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Synthesis of Pyrazoles via CuI-Mediated Electrophilic Cyclizations of α,β-Alkynic Hydrazones

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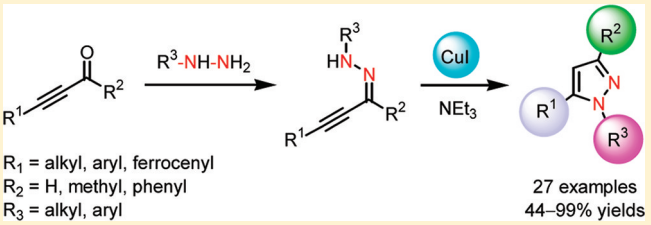
Supporting Information

ABSTRACT: Synthesis of pyrazoles via electrophilic cyclization of α,β-alkynic hydrazones by copper(I) iodide is described. When treated with copper(I) iodide in the presence of triethylamine in refluxing acetonitrile, α,β-alkynic hydrazones, prepared readily from hydrazines and propargyl aldehydes and ketones, undergo electrophilic cyclization to afford pyrazole derivatives in good to excellent yields. The reaction appears to be general for a variety of α,β-alkynic hydrazones and tolerates the presence of aliphatic, aromatic, and ferrocenyl moieties with electron-withdrawing and electron-donating substituents.



INTRODUCTION

Pyrazoles are popular targets for synthetic chemists primarily because of their diverse and potent biological properties.[1] In fact, pyrazoles have been extensively studied in the last few decades as a prominent class of heterocycles[2] and still receive great attention for both pharmaceutical and agricultural benefits. Pyrazoles have been reported to exhibit a wide range of biological properties, including analgesic,[3] antibacterial,[4] antidepressant,[5] anti-inflammatory,[6,7] antimicrobial,[8] antiobesity,[9] antiviral,[10] appetite suppressant,[11] cholesterol-lowering,[12] antihyperglycemic,[13] antihypertensive,[14] and anticancer[15] activities. In addition, they are present as the core structure in a large variety of leading drugs and pesticides, such as Celebrex,[7] Viagra[16] and Zometapine,[17] and Cyenopyrafen,[18] Fenpyroximate,[19] and Tebufenpyrad.[20] Typical methods for the synthesis of pyrazoles involve the approaches based either on the condensation of hydrazines with 1,3-dicarbonyl compounds[21] and their 1,3-dielectrophilic equivalents including α,β-unsaturated aldehydes and ketones[22] or on the intermolecular 1,3-dipolar cycloaddition of diazoalkanes and nitrilimines with alkenes and alkynes.[23] Some drawbacks of these protocols, such as the poor reactivity and regioselectivity and the potential hazardousness and detonation of the substrates, limit their practical application to some extent. Notably, pyrazoles are rarely prepared by the functionalization of unsubstituted or less substituted pyrazoles because they often require a laborious multistep synthesis.[24] Consequently, there still exists a great demand to develop new methodologies for the synthesis of substituted pyrazole derivatives. Although over the years, diverse methodologies have been developed,[25] the regiocontrolled and broadly applicable synthesis of pyrazoles remains a noteworthy challenge for synthetic chemists.

We have recently investigated the reactions of 3-ferrocenylpropynal (**1**) with hydrazinium salts (**2**) (Scheme 1).[26] Depending upon the substitution pattern of hydrazines, these reactions furnished 1-alkyl/aryl-5-ferrocenylpyrazoles (**3**, 1,5-isomer) and/or 1-alkyl/aryl-3-ferrocenylpyrazoles (**4**, 1,3-isomer), the former being the single or the major product of the reaction in most cases. Interestingly, if hydrazines are employed instead of hydrazinium salts, pyrazoles are obtained in very low yields. When hydrazinium salts, however, are used, the reaction medium becomes somewhat acidic, and pyrazoles are formed in good yields. Obviously, acid catalysis favors the reaction, but in this case, the proportion of 1,3-pyrazole isomer **4** increases at the expense of 1,5-pyrazole isomer **3**, consistent with the observations of other researchers using analogous systems.[27] As previously proposed, these reactions go through the corresponding acetylenic hydrazone and/or conjugated addition intermediates, depending upon the reaction conditions and/or the identity of the substituent in hydrazine derivatives **2**.[28] We anticipated that electrophilic cyclization of such acetylenic hydrazones, which can be easily prepared from hydrazines and acetylenic aldehydes and ketones, would provide a rapid entry to a wide variety of pyrazole derivatives.

Recently, an explosive increase of interest in electrophilic cyclizations of functionally substituted alkynes has happened,[29] thus becoming an enormously active and inventive field of heterocyclic synthesis because they often take place in a regioselective manner as well as in very mild reaction conditions.[30] By employing such electrophilic cyclizations, a large variety of important heterocycles and carbocycles have been synthesized, including furans,[31] benzofurans,[32] thiophenes,[33] benzothiophenes,[34] bicyclic β-lactams,[35] chromones,[36] cyclic carbonates,[37] isoxazoles,[38] indoles,[39] isocoumarins,[40] isochromenes,[41] isoindolinones,[42] naphthalenes,[43] and quinolines.[44] In this regard, we have recently reported the synthesis of α,β-alkynic hydrazones **7** and their electrophilic

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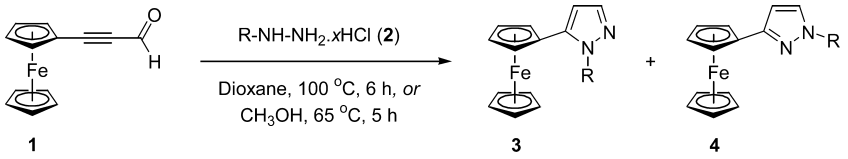
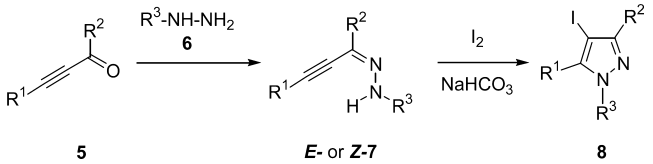
Scheme 1



cyclization into 4-iodopyrazole derivatives **8** in good to excellent yields by using molecular iodine in the presence of sodium bicarbonate (Scheme 2).[45] Iodocyclizations have been found to be general for a wide range of α,β-alkynic hydrazones and tolerated the presence of aliphatic, aromatic, heteroaromatic, and ferrocenyl moieties with electron-withdrawing and electron-donating substituents.

Scheme 2



Amazingly, electrophilic cyclizations of such acetylenic hydrazones were not utilized amply for the synthesis of pyrazoles since a literature search on this subject exposed very few reports. Gonzales-Nogal reported the synthesis of 5-silylpyrazoles by electrophilic cyclization of β-silyl-substituted acetylenic hydrazones with ethyl chloroformate and aluminum chloride, and molecular iodine.[46] Although the Larock research group planned to study electrophilic cyclization of acetylenic *N,N*-dimethylhydrazones to furnish 4-halopyrazoles, they were unable to prepare the required hydrazones.[47] Thus, they develop another method to 4-halopyrazoles, but it does not incorporate electrophilic cyclization. The Wada research group synthesized pyrazoles and dihydropyrazoles by a reagent-controlled iodocyclization of propargylic hydrazides.[48] Lately, Liu and Xu and co-workers developed a method for the synthesis of fluorinated pyrazoles via gold(I)-catalyzed electrophilic cyclization of acetylenic hydrazones in the presence of Selectfluor.[49]

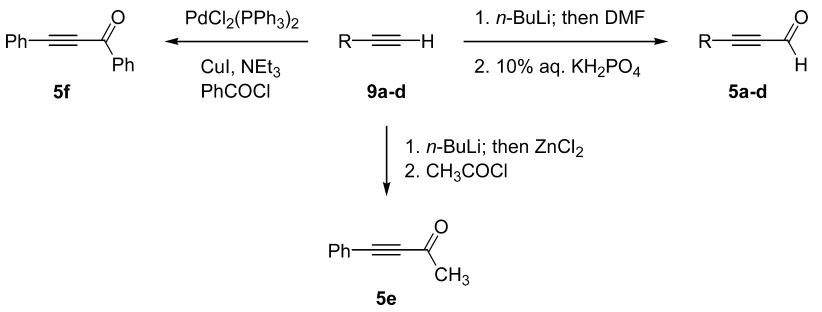
Recently, copper-mediated (both stoichiometric and catalytic) reactions have attracted great attention because the ability of these compounds to promote a wide range of reactions has allowed for their broad application.[50,51] In particular, electrophilic cyclization of functionally substituted alkynes by copper Lewis acids has been recognized as an attractive way to produce a variety of important heterocycles.[52] However, to the best of our knowledge, copper-mediated electrophilic cyclizations of α,β-alkynic hydrazones have not been explored, which in fact could provide a rapid entry to the generation of pyrazole libraries. As part of a program to synthesize new pyrazole derivatives as potential pharmaceuticals, we have further explored the electrophilic cyclizations of such alkynic hydrazones. We have disclosed that upon treatment with copper(I) iodide in the presence of triethylamine in refluxing acetonitrile, α,β-alkynic hydrazones, prepared readily from hydrazines and acetylenic aldehydes and ketones, undergo electrophilic cyclization to afford pyrazole derivatives in good to excellent yields.[53] We herein report the results of this study.

RESULTS AND DISCUSSION

The required α,β-acetylenic aldehydes and ketones can be easily prepared according to standard literature procedures as shown in Scheme 3. The lithiation of terminal alkynes **9a–d** with *n*-BuLi, followed by the formylation of in situ generated lithium acetylides with DMF, affords α,β-acetylenic aldehydes **5a–d** in good to excellent yields.[54] It is noteworthy to mention that these high yielding formylation reactions have required a reverse quench into a phosphate buffer as the key. 3-Ferrocenylpropynal (**1**) can be synthesized from ethynylferrocene by a similar formylation reaction.[55] On the other hand, the reaction of in situ generated lithium acetylide with $ZnCl_2$ yields zinc acetylide, the coupling of which with acetyl chloride leads to acetylenic methyl ketone **5e** (Scheme 3).[56] Acetylenic phenyl ketone **5f** can be prepared directly from the terminal alkyne and benzoyl chloride by a palladium-catalyzed coupling reaction.[57]

Subsequently, we synthesized a variety of α,β-acetylenic hydrazones **7** from alkynals and alkynones **5**. In fact, we prepared 27 kinds of hydrazone derivatives, 8 of which (**Z-7e–g**, **Z-7j**, **Z-7n–p**, and **Z-7v**) were synthesized for the first time (Scheme 4 and Table 1). Note that we reported the synthesis of the remaining 19 hydrazone derivatives (**Z-7a–d**, **Z-7h–i**, **Z-7k–m**, **Z-7q–u**, and **Z-7w–aa**) in a recent study,[45] which were prepared in refluxing dioxane at 100 °C or in the absence of solvent at 80 °C (see Tables 2 and 3 for the structures of these hydrazones). In light of the previous study, condensation reactions for the synthesis of new hydrazones were conducted

Scheme 3



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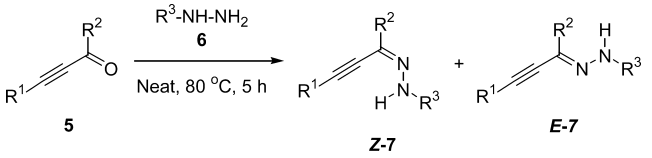
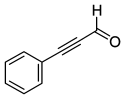
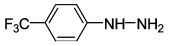
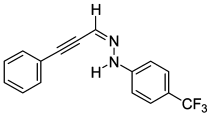
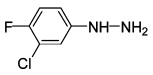
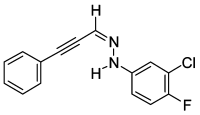
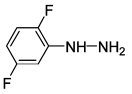
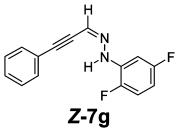
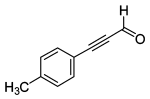
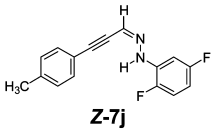
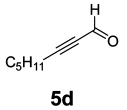
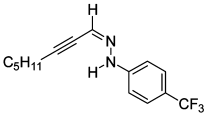
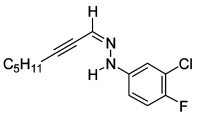
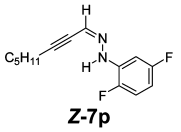
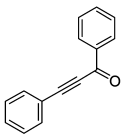
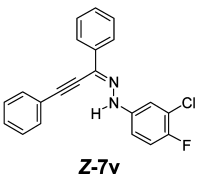
Scheme 4



in the neat conditions (without solvent) at 80 °C (Scheme 4). As illustrated in Table 1, the yields of hydrazones changed from 47 to 93%. As noted in both this study and earlier work,[45] from the reactions of 3-alkyl- or aryl-substituted propargyl aldehydes and ketones **5**, Z isomers of acetylenic hydrazones, ***Z*-7**, were resulted as major products, whereas E isomers, ***E*-7**, were obtained as minor products. Notably, E isomers ***E*-7** were not so stable in the reaction conditions, on silica gel during flash chromatography and/or on standing at room temperature in a solvent, that they partially converted into Z isomers ***Z*-7**. For this reason, we kept the reaction time longer and minimized the formation of E isomers to some level since they changed into Z isomers. As indicated by theoretical calculations at the density functional theory (DFT) level,[45] Z isomers of acetylenic hydrazones are thermodynamically more stable than their E isomers. As a result, the isolation of E isomers ***E*-7** was not attempted, and the electrophilic cyclizations were carried out with Z isomers ***Z*-7**.

As mentioned previously, E and Z isomers of acetylenic hydrazones can easily be identified on the basis of their ^{13}C

Table 1. Synthesis of Acetylenic Hydrazones

entry	aldehyde or ketone	hydrazine	hydrazone	% yield[a]
1	 **5a**	 **6b**	 ***Z*-7e**	59
2	**5a**	 **6c**	 ***Z*-7f**	80
3	**5a**	 **6d**	 ***Z*-7g**	47
4	 **5b**	**6d**	 ***Z*-7j**	80
5	 **5d**	**6b**	 ***Z*-7n**	70
6	**5d**	**6c**	 ***Z*-7o**	93
7	**5d**	**6d**	 ***Z*-7p**	88
8	 **5f**	**6c**	 ***Z*-7v**	65

[a]Isolated yield.

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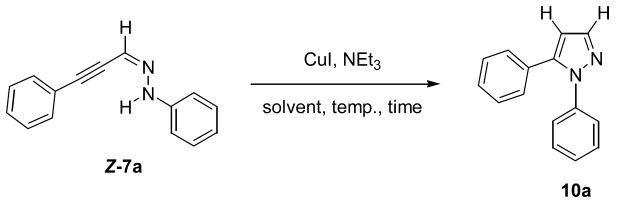
Table 2. Electrophilic Cyclization of Acetylenic Hydrazone *Z*-7a



entry	CuI (amt (equiv))	NEt_3(amt (equiv))	solvent	temp. (°C)	time (h)	% yield[a]
1	1		CH_3CN	rt	2	
2	1		CH_3CN	82	8	60
3	1	1	CH_3CN	rt	2	
4	1	1	CH_3CN	82	1.5	64
5	1	1	CH_3CN	82	2	73
6	2	1	CH_3CN	82	2	66
7	1	1	CH_2Cl_2	40	2	
8	0.05	1	CH_3CN	rt	2	
9[b]	0.05	1	CH_3CN	82	2	20
10	0.05	1	CH_3CN	82	23	61
11	0.10	1	CH_3CN	82	15	62
12	0.10	2	CH_3CN	82	6.5	62
13	0.15	1	CH_3CN	82	12	72
14	0.05	1	dioxane	100	10	55
15	0.10	1	dioxane	100	9	69
16	0.10	1	toluene	110	9	66

[a]Isolated yield. [b]Starting hydrazone *Z*-7a was recovered in 72% yield.

NMR spectra.[45,58] Two alkynic carbons in the E isomer resonate closely, and the chemical shift difference between these carbons is about 3−12 ppm. On the other hand, in the Z isomer, the alkynic carbon adjacent to the carbonyl group is comparatively upfield while the other alkynic carbon is relatively downfield, and the chemical shift difference between these carbons is roughly 22−30 ppm. In brief, the absolute value of chemical shift difference between alkynic carbons in the Z isomer is typically bigger as compared to that in the E isomer.

After synthesizing the requisite hydrazones 7, we investigated their electrophilic cyclizations to pyrazoles. Initially, electrophilic cyclization of phenylpropynal phenylhydrazone (*Z*-7a), prepared from 3-phenyl-2-propynal (**5a**) and phenylhydrazine (**6a**), was examined under several conditions to find optimal reaction conditions (Table 2). It is well-known that copper salts have mild Lewis acidity and have been commonly used as catalysts in organic synthesis.[51] Among these salts, we preferred CuI, one of the most employed reagents for inducing transformations, because it takes advantage of its affinity to carbon−carbon unsaturated bonds rather than oxygen functional groups. In addition, CuI was used effectively in the electrophilic cyclization of functionally substituted alkynes.[59] In the light of literature studies, we chose NEt_3 as a base and CH_3CN as a reaction solvent because they are one of the most commonly used bases and solvents in such transformations.[60] As a result, we carried out the optimization reactions with CuI/NEt_3 system in CH_3CN. When the hydrazone *Z*-7a was reacted with 1 equiv of CuI in CH_3CN for 2 h at room temperature, no conversion to pyrazole **10a** was observed, as indicated by TLC (Table 2, entry 1). In fact, all reactions conducted at room temperature failed to afford pyrazole **10a** (Table 2, entries 3 and 8). When the same reaction was performed in refluxing CH_3CN, pyrazole **10a** was obtained in 60% yield, but the reaction took approximately 8 h (Table 2, entry 2). On the other hand, the reaction of hydrazone *Z*-7a with 1 equiv of CuI in the presence of 1 equiv of NEt_3 in CH_3CN at 82 °C for 1.5 h provided pyrazole **10a** in 64% yield (Table 2, entry 4). When the same reaction was carried out for 2 h, pyrazole **10a** was obtained in 73% yield (Table 2, entry 5). Notably, electrophilic cyclization was quite fast in the presence of NEt_3 in refluxing CH_3CN and went to completion in nearly 2 h. On the other hand, in refluxing CH_2Cl_2, no reaction occurred (Table 2, entry 7). The reaction conducted with 0.05 equiv of CuI in refluxing CH_3CN was relatively slow and afforded pyrazole **10a** in 20% yield in 2 h, along with the recovered hydrazone *Z*-7a (72%) (Table 2, entry 9). However, the same reaction carried out for 23 h went to completion and provided **10a** in 61% yield (Table 2, entry 10). The reaction performed with 0.10 equiv of CuI afforded **10a** in 62% yield in 15 h (Table 2, entry 11). Interestingly, the use of 2 equiv of NEt_3 in the reaction did not improve the yield (62%), but it shortened the reaction time considerably (6.5 h) (Table 2, entry 12). When the reaction was carried out with 0.15 equiv of CuI, pyrazole **10a** was obtained in 72% yield (Table 2, entry 13), very close to that (73%) obtained with the stoichiometric amount of CuI (Table 2, entry 5). Electrophilic cyclization of *Z*-7a was also tested at relatively higher temperatures, such as in dioxane at 100 °C and toluene at 110 °C. The reactions conducted with 0.05 and 0.10 equiv of CuI in refluxing dioxane yielded pyrazole **10a** in 55 and 69% yields, respectively (Table 2, entries 14 and 15). When the latter reaction was carried out in refluxing toluene, **10a** was formed in 66% yield (Table 2, entry 16). Higher temperatures did not increase the yield of **10a** significantly. Notably, the catalytic usage of CuI has increased the reaction time as compared to its stoichiometric amount. Hence, the electrophilic cyclizations were performed with 1 equiv of CuI in the presence of 1 equiv of NEt_3 in refluxing CH_3CN. The results from a systematic study are given in Table 3.

As depicted in Table 3, a variety of *α,β*-alkynic hydrazone derivatives *Z*-7a−aa were employed in these pyrazole-forming electrophilic cyclizations. 1,5-Dialkyl/aryl-substituted pyrazoles **10a−p** were obtained in 57−96% yields (Table 3, entries 1−16), whereas 1,3,5-trialkyl/aryl-substituted pyrazoles **10q−w** were isolated in 54−99% yields (Table 3, entries 17−23). On the other hand, 5-ferrocenyl-1-aryl-substituted pyrazoles **10x−aa** were resulted in 44−86% yields (Table 3, entries 24−27). It is worth mentioning that ferrocenyl-substituted pyrazoles have potential for biological and medicinal studies because, according to recent studies, the incorporation of a ferrocenyl group into such structures may enhance their current biological activities or bring new medicinal properties.[26,28,61] In general, CuI-mediated electrophilic cyclizations proceed well and yielded pyrazole derivatives in good to excellent yields. In addition, these cyclizations were found to be general for a wide range of *α,β*-alkynic hydrazones and tolerated the presence of aliphatic, aromatic, and ferrocenyl moieties with electron-withdrawing and electron-donating substituents.

A possible mechanism for the formation of pyrazoles **10** is given in Scheme 5. The activation of the alkyne moiety of hydrazone *Z*-7 by CuI is followed by the nucleophilic addition of the secondary nitrogen atom to form protonated pyrazole **12**. Then, hydrogen atom transfer into copper gives intermediate **13**. Finally, reductive elimination yields pyrazole derivative **10**.

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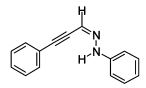
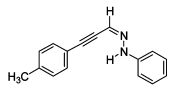
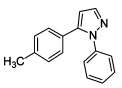
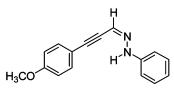
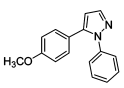
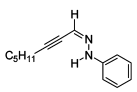
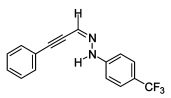
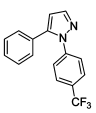
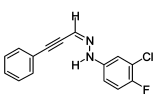
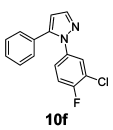
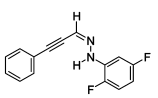
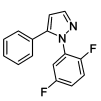
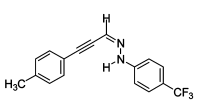
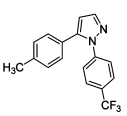
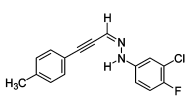
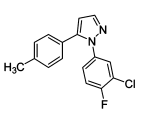
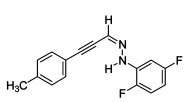
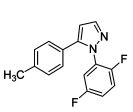
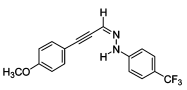
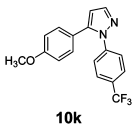
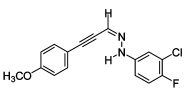
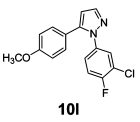
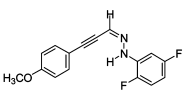
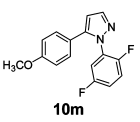
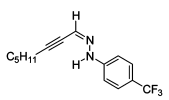
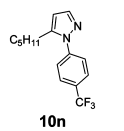
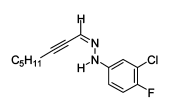
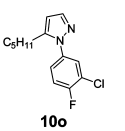
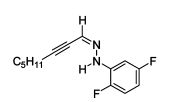
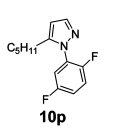
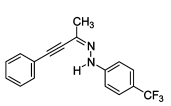
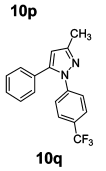
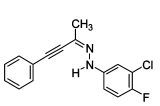
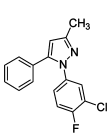
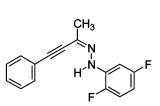
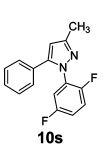
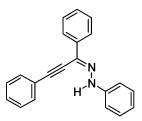
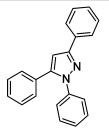
Table 3. Synthesis of Pyrazoles via CuI-Mediated Electrophilic Cyclization

entry	hydrazone	pyrazole	% yield[a]
1	 Z-7a	 10a	73
2	 Z-7b	 10b	77
3	 Z-7c	 10c	85
4	 Z-7d	 10d	65
5	 Z-7e	 10e	83
6	 Z-7f	 10f	72
7	 Z-7g	 10g	87
8	 Z-7h	 10h	71
9	 Z-7i	 10i	76
10	 Z-7j	 10j	95
11	 Z-7k	 10k	87
12	 Z-7l	 10l	96
13	 Z-7m	 10m	86
14	 Z-7n	 10n	89
15	 Z-7o	 10o	57
16	 Z-7p	 10p	85
17	 Z-7q	 10q	78
18	 Z-7r	 10r	54
19	 Z-7s	 10s	77
20	 Z-7t	 10t	99
21	Z-7u	10u	88
22	Z-7v	10v	95
23	Z-7w	10w	98
24	Z-7x	10x	44
25	Z-7y	10y	83
26	Z-7z	10z	67
27	Z-7aa	10aa	86

[a]Isolated yield.

Scheme 5

CONCLUSION

In summary, we have developed a simple and efficient copper-mediated electrophilic cyclization for the synthesis of pyrazoles. We have first prepared α,β-alkynic hydrazone derivatives by the condensation reactions of hydrazines with acetylenic aldehydes and ketones in neat condition at 80 °C, and then investigated their electrophilic cyclizations with copper(I) iodide. When reacted with copper(I) iodide in the presence of triethylamine in refluxing acetonitrile, α,β-alkynic hydrazones smoothly underwent electrophilic cyclization to furnish pyrazole derivatives in good to excellent yields. The reaction has been found to be general for a wide range of α,β-alkynic hydrazones and allowed the presence of aliphatic, aromatic, and ferrocenyl groups with electron-withdrawing and electron-donating moieties. It is anticipated that the efficiency and operational

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simplicity of the method could make it potentially attractive for library construction of pyrazoles, particularly in the area of pharmaceuticals.

EXPERIMENTAL SECTION

General information. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts are reported in parts per million (ppm) downfield from an internal TMS (trimethylsilane) reference. Coupling constants (J) are reported in hertz (Hz), and spin multiplicities are presented by the following symbols: s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet). DEPT ^{13}C NMR information is given in parentheses as C, CH, CH_2, and CH_3. Infrared spectra (IR) were recorded by using attenuated total reflection (ATR). Band positions are reported in reciprocal centimeters (cm^{-1}). Band intensities are indicated relative to the most intense band and are listed as br (broad), vs (very strong), s (strong), m (medium), w (weak), and vw (very weak). Mass spectra (MS) were obtained by using electrospray ionization (ESI) with Micro-Tof; m/z values are reported (for each measurement, the mass scale was recalibrated with sodium formiate clusters, and samples were dissolved and measured in MeOH). High resolution mass spectra (HRMS) were also obtained by using electrospray ionization (ESI) with Micro-Tof. Flash chromatography was performed using thick-walled glass columns and "flash grade" silica (230−400 mesh). Thin layer chromatography (TLC) was performed by using commercially prepared 0.25 mm silica gel plates, and visualization was effected with short wavelength UV lamp (254 nm). The relative proportions of solvents in chromatography solvent mixtures refer to the volume/volume ratio. All commercially available reagents were used directly without purification unless otherwise stated. All the solvents used in reactions were distilled for purity. The inert atmosphere was created by slight positive pressure (ca. 0.1 psi) of argon. All glassware was dried in an oven prior to use. 3-Ferrocenylpropynal (**1**),[54,55] 3-phenyl-2-propynal (phenylpropiolaldehyde or phenylpropargyl aldehyde) (**5a**),[54,62] 3-(*p*-tolyl)propiolaldehyde (**5b**),[54,62] 3-(4-methoxyphenyl)-propiolaldehyde (**5c**),[54,63] oct-2-ynal (**5d**),[54,64] 4-phenylbut-3-yn-2-one (**5e**),[56] and 1,3-diphenylprop-2-yn-1-one (**5f**)[57] were prepared according to standard literature protocols. α,β-Alkynic hydrazones **Z-7a−d**, **Z-7h−i**, **Z-7k−m**, **Z-7q−u**, and **Z-7w−aa** were synthesized according to recent literature procedures.[45]

General Procedure for the Synthesis of α,β-Alkynic Hydrazones (*Z*-7). A mixture of arylhydrazine (2 mmol) and propargyl aldehyde or ketone (2 mmol) in a round-bottom flask was heated at 80 °C under argon for 5 h. After the reaction was over, the residue was purified by flash column chromatography on silica gel using hexane/ethyl acetate (9:1) as the eluent to afford the desired product.

(*Z*)-1-(3-Phenylprop-2-yn-1-ylidene)-2-(4-(trifluoromethyl)-phenyl)hydrazine (*Z*-7e). 3-Phenyl-2-propynal (136 mg, 1.05 mmol) and (4-(trifluoromethyl)phenyl)hydrazine (184.1 mg, 1.05 mmol) were employed to afford 178.5 mg (59%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (br s, 1H, NH), 7.53 (m, 4H), 7.41 (m, 3H), 7.15 (d, J = 8.44 Hz, 2H), 6.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0 (C), 131.8 (CH), 129.8 (CH), 128.7 (CH), 126.7 (m, CH), 124.6 (d, J = 269 Hz, C), 122.8 (q, J = 30 Hz, C), 121.2 (C), 116.9 (CH), 112.9 (CH), 102.5 (C), 79.0 (C); IR (neat) 3323, 3070, 3039, 2185, 1614, 1541, 1523, 1488, 1326, 1259, 1159, 1093, 1058, 819, 754, 686 cm^{-1}; MS (ESI, m/z) 311.08 [M + Na]$^+$, 289.10 [M + H]$^+$; HRMS (ESI) calcd. for $C_{16}H_{11}F_3N_2Na$ 311.0771 [M + Na]$^+$, found 311.0767; calcd. for $C_{16}H_{12}F_3N_2$ 289.0953 [M + H]$^+$, found 289.0947.

(*Z*)-1-(3-Chloro-4-fluorophenyl)-2-(3-phenylprop-2-yn-1-ylidene)hydrazine (*Z*-7f). 3-Phenyl-2-propynal (185 mg, 1.42 mmol) and (3-chloro-4-fluorophenyl)hydrazine (228 mg, 1.42 mmol) were employed to afford 309 mg (80%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (br s, 1H, NH), 7.50 (m, 2H), 7.39 (m, 3H), 7.17 (m, 1H), 7.03 (m, 1H), 6.94 (m, 1H), 6.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5 (d, J = 18 Hz, C), 139.9 (C), 131.3 (CH), 129.2 (CH), 128.2 (CH), 121.1 (d, J = 18 Hz, C), 120.8 (C), 116.4 (d, J = 22.5 Hz, CH), 115.5 (CH), 114.4 (CH), 111.8 (d, J = 25.2 Hz, CH), 101.8 (C), 78.6(C); IR (neat) 3313, 3053, 2183, 1604, 1533, 1504, 1488, 1440, 1344, 1257, 1207, 1101, 1047, 858, 802, 746, 682 cm^{-1}; MS (ESI, m/z) 295.04 [M + Na]$^+$, 273.06 [M + H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{10}ClFN_2Na$ 295.0413 [M + Na]$^+$, found 295.0409; calcd. for $C_{15}H_{11}ClFN_2$ 273.0595 [M + H]$^+$, found 273.0589.

(*Z*)-1-(2,5-Difluorophenyl)-2-(3-phenylprop-2-yn-1-ylidene)-hydrazine (*Z*-7g). 3-Phenyl-2-propynal (200 mg, 1.55 mmol) and (2,5-difluorophenyl)hydrazine (223.3 mg, 1.55 mmol) were employed to afford 186.5 mg (47%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (br s, 1H, NH), 7.52 (m, 2H), 7.40 (m, 3H), 7.20 (m, 1H), 6.97 (m, 1H), 6.72 (s, 1H), 6.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (d, J = 240 Hz, C), 145.9 (d, J = 232 Hz, C), 133.1 (t, J = 11.5 Hz, C), 131.9 (CH), 129.8 (CH), 128.6 (CH), 121.2 (CH), 118.0 (CH), 115.5 (dd, J = 20.4 and 10.4 Hz, CH), 106.0 (dd, J = 24.5 and 6.9 Hz, CH), 103.0 (C), 102.0 (d, J = 28 Hz, CH), 79.0 (C); IR (neat) 3334, 3078, 2185, 1633, 1541, 1519, 1461, 1440, 1350, 1247, 1155, 1120, 975, 839, 796, 773, 748, 715, 680 cm^{-1}; MS (ESI, m/z) 279.07 [M + Na]$^+$, 257.09 [M + H]^4; HRMS (ESI) calcd. for $C_{15}H_{10}F_2N_2Na$ 279.0709 [M + Na]$^+$, found 279.0704; calcd. for $C_{15}H_{11}F_2N_2$ 257.0891 [M + H]$^+$, found 257.0885.

(*Z*)-1-(2,5-Difluorophenyl)-2-(3-(*p*-tolyl)prop-2-yn-1-ylidene)hydrazine (*Z*-7j). 3-*p*-Tolylpropiolaldehyde (200 mg, 1.38 mmol) and (2,5-difluorophenyl)hydrazine (198.7 mg, 1.38 mmol) were employed to afford 298.2 mg (80%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (br s, 1H), 7.41 (d, J = 7.9 Hz, 2H), 7.19 (m, 1H), 7.18 (d, J = 7.7 Hz, 2H), 6.96 (m, 1H), 6.71 (s, 1H), 6.47 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (d, J = 239.5 Hz, C), 145.9 (d, J = 234.5 Hz, C), 140.3 (C), 133.2 (t, J = 10.8 Hz, C), 131.8 (CH), 129.5 (CH), 118.3 (CH), 118.1 (C), 115.5 (dd, J = 9.7 Hz, 20.2 Hz, CH), 105.9 (dd, J = 6.9, J = 24.8 Hz, CH), 103.0 (C), 102.0 (dd, J = 28.8, J = 2.5 Hz, CH), 78.6 (C), 21.6 (CH_3); IR (neat) 3330, 3078, 2920, 2181, 1631, 1542, 1515, 1456, 1342, 1247, 1153, 1116, 1078, 844, 813, 794, 756 cm^{-1}; MS (ESI, m/z) 293.09 [M + Na]$^+$; HRMS (ESI) calcd. for $C_{16}H_{12}F_2N_2Na$ 293.0866 [M + Na]$^+$, found 293.0861.

(*Z*)-1-(Oct-2-yn-1-ylidene)-2-(4-(trifluoromethyl)phenyl)-hydrazine (*Z*-7n). Oct-2-ynal (200 mg, 1.61 mmol) and (4-(trifluoromethyl)phenyl)hydrazine (283.8 mg, 1.61 mmol) were employed to afford 317.9 mg (70%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (br s, 1H, NH), 7.49 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.45 (s, 1H), 2.49 (td, J = 7.1 and 1.4 Hz, 2H), 1.63 (p, J = 7.4 Hz, 2H), 1.42 (m, 4H), 0.93 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3 (C), 126.6 (m, CH), 124.6 (d, J = 269.5 Hz, C), 122.3 (q, J = 32.5 Hz, C), 117.9 (CH), 112.6 (CH), 105.0 (C), 71.5 (C), 31.1 (CH_2), 28.0 (CH_2), 22.2 (CH_2), 19.6 (CH_2), 13.3 (CH_3); IR (neat) 3315, 2958, 2933, 2861, 2198, 1614, 1527, 1481, 1317, 1263, 1157, 1109, 1060, 833 cm^{-1}; MS (ESI, m/z) 283.14 [M + H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{18}F_3N_2$ 283.1422 [M + H]$^+$, found 283,1417.

(*Z*)-1-(3-Chloro-4-fluorophenyl)-2-(oct-2-yn-1-ylidene)-hydrazine (*Z*-7o). Oct-2-ynal (200 mg, 1.61 mmol) and (3-chloro-4-fluorophenyl)hydrazine (294.6 mg, 1.61 mmol) were employed to afford 398.4 mg (93%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (br s, 1H, NH), 6.94 (m, 1H), 6.82 (t, J = 8.7 Hz, 1H), 6.66 (m, 1H), 6.20 (s, 1H), 2.25 (td, J = 7.1 and 1.0 Hz, 2H), 1.44 (p, J = 7.4 Hz, 2H), 1.21 (m, 4H), 0.75 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8 (J = 239.5 Hz, C), 140.72 (C), 121.5 (d, J = 18.3 Hz, C), 117.0 (CH), 116.8 (J = 22.8 Hz, CH), 114.7 (CH), 112.2 (J = 6.8 Hz, CH), 104.8 (C), 71.5 (C), 31.1 (CH_2), 28.1 (CH_2), 22.2 (CH_2), 19.7 (CH_2), 13.9 (CH_3); IR (neat) 3315, 2956, 2931, 2860, 2198, 1610, 1502, 1340, 1253, 1207, 1091, 844, 804, 731 cm^{-1}; MS (ESI, m/z) 267.11 [M + H]$^+$; HRMS (ESI) calcd. for $C_{14}H_{17}ClFN_2$ 267.1065 [M + H]$^+$, found 267.1059.

(*Z*)-1-(2,5-Difluorophenyl)-2-(oct-2-yn-1-ylidene)hydrazine (*Z*-7p). Oct-2-ynal (200 mg, 1.61 mmol) and (2,5-difluorophenyl)-hydrazine (231.8 mg, 1.61 mmol) were employed to afford 354.4 mg (88%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (br s, 1H), 7.16 (m, 1H), 6.85 (m, 1H), 6. 48 (s, 1H), 6.43 (m, 1H),

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2.48 (t, J = 6.87 Hz, 2H), 1.62 (p, 2H), 1.43 (m, 2H), 1.36 (m, 2H), 0.92 (t, J = 7.16 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, J = 203.6 Hz, C), 145.7 (d, J = 235.9 Hz, C), 133.4 (t, J = 11 Hz, C), 118.9 (CH), 115.4 (dd, J = 20.3, 10.4 Hz, CH), 105.5 (dd, J = 24.5, 7.4 Hz, CH), 105.4 (C), 101.9 (d, J = 31.5 Hz, CH), 71.4 (C), 31.0 (CH_2), 28.0 (CH_2), 22.2 (CH_2), 19.6 (CH_2), 13.8 (CH_3); IR (neat) 3328, 2958, 2931, 2862, 2198, 1631, 1542, 1517, 1456, 1338, 1288, 1244, 1157, 1107, 1066, 852, 790 cm^{-1}; MS (ESI, m/z) 273.12 [M + Na]$^+$, 251.14 [M + H]$^+$; HRMS (ESI) calcd. for $C_{14}H_{16}F_2N_2Na$ 273.1178 [M + Na]$^+$, found 273.1174; calcd. for $C_{14}H_{17}F_2N_2$ 251.1360 [M + H]$^+$, found 251.1354.

(*Z*)-1-(3-Chloro-4-fluorophenyl)-2-(1,3-diphenylprop-2-yn-1-ylidene)hydrazine (*Z*-7v). 1,3-Diphenyl-2-propyn-1-one (diphenylpropynone) (200 mg, 0.97 mmol) and (3-chloro-4-fluorophenyl)-hydrazine (155 mg, 0.97 mmol) were employed to afford 219.5 mg (65%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (br s, 1H), 7.98 (d, J = 7.6 Hz, 2H), 7.64 (m, 2H), 7.46 (m, 5H), 7.37 (d, J = 6.9 Hz, 1H), 7.31 (m, 1H), 7.09 (t, J = 8.7 Hz, 1H), 7.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0 (d, J = 240.5 Hz, C), 140.5 (C), 135.5 (C), 131.9 (CH), 129.8 (CH), 128.8 (CH), 128.6 (CH), 128.4 (CH), 126.9 (CH), 125.6 (CH), 121.6 (d, J = 18.5 Hz, C), 121.3 (C), 116.9 (d, J = 22.3 Hz, CH), 115.0 (CH), 112.6 (d, J = 6.2 Hz, CH), 104.1 (C), 78.6 (C); IR (neat) 3305, 3053, 3024, 2185, 1606, 1506, 1488, 1442, 1207, 1157, 835, 812, 752, 680 cm^{-1}; MS (ESI, m/z) 371.07 [M + Na]$^+$; HRMS (ESI) calcd. for $C_{21}H_{14}ClFN_2Na$ 371.0727 [M + Na]$^+$, found 371.0722.

General Procedure for the Synthesis of Pyrazoles (10). To a stirred solution of α,β-alkynic hydrazone *Z*-7 (0.25 mmol) in CH_3CN (7 mL) under argon was added CuI (0.25 mmol) and Et_3N (0.25 mmol), and the resulting solution was allowed to stir under reflux at 82 °C for 2 h. After the reaction was over, the solvent was evaporated, and the residue was purified by flash chromatography on silica gel using hexane/ethyl acetate (9:1) as the eluent to afford the desired product.

1,5-Diphenyl-1*H*-pyrazole (10a). Hydrazone *Z*-7**a** (55 mg, 0.25 mmol), CuI (47.5 mg, 0.25 mmol), and NEt_3 (25 mg, 0.25 mmol) were employed to afford 42.4 mg (77%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, J = 1.6 Hz, 1H), 7.32 (m, 8H), 7.27 (m, 2H), 6.53 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 140.3, 140.2, 130.6, 128.9, 128.8, 128.4, 128.2, 127.4, 125.2, 107.8. The spectral data were in agreement with those reported previously for this compound.[65]

1-Phenyl-5-(*p*-tolyl)-1*H*-pyrazole (10b). Hydrazone *Z*-7**b** (90 mg, 0.38 mmol), CuI (72.2 mg, 0.38 mmol), and NEt_3 (39 mg, 0.38 mmol) were employed to afford 76.5 mg (85%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 1.4 Hz, 1H), 7.35 (m, 5H), 7.15 (m, 4H), 6.51 (d, J = 1.5 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1 (C), 140.3 (C), 140.2 (CH), 138.1 (C), 129.2 (CH), 128.9 (CH), 128.7 (CH), 127.8 (C), 127.3 (CH), 125.2 (CH), 107.6 (CH), 21.2 (CH_3); IR (neat) 3124, 2979, 2869, 1596, 1496, 1446, 1382, 1128, 1072, 1022, 960, 923, 821, 785, 759 cm^{-1}; MS (ESI, m/z) 257.11 [M + Na]$^+$, 235.12 [M + H]$^+$; HRMS (ESI) calcd. for $C_{16}H_{14}N_2Na$ 257.1054 [M + Na]$^+$, found 257.1049; calcd. for $C_{16}H_{15}N_2$ 235.1236 [M + H]$^+$, found 235.1230. The spectral data were in agreement with those reported previously for this compound.[66]

5-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazole (10c). Hydrazone *Z*-7**c** (40 mg, 0.16 mmol), CuI (30.4 mg, 0.16 mmol), and NEt_3 (17 mg, 0.16 mmol) were employed to afford 34 mg (85%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 1.0 Hz, 1H), 7.30 (m, 5H), 7.14 (d, J = 8.67 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 6.43 (d, J = 1.0 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6 (C), 142.87 (C), 140.3 (C), 140.2 (CH), 130.0 (CH), 128.9 (CH), 127.3 (CH), 125.2 (CH), 123.0 (C), 113.9 (CH), 107.3 (CH), 55.3 (CH_3); IR (neat) 3134, 2929, 2835, 1598, 1496, 1442, 1384, 1288, 1245, 1178, 1130, 1029, 960, 925, 835, 786, 759, 692 cm^{-1}. The spectral data were in agreement with those reported previously for this compound.[67]

5-Pentyl-1-phenyl-1*H*-pyrazole (10d). Hydrazone *Z*-7**d** (114 mg, 0.53 mmol), CuI (100.7 mg, 0.53 mmol), and NEt_3 (53.5 mg, 0.53 mmol) were employed to afford 74.1 mg (65%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 1.4 Hz, 1H), 7.40 (m, 5H), 6.19 (s, 1H), 2.62 (t, J = 7.6 Hz, 2H), 1.57 (p, J = 7.3 Hz, 2H), 1.26 (m, 4H), 0.83 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8 (C), 140.1 (C), 139.8 (CH), 129.0 (CH), 127.8 (CH), 125.4 (CH), 105.3 (CH), 31.4 (CH_2), 28.5 (CH_2), 26.2 (CH_2), 22.3 (CH_2), 13.3 (CH_3); IR (neat) 2954, 2929, 286, 1598, 1537, 1500, 1454, 1394, 1201, 1070, 1012, 923, 761, 694 cm^{-1}; MS (ESI, m/z) 237.14 [M + Na]$^+$, 215.15 [M + H]$^+$; HRMS (ESI) calcd. for $C_{14}H_{18}N_2Na$ 237.1367 [M + Na]$^+$, found 237.1362; calcd. for $C_{14}H_{19}N_2$ 215.1549 [M + H]$^+$, found 215.1543.

5-Phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (10e). Hydrazone *Z*-7**e** (45 mg, 0.16 mmol), CuI (30.4 mg, 0.16 mmol), and NEt_3 (16.6 mg, 0.16 mmol) were employed to afford 38.2 mg (83%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.27 (m, 3H), 7.16 (m, 2H), 6.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3 (C), 142.8 (C), 141.1 (CH), 130.3 (C), 129.1 (q, J = 32.8 Hz, C), 128.9 (CH), 128.7 (CH), 128.6 (CH), 126.0 (CH), 124.8 (CH), 123.8 (d, J = 270.5 Hz, C), 108.9 (CH); IR (neat) 3085, 3064, 1618, 1521, 1452, 1421, 1379, 1321, 1164, 1101, 1060, 1014, 956, 920, 846, 827, 794, 758 cm^{-1}; MS (ESI, m/z) 311.08 [M + Na]$^+$, 289.10 [M + H]$^+$; HRMS (ESI) calcd. for $C_{16}H_{11}F_3N_2Na$ 311.0771 [M + Na]$^+$, found 311.0767; calcd. for $C_{16}H_{12}F_3N_2$ 289.0953 [M + H]$^+$, found 289.0947.

1-(3-Chloro-4-fluorophenyl)-5-phenyl-1*H*-pyrazole (10f). Hydrazone *Z*-7**f** (100 mg, 0.37 mmol), CuI (70.3 mg, 0.37 mmol), and NEt_3 (37.4 mg, 0.37 mmol) were employed to afford 72.4 mg (72%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 1.6 Hz, 1H), 7.50 (dd, J = 6.3, J = 2.1 Hz, 1H), 7.37 (m, 3H), 7.26 (m, 2H), 7.09 (m, 2H), 6.52 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1 (d, J = 248 Hz, C), 143.2 (C), 140.7 (CH), 136.7 (C), 130.0 (C), 128.8 (CH), 128.7 (CH), 128.6 (CH), 127.4 (CH), 124.7 (d, J = 7.5 Hz, CH), 123.4 (d, J = 18.6 Hz, C), 116.5 (d, J = 22.2 Hz, CH), 108.3 (CH); IR (neat) 2989, 2869, 2360, 1502, 1415, 1261, 1218, 1134, 1074, 925, 879, 823, 786, 756, 702 cm^{-1}; MS (ESI, m/z) 295.04 [M + Na]$^+$, 273.06 [M + H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{10}ClFN_2Na$ 295.0413 [M + Na]$^+$, found 295.0409; calcd. for $C_{15}H_{11}ClFN_2$ 273.0595 [M + H]$^+$, found 273.0589.

1-(2,5-Difluorophenyl)-5-phenyl-1*H*-pyrazole (10g). Hydrazone *Z*-7**g** (51.2 mg, 0.2 mmol), CuI (38 mg, 0.2 mmol), and NEt_3 (20.2 mg, 0.2 mmol) were employed to afford 44.5 mg (87%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 1.2 Hz, 1H), 7.22 (m, 3H), 7.15 (m, 3H), 6.96 (m, 2H), 6.45 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3 (d, J = 244.6 Hz, C), 152.7 (d, J = 244.5 Hz, C), 145.0 (C), 141.5 (CH), 130.0 (C), 129.0 (t, J = 13.6 Hz, C), 128.6 (CH), 128.5 (CH), 127.8 (CH), 117.5 (dd, J = 22 and 9 Hz, CH), 116.6 (dd, J = 24.1 and 7.5 Hz, CH), 115.9 (d, J = 25.6 Hz, CH), 107.1 (CH); IR (neat) 3082, 1508, 1433, 1369, 1251, 1180, 1130, 923, 887, 871, 812, 763 cm^{-1}. The spectral data were in agreement with those reported previously for this compound.[67]

5-(*p*-Tolyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (10h). Hydrazone *Z*-7**h** (67 mg, 0.22 mmol), CuI (42 mg, 0.22 mmol), and NEt_3 (22.2 mg, 0.22 mmol) were employed to afford 47.2 mg (71%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 1.4 Hz, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.48 (d, J = 1.4 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4 (C), 142.9 (C), 141.0 (CH), 138.7 (C), 129.4 (CH), 129.0 (d, J = 32.5 Hz, C), 128.7 (CH), 127.4 (C), 125.9 (m, CH), 124.8 (CH), 123.9 (d, J = 270 Hz, C), 108.6 (CH), 21.2 (CH_3); IR (neat) 2921, 1616, 1521, 1419, 1379, 1319, 1122, 1060, 956, 920, 844, 817, 777 cm^{-1}; MS (ESI, m/z) 325.09 [M + Na]$^+$, 303.11 [M + H]$^+$; HRMS (ESI) calcd. for $C_{17}H_{13}F_3N_2Na$ 325.0929 [M + Na]$^+$, found 325.0923; calcd. for $C_{17}H_{14}F_3N_2$ 303.1109 [M + H]$^+$, found 303.1104.

1-(3-Chloro-4-fluorophenyl)-5-(*p*-tolyl)-1*H*-pyrazole (10i). Hydrazone *Z*-7**i** (72 mg, 0.25 mmol), CuI (47.5 mg, 0.25 mmol), and NEt_3 (25.3 mg, 0.25 mmol) were employed to afford 54.7 mg (76%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 1.4 Hz, 1H), 7.50 (dd, J = 6.25 and 1.9 Hz, 1H), 7.13 (m, 4H), 7.08 (m, 2H), 6.47 (d, J = 1.6 Hz, 1H), 2.37 (s, 1H); ^{13}C NMR (100

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MHz, $CDCl_3$) δ 157.0 (d, J = 248.5 Hz, C), 143.9 (C), 140.7 (CH), 138.6 (C), 136.8 (C), 129.4 (CH), 128.6 (CH), 127.4 (CH), 127.1 (C), 124.8 (d, J = 6.9 Hz, CH), 121.4 (d, J = 19.7 Hz, C), 116.5 (d, J = 22.7 Hz, CH), 107.9 (CH), 21.2 (CH_3); IR (neat) 3066, 2923, 1496, 1417, 1257, 1220, 1136, 1082, 1058, 970, 923, 887, 817, 781, 713 cm^{-1}; MS (ESI, m/z) 309.06 $[M + Na]^+$, 287.08 $[M + H]^+$; HRMS (ESI) calcd. for $C_{16}H_{12}ClFN_2Na$ 309.0571 $[M + Na]^+$, found 309.0565; calcd. for $C_{16}H_{13}ClFN_2$ 287.0751 $[M + H]^+$, found 287.0746.

1-(2,5-Difluorophenyl)-5-(*p*-tolyl)-1*H*-pyrazole (10j). Hydrazone ***Z*-10j** (65 mg, 0.24 mmol), CuI (45.6 mg, 0.24 mmol), and NEt_3 (25 mg, 0.24 mmol) were employed to afford 61.8 mg (95%) of the indicated product: ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 1.0 Hz, 1H), 7.20 (m, 1H), 7.09 (m, 4H), 7.02 (m, 2H), 6.48 (d, J = 1.0 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2 (d, J = 244 Hz, C), 152.8 (d, J = 247.3 Hz, C), 145.1 (C), 141.4 (CH), 138.5 (C), 129.3 (CH), 129.2 (t, J = 10.8 Hz, C), 127.7 (CH), 127.1 (CH), 117.5 (dd, J = 22.4, 9 Hz, CH), 116.5 (dd, J = 23.2, 7.7 Hz, CH), 115.9 (d, J = 25.8 Hz, CH), 106.9 (CH), 21.2 (CH_3); IR (neat) 3074, 2869, 2623, 1508, 1469, 1433, 1365, 1257, 1180, 1130, 923, 871, 821, 788, 765 cm^{-1}; MS (ESI, m/z) 293.09 $[M + Na]^+$, 271.10 $[M + H]^+$; HRMS (ESI) calcd. for $C_{16}H_{12}F_2N_2Na$ 293.0866 $[M + Na]^+$, found 293.0861; calcd. for $C_{16}H_{13}F_2N_2$ 271.1047 $[M + H]^+$, found 271.1041.

5-(4-Methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (10k). Hydrazone ***Z*-10k** (55 mg, 0.17 mmol), CuI (32.3 mg, 0.17 mmol), and NEt_3 (18 mg, 0.17 mmol) were employed to afford 47.9 mg (87%) of the indicated product: ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 1.2 Hz 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.44 (d, J = 1 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (C), 143.2 (C), 142.9 (C), 141.0 (CH), 130.1 (CH), 129.1 (q, J = 32.5 Hz, C), 126.0 (m, CH), 124.8 (CH), 123.9 (d, J = 270 Hz, C), 122.6 (C), 114.2 (CH), 108.4 (CH), 55.3 (CH_3); IR (neat) 2846, 1614, 1521, 1498, 1456, 1419, 1384, 1323, 1251, 1161, 1120, 1101, 1062, 1029, 960, 923, 837, 792 cm^{-1}; MS (ESI, m/z) 341.09 $[M + Na]^+$, 319.11 $[M + H]^+$; HRMS (ESI) calcd. for $C_{17}H_{13}F_3N_2NaO$ 341.0878 $[M + Na]^+$, found 341.0872; calcd. for $C_{17}H_{14}F_3N_2O$ 319.1058 $[M + H]^+$, found 319.1053.

1-(3-Chloro-4-fluorophenyl)-5-(4-methoxyphenyl)-1*H*-pyrazole (10l). Hydrazone ***Z*-7l** (50 mg, 0.17 mmol), CuI (32.3 mg, 0.17 mmol), and NEt_3 (18 mg, 0.17 mmol) were employed to afford 48 mg (96%) of the indicated product: ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 1.5 Hz, 1H), 7.48 (m, 1H), 7.14 (d, J = 8.6 Hz, 2H), 7.07 (m, 2H), 6.85 (d, J = 8.6 Hz, 2H), 6.43 (d, J = 1.3 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (C), 157.0 (d, J = 248.3 Hz, C), 143.1 (C), 140.7 (CH), 136.9 (C), 130.0 (CH), 127.4 (CH), 124.7 (d, J = 7.1 Hz, CH), 122.4 (C), 121.4 (d, J = 19.3 Hz, C), 116.5 (d, J = 22.6 Hz, CH), 114.2 (CH), 107.7 (CH), 55.3 (CH_3); IR (neat) 2960, 2840, 1610, 1548, 1496, 1467, 1442, 1419, 1375, 1301, 1245, 1174, 1134, 1080, 1028, 966, 923, 875, 833, 790, 719 cm^{-1}; MS (ESI, m/z) 325.05 $[M + Na]^+$, 303.07 $[M + H]^+$; HRMS (ESI) calcd. for $C_{16}H_{12}ClFN_2NaO$ 325.0520 $[M + Na]^+$, found 325.0514; calcd. for $C_{16}H_{13}ClFN_2O$ 303.0700 $[M + H]^+$, found 303.0695.

1-(2,5-Difluorophenyl)-5-(4-methoxyphenyl)-1*H*-pyrazole (10m). Hydrazone ***Z*-7m** (70 mg, 0.24 mmol), CuI (45.6 mg, 0.24 mmol), and NEt_3 (24.3 mg, 0.24 mmol) were employed to afford 60.2 mg (86%) of the indicated product: ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (br s, 1H), 7.19 (m, 1H), 7.13 (d, J = 8.3 Hz, 2H), 7.02 (m, 2H), 6.80 (d, J = 8.5 Hz, 2H), 6.45 (s,1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (C), 158.2 (d, J = 244.3 Hz, C), 152.8 (d, J = 248.5 Hz, C), 144.9 (C), 141.4 (CH), 129.2 (CH), 129.0 (C), 122.4 (C), 117.5 (dd, J = 22 and 9 Hz, CH), 116.5 (dd, J = 24.3 and 7.5 Hz, CH), 115.9 (d, J = 25.8 Hz, CH), 114.0 (CH), 106.6 (CH), 55.2 (CH_3); IR (neat) 3136, 3076, 2972, 2842, 1614, 1573, 1508, 1494, 1434, 1365, 1249, 1178, 1026, 925, 875, 835, 790, 765 cm^{-1}; MS (ESI, m/z) 309.08 $[M + Na]^+$, 287.10 $[M + H]^+$; HRMS (ESI) calcd. for $C_{16}H_{12}F_2N_2NaO$ 309.0815 $[M + Na]^+$, found 309.0810; calcd. for $C_{16}H_{13}F_2N_2O$ 287.0996 $[M + H]^+$, found 287.0990.

5-Pentyl-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (10n). Hydrazone ***Z*-7n** (70 mg, 0.25 mmol), CuI (47.5 mg, 0.25 mmol), and NEt_3 (26 mg, 0.25 mmol) were employed to afford 62.3 mg (89%) of the indicated product: ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.31 Hz, 2H), 7.59 (s, 1H), 7.56 (d, J = 8.3 Hz, 2H), 6.23 (s, 1H), 2.67 (t, J = 7.82 Hz, 2H), 1.60 (p, J = 7.3 Hz, 2H), 1.28 (m, 4H), 0.84 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0 (C), 142.9 (C), 140.6 (CH), 129.6 (q, J = 33.1 Hz, C), 126.3 (m, CH), 125.1 (CH), 123.9 (d, J = 270 Hz, C), 106.3 (CH), 31.3 (CH_2), 28.5 (CH_2), 26.4 (CH_2), 22.3 (CH_2), 13.8 (CH_3); IR (neat) 2958, 2931, 2862, 1618, 1523, 1463, 1419, 1394, 1321, 1164, 1122, 1064, 1010, 923, 844, 781 cm^{-1}; MS (ESI, m/z) 305.12 $[M + Na]^+$, 283.14 $[M + H]^+$; HRMS (ESI) calcd. for $C_{15}H_{17}F_3N_2Na$ 305.1240 $[M + Na]^+$, found 305.1236; calcd. for $C_{15}H_{18}F_3N_2$ 283.1422 $[M + H]^+$, found 283.1417.

1-(3-Chloro-4-fluorophenyl)-5-pentyl-1*H*-pyrazole (10o). Hydrazone ***Z*-7o** (60 mg, 0.23 mmol), CuI (43.7 mg, 0.23 mmol), and NEt_3 (23.2 mg, 0.23 mmol) were employed to afford 34.2 mg (57%) of the indicated product: ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.51 (m, 1H), 7.27 (m, 1H), 7.21 (t, J = 8.6 Hz, 1H), 6.18 (s, 1H), 2.59 (t, J = 7.8 Hz, 2H), 1.57 (p, J = 7.4 Hz, 2H), 1.27 (m, 4H), 0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4 (J = 248.5 Hz, C), 144.0 (C), 140.3 (CH), 136.6 (C), 127.8 (CH), 125.0 (d, J = 9.5 Hz, CH), 121.6 (d, J = 18 Hz, C), 116.7 (d, J = 22.7 Hz, CH), 105.8 (CH), 31.3 (CH_2), 28.4 (CH_2), 26.1 (CH_2), 22.3 (CH_2), 13.8 (CH_3); IR (neat) 2956, 2929, 2860, 1598, 1504, 1463, 1413, 1259, 1222, 1064, 923, 879, 819, 781, 731 cm^{-1}. MS (ESI, m/z) 289.09 $[M + Na]^+$, 267.11 $[M + H]^+$; HRMS (ESI) calcd. for $C_{14}H_{16}ClFN_2Na$ 289.0883 $[M + Na]^+$, found 289.0878; calcd. for $C_{14}H_{17}ClFN_2$ 267.1065 $[M + H]^+$, found 267.1059.

1-(2,5-Difluorophenyl)-5-pentyl-1*H*-pyrazole (10p). Hydrazone ***Z*-7p** (50 mg, 0.20 mmol), CuI (38 mg, 0.20 mmol), and NEt_3 (20.2 mg, 0.20 mmol) were employed to afford 42.5 mg (85%) of the indicated product: ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.14 (m, 2H), 7.05 (m, 1H), 6.17 (s, 1H), 2.49 (t, J = 7.73 Hz, 2H), 1.54 (p, 2H), 1.23 (m, 4H), 0.81 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2 (d, J = 244 Hz, C), 153.2 (d, J = 249.3 Hz, C), 145.6 (C), 141.0 (CH), 128.5 (m, C), 117.3 (dd, J = 22.7 and 9 Hz, CH), 116.8 (dd, J = 23.4 and 7.7 Hz, CH), 116.2 (d, J = 24.8 Hz, CH), 105.0 (CH), 31.2 (CH_2), 28.1 (CH_2), 25.4 (CH_2), 22.2 (CH_2), 13.8 (CH_3); IR (neat) 2956, 2931, 2862, 1625, 1596, 1510, 1458, 1377, 1251, 1174, 923, 894, 867, 813, 763 cm^{-1}; MS (ESI, m/z) 273.12 $[M + Na]^+$, 251.14 $[M + H]^+$; HRMS (ESI) calcd. for $C_{14}H_{16}F_2N_2Na$ 273.1178 $[M + Na]^+$, found 273.1174; calcd. for $C_{14}H_{17}F_2N_2$ 251.1360 $[M + H]^+$, found 251.1354.

3-Methyl-5-phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (10q). Hydrazone ***Z*-7q** (70 mg, 0.23 mmol), CuI (43.7 mg, 0.25 mmol), and NEt_3 (23.2 mg, 0.25 mmol) were employed to afford 54.6 mg (78%) of the indicated product: ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.24 (m, 3H), 7.14 (m, 2H), 6.23 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (C), 144.0 (C), 142.9 (C), 130.5 (C), 129.0 (q, J = 9.1 Hz, C), 128.7 (CH), 128.6 (CH), 128.5 (CH), 125.9 (m, CH), 124.6 (CH), 124.6 (d, J = 270 Hz, C), 108.9 (CH), 13.5 (CH_3); IR (neat) 3060, 2925, 2850, 1616, 1519, 1496, 1448, 1411, 1361, 1323, 1162, 1105, 1062, 1036, 966, 840, 760 cm^{-1}; MS (ESI, m/z) 325.09 $[M + Na]^+$, 303.11 $[M + H]^+$; HRMS (ESI) calcd. for $C_{17}H_{13}F_3N_2Na$ 325.0929 $[M + Na]^+$, found 325.0923; calcd. for $C_{17}H_{14}F_3N_2$ 303.1109 $[M + H]^+$, found 303.1104.

1-(3-Chloro-4-fluorophenyl)-3-methyl-5-phenyl-1*H*-pyrazole (10r). Hydrazone ***Z*-7r** (70 mg, 0.25 mmol), CuI (47.5 mg, 0.25 mmol), and NEt_3 (25 mg, 0.25 mmol) were employed to afford 37.8 mg (54%) of the indicated product: ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 5.5 Hz, 1H), 7.35 (m, 3H), 7.24 (m, 2H), 7.05 (m, 2H), 6.32 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (J = 248.3 Hz, C), 149.9, 143.9, 136.7, 131.4, 130.2, 128.6, 128.5, 127.2, 124.6 (d, J = 7.3 Hz), 121.3, 116.4 (d, J = 22.8 Hz), 108.2, 13.5; IR (neat) 3062, 2923, 1602, 1556, 1504, 1452, 1404, 1363, 1259, 1226, 1191, 1080, 1055, 1016, 977, 910, 875, 817, 759 cm^{-1}; MS (ESI, m/z) 309.06 $[M + Na]^+$, 287.08 $[M + H]^+$; HRMS (ESI) calcd. for $C_{16}H_{12}ClFN_2Na$ 309.0571 $[M + Na]^+$, found 309.0565; calcd. for $C_{16}H_{13}ClFN_2$ 287.0751 $[M + H]^+$, found 287.0746.

1-(2,5-Difluorophenyl)-3-methyl-5-phenyl-1*H*-pyrazole (10s). Hydrazone *Z*-**7s** (68 mg, 0.25 mmol), CuI (47.5 mg, 0.25 mmol), and NEt_3 (25 mg, 0.25 mmol) were employed to afford 52.4 mg (77%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 3H), 7.23 (m, 3H), 7.02 (m, 2H), 6.35 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2 (d, J = 241.5 Hz, C), 152.8 (d, J = 248.5 Hz, C), 150.7 (C), 145.8 (C), 130.2 (C), 129.1 (t, J = 10.6 Hz, C), 128.5 (CH), 128.4 (CH), 127.7 (CH), 117.4 (dd, J = 9.2 and 22.9 Hz, CH), 116.3 (dd, J = 23.9 and 7.5 Hz, CH), 115.8 (d, J = 25.1 Hz, CH), 107.1 (CH), 13.6 (CH_3); IR (neat) 3080, 2925, 1623, 1556, 1508, 1496, 1359, 1251, 1201, 1174, 1014, 981, 889, 871, 819, 800, 761 cm^{-1}; MS (ESI, m/z) 293.09 [M + Na]$^+$, 271.10 [M + H]$^+$; HRMS (ESI) calcd. for $C_{16}H_{12}F_2N_2Na$ 293.0861 [M + Na]$^+$, found 293.0861; calcd. for $C_{16}H_{13}F_2N_2$ 271.1047 [M + H]$^+$, found 271.1041.

1,3,5-Triphenyl-1*H*-pyrazole (10t). Hydrazone *Z*-**7t** (70 mg, 0.24 mmol), CuI (45.6 mg, 0.24 mmol), and NEt_3 (24 mg, 0.24 mmol) were employed to afford 69.3 mg (99%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0 (d, J = 7.4 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.43 (m, 3H), 7.35 (m, 8H), 6.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0 (C), 144.5 (C), 140.3 (C), 133.2 (C), 130.7 (C), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 128.0 (CH), 127.4 (CH), 125.9 (CH), 125.4 (CH), 105.3 (CH); IR (neat) 3120, 2923, 1595, 1494, 1456, 1361, 1213, 1174, 1066, 970, 920, 791 cm^{-1}; MS (ESI, m/z) 297.14 [M + H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{17}N_2$ 297.1392 [M + H]$^+$, found 297.1386.

3,5-Diphenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (10u). Hydrazone *Z*-**7u** (47 mg, 0.13 mmol), CuI (24.7 mg, 0.13 mmol), and NEt_3 (13 mg, 0.13 mmol) were employed to afford 41.4 mg (88%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.3 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.27 (m, 4H), 7.20 (m, 2H), 6.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7 (C), 144.7 (C), 142.9 (C), 132.7 (C), 130.3 (C), 129.0 (d, J = 33 Hz, C), 128.85 (CH), 128.8 (CH), 128.7 (CH), 128.3 (CH), 128.0 (CH), 126.0 (m, CH), 125.9 (CH), 124.8 (CH), 123.9 (d, J = 270 Hz, C), 106.3 (CH); IR (neat) 3064, 1612, 1550, 1523, 1483, 1458, 1409, 1363, 1323, 1166, 1107, 1056, 1016, 968, 916, 846, 810, 763 cm^{-1}; MS (ESI, m/z) 387.11 [M + Na]$^+$, 365.13 [M + H]$^+$; HRMS (ESI) calcd. for $C_{22}H_{15}F_3N_2Na$ 387.1085 [M + Na]$^+$, found 387.1080; calcd. for $C_{22}H_{16}F_3N_2$ 365.1266 [M + H]$^+$, found 365.1260.

1-(3-Chloro-4-fluorophenyl)-3,5-diphenyl-1*H*-pyrazole (10v). Hydrazone *Z*-**7v** (50 mg, 0.14 mmol), CuI (26.6 mg, 0.14 mmol), and NEt_3 (15 mg, 0.14 mmol) were employed to afford 47.5 mg (95%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 6.8 Hz, 2H), 7.59 (m, 1H), 7.46 (m, 2H), 7.39 (m, 4H), 7.30 (m, 2H), 7.15 (m, 1H), 7.08 (m, 1H), 6.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1 (d, J = 248.5 Hz, C), 152.5 (C), 144.6 (C), 136.8 (C), 136.7 (CH), 132.7 (C), 130.1 (C), 128.8 (CH), 128.7 (2 × CH), 128.5 (CH), 127.8 (CH), 125.9 (CH), 124.8 (d, J = 7.5 Hz, CH), 121.4 (d, J = 19.5 Hz, C), 116.5 (d, J = 21.8 Hz, CH), 105.7 (CH); IR (neat) 3060, 1602, 1550, 1498, 1460, 1402, 1363, 1257, 1230, 1209, 1178, 1072, 1028, 979, 954, 908, 875, 852, 817, 758 cm^{-1}; MS (ESI, m/z) 371.07 [M + Na]$^+$, 349.09 [M + H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{14}ClFN_2Na$ 371.0727 [M + Na]$^+$, found 371.0722; calcd. for $C_{21}H_{15}ClFN_2$ 349.0908 [M + H]$^+$, found 349.0902.

1-(2,5-Difluorophenyl)-3,5-diphenyl-1*H*-pyrazole (10w). Hydrazone *Z*-**7w** (75 mg, 0.23 mmol), CuI (43.7 mg, 0.23 mmol), and NEt_3 (23.2 mg, 0.23 mmol) were employed to afford 73.5 mg (98%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.5 Hz, 2H), 7.47 (t, J = 7.4 Hz, 2H), 7.35 (m, 7H), 7.06 (m, 2H), 6.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3 (d, J = 243.8, Hz, C), 153.2 (C), 152.8 (d, J = 247 Hz, C), 146.5 (C), 132.7 (C), 130.0 (C), 129.8 (t, J = 14.3 Hz, C), 128.7 (CH), 128.65 (CH), 128.6 (CH), 128.3 (CH), 127.8 (CH), 125.9 (CH), 117.5 (dd, J = 22 and 9.1 Hz, CH), 116.6 (dd, J = 23.2 and 7.6 Hz, CH), 116.0 (d, J = 25.5 Hz, CH), 104.6 (CH); IR (neat) 3078, 1625, 1602, 1546, 1508, 1487, 1456, 1359, 1253, 1215, 1176, 1076, 954, 889, 869, 812, 758 cm^{-1}; MS (ESI, m/z) 355.10 [M + Na]$^+$, 333.12 [M + H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{14}F_2N_2Na$ 355.1023 [M + Na]$^+$, found 355.1017; calcd. for $C_{21}H_{15}F_2N_2$ 333.1203 [M + H]$^+$, found 333.1198.

5-Ferrocenyl-1-phenyl-1*H*-pyrazole (10x). Hydrazone *Z*-**7x** (72 mg, 0.22 mmol), CuI (41.8 mg, 0.22 mmol), and NEt_3 (22.2 mg, 0.22 mmol) were employed to afford 31.7 mg (44%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.40 (m, 5H), 6.50 (s,1H), 4.17 (s, 2H), 4.14 (s, 2H), 4.05 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5 (C), 140.4 (C), 140.0 (CH), 128.8 (CH), 128.0 (CH), 126.1 (CH), 106.8 (CH), 75.1 (C), 69.9 (CH), 68.8 (CH), 68.6 (CH). The spectral data were in agreement with those reported previously for this compound.[26]

5-Ferrocenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (10y). Hydrazone *Z*-**7y** (78 mg, 0.20 mmol), CuI (38 mg, 0.20 mmol), and NEt_3 (20.2 mg, 0.20 mmol) were employed to afford 64.7 mg (83%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.64 (d, J = 7.3 Hz, 2H), 7.49 (d, J = 7.2 Hz, 2H), 6.51 (s, 1H), 4.32 (s, 2H), 4.28 (s, 2H), 4.18 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143,0 (C), 141.7 (C), 140.8 (CH), 129.3 (q, J = 32.3 Hz, C), 125.8 (m, CH), 123.8 (d, J = 270.5 Hz, C), 108.7 (CH), 75.9 (C), 70.6 (CH), 69.8 (CH), 69.4 (CH); IR (neat) 1614, 1521, 1411, 1396, 1384, 1321, 1226, 1174, 1157, 1136, 1107, 1085, 1066, 1004, 972, 920, 871, 846, 817, 790 cm^{-1}; MS (ESI, m/z) 419.04 [M + Na]$^+$, 397.06 [M + H]$^+$, 396.05 [M]$^+$; HRMS (ESI) calcd. for $C_{20}H_{15}F_3FeN_2Na$ 419.0433 [M + Na]$^+$, found 419.0429; calcd. for $C_{20}H_{16}F_3FeN_2$ 397.0615 [M + H]$^+$, found 397.0610; calcd. for $C_{20}H_{15}F_3FeN_2$ 396.0536 [M] $^+$, found 396.0537.

1-(3-Chloro-4-fluorophenyl)-5-ferrocenyl-1*H*-pyrazole (10z). Hydrazone *Z*-**7z** (60 mg, 0.16 mmol), CuI (30.4 mg, 0.16 mmol), and NEt_3 (17 mg, 0.16 mmol) were employed to afford 40.2 mg (67%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.50 (m, 1H), 7.17 (m, 2H), 6.48 (s, 1H), 4.29 (s, 2H), 4.23 (s, 2H), 4.15 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3 (d, J = 248.5 Hz, C), 1441.8 (C), 140.5 (CH), 136.9 (C), 128.1 (CH), 125.5 (d, J = 7.2 Hz, CH), 121.2 (d, J = 18.8 Hz, C), 116.4 (d, J = 22.5 Hz, CH), 107.5 (CH), 75.1 (C), 70.2 (CH), 69.2 (2 × CH); IR (neat) 3043, 1600, 1562, 1502, 1407, 1263, 1215, 1143, 1107, 1085, 1062, 1024, 1002, 975, 921, 867, 815, 783 cm^{-1}; MS (ESI, m/z) 403.01 [M + Na]$^+$, 381.03 [M + H]$^+$, 380.02 [M]$^+$; HRMS (ESI) calcd. for $C_{19}H_{14}ClFFeN_2Na$ 403.0076 [M + Na]$^+$, found 403.0072; calcd. for $C_{19}H_{15}ClFFeN_2$ 381.0258 [M + H]$^+$, found 381.0152; calcd. for $C_{19}H_{14}ClFFeN_2$ 380.0179 [M]$^+$, found 380.0179.

1-(2,5-Difluorophenyl)-5-ferrocenyl-1*H*-pyrazole (10aa). Hydrazone *Z*-**7aa** (70 mg, 0.20 mmol), CuI (38 mg, 0.20 mmol), and NEt_3 (20.2 mg, 0.20 mmol) were employed to afford 60.2 mg (86%) of the indicated product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.17 (m, 3H), 6.51 (s, 1H), 4.24 (s, 4H), 4.11 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1 (d, J = 244.6 Hz, C), 153.9 (d, J = 250.9 Hz, C), 143.6 (C), 141.2 (CH), 129.0 (m, C), 117.3 (m, 2 × CH), 116.6 (d, J = 25.2 Hz, CH), 105.9 (CH), 74.1 (C), 69.9 (CH), 69.0 (CH), 67.7 (CH); IR (neat) 3083, 2989, 2869, 1625, 1508, 1473, 1454, 1415, 1253, 1180, 1141, 1103, 999, 925, 879, 819, 794, 765 cm^{-1}; MS (ESI, m/z) 387.04 [M + Na]$^+$, 365.06 [M + H]$^+$; HRMS (ESI) calcd. for $C_{19}H_{14}F_2FeN_2Na$ 387.0371 [M + Na]$^+$, found 387.0367; calcd. for $C_{19}H_{15}F_2FeN_2$ 365.0553 [M + H]$^+$, found 365.0547.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ^{1}H and ^{13}C NMR spectra of new acetylenic hydrazones and pyrazoles. This material is available free of charge via Internet at http://pubs.acs.org.

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