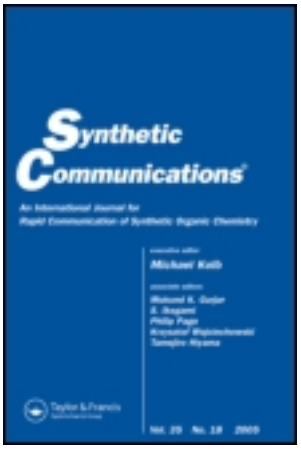

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Solvent-Free Microwave-Assisted Preparation of N-(2-(Pyridin-2-yl)-ethyl)sulfonamides

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SOLVENT-FREE MICROWAVE-ASSISTED PREPARATION OF *N*-(2-(PYRIDIN-2-YL)-ETHYL)SULFONAMIDES

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GRAPHICAL ABSTRACT

(2) **(3)** **(1)**

Abstract *Although nitrogen-containing heterocycles and sulfonamides both play crucial roles in the chemical and pharmaceutical industries, surprisingly little research exists that examines the bifunctional N-(2-(pyridin-2-yl)ethyl)sulfonamide scaffold for any potential applications. Retrosynthetic analysis indicates that this skeleton would be well suited for a conjugate addition reaction. However, the ability of 2-vinylpyridine to behave as an acceptor, and of sulfonamides to behave as donors, has very limited literature precedent, and thus required some preliminary investigations into their mutual reactivity. Herein outlines our laboratory's discovery of a novel and efficient solvent-free 1,4-aza-conjugate addition reaction between sulfonamides and 2-vinylpyridines that provides expedient access to various N-(2-(pyridin-2-yl)ethyl)sulfonamide derivatives. The products, possessing multiple sites of Brønsted acidity and basicity in close proximity, could display a wide array of valuable host–guest properties and should thus be investigated for potent pharmaceutical or agrochemical properties.*

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications® *for the following free supplemental resource(s): Full experimental and spectral details.]*

Keywords Conjugate addition; microwave-assisted synthesis; sulfonamide; 2-vinylpyridine

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INTRODUCTION

Pyridine rings are linchpins of the pharmaceutical and chemical industries.[1] Like their phenyl cousins, these heterocycles are rigid and planar, allowing for hydrophobic interactions within enzyme binding pockets; however, the addition of an electron-rich heteroatom concomitantly provides sites for hydrogen bonding, improving solvation properties[2] while encouraging interactions with more polar substrates.

Similarly, perhaps no medicinal pharmacophore has enjoyed as much success in pharmaceuticals as the sulfonamide. The dual proximal functionalities of (a) a strong hydrogen bond donor that can also be ionized at physiological pH and (b) a weakly basic sulfonyl hydrogen bond acceptor allows for myriad electrostatic interactions with biological targets,[3–6] while the tetrahedral geometry of the sulfur atom provides for a high degree of conformational flexibility.[6]

The marriage of these two functionalities into an *N*-(2-(pyridin-2-yl)ethyl)sulfonamide **(1)** scaffold promises much more than merely imparting the well-known chemical and pharmacokinetic properties of the individual pharmacophores. The ideal proximal placement of two basic nitrogen heteroatoms should welcome strong substrate–metal host–guest chelation interactions. Such metal ligation has repeatedly demonstrated significance in a number of chemical processes,[7,8] and the presence of at least two nitrogen atoms should give *N*-(2-(pyridin-2-yl)ethyl)sulfonamide scaffolds a strong chelation affinity for metal cations.[9,10] This potential for tight chelation elucidates molecules containing this unique scaffold as good candidates for water[11,12] and environmental purification and analysis,[13,14] medical diagnostics and therapies,[12,15–26,10,27–30] and organocatalysis.[8]

Despite this vast potential, surprisingly little research exists that examines a straightforward synthetic approach to the *N*-(2-(pyridin-2-yl)ethyl)sulfonamide **(1)** scaffold. Our laboratory envisions this target as an opportunity to investigate the viability of an *aza*-conjugate addition between 2-vinylpyridines **(2)** as electron acceptors and sulfonamides **(3)** as electron donors. 1,4-Conjugate additions are remarkably efficient reactions used ubiquitously in organic synthesis for the construction of diversified molecular skeletons, particularly those with ethylene connectors between two functionalities. However, the innately poor behavior of sulfonamides as electron donors and 2-vinylpyridines as acceptors poses a significant challenge. Conjugate addition with weakly nucleophilic sulfonamides has been severely limited to activated acrylate substrates with electron-withdrawing substituents, and further activation of either the nucleophile[31–37] or electrophile[38–41] is required. Alternatively, although not widespread within the synthetic literature, 2-vinylpyridine has demonstrated limited success as an acceptor in conjugate addition reactions,[42] most recently using sodium methanesulfinate as a nucleophile.[43] In most of these examples, however, the success of the reaction is reliant on activation of 2-vinylpyridine via Brønsted acid,[43–47] Lewis acid,[48,49] or Morita–Baylis–Hillman-type activation.[50]

Despite these inherent limitations, our laboratory has recently discovered a facile and efficient *aza*-conjugate addition for the synthesis of the *N*-(2-(pyridin-2-yl)ethyl)sulfonamide **(1)** scaffold (Scheme 1). We herein describe the development of the solvent-free protocol, demonstrate its utility in the synthesis of various derivatives, and propose a rational mechanism based on our studies.

Scheme 1. 1,4-Conjugate addition of sulfonamides **3** to 2-vinylpyridines **2**.

DISCUSSION

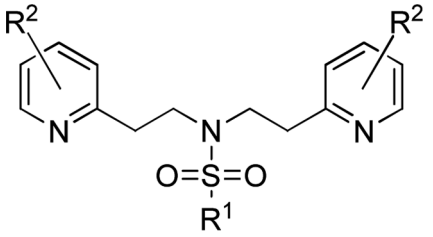
The *aza*-conjugate addition of benzensulfonamide **3a** to 2-vinylpyridine **2a** was initially employed as a model system. Surprisingly, a clean reaction was observed when the reagents were heated neat in a sealed tube (Table 1). However, this initial protocol suffered from (a) the necessity for very high temperatures, wherein no reaction would occur below 120 °C, and (b) extended reaction times longer than 24 h, after which (c) equilibration would occur between the individual starting materials, products, and a by-product, presumably bis-alkylated sulfonamide **4a** (Fig. 1) resulting from a second conjugate addition on unreacted 2-vinylpyridine (Table 1, entries 1–4).

The high temperature and solventless conditions suggested that this novel 1,4-conjugate addition reaction would be a perfect candidate for microwave-assisted synthesis. Conjugate additions of sulfonamides in particular have been significantly enabled by microwave radiation, often yielding products in good yields in no longer

Table 1. Impact of various additives, reaction temperatures, heat sources, reaction lengths, and reagent stoichiometries, on progress of *aza*-conjugate addition reactions between **2a** and **3a**

						Product ratios[a]	
Ex.	Heat	Temp. (°C)	Additives (eqv)	**3a:2a**	Time (h)	**1a:2a**	**1a:4a**
1	Oil	125	—	1:1	24	1.7:1	2.8:1
2	Oil	140	—	1:1	24	2.9:1	6.7:1
3	Oil	165	—	1:1	24	25:1	10:1
4	Oil	165	—	1:1	40	6.3:1	7.7:1
5	MW	170	—	1:1	.75	5.9:1	17:1
6	**MW**	**170**	—	**1.5:1**	**.75**	**17:1**	**33:1**
7	MW	170	TBAI (50–100 mg)	1.5:1	1	6.7:1	—
8	MW	170	TBAB (100 mg)	1.5:1	.75	4.5:1	—
9	MW	170	$BnEt_3NCl$ (100 mg)	1.5:1	.75	3.4:1	—
10	MW	170	KF (0.25)	1.5:1	.75	5.0:1	17:1
11	MW	170	Cs_2CO_3 (0.25)	1:1	.5	.05:1	—
12	MW	170	Cs_2CO_3 (0.75–2)	1:1	.75	No addition	
13	Oil	60	HOAc (5) in EtOH	5:1	2	No addition	
14	Oil	60	TFA (5) in CH_2Cl_2	5:1	2	No addition	
15	—	−78 to rt	$TiCl_4$ (1–5) in CH_2Cl_2	5:1	2	No addition	
16	—	−78 to 40	$AlCl_3$ (1–5) in CH_2Cl_2	5:1	2	No addition	

[a]Ratios of **1a:2a** and **1a:4a** determined by ^{1}H NMR integration analysis.



4

Figure 1. Proposed structure of by-product observed in conjugate addition reactions between sulfonamides **(3)** and 2-vinylpyridines **(2)**.

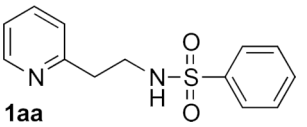
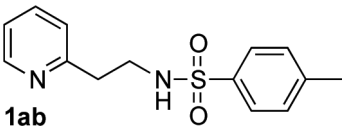
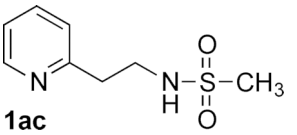
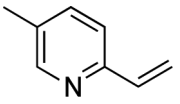
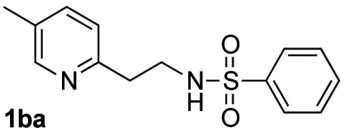
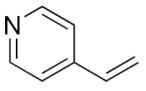
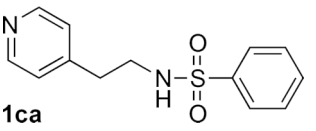
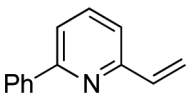
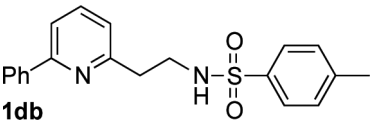
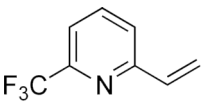
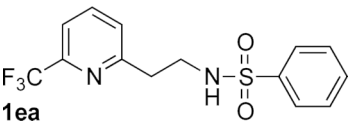
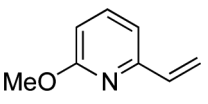
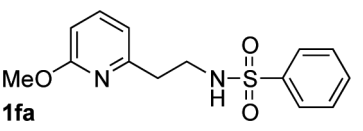
than 0.5 h.[31,34,37,51] Encouraged by this literature precedent, microwave heating was introduced to our conjugate addition reactions. Gratifyingly, 60 W of power allows the systems to reach and maintain a temperature of 170 °C, and after 30–45 min the mixtures achieve their maximum conversion, as opposed to days using conventional heating. This vastly truncated reaction time not only increases the overall attraction and utility of this reaction in the laboratory, but it is inherently responsible for the reaction's success: reaction times of 30–45 min allow for interception of products **1a**, with excellent purities, prior to the long-term equilibration described previously (Table 1, entries 5 and 6).

Next, we examined the effect of various additives on the reaction progression (Table 1, entries 7–18). The extent of reaction **(1a:2a)** and by-product formation **(1a:4a)** were facilely monitored by comparing the normalized ^{1}H NMR integrations between 2-vinylpyridine **2a** (three distinct vinyl peaks at 5.41, 6.13, and 6.77 pm), the desired product **1a** (two ethylene peaks at 3.32 and 2.86 ppm), and by-product **4a** (two ethylene peaks directly downfield from the ethylene peaks of **1a**). Surprisingly, adjuvants that typically promote thermally controlled reactions do not improve the reaction outcome. It was originally theorized that an ionic salt[34,51] would be required to solubilize the solid sulfonamide reactant, help promote conjugate addition via participation in a Morita–Baylis–Hillman-type fashion, or even behave as a highly efficient microwave absorber. However, parallel rate experiments with various ionic salts demonstrate no impact on the reaction rate or extent of completion (Table 1, entries 7–9), and inherently increase the complexity of product isolation.

We also initially proposed that the addition of an inorganic base would enhance the nucleophilicity of the poorly reactive sulfonamide.[31–34,36,37,51,52] However, increasing amounts of base are surprisingly detrimental to the reaction progression (Table 1, entries 10–12). Alternatively, additional Brønsted and Lewis acids do not appear to activate the pyridine electrophile either, as no trace of addition product is observed under these conditions (Table 1, entries 13–16).

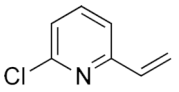
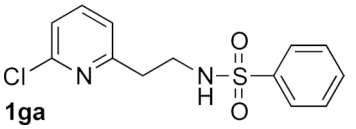
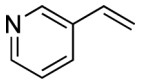
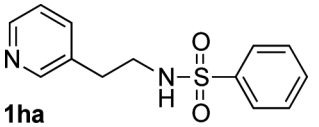
Since the optimal microwave protocol merely requires the neat mixing of the two starting materials, with greatest rates of completion observed when the sulfonamide is in excess (Table 1, entry 6), the reaction workup is also simplified, obviating the need for any chromatography or extractions. The crude mixture can be merely triturated with hot chloroform and hexanes, wherein excess sulfonamide starting

Table 2. Substrate scope for *aza*-conjugate addition reactions between various vinylpyridines **(2)** and sulfonamides **(3)**[a]

Ex.	Pyridine	Sulfonamide R^1	Product	1:2[b]	Yield[c] (%) (brsm)[d]
1	**2a**	Ph **(3a)**	 **1aa**	17:1	63 (100)
2	**2a**	Tol **(3b)**	 **1ab**	20:1	71 (100)
3	**2a**	Me **(3c)**	 **1ac**	5.0:1	53 (100)
4	 **2b**	**3a**	 **1ba**	20:1	34 (75)
5	 **2c**	**3a**	 **1ca**	3.2:1	13 (100)
6	 **2d**	**3b**	 **1db**	5.8:1	15 (35)
7[e]	 **2e**	**3a**	 **1ea**	6.3:1	32 (71)
8	 **2f**	**3a**	 **1fa**	No addition	

(*Continued*)

Table 2. Continued

Ex.	Pyridine	Sulfonamide R^1	Product	1:2[b]	Yield[c] (%) (brsm)[d]
9	 **2g**	**3a**	 **1ga**		No addition
10	 **2h**	**3a**	 **1ha**		No addition

[a]All reactions displayed minimal, if any, by-product via ^{1}H NMR integration analysis.
[b]Ratios of 1:2 determined by ^{1}H NMR integration analysis.
[c]Isolated product yield.
[d]Yield based on recovered sulfonamide **3**.
[e]0.25 equivalents of Cs_2CO_3 was added.

material cleanly crashes out and can be recovered. Next, upon cooling the filtrate, the desired *N*-(2-(pyridin-2-yl)ethyl)sulfonamide typically crystallizes out, separating the stable product from any remaining 2-vinylpyridine. This streamlined workup procedure was only made possible by the elimination of by-product formation: mono- and bis-alkylated products **1** and **4** co-crystallize and can only be separated by careful chromatography.

With the conditions for the conjugate addition reaction significantly optimized, we have had the opportunity to explore the substrate scope and synthesize other *N*-(2-(pyridin-2-yl)ethyl)sulfonamide derivatives (Table 2). First the microwave protocol has been expanded to include reactions with methane- and toluene sulfonamide **(3b and 3c)** nucleophiles, providing products in excellent purity and yields based on recovered starting material (Table 2, entries 2 and 3). Moreover, we have recently focused our efforts on employing differentially substituted 2-vinylpyridine electrophiles and have demonstrated the successful coupling of sulfonamides with alkyl- and aryl-substituted 2-vinylpyridines (Table 2, entries 4 and 6).

The mechanistic assumption that this reaction does indeed take place via conjugate addition has been validated by the successful coupling of benzene sulfonamide **3a** with 4-vinylpyridine **2c** (albeit with poor yield of the corresponding 1,6-addition product) while 3-vinylpyridine **2h** fails to react under the same conditions (Table 2, entries 5 and 10). On this account, it was reasonably predicted that the attachment of an electron-withdrawing group to the 6-position of 2-vinylpyridine would improve its electrophilicity and thus hasten the reaction, while an electron-donating substituent would inherently diminish the reactivity of the pyridine acceptor. In the event, however, it was observed that both withdrawing and donating substituents deter any conjugate addition from occurring. Surprisingly, 6-trifluoromethyl-2-vinylpyridine **2e** can be prompted to react with the addition of

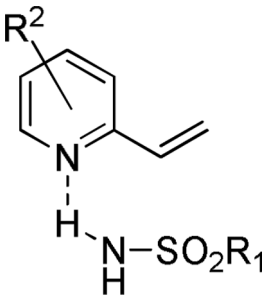


Figure 2. Proposal for initial mutual activation between sulfonamides **(3)** and 2-vinylpyridines **(2)** that occurs prior to conjugate addition.

a substoichiometric quantity of base, while 6-methoxy- and 6-chloro-2-vinylpyridine **(2f and 2g)** fail to react neat or in the presence of any adjuvants (Table 2, entries 7–9). These results strongly suggest that (a) resonance donors disable the overall electrophilicity of 2-vinylpyridines, but even more intriguingly (b) the conjugate addition must initially involve mutual activation, likely via hydrogen bonding, between the pyridine nitrogen and sulfonamide proton (Fig. 2).[53,54] This mechanistic feature accounts for the observation that pyridine substituents that withdraw electrons inhibit the nitrogen's ability to protonate and become an activated conjugate acceptor, although this inactivity can be overcome by instead increasing the sulfonamide's nucleophilicity via deprotonation. The nature of this mechanism is currently under investigation in our laboratory.

In summary, our laboratory has developed a novel, generalized method for the synthesis of *N*-(2-(pyridin-2-yl)ethyl)sulfonamides **(1)**, via the *aza*-conjugate addition of sulfonamides **(3)** to 2-vinylpyridine derivatives **(2)**. The inherent success of this microwave-assisted reaction without any adjuvant reagents or solvents, as well as the ease of product workup and isolation, makes this protocol highly advantageous and viable, despite the unavoidable thermodynamic equilibration.

EXPERIMENTAL

Benzenesulfonamide (219 mg, 1.39 mmol, 1.5 eqv) and 2-vinylpyridine (0.1 mL, 0.93 mmol, 1.0 eqv) were added to a microwave vial equipped with stir bar. The vial was irradiated in the microwave for 45 min (170 °C at a maximum of 60 W), after which the crude reaction mixture was dissolved in acetone, transferred to a round-bottom flask, and concentrated via rotary evaporation. The resultant brown residue was dissolved in a minimal amount of hot chloroform and cooled in an ice bath. The excess sulfonamide precipitate was removed via vacuum filtration, and the filtrate was concentrated under vacuum. Subsequently, the residue was redissolved in a minimal amount of hot chloroform and then triturated with cold hexanes until a sticky residue formed and the mother liquor became clear. The mother liquor containing excess 2-vinylpyridine was decanted, whereas the sticky residue was recrystallized from ethyl acetate/hexanes to afford 150 mg (63% yield, 100% brsm) of **1aa** as a light brown solid: IR (neat) ν 3082, 2854, 1595, 1441, 1314, 1144,

1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.45 (1H, d, $J = 2.4$ Hz), 7.83 (2H, m), 7.59–7.42 (4H, m), 7.15–7.09 (1H, m), 7.04 (1H, d, $J = 8.1$ Hz), 6.16 (1H, t, $J = 5.1$ Hz), 3.36 (2H, q, $J = 6$ Hz), 2.91 (2H, t, $J = 6$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 136.7, 132.4, 129.0, 127.0, 123.5, 121.8, 42.1, 35.9. HRMS (TOF) calculated for $C_{13}H_{15}N_2O_2S$ $[M + H]^+$: 262.07760; found: 262.07786.

SUPPORTING INFORMATION

The following material can be found via the Supplementary Content section of this article's webpage: (1) example of ^1H NMR used in determining extent of reaction completion; (2) general procedure for syntheses and characterization data for compounds **1aa, 1ab, 1ac, 1ba, 1ca, 1db**, and **1ea**; and (3) ^1H and ^{13}C NMR spectra for all *N*-(2-(pyridinyl)ethyl)sulfonamide products.

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REFERENCES

1. Bonnet, V.; Mongin, F.; Trecourt, F.; Breton, G.; Marsais, F.; Knochel, P.; Queginer, G. *Synlett* **2002**, 1008–1010.
2. Attwood, D. *Adv. Coll. Inter. Sci.* **1995**, *55*, 271–303.
3. De Benedetti, P. G. *Adv. Drug. Res.* **1987**, *16*, 227–279.
4. Elgersma, R.C.; Meijneke, T.; de Jong, R.; Brouwer, A. J.; Posthuma, G.; Rijkers, D. T. S.; Liskamp, R. M. J. *Org. Biomol. Chem.* **2006**, *4*, 3587–3597.
5. Weidner-Wells, M. A.; Macielag, M. J. Sulfonamides. In *Kirk-Othmer Encyclopedia of Chemical Technology,* 5th ed.; J. I. Kroschwitz; A. Seidel (Eds.); John Wiley & Sons: New York, 2007; vol. 23, pp. 493–513.
6. Reitz, A. B.; Smith, G. R.; Parker, M. H. *Expert. Opin. Ther. Patents* **2009**, *19*, 1449–1453.
7. Bianchi, A.; Micheloni, M.; Paoletti, P. *Coord. Chem. Rev.* **1991**, *110*, 17–113.
8. Kimura, E. *Tetrahedron* **1992**, *48*, 6175–6217.
9. Siaugue, J.-M.; Segat-Dioury, F.; Favre-Reguillon, A.; Madic, C.; Foos, J.; Guy, A. *Tetrahedron Lett.* **2000**, *41*, 7443–7446.
10. Bridger, G. J.; Skerlj, R. T.; Padmanabhan, S.; Martellucci, S. A.; Henson, G. W.; Struyf, S.; Witvrouw, M.; Schols, D.; De Clercq, E. *J. Med. Chem.* **1999**, *42*, 3971–3981.
11. Karigiannis, G.; Papaioannou, D. *Eur. J. Org. Chem.* **2000**, 1841–1863.
12. Liang, X.; Sadler, P. J. *Chem Soc Rev* **2004**, *33*, 246–266.
13. Kimura, E.; Kurogi, Y.; Takahashi, T. *Inorg Chem* **1991**, *30*, 4117–4121.
14. Guilard, R.; Chollet, H.; Guiberteau, P.; Cocolios, P. Polyazacycloalkanes, tri, tetra or pentaazamacrocyclic complexes grafted to a support. W01996011056, **1996**.
15. Caravan, P.; Ellison, J. J.; McMurry, J.; Lauffer, R. B. *Chem. Rev.* **1999**, *99*, 2293–2352.
16. Guo, Z.; Sadler, P. J. *Angew. Chem. Int. Ed.* **1999**, *38*, 1512–1531.
17. Reichert, D. E.; Lewis, J. S.; Anderson, C. J. *Coord. Chem. Rev.* **1999**, *184*, 3–66.

18. Jeon, H. L.; Choi, M. G.; Choe, J.-I.; Chang, S.-K. *Bull. Korean. Chem. Soc.* **2009**, *30*, 1093–1096.
19. Kamioka, S.; Sugiyama, S.; Takahashi, T.; Doi, T. *Org. Biomol. Chem.* **2010**, *8*, 2529–2536.
20. Jackson, G. E.; Mkhonta-Gama, L.; Voye, A.; Kelly, M. *J. Inorg. Biochem.* **2000**, *79*, 147–152.
21. Kramer, R. *Angew. Chem. Int. Ed.* **2000**, *39*, 4469–4470.
22. De Clercq, E. *Nat. Rev. Drug Discov.* **2002**, *1*, 13–25.
23. Liang, F.; Wan, S.; Li, Z.; Xiong, X.; Yang, L.; Zhou, X.; Wu, C. *Curr. Med. Chem.* **2006**, *13*, 711–727.
24. Xiong, X.-Q.; Liang, F.; Yang, L.; Wang, X.-L.; Zhou, X.; Zheng, C. Y.; Cao, X.-P. *Chem. Biodivers.* **2007**, *4*, 2791–2797.
25. De Clercq, E.; Yamamoto, N.; Pauwels, R.; Baba, M.; Schols, D.; Nakashima, H.; Balzarini, J.; Debyser, Z.; Burrer, B. A.; Schwartz, D.; Thornton, D.; Bridger, G. J.; Fricker, S.; Henson, G. W.; Abrams, M.; Picker, D. *Proc. Natl. Acad. Sci. USA* **1992**, *89*, 5286–5290.
26. Inouye, T.; Kanamori, T.; Sugiyama, M.; Yoshida, T.; Kolke, T.; Shionoya, K.; Enomoto, K.; Suchiro, K.; Kumura, E. *Antivir. Chem. Chemother.* **1995**, *6*, 337–344.
27. Maryanoff, B. E.; Zhang, H.-C. *Arkivoc* **2007**, 7–35.
28. Ross, A.; Soares, D. C.; Covelli, D.; Pannecouque, C.; Budd, L.; Collins, A.; Robertson, N.; Parsons, S.; De Clercq, E.; Kennepohl, P.; Sadler, P. J. *Inorg Chem* **2010**, *49*, 1122–1132.
29. Herzog, K. M.; Deutsch, E.; Deutsch, K.; Silberstein, E. B.; Saragarajan, R.; Cacini, W. *J. Nucl. Med.* **1992**, *33*, 2190–2195.
30. Siaugue, J.-M.; Segat-Dioury, F.; Sylvestre, I.; Favre-Reguillon, A.; Foos, J.; Madic, C.; Guy, A. *Tetrahedron* **2001**, *57*, 4713–4718.
31. Hasaninejad, A.; Zare, A.; Khalafi-Nezhadad, A.; Sharghi, H.; Moosavi-Zare, A. R.; Parhami, A. *J. Chil. Chem. Soc.* **2008**, *53*, 1663–1666.
32. Zhao, G.-L.; Shi, M. *Tetrahedron* **2005**, *61*, 7277–7288.
33. Park, D. Y.; Lee, M. J.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett* **2005**, *46*, 8799–8803.
34. Imanzadeh, G. H.; Zare, A.; Khalafi-Nezhadad, A.; Hasaninejad, A.; Moosavi-Zare, A. R.; Parhami, A. *J. Iran. Chem. Soc.* **2007**, *4*, 467–475.
35. Gai, X.; Grigg, R.; Khamnaen, T.; Rajviroongit, S.; Sridharan, V.; Zhang, L.; Collard, S.; Keep, A. *Tetrahedron Lett.* **2003**, *44*, 7441–7443.
36. Okamoto, Y.; Yokota, M.; Kawazoe, S.; Kubota, H.; Nagaoka, H.; Arakida, Y.; Takeuchi, M. *Chem. Pharm. Bull.* **2006**, *54*, 603–610.
37. Zare, A.; Hasaninejad, A.; Khalafi-Nezhadad, A.; Moosavi-Zare, A. R.; Parhami, A. *Arkivoc* **2007**, *13*, 105–115.
38. Reitz, A. B.; Sonveaux, E.; Rosenkranz, R. P.; Verlander, M. S.; Melmon, K. L.; Hoffman, B. B.; Akita, Y.; Castagnoli, N.; Goodman, M. *J. Med. Chem.* **1985**, *28*, 634–642.
39. Lin, Y.-D.; Kao, J. Q.; Chen, C.-T. *Org. Lett.* **2007**, *9*, 5195–5198.
40. Kim, J. M.; Lee, K. Y.; Lee, S.; Kim, J. N. *Tetrahedron Lett.* **2004**, *45*, 2805–2808.
41. Gimbert, C.; Moreno-Manas, M.; Perez, E.; Vallribera, A. *Tetrahedron* **2007**, *63*, 8305–8310.
42. Klumpp, D. *Synlett* **2012**, *23*, 1590–1604.
43. Schaaf, G. M.; Mukherjee, S.; Waterson, A. G. *Tetrahedron Lett.* **2009**, *50*, 1928–1933.
44. Champloy, F.; Benali-Cherif, N.; Bruno, P.; Blain, I.; Pierrot, M.; Reglier, M.; Michalowicz, A. *Inorg. Chem.* **1998**, *37*, 3910–3918.
45. Gebbink, R. J. M. K.; Bosman, A. W.; Feiters, M. C.; Meijer, E. W.; Nolte, R. J. M. *Chem. Eur. J.* **1999**, *5*, 65–69.

46. Gonschior, M.; Kotteritzsch, M.; Rost, M.; Schonecker, B.; Wyrwa, R. *Tetrahedron: Asym.* **2000**, *11*, 2159–2182.
47. Ladomenou, K.; Charalambidis, G.; Coutsolelos, A. G. *Tetrahedron* **2007**, *63*, 2882–2887.
48. Nelson, J. H.; Howells, P. N.; DeLullo, G. C.; Landen, G. L.; Henry, R. A. *J. Org. Chem.* **1980**, *45*, 1246–1249.
49. Clariana, J.; Galvez, N.; Marchi, C.; Moreno-Manas, M.; Vallribera, A.; Molins, E. *Tetrahedron* **1999**, *55*, 7331–7344.
50. Gimbert, C.; Lumbierres, M.; Marchi, C.; Moreno-Manas, M.; Sebastian, R. M.; Vallribera, A. *Tetrahedron* **2005**, *61*, 8598–8605.
51. Hasaninejad, A.; Zare, A.; Parhami, A.; Moosavi-Zare, A. R.; Bargebid, R.; Beyzavi, M. H.; Khalafi-Nezhadad, A.; Arghoon, A.; Merajoddin, M.; Moosavi, S. A.; Dara, A.; Shekouhy, M. *Org. Prep. Proc. Int.* **2009**, *41*, 291–299.
52. Zare, A.; Hasaninejad, A.; Beyzavi, M. H.; Moosavi-Zare, A. R.; Khalafi-Nezhadad, A.; Roshankar, M.; Fiouzi, F.; Azad, S. *Phosphorus, Sulfur Silicon Relat. Elem.* **2009**, *184*, 1702–1712.
53. Niu, R.; Xiao, J.; Liang, T.; Li, X. *Org. Lett.* **2012**, *14*, 676–679.
54. Komai, H.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Org. Lett.* **2011**, *13*, 1706–1709.