Tetrahedron Letters 54 (2013) 5500–5504

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

One-pot solid phase synthesis of (*E*)-nitroalkenes

Lalthazuala Rokhum, Ghanashyam Bez *

Department of Chemistry, North Eastern Hill University, Shillong 793022, India

ARTICLE INFO

Article history:
Received 14 May 2013
Revised 24 July 2013
Accepted 28 July 2013
Available online 3 August 2013

Keywords:
(*E*)-Nitroalkenes
Polymer-bound triphenylphosphine
Iodine
Imidazole
Solid phase synthesis

ABSTRACT

An efficient one-pot protocol for the synthesis of (*E*)-nitroalkenes by reaction of aldehydes and nitroalkanes in the presence of polymer-bound triphenylphosphine, iodine and imidazole is described. Although the reaction works with similar efficiency with triphenylphosphine and its polymer-bound version, easy removal of the unwanted polymer-bound triphenylphosphine oxide and its recovery as triphenylphosphine provide the edge for practical application of the method.

Nitroalkene is an important building block in organic synthesis. Many β-nitrostyrene derivatives are valuable intermediates for the preparation of numerous products including insecticides,[1a] fungicides,[1b,c] and pharmacologically active substances.[1d–i] It can also be used to synthesize a range of derivatives by 1,4-addition,[2a–c] reduction,[2d–g] Diels–Alder reaction,[2h–l] etc. Recent studies revealed that *trans*-β-nitrostyrene (TBNS) derivatives (Fig. 1) act as slow-binding, reversible inhibitors of protein tyrosine phosphatases (PTPs).[3] Moreover various nitroalkenes derived from aromatic aldehydes are found to be useful for natural product synthesis.[4]

Synthesis of nitroalkene from condensation (Henry condensation) of aldehyde and nitroalkane is a very important strategy for carbon–carbon bond forming reaction. Generally, nitroalkenes are synthesized by base-catalyzed reaction of the corresponding aldehydes with nitroalkanes[5] in a two step-base catalyzed synthesis of β-nitro alcohols followed by dehydration in the presence of dehydrating agents, such as phthalic anhydride,[6] dicyclohexylcarbodiimide,[7] PPh_3-CCl_4,[8] Ac_2O-AcONa,[9] CH_3SO_2Cl-NEt_3,[10] TFAA-NEt_3,[11] and Al_2O_3.[12] In spite of being effective, the problems associated with many of these methods include unwanted side products derived from the reagent, highly hygroscopic nature of the reagents, and requirement of high temperature. In search of one-step protocol, Ballini et al.[13] reported an interesting method for one step Henry condensation by heating a mixture of aldehyde and nitroalkane at 40–60 °C in the presence of heterogeneous catalysts based on Al_2O_3 in super critical CO_2 at 80–140 bar. But special apparatus is required to carry out the reaction with super critical CO_2 at high pressure. Other methods from starting materials other than conventional Henry adducts have also appeared in the literature.[14] Concellón et al.[15] reported a samarium-promoted synthesis of (*E*)-nitroalkenes from 1-bromo-1-nitroalkan-2-ols in high yields, but required two steps to achieve the desired nitroalkenes. There are a few methods[16] for the synthesis of nitroalkenes from nitric oxide (NO) and alkenes, but they have regioselectivity issues unlike Henry condensation. Recently, Pujol and co-workers[17] have reported a novel one-pot synthesis of nitroalkenes from aryl aldehydes using ammonium acetate as a catalyst without solvent under microwave irradiation. This method often gives a mixture of nitroalkenes and nitroalcohols and hence gives poor yield in many cases. Moreover, the reaction is useful only for aromatic aldehydes, not for aliphatic aldehydes. Given the existing literature, there is every scope to develop new methodologies to simplify the reaction conditions for the synthesis of nitroalkenes from aldehydes.

Solid-phase synthesis continues to evolve as a means to facilitate the manipulation of compound libraries via combinatorial chemistry.[18] The important features of solid-phase synthesis such as purification of the product by filtration of the solid matrix, easy handling, low moisture susceptibility, minimum side reaction, and recyclability of the solid matrix for repeated use have drawn huge attention from industry and academia.[19] Although triphenylphosphine is considered one of the worst atom-economic reagents due to its high carbon content, polymer-bound triphenylphosphine is getting a lot of applications in recent years.[20] The commonly encountered problems in solution-phase chemistry involving triphenylphosphine, such as removal of excess triphenylphosphine, triphenylphosphine complexes, and the by-product triphenylphosphine oxide can be overcome easily with polymer-bound triphenylphosphine. Moreover, for the reactions where polymer-bound triphenylphosphine acts as an oxygen-acceptor, the byproduct

* Corresponding author.
E-mail addresses: ghanashyambez@yahoo.com, bez@nehu.ac.in (G. Bez).

0040-4039/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2013.07.146

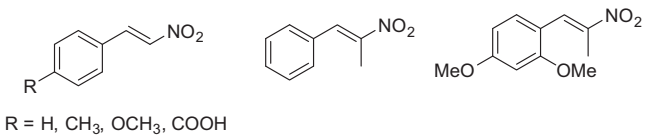
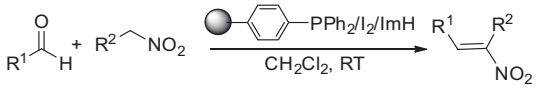
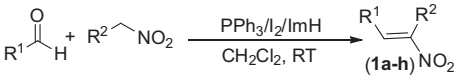


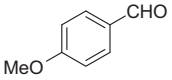
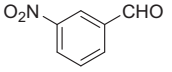
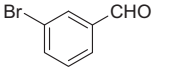
Figure 1. Structures of PTP inhibitors.



Scheme 1. Synthesis of nitroalkene.

Table 1
Synthesis of nitroalkenes in solution phase[a,b]



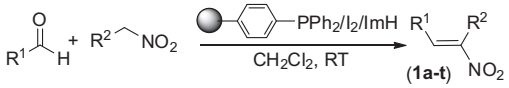
Entry	Aldehyde	R^2	Product	Yield[c] (%)
1	PhCHO	H	**1a**	82
2		CH_3	**1b**	85
3		H	**1c**	78
4		CH_3	**1d**	82
5		H	**1e**	85
6		CH_3	**1f**	88
7		H	**1g**	89
8		CH_3	**1h**	84

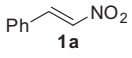
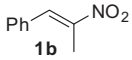
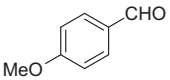
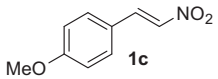
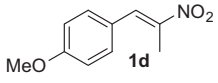
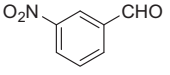
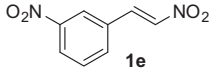
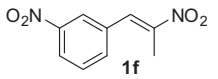
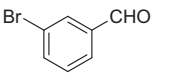
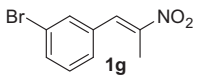
[a] Aldehyde:nitroalkane:triphenylphosphine:iodine:imidazole = 1.0:1.5:1.5:1.5:2.0.
[b] Reaction time is 30 min.
[c] Yields are calculated from pure isolated product.

triphenylphosphine oxide can be reduced to triphenylphosphine by treatment with trichlorosilane.[21] Here we wish to report a two-step one-pot methodology involving polymer-bound triphenylphosphine/iodine/imidazole reagent system for the synthesis of nitroalkenes in very good yields (Scheme 1). To our knowledge, solid phase synthesis of nitroalkene from the reaction of aldehyde and nitroalkane is not known in the literature.

In continuation of our recent interest in the catalytic application of triphenylphosphine (TPP) and iodine[22] in useful organic transformations, we assumed that if a mild base is used to abstract the β-hydrogen of β-nitroalcohol, nitroalkenes can be synthesized without use of commonly used dehydrating agents. Here, the hydroxy group was expected to react with the in situ generated iodotriphenylphosphonium iodide, from the reaction of TPP with iodine, to make itself a good leaving group. We initially wanted to test our assumption in solution phase to make sure that the reagent system works. For that purpose, we took a mixture of benzaldehyde (1 mmol) and nitromethane (1.5 equiv) in dry dichloromethane (5 mL) and stirred with 0.2 equiv of imidazole (ImH). After stirring for 4 h, the formation of β-nitroalcohol was found to be complete. Without isolating the product, triphenylphosphine (1.5 equiv) and iodine (1.5 equiv) were added to the solution and stirred for additional 30 min. Slight formation of the desired nitroalkene was observed, which did not increase even after stirring for 3 h. Then we added additional imidazole (1 mmol) and stirred for 30 min to find that the starting nitroalcohol got completely converted into its nitroalkene derivative. We reasoned that if the imidazole is used in excess, both C–C coupling and dehydration can occur simultaneously to generate the desired nitroalkene. With that idea in mind, we added 2.0 equiv of imidazole to a solution of benzaldehyde (1 mmol) and nitromethane (1.5 equiv) in anhydrous dichloromethane (5 mL) and stirred for 10 min. To the resulting solution, triphenylphosphine (0.5 g, 1.5 mmol) and iodine (1.5 equiv) were added under argon atmosphere at 0 °C. The reaction took only 30 min to generate nitroalkene in 82% isolated yield. We extended the method[23] for the synthesis of a few

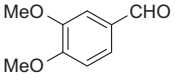
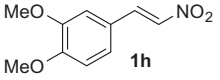
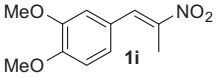
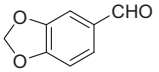
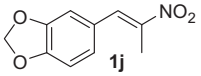
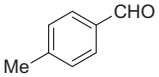
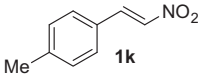
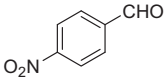
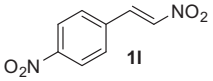
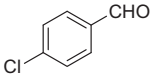
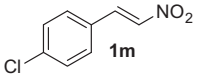
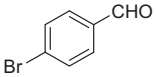
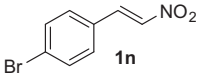
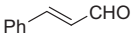
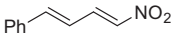
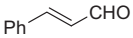
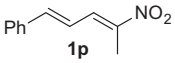
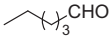
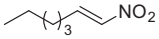
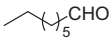
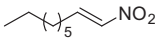
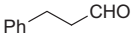
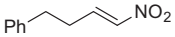
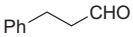
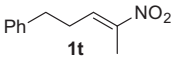
Table 2
Solid phase synthesis of nitroalkenes[a]



Entry	Aldehyde	R^2	t/h	Product	Yield[b] (%)
1	PhCHO	H	1	 **1a**	90
2		CH_3	1	 **1b**	89
3		H	1	 **1c**	84
4		CH_3	1	 **1d**	84
5		H	1	 **1e**	93
6		CH_3	1	 **1f**	91
7		CH_3	1	 **1g**	89

(*continued on next page*)

Table 2 (*continued*)

Entry	Aldehyde	R^2	*t*/h	Product	Yield[b] (%)
8		H	3	 **1h**	55
9		CH_3	3	 **1i**	54
10		CH_3	3	 **1j**	58
11		H	1	 **1k**	86
12		H	1	 **1l**	93
13		H	1	 **1m**	93
14		H	1	 **1n**	90
15		H	1	 **1o**	84
16		CH_3	1	 **1p**	89
17		H	3	 **1q**	75
18		H	3	 **1r**	81
19		H	3	 **1s**	87
20		CH_3	3	 **1t**	89

[a] Aldehyde:nitroalkane:triphenylphosphine:iodine:imidazole = 1.0:1.5:1.5:1.5:2.0.
[b] Isolated yield.

more nitroalkenes starting from aromatic aldehydes (Table 1, entries 2–8) with nitromethane/nitroethane. In all the cases, we found good yield of the corresponding nitroalkenes without formation of any side product.

Encouraged by the result in solution phase synthesis and the advantage of using polymer-bound triphenylphosphine (PBTPP) over simple triphenylphosphine (vide infra), we carried out the reaction of benzaldehyde with nitromethane under similar reaction conditions except for changing triphenylphosphine with PBTPP (1.5 equiv). For this purpose, polymer-bound triphenylphosphine, a diphenylphosphinated copolymer of styrene and 2% divinylbenzene (DVB) with loading of 3.2 mmol/g was used. Here it took comparatively longer time (1 h) to drive the reaction into completion and gave very good yield (85%). The reaction was generalized[24] for diverse aromatic aldehydes (entries 2–19) and found to work well under similar conditions to give very good yield. Only a few less electrophilic aldehydes, such as *m*, *p*-dimethoxybenzaldehyde (entries 8 and 9) and *m*, *p*-methylenedioxybenzaldehyde (entry 10) took longer reaction time (3 h) for complete conversion. All the products revealed exclusive formation of only the (*E*)-nitroalkenes. The (*E*)-configuration for 1,2-disubstututed nitroalkenes was confirmed from the coupling constant values of *trans*-coupled vicinal protons, while (*E*)-configuration of the trisubstituted nitroalkenes was determined by comparing the chemical shift values of the vinylic protons with literature data. It may be noted that, the vinylic proton of (*E*)-isomer appears downfield than the corresponding proton of the (*Z*)-isomer because of the strong anisotropic effect of the nitro group.[14c, 25] We observed similar efficiency in the synthesis of nitroalkene from α,β-unsaturated aldehyde (entries 15 and 16) and aliphatic aldehydes (Table 2, entries 17–20) as well under similar reaction conditions.

The probable mechanism for the exclusive formation of (*E*)-alkenes might be due to the formation of cyclic intermediate '**B**', where the nitro group is *syn* to the leaving group, that is, the phosphonium salt activated hydroxy group (Fig. 2). The absence of (*Z*)-nitroalkene, if formed, may additionally be explained by Stanetty and Kremslehner's report[26] that the (*Z*)-nitroalkenes undergo isomerization to give (*E*)-nitroalkenes in the presence of polymer-bound triphenylphosphine.

In summary, we have developed the first solid phase method for the synthesis of (*E*)-nitroalkenes from both aliphatic and aromatic aldehydes. Unlike most of the methods used for the synthesis of nitroalkene, the isolation of β-nitroalcohol is not required before converting it into nitroalkene in the successive step. Use of resin-bound triphenylphosphine simplified the purification process, because the triphenylphosphine oxide byproduct could be removed by simple filtration as against tedious purification process

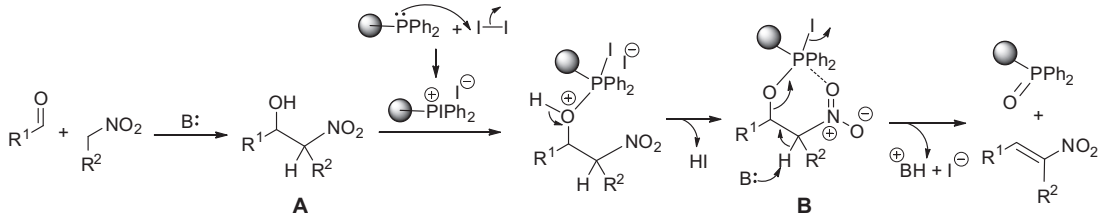


Figure 2. Plausible mechanism for the formation of exclusively (*E*)-nitroalkene.

encountered in many reported methods. Good yield, mild reaction conditions, no inert atmosphere, and two-step one-pot strategy are some major advantages over conventional dehydrating reagents used in solution chemistry.

Acknowledgements

Thanks are due to the Department of Science and Technology (DST), New Delhi [Grant No. SR/S1/OC-25/2007] for providing financial supports to carry out this work. The analytical services provided by the Sophisticated Analytical Instrumentation Facility (SAIF), North Eastern Hill University, Shillong and Central Instrumentation Facility (CIF), Indian Institute of Technology, Guwahati, India are acknowledged. The authors gratefully acknowledge the suggestions made by the reviewers to improve the content.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.07.146.

References and notes

1. (a) Boelle, J.; Schneider, R.; Gerardin, P.; Loubinoux, B.; Maienfisch, P.; Rindlisbacher, A. *Pestic. Sci.* **1998**, *54*, 304; (b) Brian, P. W.; Grove, J. F.; McGowan, J. C. *Nature* **1946**, *158*, 876; (c) McGowan, J. C.; Brian, P. W.; Hemming, H. G. *Ann. Appl. Biol.* **1948**, *35*, 25; (d) Schales, O.; Graefe, H. A. *J. Am. Chem. Soc.* **1952**, *74*, 4486; (e) Dann, O.; Moller, E. F. *Chem. Ber.* **1949**, *82*, 76; (f) Zee-Cheng, K.-Y.; Cheng, C. C. *J. Med. Chem.* **1969**, *12*, 157; (g) Plenevaux, A.; Dewey, S. L.; Fowler, J. S.; Guillaume, M.; Wolf, A. P. *J. Med. Chem.* **1990**, *33*, 2015; (h) Rosowsky, A.; Mota, C. E.; Wright, J. E.; Freisheim, J. H.; Heusner, J. J.; McCormack, J. J.; Queener, S. F. *J. Med. Chem.* **1993**, *36*, 3103; (i) Vallejos, G.; Fierro, A.; Rezende, M. C.; Sepulveda-Boza, S.; Reyes-Parada, M. *Bioorg. Med. Chem.* **2005**, *13*, 4450.
2. (a) Berner, O. M.; Tedeschi, L. *Eur. J. Org. Chem.* **2002**, 1877; (b) Tsogoeva, S. B. *Eur. J. Org. Chem.* **2007**, 1701; (c) Christoffers, J.; Koripelly, G.; Rosiak, A.; Rössle, M. *Synthesis* **2007**, 1279; (d) Laso, N. M.; Quiclet-Sire, B.; Zard, S. Z. *Tetrahedron Lett.* **1996**, *37*, 1605; (e) Fryszkowska, A.; Fisher, K.; Gardiner, J. M.; Stephens, G. M. *J. Org. Chem.* **2008**, *73*, 4295; (f) Czekelius, C.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 4793; (g) Czekelius, C.; Carreira, E. M. *Org. Lett.* **2005**, *6*, 4575; (h) Narcis, M. J.; Sprague, D. J.; Captain, B.; Takenaka, N. *Org. Biomol. Chem.* **2012**, *10*, 9134; (i) Çelebi-Ölçüm, N.; Ess, D. H.; Aviyente, V.; Houk, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 4528; (j) Takenaka, N.; Sarangthem, R. S.; Seerla, S. K. *Org. Lett.* **2007**, *9*, 2819; (k) Wu, L.-Y.; Bencivenni, G.; Mancinelli, M.; Mazzanti, A.; Bartoli, G.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 7196; (l) Bartelson, K. J.; Singh, R. P.; Foxman, B.; Deng, L. *Chem. Sci.* **2011**, *2*, 1940.
3. Park, J.; Pei, D. *Biochemistry* **2004**, *43*, 15014.
4. (a) Novellino, L.; d'Ischia, M.; Prota, G. *Synthesis* **1999**, 793; (b) He, F.; Bo, Y.; Altom, J. D.; Corey, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 6771.
5. (a) Drehal, G.; Ehrhardt, H. *Chem. Ber.* **1960**, *93*, 500; (b) Heinzelman, R. V. *Org. Synth.* **1963**, *4*, 573; (c) McDonald, E.; Martin, R. T. *Tetrahedron Lett.* **1977**, *18*, 1317; (d) Ono, N.; Kawamura, H.; Bougauchi, M.; Maruyama, K. *Tetrahedron* **1990**, *46*, 7483; (e) Yan, S.; Gao, Y.; Xing, R.; Shen, Y.; Liu, Y.; Wu, P.; Wu, H. *Tetrahedron* **2008**, *64*, 6294; (f) Alizadeh, A.; Khodaei, Md. M.; Eshghi, A. *J. Org. Chem.* **2010**, *75*, 8295; (g) Ballini, R.; Palmieri, A. *Curr. Org. Chem.* **2006**, *10*, 2145; (h) Gairand, C. B.; Lappin, G. R. *J. Org. Chem.* **1953**, *18*, 1–3.
6. (a) Noland, E. *Org. Synth.* **1973**, *5*, 833; (b) Miyashita, M.; Yanami, T.; Yoshikoshi, A. *Org. Synth.* **1990**, *7*, 396.
7. (a) Knochel, P.; Seebach, D. *Synthesis* **1982**, 1017; (b) Lucet, D.; Sabelle, S.; Kostelitz, O.; Le Gall, T.; Mioskowski, C. *Eur. J. Org. Chem.* **1999**, 2583.
8. Saikia, A. K.; Barua, N. C.; Sharma, R. P.; Ghosh, A. C. *Synthesis* **1994**, 685.
9. Hass, H. B.; Susie, A. G.; Heider, R. L. *J. Org. Chem.* **1950**, *15*, 8.
10. (a) Melton, J.; McMurry, J. E. *J. Org. Chem.* **1975**, *40*, 2138; (b) Palomo, C.; Aizpurua, J. M.; Cossío, F. P.; García, J. M.; López, M. C.; Oiarbide, M. *J. Org. Chem.* **1990**, *55*, 2070.
11. (a) Denmark, S. E.; Marcin, L. R. *J. Org. Chem.* **1993**, *58*, 3850; (b) Duursma, A.; Minnaard, A. J.; Feringa, B. L. *Tetrahedron* **2002**, *58*, 5773.
12. (a) Rosini, G.; Ballini, R.; Oetrini, M.; Sorrenti, P. *Synthesis* **1985**, 515; (b) Ballini, R.; Castagnani, R.; Petrini, M. *J. Org. Chem.* **1992**, *57*, 2160.
13. Ballini, R.; Noè, M.; Perosa, A.; Selva, M. *J. Org. Chem.* **2008**, *73*, 8520.
14. (a) Sakakibara, T.; Takai, I.; Ohara, E.; Sudoh, R. *J. Chem. Soc., Chem. Commun.* **1981**, *6*, 261; (b) Retherford, C.; Knochel, P. *Tetrahedron Lett.* **1991**, *32*, 441; (c) Hayama, T.; Tomoda, S.; Takeuchi, Y.; Nomura, Y. *Tetrahedron Lett.* **1982**, *23*, 4733; (d) Myers, A. G.; Barbay, J. K.; Zhong, B. *J. Am. Chem. Soc.* **2001**, *123*, 7207; (e) Ochiai, M.; Fujita, E.; Arimoto, M.; Yamaguchi, H. *Chem. Pharm. Bull.* **1984**, *32*, 5027; (f) Kantam, M. L.; Sreekanth, P. *Catal. Lett.* **1999**, *57*, 227.
15. Concellón, J. M.; Bernad, P. L.; Rodríguez-Solla, H.; Concellón, C. *J. Org. Chem.* **2007**, *72*, 5421.
16. (a) Jovel, I.; Prateeptongkum, S.; Jackstell, R.; Vogl, N.; Weckbecker, C.; Beller, M. *Adv. Synth. Catal.* **2008**, *350*, 2493; (b) Sreekumar, R.; Padmakumar, R.; Rugmini, P. *Tetrahedron Lett.* **1998**, *39*, 2695.
17. Rodríguez, J. M.; Pujol, M. D. *Tetrahedron Lett.* **2011**, *52*, 2629.
18. (a) Boas, U.; Brask, J.; Jensen, K. J. *Chem. Rev.* **2009**, *109*, 2092; (b) Thompson, A. A.; Ellman, J. A. *Chem. Rev.* **1996**, *96*, 555; (c) Hermkens, P. H. H.; Ottenheim, H. C. J.; Rees, D. *Tetrahedron* **1996**, *53*, 5643; (d) Balkenhohl, F.; von dem Bussche-Hünnefeld, C.; Lansky, A.; Zechel, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2288.
19. (a) Araya, J. J.; Montenegro, G.; Mitscher, L. A.; Timmermann, B. N. *J. Nat. Prod.* **2010**, *73*, 1568; (b) Harned, A. M.; Mukherjee, S.; Flynn, D. L.; Hanson, Paul R. *Org. Lett.* **2003**, *5*, 15; (c) Mothana, S.; Chahal, N.; Vanneste, S.; Hall, D. G. *J. Comb. Chem.* **2007**, *9*, 193; (d) Nandy, J. P.; Prakesch, M.; Khadem, S.; Thirupathi Reddy, P.; Sharma, U.; Arya, P. *Chem. Rev.* **1999**, *2009*, 109.
20. (a) Michaelidou, S. S.; Koutentis, P. A. *Tetrahedron* **2009**, *65*, 8428; (b) Delvare, C.; Harris, C. S.; Hennequin, L.; Koza, P.; Lambert-van der Brempt, C.; Pelleter, J.; Willerval, O. *ACS Comb. Sci.* **2011**, *13*, 449; (c) El-Dahshan, A.; Ahsanullah; Rademann, J. *Pept. Sci.* **2010**, *94*, 220; (d) Christoforou, I. C.; Kalogirou, A. S.; Koutentis, P. A. *Tetrahedron* **2009**, *65*, 9967; (e) Comely, A. C.; Gibson, S. E.; Hales, N. J. *Chem. Commun.* **2000**, 305; (f) Tunoori, A. R.; Dutta, D.; Georg, G. I. *Tetrahedron Lett.* **1998**, *39*, 8751; (g) Classon, B.; Liu, Z. *J. Org. Chem.* **1988**, *53*, 6126; (h) Holletz, T.; Cech, D. *Synthesis* **1994**, 789.
21. Regen, S. L.; Lee, D. P. *J. Org. Chem.* **1975**, *40*, 1669.
22. (a) Rokhum, L.; Bez, G. *Can. J. Chem.* **2013**, *91*, 1. http://dx.doi.org/10.1139/cjc-2012-0164; (b) Rokhum, L.; Bez, G. *J. Chem. Sci.* **2012**, *124*, 687.
23. *Typical procedure for solution phase synthesis of nitroalkene*: To a solution of benzaldehyde (0.106 g, 1.0 mmol) and nitromethane (0.091 g, 1.5 mmol) in anhydrous dichloromethane (5.0 mL) was added imidazole (0.136 g, 2.0 mmol) and stirred for 10 min. The resulting mixture was cooled to 0 °C and triphenylphosphine (0.5 g, 1.5 mmol) and iodine (0.380 g, 1.5 mmol) were added under argon atmosphere. After stirring for additional 30 min, the reaction was complete. The solution was diluted with dichloromethane (20.0 mL) and washed with a saturated solution of sodium thiosulphate (20.0 mL) to remove the unreacted iodine. The organic layer was separated, washed with brine (20 mL), dried over anhydrous sodium sulfate, and concentrated under vacuo. The resultant crude product was purified by column chromatography using 10% ethyl acetate in hexane to get the pure product in 82% (0.122 g, 0.82 mmol) yield.
24. *Typical procedure for solid phase synthesis of nitroalkene:* To a solution of benzaldehyde (0.106 g, 1 mmol) and nitromethane (0.091 g, 1.5 mmol) in anhydrous dichloromethane (10.0 mL) was added imidazole (0.136 g, 2.0 mmol) and stirred for 10 min. To the resulting mixture, polymer-bound triphenylphosphine (0.5 g, 1.5 mmol) and iodine (0.380 g, 1.5 mmol) were added and allowed to stir for additional 50 min. After completion of the reaction, the solution was filtered through a sintered funnel and the resin was washed successively with dichloromethane (30.0 mL) and saturated aqueous sodium thiosulfate solution (10.0 mL) thrice. The combined dichloromethane and sodium thiosulfate solution was vigorously shaken in a separating funnel to remove any unreacted iodine. The organic layer was washed with brine (20.0 mL) and separated, dried over anhydrous sodium sulfate, and concentrated under vacuo. The resultant crude product was purified by column chromatography using 10% ethyl acetate in hexane to get the pure product in 85% (0.127 g, 0.85 mmol) yield.
Spectroscopic data of the new compounds: 1-Bromo-3-((E)-2-nitroprop-1-enyl)benzene, ***1g***: Pale yellow liquid; IR (KBr): ν 3025, 2952, 1643, 1600, 1527, 1434, 1381, 1222, 1122, 1043, 930, 758, 678, 545, 446 cm^{-1}. ^1H NMR

(400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.64–7.23 (m, 4H), 2.36 (s, 3H). ^{13}C NMR (100 Hz, $CDCl_3$): δ 134.44, 132.79, 132.50, 131.86, 130.40, 128.37, 122.95, 14.02. ESI-MS: m/z 242.2 (M^+). Anal. Calcd for $C_9H_8BrNO_2$: C, 44.66; H, 3.33; Br, 33.01; N 5.79. Found: C, 44.62; H, 3.35; Br, 33.03; N, 5.77.

5-((E)-2-Nitroprop-1-enyl)benzo[d][1,3]dioxole, ***1j****:* Pale yellow solid. Mp 101–102; IR (KBr): ν 3605, 3025, 2402, 1643, 1525, 1434, 1374, 1210, 1116, 1043, 930, 758, 545, 543 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 6.99–6.88 (m, 3H), 6.04 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (100 Hz, $CDCl_3$): δ 149.29, 148.25, 146.15, 133.67, 125.95, 125.51, 109.53, 108.86, 101.77, 14.17. ESI-MS: m/z 207.2 (M^+). Anal. Calcd for $C_{10}H_9N0_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.94; H, 4.37; N, 6.79.

1-Chloro-4(2-nitrovinyl)benzene, ***1m****:* Yellowish solid. Mp 113–114 °C; IR (KBr): ν 3041, 2932, 2849, 1633, 1573, 1452, 1192, 1093, 824, 769, 751, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 13.6 Hz, 1H), 7.49 (d, J = 13.6 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.36, 137.71, 137.41, 130.27, 129.78, 128.52. MS-EI:m/z (%) 183.03 (M^+). Anal. Calcd for $C_8H_6ClNO_2$: C, 52.34; H, 3.29; Cl, 19.31; N, 7.63. Found: C, 52.36; H, 3.31; Cl, 19.29; N, 7.65.

((1E,3E)-4-Nitropenta-1, 3-dien-1-yl)benzene, ***1p****:* Yellow solid. Mp 65–66; IR (KBr): ν 3015, 2974, 2331, 1645, 1526, 1401, 1121, 1075, 865, 781, 656 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 12.4 Hz, 1H), 7.52–7.36 (m, 5H), 7.04 (d, J = 12.8, 1H), 6.90 (dd, J = 12.0, 2, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.29, 143.97, 135.65, 133.76, 129.88, 128.98, 127.54, 121.26, 13.06. MS-EI: m/z (%) 198.03 (M^+). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.62; H, 5.75; N, 7.68.

25. Hayama, T.; Tomoda, S.; Takeuchi, Y.; Nomura, Y. *Chem. Lett.* **1982**, 1109.
26. Stanetty, P.; Kremslehner, M. *Tetrahedron Lett.* **1998**, *39*, 811.