield (*E*/*Z* = 1/1), white solid; isomer 1, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.46 (m, 4H), 7.39−7.29 (m, 6H), 7.11 (d, J = 16.0 Hz, 1H), 7.08 (d, J = 16.0 Hz, 1H), 6.90 (d, J = 16.0 Hz, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 137.6, 136.2, 135.4, 135.3, 133.9, 131.9, 128.7, 128.4, 127.0, 122.7, 121.7, 116.6; isomer 2, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.46 (m, 4H), 7.39−7.29 (m, 6H), 7.13 (d, J = 16.0 Hz, 1H), 7.06 (d, J = 16.0 Hz, 1H), 6.90 (d, J = 16.0 Hz, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 137.6, 136.0, 135.4, 135.0, 133.9, 131.8, 129.1, 128.6, 127.3, 123.1, 122.4, 117.4; IR (thin film) 3167, 3055, 1637,

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1582, 1486, 1255, 970, 749, 687 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{15}BrNO$ $(M + H)^+$ 328.0337, found 328.0328; mp 136−137 °C.

*(1E,4E)-1-(3-Bromophenyl)-5-phenylpenta-1,4-dien-3-one oxime (**1l**):* 1.42 g, 43% yield (*E*/*Z* = 1/1), white solid; isomer 1, ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.45−7.29 (m, 6H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 16.0 Hz, 1H), 7.07 (d, *J* = 16.0 Hz, 1H), 6.91 (d, *J* = 16.5 Hz, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 138.5, 137.7, 136.0, 135.4, 133.5, 131.8, 130.2, 129.7, 128.8, 127.0, 125.6, 123.4, 121.8, 118.1; isomer 2, ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.45−7.29 (m, 6H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 16.5 Hz, 1H), 7.05 (d, *J* = 16.5 Hz, 1H), 6.90 (d, *J* = 16.5 Hz, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 138.3, 137.7, 136.2, 136.0, 133.5, 131.3, 130.1, 129.1, 128.6, 127.4, 125.9, 122.9, 121.8, 116.5; IR (thin film) 3174, 3055, 1639, 1584, 1445, 1256, 968, 774, 681 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{15}BrNO$ $(M + H)^+$ 328.0337, found 328.0328; mp 109−111 °C.

*(1E,4E)-1-(2-Bromophenyl)-5-phenylpenta-1,4-dien-3-one oxime (**1m**):* 1.04 g, 33% yield (*E*/*Z* = 1/1), white solid; isomer 1, ^1H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.60−7.46 (m, 3H), 7.43−7.28 (m, 5H), 7.21−7.09 (m, 2H), 6.96 (d, *J* = 16.0 Hz, 1H), 6.85 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 149.4, 137.7, 136.4, 135.4, 133.0, 130.0, 128.7, 128.5, 127.3, 127.0, 125.2, 123.8, 122.1, 119.5; isomer 2, ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.60−7.46 (m, 3H), 7.43−7.28 (m, 5H), 7.21−7.09 (m, 2H), 6.98 (d, *J* = 16.0 Hz, 1H), 6.88 (d, *J* = 16.0 Hz, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 149.4, 137.7, 136.2, 135.4, 132.8, 129.5, 129.0, 128.5, 127.4, 127.1, 125.1, 124.6, 122.2, 116.5; IR (thin film) 3163, 3057, 1623, 1491, 1461, 1292, 966, 749, 690 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{15}BrNO$ $(M + H)^+$ 328.0337, found 328.0328; mp 68−70 °C.

*(1E,4E,6E)-1,7-Diphenylhepta-1,4,6-trien-3-one oxime (**1n**):* 1.5 g, 55% yield (*E*/*Z* = 1/1), white solid; isomer 1, ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.44−7.42 (m, 2H), 7.38−7.31 (m, 6H), 7.30−7.24 (m, 2H), 7.11 (d, *J* = 16.5 Hz, 1H), 7.00−6.91 (m, 2H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.69 (d, *J* = 15.0 Hz, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 138.0, 137.3, 136.9, 135.4, 134.8, 128.9, 128.7, 128.6, 128.4, 128.3, 127.3, 126.8, 125.7, 120.1; isomer 2, ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 2H), 7.44−7.42 (m, 2H), 7.38−7.31 (m, 6H), 7.30−7.24 (m, 2H), 7.12 (d, *J* = 16.5 Hz, 1H), 7.00−6.91 (m, 2H), 6.84 (d, *J* = 16.0 Hz, 1H), 6.50 (d, *J* = 15.0 Hz, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 136.9, 136.5, 136.4, 135.4, 134.8, 128.9, 128.7, 128.6, 128.5, 128.0, 127.0, 126.6, 122.0, 116.8; IR (thin film) 3241, 3021, 1605, 1490, 1297, 985, 750, 689 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{18}NO$ $(M + H)^+$ 276.1388, found 276.1380; mp 137−139 °C.

General Procedure for the Preparation of Diaryliodonium Salts 2. Arylboronic acid (10 mmol, 1.0 equiv) and CH_2Cl_2 (40 mL) were combined in a dried round-bottom flask. The mixture was cooled to 0 °C for 5 min, $BF_3{\cdot}OEt_2$ (1.12 mL, 1.10 equiv) was added, and the mixture was stirred for 10 min. A solution of 2-(diacetoxyiodo)arene (1.05 equiv) in CH_2Cl_2 (20 mL) was added slowly for 10−15 min and stirred for an additional 10 min. The mixture was then warmed to room temperature and stirred for 1 h. The reaction mixture was cooled to 0 °C again and TfOH (1.67 mL, 1.1 equiv) was added slowly into the mixture. Then the mixture was stirred for 10 min and warmed to room temperature for an additional 10 min. At this time, the solvent was removed under reduced pressure and the residue quickly run through a short SiO_2 column (about 5 cm high) with 5% of MeOH in CH_2Cl_2. The eluate was concentrated under vacuum, and Et_2O (100 mL) was added to the residue to precipitate a white solid. The precipitate was filtered to give the diaryliodonium salts **2** as white solids.

*(2-Bromophenyl)(4-methoxyphenyl)iodonium triflate (**2m**):* 4.0 g, 74% yield, white solid; ^1H NMR (500 MHz, DMSO-d_6) δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 9.0 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.5, 139.2, 137.5, 134.8, 134.0, 131.0, 127.2, 123.4, 118.0, 106.3, 56.1; IR (thin film) 3466, 3085, 2941, 2846, 1575, 1486, 1250, 828, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}BrIO$ $(M - OTf)^+$ 388.9038, found 388.9028; mp 171−172 °C.

*(4-Methoxyphenyl)(thiophen-3-yl)iodonium triflate (**2n**):* 2.7 g, 59% yield, white solid; ^1H NMR (500 MHz, DMSO-d_6) δ 8.57 (d, *J* = 6.5 Hz, 1H), 8.15 (d, *J* = 9.0 Hz, 2H), 7.79−7.77 (m, 1H), 7.67 (d, *J* = 4.5 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.8, 136.9, 135.3, 131.4, 130.6, 117.3, 106.2, 101.5, 55.6; IR (thin film) 3452, 3097, 2970, 2841, 1578, 1488, 1256, 823 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}IOS$ $(M - OTf)^+$ 316.9497, found 316.9486; mp 125−126 °C.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01716.

DFT calculation studies and NMR spectra of compounds **3a−r**, **3ab−ao**, **4a**, **5−7**, oximes **1d−f,k−n**, and diaryliodonium salts **2m,n** (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for B.C.: cberic@hotmail.com.
*E-mail for G.-F.S.: gfysglgx@163.com.
*E-mail for D.-L.M.: moeastlight@mailbox.gxnu.edu.cn.

Notes

The authors declare no competing financial interest.

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(15) Without KOH, no nitrone product was observed for 72 h or 5 days. The yield of *O*-arylation product was not improved even after 5 days, but some unknown byproducts were observed.

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