Palladium and radical routes to phenanthridines

W. Russell Bowman, Jessica E. Lyon, and Gareth J. Pritchard*

Department of Chemistry, University of Loughborough,
Loughborough, Leicestershire, LE11 3TU, UK
E-mail: G.J.Pritchard@lboro.ac.uk

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

DOI: http://dx.doi.org/10.3998/ark.5550190.0013.714

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

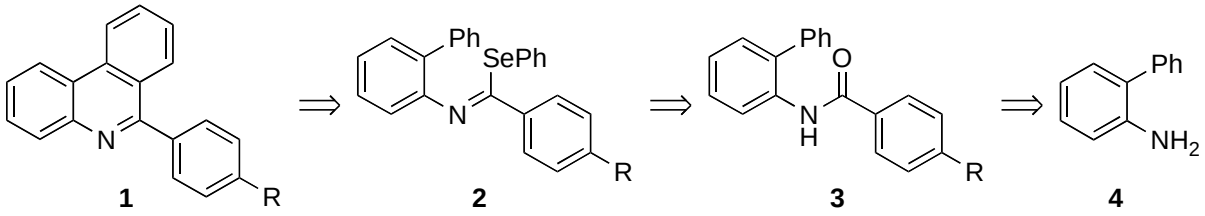
Phenanthridines are an important class of heterocyclic compounds first discovered in 1891 by Pictet and Ankersmit. They show a range of biological activities,[1] and are currently attracting significant interest from synthetic chemists. The majority of established synthetic routes utilise anionic ring closure reactions,[2] Bischler-Napieralski reactions,[3] reduction of phenanthridones,[4] palladium chemistry,[5] or free radical methodology.[6,7] A number of new syntheses of the phenanthridines have been reported recently, underlining their importance.[8]

Recently we have published a palladium-mediated route to phenanthridine,[9] as part of our interest in the development of new methods to prepare heterocyclic systems which include stoichiometric organometallics,[10] biomimetic methods,[11] condensation of reactive electrophilic systems,[12] and radical chemistry.[13] We now wish to disclose the full details of our palladium work together with an improved phenanthridine synthesis by a radical method from imines.

Results and Discussion

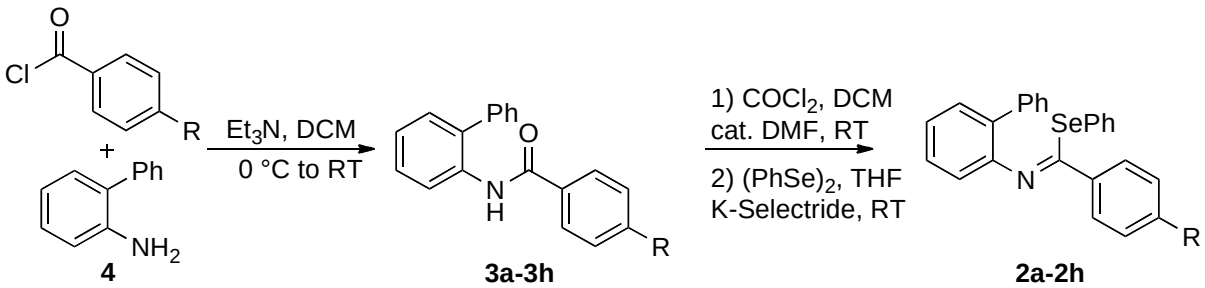
Our first proposed route to phenanthridines **1** involves the key Pd-mediated C-C bond formation of the central pyridine ring from the imidoyl-selanides **2**. The imidoyl-selanides **2** can in turn be

derived from the corresponding amides **3** 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.[14] Also it has been shown that transition metals can insert into the carbon-selenium bond.[15]



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 α–chloroimines by treatment with phosgene and catalytic DMF.[16] We found other methods of preparing the α–chloroimines were unsatisfactory for further reactions. The potassium salt of phenylselanide was prepared *in situ* by reduction of diphenyl diselanide with K-Selectride® and added directly to the un-purified α-chloroimines to give the imidoyl-selanides **2** (Scheme 2, Table 1).[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.



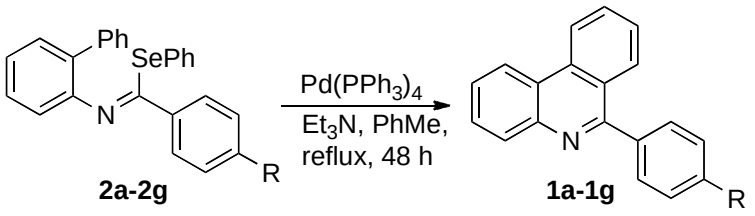
Scheme 2. Synthetic route to imidoyl-selanides **2a-2h**.

Table 1. Yields of amides **3a-3h** and imidoyl-selanides **2a-2h**

Derivative	R Group	Amide **3** Yield (%)	Selanide **2** Yield (%)
a	H	52	54
b	Me	64	44
c	*t*-Bu	59	66
d	OMe	70	51
e	Cl	64	60
f	CF_3	77	60
g	NMe_2	61	62
h	NO_2	47	Decomposed

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,[17] so in order to limit the number of variables in the preliminary reactions we initially used the conventional $Pd(PPh_3)_4$ 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% $Pd(PPh_3)_4$ 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 phenanthridine **1a** was detected in the crude mixture. The ^{1}H NMR spectrum of the crude mixture clearly showed the characteristic peaks of the phenanthridine 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 $Pd(PPh_3)_4$ (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).



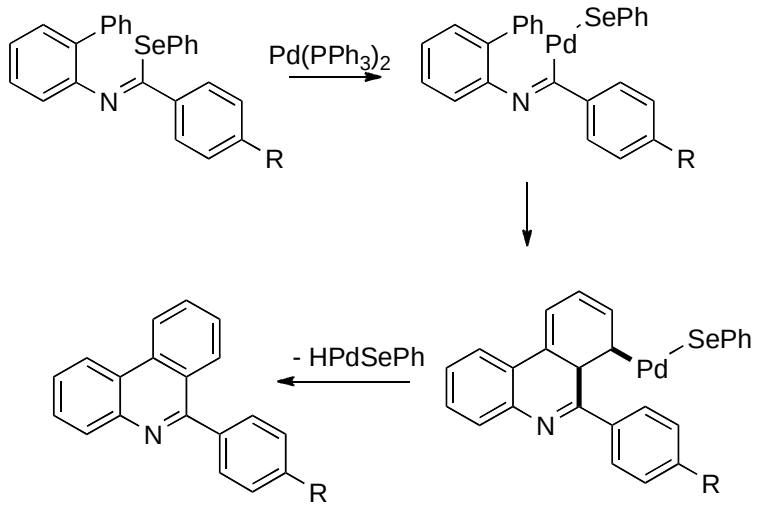
Scheme 3. Pd-mediated cyclisation to phenanthridines **1a-1g**.

Table 2. Yields of phenanthridines **1a-1g**

Phenanthridine	R Group	Yield (%)
1a	H	28
1b	Me	34
1c	*t*-Bu	47
1d	OMe	39
1e	Cl	46
1f	CF_3	48
1g	NMe_2	22

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.

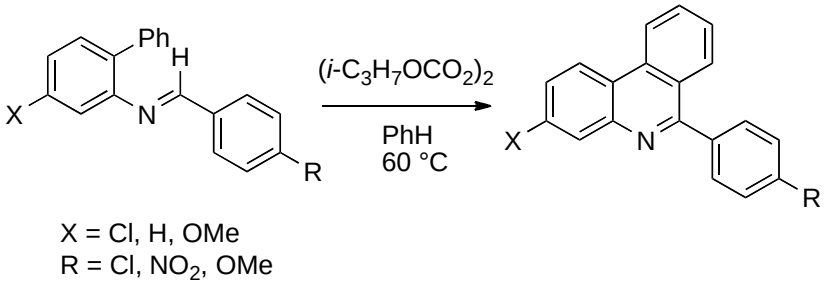
Mechanistically, we propose insertion of a Pd(0) species into the carbon selenium bond followed by carbo-palladation onto the phenyl ring. This intermediate then undergoes rapid rearomatization with the loss of HPdSePh to give the phenanthridine system (Scheme 4).



Scheme 4. Proposed mechanism of Pd-mediated cyclisation of phenanthridine **1**.

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

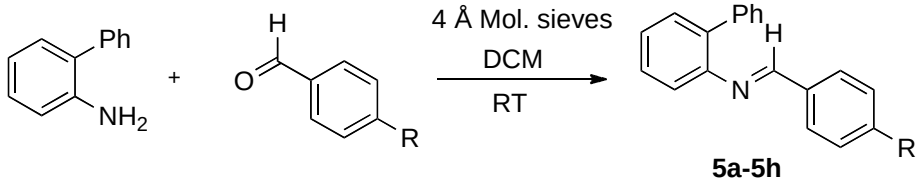
Leardini *et al.* in the 1980s.[7] These workers had shown under radical conditions imines were suitable precursors to a range of phenanthridines (Scheme 5). Using di-*iso*-propyl peroxy carbonate (DPDC) they showed that a range of imines (Scheme 5) could be cyclised to give phenanthridines in good yields, 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 phenanthridine 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 peroxycarbonate (DPDC) is somewhat of a drawback due to its explosive nature, thus requiring additional safety precautions and limiting its potential application.[18] In place of di-*iso*-propyl peroxycarbonate (DPDC), we planned to use di-(*tert*-butyl)peroxide, which is reported not to be explosive under normal conditions, as a safer alternative.[18] 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**.

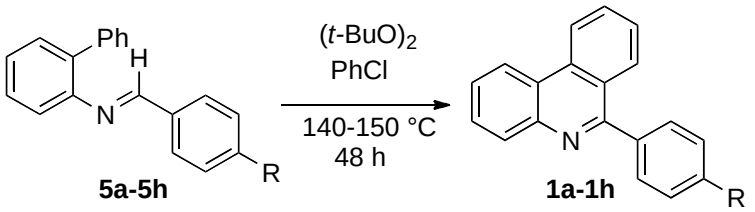
With the imines in hand we could attempt the improved radical conditions for the reaction. Homolysis of the di-(*tert*-butyl)peroxide occurs at 120 °C, therefore a high boiling point solvent was required. Our initial attempts to cyclise the imine **5a** was carried out in chlorobenzene using two equivalents of the peroxide at 125 °C. The ^{1}H 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**

Imine	R Group	Yield (%)
5a	H	60
5b	Me	66
5c	*t*-Bu	68
5d	OMe	78
5e	Cl	79
5f	CF_3	58
5g	NMe_2	66
5h	NO_2	86

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.

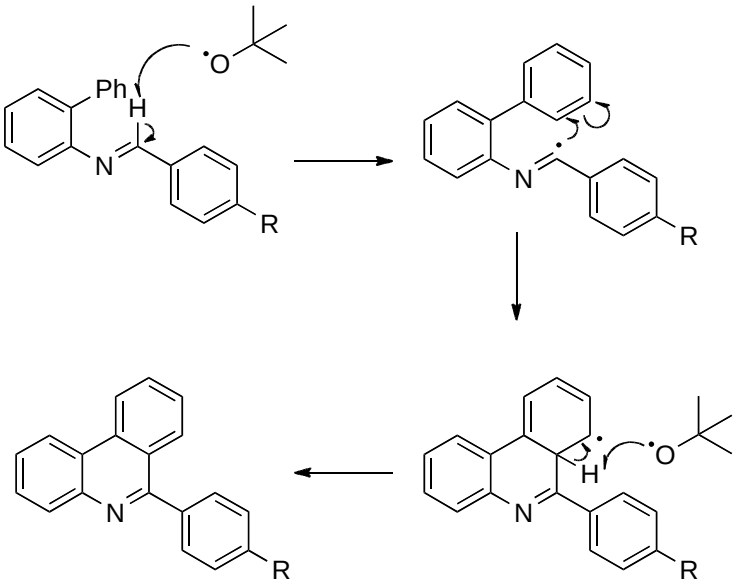


Scheme 7. Synthesis of phenanthridines **1a-1h** by radical cyclisation.

Table 4. Yields of phenanthridines **1a-1h**

Phenanthridine	R Group	Yield (%)
1a	H	40
1b	Me	44
1c	*t*-Bu	39
1d	OMe	50
1e	Cl	48
1f	CF_3	51
1g	NMe_2	42
1h	NO_2	46

The mechanism for the formation of the phenanthridines is that of homolytic aromatic substitution.[19] 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.

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-selanides/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.

^{1}H NMR spectra were measured at 400 MHz and ^{13}C NMR spectra were measured at 100 MHz (unless stated otherwise), using a Bruker AC 400 MHz spectrometer. The solvent used for spectroscopy was $CDCl_3$ (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 ^{1}H 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 Et_3N (2.0 equiv.) in CH_2Cl_2 (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. $NaHCO_3$ solution, and brine. The organics were dried over $MgSO_4$, 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. δ_H (400 MHz, $CDCl_3$) 7.43 (13H, m, Ar-*H*), 8.00 (1H, s, N*H*), 8.54 (1H, d, *J* 8.4, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 121.1 (Ar-*C*H), 124.4 (Ar-*C*H), 126.8 (2 x Ar-*C*H), 128.2 (Ar-*C*H), 128.6 (Ar-*C*H), 128.7 (2 x Ar-*C*H), 129.2 (2 x Ar-*C*H), 129.4 (2 x Ar-*C*H), 130.0 (Ar-*C*H), 131.7 (Ar-*C*H), 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. $C_{19}H_{16}NO$ 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. ν_{max} (KBr)/cm^{-1} 3190, 1620, 1590; δ_H (400 MHz, $CDCl_3$) 2.37 (3H, s, C*H*$_3$), 7.23 (4H, m, Ar-*H*), 7.47 (8H, m, Ar-*H*), 7.98 (1H, s, N*H*), 8.54 (1H, dd, *J* 0.8, 8, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 21.4 (*C*H$_3$), 121.0 (Ar-*C*H), 124.2 (Ar-*C*H), 126.8 (2 x Ar-*C*H), 128.1 (Ar-*C*H), 128.6 (Ar-*C*H), 129.2 (2 x Ar-*C*H), 129.4 (4 x Ar-*C*H), 130.0 (Ar-*C*H), 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*-butylbenzamide (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°C. ν_{max} (KBr)/cm^{-1} 3370, 1620; δ_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, N*H*), 8.57 (1H, d, *J* 8, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 31.1 (C(*C*H$_3$)$_3$), 34.9 [*C*(CH$_3$)$_3$], 121.0 (Ar-*C*H), 124.2 (Ar-*C*H), 125.7 (2 x Ar-*C*H), 126.7 (2 x Ar-*C*H), 128.2 (Ar-*C*H), 128.6 (Ar-*C*H), 129.2 (2 x Ar-*C*H), 129.4 (2 x Ar-*C*H), 130.0 (Ar-*C*H), 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. $C_{23}H_{23}NO$ 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 °C. δ_H (400 MHz, $CDCl_3$) 3.82 (3H, s, CH_3) 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, N*H*), 8.52 (1H, m, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 55.4 (O*C*H$_3$), 113.9 (2 x Ar-*C*H), 121.0 (Ar-*C*H), 124.1 (Ar-*C*H), 127.0 (Ar-*C*), 128.1 (Ar-*C*H), 128.6 (2 x Ar-*C*H), 128.7 (2 x Ar-*C*H), 129.2 (2 x Ar-*C*H), 129.4 (Ar-*C*H), 129.9 (Ar-*C*H), 132.1 (Ar-*C*), 135.1 (Ar-*C*), 138.1 (Ar-*C*), 162.4 (Ar-*C*OMe), 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** (3.57g, 64%) as white crystals mp 104-105 °C. ν_{max} (KBr)/cm^{-1} 3253, 1650, 1050; δ_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, N*H*), 8.49 (1H, d, *J* 8.0, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 121.1 (Ar-*C*H), 124.6 (Ar-*C*H), 128.2 (2 x Ar-*C*H), 128.3 (Ar-*C*H), 128.6 (Ar-*C*H), 129.0 (2 x Ar-*C*H), 129.2 (2 x Ar-*C*H), 129.3 (2 x Ar-*C*H), 130.0 (Ar-*C*H), 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 °C. ν_{max} (KBr)/cm^{-1} 3325, 1650; δ_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, N*H*), 8.51 (1H, d, *J* 8.4, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 121.2 (Ar-C),

124.8 (CF_3), 125.8 (2 x Ar-*C*H), 125.9 (2 x Ar-*C*H), 127.3 (2 x Ar-*C*H), 128.4 (2 x Ar-*C*H), 128.7 (2 x Ar-*C*H), 129.3 (2 x Ar-*C*H), 130.1 (Ar-*C*H), 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. $C_{20}H_{14}F_3NO$ 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. ν_{max} (KBr)/cm^{-1} 3370, 1650; δ_H (400 MHz, $CDCl_3$) 2.99 [6H, s, N(CH_3)$_2$], 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, N*H*), 8.57 (1H, dd, *J* 1.2, 8.4, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 40.1 (2 x CH_3), 111.1 (2 x Ar-*C*H), 120.8 (Ar-*C*H), 121.2 (Ar-*C*), 123.6 (Ar-*C*H), 128.0 (Ar-*C*H), 128.4 (2 x Ar-*C*H), 128.5 (Ar-*C*H), 129.2 (2 x Ar-*C*H), 129.4 (2 x Ar-*C*H), 129.9 (Ar-*C*H), 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. $C_{21}H_{21}N_2O$ 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. ν_{max} (KBr)/cm^{-1} 1364; δ_H (400 MHz, $CDCl_3$) 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, N*H*), 8.24 (2H, m, Ar-*H*), 8.50 (1H, d, *J* 8, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 121.2 (Ar-*C*H), 124.0 (2 x Ar-*C*H), 125.1 (Ar-*C*H), 128.0 (2 x Ar-*C*H), 128.5 (Ar-*C*H), 128.9 (Ar-*C*H), 129.3 (2 x Ar-*C*H), 129.4 (2 x Ar-*C*H), 130.1 (Ar-*C*H), 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. $C_{19}H_{14}N_2O_3$ 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 CH_2Cl_2 (8 ml/mmol) under inert atmosphere was added dry DMF (1 drop/mmol) 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/mmol) to form a white suspension. In a separate flask, the crude imidoyl chloride was re-dissolved in dry THF (8 ml/mmol) 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/mmol) and CH_2Cl_2 (8 ml/mmol). The organics were separated, dried over $MgSO_4$, 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-ylbenzimidoselenoate (**2a).** Amide **3a** (1.39 g, 5.09 mmol) yielded phenyl-*N*-biphenyl-2-ylbenzimidoselenoate **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. ν_{max} (KBr)/cm^{-1} 1627, 1535; δ_H (400 MHz, $CDCl_3$) 2.21 (3H, s, CH_3), 7.22 (18H, m, Ar-H); δ_C (100 MHz, $CDCl_3$) 21.3 (CH_3), 120.1 (Ar-*C*H), 125.1 (2 x Ar-*C*H), 126.9 (Ar-*C*H), 127.4 (2 x Ar-*C*H), 127.9 (2 x Ar-*C*H), 128.0 (2 x Ar-*C*H), 128.4 (2 x Ar-*C*H), 128.7 (2 x Ar-*C*H), 129.1 (Ar-*C*H), 129.7 (Ar-*C*), 129.8 (2 x Ar-*C*H), 130.4 (Ar-*C*H), 131.8 (Ar-*C*), 134.9 (Ar-*C*H), 135.3 (Ar-*C*), 139.7 (Ar-*C*), 140.0 (Ar-*C*), 149.1 (*C*=N); HRMS (FAB$^+$) Found: [M+H$^+$] 428.0916. $C_{26}H_{22}NSe$ requires 428.0917; *m/z* (FAB$^+$) 428 ([M+H$^+$], 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%) and it was isolated as pale yellow crystals mp 100-101 °C. ν_{max} (KBr)/cm^{-1} 1627, 1573; δ_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*); δ_C (100 MHz, $CDCl_3$) 119.6 (Ar-*C*H), 124.5 (Ar-*C*H), 124.6 (Ar-*C*H), 125.1 (Ar-*C*), 125.5 (Ar-*C*H), 127.1 (Ar-*C*H), 127.9 (2 x Ar-*C*H), 128.1 (Ar-*C*H), 128.2 (Ar-*C*H), 128.5 (Ar-*C*), 128.9 (2 x Ar-*C*H), 129.1 (Ar-*C*H), 129.6 (Ar-*C*H), 129.8 (2 x Ar-*C*H), 130.6 (Ar-*C*H), 131.0 (Ar-*C*H), 131.3 (Ar-*C*), 131.8 (Ar-*C*), 135.5 (Ar-*C*H), 139.5 (Ar-*C*), 141.3 (Ar-*C*), 148.7 (Ar-*C*), 163.5 (*C*=N); HRMS (FAB$^+$) Found: [M+H$^+$] 482.0638. $C_{26}H_{18}F_3N^{80}Se$ requires 482.0635); *m/z* (FAB$^+$) 482 ([M+H$^+$] ^{80}Se, 13%), 480 (^{78}Se, 7), 325 (70), 324 (100), 178 (24), 152 (52).

Phenyl-*N*-biphenyl-2-yl-4-(dimethylamino)benzimidoselenoate (2g). Amide **3g** (1.50 g, 4.74 mmol) yielded phenyl-*N*-biphenyl-2-yl-4-(dimethylamino) benzimidoselenoate **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_2Cl_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).[7] 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. ν_{max} (KBr)/cm^{-1} 2260; δ_H (400 MHz, $CDCl_3$) 2.37 (3H, s, C*H*$_3$), 7.06 (1H, dd, *J* 0.12, 7.6, Ar-*H*), 7.21 (2H, d, *J* 7.6, Ar-*H*), 7.47 (3H, m, Ar-*H*), 7.68 (2H, d, *J* 8.4, Ar-*H*), 8.41 (1H, s, imine-*H*); δ_C (100 MHz, $CDCl_3$) 21.6 (*C*H$_3$), 119.0 (Ar-CH), 125.8 (Ar-CH), 126.7 (Ar-CH), 127.6 (2 x Ar-CH), 128.3 (Ar-CH), 128.8 (2 x Ar-CH), 129.4 (2 x Ar-*C*H), 130.2 (2 x Ar-*C*H), 130.3 (Ar-*C*H), 133.9 (Ar-*C*), 135.2 (Ar-*C*), 139.5 (Ar-*C*), 141.7 (Ar-*C*), 149.9 (Ar-*C*), 160.2 (imine-*C*); HRMS (FAB$^+$) Found: [M+H$^+$] 272.1439. $C_{20}H_{18}N$ requires 272.1439; *m/z* (FAB$^+$) 272 ([M+H$^+$], 100%), 271 (55), 270 (31), 180 (56).

Biphenyl-2-yl-(4-*tert*-butylbenzylidene) amine (5c). 4-*t*-Butylbenzaldehyde (0.49 ml, 2.95 mmol) yielded biphenyl-2-yl-(4-t-butylbenzylidene) amine **5c** (770 mg, 86%) as a yellow oil. ν_{max} (neat)/cm^{-1} 1630, 1540; δ_H (400 MHz, $CDCl_3$) 1.34 (9H, s, ^{t}Bu-*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(*C*H$_3$)$_3$), 35.0 (*C*(CH$_3$)$_3$), 119.0 (Ar-*C*H), 125.7 (2 x Ar-*C*H), 125.8 (Ar-*C*H), 126.0 (Ar-*C*H), 127.7 (2 x Ar-*C*H), 128.3 (Ar-*C*H), 128.7 (2 x Ar-*C*H), 130.2 (2 x Ar-*C*H), 130.3 (Ar-*C*H), 133.9 (Ar-*C*), 135.3 (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. $C_{23}H_{24}N$ requires 314.1909; *m/z* (FAB$^+$) 314 ([M+H$^+$], 64%), 169 (44), 148 (100), 57 (20).

Biphenyl-2-yl-(4-methoxybenzylidene) amine (5d).[7] 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).[7] 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). ν_{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-*C*H), 126.8 (Ar-*C*H), 127.7 (2 Ar-*C*H), 128.4 (Ar-*C*H), 129.0 (2 Ar-*C*H), 129.9 (2 Ar-*C*H), 130.2 (2 Ar-*C*H), 130.4 (Ar-*C*H), 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. $C_{19}H_{15}NCl^{35}$ 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. ν_{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-*C*H), 125.5 (*C*F$_3$), 125.6 (Ar-*C*H), 125.7 (Ar-*C*H), 125.8 (Ar-*C*), 126.6 (Ar-*C*H), 126.9 (Ar-*C*H), 127.8 (2 x Ar-*C*H), 128.4 (Ar-*C*H), 129.0 (2 x Ar-*C*H), 130.2 (2 x Ar-*C*H), 130.5 (Ar-*C*H), 135.6 (Ar-*C*), 139.3 (Ar-

C), 139.4 (Ar-*C*), 149.0 (Ar-*C*), 158.6 (imine-*C*); HRMS (FAB$^+$) Found: [M+H$^+$] 326.1157. $C_{20}H_{14}F_3N$ requires 326.1157); *m/z* (FAB$^+$) 326 ([M+H$^+$], 100%), 325 (67), 324 (39), 180 (92), 152 (26).

Biphenyl-2-yl-(4-dimethylaminobenzylidene) amine (5g). 4-Dimethylaminobenzaldehyde (440 mg, 2.95 mmol) yielded biphenyl-2-yl-(4-dimethylamino benzylidene) amine **5g** (588 mg, 66%) as a yellow crystals mp 82-83 °C. ν_{max} (KBr)/cm^{-1} 1690; δ_H (400 MHz, $CDCl_3$) 3.00 (6H, s, N(C*H*$_3$)$_2$), 6.68 (2H, dd, *J* 1.6, 6.8, Ar-*H*), 7.06 (1H, dd, *J* 1.2, 7.6, Ar-*H*), 7.25 (2H, m, Ar-*H*), 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*); δ_C (100 MHz, $CDCl_3$) 40.1 (2 x *C*H$_3$), 111.5 (2 x Ar-*C*H), 119.2 (Ar-*C*H), 124.8 (Ar-*C*), 125.1 (Ar-*C*H), 126.5 (Ar-*C*H), 127.6 (2 x Ar-*C*H), 128.3 (Ar-*C*H), 130.2 (Ar-*C*H), 130.3 (2 x Ar-*C*H), 130.4 (2 x Ar-*C*H), 135.1 (Ar-*C*), 139.8 (Ar-*C*), 150.6 (Ar-*C*), 152.4 (Ar-*C*), 160.0 (imine-*C*); HRMS (FAB$^+$) Found: [M+H$^+$] 301.1704. $C_{21}H_{21}N_2$ requires 301.1705; *m/z* (FAB$^+$) 301 ([M+H$^+$], 100%), 300 (88), 299 (61), 180 (66).

Biphenyl-2-yl-(4-nitrobenzylidene) amine (5h).[7] 4-Nitrobenzaldehyde (446 mg, 2.95 mmol) yielded biphenyl-2-yl-(4-nitrobenzylidene) amine **5h** (770 mg, 86%) as yellow crystals mp 105-106 °C (lit.[7] 106-107°C). δ_H (400 MHz, $CDCl_3$) 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, 88, Ar-*H*), 8.28 (2H, dt, *J* 2, 8.8, Ar-*H*), 8.56 (1H, s, imine-*H*); δ_C (100 MHz, $CDCl_3$) 118.4 (Ar-*C*H), 124.0 (2 x Ar-*C*H), 127.0 (Ar-*C*H), 127.1 (Ar-*C*H), 127.8 (2 x Ar-*C*H), 128.5 (Ar-*C*H), 129.4 (2 x Ar-*C*H), 130.2 (2 x Ar-*C*H), 130.6 (Ar-*C*H), 136.0 (Ar-*C*), 139.2 (Ar-*C*), 141.7 (Ar-*C*), 148.5 (Ar-*C*), 149.2 (Ar-*C*), 157.5 (imine-*C*); HRMS (FAB$^+$) Found: [M$^+$] 303.1136. $C_{19}H_{14}N_2O_2$ 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 $Pd(PPh_3)_4$ (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. $NaHCO_3$ solution and brine. The organics were 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).[7] 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.[7] 103-105 °C). ν_{max} (KBr)/cm^{-1} 2400; δ_H (400 MHz, $CDCl_3$) 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*); δ_C (100 MHz, $CDCl_3$) 122.0 (2 x Ar-*C*H), 122.2 (2 x Ar-*C*H), 123.8 (Ar-*C*), 125.2 (Ar-*C*), 127.0 (Ar-*C*H), 127.2 (Ar-*C*H), 128.5 (2 x Ar-*C*H), 128.8 (Ar-*C*H), 128.9 (Ar-*C*H), 129.0 (Ar-*C*H), 129.8 (2 x Ar-*C*H), 130.7 (Ar-*C*H), 133.5 (Ar-*C*), 137.0 (Ar-*C*), 161.3 (Ar-*C*=N); HRMS (FAB$^+$) Found: [M$^+$] 255.1049. $C_{19}H_{13}N$ requires 255.1048; *m/z* (FAB$^+$) 255 ([M$^+$], 87%), 77 (100).

6-(4-Tolyl)phenanthridine (1b).[2b] Imidoyl-selanide **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.[20] 107.5-108 °C). ν_{max} (KBr)/cm^{-1} 2925, 1610; δ_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*); δ_C (100 MHz, $CDCl_3$) 21.4 (*C*H_3), 121.9 (Ar-*C*H), 122.2 (Ar-*C*H), 123.7 (Ar-*C*), 125.3 (Ar-*C*), 126.8 (Ar-*C*H), 127.1 (Ar-*C*H), 128.8 (Ar-*C*H), 129.0 (Ar-*C*H), 129.1 (2 x Ar-*C*H), 129.7 (2 x Ar-*C*H), 130.3 (Ar-*C*H), 130.5 (Ar-*C*H), 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*-butylphenyl)phenanthridine (1c). Imidoyl-selanide **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. ν_{max} (KBr)/cm^{-1} 1560; δ_H (400 MHz, $CDCl_3$) 1.41 (9H, s, C(C*H*$_3$)$_3$), 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*); δ_C (100 MHz, $CDCl_3$) 31.5 (C(*C*H$_3$)$_3$), 34.8 (*C*(CH$_3$)), 121.9 (Ar-*C*H), 122.2 (Ar-*C*H), 123.7 (Ar-*C*), 125.2 (Ar-*C*), 125.4 (2 x Ar-*C*H), 126.7 (Ar-*C*H), 126.8 (Ar-*C*H), 128.8 (Ar-*C*H), 129.1 (Ar-*C*H), 129.5 (2 x Ar-*C*H), 130.2 (Ar-*C*H), 130.6 (Ar-*C*H), 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)[7] Imidoyl-selanide **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). ν_{max} (KBr)/cm^{-1} 1650, 1575; δ_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*); δ_C (100 MHz, $CDCl_3$) 56.7 (O*C*H$_3$), 114.5 (2 x Ar-*C*H), 121.9 (Ar-*C*), 124.2 (Ar-*C*H), 126.9 (Ar-*C*), 128.4 (Ar-*C*H), 128.6 (2 x Ar-*C*H), 128.9 (2 x Ar-*C*H), 129.1 (2 x Ar-*C*H), 129.3 (Ar-*C*H), 130.2 (Ar-*C*H), 132.3 (Ar-*C*), 135.6 (Ar-*C*), 137.4 (Ar-*C*), 138.5 (Ar-*C*), 161.7 (Ar-*C*OMe),; 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).[7] Imidoyl-selanide **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). ν_{max} (neat)/cm^{-1} 2358; δ_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*); δ_C (100 MHz, $CDCl_3$) 122.0 (Ar-*C*H), 122.4 (Ar-*C*H), 123.8 (Ar-*C*), 125.0 (Ar-*C*), 127.2 (Ar-*C*H), 127.3 (Ar-*C*H), 128.5 (Ar-*C*H), 128.7 (2 x Ar-*C*H), 129.0 (Ar-*C*H), 130.4 (Ar-*C*H), 130.7 (Ar-*C*H), 131.1 (2 x Ar-*C*H), 133.5 (2 x Ar-*C*), 134.9 (Ar-*C*), 143.8 (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-selanide **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, dd, *J* 0.8, 8.4, Ar-*H*), 8.24 (1H, m, Ar-*H*), 8.65 (1H, dd, *J* 1.6, 8.0, Ar-*H*), 8.74 (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 (*C*F_3), 125.5 (2 x Ar-*C*H), 125.6 (Ar-*C*), 127.4 (2 x Ar-*C*H), 128.3 (Ar-*C*H), 129.1 (Ar-*C*H), 130.2 (2 x Ar-*C*H), 130.4 (Ar-*C*H), 130.9 (Ar-*C*H), 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-selanide **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(C*H*$_3$)$_2$), 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 *C*H_3), 112.1 (2 x Ar-*C*H), 118.9 (Ar-*C*H), 124.8 (Ar-*C*), 124.9 (Ar-*C*H), 126.5 (3 x Ar-*C*H), 128.1 (Ar-*C*H), 129.9 (Ar-*C*H), 130.1 (2 x Ar-*C*H), 130.2 (2 x Ar-*C*H), 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).[7] 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).[2b] 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).[7] 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).[7] Imine **5e** (300mg, 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).[7] Imine **5h** (350 mg, 1.16 mmol) yielded 6-(4-nitrophenyl)phenanthridine **1g** (160 mg, 46%) after column chromatography (silica, 1:1 DCM:hexane) as white crystals mp 192-193 °C (lit.[7] 191-192 °C). ν_{max} (KBr)/cm^{-1} 1550, 1520, 1350; δ_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*); δ_C (100 MHz, $CDCl_3$) 121.6 (Ar-*C*H), 122.7 (Ar-*C*H), 123.6 (Ar-*C*), 125.0 (Ar-*C*), 125.5 (2 x Ar-*C*H), 125.7 (Ar-*C*), 127.6 (2 x Ar-*C*H), 128.1 (Ar-*C*H), 128.7 (Ar-*C*H), 130.1 (2 x Ar-*C*H), 130.3 (Ar-*C*H), 131.0 (Ar-*C*H), 134.0 (Ar-*C*), 143.6 (Ar-*C*), 144.1 (Ar-*C*), 160.0 (Ar-*C*=N); HRMS (FAB$^+$) Found: [M$^+$] 300.0896. $C_{19}H_{12}N_2O_2$ requires 300.0899; *m/z* (FAB$^+$) 300 ([M$^+$], 90%), 122 (100).

References

1. For example see:- (a) Li, D.; Zhao, B.; Sim, S.-P.; Li, T.-K.; Liu, A.; Liu, L. F.; LaVoie, E. J. *Bioorg. Med. Chem.* **2003**, *11*, 521. (b) Lynch, M. A.; Duval, O.; Sukhanova, A.; Devy. J.; MacKay, S. P.; Waigh, R. D.; Nabiev, I. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2643. (c) Ishikawa, T. *Med. Res. Rev.* **2001**, *21*, 61.
2. (a) Lysén, M.; Kristensen, J. L.; Vedsø, P.; Begtrup, M. *Org. Lett.* **2002**, *4*, 257. (b) Pawlas, J.; Begtrup, M. *Org. Lett.* **2002**, *4*, 2687. (c) Lysén, M.; Madden, M.; Kristensen, J. L.; Vedsø, P.; Zøllner, C.; Begtrup, M. *Synthesis* **2006**, 3478.
3. (a) Mamalis, P.; Petrow, V. J. *J. Chem. Soc.* **1950**, 703. (b) Buu-Hoï, N. P.; Jaquignon, P.; Long, C. T. *J. Chem. Soc.* **1957**, 505.
4. Narasimham, N. S.; Chandrachood, P. S.; Shete N. R. *Tetrahedron* **1981**, *37*, 825.

5. (a) Ishida, N.; Nakanishi Y.; Moriya T.; Murakami M. *Chem. Lett*. **2011**, *40*, 1047. (b) Peng, J.; Chen, T.; Chen, C.; Li, B. *J. Org. Chem*. **2011**, *76*, 9507. (c) Blanchot, M., Candito, D. A.; Larnaud, F.; Lautens M. *Org. Lett*. **2011**, *13*, 1486. (d) Candito, D. A.; Lautens, M. *Angew. Chem. Int. Ed*. **2009**, *48*, 6713. (e) Shabashov, D.; Daugulis, O. *J. Org. Chem*. **2007**, *72*, 7720. (f) Xie, C.; Zhang, Y.; Huang, Z.; Xu, O. *J. Org. Chem*. **2007**, *72*, 5431. (g) Shou, W.-G.; Yang, Y.-Y.; Wang, Y.-G. *J. Org. Chem*. **2006**, *71*, 9241.
6. (a) Katritzky, A. R.; Yang B. Z. *J. Heterocycl. Chem*. **1996**, *33*, 607. (b) Rosa, A. M.; Lobo A. M.; Branco P. S.; Prabhakar, S.; Pereira A. M. D. L. *Tetrahedron* **1997**, *53*, 269. (c) Nakanishi, T.; Suzuki, M.; Mashiba, A.; Ishikawa, K.; Yokotsuka T. J. *Org. Chem*. **1998**, *63*, 4235. (d) Ellis, M. J.; Stevens, M. F. G. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3180. (e) Portela-Cubillo, F.; Scott, J. S.; Walton, J. C. *J. Org. Chem*. **2008**, *73*, 5558.
7. Leardini R.; Tundo A.; Zanardi G.; Pedulli G. F. *Synthesis* **1985**, 107-110.
8. For recent examples see:- (a) Mondal, P.; Thander L,; Chattopadhyay, S. K. *Tetrahedron Lett*. **2012**, *53*, 1328. (b) Jana, G. P.; Mukherjee, S.; Ghorai, B. K. *Synthesis* **2010**, 3179. (c) Zhang, L.; Ang, G. Y.; Chiba, S. *Org. Lett*. **2010**, *12*, 3682. (d) Xi, J.; Dong, Q.-L.; Liu G.-S.; Wang, S.; Chen, L., Yao, Z.-J. *Synlett* **2010**, 1674. (e) Budén, M. E.; Dorn, V. B.; Gamba, M.; Pierini, A. B.; Rossi, R. A. *J. Org. Chem*. **2010**, *75*, 2206. (f) Youn, S. W.; Bihn J. H. *Tetrahedron Lett*. **2009**, *50*, 4598. (g) Jana, G. P.; Ghorai B. K. *Lett. Org. Chem*. **2009**, *6*, 372.
9. Bowman, W. R.; Lyon, J. E.; Pritchard, G. J. *Synlett* **2008**, 2169.
10. Christie, S. D. R.; Davoile, R. J.; Elsegood, M. R. J.; Fryatt, R.; Jones, R. C. F.; Pritchard, G. *J. Chem. Commun.* **2004**, 2474; Ellart, E. A.; Christie, S. D. R.; Pritchard, G. *J*.; Elsegood, M. R. *J. Chem. Commun*. **2009**, 7339.
11. For example see:- Irlapati, N. R.; Baldwin, J. E.; Adlington, R. M.; Pritchard, G. J.; Cowley, A. R. *Tetrahedron* **2006**, *62*, 4603; Adlington, R. M.; Baldwin, J. E.; Mayweg A. V. W.; Pritchard, G. J. *Org. Lett*. **2002**, *4*, 3009; Adlington, R. M.; Baldwin, J. E.; Williams A. J.; Watkin, D. J. *Org. Lett*. **1999**, *1*, 1937; Irlapati, N. R.; Baldwin, J. E.; Adlington R. M.; G. J. Pritchard, *Org. Lett*. **2003**, *5*, 2351.
12. For examples see:- Adamo, M. F. A.; Adlington, R. M.; Baldwin, J. E.; Pritchard G. J.; Rathmell, R. E. *Tetrahedron* **2003**, *59*, 2197; Baldwin, J. E.; Fryer A. M.; Pritchard, G. J. *Bioorg. Med. Chem. Lett*. **2000**, *10*, 309; Adlington, R. M.; Baldwin, J. E.; Catterick, D.; Pritchard, G. J. *Chem. Commun*. **1997**, 1757.
13. Pedersen, J. M.; Bowman, W. R.; Elsegood, M. R. J.; Fletcher, A. J.; Lovell, P. J. *J. Org. Chem.* **2005**, *70*, 10615; Bowman, W. R.; Elsegood, M. R. J.; Stein, T; Weaver, G. W. *Org. Biomol. Chem*. **2007**, *5*, 103; Allin, S. M.; Barton W. R. S.; Bowman, W. R.; Bridge, E.; Elsegood, M. R. J.; McInally, T.; McKee, V. *Tetrahedron* **2008**, *64*, 7745.
14. Bowman, W. R.; Fletcher, A. J.; Pedersen, J. M.; Lovell, P. J.; Elsegood, M. R. J.; Lopez, E. H.; McKee, V.; Potts, G. B. S. *Tetrahedron* **2007**, *63*, 191.
15. Fujiwara S.; Toyofuku M.; Kuniyasu H.; Kambe N. *Pure Appl. Chem.* **2010**, *82*, 565.
16. Newcomb, M; Esker, J. L. *Tetrahedron Lett*. **1991**, 32, 1035.

17. (a) Li, J. J.; Gribble, G. W. *Palladium in Heterocyclic Chemistry*; Pergamon: Oxford, 2000. (b) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, 2004.
18. Bowman, W. R.; Bridge, C. F.; Brookes, P.; Cloonan, M. O.; Leach, D. C. *J. Chem. Soc., Perkins Trans. 1* **2002**, 58.
19. Bowman, W. R.; Storey, J. M. D. *Chem. Soc. Rev.* **2007**, *36*, 1803.

