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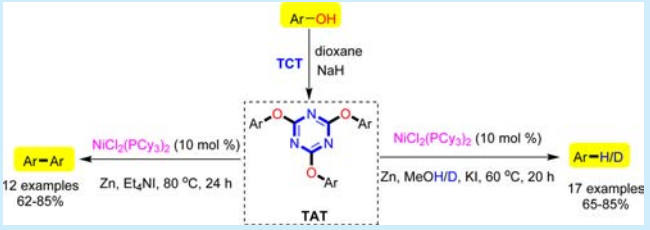
Nickel-Catalyzed One-Pot Deoxygenation and Reductive Homocoupling of Phenols via C−O Activation Using TCT Reagent

Nasser Iranpoor* and Farhad Panahi

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

Supporting Information

ABSTRACT: A new method for C−O bond activation of phenolic compounds has been achieved using 2,4,6-trichloro-1,3,5-triazine to utilize in one-pot Ni-catalyzed deoxygenation and reductive homocoupling reactions. With this simple method, phenolic compounds were converted to their corresponding arenes or biaryl compounds under mild conditions. The introduced methodology has a broad scope and demonstrates good functional group compatibility.



Carbon−oxygen bond activation is one of the most important strategies in organic chemistry applied in organic transformations.[1] Phenolic compounds (widely found in nature) can be converted to aryl C−O electrophiles using C−O bond-activating agents. This strategy makes the C−O electrophiles more suitable alternatives than aryl halides in carbon−carbon and carbon−heteroatom bond formation reactions due to their higher diversity, abundance, and availability.[2] Along this line, a range of aryl C−O electrophiles such as ethers,[3,4] esters,[4] pivalates,[5,6] acetates,[6,7] phosphonates,[7] triflates,[7] carbamates,[4,8−10] carbonates,[4,10,11] phosphoramides,[12] phosphates,[13] tosylates,[7,14] mesylates,[4,14−16] sulfamates,[4,9,10,16−18] and heteroaryl ethers[19] have been introduced for application in metal-catalyzed cross-coupling reactions as coupling partners. To use phenolic compounds in coupling reactions, there are two strategies. In the most widely used method (stepwise), phenols are first converted to the corresponding aryl C−O electrophile and then used for the next reaction.[3−19] One-pot activation of phenols is another approach for the generation of an active coupling partner in metal-catalyzed cross-coupling reactions.[20−22] Bromo-trispyrrolidino phosphoniumhexafluorophosphate is the most widely used reagent for one-pot activation of phenolic compounds.[20] In some cases, phenolic salts were used in the one-pot activation process.[21] Recently, Chen et al. reported an efficient nickel-catalyzed one-pot Suzuki−Miyaura cross-coupling of phenols and arylboronic acids mediated by *N*,*N*-ditosylaniline.[22] The one-pot activation strategy possesses important advantages in comparison to a stepwise method. First, the preactivation step limits the efficiency of a two-step protocol in view of overall yields and step economy. On the other hand, conversion of some of the phenolic compounds to aryl C−O electrophiles is difficult and has restrictions.[1k] For these reasons, the one-pot phenol activation strategy has received more attention recently.[20−22]

In our previous study, we reported that 2,4,6-trichloro-1,3,5-triazine (TCT) is an efficient reagent for Ni-catalyzed amination of phenols.[23] There are some important features in the structure of TCT which encouraged us in the development of its application in one-pot conversion of phenolic compounds to other products. First, 3 equiv of phenols immediately reacts with 1 equiv of TCT to generate the corresponding 2,4,6-triaryloxy-1,3,5-triazine (TAT),[24] providing an atom-economical approach. In fact, TAT was the introduced aryl C−O electrophile in our strategy. To the best of our knowledge, there is no report in the literature on the use of TAT as an aryl C−O electrophile in metal-catalyzed coupling reactions. These materials possess a range of physical and chemical properties.[25] Second, the C−O bond in TAT (1.42 Å) is longer than that in phenol (1.36 Å), making its strength weaker and demonstrating that TCT acts as a C−O bond activator (Figure 1).[26] Finally, the *ortho*-nitrogen atom in the structure of TAT can coordinate with metals to facilitate the oxidative addition step.[27]

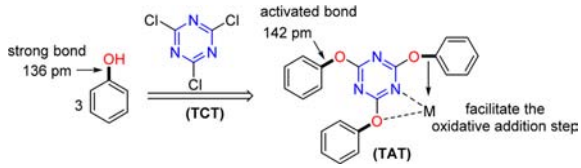


Figure 1. Phenol activation using TCT.

As part of our program aimed at activating phenolic compounds for participation in metal-catalyzed coupling reactions,[23] we demonstrate a user-friendly and operationally simple Ni-catalyzed deoxygenation and homocoupling of phenols using TCT (Scheme 1). To the best of our knowledge, this strategy represents the first one-pot Ni-catalyzed deoxygenation[28,29] and homocoupling[30] of phenols.

Deoxygenation of phenolic compounds into the arene counterparts plays a key role in organic synthesis. In most cases, the function of the hydroxyl group is to increase the reactivity of the substrate toward functionalization as well as

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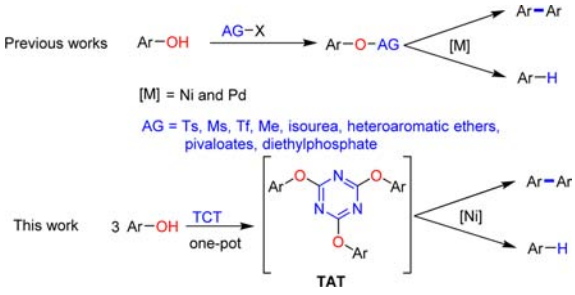
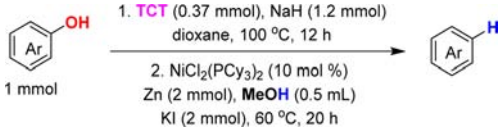
Scheme 1. Stepwise and One-Pot Deoxygenation/ Homocoupling of Phenols



acting as a directing group. Afterward, efficient catalytic deoxygenation methods are needed to remove the hydroxyl group to obtain the target product.[31] Note that the deoxygenation method should be applicable to a range of substrates with various functional groups. The frequently used protocol for deoxygenation of phenols is their conversion into aryl C−O electrophiles followed by metal-catalyzed reductive cleavage. However, the selective, simple, and efficient deoxygenation of phenolic compounds is still a challenge.[28]

We first set out to obtain proper conditions for one-pot Ni-catalyzed deoxygenation of phenolic compounds using 2-naphthol as a simple model substrate (Table 1S, Supporting Information). Conditions for the TAT preparation step were selected based on our previous work.[23] Next, different reduction systems were checked to find the most suitable conditions. According to the work of Sasaki et al., the MeOH/Zn/KI system[29] was selected as a reducing agent at the beginning, and in the presence of $NiCl_2(PCy_3)_2$ catalyst, 85% of arene was obtained. Also, other hydrogen donor systems such as Et_3SiH [$NiCl_2(PCy_3)_2$], Ph_3SiH [$NiCl_2(PCy_3)_2$],[28e] Mg/MeOH/NH_4OAc (Pd/C),[28c] *N*-(*n*-Pr)$_3$/HCOOH [Pd(OAc)$_2$(PPh$_3$)$_2$],[28h] K_2CO_3/*i*-PrOH [$PdCl_2(dppf)_2$],[28d] and $NaBH_4$ [$NiCl_2(PCy_3)_2$][28a] were investigated, but no superiority was observed. Then, diverse Ni catalysts was tested, among which $NiCl_2(PCy_3)_2$ was recognized as the best one. The optimum amount of catalyst was found to be 10 mol %. As a result, the optimized conditions for the efficient deoxygenation of phenols using TCT is shown in Scheme 2.

Scheme 2. Optimized Reaction Conditions for Deoxygenation of Phenolic Compounds Using TCT



Under the optimized conditions, various phenolic compounds were successfully deoxygenated in good to excellent yields (Figure 2).

As shown in Figure 2, 2-naphthol gave naphthalene in 85% isolated yield. The lower yield obtained for 1-naphthol may be due to the presence of some steric hindrance.[28g,h] The effect of steric hindrance on the progress of the reaction is more observable in the synthesis of **2c**. Next, we studied the electronic effects of substituents on the aryl ring. Interestingly, phenolic substrates with electron-donating and -deficient substituents gave corresponding products in moderate to good yields. This one-pot Ni-catalyzed deoxygenation of phenols shows an

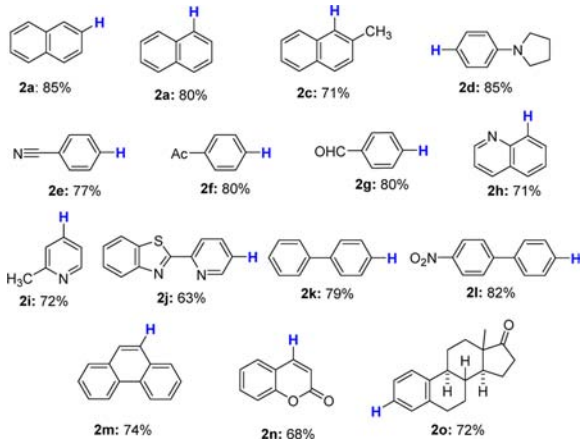
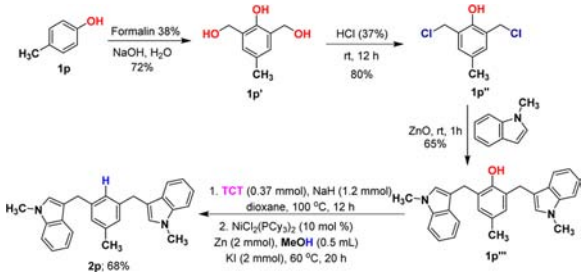


Figure 2. Ni-catalyzed deoxygenation of phenols via C−O activation using TCT under optimized conditions. All yields are isolated.

excellent chemoselectivity profile. Methoxy, amino, nitro, cyano, and keto, and aldehyde substituents tolerated the reaction conditions well. For substrates containing nitro and aldehyde functionalities, no reduced products were observed. As shown for **2h−j**, the method is also applicable for heterocyclic substrates.[32] The methodology could be extended to biphenyls and phenanthrene phenolic substrates,[33] and their corresponding products (**2k−m**) were obtained in moderate yields. Interestingly, coumarin (**2n**) was obtained in 68% yield from 4-hydroxycoumarin. The structural diversity of this reaction was further increased using estrone, leading to the formation of 3-deoxyestrone (**2o**) in 72% yield.

The potential utility of this method in organic synthesis was demonstrated in Scheme 3. As shown in Scheme 3, **2p** could be

Scheme 3. Hydroxy Group as a Removal Handle for Regioselective Arene Functionalization and Synthesis of 2p Using Our Method



selectively prepared in high yield from *p*-cresol (**1p**) in a four-step process. First, **1p′** was synthesized using the ability of the hydroxyl group to direct functionalization in the *ortho* position of the aromatic ring.[34] Then, **1p′** was converted to its corresponding benzyl chloride substrate (**1p″**).[35] Nucleophilic addition of 1-methyl-1*H*-indole to **1p″** resulted in the production of compound **1p‴** in 65% isolated yield.[36] In the final step, **1p‴** was deoxygenated using our procedure, and **2p** was obtained as a novel bisindole derivative.[37]

Subsequently, we carried out a deuterium-labeling experiment to assemble evidence regarding the reaction pathway (Scheme 4). The successful synthesis of **2a′** indicates that our procedure can be used to introduce deuterium in the structure of aromatic backbones from readily available precursors.[38]

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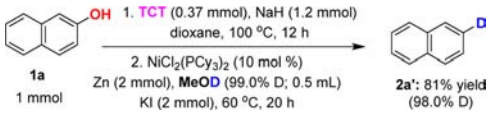
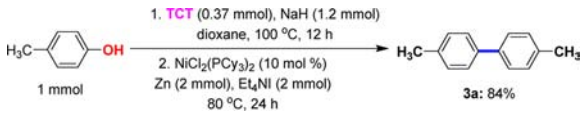
Scheme 4. Deuterium Labeling of 2-Naphthol Using Ni-Catalyzed Reductive Deoxygenation via C−O Bond Activation Using TCT



Here, we report another important application of TCT as an efficient reagent for the one-pot homocoupling reaction of phenolic compounds. The C−C bond formation using an aryl C−O electrophile is an important strategy in terms of accessibility of phenolic compounds and environmental impact.[39] One of the significant applications of this strategy is the synthesis of biaryls. Biaryl compounds have an imperative structural motif, which exists extensively in pharmaceuticals, advanced materials, and natural compounds.[40] Transition-metal-catalyzed homocoupling of aryl C−O electrophiles such as aryl triflates, aryl tosylates, and aryl mesylates, has been known as a potent and essential method for the synthesis of symmetrical biaryls.[30] However, in the reported methods for the homocoupling of aryl C−O electrophiles, phenolic compounds were first converted to their corresponding electrophiles and then used in the metal-catalyzed reactions. Clearly, a one-pot transformation from phenol would be the best option to resolve complication as it avoids the additional steps of group transfer and the production of organic waste.

The efficiency of this method for homocoupling of *p*-cresol as a simple model substrate was first evaluated. According to the data obtained from the deoxygenation reaction and pioneering work of Percec et al.,[30c] the following conditions were first tested and the homocoupling product was obtained in 84% isolated yield (Scheme 5).

Scheme 5. One-Pot Homocoupling Reaction of 4-Methylphenol Using TCT as the Model Reaction



Further changes to the catalyst, solvent, and reaction temperature did not result in any noticeable improvement in the performance of the reaction, thus the above condition was selected as the optimum. To determine the scope of the reaction for the preparation of symmetrical biaryls, a number of commercially available phenols were coupled under our optimized reaction conditions, and the results are shown in Figure 3.

As shown in Figure 3, phenols with electron-donating groups furnished the coupling product in good yield (**3a** and **3c**). Functional groups such as $-NO_2$, $-CN$, and $-CO_2Me$ were compatible under these reaction conditions (**3d−f**). Sterically hindered substrates also coupled smoothly to give the desired product in moderate yields (**3g** and **3h**). Heterocyclic substrates also provided moderate to good yields of the corresponding coupled products (**3i−l**).

Some experiments were also performed to achieve a deeper insight into the reaction mechanism. In an experiment, under optimized conditions, 2,4,6-tris(*p*-tolyloxy)-1,3,5-triazine (**4**)[24] was converted to **3a** and **2q**, demonstrating that the generated

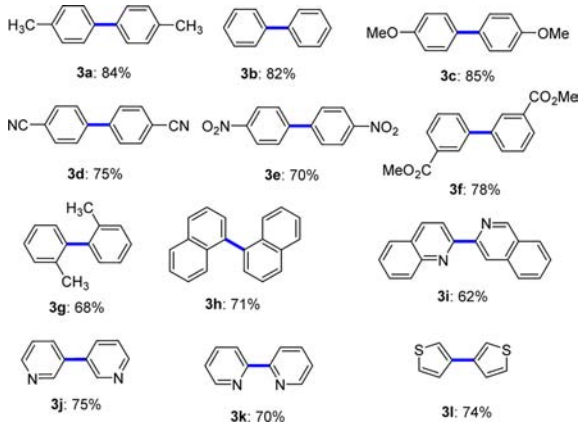
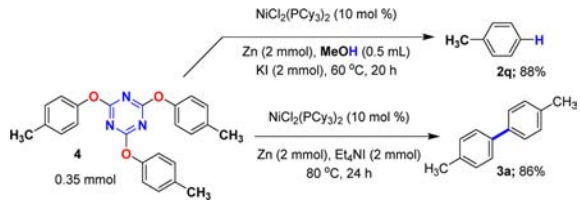


Figure 3. Products of the one-pot homocoupling reaction of phenolic compounds using TCT. All yields are isolated.

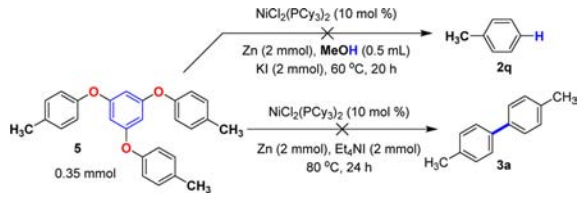
TAT during the reaction process can act as an aryl C−O electrophile (Scheme 6).

Scheme 6. Conversion of TAT to Deoxygenated and/or Homocoupling Product



When 1,3,5-tris(*p*-tolyloxy)benzene (**5**)[41] was used instead of **4**, no product was observed. This experiment clarifies that the *ortho*-nitrogen atom in the structure of TAT plays an important role in the activation of the C−O bond (Scheme 7).

Scheme 7. Effect of Nitrogen on TAT in C−O Activation



In conclusion, TCT was found to be an efficient reagent for C−O activation of phenolic compounds to convert them into the corresponding aryl and biaryl compounds. These methods are characterized by their simplicity, wide preparative scope, and the availability of the substrates employed. Remarkably, this study does not require the use of toxic reagents and preactivation of phenolic compounds, thus representing an additional benefit when compared to current methods.

■ ASSOCIATED CONTENT

Supporting Information

Table of optimization study, experimental procedures, and copies of ^1H and ^{13}C NMR for all synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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AUTHOR INFORMATION

Corresponding Author

*E-mail: iranpoor@susc.ac.ir.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Wenkert, E.; Michelotti, E. L.; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2246. (b) Hirano, M.; Kurata, N.; Marumo, T.; Komiya, S. *Organometallics* **1998**, *17*, 501. (c) Li, Z.; Zhang, S.-L.; Fu, Y.; Guo, Q.-X.; Liu, L. *J. Am. Chem. Soc.* **2009**, *131*, 8815. (d) Yan, W.; Wang, Q.; Chen, Y.; Petersen, J. L.; Shi, X. *Org. Lett.* **2010**, *12*, 3308. (e) Yu, D.-G.; Wang, X.; Zhu, R.-Y.; Luo, S.; Zhang, X.-B.; Wang, B.-Q.; Wang, L.; Shi, Z.-J. *J. Am. Chem. Soc.* **2012**, *134*, 14638. (f) Kiernicki, J. J.; Newell, B. S.; Matson, E. M.; Anderson, N. H.; Fanwick, P. E.; Shores, M. P.; Bart, S. C. *Inorg. Chem.* **2014**, *53*, 3730. (g) Fan, X.; Cui, X.-M.; Guan, Y.-H.; Fu, L.-A.; Lv, H.; Guo, K.; Zhu, H.-B. *Eur. J. Org. Chem.* **2014**, 498. (h) Lu, Y.; Li, X.; Wang, L.; Sun, H. *Inorg. Chem. Commun.* **2014**, *41*, 51. (i) Langer, N. N. P.; Bindrab, G. S.; Budzelaar, P. H. M. *Dalton Trans.* **2014**, *43*, 11286. (j) Miller, A. J. M.; Kaminsky, W.; Goldberg, K. I. *Organometallics* **2014**, *33*, 1245. (k) Tan, G.; Szilvási, T.; Inoue, S.; Blom, B.; Driess, M. *J. Am. Chem. Soc.* **2014**, *136*, 9732.

(2) (a) Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A.-M.; Garg, N. K.; Percec, V. *Chem. Rev.* **2011**, *111*, 1346. (b) Yamaguchi, J.; Muto, K.; Itami, K. *Eur. J. Org. Chem.* **2013**, 19. (c) Yu, D.-G.; Li, B.-J.; Shi, Z.-J. *Acc. Chem. Res.* **2010**, *43*, 1486. (d) Tobisu, M.; Chatani, N. *Top. Organomet. Chem.* **2013**, *44*, 35.

(3) Tobisu, M.; Shimasaki, T.; Chatani, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 4866.

(4) Leowanawat, P.; Zhang, N.; Percec, V. *J. Org. Chem.* **2012**, *77*, 1018.

(5) Quasdorf, K. W.; Tian, X.; Garg, N. K. *J. Am. Chem. Soc.* **2008**, *130*, 14422.

(6) Guan, B.-T.; Wang, Y.; Li, B.-J.; Yu, D.-G.; Shi, Z.-J. *J. Am. Chem. Soc.* **2008**, *130*, 14468.

(7) Firouzabadi, H.; Iranpoor, N.; Gholinejad, M.; Samadi, A. *J. Mol. Catal. A: Chem.* **2013**, *377*, 190.

(8) Quasdorf, K. W.; Antoft-Finch, A.; Liu, P.; Silberstein, A. L.; Komaromi, A.; Blackburn, T.; Ramgren, S. D.; Houk, K. N.; Snieckus, V.; Garg, N. K. *J. Am. Chem. Soc.* **2011**, *133*, 6352.

(9) Baghbanzadeh, M.; Pilger, C.; Kappe, C. O. *J. Org. Chem.* **2011**, *76*, 1507.

(10) Quasdorf, K. W.; Riener, M.; Petrova, K. V.; Garg, N. K. *J. Am. Chem. Soc.* **2009**, *131*, 17748.

(11) Kuwano, R.; Shimizu, R. *Chem. Lett.* **2011**, *40*, 913.

(12) Zhao, Y.-L.; Li, Y.; Li, Y.; Gao, L.-X.; Han, F.-S. *Chem.—Eur. J.* **2010**, *16*, 4991.

(13) (a) Chen, H.; Huang, Z.; Hu, X.; Tang, G.; Xu, P.; Zhao, Y.; Cheng, C.-H. *J. Org. Chem.* **2011**, *76*, 2338. (b) Shi, C.; Aldrich, C. C. *Org. Lett.* **2010**, *12*, 2286.

(14) Gao, H.; Li, Y.; Zhou, Y.-G.; Han, F.-S.; Lin, Y.-J. *Adv. Synth. Catal.* **2011**, *353*, 309.

(15) Percec, V.; Bae, J.-Y.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 1060.

(16) Zhang, N.; Hoffman, D. J.; Gutsche, N.; Gupta, J.; Percec, V. *J. Org. Chem.* **2012**, *77*, 5956.

(17) Chen, G.-J.; Han, F.-S. *Eur. J. Org. Chem.* **2012**, 3575.

(18) Xing, C.-H.; Lee, J.-R.; Tang, Z.-Y.; Zheng, J. R.; Hu, Q. S. *Adv. Synth. Catal.* **2011**, *353*, 2051.

(19) Li, X.-J.; Zhang, J.-L.; Geng, Y.; Jin, Z. *J. Org. Chem.* **2013**, *78*, 5078.

(20) (a) Kang, F.-A.; Sui, Z.; Murray, W. V. *J. Am. Chem. Soc.* **2008**, *130*, 11300. (b) Kang, F.-A.; Lanter, J. C.; Cai, C.; Sui, Z.; Murray, W. V. *Chem. Commun.* **2010**, *46*, 1347. (c) Mehta, V. P.; Modha, S. G.; Van der Eycken, E. V. *J. Org. Chem.* **2010**, *75*, 976. (d) Sharma, A.; Vachhani, D.; Van der Eycken, E. *Org. Lett.* **2012**, *14*, 1854. (e) Zhao, Y.-L.; Wub, G.-J.; Han, F.-S. *Chem. Commun.* **2012**, *48*, 5868. (f) Chen, G.-J.; Huang, J.; Gao, L.-X.; Han, F.-S. *Chem.—Eur. J.* **2011**, *17*, 4038. (g) Li, S.-M.; Huang, J.; Chen, G.-J.; Han, F.-S. *Chem. Commun.* **2011**, *47*, 12840.

(21) (a) Yu, D.-G.; Li, B.-J.; Zheng, S.-F.; Guan, B.-T.; Wang, B.-Q.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2010**, *49*, 4566. (b) Yu, D.-G.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2011**, *50*, 7097.

(22) Chen, L.; Lang, H.; Fang, L.; Zhu, M.; Liu, J.; Yu, J.; Wang, L. *Eur. J. Org. Chem.* **2014**, 4953.

(23) Iranpoor, N.; Panahi, F. *Adv. Synth. Catal.* **2014**, *356*, 3067.

(24) Dainyte, A.; Gudeika, D.; Buika, G.; Grazulevicius, J. V. *Mol. Cryst. Liq. Cryst.* **2014**, *590*, 73.

(25) (a) Ak, M.; Toppare, L. *Mater. Chem. Phys.* **2009**, *114*, 789. (b) Zhong, H.; Xu, E.; Zeng, D.; Du, J.; Sun, J.; Ren, S.; Jiang, B.; Fang, Q. *Org. Lett.* **2008**, *10*, 709. (c) Zhang, Y. D.; Jespersen, K. G.; Kempe, M.; Kornfield, J. A.; Barlow, S.; Kippelen, B.; Marder, S. R. *Langmuir* **2003**, *19*, 6534.

(26) (a) Thalladi, V. R.; Brasselet, S.; Weiss, H.-C.; Bläser, D.; Katz, A. K.; Carrell, H. L.; Boese, R.; Zyss, J.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 2563. (b) Suter, H. U.; Nonella, M. *J. Phys. Chem. A* **1998**, *102*, 10128.

(27) Ueno, S.; Mizushima, E.; Chatani, N.; Kakiuchi, F. *J. Am. Chem. Soc.* **2006**, *128*, 16516.

(28) (a) Kogan, V. *Tetrahedron Lett.* **2006**, *47*, 7515. (b) Herrmann, J. M.; König, B. *Eur. J. Org. Chem.* **2013**, 7017. (c) Sajiki, H.; Mori, A.; Mizusaki, T.; Ikawa, T.; Maegawa, T.; Hirota, K. *Org. Lett.* **2006**, *8*, 987. (d) Chow, W. K.; So, C. M.; Lau, C. P.; Kwong, F. Y. *Org. Chem. Front.* **2014**, *1*, 464. (e) Tobisu, M.; Yamakawa, K.; Shimasakia, T.; Chatani, N. *Chem. Commun.* **2011**, *47*, 2946. (f) Mori, A.; Mizusaki, T.; Ikawa, T.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Chem.—Eur. J.* **2007**, *13*, 1432. (g) Alvarez-Bercedo, P.; Martin, R. *J. Am. Chem. Soc.* **2010**, *132*, 17352. (h) Saa, J. M.; Dopico, M.; Martorell, G.; Garcia-Raso, A. *J. Org. Chem.* **1990**, *55*, 991. (i) Ganji, P.; Ibrahim, H. *J. Org. Chem.* **2012**, *77*, 511.

(29) Sasaki, K.; Kubo, T.; Sakai, M.; Kuroda, Y. *Chem. Lett.* **1997**, 617.

(30) Bergeron-Brlek, M.; Giguère, D.; Shiao, T. C.; Saucier, C.; Roy, R. *J. Org. Chem.* **2012**, *77*, 2971. (b) Jutand, A.; Mosleh, A. *J. Org. Chem.* **1997**, *62*, 261. (c) Percec, V.; Bae, J.-Y.; Zhao, M.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 176. (d) Bae, L. Y.; Percec, V. *J. Ind. Eng. Chem.* **1998**, *4*, 64.

(31) (a) Burns, N. Z.; Krylova, I. N.; Hannoush, R. N.; Baran, P. S. *J. Am. Chem. Soc.* **2009**, *131*, 9172. (b) Rohbogner, C. J.; Clososki, G. C.; Knochel, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 1503. (c) Cianci, J.; Baell, J. B.; Flynn, B. L.; Gable, R. W.; Mould, J. A.; Paul, D.; Harvey, J. A. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 2055. (d) Si, Y.-G.; Gardner, M. P.; Tarazi, F. I.; Baldessarini, R. J.; Neumeyer, J. L. *J. Med. Chem.* **2008**, *51*, 983. (e) Cianci, J.; Baell, J. B.; Flynn, B. L.; Gable, R. W.; Mould, J. A.; Paul, D.; Harvey, J. A. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 2055.

(32) Chen, X.; Zhou, L.; Li, Y.; Xie, T.; Zhou, S. *J. Org. Chem.* **2014**, *79*, 230.

(33) Anton-Torrecillas, C.; Gonzalez-Gomez, J. C. *Org. Biomol. Chem.* **2014**, *12*, 7018.

(34) Van Der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531.

(35) Sorrell, T. N.; Jameson, D. L.; O'Connor, C. J. *Inorg. Chem.* **1984**, *23*, 190.

(36) Westermaier, M.; Mayr, H. *Org. Lett.* **2006**, *8*, 4791.

(37) Lounasmaa, M.; Tolvanen, A. *Nat. Prod. Rep.* **2000**, *17*, 175.

(38) (a) Amatore, C.; Jutand, A. *Organometallics* **1988**, *7*, 2203−2214. (b) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627.

(39) (a) Li, Z.; Zhang, S.-L.; Fu, Y.; Guo, Q.-X.; Liu, L. *J. Am. Chem. Soc.* **2009**, *131*, 8815. (b) Soa, C. M.; Kwong, F. Y. *Chem. Soc. Rev.* **2011**, *40*, 4963.

(40) Bringmann, G.; Gulder, T.; Gulder, T. A. M.; Breuning, M. *Chem. Rev.* **2011**, *111*, 563.

(41) Jeon, I. Y.; Tan, L.-S.; Baek, J.-B. *Polym. Prepr.* **2008**, *49*, 89.

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