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# Thermal rearrangements of tetrahydroimidazo[1,5-*b*]isoxazole-2,3-dicarboxylates. Synthesis of 3*H*-imidazol-1-ium ylides and their silver derivatives

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ABSTRACT

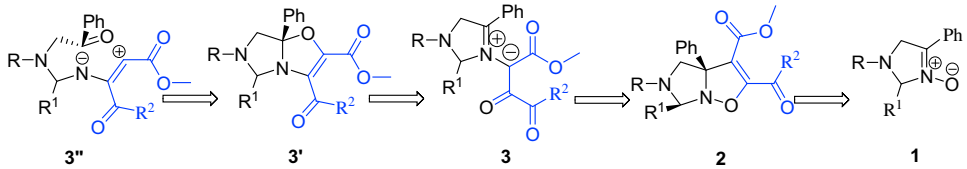
Isoxazolines **2** from the cycloaddition of imidazoline 3-oxides **1** with DMAD undergo rearrangement to 3,4-dihydro-2*H*-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxo-ethanides) **3**, which spontaneously undergo elimination to give 3*H*-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxo-ethanides) **5** or 1*H*-imidazoles **6** when heated in toluene at reflux. The presence of the aromatic ring at C-6 decelerated the conversion and enhanced the yield of **5**. Solvents more polar than toluene (e.g., DMSO) provided quantitative conversion of **2** into **6** in mild conditions, while in less polar solvents such as $CCl_4$, the reaction rate was lowered and the yield of **5** enhanced. C-2 unsubstituted ylides **5** were treated with $Ag_2O$ or $AgNO_3$ in the presence of $Et_3N$ at room temperature to give C-2 metallated derivatives **9** in excellent yields.



## 1. Introduction

The cycloadducts of di- and triarylimidazoline 3-oxides[1] with a variety of dipolarophiles[2] are bicyclic compounds with potentially interesting biological activities. They are also a source of new heterocyclic compounds via interesting ring-opening reactions.[3] Previously we reported the synthesis of stable adducts of 3-imidazoline 3-oxides with dimethyl acetylenedicarboxylate (DMAD)[2d,e] and alkyl 3-phenylpropiolates.[2f] Isoxazolines **2** undergo diastereoselective rearrangement into 3-methoxy-7-(methoxycarbonyl)-2,7a-diaryl-5-oxo-2,3,5,7a-tetrahydro-1*H*-pyrrolo[1,2-*e*]imidazol-6-olates in the presence of methoxide in methanol. The latter were converted to highly functionalized pyrrole derivatives.[2i] The synthesis and rearrangements of the alkyne adducts of some nitrones have been reviewed.[4] 4,5-Dihydroimidazole *N*-oxides undergo 1,3-dipolar cycloaddition with alkyne dipolarophiles and the cycloadducts were shown to convert into the corresponding ene-1,1-diamines.[5] There is still a large interest for 4-isoxazolines due to their biological activities[6a] and as a source of interesting rearrangements.[6b,c] In recent reports from our laboratory we described the utility of isoxazolo[3,2-*a*]isoquinolines as precursors for the synthesis of stable azomethine ylides[7a] while the adducts of acyclic nitrones were shown to undergo a cascade reaction to form reactive iminocarbenes.[7b] The reactions of 2-alkynylbenzaldoximes, DMAD and bromine was reported to afford the unexpected isoquinoline based azomethine ylides in good to excellent yields.[7c]

To assess the scope of these rearrangements for the synthesis of cyclic azomethine ylides **3**, or isoazomethine ylides **3′** we developed the retrosynthetic analysis depicted in Scheme 1. The treatment of imidazoline 3-oxides **1** with DMAD will produce




**Scheme 1.** Retrosynthetic analysis of cyclic ylides **3** and iminocarbenes **3**.

compounds **2**, the heating of which in toluene at reflux would give stable ylides **3**. In case that the corresponding ylides are prone to further rearrangements the formation of iminocarbenes **3′** is

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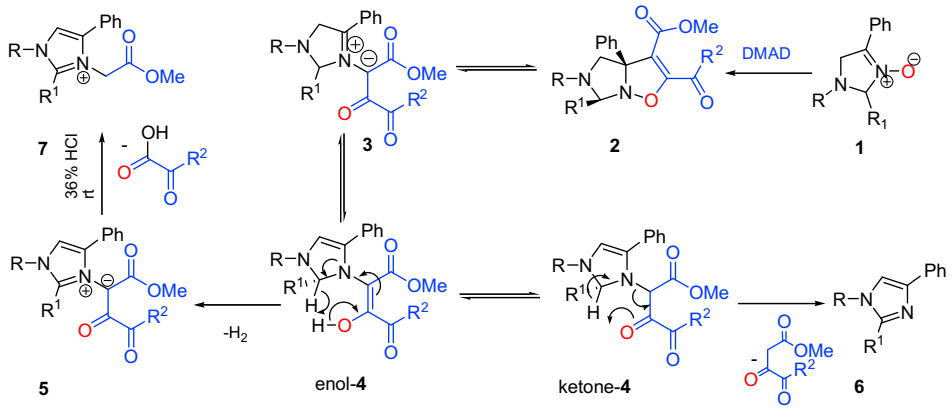


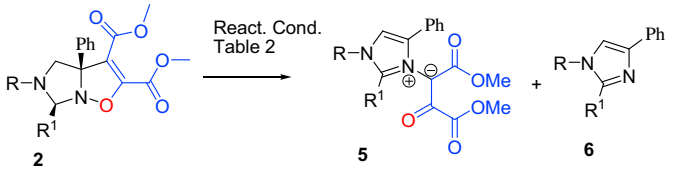

**Scheme 2.** Synthesis and probable mechanism for the formation of ylides **3** and their elimination reactions to imidazolium ylides **5** or to imidazoles **6**.

expected as we have recently reported for acyclic nitrone DMAD adducts.[7b]

Here we report on the rearrangement of isoxazolines **2** and solvent dependent competing elimination reactions of the rearrangement products to the corresponding 3*H*-imidazol-1-ium ylides **5** and 1*H*-imidazoles **6** (Scheme 2). The reaction of C-2 unsubstituted ylides **5** with Ag(I) in the presence of $Et_3N$ at room temperature provides C-2 metallated derivatives **9** precursors of useful coupling reaction catalysts.

## 2. Results and discussion

Nitrones **1** were heated at reflux in toluene in the presence of equimolar amounts of DMAD to give the corresponding imidazolium ylides **5** and imidazoles[2d,e,3a] **6** (Schemes 2 and 3). The formed ylides **5** (Table 1) and imidazoles **6** (Table 2) were characterized by analytical methods and spectroscopy as well as comparison with authentic samples in the cases of known imidazoles. The IR and NMR spectroscopic characteristics of ylides **5** are similar to the ylides obtained from the rearrangements of 3,4-dihydroisoquinolin-2-oxide DMAD adducts.[7a] All compounds have 3-proton singlets ca. 3.33




**Scheme 3.** Synthesis of ylides **5** and 1*H*-imidazoles **6**.

**Table 2**
Solvent effect on the rearrangements of compounds **2**

| Starting material | Solvent | RT (h) and T (°C) | Product[a] Yield (%) | | Mp (°C) **6** |
|---|---|---|---|---|---|
| | | | **5** | **6** | |
| **2a** | DMSO | 0.5, 77 | 0 | 100 | 93–94 |
| **2b** | DMSO | 0.5, 77 | 0 | 100 | 132–133 |
| **2c** | DMSO | 0.5, 77 | 0 | 100 | 103–104 |
| **2d** | DMSO | 0.5, 77 | 0 | 100 | 139–140 |
| **2e** | DMSO | 0.5, 77 | 0 | 100 | 151–152 |
| **2f** | DMSO | 0.5, 77 | 0 | 100 | 128–130 |
| **2a** | DMSO-$d_6$ | 24, rt | 0 | 72 | |
| **2b** | DMSO-$d_6$ | 24, rt | 0 | 80 | |
| **2c** | DMSO-$d_6$ | 24, rt | 0 | 77 | |
| **2d** | DMSO-$d_6$ | 24, rt | 0 | 82 | |
| **2e** | DMSO-$d_6$ | 24, rt | 0 | 81 | |
| **2b** | $CCl_4$ | 40, 77 | 54 | 46 | |
| **2b** | Degassed $CCl_4$ | 40, 77 | 54 | 46 | |
| **2c** | $CCl_4$ | 40, 77 | 50 | 50 | |
| **2i** | DMSO | 20, 77 | 0 | 100 | 110 |
| **2j** | DMSO | 20, 77 | 0 | 100 | 144 |
| **2k** | DMSO | 20, 77 | 0 | 100 | 122–123 |
| **2l** | DMSO | 20, 77 | 0 | 100 | 121–122 |
| **2m** | DMSO | 20, 77 | 0 | 100 | 158–159 |

[a] The yields were determined by $^1H$ NMR.

**Table 1**
Synthesis of 3*H*-imidazol-1-ium ylides **5a–n**

| **1–6** | R | $R^1$ | $R^2$ | RT[a] | Yield[b] | Mp (°C) |
|---|---|---|---|---|---|---|
| **a** | $C_6H_5$ | H | OMe | 13 | 14 | 273–274 |
| **b** | 4-$MeC_6H_4$ | H | OMe | 10 | 22[c] | 289–291 |
| **c** | 4-$MeOC_6H_4$ | H | OMe | 7 | 25[d] | 302–303 |
| **d** | 4-$ClC_6H_4$ | H | OMe | 5 | 40 | 292–293 |
| **e** | 4-$BrC_6H_4$ | H | OMe | 5 | 40 | 305–306 |
| **f** | 3,4$(MeO)_2C_6H_3$ | H | OMe | 11 | 19 | 255–257 |
| **g**[e] | 4-$MeC_6H_4$ | H | (−)-*O*-Menthyl | 10 | 15 | 242–245 |
| **h** | 4-$MeOC_6H_4$ | H | (−)-*O*-Menthyl | 4 | 14 | 253–255 |
| **i** | 4-$MeOC_6H_4$ | Ph | OMe | 23 | 48 | 149–150 |
| **j** | 4-$MeC_6H_4$ | Ph | OMe | 16 | 49 | 117–118 |
| **k** | 4-$MeC_6H_4$ | 4-$MeOC_6H_4$ | OMe | 19 | 52 | 140–142 |
| **l** | 4-$MeC_6H_4$ | 4-$ClC_6H_4$ | OMe | 6 | 38 | 155–156 |
| **m** | 4-$MeC_6H_4$ | 3-$NO_2C_6H_4$ | OMe | 14 | 60 | 222–223 |
| **n** | 4-$MeC_6H_4$ | 3,4$(MeO)_2C_6H_3$ | OMe | 15 | 57 | 128–130 |

[a] The reaction times in hours for the reaction in toluene at reflux temperatures.
[b] The isolated yields of **5** from the reaction in toluene (%).
[c] The yield remained the same when the reaction was performed passing air through the reaction mixture.
[d] The yields of **5** were 25 and 22% when the reaction was performed under nitrogen atmosphere and the solvent was degassed, respectively.
[e] Compounds **5g**,**h** were prepared from the corresponding **2g**,**h** (unseparable diastereomeric mixtures of 2-(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-methyl 3a-phenyl-5-aryl-3a,4,5,6-tetrahydroimidazo[1,5-*b*]isoxazole-2,3-dicarboxylates).

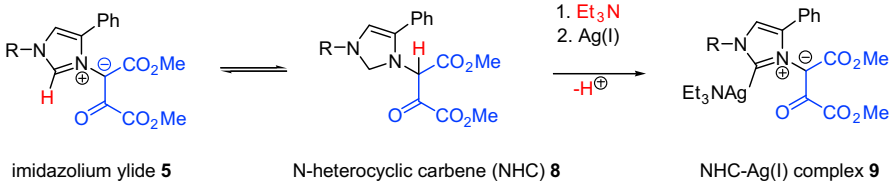
and 3.70 ppm in their $^1$H NMR spectra corresponding to the ester methoxy groups. The doublets at ca. 8.49 and 9.77 ppm ($J$=2.0 Hz) belong to the imidazolium ring protons at C4-H and C2-H, respectively in the spectra of 2-unsubstituted ylides **5** recorded in DMSO-$d_6$. In the $^{13}$C spectra, the carbonyls of the ester functional groups have signals at ca. 165.0 and 168.7 ppm, while the ketone carbonyl resonates at ca. 173.7. The ylide carbons' peaks appear at ca. 95 ppm in the $^{13}$C NMR spectra of compounds **5**.

The formation of adducts **2** and their further conversions was monitored by TLC and $^1$H NMR. The probable mechanism for the formation of ylides **5** and imidazoles **6** is depicted in Scheme 2. Ylides **3** formed as we have discussed previously[7a,b] probably isomerize to 2-hydroxy-3-(2,3-dihydroimidazol-1-yl)maleates **4**.

Compounds **5** were assumed to be products from the dehydrogenation (most probably proceeding as synchronous 1,5-elimination as shown in Scheme 2) of enol-**4** while the keto-**4** isomer undergoes 1,2-elimination to give **6** and dimethyloxaloacetate. Performing the reaction under nitrogen and in degassed toluene did not affect the yield (See the legend of Table 1). Performing the reaction passing air through the mixture in the case of **4c** also did not lead to new product distribution. The latter facts confirm that oxygen has no effect on the mechanism of the reaction and support the proposed non-radical eliminations. Other possibilities such as disproportionation[8] of **3** or reduction of unsaturated reagents and products in the reaction were also considered, however no adequate structures in the crude reaction mixtures were detected.

To understand the mechanism of the eliminations outlined in Scheme 2 we heated adducts **2** in solvents more and less polar than toluene. The reaction of adducts **2** in DMSO-$d_6$ at 77 °C proceeded quantitatively to the corresponding imidazoles (Scheme 3, Table 2) and dimethyloxaloacetate. The conversions of **2a**–**e** to **6a**–**e** in DMSO-$d_6$ at room temperature after 24 h were 72, 80, 77, 82, 81%, respectively. In the cases of chlorosubstituted adduct **2d**, an intermediate was detected whose $^1$H NMR characteristics are in agreement with structures **4**. The compound has the following resonances in DMSO-$d_6$, $\delta$ 3.29 (3H, s), 3.40 (3H, s), 4.67 (2H, d, $J$=6.0 Hz, C2-H), 6.11 (1H, t, $J$=6.0 Hz, C4-H), 6.68 (2H, d, $J$=8.8 Hz, N2-Ar-o), 7.08 (2H, d, $J$=8.8 Hz, N2-Ar-m), 7.55 (2H, t, $J$=8.0 Hz, C5-Ar-m), 8.05 (2H, d, $J$=8.0 Hz, C5-Ar-o). Some characteristic peaks for dimethyloxaloacetate are as follows; $\delta$ 3.38–3.90 (6H, 10 peaks, MeO groups of oxaloacetate tautomers), 4.67, 4.69, 4.99, 5.17, 5.81 (1H, 5 peaks), 9.42, 11.21 (1H, 2 br s). The reaction in the less polar $CCl_4$ at 77 °C proceeded with increased yield of **5** (Table 2). The conversion rate of **2b** when 0.083 M solution was heated at reflux in $CCl_4$ was nearly half the rate of the reaction performed with 0.17 M solution and the imidazole ylide ratio was 1:0.6. The reaction in degassed $CCl_4$ under nitrogen atmosphere proceeded with the same rate and product ratio. The reaction rate in the $CCl_4$ was 80 times lower than in DMSO, and the rate limiting step in the cascade was the ring-opening reaction of **2**. To separate the ylide **5b** from the corresponding imidazole we dissolved the mixture of **5**/**6b** in 36% HCl at room temperature and stirred for several minutes then the mixture was diluted with water. The formed imidazole hydrochloride was separated by filtration and the filtrate was basified with ammonia and extracted with $CHCl_3$. The extract contained 1-methoxycarbonylmethyl-3,5-diphenyl-3H-imidazol-1-ium **7b** the structure of which was confirmed by spectroscopy.[9] The chemoselective imidazole formations ensured by the polar solvent can be rationalized by assuming that the transition state of ketone-**4** conversion to **6** probably involves much more charge separation than the case of enol-**4** to **5**. The apolar solvents probably stabilize better the transition state of enol-**4** to **5** than polar solvents. Certainly the formation of compounds **4**, by a cascade reaction involving initial homolysis of the corresponding C–C bond in adducts **2**, is not excluded.

In fact, ylides **5** are isomeric structures with **8**, which we were planning to use as ligands for catalyst of Heck, Suzuki etc. coupling reactions. To convert compounds **5** to NHCs **8** we treated them with an excess of $Et_3N$ in $CH_2Cl_2$ at room temperature for several hours, however no change was detected. The treatment of ylide **5b** with $Ag_2O$ in $CH_2Cl_2$ at room temperature in the dark for 22 h also did not lead to any change of the starting **5b**. However, addition of an excess of $Et_3N$ to the latter mixture and stirring for 2 h induced a metallation of **5b** at C-2 carbon to give compound **9b** quantitatively. Compounds **9a**–**f** were prepared (Scheme 4, Table 3) by the use of $AgNO_3$ as a metal source. The first structurally characterized silver–NHC complex was made by using a free carbene and a silver salt,[10] however, generally silver bases were reacted with imidazolium salts formed in situ. The silver salts reported so far in the formation of Ag(I)–NHC complexes are silver acetate,[11] $Ag_2O$[12] and $Ag_2CO_3$.[13] Silver *N*-heterocyclic carbene complexes have played an important role in the development of other metal-carbene systems. Transmetalation reactions using silver carbenes have been reported for a wide variety of transition metals.[14]




imidazolium ylide **5** N-heterocyclic carbene (NHC) **8** NHC-Ag(I) complex **9**

**Scheme 4.** Metallation of ylides **5a**–**f**.

**Table 3**
Synthesis of 3*H*-imidazol-1-ium ylides Ag(I) derivatives **9a**–**f**

| Entry | R | Yield[a] (%) | Mp[b] (°C) | Entry | R | Yield[a] (%) | Mp[b] (°C) |
|---|---|---|---|---|---|---|---|
| **a** | $C_6H_5$ | 91 | 268–269 | **d** | 4-$ClC_6H_4$ | 97 | 287–288 |
| **b** | 4-$MeC_6H_4$ | 99[c] | 282–283 | **e** | 4-$BrC_6H_4$ | 98 | 286–288 |
| **c** | 4-$MeOC_6H_4$ | 87 | 285–286 | **f** | 3,4$(MeO)_2C_6H_3$ | 98 | 258–260 |

[a] The yields of **9a**–**f** from the reactions of **5a**–**f** with $AgNO_3$ in $CH_2Cl_2$ at room temperature for 2 h.
[b] The decomposition temperatures of the compounds, which first loss $Et_3N$ as revealed by their TGA data.
[c] The yield from the reaction with $Ag_2O$ is the same.

The IR spectra of compounds **9** have stretches at ca. 1729 and 1679 cm$^{-1}$ corresponding to the carbonyl groups. A comparison with the frequencies of the same groups in the starting **5** (Table 4, columns 7, 13) reveal that, except in the cases **9a**,**b** where $\nu_{C=O(1)}$ increases while $\nu_{C=O(2)}$ decreases by ca. 15 cm$^{-1}$, there are no significant changes in the carbonyl frequencies.

**Table 4**
Comparison of the characteristic chemical shifts and C=O stretching of ylides **5** and their Ag(I)-complexes **9**

| | **5** | | | | | | **9** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C2(H) | C4(H) | C=O[a] | C=O(1) | C=O(2) | $\nu_{C=O}$ | C2[b] | C4(H)[b] | C=O | C=O(1) | C=O(2) | $\nu_{C=O}$ |
| **a** | 138.9 | 118.2 | 172.8 | 164.8 | 168.6 | 1736; | | 118.7 | 174.1 | 166.3 | 169.5 | 1728; |
| | 9.91 | 8.59 | | 3.38 | 3.63 | 1659 | | 7.99 | | 3.27 | 3.60 | 1671 |
| **b** | 138.7 | 118.2 | 174.5 | 164.8 | 168.7 | 1742; | 184.3 | 118.7 | 174.1 | 166.3 | 169.5 | 1729; |
| | 9.84 | 8.54 | | 3.38 | 3.63 | 1663 | | 7.94 | | 3.26 | 3.59 | 1679 |
| **c** | 138.5 | 118.5 | 172.9 | 164.7 | 168.4 | 1726; | 183.9 | 118.9 | 174.1 | 166.3 | 169.5 | 1728; |
| | 9.77 | 8.49 | | 3.38 | 3.62 | 1663 | | 7.90 | | 3.25 | 3.60 | 1663 |
| **d** | 137.5 | 118.3 | 173.6 | 164.7 | 168.6 | 1740; | 184.8 | 118.6 | 174.1 | 166.3 | 169.6 | 1736; |
| | 9.90 | 8.58 | | 3.29 | 3.63 | 1659 | | 8.01 | | 3.25 | 3.60 | 1650 |
| **e** | 137.5 | 118.3 | 173.5 | 164.7 | 168.6 | 1740; | 184.8 | 118.6 | 174.1 | 166.3 | 169.6 | 1732; |
| | 9.90 | 8.58 | | 3.38 | 3.63 | 1657 | | 8.01 | | 3.25 | 3.60 | 1655 |
| **f** | 138.5 | 118.2 | 173.6 | 164.8 | 168.6 | 1732; | | 119.1 | 174.1 | 166.3 | 169.6 | 1732; |
| | 9.81 | 8.54 | | 3.33 | 3.63 | 1667 | | 7.93 | | 3.26 | 3.59 | 1667 |

[a] C=O; C=O(1) and C=O(2) are the ketone and ester carbonyls at C1 and C2 of the ethanide carbons, respectively.
[b] The C2(Ag) carbons are not observed in the $^{13}C$ NMR spectra, however in the case of **9b–e** it was deduced from their g-HMBC spectra.

The comparison of the NMR data for **5a–f** and **9a–f** reveals also that the electronic density changes around the ylide carbon are very small (Table 4, a comparison of the characteristic NMR data for **5b** and **9b** is given in Fig. 1), which implies that the ketone carbonyl oxygen in **9** is slightly interacting with the metal centre. The elemental analysis data and the $^1H$ NMR data (400 MHz, DMSO-$d_6$) reveal the presence of 1 mol of $Et_3N$ coordinated to the metal centre. The peaks corresponding to C2-H in **5** are absent in **9** and the peaks of C4-H at ca. 8.53 ppm are up fielded by 0.60 ppm due to substitution of C2-H for the less electronegative Ag (Table 4, columns 3,9). The hydrolysis of **9b** in DMSO-$d_6$ at room temperature provided the starting **5b**, while the reaction with $D_2O$ in DMSO-$d_6$ allowed us to prepare C-2-deuterated **5b**. The resonance for the C2-H was absent, while the C4-H signal was shifted up-field by ca. 0.15 ppm.

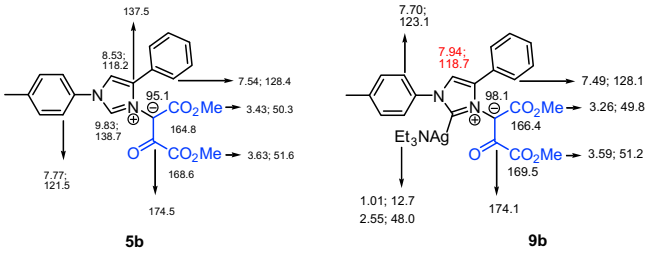



**Figure 1.** Comparison of the characteristic chemical shifts of ylide **5b** and its metallated analog **9b**.[15]

The thermal behaviour of complexes **9** were studied by thermal gravimetry (TG) and differential thermal gravimetry (DTG) in a dynamic $N_2$ atmosphere. The thermal decompositions of **9** occur in multiple steps (Scheme 5, Table 5). The compounds first lose $Et_3N$ to give intermediate **A** then lose the corresponding 1,3-diarylimidazole derivative to give structures **B**. The final product detected is corresponding to $Ag_2O$.

**Table 5**
Thermal analysis data for complexes **9a–f**

| Complex | TG | | | | DTG | |
|---|---|---|---|---|---|---|
| | Theoretical[a] | | Observed[a] | | Peak temperature (°C) | |
| **9a** | 17.2[b] | 45.2[c] | 16.5[b] | 48.0[c] | 106.3[b] | 262.1[c] |
| **9b** | 16.8 | 39.0 | 14.3 | 40.2 | 117.6 | 279.6; 291.5 |
| **9c** | 16.4 | 40.6 | 13.0 | 37.6 | 115.5 | 291.3 |
| **9d** | 16.3 | 40.9 | 14.1 | 38.8 | 133.2 | 287.3; 289.7 |
| **9e** | 15.1 | 44.8 | 15.7 | 40.6 | 128.8 | 292.6; 302.7 |
| **9f** | 15.6 | 43.3 | 15.4 | 40.6 | 104.2 | 256.9 |

[a] wt. loss (%).
[b] The loss of $Et_3N$.
[c] The loss of the corresponding 1,3-diarylimidazole.

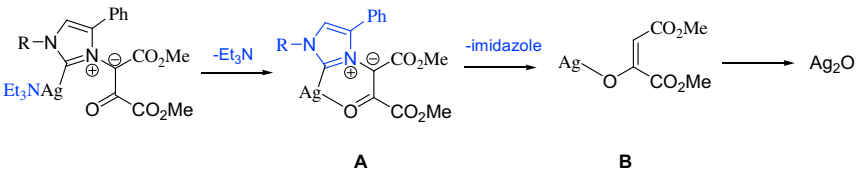
## 3. Conclusions

The thermal rearrangements of 1,2,4-triaryl- and 1,4-diaryl-2,5-dihydro-1*H*-imidazole 3-oxide **1** DMAD adducts **2** lead to 3,4-dihydro-2*H*-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxo-ethanides) **3**, which spontaneously undergo competing 1,5- and 1,2-eliminations to give 3*H*-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxo-ethanides) **5** or 1*H*-imidazole **6** when heated in toluene at reflux. Adducts **2** was shown to convert quantitatively to imidazoles **6** in polar solvent such as DMSO. For the first time ylides **5** were metallated at C-2 with Ag(I). The latter compounds will be used as precursors in the preparation of Pd–NHC complexes.

## 4. Experimental

### 4.1. General

The solvents and the reagents used in the syntheses were purchased from Merck (MeOH, $CHCl_3$, $CH_2Cl_2$, petroleum ether 40–60 °C, EtOH, benzene and the aromatic amines, $Et_3N$ and $Ag_2O$), Aldrich (formaldehyde, DMAD and $AgNO_3$), Fluka (phenacyl bromide and $(NH_2OH)_2H_2SO_4$). Melting points were recorded on an Electrothermal Digital melting point apparatus. Infrared spectra were recorded on a Thermo-Nicolet 6700 FTIR. 1D and 2D NMR experiments were performed on a Varian Mercury Plus 400 MHz




**Scheme 5.** Thermal decomposition pattern of compounds **9**.

spectrometer. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained using a SII Exstar TG/DTA 6200 analyser in the range 25–100 °C in platinum crucibles under nitrogen at a heating rate of 10 °C $min^{-1}$ using alumina as reference. The elemental analyses were performed on a EuroEA 3000 CHNS analyser. The compounds prepared were dried in a vacuum oven at room temperature. Nitrones **1a**–**l** were prepared according to the previously reported methods.[1,2i]

### 4.2. Synthesis of 4-phenyl-1-aryl-2,5-dihydro-1*H*-imidazole 3-oxides 1

*4.2.1. 1-(3,4-Dimethoxyphenyl)-4-phenyl-2,5-dihydro-1H-imidazole 3-oxide* ***1f***. Yield 0.320 g, 9%. Colourless powder, mp 183–184 °C. IR (KBr) $\nu_{C=N-O}$ 1579, $\nu_{C=N-O}$ 1245 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.65 (3H, s), 3.78 (3H, s), 4.75 (2H, t, $J$=4.0), 5.26 (2H, t, $J$=4.0), 6.17 (1H, dd, $J$=8.4; 2.8), 6.39 (1H, d, $J$=2.8), 6.86 (1H, d, $J$=8.4), 7.49–7.52 (3H, m), 8.36–8.38 (2H, m). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 53.6; 56.1; 56.8; 78.8; 98.8; 103.7; 114.5; 126.9; 127.8; 129.0; 131.0; 136.4; 140.4; 142.1; 150.5. Anal. Calcd for $C_{17}H_{18}N_2O_3$ (298.34): C, 68.44; H, 6.08; N, 9.39. Found: C, 68.50; H, 5.90; N, 9.49.

### 4.3. Synthesis of (*R*)- and (*S*)-2-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) 3-methyl 3a-phenyl-5-aryl-3a,4,5,6-tetrahydroimidazo[1,5-*b*]isoxazole-2,3-dicarboxylates 2g,h

Compounds **2b**,**c** were reacted with the Reformatsky reagent prepared from (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-bromoacetate according to the transesterification procedure we have recently reported.[2h]

*4.3.1. (R)- and (S)-2-((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl) 3-methyl 3a-phenyl-5-p-tolyl-3a,4,5,6-tetrahydroimidazo[1,5-b]isoxazole-2,3-dicarboxylate* ***2g***. Yield 0.830 g, 80%. Yellowish oil. IR (neat) $\nu_{C=O}$ 1753, 1711, $\nu_{C=C}$ 1656 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ ppm 0.78–2.07 (18H, m), 2.28 (3H, s), 3.43 (0.5H, d, $J$=10.0); 3.44 (0.5H, d, $J$=10.0), 3.62 (3H, s), 4.23 (0.5H, d, $J$=10.8), 4.24 (0.5H, d, $J$=10.8), 4.66 (0.5H, d, $J$=10.0), 4.68 (0.5H, d, $J$=10.0), 4.88 (1H, dt, $J$=11.2, 4.8), 5.04 (0.5H, d, $J$=10.8), 5.05 (0.5H, d, $J$=10.8), 6.71 (2H, d, $J$=8.4), 7.09 (2H, d, $J$=8.4), 7.28–7.32 (1H, m), 7.36–7.40 (2H, m), 7.60–7.63 (2H, m). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ ppm 16.1; 16.2; 16.3; 20.4; 20.6; 20.7; 21.0; 22.0; 22.2; 23.1; 23.2; 23.5; 25.8; 25.9; 26.1; 29.7; 31.4; 31.6; 34.0; 34.1; 34.5; 40.3; 45.0; 46.6; 50.1; 51.6; 57.1; 57.2; 71.5; 76.0; 76.1; 82.3; 82.4; 109.3; 109.4; 115.1; 115.2; 121.3; 124.9; 126.9; 128.0; 128.3; 129.0; 129.8; 141.0; 143.9; 144.0; 152.7; 152.9; 158.4; 158.5; 162.6. Anal. Calcd for $C_{31}H_{38}N_2O_5$ (518.64): C, 71.79; H, 7.38; N, 5.40. Found: C, 71.50; H, 7.22; N, 5.24.

*4.3.2. (R)- and (S)-2-((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl) 3-methyl 5-(4-methoxyphenyl)-3a-phenyl-3a,4,5,6-tetrahydroimidazo [1,5-b]isoxazole-2,3-dicarboxylate* ***2h***. Yield 0.802 g, 75%. Yellowish oil. IR (neat) $\nu_{C=O}$ 1753, 1711, $\nu_{C=C}$ 1656 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ ppm 0.78–2.07 (18H, m), 3.40 (0.5H, d, $J$=10.0); 3.39 (0.5H, d, $J$=10.0), 3.77 (3H, s), 3.622 (1.5H, s); 3.619 (1.5H, s), 4.18 (0.5H, d, $J$=10.8), 4.19 (0.5H, d, $J$=10.8), 4.63 (0.5H, d, $J$=10.0), 4.64 (0.5H, d, $J$=10.0), 4.89 (1H, dt, $J$=11.0, 4.4), 5.01 (0.5H, d, $J$=10.8), 5.02 (0.5H, d, $J$=10.8), 6.75–6.77 (2H, m), 6.84–6.87 (2H, m), 7.28–7.32 (1H, m), 7.36–7.40 (2H, m), 7.60–7.63 (2H, m). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ ppm 16.0; 16.1; 16.3; 20.6; 20.7; 21.0; 22.0; 22.2; 23.1; 23.3; 23.5; 25.8; 26.1; 29.7; 31.4; 31.6; 34.0; 34.5; 40.3; 45.0; 46.6; 50.1; 51.8; 55.6; 57.7; 71.5; 82.4; 82.5; 109.2; 109.4; 114.8; 116.5; 116.6; 123.2; 125.0; 127.0; 128.0; 128.3; 140.3; 141.1; 152.7; 152.9; 153.5; 158.4; 158.5; 162.6. Anal. Calcd for $C_{31}H_{38}N_2O_6$ (534.64): C, 69.64; H, 7.16; N, 5.24. Found: C, 69.35; H, 7.00; N, 5.00.

### 4.4. Synthesis of 3*H*-imidazol-1-ium ylides 5a–n

*4.4.1. General procedure.* DMAD (1 mmol, 0.145 g, 98%) was added to a solution of imidazoline 3-oxide **1** (1 mmol) in toluene (25 mL) and the reaction mixture heated at reflux for the specified time. In the cases of **5a**–**f** the precipitated products were filtered and dried in a vacuum oven. In the other cases the solvent was evaporated and the reaction mixture was extracted with petroleum ether (3×15 mL) heating at reflux. The residue was dissolved in hot THF–petroleum ether (25 mL, 1:4) and left to crystallize. The amorphous solid was filtered and dried under vacuum to give compounds **5**. The petroleum ether extracts were combined and the solvent evaporated. The residue contained mainly the corresponding imidazoles.

*4.4.2. 3,5-Diphenyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5a***. Gold coloured powder, mp 273–274 °C. IR (KBr) $\nu_{C=O}$ 1736 and 1659 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.33 (3H, s), 3.63 (3H, s), 7.46–7.58 (6H, m), 7.65 (2H, t, $J$=7.6), 7.89 (2H, d, $J$=7.6), 8.59 (1H, d, $J$=1.6), 9.91 (1H, d, $J$=1.6). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 50.3; 51.6; 118.2; 121.7; 126.7; 128.4; 129.1; 129.4; 130.1; 130.7; 135.0; 137.5; 138.9; 164.8; 168.6; 172.8. Anal. Calcd for $C_{21}H_{18}N_2O_5$ (378.4): C, 66.66; H, 4.79; N, 7.40. Found: C, 66.45; H, 4.55; N, 7.15.

*4.4.3. 5-Phenyl-3-p-tolyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5b***. White powder, mp 289–291 °C. IR (KBr) $\nu_{C=O}$ 1742 and 1663 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.47 (3H, s), 3.45 (3H, s), 3.86 (3H, s), 7.39–7.47 (8H, m), 7.55–7.57 (2H, m), 8.44 (1H, d, $J$=2.0). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.2; 50.5; 52.0; 95.1; 116.7; 121.8; 125.7; 128.4; 128.8; 130.2; 131.2; 132.4; 136.4; 139.4; 141; 165.0; 168.7; 173.7. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 2.38 (3H, s), 3.33 (3H, s), 3.63 (3H, s), 7.44–7.47 (5H, m), 7.53–7.55 (2H, m), 7.77 (2H, d, $J$=8.4), 8.54 (1H, d, $J$=2.0), 9.84 (1H, d, $J$=2.0). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 21.0; 50.3; 51.6; 93.9; 118.2; 121.5; 126.7; 128.4; 129.1; 130.1; 131.1; 132.7; 137.5; 138.7; 139.9; 164.8; 168.7; 174.5. Anal. Calcd for $C_{22}H_{20}N_2O_5$ (392.4): C, 67.34; H, 5.14; N, 7.14. Found: C, 66.98; H, 5.17; N, 7.00.

*4.4.4. 3-(4-Methoxyphenyl)-5-phenyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5c***. Cream coloured powder, mp 302–303 °C. IR (KBr) $\nu_{C=O}$ 1726 and 1663 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.33 (3H, s), 3.62 (3H, s), 3.83 (3H, s), 7.17 (2H, d, $J$=8.4), 7.45–7.53 (5H, m), 7.80 (2H, d, $J$=8.4), 8.49 (1H, s), 9.77 (1H, s). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 50.4; 51.7; 56.2; 94.3; 115.7; 118.5; 123.2; 126.7; 128.1; 128.4; 129.1; 130.1; 137.3; 138.5; 160.3; 164.7; 168.4; 172.9. Anal. Calcd for $C_{22}H_{20}N_2O_6$ (408.4): C, 64.70; H, 4.94; N, 6.86. Found: C, 64.60; H, 5.12; N, 6.75.

*4.4.5. 3-(4-Chlorophenyl)-5-phenyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5d***. Cream coloured powder, mp 292–293 °C. IR (KBr) $\nu_{C=O}$ 1740 and 1659 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.29 (3H, s), 3.63 (3H, s), 7.47–7.53 (5H, m), 7.74 (2H, d, $J$=8.0), 7.94 (2H, d, $J$=8.0), 8.58 (1H, d, $J$=2.0), 9.90 (1H, d, $J$=2.0). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 50.3; 51.6; 118.3; 123.5; 126.6; 128.4; 129.2; 130.2; 130.6; 133.9; 134.5; 137.5; 139.1; 164.7; 168.6; 173.6. Anal. Calcd for $C_{21}H_{17}ClN_2O_5$ (412.8): C, 61.10; H, 4.15; N, 6.79. Found: C, 60.75; H, 4.04; N, 6.62.

*4.4.6. 3-(4-Bromophenyl)-5-phenyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5e***. Cream coloured powder, mp 305–306 °C. IR (KBr) $\nu_{C=O}$ 1740 and 1657 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.33 (3H, s), 3.63 (3H, s), 7.46–7.48 (3H, m), 7.52–7.55 (2H, m), 7.87 (4H, s), 8.58 (1H, d, $J$=2.0), 9.90 (1H, d, $J$=2.0). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 50.3; 51.6; 118.3; 123.0; 123.8; 126.5; 128.4; 129.2; 130.2; 133.6; 134.3; 137.5; 139.0; 164.7; 168.6; 173.5. Anal.

Calcd for $C_{21}H_{17}BrN_2O_5$ (457.3): C, 55.16; H, 3.75; N, 6.13. Found: C, 55.19; H, 3.50; N, 5.95.

*4.4.7. 3-(3,4-Dimethoxyphenyl)-5-phenyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5f***. Cream coloured powder, mp 255–257 °C. IR (KBr) $\nu_{C=O}$ 1732 and 1667 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.33 (3H, s), 3.63 (3H, s), 3.82 (3H, s), 3.87 (3H, s), 7.17 (1H, d, $J$=8.4), 7.41 (1H, d, $J$=2.4), 7.43 (1H, d, $J$=2.8), 7.46–7.49 (3H, m), 7.54–7.60 (2H, m), 8.54 (1H, d, $J$=2.0), 9.81 (1H, d, $J$=2.0). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 50.3; 51.6; 56.3; 51.6; 105.7; 112.5; 113.3; 118.2; 126.7; 128.1; 128.4; 129.1; 130.1; 137.3; 138.5; 149.8; 150.0; 164.8; 168.6; 173.6. Anal. Calcd for $C_{23}H_{22}N_2O_7$ (438.4): C, 63.01; H, 5.06; N, 6.39. Found: C, 63.08; H, 5.06; N, 6.09.

*4.4.8. 5-Phenyl-3-p-tolyl-3H-imidazol-1-ium-1-[(1-methoxycarbonyl)-2-menthyloxycarbonyl]-2-oxoethanide* ***5g***. White powder, mp 242–245 °C. IR (KBr) $\nu_{C=O}$ 1728 and 1665 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.82–2.32 (18H, m), 2.46 (3H, s), 3.48 (3H, s), 4.76–4.85 (1H, m), 7.38–7.41 (8H, m), 7.57–7.99 (2H, m), 8.41 (1H, s). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 16.5; 20.9; 21.2; 22.1; 23.6; 25.8; 31.4; 34.3; 40.4; 47.0; 50.4; 74.8; 94.9; 116.7; 121.9; 125.8; 128.5; 128.7; 130.0; 131.1; 132.4; 136.6; 139.3; 140.9; 159.7; 167.8; 173.9. Anal. Calcd for $C_{31}H_{36}N_2O_5$ (516.63): C, 72.07; H, 7.02; N, 5.42. Found: C, 72.00; H, 6.90; N, 5.68.

*4.4.9. 5-Phenyl-3-p-methoxyphenyl-3H-imidazol-1-ium-1-[(1-methoxycarbonyl)-2-menthyloxycarbonyl]-2-oxoethanide* ***5h***. White powder, mp 253–255 °C. IR (KBr) $\nu_{C=O}$ 1729 and 1665 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.82–2.28 (18H, m), 3.48 (3H, s), 3.90 (3H, s), 4.76–4.85 (1H, m), 7.07 (2H, d, $J$=8.8), 7.41–7.47 (6H, m), 7.57–7.59 (2H, m), 8.36 (1H, s). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 16.5; 20.9; 22.1; 23.6; 25.9; 31.4; 34.3; 40.4; 47.0; 50.4; 55.8; 74.9; 115.6; 117.0; 123.7; 125.8; 127.8; 128.4; 128.7; 130.0; 136.6; 139.1; 155.5; 160.9; 167.8; 173.9. Anal. Calcd for $C_{31}H_{36}N_2O_6$ (532.63): C, 69.90; H, 6.81; N, 5.26. Found: C, 69.60; H, 6.66; N, 5.40.

*4.4.10. 3-(4-Methoxyphenyl)-2,5-diphenyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5i***. Brown powder, mp 149–150 °C. IR (KBr) $\nu_{C=O}$ 1736 and 1674 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.37 (3H, s), 3.72 (3H, s), 3.82 (3H, s), 6.90 (2H, d, $J$=8.8), 7.24 (2H, d, $J$=8.8), 7.35–7.39 (5H, m), 7.44–7.47 (4H, m), 7.61–7.63 (2H, m). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 50.5; 51.7; 55.6; 95.6; 115.0; 119.0; 122.4; 125.9; 126.8; 128.2; 128.72; 128.73; 129.0; 130.05; 130.09; 131.7; 138.7; 147.8; 160.4; 165.2; 168.5; 174.5. Anal. Calcd for $C_{28}H_{24}N_2O_6$ (484.5): C, 69.41; H, 4.99; N, 5.78. Found: C, 69.10; H, 5.05; N, 5.65.

*4.4.11. 3-(p-Tolyl)-2,5-diphenyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5j***. Yellow powder, mp 117–118 °C. IR (KBr) $\nu_{C=O}$ 1736 ad 1679 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.38 (3H, s), 3.36 (3H, s), 3.72 (3H, s), 7.16–7.22 (4H, m), 7.35–7.38 (4H, m), 7.43–7.47 (5H, m), 7.61–7.63 (2H, m). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.2; 50.5; 51.8; 95.0; 113.9; 118.8; 122.3; 125.2; 125.9; 128.72; 128.73; 129.0; 130.1; 130.5; 131.8; 133.0; 138.8; 140.4; 147.8; 165.2; 168.5; 174.5. Anal. Calcd for $C_{28}H_{24}N_2O_5$ (468.5): C, 71.78; H, 5.16; N, 5.98. Found: C, 71.50; H, 5.30; N, 5.71.

*4.4.12. 3-(p-Tolyl)-2-(4-methoxyphenyl)-5-phenyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5k***. Cream coloured powder, mp 140–142 °C. IR (KBr) $\nu_{C=O}$ 1740 and 1679 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.32 (3H, s), 3.30 (3H, s), 3.68 (3H, s), 3.73 (3H, s), 6.79 (2H, d, $J$=8.8), 7.10–7.19 (6H, m), 7.30 (2H, d, $J$=9.2), 7.38–7.39 (2H, m), 7.53–7.56 (2H, m). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.2; 50.5; 51.8; 55.3; 95.1; 114.1; 114.3; 118.6; 125.2; 128.7; 129.0; 130.0; 130.6; 131.8; 133.2; 138.7; 140.3; 147.9; 162.0; 165.0; 165.2; 168.6; 174.6. Anal. Calcd for $C_{29}H_{26}N_2O_6$ (498.53): C, 69.87; H, 5.26; N, 5.62. Found: C, 69.75; H, 5.33; N, 5.54.

*4.4.13. 2-(4-Chlorophenyl)-5-phenyl-3-p-tolyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5l***. Cream coloured powder, mp 155–156 °C. IR (KBr) $\nu_{C=O}$ 1738 and 1682 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.37 (3H, s), 3.39 (3H, s), 3.71 (3H, s), 7.22 (4H, s), 7.29–7.32 (2H, m), 7.37–7.39 (3H, m), 7.42–7.46 (3H, m), 7.57–7.59 (2H, m). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.2; 50.8; 51.9; 95.5; 119.5; 120.6; 125.4; 125.6; 128.8; 129.1; 129.2; 130.2; 130.7; 131.5; 132.7; 138.3; 138.7; 140.7; 146.5; 165.0; 167.8; 173.3. Anal. Calcd for $C_{28}H_{23}ClN_2O_5$ (502.95): C, 66.87; H, 4.61; N, 5.57. Found: C, 66.75; H, 4.73; N, 5.32.

*4.4.14. 2-(3-Nitrophenyl)-5-phenyl-3-p-tolyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5m***. Cream coloured powder, mp 222–223 °C. IR (KBr) $\nu_{C=O}$ 1732 and 1662 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.33 (3H, s), 3.34 (3H, s), 3.64 (3H, s), 7.15–7.21 (4H, m), 7.38–7.42 (4H, m), 7.54–7.60 (3H, m), 7.93 (1H, d, $J$=8.0), 8.09 (1H, s), 8.26 (1H, d, $J$=8.8). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.2; 50.7; 51.8; 95.5; 110.0; 119.5; 123.9; 125.3; 125.4; 126.5; 128.9; 129.0; 130.3; 130.4; 131.0; 132.2; 136.3; 139.3; 141.4; 145.0; 147.8; 165.0; 168.2; 174.4. Anal. Calcd for $C_{28}H_{23}N_3O_7$ (513.5): C, 65.49; H, 4.51; N, 8.18. Found: C, 65.28; H, 4.70; N, 7.95.

*4.4.15. 2-(3,4-Dimethoxyphenyl)-5-phenyl-3-p-tolyl-3H-imidazol-1-ium-1-(1,2-bis-methoxycarbonyl-2-oxoethanide)* ***5n***. Cream coloured powder, mp 128–130 °C. IR (KBr) $\nu_{C=O}$ 1732 and 1687 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.40 (3H, s), 3.37 (3H, s), 3.75 (3H, s), 3.86 (3H, s), 3.88 (3H, s), 6.74–6.76 (2H, m), 7.19–7.28 (5H, m), 7.46–7.48 (4H, m), 7.61–7.63 (2H, m). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.2; 50.5; 51.7; 55.8; 56.1; 95.4; 110.7; 112.8; 114.2; 118.6; 123.5; 125.2; 126.1; 128.7; 129.0; 130.0; 130.5; 133.3; 138.8; 140.3; 147.9; 149.1; 151.6; 165.2; 168.6; 174.2. Anal. Calcd for $C_{30}H_{28}N_2O_7$ (528.55): C, 68.17; H, 5.34; N, 5.30. Found: C, 68.00; H, 5.30; N, 5.35.

### 4.5. Synthesis of 1*H*-imidazoles 6

*4.5.1. General procedure.* Imidazoline 3-oxide **1** (1 mmol) was reacted with DMAD (1.5 mmol) in benzene (7 mL) for 1 h heating at reflux. The solvent was evaporated and the residue dissolved in DMSO (5 mL). The mixture was heated at 77 °C for 0.5 h in the cases of **1a**–**f** and 20 h in the cases of **1i**–**m**. The mixture was poured into crushed ice (8 g) and the precipitated product filtered, washed several times with water and dried in a vacuum oven. The yields are quantitative.

*4.5.2. 1,4-Diphenyl-1H-imidazole* ***6a***. Recrystallized from ether–hexane (1:2). Yellowish crystals, mp 93–94 °C. Lit[3a] mp 93–94.2 °C. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.23–7.27 (1H, m), 7.37–7.42 (3H, m), 7.55 (2H, t, $J$=8.0), 7.73 (2H, d, $J$=7.6), 7.87 (2H, d, $J$=6.8), 8.30 (1H, d, $J$=1.2), 8.35 (1H, d, $J$=1.2). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 114.5; 120.6; 124.9; 127.2; 127.4; 129.0; 130.4; 134.4; 136.4; 137.3; 142.3. Anal. Calcd for $C_{15}H_{12}N_2$ (220.27): C, 81.79; H, 5.49; N, 12.72. Found: C, 81.65; H, 5.45; N, 12.65.

*4.5.3. 4-Phenyl-1-p-tolyl-1H-imidazole* ***6b***. Recrystallized from ether. White crystals, mp 132–133 °C. Lit[3a] mp 134–135 °C. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 2.36 (3H, s), 7.24 (1H, t, $J$=7.6), 7.34–7.42 (4H, m), 7.61 (2H, t, $J$=8.4), 7.87 (2H, d, $J$=8.0), 8.25 (1H, d, $J$=1.2), 8.30 (1H, d, $J$=1.2). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 20.9; 114.5; 120.5; 124.9; 127.1; 129.0; 130.7; 134.5; 134.9; 136.3; 136.8; 142.1. Anal. Calcd for $C_{16}H_{14}N_2$ (234.30): C, 82.02; H, 6.02; N, 11.96. Found: C, 81.95; H, 6.03; N, 11.90.

*4.5.4. 1-(4-Methoxyphenyl)-4-phenyl-1H-imidazole* ***6c***. Recrystallized from ether–hexane (1:2). White crystals, mp 103–104 °C. Lit[3a] mp

100–101 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.79 (3H, s), 7.08 (2H, d, $J$=9.2), 7.22 (1H, t, $J$=7.6), 7.37 (2H, t, $J$=7.6), 7.61 (2H, t, $J$=9.2), 7.84 (2H, d, $J$=8.8), 8.17 (1H, d, $J$=1.2), 8.2 (1H, d, $J$=1.2). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 55.9; 114.9; 115.4; 122.3; 124.9; 127.0; 129.0; 130.6; 134.6; 136.4; 142.0; 158.5. Anal. Calcd for $C_{16}H_{14}N_2O$ (250.30): C, 76.78; H, 5.64; N, 11.19. Found: C, 76.70; H, 5.58; N, 11.10.

*4.5.5. 1-(4-Chlorophenyl)-4-phenyl-1H-imidazole* ***6d***. Recrystallized from ethanol. White crystals, mp 139–140 °C. IR (KBr) $\nu_{C=N}$ 1597 and $\nu_{C=C}$ 1552 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.24 (1H, t, $J$=7.2), 7.39 (2H, t, $J$=7.6), 7.61 (2H, $J$=8.4), 7.77 (2H, d, $J$=8.4), 7.84 (2H, d, $J$=7.6), 8.32 (1H, s), 8.37 (1H, s). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 114.4; 122.2; 124.9; 127.2; 129.0; 130.2; 131.5; 134.3; 136.1; 136.5; 142.5. Anal. Calcd for $C_{15}H_{11}ClN_2$ (254.71): C, 70.73; H, 4.35; N, 11.00. Found: C, 70.65; H, 4.30; N, 11.03.

*4.5.6. 1-(4-Bromophenyl)-4-phenyl-1H-imidazole* ***6e***. Recrystallized from ethanol. Orange crystals, mp 151–152 °C. IR (KBr) $\nu_{C=N}$ 1597 and $\nu_{C=C}$ 1552 cm$^{-1}$; NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.26 (1H, t, $J$=7.2), 7.41 (2H, t, $J$=8.0), 7.71–7.77 (4H, m), 7.86 (2H, dd, $J$=8.0, 1.2), 8.33 (1H, d, $J$=1.2), 8.39 (1H, d, $J$=1.2). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 114.4; 119.7; 122.5; 125.0; 127.3; 129.0; 133.2; 134.3; 136.4; 136.5; 142.5. Anal. Calcd for $C_{15}H_{11}BrN_2$ (299.17): C, 60.22; H, 3.71; N, 9.36. Found: C, 60.15; H, 3.69; N, 9.30.

*4.5.7. 1-(3,4-Dimethoxyphenyl)-4-phenyl-1H-imidazole* ***6f***. Recrystallized from DMSO–water. Cream coloured powder, mp 128–130 °C. IR (KBr) $\nu_{C=N}$ 1601 and $\nu_{C=C}$ 1552 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.94 (3H, s), 3.96 (3H, s), 6.93–7.00 (3H, m), 7.28 (1H, t, $J$=7.6), 7.41 (2H, t, $J$=7.6), 7.50 (1H, d, $J$=1.2), 7.84 (2H, d, $J$=7.6), 7.85 (1H, d, $J$=1.2). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 56.2 (2C); 106.0; 111.6; 114.0; 114.5; 124.9; 127.1; 128.7; 130.7; 133.6; 136.1; 142.7; 148.7; 149.8. Anal. Calcd for $C_{17}H_{16}N_2O_2$ (280.32): C, 72.84; H, 5.75; N, 9.99. Found: C, 72.60; H, 5.65; N, 9.86.

*4.5.8. 1-(4-Methoxyphenyl)-2,4-diphenyl-1H-imidazole* ***6i***. Recrystallized from hexane. White crystals, mp 110 °C. Lit[3a] mp 110 °C.

*4.5.9. 2,4-Diphenyl-1-p-tolyl-1H-imidazole* ***6j***. Recrystallized from hexane. White crystals, mp 144 °C. Lit[3a] mp 144.5–145 °C.

*4.5.10. 2-(4-Methoxyphenyl)-4-phenyl-1-p-tolyl-1H-imidazole* ***6k***. Recrystallized from ethanol–water. White crystals, mp 122–123 °C. IR (KBr) $\nu_{C=N}$ 1610 and $\nu_{C=C}$ 1579 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.41 (3H, s), 3.79 (3H, s), 6.80 (2H, d, $J$=8.0), 7.13–7.28 (4H, m), 7.39–7.41 (6H, m), 7.82 (2H, d, $J$=8.0). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 21.2; 55.2; 113.6; 118.3; 122.9; 124.9; 125.6; 126.9; 128.6; 130.1; 130.2; 133.9; 136.1; 138.1; 141.2; 146.9; 159.7. Anal. Calcd for $C_{23}H_{20}N_2O$ (340.42): C, 81.15; H, 5.92; N, 8.23. Found: C, 81.20; H, 5.95; N, 8.30.

*4.5.11. 2-(4-Chlorophenyl)-4-phenyl-1-p-tolyl-1H-imidazole* ***6l***. Recrystallized from EtOH–ether. White crystals, mp 121–122 °C. IR (KBr) $\nu_{C=N}$ 1605 and $\nu_{C=C}$ 1575 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.42 (3H, s), 7.14 (2H, d, $J$=8.0), 7.22–7.29 (5H, m), 7.39–7.42 (5H, m), 7.87 (2H, d, $J$=8.0). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 21.2; 118.9; 125.0; 125.6; 127.1; 128.5; 128.6; 128.9; 130.0; 130.2; 133.7; 134.4; 135.7; 138.5; 141.7; 145.8. Anal. Calcd for $C_{22}H_{17}ClN_2$ (344.84): C, 76.63; H, 4.97; N, 8.12. Found: C, 76.62; H, 4.97; N, 8.24.

*4.5.12. 2-(3-Nitrophenyl)-4-phenyl-1-p-tolyl-1H-imidazole* ***6m***. Recrystallized from EtOH–ether. Yellow crystals, mp 158–159 °C. IR (KBr) $\nu_{C=N}$ 1601 and $\nu_{C=C}$ 1575 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.43 (3H, s), 7.18 (2H, d, $J$=8.4), 7.26–7.32 (3H, m), 7.41–7.47 (4H, m), 7.78–7.81 (1H, m), 7.89 (2H, d, $J$=8.0; 1.2), 8.11–8.13 (1H, m), 8.35 (1H, t, $J$=2.0). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 21.2; 119.6; 122.9; 123.4; 125.0; 125.7; 127.3; 128.7; 129.2; 130.5; 132.0; 133.4; 134.1; 135.3; 139.2; 142.1; 144.4; 148.1. Anal. Calcd for $C_{22}H_{17}N_3O_2$ (355.39): C, 74.35; H, 4.77; N, 11.73. Found: C, 74.00; H, 4.82; N, 11.82.

### 4.6. Synthesis of C2-metallated 3*H*-imidazol-1-ium ylides 9

*4.6.1. General procedure.* To a solution of **5a–f** (0.15 mmol) in $CH_2Cl_2$ (25 mL), $AgNO_3$ (0.173 mmol, 0.029 g) or $Ag_2O$ (0.08 mmol, 0.019 g) and $Et_3N$ (10.8 mmol, 1.095 g, 1.5 mL, 0.73 kg/L) were added successively and the reaction mixture stirred for 3 h in the dark. The reaction mixture was washed with water (25 mL) and the organic phase separated and dried over $Na_2SO_4$. The solvent was evaporated and the residual solid was dried under vacuum in the dark.

*4.6.2.* ***5a*** *Ag(I) complex,* ***9a***. Brown powder, mp 268–269 °C. IR (KBr) $\nu_{C=O}$ 1728 and 1671 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 0.99 (9H, t, $J$=7.2), 2.50 (6H, q, $J$=7.2), 3.27 (3H, s), 3.60 (3H, s), 7.34–7.39 (3H, m), 7.44 (1H, t, $J$=6.8), 7.49–7.55 (4H, m), 7.82 (2H, d, $J$=6.8), 7.99 (1H, s). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 12.5; 47.4; 49.8; 51.2; (Ylide C not observed) 118.7; 123.3; 128.1; 128.4; 128.7; 128.8; 129.1; 130.2; 138.0; 140.0; 166.3; 169.5; 174.1. Anal. Calcd for $C_{27}H_{32}AgN_3O_5$ (586.43): C, 55.30; H, 5.50; N, 7.17. Found: C, 55.00; H, 5.55; N, 7.07.

*4.6.3.* ***5b*** *Ag(I) complex,* ***9b***. Brown powder, mp 282–283 °C. IR (KBr) $\nu_{C=O}$ 1729 and 1679 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 1.01 (9H, t, $J$=7.2), 2.33 (3H, s), 2.53 (6H, q, $J$=7.2), 3.26 (3H, s), 3.59 (3H, s), 7.31–7.39 (5H, m), 7.49 (2H, dd, $J$=8.0; 2.0 Hz), 7.70 (2H, d, $J$=8.4), 7.94 (1H, s). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 12.8; 21.0; 48.0; 49.8; 51.2; 98.1; 118.7; 121.5; 123.1; 128.1; 128.7; 129.2; 130.6; 137.7 (2C); 137.8; 166.3; 169.5; 174.1; 184.3 (Deduced from the g-HMBC spectrum). Anal. Calcd for $C_{28}H_{34}AgN_3O_5$ (600.50): C, 56.01; H, 5.71; N, 7.00. Found: C, 55.95; H, 5.52; N, 7.26.

*4.6.4.* ***5c*** *Ag(I) complex,* ***9c***. Brown powder, mp 285–286 °C. IR (KBr) $\nu_{C=O}$ 1728 and 1663 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 1.01 (9H, t, $J$=7.2), 2.58 (6H, q, $J$=7.2), 3.25 (3H, s), 3.60 (3H, s), 3.78 (3H, s), 7.07 (2H, d, $J$=9.2), 7.34–7.39 (3H, m), 7.48–7.51 (2H, m), 7.73 (2H, d, $J$=9.2), 7.90 (1H, s). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 12.4; 47.5; 49.8; 51.2; 55.9; 98.2; 115.2; 118.9; 124.7; 128.1; 128.7; 129.1; 129.2; 133.3; 137.7; 159.2; 166.3; 169.5; 174.1; 183.9 (Deduced from the g-HMBC spectrum). Anal. Calcd for $C_{28}H_{34}AgN_3O_6$ (616.45): C, 54.55; H, 5.56; N, 6.82. Found: C, 54.45; H, 5.43; N, 7.00.

*4.6.5.* ***5d*** *Ag(I) complex,* ***9d***. Brown powder, mp 287–288 °C. IR (KBr) $\nu_{C=O}$ 1736 and 1650 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 0.99 (9H, t, $J$=6.8), 2.50 (6H, q, $J$=6.8), 3.25 (3H, s), 3.60 (3H, s), 7.34–7.39 (3H, m), 7.48–7.51 (2H, m), 7.59 (2H, d, $J$=9.2), 7.88 (2H, d, $J$=9.2), 8.01 (1H, s). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 12.6; 47.5; 49.8; 51.3; (Ylide C not observed) 118.6; 125.0; 128.2; 128.7; 128.8; 129.0; 130.2; 132.7; 138.1; 138.8; 166.3; 169.6; 174.1; 184.8 (Deduced from the g-HMBC spectrum). Anal. Calcd for $C_{27}H_{31}AgClN_3O_5$ (620.87): C, 52.23; H, 5.03; N, 6.77. Found: C, 52.09; H, 5.08; N, 7.01.

*4.6.6.* ***5e*** *Ag(I) complex,* ***9e***. Brown powder, mp 286–288 °C. IR (KBr) $\nu_{C=O}$ 1732 and 1655 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 1.00 (9H, t, $J$=7.2), 2.53 (6H, q, $J$=7.2), 3.25 (3H, s), 3.60 (3H, s), 7.35–7.39 (3H, m), 7.48–7.51 (2H, m), 7.71 (2H, d, $J$=8.8), 7.82 (2H, d, $J$=8.8), 8.01 (1H, s). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 12.5; 47.4; 49.8; 51.3; (Ylide C not observed) 118.6; 121.1; 125.3; 128.2; 128.7; 130.0; 133.1; 138.2; 139.3; 142.8; 166.3; 169.6; 174.1; 184.8

(Deduced from the g-HMBC spectrum). Anal. Calcd for $C_{27}H_{31}AgBrN_3O_5$ (665.32): C, 48.74; H, 4.70; N, 6.32. Found: C, 48.33; H, 4.77; N, 6.50.

*4.6.7.* ***5f*** *Ag(I) complex,* ***9f***. Brown powder, mp 258–260 °C. IR (KBr) $\nu_{C=O}$ 1732 and 1667 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 0.99 (9H, t, $J$=7.2), 2.50 (6H, q, $J$=7.2), 3.26 (3H, s), 3.59 (3H, s), 3.78 (3H, s), 3.82 (3H, s), 7.06–7.50 (8H, m), 7.93 (1H, s). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 12.6; 47.4; 49.8; 51.2; 56.2; 56.3; 107.7; 115.2; 119.1; 124.1; 128.1; 128.6; 129.1; 133.5; 137.6; 148.8; 149.6; 166.3; 169.6; 174.1 (Ylide C and C-Ag are not observed). Anal. Calcd for $C_{29}H_{36}AgN_3O_7$ (646.48): C, 53.88; H, 5.61; N, 6.50. Found: C, 54.00; H, 5.87; N, 6.70.

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9. A mixture of **5b** and **6b** (0.120 g, 1.17:1) was dissolved in concd HCl (0.5 mL, 36%) and stirred for 5 min then water was added (1 mL) and the mixture filtered. The solid separated was the hydrochloride of **6b**. The filtrate was basified with ammonia (1.5 mL, 26%) and extracted with $CHCl_3$ (2×5 mL). The combined extracts were dried over $Na_2SO_4$ and filtered. The solvent was evaporated under vacuum and the remaining solid washed with warm ether. *1-Methoxycarbonylmethyl-5-phenyl-3-p-tolyl-3H-imidazol-1-ium* **7b**. Yield, 0.056 g, 83% purity, the impurity is from the starting **5b**. Mp 127–128 °C. IR (KBr) $\nu_{C=O}$ 1738 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.43 (3H, s), 3.73 (3H, s), 5.61 (2H, s), 7.36–7.45 (4H, m), 7.52–7.58 (4H, m), 7.67 (2H, d, $J$=7.2), 11.2 (1H, s). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.1; 48.4; 53.3; 117.4; 121.6; 123.9; 129.5; 129.6; 131.0; 131.1; 131.2; 132.0; 136.4; 140.9; 166.9. *5-Phenyl-3-p-tolyl-3H-imidazol-1-ium chloride* **6b**·*HCl*. Yield, 0.023g. Mp 230–232 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.38 (3H, s), 7.42–7.52 (5H, m), 7.72 (2H, d, $J$=8.4), 7.92 (2H, d, $J$=8.4), 8.67 (1H, s), 9.52 (1H, s).
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15. The $^1H$ NMR chemical shifts of the free amine in DMSO-$d_6$ are $\delta$ 0.90 (9H, t, $J$=7.6), 2.39 (6H, q, $J$=7.6).