

Efficient and Regioselective Synthesis of 2-Alkyl-2H-indazoles

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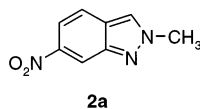
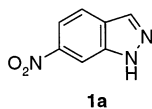
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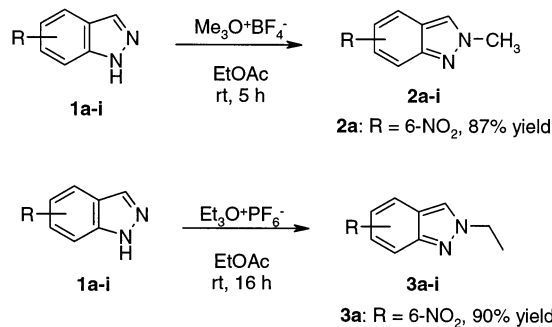
Abstract: An efficient and regioselective synthesis of 2-methyl-2H-indazoles and 2-ethyl-2H-indazoles using trimethyloxonium tetrafluoroborate or triethyloxonium hexafluorophosphate is reported.

As part of a drug discovery program, we needed to prepare a large quantity of 2-methyl-6-nitro-2H-indazole (**2a**) as a synthetic intermediate. Morel et al. and Boyer et al. reported the methylation of 6-nitro-1H-indazole (**1a**) using dimethyl sulfate in the presence of potassium hydroxide at 45 °C.¹ However, due to a lack of regioselectivity of the reaction, approximately 1:1 mixtures of 1-methyl-6-nitro-1H-indazole (42% yield) and 2-methyl-6-nitro-2H-indazole (44% yield) were obtained.



Auwers et al. reported a regioselective methylation at the 2-position of 6-nitro-1H-indazole by heating with methyl iodide (4 equiv) at 100 °C in a sealed tube for 4 h;² however, no yield was mentioned in the report. When we repeated this experiment, 2-methyl-6-nitro-2H-indazole was isolated in about 30% yield with a trace of 1-methylated product. Upon heating the reaction for 15 h, only dimethylated product (1,2-dimethyl-6-nitroindazolium iodide) was observed. Jaffari et al. also reported the regioselective methylation of 6-nitro-1H-indazole using alkylating agents such as methyl iodide, methyl toluene-*p*-sulfonate, or diazomethane.³ Interestingly, the regioselectivity of the indazoles was highly dependent on the nature of the methylating agents. For example, methylation of 6-nitro-1H-indazole using methyl iodide (MeI, Me₂SO, 70 °C, 5 h) resulted in mixtures of 2-methyl-6-nitro-2H-indazole (50% yield), 1-methyl-6-nitro-1H-indazole (10% yield), and dimethylated product (17% yield). Methylation of 6-nitro-1H-indazole using methyl toluene-*p*-sulfonate (*p*-TsOMe, PhNO₂, 90 °C, 5 h) re-

SCHEME 1. Synthesis of 2-Alkyl-substituted 2H-Indazoles



sulted in 50% yield of 2-methylated product with 25% yield of recovered starting material. On the contrary, methylation of 6-nitro-1H-indazole using diazomethane in the presence of BF₃ (CH₂N₂, BF₃-Et₂O, 70 °C, 6 h) resulted in a 75% yield of 1-methylated product. In addition to regioselective methodology, Boyer et al. reported a slow and clean conversion of (2,4-dinitrophenyl)-*N,N*-dimethylmethanamine to 2-methyl-6-nitro-2H-indazole at room temperature.⁴ However, the reaction required 2 months to go to completion.

After failing to find a literature procedure for an efficient synthesis of 2-methyl-6-nitro-2H-indazole, we initiated our own efforts to develop a more satisfactory method. Since the regioselectivity of the indazoles was highly dependent on the nature of the methylating agents, we turned our attention to other known alkylating agents. Trimethyloxonium tetrafluoroborate is a powerful methylating agent that has been used to methylate many different functional groups.⁵ As shown in Scheme 1, treatment of 6-nitro-1H-indazole (**1a**) with trimethyloxonium tetrafluoroborate (1.3 equiv) at room temperature for 5 h in ethyl acetate gave exclusively 2-methyl-6-nitro-2H-indazole (**2a**) in 87% yield. We also investigated ethylation using triethyloxonium tetrafluoroborate (Meerwein's salt).⁶ When **1a** was treated with a solution of triethyloxonium tetrafluoroborate in CH₂-Cl₂ (1.5 or 2.5 equiv) at room temperature for 16 h, 2-ethyl-6-nitro-2H-indazole was isolated in ~50% yield with starting material recovered. However, when **1a** was treated with triethyloxonium hexafluorophosphate at room temperature for 16 h in ethyl acetate, 2-ethyl-6-nitro-2H-indazole (**3a**) was isolated in 90% yield.

The scope of this regioselective alkylation was explored using a variety of indazoles (**1a-i**), containing either electron-donating (e.g., methoxy) or electron-withdrawing (e.g., chloro, nitro) groups or no aromatic substituent at all (**1e**). The regioselective alkylation can be applied to all substrates regardless of the electronic properties of the indazole rings. As shown in Table 1, 2-methyl deriv-

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(1) (a) Morel, S.; Boyer, G.; Coulet, F.; Galy, J.-P. *Synth. Commun.* **1996**, 26, 2443. (b) Boyer, G.; Galy, J. P.; Barbe, J. *Heterocycles* **1995**, 41, 487.

(2) (a) Auwers, K.V.; Schwegler, K. *Chem. Ber.* **1920**, 53, 1211. (b) Witt, O. N.; Nölting, E.; Grandmougin, E. *Chem. Ber.* **1890**, 23, 3635.

(3) Jaffari, G. A.; Nunn, A. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2371.

(4) Boyer, J. H.; Pagoria, P. F.; Pillai, T. P.; Pace, M. D.; Stec, D. J. *Chem. Res., Synop.* **1986**, 416.

(5) Stahl, I. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: Chichester, 1995; Vol. 7, pp 5213–5216.

(6) Perst, H. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: Chichester, 1995; Vol. 7, pp 5105–5112.

TABLE 1. Preparation of 2-Alkyl-substituted 2H-Indazoles

entry	1H-indazole 1	2-methyl-2H-indazole ^a 2 (% yield) ^b	2-ethyl-2H-indazole ^a 3 (% yield) ^b
a	R = 6-NO ₂	87	90
b	R = 4-NO ₂	90	82
c	R = 5-NO ₂	90	94
d	R = 7-NO ₂	93	91
e	R = H	93	90
f	R = 5-Cl	88	88
g	R = 6-Cl	86	93
h	R = 5-OMe	96	95
i	R = 6-OMe	94	90

^a Typical procedures are provided in the Experimental Section. Conditions for the synthesis of 2-methyl-2H-indazoles **2a–i**: **1** (1 mmol), Me₃OPF₆ (1.3 mmol), EtOAc (3 mL), rt, 5 h. Conditions for the synthesis of 2-ethyl-2H-indazoles **3a–i**: **1** (1 mmol), Et₃OPF₆ (1.5 mmol), EtOAc (3 mL), rt, 16 h. ^b Satisfactory spectroscopic data were obtained for all products.

atives (**2a–i**) were isolated in 86–96% yield, and 2-ethyl derivatives (**3a–i**) were isolated in 82–95% yield.⁷

In conclusion, we have developed an efficient and regioselective synthesis of 2-methyl-2H-indazoles and 2-ethyl-2H-indazoles using trimethyloxonium tetrafluoroborate or triethyloxonium hexafluorophosphate as alkylating agents. This methodology can be applied to various indazoles regardless of the electronic properties of the indazole rings.

Experimental Section

NMR spectra were recorded at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR. NMR chemical shifts are expressed in parts per million relative to the internal solvent peak. Coupling constants were calculated in hertz. MS spectra were obtained by using electrospray ionization (ESI). Melting points were recorded when applicable. Elemental analysis data were obtained for all compounds.

General Procedure for the Synthesis of 2-Methyl-substituted 2H-Indazoles: Preparation of 2-Methyl-6-nitro-2H-indazole (2a). To a stirred mixture of 6-nitro-1H-indazole (163 mg, 1 mmol) in EtOAc (3 mL) was added trimethyloxonium tetrafluoroborate (192 mg, 1.3 mmol). The mixture was stirred at room temperature for 5 h under N₂. The reaction mixture was diluted with 20 mL of EtOAc and washed with 20 mL of saturated NaHCO₃ solution. The organic layer was separated, and the aqueous layer was extracted with EtOAc (20 mL X 2). The combined organic layers were dried over anhydrous MgSO₄, filtered, and evaporated. Purification of the product by column chromatography (1:1 EtOAc/hexane) gave 2-methyl-6-nitro-2H-indazole (154 mg, 87%) as a yellow solid: mp 158–160 °C (EtOAc) (lit.³ mp 160 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.58 (s, 2H), 7.94 (d, 1H, *J* = 9.1 Hz), 7.78 (dd, 1H, *J* = 9.1 and 1.9 Hz), 4.25 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 146.58, 146.36, 126.97, 124.94, 123.12, 115.21, 115.12, 41.49; MS (+ve ES) 178 (M + H). Anal. Calcd for C₈H₇N₃O₂: C, 54.24; H, 3.98; N, 23.72; O, 18.06. Found: C, 54.25; H, 3.97; N, 23.68; O, 17.88.

General Procedure for the Synthesis of 2-Ethyl-substituted 2H-Indazoles: Preparation of 2-Ethyl-6-nitro-2H-indazole (3a). To a stirred mixture of 6-nitro-1H-indazole (163 mg, 1 mmol) in EtOAc (3 mL) was added triethyloxonium hexafluorophosphate (372 mg, 1.5 mmol). The mixture was stirred at room temperature for 16 h under N₂. The reaction

mixture was diluted with 20 mL of EtOAc and washed with 20 mL of saturated NaHCO₃ solution. The organic layer was separated, and the aqueous layer was extracted with EtOAc (20 mL X 2). The combined organic layers were dried over anhydrous MgSO₄, filtered, and evaporated. Purification of the product by column chromatography (1:1 EtOAc/hexane) gave 2-ethyl-6-nitro-2H-indazole (172.3 mg, 90%) as a yellow solid: mp 87–89 °C (EtOAc) (lit.⁸ mp 89–90 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.64 (s, 1H), 8.60 (s, 1H), 7.94 (d, 1H, *J* = 9.1 Hz), 7.79 (dd, 1H, *J* = 9.1 and 2.0 Hz), 4.54 (q, 2H, *J* = 7.3 Hz), 1.52 (t, 3H, *J* = 7.3 Hz); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 146.44, 146.37, 125.62, 124.75, 123.22, 115.34, 115.22, 49.35, 16.27; MS (+ve ES) 192 (M + H). Anal. Calcd for C₉H₉N₃O₂: C, 56.54; H, 4.74; N, 21.98; O, 16.74. Found: C, 56.69; H, 4.78; N, 22.04; O, 16.74.

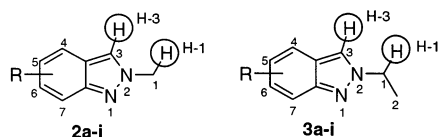
2-Methyl-4-nitro-2H-indazole (2b). Yellow solid: mp 100–102 °C (EtOAc) (lit.³ mp 101 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.84 (s, 1H), 8.16 (m, 2H), 7.46 (t, 1H, *J* = 8.0 Hz), 4.26 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 149.91, 140.59, 126.69, 126.19, 125.05, 120.98, 114.74, 41.19; MS (+ve ES) 178 (M + H). Anal. Calcd for C₈H₇N₃O₂: C, 54.24; H, 3.98; N, 23.72; O, 18.06. Found: C, 54.04; H, 3.95; N, 23.54; O, 18.21.

2-Methyl-5-nitro-2H-indazole (2c). Yellow solid: mp 127–129 °C (EtOAc) (lit.⁹ mp 129 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.86 (d, 1H, *J* = 2.1 Hz), 8.74 (s, 1H), 7.97 (dd, 1H, *J* = 9.5 and 2.1 Hz), 7.74 (d, 1H, *J* = 9.5 Hz), 4.22 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 149.77, 142.47, 130.54, 121.00, 120.68, 120.11, 118.45, 41.30; MS (+ve ES): 178 (M + H). Anal. Calcd for C₈H₇N₃O₂: C, 54.24; H, 3.98; N, 23.72; O, 18.06. Found: C, 54.28; H, 4.06; N, 23.71; O, 17.94.

2-Methyl-7-nitro-2H-indazole (2d). Yellow solid: mp 144–145 °C (EtOAc) (lit.³ mp 143 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.73 (s, 1H), 8.26 (m, 2H), 7.23 (t, 1H, *J* = 8.0 Hz), 4.26 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 140.28, 137.04, 130.67, 128.47, 126.06, 125.33, 120.34, 41.27; MS (+ve ES) 178 (M + H). Anal. Calcd for C₈H₇N₃O₂: C, 54.24; H, 3.98; N, 23.72; O, 18.06. Found: C, 54.29; H, 3.98; N, 23.82; O, 17.95.

2-Methyl-2H-indazole (2e). White solid: mp 55–57 °C (EtOAc) (lit.¹⁰ mp 56 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.29 (s, 1H), 7.66 (d, 1H, *J* = 8.4 Hz), 7.56 (d, 1H, *J* = 8.5 Hz), 7.19 (t, 1H, *J* = 7.5 Hz), 6.99 (t, 1H, *J* = 7.5 Hz), 4.14 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 148.76, 125.87, 125.05, 122.29, 121.48, 121.06, 117.38, 40.61; MS (+ve ES) 133 (M + H). Anal. Calcd for C₈H₈N₂·0.4H₂O: C, 68.94; H, 6.36; N, 20.10. Found: C, 69.07; H, 6.23; N, 20.19.

5-Chloro-2-methyl-2H-indazole (2f). White solid: mp 62–64 °C (EtOAc); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.37 (s, 1H), 7.73 (d, 1H, *J* = 8.9 Hz), 7.64 (s, 1H), 6.98 (dd, 1H, *J* = 8.9 and 1.8 Hz), 4.14 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 148.81, 130.76, 126.09, 123.19, 122.42, 120.79, 116.23, 40.83; MS (+ve



(8) Kametani, T.; Kigasawa, K.; Hirragi, M.; Wakisaka, K.; Kusama, O.; Sugi, H.; Kawasaki, K. *J. Heterocycl. Chem.* **1977**, *14*, 1175.

(9) Barclay, I. M.; Campbell, N.; Dodds, G. *J. Chem. Soc.* **1941**, 113.

(10) Frontana-Urbe, B. A.; Moinet, C. *Tetrahedron* **1998**, *54*, 3197.

ES) 167 (M + H). Anal. Calcd for $C_8H_7ClN_2$: C, 57.67; H, 4.23; Cl, 21.28; N, 16.81. Found: C, 57.41; H, 4.20; Cl, 21.01; N, 16.83.

6-Chloro-2-methyl-2H-indazole (2g). Tan solid: mp 70 °C (EtOAc); 1H NMR (400 MHz, DMSO- d_6) δ 8.30 (s, 1H), 7.76 (d, 1H, J = 1.8 Hz), 7.60 (d, 1H, J = 9.1 Hz), 7.17 (dd, 1H, J = 9.1 and 1.9 Hz), 4.14 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 147.05, 126.76, 125.98, 125.27, 122.69, 119.96, 119.47, 40.83. MS (+ve ES) 167 (M + H). Anal. Calcd for $C_8H_7ClN_2$: C, 57.67; H, 4.23; Cl, 21.28; N, 16.81. Found: C, 57.41; H, 4.26; Cl, 21.49; N, 16.65.

5-Methoxy-2-methyl-2H-indazole (2h). Yellow oil: 1H NMR (400 MHz, DMSO- d_6) δ 8.16 (s, 1H), 7.52 (d, 1H, J = 9.1), 6.88 (d, 1H, J = 1.8 Hz), 6.66 (dd, 1H, J = 9.1 and 1.8 Hz), 4.06 (s, 3H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 158.47, 149.74, 125.10, 121.87, 117.67, 115.90, 95.10, 55.62, 40.33; MS (+ve ES) 163 (M + H). Anal. Calcd for $C_9H_{10}N_2O \cdot 0.3 H_2O$: C, 64.50; H, 6.38; N, 16.72. Found: C, 64.63; H, 6.33; N, 16.74.

6-Methoxy-2-methyl-2H-indazole (2i). White solid: mp 72–74 °C (EtOAc); 1H NMR (400 MHz, DMSO- d_6) δ 8.11 (s, 1H), 7.46 (d, 1H, J = 9.3 Hz), 6.96 (d, 1H, J = 2.3 Hz), 6.86 (dd, 1H, J = 9.3 and 2.3 Hz), 4.08 (s, 3H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 154.73, 145.35, 124.06, 122.20, 120.19, 118.77, 97.80, 55.71, 40.49; MS (+ve ES) 163 (M + H). Anal. Calcd for $C_9H_{10}N_2O \cdot 0.4 H_2O$: C, 63.81; H, 6.43; N, 16.54. Found: C, 63.95; H, 6.37; N, 16.54.

2-Ethyl-4-nitro-2H-indazole (3b). Yellow solid: mp 75–77 °C (EtOAc); 1H NMR (400 MHz, DMSO- d_6) δ 8.87 (s, 1H), 8.16 (m, 2H), 7.46 (t, 1H, J = 8.0 Hz), 4.56 (q, 2H, J = 7.3 Hz), 1.52 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, DMSO- d_6) δ 149.81, 140.68, 126.86, 125.00, 124.87, 120.98, 114.55, 49.07, 16.36; MS (+ve ES) 192 (M + H). Anal. Calcd for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98; O, 16.74. Found: C, 56.68; H, 4.78; N, 21.98; O, 16.68.

2-Ethyl-5-nitro-2H-indazole (3c). Yellow solid: mp 62–64 °C (EtOAc); 1H NMR (400 MHz, DMSO- d_6) δ 8.83 (s, 1H), 8.78 (s, 1H), 7.97 (d, 1H, J = 9.4 Hz), 7.74 (d, 1H, J = 9.4 Hz), 4.53 (q, 2H, J = 7.3 Hz), 1.50 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, DMSO- d_6) δ 149.64, 142.46, 129.18, 121.03, 120.44, 120.05, 118.61, 49.14, 16.05; MS (+ve ES) 192 (M + H). Anal. Calcd for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98; O, 16.74. Found: C, 56.61; H, 4.75; N, 21.98; O, 16.62.

2-Ethyl-7-nitro-2H-indazole (3d). Yellow solid: mp 74–76 °C (EtOAc) (lit.¹¹ mp 73–74 °C); 1H NMR (400 MHz, DMSO- d_6) δ 8.78 (s, 1H), 8.28 (d, 1H, J = 7.7 Hz), 8.24 (d, 1H, J = 8.2 Hz), 7.22 (m, 1H), 4.55 (q, 2H, J = 7.3 Hz), 1.52 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, DMSO- d_6) δ 140.13, 137.22, 130.73, 127.02, 125.93, 125.32, 120.32, 49.12, 16.33; MS (+ve ES) 192 (M + H). Anal. Calcd for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98; O, 16.74. Found: C, 56.67; H, 4.80; N, 21.98; O, 16.56.

2-Ethyl-2H-indazole (3e). Colorless oil (lit.¹⁰ colorless oil); 1H NMR (400 MHz, DMSO- d_6) δ 8.34 (s, 1H), 7.66 (d, 1H, J = 8.4 Hz), 7.57 (d, 1H, J = 8.7 Hz), 7.19 (m, 1H), 6.99 (m, 1H), 4.42 (q, 2H, J = 7.3 Hz), 1.48 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, DMSO- d_6) δ 148.59, 125.82, 123.59, 122.07, 121.45, 121.16, 117.57, 48.38, 16.44; MS (+ve ES) 147 (M + H). Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.84; H, 6.93; N, 19.24.

2-Ethyl-5-chloro-2H-indazole (3f). Yellow oil; 1H NMR (400 MHz, DMSO- d_6) δ 8.36 (s, 1H), 7.77 (d, 1H, J = 1.9 Hz), 7.62 (d, 1H, J = 9.1 Hz), 7.18 (dd, 1H, J = 9.1 and 1.9 Hz), 4.43 (q, 2H, J = 7.3 Hz), 1.47 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, DMSO- d_6) δ 146.89, 126.74, 125.95, 123.87, 122.45, 120.05, 119.67, 48.62, 16.33; MS (+ve ES) 181 (M + H). Anal. Calcd for $C_9H_9N_2Cl$: C, 59.84; H, 5.02; N, 15.51; Cl, 19.63. Found: C, 59.87; H, 4.94; N, 15.61; Cl, 19.61.

2-Ethyl-6-chloro-2H-indazole (3g). Off-white solid: mp 59–61 °C (EtOAc); 1H NMR (400 MHz, DMSO- d_6) δ 8.42 (s, 1H), 7.72 (d, 1H, J = 8.8 Hz), 7.66 (s, 1H), 6.99 (d, 1H, J = 8.8 Hz), 4.52 (q, 2H, J = 7.2 Hz), 1.47 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, DMSO- d_6) δ 148.66, 130.75, 124.66, 123.26, 122.41, 120.57, 116.42, 48.60, 16.30; MS (+ve ES) 181 (M + H). Anal. Calcd for $C_9H_9N_2Cl$: C, 59.84; H, 5.02; N, 15.51; Cl, 19.63. Found: C, 59.96; H, 4.94; N, 15.69; Cl, 19.48.

2-Ethyl-5-methoxy-2H-indazole (3h). Off-white solid: mp 79–81 °C (EtOAc); 1H NMR (400 MHz, DMSO- d_6) δ 8.15 (s, 1H), 7.48 (d, 1H, J = 9.1 Hz), 6.96 (s, 1H), 6.87 (dd, 1H, J = 9.1 and 1.6 Hz), 4.36 (q, 2H, J = 7.3 Hz), 3.73 (s, 3H), 1.45 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, DMSO- d_6) δ 154.74, 145.21, 122.59, 121.97, 120.18, 118.96, 97.89, 55.72, 48.22, 16.46; MS (+ve ES) 177 (M + H). Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90; O, 9.08. Found: C, 68.23; H, 6.89; N, 15.89; O, 8.98.

2-Ethyl-6-methoxy-2H-indazole (3i). Yellow oil; 1H NMR (400 MHz, DMSO- d_6) δ 8.20 (s, 1H), 7.52 (d, 1H, J = 9.1 Hz), 6.90 (s, 1H), 6.66 (dd, 1H, J = 9.1 and 2.2 Hz), 4.34 (q, 2H, J = 7.3 Hz), 3.75 (s, 3H), 1.45 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, DMSO- d_6) δ 158.44, 149.54, 123.64, 121.95, 117.44, 115.89, 95.31, 55.62, 48.05, 16.41; MS (+ve ES) 177 (M + H). Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90; O, 9.08. Found: C, 68.21; H, 6.84; N, 15.90; O, 9.00.

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Supporting Information Available: Data from 1H NMR and ROESY experiments for 1-methyl-6-nitro-1H-indazole and 2-methyl-6-nitro-2H-indazole. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(11) Balasubrahmanyam, S. N.; Radhakrishna, A. S. *J. Org. Chem.* **1977**, *42*, 897.