Supporting Information

Cascade intramolecular imidoylation and C–H activation/annulation
of benzimidoyl chlorides with alkynes: one-pot synthesis of 7H-
dibenzo[de,h]quinoline analogues

Jiao Liu, Hao Fang, Rui Cheng, Zhishuo Wang, Yudong Yang,* Jingsong You*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of
Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064, P.R. China

E-mail: yangyudong@scu.edu.cn; jsyou@scu.edu.cn
# Table of Contents

I. General remarks ............................................................................................................. S1
II. List of substrates ............................................................................................................. S1
III. General procedure for the synthesis of substrates ............................................................ S2
IV. Optimization of the cascade cyclization of N-hydroxy-2-phenoxybenzimidoyl chloride with 1,2-diphenylethylene ........................................................ S4
V. Optimization of the cascade cyclization of 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride with 1,2-diphenylethylene .................................................. S6
VI. Optimization of the cascade cyclization of 2-benzyl-N-methoxybenzimidoyl chloride with 1,2-diphenylethylene .............................................................. S7
VII. General procedure for the synthesis of chromeno[2,3,4-ij]isoquinolines and analogues ............................................................................................................................. S8
VIII. Mechanistic study ........................................................................................................ S9
IX. Experimental data for the described substances .............................................................. S12
X. Single crystal X-ray structures of 3b, 3d, 3e, 3f, 5g, 5h, 7d ........................................... S36
XI. References .................................................................................................................... S37
XII. Copies of NMR spectra ............................................................................................... S38
I. General remarks

NMR spectra were recorded on an Agilent 400-MR DD2 spectrometer. The $^1$H NMR (400 MHz) chemical shifts were recorded relative to CDCl$_3$ or CD$_2$Cl$_2$ as the internal reference (CDCl$_3$: $\delta =$ 7.26 ppm; CD$_2$Cl$_2$: $\delta =$ 5.32 ppm). The $^{13}$C NMR (100 MHz) chemical shifts were given using CDCl$_3$ or CD$_2$Cl$_2$ as the internal standard (CDCl$_3$: $\delta =$ 77.16 ppm; CD$_2$Cl$_2$: $\delta =$ 54.00 ppm). X-Ray single-crystal diffraction data were obtained on an Agilent Technologies Gemini plus single crystal diffraction. High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI) or a Waters-Q-TOF-Premier (ESI). Melting points were tested with an SGW S-4 and were uncorrected. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. [RhCp*Cl$_2$]$_2$ were prepared according to the literature procedures. The solvents were dried and purified using an Innovative Technology PS-MD-5 Solvent Purification System. RhCl$_3$$ \cdot $xH$_2$O was purchased from Shanxi Kaida Chemical Engineering (China) CO. Ltd.

II. List of substrates

1. List of N-hydroxy-2-phenoxybenzimidoyl chloride derivatives 1

2. List of alkynes 2
III. General procedure for the synthesis of substrates

1. General procedure for the synthesis of N-hydroxy-2-phenoxybenzimidoyl chlorides 1

N-hydroxy-2-phenoxybenzimidoyl chloride 1a, 1b, 1c, 1d and 1e were prepared according to the literature procedures.\(^2\)

General procedure for the synthesis of N-acetoxy-2-phenoxybenzimidoyl chloride 1f.\(^3\)

\[
\begin{align*}
\text{Acetyl chloride} & \quad \text{rt, 2 h} \\
1a & \quad 1f
\end{align*}
\]

The N-hydroxy-2-phenoxybenzimidoyl chloride 1a (2 mol, 494 mg) was stirred at room temperature with an excess of acetyl chloride (2 ml) for 2 h. The excess of acetylating agent was removed under reduced pressure to afford yellow oil 1f.

General procedure for the synthesis of N-methoxy-2-phenoxybenzimidoyl chloride 1g.:\(^2\)

\[
\begin{align*}
\text{MeO} & \quad \text{OH} \\
& \quad \text{K}_2\text{CO}_3, \text{DMF}, 160 ^\circ \text{C} \\
& \quad 1g
\end{align*}
\]

A mixture of 2-fluoro-N-methoxybenzimidoyl chloride (40.3 mmol, 374 mg), phenol (2.2 mmol, 207 mg) and K\(_2\)CO\(_3\) (2.5 mmol 346) in DMF (2 mL) was refluxed for 13 h. The mixture was cooled to room temperature and diluted with EA and quenched by the addition of water. The organic layer was washed with water, dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The crude residue was purified through a silica gel column (petroleum ether/ethyl acetate = 100:1, v/v) to give N-methoxy-2-phenoxybenzimidoyl chloride 1g.

2. General procedure for the synthesis of Alkynes 2

Alkynes 2a, 2f, 2g and 2o were obtained from commercial suppliers and used without further purification. Alkynes 2h, 2i, 2j, 2k, 2l, 2m, 2n, 2p, 2q and 2r were prepared according to the literature procedures.\(^4,5\)

3. General procedure for the synthesis of 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)
benzimidoyl chloride derivatives 4

\[
\begin{align*}
\text{MeONH}_2\text{HCl} & \quad \text{K}_2\text{CO}_3 \\
\text{K}_2\text{CO}_3 & \quad \text{PCl}_5 \\
\text{NH}_3\text{Li, THF} & \quad \text{PCl}_5
\end{align*}
\]

In a 250 mL round-bottom flask with a magnetic stir bar, a solution of O-methylhydroxylamine hydrochloride (2.00 g, 24.0 mmol, 1.2 equiv) and K₂CO₃ (5.98 g, 48.0 mmol, 2.4 equiv) in water (40 mL) was added to a solution of 2,6-difluorobenzoyl chloride (2.5 mL, 20.0 mmol, 1.0 equiv) in ethyl acetate (80 mL) drop by drop at 0 °C. Then the reaction mixture was stirred at room temperature for 8 h. After the completion of reaction, the organic layer was separated and washed with water (60 mL×2) and brine (60 mL). Then the organic phase was dried over Na₂SO₄, filtered, and concentrated in vacuo. The resulting crude was recrystallized in a mixture of ethyl acetate and petroleum ether to get a white solid.

The white solid was transferred into a round-bottom flask under an N₂ atmosphere. Then dry toluene (60 mL) was added. The mixture was cooled to 0 °C and PCl₅ (6.25 g, 30.0 mmol, 1.5 equiv) was added. The reaction mixture was stirred at room temperature overnight. Then the mixture was cooled to 0 °C and stirred in a mixture of water (60 mL) and ethyl acetate (60 mL) for 10 minutes. The separated organic layer was sequentially washed with water (60 mL×2) and brine (60 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude residue was purified through a silica gel column (petroleum ether/ethyl acetate = 100:1, v/v) to give 2,6-difluoro-N-methoxybenzimidoyl chloride.

A 100 mL Schlenk tube was evacuated and back filled with argon, N-alkylanilines (5.0 mmol, 1 equiv), 2,6-difluoro-N-methoxybenzimidoyl chloride (1.13 g, 5.5 mmol, 1.1 equiv), lithium amide (0.25 g, 11 mmol, 2.2 equiv) and THF (20 mL) were added successively at 0 °C. The reaction mixture was heated at 50 °C for 8 h and then cooled to room temperature. The reaction was quenched with saturated ammonium chloride solution (25 mL). Then the water phase was extracted with ethyl acetate (2 × 30 mL). The combined organic layer was washed with water (30 mL×2), brine (30 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude residue was purified through a silica gel column (petroleum ether/ethyl acetate = 100:1, v/v) to give 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride derivatives 4.

4. General procedure for the synthesis of 2-benzyl-N-methoxybenzimidoyl chloride 6

S3
In a 250 mL round-bottom flask with a magnetic stir bar, a solution of O-methylhydroxylamine hydrochloride (498 mg, 6.0 mmol, 1.2 equiv) and K$_2$CO$_3$ (1.66 g, 12 mmol, 2.4 equiv) in water (10 mL) was added to a solution of 2-benzylbenzoyl chloride (1.27 g, 5.0 mmol, 1.0 equiv) in ethyl acetate (20 ml) dropwise at 0 °C. Then the reaction mixture was stirred at room temperature for 8 h. After the completion of reaction, the organic layer was separated and washed with water (15 mL×2) and brine (15 mL). Then the organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The resulting crude was recrystallized in a mixture of ethyl acetate and petroleum ether to afford 2-benzyl-N-methoxybenzamide as a white solid.

The white solid was transferred into a round-bottom flask under an N$_2$ atmosphere. Then dry toluene (15 mL) was added. The mixture was cooled to 0 °C and PCl$_5$ (1.54 g, 7.5 mmol, 1.5 equiv) was added. The reaction mixture was stirred at room temperature overnight. Then the mixture was cooled to 0 °C and stirred in a mixture of water (15 mL) and ethyl acetate (15 mL) for 10 minutes. The separated organic layer was sequentially washed with water (15 mL×2) and brine (15 mL), dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude residue was purified through a silica gel column (petroleum ether/ethyl acetate = 100:1, v/v) to give 2-benzyl-N-methoxybenzimidoyl chloride 6.

IV. Optimization of the cascade cyclization of N-hydroxy-2-phenoxybenzimidoyl chloride with 1,2-diphenylethyne

A 25 mL Schlenk tube with a magnetic stir bar was charged with [RhCp*Cl$_2$]$_2$ (3.1 mg, 5 µmol, 5 mol %), AgSbF$_6$ (7.2 mg, 20 µmol, 20 mol %), additives, N-hydroxy-2-phenoxybenzimidoyl chloride 1a (0.15 mol, 37.1 mg), 1,2-diphenylethyne 2a (0.1 mol, 17.8 mg) and DCE (2.0 mL) under an N$_2$ atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the indicated temperature for 24 h. Subsequently, it was diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 50 mL of dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on aluminum oxide to provide the desired product 3a.

Table S1. Optimization of the reaction conditions for the cascade cyclization of N-hydroxy-2-phenoxybenzimidoyl chloride with 1,2-diphenylethyne
<table>
<thead>
<tr>
<th>Entry</th>
<th>1a : 2a</th>
<th>Additives (equiv)</th>
<th>Temp (°C)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 : 1.5</td>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O (1), PivOH (2)</td>
<td>140</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>1 : 1.5</td>
<td>Zn(OTf)&lt;sub&gt;2&lt;/sub&gt; (1), PivOH (2)</td>
<td>140</td>
<td>&lt;10</td>
</tr>
<tr>
<td>3</td>
<td>1 : 1.5</td>
<td>Mn(OAc)&lt;sub&gt;2&lt;/sub&gt; (1), PivOH (2)</td>
<td>140</td>
<td>&lt;10</td>
</tr>
<tr>
<td>4</td>
<td>1 : 1.5</td>
<td>Ni(OAc)&lt;sub&gt;2&lt;/sub&gt;·4H&lt;sub&gt;2&lt;/sub&gt;O (1), PivOH (2)</td>
<td>140</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>1 : 1.5</td>
<td>Mg(OAc)&lt;sub&gt;2&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O (1), PivOH (2)</td>
<td>140</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>1 : 1.5</td>
<td>LiOAc (1), PivOH (2)</td>
<td>140</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>1 : 1.5</td>
<td>CsOAc (1), PivOH (2)</td>
<td>140</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>1 : 1.5</td>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt; (1), PivOH (2)</td>
<td>120</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>1 : 1.5</td>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt; (1), PivOH (2)</td>
<td>100</td>
<td>38</td>
</tr>
<tr>
<td>10</td>
<td>1 : 1.5</td>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O (1), PivOH (2)</td>
<td>80</td>
<td>21</td>
</tr>
<tr>
<td>11</td>
<td>1 : 1.5</td>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt; (1)</td>
<td>120</td>
<td>67</td>
</tr>
<tr>
<td>12</td>
<td>1 : 1</td>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt; (1)</td>
<td>120</td>
<td>57</td>
</tr>
<tr>
<td>13</td>
<td>1.5 : 1</td>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt; (1)</td>
<td>120</td>
<td>87</td>
</tr>
<tr>
<td>14&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.5 : 1</td>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt; (1)</td>
<td>120</td>
<td>N.D.</td>
</tr>
<tr>
<td>15&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.5 : 1</td>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt; (1)</td>
<td>120</td>
<td>N.D.</td>
</tr>
<tr>
<td>16</td>
<td>1.5 : 1</td>
<td>--</td>
<td>120</td>
<td>N.D.</td>
</tr>
<tr>
<td>17&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1.5 : 1</td>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt; (1)</td>
<td>120</td>
<td>trace</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 1a, 2a, [RhCp*Cl<sub>2</sub>]<sub>2</sub> (5 mol %), AgSbF<sub>6</sub> (20 mol %), additives and DCE at indicated temperature under N<sub>2</sub> for 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>Without AgSbF<sub>6</sub>. <sup>d</sup>Without [RhCp*Cl<sub>2</sub>]. <sup>e</sup> [Cp*Co(CO)<sub>2</sub>]<sub>2</sub> (5 mol %) was used. DCE = 1,2-dichloroethane, Cp* = C<sub>5</sub>Me<sub>5</sub>, N.D.: not detected.
V. Optimization of the cascade cyclization of 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride with 1,2-diphenylethyne

A 25 mL Schlenk tube with a magnetic stir bar was charged with [RhCp*Cl₂]₂ (3.1 mg, 10 µmol, 5 mol %), AgSbF₆ (17.9 mg, 50.0 µmol, 50 mol %), additives 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a (29.2 mg, 0.1 mmol), 1,2-diphenylethyne 2a (26.7 mg, 0.15 mmol), and DCE (2.0 mL) under an N₂ atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the indicated temperature for 24 h. Subsequently, it was diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 50 mL of dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on aluminum oxide to provide the desired product 5a.

Table S2. Optimization of the reaction conditions for the cascade cyclization of 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride with 1,2-diphenylethyne

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additives (equiv)</th>
<th>Temp °C</th>
<th>Yield (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PivOH (1), Cu(OAc)₂ (2), NaSbF₆ (2)</td>
<td>80</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>PivOH (5), Cu(OAc)₂ (2), NaSbF₆ (2)</td>
<td>80</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>PivOH (5), Cu(OAc)₂ (2), NaBF₄ (2)</td>
<td>80</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>PivOH (1), Cu(OAc)₂ (2)</td>
<td>80</td>
<td>69</td>
</tr>
<tr>
<td>5</td>
<td>PivOH (5), CuO (2), NaSbF₆ (2)</td>
<td>140</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>PivOH (2.5), CuO (2), NaSbF₆ (1)</td>
<td>140</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>PivOH (2), Zn(OAc)₂·2H₂O (1)</td>
<td>140</td>
<td>87</td>
</tr>
<tr>
<td>8c</td>
<td>PivOH (2), Zn(OAc)₂·2H₂O (1)</td>
<td>140</td>
<td>88</td>
</tr>
<tr>
<td>9c</td>
<td>PivOH (2), Zn(OAc)₂·2H₂O (1)</td>
<td>140</td>
<td>89</td>
</tr>
</tbody>
</table>

aReaction conditions: 4a (0.10 mmol), 2a (0.15 mmol), [RhCp*Cl₂]₂ (5 mol %), AgSbF₆ (50 mol %), additives, and DCE at the indicated temperature under N₂ for 24 h. bIsolated yields. cAgSbF₆ (20
mol %) was used.  

VI. Optimization of the cascade cyclization of 2-benzyl-N-methoxybenzimidoyl chloride with 1,2-diphenylethyne

A 25 mL Schlenk tube with a magnetic stir bar was charged with [RhCp*Cl₂]₂ (3.1 mg, 5 µmol, 5 mol %), AgSbF₆ (7.2 mg, 20 µmol, 20 mol %), additives, 2-benzyl-N-methoxybenzimidoyl chloride 6 (0.15 mmol, 38.9 µg), 1,2-diphenylethyne 2a (0.1 mmol, 17.8 mg) and solvent (2.0 mL) under an indicated atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the indicated temperature for 24 h. After the reaction, it was diluted with 10 mL of dichloromethane. The reaction mixture was filtered through a celite pad and washed with 50 mL of dichloromethane. Then the solution was concentrated and the residue was purified by column chromatography on aluminum oxide to provide the desired product 7a.

Table S3: Optimization of the cascade cyclization of 2-benzyl-N-methoxybenzimidoyl chloride with 1,2-diphenylethyne

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additives</th>
<th>solvent</th>
<th>Temp(℃)</th>
<th>Atmosphere</th>
<th>Yield (%)^[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zn(OAc)₂(1.0), PivOH (2.0)</td>
<td>DCE</td>
<td>140</td>
<td>N₂</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>2</td>
<td>Zn(OAc)₂(1.0)</td>
<td>DCE</td>
<td>140</td>
<td>N₂</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>3</td>
<td>Cu(OAc)₂(2.0), PivOH (2.0)</td>
<td>DCE</td>
<td>140</td>
<td>N₂</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>Cu(OAc)₂(2.0), PivOH (2.0)</td>
<td>TFE</td>
<td>140</td>
<td>N₂</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>Cu(OAc)₂(2.0), PivOH (2.0)</td>
<td>TFE</td>
<td>140</td>
<td>O₂</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>Cu(OAc)₂(5.0), PivOH (2.0)</td>
<td>TFE</td>
<td>140</td>
<td>N₂</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>Cu(OAc)₂(4.0), PivOH (2.0)</td>
<td>TFE</td>
<td>140</td>
<td>N₂</td>
<td>47</td>
</tr>
<tr>
<td>8</td>
<td>Cu(OAc)₂(3.0), PivOH (2.0)</td>
<td>TFE</td>
<td>140</td>
<td>N₂</td>
<td>41</td>
</tr>
<tr>
<td>9</td>
<td>Cu(OAc)₂(3.0), PivOH (2.0)</td>
<td>TFE</td>
<td>140</td>
<td>O₂</td>
<td>78</td>
</tr>
<tr>
<td>10</td>
<td>Cu(OAc)₂(2.0), PivOH (2.0)</td>
<td>TFE</td>
<td>120</td>
<td>O₂</td>
<td>83</td>
</tr>
</tbody>
</table>

^[a]Reaction conditions: 6 (0.15 mmol), 2a (0.10 mmol), [RhCp*Cl₂]₂ (5 mol %), AgSbF₆ (20 mol %), additives, and solvent at the indicated temperature under N₂ or O₂ for 24 h.^[b]Isolated yields. DCE = 1,2-dichloroethane, Cp* = C₅Me₅.
VII. General procedure for the synthesis of chromeno[2,3,4-ij]isoquinolines and analogues

1. General procedure for the synthesis of chromeno[2,3,4-ij]isoquinolines (Procedure I)

A 25 ml Schlenk tube with a magnetic stir bar was charged with [RhCp*Cl₂]₂ (3.1 mg, 5 mol %), AgSbF₆ (7.2 mg, 20 mol %), Zn(OAc)₂ (18.4 mg, 0.1 mmol, 1.0 equiv), 1 (0.15 mmol), alkyne 2 (0.10 mmol), and DCE (2.0 mL) under an N₂ atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 120 °C for 24 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide to provide the desired product 3.

2. General procedure for the synthesis of pyrido[4,3,2-kl]acridine derivatives (Procedure II)

A 25 ml Schlenk tube with a magnetic stir bar was charged with [RhCp*Cl₂]₂ (3.1 mg, 5 mol %), AgSbF₆ (7.2 mg, 20 mol %), Zn(OAc)₂·2H₂O (21.9 mg, 0.1 mmol, 1.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), 4 (0.10 mmol), alkyne 2 (0.15 mmol), and DCE (2.0 mL) under an N₂ atmosphere. The reaction mixture was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide to provide the desired product 5.

3. Procedure for the synthesis of 5a on 1 mmol scale
A 100 ml Schlenk tube with a magnetic stir bar was charged with [RhCp*Cl₂]₂ (31.0 mg, 5 mol %), AgSbF₆ (71.6 mg, 20 mol %), Zn(OAc)₂·2H₂O (219.5 mg, 1.0 mmol, 1.0 equiv), PivOH (204.3 mg, 2 mmol, 2.0 equiv), 4a (1.0 mmol, 291.1 mg), 1,2-diphenylethyne 2a (1.5 mmol, 267.1 mg), and DCE (5.0 mL) under an N₂ atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 20 mL of dichloromethane. The solution was filtered through a celite pad and washed with 50-80 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) to afford 5a as a yellow solid (349.7 mg, 87%).

4. General procedure for the synthesis of 7H-dibenzo[d,e,h]quinolin-7-one derivatives (Procedure III)

A 25 ml Schlenk tube with a magnetic stir bar was charged with [RhCp*Cl₂]₂ (3.1 mg, 5 mol %), AgSbF₆ (7.2 mg, 20 mol %), Cu(OAc)₂ (54.5 mg, 0.3 mmol, 3.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), 6 (0.15 mmol), alkyne 2 (0.10 mmol), and TFE (2.0 mL) under an O₂ atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 120 °C for 24 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide to provide the desired product 7.

VIII. Mechanistic study

1. Control experiments for cascade cyclization of 2-Fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a with 1,2-diphenylethyne 2a
A 25 ml Schlenk tube with a magnetic stir bar was charged with [RhCp*Cl₂]₂ (3.1 mg, 5 mol %), AgSbF₆ (7.2 mg, 20 mol %), Zn(OAc)₂·2H₂O (21.9 mg, 0.1 mmol, 1.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), 4a (0.10 mmol, 29.2 mg) and DCE (2.0 mL) under an N₂ atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) to provide the desired product 8 as a white solid (13.1 mg, 51%).

A 25 ml Schlenk tube with a magnetic stir bar was charged with [RhCp*Cl₂]₂ (3.1 mg, 5 mol %), AgSbF₆ (7.2 mg, 20 mol %), Zn(OAc)₂·2H₂O (21.9 mg, 0.1 mmol, 1.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), 8 (0.10 mmol, 25.6 mg), 1,2-diphenylethyne 2a (0.15 mmol, 26.7 mg) and DCE (2.0 mL) under an N₂ atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) to afford the desired product 1a as a yellow solid (36.9 mg, 92%).

A 25 ml Schlenk tube with a magnetic stir bar was charged with Zn(OAc)₂·2H₂O (21.9 mg, 0.1 mmol, 1.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), 4a (0.10 mmol, 29.2 mg) and DCE (2.0 mL) under an N₂ atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) to provide the desired product 8 as a white solid (15.6 mg, 61%).
A 25 ml Schlenk tube with a magnetic stir bar was charged with \([\text{RhCp}^*\text{Cl}_2]\) (3.1 mg, 5 mol %), AgSbF$_6$ (7.2 mg, 20 mol %), 4a (29.2 mg, 0.10 mmol) and DCE (2.0 mL) under an N$_2$ atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. Trace amounts of the 8a were detected.

2. Control experiments for cascade cyclization of 2-benzyl-N-methoxybenzimidoyl chloride with 1,2-diphenylethyne

A 25 ml Schlenk tube with a magnetic stir bar was charged with \([\text{RhCp}^*\text{Cl}_2]\) (3.1 mg, 5 mol %), AgSbF$_6$ (7.2 mg, 20 mol %), Cu(OAc)$_2$ (54.5 mg, 0.3 mmol, 3.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), 9 (35.6 mg, 0.15 mmol), alkyne 2a (17.8 mg, 0.10 mmol), and TFE (2.0 mL) under an O$_2$ atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 120 °C for 24 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide to provide the desired product 7a (29.5 mg, 77%). Note: Oxime 9 was synthesized by the reaction of anthracene-9,10-dione (208 mg, 1 mmol) with O-methylhydroxylamine hydrochloride (84 mg, 1 mmol) in pyridine (1 mL) at 115 °C for 48 h under air.

3. ESI-HRMS analysis.

A 25 ml Schlenk tube with a magnetic stir bar was charged with \([\text{RhCp}^*\text{Cl}_2]\) (31 mg, 50 mol %), Zn(OAc)$_2$·2H$_2$O (21.9 mg, 0.1 mmol, 1.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), 4a (29.2
mg, 0.10 mmol) and DCE (2.0 mL) under an N₂ atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 120°C for 12 h. The reaction mixture was cooled to ambient temperature. The ESI-HRMS analysis of the resultant solution was then performed immediately ([M⁺] calcd. 493.1157, found 493.1157).

IX. Experimental data for the described substances

1. Experimental data for the described substrates

**Methyl-4-(2-chloro(hydroxyimino)methyl)phenoxy)benzoate (1b)**

White solid, M.p.: 99-102 °C. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 9.06 (brs, 1H), 8.00-7.96 (m, 2H), 7.63 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.47-7.42 (m, 1H), 7.29-7.23 (m, 1H), 7.04 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 6.98-6.93 (m, 2H), 3.88 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 166.8, 161.5, 153.3, 135.9, 132.1, 131.8, 131.3, 126.3, 124.9, 121.3, 117.4, 52.3. HRMS (ESI⁺): calcd for C₁₅H₁₂Cl₂NO₄ [M⁺35Cl]⁻ 340.0149, found 340.0144.

**2-(4-Bromophenoxy)-N-hydroxybenzimidoyl chloride (1c)**

White solid, M.p.: 80-83°C. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.63 (brs, 1H), 7.60 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.45-7.38 (m, 3H), 7.23-7.17 (m, 1H), 6.94 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 6.90-6.85 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 156.3, 154.4, 136.5, 132.9, 132.0, 131.2, 125.5, 124.1, 120.5, 119.9, 116.2. HRMS (ESI⁺): calcd for C₁₃H₉Br₅Cl₂NO₂ [M⁺35Cl]⁻ 359.9199, found 359.9193; calcd for C₁₃H₉Br₅Cl₂NO₂ [M⁺35Cl]⁻ 361.9179, found 361.9169.
**N-Hydroxy-2-(p-tolyloxy)benzimidoyl chloride (1d)**

White solid, M.p.: 75-78 °C. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 9.05 (brs, 1H), 7.58 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.38-7.31 (m, 1H), 7.16-7.10 (m, 3H), 6.95-6.90 (m, 2H), 6.89 (d, J = 8.4 Hz, J = 1.2 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.7, 154.4, 136.8, 133.5, 131.8, 131.0, 130.4, 124.7, 123.0, 119.3, 118.9, 20.9. HRMS (ESI⁺): calcd for C₁₄H₁₂Cl₂NO₂ [M+35Cl]⁺ 296.0251, found 296.0241.

**N-Hydroxy-2-(4-methoxyphenoxy)benzimidoyl chloride (1e)**

White solid (ratio of oxime isomers = 1:1), M.p.: 90-93 °C. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 9.12 (brs, 1H for one isomer), 9.10 (s, 1H for one isomer), 7.60-7.55 (m, 2H for two isomers), 7.39-7.30 (m, 2H for two isomers), 7.18-6.93 (m, 6H for two isomers), 6.92-6.80 (m, 6H for two isomers), 3.88 (s, 3H for one isomer), 3.80 (s, 3H for one isomer). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) for two isomers, 156.3, 156.2, 155.5, 151.8, 150.0, 149.8, 136.9, 136.6, 131.9, 131.8, 131.2, 131.0, 124.6, 124.1, 123.4, 123.2, 122.6, 121.8, 121.0, 118.7, 118.5, 117.9, 115.0, 112.8, 56.7, 55.8. HRMS (ESI⁺): calcd for C₁₄H₁₂Cl₂NO₃⁺ [M+35Cl]⁺ 312.0398, found 312.0393.

**Yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.57 (dd, J = 7.8 Hz, J = 1.8 Hz, 1H), 7.44-7.38 (m, 1H), 7.37-7.32 (m, 2H), 7.17-7.11 (m, 2H), 7.06-7.02 (m, 2H), 6.92 (dd, J = 7.8 Hz, J = 0.8 Hz, 1H), 2.25 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 167.41, 156.59, 155.70, 144.79, 132.73, 131.16, 129.97, 124.41, 124.06, 123.22, 119.36, 119.00, 19.41. HRMS (ESI⁺): calcd for C₁₅H₁₂ClNNaO₃⁺ [M+Na]⁺ 312.0398, found 312.0393.
2-Fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride (4a)

White solid, M.p.: 65-67 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.44-7.38 (m, 1H), 7.23-7.17 (m, 2H), 7.06-7.03 (m, 1H), 7.01-6.96 (m, 1H), 6.86-6.81 (m, 1H), 6.75-6.72 (m, 2H), 3.92 (s, 3H), 3.25 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 161.1 (d, $J = 251.5$ Hz), 150.1 (d, $J = 4.0$ Hz), 148.8, 132.4 (d, $J = 11.0$ Hz), 129.0, 128.9, 123.4 (d, $J = 4.0$ Hz), 120.8 (d, $J = 15.0$ Hz), 119.5, 116.4, 112.6 (d, $J = 22.0$ Hz), 61.2, 40.7. $^{19}$F NMR (CDCl$_3$, 376 MHz): $\delta$ (ppm) -112.2 (dd, $J = 8.6$ Hz, $J = 6.4$ Hz, 1F). HRMS (ESI$^+$): calcd for C$_{13}$H$_{15}$ClFN$_2$O$^+$ [M+H]$^+$ 293.0851, found 293.0851.

2-((4-Chlorophenyl)(methyl)amino)-6-fluoro-N-methoxybenzimidoyl chloride (4b)

White solid, M.p.: 64-65 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.46-7.39 (m, 1H), 7.16-7.11 (m, 2H), 7.05-6.99 (m, 2H), 6.65-6.61 (m, 2H), 3.93 (s, 3H), 3.22 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 161.1 (d, $J = 252.0$ Hz), 149.4 (d, $J = 3.2$ Hz), 147.4, 132.6 (d, $J = 10.0$ Hz), 128.8, 128.7, 124.2, 123.5 (d, $J = 3.2$ Hz), 121.1 (d, $J = 14.6$ Hz), 117.1, 113.2 (d, $J = 21.3$ Hz), 63.2, 40.7. $^{19}$F NMR (CDCl$_3$, 376 MHz): $\delta$ (ppm) -111.8 (dd, $J = 8.8$ Hz, $J = 6.4$ Hz, 1F). HRMS (ESI$^+$): calcd for C$_{15}$H$_{14}$Cl$_2$FN$_2$O$^+$ [M+H]$^+$ 327.0462, found 327.0467.

2-((3-Chlorophenyl)(methyl)amino)-6-fluoro-N-methoxybenzimidoyl chloride (4c)

White solid, M.p.: 62-64 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.48-7.41 (m, 1H), 7.10-7.03 (m, 3H), 6.78-6.74 (m, 1H), 6.65 (t, $J = 2.4$ Hz, 1H), 6.55-6.50 (m, 1H), 3.94 (s, 3H), 3.22 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 161.0 (d, $J = 252.2$ Hz), 149.7, 149.8 (d, $J = 3.3$ Hz), 134.7, 132.6 (d, $J = 10.0$ Hz), 129.8, 128.5, 124.1 (d, $J = 3.3$ Hz), 121.4, 118.8, 115.0, 113.7 (d, $J = 21.4$ Hz), 113.5, 63.3, 40.5. $^{19}$F NMR (CDCl$_3$, 376 MHz): $\delta$ (ppm) -111.5 (dd, $J = 8.3$ Hz, $J = 6.4$ Hz, 1F). HRMS (ESI$^+$): calcd for C$_{15}$H$_{14}$Cl$_2$FN$_2$O$^+$ [M+H]$^+$ 327.0462, found 327.0464.
2-((4-Bromophenyl)(methyl)amino)-6-fluoro-N-methoxybenzimidoyl chloride (4d)

White solid, M.p.: 72-73 °C. 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.46-7.40 (m, 1H), 7.29-7.27 (m, 1H), 7.26-7.24 (m, 1H), 7.06-7.00 (m, 2H), 6.60-6.55 (m, 2H), 3.93 (s, 3H), 3.21 (s, 3H). 13C NMR (CDCl3, 100 MHz): δ (ppm) 161.1 (d, J = 252.0 Hz), 149.2 (d, J = 3.3 Hz), 147.8, 132.6 (d, J = 10.0 Hz), 131.7, 128.6, 123.7 (d, J = 3.3 Hz), 121.2 (d, J = 14.4 Hz), 117.4, 113.3 (d, J = 21.4 Hz), 111.4, 63.3, 40.6. 19F NMR (CDCl3, 376 MHz): δ (ppm) -111.7 (dd, J = 8.6 Hz, J = 6.4 Hz, 1F). HRMS (ESI+): calcd for C15H14Br35ClFN2O+ [M+H]+ 372.9936, found 372.9949.

2-Fluoro-N-methoxy-6-(methyl(m-tolyl)amino)benzimidoyl chloride (4e)

White solid, M.p.: 69-71 °C. 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.43-7.36 (m, 1H), 7.12-7.06 (m, 1H), 7.10-6.95 (m, 2H), 6.66 (d, J = 7.6 Hz, 1H), 6.57-6.53 (m, 2H), 3.93 (s, 3H), 3.23 (s, 3H), 2.27 (s, 3H). 13C NMR (CDCl3, 100 MHz): δ (ppm) 161.1 (d, J = 251.1 Hz), 150.1 (d, J = 3.5 Hz), 148.8, 138.6, 132.3 (d, J = 10.2 Hz), 129.1, 128.8, 123.2 (d, J = 3.3 Hz), 120.5, 117.2, 113.7, 112.4 (d, J = 21.5 Hz), 63.1, 40.8, 21.8. 19F NMR (CDCl3, 376 MHz): δ (ppm) -112.2 (dd, J = 8.8 Hz, J = 6.4 Hz, 1F). HRMS (ESI+): calcd for C16H17Br35ClFN2O+ [M+H]+ 307.1008, found 307.1009.

2-((3,4-Dimethoxyphenyl)(methyl)amino)-6-fluoro-N-methoxybenzimidoyl chloride (4f)

White solid, M.p.: 103-105 °C. 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.39-7.33 (m, 1H), 6.97-6.94 (m, 1H), 6.92-6.86 (m, 1H), 6.77-6.74 (m, 1H), 6.42-6.37 (m, 2H), 3.90 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 3.23 (s, 3H). 13C NMR (CDCl3, 100 MHz): δ (ppm) 161.1 (d, J = 250.3 Hz), 150.7 (d, J = 3.7 Hz), 149.3, 144.1, 143.5, 132.1 (d, J = 10.3 Hz), 129.3, 120.5, 111.9, 111.0 (d, J = 21.6 Hz), 110.9, 104.8, 63.1, 56.4, 56.0, 41.8. 19F NMR (CDCl3, 376 MHz): δ (ppm) -112.6 (dd, J = 8.6 Hz, J
= 6.4 Hz, 1F). HRMS (ESI+): calcd for C_{17}H_{19}^{35}ClFN_{2}O_{3}^{+} [M+H]^+ 353.1063, found 353.1045.

![Structure 1](image1)

**2-(Ethyl(phenyl)amino)-6-fluoro-N-methoxybenzimidoyl chloride (4g)**

White solid, M.p.: 62-64 °C. 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.42-7.37 (m, 1H), 7.21-7.16 (m, 2H), 7.04-7.01 (m, 1H), 7.00-6.95 (m, 1H), 6.84-6.79 (m, 1H), 6.76-6.72 (m, 2H), 3.91 (s, 3H), 3.70 (q, J = 7.2 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H). 13C NMR (CDCl3, 100 MHz): δ (ppm) 161.2 (d, J = 251.1 Hz), 149.0 (d, J = 3.6 Hz), 147.8, 132.1 (d, J = 10.1 Hz), 129.1, 128.9, 124.0 (d, J = 3.2 Hz), 121.0 (d, J = 7.6 Hz), 119.4, 117.4, 112.4 (d, J = 21.6 Hz), 63.1, 47.0, 12.8. 19F NMR (CDCl3, 376 MHz): δ (ppm) -112.0 (dd, J = 8.8 Hz, J = 6.4 Hz, 1F). HRMS (ESI+): calcd for C_{16}H_{17}^{35}ClFN_{2}O^{+} [M+H]^+ 307.0808, found 307.1003.

![Structure 2](image2)

**2-Fluoro-6-(indolin-1-yl)-N-methoxybenzimidoyl chloride (4h)**

White solid, M.p.: 138-140 °C. 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.39-7.32 (m, 1H), 7.26-7.24 (m, 1H), 7.16 (d, J = 6.8 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H), 6.89 (t, J = 8.4 Hz, 1H), 6.77 (t, J = 7.2 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 4.04 (s, 3H), 3.86 (t, J = 8.4 Hz, 2H), 3.14 (t, J = 8.4 Hz, 2H). 13C NMR (CDCl3, 100 MHz): δ (ppm) 161.2 (d, J = 251.1 Hz), 148.5, 146.7, 132.0 (d, J = 10.2 Hz), 130.9, 129.6, 127.1, 125.0, 119.7, 118.7 (d, J = 13.3 Hz), 111.2 (d, J = 21.5 Hz), 110.1, 63.3, 55.0, 29.2. HRMS (ESI+): calcd for C_{16}H_{15}^{35}ClFN_{2}O^{+} [M+H]^+ 305.0851, found 305.0847.

![Structure 3](image3)

**2-Benzyl-N-methoxybenzimidoyl chloride (6)**

White solid, M.p.: 55-53 °C. 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.48 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.37-7.32 (m, 1H), 7.30-7.26 (m, 3H), 7.22-7.12 (m, 4H), 4.18 (s, 2H), 4.02 (s, 3H). 13C NMR (CDCl3, 100 MHz): δ (ppm) 140.5, 140.0, 135.8, 133.8, 130.9, 130.3, 130.0, 129.2, 128.5, 126.6, 126.2, 63.1, 39.2. HRMS (ESI+): calcd for C_{15}H_{15}ClNO^{+} [M+H]^+ 260.0837, found 260.0840.

S16
2. Experimental data for the described products

\[
\text{2,3-Diphenylchromeno[2,3,4-ij]isoquinoline (3a)}
\]

Following the general procedure I, \(N\)-hydroxy-2-phenoxybenzimidoyl chloride 1a (37.1 mg, 0.15 mmol) and 1,2-diphenylethyne 2a (32.3 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3a as a yellow solid (27.0 mg, 87\% yield). M.p.: 218–219 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) 8.62 (dd, \(J = 8.4\) Hz, \(J = 1.6\) Hz, 1H), 7.55-7.45 (m, 4H), 7.40-7.31 (m, 3H), 7.29-7.20 (m, 7H), 7.19-7.12 (m, 2H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm) 154.2, 152.5, 151.4, 147.3, 141.1, 137.8, 137.6, 131.9, 131.6, 131.2, 130.6, 128.7, 128.5, 127.6, 127.4, 127.3, 125.1, 124.0, 121.8, 117.5, 117.1, 116.4, 109.5. HRMS (ESI\(^+\)): calced for \(\text{C}_{27}\text{H}_{18}\text{NO}\) \([\text{M+H}]^+\) 372.1383, found 372.1383.

\[
\text{Methyl 2,3-diphenylchromeno[2,3,4-ij]isoquinoline-10-carboxylate (3b)}
\]

Following the general procedure I, methyl-4-(2-(chloro(hydroxyimino)methyl)phenoxy)benzoate 1b (45.8 mg, 0.15 mmol) and 1,2-diphenylethyne 2a (17.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3b as a yellow solid (25.3 mg, 59\% yield). M.p.: > 250 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) 9.22 (d, \(J = 2.0\) Hz, 1H), 8.14 (dd, \(J = 8.8\) Hz, \(J = 2.4\) Hz, 1H), 7.53 (t, \(J = 8.4\) Hz, 1H), 7.49-7.44 (m, 2H), 7.41-7.33 (m, 3H), 7.28 (d, \(J = 8.8\) Hz, 1H), 7.25-7.20 (m, 6H), 7.14 (d, \(J = 7.6\) Hz, 1H), 3.95 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm) 166.5, 157.2, 151.9, 151.7, 146.4, 140.8, 137.54, 137.50, 133.1, 131.7, 131.09, 130.7, 129.0, 128.7, 127.7, 127.5, 127.5, 127.1, 126.1, 121.8, 118.3, 117.4, 116.3, 109.8, 52.3. HRMS (ESI\(^+\)): calced for \(\text{C}_{29}\text{H}_{28}\text{NO}_3\) \([\text{M+H}]^+\) 430.1438, found 430.1446.
10-Bromo-2,3-diphenylchromeno[2,3,4-ij]isoquinoline (3c)

Following the general procedure I, 2-(4-bromophenoxy)-N-hydroxybenzimidoyl chloride 1c (48.8 mg, 0.15 mmol) and 1,2-diphenylethyne 2a (17.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3c as a yellow solid (24.2 mg, 54% yield). M.p.: 215-216 °C. $^{1}H$ NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.71 (d, $J$ = 2.4 Hz, 1H), 7.56-7.51 (m, 2H), 7.46-7.43 (m, 2H), 7.40-7.34 (m, 3H), 7.25-7.21 (m, 5H), 7.19 (d, $J$ = 8.4 Hz, 1H), 7.14-7.10 (m, 2H). $^{13}C$ NMR (CDCl$_3$, 100 MHz): δ (ppm) 153.1, 152.1, 151.6, 146.0, 140.8, 137.6, 137.5, 134.6, 131.8, 131.1, 130.6, 129.1, 128.7, 127.7, 127.6, 127.52, 127.49, 123.5, 119.0, 117.9, 117.1, 116.3, 109.7. HRMS (ESI$^+$): calcd for C$_{27}$H$_{17}$BrNO$^+$ [M+H]$^+$ 450.0488, found 450.0486.

10-Methyl-2,3-diphenylchromeno[2,3,4-ij]isoquinoline (3d)

Following the general procedure I, N-hydroxy-2-(p-tolyloxy)benzimidoyl chloride 1d (39.2 mg, 0.15 mmol) and 1,2-diphenylethyne 2a (17.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3d as a yellow solid (32.7 mg, 84% yield). M.p.: 211-212 °C. $^{1}H$ NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.41 (d, $J$ = 1.6 Hz, 1H), 7.53 (t, $J$ = 8.2 Hz, 1H), 7.49-7.43 (m, 2H), 7.40-7.32 (m, 3H), 7.31-7.27 (m, 2H), 7.25-7.19 (m, 4H), 7.19-7.11 (m, 3H), 2.44 (s, 3H). $^{13}C$ NMR (CDCl$_3$, 100 MHz): δ (ppm) 152.6, 152.3, 151.4, 147.5, 141.2, 137.8, 137.6, 133.6, 132.9, 131.6, 131.2, 130.6, 128.6, 128.4, 127.7, 127.3, 124.8, 121.2, 117.3, 116.8, 116.4, 109.4, 21.1. HRMS (ESI$^+$): calcd for C$_{28}$H$_{20}$NO$^+$ [M+H]$^+$ 386.1539, found 386.1547.
4-Methoxy-2,3-diphenylchromeno[2,3,4-ij]isoquinoline (3e)

Following the general procedure I, *N*-hydroxy-2-(4-methoxyphenoxy)benzimidoyl chloride 1e (41.6 mg, 0.15 mmol) and 1,2-diphenylethyne 2a (17.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3e as a yellow solid (31.3 mg, 78% yield). M.p.: 219-220 ℃.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 8.07 (d, $J = 2.8$ Hz, 1H), 7.53 (t, $J = 8.4$ Hz, 1H), 7.48-7.44 (m, 2H), 7.38-7.32 (m, 3H), 7.27-7.26 (m, 1H), 7.25-7.20 (m, 5H), 7.17-7.12 (m, 2H), 7.10-7.06 (m, 1H), 3.92 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 156.3, 152.6, 151.4, 148.9, 147.4, 141.2, 137.9, 137.6, 131.6, 131.2, 130.7, 128.6, 127.6, 127.4, 127.3, 122.1, 120.2, 118.3, 117.1, 116.2, 110.2, 109.4, 106.7, 56.1.

HRMS (ESI$^+$): calcd for C$_{28}$H$_{20}$NO$_2$ [M+H]$^+$ 402.1489, found 402.1493.

3-Ethyl-2-phenylchromeno[2,3,4-ij]isoquinoline (3f)

Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride 1a (37.1 mg, 0.15 mmol) and but-1-yn-1-ylbenzene 2f (13.0 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3f as a yellow solid (23.9 mg, 74% yield). M.p.: 242-244 ℃.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 8.51 (d, $J = 7.6$ Hz, 1H), 7.71-7.66 (m, 1H), 7.63-7.59 (m, 2H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.52-7.47 (m, 2H), 7.46-7.41 (m, 2H), 7.25-7.18 (m, 2H), 7.17-7.13 (m, 1H), 2.96 (q, $J = 7.6$ Hz, 2H), 1.28 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 154.0, 153.0, 152.8, 145.6, 142.0, 136.7, 131.6, 131.59, 135.56, 129.5, 128.2, 127.7, 125.0, 123.9, 121.9, 116.9, 116.7, 115.7, 109.3, 22.3, 14.8.

HRMS (ESI$^+$): calcd for C$_{23}$H$_{18}$NO$^+$ [M+H]$^+$ 324.1383, found 324.1386.
3-Methyl-2-phenylchromeno[2,3,4-ij]isoquinoline (3g)

Following the general procedure I, N-hydroxy-2-phenoxybenzimidoyl chloride 1a (37.1 mg, 0.15 mmol) and prop-1-yn-1-ylbenzene 2g (11.6 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3g as a yellow solid (21.0 mg, 68% yield). M.p.: 184-185 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 8.54 (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 1H), 7.72-7.66 (m, 3H), 7.54-7.48 (m, 3H), 7.47-7.41 (m, 2H), 7.27-7.20 (m, 2H), 7.17 (d, $J = 8.0$ Hz, 1H), 2.55 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 153.9, 152.8, 152.6, 145.6, 141.7, 137.7, 131.7, 131.5, 130.2, 128.1, 127.8, 124.9, 123.9, 122.0, 121.9, 117.0, 116.1, 115.7, 109.4, 16.1. HRMS (ESI$^+$): calcd for C$_{22}$H$_{16}$NO$^+$ [M+H]$^+$ 310.1228, found 310.1228.

2,3-Di-p-tolychromeno[2,3,4-ij]isoquinoline (3h)

Following the general procedure I, N-hydroxy-2-phenoxybenzimidoyl chloride 1a (37.1 mg, 0.15 mmol) and 1,2-di-p-tolylethyne 2h (20.6 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3h as a yellow solid (27.9 mg, 70% yield). M.p.: 240-241 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 8.62 (d, $J = 8.0$ Hz, 1H), 7.53-7.45 (m, 2H), 7.39 (d, $J = 7.6$ Hz, 2H), 7.29-7.27 (m, 1H), 7.25-7.23 (m, 1H), 7.21-7.10 (m, 6H), 7.05 (d, $J = 7.6$ Hz, 2H), 2.41 (s, 3H), 2.33 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 154.2, 152.5, 151.3, 147.0, 138.3, 137.8, 137.0, 136.97, 136.92, 134.9, 131.8, 131.4, 130.9, 130.5, 129.4, 128.4, 128.2, 125.0, 123.9, 121.8, 117.5, 117.0, 116.3, 109.2, 21.5, 21.4. HRMS (ESI$^+$): calcd for C$_{29}$H$_{22}$NO$^+$ [M+H]$^+$ 400.1696, found 400.1699.
2,3-Bis(4-methoxyphenyl)chromeno[2,3,4-ij]isoquinoline (3i)

Following the general procedure I, N-hydroxy-2-phenoxybenzimidoyl chloride 1a (37.1 mg, 0.15 mmol) and 1,2-bis(4-methoxyphenyl)ethyne 2i (23.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3i as a yellow solid (20.3 mg, 47% yield). M.p.: 211-212 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 8.61 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.53-7.39 (m, 4H), 7.28-7.23 (m, 2H), 7.19-7.15 (m, 3H), 7.12-7.10 (m, 1H), 6.96-6.91 (m, 2H), 6.80-6.76 (m, 2H), 3.86 (s, 3H), 3.80 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 158.89, 158.84, 154.2, 152.5, 151.1, 147.0, 138.1, 133.8, 132.2, 131.9, 131.8, 131.5, 130.2, 127.6, 125.0, 124.0, 121.9, 117.4, 117.1, 116.2, 114.2, 113.2, 109.6, 55.4, 55.3. HRMS (ESI$^+$): calcd for C$_{29}$H$_{22}$NO$_3$+ [M+H]$^+$ 432.1594, found 432.1597.

2,3-Bis(4-(tert-butyl)phenyl)chromeno[2,3,4-ij]isoquinoline (3j)

Following the general procedure I, N-hydroxy-2-phenoxybenzimidoyl chloride 1a (37.1 mg, 0.15 mmol) and 1,2-bis(4-(tert-butyl)phenyl)ethyne 2j (29.0 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3j as a yellow solid (36.7 mg, 76% yield). M.p.: > 250 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 8.36 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.54-7.45 (m, 2H), 7.42-7.36 (m, 4H), 7.30-7.17 (m, 7H), 7.11 (d, J = 7.6 Hz, 1H), 1.36 (s, 9H), 1.28 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 154.2, 152.5, 151.3, 150.3, 150.1, 147.0, 138.2, 137.8, 134.8, 131.8, 131.4, 130.7, 130.2, 128.4, 125.5, 125.1, 124.5, 123.9, 121.9, 117.7, 117.0, 116.3, 109.2, 34.7, 34.6, 31.5, 31.4. HRMS (ESI$^+$): calcd for C$_{35}$H$_{34}$NO$_3$+ [M+H]$^+$ 484.2635, found 484.2638.
2,3-Bis(4-chlorophenyl)chromeno[2,3,4-ij]isoquinoline (3k)

Following the general procedure I, N-hydroxy-2-phenoxybenzimidoyl chloride 1a (37.1 mg, 0.15 mmol) and 1,2-bis(4-chlorophenyl)ethyne 2k (24.6 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3k as a yellow solid (30.3 mg, 69% yield). M.p.: 230-231 °C. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.57 (dd, J = 8.2 Hz, J = 1.4 Hz, 1H), 7.56 (t, J = 8.2 Hz, 1H), 7.53-7.47 (m, 1H), 7.41-7.35 (m, 1H), 7.31-7.21 (m, 4H), 7.20-7.15 (m, 3H), 7.12 (d, J = 8.4 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 154.2, 152.6, 150.3, 147.8, 139.3, 137.3, 136.0, 133.7, 133.6, 132.5, 132.3, 132.0, 131.9, 129.2, 128.1, 127.3, 125.0, 124.2, 121.5, 117.2, 117.1, 116.4, 110.0. HRMS (ESI⁺): calcd for C₂₇H₁₆Cl₂NO⁺ [M+H]⁺ 440.0603, found 440.0613.

2,3-Bis(4-bromophenyl)chromeno[2,3,4-ij]isoquinoline (3l)

Following the general procedure I, N-hydroxy-2-phenoxybenzimidoyl chloride 1a (37.1 mg, 0.15 mmol) and 1,2-bis(4-bromophenyl)ethyne 2l (33.4 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3l as a yellow solid (35.8 mg, 68% yield). M.p.: > 250 °C. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.58-8.55 (m, 1H), 7.58-7.48 (m, 4H), 7.40-7.36 (m, 2H), 7.33-7.27 (m, 4H), 7.19-7.16 (m, 1H), 7.14-7.10 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 154.2, 152.6, 150.3, 147.9, 139.7, 137.3, 136.5, 132.8, 132.2, 132.2, 132.1, 131.0, 127.2, 125.0, 124.2, 122.0, 121.8, 121.4, 117.2, 117.1, 116.3, 110.0. HRMS (ESI⁺): calcd for C₂₇H₁₆Br₂NO⁺ [M+H]⁺ 527.9593, found 527.9594; calcd for C₂₇H₁₆Br₂NO⁺ [M+H]⁺ 529.9573, found 529.9575; calcd for C₂₇H₁₆Br₂NO⁺ [M+H]⁺ 531.9552, found 531.9554.
2,3-Di-m-tolylchromeno[2,3,4-ij]isoquinoline (3m)

Following the general procedure I, N-hydroxy-2-phenoxybenzimidoyl chloride 1a (37.1 mg, 0.15 mmol) and 1,2-di-m-tolylethyne 2m (20.6 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3m as a yellow solid (31.9 mg, 80% yield). M.p.: > 250 °C. $^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.63 (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 1H), 7.55-7.46 (m, 2H), 7.36 (s, 1H), 7.32-7.27 (m, 2H), 7.25-7.23 (m, 1H), 7.21-7.16 (m, 2H), 7.15-7.12 (m, 2H), 7.10-7.06 (m, 2H), 7.04-7.00 (m, 2H), 2.34 (s, 3H), 2.28 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ (ppm) 154.2, 152.5, 151.4, 147.1, 141.0, 138.1, 137.7, 137.69, 137.1, 131.9, 131.7, 131.5, 131.4, 128.7, 128.5, 128.2, 128.07, 128.06, 127.7, 127.4, 125.1, 124.0, 121.8, 117.6, 117.1, 116.3, 109.4, 21.6. HRMS (ESI$^+$): calcd for C$_{29}$H$_{22}$NO$_2$ [M+H]+ 400.1696, found 400.1698.

2,3-Bis(3-methoxyphenyl)chromeno[2,3,4-ij]isoquinoline (3n)

Following the general procedure I, N-hydroxy-2-phenoxybenzimidoyl chloride 1a (37.1 mg, 0.15 mmol) and 1,2-bis(3-methoxyphenyl)ethyne 2n (23.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3n as a yellow solid (34.0 mg, 79% yield). M.p.: 191-192 °C. $^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.62 (d, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 8.0$ Hz, 1H), 7.50-7.46 (m, 1H), 7.33-7.24 (m, 3H), 7.21 (d, $J = 8.0$ Hz, 1H), 7.18-7.10 (m, 3H), 7.04 (s, 1H), 6.91-6.85 (m, 2H), 6.81-6.74 (m, 2H), 3.72 (s, 3H), 3.64 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ (ppm) 159.9, 159.0, 154.2, 152.5, 151.0, 147.3, 142.4, 139.2, 137.5, 132.0, 131.7, 129.7, 128.7, 128.4, 125.1, 124.0, 123.6, 123.1, 121.7, 117.6, 117.1, 116.5, 116.4, 115.5, 113.9, 113.2, 109.6, 55.4, 55.3. HRMS (ESI$^+$): calcd for...
C_{29}H_{22}NO_{3}^{+} [M+H]^+ 432.1594, found 432.1597.

2,3-Diethylchromeno[2,3,4-ij]isoquinoline (3o)

Following the general procedure I, N-hydroxy-2-phenoxybenzimidoyl chloride 1a (37.1 mg, 0.15 mmol) and hex-3-yne 2o (8.2 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 3o as a yellow solid (17.3 mg, 63% yield). M.p.: 149-150 °C. \(^1^H\) NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) 8.52 (dd, \(J = 8.0\) Hz, \(J = 1.6\) Hz, 1H), 7.59 (t, \(J = 8.0\) Hz, 1H), 7.45-7.40 (m, 2H), 7.25-7.18 (m, 2H), 7.04 (d, \(J = 7.6\) Hz, 1H), 3.02-2.94 (m, 4H), 1.41 (t, \(J = 7.6\) Hz, 3H), 1.27 (t, \(J = 7.6\) Hz, 3H). \(^{13}C\) NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm) 154.9, 153.9, 153.0, 145.4, 136.6, 131.3, 127.1, 124.5, 123.8, 122.2, 116.9, 116.3, 114.8, 108.2, 28.5, 21.2, 14.5, 14.3. HRMS (ESI\(^{+}\)): calcd for C\(_{19}\)H\(_{18}\)NO\(^{+}\) [M+H]^+ 276.1383, found 276.1385.

11-Fluoro-7-methyl-2,3-diphenyl-7H-pyrido[4,3,2-kl]acridine (5a)

Following the general procedure II, 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a (29.2 mg, 0.1 mmol) and 1,2-diphenylethyne 2a (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5a as a yellow solid (35.8 mg, 89% yield). M.p.: 234-236 °C. \(^1^H\) NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) 7.57-7.52 (m, 2H), 7.45 (t, \(J = 8.0\) Hz, 1H), 7.41-7.33 (m, 4H), 7.28-7.27 (m, 2H), 7.21-7.16 (m, 3H), 6.98 (t, \(J = 8.0\) Hz, 2H), 6.88-6.81 (m, 1H), 6.75 (d, \(J = 8.0\) Hz, 1H), 3.57 (s, 3H). \(^{13}C\) NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm) 162.3 (d, \(J = 260.0\) Hz), 151.0, 148.6 (d, \(J = 8.0\) Hz), 144.2 (d, \(J = 4.0\) Hz), 141.2, 138.5, 138.1, 131.29, 131.28 (d, \(J = 11.2\) Hz), 131.2, 130.9 (d, \(J = 16.4\) Hz), 130.8, 128.75, 128.70, 127.6, 127.5, 127.2 (d, \(J = 4.3\) Hz), 119.1, 114.4, 109.5, 109.4 (d, \(J = 4.0\)Hz), 109.3, 105.0, 35.0. \(^{19}F\) NMR (CDCl\(_3\), 376 MHz): \(\delta\) (ppm) -107.1 (dd, \(J = 11.6\) Hz, \(J = 5.6\) Hz, 1F). HRMS (ESI\(^{+}\)): calcd for C\(_{29}\)H\(_{20}\)FN\(_{2}\) [M+H]^+ 403.1605, found 403.1607.
4-Chloro-11-fluoro-7-methyl-2,3-diphenyl-7H-pyrido[4,3,2-kl]acridine (5b)

Following the general procedure II, 2-((4-chlorophenyl)(methyl)amino)-6-fluoro-N-methoxybenzimidoyl chloride 4b (32.6 mg, 0.1 mmol) and 1,2-diphenylethene 2a (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5b as a yellow solid (17.4 mg, 40% yield). M.p.: >250 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.53 (d, J = 8.8 Hz, 1H), 7.43-7.36 (m, 1H), 7.35-7.32 (m, 2H), 7.24-7.14 (m, 8H), 6.98 (d, J = 8.8 Hz, 1H), 6.86-6.81 (m, 1H), 6.71 (d, J = 8.8 Hz, 1H), 3.57 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ (ppm) 162.2 (d, J = 260.8 Hz), 154.4, 148.7 (d, J = 8.0 Hz), 143.6 (d, J = 4.0 Hz), 141.5, 140.6, 139.1, 134.6, 133.4, 132.3, 131.6 (d, J = 11.2 Hz), 130.6, 127.3, 127.2, 126.9 (d, J = 6.0 Hz), 125.7, 120.7, 117.8, 109.7, 109.2 (d, J = 4.0 Hz), 106.7, 35.3.

$^{19}$F NMR (CDCl$_3$, 376 MHz): δ (ppm) -106.6 (dd, J = 11.6 Hz, J = 5.2 Hz, 1F). HRMS (ESI$^+$): calcd for C$_{28}$H$_{19}$ClFN$_2$ [M+H]$^+$ 437.1215, found 437.1221.

5-Chloro-11-fluoro-7-methyl-2,3-diphenyl-7H-pyrido[4,3,2-kl]acridine (5c)

Following the general procedure II, 2-((3-chlorophenyl)(methyl)amino)-6-fluoro-N-methoxybenzimidoyl chloride 4c (32.6 mg, 0.1 mmol) and 1,2-diphenylethene 2a (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5c as a yellow solid (17.4 mg, 35% yield). M.p.: 242-243 °C.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): δ (ppm) 7.50-7.35 (m, 6H), 7.28-7.18 (m, 5H), 7.07 (d, J = 9.3 Hz, 1H), 6.91-6.85 (m, 2H), 6.76 (s, 1H), 3.57 (s, 3H). $^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz): δ (ppm) 162.4 (d, J = 259.7 Hz), 160.2, 144.2 (d, J = 4.0 Hz), 142.8, 139.4, 138.1, 132.1 (d, J = 11.0 Hz), 131.5, 130.9, 129.3, 127.9, 127.6, 117.7, 113.5, 110.4 (d, J = 3.4 Hz), 110.3, 110.1, 106.1, 35.6. $^{19}$F NMR (CD$_2$Cl$_2$, 376 MHz): δ (ppm) -107.7 (s, 1F). HRMS (ESI$^+$): calcd for C$_{28}$H$_{19}$ClFN$_2$ [M+H]$^+$ 437.1221, found 437.1223.
4-Bromo-11-fluoro-7-methyl-2,3-diphenyl-7H-pyrido[4,3,2-kl]acridine (5d)

Following the general procedure II, 2-((4-bromophenyl)(methyl)amino)-6-fluoro-N-methoxybenzimidoyl chloride 4d (37.0 mg, 0.1 mmol) and 1,2-diphenylethyne 2a (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5d as a yellow solid (18.2 mg, 38% yield). M.p.: >250 ºC.

1H NMR (CDCl3, 400 MHz): δ (ppm) 7.53 (d, J = 8.8 Hz, 1H), 7.42-7.32 (m, 3H), 7.25-7.13 (m, 8H), 6.97 (d, J = 8.8 Hz, 1H), 6.87-6.79 (m, 1H), 6.70 (d, J = 8.8 Hz, 1H), 3.65 (s, 3H).

13C NMR (CDCl3, 100 MHz): δ (ppm) 162.2 (d, J = 259.6 Hz), 151.2, 148.3 (d, J = 9.2 Hz), 144.2 (d, J = 4.8 Hz), 141.6, 141.3, 141.0, 138.6, 138.2, 131.3, 131.1 (d, J = 12.0 Hz), 130.8, 128.7, 127.5, 127.1 (d, J = 4.5 Hz), 126.3 (d, J = 1.9 Hz), 117.6, 114.0, 112.3 (d, J = 7.8 Hz), 109.43 (d, J = 3.0 Hz), 109.37, 109.2, 106.8, 34.9, 23.1.

19F NMR (CDCl3, 376 MHz): δ (ppm) -107.2 (dd, J = 11.6 Hz, J = 5.4 Hz, 1F).

11-Fluoro-4,7-dimethyl-2,3-diphenyl-7H-pyrido[4,3,2-kl]acridine (5e)

Following the general procedure II, 2-fluoro-N-methoxy-6-(methyl(p-tolyl)amino)benzimidoyl chloride 4e (30.6 mg, 0.1 mmol) and 1,2-diphenylethyne 2a (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5e as a yellow solid (18.3 mg, 44% yield). M.p.: 242-243 ºC. 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.55-7.50 (m, 2H), 7.42-7.33 (m, 4H), 7.29-7.25 (m, 2H), 7.21-7.15 (m, 3H), 6.96 (d, J = 8.4 Hz, 1H), 6.86-6.80 (m, 1H), 6.79 (s, 1H), 6.58 (s, 1H), 3.55 (s, 3H), 2.39 (s, 3H).

13C NMR (CDCl3, 100 MHz): δ (ppm) 162.2 (d, J = 259.6 Hz), 151.2, 148.3 (d, J = 9.2 Hz), 144.2 (d, J = 4.8 Hz), 141.6, 141.3, 141.0, 138.6, 138.2, 131.3, 131.1 (d, J = 12.0 Hz), 130.8, 128.7, 127.5, 127.1 (d, J = 4.5 Hz), 126.3 (d, J = 1.9 Hz), 117.6, 114.0, 112.3 (d, J = 7.8 Hz), 109.43 (d, J = 3.0 Hz), 109.37, 109.2, 106.8, 34.9, 23.1.

19F NMR (CDCl3, 376 MHz): δ (ppm) -107.2 (dd, J = 11.6 Hz, J = 5.4 Hz, 1F).
Hz, J = 5.6 Hz, 1F). HRMS (ESI⁺): calcd for C_{29}H_{22}FN_{2}⁺ [M+H]⁺ 417.1762, found 417.1769.

11-Fluoro-4,5-dimethoxy-7-methyl-2,3-diphenyl-7H-pyrido[4,3,2-kl]acridine (5f)
Following the general procedure II, 2-((3,4-dimethoxyphenyl)(methyl)amino)-6-fluoro-N-methoxybenzimidoyl chloride 4f (35.2 mg, 0.1 mmol) and 1,2-diphenylethyne 2a (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5f as a yellow solid (33.7 mg, 73% yield). M.p.: 211-212 ºC. 

\[ \text{HRMS (ESI}^+\text{): calcd for C}_{30}\text{H}_{24}\text{FN}_{2}O_{2}^+ \text{[M+H]}^+ 463.1816, \text{found 463.1820.} \]

7-Ethyl-11-fluoro-2,3-diphenyl-7H-pyrido[4,3,2-kl]acridine (5g)
Following the general procedure II, 2-(ethyl(phenyl)amino)-6-fluoro-N-methoxybenzimidoyl chloride 4g (30.6 mg, 0.1 mmol) and 1,2-diphenylethyne 2a (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5g as a yellow solid (39.5 mg, 95% yield). M.p.: 204-205 ºC. 

\[ \text{HRMS (ESI}^+\text{): calcd for C}_{30}\text{H}_{24}\text{FN}_{2}O_{2}^+ \text{[M+H]}^+ 463.1816, \text{found 463.1820.} \]
12.0 Hz), 131.26, 130.8, 128.8, 127.5, 127.2 (d, \( J = 4.0 \) Hz), 126.7 (d, \( J = 2.0 \) Hz), 119.0, 114.2, 112.4 (d, \( J = 7.0 \) Hz), 109.4, 109.2, 108.9 (d, \( J = 4.0 \) Hz), 104.3, 42.1, 11.0. \(^{19}\)F NMR (CDCl\(_3\), 376 MHz): \( \delta \) (ppm) -106.4 (dd, \( J = 11.7 \) Hz, \( J = 5.5 \) Hz, 1F). HRMS (ESI\(^+\)): calcd for C\(_{29}\)H\(_{22}\)FN\(_2\)\(^+\)[M+H]\(^+\) 417.1762, found 417.1769.

12-Fluoro-2,3-diphenyl-6,7-dihydropyrido[2,3,4-\(mn\)]pyrrolo[3,2,1-de]acridine (5h)

Following the general procedure II, 2-fluoro-6-(indolin-1-yl)-N-methoxybenzimidoyl chloride 4h (30.4 mg, 0.1 mmol) and 1,2-diphenylethylene 2a (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5h as a yellow solid (23.2 mg, 56% yield). M.p.: > 250 °C. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz): \( \delta \) (ppm) 7.43-7.27 (m, 7H), 7.25-7.15 (m, 5H), 6.73-6.59 (m, 3H), 4.28 (t, \( J = 8.4 \) Hz, 2H), 3.44 (t, \( J = 8.4 \) Hz, 2H). The \(^{13}\)C NMR data could not be recorded due to its poor solubility, but the X-ray single crystal diffraction of 5h confirmed its structures. HRMS (ESI\(^+\)): calcd for C\(_{29}\)H\(_{20}\)FN\(_2\)\(^+\)[M+H]\(^+\) 415.1605, found 415.1609.

11-Fluoro-7-methyl-2,3-di(naphthalen-2-yl)-7\(H\)-pyrido[4,3,2-\(kl\)]acridine (5i)

Following the general procedure II, 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a (29.2 mg, 0.1 mmol) and 1,2-di(naphthalen-2-yl)ethyne 2p (41.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5i as a yellow solid (42.6 mg, 85% yield). M.p.: > 185 °C. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz): \( \delta \) (ppm) 8.04 (s, 1H), 7.87 (d, \( J = 8.4 \) Hz, 2H), 7.82 (s, 1H), 7.76 (d, \( J = 8.0 \) Hz, 1H), 7.71 (d, \( J = 8.0 \) Hz, 1H), 7.68-7.56 (m, 3H), 7.54-7.32 (m, 7H), 7.09 (d, \( J = 8.0 \) Hz, 1H),
6.98 (d, \( J = 8.4 \) Hz, 1H), 6.93\--6.84 (m, 2H), 3.62 (s, 3H). \(^{13}\text{C}\) NMR (CD\(_2\)Cl\(_2\), 100 MHz): \( \delta \) (ppm) 162.5 (d, \( J = 258.0 \) Hz), 158.9, 153.5, 151.0, 149.1 (d, \( J = 7.9 \) Hz), 146.7, 144.8, 141.6, 138.6, 136.3, 134.1, 133.4, 133.0 (d, \( J = 8.5 \) Hz), 132.1, 132.0, 130.5 (d, \( J = 5.3 \) Hz), 129.9, 128.8, 128.4, 128.2, 127.8, 127.1, 126.6 (d, \( J = 4.2 \) Hz), 126.5, 126.2, 119.4, 114.7, 110.3 (d, \( J = 3.5 \) Hz), 109.6 (d, \( J = 22.6 \) Hz), 105.9, 35.5. \(^{19}\text{F}\) NMR (CD\(_2\)Cl\(_2\), 376 MHz): \( \delta \) (ppm) -107.9\--108.0 (m, 1F). HRMS (ESI\(^{+}\)): calcd for C\(_{36}\)H\(_{24}\)FN\(_2\)\([\text{M+H}]^{+}\) 503.1918, found 503.1921.

\[11\text{-Fluoro-7-methyl-2,3-di-p-tolyl-7H-pyrido}[4,3,2-kl]\text{acridine (5j)}\]

Following the general procedure II, 2-fluoro-\(N\)-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a (29.2 mg, 0.1 mmol) and 1,2-di-\(p\)-tolylenethyne 2h (30.9 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5j as a yellow solid (41.7 mg, 97% yield). M.p.: 237-238 °C. \(^{1}\text{H}\) NMR (CD\(_3\)Cl, 400 MHz): \( \delta \) (ppm) 7.47 (d, \( J = 8.0 \) Hz, 2H), 7.41 (t, \( J = 8.0 \) Hz, 1H), 7.38\--7.32 (m, 1H), 7.22\--7.15 (m, 4H), 7.02 (d, \( J = 8.0 \) Hz, 2H), 6.97 (d, \( J = 8.4 \) Hz, 1H), 6.94 (d, \( J = 8.4 \) Hz, 1H), 6.86\--6.79 (m, 1H), 6.70 (d, \( J = 7.6 \) Hz, 1H), 3.54 (s, 3H), 2.42 (s, 3H), 2.29 (s, 3H). \(^{13}\text{C}\) NMR (CD\(_3\)Cl, 100 MHz): \( \delta \) (ppm) 162.2 (d, \( J = 259.9 \) Hz), 150.9, 148.3 (d, \( J = 7.8 \) Hz), 144.2 (d, \( J = 4.4 \) Hz), 141.1, 138.3 (d, \( J = 8.6 \) Hz), 136.8 (d, \( J = 5.3 \) Hz), 135.5, 131.2 (d, \( J = 11.2 \) Hz), 131.1, 131.0, 130.7, 129.5, 128.3, 126.5 (d, \( J = 2.0 \) Hz), 118.9, 114.4, 112.5 (d, \( J = 7.8 \) Hz), 109.5, 109.3 (d, \( J = 3.8 \) Hz), 109.2, 104.8, 34.9, 21.5. \(^{19}\text{F}\) NMR (CD\(_3\)Cl, 376 MHz): \( \delta \) (ppm) -107.2 (dd, \( J = 11.7, J = 5.4 \) Hz, 1F). HRMS (ESI\(^{+}\)): calcd for C\(_{30}\)H\(_{22}\)FN\(_2\)\([\text{M+H}]^{+}\) 431.1918, found 431.1925.
11-Fluoro-7-methyl-2,3-di-\(m\)-tolyl-7\(H\)-pyrido[4,3,2-\(kl\)]acridine (5k)

Following the general procedure II, 2-fluoro-\(N\)-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a (29.2 mg, 0.1 mmol) and 1,2-di-\(m\)-tolylethyne 2m (30.9 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5k as a yellow solid (42.5 mg, 99% yield). M.p.: > 250 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) 7.48-7.42 (m, 2H), 7.40-7.33 (m, 1H), 7.31-7.23 (m, 2H), 7.18-7.09 (m, 2H), 7.08-6.93 (m, 5H), 6.29-6.81 (m, 1H), 6.73 (d, \(J = 8.0\) Hz, 1H), 3.56 (s, 3H), 2.35 (s, 3H), 2.27 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm) 162.2 (d, \(J = 259.6\) Hz), 150.9, 148.3 (d, \(J = 7.9\) Hz), 144.2 (d, \(J = 4.4\) Hz), 141.0 (d, \(J = 12.6\) Hz), 138.4, 138.2, 138.1, 136.9, 131.8, 131.6, 131.2 (d, \(J = 11.2\) Hz), 131.1, 128.6, 128.3, 127.9 (d, \(J = 3.0\) Hz), 127.8, 127.3, 126.9 (d, \(J = 2.1\) Hz), 119.0, 114.5, 112.4 (d, \(J = 7.7\) Hz), 109.5, 109.4 (d, \(J = 3.7\) Hz), 109.3, 104.9, 35.0, 21.66, 21.64. \(^{19}\)F NMR (CDCl\(_3\), 376 MHz): \(\delta\) (ppm) -107.1 (dd, \(J = 11.6\) Hz, \(J = 5.6\) Hz, 1F). HRMS (ESI\(^{+}\)): calcd for C\(_{30}\)H\(_{24}\)FN\(_2\)\(^{+}\) [M+H\(^{+}\)]\(^{+}\) 431.1918, found 431.1925.

\[\text{11-Fluoro-7-methyl-2,3-di-}m\text{-toly1-7H-pyrido[4,3,2-kl]acridine (5l)}\]

Following the general procedure II, 2-fluoro-\(N\)-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a (29.2 mg, 0.1 mmol) and 1,2-bis(4-methoxyphenyl)ethyne 2l (35.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5l as a yellow solid (37.0 mg, 80% yield). M.p.: 242-243 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) 7.54-7.51 (m, 2H), 7.43 (t, \(J = 8.2\) Hz, 1H), 7.40-7.34 (m, 1H), 7.21-7.17 (m, 2H), 7.01-6.94 (m, 4H), 6.87-6.81 (m, 1H), 6.77-6.74 (m, 2H), 6.72 (d, \(J = 8.0\) Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.57 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm) 162.2 (d, \(J = 259.5\) Hz), 150.8 (d, \(J = 9.5\) Hz), 150.6, 144.2 (d, \(J = 4.5\) Hz), 141.2, 138.5, 133.8, 132.3, 132.0, 131.2 (d, \(J = 11.3\) Hz), 131.1, 130.8, 125.7, 118.9, 114.32, 114.29, 113.1, 112.5 (d, \(J = 7.7\) Hz), 109.5, 109.4 (d, \(J = 3.7\) Hz), 109.3, 104.7, 55.4, 55.3, 35.0. \(^{19}\)F NMR (CDCl\(_3\), 376 MHz): \(\delta\) (ppm) -107.4 (dd, \(J = 11.6\) Hz, \(J = 5.2\) Hz, 1F). HRMS (ESI\(^{+}\)): calcd for C\(_{30}\)H\(_{24}\)FN\(_2\)\(^{+}\) [M+H\(^{+}\)]\(^{+}\) 463.1816, found 463.1822.
11-Fluoro-2,3-bis(3-methoxyphenyl)-7-methyl-7H-pyrido[4,3,2-kl]acridine (5m)
Following the general procedure II, 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a (29.2 mg, 0.1 mmol) and 1,2-bis(3-methoxyphenyl)ethyne 2n (35.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5m as a yellow solid (45.7 mg, 99% yield). M.p.: 207-208 °C. ^1H NMR (CDCl₃, 400 MHz): δ (ppm) 7.46 (t, J = 8.2 Hz, 1H), 7.41-7.31 (m, 2H), 7.24 (s, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.92-6.81 (m, 4H), 6.77 (s, 1H), 6.75 (s, 1H), 3.74 (s, 3H), 3.66 (s, 3H), 3.57 (s, 3H). ^13C NMR (CDCl₃, 100 MHz): δ (ppm) 162.3 (d, J = 259.9 Hz), 160.0, 158.9, 150.4 (d, J = 1.6 Hz), 148.5 (d, J = 8.1 Hz), 144.2 (d, J = 4.5 Hz), 142.3, 141.1, 139.9, 138.0, 131.3 (d, J = 11.3 Hz), 131.2, 129.9, 128.5, 126.5 (d, J = 1.9 Hz), 123.7, 123.3, 119.0, 116.5, 115.2, 114.4 (d, J = 10.0 Hz), 113.1, 109.5, 109.4 (d, J = 3.8 Hz), 109.3, 105.1, 55.4, 55.2, 35.0. ^19F NMR (CDCl₃, 376 MHz): δ (ppm) -107.2 (dd, J = 11.6 Hz, J = 5.3 Hz, 1F). HRMS (ESI^+): calced for C₃₀H₂₄F₅N₂O₂^+ [M+H]^+ 463.1816, found 463.1824.

11-Fluoro-2,3-bis(4-fluorophenyl)-7-methyl-7H-pyrido[4,3,2-kl]acridine (5n)
Following the general procedure II, 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a (29.2 mg, 0.1 mmol) and 1,2-bis(4-fluorophenyl)ethyne 2q (32.1 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5n as a yellow solid (41.2 mg, 94% yield). M.p.: 224-226 °C. ^1H NMR (CDCl₃, 400 MHz): δ (ppm) 7.51-7.45 (m, 3H), 7.42-7.26 (m, 1H), 7.25-7.19 (m, 2H), 7.14-7.07
(m, 2H), 6.99 (d, J = 8.8 Hz, 1H), 6.95-6.82 (m, 4H), 6.77 (d, J = 8.0 Hz, 1H), 3.58 (s, 3H). 13C NMR (CDCl₃, 100 MHz): δ (ppm) 162.3 (d, J = 251.2 Hz), 162.2 (d, J = 253.9 Hz), 162.1 (d, J = 245.3 Hz), 150.2, 148.8 (d, J = 7.8 Hz), 144.2 (d, J = 4.5 Hz), 141.2, 138.1, 137.1 (d, J = 3.7 Hz), 134.1 (d, J = 3.6 Hz), 132.9 (d, J = 7.8 Hz), 132.5 (d, J = 8.1 Hz), 131.5 (d, J = 10.2 Hz), 125.4 (d, J = 1.8 Hz), 119.0, 116.0 (d, J = 21.2 Hz), 114.6 (d, J = 21.2 Hz), 114.0, 112.2 (d, J = 7.7 Hz), 109.6, 109.5 (d, J = 3.8 Hz), 109.4, 105.2, 35.0. 19F NMR (CDCl₃, 376 MHz): δ (ppm) -107.2 (dd, J = 11.7 Hz, J = 5.5 Hz), -114.6 - -114.7 (m, 1F), -115.07 - -115.16 (m, 1F). HRMS (ESI⁺): calcd for C₂₉H₁₈F₃N₂⁺ [M+H]⁺ 439.1417, found 439.1420.

2,3-Bis(ethoxymethyl)-11-fluoro-7-methyl-7H-pyrdo[4,3,2-kl]acridine (5o)

Following the general procedure II, 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a (29.2 mg, 0.1 mmol) and 1,4-diethoxybut-2-yne 2r (21.3 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5o as a yellow solid (24.2 mg, 66% yield). M.p.: 119-120 °C. 1H NMR (CDCl₃, 400 MHz): δ (ppm) 7.59 (t, J = 8.0 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.39-7.32 (m, 1H), 6.95 (d, J = 8.8 Hz, 1H), 6.84-6.78 (m, 1H), 6.76 (d, J = 8.0 Hz, 1H), 4.92 (s, 2H), 4.88 (s, 2H), 3.70 (q, J = 7.2 Hz, 2H), 3.64 (q, J = 7.2 Hz, 2H), 3.54 (s, 3H), 1.29-1.23 (m, 6H). 13C NMR (CDCl₃, 100 MHz): δ (ppm) 162.2 (d, J = 259.7 Hz), 151.1, 148.9 (d, J = 7.7 Hz), 144.0 (d, J = 4.5 Hz), 141.1, 138.0, 131.4, 131.3 (d, J = 11.1 Hz), 122.2 (d, J = 1.7 Hz), 120.0, 112.8, 109.4, 109.3 (d, J = 27.1 Hz), 105.0, 73.6, 66.2, 65.84, 65.79, 34.9, 15.5, 15.4. 19F NMR (CDCl₃, 376 MHz): δ (ppm) -107.0 (dd, J = 12.0 Hz, J = 5.6 Hz, 1F). HRMS (ESI⁺): calcd for C₂₈H₂₃FN₂O₂⁺ [M+H]⁺ 367.1816, found 367.1815.
2,3-Diethyl-11-fluoro-7-methyl-7H-pyrido[4,3,2-kl]acridine (5p)

Following the general procedure II, 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a (29.2 mg, 0.1 mmol) and hex-3-yne 2o (12.3 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded 5p as a yellow oil (29.7 mg, 97% yield). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) 7.53 (t, \(J = 8.2\) Hz, 1H), 7.36-7.28 (m, 1H), 7.24 (d, \(J = 8.4\) Hz, 1H), 6.92 (d, \(J = 8.8\) Hz, 1H), 6.84-6.77 (m, 1H), 6.66 (d, \(J = 8.0\) Hz, 1H), 3.52 (s, 3H), 3.01-2.91 (m, 4H), 1.43 (t, \(J = 7.6\) Hz, 3H), 1.25 (t, \(J = 7.6\) Hz, 3H). \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm) 162.0 (d, \(J = 259.0\) Hz), 154.7, 146.8 (d, \(J = 8.6\) Hz), 144.0 (d, \(J = 4.6\) Hz), 141.7, 136.8, 130.8, 130.6 (d, \(J = 11.3\) Hz), 125.6, 119.1, 111.7, 109.4, 109.3 (d, \(J = 3.5\) Hz), 109.2, 103.7, 34.9, 28.5, 21.2, 14.2, 13.9. \(^{19}\)F NMR (CDCl\(_3\), 376 MHz): \(\delta\) (ppm) -108.1 (dd, \(J = 12.0\) Hz, \(J = 5.6\) Hz, 1F). HRMS (ESI\(^+\)): calcd for C\(_{20}\)H\(_{20}\)FN\(_2\) [M+H]\(^+\) 307.1605, found 307.1609.

[Structure image of 2,3-Diethyl-11-fluoro-7-methyl-7H-pyrido[4,3,2-kl]acridine (5p)]

2,3-Diphenyl-7H-dibenzo[de,h]quinolin-7-one (7a)

Following the general procedure III, 2-benzyl-N-methoxybenzimidoyl chloride 6 (38.9 mg, 0.15 mmol) and 1,2-diphenylethyne 2a (17.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 7a as a yellow solid (31.8 mg, 83% yield). M.p.: > 250 °C. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz): \(\delta\) (ppm) 9.03 (d, \(J = 7.6\) Hz, 1H), 8.56 (d, \(J = 7.6\) Hz, 1H), 8.42 (d, \(J = 8.4\) Hz, 1H), 8.03 (d, \(J = 8.4\) Hz, 1H), 7.89-7.81 (m, 2H), 7.70 (t, \(J = 8.0\) Hz, 1H), 7.56-7.49 (m, 2H), 7.46-7.39 (m, 3H), 7.35-7.31 (m, 2H), 7.30-7.24 (m, 3H). The \(^{13}\)C NMR data could not be recorded due to its poor solubility. HRMS (ESI\(^+\)): calcd for C\(_{28}\)H\(_{18}\)NO\(_3\) [M+H]\(^+\) 384.1383, found 384.1383.
2,3-Bis(4-(tert-butyl)phenyl)-7H-dibenzo[de,h]quinolin-7-one (7b)

Following the general procedure III, 2-benzyl-N-methoxybenzimidoyl chloride 6 (38.9 mg, 0.15 mmol) and 1,2-bis(4-(tert-butyl)phenyl)ethyne 2j (29.0 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 7b as a yellow solid (37.1 mg, 75% yield). M.p.: > 250 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 9.08-9.06 (m, 1H), 8.67-8.65 (m, 1H), 8.46-8.44 (m, 1H), 8.09 (dd, $J = 8.4$ Hz, $J = 1.0$ Hz, 1H), 7.84-7.78 (m, 2H), 7.68-7.64 (m, 1H), 7.47-7.41 (m, 4H), 7.29-7.27 (m, 1H), 7.25-7.20 (m, 3H), 1.39 (s, 9H), 1.31 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 184.0, 151.6, 150.9, 150.5, 147.3, 137.7, 137.2, 136.0, 134.0, 133.9, 133.1, 132.5, 131.4, 131.2, 130.32, 130.28, 129.3, 129.1, 127.5, 125.8, 125.4, 124.7, 121.6, 34.8, 34.7, 31.5, 31.4. HRMS (ESI$^+$): calcd for C$_{36}$H$_{34}$NO$^+$ [M+H]$^+$ 496.2635 found 496.2642.

2,3-Di-m-tolyl-7H-dibenzo[de,h]quinolin-7-one (7c)

Following the general procedure III, 2-benzyl-N-methoxybenzimidoyl chloride 6 (38.9 mg, 0.15 mmol) and 1,2-di-m-tolylyne 2m (20.6 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 7c as a yellow solid (31.2 mg, 76% yield). M.p.: > 250 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 9.07 (d, $J = 7.6$ Hz, 1H), 8.67 (d, $J = 7.2$ Hz, 1H), 8.46 (d, $J = 7.6$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.85-7.80 (m, 2H), 7.70-7.64 (m, 1H), 7.41 (s, 1H), 7.33-7.26 (m, 2H), 7.21 (d, $J = 7.6$ Hz, 1H), 7.17-7.11 (m, 2H), 7.10-7.05 (m, 2H), 2.37 (s, 3H), 2.31 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 184.0, 151.6, 147.4, 140.5, 138.1, 137.3, 137.1, 136.9, 135.8, 134.1, 133.1, 132.5, 132.1, 131.6,

2,3-Bis(4-bromophenyl)-7H-dibenzo[de,h]quinolin-7-one (7d)

Following the general procedure III, 2-benzyl-N-methoxybenzimidoyl chloride 6 (38.9 mg, 0.15 mmol) and 1,2-bis(4-bromophenyl)ethyne 2l (33.4 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded 7d as a yellow solid (51.2 mg, 95% yield). M.p.: > 250 °C. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 9.01-8.98 (m, 1H), 8.68 (dd, J = 7.2 Hz, J = 0.8 Hz, 1H), 8.46-8.42 (m 1H), 7.98 (dd, J = 8.8 Hz, J = 1.2 Hz, 1H), 7.88-7.80 (m, 2H), 7.70-7.66 (m, 1H), 7.61-7.57 (m, 2H), 7.46-7.42 (m, 2H), 7.39-7.35 (m, 2H), 7.20-7.16 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 183.6, 150.3, 148.2, 139.3, 136.7, 135.6, 135.5, 134.2, 133.0, 132.5, 132.3, 132.2, 132.1, 131.3, 131.0, 130.8, 130.1, 129.8, 129.2, 127.7, 125.7, 122.5, 122.4, 121.8. HRMS (ESI⁺): calcd for C₂₈H₁₆Br₂NO⁺ [M+H]⁺ 529.9593, found 539.9602; calcd for C₂₈H₁₆Br₂BrNO⁺ [M+H]⁺ 541.9573, found 541.9573; calcd for C₂₈H₁₆Br₂NO⁺ [M+H]⁺ 543.9552, found 543.9558.

1-Fluoro-10-methylacridin-9(10H)-one O-methyl oxime (8)

Following the general procedure II, reaction of 2-fluoro-N-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a (29.2 mg, 0.1 mmol) was conducted in the absence of an alkyne component. Purification via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded 8 as a white solid (13.1 mg, 51% yield, major isomer: minor isomer = 1.7:1) M.p.: 119-121 °C. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.41 (dd, J = 8.0 Hz, J =
1.6 Hz, 1H for major isomer), 7.85 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H for minor isomer), 7.45-7.26 (m, 2H for two isomers), 7.15-7.04 (m, 2H for two isomers), 6.90-6.76 (m, 2H for two isomers), 4.06 (s, 3H, for minor isomer), 4.05 (s, 3H, for major isomer), 3.53 (s, 3H for two isomers). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ (ppm) for two isomers, 160.0 (d, J = 254.2 Hz), 159.7 (d, J = 251.3 Hz), 144.7 (d, J = 8.0 Hz), 144.0 (d, J = 4.8 Hz), 143.2 (d, J = 3.5 Hz), 142.8 (d, J = 6.0 Hz), 142.4, 141.1, 131.1 (d, J = 10.5 Hz), 130.9, 130.7, 129.8 (d, J = 11.0 Hz), 129.6, 124.8, 121.9, 120.0, 117.7, 113.5, 112.9, 109.7 (d, J = 14.7 Hz), 108.8, 108.7 (d, J = 3.5 Hz), 108.6 (d, J = 2.9 Hz), 108.6, 108.0, 107.8, 62.7, 62.6, 34.7, 34.4. $^{19}$F NMR (CDCl$_3$, 376 MHz): δ (ppm) -96.1 (dd, J = 9.6, J = 6.1 Hz), -114.7 (dd, J = 10.4, J = 5.7 Hz). HRMS (ESI$^+$): calcd for C$_{15}$H$_{14}$FN$_2$O$^+ [M+H]$^+$ 257.1085 found 257.1086.

X. Single crystal X-ray structures of 3b, 3d, 3e, 3f, 5g, 5h, 7d

Figure S1. ORTEP diagrams of 3b, 3d, 3e, 3f, 5h, 5i and 7d. Thermal ellipsoids are shown at the 50% probability level. CCDC 1899576 (3b), CCDC 1913390 (3d), CCDC 1899575 (3e), CCDC
1899578 (3f), CCDC 1899572 (5g), CCDC 1899579 (5h), and CCDC 1899574 (7d) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**XI. References**

XII. Copies of NMR spectra:

$^1$H NMR spectra of 1b (CDCl$_3$)

$^{13}$C NMR spectra of 1b (CDCl$_3$)
$^1$H NMR spectra of 1e (CDCl$_3$)

$^{13}$C NMR spectra of 1e (CDCl$_3$)
$^1$H NMR spectra of 1d (CDCl₃)

$^{13}$C NMR spectra of 1d (CDCl₃)
$^1$H NMR spectra of 1e (CDCl$_3$)

$^{13}$C NMR spectra of 1e (CDCl$_3$)
$^1$H NMR spectra of 1f (CDCl$_3$)

$^{13}$C NMR spectra of 1f (CDCl$_3$)
$^1$H NMR spectra of 4a (CDCl$_3$)

$^{13}$C NMR spectra of 4a (CDCl$_3$)
$^{19}$F NMR spectra of 4a (CDCl$_3$)

$^1$H NMR spectra of 4b (CDCl$_3$)
$^{13}$C NMR spectra of 4b (CDCl$_3$)

$^{19}$F NMR spectra of 4b (CDCl$_3$)
$^1$H NMR spectra of 4c (CDCl$_3$)

$^{13}$C NMR spectra of 4c (CDCl$_3$)
$^{19}$F NMR spectra of 4c (CDCl$_3$)

$^1$H NMR spectra of 4d (CDCl$_3$)
$^{13}$C NMR spectra of 4d (CDCl$_3$)

$^{19}$F NMR spectra of 4d (CDCl$_3$)
$^1$H NMR spectra of 4e (CDCl$_3$)

$^{13}$C NMR spectra of 4e (CDCl$_3$)
$^{19}$F NMR spectra of 4e (CDCl$_3$)

$^1$H NMR spectra of 4f (CDCl$_3$)
$^{13}$C NMR spectra of 4f (CDCl$_3$)

$^{19}$F NMR spectra of 4f (CDCl$_3$)
$^1$H NMR spectra of 4g (CDCl$_3$)

$^{13}$C NMR spectra of 4g (CDCl$_3$)
$^{19}$F NMR spectra of 4g (CDCl$_3$)

$^1$H NMR spectra of 4h (CDCl$_3$)
$^{13}$C NMR spectra of 4h (CDCl$_3$)

$^1$H NMR spectra of 6 (CDCl$_3$)
$^{13}$C NMR spectra of 6 (CDCl$_3$)

$^1$H NMR spectra of 3a (CDCl$_3$)
$^{13}$C NMR spectra of 3a (CDCl$_3$)

$^1$H NMR spectra of 3b (CDCl$_3$)
$^{13}$C NMR spectra of 3b (CDCl$_3$)

$^1$H NMR spectra of 3c (CDCl$_3$)
$^{13}$C NMR spectra of 3c (CDCl$_3$)

$^1$H NMR spectra of 3d (CDCl$_3$)
$^{13}$C NMR spectra of 3d (CDCl$_3$)

$^1$H NMR spectra of 3e (CDCl$_3$)
$^{13}$C NMR spectra of 3e (CDCl$_3$)

$^1$H NMR spectra of 3f (CDCl$_3$)
$^{13}$C NMR spectra of $3f$ (CDCl$_3$)

$^1$H NMR spectra of $3g$ (CDCl$_3$)
$^{13}$C NMR spectra of 3g (CDCl₃)

$^1$H NMR spectra of 3h (CDCl₃)
$^{13}$C NMR spectra of 3h (CDCl$_3$)

$^1$H NMR spectra of 3i (CDCl$_3$)
$^{13}$C NMR spectra of 3i (CDCl$_3$)

$^1$H NMR spectra of 3j (CDCl$_3$)
$^1$H NMR spectra of 3j (CDCl$_3$)

$^{13}$C NMR spectra of 3k (CDCl$_3$)
$^1$H NMR spectra of 3l (CDCl$_3$)

$^{13}$C NMR spectra of 3k (CDCl$_3$)
$^{13}$C NMR spectra of 3l (CDCl$_3$)

$^1$H NMR spectra of 3m (CDCl$_3$)
$^{13}$C NMR spectra of 3m (CDCl$_3$)

$^1$H NMR spectra of 3n (CDCl$_3$)
$^{13}$C NMR spectra of 3n (CDCl$_3$)

$^1$H NMR spectra of 3o (CDCl$_3$)
$^{13}$C NMR spectra of 3o (CDCl$_3$)

$^1$H NMR spectra of 5a (CDCl$_3$)
$^{13}$C NMR spectra of 5a (CDCl$_3$)

$^{19}$F NMR spectra of 5a (CDCl$_3$)
$^1$H NMR spectra of 5b (CDCl$_3$)

$^{13}$C NMR spectra of 5b (CDCl$_3$)
$^{19}$F NMR spectra of $5b$ (CDCl$_3$)

$^1$H NMR spectra of $5c$ (CD$_2$Cl$_2$)
$^{13}$C NMR spectra of 5c (CD$_2$Cl$_2$)

$^{19}$F NMR spectra of 5c (CD$_2$Cl$_2$)
$^1$H NMR spectra of 5d (CDCl$_3$)

$^{13}$C NMR spectra of 5d (CDCl$_3$)
$^{19}$F NMR spectra of 5d (CDCl$_3$)

$^1$H NMR spectra of 5e (CDCl$_3$)
$^{13}$C NMR spectra of 5e (CDCl$_3$)

$^{19}$F NMR spectra of 5e (CDCl$_3$)
$^1$H NMR spectra of 5f (CDCl$_3$)

$^{13}$C NMR spectra of 5f (CDCl$_3$)
$^{19}$F NMR spectra of $5f$ (CDCl$_3$)

$^1$H NMR spectra of $5g$ (CDCl$_3$)
$^{13}$C NMR spectra of 5g (CDCl$_3$)

$^{19}$F NMR spectra of 5g (CDCl$_3$)
$^1$H NMR spectra of 5h (CD$_2$Cl$_2$)

$^1$H NMR spectra of 5i (CD$_2$Cl$_2$)
$^{13}$C NMR spectra of $5i$ (CD$_2$Cl$_2$)

$^{19}F$ NMR spectra of $5i$ (CD$_2$Cl$_2$)
$^1$H NMR spectra of 5j (CDCl$_3$)

$^{13}$C NMR spectra of 5j (CDCl$_3$)
$^{19}$F NMR spectra of 5j (CDCl$_3$)

$^1$H NMR spectra of 5k (CDCl$_3$)
$^{13}$C NMR spectra of 5k (CDCl$_3$)

$^{19}$F NMR spectra of 5k (CDCl$_3$)
$^1$H NMR spectra of 5l (CDCl$_3$)

$^{13}$C NMR spectra of 5l (CDCl$_3$)
$^{19}$F NMR spectra of 5l (CDCl₃)

$^1$H NMR spectra of 5m (CDCl₃)
$^{13}$C NMR spectra of 5m (CDCl$_3$)

$^{19}$F NMR spectra of 5m (CDCl$_3$)
$^1$H NMR spectra of 5n (CDCl₃)

$^{13}$C NMR spectra of 5n (CDCl₃)
$^{19}$F NMR spectra of $5n$ (CDCl$_3$)

$^1$H NMR spectra of $5o$ (CDCl$_3$)
$^{13}$C NMR spectra of 5o (CDCl$_3$)

$^{19}$F NMR spectra of 5o (CDCl$_3$)
$^1$H NMR spectra of 5p (CDCl$_3$)

$^{13}$C NMR spectra of 5p (CDCl$_3$)
$^{19}$F NMR spectra of 5p (CDCl$_3$)

$^1$H NMR spectra of 7a (CD$_2$Cl$_2$)
$^1$H NMR spectra of 7b (CDCl$_3$)

$^{13}$C NMR spectra of 7b (CDCl$_3$)
$^1$H NMR spectra of 7c (CDCl$_3$)

$^{13}$C NMR spectra of 7c (CDCl$_3$)
$^1$H NMR spectra of 7d (CDCl$_3$)

$^{13}$C NMR spectra of 7d (CDCl$_3$)
$^1$H NMR spectra of 8 (CDCl$_3$)

$^{13}$C NMR spectra of 8 (CDCl$_3$)
$^{19}$F NMR spectra of 8 (CDCl₃)