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Electrochemically induced Henry reaction of nitromethane and carbonyl compounds

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ABSTRACT

The electrolysis of carbonyl compounds and nitromethane in methanol or in the mixture of methanol and DMF in an undivided cell results in the formation of corresponding β-nitroalcohols in 60–75% yields. Thus, the simple electrocatalytic system can produce under mild conditions an electrochemically induced Henry reaction.

1. Introduction

The Henry reaction is a base-catalyzed C–C bond-forming reaction between nitroalkanes and aldehydes or ketones.[1] The Henry reaction is one of the most useful carbon–carbon bond-forming reactions and has wide synthetic applications in organic synthesis.[2] The β-nitroalcohols, thus formed, are useful intermediates in synthesis of nitroalkenes, α-nitroketones, and β-aminoalcohols.[3] β-Aminoalcohols are of particular significance in the synthesis of biologically important compounds such as ephedrine,[4] norephedrine,[5] epinephrine,[6] anthracycline,[7] ezomycin,[8] and tunicamycin[9] antibiotics, while α-nitroketones are valuable intermediates in the synthesis of many natural products.[10] The β-nitroalcohols are also important because of their utility as intermediates in the synthesis of pharmaceuticals such as (*S*)-propranolol[11] and (*S*)-pindolol,[12] amino sugars,[13] and alkaloids.[14]

Classical methods for preparing β-nitroalcohols include the condensation of the carbonyl compounds and nitroalkane in the presence of an ionic base, such as alkali metal hydroxides, alkaline earth oxides, carbonates, alkoxides or magnesium or aluminum alkoxides. While this approach is quite simple, its limitations often render it unattractive. Thus, careful control of the basicity of the reaction medium is crucial to achieve good yields of β-nitroalcohols. Such efforts require longer reaction times but only give moderate yields.[15] β-Nitroalcohols formed from aryl aldehydes tend to eliminate water to form niroalkenes,[16] which readily polymerize. Moreover, it is not easy to remove the base before workup because acidification of the reaction mixture may lead to the Nef reaction.[17]

Heterogeneous catalysis induced by solid catalysts such as basic alumina,[18] alumina-KF,[19] Mg-Al-O-*t*-Bu hydrotalcite[20] and phase transfer catalysis with surfactans[21] are the two divergent approaches applied to obtain improved selectivity. The former approach requires longer reaction times and in some cases affords condensed olefins.[22] Although good selectivity has been achieved in phase transfer reactions, the reaction still requires a soluble base, which tends to give salts upon neutralization at the end of reaction.[21]

Nevertheless, the development of new catalysts and procedures for the Henry reaction have been constantly in focus, because of the need to reduce the amount of toxic waste materials and by-products, to develop new catalysts or catalytic systems, and to use less toxic 'green' promoters.

Only in the last years phosphines,[23] SmI_2,[24] and biocatalytic[25] and microwave assisted[26] variants of Henry reaction have been suggested.

Within the domain of *green chemistry*, electrochemical technology can provide a valuable alternative to the use of the conventional reagents for fine chemical synthesis.[27] Thanks to the electron transfer between an electrode and the substrate molecules; the

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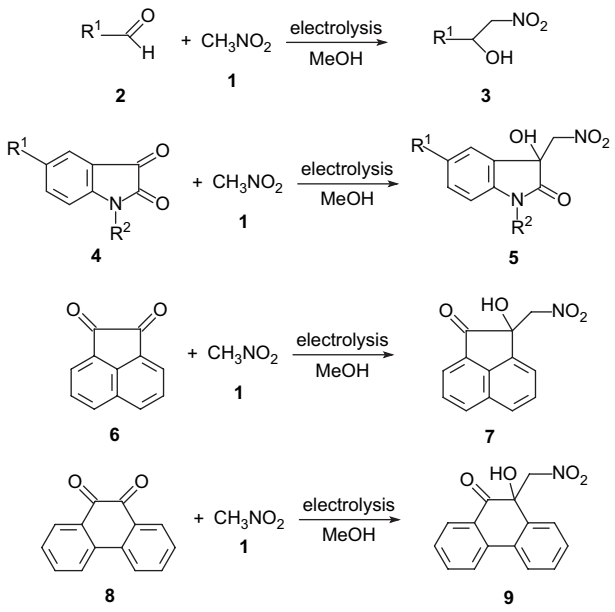
formation of highly reactive intermediates is achieved under mild conditions, avoiding reductive or oxidant agents as well as acids, bases, and related waste by-products.

In the present time two variants of the electrochemically induced Henry reaction are known.[28,29] Both of which concern the addition of nitromethane to only aldehydes and the divided cell was used in both cases. The last circumstance makes the difficulties for use the above procedures in the organic chemistry laboratories, and especially in industry because of the necessity employing special equipment and knowledge of complex electrochemical technique. The procedure in an undivided cell, employing a sacrificial Mg anode is also described,[28] but this variant makes specific problems for isolation of the corresponding nitroaldol and change of the unstable anode is also necessary. One more disadvantage of the reported procedures[28,29] is the necessity to use nitromethane as a solvent.

Recently we have published several variants of electrochemically generated base induced tandem Knoevenagel–Michael reaction, which necessarily proceeds with further cyclization in alcohol solution in an undivided cell.[30–32] Now we wish to report the electrochemically induced addition of nitromethane to carbonyl compounds in methanol solution in an undivided cell (Scheme 1, Table 1).



Scheme 1.

First, to evaluate the synthetic potential of the procedure proposed and to optimize the electrolysis conditions, the electrocatalytic addition of nitromethane **1** to benzaldehyde **2a** in methanol solution in an undivided cell was studied (Table 1).

Under the optimal conditions (current density 10 mA/cm^2, 0.15 F/mol passed, NaI–MeOH as electrolyte–solvent system) the electrolysis of nitromethane **1** and aryl aldehydes **2b–h** in methanol in an undivided cell resulted in the formation of corresponding 2-nitroethanols **3b–h** in 60–76% yields (Table 2).

The procedure found also gave good yields of β-nitroalcohols **5a–f** starting from nitromethane and isatin **4a** or substituted isatins **4b–f**, but in the case of **4d–f** DMF was added to methanol to increase the solubility of starting compound (Table 3).

The electrochemically induced addition of nitromethane to acenaphthoquinone **6** and phenanthrene-9,10-dione **8** under conditions studied resulted in the formation of 2-hydroxy-2-(nitromethyl)acenaphthylen-1(2*H*)-one **7** and 10-hydroxy-10-(nitromethyl)phenanthren-9(10*H*)-one **9** in yields 78 and 71%, respectively.

Table 1
Electrocatalytic addition of nitromethane **1a** and benzaldehyde **2a** with the formation of 2-nitro-1-phenylethanol **3a**[a]

Electrolyte	*I* (mA)	Current density (mA/cm^2)	Time (min)	Electricity passed (F/mol)	Yield of **3a**[b] (%)
NaBr	50	10	48	0.10	59
NaI	50	10	48	0.10	72
KI	50	10	48	0.10	67
NaI	20	4	120	0.10	52
NaI	100	20	24	0.10	63
NaI	50	10	72	0.15	82 (75)
NaI	50	10	96	0.20	79

[a] **1a** (10 mmol), **2a** (10 mmol), electrolyte (1 mmol), MeOH (20 ml), iron cathode (5 cm^2), graphite anode (5 cm^2), 20 °C.
[b] Yield based on NMR data, in parenthesis—isolated yield (method of isolation A).

Taking into consideration the data obtained and our previous results on the electrochemically generated base induced tandem Knoevenagel–Michael reaction with further cyclization in alcohol solution in an undivided cell,[30–32] the following reaction scheme for the electrochemically induced addition of nitromethane **1** to carbonyl compounds **2a–h**, **4a–f**, **6**, and **8** is proposed (Scheme 2). The deprotonation of methanol at the cathode as result of direct or indirect cathode process leads to the formation of methoxide anion. The evolution of hydrogen at the cathode is observed, especially when electrolysis is conducted without stirring of the reaction mixture. The subsequent reaction in solution between methoxide anion and nitromethane gives rise to nitromethane anion (Scheme 2). Then addition of nitromethane anion to carbonyl anion takes place in the solution with the formation of intermediate β-nitroalkoxide anion **A**. The following reaction of β-nitroalkoxide anion **A** with methanol leads to the end product of the electrocatalytic process—the corresponding β-nitroalcohols **3a–h**, **5a–f**, **7** or **9** with the regeneration at this stage of new methoxide anion. This methoxide anion continues the catalytic chain process by the interaction with the next molecule of nitromethane. Thus, the generation of even single methoxide anion at the cathode is theoretically sufficient for the total conversion of carbonyl compounds **2a–h**, **4a–f**, **6**, and **8** and nitromethane **1** into corresponding β-nitroalcohols **3a–h**, **5a–f**, **7** or **9**.

The larger yield of β-nitroalcohols **3a–h**, **5a–f**, **7** or **9** in the presence of iodides as electrolyte could be associated with the competitive mechanism presented in Scheme 3.

It should also be mentioned that recently results concerning with the catalysis of Henry reaction by I_2/I^- in the presence of K_2CO_3 in alcohols have been published without any discussion about mechanistic aspects of the process.[33]

Table 2
Electrocatalytic addition of nitromethane to aldehydes with the formation of 1-substituted 2-nitroethanols **3b–h**[a]

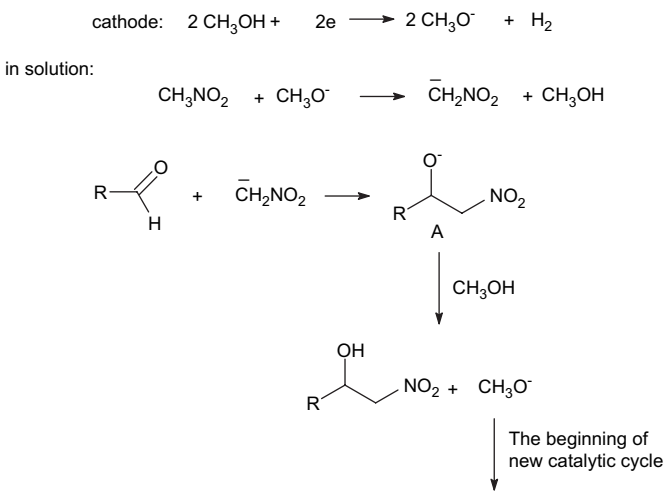
R	*I* (mA)	Current density (mA/cm^2)	Time (min)	Electricity passed (F/mol)	Product, yield[b] (%)
4-MePh	50	10	72	0.15	**3b**, 67
Furyl	50	10	72	0.15	**3c**, 59
$Me(CH_2)_5$–	50	10	72	0.15	**3d**, 71
3-BrC_6H_4	50	10	72	0.15	**3e**, 68
4-ClC_6H_4	50	10	72	0.15	**3f**, 73
4-$O_2NC_6H_4$	50	10	72	0.15	**3g**, 62
3-$O_2NC_6H_4$	50	10	72	0.15	**3h**, 73

[a] **1** (10 mmol), **2** (10 mmol), NaI (1 mmol), MeOH (20 ml), iron cathode (5 cm^2), graphite anode (5 cm^2), 20 °C.
[b] Isolated yields (method of isolation A).

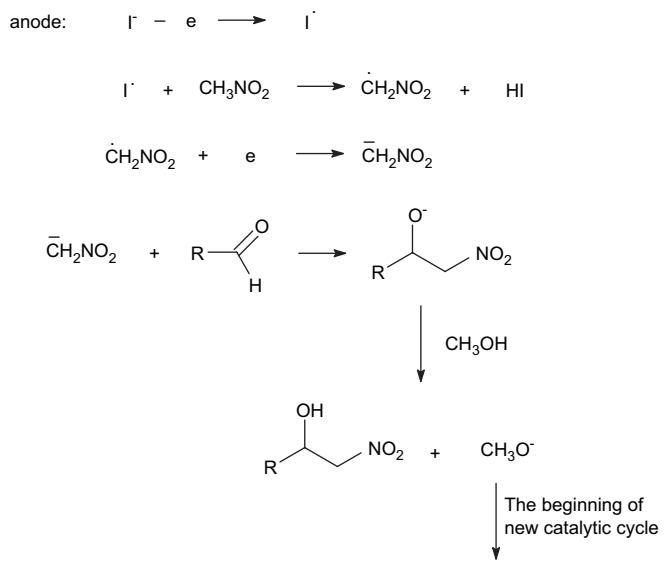
Table 3
Electrocatalytic addition of nitromethane to isatin **4** and substituted isatins **4b–f**[a]

R^1	R^2	I (mA)	Current density (mA/cm^2)	Solvent	Time (min)	Electricity passed (F/mol)	Product, yield (%),[b] method of isolation
H	H	50	10	MeOH	72	0.15	**5a**, 70, B
H	Me	50	10	MeOH	72	0.15	**5b**, 60, C
H	CH_2Ph	50	10	MeOH	72	0.15	**5c**, 69, D
Me	H	50	10	MeOH–DMF	72	0.15	**5d**, 62, D
Cl	H	50	10	MeOH–DMF	72	0.15	**5e**, 75, D
Br	H	50	10	MeOH–DMF	72	0.15	**5f**, 71, D

[a] **1** (10 mmol), **2** (10 mmol), NaI (1 mmol), solvent (20 ml) MeOH or MeOH–DMF (7:3), iron cathode (5 cm^2), graphite anode (5 cm^2), 20 °C.
[b] Isolated yields.



Scheme 2.



Scheme 3.

2. Conclusion

In conclusion, the simple electrocatalytic system can produce, under mild conditions in an undivided cell, a fast and selective transformation of carbonyl compounds and nitromethane into corresponding β-nitroalcohols in good yields. This electrocatalytic chain process is an efficient and convenient way to β-nitroalcohols—promising compounds for different biomedical applications. The procedure utilizes inexpensive reagents, simple equipment, and an undivided cell; it is easily carried out and is fully beneficial from the viewpoint of ecological organic synthesis and large-scale processes. In this electrocatalytic system, methanol and the mixtures of methanol and DMF were used as solvent, so it is not necessary to use nitromethane as the solvent.

3. Experimental section

3.1. General remarks

All melting points were measured with a Gallenkamp melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded with Bruker AC-300 spectrometers at ambient temperature. Chemical shifts values are relative to Me_4Si. IR spectra were registered with a SPECORD M82 spectrometer in KBr pellets. Mass spectra (EI=70 eV) were obtained directly with a Finningan MAT INCOS 50 spectrometer.

3.2. Typical procedure

A solution of carbonyl compound (10 mmol), nitromethane **1** (10 mmol), and alkali metal halide (1 mmol) in 20 ml of methanol or 20 ml mixture methanol–DMF (7:3) was electrolyzed in an undivided cell equipped with a magnetic stirrer, a graphite anode, and an iron cathode at ambient temperature under constant current density 10 mA/cm^2 (I=50 mA, electrode square 5 cm^2) until the catalytic quantity of the electricity 0.15 F/mol was passed. After the end of the electrolysis, the solution was evaporated to dryness in vacuo at 30 °C and worked up by one of the methods A–E, which are indicated below.

In the case of acenaphthoquinone **6** and phenanthrene-9,10-dione **8** electrolysis was accomplished in 5 mmol scale, isolation was in according the method E.

(A) The crude reaction product was diluted with $CHCl_3$ (20 ml), the solid was filtered, and washed with $CHCl_3$ (2×5 ml). Chloroform solutions were combined and evaporated in vacuo at 30 °C. The residue was purified by flash chromatography on silica gel (40–60 mesh), eluent light petroleum–EtOAc (9:1)
(B) The crude reaction product was diluted with $CHCl_3$ (20 ml), the solid was filtered, washed with $CHCl_3$ (2×5 ml) and water (2×5 ml), and dried under vacuum at 30 °C.
(C) The residue obtained according to procedure B was purified by column chromatography on silica gel (40–60 mesh), eluent light petroleum–EtOAc (9:1).
(D) The crude reaction product was diluted with Et_2O (100 ml) and water (50 ml). The etheric extract was filtered from insoluble material, washed with water (2×20 ml), dried ($MgSO_4$), and evaporated in vacuo at 30 °C. The residue was recrystallized from Et_2O or $CHCl_3$.
(E) The residue obtained according to procedure A was purified by column chromatography on silica gel (40–60 mesh), eluent chloroform–hexane (5:2).

*3.2.1. 2-Nitro-1-phenylethanol (**3a**)*[24]

Light yellow oil; yield 1.25 g (75%); δ_H (300 MHz, $CDCl_3$) 2.98 (1H, br s, OH), 4.42–4.62 (2H, m, CH_2), 5.40–5.52 (1H, m, CH), 7.15–7.20 (5H, m, Ph).

*3.2.2. 1-(4-Methylphenyl)-2-nitroethanol (**3b**)*

Light yellow solid; yield 1.21 g (67%); mp 44–45 °C; lit. mp[34] 46 °C; δ_H (300 MHz, $CDCl_3$) 2.27 (3H, s, CH_3), 2.98 (1H, br s, OH), 4.38–4.60 (2H, m, CH_2), 5.40–5.52 (1H, m, CH), 7.15–7.18 (2H, d, *J* 9.2 Hz, Ar), 7.23 (2H, d, *J* 9.2 Hz, Ar).

*3.2.3. 1-(2-Furyl)-2-nitroethanol (**3c**)*[35]

Light yellow oil; yield 0.93 g (59%); δ_H (300 MHz, $CDCl_3$) 3.08 (1H, br s, OH), 4.64–4.82 (2H, m, CH_2), 5.42–5.52 (1H, m, CH), 6.30–6.43 (2H, m, Fur), 7.42 (1H, d, *J* 2.3 Hz, Fur).

*3.2.4. 1-Nitroheptan-2-ol (**3d**)*[36]

Light yellow oil; yield 1.14 g (71%); δ_H (300 MHz, $CDCl_3$) 0.90 (3H, t, *J* 7.0 Hz, CH_3), 1.25–1.55 (8H, m, CH_2), 2.65 (1H, br s, OH), 4.30–4.45 (3H, m, CH_2 and CH).

*3.2.5. 1-(3-Bromophenyl)-2-nitroethanol (**3e**)*

Light yellow solid; yield 1.67 g (68%); mp 67–69 °C; lit. mp[34] 68–69 °C; δ_H (300 MHz, $CDCl_3$) 3.10 (1H, br s, OH), 4.52–4.62 (2H, m, CH_2), 5.50–5.65 (1H, m, CH), 7.25–7.35 (2H, m, Ar), 7.47–7.50 (1H, m, Ar), 7.58 (1H, s, Ar).

*3.2.6. 1-(4-Chlorophenyl)-2-nitroethanol (**3f**)*[37]

Light yellow oil; yield 1.47 g (73%); δ_H (300 MHz, $CDCl_3$) 3.09 (1H, br s, OH), 4.42–4.60 (2H, m, CH_2), 5.42–5.52 (1H, m, CH), 7.25–7.40 (4H, m, Ar).

*3.2.7. 1-(4-Nitrophenyl)-2-nitroethanol (**3g**)*

Light yellow solid; yield 1.31 g (62%); mp 82–83 °C; lit. mp[38] 84 °C; δ_H (300 MHz, $CDCl_3$) 3.12 (1H, br s, OH), 4.55–4.59 (2H, m, CH_2), 5.50–5.65 (1H, m, CH), 7.61 (2H, d, *J* 8.5 Hz, Ar), 8.28 (2H, d, *J* 8.5 Hz, Ar).

*3.2.8. 1-(3-Nitrophenyl)-2-nitroethanol (**3h**)*

Light yellow solid; yield 1.54 g (73%); mp 70–71 °C; lit. mp[38] 70–71 °C; δ_H (300 MHz, $CDCl_3$) 3.10 (1H, br s, OH), 4.52–4.62 (2H, m, CH_2), 5.50–5.65 (1H, m, CH), 7.58 (1H, t, *J* 7.9 Hz, Ar), 7.75 (1H, d, *J* 7.9 Hz, Ar), 8.17 (1H, d, *J* 7.9 Hz, Ar), 8.28 (1H, s, Ar).

*3.2.9. 3-Hydroxy-3-(nitromethyl)-1,3-dihydro-2H-indol-2-one (**5a**)*

Yellow solid; yield 1.46 g (70%); mp 143–145 °C (dec); lit. mp[39] 135–140 °C (dec); δ_H (300 MHz, DMSO-d_6) 4.97 (1H, d, *J* 12.7 Hz), 5.01 (1H, d, *J* 12.7 Hz), 6.71 (1H, s, OH), 6.83 (1H, d, *J* 7.6 Hz), 6.98 (1H, t, *J* 7.6 Hz), 7.24 (1H, t, *J* 7.6 Hz), 7.39 (1H, d, *J* 7.6 Hz), 10.53 (1H, s, NH).

*3.2.10. 3-Hydroxy-1-methyl-3-(nitromethyl)-1,3-dihydro-2H-indol-2-one (**5b**)*

Yellow solid; yield 1.33 g (60%); mp 103–105 °C (dec); lit. mp[39] 98–99 °C; δ_H (300 MHz, $CDCl_3$) 3.22 (3H, s, CH_3), 4.58 (1H, s, OH), 4.88 (2H, m, CH_2), 6.89 (1H, d, *J* 8.1 Hz, Ar), 7.13 (1H, t, *J* 8.1 Hz, Ar), 7.40 (1H, t, *J* 8.1 Hz, Ar), 7.42 (1H, d, *J* 8.1 Hz, Ar).

*3.2.11. 1-Benzyl-3-hydroxy-3-(nitromethyl)-1,3-dihydro-2H-indol-2-one (**5c**)*

Yellow solid; yield 2.05 g (69%); mp 133–136 °C lit. mp[40] 125–127 °C; δ_H (300 MHz, DMSO-d_6) 4.87–4.96 (2H, m, CH_2), 5.11–5.19 (2H, m, CH_2), 6.88 (1H, d, *J* 7.3 Hz, Ar), 6.97 (s, 1H, OH), 7.06 (1H, t, *J* 7.3 Hz, Ar), 7.23–7.44 (m, 6H, Ar), 7.50 (1H, d, *J* 7.3 Hz, Ar).

*3.2.12. 3-Hydroxy-5-methyl-3-(nitromethyl)-1,3-dihydro-2H-indol-2-one (**5d**)*

Yellow solid; yield 1.28 g (62%); mp 153 °C (dec); δ_H (300 MHz, DMSO-d_6) 2.25 (s, 3H, CH_3), 4.93–4.12 (2H, m, CH_2), 6.70 (1H, s, OH), 6.74 (1H, d, *J* 8.2 Hz, Ar), 7.08 (1H, d, *J* 7.8 Hz, Ar), 7.23 (1H, s, Ar), 10.45 (1H, s, NH); δ_C (75 MHz, DMSO-d_6) 21.0, 73.3, 78.8, 110.2, 125.6, 128.4, 130.8, 131.1, 140.5, 176.3; MS (70 eV) *m*/*z* (relative intensity %): 222 ($[M]^+$, 7), 162 (22), 161 (44), 147 (18), 133 (100), 130 (22), 105 (25), 104 (88), 78 (49), 77 (50), 51 (45); IR (KBr): ν_{max} 3328, 3028, 2860, 1704, 1628, 1560, 1496, 1384, 1160, 1088 cm^{-1}. Anal. Calcd (%) for $C_{10}H_{10}N_2O_4$: C, 54.05; H, 4.54; N, 12.61. Found (%): C, 53.87; H, 4.35; N, 12.52.

*3.2.13. 5-Chloro-3-hydroxy-3-(nitromethyl)-1,3-dihydro-2H-indol-2-one (**5e**)*

Yellow solid; yield 1.82 g (75%); mp 160–162 °C (dec); δ_H (300 MHz, DMSO-d_6) 5.03–5.13 (2H, m, CH_2), 6.87 (1H, d, *J* 8.1 Hz, Ar), 6.90 (1H, s, OH), 7.33 (1H, dd, J_1 8.1 Hz, J_2 2.2 Hz, Ar), 7.53 (1H, d, *J* 2.2 Hz, Ar), 10.72 (1H, s, NH); δ_C (75 MHz, DMSO-d_6) 73.2, 78.4, 112.0, 125.4, 126.3, 130.5, 130.6, 142.0, 176.1; MS (70 eV) *m*/*z* (relative intensity %): 242 ($[M]^+$, 37), 196 (10), 184 (12), 183 (16), 182 (39), 181 (40), 167 (49), 155 (32), 153 (100), 150 (41), 133 (36), 63 (89), 61 (70); IR (KBr): ν_{max} 3348, 3244, 1716, 1624, 1560, 1484, 1440, 1192 cm^{-1}. Anal. Calcd (%) for $C_9H_7ClN_2O_4$: C, 44.56; H, 2.91; N, 11.54. Found (%): C, 44.34; H, 2.77; N, 11.30.

*3.2.14. 5-Bromo-3-hydroxy-3-(nitromethyl)-1,3-dihydro-2H-indol-2-one (**5f**)*

Yellow solid; yield 2.03 g (71%); mp 163–165 °C (dec); δ_H (300 MHz, DMSO-d_6) 5.02–5.12 (2H, m, CH_2), 6.83 (1H, d, *J* 8.1 Hz, Ar), 6.88 (1H, s, OH), 7.46 (1H, dd, J_1 8.1 Hz, J_2 2.2 Hz, Ar), 7.64 (1H, d, *J* 2.2 Hz, Ar), 10.69 (s, 1H, NH); δ_C (75 MHz, DMSO-d_6) 72.7, 77.9, 112.1, 113.5, 127.7, 130.5, 132.9, 142.0, 175.6; MS (70 eV) *m*/*z* (relative intensity %): 288 ($[M]^+$, 1), 286 ($[M]^+$, 1), 227 (24), 225 (24), 199 (71), 197 (73), 171 (19), 170 (22), 169 (19), 90 (34), 63 (69), 61 (100); IR (KBr): ν_{max} 3344, 1720, 1616, 1560, 1552, 1480, 1376, 1148, 1088 cm^{-1}. Anal. Calcd (%) for $C_9H_7BrN_2O_4$: C, 37.66; H, 2.46; N, 9.76. Found (%): C, 37.48; H, 2.30; N, 9.61.

*3.2.15. 2-Hydroxy-2-(nitromethyl)acenaphthylen-1(2H)-one (**7**)*[41]

Yellow solid; yield 0.96 g (78%); mp 134–136 °C, lit. mp[41] 127–128 °C; δ_H (300 MHz, $CDCl_3$) 3.90 (1H, br s, OH), 4.94 (1H, d, *J* 12.9 Hz), 4.99 (1H, d, *J* 12.9 Hz), 7.68–7.73 (2H, m), 7.77–7.80 (1H, m), 7.97 (1H, d, *J* 8.0 Hz), 8.04 (1H, d, *J* 7.1 Hz), 8.18 (1H, d, *J* 8.0 Hz).

*3.2.16. 10-Hydroxy-10-(nitromethyl)phenanthren-9(10H)-one (**9**)*

Yellow solid; yield 0.95 g (71%); mp 159–160 °C, lit. mp[42] 148–149 °C; δ_H (300 MHz, $CDCl_3$) 4.54 (1H, br s, OH), 4.61 (1H, d, *J* 12.1 Hz), 4.64 (1H, d, *J* 12.1 Hz), 7.42–7.51 (3H, m), 7.72–7.75 (1H, m), 7.79–7.84 (2H, m), 7.91 (1H, d, *J* 8.0 Hz), 7.97 (1H, d, *J* 7.1 Hz).

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