Copper catalyzed synthesis of quinolinopyrano[2,3-*b*]carbazole derivatives via Povarov reaction

SUBBURETHINAM RAMESH and RAJAGOPAL NAGARAJAN*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India
e-mail: rnsch@uohyd.ernet.in; naga_indole@yahoo.co.in

MS received 6 January 2014; revised 9 January 2014; accepted 12 February 2014

Abstract. An efficient procedure for the synthesis of pyranocarbazole derivatives using copper catalysed Povarov reaction between aromatic amines and *O*-propargyl carbazole carboxaldehyde has been developed. Ionic liquid is found to be a good solvent medium.

Keywords. Povarov reaction; copper(I)iodide; ionic liquid; pyranocarbazole.

1. Introduction

Carbazoles represent an important family of heterocyclic compounds that are present in many natural products.¹ Naturally occurring carbazoles and synthetic carbazole analogues are known to exhibit promising biological applications.¹ Among these, pyranocarbazole alkaloids have spared in the natural product synthesis due to their wide isolation from various plants.^{1,2} Some of the important pyranocarbazole alkaloids are shown in figure 1.

Pyranocarbazole analogues showed antioxidant activity at 33.1 µg/mL,^{3a} antiosteoporotic activity in the CAT-B model^{3b} and cytotoxicity against leukemia and colon cancer cell lines.^{3c} Usually, an oxidative cyclization of a hydroxy prenyl or hydroxy geranylcarbazole has been used for the construction of pyran ring present in this class of alkaloids. 2-Hydroxy-3-methylcarbazole is recognized as an efficient reaction precursor for the synthesis of Mahanimbine^{4a} and Girinimbine.^{4b} Knölker *et al.* utilised palladium catalysed Buchwald–Hartwig amination followed by double aromatic C–H bond activation of biaryl compound.^{4c} The same group reported tandem C–C and C–N bond formation using aromatic substitution of aminochromene with iron carbonyl complex followed by I₂ mediated oxidative coupling of biaryl compound.^{4d} Lebold *et al.* demonstrated the synthesis of pyrano[2,3-*c*]carbazole alkaloids (Eustifoline-A and Eustifoline-B) using a Diels–Alder reaction of quinone imine followed by Plieninger indolization reaction.^{4e} Recently, our group utilized Larock's iodocyclization of *O*-propargylated

carbazoles for the synthesis of pyrano[3,2-*b*] and pyrano[2,3-*c*] carbazole derivatives.^{4f}

Chromenes and chromenoquinolines are an important class of heterocyclic compounds which have attracted considerable attention, due to their diverse biological activities⁵ and hence many synthetic strategies have been developed by various groups.⁶ We anticipated as in figure 2 that the presence of both pyranocarbazole and chromenoquinoline units in a single molecule could make more biological applications. Povarov reaction has been recognized as a practical method to construct quinoline or tetrahydroquinoline compounds.⁷ We envisioned that such a strategy if applied to an appropriate precursor could make interesting synthetic application for the pyranocarbazole derivatives. Though there are many synthetic approaches for making pyrano[3,2-*a*], [2,3-*c*] and [3,2-*b*] carbazoles,⁴ synthesis of pyrano[2,3-*b*]carbazole derivatives have been scarcely studied. Based on the important biological profile of pyranocarbazoles and our continuing interest in Povarov reaction,^{6c–g} we report here Povarov reaction between *O*-propargyl carbazole carboxaldehyde and anilines to give quinolinopyrano[2,3-*b*]carbazole derivatives.

2. Experimental

2.1 General information

The melting point of the products was recorded on a Superfit (India) capillary melting point apparatus and is uncorrected. Infrared spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. All the spectra were calibrated against polystyrene absorption at

*For correspondence

Figure 1. Some of the important pyranocarbazole alkaloids.

Figure 2. Quinolinopyranocarbazole.

1601 cm^{-1} . Solid samples were recorded as KBr wafers and liquid samples as thin film between NaCl plates or solution spectra in DCM. ^1H NMR and ^{13}C NMR spectra were recorded on BRUKER-AVANCE-400/500 spectrometers. ^1H NMR (400 or 500 MHz) spectra for all the samples were measured in chloroform- d , unless otherwise mentioned ($\delta = 2.50$ ppm for ^1H NMR in the case of DMSO- d_6), with TMS ($\delta = 0$ ppm) as an internal standard. ^{13}C NMR (100 or 125 MHz) spectra for all the samples were measured in chloroform- d , unless otherwise mentioned (in the case of DMSO- d_6 , $\delta = 39.70$ ppm its middle peak of the septet), with its middle peak of the triplet ($\delta = 77.10$ ppm) as an internal standard. Mass spectral data were obtained from HRMS (ESI). The TOF and quadrupole mass analyzer types are used for the HRMS measurements. All the cases DCM or MeOH were used to dissolve the compounds.

2.1a Procedure for the preparation of 2-hydroxy-9-methyl-9H-carbazole-3-carbaldehyde (2): The reaction mixture of aldehyde (1) (1.0 mmol) and pyridine HCl salt (10 equiv.) was heated under microwave condition for 10 min. The crude was extracted using dichloromethane and evaporated under reduced pressure. Pure product was obtained as a colourless solid through silica gel column chromatography using 3% ethyl acetate in hexanes as eluent; Yield: 63%; m.p. 165–167°C; IR (KBr): 3357, 1936, 1147, 665 cm^{-1} ; ^1H

NMR (400 MHz, CDCl_3 , TMS) δ : 11.53 (1H, s), 9.92 (1H, s), 8.13 (1H, s), 7.99 (1H, d, $J = 7.6$ Hz), 7.47 (1H, t, $J = 7.2$ Hz), 7.36 (1H, d, $J = 8.4$ Hz), 7.29 (1H, t, $J = 7.6$ Hz), 6.79 (1H, s), 3.77 (3H, s); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ : 195.0, 161.3, 146.9, 142.1, 127.1, 126.0, 123.1, 120.7, 119.7, 117.2, 115.0, 108.9, 94.9 (Aromatic C); 29.4 (Aliphatic C); HRMS (ESI-MS) calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}_2$ (M+H); 226.0868, found: 226.0865

2.1b Procedure for the preparation of 9-methyl-2-(prop-2-yn-1-yloxy)-9H-carbazole-3-carbaldehyde (3): To the reaction mixture of 2-hydroxy-9-methyl-9H-carbazole-3-carbaldehyde (2) (1 mmol) and K_2CO_3 (5 equiv.) in acetone was added propargyl bromide (1.5 mmol). Then the reaction mixture was heated at reflux temperature of acetone. After completion of the reaction as indicated by TLC, the solvent was evaporated and extracted with ethylacetate. The solvent was removed under reduced pressure and pure product was obtained through silica gel column chromatography with 2% ethyl acetate in hexanes. m.p. 124–126°C; IR (KBr): 3457, 2829, 1697, 1147, 645 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS) δ : 10.49 (1H, s), 8.65 (1H, s), 8.01 (1H, d, $J = 7.6$ Hz), 7.45 (1H, t, $J = 6.8$ Hz), 7.34 (1H, d, $J = 8.0$ Hz), 7.26–7.29 (1H, m), 6.86 (1H, s), 4.91 (2H, s), 3.78 (3H, s), 2.62 (1H, s); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ : 189.2, 159.4, 145.7, 141.8, 125.9, 123.2, 121.5, 120.5, 120.2, 118.9, 117.6, 108.8, 92.1 (Aromatic C); 77.9, 76.6, 56.9, 29.4 (Aliphatic C); HRMS (ESI-MS) calcd. for $\text{C}_{17}\text{H}_{13}\text{NO}_2$ (M+H); 264.1024, found: 264.1024

2.2 General procedure for the synthesis of dihydroquinalopyran[2,3-b]carbazoles (5a–f)

In a round bottom flask equipped with a magnetic stirring bar, 1.0 mmol of aniline and 1.0 mmol of *O*-propargyl salicylaldehyde in 5 mL of ionic liquid $[\text{Bmim}][\text{BF}_4]$ as solvent, was added 10 mol% of CuI. Reaction mixture was stirred at 90–95°C. After completion of the reaction, as indicated by the TLC, water

(20 mL) was added to the crude reaction mass. Then aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under the reduced pressure. Product was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate).

2.2a *9-Methyl-6,9-dihydroquinolino[2',3':4,5]pyrano[2,3-*b*]carbazole (5a)*: m.p. 198–200°C; IR (KBr): 3024, 2841, 1174, 1059, 634 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, TMS) δ: 9.21 (1H, s), 8.21 (2H, d, *J* = 8.0 Hz), 7.88 (1H, s), 7.78 (1H, d, *J* = 8.0 Hz), 7.31 (1H, dt, *J*₁ = 1.5 Hz and *J*₂ = 7.0 Hz), 7.46–7.52 (2H, m), 7.38 (1H, d, *J* = 8.0 Hz), 7.30 (1H, d, *J* = 7.5 Hz), 6.99 (1H, s), 5.41 (2H, s), 3.82 (3H, s); ¹³C NMR (125 MHz, CDCl₃, TMS) δ: 156.9, 150.4, 148.6, 144.0, 141.9, 130.7, 129.5, 129.1, 127.4, 127.2, 125.7, 125.3, 125.2, 123.5, 120.4, 119.7, 119.2, 117.8, 116.0, 108.4, 96.0 (Aromatic C); 68.9, 29.2 (Aliphatic C); HRMS (ESI-MS) calcd. for C₂₃H₁₆N₂O (M+H); 337.1341, found: 337.1344.

2.2b *3,9-Dimethyl-6,9-dihydroquinolino[2',3':4,5]pyrano[2,3-*b*]carbazole (5b)*: m.p. 254–256°C; IR (KBr): 3187, 2829, 1148, 1025, 659 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ: 9.16 (1H, s), 8.19 (1H, d, *J* = 8.0 Hz), 8.09 (1H, d, *J* = 8.4 Hz), 7.76 (1H, s), 7.53–7.57 (2H, m), 7.47 (1H, t, *J* = 7.6 Hz), 7.37 (1H, d, *J* = 8.0 Hz), 7.27–7.31 (1H, m), 6.97 (1H, s), 5.38 (2H, s), 3.80 (3H, s), 2.56 (3H, s); ¹³C NMR (100 MHz, CDCl₃, TMS) δ: 156.7, 149.6, 147.1, 143.8, 141.8, 135.5, 131.8, 130.2, 128.7, 127.2, 126.4, 125.3, 125.2, 123.5, 120.4, 119.6, 119.0, 117.6, 116.1, 108.4, 96.1 (Aromatic C); 69.0, 29.3, 21.6 (Aliphatic C); HRMS (ESI-MS) calcd. for C₂₄H₁₈N₂O (M+H); 351.1497, found: 351.1499.

2.2c *3-Methoxy-9-methyl-6,9-dihydroquinolino[2',3':4,5]pyrano[2,3-*b*]carbazole (5c)*: m.p. 228–230°C; IR (KBr): 3149, 2837, 1249, 1164, 618 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ: 9.09 (1H, s), 8.17 (1H, d, *J* = 7.6 Hz), 8.08 (1H, d, *J* = 9.2 Hz), 7.72 (1H, s), 7.44 (1H, d, *J* = 7.2 Hz), 7.34–7.38 (2H, m), 7.25–7.28 (1H, m), 7.01 (1H, d, *J* = 2.4), 6.93 (1H, s), 5.36 (2H, s), 3.93 (3H, s), 3.77 (3H, s); ¹³C NMR (100 MHz, CDCl₃, TMS) δ: 157.3, 156.5, 148.1, 144.5, 143.6, 141.8, 130.5, 129.6, 128.1, 125.5, 125.2, 123.5, 121.8, 120.4, 119.6, 119.0, 117.3, 116.1, 108.3, 105.4, 96.0 (Aromatic C); 68.9, 55.5, 29.2 (Aliphatic C); HRMS (ESI-MS) calcd. for C₂₄H₁₈N₂O₂ (M+H); 367.1446, found: 367.1451.

2.2d *3-Fluoro-9-methyl-6,9-dihydroquinolino[2',3':4,5]pyrano[2,3-*b*]carbazole (5d)*: m.p. 241–243°C; IR (KBr): 3125, 2835, 1451, 1179, 632 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, TMS) δ: 9.08 (1H, s), 8.16–8.18 (2H, m), 7.69 (1H, s), 7.45–7.47 (2H, m), 7.28–7.35 (3H, m), 6.91 (1H, s), 5.34 (2H, s), 3.74 (3H, s); ¹³C NMR (125 MHz, CDCl₃, TMS) δ: 161.0, 159.0, 156.7, 149.8, 145.5, 143.9, 141.8, 131.4, 131.3, 129.91, 129.9, 127.7, 127.6, 126.0, 125.3, 123.4, 120.7, 120.3, 119.7, 119.5, 119.3, 119.1, 117.5, 115.7, 110.6, 110.5, 108.8, 108.4, 96.0, 94.9 (Aromatic C); 68.7, 29.1 (Aliphatic C); HRMS (ESI-MS) calcd. for C₂₃H₁₅FN₂O (M+H); 355.1246, found: 355.1246.

2.2e *3-Chloro-9-methyl-6,9-dihydroquinolino[2',3':4,5]pyrano[2,3-*b*]carbazole (5e)*: m.p. 212–214°C; IR (KBr): 3032, 2857, 1364, 1157, 629 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆, TMS) δ: 9.05 (1H, s), 8.23 (1H, d, *J* = 7.5 Hz), 8.19 (1H, s), 8.15 (1H, s), 8.01 (1H, d, *J* = 8.5 Hz), 7.85 (1H, d, *J* = 8.5 Hz), 7.56 (1H, d, *J* = 8.0 Hz), 7.46 (1H, t, *J* = 7.0 Hz), 7.21–7.26 (2H, m), 5.45 (2H, s), 3.84 (3H, s); ¹³C NMR (125 MHz, CDCl₃, TMS) δ: 157.1, 150.6, 146.9, 144.3, 142.1, 133.1, 131.1, 130.9, 130.2, 128.7, 126.7, 126.0, 123.0, 120.5, 120.1, 118.9, 118.6, 117.6, 115.6, 109.7, 97.2 (Aromatic C); 68.4, 29.7 (Aliphatic C); HRMS (ESI-MS) calcd. for C₂₃H₁₅ClN₂O (M+H); 371.0951, found: 371.0953.

2.2f *3-Bromo-9-methyl-6,9-dihydroquinolino[2',3':4,5]pyrano[2,3-*b*]carbazole (5f)*: m.p. 223–225°C; IR (KBr): 3048, 2874, 1483, 1148, 625 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ: 9.06 (1H, s), 8.15 (1H, d, *J* = 7.2 Hz), 8.00 (1H, d, *J* = 8.8 Hz), 7.82 (1H, s), 7.74 (1H, dd, *J*₁ = 7.2 Hz, *J*₂ = 2.0 Hz), 7.65 (1H, s), 7.46 (1H, t, *J* = 7.6 Hz), 7.34 (1H, d, *J* = 7.6 Hz), 7.26–7.29 (1H, m), 6.89 (1H, s), 5.35 (2H, s), 3.74 (3H, s); ¹³C NMR (100 MHz, CDCl₃, TMS) δ: 156.7, 150.7, 147.0, 144.0, 141.8, 132.8, 130.6, 129.6, 129.4, 128.2, 126.1, 125.4, 123.4, 120.4, 119.7, 119.2, 119.1, 117.7, 115.5, 108.4, 96.0 (Aromatic C); 68.7, 29.2 (Aliphatic C); HRMS (ESI-MS) calcd. for C₂₃H₁₅BrN₂O (M+H); 415.0446, found: 415.0446.

3. Results and Discussion

We choose 2-hydroxy-3-formylcarbazole (**1**) which would be a potential starting material for making pyrano[2,3-*b*]carbazole derivatives. The synthesis of *O*-propargylaldehyde precursor **3** is shown in scheme 1. Demethylation of 2-methoxy-3-formylcarbazole⁸ (**1**)

Scheme 1. Synthesis of 9-methyl-2-(prop-2-yn-1-yloxy)-9H-carbazole-3-carbaldehyde (**3**).

Table 1. Optimization of the reaction conditions.

Entry	Solvent	Time (h)	Yield (%) ^a
1	CH ₃ CN	3	61
2	Toluence	10	37
3	DMSO	2.5	66
4	Dioxane	8	34
5	THF	10	47
6	[Bmim][BF ₄]	2.5	78
7 ^b	[Bmim][BF ₄]	24	42

General condition: aldehyde (**1**) (1 mmol), aniline (**2a**) (1.2 mmol) and CuI (10 mol%). For entries 1, 2 and 4, 5 reflux temperature of corresponding solvents were maintained. For entries 3, 6 and 7 the reaction temperature 90–95°C were maintained.

^aYield of isolated product.

^bWithout CuI.

Scheme 2. Synthesis of pyranocarbazole derivatives (**5a–f**).

Scheme 3. Proposed mechanism for the Povarov reaction.

using pyridine hydrochloride salt under microwave condition afforded 2-hydroxy-3-formylcarbazole (**2**). *O*-Propargylation of compound **2** provided propargylated 3-formylcarbazole **3** in quantitative yield using propargyl bromide/acetone under reflux condition.

Then, we carried out the cyclization reaction of *O*-propargyl derivative **3** with aniline **4a** in the presence of CuI as it showed better catalytic activity in the synthesis of chrominoquinoline and pyrroloquinoline derivatives.^{6e-g} We screened various solvents such as CH₃CN, toluene, THF, dioxane, DMSO and [Bmim][BF₄] (table 1, entries 1–7). We found that the conditions using [Bmim][BF₄] as solvent with 10 mol% of CuI at 90°C gave comparatively good yield (entry 6). Notably, without CuI in the presence of ionic liquid [Bmim][BF₄], the yield decreased.

With acceptable conditions in hand (table 1, entry 6), we tested the scope of this methodology for different aromatic amines (scheme 2). As shown in scheme 2, electron donating (-Me, -OMe) as well as electron withdrawing (-F, -Cl, -Br) groups containing anilines worked well in the present system to give quinolinopyranocarbazole derivatives in good yields. The proposed reaction mechanism is shown in scheme 3.

4. Conclusions

Copper catalysed Povarov reaction to synthesize quinolinopyrano[2,3-*b*]carbazole derivatives has been developed. Applying various aromatic amines with *O*-propargylated carbazole aldehyde in the presence of CuI and [Bmim][BF₄] afford the corresponding pyranocarbazole products in a straightforward manner. This simple, efficient, one-pot and high yielding procedure would be a useful synthetic tool for the synthesis of pyranocarbazoles.

Supplementary Information

¹H, ¹³C spectra and HRMS of compounds **2,3** and **5a–f** are mentioned in the supporting information. The

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

Acknowledgements

We thank the Department of Science and Technology (DST) for financial assistance (Project number: SR/S1/OC-70/2008). SR thanks the Council of Scientific and Industrial Research (CSIR) for Senior Research Fellowship.

References

- (a) Schmidt A W, Reddy K R and Knölker H-J 2012 *Chem. Rev.* **112** 3193; (b) Cordell G A 2008 *The Alkaloids* **65**; (c) Knölker H-J 2008 *The Alkaloids* (Cordell G A ed.) Academic Press, Amsterdam **65** 1; (d) Knölker H-J and Reddy K R 2002 *Chem. Rev.* **102** 4303; (e) Gribble G W 1990 *The Alkaloids*; Brossi A (ed.) (San Diego, CA: Academic Press) p 239
- (a) Jana A and Mal D 2010 *Chem. Commun.* **46** 4411; (b) Lebold T P and Kerr M A 2008 *Org. Lett.* **10** 997; (c) Mal D, Senapati B K and Pahari P 2007 *Tetrahedron* **63** 3768; (d) Forke R, Krah M P, Krause T, Schlechtingen G and Knölker H-J 2007 *Synlett.* 268; (e) Czerwonka R, Reddy K R, Baum E and Knölker H-J 2006 *Chem. Commun.* 711; (f) Knölker H-J, Fröhner W and Wagner A 1998 *Tetrahedron Lett.* **39** 2947; (g) Krah M P, Jäger A, Krause T and Knölker H-J 2006 *Org. Biomol. Chem.* **4** 3215; (h) Knölker H-J and Wolfgang F 1997 *Synlett.* 1108
- (a) Ramsewak R S, Nair M G, Strasburg G M, DeWitt D L and Nitiss J L 1999 *J. Agric. Food Chem.* **47** 444; (b) Wang Y S, He H P, Shen M Y, Hong X and Hao X J 2003 *J. Nat. Prod.* **66** 416; (c) Itoigawa M, Kashiwada Y, Ito C, Furukawa H, Tachibana Y, Bastow K F and Lee K-H 2000 *J. Nat. Prod.* **63** 893
- (a) Crombie L and Ponsford R 1968 *Chem. Commun.* 894; (b) Chakraborty D P, Chatterji D and Ganguli S N 1969 *Chem. Ind. (London)* 1662; (c) Gruner K K and Knölker H-J 2008 *Org. Biomol. Chem.* **6** 3902; (d) Gruner K K, Hopfmann T, Matsumoto K, Jäger A, Katsuki T and Knölker H-J 2011 *Org. Biomol. Chem.* **9** 2057; (e) Lebold T P and Kerr M A 2007 *Org. Lett.* **9** 1883; (f) Talluri K C and Nagarajan R 2012 *J. Chem. Sci.* **124** 487

5. (a) Shaheen F, Ahmad M, Khan S N, Hussain S S, Anjum S, Tashkhodjaev B, Turgunov K, Sultankhodzhaev M N, Choudhary M I and Rahman A-U 2006 *Eur. J. Org. Chem.* **10** 2371; (b) Nikolai M E, Artem S K, Andrey A Y, Mikhail Y A, Igor V M and Alexander K 2007 *J. Org. Chem.* **72** 3443; (c) María E, Benito R, Paula G, Juan R, Carlos C, Humberto C and Jesus A 2010 *Fitoterapia* **81** 66; (d) Zhi L, Tegley C M, Pio B, Edward J P, Motamedi M, Jones T D, Marschke K B, Mais D E, Risek B and Schrader W T 2003 *J. Med. Chem.* **46** 4104; (e) Coghlan M J, Kym P R, Elmore S W, Wang A X, Luly J R, Wilcox D, Stashko M, Lin C W, Miner J, Tyree C, Nakane M, Jacobson P and Lane B C 2001 *J. Med. Chem.* **44** 2879; (f) Ku Y Y, Grieme T, Raje P, Sharma P, Morton H E, Rozema M and King S A 2003 *J. Org. Chem.* **68** 3238
6. (a) Tomashevskaya M M, Tomashenko O A, Tomashevskii A A, Sokolov V V and Potekhin A A 2007 *Russ. J. Org. Chem.* **43** 77; (b) Sabitha G, Babu R S, Reddy B V S and Yadav J S 1999 *Synth. Commun.* **29** 4403; (c) Rabin B, Dhananjaya S N S, Ramu B, Sai U K, Rajender K, Mukkanti K and Pal M 2008 *Tetrahedron* **64** 582; (d) Vu A T, Campbell A N, Harris H A, Unwalla R J, Manas E S and Mewshaw R E 2007 *Bioorg. Med. Chem. Lett.* **17** 4053; (e) Ramesh S, Gaddam V and Nagarajan R 2010 *Synlett.* 757; (f) Gaddam V, Ramesh S and Nagarajan R 2010 *Tetrahedron* **66** 4218; (g) Ramesh S and Nagarajan R 2011 *Tetrahedron Lett.* **52** 4857
7. (a) Babu G and Perumal P T 2000 *Aldrichimica Acta* 33 16; (b) Kouznetsov V V 2009 *Tetrahedron* **65** 2721; (c) Sridharan V, Suryavanshi P A and Menéndez J C 2011 *Chem. Rev.* **111** 7157; (d) Povarov L S 1967 *Russ. Chem. Rev.* **36** 656
8. Díaz J L, Villacampa B, López-Calahorra, F and Velasco D 2002 *Chem. Mater.* **14** 2240