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Oxygenation of 2,3-dihydroindoles

Johnny Slätt and Jan Bergman*

Unit for Organic Chemistry, Department of Biosciences, Karolinska Institute and Södertörn University College, Novum Research Park, SE-141 57 Huddinge, Sweden

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Abstract—Isatogens (3-oxo-3*H*-indole 1-oxides) possess interesting biological properties and development of a general method to construct these derivatives has now been developed. Indolines (2,3-dihydroindoles) and isatogens have been prepared in an efficient route starting from indoles substituted in position 2. Reduction of the 2-substituted indoles was performed with tin and hydrochloric acid to give racemic indolines, which were converted to isatogens by 3-chloroperoxybenzoic acid (*m*-CPBA).

1. Introduction

Isatogens, more comprehensively named as 3-oxo-3*H*-indole 1-oxides (**1**), are brightly coloured solids that do not occur naturally. Although the first isatogen (3-oxo-1-oxy-3*H*-indole-2-carboxylic acid ethyl ester) was reported as early as 1881,[1,2] no generally applicable synthetic methodology is available for this chemically interesting class of compounds, which have properties similar to those of quinones.[3] Isatogen and indoxyl form adducts analogous with quinhydrones.[4] Isatogens form spin trap adducts capable of trapping hydroxyl and superoxide radicals.[5] Isatogens can readily undergo nucleophilic attack in the 2-position.[6] In mammalian systems isatogens are known as inhibitors of the synthesis of adenosine triphosphate (ATP) from mitocondrial preparations.[7] Many isatogens are antifungal[8] and augment smooth muscle dilatation.[9] In vitro screening tests have shown that isatogens possess moderate antibacterial effects (Fig. 1).[10]

Direct oxidation of indole to isatogen is only possible if MoO_5·HMPA is used.[11] Isatogens have most frequently been synthesised via alkynic derivatives such as **2**. Kröhnke's route via pyridinium salt **3** is also commonly used. A less common route goes via α-(*o*-nitrobenzoyl)-β-morpholinostyrenes (**4**).[12] Sometimes the cyclisation, **5** to **1**, is useful (Scheme 1).[13]

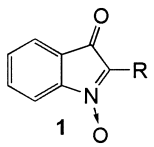
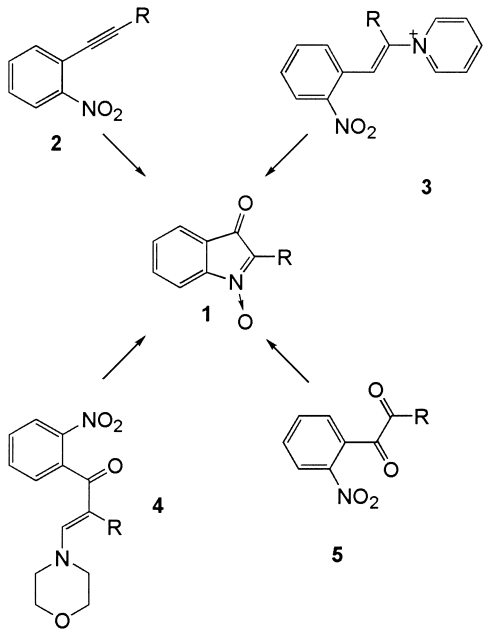


Figure 1.



Scheme 1.

Oxidative transformations of 2,3-dihydroindoles (indolines) to isatogens have only briefly been indicated as a useful route.[14–17] Reductions of indole or 2-alkylindole have been performed in acetic acid with sodium cyanoborohydride, whereas 2-phenylindoles require a stronger acid.[18–21] Enantioselective reduction is also possible but requires high pressure and use of the $[Rh(nbd)_2]SbF_6$ complex.[22] Indoline derivatives are also useful precursors for 1-hydroxyindoles[23] which gives isatogen when oxidised with benzoperoxoic acid.[17,24]

Keywords: isatogen; 2,3-dihydroindoles; quinhydrones.

* Corresponding author. Tel.: +46-8-608-9204; fax: +46-8-608-1501; e-mail: jabe@biosci.ki.se

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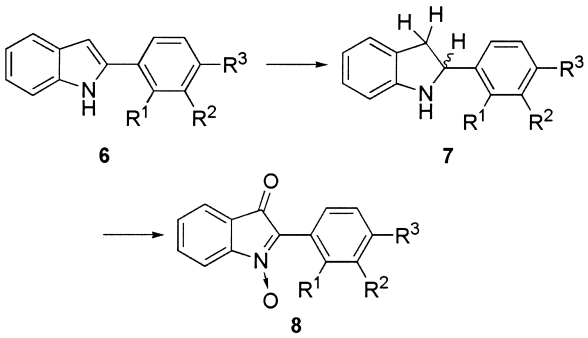

Scheme 2.

2. Results and discussion

We have, via Fischer indole synthesis, obtained 2-phenylindoles **6** in good yields. This reaction works very well with electron donating precursors. If the synthesis is performed via the phenylhydrazone the yields become higher, and the products are generally very pure and no further purification is necessary. Reductions of indoles **6** to indoline derivatives **7** has been performed in a mixture containing hydrochloric acid, ethanol and excess of tin. The indolines obtained are often very pure, and if not they can easily be purified by distillation. Oxidation of the indolines with 3 equiv. of *m*-CPBA in methanol gave the corresponding isatogens **8**. Pure products could be obtained by flash column chromatography with hexane and ethyl acetate (80/20) as eluent. Recrystallisation in a polar solvent like ethanol often gave crystals as long brightly coloured needles (Scheme 2).

	R^1	R^2	R^3	**6** (%)	**7** (%)	**8** (%)
a	H	H	H	–	87.1	68.0
b	H	H	OMe	80.6	55.2	63.5
c	H	OMe	OMe	60.0	69.6	53.0
d	OH	H	H	99.3	47.2	64.0
e	H	H	Cl	99.1	97.3	60.0

3. Conclusion

In summary, we have demonstrated the application and versatility of 2-substituted indolines **7** as precursors for 2-substituted isatogen derivatives **8**.

4. Experimental

4.1. General aspects

NMR spectra were recorded at 300 MHz for ^{1}H and 75 or 125 MHz for ^{13}C; δ values are given in ppm, coupling constants are reported in Hertz. Infrared spectra were recorded on a FT-IR instrument. All reagents were of commercial quality and were used as received. All solvents were purified by distillation or were HPLC grade.

4.1.1. 2-(4-Methoxyphenyl)-1*H*-indole (6b). 4-Methoxyacetophenone (15 g, 0.1 mol) was mixed with phenylhydrazine (9.8 ml, 0.1 mol) in EtOH (20 ml) and glacial AcOH 8 drops and heated for 1 h at 80°C. The solvent was evaporated to yield a grey solid, which was added to PPA (50 ml) and an exothermic reaction ensured whereupon the mixture was heated slowly to 120°C and kept at this temperature for 1 h. The mixture was poured into ice and neutralised with 2 M NaOH to give a beige solid which was collected and dried. Yield 18.0 g (80.6%). Mp. 233–234°C (Lit.,[25] 232–233°C). IR (KBr) 3431.1, 1607.5, 1545.4, 1499.8, 1454.0, 1431.0, 1397.3, 1350.3, 1310.0, 1287.8, 1254.1, 1180.7, 1113.2, 1051.3, 1026.5, 833.6, 786.1, 748.9, 739.9, 529.6 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) 3.83 (s, 3H), 6.74 (s, 1H), 6.94–7.07 (m, 4H), 7.35–7.37 (m, 1H), 7.77–7.80 (m, 1H), 7.78–7.81 (m, 2H), 11.45 (1H, br s) ppm. ^{13}C NMR (DMSO-d$_6$) 55.1, 97.2, 111.0, 114.3, 119.1, 119.6, 120.9, 124.9, 126.3, 128.8, 136.9, 137.7, 158.7 ppm.

4.1.2. 2-(3-Methoxyphenyl)-1*H*-indole (6c). 3-Methoxyacetophenone (5.5 g, 36.6 mmol) and phenylhydrazine (3.6 ml, 36.6 mmol) were added to a mixture with EtOH (10 ml) and glacial AcOH 10 drops. The phenylhydrazone obtained was then treated as described for compound **6b**. Yield 6.7 g (81.9%). Mp 131°C (Lit.,[26] 141°C). IR (KBr) 3393.9, 1601.2, 1481.8, 1434.1, 1349.9, 1303.0, 1263.8, 1219.8, 1175.7, 1165.2, 1088.1, 1036.4, 851.5, 808.7, 783.8, 757.8, 677.8, 506.2 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) 3.84 (s 1H), 6.87–6.92 (m, 2H), 6.97–7.02 (m, 1H), 7.08–7.12 (m, 1H), 7.33–7.46 (m, 4H), 7.51–7.54 (m, 1H), 11.51 (s, NH) ppm. ^{13}C NMR (DMSO-d$_6$) 3.84, 55.1, 98.9, 110.3, 111.2, 113.0, 117.4, 119.3, 120.0, 121.6, 128.5, 129.9, 133.5, 137.0, 137.4, 159.7 ppm.

4.1.3. 2-(3,4-Dimethoxyphenyl)-1*H*-indole (6d). 3,4-Dimethoxyacetophenone (3.0 g, 16.7 mmol) and phenylhydrazine (1.6 ml, 16.7 mmol) were added to a mixture of EtOH (10 ml) and glacial AcOH 5 drops and heated subsequently 80°C 1 h. The solvent was evaporated to give a yellow solid. PPA (10 ml) was added and the mixture was heated at 120°C for 15 min and poured on ice and neutralised with 2 M NaOH to give a yellow solid. Yield 2.21 g (60%). Mp 184–185°C (Lit.,[27] 185–186°C). IR (KBr) 3372.2, 1592.1, 1507.3, 1455.7, 1345.7, 1259.1, 1164.2, 1141.9, 1020.7, 897.2, 797.0, 750.3, 518.0 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) 3.79 (s, 3H), 3.86 (s, 3H), 6.80 (s, 1H), 6.94–7.08 (m, 3H), 7.36–7.50 (m, 4H), 11.42 (bs, NH) ppm. ^{13}C NMR (DMSO-d$_6$) 55.6, 55.7, 97.7, 109.0, 111.0, 112.2, 117.2, 119.3, 119.7, 121.1, 125.2, 128.8, 136.9, 138.0, 148.5, 149.1 ppm.

4.1.4. 2-(1*H*-Indol-2-yl)-phenol (6e). 2-Hydroxyacetophenone (5.95 g, 43.7 mmol) and phenylhydrazine (4.2 ml, 43.7) were added to a mixture of EtOH (20 ml) and glacial AcOH 8 drops, and then treated with PPA (25 ml) as described above. Yield 9.08 g (99.3%). Mp 167°C (Lit.,[28] 180°C). IR (KBr) 3426.6, 1606.4, 1481.3, 1460.0, 1305.0, 1280.7, 1231.8, 1100.5, 789.5, 749.8, 738.0, 667.6, 555.2, 525.9 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) 6.88–7.21 (m, 7H), 7.45–7.53 (m, 2H), 7.73–7.77 (m, 1H), 11.1 (bs, NH) ppm. ^{13}C NMR (DMSO-d$_6$) 100.7, 111.3, 116.5, 118.8, 118.9, 119.4, 119.7, 120.9, 127.4, 128.2, 128.3, 135.3, 136.2, 154.3 ppm.

4.1.5. 2-(4-Chlorophenyl)-1*H*-indole (6f). 4-Chloroacetophenone (6.22 g, 40.2 mmol) and phenylhydrazine (3.95 ml,

40 mmol) were added to a mixture of EtOH (10 ml) and glacial AcOH 8 drops, and then treated as described for **6e**. Yield 9.18 g (99.1%). Mp 207°C (Lit.,[29] 204–205°C). IR (KBr) 3426.4, 1540.2, 1480.6, 1450.2, 1424.0, 1348.2, 1299.3, 1241.8, 1188.1, 1096.0, 1010.0, 933.3, 831.8, 794.0, 749.1, 725.2, 657.2, 512.1 cm^{-1}. ^1H NMR (DMSO-d_6) 6.90 (bs, 1H), 6.97–7.01 (m, 1H), 7.07–7.12 (m, 1H), 7.39–7.41 (m, 1H), 7.48–7.53 (m, 3H), 7.85–7.88 (m, 2H), 11.56 (bs, NH). ^{13}C NMR (DMSO-d_6) 99.2, 111.2, 119.4, 120.1, 121.8, 126.5, 128.5, 128.8, 131.1, 131.7, 136.3, 137.2.

4.1.6. 2-Phenyl-2,3-dihydro-1*H*-indole (7a). 2-Phenylindole (**6a**) (1.5 g, 7.8 mmol) was dissolved a mixture of EtOH (9 ml) and conc. hydrochloric acid (6 ml) and refluxed in the presence of tin (5 g, 42.1 mmol) for 6 h. The cooled solution was then decanted from excess of tin into KOH (20%, aqueous) to give a white solid. The basic mixture was extracted with ether (3×30 ml), and the combined ether layers were filtered through celite, dried with $MgSO_4$ and evaporated to give 2-phenylindoline 1.32 g (87.1%). Mp. 54–55°C (Lit.,[18] 46–47°C). IR (KBr) 3367, 1608, 1483, 1463, 1454, 1362, 1246, 747, 705 cm^{-1}. ^1H NMR (DMSO-d_6) 2.74 (dd, 1H, *J*=9.0, 15.5 Hz), 3.28 (dd, 1H, *J*=9.0, 15.5 Hz), 4.83–4.90 (m, 1H), 6.09 (s, NH), 6.52–6.57 (m, 2H),6.92–7.00 (m, 2H), 7.21–7.46 (m, 5H) ppm. ^{13}C NMR (DMSO-d_6) 38.9, 62.3, 107.9, 117.1, 124.1, 126.2, 126.8, 127.2, 127.4, 128.3, 145.1, 151.9 ppm.

4.1.7. 2-(4-Methoxyphenyl)-2,3-dihydro-1*H*-indole (7b). 2-(4-Methoxyphenyl)-1*H*-indole (7.5 g, 33.6 mmol) was added to a solution of EtOH (30 ml), conc. hydrochloric acid (25 ml) and tin (0.25 mol 30 g), and then treated as described for **7a**. Yield 4.18 g (55.2%). Mp. 57°C (Lit.,[30] 61–62°C). IR (KBr) 3377.5, 1607.4, 1511.8, 1483.0, 1461.7, 1290.5, 1246.8, 1167.0, 1030.2, 832.5, 813.0, 749.3, 680.5, 631.9, 600.0, 539.7 cm^{-1}. ^1H NMR (DMSO-d_6) 2.68–2.76 (m, 1H), 3.27–3.37 (m, 1H), 3.73 (s, 3H), 4.78–4.84 (m, 1H), 6.03 (s, NH), 6.52–6.56 (m, 2H), 6.87–7.05 (m, 4H), 7.29–7.34 (m, 2H) ppm. ^{13}C NMR (DMSO-d_6) 39.1, 55.0, 61.9, 107.9, 113.6, 113.9, 117.0, 124.1, 127.2, 127.3, 127.5, 127.6, 136.9, 151.9, 158.3 ppm.

4.1.8. 2-(3-Methoxyphenyl)-2,3-dihydro-1*H*-indole (7c). 2-(3-Methoxy-phenyl)-indole (3.0 g, 13.4 mmol) was dissolved in a mixture of EtOH (30 ml), conc. hydrochloric acid (25 ml) and tin (10.0 g, 84.3 mmol), and then treated as described for **7a**. Compound **7c** was obtained as a colourless liquid. Bp 169–171°C/0.1 mm. Yield 2.1 g (69.6%). IR (KBr) 3366.9, 1608.8, 1483.2, 1464.3, 1433.6, 1399.4, 1349.7, 1319.9, 1248.5, 1153.9, 1040.0, 1018.0, 994.6, 958.5, 877.6, 781.4, 748.7, 697.0, 532.5 cm^{-1}. ^1H NMR (DMSO-d_6) 2.69–2.77 (m, 1H), 3.29–3.40 (m, 1H), 4.84–4.85 (m, 1H), 6.09 (s, NH), 6.52–6.56 (m, 2H), 6.81–6.82 (m, 1H), 6.91–6.99 (m, 4H), 7.21–7.26 (m, 1H) ppm. ^{13}C NMR (DMSO-d_6) 38.9, 54.9, 62.3, 107.9, 111.8, 112.2, 117.1, 118.4, 124.1, 127.2, 127.4, 129.6, 146.8, 151.9, 159.3 ppm. Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.01; H, 6.69; N, 6.28.

4.1.9. 2-(3,4-Dimethoxyphenyl)-2,3-dihydro-1*H*-indole (7d). 2-(3,4-Dimethoxyphenyl)-1*H*-indole (2.5 g, 11.9 mmol) was dissolved in a mixture of EtOH (30 ml), conc. hydrochloric acid (25 ml) and tin (10.0 g, 84.3 mmol), and then treated as described for compound **7a**. Compound **7c** was obtained as a colourless liquid. Yield 1.25 g (47%). Bp 194–195°C/0.1 mm. IR (KBr) 2931.9, 1606.2, 1516.3, 1482.1, 1462.2, 1417.5, 1371.7, 1260.3, 1234.0, 1184.3, 1135.8, 1027.3, 892.4, 859.9, 810.2, 748.3 cm^{-1}. ^1H NMR (DMSO-d_6) 2.73–2.78 (m, 1H), 3.19–3.323 (m, 1H), 3.73 (s, 3H), 3.74 (s, 3H), 4.54–4.60 (m, 1H), 6.0 (s, NH), 6.47–6.60 (m, 2H), 6.89–7.05 (m, 5H) ppm. ^{13}C NMR (DMSO-d_6) 55.3, 55.4, 66.2, 67.0, 106.5, 110.3, 111.6, 117.0, 119.5, 123.8, 127.3, 128.1, 134.8, 148.2, 148.8, 151.3 ppm.

4.1.10. 2-(2,3-Dihydro-1*H*-indol-2-yl)-phenol (7e). 2-(1*H*-Indol-2-yl)-phenol (3.0 g, 14.3 mmol) was dissolved a mixture of EtOH (20 ml) and conc. hydrochloric acid (25 ml) and tin (15.0 g, 0.13 mol) and then treated as described for compound **7d**. Yield 1.53 g (47.2%). Mp. 112°C. IR (KBr) 3328.9, 2894.2, 1608.1, 1590.1, 1493.4, 1461.4, 1388.2, 1357.7, 1244.8, 1236.1, 1030.1, 993.6, 923.3, 869.6, 841.9, 764.1, 752.1, 707.4, 645.9, 593.3, 532.7, 496.0 cm^{-1}. ^1H NMR (DMSO-d_6) 2.61–2.69 (m, 1H), 3.38–3.47 (m, 1H), 5.02–5.07 (m, 1H), 5.92 (bs, NH), 6.52–6.61 (m, 2H), 6.72–6.82 (m, 2H), 6.92–7.08 (m, 3H), 7.31–7.33 (m, 1H), 9.54 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6) 57.3, 66.4, 108.3, 115.0, 117.2, 118.7, 124.2, 126.3, 127.1, 127.5, 127.9, 130.6, 151.8, 154.6 ppm. Calcd for $C_{14}H_{13}N$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.52; H, 6.28; N, 6.70.

4.1.11. 2-(4-Chlorophenyl)-2,3-dihydro-1*H*-indole (7f). 2-(4-Chlorophenyl)-1*H*-indole (4.28, 18.8 mmol) was dissolved in a mixture of EtOH (25 ml) and conc. hydrochloric acid (25 ml) and tin (15.0 g, 12.6 mol). Yield 4.2 g (97.3%). Mp 69°C. IR (KBr) 3344.3, 1607.3, 1481.5, 1484.0, 1409.7, 1346.0, 1321.5, 1291.4, 1242.9, 1143.8, 1085.8, 1042.0, 1012.6, 919.1, 850.3, 825.4, 751.7, 719.7, 704.3, 670.4, 628.1, 579.5, 543.3, 529.9 cm^{-1}. ^1H NMR (DMSO-d_6) 2.66–2.75 (m, 1H), 3.34–3.48 (m, 1H), 4.36–4.39 (m, 1H), 6.13 (bs, NH), 6.52–6.57 (m, 2H), 6.92–7.00 (m, 2H), 7.36–7.43 (m, 4H) ppm. ^{13}C NMR (DMSO-d_6) 38.9, 61.6, 108.0, 117.3, 124.2, 127.2, 127.3, 128.1, 128.2, 131.3, 144.2, 151.8 ppm. Calcd for $C_{14}H_{12}N$: C, 73.20; H, 5.27; N, 6.10. Found: C, 73.25; H, 5.21; N, 6.06.

4.1.12. 1-Oxy-2-phenyl-indol-3-one (8a). 2-Phenyl-2,3-dihydro-1*H*-indole (100 mg, 0.51 mmol) was dissolved in MeOH (20 ml) and *m*-CPBA (60 mg) and was added in aliquots. After approximately 5 min the solution turns deep red and the reaction mixture was left over night. The solvent was evaporated and the residue was extracted with EtOAc and Na_2CO_3 until the water phase was colourless. The solvent was evaporated to give a bright orange solid, which was recrystallised from EtOH, to give small orange flakes. Yield 78 mg (68%). Mp. 185°C (Lit.,[31] 186°C). IR (KBr) 1705.7, 1597.5, 1523.4, 1481.3, 1447.0, 1388.2, 1314.0, 1283.3, 1181.8, 1073.8, 875.6, 759.9, 686.1, 668.2, 536.9, 510.2 cm^{-1}. ^1H NMR ($CDCl_3$) 7.49–7.27 (m, 7H), 8.63–8.67 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$) 114.2, 121.6, 127.8, 128.5, 129.8, 130.2, 130.7, 131.2, 134.8, 135.1, 147.8, 186.9 ppm.

4.1.13. 2-(4-Methoxyphenyl)-1-oxy-indol-3-one (8b). 2-(4-Methoxyphenyl)-2,3-dihydro-1*H*-indole (210 mg, 0.93 mmol) was dissolved in MeOH (20 ml) and *m*-CPBA

(0.6 g), was added as described for compound **8a**. The crude product purified by flash chromatography with hexane/EtOAc 80/20, gave deep red long needles. Yield 150 mg (63.5%). Mp. 192°C (Lit.,[32] 187°C). IR (KBr) 1689.9, 1598.9, 1557.8, 1529.9, 1492.9, 1456.0, 1379.5, 1301.8, 1261.5, 1178.5, 1019.8, 876.1, 876.1, 832.7, 784.5, 756.1, 697.9, 522.1 cm^{-1}. ^1H NMR ($CDCl_3$) 3.89 (s, 3H), 7.01–7.04 (m, 2H), 7.42–7.68 (m, 4H), 8.72–8.75 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$) 55.3, 113.8, 114.0, 118.7, 121.4, 122.7, 129.7, 130.6, 131.9, 134.7, 147.9, 161.2, 187.3 ppm.

4.1.14. 2-(3-Methoxyphenyl)-1-oxy-indol-3-one (8c). 2-(3-Methoxyphenyl)-2,3-dihydro-1*H*-indole (250 mg, 1.1 mmol) was dissolved in MeOH (50 ml) and *m*-CPBA (0.70 g), was added as described for compound **8a**. The product purified by flash chromatography with hexane/EtOAc 80/20 appeared as long deep red needles. Yield 180 mg (64%). Mp. 140–141°C). IR (KBr) 1715.4, 1702.6, 1600.0, 1575.0, 1519.7, 1480.1, 1453.9, 1380.1, 1299.0, 1252.2, 1181.8, 1050.0, 873.9, 775.5, 760.5, 680.5, 613.4, 536.3 cm^{-1}. ^1H NMR ($CDCl_3$) 3.90 (s, 3H), 7.05 (dd, 1H, J=2.5, 5.8 Hz), 7.40–7.76 (m, 1H), 7.53–7.61 (m, 1H), 7.67–7.71 (m, 3H), 8.26–8.33 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$) 55.3, 112.0, 114.2, 117.7, 120.5, 121.6, 122.7, 126.9, 129.5, 131.2, 132.0, 134.8, 147.8, 159.4, 186.8 ppm. Calcd for $C_{15}H_{11}N$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.04; H, 4.46; N, 5.47.

4.1.15. 2-(3,4-Dimethoxyphenyl)-1-oxy-indol-3-one (8d). 2-(3,4-Dimethoxyphenyl)-2,3-dihydro-1*H*-indole (200 mg, 0.9 mmol) was dissolved in MeOH (50 ml) and *m*-CPBA (0.50 g), was added as described for compound **8a**. The product purified by flash chromatography with hexane/EtOAc 80/20 appeared as long deep red needles. Yield 119 mg (53%). Mp. 227°C (Lit.,[33] 227°C). IR (KBr) 1703.1, 1592.7, 1569.6, 1527.9, 1492.2, 1456.9, 1439.1, 1388.2, 1362.7, 1323.0, 1285.4, 1266.2, 1239.1, 1185.6, 1148.6, 1088.2, 1023.8, 869.7, 808.5, 784.8, 759.9, 705.5, 635.8, 603.7, 535.7 cm^{-1}. ^1H NMR ($CDCl_3$) 3.97–3.99 (m, 6H), 6.95–6.95 (m, 1H), 7.49–7.54 (m, 1H), 7.60–7.63 (m, 1H), 7.67–7.69 (m, 2H), 8.41–8.44 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$) 55.9 (2C), 110.0, 110.8, 113.8, 119.1, 121.5, 122.2, 122.7, 130.7, 131.7, 134.9, 148.0, 148.5, 151.1, 187.3 ppm.

4.1.16. 2-(2-Hydroxyphenyl)-1-oxy-indol-3-one (8e). 2-(2,3-Dihydro-1*H*-indol-2-yl)-phenol (400 mg, 1.9 mmol) was dissolved in MeOH (50 ml) and *m*-CPBA (0.98 g), was added as described for compound **8a**. The product purified by flash chromatography with hexane/EtOAc 80/20 appeared as long deep red needles. Yield 289 mg (64%). Mp. 160°. IR (KBr) 3426.1, 1725.4, 1598.4, 1564.6, 1535.4, 1459.9, 1340.4, 1307.4, 1282.0, 1258.0, 1225.6, 1183.2, 1153.9, 1059.2, 1035.8, 946.4, 881.3, 756.7, 704.0, 682.0, 611.5, 532.0, 493.4 cm^{-1}. ^1H NMR ($CDCl_3$) 7.04–7.11 (m, 2H), 748–7.62 (m, 2H), 7.71–7.75 (m, 3H), 7.82–7.85 (m, 1H), 9.28 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$) 112.8, 114.7, 120.5, 120.7, 122.9, 123.0, 131.0, 131.2, 134.3, 135.6, 136.9, 147.3, 159.3, 184.8 ppm. Calcd for $C_{14}H_9N$: C, 70.29; H, 3.79; N, 5.86. Found: C, 70.21; H, 3.68; N, 5.77.

4.1.17. 2-(4-Chlorophenyl)-1-oxy-indol-3-one (8f). 2-(4-Chlorophenyl)-2,3-dihydro-1*H*-indole (0.3 g, 1.3 mmol) was added to a solution of MeOH (80 ml) and *m*-CPBA (0.9 g) was added as described for compound **8a**. Yield 202 mg (60.0%). Mp. 174°C (Lit.,[34] 174°C). IR (KBr) 1704.0, 1587.6, 1521.5, 1484.0, 1380.9, 1284.3, 1180.0, 1094.7, 1010.0, 876.6, 832.3, 784.0, 761.3, 538.6, 513.8, 466.1, 450.0 cm^{-1}. ^1H NMR ($CDCl_3$) 7.26–7.68 (m, 6H), 8.62–8.65 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$) 114.2, 121.7, 122.6, 124.3, 128.8, 128.9, 131.2, 131.3, 134.9, 136.6, 147.7, 186.6 ppm.

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