http://dx.doi.org/10.5012/bkcs.2013.34.12.3881

Smiles Rearrangement Based Practical One-pot Synthesis of *N*-Alkyl/aryl-6-aminoquinolines from 6-Hydroxylquinoline

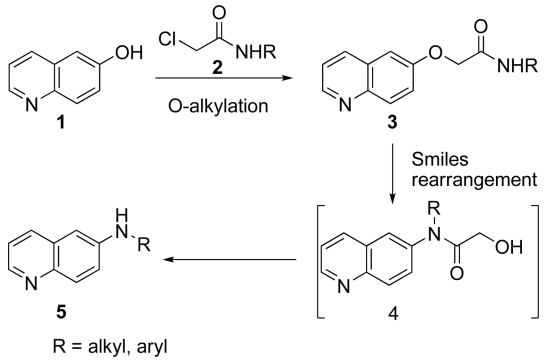
Yong-Sheng Xie,[†,‡] B. V. D. Vijaykumar,[†] Kiwan Jang,[†] Kyung-Min Choi,[†] Hua Zuo,[§] Yong-Jin Yoon,[#] and Dong-Soo Shin[†,*]

[†]*Department of Chemistry and Physics, Changwon National University, Changwon 641-773, Korea*
[*]*E-mail: dsshin@changwon.ac.kr*
[‡]*College of Chemical and Environmental Engineering, Chongqing Three Gorges University, Chongqing 404100, China*
[§]*College of Pharmaceutical Sciences, Southwest University, Chongqing 400716, China*
[#]*Department of Chemistry, Gyeongsang National University, Chinju 660-701, Korea*
Received July 3, 2013, Accepted September 20, 2013

Key Words : C-N coupling, Smiles rearrangement, 6-Aminoquinoline, 6-Hydroxylquinoline, One-pot

Aminoquinolines and their derivatives are important chemical entities that are widely used as pro-drugs and drugs due to their antimicrobial, cytotoxic and anti-malarial activities *etc*.[1] Among which, *N*-alkyl/aryl-6-aminoquinolines attracted the interest of medicinal chemists because of their exceptional significance as potential nootropics.[2] Biochemical studies have shown that these compounds possess good acetyl-cholinesterase inhibitor (AChEI) activity. *N*-Substituted-6-aminoquinoline has been considered as new lead compound for the discovery of memory and cognition facilitating drugs. Synthetic efforts to attain the 6-amino quinoline (**I**) based biologically active structures have been studied including the parent compound which itself is a fluorophore (acts as a probe in metabolite identification).[3] Generally, *N*-substituted-6-aminoquinolines can be obtained by using sodium borohydride to reduce the Schiff's base prepared by condensation of 6-aminoquinoline with different aldehydes.[4-7] Another method is the palladium-catalyzed C-*N* coupling between amines and 6-halogenated (or 6-sulfonyl) quinolines.[8-10] However, all of them have some limitation with respect to expensive starting materials and long reaction times. For example, aldehydes are highly reactive, not stable for air and absent in diversity. Although phenols are diverse to be used in laboratory for amine synthesis, palladium-catalyzed method has serious problems with respect to cost and presence of residual palladium. The lack of an efficient method to facile synthesis of *N*-substituted-6-aminoquinoline derivatives attracted us to take up their preparation.

In order to study the specific AChEI agents, one needs to synthesize a series of *N*-substituted-6-aminoquinolines by following convenient strategies that also cover economical aspects. In continuation of our efforts to develop simple and cost-effective methodologies in investigating C-N bond formation from various phenols to anilines *via* Smiles rearrangement,[11] we herein wish to report a practical one-pot synthesis of *N*-substituted-6-aminoquinolines from 6-hydroxylquinolines. The amine counterparts would be *N*-alkyl/aryl-2-chloroacetamide and the bases used for this reaction include Cs_2CO_3 and/or K_2CO_3 in DMF.

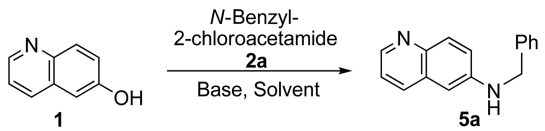


Scheme 1. The three-step one-pot process.

6-Hydroxylquinoline (**1**) is a commercial starting material to start with and very cheaper than 6-aminoquinoline. *N*-alkyl/aryl 2-chloroacetamides (**2**) can be easily prepared by acylation of amines with chloroacetylchloride and triethylamine in dichloromethane. The C-N coupling between compound **1** and **2** undergoes a tandem *O*-alkylation/Smiles rearrangement/hydrolysis sequence. The proposed three-step process has been illustrated in Scheme 1. The compound **1** was etherified with excess base and compound **2** to afford *N*-alkyl/aryl-2-(quinoline-6-yloxy)acetamide (**3**). This further underwent Smiles rearrangement to give the intermediate **4**. Finally, hydrolysis of compound **4** yielded us the *N*-alkyl/aryl-6-aminoquinolines (**5**).

To explore the optimized conditions for this reaction we chose compound **1** and *N*-benzyl-2-chloroacetamide (**2a**) as phenol and amine counterparts and the results are represented in Table 1. It was found that the compound **1** reacted with 1.2 equiv of **2a** in the presence of Cs_2CO_3 in DMF, afforded **5a** after 2 h at 150 °C in 68% yield. Changing base from Cs_2CO_3 to K_2CO_3 or Na_2CO_3 sharply decreased the reaction yields (Table 1, Entry 2 & 3). We have recently established our refurbish results for obtaining arylamines using Smiles rearrangement in presence of K_2CO_3 and catalytic KI as a better regent system, from phenols (which have

Table 1. The C-N model coupling reaction between **1** and **2a**



Entry	Base	Solvent	Reaction conditions[a]	**5a** (%)[b]
1	Cs_2CO_3	DMF	90 °C, 1h; 150 °C, 2 h	71
2	K_2CO_3	DMF	90 °C, 1h; 150 °C, 2 h	25
3	Na_2CO_3	DMF	90 °C, 1h; 150 °C, 5 h	4[c]
4	K_2CO_3/cat. KI	DMF	90 °C, 1h; 150 °C, 3 h	38
5	Cs_2CO_3	CH_3CN	Reflux, 12 h	0[d]

[a]1.0 eq. 6-Hydroxylquinoline, 1.2 eq. **2a**, 2.5 eq. base and DMF (8 mL/mmol). [b]Isolated yield. [c]The *O*-alkyl product, *N*-benzyl-2-(quinoline-6-yloxy)acetamide, was also isolated in 54% yield. [d]Only *N*-benzyl-2-(quinoline-6-yloxy)acetamide was isolated in 66% yield.

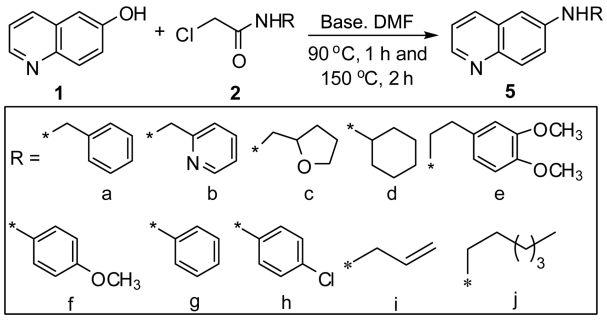
electron withdrawing group) that give lower yields with Cs_2CO_3. So we have applied the same method to find no better results (Table 1, Entry 4). It seems not all kinds of phenols follow the same reaction conditions, and position of hydroxyl group may also play major role in producing the desired products. When DMF was replaced with CH_3CN, we have ended up with isolating only the *O*-alkyl product (Table 1, Entry 5).

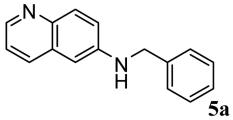
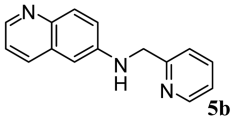
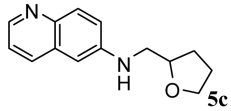
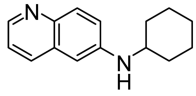
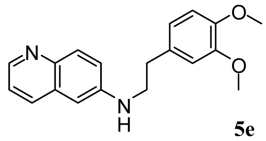
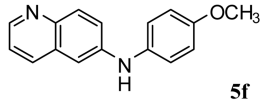
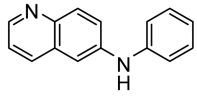
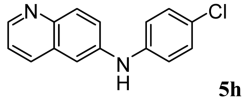
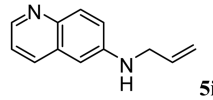
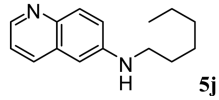
Now, the synthesis of 6-aminoquinoline (**I**) has been achieved by simple reduction of **5a** under standard hydrogenation conditions (Pd/C, H_2, MeOH, rt) in 68% overall yield from **1**. This is found to be an alternative and better method to prepare **I**, when compared to the less yielding (39%) procedure that involves more than 72 h complex process and usage of hazardous NaH along with $CsCO_3$, NMP and DMPU.[12] Thus, our method can be extended in process development for the synthesis of various aminoquinoline derivatives. However, having the optimal reaction conditions in hand, we further explored the scope of C-N coupling in the synthesis of *N*-alkyl/aryl-6-aminoquinolines from 6-hydroxylquinoline with a series of *N*-alkyl/aryl-2-chloroacetamide derivatives (Table 2).

As expected, all the *N*-substituted-2-chloroacetamide derivatives of both arylamines and alkylamines in this reaction smoothly afforded corresponding C-N coupled products **5a-5j** designed for memory-enhancing activity. There is no considerable difference in the yields to obtain *N*-aryl-6-aminoquinolines either with Cs_2CO_3 or K_2CO_3 (Table 2, Entry 6, 7 and 8). Besides, an electron-donating substituent on the aryl group of **2** brought a small increase in the yield. As a consolidated result, we would like to conclude that an electron withdrawing group in phenols[11f] or an electron donating group on the nitrogen of acetamides would favor the Smiles rearrangement sequence to afford corresponding anilines in good yields, where our present study enlightens the later.

In summary, the C-N coupling protocol reported herein represents a convenient and practical synthesis of *N*-alkyl/aryl-6-aminoquinolines in a three-step one-pot manner by simple addition of 6-hydroxyquinoline and *N*-alkyl/aryl-2-chloroacetamides with Cs_2CO_3 or K_2CO_3 in DMF at 150 °C *via* Smiles rearrangement. An electron donating substituent on the nitrogen counterpart would accelerate the rearrangement process to achieve various anilines in good yields. We currently engaged in making a chemical library including multifarious *N*-substituted-6-aminoquinolines, to be used in

Table 2. One-pot synthesis of *N*-alkyl/arylaminoquinolines



Entry	**2**	Base	Product	Yield (%)[a]
1	**2a**	Cs_2CO_3	 **5a**	71
		K_2CO_3		25
2	**2b**	Cs_2CO_3	 **5b**	68
3	**2c**	Cs_2CO_3	 **5c**	85
4	**2d**	Cs_2CO_3	 **5d**	24
5	**2e**	Cs_2CO_3	 **5e**	68
		K_2CO_3		50
6	**2f**	Cs_2CO_3	 **5f**	78
		K_2CO_3		79
7	**2g**	K_2CO_3	 **5g**	70
8	**2h**	K_2CO_3	 **5h**	65
9	**2i**	Cs_2CO_3	 **5i**	40
10	**2j**	Cs_2CO_3	 **5j**	80

[a]Isolated yield

the screening for specific AChEI activity. Furthermore, this work extends the scope of preparing different heterocyclic synthons in drug design for various biological activities.

Experimental

General. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Advance 400 FT spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C, respectively) in $CDCl_3$ with chemical shift values reported in δ units (ppm) relative to an internal standard (TMS). IR spectra were recorded on a FT-IR-6300 (JASCO, Japan). Gas chromatography-mass spectrometric (GC-MS) analyses were carried out with a Hewlett-Packard 6890 & 5973 system (AGILENT, USA). Melting points were determined on a digital SMP10 capillary melting point apparatus (SRUAT, UK). Silical gel (70-230 mesh) was used for flash column chromatography. All chemicals were used as delivered from Sigma-Aldrich.

General Procedure for the Synthesis of Compound 5. To a solution of 6-hydroxylquinoline **1** (1.0 mmol, 1.0 eq.) and *N*-alkyl/aryl 2-chloroacetamides **2** (1.2 mmol, 1.2 eq.) in DMF (8 mL) was added Cs_2CO_3/K_2CO_3 (2.5 mmol, 2.5 eq.) as indicated in Table 2. The mixture was stirred at 90 °C for 1 h followed at 150 °C for 2 h. Then, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was adsorbed onto silica gel and purified by flash column chromatography to give the product **5**.

***N*-Benzylquinolin-6-amine (5a)[9]:** Off-white solid, mp 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.0 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.34-7.43 (m, 4H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.23 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.12 (dd, *J* = 2.8, 8.8 Hz, 1H), 6.71 (d, *J* = 2.8 Hz, 1H), 4.47 (s, br, 1H), 4.42 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.27, 146.07, 143.44, 138.80, 133.81, 130.39, 130.14, 128.76, 127.53, 127.45, 121.34, 121.26, 103.44, 48.33; MS (EI) *m/z*: 235 (M^+), 234 (M^+), 233, 91 (100).

***N*-(Pyridin-2-ylmethyl)quinolin-6-amine (5b):** Brown semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58-8.63 (m, 2H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.65 (dt, *J* = 7.6, 1.8 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1 H), 7.17-7.25 (m, 3 H), 6.69 (d, *J* = 2.6 Hz, 1H), 5.25 (s, br, 1H), 4.54 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.70, 149.33, 146.28, 145.89, 143.49, 136.69, 133.82, 130.42, 130.17, 122.30, 121.66, 121.53, 121.34, 103.57, 49.16; MS (EI) *m/z*: 236 (M^+), 235 (M^+), 234, 158, 157(100).

***N*-((Tetrahydrofuran-2-yl)methyl)quinolin-6-amine (5c):** Light-brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 4.4, 1.6 Hz, 1H), 7.89 (d, *J* = 8.3, 1.6 Hz, 1H), 7.86 (d, *J* = 9.2 Hz, 1H), 7.23 (dd, *J* = 8.3, 4.4 Hz, 1H), 7.11 (dd, *J* = 9.2, 2.6 Hz, 1H), 6.70 (d, *J* = 2.6 Hz, 1H), 4.43 (s, 1H), 4.13-4.21 (m, 1H), 3.87-3.94 (m, 1H), 3.76-3.83 (m, 1H), 3.30-3.38 (m, 1H), 3.13-3.21 (m, 1H), 2.01-2.10 (m, 1H), 1.86-1.99 (m, 2H), 1.62-1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.46, 146.14, 143.44, 133.70, 130.29, 130.18, 121.57, 121.31, 103.27, 68.13, 48.19, 29.23, 25.83, 14.20; MS (EI) *m/z*: 229 (M^+), 228 (M^+), 158, 157 (100).

***N*-Cyclohexylquinolin-6-amine (5d):** Light-green solid, mp 77-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.2, 1.6 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.24 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.05 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 3.88 (s, br, 1H), 3.34-3.44 (m, 1H), 2.08-2.18 (m, 2H), 1.75-1.85 (m, 2H), 1.65-1.74 (m, 1H), 1.36-1.50 (m, 2H), 1.15-1.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.81, 145.39, 143.00, 133.69, 130.35, 130.32, 121.67, 121.31, 103.32, 51.84, 33.28, 25.97, 25.00; MS (EI) *m/z*: 227 (M^+), 226 (M^+), 184, 183 (100), 170, 169.

***N*-(3,4-Dimethoxyphenethyl)quinolin-6-amine (5e):** Off-white solid, mp 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.2, 1.6 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.26 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.05 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.79 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.75 (d, *J* = 1.9 Hz, 1H), 6.73 (d, *J* = 2.6 Hz, 1H), 4.02 (s, br, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.49 (m, 2H), 2.94 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.35, 148.03, 146.24, 146.02, 143.42, 133.74, 131.66, 130.41, 130.22, 121.44, 121.40, 120.81, 112.37, 111.83, 103.40, 56.07, 56.00, 45.11, 34.84; MS (EI) *m/z*: 309 (M^+), 308 (M^+), 158, 157 (100).

***N*-(4-Methoxyphenyl)quinolin-6-amine (5f):** Light-yellow solid, mp 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 4.2, 1.6 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.31 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.27 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.16-7.22 (m, 2H), 7.10 (d, *J* = 2.6 Hz, 1H), 6.90-6.96 (m, 2H), 5.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.20, 147.02, 144.03, 143.84, 134.93, 134.09, 130.56, 129.86, 123.46, 122.09, 121.44, 114.96, 107.06, 55.63; MS (EI) *m/z*: 251 (M^+), 250 (M^+, 100), 236, 235.

***N*-Phenylquinolin-6-amine (5g):** Light-yellow solid, mp 177-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 1.5, 4.2 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.42 (dd, *J* = 2.6, 9.0 Hz, 1H), 7.32-7.37 (m, 3H), 7.30 (dd, *J* = 4.2, 8.3 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.66, 144.53, 142.32, 141.87, 134.37, 130.72, 129.68, 129.57, 123.13, 122.34, 121.52, 119.30, 109.67; MS (EI) *m/z* 221 (M^+), 220 (M^+, 100), 219.

***N*-(4-Chlorophenyl)quinolin-6-amine (5h):** Light-yellow solid, mp 189-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* =7.5 Hz, 1H), 7.40 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.25-7.35 (m, 4H), 7.13 (m, 2H), 6.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.92, 144.62, 141.40, 141.02, 134.46, 130.86, 129.59, 129.57, 127.05, 123.12, 121.63, 120.32, 110.18; MS (EI) *m/z*: 256 (M^+), 255 (M^+), 254 (M^+, 100), 253, 219, 218.

***N*-Allylquinolin-6-amine (5i)[13]:** Light-yellow solid, mp 59-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 3.2 Hz, 1H), 7.72-7.84 (m, 2H), 7.17 (dd, *J* = 8.4, 4.4 Hz, 1H), 6.98 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 5.86-6.06 (m, 1H), 5.31 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.18 (dd, *J* = 10.1, 1.2 Hz, 1H), 4.19 (s, br, 1H), 3.85 (d, *J* = 3.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.76, 145.64, 143.44, 134.71,

133.34, 130.50, 129.95, 121.06, 121.04, 116.64, 103.22, 46.44; MS (EI) m/z 185 (M^+), 184 (M^+, 100), 183.

***N*-Hexylquinolin-6-amine (5j):** Light-yellow solid, mp 65-66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 3.2 Hz, 1H), 7.77-7.85 (m, 2H), 7.19 (dd, J = 8.0, 4.0 Hz, 1H), 7.02 (dd, J = 9.2, 2.4 Hz, 1H), 6.60 (d, J = 2.4 Hz, 1H), 5.86-6.06 (m, 1H), 5.31 (dd, J = 17.2, 1.2 Hz, 1H), 5.18 (dd, J = 10.1, 1.2 Hz, 1H), 4.11 (s, br, 1H), 1.54-1.74 (m, 2H), 1.20-1.52 (m, 6H), 0.79-0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.19, 145.34, 143.23, 133.20, 130.26, 130.11, 121.16, 120.99, 102.37, 43.82, 31.64, 29.27, 26.92, 22.06, 14.07; MS (EI) m/z 229 (M^+), 228 (M^+), 158 (100), 157.

Acknowledgments. This research is financially supported by Changwon National University, South Korea in 2011-2012.

References

1. (a) Vlahov, R.; Parushev, St.; Vlahov, J. *Pure & Appl. Chem.* **1990**, *62*, 1303. (b) Sweeney, A. W.; Blackburn, C. R. B.; Rieckmann, K. H. *Am. J. Trop. Med. Hyg.* **2004**, *71*, 187. (c) Mohana, K. N.; Mallesha, L.; Gurudatt, D. M. *International Journal of Drug Design and Discovery* **2011**, *2*, 584.
2. (a) Piplani, P.; Rania, A.; Sandhir, R.; Kulkarni, S. K. *J. Young Pharm.* **2009**, *1*, 341. (b) Piplani, P.; Rania, A.; Saihgal, R.; Sharma, M. *Arzneimittelforschung* **2011**, *61*, 373.
3. (a) Wu, Q.; Jiao, X.; Wang, L.; Xiao, Q.; Liu, X.; Xie, P. *Tetrahedron Lett.* **2010**, *51*, 4806. (b) Lan, T.; Yuan, X. X.; Yu, J. H.; Jia, C.; Wang, Y. S.; Zhang, H. J.; Maa, Z. F.; Ye, W. D. *Chin. Chem. Lett*. **2011**, *22*, 253. (c) Rajapakse, A.; Linder, C.; Morrison, R. D.; Sarkar, U.; Leigh, N. D.; Barnes, C. L.; Daniels, J. S.; Gates, K. S. *Chem. Res. Toxicol*. **2013**, *26*, 555.
4. Grassmann, S.; Apelt, J.; Sippl, W.; Ligneau, X.; Pertz, H. H.; Zhao, Y. H.; Arrang, J.-M.; Ganellin, C. R.; Schwartz, J.-C.; Schunack, W.; Stark, H. *Bioorg. Med. Chem. Lett.* **2003**, *11*, 2163.
5. Hu, Y.; Gavrin, L. K.; Janz, K.; Kaila, N.; Li, H.-Q.; Thomason, J. R.; Cuozzo, J. W.; Hall, J. P.; Hsu, S.; Nicherson-Nutter, C.; Telliez, J.-B.; Lin, L.-L.; Tam, S. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 6067.
6. Nutaitis, C. F.; Smith, Kimberly. *Org. Prep. Proced. Int.* **2007**, *39*, 611.
7. Cukalovic, A.; Stevens, C. V. *Green Chem.* **2010**, *12*, 1201.
8. Anderson, K. W.; Tundel, R. E.; Ikawa, T.; Altman, R. A.; Buchawald, S. L. *Angew. Chem. Int. Ed.* **2006**, *45*, 6523.
9. Ogata, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 13848.
10. Ueda, S.; Su, M.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2011**, *50*, 8944.
11. (a) Cho, S.-D.; Park, Y.-D.; Kim, J.-J.; Lee, S.-G.; Ma, C.; Song, S.-Y.; Joo, W.-H.; Flack, J. R.; Shiro, M.; Shin, D.-S.; Yoon, Y.-J. *J. Org. Chem.* **2003**, *68*, 7918. (b) Zuo, H.; Kam, K.-H.; Kwon, H.-J.; Meng, L.-J.; Ahn, C.; Won, T.-J.; Kim, T.-H.; Raji Reddy, Ch.; Chandrasekhar, S.; Shin, D.-S. *Bull. Korean Chem. Soc.* **2008**, *29*, 1379. (c) Zuo, H.; Meng, L.; Ghate, M.; Hwang, K.-H.; Cho, K. Y.; Chandrasekhar, S.; Raji Reddy, C.; Shin, D.-S. *Tetrahedron Lett.* **2008**, *49*, 3827. (d) Yang, H.; Li, Z.-B.; Shin, D.-S.; Wang, L.-Y.; Zhou, J.-Z.; Qiao, H.-B.; Tian, X.; Ma, X.-Y.; Zuo, H. *Syn. Lett.* **2010**, *3*, 483. (e) Meng, L.-J.; Zuo, H.; Vijaykumar, B. V. D.; Gautam, D.; Kiwan, J.; Yoon, Y.-J.; Shin, D.-S. *Bull. Korean. Chem. Soc.* **2013**, *34*, 585. (f) Xie, Y.-S.; Vijaykumar, B. V. D.; Jang, K.; Shin, H.-H.; Zuo, H.; Shin, D.-S. *Tetrahedron Lett.* **2013**, *54*, 5151.
12. Peet, N. P.; Weidner, J. J. US6034241(A), March 7, 2000.
13. Wang, D.-P.; Ding, K. *Chem Commun.* **2009**, 1891.