13. Palladium-promoted Cyclization of Tetra-alkylated 1-Arylazonaphthalenes to 2-Aryl-benzo[*g*]indazoles

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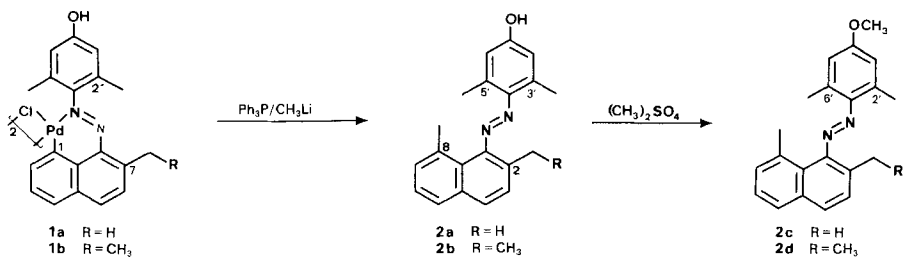
(9.XI.83)

Summary

1-Arylazonaphthalenes with all the potential cyclopalladation sites (one *peri*- and three *ortho*-positions) substituted by methyl or ethyl groups react with stoicheiometric or catalytic amounts of sodium tetrachloropalladate(II) to the corresponding 2-aryl-benzo[*g*]indazoles. Possible mechanisms for the catalytic cyclization reaction are proposed.

In our attempt to cyclopalladate the *peri*-position C(8) in a 1-arylazonaphthalene the potential *ortho*-palladation sites in the naphthyl and the phenyl moiety were blocked with methyl substituents [1] [2]. The cleavage of the Pd-C bond of the resulting *peri*-cyclopalladated complex **1a** with CH_3Li led to the tetra-methylated 1-arylazonaphthalene **2a** [3], which in turn was reacted with a stoicheiometric amount of tetrachloropalladate(II) in MeOH [4]. This reaction did not result in the formation of a Pd-complex with a Pd-alkyl bond as could have been expected from the well-known alkyl-palladation of 8-methylquinolines [5]. Instead, a colourless crystalline compound was isolated and identified as the 2-aryl-benzo[*g*]indazole **3a** [4].

Scheme 1



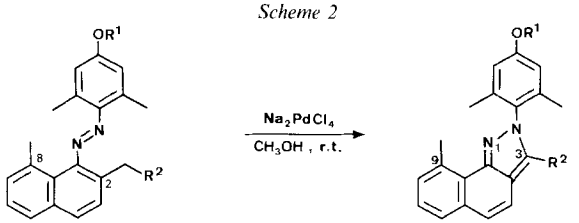
1a R = H
1b R = CH_3

2a R = H
2b R = CH_3

2c R = H
2d R = CH_3

For a further investigation of this unexpected cyclization complex **1b,** the 2-ethyl analogue of the *peri*-palladated complex **1a** was synthesized. Cleavage of the Pd-C bond with CH_3Li yielded the 2-ethyl-8,3′,5′-trimethylazonaphthalene **2b** *(Scheme 1)*. The hydroxy-substituted azo compounds **2a** and **2b** were converted to the methoxy derivatives **2c** and **2d,** respectively, by *O*-methylation with $(CH_3)_2SO_4$ *(Scheme 1)*.

Scheme 2



2a $R^1 = R^2 = H$
2b $R^1 = H$, $R^2 = CH_3$
2c $R^1 = CH_3$, $R^2 = H$
2d $R^1 = R^2 = CH_3$

3a $R^1 = R^2 = H$
3b $R^1 = H$, $R^2 = CH_3$
3c $R^1 = CH_3$, $R^2 = H$
3d $R^1 = R^2 = CH_3$

Table. *Cyclization of Azo Compounds* **2a–d** *to the Indazoles* **3a–d** *in MeOH at Room Temperature*[1]) (Catalyst: 5 mol% Na_2PdCl_4)

Compounds	Reaction time [h]	Yield [%][a])	Conversion [%][b])	$Yield_{corr}$ [%][c])
2a→3a	190	61	80	76
2b→3b	120	44	not determined	–
2c→3c	52	31	35	91
2d→3d	48	75	not determined	–

[a]) Relative to total amount of starting material.
[b]) None of the reactions was completed.
[c]) Relative to amount of reacted starting material.

The tetra-alkylated 1-arylazonaphthalenes **2a–d** reacted with catalytic amounts (5 mol%) of Na_2PdCl_4 to the corresponding indazoles **3a–d** *(Scheme 2)*. The reaction parameters of these conversions are shown in the *Table*. All the cyclization reactions proceeded with precipitation of metallic Pd.

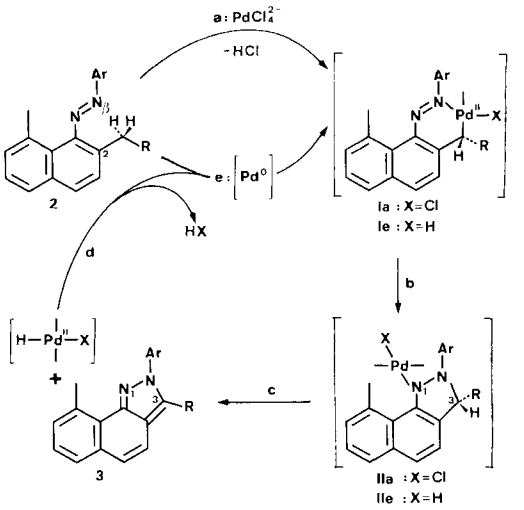
Tentatively, for the Pd-promoted cyclization, the pathway shown in *Scheme 3* can be envisaged.

First $PdCl_4^{2-}$ reacts electrophilically in a cyclopalladation reaction (step a) similar to that of alkyl-arenes [5], followed by insertion of the N=N bond into the Pd-C bond[2]) (step b), concluded by a 'δ-H-elimination'[3]) (step c) in which a Pd-hydride species is expelled to yield the indazole **3.** The Pd-hydride complex generates a Pd(0)-species by reductive elimination of HCl (step d, X = Cl).

In the reaction sequence a–b–c–d the Pd(II)-salt acts as a catalyst precursor that is reduced to the catalytically active Pd(0)-species which initiates the catalytic cycle e–b–c–d *(Scheme 3)*: 'Pd(0)' is oxidatively added to the α-C–H bond of the C(2)-alkyl substituent in **2** (step e), thus forming the intermediate Pd(II)-hydride complex **Ie** that is stabilized by chelating with the β-N-atom of the azo bridge. In the following steps a Pd(II)-dihydride complex is expelled from the insertion product **IIe** in a 'δ-H-elimi-

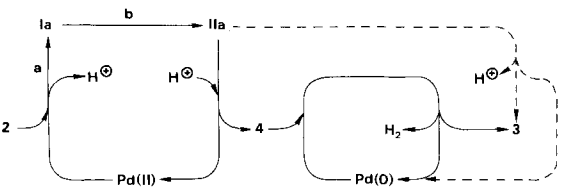
[1]) No precautions were taken to preclude air from the reaction mixtures.
[2]) In analogy to the olefin insertion in the Pd-promoted syntheses of heterocycles [6].
[3]) This 'δ-hydride elimination' can be understood as a vinylogous β-H-elimination. Whereas for the latter a 4-membered transition state has been proposed [7], the former may proceed *via* a 6-centre transition state, which requires a *cis*-arrangement of the Pd-X and the hydride substituent in the intermediate **II** *(Scheme 3)*.

Scheme 3

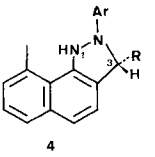


a: Cyclopalladation
b: Insertion (addition of Pd–C to N=N bond)
c: δ-Hydride elimination
d: Reductive elimination
e: Oxidative addition

Scheme 4



Structures of **2**, **Ia**, **IIa**, and **3** and steps a and b as shown in *Scheme 3*.



nation' to yield the indazole **3.** Finally, the Pd(II)-dihydride species reductively eliminates H_2 (step d, X = H) regenerating the Pd(0)-catalyst. However, for the proposed oxidative addition of 'Pd(0)' to C–H and the stabilization of the intermediate by a chelate structure no analogy has been found in the literature so far. Furthermore, in additional experiments with catalytic amounts of the soluble Pd(0)-complex $Pd(Ph_3P)_4$ in the absence of a Pd(II)-species the azo compound **2a** did *not* cyclize. Considering

these facts we tend to believe that the mechanism of the catalytic cyclization is more complex than that visualized in *Scheme 3* and that a Pd(II)- as well as a Pd(0)-species is operating simultaneously in two catalytic cycles *(Scheme 4)*.

First the azo compound **2** is converted to the 1,3-dihydroindazole **4** by cyclopalladation (step a) and insertion (step b), followed by the release of Pd(II) from the insertion product **IIa** by protolysis of the Pd-N(1) bond. This Pd(II)-species is recycled to catalyze the conversion of **2** into the 1,3-dihydroindazole **4,** whereas some Pd(II) is reduced to Pd(0) (dashed line in *Scheme 4*). Once Pd(0) is formed, it can catalyze the oxidation of **4** to **3** by way of dehydrogenation. The overall reaction **2**→**3** would therefore consist of two catalytic cycles (one with Pd(II) and the other with Pd(0) as catalyst) running simultaneously with the 1,3-dihydroindazole **4** as the common intermediate.

Conclusion. – The cyclization of the tetra-alkylated 1-arylazonaphthalenes **2a–d** to the 2-aryl-benzo[*g*]indazoles **3a–d** seems to be catalyzed by yet unknown Pd-species. The mechanism put forward in *Scheme 3* would require the Pd(II)-salt as a catalyst precursor from which the active catalyst 'Pd(0)' is formed. In the second pathway *(Scheme 4)* the Pd(II)-species is regarded as the catalyst for the cyclization of the azo compound **2** to the 1,3-dihydroindazole **4,** which is oxidized catalytically to the indazole **3** in a subsequent fast reaction. The catalyst for this dehydrogenation would be Pd(0) that was formed initially by reduction of some Pd(II)-salt.

The oxidative addition step e of the former mechanism *(Scheme 3)* resembles strongly a nucleophilic cyclometalation reaction and might thus be the rate-determining step of the catalytic cycle, because the insertion and the hydride elimination are usually fast reactions, especially in the absence of stabilizing ligands such as phosphines [7] [8].

The elucidation of the mechanism of this Pd-promoted cyclization, especially the identification of the catalytically active Pd-species, is in progress. Further studies on the obvious influence (see the *Table*) of the substituent (OH *vs.* CH_3O) in the phenyl ring and of the C(2)-alkyl group involved in the ring closure (CH_3 *vs.* CH_3CH_2) will give some insight into the nature of the cyclopalladation step. In addition, 1-arylazonaphthalenes with 2-alkyl groups that do not bear a second H-atom at the α-C-atom will provide more detailed information on a possible hydride elimination step c *(Scheme 3)*. Finally, the potential role of oxygen and of co-catalysts in the catalytic cycles will be investigated.

Partial financial support of this work by *Ciba-Geigy AG,* Basel and by the *Eidgenössische Technische Hochschule,* Zürich (project No. 0.330.082.09/0) is gratefully acknowledged. We also thank Mr. *Felix Bangerter* for his invaluable contributions to our NMR investigations.

Experimental Part

General. See [9]. Abbreviations: *i.v.* = in vacuum; r.t. = room temperature. ^{1}H-NMR spectra (300 MHz) were recorded by Mr. *F. Bangerter* on the *Bruker AM 300-WB* spectrometer.

Syntheses of the *peri*-Palladated Complexes 1a and 1b. – *Di-μ-chlorobis{[8-(4'-hydroxy-2',6'-dimethylphenylazo)-7-methyl-1-naphthyl-C(1),N_β]palladium(II)}* (**1a**). Synthesized by cyclopalladation of 2-methyl-

naphthalene-1-azo-4'-(3',5'-dimethylphenol)[4]) with Na_2PdCl_4 in MeOH[2], 24 h at r.t.; yield 76%, m.p. 283° (dec.). ^{1}H-NMR (90 MHz, (D_6)DMSO): 2.29 (*m*, CH_3–Ph); 2.74 (*s*, CH_3–C(7)); 6.57 (*m*, H–C(3' and 5')); 7.22 (*t*, J = 7.6, H–C(3)); 7.60 (*d*, J = 8.3, H–C(6)); 7.64–7.73 (*m*, H–C(4)); 8.17 (*dd*, J = 7.5 and 1.2, H–C(2)); 8.20 (*d*, J = 8.3, H–C(5)); 9.54 (*s*, OH).

Di-μ-chlorobis{[7-ethyl-8-(4'-hydroxy-2',6'-dimethylphenylazo)-1-naphthyl-C(1),N_β]palladium(II)} (**1b**)[5]). Synthesized by cyclopalladation of 1.60 g (5.25 mmol) *2-ethylnaphthalene-1-azo-4'-(3',5'-dimethylphenol)*[6]) with 1.55 g (5.27 mmol) Na_2PdCl_4 in 147 ml MeOH, 3 days at r.t.; yield 80%, m.p. > 250°. ^{1}H-NMR (300 MHz, (D_6)DMSO): 1.26 (*t*, J = 7.5, 3H, CH_3CH_2); 2.27 (*s*, 6H, CH_3-Ph); 3.16 (*q*, J = 7.5, 2H, CH_3CH_2); 6.58 (br.*s*, 2H, H–C(3' and 5')); 7.25 (*t*, J = 7.6, 1H, H–C(3)); 7.66 (*d*, J = 8.4, 1H, H–C(6)); 7.70 (br. *d*, J = 7.4, 1H, H–C(4)); 8.17 (br. *d*, J = 7.5, 1H, H–C(2)); 8.27 (*d*, J = 8.4, 1H, H–C(5)); 9.56 (*s*, 1H, OH).

Syntheses of the Tetra-alkylated 1-Arylazonaphthalenes 2a–d. – *2,8-Dimethylnaphthalene-1-azo-4'-(3',5'-dimethylphenol)* (**2a**). The suspension of 1.724 g (2 mmol) **1a** and 4.20 g (16 mmol) Ph_3P *(Fluka, puriss.)* in 75 ml dry Et_2O was stirred under a N_2-atmosphere at r.t. After 30 min the clear red solution was cooled to 0° and 11 ml (*ca.* 17 mmol) of a 5% solution of MeLi in Et_2O *(EGA)* were added slowly. After 1 h excess MeLi was destroyed with H_2O and the reaction mixture extracted with Et_2O. The org. layer was separated and washed with dil. aq. HCl and H_2O. The ethereal solution was then dried and evaporated, and the residue chromatographed with CH_2Cl_2 on silica gel. Recrystallization from benzene/light petroleum ether yielded 0.88 g (72%) **2a** as red crystals, m.p. 69–70°. UV/VIS (EtOH): 326 (17900). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.28 (*s*, CH_3–C(2)); 2.37 (*s*, CH_3–C(8)); 2.49 (*s*, CH_3-Ph); 4.90 (*s*, OH); 6.64 (*s*, H–C(2' and 6')); 7.24 (br. *d*, H–C(7)); 7.31 (*m*, H–C(6)); 7.35 (*d*, J = 8.4, H–C(3)); 7.67 (*d*, J = 8.4, H–C(4)); 7.68 (br. *d*, H–C(5)). MS: 304 (70, M^+), 290 (10), 289 (10), 170 (11), 169 (72), 168 (100), 155 (34), 154 (15), 153 (14), 141 (16), 137 (19), 136 (35), 122 (10), 121 (83), 115 (10), 91 (11), 77 (17).

2-Ethyl-8-methylnaphthalene-1-azo-4'-(3',5'-dimethylphenol) (**2b**). The mixture of 1.60 g (3.59 mmol) **1b** and 3.85 g (14.6 mmol) Ph_3P *(Fluka, puriss.)* was dried *i.v.* overnight. Then the reaction vessel was flushed with dry N_2, 65 ml dry Et_2O were added, and the mixture stirred at r.t. After 30 min the clear red solution was cooled to 0° and 7.1 ml (10.9 mmol) of a 5% solution of MeLi in Et_2O *(EGA)* were added slowly. After 10 min the ice-bath was removed and the mixture stirred at r.t. After 60 min H_2O was carefully added and the mixture extracted with Et_2O. The org. layer was dried and evaporated, and the residue was chromatographed with CH_2Cl_2 on silica gel. Recrystallization from toluene/light petroleum ether yielded 1.0 g (86%) **2b** as red crystals, m.p. 112°. UV/VIS (DMF/HCl): 328 (20100), 467 (2300). ^{1}H-NMR (90 MHz, $CDCl_3$): 1.20 (*t*, J = 7.5, CH_3CH_2); 2.35 (*s*, CH_3–C(8)); 2.48 (*s*, CH_3–Ph); 2.54 (*q*, J = 7.6, CH_3CH_2); 6.49 (*s*, H–C(2' and 6')); 7.23–7.41 (*m*, H–C(6 and 7)); 7.28 (*d*, J = 8.4, H–C(3)); 7.70 (*d*, J = 8.4, H–C(4)); 7.63–7.73 (*m*, H–C(5)). MS: 318 (51, M^+), 316 (19), 303 (21), 301 (16), 184 (12), 183 (69), 182 (84), 180 (10), 170 (15), 169 (16), 168 (32), 167 (35), 155 (34), 153 (23), 152 (12), 149 (46), 141 (13), 137 (33), 136 (45), 128 (10), 122 (14), 121 (100), 120 (18), 91 (20), 77 (33).

2,8-Dimethylnaphthalene-1-azo-1'-(4'-methoxy-2',6'-dimethylbenzene) (**2c**). A mixture of 10 ml CH_2Cl_2, 10 ml H_2O, 0.304 g (1 mmol) **2a**, 0.12 g (3 mmol) NaOH, 0.37 ml (4 mmol) $(CH_3)_2SO_4$ *(Fluka, puriss.)* and *ca.* 4 mg (*ca.* 0.15 mmol) tetrabutylammonium chloride *(Fluka, pract.)* was vigorously stirred for 2 h at r.t. Then the org. layer was separated and the aq. layer extracted three times with 10 ml CH_2Cl_2. The combined org. extracts were evaporated, the residue dissolved in 15 ml Et_2O and washed three times with 15 ml 2*M* NH_3-solution and three times with 15 ml sat. NaCl-solution. The ethereal solution was dried ($MgSO_4$) and evaporated. Chromatography with CH_2Cl_2 on silica gel yielded 0.276 g (87%) **2c** as an orange-red oil[7]). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.28 (*s*, 3H, CH_3–C(2)); 2.38 (*s*, 3H, CH_3–C(8)); 2.52 (*s*, 6H CH_3-Ph); 3.85 (*s*, 3H, CH_3O); 6.71 (br. *s*, 2H, H–C(3' and 5')); 7.22 (br. *d*, J = 6.6, 1H, H–C(7)); 7.30 (*dd*, J = 7.6 and 6.6, 1H, H–C(6)); 7.34 (*d*, J = 8.3, 1H, H–C(3)); 7.66 (*d*, J = 8.3, 1H, H–C(4)); 7.67 (br. *d*, J = 7.6, 1H, H–C(5)). MS: 319 (6), 318 (27, M^+), 304 (5), 303 (5), 169 (8), 168 (40), 155 (18), 154 (8), 153 (11), 152 (9), 151 (30), 150 (77), 141 (11), 139 (6), 136 (16), 135 (100), 129 (5), 128 (8), 127 (6), 120 (5), 115 (12), 105 (8), 103 (9), 92 (7), 91 (24), 79 (11), 77 (14), 65 (7), 39 (7).

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[4]) Synthesized by cleaving the Pd-C bond in di-μ-chlorobis{[1-(4'-hydroxy-2',6'-dimethylphenylazo)-2-naphthyl-C(2),N_β]palladium(II)} with Ph_3P/CH_3Li in Et_2O [2].

[5]) N_β-coordination is postulated in analogy to the structure of **1a** that was established by ^{15}N-NMR spectroscopy [1].

[6]) Synthesized by cleaving the Pd-C bond in di-μ-chlorobis{[1-(4'-hydroxy-2',6'-dimethylphenylazo)-2-naphthyl-C(2),N_β]palladium(II)} with Ph_3P/EtMgBr in Et_2O (yield 38%).

[7]) M.p. is expected to be around 100° (*cf.* m.p. of **2d**), but the oil has not yet been brought to crystallize.

2-Ethyl-8-methylnaphthalene-1-azo-1'-(4'-methoxy-2',6'-dimethylbenzene) (**2d**). A mixture of 0.63 ml CH_2Cl_2, 0.63 ml H_2O, 20 mg (0.063 mmol) **2b**, 7.5 mg (0.12 mmol) NaOH, 0.04 ml (0.38 mmol) $(CH_3)_2SO_4$ *(Fluka, puriss.)* and *ca.* 0.25 mg (*ca.* 0.01 mmol) tetrabutylammonium chloride *(Fluka, pract.)* was vigorously stirred for 3 h at r.t. Then the org. layer was separated and the aq. layer extracted three times with 5 ml CH_2Cl_2. The combined org. extracts were evaporated, the residue dissolved in 5 ml Et_2O and washed twice with 5 ml 2M NH_3-solution and 5 ml sat. NaCl-solution. The ethereal solution was dried ($MgSO_4$) and evaporated. Chromatography (CH_2Cl_2, silica gel) and recrystallization from Et_2O/MeOH yielded 18 mg (86%) **2d**, m.p. 110°. UV/VIS (DMF): 324 (18000), 470 (1850). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.20 (*t*, *J* = 7.5, 3H, CH_3CH_2); 2.36 (*s*, 3H, CH_3–C(8)); 2.50–2.58 (*m*, 8H), including 2.53 (br. *s*, CH_3-Ph) and 2.54 (*q*, *J* = 7.5, CH_3CH_2); 3.88 (*s*, 3H, CH_3O); 6.72 (br. *s*, 2H, H–C(3' and 5')); 7.23 (br. *d*, *J* = 6.8, 1H, H–C(7)); 7.31 (*dd*, *J* = 8.0 and 7.1, 1H, H–C(6)); 7.39 (*d*, *J* = 8.4, 1H, H–C(3)); 7.68 (br. *d*, *J* = 8.3, 1H, H–C(5)); 7.71 (*d*, *J* = 8.4, 1H, H–C(4)). MS: 333 (13), 332 (49, M^+), 317 (26), 182 (44), 167 (13), 154 (16), 153 (13), 152 (10), 151 (37), 150 (100), 136 (17), 135 (87), 91 (14).

General Procedure for the Syntheses of the Indazoles **3a–d**. To the tetra-alkylated azo compound dissolved in MeOH 5 mol% of Na_2PdCl_4 are added at r.t. without preclusion of air from the mixture. In all cyclizations Pd(0) metal is precipitated. Workup by chromatography on silica gel with a 24:1- or 6:1- mixture of CH_2Cl_2/AcOEt for **3a** and **3b**, respectively, with CH_2Cl_2 for **3c** and **3d**.

3,5-Dimethyl-4-(9'-methylbenzo[g]indazol-2'-yl)phenol (**3a**). From 30.6 mg (0.10 mmol) **2a** in 3 ml MeOH, 18.4 mg (61%) **3a** after 8 days (reaction not completed[8]), m.p. 270° (dec.). UV/VIS (EtOH): 242 (32300), 249 (31700), 282 (9500), 294 (8300), 303 sh, 318 (5900), 332 (6200). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.98 (*s*, CH_3-Ph); 3.09 (*s*, CH_3–C(9')); 5.17 (*s*, OH); 6.63 (*s*, H–C(2 and 6)); 7.40–7.48 (*m*, H–C(7' and 8')); 7.43 (*d*, *J* = 8.8, H–C(5')); 7.60 (*d*, *J* = 8.8, H–C(4')); 7.70 (*dd*, *J* = 7.1 and 2.4, H–C(6')); 7.94 (*s*, H–C(3')). MS: 302 (100, M^+), 286 (5), 274 (4), 259 (3), 181 (4), 179 (4), 167 (3), 154 (8), 151 (6), 127 (4), 91 (3), 77 (4).

3,5-Dimethyl-4-(3',9'-dimethylbenzo[g]indazol-2'-yl)phenol (**3b**). From 80 mg (0.25 mmol) **2b** in 8 ml MeOH, 35.3 mg (44%) **3b** after 5 days (reaction not completed), m.p. 215°. UV/VIS (EtOH): 244 (31000), 282 (9100), 297 (9100), 317 (6900), 333 (7000), 348 (1300). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.87 (*s*, CH_3-Ph); 2.38 (*s*, CH_3–C(3')); 3.10 (*s*, CH_3–C(9')); 6.58 (*s*, H–C(2 and 6)); 7.39 (*t*, *J* = 8.9 and 8.4, H–C(7')); 7.40 (*d*, *J* = 8.3, H–C(5' or 8')); 7.45 (*d*, *J* = 7.3, H–C(8' or 5')); 7.51 (*d*, *J* = 8.8, H–C(4')); 7.70 (*dd*, *J* = 7.3 and 1.4, H–C(6')). MS: 317 (24), 316 (100, M^+), 315 (16), 302 (16), 301 (69), 300 (5), 299 (5), 287 (5), 286 (10), 285 (5), 274 (8), 180 (5), 158 (6), 154 (7), 150 (6), 149 (7), 121 (3), 91 (4), 77 (7).

2-(4'-Methoxy-2',6'-dimethylphenyl)-9-methylbenzo[g]indazole (**3c**). From 35.2 mg (0.11 mmol) **2c** in 2.5 ml MeOH, 10.8 mg (31%) **3c** after 2 days (reaction not completed[9]). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.02 (*s*, 6H, CH_3-Ph); 3.07 (*s*, 3H, CH_3–C(9)); 3.85 (*s*, 3H, CH_3O); 6.72 (br. *s*, 2H, H–C(3' and 5')); 7.40–7.45 (*m*, H–C(7 and 8)); 7.42 (*d*, *J* = 8.9, H–C(5)); 7.60 (*d*, *J* = 8.9, 1H, H–C(4)); 7.70 (*dd*, *J* = 7.2 and 2.0, 1H, H–C(6)); 7.93 (*s*, 1H, H–C(3)). MS: 318 (6), 317 (24), 316 (100, M^+), 315 (6), 302 (6), 301 (24), 273 (16), 168 (5), 158 (7), 154 (8), 153 (6), 151 (5), 150 (12), 149 (6), 136 (5), 135 (22), 128 (6), 127 (8), 91 (13), 79 (5), 77 (9), 65 (5), 57 (6), 55 (6), 43 (6), 41 (7), 39 (6).

2-(4'-Methoxy-2',6'-dimethylphenyl)-3,9-dimethylbenzo[g]indazole (**3d**). From 7 mg (0.021 mmol) **2d** in 1 ml MeOH, 5.2 mg (75%) **3d** after 2 days (reaction not completed), m.p. 122°. UV/VIS (EtOH): 250 (40000), 288 (9500), 302 (10300), 305 sh (9000), 321 (7400), 339 (6900). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.92 (*s*, 6H, CH_3-Ph); 2.36 (*s*, 3H, CH_3–C(3)); 3.06 (*s*, 3H, CH_3–C(9)); 3.85 (*s*, 3H, CH_3O); 6.74 (br. *s*, 2H, H–C(3' and 5')); 7.36 (*d*, *J* = 8.9, 1H, H–C(5)); *ca.* 7.38 (ev. br. *d*, H–C(8)); 7.42 (ev. *t*, *J* = 7.3, H–C(7)); 7.50 (*d*, *J* = 8.8, 1H, H–C(4)); 7.68 (*dd*, *J* = 7.4 and 1.6, 1H, H–C(6)). MS: 332 (12), 331 (26), 330 (100, M^+), 329 (11), 316 (17), 315 (72), 300 (15), 150 (19), 149 (11), 135 (17).

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[8]) 6.5 mg (0.02 mmol) of unreacted starting product **2a** were recovered (yield 76% relative to reacted **2a**).

[9]) 23.3 mg (0.073 mmol) of unreacted starting product **2c** were recovered (yield 91% relative to reacted **2c**).

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