An optimized procedure for direct access to 1H-Indazole-3-carboxaldehyde derivatives by nitrosation of indoles.

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I. Materials and Methods

Commercially available reagents were used without further purification. Column chromatography purifications were performed on silica gel (40-63 μm). Thin-layer chromatography (TLC) analyses were carried out on Merck DC Kieselgel 60 F-254 aluminum sheets. The spots were visualized through illumination with UV lamp (λ = 254 nm and 360 nm) and/or staining with 4-hydrazinobenzenesulfonic acid. IR spectra were recorded with an ATR diamant Perkin Elmer. 1H and 13C NMR spectra (C13APT or C13CPD experiments) were recorded on a Bruker AVIII 300 MHz spectrometer (BBFO). Chemical shifts are expressed in parts per million (ppm) from the residual non-deuterated solvent signal contained in CDCl3 (δH = 7.26, δC = 77.16), in Acetone-d6 (δH = 2.05, δC = 29.84) and in DMSO-d6 (δH = 2.50, δC = 39.52). Multiplicities are described as s (singlet), d (doublet), t (triplet), brs (broad peak) etc. Coupling constants, J values, are reported in Hz. High-resolution mass spectra (HRMS) were obtained using an orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer equipped with an electrospray source and in the positive and negative modes (ESI+/-).
II. Copies of 1H and 13C NMR

1H-Indazole-3-carboxaldehyde (1b)
5-Bromo-1H-Indazole-3-carboxaldehyde (11b)
5-chloro-1H-indazole-3-carboxaldehyde (12b)
5-iodo-1H-indazole-3-carboxaldehyde (13b)
5-fluoro-1H-indazole-3-carboxaldehyde (14b)
6-bromo-1H-Indazole-3-carboxaldehyde (15b)
6-fluoro-1H-indazole-3-carboxaldehyde (16b).
5-Methoxy-1H-Indazole-3-carboxaldehyde (17b)
5-Benzylxoy-1H-indazole-3-carboxaldehyde (18b)
1-(1H-indazol-3-yl)ethanone (19b)
7-methyl-1H-indazole-3-carboxaldehyde (20b)
5-carboxy-1H-Indazole-3-carboxaldehyde (21b)
5-NHBOc -1H-indazole-3-carboxaldehyde (22b)
5-piperidyl-1H-indazole-3-carboxaldehyde (23b)
1H-indazole-3,5-dicarboxaldehyde (24b)
5-cyano-1H-indazole-3-carboxaldehyde (25b)
5-nitro-1H-indazole-3-carboxaldehyde (26b).
6-nitro-1H-indazole-3-carboxaldehyde (27b)
