A Novel and Efficient Method for the Synthesis of 1*H*-Indol-3-yl Acetates

Kexin Liu, Ping Wen, Jin Liu, Guosheng Huang*

State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. of China
Fax +86(931)8912582; E-mail: hgs2368@163.com

Received 30 June 2010; revised 29 July 2010

Abstract: A catalyst-free method for the synthesis of 1*H*-indol-3-yl acetates from 1*H*-indoles is described. The reaction takes place in the presence of (diacetoxyiodo)benzene (DIB) and potassium hydroxide as the base under mild conditions (MeCN, 35 °C, 1.5 h). This represents a simple and efficient new method for 1*H*-indol-3-yl acetate synthesis.

Key words: indoles, (diacetoxyiodo)benzene (DIB), 1*H*-indol-3-yl acetates, oxidation

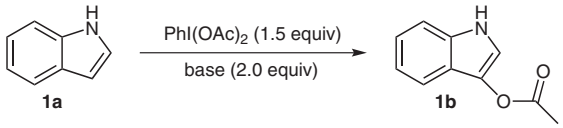
The direct formation of C–O bonds from C–H bonds is one of the most challenging projects in organic synthesis.[1] Recently, the direct formation of C–O bonds based on the β-C–H activation of amines has received great attention.[2] In this context, the functionalization of C–H bonds adjacent to a nitrogen atom is of great importance. It has been widely proved that the C3-position of indole has the priority in substitution reactions.[3] During the past few years, much attention has been devoted to 1*H*-indol-3-yl acetates because of their potential applications in medicinal and bioorganic chemistry. For example, 1*H*-indol-3-yl acetates are important materials for the preparation of biochemical reagents for the identification of campylobacter. Meanwhile, as starting materials, 1*H*-indol-3-yl acetates can be used to synthesize *N*-hydroxysuccinimidylindol-3-yl acetates, which are used for amino acid analysis.[4]

During a literature search we found only little information on the synthesis of 1*H*-indol-3-yl acetate. Arnold and coworkers revealed that indole reacts with iodine–potassium iodide. Subsequent stirring of the resulting crude 3-iodoindole with acetic acid for 20 hours results in the 1*H*-indol-3-yl acetate product;[5] however, the reported procedures are complex to perform and also need harsh reaction conditions.

Our efforts have been aimed at achieving this transformation by oxidation using hypervalent iodine(III) reagents. Hypervalent iodine reagents have recently received much attention due to their low toxicity, ease of handling and high reactivity.[6] The most well known representative of this class is (diacetoxyiodo)benzene (DIB), which is useful for the oxidative functionalization of various functional groups.[7]

Our initial study began with the reaction of 1*H*-indole (**1a**; 0.2 mmol) and DIB (1.5 equiv) in acetonitrile (2 mL) at 20 °C under air atmosphere for one hour. During the reaction, iodobenzene was detected by TLC. The desired product **1b** was isolated in 35% yield (Table 1, entry 1). After that, we found that the yield was increased when the reaction was undertaken in the presence of base. The reason for this increase is that base can neutralize acetic acid, keeping the reaction under an alkaline environment. Thus, base is suitable for the reaction and the effect of different bases on the reaction was tested. It can be seen from Table 1 that potassium hydroxide gave the best result, superior to Cs_2CO_3, NaH, K_2CO_3, Et_3N, pyridine and *t*-BuOK (entries 2–8). This revealed that potassium hydroxide is by far the best base for the reaction.

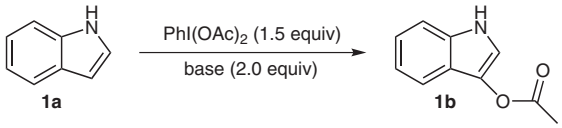
Table 1 Optimization of the Reaction of 1*H*-Indole with DIB[a]



Entry	Solvent	Base	Temp (°C)	Time (h)	Yield[b] (%)
1	MeCN	–	20	1	35
2	MeCN	Cs_2CO_3	20	1	53
3	MeCN	KOH	20	1	63
4	MeCN	NaH	20	1	57
5	MeCN	K_2CO_3	20	1	28
6	MeCN	Et_3N	20	1	30
7	MeCN	pyridine	20	1	27
8	MeCN	*t*-BuOK	20	1	31
9	MeCN	KOH	35	1	68
10	MeCN	KOH	45	1	65
11	MeCN	KOH	55	1	51
12	MeCN	KOH	75	1	28
13	**MeCN**	**KOH**	**35**	**1.5**	**76**
14	MeCN	KOH	35	2	74
15	MeCN	KOH	35	6	68
16[c]	MeCN	KOH	35	1.5	72
17[d]	MeCN	KOH	35	1.5	75

SYNTHESIS 2010, No. 21, pp 3623–3626
Advanced online publication: 01.09.2010
DOI: 10.1055/s-0030-1258240; Art ID: F11410SS

Table 1 Optimization of the Reaction of 1*H*-Indole with DIB[a] (continued)



Entry	Solvent	Base	Temp (°C)	Time (h)	Yield[b] (%)
18[e]	MeCN	KOH	35	1.5	67
19[f]	MeCN	KOH	35	1.5	74
20[g]	MeCN	KOH	35	1.5	0
21	CH_2Cl_2	KOH	35	1.5	40
22	DCE	KOH	35	1.5	51
23	THF	KOH	35	1.5	38
24	*i*-PrOH	KOH	35	1.5	43
25	Et_2O	KOH	35	1.5	32
26	DMF	KOH	35	1.5	35
27	DMSO	KOH	35	1.5	0
28	1,4-dioxane	KOH	35	1.5	65
29	AcOH	–	35	1.5	trace

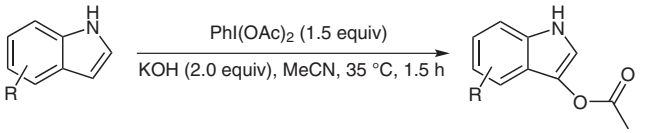
[a] Reaction conditions: 1*H*-indole (0.2 mmol), $PhI(OAc)_2$ (DIB, 1.5 equiv), base (2.0 equiv), solvent (2 mL), air atmosphere.
[b] Isolated yield of **1b**.
[c] KOH (1.5 equiv) was added.
[d] KOH (2.5 equiv) was added.
[e] $PhI(OAc)_2$ (1.0 equiv) was added.
[f] $PhI(OAc)_2$ (2.0 equiv) was added.
[g] MCPBA (1.0 equiv) was added.

Next, we evaluated the influence of the reaction temperature and time. As is obvious from the results in Table 1 (entries 3, 9–15), the best yield was obtained at 35 °C after reaction for 1.5 hours (entry 13). Furthermore, the quantity of potassium hydroxide did not obviously affect the reaction yield (Table 1, entries 16, 17).

According to our investigation, the optimal ratio of 1*H*-indole to DIB is 1:1.5, which gives the highest yield. Changes in the amount of DIB had little effect on the yield (Table 1, entries 18, 19). Further optimization of the reaction conditions revealed that acetonitrile as solvent is more effective than CH_2Cl_2, DCE, THF, *i*-PrOH, Et_2O, DMF, DMSO, 1,4-dioxane and AcOH (Table 1, entries 21–29). In addition, excessively strong oxidant may hinder the reaction (Table 1, entry 20).

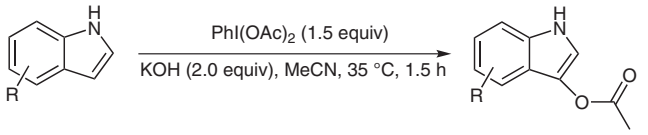
Having optimized the reaction conditions, we examined the scope and limitations of the procedure. As shown in Table 2, compounds **1a**, **7a**, **8a** and **9a** produced the corresponding acetates in moderate to good yields when reacted with DIB (entries 1, 7–9), while compounds **2a**, **3a**, **4a**, **5a** and **6a** produced the corresponding acetates in moderate yields (entries 2–6). In general, the reaction is mainly influenced by the electronic effect.[8] Electron-withdrawing or electron-donating groups may affect the activity of the 3-position of indoles and the activity of the N–H bond. Strongly electron-withdrawing substituents on the aryl moiety of the indole nucleus affect the efficiency of the reaction as lower yields are observed (Table 2, entries 10, 11). This is probably due to the strong modification of the electronic density at the C3-position of the nucleus due to the presence of such substituents.[9] On the other hand, different substituent positions of a substituent group may have a greater or lesser effect on the yield (Table 2, entries 2–5 and 7, 8).[10] In all cases, the indoles are inevitably consumed by oxidation. Finally, 1-phenyl-1*H*-indole (**12a**) gave no reaction (Table 2, entry 12), probably because it does not have a N–H bond like the N-unsubstituted indoles.[11]

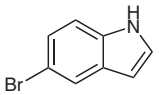
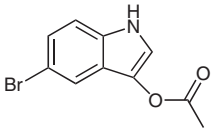
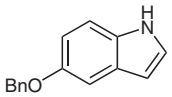
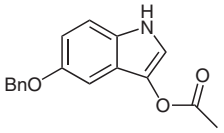
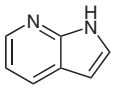
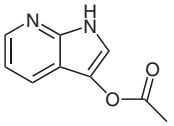
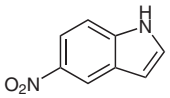
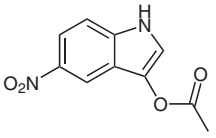
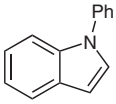
Table 2 Synthesis of 1*H*-Indol-3-yl Acetates[a]



Entry	Indole	Product	Yield[b] (%)
1	**1a**	**1b**	76
2	**2a**	**2b**	66
3	**3a**	**3b**	62
4	**4a**	**4b**	67
5	**5a**	**5b**	61
6	**6a**	**6b**	68
7	**7a**	**7b**	82

Table 2 Synthesis of 1*H*-Indol-3-yl Acetates[a] (continued)



Entry	Indole	Product	Yield[b] (%)
8	**8a** 	**8b** 	78
9	**9a** 	**9b** 	72
10	**10a** 	**10b** 	43
11	**11a** 	**11b** 	36
12	**12a** 	– –	n.r.[c]

[a] Reaction conditions: indole (0.3 mmol), $PhI(OAc)_2$ (DIB, 1.5 equiv), KOH (2.0 equiv), MeCN (3 mL), air atmosphere, 35 °C, 1.5 h.
[b] Isolated yield.
[c] No reaction.

In conclusion, we have developed a novel and mild methodology for the synthesis of 1*H*-indol-3-yl acetates. The reaction of 1*H*-indoles with DIB, without the presence of any catalyst, affords moderate to good yields of 1*H*-indol-3-yl acetates. This is a better option than the known method for 1*H*-indol-3-yl acetate synthesis.

NMR spectra were recorded on a Bruker Avance III 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz), using $CDCl_3$ as the solvent and TMS as the internal standard. IR spectra were recorded as KBr pellets or neat on a Nicolet Nexus 670 FT-IR spectrophotometer. Mass spectra were recorded using the EI method on a HP 5988A mass spectrometer. Elemental analyses were performed on an Elementar vario EL analyzer. Melting points are uncorrected.

1*H*-Indol-3-yl Acetate (1b); Typical Procedure

A mixture of 1*H*-indole (**1a**; 35.1 mg, 0.3 mmol), DIB (144.9 mg, 0.45 mmol) and KOH (33.6 mg, 0.6 mmol) was stirred in MeCN (3 mL) at 35 °C for 1.5 h (the progress of the reaction was monitored by TLC). During this time, the color of the mixture changed from colorless to orange. When the reaction was completed, the liquid was extracted with EtOAc (3 × 40 mL). The combined organic extracts were washed with H_2O (50 mL) and saturated brine (100 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated on a rotary evaporator. The residue was purified by chromatography on a silica gel column to obtain 1*H*-indol-3-yl acetate (the silica gel should be washed once with Et_3N before being used). The product was decolorized with activated carbon to give pure white needles; yield: 39.6 mg (76%); mp 128 °C.

IR (KBr): 3345, 1751, 1350, 1222, 741 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1 H), 7.54 (d, *J* = 7.6 Hz, 1 H), 7.29 (s, 1 H), 7.22 (d, *J* = 4.8 Hz, 1 H), 7.20 (t, *J* = 7.4 Hz, 1 H), 7.12 (t, *J* = 7.2 Hz, 1 H), 2.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.9, 133.1, 130.4, 122.7, 120.0, 119.8, 117.4, 113.4, 111.4, 20.94.

MS (EI): *m*/*z* = 175 [M$^+$], 133 (fission of C–O bond), 104, 77, 51, 43.

Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.55; H, 5.20; N, 8.04.

2-Methyl-1*H*-indol-3-yl Acetate (2b)

Yield: 37.1 mg (66%); yellow oil.

IR (neat): 3393, 1743, 1217, 742 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.34 (d, *J* = 7.2 Hz, 1 H), 7.21 (d, *J* = 7.2 Hz, 1 H), 7.14–7.06 (m, 2 H), 2.39 (s, 3 H), 2.27 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.5, 132.8, 126.7, 123.8, 121.7, 121.5, 119.9, 116.6, 110.8, 20.57, 10.40.

MS (EI): *m*/*z* = 189 [M$^+$], 147, 91, 77, 43.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86, N, 7.40. Found: C, 69.76; H, 5.84, N, 7.46.

4-Methyl-1*H*-indol-3-yl Acetate (3b)

Yield: 34.9 mg (62%); yellow needles; mp 120–121 °C.

IR (KBr): 3310, 1727, 1341, 1258, 1069, 736 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (s, 1 H), 7.18 (d, *J* = 2.4 Hz, 1 H), 7.10–7.04 (m, 2 H), 6.85 (t, *J* = 0.6 Hz, 1 H), 2.61 (s, 3 H), 2.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.5, 133.3, 131.1, 129.3, 122.8, 121.1, 118.9, 113.4, 109.1, 21.10, 18.71.

MS (EI): *m*/*z* = 189 [M$^+$], 147, 91, 43.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.82; H, 5.92; N, 7.45.

5-Methyl-1*H*-indol-3-yl Acetate (4b)

Yield: 37.5 mg (67%); white needles; mp 117–118 °C.

IR (KBr): 3357, 1747, 1222, 798, 604 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 1 H), 7.30 (s, 1 H), 7.19–7.13 (m, 2 H), 7.01 (d, *J* = 8.0 Hz, 1 H), 2.43 (s, 3 H), 2.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.9, 131.5, 130.0, 129.1, 124.4, 120.1, 116.8, 113.5, 111.1, 21.36, 20.90.

MS (EI): *m*/*z* = 189 [M$^+$], 147, 118, 91, 65, 43.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.77; H, 5.98; N, 7.36.

7-Methyl-1*H*-indol-3-yl Acetate (5b)

Yield: 34.1 mg (61%); yellow solid; mp 118–119 °C.

IR (KBr): 3291, 1729, 1250, 1222, 776 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 1 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 7.36 (d, *J* = 2.8 Hz, 1 H), 7.09–7.02 (m, 2 H), 2.47 (s, 3 H), 2.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.0, 132.6, 130.8, 123.1, 120.5, 120.0, 119.4, 115.0, 113.1, 20.91, 15.95.

MS (EI): *m*/*z* = 189 [M$^+$], 147, 118, 91, 65, 43.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.74; H, 5.79; N, 7.51.

5-Methoxy-1*H*-indol-3-yl Acetate (6b)
Yield: 41.2 mg (68%); white needles; mp 82–84 °C.

IR (KBr): 3378, 2934, 1753, 1457, 1225, 1028, 797 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (s, 1 H), 7.32 (d, *J* = 2.8 Hz, 1 H), 7.20 (s, 1 H), 6.96–6.86 (m, 2 H), 3.86 (s, 3 H), 2.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 154.2, 130.4, 128.3, 120.1, 114.1, 113.6, 112.3, 98.5, 55.77, 21.01.

MS (EI): *m*/*z* = 205 [M^+], 163, 148, 63, 43.

Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.32; H, 5.55; N, 6.86.

4-Bromo-1*H*-indol-3-yl Acetate (7b)
Yield: 61.9 mg (82%); yellow solid; mp 112–113 °C.

IR (KBr): 3311, 1749, 1370, 1333, 1221, 1190, 906, 732, 672 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 7.20 (d, *J* = 0.4 Hz, 1 H), 7.02 (d, *J* = 8.0 Hz, 1 H), 6.91 (t, *J* = 8.0 Hz, 1 H), 6.83 (d, *J* = 2.8 Hz, 1 H), 2.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 134.7, 129.0, 123.9, 123.4, 118.7, 115.8, 111.1, 111.0, 21.11.

MS (EI): *m*/*z* = 253 [M^+], 211, 131, 103, 75, 43.

Anal. Calcd for $C_{10}H_8BrNO_2$: C, 47.27; H, 3.17; N, 5.51. Found: C, 47.36; H, 3.14; N, 5.60.

5-Bromo-1*H*-indol-3-yl Acetate (8b)
Yield: 58.9 mg (78%); yellow solid; mp 118–119 °C.

IR (KBr): 3331, 1746, 1216, 1080, 795 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1 H), 7.56 (s, 1 H), 7.16–7.13 (m, 2 H), 7.01 (d, *J* = 8.8 Hz, 1 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.8, 131.7, 129.7, 125.7, 121.5, 120.0, 114.7, 113.1, 112.9, 20.87.

MS (EI): *m*/*z* = 253 [M^+], 211, 132, 75, 43.

Anal. Calcd for $C_{10}H_8BrNO_2$: C, 47.27; H, 3.17; N, 5.51. Found: C, 47.33; H, 3.21; N, 5.57.

5-(Benzyloxy)-1*H*-indol-3-yl Acetate (9b)
Yield: 60.1 mg (72%); yellow needles; mp 84–85 °C.

IR (KBr): 3411, 1745, 1490, 1455, 1220, 1062, 739 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 1 H), 7.48 (d, *J* = 7.2 Hz, 2 H), 7.42–7.31 (m, 4 H), 7.21 (d, *J* = 8.8 Hz, 1 H), 7.07 (d, *J* = 2.0 Hz, 1 H), 6.95 (dd, *J* = 2.4, 2.4 Hz, 1 H), 5.11 (s, 2 H, CH_2), 2.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 153.4, 137.4, 130.4, 128.52, 128.47, 127.79, 127.60, 120.1, 114.20, 114.05, 112.3, 100.3, 70.8, 20.9.

MS (EI): *m*/*z* = 281 [M^+], 239, 149, 91, 43.

Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.38; N, 4.98. Found: C, 72.61; H, 5.41; N, 5.01.

1*H*-Pyrrolo[2,3-*b*]pyridin-3-yl Acetate (10b)
Yield: 22.4 mg (43%); yellow solid; mp 132–134 °C.

IR (KBr): 2919, 1713, 1265, 662 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 11.24 (s, 1 H), 7.98–7.90 (m, 2 H), 7.40 (d, *J* = 3.6 Hz, 1 H), 6.47 (t, *J* = 7.8 Hz, 1 H), 3.70 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.2, 148.0, 141.4, 129.4, 125.4, 120.8, 115.5, 100.5, 21.75.

MS (EI): *m*/*z* = 176 [M^+], 134, 118, 91, 63, 43.

Anal. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.58; H, 4.78; N, 15.66.

5-Nitro-1*H*-indol-3-yl Acetate (11b)
Yield: 23.4 mg (36%); yellow solid; mp 172–173 °C.

IR (KBr): 3368, 2914, 1744, 1519, 1332, 1213, 743 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.95 (s, 1 H), 7.71 (s, 1 H), 7.44–7.31 (m, 3 H), 2.05 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.8, 137.5, 132.7, 131.8, 130.2, 127.4, 118.0, 117.6, 111.0, 29.67.

MS (EI): *m*/*z* = 220 [M^+], 178, 162, 132, 116, 104, 89.

Anal. Calcd for $C_{10}H_8N_2O_4$: C, 54.55; H, 3.66; N, 12.72. Found: C, 54.75; H, 3.42; N, 12.98.

Acknowledgment

The authors thank the State Key Laboratory of Applied Organic Chemistry for financial support.

References

(1) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077.
(2) Xingzhong, S.; Xiaofeng, X.; Yanfang, Y.; Kegong, J.; Xueyuan, L.; Yongmin, L. *J. Org. Chem.* **2009**, *74*, 7464.
(3) (a) Ohno, M.; Oguri, I.; Eguchi, S. *J. Org. Chem.* **1999**, *64*, 8995. (b) Prakash, O.; Kaur, H.; Sharma, V.; Bhardwaj, V.; Pundeer, R. *Tetrahedron Lett.* **2004**, *45*, 9065. (c) Bandini, M.; Melloni, A.; Umani, R. A. *Angew. Chem. Int. Ed.* **2004**, *43*, 550. (d) Cacchi, S.; Fabrizi, G. *Chem. Rev.* **2005**, *105*, 2873. (e) Ramesh, G.; BingFeng, S.; Keary, M.; Nathan, M.; Jinquan, Y. *Chem. Soc. Rev.* **2009**, *38*, 3242. (f) Mi, Z.; Qiang, K.; Qingli, H.; Shuli, Y. *Adv. Synth. Catal.* **2008**, *350*, 2169. (g) Verma, A. K.; Kesharwani, T.; Singh, J.; Tadon, V.; Larock, R. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 1138. (h) Kruger, K.; Tillack, A.; Beller, M. *Adv. Synth. Catal.* **2008**, *350*, 2153.
(4) (a) Bandini, M.; Eichholzer, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 9608. (b) Joucla, L.; Djakovitch, L. *Adv. Synth. Catal.* **2009**, *351*, 673. (c) Hong, J.; Xun, L.; Hong, W.; Huashan, Z.; Jieke, C. *J. Wuhan Univ. (Nat. Sci. Ed.)* **1998**, *44*, 175.
(5) Arnold, R. D.; Nutter, W. M.; Stepp, W. L. *J. Org. Chem.* **1959**, *24*, 117.
(6) (a) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299. (b) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523. (c) Mutule, I.; Suna, E.; Olofsson, K.; Pelcman, B. *J. Org. Chem.* **2009**, *74*, 7195.
(7) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123.
(8) (a) Yadav, J. S.; Subba Reddy, B. V.; Raghavendra Rao, K. V.; Narayana Kumar, G. G. K. S. *Tetrahedron Lett.* **2007**, *48*, 5573. (b) Taoan, L.; Pingzou, J.; Lizhang, L.; Yong, Z. *Tetrahedron Lett.* **2007**, *48*, 4297.
(9) (a) Lane, B. S.; Brown, M. A.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 8050. (b) Zhiping, L.; Chaojun, L. *J. Am. Chem. Soc.* **2005**, *127*, 6968.
(10) (a) Xiang, W.; Gribkov, D. V.; Sames, D. *J. Org. Chem.* **2007**, *72*, 1476. (b) Yanlong, G.; Ogawa, C.; Kobayashi, S. *Org. Lett.* **2007**, *9*, 175.
(11) (a) Bartoli, G.; Bosco, M.; Carlone, A.; Pesciaioli, F.; Sambri, L.; Melchiorre, P. *Org. Lett.* **2007**, *9*, 1403. (b) Hyeyeon, Y.; Youngtaek, H.; Sunggak, K. *Org. Lett.* **2007**, *9*, 2281. (c) Blay, G.; Fernández, I.; Pedro, J. R.; Vila, C. *Org. Lett.* **2007**, *9*, 2601.