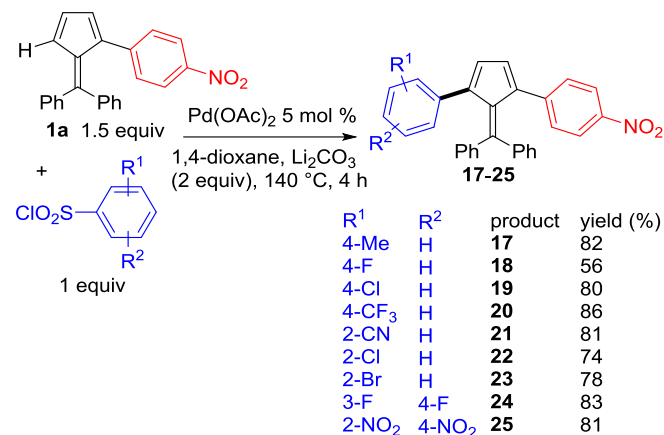


bromobenzenesulfonyl chloride gave **23** in 78% yield, again without cleavage of the C-Br bond.

Scheme 4. Palladium-catalysed direct C4-arylation of C1-arylated 6,6-diphenylfulvene 1a.



In summary, we have demonstrated that the Pd-catalysed C-H bond functionalisation of fulvenes is possible when appropriate reaction conditions are employed. The reaction of 6,6-diphenylfulvene with a set of benzenesulfonyl chlorides in the presence of Pd(OAc)₂ catalyst affords regioselectively the C1-arylated fulvenes. Moreover using an excess of benzenesulfonyl chlorides or from C1-arylated fulvenes, the formation of C1,C4-diarylated fulvenes also proceed in good yields. The reported conditions offer routes for fast and direct access to arylated fulvene derivatives from commercially available compounds, catalyst and inexpensive base. This protocol is applicable to a range of functions on the benzenesulfonyl chloride, including reactive ones. Such functional group tolerance should allow the easy modification of these products, a strategy enabling the tuning of their properties.

ASSOCIATED CONTENT

Supporting Information

Proposed catalytic cycle, experimental procedure and ¹H and ¹³C NMR of all compounds, UV-vis absorption spectra of products **3**, **9**, **10**, **13**, **14**, **19**, **21**, X-ray analysis of **10**. The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

* E-mail: jean-francois.soulé@univ-rennes1.fr; henri.doucet@univ-rennes1.fr

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

We thank the “CNRS”, “Rennes Metropole”, “UTIQUE” and Scientific Ministry of Higher Education Research of Tunisia for providing financial support.

REFERENCES

- (a) Bergmann, E. D. *Chem. Rev.* **1968**, 68, 41; (b) Hopf, H.; Sherburn, M. S. *Cross Conjugation: Modern Dendralene, Radialene and Fulvene Chemistry*, Wiley-VCH, 2016.
- (a) Butler, M. S. *Nat. Prod. Rep.* **2008**, 25, 475; (b) Pelloquin, A. J.; Stone, R. L.; Avila, S. E.; Rudico, E. R.; Horn, C. B.; Gardner, K. A.; Ball, D. W.; Johnson, J. E. B.; Iacono, S. T.; Balaich, G. J. *J. Org. Chem.* **2012**, 77, 6371; (c) Godman, N. P.; Balaich, G. J.; Iacono, S. T. *Chem. Commun.* **2016**, 52, 5242; (d) Kreindlin, A. Z.; Rybinskaya, M. I. *Russ. Chem. Rev.* **2004**, 73, 417.
- For reviews on metal-catalysed C-H bond functionalisation: (a) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, 107, 174-238; (b) Satoh, T.; Miura, M. *Chem. Lett.* **2007**, 36, 200-205; (c) Li, B.-J.; Yang, S.-D.; Shi, Z.-J. *Synlett* **2008**, 949-977; (d) Bellina, F.; Rossi, R. *Tetrahedron* **2009**, 65, 10269-10310; (e) Ackermann, L.; Vicente, R.; Kapdi, A. *Angew. Chem., Int. Ed.* **2009**, 48, 9792-9826; (f) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, 48, 5095-5115; (g) Wencel-Delord, J.; Glorius, F. *Nature Chem.* **2013**, 5, 267-275; (h) Rouquet, G.; Chatani, N. *Angew. Chem., Int. Ed.* **2013**, 52, 11726-11743; (i) Rossi, R.; Bellina, F.; Alessi, M.; Mazzini, C. *Adv. Synth. Catal.* **2014**, 356, 170-177; (j) Zhang, M.; Zhang, Y.; Jie, X.; Zhao, H.; Li, G.; Su, W. *Org. Chem. Front.* **2014**, 1, 843-895; (k) Bheeter, C. B.; Chen, L.; Soule, J.-F.; Doucet, H. *Cat. Sci. Technol.* **2016**, 6, 2009-2049.
- For metal-catalysed functionalization of the 5-membered ring C-H bonds of azulenes and acenaphthylene: (a) Dyker, G. *Tetrahedron Lett.* **1991**, 32, 723-724; (b) Dyker, G.; Borowski, S.; Heiermann, J.; Körning, U.; Oppel, K.; Henkel, G.; Köckerling, M. *J. Organomet. Chem.* **2000**, 606, 108; (c) Pletnev, A. A.; Tian, Q.; Larock, R. C. *J. Org. Chem.* **2002**, 67, 9276; (d) Sugihara, T.; Satoh, T.; Miura, M.; Nomura, M. *Adv. Synth. Catal.* **2004**, 346, 1735; (e) Dyker, G.; Merz, K.; Oppel, I. M.; Muth, E. *Synlett* **2007**, 89; (f) Pillekamp, M.; Aniol, A.; Heppekausen, J.; Neukirchen, S.; Seel, S.; Oppel, I. M.; Dyker, G. *Synlett* **2009**, 133; (g) Zhang, L.; Bruneau, C.; Doucet, H. *Chem. Commun.* **2013**, 49, 5353; (h) Murai, M.; Takami, K.; Takeshima, H.; Takai, K. *Org. Lett.* **2015**, 17, 1798; (i) Murai, M.; Yanagawa, M.; Nakamura, M.; Takai, K. *Asian J. Org. Chem.* **2016**, 5, 629.
- (a) Hong, B.-C.; Sun, H.-I.; Chen, Z.-Y. *Chem. Commun.* **1999**, 2125; (b) Pelloquin, A. J.; Stone, R. L.; Avila, S. E.; Rudico, E. R.; Horn, C. B.; Gardner, K. A.; Ball, D. W.; Johnson, J. E. B.; Iacono, S. T.; Balaich, G. J. *J. Org. Chem.* **2012**, 77, 6371.
- (a) Antras, F.; Ahmar, M.; Cazes, B. *Tetrahedron Lett.* **2002**, 43, 5029; See also (b) Andrew, T. L.; Cox, J. R.; Swager, T. M. *Org. Lett.* **2010**, 12, 5302; (c) Eshdat, L.; Berger, H.; Hopf, H.; Rabinovitz, M. *J. Am. Chem. Soc.* **2002**, 124, 3822; (d) Sinu, C. R.; Suresh, E.; Nair, V. *Org. Lett.* **2013**, 15, 6230.
- Mohand, A.; Belkessam, F.; Soule, J.-F.; Doucet, H. *ChemCatChem* **2016**, 8, 1583.
- For a review on transition-metal catalysed desulfurative couplings: Yuan, K.; Soule, J.-F.; Doucet, H. *ACS Catal.* **2015**, 5, 978.
- For Heck reaction with benzenesulfonyl chlorides: (a) Miura, M.; Hashimoto, H.; Itoh, K.; Nomura, M. *Tetrahedron Lett.* **1989**, 30, 975; (b) Miura, M.; Hashimoto, H.; Itoh, K.; Nomura, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2207; (c) Dubbaka, S. R.; Vogel, P.; *Chem. Eur. J.* **2005**, 11, 2633.
- (a) Zhao, X.; Dimitrijevic, E.; Dong, V. M. *J. Am. Chem. Soc.* **2009**, 131, 3466; (b) Zhao, X.; Dong, V. M. *Angew. Chem., Int. Ed.* **2011**, 50, 932; (c) Chen, R.; Liu, S.; Liu, X.; Yang, L.; Deng, G.-J. *Org. Biomol. Chem.* **2011**, 9, 7675.
- For a review on transition-metal mediated C-S bond activation: Wang, L.; He, W.; Yu, Z. *Chem. Soc. Rev.* **2013**, 42, 599.
- (a) Yuan, K.; Doucet, H. *Chem. Sci.* **2014**, 5, 392; (b) Loukotova, L.; Yuan, K.; Doucet, H. *ChemCatChem* **2014**, 6, 1303; (c) Jin, R.; Yuan, K.; Chatelain, E.; Soule, J.-F.; Doucet, H. *Adv. Synth. Catal.* **2014**, 356, 3831; (d) Skhiri, A.; Beladhria, A.; Yuan, K.; Soule, J.-F.; Ben Salem, R.; Doucet, H. *Eur. J. Org. Chem.* **2015**, 4428.