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Supporting Information

New Organic Materials Based on Multitask 2*H*-benzo[*d*]1,2,3-triazole Moiety

Iván Torres-Moya *, José Ramón Carrillo, Ángel Díaz-Ortiz and Pilar Prieto

Department of Inorganic, Organic Chemistry and Biochemistry, Faculty of Science and Chemical Technologies, University of Castilla-La Mancha, 13071 Ciudad Real, Spain; Joseramon.carrillo@uclm.es (J.R.C.); Angel.Diaz@uclm.es (Á.D.-O.); MariaPilar.Prieto@uclm.es (P.P.)

* Correspondence: Ivan.TorresMoya@uclm.es

1. General Procedure for the Preparation of Derivatives 1.

A mixture of 2-aryl-4,7-dibromo-2*H*-benzo[*d*][1,2,3]triazole (**3**) (1 eq.), the corresponding acetylene derivative (**4**) (2 or 3.5 eq.), DBU (2 eq.), CuI (0.05 eq.) and Pd-Encat™ TPP30 (0.035 eq.) was charged under argon to a dried microwave vessel. CH_3CN (1 mL) was added. The vessel was closed and irradiated at 130ºC (170ºC in the case of 1g) for 20 min. The crude product was purified by column chromatography, eluting with hexane/ethyl acetate (9:1), to give analytically pure products **1**. [24]

2. General Procedure for the Preparation of Derivatives 5.

A mixture of 2-(3,5-bis(trifluoromethyl)phenyl)-4,7-dibromo-2*H*-benzo[*d*][1,2,3]triazole (0.100 g, 0.2 mmol), the corresponding acetylene derivative (0.4 mmol), DBU (0.061 g, 0.40 mmol), CuI (0.002 g, 0.01 mmol) and Pd-EncatTM TPP30 (0.018 g, 0.007 mmol) was charged under argon to a dried microwave vessel. CH_3CN (1 mL) was added. The vessel was closed and irradiated at 130ºC for 20 min. The crude reaction product was purified by chromatography, eluting with hexane/ethyl acetate to give analytically pure products **5**. [30,55]

3. General Procedure for the Preparation of Derivatives 6.

3.1. General Procedure for the Synthesis of derivatives 6a, 6c, and 6d

A mixture of 2-(3,5-bis(trifluoromethyl)phenyl)-4,7-dibromo-2*H*-benzo[*d*][1,2,3]triazole (0.200 g, 0.41 mmol), $Pd(OAc)_2$ (0.9 mg, 0.0041 mmol), NaOAc (0.168 g, 2.05 mmol), nBu4NBr (0.0258 g, 0.082 mmol), and DMF (3 mL) was heated at 100 °C with efficient stirring for 24 h. The fluorescent solution was poured into water. The precipitate was filtered, washed with water, dissolved in dichloromethane, and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the residue was purified by means of column chromatography on silica gel to give pure products **6a**, **6c**, or **6d**. [45]

3.2. Synthesis of 6b

A mixture of **5f** (0.156 g, 0.24 mmol), $HSiEt_3$ (0.14 g, 0.0012 mmol), [$PdCl_2$(dppf)] (0.008 g, 0.001 mmol), dppf (0.017 g, 0.00003 mmol), $CuSO_4$ (0.035 g, 0.0001 mmol), and toluene/H_2O (5 mL/1 mL) was heated at 120 °C for 12 h. The end of the reaction was detected by TLC. Finally, an orange solid was obtained by chromatography, eluting with hexane/ethyl acetate (50:1). [45]

4. General Procedure for the Preparation of Derivatives 7.

A mixture of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (6) (0.001 g, 0.34 mmol), the corresponding alkynyl derivative (1.68 mmol), DBU (0.102 g, 1.34 mmol), CuI (0.003 g, 0.017

mmol) and Pd-EncatTM TPP30 (0.03 g, 0.012 mmol) was charged under argon to a dried microwave vessel. Then CH_3CN (1 mL) was added. The vessel was closed and irradiated at 130 °C for 25 min. The crude reaction product was purified by chromatography, eluting with hexane/ethyl acetate (3:1) to give derivatives **7** in good yields. [44]

5. Synthesis of the CPE 12

Monomers, **10** (0.3 mmol), **3a** (0.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.005 mmol) were mixed in a microwave (MW) tube in an inert atmosphere. Subsequently, 4 mL of toluene was added together with 1 drop of Aliquat® 336 (phase-transfer catalyst), the mixture was stirred until completely dissolved and 2 mL of potassium carbonate (water solution, 2 M) was added. Finally, it was left to react in a MW reactor under the following conditions: 135 °C, 22 min and 150 W of power. The organic solvents were removed by evaporation and the product was solubilized in 2 mL of chloroform, precipitated in 250 mL of methanol and filtered under vacuum. The final precipitated product **11** is left to dry under vacuum at 40 °C to give 120 mg yellow-green solid.

11 (0.11 mmol) was dissolved in tetrahydrofuran (50 mL) at –78 °C (dry ice-acetone bath) in an inert atmosphere. Meanwhile, in a different flask, a solution of trimethylamine in water was heated up to 50 °C. Trimethylamine (~7 mL) was added in tetrahydrofuran drop by drop, by using a coldfinger condenser. The mixture was left stirring at room temperature for 24 h. Afterwards, 50 mL of water was added to the reaction flask and the previous procedure was repeated by adding more trimethylamine (~7 mL) and the mixture left stirring for 24 h at room temperature. The solvent and the excess of trimethylamine were evaporated. Approximately 80 mg of solid polymer **12** with yellow colour was precipitated in acetone. Polymer was collected by filtration and dried under vacuum at 40 °C. [68]