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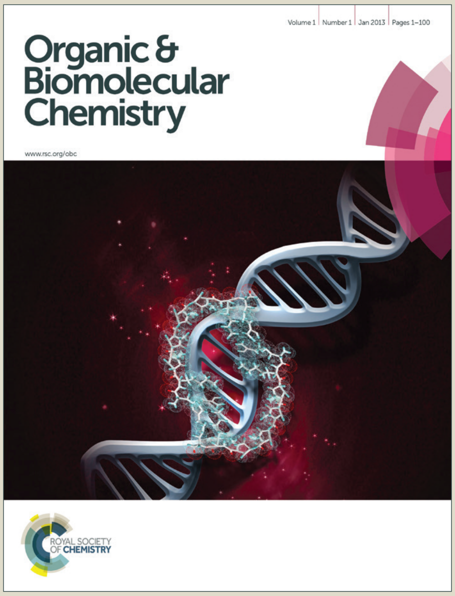

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ARTICLE TYPE

Efficient Silver-catalyzed Direct Sulfenylation and Selenylation of Rich Arenes

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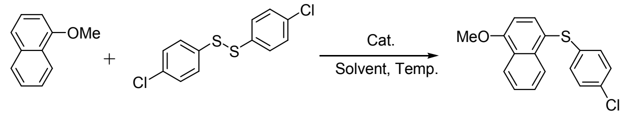
An efficient protocol for silver/copper-cocatalyzed direct sulfenylation and selenylation of arenes with aryl disulfides and diselenides has been developed. This strategy exhibits excellent functional group tolerance and high regioselectivity. Mono sulfenylation and selenylation products can be exclusively achieved. This reaction provides a simple and practical route to the preparation of aryl sulfides and selenides.

Organochalcogenides are very important molecules frequently found in the biological and pharmaceutical field.[1] Apart from the conventional methods of coupling aryllithiums/aryl Grignard reagents with chalcogenide precursors towards formation of carbon-chalcogen (S, Se) bond,[2] one of the more powerful approach is based on transition-metal-catalyzed coupling of aryl halides,[3-11] triflates[4d,12] or Boronic acids[13] with a suitable chalcogenide precursors. Complexes and salts of Pd[4,12] Ni,[5] Cu,[6,13] Fe,[7] Co,[8] Rh,[9] In,[10] and Ru[11] have been introduced as efficient catalyst for this type of reaction. However prefunctionlization of the starting material can be considered as a drawback of this approach in comparison to an another approach i.e. through direct C-H bond activation process. While in the area of C-H bond functionalization, much attention has been paid to transition metal catalyzed C-C, C-O, and C-N bond-forming reactions,[14] the formation of intermolecular C-S/ C-Se bond through transition-metal catalyzed direct C-H activation is relatively rare.[15] Metal-free such C-S bond formation is also reported but to a very small extent.[16]

In general, the metal-catalyzed processes involve dominantly use of thiol or disulfides as coupling partner. However, thiols are prone to undergo oxidative S-S coupling reactions, resulting in the undesired formation of disulfides. So use of dichalcogenides is more useful. Since pioneering Cu-mediated direct intermolecular thioetherification of the arene C-H bond, reported by Yu and co-workers,[15a] a few numbers of chelation-assisted C-S bond formation has been reported.[15b-f] Though these methods are highly regioselective but success depends on requiring a heteroatom in the molecule that acts as directing group. The direct C-S/Se bond formation of non acidic C-H bonds of arenes is very challenging in comparision to acidic heterocycles.[15g, h, j, n, o]Cheng et al.[15k] and Beller[15m] reported a nonchelation-assisted $C(sp^2)$-H functionalization of electron-erich arenes using Cu and Pd as catalyst respectively. With these methods, the yields of the products were found to be moderate and corresponding selenide analogues are less available. Recently Lee and his co-workers[15p] reported the Cu-catalyzed highly regioselective synthesis of aryl chalcogenides using arenes as coupling partner. However it proceeds through tandem C-H borylation and copper-catalyzed C-S coupling reaction. In continuation to the metal catalyzed C-S/Se bond formation of arens, here in this paper we have introduced silver in combination with copper as cocatalyst that can efficiently carried out the formation of C-S/Se bond in presence of various dichalocogenides.

Initially we have carried out sulfenylation of 1-methoxynapthalene using diarydsulfide (**2a**) with $AgSbF_6$ as a Lewis acid catalyst at room temperature (Table 1, entry 1). The reaction was carried out in 1,2-dichloroethane (DCE) as solvent, but trace amount of product was detected by GC-Mass. To our delight, increasing the temperature to 100°C (Table 1, entry 2), the sulfenylation was found to occur with 47% yield (product **3a**). The NMR spectral data revealed the sulfenylation process at *para* position of the naphthalene ring. Then we have planned to change the Ag source under this improved reaction condition to get better yield (Table 1, entries 3-5). But in all cases, the reaction did not occur. In an attempt using $Cu(OAc)_2 \cdot H_2O$ as an additive[15k] (Table 1, entry 6) at 100° C , the product **3a** was isolated with excellent yield (85%) within 12h of reaction time. However $Cu(OAc)_2 \cdot H_2O$ itself can not provide the sulfide product **3a**. (Table 1, entry 7). So use of this additive is essential for the Ag catalyzed process. $Cu(OAc)_2 \cdot H_2O$ is an oxidant and used in catalytic amount in presence of air. Then we examined the reaction using $Cu(OAc)_2 \cdot H_2O$ at other temperatures (Table 1, entries 11-12). But low yield in comparision to entry 6 was recorded. Screening of different solvents had shown that toluene (Table 1, entry 8) can provide 68% yield while in DMF (Table 1, entry 9) and DMSO (Table 1, entry 10), the desired product could not be obtained. Though decreased amount of diarydisulfide (**2a**) results comparatively lower yield during the process (Table 1, entries 13), however with higher loading of the catalyst (Table 1, entry 14), the system enables the use of two RS in $(RS)_2$. Hence the catalyst $AgSbF_6$ in combination with $Cu(OAc)_2 \cdot H_2O$ at 100°C using DCE as solvent was found to be the best reaction condition (Table 1, entry 6).

Table 1: Optimization of the reaction conditions[a]



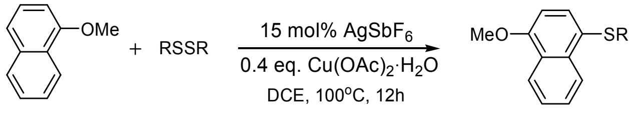
1a **2a** **3a**

Entry	Catalyst	Solvent	T(°C)	Yield (%)[b]
1	$AgSbF_6$	DCE	rt	Trace
2	$AgSbF_6$	DCE	100	47
3	Ag_2CO_3	DCE	100	-
4	AgOAc	DCE	100	-
5	$AgNO_3$	DCE	100	-
6[c]	**$AgSbF_6$**	**DCE**	**100**	**85**
7[c]	$Cu(OAc)_2\cdot H_2O$	DCE	100	-
8[c]	$AgSbF_6$	PhMe	100	68
9 [c]	$AgSbF_6$	DMF	100	-
10[c]	$AgSbF_6$	DMSO	100	-
11[c]	$AgSbF_6$	DCE	80	57
12[c]	$AgSbF_6$	DCE	120	72
13[c,d]	$AgSbF_6$	DCE	100	78
14[c,d,e]	$AgSbF_6$	DCE	100	87

[a]Unless otherwise noted, the reaction conditions are: **1a** (0.3 mmol), **2a** (0.3 mmol), catalyst (0.15 eq.), solvent (2 mL), 12h. [b]Isolated yield. [c] $Cu(OAc)_2\cdot H_2O$ (0.4 eq.), 12h. [d]**2a** (0.2 mmol), [e] $AgSbF_6$ (0.3 eq.).

Having identified the optimal reaction condition, this approach was then applied to the coupling of 1-methoxynapthalene to a variety of disulfides, the results of which are shown in Table 2. The electronic effects of the substituents on the aromatic ring of disulfides hardly influenced the reactivity (Table 2, Entries 1-10) and provided the sulfides in good to excellent yield. However, NO_2 substituent on the aromatic ring of disulfide provided only 21% yield of the product (**3k**), while amine group (product **3l**) provided trace amount. The position of substituent on the benzene ring had a slight impact on the reaction yield. Substituent at *para* position provided more yield in comparision to *ortho* and *meta*. This is due to steric reason of the disulfides. No regioisomeric products as well as disulfenation products were observed by ^{1}H NMR spectroscopy. The process was also extended to disulfides bearing heteroarenes (entries 14, 15), but trace amount of product was obtained.

Table 2: Direct Sulfenylation of 1-methoxynapthalene with disulfides [a]



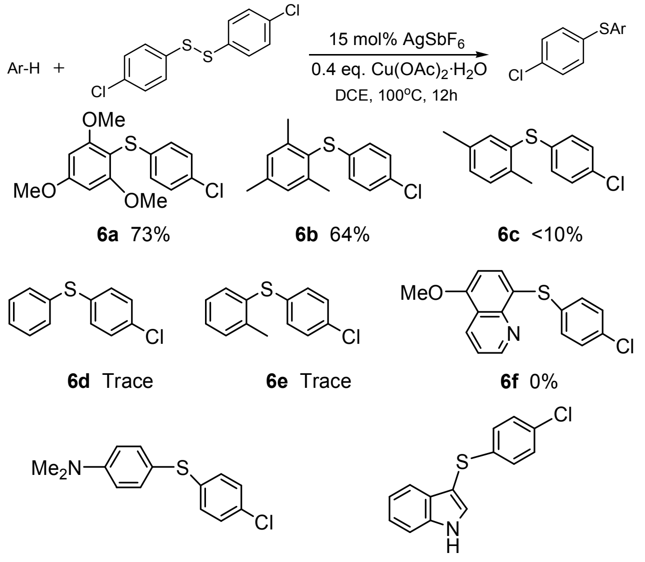
1a **2a-p** **3a-p**

Entry	RSSR (2a-p)	Product (3a-p)	Yield(%)[b]
1	R= 4-ClC_6H_4 **2a**	**3a**	85
2	R= 3-ClC_6H_4 **2b**	**3b**	79
3	R= 2-ClC_6H_4 **2c**	**3c**	69
4	R= 4-BrC_6H_4 **2d**	**3d**	78
5	R= 2-BrC_6H_4 **2e**	**3e**	67
6	R= 4-FC_6H_4 **2f**	**3f**	83
7	R= 2-FC_6H_4 **2g**	**3g**	69
8	R= 4-MeC_6H_4 **2h**	**3h**	95
9	R= 3-MeC_6H_4 **2i**	**3i**	78
10	R= 2-MeC_6H_4 **2j**	**3j**	64
11	R= 4-$NO_2C_6H_4$ **2k**	**3k**	21
12	R= 2-$NH_2C_6H_4$ **2l**	**3l**	Trace
13	R= C_6H_5 **2m**	**3m**	80
14	R=2-Pyridinyl **2o**	**3o**	Trace
15	R=4-Pyridinyl **2p**	**3p**	Trace

[a]The reaction conditions are : **1a** (0.3 mmol), **2a-p** (0.3 mmol), $AgSbF_6$(0.15 eq.), $Cu(OAc)_2\cdot H_2O$ (0.4 eq.), DCE (2 mL), 100°C, 12h. [b]Isolated yield

After successful investigation of the sulfenylation of 1-metyhoxynapthalene, we also observed the efficiency of the process with different aromatic system as coupling partner to **2a**. However it reveals that only electron rich arenes (**Scheme 1**) are suitable for the sulfenylation process. Disappointingly, the scope of the arenes is limited.

Scheme 1: Scope of the sulfenylation process of rich arenes with diaryldisulfide (**2a**)



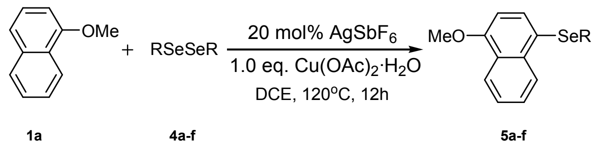
6a 73% **6b** 64% **6c** <10%

6d Trace **6e** Trace **6f** 0%

6g 0% **6h** 0%

We next turned our attention towards formation of C-Se bond. Under similar reaction conditions using diaryldiselenides, selenide products of 1-methoxynapthalene (Table 3, **5a-5f**) were isolated in very good yield of 60-87%. However use of 1 equivalent $Cu(OAc)_2\cdot H_2O$ at 120°C was found to be the best condition for the selenylation process and also requires slightly more catalyst loading (20 mol%) in comparision to the sulfenylation process. Both electron withdrawing and electron donating substituents on the aryl ring of the diselenide are equally effective and does not exhibit significant differences. The extension of the process with an another electron rich arene was found to be effective under the reaction condition (**Scheme 2**).

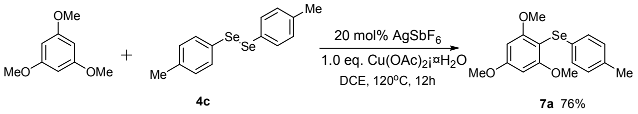
Table 3: Direct Selenylation of 1-methoxynapthalene with diaryl diselenides [a]



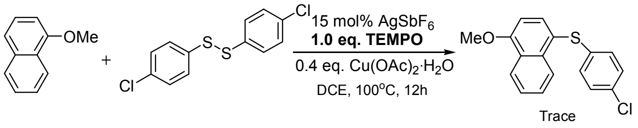
Entry	RSeSeR (4a-f)		Product (5a-f)	Yield(%)[b]
1	R= 4-ClC$_6$H$_4$	**4a**	**5a**	83
2	R= 4-FC$_6$H$_4$	**4b**	**5b**	78
3	R= 4-MeC$_6$H$_4$	**4c**	**5c**	87
4	R= 2-MeC$_6$H$_4$	**4d**	**5d**	60
5	R= 2-OMeC$_6$H$_4$	**4e**	**5e**	75
6	R= 3-CF$_3$C$_6$H$_4$	**4f**	**5f**	71

[a]The reaction conditions are as: **1a** (0.3 mmol), **4a-f** (0.3 mmol), AgSbF$_6$(0.20 eq.), Cu(OAc)$_2$·H$_2$O (1.0 eq.), DCE (2 mL), 120°C, 12h. [b]Isolated yield.

Scheme 2: Direct Selenylation of 1,3,5-trimethoxybenzene with 1,2-di*p*-tolyldiselane.



The exact mechanistic path of the reaction is not clear at this moment. We believe a radical reaction path as use of TEMPO (**Scheme 3**), a radical-trapping reagent completely suppressed the formation of the desired product **3a.** However under the reaction condition it was not possible to detect formation of TEMPO adduct.



Scheme 3

On the basis of our observations, a plausible mechanism has been proposed (**Figure 1**). Initially, the interaction between 1-methoxynapthalene and Ag(I) salt generated aryl-Ag(I) species **A** at 4-position of the ring, which reacted with diarydsulfide to afford intermediate **B** through a single-electron transfer process. Subsequent reductive elimination of intermediate **B** gave the desired product, along with Ag (0) species which can be oxidized to Ag(I) by Cu(II) and/or air to complete the catalytic cycle. Therefore Ag(I) is used as a Lewis acid through the classical electrophilic substitution providing highly regioselective sulfenylation of 1-methoxynapthalene at 4-position of napthalene ring and only electron-rich arenes were suitable under the reaction condition. In addition, the use of oxidant Cu(OAc)$_2$ in catalytic amount improves the reaction yield. We speculate the reduced Cu(I) to be oxidized back to Cu(II) in the presence of air.

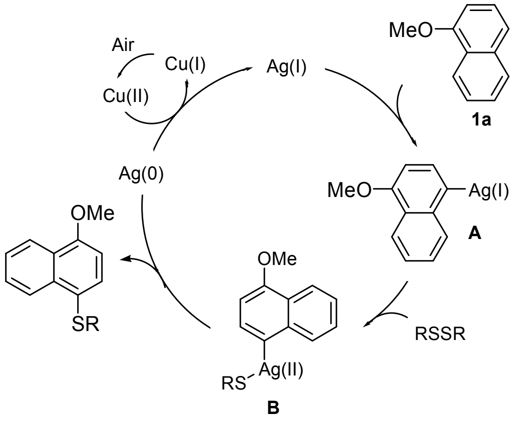


Figure 1 Proposed mechanism of the reaction

In conclusion, we have developed a direct sulfenylation and selenylation process of arenes using silver in combination with copper as cocatalyst. The present method is very effective with a number of dichalcogenides. However, only electron rich arenes were found to be successfull under the reaction conditions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI:10.1039/b000000x/

‡ **Typical procedure for the sulfenylation and selenylation of rich arenes:** Under air atmosphere, 1-methoxynaphthalene (47.4 mg, 0.3 mmol), diaryl disulfides or diaryl diselenides (0.3 mmol), AgSbF$_6$ (0.15 eq. or 0.20 eq.), Cu(OAc)$_2$ ·H$_2$O (0.4 eq. or 1.0 eq.) were added to a screw-capped vial, followed by addition of a stir bar and DCE (2 mL). The reaction vial was placed in a temperature-controlled aluminum-heating block set at 100 °C. After 12 h of stirring, the vial was removed from the heating block and was left to the ambient temperature. The solvents were removed under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography with Petroleum ether/EtOAc as an eluent to give the desired product.

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[1] a) G. Mugesh, H. B. Singh, *Chem. Soc. Rev.* 2000, **29**, 347-357; b) G. Mugesh, W. W. du Mont, H. Sies, *Chem. Rev.* 2001, **101**, 2125-2179; c) G. Liu, J. R. Huth, E. T. Olejniczak, R. Mendoza, P. DeVries, S. Leitza, E. B. Reilly, G. F. Okasinski, S. W. Fesik, T. W. von Geldern, *J. Med. Chem.* 2001, **44**, 1202-1210; d) C. W. Nogueira, G. Zeni, J. B. T. Rocha, *Chem. Rev.* 2004, **104**, 6255-6285; e) G. De Martino, M. C. Edler, G. La Regina, A. Coluccia, M. C. Barbera, D. Barrow, R. I. Nicholson, G. Chiosis, A. Brancale, E. Hamel, M. Artico, R. Silvestri, *J. Med. Chem.* 2006, **49**, 947-954; f) A. Gangjee, Y. Zeng, T. Talreja, J. J. McGuire, R. L. Kisliuk, S. F. Queener, *J. Med. Chem.* 2007, **50**, 3046-3053.

[2] a) V. A. Vu, L. Bérillon, P. Knochel, *Tetrahedron Lett.* 2001, **42**, 6847-6850; b) G. Mugesh, H. B. Singh, *Acc. Chem. Res.* 2002, **35**, 226-236; c) J. Ham, I. Yang, H. Kang, *J. Org. Chem.* 2004, **69**, 3236-3239; d) S. Kumar, H. B. Singh, G. Wolmershäuser, *Organometallics* 2006, **25**, 382-393.

[3] a) T. Kondo, T. Mitsudo, *Chem. Rev*. 2000, **100**, 3205-3220; b) S. V. Ley, A. W. Thomas, *Angew. Chem. Int. Ed*. 2003, **42**, 5400-5449; c) J. F. Hartwig, *Acc. Chem. Res*. 2008, **41**, 1534-1544; d) I. P. Beletskaya, V. P. Ananikov, *Chem. Rev*. 2011, **111**, 1596-1636.

[4] **Selected references on Pd-catalyzed synthesis**: a) T. Migita, T. Shimizu, Y. Asami, J. Shiobara, Y. Kato, M. Kosugi, *Bul. Chem. Soc. Jpn*. 1980, **53**, 1385-1389; b) G. Y. Li, *Angew. Chem., Int. Ed*. 2001, **40**, 1513-1516; c) F. Y. Kwong, S. L. Buchwald, *Org. Lett*. 2002, **4**, 3517-3520; d) T. Itoh, T. Mase, *Org. Lett*. 2004, **6**, 4587-4590; e) X. Moreau, J. M. Campagne, G. Meyer, A. Jutand, *Eur. J. Org. Chem*. 2005, 3749-3769; f) M. A. Fernández-Rodríguez, Q. Shen, J. F. Hartwig, *J. Am. Chem. Soc*. 2006, **128,** 2180-2181; g) J.-Y. Lee, P.-H. Lee, *J. Org. Chem*. 2008, **73**, 7413-7416; h) E. Alvaro, J. F. Hartwig, *J. Am. Chem. Soc*. 2009, **131**, 7858-7868; i) M. A. Fernández-Rodríguez, J. F. Hartwig, *Chem. Eur. J*. 2010, **16**, 2355-2359; j) J.-M. Becht, C. L. Drian, *J. Org. Chem*. 2011, **76**, 6327-6330; k) G. Teverovskiy, S. L. Buchwald, *Angew. Chem., Int. Ed*. 2011, **50**, 7312-7314; l) M. Sayah, M. G. Organ, *Chem. Eur. J*. 2011, **17**, 11719-11722; m) L. Wang, W.-Y. Zhou, S.-C. Chen, M.-Y. He, Q. Chena, *Adv. Synth. Catal*. 2012, **354**, 839-845; n) Z. Qiao, J. Wei, X. Jiang, *Org. Lett*. 2014, **16**, 1212-1215.

[5] **Selected references on Ni-catalyzed synthesis**: a) H. J. Cristau, B. Chabaud, R. Labaudiniere, H. Christol, *J. Org. Chem*. 1986, **51**, 875-878; b) N. Taniguchi, *J. Org. Chem*. 2004, **69**, 6904-6906; c)Y. Zhang, K. N. Ngeow, J. Y. Ying, *Org. Lett*. 2007, **9**, 3495-3498; d) S. Jammi, P. Barua, L. Rout, P. Saha, T. Punniyamurthy, *Tetrahedron Lett*. 2008, **49**, 1484-1487; e) C.-P. Zhang, D. A. Vicic, *J. Am. Chem. Soc*. 2012, **134**, 183-185.

[6] **Selected references on Cu-catalyzed synthesis**: a) N. Taniguchi, T. Onami, *J. Org. Chem*. 2004, **69**, 915-920; b) W. Zhu, D. Ma, *J. Org. Chem*. 2005, **70**, 2696-2700; c) N. Taniguchi, *J. Org. Chem*. 2006, **71**, 7874-7876; d) S. Kumar, L. Engman, *J. Org. Chem*. 2006, **71**, 5400-5403; e)Y. J. Chen, H. H.Chen, *Org. Lett*. 2006, **8**, 5609-5612; f) M. S. Kabir, M. L. V. Linn, A. Monte, J. M. Cook, *Org. Lett*. 2008, **10**, 3363-3366; g) L. Liang, Z. Li, X. Zhou, *Org. Lett*. 2009, **11**, 3294-3297; h) J. Gan, D. Ma, *Org. Lett*. 2009, **11**, 2788-2790; i) A. Saha, D. Saha, B. C. Ranu, *Org. Biomol. Chem*. 2009, **7**, 1652-1657; j) D. Ma, S. Xie, P. Xue, X. Zhang, J. Dong, Y. Jiang, *Angew. Chem., Int. Ed*. 2009, **48**, 4222-4225; k) D. Ma, Q. Geng, H. Zhang, Y. Jiang, *Angew. Chem., Int. Ed*. 2010, **49**, 1291-1294; l) D. Ma, X. Lu, L. Shi, H. Zhang, Y. Jiang, X. Liu, *Angew. Chem., Int. Ed*. 2011, **50**, 1118-1121; m) F. Ke, Y. Qu, Z. Jiang, Z. Li, D. Wu, X. Zhou, *Org. Lett*. 2011, **13**, 454-457; n)H.-L. Kao, C.-F. Lee, *Org. Lett*. 2011, **13**, 5204-5207; o) H. Deng, Z. Li, F. Ke, X. Zhou, *Chem. Eur. J*. 2012, **18**, 4840-4843.

[7] **Selected references on Fe-catalyzed synthesis**: a) A. Correa, O. Garcia Mancheño, C. Bolm, *Chem. Soc. Rev*. 2008, **37**, 1108-1117; b) A. Correa, M. Carril, C. Bolm, *Angew. Chem. Int. Ed*. 2008, **47**, 2880-2883; c) W. Y. Wu, J. C. Wang, F. Y. Tsai, *Green Chem*. 2009, **11**, 326-329; d) C. F. Lee, J.R.Wu, C.H. Lin, *Chem. Commun*. 2009, 4450-4452; e) Y.-Y. Lin, Y.-J. Wang, C.-H. Lin, J.-H. Cheng, C.-F. Lee, *J. Org. Chem*. 2012, **77**, 6100-6106.

[8] Y. C. Wong, T. T. Jayanth, C. H. Cheng, *Org. Lett*. 2006, **8**, 5613-5616.

[9] a) K. Ajiki, M. Hirano, K. Tanaka, *Org. Lett*. 2005, **7**, 4193-4195; b)M. Arisawa, T. Suzuki, T. Ishikawa, M. Yamaguchi, *J. Am. Chem. Soc*. 2008, **130**, 12214-12215; c) C.-S. Lai, H.-L. Kao, Y.-J. Wang, C.-F. Lee, *Tetrahedron Lett*. 2012, **53**, 4365-4367.

[10] a) B. C. Ranu, T. Mandal, S. Samanta, *Org. Lett*. 2003, **5**, 1439-1441; b) B. C. Ranu, T. Mandal, *J. Org. Chem*. 2004, **69**, 5793-5795; c) B. C. Ranu, K. Chattopadhyay, S. Banejee, *J. Org. Chem*. 2006, **71**, 423-425; d) V. P. Reddy, K. Swapna, A. V. Kumar, K. R. Rao, *J. Org. Chem*. 2009, **74**, 3189-3191; e) V. P. Reddy, A. V. Kumar, K. Swapna**,** K. R. Rao, *Org. Lett*., 2009, **11**, 1697-1700;

[11] X. Zhao, Z. Yu, S. Yan, S. Wu, R. Liu, W. He, L. Wang, *J. Org. Chem*. 2005, **70**, 7338-7341.

[12] a) N. Zheng, J. C. McWilliams, F. J. Fleitz, J. D. Armstrong III, R. P. Volante, *J. Org. Chem*. 1998, **63**, 9606-9607; b) T. Itoh and T. Mase, *Org. Lett*. 2004, **6**, 4587-4590; c) C. Mispelaere-Canivet, J.-F. Spindler, S. Perrio and P. Beslin, *Tetrahedron*, 2005, **61**, 5253-5259.

[13] a) P. S. Herradura, K. A. Pendola and R. K. Guy, *Org. Lett*. 2000, **2**, 2019-2022; b) C. Savarin, J. Srogl and L. S. Liebeskind, *Org. Lett*. 2002, **4**, 4309-4312; c) N. Taniguchi, *J. Org. Chem*. 2007, **72**, 1241-1245.

[14] a) Bergman, R. G. *Nature*, 2007, **446**, 391-393; b) G. Song, F. Wang, X. Li, *Chem. Soc. Rev*. 2012, **41**, 3651-3678; c) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev*. 2011, **40**, 5068-5083; d) J. Wencel-Delord, T. Droge, F. Liu, F. Glorius, *Chem. Soc. Rev*. 2011, **40**, 4740-4761.

[15] **Chelation-assisted C-H activation**: a) X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *J. Am. Chem. Soc*. 2006, **128**, 6790-6791; b) L. Chu, X. Yue, F.-L. Qing, *Org. Lett*. 2010, **12**, 1644-1647; c)O. Saidi, J. Marafie, A. E. W. Ledger, P. M. Liu, M. F. Mahon, G. Kociok-Köhn, M. K. Whittlesey, C. G. Frost, *J. Am. Chem. Soc*. 2011, **133**, 19298-19301; d) L. D. Tran, I. Popov, O. Daugulis, *J. Am. Chem. Soc*. 2012, **134**, 18237-18240; e) X. Zhao, E. Dimitrijevic, V. M. Dong, *J. Am. Chem. Soc*. 2009, **131**, 3466-3467; f) Z. Wu, H. Song, X. Cui, C. Pi, W. Du, Y. Wu, *Org. Lett*. 2013, **15**, 1270-1273; **Non chelation-assisted C-H bond activation:** g) D. Crich, J. W. Davies, *Tetrahedron Lett*. 1989, **30**, 4307-4308; h) M. Tiecco, L. Testaferri, L. Bagnoli, F. Marini, A. Temperini, C. Tomassini, C. Santi, *Tetrahedron* 2000, **56**, 3255-3260; i) M. Abdo, S. Knapp, *J. Am. Chem. Soc*. 2008, **130**, 9234-9235; j) S.-I. Fukuzawa,; E. Shimizu, Y. Atsuumi, M. Haga, K. Ogata, *Tetrahedron Lett*. 2009, **50**, 2374-2376; k)S. Zhang, P. Qian, M. Zhang, M. Hu, J. Cheng, *J. Org. Chem*. 2010, **75**, 6732-6735; l) M. Abdo, Y. Zhang, V. L. Schramm, S. Knapp, *Org. Lett*. 2010, **12**, 2982-2985; m) P. Anbarasan, H. Neumann, M. Beller, *Chem. Commun*. 2011, **47**, 3233-3235; n) S. Ranjit, R. Lee, D. Heryadi, C. Shen, J. Wu, P. Zhang, K.-W. Huang, X. Liu, *J. Org. Chem*. 2011, **76**, 8999-9007; o) C. Dai, Z. Xu, F. Huang, Z. Yu, Y.-F. Gao, *J. Org. Chem*. 2012, **77**, 4414-4419; p) J.-H. Cheng, C.-L. Yi, T.-J. Liu, C.-F. Lee, *Chem. Commun*. 2012, **48**, 8440-8442.

[16] a) Q. Wu, D. Zhao, X. Qin, J. Lan, J. You, *Chem. Commun*. 2011, **47**, 9188-9190; b) R. Tang, Y. Xie, Y. Xie, J. Xiang, J. Li, *Chem. Commun*. 2011, **47**, 12867-12869; c) Y. P. Zhu, M. Lian, F. C. Jia, M. C. Liu, J. J. Yuan, Q. H. Gao, A. X. Wu, *Chem. Commun*. 2012, **48**, 9086-9088; d) L. -H. Zou, J. Reball, J. Mottweiler, C. Bolm, *Chem. Commun*. 2012, **48**, 11307–11309; e) S. Guo, Y. Yuan, J. Xiang, *Org. Lett*. 2013, **15**, 4654-4657; f) F. Yang, S. Tian, *Angew. Chem., Int. Ed*. 2013, **52**, 4929-4932;

g)B. Du, B. Jin, P. Sun *Org. Lett.* 2014, **16**, 3032-3035; h) C. Ravi, D. C. Mohan, S. Adimurth, *Org. Lett*. 2014, **16**, 2978-2981.