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Copper mediated cyclization of 1-substituted enamides, dienamides and trienamides: regiochemistry, indigoid formation and methyl migration-aromatisation

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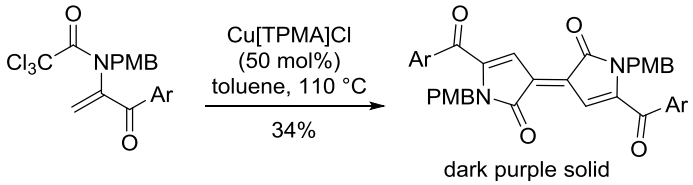
Joanna V. Geden, Andrew J. Clark* , Stuart R. Coles, Collette S. Guy, Franco Ghelfi and Stephen Thom*



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Copper mediated cyclization of 1-substituted enamides, dienamides and trienamides: regiochemistry, indigoid formation and methyl migration-aromatization.

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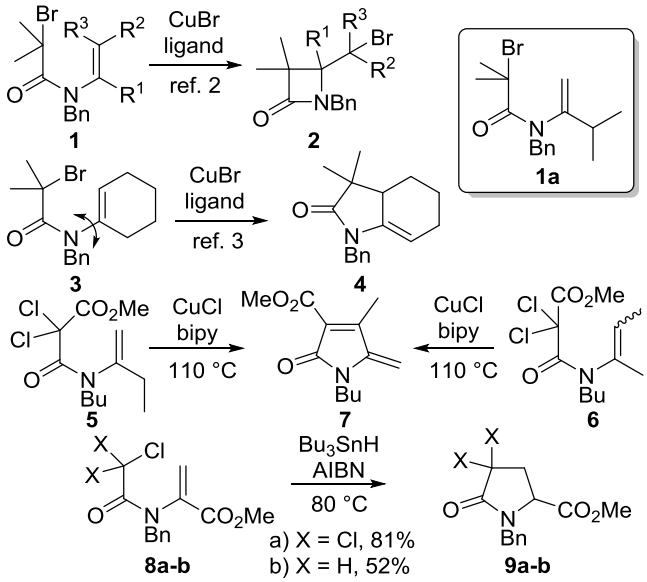
ABSTRACT

Copper mediated cyclization of activated 1-substituted enamides occurs *via* a 5-*endo* radical-polar crossover process. Trichloroacetyl derivatives can undergo further reactions post cyclization (elimination of HCl or dimerization potentially *via* copper carbenoid intermediates). Reaction of α-halo trienamides derived from β-ionone furnish either β- or γ-lactams *via* 4-*exo* or 5-*exo* cyclizations respectively depending upon the enamide tautomer undergoing reaction. For the less reactive dichloroacetamide derivative a competing regioselective methyl migration–aromatization prior to cyclization is observed.

1. Introduction

The copper-mediated cyclization of α–haloenamides has attracted considerable interest in recent years.[1] The regioselective outcome of cyclization is primarily dependent upon the substitution of the alkene. Thus, for **1** (R^1 = H and R^2, $R^3 \neq$ H), 4-*exo* atom transfer cyclization is the major pathway,[2] while for **3** 5-*endo* cyclization to give **4** predominates, *via* a radical-polar crossover pathway.[3] That enamides like **3** can undergo **5**-*endo*-*trig* radical cyclization processes with ease[4] has recently been attributed to their ground state conformations.[5] Enamides prefer the *E*-amide rotamer and exhibit transient axial chirality on the NMR timescale.[5] The twisting of the *N*-alkenyl bond away from planarity favours cyclization as it positions the reacting radical in the correct geometry to interact with the alkene π* orbital.[5] Copper mediated cyclization of 1-functionalised enamides (**1** R^2, R^3 = H) has received less attention.[3b-c] While cyclization of **1a** failed with a range of copper catalysts,[6] cyclization of the more reactive enamides **5** or **6** with Cu[bipy]Cl produced **7**.[3b] Both **5** and **6** were found to be interconverting under the reaction conditions and cyclization appeared to preferentially proceed *via* the more substituted **6**. Replacing the 1-alkyl group in **1a** with a group capable of stabilizing thermodynamically (captodatively)[7] the cyclized radical will facilitate 5-*endo* cyclization. Cyclizations of **8a-b** using Bu_3SnH were found to be acyl group dependent, with **8a** providing better yields than **8b**.[7]

Scheme 1. Radical cyclization of enamides



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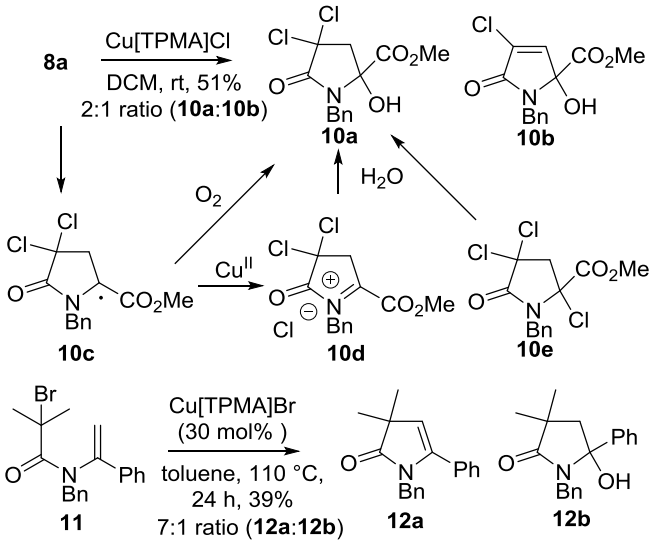
2. Results and Discussion

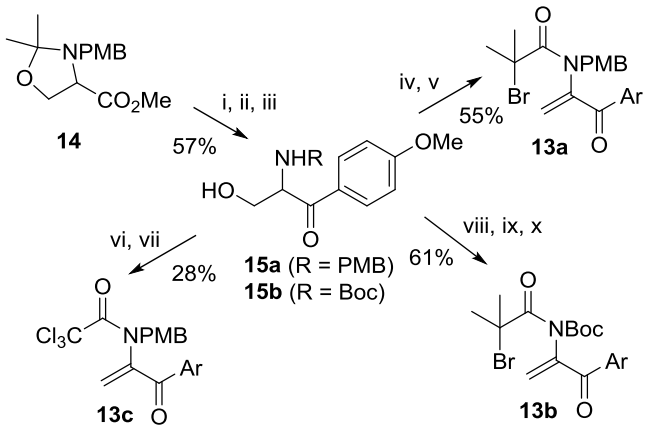
1-Substituted enamides: We initially probed the cyclization of the known substrate **8a**.[7d] While a range of copper catalysts have been reported to mediate 5-*endo* cyclizations,[3] we chose the more active redox system based upon the tripyridylmethanamine (TPMA) ligand.[8] Cyclizations normally require 5-30 mol% of catalyst but it was necessary to use 1 equivalent of Cu[TPMA]Cl in DCM (rt, 24 h) to give a 51% combined yield of **10a**:**10b** (2:1 ratio, 15% recovered starting material). Mechanistically, **10a** could be formed by reaction of the stabilized captodative radical **10c** with advantageous O_2, followed by reduction. However, this is unlikely as the reactions were performed under nitrogen. Most probably, oxidation of the radical **10c** by Cu[TPMA]Cl_2 occurs to give the acyl iminium ion **10d** (despite the neighbouring carbonyl group) which upon work-up with water furnishes **10a**.[3] Alternatively, atom transfer to **10c** could give unstable chloride **10e** which after reaction with water would give **10a**. Elimination of HCl from **10a** gives the observed minor product **10b**. In any case, the generation of two equivalents of HCl deactivates the catalyst system which is why 1 equivalent was necessary.[3f] Unlike **1a** reaction of the less reactive bromide **11** could be accomplished with 30 mol% Cu[TPMA]Br if the reaction was heated to 110 °C in toluene. At this higher temperature, elimination to the alkene **12a** predominates either *via* **12b** or directly from an acyl-iminium ion intermediate.

Scheme 2. Cu[TPMA]Cl mediated cyclization of **8a** and **11**.

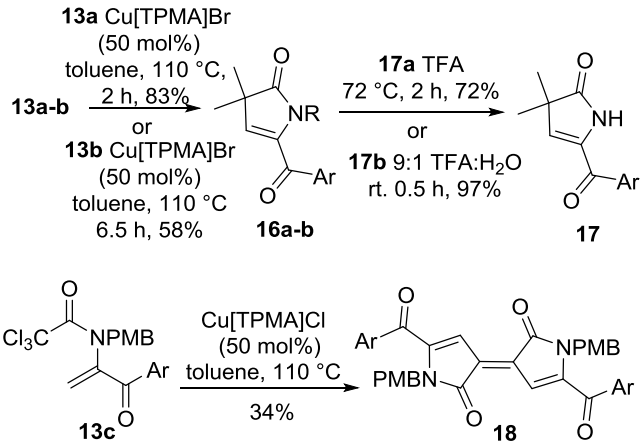


Having shown that activating substituents at the 1-position facilitate the copper mediated cyclization process, we next investigated the effect of the initiating acetyl group and nitrogen protecting group upon the cyclization of 1-substituted ketones **13a-c**. In order to encourage potential radical-polar crossover we added the electron rich 4-methoxyphenyl group to the ketone. Direct conversion of the known ester **14**[9] to **15a** was achieved *via* the Weinreb amide followed by the Grignard addition of 4-methoxyphenylmagnesium bromide and deprotection (4:1 AcOH:H_2O) in 57% overall yield. It was then relatively straight forward to prepare the radical-polar crossover precursors **13a** and **13c**. Reaction of **15a** with excess 2-bromo-2-methylpropionyl bromide (3 eq) initially furnished the diacylated compound which, when treated with potassium *t*-butoxide, underwent elimination of the ester to give **13a**.[7e] The same approach could be used to prepare the trichloro derivative **13c** if trichloroacetyl chloride was used. It was not possible to make **13b** using this approach. Instead treatment of known **15b**[10] with excess dichloroacetyl chloride led to mono acylation on oxygen. Elimination with DBU furnished the *N*-unsubstituted enamide which after deprotonation (LDA) and further acylation furnished **13b**. Compounds **13a** and **13c** exhibited broad peaks in their NMR spectra, indicative of slow rotation about the C-N bond of the enamide functionality.[5b-c]

Scheme 3. Preparation and cyclization of **13a-c**.



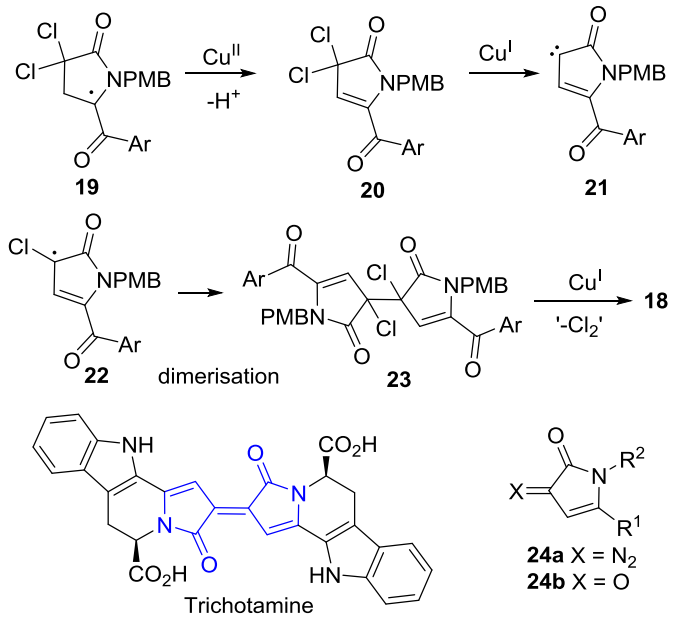
i) MeNH(OMe).HCl, ^{i}PrMgCl, THF -10 °C. ii) THF, *p*-$MeOC_6H_4MgBr$, -78 °C. iii) 4:1 AcOH:H_2O, rt, 1 h. iv) $Me_2BrCCOBr$, Et_3N, MeCN, 0 °C. v) KO^{t}Bu, THF, reflux, 2 h. vi) Cl_3CCOCl, Et_3N, MeCN, 0 °C. vii) KO^{t}Bu, THF, rt, 2 h. viii) $Cl_2HCCOCl$, Et_3N, MeCN, 0 °C. ix) DBU, MeCN, reflux, 2 h. x) LDA, THF -78 °C, $Me_2BrCCOBr$.



Efficient cyclization of **13a** was achieved using 50 mol% Cu[TPMA]Br in refluxing toluene for 2 hours, while **13b** required longer (6 hours). Both produced the expected cyclized lactams **16a-b** which could be deprotected to **17** in high yields **17a** (TFA, reflux, 2 h, 72%), **17b** (9:1 TFA:H_2O, rt, 0.5 h, 97%). By analogy we expected that cyclization of the derivative **13c** would lead to the dichloro derivative **20**. However, heating **13c** for 5 hours under the same conditions as before led to a dark purple product, identified as the indigoid derivative **18** in 34% yield (as a single isomer around the central tetrasubstituted alkene).[11] Attempts to increase the yield by varying the amount of CuCl or the reaction time failed, and the rest of the mass balance was uncharacterized baseline material. Possible mechanisms for the formation of **18** are outlined in Scheme 4. Reaction of **13c** with Cu[TPMA]Cl generates the initial radical which undergoes 5-*endo* cyclization to give the captodative radical **19**. Oxidation of this captodative radical to the cation followed by elimination of a proton furnishes **20** while regenerating Cu[TPMA]Cl. At this point, the gem dichloride **20** may react rapidly with Cu[TPMA]Cl to furnish the copper carbenoid species **21** which undergoes dimerization to the observed product **18**.[12] This potentially represents a formal

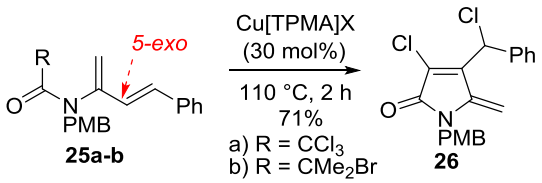
radical-polar-carbene triple crossover reaction. However, it proved impossible to determine the stereochemistry of the tetrasubstituted alkene component of **18** directly, as suitable crystals for X-ray determination could not be obtained.

Scheme 4. Possible mechanisms for the formation of **18**.



Structurally related molecules, such as trichotamine,[13] have been reported to possess the (*E*)-geometry and have been accessed by dimerization of appropriate α-keto carbene-carbenoid precursors, (e.g. copper assisted thermolysis of azo lactams **24a** or carbene mediated olefination of keto lactams **24b** using trimethylphosphite).[14] Similarly, CuCl mediated carbene formation / dimerization of structurally related α,α-dichloroesters have been reported to provide mainly (*E*)-isomers.[12] Compounds of the indigo group,[15] which have the same [3,3']-bipyrrolidene-2,2-dione core as **18**, have been reported in the literature as highly coloured dyes. Thus, in the absence of X-ray data we tentatively assigned the central alkene geometry of **18** as (*E*). Molecules of this type have shown promise in molecular bulk heterojunction solar cell devices.[16] An alternative mechanism for the generation of **18** from **20** can be envisaged where Cu[TPMA]Cl generates the radical **22** which after dimerization to **23** and CuCl mediated elimination of chlorine provides the observed product **18**.

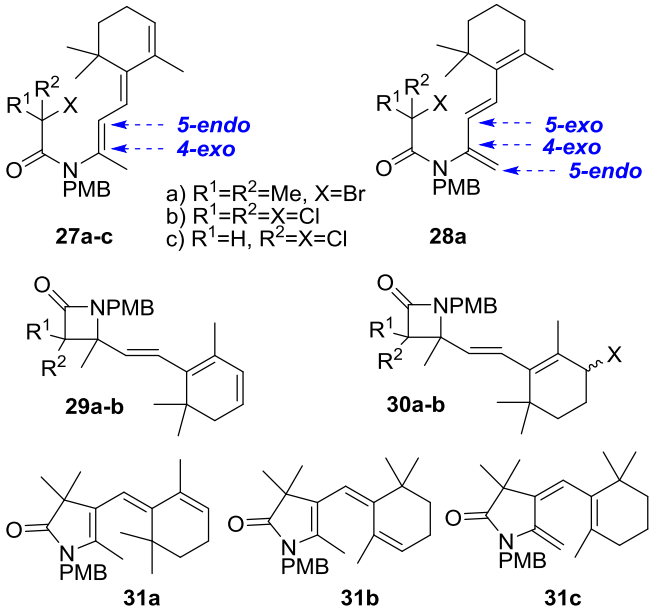
Scheme 5. Cyclization of dienamide **25a**



Dienamides and trienamides: Dienamides **25a-b** were prepared by acylation of the benzyl imine of *trans*-4-phenyl-3-but-2-one. Cyclization of the more reactive substrate **25a** occurred with 30 mol% Cu[TPMA]Cl exclusively in a 5-*exo* manner *via* the intermediacy of a benzyl radical, followed by elimination of HCl to give **26**. Cyclization was also possible using a polystyrene bound solid supported catalyst based upon the hexamethyl triethylenediamine ligand (albeit in a slightly lower 61% yield in 5 hours).[17] Reaction of bromide **25b** under either conditions led to decomposition of the starting material and a complex mixture of unidentified products.

Trienamides **27a-c** and **28a** were prepared by acylation of the 4-methoxybenzyl imine of β-ionone. Reaction of β-ionone with 4-methoxybenzylamine in benzene at reflux, with 10 mol% $ZnCl_2$ for two days, furnished the imine in 80% yield. Acylation of the imine with either 2-bromo-2-methylpropionyl bromide, trichloroacetyl chloride or dichloroacetyl chloride and triethylamine in DCM furnished the desired enamides **27a-c** and **28a**. Acylation with either trichloroacetyl or dichloroacetyl chloride provided only one enamide regioisomer **27b-c** while reaction with 2-bromo-2-methylpropionyl bromide furnished both regioisomers **27a** and **28a** in a 2:1 ratio. It was possible to separate both isomers by careful chromatography, although the sensitivity of the enamides led to low yields of purified compounds (12-30%).

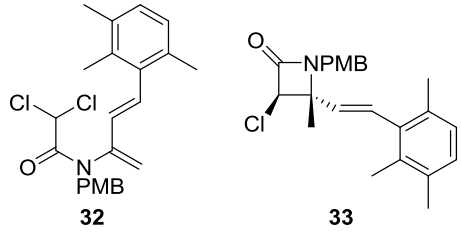
Scheme 6. Cyclization of trienamides **27a-b** and **28a**.



Cyclization of the more substituted bromotrienamide **27a** was attempted first by using 30 mol% Cu[TPMA]Br in toluene at reflux. After 5 hours no starting material remained and the β–lactam product **29a** was isolated in 26% yield. No bromide **30a** (X = Br) arising from atom transfer to the 4-*exo* cyclized radical was detected suggesting termination either occurred *via* oxidation to the allylic cation by Cu[TPMA]Br_2 followed by elimination, or by direct elimination of HBr from **30a** at elevated temperature. No products arising from the alternative 5-*endo* or 5-*exo* cyclization modes were detected. The rest of the mass balance after chromatography was uncharacterized baseline material (presumably oligomeric products).[6] Cyclization of the tautomeric enamide **28a** gave rise to the same β–lactam **29a** (37%) and the three 5-*exo* products **31a-c** in 84% combined yield (**31a** = 8%, **31b** = 27%, **31c** = 12%). No evidence of 6-*endo*, 7-*exo* or 8-*endo* cyclization was observed. NOE measurements confirmed the stereoselectivity of the alkenes in the products **31a-c**. This suggests that **28a** is converting to **27a** under the reaction conditions and that **27a** cyclizes exclusively in the 4-*exo* mode. Reacting the trichloroacetyl derivative **27b** under the same conditions as **27a** led to complete disappearance of starting material in only 3 hours and the chlorine atom transfer product **30b** (X = Cl) was isolated as a 1:1 mixture of diastereomers (29%) along with the triene **29b** (7%) arising from elimination of HCl from **30b**. As for **27a**, only 4-*exo* cyclization was observed, although in poor overall yield. The fact that atom transfer product **30b** was isolated for **27b** and not **27a** suggests that the trienes **29a-b** arise from elimination of HX from **30a-b** rather

than Cu[TPMA]Cl_2 mediated oxidation of the resonance stabilized radical directly to a cation and loss of a proton.

Scheme 8. Cyclization of trienamide **27c**.



32 **33**

Finally we investigated the cyclization of the substrate **27c**. Reaction and cyclization of dichloroacetyl derivatives under atom transfer conditions are often problematic as both initiation and cyclization can be slow.[18] Heating **27c** with 30 mol% Cu[TPMA]Cl in toluene at reflux for 5 hours led to only recovered starting material. Heating for a further 6 days led to a complex mixture of products, but no starting material remained. The two products isolated pure enough for accurate identification (compounds **32** and **33**) indicated that both oxidation of the cyclohexene ring and regioselective methyl migration had taken place. The stereochemistry of the β-lactam **33** was determined by NOE measurements. In this case initiation and cyclization are so slow that competing processes occur. Methyl migration and aromatization of conjugate carotenoid systems is important in the biosynthesis of aromatic carotenoids[19] and the same rearrangement can be accomplished by reacting β-ionone with 2-4 equivalents $CuCl_2$ (30%) in DMF as solvent, albeit in low yields.[20] It is likely that any build-up of Cu[TPMA]Cl_2 in our reaction is responsible for this migration.

Conclusions

Copper mediated cyclization of activated 1-substituted enamides occurs *via* a 5-*endo* radical-polar crossover process. Trichloroacetyl derivatives can undergo further reactions post cyclization (elimination of HCl or dimerization potentially *via* copper carbenoid intermediates). Reaction of α-halo trienamides derived from β-ionone furnish either β- or γ-lactams *via* 4-*exo* or 5-*exo* cyclizations respectively depending upon the enamide tautomer undergoing reaction. For the less reactive dichloroacetamide derivative a competing regioselective methyl migration-aromatization prior to cyclization is observed.

Acknowledgments

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References and notes

1. (a) Clark, A. J. *Chem. Soc. Rev*. **2002**, *31*, 1–11. (b) Clark, A. J. *Eur. J. Org. Chem.* **2016**, DOI: 10.1002/ejoc.201501571.
2. (a) Clark, A. J.; Battle, G. M.; Bridge, A. *Tetrahedron Lett*. **2001**, 42, 4409–4412. (b) Bryans, J. S.; Chessum, N. E. A.; Parsons, A. F.; Ghelfi, F. *Tetrahedron Lett.* **2001**, *42*, 2901–2905.
3. Radical polar crossover reaction: (a) Bashir, N.; Patro, B.; Murphy, J. A. *Advances in Free Radical Chemistry*; Zard, S. Z., Ed.; Jai Press: Stamford, CT, 1999; Vol. 2. 123. Copper mediated: (b) Davies, D. T.; Kapur, N.; Parsons, A. F. *Tetrahedron Lett.* **1999**, *40*, 8615–8618. (c) Clark, A. J.; Dell, C. P.; Ellard, J. M.; Hunt, N. A.; McDonagh, J. P. *Tetrahedron Lett.* **1999**, 40, 8619–8623. (d) Clark, A. J.; Dell, C. P. *C. R. Acad. Sci. Ser. IIC: Chim*. **2001**, *4*, 575–579. (e) Clark, A. J.; Collis, A. E. C.; Fox, D. J.; Halliwell, L. L.; James, N.; O'Reilly, R. K.; Parekh, H.; Ross, A. Sellars, A. B; Willcock, H.; Wilson, P. *J. Org. Chem.* **2012**, *77*, 6778–6788. (f) Cornia, A.; Felluga, F.; Frenna, V.; Ghelfi, F.; Parsons, A.F.; Pattarozzi, M.; Roncaglia, F.; Spinelli, D. *Tetrahedron*, **2012**, *68*, 5863–5881. Tin mediated: (g) Ishibashi, H.; Higuchi, M.; Ohba, M.; Ikeda, M. *Tetrahedron Lett.* **1998**, *39*, 75–78. (h) Tamura, O.; Matsukida, H.; Toyao, A.; Takeda, Y.; Ishibashi, H. *J. Org. Chem.* **2002**, *67*, 5537–5545. (i) Curran, D. P.; Guthrie, D. B.; Geib, S. J. *J. Am. Chem. Soc.* **2008**, *130*, 8437–8445. Nickel Mediated: (j) Cassayre, J.; Quiclet-Sire, B.; Saunier, J-B.; Zard, S. Z. *Tetrahedron*, **1998**, *54*, 1029–1040.
4. (a) Ishibashi, H.; Nakamura, N.; Sato, T.; Takeuchi, M.; Ikeda, M. *Tetrahedron Lett*. **1991**, 32, 1725–1728. (b) Sato, T.; Nakamura, N.; Ikeda, K.; Okada, M.; Ishibashi, H.; Ikeda, M. *J. Chem. Soc. Perkin Trans. 1*. **1992**, 2399–2407. (c) Ikeda, M.; Ohtani, S.; Yamamoto, T.; Sato, T, Ishibashi, H. *J. Chem. Soc. Perkin Trans. 1*. **1998**, 1763–1768. (d) Parsons, A. F.; Williams, D. A. J. *Tetrahedron*, **2000**, *56*, 7217–7228.
5. (a) Chatgilialoglu, C.; Ferreri, C.; Guerra, M.; Timokhin, V.; Froudakis, G.; Gimisis, T. *J. Am. Chem. Soc.* **2002**, *124*, 10765–10772. (b) Guthrie, D. B.; Damodaran, K.; Curran, D. P.; Wilson, P.; Clark, A. J. *J. Org. Chem.* **2009**, *74,* 4262–4266. (c) Clark, A.J.; Curran, D. P.; Geden, J. V.; James, N.; Wilson, P. *J. Org. Chem*. **2011**, *76*, 4546–4551.
6. Clark, A. J.; Geden, J.V.; Thom, S.; Wilson, P. *J. Org.Chem.* **2007**, *72*, 5923–5926.
7. (a) Viehe, H. G.; Janousek, Z.; Merényi, R.; Luciens, S. *Acc. Chem. Res*. **1985**, *18*, 148–154. (b) Goodall, K.; Parsons, A. F.*; J. Chem. Soc. Perkin Trans. 1* **1994**, 3257-3259. (c) Sato, T.; Chono, N.; Ishibashi, H.; Ikeda, M. *J. Chem. Soc. Perkin Trans. 1*. **1995**, 1115–1120. (d) Goodall, K.; Parsons, A. F. *Tetrahedron Lett.* **1995**, *36*, 3259–3260. (e) Goodall, K.; Parsons, A. F. *Tetrahedron* **1996**, *52*, 6739–6758. (f) Baker, S. R.; Parsons, A. F.; Wilson, M. *Tetrahedron Lett.* **1998**, *39*, 2815–2818. (g) Baker, S. R.; Burton, K. I.; Parsons, A. F.; Pons, J-F.; Wilson, M. *J. Chem. Soc. Perkin Trans. 1*. **1999**, 427–436.
8. (a) De Campo, F. ; Lastécouères, D.; Verlac J-B. *Chem. Commun.* **1998**, 2117–2118. (b) Clark, A. J.; De Campo, F.; Deeth, R. J.; Filik, R. P.; Gatard, S.; Hunt, N. A.; Lastécouères, D.; Thomas, G. H.; Verlac J-B.; Wongtap H. *J. Chem. Soc., Perkin Trans. 1* **2000**, 671–680. (c) Clark, A. J. ; Wilson, P. *Tetrahedron Lett*. **2008**, 49, 4848–4850. (d) Diaba, F. ;Montiel, J. A.; Bonjoch, J. *Tetrahedron* **2013**, *69*, 4883–4889; (e) Diaba, F.; Martinez-Laporta, A.; Bonjoch, J. *Eur. J. Org. Chem.* **2014**, 2371–2378. (f) Clark, A. J.; Cornia, A.; Felluga, F.; Gennaro, A.; Ghelfi, F.;Isse, A. A.; Menziani, M. C.; Muniz-Miranda, F.; Roncaglia, F.; Spinelli,D. *Eur. J. Org. Chem.* **2014**, 6734–6745. (g) Isse, A. A.; Visona, G.; Ghelfi, F.; Roncaglia, F.; Gennaro, A. *Adv. Synth. Catal*. **2015**, *357*, 782–792.
9. Chung, S-K.; Lee, J-M. *Tetrahedron Asymm*etry **1999**, *10*, 1441–1444.
10. Myers, M. C.; Wang, J.; Iera, J. A.; Bang, J-K.; Haa, T.; Saito, S.; Zambetti, G. P.; Appella, D. H. *J. Am. Chem. Soc.* **2005**, *127*, 6152–6153.
11. m.p. 184.0-186.0°C; λ_{max} ($CHCl_3$) 273 nm (ε = 29,853), 375 nm (ε = 6,931), 567 nm (ε = 11,018); υmax (film)/cm^{-1} 2956, 1718, 1684, 1635, 1597; δH (400 MHz, $CDCl_3$) 7.78 (4H, d, J 8.8 Hz), 7.12 (4H, d, J 8.8 Hz), 7.08 (2H, s), 6.93 (4H, d, J 8.8 Hz), 6.72 (4H, d, J 8.8 Hz), 4.99 (4H, s), 3.89 (6H, s), 3.71 (6H, s); δC (125.8 MHz, $CDCl_3$) 186.3, 169.1, 164.3, 158.9, 147.4, 132.8, 129.3, 129.2, 132.3, 129.5, 114.0, 113.9, 111.5, 55.7, 55.2, 43.5; m/z 671 $(MH)^+$, 523, 460, 391, 341; [Found: $(MH)^+$ 671.2388, $C_{40}H_{35}N_2O_8$ requires $(MH)^+$ 671.2393].
12. Tezuka, Y.; Hashimoto, A.; Ushizaka, K.; Imai, K. *J. Org. Chem.* **1990**, *55*, 329–333.
13. Iwadare, S.; Shizuri, Y.; Sasaki, K.; Hirata, Y. *Tetrahedron*, **1974**, *30*, 4105–4111.
14. Palmisano, G.; Danieli, B.; Lesma, G.; Riva. R. *J. Org. Chem*. **1985**, *50*, 3322–3325.
15. Irikawa, H.; Shiratori, K.; Adachi, K.; Adachi, N.; Kawata, S. *Bull. Chem. Soc. Jpn*. **2001**, *74*, 555–559.
16. (a) Mei, J.; Graham, K. R.; Stalder, R.; Reynolds, J. R. *Org. Lett*. **2010**, *12*, 660–663. (b) Porada, J. H.; Blunk, D. *J. Mat. Chem*. **2010**, *20*, 2956–2958.
17. Clark, A. J.; Geden, J.; Thom, S. *J. Org.Chem.* **2006**, *71*, 1471–1479.
18. Ghelfi, F.; Parsons, A. F. *J. Org. Chem*. **2000**, *65*, 6249–6253.
19. (a) Moshier, S. E.; Chapman, D. J. *Biochem. J*. **1973**, *136*, 395–404. (b) Krügel, H.; Krubasik, P.; Weber, K.; Saluz, H. P.; Sandmann, G. *Biochim. Biophys. Acta*, **1999**, *1439*, 57–64.
20. Valla, A.; Andriamialisoa, Z.; Valla, B.; Labia, R.; Le Guillou, R.; Dufossé, L.; Cartier, D. *Eur. J. Org. Chem.* **2007**, 711–715.