General Experimental Details

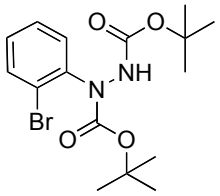
Commercially available reagents were used throughout without purification unless otherwise stated. Anhydrous DMF, DMSO, acetonitrile, chloroform and methanol were used as supplied. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen atmosphere. Dichloromethane was distilled from calcium hydride under a nitrogen atmosphere. Light petroleum refers to the fraction with bp 40-60 °C. Ether refers to diethyl ether. Reactions were routinely carried out under a nitrogen or argon atmosphere. Analytical thin layer chromatography was carried out on aluminum backed plates coated with silica gel, and visualized under UV light at 254 and/or 360 nm and/or potassium permanganate or ethanolic vanillin dip. Chromatography was carried out on silica gel. Fully characterized compounds were chromatographically homogeneous. Infrared spectra were recorded in the range 4000-600 cm^{-1} as solutions in chloroform. NMR spectra were recorded on a 400 MHz (^{1}H frequency) spectrometer. Chemical shifts are quoted in ppm and *J* values in Hz. Chemical shift values are referenced against residual proton in the deuterated solvents. In the ^{13}C NMR spectra, signals corresponding to CH, CH_2, or CH_3 are assigned from DEPT spectra; all others are quaternary C. High and low resolution mass spectra were recorded on a time-of-flight spectrometer.

General procedure: Synthesis of aryl hydrazides from aryl iodides

An oven-dried flask was cooled to room temperature under argon and charged with a solution of aryl iodide (1.0 mol equiv) in THF (4-20 mL/mmol), then cooled to -20 °C. A solution of isopropylmagnesium chloride in THF (2.0 M; 1.1 mol equiv) was added dropwise over 5 min, and the resulting mixture was stirred at -20 °C for 1 h then 0 °C for 1 h. A solution of di-*tert*-butyl azodicarboxylate (1.3 mol equiv) in THF

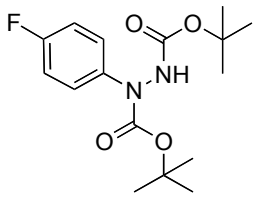
(4 mL/mmol) was added dropwise over 5 min at 0 °C, and the resulting mixture was stirred at 0 °C to room temperature for 3 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution (20 ml/10 mmol)), diluted with water (50 mL/10 mmol), and extracted with ethyl acetate (3 × 40 mL/10 mmol). The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Column chromatography of the residue gave the product.

Di-*tert*-Butyl 1-(2-bromophenyl)hydrazine-1,2-dicarboxylate 2a



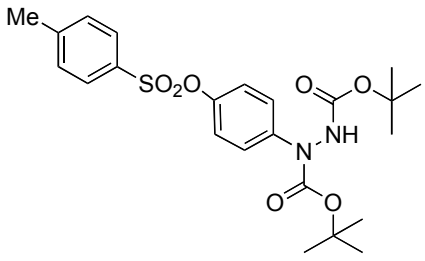
Prepared by the general procedure from 2-bromoiodobenzene (2.83 g, 10 mmol) and di-*tert*-butyl azodicarboxylate (2.99 g, 13 mmol), and isolated by chromatography eluting with light petroleum and ethyl acetate (11:1 v/v) as a mixture of rotamers, as a colorless oil (2.771 g, 72%), mp 94-96 °C; (Found: $M+Na^+$, 409.0737. $C_{16}H_{23}{}^{79}BrNaN_2O_4$ requires 409.0739); ν_{max} ($CHCl_3$)/cm^{-1} 3401, 2983, 1716, 1480, 1370, 1244, 1155; δ_H (400 MHz; $CDCl_3$) 7.71 (1H, br s, ArH), 7.58 (1H, d, *J* 7.9, ArH), 7.33 (1H, m, ArH), 7.18 (1H, td, *J* 7.5, 1.5, ArH), 6.97 (1H, br s, NH), 1.49 (18H, s, *t*Bu); δ_C (100 MHz; $CDCl_3$) 155.3, 154.8, 153.7, 141.2, 140.6, 132.8 (CH), 132.6 (CH), 131.2 (CH), 129.5 (CH), 129.4 (CH), 128.3 (CH), 128.1 (CH), 122.7 (CH), 122.6 (CH), 82.3, 81.6, 81.5, 28.2 (Me), 28.1 (Me), 28.0 (Me); *m/z* (EI) 409 ($M+Na^+$, 99%), 411 ($M+Na^+$, 100).

Di-*tert*-Butyl 1-(4-fluorophenyl)hydrazine-1,2-dicarboxylate 2b



Prepared by the general procedure from 4-fluoroiodobenzene (2.22 g, 10 mmol) and di-*tert*-butyl azodicarboxylate (2.99 g, 13 mmol), and isolated by chromatography eluting with light petroleum and ethyl acetate (9:1 v/v) as a colorless oil (3.03 g, 93%), mp 128-130 °C; (Found: M+Na^+, 349.1541. $C_{16}H_{23}FNaN_2O_4$ requires 349.1534); ν_{max} ($CHCl_3$)/cm^{-1} 3402, 2983, 1746, 1716, 1510, 1370, 1152; δ_H (400 MHz; $CDCl_3$) 7.39 (2H, br s, ArH), 7.02 (2H, dd, *J* 8.8, 8.6, ArH), 6.77 (1H, br s, NH), 1.51 (18H, s, *t*Bu); δ_C (100 MHz; $CDCl_3$) 160.5 (d, *J* 246, CF), 155.4, 153.7, 138.3, 125.9 (CH), 115.2 (d, *J* 23, CH), 85.5, 81.7, 28.2 (Me), 28.1 (Me); *m/z* (EI) 349 (M+Na^+, 100).

Di-*tert*-Butyl 1-(4-(tosyloxy)phenyl)hydrazine-1,2-dicarboxylate 2c

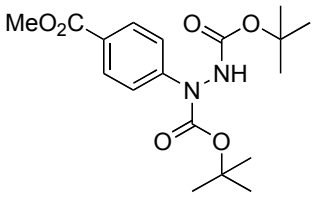


(a) Prepared by the general procedure from 4-iodophenyl 4-toluenesulfonate (3.74 g, 10 mmol) and di-*tert*-butyl azodicarboxylate (2.99 g, 13 mmol), and isolated by chromatography eluting with light petroleum and ethyl acetate (6:1 v/v) as a colorless solid (4.16 g, 87%), mp 110-112 °C; (Found: M+Na^+, 501.1679, $C_{23}H_{30}NaN_2O_7S$ requires 501.1671); ν_{max} ($CHCl_3$)/cm^{-1} 3403, 2934, 1720, 1371; δ_H (400 MHz; $CDCl_3$) 7.71 (2H, d, *J* 8.0, ArH), 7.36 (2H, d, *J* 8.6, ArH), 7.31 (2H, d, *J* 8.0, ArH), 6.93 (2H, d, *J* 8.6, ArH), 2.46 (3H, s, Me), 1.49 (18H, s, *t*Bu); δ_C (100 MHz; $CDCl_3$) 155.3,

153.2, 146.6, 145.3, 140.9, 132.3, 129.8 (CH), 128.6 (CH), 124.2 (CH), 122.3 (CH), 82.7, 81.9, 28.2 (Me), 28.1 (Me), 21.7 (Me); *m/z* (EI) 979 (2M+Na^+, 90%), 580 (100), 501 (M+Na^+, 45).

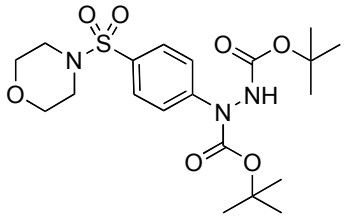
(b) Prepared by the general procedure from 4-bromophenyl 4-toluenesulfonate with the metalation step carried out at room temperature for 6 h before the addition of the di-*tert*-butyl azodicarboxylate at 0 °C, Following work up and chromatography, the title compound was obtained in 76% yield.

Di-*tert*-Butyl 1-(4-(methoxycarbonyl)phenyl)hydrazine-1,2-dicarboxylate 2d



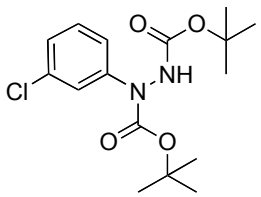
Prepared by the general procedure from methyl 4-iodobenzoate (2.62 g, 10 mmol) and di-*tert*-butyl azodicarboxylate (2.99 g, 13 mmol), and isolated by chromatography eluting with light petroleum and ethyl acetate (7:1 v/v) as a colorless solid (2.609 g, 71%), mp 104-106 °C; (Found: M+Na^+, 389.1693. $C_{18}H_{26}NaN_2O_6$ requires 389.1683); ν_{max} ($CHCl_3$)/cm^{-1} 3402, 3011, 2983, 1747, 1719, 1283; δ_H (400 MHz; $CDCl_3$) 8.00 (2H, d, *J* 7.6, ArH), 7.55 (2H, d, *J* 7.6, ArH), 6.76 (1H, br s, NH), 3.92 (3H, s, OMe), 1.54 (18H, s, *t*Bu); δ_C (100 MHz; $CDCl_3$) 166.7, 155.3, 152.9, 146.1, 130.0 (CH), 126.2, 121.6 (CH), 83.1, 82.0, 52.0 (Me), 28.2 (Me), 28.1 (Me); *m/z* (EI) 755 (2M+Na^+, 100%), 389 (M+Na^+, 11).

Di-*tert*-Butyl 1-(4-(morpholinosulfonyl)phenyl)hydrazine-1,2-dicarboxylate 2e



Prepared by the general procedure from *N-(*4-iodobenzenesulfonyl)morpholine (2.118 g, 6 mmol) and di-*tert*-butyl azodicarboxylate (1.794 g, 7.8 mmol), and isolated by chromatography eluting with light petroleum and ethyl acetate (3:1 v/v) as a colorless solid (2.031 g, 74%), mp 179-181 °C; (Found: M+Na^+, 480.1763. $C_{20}H_{31}NaN_3O_7S$ requires 480.1775); ν_{max} ($CHCl_3$)/cm^{-1} 3401, 2930, 1747, 1726, 1320, 1163; δ_H (400 MHz; $CDCl_3$) 7.70 (4H, m, ArH), 6.74 (1H, br s, NH), 3.75 (4H, t, *J* 4.6, CH_2O), 3.02 (4H, t, *J* 4.6, CH_2N), 1.54 (18H, s, *t*Bu); δ_C (100 MHz; $CDCl_3$) 155.2, 152.7, 146.3, 130.5, 128.4 (CH), 121.8 (CH), 83.6, 82.4, 66.1 (CH_2), 46.0 (CH_2), 28.2 (Me), 28.1 (Me); *m/z* (EI) 480 (M+Na^+, 100%).

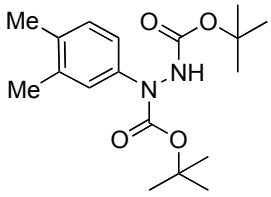
Di-*tert*-Butyl 1-(3-chlorophenyl)hydrazine-1,2-dicarboxylate 2f



Prepared by the general procedure from 3-chloroiodobenzene (2.38 g, 10 mmol) and di-*tert*-butyl azodicarboxylate (2.99 g, 13 mmol), and isolated by chromatography eluting with light petroleum and ethyl acetate (9:1 v/v) as a colorless solid (2.76 g, 81%), mp 95-97 °C (Found: M+Na^+, 365.1241. $C_{16}H_{23}{}^{35}ClNaN_2O_4$ requires 365.1239); ν_{max} ($CHCl_3$)/cm^{-1} 3403, 2971, 1721; δ_H (400 MHz; $CDCl_3$) 7.49 (1H, br s, ArH), 7.33 (1H, br, ArH), 7.25 (t, *J* 8.0, ArH), 7.14 (1H, d, *J* 8.0), 6.74 (1H, br s, NH), 1.53 (18H, *t*Bu); δ_C (100 MHz; $CDCl_3$) 155.3, 153.2, 143.2, 133.9 (CH), 129.3

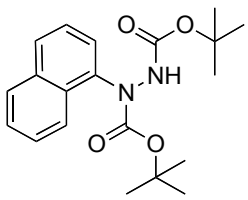
(CH), 125.4 (CH), 123.3 (CH), 121.2 (CH), 82.9, 82.0, 28.2 (Me), 28.1 (Me); *m/z* (EI) 707 ($2M+Na^+$, 100%), 365 ($M+Na^+$, 63).

Di-*tert*-Butyl 1-(3,4-dimethylphenyl)hydrazine-1,2-dicarboxylate 2g



Prepared by the general procedure from 4-iodo-*o*-xylene (2.32 g, 10 mmol) and di-*tert*-butyl azodicarboxylate (2.99 g, 13 mmol), and isolated by chromatography eluting with light petroleum and ethyl acetate (9:1 v/v) as a colorless solid (2.551 g, 76%), mp 94-96 °C; (Found: $M+Na^+$, 359.1947. $C_{18}H_{28}NaN_2O_4$ requires 359.1947); ν_{max} ($CHCl_3$)/cm^{-1} 3404, 3011, 2982, 1934, 1715, 1370; δ_H (400 MHz; $CDCl_3$) 7.21 (1H, br, ArH), 7.13 (1H, br, ArH), 7.08 (d, *J* 8.1, ArH), 6.85 (1H, br s, NH); 2.25 (3H, s, Me), 2.23 (3H, s, Me), 1.49 (18H, s, *t*Bu); δ_C (100 MHz; $CDCl_3$) 155.7, 155.4, 139.9, 136.6, 134.1, 129.5 (CH), 125.3 (CH), 121.5 (CH), 81.9, 81.3, 28.3 (Me), 28.2 (Me), 19.9 (Me), 19.2 (Me); *m/z* (EI) 695 (100%), 359 ($M+Na^+$, 10).

Di-*tert*-Butyl 1-(naphthalen-1-yl)hydrazine-1,2-dicarboxylate 2h

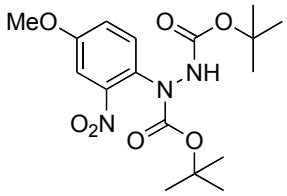


(a) Prepared by the general procedure from 1-iodonaphthalene (2.54 g, 10 mmol) and di-*tert*-butyl azodicarboxylate (2.99 g, 13 mmol), and isolated by chromatography eluting with light petroleum and ethyl acetate (11:1 v/v) as a colorless solid (3.52 g, 98%), mp 144-146 °C; (Found: $M+Na^+$, 381.1793. $C_{20}H_{26}NaN_2O_4$ requires

381.1785); ν_{max} ($CHCl_3$)/cm^{-1} 3401, 2983, 1745, 1714, 1370, 1153; δ_H (400 MHz; $CDCl_3$) 7.98 (1H, br, ArH), 7.88 (1H, d, *J* 8.0, ArH), 7.83 (1H, d, *J* 8.4, ArH), 7.70 (1H, br, ArH), 7.57-7.47 (3H, m, ArH); 7.01 (1H, br s, NH); 1.57 (18H, s, *t*Bu); δ_C (100 MHz; $CDCl_3$) 155.6, 155.0, 138.8, 134.3, 130.2, 128.3 (CH), 126.5 (CH), 126.0 (CH), 125.6 (CH), 122.9 (CH), 82.0, 81.4, 28.3 (Me), 28.1 (Me); two C unobserved; *m/z* (EI) 739 ($2M+Na^+$, 66%), 734 (49), 418 (100), 381 ($M+Na^+$, 86).

(b) Prepared by the general procedure from 1-bromonaphthalene with the metalation step carried out at room temperature for 9 h before the addition of the di-*tert*-butyl azodicarboxylate at 0 °C, Following work up and chromatography, the title compound was obtained in 66% yield.

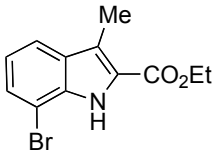
Di-*tert*-Butyl 1-(4-methoxy-2-nitrophenyl)hydrazine-1,2-dicarboxylate 2i



Phenylmagnesium chloride (2 M solution in THF; 13.75 mL, 27.5 mmol) was added dropwise over 10 min to a stirred solution of 4-iodo-3-nitroanisole (6.975 g, 25 mmol) in THF (100 mL) at -40 °C under argon. The resulting mixture was stirred at that temperature for 25 min, then di-*tert*-butyl azodicarboxylate (7.475 g, 32.5 mmol) in THF (25 mL) was added dropwise over 15 min. The resulting mixture was stirred at -40 °C for 30 min, then at room temperature for 4 h, then quenched with saturated aqueous ammonium chloride solution (20 mL), diluted with H_2O (100 mL) and extracted with ethyl acetate (3 × 100 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography of the residue eluting with light petroleum and ethyl acetate (7:1 v/v) gave the *title compound* as mixture of

rotamers, as a viscous pale orange oil (7.62 g, 80%); (Found: M+Na^+, 406.1599. $C_{17}H_{25}NaN_3O_7$ requires 406.1590); ν_{max} ($CHCl_3$)/cm^{-1} 3394, 2935, 1725, 1536, 1370; δ_H (400 MHz; $CDCl_3$) 7.73 (1H, d, *J* 8.1, ArH), 7.54 (0.5H, br s), 7.48 (0.5H, d, *J* 2.9), 7.19-7.15 (1H, m, ArH), 7.01 (1H, br s, NH), 3.90 (1.5H, s, Me), 3.88 (1.5H, s, Me), 1.54 (13.5H, s, *t*Bu), 1.34 (4.5H, s, *t*Bu); δ_C (100 MHz; $CDCl_3$) 159.0, 158.9, 155.5, 155.0, 153.9, 153.1, 145.5, 145.3, 132.2 (CH), 131.9 (CH), 128.9, 128.4, 120.1 (CH), 119.8 (CH), 109.8 (CH), 109.5 (CH), 82.8, 82.7, 81.5, 81.4, 56.0 (Me), 59.9 (Me), 28.2 (Me), 28.1 (Me), 28.0 (Me), 27.7 (Me); *m/z* (EI) 789 (2M+Na^+, 92%), 406 (M+Na^+, 100).

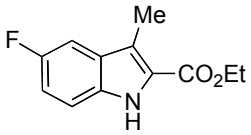
Ethyl 7-bromo-3-methyl-1H-indole-2-carboxylate 3a



Hydrochloric acid (35%; 5 mL) was added to a suspension of di-*tert*-butyl 1-(2-bromophenyl)hydrazine-1,2-dicarboxylate **2a** (0.386 g, 1.0 mmol), 2-ketobutyric acid (0.102 g, 1.0 mmol), and ethanol (5 mL), and the mixture was stirred at 70 °C for 16 h, cooled to room temperature, diluted with water (50 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated. Column chromatography eluting with ethyl acetate and light petroleum (1:50) gave the *title compound* as a colorless solid (0.196 g, 70%), mp 81-83 °C; (Found: M+Na^+, 303.9965. $C_{12}H_{12}{}^{79}BrNaNO_2$ requires 303.9949); ν_{max} ($CHCl_3$)/cm^{-1} 3452, 2985, 2938, 1700, 1311, 1242; δ_H (400 MHz; $CDCl_3$) 8.78 (1H, br s, NH), 7.62 (1H, dd, *J* 8.0, 0.7, ArH), 7.49 (1H, dd, *J* 7.5, 0.7, ArH), 7.04 (1H, dd, *J* 8.0, 7.5, ArH), 4.47 (2H, q, *J* 7.2, CH_2), 2.62 (3H, s, Me), 1.47 (3H, t, *J* 7.2, Me); δ_C (100

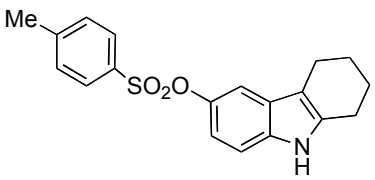
MHz; $CDCl_3$) 162.2, 134.6, 129.6, 127.7 (CH), 124.1, 121.0, 120.9 (CH), 120.0 (CH), 105.0, 61.0 (CH_2), 14.5 (Me), 10.2 (Me); *m/z* (EI) 304 ($M+Na^+$, 100%), 305 ($M+Na^+$, 98).

Ethyl 5-fluoro-3-methyl-1H-indole-2-carboxylate 3b



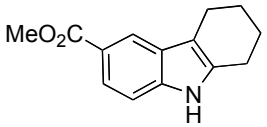
Hydrochloric acid (35%; 5 mL) was added to a suspension of di-*tert*-butyl 1-(4-fluorophenyl)hydrazine-1,2-dicarboxylate **2b**(0.386 g, 1.0 mmol), 2-ketobutyric acid (0.102 g, 1.0 mmol), and ethanol (5 mL), and the mixture was stirred at 70 °C for 16 h, cooled to room temperature, diluted with water (50 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated. Column chromatography eluting with ethyl acetate and light petroleum (1:14) gave the *title compound* as a colorless solid (0.146 g, 66%), mp 121-123 °C; (Found: $M+Na^+$, 244.0745. $C_{12}H_{12}FNaNO_2$ requires 244.0750); ν_{max} ($CHCl_3$)/cm^{-1} 3463, 2985, 2938, 1695, 1456, 1242; δ_H (400 MHz; DMSO-d_6) 7.43-7.39 (2H, m, ArH), 7.12 (1H, ddd, *J* 9.4, 8.9, 2.4, ArH), 4.34 (2H, q, *J* 7.2, CH_2), 2.51 (3H, s, Me), 1.34 (3H, t, *J* 7.2, Me); δ_C (100 MHz; DMSO-d_6) 162.2, 127.3 (d, *J* 233, CF), 133.4, 128.2 (d, *J* 9.6, C), 125.3, 118.7 (d, *J* 5.8, C), 114.2 (d, *J* 24, CH), 114.1 (d, *J* 12, CH), 105.0 (d, *J* 23, CH), 60.7 (CH_2), 14.7 (Me), 10.2 (Me); *m/z* (EI) 244 ($M+Na^+$, 100%).

6-(4-Toluenesulfonyloxy)-2,3,4,9-tetrahydrocarbazole 3c



Hydrochloric acid (35%; 2 mL) was added to a suspension of di-*tert*-butyl 1-(4-(tosyloxy)phenyl)hydrazine-1,2-dicarboxylate **2c** (0.239 g, 0.5 mmol), cyclohexanone (0.098 g, 1.0 mmol), and ethanol (2 mL), and the mixture was stirred at 70 °C for 2 h, cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated. Column chromatography eluting with ethyl acetate and light petroleum (1:6) gave the *title compound* as a pale yellow solid (0.154 g, 90%); mp 112-114 °C; (Found: $M+H^+$, 342.1166. $C_{19}H_{20}NO_3S$ requires 342.1164); ν_{max} ($CHCl_3$)/cm^{-1} 3605, 3011, 2941, 1600, 1477, 1369; δ_H (400 MHz; $CDCl_3$) 7.80 (1H, br s, NH), 7.72 (2H, d, *J* 7.8, ArH), 7.29 (2H, d, *J* 7.8, ArH), 7.10-7.08 (2H, m, ArH), 6.65 (1H, dd, *J* 8.8, 2.4, ArH), 2.71 (2H, t, *J* 6.0, CH_2), 2.60 (2H, t, *J* 5.8, CH_2), 2.07 (3H, s, Me), 1.92-1.84 (4H, m, 2 × CH_2); δ_C (100 MHz; $CDCl_3$) 144.9, 143.1, 136.3, 134.0, 132.7, 129.6 (CH), 128.6 (CH), 128.0, 115.2 (CH), 111.3 (CH), 110.7 (CH), 110.6, 23.2 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 21.7 (Me), 20.7 (CH_2); *m/z* (EI) 364 ($M+Na^+$, 100%), 342 ($M+H^+$, 63).

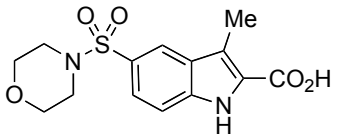
Methyl 5,6,7,8-tetrahydrocarbazole-3-carboxylate 3d



A suspension of di-*tert*-butyl 1-(4-(methoxycarbonyl)phenyl)hydrazine-1,2-dicarboxylate **2d** (0.183 g, 0.5 mmol), cyclohexanone (0.098 g, 1.0 mmol), and trifluoroacetic acid (2 mL) was stirred at 70 °C for 4 h, cooled to room temperature, diluted with saturated sodium hydrogen solution (30 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated. Column chromatography eluting with ethyl acetate and light petroleum

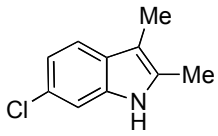
(1:7) gave the *title compound* as a colorless solid (0.102 g, 89%); mp 153-155 °C (lit.,[1] mp 155-157 °C); (Found: $M+H^+$, 230.1174. $C_{14}H_{16}NO_2$ requires 230.1181); ν_{max} ($CHCl_3$)/cm^{-1} 3468, 3011, 2946, 2846, 1703, 1312, 1243; δ_H (400 MHz; $CDCl_3$) 8.26 (1H, s, ArH), 8.03 (1H, br s, NH), 7.86 (1H, dd, *J* 8.6, 1.6, ArH), 7.29 (1H, d, *J* 8.6, ArH), 3.96 (3H, s, Me), 2.77-2.75 (4H, m, 2 × CH_2), 1.97-1.67 (4H, m, 2 × CH_2); δ_C (100 MHz; $CDCl_3$) 168.5, 138.4, 135.6, 127.5, 122.6 (CH), 121.0, 120.7 (CH), 111.5, 110.0 (CH), 51.8 (Me), 23.2 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 20.8 (CH_2); *m/z* (EI) 481 ($2M+Na^+$, 100%), 252 ($M+Na^+$, 33), 230 ($M+H^+$, 25).

3-Methyl-5-(morpholinosulfonyl)-1H-indole-2-carboxylic acid 3e



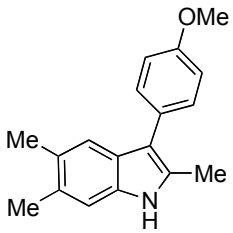
Hydrochloric acid (35%; 2 mL) was added to a suspension of di-*tert*-butyl 1-(4-(morpholinosulfonyl)phenyl)hydrazine-1,2-dicarboxylate **2e** (0.229 g, 0.5 mmol), 2-ketobutyric acid (0.051 g, 0.5 mmol), and acetic acid (2 mL), and the mixture was stirred at 70 °C for 3 h, cooled to room temperature and diluted with water (25 mL). The resulting precipitate was collected by filtration and dried *in vacuo* to give the *title compound* as a grey solid (0.134 g, 83%), mp >250 °C; (Found: $M+H^+$, 325.0862. $C_{14}H_{17}N_2O_5S$ requires 325.0858); ν_{max} ($CHCl_3$)/cm^{-1} 3320, 2987, 2845, 1683, 1363; δ_H (400 MHz; $CDCl_3$) 8.05 (1H, s, ArH), 7.61-7.55 (2H, m, ArH), 3.62 (4H, t, *J* 4.6, CH_2O), 2.85 (4H, t, *J* 4.6, CH_2N), 2.59 (3H, s, Me); δ_C (100 MHz; $CDCl_3$) 163.5, 138.2, 127.7, 127.0, 125.5, 123.6 (CH), 122.1 (CH), 119.7, 113.5 (CH), 65.8 (CH_2), 46.5 (CH_2), 10.1 (Me); *m/z* (EI) 347 ($M+Na^+$, 100%), 325 (56).

6-Chloro-2,3-dimethyl-1H-indole 3f



Hydrochloric acid (35%; 4 mL) was added to a suspension of di-*tert*-butyl 1-(3-chlorophenyl)hydrazine-1,2-dicarboxylate **2f** (0.342 g, 1.0 mmol), 2-butanone (0.144 g, 2.0 mmol), and ethanol (4 mL), and the mixture was stirred at reflux for 4 h, cooled to room temperature, diluted with water (40 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated. Column chromatography eluting with ethyl acetate and light petroleum (1:19) gave the *title compound* as a pale yellow solid (0.137 g, 76%); mp 151-153 °C (lit.,[2] mp 166-167 °C); (Found: $M+H^+$, 180.0577. $C_{10}H_{11}{}^{35}ClN$ requires 180.0580); ν_{max} ($CHCl_3$)/cm^{-1} 3472, 3011, 2920, 1624, 1464; δ_H (400 MHz; $CDCl_3$) 7.61 (1H, br s, NH), 7.38 (1H, d, *J* 8.3, ArH), 7.25 (1H, d, *J* 1.7, ArH), 7.07 (1H, dd, *J* 8.3, 1.7, ArH), 2.37 (3H, s, Me), 2.23 (3H, s, Me); δ_C (100 MHz; $CDCl_3$) 135.5, 131.4, 128.1, 126.7, 119.6 (CH), 118.7 (CH), 110.0 (CH), 107.3, 11.6 (Me), 8.4 (CH); *m/z* (EI) 396 (100%), 180 (27).

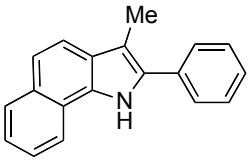
3-(4-Methoxyphenyl)-2,5,6-trimethyl-1H-indole 3g



Hydrochloric acid (35%; 2 mL) was added to a suspension of di-*tert*-butyl 1-(3,4-dimethylphenyl)hydrazine-1,2-dicarboxylate **2g** (0.336 g, 1.0 mmol), 4-methoxyphenylacetone (0.164 g, 1.0 mmol), and ethanol (2 mL), and the mixture was stirred at reflux for 4 h, cooled to room temperature, diluted with water (20 mL) and

extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated. Column chromatography eluting with ethyl acetate and light petroleum (1:49) gave the *title compound* as a colorless solid (0.180 g, 68%), mp 119-121 °C; (Found: $M+Na^+$, 288.1355. $C_{18}H_{19}NaNO$ requires 288.1359); ν_{max} ($CHCl_3$)/cm^{-1} 3471, 3009, 1512, 1243; δ_H (400 MHz; $CDCl_3$) 7.73 (1H, br s, NH), 7.43 (2H, d, *J* 8.6, ArH), 7.42 (1H, s, ArH), 7.12 (1H, s, ArH), 7.06 (2H, d, *J* 8.6, ArH), 3.91 (3H, s, Me), 2.48 (3H, s, Me), 2.40 (3H, s, Me), 2.37 (3H, s, Me); δ_C (100 MHz; $CDCl_3$) 157.7, 134.1, 130.4 (CH), 130.1, 128.3, 118.9 (CH), 114.0 (CH), 113.1, 113.0, 110.8 (CH), 55.3 (Me), 20.4 (Me), 20.1 (Me), 12.4 (Me); two C unobserved; *m/z* (EI) 288 ($M+Na^+$, 100%), 266 ($M+H^+$, 70).

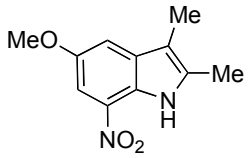
3-Methyl-2-phenyl-1H-benz[*g*]indole 3h



Hydrochloric acid (35%; 2 mL) was added to a suspension of di-*tert*-butyl 1-(naphthalen-1-yl)hydrazine-1,2-dicarboxylate **2h** (0.179 g, 0.5 mmol), propiophenone (0.134 g, 1.0 mmol), and ethanol (2 mL), and the mixture was stirred at 70 °C for 2 h, cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated. Column chromatography eluting with ethyl acetate and light petroleum (1:49) gave the *title compound* as a pale yellow solid (0.114 g, 92%); mp 115-117 °C (lit.,[3] mp 117 °C); (Found: $M+H^+$, 258.1274. $C_{19}H_{16}N$ requires 258.1277); ν_{max} ($CHCl_3$)/cm^{-1} 3466, 3058, 3011, 2974, 1387; δ_H (400 MHz; $CDCl_3$) 8.75 (1H, br s, NH), 8.06 (1H, d, *J* 8.4, ArH), 7.96 (1H, d, *J* 8.4, ArH), 7.73 (1H, d, *J* 8.4, ArH),

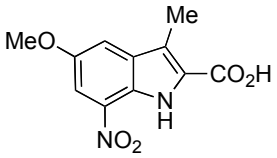
7.68-7.52 (6H, m, ArH), 7.45 (1H, t, *J* 7.6, ArH), 7.39 (1H, dd, *J* 7.6, 7.2, ArH), 2.57 (3H, s, Me); δ_C (100 MHz; $CDCl_3$) 133.5, 132.6, 130.7, 130.4, 129.0 (CH), 128.9 (CH), 127.7 (CH), 127.1 (CH), 125.7, 125.5 (CH), 123.9 (CH), 121.5, 120.5 (CH), 119.5 (CH), 119.1 (CH), 110.5, 9.9 (Me); *m/z* (EI) 258 ($M+H^+$, 100%).

5-Methoxy-2,3-dimethyl-7-nitro-1H-indole 3i



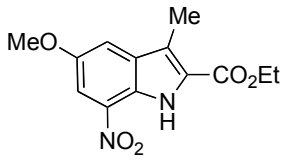
A mixture of di-*tert*-butyl 1-(4-methoxy-2-nitrophenyl)hydrazine-1,2-dicarboxylate **2i** (1.915 g, 5 mmol), butan-2-one (0.70 g, 10 mmol), hydrochloric acid (35%; 25 mL) and acetic acid (25 mL) was stirred at 70 °C for 4 h, cooled to room temperature, neutralized with saturated aqueous sodium hydrogen solution (400 mL) and extracted with ethyl acetate (4 × 150 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the product as a brown solid (1.06 g, 96%), mp 146-148 °C; (Found: $M+Na^+$, 243.0735. $C_{11}H_{12}NaN_2O_3$ requires 243.0746); ν_{max} ($CHCl_3$)/cm^{-1} 3467, 2922, 1518, 1289; δ_H (400 MHz; $CDCl_3$) 9.30 (1H, br s, NH), 7.66 (1H, d, *J* 2.4, ArH), 7.35 (1H, d, *J* 2.4, ArH), 3.93 (3H, s, OMe), 2.44 (3H, s, Me), 2.24 (3H, s, Me); δ_C (100 MHz; $CDCl_3$) 152.7, 134.8, 133.9, 131.3, 124.9, 111.9 (CH), 108.0, 103.9 (CH), 56.5 (Me), 11.7 (Me), 3.4 (Me); *m/z* (EI) 243 ($M+Na^+$, 100%).

5-Methoxy-3-methyl-7-nitro-1H-indole-2-carboxylic acid 3j



A suspension of di-*tert*-butyl 1-(4-methoxy-2-nitrophenyl)hydrazine-1,2-dicarboxylate **2i** (0.038 g, 0.1 mmol), 2-ketobutyric acid (0.020 g, 0.2 mmol), hydrochloric acid (35%; 0.5 mL) and acetic acid (0.5 mL) was stirred at 70 °C for 5 h, cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated. Column chromatography eluting with ethyl acetate and light petroleum (2:1 then 1:0) gave the *title compound* as a bright yellow solid (0.025 g, 100%); mp 236-238 °C; (Found: M-H$^-$, 249.0434. $C_{11}H_9N_2O_5$ requires 249.0511); ν_{max} ($CHCl_3$)/cm^{-1} 3476, 2937, 1920, 1662, 1562; δ_H (400 MHz; DMSO-d_6) 10.4 (1H, br s, NH), 7.80 (1H, s, ArH), 7.76 (1H, s, ArH), 3.90 (3H, s, OMe), 2.54 (3H, s, Me); δ_C (100 MHz; $CDCl_3$) 163.1, 152.8, 132.9, 132.8, 128.6, 124.0, 118.7, 113.0 (CH), 110.3 (CH), 56.8 (Me), 10.0 (Me); *m/z* (EI) 249 (M-H$^-$, 46%), 205 (M-$CO_2H^=$, 100%).

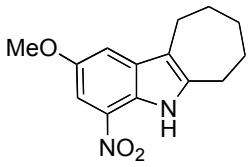
Ethyl 5-methoxy-3-methyl-7-nitro-1H-indole-2-carboxylate 3k



A suspension of di-*tert*-butyl 1-(4-methoxy-2-nitrophenyl)hydrazine-1,2-dicarboxylate **2i** (0.038 g, 0.1 mmol), ethyl 2-ketobutyrate (0.026 g, 0.2 mmol) and trifluoroacetic acid (0.5 mL) was stirred at 70 °C for 16 h and concentrated *in vacuo*. Column chromatography eluting with ethyl acetate and light petroleum (1:11) gave the *title compound* as a bright yellow solid (0.027 g, 97%); mp 123-125 °C; (Found: M+Na$^+$, 301.0827. $C_{13}H_{15}NaN_2O_5$ requires 301.0819); ν_{max} ($CHCl_3$)/cm^{-1} 3465, 2985, 1704, 1568, 1523; δ_H (400 MHz; $CDCl_3$) 9.95 (1H, br s, NH), 7.95 (1H, d, *J* 2.0, ArH), 7.51 (1H, d, *J* 2.0, ArH, 4.47 (2H, q, *J* 7.1, CH_2), 3.96 (3H, s, OMe), 2.63 (3H,

s, Me), 1.47 (3H, t, *J* 7.1, Me); δ_C (100 MHz; $CDCl_3$) 161.5, 153.0, 132.8, 132.6, 126.6, 124.6, 120.0, 112.6 (CH), 110.7 (CH), 61.2 (CH_2), 56.5 (Me), 14.4 (Me), 9.8 (Me); *m/z* (EI) 301 ($M+Na^+$, 100%).

2-Methoxy-4-nitro-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole 3l



Hydrochloric acid (35%; 12 mL) was added to a suspension of di-*tert*-butyl 1-(4-methoxy-2-nitrophenyl)hydrazine-1,2-dicarboxylate **2i** (1.532 g, 4.0 mmol), cycloheptanone (0.448 g, 4.0 mmol), and acetic acid (12 mL), and the mixture was stirred at 70 °C for 6 h, cooled to room temperature, diluted with water (150 mL) and extracted with dichloromethane (3 × 80 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated. Column chromatography eluting with ethyl acetate and light petroleum (1:24) gave the *title compound* as an orange solid (0.781 g, 75%); mp 134-136 °C; (Found: $M+Na^+$, 283.1059. $C_{14}H_{16}NaN_2O_3$ requires 283.1053); ν_{max} ($CHCl_3$)/cm^{-1} 3465, 2928, 2851, 1514, 1316; δ_H (400 MHz; $CDCl_3$) 9.28 (1H, br s, NH), 7.66 (1H, d, *J* 2.4, ArH), 7.36 (1H, d, *J* 2.4, ArH), 3.92 (3H, s, OMe), 2.91 (2H, t, *J* 5.7, CH_2), 2.79 (2H, t, *J* 5.7, CH_2), 1.94-1.91 (2H, m, CH_2), 1.85-1.78 (4H, m, 2 × CH_2); δ_C (100 MHz; $CDCl_3$) 152.7, 141.5, 133.6, 131.5, 123.9, 114.5, 111.6 (CH), 104.0 (CH), 56.5 (Me), 31.5 (CH_2), 29.4 (CH_2), 28.4 (CH_2), 27.2 (CH_2), 24.6 (CH_2); *m/z* (EI) 283 ($M+Na^+$, 100%).

References for Supporting Information

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[2] D. W. Ockenden, K. Schofield, *J. Chem. Soc.* **1957**, 3175.

[3] N. P. Buu-Hoi, N. D. Xuong, *J. Chem. Soc.* **1952**, 2225.