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Metal-free synthesis of amides by oxidative amidation of aldehydes with amines in PEG/oxidant system

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ABSTRACT

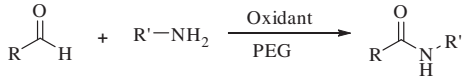
A simple, inexpensive, and efficient one-pot synthesis of amide derivatives were achieved in good to excellent yields via the directly oxidative amidation of aldehydes with amines under PEG/Oxidant system.

1. Introduction

The amides are one class of most common intermediates in synthetic organic chemistry and biological chemistry.[1] One of the most traditional methods for the preparation of amides is condensation of activated carboxylic acids with amines. However, the application scope of this method is still limited by some flaws, such as the demand on activated carboxylic acids, harsh conditions, and tedious workup, etc.[2] Therefore, development of facile, effective and more economical methods for the synthesis of amide has been attracting a great deal of attention. Various unconventional strategies have been devised and displayed practical utilities in synthesizing diverse amides. Typical examples including transition metal-catalyzed aminocarbonylation of aryl halides,[3] nitriles,[4] aldehydes,[5] aldoximes,[6] alcohols,[7] alkenes,[8] alkynes[9] as well as the Staudinger reaction using thioacids in the presence of azides.[10] The acid-promoted Schmidt reaction between ketones and alkyl azides or hydrazoic acids have been also reported.[11] Although effective and significant results were obtained, the high cost of transition metals greatly restricted the large scale application of these kinds of methodologies.

Considering the atom economics, a promising access to amides is employing aldehyde and amine as starting materials via direct oxidative amidation. Although this reaction was early declared to proceed in the presence of transition metals such as palladium and ruthenium under the assistance of oxidant like iodine and H_2O_2, lanthanide and lithium metals as the catalyst for amidation of aldehydes with amines,[12] radical mediated oxidant NBS/AIBN or oxone, etc.,[13] Metal-free oxidative protocol has been recently achieved.[14]

Poly(ethylene glycol) (PEG) and its monomethyl ethers are inexpensive, thermally stable, recoverable and nontoxic media frequently used in phase transfer catalysis.[15] Developing efficient catalyst systems, which utilizing PEG as reaction medium is highly desirable in terms of environmental friendliness as well as atom economics due to the unique advantages of PEG. As our continuous endeavor in exploring practical PEG mediated synthesis,[16] we wish to describe herein the reaction of aldehydes with amines for direct synthesis of amides in PEG/oxidant system. To the best of our knowledge, there are no examples using PEG/oxidant system for the direct oxidative amidation of aldehydes with amines is presently available (Scheme 1).



R, R'=Alkyl, Aryl

Scheme 1.

2. Results and discussion

In our initial attempt, we chose the reaction of benzaldehyde with aniline as the model reaction. Generally, a mixture of

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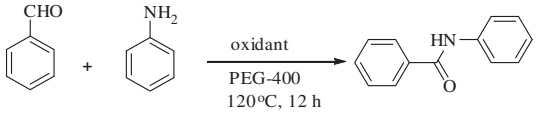
benzaldehyde (1 mmol), aniline (1 mmol) has been vigorously stirred at 120 °C for 12 h in the presence of oxidant in different media. The results on reaction condition optimization were shown in Table 1, it can be found in these data that NaOCl is favored as the best oxidant for this reaction by providing a yield of 90% **3a** with the assistance of Bu_4NHSO_4 (entry 5, Table 1). The results obtained in other conditions, such as different oxidants (entries 1–4 and 10–12, Table 1) as well as other solvents (entries 6–9, Table 1) were all evidently poorer. Further investigation on the effect of catalyst loading implied that 1.5 equiv of $NaOCl/Bu_4NHSO_4$ is most proper for optimal results.

Table 1
Oxidative amidation of benzaldehyde with aniline under different conditions[a]



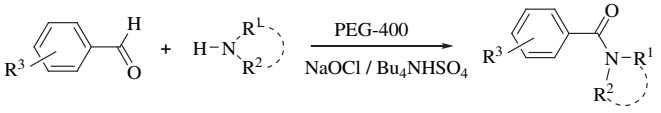
1a **2a** **3a**

Entry	Oxidant	Solvent	Yield[b] (%)
1	SeO_2	PEG-400	55
2	MnO_2	PEG-400	46
3	I_2	PEG-400	0
4	Al_2O_3/KF	PEG-400	12
5	$NaOCl/Bu_4NHSO_4$	PEG-400	90
6	$NaOCl/Bu_4NHSO_4$	No	68
7	$NaOCl/Bu_4NHSO_4$	CH_3CN[c]	49
8	$NaOCl/Bu_4NHSO_4$	$CHCl_3$[c]	42
9	$NaOCl/Bu_4NHSO_4$	Toluene[c]	31
10	$K_2S_2O_8/Bu_4NHSO_4$	PEG-400	57
11	K_2SO_5/Bu_4NHSO_4	PEG-400	61
12	H_2O_2/NBS	PEG-400	39

[a] Reaction conditions: (1 mmol) benzaldehyde, (1 mmol) aniline, (1.5 equiv) oxidants in 2g PEG-400 at 120 °C.
[b] Isolated yields after column chromatography.
[c] Reaction in corresponding solvents (3 ml).

Based on the optimized reaction conditions in hand, the scope and generality of this PEG-400/$NaOCl/Bu_4NHSO_4$ promoted amidation was subsequently examined. A wide range of substituted aromatic aldehydes with various amines were subjected for reaction. The amidation results were shown in Table 2. In general,

Table 2
Synthesis of various aldehydes and amines in PEG-400/$NaOCl/Bu_4NHSO_4$ system[a]



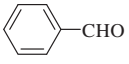
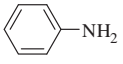
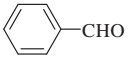
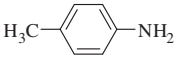
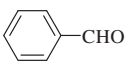
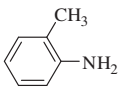
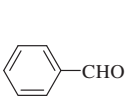
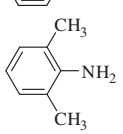
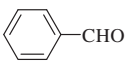
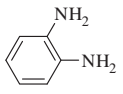
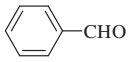
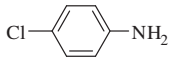
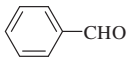
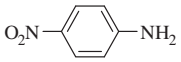
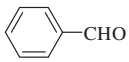
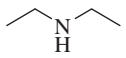
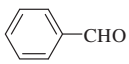
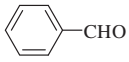
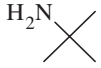
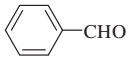
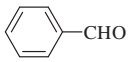
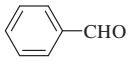
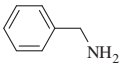
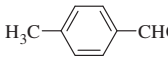
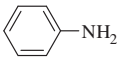
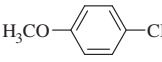
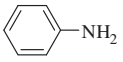
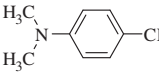
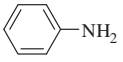
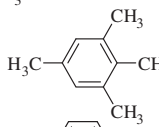
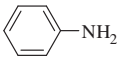
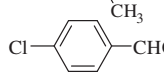
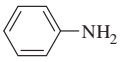
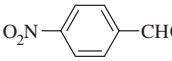
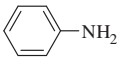
Entry	Aldehydes	Amines	Yield[b] (%)
1			90 (**3a**)
2			91 (**3b**)
3			89 (**3c**)
4			81 (**3d**)
5			63 (**3e**)

Table 2 (*continued*)

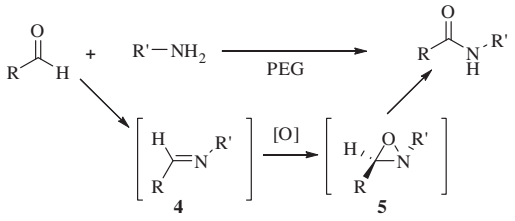
Entry	Aldehydes	Amines	Yield[b] (%)
6			70 (**3f**)
7			52 (**3g**)
8			83 (**3h**)
9			66 (**3i**)
10			45 (**3j**)
11			77 (**3k**)
12			81 (**3l**)
13			80 (**3m**)
14			88 (**3n**)
15			74 (**3o**)
16			76 (**3p**)
17			69 (**3q**)
18			93 (**3r**)
19			94 (**3s**)
20			93 (**3t**)
21			N.R
22			Trace

[a] Reaction perform with (1 mmol) aldehydes, (1 mmol) amines, (1.5 equiv) $NaOCl/Bu_4NHSO_4$ in 2 g PEG-400 at 120 °C.
[b] Isolated yields after column chromatography.

aromatic aldehydes and aromatic/aliphatic were well tolerated in this reaction system, while aliphatic aldehydes didn't provide corresponding products under present conditions (entries 21 and 22, Table 2). Based on the obtained results, the electronic effects and the steric effects of the substituents both in amines and aldehydes played significant role in the yields of products. Electron donating group such as CH_3 on the amine was able to facilitate the transformation by giving evidently higher yield of products than the entries using electron withdrawing groups functionalized anilines

(entries 2, 6, and 7, Table 2), while electron donating effect in aromatic aldehydes displayed remarkable hindering effect by leading to lower yields of products than equivalent entries using electron withdrawing aldehydes (entries 14–16 and 19, Table 2). One the other hand, steric effects from both amines and aldehydes undermined the efficiency of corresponding reactions (entries 1, 3–5 and 1, 17, Table 2). Finally, in order to further demonstrate the wide application scope of the present methodology, we investigated the reactions using both aliphatic aldehydes and amines as starting materials. While aliphatic aldehydes could not undergo the amidation transformation as mentioned above, aliphatic amines of different frameworks were successfully converted to corresponding amides in moderate to good yields (entries 8–13, Table 2), and the yields provided by aliphatic amines were generally inferior to their aromatic counterparts.

According to the known literature and results obtained in our experiments, a mechanism is proposed for this amidation reaction as shown in Scheme 2. First, the imine intermediates **4** were formed via the condensation of the aldehydes and amines. Subsequently, **4** was oxidized to give oxaziridine intermediates **5** in the presence of oxidant. The tautomerization of **5** led to the final formation of amide products.



Scheme 2. Proposed mechanism for the reaction oxidized by PEG/NaOCl/Bu_4NHSO_4 system.

3. Conclusion

In summary, we have developed a green and efficient new approach for the synthesis of amides via direct oxidative amidation of aldehydes and amines. The features of environmentally benign solvent, cheap oxidant, wide range of reactant tolerance and satisfactory product yields of our method should reasonably make it a useful supplement for those known strategies.

4. Experimental

4.1. General

All chemicals were purchased from Aldrich. Mps were determined on a WRR/X-4 digital mp apparatus and were not corrected, NMR spectra were recorded on a Bruker Avance DMX 500 MHz (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer in $CDCl_3$ using TMS as internal standard. Chemical shifts (δ) are reported in parts per million. IR spectra were obtained with a NICOLET 560 type FT-IR spectrometer, GC–MS spectra were recorded on HP6890. All data are in full agreement with those previously reported in the literature.[12,14]

4.2. General procedure for the synthesis of amides from the reaction of aldehydes with amines

Typically reactions were carried out as follows: A mixture of aldehydes (1 mmol), amines (1 mmol), NaOCl/Bu_4NHSO_4 (1.5 equiv), and PEG (2 g) was placed in a 15 mL round-bottomed flask, stirring at 120 °C for 12 h. After the reaction was completed, the mixture was extracted with ethyl acetate (3×10 mL), dried over anhydrous Na_2SO_4, and filtered. After the solvents were evaporated, the crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (9:1) as the eluent to give corresponding amides in analytical purity.

*4.2.1. Compound **3a**: N-phenylbenzamide.* Mp 164–165 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24 (t, J=14.2 Hz, 2H), 7.53–7.59 (m, 3H), 7.66–7.71 (m, 3H), 7.98 (d, J=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 120.2, 124.6, 126.7, 128.4, 128.8, 132.1, 134.6, 137.9, 165.4; IR (KBr) 3301, 1645, 1552, 1492, 1452, 1415, 727, 695 cm^{-1}; GC–MS: m/z, 197.

*4.2.2. Compound **3b**: N-p-tolylbenzamide.* Mp 156–157 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.35 (s, 3H), 7.20 (d, J=8.7 Hz, 2H), 7.56–7.67 (m, 5H), 8.03 (d, J=7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 121.5, 128.6, 128.8, 129.4, 132.2, 134.4, 135.3, 137.1, 165.2; IR (KBr) 3335, 1652 cm^{-1}; GC–MS: m/z, 211.

*4.2.3. Compound **3c**: N-o-tolylbenzamide.* Mp 143–145 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.42 (s, 3H), 7.16–7.21 (m, 1H), 7.25–7.38 (m, 2H), 7.63–7.71 (m, 3H), 7.92 (d, J=7.4 Hz, 2H), 10.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.6, 126.4, 126.2, 126.8, 127.6, 128.8, 130.7, 132.2, 134.7, 134.9, 136.6, 164.9; IR (KBr) 3296, 1644 cm^{-1}; GC–MS: m/z, 211.

*4.2.4. Compound **3d**: N-(2,6-dimethylphenyl)benzamide.* Mp 157–158 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.29 (d, J=7.5 Hz, 6H), 7.20–7.36 (m, 3H), 7.63–7.70 (m, 3H), 7.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 131.2, 132.4, 133.2, 134.0, 137.2, 139.7, 140.6, 142.3, 165.7; IR (KBr) 3271, 1654 cm^{-1}; GC–MS: m/z, 225.

*4.2.5. Compound **3e**: N-(2-aminophenyl)benzamide.* Mp 154–155 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.08 (s, 2H), 6.85–6.89 (m, 2H), 7.21 (t, J=12.5 Hz, 1H), 7.36 (d, J=9.5 Hz, 1H), 7.6–7.68 (m, 3H), 7.99 (s, 1H), 8.12 (d, J=9.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 115.6, 117.8, 124.6, 127.7, 127.7, 128.4, 128.9, 132.1, 134.7, 145.6, 170.9; IR (KBr) 3271, 1643 cm^{-1}; GC–MS: m/z, 212.

*4.2.6. Compound **3f**: N-(4-chlorophenyl)benzamide.* Mp 199–200 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.45 (d, J=11.2 Hz, 2H), 7.83 (d, J=11.2 Hz, 2H), 7.85–7.48 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 122.4, 127.8, 128.2, 128.8, 129.0, 133.2, 135.1, 137.9, 166.8; IR (KBr) 3348, 1654 cm^{-1}; GC–MS: m/z, 231.

*4.2.7. Compound **3g**: N-(4-nitrophenyl)benzamide.* Mp 198–199 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.63–7.52 (m, 4H), 7.84–8.03 (m, 3H), 8.24 (d, J=15.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 120.2, 124.6, 127.9, 129.1, 132.7, 134.6, 143.9, 145.8, 167.2; IR (KBr) 3336, 1658 cm^{-1}; GC–MS: m/z, 242.

*4.2.8. Compound **3h**: N, N-diethylbenzamide.* Colorless, liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.29 (t, 3H), 1.34 (t, 3H), 3.35 (q, 2H), 3.57 (q, 2H), 7.67–7.87 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.9, 13.9, 39.2, 43.2, 127.2, 128.5, 128.8, 129.7, 137.1, 170.2; IR (KBr) 2974, 2935, 1627, 1427, 1381, 1288, 1219, 1099, 786, 736, 705 cm^{-1}; GC–MS: m/z, 177.

*4.2.9. Compound **3i**: N-isopropylbenzamide.* Mp 99–101 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.27 (d, J=9.6 Hz, 6H), 4.25–4.31 (m, 1H), 5.83 (br, 1H), 7.53–7.61 (m, 3H), 7.84 (d, J=9.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.2, 41.5, 127.9, 128.5, 132.3, 134.9, 167.8; IR (KBr) 3298, 2970, 2874, 1631, 1535, 1489, 1458, 1346, 1288, 698 cm^{-1}; GC–MS: m/z, 163.

*4.2.10. Compound **3j**: N-tert-butylbenzamide.* Mp 135–136 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.48 (s, 9H), 7.54–7.61 (m, 3H), 7.78 (d, J=12 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.2, 51.7, 126.8, 128.2,

131.7, 135.6, 169.4; IR (KBr) 3325, 2966, 2928, 1635, 1532, 1492, 1458, 1278, 692 cm^{-1}; GC–MS: *m*/*z*, 177.

4.2.11. Compound ***3k****: phenyl(pyrrolidin-1-yl)methanone.* Colorless, liquid; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.62 (t, 2H), 1.71 (t, 2H), 3.43 (t, 2H), 3.50 (t, 2H), 7.63–7.84 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.5. 45.4, 127.8, 128.6, 129.4, 129.8, 135.2, 170.1; IR (KBr) 2936, 2856, 1643, 1578, 1492, 1429, 1273, 781, 722, 710 cm^{-1}; GC–MS: *m*/*z*, 175.

4.2.12. Compound ***3l****: phenyl(piperidin-1-yl)methanone.* Colorless, liquid; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.53–1.59 (m, 6H), 3.53 (t, 2H), 3.70 (t, 2H), 7.64–7.85 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.2, 25.6, 26.5, 43.1, 48.7, 126.8, 128.4, 128.5, 129.3, 136.5, 170.3; IR (KBr) 2939, 2861, 1642, 1579, 1492, 1437, 1281, 786, 732, 709 cm^{-1}; GC–MS: *m*/*z*, 189.

4.2.13. Compound ***3m****: N-benzylbenzamide.* Mp 105–106 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 4.65 (d, *J*=9.4 Hz, 2H) 6.40 (s, 1H), 7.23–7.26 (m, 5H), 7.63–7.69 (m, 3H), 7.86 (d, *J*=11.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 44.8, 126.7, 127.2127.5, 128.3, 128.5, 135.2, 134.1, 137.9, 167.8; IR (KBr) 3313, 1649, 1598, 1525, 1515, 1491, 1475, 698, 675 cm^{-1}; GC–MS: *m*/*z*, 211.

4.2.14. Compound ***3n****: 4-methyl-N-phenylbenzamide.* Mp 145–146 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.37 (s, 3H), 7.22–7.27 (m, 3H), 7.38 (t, *J*=13.2 Hz, 2H), 7.64 (d, *J*=13.2 Hz, 2H), 7.89 (d, *J*=13.5 Hz, 2H), ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 121.2, 124.4, 126.8, 127.1, 129.1, 129.4, 132.1, 138.2, 142.4, 165.8; IR (KBr) 3348, 1651 cm^{-1}; GC–MS: *m*/*z*, 211.

4.2.15. Compound ***3o****: 4-methoxy-N-phenylbenzamide.* Mp 174–175 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.83 (s, 3H), 7.15 (d, *J*=14.5 Hz, 2H), 7.21 (t, 1H), 7.37 (t, 2H), 7.63 (d, *J*=13.1 Hz, 2H), 7.88 (d, *J*=14.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.8, 114.4, 121.6, 123.9, 127.4, 129.0, 130.0, 139.7, 163.4, 165.5; IR (KBr) 3329, 1654 cm^{-1}; GC–MS: *m*/*z*, 227.

4.2.16. Compound ***3p****: 4-(dimethylamino)-N-phenylbenzamide.* Mp 182–183 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.06 (s, 6H), 7.19 (t, 1H), 7.43–7.56 (m, 3H), 7.36 (t, *J*=12.8 Hz, 2H), 7.63 (d, *J*=13.3 Hz, 2H), 7.78 (d, *J*=14.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 41.6, 112.3, 124.5, 125.2, 127.3, 127.6, 132.7, 133.4, 143.9, 155.6, 168.7; IR (KBr) 3267, 1643, 1604, 1519, 1489, 1435, 1323, 759 cm^{-1}; GC–MS: *m*/*z*, 240.

4.2.17. Compound ***3q****: 2,4,6-trimethyl-N-phenylbenzamide.* Mp 156–157 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.34–2.46 (m, 9H), 6.89 (s, 2H), 7.31 (br, 1H), 7.38–7.43 (m, *J*=7.7 Hz, 3H), 7.62 (d, *J*=12.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.9, 21.8, 121.2, 124.6, 128.4, 129.1, 134.6, 135.3, 137.9, 138.9, 169.8; IR (KBr) 3279, 3255, 1654, 1597, 1543, 1492, 1442, 1323, 756 cm^{-1}; GC–MS: *m*/*z*, 239.

4.2.18. Compound ***3r****: 4-chloro-N-phenylbenzamide.* Mp 199–200 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.19 (t, 1H), 7.43–7.57 (m, 4H), 7.75 (d, *J*=13.6 Hz, 2H), 7.91 (d, *J*=14 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 121.6, 124.3, 128.9, 129.1, 131.1, 134.5, 137.4, 139.7, 164.7; IR (KBr) 3351, 1654 cm^{-1}; GC–MS: *m*/*z*, 231.

4.2.19. Compound ***3s****: 4-nitro-N-phenylbenzamide.* Mp 214–216 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.17–7.27 (t, 1H), 7.43 (t, *J*=12.6 Hz, 2H), 7.65 (d, *J*=13.2 Hz, 2H), 8.11 (d, *J*=13.8 Hz, 2H), 8.43 (d, *J*=14 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 121.5, 124.0, 124.7, 128.2, 138.1, 141.1, 151.6, 164.4; IR (KBr) 3321, 1651 cm^{-1}; GC–MS: *m*/*z*, 242.

4.2.20. Compound ***3t****: 2,4-dichloro-N-phenylbenzamide.* Mp 153–154 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.19 (t, 1H), 7.43–7.48(m, 4H), 7.63(d, *J*=13 Hz, 2H), 7.73(d, *J*=13.8 Hz, 1H), 7.90(s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 122.3, 125.1, 127.6, 129.2, 130.1, 131.2, 131.5, 133.6, 137.1, 137.9, 164.7; IR (KBr) 3344, 1659 cm^{-1}; GC–MS: *m*/*z*, 265.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.08.091.

References and notes

1. (a) Humphrey, J. M.; Chamberlin, A. R. *Chem. Rev.* **1997**, *97*, 2243–2266.
2. (a) Kang, Y.; Chung, H.; Kim, J.; Yoon, Y. *Synthesis* **2002**, 733–738; (b) Azumaya, I.; Okamoto, T.; Imabeppu, F.; Takayanagi, H. *Tetrahedron* **2003**, *59*, 2325–2331; (c) Wu, X.; Hu, L. *J. Org. Chem.* **2007**, *72*, 765–774; (d) Daniel, G.; David, B.; Simon, W. *Tetrahedron Lett.* **2008**, *49*, 5687–5688; (e) Teichert, A.; Jantos, K.; Harms, K.; Studer, A. *Org. Lett.* **2004**, *6*, 3477–3480; (f) Naik, S.; Bhattacharjya, G.; Talukdar, B.; Patel, B. K. *Eur. J. Org. Chem.* **2004**, 1254–1260; (g) Shendage, D. M.; Froehlich, R.; Haufe, G. *Org. Lett.* **2004**, *6*, 3675–3678; (h) Black, D. A.; Arndtsen, B. A. *Org. Lett.* **2006**, *8*, 1991–1993; (i) Katritzky, A. R.; Cai, C.; Singh, S. K. *J. Org. Chem.* **2006**, *71*, 3375–3380.
3. (a) Fukuoka, S.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1971**, *36*, pp 2721–2721; (b) Uozumi, Y.; Arii, T.; Watanabe, T. *J. Org. Chem.* **2001**, *66*, 5272–5274; (c) Namayakkara, P.; Alper, H. *Chem. Commun.* **2003**, 2384–2385; (d) Lin, Y. S.; Alper, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 779–781.
4. (a) Murahashi, S. I.; Naota, T.; Saito, E. *J. Am. Chem. Soc.* **1986**, *108*, 7846–7847; (b) Cobley, C. J.; van den Heuvel, M.; Abbadi, A.; de Vries, J. G. *Tetrahedron Lett.* **2000**, *41*, 2467–2470.
5. Tillack, A.; Rudloff, I.; Beller, M. *Eur. J. Org. Chem.* **2001**, 523–528.
6. Park, S.; Choi, Y.; Han, H.; Yang, S. H.; Chang, S. *Chem. Commun.* **2003**, 1936–1937.
7. Owston, N. A.; Parker, A. J.; Williams, J. M. J. *Org. Lett.* **2007**, *9*, 73–75.
8. Beller, M.; Cornils, B.; Frohning, C. D. *J. Mol. Catal. A: Chem.* **1995**, *104*, 17–85.
9. (a) Ali, B. E.; Tijani, J. *Appl. Organomet. Chem.* **2003**, *17*, 921–931; (b) Knapton, D. J.; Meyer, T. Y. *Org. Lett.* **2004**, *6*, 687–689; (c) Uenoyama, Y.; Fukuyama, T.; Nobuta, O.; Matsubara, H.; Ryu, I. *Angew. Chem., Int. Ed.* **2005**, *44*, 1075–1078; (d) Zhang, C.; Jiao, N. *J. Am. Chem. Soc.* **2010**, *132*, 28–29.
10. (a) Nilson, B. L.; Kiessling, L. L.; Raines, R. T. *Org. Lett.* **2000**, *2*, 1939–1941; (b) Damkaci, F.; DeShong, P. *J. Am. Chem. Soc.* **2003**, *125*, 4408–4409; (c) Shangguan, N.; Katukojvala, S.; Greenberg, R.; Williams, L. J. *J. Am. Chem. Soc.* **2003**, *125*, 7754–7755; (d) Merkx, R.; Brouwer, A. J.; Rijkers, D. T. S.; Liskamp, R. M. J. *Org. Lett.* **2005**, *7*, 1125–1128.
11. (a) Schmidt, R. F. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 704–706; (b) Yao, L.; Aube, J. *J. Am. Chem. Soc.* **2007**, *129*, 2766–2767; (c) Cho, S. H.; Yoo, E. J.; Bae, I.; Chang, S. *J. Am. Chem. Soc.* **2005**, *127*, 16046–16047.
12. (a) Qian, C. W.; Zhang, X. M.; Zhang, Y.; Shen, Q. *J. Organomet. Chem.* **2010**, *695*, 747–752; (b) Zhang, L. J.; Su, S. P.; Wu, H. P.; Wang, S. W. *Tetrahedron* **2009**, *65*, 10022–10024; (c) Seo, S. Y.; Marks, T. J. *Org. Lett.* **2008**, *10*, 317–319; (d) Wang, J. F.; Li, J. M.; Xu, F.; Shen, Q. *Adv. Synth. Catal.* **2009**, *351*, 1363–1370; (e) Wu, Y. J.; Wang, S. W.; Zhang, L. J.; Yang, G. S.; Zhu, X. C.; Zhou, Z. H.; Zhu, H.; Wu, S. H. *Eur. J. Org. Chem.* **2010**, 326–332.
13. (a) Annegret, T.; Ivo, R.; Matthias, B. *Eur. J. Org. Chem.* **2001**, 523–528; (b) Shie, J.; Fang, J. *J. Org. Chem.* **2003**, *68*, 1158–1160; (c) Markó, I. E.; Mekhalfia, A. *Tetrahedron Lett.* **1990**, *31*, 7237–7240; (d) Gao, J.; Wang, G. W. *J. Org. Chem.* **2008**, *73*, 2955–2958.
14. Kekeli, E. K.; Christian, W. *Org. Lett.* **2007**, *9*, 3426–3432.
15. (a) Harris, J. M. *Polyethylene Glycol: Chemistry and Biological Application*; Plenum: New York, NY, 1992; p 3; (b) Harris, J. M. In *Poly(ethylene Glycol) Chemistry, Biotechnological and Biomedical Applications*; ACS Books: Washington, DC, 1997; (c) Kochi, M. *Green Reaction Media for Organic Synthesis*; Blackwell: Oxford, 2005, pp 1–187.
16. Liang, J.; Lv, J.; Fan, J. C.; Shang, Z. C. *Synth. Commun.* **2009**, *39*, 2822–2828.