Study and application of graphene oxide on the synthesis of 2,3-disubstituted quinolines via Povarov multicomponent reaction and subsequent oxidation

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General methods

$^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz, and 75 MHz respectively) or on JEOL 400 (at 400 MHz and 101 MHz respectively).

Unless otherwise stated, NMR spectra were recorded using residual solvent as the internal standard $^1$H NMR: CDCl$_3$ = 7.26, CD$_3$OD = 4.87; (CD$_3$)$_2$SO = 2.50; and $^{13}$C NMR: CDCl$_3$ = 77.0; CD$_3$OD =49.0;(CD$_3$)$_2$SO = 39.52. Data for $^1$H NMR spectra are reported as follows: chemical shift (δ ppm), integration, multiplicity and coupling constants (Hz). Data for $^{13}$C NMR spectra are reported in terms of chemical shift (δ ppm). Interpretation of spectra has been made also with the aid of gCOSY and gHSQC experiments. The following abbreviations are used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

I.R. spectra were recorded as solid, oil, or foamy samples, with the ATR (attenuated total reflectance) method.

TLC analyses were carried out on pre-coated Merck silica gel 60 F254 plates and viewed at UV (254 nm) and developed with Hanessian stain (dipping into a solution of (NH$_4$)$_4$MoO$_4$·4H$_2$O (21 g) and Ce(SO$_4$)$_2$·4H$_2$O (1 g) in H$_2$SO$_4$ (31 mL) and H$_2$O (469 mL) and warming). $R_f$ were measured after an elution of 7–9 cm.

Column chromatographies were done with the "flash" methodology using 220–400 mesh silica. Petroleum ether (40–60 °C) is abbreviated as PE. In extractive work-up, aqueous solutions were always re-extracted three time with the appropriate organic solvent. Organic extracts were always dried over Na$_2$SO$_4$ and filtered, before evaporation of the solvent under reduced pressure.

All reactions using dry solvents were carried out under a nitrogen (or argon if specified) atmosphere. Unless otherwise noted, analytical grade solvents and commercially available reactants were used without further purification. Common reagents were purchased from commercial sources and were used without further purification. Graphene oxide (GO) was purchased from Graphenea and Abalonyx companies.

All products were characterized by $^1$H, $^{13}$C NMR, IR and elemental analysis. The spectroscopic data of products were identical with the data reported in the literature.
Control experiments

Determination of the amount of Mn on GO (Graphenea): Quantification of the trace of Mn impurities contained within GO has been determined by using two methods. With ICP-OES (Inductively coupled plasma - optical emission spectrometry), we detected low quantities of Mn (4740 ppm) in GO Graphenea. Sample preparation: acidic digestion of Graphene oxide (10.3 mg, Graphenea) was dissolved in a mixture of HCl/HNO₃ (1 mL, 3:1) and heated at 110 °C for 24 h, then at 150 °C for 6 h. The mixture was cooled and diluted to 10 mL with milliQ water, and subsequently analyzed by ICP-OES, founding 4740 ppm of Mn. Alternatively, the sample has been digested by MW heating, obtaining similar results. Similar results (4400 ppm) were obtained by performing UV-Vis analysis of KMnO₄ after treatment of the sample with sulphuric acid and potassium periodate.

Povarov reaction with MnCl₂•4H₂O: to a solution of 4-chlorobenzaldehyde (35 mg, 0.25 mmol), aniline (30 mg, 30 μL, 0.33 mmol) and 2,3-dihydrofuran (26 mg, 28 μL, 0.38 mmol) in CH₃CN (0.3 mL), 6 μL of aq. solution of MnCl₂•4H₂O (5mg/ml) was added and the mixture was stirred at rt for 24 h. Then, the solvent was removed under vacuo and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (95:5 to 90:10) to afford 1a (14 mg, 20%) as a mixture of diastereoisomers (endo/exo 80:20).

Oxidation reaction with MnCl₂•4H₂O: to a solution of pure endo 1a (30 mg, 0.10 mmol) in CH₃CN/H₂O (1.00 mL), 10 μL of aq. solution of MnCl₂•4H₂O (5mg/ml) was added and the mixture was stirred at 120 °C for 48 h. Then, the solvent was removed under vacuo to afford only unreacted endo 1a.

GO recyclability experiments

GO reusability in Povarov reaction: reusability of GO (Graphenea) was verified for the standard reaction of 4-chlorobenzaldehyde (351 mg, 2.5 mmol), aniline (296 μL, 3.25 mmol) with 2,3-dihydrofuran (473 μL, 6.25 mmol) at room temperature for 24 h. The catalyst was recovered by dissolving the mixture in DCM/EtOAc 1:1 (10 mL) followed by centrifugation (5 min at 7800 rpm) for 4 times. The collected solutions were evaporated and the residue purified by column chromatography, giving 1a (492 mg, 66%) as a mixture of diastereoisomers (endo/exo 80:20). The catalyst was washed with H₂O (20 mL), MeOH (20 mL) and acetone (20 mL), dried under vacuum.
overnight, and reused. This procedure was repeated for five reactions and 1a was obtained with the yield of 48, 48, 41, 29 and 22%, respectively. The selectivity endo/exo resulted 80:20 by NMR of the crude after every run. The reusability experiments have been repeated by using commercial Abalonyx (S-126/36, No product 18000) affording 1a in 60%, 46% and 45% yield, respectively. After the recyclability experiments, the recovered catalyst after the first and the last run were analyzed by XPS analysis.

**GO reusability in oxidation reaction**: reusability of GO (Graphenea) was verified for the standard reaction of endo 1a (143 mg, 0.5 mmol) in CH$_3$CN/H$_2$O (4:1, 5.00 mL) at 120 °C for 48 h. The catalyst was recovered by dissolving the mixture in DCM/EtOAc 1:1 (10 mL) followed by centrifugation (5 min at 7800 rpm) for 4 times. The collected solutions were evaporated and the residue purified by column chromatography, giving 2a (105 mg, 74%). The catalyst was washed with H$_2$O (2x5 mL), MeOH (2x5 mL) and acetone (2x5 mL), dried under vacuum overnight, and reused. This procedure was repeated for two reactions and 2a was obtained with the yield of 49 and 49 %, respectively. After the recyclability experiments, the recovered catalyst after the first and the last run were analyzed by XPS analysis.

Note that GO Abalonyx must be sonicated for 30 min before used, as suggested by the vendor.
XPS analysis of GO (Graphenea and Abalonyx)

**Figure S1.** XPS Survey spectra of GO (Graphenea); GO after CH$_3$CN at room temperature for 24 h; GO after 1st cycle; GO after 6th cycle.

<table>
<thead>
<tr>
<th>Elements Transition</th>
<th>Binding Energies eV</th>
<th>GO Graphenea</th>
<th>Control</th>
<th>1st cycle</th>
<th>6th cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>285</td>
<td>72.1 ± 0.9</td>
<td>71.8 ± 0.9</td>
<td>72.5 ± 0.9</td>
<td>73.4 ± 0.9</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.7</td>
<td>26.1 ± 0.9</td>
<td>27.3 ± 0.9</td>
<td>26.2 ± 0.9</td>
<td>24.6 ± 0.9</td>
</tr>
<tr>
<td>N 1s</td>
<td>401-399</td>
<td>0.4±0.1</td>
<td>0.3±0.1</td>
<td>0.7±0.1</td>
<td>1.1±0.1</td>
</tr>
<tr>
<td>S 2p / S-O</td>
<td>168.5</td>
<td>0.40±0.05</td>
<td>0.4±0.1</td>
<td>0.4±0.0.1</td>
<td>0.20±0.05</td>
</tr>
<tr>
<td>Si 2p / Si-O</td>
<td>101.7</td>
<td>0.9±0.1</td>
<td>0.2±0.1</td>
<td>0.10±0.05</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td>Mn 2p$_{3/2}$ MnOx</td>
<td>641.8</td>
<td>0.15±0.03*</td>
<td>0.05±0.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cl 2p</td>
<td>199.8</td>
<td>-</td>
<td>-</td>
<td>0.20±0.05</td>
<td>0.4±0.1</td>
</tr>
<tr>
<td>O/C Area</td>
<td>0.36±0.01</td>
<td>0.38±0.01</td>
<td>0.36±0.01</td>
<td>0.34±0.01</td>
<td></td>
</tr>
</tbody>
</table>

**Table S1.** XPS Atomic composition of GO (Graphenea); GO after CH$_3$CN at room temperature for 24 h; GO after 1st cycle; GO after 6th cycle. *Mn sensitivity c.a. 0.03%.
Figure S2. XPS Survey spectra of GO (Abalonyx GO); GO after CH₃CN at room temperature for 24 h; GO after 1st cycle; GO after 3rd cycle.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Binding Energies eV</th>
<th>GO Aba</th>
<th>Control</th>
<th>1ˢᵗ cycle</th>
<th>3ʳᵈ cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>285</td>
<td>65.9 ± 0.9</td>
<td>70.3 ± 0.9</td>
<td>73.9 ± 0.9</td>
<td>73.5 ± 0.9</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.7</td>
<td>30.3 ± 0.9</td>
<td>28.5 ± 0.9</td>
<td>24.5 ± 0.9</td>
<td>24.7 ± 0.9</td>
</tr>
<tr>
<td>N 1s</td>
<td>401-399</td>
<td>1.0±0.1</td>
<td>0.3±0.03</td>
<td>0.7±0.1</td>
<td>1.0±0.1</td>
</tr>
<tr>
<td>S 2p / S-O</td>
<td>168.5</td>
<td>1.8±0.2</td>
<td>0.20±0.05*</td>
<td>0.20±0.05</td>
<td>0.20±0.05</td>
</tr>
<tr>
<td>Si 2p / Si-O</td>
<td>101.7</td>
<td>0.4±0.1</td>
<td>0.3±0.1</td>
<td>0.2±0.1</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td>Cl 2p</td>
<td>199.8</td>
<td>0.6±0.1</td>
<td>0.5±0.03</td>
<td>0.5±0.05</td>
<td>0.4±0.1</td>
</tr>
</tbody>
</table>

Table S2. XPS Atomic composition of GO (Abalonyx GO); GO after CH₃CN at room temperature for 24 h; GO after 1st cycle; GO after 3rd cycle. O/C decrease mainly due to decrease of SO₄, not due reduction of C-O groups.
**Table S3.** XPS C 1s fitting of GO (Abalonyx GO); GO after CH$_3$CN at room temperature for 24 h; GO after 1st cycle; GO after 3rd cycle.

<table>
<thead>
<tr>
<th>C groups</th>
<th>GO Aba</th>
<th>Control</th>
<th>1$^{st}$ cycle</th>
<th>3$^{rd}$ Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C sp$^2$ 284.4 eV</td>
<td>32.9±0.9</td>
<td>30.0±0.9</td>
<td>29.6±0.9</td>
<td>31.5±0.9</td>
</tr>
<tr>
<td>C=C* -0.8 eV</td>
<td>4.4±0.4</td>
<td>5.4±0.9</td>
<td>4.8±0.9</td>
<td>4.3±0.5</td>
</tr>
<tr>
<td>C-C sp$^3$ +0.6</td>
<td>7.7±0.5</td>
<td>8.1±0.5</td>
<td>18.0±0.5</td>
<td>17.8±0.5</td>
</tr>
<tr>
<td>C-OH +1.8</td>
<td>18.0±0.4</td>
<td>19.8±0.4</td>
<td>11.8±0.4</td>
<td>11.0±0.4</td>
</tr>
<tr>
<td>C-O-C +2.4</td>
<td>28.3±0.9</td>
<td>28.3±0.9</td>
<td>28.7±0.9</td>
<td>29.0±0.9</td>
</tr>
<tr>
<td>C=O +3.8</td>
<td>6.6±0.5</td>
<td>7.2±0.5</td>
<td>5.1±0.5</td>
<td>4.6±0.5</td>
</tr>
<tr>
<td>O-C=O +4.7</td>
<td>2.2±0.2</td>
<td>1.1±0.2</td>
<td>2.0±0.2</td>
<td>1.9±0.2</td>
</tr>
<tr>
<td>O/C fit</td>
<td>0.43±0.02</td>
<td>0.43±0.02</td>
<td>0.35±0.02</td>
<td>0.34±0.02</td>
</tr>
</tbody>
</table>

**Figure S3.** XPS Mn 2p spectra of GO (Graphenea); GO after CH$_3$CN at room temperature for 24 h; GO after 6th cycle (left). GO (Abalonyx); GO after CH$_3$CN at room temperature for 24 h; GO after 3rd cycle (right).
Figure S4. XPS C 1s signal of: a) commercial Abalonyx GO; b) GO after CH$_3$CN at room temperature for 24 h; c) GO after 1st cycle; d) GO after 3rd cycle.
C groups
In C1s XPS | GO Graphenea | Control | 1st cycle | 6th cycle
--- | --- | --- | --- | ---
C=C sp² | 284.4 eV | 42.2±0.9 | 35.4±0.9 | 43.7±0.9 | 45.5±0.9
C=C* | -0.8 eV | 4.3±0.4 | 7.2±0.9 | 6.0±0.9 | 5.6±0.5
C-C sp³ | +0.6 | 3.9±0.5 | 6.4±0.5 | 3.4±0.5 | 7.0±0.5
C-OH | +1.8 | 12.6±0.4 | 16.1±0.4 | 20.0±0.4 | 12.3±0.4
C-O-C | +2.4 | 29.1±0.9 | 25.6±0.9 | 22.0±0.9 | 24.5±0.9
C=O | +3.8 | 6.0±0.5 | 7.8±0.5 | 4.2±0.5 | 3.8±0.5
O-C=O | +4.7 | 1.9±0.2 | 1.4±0.2 | 0.7±0.2 | 1.3±0.2

| O/C fit | 0.37±0.02 | 0.41±0.02 | 0.37±0.02 | 0.31±0.02 |

**Table S4.** XPS C 1s fitting of GO (Graphenea GO); GO after CH₃CN at room temperature for 24 h; GO after 1st cycle; GO after 6th cycle.

**Figure S5.** XPS C 1s signal of: a) commercial Graphenea GO; b) GO after CH₃CN/H₂O 4:1 at 120°C for 48 h; c) GO after oxidation. Sp² fraction was 42%, 54% and 78%, respectively.
Figure S6. XPS survey spectra of commercial Abalonyx GO; GO after CH$_3$CN/H$_2$O 4:1 at 120°C for 48 h; GO after oxidation.

<table>
<thead>
<tr>
<th>Elements</th>
<th>GO Graphenea</th>
<th>Control</th>
<th>GO after oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>72.1 ± 0.9</td>
<td>78.3 ± 0.9</td>
<td>88.2 ± 0.9</td>
</tr>
<tr>
<td>O</td>
<td>26.1 ± 0.9</td>
<td>21.4 ± 0.9</td>
<td>10.7 ± 0.9</td>
</tr>
<tr>
<td>N</td>
<td>0.4±0.1</td>
<td>0.3±0.1</td>
<td>0.4±0.1</td>
</tr>
<tr>
<td>S-O</td>
<td>0.40±0.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si-O</td>
<td>0.9±0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MnOx</td>
<td>0.15±0.03*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>-</td>
<td>0.70±0.05</td>
</tr>
<tr>
<td>O/C Area</td>
<td>0.36±0.01</td>
<td>0.28±0.01</td>
<td>0.12±0.01</td>
</tr>
</tbody>
</table>

Table S5. XPS Atomic composition of GO (Graphenea); GO after CH$_3$CN/H$_2$O 4:1 at 120°C for 48 h; GO after oxidation. *Mn sensitivity c.a. 0.03%.
### ssNMR analysis of GO (Graphenea and Abalonyx)

<table>
<thead>
<tr>
<th>conditions</th>
<th>Csp2 130 ppm</th>
<th>C sp3 31 ppm</th>
<th>COH 70 ppm</th>
<th>C-O-C 60 ppm</th>
<th>O-C=O 167 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO Graphenea control in ACN, 24h, 20°C</td>
<td>30.0±0.9</td>
<td>-</td>
<td>25.9±0.9</td>
<td>43.3±0.9</td>
<td>0.8±0.3</td>
</tr>
<tr>
<td>GO Graphenea after 1 cycle</td>
<td>27.8±0.9</td>
<td>13.0±0.9</td>
<td>18.5±0.9</td>
<td>39.0±0.9</td>
<td>1.8±0.3</td>
</tr>
<tr>
<td>GO Graphenea after 6 cycles</td>
<td>30.1±0.9</td>
<td>14.4±0.9</td>
<td>20.7±0.9</td>
<td>34.6±0.9</td>
<td>0.3±0.2</td>
</tr>
<tr>
<td>GO Abalonyx control in ACN, 24h, 20°C</td>
<td>28.0±0.9</td>
<td>-</td>
<td>23.5±0.9</td>
<td>38.5±0.9</td>
<td>9.9±0.3</td>
</tr>
<tr>
<td>GO Abalonyx after 1 cycle</td>
<td>26.5±0.9</td>
<td>14.4±0.9</td>
<td>20.3±0.9</td>
<td>33.7±0.9</td>
<td>5.1±0.3</td>
</tr>
<tr>
<td>GO Abalonyx after 3 cycles</td>
<td>29.2±0.9</td>
<td>13.9±0.9</td>
<td>20.9±0.9</td>
<td>33.0±0.9</td>
<td>3.0±0.3</td>
</tr>
</tbody>
</table>

**Table S6.** Quantitative composition of GO in different conditions obtained by using ssNMR 13C direct excitation.
Figure S7. 13C direct excitation ssNMR spectra of GO (Graphenea) after CH$_3$CN at room temperature for 24 h; GO after 1st cycle; GO after 6th cycle. Spinning side bands are marked with *.
Figure S8. $^{13}$C direct excitation ssNMR spectra of GO (Abalonyx) after CH$_3$CN at room temperature for 24 h; GO after 1st cycle; GO after 3rd cycle.
Structural assignment of tetrahydroquinoline derivatives

The stereochemistry of the furo- and pyrano- tetrahydroquinolines has been determined comparing coupling constants of protons 3a-9b and 3a-4, or 4a-10b and 4a-5 with the data reported on the literature.¹

The stereochemistry of cyclopentatetrahydroquinoline and of ethoxy-tetrahydroquinoline has been determined comparing coupling constants of protons 3a-9b and 3a-4, or 2-3 and 3-4 with the data reported on the literature.²

Synthesis of 1 via Povarov reaction

Synthesis of 4-(4-chlorophenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1a.

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH₃CN (300 μL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath,
then 4-chlorobenzaldehyde (35 mg, 0.25 mmol), aniline (30 mg, 30 µL, 0.325 mmol) and 2,3-dihydrofuran (26 mg, 28 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 4 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (95:5 to 85:15) to afford 1a as a mixture of diastereoisomers (endo/exo 80:20 determined by ¹H NMR) as white solid (44 mg, 62%). Trituration from CH₃CN gave the pure endo 1a as white powder. The physical and spectral data agreed with those reported.

endo 1a: Rf = 0.46 (PE/acetone 85:15); m.p. 204 - 206°C (CH₃CN) (Lit.³ mp: 152–153 °C); I.R.: ṽ (cm⁻¹) = 3388, 3317, 3059, 2978, 2923, 2880, 2851, 2851, 1608, 1588, 1486, 1410, 1366, 1319, 1297, 1262, 1185, 1145, 1085, 1057, 1035, 1022, 1013, 996, 973, 942, 914, 884, 843, 824, 704, 751, 673; ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.32 (m, 5H, 9-H, 4H-Ar), 7.10 (t, J = 7.5 Hz, 1H, 7-H), 6.83 (td, J = 7.4, 1.2 Hz, 1H, 8-H), 6.61 (dd, J = 8.0, 1.1 Hz, 1H, 6-H), 5.27 (d, J = 7.9 Hz, 1H, 9b-H), 4.68 (d, J = 3.1 Hz, 1H, 4-H), 3.88 – 3.77 (m, 2H, N-H and 2-H), 3.72 (td, J = 8.5, 6.9 Hz, 1H, 2-H), 2.81 – 2.70 (m, 1H, 3a-H), 2.23 – 2.10 (m, 1H, 3-H), 1.57 – 1.45 (m, 1H, 3-H); ¹³C NMR (101 MHz, CDCl₃) δ 144.7, 140.8, 133.4, 130.2, 128.9, 128.6, 128.0, 122.7, 119.5, 115.2, 75.9, 66.9, 57.0, 45.7, 24.7; Anal. Calcd. for C₁₇H₁₆ClNO: % C 71.45; H 5.64; N 4.90; O 5.60: C 71.46; H 5.73; N 4.80; O 5.64.

Synthesis of 4-(4-chlorophenyl)-8-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1b.

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH₃CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 4-chlorobenzaldehyde (35 mg, 0.25 mmol), p-toluidine (35 mg, 36 µL, 0.33 mmol) and 2,3-dihydrofuran (26 mg, 28 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 24 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (95:5 to 85:15) to afford 1b as a mixture of diastereoisomers (endo/exo 68:32 determined by ¹H NMR) as cream amorphous solid (30 mg, 40%). The physical and spectral data agreed with those
reported.4, 5 Rf = 0.30 (PE/acetone 90:10); I.R.: ū (cm−1) = 3304, 2973, 2942, 2910, 2876, 1621, 1509, 1489, 1409, 1362, 1299, 1261, 1159, 1085, 1034, 819; 1H NMR (300 MHz, CDCl3) selected data for endo 1b: δ 7.44 – 7.32 (m, 4H, 4-H-Ar), 7.17 (d, J = 1.6 Hz, 1H, 9-H), 6.97 – 6.88 (m, 1H, 7-H), 6.55 (t, J = 7.8 Hz, 1H, 6-H), 5.24 (d, J = 8.0 Hz, 1H, 9b-H), 4.62 (d, J = 3.1 Hz, 1H, 4-H), 3.89 – 3.77 (m, 1H, 2-H), 3.77 – 3.66 (m, 2H, N-H and 2-H), 2.81 – 2.68 (m, 1H, 3a-H), 2.27 (s, 3H, CH3), 2.24 – 2.09 (m, 1H, 3-H), 1.55 – 1.43 (m, 1H, 3-H); 13C NMR (75 MHz, CDCl3) selected data for endo 1b: δ 142.5, 141.0, 133.3, 130.5, 129.7, 129.3, 128.9, 128.0, 122.7, 115.2, 76.0, 66.9, 57.3, 45.9, 24.7, 20.7.

**Synthesis of 4-phenyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1c.**

![Chemical structure of 1c](attachment:image.png)

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH3CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then benzaldehyde (26 mg, 25 µL, 0.25 mmol), aniline (30 mg, 30 µL, 0.33 mmol) and 2,3-dihydrofuran (26 mg, 28 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 4 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO2), eluting with PE/acetone (95:5 to 85:15) to afford 1c as a mixture of diastereoisomers (endo/exo 79:21) as amber foam (39 mg, 62%). The physical and spectral data agreed with those reported.6, 7 Rf = 0.49 (PE/acetone 80:20); I.R.: ū (cm−1) =3345, 3293, 3059, 3027, 2971, 2939, 2881, 1609, 1588, 1484, 1451, 1368, 1337, 1294, 1253, 1197, 1159, 1143, 1082, 1058, 1038, 1020, 994, 967, 941, 912, 855, 752, 708, 646; 1H NMR (400 MHz, CDCl3) selected data for endo 1c: δ 7.50 – 7.30 (m, 6H, 9-H and 5-H-Ph), 7.10 (t, J = 7.6 Hz, 1H, 7-H), 6.83 (td, J = 7.5, 1.2 Hz, 1H, 8-H), 6.61 (dd, J = 8.1, 1.2 Hz, 1H, 6-H), 5.29 (d, J = 8.0 Hz, 1H, 9b-H), 4.71 (d, J = 3.1 Hz, 1H, 4-H), 3.90 – 3.78 (m, 2H, N-H and 2-H), 3.73 (td, J = 8.5, 6.8 Hz, 1H, 2-H), 2.85 – 2.74 (m, 1H, 3a-H), 2.29 – 2.15 (m, 1H, 3-H), 1.53 (ddddd, J = 11.8, 8.1, 6.9, 3.4 Hz, 1H, 3-H); 13C NMR (101 MHz, CDCl3) selected data for endo 1c: δ 145.1, 142.2, 130.2, 128.8, 128.5, 127.8, 126.6, 122.8, 119.3, 115.1, 76.1, 66.9, 57.6, 45.9, 24.8.

**Synthesis of 4-(naphthalen-1-yl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1d.**
A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH$_3$CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 1-naphthaldehyde (39 mg, 34 µL, 0.25 mmol), aniline (30 mg, 30 µL, 0.33 mmol) and 2,3-dihydrofuran (26 mg, 28 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 4 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO$_2$), eluting with PE/acetone (95:5 to 85:15) to afford 1d as a mixture of diastereoisomers (endo/exo 81:19) as white foam (35 mg, 47%); R$_f$ = 0.40 (PE/acetone 80:20); I.R.: δ (cm$^{-1}$) = 3354, 3312, 3049, 2972, 2931, 2872, 1609, 1589, 1478, 1382, 1339, 1295, 1257, 1191, 1169, 1156, 1138, 1061, 1026, 979, 908, 802, 782, 749, 641; $^1$H NMR (300 MHz, CDCl$_3$) selected data for endo 1d: δ 8.13 – 8.05 (m, 1H, 1$\text{H}$-Ar), 7.96 – 7.81 (m, 3H, 3$\text{H}$-Ar), 7.61 – 7.48 (m, 3H, 3$\text{H}$-Ar), 7.41 (dd, J = 7.7, 1.6 Hz, 1H, 9-H), 7.13 (t, J = 7.6 Hz, 1H, 7-H), 6.86 (td, J = 7.4, 1.2 Hz, 1H, 8-H), 6.68 (dd, J = 8.0, 1.2 Hz, 1H, 6-H), 5.53 (d, J = 2.7 Hz, 1H, 4-H), 5.40 (d, J = 8.1 Hz, 1H, 9b-H), 3.90 – 3.76 (m, 2H, N-H and 2-H), 3.67 (td, J = 8.6, 6.7 Hz, 1H, 2-H), 3.17 – 3.02 (m, 1H, 3a-H), 2.32 – 2.14 (m, 1H, 3-H), 1.35 (dddd, J = 12.0, 8.4, 6.8, 3.5 Hz, 1H, 3-H); $^{13}$C NMR (75 MHz, CDCl$_3$) selected data for endo 1d: δ 145.7, 137.7, 134.0, 130.4, 129.3, 128.6, 128.2, 126.5, 125.9, 125.7(x2), 123.2, 123.2, 122.3, 119.5, 115.39, 76.1, 67.0, 53.4, 43.9, 25.3.

**Synthesis of 8-fluoro-4-phenyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1e.**

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH$_3$CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then benzaldehyde (26 mg, 25 µL, 0.25 mmol), 4-fluoroaniline (36 mg, 31 µL, 0.33 mmol) and 2,3-dihydrofuran (26 mg, 28 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 4 h. After completion of the reaction, the reaction mixture was filtered through a...
celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO$_2$), eluting with PE/acetone (95:5 to 85:15) to afford 1e as a mixture of diastereoisomers (endo/exo 82:18) as yellow foam (35 mg, 52%); $R_l = 0.27$ (PE/acetone 90:10); I.R.: $\tilde{\nu}$ (cm$^{-1}$) = 3371, 3291, 3032, 2974, 2921, 2888, 1601, 1496, 1479, 1451, 1368, 1356, 1333, 1298, 1248, 1213, 1150, 1136, 1092, 1058, 1028, 997, 979, 937, 923, 875, 808, 776, 734, 705; $^1$H NMR (400 MHz, CDCl$_3$) selected data for endo 1e: $\delta$ 7.48 – 7.30 (m, 5H, Ph), 7.07 (d, $J = 9.2$, 2.9, 0.7 Hz, 1H, 9-H), 6.81 (td, $J = 8.5$, 3.0 Hz, 1H, 7-H), 6.54 (dd, $J = 8.8$, 4.6 Hz, 1H, 6-H), 5.23 (d, $J = 7.9$ Hz, 1H, 9b-H), 4.66 (d, $J = 3.0$ Hz, 1H, 4-H), 3.88 – 3.69 (m, 3H, N-H and 2-C$_2$H$_2$), 2.84 – 2.71 (m, 1H, 3a-H), 2.26 – 2.12 (m, 1H, 3-H), 1.53 (dddd, $J = 11.9$, 8.2, 6.9, 3.4 Hz, 1H, 3-H); $^{13}$C NMR (101 MHz, CDCl$_3$) selected data for endo 1e: $\delta$ 156.7, 142.1, 141.2, 128.8, 128.4, 127.9, 126.6, 116.0, 115.9, 115.5, 75.9, 67.1, 57.8, 45.6, 24.5.

**Synthesis of 1-phenyl-1,2,3a,10,11,11a-hexahydrobenzo[h]furo[3,2-c]quinoline 1f**

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH$_3$CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then benzaldehyde (26 mg, 25 µL, 0.25 mmol), 1-naphthylamine (47 mg, 0.33 mmol) and 2,3-dihydrofuran (26 mg, 28 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 24 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO$_2$), eluting with PE/acetone (95:5 to 80:20) to afford 1f as a mixture of diastereoisomers (endo/exo 46:54) as pink foam (22 mg, 29%); $R_l = 0.54$ (PE/acetone 80:20); I.R.: $\tilde{\nu}$ (cm$^{-1}$) = 3356, 3057, 2930, 2872, 1626, 1576, 1520, 1463, 1453, 1407, 1366, 1339, 1317, 1297, 1145, 1090, 1038, 952, 907, 857, 803, 764, 732, 700, 662; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.84 – 7.29 (m, 22H, aromatics, endo and exo), 5.49 (d, $J = 7.8$ Hz, 1H, 9b-H of endo), 4.90 (brs, 1H, N-H, exo), 4.83 (d, $J = 3.0$ Hz, 1H, 4-H, endo), 4.73 (d, $J = 5.0$ Hz, 1H, 9b-H, exo), 4.58 (brs, 1H, N-H, endo), 4.09 (td, $J = 8.5$, 5.9 Hz, 1H, 2-H, exo), 3.95 – 3.85 (m, 2H, 2-H and 4-H, exo), 3.81 – 3.74 (m, 2H, 2-CH$_2$, endo), 2.95 – 2.82 (m, 1H, 3a-H, endo), 2.56 (dddd, $J = 11.1$, 8.2, 6.9, 3.4 Hz, 1H, 3-H); $^{13}$C NMR (101 MHz, CDCl$_3$) selected data for endo 1f: $\delta$ 156.7, 144.2, 141.2, 128.8, 128.4, 127.9, 126.6, 116.0, 115.9, 115.5, 75.9, 67.1, 57.8, 45.6, 24.5.
7.6, 5.1, 2.1 Hz, 1H, 3a-H, exo), 2.10 (dddd, J = 13.1, 9.2, 8.0, 5.9 Hz, 1H, 3-H, exo), 2.35 – 2.24 (m, 1H, 3-H, endo), 1.85 – 1.72 (m, 1H, 3-H, exo), 1.61 (dddd, J = 12.5, 8.3, 6.1, 4.5 Hz, 1H, 3-H, endo).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 142.5, 141.8, 140.8, 139.6, 134.2, 133.8, 128.95, 128.93, 128.9, 128.8, 128.7, 128.6, 128.4, 128.0, 127.6, 126.9, 126.1, 126.0, 125.3, 125.1, 122.9, 122.9, 120.2, 120.0, 119.0, 118.2, 116.8, 114.3, 76.8 (endo), 76.7 (exo), 66.8 (endo), 65.4 (exo), 58.2 (exo), 57.7 (endo), 45.5 (endo), 43.1 (exo), 29.0 (exo), 24.6 (endo).

**Synthesis of 4-(p-tolyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1g.**

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH\(_3\)CN (300 \(\mu\)L). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then \(p\)-tolualdehyde (30 mg, 29 \(\mu\)L, 0.25 mmol), aniline (30 mg, 30 \(\mu\)L, 0.33 mmol) and 2,3-dihydrofuran (26 mg, 28 \(\mu\)L, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 4 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO\(_2\)), eluting with PE/acetone (95:5 to 85:15) to afford 1g as a mixture of diastereoisomers (endo/exo 85:15) as white foam (44 mg, 66%). The physical and spectral data agreed with those reported;\(^8\) \(R_f = 0.48\) (PE/acetone 80:20); I.R.: \(\tilde{\nu}\) (cm\(^{-1}\)) = 3367, 3327, 3052, 3027, 2978, 2936, 2883, 1905, 1796, 1609, 1587, 1515, 1488, 1469, 1420, 1364, 1336, 1318, 1296, 1253, 1186, 1147, 1129, 1112, 1087, 1049, 1038, 1020, 995, 971, 942, 911, 849, 820, 748, 685, 634; \(^1\)H NMR (400 MHz, CDCl\(_3\)) selected data for endo 1g: \(\delta\) 7.38 – 7.32 (m, 3H, 9-H and 2-H-Ar), 7.24 – 7.18 (m, 2H, 2-H-Ar), 7.09 (t, \(J = 7.8\) Hz, 1H, 7-H), 6.82 (td, \(J = 7.4, 1.1\) Hz, 1H, 8-H), 6.60 (dd, \(J = 8.1, 1.2\) Hz, 1H, 6-H), 5.28 (d, \(J = 8.0\) Hz, 1H, 9b-H), 4.67 (d, \(J = 3.0\) Hz, 1H, 4-H), 3.88 – 3.78 (m, 2H, N-H and 2-H), 3.72 (td, td, \(J = 8.5, 6.8\) Hz, 1H, 2-H), 2.82 – 2.73 (m, 1H, 3a-H), 2.38 (s, 3H, CH\(_3\)), 2.28 – 2.16 (m, 1H, 3-H), 1.55 (dddd, \(J = 11.8, 8.1, 6.8, 3.4\) Hz, 1H, 3-H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) selected data for endo 1g: \(\delta\) 145.2, 139.3, 137.5, 130.2, 129.4, 128.4, 126.6, 122.8, 119.2, 115.0, 76.1, 57.4, 45.9, 24.8, 21.2.

**Synthesis of 4-(4-methoxyphenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1h.**
A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH$_3$CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 4-methoxybenzaldehyde (34 mg, 30 µL, 0.25 mmol), aniline (30 mg, 30 µL, 0.33 mmol) and 2,3-dihydrofuran (26 mg, 28 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 4 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO$_2$), eluting with PE/acetone (95:5 to 85:15) to afford 1h as a mixture of diastereoisomers (endo/exo 85:15) as white foam (50 mg, 71%). The physical and spectral data agreed with those reported; $^8$ R$_f$ = 0.31 (PE/acetone 80:20); I.R.: $\tilde{\nu}$ (cm$^{-1}$) = 3349, 2968, 2925, 2877, 2835, 1606, 1587, 1512, 1479, 1452, 1436, 1366, 1331, 1290, 1240, 1175, 1156, 1111, 1065, 1027, 994, 967, 928, 828, 796, 775, 749, 696, 638; $^1$H NMR (400 MHz, CDCl$_3$) selected data for endo 1h: $\delta$ 7.44 – 7.33 (m, 3H, 9-H, 2H-Ar), 7.09 (t, 1H, 7-H), 6.96 – 6.88 (m, 2H, 2H-Ar), 6.81 (td, $J$ = 7.4, 1.2 Hz, 1H, 8-H), 6.59 (dd, $J$ = 8.1, 1.1 Hz, 1H, 6-H), 5.27 (d, $J$ = 7.9 Hz, 1H, 9b-H), 4.65 (d, $J$ = 3.0 Hz, 1H, 4-H), 3.88 – 3.79 (m, 5H, CH$_3$, N-H and 2-H), 3.72 (td, $J$ = 8.6, 6.8 Hz, 1H, 2-H), 2.82 – 2.68 (m, 1H, 3a-H), 2.30 – 2.12 (m, 1H, 3-H), 1.62 – 1.49 (m, 1H, 3-H); $^{13}$C NMR (101 MHz, CDCl$_3$) selected data for endo 1h: $\delta$ 159.2, 145.2, 134.4, 130.3, 128.5, 127.8, 122.8, 119.2, 115.0, 114.1, 76.1, 67.0, 57.1, 55.5, 46.1, 24.8.

Synthesis of 4-(2-(benzyloxy)phenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1i

A 5 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (20 mg) and CH$_3$CN (1 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 2-benzyloxybenzaldehyde (212 mg, 158 µL, 1.00 mmol), aniline (121 mg, 118 µL, 1.30 mmol) and 2,3-dihydrofuran (105 mg, 113 µL, 1.50 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 24 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (30 mL). The filtrate was evaporated to
dryness in vacuo and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (95:5 to 80:20) to afford 1i as a mixture of diastereoisomers (endo/exo 60:40) as white foam (64 mg, 60%). The diastereoisomers were separated by a second flash column chromatography, eluting with PE/EtOAc (95:5 to 90:10) to afford endo 1i (128 mg, 36%) as white solid and then exo 1i (86 mg, 24%) as white foam; endo 1i: mp 119-121°C (DCM); Rᵣ = 0.35 (PE/EtOAc 90:10); I.R.: ʋ (cm⁻¹) = 3335, 3045, 2960, 2922, 2896, 1629, 1599, 1551, 1492, 1452, 1400, 1375, 1336, 1283, 1240, 1164, 1114, 1079, 1025, 1001, 971, 927, 910, 864, 802, 753, 704, 670, 644, 620; ¹H NMR (300 MHz, CDCl₃) δ 7.68 (dd, J = 7.8, 1.8 Hz, 1H, 1H-Ar), 7.47 – 7.25 (m, 7H, 5H-benzyl, 1H-Ar, 9-H), 7.13 – 6.97 (m, 3H, 2H-Ar and 7-H), 6.82 (td, J = 7.4, 1.2 Hz, 1H, 8-H), 6.61 (dd, J = 8.0, 1.2 Hz, 1H, 6-H), 5.26 (d, J = 8.1 Hz, 1H, 9b-H), 5.21 – 5.06 (m, 3H, 4-H and CH₂ of benzyl), 3.83 (td, J = 8.5, 3.6 Hz, 1H, 2-H), 3.78 – 3.67 (m, 2H, N-H and 2-H), 3.11 – 2.97 (m, 1H, 3a-H), 2.27 – 2.10 (m, 1H, 3-H), 1.51 (dddd, J = 12.1, 8.3, 6.9, 3.6 Hz, 1H, 3-H); ¹³C NMR (75 MHz, CDCl₃) δ 155.5, 145.7, 137.0, 130.8, 130.3, 128.8, 128.4, 128.3, 128.1, 127.1, 126.7, 123.1, 121.1, 119.2, 115.2, 111.7, 76.0, 70.0, 66.9, 51.0, 42.5, 25.1; Anal. Calcd. for C₂₄H₂₁NO₂: % C 80.64; H 6.49; N 3.92; O 8.95; found: C 80.70; H 6.52; N 3.80; O 8.96; exo 1i: Rᵣ = 0.29 (PE/EtOAc 90:10); I.R.: ʋ (cm⁻¹) = 3372, 3326, 3032, 2926,2857, 1602, 1587, 1488, 1451, 1364, 1287, 1237, 1158, 1086, 1039, 909, 852, 796, 748, 696, 633; ¹H NMR (300 MHz, CDCl₃) δ 7.58 (dd, J = 7.6, 1.8 Hz, 1H, 1H-Ar), 7.46 – 7.26 (m, 7H, 5H-benzyl, 1H-Ar and 9-H), 7.16 – 7.00 (m, 3H, 2H-Ar and 7-H), 6.79 (td, J = 7.4, 1.2 Hz, 1H, 8-H), 6.60 (dd, J = 8.1, 1.1 Hz, 1H, 6-H), 5.11 (s, 2H, CH₂-benzyl), 4.64 (d, J = 5.0 Hz, 1H, 9b-H), 4.57 (d, J = 11.0 Hz, 1H, 4-H), 4.07 (burs, 1H, N-H), 3.98 – 3.87 (m, 1H, 2-H), 3.82 (ddd, J = 9.3, 8.3, 5.4 Hz, 1H, 2-H), 2.51 (dddd, J = 11.0, 7.5, 5.0, 2.1 Hz, 1H, 3a-H), 2.06 (dddd, J = 12.8, 9.2, 7.8, 6.9 Hz, 1H, 3-H), 1.85 (dddd, J = 13.0, 7.8, 5.4, 2.1 Hz, 1H, 3-H); ¹³C NMR (75 MHz, CDCl₃) δ 156.8, 145.9, 136.8, 131.2, 130.8, 128.9, 128.79, 128.77, 128.6, 128.2, 127.5, 121.6, 120.3, 118.3, 114.9, 112.2, 76.3, 70.5, 65.6, 49.1, 43.4, 29.1; Anal. Calcd. for C₂₄H₂₃NO₂: % C 80.64; H 6.49; N 3.92; O 8.95; found: C 80.72; H 6.54; N 3.85; O 8.85.

**Synthesis of 4-cyclopropyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1j**

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH₃CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then cyclopropanecarboxaldehyde (18 mg, 19 µL, 0.25 mmol), aniline (30 mg, 30 µL, 0.33 mmol)
and 2,3-dihydrofuran (26 mg, 28 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 24 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (95:5 to 85:15) to afford endo 1j (25 mg, 47%) as white solid and exo 1j (6 mg, 11%) as white foam. The ratio endo/exo was determined by ¹H NMR of the crude and resulted 80:20; endo 1j: mp 130-133°C (DCM); Rf = 0.40 (PE/EtOAc 90:10); I.R.: ῡ (cm⁻¹) = 3314, 3079, 3061, 3007, 2977, 2952, 2928, 1607, 1590, 1500, 1490, 1452, 1428, 1397, 1363, 1328, 1300, 1268, 1257, 1201, 1148, 1115, 1059, 1045, 1034, 1023, 1015, 1005, 973, 937, 926, 911, 876, 826, 784, 752, 704, 672; ¹H NMR (300 MHz, CDCl₃) δ 7.29 (dd, J = 7.7, 1.6 Hz, 1H, 9-H), 7.04 (td, J = 7.7, 1.6 Hz, 1H, 7-H), 6.74 (td, J = 7.4, 1.2 Hz, 1H, 8-H), 6.53 (dd, J = 8.1, 1.2 Hz, 1H, 6-H), 5.08 (d, J = 8.0 Hz, 1H, 9b-H), 3.87 – 3.79 (m, 2H, 2-CH₂), 3.77 (brs, 1H, N-H), 2.81 – 2.68 (m, 1H, 3a-H), 2.50 (dd, J = 9.6, 3.0 Hz, 1H, 4-H), 2.26 – 2.10 (m, 1H, 3-H), 2.10 – 1.94 (m, 1H, 3-H), 1.06 – 0.92 (m, 1H, CH-cyclopropyl), 0.67 – 0.51 (m, 2H, CH₂-cyclopropyl), 0.32 – 0.17 (m, 2H, CH₂-cyclopropyl); ¹³C NMR (75 MHz, CDCl₃) δ 145.1, 130.2, 128.4, 122.8, 118.7, 114.5, 75.9, 66.8, 59.1, 43.0, 25.0, 15.1, 3.6, 2.1; Anal. Calcd. for C₁₄H₁₇NO: % C 78.10; H 7.96; O 7.43, found: C 78.16; H 8.05; O 6.53; O 7.43; exo 1j: Rf = 0.34 (PE/EtOAc 90:10); I.R.: ῡ (cm⁻¹) = 3327, 3075, 2996, 2928, 2861, 2810, 2762, 1610, 1587, 1492, 1453, 1365, 1301, 1265, 1199, 1138, 1104, 1028, 996, 979, 918, 881, 826, 748, 647; ¹H NMR (400 MHz, CDCl₃) 7.33 (dd, J = 7.6, 1.3 Hz, 1H, 9-H), 7.09 (t, J = 7.4 Hz, 1H, 7-H), 6.74 (td, J = 7.5, 1.2 Hz, 1H, 8-H), 6.63 (dd, J = 8.0, 0.8 Hz, 1H, 6-H), 4.57 (d, J = 5.2 Hz, 1H, 9b-H), 4.08 (brs, 1H, N-H), 3.95 – 3.78 (m, 2H, 2-CH₂), 2.35 – 2.28 (m, 1H, 3a-H), 2.26 – 2.18 (m, 2H, 3-CH₂), 2.02 (t, J = 9.7 Hz, 1H, 4-H), 0.93 (dtt, J = 9.1, 8.1, 5.1 Hz, 1H, CH-cyclopropyl), 0.72 (ddddd, J = 8.9, 8.0, 5.8, 4.5 Hz, 1H, 1H of CH₂-cyclopropyl), 0.53 (dddd, J = 8.8, 7.9, 5.5, 4.2 Hz, 1H, 1H of CH₂-cyclopropyl), 0.48 – 0.39 (m, 1H, 1H of CH₂-cyclopropyl), 0.25 – 0.16 (m, 1H, 1H of CH₂-cyclopropyl); ¹³C NMR (101 MHz, CDCl₃) δ 145.2, 131.1, 129.0, 120.5, 118.2, 114.7, 76.3, 65.4, 57.24, 43.3, 28.7, 16.1, 4.5, 1.1; Anal. Calcd. for C₁₄H₁₇NO: % C 78.10; H 7.96; O 7.43, found: C 78.12; H 8.01; O 6.52; O 7.43.

**Synthesis of 4-isopropyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1k**

![Diagram of 4-isopropyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1k]
A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH₃CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then isobutyraldehyde (18 mg, 23 µL, 0.25 mmol), aniline (30 mg, 30 µL, 0.33 mmol) and 2,3-dihydrofuran (26 mg, 28 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 24 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (95:5) to afford endo 1k (27 mg, 50%) as amorphous solid and then 1k as a mixture of diastereoisomers (endo/exo 50:50) as white foam (7 mg, 13%). The physical and spectral data agreed with those reported; ⁹ endo 1k: Rₜ = 0.41 (PE/EtOAc 90:10); I.R.: ν (cm⁻¹) = 3348, 3059, 3021, 2957, 2885, 1609, 1591, 1489, 1469, 1387, 1365, 1333, 1304, 1288, 1256, 1245, 1198, 1156, 1142, 1095, 1061, 1035, 1020, 971, 936, 910, 849, 801, 750, 705, 639; ¹H NMR (300 MHz, CDCl₃): δ 7.29 (dd, J = 7.6, 1.6 Hz, 1H, 9-H), 7.04 (t, J = 7.6, 1H, 7-H), 6.74 (td, J = 7.4, 1.2 Hz, 1H, 8-H), 6.53 (dd, J = 8.1, 1.2 Hz, 1H, 6-H), 5.12 (d, J = 8.0 Hz, 1H, 9b-H), 3.85 – 3.73 (m, 2H, 2-CH₂), 3.69 (brs, 1H, N-H), 3.04 (dd, J = 9.1, 2.8 Hz, 1H, 4-H), 2.82 – 2.69 (m, 1H, 3a-H), 2.10 – 1.94 (m, 1H, 3-H), 1.91 – 1.79 (m, 1H, 3-H), 1.78 – 1.64 (m, 1H, CH-CH₃), 1.06 (d, J = 6.5 Hz, 3H, CH₃), 1.02 (d, J = 6.8 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 145.2, 130.0, 128.3, 122.8, 118.8, 114.6, 76.1, 66.6, 59.0, 40.8, 31.3, 23.9, 20.0, 19.2; Anal. Calcd. for C₁₄H₁₉NO: % C 77.38; H 8.81; N 6.45; O 7.36, found: C 77.43; H 8.65; N 6.42; O 7.69.

**Synthesis of (E)-4-styryl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1l.**

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (10 mg) and CH₃CN (600 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then trans-cinnamaldehyde (66 mg, 63 µL, 0.50 mmol), aniline (61 mg, 59 µL, 0.65 mmol) and 2,3-dihydrofuran (53 mg, 57 µL, 0.75 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 24 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (95:5 to 85:15) to afford 1l as a mixture of diastereoisomers (endo/exo 83:17) as
yellow foam (69 mg, 50%). The physical and spectral data agreed with those reported;\textsuperscript{10} \( R_f = 0.42 \) (PE/acetone 80:20); I.R.: \( \tilde{\nu} (\text{cm}^{-1}) = 3373, 3326, 3024, 2970, 2925, 2873, 1674, 1609, 1589, 1479, 1449, 1364, 1293, 1259, 1190, 1155, 1127, 1062, 1038, 1026, 967, 908, 748, 728, 691, 646; \) \( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) selected data for \textit{endo 1}: \( \delta = 7.46 - 7.27 \) (m, 6H, 5H-Ar and 9-H), 7.09 (t, \( J = 7.6 \) Hz, 1H, 7-H), 6.80 (td, \( J = 7.5, 1.2 \) Hz, 1H, 8-H), 6.64 (d, \( J = 16.0 \) Hz, 1H, 1H-stryryl), 6.58 (dd, \( J = 8.0, 1.1 \) Hz, 1H, 6-H), 6.30 (dd, \( J = 15.9, 7.9 \) Hz, 1H, 1H-styryl), 5.08 (d, \( J = 7.3 \) Hz, 1H, 9b-H), 4.16 (ddd, \( J = 7.9, 3.7, 1.0 \) Hz, 1H, 4-H), 3.86 – 3.77 (m, 3H, 2-CH\(_2\) and N-H), 2.79 – 2.70 (m, 1H, 3a-H), 2.18 – 2.11 (m, 1H, 3-H), 2.06 – 1.98 (m, 1H, 3-H); \( ^{13}\text{C} \) NMR (101 MHz, CDCl\(_3\)) selected data for \textit{endo 1}: \( \delta = 144.4, 136.7, 131.6, 130.5, 129.8, 128.8, 128.7, 127.9, 126.6, 122.1, 119.1, 115.0, 75.5, 66.6, 55.9, 42.8, 25.7.

\textbf{Synthesis of 4-ethoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 1m}

![Diagram of 4-ethoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 1m]

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (10 mg) and CH\(_3\)CN (600 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then using benzaldehyde (26 mg, 25 µL, 0.25 mmol), aniline (30 mg, 30 µL, 0.33 mmol) and ethyl vinyl ether (27 mg, 36 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 24 h. After completion of the reaction, the mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO\(_2\)), eluting with PE/EtOAc (95:5 to 90:10) to afford \textit{1m} as a mixture of diastereoisomers (\textit{endo/exo} 95:5) as a white foam (32 mg, 51%). The physical and spectral data agreed with those reported; \( R_f = 0.31 \) (PE/EtOAc 95:5); I.R.: \( \tilde{\nu} (\text{cm}^{-1}) = 3340, 3061, 3030, 2973, 694, 642, 6152926, 2849, 1608, 1582, 1488, 1452, 1358, 1338, 1310, 1262, 1210, 1174, 1119, 1086, 1028, 947, 907, 863, 843, 775, 747, 722; \) \( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) selected data for \textit{endo 1m}: \( \delta = 7.50 - 7.29 \) (m, 6H, 9-H, 5-H-Ar), 7.06 (t, \( J = 7.6 \) Hz, 1H, 7-H), 6.76 (td, \( J = 7.5, 1.2 \) Hz, 1H, 8-H), 6.53 (dd, \( J = 8.0, 1.2 \) Hz, 1H, 6-H), 4.83 (dd, \( J = 10.6, 5.6 \) Hz, 1H, 2-H), 4.54 (dd, \( J = 11.6, 2.7 \) Hz, 1H, 4-H), 3.95 (brs, 1H, N-H), 3.71 (dq, \( J = 9.0, 6.9 \) Hz, 1H, CH\(_2\) of ethyl), 3.58 (dq, \( J = 9.0, 7.0 \) Hz, 1H, CH\(_2\) of ethyl), 2.43 (ddd, \( J = 12.3, 5.7, 2.7 \) Hz, 1H, 3-H), 2.09 (ddd, \( J = 12.4, 11.6, 10.6 \) Hz, 1H, 3-H), 1.27 (t, \( J = 7.0 \) Hz, 3H, CH\(_3\) of ethyl); \( ^{13}\text{C} \) NMR (101 MHz,
CDCl₃) selected data for **endo 1m**: δ 144.7, 143.8, 128.8, 128.4, 127.9, 127.4, 126.8, 122.7, 117.9, 114.2, 74.1, 63.6, 56.0, 37.2, 15.8.

**Synthesis of 4-ethoxy-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline 1n**

![Chemical Structure](image)

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH₃CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 4-methoxybenzaldehyde (34 mg, 30 µL, 0.25 mmol), aniline (30 mg, 30 µL, 0.33 mmol) and ethyl vinyl ether (27 mg, 36 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 48 h. After this time, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (95:5 to 90:10) to afford 1n as a mixture of diastereoisomers (endo/exo 75:25) as white foam (45 mg, 64%); **endo 1n** was separated by a second flash column chromatography, eluting with PE/EtOAc (95:5). The physical and spectral data agreed with those reported.\(^\text{11}\) **endo 1n**: Rᵓ = 0.40 (PE/EtOAc 80:20); l.R.: ν (cm⁻¹) = 3363, 3346, 3058, 3032, 2970, 2935, 2869, 2835, 1606, 1583, 1511, 1488, 1464, 1441, 1370, 1333, 1311, 1297, 1264, 1241, 1176, 1110, 1083, 1064, 1028, 945, 904, 864, 825, 780, 768, 746, 722, 672, 632, 607; \(^1\)H NMR (300 MHz, CDCl₃): δ 7.43 – 7.32 (m, 3H, 9-H, 2H-Ar), 7.05 (t, J = 7.6 Hz, 1H, 7-H), 6.93 – 6.88 (m, 2H, 2H-Ar), 6.74 (td, J = 7.4, 1.2 Hz, 1H, 8-H), 6.50 (dd, J = 7.9, 1.2 Hz, 1H, 6-H), 4.87 – 4.78 (m, 1H, 2-H), 4.48 (dd, J = 11.7, 2.6 Hz, 1H, 4-H), 3.88 (brs, 1H, N-H), 3.82 (s, 3H, O-CH₃), 3.71 (dq, J = 9.2, 7.0 Hz, 1H, CH₂ of ethyl), 3.58 (dq, J = 9.1, 7.0 Hz, 1H, CH₂ of ethyl), 2.38 (ddd, J = 12.3, 5.7, 2.7 Hz, 1H, 3-H), 2.12 – 1.98 (m, 1H, 3-H), 1.27 (t, J = 7.0 Hz, 3H, CH₃ of ethyl); \(^{13}\)C NMR (75 MHz, CDCl₃): δ 159.3, 144.8, 135.9, 128.3, 127.9, 127.3, 122.7, 117.9, 114.2, 114.1, 74.2, 63.6, 55.5 (x2), 37.3, 15.8; Anal. Calcd. for C₁₈H₂₁NO₂: % C 76.29; H 7.47; N 4.94; O 11.29, found: C 76.33; H 7.52; N 4.94; O 11.42.

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**Synthesis of 2-(4-chlorophenyl)-4-ethoxy-1,2,3,4-tetrahydroquinoline 1o.**
A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH$_3$CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 4-chlorobenzaldehyde (35 mg, 0.25 mmol), aniline (30 mg, 30 µL, 0.33 mmol) and ethyl vinyl ether (27 mg, 36 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 24 h. After this time, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO$_2$), eluting with PE/EtOAc (95:5) to afford 1o as a mixture of diastereoisomers (endo/exo 91:9) as white foam (31 mg, 45%). The physical and spectral data agreed with those reported;\textsuperscript{11} $R_f = 0.33$ (PE/EtOAc 95:5); I.R.: $\tilde{\nu}$ (cm$^{-1}$) = 3364, 3334, 3055, 3031, 2973, 2868, 2843, 1607, 1585, 1488, 1406, 1331, 1310, 1263, 1208, 1173, 1120, 1086, 1029, 1012, 865, 844, 813, 775, 748, 725, 696, 630, 615; $^1$H NMR (300 MHz, CDCl$_3$) selected data for endo 1o: $\delta$ 7.43 – 7.29 (m, 5H, 9-H, 4H-Ar), 7.06 (t, $J = 7.5$ Hz, 1H, 7-H), 6.75 (td, $J = 7.5$, 1.2 Hz, 1H, 8-H), 6.53 (dd, $J = 8.0$, 1.1 Hz, 1H, 6-H), 4.79 (dd, $J = 10.2$, 5.7 Hz, 1H, 2-H), 4.52 (dd, $J = 11.3$, 2.8 Hz, 1H, 4-H), 3.91 (brs, 1H, N-H), 3.74 – 3.49 (m, 2H, CH$_2$ of ethyl), 2.37 (ddd, $J = 12.4$, 5.7, 3.0 Hz, 1H, H-3), 2.04 (ddd, $J = 12.4$, 11.3, 10.3 Hz, 1H, H-3), 1.24 (t, $J = 7.0$ Hz, 3H, CH$_3$ of ethyl). $^{13}$C NMR (75 MHz, CDCl$_3$) selected data for endo 1o: $\delta$ 144.5, 142.4, 133.5, 128.9, 128.5, 128.1, 127.6, 122.7, 118.2, 114.3, 73.9, 63.7, 55.4, 37.2, 15.8.

**Synthesis of 8-bromo-4-phenyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline 1p**

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH$_3$CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then benzaldehyde (26 mg, 25 µL, 0.25 mmol), 4-bromoaniline (56 mg, 0.33 mmol) and 2,3-dihydrofuran (26 mg, 28 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 4 h. After this time, the reaction mixture was filtered through a celite cake,
washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO$_2$), eluting with PE/acetone (95:5 to 85:15) to afford 1p as a mixture of diastereoisomers (endo/exo 74:26) as cream color foam (30 mg, 36%). The physical and spectral data agreed with those reported;\textsuperscript{12} $R_f = 0.47$ (PE/acetone 80:20); I.R.: $\tilde{\nu}$ (cm$^{-1}$) = 3370, 3293, 3051, 3030, 2980, 2925, 2893, 2877, 1596, 1483, 1449, 1367, 1353, 1332, 1296, 1259, 1174, 1057, 1026, 994, 973, 915, 878, 806, 775, 759, 726, 700, 671; $^1$H NMR (400 MHz, CDCl$_3$) selected data for endo 1p: $\delta$ 7.47 – 7.29 (m, 6H, 5H-Ph and 9-H), 7.16 (dd, $J = 8.5$, 2.3 Hz, 1H, 7-H), 6.48 (d, $J = 8.5$ Hz, 1H, 6-H), 5.21 (d, $J = 7.8$ Hz, 1H, 9b-H), 4.68 (d, $J = 3.0$ Hz, 1H, 4-H), 3.91 – 3.79 (m, 2H, N-H and 2-H), 3.79 – 3.69 (m, 1H, 2-H), 2.81 – 2.72 (m, 1H, 3a-H), 2.23 – 2.10 (m, 1H, 3-H), 1.53 (dddd, $J = 11.8$, 8.1, 7.0, 3.4 Hz, 1H, 3-H). $^{13}$C NMR (101 MHz, CDCl$_3$) selected data for endo 1p: $\delta$ 144.2, 142.2, 133.1, 131.6, 129.2, 128.3, 126.9, 125.1, 117.0, 111.2, 75.9, 67.4, 57.6, 45.8, 24.9.

**Synthesis of 5-(4-chlorophenyl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline 1q**

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH$_3$CN (300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 4-chlorobenzaldehyde (25 mg, 0.25 mmol), aniline (30 mg, 30 µL, 0.33 mmol) and 3,4-dihydropyran (32 mg, 34 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 48 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO$_2$), eluting PE/Et$_2$O/DCM (90:5:5 to 80:10:10) to afford endo 1q (14 mg, 19%) as cream color solid and exo 1q (7 mg, 9%) as white solid. The ratio endo/exo was determined by $^1$H NMR of the crude and resulted 65:35. The physical and spectral data agreed with those reported;\textsuperscript{13} endo 1q: mp 153-155°C (DCM); $R_f = 0.35$ (PE/Et$_2$O/DCM 80:10:10); I.R.: $\tilde{\nu}$ (cm$^{-1}$) = 3387, 3049, 3022, 2985, 2940, 2894, 2850, 1602, 1582, 1483, 1460, 1435, 1407, 1375, 1342, 1317, 1275, 1256, 1205, 1185, 1142, 1121, 1084, 1069, 1041, 1014, 969, 943, 926, 861, 843, 814, 747, 705, 664; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 – 7.40 (m, 1H, 10-H), 7.40 – 7.31 (m, 4H, Ar), 7.10 (t, $J = 7.5$ Hz, 1H, 8-H), 6.81 (td, $J = 7.5$, 1.2 Hz, 1H, 9-H), 6.61 (dd, $J = 8.0$, 1.2 Hz, 1H, 7-H), 5.32 (d, $J = 5.7$ Hz, 1H, 10b-H), 4.67 (d, $J = 2.6$ Hz, 1H, 5-H), 3.82 (brs, S27
1H, N-H), 3.65 – 3.54 (m, 1H, 2-H), 3.48 – 3.37 (m, 1H, 2-H), 2.21- 2.05 (m, 1H, 4a-H), 1.63 – 1.39 (m, 3H, 2H-3 and H-4, overlapped with H2O signal), 1.37 – 1.22 (m, 1H, H-4); 13C NMR (101 MHz, CDCl3) δ 145.0, 139.8, 133.3, 128.7, 128.3 (x2), 127.8, 120.1, 118.7, 114.7, 72.8, 60.8, 58.9, 39.0, 25.5, 18.1; Anal. Calcd. for C18H18ClNO: % C 72.11; H 6.05; N 4.67; O 5.34, found: C 72.15; H 6.05; N 4.75; O 5.45; exo 1q: mp 125-127 °C (DCM); RI = 0.28 (PE/Et2O/DCM 80:10:10); I.R.: υ (cm⁻¹) = 3365, 3020, 2954, 2937, 2916, 2855, 2827, 1609, 1591, 1484, 1447, 1441, 1364, 1341, 1321, 1299, 1263, 1255, 1212, 1204, 1185, 1157, 1121, 1107, 1078, 1050, 1031, 1014, 1003, 973, 962, 936, 914, 884, 839, 817, 791, 748, 727, 713, 662, 640, 625; 1H NMR (400 MHz, CDCl3) δ 7.40 – 7.31 (m, 4H, Ar), 7.23 (dd, J = 7.6, 1.6 Hz, 1H, 10-H), 7.10 (t, J = 8.0 Hz, 1H, 8-H), 6.72 (td, J = 7.4, 1.1 Hz, 1H, 9-H), 6.54 (dd, J = 8.0, 1.1 Hz, 1H, 7-H), 4.71 (d, J = 10.80 Hz, 1H, 5-H), 4.39 (d, J = 2.7 Hz, 1H, 10b-H), 4.15 – 4.06 (m, 1H, 2-H), 4.04 (brs, 1H, N-H), 3.73 (td, J = 11.5, 2.6 Hz, 1H, 2-H), 2.05 (ddt, J = 10.6, 5.2, 2.8 Hz, 1H, 4a-H), 1.91 – 1.74 (m, 1H, 3-H), 1.66 (tt, J = 13.4, 4.6 Hz, 1H, 4-H), 1.49 – 1.42 (m, 1H, 4-H), 1.40 – 1.31 (m, 1H, 3-H); 13C NMR (101 MHz, CDCl3) δ 144.7, 141.0, 133.7, 131.1, 129.6, 129.3, 129.0, 120.8, 117.9, 114.4, 74.5, 68.8, 54.4, 39.1, 24.2, 22.1; Anal. Calcd. for C18H18ClNO: % C 72.11; H 6.05; N 4.67; O 5.34, found: C 72.17; H 6.06; N 4.74; O 5.40.

**Synthesis of 5-(4-methoxyphenyl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline 1r**

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH3CN/H2O (4:1, 300 µL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 4-methoxybenzaldehyde (34 mg, 0.25 mmol), aniline (30 mg, 30 µL, 0.33 mmol) and 3,4-dihydropyran (32 mg, 34 µL, 0.38 mmol) were added to the mixture. The sealed reaction vial was stirred at 60 °C for 48 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO2), eluting with PE/DCM/Et2O (80:10:10) to afford a mixture of aldehyde/imine/endo 1r (65:10:25, 13 mg, 5%) and then exo 1r (26 mg, 35%) as pale yellow solid (26 mg, 35%). The ratio endo/exo was determined by 1H NMR of the crude and resulted 25:75. The physical and spectral data agreed with those reported;14 exo 1r: m.p. = 121 - 123°C (DCM); RI = 0.18 (PE/DCM/Et2O 80:10:10); I.R.: υ (cm⁻¹) = 3385, 2931, 2838, 1607, 1588, 1510, 1487, 1463, 1441, 1366, 1351, 1303,
1287, 1257, 1239, 1222, 1182, 1111, 1081, 1057, 1004, 915, 888, 852, 838, 814, 797, 765, 748, 733, 693, 651; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.30 (m, 2H, 2H-Ar), 7.22 (dd, \(J = 7.6, 1.6\) Hz, 1H, 10-H), 7.09 (t, \(J = 7.5\) Hz, 1H, 8-H), 6.95 – 6.88 (m, 2H, 2H-Ar), 6.70 (td, \(J = 7.4, 1.1\) Hz, 1H, 9-H), 6.52 (dd, \(J = 8.1, 1.1\) Hz, 1H, 7-H), 4.68 (d, \(J = 10.9\) Hz, 1H, 5-H), 4.39 (d, \(J = 2.8\) Hz, 1H, 10b-H), 4.15 – 4.06 (m, 1H, 2-H), 4.03 (burs, 1H, N-H), 3.83 (s, 3H, CH\(_3\)), 3.73 (td, \(J = 11.5, 2.5\) Hz, 1H, 2-H), 2.06 (ddt, \(J = 10.8, 5.2, 2.8\) Hz, 1H, 4a-H), 1.93 – 1.75 (m, 1H, 3-H), 1.65 (tt, \(J = 13.2, 4.6\) Hz, 1H, 4-H), 1.59 – 1.44 (m, 1H, 4-H), 1.38 – 1.28 (m, 1H, 3-H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 159.4, 145.0, 134.4, 131.1, 129.5, 129.0, 120.8, 117.5, 114.2, 114.1, 74.8, 68.9, 55.5, 54.2, 39.1, 24.3, 22.1; Anal. Calcd.

Synthesis of 4-(4-chlorophenyl)-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline 1s.

A 2 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH\(_3\)CN (300 \(\mu\)L). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 4-chlorobenzaldehyde (34 mg, 0.25 mmol), aniline (30 mg, 30 \(\mu\)L, 0.33 mmol) and freshly distilled cyclopentadiene (66 mg, 84 \(\mu\)L, 1.00 mmol) were added to the mixture. The sealed reaction vial was stirred at 60 °C for 24 h. After completion of the reaction, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness in vacuo and the residue was purified by flash column chromatography (SiO\(_2\)), eluting with PE/acetone (95:5) to afford 1s as a mixture of diastereoisomers (endo/exo 90:10) as white foam (49 mg, 70%). Crystallization from Et\(_2\)O/pentane gave the pure endo 1s as white crystals. The physical and spectral data agreed with those reported;\(^2\) endo 1s: m.p. = 137-139°C (Et\(_2\)O/pentane); \(R_t = 0.63\) (PE/acetone 90:10); I.R.: \(\nu\) (cm\(^{-1}\)) = 3360, 3046, 2961, 2929, 2871, 2849, 1604, 1591, 1489, 1469, 1435, 1419, 1408, 1354, 1318, 1289, 1264, 1226, 1203, 1177, 1160, 1129, 1113, 1086, 1033, 1014, 1001, 968, 956, 939, 890, 866, 843, 810, 794, 752, 725, 697, 680, 632, 621; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 – 7.31 (m, 4H, 4H-Ar), 7.07 (d, \(J = 7.6\) Hz, 1H, 9-H), 7.00 (t, \(J = 7.6\) Hz, 1H, 7-H), 6.77 (td, \(J = 7.4, 1.3\) Hz, 1H, 8-H), 6.64 (dd, \(J = 8.0, 1.3\) Hz, 1H, 6-H), 5.89 – 5.82 (m, 1H, 1-H), 5.71 – 5.60 (m, 1H, 2-H), 4.62 (d, \(J = 3.3\) Hz, 1H, 4-H), 4.12 (d, \(J = 9.2\) Hz, 1H, 9b-H), 3.70 (burs, 1H, N-H), 2.97 (ddddd, \(J = 8.9, 3.3\) Hz, 1H, 3a-H), 2.60 (ddddd, \(J = 16.5, 9.4, 2.4\) Hz, 1H, 3-H), 1.80 (ddddd, \(J = 16.3, 8.7, 2.7, 1.5\) Hz, 1H, 3-H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.4, 141.5, 134.1,
133.0, 130.4, 129.2, 128.8, 128.0, 126.5, 126.1, 119.5, 116.1, 57.6, 46.4, 46.0, 31.5; Anal. Calcd. for C_{18}H_{16}ClN: % C 76.72; H 5.72; N 4.97, found: C 76.62; H 5.63; N 5.03.

**Synthesis of quinolines 2 via oxidation of Povarov products**

**Synthesis of 2-(2-(4-chlorophenyl)quinolin-3-yl)ethan-1-ol 2a.**

A 10 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (16 mg) and CH$_3$CN/H$_2$O (4:1, 1.6 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath. 1a (45 mg, 0.16 mmol, endo/exo = 80:20) was added and the mixture was stirred at 120 °C for 24 h. After completion of the reaction, as indicated by thin-layer chromatography (TLC), the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL) and MeOH (5 mL). The filtrate was evaporated to dryness and the residue was purified by flash column chromatography (SiO$_2$), eluting with PE/acetone (90:10 to 60:40) to afford unreacted endo 1a (6 mg, 13%) and then 2a (33 mg, 73%) as white solid.

Quinoline 2a has been obtained in 92 % isolated yield, following the same procedure starting from pure endo 1a.

Quinoline 2a has been obtained in 88 % isolated yield, starting from pure endo 1a and using microwaves irradiation as described below: a suspension of GO (10 mg) and endo 1a (30 mg, 0.10 mmol) in CH$_3$CN/H$_2$O (2:1, 1.0 mL) was sonicated for 2 min using an ultrasonic bath and then heated at 120 °C under MW irradiation for 3 h. The reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness and the residue was purified by flash column chromatography (SiO$_2$), eluting with PE/acetone (90:10 to 60:40) to afford unreacted endo 1a (2 mg, 8%) and then 2a (25 mg, 88%) as white solid.

2a: mp 116-119°C (PE/acetone); R$_f$ = 0.37 (PE/acetone 75:25); I.R.: v (cm$^{-1}$) = 3351, 3176, 3055, 2934, 1622, 1598, 1559, 1485, 1423, 1395, 1338, 1264, 1161, 1121, 1089, 1042, 1005, 958, 907, 841, 793, 751, 618; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.10 (s, 1H, 4-H), 8.07 (d, $J = 7.9$ Hz, 1H, 8-H), 7.89 (d, $J = 8.2$ Hz, 1H, 5-H), 7.71–7.62 (m, 1H, 7-H), 7.53 (tt, $J = 8.3$, 1.5 Hz, 1H, 6-H), 7.48–7.37 (m, 4H, Ar), 3.69 (td, $J = 6.6$, 1.9 Hz, 2H, CH$_2$-O), 2.97 (td, $J = 6.7$, 2.0 Hz, 2H, CH$_2$-C), 2.19 (brs, 1H, OH); $^{13}$C
NMR (75 MHz, CDCl₃) δ 159.4, 146.6, 139.0, 134.5, 130.4, 129.9, 129.5, 129.1, 128.7, 127.6, 127.2, 126.9, 62.4, 35.8; Anal. Calcd. for C₁₇H₁₄ClNO: % C 71.96; H 4.97; N 4.94; O 5.64, found: C 72.03; H 5.05; N 5.03; O 5.74.

2-{2-[4-methoxyphenyl]quinolin-3-yl}ethan-1-ol 2h

![Structure](image)

A 10 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (10 mg) and CH₃CN/H₂O (4:1, 1.0 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath. 1h (28 mg, 0.10 mmol, endo/exo = 80:20) was added and the mixture was stirred at 120 °C for 24 h. After completion of the reaction, as indicated by thin-layer chromatography (TLC), the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (90:10 to 60:40) to afford unreacted exo 1h (4 mg, 14%) and then 2h (21 mg, 75%) as cream color solid: mp 127 -130 °C (PE/acetone); Rᵋ = 0.21 (PE/acetone 80:20); I.R.: ῡ (cm⁻¹) = 3278, 3014, 2962, 2929, 2864, 2836, 1610, 1516, 1488, 1456, 1441, 1421, 1374, 1340, 1291, 1246, 1176, 1136, 1107, 1041, 1021, 970, 917, 869, 840, 815, 800, 763, 734, 636, 619; ¹H NMR (300 MHz, CDCl₃) δ 8.13 – 8.07 (m, 2H, 4-H and 8-H), 7.79 (dd, J = 8.0, 1.4 Hz, 1H, 5-H), 7.67 (ddd, J = 8.6, 6.9, 1.5 Hz, 1H, 7-H), 7.55 – 7.46 (m, 3H, 6-H and 2-H-Ar), 7.04 – 6.96 (m, 2H, 2-H-Ar), 3.86 (s, 3H, CH₃), 3.78 – 3.70 (m, 2H CH₂-O), 3.07 (t, J = 6.7 Hz, 2H, CH₂-C), 1.67 (brs, 1H, O-H, overlapped with H₂O signal); ¹³C NMR (75 MHz, CDCl₃) δ 160.5, 159.8, 146.8, 137.0, 133.2, 130.3, 130.1, 129.3 (x2), 127.4, 127.1, 126.6, 114.0, 62.7, 55.5, 36.2; Anal. Calcd. for C₁₈H₁₇NO₂: % C 77.40; H 6.13; N 5.01; O 11.46, found: C 77.38; H 6.12; N 5.03; O 11.54.

2-{2-{2-(benzyloxy)phenyl}quinolin-3-yl}ethan-1-ol 2i

![Structure](image)

A 10 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (10 mg) and CH₃CN/H₂O (4:1, 1.0 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath. 1i (36 mg, 0.10 mmol, endo/exo = 60:40) was added and the mixture was stirred at
120 °C for 24 h. After completion of the reaction, as indicated by thin-layer chromatography (TLC), the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL) and MeOH (10 mL). The filtrate was evaporated to dryness and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (90:10 to 60:40) to afford unreacted exo 1i (4 mg, 6%) and then 2i (28 mg, 79%) as colorless oil: Rf = 0.21 (PE/acetone 80:20); I.R.: ū (cm⁻¹) = 3274, 3061, 3033, 2929, 2868, 1700, 1602, 1583, 1489, 1447, 1418, 1378, 1341, 1312, 1291, 1262, 1222, 1161, 1129, 1111, 1048, 1019, 908, 854, 793, 749, 727, 695, 644, 618; ¹H NMR (300 MHz, CDCl₃) δ 8.14 (d, J = 8.4 Hz, 1H, H-8), 8.08 (s, 1H, H-4), 7.83 (dd, J = 8.0, 1.5 Hz, 1H, H-5), 7.68 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H, H-7), 7.54 (ddd, J = 3.4 Hz, 2H, CH₂-benzyl), 7.12 – 7.03 (m, 2H, Ar), 7.03 – 6.93 (m, 2H, Ar), 5.04 (d, J = 3.4 Hz, 2H, CH₂-benzyl), 3.71 (t, J = 6.1 Hz, 2H, CH₂-O), 2.94 (t, J = 6.6 Hz, 2H, CH₂-C), 1.44 (t, J = 6.0 Hz, 1H, O-H); ¹³C NMR (75 MHz, CDCl₃) δ 159.1, 155.9, 146.9, 137.0, 135.9, 131.5, 130.8, 130.7, 130.0, 129.4, 129.1, 128.5, 127.8, 127.7, 127.2, 126.9, 126.6, 121.8, 113.3, 70.6, 62.6, 36.0; Anal. Calcd. for C₂₄H₂₁NO₂: % C 81.10; H 5.96; N 3.94; O 9.00, found: C 81.23; H 6.03; N 3.96; O 9.12.

2-([2-cyclopropylquinolin-3-yl]ethan-1-ol 2j

A 10 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (10 mg) and CH₃CN/H₂O (4:1, 1.0 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath. 1j (22 mg, 0.10 mmol, endo/exo = 85:15) was added and the mixture was stirred at 120 °C for 24 h. After completion of the reaction, as indicated by thin-layer chromatography (TLC), the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (90:10 to 60:40) to afford unreacted 1j (endo/exo 1:1, 3 mg, 14%) and then 2j (13 mg, 61%) as colorless oil: Rf = 0.24 (PE/acetone 75:25); I.R.: ū (cm⁻¹) = 3426, 3057, 3007, 2937, 2873, 1619, 1601, 1562, 1492, 1425, 1345, 1224, 1143, 1063, 1047, 1022, 911, 852, 788, 753, 618; ¹H NMR (300 MHz, CDCl₃) δ 7.91 (d, J = 8.4 Hz, 1H, H-8), 7.87 (s, 1H, H-4), 7.76 (d, J = 8.5 Hz, 1H, H-5), 7.59 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H, H-7), 7.41 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H, H-6), 4.03 (t, J = 6.7 Hz, 2H, CH₂-O), 3.23 (t, J = 6.7 Hz, 2H, CH₂-C), 3.20 (tt, J = 8.0, 4.8 Hz, 1H, CH-cyclopropyl), 1.64-1.48 (m, 1H, O-H, overlapped with H₂O signal), 1.32 – 1.25 (m, 2H, CH₂-cyclopropyl), 1.09 – 0.99 (m, 2H, CH₂-cyclopropyl); ¹³C NMR (75 MHz, CDCl₃) δ 161.8, 147.0, 135.7,
A 10 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (14 mg) and CH₃CN/H₂O (4:1, 1.4 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath. 1k (30 mg, 0.14 mmol, endo/exo = 90:10) was added and the mixture was stirred at 120 °C for 24 h. After completion of the reaction, as indicated by thin-layer chromatography (TLC), the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL) and MeOH. The filtrate was evaporated to dryness and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (90:10 to 70:30) to afford unreacted 1k (endo/exo 1:1, 6 mg, 20%) and then 2k (21 mg, 70%) as colorless oil: $R_f = 0.33$ (PE/acetone 75:25); I.R.: $\tilde{\nu}$ (cm⁻¹) = 3322, 3061, 2961, 2930, 2871, 1621, 1600, 1563, 1491, 1455, 1422, 1378, 1359, 1219, 1137, 1043, 955, 908, 854, 796, 753, 729, 646, 618; ¹H NMR (300 MHz, CDCl₃) $\delta$ 8.03 (d, 1H, 8-H), 7.90 (s, 1H, 4-H), 7.72 (dd, $J = 8.1, 1.2$ Hz, 1H, 5-H), 7.62 (ddd, $J = 8.4, 6.9, 1.5$ Hz, 1H, 7-H), 7.44 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H, 6-H), 3.99 – 3.88 (m, 2H, CH₂-O), 3.45 (hept, $J = 6.7$ Hz, 1H, CH-isopropyl), 3.11 (td, $J = 6.8, 0.7$ Hz, 2H, CH₂-C), 1.68 – 1.56 (m, 1H, O-H, overlapped with H₂O signal), 1.39 (d, $J = 6.7$ Hz, 6H, 2CH₃); ¹³C NMR (75 MHz, CDCl₃) $\delta$ 166.4, 147.2, 136.3, 129.2, 129.0, 128.7, 127.0, 127.0, 125.8, 63.1, 35.6, 31.7, 22.5; Anal. Calcd. for C₁₄H₁₇NO: % C 78.10; H 7.98; N 6.51; O 7.43, found: C 78.14; H 7.98; N 6.54; O 7.56.

(E)-2-(2-styrylquinolin-3-yl)ethan-1-ol 2l

A 10 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (10 mg) and CH₃CN/H₂O (4:1, 1.0 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath. 1l (28 mg, 0.14 mmol, endo/exo = 80:20) was added and the mixture was stirred at 120 °C for 24 h. After completion of the reaction, as indicated by thin-layer chromatography (TLC), the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL). The filtrate was evaporated to dryness and the residue was purified by flash column chromatography.
(SiO$_2$), eluting with PE/acetone (90:10 to 60:40) to afford unreacted **exo 1I** (2 mg, 9%) and then **2I** (16 mg, 58%) as cream solid: mp 113-114 °C (PE/acetone); $R_f = 0.26$ (PE/acetone 75:25); I.R.: $\tilde{\nu}$ (cm$^{-1}$) = 3152, 3042, 2953, 2924, 2873, 1643, 1616, 1601, 1576, 1559, 1494, 1451, 1418, 1376, 1340, 1313, 1243, 1222, 1174, 1144, 1100, 1068, 1029, 988, 912, 875, 847, 820, 786, 751, 716, 689, 676, 626, 603; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 8.8$ Hz, 1H, 8-$H$), 7.98 (d, $J = 15.6$ Hz, 1H, CH-styryl), 7.90 (s, 1H, 4-$H$), 7.70 – 7.60 (m, 4H, 5-$H$, 7-$H$ and 2H-Ph), 7.51 (d, $J = 15.5$ Hz, 1H, CH-styryl), 7.46 – 7.31 (m, 4H, 6-H and 3H-Ph), 4.01 (t, $J = 6.5$ Hz, 2H, O$_2$CH), 3.18 (t, $J = 6.5$ Hz, 2H, CH$_2$-CO), 2.21 – 2.09 (m, 1H, OH); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 154.7, 147.1, 137.2, 137.0, 136.2, 130.0, 129.3, 129.0, 128.9, 128.7, 127.6, 127.6, 127.1, 126.3, 124.1, 62.7, 36.1; Anal. Calcd. for C$_{19}$H$_{17}$NO: % C 82.88; H 6.22; N 5.09; O 5.81, found: C 83.01; H 6.28; N 5.02; O 5.89.

**2-(4-chlorophenyl)quinoline 2o**

A 10 mL screw-capped vial was equipped with a magnetic stirring bar and charged with GO (9 mg) and CH$_3$CN/H$_2$O (4:1, 0.9 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath. **1o** (25 mg, 0.09 mmol, endo/exo = 90:10) was added and the mixture was stirred at 120 °C for 24 h. After completion of the reaction, as indicated by thin-layer chromatography (TLC), the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL) and MeOH. The filtrate was evaporated to dryness and the residue was purified by flash column chromatography (SiO$_2$), eluting with PE/acetone (90:10 to 70:30) to afford unreacted **2o** (4 mg, 19%) as white solid. The physical and spectral data agreed with those reported;$^{15}$ mp 112-114 °C (PE/acetone); $R_f = 0.52$ (PE/EtOAc 90:10); I.R.: $\tilde{\nu}$ (cm$^{-1}$) = 3057, 2919, 2850, 1617, 1588, 1578, 1553, 1509, 1486, 1431, 1399, 1378, 1318, 1286, 1263, 1244, 1211, 1158, 1128, 1106, 1089, 1050, 1007, 940, 815, 787, 771, 751, 733, 715, 672, 635, 621; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.23 (d, $J = 8.6$ Hz, 1H, 4-$H$), 8.18 – 8.09 (m, 3H, 2H-Ar and 8-$H$), 7.87 – 7.81 (m, 2H, 5-$H$ and 3-$H$), 7.74 (ddd, $J = 8.5$, 6.9, 1.5 Hz, 1H, 7-$H$), 7.58 – 7.45 (m, 3H, 2H-Ar and 6-$H$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 156.2, 148.4, 138.2, 137.1, 135.7, 130.0, 129.9, 129.2, 129.0, 127.6, 127.4, 126.7, 118.7; Anal. Calcd. for C$_{15}$H$_{10}$ClN: % C 75.16; H 4.21; N 5.84, found: C 75.19; H 4.28; N 5.80.
One-pot synthesis of 2,3-disubstituted quinolines 2

Synthesis of 2-(2-(4-chlorophenyl)quinolin-3-yl)ethan-1-ol 2a.

A screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH$_3$CN (1.3 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 4-chlorobenzaldehyde (35 mg, 0.25 mmol), aniline (30 mg, 30 µL, 0.323 mmol) and 2,3-dihydrofuran (44 mg, 47 µL, 0.62 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 6 h. After completion of the reaction, GO (20 mg), CH$_3$CN (0.7 mL) and H$_2$O (0.5 mL) were added and the resulting suspension was stirred at 120 °C for 48 h. Then, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL) and MeOH (5 mL). The filtrate was evaporated to dryness and the residue was purified by flash column chromatography (SiO$_2$), eluting with PE/acetone (90:10 to 60:40) to afford unreacted 1a (17 mg, 24%, endo/exo 25:75) and then 2a (30 mg, 42%) as white solid.

2-(2-(4-methoxyphenyl)quinolin-3-yl)ethan-1-ol 2h

A screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH$_3$CN (1.3 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 4-methoxybenzaldehyde (34 mg, 0.25 mmol), aniline (30 mg, 30 µL, 0.32 mmol) and 2,3-dihydrofuran (44 mg, 47 µL, 0.62 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 24 h. After completion of the reaction, GO (20 mg), CH$_3$CN (0.7 mL) and H$_2$O (0.5 mL) were added and the resulting suspension was stirred at 120 °C for 48 h. Then, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL) and MeOH (5 mL). The filtrate was evaporated to dryness and the residue was purified by flash column chromatography (SiO$_2$), eluting with PE/acetone (90:10 to 60:40) to afford unreacted 1h (11 mg, 16%, endo/exo 10:90) and then 2h (28 mg, 40%) as cream color solid.
A screw-capped vial was equipped with a magnetic stirring bar and charged with GO (6 mg) and CH₃CN (1.5 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, then 2-benzzyloxobenzaldehyde (64 mg, 0.30 mmol), aniline (36 mg, 36 µL, 0.39 mmol) and 2,3-dihydrofuran (53 mg, 57 µL, 0.75 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 24 h. After completion of the reaction, GO (24 mg), CH₃CN (0.9 mL) and H₂O (0.6 mL) were added and the resulting suspension was stirred at 120 °C for 48 h. Then, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL) and MeOH (5 mL). The filtrate was evaporated to dryness and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (90:10 to 60:40) to afford unreacted 1i (26 mg, 29%, endo/exo 20:80) and then 2i (37 mg, 42%) as colorless oil.

**2-(2-cyclopropylquinolin-3-yl)ethan-1-ol 2j**

A screw-capped vial was equipped with a magnetic stirring bar and charged with GO (5 mg) and CH₃CN (1.3 mL). The resulting suspension was sonicated for 2 min, using an ultrasonic bath, cyclopropanecarboxaldehyde (18 mg, 19 µL, 0.25 mmol), aniline (30 mg, 30 µL, 0.33 mmol) and 2,3-dihydrofuran (44 mg, 47 µL, 0.62 mmol) were added to the mixture. The sealed reaction vial was stirred at rt for 24 h. After completion of the reaction, GO (20 mg), CH₃CN (0.7 mL) and H₂O (0.5 mL) were added and the resulting suspension was stirred at 120 °C for 48 h. Then, the reaction mixture was filtered through a celite cake, washing with DCM/EtOAc 1:1 (15 mL) and MeOH (5 mL). The filtrate was evaporated to dryness and the residue was purified by flash column chromatography (SiO₂), eluting with PE/acetone (90:10 to 60:40) to afford unreacted 1j (18 mg, 33%, endo/exo 80:20) and then 2j (9 mg, 17%) as colorless oil.

**Synthesis of endo 3 and 4**

*Synthesis of 4-(4-chlorophenyl)-5-propyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline endo 3*
A solution of endo 1a (50 mg, 0.17 mmol) in dry DCM (2 mL) was treated with propionaldehyde (51 mg, 0.63 μL, 0.87 mmol) and AcOH (42 mg, 40 μL, 0.70 mmol) at rt under N\textsubscript{2}. After stirring 15 min, NaBH(OAc)\textsubscript{3} (111 mg, 0.53 mmol) was added portion wise and the suspension was stirred for 2 h at rt. Then, the reaction mixture was diluted with saturated NaHCO\textsubscript{3} solution (5 mL) and extracted with DCM (10-15 mL). The combined organic phases were washed with brine, dried with anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtrated and the solvent was removed. The desired product was isolated by flash chromatography over silica gel (PE/acetone 95:5 to 90:10) to afford endo 3 as colorless oil (25 mg, Y = 45%); \textit{R} \textsubscript{f} = 0.59 (PE/acetone 85:15); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \delta 7.37 (dd, J = 7.5, 1.2 Hz, 1H, 7-H), 7.26 – 7.16 (m, 5H, 4H-Ar and 9-H), 6.81 – 6.70 (m, 2H, 6-H and 8-H), 4.91 (d, J = 6.0 Hz, 1H, 9b-H), 4.45 (d, J = 5.5 Hz, 1H, 4-H), 3.66 (td, J = 8.4, 6.5 Hz, 1H, H-2) 3.31 (ddd, J = 14.8, 8.8, 6.1 Hz, 1H, 1H of CH\textsubscript{2}-N), 3.19 (td, J = 8.5, 5.5 Hz, 1H, 1H of H-2), 2.84 (ddd, J = 14.8, 9.1, 6.9 Hz, 1H, 1H of CH\textsubscript{2}-N), 2.78 – 2.67 (m, 1H, 3a-H), 2.05 – 1.81 (m, 2H, CH\textsubscript{2}-3), 1.56 – 1.43 (m, 2H, CH\textsubscript{2}-CH\textsubscript{3}), 0.81 (t, J = 7.4 Hz, 3H, CH\textsubscript{3}); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \delta 144.7, 140.0, 133.0, 130.5, 129.8, 129.2, 128.4, 121.9, 117.2, 112.3, 75.4, 65.6, 62.2, 51.5, 42.5, 27.4, 19.4, 11.6; Anal. Calcd. for C\textsubscript{20}H\textsubscript{22}ClNO: % C 73.27; H 6.76; N 4.27; O 4.88, found: C 73.35; H 6.58; N 4.80; O 4.95.

**Synthesis of 6,7-dihydrobenzo[2,3]oxepino[4,5-b]quinolone 4**

A solution of 2i (50 mg, 0.14 mmol) in EtOH (96%, 2.5 mL) was treated with 10% Pd/C (15 mg, 30 wt. %) and hydrogenated at rt under the slight overpressure of an inflated balloon. After stirring overnight, the suspension was filtered through a celite cake, washing with a mixture of EtOH/DCM 1:1 and evaporated under reduced pressure. The crude filtrated on SiO\textsubscript{2} washing with EtOAc + 10%MeOH to afford debenzylated derivative (30 mg, 81%), which was taken up in dry THF (3 mL), cooled to 0 °C, and treated with triphenylphosphine (39 mg, 0.15 mmol) and t-butyl azodicarboxylate (35 mg, 0.15 mmol). The mixture was stirred for 30 min at rt. Then, the solvent was removed under reduced pressure and the resulting crude was purified by silica gel column.
chromatography, eluting with PE/EtOAc (95:5 to 85:15) to afford 4 as white solid (22 mg, 89%); mp 138-139 °C (PE/EtOAc); \( R_f = 0.53 \) (PE/EtOAc 80:20); I.R.: \( \bar{\nu} \) (cm\(^{-1}\)) = 3049, 2967, 2938, 2876, 1620, 1603, 1577, 1558, 1488, 1451, 1428, 1417, 1348, 1314, 1296, 1233, 1207, 1196, 1141, 1130, 1104, 1066, 1049, 1030, 1011, 949, 937, 921, 866, 852, 818, 796, 784, 766, 752, 725, 707, 660, 634, 615; \( ^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 8.19 (ddt, \( J = 8.4, 1.3, 0.7 \) Hz, 1H, 16-H), 8.01 (s, 1H, 8-H), 7.97 (dd, \( J = 7.6, 1.9 \) Hz, 1H, 12-H), 7.82 (dd, \( J = 8.0, 1.5 \) Hz, 1H, 19-H), 7.71 (dddd, \( J = 8.4, 6.9, 1.5, 0.5 \) Hz, 1H, 17-H), 7.54 (dddd, \( J = 8.1, 6.9, 1.3, 0.5 \) Hz, 1H, 18-H), 7.45 (dddd, \( J = 7.9, 7.3, 1.9, 0.5 \) Hz, 1H, 14-H), 7.34 (tdt, \( J = 7.5, 1.3, 0.5 \) Hz, 1H, 13-H), 7.17 (dd, \( J = 7.9, 1.3 \) Hz, 1H, 15-H), 4.59 (t, \( J = 6.3 \) Hz, 2H, \( \text{CH}_2\)-O), 3.01 (t, \( J = 6.3 \), 2H, \( \text{CH}_2\)-C); \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 158.1, 155.0, 147.8, 134.7, 134.4, 131.3, 131.1, 130.4, 129.7, 129.2, 127.6, 127.2, 126.6, 125.0, 122.3, 76.3, 32.7; Anal. Calcd. for C\(_{17}\)H\(_{13}\)NO: % C 82.57; H 5.30; N 5.66; O 6.47, found: C 82.63; H 5.29; N 5.64; O 6.49.

Copies of \(^1\)H- and \(^{13}\)C-NMR Spectra of Compounds
References


