



Ultrasound-assisted synthesis of symmetrical biaryls by palladium-catalyzed detelluration of 1,2-diarylditellanes

Fateh V. Singh, Hélio A. Stefani *

Faculdade de Ciências Farmacêuticas, Universidade de São Paulo, São Paulo, SP, Brazil

ARTICLE INFO

Article history:

Received 2 November 2009

Revised 5 December 2009

Accepted 7 December 2009

Available online 11 December 2009

Keywords:

Detelluration reaction

Biaryls

Diarylditellurides

ABSTRACT

An ultrasound-assisted synthesis of functionalized symmetrical biaryls with electron-withdrawing or electron-donating substituents is described and illustrated by the palladium-catalyzed detelluration of 1,2-diarylditellanes. This procedure offers easy access to symmetrical biaryls in short reaction time and the products are achieved in good to excellent yields.

© 2009 Published by Elsevier Ltd.

Biaryl scaffolds are important structural motifs for both synthetic and medicinal purposes. These scaffolds are also common structural features found in a large number of biologically important natural products.¹ Aside from their occurrence in complex natural products and pharmaceutical agents,² these compounds are also applied as chiral ligands,³ liquid crystal materials,⁴ and organic conductors.⁵

Several synthetic biaryl compounds have been reported to have diverse biological activities⁶ such as antidiabetic,⁷ anticancer,⁸ antibacterial,⁹ and γ -secretase inhibitory activity.¹⁰ Some symmetric and asymmetric biaryls such as α -DDB (methyl 4,40-dimethoxy-5,6,50,60-dimethylenedioxy biphenyl-2,2-dicarboxylate) and bicyclicol (Fig. 1) are used as leading hepatoprotective agents.¹¹ Recently, some biaryl scaffolds have been identified as a new class of antileishmanial agents.¹²

Aryl–aryl bond formation for the preparation of symmetrical and unsymmetrical biaryl compounds is one of the most useful and important tools in modern organic chemistry. The synthesis of some unsymmetrical biaryl compounds has been achieved by metal-catalyzed¹³ and non-metal-catalyzed¹⁴ approaches in the past few years. Symmetrical biaryls are traditionally obtained using the Ullmann reaction¹⁵ and some other methods.¹⁶ In the past decade, the synthesis of symmetrical biaryl scaffolds has continued using metal-assisted homocoupling of aryl halides,¹⁷ boronic acids,¹⁸ aryl Grignard reagents,¹⁹ and arene diazonium salts.²⁰ Wong and Zhang reported the synthesis of these systems through the palladium-catalyzed homocoupling of aryl boronic acids, but

this method requires phosphine or phosphate ligands and harsh reaction conditions.²¹ In the past few years, Yamamoto et al. reported an efficient method to obtain symmetrical biaryls through

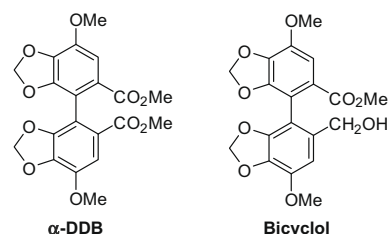


Figure 1. Structures of biologically active biaryl scaffolds.

Table 1
Study of the catalyst effect on detelluration of 1,2-diphenylditellane **1a**

Entry	Catalyst ^a	Yield ^b (%)
1	—	nr
2	PdCl ₂	95
3	Pd(AcO) ₂	82
4	Pd(dba) ₃	20
5	Pd(BzCN) ₂	62
6	PdCl ₂ (PEPPSI)	46
7	Fe(acac) ₃	nr
8	Cu(OAc) ₂	nr

Reaction conditions: diphenylditelluride (1 equiv), catalyst (10 mol %), Na₂CO₃ (2 equiv), Ag₂O (2 equiv), MeOH, irradiate in ultrasonic bath.

^a 10 mol % of catalyst was used.

^b The yields were determined by GC analysis.

* Corresponding author. Tel.: +55 11 3091 3654; fax: 55 11 3815 4418.

E-mail address: hstefani@usp.br (H.A. Stefani).

Table 2
Study of the effects of additive and base on the detelluration of 1,2-diphenylditellane **1a**

Entry	Base	Additive (equiv)	Pd(PPh ₃) ₄ (mol %)	Yield ^a (%)
1	—	AgOAc (2)	PdCl ₂ (10)	nr
2	Na ₂ CO ₃	AgOAc (2)	PdCl ₂ (10)	95
3	CS ₂ CO ₃	AgOAc (2)	PdCl ₂ (10)	92
4	NaHCO ₃	AgOAc (2)	PdCl ₂ (10)	72
5	DIPEA	AgOAc (2)	PdCl ₂ (10)	79
6	Et ₃ N	AgOAc (2)	PdCl ₂ (10)	84
7	Na ₂ CO ₃	—	PdCl ₂ (10)	nr
8	Na ₂ CO ₃	AgOAc (2)	PdCl ₂ (10)	95
9	Na ₂ CO ₃	Ag ₂ O (2)	PdCl ₂ (10)	98
10	Na ₂ CO ₃	CuI (2)	PdCl ₂ (10)	35
11	Na ₂ CO ₃	Ag ₂ O (2)	PdCl ₂ (10)	55
12	Na ₂ CO ₃	Ag ₂ O (2)	PdCl ₂ (8)	78
13	Na ₂ CO ₃	Ag ₂ O (2)	PdCl ₂ (10)	70

Reaction conditions: diphenylditelluride (1 equiv), PdCl₂ (10 mol %), base (2 equiv), additive (2 equiv), MeOH, irradiate in ultrasonic bath.

^a The yields were determined by GC analysis.

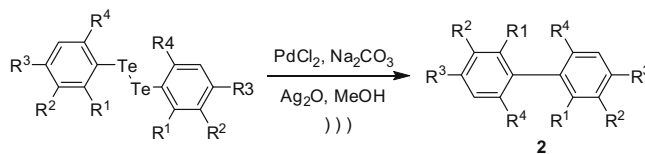
Table 3
Study of the solvent effect on the detelluration of 1,2-diphenylditellane **1a**

Entry	Solvent	Yield ^a (%)
1	MeOH	98
2	MeCN	38
3	THF	35
4	1,4-Dioxane	17
5	Toluene	23

Reaction conditions: diphenylditelluride (1 equiv), PdCl₂ (10 mol %), Na₂CO₃ (2 equiv), Ag₂O (2 equiv), solvent, irradiate in ultrasonic bath.

^a The yield was determined by GC analysis.

Table 4
Detelluration of functionalized 1,2-diarylditellanes **1a–j**



Entry	Diarylditellurides (1)	Biaryls (2)	Reaction time (min)	Yield ^a (%)
a			30	95
b			30	92
c			30	88
d			25	82
e			45	84
f			45	78
g			30	83

the homocoupling of aryl boronic acids, but this method suffers from low yields with electron-withdrawing functionalities as aryl boronic acids.²²

Organotellurium compounds have undergone remarkable development as intermediates in synthetic organic chemistry. Organotellurium compounds have been used instead of halogens as electrophilic partners in some palladium-catalyzed cross-coupling reactions.^{23,24} Recently, we reported the synthesis of symmetrical biaryls²⁵ through the palladium-catalyzed homocoupling of *n*-butyl aryltellurides, which proceeds in a few minutes using ultrasonic waves as a source of energy. The ultrasound effects are attributed to a physical process called cavitation.²⁶

Herein, we report a new protocol for the synthesis of symmetrical biaryls using a palladium-catalyzed detelluration reaction of functionalized 1,2-diarylditellanes with ultrasonic waves as a source of energy. The strength of the procedure lies in the formation of a C–C bond and the introduction of electron-donor or -acceptor functionalities into the products.

The approach to prepare biaryl compounds **2a–i** was based on a palladium-catalyzed detelluration reaction of functionalized 1,2-diarylditellanes **1a–i**. The parent precursors 1,2-diarylditellanes **1a–j** were conveniently prepared in high yields through the Grignard reaction of aryl halides followed by the addition of tellurium and oxidation by air.²⁷

Initially, we optimized the conditions for the detelluration of functionalized 1,2-diarylditellanes **1**. In order to find appropriate conditions for the detelluration reaction of 1,2-diarylditellanes, 1,2-diphenylditellane **1a** was selected as a model substrate and a variety of conditions were screened, as described in Tables 1–3. The reactions were monitored by TLC or GC.

Initially, we surveyed palladium catalysts for this detelluration reaction. We attempted reactions with some palladium (Table 1,

Table 4 (continued)

Entry	Diarylditellurides (1)	Biaryls (2)	Reaction time (min)	Yield ^a (%)
h			30	92
i			40	82
j			60	—

Reaction conditions: diarylditelluride (1 equiv), PdCl₂ (10 mol %), Na₂CO₃ (2 equiv), Ag₂O (2 equiv), MeOH, irradiate in ultrasonic bath.

^a Isolated yields.

entries 2–6) and non-palladium (Table 1, entries 7 and 8) catalysts, but the reaction only worked with palladium catalysts. Pd(II) and (0) species were used in these detelluration reactions, but the best results were obtained with Pd(II) species (Table 1, entries 2, 3 and 5). Two equivalents of Ag₂O as an additive were used, with 2 equiv of sodium carbonate and methanol as the solvent. The reaction was irradiated for 30 min in an ultrasound bath. The best result was obtained with PdCl₂ (Table 1, entry 2).

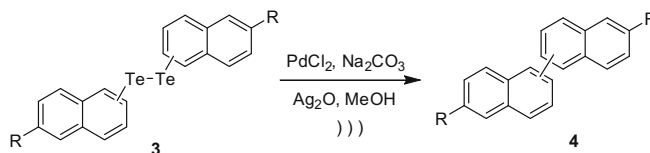
The next step was the determination of the best base and the necessity of an additive in the reaction. Initially, we used sodium carbonate as a base in the presence of Ag₂O, and the desired compound was observed in 95% yield (Table 2, entry 2). We attempted the same reaction with some other inorganic bases such as cesium carbonate and sodium bicarbonate and observed a slight decrease in the yield of the desired biaryl compound (Table 2, entries 3 and 4). When the same reaction was performed with organic bases such as DIPEA and triethylamine, the desired compound was isolated in 79% and 84% yields (Table 2, entries 5 and 6). We also performed the reaction without using any base, but no reaction was observed (Table 2, entry 1).

To observe the influence of the additive, we performed the same reaction with three different additives: AgOAc, Ag₂O, and CuI. The desired biphenyl product **2a** was observed in 95%, 98%, and 35% yields, respectively (Table 2, entries 8–10). To establish the correct stoichiometry of the reaction, we performed it with 1 equiv of Ag₂O and the desired product was observed in 55% yield (Table 2, entry 11), while the intermediate diphenyltellane was also observed in 45% yield. No reaction was observed in the absence of an additive (Table 2, entry 7).

In order to determine the best solvent for the biaryl formation, we performed different reactions with different types of solvents. The best result was achieved with a polar protic solvent (methanol), which furnished the desired product in 98% yield (Table 3, entry 1). The optimization results with different solvents are described in Table 3.

Finally, to observe the effect of ultrasonic waves in this reaction, we attempted the same reaction under reflux conditions. The reaction was completed in 6 h and desired compound **2a** was isolated in 70% yield (Table 2, entry 13). The role of Ag₂O can be attributed to the removal of phosphine ligands from the catalyst or from one

Table 5
Detelluration reaction of dinaphthyl ditellurides **3a–c**



Entry	Dinaphthyl ditellurides (3)	Binaphthyls (4)	Reaction time (min)	Yield ^a (%)
a			60	72
b			30	81
c			35	85

Reaction conditions: dinaphthyl ditelluride (1 equiv), PdCl₂ (10 mol %), Na₂CO₃ (2 equiv), Ag₂O (2 equiv), MeOH, irradiate in ultrasonic bath.

^a Isolated yields.

of the catalytic intermediates formed in the course of the reaction.^{13a}

The catalyst loadings were analyzed, and the best result was obtained with 10 mol% of PdCl₂, which provided a 98% yield. During the optimization studies for biphenyl **2a**, was observed that a reaction mixture of 1.0 equiv of 1,2-diphenylditellane **1a**, 2.0 equiv of Ag₂O, 2.0 equiv of sodium carbonate, and 10 mol% of PdCl₂ in methanol irradiated under ultrasonic waves for 30 min were the best conditions for the synthesis of biphenyl **2a**. After optimizing the conditions for the synthesis of biphenyl **2a**, we synthesized a series of functionalized biaryl compounds (**2a–i**) using the optimized conditions in 78–95% yields (see Table 4). Interestingly, the reaction proceeded nicely with both electron-withdrawing and electron-donating substituents in the biaryl architecture. When we attempted the same reaction with more hindered 1,2-dimesitylditellane **1j** under similar reaction conditions, we isolated the dimesityltellane instead of corresponding biaryl derivative 2,2',4,4',6,6'-hexamethylbiphenyl **2j**. All of the synthesized compounds were characterized by spectroscopic analysis.³⁰

In order to demonstrate the utility of this approach, we prepared 1,2-naphthylditellanes **3a–c** from functionalized bromonaphthalenes using a Grignard reaction followed by the addition of tellurium and air oxidation,²⁷ and prepared binaphthyls **4a–c** in good yields (Table 5).

On the basis of the available literature³¹ we propose a possible catalytic cycle for the detelluration reaction of diarylditellurides as described in Figure 2. According to this cycle, the reaction proceeds with the formation of a telluride–palladium(II) complex (**A**) followed by the conversion of this intermediate into another palladium species (**B**), which leads the formation of diaryl telluride (**C**) along with Pd(0). Further, Pd(0) oxidized into Pd(II) by Ag⁺ ions and Pd(II) formed a telluride–palladium(II) complex (**D**) with diaryl telluride (**C**). After that telluride–palladium(II) complex (**D**) converted into an intermediate (**E**), which finally offered biaryl compounds along with Pd(0) and metallic tellurium. The palladium species is later oxidized with Ag₂O to give palladium(II) thus completing the cycle. We observed the formation of diaryl telluride in one reaction during the screening by GC–MS.

In summary, we demonstrated the ultrasound-assisted synthesis of functionalized symmetrical biaryls through the homocoupling reaction of easily accessible aryltellurides. This methodology has the flexibility of introducing electron-donor or electron-acceptor functionalities in the biaryl architecture. Further applications of our methodology for the synthesis of biaryls are currently in progress.

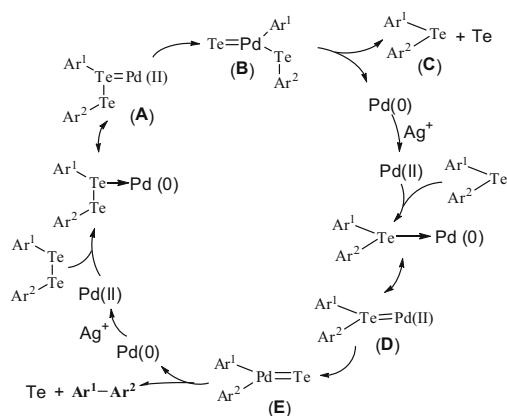


Figure 2. Possible catalytic cycle of detelluration reaction of 1,2-diarylditellurides.

Acknowledgments

The authors are grateful to FAPESP (07/51466-9, 07/59404-2) and CNPq for financial support.

References and notes

- (a) Nising, C. F.; Schmid, U. K.; Nieger, M.; Brase, S. *J. Org. Chem.* **2004**, *69*, 6830; (b) Bringmann, G.; Ochse, M.; Schupp, O.; Tasler, S. In *Progress in the Chemistry of Organic Natural Products*; Springer: Wien, Germany, 2001; Vol. 82; (c) Bringmann, G.; Tasler, S. *Tetrahedron* **2001**, *57*, 331; (d) Franck, B.; Gottschalk, E. M.; Ohnsorge, U.; Huper, F. *Chem. Ber.* **1966**, *99*, 3842; (e) Torsell, K. B. G. *Natural Product Chemistry*; Taylor and Francis: New York, 1997; (f) Thomson, R. H. *The Chemistry of Natural Products*; Blackie and Son: Glasgow, 1985.
- (a) Nicolaou, K. C.; Boddy, N. C.; Brase, S.; Winessinger, N. *Angew. Chem.* **1999**, *111*, 2230; *Angew. Chem., Int. Ed.* **1999**, *38*, 2096; (b) Birkenhager, W. H.; de Leeuw, P. W. *J. Hypertens.* **1999**, *17*, 873; (c) Goa, K. L.; Wagstaff, A. *J. Drugs* **1996**, *51*, 820; (d) François, G.; Timperman, G.; Holenz, J.; Aké Assi, L.; Geuder, T.; Maes, L.; Dubois, J.; Hanocq, M.; Bringmann, G. *Ann. Trop. Med. Parasitol.* **1996**, *90*, 115.
- (a) Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187; (b) Andersen, N. G.; Maddaford, S. P.; Keay, B. A. *J. Org. Chem.* **1996**, *61*, 9556; (c) Buchwald, S. L.; Surry, D. S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338; (d) Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653; (e) Goel, A.; Singh, F. V. *Tetrahedron Lett.* **2005**, *46*, 5585.
- (a) Yamamura, K.; Ono, S.; Tabushi, I. *Tetrahedron Lett.* **1988**, *29*, 1797; (b) Yamamura, K.; Ono, S.; Ogoshi, H.; Masuda, H.; Kuroda, Y. *Synlett* **1989**, 18.
- Bringmann, G.; Breuning, M.; Tasler, S. *Synthesis* **1999**, 525. and references are cited therein.
- (a) Chen, Y. X.; Li, Y. M.; Lam, K. H.; Chan, A. S. C. *Chin. J. Chem.* **2001**, *19*, 794; (b) Arlt, M.; Böttcher, H.; Riethmüller, A.; Schneider, G.; Bartoszyk, G. D.; Greiner, H.; Seyfried, C. A. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 2033.
- (a) Singh, F. V.; Parihar, A.; Chaurasia, S.; Singh, A. B.; Singh, S. P.; Tamrakar, A. K.; Srivastava, A. K.; Goel, A. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 2158; (b) Singh, F. V.; Kumar, A.; Goel, A. *Tetrahedron Lett.* **2006**, *47*, 7767. and references are cited therein.
- (a) Kuo, Y. H.; Kuo, L. M.; Chen, C. F. *J. Org. Chem.* **1997**, *62*, 3242; (b) Yasukawa, K.; Ikeya, Y.; Mitsuhashi, H.; Iwasaki, M.; Aburada, M.; Nakagawa, S.; Takeuchi, M.; Takido, M. *Oncology* **1992**, *49*, 68.
- Look, G. C.; Vacin, C.; Dias, T. M.; Ho, S.; Tran, T. H.; Lee, L. L.; Wiesner, C.; Fang, F.; Marra, A.; Westmacott, D.; Hromockyj, A. E.; Murphy, M. M.; Schullek, J. R. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 1423.
- Thompson, L. A.; Liauw, A. Y.; Ramanjulu, M. M.; Kasireddy-Polam, P.; Mercer, S. E.; Maduskuie, T. P.; Glicksman, G.; Roach, A. H.; Meredith, J. E.; Liu, R. Q.; Combs, A. P.; Higaki, J. N.; Cordell, B.; Seiffert, D.; Zaczek, R. C.; Robertson, D. W.; Olson, R. E. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 2357.
- Wu, G.; Guo, H. F.; Gao, K.; Liu, Y.; Bastow, K. F.; Morris-Natschke, S. L.; Lee, K. H.; Xie, L. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 5272.
- Singh, F. V.; Vatsyayan, R.; Roy, U.; Goel, A. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 2734.
- (a) Cella, R.; Cunha, R. L. O. R.; Reis, A. E. S.; Pimenta, D. C.; Klitzke, C. F.; Stefani, H. A. *J. Org. Chem.* **2006**, *71*, 244; (b) Wolf, C.; Xu, H. *J. Org. Chem.* **2008**, *73*, 162; (c) Yin, J.; Rainka, M. P.; Zhang, X.-X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162; (d) Jensen, J. F.; Johannsen, M. *Org. Lett.* **2003**, *5*, 3025; (e) Navarro, O.; Kelly, R. A., III; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194; (f) Altenhoff, G.; Goddard, R.; Lehmann, C.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195; (g) Wolf, C.; Mei, X. *J. Am. Chem. Soc.* **2003**, *125*, 10651; (h) Tumambac, G. E.; Wolf, C. *J. Org. Chem.* **2004**, *69*, 2048; (i) Mei, X.; Martin, R. M.; Wolf, C. *J. Org. Chem.* **2006**, *71*, 2854; (j) Milne, J. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 13028.
- (a) Goel, A.; Singh, F. V.; Dixit, M.; Verma, D.; Raghunandan, R.; Maulik, P. R. *Chem. Asian J.* **2007**, *2*, 239; (b) Kumar, A.; Singh, F. V.; Goel, A. *Tetrahedron Lett.* **2007**, *48*, 7283; (c) Singh, F. V.; Kumar, V.; Kumar, B.; Goel, A. *Tetrahedron* **2007**, *63*, 10971.
- (a) Pier, E.; Yee, J. G. K.; Gladstone, P. L. *Org. Lett.* **2000**, *2*, 481; (b) Fanta, P. E. *Synthesis* **1974**, *1*, 9; (c) Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327; (d) Lindley, J. *Tetrahedron* **1984**, *40*, 1433.
- (a) Cravotto, G.; Beggiano, M.; Penoni, A.; Palmisano, G.; Tollari, S.; Lévêque, J.-M.; Bonrath, W. *Tetrahedron Lett.* **2005**, *46*, 2267; (b) Yoshida, H.; Yamaryo, Y.; Ohshita, J.; Kunai, A. *Tetrahedron Lett.* **2003**, *44*, 1541; (c) Punna, S.; Diaz, D. D.; Finn, M. G. *Synlett* **2004**, 2351; (d) Kabalka, G. W.; Wang, L. *Tetrahedron Lett.* **2002**, *43*, 3067; (e) Lei, A.; Zhang, X. *Tetrahedron Lett.* **2002**, *43*, 2525; (f) Percec, V.; Bae, J.-Y.; Zhao, M.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 176.
- (a) Miyake, Y.; Wu, M.; Rahman, M. J.; Kuwatani, Y.; Iyoda, M. *J. Org. Chem.* **2006**, *71*, 6110; (b) Xu, X.; Cheng, D.; Pei, W. *J. Org. Chem.* **2006**, *71*, 6637.
- Xu, Z.; Mao, J.; Zhang, Y. *Catal. Commun.* **2008**, *9*, 97. and references cited therein.
- Cahiez, G.; Moyeux, A.; Buendia, J.; Duplais, C. *J. Am. Chem. Soc.* **2007**, *129*, 13788. and references cited therein.
- Robinson, M. K.; Kochurina, V. S.; Hanna, J. M. *Tetrahedron Lett.* **2007**, *48*, 7687. and references cited therein.
- Wong, M. S.; Zhang, X. L. *Tetrahedron Lett.* **2001**, *42*, 4087.
- Yamamoto, Y.; Suzuki, R.; Hattori, K.; Nishiyama, H. *Synlett* **2006**, 1027.

23. For review: (a) Petragnani, N.; Stefani, H. A. *Tetrahedron* **2005**, *61*, 1613; (b) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373; (c) Zeni, G.; Braga, A. L.; Stefani, H. A. *Acc. Chem. Res.* **2003**, *36*, 731.
24. (a) Zeni, G.; Perin, G.; Cella, R.; Jacob, R. G.; Braga, A. L.; Silveira, C. C.; Stefani, H. A. *Synlett* **2002**, 975; (b) Braga, A. L.; Lüdtke, D. S.; Vargas, F.; Donato, R. K.; Silveira, C. C.; Stefani, H. A.; Zeni, G. *Tetrahedron Lett.* **2003**, *44*, 1779; (c) Nishibayashi, Y.; Cho, C.-S.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **1996**, *507*, 197; (d) Nishibayashi, Y.; Cho, C.-S.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **1996**, *526*, 335.
25. Singh, F. V.; Stefani, H. A. *Synlett* **2008**, 3221.
26. (a) Margulis, M. A. *High Energ. Chem.* **2004**, *38*, 135; (b) Mason, T. J. *Chem. Soc. Rev.* **1997**, *26*, 443.
27. *General experimental procedure for diarylditellurides 1a–j and 3a–c*: Mg (0.240 g, 20 mmol) and catalytic amounts of I₂ were heated under N₂ in a two-necked round-bottomed flask. A solution of aryl halide (10 mmol) in dry THF (20 mL) was added dropwise and the mixture stirred for 1 h at room temperature. Activated elemental Te (2.54 g, 20 mmol) was added, and after 1 h the system was opened to allow oxidation. The reaction mixture was diluted with ethyl acetate, a solution of NH₄Cl was added dropwise, and stirred for 2 h. The reaction was monitored by TLC and GC. The reaction mixture was extracted with ethyl acetate (30 mL) and washed with a solution of brine. The organic layer was dried over MgSO₄, filtered over Celite, and concentrated under vacuum. Finally, the red solid crystalline compounds **1a–j** and **3a–c** were obtained without using column chromatography.
28. Cahiez, G.; Chaboche, C.; Mahuteau-Betzer, F.; Ahr, M. *Org. Lett.* **2005**, *7*, 1943.
29. Kirai, N.; Yamamoto, Y. *Eur. J. Org. Chem.* **2009**, 1864.
30. *General experimental procedure for biaryls 2a–i and 4a–c*: A suspension of 1,2-diphenylditellane **1a** (0.204 g, 0.5 mmol), PdCl₂ (0.09 g, 10 mol %), sodium carbonate (0.106 g, 1 mmol), and silver oxide (0.232 g, 1.0 mmol) in 5 mL of methanol was irradiated in a water bath of an ultrasonic cleaner (Branson Ultrasonic Cleaner) at room temperature for 30 min. After the completion of reaction, the reaction mixture was diluted with ethyl acetate (20 mL). The organic layer was washed with saturated solution of NH₄Cl (2 × 10 mL) and water (2 × 10 mL), dried over MgSO₄, and concentrated under vacuum. The crude product was purified by flash silica column chromatography using hexane as an eluent and characterized as biphenyl²⁸ **2a**: white solid; mp 70–72 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.21–7.44 (m, 6H, ArH), 7.65 (d, J = 7.2 Hz, 4H, ArH); ¹³C NMR (75.5 MHz, CDCl₃) δ 127.6, 128.76, 141.29; GC–MS (%) 154 (100), 153 (44), 152 (29), 76 (32). 4,4'-Dibromobiphenyl²⁹ **2b**: white solid; mp 160–162 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.41 (d, J = 8.2 Hz, 4H, ArH), 7.52 (d, J = 8.2 Hz, 4H, ArH); ¹³C NMR (75.5 MHz, CDCl₃) δ 121.93, 128.48, 132.00, 138.91; GC–MS (%) 312 (66), 152 (100), 151(25), 76 (94). 1,1'-Binaphthyl²⁵ **4a**: white solid; mp 138–140 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.20 (t, J = 7.8 Hz, 2H, ArH), 7.36–7.52 (m, 4H, ArH); 7.65–7.76 (m, 6H, ArH); 8.18 (d, J = 8.4 Hz, 2H, ArH); ¹³C NMR (75.5 MHz, CDCl₃) δ 122.93, 126.25, 126.78, 127.19, 127.42, 128.03, 128.40, 129.99, 132.09, 134.56; GC–MS (%) 254 (90), 253 (100), 252 (80), 250 (25), 126 (98), 125 (47).
31. Barton, D. H. R.; Ozbalik, N.; Ramesh, M. *Tetrahedron Lett.* **1988**, *29*, 3533.