ChemInform Abstract: Microwave-Assisted Copper Powder-Catalyzed Coupling and Cyclization of β-Bromo-α,β-Unsaturated Amides with Amidine Hydrochlorides Leading to Pyrimidinones.

ARTICLE *in* APPLIED ORGANOMETALLIC CHEMISTRY · MARCH 2015

Impact Factor: 2.25 · DOI: 10.1002/aoc.3301

Full Paper

Applied Organometallic Chemistry

Received: 14 January 2015 Revised: 28 January 2015 Accepted: 29 January 2015 Published online in Wiley Online Library: 16 March 2015

(wileyonlinelibrary.com) DOI 10.1002/aoc.3301

Microwave-assisted copper powder-catalyzed coupling and cyclization of β-bromo-α,β-unsaturated amides with amidine hydrochlorides leading to pyrimidinones

Yang Jiao and Chan Sik Cho*

β-Bromo-α,β-unsaturated amides are coupled and cyclized with amidine hydrochlorides using microwave irradiation in the presence of a catalytic amount of copper powder and a base to give the corresponding pyrimidinones in good yields.

Keywords: heterogeneous catalysis; copper powder; cyclization; heterocycles; microwaves

Introduction

It is known that pyrimidinone-containing compounds exhibit a wide spectrum of biological activities, such as antitumor,[1–3] antituberculous,[4] antipsychotic,[5,6] antiviral,[7] antifungal,[8] antagonist[9,10] and anti-HIV (human immunodeficiency virus) properties.[11,12] Thus, such scaffold-containing compounds have been synthesized and tested for biological activity. During the course of our continuing studies directed towards transition metal-catalyzed cyclization reactions of β-bromo-α,β-unsaturated aldehydes and their derivatives, we have identified several new methods for the synthesis of carbocyclic and heterocyclic compounds.[13–27] β-Bromo-α,β-unsaturated aldehydes and their derivatives are readily prepared from α-methylene group-containing ketones by bromination under Vilsmeier–Haack conditions[28,29] and subsequent transformation, and the products can serve as valuable building blocks for the construction of various cyclic compounds.[20–38] Among such heterocyclic compounds, we also have shown two examples for the synthesis of pyrimidinone scaffold. It is reported that β-bromo-α,β-unsaturated amides are coupled and cyclized with formamide in the presence of CuI and a base without an additional ligand to give pyrimidinones.[39] Such a similar coupling and cyclization leading to pyrimidinones is also exemplified by the reaction of β-bromo-α,β-unsaturated carboxylic acids and amidine hydrochlorides in the presence of copper powder under microwave irradiation conditions.[40] It is also reported that quinazolin-4(3*H*)-ones can be synthesized by CuI-catalyzed coupling of 2-iodobenzamides with amidine acetates followed by condensation cyclization.[41] However, no reports are known for such a coupling and cyclization between β-bromo-α,β-unsaturated amides and amidine hydrochlorides. In these circumstances, with an effort to develop another protocol for the construction of pyrimidinone scaffolds, herein this report describes a quick copper powder-catalyzed coupling and cyclization of β-bromo-α,β-unsaturated amides with amidine hydrochlorides leading to pyrimidinones under microwave irradiation conditions.

Results and Discussion

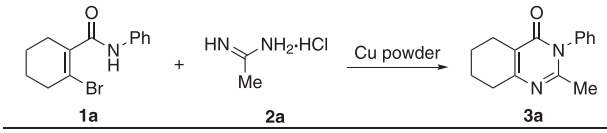
Table 1 shows several results for the attempted coupling and cyclization of 2-bromo-*N*-phenylcyclohex-1-enecarboxamide (**1a**) with acetamidine hydrochloride (**2a**), leading to 5,6,7,8-tetrahydro-2-methyl-3-phenylquinazolin-4(3*H*)-one (**3a**) under various reaction conditions such as molar ratio of **2a** to **1a**, several kinds of base and solvent, and reaction time. Treatment of **1a** with equimolar amount of **2a** in *N*,*N*-dimethylformamide (DMF) at 150°C for 1 h in the presence of 10 mol% of copper powder along with sodium *tert*-butoxide under microwave irradiation (200 W of initial power) affords **3a** in 38% yield (entry 1). The molar ratio of **2a** to **1a** affects the yield of **3a** with the yield increasing with an increase of the molar ratio up to 1.5 (entries 1–3). The yield of **3a** increases on prolonging the reaction time to 2 h (entry 4). The reaction also proceeds in the presence of other bases, such as tripotassium phosphate, potassium carbonate, cesium carbonate or sodium acetate, but the yields of **3a** are generally lower than that obtained in the presence of sodium *tert*-butoxide (entries 5–8). Among the solvents examined, DMF is found to be that of choice (entries 4, 9, 10). Also, performing the reaction under usual heating conditions results in lower yield of **3a** along with many unidentifiable side products (entry 11). The best result in terms of the yield of product **3a** and complete conversion of **1a** is obtained with the standard set of reaction conditions shown in entry 4 of Table 1.

After the reaction conditions had been optimized, various β-bromo-α,β-unsaturated amides **1** were subjected to the reaction with amidine hydrochlorides **2** in order to investigate the reaction scope. Several representative results are summarized in Table 2.

* *Correspondence to: Chan Sik Cho, Department of Applied Chemistry, Kyungpook National University, Daegu 702-701, Republic of Korea. E-mail: cscho@knu.ac.kr*

Department of Applied Chemistry, Kyungpook National University, Daegu 702-701, Republic of Korea

Table 1. Optimization of conditions for the reaction of 1a with 2a[a]

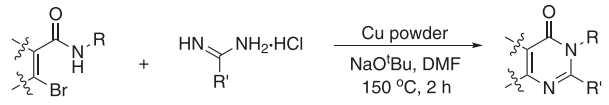


1a 2a 3a

Entry	[**2a**]/[**1a**]	Base	Solvent	Time (h)	Yield (%)
1	1	NaO^{t}Bu	DMF	1	38
2	1.5	NaO^{t}Bu	DMF	1	55
3	2	NaO^{t}Bu	DMF	1	53
4	1.5	NaO^{t}Bu	DMF	2	66
5	1.5	K_3PO_4	DMF	2	21
6	1.5	K_2CO_3	DMF	2	27
7	1.5	Cs_2CO_3	DMF	2	38
8	1.5	NaOAc	DMF	2	49
9	1.5	NaO^{t}Bu	DMSO	2	50
10	1.5	NaO^{t}Bu	DMAc	2	40
11[b]	1.5	NaO^{t}Bu	DMF	3	10

[a]Reaction conditions: **1a** (0.5 mmol), copper powder (0.05 mmol), base (1.5 mmol), solvent (3 ml), 150°C, microwave irradiation (200 W of initial power).
[b]Under usual heating conditions.

Table 2. Copper powder-catalyzed synthesis of pyrimidinones 3 from β-bromo-α,β-unsaturated amides 1 and amidine hydrochlorides 2a[a]

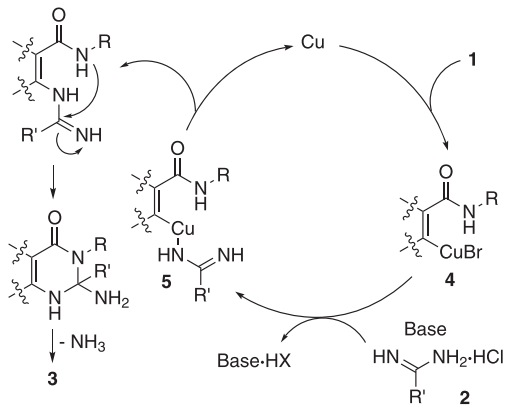


1 **2a** R' = Me, **2b** R' = Ph **3**

Amide (**1**)	Amidine hydrochloride (**2**)	Pyrimidinone (**3**)	Yield (%)
1a (R = Ph)	**2a**	**3a**	66
1a	**2b**	**3b** (R = H)	66
1b (R = benzyl)	**2a**	**3c**	63
1b	**2b**	**3b**	60
1c	**2a**	**3d**	52
1d	**2a**	**3e**	63
1e	**2a**	**3f**	55
1f	**2a**	**3g**	57
1g	**2a**	**3h**	52
1h	**2a**	**3i**	64
1i	**2a**	**3j**	52
1j	**2a**	**3k**	52

[a]Reaction conditions: **1a** (0.5 mmol), **2** (0.75 mmol), copper powder (0.05 mmol), NaO^{t}Bu (1.5 mmol), DMF (3 ml), 150°C, for 2 h, microwave irradiation (200 W of initial power).

N-Benzyl-substituted β-bromo-α,β-unsaturated amide **1b** also couples and cyclizes with **2a** under the employed conditions to give the corresponding pyrimidinone **3c** in similar yield. However, similar treatment of **1a** and **1b** with benzamidine hydrochloride (**2b**) affords 2-phenyl-5,6,7,8-tetrahydroquinazolin-4(3*H*)-one (**3b**, R = H) irrespective of N-substituents on **1a** and **1b** in 66 and 60% yields, respectively. It is known that 2-iodobenzamides having N-methyl and phenyl substituents react with benzamidine acetate in the presence of copper(I) iodide to give N-substituent-



Scheme 1. Reaction pathway.

eliminated 2-phenylquinazolin-4(3*H*)-one as major product irrespective of N-substituents on starting amides.[41] From the reaction of six-membered β-bromo-α,β-unsaturated amides (**1c** and **1d**) with **2a**, the corresponding pyrimidinones (**3d** and **3e**) are also formed in similar yields irrespective of methyl and phenyl substituents on **1c** and **1d**. With cyclic *N*-phenyl-substituted β-bromo-α,β-unsaturated amides (**1e–h**) having various ring sizes, the coupled and cyclized products (**3f–i**) are produced with yields in the range 55–64%, and the product yield is not significantly affected by the ring size. To test for the effect of the position of bromide and amide groups in β-bromo-α,β-unsaturated amides, **1i** and **1j** were employed. The coupling and cyclization similarly take place with both **1i** and **1j**.

As to the reaction pathway, it seems to proceed via initial formation of vinylcopper(II) intermediate **4** by oxidative addition of C–Br bond of **1** to copper (Scheme 1).[41] The intermediate **4** then undergoes coupling with **2** to give amidocopper(II) intermediate **5**, which triggers reductive elimination, cyclization and deamination to afford product **3**.

Conclusions

It has been shown that β-bromo-α,β-unsaturated amides react with amidine hydrochlorides in the presence of copper powder and a base under microwave irradiation to give the corresponding pyrimidinones. This reaction provides a new method for synthesizing the pyrimidinone scaffold from readily available ketones. Further studies on synthetic applications to produce heterocycles starting from ketones as well as using the copper powder–microwave irradiation system are underway.

Experimental

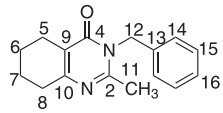
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a Bruker Avance Digital 400 spectrometer using tetramethylsilane as an internal standard in $CDCl_3$. Melting points were determined with a Standford Research Inc. MPA100 automated melting point apparatus. High-resolution mass spectrometry (HRMS) was performed with a Jeol JMS-700 spectrometer at the Korea Basic Science Center, Daegu, Korea. The isolation of pure products was carried out via thin layer (silica gel 60 GF_{254}, Merck) chromatography. The starting β-bromo-α,β-unsaturated amides were synthesized via three steps from the corresponding ketones according to literature procedures, and all are known.[24,28,29,39,42,43]

Commercially available organic and inorganic compounds were used without further purification.

General Procedure for Copper Powder-Catalyzed Coupling and Cyclization of β-Bromo-α,β-unsaturated Amides with Amidine Hydrochlorides

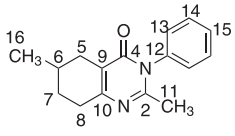
A 10 ml microwave reaction tube was charged with β-bromo-α,β-unsaturated amide **1** (0.5 mmol) and amidine hydrochloride **2** (0.75 mmol), together with copper powder (0.003 g, 0.05 mml), NaO^{t}Bu (0.144 g, 1.5 mmol) and DMF (3 ml). The reaction mixture was heated to 150°C for 2 h using microwave irradiation (CEM Discover Microwave System) at 200 W initial power. The reaction mixture was then cooled to room temperature and filtered through a short column of silica gel (ethyl acetate–hexane mixture) to remove inorganic salts. Evaporation of the solvent gave a crude mixture that was purified using TLC (ethyl acetate–hexane). Except for known **3a**[44] and **3b**,[40] all new products prepared by the above procedure were characterized spectroscopically as described below.

*3-Benzyl-2-methyl-5,6,7,8-tetrahydroquinazolin-4(3H)-one (**3c**)*



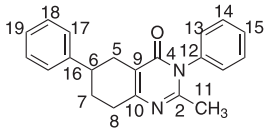
Oil. ^{1}H NMR (δ, ppm): 1.67–1.76 (m, 4H, H6 and H7), 2.34 (s, 3H, H11), 2.46–2.53 (m, 4H, H5 and H8), 5.21 (s, 2H, H12), 7.10–7.12 (m, 2H, H14), 7.18–7.28 (m, 3H, H15 and H16). ^{13}C NMR (δ, ppm): 22.02 (C7), 22.41 (C6), 22.80 (C5), 23.06 (C11), 31.64 (C8), 47.29 (C12), 119.65 (C9), 126.91 (C16), 127.87 (C14), 129.10 (C15), 135.90 (C13), 155.70 (C10), 159.24 (C2), 162.90 (C4), assignments to C14 and C16 are interchangeable. Anal. Calcd for $C_{16}H_{18}N_2O$ (%): C, 75.56; H, 7.13; N, 11.01. Found (%): C, 75.48; H, 7.17; N, 10.95.

*2,6-Dimethyl-3-phenyl-5,6,7,8-tetrahydroquinazolin-4(3H)-one (**3d**)*



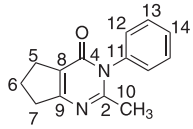
Solid; m.p. 95–96°C (from hexane–$CHCl_3$). ^{1}H NMR (δ, ppm): 1.08 (d, J_{HH} = 6.8 Hz, 3H, H16), 1.37–1.48 (m, 1H, H7), 1.74–1.84 (m, 1H, H7), 1.87–1.93 (m, 1H, H6), 1.99–2.06 (m, 1H, H5), 2.12 (s, 3H, H11), 2.66–2.75 (m, 3H, H5 and H8), 7.17–7.20 (m, 2H, H13), 7.45–7.55 (m, 3H, H14 and H15). ^{13}C NMR (δ, ppm): 21.65 (C16), 23.97 (C11), 28.29 (C6), 30.57 (C7), 30.72 (C8), 31.61 (C5), 119.65 (C9), 127.86 (C13), 129.38 (C15), 130.16 (C14), 137.97 (C12), 155.29 (C10), 159.13 (C2), 162.87 (C4), assignments to C7 and C8 are interchangeable, assignments to C14 and C15 are interchangeable. Anal. Calcd for $C_{16}H_{18}N_2O$ (%): C, 75.56; H, 7.13; N, 11.01. Found (%): C, 75.45; H, 7.08; N, 11.06.

*2-Methyl-3,6-diphenyl-5,6,7,8-tetrahydroquinazolin-4(3H)-one (**3e**)*



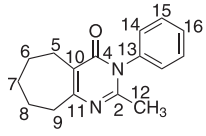
Solid; m.p. 121–122°C (from hexane–$CHCl_3$). ^{1}H NMR (δ, ppm): 1.84–1.95 (m, 1H, H7), 2.09 (s, 3H, H11), 2.10–2.14 (m, 1H, H7), 2.44–2.50 (m, 1H, H8), 2.69–2.77 (m, 2H, H5 and H8), 2.81–2.95 (m, 2H, H5 and H6), 7.12–7.28 (m, 7H, H17–19 and H13), 7.39–7.49 (m, 3H, H14 and H15). ^{13}C NMR (δ, ppm): 24.01 (C11), 29.64 (C7), 30.29 (C8), 32.19 (C5), 39.64 (C6), 119.67 (C9), 126.61 (C13), 127.09 (C19), 127.84 (C15), 128.74 (C17), 129.46 (C18), 130.22 (C14), 137.88 (C12), 145.72 (C16), 155.66 (C10), 158.98 (C2), 162.72 (C4), assignments to C7 and C8 are interchangeable, assignments to C13–15 and C17–19 are interchangeable. Anal. Calcd for $C_{21}H_{20}N_2O$ (%): C, 79.72; H, 6.37; N, 8.85. Found (%): C, 79.60; H, 6.30; N, 8.92.

*2-Methyl-3-phenyl-6,7-dihydro-3H-cyclopenta[d]pyrimidin-4(5H)-one (**3f**)*



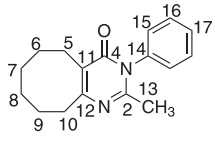
Solid; m.p. 91–92°C (from hexane–$CHCl_3$). ^{1}H NMR (δ, ppm): 2.05–2.13 (m, 2H, H6), 2.14 (s, 2H, H10), 2.80–2.90 (m, 4H, H5 and H7), 7.16–7.19 (m, 2H, H12), 7.44–7.53 (m, 3H, H13 and H14). ^{13}C NMR (δ, ppm): 21.45 (C6), 24.36 (C10), 28.02 (C5), 35.16 (C7), 122.88 (C8), 127.77 (C12), 129.39 (C14), 130.15 (C13), 137.98 (C11), 158.92 (C9), 161.05 (C2), 167.90 (C4). Anal. Calcd for $C_{14}H_{14}N_2O$ (%): C, 74.31; H, 6.24; N, 12.38. Found (%): C, 74.21; H, 6.20; N, 12.36.

*2-Methyl-3-phenyl-6,7,8,9-tetrahydro-3H-cyclohepta[d]pyrimidin-4(5H)-one (**3g**)*



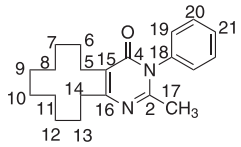
Solid; m.p. 106–107°C (from hexane–$CHCl_3$). ^{1}H NMR (δ, ppm): 1.57–1.61 (m, 2H, H7), 1.67–1.72 (m, 2H, H6), 1.82–1.87 (m, 2H, H8), 2.10 (s, 3H, H12), 2.74–2.76 (m, 2H, H5), 2.78–2.80 (m, 2H, H9), 7.16–7.18 (m, 2H, H15), 7.43–7.46 (m, 1H, H16), 7.48–7.52 (m, 2H, H14), H5 and H9 are interchangeable. ^{13}C NMR (δ, ppm): 24.06 (C12), 24.72 (C8), 25.57 (C5), 26.58 (C6), 32.50 (C7), 38.38 (C9), 124.64 (C10), 127.65 (C14), 129.31 (C16), 130.12 (C15), 138.31 (C13), 155.29 (C11), 163.07 (C2), 165.27 (C4), assignments to C5, C6 and C8 are interchangeable. Anal. Calcd for $C_{16}H_{18}N_2O$ (%): C, 75.56; H, 7.13; N, 11.01. Found (%): C, 75.50; H, 7.05; N, 11.08.

*2-Methyl-3-phenyl-5,6,7,8,9,10-hexahydrocycloocta[d]pyrimidin-4(3H)-one (**3h**)*



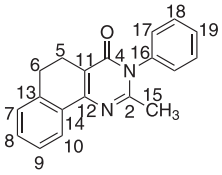
Solid; m.p. 114–115°C (from hexane–$CHCl_3$). ^{1}H NMR (δ, ppm): 1.44–1.52 (m, 4H, H7 and H8), 1.64–1.70 (m, 2H, H6), 1.77–1.82 (m, 2H, H9), 2.11 (s, 3H, H13), 2.67–2.73 (m, 4H, H5 and H10), 7.16–7.19 (m, 2H, H16), 7.42–7.46 (m, 1H, H17), 7.47–7.52 (m, 2H, H15), H6 and H9 are interchangeable. ^{13}C NMR (δ, ppm): 23.99 (C13), 24.34 (C9), 26.36 (C7), 26.56 (C8), 29.21 (C6), 29.58 (C5), 34.26 (C10), 122.44 (C11), 127.70 (C15), 129.18 (C17), 130.00 (C16), 138.09 (C14), 155.77 (C2 and C12), 162.50 (C4), assignments to C5–9 are interchangeable. Anal. Calcd for $C_{17}H_{20}N_2O$ (%): C, 76.09; H, 7.51; N, 10.44. Found (%): C, 76.00; H, 7.57; N, 10.51.

*2-Methyl-3-phenyl-5,6,7,8,9,10,11,12,13,14-decahydrocyclododeca[d]pyrimidin-4(3H)-one (**3i**)*



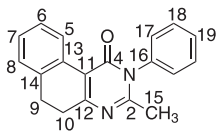
Solid; m.p. 140–141°C (from hexane–$CHCl_3$). ^{1}H NMR (δ, ppm): 1.28–1.51 (m, 12H, H7–12), 1.68–1.74 (m, 2H, H6), 1.83–1.89 (m, 2H, H13), 2.12 (s, 3H, H17), 2.55–2.62 (m, 4H, H5 and H14), 7.19–7.22 (m, 2H, H20), 7.43–7.47 (m, 1H, H21), 7.49–7.53 (m, 2H, H19), assignments to H6 and H13 are interchangeable. ^{13}C NMR (δ, ppm): 22.36 (C17), 22.98 (C7), 23.98 (C9), 24.10 (C10), 24.45 (C12), 25.65 (C8 and C11), 26.08 (13), 26.10 (C5), 26.35 (C14), 31.46 (C6), 122.98 (C15), 127.82 (C20), 129.20 (C21), 130.04 (C19), 138.13 (C18), 155.10 (C16), 162.15 (C2), 163.3 (C4), assignments to C5–14 are interchangeable. Anal. Calcd for $C_{21}H_{28}N_2O$ (%): C, 77.74; H, 8.70; N, 8.63. Found (%): C, 77.50; H, 8.65; N, 8.69.

*2-Methyl-3-phenyl-5,6-dihydrobenzo[h]quinazolin-4(3H)-one (**3j**)*



Solid; m.p. 193–195°C (from hexane–$CHCl_3$). ^{1}H NMR (δ, ppm): 2.16 (s, 3H, H15), 2.76–2.80 (m, 2H, H5), 2.85–2.89 (m, 2H, H6), 7.16–7.18 (m, 3H, H7–9), 7.25–7.30 (m, 2H, H17), 7.39–7.44 (m, 1H, H19), 7.45–7.50 (m, 2H, H18), 8.13–8.16 (m, 1H, H10). ^{13}C NMR (δ, ppm): 20.14 (C15), 24.41 (C5), 27.37 (C6), 117.75 (C11), 125.52 (C19), 127.06 (C9), 127.77 (C17), 128.10 (C10), 129.41 (C7), 130.17 (C18), 130.44 (C8), 132.68 (C14), 138.10 (C16), 138.92 (C13), 153.28 (C12), 156.66 (C2), 163.00 (C4), assignments to C7–10 and C19 are interchangeable, assignments to C13 and C16 are interchangeable. HRMS (EI): calcd for $C_{19}H_{16}N_2O$ (M^+): 288.1263; found: 288.1260. Anal. Calcd for $C_{19}H_{16}N_2O$ (%): C, 79.14; H, 5.59; N, 9.72. Found (%): C, 79.10; H, 5.53; N, 9.84.

*3-Methyl-2-phenyl-5,6-dihydrobenzo[f]quinazolin-1(2H)-one (**3k**)*



Solid; m.p. 194–196°C (from hexane–$CHCl_3$). ^{1}H NMR (δ, ppm): 2.14 (s, 3H, H15), 2.79–2.83 (m, 2H, H10), 2.87–2.91 (m, 2H, H9), 7.12–7.20 (m, 5H, H6–8 and H18), 7.41–7.46 (m, 1H, H19), 7.47–7.52 (m, 2H, H17), 8.53–8.55 (m, 1H, H5). ^{13}C NMR (δ, ppm): 24.28 (C15), 28.13 (C9), 31.34 (C10), 116.60 (C11), 126.80 (C19), 127.25 (C6), 127.38 (C5), 127.72 (C17), 129.53 (C8), 130.26 (C18), 130.64 (C16), 135.66 (C13), 137.97 (C14), 157.14 (C12), 160.73 (C2), 161.78 (C4), assignments to C5–8 and C19 are interchangeable and signal of C7 is eclipsed. HRMS (EI): calcd for $C_{19}H_{16}N_2O$ (M^+): 288.1263; found: 288.1261. Anal. Calcd for $C_{19}H_{16}N_2O$ (%): C, 79.14; H, 5.59; N, 9.72. Found (%): C, 79.05; H, 5.50; N, 9.80.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0007563).

References

[1] C. Langer, J. Dansker, A. Ridgo, *Clin. Adv. Hematol. Oncol.* **2003**, *1*, 424.
[2] D. Smaniotto, G. D'Agostino, S. Luzi, V. Valentini, G. Macchia, M. G. Mangiacotti, P. A. Margoriti, G. Ferrandiono, G. Scambia, *Tumori* **2005**, *91*, 215.
[3] J. S. Driscoll, V. E. Marquez, J. Plowman, P. S. Liu, J. A. Kelley, J. J. Barchi, *J. Med. Chem.* **1991**, *34*, 3280.
[4] A. Nayyar, R. Jain, *Curr. Med. Chem.* **2005**, *12*, 1873.
[5] G. Faludi, *Neuropsychopharmacol. Hung.* **2005**, *7*, 22.
[6] J. A. Lieberman, T. S. Stroup, J. P. McEvoy, M. S. Suartz, R. A. Rosenheck, D. O. Perkins, R. S. Keefe, S. M. Davis, C. E. Davis, B. D. Lebowitz, J. Severe, J. K. Hsiao, *N. Engl. J. Med.* **2005**, *353*, 1209.
[7] R. Saladino, C. Crestini, A. T. Palamara, M. C. Danti, F. Manetti, F. Corelli, E. Garaci, M. Botta, *J. Med. Chem.* **2001**, *44*, 4554.
[8] J.-B. Bher, T. Gourlain, A. Helimi, G. Guillerm, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 1713.
[9] A. Salimbeni, R. Canevotti, F. Paleari, D. Poma, S. Caliari, F. Fici, R. Cirillo, A. R. Renzetti, A. Subissi, L. Belvisi, G. Bravi, C. Scolastico, A. Giachetti, *J. Med. Chem.* **1995**, *38*, 4806.
[10] G. R. Madhavan, R. Chakrabarti, R. K. Vikramadithyan, R. N. V. S. Mamidi, V. Balraju, B. M. Rajesh, P. Misra, S. K. B. Kumar, B. B. Lohray, V. B. Lohray, R. Rajagopalan, *Bioorg. Med. Chem.* **2002**, *10*, 2671.
[11] E. Petricci, C. Mugnaini, M. Radi, A. Togninelli, C. Bernardini, F. Manetti, M. C. Parlato, M. L. Renzulli, M. Alongi, C. Falciani, F. Corelli, M. Botta, *Arkivoc* **2006**, 452.
[12] A. Mai, M. Artico, D. Rotili, D. Tarantino, I. Clotet-Codina, M. Armand-Ugón, R. Ragno, S. Simeoni, G. Sbardella, M. B. Nawrozkij, A. Samuele, G. Maga, J. A. Esté, *J. Med. Chem.* **2007**, *50*, 5412.
[13] C. S. Cho, D. B. Patel, S. C. Shim, *Tetrahedron* **2005**, *61*, 9490.
[14] C. S. Cho, H. S. Shim, *Tetrahedron Lett.* **2006**, *47*, 3835.
[15] C. S. Cho, D. B. Patel, *Tetrahedron* **2006**, *62*, 6388.
[16] C. S. Cho, J. U. Kim, H.-J. Choi, *J. Organometal. Chem.* **2008**, *693*, 3677.
[17] C. S. Cho, H. B. Kim, S. Y. Lee, *J. Organometal. Chem.* **2010**, *695*, 1744.
[18] C. S. Cho, H. B. Kim, *Catal. Lett.* **2010**, *140*, 116.
[19] C. S. Cho, H. B. Kim, *J. Organometal. Chem.* **2011**, *696*, 3264.
[20] H. K. Lee, C. S. Cho, *Appl. Organometal. Chem.* **2012**, *26*, 185.
[21] H. K. Lee, C. S. Cho, *Appl. Organometal. Chem.* **2012**, *26*, 406.
[22] C. S. Cho, J. I. Son, N. S. Yoon, *Appl. Organometal. Chem.* **2012**, *26*, 499.
[23] H. K. Lee, C. S. Cho, *Appl. Organometal. Chem.* **2012**, *26*, 570.
[24] J. I. Son, C. S. Cho, H.-J. Choi, *Appl. Organometal. Chem.* **2013**, *27*, 380.
[25] Y. K. Bae, C. S. Cho, *Synlett* **2013**, *24*, 1848.
[26] Y. K. Bae, C. S. Cho, *Appl. Organometal. Chem.* **2014**, *28*, 225.
[27] S. L. Ho, C. S. Cho, H.-S. Sohn, *Synthesis* **2015**, *47*, 216.
[28] Z. Arnold, A. Holly, *Collect. Czech. Chem. Commun.* **1961**, *26*, 3059.
[29] R. M. Coates, P. D. Senter, W. R. Baker, *J. Org. Chem.* **1982**, *47*, 3597.
[30] S. Brahma, J. K. Ray, *Tetrahedron* **2008**, *64*, 2883.
[31] R. Jana, I. Chatterjee, S. Samanta, J. K. Ray, *Org. Lett.* **2008**, *10*, 4795.
[32] P. Karthikeyan, A. Meena Rani, R. Saiganesh, K. K. Balasubramanian, S. Kabilan, *Tetrahedron* **2009**, *65*, 811.
[33] S. Samanta, R. Jana, J. K. Ray, *Tetrahedron Lett.* **2009**, *50*, 6751.
[34] S. Nandi, J. K. Ray, *Tetrahedron Lett.* **2009**, *50*, 6993.
[35] R. Jana, S. Paul, A. Biswas, J. K. Ray, *Tetrahedron Lett.* **2010**, *51*, 273.
[36] S. Samanta, N. Yasmin, D. Kundu, J. K. Ray, *Tetrahedron Lett.* **2010**, *51*, 4132.
[37] N. Yasmin, J. K. Ray, *Synlett* **2010**, 924.
[38] S. Paul, T. Gorai, A. Koley, J. K. Ray, *Tetrahedron Lett.* **2011**, *52*, 4051.
[39] S. L. Ho, C. S. Cho, *Appl. Organometal. Chem.* **2013**, *27*, 507.
[40] S. L. Ho, C. S. Cho, *Synlett* **2013**, *24*, 2705.
[41] J. Zhou, L. Fu, M. Lv, J. Liu, D. Pei, K. Ding, *Synthesis* **2008**, 3974.
[42] E. Dalcanale, F. Montanari, *J. Org. Chem.* **1986**, *51*, 567.
[43] T. Harayama, H. Toko, H. Nishioka, H. Abe, Y. Takeuch, *Heterocycles* **2003**, *59*, 541.
[44] E. Zoltan, H. Voeroes, T. Zoltan, German Patent, DE2943568, **1986**.