

Bibliography

I.A.5. References

- (1) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666-669.
- (2) C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First and W. A. de Heer, *Science*, 2006, **312**, 1191-1196.
- (3) C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam and A. Govindaraj, *Angew. Chem. Int. Ed.*, 2009, **48**, 7752-7777.
- (4) K. P. Loh, Q. L. Bao, P. K. Ang and J. X. Yang, *J. Mater. Chem.*, 2010, **20**, 2277-2289.
- (5) V. Georgakilas, J. N. Tiwari, K. C. Kemp, J. A. Perman, A. B. Bourlinos, K. S. Kim and R. Zboril, *Chem. Rev.*, 2016, **116**, 5464-5519.
- (6) V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril and K. S. Kim, *Chem. Rev.*, 2012, **112**, 6156-6214.
- (7) M. Inagaki and F. Kang, *J. Mater. Chem. A.*, 2014, **2**, 13193-13206.
- (8) L. Zhang, J. Liang, Y. Huang, Y. Ma, Y. Wang and Y. Chen, *Carbon*, 2009, **47**, 3365-3368.
- (9) A. Vul and A. T. Dideikin, *Front. Phys.*, 2018, **6**, 1-24.
- (10) O. Mohammadi, M. Golestanzadeh and M. Abdouss, *New J. Chem.*, 2017, **41**, 11471-11497.
- (11) J. H. Bitter, *J. Mater. Chem.*, 2010, **20**, 7312-7321.
- (12) D. S. Su, J. Zhang, B. Frank, A. Thomas, X. C. Wang, J. Paraknowitsch and R. Schlogl, *ChemSusChem.*, 2010, **3**, 169-180.
- (13) B. Brodie, *Ann. Chim. Phys.*, 1855, **45**, 351-353.

- (14) D.Li and Kaner, R. B. *Science*, 2008, **320**, 1170-1171.
- (15) L. Staudenmaier, *Ber. Dtsch. Chem. Ges.*, 1898, **31**, 1481-1487.
- (16) D. C.Marcano, D. V.Kosynkin, J. M.Berlin, A.Sinitiskii, Z.Sun, A.Slesarev, L. B.Aleman, W.Luand J. M. Tour, *ACS Nano*, 2010, **8**, 4806-4814.
- (17) A. M.Dimiev, L. B.Aleman and J. M. Tour, *ACS Nano*, 2013, **7**, 576-588.
- (18) C. Su and K. P.Loh, *Acc. Chem. Res.*, 2013, **46**, 2275-2285.
- (19) S.Rana and S. B.Jonnalagadda, *Catal. Commun.*, 2017, **92**, 31-34.
- (20) H. Yang, C. Shan, F. Li, D. Han, Q. Zhang and L. Niu, *Chem. Commun.*, 2009, **26**, 3880–3882.
- (21) W. Lee, J.U. Lee, B.M. Jung, B. J-Hyung, J.W. Yi, S.B. Lee and B.S.Kim, *Carbon*, 2013, **65**, 296–304.
- (22) E. Bekyarova, M.E. Itkis, P. Ramesh, C. Berger, M. Sprinkle, W.A. De Heer and R.C. Haddon, *J. Am. Chem. Soc.*, 2009, **131**, 1336-1337.
- (23) A.C. Obreja, D. Cristea, R. Gavrilă, V. Schiopu, A. Dinescu, M. Danila and F. Comanescu, *Science*, 2013, **276**, 458– 467.
- (24) S. Rani, M. Kumar, R. Kumar, D. Kumar, S. Sharma and G. Singh, *Mater. Res. Bull.*, 2014, **60**, 143-149.
- (25) A. Gholampour, M. V. Kiamahalleh, D. N. H. Tran, T. Ozbakkaloglu, and D. Losic, *ACS Appl. Mater. Interfaces.*, 2017, **9**, **49**, 43275–43286.
- (26) R. Kumar, M. Kumar, A. Kumar, R. Singh, R. Kashyap, S. Rani and D. Kumar, *Mater Today: Proc.*, 2019, **18**, 1556-1561.
- (27) H. Tondro, H. Zilouei, K. Zargoosh and M. Bazarganipour, *Bioresour. Technol.*, 2020, **306**, 123124-123159.
- (28) V.Polshettiwar., R. Luque., A.Fihri., H.Zhu., M.Bouhrara and J.-M. Basset, *Chem. Rev.*, 2011, **111**, 3036-3075.

-
- (29) D. R.Dreyer, H. P. Jia and C. W. Bielawski, *Angew. Chem. Int. Ed.*, 2010, **49**, 6813-6816.
- (30) D. R.Dreyer, H. P.Jia, A. D.Todd, G.Jeng and Bielawski, C. W. *Org. Biomol. Chem.*, 2011, **9**, 7292-7295.
- (31) H.Huang, J.Huang, Y. M.Liu, H. Y.He, Y. Cao and K. N. Fan, *Green Chem.*, 2012, **14**, 930-934.
- (32) Y. Gao, P.Tang, H.Zhou, W.Zhang, H.Yang, N.Yan, G. Hu, D.Mei, J. Wang and D. Ma, *Angew. Chem. Int. Ed.*, 2016, **55**, 3124-3128.
- (33) K. B.Dhopte, R. S.Zambare, A. V.Patwardhan and P. R. Nemade, *RSC Adv.*, 2016, **6**, 8164-8172.
- (34) S. Bhattacharya, P.Ghosh and B. Basu, *Tetrahedron Lett.*, 2018, **59**, 899-903.
- (35) V. D. Ebajo Jr., C. R. L.Santos, G. V.Alea, Y. A.Lin and C.-H. Chen, *Sci Rep.*, 2019, **9**, 15579-15590.
- (36) M. Karthik and P. Suresh, *ACS Sustainable Chem. Eng.*, 2019, **7**, 9028-9034.
- (37) H.Wu, C.Qiu, Z.Zhang, B.Zhang, S.Zhang, Y.Xua, H.Zhou, C.Sua and K. P. Loh, *Adv. Synth. Catal.*, 2020, **362**, 789-794.
- (38) F.Hu, M.Patel, F.Luo, C.Flach, R. Mendelsohn, E.Garfunkel, H. He and M. Szostak, *J. Am. Chem. Soc.*, 2015, **137**, 14473-14480.
- (39) H. Yang, X.Cui, X.Dai, Y.Deng and F. Shi, *Nat. Commun.*, 2015, **6**, 6478-6487.
- (40) G. A. B.Gon alves, S. M. G. Pires, M. M. Q.Simoes, M. G. P. M. S.Neves and P. A. A. P. Marques, *Chem Commun.*, 2014, **50**, 7673-7676.
- (41) T. A. J. Siddiqui, B. G.Ghule, S.Shaikh, P. V. Shinde, K. C. Gunturu, P. K.Zubaidha, J. M. Yun, C. O'Dwyer, R. S.Mane, K. H.Kim, *RSC Adv.*, 2018, **8**, 17373-17379.

- (42) G.Lv,H. Wang,Y.Yang,T.Deng,C.Chen,Y.Zhu and X. Hou,*ACS Catal.*, 2015, **5**, 5636-5646.
- (43) C.Su, R.Tandiana, J.Balapanuru, W. Tang, K.Pareek, C. T.Nai, T.Hayashi and Loh, K. P. *J. Am. Chem. Soc.*,2015, **137**, 685-690.
- (44) B.Majumdar, D.Sarma, T.Bhattacharya and T. K. Sarmsa, *ACS Sustainable Chem. Eng.*, 2017, **5**, 9286-9294.
- (45) S. Bhattacharya, P. Ghosh and B. Basu, *Tetrahedron Lett.*, 2017, **58**, 926-931.
- (46) P. Choudhury and B. Basu, *J. Flow Chem.*, 2020, **10**, 389-396.
- (47) M.Atarod, M.Nasrollahzadeh and S.M. Sajadi, *J. Colloid Interface Sci.*,2016,**465**, 249-258.
- (48) S.Naghdi, K. Y. Rhee and Jaleh, B. *Appl. Surf. Sci.*, 2016,**364**, 686-693.
- (49) S. Lowa and Y.-S. Shon, *Adv Nano Res.*, 2018, **6**, 357–375.
- (50) D. R.Dreyer,S. Park,C. W.Bielawski and R. S. Ruoff,*Chem. Soc. Rev.*, 2010, **39**, 228-240.
- (51) M. N. Groves, C. Malardier-Jugroot and M. Jugroot,*J. Phys. Chem. C.*, 2012, **116**, 10548-10556.
- (52) D.Astruc, F. Lu and J. R. Aranzaes, *Angew. Chem. Int. Ed.*,2005, **44**, 7852-7872.
- (53) V.K.Gupta, A.Mittal, D.Jhare and J. Mittal, *RSC Adv.*, 2012,**2**, 8381-8389.
- (54) R.Saravanan, E.Thirumal, V.K.Gupta, V. Narayanan and A. Stephen, *J. Mol. Liq.*, 2013,**177**, 394-401.
- (55) R.Saravanan, V.K.Gupta, E. Mosquera and F. Gracia, *J. Mol. Liq.*, 2014, **198**, 409-412.

- (56) R.Saravanan, S.Joicy, V.K.Gupta, V. Narayanan and A. Stephen, *Mater. Sci. Eng. CMater. Biol. Appl.*, 2013,**33**, 4725-4731.
- (57) R.Saravanan, S.Karthikeyan, V.K.Gupta, G.Sekaran, V. Narayanan and A. Stephen, *Mater. Sci. Eng. CMater. Biol. Appl.*, 2013,**33**, 91-98.
- (58) R.Saravanan,V.K.Gupta, V. Narayanan and A. Stephen, *J. Taiwan Inst. Chem. Eng.* 2014,**45**, 1910-1917.
- (59) T. A. Saleh and V.K. Gupta, *J. Colloid Interface Sci.*, 2011,**362**, 337-344.
- (60) T. A. Saleh and V.K. Gupta, *J. Colloid Interface Sci.*,2012,**371**, 101-106.
- (61) R.Saravanan, V.K.Gupta, V. Narayanan and A. Stephen, *J. Mol. Liq.*, 2013,**181**, 133-141.
- (62) R.Saravanan, M. M. Khan, F.Gracia, J.Qin, V.K. Gupta and S. Arumainathan, *Sci. Rep.*, 2016,**6**, 31641-31652.
- (63) M. Pe´rez-Lorenzo, *J. Phys. Chem. Lett.*, 2012, **3**, 167-174.
- (64) P.Taladriz-Blanco, P. Herve´s and J. Pe´rez-Juste, *Top. Catal.*, 2013, **56**, 1154-1170.
- (65) Negishi, E.;deMeijere, A.; Handbook of Organopalladium Chemistry for Organic Synthesis, Wiley, **2003**.
- (66) N.Miyaura, K.Yamada, A. Suzuki, *Tetrahedron Lett.*, 1979, **20**, 3437-3440.
- (67) E.-I.Negishi and S.Baba, *J. Chem. Soc., Chem. Commun.*, 1976, 596b-597b.
- (68) D.Milstein andJ. K. Stille, *J. Am. Chem. Soc.*, 1978, **100**, 3636-3638.
- (69) T. R. Kelly, Q.Li and V. Bhushan, *Tetrahedron Lett.*, 1990, **31**, 161-164
- (70) K.Tamao, K.Sumitani and M. Kumada, *J. Am. Chem. Soc.*, 1972, **94**, 4374-4376.
- (71) T. Hiyama, *J. Organomet. Chem.*, 2002, **653**, 58-61.

- (72) K.Sonogashira, Y.Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, **16**, 4467-4470.
- (73) R.Martin and S.L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1461-1473.
- (74) G.M.Scheuermann, L.Rumi, P.Steurer, W.Bannwarth and R. Mülhaupt, *J. Am. Chem. Soc.*, 2009, **131**, 8262-8270.
- (75) L.Rumi, G.M.Scheuermann, R.Mülhaupt and W. Bannwarth, *Helv. Chim. Acta.*, 2011, **94**, 966-976.
- (76) A. R.Siamaki, A-El-R. S.Khder, V. Abdelsayed, M. S. El-Shall and B. F.Gupton, *J. Catal.*, 2011, **279**, 1-11.
- (77) A. Khannanov, I. Il'yasov, A. Kiiamov, I. Vakhitov, A. Kirgizov, A. Lamberovb, A. M.Dimiev, *New J. Chem.*, 2019, **43**, 19035-19043.
- (78) M. Gómez-Martínez, E. Buxaderas, I. M. Pastor and D. A. Alonso, *J. Mol. Catal. A Chem.*, 2015, **1**, 404-405.
- (79) N. Shang, C. Feng, H. Zhang, S. Gao, R. Tang, C. Wang and Z.Wang, *Catal. Commun.*, 2013, **40**, 111-115.
- (80) A. H.Al-Marri, M. Khan, M. R. Shaik, N. Mohri, S. F. Adil, M. Kuniyil, H. Z.Alkathlan, A. Al-Warthan, W. Tremel, M. N. Tahir, M. Khan, M. R. H. Siddiqui, *Arab. J. Chem.*, 2016, **9**, 835-845.
- (81) K. S.Gayen, T. Sengupta, Y.Saima, A. Das, D. K.Maiti and A. Mitra, *Green Chem.*, 2012, **14**, 1589-1592.
- (82) M. Meldal and C. W.Tornøe, *Chem. Rev.*, 2008, **108**, 2952-3015.
- (83) K. Zhou, J. Zhang, G. Qiu and J.Wu, *Org. Lett.*, 2019, **21**, 275-278.
- (84) N. Ichiishi, A. J.Canty, B. F. Yates and M. S. Sanford, *Organometallics*, 2014, **33**, 5525-5534.
- (85) K. Zhang, J.M. Suh, T. H. Lee, C.J. Hwan, J. W. Choi, H. W. Jang and R. S.Varma, *Nano Converg.*, 2019, **6**, 1-7.

-
- (86) V. S.Sadu, H.-R.Bin, D.-M.Lee, K.-I. Lee,*Sci. Rep.*,2017,**7**, 242-252.
- (87) A.Mittal, S.; Kumari, Parmanand,D. Yadav and S. K.Sharma, *Appl. Organomet. Chem.*, 2020, **34**, 5362-5374.
- (88) M.Tobisu and N. Chatani,*Angew. Chem.*,2006, **118**, 1713-1715.
- (89) Yu. M.Shafran, V. A.Bakulev and V. S. Mokrushin,*Russ. Chem. Rev.*, 1989, **58**, 148-162.
- (90) E. J.Martinez, E. J.Corey,*Org. Lett.*, 1999, **1**, 75-78.
- (91) D. Verma, S. Verma, A. K.Sinha and S. L. Jain,*ChemPlusChem.*, 2013, **78**, 860-865.
- (92) X.Tian, F.Su and X. S. Zhao,*Green Chem.*, 2008, **10**, 951-956.
- (93) M.Kitano, K.Nakajima, J. N.Kondo, S.Hayashi and M. Hara,*J. Am. Chem. Soc.*, 2010, **132**, 6622-6623.
- (94) H. I.Ryoo, L. Y.Hong, S. H.Jung and D.-P. Kim,*J. Mater. Chem.*,2010, **20**, 6419-6421.
- (95) Y.Zhao, H.Wang, Y.Zhao and J. Shen,*Catal. Commun.*, 2010, **11**, 824-828.
- (96) H.Xiao, Y.Guo, X.Liang and C. Qi *J. Solid State Chem.*, 2010, **183**, 1721-1725.
- (97) H. T.Gomes, S. M.Miranda, M. J.Sampaio, A. M. T.Silva and J. L.Faria,*Catal. Today.*, 2010,**151**, 153-158.
- (98) R.Fareghi-Alamdari, M.Golestanzadeh, F.Agend and N. Zekri,*C. R. Chim.*, 2013, **16**, 878-887.
- (99) R.Fareghi-Alamdari, M.Golestanzadeh, F.Agend and N. Zekri,*Can. J. Chem.*, 2013, **91**, 982-991.
- (100) M.Toda, A.Takagaki, M.Okamura, J. N.Kondo, S.Hayashi, K.Domen and M. Hara,*Nature*, 2005, **438**, 178-178.

- (101) S.Suganuma, K.Nakajima, M.Kitano, D.Yamaguchi, H.Kato and S.Hayashi,*J. Am. Chem. Soc.*,2008, **130**, 12787-12793.
- (102) F.Liu, J. Sun, L.Zhu, X.Meng, C. Qi and F.-S. Xiao, *J. Mater. Chem.*,2012, **22**, 5495-5502.
- (103) P. P.Upare, J.-W.Yoon, M. Y.Kim, H.-Y.Kang, D. W.Hwang, Y. K. Hwang, H. H. Kung and J.-S. Chang, *Green Chem.*, 2013, **15**, 2935-2943.
- (104) P. Gao, D. D. Sun and W. J. Ng, *RSC Adv.*,2013, **3**, 15202-15210.
- (105) H. Naeimi and M. Golestanzadeh, *RSC Adv.*,2014, **4**, 56475-56488.
- (106) E. Vessally, A. Hassanpour, R. Hosseinzadeh-Khanmiri, M. Babazadeh and J.Abolhasani, *Monatsh. Chem.*, 2017, **148**, 321-326.
- (107) A. Sengupta, C. Su, C. Bao, C. T. Nai and K. P.Loh,*ChemCatChem.*,2014, **6**, 2507-2511.
- (108) E. Lam, J.H.Chong, E. Majid, Y. Liu, S. Hrapovic, A. C. W. Leung and J. H. T. Luong,*Carbon*, 2012, **50**, 1033-1043.
- (109) M.-S. Hosseini, M.Masteri-Farahani, *Tetrahedron*, 2021, **83**, 132083-132106.
- (110) M. Mirza-Aghayana,N.Ganjbakhsh,M. M.Tavanaa and R. Boukherroub, *Ultrason.Sonochem.*,2016,**29**, 371-379.
- (111) M. C. Nongbeab, T. Ekou, L. Ekou, K. B. Yao,E.L. Grogneca and F.-X. Felpin, *Renew. Energy.*, 2017,**106**, 135-140.
- (112) M-S.Hosseini, M. M.Farahani and S.ShahsavariFar, *J. Taiwan Inst. Chem. Eng.*, 2019, **102**, 34-40.
- (113) Q. Hou, W.Li, M.Ju, L.Liu, Y.Chen and Q. Yang, *RSC Adv.*,2016, **6**, 104016-104024.
- (114) X.Zhao, J. Wang, C.Chen, Y.Huang, A.Wang and T. Zhang, *Chem. Commun.*, 2014, **50**, 3439-3442.

- (115) E.Vessally, A.Hassanpour, R.Hosseinzadeh-Khanmiri, M.Babazadeh and Abolhasani, *J. Monatsh. Chem.*, 2017, **148**, 321-326.
- (116) M.Brahmayya, S. A.Dai and S.-Y. Sue, *Sci. Rep.*, 2017, **7**, 4675-4688.
- (117) M.Brahmayya, S.-Y. Suen and S. A. Dai, *J. Taiwan Inst. Chem. Eng.*, 2018, **83**, 174-183.
- (118) P.Basak, S.Dey and P. Ghosh, *ChemistrySelect*, 2020, **5**, 626-636.
- (119) M. M.Antunes, P. A.Russo, P. V.Wiper, J. M.Veiga, M. Pillinger, L. Mafra, D. V.Evtuguin, N. Pinna and A. A. Valente, *ChemSusChem*, 2014, **7**, 804-812.

I.B.6. References

- (1) M. Carbone, Y. Li, C.Irace, E.Mollo, F.Castelluccio, D. A. Pascale, G. Cimino, R. Santamaria, W. Y.Guo and M. Gavagnin, *Org. Lett.*, 2011, **13**, 2516-2519.
- (2) A. V.Gulevich, A. S. Dudnik, N.Chernyak, V. Gevorgyan, *Chem. Rev.*, 2013, **113**, 3084-3213.
- (3) R. J.Mathvink, A. M.Barritta, M. R.Candelore, M. A.Cascieri, L. Deng, L.Tota, C. D. Strader, M. J.Wyvrat, M. H. Fisher and A. E. Weber, *Bioorg. Med. Chem. Lett.*, 1999, **9**, 1869-1874.
- (4) G. D. Diana, D. L.Volkots, T. J. Nitz, T. R. Bailey, M. A. Long, N.Vescio, S. Aldous, D. C. Pevear and F. J. Dutko, *J. Med. Chem.*, 1994, **37**, 2421-2436.
- (5) H. Z. Zhang, S.Kasibhatla, J.Kuemmerle, W. Kemnitzer, K.OllisMason, L.Qiu, C.Crogan-Grundy, B. Tseng, J. Drewe and S. X. Cai, *J. Med. Chem.*, 2005, **48**, 5215-5223.
- (6) F. I. Carroll, J. L. Gray, P. Abrahm, M. A.Kuzemko, A. H. Lewin, J. W.Boja and M. J. Kuhar, *J. Med. Chem.*, 1993, **36**, 2886-2890.

- (7) L. J. Street, R. Baker, T. Book, A. J. Reeve, J. Saunders, T. Willson, R. S. Marwood, S. Patel and S. B. Freedman, *J. Med. Chem.*, 1992, **35**, 295–305.
- (8) J. W. Clitherow, P. Beswick, W. J. Irving, D. I. C. Scopes, J. C. Barnes, J. Clapham, J. D. Brown, D. J. Evans and A. G. Hayes, *Bioorg. Med. Chem. Lett.*, 1996, **6**, 833-838.
- (9) C. B. Vu, E. G. Corpuz, T. J. Merry, S. G. Bartlett, C. Pradeepan, R. S. Bohacek, M. C. Botfield, C. J. Eyermann, B. A. Lynch, I. A. MacNeil and M. K. Ram, *J. Med. Chem.*, 1999, **42**, 4088-4094.
- (10) J. Matsumoto, T. Takahashi, M. Agata, H. Toyofuku and N. Sasada, *Jpn. J. Pharmacol.*, 1994, **65**, 51-58.
- (11) B. L. Mylari, T. A. Beyer, P. J. Scott, C. E. Aldinger, M. F. Dee, T. W. Siegel and W. J. Zembrowski, *J. Med. Chem.*, 1992, **35**, 457-465.
- (12) B. S. Orlek, F. E. Blaney, F. Brown, M. S. G. Clark, M. S. Hadley, J. Hatcher, G. J. Riley, H. E. Rosenberg, H. J. Wadsworth and P. Wyman, *J. Med. Chem.*, 1991, **34**, 2726-2735.
- (13) T. Nakamura, M. Asano, Y. Sekiguchi, Y. Mizuno, K. Tamaki, F. Nara, Y. Kawase, Y. Yabe, D. Nakai, E. Kamiyama, Y. Urasaki-Kaneno, T. Shimozato, H. Doi-Komuro, T. Kagari, W. Tomisato, R. Inoue, M. Nagasaki, H. Yuita, K. Oguchi-Oshima, R. Kaneko and T. Nishi, *Eur. J. Med. Chem.*, 2012, **51**, 92-98.
- (14) A. Domling, *Chem. Rev.*, 2006, **106**, 17-89.
- (15) D. Tejedor and F. Garcia-Tellado, *Chem. Soc. Rev.*, 2007, **36**, 484-491.
- (16) B. Kaboudin and L. Malekzadeh, *Tetrahedron Lett.*, 2011, **52**, 6424-6426.
- (17) J. K. Augustine, V. Akabote, S. G. Hegde and P. Alagarsamy, *J. Org. Chem.*, 2009, **74**, 5640-5643.

- (18) Srivastava, R. M.; Freire, M. V. S.; Chaves, A. S. S. C.; Beltrao, T. M. J. *Heterocycl. Chem.*, **1987**, *24*, 101.
- (19) Adib, M.; Jahromi, A. H.; Tavoosi, N.; Mahdavi, M.; Bijanzadeh, H. R. *Tetrahedron Lett.*, **2006**, *47*, 2965.
- (20) S.Kandre, P. R. Bhagat, R. Sharma and A. Gupte, *Tetrahedron Lett.*, 2013, **54**, 3526-3529.
- (21) J. J. Lade, B. N. Patil, K. S. Vadagaonkar and A. C.Chaskar, *Tetrahedron Lett.*, 2017, **58**, 2103-2108.
- (22) Y. Wang, R. L. Miller, D. R. Sauer and S. Djuric, W. *Org. Lett.*, 2005, **7**, 925-928.
- (23) (a) R. F. P. Poulin, A. L.; Tartar and B. P. De'prez, *Tetrahedron Lett.*, 2001, **42**, 1495-1498.
(b) R.Milcent and G. Barbier, *J. Heterocycl. Chem.*, 1983, **20**, 77-80.
- (24) F.Eloy and R. Lenaers, *Chem. Rev.*, 1962, **62**, 155-183.
- (25) B.Kaboudin and F. Saadati, *Tetrahedron Lett.*, 2007, **48**, 2829-2832.
- (26) W. Wang, H. Xu, Y. Xu, T. Ding, W. Zhang, Y. Ren and H. Chang, *Org. Biomol. Chem.*, 2016, **14**, 9814-9822.
- (27) M. R.Kuram, W. G. Kim, K.Myung and S. Y. Hong, *Eur. J. Org. Chem.*, **2016**, 438-442.
- (28) K. B.Dhopte, R. S.Zambare, A. V. Patwardhan and P. R.Nemade, *RSC Adv.*, 2016, **6**, 8164-8172.
- (29) D. C.Marcano, D. V.Kosynkin, J. M. Berlin, A.Sinitskii, Z. Sun, A.Slesarev, L. B.Aleman, W.Luand J. M. Tour, *ACS Nano*, 2010, **8**, 4806-4814.
- (30) D. S.Bolotin, K. I.Kulish, N. A.Bokach, G. L.Starova, V. V.Gurzhiy and V. Y.Kukushkin, *Inorg. Chem.*, 2014, **53**, 10312-10324.

I.C.6. References

- (1) A. R. Katritzky, C. W. Rees and E. F. V. Scriven, *Comprehensive Heterocyclic Chemistry II*, Oxford, London, 1996.
- (2) B. Y. Kim, J. B. Ahn, H. W. Lee, S. K. Kang, J. H. Lee, J. S. Shin, S. K. Ahn, C. I. Hong and S. S. Yoon, *Eur. J. Med. Chem.*, 2004, **39**, 433-447.
- (3) I. J. Enyedy, S. Sakmuri, W. A. Zaman, K. M. Johnson and S. Wang, *Bioorg. Med. Chem. Lett.*, 2004, **13**, 513-517.
- (4) V. Klimesova', M. Svoboda, K. Waisser, M. Pour and J. Kaustova', *Framaco*, 1999, **54**, 666-672.
- (5) E. Figgemeier, E. C. Constable, C. E. Housecroft and Y. C. Zimmermann, *Langmuir*, 2004, **20**, 9242-9248.
- (6) E. C. Constable, C. E. Housecroft, M. Neuburger, D. Phillips, P. R. Raithby, E. Schofield, E. Sparr, D. A. Tocher, M. Zehnder, and Y. Zimmermann, *Dalton Trans.*, 2000, **13**, 2219-2228.
- (7) R. W. Armstrong, A. P. Combs, P. A. Tempest, S. D. Brown and T. A. Keating, *Acc. Chem. Res.*, 1996, **29**, 123-131.
- (8) F. Krohnke, *Angew. Chem. Int. Ed.*, 1963, **2**, 225-276.
- (9) N. Montazeri and S. Mahjoob, *Chin. Chem. Lett.*, 2012, **23**, 419-422.
- (10) M. M. Heravi, K. Bakhtiari, Z. Daroogheha and F. F. Bamoharram, *Catal. Commun.*, 2007, **8**, 1991-1994.
- (11) L. Nagarapu, A. R. Peddiraju and S. Apuri, *Catal. Commun.*, 2007, **8**, 1973-1976.
- (12) A. Davoodnia, M. Bakavoli, R. Moloudi, N. Tavakoli-Houseini and M. Khashi, *Monatsh Chem.*, 2010, **141**, 867-870.
- (13) A. Maleki and R. Firouzi-Haji, *Sci Rep.*, 2018, **8**, 17303-17311.

-
- (14) J. Safari, S. Gandomi-Ravandi and M. Borujeni, *Chem. Sci.*, 2013, 125, 1063-1070.
- (15) M. Adib, H. Tahermansouri, S. A. Koloogani, B. Mohammadia and H. R. Bijanzadeh, *Tetrahedron Lett.*, 2006, **47**, 5957–5960.
- (16) R. Nagase, J. Osada, H. Tamagaki and Y. Tanabe, *Adv. Synth. Catal.*, 2010, **352**, 1128-1134.
- (17) T. Funatomi, K. Wakasugi T. Misaki and Y. Tanabe, *Green Chem.*, 2006, 8, 1022-1027.
- (18) N. Montazeri, S. Khaksar, A. Nazari, S. S. Alavia, S. M. Vahdat and M. TajbakhshcJ, *Fluorine Chem.*, 2011, **132**, 450-452.
- (19) C. W. Fairhurst, *Adv. Dent. Res.*, 1992, **6**, 78-81.
- (20) L. Thomé, A. Gentils, J. Jagielski, F. Garrido and T. Thomé, *Vacuum*, 2007, **81**, 1264-1270.
- (21) L. Koroleva, *Glass. Ceram.*, 2004, **61**, 299-302.
- (22) A. E. Navaei, M. Rezaei, A. H. Navaei, H. Feyzallahzadeh and Z. F. Yan, *Chem. Eng. Commun.*, 2009, **196**, 1417-1424.
- (23) E. Tabrizian, A. Amoozadeh, S. Rahmani, E. Imanifar, S. Azhari and M. Malmir, *Chin. Chem. Lett.*, 2015, **26**, 1278-1282.
- (24) M. Ghaedi, S. Hajjatia, Z. Mahmudia, I. Tyagib, S. Agarwal, A. Maity and V. K. Gupta *Chem. Eng. J.*, 2015, **268**, 28-37.
- (25) A. Maleki and T. Kari, *Catal. Lett.*, 2018, **148**, 2929-2934.
- (26) A. Asfaram, M. Ghaedi, S. Agarwal, I. Tyagi and V. K. Gupta, *RSC Adv.*, 2015, **5**, 18438-18450.
- (27) V. K. Gupta, N. Atar, M. L. Yola, Z. Üstündağ and L. Uzun, *Water Res.*, 2014, **48**, 210-2017.
- (28) H. Wang, W. Zhao, J. Du, F. Wei, Q. Chen and X. Wang, *RSC Adv.*, 2019, **9**, 5158-5163.

II.A.5. References

- (1) H.Kolbe,*Ann. Chem. Pharm.*, 1849, **69**, 257-294.
- (2) R.Breslow,*Acc. Chem. Res.*, 1991, **24**, 159-164.
- (3) C. J. Li, T. H.Chan, New York, John Wiley & Sons, 1997.
- (4) M. Siskin,A. R.Katritzky,*Science*, 1991, **254**, 231-237.
- (5) A.Wurtz,*Justus Liebigs Ann. Chem.*, 1855, **96**, 364-375.
- (6) R.Fittig,*Justus Liebigs Ann. Chem.*, 1859, **110**, 23-45.
- (7) C.Glaser,*Justus Liebigs Ann. Chem.*, 1870, **154**, 137-171.
- (8) F.Ullmann, J. Bielecki,*Chemische Berichte*, 1901, **34**, 2174-2185.
- (9) Cadot P, Chodkiewicz W. In chemistry of acetylenes. Viehe HG, Dekker M. ed. New York, 1969, 597-647.
- (10) R. D.Stephens, C. E.Castro,*J. Org. Chem.* 1963, **28**, 3313-3315.
- (11) E. J.Corey, G. H.Posner,*J. Am. Chem. Soc.*, 1967, **89**, 3911-3912.
- (12) K.Tamao,K. Sumitani,M.Kumada,*J. Am. Chem. Soc.*, 1972, **94**, 4374-4376.
- (13) R. F.Heck, *Org. React.*, 1982, **27**, 345-390.
- (14) K.Sonogashira,*J.Organomet. Chem.*, 2002, **653**, 46-49.
- (15) A. O.King, N. Okukado, E. Negishi,*J. C. S. Chem. Comm.*, 1977, **19**, 683-684.
- (16) J. K.Stille,*Angew. Chem. Int. Ed.*, 1986, **25**, 508-524.
- (17) N.Miyaura, K.Yamada, A.Suzuki,*Tetrahedron Lett.*, 1979, **20**, 3437-3440.
- (18) S. Murahashi, M.Yamamura, K.Yanagisawa,N.Mita, K.Kondo, *J. Org. Chem.* 1979, **44**, 2408-2417.
- (19) Y.Hatanaka,T.Hiyama,*J. Org. Chem.*, 1988, **53**, 918-920.

-
- (20) H.Tokuyama, S.Yokoshima, T.Yamashita, T.Fukuyama, *Tetrahedron Lett.*, 1998, **39**, 3189-3192.
- (21) L. Liebeskind, J.Srogl, *J. Am. Chem. Soc.*, 2000, **122**, 11260-11261.
- (22) D.Astruc, F.Lu, J. R.Aranzaes, *Angew. Chem. Int. Ed.*, 2005, **44**, 7852-7872.
- (23) R.Saravanan, E.Thirumal, V. K.Gupta, V.Narayanan, A.Stephen, *J. Mol. Liq.*, 2013, **177**, 394-401.
- (24) R.Saravanan, V. K.Gupta, E.Mosquera, F.Gracia, *J. Mol. Liq.*, 2014, **198**, 409-412.
- (25) T. A.Saleh, V. K. Gupta, *J. Colloid. Interface. Sci.*, 2011, **362**, 337-344.
- (26) T. A.Saleh, V. K.Gupta, *J. Colloid. Interface. Sci.*, 2012, **371**, 101-106.
- (27) D.Astruc, *Inorg. Chem.*, 2007, **46**, 1884-1894.
- (28) J. Liu, *Acs Catal.*, 2017, **7**, 34-59.
- (29) D.Wang, D.Astruc, *Chem. Soc. Rev.*, 2017, **46**, 816-854.
- (30) N. B.Singh, S. Agarwal, *Emerg. Mater. Res.*, 2016, **5**, 5-43.
- (31) N.Miyaura, A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457-2483.
- (32) S.Budagumpi, R. A.Haque, A. W.Salman, *Coord. Chem. Rev.*, 2012, **256**, 1787-1830.
- (33) E. A. B.Kantchev, C. J.O'Brien, M. G.Organ, *Angew. Chem. Int. Ed.*, 2007, **46**, 2768-2813.
- (34) A.de Meijere, F. E.Meyer, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 2379-2411.
- (35) A. O.King, N. Yasuda, *Org. Process. Res. Dev.*, 2005, **9**, 646-650.
- (36) A. O.King, N.Yasuda, *Top Organomet. Chem.*, 2004, **6**, 205-245.
- (37) P.Veerakumar, P.Thanasekaran, K. L.Lu, K. C.Lin, S. Rajagopal, *ACS Sustain. Chem. Eng.*, 2017, **5**, 8475-8490.

- (38) N. T. S.Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* 2006, **348**, 609-679.
- (39) V. P. Ananikov, I. P. Beletskaya, *Organometallics*, 2012, **31**, 1595-1604.
- (40) F. Amoroso, S. Colussi, *Catal. Lett.* 2013, **143**, 547-554.
- (41) S. R. Sanjaykumar, B. D. Mukri, S. Patil, G. Madras, M. S. Hegde., *J. Chem. Sci.* 2011, **123**, 47-54.
- (42) D. Khalili, A. R. Banazadeh, E. Etemadi-Davan, *Catal. Lett.*, 2017, **147**, 2674-2687.
- (43) I. B. Chorkendorff, J. W. Niemantsverdriet, WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2003, 1-22.
- (44) A. V. Astakhov, O. V. Khazipov, A. Y. Chernenko, D. V. Pasyukov, A. S. Kashin, E. G. Gordeev, V. N. Khrustalev, V. M. Chernyshev, V. P. Ananikov, *Organometallics*, 2017, **36**, 1981-1992.
- (45) F. X. Felpin, T. Ayad, S. Mitra, *Eur. J. Org. Chem.* 2006, **2006**, 2679-2690.
- (46) F. X. Felpin, *Synlett.*, 2014, **25**, 1055-1067.
- (47) E. Cini, E. Petricci, M. Taddei, *Catalysts*, 2017, **7**, 89.
- (48) Z. Wu, Y. Wang, L. Sun, Y. Mao, M. Wang and C. Lin, *J. Mater. Chem. A*, 2014, **2**, 8223-8229.
- (49) G. Lu, R. Franzen, Q. Zhang, Y. Xu, *Tetrahedron Lett.*, 2005, **46**, 4255-4259.
- (50) M. Lysen and K. Kohler, *Synthesis*, 2006, **17**, 692-698.
- (51) K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature*, 2012, **490**, 192-200.
- (52) (a) G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, *J. Am. Chem. Soc.*, 2009, **131**, 8262-8270; (b) L. Rumi, G.

- M.Scheuermann, R. Mülhaupt, W. Bannwarth, *Helv. Chim. Acta.*, 2011, **94**, 966-976.
- (53) (a) G.Xiang, J.He, T.Li, J.Zhuang, X. Wang, *Nanoscale*, 2011, **3**, 3737-3742; (b) S. J. Hoseini, M. Dehghani, H.Nasrabadi, *Catal. Sci. Technol.*, 2014, **4**, 1078-1083.
- (54) S.Moussa, A. R.Siamaki, B. F.Gupton, M. S.El-Shall, *ACS Catal.*, 2012, **2**, 145-154.
- (55) J.Hu, Y.Wang, M.Han, Y.Zhou, X.Jiang, P.Sun, *Catal. Sci. Technol.* 2012, **2**, 2332-2340.
- (56) N.Shang, S.Gao, C.Feng, H.Zhang, C.Wang, Z.Wang, *RSC Adv.*, 2013, **3**, 21863-21868.
- (57) N.Shang, C.Feng, H.Zhang, S.Gao, R.Tang, C.Wang, Z.Wang, *Catal. Commun.*, 2013, **40**, 111-115.
- (58) Y.Li, X.Fan, J.Qi, J.Ji, S.Wang, G.Zhang, F.Zhang, *Nano Res.*, 2010, **3**, 429-437.
- (59) S. S. Shendage, U. B.Patil, J. M.Nagarkar, *Tetrahedron Lett.*, 2013, **54**, 3457-3461.
- (60) J.Li, A.Corma, J.Yu, *Chem. Soc. Rev.*, 2015, **44**, 7112-7127.
- (61) S.Bhattacharyya, D.Samanta, S.Roy, V. P.Haveri Radhakantha, T. K.Maji, *ACS Appl. Mater. Interfaces.*, 2019, **11**, 5455-5461.
- (62) A. Kumbhar, *Top Curr. Chem.*, 2017, **375**, No. 2.
- (63) Y.Wang, J.Liao, Z. Xie, K.Zhang, Y.Wu, P. Zuo, W.Zhang, J.Li, *ACS Appl. Mater. Interfaces.*, 2020, **12**, 11419-11427.
- (64) M.Shamzhy, M.Opanasenko, P.Concepcion, A. Martínez, *Chem. Soc. Rev.*, 2019, **48**, 1095-1149.
- (65) N.Wang, Q.Sun, R.Bai, X.Li, G.Guo, J.Yu, *J. Am. Chem. Soc.*, 2016, **138**, 7484-7487.

- (66) C. Baleizao, A. Corma, H. Garcia, A. Leyva, *Chem. Commun.*, 2003, **85**, 606-607; (b) C. Baleizao, A. Corma, H. Garcia, A. Leyva, *J. Org. Chem.*, 2004, **69**, 439-446.
- (67) V. H. Pham, T. T. Dang, S. H. Hur, E. J. Kim, J. S. Chung, *ACS Appl. Mater. Interfaces.*, 2012, **4**, 2630-2636.
- (68) P. Cotugno, M. Casiello, A. Nacci, P. Mastrorilli, M. M. Dell'Anna, A. Monopoli, *J. Organomet. Chem.*, 2014, **752**, 1-5.
- (69) J. Mondal, A. Modak, A. Bhaumik, *J. Mol. Catal. A Chem.*, 2011, **350**, 40-48.
- (70) Y. L. Zhang, S. Wei, F. J. Liu, Y. C. Du, S. Liu, Y. Y. Ji, T. Yokoi, T. Tatsumi, F. S. Xiao, *Nano Today*, 2009, **4**, 135-142.
- (71) J. K. Cho, R. Najman, T. W. Dean, O. Ichihara, C. Muller, M. Bradley, *J. Am. Chem. Soc.*, 2006, **128**, 6276-6277.
- (72) Y. Lee, M. C. Hong, H. Ahn, J. Yu, H. Rhee, *J. Organomet. Chem.*, 2014, **769**, 80-93.
- (73) (a) Y. Hirokawa, T. Tanaka, E. S. Matsuo, *J. Chem. Phys.*, 1984, **81**, 6379-6380; (b) K. Kubota, S. Fujishige, I. Ando, *J. Phys. Chem.* 1990, **94**, 5154-5158.
- (74) M. Shibayama, Y. Suetoh, S. Nomura, *Macromolecules*, 1996, **29**, 6966-6968.
- (75) D. E. Bergbreiter, B. L. Case, Y. S. Liu, J. W. Caraway, *Macromolecules*, 1998, **31**, 6053-6062.
- (76) (a) Y. Mei, Y. Lu, F. Polzer, M. Ballauff, M. Drechsler, *Chem. Mater.*, 2007, **19**, 1062-1069; (b) D. E. Bergbreiter, P. L. Osburn, A. Wilson, E. M. Sink, *J. Am. Chem. Soc.* 2000, **122**, 9058-9064.

- (77) (a) H. I. Melendez-Ortiz, E. Bucio, G. Burillo, *Radiat. Phys. Chem.* 2009, **78**, 1-7; (b) H. Nur, V. T. Pinkrah, J. C. Mitchell, L. S. Bence, M. J. Snowden, *Adv. Colloid. Interface. Sci.*, 2010, **158**, 15-20.

II.B.6. References

- (1) (a) A. Suzuki, *In Modern Arene Chemistry*, ed. D. Astruc, Wiley-VCH, Weinheim, 1st edn, 2004, vol. 80, ch. 3, pp 53-106; (b) R. F. Heck, *Acc. Chem. Res.*, 1979, **12**, 146-151.
- (2) A. Fihri, M. Bouhrara, B. Nekoueishahraki, J. M. Basset and V. Polshettiwar, *Chem. Soc. Rev.*, 2011, **40**, 5181-5203.
- (3) Z. Z. F. S. Zhou, D. S. Liu, Ch. Shen and L. Y. Tan, Luo, *Inorg. Chem. Commun.*, 2011, **14**, 659-664.
- (4) P. J. M. Hajduk, J. Bures, Prastgaard and S. W. Fesik, *J. Med. Chem.*, 2000, **43**, 3443-3447.
- (5) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem Rev.*, 2002, **102**, 1359-1470.
- (6) A. Fihri, M. Bouhrara, B. Nekoueishahraki, J. M. Basset and V. Polshettiwar, *Chem. Soc. Rev.*, 2011, **40**, 5181-5203.
- (7) V. P. W. Böhm and W. A. Herrmann, *Chem. Eur. J.*, 2000, **6**, 3679-3681.
- (8) J. H. Park, F. Raza, S. J. Jeon, H. I. Kim, T. W. Kang, D. Yim and J. H. Kim, *Tetrahedron Lett.*, 2014, **55**, 3426-3430.
- (9) S. Paul, Md. M. Islam and Sk. M. Islam, *RSC Adv.*, 2015, **5**, 42193-42221.
- (10) L. Yin and J. Liebscher, *Chem. Rev.* 2007, **107**, 133-173.
- (11) Q. Sun, L. F. Zhu, Z. H. Sun, X. Ju. Meng and F. S. Xiao, *Sci. China Chem.*, 2012, **55**, 2095-2103.

- (12) C. Pan, M. Liu, L. Zhao, H. Wu, J. Ding and J. Cheng, *Catcom.*, 2008, **9**, 1685-1687.
- (13) R. B. Bedford, U. G. Singh, R. I. Walton, R. T. Williams and S. A. Davis, *Chem. Mater.*, 2005, **17**, 701-707.
- (14) M. J. Jin, A. Taher, H. J. Kang, M. Choi and R. Ryoo, *Green Chem.*, 2009, **11**, 309-313.
- (15) X. Jin, J. Li and H. Li, *J. Exp. Nanosci.*, 2018, **13**, 95-106.
- (16) R. K. Ramchandani, B. S. Uphade, M. P. Vinod, R. D. Wakharkar, V. R. Choudhary and A. Sudalai, *Chem. Commun.*, 1997, 2071-2072.
- (17) Y. Wan, H. Wang, Q. Zhao, M. Klingstedt, O. Terasaki and D. Zhao, *J. Am. Chem. Soc.*, 2009, **131**, 4541-4550.
- (18) Y. L. Nong, N. Qiao, T.H. Deng, Z. Pan and Y. Liang, *Catal. Commun.*, 2017, **100**, 139-143.
- (19) A. Wali, S. M.; Pillai, V. K. Kaushik and S. Satish, *Appl. Catal. A.*, 1996, **135**, 83-93.
- (20) W. K. Kundhikanjana, J. Lai, H. L. Wang, H. J. Dai, M. A. Kelly and Z. X. Shen, *Nano Lett.*, 2009, **9**, 3762-3765.
- (21) J. Wang, H. Hu, X. Wang, C. Xu, M. Zhang and X. Shang, *J. Appl Polm Sci.*, 2011, **122**, 1866-1871.
- (22) T. Kuila, S. Bose, P. Khanra, N. H. Kim and J. H. Lee, *Compos.-A:Appl.Sci. Manuf.*, 2011, **42**, 1856-1861.
- (23) J. Yang, X. Yan, M. Wu, F. Chen, Z. Fei and M. Zhong, *J Nanopart Res.*, 2012, **14**, 717-726.
- (24) J. Hass, W. A. Heer and E. H. Conrad, *J. Phys. Condens. Matter.*, 2008, **20**, 1-27.
- (25) S. S. Shendage, A. S. Singh and J. M. Nagarkar, *Tetrahedron Lett.*, 2014, **55**, 857-860.

-
- (26) M. G'omez-Mart'inez, E. Buxaderas, M. I. Pastor and D. A. Alonso, *J. Mol. Catal. A. Chem.*, 2015, **404**, 1-7.
- (27) G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth and R. Mu'llhaupt, *J. Am. Chem. Soc.*, 2009, **131**, 8262-8270.
- (28) S.-H. Kim, G. H. Jeong, D. Choi, S. Yoon, H. B. Jeon, S.-M. Lee and S.-W. Kim, *J. Colloid Interface Sci.*, 2013, **389**,85-90.
- (29) S. S. Shendage, U. B. Patil and J. M. Nagarkar, *Tetrahedron Lett.*, 2013, **54**, 3457–3461.
- (30) V.Sharavath and S. Ghosh, *RSC Adv.*, 2014, **4**, 48322–48330
- (31) C. Premi and N. Jain, *RSC Adv.*, 2016, **6**, 74961-74967.
- (32) J. R. Anasdass, P. Kannaiyan, R. Raghavachary, S. C. B. Gopinath and Y. Chen, *PLOS ONE*, 2018, **13**, 0193281-0193294.
- (33) A. Zarnegaryan and D. Elhamifar, *Heliyon*, 2020, **6**, 03741-03749.
- (34) J.Y. Jang, H. M. Jeong and B. K. Kim, *Macromol. Res.*, 2009, **17**, 626-629.
- (35) C. H. Chen, W. H. Yen, C. F. Kuan and C. L. Chiang, *Polym. Compos.*, 2010, **31**, 18-24.
- (36) J. R. Potts, S. H. Lee, T. M. Alam, J. An, M. D. Stoller and R. D. Piner, *Carbon*, 2011, **49**, 2615-2623.
- (37) X. Zeng, J. Yang and W. Yuan, *Eur. Polym. J.*, 2012, **48**, 1674-1682.
- (38) V. H. Pham, T. T. Dang, S. H. Hur, E. J. Kim and J. S. Chung, *ACS Appl. Mater. Interfaces.*,2012, **4**, 2630-2636.
- (39) J. M. Thomassin, M. Trifkovic, W. Alkarmo, C. Detrembleur, C. J r me and C. Macosko, *Macromolecules*, 2014, **47**, 2149-2155.
- (40) D. L. Trimm, ed. C. H. Bartholomew, *Elsevier*, Amsterdam, 1991, 68, 29-51.

- (41) R. K. Gupta, Z. A. Alhamed and F. Yakuphanoglu, *Mater. Lett.*, 2013, **112**, 75-77.
- (42) F. Chekin, *Bull. Mater. Sci.*, 2015, **38**, 887-893.
- (43) J. Xu, S. Gai, F. He, N. Niu, P. Gao, Y. Chen and P. Yang, *Dalton Trans.*, 2014, **43**, 11667-11675.
- (44) D. R. Anton and R. H. Crabtree, *Organometallics*, 1983, **2**, 855-859.
- (45) B. Basu, K. Biswas, S. Kundu and S. Ghosh, *GreenChem.* 2010, **12**, 1734-1738.
- (46) A. Mahanta, M. Mondal, A. J. Thakur and U. Bora, *Tetrahedron Lett.*, 2016, **57**, 3091-3095.
- (47) S. Bhattacharya, A. Srivastava and S. Sengupta, *Tetrahedron Lett.*, 2005, **46**, 3557-3560.
- (48) A. Ohtaka, T. Okagaki, G. Hamasaka, Y. Uozumi, T. Shinagawa, O. Shimomura and R. Nomura, *Catalysts*, 2015, **5**, 106-118.
- (49) S. R. Sanjaykumar, B. D. Kumari, S. Patil, G. Madras and M. S. Hegde, *J. Chem. Sci.*, 2011, **123**, 47-54.
- (50) M. Bakherad, A. Keivanloo and S. Samangooei, *Tetrahedron Lett.*, 2012, **53**, 5773-5776.
- (51) V. Calo, A. Nacci, A. Monopoli, A. Fornaro, L. Sabbatini, N. Cioffi, N. Ditaranto, *Organometallics*, 2004, **23**, 5154-5158.
- (52) I. Bin, W. J. Qing, G. D. Hua, L. X. Ming, C. X. Qin, P. Yue and G. H. Wei, *Sci China Chem.*, 2014, **57**, 1310-1314.

III.A.6. References

- (1) E. Vitaku, D. T. Smith and J. T. Njardarson, *J. Med. Chem.*, 2014, **57**, 10257-10274.

-
- (2) P. J. J. Martins, S. Santos, L. R. Raposo, C. Roma-Rodrigues, P. V. Baptista and A. R. Fernandes, *Molecules*, 2015, **20**, 16852-16891.
- (3) T. Karabasanagouda, A. V. Adhikari and M. Girisha, *Indian J. Chem.*, 2009, **48**, 430-437.
- (4) (a) Q. Liu and Y. N. Zhang, *Bull. Korean Chem. Soc.*, 2011, **32**, 3559-3560, (b) A. Domling, *Curr. Opin. Chem. Biol.*, 2002, **6**, 306-313, (c) C. O. Kappe, *Curr. Opin. Chem. Biol.*, 2002, **6**, 314-320.
- (5) E. Rafiee and H. Jafari, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 2463-2466.
- (6) G. Abbiati, E. M. Beccalli, G. Brogginini and C. Zoni, *Tetrahedron*, 2003, **59**, 9887-9893.
- (7) S. Batra, S. K. Rastogi, B. Kundu, A. Patra and A. P. Bhaduri, *Tetrahedron Lett.*, 2000, **41**, 5971-5974.
- (8) A. Barria, V. Derkach and T. Soderling, *J. Biol. Chem.*, 1997, **272**, 32727-32730.
- (9) B. Kafle, N. G. Aher, D. Khadka, H. Park and H. Cho, *Chem. Asian J.*, 2011, **6**, 2073-2079.
- (10) J. Han, H. Guo, X. G. Wang, M. L. Pang and J. B. Meng, *Chin. J. Chem.*, 2007, **25**, 129-131.
- (11) M. Pinerio and T. M. Pinho-e-Melo, *Eur. J. Org. Chem.*, 2009, **31**, 5287-5307.
- (12) O. H. Kan, I. Adachi, R. Kido and K. Hirose, *J. Med. Chem.*, 1967, **10**, 411-418.
- (13) X. H. Zhang, Y. H. Zhan, D. Chen, F. Wang and L. Y. Wang, *Dyes Pigm.*, 2012, **93**, 1408-1415.
- (14) (a) E. Aret, H. Meekes, E. Vlieg and G. Deroover, *Dyes Pigm.*, 2007, **72**, 339-344 (b) Y. K. Kang, K. J. Shin and K. H. Yoo, *Bioorg. Med. Chem. Lett.*, 2000, **10**, 95-99.

- (15) (a) P. Conti, C. Dallanoce, M. D. Amici, C. D. Micheli and K. N. Klotz, *Bioorg. Med. Chem.*, 1998, **6**, 401-408; (b) M. G. Gordaliza, T. Faircloth, M. A. Castro, J. M. M. DelCorral, M. L. López-Vázquez and A. San Feliciano, *J. Med. Chem.*, 1996, **39**, 2865-2868.
- (16) T. Ishioka, A. Kubo, Y. Koiso, K. Nagasawa, A. Itai and Y. Hashimoto, *Bioorg. Med. Chem.*, 2002, **10**, 1555-1566.
- (17) I. Nakamura, M. Okamoto and M. Terada, *Org Lett.*, 2010, **12**, 2453-2455.
- (18) D. B. Lowe, S. Magnuson, N. Qi, et al. *Bioorg. Med. Chem. Lett.*, 2004, **14**, 3155-3159.
- (19) D. Villemin, B. Martin and B. Garrigues, *Synth. Commun.*, 1993, **23**, 2251-2257.
- (20) (a) Y. Q. Zhang and C. Wang, *Chin. J. Org. Chem.*, 2008, **28**, 141-144; (b) Q. Liu and R. T. Wu, *J. Chem. Res.*, 2011, **35**, 598-599.
- (21) Y. Q. Zhang and C. Wang, *Chin. J. Org. Chem.*, 2008, **28**, 1267-1271.
- (22) S. Tu, J. Zhang, R. Jia, B. Jiang, Y. Zhang and H. Jiang, *Org. Biomol. Chem.*, 2007, **5**, 1450-1453.
- (23) K. Ablajan and H. Xiamuxi, *Synth. Commun.*, 2012, **42**, 1128-1136.
- (24) F. Saikh, J. Das and S. Ghosh, *Tetrahedron Lett.*, 2013, **54**, 4679-4682.
- (25) Q. Liu and X. Hou, *Phosphorus Sulfur Silicon Relat. Elem.*, 2012, **187**, 448-453.
- (26) H. Kiyani and F. Ghorbani, *J. Chem. Soc.*, 2017, **21**, 112-119.
- (27) M. S. Patil, C. Mudaliar and G. U. Chaturbhuj, *Tetrahedron Lett.*, 2017, **58**, 3256-3261.
- (28) H. Kiyani and F. Ghorbani, *Res. Chem. Intermed.*, 2015, **41**, 2653-2664.
- (29) H. Kiyani, F. Ghorbani, *Elixir Org. Chem. A.*, 2013, **58**, 14948-14950.

-
- (30) M. Ahmadzadeh, Z. Zarnegar and J. Safari, *Green Chem. Lett. Rev.*, 2018, 11, 78-85.
- (31) Q. Liu, H. M. Ai, Z. Li, *Ultrason. Sonochem.*, 2011, **18**, 477-479.
- (32) M. Mirzazadeh and G. Mahdavinia, *H. J. Chem.*, 2012, 9, 425-429.
- (33) S. Tu, J. Zhang, R. Jia, B. Jiang, Y. Zhang and H. Jiang, *Org. Biomol. Chem.*, 2007, **5**, 1450-1453.
- (34) S. N. Maddila, S. Maddila, W. E. Zyl and S. B. Jonnalagadda, *Res. Chem. Intermed.*, 2016, **42**, 2553.
- (35) H. Kiyani, A. Kanaani, D. Ajloo, F. Ghorbani and M. Vakili, *Res. Chem. Intermed.*, 2015, **41**, 7739-7773.
- (36) G. Minunni and S. D'Urso, *Cuss. chim. it&.*, 68, 485 (1928); *c. A.*, 43, 1120 (1929)
- (37) R. Schiff and M. Betti, *Ber.* 1897, **80**, 1885-1887.
- (38) M. S. Patil, C. Mudaliar and G. U. Chaturbhuji, *Tetrahedron Lett.*, 2017, **58**, 3256-3261
- (39) Q. Liu and X. Hou, *Phosphorus Sulfur Silicon Relat. Elem.*, 2012, **187**, 448-453.
- (40) M. M. Heravi, K. Bakhtiari, S. Taheri and H. A. Oskooie, *J. Chin. Chem. Soc.*, 2007, **54**, 1557-1560.
- (41) M. Fagnoni, D. Dondi, D. Ravelli and A. Albini, *Chem. Rev.*, 2007, **107**, 2725-2756.
- (42) F. Saikh, J. Das and S. Ghosh, *Tetrahedron Lett.*, 2013, **54**, 4679-4682.
- (43) H. Kiyani and F. Ghorbani, *J. Saudi Chem. Soc.*, 2017, **21**, 112-119.
- (44) P. L. Salzberg and J.V. Supniewski, *In Organic Synthesis Collection*, John Wiley, New York, USA, 1995.
- (45) B. Zwanenburg and A.S. Mwakaboko, *Bioorg. Med. Chem.*, 2011, **19**, 7394-7400.

- (46) S. G. Stewart, D. Spagnolo, M. E. Polomska, M. Sin, M. Karimi and L. Abraham, *J. Bioorg. Med. Chem. Lett.*, 2007, **17**, 5819-5824.
- (47) M. G. Dekamin and Z. Karimi, *J. Organomet. Chem.*, 2009, **694**, 1789-1794.
- (48) D. R. Dreyer and C. W. Bielawski, *Chem. Sci.*, 2011, **2**, 1233-1240.
- (49) F. Hu, M. Patel, F. Luo, C. Flach, R. Mendelsohn, E. Garfunkel, H. He and M. Szostak, *J. Am. Chem. Soc.*, 2015, **137**, 14473-14480.
- (50) D. R. Dreyer, H.-P. Jia and C. W. Bielawski, *Angew. Chem. Int. Ed.*, 2010, **49**, 6813-6816.
- (51) C. Su, R. Tandiana, J. Balapanuru, W. Tang, K. Pareek, C. T. Nai, T. Hayashi and K. P. Loh, *J. Am. Chem. Soc.*, 2015, **137**, 685-690.
- (52) B. Majumdar, D. Sarma, T. Bhattacharya and T. K. Sarma, *ACS Sustainable Chem. Eng.*, 2017, **5**, 9286-9294.
- (53) C. Su and K. P. Loh, *Acc. Chem. Res.*, 2013, **46**, 2275-2285.
- (54) S. Navalon, A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *Chem. Rev.*, 2014, **114**, 6179-6212.
- (55) Q. Hou, W. Li, M. Ju, L. Liu, Y. Chen and Q. Yang, *RSC Adv.*, 2016, **6**, 104016-104024.
- (56) M. Mirzazadeh and G. H. Mahdavinia, *J. Chem.*, 2012, **9**, 425-429.

III.B.5. References

- (1) W. P. Smith, L. S. Sollis, D. P. Howes, P. C. Cherry, I. D. Starkey, K. N. Cobley, H. Weston, J. Scicinski, A. Merritt and A. Whittington, et al. *J. Med. Chem.*, 1998, **41**, 787-797.
- (2) J. L. Wang, D. Liu, Z. J. Zheng, S. Shan, X. Han, S. M. Srinivasula, C. M. Croce, E. S. Alnemri and Z. Huang, *Proc. Natl. Acad. Sci.*, 2000, **97**, 7124-7129.

-
- (3) A. M. Grumezescu, E. Andronesu, A. Fikai, C. Bleotu, D. E. Mihaiescu and M. C. Chifiriuc, *Int. J. Pharm.*, 2012, **436**, 771-777.
 - (4) K. Mazaahir, S. Shilpi, R. K. Khalilur and S. T. Sharanjit, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 4295-4298.
 - (5) C. K. Sheng, J. H. Li and N. J. Hideo, *Med. Chem.*, 1984, **27**, 539-544.
 - (6) M. Bihani, P. P. Bora, G. Bez and H. Askari, *ACS Sustainable. Chem. Eng.*, 2013, **1**, 440-447.
 - (7) M. Fatahpour, F. N. Sadeh, N. Hazeri, M. T. Maghsoodlou, Md. S. Hadavi and S. Mahnaei, *Jour. of Saudi Chem. Soc.*, 2017, **21**, 998-1006.
 - (8) S. C. Kuo, L. J. Huang and H. J. Nakamura, *Med. Chem.*, 1984, **27**, 539-544.
 - (9) H. Junek and H. Aigner, *Chem. Ber.*, 1973, **106**, 914-921.
 - (10) G. Tacconi, G. Gatti and G. J. Desimoni, *Prakt. Chem.*, 1980, **322**, 831-834.
 - (11) A. Sharanin, L. Yu, G. Sharanina and V. V. Zh. Puzanova, *Org. Khim.*, 1983, **19**, 2609.
 - (12) G. Kaupp, M. R. Naimi-Jamal and J. Schmeyers, *Tetrahedron*, 2003, **59**, 3753-3760.
 - (13) L. He, Z. Tang, L. F. Cun, A. Q. Mi, Y. Z. Jiang and L. Z. Gong, *Tetrahedron*, 2006, **62**, 346-351.
 - (14) S. R. Meghana, K. P. Mahesh, S. M. Swapnil and M. S. Manikrao, *J. Mol. Catal. A*, 2005, **235**, 267-270.
 - (15) S.-B. Guo, S.-X. Wang and J.-T. Li, *Synth. Commun.*, 2007, **37**, 2111-2120.
 - (16) B. List, *Tetrahedron*, 2002, **58**, 5573-5590.
 - (17) G. Vasuki and K. Kumaravel, *Tetrahedron Lett.*, 2008, **49**, 5636-5638.
 - (18) M. Babaie and H. Sheibani, *Arab. J. Chem.*, 2011, **4**, 159-162.

- (19) M. Kangani, N. Hazeri, M. T. Mghsoodlou, S. M. Habibi-khorasani and S. Salahi, *Res. Chem. Intermed.*, 2015, **41**, 2513-2519.
- (20) G. Nagendrappa, *Resonance*, 2002, **7**, 59-63.
- (21) D. R. Park, H. Kim, J. C. Jung, S. H. Lee and I. K. Song, *Chem. Res. Intermed.*, 2008, **34**, 2-5.
- (22) A. Vafae, A. Davoodnia and M. Pordel, *Chem. Res. Intermed.*, 2015, **41**, 8343-8354.
- (23) P. H. Li, B. L. Li, Z. M. An, L. P. Mo, Z. S. Cui and Z. H. Zhang, *Adv. Synth. Catal.*, 2013, **355**, 2952-2959.
- (24) B. Maleki, H. Eshghi, M. Barghamadi, N. Nasiri, A. Khojastehnezhad, S. S. Ashrafi and O. Pourshiani, *Res. Chem. Intermed.*, 2016, **42**, 3071-3093.
- (25) R. Konakanchi, R. Gondru, V. B. Nishtala and L. R. Kotha, *Synth. Commun.*, 2018, **48**, 1994-2001.
- (26) A. Iskalieva, B. M. Yimmou, P. R. Gogate, M. Horvath, P. G. Horvath and L. Csoka, *Ultrason. Sonochem.*, 2012, **19**, 984-993.
- (27) S. Zhu, J. Wang and W. Fan, *Catal. Sci. Technol.*, 2015, **5**, 3845-3858.
- (28) Q. Hou, W. Li, M. Ju, L. Liu, Y. Chen and Q. Yang, *RSC Adv.*, 2016, **6**, 104016-104024.
- (29) D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **8**, 4806-4814.

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Puja Basak & Pranab Ghosh

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Poly (methyl methacrylate)-graphene oxide supported palladium catalyst: A ligand free protocol for Suzuki and Heck coupling reaction in water medium

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ABSTRACT

A green and efficient approach for the ligand free Suzuki–Miyaura and Mizoroki–Heck C–C cross coupling reaction using low palladium loaded Graphene oxide-polymer composite catalyst has been described. High yields, easy work-up, easy availability and handling, eco-friendly and reusability of the catalysts are the main aspects of the present method. The simplicity of the entire sequence has made the protocol meritorious as a reasonable contribution to the existing methods in the field of substituted biphenyls and olefins. The supported heterogeneous catalyst was characterized using HRTEM, ICP-AES, PXRD, XPS, TGA, and FT-IR spectroscopy.

GRAPHICAL ABSTRACT

Heck Coupling

Suzuki Coupling



ARTICLE HISTORY

Received 9 May 2018

KEYWORDS


Aqueous medium; GO-PMMA-Pd catalyst; Heck reaction; ligand free; Suzuki–Miyaura coupling

Introduction

Heterogeneous palladium catalyzed C–C cross coupling reactions have attracted much attention over past two decades. As a representative of this class of reaction, Suzuki and Heck coupling are most significant because biaryl moieties and substituted olefins are present in pharmaceuticals,^[1–4] wide range of natural products such as alkaloids and many agrochemicals and biologically active compounds.^[2,5] Although homogeneous catalyst offers excellent result, they have some drawbacks because of difficult separation procedure that often contaminates the products. However, most of them employ different types of ligands such as sterically hindered trialkyl phosphines, triarylphosphines,^[6] *N*-heterocyclic carbenes,^[7] based Pd (II) complexes. Use of these ligands is unenviable

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because they are toxic and moisture sensitive. However, with growing interest towards greener reactions, ligand free solid supported heterogeneous catalysts are in demand. They have the advantage of enhanced synthetic efficiency and operational simplicity.^[8–11] Previous reports include the immobilization of Pd on activated carbon,^[12] polymers,^[13,14] zeolites,^[15] mesoporous carbon,^[16] silica, alumina or titania.^[17,18]

In the recent years, graphene oxide (GO) has attracted much attention owing to its wide range of application in different fields such as fuel cells,^[19] nanocomposite materials,^[20–23] and electronic devices.^[24] GO has two dimensional layered sheets with several oxygen containing functional groups like epoxy, hydroxy, carbonyl, carboxyl, etc. Palladium nanoparticles supported on graphene and graphene derivatives enlarge the surface area of the composite,^[25] increasing the distance between the sheets. Utilising this phenomenon, catalytic activity of GO-Pd/SGO-Pd,^[25,26] Pd NPs supported on single layer-GO^[27] and polyamine modified GO-Pd^[28] have been successfully tested in Suzuki–Miyaura coupling. Reports regarding GO-supported palladium catalyst using ethanol at refluxed condition,^[29] and GO-supported NHC-Palladium catalyst using aqueous-organic mixed solvents^[7] are very scanty. In some cases, it is reported that,^[7,29] the activity of GO-supported palladium catalyst reduces gradually due to the agglomeration and leaching of metal nanoparticles (NPs). In view of that and to overcome the drawbacks of the previously reported protocols, we have developed a new GO-based heterogeneous catalyst and employed it in Suzuki–Miyaura and Mizoroki–Heck reaction. The reaction conditions are mild and the catalyst can be recycled for five runs without significant loss in its catalytic activity.

Preliminary studies on polymer supported GO has revealed significant increase in mechanical and thermal properties of the composite.^[30–33] Driven by this fact, the idea of a new solid support, which allows better stability, easy recovery of products and simple separation procedure is hypothesized. Poly (methyl methacrylate) [PMMA] is a non-conductive polymer and its composite with GO enhances the thermal stability of the material. Based on the above perspective, our present explorative work involves the deposition of Pd NPs on GO-PMMA composite through *in situ* polymerization of MMA. Wielded by the environmental concerns, water is selected as solvent instead of hazardous solvents such as DMF, DMA, NMP, etc. Utility of GO enhances the thermal stability of poly (methyl methacrylate)^[34,35] and Pd NPs are strongly immobilized in between the layers of graphene oxide–PMMA composite.^[24,29] To the best of our knowledge, GO-PMMA supported Pd catalyst has not been employed in Suzuki and Heck coupling reactions. Simpler reaction conditions, ligand free protocol, low Pd content and tolerance to wide range of functional groups are the salient features of our work.

Results and discussion

The morphology of the catalyst (GO-PMMA-Pd) was analyzed by transmission electron microscope (TEM). The micrograph and particle size distribution curve of *in situ* prepared GO-PMMA-Pd catalyst is represented in [Figure 1](#). The TEM images show the mono dispersed palladium without agglomeration on the GO-PMMA-sheet during *in situ* polymerization of MMA. The average size of the Pd NPs has been determined from the TEM images and was found to be around 4.8 nm.

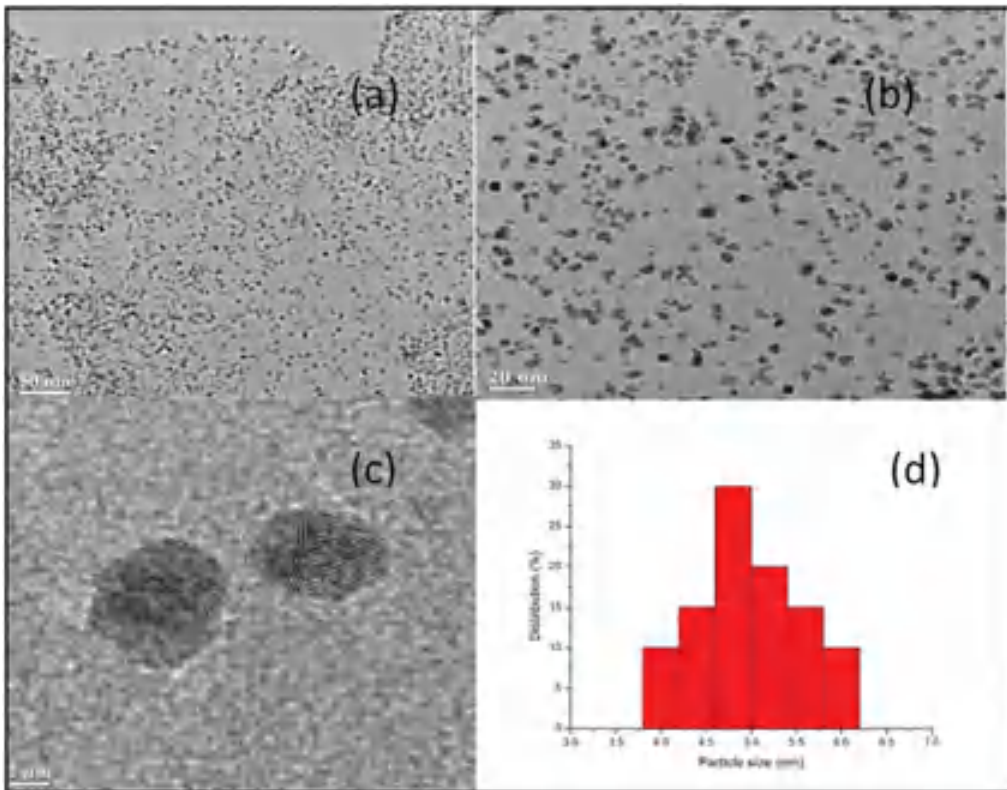


Figure 1. TEM image of GO-PMMA-Pd composite catalyst (a) at 50 nm (b) at 20 nm (c) at 2 nm (d) Particle size distribution curve of GO-PMMA-Pd catalyst.

The catalyst life is a factor that can control the economic viability of industrial processes and as a consequence high thermal resistance of a catalyst support is found to be suitable for different kinds of thermal reaction.^[36]

Thermogravimetric Analysis (TGA) of the solid support has been analyzed for several samples with different *wt %* of GO loading as shown in Figure 2. It is very interesting to observe that composite with the lowest *wt %* of GO exhibited maximum thermal stability (Fig. 2).

The catalyst was subjected to powder X-ray diffraction (XRD) for composition analysis (Fig. 3). Three sharp peaks at around $2\theta = 40.1^\circ$, 46.6° and 68.9° represents the crystalline planes (111), (200) and (220), respectively, in fcc structure of Pd.^[29] However the intensity of (111) plane is higher than (200) and (220) plane. The absence of strong GO peak at $2\theta = 10.63^\circ$ ^[37] and the appearance of characteristic broad PMMA peak at $2\theta = 14.8^\circ$ indicated the formation of GO-polymer composite. The FTIR spectrum of GO has a peak at 1735 cm^{-1} which is assigned to the carbonyl stretching frequency. The FT-IR peak of PMMA at 1148 cm^{-1} is associated with the stretching vibration of the C–O bond in the C–O–C moiety, whereas the peak at 1731 cm^{-1} is due to the acrylate carbonyl groups. FT-IR spectrum (Fig. 4) revealed that the resultant GO-PMMA-Pd composite catalyst contained several functional groups like –OH (3454 cm^{-1}) and C=O (1731 cm^{-1}). Therefore, it has a strong tendency to readily

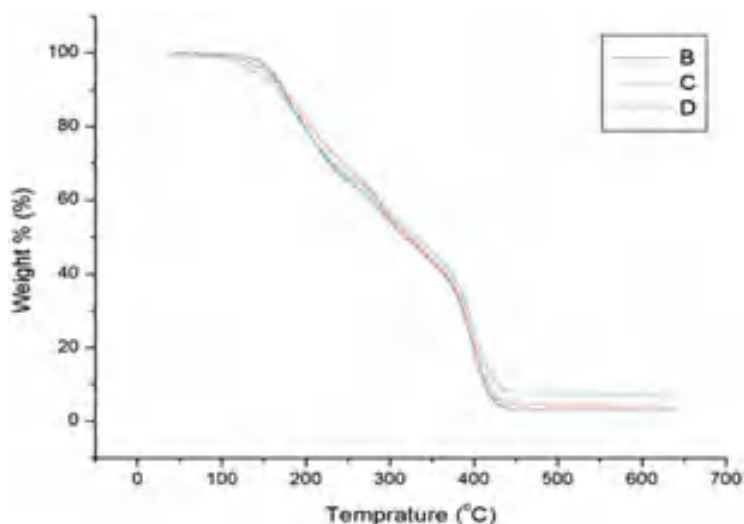


Figure 2. TGA results of (B) 2 wt% (C) 5 wt% (D) 10 wt% GO in PMMA.

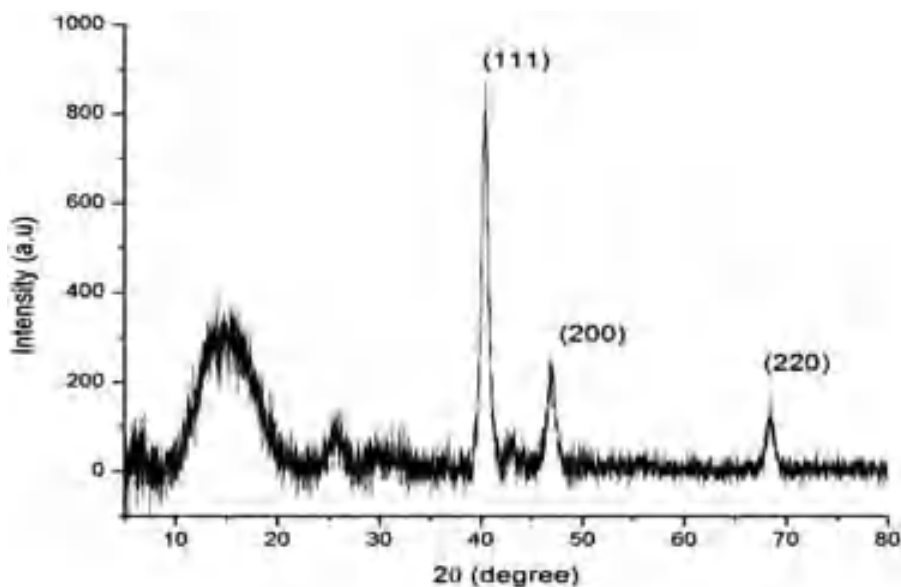


Figure 3. XRD pattern of GO-PMMA-Pd composite catalyst.

interact with metal ions by hydroxyl and carboxyl group. It is considered that the bond between Pd and GO-PMMA can be formed through some physical/chemical interactions such as Vander Waals force, H-bonding and other bonds.^[38] The shift of other stretching frequencies also points towards the association of PMMA with GO (Fig. 4). Furthermore, a hump obtained at around $2\theta = 23^\circ$ suggests the presence of reduced graphene oxide (RGO).^[39] Hence, it can be concluded that a small amount of GO has been converted into RGO when HCOOH was employed. GO-PMMA-Pd catalyst was further characterized by XPS, as shown in Figure 5. High-resolution XPS spectrum was corrected with reference to the carbon 1s peak at 284.8 eV shown in Figure 5(b).

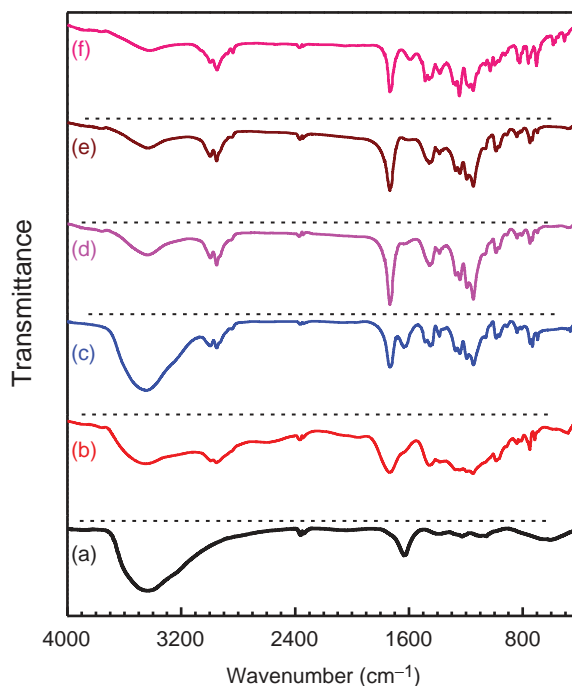


Figure 4. Comparison of FT-IR spectra of (a) GO (b) GO-PMMA (c) GO-PMMA-Pd (d) PMMA-Pd (e) PMMA and (f) recycled catalyst after fifth run.

The binding energies of Pd 3d at 335.87 and 341.2 eV for GO-PMMA-Pd corresponded to the Pd⁰ Pd 3d_{5/2} and Pd 3d_{3/2}, respectively. Thus, the presence of metallic Pd in the composite is confirmed (Fig. 5(c)).

Leaching of metal from the heterogeneous GO-PMMA support was examined by hot filtration test as described in the literature.^[40] After 1 h completion of reaction, the reaction mixture was filtered to separate out the catalyst and HPLC was carried out with the obtained filtrate (38% conversion). The ICP-AES analysis of the filtrate showed the absence of any palladium. The filtrate was then heated for another 4 h at 90 °C without the addition of catalyst and the corresponding HPLC pattern (Fig. 6) did not show any noticeable conversion which implied that metals are not getting leached from the solid GO-PMMA support during first 1 h of the reaction.

The Pd content was found to be 5.559 wt% in this heterogeneous catalyst. The recyclability of the catalyst was tested for Suzuki coupling reaction and the catalyst was recyclable for five consecutive runs without significant drop in activity. The sudden drop in Pd content (Fig. 7) after the fifth run may be attributed to the leaching of Pd from the catalyst. The development of recoverable catalyst is one of the indispensable principles of the green synthetic organic chemistry and the key purpose of this study was to place a recyclable catalyst for Suzuki and Heck reaction in aqueous medium. Initially, for screening the reaction, phenylboronic acid and 4-iodo anisole has been chosen as the model substrates in presence of GO-PMMA-Pd catalyst. The favorable condition of the reaction was achieved by varying the parameters such as catalyst loading, solvent, time, base and temperature. Finally the protocol was optimized by using water as solvent, K₂CO₃ as base and catalyst loading (0.3 mol % Pd) in 6 mg of

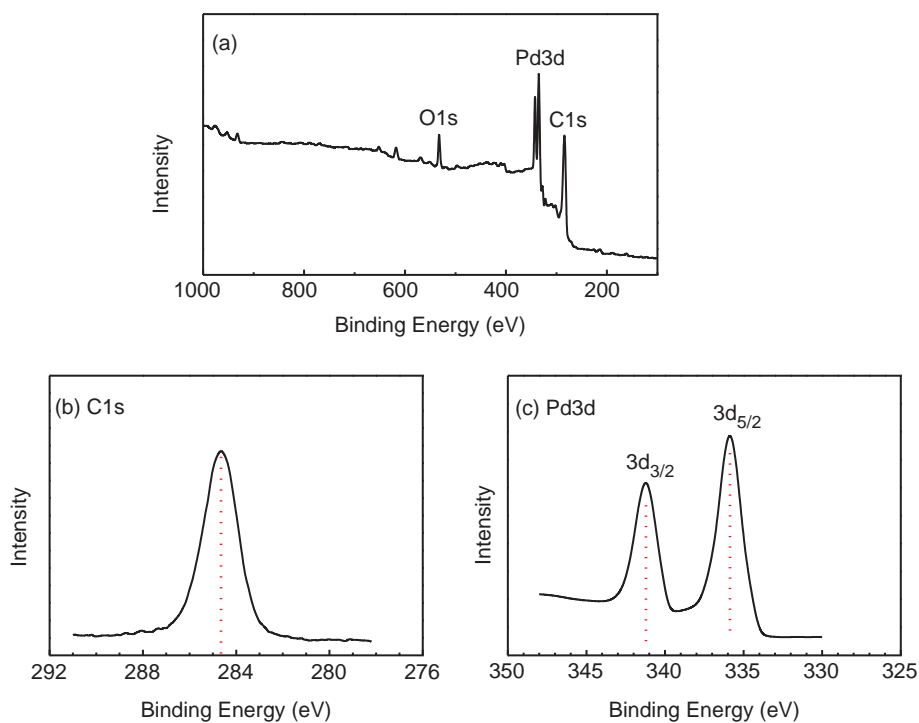


Figure 5. (a) Full-range XPS spectrum of GO-PMMA-Pd catalyst. C 1s peak at 284.8 eV shown in (b). In (c) the binding energies of Pd 3d at 335.87 and 341.2 eV for GO-PMMA-Pd corresponded to the Pd⁰ Pd 3d_{5/2} and Pd 3d_{3/2}, respectively.

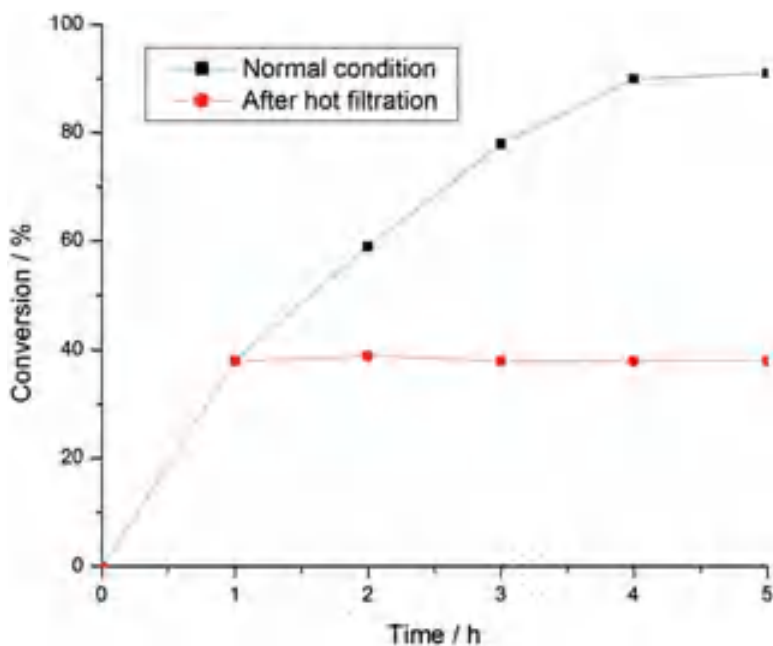


Figure 6. Comparison of normal time profile with hot filtration test. Conversions ($\pm 2\%$) at different time intervals for each plot were measured by HPLC.

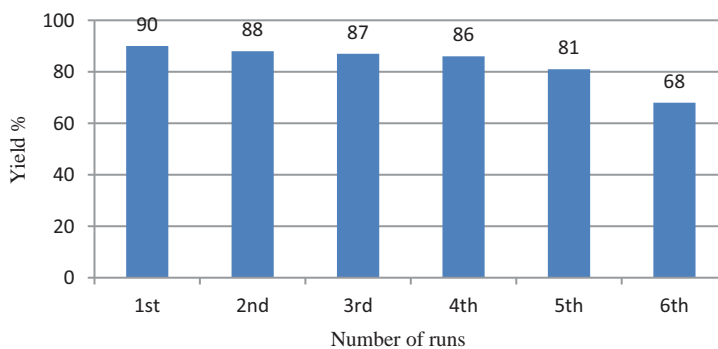


Figure 7. Recycling efficiencies of GO-PMMA-Pd catalyst for Suzuki coupling reaction.

Table 1. Optimization of reaction parameters for Suzuki reaction based on the result of the following combination in the protocol^a.

Entry	Solvent	Base	Pd loading (mol%)	Additive	Time (h)	Yield ^b (%)
1	DMF	K ₂ CO ₃	0.1	Bu ₄ NBr	1	42
2	DMSO	K ₂ CO ₃	0.1	Bu ₄ NBr	2	29
3	Water	K ₂ CO ₃	0.2	Bu ₄ NBr	3	63
4	Ethanol	K ₂ CO ₃	0.2	Bu ₄ NBr	3	58
5	Water	K ₂ CO ₃	0.3	SDS	4	72
6	Water	K ₂ CO ₃	0.3	Bu ₄ NBr	4	90
7	Water	Na ₂ CO ₃	0.3	Bu ₄ NBr	6	76
8	Water	Cs ₂ CO ₃	0.3	Bu ₄ NBr	6	75
9	Water	Et ₃ N	0.3	Bu ₄ NBr	6	78
10	Water	KOH	0.3	Bu ₄ NBr	4	62
11	Water	K ₂ CO ₃	0.3	CTAB	6	72
12	Water	K ₂ CO ₃	0.3	TMAI	4	52
13	Water	K ₂ CO ₃	0.3	Bu ₄ NBr	24	25 ^c
14	Water	K ₂ CO ₃	0.5	Bu ₄ NBr	12	86 ^d

^aReaction of 4-Iodo anisole (1 mmol), Phenyl boronic acid (1.5 mmol), Pd loading (0.3 mol%), K₂CO₃ (1 mmol), TBAB (10 mol%), water (2 mL) at 90 °C;

^bIsolated yields.

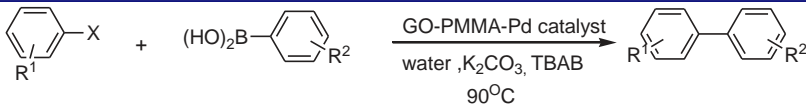
^cRoom temperature reaction;

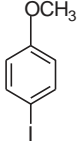
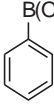
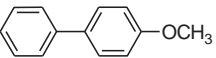
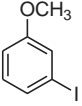
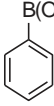
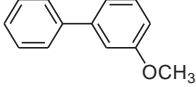
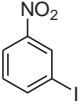
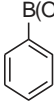
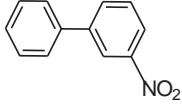
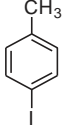
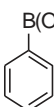
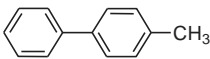
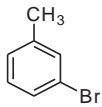
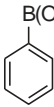
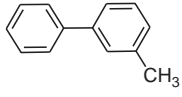
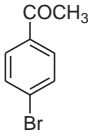
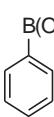

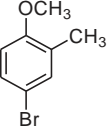
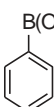
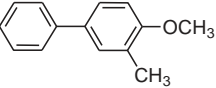
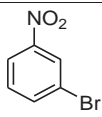
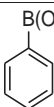
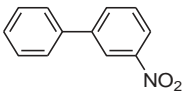
^dTemp of the reaction 100 °C.

GO-PMMA-Pd catalyst at 90 °C (Table 1). In order to enhance the yield of 4-methoxy-1,1' biphenyl in water, different surfactants were employed in the study (Table 1). It is established that the yield of the product can be improved by increasing the reaction time. We started increasing the reaction time by keeping all parameters similar and found that the best yield is achieved in 4 h of reaction (Table 1, entry 6). However, *ortho*-substituted compounds require longer reaction time.

The synthetic efficacy of this catalyst in water mediated Suzuki coupling reaction was conducted with a number of different aryl halides and arylboronic acids under optimized condition (Table 2, entries 1–16). The electron withdrawing aryl iodides and bromides gave excellent yields of corresponding products (entries 3, 6 and 8). Although relatively longer reaction time was required for electron donating aryl iodides and bromides but each of them offered an excellent yield of products (entries 1–2 and 4–5). The aryl chlorides gave only trace amount of the corresponding product even after 24 h of exertion of reaction. The arylboronic acids with methoxy, methyl, nitro groups were rapidly converted to their corresponding products at high to moderate yield at 90 °C as shown in Table 2 (entries 9, 15 and 16).

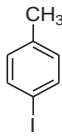
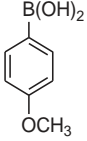
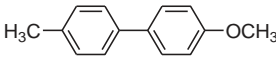

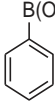
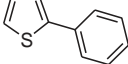
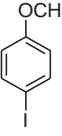
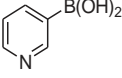
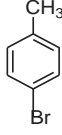
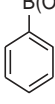
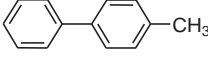
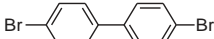
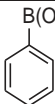

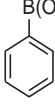
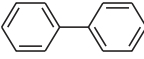

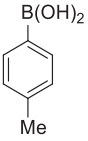
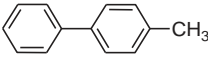

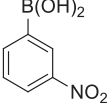
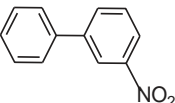
Table 2. GO-PMMA-Pd catalyzed Suzuki reaction of different aryl halides with phenyl boronic acid^a.



Entry	Aryl halide	Boronic acid	Products	Time (h)	Yield ^b (%)
1.				4	90
2.				4	88
3.				2	92
4.				6	86
5.				6	84
6.				1.5	93
7.				4	85
8.				3	89

continued

Table 2. Continued.

9.				4	86
10.				6	58
11.			No reaction	–	Nil
12.				6	79
13.			No reaction	–	Nil
14.				24	35 ^c
15.				4	88
16.				4	71

^aReaction of aryl halide (1 mmol), Phenyl boronic acid (1.5 mmol), palladium loading (0.3 mol%), K₂CO₃ (1 mmol), TBAB (10 mol%), water (2 mL) at 90 °C.

^bIsolated yields.

^cReaction temperature 120 °C.

The above success in Suzuki coupling reaction prompted us to look for such expectancy in Heck coupling reaction too. The Heck reaction was optimized by varying the reaction parameters temperature, solvent, base, catalyst loading (Table 3). In that instance, 4-iodo anisole was successfully coupled with methyl acrylate in presence of TBAB and 0.2 mol% Pd in GO-PMMA-Pd catalyst at 100 °C. All types of aryl halides

Table 3. Optimization of reaction parameters of Heck reaction^a.

Entry	Solvent	Base	Temp (°C)	Pd-loading (mol%)	Time (h)	Yield (%) ^b
1	DMF	K ₂ CO ₃	120	0.1	4	75 ^c
2	Water	K ₂ CO ₃	100	0.1	5	72
3	Water	Et ₃ N ^d	100	0.2	5	80
4	Water	K ₂ CO ₃	100	0.2	4	85
5	Water	K ₂ CO ₃	80	0.3	5	78
6	Water	K ₂ CO ₃	Rt	0.3	24	25 ^e

^aReaction of 4-Iodo anisole(1 mmol), methyl acrylate (2 mmol), Pd loading (0.2 mol%), K₂CO₃ (1 mmol), TBAB (10 mol%), water 3 mL.

^bIsolated yields.

^csolvent was DMF.

^dtriethyl amine was used as base.

^eroom temperature.

gave good to excellent yield, which indicates the high efficiency of this heterogeneous catalyst (Table 4) in Heck coupling too.

Figure 7 represents the recyclability of the GO-PMMA-Pd catalyst for Suzuki coupling reaction upto the sixth run. The reduction of yield after fifth run could be due to the leaching of Pd NPs from GO-PMMA surface. The palladium content after fifth run was confirmed by ICP-AES and it was found to be 1.357 wt%. However, when the reaction was performed with only PMMA-Pd⁰, a drastic change in yield was observed from 88% to 56% in second run. This observation clearly indicated that presence of GO in the composite plays a vital role to improve the catalytic ability of GO-PMMA-Pd system.

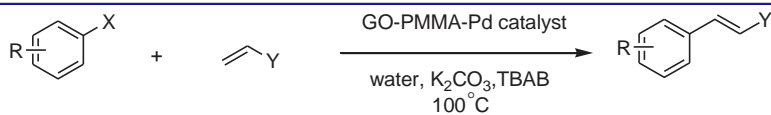
Experimental

Materials and physical measurements

Palladium (II) acetate 99.98% was purchased from Sigma Aldrich. Graphite powder, H₂O₂ (solution 30%), 98.5% pure methyl methacrylate were purchased from commercial supplier. The morphology of the catalyst (GO-PMMA-Pd) was analyzed by TEM, (Model: JEM-2100, accelerating voltages 60–200 KV in 50 V steps; resolution: 1.9 Å to 1.4 Å). Inductively coupled plasma spectroscopy (ICP) was analyzed on ARCOS, Simultaneous ICP spectrometer (SPECTRO analytical instruments GmbH, Germany). Powder XRD data and X-ray photoelectron spectroscopy (XPS) was obtained from Bruker D8 Advanced X-ray Powder Diffractometer (Cu K α radiation, $\lambda = 1.54 \text{ \AA}$) and an XPS instrument (Omicron: Serial no. 0571) respectively. NMR spectra were taken in CDCl₃ using a Bruker AV-300 spectrometer operating for ¹H at 300 MHz and for ¹³C at 75 MHz. Splitting patterns of protons were described as s (singlet), d (doublet), t (triplet), br (broad) and m (multiplet). Chemical shifts were reported in parts per million (ppm) relative to TMS as internal standard.

General procedure for preparation of GO-PMMA-supported Pd catalyst

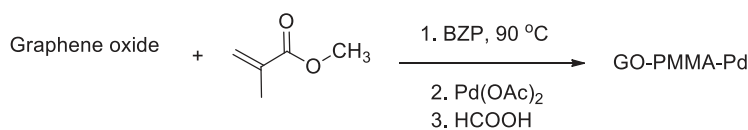
Initially for the preparation of catalyst 20 mg of GO was suspended in 20 mL of toluene. The slurry was then dispersed through ultrasonication for 60 min. After ultrasonication methyl methacrylate was injected to a well dispersed solution of GO. Benzoyl peroxide

Table 4. Reaction of aryl halides with different vinyl compounds^a.

Entry	Aryl halides	Olefins	Product	Time (h)	Yield ^b (%)
1				4	85
2				4	83
3				6	84
4				4	88
5				5	90
6				5	79
7				4	80
8				4	84

^aReaction of aryl halide (1 mmol), vinyl compound (2 mmol), GO-PMMA-Pd catalyst (0.2 mol%), K₂CO₃ (1 mmol), TBAB (10 mol%), water 3 mL.

^bIsolated yields.



Scheme 1. Preparation of GO-PMMA-Pd catalyst.

(BZP, 0.1 mol%) was added to initiate the polymerization of methyl methacrylate (MMA). The resulting mixture was then stirred well at 90 °C for 4 h. The temp of the solution was maintained at 90 °C. Stirring was continued for another 3 h followed by the addition of 40 mg Pd(OAc)₂ and 100 mg of HCOOH as shown in Scheme 1. The dark brown precipitate instantly turned into black after the addition of HCOOH. The obtained residue was washed several times with water and residual solvent was shuffled off by rotary evaporator, and dried at 60 °C.

Procedure for cross coupling of 4-iodo anisole and phenyl boronic acid using GO-PMMA-Pd catalyst

A 25 mL RB was charged with 4-iodo anisole (1.0 mmol), phenylboronic acid (1.5 mmol), GO-PMMA-Pd catalyst (0.3 mol % Pd), K₂CO₃ (1 mmol), TBAB (10 mol %) and 2 mL water. The mixture was allowed to stir at 90 °C for an appropriate time (Table 1) and the extent of the reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, the reaction mixture was extracted by ethyl acetate (2 × 25 ml) and washed with water repeatedly. The catalyst was filtered off and washed several times with ether and water (1:1) until no significant product was obtained in the wash. The recovered catalyst was reused for the next coupling experiment. The reaction mixture was dried over anhydrous Na₂SO₄, concentrated in vacuum and purified by column chromatography on silica gel 60–120 mesh using petroleum ether as eluent to obtain pure product. The catalyst recovered after fifth run was subjected to ICP-AES for Pd content analysis. The isolated products were analyzed by ¹H NMR and ¹³C NMR spectroscopy.

4-methoxy-1,1' biphenyl^[41]: ¹H NMR (CDCl₃, 300 MHz) δ 3.85 (s, 3H), 6.98 (d, 2H, *J* = 6.9 Hz), 7.238–7.319 (1H, m), 7.397 (d, 2H, *J* = 7.8 Hz), 7.511–7.564 (m, 4H, *J* = 8.7 Hz); ¹³C NMR δ 55.37, 114.22, 126.68, 126.76, 128.18, 128.75, 133.80, 140.85, 159.16.

General procedures for the heck coupling reactions

A mixture of 4-iodo anisole (1 mmol), methyl acrylate (2 mmol), GO-PMMA-Pd catalyst (0.2 mol % Pd), K₂CO₃ (1 mmol), TBAB (10 mol %) and 3 ml water was stirred under 100 °C. The reaction took significant time for completion (Table 3) and the progress of the reaction was monitored by TLC. After completion, the reaction mixture was extracted with ethyl acetate and washed with water repeatedly. The combined organic mixture was dried over anhydrous Na₂SO₄ and purified by column chromatography using petroleum ether/ethyl acetate as eluent to afford pure product. The catalyst was separated and washed for several times with ether and water. The recovered catalyst was

used in next cycles and the isolated products were characterized by ^1H and ^{13}C NMR spectroscopy.

(E)-methyl 3-(4-methoxyphenyl) acrylate^[42]: ^{13}C NMR δ 51.27, 55.29, 114.33, 115.03, 126.57, 130.13, 144.31, 161.11, 166.91.

Conclusion

A greener protocol using ligand free GO-PMMA-Pd catalyst is proposed. The prepared catalyst was characterized by different spectroscopic and microscopic techniques. The newly made catalyst effectively generates different C–C cross coupled product even at a very low Pd content in high yields at optimal condition. The simple operational procedure, easy removal of catalyst, reusability of the catalyst and environmentally benign process are the most significant and outwit factors of our proposed scheme in comparison to the existing protocols.

Acknowledgments

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References

- [1] (a) Suzuki, A. The Suzuki Reaction with Arylboron Compounds in Arene Chemistry. In *Modern Arene Chemistry*, 1st ed.; Wiley-VCH: Weinheim, **2004**; pp 53–106; b) Heck, R. F. Palladium-Catalyzed Reactions of Organic Halides with Olefins. *Acc. Chem. Res.* **1979**, *12*, 146. DOI: [10.1002/chin.197937153](https://doi.org/10.1002/chin.197937153). c) Yahiaoui, S.; Fardost, A.; Trejos, A.; Larhed, M. Chelation-Mediated Palladium(II)-Catalyzed Domino Heck–Mizoroki/Suzuki–Miyaura Reactions Using Arylboronic Acids: Increasing Scope and Mechanistic Understanding. *J. Org. Chem.* **2011**, *76*, 2433–2438.
- [2] Fihri, A.; Bouhrara, M.; Nekoueishahraki, B.; Basset, J. M.; Polshettiwar, V. Nanocatalysts for Suzuki Cross-Coupling Reactions. *Chem. Soc. Rev.* **2011**, *40*, 5181–5203. DOI: [10.1039/c1cs15079k](https://doi.org/10.1039/c1cs15079k).
- [3] Zhou, Z. Z.; Liu, F. S.; Shen, D. S.; Tan, C.; Luo, L. Y. Efficient Palladium-Catalyzed Suzuki Cross-Coupling Reaction with β -Ketoamine Ligands. *Inorg. Chem. Commun.* **2011**, *14*, 659–662. DOI: [10.1016/j.inoche.2011.01.044](https://doi.org/10.1016/j.inoche.2011.01.044).
- [4] Hajduk, P. J.; Bures, M.; Praestgaard, J.; Fesik, S. W. Privileged Molecules for Protein Binding Identified from NMR-Based Screening. *J. Med. Chem.* **2000**, *43*, 3443–3447. DOI: [10.1021/jm000164q](https://doi.org/10.1021/jm000164q).
- [5] Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. Aryl–Aryl Bond Formation One Century after the Discovery of the Ullmann Reaction. *Chem. Rev.* **2002**, *102*, 1359–1470. DOI: [10.1021/cr000664r](https://doi.org/10.1021/cr000664r).
- [6] Böhm, V. P. W.; Herrmann, W. A. Nonaqueous Ionic Liquids: superior Reaction Media for the Catalytic Heck-Vinylation of Chloroarenes. *Chemistry* **2000**, *6*, 1017–1025. DOI: [10.1002/\(SICI\)1521-3765\(20000317\)6:6<1017::AID-CHEM1017>3.0.CO;2-8](https://doi.org/10.1002/(SICI)1521-3765(20000317)6:6<1017::AID-CHEM1017>3.0.CO;2-8).

- [7] Park, J. H.; Raza, F.; Jeon, S. J.; Kim, H. I.; Kang, T. W.; Yim, D.; Kim, J. H. Recyclable N-Heterocyclic Carbene/Palladium Catalyst on Graphene Oxide for the Aqueous-Phase Suzuki Reaction. *Tetrahed. Lett.* **2014**, *55*, 3426–3430. DOI: [10.1016/j.tetlet.2014.04.078](https://doi.org/10.1016/j.tetlet.2014.04.078).
- [8] Paul, S.; Islam, M. M.; Islam, S. M. Suzuki–Miyaura Reaction by Heterogeneously Supported Pd in Water: Recent Studies. *RSC Adv.* **2015**, *5*, 42193–42221. DOI: [10.1039/C4RA17308B](https://doi.org/10.1039/C4RA17308B).
- [9] Yin, L.; Liebscher, J. Carbon-Carbon Coupling Reactions Catalyzed by Heterogeneous Palladium Catalysts. *Chem. Rev.* **2007**, *107*, 133–173. DOI: [10.1021/cr0505674](https://doi.org/10.1021/cr0505674).
- [10] Sun, Q.; Zhu, L. F.; Sun, Z. H.; Meng, X. J.; Xiao, F. S. Porous Polymer Supported Palladium Catalyst for Cross Coupling Reactions with High Activity and Recyclability. *Sci. China Chem.* **2012**, *55*, 2095–2103. DOI: [10.1007/s11426-011-4491-8](https://doi.org/10.1007/s11426-011-4491-8).
- [11] Pan, C.; Liu, M.; Zhao, L.; Wu, H.; Ding, J.; Cheng, J. Palladium Chloride Catalyzed Hiyama Cross-Coupling Reaction Using Phenyltrimethoxysilane. *Catcom.* **2008**, *9*, 1685–1687.
- [12] Bedford, R. B.; Singh, U. G.; Walton, R. I.; Williams, R. T.; Davis, S. A. Nanoparticulate Palladium Supported by Covalently Modified Silicas: Synthesis, Characterization, and Application as Catalysts for the Suzuki Coupling of Aryl Halides. *Chem. Mater.* **2005**, *17*, 701–707. DOI: [10.1021/cm048860s](https://doi.org/10.1021/cm048860s).
- [13] Jin, M. J.; Taher, A.; Kang, H. J.; Choi, M.; Ryoo, R. Palladium Acetate Immobilized in a Hierarchical MFI Zeolite-Supported Ionic Liquid: A Highly Active and Recyclable Catalyst for Suzuki Reaction in Water. *Green Chem.* **2009**, *11*, 309–313. DOI: [10.1039/b817855k](https://doi.org/10.1039/b817855k).
- [14] Jin, X.; Li, J.; Li, H. An Efficient Poly(Amic Acid) Salt-Stabilised Palladium Nanocatalyst with Excellent Recyclable Performance for Suzuki–Miyaura Coupling Reactions under Mild Conditions. *J. Exper. Nanosci.* **2018**, *13*, 95–106. DOI: [10.1080/17458080.2017.1413600](https://doi.org/10.1080/17458080.2017.1413600).
- [15] Ramchandani, R. K.; Uphade, B. S.; Vinod, M. P.; Wakharkar, R. D.; Choudhary, V. R.; Sudalai, A. Pd–Cu–Exchanged Montmorillonite K10 Clay: an Efficient and Reusable Heterogeneous Catalyst for Vinylation of Aryl Halides. *Chem. Commun.* **1997**, *21*, 2071–2072. DOI: [10.1039/a705870e](https://doi.org/10.1039/a705870e).
- [16] Wan, Y.; Wang, H.; Zhao, Q.; Klingstedt, M.; Terasaki, O.; Zhao, D. Ordered Mesoporous Pd/Silica-Carbon as a Highly Active Heterogeneous Catalyst for Coupling Reaction of Chlorobenzene in Aqueous Media. *J. Am. Chem. Soc.* **2009**, *131*, 4541–4550. DOI: [10.1021/ja808481g](https://doi.org/10.1021/ja808481g).
- [17] Nong, Y. L.; Qiao, N.; Deng, T. H.; Pan, Z.; Liang, Y. Solid Sheet of Anodic Aluminium Oxide Supported Palladium Catalyst for Suzuki Coupling Reactions. *Catalys. Commun.* **2017**, *100*, 139–143. DOI: [10.1016/j.catcom.2017.06.032](https://doi.org/10.1016/j.catcom.2017.06.032).
- [18] Wali, A.; Pillai, S. M.; Kaushik, V. K.; Satish, S. Arylation of Acrylonitrile with Iodobenzene over Pd/MgO Catalyst. *Appl. Catal. A.* **1996**, *135*, 83. DOI: [10.1016/0926-860X\(95\)00190-5](https://doi.org/10.1016/0926-860X(95)00190-5).
- [19] Kundhikanjana, W. K.; Lai, J.; Wang, H. L.; Dai, H. J.; Kelly, M. A.; Shen, Z. X. Hierarchy of Electronic Properties of Chemically Derived and Pristine Graphene Probed by Microwave Imaging. *Nano Lett.* **2009**, *9*, 3762–3765. DOI: [10.1021/nl901949z](https://doi.org/10.1021/nl901949z).
- [20] Wang, J.; Hu, H.; Wang, X.; Xu, C.; Zhang, M.; Shang, X. Preparation and Mechanical and Electrical Properties of Graphene Nanosheets-Poly(Methyl Methacrylate) Nanocomposites via in Situ Suspension Polymerization. *J. Appl. Polym. Sci.* **2011**, *122*, 1866–1871. DOI: [10.1002/app.34284](https://doi.org/10.1002/app.34284).
- [21] Kuila, T.; Bose, S.; Khanra, P.; Kim, N. H.; Rhee, K. Y.; Lee, J. H. Characterization and Properties of in Situ Emulsion Polymerized Poly(Methyl Methacrylate)/Graphene Nanocomposites. *Compos A. APPL Sci Manuf.* **2011**, *42*, 1856–1861. DOI: [10.1016/j.compositesa.2011.08.014](https://doi.org/10.1016/j.compositesa.2011.08.014).
- [22] Yang, J.; Yan, X.; Wu, M.; Chen, F.; Fei, Z.; Zhong, M. Self-Assembly between Graphene Sheets and Cationic Poly(Methyl Methacrylate) (PMMA) Particles: preparation and Characterization of PMMA/Graphene Composites. *J. Nanopart. Res.* **2012**, *14*, 717–724. DOI: [10.1007/s11051-011-0717-0](https://doi.org/10.1007/s11051-011-0717-0).

- [23] Hass, J.; Heer, W. A.; Conrad, E. H. The Growth and Morphology of Epitaxial Multilayer Graphene. *J. Phys: Condens. Matter*. **2008**, *20*, 323202. DOI: [10.1088/0953-8984/20/32/323202](https://doi.org/10.1088/0953-8984/20/32/323202).
- [24] Shendage, S. S.; Singh, A. S.; Nagarkar, J. M. Facile Approach to the Electrochemical Synthesis of Palladium-Reduced Graphene Oxide and Its Application for Suzuki Coupling Reaction. *Tetrahedron Lett*. **2014**, *55*, 857–860. DOI: [10.1016/j.tetlet.2013.12.022](https://doi.org/10.1016/j.tetlet.2013.12.022).
- [25] Omez-Mart, G.; Inez, M.; Buxaderas, E.; Pastor, M. I.; Alonso, D. A. Palladium Nanoparticles Supported on Graphene and Reduced Graphene Oxide as Efficient Recyclable Catalyst for the Suzuki–Miyaura Reaction of Potassium Aryltrifluoroborates. *J. Mol. Catal. A: Chem*. **2015**, *404–405*, 1–7. DOI: [10.1016/j.molcata.2015.03.022](https://doi.org/10.1016/j.molcata.2015.03.022).
- [26] Scheuermann, G. M.; Rumi, L.; Steurer, P.; Bannwarth, W.; Mülhaupt, R. Palladium Nanoparticles on Graphite Oxide and Its Functionalized Graphene Derivatives as Highly Active Catalysts for the Suzuki–Miyaura Coupling Reaction. *J. Am. Chem. Soc*. **2009**, *131*, 8262–8270. DOI: [10.1021/ja901105a](https://doi.org/10.1021/ja901105a).
- [27] Yamamoto, S-i.; Kinoshita, H.; Hashimoto, H.; Nishina, Y. *Nanoscale* **2012**, *00*, 1–3.
- [28] Shang, N.; Feng, C.; Zhang, H.; Gao, S.; Tang, R.; Wang, C.; Wang, Z. Suzuki–Miyaura Reaction Catalyzed by Graphene Oxide Supported Palladium Nanoparticles. *Catal. Commun*. **2013**, *40*, 111–115. DOI: [10.1016/j.catcom.2013.06.006](https://doi.org/10.1016/j.catcom.2013.06.006).
- [29] Shendage, S.; Patil, B. U.; Nagarkar, J. M. Electrochemical Synthesis and Characterization of Palladium Nanoparticles on Nafion–Graphene Support and Its Application for Suzuki Coupling Reaction. *Tetrahedron Lett*. **2013**, *54*, 3457–3461. DOI: [10.1016/j.tetlet.2013.04.092](https://doi.org/10.1016/j.tetlet.2013.04.092).
- [30] Jang, J. Y.; Jeong, H. M.; Kim, B. K. Compatibilizing Effect of Graphite Oxide in Graphene/PMMA Nanocomposites. *Macromol. Res*. **2009**, *17*, 626–635. DOI: [10.1007/BF03218920](https://doi.org/10.1007/BF03218920).
- [31] Chen, C. H.; Yen, W. H.; Kuan, C. F.; Chiang, C. L. *Polym. Compos*. **2010**, *31*, 18–24.
- [32] Potts, J. R.; Lee, S. H.; Alam, T. M.; An, J.; Stoller, M. D.; Piner, R. D.; Ruoff, R. S. Thermomechanical Properties of Chemically Modified Graphene/Poly(Methyl Methacrylate) Composites Made by in Situ Polymerization. *Carbon* **2011**, *49*, 2615–2623. DOI: [10.1016/j.carbon.2011.02.023](https://doi.org/10.1016/j.carbon.2011.02.023).
- [33] Zeng, X.; Yang, J.; Yuan, W. Preparation of a Poly(Methyl Methacrylate)-Reduced Graphene Oxide Composite with Enhanced Properties by a Solution Blending Method. *European Polym. J*. **2012**, *48*, 1674–1682. DOI: [10.1016/j.eurpolymj.2012.07.011](https://doi.org/10.1016/j.eurpolymj.2012.07.011).
- [34] Pham, V. H.; Dang, T. T.; Hur, S. H.; Kim, E. J.; Chung, J. S. Highly Conductive Poly(Methyl Methacrylate) (PMMA)-Reduced Graphene Oxide Composite Prepared by Self-Assembly of PMMA Latex and Graphene Oxide through Electrostatic Interaction. *ACS Mater. Interfaces Appl. Mater. Interfaces* **2012**, *4*, 2630–2636. — DOI: [10.1021/am300297j](https://doi.org/10.1021/am300297j).
- [35] Thomassin, J.-M.; Trifkovic, M.; Alkarmo, W.; Detrembleur, C.; Jérôme, C.; Macosko, C. Poly(Methyl Methacrylate)/Graphene Oxide Nanocomposites by a Precipitation Polymerization Process and Their Dielectric and Rheological Characterization. *Macromol*. **2014**, *47*, 2149–2155. DOI: [10.1021/ma500164s](https://doi.org/10.1021/ma500164s).
- [36] Trimm, D. L. Thermal stability of catalyst support In *Catalyst Deactivation*; , Ed.; Elsevier Science Publishers, **1991**.; pp 29–51.
- [37] Gupta, R. K.; Alahmed, Z. A.; Yakuphanoglu, F. Graphene Oxide Based Low Cost Battery. *Mater. Lett*. **2013**, *112*, 75–77. DOI: [10.1016/j.matlet.2013.09.011](https://doi.org/10.1016/j.matlet.2013.09.011).
- [38] Chekin, F. Sol–Gel Synthesis of Palladium Nanoparticles Supported on Reduced Graphene Oxide: An Active Electrocatalyst for Hydrogen Evolution Reaction. *Bull. Mater. Sci*. **2015**, *38*, 887–893. DOI: [10.1007/s12034-015-0954-4](https://doi.org/10.1007/s12034-015-0954-4).
- [39] Xu, J.; Gai, S.; He, F.; Niu, N.; Gao, P.; Chen, Y.; Yang, P. Reduced Graphene Oxide/Ni(1-x)Co(x)Al-Layered Double Hydroxide Composites: Preparation and High Supercapacitor Performance. *Dalton Trans*. **2014**, *43*, 11667–11675. DOI: [10.1039/C4DT00686K](https://doi.org/10.1039/C4DT00686K).

- [40] Anton, D. R.; Crabtree, R. H. Dibenzo[a,e]Cyclooctatetraene in a Proposed Test for Heterogeneity in Catalysts Formed from Soluble Platinum-Group Metal Complexes. *Organometallics* **1983**, *2*, 855–859. DOI: [10.1021/om50001a013](https://doi.org/10.1021/om50001a013).
- [41] Mahanta, A.; Mondal, M.; Thakur, A. J.; Bora, U. An Improved Suzuki–Miyaura Cross-Coupling Reaction with the Aid of in Situ Generated PdNPs: Evidence for Enhancing Effect with Biphasic System. *Tetrahedron Lett.* **2016**, *57*, 3091–3095. DOI: [10.1016/j.tetlet.2016.05.098](https://doi.org/10.1016/j.tetlet.2016.05.098).
- [42] Sanjaykumar, S. R.; Mukri, B. D.; Patil, S.; Madras, G.; Hegde, M. S. CeO₂-98PdO-02O₂-δ: Recyclable, Ligand Free Palladium(II) Catalyst for Heck Reaction. *J. Chem. Sci.* **2011**, *123*, 47–54. DOI: [10.1007/s12039-011-0103-6](https://doi.org/10.1007/s12039-011-0103-6).

Catalysis

Sulfonated Graphene-Oxide as Metal-Free Efficient Carbocatalyst for the Synthesis of 3-Methyl-4-(hetero)arylmethylene isoxazole-5(4H)-ones and Substituted Pyrazole

Puja Basak, Sourav Dey, and Pranab Ghosh*^[a]

A straightforward, simple and unprecedented transformative protocol has been accomplished towards furnishing a wide variety of pharmaceutically promising functionalised 3-methyl-4-(hetero)arylmethylene isoxazole-5(4H)-ones and 6-Amino-3-methyl-4-phenyl-1,4-[2,3-*c*]pyrazole-5-carbonitriles. Sulfonated graphene oxide (SGO), a new class of heterogeneous carbocatalyst, was found to be efficient for this one pot rapid

conversion of isoxazoles and pyranopyrazoles from aldehyde. The prepared SGO was characterised by FEG-SEM, HR-TEM, FTIR and was recyclable up to 5th run without a significant drop in its catalytic activity. Metal free synthesis, good to excellent yield, high atom economy, usage of readily available starting material, operational simplicity, easy workup, and recyclable catalyst are the fundamental features of this protocol.

Introduction

In recent times, multicomponent reactions (MCR) are emerging as ecologically sustainable processes in pharmaceutical chemistry, drug designing, and fine chemical synthesis. Due to the increasing demand in green chemistry, MCRs have been paid much attention to achieve high yield, high selectivity and synthetic simplicity in various research fields, such as the discovery of lead compounds in medicinal chemistry or combinatorial chemistry.

Substituted isoxazoles display beneficial biological properties such as antitumor,^[1] antifungal,^[2] cytotoxic, anti-inflammatory,^[3] antibacterial and anti-HIV activities.^[4–6] Furthermore, compounds belonging to this class have been employed as versatile building blocks of a variety of natural products,^[7] synthetic drug molecules,^[8(a,b)] fungicides and insecticides.^[8] In particular, isoxazoles are privileged scaffolds in various organic synthesis,^[9] liquid crystalline material,^[10] optical storage as well as nonlinear optical research^[11] and filter dyes in photographic films^[12(a–d)] (Figure 1). A series of androgen antagonists with isoxazole motifs are found to have medicinal utility^[13(a–c)] and some of them also exhibit full antagonistic activity towards human prostate tumor cells and human metastatic breast cancer cells (Figure 1).^[14]

As a consequence of the above, a number of researchers have set their goal to synthesize isoxazole derivatives. The most common approaches to 3-methyl-4-(hetero)arylmethylene

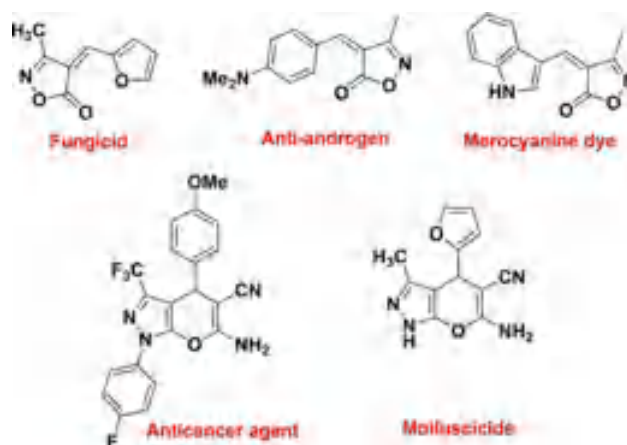


Figure 1. Some example of compounds containing isoxazole and pyranopyrazole moiety.

isoxazole-5(4H)-ones are the multistep condensation of ethyl acetoacetate with hydroxylamine hydrochloride followed by Knoevenagel type reaction with aromatic aldehydes.^[15] The convenient methodologies demand solid state heating, solid-state grinding,^[16] ultrasonic irradiation,^[17] microwave heating,^[18] application of visible light in the presence of sodium acetate in ethanol.^[19] Nevertheless, different moisture sensitive reagents are also employed for the synthesis of isoxazole derivatives like phthalimide-N-oxyl salts,^[20] sodium sulphide,^[21] boric acid,^[22] sulphated polyborate,^[23] sodium azide,^[24] potassium sorbate,^[25] SnII-montmorillonite,^[26] etc.^[27–33] Most of the conditions, however, suffer from drawbacks such as harsh reaction conditions, high temperature, strongly acidic/basic condition, prolonged reaction time, use of homogeneous catalyst, low yield and suffer from rapid loss of catalytic activity. Although, the acceptable yield of isoxazole has been reported in most of the

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protocols where either toxic metal catalyst and costly reagents were used,^[23,24] or people had to suffer handling tedious reaction conditions and work up process.^[19,24, 26] To avoid these drawbacks it is imperative to develop a high yielding greener, radiation and metal-free efficient method for its synthesis with a broad range of substrate applicability.

Another organic moiety pyranopyrazoles, ubiquitous in many biologically active heterocyclic compounds, have attracted much consideration because of its wide range of activity like antimicrobial,^[34] antitumor,^[35] anticancer,^[36] anticoagulant,^[37] diuretic, anti-inflammatory and so on.^[38,39] Some important Pharmaceutical agents and drug molecules containing dihydropyrano[2,3-*c*]pyrazole ring in their core structure were shown in (Figure 1). Due to 'broad spectrum of biological activity, several methods have emerged to synthesize these promising drug molecules. Most of the conventional method for the preparation of dihydropyrano[2,3-*c*]pyrazole involves four-component reaction using various catalytic system such as tungstate sulphuric acid,^[40] Cesium carbonate supported on hydroxyapatite coated Ni_{0.5}Zn_{0.5}Fe₂O₄ magnetic nanoparticles,^[41] nano MgO,^[42] glycerol,^[43] silica coated magnetic NiFe₂O₄ nanoparticles supported H₃PW₁₂O₄₀ (NFSPWA),^[44] maltose,^[45] trichloroacetic acid,^[46] γ-Fe₂O₃@Cu₃Al-LDH,^[47] NaF.^[48] However, considering ecological issues avoidance of the use of hazardous homogeneous catalyst^[46] and toxic metal catalyst^[40-44] is essential to prevent environmental pollution. Based on this conception, it was felt to explore a one pot four-component, environmentally benign, high yielding MCR route of pyranopyrazoles.

As a part of our ongoing efforts, presently we have employed a well documented environmentally benign nanomaterial to synthesize substituted isoxazoles and pyranopyrazoles. As an alternative of nonmetal for important organic transformation, carbonaceous nanomaterials have received considerable attention owing to their sustainability and affordability.^[49] Graphene oxide (GO), a two dimensional unique nanomaterial, upon exhaustive oxidation during preparation, contains a variety of oxygen containing functionalities (e.g. alcohols, epoxides, carboxylates, sulphate groups), these extrinsic functional groups provides moderate acidic properties (pH=4.2) and makes GO an excellent heterogeneous acidic catalyst for various synthetic transformation reactions. Compared with other conventional solid acid catalysts, GO and its derivatives are interesting due to the presence of high surface

area and abundant functional group inactive sites. Previously, GO and its derivative sulfonated graphene oxide (SGO) has been used as an efficient carbocatalyst in hydration, oxidation, Aza-Michael addition, condensation, hydrolysis of cellulose and hydration of alkynes^[50-59] However, synthesis of SGO requires complicated post functionalization process with fuming H₂SO₄ or Chlorosulfonic acid^[57] and to avoid these harsh processes we have reported herein a one pot synthesis of SGO.^[58,59] Among metal free catalysts, sulfonated graphene oxide (SGO) is a highly air-stable, environmentally friendly acid catalyst for use in various chemical reactions.

Considering all these aspects, it was felt to explore the ingenious role of SGO for the synthesis of 3-methyl-4-(hetero) arylmethylene isoxazole-5(4*H*)-ones and 6-Amino-3-methyl-4-phenyl-1,4-[2,3-*c*]pyrazole-5-carbonitriles. Our results indeed show that SGO alone is capable of achieving different types of isoxazoles and pyranopyrazoles with diverse functional groups of pharmaceutical interest.

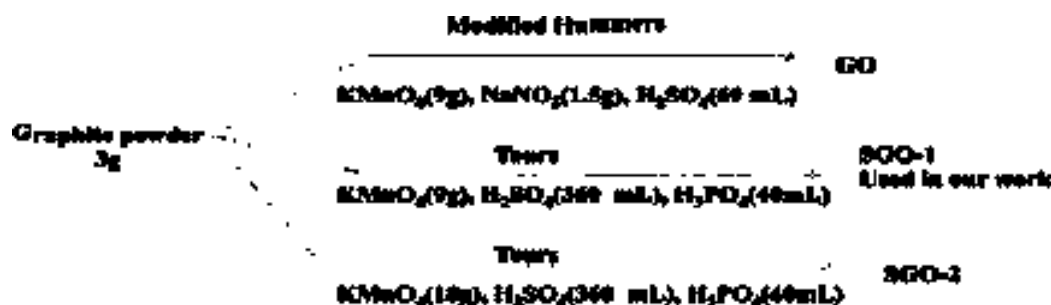
Morphological studies and recyclability experiment of the catalyst SGO has also been carried out. To reduce the environmental hazards and the shortcomings of the previously reported methods a metal free cyclisation pathway has been established in our present work. A possible route of the reaction is also established which implies the profound effect of SGO in governing the reaction.

Result and discussion

We have assessed the catalytic activity of SGO as an acid catalyst in promotion of isoxazole and pyranopyrazole synthesis. SGO was synthesised by the Tours method shown in scheme 1 and was extensively purified to remove any metal impurity.

Fourier-transform infrared spectroscopy (FTIR) studies

The presence of various oxygen containing functional groups, namely hydroxyl, epoxide, carbonyl, sulfonic and carboxylic acid in the synthesised SGO was confirmed by FTIR spectra. FTIR spectra of SGO-1 show significant bands at 1393, 1057 and 857 cm⁻¹ which are accounted for the O=S=O stretching, -SO₃ symmetrical stretching and S-OH stretching vibration respectively. Another vibration modes in SGO comprises of hydroxyls (between 3100–3800 cm⁻¹), carboxyls (1640-1760 cm⁻¹), C-OH



Scheme 1. Preparation of GO, SGO-1, and SGO-2 by different approaches.

vibration (between 3000–3600 cm^{-1}), epoxides (C–O–C at 840 and 1220–1340 cm^{-1}), etc (Figure 7).^[55,59]

Evaluation of catalytic activity of SGO through the synthesis of substituted isoxazoles and pyranopyrazoles

As a first instance, we focused our study on the synthesis of 3-methyl-4-arylmethyleneisoxazole-5(4*H*)-ones. For screening the reaction condition, benzaldehyde, ethyl acetoacetate and hydroxylamine hydrochloride were selected for the model reaction. The effects of the reaction parameters such as solvent, temperature, amount of the catalyst are discussed briefly in Table 1. It was noticed that except toluene other solvents produced the desired product in moderate to good yield. Further investigation revealed that solvent free stirring yielded the corresponding products with an excellent yield at room temperature (Table 1). Inspired by this expectancy, we altered the amount of the catalyst SGO under solvent free condition to achieve the optimal condition of the reaction. Depending upon the time, yield and temperature, 25 mg SGO-1 displayed the best result (entry 8, Table 1) and was opted as optimum quantity for the promotion of the reaction (Table 1). In order to show catalytic efficiency, SGO-1 was also compared with GO and SGO-2 (entry 9, 10 Table 1) and results revealed that SGO-1 exerted the desired product with high yield.

In order to test the water tolerance of the catalyst, we have also carried out the reaction in an aqueous medium (entry 2, Table 1). Upto 82% yield of the entry suggested that there is no chance of poisoning the catalyst by water. To reconfirm the anticipation, after the 1st run the recovered catalyst was dried in a rotary evaporator at 50 °C and reused under the identical

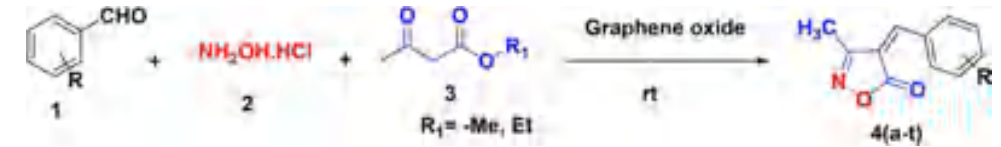
condition and in each case, we observed almost identical yield upto 3rd run.

After achieving the optimised condition, we used some substituted aromatic aldehydes in order to get different substituted 3-methyl-4-(hetero)arylmethylene isoxazole-5(4*H*)-ones. The study also indicated that various aromatic aldehydes afforded the corresponding products with high yield (except 2-nitro and 4-nitrobenzaldehyde). Aldehydes with electron donating groups considerably increase the nucleophilicity on carbonyl oxygen, thereby efficiently yielding the desired product with excellent yield (Table 2, entries 2, 4, 8, 13, 18 and 22), whereas, the aldehydes with electron withdrawing groups affording relatively poor yield of the product. 2-Naphthaldehyde (Table 2, entry 9) gave moderate yield whereas 1-Naphthaldehyde (Table 2, entry 10) did not respond to reaction and the reason may be due to the hindrance offered by steric factor. Again, we examined the reaction in the case of aliphatic aldehyde also (Table 2, entry 20) which gave a trace amount of product. The generality of the reaction was further extended in case of heterocyclic and α,β unsaturated aldehydes which also afforded the corresponding product with good yield (Table 2, entries 7, 11 and 17, 19). The versatility of the reaction was further tested by using methyl acetoacetate instead of ethyl acetoacetate. As expected we get the same product and with almost identical yield (Table 2, entry 21, 22, 23).

Mechanism

A probable mechanism for the synthesis of 3-methyl-4-arylmethylene isoxazole-5(4*H*)-ones by SGO is depicted below (Scheme 2). It is suggested that acid catalysed oxime (I) formation actually initiated the reaction. The oxime so formed

Table 1. Optimization of reaction parameters for the synthesis of 3-methyl-4-(hetero)arylmethylene isoxazole-5(4*H*)-ones based on the result of the following combination in the protocol.^[a]



Entry	Catalyst (SGO-1) mg	Solvent	Temperature °C	Time(h)	Yield (%) ^b
1.	None ^c	Water	Rt	8	Trace
2.	50	Water	Rt	2	82%
3.	50 ^d	Water	100	1	84%
4.	50	Ethanol	Rt	2	74%
5.	50	MeCN	Rt	2	52%
6.	50	Neat	Rt	2	91%
7.	50	Toluene	Rt	2	NR
8.	25	Neat	Rt	1	90%
9.	25 (GO)	Neat	Rt	1	84% ^e
10	25 (SGO-2)	Neat	Rt	1	87% ^f
11.	25	Neat	Rt	12	86%
12.	15	Neat	Rt	4	60%
13.14.	10	Neat	rt	12	49%
	100 ^g	Neat	rt	4	81%

[a] Reaction of benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol), hydroxylamine hydrochloride (2.5 mmol) at room temperature (rt). [b] Isolated yield after purification through column chromatography on silica gel. [c] No sulfonated graphene oxide (SGO) was added. [d] Temperature of the reaction 100 °C.^[e] GO was used as catalyst, [f] SGO-2 was used as catalyst. [g] The reactants are used 5 mmol each.

Table 2. SGO catalysed synthesis of different substituted 3-methyl-4-(hetero)arylmethylene isoxazole-5(4*H*)-ones.^[a]

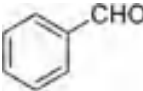
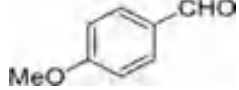
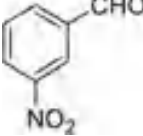
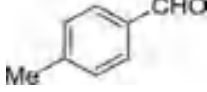
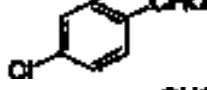
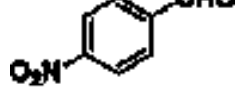
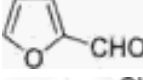
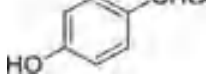
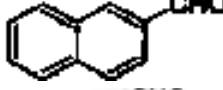
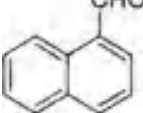
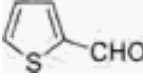
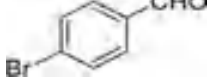
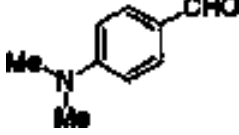
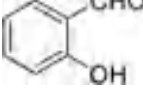
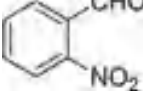
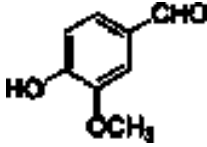
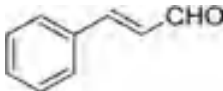
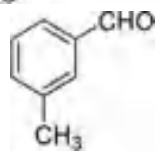
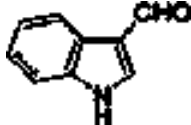

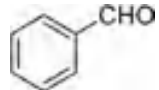
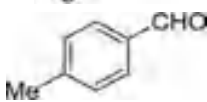
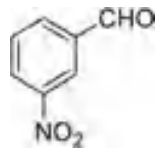
Entry	Aldehyde	R	Product	Time	Yield(%) ^b	Mp (°C) Found	Reported
1.		Et	4a	1	90	141-142	141-143
2.		Et	4b	1.5	89	176-178	174-176
3.		Et	4c	1.5	80	141-143	142-144
4.		Et	4d	1.5	87	135-136	135-136
5.		Et	4e	2	84	119-121	118-120
6.		Et	4f	4	Trace	-	-
7.		Et	4 g	1.5	91	237-239	238-241
8.		Et	4 h	1.5	84	215-216	214-216
9.		Et	4i	3	64	165-166	-
10.		Et	4j	8	NR	-	-
11.		Et	4k	1.5	90	144-146	146-147
12.		Et	4 l	2.5	82	122-125	120-122
13.		Et	4 m	1	93	225-227	227-228
14.		Et	4n	2	82	200-202	198-201
15.		Et	4o	8	Trace	-	-

Table 2. continued							
Entry	Aldehyde	R	Product	Time	Yield(%) ^b	Mp (°C) Found	Reported
16.		Et	4p	2.5	90	214-216	211-214
17.		Et	4q	2	84	172-174	171-173
18.		Et	4r	2.5	87	108-110	-
19.		Et	4 s	2.5	86	239-240	240-242
20.		Et	4 t	8	Trace	-	-
21.		Me	4a	2	84	141-142	141-143
22.		Me	4d	2	86	135-136	135-136
23.		Me	4c	2	78	141-143	142-144

[a] Reaction of aldehyde (1 mmol), ethyl acetoacetate (2 mmol), hydroxylamine hydrochloride (2.5 mmol), SGO (25 mg) at room temperature.
[b] Isolated yield after purification through column chromatography on silica gel.

subsequently guided the Knoevenagel condensation between aromatic aldehyde and intermediate (I). This will be followed by successive cyclisation along with the elimination of ethanol to yield the desired product.

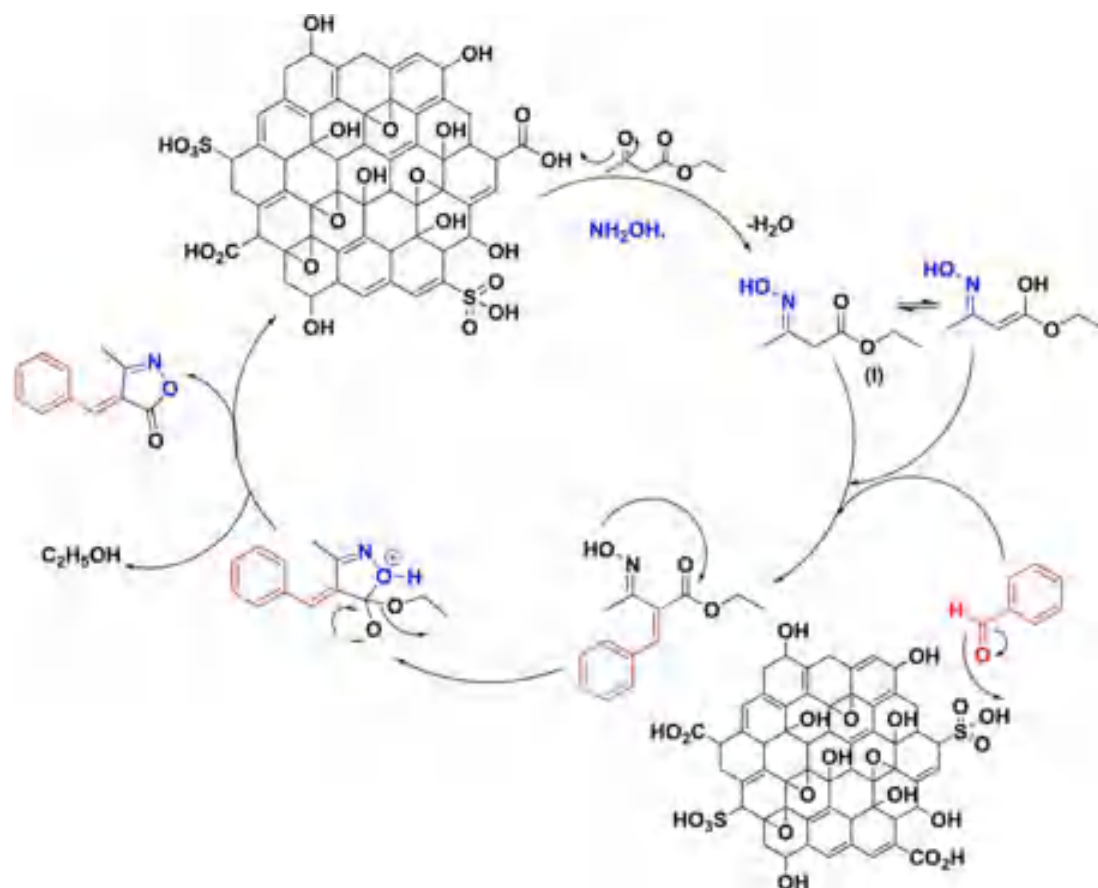
The versatility and the catalytic performance of the prepared catalyst SGO were also observed in one pot-four component synthesis of 1,4-dihydropyrano[2,3-c]pyrazoles using hydrazine hydrate/phenylhydrazine, aromatic aldehyde, malononitrile, ethyl acetoacetate, and the results are summarised below.

To examine the feasibility of the reaction and to optimize the reaction parameters, a model reaction was carried out using phenylhydrazine, ethyl acetoacetate, malononitrile and 4-bromo benzaldehyde as the starting components. Different solvents EtOH, DMF, DCM, CH₃CN, THF (Table 3. Entry 2–6) were implemented to get the desired product in high yield, but H₂O, the green solvent was proved to be more appropriate for this reaction (Table 3 entry 8). However, temperature has a considerable effect on the reaction, as can be seen from (Table 3.

entry 11) that room temperature reaction exerted less than 40% yield.

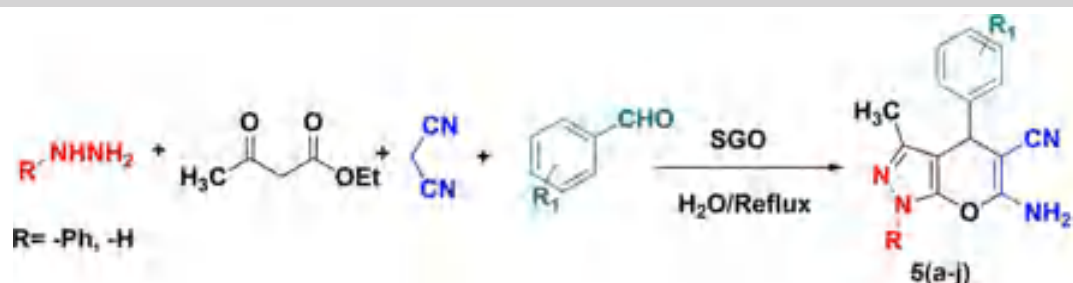
Investigating the catalytic efficiency of synthesized SGO-1, it was compared with GO and SGO-2, but SGO-1 afforded the desired product with high yield. Other Lewis acids were also employed to get the desired product. The results indeed showed that high yield was only achieved in the presence of SGO-1 (Table 4. Entry 3)

After optimizing the reaction parameters, the versatility of the reaction was examined by varying different aromatic aldehydes and the results were summarized in Table 5. Aldehydes with electron withdrawing groups, however, exerted the desired product with high yield and quicken the entire process (Table 5. entry 5, 6, 7, 10). As an extension of our present work we have replaced phenylhydrazine with hydrazine hydrate and the results were satisfactory as shown in (Table 5. entry 8–10).



Scheme 2. A possible route for SGO catalysed synthesis of 3-methyl-4-(hetero) arylmethylene isoxazole-5(4H)-ones.

Table 3. Optimization of reaction condition for the synthesis of 1,4-dihydropyrano[2,3-c]pyrazoles.^[a]



Entry	Time (min)	solvent	Catalyst amount(mg)	Yield(%)
1	120	No solvent	20	< 50
2	60	EtOH /Reflux	20	55
3	60	DMF/Reflux	20	45
4	60	CH ₃ CN/Reflux	20	40
5	120	DCM/Reflux	20	< 40
6	120	THF/Reflux	20	< 30
7	60	H ₂ O/Reflux	20	65
8	60	H ₂ O/Reflux	30	91
9	60	H ₂ O/Reflux	50	94
10	60	H ₂ O/Reflux	10	< 50
11	120	H ₂ O/r.t	40	< 40 ^b

[a] Reaction of phenylhydrazine (1.5 mmol), ethyl acetoacetate (1 mmol), malononitrile (1 mmol), 4-bromo benzaldehyde (1 mmol) and SGO-1 with varying amount at refluxed condition. [b] Room temperature reaction.

Table 4. Comparison of the efficiency of the present catalyst with a different catalytic system.

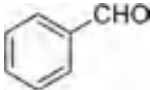
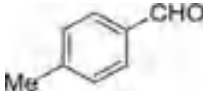
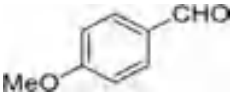
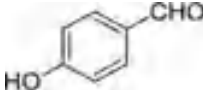
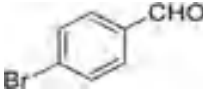
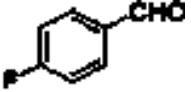
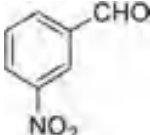
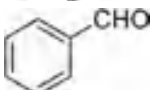
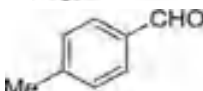
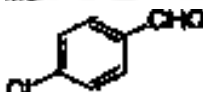
Entry	Condition	Catalyst	Yield(%)
1	No solvent	-	< 30
2	H ₂ O/Reflux	GO	78 ^b
3	H ₂ O/Reflux	SGO-1	91 ^c
3	H ₂ O/Reflux	SGO-2	85
4	H ₂ O/Reflux	Al ₂ O ₃	< 40
5	H ₂ O/Reflux	FeCl ₃	70
6	H ₂ O/Reflux	ZnCl ₂	< 50

[a] Reaction of phenylhydrazine (1.5 mmol), ethyl acetoacetate (1 mmol), malononitrile (1 mmol), 4-bromo benzaldehyde (1 mmol), catalyst 30 mg at refluxed condition in water. [b] GO was prepared by Modified hummers method. [c] SGO-1 by Tours method.

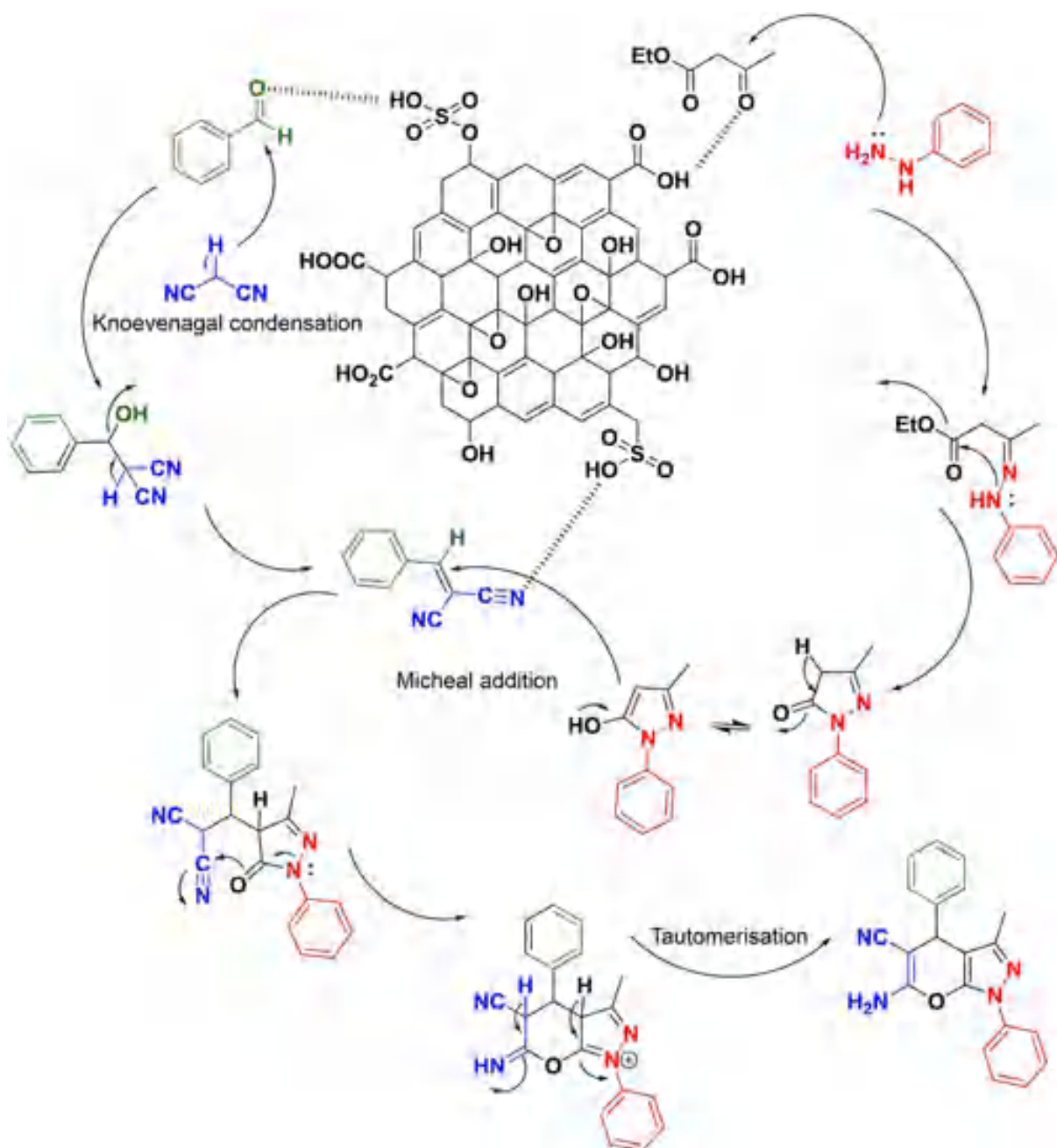
Mechanism

A plausible mechanism for the synthesis of 1,4-dihydropyrano [2,3-*c*]pyrazoles using SGO was shown here (Scheme 3). At first, 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazole-3-one was formed by the condensation of phenylhydrazine and ethyl acetoacetate. Subsequently, Knoevenagel condensation between aromatic aldehyde and malononitrile exerted 2-benzylidenemalonitrile. After that, pyrazolone and benzylidenemalonitrile participated in Michael addition followed by cyclisation. Finally, the desired 1,4-dihydropyrano[2,3-*c*]pyrazole was obtained through tautomerisation in the last step of the reaction mechanism.

Table 5. Synthesis of different substituted 1,4-dihydropyrano[2,3-*c*]pyrazoles.^[a]

Entry	Product	R	Aldehyde	Time	Yield	Mp (°C) Found	Reported
1	5a	-Ph		60	80	169-170	170-172
2	5b	-Ph		60	82	180-182	180-182
3	5c	-Ph		60	84	175-176	177-179
4	5d	-Ph		60	83	197-198	195-197
5	5e	-Ph		50	89	180-182	180-182
6	5f	-Ph		50	91	177-178	174-177
7	5g	-Ph		60	88	188-190	190-191
8	5h	-H		50	77	240-241	240-242
9	5i	-H		50	80	203-205	205-207
10	5j	-H		50	88	231-232	231-233

[a] Reaction of R-NHNH₂ (1.5 mmol), ethyl acetoacetate (1 mmol), malononitrile (1 mmol), aromatic benzaldehyde (1 mmol), 30 mg of SGO at refluxed condition in H₂O.



Scheme 3. A plausible route for the synthesis of 1,4-dihydropyrano[2,3-c]pyrazoles.

HR-TEM and SEM analysis

Morphological study of graphene oxide (SGO) and SGO after 5th run was carried out by HR-TEM microscopy to investigate the disintegration of SGO sheets due to the reactions (Figure 2). After reuse SGO sheets appear to have disintegrated along with slight aggregation. The possible explanation may be put forward that, after catalysis, its reduction to rGO leads disintegration into smaller sheets. Furthermore, the morphological study (SEM images) confirms the formation of multiple

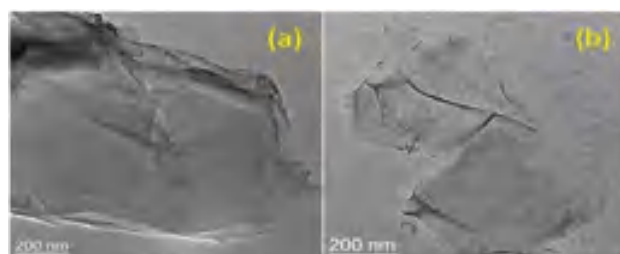


Figure 2. HR-TEM images of (a) SGO and (b) SGO after 5th run.

SGO sheets (Figure 3). Thus, from the above, it may be included that SGO has really taken part in the reaction.

The S content in fresh SGO and the residue left after 5th run was 3.12 and 0.68 wt% respectively (Figure 4). The decreased percentage of S in SGO after 5th run reveals that the functional groups containing sulfur have had participated in the reaction.

For structural studies, XRD spectra of the synthesized catalyst SGO, and that of it after 5th run are shown in Figure 5. A comparison indicates a reduction in intensity of the first peak ($2\theta=9.98$) which is a characteristic peak of sulfonated graphene oxide. After 5th cycle, a new peak appears at $2\theta=$

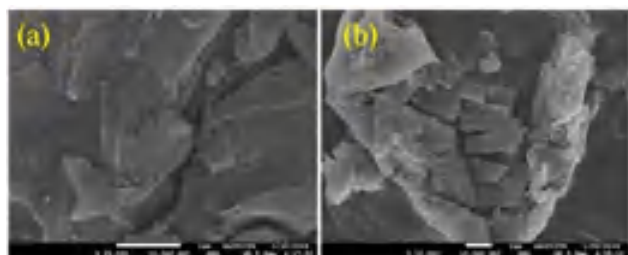


Figure 3. SEM images of (a) SGO and (b) SGO after 5th run.

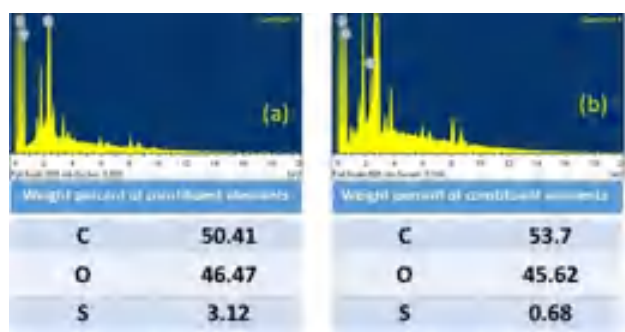


Figure 4. EDX spectra of (a) SGO and (b) SGO after 5th run.

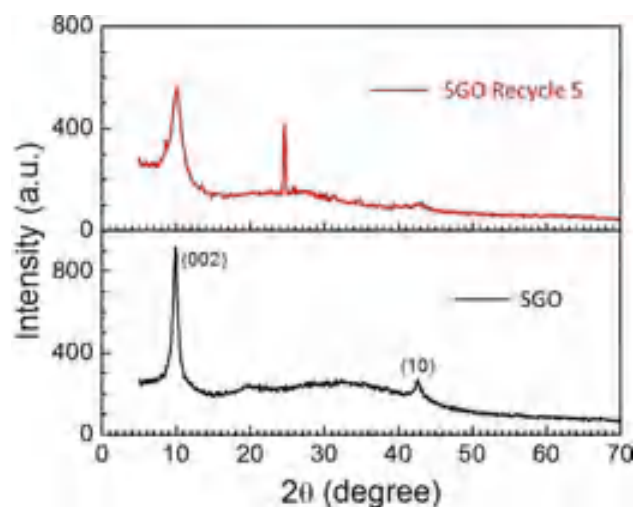


Figure 5. XRD spectra of synthesized SGO and SGO catalyst after 5th recycle.

24.64, which indicates the partial formation of rGO. These results show proportional reduction of the content of functional groups on SGO during the reaction.

The Raman spectra of both SGO and used SGO after 5th run showed a characteristic D peak at 1346 cm^{-1} and G peak at 1582 cm^{-1} (Figure 6). The ratio of intensities of D and G band (I_D/I_G) of SGO and used SGO after 5th run displayed 0.91 and 0.93 respectively. However, the slight increased (I_D/I_G) ratio suggested that during successive runs partial formation of rGO has occurred through the restoration of some C=C bonds.

Recyclability experiment

To check the recyclability of the catalyst SGO, a model reaction between benzaldehyde, ethylacetoacetate and hydroxylamine hydrochloride in presence of 100 mg of SGO was carried out. After the completion of the reaction, ethyl acetate (20 ml) was added into the reaction mixture and centrifuged at 4000 rpm for 5 minutes. The supernatant liquid containing the product was decanted off and the process was repeated thrice. The recovered catalyst was then washed with water and acetone repeatedly to obtain dry SGO. The SGO catalyst could easily be separated from the reaction mixture by simple centrifugation and was found to retain its acidic property, even after 5 runs (Figure 8). This was further supported by comparing the FTIR data of fresh SGO and recovered catalyst (Figure 7). This may be attributed that the involvement of the nucleophilic oxo groups in SGO during the reaction may reduce the catalytic activity of SGO after 5th run.

Conclusion

In conclusion, a green and efficient methodology for the synthesis of a variety of isoxazoles and pyranopyrazoles from commercially available aldehydes has been established. We have unfolded a new role of sulfonated graphene oxide as an efficient and heterogeneous carbocatalyst. SGO, itself is capable of furnishing the desired 3-methyl-4-(hetero)arylmethylene isoxazole-5(4*H*)-ones and 6-Amino-3-methyl-4-phenyl-1,4-[2,3-*c*]

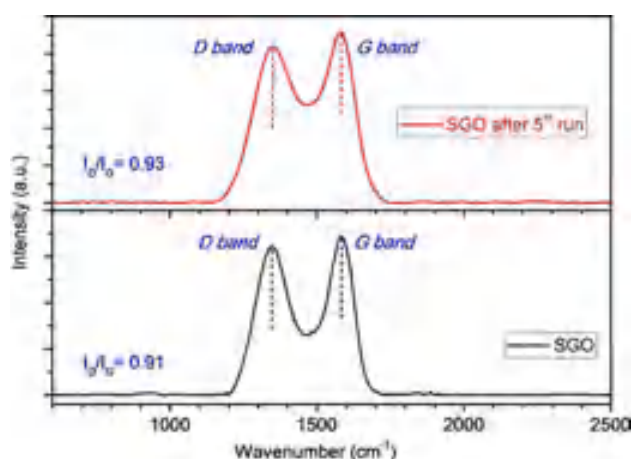


Figure 6. Raman spectra of SGO and SGO after 5th run.

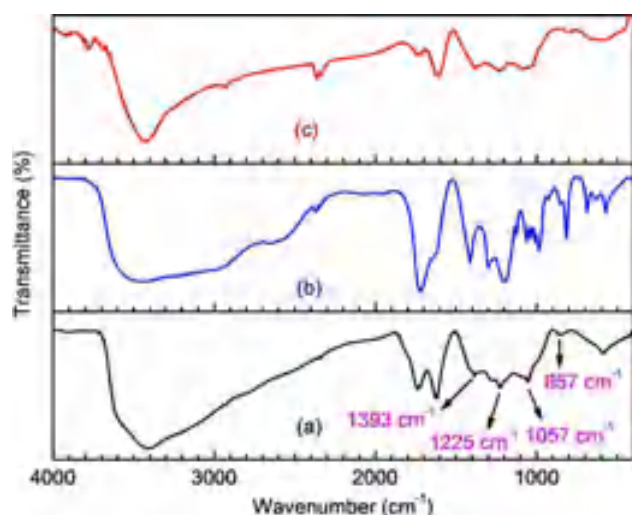


Figure 7. FTIR spectra of SGO (a) fresh (b) after 2nd run (c) after 5th run.

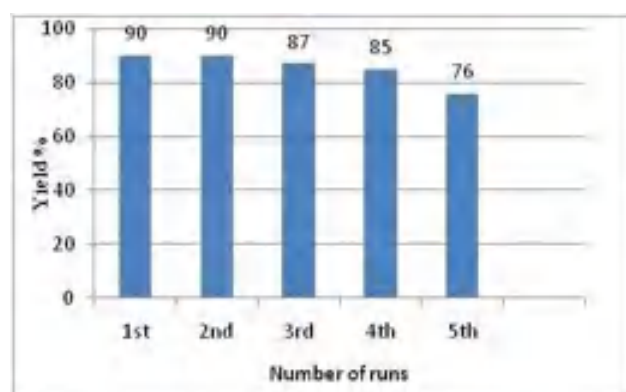


Figure 8. Recyclability experiment of catalyst SGO.

pyrazole-5-carbonitriles with excellent yield. It can be envisioned that such a cheap and robust solid acid catalyst SGO holds great potential for a wide range of acid-catalysed reactions.

Supporting Information Summary

Supplementary data include experimental details, ¹HNMR, ¹³CNMR spectra and IR data of all the synthesized compounds (4a-4s, 5a-5j). HRMS of few compounds have also been presented.

Acknowledgment

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Keywords: Aldehyde · Carbocatalyst · Ethyl acetoacetate · Isoxazole · Pyranopyrazole · Sulfonated graphene oxide.

- [1] E. Vitaku, D. T. Smith, J. T. Njardarson, *J. Med. Chem.* **2014**, *57*, 10257–10274.
- [2] P. Martins, J. Jesus, S. Santos, L. R. Raposo, C. Roma-Rodrigues, P. V. Baptista, A. R. Fernandes, *Molecules* **2015**, *20*, 16852–16891.
- [3] T. Karabasanagouda, A. V. Adhikari, M. Girisha, *Indian J. Chem.* **2009**, *48*, 430–437.
- [4] a) Q. Liu, Y. N. Zhang, *Bull. Korean Chem. Soc.* **2011**, *32*, 3559–3560; b) A. Domling, *Curr. Opin. Chem. Biol.* **2002**, *6*, 306–308; c) C. O. Kappe, *Curr. Opin. Chem. Biol.* **2002**, *6*, 314–320.
- [5] a) E. Rafiee, H. Jafari, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 2463–2466; b) M. S. Patil, C. Mudaliar, G. U. Chaturbhuj, *Tetrahedron Lett.* **2017**, *58*, 3256–3261.
- [6] G. Abbiati, E. M. Beccalli, G. Broggin, C. Zoni, *Tetrahedron* **2003**, *59*, 9887–9893.
- [7] J. Han, H. Guo, X. G. Wang, M. L. Pang, J. B. Meng, *Chin. J. Chem.* **2007**, *25*, 129–131.
- [8] a) X. H. Zhang, Y. H. Zhan, D. Chen, F. Wang, L. Y. Wang, *Dyes Pigm.* **2012**, *93*, 1408–1415; b) B. Kaffle, N. G. Aher, D. Khadka, H. Park, H. Cho, *Chem. Asian J.* **2011**, *6*, 2073–2079.
- [9] M. Pinerio, T. M. Pinho-e-Melo, *Eur. J. Org. Chem.* **2009**, *31*, 5287–5307.
- [10] a) B. Kaffle, N. G. Aher, D. Khadka, H. Park, H. Cho, *Chem. Asian J.* **2011**, *6*, 2073–2079; b) O. H. Kan, I. Adachi, R. Kido, K. Hirose, *J. Med. Chem.* **1967**, *10*, 411–418; c) T. Karabasanagouda, A. V. Adhikari, M. Girisha, *Indian J. Chem.* **2009**, *48*, 430–437; d) M. M. Santos, N. Faria, J. Iley, *Bioorg. Med. Chem. Lett.* **2010**, *20*, 193–195; e) A. Kamal, E. V. Bharathi, J. S. Reddy, *Eur. J. Med. Chem.* **2011**, *46*, 691–703.
- [11] a) X. H. Zhang, Y. H. Zhan, D. Chen, F. Wang, L. Y. Wang, *Dyes Pigm.* **2012**, *93*, 1408–1415; b) P. Diana, A. Carbone, P. Barraja, G. Kelter, H. H. Fiebig, G. Cirrincione, *Bioorg. Med. Chem.* **2010**, *18*, 4524–4529; c) T. Kwon, A. S. Heimann, E. T. Oriaku, K. Yoon, H. Lee, *J. Med. Chem.* **1995**, *38*, 1048–1051.
- [12] a) E. Aret, H. Meekes, E. Vlieg, G. Deroover, *Dyes Pigm.* **2007**, *72*, 339–344; b) Y. K. Kang, K. J. Shin, K. H. Yoo, *Bioorg. Med. Chem. Lett.* **2000**, *10*, 95–99; c) X. H. Zhang, Y. H. Zhan, D. Chen, F. Wang, L. Y. Wang, *Dyes Pigm.* **2012**, *93*, 1408–1415.
- [13] a) P. Conti, C. Dallanoce, M. D. Amici, C. D. Micheli, K. N. Klotz, *Bioorg. Med. Chem.* **1998**, *6*, 401–409; b) M. G. Gordaliza, T. Faircloth, M. A. Castro, J. M. M. Del Corral, M. L. López-Vázquez, A. San Feliciano, *J. Med. Chem.* **1996**, *39*, 2865–2868; c) T. Kwon, A. S. Heimann, E. T. Oriaku, K. Yoon, *J. Med. Chem.* **1995**, *38*, 1048–1051.
- [14] T. Ishioka, A. Kubo, Y. Koiso, K. Nagasawa, A. Itai, Y. Hashimoto, *Bioorg. Med. Chem.* **2002**, *10*, 1555–1566.
- [15] a) Y. Q. Zhang, C. Wang, *Chin. J. Org. Chem.* **2008**, *28*, 141–144; b) Q. Liu, R. T. Wu, *J. Chem. Res.* **2011**, *35*, 598–599.
- [16] Y. Q. Zhang, C. Wang, *Chin. J. Org. Chem.* **2008**, *28*, 1267–1271.
- [17] K. Ablajan, H. Xiamuxi, *Synth. Commun.* **2012**, *42*, 1128–1136.
- [18] S. Tu, J. Zhang, R. Jia, B. Jiang, Y. Zhang, H. Jiang, *Org. Biomol. Chem.* **2007**, *5*, 1450–1453.
- [19] F. Saikh, J. Das, S. Ghosh, *Tetrahedron Lett.* **2013**, *54*, 4679–4682.
- [20] H. Kiyani, F. Ghorbani, *J. Chem. Soc.* **2017**, *21*, 112–119.
- [21] Q. Liu, X. Hou, *Phosphorus Sulfur Silicon Relat. Elem.* **2012**, *187*, 448–453.
- [22] H. Kiyani, F. Ghorbani, *Res. Chem. Intermed.* **2015**, *41*, 2653–2664.
- [23] M. S. Patil, C. Mudaliar, G. U. Chaturbhuj, *Tetrahedron Lett.* **2017**, *58*, 3256–3261.
- [24] H. Kiyani, F. Ghorbani, *Elixir Org. Chem. A.* **2013**, *58*, 14948–14950.
- [25] Q. Liu, H. M. Ai, Z. Li, *Ultrason. Sonochem.* **2011**, *18*, 477–479.
- [26] M. Ahmadzadeh, Z. Zarnegar, J. Safari, *Green Chem. Lett. Rev.* **2018**, *11*, 78–85.
- [27] a) Q. Liu, Y. N. Zhang, *Bull. Korean Chem. Soc.* **2011**, *32*, 3559–3560; b) C. M. Moorhoff, D. F. Schneider, *Monatsh. Chem.* **1998**, *129*, 409–417.
- [28] M. Mirzazadeh, G. H. Mahdavinia, *J. Chem.* **2012**, *9*, 425–429.
- [29] S. Tu, J. Zhang, R. Jia, B. Jiang, Y. Zhang, H. Jiang, *Org. Biomol. Chem.* **2007**, *5*, 1450–1453.
- [30] S. N. Maddila, S. Maddila, W. E. Zyl, S. B. Jonnalagadda, *Res. Chem. Intermed.* **2016**, *42*, 2553–2566.
- [31] H. Kiyani, A. Kanaani, D. Ajloo, F. Ghorbani, M. Vakili, *Res. Chem. Intermed.* **2015**, *41*, 7739–7773.


- [32] D. Setamdideh, *J. Mex. Chem. Soc.* **2015**, *59*, 191–197.
- [33] A. U. Khandebharad, C. H. Gill, B. R. Agrawal, *Res. J. Chem. Sci.* **2015**, *5*, 27–32.
- [34] W. P. Smith, L. S. Sollis, D. P. Howes, P. C. Cherry, I. D. Starkey, K. N. Cobley, H. Weston, J. Scicinski, A. Merritt, A. Whittington, P. Wyatt, N. Taylor, D. Green, R. Bethell, S. Madar, R. J. Fenton, P. J. Morley, T. Pateman, A. Beresford, *J. Med. Chem.* **1998**, *41*, 787–797.
- [35] J. L. Wang, D. Liu, Z. J. Zheng, S. Shan, X. Han, S. M. Srinivasula, C. M. Croce, E. S. Alnemri, Z. Huang, *Proc. Mont. Acad. Sci.* **2000**, *97*, 7124–7129.
- [36] A. M. Grumezescu, E. Andronescu, A. Fica, C. Bleotu, D. E. Mihaiescu, M. C. Chifiriuc, *Int. J. Pharm.* **2012**, *436*, 771–777.
- [37] K. Mazaahir, S. Shilpi, R. K. Khalilur, S. T. Sharanjit, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 4295–4298.
- [38] C. K. Sheng, J. H. Li, N. Hideo, *J. Med. Chem.* **1984**, *27*, 539–544.
- [39] M. Bihani, P. P. Bora, G. Bez, H. Askari, *ACS Sustainable Chem. Eng.* **2013**, *1*, 440–447.
- [40] M. Farahi, B. Karami, I. Sedighimehr, H. M. Tanuraghaj, *Chin. Chem. Lett.* **2014**, *25*, 1580–1582.
- [41] F. Moeinpour, A. Khojastehnezhad, *Chin. Chem. Lett.* **2015**, *26*, 575–579.
- [42] M. Babaie, H. Sheibani, *Arabian J. Chem.* **2011**, *4*, 159–162.
- [43] H. S. Sohal, A. Goyal, R. Sharma, R. Khare, S. Kumar, *Eur. J. Chem.* **2013**, *4*, 450–453.
- [44] B. Maleki, H. Eshghi, M. Barghamadi, N. Nasiri, A. Khojastehnezhad, S. Sedigh Ashrafi, O. Pourshiani, *Res. Chem. Intermed.* **2016**, *42*, 3071–3093.
- [45] M. Kangani, N. Hazeri, M. T. Mghsoodlou, S. M. Habibi-khorasani, S. Salahi, *Res. Chem. Intermed.* **2015**, *41*, 2513–2519.
- [46] Z. Karimi-Jaberi, M. M. ReyazoShams, *Heterocycl. Commun.* **2011**, *17*, 177–179.
- [47] D. Azarifar, M. Tadayoni, M. Ghaemi, *Appl. Organomet. Chem.* **2018**, *32*, 4293.
- [48] R. Konakanchi, R. Gondru, V. B. Nishtala, L. R. Kotha, *Synth. Commun.* **2018**, *48*, 1994–2001.
- [49] D. R. Dreyer, C. W. Bielawski, *Chem. Sci.* **2011**, *2*, 1233–1240.
- [50] C. Su, K. P. Loh, *Acc. Chem. Res.* **2013**, *46*, 2275–2280.
- [51] S. Navalon, A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *Chem. Rev.* **2014**, *114*, 6179–6212.
- [52] F. Hu, M. Patel, F. Luo, C. Flach, R. Mendelsohn, E. Garfunkel, H. He, M. Szostak, *J. Am. Chem. Soc.* **2015**, *137*, 14473–14480.
- [53] D. R. Dreyer, H.-P. Jia, C. W. Bielawski, *Angew. Chem. Int. Ed.* **2010**, *49*, 6813–6816; *Angew. Chem.* **2010**, *122*, 6965–6968.
- [54] C. Su, R. Tandiana, J. Balapanuru, W. Tang, K. Pareek, C. T. Nai, T. Hayashi, K. P. Loh, *J. Am. Chem. Soc.* **2015**, *137*, 685–690.
- [55] B. Majumdar, D. Sarma, T. Bhattacharya, T. K. Sarmsa, *ACS Sustainable Chem. Eng.* **2017**, *5*, 9286–9294.
- [56] Z. Wei, Y. Yang, Y. Hou, Y. Liu, X. He, S. Deng, *ChemCatChem.* **2014**, *6*, 2354–2363.
- [57] S. Zhu, J. Wang, W. Fan, *Catal. Sci. Technol.* **2015**, *5*, 3845–3858.
- [58] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, *ACS Nano* **2010**, *8*, 4806–4814.
- [59] Q. Hou, W. Li, M. Ju, L. Liu, Y. Chen, Q. Yang, *RSC Adv.* **2016**, *6*, 104016–104024.

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Convenient one-pot synthesis of 1,2,4-oxadiazoles and 2,4,6-triarylpyridines using graphene oxide (GO) as a metal-free catalyst: importance of dual catalytic activity†

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A convenient and efficient process for the synthesis of 3,5-disubstituted 1,2,4-oxadiazoles and 2,4,6-triarylpyridines has been described using an inexpensive, environmentally benign, metal-free heterogeneous carbocatalyst, graphene oxide (GO). GO plays a dual role of an oxidizing agent and solid acid catalyst for synthesizing 1,2,4-oxadiazoles and triarylpyridines. This dual catalytic activity of GO is due to the presence of oxygenated functional groups which are distributed on the nanosheets of graphene oxide. A broad scope of substrate applicability and good sustainability is offered in this developed protocol. The results of a few control experiments reveal a plausible mechanism and the role of GO as a catalyst was confirmed by FTIR, XRD, SEM, and HR-TEM analysis.

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Introduction

Nitrogen-containing heterocyclic compounds are valuable due to their potential application as a key intermediate in the synthesis of numerous drugs.¹ 3,5-Disubstituted 1,2,4-oxadiazoles are a remarkably important class of nitrogen-containing heterocyclic scaffold as they are widely used as pharmacophores, bioactive molecules, and functional materials.^{1,2} Among the oxadiazole derivatives, the 1,2,4-oxadiazole motif has received interest due to its application as a stable bioisostere in place of an amide, ester, or urea functionality.³ These compounds when selectively functionalized, have performed as various muscarinic agonists,⁴ benzodiazepine receptor partial agonists,⁵ serotonergic (5-HT₃) antagonists,⁶ dopamine transporters,⁷ antischistosomal drugs,⁸ G-quadruplex ligands for probing DNA superstructure in antitumor research.^{9,10} Another nitrogen-containing heterocycle, pyridines are ubiquitous and have attracted much attention due to their unique biological, medicinal, and pharmaceutical properties.^{11–13} 2,4,6-Triarylpyridines are frequently used as a synthon in supramolecular chemistry owing to their π -stacking ability.¹⁴ In addition, pyridines have received a growing interest as monomeric building blocks in thin films and organometallic polymers.¹⁵

It is noteworthy that, in the last decade many efficient protocols have been developed to synthesize these significant heterocyclic moieties. Among the known synthetic strategies of

1,2,4-oxadiazoles, the most conventional approach involves the use of amidoximes as starting materials or intermediates. Other common approaches involve *O*-acylation of amidoximes by an activated carboxylic acid derivative, followed by cyclodehydration,¹⁶ the 1,3-dipolar cycloaddition of nitrile oxide to nitriles, and intermolecular cyclodehydration reaction of amidoximes with aldehydes followed by oxidative dehydrogenation.^{17,18} Besides this, base-mediated one-pot synthesis, MnO₂/GO based synthesis, microwave-assisted efficient synthesis of oxadiazoles using PTSA and ZnCl₂ have also been reported.^{17,19–21} On the other hand, efficient protocols for the synthesis of another important heterocycle 2,4,6-triarylpyridines involve condensation reaction between benzaldehydes, acetophenones, and ammonium acetate in presence of different acid catalysts^{22–24} *e.g.* pentafluorophenylammonium triflate,²³ heteropolyacid,²⁵ HClO₄-SiO₂,²⁶ Brønsted-acidic ionic liquid,²⁷ and nano-metal catalyst.^{23,28,29} Nevertheless, most of the traditional synthetic method requires harsh reaction condition, prolonged heating, and use of toxic transition metal catalyst. However, only a few protocols have shown greener context and high atom economy. Multicomponent reaction (MCR) is considered to be an effective and straightforward approach for the synthesis of heterocycles in an atom economical way. Considering the efficiency of MCRs and the aspects of green chemistry,^{30–33} there is a need for new methods which involve metal-free, environmentally friendly catalytic protocol to synthesize 1,2,4-oxadiazoles and 2,4,6-triarylpyridines.

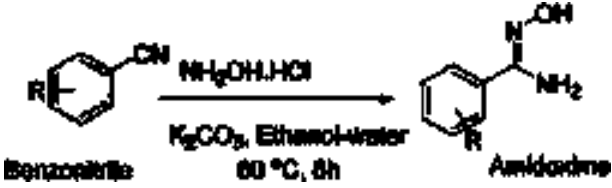
Recently, carbonaceous nanomaterials have gained considerable attention in green chemistry, especially in the development of metal-free sustainable heterogeneous catalysts.^{34–36} Among the carbonaceous nanomaterials, graphene oxide (GO)

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† Electronic supplementary information (ESI) available: The scanned copies of ¹H and ¹³C NMR are included in this section. See DOI: 10.1039/d1ra06331f



Table 1 Optimization of reaction condition for the synthesis of amidoxime (intermediate)^a



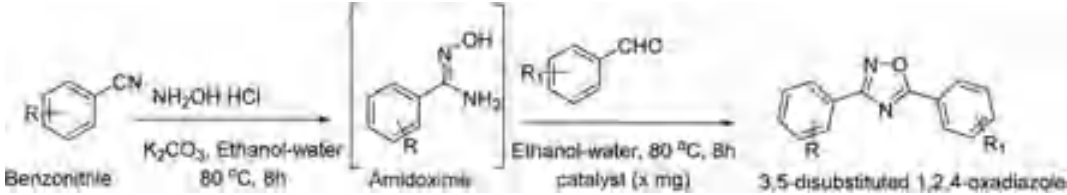
Entry	Solvent	Temp (°C)	Base	Yield ^b (%)
1	Water	100	K ₂ CO ₃	68
2	Water	100	CS ₂ CO ₃	72
3	Ethanol	80	K ₂ CO ₃	66
4	Ethanol	80	TEA	70
5	Ethanol-water	80	TEA	80
6	Ethanol-water	80	—	<50 ^c
7	Ethanol-water	80	K ₂ CO ₃	91
8	Ethanol-water	80	K ₂ CO ₃	94 ^d
9	Ethanol-water	80	CS ₂ CO ₃	93
10	THF	120	K ₂ CO ₃	54
11	Toluene	110	K ₂ CO ₃	<50
12	CH ₃ CN	82	K ₂ CO ₃	68
13	DMF	120	K ₂ CO ₃	76

^a Reaction condition: benzonitrile (1.5 mmol), hydroxylamine hydrochloride (1.5 mmol), base (1.5 mmol) and solvent (5 mL).

^b Isolated yield. ^c No base was added. ^d The reaction was carried out for 24 h.

has been reported to accelerate several organic transformation reactions replacing different hazardous chemical reagents. GO, a thin two-dimensional unique nanomaterial contains different oxygen functionalities like carbonyl (C=O), carboxyl (COOH), epoxy (O), and hydroxyl (OH) on its edges and basal plane.^{37–39} On account of the presence of large surface area, and diverse oxygen functionalities, GO has been identified as a heterogeneous solid acid catalyst (pH 4.5 at 0.1 mg mL⁻¹) as well as a benign oxidizing agent.^{40–42} Its abundance from low-cost natural carbon sources, low toxicity, reusability, and metal-free catalytic activity makes this heterogeneous carbon material (GO) as a promising carbocatalyst. Due to the inherent acidic and oxidation property of GO, it is explored as a catalyst in different organic transformations like C–H oxidations,⁴³ oxidative coupling of amines⁴⁴ to the imines, oxidation of thioanisole,⁴⁵ glutaraldehyde to glutaric acid,⁴⁶ 5-hydroxymethylfurfural,⁴⁷ benzylpyrazolyl coumarins,⁴⁸ Fisher esterification,⁴⁹ and transamidation.^{50–54} The versatility and sustainability of GO as a catalyst leads us to employ GO as a metal-free catalyst for the synthesis of substituted 1,2,4-oxadiazoles and 2,4,6-triarylpyridines to overcome the drawbacks of the reported protocols and reduce environmental hazards. Our present study explores the role of GO as an acid catalyst as well as an oxidizing agent using the surface-bound oxygen-containing functional groups. To unleash the dual catalytic activity of GO, a plausible oxidative cyclization pathway to the

Table 2 Optimization of reaction condition for the synthesis of 3,5-disubstituted 1,2,4-oxadiazole from amidoxime^a

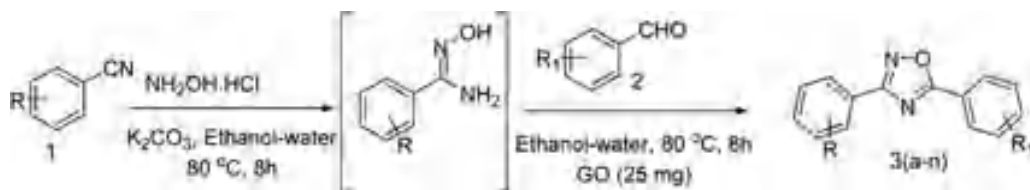


Entry	Catalyst (mg)	Solvent	Temperature	Time (h)	Yield ^a
1	—	Ethanol	80	12	Trace
2	15 (GO)	Ethanol	80	12	73
3	15 (GO)	Water	100	12	77
4	15 (GO)	DMF	100	12	60
5	15 (GO)	Ethanol-water	80	12	79
6	15 (GO)	Ethanol-water	80	24	83
7	25 (GO)	Ethanol-water	80	12	89
8	25 (GO)	Ethanol-water	80	8	88
9	25 (GO)	Ethanol-water	RT	12	52
10	25 (graphite)	Ethanol-water	80	8	40 ^b
11	25 (rGO)	Ethanol-water	80	8	45 ^c
12	25 (GO)/oxidant	Ethanol-water	80	8	67 ^d
13	Oxidant	Ethanol-water	80	8	<40 ^e
14	25 (GO)	Neat	80	8	69
15	25 (GO)	Ethanol-water	80	8	85 ^f
16	—	Ethanol-water	80	8	Nil ^f

^a Reaction condition: benzaldehyde (1 mmol), amidoxime (1 mmol) and ethanol-water (5 mL), pristine GO (25 mg). ^b Graphite powder was used.

^c Reduced graphene oxide (rGO). ^d GO and extra oxidant 30% H₂O₂ (1 mmol) were used. ^e Only H₂O₂ was used. ^f Under inert atmospheric condition.

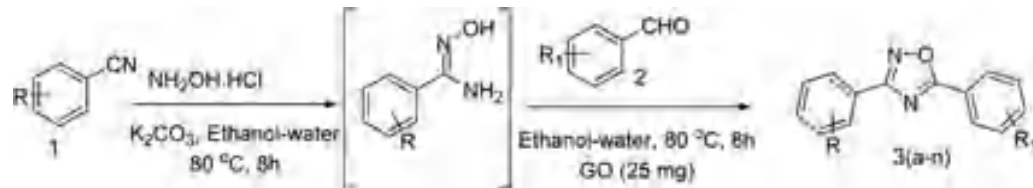


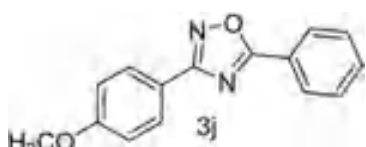
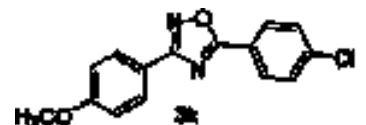
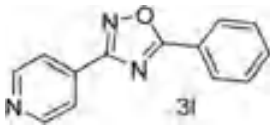
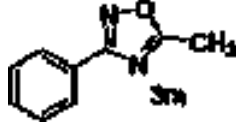
Table 3 Synthesis of diversely functionalised 3,5-disubstituted 1,2,4-oxadiazole^a

Entry	R	R ₁	Product	Yield ^b (%)
1	4-H	4-H		83
2	4-H	4-CH ₃		81
3	4-H	4-OCH ₃		80
4	4-H	4-F		78
5	4-H	3-NO ₂		75
6 ^c	4-H	4-N(CH ₃) ₂	No 1,2,4-oxadiazole, only imine formation	—
7	4-H	1-Napthaldehyde		62
8	4-H	Furan-2-carbaldehyde		72
9	4-H	Thiophene-2-carbaldehyde		70
10	4-CH ₃	4-H		80



Table 3 (Contd.)



Entry	R	R ₁	Product	Yield ^b (%)
11	4-OCH ₃	4-H		78
12	4-OCH ₃	4-Cl		82
13	4-Pyridinecarbonitrile	4-H		68
14	4-H	CH ₃ CHO		75
15 ^d	4-H	Heptaldehyde	NR	—
16 ^e	CH ₃ CN	4-H	NR	—

^a In the first step, benzonitrile (1 mmol), hydroxylamine hydrochloride (1.5 mmol), K₂CO₃ (1.5 mmol), and ethanol–water (5 mL) were stirred for 8 h and in the 2nd step benzaldehyde (1 mmol) and GO (*x* mg) were added and stirred for another 8 h. ^b Isolated yield after purification through column chromatography. ^c 4-(Dimethylamino)benzaldehyde (1 mmol) was used. ^d Heptaldehyde was used. ^e Acetonitrile (1 mmol) was used.

synthesis of oxadiazoles and triarylpyridines under benign conditions has also been established.

Results and discussion

For screening the reaction parameter benzonitrile (1.5 mmol), hydroxylamine hydrochloride (1.5 mmol), and base (1.5 mmol) were taken as model substrates to find out suitable conditions for the synthesis of amidoxime (intermediate). To satisfy our curiosity, the reaction was performed in different solvents *e.g.* polar protic, polar aprotic, and nonpolar. However, in absence of a base, a low yield was obtained (Table 1, entry 6). Gratifyingly, the reaction results showed (Table 1) the formation of amidoxime is highly favored in mixed solvent ethanol–water (1 : 3) using K₂CO₃ as a base. To control the reaction conditions, after completion of the reaction, the solvent was removed by a rotary evaporator to separate the intermediate. While monitoring the TLC, only one spot was observed other than the reactant. After workup and purification by column

chromatography, 91% yield of the intermediate (amidoxime) was obtained (Table 1, entry 7). Although other bases were also employed (Table 1, entries 2, 5 and 9), K₂CO₃ exerted the best result in an ethanol–water solvent. The synthesized amidoxime was characterized by NMR (300 MHz) and the spectral data was shown in ESI.†

In the second step of the reaction, benzaldehyde (1 mmol) and the catalyst were added to the reaction mixture to prioritize the synthesis of 3,5-disubstituted 1,2,4-oxadiazole. In presence of a small amount of GO, 73% yield of the product was obtained at 80 °C temperature (entry 2). Further increase in the amount of GO, proved to be favorable in the formation of 1,2,4-oxadiazole. No product was obtained when the reaction was carried out in absence of GO (Table 2, entry 1). High yield of the product was observed in aqueous ethanolic solution with a ratio ethanol–water (1 : 3). The outstanding catalytic activity of GO in ethanol–water (1 : 3) is revealed due to its better dispersibility. To establish the catalytic activity of GO, few controlled experiments were carried out using various catalysts. Other



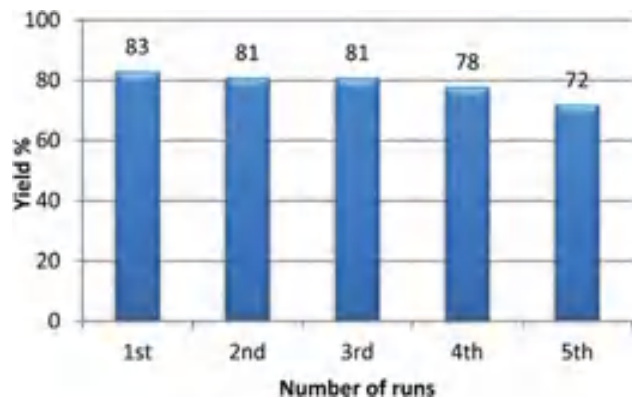


Fig. 1 Recyclability study of GO for the synthesis of 3,5-disubstituted 1,2,4-oxadiazole.

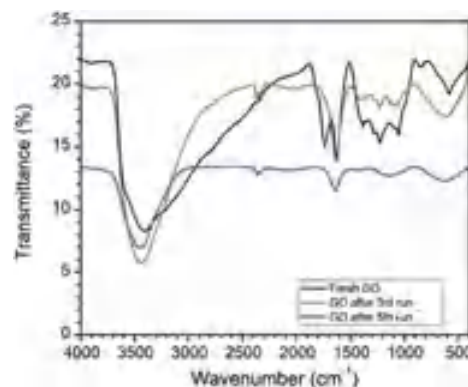


Fig. 3 Comparative FTIR of fresh GO, after 3rd run and 5th run.

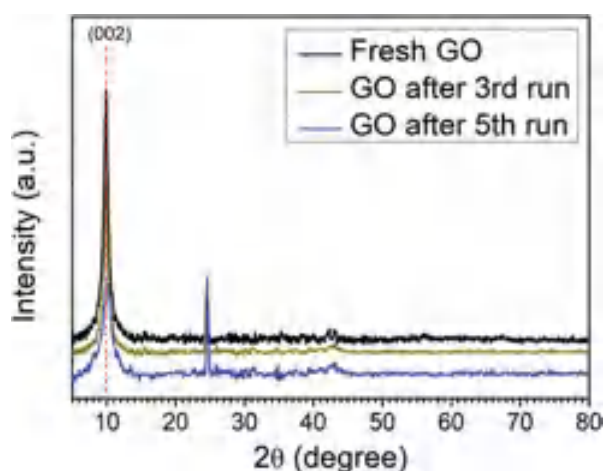


Fig. 2 XRD spectra of fresh GO, after 3rd run and 5th run.

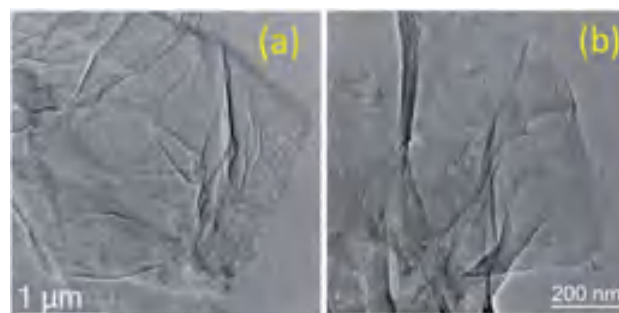


Fig. 4 HR-TEM images of (a) GO and (b) GO after the 5th run.

carbonaceous nanomaterials *e.g.* powdered graphite, reduced graphene oxide (rGO) showed less catalytic activity than GO because they do not contain as many hydroxyl and carboxylic groups, indicating oxygen-containing functional groups in graphene oxide have a profound effect in catalyzing the synthesis of 3,5-disubstituted 1,2,4-oxadiazole. The reaction was also carried out in presence of GO and an oxidant H_2O_2 , the reason for the low yield may be due to the oxidation of benzaldehyde to benzoic acid in presence of H_2O_2 (Table 2, entry 12). The yield was not improved when only an H_2O_2 oxidant was used (entry 13). These control experiments infer the significant catalytic role of GO in the reaction.

The scope and the substrate applicability of the reaction were also examined and results were summarized in Table 3.

With the optimized condition in hand, we have extended the substrate scope in organic transformations and a series of diversely substituted aldehydes and benzonitriles are subjected to the synthesis of 3,5-disubstituted 1,2,4-oxadiazole (Table 3). Both the electron-donating (Table 3, entries 2, 3, 10 and 11) and electron-withdrawing groups (entries 4 and 5) in the substituents afforded the corresponding product in good to excellent

yield which indicates that the electronic nature of the substituents is not much influential to determine the yield of the reaction. 1-Naphthaldehyde offered the product with low yield and the reason may be due to steric hindrance (Table 3, entry 7). In the case of 4-*N,N*-(dimethylamino) benzaldehyde, the reaction was stopped at amidoxime, no desired oxadiazole is obtained (Table 3, entry 6). The present catalytic condition showed a wide tolerance to heterocyclic aldehydes (Table 3 entries 8, 9) and they were found to be highly effective to afford the corresponding product. The generality of the reaction was examined in the case of aliphatic aldehydes also. Interestingly, acetaldehyde was equally effective to yield the product with excellent quantity (entry 14). However, no product was found with increasing the side chain of aliphatic aldehydes (entry 15). It was disappointing that acetonitrile did not exert the corresponding product (entry 16). Due to the heterogeneous nature

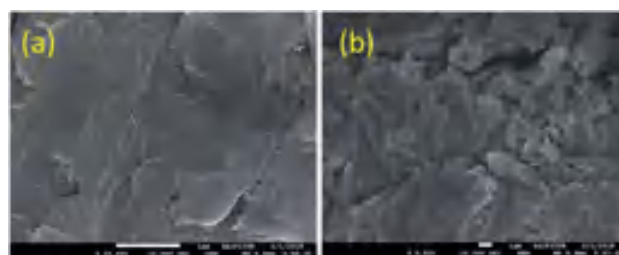


Fig. 5 SEM images of (a) GO and (b) GO after the 5th run.



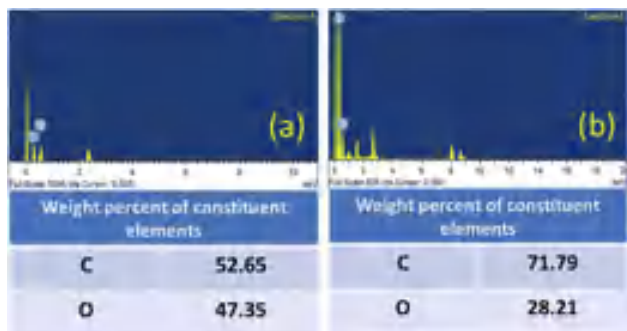
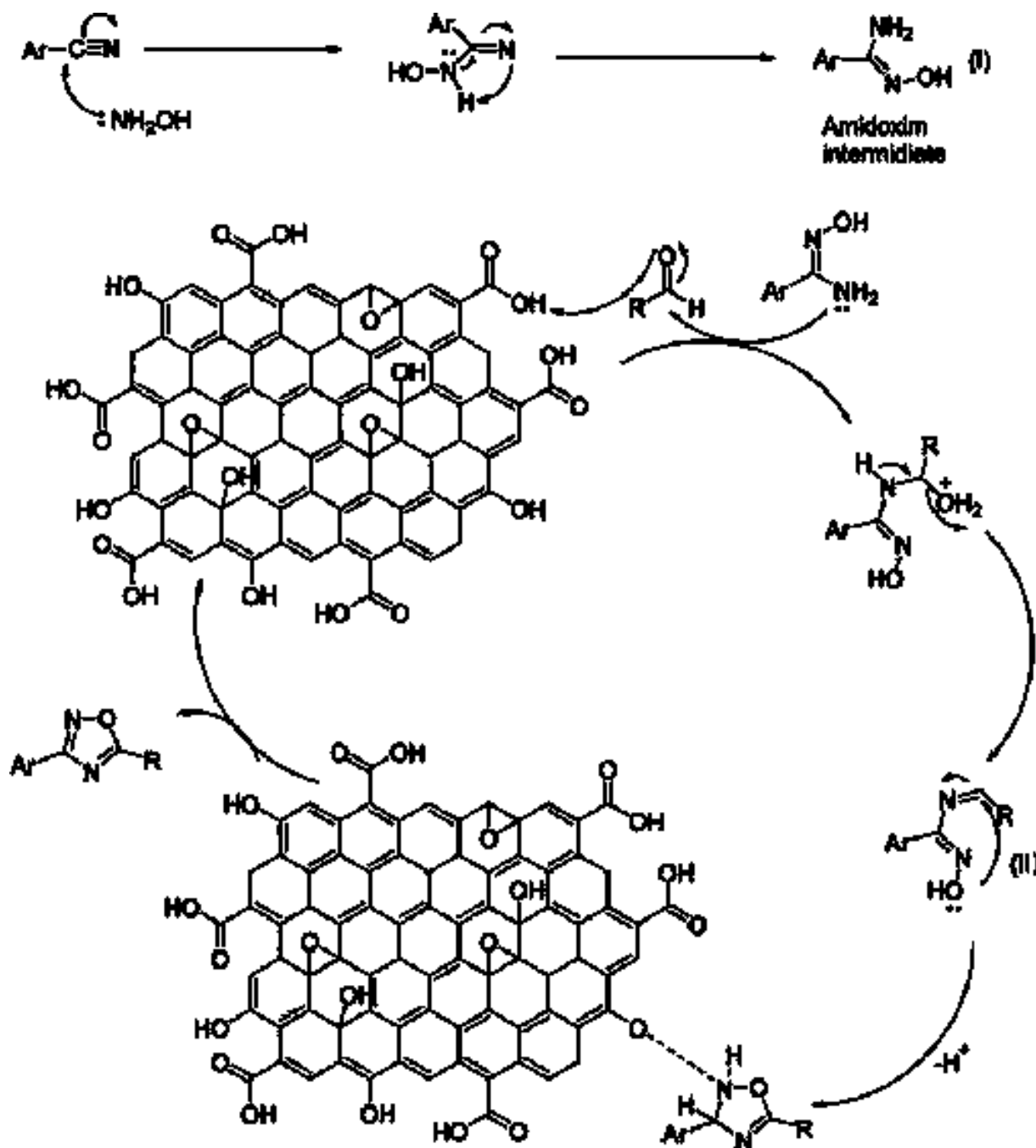


Fig. 6 EDX spectra of (a) GO and (b) GO after the 5th run.

of GO, it can be easily isolated from the reaction mixture and reused. The catalytic activity of GO was examined for five consecutive cycles for the synthesis of 3,5-disubstituted 1,2,4-oxadiazole from benzaldehyde and amidoxime under reflux conditions for 8 h to ascertain the recyclability potential of graphene oxide. The catalyst was separated after each recycle and washed thoroughly with ethanol and reused. A marginal decrease in the yield of oxadiazole is observed after each cycle which indicates a slight loss of catalytic activity of GO with recycling (Fig. 1).



Scheme 1 A plausible route to the synthesis of 3,5-disubstituted 1,2,4-oxadiazole.



The catalytic activity arises some structural changes in GO which were analyzed by FTIR, XRD, SEM, HR-TEM, and EDX analysis. The XRD spectra of fresh GO and recycled catalyst (GO after 3rd run and 5th run) are shown in Fig. 2. A comparison of spectra indicates the reduction in the intensity of the first characteristic peak of GO ($2\theta = 10.01$) and the appearance of a new peak at ($2\theta = 24.62$) due to the formation of partially reduced GO/reduced graphene oxide upon reuse. These results confirm the reduction of the functional groups of GO during the reaction.

The comparison of the FTIR spectra revealed that the peak at 1720 cm^{-1} in fresh GO has completely disappeared after reuse. In addition to this, the peak intensity of the hydroxyl group at 3400 cm^{-1} decreases after reuse. FTIR data strongly support the reduction of GO to rGO in this oxidative cyclization reaction (Fig. 3).

A morphological study of GO and GO after the 5th run was carried out using SEM and HR-TEM to investigate the disintegration of graphene oxide sheets after the reaction. In HR-TEM, the graphene oxide sheets are disintegrated into smaller sheets with slight aggregation after recycle (Fig. 4).

Moreover, the SEM images (Fig. 5) also reveal the formation of multiple small GO sheets after reuse. As GO catalyzes the reaction, its reduction to reduced graphene oxide possibly leads to its disintegration into smaller sheets.

The contribution of oxygen-containing functionalities during the reaction was further confirmed by the EDX analysis (Fig. 6). The carbon content was increased from 52.65% (fresh GO) to 71.79% (GO after 5th run) and the oxygen content was decreased from 47.35% (fresh GO) to 28.21% (GO after 5th run). The decrease in the oxygen content, therefore, indicates the role of GO in this cyclization reaction as an oxidizing agent. The universality and the dual catalytic activity of GO were established by a plausible mechanism (Scheme 1).

Mechanism

A plausible mechanism of GO catalyzed synthesis of 3,5-disubstituted 1,2,4-oxadiazole has been proposed (Scheme 1) based on literature reports⁵⁵ and our controlled experiments (Table 2). Now, we propose the formation of amidoxime intermediate (I) from benzonitrile and hydroxylamine hydrochloride. However, in the first step, a base is required to neutralize hydroxylamine hydrochloride. In the 2nd step protonation of aldehyde, oxygen occurs and subsequently, a nucleophilic attack by amidoxime occurs at the electrophilic center of aldehyde. After that, the intermediate (II) undergoes an oxidative cyclization in presence of GO to produce 1,2,4-oxadiazoles. This mechanism is in good agreement with the control experiments as described in Table 2. However, in presence of only H₂O₂ oxidant the yield of the reaction was diminished (Table 2, entry 11). The role of GO as an acid catalyst and an oxidant was confirmed as its absence did not lead to the oxadiazole product. The oxygen containing functional groups of GO are consumed during the reaction and the activity of GO gradually decreases. The activity of recycled GO is lower than that of the pristine GO. Good yield of the product was obtained even under an inert atmosphere which strongly establish (Table 2, entry 15), the prime role of GO in absence of atmospheric oxygen.

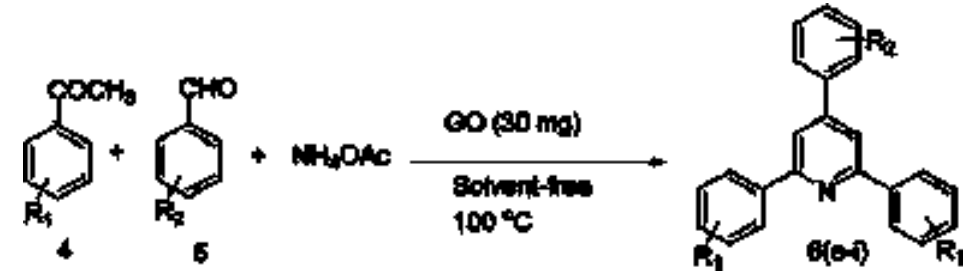
In connection to our previous work, the catalytic activity of synthesized GO was investigated in the case of 2,4,6-triarylpyridine synthesis. To find out the optimized condition of the reaction, acetophenone (2 mmol), benzaldehyde (1 mmol), and ammonium acetate (2 mmol) were selected as model substrates and the results were summarized in Table 4. As can be seen from Table 4 that neither polar nor non-polar solvents were found suitable for the reaction. The best result was obtained under neat or solvent-free conditions (Table 4, entry 11). The effect of temperature and the amount of catalyst was also examined to find out the optimized condition. Studies reveal

Table 4 Optimization of reaction condition for the reaction of 2,4,6-triarylpyridine^a

Entry	Temp (°C)	Solvent	Catalyst GO (mg)	Ammonia source	Yield ^b (%)
1	100	H ₂ O	15	NH ₄ OAc	65
2	80	Ethanol	15	NH ₄ OAc	55
3	100	DMF	15	NH ₄ OAc	53
4	100	DMSO	15	NH ₄ OAc	45
5	100	Toluene	15	NH ₄ OAc	50
6	80	CH ₃ CN	15	NH ₄ OAc	30
7	100	Ethylene glycol	15	NH ₄ OAc	60
8	100	Neat	15	NH ₄ OAc	83
9	120	Neat	30	NH ₄ OAc	90
10	150	Neat	30	NH ₄ OAc	86
11	100	Neat	30	NH ₄ OAc	92
12	80	Neat	30	NH ₄ OAc	80
13	100	Neat	—	NH ₄ OAc	Trace
14	100	Neat	30	(NH ₄) ₂ CO ₃	48
15	100	Neat	30	(NH ₄) ₂ SO ₄	Trace
16	RT	Neat	30	NH ₄ OAc	<20

^a Reaction condition: acetophenone (2 mmol), benzaldehyde (1 mmol), ammonium acetate (2 mmol), reaction time: 2 h ^b Isolated yields.



Table 5 Synthesis of 2,4,6-triarylpyridine derivatives in presence of GO^a

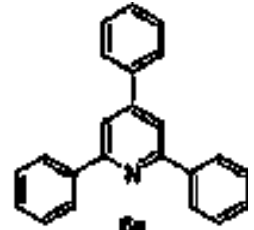
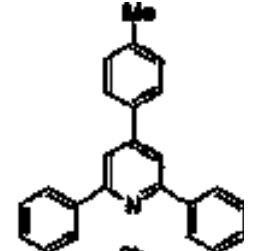
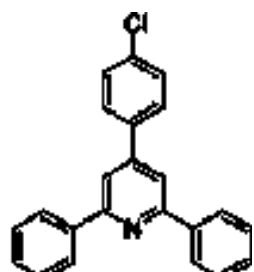
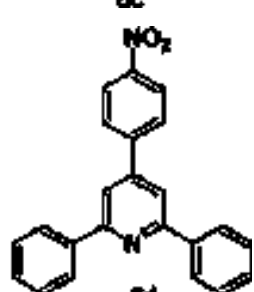
Entry	R ₁	R ₂	Product	Time (h)	Yield ^b (%)
1	4-H	4-H		2 h	92
2	4-H	4-Me		2 h	86
3	4-H	4-Cl		1 h	93
4	4-H	4-NO ₂		1 h	88



Table 5 (Contd.)

Entry	R ₁	R ₂	Product	Time (h)	Yield ^b (%)
5	4-H	4-OMe		2 h	83
6	4-H	Furan-2-carbaldehyde		2 h	78
7	4-Me	4-H		2 h	87
8	4-Br	4-H		1 h	90



Table 5 (Contd.)

Entry	R ₁	R ₂	Product	Time (h)	Yield ^b (%)
9	4-Br	4-Cl		1 h	94

^a Reaction condition: acetophenone (2 mmol), benzaldehyde (1 mmol), ammonium acetate (2 mmol) and GO (30 mg). ^b Isolated yields after purification through column chromatography on silica gel.

that the yield increases with increasing temperature. Room-temperature reaction afforded only 20% of the product which strongly indicates the vital role of temperature in governing the reaction (entry 16). However, after 120 °C the yield decreases with a further increase in temperature (Table 4, entry 10). To ascertain the catalytic function of GO, the reaction was performed in absence of catalyst and only a trace amount of product was obtained. The amount of the catalyst was also altered and optimum condition offered a neat reaction with 30 mg of GO at 100 °C temperature. Ammonia sources other than ammonium acetate produced the corresponding product with a low yield (Table 4, entries 14 and 15).

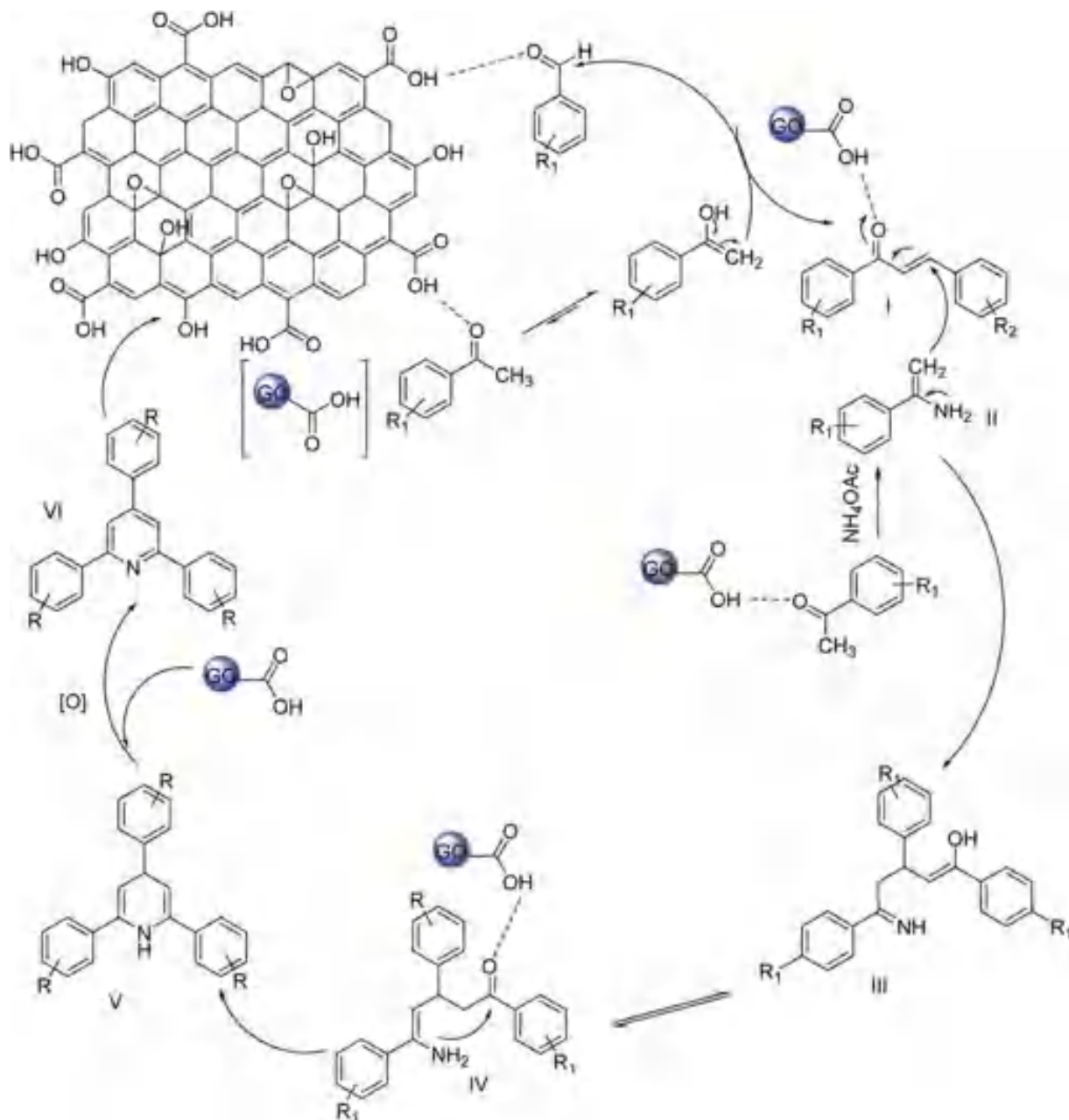
To explore the catalytic activity of GO, a wide variety of aromatic aldehydes and substituted acetophenones were subjected to synthesize 2,4,6-triarylpyridines. Based on the above-optimized results, GO catalyzed reaction was carried out at 100 °C temperature under solvent-free condition and the results are summarized in Table 5. First, the compatibility of the substituents in the phenyl ring of acetophenone and benzaldehyde was examined. All the electron-donating and electron-withdrawing substituents on the aromatic ring are equally capable of producing the corresponding product with a good yield. However, aldehydes with electron-withdrawing groups (Table 5, entries 3, 4 and 9) exerted excellent yield and reacted faster than the aromatic aldehydes with electron-donating groups (Table 5, entries 2, 5, 7). In the case of heterocyclic

aldehydes, the reaction has smoothly proceeded as can be seen from entry 6.

The probable mechanism for the synthesis of 2,4,6-triarylpyridines using GO is described in Scheme 2. At the very first step, aldol condensation occurs between acetophenone and aromatic aldehyde. Acetophenone is activated by the acidic group of GO and the nucleophilic attack occurs at the carbonyl carbon of aromatic aldehyde. After that, an acetophenone molecule is reacted with an ammonia source to form enamine (II). In the third stage, Michael's addition between enamine (II) and the aldol condensation product (I) occurs. GO protonates the condensation product (I), thereby facilitating the Michael addition by enamine (II). The intermediate (III) is formed by Michael's addition and undergoes cyclization to form dihydropyridine (V). At the last step, oxidation to dihydropyridine occurs and gives the ultimate product 2,4,6-triarylpyridine (VI).

The main advantage of heterogeneous catalysts is their reusability in organic transformation. For this purpose, acetophenone, benzaldehyde, and ammonium acetate were taken in a reaction vial in presence of 120 mg of GO. The model reaction was carried out for an adequate time and after completion of the reaction, ethyl acetate (30 mL) was added into the reaction vial and centrifuged for four times. The supernatant liquid after centrifugation was decanted off and the residual catalyst was washed repeatedly with water and acetone. The dry GO was then collected and reused for the 2nd run. It was observed that GO





Scheme 2 A possible route of GO catalyzed synthesis of 2,4,6-triarylpyridine.

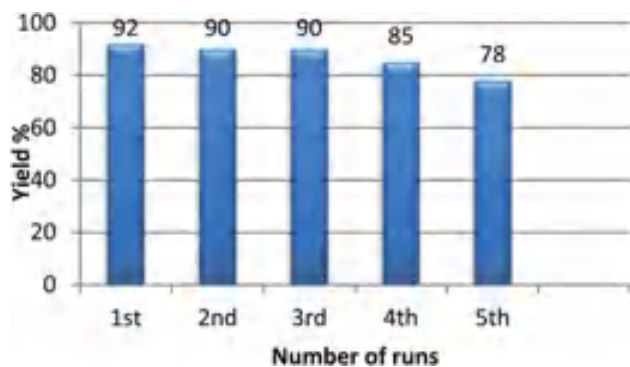


Fig. 7 Recyclability experiment of catalyst GO for the synthesis of 2,4,6-triarylpyridines.

could easily retain its acidic property without significant loss in its catalytic activity even after 5 successive runs (Fig. 7). Although there may be loss of some oxygenated groups due to subsequent runs, the recovered catalyst shows almost equal efficiency with the fresh GO.

Conclusion

In conclusion, carbocatalyst based metal-free catalytic pathway for the synthesis of 3,5-disubstituted 1,2,4-oxadiazoles and 2,4,6-triarylpyridines has been established. The solid acid catalyst, GO facilitates the synthesis of oxadiazoles and triarylpyridines with good yield, easy recovery, and under mild



reaction conditions. The dual catalytic activity of GO has been demonstrated without any undesired by-product under benign conditions. The present protocol gives a clean strategy to provide a wide variety of substituted oxadiazoles and pyridines.

Conflicts of interest

The authors declare no competing financial interest.

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References

- M. Carbone, Y. Li, C. Irace, E. Mollo, F. Castelluccio, D. A. Pascale, G. Cimino, R. Santamaria, W. Y. Guo and M. Gavagnin, *Org. Lett.*, 2011, **13**, 2516–2519.
- A. V. Gulevich, A. S. Dudnik, N. Chernyak and V. Gevorgyan, *Chem. Rev.*, 2013, **113**, 3084–3213.
- R. J. Mathvink, A. M. Barritta, M. R. Candelore, M. A. Cascieri, L. Deng, L. Tota, C. D. Strader, M. J. Wyvratt, M. H. Fisher and A. E. Weber, *Bioorg. Med. Chem. Lett.*, 1999, **9**, 1869–1874.
- F. I. Carroll, J. L. Gray, P. Abrahm, M. A. Kuzemko, A. H. Lewin, J. W. Boja and M. J. Kuhar, *J. Med. Chem.*, 1993, **36**, 2886–2890.
- J. W. Clitherow, P. Beswick, W. J. Irving, D. I. C. Scopes, J. C. Barnes, J. Clapham, J. D. Brown, D. J. Evans and A. G. Hayes, *Bioorg. Med. Chem. Lett.*, 1996, **6**, 833–838.
- C. B. Vu, E. G. Corpuz, T. J. Merry, S. G. Pradeepan, C. Bartlett, R. S. Bohacek, M. C. Botfield, C. J. Eyermann, B. A. Lynch, I. A. MacNeil and M. K. Ram, *J. Med. Chem.*, 1999, **42**, 4088–4098.
- J. Matsumoto, T. Takahashi, M. Agata, H. Toyofuku and N. Sasada, *Jpn. J. Pharmacol.*, 1994, **65**, 51–57.
- B. L. Mylari, T. A. Beyer, P. J. Scott, C. E. Aldinger, M. F. Dee, T. W. Siegel and W. J. Zembrowski, *J. Med. Chem.*, 1992, **35**, 457–465.
- B. S. Orlek, F. E. Blaney, F. Brown, M. S. G. Clark, M. S. Hadley, J. Hatcher, G. J. Riley, H. E. Rosenberg, H. J. Wadsworth and P. Wyman, *J. Med. Chem.*, 1991, **34**, 2726–2735.
- T. Nakamura, M. Asano, Y. Sekiguchi, Y. Mizuno, K. Tamaki, F. Nara, Y. Kawase, Y. Yabe, D. Nakai, E. Kamiyama, Y. Urasaki-Kaneno, T. Shimozato, H. Doi-Komuro, T. Kagari, W. Tomisato, R. Inoue, M. Nagasaki, H. Yuita, K. Oguchi-Oshima, R. Kaneko and T. Nishi, *Eur. J. Med. Chem.*, 2012, **51**, 92–98.
- B. Y. Kim, J. BokAhn, H. W. Lee, S. K. Kang, J. H. Lee, J. S. Shin, S. K. Ahn, C. Hong and S. S. Yoon, *Eur. J. Med. Chem.*, 2004, **39**, 433–447.
- L. Tian, J. Song, J. Wang and B. Liu, *Chin. Chem. Lett.*, 2009, **20**, 288–291.
- R. D. Allen and G. A. R Johnston, *Med. Res. Rev.*, 1983, **3**, 91–118.
- E. C. Constable, C. E. Housecroft, M. Neuburger, D. Phillips, P. R. Raithby, E. Schofield, E. Sparr, D. A. Tocher, M. Zehnder and Y. Zimmermann, *Dalton Trans.*, 2000, **13**, 2219–2228.
- E. Figgemeier, E. C. Constable, C. E. Housecroft and Y. C. Zimmermann, *Langmuir*, 2004, **20**, 9242–9248.
- (a) Y. Wang, R. L. Miller, D. R. Sauer and S. W. Djuric, *Org. Lett.*, 2005, **7**, 925–928; (b) S. Kandre, P. R. Bhagat, R. Sharma and A. Gupte, *Tetrahedron Lett.*, 2013, **54**, 3526–3529; (c) B. Kaboudin and L. Malekzadeh, *Tetrahedron Lett.*, 2011, **52**, 6424–6426; (d) B. Kaboudin and F. Saadati, *Tetrahedron Lett.*, 2007, **48**, 2829–2832.
- J. K. Augustine, V. Akabote, S. G. Hegde and P. Alagarsamy, *J. Org. Chem.*, 2009, **74**, 5640–5643.
- D. S. Bolotin, K. I. Kulish, N. A. Bokach, G. L. Starova, V. V. Gurzhiy and V. Y. Kukushkin, *Inorg. Chem.*, 2014, **53**, 10312–10324.
- (a) M. Okimoto and Y. Takahashi, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 427–428; (b) D. B. Repke, H. P. Albrecht and J. G. Moffat, *J. Org. Chem.*, 1975, **40**, 2481–2487.
- W. Wang, H. Xu, Y. Xu, T. Ding, W. Zhang, Y. Ren and H. Chang, *Org. Biomol. Chem.*, 2016, **14**, 9814–9822.
- F. Saadati, B. Kaboudin, R. Hasanloei, Z. Namazifar, X. Marset and G. Guillena, *Appl. Organomet. Chem.*, 2020, **34**, 5838–5849.
- M. Adib, A. H. Jahromi, N. Tavoosi, M. Mahdavi and H. R. Bijanzadeh, *Tetrahedron Lett.*, 2006, **47**, 2965–2967.
- N. Montazeri and S. Mahjoob, *Chin. Chem. Lett.*, 2012, **23**, 419–422.
- J. Safari, S. Gandomi-Ravandi and M. Borujeni, *Chem. Sci.*, 2013, **125**, 1063–1070.
- M. M. Heravi, K. Bakhtiari, Z. Daroogheha and F. F. Bamoharram, *Catal. Commun.*, 2007, **8**, 1991–1994.
- L. Nagarapu, A. R. Peddiraju and S. Apuri, *Catal. Commun.*, 2007, **8**, 1973–1976.
- A. Davoodnia, M. Bakavoli, R. Moloudi, N. Tavakoli-Houseini and M. Khashi, *Monatsh. Chem.*, 2010, **141**, 867–870.
- A. Maleki and R. Firouzi-Haji, *Sci. Rep.*, 2018, **8**, 17303–17311.
- E. Tabrizian, A. Amoozadeh, S. Rahmani, E. Imanifar, S. Azhari and M. Malmir, *Chin. Chem. Lett.*, 2015, **26**, 1278–1282.
- G.-L. Wu and Q.-P. Wu, *Adv. Synth. Catal.*, 2018, **360**, 1949–1953.
- R. Mishra, A. Jana, A. K. Panday and L. H. Choudhury, *Org. Biomol. Chem.*, 2018, **16**, 3289–3302.
- C.-Y. Chen, W.-P. Hu, P.-C. Yan, G. C. Senadi and J.-J. Wang, *Org. Lett.*, 2013, **15**, 6116–6119.
- C. C. Răzvan, R. Eelco and V. A. O. Romano, *Green Chem.*, 2014, **16**, 2958–2975.
- D. S. Su, S. Perathoner and G. Centi, *Chem. Rev.*, 2013, **113**, 5782–5816.
- O. Mohammadi, M. Golestanzadeh and M. Abdouss, *New J. Chem.*, 2017, **41**, 11471–11497.
- N. Oger, Y. F. Lin, E. L. Grogneec, F. Rataboul and F. X. Felpin, *Green Chem.*, 2016, **18**, 1531–1537.



- 37 D. R. Dreyer and C. W. Bielawski, *Chem. Sci.*, 2011, **2**, 1233–1240.
- 38 S. Navalon, A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *Chem. Rev.*, 2014, **114**, 6179–6212.
- 39 S. Zhu, J. Wang and W. Fan, *Catal.: Sci. Technol.*, 2015, **5**, 3845–3858.
- 40 C. Su and K. P. Loh, *Acc. Chem. Res.*, 2013, **46**, 2275–2285.
- 41 (a) D. R. Dreyer, H. P. Jia and C. W. Bielawski, *Angew. Chem., Int. Ed.*, 2010, **49**, 6813–6816; (b) D. R. Dreyer, H. P. Jia, A. D. Todd, G. Jeng and C. W. Bielawski, *Org. Biomol. Chem.*, 2011, **9**, 7292–7295.
- 42 T. Szabo, E. Tombacz, E. Illes and I. Dekany, *Carbon*, 2006, **44**, 537–545.
- 43 H. P. Jia, D. R. Dreyer and C. W. Bielawski, *Tetrahedron*, 2011, **67**, 4431–4434.
- 44 H. Huang, J. Huang, Y. M. Liu, H. Y. He, Y. Cao and K. N. Fan, *Green Chem.*, 2012, **14**, 930–934.
- 45 G. A. B. Gonçalves, S. M. G. Pires, M. M. Q. Simoes, M. G. P. M. S. Neves and P. A. A. P. Marques, *Chem. Commun.*, 2014, **50**, 7673–7676.
- 46 X. Chu, Q. Zhu, W.-L. Dai and K. Fan, *RSC Adv.*, 2012, **2**, 7135–7139.
- 47 G. Lv, H. Wang, Y. Yang, T. Deng, C. Chen, Y. Zhu and X. Hou, *ACS Catal.*, 2015, **5**, 5636–5646.
- 48 T. A. J. Siddiqui, B. G. Ghule, S. Shaikh, P. V. Shinde, K. C. Gunturu, P. K. Zubaidha, J. M. Yun, C. O. Dwyer, R. S. Mane and K. H. Kim, *RSC Adv.*, 2018, **8**, 17373–17379.
- 49 B. Roy, D. Sengupta and B. Basu, *Tetrahedron Lett.*, 2014, **55**, 6596–6600.
- 50 R. Wang, Z. Wu, Z. Qin, C. Chen, H. Zhu, J. Wu, G. Chen, W. Fan and J. Wang, *Catal.: Sci. Technol.*, 2016, **6**, 993–997.
- 51 S. Bhattacharya, P. Ghosh and B. Basu, *Tetrahedron Lett.*, 2018, **59**, 899–903.
- 52 Z. Chen, Y. Wen, Y. Fu, H. Chen, M. Ye and G. Luo, *Synlett*, 2017, **28**, 981–985.
- 53 J. Porwal, N. Karanwal, S. Kaul and S. L. Jain, *New J. Chem.*, 2016, **40**, 1547–1553.
- 54 H. P. Mungse, N. Bhakuni, D. Tripathi, O. P. Sharma, B. Sain and O. P. Khatri, *J. Phys. Org. Chem.*, 2014, **27**, 944–951.
- 55 K. B. Dhopte, R. S. Zambare, A. V. Patwardhan and P. R. Nemade, *RSC Adv.*, 2016, **6**, 8164–8172.

