Silylation of 2*H*-Indazoles by Photoinduced Hydrogen-Atom Transfer Catalysis

Krishna Kanta Das and Alakananda Hajra*

Department of Chemistry, Visva-Bharati (A Central University), Santiniketan 731235, India; Tel./Fax: +913463 261526; E-mail: <u>alakananda.hajra@visva-bharati.ac.in</u>

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1. General Information:

All reagents were purchased from commercial sources and used without further purification. ¹H NMR spectra were determined on 400 MHz spectrometer as solutions in CDCl₃. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplate) and coupling constants (J) were given in Hz. ¹³C{¹H} NMR spectra were recorded at 100 MHz in CDCl₃ solution. NMR data are reported relative to residual CHCl₃ (¹H, δ = 7.26 ppm) and CDCl₃ (¹³C, δ = 77.16 ppm). TLC was done on silica gel coated glass slide. All 2-arylindazoles¹ were prepared by the reported methods. All solvents were dried and distilled before use. Commercially available solvents were freshly distilled before the reaction. All reactions involving moisture sensitive reactants were executed using oven dried glassware. Melting points (M.p's) were determined after recrystallization of solid compounds from a solution of dichloromethane/petroleum ether (1:3).

1.2. Light Information:

Kessil 34 W blue LED (Model No. H150-BLUE) was used as a light source for light promoted reactions.

Rating of LED: 24VDC 1.5A 34W

Model: H150-BLUE

Range of wavelength: 450-530 nm. Manufacturer: Kessil, 1689 Regatta blvd, Richmond, CA94804 (www.kessil.com).

2. Experimental Procedures:

2.1. Typical Experimental Procedure for 3b:



A mixture of 2-(*p*-tolyl)-2*H*-indazole (**1b**) (0.25 mmol, 52.0 mg), Ph₃SiH (**2**) (2.0 equiv., 130.2 mg), 4CzIPN (3 mol%, 5.9 mg), ⁱPr₃SiSH (10 mol%, 4.8 mg), K₂CO₃ (10 mol%, 3.5 mg) and CH₃CN (2 ml) were added to an oven-dried reaction vessel (tube) equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under open air atmosphere for 24 h. The progress of the reaction was monitored by TLC, the reaction was cooled to room temperature and extracted with ethyl acetate. The organic phase was dried over anhydrous Na₂SO₄. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate to afford the pure products.

3. Gram-Scale Synthesis for 3b:



A mixture of 2-(*p*-tolyl)-2*H*-indazole (**1b**) (5.0 mmol, 1.04 g), Ph₃SiH (2.0 equiv., 2.60 g), 4CzIPN (3 mol%, 118.3 mg), i Pr₃SiSH (10 mol%, 95.2 mg), K₂CO₃ (10 mol%, 69.1 mg) and CH₃CN (20 ml) were added to an oven-dried reaction vessel (tube) equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under open air atmosphere for 24 h. The progress of the reaction was monitored by TLC, the reaction was cooled to room temperature and extracted with ethyl acetate. The organic phase was dried over anhydrous Na₂SO₄. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture

of petroleum ether and ethyl acetate (92:08) as an eluting solvent to afford the pure product **3b** (1.72 g, 74%) as a white solid.

4. Synthetic Utility:²



A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with N-Bromosuccinimide (NBS) (177.9 mg, 5.0 equiv.), **3b** (93.3 mg, 0.2 mmol), fresh distilled CH_2Cl_2 or MeCN (2.0 mL) were then added under argon atmosphere. The reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was diluted with ethyl acetate. The residue was purified by silica gel flash chromatography to afford the corresponding compound **4b** in 83% yield.

5. Starch-Iodide Test for the Detection of Hydrogenperoxide:³

After the completion of reaction (monitored by TLC), aqueous potassium iodide solution was added to the reaction mixture. The aqueous layer turned to light brown-blue colour and the colour was enhanced by addition of starch. To the same aqueous layer, aqueous sodium thiosulfate solution was added and the aqueous layer immediately turned colourless.

The chemical equations involved in this reaction:

 $H_2O_2 + 2KI_{(aq)} \longrightarrow I_{2(aq)} + 2K^+_{(aq)} \text{ (brown-blue colour solution)}$ $I_{2(aq)} + 2S_2O_3^{2-}_{(aq)} \longrightarrow 2I^-_{(aq)} + S_4O_6^{2-}_{(aq)} \text{ (colourless solution)}$

6. Characterization Data for the Synthesized Products:



2-Phenyl-3-(triphenylsilyl)-2H-indazol (3a): White solid (82%, 92.7 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 151-152 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 6.8 Hz, 6H), 7.38 (t, J = 7.6 Hz, 3H), 7.34-7.27 (m, 7H), 7.15-7.09 (m, 3H), 6.98 (d, J = 7.6 Hz, 2H), 6.91-6.86 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.4, 142.0, 136.2, 132.9, 131.9, 131.5, 129.9, 128.7, 128.3, 128.1, 126.8, 126.2, 122.7, 122.2, 117.9; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₃₁H₂₅N₂Si]⁺: 453.1782; found: 453.1794.



2-(p-Tolyl)-3-(triphenylsilyl)-2H-indazole (3b): White solid (85%, 99.0 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 177-178 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 6.8 Hz, 6H), 7.37 (t, J = 7.6 Hz, 3H), 7.32-7.29 (m, 1H), 7.27-7.24 (m, 6H), 6.97 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 3.6 Hz, 2H), 6.72 (d, J = 8.0 Hz, 2H), 2.21 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.3, 139.5, 138.6, 136.2, 135.1, 132.9, 131.7, 129.7, 128.8, 128.0, 126.5, 126.1, 122.6, 122.1, 117.9, 21.1; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₃₂H₂₇N₂Si]⁺: 467.1938; found: 467.1940.



2-(4-Methoxyphenyl)-3-(triphenylsilyl)-2H-indazole (3c): White solid (70%, 84.4 mg); $R_f = 0.50$ (PE/EA = 88 : 12), M.P. 198-199 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, J = 8.0 Hz, 1H), 7.45-7.43 (m, 6H), 7.36 (t, J = 7.6 Hz, 3H), 7.31-7.24 (m, 7H), 6.99-6.95 (m, 2H), 6.88-6.82 (m, 2H), 6.43-6.39 (m, 2H), 3.69 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.6, 149.3, 136.2, 135.1, 132.9, 131.9, 131.7, 129.8, 128.0, 127.9, 126.1, 122.6, 122.1, 117.8, 113.4, 55.5; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₃₂H₂₇N₂OSi]⁺: 483.1887; found: 483.1901.



2-(4-(tert-Butyl)phenyl)-3-(triphenylsilyl)-2H-indazole (3d): White solid (81%, 103.0 mg); $R_f = 0.50$ (PE/EA = 93 : 07), M.P. 155-156 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, J = 8.8 Hz, 1H), 7.49-7.47 (m, 6H), 7.38-7.34 (m, 3H), 7.32-7.29 (m, 1H), 7.28-7.24 (m, 6H),

7.06 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.88-6.87 (m, 2H), 1.22 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.5, 149.3, 139.4, 136.2, 133.0, 131.8, 131.4, 129.8, 128.0, 126.27, 126.20, 125.3, 122.6, 122.1, 117.9, 34.6, 31.3; Anal. Calcd for C₃₅H₃₂N₂Si: C, 82.63; H, 6.34; N, 5.51; Found: C, 82.78; H, 6.37; N, 5.61%.



Ethyl 4-(3-(triphenylsilyl)-2H-indazol-2-yl)benzoate (3e): White solid (83%, 108.8 mg); $R_f = 0.50$ (PE/EA = 88 : 12), M.P. 162-163 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 6.8 Hz, 6H), 7.38 (d, J = 7.6 Hz, 3H), 7.34-7.30 (m, 1H), 7.28-7.24 (m, 6H), 7.20 (d, J = 8.4 Hz, 2H), 6.91-6.85 (m, 2H), 4.38-4.33 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 165.7, 149.7, 145.4, 136.2, 132.6, 132.1, 131.8, 130.4, 130.0, 129.7, 128.2, 126.7, 126.6, 122.7, 122.5, 118.0, 61.2, 14.4; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₃₄H₂₉.N₂O₂Si]⁺: 525.1993; found: 525.1998.



2-(4-(Trifluoromethyl)phenyl)-3-(triphenylsilyl)-2H-indazole (3f): White solid (79%, 102.8 mg); $R_f = 0.50$ (PE/EA = 90 : 10), M.P. 171-172 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, J = 8.4 Hz, 1H), 7.49-7.47 (m, 6H), 7.41-7.37 (m, 3H), 7.36-7.32 (m, 2H), 7.29 (d, J = 7.6 Hz, 5H), 7.25-7.21 (m, 4H), 6.94-6.91 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.6, 144.6, 136.1, 132.4, 132.2 (q, J = 226.0 Hz), 132.0, 130.6 (d, J = 32.0 Hz), 130.1, 128.2, 127.2, 126.7, 126.2 (q, J = 271.0 Hz), 125.4 (q, J = 4.0 Hz), 122.7, 122.6, 117.9; Anal. Calcd for C₃₂H₂₃F₃N₂Si: C, 73.82; H, 4.45; N, 5.38%; Found: C, 74.00; H, 4.43; N, 5.30%.



2-(4-Fluorophenyl)-3-(triphenylsilyl)-2H-indazole (3g): White solid (78%, 91.7 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 162-163 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, J = 8.8 Hz, 1H), 7.35-7.33 (m, 6H), 7.27 (t, J = 7.6 Hz, 3H), 7.22-7.13 (m, 7H), 6.95-6.92 (m, 2H), 6.79-6.73 (m, 2H), 6.53-6.47 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 162.4 (C-F, ¹ $J_{C-F} = 247.0$ Hz), 149.4, 138.13, 138.11, 136.1, 135.1, 132.6, 132.1, 131.8, 130.0, 128.6 (C-F, ³ $J_{C-F} = 9.0$ Hz), 128.1, 126.5, 122.5 (C-F, ² $J_{C-F} = 25.0$ Hz), 117.9, 115.1 (C-F, ² $J_{C-F} = 23.0$ Hz); HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₃₁H₂₄.FN₂Si]⁺: 471.1687; found: 471.1703.



2-(4-Chlorophenyl)-3-(triphenylsilyl)-2H-indazole (3h): White solid (69%, 84.0 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 184-185 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, J = 8.8 Hz,

1H), 7.46 (d, J = 6.8 Hz, 6H), 7.40 (t, J = 7.6 Hz, 3H), 7.34-7.27 (m, 7H), 7.01 (d, J = 8.8 Hz, 2H), 6.90-6.86 (m, 4H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.5, 140.5, 136.2, 134.7, 132.6, 132.1, 131.9, 130.0, 128.4, 128.2, 128.1, 126.5, 122.6, 122.4, 117.9; Anal. Calcd for C₃₁H₂₃ClN₂Si: C, 76.44; H, 4.76; N, 5.75; Found: C, 76.24; H, 4.81; N, 5.63%.



2-(4-Bromophenyl)-3-(triphenylsilyl)-2H-indazole (3i): White solid (75%, 99.6 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 187-188 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 7.2 Hz, 6H), 7.41 (t, J = 7.2 Hz, 3H), 7.33-7.27 (m, 7H), 7.04 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 6.91-6.86 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.5, 140.9, 136.1, 132.5, 132.1, 131.9, 131.4, 130.0, 128.3, 128.2, 126.5, 123.0, 122.6, 122.4, 117.9; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₁H₂₃BrN₂NaSi]⁺: 553.0706; found: 553.0706.



2-(m-Tolyl)-3-(triphenylsilyl)-2H-indazole (3j): White solid (83%, 96.8 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 183-184 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, J = 8.8 Hz, 1H), 7.49-7.47 (m, 6H), 7.39-7.35 (m, 3H), 7.33-7.27 (m, 7H), 6.99-6.97 (m, 1H), 6.90-6.87 (m, 5H), 2.02 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.4, 141.9, 138.3, 136.2, 135.9, 132.9, 131.8, 129.8, 129.5, 128.2, 128.0, 127.6, 126.1, 123.8, 122.6, 122.1, 117.9, 20.9; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₃₂H₂₇N₂Si]⁺: 467.1938; found: 467.1936.



2-(3-Methoxyphenyl)-3-(triphenylsilyl)-2H-indazole (3k): White solid (85%, 102.5 mg); $R_f = 0.50$ (PE/EA = 88 : 12), M.P. 196-197 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, J = 8.8 Hz, 1H), 7.50-7.48 (m, 6H), 7.38 (t, J = 7.6 Hz, 3H), 7.33-7.26 (m, 7H), 6.91-6.83 (m, 3H), 6.74 (d, J = 8.0 Hz, 1H), 6.66-6.62 (m, 2H), 3.38 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.2, 149.4, 143.0, 136.2, 132.9, 131.8, 131.5, 129.9, 129.3, 128.0, 126.2, 122.7, 122.2, 119.2, 118.0, 115.9, 111.6, 55.0; Anal. Calcd for C₃₂H₂₆N₂OSi: C, 79.63; H, 5.43; N, 5.80; Found: C, 79.79; H, 5.39; N, 5.88%.



2-(3-Chlorophenyl)-3-(triphenylsilyl)-2H-indazole (3l):): White solid (73%, 88.0 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 168-169 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, J = 8.8 Hz, 1H), 7.50-7.48 (m, 6H), 7.39 (t, J = 7.2 Hz, 3H), 7.33-7.27 (m, 7H), 7.11-7.10 (m, 1H), 7.07-7.04 (m, 2H), 6.92-6.87 (m, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.5, 142.9, 136.1, 134.0, 132.6, 132.0, 131.9, 130.1, 129.4, 129.0, 128.2, 127.4, 126.6, 125.0, 122.7, 122.5, 118.0; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₃₁H₂₄ClN₂Si]⁺: 487.1392; found: 487.1387.



2-(3-Chloro-4-fluorophenyl)-3-(triphenylsilyl)-2H-indazole (**3m**): White solid (87%, 109.8 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 177-178 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, J = 8.8 Hz, 1H), 7.50 (d, J = 6.8 Hz, 6H), 7.42 (t, J = 7.6 Hz, 3H), 7.35-7.30 (m, 7H), 7.14-7.12 (m, 1H), 7.04-7.00 (m, 1H), 6.93-6.88 (m, 2H), 6.71 (t, J = 8.8 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 158.0 (C-F, ¹ $J_{C-F} = 251.0$ Hz), 149.5, 138.56, 138.53, 136.1, 132.4 (C-F, ³ $J_{C-F} = 9.0$ Hz), 131.8, 130.2, 129.6, 128.2, 126.79, 126.76, 126.72, 122.6 (C-F, ³ $J_{C-F} = 3.0$ Hz), 120.8 (C-F, ² $J_{C-F} = 19.0$ Hz), 117.9, 116.0 (C-F, ² $J_{C-F} = 22.0$ Hz); Anal. Calcd for C₃₁H₂₂ClFN₂Si: C, 73.72; H, 4.39; N, 5.55; Found: C, 73.91; H, 4.36; N, 5.61%.



5-Fluoro-2-phenyl-3-(triphenylsilyl)-2H-indazole (**3n**): White solid (72%, 84.6 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 157-158 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.85-7.82 (m, 1H), 7.46-7.44 (m, 6H), 7.40-7.36 (m, 3H), 7.27 (t, J = 8.0 Hz, 6H), 7.13-7.08 (m, 4H), 6.99-6.95 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 158.3 (C-F, ¹ $J_{C-F} = 238.0$ Hz), 146.8, 141.9, 136.1, 132.5, 131.7, 131.5 (C-F, ³ $J_{C-F} = 11.0$ Hz), 130.0, 128.9, 128.5, 128.2, 126.7, 119.9 (C-F, ³ $J_{C-F} = 10.0$ Hz), 117.8 (C-F, ² $J_{C-F} = 29.0$ Hz), 105.2 (C-F, ² $J_{C-F} = 24.0$ Hz); Anal. Calcd for C₃₁H₂₃FN₂Si: C, 79.12; H, 4.93; N, 5.95; Found: C, 79.33; H, 4.97; N, 5.86%.



5-Fluoro-2-(p-tolyl)-3-(triphenylsilyl)-2H-indazole (**3o**): White solid (76%, 92.0 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 183-184 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.83-7.80 (m, 1H), 7.43-7.41 (m, 6H), 7.37 (t, *J* = 7.6 Hz, 3H), 7.27 (d, *J* = 7.6 Hz, 4H), 7.24 (d, *J* = 3.2 Hz, 2H), 7.11-7.06 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.35-6.32 (m, 1H), 2.19 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 158.2 (C-F, ¹*J*_{C-F} = 239.0 Hz), 146.7, 139.4, 138.8, 136.1, 132.5, 131.8, 131.3 (C-F, ³*J*_{C-F} = 11.0 Hz), 129.8, 128.9, 128.1, 126.4, 119.8 (C-F, ³*J*_{C-F} = 10.0 Hz), 117.6 (C-F, ²*J*_{C-F} = 29.0 Hz), 105.2 (C-F, ²*J*_{C-F} = 24.0 Hz), 21.1;

Anal. Calcd for C₃₂H₂₅FN₂Si: C, 79.31; H, 5.20; N, 5.78; Found: C, 79.14; H, 5.22; N, 5.88%.



5-Fluoro-2-(4-methoxyphenyl)-3-(triphenylsilyl)-2H-indazole (**3p**): White solid (68%, 85.1 mg); $R_f = 0.50$ (PE/EA = 87 : 13), M.P. 202-203 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.84-7.81 (m, 1H), 7.46-7.44 (m, 6H), 7.39 (t, J = 7.6 Hz, 3H), 7.30-7.26 (m, 6H), 7.12-7.07 (m, 1H), 7.00-6.96 (m, 2H), 6.44-6.41 (m, 2H), 6.36-6.33 (m, 1H), 3.70 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.8, 158.3 (C-F, ${}^{1}J_{C-F} = 239.0$ Hz), 146.6, 136.2, 134.9, 132.6, 132.2, 131.3 (C-F, ${}^{3}J_{C-F} = 11.0$ Hz), 130.0, 128.1, 127.9, 119.8 (C-F, ${}^{3}J_{C-F} = 9.0$ Hz), 117.8 (C-F, ${}^{2}J_{C-F} = 29.0$ Hz), 113.6, 105.2 (C-F, ${}^{2}J_{C-F} = 25.0$ Hz), 55.6; Anal. Calcd for C₃₂H₂₅FN₂OSi: C, 76.77; H, 5.03; N, 5.60; Found: C, 76.64; H, 4.99; N, 5.53%.



2-(4-Chlorophenyl)-5-fluoro-3-(triphenylsilyl)-2H-indazole (3q): White solid (79%, 99.7 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 204-205 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.85-7.81 (m, 1H), 7.47-7.40 (m, 9H), 7.30 (t, J = 7.6 Hz, 6H), 7.14-7.09 (m, 1H), 7.01 (d, J = 7.2 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 6.38 (d, J = 10.0 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 158.4 (C-F, ¹ $J_{C-F} = 239.0$ Hz), 146.9, 140.3, 136.1, 134.9, 132.3, 132.2, 131.5 (C-F, ³ $J_{C-F} = 12.0$ Hz), 130.1, 128.5, 128.3, 128.0, 119.9 (C-F, ³ $J_{C-F} = 10.0$ Hz), 118.1 (C-F, ² $J_{C-F} = 29.0$ Hz), 105.2 (C-F, ² $J_{C-F} = 25.0$ Hz); Anal. Calcd for C₃₁H₂₂ClFN₂Si: C, 73.72; H, 4.39; N, 5.55; Found: C, 73.91; H, 4.44; N, 5.63%.



5-Chloro-2-phenyl-3-(triphenylsilyl)-2H-indazole (**3r**): White solid (81%, 98.6 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 163-164 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 7.2 Hz, 6H), 7.38 (t, J = 7.6 Hz, 3H), 7.28 (d, J = 7.6 Hz, 6H), 7.24-7.21 (m, 1H), 7.12-7.08 (m, 3H), 6.96 (t, J = 8.0 Hz, 2H), 6.68 (d, J = 1.2 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 147.7, 141.7, 136.1, 135.0, 132.3, 131.6, 130.1, 128.9, 128.5, 128.2, 127.7, 127.6, 126.6, 121.4, 119.4; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for [C₃₁H₂₄ClN₂Si]⁺: 487.1392; found: 487.1391.



5-Chloro-2-(p-tolyl)-3-(triphenylsilyl)-2H-indazole (3s): White solid (65%, 81.4 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 196-197 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, J = 9.2 Hz,

1H), 7.43 (d, J = 6.8 Hz, 6H), 7.39 (t, J = 7.6 Hz, 3H), 7.27 (d, J = 8.0 Hz, 6H), 7.23-7.21 (m, 1H), 6.94 (d, J = 8.4 Hz, 2H), 6.73-6.69 (m, 3H), 2.20 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 147.7, 139.3, 138.9, 136.2, 132.5, 132.2, 131.8, 129.9, 128.9, 128.1, 127.7, 127.5, 126.4, 121.4, 119.4, 21.1; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₃₂H₂₆ClN₂Si]⁺: 501.1548; found: 501.1558.



5-Chloro-2-(4-methoxyphenyl)-3-(triphenylsilyl)-2H-indazole (3t): White solid (84%, 108.5 mg); $R_f = 0.50$ (PE/EA = 87 : 13), M.P. 199-200 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, J = 9.2 Hz, 1H), 7.47-7.45 (m, 6H), 7.42-7.38 (m, 3H), 7.30 (t, J = 7.6 Hz, 6H), 7.24-7.22 (m, 1H), 7.01-6.97 (m, 2H), 6.71 (d, J = 1.2 Hz, 1H), 3.70 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.8, 147.7, 136.2, 134.9, 132.5, 132.1, 132.0, 130.0, 128.1, 127.8, 127.7, 127.5, 121.3, 119.3, 113.5, 55.5; Anal. Calcd for C₃₂H₂₅ClN₂OSi: C, 74.33; H, 4.87; N, 5.42; Found: C, 74.47; H, 4.84; N, 5.31%.



5-Chloro-2-(4-chlorophenyl)-3-(triphenylsilyl)-2H-indazole (**3u**): White solid (89%, 116.0 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 154-155 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, J = 8.8 Hz, 1H), 7.48-7.46 (m, 6H), 7.43 (d, J = 7.6 Hz, 3H), 7.32 (t, J = 7.6 Hz, 6H), 7.27-7.24 (m, 1H), 7.02 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 1.6 Hz, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 147.9, 140.2, 136.1, 135.1, 135.0, 132.3, 132.2, 130.2, 128.5, 128.3, 128.0, 127.99, 127.95, 121.3, 119.4; Anal. Calcd for C₃₁H₂₂Cl₂N₂Si: C, 71.40; H, 4.25; N, 5.37; Found: C, 71.25; H, 4.23; N, 5.27%.



6-Methyl-2-phenyl-3-(triphenylsilyl)-2H-indazole (3v): White solid (74%, 86.3 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 178-179 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, J = 0.8 Hz, 1H), 7.47-7.45 (m, 6H), 7.38-7.34 (m, 3H), 7.26 (t, J = 2.0 Hz, 6H), 7.12-7.07 (m, 3H), 6.95 (t, J = 8.0 Hz, 2H), 6.73 (s, 2H), 2.43 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.7, 141.8, 136.2, 135.1, 132.9, 131.6, 130.3, 129.9, 128.7, 128.4, 128.1, 126.8, 125.2, 122.2, 116.1, 22.1; Anal. Calcd for $C_{32}H_{26}N_{2}Sii$ C, 82.36; H, 5.62; N, 6.00; Found: C, 82.52; H, 5.58; N, 6.12%.



6-Methyl-2-(p-tolyl)-3-(triphenylsilyl)-2H-indazole (3w): White solid (71%, 85.3 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 189-190 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.60 (s, 1H), 7.44-7.42 (m, 6H), 7.37-7.33 (m, 3H), 7.24 (t, J = 7.6 Hz, 6H), 6.94 (d, J = 8.0 Hz, 2H), 6.72-6.68 (m, 4H), 2.42 (s, 3H), 2.18 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.9, 139.6, 138.5, 136.2, 136.0, 133.0, 131.5, 130.2, 129.7, 128.8, 128.0, 126.6, 125.0, 122.1, 116.2, 22.18, 21.15; Anal. Calcd for C₃₃H₂₈N₂Si: C, 82.46; H, 5.87; N, 5.83; Found: C, 82.26; H, 5.89; N, 5.75%.



6-Chloro-2-phenyl-3-(triphenylsilyl)-2H-indazole (**3x**): White solid (67%, 81.5 mg); $R_f = 0.50$ (PE/EA = 92 : 08), M.P. 166-167 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, J = 0.3 Hz, 1H), 7.45-7.43 (m, 6H), 7.41-7.35 (m, 3H), 7.29-7.25 (m, 6H), 7.13-7.09 (m, 3H), 6.99-6.95 (m, 2H), 6.83-6.80 (m, 1H), 6.74 (d, J = 8.8 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.6, 141.7 136.1, 132.6, 132.5, 132.3, 130.2, 130.1, 128.9, 128.5, 128.2, 126.7, 123.9, 123.7, 116.8; Anal. Calcd for C₃₁H₂₃ClN₂Si: C, 76.44; H, 4.76; N, 5.75; Found: C, 76.30; H, 4.79; N, 5.81%.



3-Bromo-2-(p-tolyl)-2H-indazole (4b)⁴ : White solid (83%, 47.6 mg); R_f = 0.50 (PE/EA = 96 : 04); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.8 Hz, 1 H), 7.59-7.54 (m, 3H), 7.38-7.33 (m, 3H), 7.19-7.15 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 149.1, 139.4, 136.7, 129.6, 127.5, 125.9, 122.8, 122.9, 119.7, 118.1, 106.3, 21.3.

7. Structure Determination (X-ray Crystallographic Data for 3p):

The white crystal of 3p was obtained by crystallization from a solution in dichloromethane/petroleum ether after purification by column chromatography. Chemical Formula: $C_{32}H_{25}FN_2OSi$.

View of ORTEP (with 50% probability) diagram for the structure 5-fluoro-2-(4-methoxyphenyl)-3-(triphenylsilyl)-2H-indazole (**3p**).



Datablock AKBKKD_2 - ellipsoid plot



| Wavelength | 0.71073 Å | | |
|----------------------|---|-------------------------------|--|
| Formula | C ₃₂ H ₂₅ FN ₂ OSi | | |
| Crystal system | Triclinic | | |
| Space group | P -1 | | |
| Unit cell dimensions | a = 9.840(2)Å | $\alpha = 102.890(7)^{\circ}$ | |
| | b = 12.074(3) Å | $\beta = 107.408(7)^{\circ}$ | |
| | c = 13.093(3) Å | $\gamma = 110.200(6)^{\circ}$ | |
| Volume | 1297.2 Å ³ | | |
| Ζ | 2 | | |
| R factor | 5.69 | | |

The crystallographic data have been deposited with the Cambridge Crystallographic Data centre as a supplementary publication with a CCDC reference number 2308886.

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9. NMR Spectra for the Synthesized Products





S16























S26

S52

