JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

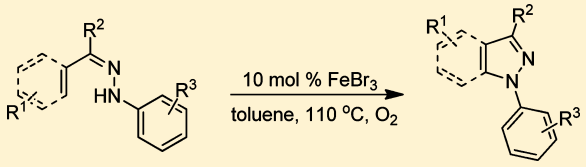
Synthesis of 1*H*-Indazoles and 1*H*-Pyrazoles via $FeBr_3/O_2$ Mediated Intramolecular C−H Amination

Tianshui Zhang and Weiliang Bao*

Department of Chemistry, Xixi Campus, Zhejiang University, Hangzhou 310028, P. R. China

Supporting Information

ABSTRACT: A new synthesis of substituted 1*H*-indazoles and 1*H*-pyrazoles from arylhydrazones via $FeBr_3/O_2$ mediated C−H activation/C−N bond formation reactions is reported. The corresponding 1,3-diaryl-substituted indazoles and trisubstituted pyrazoles were obtained in moderate to excellent yields under mild conditions.



N-Heterocycles, because of their ubiquitous nature, are key scaffolds of many biological molecules and pharmaceutical products. Among them, 1*H*-indazoles[1] and 1*H*-pyrazoles[2] with a broad spectrum of pharmacological activities are very important. Presently many of their derivatives have been reported with fantastic bioactivities, and some typical examples are outlined in Figure 1. 5-Aminomethyl-1*H*-indazole (**A**) is an

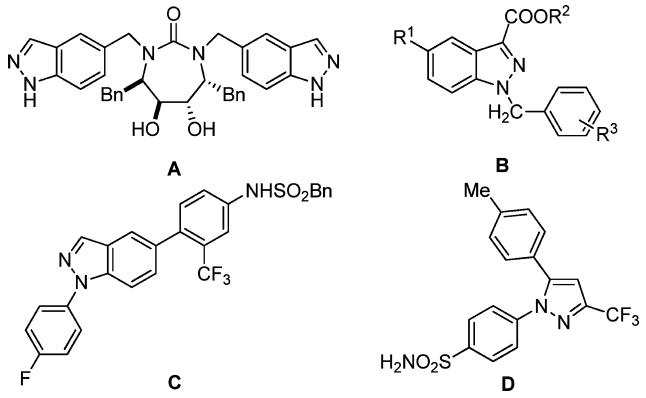


Figure 1. Structures of some pharmacologically important indazoles and pyrazols.

extremely potent HIV protease inhibitor with excellent antiviral activity;[3] 1*H*-indazole-3-carboxylic acid (**B**) has a selective and potent antispermatogenic activity;[4] 1-(4-fluoro-phenyl)-1*H*-indazole (**C**) has been used as the most effective treatment of acute and chronic inflammatory conditions;[5] 1*H*-pyrazol-1-benzenesulfonamide (**D**) is currently in phase III clinical trials for treatment of rheumatoid arthritis and osteoarthritis;[6] and so on. As a class of privileged substructures, numerous efforts have been devoted to pursue efficient methods for synthesis of the above-mentioned frameworks.

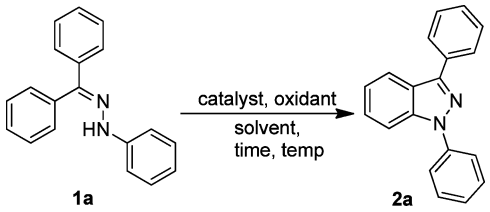
The primal synthetic method of indazoles is the diazotization of *o*-alkyl-substituted anilines followed by base-[7] or acid-promoted[8] cyclization. Recently, a new approach of 1,3-dipolar cycloaddition of arynes with different nitrogen sources was developed. For instance, Yamamoto[8c] and Larock[9] have independently reported the cycloaddition of arynes with diazo compounds, and Moses[10] has disclosed a 1,3-dipolar cycloaddition of in situ generated nitrile imines with benzyne. Later, a variety of *N*-aryl-1*H*-indazoles were synthesized via intramolecular dehydration from common arylamino oximes,[11] coupling reaction of *N*-acyl-*N*-substituted hydrazines with 2-bromoarylcarbonylic compounds,[12] and a [3 + 2] annulation approach from arynes and hydrazones.[13] At the same time, a one-pot synthetic protocol for the synthesis of substituted pyrazoles was achieved through cyclocondensation of ketones/aldehydes with hydrazines.[14] Early in 1965, Gladstone and Norman[15] had treated hydrazone with $Pb(OAc)_4$ to give azo-compounds that then cyclized to the indazole. Very recently, Kou Hiroya and Yu Rao[16] also obtained the corresponding *N*-heterocycles from hydrazones via an orthometalation process.

As an abundant, cheap, and less toxic element, iron is an ideal candidate to replace precious metals in organic synthesis, especially for practical large scale preparation. The use of iron as a catalyst for organic synthesis has recently been increasingly attracting the interest of chemists from economical and ecological points of view.[17] Herein, we report a new cost-effective synthesis of substituted 1*H*-indazoles and 1*H*-pyrazoles from arylhydrazones catalyzed by cheap iron(III) tribromide with oxygen as an ultimate oxidative agent under mild conditions.

Benzophenone phenylhydrazone (**1a**) was chosen as the substrate to investigate the reaction conditions (Table 1). First, $Pd(OAc)_2$ was used as a catalyst and the reaction was conducted in 2 mL of toluene under O_2 atmosphere at 110 °C; 24 h later, 41% yield of the desired product (**2a**) was obtained (Table 1, entry 1). When $Cu(OTf)_2$ or $Cu(OAc)_2$ replaced the $Pd(OAc)_2$, the yield declined to 10% or 22% (Table 1, entries 2 and 4). The yield of **2a** also decreased a little when $PhI(OAc)_2$, Ag_2CO_3, or DDQ was used as the oxidant (Table 1, entries 3, 5, and 8). With addition of MS 4 Å or DIC to the reaction mixture, no change was made in the yield (Table

Received: December 13, 2012
Published: January 9, 2013

Table 1. Reaction Conditions Optimization[a]



1a 2a

entry	catalyst	oxidant	time (h)	temp (°C)	yield (%)
1	$Pd(OAc)_2$	O_2	24	110	41
2	$Cu(OTf)_2$	O_2	24	110	10
3	$Cu(OTf)_2$	$PhI(OAc)_2$	24	110	tr
4	$Cu(OAc)_2$	O_2	24	110	22
5	$Cu(OAc)_2$	Ag_2CO_3	24	110	16
6[b]	$Cu(OAc)_2$	O_2	24	110	20
7[c]	$Cu(OAc)_2$	O_2	24	110	24
8	$Cu(OAc)_2$	DDQ	18	110	13
9	$FeCl_3$	DDQ	18	110	34
10	$FeCl_3$	BQ	18	110	43
11	$FeBr_3$	DDQ	18	110	31
12	$FeBr_3$	BQ	18	110	49
13[d]	$FeCl_3$	BQ	18	110	37
14[e]	$FeBr_3$	BQ	18	110	37
15	$FeCl_3$	O_2	16	110	22
16	**$FeBr_3$**	**O_2**	**16**	**110**	**82**
17	$FeBr_3$	O_2	16	80	65
18[f]	$FeBr_3$	O_2	16	110	tr
19[g]	$FeBr_3$	O_2	16	110	25
20[h]	$FeBr_3$	O_2	16	110	75

[a]Reaction conditions: phenylhydrazone (0.25 mmol) and catalyst (0.025 mmol), oxidant (0.3 mmol) or under an atmosphere of dry oxygen, 2.0 mL toluene (reflux). [b]MS 4 Å (200 mg) was added. [c]2 equiv of diisopropyl-carbodiimide (DIC) (126 mg) was added. [d]0.3 equiv of $FeCl_3$ was used. [e]0.3 equiv of $FeBr_3$ was used. [f]2 mL of DMF as solvent. [g]2 mL of DMSO as solvent. [h]2 mL of PhCl as solvent.

1, entries 6 and 7). However, when iron(III) was used as catalyst, moderate yield was obtained (Table 1, entries 9–12). Increasing the amount of catalyst did not improve the yield (Table 1, entries 13 and 14). Interestingly, oxidant had a significant effect on product yield, and environmentally friendly oxidant molecular O_2 showed the best effect. Further investigation found that $FeBr_3$ was the best catalyst (Table 1, entries 15 and 16). Reducing the temperature to 80 °C decreased the yield slightly (Table 1, entry 17). Among the solvents investigated, toluene was the best choice (Table 1, entries 16, 18–20). Finally, the reaction was best promoted by $FeBr_3$ (10 mol %) /O_2 in toluene (2 mL) at 110 °C for 16 h (Table 1, entry 16).

With these optimized reaction conditions in hand, the substrate scope was surveyed, and the results are summarized in Table 2. Various substituted phenylhydrazones generated the corresponding products in moderate to excellent yields. The electronic properties of the phenylhydrazone substituents affected the efficiency of the reaction. The phenylhydrazones disubstituted by electron-donating groups gave the products in good to excellent yields (Table 2, **2b–2d**), while the reactions of the phenylhydrazones disubstituted by electron-withdrawing groups proceeded more slowly and afforded moderate yields after 21 h (Table 2, **2e** and **2f**). Impressively, the substrate disubstituted by chloro and methyl groups also had a satisfactory yield of 78% and no isomer was found (Table 2, **2g**). As can be anticipated, the substrates singly substituted by methyl or chloro group had isomers (Table 2, **2h** and **2l**). Interestingly, when the phenylhydrazones substituted by methoxy group were subjected to this procedure, the benzene ring with methoxy group was preferentially activated, and the reaction proceeded in high regioselectivity (Table 2, **2i–2k**), contrary to nitro group substituted substrate (Table 2, **2m**). As for substrates with substituents in the phenylhydrazines, the yields were slightly reduced (Table 2, **2n–2p**) and no distinct electronic effect was observed.

Excitingly, this facile method can also be applied to the construction of a pyrazole scaffold. A variety of substrates derived from α,β-unsaturated ketones and phenylhydrazine were surveyed to prepare different trisubstituted pyrazoles. As shown in Table 3, the optimum reaction condition was also successful in providing highly diversified trisubstituted pyrazoles (compounds **3a–3h**) with satisfactory yields. Apparently, in terms of R^2 substituents, the substrates with alkyl group easily produced excellent yields of the corresponding pyrazole products. It was found that both the electron-rich and electron-deficient aryl groups were well tolerated and did not show distinct electronic effect.

On the basis of these observations, a plausible mechanism is proposed in Scheme 1. The reaction proceeded via one-electron transfer from substrate **1** to $FeBr_3$ to give the reduced form (Fe^{2+}) and a radical cationic species (**A**), which underwent electrophilic attack to the electron-rich double bond to form a C–N bond. At last, **C** lost one electron and dehydrogenated to give the product **2 or 3**. The reduced catalyst reacted with O_2 to regenerate the oxidized form (Fe^{3+}) with the formation of water.

In conclusion, we have developed a new synthetic method for substituted 1*H*-indazoles and 1*H*-pyrazoles via $FeBr_3/O_2$ mediated oxidative C–N bond formation reactions. Using molecular oxygen as an environmentally friendly oxidant and the inexpensive and nontoxic iron(III) as the catalyst, this protocol is an efficient method for the direct construction of *N*-heterocycles and fits to be largely employed for industrial applications.

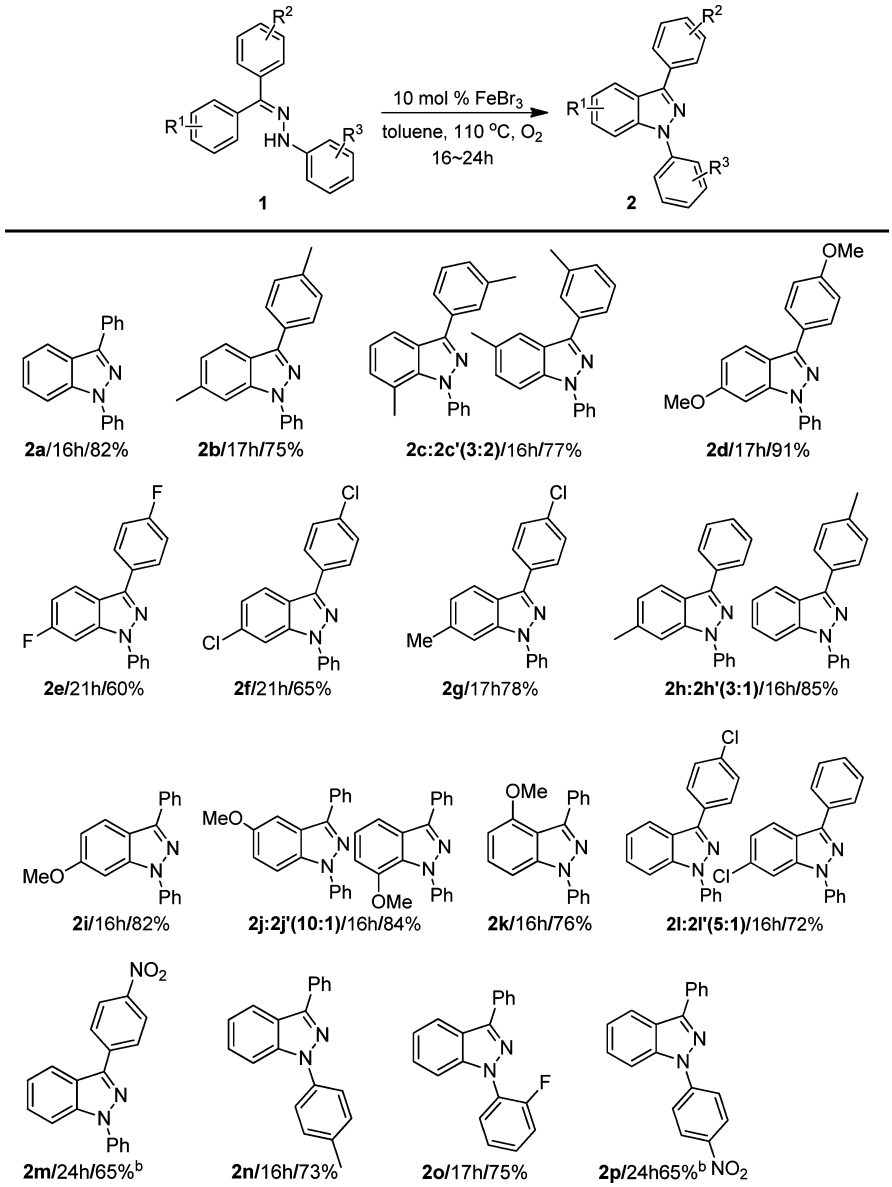
EXPERIMENTAL SECTION

General Remarks. All reactions were carried out under oxygen with oxygen balloon in oven-dried Schlenk tubes. All the reagents were commercially available, and toluene was distilled from sodium. The catalyst $FeBr_3$ was anhydrous (>98%) from Alfa Aesar. The analytical thin-layer chromatography (TLC) was performed on precoated silica gel plates (GF 254), visualized with a UV254 lamp. Column chromatography was performed on silica gel 60 (200–300 mesh) with petroleum ether/dichloromethane (or petroleum ether/ethyl acetate) as eluent. All products were confirmed by ^1H NMR, ^{13}C NMR, MS, and IR. Unknown compounds were additionally confirmed by high resolution mass spectrometry (HRMS). ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR at 100 MHz. Chemical shifts (δ, ppm) were determined with TMS as internal standard. Coupling constants are reported in hertz (Hz). Mass spectra were obtained using EI ionization. Melting points are uncorrected.

Synthesis of Benzophenone Phenylhydrazone. Benzophenone (5 mmol, 1.0 equiv) was added to a solution of phenylhydrazine (6 mmol, 1.2 equiv) in EtOH, and then two or three drops of acetic acid were added if necessary. It was stirred at 80 °C for about 10 h equipped with a reflux condenser until most disappearance of the benzophenone by TLC, purified by chromatography on a column of silica gel with PE/DCM = 3:1 as eluent to give benzophenone phenylhydrazone.

dx.doi.org/10.1021/jo3026862 | J. Org. Chem. 2013, 78, 1317–1322

Table 2. Scope of C−H Activation/C−N Cyclization[a]



[a]Unless otherwise specified, the reactions were carried out with phenylhydrazone (0.25 mmol), $FeBr_3$ (0.025 mmol), and toluene (2.0 mL) under an atmosphere of dry oxygen. [b]Temperature, 140 °C; solvent, *p*-xylene.

Synthesis of Phenylhydrazone of *α,β*-unsaturated ketones. NaOAc (1.3 equiv) was added to a stirred solution of hydrazine hydrochloride (1.2 equiv) in EtOH. After stirring at room temperature for 15−20 min, ketones (1.0 equiv) were added to the upper solution (warm to 40 °C or higher temp if necessary). If most of the ketone disappeared from TLC, the reaction was quenched, purified by chromatography on a column of silica gel with PE/EA = 20:1 as eluent to give the phenylhydrazone. If a lot of solid precipitated from the solution, the solid was collected by filtration and washed with cold water and MeOH, followed by further purification by recrystallization in EtOAc/MeOH cosolvent system.

General Procedure for the Synthesis of Substituted 1*H*-Indazoles 2a−2p. An oven-dried Schlenk tube was charged with $FeBr_3$ (8 mg, 10 mol %) and phenylhydrazone (0.25 mmol), then 2 mL toluene was added as solvent, the reaction tube was sealed, and the contents were stirred at 110 °C for 16 h under oxygen with oxygen balloon. After the reaction was complete, the mixture was filtrated and washed with EtOAc. Then the solvent was removed, and the crude product was purified through column chromatography with PE/DCE = 3:1 as eluent to give the pure product.

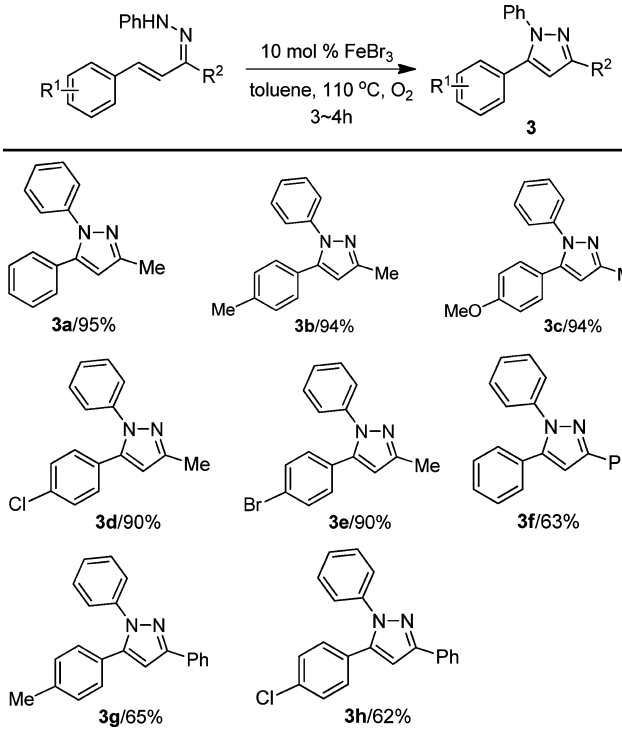
1,3-Diphenyl-1*H*-indazole (2a).[8c,10] Compound **2a** (55 mg, 82%) was obtained as a white solid; mp 96−98 °C ; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, J = 8 Hz, 1H), 8.04 (d, J = 8 Hz, 2H), 7.80−7.76 (m, 3H), 7.55−7.50 (m, 4H), 7.46−7.41 (m, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.0, 140.2, 140.0, 133.1, 129.4, 128.8, 128.2, 127.8, 127.1, 126.6, 123.0, 122.9, 121.9, 121.5, 110.6; IR (neat, cm^{-1}) 3052, 1613, 1595, 1498, 1392, 1228, 1110, 1071, 837, 772, 743, 694.

6-Methyl-1-phenyl-3-*p*-tolyl-1*H*-indazole (2b). Compound **2b** (56 mg, 75%) was obtained as a light yellow solid; mp 86−88 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, J = 8 Hz, 3H), 7.83 (d, J = 7.6, 2H), 7.60−7.56 (m, 3H), 7.41−7.36 (m, 3H), 7.14 (d, J = 8 Hz, 1H), 2.54 (s, 3H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.9, 140.8, 140.2, 138.0, 137.4, 130.4, 129.5, 129.4, 127.5, 126.4, 123.9, 123.0, 121.3, 121.2, 110.1, 22.0, 21.3; IR (neat, cm^{-1}) 3036, 2919, 2859, 1613, 1596, 1531, 1499, 1415, 1164, 850, 823, 759, 730; HRMS (EI-TOF) [M]$^+$ calculated for $C_{21}H_{18}N_2$ 298.1470, found 298.1470.

7-Methyl-1-phenyl-3-*m*-tolyl-1*H*-indazole (2c). Compound **2c** (33 mg, 44%) was obtained as a light yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85−7.77 (m, 5H), 7.66 (d, J = 8.8 Hz, 1H), 7.53 (t, J =

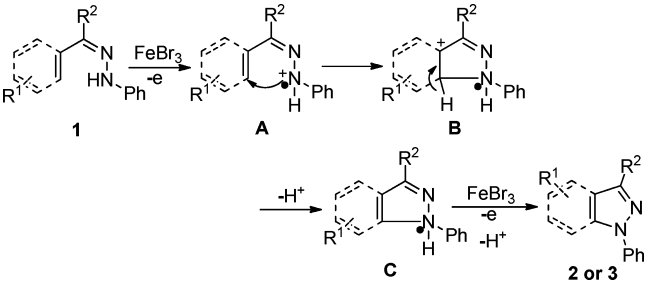
dx.doi.org/10.1021/jo3026862 | J. Org. Chem. 2013, 78, 1317−1322

Table 3. Synthesis of Trisubstituted Pyrazoles[a]



[a]Conditions: phenylhydrazone (0.3 mmol), $FeBr_3$ (9 mg, 10 mol %,), toluene (2.0 mL) under an atmosphere of dry oxygen.

Scheme 1. Tentative Mechanism



8 Hz, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 8.4, 1H), 7.24 (d, J = 4.4 Hz, 1H), 2.51 (s, 3H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.6, 140.2, 138.9, 138.4, 133.2, 131.3, 129.3, 129.0, 128.9, 128.6, 128.3, 126.3, 124.8, 123.5, 122.7, 120.6, 110.3, 21.5, 21.4; IR (neat, cm^{-1}) 3043, 2920, 2857, 1653, 1596, 1498, 1455, 1306, 1209, 1116, 815, 792, 756, 694; HRMS (EI-TOF) $[M]^+$ calculated for $C_{21}H_{18}N_2$ 298.1472, found 298.1470.

5-Methyl-1-phenyl-3-*m*-tolyl-1*H*-indazole (2c′). Compound **2c′** (25 mg, 33%) was obtained as a light yellow solid, mp 86–88 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (dd, J_1 = 6.4 Hz, J_2 = 2.8 Hz, 1H), 7.82 (s, 1H), 7.78 (d, J = 8 Hz, 1H), 7.55–7.45 (m, 5H), 7.40 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.17 (d, J = 2.8 Hz, 1H), 7.16 (s, 1H), 2.44 (s, 3H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.8, 141.3, 141.0, 138.4, 133.1, 128.8, 128.7, 128.59, 128.56, 128.5, 128.4, 128.0, 125.0, 122.7, 121.6, 121.2, 119.2, 21.5, 19.4; IR (neat, cm^{-1}) 3044, 2921, 2858, 1654, 1597, 1501, 1453, 1210, 1125, 836, 796, 749, 697; HRMS (EI-TOF) $[M]^+$ calculated for $C_{21}H_{18}N_2$ 298.1467, found 298.1470.

6-Methoxy-3-(4-methoxy-phenyl)-1-phenyl-1*H*-indazole (2d). Compound **2d** (75 mg, 91%) was obtained as a light yellow solid; mp 132–134 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 9.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.12 (d, J = 1.6 Hz, 1H), 7.07 (d, J = 8.8 Hz, 2H), 6.93 (dd, J_1 = 8.4 Hz, J_2 = 1.6, 1H), 3.880 (s, 3H), 3.876 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.8, 159.7, 145.8, 141.5, 140.2, 129.4, 128.8, 126.4, 125.8, 122.9, 122.3, 117.6, 114.2, 113.3, 91.8, 55.5, 55.3; IR (neat, cm^{-1}) 3068, 3000, 2931, 2835, 1615, 1597, 1530, 1499, 1418, 1248, 1173, 1110, 1032, 860, 835, 814, 757, 698; HRMS (EI-TOF) $[M]^+$ calculated for $C_{21}H_{18}N_2O_2$ 330.1370, found 330.1368.

6-Fluoro-3-(4-fluoro-phenyl)-1-phenyl-1*H*-indazole (2e). Compound **2e** (46 mg, 60%) was obtained as a light yellow solid; mp 130–132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97–7.91 (m, 3H), 7.72 (d, J = 8 Hz, 2H), 7.55 (t, J = 7.6 Hz, 2H), 7.41–7.36 (m, 2H), 7.20 (t, J = 8.8 Hz, 2H), 7.03 (td, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.2, 163.8, 161.7, 161.3, 145.3, 140.6, 140.5, 139.6, 129.5, 129.4, 129.3, 128.82, 128.78, 127.0, 122.7, 122.6, 119.7, 115.9, 115.7, 111.8, 111.5, 96.7, 96.4; IR (neat, cm^{-1}) 3064, 2956, 2924, 2853, 1621, 1599, 1528, 1501, 1417, 1224, 1177, 1157, 1106, 862, 839, 807, 758; HRMS (EI-TOF) $[M]^+$ calculated for $C_{19}H_{12}F_2N_2$ 306.0966, found 306.0969.

6-Chloro-3-(4-chloro-phenyl)-1-phenyl-1*H*-indazole (2f). Compound **2f** (55 mg, 65%) was obtained as a white solid; mp 148–150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91–7.87 (m, 3H), 7.72–7.69 (m, 3H), 7.54 (t, J = 7.6 Hz, 2H), 7.47 (d, J = 8 Hz, 2H), 7.39 (t, J = 7.2 Hz,1H), 7.21 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.9, 140.6, 139.3, 134.4, 133.6, 131.1, 129.6, 129.0, 128.7, 127.2, 123.03, 129.96, 122.1, 121.3, 110.5; IR (neat, cm^{-1}) 3063, 2923, 1650, 1601, 1499, 1413, 1164, 1117, 827, 805, 753, 717; HRMS (EI-TOF) $[M]^+$ calculated for $C_{19}H_{12}Cl_2N_2$ 338.0378, found 338.0378.

3-(4-Chloro-phenyl)-6-methyl-1-phenyl-1*H*-indazole (2g). Compound **2g** (57 mg, 78%) was obtained as a light yellow solid; mp 118–120 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8 Hz, 1H), 7.75 (d, J = 8 Hz, 2H), 7.55–7.51 (m, 3H), 7.46 (d, J = 8 Hz, 2H), 7.35 (t, J = 8 Hz, 1H), 7.09 (d, J = 8 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.6, 140.9, 140.0, 137.6, 133.9, 131.8, 129.4, 128.9, 128.7, 126.7, 124.2, 123.0, 121.0, 120.8, 110.2, 22.0; IR (neat, cm^{-1}) 3065, 2920, 2857, 1618, 1597, 1498, 1413, 1388, 1238, 1118, 1092, 832, 803, 758, 696; HRMS (EI-TOF) $[M]^+$ calculated for $C_{20}H_{15}ClN_2$ 318.0928, found 318.0924.

6-Methyl-1,3-diphenyl-1*H*-indazole (2h) and 1-Phenyl-3-*p*-tolyl-1*H*-indazole (2h′). Compounds **2h** and **2h′** (60 mg, 85%) were obtained as a light yellow oil, the regioisomer ratio was got from ^{1}H NMR spectrum about (3: 1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06–8.02 (m, 1.75 H), 7.93 (d, J = 8.4 Hz, 1.25H), 7.78–7.74 (m, 2.25H), 7.54–7.48 (m, 4.25H), 7.43–7.38 (m, 1H), 7.36–7.31 (m, 1.5H), 7.25 (t, J = 8 Hz, 0.25H, **2h′**-isomer), 7.09 (d, J = 8.8 Hz, 0.75H, **2h**-isomer), 2.49 (s, 2.25H, **2h**-isomer), 2.42 (s, 0.75H, **2h′**-isomer); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.9, 140.9, 140.2, 137.4, 133.3, 129.4, 128.7, 128.1, 127.6, 126.5, 124.0, 123.0, 121.2, 121.1, 110.1, 22.0 (**2h**-isomer); IR (neat, cm^{-1}) 3057, 2958, 2921, 2859, 1615, 1598, 1561, 1500, 1417, 1260, 1237, 1164, 1115, 803, 753, 695; HRMS (EI-TOF) $[M]^+$ calculated for $C_{20}H_{16}N_2$ 284.1310, found 284.1313.

6-Methoxy-1,3-diphenyl-1*H*-indazole (2i). Compound **2i** (62 mg, 82%) was obtained as a light yellow solid; mp 134–136 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, J = 7.2 Hz, 2H), 7.90 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8 Hz, 2H), 7.55–7.47 (m, 4H), 7.40 (t, J = 6.8 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.08 (s, 1H), 6.91 (dd, J_1 = 8.8 Hz, J_2 = 1.2 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.9, 146.0, 141.6, 140.1, 133.2, 129.5, 128.8, 128.2, 127.6, 126.6, 123.0, 122.3, 117.7, 113.5, 91.9, 55.5; IR (neat, cm^{-1}) 3058, 2956, 2926, 1615, 1597, 1500, 1455, 1276, 1207, 1169, 1111,860, 814, 763, 694; HRMS (EI-TOF) $[M]^+$ calculated for $C_{20}H_{16}N_2O$ 300.1266, found 300.1263.

5-Methoxy-1,3-diphenyl-1*H*-indazole (2j).[15,18] Compound **2j** (63 mg, 84%) was obtained as a light yellow solid; mp 86–88 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) (main isomer) δ 8.00 (d, J = 7.2 Hz, 2H), 7.78 (d, J = 8 Hz, 2H), 7.68 (d, J = 9.2 Hz, 1H), 7.53 (t, J = 7.6 Hz, 4H), 7.43 (t, J = 6.8 Hz, 1H), 7.39 (d, J = 2 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.12 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H); 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.5, 145.3, 140.1, 136.0, 133.4, 129.4, 128.8, 128.0, 127.5, 126.4, 123.4, 122.6, 118.8, 111.7, 100.9, 55.7; IR

dx.doi.org/10.1021/jo3026862 | J. Org. Chem. 2013, 78, 1317–1322

(neat, cm^{-1}) 3060, 2926, 2863, 1613, 1596, 1497, 1455, 1416, 1261, 1115, 1071, 855, 835, 804, 754.

4-Methoxy-1,3-diphenyl-1*H*-indazole (2k).[13] Compound **2k** (57 mg, 76%) was obtained as a light yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.81−7.75 (m, 4H), 7.71 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.53 (t, J = 8 Hz, 2H), 7.45−7.40 (m, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.12−7.06 (m, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.3, 144.7, 140.2, 139.7, 131.6, 129.9, 129.3, 126.8, 126.4, 124.5, 122.9, 122.0, 121.1, 120.8, 111.2, 110.3, 55.4; IR (neat, cm^{-1}) 3056, 2927, 2864, 1595, 1499, 1461, 1245, 1098, 1071, 1023, 850, 799, 743, 695.

3-(4-Chloro-phenyl)-1-phenyl-1*H*-indazole (2l).[19] Compound **2l** (55 mg, 72%) was obtained as a light yellow solid; mp 120−122 °C; ^1H NMR (DMSO, 400 MHz) (main isomer) δ 8.17 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.65−7.61 (m, 4H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H); ^{13}C NMR (DMSO, 100 MHz) δ 144.1, 140.1, 139.7, 133.5, 131.8, 130.0, 129.4, 129.2, 128.1, 127.2, 123.0, 122.9, 122.5, 121.6, 111.3; IR (neat, cm^{-1}) 3050, 2961, 2925, 1652, 1597, 1499, 1414, 1389, 1164, 1111, 1093, 834, 807, 746, 695; HRMS (EI-TOF) $[M]^+$ calculated for $C_{19}H_{13}ClN_2$ 304.0763, found 304.0767.

3-(4-Nitro-phenyl)-1-phenyl-1*H*-indazole (2m).[15] Compound **2m** (51 mg, 65%) was obtained as a yellow solid; mp 136−138 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, J = 8.4 Hz, 2H), 8.23 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 8 Hz, 1H), 7.81−7.78 (m, 3H), 7.58 (t, J = 7.6 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ147.2, 143.3, 140.5, 139.7, 139.5, 129.5, 127.8, 127.4, 127.3, 124.1, 123.1, 122.82, 122.76, 120.9, 111.0; IR (neat, cm^{-1}) 3076, 2925, 2852, 1653, 1595, 1501, 1342, 1228, 1166, 1105, 854, 747, 695.

3-Phenyl-1-*p*-tolyl-1*H*-indazole (2n). Compound **2n** (52 mg, 73%) was obtained as a light yellow solid; mp 88−90 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.07−8.03 (m, 3H), 7.72 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8 Hz, 2H), 7.53−7.50 (m, 2H), 7.43−7.40 (m, 2H), 7.33 (d, J = 8 Hz, 2H), 7.25 (t, J = 7.6 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.7, 140.3, 137.6, 136.5, 133.3, 129.3, 128.8, 128.1, 127.7, 126.9, 123.0, 122.9, 121.7, 121.5, 110.6, 21.1; IR (neat, cm^{-1})3061, 2953, 2920, 2852, 1604, 1513, 1479, 1227, 1163, 1102, 1072, 844, 819, 800, 775, 746; HRMS (EI-TOF) $[M]^+$ calculated for $C_{20}H_{16}N_2$ 284.1312, found 284.1313.

1-(2-Fluoro-phenyl)-3-phenyl-1*H*-indazole (2o). Compound **2o** (54 mg, 75%) was obtained as a light yellow solid; mp 76−78 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, J = 8 Hz, 1H), 8.03 (d, J = 8 Hz, 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 8 Hz, 2H), 7.47−7.39 (m, 4H), 7.33−7.27 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.4, 154.8, 146.9, 141.6, 133.0, 129.3, 129.2, 128.8, 128.3, 128.2, 127.8, 127.5, 127.4, 127.1, 124.90, 124.86, 122.5, 121.9, 121.3, 117.0, 116.8, 110.82, 110.77; IR (neat, cm^{-1}) 3066, 2958, 2924, 2863, 1610, 1505, 1464, 1267, 1241, 1113, 844, 820, 747, 697; HRMS (EI-TOF) $[M]^+$ calculated for $C_{19}H_{13}FN_2$ 288.1061, found 288.1063.

1-(4-Nitro-phenyl)-3-phenyl-1*H*-indazole (2p).[15] Compound **2p** (51 mg, 65%) was obtained as a yellow solid; mp 160−162 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.38 (d, J = 9.6 Hz, 2H), 8.09 (d, J = 8 Hz, 1H), 8.01 (d, J = 8.4 Hz, 4H), 7.86 (d, J = 8.8 Hz, 1H), 7.57−7.52 (m, 3H), 7.47 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.2, 145.3, 144.8, 139.9, 132.2, 128.9, 128.1, 127.8, 125.2, 124.2, 123.0, 122.1, 121.3, 110.7; IR (neat, cm^{-1}) 3059, 2924, 2853, 1653, 1592, 1502, 1326, 1108, 852, 818, 765, 745, 695.

General Procedure for the Synthesis of Substituted 1*H*-Pyrazoles 3a−3h. An oven-dired Schlenk tube was charged with $FeBr_3$ (9 mg, 10 mol %) and phenylhydrazone (0.3 mmol), then 2 mL toluene was added as solvent, the reaction tube was sealed, and the contents were stirred at 110 °C for 4 h under oxygen with oxygen balloon. After the reaction was complete, the mixture was filtrated and washed with EtOAc. Then the solvent was removed, and the crude product was purified through column chromatography with PE/EA = 20:1 as eluent to give the pure product.

3-Methyl-1,5-diphenyl-1*H*-pyrazole (3a).[16b,20] Compound **3a** (67 mg, 95%) was obtained as a light yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.31−7.19 (m, 10H), 6.30 (s, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.4, 143.6, 140.1, 130.7, 128.8, 128.6, 128.3, 128.0, 127.0, 125.0, 107.7, 13.5; IR (neat, cm^{-1}) 3059, 2925, 1597, 1551, 1502, 1456, 1417, 1364, 969, 912, 763.

3-Methyl-1-phenyl-5-(*p*-tolyl)-1*H*-pyrazole (3b).[16b] Compound **3b** (70 mg, 94%) was obtained as a light yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.32−7.22 (m, 5H), 7.11−7.06 (m, 4H), 6.27 (s, 1H), 2.37 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.3, 143.7, 140.2, 137.9, 129.0, 128.7, 128.4, 127.7, 126.9, 125.1, 107.4, 21.2, 13.5; IR (neat, cm^{-1}) 3057, 2922, 1598, 1504, 1456, 1428, 1366, 1316, 970, 762.

5-(4-Methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazole (3c).[16b,20] Compound **3c** (75 mg, 94%) was obtained as a light yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.32−7.23 (m, 5H), 7.13 (d, J = 7.6 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 6.25 (s, 1H), 3.78 (s, 3H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 149.3, 143.4, 140.2, 129.8, 128.7, 126.9, 125.0, 123.1, 113.7, 107.1, 55.1, 13.5; IR (neat, cm^{-1}) 3060, 2925, 1598, 1576, 1505, 1459, 1433, 1363, 969,762.

5-(4-Chloro-phenyl)-3-methyl-1-phenyl-1*H*-pyrazole (3d).[14a,21] Compound **3d** (73 mg, 90%) was obtained as a light yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.34−7.24 (m, 7H), 7.13 (d, J = 8.4 Hz, 2H), 6.30 (s, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.5, 142.4, 139.8, 134.0, 129.7, 129.1, 128.9, 128.6, 127.3, 125.1, 107.8, 13.5; IR (neat, cm^{-1}) 3055, 2924, 1598, 1499, 1460, 1428, 1397, 1364, 969, 794.

5-(4-Bromo-phenyl)-3-methyl-1-phenyl-1*H*-pyrazole (3e).[22] Compound **3e** (85 mg, 90%) was obtained as a light yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.40 (d, J = 8.4 Hz, 2H), 7.34−7.24 (m, 5H), 7.07 (d, J = 8.4 Hz, 2H), 6.30 (s, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.5, 142.4, 139.8, 131.6, 130.0, 129.5, 128.9, 127.3, 125.1, 122.3, 107.8, 13.5; IR (neat, cm^{-1}) 3053, 2923, 1596, 1501, 1460, 1427, 1393, 1364, 969, 765.

1,3,5-Triphenyl-1*H*-pyrazole (3f).[14b,16b] Compound **3f** (56 mg, 63%) was obtained as a light yellow solid; mp 130−132 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, J = 6.8 Hz, 2H), 7.42 (t, J = 7.2 Hz, 2H), 7.38−7.26 (m, 11H), 6.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.9, 144.3, 140.1, 133.0, 130.5, 128.8, 128.7, 128.6, 128.4, 128.2, 127.9, 127.3, 125.7, 125.2, 105.1; IR (neat, cm^{-1}) 3060, 2930, 1596, 1550, 1498, 1458, 1411, 1363, 972, 763.

1,3-Diphenyl-5-(*p*-tolyl)-1*H*-pyrazole (3g).[14b] Compound **3g** (60 mg, 65%) was obtained as a light yellow solid; mp 110−112 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, J = 7.6 Hz, 2H), 7.44−7.27 (m, 8H), 7.16 (d, J = 6.8 Hz, 2H), 7.11 (d, J = 8 Hz, 2H), 6.79 (s, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8, 144.4, 140.2, 138.1, 133.1, 129.1, 128.8, 128.6, 127.8, 127.6, 127.3, 125.7, 125.2, 104.9, 21.2; IR (neat, cm^{-1}) 3049, 2922, 1597, 1496, 1458, 1429, 1398, 1362, 972, 764.

5-(4-Chloro-phenyl)-1,3-diphenyl-1*H*-pyrazole (3h).[23] Compound **3h** (61 mg, 62%) was obtained as a light yellow solid; mp 100−102 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, J = 7.2 Hz, 2H), 7.43 (t, J = 7.2 Hz, 2H), 7.37−7.28 (m, 8H), 7.20 (d, J = 8 Hz, 2H), 6.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 143.1, 139.8, 134.3, 132.8, 129.9, 129.0, 128.7, 128.6, 128.0, 127.6, 125.7, 125.2, 105.2; IR (neat, cm^{-1}) 3051, 2923, 1598, 1497, 1482, 1457, 1391, 1361, 971,761.

■ ASSOCIATED CONTENT

Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wlbao@css.zju.edu.cn.

Notes

The authors declare no competing financial interest.

dx.doi.org/10.1021/jo3026862 | J. Org. Chem. 2013, 78, 1317−1322

■ ACKNOWLEDGMENTS

This work was financially supported by the Natural Science Foundation of China (No. 21072168).

■ REFERENCES

(1) (a) Bermudez, J.; Fake, C. S.; Joiner, G. F.; Joiner, K. A.; King, F. D.; Miner, W. D.; Sanger, G. J. *J. Med. Chem.* **1990**, *33*, 1924−1929. (b) Moore, P. K.; Babbedge, R. C.; Wallace, P.; Gaffen, Z. A.; Hart, S. L. *Br. J. Pharmacol.* **1993**, *108*, 296−297. (c) Boehm, H. -J.; Boehringer, M.; Bur, D.; Gmuender, H.; Huber, W.; Klaus, W.; Kostrwa, D.; Kuehne, H.; Luebbers, T.; Meunier-Keller, N.; Mueller, F. *J. Med. Chem.* **2000**, *43*, 2664−2674. (d) Hartmann, M.; Sommer, M. E.; Keppler, B. K.; Kratz, F.; Einhäuser, Th. J. *J. Inorg. Biochem.* **1995**, *59*, 214. (e) Clarke, M. J. *Coord. Chem. Rev.* **2003**, *236*, 209−233. (f) Goodman, K. B.; Cui, H.; Dowdell, S. E.; Gaitanopoulos, D. E.; Ivy, R. L.; Sehon, C. A.; Stavenger, R. A.; Wang, G. Z.; Viet, A. Q.; Xu, W.; Ye, G.; Semus, S. F.; Evans, C.; Fries, H. E.; Jolivette, L. J.; Kirkpatrick, R. B.; Dul, E.; Khandekar, S. S.; Yi, T.; Jung, D. K.; Wright, L. L.; Smith, G. K.; Behm, D. J.; Bentley, R.; Doe, C. P.; Hu, E.; Lee, D. *J. Med. Chem.* **2007**, *50*, 6−9.

(2) (a) Bekhit, A. A.; Abdel-Aziem, T. *Bioorg. Med. Chem.* **2004**, *12*, 1935−1945. (b) Fustero, S.; Rosell, M. S.; Barrio, P.; Fuentes, A. S. *Chem. Rev.* **2011**, *111*, 6984. (c) Selvam, C.; Jachak, S. M.; Thilagavathi, R.; Chakraborti, A. K. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1793−1797. (d) Sperandeo, N. R.; Brun, R. *ChemBioChem* **2003**, *4*, 69. (e) Terrett, N. K.; Bell, A. S.; Brown, D.; Ellis, P. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 1819−1824.

(3) (a) Sun, J. -H.; Teleha, C. A.; Yan, J. -S.; Rodgers, J. D.; Nugiel, D. A. *J. Org. Chem.* **1997**, *62*, 5627−5629. (b) Rodgers, J. D.; Johnson, B. L.; Wang, H.; Greenberg, R. A.; Erickson-Viitanen, S.; Klabe, R. M.; Cordova, B. C.; Rayner, M. M.; Lam, G. N.; Chang, C.-H. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2919−2921.

(4) Corsi, G.; Palazzo, G.; Germani, C.; Barcellona, P. S.; Silvestrini, B. *J. Med. Chem.* **1976**, *19*, 778−783.

(5) (a) Guglielmotti, A.; De Joannon, A. C.; Cazzolla, N.; Marchetti, M.; Soldo, L.; Cavallo, G.; Pinza, M. *Pharmacol. Res.* **1995**, *32*, 369−373. (b) Wrobleski, S. T.; Chen, P.; Hynes, J., Jr.; Lin, S.; Norris, D. J.; Pandit, C. R.; Spergel, S.; Wu, H.; Tokarski, J. S.; Chen, X.; Gilloly, K. M.; Kiener, P. A.; McIntyre, K. W.; Patil-Koota, V.; Shuster, D. J.; Turk, L. A.; Yang, G.; Leftheris, K. *J. Med. Chem.* **2003**, *46*, 2110−2116. (c) Yates, C. M.; Brown, P. J.; Stewart, E. L.; Patten, C.; Austin, R. J. H.; Holt, J. A.; Maglich, J. M.; Angell, D. C.; Sasse, R. Z.; Taylor, S. J.; Uings, I. J.; Trump, R. P. *J. Med. Chem.* **2010**, *53*, 4531.

(6) Penning, T. D.; Talley, J. J.; Bertenshaw, S. R.; Carter, J. S.; Collins, P. W.; Docter, S.; Graneto, M. J.; Lee, L. F.; Malecha, J. W.; Miyashiro, J. M.; Rogers, R. S.; Rogier, D. J.; Yu, S. S.; Anderson, G. D.; Burton, E. G.; Cogburn, J. N.; Gregory, S. A.; Koboldt, C. M.; Perkins, W. E.; Seibert, K.; Veenhuizen, A. W.; Zhang, Y. Y.; Isakson, P. C. *J. Med. Chem.* **1997**, *40*, 1347−1365.

(7) Huisgen, R.; Bast, K. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. *V*, 650

(8) (a) Stadlbauer, W. *Sci. Synth.* **2002**, *12*, 227−324. (b) Crestey, F.; Collot, V.; Stiebing, S.; Rault, S. *Tetrahedron* **2006**, *62*, 7772. (c) Jin, T.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 3323−3325.

(9) Liu, Z.; Shi, F.; Martinez, P. D. G.; Raminelli, C.; Larock, R. C. *J. Org. Chem.* **2008**, *73*, 219−226.

(10) Spiteri, C.; Keeling, S.; Moses, J. E. *Org. Lett.* **2010**, *12*, 3368−3371.

(11) Wray, B. C.; Stambuli, J. P. *Org. Lett.* **2010**, *12*, 4576−4579.

(12) Xiong, X.; Jiang, Y.; Ma, D. *Org. Lett.* **2012**, *14*, 2552−2555.

(13) Li, P.; Wu, C.; Zhao, J.; Rogness, D. C.; Shi, F. *J. Org. Chem.* **2012**, *77*, 3149−3158.

(14) (a) Jin, W.; Yu, H.; Yu, Z. *Tetrahedron Lett.* **2011**, *52*, 5884−5887. (b) Liu, P.; Pan, Y.; Xu, Y.; Wang, H. *Org. Biomol. Chem.* **2012**, *10*, 4696−4698. (c) Guo, S.; Wang, J.; Guo, D.; Zhang, X.; Fan, X. *RSC Adv.* **2012**, *2*, 3772−3777. (d) Gosselin, F.; O'Shea, P. D.; Webster, R. A.; Reamer, R. A.; Tillyer, R. D.; Grabowski, E. J. *Synlett* **2006**, *19*, 3267−3270.

(15) Gladstone, W. A. F.; Norman, R. O. C. *J. Chem. Soc.* **1965**, 3048−3052.

(16) (a) Inamoto, K.; Saito, T.; Katsuno, M.; Sakamoto, T.; Hiroya, K. *Org. Lett.* **2007**, *9*, 2931−2934. (b) Hu, J.; Chen, S.; Sun, Y.; Yang, J.; Rao, Y. *Org. Lett.* **2012**, *14*, 5030−5033.

(17) (a) Correa, A.; Mancheño, O. G.; Bolm, C. *Chem. Soc. Rev.* **2008**, *37*, 1108−1117. (b) Bolm, C.; Legros, J.; Paih, J. L.; Zani, L. *Chem. Rev.* **2004**, *104*, 6217−6254. (c) Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3317−3321.

(18) Salovich, J. M.; Lindsley, C. W.; Hopkins, C. R. *Tetrahedron Lett.* **2010**, *51*, 3796−3799.

(19) Hattori, K.; Yamaguchi, K.; Yamaguchi, J.; Itami, K. *Tetrahedron* **2012**, *68*, 7605−7612.

(20) Dvorak, C. A.; Rudolph, D. A.; Ma, S.; Carruthers, N. I. *J. Org. Chem.* **2005**, *70*, 4188−4190.

(21) Kovelesky, A. C.; H. Shine, J. *J. Org. Chem.* **1988**, *53*, 1973.

(22) Moegel, L.; Schulz, M.; Radeglia, R.; Osten, H. J. *J. Prakt. Chem. (Leipzig)* **1984**, *326*, 54−62.

(23) Sabitha, G.; Kiran Kumar Reddy, G. S.; Reddy, Ch. S.; Fatima, N.; Yadav, J. S. *Synthesis* **2003**, *8*, 1267−1271.