SUPPORTING INFORMATION

Lewis Acid Catalyzed Reactivity Switch: Pseudo Three-Component Annulation of Nitrosoarenes and (Epoxy)styrenes

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Experimental:

General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware under an argon atmosphere. Dichloromethane (CH₂Cl₂) was freshly distilled from phosphorus (V) oxide (P₂O₅). Commercial grade DCE, xylene, benzene and toluene were distilled over CaH₂ before use. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Acros, Merck and Spectrochem. ¹H, ¹³C NMR spectroscopy: Bruker 600 MHz and Bruker 400 MHz (at 298 K). Chemical shifts, δ (in ppm), are reported relative to TMS δ (¹H) 0.0 ppm, δ (¹³C) 0.0 ppm) which was used as the inner reference. Otherwise the solvents residual proton resonance and carbon resonance (CHCl₃, δ (¹H) 7.26 ppm, δ (¹³C) 77.23 ppm) were used for calibration. Column chromatography: Merck or Spectrochem silica gel 60-120 under gravity. IR: spectra were recorded on Perkin Elmer Instrument at normal temperature. MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-Mass Q-TOF LC/MS 6520, and peaks are given in m/z (% of basis peak). Nitrosoarenes were prepared from the reported method.
Table S1: Optimization of reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Yield of 5b (%)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Yield of 5b' (%)&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sc(OTf)&lt;sub&gt;3&lt;/sub&gt; (30 mol%), toluene, reflux, 24 h</td>
<td>36</td>
<td>11</td>
</tr>
<tr>
<td>2.</td>
<td>Sc(OTf)&lt;sub&gt;3&lt;/sub&gt; (30 mol%), toluene, reflux, 24 h</td>
<td>43</td>
<td>18</td>
</tr>
<tr>
<td>3.</td>
<td>Sc(OTf)&lt;sub&gt;3&lt;/sub&gt; (30 mol%), toluene, reflux, 24 h</td>
<td>46</td>
<td>22</td>
</tr>
<tr>
<td>4.</td>
<td>Sc(OTf)&lt;sub&gt;3&lt;/sub&gt; (30 mol%), toluene, reflux, 36 h</td>
<td>47</td>
<td>25</td>
</tr>
<tr>
<td>5.</td>
<td>Sc(OTf)&lt;sub&gt;3&lt;/sub&gt; (15 mol%), toluene, reflux, 36 h</td>
<td>45</td>
<td>18</td>
</tr>
<tr>
<td>6.</td>
<td>Sc(OTf)&lt;sub&gt;3&lt;/sub&gt; (15 mol%), DCE, reflux, 36 h</td>
<td>49</td>
<td>28</td>
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<tr>
<td>7.</td>
<td>Sc(OTf)&lt;sub&gt;3&lt;/sub&gt; (15 mol%), DCM, reflux, 36 h</td>
<td>46</td>
<td>21</td>
</tr>
<tr>
<td>8.</td>
<td>Yb(OTf)&lt;sub&gt;3&lt;/sub&gt; (15 mol%), DCE, reflux, 36 h</td>
<td>48</td>
<td>28</td>
</tr>
<tr>
<td>9.</td>
<td>Yb(OTf)&lt;sub&gt;3&lt;/sub&gt; (15 mol%), DCE, reflux, 36 h</td>
<td>44</td>
<td>25</td>
</tr>
<tr>
<td>10.</td>
<td>Yb(OTf)&lt;sub&gt;3&lt;/sub&gt; (5 mol%), DCE, reflux, 36 h</td>
<td>34</td>
<td>15</td>
</tr>
<tr>
<td>11.</td>
<td>Yb(OTf)&lt;sub&gt;3&lt;/sub&gt; (5 mol%), DCE, reflux, 72 h</td>
<td>34</td>
<td>12</td>
</tr>
<tr>
<td>12.</td>
<td>Yb(OTf)&lt;sub&gt;3&lt;/sub&gt; (15 mol%), DCE, reflux, 72 h</td>
<td>42</td>
<td>22</td>
</tr>
<tr>
<td>13.</td>
<td>Bi(OTf)&lt;sub&gt;3&lt;/sub&gt; (15 mol%), DCE, reflux, 36 h</td>
<td>36</td>
<td>19</td>
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<tr>
<td>14.</td>
<td>Cu(OTf)&lt;sub&gt;2&lt;/sub&gt; (15 mol%), DCE, reflux, 36 h</td>
<td>35</td>
<td>11</td>
</tr>
<tr>
<td>15.</td>
<td>TfOH (15 mol%), DCE, reflux, 36 h</td>
<td>33</td>
<td>21</td>
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<tr>
<td>16.</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt; (15 mol%), DCE, reflux, 36 h</td>
<td>-</td>
<td>-</td>
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<tr>
<td>17.</td>
<td>Yb(OTf)&lt;sub&gt;3&lt;/sub&gt; (15 mol%), THF, reflux, 36 h</td>
<td>37</td>
<td>18</td>
</tr>
<tr>
<td>18.</td>
<td>Yb(OTf)&lt;sub&gt;3&lt;/sub&gt; (15 mol%), EtOAc, reflux, 36 h</td>
<td>39</td>
<td>22</td>
</tr>
<tr>
<td>19.</td>
<td>Yb(OTf)&lt;sub&gt;3&lt;/sub&gt; (15 mol%), benzene, reflux, 36 h</td>
<td>45</td>
<td>11</td>
</tr>
</tbody>
</table>
Accordingly, nitrosobenzene 4 was reacted with styrene 2 in the presence of 30 mol% of Sc(OTf)₃ in refluxing toluene for 24 h. As expected, the 2,4-diarylquinoline 5b and 4-arylquinoline 5b' were isolated as 3:1 ratio with a 47% combined yield (SI, Table S1). The better yield of the desired products was obtained by increasing the stoichiometry of styrene and the reaction time (entry 2-4). A significant decrease in the yield was observed on lowering the catalyst loading to 15 mol% (entry 5). However, the best yield of the desired quinoline was observed when the reaction with reduced catalyst loading was carried out in refluxing DCE instead of refluxing toluene (entry 6). A similar result was obtained when Yb(OTf)₃ was used as the catalyst. Further screening of reaction conditions was carried out using Yb(OTf)₃, which is cost-effective than Sc(OTf)₃ (entry 8-12, 17-20). Although the lower yield of the desired product was obtained in the presence of a catalytic amount of TfOH, the use of other acids like AcOH and dinitrobenzoic acid failed to provide the quinolines. Other solvents such as THF, EtOAc, CH₃CN, etc. were also found to be suitable for this reaction.
Table S2. Screening of reaction conditions.

<table>
<thead>
<tr>
<th>entry</th>
<th>conditions</th>
<th>Yield (%)^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1^a</td>
<td>Cu(OTf)$_2$ (15 mol%), toluene, reflux, 24 h</td>
<td>39</td>
</tr>
<tr>
<td>2</td>
<td>Cu(OTf)$_2$ (15 mol%), toluene, reflux, 24 h</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>Cu(OTf)$_2$ (15 mol%), DCE, reflux, 24 h</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>Sc(OTf)$_3$ (15 mol%), DCE, reflux, 24 h</td>
<td>64</td>
</tr>
<tr>
<td>5</td>
<td>Cu(OTf)$_2$ (15 mol%), DCE, reflux, 36 h</td>
<td>61</td>
</tr>
<tr>
<td>6</td>
<td>Cu(OTf)$_2$ (15 mol%), DCE, reflux, 72 h</td>
<td>56</td>
</tr>
<tr>
<td>7</td>
<td>Cu(OTf)$_2$ (15 mol%), DCE, reflux, 12 h</td>
<td>51</td>
</tr>
<tr>
<td>8^b</td>
<td>Cu(OTf)$_2$ (15 mol%), DCE, reflux, 24 h</td>
<td>61</td>
</tr>
<tr>
<td>9</td>
<td>Yb(OTf)$_3$ (15 mol%), DCE, reflux, 24 h</td>
<td>53</td>
</tr>
<tr>
<td>10</td>
<td>CuBr$_2$ (15 mol%), DCE, reflux, 24 h</td>
<td>-</td>
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<tr>
<td>11</td>
<td>Cu(OTf)$_2$ (15 mol%), benzene, reflux, 24 h</td>
<td>42</td>
</tr>
<tr>
<td>12</td>
<td>Cu(OTf)$_2$ (15 mol%), THF, reflux, 24 h</td>
<td>37</td>
</tr>
</tbody>
</table>

All reactions were carried out 0.33 mmol (1 eq.) of nitrosobenzene, 2 eq. of styrene epoxide and solvent (3 mL). ^a1 eq. epoxide was used. ^b2.5 eq. epoxide was used. ^cSeparated yield.

Scheme S1: Additional substrates
Scheme S2: Attempted reactions with various additional alkenes and epoxide.
Scheme S3: Additional controlled experiments.

Scheme S4: Proposed mechanism for the formation of nitrone from nitrosoarene and styrene

Scheme S5: Probable stepwise pathway to form intermediate 20.
Procedure for the Synthesis of 2-phenyl-4-(p-tolyl)quinoline (3):

2-phenyl-4-(p-tolyl)quinoline (3): Freshly prepared (Z)-N,1-diphenylmethanimine oxide (79 mg, 0.40 mmol) and Sc(OTf)₃ (29 mg, 0.06 mmol) were successively added to a solution of 4-methyl styrene (57 mg, 0.48 mmol) in dry DCE (3 mL). Then the reaction mixture was refluxed for 36 h under argon atmosphere. Then the solvent was evaporated under reduced pressure. The reaction mixture was diluted with water (1X20 mL) and the reaction mixture was extracted with DCM (3X20 mL). The organic layer was washed with brine solution (1X30 mL) and evaporated under vaccum. The crude mixture was subjected to column chromatography (silica gel; EtOAc : hexane, 1:30) gave 3 as yellow gum (0.10 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ = 8.28 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 7.2 Hz, 2H), 7.95 (d, J = 7.6 Hz, 1H), 7.82 (s, 1H), 7.76 - 7.72 (m, 1H), 7.56 - 7.52 (m, 2H), 7.49 - 7.47 (m, 4H), 7.37 (d, J = 8.0 Hz, 2H), 2.49 (s, 3H) ppm. HRMS: Exact mass calculated for C₂₂H₁₈N ([M+H]+): 296.1434, Found: 296.1432.

General Procedure for the Synthesis of mono and di substituted quinolines (I):

Freshly prepared nitrosoarenes (1 equiv.) and Yb(OTf)₃ (15 mol%) were successively added to a solution of styrene derivatives (2.2 equiv.) in dry DCE (3 mL). Then the reaction mixture was refluxed for 36 h under argon atmosphere. The reactions were carried out under an argon environment; however, without strictly maintaining the oxygen-free conditions. Then the solvent was evaporated under reduced pressure. The reaction mixture was diluted with water (1x20 mL) and the reaction mixture was extracted with DCM (3X20 mL). The organic layer was washed with brine solution (1X30 mL) and evaporated under vaccum. The crude mixture was subjected to column chromatography (silica gel) to afford analytically pure products.

2,4-diphenylquinoline (5a) and 4-phenylquinoline (5a'): According to GP I, nitrosobenzene (43 mg, 0.40 mmol), styrene (92 mg, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5a as yellow gum (48 mg, 43%) and (silica gel; EtOAc : hexane, 1:7) gave 5a' as yellow gum (21 mg, 25%). Analytical data for 5a: ¹H NMR (400 MHz, CDCl₃) δ =
8.33 (d, $J = 8.4$ Hz, 1H), 8.23 - 8.18 (m, 2H), 7.92 (d, $J = 8.4$ Hz, 1H), 7.83 (s, 1H), 7.78 - 7.74 (m, 1H), 7.58 - 7.46 (m, 9H) ppm. HRMS: Exact mass calculated for C$_{21}$H$_{16}$N ([M+H]$^+$): 282.1277, Found: 282.1285.

Analytical data for 5a': $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.96 (d, $J = 3.6$ Hz, 1H), 8.32 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.82 - 7.78 (m, 1H), 7.59 - 7.46 (m, 6H), 7.43 (d, $J = 4.4$ Hz, 1H) ppm. HRMS: Exact mass calculated for C$_{15}$H$_{12}$N ([M+H]$^+$): 206.0964, Found: 206.0974.

2,4-di-p-tolylquinoline (5b)$^c$ and 4-(p-tolyl)quinoline (5b')$^d$: According to GP I, nitrosobenzene (43 mg, 0.40 mmol), 4-methyl styrene (0.10 g, 0.88 mmol) and Yb(OTf)$_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5b as yellow gum (59 mg, 48%) and (silica gel; EtOAc : hexane, 1:7) gave 5b' as yellow gum (25 mg, 28%). Analytical data for 5b: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.27 (d, $J = 8.0$ Hz, 1H), 8.11 (d, $J = 8.4$ Hz, 2H), 7.94 - 7.92 (m, 1H), 7.80 (s, 1H), 7.75 - 7.71 (m, 1H), 7.48 - 7.45 (m, 3H), 7.38 - 7.33 (m, 4H), 2.49 (s, 3H), 2.44 (s, 3H) ppm. HRMS: Exact mass calculated for C$_{23}$H$_{20}$N ([M+H]$^+$): 310.1590, Found: 310.1604.

Analytical data for 5b': $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.94 (d, $J = 4.8$ Hz, 1H), 8.31 (d, $J = 8.4$ Hz, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.81 - 7.76 (m, 1H), 7.58 - 7.54 (m, 1H), 7.44 - 7.40 (m, 3H), 7.36 (d, $J = 7.6$ Hz, 2H), 2.48 (s, 3H) ppm. HRMS: Exact mass calculated for C$_{16}$H$_{14}$N ([M+H]$^+$): 220.1121, Found: 220.1127.

2,4-di-m-tolylquinoline (5c) and 4-(m-tolyl)quinoline (5c')$^k$: According to GP I, nitrosobenzene (43 mg, 0.40 mmol), 3-methyl styrene (0.10 g, 0.88 mmol) and Yb(OTf)$_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5c as yellow gum (40 mg, 32%) and (silica gel; EtOAc : hexane, 1:7) gave 5c' as yellow gum (17 mg, 19%). Analytical data for 5c: FT-IR: $\tilde{\nu}$ = 2960, 2927, 2857, 1670, 1593, 1548, 1488, 1353, 1261, 1096, 876, 766 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.26 (d, $J = 8.8$ Hz, 1H), 8.04 (s, 1H), 7.97 (d, $J = 7.6$ Hz,
1H), 7.92 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.76 - 7.72 (m, 1H), 7.50 - 7.42 (m, 3H), 7.40 - 7.32 (m, 3H), 7.29 (d, J = 7.6 Hz, 1H), 2.48 (s, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 157.3, 149.5, 149.0, 139.8, 138.7, 138.6, 138.5, 130.4, 130.3, 130.2, 129.7, 129.3, 128.9, 128.7, 128.5, 126.9, 126.4, 126.0, 125.9, 124.9, 119.7, 21.82, 21.75 ppm. HRMS: Exact mass calculated for C$_{23}$H$_{20}$N ([M+H]$^+$): 310.1590, Found: 310.1590.

Analytical data for 5c': $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.96 (d, J = 4.8 Hz, 1H), 8.41 (d, J = 8.4 Hz, 1H), 7.48 - 7.44 (m, 2H), 7.37 - 7.32 (m, 3H), 2.47 (s, 3H) ppm. HRMS: Exact mass calculated for C$_{16}$H$_{14}$N ([M+H]$^+$): 220.1122, Found: 220.1122.

2,4-bis(4-chlorophenyl)quinoline (5d) and 4-(4-chlorophenyl)quinoline (5d')$^1$: According to GP I, nitrosobenzene (43 mg, 0.40 mmol), 4-chloro styrene (0.12 g, 0.88 mmol) and Yb(OTf)$_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5d as yellow gum (45 mg, 32%) and (silica gel; EtOAc : hexane, 1:7) gave 5d' as yellow gum (21mg, 22%).

Analytical data for 5d: FT-IR: $\tilde{\nu}$ = 2962, 2925, 2855, 1596, 1544, 1487, 1420, 1357, 1091, 1014, 830, 765 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.24 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.78 - 7.74 (m, 2H), 7.55 - 7.49 (m, 7H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 155.5, 149.2, 148.0, 137.0, 136.5, 136.4, 135.2, 131.0, 130.6, 129.6, 129.4, 129.3, 129.2, 127.3, 125.8, 125.6, 119.3 ppm. HRMS: Exact mass calculated for C$_{21}$H$_{14}$NCl$_2$ ([M+H]$^+$): 350.0498, Found: 350.0497.

Analytical data for 5d': $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.97 (d, J = 4.4 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.63 - 7.48 (m, 1H), 7.56 - 7.54 (m, 2H), 7.48 - 7.46 (m, 2H), 7.43 (d, J = 4.4 Hz, 1H) ppm. HRMS: Exact mass calculated for C$_{15}$H$_{11}$NCl ([M+H]$^+$): 240.0575, Found: 240.0576.
2,4-bis(4-fluorophenyl)quinoline (5e) and 4-(4-fluorophenyl)quinoline (5e')

According to GP I, nitrosobenzene (43 mg, 0.40 mmol), 4-fluoro styrene (0.11 g, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5e as yellow gum (47 mg, 37%) and (silica gel; EtOAc : hexane, 1:7) gave 5e' as yellow gum (22 mg, 24%). Analytical data for 5e: ¹H NMR (600 MHz, CDCl₃) δ = 8.27 - 8.23 (m, 1H), 8.21 - 8.16 (m, 2H), 7.87 - 7.83 (m, 1H), 7.77 - 7.75 (m, 2H), 7.55 - 7.49 (m, 3H), 7.27 - 7.20 (m, 4H) ppm. HRMS: Exact mass calculated for C₂₁H₁₄NF₂ ([M+H]⁺): 318.1089, Found: 318.1090.

Analytical data for 5e': ¹H NMR (400 MHz, CDCl₃) δ = 8.96 (d, J = 4.8 Hz, 1H), 8.34 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.83 - 7.79 (m, 1H), 7.61 - 7.57 (m, 1H), 7.53 - 7.49 (m, 2H), 7.41 (d, J = 4.4 Hz, 1H), 7.28 - 7.27 (m, 1H), 7.26 - 7.24 (m, 1H) ppm. HRMS: Exact mass calculated for C₁₅H₁₁NF ([M+H]⁺): 224.0870, Found: 224.0871.

2,4-bis(4-(tert-butyl)phenyl)quinoline (5f) and 4-(4-(tert-butyl)phenyl)quinoline (5f')

According to GP I, nitrosobenzene (43 mg, 0.40 mmol), 4-tert butyl styrene (0.14 g, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:40) gave 5f as yellow gum (38 mg, 24%) and (silica gel; EtOAc : hexane, 1:10) gave 5f' as yellow gum (22 mg, 21%). Analytical data for 5f: FT-IR: ν = 2961, 2930, 2867, 1660, 1591, 1497, 1363, 1268, 1018, 838, 765, 701 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.24 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 1H), 7.83 (s, 1H), 7.74 - 7.70 (m, 1H), 7.59 - 7.57 (m, 3H), 7.55 - 7.51 (m, 3H), 7.48 - 7.45 (m, 1H), 1.44 (s, 9H), 1.39 (s, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 157.2, 152.7, 151.7, 149.2, 149.1, 137.2, 135.8, 130.3, 129.5, 127.5, 126.2, 126.04, 125.99, 125.7, 119.5, 34.98, 34.96, 31.6, 31.5 ppm. Total count of 13C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for C₂₉H₃₂N ([M+H]⁺): 394.2529, Found: 394.2533.
Analytical data for 5f′: FT-IR: $\tilde{\nu} = 2960, 2930, 2866, 1611, 1585, 1501, 1462, 1389, 1201, 1056, 873, 747 \text{ cm}^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.93$ (d, $J = 4.4$ Hz, 1H), 8.17 (d, $J = 8.4$ Hz, 1H), 8.00 (d, $J = 6.4$ Hz, 1H), 7.74 - 7.70 (m, 1H), 7.56 - 7.54 (m, 2H), 7.52 - 7.48 (m, 1H), 7.47 - 7.45 (m, 2H), 7.34 (d, $J = 4.4$ Hz, 1H), 1.41 (s, 9H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 151.8, 150.2, 149.0, 148.8, 135.3, 130.0, 129.51, 129.45, 127.1, 126.7, 126.3, 125.7, 121.5, 35.0, 31.6$ ppm. HRMS: Exact mass calculated for C$_{19}$H$_{20}$N ([M+H]$^+$): 262.1590, Found: 262.1595.

2,4-di([1,1'-biphenyl]-4-yl)quinoline (5g) and 4-([1,1'-biphenyl]-4-yl)quinoline (5g′):

According to GP I, nitrosobenzene (43 mg, 0.40 mmol), 4-vinyl biphenyl (0.16 g, 0.88 mmol) and Yb(OTf)$_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5g as yellow gum (58 mg, 33%) and (silica gel; EtOAc : hexane, 1:10) gave 5g′ as yellow gum (24 mg, 21%). Analytical data for 5g: FT-IR: $\tilde{\nu} = 2927, 2860, 1628, 1600, 1449, 1299, 1076, 907, 844, 734 \text{ cm}^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.32 - 8.29$ (m, 3H), 8.02 - 8.00 (m, 1H), 7.92 (s, 1H), 7.81 - 7.75 (m, 5H), 7.73 - 7.67 (m, 6H), 7.54 - 7.47 (m, 5H), 7.44 - 7.37 (m, 2H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta = 156.7, 149.1, 149.0, 142.3, 141.6, 140.8, 140.7, 138.7, 137.5, 130.4, 130.3, 129.9, 129.2, 129.1, 128.2, 127.9, 127.81, 127.79, 127.6, 127.41, 127.37, 126.6, 126.0, 125.9, 119.5 ppm. HRMS: Exact mass calculated for C$_{33}$H$_{24}$N ([M+H]$^+$): 434.1903, Found: 434.1910.

Analytical data for 5g′: FT-IR: $\tilde{\nu} = 2957, 2920, 2847, 1633, 1596, 1486, 1388, 1261, 1007, 839, 766 \text{ cm}^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.97$ (d, $J = 4.8$ Hz, 1H), 8.24 (d, $J = 8.4$ Hz, 1H), 8.03 (d, $J = 9.2$ Hz, 1H), 7.79 - 7.75 (m, 3H), 7.71 - 7.69 (m, 2H), 7.62 - 7.60 (m, 2H), 7.58 - 7.54 (m, 1H), 7.52 - 7.49 (m, 2H), 7.43 - 7.39 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 149.7, 149.0, 148.3, 141.8, 140.6, 136.9, 130.2, 129.9, 129.7, 129.2, 128.0, 127.6, 127.4, 127.1, 127.0, 126.2, 121.5 ppm. HRMS: Exact mass calculated for C$_{21}$H$_{16}$N ([M+H]$^+$): 282.1277, Found: 282.1270.
6-methyl-2,4-diphenylquinoline (5h)\(^b\) and 6-methyl-4-phenylquinoline (5h')\(^a\): According to GP I, 1-methyl-4-nitrosobenzene (48 mg, 0.40 mmol), styrene (92 mg, 0.88 mmol) and Yb(OTf)\(_3\) (37 mg, 0.06 mmol) was reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5h as yellow gum (34 mg, 29%) and (silica gel; EtOAc : hexane, 1:7) gave 5h' as yellow gum (17 mg, 19%). Analytical data for 5h': \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.21 - 8.17 (m, 3H), 7.78 (s, 1H), 7.66 - 7.51 (m, 8H), 7.48 - 7.44 (m, 1H), 2.48 (s, 3H) ppm. HRMS: Exact mass calculated for C\(_{22}\)H\(_{18}\)N ([M+H]\(^+\): 296.1434, Found: 296.1438.

Analytical data for 5h': \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 8.88 (d, J = 4.2 Hz, 1H), 8.22 (d, J = 9.0 Hz, 1H), 7.70 (s, 1H), 7.63 - 7.62 (m, 1H), 7.57 - 7.51 (m, 5H), 7.38 (d, J = 4.2 Hz, 1H), 2.49 (s, 3H) ppm. HRMS: Exact mass calculated for C\(_{16}\)H\(_{14}\)N ([M+H]\(^+\): 220.1121, Found: 220.1123.

6-ethyl-2,4-diphenylquinoline (5i)\(^f\) and 6-ethyl-4-phenylquinoline (5i')\(^o\): According to GP I, 1-ethyl-4-nitrosobenzene (54 mg, 0.40 mmol), styrene (92 mg, 0.88 mmol) and Yb(OTf)\(_3\) (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5i as yellow gum (44 mg, 36%) and (silica gel; EtOAc : hexane, 1:7) gave 5i' as yellow gum (19 mg, 20%). Analytical data for 5i: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.24 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 7.2 Hz, 2H), 7.79 (s, 1H), 7.68 (s, 1H), 7.64 - 7.62 (m, 1H), 7.58 - 7.51 (m, 7H), 7.48 - 7.45 (m, 1H), 2.78 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H) ppm. HRMS: Exact mass calculated for C\(_{23}\)H\(_{20}\)N ([M+H]\(^+\): 310.1590, Found: 310.1591.

Analytical data for 5i': \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.88 (d, J = 4.4 Hz, 1H), 8.21 (d, J = 8.8 Hz, 1H), 7.71 (s, 1H), 7.66 - 7.64 (m, 1H), 7.56 - 7.51 (m, 5H), 7.36 (d, J = 4.8 Hz, 1H), 2.78 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H) ppm. HRMS: Exact mass calculated for C\(_{17}\)H\(_{16}\)N ([M+H]\(^+\): 234.1277, Found: 234.1285.
6-isopropyl-2,4-diphenylquinoline (5j) and 6-isopropyl-4-phenylquinoline (5j')\(^p\): According to GP I, 1-isopropyl-4-nitrosobenzene (60 mg, 0.40 mmol), styrene (92 mg, 0.88 mmol) and Yb(OTf)\(_3\) (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5j as yellow gum (48 mg, 37%) and (silica gel; EtOAc : hexane, 1:7) gave 5j' as yellow gum (20 mg, 20%). Analytical data for 5j: FT-IR: \(\tilde{\nu} = 2960, 2930, 2867, 1623, 1589, 1491, 1027, 835, 693\) cm\(^{-1}\). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 8.20 - 8.16\) (m, 3H), 7.78 (s, 1H), 7.67 - 7.66 (m, 1H), 7.59 - 7.56 (m, 4H), 7.54 - 7.51 (m, 3H), 7.47 - 7.45 (m, 1H), 3.06 - 3.01 (m, 1H), 1.29 (d, \(J = 7.2\) Hz, 6H) ppm. \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta = 156.4, 148.9, 147.9, 147.2, 140.0, 138.8, 130.3, 129.8, 129.3, 129.2, 129.0, 128.8, 128.5, 127.7, 125.8, 122.1, 119.7, 34.6, 24.1\) ppm. HRMS: Exact mass calculated for C\(_{24}\)H\(_{22}\)N ([M+H]+): 324.1747, Found: 324.1749.

Analytical data for 5j': \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.88\) (d, \(J = 4.8\) Hz, 1H), 8.22 (d, \(J = 8.8\) Hz, 1H), 7.74 (s, 1H), 7.51 - 7.68 (m, 1H), 7.56 - 7.52 (m, 5H), 7.36 (d, \(J = 4.4\) Hz, 1H), 3.07 - 3.05 (m, 1H), 1.28 (d, \(J = 6.8\) Hz, 6H) ppm. HRMS: Exact mass calculated for C\(_{18}\)H\(_{18}\)N ([M+H]+): 248.1434, Found: 248.1432.

6-(tert-butyl)-2,4-diphenylquinoline (5k)\(^\#\) and 6-(tert-butyl)-4-phenylquinoline (5k')\(^p\): According to GP I, 1-tert butyl-4-nitrosobenzene (65 mg, 0.40 mmol), styrene (92 mg, 0.88 mmol) and Yb(OTf)\(_3\) (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5k as yellow gum (55 mg, 41%) and (silica gel; EtOAc : hexane, 1:7) gave 5k' as yellow gum (19 mg, 18%). Analytical data for 5k: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.21\) (d, \(J = 8.8\) Hz, 1H), 8.19 - 8.17 (m, 2H), 7.87 - 7.83 (m, 2H), 7.79 (s, 1H), 7.60 - 7.51 (m, 7H), 7.48 - 7.44 (m, 1H), 1.35 (s, 9H) ppm. HRMS: Exact mass calculated for C\(_{25}\)H\(_{24}\)N ([M+H]+): 338.1903, Found: 338.1921.
Analytical data for 5k': $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.89$ (d, $J = 4.8$ Hz, 1H), 8.25 (d, $J = 8.8$ Hz, 1H), 7.92 - 7.87 (m, 2H), 7.56 - 7.53 (m, 5H), 7.39 (d, $J = 4.8$ Hz, 1H), 1.34 (s, 9H) ppm. HRMS: Exact mass calculated for C$_{10}$H$_{20}$N ([M+H]$^+$): 262.1590, Found: 262.1594.

6-methyl-2,4-di-p-tolylquinoline (5l)$^b$ and 6-methyl-4-(p-tolyl)quinoline (5l')$^b$: According to GP I, 1-methyl-4-nitrosobenzene (48 mg, 0.4 mmol), 4-methylstyrene (0.10 g, 0.88 mmol) and Yb(OTf)$_3$ (37 mg, 0.06 mmol) was reacted for 36 h in dry DCE (3 mL) and column chromatography (silica gel; EtOAc : hexane, 1:30) gave 5l as yellow gum (58 mg, 45%) and (silica gel; EtOAc : hexane, 1:7) gave 5l' as yellow gum (22 mg, 24%). Analytical data for 5l: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.18$ (d, $J = 8.4$ Hz, 1H), 8.08 (d, $J = 8.0$ Hz, 2H), 7.75 (s, 1H), 7.67 (s, 1H), 7.58 - 7.55 (m, 1H), 7.47 - 7.45 (m, 2H), 7.38 - 7.36 (m, 2H), 7.3 (d, $J = 8.0$ Hz, 2H), 2.49 (s, 3H), 2.48 (s, 3H), 2.43 (s, 3H) ppm. HRMS: Exact mass calculated for C$_{24}$H$_{22}$N ([M+H]$^+$): 324.1747, Found: 324.1757.

Analytical data for 5l': $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.85$ (d, $J = 4.4$ Hz, 1H), 8.12 (d, $J = 8.4$ Hz, 1H), 7.71 (s, 1H), 7.59 - 7.56 (m, 1H), 7.42 - 7.40 (m, 2H), 7.36 - 7.34 (m, 2H), 7.31 (d, $J = 4.8$ Hz, 1H), 2.48 (s, 6H) ppm. HRMS: Exact mass calculated for C$_{17}$H$_{16}$N ([M+H]$^+$): 234.1277, Found: 234.1287.

6-ethyl-2,4-di-p-tolylquinoline (5m) and 6-ethyl-4-(p-tolyl)quinoline (5m')$: According to GP I, 1-ethyl-4-nitrosobenzene (54 mg, 0.4 mmol), 4-methylstyrene (0.10 g, 0.88 mmol) and Yb(OTf)$_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5m as yellow gum (62 mg, 46%) and (silica gel; EtOAc : hexane, 1:7) gave 5m' as yellow gum (26 mg, 26%). Analytical data for 5m: FT-IR: $\tilde{\nu} =$ 2963, 2922, 2870, 1613, 1588, 1494, 1358, 1211, 1183, 1090, 890, 725 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.21$ (d, $J = 8.8$ Hz, 1H), 8.09 (d, $J = 8.0$ Hz, 2H), 7.75 (s, 1H), 7.70 (d, $J = 1.2$ Hz, 1H), 7.62 - 7.59 (m, 1H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 7.6$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 2.77 (q, $J = 7.6$ Hz, 2H), 2.50 (s, 3H), 2.43 (s, 3H), 1.27 (t, $J = 7.6$ Hz, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 156.0, 149.5, 147.0, 142.8, 139.8, 138.6, 136.3, 135.7, 131.1, 129.8, 129.7,
129.5, 129.4, 127.8, 126.0, 123.5, 119.6, 29.3, 21.56, 21.54, 15.8 ppm. HRMS: Exact mass calculated for C_{25}H_{24}N ([M+H]^+): 338.1903, Found: 338.1903.

Analytical data for 5m: FT-IR: $\tilde{\nu} = 2964, 2927, 2872, 1615, 1584, 1454, 1372, 1260, 1184, 1021, 817, 723 \text{ cm}^{-1}$. $^1$H NMR (600 MHz, CDCl$_3$) $\delta = 8.86$ (d, $J = 4.8$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 1H), 7.75 (s, 1H), 7.64 (d, $J = 8.4$ Hz, 1H), 7.42 (d, $J = 7.8$ Hz, 2H), 7.37 - 7.34 (m, 3H), 2.78 (q, $J = 7.8$ Hz, 2H), 2.48 (s, 3H), 1.26 (t, $J = 7.8$ Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta = 149.2, 148.4, 146.7, 143.3, 138.7, 135.2, 131.1, 129.63, 129.55, 129.1, 127.1, 123.8, 121.5, 29.4, 21.5, 15.8 ppm. HRMS: Exact mass calculated for C_{18}H_{18}N ([M+H]^+): 248.1434, Found: 248.1434.

2,4-bis(4-(tert-butyl)phenyl)-6-ethylquinoline (5n) and 4-(4-(tert-butyl)phenyl)-6-ethylquinoline (5n'): According to GP I, 1-ethyl-4-nitrosobenzene (54 mg, 0.4 mmol), 4-tert-butylstyrene (0.14 g, 0.88 mmol) and Yb(OTf)$_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:40) gave 5n as yellow gum (57 mg, 34%) and (silica gel; EtOAc : hexane, 1:10) gave 5n' as yellow gum (24 mg, 21%). Analytical data for 5n: FT-IR: $\tilde{\nu} = 2962, 2904, 2868, 1589, 1460, 1394, 1261, 1186, 1081, 965, 892, 799 \text{ cm}^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.16$ (d, $J = 8.8$ Hz, 1H), 8.10 (d, $J = 8.4$ Hz, 2H), 7.77 (s, 1H), 7.74 (s, 1H), 7.61 - 7.57 (m, 3H), 7.55 - 7.51 (m, 4H), 2.78 (q, $J = 7.6$ Hz, 2H), 1.44 (s, 9H), 1.38 (s, 9H), 1.28 (t, $J = 7.6$ Hz, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 156.4, 152.5, 151.6, 148.6, 147.9, 142.4, 137.4, 136.0, 130.6, 130.2, 129.5, 127.4, 126.0, 125.9, 125.7, 123.6, 119.6, 35.0, 34.9, 31.6, 31.5, 29.4, 15.9 ppm. HRMS: Exact mass calculated for C_{31}H_{36}N ([M+H]^+): 422.2822, Found: 422.2851.

Analytical data for 5n': FT-IR: $\tilde{\nu} = 2962, 2929, 2868, 1611, 1582, 1501, 1455, 1363, 1260, 1102, 1018, 891, 736 \text{ cm}^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.86$ (d, $J = 4.4$ Hz, 1H), 8.09 (d, $J = 8.8$ Hz, 1H), 7.76 (s, 1H), 7.61 - 7.59 (m, 1H), 7.57 - 7.55 (m, 2H), 7.48 - 7.46 (m, 2H), 7.29 (d, $J = 4.4$ Hz, 1H), 2.78 (q, $J = 7.6$ Hz, 2H), 1.42 (s, 9H), 1.27 (t, $J = 7.6$ Hz, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 151.6, 149.3, 148.2, 147.7, 142.9, 135.5, 130.6, 129.8, 129.5, 127.0,
125.7, 123.8, 121.7, 35.0, 31.6, 29.4, 15.9 ppm. HRMS: Exact mass calculated for C_{21}H_{24}N ([M+H]^+): 290.1903, Found: 290.1900.

**6-propyl-2,4-di-p-tolylquinoline (5o) and 6-propyl-4-(p-tolyl)quinoline (5o’):** According to GP I, 1-propyl-4-nitrosobenzene (60 mg, 0.4 mmol), 4-methylstyrene (0.10 g, 0.88 mmol) and Yb(OTf)$_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5o as yellow gum (55 mg, 39%) and (silica gel; EtOAc : hexane, 1:10) gave 5o’ as yellow gum (20 mg, 19%). Analytical data for 5o: FT-IR: $\tilde{\nu}$ = 2960, 2925, 2870, 1618, 1590, 1496, 1361, 1261, 1018, 820, 669 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.15 (d, $J$ = 8.8 Hz, 1H), 8.08 (d, $J$ = 8.4 Hz, 2H), 7.75 (s, 1H), 7.68 - 7.67 (m, 1H), 7.59 - 7.56 (m, 1H), 7.47 (d, $J$ = 8.0 Hz, 2H), 7.37 (d, $J$ = 7.6 Hz, 2H), 7.33 (d, $J$ = 8.0 Hz, 2H), 2.71 (t, $J$ = 7.6 Hz, 2H), 2.50 (s, 3H), 2.43 (s, 3H), 1.73 - 1.64 (m, 2H), 0.95 (t, $J$ = 7.6 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 156.3, 148.7, 147.8, 140.9, 139.3, 138.4, 137.3, 136.0, 131.1, 129.9, 129.73, 129.68, 129.5, 127.6, 125.9, 124.2, 119.5, 38.4, 24.8, 21.6, 14.1 ppm. Total count of 13C is less than expected due to the merging of signals in the aliphatic region. HRMS: Exact mass calculated for C$_{26}$H$_{26}$N ([M+H]^+): 352.2060, Found:352.2056.

Analytical data for 5o’: FT-IR: $\tilde{\nu}$ = 2958, 2923, 2854, 1615, 1585, 1501, 1456, 1260, 1184, 1089, 858, 724 cm$^{-1}$. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 8.86 (d, $J$ = 4.8 Hz, 1H), 8.24 (d, $J$ = 8.4 Hz, 1H), 7.74 (s, 1H), 7.64 (d, $J$ = 8.4 Hz, 1H), 7.43 (d, $J$ = 7.8 Hz, 2H), 7.38 - 7.37 (m, 3H), 2.72 (t, $J$ = 7.2 Hz, 2H), 2.49 (s, 3H), 1.70 - 1.64 (m, 2H), 0.94 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 150.1, 147.6, 145.7, 142.2, 139.0, 135.0, 132.0, 129.6, 128.3, 127.1, 124.6, 121.5, 38.4, 24.7, 21.6, 14.0 ppm. Total count of 13C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for C$_{19}$H$_{20}$N ([M+H]^+): 262.1590, Found:262.1596.
6-isopropyl-2,4-di-p-tolylquinoline (5p) and 6-isopropyl-4-(p-tolyl)quinoline (5p’): According to GP I, 1-isopropyl-4-nitrosobenzene (60 mg, 0.4 mmol), 4-methylstyrrene (0.10 g, 0.88 mmol) and Yb(OTf)$_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5p as yellow gum (59 mg, 42%) and (silica gel; EtOAc : hexane, 1:7) gave 5p’ as yellow gum (30 mg, 29%). Analytical data for 5p: FT-IR: $\tilde{\nu}$ = 2960, 2922, 2867, 1613, 1593, 1548, 1456, 1358, 1266, 821, 751 cm$^{-1}$. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 8.17 (d, $J$ = 8.4 Hz, 1H), 8.08 (d, $J$ = 7.8 Hz, 2H), 7.76 (s, 1H), 7.73 (s, 1H), 7.66 - 7.64 (m, 1H), 7.49 (d, $J$ = 8.4 Hz, 2H), 7.38 (d, $J$ = 7.8 Hz, 2H), 7.33 (d, $J$ = 7.8 Hz, 2H), 3.06 - 3.01 (m, 1H), 2.50 (s, 3H), 2.44 (s, 3H), 1.29 (d, $J$ = 7.2 Hz, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 156.3, 148.8, 147.9, 146.9, 139.3, 138.4, 129.7, 136.0, 130.1, 129.72, 129.67, 129.5, 129.1, 127.6, 125.8, 122.2, 119.5, 34.6, 24.1, 21.6 ppm. Total count of 13C is less than expected due to the merging of signals in the aliphatic region. HRMS: Exact mass calculated for C$_{26}$H$_{26}$N ([M+H]$^+$): 352.2060, Found: 352.2072.

Analytical data for 5p’: FT-IR: $\tilde{\nu}$ = 2960, 2925, 2867, 1618, 1584, 1501, 1457, 1385, 1185, 1043, 859, 818, 684 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.86 (d, $J$ = 4.4 Hz, 1H), 8.18 (d, $J$ = 8.8 Hz, 1H), 7.77 (d, $J$ = 1.6 Hz, 1H), 7.69 - 7.66 (m, 1H), 7.44 - 7.42 (m, 2H), 7.37 - 7.32 (m, 3H), 3.07 - 3.00 (m, 1H), 2.48 (s, 3H), 1.28 (d, $J$ = 6.8 Hz, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 149.4, 148.4, 147.8, 146.7, 138.8, 135.2, 129.7, 129.6, 129.1, 127.1, 122.5, 121.5, 34.6, 24.1, 21.6 ppm. Total count of 13C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for C$_{19}$H$_{20}$N ([M+H]$^+$): 262.1590, Found: 262.1591.
2,4-bis(4-(tert-butyl)phenyl)-6-isopropylquinoline (5q) and 4-(4-(tert-butyl)phenyl)-6-isopropylquinoline (5q’): According to GP I, 1-isopropyl-4-nitroso benzene (60 mg, 0.4 mmol), 4-tert-butylstyrene (0.14 g, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:40) gave 5q as yellow gum (81 mg, 47%) and (silica gel; EtOAc : hexane, 1:10) gave 5q’ as yellow gum (21 mg, 17%). Analytical data for 5q: FT-IR: \( \tilde{\nu} \) = 2962, 2902, 2867, 1610, 1590, 1463, 1368, 1273, 1113, 1016, 838, 750, 604 cm⁻¹. \(^1\)H NMR (400 MHz, CDCl₃) δ = 8.17 (d, \( J = 8.4 \) Hz, 1H), 8.09 (d, \( J = 8.4 \) Hz, 2H), 7.77 - 7.76 (m, 2H), 7.66 - 7.63 (m, 1H), 7.60 - 7.58 (m, 2H), 7.55 - 7.52 (m, 4H), 3.09 - 3.02 (m, 1H), 1.44 (s, 9H), 1.38 (s, 9H), 1.30 (d, \( J = 7.2 \) Hz, 6H) ppm. \(^1\)C NMR (101 MHz, CDCl₃) δ = 156.4, 152.5, 151.6, 148.7, 148.1, 146.9, 137.4, 136.0, 130.3, 129.5, 128.9, 127.4, 126.0, 125.7, 125.9, 122.3, 119.7, 35.0, 34.9, 34.6, 31.6, 31.5, 24.2 ppm. HRMS: Exact mass calculated for C₃₂H₃₈N ([M+H]⁺): 436.2999, Found: 436.2992.

Analytical data for 5q’: FT-IR: \( \tilde{\nu} \) = 2961, 2905, 2870, 1613, 1583, 1501, 1460, 1363, 1267, 1106, 1021, 838, 750 cm⁻¹. \(^1\)H NMR (400 MHz, CDCl₃) δ = 8.86 (d, \( J = 4.4 \) Hz, 1H), 8.11 (d, \( J = 8.8 \) Hz, 1H), 7.79 (d, \( J = 2.0 \) Hz, 1H), 7.66 - 7.63 (m, 1H), 7.56 (d, \( J = 8.4 \) Hz, 2H), 7.48 - 7.46 (m, 2H), 7.29 (d, \( J = 4.4 \) Hz, 1H), 3.08 - 3.01 (m, 1H), 1.43 (s, 9H), 1.29 (d, \( J = 7.2 \) Hz, 6H) ppm. \(^1\)C NMR (101 MHz, CDCl₃) δ = 151.7, 149.4, 148.2, 147.9, 147.4, 135.5, 130.0, 129.5, 128.9, 127.0, 125.7, 122.5, 121.7, 35.0, 34.6, 31.6, 24.2 ppm. HRMS: Exact mass calculated for C₂₂H₂₆N ([M+H]⁺): 304.2060, Found: 304.2064.

6-tert-butyl-2,4-di-p-tolylquinoline (5r) and 6-tert-butyl-4-(p-tolyl)quinoline (5r’): According to GP I, 1-tert-butyl-4-nitroso benzene (65 mg, 0.4 mmol), 4-methylstyrene (0.10 g, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 5r as yellow gum (65 mg, 45%) and (silica gel; EtOAc : hexane, 1:7) gave 5r’ as yellow gum (24 mg, 22%). Analytical data for 5r: FT-IR: \( \tilde{\nu} \) =
2962, 2927, 2867, 1615, 1590, 1544, 1462, 1389, 1260, 1114, 1020, 820, 746 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.23\) (d, \(J = 8.8\) Hz, 1H), 8.09 (d, \(J = 8.4\) Hz, 2H), 7.91 (d, \(J = 2.0\) Hz, 1H), 7.85 - 7.82 (m, 1H), 7.77 (s, 1H), 7.50 (d, \(J = 8.0\) Hz, 2H), 7.39 - 7.32 (m, 4H), 2.50 (s, 3H), 2.44 (s, 3H), 1.36 (s, 9H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 156.3, 149.7, 149.3, 146.9, 139.7, 138.6, 136.6, 135.8, 129.8, 129.6, 129.5, 129.3, 128.8, 127.7, 125.5, 120.9, 119.6, 35.3, 31.4, 21.6 ppm. Total count of 13C is less than expected due to the merging of signals in the aliphatic region. HRMS: Exact mass calculated for C\(_{27}\)H\(_{28}\)N ([M+H]\(^+\)): 366.2216, Found: 366.2219.

Analytical data for 5r': FT-IR: \(\tilde{\nu} = 2962, 2869, 1614, 1583, 1500, 1372, 1260, 1185, 1022, 859, 817, 724\) cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.87\) (s, 1H), 8.15 (d, \(J = 8.8\) Hz, 1H), 7.93 (s, 1H), 7.85 - 7.82 (m, 1H), 7.45 - 7.43 (m, 2H), 7.36 - 7.31 (m, 3H), 2.48 (s, 3H), 1.35 (s, 9H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 149.2, 149.0, 146.9, 138.6, 135.4, 129.7, 129.5, 129.1, 128.6, 126.6, 121.6, 121.1, 35.3, 31.4, 21.5 ppm. HRMS: Exact mass calculated for C\(_{20}\)H\(_{22}\)N ([M+H]\(^+\)): 276.1747, Found: 276.1751.

2,4-bis(4-(tert-butyl)phenyl)-6-tert-butylquinoline (5s) and 4-(4-(tert-butyl)phenyl)-6-tert-butylquinoline (5s'): According to GP I, 1-tert-butyl-4-nitrosobenzene (65 mg, 0.4 mmol), 4-tert-butylstyrene (0.14 g, 0.88 mmol) and Yb(OTf)\(_3\) (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:40) gave 5s as yellow gum (76 mg, 42%) and (silica gel; EtOAc : hexane, 1:10) gave 5s' as yellow gum (20 mg, 16%). Analytical data for 5s: FT-IR: \(\tilde{\nu} = 2961, 2905, 2868, 1589, 1514, 1493, 1393, 1201, 1110, 1017, 894, 834, 669\) cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.24\) (d, \(J = 8.4\) Hz, 2H), 8.11 (d, \(J = 8.4\) Hz, 2H), 7.95 (d, \(J = 2.0\) Hz, 2H), 7.85 - 7.82 (m, 1H), 7.79 (s, 1H), 7.61 - 7.54 (m, 6H), 1.44 (s, 9H), 1.39 (s, 9H), 1.38 (s, 9H) ppm. \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta = 156.5, 152.6, 151.6, 149.1, 147.4, 137.2, 135.9, 129.6, 129.5, 128.5, 127.5, 126.0, 125.7, 125.4, 120.8, 119.7, 35.3, 35.0, 34.9, 31.6, 31.5, 31.4 ppm. Total count of 13C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for C\(_{33}\)H\(_{40}\)N ([M+H]\(^+\)): 450.3155, Found: 450.3172.
Analytical data for 5s’: FT-IR: $\tilde{\nu} = 2962, 2909, 2870, 1613, 1583, 1500, 1372, 1266, 1111, 1023, 839, 771$ cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.87$ (d, $J = 4.4$ Hz, 1H), 8.11 (d, $J = 9.2$ Hz, 1H), 7.96 (d, $J = 2.0$ Hz, 1H), 7.84 - 7.81 (m, 1H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 4.4$ Hz, 1H), 1.43 (s, 9H), 1.36 (s, 9H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 151.7, 149.5, 149.4, 148.6, 147.4, 135.5, 129.49, 129.45, 128.4, 126.6, 125.7, 121.7, 121.1, 135.3, 35.0, 31.6, 31.4$ ppm. HRMS: Exact mass calculated for C$_{23}$H$_{28}$N ([M+H]$^+$): 318.2216, Found: 318.2206.

2,4-bis(4-bromophenyl)quinoline (5t) and 4-(4-bromophenyl)quinoline (5t’): According to GP I, nitrosobenzene (43 mg, 0.40 mmol), 4-bromo styrene (0.16 g, 0.88 mmol) and Yb(OTf)$_3$ (74 mg, 0.12 mmol) were reacted for 48 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:40) gave 5t as yellow gum (43 mg, 25%) and (silica gel; EtOAc : hexane, 1:10) gave 5t’ as yellow gum (12 mg, 11%).

Analytical data for 5t: FT-IR = 2958, 2924, 2851, 1596, 1542, 1485, 1355, 1072, 825, 764, 578, 470 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.24$ (d, $J = 8.4$ Hz, 1H), 8.08 (d, $J = 8.8$ Hz, 2H), 7.84 (d, $J = 8.4$ Hz, 1H), 7.78 – 7.74 (m, 2H), 7.71 – 7.65 (m, 4H), 7.51 (t, $J = 8.0$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 155.7, 148.8, 148.6, 138.3, 137.2, 132.3, 132.1, 131.3, 130.2, 129.4, 127.1, 125.7, 125.5, 124.4, 123.2, 119.0$ ppm. Total count of $^{13}$C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for C$_{21}$H$_{14}$Br$_2$N ([M+H]$^+$): 437.9488, Found: 437.9484.

Analytical data for 5t’: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.96$ (s, 1H), 8.28 (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.79 (t, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.58 – 7.54 (m, 1H), 7.41 – 7.38 (m, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 149.0, 148.8, 136.7, 132.2, 131.3, 130.4, 129.2, 127.6, 125.9, 123.5, 121.4$ ppm. Total count of $^{13}$C is less than expected due to the merging of signals in the aromatic region.
4,4'-(quinoline-2,4-diyl)dibenzonitrile (5u): According to GP II, nitrosobenzene (43 mg, 0.40 mmol), 4-cyano styrene (0.11 g, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 5 days in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 5u as yellow gum (13 mg, 10%). Analytical data for 5u: FT-IR = 2960, 2930, 2852, 2228, 1595, 1499, 1451, 1278, 1188, 1076, 844, 747, 699 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.35 – 8.32 (m, 3H), 7.89 – 7.78 (m, 7H), 7.69 (d, J = 8.4 Hz, 2H), 7.61 – 7.57 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 154.6, 148.4, 142.7, 132.9, 132.8, 131.0, 130.5, 130.4, 128.5, 128.2, 119.1, 118.8, 118.5, 113.5, 113.1 ppm. Total count of ¹³C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for C₂₃H₁₄N₃ ([M+H]+): 332.1182, Found: 332.1177.

4,4'-(propane-1,3-diylbis(oxy))dibenzaldehyde: 4-hydroxy benzaldehyde (1.47 g, 12.05 mmol) was added to the solution of 1,3-dibromopropoape (1.0 g, 5.00 mmol) in DMF (5 mL) followed by the addition of K₂CO₃ (2.08 g, 15.07 mmol). The reaction mixture was heated at 100 °C for 12 h. After that, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with cold water (70 mL) and extracted with DCM (3 X 50 mL). The organic layer was washed with brine solution (1 X 50 mL), dried over anhydrous Na₂SO₄ and evaporated under vaccum to provide 4,4'-(propane-1,3-diylbis(oxy))dibenzaldehyde as a light yellow solid (1.28 g, 90%) which was used for the next step. ¹H NMR (600 MHz, CDCl₃) δ = 9.87 (s, 2H), 7.82 (d, J = 8.4 Hz, 4H), 7.01 (d, J = 9.0 Hz, 4H), 4.25 (t, J = 6.0 Hz, 4H), 2.36 - 2.32 (m, 2H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 191.0, 163.9, 132.2, 130.2, 114.9, 64.7, 29.1 ppm.

1,3-bis(4-vinylphenoxy)propane (6): Methyltriphenylphosphonium iodide (2.19 g, 5.41 mmol) and sodium hydride (60% in mineral oil) (0.81 g (0.49 g), 20.29 mmol) were taken in 100 mL R.B. under argon. A solution of 4,4'-(propane-1,3-diylbis(oxy))dibenzaldehyde (1.28 g, 4.51 mmol) in dry THF (20 mL) was added slowly to the mixture at 0 °C. Then the reaction mixture was stirred at room temperature for 12 h. Then the reaction was quenched with cold water (50 mL) and the mixture was extracted with DCM (3 X 50 mL). The organic layer was washed with
brine solution (1X50 mL), dried over anhydrous Na₂SO₄ and evaporated under vaccum. The column chromatography of the crude product (silica gel; EtOAc : hexane, 1:50) gave 6 as white solid (0.33 g, 26%). FT-IR: $\tilde{\nu}$ = 2955, 2922, 2853, 1603, 1509, 1468, 1378, 1289, 1242, 1176, 1065, 992, 903, 836 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ = 7.34 (d, $J$ = 8.4 Hz, 4H), 6.87 (d, $J$ = 9.0 Hz, 4H), 6.69 - 6.64 (m, 2H), 5.61 (d, $J$ = 17.4 Hz, 2H), 5.13 (d, $J$ = 10.8 Hz, 2H), 4.17 (t, $J$ = 6.0 Hz, 4H), 2.29 - 2.25 (m, 2H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 158.8, 136.4, 130.7, 127.6, 114.7, 111.8, 64.6, 29.5 ppm.

2,4-bis(4-(3-(4-vinylphenoxy)propoxy)phenyl)quinoline (7a) and 4-(4-(3-(4-vinylphenoxy)propoxy)phenyl)quinoline (7b):

Nitrosobenzene (43 mg, 0.40 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were successively added to a solution of styrene derivative 6 (0.25 g, 0.88 mmol) in dry DCE (3 mL). Then the reaction mixture was refluxed for 36 h under argon atmosphere. Then the solvent was evaporated under reduced pressure. The reaction mixture was diluted with water (20 mL) and the mixture was extracted with DCM (3 X 20 mL). The combined organic layer was washed with brine solution (1 X 30 mL), dried over anhydrous Na₂SO₄ and evaporated under vaccum. Column chromatography of the crude product (silica gel; EtOAc : hexane, 1:10) gave 7a as yellow gum (75 mg, 30%) and (silica gel; EtOAc : hexane, 1:4) gave 7b as yellow gum (34 mg, 22%). Analytical data for 7a: FT-IR: $\tilde{\nu}$ = 2958, 2923, 2879, 2848, 1606, 1544, 1509, 1498, 1401, 1288, 1175, 1059, 833 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.25 (d, $J$ = 8.0 Hz, 1H), 8.16 (d, $J$ = 8.8 Hz, 2H), 7.92 (d, $J$ = 8.0 Hz, 1H), 7.73 - 7.70 (m, 1H), 7.49 (d, $J$ = 8.8 Hz, 2H), 7.47 - 7.43 (m, 1H), 7.37 - 7.34 (m, 4H), 7.10 - 7.05 (m, 4H), 6.91 - 6.88 (m, 4H), 6.70 - 6.62 (m, 2H), 5.64 - 5.59 (m, 2H), 5.15 - 5.11 (m, 2H), 4.29 - 4.18 (m, 8H), 2.37 - 2.28 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 160.6, 159.5, 158.8, 156.3, 136.41, 136.38, 131.0, 130.82, 130.78, 130.7, 130.0, 129.4, 127.6, 126.3, 126.0, 125.9, 119.2, 115.1, 114.9, 114.73, 114.72, 111.9, 111.8, 64.81, 64.80, 64.65, 64.56, 29.52, 29.50 ppm. Total count of ¹³C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for C₄₃H₄₀N⁴O₄ ([M+H]⁺): 634.2952, Found: 634.2945.
Analytical data for 7b: FT-IR: $\tilde{\nu} = 2961, 2905, 2870, 1613, 1583, 1501, 1460, 1363, 1267, 1106, 1021, 838, 750 \text{ cm}^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.92$ (d, $J = 4.8$ Hz, 1H), 8.29 (d, $J = 8.4$ Hz, 1H), 8.01 (d, $J = 8.4$ Hz, 1H), 7.80 - 7.76 (m, 1H), 7.58 - 7.54 (m, 1H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.40 - 7.34 (m, 3H), 7.09 (d, $J = 8.4$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 6.70 - 6.63 (m, 1H), 5.62 (d, $J = 17.6$ Hz, 1H), 5.13 (d, $J = 10.8$ Hz, 1H), 4.29 - 4.20 (m, 4H), 2.36 - 2.30 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 159.8, 158.8, 148.6, 147.2, 136.4, 131.1, 130.8, 130.4, 130.0, 128.8, 128.7, 127.6, 127.3, 127.2, 126.3, 121.4, 115.0, 114.7, 111.9, 64.8, 64.5, 29.5$ ppm. HRMS: Exact mass calculated for C$_{26}$H$_{24}$NO$_2$ ([M+H]$^+$): 382.1802, Found: 382.1818.

2-phenylquinoline (7c): According to GP I, nitrosobenzene (43 mg, 0.40 mmol), trans β- methyl styrene (0.10 g, 0.88 mmol) and Yb(OTf)$_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave 7c as yellow gum (18 mg, 22%) $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.23$ (d, $J = 8.4$ Hz, 1H), 8.19 – 8.16 (m, 3H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.76 – 7.71 (m 1H), 7.56 – 7.52 (m, 3H), 7.49 – 7.45 (m, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 157.6, 148.5, 139.9, 137.0, 129.94, 129.88, 129.5, 129.1, 127.8, 127.7, 127.4, 126.5, 119.3$ ppm.

General Procedure for the Synthesis of 3-substituted quinolines (II):

Freshly prepared nitrosoarenes (1 equiv.) and Cu(OTf)$_2$ (15 mol%) were successively added to a solution of styrene oxide derivatives (2 equiv.) in dry DCE (3 mL). Then the reaction mixture was refluxed for 20 - 28 h under argon atmosphere. Then the solvent was evaporated under reduced pressure. The reaction mixture was diluted with water (1X20 mL) and the reaction mixture was extracted with DCM (3X20 mL). The organic layer was washed with brine solution (1X30 mL) and evaporated under vaccum. The crude mixture was subjected to column chromatography (silica gel) to afford analytically pure products.
3-phenylquinoline (9a): According to GP II, nitrosobenzene (35 mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9a as yellow gum (42 mg, 62%). ¹H NMR (400 MHz, CDCl₃) δ = 9.19 (d, J = 2.4 Hz, 1H), 8.32 (d, J = 2.0 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.89 - 7.71 (m, 3H), 7.61 - 7.57 (m, 1H), 7.55 - 7.51 (m, 2H), 7.46 - 7.43 (m, 1H) ppm. HRMS: Exact mass calculated for C₁₅H₁₂N ([M+H]⁺): 206.0964, Found: 206.0974.

3-(m-tolyl)quinoline (9b): According to GP II, nitrosobenzene (35 mg, 0.33 mmol), 3-methylstyrene oxide (88 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 20 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9b as yellow gum (39 mg, 54%). ¹H NMR (400 MHz, CDCl₃) δ = 9.19 (d, J = 2.0 Hz, 1H), 8.37 (d, J = 2.0 Hz, 1H), 8.21 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.63 - 7.60 (m, 1H), 7.53 - 7.51 (m, 2H), 7.45 - 7.41 (m, 1H), 7.28 (s, 1H), 2.48 (s, 3H) ppm. HRMS: Exact mass calculated for C₁₆H₁₄N ([M+H]⁺): 220.1121, Found: 220.1114.

3-(p-tolyl)quinoline (9c): According to GP II, nitrosobenzene (35 mg, 0.33 mmol), 4-methylstyrene oxide (88 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 20 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9c as yellow gum (49 mg, 68%). ¹H NMR (400 MHz, CDCl₃) δ = 9.19 (d, J = 1.2 Hz, 1H), 8.36 (d, J = 1.6 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.77 - 7.73 (m, 1H), 7.63 - 7.59 (m, 3H), 7.35 (d, J = 7.6 Hz, 2H), 2.45 (s, 3H) ppm. HRMS: Exact mass calculated for C₁₆H₁₄N ([M+H]⁺): 220.1121, Found: 220.1122.

3-(4-chlorophenyl)quinoline (9d): According to GP II, nitrosobenzene (35 mg, 0.33 mmol), 4-chlorostyrene oxide (0.10 g, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 20 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9d as yellow gum (44 mg, 56%). ¹H NMR (400 MHz, CDCl₃) δ = 9.15 (d, J = 2.0 Hz, 1H), 8.33 (d, J = 2.0 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz,
3-(4-fluorophenyl)quinoline (9e): According to GP II, nitrosobenzene (35 mg, 0.33 mmol), 4-fluorostyrene oxide (91 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 15 mol %, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9e as yellow gum (45 mg, 61%). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta = 9.16 (d, J = 2.0 \text{ Hz}, 1\text{H}), 8.36 (s, 1\text{H}), 8.25 (d, J = 8.4 \text{ Hz}, 1\text{H}), 7.92 (d, J = 8.0 \text{ Hz}, 1\text{H}), 7.80 - 7.76 (m, 1\text{H}), 7.70 - 7.62 (m, 3\text{H}), 7.24 - 7.22 (m, 2\text{H}) \text{ ppm. HRMS: Exact mass calculated for C}_{15}H_{11}NF ([M+H]^+) : 224.0870, Found: 224.0869.

6-methyl-3-phenylquinoline (9f): According to GP II, 1-methyl-4-nitrosobenzene (40 mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9f as yellow gum (45 mg, 62%). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta = 9.12 (d, J = 2.0 \text{ Hz}, 1\text{H}), 8.32 (d, J = 2.0 \text{ Hz}, 1\text{H}), 8.12 (d, J = 8.4 \text{ Hz}, 1\text{H}), 7.72 - 7.68 (m, 3\text{H}), 7.61 - 7.58 (m, 1\text{H}), 7.56 - 7.52 (m, 2\text{H}), 7.47 - 7.43 (m, 1\text{H}), 2.58 (s, 3\text{H}) \text{ ppm. HRMS: Exact mass calculated for C}_{16}H_{14}N ([M+H]^+) : 220.1121, Found: 220.1124.

6-ethyl-3-phenylquinoline (9g): According to GP II, 1-ethyl-4-nitrosobenzene (45 mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 20 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9g as yellow gum (42 mg, 55%). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta = 9.13 (d, J = 2.0 \text{ Hz}, 1\text{H}), 8.32 (d, J = 2.0 \text{ Hz}, 1\text{H}), 8.14 (d, J = 8.4 \text{ Hz}, 1\text{H}), 7.73 - 7.69 (m, 3\text{H}), 7.64 - 7.61 (m, 1\text{H}), 7.55 - 7.52 (m, 2\text{H}), 7.47 - 7.43 (m, 1\text{H}), 2.88 (q, J = 7.6 \text{ Hz}, 2\text{H}), 1.36 (t, J = 7.6 \text{ Hz}, 3\text{H}) \text{ ppm. HRMS: Exact mass calculated for C}_{17}H_{16}N ([M+H]^+) : 234.1277, Found: 234.1280.
6-isopropyl-3-phenylquinoline (9h): According to GP II, 1-isopropyl-4-nitrosobenzene (49 mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9h as yellow gum (55 mg, 67%). ¹H NMR (400 MHz, CDCl₃) δ = 9.12 (d, J = 2.0 Hz, 1H), 8.27 (d, J = 2.4 Hz, 1H), 7.72 - 7.71 (m, 2H), 7.68 (s, 1H), 7.65 - 7.63 (m, 1H), 7.55 - 7.51 (m, 2H), 7.45 - 7.42 (m, 1H), 3.16 - 3.09 (m, 1H), 1.37 (d, J = 6.8 Hz, 6H) ppm. HRMS: Exact mass calculated for C₁₈H₁₈N ([M+H]+): 248.1434, Found: 248.1429.

3-phenyl-6-propylquinoline (9i): According to GP II, 1-nitroso-4-propylbenzene (49 mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 22 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9i as yellow gum (57 mg, 70%). FT-IR: ν = 2959, 2929, 2871, 1600, 1494, 1455, 1349, 1260, 1026, 800, 627 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ = 9.13 (d, J = 1.8 Hz, 1H), 8.33 (d, J = 1.2 Hz, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.68 (s, 1H), 7.62 - 7.61 (m, 1H), 7.55 - 7.53 (m, 2H), 7.47 - 7.44 (m, 1H), 2.81 (t, J = 7.8 Hz, 2H), 1.79 - 1.75 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 148.1, 144.9, 142.5, 137.7, 134.21, 134.15, 132.0, 129.5, 128.5, 128.4, 128.1, 127.6, 126.6, 38.2, 24.5, 14.0 ppm. HRMS: Exact mass calculated for C₁₈H₁₈N ([M+H]+): 248.1434, Found: 248.1433.

5,7-dimethyl-3-phenylquinoline (9j): According to GP II, 1,3-dimethyl-5-nitrosobenzene (45 mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 28 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9j as yellow gum (45 mg, 58%). ¹H NMR (400 MHz, CDCl₃) δ = 9.13 (d, J = 2.4 Hz, 1H), 8.44 (d, J = 2.0 Hz, 1H), 7.82 (s, 1H), 7.73 - 7.71 (m, 2H), 7.56 - 7.52 (m, 2H), 7.46 - 7.42 (m, 1H), 7.28 (s, 1H), 2.72 (s, 3H), 2.55 (s, 3H) ppm. HRMS: Exact mass calculated for C₁₇H₁₆N ([M+H]+): 234.1277, Found: 234.1280.
6-(tert-butyl)-3-phenylquinoline (9k): According to GP II, 1-(tert-butyl)-4-nitrosobenzene (54 mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)$_2$ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9k as yellow gum (56 mg, 65%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 9.13 (s, 1H), 8.35 (d, $J$ = 1.6 Hz, 1H), 8.15 (d, $J$ = 8.8 Hz, 1H), 7.86 - 7.83 (m, 2H), 7.73 - 7.71 (m, 2H), 7.55 - 7.52 (m, 2H), 7.47 - 7.43 (m, 1H), 1.45 (s, 9H) ppm. HRMS: Exact mass calculated for C$_{19}$H$_{20}$N ([M+H]$^+$): 262.1590, Found: 262.1593.

6-chloro-3-phenylquinoline (9l): According to GP II, 1-chloro-4-nitrosobenzene (47 mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)$_2$ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9l as yellow gum (29 mg, 37%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 9.17 (d, $J$ = 2.0 Hz, 1H), 8.23 (d, $J$ = 2.0 Hz, 1H), 8.10 (d, $J$ = 9.2 Hz, 1H), 7.87 (d, $J$ = 2.4 Hz, 1H), 7.71 - 7.65 (m, 3H), 7.56 - 7.52 (m, 2H), 7.48 - 7.44 (m, 1H) ppm. HRMS: Exact mass calculated for C$_{15}$H$_{11}$NCl ([M+H]$^+$): 240.0575, Found: 240.0574.

7-ethyl-3-phenylquinoline (9m): According to GP II, 1-ethyl-3-nitrosobenzene (45 mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)$_2$ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9m as yellow gum (41 mg, 53%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 9.15 (d, $J$ = 2.4 Hz, 1H), 8.35 (d, $J$ = 2.0 Hz, 1H), 8.02 (s, 1H), 7.84 (d, $J$ = 8.4 Hz, 1H), 7.72 - 7.70 (m, 2H), 7.55 - 7.43 (m, 4H), 2.90 (q, $J$ = 7.6 Hz, 2H), 1.37 (t, $J$ = 7.6 Hz, 3H) ppm. HRMS: Exact mass calculated for C$_{17}$H$_{16}$N ([M+H]$^+$): 234.1277, Found: 234.1279.

6-ethyl-3-(p-tolyl)quinoline (9n): According to GP II, 1-ethyl-4-nitrosobenzene (45 mg, 0.33 mmol), 4-methyl styrene oxide (88 mg, 0.66 mmol) and Cu(OTf)$_2$ (18 mg, 0.05 mmol) were reacted for 20 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9n as yellow gum (52 mg, 64%). FT-IR: $\tilde{\nu}$ = 2964, 2927, 2871, 1604, 1516, 1455, 1374, 1261, 1040, 914, 834, 724 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 9.11 (d, $J$ = 2.0 Hz, 1H), 8.29 (d,
$J = 2.0$ Hz, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 7.67 (s, 1H), 7.63 - 7.60 (m, 3H), 7.34 (d, $J = 8.0$ Hz, 2H), 2.87 (q, $J = 7.6$ Hz, 2H), 2.44 (s, 3H), 1.36 (t, $J = 7.6$ Hz, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 148.1, 144.8, 143.9, 138.5, 134.8, 134.1, 133.8, 131.5, 130.2, 128.6, 128.2, 127.4, 125.7, 29.1, 21.4, 15.5$ ppm. HRMS: Exact mass calculated for C$_{18}$H$_{18}$N ([M+H]$^+$): 248.1434, Found: 248.1435.

6-isopropyl-3-(p-tolyl)quinoline (9o): According to GP II, 1-isopropyl-4-nitrosobenzene (49 mg, 0.33 mmol), 4-methyl styrene oxide (88 mg, 0.66 mmol) and Cu(OTf)$_2$ (18 mg, 0.05 mmol) were reacted for 2 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9o as yellow gum (57 mg, 66%). FT-IR: $\tilde{\nu} = 2960, 2927, 2872, 1607, 1516, 1256, 1128, 817, 748$ cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.12$ (d, $J = 2.4$ Hz, 1H), 8.36 (d, $J = 8.4$ Hz, 1H), 7.71 - 7.67 (m, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 7.6$ Hz, 2H), 3.17 - 3.10 (m, 1H), 2.44 (s, 3H), 1.37 (d, $J = 6.8$ Hz, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 148.9, 147.4, 144.0, 138.8, 134.7, 134.4, 134.2, 130.7, 130.3, 128.7, 127.6, 127.4, 124.3, 34.4, 24.0, 21.4$ ppm. HRMS: Exact mass calculated for C$_{19}$H$_{20}$N ([M+H]$^+$): 262.1592, Found: 262.1592.

3-butylquinoline (9p): According to GP II, nitrosobenzene (43 mg, 0.4 mmol), 1,2-epoxyhexane (80 mg, 0.8 mmol) and Cu(OTf)$_2$ (22 mg, 0.06 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (neutral alumina; EtOAc : hexane, 1:30) gave 9p as yellow gum (8 mg, 11%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.78$ (d, $J = 2.0$ Hz, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 7.95 (s, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.67 (t, $J = 8.0$ Hz, 1H), 7.53 (t, $J = 8.0$ Hz, 1H), 2.83 - 2.67 (m, 2H), 1.77 - 1.67 (m, 2H), 1.44 - 1.38 (m, 2H), 1.00 - 0.94 (m, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 151.8, 146.4, 135.7, 134.9, 129.0, 128.9, 128.5, 127.5, 126.9, 33.4, 33.1, 22.5, 14.1$ ppm.

General Procedure for preparation of nitrone 10 and its reaction with 2-phenylacetaldehyde or styrene oxide (GP III): Formalin (37%, 1 eq) solution was added to a mixture of nitrobenzene derivatives (1 eq), ethanol, water and NH$_4$Cl (1 eq). After the mixture was stirred 15 min, Zn powder (2 eq) was added under 0 °C. The reaction mixture was stirred overnight at room temperature. Then the solid was filtered, the filtrate was extracted with DCM (3X30 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The crude product was
dissolved in DCE. 2-phenylacetaldehyde (1 eq) or styrene epoxide (1 eq) and Cu(OTf)_2 (15 mol%) were added and the mixture was refluxed for 24 h. Then the solvent was evaporated under reduced pressure. The reaction mixture was diluted with water and the reaction mixture was extracted with DCM. The organic layer was washed with brine solution and evaporated under vacuum. The crude mixture was subjected to column chromatography (silica gel) to afford analytically pure products.

3-phenylquinoline (9a): According to the GP III: 37% aq. Formalin (0.11 g (40 mg), 1.35 mmol), nitrobenzene (0.17 g, 1.35 mmol), ethanol (5 mL), water (5 mL) and NH_4Cl (72 mg, 1.35 mmol), Zn powder (0.18 g, 2.70 mmol), 2-phenylacetaldehyde (0.16 g, 1.35 mmol) and Cu(OTf)_2 (73 mg, 0.20 mmol) were reacted for 24 h in dry DCE (5 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9a as yellow gum (0.14 g, 52%) and styrene oxide (0.16 g, 1.35 mmol) and Cu(OTf)_2 (73 mg, 0.20 mmol) were reacted for 24 h in dry DCE (5 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9a as yellow gum (0.20 g, 73%).

8-methyl-3-phenylquinoline (9q): According to the GP III: 37% aq. Formalin (0.11 g (40 mg), 1.35 mmol), 1-methyl-2-nitrobenzene (0.19 g, 1.35 mmol), ethanol (5 mL), water (5 mL) and NH_4Cl (72 mg, 1.35 mmol), Zn powder (0.18 g, 2.70 mmol), 2-phenylacetaldehyde (0.16 g, 1.35 mmol) and Cu(OTf)_2 (73 mg, 0.20 mmol) were reacted for 24 h in dry DCE (5 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave 9q as yellow gum (92 mg, 31%). Analytical data for 9q: ^1^H NMR (400 MHz, CDCl_3) δ = 9.25 (s, 1H), 8.34 (d, J = 2.0 Hz, 1H), 7.77 – 7.72 (m, 3H), 7.61 – 7.52 (m, 3H), 7.50 – 7.43 (m, 2H), 2.88 (s, 3H) ppm. HRMS: Exact mass calculated for C_{16}H_{14}N ([M+H]^+): 220.1121, Found: 220.1135.

2,6-diphenyl-3,6-dihydro-2H-1,2-oxazine: According to GP I, nitrosobenzene (43 mg, 0.4 mmol), phenylbutadiene (0.11 g, 0.88 mmol) and Yb(OTf)_3 (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave oxazine as yellow gum (29 mg, 31%). ^1^H NMR (400 MHz, CDCl_3) δ = 7.40 – 7.38 (m, 2H), 7.32 – 7.25 (m, 3H), 7.22 – 7.18 (m, 2H), 7.04 – 7.02 (m, 2H), 6.89 (t, J = 7.2 Hz, 1H), 6.08 – 5.99 (m, 2H), 5.55 – 5.54 (m, 1H), 3.93 – 3.79 (m, 2H)
ppm. $^{13}\text{C}$ NMR (101 MHz, CDCl$_3$) $\delta$ = 150.5, 139.1, 129.2, 129.0, 128.7, 128.6, 128.4, 124.0, 122.4, 116.0, 80.1, 51.8 ppm.

References:


(c) V. Fasano, J. E. Radcliffe and M. J. Ingleson, Organometallics, 2017, 36, 1623.


The image shows a chemical structure labeled as 5c, with an associated NMR spectrum. The spectrum indicates various chemical shifts in parts per million (ppm), ranging from 0.5 to 10.0 ppm, and specific peaks at different chemical shifts.