A VERSATILE SYNTHESIS OF SUBSTITUTED INDAZOLES

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Abstract - A four-step synthetic sequence for substituted indazoles was presented from 2-acylcyclohexane-1,3-diones *via* either simultaneous or stepwise dehydration and dehydrogenation of 4-substituted 4-hydroxy-4,5,6,7-tetrahydroindazoles as a key step.

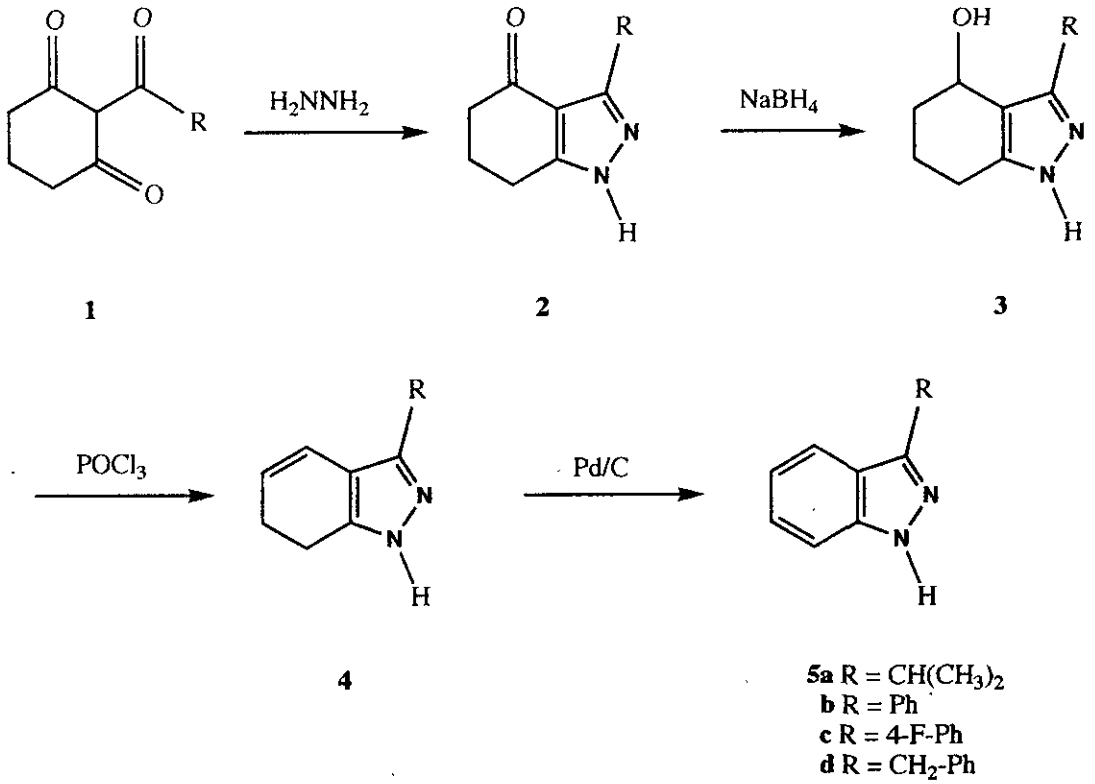
The synthetic methods for indazole nucleus are somewhat limited to involve condensation of hydrazino group,[1] generated by *in situ* reduction of diazo group in *o*-diazophenyl ketones, with C=O of the substituent at the neighboring position, and dehydrogenation of 4,5,6,7-tetrahydroindazoles.[2] The former method, however, is suffering from low yields, limitations of employable diazophenyl ketones,[3] explosive intermediates,[4] and the latter method is also suffering from extreme reaction conditions[5] as well as low yields.[2] Other methods have been reported, but so far not so effective to overcome the limitations of introducing substituent on indazole skeletons, especially at C_3 and/or C_4.[6] In the present paper, we describe a facile and efficient route for the preparation of indazoles, in which substituents can be easily introduced at C_3 and/or C_4.

RESULTS AND DISCUSSION

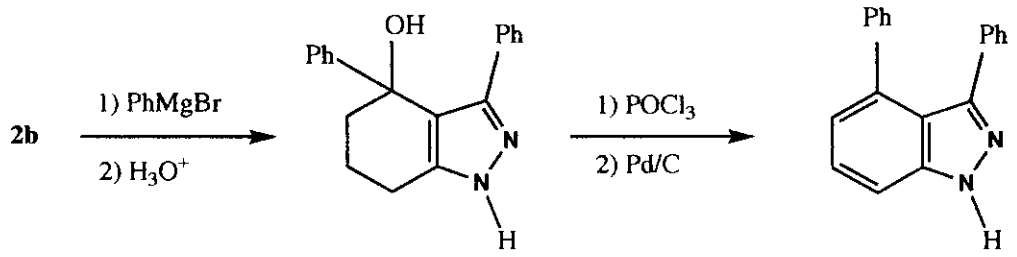
Our strategy stems from the idea that the introduction of a proper leaving group on the tetrahydroindazole system may affect the dehydrogenation step. Upon this rationale, 4-hydroxy-4,5,6,7-tetrahydroindazoles were selected as key intermediates, which may readily undergo either stepwise or simultaneous dehydration and dehydrogenation. The synthetic sequence is, thus, quite straightforward as shown in Scheme I. The prerequisite 2-acylcyclohexane-1,3-diones (1) were prepared by previously reported methods either direct acylation[7] of cyclohexane-1,3-dione or *via* Fries rearrangement[8] of 3-acyloxy-2-cyclohexenones[9] in 88-92% yields. The latter procedure gave better yields, as reported.[8] It is worthy to note that ^{13}C nmr spectral data provided information for the enol-keto tautomerism on 2-acylcyclohexane-1,3-diones. The presence of one sp^2 carbon resonance (δ 112.0) and three carbonyl resonances at δ 194.9, 199.0, and 210.3 implies that keto form is the major component in compound (**1a**) on the ^{13}C nmr scale. In the system with aromatic ring, compound (**1b**), however, four additional sp^2 carbon resonances appeared at δ 127.5, 128.1, 131.9, 134.2 with disappearance of the two sp^3 carbon resonances at δ 32.1, and 37.9, representing C_4 and C_6, respectively, and one carbonyl resonance was shown at δ 198.7. This impies that enol form is the major component in compound (**1b**). On

the other hand, ^{13}C nmr spectrum of compound (**1c**) showed a pair of resonances for each carbon indicates the presence of two tautomers, which implies the keto and enol forms are at equilibrium in compound (**1c**). The direction of equilibrium, thus, is dependent on the substituent presumably due to the electronic effect of the substituents. The reaction of 2-acylcyclohexane-1,3-diones with hydrazine afforded 82-88% yields of 4-oxo-4,5,6,7-tetrahydroindazoles (**2**), which can be readily reduced by $NaBH_4$ to provide 4-hydroxy-4,5,6,7-tetrahydroindazoles (**3**) over 90% yields. The dehydration of **3** by $POCl_3$[10] at 0 °C yielded 6,7-dihydroindazoles (**4**) over 95% yields. These dihydro systems are usally labile, thus need directly to undergo dehydrogenation for better yields. Subsequent dehydrogenation of **4** by 10% Pd/C at 100 °C in dioxane led to excellent yields of indazoles (**5**), whose spectral as well as elemental analysis data were satisfactory to the presented structure. On the other hand, heating **3** with catalytic amounts of *p*-TsOH in the presence of 10% Pd/C at 100 °C in dioxane afforded **4** and **5** in a ratio of 3-4:7-6 with 78-86% yields. In this step, the ratios of the products were highly dependent on reaction time. The longer reaction time increased the portion of aromatized system, which implies that dehydration step is followed by dehydrogenation step. In general, 20 h is the limit to obtain the maximum yields of indazoles (**5**).

Scheme 1.



In addition, the substituents at C_4 can be readily introduced by the reactions of **2** with Grignard reagents, followed by either stepwise or simultaneous dehydration and dehydrogenation.



6 **8**

In conclusion, the present method offers advantages over the methods,[1-3] previously reported. The reaction requires readily available reagents, and is applicable to the synthesis of various 3- and/or 4-substituted indazoles with high yields, as well as is able to carry our under relatively mild conditions.

EXPERIMENTAL

General. Melting points were determined on Yanaco micro melting point apparatus and are uncorrected. Ir spectra were obtained on a Perkin Elmer 1310 spectrophotometer in KBr, except where noted. Nuclear magnetic resonance(nmr) spectra were obtained on a Bruker AM-300 (300 MHz for ^1H nmr and 75.5 MHz for ^{13}C nmr) spectrometer and chemical shift are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard. Dry pyridine was obtained by distilling over CaH_2 and all other solvents were reagent grade and used directly without further purification. The enol esters, 3-benzoyloxy-2-cyclohexeone and 3-phenylacetyloxy-2-cyclohexenone, and corresponding 2-acylcyclohexane-1,3-diones (**1c**) and (**1d**) were prepared by known methods.[8]

General Synthetic Procedure:

2-Acylcyclohexane-1,3-diones (1). To the suspension of 2.66 g(0.02 mol) of anhyd. $AlCl_3$ in 100 ml of freshly distilled 1,2-dichloroethane was slowly added by dropping 0.01 mol of enol ester, and resulting mixture was stirred for 2-24 h under N_2 gas at room temperature. Reaction mixture was poured into the mixture of ice and conc. H_2SO_4. Organic layer was separated and aqueous layer was extracted with $CHCl_3$. The combined organic layer was washed with water and dried over anhyd. $MgSO_4$. Evaporation of the solvent afforded pale yellow liquid, which was purified by column chromatography on silica gel, eluting with hexane:CH_2Cl_2(2:1). The early fractions provide products.

4-Oxo-4,5,6,7-tetrahydroindazles (2). The ice-cold mixture of 0.05 g(0.01 mol) of hydrazine and 0.01 mol of 1 in 25 ml of EtOH was allowed to be stirred at room temperature for 4-6 h and the solvent removed. The crude product was purified by either column chromatography [hexane:EtOAc(3:1)] on silica gel or recrystallization from hexane:EtOAc(1:1).

4-Hydroxy-4,5,6,7-tetrahydroindazles (3). To a stirred suspension of 0.38 g(0.01 mol) of $NaBH_4$ in 25 ml of EtOH was added 0.01 mol of **2**, and resulting mixture was stirred for 6-8 h. After removal of the solvent, the resulting residue was dissolved in 25 ml of $CHCl_3$ and washed with 20 ml of 10% AcOH. The organic layer was washed with water, and dried over anhyd. $MgSO_4$. Evaporation of the solvent afforded the crude product, which was purified by recrystallization from hexane:EtOAc(1:1).

6,7-Dihydroindazles (4). To the ice-cold solution of 0.01 mol of **3** in 25 ml of dry pyridine was added 3.06 g(0.02 mol) of $POCl_3$. The resulting mixture was allowed to stand 8 h at room temperature and was heated at 80 °C for 1.5 h on water bath. The cooled mixture was poured into ice water and extracted with EtOAc. The combined organic layer was washed with water, and dried. After removal of the solvent, the residue was purified by column chromatography on silica gel [hexane:EtOAc (5:1)]. The 6,7-dihydro-indazoles turn dark almost immediately after column chromatography, thus are subject to undergo dehyrogenation directly without full chracterization.

Indazoles (5). Method A: A suspension of 0.01 mol of **4** and 100 mg of 10% Pd/C in 25 ml of dioxane was heated at 100 °C for 6-8 h. Removal of the catalyst and evaporation of the solvent afforded a residue, which was dissolved in 25 ml of CH_2Cl_2 and washed with water. The organic layer was concentrated and chromatographed on silica gel eluting with hexane:EtOAc(5:1). The latter fractions provide the indazoles.

Method B: A suspension of 0.01 mol of 4, 100 mg of 10% Pd/C, and 100 mg of *p*-TsOH in 25 ml of dioxane was heated at 100 °C for 6-8 h. Work-up and purification as given in Method A gave 6,7-dihydroindazoles and indazoles.

2-Isobutyrylcyclohexane-1,3-dione (1a): Pale yellow liquid(89%). Ir(thin film) ν 2940, 2860, 1645, 1580-1500, 1410, 1310, 1240, 1180, 1130, 1080, 1040, 995, 955, 915, 870, 810, 770 cm^{-1}; ^1H nmr($CDCl_3$, 300 MHz) δ 1.13(d, 6H, J=6.7 Hz), 2.00(quintet, 2H, J=6.4 Hz), 2.49(t, 2H, J=6.4 Hz), 2.67(t, 2H, J=6.4 Hz), 3.97(septet, 1H, J=6.7 Hz), 17.38(s, OH) ppm; ^{13}C nmr($CDCl_3$, 75.5 MHz) δ 18.7, 18.9, 33.4, 36.2, 39.0, 112.0, 194.9, 199.0, 210.3. Anal. Calcd for $C_{10}H_{14}O_3$ C:65.91, H:7.74. Found C:66.03 H:7.59.

2-(4-Fluorobenzoyl)cyclohexane-1,3-dione (1c): Pale yellow liquid(86%). Ir(thin film) ν 3050, 2940, 2880, 1645, 1590-1500, 1400, 1340, 1320, 1285, 1250, 1220, 1180, 1145, 1090, 1060, 1040, 1000, 980, 920, 840, 820, 780, 770, 730, 690, 620 cm^{-1}; ^1H nmr($CDCl_3$, 300 MHz) δ 2.03(quintet, 2H, J=6.4 Hz), 2.48(br s, 2H), 2.69(br s, 2H), 7.04(dm, 2H, J=8.6 Hz), 7.54(dm, 2H, J=8.6 Hz), 16.80(s, OH) ppm; ^{13}C nmr($CDCl_3$, 75.5 MHz) δ 18.9, 32.2, 38.09, 113.0, 114.7(d, $^3J_{C-F}$=8 Hz), 131.4(d, $^2J_{C-F}$=22 Hz), 164.9(d, $^1J_{C-F}$=249 Hz), 194.0, 196.0, 197.3; another set(enol form) δ 18.9, 32.1, 37.9, 113.0, 114.7(d, $^2J_{C-F}$=22 Hz), 127.5, 128.1, 131.0(d, $^3J_{C-F}$=8 Hz), 131.7, 134.1, 164.9(d, $^1J_{C-F}$=250 Hz), 197.3. Anal. Calcd for $C_{13}H_{11}O_3F$ C:66.66, H:4.73. Found C:67.03, H:4.28.

4-Oxo-4,5,6,7-tetrahydro-3-isopropylindazole (2a): White platelets(94%), mp 96-98 °C. Ir(thin film) ν 3150, 3080, 2940, 2860, 1625, 1555, 1475, 1410, 1350, 1315, 1290, 1260, 1175, 1150, 1100, 1070, 1055, 1025, 1010, 890, 850, 760, 720 cm^{-1}; ^1H nmr($CDCl_3$, 300 MHz) δ 1.30(d, 6H, J=6.8 Hz), 2.10(quintet, 2H, J=6.2 Hz), 2.50(t, 2H, J=6.2 Hz), 2.82(t, 2H, J=6.2 Hz), 3.56(septet, 1H, J=6.8 Hz), 12.45(br, NH): ^{13}C nmr($CDCl_3$, 75.5 MHz) δ 20.9, 22.5, 23.5, 26.6, 39.1, 114.2, 154.9, 155.2, 194.6. Anal. Calcd for $C_{14}H_{14}N_2O$ C:67.39, H:7.92, N:15.72. Found C:67.03, H:8.02, N:15.93.

4-Oxo-4,5,6,7-tetrahydro-3-phenylindazole (2b): White platelets(89%), mp 193-194 °C. Ir(KBr) ν 3160, 3080, 2920, 1580, 1550, 1430, 1350, 1310, 1260, 1165, 1125, 1060, 1015, 970, 890, 775, 745, 690 cm^{-1}; ^1H nmr($CDCl_3$ in DMSO-d_6, 300 MHz) δ 2.08(quintet, 2H, J=6.2 Hz), 2.45(t, 2H, J=6.2 Hz), 2.85(t, 2H, J=6.2 Hz), 7.37(m, 3H), 8.05(m, 2H), 13.20(br s, NH): ^{13}C nmr($CDCl_3$ in DMSO-d_6, 75.5 MHz) δ 21.3, 25.6, 36.3, 119.3, 127.1, 127.7, 131.3, 132.0, 164.8, 165.6, 195.9. Anal. Calcd for $C_{13}H_{12}N_2O$ C:73.57, H:5.70, N:13.20. Found C:73.63, H:6.04, N:13.17.

4-Oxo-4,5,6,7-tetrahydro-3-(4-fluorophenyl)indazole (2c): White platelets(92%), mp 223-224° C. Ir(KBr) ν 3180, 3070, 2920, 1490, 1550, 1500, 1460, 1430, 1210, 1140, 1125, 1080, 1060, 1035, 1005, 970, 890, 830, 810, 750 cm^{-1}; ^1H nmr($CDCl_3$ in DMSO-d_6, 300 MHz) δ 2.10(quintet, 2H, J=6.2 Hz), 2.49(t, 2H, J=6.2 Hz), 2.86(t, 2H, J=6.2 Hz), 7.08(dm, 2H, J=8.8 Hz), 8.12(dm, 2H, J=8.8 Hz), 13.05 (br, NH): ^{13}C nmr ($CDCl_3$ in DMSO-d_6, 75.5 MHz) δ 21.7, 22.9, 39.2, 113.9, 114.4(d, $^2J_{C-F}$=22 Hz), 127.5, 128.2, 130.1, 130.2(d, $^3J_{C-F}$=8 Hz), 162.4(d, $^1J_{C-F}$=242 Hz), 192.8. Anal. Calcd for $C_{13}H_{11}N_2OF$ C:67.82, H:4.82, N:12.17. Found C:68.07, H:4.98, N:13.07.

4-Oxo-4,5,6,7-tetrahydro-3-benzylindazole (2d): White platelete(91%), mp 165-166 °C. Ir(KBr) ν 3200, 3100, 3010, 2940, 2900, 1600, 1550, 1465, 1445, 1415, 1350, 1310, 1270, 1160, 1130, 1060, 1010, 930, 890, 870, 765, 730, 695 cm^{-1}; ^1H nmr($CDCl_3$ in DMSO-d_6, 300 MHz) δ 2.03(quintet, 2H, J=6.2 Hz), 2.40(t, 2H, J=6.2 Hz), 2.68(t, 2H, J=6.2 Hz), 4.22(s, 2H), 7.24-7.12(m, 5H), 13.00(br s, NH): ^{13}C nmr($CDCl_3$ in DMSO-d_6, 75.5 MHz) δ 22.1, 23.5, 32.4, 38.8, 115.1, 126.4, 128.4, 128.7, 137.7, 148.3, 154.3, 194.8. Anal. Calcd for $C_{14}H_{14}N_2O$ C:74.31, H:6.24, N:12.38. Found C:73.93, H:6.64, N:12.93.

4-Hydroxy-4,5,6,7-tetrahydro-3-isopropylindazole (3a): White platelets(95%), mp 178-180 °C. Ir(KBr) ν 3300, 3180, 2910, 2850, 1575, 1470-1420, 1350, 1260, 1060, 1030, 980, 950, 900, 825, 780, 720 cm^{-1}; ^1H nmr($CDCl_3$ in DMSO-d_6, 300 MHz) δ 1.32(d, 6H, J=7.0 Hz), 1.75-1.80(m, 1H), 1.82-1.87(m, 1H), 1.89-1.96(m, 1H), 2.50-2.56(m, 1H), 2.61-2.73(m, 2H), 3.17(septet, 1H, J=7.0 Hz), 4.81(br. s, OH), 4.83(d, J=6.7 Hz, H_4), 11.10(br, NH): ^{13}C nmr($CDCl_3$ in DMSO-d_6, 75.5 MHz) δ 18.1, 21.5, 22.0, 25.6, 33.2(2 C's), 60.9, 114.2, 133.7, 140.6. Anal. Calcd for $C_{10}H_{16}N_2O$ C:66.64, H:8.95, N:15.54. Found C:67.08, H:9.01, N:15.31.

4-Hydroxy-4,5,6,7-tetrahydro-3-phenylindazole (3b): White platelets(85%), mp: 212-214 °C. Ir(KBr) ν 3170-3100, 3050, 2910-2880, 1430, 1390, 1330, 1265, 1150, 1095, 1050, 980, 945, 865, 830, 755, 725, 690 cm^{-1}; ^1H nmr($CDCl_3$ in DMSO-d_6, 300 MHz) δ 1.69-1.79(m, 2H), 1.95-2.09(m, 2H), 2.47-2.58(m, 1H), 2.75(dt, 1H, J=16.0, 4.5 Hz), 4.60(d, J=6.0 Hz, H_4), 4.79(t, 1H, J=5.4 Hz), 7.26(t, 1H, J=7.5 Hz), 7.37(t, 2H, J=7.5 Hz), 7.97(dm, 2H, J=7.5 Hz), 12.40(br s, NH); ^{13}C nmr($CDCl_3$ in DMSO-d_6, 75.5 MHz) δ 16.6, 32.9, 39.5, 60.2, 78.3, 108.2, 115.0, 126.4, 126.6, 127.9, 130.8, 137.1, 150.3. Anal. Calcd for $C_{13}H_{14}N_2O$ C:72.87, H:6.59, N:13.07. Found C:73.10, H:6.65, N:12.86.

4-Hydroxy-4,5,6,7-tetrahydro-3-(4-fluorophenyl)indazole (3c): White platelets (92%), mp 236-238 °C. Ir(KBr) ν 3100, 2920, 2880, 1565, 1475, 1420, 1370, 1320, 1260, 1190, 1140, 1075, 1045, 975, 940, 895, 860, 800, 770, 705, 620 cm^{-1}; ^1H nmr($CDCl_3$ in DMSO-d_6, 300 MHz) δ 1.68-1.76(m, 2H), 1.91-2.04(m, 2H), 2.48-2.52(m, 1H), 2.70(dd, 1H, J=15.0, 3.0 Hz), 4.71(br s, OH), 4.81(d, J=6.8 Hz, H_4), 7.13-7.18(m, 2H), 7.95-8.02(m, 2H), 12.40(br s, NH); ^{13}C nmr($CDCl_3$ in DMSO-d_6, 75.5 MHz) δ 16.6, 33.0, 39.5, 60.0, 108.2, 114.9(d, $^2J_{C-F}$=22 Hz), 128.3(d, $^3J_{C-F}$=8 Hz), 130.2(d, $^4J_{C-F}$=3 Hz), 138.7, 159.7, 162.4(d, $^1J_{C-F}$=242 Hz). Anal. Calcd for $C_{13}H_{13}N_2OF$ C:68.11, H:5.72, N:12.22. Found C:69.04, H:5.65, N:12.76.

4-Hydroxy-4,5,6,7-tetrahydro-3-benzylindazole (3d): White platelets(88%), mp 173-175 °C: Ir(KBr) ν 3170-3100, 2910, 1570, 1480, 1415, 1390, 1325, 1265, 1225, 1205, 1135, 1095, 1050, 970, 895, 820, 750, 710, 690 cm^{-1}; ^1H nmr($CDCl_3$ in DMSO-d_6, 300 MHz) δ 1.73-1.77(m, 2H), 1.81-1.90(m, 2H), 2.46-2.56(m, 1H), 2.60(dt, 1H, J=16.0, 4.5 Hz), 3.15(br s, OH), 4.05(AB quartet, J = 9.6, 4.1 Hz, 2H, benzylic H), 4.69(overlapped d, J=6.4 Hz, H_4), 7.21-7.35(m, 5H), 12.56(br s, NH). Anal. Calcd for $C_{14}H_{16}N_2O$ C:73.66, H:7.06, N:12.27. Found C:74.02, H:6.98, N:12.76.

***3-Isopropyl-6,7-dihydroindazole* (4a)**: *Pale yellow oil(98%).* Ir(thin film) ν 3150, 3030, 2920, 1685, 1605, 1480, 1430, 1300, 1210, 1150, 1065, 1005, 975, 910, 865, 780, 760, 725, 690 cm^{-1}; ^1H nmr($CDCl_3$, 300 MHz) δ 1.43(d, 6H, J=6.7 Hz), 2.35(td, 2H, J=8.5, 4.3 Hz, H_6), 2.74(t, 2H, J=8.3 Hz, H_7), 3.65(septet, 6H, J=6.7 Hz), 5.66(dt, 1H, J=9.8, 4.3 Hz, H_5), 6.65(dd, 1H, J=9.8, 1.8 Hz, H_4), 10.65(br s, NH); ^{13}C nmr($CDCl_3$, 75.5 MHz) δ 20.9, 22.1, 23.6, 28.0, 113.1, 119.7, 124.0, 126.9, 130.9. Anal. Calcd for $C_{10}H_{14}N_2$ C:74.03, H:8.70, N:17.27. Found C:74.10, H:8.74, N:17.16.

3-Phenyl-6,7-dihydroindazole (4b): Oil(98%). Ir(thin film) ν 3150, 3090, 3030, 2920, 1685, 1600, 1485, 1425, 1310, 1210, 1130, 1065, 1005, 975, 910, 860, 780, 760, 725, 690, 665 cm^{-1}; ^1H nmr($CDCl_3$, 300 MHz) δ 2.36-2.43(m, 2H, H_6), 2.73(td, 2H, J=8.3, 1.8 Hz, H_7), 5.78(dt, J=9.7, 4.3 Hz, H_5), 6.64(dt, J=9.7, 2.1 Hz, H_4), 7.35(m, 3H), 7.57(m, 2H), 10.55(br s, NH); ^{13}C nmr($CDCl_3$, 75.5 MHz) δ 20.9, 23.6, 113.1, 119.7, 124.0, 126.9, 127.8, 128.7, 130.8, 139.1, 148.0. Anal. Calcd for $C_{13}H_{12}N_2$ C:79.56, H:6.16, N:14.27. Found C:79.63, H:6.17, N:14.29.

3-(4-Fluorophenyl)indazole (5c): White platelets(95%), mp 135-136 °C. Ir(KBr) ν 3100, 1590, 1470, 1400, 1325, 1205, 1145, 1125, 1090, 990, 900, 835, 810, 770, 730 cm^{-1}; ^1H nmr($CDCl_3$, 300 MHz) δ 7.19(m, 4H), 7.31(dd, 1H, J=8.4, 7.0 Hz), 7.95(m, 3H), 12.04(br s, NH); ^{13}C nmr($CDCl_3$, 75.5 MHz) δ 110.3, 116.0(d, $^2J_{C-F}$=22 Hz), 120.8, 121.4, 126.9, 129.4(d, $^3J_{C-F}$=8 Hz), 129.6, 129.7, 141.7, 144.7, 162.9(d, $^1J_{C-F}$=256 Hz). Anal. Calcd for $C_{13}H_9N_2F$ C:73.57, H:4.27, N:13.20. Found C:73.63, H:4.28, N:13.17.

3-Benzylindazole (5d): White platelets(94%), mp 115-116 °C. Ir(KBr) ν 3125, 2920, 2860, 1590, 1480, 1440, 1420, 1360, 1330, 1245, 1170, 1140, 1105, 1060, 1025, 990, 930, 890, 735, 715, 690, cm^{-1}; ^1H nmr($CDCl_3$, 300 MHz) δ 4.37(s, methylene H), 7.01(m, 1H), 7.22(m, 7H), 7.49(d, J = 8.2 Hz, 1H), 11.35(br, NH); ^{13}C nmr($CDCl_3$, 75.5 MHz) δ 33.6, 109.9, 120.3, 120.4, 122.1, 126.3, 126.6, 128.4, 128.7, 139.0, 141.4, 145.6. Anal. Calcd for $C_{14}H_{12}N_2$ C:80.74, H:5.81, N:13.45. Found C:80.66, H:5.84, N:13.50.

3,5-Diphenyl-4-hydroxy-4,5,6,7-tetrahydroindazole (6): Into 50 ml of THF contaning 2.43 g(0.1 mol) of Mg tunnings, a solution of 15.7 g(0.01 mol) of bromobenzene in 60 ml of THF was added with stirring. The Grignard reagent formation was completed, a solution of 6.36 g(0.03 mol) of **2b** in 80 ml of THF was added at 60 °C for 2 h. The mixture was stirred under reflux for additional 2 h and quenched by adding 50 ml of saturated NH_4Cl solution. Work up as usual afforded white platelets (86%), mp 137-138 °C: Ir(KBr) ν 3200, 2900, 1430, 1060, 980, 750, 690 cm^{-1}; ^1H nmr($CDCl_3$, 300 MHz) δ 1.87(m, 2H), 2.10(m, 2H), 2.72(m, 4H), 4.27(s, OH), 7.08(m, 5H), 7.32(m, 3H), 12.15(s, NH). Anal. Calcd for $C_{19}H_{18}N_2$ C:83.48, H:6.64, N:10.25. Found C:84.02, H:7.02, N:9.97.

3,5-Diphenyl-4,5,6,7-tetrahydroindazole (7): The same method described previously for **4** was provided semisolid as a desired product in 70% of yield. Ir(KBr) ν 3020, 2900, 1470, 1410, 1250, 1020, 720, 680 cm^{-1}; ^1H nmr($CDCl_3$, 300 MHz) δ 2.49(td, 2H, J=8.0, J=4.8 Hz), 2.70(t, 2H, J=8.0 Hz), 5.89(t, 1H, J=4.8 Hz), 7.01-7.24(m, 10H), 9.53(s, NH). Anal. Calcd for $C_{13}H_{12}N_2$ C:79.56, H:6.16, N:14.27. Found C:80.02, H:6.08, N:13.90.

3,5-Diphenylindazole (8): The same method described previously for **5** was provided white platelets (78%), mp > 200 °C. Ir(KBr) ν 3020, 1470, 1430, 1020, 740, 680 cm^{-1}. Anal. Calcd for $C_{13}H_{10}N_2$ C:80.39, H:5.19, N:14.42. Found C:80.44, H:5.11, N:14.45.

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