Ligand-Free Copper(I) Oxide Nanoparticle Catalyzed Three-Component Synthesis of 2*H*-Indazole Derivatives from 2-Halobenzaldehydes, Amines and Sodium Azide in Polyethylene Glycol as a Green Solvent

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Abstract: An efficient synthesis of 2*H*-indazole derivatives based on the one-pot three-component reaction of 2-chloro- and 2-bromobenzaldehydes, primary amines and sodium azide is described. The reaction is catalyzed by copper(I) oxide nanoparticles (Cu_2O-NP) under ligand-free conditions in polyethylene glycol (PEG 300) as a green solvent.

Key words: Cu_2O nanoparticle, 2*H*-indazole derivatives, ligand-free, three-component, green solvent

Indazole derivatives represent a class of pharmacologically important compounds exhibiting a broad range of biological activities including HIV protease inhibition,[1] anti-inflammatory,[2] antitumor,[3] antimicrobial,[4] antiplatelet[5] and anticancer activities.[6]

In addition to the use of these heterocyclic compounds as electronically active materials,[7] they have been also reported to have agricultural applications.[8] Considering their wide range of applications, indazoles have become the center of attention in many research studies.

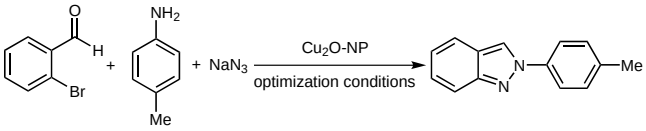
Due to difficulties in the synthesis of 2*H*-indazoles compared to that of 1*H*-indazoles, their preparation has been much less studied. In this regard, most existing protocols give mixtures of 1*H*- and 2*H*-indazoles and therefore their selective synthesis remains a challenging subject.[9]

Several modifications for preparing indazole derivatives have been reported.[10] However, all of these procedures have drawbacks such as the requirement for expensive ligands, requiring several steps to prepare the starting materials and long reaction times. Therefore the need for direct, and effective, multicomponent, selective procedures for the synthesis of 2*H*-indazoles using readily available starting materials still exists.

Recently, Cu_2O catalysts have shown wide applicability for conversions such as cross-couplings of aryl halides and heteroaryl halides with terminal alkynes,[11] C–S cross-coupling,[12] tandem ring-opening/coupling cyclization processes for the synthesis of 2,3-dihydro-1,4-benzodioxins,[13] Ullmann-type reaction of vinyl bromides with imidazole and benzimidazole,[14] synthesis of benzimidazole derivatives from amidine hydrochlorides and *o*-haloaniline[15] and synthesis of triazoles.[16] Furthermore it has been reported that Cu_2O can be used in ligand-free cross-coupling procedures.[17] Owing to the low cost of Cu_2O and its low sensitivity to light and air it is interesting to investigate its efficiency as a copper source in different organic reactions.[14]

In continuation of our previous studies,[18] we herein report an efficient route to the synthesis of 2*H*-indazole derivatives by the reaction of 2-halobenzaldehydes, primary amines and NaN_3 using stable and cheap Cu_2O-NP under ligand-free conditions. The reactions are performed in polyethylene glycols (PEG) as cheap and commercially available solvents, which have been widely used as substitutes for volatile organic solvents.[19]

To optimize the catalyst and conditions for the synthesis of 2*H*-indazole derivatives, the reaction of 2-bromobenzaldehyde (1.0 mmol), *p*-toluidine (1.1 mmol) and NaN_3 (2.0 mmol) was chosen as a model (Scheme 1) under a variety of conditions (Table 1).



Scheme 1 Model reaction for one-pot synthesis of 2-*p*-tolyl-2*H*-indazole using 2-bromobenzaldehyde, *p*-toluidine and NaN_3 in the presence of Cu_2O-NP in PEG

As expected, no product was obtained in the absence of catalyst even after 12 hours (Table1, entry 1); so, we employed Cu_2O-NP as catalyst. These observations show that the catalyst plays an important role in the preparation of 2*H*-indazole derivatives. Using the catalyst at 2 mol%, 5 mol% and 10 mol% concentrations gave 53%, 82% and 82% yields, respectively at 120 °C in PEG (Table 1, entries 2–4). We therefore chose 5 mol% of Cu_2O-NP as the optimal amount of the catalyst.

We then examined the effect of varying solvent and discovered that the use of dipolar aprotic solvents, such as DMF and DMSO, in the presence of catalyst led to the formation of the product in moderate yield, but that PEG was the best choice (Table 1, entries 3, 5 and 6). No reaction was observed in nonpolar solvents, such as toluene (Table 1, entry 7). Finally, we studied the catalytic efficiency of Cu_2O-NP for the synthesis of 2*H*-indazole derivatives at

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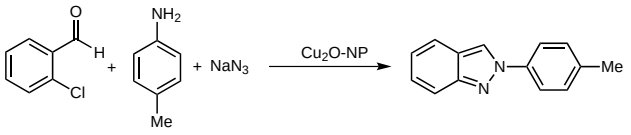
various temperatures, and 120 °C was selected as the optimal temperature for this reaction. Therefore, the most suitable reaction conditions for the synthesis of 2*H*-indazole derivatives were obtained at 120 °C in PEG in the presence of Cu_2O-NP (5 mol%) as catalyst (Table 1, entry 3).

Table 1 Effect of Different Solvents and the Amount of Catalyst on the Preparation of 2-*p*-Tolyl-2*H*-indazole under a Variety of Reaction Conditions at 120 °C

Entry	Catalyst	Solvent	Time (h)	Yield (%)[a]
1	–	PEG	12	–
2	2 mol%	PEG	6	53
3	5 mol%	PEG	6	82
4	10 mol%	PEG	6	82
5	5 mol%	DMF	8	55
6	5 mol%	DMSO	8	63
7	5 mol%	toluene	12	–
8	5 mol%	H_2O[b]	12	–
9	5 mol%	EtOH[b]	12	–

[a] Isolated yield.
[b] The reaction was carried out under reflux.

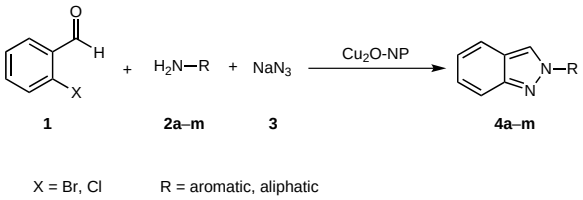
However, when we applied these conditions using 2-chlorobenzaldehyde (1.0 mmol), *p*-toluidine (1.1 mmol) and NaN_3 (2.0 mmol) as starting materials, the reaction failed. However, during these studies, we observed that Cu_2O-NP could catalyze the conversion at 170 °C (Scheme 2); the reaction was complete within six hours with 2-*p*-tolyl-2*H*-indazole being obtained in good yield (80%). From an economic point of view, 2-chlorobenzaldehyde is preferable to 2-bromobenzaldehyde as starting material.



Scheme 2 Synthesis of 2-*p*-tolyl-2*H*-indazole using 2-chlorobenzaldehyde, *p*-toluidine and NaN_3

In the next step, using the optimized conditions, 2-bromobenzaldehyde and 2-chlorobenzaldehyde were tested in one-pot reactions with a variety of substituted amines and NaN_3 in the presence of Cu_2O-NP in PEG to give the corresponding 2*H*-indazole derivatives in good yields (Scheme 3).

As shown, various anilines with substituents such as Me, Et, OMe, OEt, $N(Me)_2$ and Cl were treated with 2-bromobenzaldehyde and NaN_3 under the optimized reaction conditions. The yield of the 2*H*-indazole derivatives are shown in Table 2. In addition, aliphatic amines such as



Scheme 3 Synthesis of 2*H*-indazole derivatives using 2-halobenzaldehydes (1.0 mmol), amines (1.1 mmol) and NaN_3 (2.0 mmol) in the presence of Cu_2O-NP (5.0 mol%) under ligand-free conditions in PEG

tert-butylamine gave the corresponding 2*H*-indazoles in good yield under similar reaction conditions (Table 2, entry 9). The present procedure was also examined for 2-chlorobenzaldehyde with different amines and NaN_3, and the desired 2*H*-indazole derivatives were obtained at 170 °C (Table 3). Similar to the reactions of 2-bromobenzaldehyde, the use of 2-chlorobenzaldehyde produced the desired products with good yields. The 2*H*-indazole derivatives were characterized by their melting points, IR, ^1H NMR, ^{13}C NMR spectroscopic, mass spectrometric and elemental analysis data.

Table 2 One-Pot Synthesis of 2*H*-Indazole Derivatives Using 2-Bromobenzaldehyde, Amines and NaN_3 in the Presence of Cu_2O-NP in PEG at 120 °C

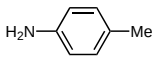
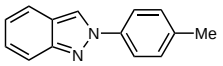
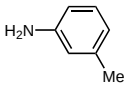
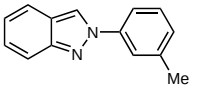
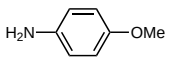
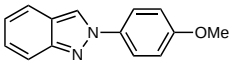
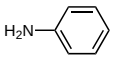
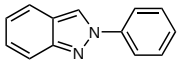
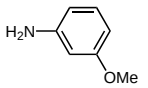
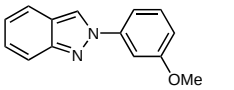
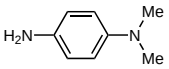
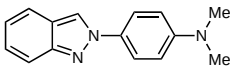
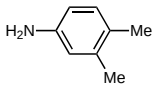
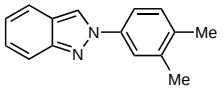
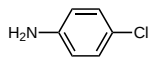
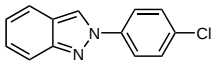
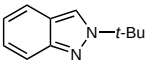
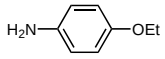
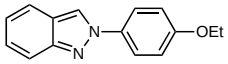
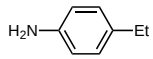
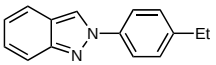
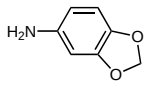
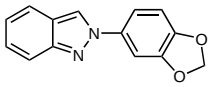
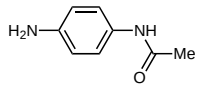
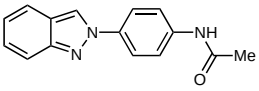
Entry	Amine	Product	Yield (%)[a]
1	 **2a**	 **4a**	82
2	 **2b**	 **4b**	83
3	 **2c**	 **4c**	88
4	 **2d**	 **4d**	90
5	 **2e**	 **4e**	85
6	 **2f**	 **4f**	90
7	 **2g**	 **4g**	91

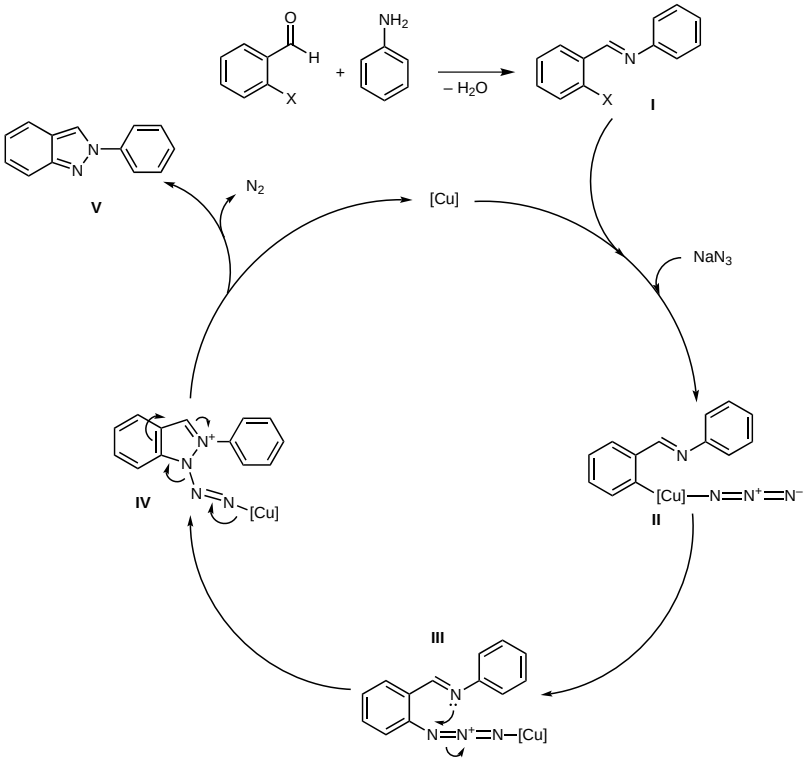
Table 2 One-Pot Synthesis of 2*H*-Indazole Derivatives Using 2-Bromobenzaldehyde, Amines and NaN_3 in the Presence of Cu_2O-NP in PEG at 120 °C (continued)

Entry	Amine	Product	Yield (%)[a]
8			78
	2h	**4h**	
9			79
	2i	**4i**	
10			85
	2j	**4j**	
11			83
	2k	**4k**	
12			87
	2l	**4l**	
13			83
	2m	**4m**	

[a] Isolated yield.

We propose a mechanism, for the formation of the 2*H*-indazole derivatives using 2-halobenzaldehydes, amines and NaN_3 in the presence of Cu_2O-NP (Scheme 4). This mechanism is analogous to the established mechanisms reported in the literature,[10a,c] although Cu_2O-NP in PEG appears to exhibit better activity for the one-pot three-component synthesis of 2*H*-indazole derivatives. In the presence of Cu_2O-NP, 2-halobenzaldehyde reacts with aniline to give imine **I** by elimination of H_2O. We believe that the catalyst helps to form imine **I** in this reaction. Then addition of NaN_3 to imine **I** forms the intermediate **II** followed by generation of intermediate **III**. Cyclization of the intermediate **III** gives the intermediate **IV**, which subsequently forms product **V** by elimination of N_2.

In conclusion, a facile and efficient Cu_2O nanoparticle catalyzed protocol for the synthesis of 2*H*-indazole derivatives from 2-halobenzaldehydes, primary amines and NaN_3 as a nitrogen source in the absence of any supplementary ligand in polyethylene glycol (PEG 300) as a green solvent, has been developed.[20] This procedure allows the use of a wide range of amines and 2-halobenzaldehydes to assemble various 2*H*-indazole derivatives in moderate to good yields. The methodology has the advantages of using commercially available reagents. It occurs under ligand-free reaction conditions in short reaction time and, in addition, does not require the purification of intermediates. The methodology is applicable to 2-bromobenzaldehyde and 2-chlorobenzaldehyde and a wide variety of amines.



Scheme 4 A plausible mechanism for the synthesis of 2*H*-indazole derivatives

Table 3 One-Pot Synthesis of 2*H*-Indazole Derivatives Using 2-Chlorobenzaldehyde, Amines and NaN_3 in the Presence of Cu_2O-NP in PEG at 170 °C

Entry	Amine	Product	Yield (%)[a]
1	**2a**	**4a**	79
2	**2b**	**4b**	80
3	**2c**	**4c**	85
4	**2d**	**4d**	87
5	**2e**	**4e**	83
6	**2f**	**4f**	89
7	**2g**	**4g**	88
8	**2h**	**4h**	67
9	**2i**	**4i**	74
10	**2j**	**4j**	82
11	**2k**	**4k**	80
12	**2l**	**4l**	84
13	**2m**	**4m**	81

[a] Isolated yield.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

References and Notes

(1) Han, W.; Pelletier, J. C.; Hodge, C. N. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 3615.
(2) Picciola, G.; Ravenna, F.; Carenini, G.; Gentili, P.; Riva, M. *Farmaco Ed. Sci.* **1981**, *36*, 1037.
(3) (a) Qian, S.; Cao, J.; Yan, Y.; Sun, M.; Zhu, H.; Hu, Y.; He, Q.; Yang, B. *Mol. Cell. Biochem.* **2010**, *345*, 13. (b) Baraldi, P. G.; Balboni, G.; Pavani, M. G.; Spalluto, G.; Tabrizi, M. A.; De Clercq, E.; Balzarini, J.; Bando, T.; Sugiyama, H.; Romagnoli, R. *J. Med. Chem.* **2001**, *44*, 2536.
(4) (a) Cerecetto, H.; Gerpe, A.; Gonzalez, M.; Aran, V. J.; Ochoa de Ocariz, C. *Mini-Rev. Med. Chem.* **2005**, *5*, 869. (b) De Angelis, M.; Stossi, F.; Carlson, K.; Katzenellenbogen, B.; Katzenellenbogen, J. *J. Med. Chem.* **2005**, *48*, 1132. (c) Li, X.; Chu, S.; Feher, V. A.; Khalili, M.; Nie, Z.; Margosiak, S.; Nikulin, V.; Levin, J.; Sparankle, K. G.; Fedder, M. E.; Almassy, R.; Appelt, K.; Yager, K. M. *J. Med. Chem.* **2003**, *46*, 5663.
(5) Lee, F. Y.; Lien, J. C.; Huang, L. J.; Huang, T. M.; Tsai, S. C.; Teng, C. M.; Wu, C. C.; Cheng, F. C.; Kuo, S. C. *J. Med. Chem.* **2001**, *44*, 3746.
(6) (a) Chen, C. J.; Hsu, M. H.; Huang, L. J.; Yamori, T.; Chung, F. G.; Lee, F. Y.; Teng, C. M.; Kuo, S. C. *Biochem. Pharm.* **2008**, *75*, 360. (b) Yakaiah, T.; Lingaiah, B. P. V.; Narsaiah, B.; Shireesha, B.; Kumar, B. A.; Gururaj, S.; Parthasarathy, T.; Sridhar, B. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 3445.
(7) Cekaviciute, M.; Simokaitiene, J.; Grazulevicius, J. V.; Buika, G.; Jankauskas, V. *Dyes Pigments* **2011**, *92*, 654.
(8) (a) Mills, A. D.; Maloney, P.; Hassanein, E.; Haddadin, M. J.; Kurth, M. J. *J. Comb. Chem.* **2007**, *9*, 171. (b) Grimmet, M. R.; Barton, S. D.; Ollis, W. D. *Comprehensive Organic Chemistry*; Pergamon Press: New York, **1997**, Vol. 4 357. (c) Stadlbauer, W. *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations*; Vol. 12; Neier, R., Ed.; Thieme: Stuttgart, **2002**, 227. (d) Huang, L. J.; Shih, M. L.; Chen, H. S.; Pan, S. L.; Teng, C. M.; Lee, F. Y.; Kuo, S. C. *Bioorg. Med. Chem.* **2006**, *14*, 528.
(9) (a) Wu, C.; Fang, Y.; Larock, R. C.; Shi, F. *Org. Lett.* **2010**, *12*, 2234. (b) Lam, P. Y. S.; Clark, C. G.; Saubern, S.; Adams, J.; Winters, M. P.; Chan, D. M. T.; Combs, A. *Tetrahedron Lett.* **1998**, *39*, 2941. (c) Lopez-Alvarado, P.; Avendano, C.; Menendez, J. C. *J. Org. Chem.* **1995**, *60*, 5678. (d) Fedorov, A. Y.; Finet, J.-P. *Tetrahedron Lett.* **1999**, *40*, 2747. (e) Claramunt, R. M.; Elguero, J.; Garceran, R. *Heterocycles* **1985**, *23*, 2895. (f) Slade, D. J.; Pelz, N. F.; Bodnar, W.; Lampe, J. W.; Watson, P. S. *J. Org. Chem.* **2009**, *74*, 6331.
(10) (a) Kumar, M. R.; Park, A.; Park, N.; Lee, S. *Org. Lett.* **2011**, *13*, 3542. (b) Halland, N.; Nazare, M.; Rkyek, O.; Alonso, J.; Urmann, M.; Lindenschmidt, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 6879. (c) Stokes, B. J.; Vogel, C. V.; Urnezis, L. K.; Pan, M.; Driver, T. G. *Org. Lett.* **2010**, *12*, 2884. (d) Haag, B.; Peng, Z.; Knochel, P. *Org. Lett.* **2009**, *11*, 4270. (e) Lee, K. Y.; Gowrisankar, S.; Kim, J. N. *Tetrahedron Lett.* **2005**, *46*, 5387. (f) Song, J. J.; Yee, N. K. *Org. Lett.* **2000**, *2*, 519. (g) Prasad, A. N.; Srinivas, R.; Reddy, B. M. *Catal. Sci. Technol.* **2013**, *3*, 654.
(11) Tang, B. X.; Wang, F.; Li, J. H.; Xie, Y. X.; Zhang, M. B. *J. Org. Chem.* **2007**, *72*, 6294.
(12) Xu, H. J.; Zhao, X. Y.; Deng, J.; Fu, Y.; Feng, Y. S. *Tetrahedron Lett.* **2009**, *50*, 434.
(13) Bao, W.; Liu, Y.; Lv, X.; Qian, W. *Org. Lett.* **2008**, *10*, 3899.
(14) Shen, G.; Lv, X.; Qian, W.; Bao, W. *Tetrahedron Lett.* **2008**, *49*, 4556.
(15) Qu, Y.; Pan, L.; Wu, Z.; Zhou, X. *Tetrahedron* **2013**, *69*, 1717.
(16) Wang, J. H.; Pan, C. W.; Li, Y. T.; Meng, F. F.; Zhou, H. G.; Yang, C.; Zhang, Q.; Bai, C. G.; Chen, Y. *Tetrahedron Lett.* **2013**, *54*, 3406.
(17) Correa, A.; Bolm, C. *Adv. Synth. Catal.* **2007**, *349*, 2673.
(18) (a) Sharghi, H.; Aberi, M.; Doroodmand, M. M. *Adv. Synth. Catal.* **2008**, *350*, 2380. (b) Sharghi, H.; Beyzavi, M. H.; Doroodmand, M. M. *Eur. J. Org. Chem.* **2008**, 4126. (c) Sharghi, H.; Aberi, M.; Doroodmand, M. M. *J. Iran Chem. Soc.* **2012**, *9*, 189. (d) Sharghi, H.; Beyzavi, M. H.; Safavi, A.; Doroodmand, M. M.; Khalifeh, R. *Adv. Synth. Catal.* **2009**, *351*, 2391. (e) Sharghi, H.; Khalifeh, R.; Doroodmand, M. M. *Adv. Synth. Catal.* **2009**, *351*, 207. (f) Sharghi, H.; Khalifeh, R.; Mansouri, S. G.; Aberi, M.; Eskandari, M. M. *Catal Lett.* **2011**, *141*, 1845. (g) Sharghi, H.; Khoshnood, A.; Doroodmand, M. M.; Khalifeh, R. *J. Iran. Chem. Soc.* **2012**, *9*, 231. (h) Sharghi, H.; Ebrahimpourmoghaddam, S.; Doroodmand, M. M. *J. Organomet. Chem.* **2013**, *738*, 41. (i) Sharghi, H.; Ebrahimpourmoghaddam, S.; Doroodmand, M. M. *Tetrahedron* **2013**, *69*, 4708. (j) Khalifeh, R.; Sharghi, H.; Rashidi, Z. *Heteroat. Chem.* **2013**, *24*, 372.
(19) Colacino, E.; Villebrun, L.; Martinez, J.; Lamaty, F. *Tetrahedron* **2010**, *66*, 3730.
(20) **General Procedure**: To a mixture of 2-bromobenzaldehyde (1.0 mmol) or 2-chlorobenzaldehyde (1.0 mmol), amine (1.1

mmol) and NaN_3 (2.0 mmol) in polyethylene glycol (PEG 300; 3.0 mL) was added the Cu_2O-NP catalyst (5 mol%) and the mixture was stirred at 120 °C for 2-bromobenzaldehyde or at 170 °C for 2-chlorobenzaldehyde. The progress of the reaction was monitored by TLC using *n*-hexane–EtOAc (10:1). After completion of the reaction, the reaction mixture was cooled to r.t., the mixture was poured into EtOAc (30.0 mL) and washed with deionized H_2O (3 × 20.0 mL) and brine (3 × 20.0 mL). The organic layer was dried ($CaCl_2$), filtered and evaporated in vacuo to give the crude product, which was purified by silica gel column chromatography employing *n*-hexane–EtOAc (10:1) as eluent.

Typical Characterization Data for Some Compounds:

2-*p*-Tolyl-2*H*-indazole (4a): pale yellow solid; mp 98–100 °C. IR (KBr): 748, 786, 817, 1041, 1118, 1195, 1380, 1450, 1519, 1620, 2947, 3039, 3129 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 7.08–7.14 (m, 1 H), 7.30–7.35 (m, 3 H), 7.71 (d, *J* = 8.5 Hz, 1 H), 7.77–7.82 (m, 3 H), 8.37 (d, *J* = 0.7 Hz, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.0, 117.8, 120.3, 120.4, 120.8, 122.3, 122.7, 126.7, 130.1, 137.9, 138.2, 149.6. MS: *m*/*z* (%) = 210 (9.0) [M^+ + 2], 209 (89.6) [M^+ + 1], 208 (100.0) [M^+], 165 (51.4), 91 (61.1), 65 (68.1). Anal. Calcd for $C_{14}H_{12}N_2$ (208.262): C, 80.74; H, 5.81; N, 13.45. Found: C, 80.70; H, 5.87; N, 13.51.

4-(2*H*-Indazol-2-yl)-*N*,*N*-dimethylaniline (4f): orange solid; mp 185–187 °C. IR (KBr): 732, 779, 817, 941, 1049, 1141, 1195, 1226, 1350, 1434, 1519, 1596, 2923, 3055 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 3.02 (s, 6 H), 6.80 (d, *J* = 9.0 Hz, 2 H), 7.07–7.13 (m, 1 H), 7.27–7.33 (m, 1 H), 7.68–7.75 (m, 3 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 8.29 (s, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 40.5, 111.7, 112.4, 117.6, 119.9, 120.2, 121.9, 122.1, 122.6, 124.0, 126.1, 130.4, 149.3, 150.1. MS: *m*/*z* (%) = 239 (13.7) [M^+ + 2], 238 (73.4) [M^+ + 1], 237 (100.0) [M^+], 208 (47.5), 165 (32.0), 118 (21.3), 69 (38.2). Anal. Calcd for $C_{15}H_{15}N_2$ (237.304): C, 75.92; H, 6.37; N, 17.71. Found: C, 75.97; H, 6.48; N, 17.82.

2-(4-Chlorophenyl)-2*H*-indazole (4h): white solid; mp 139–141 °C. IR (KBr): 748, 817, 948, 1002, 1087, 1195, 1380, 1419, 1488, 15.21, 1627, 3062, 3132 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.09–7.15 (m, 1 H), 7.30–7.36 (m, 1 H), 7.47–7.50 (m, 2 H), 7.69 (d, *J* = 8.5 Hz, 1 H), 7.78 (d, *J* = 8.7 Hz, 1 H), 7.83–7.86 (m, 2 H), 8.36 (s, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 117.9, 120.2, 120.4, 121.9, 122.7, 122.9, 127.1, 129.6, 133.5, 138.9, 149.9. MS: *m*/*z* (%) = 230 (35.1) [M^+ + 2], 229 (79.8) [M^+ + 1], 228 (100.0) [M^+], 193 (57.4), 166 (77.7), 139 (24.5), 111 (51.1), 75 (60.6). Anal. Calcd for $C_{13}H_9ClN_2$ (228.681): C, 68.28; H, 3.97; N, 12.25. Found: C, 68.22; H, 4.07; N, 12.32.