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Hg cathode-free electrochemical detosylation of *N*,*N*-disubstituted *p*-toluenesulfonamides: mild, efficient, and selective removal of *N*-tosyl group

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ABSTRACT

Hg cathode-free electrochemical detosylation of *N*,*N*-disubstituted *p*-toluenesulfonamides was successfully carried out by a constant current electrolysis using an undivided cell equipped with a platinum cathode and a magnesium anode in the presence of an arene mediator. The deprotection proceeded efficiently and selectively under neutral and mild conditions with a stoichiometric amount of electricity without the use of an Hg cathode to obtain the corresponding secondary amines in good to excellent yields.

Arenesulfonyl groups, particularly a *p*-toluenesulfonyl (tosyl, Ts) group, are useful and important protecting groups for primary and secondary amines and have been widely used for organic transformations.[1] Due to the stability of the resulting arenesulfonamides, desulfonylation reaction is frequently troublesome and harmful reagents or harsh reaction conditions have been required for reproducing amine function. Desulfonylation of benzene- or *p*-toluenesulfonamides has been classically performed by using reagents such as strong acids,[2] sodium or lithium metal in liquid ammonia,[2a,3] sodium amalgam,[4] and sodium naphthalenide and the related arenides.[2b,5] Various efforts have been made to improve the utilities of arenesulfonyl groups as protecting groups. For example, efforts have been made to modify arenesulfonyl groups to make the resulting amides more labile. Consequently, 2- or 4-nitro-,[6] 2,4-dinitro-,[7] and electron-donating group-substituted benzenesulfonyl groups,[8] 2,2,5,7,8-pentamethylchloman-6-sulfonyl group[9] and heteroarene-2-sulfonyl groups[10] were developed as alternative arenesulfonyl groups. Efforts have also been made to develop new and efficient methods for desulfonylation of conventional benzene- and *p*-toluenesulfonamides under milder conditions than the classical conditions. Several reagents such as Bu_3SnH/AIBN,[11] SmI_2,[12] TMSI,[13] $TiCl_4$/Zn,[11b] $TiCl_4$/mischmetal,[14] $TiCl_3$/Li,[15] Mg/MeOH,[16] Me_3CoLi, Me_3FeLi and Me_3MnLi with Mg,[17] Ni(0)acac/*i*-PrMgCl,[18] photolysis,[19] TBAF,[20] phase-transfer catalyst,[21] alkali metals on silica gel,[22] and microwave irradiation in the presence of acid[23] were found to be applicable for desulfonylation. However, many of these reagents were effective only for arenesulfonamides having an activating group such as a phenyl, acyl, and Boc group on nitrogen, and were ineffective for stable amides such as *N*,*N*-dialkyltosylamides. Electrochemical reduction of tosylamides is also known to be a useful method for detosylation under mild conditions and has been extensively studied.[2a,10a,24,25] However, in most cases the electrolysis has been performed by using mercury as a cathode and/or a divided cell. The use of mercury is unfavorable nowadays from the viewpoint of green chemistry and a divided cell sometimes gives rise to complications in choice of diaphragm and its structure. The divider usually increases the cell resistance and the power loss (dissipated as heat) in the cell sometimes causes the problem of undesirable reactions taking place at the counter electrode. Therefore, powerful, efficient, and selective detosylation under mild conditions without harmful and toxic reagents has been still desirable. During the course of our studies on electrochemical reduction in organic transformations,[26] we recently found that electrolysis of *N*,*N*-disubstituted tosylamides using an undivided cell, which is easier to construct and to apply to large-scale synthesis, in the presence of an arene mediator resulted in efficient detosylation of the amides without the use of a mercury electrode to obtain secondary amines in high yields. In this communication, we report mild, efficient, and Hg electrode-free electrochemical detosylation of *N*,*N*-disubstituted tosylamides in the presence of an arene mediator.

A constant current electrolysis of *N*,*N*-dihexyltosylamide (**1a**) was carried out in DMF containing 0.1 M Et_4NBr as a supporting electrolyte by using a test tube-like undivided cell equipped with a platinum plate cathode and a magnesium rod anode. The results of optimization of reaction conditions are partly shown in Table 1. Electrolysis of **1a** with a stoichiometric amount of electricity (2 F/mol) without any mediator gave dihexylamine (**2**) in 77% yield along with 13% of recovered **1a** (Table 1, entry 1). The yield of **2** increased to 87% when 5 F/mol of electricity was passed. However, a trace amount of **1a** remained (Table 1, entry 2). On the other hand, **1a** was consumed completely with 2 F/mol of electricity and amine **2** was obtained in 88% yield when the electrolysis was carried out in the presence of 1.0 equiv of naphthalene as an electron-transfer mediator (Table 1, entry 3). Even 0.5 equiv of naphthalene effectively played a role of mediator to give **2** in 90% yield (Table 1, entry 4). Biphenyl was also usable as a mediator, though there was a

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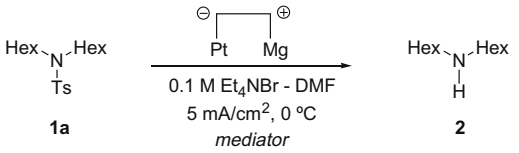
Table 1
Optimization of reaction conditions



Entry	Mediator (equiv)	Electricity (F/mol)	Yield[a] (%)
1	—	2.0	77[b]
2	—	5.0	87
3	Naphthalene (1.0)	2.0	88
4	Naphthalene (0.5)	2.0	90
5	Biphenyl (0.5)	3.0	80

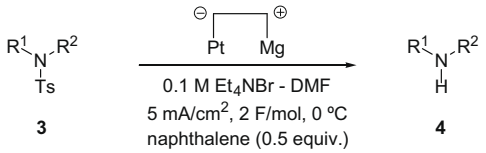
[a] All reactions were performed on a 1 mmol scale. The yields refer to isolated amine **2**.
[b] Amide **1a** was recovered in 13% yield.

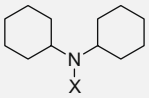
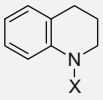
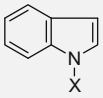
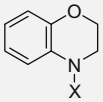
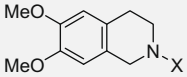
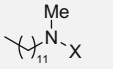
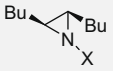
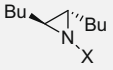
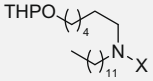
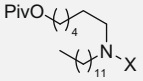
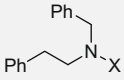
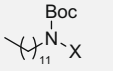
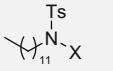
slight decrease in the yield (Table 1, entry 5). Although pyren[25j] and anthracene[25g] have already been used as an electron-transfer mediator in electrochemical detosylation, naphthalene, and biphenyl are more convenient and also works as a mediator. These results indicated that neither a mercury electrode nor a divided cell is critical for the efficient electrochemical detosylation. We also found that detosylation can be accomplished more easily and friendly than a conventional method by using the present electrochemical detosylation. It should also be noted that naphthalene, used as an electron-transfer mediator, could be recovered quantitatively by usual work up including extraction followed by column chromatography on silica gel, and could also be reused as a mediator.

Desulfonylation of other representative arenesulfonamides was next investigated, and the results are summarized in Scheme 1. A similar electrolysis of benzenesulfonamide **1b** with 2 F/mol of electricity gave deprotected amine **2** in 88% yield. In the case of 4-bromobenzenesulfonamide (brosylate) **1c**, probably due to competitive reduction with a C–Br bond, 6 F/mol of electricity was necessary for consumption of amide **1c** to obtain **2** in 78% yield. These results also showed that the present desulfonylation is effective for benzene- and 4-bromobenzenesulfonamides.

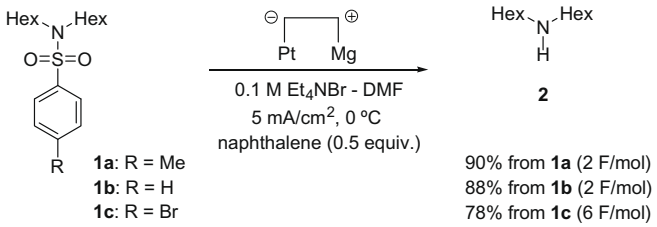
The results of the present electrochemical detosylation of various *N*,*N*-disubstituted tosylamides **3** are shown in Table 2. In all cases, detosylation proceeded efficiently under neutral and mild conditions to afford the corresponding secondary amines **4** in good to excellent yields. Thus, dicyclohexylamine (**4a**), tetrahydroquinoline (**4b**), indole (**4c**), and 3,4-dihydro-2*H*-1,4-benzoxazine (**4d**) were obtained in 96%, 90%, 97%, and 87% yields, respectively, from the corresponding tosylamides **3a**, **3b**, **3c**, and **3d** (Table 2, entries 1–4). When electrolysis of *N*-tosyltetrahydroisoquinoline (**3e**) and *N*-dodecyl-*N*-methyltosylamide (**3f**) was carried out in DMF under similar conditions, detosylation also took place efficiently and amines were surprisingly obtained as the corresponding formamides.[27] Instead of DMF, the use of acetonitrile as a solvent resulted in exclusive formation of **4e** and **4f** in 84% and 82% yields,

Table 2
Scope of Hg cathode-free electrochemical detosylation



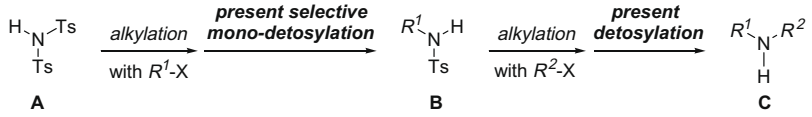
Entry	Substrate, product, and yield[a]	
1		**3a**; X = Ts **4a**; X = H — 96%
2		**3b**; X = Ts **4b**; X = H — 90%
3		**3c**; X = Ts **4c**; X = H — 97%
4		**3d**; X = Ts **4d**; X = H — 87%
5[b]		**3e**; X = Ts **4e**; X = H — 84%
6[b]		**3f**; X = Ts **4f**; X = H — 82%
7		**3g**; X = Ts **4g**; X = H — 80%
8		**3h**; X = Ts **4h**; X = H — 90%
9		
10		**3j**; X = Ts **4j**; X = H — 70%
11[b,c]		**3k**; X = Ts **4k**; X = H — 94%
12[d]		**3l**; X = Ts **4l**; X = H — 71%
13[c]		**3m**; X = Ts **4m**; X = H — 95%

[a] All reactions were performed on a 1 mmol scale. The yields refer to isolated amine **4**.
[b] Instead of DMF, acetonitrile was used as a solvent.
[c] 2.5 F/mol of electricity was passed.
[d] Electrolysis was carried out in the presence of 1.0 equiv of naphthalene.

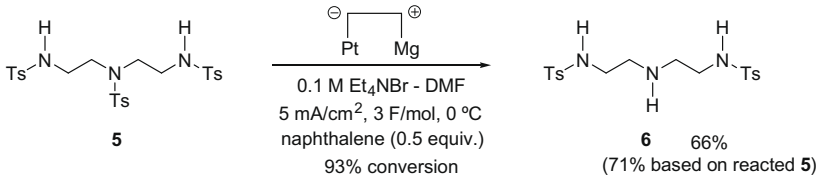


Scheme 1. Desulfonylation of arenesulfonamides.

respectively (Table 2, entries 5 and 6). *N*-Tosylaziridines **3g** and **3h** could also be deprotected efficiently without isomerization of the stereochemistry and ring opening to give *cis*- and *trans*-dialkylaziridines **4g**–**h** in 80% and 90% yields, respectively (Table 2, entries 7 and 8). Chemoselective detosylation was also achieved by using tosylamides **3i**–**l** having a functional group such as tetrahydropyranyl ether, pivalate, *N*-benzyl or *N*-Boc group to afford functionalized amines **4i**–**l** in good yields (Table 2, entries 9–12). Notably, selective mono-detosylation of *N*-dodecyl-di-tosylamide



Scheme 2. New protocol for the synthesis of *N*,*N*-dialkylamine.



Scheme 3. Selective detosylation of triamide **5**.

(**3m**) was found to proceed efficiently under similar conditions to give *N*-dodecyltosylamide (**4m**) in 95% yield (Table 2, entry 13). It has been shown that mono-detosylation of *N*-alkyl-di-tosylamides required harsh reaction conditions,[28] whereas mono-detosylation of *N*-aryl derivatives could take place under relatively mild conditions.[20b,29] The present method enables selective mono-detosylation of *N*-alkyl-di-tosylamides under neutral and quite mild conditions without a mercury electrode to afford *N*-alkyltosylamides in high yields. These accomplishments of detosylation should enable the establishment of a new general protocol for the synthesis of *N*,*N*-dialkylamines as shown in Scheme 2. Thus, alkylation of a commercial ditosylamide **A** gives *N*-alkyl-di-tosylamide, which can be selectively mono-detosylated by the present method (entry 13 in Table 2) to give *N*-alkyltosylamide **B**. Successive alkylation of the resulting **B** gives *N*,*N*-dialkyltosylamide, which can also be detosylated by the present method (entry 6 in Table 2) to produce *N*,*N*-dialkylamine in high yield.

Finally, selective detosylation of *N*,*N*-disubstituted tosylamide in the presence of *N*-mono-substituted tosylamide was attempted, and the results are shown in Scheme 3. Electrolysis of triamide **5** in the presence of 0.5 equiv of naphthalene with 3.0 F/mol of electricity[30] resulted in selective detosylation of disubstituted tosylamide to give a high yield of amino ditosylamide **6**, which is a useful component for the synthesis of polyaza macrocycles and was prepared by four steps.[31] By using the present method, **6** could be prepared from commercially available **5** in one step. Moreover, it should be noted that this selective detosylation cannot be achieved by reported conventional methods.

In conclusion, Hg cathode-free electrochemical detosylation has been accomplished under neutral and mild conditions. Efficient detosylation of *N*,*N*-disubstituted tosylamides was successfully carried out by a constant current electrolysis using an undivided cell equipped with a Pt cathode and an Mg anode in the presence of naphthalene as an electron-transfer mediator. The present method also enabled selective detosylation of *N*,*N*-disubstituted tosylamide in the presence of *N*-mono-substituted tosylamides. Consequently, it should become a powerful tool for synthesis of various nitrogen-containing organic compounds.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.11.056.

References and notes

1. Wuts, P. G. M.; Greene, T. W. *Greene's Protective Groups in Organic Synthesis*, 4th ed.; John Wiely & Sons, Inc.: Hoboken, New Jersey, 2007. pp 855.
2. (a) Roemmele, R. C.; Rapoport, H. *J. Org. Chem.* **1988**, *53*, 2367; (b) Alonso, D. A.; Andersson, P. G. *J. Org. Chem.* **1998**, *63*, 9455; (c) Jordis, U.; Sauter, F.; Siddiqi, S. M.; Küenburg, B.; Bhattacharya, K. *Synthesis* **1990**, 925; (d) Compagnone, R. S.; Rapoport, H. *J. Org. Chem.* **1986**, *51*, 1713; (e) Kudav, D. P.; Samant, S. P.; Hosangadi, B. D. *Synth. Commun.* **1987**, *17*, 1185; (f) Portoghese, P. S.; Mikhail, A. A. *J. Org. Chem.* **1966**, *31*, 1059.
3. (a) Heathcock, C. H.; Smith, K. M.; Blumenkopf, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 5022; (b) Schultz, A. G.; McCloskey, P. J.; Court, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 6493; (c) Yamazaki, N.; Kibayashi, C. *J. Am. Chem. Soc.* **1989**, *111*, 1396; (d) Dalko, P. I.; Burn, V.; Langlois, Y. *Tetrahedron Lett.* **1998**, *39*, 8979.
4. (a) Birkinshaw, T. N.; Holmes, A. B. *Tetrahedron Lett.* **1987**, *28*, 813; (b) Chavez, F.; Sherry, A. D. *J. Org. Chem.* **1989**, *54*, 2990; (c) Forshee, P. B.; Sibert, J. W. *Synthesis* **2006**, 756.
5. (a) McIntosh, J. M.; Matassa, L. C. *J. Org. Chem.* **1988**, *53*, 4452; (b) Heathcock, C. H.; Blumenkopf, T. A.; Smith, K. M. *J. Org. Chem.* **1989**, *54*, 1548; (c) Bergmeier, S. C.; Seth, P. P. *Tetrahedron Lett.* **1999**, *40*, 6181; (d) Nagashima, H.; Ozaki, N.; Washiyama, M.; Itoh, K. *Tetrahedron Lett.* **1985**, *26*, 657; (e) Henry, J. R.; Marcin, L. R.; McIntosh, M. C.; Scola, P. M.; Harris, G. D., Jr.; Weinreb, S. M. *Tetrahedron Lett.* **1989**, *30*, 5709; (f) Katoh, T.; Itoh, E.; Yoshino, T.; Terashima, S. *Tetrahedron Lett.* **1996**, *37*, 3471; (g) Zhou, W.-S.; Xie, W.-G.; Liu, Z.-H.; Pan, X. F. *Tetrahedron Lett.* **1995**, *36*, 1291; (h) Magnus, P.; Giles, M.; Bonnert, R.; Kim, C. S.; McQuire, L.; Merritt, A.; Vicker, N. *J. Am. Chem. Soc.* **1992**, *114*, 4403; (i) Alonso, E.; Ramón, D. J.; Yus, M. *Tetrahedron* **1997**, *53*, 14355; (j) Chowdhury, M. A.; Reissig, H.-U. *Synlett* **2006**, 2383.
6. (a) Fukuyama, T.; Jow, C.-K.; Cheung, M. *Tetrahedron Lett.* **1995**, *36*, 6373; (b) Kan, T.; Fukuyama, T. *Chem. Commun.* **2004**, 353.
7. Fukuyama, T.; Cheung, M.; Jow, C.-K.; Hidai, Y.; Kan, T. *Tetrahedron Lett.* **1997**, *38*, 5831.
8. (a) Wakimasu, M.; Kitada, C.; Fujino, M. *Chem. Pharm. Bull.* **1981**, *29*, 2592; (b) Milburn, R. R.; Snieckus, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 892.
9. Ramage, R.; Green, J. *Tetrahedron Lett.* **1987**, *28*, 2287.
10. (a) Goulaouic-Dubois, C.; Guggisberg, A.; Hesse, M. *J. Org. Chem.* **1995**, *60*, 5969; (b) Goulaouic-Dubois, C.; Guggisberg, A.; Hesse, M. *Tetrahedron* **1995**, *51*, 12573; (c) Vedjs, E.; Lin, S.; Klapars, A.; Wang, J. *J. Am. Chem. Soc.* **1996**, *118*, 9796; (d) Park, J. K.; Guggisberg, A.; Hesse, M. *Tetrahedron* **1998**, *54*, 8035; (e) Wuts, P. G. M.; Gu, R. L.; Northuis, J. M.; Thomas, C. L. *Tetrahedron Lett.* **1998**, *39*, 9155; (f) Wuts, P. G. M.; Gu, R. L.; Northuis, J. M. *Lett. Org. Chem.* **2004**, *1*, 372.
11. (a) Parsons, A. F.; Pettifer, R. M. *Tetrahedron Lett.* **1996**, *37*, 1667; (b) Knowles, H. S.; Parsons, A. F.; Pettifer, R. M.; Rickling, S. *Tetrahedron* **2000**, *56*, 979.
12. (a) Vedejs, E.; Lin, S. *J. Org. Chem.* **1994**, *59*, 1602; (b) Hill, D. C.; Flugge, L. A.; Petillo, P. A. *J. Org. Chem.* **1997**, *62*, 4864; (c) Knowles, H.; Parsons, A. F.; Pettifer, R. M. *Synlett* **1997**, 271; (d) Moussa, Z.; Romo, D. *Synlett* **2006**, 3294; (e) Ankner, T.; Hilmersson, G. *Org. Lett.* **2009**, *11*, 503.
13. Sabitha, G.; Reddy, B. V. S.; Abraham, S.; Yadav, J. S. *Tetrahedron Lett.* **1999**, *40*, 1569.
14. Vellemäe, E.; Lebedev, O.; Mäeorg, U. *Tetrahedron Lett.* **2008**, *49*, 1373.
15. Nayak, S. K. *Synthesis* **2000**, 1575.
16. Nyasse, B.; Grehn, L.; Ragnarsson, U. *Chem. Commun.* **1997**, 1017.
17. Uchiyama, M.; Matsumoto, Y.; Nakamura, S.; Ohwada, T.; Kobayashi, N.; Yamashita, N.; Matsumiya, A.; Sakammoto, T. *J. Am. Chem. Soc.* **2004**, *126*, 8755.
18. Millburn, R. R.; Snieckus, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 892.
19. (a) Liu, Q.; Liu, Z.; Zhou, Y.-L.; Zhang, W.; Yang, L.; Liu, Z.-L.; Yu, W. *Synlett* **2005**, 2510; (b) Abad, A.; Mellier, D.; Pète, J. P.; Portella, C. *Tetrahedron Lett.* **1971**, *12*, 4555; (c) Yuan, W.; Fearson, K.; Gelb, M. H. *J. Org. Chem.* **1989**, *54*, 906; (d) Hamada, T.; Nishida, A.; Yonemitsu, O. *J. Am. Chem. Soc.* **1986**, *108*, 140; (e) Urjasz, W.; Celewicz, L. *J. Phys. Org. Chem.* **1998**, *11*, 618; (f) Ayadim, M.; Jiwan, J. L. H.; Soumillion, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 10436; (g) Art, J. F.; Kestemont, J. P.; Soumillion, J. P. *Tetrahedron Lett.* **1991**, *32*, 1425.
20. (a) Yasuhara, A.; Sakamoto, T. *Tetrahedron Lett.* **1998**, *39*, 595; (b) Yasuhara, A.; Kameda, M.; Sakamoto, T. *Chem. Pharm. Bull.* **1999**, *47*, 809.
21. Liu, Y.; Shen, L.; Prashad, M.; Tibbatts, J.; Repič, O.; Blacklock, T. J. *Org. Process Res. Dev.* **2008**, *12*, 778.

22. Nandi, P.; Redko, M. Y.; Peterson, K.; Dye, J. L.; Lefenfeld, M.; Vogt, P. F.; Jackson, J. E. *Org. Lett.* **2008**, *10*, 5441.
23. Wellner, E.; Sandin, H.; Pääkkönen, L. *Synthesis* **2003**, 223.
24. (a) Mairanovsky, V. G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 281; (b) Lund, H. In *Organic Electrochemistry, Fourth Edition, Revised and Expanded*; Lund, H., Hammerich, O., Eds.; Clearvage and Deprotection; Marcel Dekker: New York, 2001; p 969. and references cited therein.
25. (a) Horner, L.; Neumann, H. *Chem. Ber.* **1965**, *98*, 1715; (b) Horner, L.; Neumann, H. *Chem. Ber.* **1965**, *98*, 3462; (c) Okumura, K.; Iwasaki, T.; Matsuoka, M.; Matsumoto, K. *Chem. Ind.* **1971**, 929; (d) Iwasaki, T.; Matsumoto, K.; Matsuoka, M.; Miyoshi, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 852; (e) Kossai, R.; Jeminet, G.; Simonet, J. *Electrochim. Acta* **1977**, *22*, 1395; (f) Kossai, R.; Simonet, J.; Jeminet, G. *Tetrahedron Lett.* **1979**, *20*, 1059; (g) Oda, K.; Ohnuma, T.; Ban, Y. *J. Org. Chem.* **1984**, *49*, 953; (h) Moriwaki, T.; Saito, S.; Tamai, H.; Fujita, S.; Inaba, M. *Heterocycles* **1985**, *23*, 2525; (i) Lebouc, A.; Martigny, P.; Carlier, R.; Simonet, J. *Tetrahedron* **1985**, *41*, 1251; (j) Kossai, R. *Electrochim. Acta* **1986**, *31*, 1643; (k) Kossai, R.; Emir, B.; Simonet, J.; Mousset, G. *J. Electroanal. Chem.* **1989**, *270*, 253; (l) Grehn, L.; Maia, L. S.; Monteiro, L. S.; Montenegro, M. I.; Ragnarsson, U. *J. Chem. Res. (S)* **1991**, 144; (m) Scialdone, O.; Belfiore, C.; Filardo, G.; Galia, A.; Sabatino, M. A.; Silvestri, G. *Electrochim. Acta* **2005**, *51*, 598; (n) Coeffard, V.; Thobie-Gautier, C.; Beaudet, I.; Le Grognec, E.; Quintard, J.-P. *Eur. J. Org. Chem.* **2008**, 383.
26. Senboku, H.; Takahashi, M.; Fukuhara, T.; Hara, S. *Chem. Lett.* **2007**, *36*, 228. and references cited therein.
27. In the reaction of **3e** in DMF, *N*-formyl-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinoline was obtained in 72% yield. *N*-Dodecyl-*N*-methylformamide was also obtained in 52% yield along with **4f** in 44% yield when the reaction of **3f** was carried out in DMF.
28. Hutchins, R. O.; Cistone, F.; Goldsmith, B.; Heuman, P. *J. Org. Chem.* **1975**, *40*, 2018.
29. for example: Klein, M.; König, B. *Tetrahedron* **2004**, *60*, 1087.
30. An excess electricity would be used for the reduction of N–H bond of mono-substituted tosylamide moiety in **5** resulting in generation of hydrogen and amide enolates.
31. (a) Martin, A. E.; Ford, T. M.; Bulkowski, J. E. *J. Org. Chem.* **1982**, *47*, 412; (b) Zhang, Z.; Mikkola, S.; Lönnberg, H. *Org. Biomol. Chem.* **2003**, 854.