Taylor & Francis
Taylor & Francis Group

Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

Montmorillonite K-10 catalyzed Mannich reaction: Synthesis of aminonaphthoquinone derivatives from Lawsone

Sankaranarayanan Jayashree & Kalegowda Shivashankar

To cite this article: Sankaranarayanan Jayashree & Kalegowda Shivashankar (2018): Montmorillonite K-10 catalyzed Mannich reaction: Synthesis of aminonaphthoquinone derivatives from Lawsone, Synthetic Communications, DOI: 10.1080/00397911.2018.1466334

To link to this article: https://doi.org/10.1080/00397911.2018.1466334

SYNTHETIC COMMUNICATIONS®
https://doi.org/10.1080/00397911.2018.1466334

Taylor & Francis
Taylor & Francis Group

Montmorillonite K-10 catalyzed Mannich reaction: Synthesis of aminonaphthoquinone derivatives from Lawsone

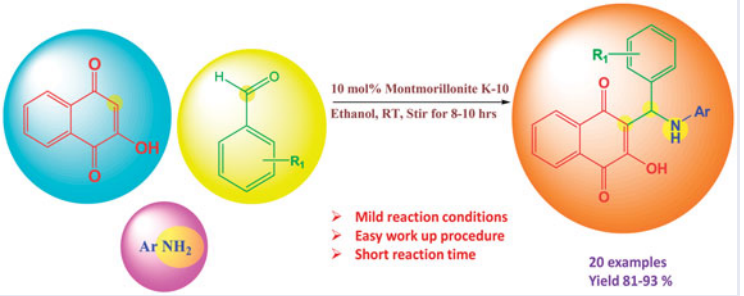
Sankaranarayanan Jayashree and Kalegowda Shivashankar

P.G. Department of Chemistry, Central College Campus, Bangalore University, Bangalore, Karnataka, India

ABSTRACT

An efficient one-pot protocol for the synthesis of 2-((substituted amino)(4-phenyl)methyl)-3-hydroxy-naphthalene-1,4-dione derivatives has been developed by the three-component reaction of 2-hydroxy-naphthalene-1,4-dione, aromatic aldehydes and anilines/heterocyclic amines using montmorillonite K-10 as a catalyst. The advantages of this method include short reaction time, excellent yield and easy work-up.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received 21 February 2018

KEYWORDS
Lawsone; Mannich reaction; montmorillonite K-10; naphthoquinone; pigment

Introduction

Multicomponent reactions which combine three or more substrates in one pot have gained considerable attention in recent times. These reactions have avoided the tedious steps of protection and deprotection of functional groups, isolation of intermediates, thereby reducing the generation of waste.[1–11]

Naphthoquinones constitute a main class of naturally occurring compounds and exhibit wide variety of fluorescent, pharmacological and medicinal properties such as antidiabetic,[12] anti-HIV,[13] anticancer,[14] trypsin inhibitor,[15] anti-inflammatory,[16] molluscicidal,[17] antiallergic,[18] anticoagulant,[19] antiacute pancreatitis,[20] antibacterial,[21] antimalarial[22] and antifungal activities.[23] Recently, bis-aziridinyl dimeric naphthoquinone

CONTACT Kalegowda Shivashankar shivashankark@gmail.com P.G. Department of Chemistry, Central College Campus, Bangalore University, Bangalore – 560 001, Karnataka, India.
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lsyc.
Supplemental data for this article can be accessed on the publisher's website.

derivatives displayed potent antileukemic activities[24] and the coumarin-naphthoquinone conjugates targeted the human topoisomerase II effectively.[25] The presence of secondary amino group in naphthoquinones has led to interesting biologically active compounds such as 2,2-dimethyl-3-phenylamino-2,3-dihydronaphtho[1,2-*b*]furan-4,5-diones which are active against Chagas disease[26] and phenylaminonaphthoquinones with excellent cytotoxic activities.[27] Naphthoquinones also exhibited electrochemical properties,[28] nonlinear optical properties,[29] potent organic fluorescent switching property[30] and orange/red light emitting property in OLEDs.[31]

Lawsone (2-hydroxy-naphthalene-1,4-dione) is a natural dye (orange color) present in henna plants. People have been using Lawsone as cosmetic dye for hair, finger nails, silk, wool, leather, skin, etc., since the Bronze age[32] and for the detection of latent finger marks on paper surfaces.[33] A literature survey revealed that one pot synthesis of these scaffolds have been achieved by employing catalysts such as $InCl_3$,[34] *p*-toluene sulfonic acid,[35] phenylphosphinic acid,[36] ionic liquids,[37] copper oxide[38] and dendrimers.[39] But these methods involved the use of costly reagents, toxic solvents, long reaction time and harsh conditions. Therefore, there is a need for efficient protocol to obtain these valuable organic pigments.

In recent years, montmorillonite K-10 has gained extensive attention in organic synthesis due to its unique properties of readily affordable, commercially available, non-hazardous and tolerance to moisture as well as air making it the ideal catalyst. Owing to these advantages, montmorillonite K-10 has been explored as an efficient catalyst for various organic transformations such as Diels-Alder reaction,[40] Pinacol-Pinacolone rearrangement,[41] Friedlander synthesis,[42] Fischer indole synthesis,[43] pyrolytic elimination reaction[44] Friedel-Crafts acylation and alkylation,[45] Heck vinylation,[46] and formylation of phenols[47] without loss of its activity.

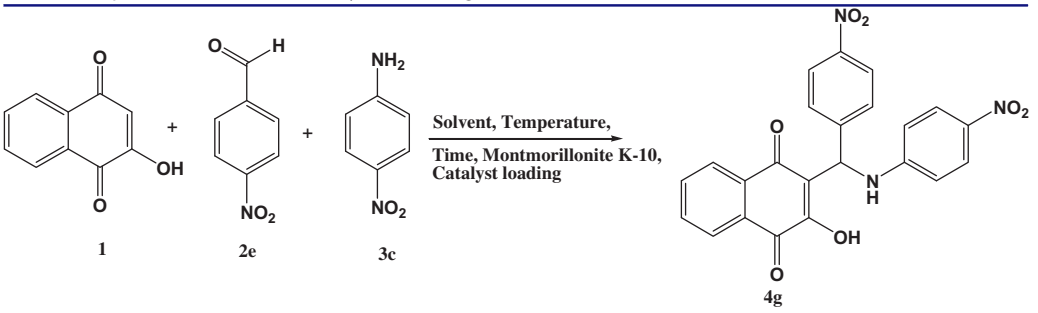
In connection with our consistent interest in the development of efficient synthetic methodologies,[48–59] we report herein a new and efficient protocol using clay catalytic system to access the synthesis of relevant scaffolds and some novel aminonaphthoquinone derivatives with benzothiazole moiety from readily available substrates.

Results and discussion

First, to find the standard conditions, the reaction of Lawsone (**1**), 4-nitrobenzaldehyde (**2e**) and 4-nitroaniline (**3c**) in acetonitrile was selected as a model. When the reaction was carried without any catalyst at ambient temperature and reflux, no desirable product (**4g**) was obtained even after prolonged reaction time. This pointed out clearly that a catalyst shall absolutely be needed for this reaction. When this three-component reaction was attempted using L-proline (10 mol%) as a catalyst at ambient temperature, it was observed that the reaction was end after 12 h yielding 45% of the product. We then focused on Lewis acid catalysts and among these, zinc chloride, iodine, bismuth nitrate pentahydrate and montmorillonite K-10 has resulted in 20%, 33%, 38% and 58% of target product (**4g**), respectively.

We next performed a screening of various solvents such as water, chloroform, toluene, xylene, dichloromethane, tetrahydrofuran and ethanol. The results of Table 1 revealed that ethanol was the most suitable solvent for the reaction in terms of time, temperature and yield. Subsequent experiments revealed that catalyst loading could be

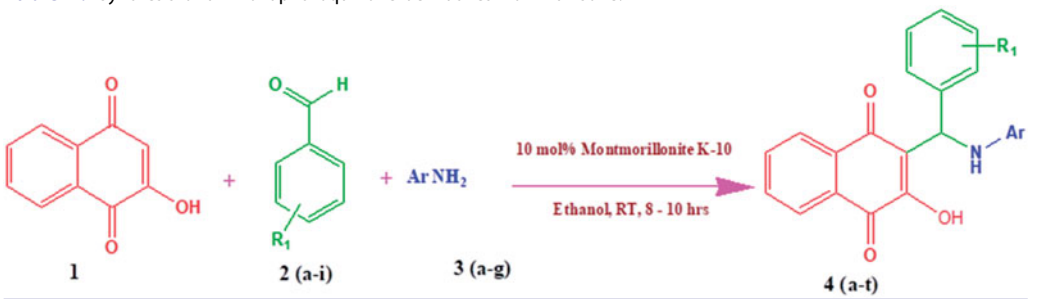
Table 1. Optimization studies for the synthesis of (**4g**).



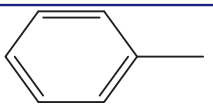
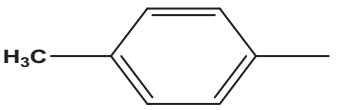
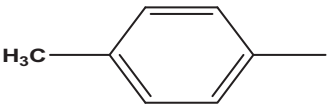
1 2e 3c 4g

Entry	Solvent	Temp (°C)	Time (h)	Catalyst (mol%)	Yield (%)
1	Water	Reflux	8	10	60
2	Chloroform	Reflux	12	10	20
3	Toluene	Reflux	15	10	30
4	Acetonitrile	Reflux	12	10	58
5	Xylene	Reflux	16	10	27
6	Dichloromethane	Reflux	12	10	25
7	THF	Reflux	15	10	15
8	Ethanol	Reflux	8	10	84
9	Ethanol	60	8	10	86
10	Ethanol	40	8	10	90
11	Ethanol	RT	8	10	93
12	Ethanol	RT	8	5	62
13	Ethanol	RT	8	3	41
14	Ethanol	RT	8	2	34
15	Ethanol	RT	8	15	93

Table 2. Synthesis of aminonaphthoquinone derivatives from Lawsone.

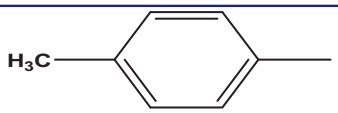
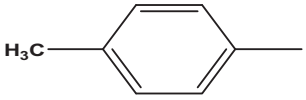
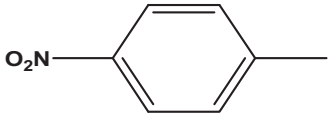
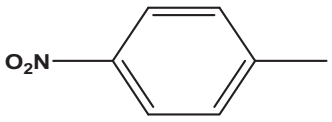
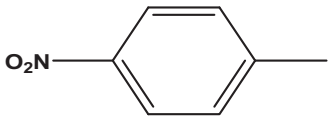
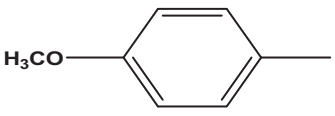
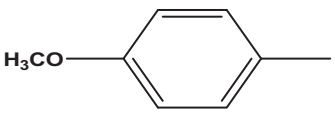
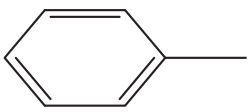
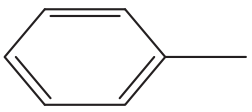
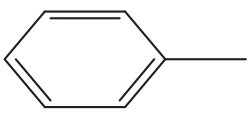
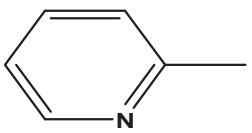


1 2 (a-i) 3 (a-g) 4 (a-t)

S.No.	R_1	Ar	Product	Time (h)	Yield (%)
1	**H**		**4a**	**8**	**93**
2	**H**		**4b**	**8**	**85**
3	**4-CH_3**		**4c**	**8.5**	**88**

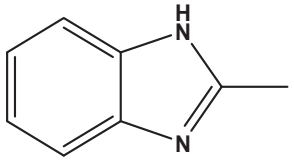
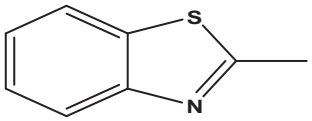
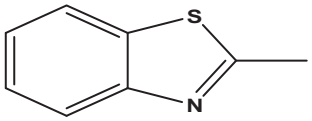
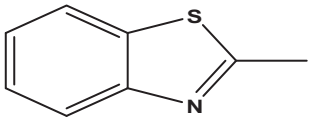
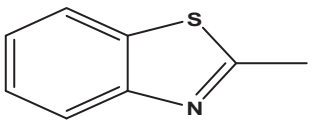
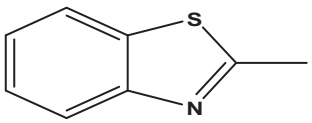
(*continued*)

Table 2. Continued.

S.No.	R_1	Ar	Product	Time (h)	Yield (%)
4	**4-Cl**		**4d**	**10**	**83**
5	**4-Br**		**4e**	**10**	**90**
6	**4-CH_3**		**4f**	**8**	**81**
7	**4-NO_2**		**4g**	**8**	**93**
8	**4-Cl**		**4h**	**8.5**	**90**
9	**4-Cl**		**4i**	**9**	**85**
10	**4-NO_2**		**4j**	**8.25**	**83**
11	**2-NO_2**		**4k**	**8**	**90**
12	**2,6-$(CH_3)_2$**		**4l**	**8.25**	**81**
13	**3,4,5-$(OCH_3)_3$**		**4m**	**10**	**83**
14	**4-NO_2**		**4n**	**8**	**91**

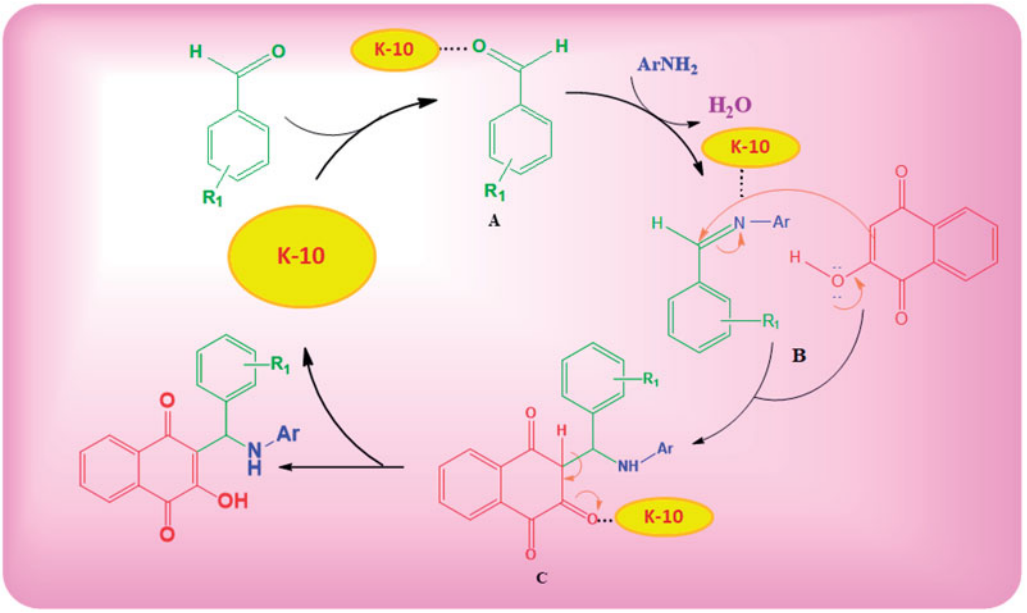
(*continued*)

Table 2. Continued.

S.No.	R_1	Ar	Product	Time (h)	Yield (%)
15	**4-NO_2**		**4o**	**8**	**93**
16	**H**		**4p**	**8.25**	**89**
17	**4-NO_2**		**4q**	**8**	**92**
18	**4-OH**		**4r**	**8**	**90**
19	**4-Br**		**4s**	**8.5**	**93**
20	**4-CH_3**		**4t**	**8**	**87**

optimum at 10 mol% (Table 1, entry 11), but lower amounts were detrimental. It is noteworthy that the ratio of the three starting substrates has important influence on the yield of this reaction. When the ratio of **1/2e/3c** was 1:1:1, the yield was raised to 93%. Further altering the ratio, no progress of yield was observed.

In order to extend the above reaction to the library system, different substituted benzaldehydes **2**(**a–i**) and aromatic amines **3**(**a–g**) were allowed to react with Lawsone to give the aminonaphthoquinone derivatives **4(a–t)** and representative examples are presented in Table 2. Benzaldehydes carrying both electron-donating and electron-withdrawing substituents displayed high reactivity under this optimized conditions to afford the desired products. Aromatic amines tethered with electron-donating and electron-withdrawing substituents showed similar reactivity and reacted efficiently to afford the target products. Heterocyclic amines also exhibited a high reactivity under this standard condition to yield the final products. The aminonaphthoquinones reported by Dabiri et al.[34] (**4a**, **4b**, **4c**, **4e**) and the compounds reported by Shahram et al.[39] (**4d**, **4f**, **4g**, **4h**, **4i**, **4j**, **4h**, **4n**, **4o**) are also obtained efficiently using this current protocol. It



Scheme 1. Plausible mechanism for the synthesis of aminonaphthoquinone derivatives.

is noteworthy that it is possible to synthesize a series of aminonaphthoquinones containing phenyl, pyridyl, benzimidazolyl and benzothiazolyl moieties. To the best of our knowledge, this is the first report for the synthesis of aminonaphthoquinone derivatives with benzothiazolyl moiety.

A speculative mechanistic explanation for this reaction based on previously reported literature[34,39] is provided in Scheme 1. In the first step, aromatic amines attacked the activated benzaldehydes (A) to form activated imines (B). The latter compounds reacted with Lawsone, to give an intermediate (C) that underwent tautomerization to yield the products. Montmorillonite K-10 is likely to enhance the rate of Mannich reaction.

Conclusion

To concise, we reported a range of aminonapthoquinone derivatives with complete control over the substitution pattern. Mild reaction conditions, easy work-up and catalyst recovery are prominent features of this protocol. Furthermore, a promising pathway for the introduction of heterocyclic amines like 2-aminopyridine, 2-aminobenzimidazole and 2-aminobenzothiazole is explored.

Experimental

General information

The melting points were recorded on an Electrothermal melting point apparatus. The FT-IR (ATR) analysis was carried out on Cary 630 FT-IR spectrophotometer (Agilent Technologies, Stevens Creek Blvd, Santa Clara, USA). ^{1}H NMR (for 400 MHz) and ^{13}C NMR (for 100 MHz) spectra were recorded on a Bruker spectrometer using DMSO-d_6

as a solvent and Tetra Methyl Silane (TMS) as an internal standard. The chemical shifts are expressed in δ ppm. The mass analysis was recorded on a Micro Mass QTOF mass spectrometer. The purity of the compounds was checked by Thin Layer Chromatography (TLC).

Typical experimental procedure for the preparation of 2-hydroxy-3-((4-nitrophenyl)(4-nitrophenyl)amino)methyl)naphthalene-1,4-dione (4g)

A mixture of 4-nitrobenzaldehyde (0.151 g, 1 mmol), 4-nitroaniline (0.138 g, 1 mmol), 2-hydroxy-naphthalene-1,4-dione (0.174 g, 1mmol) and montmorillonite K-10 (0.005 g, 10 mol %) was stirred in ethanol (3 mL). After the completion of the reaction, as indicated by TLC, the mixture was diluted with CH_2Cl_2 and the catalyst was separated by filtration. The catalyst was washed thoroughly with acetone and dried. The recovered catalyst was reused up to four runs without any significant loss of its activity. The solvent was evaporated under reduced pressure to get the crude product that was recrystallized from ethanol.

2-Hydroxy-3-((4-nitrophenyl)(4-nitrophenyl)amino)methyl)naphthalene-1,4-dione (4g)

Yield 93%; a yellow solid; mp: 134–136 °C. IR (ATR cm^{-1}): 3408 (OH), 3334 (NH), 1685 (C=O), 1656 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.23 (s, 1H, OH), 10.13 (s, 1H, NH), 8.15–6.79 (m, 12H, Ar-H), 6.08 (s, 1H, CH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 183.1, 181.3, 153.4, 151.2, 149.2, 146.7, 136.2, 135.0 (2C), 131.4, 130.2, 128.4 (2C), 127.0 (2C), 126.7 (2C), 125.2 (2C), 117.1, 114.5 (2C), 52.3 ppm.

Acknowledgments

S.J. is thankful to CSIR for providing Senior Research Fellowship (SRF).

Funding

This study was supported by Council of Scientific and Industrial Research (CSIR), New Delhi, India [Grants Reference no. 02(0172)/13/EMR-II, Dated: 21.10.2013].

Supporting information

This material can be found via "Supplementary Content" section of this article's webpage.

ORCID

Kalegowda Shivashankar http://orcid.org/0000-0001-6419-341X

References

[1] Rajesh, S. M.; Bala B. D.; Perumal, S.; Menendez, J. C. L-Proline-Catalysed Sequential Four-Component “On Water” Protocol for the Synthesis of Structurally Complex

Heterocyclic Ortho-Quinones. *Green Chem*. **2011**, *13*, 3248–3254. DOI:10.1039/C1GC15794A.

[2] Xie, X.; Zhang, F.; Geng, D. M.; Wang, L. L.; Hao, W. J. B.; Jiang, B.; Tu, S. J. Regioselectively Synthesis of Thiazolo[4,5-*a*]Acridines and Oxazolo[5,4-*a*]Thiazolo[5,4-*j*]Acridines via Multicomponent Domino Reactions. *J. Heterocyclic Chem*. **2016**, *53*, 1046–1053. DOI:10.1002/jhet.2437.

[3] Bharti, R.; Parvin, T. Diversity Oriented Synthesis of Tri-Substituted Methane Containing Aminouracil and Hydroxynaphthoquinone/Hydroxycoumarin Moiety Using Organocatalysed Multicomponent Reactions in Aqueous Medium. *RSC Adv*. **2015**, *5*, 66833–66839. DOI:10.1039/C5RA13093J.

[4] Manickam, S.; Iyer, S. K. A New Approach for Fluorescent Tetrahydrobenzo[*f*]Pyrimido[4,5-*b*]Quinolines and Indeno Fused Pyrido[2,3-*b*]Pyrimidines. *Dyes Pig*. **2017**, *147*, 300–312. DOI:10.1016/j.dyepig.2017.07.041.

[5] Shirini, F.; Beigbaghlou, S. S.; Atghia, S. V.; Mousazadeh, S. A. Multi-Component One-Pot Synthesis of Unsymmetrical Dihydro-5H-Indeno[1,2-*b*]Quinolines as New pH Indicators. *Dyes Pig*. **2013**, *97*, 19–25. DOI:10.1016/j.dyepig.2012.11.002.

[6] Shivashankar, K.; Shastri, L. A.; Kulkarni, M. V.; Rasal, V. P.; Saindane, D. M. Multi-Component Reactions of Formyl-4-Aryloxymethylcoumarins under Microwave Irradiation. *J. Indian Chem. Soc*. **2009**, *86*, 265–271.

[7] Kavitha, C. V.; Basappa, S.; Swamy, N.; Mantelingu, K.; Doreswamy, S.; Sridhar, M. A.; Prasad, J. S.; Rangappa, K. S. Synthesis of New Bioactive Venlafaxine Analogs: Novel Thiazolidin-4-Ones as Antimicrobials. *Bioorg. Med. Chem. Lett*. **2006**, *14*, 2290–2299. DOI:10.1016/j.bmc.2005.11.017.

[8] Chougala, B. M.; Samundeeswari, S.; Holiyachi, M.; Shastri, L. A.; Dodamani, S.; Jalalpure, S.; Dixit, S. R.; Joshi, S. D.; Sunagar, V. A. Synthesis, Characterization and Molecular Docking Studies of Substituted 4-Coumarinylpyrano[2,3-*c*]Pyrazole Derivatives as Potent Antibacterial and Anti-Inflammatory Agents. *Eur. J. Med. Chem*. **2017**, *125*, 101–116. DOI:10.1016/j.ejmech.2016.09.021.

[9] Basanagouda, M.; Kulkarni, M. V. Novel One-Pot Synthesis for 2,5-Diaryl and 5-Aryl-pyridazin-3(2*H*)-Ones. *Synth. Commun*. **2011**, *41*, 2569–2582. DOI:10.1080/00397911.2010.515330.

[10] Nadaf, A. N.; Shivashankar, K. CFL Light Promoted One-Pot Synthesis of Pyrano [3,2-*c*] Chromen-5(4*H*)-Ones. *Synth. Commun*. **2018**, *48*, 809–815. DOI:10.1080/00397911.2018.1426101.

[11] Beerappa, M.; Shivashankar, K. Four Component Synthesis of Highly Functionalized Pyrano[2,3-*c*]Pyrazoles from Benzyl Halides. *Synth. Commun*. **2018**, *48*, 146–154. DOI:10.1080/00397911.2017.1386788.

[12] Ahn, J. H.; Cho, S. Y.; Ha, J. D.; Chu, S. Y.; Jung, S. H.; Jung, Y. S.; Baek, J. Y.; Choi, I. K.; Shin, E. Y.; Kang, S. K.; et al. Synthesis and PTP1B Inhibition of 1,2-Naphthoquinone Derivatives as Potent Anti-Diabetic Agents. *Bioorg. Med. Chem. Lett*. **2002**, *12*, 1941–1946. DOI:10.1016/S0960-894X(02) DOI:00331-1.

[13] Yin, J.; Liebeskind, L. S. A Synthesis of Trisquinones. *J. Org. Chem*. **1998**, *63*, 5726–5727. DOI:10.1021/jo980680c.

[14] Wellington, K. W. Understanding Cancer and the Anticancer Activities of Naphthoquinones – A Review. *RSC Adv*. **2015**, *5*, 20309–20338. DOI:10.1039/C4RA13547D.

[15] Sieveking, I.; Thomas, P.; Estevez, J. C.; Quinones, N.; Cuellar, M. A.; Villena, J.; Espinosa-Bustos, C.; Fierro, A.; Tapia, R. A.; Maya, J. D.; et al. 2-Phenylaminonaphthoquinones and Related Compounds: Synthesis, Trypanocidal and Cytotoxic Activities. *Bioorg. Med. Chem*. **2014**, *22*, 4609–4620. DOI:10.1016/j.bmc.2014.07.030.

[16] Moon, D. O.; Choi, Y. H.; Kim, N. D.; Park, Y. M.; Kim, G. Y. Anti-Inflammatory Effects of Beta-Lapachone in Lipopolysaccharide-Stimulated BV2 Microglia. *Int. Immunopharmacol*. **2007**, *7*, 506–514. DOI:10.1016/j.intimp.2006.12.006.

[17] Barbosa, T. P.; Camara, C. A.; Silva, T. M. S.; Martins, R. M.; Pinto, A. C.; Vargas, M. D. New 1,2,3,4-Tetrahydro-1-Aza-Anthraquinones and 2-Aminoalkyl Compounds from Norlapachol with Molluscicidal Activity. *Bioorg. Med. Chem.* **2005**, *13*, 6464–6469. DOI:10.1016/j.bmc.2005.06.068.

[18] Buckle, D. R.; Cantello, B. C. C.; Smith, H.; Smith, R. J.; Spicer, B. A. Synthesis and Antiallergic Activity of 2-Hydroxy-3-Nitro-1,4-Naphthoquinones. *J. Med. Chem.* **1977**, *20*, 1059–1064. DOI:10.1021/jm00218a014.

[19] Sultana, N.; Choudhary, M. I.; Khan, A. Protein Glycation Inhibitory Activities of *Lawsonia inermis* and Its Active Principles. *J. Enzyme. Inhib. Med. Chem.* **2009**, *24*, 257–261. DOI:10.1080/14756360802057500.

[20] Ghosh, P. P.; Pal, G.; Paul, S.; Das, A. R. Design and Synthesis of Benzylpyrazolyl Coumarin Derivatives via a Four-Component Reaction in Water: Investigation of the Weak Interactions Accumulating in the Crystal Structure of a Signified Compound. *Green Chem.* **2012**, *14*, 2691–2698. DOI:10.1039/C2GC36021G.

[21] Calvo, J. M. S.; Barbero, G. R.; Vasquez, G. G.; Duran, A. G.; Macias, M.; Iglesias, M. A. R.; Macias, F. A. Synthesis, Antibacterial and Antifungal Activities of Naphthoquinone Derivatives: A Structure–Activity Relationship Study. *Med. Chem. Res.* **2016**, *25*, 1274–1285. DOI:10.1007/s00044-016-1550-x.

[22] Pingaew, R.; Prachayasittikul, V.; Worachartcheewan, A.; Nantasenamat, C.; Prachayasittikul, S.; Ruchirawat, S.; Prachayasittikul, V. Novel 1,4-Naphthoquinone-Based Sulfonamides: Synthesis, QSAR, Anticancer and Antimalarial Studies. *Eur. J. Med. Chem.* **2015**, *103*, 446–459. DOI:10.1016/j.ejmech.2015.09.001.

[23] Gafner, S.; Wolfender, J. L.; Nianga, M.; Stoeckli-Evans, H.; Hostettmann, K. Antifungal and Antibacterial Naphthoquinones from Newbouldia Laevis Roots. *Phytochem.* **1996**, *42*, 1315–1320. DOI:10.1016/0031-9422(96)00135-5.

[24] Brandon, A. C. C.; Steven, F.; Dana, F.; Eun, Y. C.; Dahlia, K.; Smaraki, D.; Phuc, T.; Edward, A. S.; Rena, G. L.; Ashkan, E. Synthesis, Characterization and Antineoplastic Activity of Bis-Aziridinyl Dimeric Naphthoquinone – A Novel Class of Compounds with Potent Activity against Acute Myeloid Leukemia Cells. *Bioorg. Med. Chem. Lett.* **2017**, *27*, 6–10. DOI:10.1016/j.bmcl.2016.11.045.

[25] Idaira, H. F.; Angel, A.; Laura, A. A.; Isabel, L. C.; Felix, M.; Ana, E. B. Synthesis and Biological Evaluation of Naphthoquinone-Coumarin Conjugates as Topoisomerase II Inhibitors. *Bioorg. Med. Chem. Lett.* **2017**, *27*, 484–489. DOI:10.1016/j.bmcl.2016.12.040.

[26] Raphael, S. F. S.; Elaine, M. C.; Ursula, L. T. T.; Daniel, V. T.; Maria, F. R. P.; Gustavo, L. S.; Valeria, R. S. M.; Carlos, A. D. S.; Antonio, V. P.; Solange, L. C. Synthesis of Naphthofuranquinones with Activity against *Trypanosoma cruzi*. *Eur. J. Med. Chem.* **2006**, *41*, 526–530. DOI:10.1016/j.ejmech.2005.12.006.

[27] Benites, J.; Valderrama, J. A.; Bettega, K.; Pedrosa, R. C.; Calderon, P. B.; Verrax, J. Biological Evaluation of Donor-Acceptor Aminonaphthoquinones as Antitumor Agents. *Eur. J. Med. Chem.* **2010**, *45*, 6052–6057. DOI:10.1016/j.ejmech.2010.10.006.

[28] Sanjay, K. V.; Vinay, K. S. Synthesis, Electrochemical, Fluorescence and Antimicrobial Studies of 2-Chloro-3-Amino-1,4-Naphthoquinone Bearing Mononuclear Transition Metal Dithiocarbamate Complexes [M{κ^2S,S-S_2C–Piperazine–C_2H_4N(H)ClNQ}n]. *RSC Adv.* **2015**, *5*, 53036–53046. DOI:10.1039/C5RA08065G.

[29] Prashant, M.; Elizabeth, M.; Subramaniyan, C.; Isaac, H. J.; Nagaiyan, S. NLO Properties of 1, 4-Naphthoquinone, Juglone and Lawsone by DFT and Z-Scan Technique – A Detailed Study. *Opt. Mat.* **2017**, *72*, 549–558. DOI:10.1016/j.optmat.2017.06.058.

[30] Palanisamy, R.; Samuel, V. Synthesis of Heterocyclic Naphthoquinone Derivatives as Potent Organic Fluorescent Switching Molecules. *J. Taibah. Uni. Sci.* **2015**, *9*, 538–547. DOI:10.1016/j.jtusci.2014.12.003.

[31] Jing, W.; Dekun, Q.; Jingbo, L.; Yangyang, C.; Shuai, Z.; Qiang, G.; Jie, W.; Di, W.; Jingsong, Y. Rh-Catalysed Direct Cyclisation of 1,4-Naphthoquinone and 9,10-Phenanthraquinone with Alkyne: Facile Access to 1,8-Dioxapyrenes and

1,12-Dioxaperylenes as Orange and Red-Emitting Luminophores. *Chem. Commun*. **2015**, *51*, 6337–6339. DOI:10.1039/C5CC00312A.

[32] Jordao, A. K.; Vargas, M. D.; Pinto, A. C.; Silva, F. C.; Ferreira, V. F. Lawsone in Organic Synthesis. *RSC Adv*. **2015**, *5*, 67909–67943. DOI:10.1039/C5RA12785H.

[33] Jelly, R.; Lewis, S. W.; Lennard, C.; Lim, K. F.; Almog, J. Lawsone: A Novel Reagent for the Detection of Latent Fingermarks On Paper Surfaces. *Chem. Commun*. **2008**, *0*, 3513–3515. DOI:10.1039/B808424F.

[34] Dabiri, M.; Tisseh, Z. N.; Bazgir, A. Synthesis of Fluorescent Hydroxyl Naphthalene-1,4-Dione Derivatives by a Three-Component Reaction in Water. *Dyes Pig*. **2011**, *89*, 63–69. DOI:10.1016/j.dyepig.2010.09.004.

[35] Fiorot, R. G.; Filho, J. F. A.; Pereira, T. M. C.; Lacerda, V.; Santos, R. B.; Romão, W.; Greco, S. J. A Simple and Convenient Method for Synthesis of New Aminonaphthoquinones Derived from Lawsone by Catalytic Multicomponent Mannich Reaction. *Tetrahedron Lett*. **2014**, *55*, 4373–4377. DOI:10.1016/j.tetlet.2014.06.031.

[36] Liu, D.; Zhou, S.; Gao, J. Room-Temperature Synthesis of Hydroxylnaphthalene-1,4-Dione Derivative Catalyzed by Phenylphosphinic Acid. *Synth. Commun*. **2014**, *44*, 1286–1290. DOI:10.1080/00397911.2013.853314.

[37] Shaabani, S.; Naimi-Jamal, M. R.; Maleki, A. Synthesis of 2-Hydroxy-1,4-Naphthoquinone Derivatives via a Three-Component Reaction Catalyzed by Nanoporous MCM-41. *Dyes Pig*. **2015**, *122*, 46–49. DOI:10.1016/j.dyepig.2015.06.013.

[38] Shaterian, H. R.; Moradi, F. Mild Preparation of Hydroxyl Naphthalene-1,4-Dione Derivatives with Nano Copper(II) Oxide as Catalyst under Ambient and Solvent-Free Conditions. *Res. Chem. Intermed*. **2015**, *41*, 291–297. DOI:10.1007/s11164-013-1191-3.

[39] Asadi, B.; Baltork, I. M.; Tangestaninejad, S.; Moghadam, M.; Mirkhani, V.; Isfahani, A. L. Synthesis and Characterization of Bi(III) Immobilized on Triazine Dendrimer-Stabilized Magnetic Nanoparticles: A Reusable Catalyst for the Synthesis of Aminonaphthoquinones and Bis-Aminonaphthoquinones. *New J. Chem*. **2016**, *40*, 6171–6184. DOI:10.1039/C5NJ03050A.

[40] Adams, J. M.; Dyer, S.; Martin, K.; Matear, W. A.; McCabe, R. W. Diels–Alder Reactions Catalysed by Cation-Exchanged Clay Minerals. *J. Chem. Soc. Perkin Trans. 1*. **1994**, *0*, 761–765. DOI:10.1039/P19940000761.

[41] Shinde, A. B.; Shrigadi, N. B.; Bhat, R. P.; Samant, S. D. Pinacol-Pinacolone Rearrangement on $FeCl_3$ Modified Montmorillonite K-10. *Synth. Commun*. **2004**, *34*, 309–314. DOI:10.1081/SCC-120027268.

[42] Mogilaiah, K.; Sakram, B. Facile Clay-Induced Fischer Indole Synthesis: A New Approach to Synthesis of 1,2,3,4-Tetrahydrocarbazole and Indoles. *Appl. Catal. A*. **2005**, *292*, 305–311. DOI:10.1016/j.apcata.2005.06.011.

[43] Baran, P. S.; Richter, J. M. Enantioselective Total Syntheses of Welwitindolinone A and Fischerindoles I and G. *J. Am. Chem. Soc*. **2005**, *127*, 15394–15396. DOI:10.1021/ja056171r.

[44] Singh, V.; Khurana, A.; Kaur, I.; Sapehiyia, V.; Kad, G. L.; Singh, J. Microwave Assisted Facile Synthesis of Elvirol, Curcuphenol and Sesquichamaenol Using Montmorillonite K-10 Clay in Dry Media. *J. Chem. Soc. Perkin Trans. 1*. **2002**, *0*, 1766–1768. DOI:10.1039/B204509P.

[45] Ramchandani, R. K.; Uphade, B. S.; Vinod, M. P.; Warharkar, R. D.; Choudary, V. R.; Sudalai, A. Pd–Cu–Exchanged Montmorillonite K-10 Clay: An Efficient and Reusable Heterogeneous Catalyst for Vinylation of Aryl Halides. *Chem. Commun*. **1997**, *0*, 2071–2072. DOI:10.1039/A705870E.

[46] Anastas, P. T. *Williamson, T.C. Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes*; Oxford University Press: Madison Avenue, New York, USA, 1998.

[47] Bigi, F.; Confionti, M. L.; Maggi, R.; Sartori, G. Trialkylamine Controlled Phenol–Formaldehyde Reaction over Clay Catalysts: Selective and Environmentally Benign Synthesis of Salicylic Aldehydes. *Tetrahedron*. **2000**, *56*, 2709–2712. DOI:10.1016/S0040-4020(00)00171-X.

[48] Beerappa, M.; Shivashankar, K. One Pot Synthesis of Pyran-Based Heterocycles from Benzyl Halides as Key Reagents. *RSC Adv*. **2015**, *5*, 30364–30371. DOI:10.1039/C4RA17219A.

[49] Jagadishbabu, N.; Shivashankar, K. One Pot Synthesis of Acridine Analogues from 1,2-Diols as Key Reagents. *RSC Adv*. **2015**, *5*, 95240–95246. DOI:10.1039/C5RA19595K.

[50] Chacko, P.; Shivashankar, K. I_2-Catalyzed One-Pot Synthesis of Benzofuro/Thieno [2,3-*b*] Pyrrole Motifs. *Tetrahedron*. **2018**, *74*, 1520–1526. DOI:10.1016/j.tet.2018.02.013.

[51] Chacko, P.; Shivashankar, K. Nano Structured Spinel Co_3O_4-Catalyzed Four Component Reaction: A Novel Synthesis of Ugi Adducts from Aryl Alcohols as a Key Reagent. *Chin. Chem. Lett*. **2017**, *28*, 1619–1624. DOI:10.1016/j.cclet.2017.04.015.

[52] Jagadishbabu, N.; Shivashankar, K. Biginelli Reaction of Vicinal Diols: A New Route for One-Pot Synthesis of 3, 4-Dihydropyrimidin-2 (1*H*)-One Derivatives. *Lett. Org. Chem*. **2017**, *14*, 330–336. DOI:10.2174/1570178614666170310123511.

[53] Shivashankar, K.; Shastri, L. A.; Kulkarni, M. V. Facile Synthesis of Some Novel 4-{3-Aryl-3,4-Dihydro-2H-Benzo[*b*][1,4]Thiazin-2-yl}-2*H*-Chromen-2-Ones Derivatives. *J. Sulfur Chem*. **2007**, *28*, 625–630. DOI:10.1080/17415990701591286.

[54] Shivashankar, K.; Shastri, L. A.; Kulkarni, M. V.; Rasal, V. P.; Rajendra, S. V. Synthetic and Biological Studies on 4-Aryloxymethyl Coumarinyl Thiazolidinone. *Phosphorus Sulfur Silicon*. **2008**, *183*, 56–68. DOI:10.1080/10426500701555801.

[55] Shamala, D.; Shivashankar, K. Synthesis of Pyridazinones via Molecular-Iodine-Mediated Cleavage of 4-Bromomethylcoumarin Precursors. *Synth. Commun*. **2016**, *46*, 1735–1740. DOI:10.1080/00397911.2016.1223310.

[56] Beerappa, M.; Shivashankar, K. Multicomponent Reaction of Benzyl Halides: Synthesis of [1,2,4] Triazolo/Benzimidazolo Quinazolinones. *Synth. Commun*. **2016**, *46*, 421–432. DOI:10.1080/00397911.2016.1140784.

[57] Chacko, P.; Shivashankar, K. Montmorillonite K10-Catalyzed Synthesis of N-Fused Imino-1,2,4-Thiadiazolo Isoquinoline Derivatives. *Synth. Commun*. **2018**, *48*, 1363–1376. DOI:10.1080/00397911.2018.1448419.

[58] Shamala, D.; Shivashankar, K. Synthesis of 4-Phenyloxazinones via DBU-Catalyzed Cleavage of 4-Bromomethylcoumarins. *Synth. Commun*. **2017**, *47*, 105–110. DOI:10.1080/00397911.2016.1252045.

[59] Shamala, D.; Shivashankar, K. Synthesis of N1 and N2 Coumarin Substituted 1,2,3-Triazole Isomers via Click Chemistry Approach. *Synth. Commun*. **2016**, *46*, 433–441. DOI:10.1080/00397911.2016.1140785.