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Copper catalysed synthesis of indolylquinazolinone alkaloid bouchardatine

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Abstract. We describe the total synthesis of indolylquinazolinone alkaloid bouchardatine and some of the quinazolinone derivatives. The aerobic oxidation induced by copper(I) bromide, followed by Vilsmeier-Haack formylation gives the natural product bouchardatine alkaloid in good yield.

Keywords. Bouchardatine; Vilsmeier-Haack formylation; indolylquinazolinone alkaloid

1. Introduction

2,3-Dihydroquinazolin-4(1*H*)-ones are an important class of privileged compounds which have a range of applications in many areas of chemistry and are frequently found in many natural products.[1] As a result, numerous efforts have focused in the past few decades on the construction of quinazolinone alkaloids which are well-documented in a broad range of scientific journals.[1–6] Moreover, quinazolinone derivatives have drawn renewed attention as new drug delivery technologies and exhibit a wide range of biological and medicinal activities; used as anti-tumor, anti-defibrillatory, analgesic, diuretic, CNS stimulant, anti-histamine, anti-hypertensive, vasodilating agent, and also used as inhibitor of various enzymes (figure 1).[2]

Bouchardatine is an indolylquinazolinone alkaloid that was isolated from the aerial part of Bouchardatia neurococca. It belongs to the family of Rutaceae and subfamily rutoideae;[3] and it is a monotypic genus that has been collected from Australia.[4,5] In view of its important pharmacological as well as biological properties, a careful analysis of literature disclosed that there are only two reports available for the synthesis of the bouchardatine alkaloid.[6]

Over the last few decades, transition metal-catalyzed formation of C-C and C-N bonds has attracted increasing attention and found wide applications in organic synthesis.[7] These days, this field has been mainly dominated by palladium catalyst.[8] However, the development of less expensive and environmentally amiable catalysts is still desirable for organic synthesis. Copper catalysts are relatively cheap, easy to handle, and hold a fine position in comparison with the other transition metal catalysts used in organic synthesis. Therefore, during the past decade, large numbers of novel and useful reactions using copper catalyst have been reported in literature.[9]

The reported methods[6] for the synthesis of bouchardatine were reported, either via harsher reactions condition or multi-step sequence. Therefore, we are interested in identifying mild reaction conditions for the construction of quinazolinone alkaloids. Herein, we report a mild and effective method for the synthesis of bouchardatine, starting from indole-2-aldehyde with anthranilamide through copper(I) bromide mediated aerobic oxidation reaction as shown in scheme 1.

2. Experimental section

2.1 *General information*

All ^{1}H, ^{13}C NMR spectra were recorded on AV-400 spectrometer operating at 400 and 100 MHz respectively. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Multiplicities were indicated as follows (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and coupling constants (Hz). Chemical shifts of common trace ^{1}H NMR impurities ($CDCl_3$, ppm): H_2O, 1.56; EtOAc, 1.26, 2.05, 4.12; CH_2Cl_2, 5.30; $CDCl_3$, 7.26. IR spectra were recorded on FT/IR-5300 spectrometer; absorptions are reported in cm^{-1}. Mass spectra were recorded on either using EI technique or LCMS-2010A mass spectrometer. Elemental analyses (C, H and N) were recorded on

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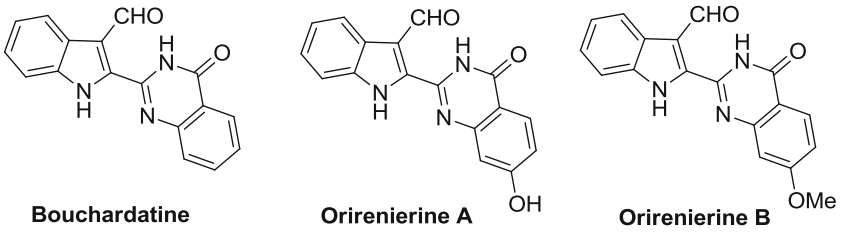
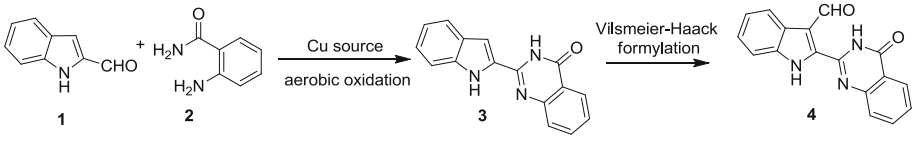


Figure 1. Indolylquinazolinone alkaloids.



Scheme 1. Schematic representation of the present work.

EA 1112 analyzer in the School of Chemistry, University of Hyderabad. Routine monitoring of the reactions was performed by TLC silica gel 60 F254 plates. Compounds were visualized with UV light at 254 nm. Further visualization was achieved by staining with iodine. Column chromatography was carried out employing neutral alumina. Commercially available reagents and solvents were used without further purification. Melting points were measured in open capillary tubes.

2.1a *General procedure for the synthesis of 2-(1H-indol-2-yl)quinazolin-4(3H)-one (3)*: An oven dried 25 mL round bottom flask was charged with a magnetic pellet and CuBr (10 mol %), indole-2-aldehyde **1** (1.0 equiv.), DMF (3 mL) along with anthranilamide **2** (1.0 equiv.), Cs_2CO_3 (3.0 equiv.) and it was stirred at 120°C for 2 h in open air. After completion of the reaction, followed by thin layer chromatography (TLC), the reaction mixture was poured into water and extracted with EtOAc (3 × 10 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a crude product. The crude product was purified by column chromatography on neutral alumina using hexanes/EtOAc as the eluent. The solvent was evaporated to dryness to get the pure product **3** in 94% yield.

2.1b *2-(1H-Indol-2-yl)quinazolin-4(3H)-one (3)*: White colored solid; yield: 94 %, Mp: 270°C, IR (KBr) ν_{max}: 3424, 2964, 2926, 2849, 1676, 1594, 1336, 1309, 865, 777 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.62 (s, 1H), 11.81 (s, 1H), 8.14 (d, 1H, J = 7.8 Hz), 7.84 (t, 1H, J = 7.6 Hz), 7.74–7.72 (m, 1H), 7.65 (s, 1H), 7.63 (d, 1H, J = 8.0 Hz), 7.53–7.49 (m, 2H), 7.22 (t, 1H, J = 7.0 Hz), 7.05 (t, 1H, J = 7.2 Hz); ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.2, 149.2, 147.0, 138.1, 135.1, 130.5, 127.9, 127.4, 126.7, 126.5, 124.5, 122.0, 121.6, 120.4, 112.8, 105.4. LC-MS (m/z): 262 $(M+H)^+$ positive mode; Anal. calcd. for $C_{16}H_{11}N_3O$: C, 73.55; H, 4.24; N, 16.18 %, found: C, 73.31; H, 4.31; N, 16.12 %.

2.1c *General procedures for the synthesis of 2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1H-indole-3-carbaldehyde (4)*: Phosphoryl chloride (9.0 equiv.) was dissolved in 3 mL of anhydrous DMF and stirred at 0°C. Then 1.0 equiv. of **3** was dissolved in 4 mL of DMF added dropwise to the reaction mixture. The mixture was stirred at 0°C for 24 h, then this solution was added dropwise to 7 mL of saturated sodium bicarbonate solution. 5 mL of 10% NaOH solution were poured onto the mixture, and the precipitated solid was filtered off and washed with water. Recrystallization from hot ethanol provided a pale yellow colored solid **4** in 91% yield.

2.1d *2-(4-Oxo-3,4-dihydroquinazolin-2-yl)-1H-indole-3-carbaldehyde (4)*: Yellow colored solid; yield: 91 %, Mp: > 280°C, IR (KBr) ν_{max}: 3462, 2986, 2875, 2821, 1718, 1693, 1562, 1432, 1317, 1223, 865, 750 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.65 (s, 1H), 13.13 (s, 1H), 10.4 (s, 1H), 8.26 (d, 1H, J = 8.0 Hz), 8.20 (d, 1H, J = 8.0 Hz), 7.92–7.89 (m, 1H), 7.85–7.83 (m, 1H), 7.68 (d, 1H, J = 8.0 Hz), 7.59 (t, 1H, J = 7.6 Hz), 7.41 (t, 1H, J = 7.2 Hz), 7.36–7.32 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 188.0, 161.6, 148.8, 145.7, 136.3, 136.2, 135.4, 128.1, 128.0, 127.9, 126.5, 125.8, 123.7, 122.2, 120.6, 115.5, 113.7; LC-MS (m/z): 290 $(M+H)^+$, positive mode; Anal.

calcd. for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.83; N, 14.53 %, found: C, 70.45; H, 3.78; N, 14.43%.

2.1e *2-(4-(Dimethylamino)phenyl)quinazolin-4(3H)-one (5)*: White solid; yield: 92%, Mp: 222°C, IR (KBr) ν_{max}: 3188, 3015, 1670, 1588, 1528, 1363, 1287, 1204, 936, 821, 766, 459 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 11.03 (s, 1H), 8.30 (d, 1H, J = 7.8 Hz), 8.11 (d, 2H, J = 8.8 Hz), 7.76–7.74 (m, 2H), 7.43–7.39 (m, 1H), 6.79 (d, 2H, J = 8.8 Hz), 3.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 152.5, 151.8, 150.1, 134.6, 128.8, 128.5, 127.4, 126.3, 125.6, 120.3, 119.2, 112.0, 111.6, 40.1; LC-MS (m/z): 266 $(M+H)^+$ positive mode; Anal Calcd for $C_{16}H_{15}N_3O$: C,72.43; H, 5.70; N, 15.84 %; found C, 72.54; H, 5.62; N, 15.76%.

2.1f *2-(1H-Pyrrol-2-yl)quinazolin-4(3H)-one (6)*: White solid; yield: 94%, Mp: 240°C, IR (neat) ν_{max}: 3430, 2252, 2126, 1665, 1539, 1501, 1468, 1052, 1024, 986, 827 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/DMSO-d_6): δ 12.01 (s, 1H), 11.17 (s, 1H), 8.08 (d, 1H, J = 7.8 Hz), 7.62–7.58 (m, 1H), 7.54–7.52 (m, 1H), 7.28–7.24 (m, 2H), 6.92 (s, 1H), 6.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ 161.5, 148.4, 145.1, 133.0, 125.3, 124.8, 123.8, 123.4, 122.1, 119.4, 111.3, 108.8; LC-MS (m/z): 212 $(M+H)^+$ positive mode, Anal Calcd for $C_{12}H_9N_3O$: C, 68.24; H, 4.29; N, 19.89 %; found C, 68.36; H, 4.35; N, 19.76 %.

2.1g *2-(Pyridin-2-yl)quinazolin-4(3H)-one (7)*: White solid, yield: 92%, Mp: 138°C, IR (KBr) ν_{max}: 3265, 1670, 1593, 1467, 1319, 1139, 991, 799, 739, 684, 601 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 10.94 (s, 1H), 8.63 (d, 1H, J = 4.6 Hz), 8.54 (d, 1H, J = 8.0 Hz), 8.32 (d, 1H, J = 8.0 Hz), 7.90–7.86 (m, 1H), 7.80–7.74 (m, 2H), 7.51–7.43 (m, 2H);^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 149.1, 148.8, 148.7, 148.3, 137.5, 134.5, 128.0, 127.2, 126.7, 126.2, 122.4, 121.9; LC-MS (m/z): 224 $(M+H)^+$ positive mode; Anal Calcd for $C_{13}H_9N_3O$: C, 69.95; H, 4.06; N, 18.82 %; found: C, 69.85; H, 4.12; N, 18.75 %.

2.1h *2-(Quinolin-2-yl)quinazolin-4(3H)-one (8)*: White solid; yield: 95%, Mp: 188°C, IR (KBr) ν_{max}: 3320, 1687, 1599, 1555, 1407, 1325, 1237, 1122, 925, 837, 739, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 11.16 (s, 1H), 8.56 (d, 1H, J = 8.4 Hz), 8.33 (d, 1H, J = 7.8 Hz), 8.28 (d, 1H, J = 8.4 Hz), 8.08 (d, 1H, J = 8.4 Hz), 7.83–7.81 (m, 2H), 7.78–7.72 (m, 2H), 7.58 (t, 1H, J = 7.4 Hz), 7.49 (t, 1H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 149.0, 148.8, 147.9, 146.6, 137.5, 134.5, 130.4, 129.6, 129.2, 128.2, 127.7, 127.5, 126.7, 122.5, 118.3; LC-MS (m/z): 274 $(M+H)^+$ positive mode; Anal Calcd for $C_{17}H_{11}N_3O$: C, 74.71; H, 4.06; N, 15.38 %; found: C 74.62; H, 4.14; N 15.42 %.

2.1i *2-(9-Ethyl-9H-carbazol-3-yl)quinazolin-4(3H)-one (9)*: White solid; yield: 91%, Mp: 232°C, IR (KBr) ν_{max}: 3051, 2853, 2328, 1682, 1589, 1556, 1506, 1468, 1287, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/DMSO-d_6): δ 12.15 (s, 1H), 9.05 (s, 1H), 8.38 (d, 1H, J = 7.6 Hz), 8.29 (d, 1H, J = 7.8 Hz), 8.21 (d, 1H, J = 7.6 Hz), 7.81–7.45 (m, 2H), 7.52–7.49 (m, 2H), 7.47–7.41 (m, 2H), 7.29 (t, 1H, J = 7.3 Hz), 4.40 (q, 2H, J = 7.2 Hz), 1.45 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ 163.1, 152.5, 149.2, 141.1, 139.9, 133.8, 126.9, 125.7, 125.6, 125.2, 124.9, 122.8, 122.4, 120.27, 120.20, 119.9, 119.0, 108.4, 108.1, 37.1, 13.3; LC-MS (m/z): 340 $(M+H)^+$ positive mode; Anal Calcd for $C_{22}H_{17}N_3O$: C, 77.86; H, 5.05; N, 12.38 %; found C, 77.69; H, 5.14, N, 12.45 %.

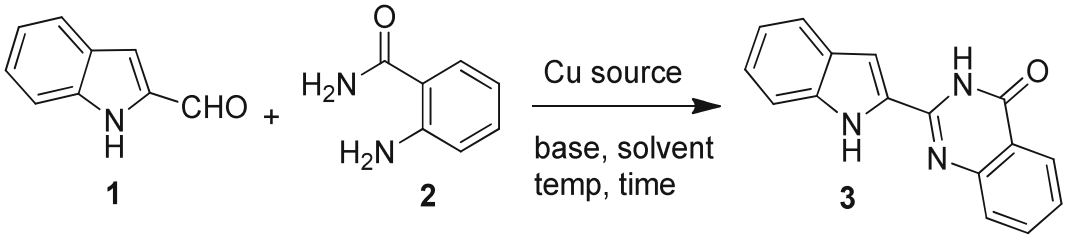
3. Results and discussion

We first examined a synthetic route starting from a reaction of indole-2-aldehyde (**1**) with anthranilamide (**2**), chosen as the model substrates to optimize the reaction conditions. In the presence of CuBr and 2.0 equivalent of K_2CO_3 (relative to the amount of indole-2-aldehyde 1) at 120°C, this coupling reaction proceeded smoothly, to give a indolylquinazolinone **3** in 74% yield.

The influence of the catalyst, ligand, base, solvent and temperature were examined as shown in table 1. In the initial screenings, different bases like Cs_2CO_3, Na_2CO_3, KOAc, and K_2CO_3 were tested in the reaction. Also, the effect of solvents were investigated and it was found that DMF afforded good yield compared to the various solvents which were investigated in this reaction. We found that Cs_2CO_3 proved to be the most effective base in DMF. It may be due to maximum solubility as well as basicity of Cs_2CO_3 particularly in DMF than that of other bases used in the optimization of the reaction.[10]

When CuI was used as the catalyst in place of CuBr, it showed weaker activity than CuBr (table 1, entry 3). Other copper catalysts were also evaluated but proved less effective than CuBr. The condensation of **1** and **2** proceed neither at room temperature nor below 70°C. No product formation was observed in the absence of catalyst (table 1, entry 12). The optimal reaction temperature was also examined, and the yield

Table 1. Optimization condition for the copper catalyzed synthesis of indolylquinazolinone.[a]



S. No	Catalyst	Base	Solvent	Time(H)	Yield[d](%)
1	CuBr	K_2CO_3	DMF	2	74
2	CuBr	KOAc	DMF	6	48
3	CuI	Cs_2CO_3	DMF	4	85
4	CuBr	Cs_2CO_3	NMP	8	10
5	$Cu(OAc)_2$	Cs_2CO_3	DMF	6	84
6[b]	**CuBr**	**Cs_2CO_3**	**DMF**	**2**	**94**
7	CuI	Cs_2CO_3	DMSO	8	20
8	CuBr	Na_2CO_3	DMF	12	72
9	CuCl	Cs_2CO_3	DMSO	12	35
10	CuBr	Cs_2CO_3	Toluene	12	22
11	CuI	K_2CO_3	DMF	4	72
12	-	Cs_2CO_3	DMF	12	-
13[c]	CuBr	Cs_2CO_3	DMF	5	68

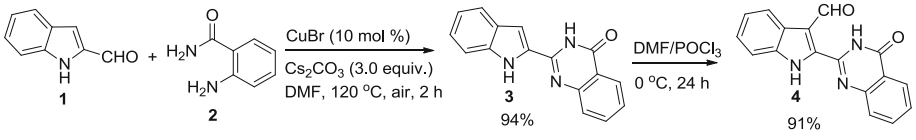
[a]Unless otherwise mentioned, all the reactions were conducted in a RB using indole-2-aldehyde **1** (1.0 equiv.), anthranilamide **2** (1.0 equiv.) catalyst (10 mol %), base (2.0 equiv.) 3 mL solvent stirred at 120 °C in open air. [b]3 equiv. of base used. [c]5 mol % catalyst used. [d]isolated yields

of the target product reached a maximum at 120°C under open air condition. Without ligand and additive the reaction proceeded well within 2 h. By decreasing the CuBr loading from 10 mol % to 5 mol %, the reaction took longer reaction time for the completion (table 1. entry 13).

Based on above findings, we concluded that the optimal condition for this reaction involves 1.0 equiv. of **1**, 1.0 equiv. of **2** and 3.0 equiv. of Cs_2CO_3 in DMF with 10 mol % of CuBr at 120°C in open air. By using the above optimized condition the product **3** was obtained in excellent yield (94%) within 2 h. To achieve the synthesis of bouchardatine alkaloid **4** we conducted the formylation reaction of **3**, following the reported procedure[6a] using $DMF/POCl_3$ at 0°C for 24 h which yielded the **4** in 91% yield (scheme 2).

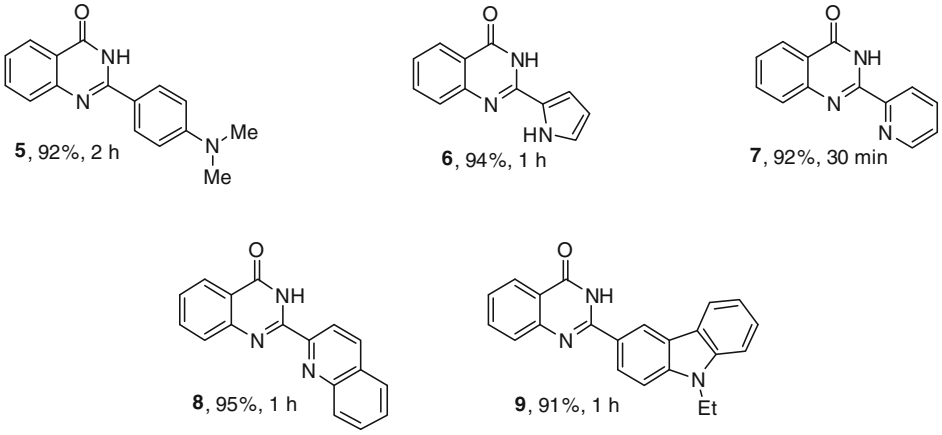
With the optimized reaction conditions in hand, we next moved to synthesis of different quinazolinone derivatives (**5–9**) by varying different (hetero)aryl aldehydes with anthranilamide **2** and the reactions proceeded well to give quinazolinone derivatives in excellent yields (table 2). The proposed mechanism is shown in scheme 3.

We proposed a plausible pathway in scheme 3, where the first step is the reaction between aldehyde **1** and the amine **2**, which led to the formation of corresponding imine (**A**). Next, the imine nitrogen is activated by the CuBr, which increases the elctrophilicity of the imine that undergoes a ready attack by the amide nitrogen to form the cyclized quinazolinone ring (**C**) and regenerate the CuBr. Then the cyclized ring is aromatized by aerobic oxidation to form **3**.

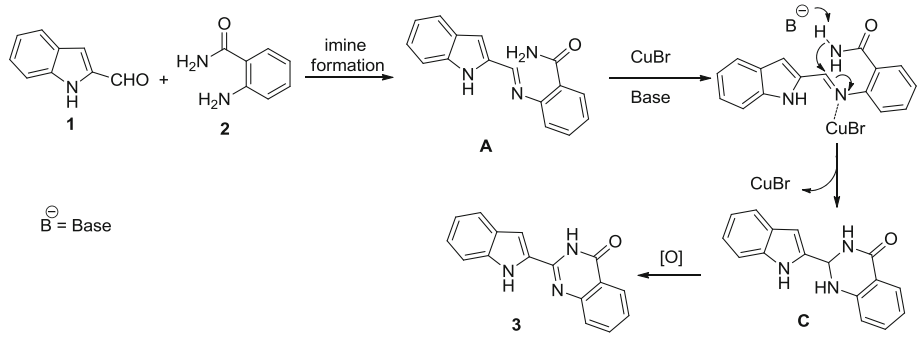


Scheme 2. Synthesis of bouchardatine alkaloid (**4**).

Table 2. Synthesis of (hetero)aryl substituted quinazolinone.[a]



[a]All the reactions were conducted in a 10 mL R.B. using anthranilamide **2**(1.0 equiv.), (hetero)arylaldehyde (1.0 equiv.), Cs_2CO_3 (3.0 equiv.), CuBr (10 mol %), DMF (3 mL), 120°C, open air.



Scheme 3. Proposed mechanism for the formation of **3**.

4. Conclusion

In summary, we have developed an efficient copper-catalyzed synthesis of indolylquinazolinone derivative in good yield. This reaction proceeds well under relatively moderate conditions with shorter reaction times. By formylation of the above product, bouchardatine was prepared in good yield. We synthesized various (hetero)aryl substituted quinazolinone derivatives in good yields using the above optimized oxidation reaction condition.

Supplementary Information

The electronic supporting information can be seen at www.ias.ac.in/chemsci.

Acknowledgements

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References

1. (a) Mhaske S B and Argade N P 2006 *Tetrahedron* **62** 9787; (b) Grundon M F 1984 *Nat. Prod. Rep. 1* 195; (c) Michael J P 2000 *Nat. Prod. Rep.* **17** 603
2. (a) Witt A and Bergman J 2003 *Curr. Org. Chem.* **7** 659; (b) Johne S Rodd's 1995 *Chemistry of Carbon Compounds* (supplements to the 2nd Ed.) (ed) Ansell M F (Amsterdam: Elsevier) Vol. IV I/J, pp 223; (c) Brown D J 1996, Quinazolines. In *The Chemistry of Heterocyclic Compounds*, Volume 55, Quinazolines: Supplement 1 (New York: Wiley); (d) Connolly D J, Cusack D, O'Sullivan T P and Guiry P J 2005 *Tetrahedron* **61** 10153; (e) Liang J L, Cha H C and Jahng Y 2011 *Molecules* **16** 4861; (f) Nacro K, Zha C, Guzzo P R, Herr R J, Peace D and Friedrich T D 2007 *Bioorg. Med. Chem.* **15** 4237
3. Wattanapiromsakul C, Forster P I and Waterman P G 2003 *Phytochemistry* **64** 609

4. Richards PG 1991 *Bouchardatia Vol. 2* Harden G, (Ed.), (Sydney: New South Wales University Press)
5. Forster P I 2002 *Rutaceae* R J F Henderson (Ed.), (Brisbane: Queensland Government, Environmental Protection Agency)
6. (a) Bubenyák M, Palfi M, Takacs M, Beni S, Eva S, Noszal B and Kokosi J 2008 *Tetrahedron Lett.* **49** 4937; (b) Naik N H, Urmode T D, Sikder A K and Kusurkar R S 2013 *Aust. J. Chem.* **66** 1112
7. (a) Jana R, Pathak T P and Sigman M S 2011 *Chem. Rev.* **111** 1417; (b) Engle K M, Mei T S, Wang X and Yu J Q 2011 *Angew. Chem., Int. Ed.* **50** 1478; (c) Bras J L and Muzart J 2011 *Chem. Rev.* **111** 1170; (d) Chen X, Wang H, Jin X, Feng J, Wang Y and Lu P 2011 *Chem. Commun.* **47** 2628; (e) Luo Y, Pan X and Wu J 2011 *Org. Lett.* **13** 1150; (f) Armstrong A and Collins J C 2010 *Angew. Chem., Int. Ed.* **49** 2282; (g) Zhao D B, You J S and Hu C W 2011 *Chem.- Eur. J.* **17** 5466
8. For general reviews on palladium-catalyzed transformations and synthesis of heterocycles, see: (a) Magano J and Dunetz J R 2011 *Chem. Rev*. **111** 2177; (b) Majumdar K C, Chattopadhyay B K, Maji P K, Chattopadhyay S and Samanta S 2010 *Heterocycles* **81** 795; (c) Song G, Wang F and Li X 2012 *Chem. Soc. Rev.* **41** 3651; (d) Neufeldt S R and Sanford M S 2012 *Acc. Chem. Res.* **45** 936; (e) Kuhl N, Hopkinson M N, Wencel D J and Glorius F 2012 *Angew. Chem., Int. Ed* **51** 10236; (f) Mousseau J J and Charette A B 2013 *Acc. Chem. Res.* **46** 412
9. For reviews and papers on copper-catalyzed coupling reactions, see: (a) Lanting X, Yinsheng P, Qiangbiao P, Yongwen J and Dawei M 2013 *J. Org. Chem.* **78** 3400; (b) Allen S E, Walvoord R R, Salinas R P and Kozlowski M 2013 *Chem. Rev.* **113** 6234; (c) Xiaolin P, Yong L and Jie W 2013 *J. Org. Chem.* 78 5756; (d) Chen D S, Dou G L, Li Y L, Liu Y and Wang X S 2013 *J. Org. Chem.* **78** 5700; (e) Biswas S and Batra S 2013 *Eur. J. Org. Chem.* 4895; (f) Jhan Y H, Kang T W and Hsieh J C 2013 *Tetrahedron Lett.* **54** 1155; (g) Chen D, Chen Q, Liu M, Dai S, Huang L, Yang J and Bao W 2013 *Tetrahedron* **69** 6461; (h) Ngi S I, Guilloteau V, Abarbri M and Thibonnet J J 2011 *Org. Chem.* **76** 8347; (i) Xu W, Jin Y, Liu H, Jiang Y and Fu H 2011 *Org. Lett.* **13** 1274; (j) Sreenivas D K, Ramkumar N and Nagarajan R 2012 *Org. Biomol. Chem.* **10** 3417
10. (a) Salvatore R N, Nagle A S and Jung K W 2002 *J. Org. Chem.* **67** 674; (b) Wolfe J P and Buchwald S L 2000 *J. Org. Chem.* **65** 1144