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Synthesis of new 2,4-disubstituted 2,3-dihydrobenzo[g]indol-5-ones by $S_{RN}1$ strategy

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Abstract: We report an original and short synthesis of substituted 2,3-dihydrobenzo[g]indol-5-ones by $S_{RN}1$ mediated synthesis of 2-nitroalkyl substituted naphthalene-1,4-diones followed by a one-pot reduction-cyclization reaction.

Key words: quinones - electron transfer - cyclization - heterocycles - 2, 3-dihydrobenzo[g]indol-5-one.

Wide-ranging therapeutic applications for quinones have inspired abundant research programs in organic chemistry. Over the last decade, for instance, these have yielded numerous potent anticancerous¹ or antiparasitic² naphthoquinone derivatives. One pharmaceutical application consists in adding an amino group on the quinonic moiety, leading to the discovery of promising molecules. For example, naphthoquinonic derivatives, which are C₁-substituted by a nitrogen, have been shown to have antioxidant and cell signaling properties as redox cycling agents,³ to have antidiabetic potency⁴ and to have anti-Alzheimer applications as heat shock protein inhibitors.⁵

Over the past decades, we have extensively studied a single-electron-transfer reaction, radical nucleophilic substitution ($S_{RN}1$ reaction). In this connection we designed mechanistic studies and described the reactivities of various molecules.⁶

Under our program for the synthesis of new quinonic compounds using single-electron-transfer methodology⁷ and aiming at the preparation of new potentially bioactive compounds, we report an

original and efficient synthesis of substituted 2,3-dihydrobenzo[g]indol-5-ones by a reduction-cyclization reaction of nitronaphthoquinonic derivatives prepared using by $S_{RN}1$ substitution strategies. Accounts of the synthesis of 2,3-dihydrobenzo[g]indol-5-ones are rare, with various structural limitations.^{4,8}

Seeking to apply these strategies to prepare substituted 2,3-dihydrobenzo[g]indol-5-one derivatives, we focused on a retrosynthetic pathway in which $S_{RN}1$ reactions are followed by a cyclization reaction. Starting materials were two 2-chloromethylated naphthoquinones, substituted in position 3 by a methyl or a methoxy group. We therefore prepared the 2-(chloromethyl)-3-methylnaphthalene-1,4-dione (**1**) from menadione as previously described following Thomson's procedure (Scheme 1).⁹

Scheme 1: Synthesis of 2-(chloromethyl)-3-methylnaphthalene-1,4-dione (**1**)

2-(Chloromethyl)-3-methoxynaphthalene-1,4-dione (**3**) was synthesized in a two-step procedure adapted from previously described procedures, and involving a radical bromination¹⁰ followed by a trans-halogenation (Scheme 2).¹¹

Scheme 2: Synthesis of 2-(chloromethyl)-3-methoxynaphthalene-1,4-dione (**3**)

Reaction of 2-methoxy-3-methylnaphthalene-1,4-dione with 1.01 equivalent of *N*-bromosuccinimide (NBS) and 0.4 equivalent of benzoyl peroxide in carbon tetrachloride for 12 hours under light

irradiation gave the 2-(bromomethyl)-3-methoxynaphthalene-1,4-dione **2** in 90% yield. The second step was the trans-halogenation of the 2-bromomethyl naphthoquinone **2** in 2-chloromethyl

naphthoquinone **3**, with 45 equivalents of lithium chloride in THF for 36 hours. This reaction gave the 2-(chloromethyl)-3-methoxynaphthalene-1,4-dione (**3**) in 85% yield.

The optimization of the $S_{RN}1$ reaction conditions with the substrates **1** and **3** was guided by our previous work on electron transfer reaction in quinonic compounds.¹² The phase-transfer conditions using tetrabutylammonium hydroxide (TBAOH) 40% in water and toluene or dichloromethane as solvent were found to be the best reaction conditions (Scheme 3).

Scheme 3: C-alkylation of chloromethyl naphthoquinones by an $S_{RN}1$ reaction

Table 1: Yields of products obtained in the $S_{RN}1$ reaction

Product	R ¹	R ²	R ³	Yield ^a
4a	-OCH ₃	-CH ₃	-CH ₃	60%
4b	-OCH ₃		-(CH ₂) ₅ -	50%
4c	-OCH ₃		-(CH ₂) ₄ -	63%
4d	-OCH ₃	-H	- <i>n</i> C ₃ H ₇	51%
4e	-OCH ₃	-CH ₃	-Ph	54%
4f	-OCH ₃	-H	-CH ₃	47%
4g	-OCH ₃	-H	-C ₂ H ₅	54%
4h	-CH ₃	-CH ₃	-CH ₃	65%
4i	-CH ₃		-(CH ₂) ₅ -	70%
4j	-CH ₃		-(CH ₂) ₄ -	51%
4k	-CH ₃	-H	- <i>n</i> C ₃ H ₇	72%
4l	-CH ₃	-CH ₃	-Ph	43%
4m	-CH ₃	-H	-CH ₃	85%
4n	-CH ₃	-H	-C ₂ H ₅	75%

^a Yield of isolated product based on the corresponding naphthoquinone

Under these conditions (Scheme 3) with various nitronate derivatives, aliphatic or alicyclic, the compounds **1** and **3** gave C-alkylation products **4a-n** in moderate to good yields (43-83%). Predictably, elimination products were not observed in this study. As previously reported,¹³ $S_{RN}1$ reaction on various nitroheterocyclic compounds can be followed by the elimination of nitrous acid, leading to an alkene. This elimination is favored by the presence of an excess of the initial nitronate anion. With quinone as $S_{RN}1$ substrate, this elimination was rarely observed,¹³ probably because of the degradation that occurs with an excess of the anion.

We also investigated several experimental conditions favoring nitrous acid elimination on the substrates when R¹ is methoxy (NaH/DMSO, toluene/DBU,

MeOH/MeONa), without success. However, under classical conditions (CH₂Cl₂/TBAOH 40%), when an excess of TBAOH 40% (6equiv) was applied overnight, demethylated products **5a-b** were observed in 60-70% yields (Scheme 4). This hydrolysis of a vinylogous ester is probably due to the action of OH⁻.

Scheme 4: One-pot naphthoquinone C-alkylation / demethylation

As a potential application for these synthesized compounds, we explored the reduction-cyclization reaction to form heterocyclic derivatives. Reduction of the nitro group with zinc in acetic acid gave, after cyclization (Scheme 5), the substituted 2,3-dihydrobenzo[*g*]indol-5-one derivatives **6a-n** in moderate to good yields (Table 2).

Scheme 5: Reduction-cyclization reactions leading to 2,3-dihydrobenzo[*g*]indol-5-one **6a-n**

Table 2: Yields of products obtained by reduction-cyclization

Product	R ¹	R ²	R ³	Yield ^a
6a	-OCH ₃	-CH ₃	-CH ₃	60%
6b	-OCH ₃		-(CH ₂) ₅ -	50%
6c	-OCH ₃		-(CH ₂) ₄ -	60%
6d	-OCH ₃	-H	- <i>n</i> C ₃ H ₇	51%
6e	-OCH ₃	-CH ₃	-Ph	54%
6f	-OCH ₃	-H	-CH ₃	54%
6g	-OCH ₃	-H	-C ₂ H ₅	56%
6h	-CH ₃	-CH ₃	-CH ₃	74%
6i	-CH ₃		-(CH ₂) ₅ -	60%
6j	-CH ₃		-(CH ₂) ₄ -	56%
6k	-CH ₃	-H	- <i>n</i> C ₃ H ₇	75%
6l	-CH ₃	-CH ₃	-Ph	58%
6m	-CH ₃	-H	-CH ₃	79%
6n	-CH ₃	-H	-C ₂ H ₅	85%

^a Yield of isolated product based on the corresponding naphthoquinone

In conclusion, we developed a new synthesis of substituted 2,3-dihydrobenzo[*g*]indol-5-ones using a two-step procedure involving $S_{RN}1$ methodology and one-pot reduction-cyclization reaction. This procedure

allows the synthesis of numerous original derivatives, due to the wide variety of nitronate anions which can react *via* an $S_{RN}1$ mechanism. 2,3-Dihydrobenzo[g]indol-5-ones while structurally very similar to other derivatives of pharmacological interest, have to date received little attention. The pharmacological properties of our compounds are therefore under active investigation.

Experimental

General

Melting points were determined with a B-540 Büchi melting point apparatus and are uncorrected. 200MHz ^1H -NMR, 250MHz ^1H -NMR and 50 MHz ^{13}C -NMR, 62.5 MHz ^{13}C -NMR spectra were recorded on a Bruker ARX 200 and 250 spectrometers in CDCl_3 or DMSO-d_6 at the Faculté de Pharmacie de Marseille. ^1H - and ^{13}C -NMR chemical shifts (δ) are reported in ppm with respect to CDCl_3 7.26 ppm (^1H), 77.2 ppm (^{13}C) or DMSO-d_6 2.50 ppm (^1H), 39.5 (^{13}C). Mass spectrometry analysis were carried out at the Spectropole, Faculté des Sciences site Saint-Jérôme. Silica gel 60 (Merck, particular size 0.063–0.200 mm, 70–230 mesh ASTM) was used for column chromatography. TLC was performed on 5 cm $\times$ 10 cm aluminium plates coated with silica gel 60F-254 (Merck) in appropriate solvent. The following substrates or subproducts were prepared and described previously: 2-(chloromethyl)-3-methyl-1,4-naphthoquinone (**1**),⁹ 2-methyl-3-(2-nitropentyl)naphthalene-1,4-dione (**4k**),¹⁴ 2-methyl-3-(2-methyl-2-nitropropyl)-1,4-naphthoquinone (**4m**),¹⁴ 2-methyl-3-(2-nitrobutyl)naphthalene-1,4-dione (**4n**).¹⁴

2-Bromomethyl-3-methoxy-1,4-naphthoquinone (2)

A solution of 2-methoxy-3-methyl-1,4-naphthoquinone (5 mmol, 1 g, 1 equiv) in 30 mL of carbon tetrachloride (CCl_4) was stirred, and N-bromosuccinimide (5.05 mmol, 900 mg, 1.01 equiv) and benzoyl peroxide (2.10 mmol, 0.50 g, 0.40 equiv) were added. The mixture was stirred under white light irradiation (60W) at 80 °C overnight. After the disappearance of the substrate (monitored by TLC), the reaction was stopped, cooled to rt, and the mixture was concentrated in vacuo. The crude product was dissolved in 60 mL of dichloromethane and washed with water (4 $\times$ 30 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated. The product was purified by chromatography on a silica gel column, eluting with dichloromethane/petroleum ether 1:1, and recrystallized from isopropanol in 90% yield, yellow solid mp 117 °C (petroleum ether).

^1H NMR (200 MHz, CDCl_3): δ = 8.04–8.15 (m, 2H, Ar-H), 7.71–7.79 (m, 2H, Ar-H), 4.48 (s, 2H, CH_2), 4.34 (s, 3H, OCH_3).

^{13}C NMR (62.5 MHz, CDCl_3): δ 180.6, 179.1, 155.8, 132.1, 131.4, 129.3, 129.2 $\times$ 2, 126.9, 124.3, 124.2, 59.5, 17.8.

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{12}\text{H}_9\text{O}_3\text{Br}$: 280.9808; found: 280.9810.

2-Chloromethyl-3-methoxy-1,4-naphthoquinone(3)

To a solution of **2** (1.78 mmol, 0.50 g, 1 equiv) in 50 mL of THF under nitrogen atmosphere, were added rapidly lithium chloride (80.10 mmol, 3.41 g, 45 equiv). The mixture was stirred at rt for 36 h, filtered and evaporated. The crude product was dissolved in 100 mL of ethyl acetate and washed with water (5 $\times$ 20 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated. The chlorinated product was purified by chromatography on a silica gel column, eluting with dichloromethane/petroleum ether 1:1, and recrystallized from isopropanol in 85% yield, yellow solid mp 102 °C (petroleum ether).

^1H NMR (200 MHz, CDCl_3): δ = 8.05–8.15 (m, 2H, Ar-H), 7.69–7.80 (m, 2H, Ar-H), 4.59 (s, 2H, CH_2), 4.32 (s, 3H, OCH_3).

^{13}C NMR (62.5 MHz, CDCl_3): δ = 183.0, 181.5, 158.5, 134.5, 133.6, 131.5, 131.4, 128.5, 126.6, 126.5, 61.9, 33.6.

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{12}\text{H}_9\text{O}_3\text{Cl}$: 237.0313; found: 237.0311.

General procedure for $S_{RN}1$ reaction of substrate 1 and 3

Corresponding nitroalkane (0.84 mmol, 2 equiv) and 0.55 mL of 40% TBAOH were stirred at rt for 1 h under nitrogen atmosphere. Then, naphthoquinone (0.42 mmol, 100 mg, 1 equiv, for example methoxy-naphthoquinone) solubilized in 5 mL of dichloromethane or toluene, was added. The mixture was rapidly stirred at rt under nitrogen atmosphere with white light irradiation (60W) for 10 min. After disappearance of the substrate (monitored by TLC), the reaction was quenched by 10 mL of water and the product was extracted with dichloromethane (4 $\times$ 30 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated. The product was purified by chromatography on a silica gel column, eluting with dichloromethane/petroleum ether 1:1, followed by recrystallization from corresponding solvent.

2-Methoxy-3-(2-methyl-2-nitropropyl)-1,4-naphthoquinone (4a)

The reaction procedure was performed as previously described by $S_{RN}1$, the solvent is dichloromethane.

Yield: 60%, yellow solid, mp 81.8 °C (isopropanol). ^1H NMR (200 MHz, CDCl_3): δ = 7.99–8.06 (m, 2H, Ar-H),

7.67-7.72 (m, 2H, Ar-H), 4.11 (s, 3H, OCH₃), 3.22 (s, 2H, CH₂), 1.58 (s, 6H, 2xCH₃).

¹³C NMR(50MHz, CDCl₃): δ =184.7, 181.2, 159.3, 134.1, 133.5, 131.5x2, 127.1, 126.5, 126.3, 87.9, 61.6, 34.2, 26.2x2.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₅H₁₅NO₅: 290.1023 ; found: 290.1026.

2-Methoxy-3-((1-nitrocyclohexyl)methyl)-1,4-naphthoquinone (4b)

The reaction procedure was performed as previously described by S_{RN}1, the solvent is dichloromethane.

Yield: 50%, yellow solid, mp 106°C (isopropanol).

¹H NMR (200MHz, CDCl₃): δ = 7.98-8.05 (m, 2H, Ar-H), 7.66-7.70 (m, 2H, Ar-H), 4.10 (s, 3H, OCH₃), 3.12 (s, 2H, CH₂), 2.40-2.49 (m, 2H, CH₂), 1.56-1.69 (m, 4H, 2xCH₂), 1.2-1.29 (m, 4H, 2xCH₂). ¹³C NMR (62.5MHz, CDCl₃): δ = 186.9, 183.3, 161.5, 136.1, 135.5, 133.6 x2, 128.9, 128.6, 128.4, 93.6, 63.8, 36.8, 36.6x2, 26.6, 24.4x2.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₈H₁₉NO₅: 330.1336 ; found : 330.1337.

2-Methoxy-3-((1-nitrocyclopentyl)methyl)-1,4-naphthoquinone (4c)

The reaction procedure was performed as previously described by S_{RN}1, the solvent is dichloromethane.

Yield: 63%, yellow oil

¹H NMR (200MHz, CDCl₃): δ = 8.00-8.08 (m, 2H, Ar-H), 7.68-7.73 (m, 2H, Ar-H), 4.11 (s, 3H, OCH₃), 3.30 (s, 2H, CH₂), 2.53-2.59 (m, 2H, CH₂), 1.65-1.94 (m, 6H, 3xCH₂).

¹³C NMR (62.5MHz, CDCl₃): δ = 184.9, 181.3, 159.3, 134.1, 133.5, 131.6, 131.5, 127.6, 126.5, 126.3, 100.0, 61.7, 36.5x2, 32.1, 23.0x2.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₇H₁₇NO₅: 316.1179 ; found : 316.1178.

2-Methoxy-3-(2-nitropentyl)-1,4-naphthoquinone(4d)

The reaction procedure was performed as previously described by S_{RN}1, the solvent is dichloromethane.

Yield: 51%, yellow oil.

¹H NMR (200MHz, CDCl₃): δ = 8.01-8.08 (m, 2H, Ar-H), 7.69-7.75 (m, 2H, Ar-H), 4.72-4.75 (m, 1H, CH), 4.14 (s, 3H, CH₃), 3.29 (dd, J = 13.6, 9.4Hz, 1H, CH), 2.96 (dd, J = 13.6, 4.6 Hz, 1H, CH), 1.69-1.84 (m, 1 H, CH), 1.34-1.45 (m, 2H, CH₂), 0.95 (t, J=7.2Hz, 3H, CH₃).

¹³C NMR (62.5MHz, CDCl₃): δ = 184.7, 181.1, 159.1, 134.1, 133.6, 131.6, 131.5, 127.9, 126.4, 126.3, 87.1, 61.8, 35.7, 28.5, 19.1, 13.4.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₆H₁₇NO₅: 304.1179 ; found : 304.1180.

2-Methoxy-3-(2-nitro-2-phenylpropyl)-1,4-naphthoquinone (4e)

The reaction procedure was performed as previously described by S_{RN}1, the solvent is dichloromethane.

Yield: 54%, yellow solid, mp 130-131 °C (isopropanol).

¹H NMR (200MHz, CDCl₃): δ = 8.00-8.05 (m, 2H, Ar-H), 7.68-7.73 (m, 2H, Ar-H), 7.35-7.46 (m, 5H, Ar-H), 3.97 (s, 3H, OCH₃), 3.87 (d, J=13.2Hz, 1H, CH), 3.76 (d, J=13.2Hz, 1H, CH), 1.86 (s, 3H, CH₃).

¹³C NMR (50MHz, CDCl₃): δ = 184.7, 181.2, 159.2, 140.1, 134.2, 133.4, 131.6, 131.4, 128.8x2, 128.5, 126.9, 126.5, 126.3, 125.8x2, 93.0, 61.3, 33.1, 24.5.

HRMS (ESI): m/z [M + NH₄]⁺ calcd for C₂₀H₁₇NO₅: 369.1445 ; found : 369.1445.

2-Methoxy-3-(2-nitropropyl)-1,4-naphthoquinone (4f)

The reaction procedure was performed as previously described by S_{RN}1, the solvent is toluene.

Yield: 47%, yellow solid, mp 87°C (isopropanol).

¹H NMR (200MHz, CDCl₃): δ = 7.99-8.05 (m, 2H, Ar-H), 7.67-7.72 (m, 2H, Ar-H), 4.74-4.87 (m, 1H, CH), 4.14 (s, 3H, OCH₃), 3.28 (dd, J=13.4, 8.7 Hz, 1H, CH), 2.97 (dd, J=13.4, 5.5Hz, 1H, CH), 1.55(d, J=6.6Hz, 3H, CH₃).

¹³C NMR (50MHz, CDCl₃): δ= 184.7, 181.1, 159.0, 134.1, 133.6, 131.5x2, 127.7, 126.4, 126.3, 81.8, 61.8, 29.6, 19.1.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₄H₁₃NO₅: 276.0866 ; found : 276.0866.

2-Methoxy-3-(2-nitrobutyl)-1,4-naphthoquinone (4g)

The reaction procedure was performed as previously described by S_{RN}1, the solvent is dichloromethane.

Yield: 54%, yellow oil.

¹H NMR(200MHz, CDCl₃):δ = 7.95-8.02 (m, 2H, Ar-H), 7.64-7.71 (m, 2H, Ar-H), 4.58-4.67(m, 1H, CH), 4.11 (s, 3H, OCH₃), 3.24 (dd, J= 13.5, 9.1Hz, 1H,CH), 2.94 (dd, J= 13.5, 4.8 Hz, 1H, CH),1.98-2.14 (m, 1H, CH), 1.14-1.90 (m, 1H, CH), 0.92-0.99 (t, J= 7.3Hz, 3H, CH₃).

¹³C NMR(50MHz, CDCl₃): δ= 184.6, 181.0, 159.0, 134.1, 133.5, 131.5, 131.4, 127.8, 126.3, 126.2, 88.7, 61.8, 28.2, 27.0, 10.2.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₅H₁₅NO₅: 290.1023 ; found : 290.1025.

2-Methyl-3-(2-methyl-2-nitropropyl)naphthalene-1,4-dione (4h)

The reaction procedure was performed as previously described by $S_{RN}1$, the solvent is dichloromethane.

Yield: 65%, Orange solid mp 112 °C (cyclohexane-toluene 8:2).

1H NMR(200MHz, $CDCl_3$): δ = 8.11 (m, 2H, Ar-H), 7.76 (m, 2H, Ar-H), 3.41 (s, 2H, CH_2), 2.18 (s, 3H, CH_3), 1.63 (s, 6H, 2x CH_3).

^{13}C NMR(62.5 MHz, $CDCl_3$): δ = 184.7, 184.5, 147.4, 141.1, 133.8 x2, 132.0, 131.8, 126.7, 126.5, 87.9, 37.0, 26.4, 14.0 x2.

Anal.Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.61; H, 5.60; N, 4.95.

2-Methyl-3-((1-nitrocyclohexyl)methyl)-1,4-naphthoquinone (4i)

The reaction procedure was performed as previously described by $S_{RN}1$, the solvent is toluene.

Yield: 70%, yellow solid, mp 135-136 °C(isopropanol).

1H NMR (200MHz, $CDCl_3$): δ = 8.03-8.08 (m, 2H, Ar-H), 7.67-7.72 (m, 2H, Ar-H), 3.23 (s, 2H, CH_2), 2.42-2.53 (m, 2H, CH_2), 2.09 (s, 3H, CH_3), 1.58-1.72 (m, 4H, 2x CH_2), 1.19-1.25 (m, 4 H, 2x CH_2). ^{13}C NMR (50MHz, $CDCl_3$): δ = 184.6, 184.5, 147.5, 140.7, 133.7, 133.6, 132.0, 131.8, 126.7, 126.4, 91.4, 37.8, 34.7x2, 24.4, 22.3x2, 13.8.

HRMS (ESI): m/z $[M + NH_4]^+$ calcd for $C_{18}H_{19}NO_4$: 331.1652 ; found: 331.1655.

2-Methyl-3-((1-nitrocyclopentyl)methyl)-1,4-naphthoquinone (4j)

The reaction procedure was performed as previously described by $S_{RN}1$, the solvent is toluene.

Yield: 51%, yellow solid, mp 90-91 °C(petroleum ether).

1H NMR (200MHz, $CDCl_3$): δ = 8.04-8.09 (m, 2H, Ar-H), 7.68-7.73 (m, 2H, Ar-H), 4.43 (s, 2H, CH_2), 2.55-2.65 (m, 2H, CH_2), 2.12 (s, 3H, CH_3), 1.65-1.94 (m, 6 H, 3x CH_2).

^{13}C NMR (50MHz, $CDCl_3$): δ = 184.7, 184.6, 147.2, 141.4, 133.7, 133.7, 132.0, 131.8, 126.6, 126.4, 100.0, 36.4x2, 34.7, 22.7x2, 13.7.

HRMS (ESI): m/z $[M + NH_4]^+$ calcd for $C_{17}H_{17}NO_4$: 317.1496 ; found: 317.1492.

2-Methyl-3-(2-nitro-2-phenylpropyl)-1,4-naphthoquinone (4l)

The reaction procedure was performed as previously described by $S_{RN}1$, the solvent is toluene.

Yield: 43%, yellow solid, mp 138-139 °C (isopropanol).

1H NMR (200MHz, $CDCl_3$): δ = 7.98-8.06 (m, 2H, Ar-H), 7.67-7.71 (m, 2H, Ar-H), 7.32 (s, 5H, Ar-H), 4.00 (d, J =13.3 Hz, 1H, CH), 3.74 (d, J =13.3Hz, 1H, CH), 1.86 (s, 3H, CH_3), 1.73 (s, 3H, CH_3).

^{13}C NMR (50MHz, $CDCl_3$): δ = 184.5x2, 147.9, 141.0, 139.6, 133.8x3, 131.9, 129.1, 128.9x2, 126.6, 126.4, 125.5x2, 93.4, 36.2, 24.6, 13.5.

HRMS (ESI): m/z $[M + NH_4]^+$ calcd for $C_{20}H_{17}NO_4$: 353.1496 ; found: 353.1492.

General procedure of one-pot $S_{RN}1$ /demethylation of naphthoquinone (3)

Corresponding nitroalkane (0.84mmol, 2 equiv) and 1.10 mL of 40% TBAOH were stirred at rt for 1 h under nitrogen atmosphere. Then, naphthoquinone 3(0.42 mmol, 100mg, 1 equiv) solubilized in 5 mL of dichloromethane, was added. The mixture was stirred at rt under nitrogen atmosphere with white light irradiation (60W) 12 h. The reaction was quenched by 10 mL of water and the product was extracted with dichloromethane (4×30 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated. The product was purified by chromatography on a silica gel column, eluting with dichloromethane/petroleum ether 1:1, followed by recrystallization from corresponding solvent.

2-Hydroxy-3-(2-methyl-2-nitropropyl)naphthalene-1,4-dione (5a)

The reaction procedure was performed as previously described by $S_{RN}1$, the solvent is dichloromethane.

Yield: 70%, yellow solid, mp 141 °C(Petroleum ether).

1H NMR(200MHz, $CDCl_3$): δ = 8.07-8.15 (m, 2H, Ar-H), 7.70-7.83 (m, 2H, Ar-H), 7.60 (s, 1H, OH), 3.29 (s, 2H, CH_2), 1.63 (s, 6H, 2x CH_3).

^{13}C NMR(50MHz, $CDCl_3$): δ = 184.1, 180.9, 154.9, 135.4, 133.3, 132.6, 129.3, 127.2, 126.4, 117.7, 88.0, 34.1, 26.1x2.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{13}NO_5$: 276.0866 ; found: 276.0866.

2-Hydroxy-3-((1-nitrocyclohexyl)methyl)-naphthalene-1,4-dione(5b)

The reaction procedure was performed as previously described by $S_{RN}1$, the solvent is dichloromethane.

Yield: 55%, yellow solid, mp 150°C(petroleum ether).

1H NMR(200MHz, $CDCl_3$): δ = 8.06-8.13 (m, 2H, Ar-H), 7.66-7.80 (m, 2H, Ar-H), 7.49 (s, 1H, OH), 3.15 (s, 2H, CH_2), 2.49-2.54(m, 2H, CH_2), 1.54-1.63 (m, 5H, CH_2 ,CH), 1.40 (s, 1H, CH), 1.21-1.29 (m, 4H, CH_2 , CH).

^{13}C NMR(50MHz, $CDCl_3$): δ = 184.1, 180.9, 154.9, 135.3, 133.3, 132.6, 129.3, 127.3, 126.4, 117.3, 91.2, 34.8, 34.4x2, 24.5, 22.3x2.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{17}NO_5$: 316.1179 ; found: 316.1181.

General procedure for cyclization of compounds (4a-n)

Corresponding naphthoquinone (0.57mmol, 1 equiv) obtained by $S_{RN}1$ was solubilized in 50mL of glacial acetic acid and stirred. Zinc powder(17.10mmol, g, 30 equiv) was added progressively and the mixture was stirred vigorously overnight at 60 °C. Reaction was cooled to rt, filtered by celite, washed with dichloromethane (6×20 mL) and concentrated in vacuo. The mixture was poured into 60 mL of dichloromethane, washed with water (4×25 mL), dried over anhydrous sodium sulfate and concentrated in vacuo. After purification on a silica gel column, eluting with dichloromethane/petroleum ether 1:1, products obtained were recrystallized from the corresponding solvent.

4-Methoxy-2,2-dimethyl-2H-benzo[g]indol-5(3H)-one (6a)

Yield: 60%, red solid, mp 75°C (isopropanol).

1H NMR (200MHz, $CDCl_3$): δ = 8.21-8.25 (m, 1H, Ar-H), 8.09-8.13 (m, 1H, Ar-H), 7.53-7.61 (m, 2H, Ar-H), 4.00 (s, 3H, OCH_3), 2.91 (s, 2H, CH_2), 1.42 (s, 6H, $2 \times CH_3$).

^{13}C NMR (50MHz, $CDCl_3$): δ = 181.1, 161.0, 149.1, 134.4, 132.5, 132.2, 131.1, 130.6, 126.8, 124.9, 74.0, 59.2, 41.8, 29.3x2.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{15}NO_2$: 242.1176 ; found: 242.1175.

4-Methoxyspiro[benzo[g]indole-2,1'-cyclohexan]-5(3H)-one (6b)

Yield: 50%, brown oil.

1H NMR (200MHz, $CDCl_3$): δ = 8.27-8.32 (m, 1H, Ar-H), 8.14-8.19 (m, 1H, Ar-H), 7.58-7.68 (m, 2H, Ar-H), 4.06 (s, 3H, OCH_3), 2.88 (s, 2H, CH_2), 1.40-1.96 (m, 10H, $5 \times CH_2$).

^{13}C NMR (50MHz, $CDCl_3$): δ = 181.3, 161.0, 149.1, 134.6, 132.5, 132.3, 131.1, 130.7, 126.8, 125.00, 77.8, 59.4, 38.9, 37.9x2, 25.4, 23.6x2.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{18}H_{19}NO_2$: 282.1489 ; found: 282.1495.

4-Methoxyspiro[benzo[g]indole-2,1'-cyclopentan]-5(3H)-one (6c)

Yield: 60%, clear red solid, mp 87°C (petroleum ether).

1H NMR (200MHz, $CDCl_3$): δ = 8.28-8.32 (m, 1H, Ar-H), 8.14-8.19 (m, 1H, Ar-H), 7.60-7.66 (m, 2H, Ar-H), 4.05 (s, 3H, OCH_3), 3.02 (s, 2H, CH_2), 1.98-2.10 (m, 4H, $2 \times CH_2$), 1.66-1.85 (m, 4H, $2 \times CH_2$). ^{13}C

NMR (50MHz, $CDCl_3$): δ = 181.3, 161.2, 148.8, 134.5, 132.5, 132.2, 131.1, 130.7, 126.8, 125.0, 59.3, 53.5, 40.9, 40.4x2, 24.7x2.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{17}NO_2$: 268.1332 ; found: 268.1332.

4-Methoxy-2-propyl-2,3-dihydrobenzo[g]indol-5-one (6d)

Yield: 54%, brown oil.

1H NMR (200MHz, $CDCl_3$): δ = 8.25-8.29 (m, 1H, Ar-H), 8.13-8.18 (m, 1H, Ar-H), 7.60-7.66 (m, 2H, Ar-H), 4.48-4.58 (m, 1H, CH), 4.05 (s, 3H, CH_3), 3.23 (dd, J = 19.3, 6.1Hz, 1H, CH), 2.71 (dd, J = 19.3, 2.4Hz, 1H, CH), 1.80-1.92 (m, 1H, CH), 1.46-1.62 (m, 2H, CH_2), 1.32-1.41 (t, J =7.0Hz, 1H, CH), 0.95-1.03 (t, J =7.0Hz, 3H, CH_3).

^{13}C NMR (50MHz, $CDCl_3$): δ = 181.3, 163.3, 149.0, 134.4, 132.5, 132.2, 131.2, 130.4, 126.8, 124.8, 73.2, 59.3, 38.8, 33.9, 19.9, 14.2.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{17}NO_2$: 256.1332 ; found: 256.1331.

4-Methoxy-2-methyl-2-phenyl-2,3-dihydrobenzo[g]indol-5-one (6e)

Yield: 51%, clear red solid, mp 102°C (isopropanol).

1H NMR (200MHz, $CDCl_3$): δ = 8.43-8.47 (m, 1H, Ar-H), 8.18-8.22 (m, 1H, Ar-H), 7.65-7.71 (m, 2H, Ar-H), 7.28-7.49 (m, 5H, Ar-H), 4.05 (s, 3H, OCH_3), 3.36 (s, 2H, CH_2), 1.71 (m, 3H, CH_3).

^{13}C NMR (50MHz, $CDCl_3$): δ = 181.1, 162.2, 149.2, 147.2, 133.4, 132.7, 132.3, 131.4, 130.6, 128.6 x2, 126.9 x2, 125.4 x2, 125.3, 78.6, 59.3, 43.8, 30.56. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{17}NO_2$: 304.1332 ; found: 304.1334.

4-Methoxy-2-methyl-2,3-dihydrobenzo[g]indol-5-one (6f)

Yield: 56%, brown oil.

1H NMR (200MHz, $CDCl_3$): δ = 8.22-8.26 (m, 1H, Ar-H), 8.10-8.14 (m, 1H, Ar-H), 7.58-7.63 (m, 2H, Ar-H), 4.52-4.67 (m, 1H, CH), 4.03 (s, 3H, OCH_3), 3.23 (dd, J = 19.2, 6.2Hz, 1H, CH), 2.72 (dd, J =19.2, 2.4Hz, 1H, CH), 1.43-1.46 (d, J =6.9Hz, 3H, CH_3).

^{13}C NMR (50MHz, $CDCl_3$): δ = 181.2, 163.3, 149.1, 134.2, 132.6, 132.1, 131.3, 130.3, 126.8, 124.9, 68.5, 59.2, 35.7, 22.2.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{13}NO_2$: 228.1019 ; found: 228.1013.

2-Ethyl-4-methoxy-2,3-dihydrobenzo[g]indol-5-one (6g)

Yield: 54%, brown oil.

1H NMR (200MHz, $CDCl_3$): δ = 8.29-8.33 (m, 1H, Ar-H), 8.13-8.18 (m, 1H, Ar-H), 7.61-7.66 (m, 2H,

Ar-H), 4.46-4.54 (m, 1H, CH), 4.06 (s, 3H, OCH₃), 3.23 (dd, J = 19.2, 6.2Hz, 1H,CH), 2.72 (dd, J = 19.2, 2.5 Hz, 1H, CH), 1.89-2.08 (m, 1H,CH), 1.59-1.75 (m, 1H, CH), 1.03-1.10 (t, J =7.4Hz, 3H, CH₃).

¹³C NMR (50MHz, CDCl₃): δ = 181.1, 163.6, 149.2, 134.1, 132.6, 132.2, 131.4, 130.1, 126.9, 125.0, 74.3, 59.3, 33.3, 29.4, 10.7.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₅H₁₅NO₂: 242.1176 ; found: 242.1174.

2,2,4-Trimethyl-2,3-dihydrobenzo[g]indol-5-one (6h)

Yield: 75%, green solid, mp 57-58 °C (isopropanol).

¹H NMR (200MHz, CDCl₃): δ = 8.30-8.34 (m, 1H, 1Ar-H), 8.16-8.20 (m, 1H, Ar-H), 7.62-7.67 (m, 2H, Ar-H), 2.76(s, 2H, CH₂), 2.07 (s, 3H, CH₃), 1.49 (s, 6H, 2xCH₃).

¹³C NMR (50MHz, CDCl₃): δ = 184.4, 160.4, 132.5x2, 131.9, 131.8, 127.0x2, 125.5, 77.2, 73.1, 42.8, 29.3, 13.1x2.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₅H₁₅NO: 226.1226 ; found: 226.1227.

4-Methylspiro[benzo[g]indole-2,1'-cyclohexan]-5(3H)-one (6i)

Yield: 85%, yellow solid, mp 82°C (isopropanol).

¹H NMR (200MHz, CDCl₃): δ = 8.27-8.31 (m, 1H, Ar-H), 8.14-8.18 (m, 1H, Ar-H), 7.59-7.64 (m, 2H, Ar-H), 2.69 (s, 2H, CH₂), 2.06(s, 3H, CH₃), 1.24-1.93 (m, 10H, 5xCH₂).

¹³C NMR (50MHz, CDCl₃): δ = 185.1, 160.1, 151.0, 132.2, 131.9, 131.2, 130.9, 126.8, 124.9, 40.1, 38.0x2, 29.7, 25.4, 23.7x2, 13.0.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₈H₁₉NO: 266.1539 ; found: 266.1539.

4-Methylspiro[benzo[g]indole-2,1'-cyclopentan]-5(3H)-one (6j)

Yield: 79%, yellow solid, mp 123°C (petroleum ether).

¹H NMR (200MHz, CDCl₃): δ = 8.28-8.32 (m, 1H, Ar-H), 8.14-8.19 (m, 1H, Ar-H), 7.60-7.66 (m, 2H, Ar-H), 4.05 (s, 3H, CH₃), 3.02 (s, 2H, CH₂), 1.98-2.10 (m, 4H, 2xCH₂), 1.66-1.85 (m, 4H, 2xCH₂).

¹³C NMR (65.2MHz, CDCl₃): δ = 185.1, 160.4, 151.2, 132.2, 131.9, 131.3, 131.1, 131.0, 126.9, 124.8, 83.7, 42.1, 40.4x2, 24.7x2, 13.1.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₇H₁₇NO : 252.1383 ; found: 252.1385.

4-Methyl-2-propyl-2,3-dihydrobenzo[g]indol-5-one (6k)

Yield: 56%, red clear solid, mp 63°C (isopropanol).

¹H NMR (200MHz, CDCl₃) : δ = 8.21-8.26 (m, 1H, Ar-H), 8.11-8.16 (m, 1H, Ar-H), 7.57-7.64 (m, 2H, Ar-H), 4.44-4.53 (m, 1H, CH), 2.99 (ddd, J = 19.4, 6.0, 1.7Hz, 1H, CH), 2.48 (dt, J = 9.4, 1.9Hz, 1H, CH), 2.03 (s, 3H, CH₃), 1.80-1.92(m, 1H, CH), 1.45-1.64 (m, 3H, CH, CH₂), 0.95-1.02 (t, J =7.1 Hz, 3H, CH₃).

¹³C NMR (50MHz, CDCl₃): δ = 185.1, 162.4, 151.2, 132.2, 131.8, 131.3, 131.2, 130.7, 126.8, 124.6, 72.5, 38.8, 35.1, 16.9, 14.2, 13.0.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₆H₁₇NO: 240.1383 ; found: 240.1383.

2,4-Dimethyl-2-phenyl-2,3-dihydrobenzo[g]indol-5-one (6l)

Yield: 58%, yellow solid, mp 144-145 °C (isopropanol).

¹H NMR (200MHz, CDCl₃): δ = 9.23-9.27 (m, 1H, Ar-H), 8.23-8.38 (m, 1H, Ar-H), 7.67-7.73 (m, 2H, Ar-H), 7.32-7.38 (m, 5H, Ar-H), 3.50 (dd, J =17.9, 1.1 Hz, 1 H, CH), 3.19 (dd, J =17.9, 1.3Hz, 1H, CH), 2.09 (dd, J = 1.3, 1.1Hz, 3H,CH₃), 2.07 (m, 3H, CH₃).

¹³C NMR (50MHz, CDCl₃): δ = 183.1, 143.7, 141.5, 132.7, 131.0, 130.5, 129.0x2, 128.7, 128.5, 127.4, 125.4, 125.2x2, 124.7, 81.3, 77.3, 41.3, 25.0, 11.9.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₀H₁₇NO: 288.1383 ; found: 288.1385.

2,4-Dimethyl-2,3-dihydrobenzo[g]indol-5-one (6m)

Yield: 74%, red clear solid, mp 104°C (isopropanol).

¹H NMR (200MHz, CDCl₃): δ = 8.23-8.27 (m, 1H, Ar-H), 8.13-8.18 (m, 1H, Ar-H), 7.60-7.64 (m, 2H, Ar-H), 4.54-4.67 (m, 1H, CH), 3.09 (ddd, J = 19.4, 6.1, 1.7Hz, 1H, 1x CH), 2.45 (dt, J = 19.4, 1.9Hz, 1H, CH), 2.05 (s, 3H, CH₃), 1.47 (d, J =6.9Hz, 3H, CH₃).

¹³C NMR (50MHz, CDCl₃): δ = 185.1, 162.3, 151.3, 132.3, 131.8, 131.5, 131.3, 130.7, 126.9, 124.7, 68.0, 36.9, 22.3, 13.1.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₄H₁₃NO: 212.1070 ; found: 212.1070.

2-Ethyl-4-methyl-2,3-dihydrobenzo[g]indol-5-one (6n)

Yield: 60%, yellow solid, mp 62-64°C (petroleum ether).

¹H NMR (200MHz, CDCl₃): δ = 8.24-8.29 (m, 1H, Ar-H), 8.14-8.18 (m, 1H, Ar-H), 7.60-7.65 (m, 2H, Ar-H), 4.40-4.50 (m, 1H, CH), 3.01 (ddd, J = 19.4, 6.0, 1.6 Hz, 1H, CH), 2.5 (dt, J = 19.4, 1.9Hz, 1H, CH) , 2.06 (s, 3H, CH₃), 1.85-2.02 (m, 1H, CH), 1.55-1.72 (m, 1H, CH), 1.07 (t, J =7.3Hz, 3 H, CH₃).

^{13}C NMR (50MHz, CDCl_3): δ = 185.2, 162.5, 151.1, 132.2, 131.8, 131.3, 131.2, 130.7, 126.8, 124.7, 73.9, 34.6, 29.5, 13.0, 10.8.

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{NO}$: 226.1226; found: 226.1226.

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