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Copper-Catalyzed Aerobic C(sp^2)−H Functionalization for C−N Bond Formation: Synthesis of Pyrazoles and Indazoles

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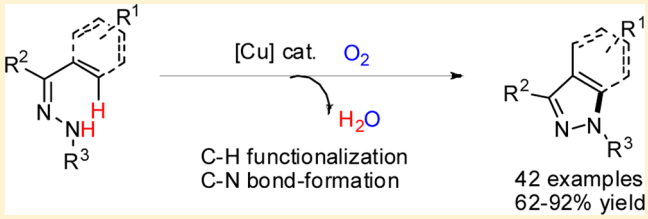
Supporting Information

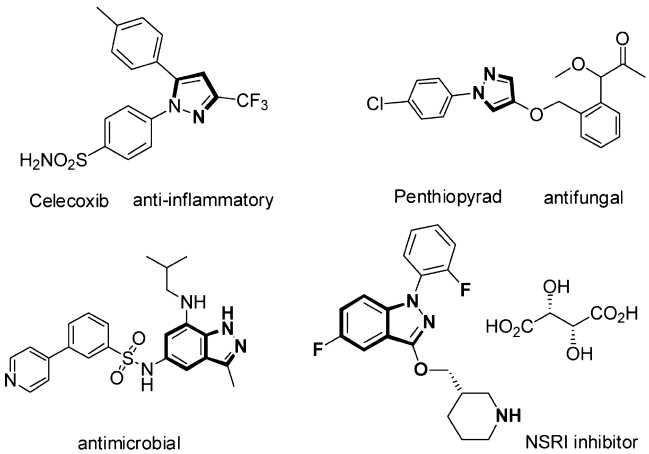
ABSTRACT: A simple, practical, and highly efficient synthesis of pyrazoles and indazoles via copper-catalyzed direct aerobic oxidative C(sp^2)−H amination has been reported herein. This process tolerated a variety of functional groups under mild conditions. Further diversification of pyrazoles was also investigated, which provided its potential for drug discovery.



INTRODUCTION

The development for the rapid access to N-heterocycles with complexity and diversity which stem from their wide occurrence in nature and broad application in chemistry, biology, and material sciences has attracted considerable attention in the studies of chemical genetics.[1] In this respect, pyrazoles and indazoles are important synthetic targets in biologically active molecules, synthetic drugs, and drug candidates, (Scheme 1), and in addition, they can be used as ligands for generating metallic complexes.[2,3]

Scheme 1. Pyrazole and Indazole Representative Biologically Active Analogues

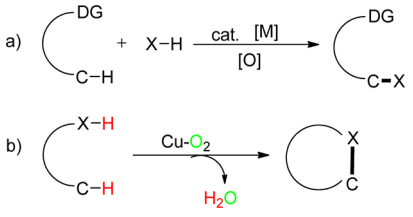


The importance of these heterocyclic moieties has prompted the development of many practical synthetic routes to construct their derivatives.[4,5] However, traditional methods for their derivatives often suffer from low regioseletivities, harsh reaction conditions (stoichiometric strong base, high reaction temperature), and the need for precious metal catalysts and stoichiometric and environmentally unfriendly oxidants. Thus, it is desirable to develop efficient methods with regard to green chemistry, regioselectivities, and synthetic practice.

Direct C−H bond amination without prefunctionalization of simple starting materials to the corresponding organic (pseudo)halides is a highly attractive synthetic strategy as an atom-economic and environmentally benign method for C−N bond formation.[6] From a synthetic standpoint, a strategy involving transition-metal-catalyzed C−H bond fuctionalization followed by C−N bond formation represents one of the most versatile and practical approaches for installing nitrogen functional groups.[7] For example, utilizing a directing group-assisted C−H bond functionalization strategy to achieve C−X bonds is a powerful and challenging area in organic synthesis.[8] However, extra steps are required for the introduction and removal of directing groups and limit its synthetic applications (Scheme 2a).

On the other hand, Cu/O_2 catalytic systems that comprise naturally occurring metalloenzyme copper and molecular oxygen as the oxidant are notable bacause they often exhibit exquisite substrate specificity as well as regioselectivity and/or stereoselectivity and operate under mild conditions through inherently "green" processes.[9] Consequently, copper-catalyzed

Scheme 2[a]



[a]Key: (a) *ortho*-assisted C−H bond functionalization for the C−X bond formation; (b) Cu-catalyzed aerobic oxidative C−X bond formation. DG = directing group, X = Nu.

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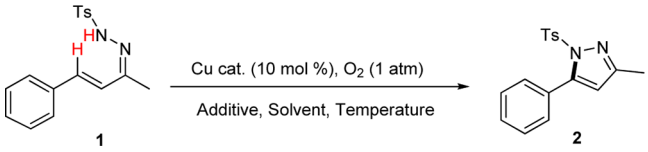
aerobic oxidative C−H bond functionalization[10] for the C−X bond formation[11] could provide an alternative route with its versatility and green chemistry (Scheme 2b). As part of our continuous efforts on copper-catalyzed aerobic oxygenation/oxidation reactions,[12] herein we report copper-catalyzed aerobic amination of the C(sp^2)−H bond for pyrazole and indazole synthesis based on *N*-tosylhydrazone **1** and **3** derivatives. This Cu-mediated aerobic oxidative transformation features great efficiency, broad substrate scope, and good functional group tolerance under mild conditions, and the use of molecular oxygen (1 atm) as the sole oxidant made this strategy even more practical and green.

RESULTS AND DISCUSSION

We commenced our investigation by studying the conversion of **1** to the desired pyrazole **2** using a combination of a copper catalyst together with 1 atm of O_2 as the stoichiometric oxidant (Table 1). Without additives, the transformation could proceed

Table 1. Optimization of Reaction Conditions[a]



1 2

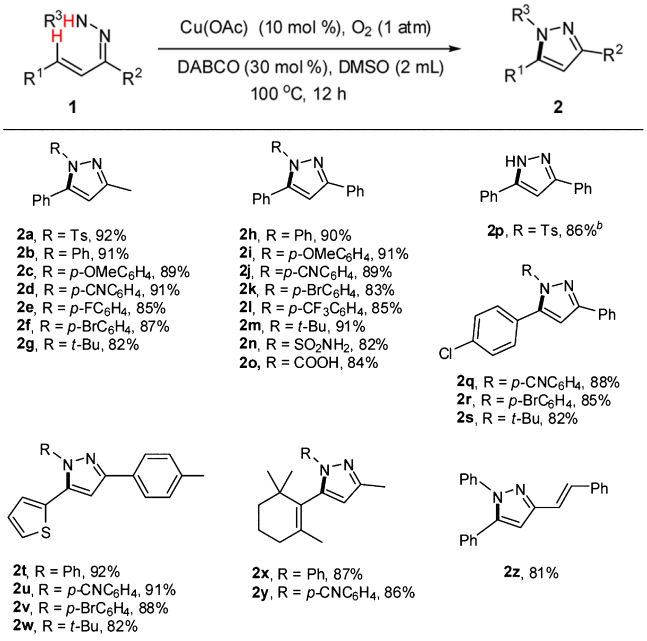
entry	copper catalyst	additive	solvent	temp (°C)	yield[b](%)
1	$Cu(OAc)_2$		DMSO	100	32
2	$Cu(OAc)_2$	HOAc	DMSO	100	12
3	$Cu(OAc)_2$	K_2CO_3	DMSO	100	65
4	$Cu(OAc)_2$	Li_2CO_3	DMSO	100	52
5	$Cu(OAc)_2$	K_2CO_3	DMSO	100	65
6	$Cu(OAc)_2$	pyridine	DMSO	100	37
7	$Cu(OAc)_2$	NEt_3	DMSO	100	42
8	$Cu(OAc)_2$	DABCO	DMSO	100	95 (92)
9	CuCl	DABCO	DMSO	100	66
10	CuBr	DABCO	DMSO	100	49
11	$Cu(OAc)_2$	DABCO	toluene	100	75
12	$Cu(OAc)_2$	DABCO	DCE	100	68
13	$Cu(OAc)_2$	DABCO	DMSO	80	76
14[c]	$Cu(OAc)_2$	DABCO	DMSO	100	72
15		DABCO	DMSO	100	<10

[a]Reaction conditions: **1** (0.2 mmol), Cu catalyst (0.02 mmol), additive (0.06 mmol) in DMSO (2 mL), 100 °C, 12 h. [b]Yield was determined by GC analysis. [c]Reaction was performed under air.

with low efficiency. When a Brønsted acid such as HOAc was used as the additive, the yield deteriorated to 12% (entry 2). Detailed examination of base as the additive suggested that the use of 30 mol % of DABCO gave the best yield and provided the optimized result (entry 8); other bases also gave moderate yields (entries 3−7). We suspected that DABCO might act as both base and ligand to facilitate the product formations. A range of copper sources were evaluated, such as CuCl; CuBr could also serve as the catalyst and led to the desired products although with inferior results (entries 9 and 10). We also optimized the solvent effect and found that DMSO gave the superior results than toluene and DCE. Lowering the temperature to 80 °C just led to a decrease in yield (entry 13). This process could also be performed under air atmosphere (entry 14). Control experiments revealed that in the absence of the copper source only trace amount of target molecular **2** was detected (entry 15). Thus, the optimal reaction conditions were $Cu(OAc)_2$ (10 mol %) and DABCO (30 mol %) in DMSO at 100 °C with molecular oxygen (1 atm) as the oxidant.

Substrate Scope for the Synthesis of Pyrazoles. With these optimized conditions in hand, we next explored the scope and generality of the process, and the results are summarized in Table 2. The scope of the process with respect to the hydrazine

Table 2. Synthesis of Pyrazole Derivatives[a]



[a]Standard reaction conditions: **1** (0.2 mmol), $Cu(OAc)_2$ (10 mol %), DABCO (30 mol %), DMSO (2 mL), 100 °C, 12 h. [b]The Ts group of the substrate was dissociated in the reaction.

reactant was examined. In general, aromatic and aliphatic R^3 under the optimized reaction conditions all form the corresponding pyrazoles in excellent yields. Various electron-donating and electron-accepting groups on aromatic R^3 substrates were tolerated well in this reaction. These results showed that electron-donating goups had more favorable effects than electron-withdrawing goups. What's more, the process tolerated functional groups such as fluorides, chlorides, bromides, nitriles, trifluoromethyls, carboxyls, sulfonamides, and ethers and, therefore, should be applicable to late-stage modifications of advanced intermediates. However, free NH_2 group substituted substrates gave no desired products. Both aromatic and aliphatic groups (Table 2, **2x**, **2y**) were tolerated and furnished the target products in comparable yields. Pyrazoles **2x** and **2y** were derived from *β*-ionone, which is known as a starting material for the synthesis of vitamin A. Interestingly, 3,5-diphenyl-1*H*-pyrazole (**2p**) was obtained when R = Ts, which was different from what we observed in product **2a**. However, there was no prededent for this in situ deprotection of the pyrrazole nitrogen. Bolotin and Larock had reported similar observations.[13] The deprotection of the Ts group still proceeded even at lower reaction tempearture or with other bases. We assumed that this result might be due to the copper catalyst or the aromatic system (R^1 = R^2 = Ph) of the obtained pyrazole products. Notably, heterocycle-substituted pyrazoles could also be obtained in high yields (Table 2, **2t**−**2w**). We could also obtain **2z** bearing a C−C double bond,

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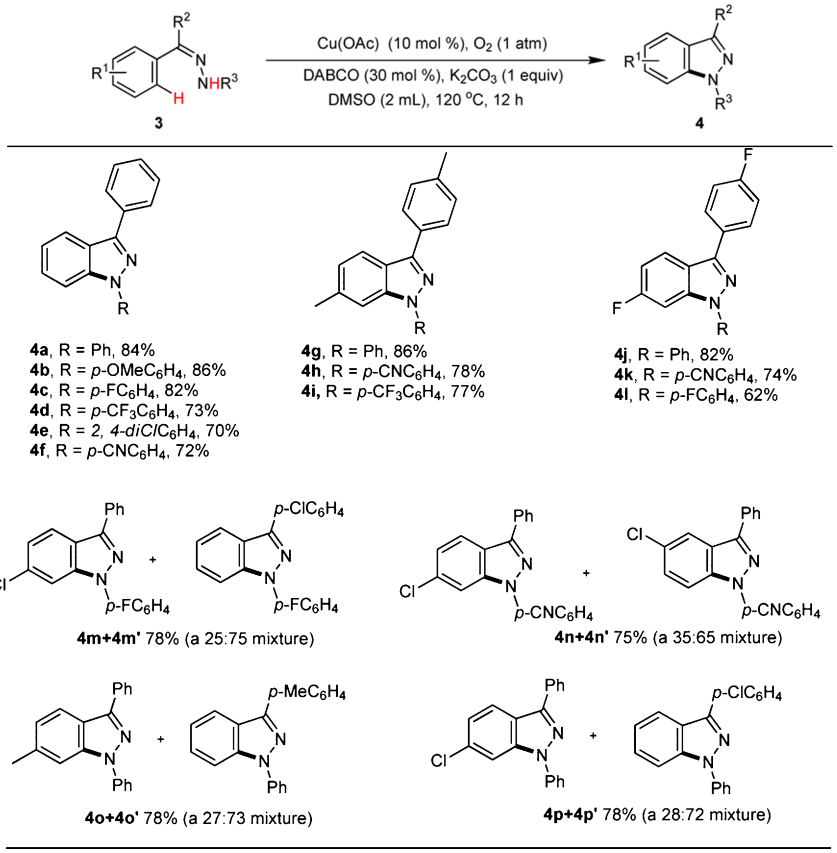
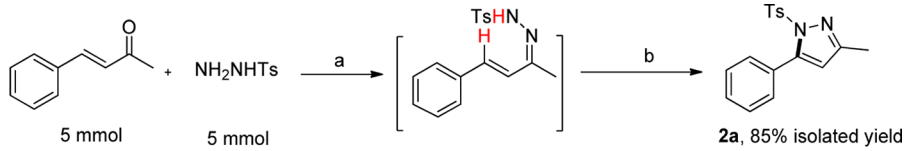
Table 3. Synthesis of Indazole Derivatives[a]



[a]Standard reaction conditions: **1** (0.2 mmol), $Cu(OAc)_2$ (10 mol %), DABCO (30 mol %), K_2CO_3 (1 equiv), DMSO (2 mL), 120 °C, 12 h.

Scheme 3. One-Pot Pyrazole Synthesis[a]



[a]Reaction conditions: (a) 1. MeOH (6 mL), reflux, 3 h; (b) $Cu(OAc)_2$ (10 mol %), DABCO (30 mol %), DMSO (2 mL), O_2 (1 atm), 100 °C, 10 h.

which could be further functionalized in various transformations. The stereochemistry of the hydrazone CN double bond did not influence the result of this reaction. Both cis- and trans-type substrates **1** could afford the responding pyrazole products, and we suspected that the (*E*)-**1** isomerizes could transform to (*Z*)-**1** with the aid of DABCO at elevated temperature.[10i]

The above results inspired us to further demonstrate the synthetic application of our developed protocol into aromatic $C(sp^2)$–H amination for the synthesis of indazole derivatives. The reaction was further optimized with the addition of 1 equiv of K_2CO_3 into the system, and indazole derivatives were obtained in good yields. With the optimized results, we embarked on an investigation of the scope of this aromatic $C(sp^2)$–H amination.

Substrate Scope for the Synthesis of Indazoles. As is depicted in Table 3, indazoles could be obtained smoothly with good results. Moreover, functional groups, like F, Cl, CF_3, and CN were all well tolerated in this transformation. In general, substrates **3** bearing electron-donating groups gave better yields than electron-withdrawing groups. These functional groups provide ample opportunity for further synthetic manipulations. The introduction of fluorine atoms or fluorine-containing groups into heterocyclic rings has made possible the discovery of new bioactive products.[14] Trifluoromethylated arenes are essential structural motifs in a great number of pharmaceuticals, agrochemicals, and organic materials.[15] The cyano group is a versatile functional group that could serve as a coordinating functional group and for versatile intermediates and valued target pharmacophores.[16] When two electronically unsymmetrical aromatic groups were present in benzophenones, a mixture of 75:25 to 65:35 isomers was observed for the formation of **4m**+**4m**′ to **4p**+**4p**′, respectively. The regioselectivity in the case of unsymmetric aryl groups was moderate, and we surmised that electron-rich substrates were favored in the insertion step and the steric factors might also affect the regioselectivities.

We then succeeded in performing the reaction on a larger scale to demonstrate the practicability of the developed methodology in a one-pot fashion (Scheme 3). By using this procedure, pyrazole product **2a** could be conveniently obtained on a 5 mmol scale in yields similar to those for the pyrazole

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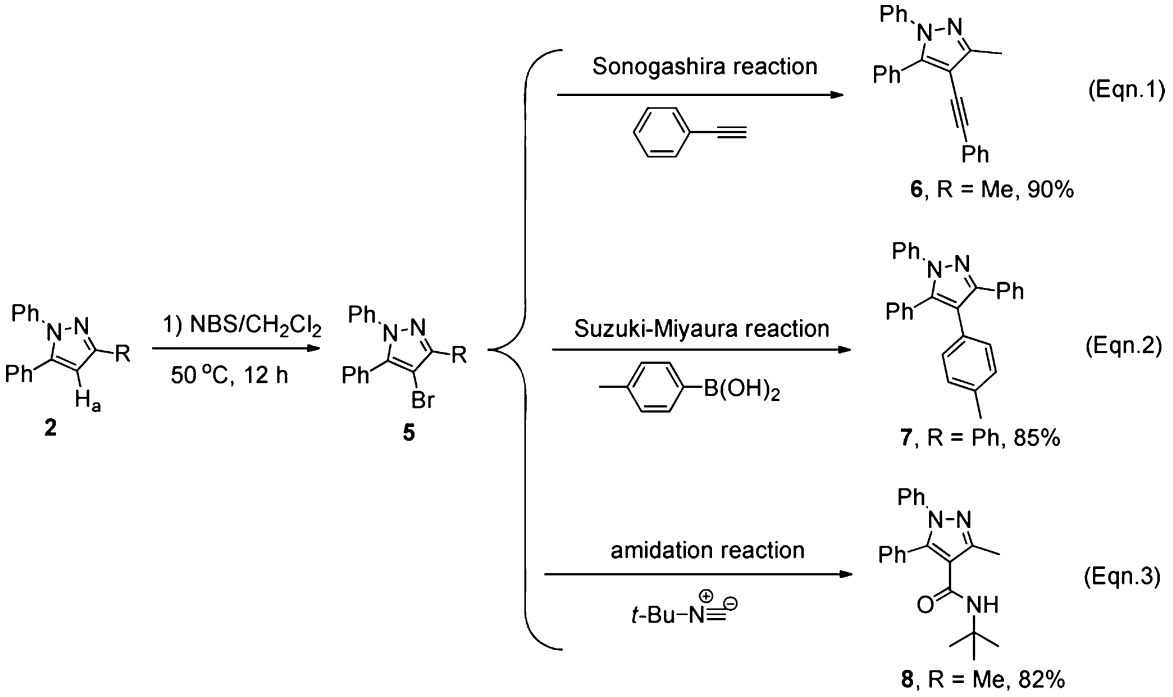
Scheme 4. Further Demonstration of the Synthetic Application of the Pyrazole Products[a]



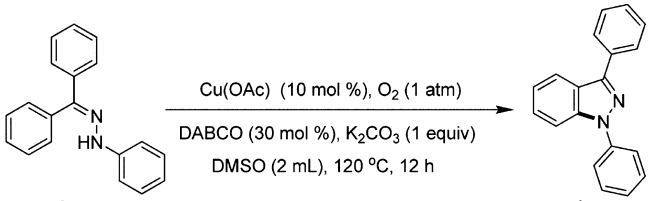
[a]Reaction conditions: (1) **2c** (0.5 mmol), NBS (0.6 mmol), CH_2Cl_2, 50 °C, 12 h, 70% (R = Me), 72% (R = Ph); (2) **5** (0.25 mmol), ethynylbenzene (1.1equiv), $PdCl_2(PPh_3)_2$ (5 mol %), CuI (10 mol %), Et_3N (2equiv), MeCN (2 mL), 70 °C, 4 h, 90%; (3) **5** (0.25 mmol), *p*-tolylboronic acid (1.5equiv), $Pd(PPh_3)_4$ (10 mol %), PPh_3 (20 mol %), K_2CO_3 (2.5equiv), tolunene/EtOH/H_2O (20:5:1) 5 mL, 80 °C, 12 h, 85%; (4) **5** (0.25 mmol), *tert*-butyl isocyanide (0.30 mmol), $PdCl_2$ (5 mol %), PPh_3 (10 mol %), CsF (1.0equiv), and 0.2 mL of H_2O in 1.5 mL of DMSO at 110 °C for 12 h, 82%.

formation step only (e.g., **2a**: 92% versus 85%, respectively). This efficient and highly modular one-pot procedure significantly increases the practicality and usefulness of this new method.

Application To Further Functionalize the Obtained Pyrazoles. To further demonstrate the synthetic application of our developed protocol, we performed experiments using **2c** as the starting materials for the diversification of pyrazole derivatives. The C−H_a bond of **2** could also be brominated with NBS to **5**, which could undergo Sonogashira and Suzuki−Miyaura reactions to afford **6** and **7**, respectively. These analogues may have potential application in materials synthesis (Scheme 4, eqs 1 and 2). We also performed amidation reactions of **5** using our previous developed palladium-catalyzed C−C coupling of aryl halides with isocyanides for the synthesis of amides, which as we know, are potential precursors for the synthesis of numerous natural products, potential pharmaceuticals, and bioactive polymers (Scheme 4, eq 3).[17]

Mechanistic Studies of the Synthesis of Pyrazoles and Indazoles. To further elucidate the reaction mechanism, we conducted several experiments by stiochiometric addition of an electron-transfer scavenger (1, 4-dinitrobenzene), a radical clock (diallyl ether), or radical inhibitor (hydroquinone, TEMPO) to the Cu-catalyzed aerobic C−H amination process. The reaction still proceeded smoothly to afford the desired product with the addition of hydroquinone, TEMPO, or 1,4-dinitrobenzene (Scheme 5). In addition, when 1.0 equiv of diallyl ether was added to the standard conditions, no radical-initiated cyclization product was observed. These results suggest that radical process is not involved in this transformation.[18]

Scheme 5. Mechanism Probing Experiments



	yield
no additive	84%
1,4-Dinitrobenzene (1.0 equiv)	77%
Diallyl ether (1.0 equiv)	68%
Hydroquinone ((1.0 equiv))	45%
TEMPO ((1.0 equiv))	72%

In the light of these preliminary results, a catalytic cycle for this transformation was hypothesized as shown in Scheme 6, while further detailed elucidation should be indispensable. Initially, the reaction of substrates **1** or **3** with $Cu(OAc)_2$ presumably led to a Cu−N adduct **A**.[11a,19] Intramolecular electrophilic aromatic substitution with the nitrogen of the Cu−N adduct **A** followed by aromatization via **C** would provide the pyrazoles **2** or indazoles **4** with generation of reduced copper species (Cu^{n-2}), which could be reoxidized by O_2 to achieve the catalytic cycle. Alternatively, formation of metallacycle **B** by electronphilic metalation or a C−H bond activation followed by reductive elimination[20,21] and aromatization gave the products **2** or **4**.[22]

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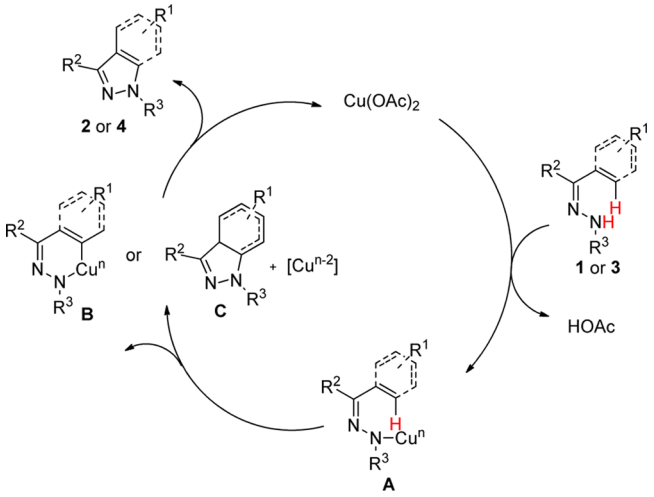
Scheme 6. Proposed Catalytic Cycle



CONCLUSION

In conclusion, we have developed a Cu-catalyzed aerobic oxidative C(sp^2)−H amination leading to pyrazoles and indazoles, which are ubiquitous structural units in a number of biological active compounds. This method is highly efficient and exhibits a good functional group tolerance. Further modification could be performed smoothly which showed its potential in organic synthesis. It is noteworthy that this reaction provides a highly attractive practical synthetic strategy for the direct C−H amination that precludes the need for prefunctionalized starting materials and the use of molecular oxygen as the oxidant make the overall chemical transformation sustainable and practical.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out in 10 mL tubes under air atmosphere. TLC was performed by using commercially prepared 100−400 mesh silica gel plates (GF_{254}) and visualization was effected at 254 nm. All reagents were purchased as reagent grade and used without further purification. Melting points were measured with a micromelting point apparatus. ^{1}H NMR spectra were recorded at 400 MHz using TMS as an internal standard and ^{13}C NMR spectra at 100, using $CDCl_3$. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with an infrared Fourier spectrometer. High-resolution mass spectra (ESI) were obtained with a LCMS−IT-TOF mass spectrometer.

Typical Procedure for the Synthesis of Hydrazone. Ketones (1.0equiv) and phenylhydrazines (1.05equiv) were mixed in MeOH or toluene to stir at room temperature (AcOH was added if necessary). After minutes, a lot of solid precipitated from the solution. After the disappearance of the enones by TLC, the solid was collected by filtration and washed with cooled MeOH. Then the solid was dissolved in DCM, and the organic layer was washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried with Na_2SO_4, filtered, and evaporated to give the solid, which was further purification by recrystallization in EtOAc/MeOH cosolvent system.

Typical Procedure for the Synthesis of Pyrazoles and Indazoles. To a dried Schlenk tube was added successively a mixture of hydrazone (0.2 mmol), $Cu(OAc)_2$ (10 mol %, 3 mg), DABCO (30 mol %, 6 mg) (1 equiv of K_2CO_3 (32 mg) was also added for the synthesis of indazoles), and 2 mL of DMSO. Then the mixture was stirred at 100 °C (or 120 °C) for 12 h under 1 atm of O_2. Upon completion, the reaction mixture was washed by saturated NaCl aqueous solution (2 × 10 mL) and then extracted with ethyl acetate (2 × 10 mL), and the organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was separated by column chromatography to give the pure products **2a−z** and **4a−q**.

*(Z)-4-Methyl-N′-((E)-4-phenylbut-3-en-2-ylidene)-benzenesulfonohydrazide (**1a**):* ^{1}H NMR (400 MHz, DMSO-d_6) δ = 10.55 (s, Br, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 7.01 (d, J = 14.8 Hz, 3H), 6.72 (d, J = 16.4 Hz, 1H), 2.34 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.2, 143.2, 135.9, 133.8, 129.4, 128.7, 128.4, 128.3, 127.5, 126.9, 21.0, 12.3; MS (EI) m/z 51, 75, 102, 116, 160, 237, 299, 314; HRMS calcd $C_{17}H_{18}N_2O_2S$, [M$^+$] 314.1089, found 314.1094.

*(Z)-1-Phenyl-2-((E)-4-phenylbut-3-en-2-ylidene)hydrazine (**1b**):*[4g,h] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, J = 8.8 Hz, 2H), 7.40−7.35 (m, 6H), 7.22 (dd, J = 1.6 Hz, 7.2 Hz, 3H), 6.33 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.4, 143.6, 140.1, 130.7, 128.6, 128.3, 128.0, 127.0, 125.1, 107.7, 13.5; MS (EI) m/z 51, 77, 102, 116, 156, 192, 236.

*(Z)-1-(4-Methoxyphenyl)-2-((E)-4-phenylbut-3-en-2-ylidene)-hydrazine (**1c**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29−7.20 (m, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.32 (s, 1H), 3.79 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.6, 149.0, 143.7, 133.5, 130.8, 128.6, 128.0, 126.6, 114.0, 107.2, 55.4, 13.6; MS (EI) m/z 64, 76, 116, 156, 192, 235, 266; HRMS calcd $C_{17}H_{18}N_2O$ [M$^+$] 266.1419, found 266.1415.

*4-((Z)-2-((E)-4-Phenylbut-3-en-2-ylidene)hydrazinyl)benzonitrile (**1d**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, J = 6.4 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.46−7.40 (m, 5H), 7.21 (d, J = 8.0 Hz, 3H), 6.62 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.3, 149.5, 145.4, 129.7, 129.4, 128.8, 128.1, 127.9, 126.5, 109.6, 21.7; MS (EI) m/z 64, 75, 102, 157, 192, 218, 245, 261; HRMS calcd $C_{17}H_{15}N_3$, [M$^+$] 261.1266, found 261.1269.

*(Z)-1-(4-Fluorophenyl)-2-((E)-4-phenylbut-3-en-2-ylidene)-hydrazine (**1e**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 7.6 Hz, 3H), 7.31−7.26 (m, 7H), 7.23−7.20 (m, 2H), 6.97 (t, J = 8.4 Hz, 1H), 6.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8, 160.4, 152.1, 144.5, 136.4, 133.0, 130.4, 128.8, 128.6, 128.5, 128.1, 127.1, 127.0, 125.9, 115.9, 115.7, 105.2; MS (EI) m/z 64, 75, 102, 117, 155, 191, 235, 254; HRMS calcd $C_{16}H_{15}FN_2$ [M$^+$] 254.1219, found 254.1223.

*(Z)-1-(4-Bromophenyl)-2-((E)-4-phenylbut-3-en-2-ylidene)-hydrazine (**1f**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42−7.37 (m, 1H), 7.33−7.29 (m, 3H), 7.25−7.22 (m, 3H), 7.18 (d, J = 8.8 Hz, 2H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.2, 144.9, 142.4, 131.6, 128.6, 127.6, 126.5, 125.8, 114.7, 110.5, 15.9; MS (EI) m/z 64, 75, 117, 155, 191, 234, 276, 314; HRMS calcd $C_{16}H_{15}BrN_2$ [M$^+$] 314.0419, found 314.0412.

*(Z)-1-(tert-Butyl)-2-((E)-4-phenylbut-3-en-2-ylidene)hydrazine (**1g**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (d, J = 7.2 Hz, 2H), 7.33−7.32 (m, 1H), 7.27 (t, J = 7.6 Hz, 2H), 7.17 (t, J = 6.8 Hz, 1H), 5.09 (t, J = 4.8 Hz, 3H), 2.16−2.11 (m, 3H), 1.29−1.24 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.8, 130.4, 128.4, 127.7, 126.8, 126.6, 109.9, 64.3, 27.3, 16.0; MS (EI) m/z 64, 79, 133, 159, 188, 216; HRMS calcd $C_{14}H_{20}N_2$ [M$^+$] 216.1626, found 216.1633.

*(E)-1-((E)-1,3-Diphenylallylidene)-2-phenylhydrazine (**1h**):*[4h] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, J = 6.8 Hz, 2H), 7.37−7.06 (m, 13H), 6.79−6.78 (m, 1H), 5.25 (dd, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.7, 144.9, 142.6, 132.8, 128.6, 125.8, 119.1, 113.4; MS (EI) m/z 75, 147, 192, 243, 269, 298.

*(E)-1-((E)-1,3-Diphenylallylidene)-2-(4-methoxyphenyl)hydrazine (**1i**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, J = 7.2 Hz, 2H), 7.38−7.22 (m, 9H), 7.00 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 9.2 Hz, 2H), 5.14 (dd, J = 8.4 Hz, 3.6 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.3, 146.3, 142.7, 139.7, 132.9, 129.1, 127.6, 125.7, 114.9, 114.4, 55.6; MS (EI) m/z 64, 77, 89, 167, 218, 269, 298, 328; HRMS calcd $C_{22}H_{20}N_2O$ [M$^+$] 328.1576, found 328.1584.

*4-((E)-2-((E)-1,3-Diphenylallylidene)hydrazinyl)benzonitrile (**1j**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79−7.75 (m, 1H), 7.66−7.55 (m, 4H), 7.49 (d, J = 8.0 Hz, 2H), 7.34−7.32 (m, 5H), 7.10 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.7, 147.5, 137.6, 133.6,

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132.1, 129.9, 128.9, 128.4, 126.9, 120.0, 113.0, 101.9; MS (EI) *m/z* 75, 145, 196, 243, 298, 323; HRMS calcd $C_{22}H_{17}N_3$ [M^+] 323.1422, found 323.1426.

*(E)-1-(4-Bromophenyl)-2-((E)-1,3-diphenylallylidene)hydrazine (**1k**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 7.2 Hz, 2H), 7.38−7.22 (m, 9H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 9.2 Hz, 2H), 5.14 (dd, *J* = 8.4 Hz, 3.6 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.3, 146.3, 142.7, 139.7, 132.9, 129.1, 127.6, 125.7, 114.9, 114.4, 55.6; MS (EI) *m/z* 75, 145, 193, 218, 267, 298, 376; HRMS calcd $C_{21}H_{17}BrN_2$ [M^+] 376.0575, found 376.0583.

*(E)-1-((E)-1,3-Diphenylallylidene)-2-(4-(trifluoromethyl)phenyl)-hydrazine (**1l**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.31−7.26 (m, 7H), 7.23−7.20 (m, 2H), 6.97 (t *J* = 8.4 Hz, 2H), 6.77(s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 62.9, 160.4, 152.1, 144.5, 136.4, 130.4, 128.7, 128.5, 127.1, 125.9, 115.9, 115.7, 105.2; MS (EI) *m/z* 55, 146, 192, 218, 267, 289, 366; HRMS calcd $C_{22}H_{17}F_3N_2$ [M^+] 366.1344, found 366.1349.

*(E)-1-(tert-Butyl)-2-((E)-1,3-diphenylallylidene)hydrazine (**1m**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 8.4 Hz, 4H), 7.29 (dd, *J* = 8.0 Hz, 4.0 Hz, 5H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.1, 146.5, 145.2, 142.8, 134.8, 134.0, 133.5, 133.0, 132.5, 132.0, 128.7, 128.4, 127.5, 125.7, 125.5, 106.9, 64.1, 27.9; MS (EI) *m/z* 55, 133, 192, 220, 278; HRMS calcd $C_{19}H_{22}N_2$ [M^+] 278.1783, found 278.1786.

*4-((E)-2-((E)-1,3-Diphenylallylidene)hydrazinyl)-benzenesulfonamide (**1n**):*[4c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78−7.69 (m, 3H), 7.31−7.29 (m, 3H), 7.14−7.05 (m, 4H), 7.03−6.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.6, 155.7, 154.0, 143.4, 137.1, 135.4, 134.9, 128.3, 127.4, 116.9.

*4-((E)-2-((E)-1,3-Diphenylallylidene)hydrazinyl)benzoic acid (**1o**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (m, 3H), 7.31−7.29 (m, 3H), 7.14−7.05 (m, 4H), 7.03−6.89 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 166.4, 151.6, 144.2, 142.8, 130.0, 128.6, 128.4, 128.1, 125.4, 124.5, 109.9, 106.1; MS (EI) *m/z* 64, 77, 165, 192, 221, 298, 342; HRMS calcd $C_{22}H_{18}N_2O_2$ [M^+] 342.1368, found 342.1371.

*(E)-N′-((E)-1,3-Diphenylallylidene)-4-methylbenzenesulfonohydrazide (**1p**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78−7.69 (m, 3H), 7.31−7.29 (m, 3H), 6.92−6.89 (m, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 156.2, 154.4, 144.1, 143.9, 141.1, 135.3, 129.5, 128.2, 127.0, 117.3, 20.9; MS (EI) *m/z* 64, 133, 192, 222, 298, 376; HRMS calcd $C_{22}H_{20}N_2O_2S$ [M^+] 376.1245, found 376.1248.

*4-((E)-2-((E)-3-(4-Chlorophenyl)-1-phenylallylidene)hydrazinyl)-benzonitrile (**1q**):*[4f] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53−7.44 (m, 5H), 7.29−7.18 (m, 7H), 7.03 (dd, *J* = 8.4 Hz, 2H), 6.80 (t, *J* = 7.2 Hz, 1H), 5.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.6, 144.5, 143.1, 142.9, 138.2, 137.1, 135.4, 133.9, 132.4, 129.7, 128.5, 127.8, 126.5, 120.5, 113.2; MS (EI) *m/z* 64, 101, 133, 167, 212, 298, 357.

*(E)-1-(4-Bromophenyl)-2-((E)-3-(4-chlorophenyl)-1-phenylallylidene)hydrazine (**1r**):*[4f] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 6.8 Hz, 2H), 7.37−7.18 (m, 10H), 6.89 (d, *J* = 7.2 Hz, 2H), 5.17 (dd, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.5, 143.5, 140.5, 133.6, 132.3, 131.8, 129.5, 128.7, 125.9, 115.0, 113.4; MS (EI) *m/z* 64, 101, 133, 212, 298, 314, 376, 410.

*(E)-1-tert-Butyl-2-((E)-3-(thiophene-2-yl)-1-p-tolylallylidene)-hydrazine (**1s**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 7.6 Hz, 2H), 7.39−7.30 (m, 6H), 7.27−7.22 (m, 5H), 6.92 (d, *J* = 8.4 Hz, 2H), 5.21 (dd, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.4, 143.7, 142.0, 131.7, 129.3, 128.9, 128.6, 127.8, 125.8, 115.0, 111.1; MS (EI) *m/z* 64, 103, 191, 219, 253, 298, 312; HRMS calcd $C_{18}H_{22}N_2S$ [M^+] 298.1504, found 298.1507.

*(E)-1-Phenyl-2-((E)-3-(thiophene-2-yl)-1-(p-tolyl)allylidene)-hydrazine (**1t**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.0 Hz, 2H), 7.45−7.33 (m, 6H), 7.25−7.20 (m, 3H), 6.91 (t, *J* = 4.0 Hz, 1H), 6.82−6.81 (m, 2H), 6.77 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.2, 143.3, 137.9, 133.1, 129.3, 128.3, 127.6, 125.9, 124.9, 111.1, 107.4, 21.5; MS (EI) *m/z* 64, 115, 198, 234, 282, 318; HRMS calcd $C_{20}H_{18}N_2S$ [M^+] 318.1191, found 318.1195.

*4-((E)-2-((E)-3-(Thiophene-2-yl)-1-(p-tolyl)allylidene)hydrazinyl)-benzonitrile (**1u**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.0 Hz, 2H), 7.43−7.33 (m, 6H), 7.25−7.20 (m, 3H), 6.91 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.82−6.81 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.5, 143.5, 138.2, 130.9, 129.8, 128.6, 126.3, 125.2, 112.2, 107.7, 21.7; MS (EI) *m/z* 64, 152, 234, 281, 327, 343; HRMS calcd $C_{21}H_{17}N_3S$ [M^+] 343.1143, found 343.1147.

*(E)-1-(4-Bromophenyl)-2-((E)-3-(thiophene-2-yl)-1-(p-tolyl)-allylidene)hydrazine (**1v**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.17−7.14 (m, 3H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 2.8 Hz, 1H), 6.88 (t, *J* = 8.4 Hz, 3H), 5.38 (dd, *J* = 2.8 Hz, 15.6 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.3, 145.6, 144.2, 139.3, 131.7, 126.0, 125.1, 124.4, 115.4, 111.6, 21.5; MS (EI) *m/z* 64, 133, 212, 281, 318, 396; HRMS calcd $C_{20}H_{17}BrN_2S$ [M^+] 396.0296, found 396.0301.

*(E)-1-(tert-Butyl)-2-((E)-3-(thiophene-2-yl)-1-(p-tolyl)allylidene)-hydrazine (**1w**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, *J* = 8.0 Hz, 2H), 7.32−7.18 (m, 2H), 7.09 (d, *J* = 5.2 Hz, 3H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 2.8 Hz, 1H), 6.84−6.82 (m, 1H), 4.84 (t, *J* = 2.8 Hz, 1H), 2.54 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.2, 145.1, 138.2, 129.1, 128.4, 128.2, 128.1, 126.5, 125.7, 125.6, 124.1, 123.0, 60.0, 27.4, 21.4; MS (EI) *m/z* 64, 133, 231, 282, 298; HRMS calcd $C_{18}H_{22}N_2S$ [M^+] 298.1504, found 298.1507.

*(Z)-1-Phenyl-2-((E)-4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-3-en-2-ylidene)hydrazine (**1x**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50−7.48 (m, 2H), 7.33−7.28 (m, 3H), 7.19−7.17 (m, 1H), 5.89 (d, *J* = 2.8 Hz, 1H), 2.40 (s, 3H), 2.02 (s, 2H), 1.71−1.62 (m, 2H), 1.47 (s, 2H), 1.01 (s, 3H), 0.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.3, 148.5, 141.2, 136.5, 131.1, 128.7, 126.3, 123.3, 108.8, 39.1, 32.0, 28.3, 191., 13.9; MS (EI) *m/z* 64, 133, 172, 199, 235, 267, 282; HRMS calcd $C_{19}H_{26}N_2$ [M^+] 282.2096, found 282.2103.

*4-((Z)-2-((E)-4-(2,6,6-Trimethylcyclohex-1-en-1-yl)but-3-en-2-ylidene)hydrazinyl)benzonitrile (**1y**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 9.2 Hz, 2H), 6.99 (d, *J* = 9.2 Hz, 2H), 4.48 (dd, *J* = 9.2 Hz, 12.8 Hz, 1H), 3.29 (dd, *J* = 14.8 Hz, 18.4 Hz, 1H), 2.06 (s, 4H), 1.87−1.85 (m, 2H), 1.74 (s, 1H), 1.58−1.52 (m, 3H), 1.32−1.29 (d, *J* = 9.2 Hz, 6H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.7, 147.7, 135.6, 133.0, 132.9, 131.8, 120.7, 112.9, 112.0, 98.8, 40.3, 34.6, 28.0, 19.2, 18.9, 15.8; MS (EI) *m/z* 64, 132, 198, 235, 282, 318, 360; HRMS calcd $C_{20}H_{25}N_3$ [M^+] 307.2048, found 307.2054.

*1-((1E,4E)-1,5-Diphenylpenta-1,4-dien-3-ylidene)-2-phenylhydrazine (**1z**):*[4h] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.0 Hz, 2H), 7.64−7.62 (m, 2H), 7.43−7.39 (m, 5H), 7.37−7.32 (m, 5H), 7.30−7.25 (m, 4H), 6.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.9, 151.6, 141.1, 139.6, 139.3, 129.0, 128.6, 128.0, 122.5, 115.5, 104.6; MS (EI) *m/z* 64, 155, 192, 298, 324.

*1-(Diphenylmethylene)-2-phenylhydrazine (**3a**):*[4f] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 6.8 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.29−7.18 (m, 7H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.80 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.8, 144.3, 138.6, 132.9, 129.9, 129.4, 129.3, 128.4, 128.2, 126.7, 120.2, 113.1; MS (EI) *m/z* 64, 167, 192, 215, 243, 272.

*1-(Diphenylmethylene)-2-(4-methoxyphenyl)hydrazine (**3b**):*.[5d,g] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06−8.01 (m, 4H), 7.65−7.62 (m, 4H), 7.50 (t, *J* = 6.8 Hz, 2H), 7.39 (t, *J* = 6.8 Hz, 2H), 7.25−7.20 (dd, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.6, 145.6, 140.7, 133.4, 127.0, 121.6, 114.7, 110.6, 55.7; MS (EI) *m/z* 64, 167, 192, 223, 245, 302.

*1-(Diphenylmethylene)-2-(4-fluorophenyl)hydrazine (**3c**):*.[5f,g] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55−7.42 (m, 5H), 7.28−7.16 (m, 3H), 7.06−6.99 (m, 2H), 6.82−6.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.4, 142.8, 138.0, 136.9, 135.2, 133.7, 132.2, 130.0, 129.4, 129.0, 128.2, 127.6, 126.4, 120.3, 113.0; MS (EI) *m/z* 64, 133, 212, 265, 290.

*1-(Diphenylmethylene)-2-(4-(trifluoromethyl)phenyl)hydrazine (**3d**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (s, 1H), 7.76−7.75 (m, 2H), 7.70−7.61 (m, 5H), 7.44−7.41 (m, 5H), 7.20 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.4, 146.4, 138.2, 128.7, 126.7, 121.8, 121.5, 112.6; MS (EI) *m/z* 64, 133, 192, 235, 317, 340; HRMS calcd $C_{20}H_{15}F_3N_2$ [M^+] 340.1187, found 340.1194.

*1-(2,4-Dichlorophenyl)-2-(diphenylmethylene)hydrazine (**3e**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 8.8 Hz, 2H), 7.83−7.75 (m, 3H), 7.69−7.60 (m, 3H), 7.46−7.44 (m, 5H), 7.34−7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.3, 139.5, 138.0, 137.9, 132.6, 132.5,

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129.9, 129.7, 128.9, 128.5, 128.2, 127.0, 124.1, 117.7, 114.9; MS (EI) *m/z* 64, 133, 215, 269, 304, 340; HRMS calcd $C_{19}H_{14}Cl_2N_2$ [M^+] 340.0534, found 340.0522.

*4-(2-(Diphenylmethylene)hydrazinyl)benzonitrile (**3f**):*[5e] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79−7.75 (m, 1H), 7.66−7.55 (m, 4H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.34−7.32 (m, 5H), 7.10 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.7, 147.5, 137.6, 133.6, 132.1, 129.9, 128.9, 128.4, 126.9, 120.0, 113.0, 101.9; MS (EI) *m/z* 64, 133, 263, 297.

*1-(Di-p-tolylmethylene)-2-phenylhydrazine (**3g**):*[4f] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (dd, *J* = 9.2 Hz, 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.73−7.69 (m, 2H), 7.54−7.47 (m, 2H), 7.46−7.37 (m, 3H), 7.32−7.26 (m, 2H), 2.61−2.51 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.0, 144.6, 139.2, 129.9, 129.2, 126.7, 120.1, 113.2, 21.6, 21.5; MS (EI) *m/z* 64, 185, 206, 269, 300.

*4-(2-(Di-p-tolylmethylene)hydrazinyl)benzonitrile (**3h**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 8.8 Hz, 2H), 7.83−7.75 (m, 3H), 7.69−7.60 (m, 3H), 7.46−7.44 (m, 5H), 7.34−7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.8, 144.1, 140.7, 138.9, 138.6, 133.6, 129.9, 129.8, 127.8, 125.0, 122.5, 122.0, 121.8, 118.9, 110.5, 108.9, 22.3, 21.6; MS (EI) *m/z* 64, 133, 205, 297, 325; HRMS calcd $C_{22}H_{19}N_3$ [M^+] 325.1579, found 325.1586.

*1-(Di-p-tolylmethylene)-2-(4-(trifluoromethyl)phenyl)hydrazine (**3i**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (s, 1H), 7.45 (dd, *J* = 8.0 Hz, 4H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.07 (dd, *J* = 8.0 Hz, 4H), 2.42 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.4, 146.8, 139.5, 138.6, 135.6, 128.9, 126.9, 126.6, 126.5, 112.4, 21.4, 21.3; MS (EI) *m/z* 64, 133, 192, 248, 298, 338, 352, 368; HRMS calcd $C_{22}H_{19}F_3N_2$ [M^+] 368.1500, found 368.1512.

*1-(Bis(4-fluorophenyl)methylene)-2-phenylhydrazine (**3j**):*[4f] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 2.0 Hz, 1H), 7.56−7.49 (m, 4H), 7.33−7.31 (m, 4H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.03 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.6, 162.1, 147.6, 145.5, 133.8, 133.7, 131.1, 128.7, 127.7, 119.9, 117.4, 117.2, 115.5, 115.3, 113.0, 102.2; MS (EI) *m/z* 64, 133, 185, 212, 247, 288, 308.

*4-(2-(Bis(4-fluorophenyl)methylene)hydrazinyl)benzonitrile (**3k**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37−7.33 (m, 3H), 7.13−7.09 (m, 5H), 6.80 (dd, *J* = 8.8 Hz, 4H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.03 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 164.4, 161.9, 143.7, 142.9, 132.0, 131.2, 128.2, 117.2, 117.0, 115.4, 115.1, 114.7, 112.0; MS (EI) *m/z* 64, 187, 210, 298, 333; HRMS calcd $C_{20}H_{13}F_2N_3$ [M^+] 333.1078, found 333.1086.

*1-(Bis(4-fluorophenyl)methylene)-2-(4-fluorophenyl)hydrazine (**3l**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (s, 1H), 7.56−7.48 (m, 3H), 7.28−7.20 (m, 4H), 7.10 (d, *J* = 12.0 Hz, 2H), 6.96 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.5, 162.0, 145.1, 139.2, 130.9, 128.5, 124.2, 117.3, 117.0, 115.5, 115.3, 114.8; MS (EI) *m/z* 64, 156, 229, 252, 293, 305, 324; HRMS calcd $C_{19}H_{13}F_3N_2$ [M^+] 326.1031, found 326.1042.

*(Z)-1-((4-Chlorophenyl)(phenyl)methylene)-2-(4-fluorophenyl)-hydrazine (**3m**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04−7.96 (m, 2H), 7.78−7.66 (m, 4H), 7.53−7.43 (m, 3H), 7.32−7.22 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.6, 160.1, 146.3, 140.6, 129.0, 127.9, 124.9, 121.8, 116.4, 110.5; MS (EI) *m/z* 64, 117, 192, 215, 286; HRMS calcd $C_{19}H_{14}ClFN_2$ [M^+] 324.0830, found 324.0837.

*(Z)-1-((4-Chlorophenyl)(phenyl)methylene)-2-phenylhydrazine (**3n**):*[4f] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.28 (d, *J* = 7.2 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.943 (d, *J* = 8.8 Hz, 2H), 7.84 (m, 1H), 7.71−7.57 (m, 5H), 7.52−7.44 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.8, 139.9, 129.2, 127.5, 126.3, 122.6, 121.3, 110.4; MS (EI) *m/z* 75, 167, 241, 297, 306.

*1-Phenyl-2-(phenyl(p-tolyl)methylene)hydrazine (**3o**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02−8.00 (m, 2H), 7.92 (t, *J* = 8.8 Hz, 3H), 7.74−7.71 (m, 2.4H), 7.51 (d, *J* = 7.2 Hz, 1.7H), 7.45−7.41 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24−7.21 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 2.50 (s, 2H), 2.43 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.5, 160.1, 146.4, 146.1, 133.4, 129.0, 127.8, 125.0, 123.2, 121.4, 116.3, 110.4, 110.0, 22.1, 21.5; MS (EI) *m/z* 64, 117, 215, 290, 324; HRMS calcd $C_{20}H_{18}N_2$ [M^+] 286.1470, found 286.1482.

*(Z)-4-(2-((4-Chlorophenyl)(phenyl)methylene)hydrazinyl)-benzonitrile (**3p**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02−8.00 (m, 2H), 7.92 (t, *J* = 8.8 Hz, 3H), 7.74−7.71 (m, 2.4H), 7.51 (d, *J* = 7.2 Hz, 1.7H), 7.45−7.41 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24−7.21 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 2.50 (s, 2H), 2.43 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.5, 160.1, 146.4, 146.1, 133.4, 129.0, 127.8, 125.0, 123.2, 121.4, 116.3, 110.4, 110.0, 22.1, 21.5; MS (EI) *m/z* 64, 222, 298, 331; HRMS calcd $C_{20}H_{14}ClN_3$ [M^+] 331.0876, found 331.0882.

*3-Methyl-5-phenyl-1-tosyl-1H-pyrazole (**2a**):* 56.7 mg, 92% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 8.0 Hz, 2H), 7.46−7.36 (m, 5H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.11 (s, 1H), 2.38 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.9, 148.9, 145.1, 134.9, 129.6, 129.3, 127.9, 127.7, 12.8, 112.7, 21.7, 13.9; MS (EI) *m/z* 51, 75, 102, 116, 158, 236, 298, 312; HRMS calcd $C_{17}H_{16}N_2O_2S$ [M^+] 312.0933, found 312.0929.

*3-Methyl-1,5-diphenyl-1H-pyrazole (**2b**):*[4d] 42.5 mg, 91% yield; slightly yellow solid; mp 129−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16−7.09 (m, *J* = 8.0 Hz, 10H), 6.18 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.5, 143.7, 140.2, 130.8, 128.9, 128.7, 128.5, 128.1, 127.1, 125.2, 107.8, 13.7; MS (EI) *m/z* 51, 75, 102, 116, 155, 190, 234.

*1-(4-Methoxyphenyl)-3-methyl-5-phenyl-1H-pyrazole (**2c**):* 47.0 mg, 89% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22−7.16 (m, 3 H), 7.81−7.73 (m, 7 H), 6.79 (m, 2H), 6.27 (s, 1 H), 3.72 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.6, 149.0, 143.7, 130.8, 128.6, 128.4, 128.0, 126.6, 114.0, 107.2, 55.3, 13.5; MS (EI) *m/z* 75, 116, 155, 190, 234, 264; HRMS calcd $C_{17}H_{16}N_2O$ [M^+] 264.1263, found 264.1258.

*4-(3-Methyl-5-phenyl-1H-pyrazol-1-yl)benzonitrile (**2d**:).* 47.1 mg, 91% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 8.4 Hz, 2H), 7.28−7.22 (m, 5H), 7.12 (s, 2H), 6.22 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.7, 143.9, 143.3, 132.7, 130.3, 128.8, 128.7, 128.6, 124.4, 118.2, 109.8, 109.6, 13.6; MS (EI) *m/z* 75, 102, 155, 190, 217, 243, 259; HRMS calcd $C_{17}H_{13}N_3$, [M^+] 259.1110, found 259.1106.

*1-(4-Fluorophenyl)-3-methyl-5-phenyl-1H-pyrazole (**2e**):* 42.8 mg, 85% yield; slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23−7.16 (m, 7H), 6.96−6.92 (m, 2H), 6.79 (m, 2H), 6.27 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.6, 160.2, 149.5, 143.8, 136.4, 128.6, 128.2, 115.8, 115.6, 107.8, 60.3, 13.5; MS (EI) *m/z* 51, 75, 102, 116, 155, 190, 234, 252; HRMS calcd $C_{16}H_{13}FN_2$, [M^+] 252.1063, found 252.1060.

*1-(4-Bromophenyl)-3-methyl-5-phenyl-1H-pyrazole (**2f**):* 54.2 mg, 87% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26−7.19 (m, 10H), 6.28 (s,1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.4, 143.7, 140.2, 130.8, 128.8, 127.1, 125.1, 107.8, 13.6; MS (EI) *m/z* 75, 116, 155, 190, 234, 312; HRMS calcd $C_{16}H_{13}BrN_2$ [M^+] 312.0262, found 312.0259.

*1-(tert-Butyl)-3-methyl-5-phenyl-1H-pyrazole (**2g**):* 35.1 mg, 82% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38−7.33 (m, 5 H), 5.92 (s, 1 H), 2.29 (s, 3H), 1.44 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.2, 143.5, 134.7, 130.4, 128.2, 127.7, 109.0, 60.6, 31.3, 13.5; MS (EI) *m/z* 63, 79, 127, 158, 214; HRMS calcd $C_{14}H_{18}N_2$ [M^+] 214.1470, found 214.147066.

*1,3,5-Triphenyl-1H-pyrazole (**2h**):*[4d] 53.2 mg, 90% yield; white solid; mp 129−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.42−7.32 (m, 11H), 6.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.0, 144.5, 140.2, 133.1, 130.6, 1299.0, 128.7, 128.5, 128.4, 128.1, 127.5, 125.9, 125.4, 105.3; MS (EI) *m/z* 77, 147, 192, 241, 267, 296.

*1-(4-Methoxyphenyl)-3,5-diphenyl-1H-pyrazole (**2i**):* 59.3 mg, 91% yield; colorless solid, mp 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.30−7.24 (m, 7H), 6.80 (t, *J* = 8.8 Hz, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.9, 151.7, 144.4, 133.5, 133.3, 130.7, 128.8, 128.3, 128.0, 126.8, 125.9, 114.2, 104.7, 55.5; MS (EI) *m/z* 77, 89, 165, 218, 267, 296, 326; HRMS calcd $C_{22}H_{18}N_2O$ [M^+] 326.1419, found 326.1416.

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4-(3,5-Diphenyl-1H-pyrazol-1-yl)benzonitrile (**2j**): 57.1 mg, 89% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.51−7.44 (m, 4H), 7.41−7.38 (m, 4H), 7.30 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.1, 144.8, 143.4, 132.9, 132.4, 128.5, 125.9, 124.8, 110.4, 106.9; MS (EI) m/z 77, 145, 218, 241, 296, 321; HRMS calcd $C_{22}H_{15}N_3$ [M^+] 321.1266, found 321.1262.

1-(4-Bromophenyl)-3,5-diphenyl-1H-pyrazole (**2k**): 62.0 mg, 83% yield; light yellow solid; mp 133−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, J = 7.2 Hz, 2H), 7.38−7.34 (m, 4H), 7.29−7.24 (m, 4H), 7.21−7.15 (m, 4H), 6.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.4, 144.5, 139.3, 128.9, 128.8, 128.7, 128.3, 126.7, 126.0, 121.0, 105.8; MS (EI) m/z 77, 165, 192, 218, 267, 296, 374; HRMS calcd $C_{21}H_{15}BrN_2$ [M^+] 374.0419, found 374.0416.

3,5-Diphenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazole (**2l**): 61.9 mg, 85% yield; yellow solid; mp 139−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.42−7.36 (m, 4H), 7.31−7.19 (m, 6H), 6.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.8, 144.7, 143.0, 132.8, 128.9, 128.4, 126.1, 126.0, 125.9, 124.8, 106.4; MS (EI) m/z 77, 146, 165, 192, 218, 267, 288, 364; HRMS calcd $C_{22}H_{15}F_3N_2$ [M^+] 364.1187, found 364.1184.

1-(tert-Butyl)-3,5-diphenyl-1H-pyrazole (**2m**): 50.2 mg, 91% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74−7.72 (m, 2H), 7.25−7.22 (m, 7H), 7.12 (t, J = 7.2 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.7, 142.9, 133.3, 132.9, 129.4, 127.3, 126.1, 124.4, 105.4, 60.3, 30.1; MS (EI) m/z 64, 133, 192, 220, 276; HRMS calcd $C_{19}H_{20}N_2$ [M^+] 276.1628, found 276.1624.

4-(3,5-Diphenyl-1H-pyrazol-1-yl)benzenesulfonamide (**2n**): 54.2 mg, 87% yield; white solid; mp 158−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.4 Hz, 3H), 7.48 (d, J = 7.6 Hz, 2H), 7.43−7.41 (m, 3H), 7.37−7.35 (m, 2H), 7.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.8, 144.4, 142.7, 142.0, 132.3, 129.7, 128.8, 128.6, 128.3, 127.0, 126.7, 125.5, 125.0, 113.4, 106.4.

4-(3,5-Diphenyl-1H-pyrazol-1-yl)benzoic acid (**2o**): 57.1 mg, 84% yield; white solid; mp 147−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (s, 4H), 7.48−7.35 (m, 10H), 7.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.6, 151.7, 144.3, 143.0, 130.2, 129.5, 128.7, 128.5, 128.2, 125.5, 124.6, 110.0, 106.2; MS (EI) m/z 77, 165, 192, 220, 296, 340; HRMS calcd $C_{22}H_{16}N_2O_2$ [M^+] 340.1212, found 340.1207.

3,5-Diphenyl-1H-pyrazole (**2p**):[4e] 37.8 mg, 86% yield; slightly yellow solid; mp 135−137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.87 (br. s, 1H), 7.72−7.70 (d, J = 6.8 Hz, 4H), 7.38−7.29 (m, 6H), 6.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.8, 131.3, 128.8, 128.2, 125.6, 100.1; MS (EI) m/z 77, 101, 133, 165, 192, 220.

4-(5-(4-Chlorophenyl)-3-phenyl-1H-pyrazol-1-yl)benzonitrile (**2q**): 62.4 mg, 88%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, J = 6.8 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.44−7.32 (m, 7H), 7.17 (d, J = 7.6 Hz, 2H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.2, 143.5, 143.1, 135.2, 132.3, 130.0, 128.5, 125.9, 124.9, 118.2, 110.7, 107.0; MS (EI) m/z 101, 133, 165, 192, 296, 355; HRMS calcd $C_{22}H_{14}ClN_3$ [M^+] 355.0876, found 355.0872.

1-(4-Bromophenyl)-5-(4-chlorophenyl)-3-phenyl-1H-pyrazole (**2r**): 69.3 mg, 85% yield; yellow solid; mp 147−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, J = 7.2 Hz, 2H), 7.47−7.40 (m, 4H), 7.36−7.29 (m, 3H), 7.23−7.17 (m, 4H), 6.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.4, 143.2, 138.9, 134.7, 132.7, 132.2, 128.8, 128.3, 126.6, 125.8, 121.3, 105.8; MS (EI) m/z 77, 101, 133, 192, 220, 296, 330, 374, 408; HRMS calcd $C_{21}H_{14}BrClN_2$ [M^+] 408.0029, found 408.0026.

1-(tert-Butyl)-5-(4-chlorophenyl)-3-phenyl-1H-pyrazole (**2s**): 50.8 mg, 82% yield; slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (d, J = 8.4 Hz, 2H), 7.38−7.27 (m, 7H), 6.43 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.0, 142.7, 131.8, 129.6, 128.6, 127.4, 125.5, 106.7, 61.6, 31.3; MS (EI) m/z 77, 103, 191, 219, 253, 297, 310; HRMS calcd $C_{19}H_{19}ClN_2$ [M^+] 310.1237, found 310.1233.

1-Phenyl-5-(thiophene-2-yl)-3-(p-tolyl)-1H-pyrazole (**2t**): 58.1 mg, 92% yield; black oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, J = 7.6 Hz, 2H), 7.58 (dd, J = 6.8 Hz, 33.2 Hz, 5H), 7.19−7.15 (m, 3H), 6.84−6.78 (m, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.1, 140.1, 138.2, 137.9, 130.2, 129.1, 127.5, 126.7, 125.9, 105.0, 21.5; MS (EI) m/z 51, 115, 198, 255, 281, 316; HRMS calcd $C_{20}H_{16}N_2S$ [M^+] 316.1034, found 316.1031.

4-(5-(Thiophene-2-yl)-3-(p-tolyl)-1H-pyrazol-1-yl)benzonitrile (**2u**:). 62.0 mg, 91% yield; dark purple oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H),7.36 (d, J = 8.8 Hz, 1H), 7.22 (d, J = 7.6 Hz, 2H), 7.00 (t, J = 4.0 Hz, 2H), 6.88 (d, J = 2.8 Hz, 1H), 6.82 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.1, 143.2, 138.5, 137.9, 133.0, 132.9, 129.5, 129.2, 128.2, 127.5, 125.9, 125.3, 124.9, 110.9, 107.4, 21.4; MS (EI) m/z 77, 152, 231, 281, 326, 341; HRMS calcd $C_{21}H_{15}N_3S$, [M^+] 341.0987, found 341.0983.

1-(4-Bromophenyl)-5-(thiophene-2-yl)-3-(p-tolyl)-1H-pyrazole (**2v**): 69.3 mg, 88% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, J = 7.0 Hz, 1H), 7.48 (dd, J = 5.6 Hz, 37.6 Hz, 2H), 7.25−7.09 (m, 5H), 6.97−6.77 (m, 4H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.4, 148.3, 145.6, 138.1, 129.5, 127.0, 111.7, 105.7, 21.6; MS (EI) m/z 77, 152, 211, 281, 316, 394; HRMS calcd $C_{20}H_{15}BrN_2S$ [M^+] 394.0139, found 394.0136.

1-tert-Butyl-5-(thiophene-2-yl)-3-(p-tolyl)-1H-pyrazole (**2w**): 48.5 mg, 82% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 5.2 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 6.79 (s, 1H), 2.54 (s, 3H), 1.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.1, 137.0, 135.7, 133.9, 131.3, 129.5, 127.3, 126.9, 125.7, 108.9, 61.8, 31.1, 21.5; MS (EI) m/z 65, 91, 130, 197, 211, 281, 296; HRMS calcd $C_{18}H_{20}N_2S$ [M^+] 296.1347, found 296.1343.

3-Methyl-1-phenyl-5-(2,6,6-trimethylcyclohex-1-en-1-yl)-1H-pyrazole (**2x**): 48.7 mg, 87% yield; slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 7.2 Hz, 2H), 7.17 (t, J = 6.8 Hz,1H), 5.88 (s, 1H), 2.32 (s, 3H), 2.01 (t, J = 6.4 Hz, 2H), 1.49−1.36 (m, 6H), 0.99 (s, 3H), 0.93 (d, J = 7.2 Hz, 1H), 0.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 141.6, 136.2, 130.8, 128.4, 126.0, 123.1, 108.6, 38.8, 34.9, 31.7, 29.2, 28.0, 18.9, 13.6; MS (EI) m/z 65, 77, 117, 170, 197, 235, 265, 280; HRMS calcd $C_{19}H_{24}N_2$ [M^+] 280.1940, found 280.1936.

1-(4-Bromophenyl)-3-methyl-5-(2,6,6-trimethylcyclohex-1-en-1-yl)-1H-pyrazole (**2y**): 61.5 mg, 86% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39−7.35 (m, 2H), 7.31 (d, J = 8.8 Hz, 2H), 5.82 (s, 1H), 2.25 (s, 3H), 1.96 (t, J = 6.4 Hz, 2H), 1.67−1.53 (m, 2H), 1.46−1.41 (m, 1H), 1.37−1.35 (m, 4H), 0.96 (s, 3H), 0.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.9. 142.6, 136.7, 126.8, 124.2, 119.5, 109.1, 38.9, 35.0, 31.8, 29.2, 28.2, 18.9, 13.7; MS (EI) m/z 77, 154, 197, 223, 280, 316, 358; HRMS calcd $C_{19}H_{23}BrN_2$ [M^+] 358.1045, found 358.1041.

(E)-1,5-Diphenyl-3-styryl-1H-pyrazole (**2z**): 51.6 mg, 81% yield; white solid; mp 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98−7.96 (d, J = 8.0 Hz, 2H), 7.48−7.44 (d, J = 7.2 Hz, 1H), 7.42−7.32 (m, 11H), 6.86(s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.0, 144.5, 140.2, 133.1, 130.6, 129.0, 128.7, 128.5, 128.4, 128.1, 127.5, 125.9, 125.4, 105.3; MS (EI) m/z 75, 155, 190, 246, 322; HRMS calcd $C_{23}H_{18}N_2$ [M^+] 322.1470, found 322.1467.

1,3-Diphenyl-1H-indazole (**4a**):[5b] 45.3 mg, 84%; yellow solid; mp 136−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (dd, J = 4.0 Hz, 16.0 Hz, 3H), 7.81 (t, J = 8.0 Hz, 3 H), 7.55 (dd, J = 7.6 Hz, 15.6 Hz, 4H), 7.46 (dd, J = 8.8 Hz, 16.4 Hz, 2 H), 7.39 (t, J = 8.4 Hz, 1H), 7.30 (t, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.1, 140.4, 140.2, 133.3, 130.1, 129.5, 128.9, 127.8, 127.1, 126.7, 123.2, 123.0, 122.0, 121.6, 110.7; MS (EI) m/z 77, 115, 167, 192, 215, 241, 270.

1-(4-Methoxyphenyl)-3-phenyl-1H-indazole (**4b**): 492. mg, 82%; yellow solid, mp 129−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (t, J = 8.8 Hz, 3H), 7.51 (t, J = 7.2 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.5, 145.6, 140.7, 128.2, 124.8, 121.5, 114.7, 110.5, 55.6; MS (EI) m/z 77, 115, 167, 192, 215, 241, 300; HRMS calcd $C_{20}H_{16}N_2O$ [M^+] 300.1263, found 300.1259.

1-(4-Fluorophenyl)-3-phenyl-1H-indazole (**4c**): 49.5 mg, 86%; yellow solid, mp 142−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (dd, J = 4.0 Hz, 22.0 Hz, 3H), 7.81−7.73 (m, 2H), 7.69 (d, J = 4.0

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Hz, 1H), 7.60−7.49(m, 2H), 7.48−7.41 (m, 2H), 7.31−7.22 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.5, 160.0, 146.2, 140.5, 136.3, 133.1, 132.4, 128.9, 128.3, 127.3, 124.8, 123.1, 122.0, 121.7, 116.5, 116.2, 110.4; MS (EI) *m*/*z* 63, 77, 95, 157, 184, 210, 267, 288; HRMS calcd $C_{19}H_{13}FN_2$ [M^+] 288.1063, found 288.1058.

3-Phenyl-1-(4-(trifluoromethyl)phenyl)-1H-indazole (**4d**):[5c] 48.6 mg, 72% yield; yellow solid; mp 145−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (t, *J* = 7.6 Hz, 5H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.48 (s, 1H), 7.26 (d, *J* = 7.6 Hz, 2 H), 7.02 (d, *J* = 8.4 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.1, 143.3, 140.7, 138.5, 138.1, 130.1, 129.6, 126.7, 126.6, 124.5, 122.0, 122.0, 121.5, 110.2, 22.1, 21.4; MS (EI) *m*/*z* 77, 145, 192, 235, 317, 338.

1-(2,4-Dichlorophenyl)-3-phenyl-1H-indazole (**4e**): 48.6 mg, 73% yield; yellow solid; mp 146−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96−7.92 (m, 3H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.36 (dd, *J* = 2.4 Hz, 9.2 Hz, 1H), 7.25−7.19 (m, 3H), 7.08−7.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.4, 164.0, 161.9, 161.6, 145.8, 138.3, 128.7, 123.8, 116.1, 115.9, 112.1, 111.8, 96.7, 96.4; MS (EI) *m*/*z* 77, 139, 192, 215, 269, 304, 338; HRMS calcd $C_{19}H_{12}Cl_2N_2$ [M^+] 338.0378, found 338.0374.

4-(3-Phenyl-1H-indazol-1-yl)benzonitrile (**4f**): 41.3 mg, 70% yield; yellow solid; mp 141−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (dd, *J* = 4.0 Hz, 22.0 Hz, 3H), 7.81−7.73 (m, 2H), 7.69 (d, *J* = 4.0 Hz, 1H), 7.60−7.49 (m, 2H), 7.48−7.41 (m, 2H), 7.31−7.22 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.5, 160.0, 146.2, 140.5, 136.3, 133.1, 132.4, 128.9, 128.3, 127.3, 124.8, 123.1, 122.0, 121.7, 116.5, 116.2, 110.4; MS (EI) *m*/*z* 77, 115, 167, 192, 215, 269, 295; HRMS calcd $C_{20}H_{13}N_3$ [M^+] 295.1110, found 295.1106.

6-Methyl-1-phenyl-3-(p-tolyl)-1H-indazole (**4g**):[4f] 51.2 mg, 86% yield; yellow solid; mp 88−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (dd, *J* = 2.0 Hz, 8.4 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.33 (dd, *J* = 7.6 Hz, 14.6 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 2.46 (d, *J* = 32.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.0, 142.9, 140.3, 138.1, 137.5, 135.3, 130.2, 129.5, 128.9, 127.6, 126.5, 124.0,123.1, 121.4, 121.2, 110.1, 22.1, 21.4; MS (EI) *m*/*z* 65, 95, 116, 183, 205, 269, 298; HRMS calcd $C_{21}H_{18}N_2$ [M^+] 298.1470, found 298.1466.

4-(6-Methyl-3-(p-tolyl)-1H-indazol-1-yl)benzonitrile (**4h**): 50.3 mg, 78% yield; yellow solid; mp 127−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95−7.89 (m, 5H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.59 (s, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 2.54 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.7, 143.9, 140.6, 138.8, 138.5, 133.5, 129.7, 129.6, 127.7, 124.8, 121.8, 118.7, 110.3, 108.7, 22.2, 21.4; MS (EI) *m*/*z* 65, 77, 91, 183, 205, 223, 295, 323; HRMS calcd $C_{22}H_{17}N_3$ [M^+] 323.1423, found 323.1420.

6-Methyl-3-(p-tolyl)-1-(4-(trifluoromethyl)phenyl)-1H-indazole (**4i**): 56.3 mg, 77% yield; yellow solid; mp 147−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03−7.98 (m, 3H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.74−7.71 (m, 3H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.42−7.38 (m, 2H), 2.38 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.2, 143.1, 140.2, 132.8, 129.0, 128.2, 127.9, 127.7, 126.6, 125.5, 123.8, 122.8, 122.6, 122.1, 121.9, 110.6; MS (EI) *m*/*z* 65, 77, 91, 145, 183, 223, 248, 282, 296, 336, 350, 366; HRMS calcd $C_{22}H_{17}F_3N_2$ [M^+] 366.1344, found 366.1340.

6-Fluoro-3-(4-fluorophenyl)-1-phenyl-1H-indazole (**4j**):[4f] 50.1 mg, 82% yield; yellow solid; mp 169−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90−7.87 (m, 2H), 7.81−7.78 (m, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.13 (t, *J* = 8.4 Hz, 2 H), 6.93 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.3, 163.9, 161.8, 161.4, 145.3, 140.7, 140.6, 139.7, 129.6, 129.5, 129.0, 127.0, 122.8, 122.7, 119.8, 116.0, 115.8, 111.8, 111.6, 96.8, 96.5 ; MS (EI) *m*/*z* 57, 77, 95, 123, 185, 210, 245, 285, 306; HRMS calcd $C_{19}H_{12}F_2N_2$ [M^+] 306.0968, found 306.0965.

4-(6-Fluoro-3-(4-fluorophenyl)-1H-indazol-1-yl)benzonitrile (**4k**): 48.9 mg, 74% yield; yellow solid; mp 172−174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01−7.94 (m, 5H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.51 (dd, *J* = 0.4 Hz, 9.2 Hz, 1H), 7.26 (t, *J* = 8.8 Hz, 2H), 7.14 (dt, *J* = 2.0 Hz, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.6, 164.3, 162.1, 161.8, 147.1, 143.3, 140.4, 140.3, 133.7, 129.6, 128.2, 123.4, 122.0, 120.7, 118.4, 116.2, 116.0, 112.7, 112.4, 109.7; MS (EI) *m*/*z* 77, 95, 149, 185, 208, 295, 331; HRMS calcd $C_{20}H_{11}F_2N_3$ [M^+] 331.0921, found 331.0918.

6-Fluoro-1,3-bis(4-fluorophenyl)-1H-indazole (**4l**): 40.1 mg, 62% yield; yellow solid; mp 170−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01−7.94 (m, 5H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.51 (dd, *J* = 0.4 Hz, 9.2 Hz, 1H), 7.26 (t, *J* = 8.8 Hz, 2H), 7.14 (dt, *J* = 2.0 Hz, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.3, 164.0, 162.6, 161.8, 160.2, 145.5, 140.8, 135.8, 132.5, 128.8, 122.8, 119.7, 115.5, 111.9, 111.7, 96.5, 96.2; MS (EI) *m*/*z* 69, 95, 121, 162, 202, 229, 251, 291, 303, 324; HRMS calcd $C_{19}H_{11}F_3N_2$ [M^+] 324.0874, found 324.0871.

6-Methyl-1,3-diphenyl-1H-indazole + 1-phenyl-3-(p-tolyl)-1H-indazole (**4m+4m′**): 44.3 mg, 78% yield; yellow solid; mp 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (dd, *J* = 8.4 Hz, 17.0 Hz, 3H), 7.90 (t, *J* = 8.8 Hz, 2.76H), 7.72−7.63 (m, 4.76H), 7.49 (t, *J* = 7.2 Hz, 2.3H), 7.40 (dd, *J* = 6.4 Hz, 3.3H), 7.30 (d, *J* = 8.0 Hz, 1.8H), 7.24−7.18 (m, 4.7H), 7.08 (d, *J* = 8.4 Hz, 1.6H), 2.48 (s, 3H), 2.41 (s, 2.2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.4, 160.0, 146.3, 146.0, 138.3, 133.3, 128.8, 127.7, 124.9, 123.1, 121.2, 116.2, 110.3, 109.8, 22.0, 21.4; MS (EI) *m*/*z* 77, 115, 167, 192, 215, 284; HRMS calcd $C_{20}H_{16}N_2$ [M^+] 284.1313, found 284.1310.

6-Chloro-1,3-diphenyl-1H-indazole 3-(4-chlorophenyl)-1-phenyl-1H-indazole (**4n+4n′**): 45.6 mg, 75% yield; yellow solid; mp 138−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 7.2 Hz, 1.9H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.94 (dd, *J* = 7.6 Hz, 18.8 Hz, 2.3H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.68−7.53 (m, 5.2H), 7.51−7.40 (m, 2.8H), 7.34 (t, *J* = 7.6 Hz, 1.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.2, 140.5, 140.4, 133.6, 131.3, 130.2, 129.6, 128.8, 128.5, 128.0, 127.3, 126.9, 126.8, 123.4, 123.0, 122.2, 121.7, 110.9; MS (EI) *m*/*z* 77, 115, 139, 167, 192, 241, 304; HRMS calcd $C_{19}H_{13}ClN_2$ [M^+] 304.0767, found 304.0763.

6-Chloro-1-(4-fluorophenyl)-3-phenyl-1H-indazole + 3-(4-chlorophenyl)-1-(4-fluorophenyl)-1H-indazole (**4o+4o′**): 50.2 mg, 78% yield; yellow solid; mp 145−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 4.9H), 7.78−7.66 (m, 7.4H), 7.59−7.43 (m, 7.5H), 7.32−7.22 (m, 6.7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.7, 162.6, 160.2, 160.1, 146.3, 145.0, 140.9, 140.5, 135.8, 133.8, 132.5, 131.5, 129.0, 128.7, 128.4, 127.4, 125.0, 124.9, 123.0, 122.6, 122.2, 121.6, 121.4, 116.6, 116.5, 116.4, 116.3, 110.5, 110.1; MS (EI) *m*/*z* 77, 115, 167, 192, 215, 241, 288, 322; HRMS calcd $C_{19}H_{12}ClFN_2$ [M^+] 322.0673, found 322.0670.

4-(6-Chloro-3-phenyl-1H-indazol-1-yl)benzonitrile + 4-(3-(4-chlorophenyl)-1H-indazol-1-yl)benzonitrile (**4p+4p′**):[4f] 51.3 mg, 78% yield; yellow solid; mp 127−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.0 Hz, 1.33H), 7.97−7.93 (m, 7.26H), 7.91 (s, 1.24H), 7.85−7.81 (m, 5.37H), 7.57−7.47 (m, 6H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 84 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.9, 146.6, 143.6, 143.2, 140.4, 140.0, 134.9, 134.6, 133.6, 131.9, 130.9, 129.1, 128.9, 128.1, 127.8, 123.9, 123.8, 123.0, 122.6, 122.1, 122.0, 121.8, 118.5, 118.4, 110.8, 110.6, 109.7, 109.4; MS (EI) *m*/*z* 77, 115, 139, 192, 215, 295, 329; HRMS calcd $C_{20}H_{12}ClN_3$ [M^+] 329.0720, found 329.0716.

4-Bromo-3-methyl-1,5-diphenyl-1H-pyrazole (**5a**): 109.2 mg, 70% yield; yellow solid; mp 146−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12−7.00 (m, 10H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.2, 140.5, 139.9, 129.8, 129.2, 128.7, 128.5, 127.1, 124.5, 97.0, 60.1, 12.5; MS (EI) *m*/*z* 51, 75, 116, 155, 190, 234, 312; HRMS calcd $C_{16}H_{13}BrN_2$ [M^+] 312.0262, found 312.0258.

4-Bromo-1,3,5-triphenyl-1H-pyrazole (**5b**): 104.6 mg, 72% yield; yellow solid; mp 147−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 5H), 7.47−7.21 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.8, 142.1, 139.9, 130.3, 129.1, 128.6, 128.4, 127.6, 124.9, 95.0; MS (EI) *m*/*z* 77, 89, 147, 165, 192, 218, 241, 267, 296, 374; HRMS calcd $C_{21}H_{15}BrN_2$ [M^+] 374.0419, found 374.0415.

3-Methyl-1,5-diphenyl-4-(phenylethynyl)-1H-pyrazole (**6**): 150.3 mg, 90% yield; yellow solid; mp 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46−7.41 (m, 4H), 7.36−7.27 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.9, 144.3, 139.8, 131.3, 128.6, 127.5, 125.2, 123.8, 104.2, 93.2, 81.6, 12.7; MS (EI) *m*/*z* 51, 75, 102, 155, 190, 234, 334; HRMS calcd $C_{24}H_{18}N_2$ [M^+] 334.1470, found 334.1466.

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*N-tert-Butyl-3-methyl-1,5-diphenyl-1H-pyrazole-4-carboxamide (**7**):* 141.5 mg, 85% yield; yellow solid; mp 149−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43−7.39 (m, 3H), 7.30−7.28 (m, 5H), 7.25−7.22 (m, 2H), 2.59 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.2, 150.8, 141.5, 139.3, 128.8, 127.5, 125.1, 116.8, 51.0, 28.6, 13.6; MS (EI) *m*/*z* 75, 102, 155, 190, 234, 333; HRMS calcd $C_{21}H_{23}N_3O$ [M^+] 333.1841, found 333.1837.

*1,3,5-triphenyl-4-(p-tolyl)-1H-pyrazole (**8**):* 158.3 mg, 82% yield; yellow solid; mp 148−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (s, 2H), 7.45−7.13 (m, 17H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.3, 141.4, 140.2, 136.3, 133.4, 130.6, 128.4, 127.3, 125.9, 125.4, 21.4; MS (EI) *m*/*z* 77, 139, 190, 263, 307, 355, 370, 386; HRMS calcd $C_{28}H_{22}N_2$ [M^+] 386.1783, found 386.1780.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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