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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

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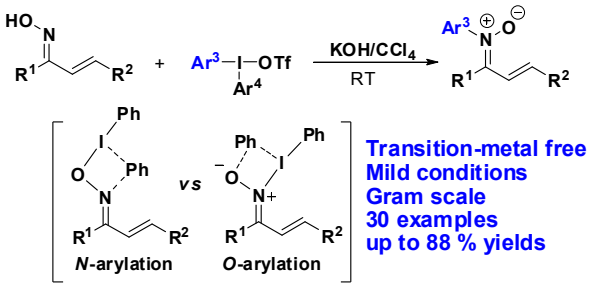


ABSTRACT: An efficient transition-metal free method for the preparation of *α,β*-unsaturated *N*-aryl ketonitrones under mild conditions has been developed. This reaction shows good functional group tolerance for both electron-rich and electron-deficient substituents on both oximes and diaryliodonium 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.

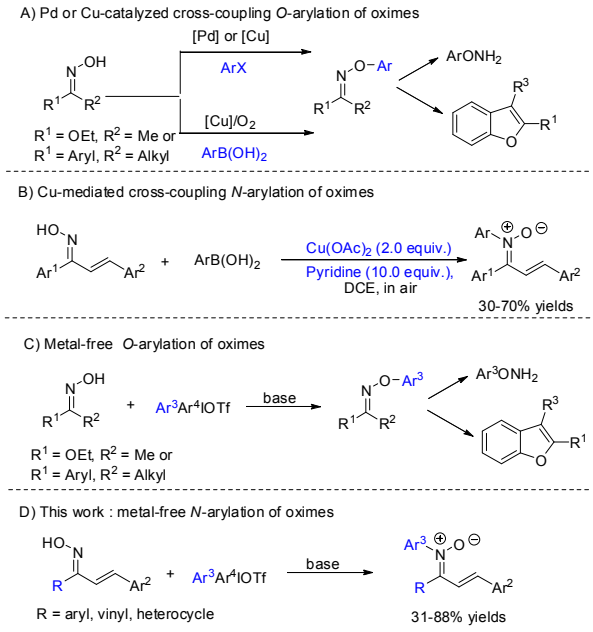
INTRODUCTION

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 aryl boronic 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 1-A).[4b] In addition, both Huang and Meyer have reported the copper-mediated coupling of oximes with arylboronic acids to form *O*-arylation products (Scheme 1-A).[5] More recently, Anderson and coworkers 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 1-B).[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 availabile reagents that exhibit high-reactivity and selectivity, good tolerance of a wide range of functional groups, and are considered to be non-toxic 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 1-C).[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 1-D). 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 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]

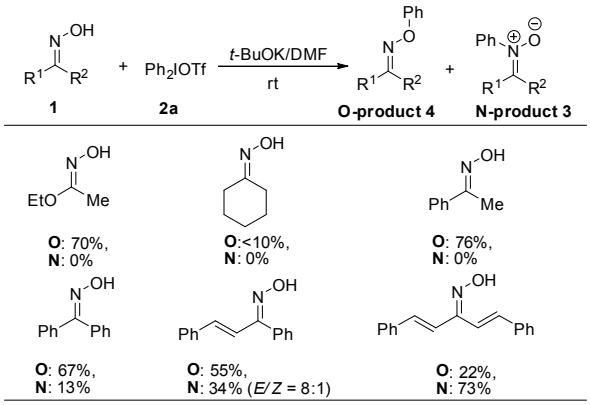


Scheme 1 Arylation Strategies of Oximes

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 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 the literature.[8b] In contrast, when cyclohexanone oxime was treated with diaryliodonium salt **2a**, the reaction mixture was complex and only <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

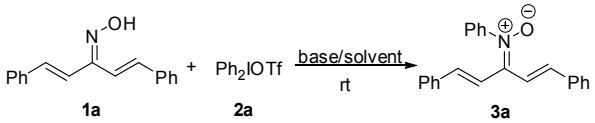
the major product. Encouraged by the observed switch in selectivity from *O*-arylation to *N*-arylation, we decided to optimize the reaction conditions of this *N*-arylation process.



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

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 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, 10 *vs* 11). The *N*-arylation reaction proceeded smoothly and provided analogous yields either in 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).

Table 1. Optimization of Reaction. [a]



Entry	Base	Solvent	Time (h)	**3a**, Yield %[b]
1	KOH	DMF	13	69

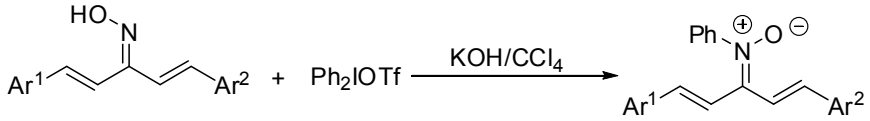
2	KOH	DMSO	13	45[c]
3	KOH	MeCN	1.5	60
4	KOH	THF	0.5	67
5	KOH	PhMe	1.6	70
6	KOH	DCE	2.5	64
7	KOH	CCl_4	2.5	75[d]
8	KOH	CCl_4	5	74[e]
9	*t*-BuOK	CCl_4	4	74
10	Cs_2CO_3	CCl_4	7.5	71
11	Pyridine	CCl_4	24	0
12	-	CCl_4	24	0

[a] Reaction conditions: oxime **1a** (0.5 mmol), Ph_2IOTf (1.5 equiv.), KOH (1.5 equiv.), CCl_4 (5 mL), rt. [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.

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 with *ortho-, meta-, 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 -1n** (*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 46% yield in CCl_4 (Table 2, entries 9). To our delight, the reaction tolerated heterocylic 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 enhances the potential synthetic applications of the nitrone products.

Table 2. The Scope of Oximes.[a]



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

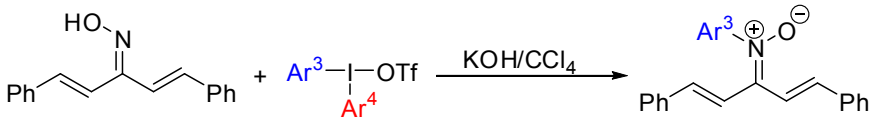
Entry	**1**	Ar^1	Ar^2	**3**	Yield %[b]
1	**1a**	Ph	Ph	**3a**	75
2	**1b**	4-MeO(C_6H_4)	4-MeO(C_6H_4)	**3b**	65 (39[c],56[d])
3	**1c**	4-Me(C_6H_4)	4-Me(C_6H_4)	**3c**	81 (41[d])
4	**1d**	4-CF_3(C_6H_4)	4-CF_3(C_6H_4)	**3d**	76 (61[d])
5	**1e**	3-Br(C_6H_4)	3-Br(C_6H_4)	**3e**	46 (52[c],50[d])
6	**1f**	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: oxime **1** (0.5 mmol), Ph_2IOTf (1.5 equiv.), KOH (1.5 equiv.), CCl_4 (5 mL), rt, 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.

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 aryl boronic acids.[13] As shown in the 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 *ortho*-methyl or *ortho*-bromo, and heterocyclic substituents also gave the desired nitrones (Table 3, entries 9, 14 and 15). Analogous challenging nitrones were obtained with 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 coworkers 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. The Scope of diaryliodionium salts [a]



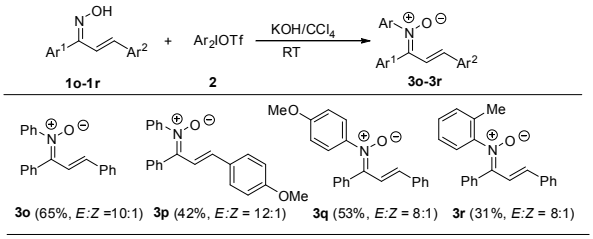
1a **2** **3ab-3ao**

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), rt, 0.5-24 h. [b] Isolated yields. [c] **3ab** was also obtained with 40% yield.

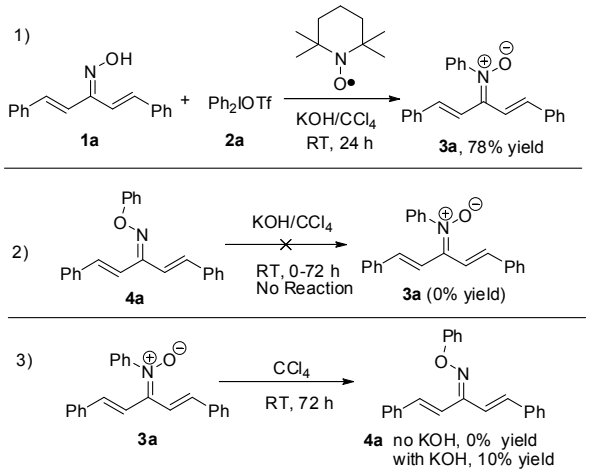
When chalcone oximes (**1o-1r**) were subjected to the optimal oxime *N*-arylation conditions described above, the desired products were obtained in moderate yields with the *E*-isomers as the major products (Scheme 3).[12] Interestingly, the *E/Z*-geometry ratio of the C=N bond in nitrones **3** ranged from 8:1 to 12:1 (**3o-3r**). 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-1r**.

When radical trap TEMPO (2.0 equiv.) was added into the reaction of oxime **1a** and iodonium salt **2a**, nitrone **3a** was still obtained in 78% yield for 24h (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

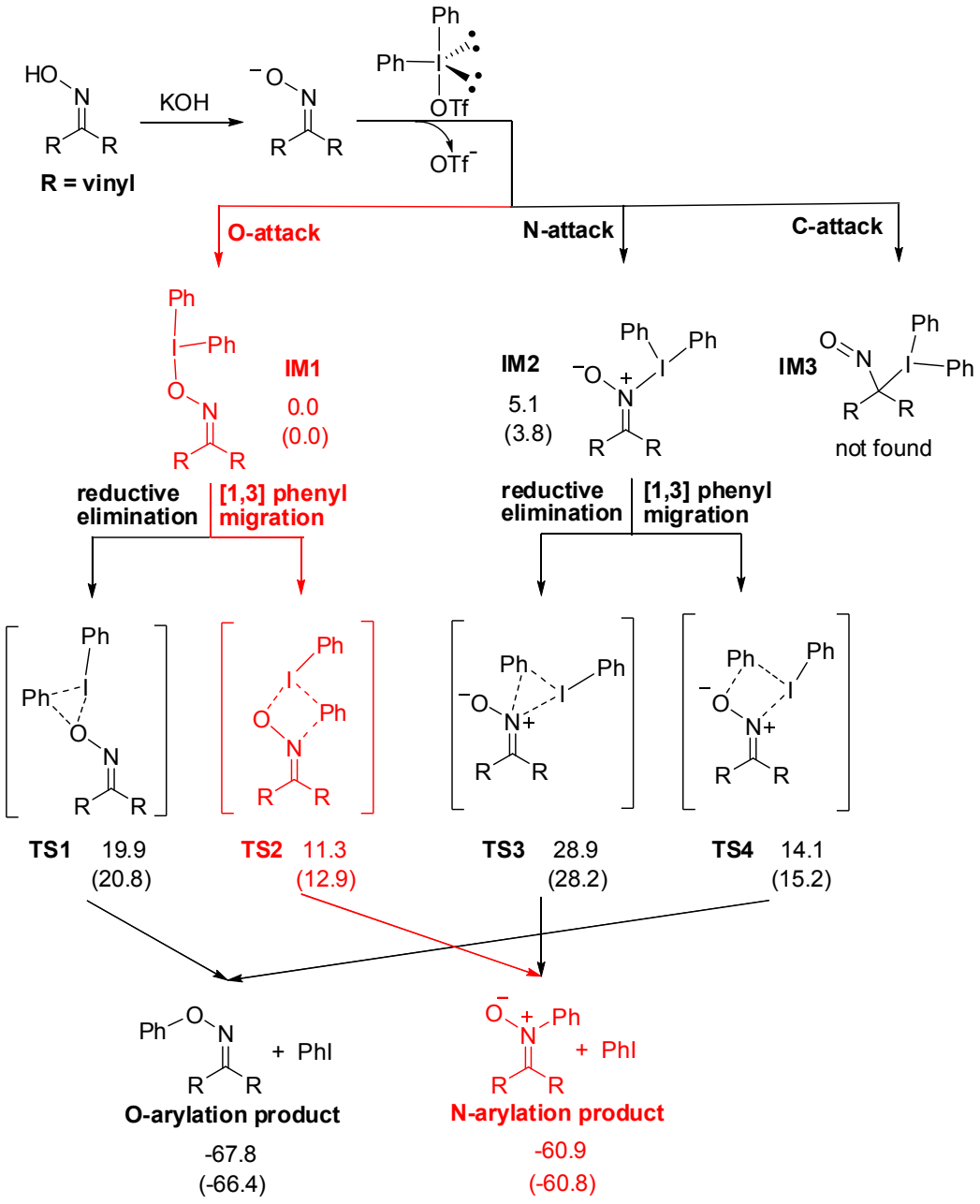
conditions for 72 h, nitrone **3a** was not observed and only starting material was recovered (Scheme 4-2). This experiment revealed that nitrone **3a** cannot be formed from a rearrangement of *O*-arylation product **4a**. However, when nitrone **3a** was subjected to the optimal condition, *O*-arylation 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.



Scheme 4. The Mechanism Studies.

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 nucleophiles, 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 **IM2** can be represented by a non-charge-separated Lewis structure while the **IM1** 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.



Scheme 5. Possible reaction pathways (R = vinyl), with calculated energies for intermediates, transition states and products. Free energies in both gas phase (ΔG_{gas})

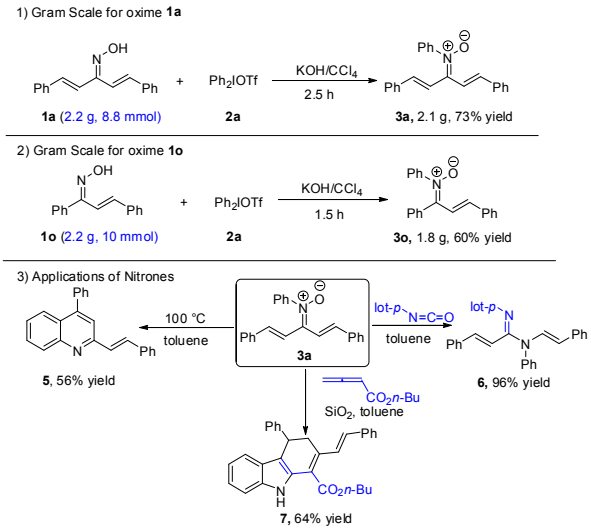
and in solvent (ΔG_{sol} in parenthesis) are given in units of kcal/mol. The most favorable pathway that gives *N*-arylation product is highlighted in red.

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 *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 *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 and 4-3).

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 oxime **1a** were 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).

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*-tolisocyanate, *N*-vinyl amidine **6** was isolated in excellent yield. When **3a** was treated with mono-substituted allenoate, dihydrocarbazole **7** was isolated with 64% yield. These quinoline, amidine and dihydrocarbazole products are important and useful intermediates in organic synthesis.[18] The facile method that we have developed for the synthesis of *N*-aryl nitrones will allow these important scaffolds to be studied more frequently.



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

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, includes 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 nitrones 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 MHz, 500MHz, or 600MHz instrument 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 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**, **1i**, **1j**, **1o** and **1p**,[6,20] **1b**,[21] **1c**,[22] **1g** and **1h**,[23] diaryliodonium salts **2a**, **2aa, 2c** and **2o**,[13a, 24] **2b**, **2d**, **2e**, **2f** and **2i**,[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 RT 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 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*-((1*E*,4*E*)-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; m.p: 163-164 ℃.

***N*-((1*E*,4*E*)-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; m.p: 150-152 °C.

***N*-((1*E*,4*E*)-1,5-Dip-tolylpenta-1,4-dien-3-ylidene)aniline oxide (3c)**, 0.143 g, 81% yield, yellow solid. ^1H 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; m.p: 146-147 °C.

***N*-((1*E*,4*E*)-1,5-Bis(4-(trifluoromethyl)phenyl)penta-1,4-dien-3-ylidene)aniline oxide (3d)**, 0.176 g, 76% yield, yellow solid. ^1H 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; m.p: 148-149 °C.

***N*-((1*E*,4*E*)-1,5-Bis(3-bromophenyl)penta-1,4-dien-3-ylidene)aniline oxide (3e)**, 0.110 g, 46% yield, yellow solid. ^1H 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 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{18}Br_2NO$ $(M+H)^+$ 481.9755, found 481.9761; m.p: 51-52 °C.

***N*-((1*E*,4*E*)-1,5-Bis(2-bromophenyl)penta-1,4-dien-3-ylidene)aniline oxide (3f)**, 0.164 g, 68% yield, yellow solid. ^{1}H 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; m.p: 118-119 °C.

***N*-((1*E*,4*E*)-1,5-Di(furan-2-yl)penta-1,4-dien-3-ylidene)aniline oxide (3g)**, 0.113 g, 74% yield, yellow solid. ^{1}H 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; m.p: 144-145 °C.

***N*-((1*E*,4*E*)-1,5-Di(thiophen-2-yl)penta-1,4-dien-3-ylidene)aniline oxide (3h)**, 0.126 g, 75% yield, yellow solid. ^{1}H 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; m.p: 140-141 °C

***N*-((1*E*,4*E*)-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*: ^{1}H 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*: ^{1}H 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; m.p: 54-55 °C.

***N*-((1*E*,4*E*)-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*: ^{1}H 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*: ^{1}H 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; m.p: 55-57 °C

***N*-((1*E*,4*E*)-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*: ^{1}H 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*: ^{1}H 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; m.p: 144-146 °C.

***N*-((1*E*,4*E*)-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; m.p: 147-149 °C.

***N*-((1*E*,4*E*)-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; m.p:125-126 °C.

***N*-((1*E*,4*E*,6*E*)-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; m.p: 62-63 °C.

***N*-((1*E*,4*E*)-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; m.p: 151-153 °C.

***N*-((1*E*,4*E*)-1,5-Diphenylpenta-1,4-dien-3-ylidene)-4-methylaniline oxide (3ac),** 0.120 g, 71% yield, yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): 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; m.p: 170-171 °C.

4-tert-Butyl-*N*-((1*E*,4*E*)-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; m.p: 150-152 °C.

4-Chloro-*N*-((1*E*,4*E*)-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; m.p: 169-170 °C.

***N*-((1*E*,4*E*)-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; m.p: 180-182 °C.

***N*-((1*E*,4*E*)-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; m.p: 135-136 °C.

***N*-((1*E*,4*E*)-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; m.p: 138-139 °C.

***N*-((1*E*,4*E*)-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; m.p: 169-170 °C.

***N*-((1*E*,4*E*)-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; m.p: 147-148 °C.

4-Bromo-*N*-((1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-ylidene)aniline oxide (3ak), 0.137 g, 68% yield, yellow solid. ^1H 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; m.p: 173-174 °C.

3-Bromo-*N*-((1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-ylidene)aniline oxide (3al), 0.145 g, 72% yield, yellow solid. ^1H 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; m.p: 149-151 °C.

2-Bromo-*N*-((1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-ylidene)aniline oxide (3am), 0.177 g, 88% yield, yellow solid. ^1H 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; m.p: 126-128 °C.

***N*-((1*E*,4*E*)-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; m.p: 154-156 °C.

***N*-((1*E*,4*E*)-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; m.p: 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)* based on: ^{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; m.p: 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 (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)* based on: ^{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; m.p: 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)* based on: ^{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; m.p: 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):* ^1H 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; m.p: 62-63 °C.

(1*E*,2*E*)-Chalcone *O*-phenyl oxime (4a) was prepared from **Table 1 entry 2** with 40% yield as yellow solid. ^1H 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; m.p: 88-89 °C.

(*E*)-4-Phenyl-2-styrylquinoline (5)[31] was prepared as follow. Nitrone **3a** (0.065 g, 0.20 mmol) was dissolved in toluene (2 mL), and the mixture was stirring 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 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 yellow oil (0.033g, 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) was prepared as follow. 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 stirring 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 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 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-3H-carbazole-1-carboxylate (7) was prepared as follow. Nitrone **3a** (0.065 g, 0.20 mmol), SiO_2 (200 mg) and allene (0.056 mg, 0.4 mmol) were placed into a round-bottle flask. Toluene (2 mL) was added and the mixture was stirring 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 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 red-brown oil (0.057g, 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), $NH_2OH{\cdot}HCl$ (1.42 g, 20.0 mmol) and pyridine (2.4 mL, 30.0 mmol) in MeOH (30 mL) was stirring at RT for about 18-24 h. The reaction mixture was evaporated to remove MeOH in vacuo, and the residue was then added water (50

mL). Extracted 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 white solid or yellow solid.

(1*E*,4*E*)-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; m.p: 164-165 °C.

(1*E*,4*E*)-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; m.p: 131-132 °C.

(1*E*,4*E*)-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; m.p: 148-149 °C.

(1*E*,4*E*)-1-(4-Bromophenyl)-5-phenylpenta-1,4-dien-3-one oxime (1k), 1.20g, 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, 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; m.p: 136-137 °C.

(1*E*,4*E*)-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:* ^{1}H 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:* ^{1}H 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; m.p: 109-111 °C.

(1*E*,4*E*)-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:* ^{1}H 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:* ^{1}H 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; m.p: 68-70 °C.

(1*E*,4*E*,6*E*)-1,7-Diphenylhepta-1,4,6-trien-3-one oxime (1n), 1.5 g, 55% yield (*E/Z* = 1:1), white solid. *isomer 1:* ^{1}H 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:* ^{1}H 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; m.p: 137-139 °C.

General Procedure for the Preparation of diaryliodonium salts 2: Aryl boronic 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•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 additional 10 min. The mixture was then warmed to room temperature and stirred for 1 h. The reaction was cooled to 0 °C again and TfOH (1.67 mL, 1.1 equiv) was added slowly into the mixture. Then stirring the mixture for 10

min and warmed to room temperature for additional 10 min. At this time, removed the solvent under reduced pressure and ran through a short SiO_2 column (about 5 cm high) with 5% of MeOH in CH_2Cl_2 quickly. Concentrated under vacuum and Et_2O (100 mL) was added to the residual to precipitate a white solid. Filtrated and obtained the diaryliodonium salts **2** as white solid.

(2-Bromophenyl)(4-methoxyphenyl)iodonium triflate (2m), 4.0 g, 74% yield, white solid. ^{1}H 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 $C_{13}H_{11}BrIO$ $(M\text{-}OTf)^+$ 388.9038, found 388.9028; m.p: 171-172 °C.

(4-Methoxyphenyl)(thiophen-3-yl)iodonium triflate (2n), 2.7 g, 59% yield, white solid. ^{1}H 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 $C_{11}H_{10}IOS$ $(M\text{-}OTf)^+$ 316.9497, found 316.9486; m.p: 125-126 °C.

ASSOCIATED CONTENT

Supporting Information: DFT calculations studies and spectra of compounds **3a-3r**, **3ab-3ao**, **4a**, **5**, **6**, **7**, oximes **1d-1f, 1k-1n,** diaryliodonium salts **2m, 2n**. These

materials are available free of charge via the Internet at http://pubs.acs.org.

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Notes

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

(16) DFT calculations were carried out with the Gaussian 09 suit of programs. The energies reported in Scheme 5 are relative free energies in gas phase (ΔG_{gas}) and in solvent (ΔG_{sol}), each consists of gas-phase free energy and solvation free energy correction, computed at ωB97XD/def2-TZVP level of theory. See supporting information for detailed computational methods.

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