

Cite this: *RSC Adv.*, 2019, 9, 13332

Received 6th March 2019

Accepted 21st April 2019

DOI: 10.1039/c9ra01715a

rsc.li/rsc-advances

Pd nanoparticle supported reduced graphene oxide and its excellent catalytic activity for the Ullmann C–C coupling reaction in a green solvent†

Surjyakanta Rana,* G. Bishwa Bidita Varadwaj and Sreekantha B. Jonnalagadda *

An efficient and easy route to synthesize reduced graphene oxide with well dispersed palladium (Pd) nanoparticles (Pd(0)-RGO) is described. The synthesized materials were fully characterized by different techniques such as: XRD, FTIR, Raman, SEM, and TEM. An average particle size of 7.5 nm for the metal particles was confirmed by TEM analysis. Pd(0)-RGO demonstrated outstanding catalytic activity for Ullmann coupling with 97% yield and good reusability (4 cycles).

Nanoparticles (NPs) proved to be efficient materials with wide applications in the fields of energy, environment, fine chemical synthesis, adsorption and sensors.^{1–3} Nano catalysts are more efficacious than traditional catalysts because of their higher surface to volume ratio, as well as increased number of active sites.^{4,5} Among all the nano catalysts, palladium and palladium based nanoparticles with many applications have gained importance in the last decade.^{6–8} Various types of Pd nanoparticle have been employed as catalysts for different coupling reactions. Due to the recovery and reusability limitations of pure nanoparticles, the use of supported Pd nanoparticles is more cost effective and eco-friendly.

Over the period, numerous carbon based materials such as activated carbon, carbon nanotubes, graphite and graphene have been explored as supports appropriate to the catalyst loading. Among the carbon supports, reduced graphene oxide has evolved as attractive option to be active support, due to its remarkable properties like optical properties, high surface area and electrical conductivity.^{9–17} Graphene and graphene oxide (GO) have also gained importance as prospective support materials for palladium-catalysed C–C coupling reactions.¹⁸ Ullmann C–C coupling reaction, involving two aryl halides yielding biphenyl as a selective product, has attracted researchers' attention in the recent past. Wang *et al.* reported that palladium modified ordered mesoporous carbon (Pd/OMC) as catalyst gave 43% biphenyl yield at 100 °C in water medium at 6 h.¹⁹ Yuan *et al.* reported excellent yields (96%) towards C–C coupling reaction at 80 °C in 20 h using Pd/MIL-101 as catalyst.²⁰ Liyu *et al.* showed that MOF-253·0.05PdCl₂ as catalyst, the

reaction gives 99% yield in DMSO/EtOH (20 : 1) at 120 °C in 10 h.²¹ Karimi *et al.*, obtained 95% yield of biphenyl by using Au supported mesoporous silica at 100 °C for 16 h.²² Varadwaj *et al.*, obtained 96% yield of biphenyl in water medium at 80 °C in 6 h, employing Pd(0) nanoparticles supported organ functionalized clay.²³

In this communication, we describe a facile and efficient route for synthesis of Pd nanoparticles supported on reduced graphene oxide and its efficacy as catalyst for Ullmann reaction in water with exceptional yields (97%). Reusability test confirms that the material is perpetual and recyclable up to four cycles.

The graphene oxide was prepared according to modified Hummers' method.²⁴ For the preparation of Pd reduced graphene oxide (Pd(0)-RGO) catalyst: 1.0 g of GO and 50 ml of distilled water was taken in a flask and sonicated for 30 min. Then palladium nitrate was added in the solution with GO, to prepare 5 and 7 wt% of Pd loaded materials. The mixture was stirred for 2 h. Then, 12 mmol of NaBH₄ with tetrahydrofuran (10 ml) solvent was added to the mixture, which was constantly stirred for 1 h. The material was filtered and washed, followed by drying at 100 °C overnight in a vacuum oven to obtain 5-Pd(0)-RGO and 7-Pd(0)-RGO materials.

Fig. 1 illustrates the XRD spectra of GO (a) and 5-Pd(0)@RGO (b). In Fig. 1(a), the spectrum represents $2\theta \approx 10.75$ corresponding to (002) plane of GO.^{25,26} In case of the Pd(0) metal modified graphene oxide material converted to Pd(0) reduced graphene oxide [Fig. 1(b)], plane (002) at $2\theta \approx 23.11$ is due to the reducing agent.²⁷ The angle at $2\theta \approx 40.11$ and 46.79 correspond to (111), (200) planes of Pd metal particles.²⁶ This confirms the presence of Pd(0) metal particles on the RGO surface.

The stretching and bending frequencies of the FT-IR spectra of GO (a) and 5-Pd(0)-RGO (b) samples are illustrated in ESI Fig. S1.† In these spectra, 3400 cm⁻¹, 1740 cm⁻¹ and 1385 cm⁻¹ represent the O–H stretching, O–H bending vibration of C–OH and C=O stretching of –COOH groups respectively, which were

School of Chemistry & Physics, College of Agriculture, Engineering & Science, University of KwaZulu-Natal, Durban, South Africa. E-mail: jonnalagaddas@ukzn.ac.za; surjya.nou@gmail.com; Fax: +27 31 260 3091; Tel: +27 31 260 7325; +27 31 260 3090

† Electronic supplementary information (ESI) available: Reaction procedure and instrumentation, FTIR figures. See DOI: 10.1039/c9ra01715a



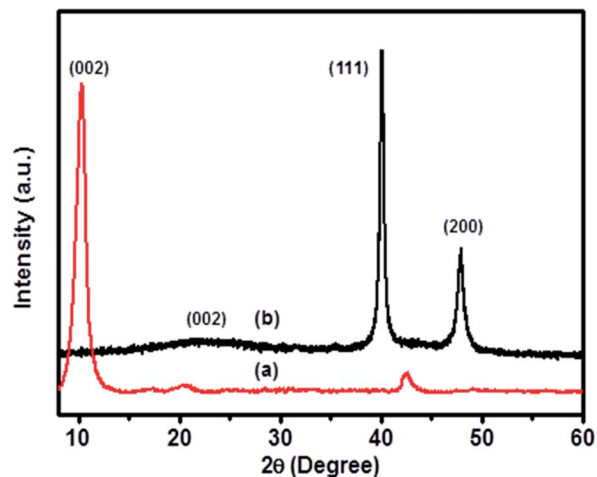


Fig. 1 XRD spectra of GO (a) and 5-Pd(0)-RGO (b) samples.

clearly attributed to graphene oxide material.²⁸ After modification of Pd metal on the GO surface, maximum number of functional groups disappeared, which is because of the reducing agent.

Fig. 2 illustrates the Raman spectra of GO (a) and 5-Pd(0)-RGO (b) samples. In the Raman spectra, all the samples showed the characteristic D-bands at 1342 cm^{-1} and G-bands at 1595 cm^{-1} .²⁹ The intensity of the I_D/I_G ratio of normal GO sample is 0.63, but in case of 5-Pd(0)-RGO sample, the intensity of the I_D/I_G ratio increased to 0.69.

The SEM, TEM and particle size distribution images of 5-Pd(0)-RGO sample are shown in Fig. 3. The SEM and TEM images give the details about the layered sheets of the Pd(0)-RGO sample. The uniform distribution of Pd nanoparticles on the RGO surface was confirmed by transmitted electron microscope monograph. The average particle size of the nanoparticles was 7.5 nm as calculated from TEM image (Fig. 3(d)).

The SEM/EDX analysis provides information on elements present on the material. Fig. 4 illustrates the SEM/EDX and colour mapping images of 5-Pd(0)-RGO catalyst. The images validate the presence of Pd, C and O on the catalyst, which is

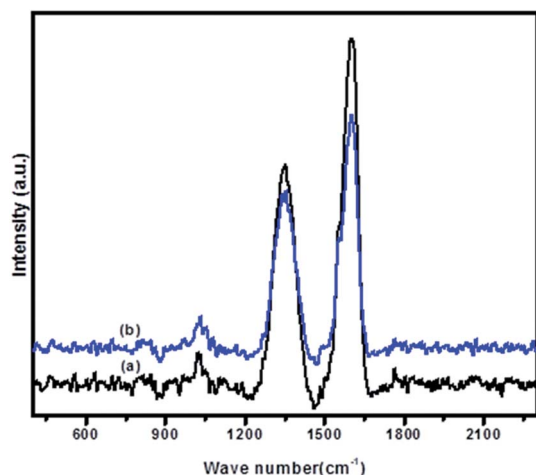


Fig. 2 Raman spectra of GO (a) and 5-Pd(0)-RGO (b) samples.

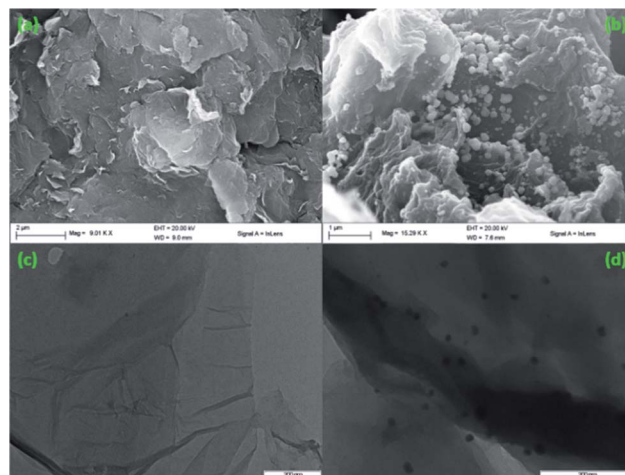


Fig. 3 SEM image of GO, scale bar = $2\text{ }\mu\text{m}$ (a), 5-Pd(0)-RGO, scale bar = $1\text{ }\mu\text{m}$ (b) and TEM image of GO, scale bar = 200 nm (c), 5-Pd(0)-RGO, scale bar = 200 nm (d) catalyst.

also highlighted through their colour mapping. Fig. S2, in the ESI† shows the binding energy of Pd. Binding energy of Pd $3d^{5/2}$ and Pd $3d^{3/2}$ were 335.7 eV and 341.08 eV , which represent the zero-oxidation state of Pd metal. The exact amount of the Pd metal loaded on the support surface was confirmed by ICP-MS analysis indicating the Pd content in materials was 4.5 wt% and 5.1 wt% respectively.

Ullmann C–C coupling is one of the valuable procedures to produce biaryls and biaryls derivatives. C–C coupling reactions are known to be accelerated by various Pd-based catalysts together with organic solvents³⁰ and aqueous inorganic bases.³¹ As reported by Li *et al.*, Pd/Ph-SBA-15 catalyst gave 75% yield towards coupling product at $100\text{ }^\circ\text{C}$ for 10 h.³² Wan *et al.* reported that, silica-carbon supported palladium catalyst gave 64% yields towards coupling product and also the reaction was performed under water medium for 6 h.³³ Gadda *et al.* reported

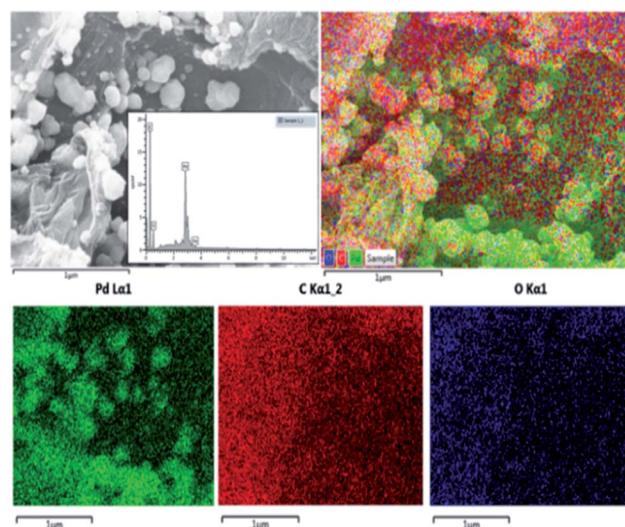


Fig. 4 SEM/EDX with color mapping of 5-Pd(0)-RGO, scale bar = $1\text{ }\mu\text{m}$ catalyst.



46% conversion and 91% selectivity towards biphenyl at 150 °C in water medium with Pd/C catalyst for Ullmann coupling reaction.³⁴ The inherent drawbacks in these reports were essentially long reaction times and high temperature requirement, which have negative impact both fiscally and environmentally.

We report an efficient Ullmann C–C coupling reaction of two molecules of iodobenzene with excellent yields, using potassium carbonate as base and Pd(0)-RGO as catalyst. No reaction was observed in absence of catalyst. In the preliminary studies, when the coupling reaction was performed in presence of graphene oxide (GO) for 5 h at 80 °C, reaction gave 4% yield. Results with reduced graphene oxide (RGO) and different wt% of Pd(0) modified RGO as catalysts, under similar conditions are summarized in Table 1. Due to the less number of functional group, the RGO gave 11% yields, but the 5-Pd(0)-RGO catalyst, showed excellent yield (97%). In the coupling reaction, the aryl radicals get trapped by the oxygen containing functional group of GO materials compared to RGO materials. So, the catalytic activity of GO is less compared to RGO materials. Using 7-Pd(0)-RGO catalyst, 1% higher activity relative to 5-Pd(0)-RGO catalyst was observed. Based on the cost effective, we choose only 5-Pd(0)-RGO catalyst for optimization of the reaction.

We investigated efficiency of C–C coupling reactions using different halo benzenes (ArX) with 5-Pd(0)-RGO catalyst (Table 2). An observation the results show that iodobenzene gave best yield (97%) compared with the chloro- and bromo benzenes. The yield of the reaction product depended upon the C–X, bond energy. The C–I bond easily breakdowns facilitating higher yield of the C–C product, than with the other halides, based on bond energies, C–I < C–Br < C–Cl.

Solvent plays a vital role in improving the catalytic activity. The effect on different solvents on the reaction yield was investigated (Table 3). While, the polar solvents THF and DMF gave excellent yields, nonpolar solvents like toluene gave lower yields. With water solvent, the yield was nearly same as with polar solvents. Therefore, water the inexpensive green solvent, was chosen as medium for the study.

The reaction mechanism of Ullmann C–C coupling reaction over 5-Pd(0)-RGO catalyst is represented in Scheme 1. In the first step followed by oxidative addition, the aryl halide reacts with Pd(0) species on catalyst surface to form a (Ar–Pd(II)–I) complex as a reactive intermediate. Then, the (I–Pd(II)–Ar) complex reacts with another aryl halide molecule to produce a Ar–Pd(II)–Ar and

Table 1 Catalytic activity of catalyst toward C–C reaction^a

Entry	Catalyst	Yield (%)
1	Without catalyst	—
2	GO	4
3	RGO	11
4	5-Pd(0)-RGO	97
5	7-Pd(0)-RGO	98

^a Reaction conditions: time, 5 h; temperature, 80 °C; catalyst, 0.03 g; solvent (DD water), 10 ml. Reactants: aryl halides (4.5 mmol); HCOONa (1.10 g); KOH (1.40 g).

Table 2 Effect of different substrates on C–C coupling reaction^a over 5-Pd(0)-RGO catalyst

Entry	Aryl halide	Time (h)	Temp (°C)	Yield (%)
1	C ₆ H ₅ I	5	80	97
2	C ₆ H ₅ Cl	5	80	79
3	C ₆ H ₅ Br	5	80	88

^a Reaction conditions: time, 5 h; temperature, 80 °C; catalyst 0.03 g; solvent (DD water), 10 ml. Reactants: different aryl halides (4.5 mmol); HCOONa (1.10 g); KOH (1.40 g).

Table 3 Effect of different solvents towards C–C coupling reaction^a by 5-Pd(0)-RGO catalyst

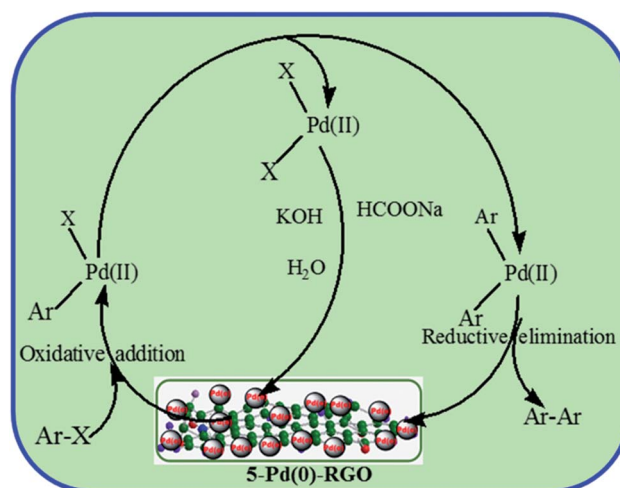
Entry	Solvent	Time (h)	Temp (°C)	Yield (%)
1	Toluene	5	80	84
2	Water	5	80	97
3	DMF	5	80	98
4	THF	5	80	96

^a Reaction conditions: time, 5 h; temperature, 80 °C; catalyst, 0.03 g; solvent, 10 ml. Reactants: aryl halides (4.5 mmol); HCOONa (1.10 g); KOH (1.40 g).

I–Pd(II)–I complex. In the intermediate state, dihydrogen was generated by sodium formate and water in presence of Pd(0). Dihydrogen can reduce I–Pd(II)–I complex to Pd(0).³⁵ Further, the Ar–Pd(II)–Ar complex gives Ar–Ar product and Pd(II) to Pd(0) through reductive elimination process.

Fig. 5 illustrates the results of reusability test for Pd(0)-RGO heterogeneous catalyst. After completion of each reaction, the used catalyst was filtered, and washed several times in ethanol, and dried at 100 °C. There was no loss of catalytic activity and it is repeatedly used for four times. The catalytic activity reduced after fourth run, due to partial leaching the metal particles.

Using a simple procedure, material with Pd nanoparticles supported on reduced graphene was successfully prepared.



Scheme 1 Possible mechanism for Ullmann C–C coupling reaction by Pd(0)-RGO catalyst.



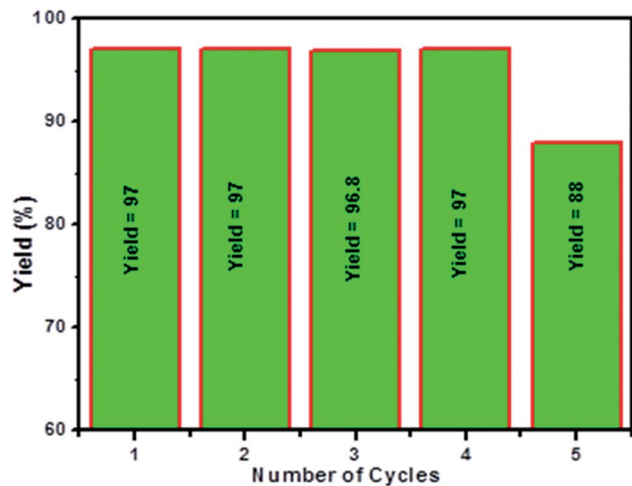


Fig. 5 Recycle experiments over Pd(0)-RGO catalyst.

Pd(0)-RGO proved to be effective, stable and recyclable material for Ullmann coupling reaction with excellent yields (79–97%) in water medium. The particle size of metal particles was confirmed by TEM analysis. XPS spectra validated the zero-valent state of Pd metal.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The authors acknowledge the support received from the School of Chemistry & Physics and College of Agriculture, Engineering & Science, University of KwaZulu-Natal, Durban, South Africa in the form of research facilities and financial support.

Notes and references

- 1 A. Balanta, C. Godard and C. Claver, *Chem. Soc. Rev.*, 2011, **40**, 4973.
- 2 A. Fihri, M. Bouhrara, B. Nekoueishahraki, J. M. Basset and V. Polshettiwar, *Chem. Soc. Rev.*, 2011, **40**, 5181.
- 3 M. Stratakis and H. Garcia, *Chem. Rev.*, 2012, **112**, 4469.
- 4 K. N. Sharma, H. Joshi, V. V. Singh, P. Singh and A. K. Singh, *Dalton Trans.*, 2013, **42**, 3908.
- 5 K. N. Sharma, H. Joshi, A. K. Sharma, O. Prakash and A. K. Singh, *Organometallics*, 2013, **32**, 2443.
- 6 S. W. Kim, M. Kim, W. Y. Lee and T. Hyeon, *J. Am. Chem. Soc.*, 2002, **124**, 7642.
- 7 L. Piccolo, A. Valcarcel, M. Bausach, C. Thomazeau, D. Uziob and G. Berhault, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5504.
- 8 J. Watt, S. Cheong, M. F. Toney, B. Ingham, J. Cookson, P. T. Bishop and R. D. Tilley, *ACS Nano*, 2010, **4**, 396.
- 9 A. K. Geim, *Science*, 2009, **324**, 1530.
- 10 D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228.
- 11 M. J. Allen, V. C. Tung and R. B. Kaner, *Chem. Rev.*, 2010, **110**, 132.
- 12 X. Huang, Z. Yin, S. Wu, X. Qi, Q. He, Q. Zhang, Q. Yan, F. Boey and H. Zhang, *Small*, 2011, **7**, 1876.
- 13 L. T. Qu, Y. Liu, J. B. Baek and L. Dai, *ACS Nano*, 2010, **4**, 1321.
- 14 D. Yu and L. Dai, *J. Phys. Chem. Lett.*, 2010, **1**, 467.
- 15 Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts and R. S. Ruoff, *Adv. Mater.*, 2010, **22**, 3906.
- 16 Z. Wei, H. Liu, Y. Chen, D. Guo, R. Pan and Y. Liu, *Chin. J. Chem. Eng.*, 2018, **26**, 2542–2548.
- 17 L. Pan, H. Zhao, W. Shen, X. Dong and J. Xu, *J. Mater. Chem. A*, 2013, **1**(24), 7159–7166.
- 18 G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth and R. Mülhaupt, *J. Am. Chem. Soc.*, 2009, **131**, 8262.
- 19 H. Wang and Y. Wan, *J. Mater. Sci.*, 2009, **44**, 6553.
- 20 B. Yuan, Y. Pan, Y. Li, B. Yin and H. Jiang, *Angew. Chem., Int. Ed.*, 2010, **49**, 4054.
- 21 L. Chen, Z. Gao and Y. weil, *Catal. Today*, 2015, **245**, 122.
- 22 B. Karimi and F. K. Esfahani, *Chem. Commun.*, 2011, **47**, 10452.
- 23 G. Bishwa Bidita Varadwaj, S. Rana and K. M. Parida, *J. Phys. Chem. C*, 2014, **118**, 1640.
- 24 G. Bishwa Bidita Varadwaj, O. A. Oyetade, S. Rana, B. S. Martincigh, S. B. Jonnalagadda and V. O. Nyamori, *ACS Appl. Mater. Interfaces*, 2017, **9**, 17290.
- 25 Y. J. Li, W. Gao, L. J. Ci, C. M. Wang and P. M. Ajayan, *Carbon*, 2010, **48**, 1124–1126.
- 26 H. K. Jeong, Y. P. Lee, R. J. W. E. Lahaye, M. H. Park, K. H. An, I. J. Kim, C.-W. Yang, C. Y. Park, R. S. Ruoff and Y. H. Lee, *J. Am. Chem. Soc.*, 2008, **130**, 1362.
- 27 R. N. Singh and R. Awasthi, *Catal. Sci. Technol.*, 2011, **1**, 778.
- 28 S. Rana, S. Maddila, K. Yalagala and S. B. Jonnalagadda, *Appl. Catal., A*, 2015, **505**, 539.
- 29 S. Rana and S. B. Jonnalagadda, *Catal. Commun.*, 2017, **92**, 31.
- 30 J. A. Corral, M. I. López, D. Esquivel, M. Mora, S. Jiménez-Sanchidrián and F. J. Romero-Salguero, *Materials*, 2013, **6**, 1554.
- 31 S. Kotha, K. Lahiri and D. Kashinath, *Tetrahedron*, 2002, **58**, 9633.
- 32 H. Li, W. Chai, F. Zhang and J. Chen, *Green Chem.*, 2007, **9**, 1223.
- 33 Y. Wan, H. Wang, Q. Zhao, M. Klingstedt, O. Terasaki and D. Zhao, *J. Am. Chem. Soc.*, 2009, **131**, 4541.
- 34 T. M. Gadda, Y. Kawanishi and A. Miyazawa, *Synth. Commun.*, 2012, **42**, 1259.
- 35 S. Mukhopadhyay, G. Rothenberg, D. Gitis, H. Wiener and Y. Sasson, *J. Chem. Soc., Perkin Trans. 2*, 1999, **2**, 2481.

