Palladium and radical routes to phenanthridines

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We wish to dedicate this paper to mark Professor Keith Smith’s retirement

Abstract
Two routes to phenanthridines are reported; a palladium-mediated route using imidoyl-selanides as precursors and a modified radical route using aryl imines as starting materials.

Keywords: Phenanthridines, palladium, imines, radicals, imidoyl-selanides

Introduction
Phenanthridines are an important class of heterocyclic compounds first discovered in 1891 by Pictet and Ankersmit. They show a range of biological activities, and are currently attracting significant interest from synthetic chemists. The majority of established synthetic routes utilise anionic ring closure reactions, Bischler-Napieralski reactions, reduction of phenanthridones, palladium chemistry, or free radical methodology. A number of new syntheses of the phenanthridines have been reported recently, underlining their importance. Recently we have published a palladium-mediated route to phenanthidine, as part of our interest in the development of new methods to prepare heterocyclic systems which include stoichiometric organometallics, biomimetic methods, condensation of reactive electrophilic systems, and radical chemistry. We now wish to disclose the full details of our palladium work together with an improved phenanthidine synthesis by a radical method from imines.

Results and Discussion
Our first proposed route to phenanthridines involves the key Pd-mediated C-C bond formation of the central pyridine ring from the imidoyl-selanides. The imidoyl-selanides can in turn be derived from the corresponding amides which are readily prepared from commercially
available 2-aminobiphenyl 4 by well-established amide bond formation chemistry, such as simple reaction with aromatic acid chlorides (Scheme 1). We chose imidoyl selanides because the weak imidoyl-Se bond was predicted to facilitate Pd(0) insertion and they had proved good precursors for radical reactions.\textsuperscript{14} Also it has been shown that transition metals can insert into the carbon-selenium bond.\textsuperscript{15}

![Scheme 1](image)

**Scheme 1.** Proposed synthesis of phenanthridines 1.

The required amides 3 were prepared, in reasonable yields, by standard methods from 2-aminobiphenyl 4 and aryl acid chlorides (Scheme 2, Table 1). A representative range of 4-substituted aryl acid chlorides was chosen to prepare the amides 3, in order to observe the electronic effect on the insertion of palladium into the Se-C bond of the imidoyl-selanides 2 (Table 1). The amides 3 were converted into the appropriate $\alpha$–chloroimines by treatment with phosgene and catalytic DMF.\textsuperscript{16} We found other methods of preparing the $\alpha$–chloroimines were unsatisfactory for further reactions. The potassium salt of phenylselanide was prepared *in situ* by reduction of diphenyl diselanide with K-Selectride\textsuperscript{®} and added directly to the un-purified $\alpha$–chloroimines to give the imidoyl-selanides 2 (Scheme 2, Table 1).\textsuperscript{14} Some hydrolysis of the imidoyl-selanides 2 was observed upon both silica and alumina chromatography, therefore the imidoyl-selanides 2 were used either after purification by crystallization, or rapid chromatography, and in some cases as the crude mixture.

![Scheme 2](image)

**Scheme 2.** Synthetic route to imidoyl-selanides 2a-2h.
Table 1. Yields of amides 3a-3h and imidoyl-selanides 2a-2h

<table>
<thead>
<tr>
<th>Derivative</th>
<th>R Group</th>
<th>Amide 3 Yield (%)</th>
<th>Selanide 2 Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>52</td>
<td>54</td>
</tr>
<tr>
<td>b</td>
<td>Me</td>
<td>64</td>
<td>44</td>
</tr>
<tr>
<td>c</td>
<td>t-Bu</td>
<td>59</td>
<td>66</td>
</tr>
<tr>
<td>d</td>
<td>OMe</td>
<td>70</td>
<td>51</td>
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<tr>
<td>e</td>
<td>Cl</td>
<td>64</td>
<td>60</td>
</tr>
<tr>
<td>f</td>
<td>CF₃</td>
<td>77</td>
<td>60</td>
</tr>
<tr>
<td>g</td>
<td>NMe₂</td>
<td>61</td>
<td>62</td>
</tr>
<tr>
<td>h</td>
<td>NO₂</td>
<td>47 Decomposed</td>
<td></td>
</tr>
</tbody>
</table>

With an array of imidoyl-selanides 2 in hand we attempted the proposed Pd-mediated cyclisation to phenanthridines 1. A large range of conditions have been reported for palladium catalyzed reactions, so in order to limit the number of variables in the preliminary reactions we initially used the conventional Pd(PPh₃)₄ as the palladium source without additional ligands. It is foreseeable that other palladium sources, or the inclusion of ligands, will also be applicable and we are keen to explore their potential in due course.

The parent imidoyl-selanide (R = H) 2a was first treated with 10% Pd(PPh₃)₄ and excess triethylamine under a range of trial reaction conditions. In DCM, THF, or MeCN, no reactions took place at either room temperature or at reflux. Complex mixtures were observed when the reactions were carried out at 80 °C in DMF or chlorobenzene, with no discernible sign of the desired product. However, when the reaction was carried out at 80 °C in the non-polar solvent, toluene, a trace of the desired phenanthidine 1a was detected in the crude mixture. The ¹H NMR spectrum of the crude mixture clearly showed the characteristic peaks of the phenanthidine ring. Encouraged by this result the reaction was repeated at reflux in toluene for 48 hours which gave a 10% isolated yield. A further improvement in yield was seen when the amount of palladium catalyst was increased to 0.4 equiv. With these positive conditions in hand, the range of imidoyl-selanides 2a-2g previously prepared were treated with Pd(PPh₃)₄ (0.4 equiv.) and excess triethylamine in toluene at reflux for 48 hours, to successfully produce the respective phenanthridines 1a-1g (Scheme 3, Table 2).

Scheme 3. Pd-mediated cyclisation to phenanthridines 1a-1g.
Table 2. Yields of phenanthridines 1a-1g

<table>
<thead>
<tr>
<th>Phenanthridine</th>
<th>R Group</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>H</td>
<td>28</td>
</tr>
<tr>
<td>1b</td>
<td>Me</td>
<td>34</td>
</tr>
<tr>
<td>1c</td>
<td>t-Bu</td>
<td>47</td>
</tr>
<tr>
<td>1d</td>
<td>OMe</td>
<td>39</td>
</tr>
<tr>
<td>1e</td>
<td>Cl</td>
<td>46</td>
</tr>
<tr>
<td>1f</td>
<td>CF₃</td>
<td>48</td>
</tr>
<tr>
<td>1g</td>
<td>NMe₂</td>
<td>22</td>
</tr>
</tbody>
</table>

The phenanthridines 1a-1g were isolated in synthetically useful yields that are currently un-optimised. The electronic effect of the substitution on the aromatic ring (R) did not appear to affect the reaction. In the absence of the base there was no reaction or significantly reduced yield. Attempts to cyclise the α-chloroimines, precursors of the imidoyl-selanides, under all conditions failed to give any signs of the phenanthridines in our hands to date. We are pleased with these initial results and a wider range of targets is currently under investigation using imidoyl-selanides and Pd-mediated conditions. We are also looking at optimising the reaction conditions by using a different base, palladium source and ligands that are known to enhance Pd-catalysis.

Mechanistically, we propose insertion of a Pd(0) species into the carbon selenium bond followed by carbo-palladation onto the phenyl ring. This intermediate then undergoes rapid rearomatization with the loss of HPdSePh to give the phenanthridine system (Scheme 4).

![Scheme 4. Proposed mechanism of Pd-mediated cyclisation of phenanthidine 1.](image)

Incidentally, while we were looking up spectral data of the phenanthridines prepared using the previously described novel palladium chemistry, we became aware of some leading work by
Leardini et al. in the 1980s. These workers had shown under radical conditions imines were suitable precursors to a range of phenanthridines (Scheme 5). Using di-iso-propyl peroxy carbonate (DPDC) they showed that a range of imines (Scheme 5) could be cyclised to give phenanthridines in good yields, in hot benzene. The reaction proceeds by initial imidoyl-H atom abstraction by the electrophilic i-PrO· radical, and subsequently the intermediate undergoes intramolecular cyclization and oxidative aromatization to form the phenanthidine ring.

Scheme 5. Radical reaction reported by Leardini et al.

With our experience in radical chemistry, we decided to enhance this methodology as part of our interests in the field of phenanthridines. We considered that the use of di-iso-propyl peroxy carbonate (DPDC) is somewhat of a drawback due to its explosive nature, thus requiring additional safety precautions and limiting its potential application. In place of di-iso-propyl peroxy carbonate (DPDC), we planned to use di-(tert-butyl)peroxide, which is reported not to be explosive under normal conditions, as a safer alternative. Homolysis of the di-(tert-butyl)peroxide, which can be facilitated by heat, yields the strongly electrophilic radical t-BuO·, which should be an ideal substitute for i-PrO· and a similar reaction followed.

The desired aryl imines were readily prepared by standard methods in decent yields. 2-Aminobiphenyl 4 and an aryl aldehyde were stirred together in dichloromethane in the presence of molecular sieves at room temperature to give the required imines 5a-5h (Scheme 6, Table 3).

Scheme 6. Preparation of imines 5a-5h.

With the imines in hand we could attempt the improved radical conditions for the reaction. Homolysis of the di-(tert-butyl)peroxide occurs at 120 °C, therefore a high boiling point solvent was required. Our initial attempts to cyclise the imine 5a was carried out in chlorobenzene using two equivalents of the peroxide at 125 °C. The 1H NMR spectrum showed no trace of the desired
product. The boiling point of di-(tert-butyl)peroxide is 109 °C and it was therefore thought that homolysis was not occurring or was undergoing evaporation prior to homolysis. This problem was solved by repeating the reaction in a sealed vessel and heating the reaction mixture to 140-150 °C (oil bath temperature) which led to the desired product in 48% yield. The purified phenanthridine showed an identical $^1$H NMR spectrum to the sample previously prepared by Pd catalysis. The un-optimised yield was somewhat lower that reported by Leardini using DPDC, but this does provide a safer alternative especially when scaling up.

**Table 3. Yields of imines 5a-5h**

<table>
<thead>
<tr>
<th>Imine</th>
<th>R Group</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>H</td>
<td>60</td>
</tr>
<tr>
<td>5b</td>
<td>Me</td>
<td>66</td>
</tr>
<tr>
<td>5c</td>
<td>$t$-Bu</td>
<td>68</td>
</tr>
<tr>
<td>5d</td>
<td>OMe</td>
<td>78</td>
</tr>
<tr>
<td>5e</td>
<td>Cl</td>
<td>79</td>
</tr>
<tr>
<td>5f</td>
<td>CF$_3$</td>
<td>58</td>
</tr>
<tr>
<td>5g</td>
<td>NMe$_2$</td>
<td>66</td>
</tr>
<tr>
<td>5h</td>
<td>NO$_2$</td>
<td>86</td>
</tr>
</tbody>
</table>

With this gratifying result in-hand we decided to look at a range of substituents on the aldehyde component of the reaction. The choice of a $p$-substituted benzaldehyde reflects the possible influence of electronic effects and also parallels our palladium chemistry. In addition it expands on the limited range of examples Leardini had reported. All the imines were prepared in reasonably yields (Table 4) and used shortly after preparation to avoid potential hydrolysis or oxidation problems. The imines 5b-5h were submitted to the radical cyclisation conditions, di-(tert-butyl)peroxide (2 equiv.) in chlorobenzene at 140-150 °C for 48 h, to yield the corresponding phenanthridines 1b-1h in moderate yields (Scheme 7, Table 4). There was no significant difference in the results with respect to the effect of the functional group on the cyclisation.

**Scheme 7. Synthesis of phenanthridines 1a-1h by radical cyclisation.**
Table 4. Yields of phenanthridines 1a-1h

<table>
<thead>
<tr>
<th>Phenanthidine</th>
<th>R Group</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>H</td>
<td>40</td>
</tr>
<tr>
<td>1b</td>
<td>Me</td>
<td>44</td>
</tr>
<tr>
<td>1c</td>
<td>t-Bu</td>
<td>39</td>
</tr>
<tr>
<td>1d</td>
<td>OMe</td>
<td>50</td>
</tr>
<tr>
<td>1e</td>
<td>Cl</td>
<td>48</td>
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<tr>
<td>1f</td>
<td>CF₃</td>
<td>51</td>
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<tr>
<td>1g</td>
<td>NMe₂</td>
<td>42</td>
</tr>
<tr>
<td>1h</td>
<td>NO₂</td>
<td>46</td>
</tr>
</tbody>
</table>

The mechanism for the formation of the phenanthridines is that of homolytic aromatic substitution. The t-BuO· radical abstracts the imine-H forming the imidoyl radical, which then adds to the phenyl ring. The homolytic aromatic substitution is then terminated by H-atom abstraction by another radical such as a t-BuO· radical.

![Scheme 8. Proposed homolytic aromatic substitution mechanism of phenanthridine 1 formation.](image)

Conclusions

We are pleased with the initial palladium results and the modified radical reaction conditions for the preparation of phenanthridines, but there is plenty of scope for optimising both the radical and palladium reaction conditions, such as using alternative palladium sources, the addition of ligands, and different base/solvent combinations. Currently, we are investigating further chemistry of the imidoyl-selenides/palladium methodology to synthesise a wide range of heterocyclic targets other than phenanthridines. Moreover, our research into the development of
new palladium reactions and radical reactions to the same target could lead to a valuable direct comparison of radical and palladium reactions in the generation of important heterocyclic compounds.

**Experimental Section**

**General.** Infrared spectra were obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer in the range of 4000-600 cm⁻¹ (with internal calibration). Samples were dissolved in the appropriate solvent and applied to sodium chloride plates as thin films. In the case of liquid samples, they were applied neat to the plates and run as thin films. Only the major absorbances have been quoted.

¹H NMR spectra were measured at 400 MHz and ¹³C NMR spectra were measured at 100 MHz (unless stated otherwise), using a Bruker AC 400 MHz spectrometer. The solvent used for spectroscopy was CDCl₃ (unless stated otherwise) using TMS as the internal reference. Chemical shifts are given in part per million (ppm) and coupling constants (J values) are given in hertz (Hz). Assignment of individual proton signals was assisted by analysis of ¹H COSY spectra.

Melting points were obtained using an electrical 9100 Thermal melting point instrument and are uncorrected.

All solvents and reagents were purified by standard technique or used as supplied from chemical sources as appropriate. Light petrol refers to the fraction which boils at 40-60 °C Reagent chemicals were purchased from Aldrich Chemical Company Ltd, Lancaster Chemical Synthesis Ltd and Acros (Fischer) Chemicals Ltd. Solvents when necessary were dried and stored over 4Å molecular sieves prior to use.

**General experimental procedure for the preparation of the benzamides 3**

To a solution of 2-aminobiphenyl 4 (1.0 equiv.) and Et₃N (2.0 equiv.) in CH₂Cl₂ (0.3 ml/mmol) at 0 °C was added acid chloride (1.0 equiv.). The reaction was warmed to rt and stirred for 5 h. The reaction mixture was then washed with water, sat. NaHCO₃ solution, and brine. The organics were dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by trituration with DCM and hexanes. The resulting solid was filtered off and dried under vacuum to yield pure benzamide 3.

**N-Biphenyl-2-yl benzamide (3a).** Benzoyl chloride (0.34 ml, 2.95 mmol) yielded N-biphenyl-2-yl benzamide 3a (419 mg, 52%) as off-white crystals mp 87-88 °C. δH (400 MHz, CDCl₃) 7.43 (13H, m, Ar-H), 8.00 (1H, s, NH), 8.54 (1H, d, J 8.4, Ar-H); δC (100 MHz, CDCl₃) 121.1 (Ar-CH), 124.4 (Ar-CH), 126.8 (2 x Ar-CH), 128.2 (Ar-CH), 128.6 (Ar-CH), 128.7 (2 x Ar-CH), 129.2 (2 x Ar-CH), 129.4 (2 x Ar-CH), 130.0 (Ar-CH), 131.7 (Ar-CH), 132.3 (Ar-C), 134.8 (Ar-C), 134.9 (Ar-C), 138.0 (Ar-C), 165.0 (C=O); HRMS (FAB⁺) Found: [M+H⁺] 274.1234. C₁₀H₁₆NO requires 274.1232; m/z (FAB⁺) 274 ([M+H⁺], 73%), 273 (46), 105 (100), 77 (25).
**N-Biphenyl-2-yl-4-methyl benzamide (3b)**. Toluoyl chloride (0.39 ml, 2.95 mmol) yielded N-biphenyl-2-yl benzamide 3b (540 mg, 64%) as off-white crystals mp 108-109 °C. $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3190, 1620, 1590; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 2.37 (3H, s, CH$_3$), 7.23 (4H, m, Ar-H), 7.47 (8H, m, Ar-H), 7.98 (1H, s, NH), 8.54 (1H, dd, J 0.8, 8, Ar-H); $\delta_{\text{C}}$ (100 MHz, CDCl$_3$) 21.4 (CH$_3$), 121.0 (Ar-CH), 124.2 (Ar-CH), 126.8 (2 x Ar-CH), 128.1 (Ar-CH), 128.6 (Ar-CH), 129.2 (2 x Ar-CH), 129.4 (4 x Ar-CH), 130.0 (Ar-CH), 131.9 (Ar-C), 132.2 (Ar-C), 135.0 (Ar-C), 138.1 (Ar-C), 142.3 (Ar-C), 164.9 (C=O); HRMS (FAB$^+$) Found: [M+H$^+$] 288.1388. C$_{20}$H$_{18}$NO requires 288.1388; $m/z$ (FAB$^+$) 288 ([M+H$^+$], 75%), 119 (100), 102 (44).

**N-Biphenyl-2-yl-4-(tert-butyl)benzamide (3c)**. 4-tert-Butylbenzoyl chloride (2.16 ml, 11.82 mmol) yielded N-biphenyl-2-yl-4-(tert-butyl) benzamide 3c (2.29 g, 59%) as off white crystals mp 160-161 ºC. $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3370, 1620; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 1.31 [9H, s, C(CH$_3$)$_3$-H], 7.21 (1H, dt, J 1.2, 7.2, Ar-H), 7.29 (1H, dd, J 1.6 7.2, Ar-H), 7.24 (6H, m, Ar-H), 7.53 (4H, m, Ar-H), 8.02 (1H, s, NH), 8.57 (1H, d, J 8, Ar-H); $\delta_{\text{C}}$ (100 MHz, CDCl$_3$) 31.1 (C(CH$_3$)$_3$), 34.9 [C(CH$_3$)$_3$], 121.0 (Ar-CH), 124.2 (Ar-CH), 125.7 (2 x Ar-CH), 126.7 (2 x Ar-CH), 128.2 (Ar-CH), 128.6 (Ar-CH), 129.2 (2 x Ar-CH), 130.0 (Ar-CH), 131.8 (Ar-C), 132.2 (Ar-C), 135.1 (Ar-C), 138.1 (Ar-C), 155.3 (Ar-C), 164.8 (C=O); HRMS (FAB$^+$) Found: [M+H$^+$] 330.1858. C$_{22}$H$_{23}$NO requires 330.1858; $m/z$ (FAB$^+$) 330 ([M+H$^+$], 100%), 329 (47), 161 (91).

**N-Biphenyl-2-yl-4-methoxybenzamide (3d)**. 4-Methoxybenzoyl chloride (0.40 ml, 2.95 mmol) yielded N-biphenyl-2-yl-4-methoxybenzamide 3d (630 mg, 70%) as an off white solid mp 131-132 ºC. $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 382 (3H, s, CH$_3$), 3.82 (3H, s, Ar-H), 6.87 (2H, m, Ar-H), 7.20 (1H, dt, J 1.2, 7.2, Ar-H), 7.28 (1H, m, Ar-H), 7.49 (8H, m, Ar-H), 7.93 (1H, s, NH), 8.52 (1H, m, Ar-H); $\delta_{\text{C}}$ (100 MHz, CDCl$_3$) 55.4 (OCH$_3$), 113.9 (2 x Ar-CH), 121.0 (Ar-H), 124.1 (Ar-C), 127.0 (Ar-C), 128.1 (Ar-CH), 128.6 (2 x Ar-CH), 128.7 (2 x Ar-CH), 129.2 (2 x Ar-CH), 129.4 (Ar-CH), 129.9 (Ar-CH), 132.1 (Ar-C), 135.1 (Ar-C), 138.1 (Ar-C), 162.4 (Ar-COME), 164.5 (C=O); HRMS (FAB$^+$) Found: [M+H$^+$] 303.1260. C$_{20}$H$_{17}$NO$_2$ requires 303.1259; $m/z$ (FAB$^+$) 304 ([M+H$^+$], 100%) 303 (39), 135 (9).

**N-Biphenyl-2-yl-4-chlorobenzamide (3e)**. 4-Chlorobenzoyl chloride (2.29 ml, 18.02 mmol) yielded N-biphenyl-2-yl-4-chlorobenzamide 3e (3.57 g, 64%) as white crystals mp 104-105 ºC. $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3253, 1650, 1050; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 7.23 (1H, dt, J 1.2, 7.6, Ar-H), 7.31 (1H, dd, J 1.6, 7.6, Ar-H), 7.36 (2H, m, Ar-H), 7.44 (4H, m, Ar-H), 7.52 (4H, m, Ar-H), 7.93 (1H, s, NH), 8.49 (1H, d, J 8.0, Ar-H); $\delta_{\text{C}}$ (100 MHz, CDCl$_3$) 121.1 (Ar-CH), 124.6 (Ar-CH), 128.2 (2 x Ar-CH), 128.3 (Ar-CH), 128.6 (Ar-CH), 129.0 (2 x Ar-CH), 129.2 (2 x Ar-CH), 129.3 (2 x Ar-CH), 130.0 (Ar-CH), 132.3 (Ar-C), 133.1 (Ar-C), 134.6 (Ar-C), 137.9 (Ar-C), 138.0 (Ar-C), 163.9 (C=O); HRMS (FAB$^+$) Found: [M+H$^+$] 308.0841. C$_{19}$H$_{15}$NOCl requires 308.0842; $m/z$ (FAB$^+$) 308 ([M+H$^+$], 100%), 307 (68), 154 (22), 141 (32), 139 (96).

**N-(Biphenyl-2-yl-4-trifluoromethyl)benzamide (3f)**. 4-Trifluoromethylbenzoyl chloride (1.32 ml, 8.86 mmol) yielded N-(biphenyl-2-yl-4-trifluoro methyl) benzamide 3f (2.33 g, 77%) as off-white crystals mp 127-128 ºC. $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3325, 1650; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 7.25 (1H, m, Ar-H), 7.33 (1H, dd, J 1.6, 7.6, Ar-H), 7.45 (4H, m, Ar-H), 7.53 (2H, m, Ar-H), 7.68 (4H, dd, J 8.4, 18.8 Ar-H), 8.00 (1H, s, NH), 8.51 (1H, d, J 8.4, Ar-H); $\delta_{\text{C}}$ (100 MHz, CDCl$_3$) 121.2 (Ar-C),...
124.8 (CF3), 125.8 (2 x Ar-CH), 125.9 (2 x Ar-CH), 127.3 (2 x Ar-CH), 128.4 (2 x Ar-CH), 128.7 (2 x Ar-CH), 129.3 (2 x Ar-CH), 130.1 (Ar-CH), 132.5 (Ar-C), 134.5 (Ar-C), 137.9 (Ar-C), 138.0 (Ar-C), 163.8 (C=O); HRMS (FAB⁺) Found: [M+H⁺] 342.1103. C29H14F3NO requires 342.1106; m/z (FAB⁺) 342 ([M+H⁺] 88%), 341 (57), 173 (100), 145 (44).

**N-Biphenyl-2-yl-4-dimethylaminobenzamide (3g).** 4-Dimethylaminobenzoyl chloride (1.63 g, 8.86 mmol) yielded N-biphenyl-2-yl-4-dimethylamino benzamide 3g (1.72 g, 61%) as off white crystals mp 204-205 °C. νmax (KBr)/cm⁻¹ 3370, 1650; δH (400 MHz, CDCl3) 2.99 [6H, s, N(CH3)2], 6.60 (2H, dd, J 2.0, 6.8, Ar-H), 7.17 (1H, dt, J 1.2, 7.6, Ar-H), 7.26 (1H, dd, J 1.2, 7.6, Ar-H), 7.46 (8H, m, Ar-H), 7.92 (1H, s, NH), 8.57 (1H, dd, J 1.2, 8.4, Ar-H); δC (100 MHz, CDCl3) 40.1 (2 x NH), 7.34 (2H, m, Ar-H), 7.50 (6H, m, Ar-H), 7.75 (2H, d, J 8.8, Ar-H), 8.00 (1H, s, NH), 8.24 (2H, m, Ar-H), 8.50 (1H, d, J 8, Ar-H); δC (100 MHz, CDCl3) 121.2 (Ar-CH), 124.0 (2 x Ar-CH), 125.1 (Ar-CH), 128.0 (2 x Ar-CH), 128.5 (Ar-CH), 129.2 (2 x Ar-CH), 129.4 (2 x Ar-CH), 129.9 (Ar-CH), 131.8 (Ar-C), 135.5 (Ar-C), 138.3 (Ar-C), 152.5 (Ar-C), 165.0 (C=O); HRMS (FAB⁺) Found: [M+H⁺] 317.1659. C19H19N2O requires 317.1654; m/z (FAB⁺) 317 ([M+H⁺], 46%), 316 (38), 148 (100).

**N-Biphenyl-2-yl-4-nitrobenzamide (3h).** 4-Nitrobenzoyl chloride (1.64 g, 8.86 mmol) yielded N-biphenyl-2-yl-4-nitrobenzamide 3h (1.24 g, 44%) as an off-white solid mp 109-110 °C. νmax (KBr)/cm⁻¹ 1364; δH (400 MHz, CDCl3) 7.28 (1H, m, Ar-H), 7.34 (2H, m, Ar-H), 7.50 (6H, m, Ar-H), 7.75 (2H, d, J 8.8, Ar-H), 8.00 (1H, s, NH), 8.24 (2H, m, Ar-H), 8.50 (1H, d, J 8, Ar-H); δC (100 MHz, CDCl3) 121.2 (Ar-CH), 124.0 (2 x Ar-CH), 125.1 (Ar-CH), 128.0 (2 x Ar-CH), 128.5 (Ar-CH), 129.2 (2 x Ar-CH), 129.4 (2 x Ar-CH), 130.1 (Ar-CH), 132.7 (Ar-C), 134.2 (Ar-C), 137.7 (Ar-C), 140.3 (Ar-C), 149.7 (C=O); HRMS (FAB⁺) Found: [M+H⁺] 319.1088. C19H14N2O3 requires: 319.1083; m/z (FAB⁺) 319 ([M+H⁺], 29%), 176 (40), 154 (100), 136 (58).

**General experimental procedures for the preparation of the imidoyl-selanides 2**

To a solution of amide 3 (1.0 equiv.) in dry CH2Cl2 (8 ml/mmoll) under inert atmosphere was added dry DMF (1 drop/mmoll) and phosgene (3.0 equiv.). The reaction mixture was stirred at rt for 5 h. The volatiles were then removed under reduced pressure to give the crude imidoyl chloride as a residue.

K-Selectride® (1M THF solution, 1.1 equiv.) was added to a solution of (PhSe)2 (0.5 equiv.) in THF (10 ml/mmoll) to form a white suspension. In a separate flask, the crude imidoyl chloride was re-dissolved in dry THF (8 ml/mmoll) and the solution was cannulated into the suspension. The reaction mixture was stirred at rt overnight. The solvent was then removed under reduced pressure and the residue was partitioned between water (8 ml/mmoll) and CH2Cl2 (8 ml/mmoll). The organics were separated, dried over MgSO4, filtered and concentrated under reduced pressure to give crude imidoyl-selanide product 2. No further purification was carried out in most cases.

**Phenyl-N-biphenyl-2-ylbenzimidoseleenoate (2a).** Amide 3a (1.39 g, 5.09 mmoll) yielded phenyl-N-biphenyl-2-ylbenzimidoseleenoate 2a (1.74 g crude) and it was carried on to the next reaction without further purification.
**N-Biphenyl-2-yl-4-methylselenobenzimidic acid phenyl ester (2b).** Amide 3b (1.00 g, 3.48 mmol) yielded N-biphenyl-2-yl-4-methylselenobenzimidic acid phenyl ester 2b (655 mg crude) as a pale yellow solid mp 104-105 °C. \( \nu_{\text{max}} \) (KBr)/cm\(^{-1}\) 1627, 1535; \( \delta_H \) (400 MHz, CDCl\(_3\)) 2.21 (3H, s, CH\(_3\)), 7.22 (18H, m, Ar-H); \( \delta_C \) (100 MHz, CDCl\(_3\)) 21.3 (CH\(_3\)), 120.1 (Ar-CH), 125.1 (2 x Ar-CH), 126.9 (Ar-CH), 127.4 (2 x Ar-CH), 127.9 (2 x Ar-CH), 128.0 (2 x Ar-CH), 128.4 (2 x Ar-CH), 128.7 (2 x Ar-CH), 129.1 (Ar-CH), 129.7 (Ar-C), 129.8 (2 x Ar-CH), 130.4 (Ar-CH), 131.8 (Ar-C), 134.9 (Ar-CH), 135.3 (Ar-C), 139.7 (Ar-C), 140.0 (Ar-C), 149.1 (C=\(\text{N}\)); HRMS (FAB\(^+\)) Found: [M+H\(^+\)] 428.0916. C\(_{26}\)H\(_{22}\)NSe requires 428.0917; m/z (FAB\(^+\)) 428 (67%), 427 (100), 91 (56).

**N-Biphenyl-2-yl-4-tert-butyl selenobenzimidic acid phenyl ester (2c).** Amide 3c (1.00 g, 3.04 mmol) yielded N-biphenyl-2-yl-4-tert-butyl selenobenzimidic acid phenyl ester 2c (1.53 g, crude) and it was carried on to the next reaction without further purification.

**N-Biphenyl-2-yl-4-methoxyselenobenzimidic acid phenyl ester (2d).** Amide 3d (2.10 g, 6.63 mmol) yielded N-biphenyl-2-yl-4-methoxyselenobenzimidic acid phenyl ester 2d (51% crude) and it was carried on to the next reaction without further purification.

**N-Biphenyl-2-yl-4-chloroselenobenzimidic acid phenyl ester (2e).** Amide 3e (1.00 g, 3.25 mmol) yielded N-biphenyl-2-yl-4-chloroselenobenzimidic acid phenyl ester 2e (659 mg, 60%) as yellow crystals mp 116-117 °C. It was carried on to the next reaction without further purification. Decomposition occurred before spectra could be recorded.

**N-(Biphenyl-2-yl-4-trifloromethyl)selenobenzimidic acid phenyl ester (2f).** Amide 3f (2.26 g, 6.63 mmol) yielded N-(biphenyl-2-yl-4-trifloromethyl) selenobenzimidic acid phenyl ester 2f (1.91 g, 60%) as pale yellow crystals mp 116-117 °C. \( \nu_{\text{max}} \) (KBr)/cm\(^{-1}\) 1627, 1573; \( \delta_H \) (400 MHz, CDCl\(_3\)) 7.01 (6H, m, Ar-H), 7.32 (10H, m, Ar-H), 7.56 (2H, d, J 7.2, Ar-H); \( \delta_C \) (100 MHz, CDCl\(_3\)) 119.6 (Ar-CH), 124.5 (Ar-CH), 124.6 (Ar-CH), 125.1 (Ar-C), 125.5 (Ar-CH), 127.1 (Ar-CH), 127.9 (2 x Ar-CH), 128.1 (Ar-CH), 128.2 (Ar-CH), 128.5 (Ar-C), 128.9 (2 x Ar-CH), 129.1 (Ar-CH), 129.6 (Ar-CH), 129.8 (2 x Ar-CH), 130.6 (Ar-CH), 131.0 (Ar-CH), 131.3 (Ar-C), 131.8 (Ar-C), 135.5 (Ar-CH), 139.5 (Ar-C), 141.3 (Ar-C), 148.7 (Ar-C), 163.5 (C=\(\text{N}\)); HRMS (FAB\(^+\)) Found: [M+H\(^+\)] 482.0638. C\(_{26}\)H\(_{18}\)F\(_3\)N\(_8\)O\(_{10}\)Se requires 482.0635; m/z (FAB\(^+\)) 482 ([M+H\(^+\)] 80Se, 13%), 480 (78Se, 7%), 480 (78Se, 7%), 325 (70), 324 (100), 178 (24), 152 (52).

**Phenyl-N-biphenyl-2-yl-4-(dimethylamino)benzimidoseleanoate (2g).** Amide 3g (1.50 g, 4.74 mmol) yielded phenyl-N-biphenyl-2-yl-4-(dimethylamino) benzimidoseleanoate 2g (282 mg, 62% crude) and it was carried on to the next reaction without further purification.

**General experimental procedure for the preparation of imine 5**

To a solution of 2-aminobiphenyl 4 (1.0 equiv.) in CH\(_2\)Cl\(_2\) (2 ml/mmol) in the presence of 4Å molecular sieves was added aldehyde (1.0 equiv.). The reaction mixture was stirred at rt for 5 h. It was then filtered through a pad of Celite and washed with excess DCM. The filtrate was concentrated under reduced pressure to give imine product 5 without further purification.
Benzylidene biphenyl-2-yl amine (5a). Benzaldehyde (0.30 ml, 2.95 mmol) yielded benzylidene biphenyl-2-yl amine 5a (455 mg, 60%) as a yellow oil. The crude imine 5a was directly carried on to the next reaction without isolation.

Biphenyl-2-yl-(4-methylbenzylidene) amine (5b). p-Tolualdehyde (0.35 ml, 2.95 mmol) yielded biphenyl-2-yl-(4-methylbenzylidene) amine 5b (592 mg, 66%) as yellow crystals mp 79-80 °C. v_max (KBr/cm\(^{-1}\)) 1630, 1627, 1087; δ_H (400 MHz, CDCl\(_3\)) 7.06 (1H, dd, J 1.2, 8, Ar-H), 7.29 (2H, m, Ar-H), 7.36 (3H, m, Ar-H), 7.47 (5H, m, Ar-H), 7.73 (2H, d, J 8.4, Ar-H), 8.44 (imine-H); δ_C (100 MHz, CDCl\(_3\)) 130.4 (Ar-C), 135.9 (Ar-C), 139.5 (Ar-C), 149.9 (Ar-C), 154.7 (Ar-C), 160.1 (imine-C); HRMS (FAB\(^{+}\)) Found: [M+H\(^{+}\)] 272.1439. C\(_{20}\)H\(_{19}\)N requires 272.1439; m/z (FAB\(^{+}\)) 272 ([M+H\(^{+}\]), 100%), 271 (55), 270 (31), 180 (56).

Biphenyl-2-yl-(4-tert-butylenzylidene) amine (5c). 4-tert-Butylbenzaldehyde (0.49 ml, 2.95 mmol) yielded biphenyl-2-yl-(4-tert-butylenzylidene) amine 5c (770 mg, 86%) as a yellow oil. v_max (neat)/cm\(^{-1}\) 1630, 1540; δ_H (400 MHz, CDCl\(_3\)) 1.34 (9H, s, iBu-H), 7.06 (1H, dd, J 1.2, 8, Ar-H), 7.29 (2H, m, Ar-H), 7.36 (3H, m, Ar-H), 7.47 (5H, m, Ar-H), 7.73 (2H, d, J 8.4, Ar-H), 8.44 (imine-H); δ_C (100 MHz, CDCl\(_3\)) 31.2 (C(CH\(_3\))\(_3\)), 35.0 (C(CH\(_3\))\(_3\)), 119.0 (Ar-CH), 125.7 (2 x Ar-CH), 125.8 (Ar-CH), 127.7 (2 x Ar-CH), 127.8 (Ar-CH), 127.9 (Ar-CH), 129.3 (2 x Ar-CH), 130.2 (2 x Ar-CH), 130.3 (Ar-CH), 133.9 (Ar-C), 135.3 (Ar-C), 135.9 (Ar-C), 139.5 (Ar-C), 149.9 (Ar-C), 154.7 (Ar-C), 160.1 (imine-C); HRMS (FAB\(^{+}\)) Found: [M+H\(^{+}\)] 314.1911. C\(_{23}\)H\(_{26}\)N requires 314.1909; m/z (FAB\(^{+}\)) 314 ([M+H\(^{+}\]), 64%), 169 (44), 148 (100), 57 (20).

Biphenyl-2-yl-(4-methoxybenzylidene) amine (5d). 4-Methoxybenzaldehyde (0.36 ml, 2.95 mmol) yielded biphenyl-2-yl-(4-methoxybenzylidene) amine 5d (661 mg, 78%) as a yellow oil. The crude imine 5d was directly carried on to the next reaction without isolation.

Biphenyl-2-yl-(4-chlorobenzylidene) amine (5e). 4-Chlorobenzaldehyde (378 mg, 2.69 mmol) yielded biphenyl-2-yl-(4-chlorobenzylidene) amine 5e (619 mg, 79%) as yellow crystals mp 83-84 °C (lit. 7 89-90°C). v_max (thin film)/cm\(^{-1}\) 1627, 1087; δ_H (400 MHz, CDCl\(_3\)) 7.06 (1H, dd, J 1.2, 7.6, Ar-H), 7.38 (10H, m, Ar-H), 7.70 (2H, dt, J 2, 8.8, Ar-H), 8.40 (1H, s, imine-H); δ_C (100 MHz, CDCl\(_3\)) 118.7 (Ar-C), 126.2 (Ar-CH), 126.8 (Ar-CH), 127.7 (2 Ar-CH), 128.4 (Ar-CH), 129.0 (2 Ar-CH), 129.9 (2 Ar-CH), 130.2 (2 Ar-CH), 130.4 (Ar-CH), 134.8 (Ar-C), 135.4 (Ar-C), 137.2 (Ar-C), 139.4 (Ar-C), 149.2 (2'-C), 158.8 (7-C); HRMS (FAB\(^{+}\)) Found: [M+H\(^{+}\)] 292.0897. C\(_{19}\)H\(_{15}\)NCl\(_{2}\) requires 292.0893; m/z (FAB\(^{+}\)) 292 ([M+H\(^{+}\]), 70%), 291 (32), 290 (31), 180 (100), 152 (26).

Biphenyl-2-yl-(4-trifluoromethylbenzylidene) amine (5f). 4-Trifluoromethylbenzaldehyde (0.40 ml, 2.95 mmol) yielded biphenyl-2-yl-(4-trifluoromethyl benzylidene) amine 5f (561 mg, 58%) as yellow crystals mp 97-98 °C. v_max (KBr/cm\(^{-1}\)) 1630; δ_H (400 MHz, CDCl\(_3\)) 7.09 (1H, dd, J 1.6 8.0, Ar-H), 7.32 (5H, m, Ar-H), 7.47 (3H, m, Ar-H), 7.66 (2H, d, J 8.4, Ar-H), 7.88 (2H, d, J 8.0, Ar-H), 8.49 (1H, s, imine-H); δ_C (100 MHz, CDCl\(_3\)) 118.6 (Ar-CH), 125.5 (CF\(_3\)), 125.6 (Ar-CH), 125.7 (Ar-CH), 125.8 (Ar-C), 126.6 (Ar-CH), 126.9 (Ar-CH), 127.8 (2 x Ar-CH), 128.4 (Ar-CH), 129.0 (2 x Ar-CH), 130.2 (2 x Ar-CH), 130.5 (Ar-CH), 135.6 (Ar-C), 139.3 (Ar-C), 149.9 (Ar-C), 154.7 (Ar-C), 160.1 (imine-C).
was added Pd(PPh₃)₄ as a yellow crystals mp 82-83 °C.

7.34 (3H, m, Ar-H), 7.44 (1H, dd, J 1.2, 7.2, Ar-H), 7.51 (2H, m, Ar-H), 7.67 (2H, dd, J 2.0, 7.2, Ar-H), 8.32 (1H, s, imine-H); δC (100 MHz, CDCl₃) 40.1 (2 x CH₃), 111.5 (2 x Ar-CH), 119.2 (Ar-CH), 124.8 (Ar-C), 125.1 (Ar-CH), 126.5 (Ar-CH), 127.6 (2 x Ar-CH), 128.3 (Ar-CH), 130.2 (Ar-CH), 130.3 (2 x Ar-CH), 130.4 (2 x Ar-CH), 135.1 (Ar-C), 135.8 (Ar-C), 150.6 (Ar-C), 152.4 (Ar-C), 160.0 (imine-C); HRMS (FAB⁺) Found: [M+H⁺] 301.1704. C₂₁H₂₁N₂ requires 301.1705; m/z (FAB⁺) 301 ([M+H⁺], 100%), 300 (88), 299 (61), 180 (66).

Biphenyl-2-yl-(4-dimethylaminobenzylidene) amine (5g). 4-Dimethylaminobenzaldehyde (446 mg, 2.95 mmol) yielded biphenyl-2-yl-(4-dimethylamino benzylidene) amine 5g (770 mg, 86%) as yellow crystals mp 105-106 °C (lit.° 106-107°C). δH (400 MHz, CDCl₃) 7.13 (1H, dd, J 1.2, 7.6, Ar-H), 7.39 (7H, m, Ar-H), 7.50 (1H, dd, J 2.0, 7.2, Ar-H), 7.95 (2H, dt, J 2.2, 88, Ar-H), 8.28 (2H, dt, J 2, 8.8, Ar-H), 8.56 (1H, s, imine-H); δC (100 MHz, CDCl₃) 118.4 (Ar-C), 141.7 (Ar-C), 149.2 (Ar-C), 157.5 (imine-C); HRMS (FAB⁺) Found: [M⁺] 303.1136. C₁₀H₁₄N₂O₂ requires 303.1134; m/z (FAB⁺) 303 (M⁺, 100%), 302 (63), 180 (65), 154 (47), 136 (30).

General experimental procedure for the preparation of phenanthridine 1 by Pd catalysis
To a solution of imidoyl-selanide 2 (1.0 equiv.) in toluene (5 ml/mmol) under inert atmosphere was added Pd(PPh₃)₄ (0.4 equiv.) and triethylamine (5.0 equiv.). The reaction mixture was refluxed for 48 h. The solvent was then removed under reduced pressure. The residue was dissolved in DCM (10 ml/mmol), washed with water, sat. NaHCO₃ solution and brine. The organics were dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography to yield phenanthridine product 1.

6-Phenylphenanthridine (1a).° Imidoyl-selanide 2a (400 mg, 0.97 mmol) yielded 6-phenyl phenanthridine 1a (59 mg, 24%) after column chromatography (Alumina, 25% DCM in hexanes) as white crystals mp 101-102°C (lit.° 103-105 °C). δH (400 MHz, CDCl₃) 7.66 (8H, m, Ar-H), 7.88 (1H, dt J 1.2, 7.2, Ar-H), 8.12 (1H, dd, J 0.4, 8.4, Ar-H), 8.25 (1H, dd, J 1.6, 8.4, Ar-H), 8.64 (1H, dd, J 1.2, 8.0, Ar-H), 8.72 (1H, d, J 8.4, Ar-H); δC (100 MHz, CDCl₃) 122.0 (2 x Ar-CH), 122.2 (2 x Ar-CH), 123.8 (Ar-C), 125.2 (Ar-C), 127.0 (Ar-CH), 127.2 (Ar-CH), 128.5 (2 x Ar-CH), 128.8 (Ar-CH), 128.9 (Ar-CH), 129.0 (Ar-CH), 129.8 (2 x Ar-CH), 130.7 (Ar-CH), 133.5 (Ar-C), 137.0 (Ar-C), 161.3 (Ar-C=N); HRMS (FAB⁺) Found: [M⁺] 255.1049. C₁₀H₁₃N requires 255.1048; m/z (FAB⁺) 255 ([M⁺], 87%), 77 (100).
6-(4-Tolyl)phenanthridine (1b). Imidoyl-selenide 2b (250 mg, 0.59 mmol) yielded 6-(4-tolyl)phenanthridine 1b (60 mg, 38%) after column chromatography (alumina, 25% DCM in hexanes) as white crystals mp 107-109 °C (lit.2b 107.5-108 °C). \( \nu_{\text{max}} \) (KBr)/cm\(^{-1}\) 2925, 1610; \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 2.48 (3H, s, CH\(_3\)), 7.37 (2H, m, Ar-H), 7.69 (5H, m, Ar-H), 7.86 (1H, dt, J 1.2, 7.2, Ar-H), 8.14 (1H, m, Ar-H), 8.24 (1H, dd, J 1.2, 7.6, Ar-H), 8.62 (1H, dd, J 1.6, 8.4, Ar-H), 8.71 (1H, d, J 8.0, Ar-H); \( \delta_{\text{C}} \) (100 MHz, CDCl\(_3\)) 21.4 (CH\(_3\)), 121.9 (Ar-CH), 122.2 (Ar-CH), 123.7 (Ar-C), 125.3 (Ar-C), 126.8 (Ar-CH), 127.1 (Ar-CH), 128.8 (Ar-CH), 129.0 (Ar-CH), 129.1 (2 x Ar-CH), 129.7 (2 x Ar-CH), 130.3 (Ar-CH), 130.5 (Ar-CH), 133.5 (Ar-C), 136.9 (Ar-C), 138.6 (Ar-C), 143.9 (Ar-C), 161.3 (Ar-C=N); HRMS (FAB\(^+\)) Found: [M+H\(^+\)] 270.1280. C\(_{20}\)H\(_{16}\)N requires 270.1283; m/z (FAB\(^+\)) 270 ([M+H\(^+\)], 88%), 180 (100).

6-(4-tert-Butylyphenyl)phenanthridine (1c). Imidoyl-selenide 2c (600 mg, 1.28 mmol) yielded 6-(4-tert-butylphenyl)phenanthridine 1c (187 mg, 47%) after column chromatography (alumina, 25% DCM in hexanes) as a clear oil. \( \nu_{\text{max}} \) (KBr)/cm\(^{-1}\) 1560; \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 1.41 (9H, s, C(CH\(_3\))\(_3\)), 7.63 (6H, m, Ar-H), 7.75 (1H, m, Ar-H), 7.85 (1H, m, Ar-H), 8.19 (1H, dd, J 0.8, 8.0, Ar-H), 8.27 (1H, d, J 8.0, Ar-H), 8.61 (1H, dd, J 1.2, 8.0, Ar-H), 8.70 (1H, d, J 8.0, Ar-H); \( \delta_{\text{C}} \) (100 MHz, CDCl\(_3\)) 31.5 (C(CH\(_3\))\(_3\)), 34.8 (C(CH\(_3\))), 121.9 (Ar-CH), 122.2 (Ar-CH), 123.7 (Ar-C), 125.2 (Ar-C), 125.4 (2 x Ar-CH), 126.7 (Ar-CH), 126.8 (Ar-CH), 128.8 (Ar-CH), 129.1 (Ar-CH), 129.5 (2 x Ar-CH), 130.2 (Ar-CH), 130.6 (Ar-CH), 133.5 (Ar-C), 136.7 (Ar-C), 143.7 (Ar-C), 151.8 (Ar-C), 161.3 (C=N); HRMS (FAB\(^+\)) Found: [M+H\(^+\)] 312.1753. C\(_{23}\)H\(_{22}\)N requires 312.1752; m/z (FAB\(^+\)) 312 ([M+H\(^+\)], 100%), 180 (35) 134 (50).

6-(4-Methoxyphenyl)phenanthridine (1d). Imidoyl-selenide 2d (500 mg, 1.13 mmol) yielded 6-(4-methoxyphenyl)phenanthridine 1d (128 mg, 39%) after column chromatography (alumina, 50% DCM in hexanes) as white crystals mp 144-145 °C (lit.7 149-150 °C). \( \nu_{\text{max}} \) (KBr)/cm\(^{-1}\) 1650, 1575; \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 3.80 (3H, s, CH\(_3\)), 6.63 (2H, m, Ar-H), 6.81 (1H, dd, J 1.2, 8.0, Ar-H), 6.88 (1H, m, Ar-H), 7.01 (1H, m, Ar-H), 7.11 (1H, m, Ar-H), 7.18 (1H, dd, J 1.2, 8.0, Ar-H), 7.38 (2H, m, Ar-H), 7.55 (2H, m, Ar-H), 7.71 (1H, m, Ar-H); \( \delta_{\text{C}} \) (100 MHz, CDCl\(_3\)) 56.7 (OCH\(_3\)), 114.5 (2 x Ar-CH), 121.9 (Ar-C), 124.2 (Ar-CH), 126.9 (Ar-C), 128.4 (Ar-CH), 128.6 (2 x Ar-CH), 128.9 (2 x Ar-CH), 129.1 (2 x Ar-CH), 129.3 (Ar-CH), 130.2 (Ar-CH), 132.3 (Ar-C), 135.6 (Ar-C), 137.4 (Ar-C), 138.5 (Ar-C), 161.7 (Ar-COMe); HRMS (FAB\(^+\)) Found: [M+H\(^+\)] 286.1233. C\(_{20}\)H\(_{16}\)NO requires 286.1232; m/z (FAB\(^+\)) 286 ([M+H\(^+\)], 80%), 285 (100), 254 (55), 241 (30).

6-(4-Chlorophenyl)phenanthridine (1e). Imidoyl-selenide 2e (80 mg, 0.18 mmol) yielded 6-(4-chlorophenyl)phenanthridine 1e (23 mg, 46%) after column chromatography (alumina, 20% DCM in hexanes) as white crystals mp 152-154 °C (lit.7 160-161 °C). \( \nu_{\text{max}} \) (neat)/cm\(^{-1}\) 2358; \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 7.54 (2H, m, Ar-H), 7.64 (1H, m, Ar-H), 7.70 (3H, m, Ar-H), 7.77 (1H, m, Ar-H), 7.88 (1H, m, Ar-H), 8.06 (1H, dd, J 0.8, 8.4, Ar-H), 8.23 (1H, dd, J 1.2, 8.4, Ar-H), 8.63 (1H, dd, J 1.6, 8.4, Ar-H), 8.72 (1H, d, J 8.4, Ar-H); \( \delta_{\text{C}} \) (100 MHz, CDCl\(_3\)) 122.0 (Ar-CH), 122.4 (Ar-CH), 123.8 (Ar-C), 125.0 (Ar-C), 127.2 (Ar-CH), 127.3 (Ar-CH), 128.5 (Ar-CH), 128.7 (2 x Ar-CH), 129.0 (Ar-CH), 130.4 (Ar-CH), 130.7 (Ar-CH), 131.1 (2 x Ar-CH), 133.5 (2 x Ar-C), 134.9 (Ar-C), 134.8 (Ar-C=Cl), 160.0 (Ar-C=N); HRMS (FAB\(^+\)) Found: [M+H\(^+\)] 290.0732.
C_{19}H_{13}NCl requires 290.0736; m/z (FAB^+) 290 ([M+H^+], 67%), 289 (38), 176 (22), 155 (24), 154 (100), 138 (25), 137 (48), 136 (61).

6-(4-Trifluoromethylphenyl)phenanthridine (1f). Imidoyl-selenide 2f (259 mg, 0.54 mmol) yielded 6-(4-trifluoromethylphenyl)phenanthridine 1f (84 mg, 48%) after column chromatography (alumina, 25% DCM in hexanes) as white crystals mp 174-175 °C. ν_{max} (KBr)/cm^{-1} 2368, 1111; δ_{H} (400 MHz CDCl_{3}) 7.65 (1H, dd, J 1.2, 7.2, Ar-H), 7.73 (1H, dd, J 1.6, 7.2, Ar-H), 7.79 (1H, dd, J 1.6, 7.2, Ar-H), 7.87 (5H, m, Ar-H), 8.03 (1H, d, J 8.4, Ar-H); δ_{C} (100 MHz, CDCl_{3}) 122.0 (Ar-C_{H}), 122.4 (Ar-C_{H}), 123.9 (Ar-C), 124.9 (Ar-C), 125.4 (CF_{3}), 125.5 (2 x Ar-C), 125.6 (Ar-C), 127.4 (2 x Ar-C), 128.3 (Ar-CH), 129.1 (Ar-CH), 130.2 (2 x Ar-CH), 130.4 (Ar-CH), 130.9 (Ar-CH), 133.5 (Ar-C), 143.4 (Ar-C), 143.7 (Ar-C), 159.7 (Ar-C=N); HRMS (FAB^+) Found: [M+H^+] 325.1004. C_{20}H_{13}NF_{3} requires 325.1000; m/z (FAB^+) 324 ([M+H^+], 100%), 323 (21).

6-(4-Dimethylaminophenyl)phenanthridine (1g). Imidoyl-selenide 2g (109 mg, 0.24 mmol) yielded 6-(4-dimethylaminophenyl)phenanthridine 1g (16 mg, 22%) after column chromatography (alumina, 25% DCM in hexanes) as white crystals mp 155-157 °C. ν_{max} (KBr)/cm^{-1} 1625; δ_{H} (400 MHz, CDCl_{3}) 3.00 (6H, s, N(CH_{3})_{2}), 7.55 (1H, dd, J 1.2, 7.2, Ar-H), 7.70 (1H, dd, J 1.6, 7.2, Ar-H), 7.80 (1H, dd, J 1.6, 7.2, Ar-H), 7.86 (5H, m, Ar-H), 8.01 (1H, dd, J 0.8, 8.4, Ar-H), 8.30 (1H, m, Ar-H), 8.66 (1H, dd, J 1.6, 8.0, Ar-H), 8.76 (1H, d, J 8.4, Ar-H); δ_{C} (100 MHz, CDCl_{3}) 40.7 (2 x CH_{3}), 112.1 (2 x Ar-CH), 118.9 (Ar-CH), 124.8 (Ar-C), 124.9 (Ar-CH), 126.5 (3 x Ar-CH), 128.1 (Ar-CH), 129.9 (Ar-CH), 130.1 (2 x Ar-CH), 130.2 (2 x Ar-CH), 134.9 (Ar-C), 139.9 (Ar-C), 150.0 (Ar-C), 152.7 (Ar-C), 160.0 (Ar-C=N); HRMS (FAB^+) Found: [M+H^+] 299.1548. C_{21}H_{19}N_{2} requires 299.1548; m/z (FAB^+) 299 ([M+H^+], 100%), 120 (56).

General experimental procedure for the preparation of phenanthridine 1 by radical cyclisation

To a solution of the imine 5 (1.0 equiv.) in PhCl (2 ml/mmol) in a Young’s tube was added di-tert-butylperoxide (2.0 equiv.). The reaction vessel was deoxygenated by flushing with inert gas for 15 min, then sealed and heated at 140 °C for 48 h. The reaction mixture was allowed to cool to rt and quenched with NaHSO_{3} solution to remove any unreacted peroxide. The aqueous layer was then extracted with DCM (3 x 10 ml/mmol). The combined organics were washed with water, brine, dried over MgSO_{4}, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography to yield phenanthridine product 1.

6-Phenylphenanthridine (1a). Imine 5a (350 mg, 1.36 mmol) yielded 6-phenyl phenanthridine 1a (138 mg, 40%) after purification. Characterisation data is the same as above.

6-(4-Tolyl)phenanthridine (1b). Imine 5b (320 mg, 1.11 mmol) yielded 6-(4-tolyl)phenanthridine 1b (132 mg, 44%) after purification. Characterisation data is the same as above.
6-(4-tert-butylphenyl)phenanthridine (1c). Imine 5c (350 mg, 1.12 mmol) yielded 6-(4-tert-butylphenyl)phenanthridine 1c (136 mg, 39%) after purification. Characterisation data is the same as above.

6-(4-Methoxyphenyl)phenanthridine (1d). Imine 5d (300 mg, 1.04 mmol) yielded 6-(4-methoxyphenyl)phenanthridine 1d (148 mg, 50%) after purification. Characterisation data is the same as above.

6-(4-Chlorophenyl)phenanthridine (1e). Imine 5e (300 mg, 1.03 mmol) yielded 6-(4-chlorophenyl)phenanthridine 1e (143 mg, 48%) after purification. Characterisation data is the same as above.

6-(4-Trifluoromethylphenyl)phenanthridine (1f). Imine 5f (366 mg, 1.13 mmol) yielded 6-(4-trifluoromethylphenyl)phenanthridine 1f (186 mg, 51%) after purification. Characterisation data is the same as above.

6-(4-Dimethylaminophenyl)phenanthridine (1g). Imine 5g (350 mg, 1.17 mmol) yielded 6-(4-dimethylaminophenyl)phenanthridine 1g (147 mg, 42%) after purification. Characterisation data is the same as above.

6-(4-Nitrophenyl)phenanthridine (1h). Imine 5h (350 mg, 1.16 mmol) yielded 6-(4-nitrophenyl)phenanthridine 1h (160 mg, 46%) after column chromatography (silica, 1:1 DCM:hexane) as white crystals mp 192-193 °C (lit. 191-192 °C). νmax (KBr)/cm\(^{-1}\) 1550, 1520, 1350; \(\delta\)H (400 MHz, CDCl\(_3\)) 7.69 (1H, t, J 8.0, Ar-H), 7.79 (3H, m, Ar-H), 7.98 (3H, m, Ar-H), 8.29 (1H, m, Ar-H), 8.47 (2H, m, Ar-H), 8.67 (1H, dd, J 1.6, 8.0, Ar-H), 8.77 (1H, d, J 8.4, Ar-H); \(\delta\)C (100 MHz, CDCl\(_3\)) 121.6 (Ar-C\(_\text{H}\)), 122.7 (Ar-C\(_\text{H}\)), 123.6 (Ar-C), 125.0 (Ar-C), 125.5 (2 x Ar-C\(_\text{H}\)), 125.7 (Ar-C), 127.6 (2 x Ar-C\(_\text{H}\)), 128.1 (Ar-C\(_\text{H}\)), 128.7 (Ar-C\(_\text{H}\)), 130.1 (2 x Ar-C\(_\text{H}\)), 130.3 (Ar-C\(_\text{H}\)), 131.0 (Ar-C\(_\text{H}\)), 134.0 (Ar-C), 143.6 (Ar-C), 144.1 (Ar-C), 160.0 (Ar-C=N); HRMS (FAB\(^{+}\)) Found: [M\(^{+}\)] 300.0896. C\(_{19}\)H\(_{12}\)N\(_2\)O\(_2\) requires 300.0899; m/z (FAB\(^{+}\)) 300 ([M\(^{+}\)], 90%), 122 (100).

References


