Synthesis of Substituted Tripod-Shaped Tri(p-phenylene)s

Jesús Hierrezuelo, ¹ <u>Elena Guillén,</u> ¹ J. Manuel López-Romero, *¹ Rodrigo Rico, ¹ M. Rosa López-Ramírez, ² J. Carlos Otero, ²

1 Dept. de Química Orgánica, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain
2 Dept. de Química Física, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain
E-mail: elenguillen@uma.es

For the development of organic thin films with applications in the construction of molecular scale devices it is needed i) the control of the orientation and spacing between functional groups in the film, ii) the availability of methods for the effective derivatization of the modified surface, and iii) for biological applications, the surface should resist the non-specific protein adsorption in order to avoid sensor contamination. ¹

We report here the synthesis of several tripod-shaped oligo(*p*-phenylene)s with each tripod leg composed of three or four phenylene units. Each leg is end-capped with an iodine atom, TMS or carboxyl group, and an ethoxy group is present at the functional arm. One of the tripods presents a methoxylated side substitution (Figure 1). The key step of the synthesis is the Pd-catalyzed Suzuki cross-coupling reaction² of the silicon derivative core molecule with the appropriate substituted *p*-biphenyl moiety. This synthesis represents a new and convergent strategy since iterative coupling of the substituted biphenyl buildings blocks with the first-generation tripods will allow the homologation of the tripod legs to reach giant tripod-shaped oligo(*p*-phenylene)s. Also, the iodine end-capped leg and the ethoxy group at the functional arm permit the design of the tripod for the nanostructuration of different surfaces and applications.³ Geometry of some of the synthesized tripods was optimized by theoretical calculations (B3LYP/6-31G level of theory) combined with the analysis of their Raman bands.

References:

- [1] (a) Organic Thin Films for Waveguiding Nonlinear Optics; Kajzar, F.; Swalen, J. D.; Eds.; Gordon & Breach: Amsterdam, **1996**. (b) Southern, E.; Mir, K.; Shchepinov, M. Nat. Genet. **1999**, 21, 5-9. (c) Houseman, B. T.; Mrksich, M. Angew. Chem., Int. Ed. **1999**, 38, 782-785.
- [2] Miyaura, N.; Suzuki, A. Chem. Rev., 95, 1995, 2457-2483
- [3] (a) López-Romero, J. M.; Rico, R.; Martínez-Mallorquín, R.; Hierrezuelo, J.; Guillén, E.; Cai, C.; Otero, J. C.; López-Tocón, I. *Tetrahedron Lett.* **2007**, 48, 6075-6079. (b) López-Tocón, I.; Peláez, D.; Soto, J.; Rico, R.; Cai, C.; López-Romero, J. M.; Otero, J. C. *J. Phys. Chem.* **2008**, 112, 5363-5367. (c) Deng, X.; Mayeux, A.; Cai, C. *J. Org. Chem.* **2002**, 67, 5279-5283. (d) Deng, X.; Cai, C. *Tetrahedron Lett.* **2003**, 44, 815-817.

Figures 1

$$H_3CO$$
 H_3CO
 H_3CO
 OCH_3
 OCH_3
 OCH_3
 OCH_3
 OCH_3