Supplementary Material (ESI) for Green Chemistry

Supplementary information

Alternating CO/*tert*-butylstyrene copolymerisation using soluble cationic palladium complexes in supercritical carbon dioxide

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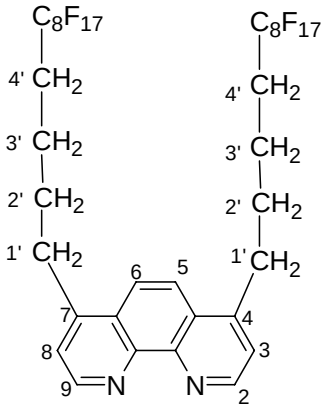
Preparation of 2



A solution of n-butyllithium 1.6 M in hexane (10.5 ml, 3.5 eq, 16.8 mmol) was added, via a syringe, to a solution of diisopropylamine (2.7 ml, 4 eq., 19.2 mmol) in tetrahydrofuran (5 ml) at –78 °C. The solution was stirred for 20 min. at –78 °C and 4,7-dimethylphenantroline (1 g, 4.8 mmol) in 75 ml of tetrahydrofuran was then added dropwise. The dark brown solution was stirred at –78 °C for 1 h. Then, 3-perfluorooctyl-1-iodopropane (6.77 g, 11.52 mmol) in 50 ml of tetrahydrofuran was added slowly via a syringe at –78 °C. The violet solution was stirred for 5 h at –78 °C and at room temperature overnight. The solvent was removed under reduced pressure. Then, 60 ml of water were added and the mixture was extracted twice with 75 ml of diethylether, and with dichloromethane (2 x 75 ml). The organic extracts are collected and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallized from

dichloromethane/pentane. The product was obtained as brown solid. Yield = 32 %. EIMS m/z: 1129.3 $[M + H]^{+\cdot}$. High resolution EIMS:1129.13, $C_{36}H_{23}F_{34}N_2$

Preparation of 3

A solution of 4,4‘-bis[4‘’-(F-octyl)-butyl]-2,2‘-bipyridine (250 mg. 0.2265 mmol) was added to a solution of [PdClMe(cod)] (50 mg, 0.1887 mmol) in 1 ml of dichloromethane. The yellow mixture was stirred at room temperature for 3.5 h. The complex was filtered off and washed with dichloromethane. This complex was not enough soluble in organic solvents to allow its NMR spectra to be recorded. Yield = 96 %. EIMS) *m/z*: 1210.0 $[M\text{-}Cl\text{-}CH_3]^+$, 1105.2 [**1**+1]

Preparation of 4

A solution of 4,7‘- Bis[4‘’-(F-octyl)-butyl]-1,10-phenantroline (300 mg. 0.026 mmol) was added to a solution of [PdClMe(cod)] (70 mg, 0.0026 mmol) in 5 ml of dichloromethane. The mixture was stirred at room temperature for 3.5 h. The product was filtered off and washed with dichloromethane. This complex was not enough soluble in common deuterated solvents to allow its NMR spectra to be recorded. Yield = 87 %. EIMS m/z: 1234.9 $[M + H\text{-}Cl\text{-}CH_3]^{+\cdot}$.

Preparation of 5

To a suspension of [4,4‘-di-[4‘’-(F-octyl)-butyl]-2,2‘-bipyrydil]chloromethylpalladium (II) (61 mg, 0.048 mmol) in 5 ml of dichloromethane were added sodium tetrakis 3,5-bis-(trifluoromethyl)phenyl borate (40.5 mg, 0.048 mmol) and 0.3 ml of acetonitrile. The mixture was heated 1h at 40 ºC. The product was filtered off over celite and the solvent was removed under reduced pressure. The product was obtained as an oil. Yield = 78 %. EIMS m/z: 1266.0 $[M - BARF]^{+\cdot}$, 1224.9 $[M – BARF\text{-} NCCH_3]^{+\cdot}$

Preparation of 6

To a suspension of 4,7‘- Bis[4‘’-(F-octyl)-butyl]-1,10‘-phenantroline (62.2 mg, 0.048 mmol) in 5 ml of dichloromethane was added sodium tetrakis-3,5-bis-(trifluoromethyl)phenyl borate (40.5 mg, 0.048 mmol) and 0.3 ml of acetonitrile. The

mixture was heated 1h at 40 ºC. The product was filtered off over celite and the solvent was removed under reduced pressure. The product was obtained as an oil. Yield = 95 %. MALDI-TOF m/z: 1233.8 $[M - NCCH_3 - CH_3 - BARF]^{+\cdot}$.