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Copper-Catalyzed Isomerization and Cyclization of *E*/*Z*-*o*-Haloaryl *N*-Sulfonylhydrazones: Convenient Access to of 1*H*-Indazoles

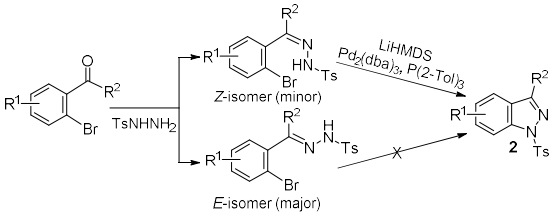
Xue-Qing Zhu, Shuai Mao, Dong-Dong Guo, Bin Li, Shi-Huan Guo, Ya-Ru Gao, Yong-Qiang Wang*[a]

Abstract: The isomerization of C=N double bond in hydrazones is a fundamental chemistry topic, and has drawn considerable attentions in the chemistry community due to its potential applied in a broad range of chemical transformations. Generally, the isomerization of C=N double bond of hydrazones can be realized by means of two processes, either photochemically or thermally. In this manuscript, we disclose a new isomerization approach, the first copper-catalyzed C=N double bond isomerization of hydrazones, which is followed by an efficient intramolecular C-N coupling reaction, providing an unprecedented catalytic approach for the synthesis of 1*H*-indazoles from readily accessible *Z*/*E* mixture of *o*-haloaryl *N*-sulfonylhydrazones.

Introduction

Hydrazone compounds being a class of important organic molecules have attracted much interest within the chemistry community.[1,2] Early researches on hydrazones led to the famous Fischer indole synthesis[3] and Wolff−Kishner reduction.[4] In the past decade, the isomerization of C=N double bond in hydrazones as a fundamental chemistry topic has drawn considerable attentions due to its potential applied in a broad range of chemical transformations.[5] Generally, the isomerization of C=N double bond can be realized by means of two processes, either photochemically or thermally.[6] Herein, we disclose a new isomerization approach for hydrazones, the first copper-catalyzed C=N double bond isomerization of *o*-haloaryl *N*-sulfonylhydrazones, which is an important complementary protocol for C=N double bond isomerization of hydrazone compounds. The isomerization is followed by an efficient intramolecular C-N coupling reaction, providing a promising access to 1*H*-indazoles.

1*H*-Indazole, as a privileged *N*-heterocyclic structure in medicinal chemistry,[7] is the key moiety in many drug substances with a wide range of pharmacological activities,[8] including anti-inflammatory, anti-depressant, anticancer, anti-HIV and antifertility activity. Consequently, great efforts have been devoted to the development of efficient methods for the construction of 1*H*-indazole frameworks.[9-13] In 2004, Inamoto et al. first reported the Pd-catalyzed 1*H*-indazoles formation from *o*-halobenzyl *N*-tosylhydrazons (Scheme 1).[14] Compared to the classical approach such as the diazotization or nitrosation of anilines and the condensation of benzaldehydes with hydrazines the approach possesses obvious advantages. Those methods often require a highly toxic or unstable reagents (e.g. hydrazine,[10] nitro,[9] diazo[9] compound) and harsh reaction conditions. However, the compatible coupling substrates for this approach have to be the *N*-tosylhydrazones with *Z* configuration at C=N double bond, while (*E*)-isomers were totally decomposed under the same conditions. Nevertheless, the principle and experiments affirm that the hydrazones with *E* configuration is the predominance in the syntheses.[15] Although later Tois et al. developed a (*Z*)-selective preparation of *o*-haloaryl hydrazones through a three-step reaction sequence,[16] the mult-step synthesis is inconvenient to access the 1*H*-indazoles. In 2013, Bolm et al. reported a base-catalyzed transition-metal-free synthesis of 1*H*-indazoles from (*Z*)-*o*-bromobenzyl *N*-tosylhydrazones.[17] In order to remove the restriction of the substrate with *Z* configuration, they tested an *in situ* photoisomeriation of the 2:3 *Z*/*E* mixture of *o*-bromacetophenone *N*-tosylhydrazone induced by UV light, and only less part of *E*-isomer was isomerized and the yield of 1*H*-indazole was improved from 40% to 60%. It is note that they also attempted to the isomerization and cyclization of the pure (*E*)-*o*-bromacetophenone *N*-tosylhydrazone and (*E*)-*o*-halobenzaldehyde *N*-tosylhydrazone by exposure to UV irradiation, but failed and resulted in decomposition of the starting materials. More recently, Tang et al. reported an elegant thermo-induced isomerization of *o*-haloaryl *N*-tosylhydrazones and Cu_2O-mediated cyclization to synthesize 1*H*-indazoles.[18] In spite of being great breakthrough to the previous methods, this approach suffer from the following challenges: 1) high temperature (140 °C) for the isomerization of C=N double bond in hydrazone; 2) stiochiometric amounts of copper loading (Cu_2O 0.5 equiv.) for the cyclization; 3) poor yield for some case (e. g. *o*-chlorobenzaldehyde *N*-tosylhydrazone gave 33% yield).



Scheme 1. Synthesis of 1*H*-Indazole from *o*-Bromobenzyl *N*-Tosylhydrazons.

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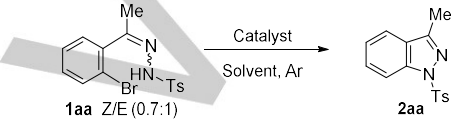
From the above researches, it is clear that UV light can induce C=N double bond isomerization of *N*-tosylhydrazones, but the efficiency is low; and thermo-induced such isomerization is effective, but it need high temperature. Therefore, it is very significant to develop an efficient C=N double bond isomerization of *N*-tosylhydrazones under mild conditions, especially at room temperature. Despite of these important advances in synthesis of 1*H*-indazoles, it is still highly desirable to develop an efficient catalytic protocol to synthesize 1*H*-indazole from readily accessible *E*/*Z* mixture of *o*-haloaryl *N*-tosylhydrazone.

Results and Discussion

Our research originated from the reaction where 0.7:1 *Z*/*E* mixture of *N*-tosylhydrazone (**1aa**) was treated with 50 mol % of $Cu(OAc)_2·H_2O$ in toluene under Ar atomsphere at room temperture for 24 h to afford 1.6:1 *Z*/*E* mixture of **1aa**. Then, with 0.7:1 *Z*/*E* mixture of **1aa** as model substrate and toluene as the solvent**,** we investigated other copper salt (e. g. CuCl, CuI, $CuBr_2$, etc.). These copper salts all could promote the isomerization of C=N double bond of **1aa**, while $Cu(OAc)_2·H_2O$ was the most efficient (for details see supporting information). At this moment, we wondered if the solvent would promote C=N double bond isomerization of *N*-tosylhydrazones. Therefore, all kinds of the solvents including toluene were employed to carry out the reaction in absence of copper salt. The reactions have been carried out at room temperature for 24 h. It turned out that the C=N double bond of of *N*-tosylhydrazones did not been isomerized at all (for details see supporting information). Later, we treated pure (*E*)-**1aa** with 50 mol % of $Cu(OAc)_2·H_2O$ in toluene at room temperture for 24 h and got 1.2:1 *Z*/*E* mixture of **1aa**. Thus, $Cu(OAc)_2·H_2O$ could be verified to promote C=N double bond isomerization of *N*-tosylhydrazones. We realized this was a new isomerization approach for C=N double bond of hydrazone compounds, and if it followed by an intramolecular dehydrohalogenation couplings, a novel catalytic synthesis of 1*H*-indazoles from readily accessible *E*/*Z* mixture of *o*-haloaryl *N*-tosylhydrazone compounds would be developed.

Accordingly, we chose the 0.7:1 *Z*/E mixture of **1aa** as model substrate to seek optimal reaction conditions for catalytic synthesis of 1*H*-indazoles via a copper-catalyzed C=N double bond isomerization and cyclization of *o*-haloaryl *N*-tosylhydrazones. First, the temperature of the reaction was investigated (Table 1, entries 1-3). To our delighted, temperature rise indeed led to the desired 1*H*-indazole (**2aa**), and 110°C provided fast reaction and the highest yield (95%). Then a variety of copper sources were tested in toluene at 110 ºC (entries 4-6). Copper(I) acetate and copper(I) oxide were turned out to be effective catalyst (entryies 4, 5). Interestingly, hydrate copper (II) acetate was better than copper(I) acetate. Further studies showed that the solvent was important, and toluene proved to be the best solvent (entries 7, 8). When the loading of $Cu(OAc)_2·H_2O$ was reduced to 20 mol%, the excellent results were maintained, while less amount of $Cu(OAc)_2·H_2O$, e.g., 10 mol%, led to longer reaction time (entries 9-11). In control experiments, under the optimized reaction conditions (20 mol% $Cu(OAc)_2·H_2O$, toluene at 110 ºC), we found that (*Z*)-**1aa** reacted fast and the cyclization accomplished within 2 h, while (*E*)-**1aa** reacted slowly and complete cyclization needed 5.5 h. Both reactions afforded the same 1*H*-indazole product (**2aa**). It is noteworthy that we always observed the C=N isomeric product of starting material in both reactions. Without the $Cu(OAc)_2·H_2O$ catalyst, only in toluene at 110 ºC, isomerization was much slow and no cyclization occurred. These results established that $Cu(OAc)_2·H_2O$ served a dual role, catalyzing both the isomerization and the cycliztion of **1aa**. Consequently, both (*Z*)- and (*E*)-isomer of **1aa** could be converted to 1*H*-indazole (**2aa**) via an efficient dynamic kinetic approach catalyzed by a single catalyst, $Cu(OAc)_2·H_2O$.

Table 1. Optimization of Reaction Conditions[a]

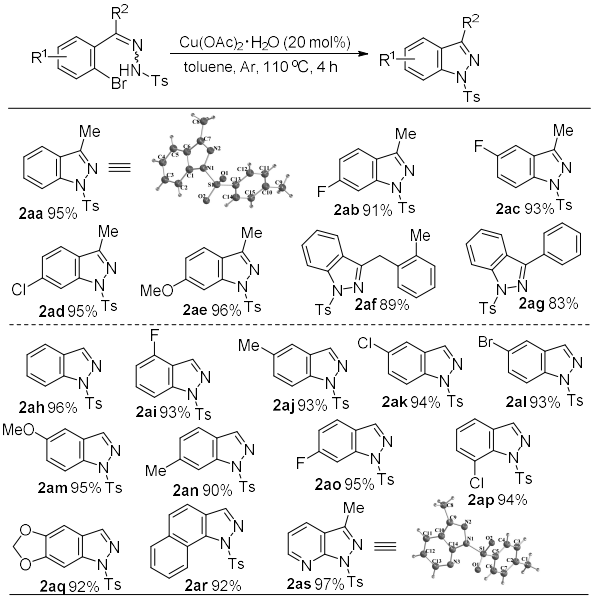


1aa Z/E (0.7:1) **2aa**

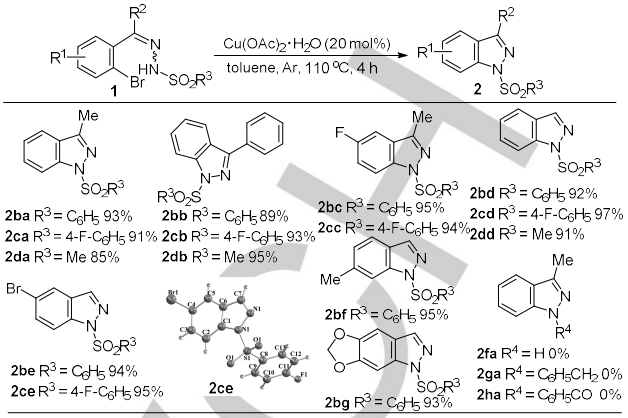
entry	Catalyst (mol %)	temp (°C)	solvent	yield (%)[b]
1	$Cu(OAc)_2·H_2O$ (50)	50	toluene	23
2	$Cu(OAc)_2·H_2O$ (50)	80	toluene	65
3	$Cu(OAc)_2·H_2O$ (50)	110	toluene	95
4	CuOAc (50)	120	toluene	79
5	Cu_2O (50)	120	toluene	75
6[c]	Other copper (50)	120	toluene	0
7	$Cu(OAc)_2·H_2O$(50)	120	xylene	89
8[d]	$Cu(OAc)_2·H_2O$ (50)	-	Other Solv.	<60
9	$Cu(OAc)_2·H_2O$ (30)	110	toluene	95
10	$Cu(OAc)_2·H_2O$ (20)	110	toluene	95
11	$Cu(OAc)_2·H_2O$ (10)	110	toluene	83
12	-	110	toluene	0

[a] Reaction conditions: **1aa**, copper catalyst in solvent (2 mL) at the specified temperature for 4 h. [b] Isolated yields. [c] Other copper: CuI, CuCl, CuCN, $CuCl_2·2H_2O$, $CuSO_4·5H_2O$, $CuBr_2$, Cu. [d] Other Solv.: DMF (120 ºC), 58% yield; MeOH (60 ºC), 58% yield; THF (65 ºC), 45% yield; CH_3CN (80 ºC), no reaction.

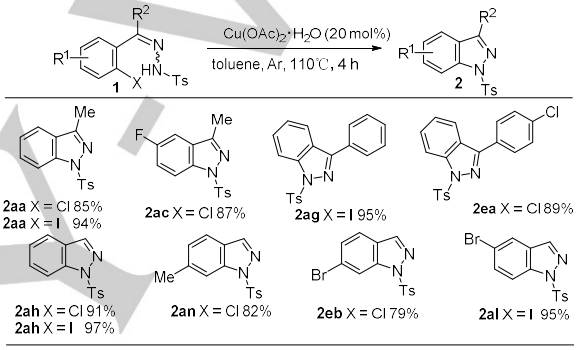
With the optimized reaction conditions in hand, we move on to explore the substrate scope of the reaction. We were pleased to observe that the dynamic kinetic approach were successful for a variety of *Z*/*E* mixture of *o*-haloaryl hydrazones. First, these conditions were applied smoothly to a series of *Z*/*E* mixture of *o*-bromoaryl *N*-tosylhydrazones derivated from *o*-bromoaryl ketones (**1ab**–**1ag**), and allowed the synthesis of a range of indazoles in good to excellent yields (Scheme 2, **2ab**–**2ag**). The cyclization was insensitive to the electronic nature of the substrate. Various *E*/*Z* mixture of *o*-bromoaryl *N*-tosylhydrazone bearing either electron-donating or electron-withdrawing groups on the aromatic ring all reacted smoothly, affording 1*H*-indazole products in 83-96% yields. Particularly noticeable is the performance of *p*-fluoro-substituted and benzyl-substituted



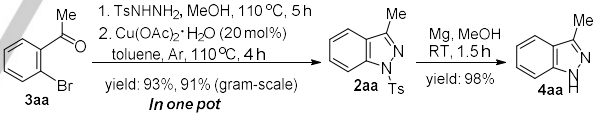
Scheme 2. Survey Substrate Scope.



Scheme 3. Survey Other *N*-Sufonylhydrazones.



Scheme 4. Survey Other Halo-subsituted Hydrazones.



Scheme 5. Synthesis 1*H*-Indazole in One Pot and Detosylation.

substrates (**1ac** and **1af**) in view of no reaction in the previous research.[17] Under these reaction conditions, they underwent a smooth reaction to afford the corresponding 1*H*-indazole products **2ac** (93% yield) and **2af** (89% yield).

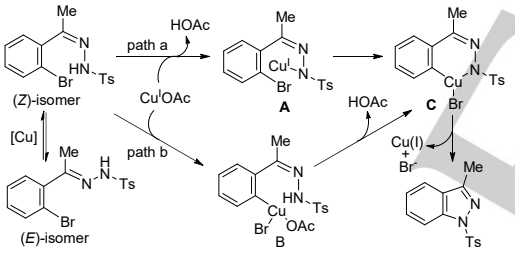
Next, we undertook the challenge of employing *o*-bromoaryl *N*-tosylhydrazone derivated from *o*-bromo arylaldehyde. Generally (*E*)-*o*-bromoaryl *N*-tosylhydrazones were exclusively produced by the condensation of the arylaldehydes with tosylhydrazine, without generation of the (*Z*)-isomer being observed. Due to unfavorable configuration for the dehydrohalogenation cyclization, it is resonable for this kind of hydrazone failing to generate 1*H*-indazole in the previous research.[17] Pleasingly, with the dynamic kinetic strategy these (*E*)-*o*-bromoaryl *N*-tosylhydrazones were found to smoothly react and provided the desired 1*H*-indazols in excellent yields (Scheme 2, **2ah**-**2as**). Several important functional groups such as –F, –Cl, –Br, –Me and –OMe were well tolerated, allowing further functionalization toward the synthesis of structural diversely 1*H*-indazoles. Notably, this transformation was not limited to phenyl hydrazone, other aromatic ring, e.g. naphthyl and pyridyl, could also be compatible to afford the expected 1*H*-indazole products, **2ar** and **2as**, in 92% and 97% yields, respectively. The structures of the products **2aa** and **2as** were confirmed by single-crystal X-ray analysis.

In previous research, the *N*-sulfonyl moiety in the substrates affected the reactivity.[18] So the *N*-sulfonyl moiety was then examined. Delightedly, replacement of the tolyl group with phenyl, 4-fluorophenyl or methyl had almost no effect on the reactivity in this approach. All kinds of *Z*/*E* hydrazones with various substituted groups, derivated from either arylketones or arylaldehydes, underwent efficient cyclizations to form the desired products in excellent yields (Scheme 3). Then, we checked other non-sulfonyl substituted hydrazones. Under the current reaction conditions, *o*-bromoaryl hydrazones bearing benzyl or without any substituents at the terminal nitrogen atom did not react, while *o*-bromoaryl *N*-benzoylhydrazone decomposed gradually and no desired product detected (**2fa**-**2ha**). We also investigated the hydrazones substituted by other halogen at ortho position. The cyclization of the *o*-chloroaryl derivatives and *o*-iodoaryl derivatives proceeded as well as that of the *o*-bromoaryl derivatives and afforded the desired 1*H*-indazoles in 79-97% yield (Scheme 4), including a previous challenge substrate,[18] *o*-chlorobenzaldehyde *N*-tosylhydrazone also to produce the desired **2ah** in 91% yield (ref.[18] 33% yield), while 2-fluoroaryl derivative did not work.

Finally, we investigated the one-pot approach to synthesize the 1*H*-indazole from *o*-bromoacetophenone and tosylhydrazine (Scheme 5). After the reaction of the condensation of *o*-bromoacetophenone and tosylhydrazine was complete, the

solvent was evaporated, then treated with $Cu(OAc)_2 \cdot H_2O$ (20 mol%) in toluene at 110 ºC under Ar atmosphere for 4 h. The one-pot approach afforded the desired 1*H*-indazole in 93% yields. A major benefit of the present protocol is its amenability to gram-scale applications. Under modified conditions (10 mol% of $Cu(OAc)_2 \cdot H_2O$, the scale up of the reaction could be carried out with a reduction of catalyst loading.), *o*-bromoacetophenone (1.98 g) and tosylhydrazine (1.86 g) condensed, then cyclized, giving **2aa** (2.60 g) in 91% yield (Scheme 5). The gram-scale synthesis without notable erosion of yield proved the practicality of this new approach. 1*H*-indazole (**2aa**) could be easily detosylated with magnesium in methanol at room temperature in high yield.

On the basis of the above experimental results and related reports, a plausible mechanism for this reaction was proposed (Scheme 6). The reaction is initiated by a copper-catalyzed isomerization of C=N double bond. Subsequently, two paths are possible. Path a starts with a ligand exchange[19] between substrate and the Cu^I species (resulted from $Cu(OAc)_2 \cdot H_2O$ disproportionation)[20] to give intermediate **A**, which undergoes an intramolecular oxidative addition to produce Cu^{III} intermediate **C**. Other path commences with Cu^I species oxidative addition of the aryl halide generated Cu^{III} intermediate **B**,[21] followed by a ligand exchange to provide the same intermediate **C**. Finally, a reductive elimination of intermediate **C** releases 1*H*-indazole product and regenerate Cu^I catalyst to complete the catalytic cycle.



Scheme 6. Plausible Mechanism.

Conclusions

In summary, the first copper-catalyzed C=N double bond isomerization and cyclization of *o*-haloaryl *N*-sulfonylhydrazones has been developed, which is an important complementary protocol for C=N double bond isomerization of hydrazone compounds. Moreover, it offered an unprecedented catalytic approach for the synthesis of 1*H*-indazoles from readily accessible *Z*/*E* mixture of *o*-haloaryl *N*-sulfonylhydrazone. The synthesis features low-cost reagents, convenient operation and broad substrate scope including hydrazones derivated from both ketone and aldehyde substrates. The copper-catalyzed C=N double bond isomerization can proceed under much mild conditions, which opens a door for hydrazone chemistry, and should have broad application.

Experimental Section

General Information

All reactions were carried out under argon. Unless otherwise noted, all commercial reagents and solvents were used as received without further purification. The progress of the reactions was monitored by TLC with silica gel plates (GF254), and the visualization was carried out under UV light. Melting points (m. p.) were measured on electrothermal digital melting point apparatus and were uncorrected. The ^1H and the ^{13}C NMR spectroscopic data were recorded with a Varian Unity Inova-400 spectrometer or Bruker Ascend 400 (400 MHz) spectrometer (^1H and ^{13}C NMR at 400 and 100 MHz, respectively). Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br. s = broad singlet. Infrared (IR) data were recorded as films on potassium bromide plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-QII mass spectrometer. X-ray crystal structure analyses were measured on Bruker Smart APEXIICCD instrument using Mo-Kα radiation. The structures were solved and refined using the SHELXTL software package. All of the *o*-haloaryl *N*-sulfonylhydrazones **1** was prepared according to General procedure **A** (see Supporting information).

Typical Procedure for Synthesis of 1*H*-Indazoles

A 10 mL round-bottom flask was charged with tosylhydrazone (0.5 mmol) $Cu(OAc)_2 \cdot H_2O$ (0.1 mmol) and toluene (3 mL). Then, the flask was degassed for 50 seconds, and then was filled with argon gas and stirred at 110 °C for 4 h under 1 atm argon. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature and the resulting mixture was filtered through a small pad of aluminum oxide (neutrality) and concentrated in vacuo. The product was separated by aluminum oxide column chromatography (neutrality) (hexanes / EtOAc = 15:1 to 8:1) to afford the corresponding product **2**.

Chemical Characterisation

3-Methyl-1-tosyl-1H-indazole (2aa):[17] 135.9 mg, 95% yield from *N'*-(1-(2-bromophenyl)ethylidene)-4-methylbenzenesulfonohydrazide; 134.5 mg, 94% yield from *N'*-(1-(2-iodophenyl)ethylidene)-4-methylbenzene sulfonohydrazide; 121.6 mg, 85% yield from *N'*-(1-(2-chlorophenyl) ethylidene)-4-methylbenzenesulfonohydrazide; White solid; m. p. = 123 - 124 °C; ^1H NMR (400 MHz, $CDCl_3$): *δ* 8.15 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.51 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.8, 145.1, 141.0, 134.6, 129.7, 129.2, 127.4, 126.2, 123.9, 120.6, 113.3, 21.6, 12.3; IR (KBr): 2991, 2924, 1601 1524, 1367, 1294, 1250, 1122, 810, 752 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{14}N_2O_2SNa$ $[M+Na]^+$: 309.0668; found 309.0664. CCDC 1505832 contains the crystallographic data for **2aa** that can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

6-Fluoro-3-methyl-1-tosyl-1H-indazole (2ab): 138.4 mg, 91% yield; Yellow solid; m. p. = 151 - 152 °C; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.75 (d, *J* = 8.0 Hz, 3H), 7.45 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H),

6.97 (td, *J* = 8.0, 2.0 Hz, 1H), 2.41 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 163.6 (d, J_{C-F} = 247.0 Hz), 150.5, 145.4, 141.7 (d, J_{C-F} = 13.0 Hz), 134.5, 129.9, 127.5, 122.7, 122.0 (d, J_{C-F} = 11.0 Hz), 113.2 (d, J_{C-F} = 25.0 Hz), 100.2 (d, J_{C-F} = 28.0 Hz), 21.7, 12.2; IR (KBr): 2962, 2924, 1674, 1614, 1524, 1489, 1279, 1250, 1173, 862 810 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{13}FN_2O_2SNa$ [M+Na]$^+$: 327.0574; found 327.0565.

5-Fluoro-3-methyl-1-tosyl-1H-indazole (2ac): 141.4 mg, 93% yield from *N′*-(1-(2-bromo-5-fluorophenyl)ethylidene)-4-methylbenzenesulfono hydrazide; 132.3 mg, 87% yield from *N′*-(1-(2-chloro-5-fluorophenyl) ethylidene)-4-methylbenzenesulfonohydrazide; White solid; m. p. = 143 - 144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.12 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.32 - 7.17 (m, 4H), 2.49 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 159.5 (d, J_{C-F} = 242.0 Hz), 150.4, 145.3, 137.8, 134.4, 129.9, 127.5, 126.9 (d, J_{C-F} = 9.0 Hz), 118.1 (d, J_{C-F} = 27.0 Hz), 114.8 (d, J_{C-F} = 9.0 Hz), 105.5 (d, J_{C-F} = 24.0 Hz), 21.7, 12.3; IR (KBr): 3066, 2962, 2926, 1645, 1597, 1529, 1444, 1325, 1267, 1170, 891, 854, 814 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{13}FN_2O_2SNa$ [M+Na]$^+$: 327.0574; found 327.0561.

6-Chloro-3-methyl-1-tosyl-1H-indazole (2ad): 152.4 mg, 95% yield; White solid; m. p. = 183 - 184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.18 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.31-7.22 (m, 3H), 2.50 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.4, 145.5, 141.5, 135.8, 134.5, 129.9, 127.6, 124.9, 124.7, 121.5, 113.4, 21.7, 12.3; IR (KBr): 3091, 2923, 1599, 1520, 1377, 1254, 1174, 1122, 1061, 978, 869, 812, 671, 606, 577 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{13}ClN_2O_2SNa$ [M+Na]$^+$: 343.0278; found 343.0275.

6-Methoxy-3-methyl-1-tosyl-1H-indazole (2ae): 151.9 mg, 96% yield; White solid; m. p. = 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.81 (d, *J* = 8.0 Hz, 2H), 7.58 (s, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.92 – 6.88 (m, 1H), 3.92 (s, 3H), 2.44 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 161.4, 150.7, 145.1, 142.9, 134.8, 129.8, 127.4, 121.3, 120.4, 114.8, 95.6, 55.9, 21.7, 12.3; IR (KBr): 3084, 3001, 2968, 2919, 2839, 1614, 1519, 1495, 1423, 1369, 1288, 1213, 1169, 1120, 1065, 1032, 979, 816, 665, 609, 581, 539 cm^{-1}; HRMS (ESI) m/z calculated for $C_{16}H_{17}N_2O_3S$ [M+H]$^+$: 317.0954; found 317.0951.

3-(2-Methylbenzyl)-1-tosyl-1H-indazole (2af): 167.4 mg, 89% yield; White solid; m. p. = 132 - 133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.15 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.20 - 6.97 (m, 7H), 4.25 (s, 2H), 2.33 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 152.7, 145.1, 141.7, 136.8, 135.1, 134.5, 130.4, 129.7, 129.5, 129.1, 127.4, 127.0, 126.0, 125.7, 124.0, 121.2, 113.5, 32.1, 21.6, 19.6; IR (KBr): 3062, 3020, 2972, 2918, 1655, 1599, 1518, 1385, 1292, 1119, 808, 756 cm^{-1}; HRMS (ESI) m/z calculated for $C_{22}H_{20}N_2O_2SNa$ [M+Na]$^+$: 399.1138; found 399.1129.

3-Phenyl-1-tosyl-1H-indazole (2ag): [17] 144.4 mg, 83% yield from *N′*-((2-bromophenyl)-(phenyl)methylene)-4-methylbenzenesulfonohydrazide; 165.3 mg, 95% yield from *N′*-((2-iodophenyl)(phenyl)methylene)-4-methylbenzenesulfonohydrazide; White solid; m. p. = 104 - 105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.20 (d, *J* = 8.0 Hz, 1H), 7.89 - 7.79 (m, 5H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 3H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 151.8, 145.3, 141.9, 134.6, 131.4, 129.8, 129.6, 129.1, 128.9, 128.3, 127.6, 124.5, 124.3, 121.7, 113.6, 21.7; IR (KBr): 3057, 2924, 1647, 1595, 1487, 1375, 1298, 1257, 1132, 810, 735 cm^{-1}; HRMS (ESI) m/z calculated for $C_{20}H_{16}N_2O_2SNa$ [M+Na]$^+$: 371.0825; found 371.0821.

1-Tosyl-1H-indazole (2ah):[18] 130.6 mg, 96% yield from *N′*-(2-bromobenzylidene)-4-methyl-benzenesulfonohydrazide; 131.9 mg, 97% yield from *N′*-(2-iodobenzylidene)-4-methylbenzenesulfonohydrazide; 123.8 mg, 91% yield from *N′*-(2-chloro-benzylidene)-4-methylbenzene sulfonohydrazide; White solid; m. p. = 97 - 98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.23 - 8.16 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.4, 141.4, 140.2, 134.5, 129.9, 129.3, 127.5, 125.8, 124.2, 121.4, 113.1, 21.6; IR (KBr): 2922, 1649, 1599, 1498, 1371, 1290, 1176, 1126, 806, 737 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{12}N_2O_2SNa$ [M+Na]$^+$: 295.0512; found 295.0508.

4-Fluoro-1-tosyl-1H-indazole (2ai): 134.9 mg, 93% yield; White solid; m p. = 157 - 158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.25 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.51 (td, *J* = 8.2, 5.1 Hz, 1H), 7.30 - 7.24 (m, 2H), 7.03 - 6.94 (m, 1H), 2.37 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 155.4 (J_{C-F} = 253.0 Hz), 145.9, 142.4 (J_{C-F} = 7.0 Hz), 137.2, 134.4, 130.6 (J_{C-F} = 7.0 Hz), 130.0, 127.7, 115.9 (J_{C-F} = 22.0 Hz), 109.3 (J_{C-F} = 5.0 Hz), 109.0 (J_{C-F} = 18.0 Hz), 21.7; IR (KBr): 3120, 2924, 2854, 1629, 1589, 1502, 1464, 1412, 1373, 1294, 1213, 1171, 1113, 1041, 964 872, 808, 775, 675, 579, 540 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{11}FN_2O_2SNa$ [M+Na]$^+$: 313.0417; found 313.0423.

5-Methyl-1-(p-tolylsulfinyl)-1H-indazole (2aj): 133.0 mg, 93% yield; White solid; m. p. = 137 - 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.10 (s, 1H), 8.00 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 2.54 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.3, 141.3, 140.9, 140.2, 134.7, 129.9, 127.5, 126.2, 123.9, 120.9, 112.9, 22.3, 21.7; IR (KBr): 2918, 2854, 1595 1487, 1374, 1311, 1170, 868, 814 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{14}N_2O_2SNa$ [M+Na]$^+$: 309.0668; found 309.0669.

5-Chloro-1-tosyl-1H-indazole (2ak): 144.2 mg, 94% yield; White solid; m. p. = 148 - 149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.15 (d, *J* = 8.9 Hz, 1H), 8.13 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 1.7 Hz, 1H), 7.51 (dd, *J* = 8.9, 1.7 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.8, 140.4, 138.8, 134.3, 130.1, 130.0, 129.8, 127.7, 126.9, 120.7, 114.4, 21.7; IR (KBr): 2924, 2854, 1626, 1593, 1495 1373, 1240, 1169, 1068, 883, 809, 727, 669, 584, 540 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{11}ClN_2O_2SNa$ [M+Na]$^+$: 329.0122; found 329.0116

5-Bromo-1-tosyl-1H-indazole (2al): 162.7 mg, 93% yield from *N′*-(2,5-dibromobenzyli-dene)-4-methylbenzenesulfonohydrazide; 166.2 mg, 95% yield from *N′*-(5-bromo-2-iodobenzylidene)-4-methylbenzenesulfono hydrazide; White solid; m. p. = 144 - 145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.19 - 8.03 (m, 2H), 7.88 - 7.80 (m, 3H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.8, 140.2, 139.1, 134.3, 132.3, 130.0, 127.6, 127.4, 123.9, 117.5, 114.6, 21.7; IR (KBr): 3088, 2922, 2854, 1591, 1493, 1294, 1172, 1130, 899, 812, 592 538 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{11}BrN_2O_2SNa$ [M+Na]$^+$: 372.9617; found 372.9611.

5-Methoxy-1-tosyl-1H-indazole (2am):[18] 143.6 mg, 95% yield; White solid; m. p. = 149 - 150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.18 - 8.02 (m, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.24 - 7.15 (m, 3H), 7.01 (s, 1H), 3.82 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.9, 145.3, 141.2, 135.7, 134.5, 129.8, 127.5, 126.8, 120.3, 114.2, 101.3, 55.7, 21.6; IR (KBr): 3091, 2962, 2919, 1620, 1593, 1510, 1444, 1416, 1371, 1284, 1250, 1176, 1080, 1018, 881, 823, 671, 586, 540 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{14}N_2O_3SNa$ [M+Na]$^+$: 325.0617; found 325.0618.

6-Methyl-1-tosyl-1H-indazole (2an): 128.7 mg, 90% yield from *N'*-(2-bromo-4-methyl-benzylidene)-4-methylbenzenesulfonohydrazide; 117.3 mg, 82% yield from *N'*-(2-chloro-4-methylbenzylidene)-4-methylbenzenesulfonohydrazide; White solid; m. p. = 129 - 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.10 (s, 1H), 8.00 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 2.54 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.3, 141.3, 140.9, 140.1, 134.7, 129.9, 127.5, 126.2, 123.9, 120.8, 112.9, 22.2, 21.7; IR (KBr): 3035, 2920, 2852, 1695, 1595, 1487, 1373, 1311, 870, 816 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{14}N_2O_2SNa$ $[M+Na]^+$: 309.0668; found 309.0669.

6-Fluoro-1-tosyl-1H-indazole (2ao):[18]137.9 mg, 95% yield; White solid; m. p. = 175 - 176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.14 (s, 1H), 7.97 - 7.83 (m, 3H), 7.64 (dd, *J* = 8.7, 5.1 Hz, 1H), 7.30 - 7.24 (m, 2H), 7.09 (td, *J* = 8.8, 2.1 Hz, 1H), 2.37 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 163.5 ($J_{C\text{-}F}$ = 248.0 Hz), 145.8, 141.0, 140.9 ($J_{C\text{-}F}$ = 14.0 Hz), 134.4, 130.0, 127.7, 122.8 ($J_{C\text{-}F}$ = 11.0 Hz), 122.4, 113.8 ($J_{C\text{-}F}$ = 25.0 Hz), 100.1 ($J_{C\text{-}F}$ = 28.0 Hz), 21.7; IR (KBr): 2924, 2852, 1619, 1591, 1481, 1373, 1313, 1242, 1173, 1120, 1070, 943, 856, 673, 582, 539 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{11}FN_2O_2SNa$ $[M+Na]^+$: 313.0417; found 313.0423.

7-Chloro-1-tosyl-1H-indazole (2ap): 144.4 mg, 94% yield; White solid; m. p. = 114 - 115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.23 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.4, 139.8, 137.2, 135.5, 131.4, 129.8, 129.6, 128.3, 125.1, 120.2, 118.8, 21.7; IR (KBr): 3089, 2921, 2854, 1925, 1595, 1502, 1456, 1385, 1335, 1184, 1089, 1041, 953, 819, 673, 569, 538 cm^{-1}; HRMS (ESI) m/z calculated for Chemical Formula: $C_{14}H_{11}ClN_2O_2SNa$ $[M+Na]^+$: 329.0122; found 329.0120.

1-Tosyl-1H-[1,3]dioxolo[4,5-f]indazole (2aq):[18] 145.4 mg, 92% yield; White solid; m. p. = 188 - 189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.97 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.61 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.91 (s, 1H), 6.07 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.7, 146.4, 145.4, 141.0, 137.1, 134.5, 129.9, 127.6, 120.4, 102.3, 98.2, 93.7, 21.7; IR (KBr): 2920, 2856, 1687, 1626, 1595, 1506, 1467, 1377, 1323, 808 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{12}N_2O_4SNa$ $[M+Na]^+$: 339.0410; found 339.0411.

1-Tosyl-1H-benzo[g]indazole (2ar): 148.3 mg, 92% yield; White solid; m. p. = 112 - 113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.42 (d, *J* = 8.6 Hz, 1H), 8.26 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.77 - 7.56 (m, 6H), 7.17 (d, *J* = 8.1 Hz, 2H), 2.31 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.4, 141.5, 138.9, 134.6, 134.4, 129.8, 129.0, 127.9, 127.4, 127.3, 127.1, 125.9, 124.8, 121.8, 118.1, 21.7.; IR (KBr): 3057, 2922, 2852, 1593, 1375, 1311, 1178, 1092, 1012, 866, 809, 675, 579 cm^{-1}; HRMS (ESI) m/z calculated for $C_{18}H_{15}N_2O_2S$ $[M+H]^+$: 323.0849; found 323.0845.

3-Methyl-1-tosyl-1H-pyrazolo[3,4-b]pyridine (2as): 139.2 mg, 97% yield; White solid; m. p. = 168 - 169 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.71 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.97 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.32 - 7.23 (m, 3H), 2.56 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 152.3, 150.5, 147.9, 145.4, 135.1, 130.0, 129.8, 128.0, 119.3, 118.0, 21.7, 12.8; IR (KBr): 3444, 1591, 1442, 1379, 1242, 1176, 1119, 1070, 976, 804, 760, 665, 584, 532 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{13}N_3O_2SNa$ $[M+Na]^+$: 310.0621; found 310.0614. CCDC 1505834 contains the crystallographic data for **2as** that can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

3-Methyl-1-(phenylsulfonyl)-1H-indazole (2ba): [17] 126.5 mg, 93% yield; Yellow solid; m. p. = 134 - 135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.10 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 4.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.49 - 7.43 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 151.0, 141.2, 137.7, 133.9, 129.3, 129.2, 127.5, 126.3, 124.0, 120.7, 113.4, 12.4; IR (KBr): 2958, 1647, 1608, 1524, 1443, 1373, 1292, 1252, 1182, 1124, 974, 756, 721, 681 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{12}N_2O_2SNa$ $[M+Na]^+$: 295.0512; found 295.0507.

3-Phenyl-1-(phenylsulfonyl)-1H-indazole (2bb): 148.7 mg, 89% yield; White solid; m. p. = 186 - 187 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.29 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.92 (t, *J* = 8.0 Hz, 3H), 7.62 - 7.42 (m, 7H), 7.39 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 151.9, 141.9, 137.7, 134.1, 131.4, 129.7, 129.2, 128.9, 128.3, 127.6, 124.6, 124.4, 121.8, 113.6; IR (KBr): 3062, 2924, 2856, 1065, 1520, 1485, 1444, 1369, 1292, 1254, 1170, 1130, 739, 689 cm^{-1}; HRMS (ESI) m/z calculated for $C_{19}H_{14}N_2O_2SNa$ $[M+Na]^+$: 357.0668; found 357.0663.

5-Fluoro-3-methyl-1-(phenylsulfonyl)-1H-indazole (2bc): 137.8 mg, 95% yield; White solid; m. p. = 139 - 140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.12 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.28 (td, *J* = 8.0, 4.0 Hz, 1H), 7.21 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 159.6 (d, $J_{C\text{-}F}$ = 242.0 Hz), 150.6 (d, $J_{C\text{-}F}$ = 5.0 Hz), 137.8, 137.4, 134.2, 129.2, 127.5, 126.9 (d, $J_{C\text{-}F}$ = 9.0 Hz), 118.1 (d, $J_{C\text{-}F}$ = 26.0 Hz), 114.8 (d, $J_{C\text{-}F}$ = 10.0 Hz), 105.6 (d, $J_{C\text{-}F}$ = 24.0 Hz), 12.3; IR (KBr): 3076, 2922, 2854, 1620, 1525, 1323, 1277, 1182, 891, 858, 814, 756, 725, 682 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{11}FN_2O_2SNa$ $[M+Na]^+$: 313.0417; found 313.0412.

1-(Phenylsulfonyl)-1H-indazole (2bd): 118.7 mg, 92% yield; White solid; m. p. = 83 - 84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.25 - 8.16 (m, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.56 (q, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 141.6, 140.3, 137.5, 134.2, 129.4, 129.3, 127.5, 125.9, 124.3, 121.5, 113.1; IR (KBr): 3058, 2852, 1647, 1608, 1579, 1500, 1379, 1311, 1286, 1244, 1182, 1124, 760, 725 cm^{-1}; HRMS (ESI) m/z calculated for $C_{13}H_{10}N_2O_2SNa$ $[M+Na]^+$: 281.0355; found 281.0347.

5-Bromo-1-(phenylsulfonyl)-1H-indazole (2be): 157.9 mg, 94% yield; White solid; m. p. = 93 - 94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.16 - 8.08 (m, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.84 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.4, 139.1, 137.3, 134.5, 132.4, 129.4, 127.6, 127.4, 123.9, 117.6, 114.6; IR (KBr): 2922, 2852, 1657, 1633, 1491, 1379, 1296, 1241, 1172, 903, 874, 810, 727, 702, 592, 555 cm^{-1}; HRMS (ESI) m/z calculated for $C_{13}H_9BrN_2O_2SNa$ $[M+Na]^+$: 358.9460; found 358.9453.

6-Methyl-1-(phenylsulfonyl)-1H-indazole (2bf): 129.2 mg, 95% yield; White solid; m. p. = 105 - 106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.11 (s, 1H), 8.02 - 7.95 (m, 3H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 141.5, 141.0, 140.3, 137.7, 134.1, 129.3, 127.5, 126.3, 123.9, 120.9, 112.9, 22.3; IR (KBr): 3099, 3068, 2922, 2854, 1612, 1485, 1377, 1313, 1180, 895, 810, 756, 725, 682 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{12}N_2O_2SNa$ $[M+Na]^+$: 295.0512; found 295.0507.

1-(Phenylsulfonyl)-1H-[1,3]dioxolo[4,5-g]indazole (2bg): 140.4 mg, 93% yield; White solid; m. p. = 192 - 193 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.05 - 7.90 (m, 3H), 7.63 (s, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 6.93 (s, 1H), 6.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.8, 146.5, 141.3, 137.5, 137.2, 134.2, 129.3, 127.6, 120.5, 102.4,

98.3, 93.8; IR (KBr): 3091, 3062, 2852, 1628, 1581, 1473, 1375, 1325, 1238, 1180, 1157, 839, 808, 760, 727, 685 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{10}N_2O_4SNa$ $[M+Na]^+$: 325.0253; found 325.0250.

1-(4-Fluorophenylsulfonyl)-3-methyl-1H-indazole (2ca): 131.9 mg, 91% yield; Yellow solid; m. p. = 142 - 143 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.0 Hz, 1H), 7.97 (dd, J = 8.0, 4.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 8.0Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.09 (t, J = 8.0 Hz, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8 (d, J_{C-F} = 255.0 Hz), 151.4, 141.1, 133.6 (d, J_{C-F} = 3.0 Hz), 130.4 (d, J_{C-F} = 10.0 Hz), 129.4, 126.3, 124.2, 120.8, 116.5 (d, J_{C-F} = 22.0 Hz), 113.3, 12.4; IR (KBr): 3054, 2960, 1589, 1489, 1319, 1240, 1141, 1139, 1128, 837, 773 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{11}FN_2O_2SNa$ $[M+Na]^+$: 313.0417; found 313.0414.

1-(4-Fluorophenylsulfonyl)-3-phenyl-1H-indazole (2cb): 163.7 mg, 93% yield; White solid; m. p. = 171 - 172 °C; ^1H NMR (400 MHz, $CDCl_3$): 1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.4 Hz, 1H), 8.06 (dd, J = 8.3, 5.0 Hz, 2H), 7.93 – 7.88 (m, 3H), 7.60 (t, J = 7.7 Hz, 1H), 7.56 - 7.44 (m, 3H), 7.40 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9 (J_{C-F} = 255.0 Hz), 152.3, 141.9, 133.6 (J_{C-F} = 2.0 Hz), 131.3, 130.6 (J_{C-F} = 9.0 Hz), 129.8, 129.4, 128.9, 128.3, 124.8, 124.5, 121.9, 116.7 (J_{C-F} = 23.0 Hz), 113.6; IR (KBr): 3363, 3263, 3101, 3060, 1589, 1489, 1373, 1292, 1240, 1184, 1153, 1292, 1240, 1184, 1153, 1063, 1018, 945, 847, 741, 671, 579, 534 cm^{-1}; HRMS (ESI) m/z calculated for $C_{19}H_{13}FN_2O_2SNa$ $[M+Na]^+$: 375.0574; found 375.0573.

5-Fuoro-1-(4-fluorophenylsulfonyl)-3-methyl-1H-indazole (2cc): 144.8 mg, 94% yield; White solid; m. p. = 158 - 159 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, J = 9.1, 4.1 Hz, 1H), 7.93 - 7.85 (m, 2H), 7.22 (td, J = 8.9, 2.2 Hz, 1H), 7.15 (dd, J = 7.8, 2.2 Hz, 1H), 7.04 (t, J = 8.5 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0 (d, J_{C-F} = 255.0 Hz), 159.7 (d, J_{C-F} = 242.0 Hz), 150.9 (d, J_{C-F} = 4.0 Hz), 137.7, 133.4 (d, J_{C-F} = 3.0 Hz), 130.4 (d, J_{C-F} = 9.0 Hz), 127.1 (d, J_{C-F} = 9.0 Hz), 118.3 (d, J_{C-F} = 27.0 Hz), 116.7 (d, J_{C-F} = 23.0 Hz), 114.7 (d, J_{C-F} = 9.0 Hz), 105.7 (d, J_{C-F} = 23.0 Hz), 12.4; IR (KBr): 3070, 1587, 1529, 1485, 1325, 1281, 1232, 1178, 1151, 854, 814 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{10}F_2N_2O_2SNa$ $[M+Na]^+$: 331.0323; found 331.0320.

1-(4-Fluorophenylsulfonyl)-1H-indazole (2cd): 133.9 mg, 97% yield; White solid; m. p. = 149 - 150 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.0 Hz, 2H), 8.01 (dd, J = 8.0, 4.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.12 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0 (d, J_{C-F} = 256.0 Hz), 141.8, 140.3, 133.5 (d, J_{C-F} = 3.0 Hz), 130.5 (d, J_{C-F} = 10.0 Hz), 129.5, 125.9, 124.5, 121.5, 116.7 (d, J_{C-F} = 24.0 Hz), 113.1; IR (KBr): 3103, 3064, 1643, 1589, 1495, 1373, 1292, 1238, 1180, 829, 744 cm^{-1}; HRMS (ESI) m/z calculated for $C_{13}H_9FN_2O_2SNa$ $[M+Na]^+$: 299.0261; found 299.0257.

5-Bromo-1-(4-fluorophenylsulfonyl)-1H-indazole (2ce): 168.1 mg, 95% yield; White solid; m. p. = 131 - 132 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.00 (dd, J = 8.0, 4.0 Hz, 2H), 7.85 (d, J = 4.0 Hz, 1H), 7.65 (dd, J = 8.0, 4.0Hz, 1H), 7.14 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2 (d, J_{C-F} = 256.0 Hz), 140.6, 139.1, 133.2, 132.6, 130.6 (d, J_{C-F} = 10.0 Hz), 127.5, 124.1, 117.8, 116.9(d, J_{C-F} = 23.0 Hz), 114.6; IR (KBr): 3099, 3070, 2852, 1587, 1495, 1383, 1300, 1151, 881, 842, 808, 588, 536 cm^{-1}; HRMS (ESI) m/z calculated for $C_{13}H_8BrFN_2O_2SNa$ $[M+Na]^+$: 376.9366; found 376.9357. CCDC 1505835 contains the crystallographic data for **2ce** that can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

3-Methyl-1-(methylsulfonyl)-1H-indazole (2da):[18] 89.3 mg, 85% yield; White solid; m. p. = 72 - 73 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 3.18 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 141.1, 129.4, 125.9, 124.1, 120.7, 113.3, 40.6, 12.4; IR (KBr): 3060, 3005, 2958, 2924, 1724, 1610, 1527, 1444, 1363, 1334, 1170, 1120, 756 cm^{-1}; HRMS (ESI) m/z calculated for $C_9H_{10}N_2O_2SNa$ $[M+Na]^+$: 233.0355; found 233.0354.

1-(Methylsulfonyl)-3-phenyl-1H-indazole (2db): 129.3 mg, 95% yield; White solid; m. p. = 126 - 127 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.5 Hz, 1H), 8.03 - 7.94 (m, 3H), 7.63 - 7.48 (m, 4H), 7.42 (t, J = 7.6 Hz, 1H), 3.29 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 141.7, 131.2, 129.7, 129.3, 128.9, 128.2, 124.6, 123.9, 121.8, 113.4, 40.9.; IR (KBr): 3020, 2925, 1604, 1519, 1489, 1410, 1354, 1261, 1174, 1130, 1074, 958 849, 748, 698, 665, 567, 530 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{12}N_2O_2SNa$ $[M+Na]^+$: 295.0512; found 295.0513.

1-(Methylsulfonyl)-1H-indazole (2dd):[18] 89.2 mg, 91% yield; Colorless gum; ^1H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 140.2, 129.5, 125.6, 124.4, 121.5, 113.0, 40.9; IR (KBr): 3020, 2931, 1610, 1502, 1417, 1369, 1321, 1173, 1128, 1072, 756 cm^{-1}; HRMS (ESI) m/z calculated for $C_8H_8N_2O_2SNa$ $[M+Na]^+$: 219.0199; found 219.0197.

3-(4-Chlorophenyl)-1-tosyl-1H-indazole (2ea): 170.4 mg, 89% yield; White solid; m. p. = 116 - 117 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 8.5 Hz, 1H), 7.92 - 7.83 (m, 5H), 7.64 - 7.55 (m, 1H), 7.51 - 7.44 (m, 2H), 7.38 (t, J = 7.3 Hz, 1H), 7.29 - 7.21 (m, 2H), 2.35 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 145.5, 141.9, 135.7, 134.6, 130.0, 129.9, 129.5, 129.3, 129.2, 127.7, 124.7, 124.1, 121.4, 113.7, 21.7; IR (KBr): 3059, 2922, 2854, 1590, 1481, 1377, 1261, 1173, 1076, 947, 827, 748, 687, 659, 586, 538 cm^{-1}; HRMS (ESI) m/z calculated for $C_{20}H_{15}ClN_2O_2SNa$ $[M+Na]^+$: 405.0435; found 405.0434.

6-Bromo-1-tosyl-1H-indazole (2eb): 138.7 mg, 79% yield; White solid; m. p. = 217 - 218 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.14 (s, 1H), 7.89 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 8.5 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 140.9, 140.9, 134.4, 130.1, 127.9, 127.8, 124.6, 124.0, 122.4, 116.3, 21.8; IR (KBr): 2927, 2856, 1655, 1603, 1443, 1379, 1308, 1173, 1084, 906, 802, 712, 665, 598, 573, 542 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{11}BrN_2O_2SNa$ $[M+Na]^+$: 372.9617; found 372.9603.

3-Methyl-1H-indazole (4aa):[22] 25.9 mg, 98% yield; White solid; m. p. = 115 - 116 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 11.04 (br. s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 141.2, 126.7, 122.7, 120.3, 120.2, 109.9, 12.1; IR (KBr): 3429, 3178, 2918, 1620, 1500, 1441, 1383, 1338, 1248, 1130, 1078, 744 cm^{-1}; HRMS (ESI) m/z calculated for $C_8H_9N_2$ $[M+H]^+$: 133.0760; found 133.0759..

(E)-N'-(1-(2-Bromophenyl)ethylidene)-4-methylbenzenesulfono hydrazide ((E)-1aa):[14b] 59% yield; White solid; m. p. = 152 - 153 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.43 - 8.32 (br, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.26 (s, J = 8.0 Hz, 1H), 7.21 - 7.12 (m, 2H), 2.43 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 144.2, 140.2, 135.4, 132.9, 130.3, 130.1, 129.7, 128.1, 127.4, 121.3, 21.7, 17.9; IR (KBr): 3207, 1595, 1394, 1340, 1167, 1061, 918, 816, 756, 677, 617, 550 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{15}BrN_2O_2SNa$ $[M+Na]^+$: 388.9930; found 388.9918.

(Z)-N'-(1-(2-Bromophenyl)ethylidene)-4-methylbenzenesulfono hydrazide ((Z)-1aa): [14b] 41% yield; White solid; m. p. = 152 - 153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.79 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.33 - 7.25 (m, 3H), 7.16 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 153.5, 144.0, 135.3, 135.1, 133.5, 131.3, 129.5, 128.7, 128.2, 128.0, 119.5, 24.1, 21.7; IR (KBr): 3199, 1591, 1390, 1346, 1294, 1165, 1066, 899, 816, 752, 665, 594, 546 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{15}BrN_2O_2SNa$ $[M+Na]^+$: 388.9930; found 388.9924.

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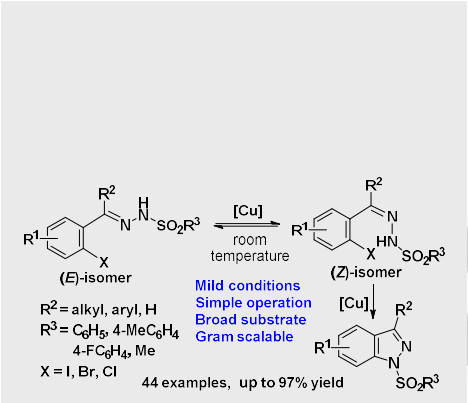

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Copper-Catalyzed Isomerization and Cyclization of *E*/*Z*-*o*-Haloaryl *N*-Sulfonylhydrazones: Convenient Access to of 1*H*-Indazoles

Copper-Catalyzed 1*H*-Indazoles synthesis: The first copper-catalyzed C=N double bond isomerization of hydrazones has been developed, followed by an efficient intramolecular C-N coupling reaction, which offered an unprecedented catalytic approach for the synthesis of 1*H*-indazoles from readily accessible *Z*/*E* mixture of *o*-haloaryl *N*-sulfonylhydrazones.