Synthesis and Properties of Oligo-/Polymers Based on a "Flexible" Swivel-Cruciform Structure

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Summary: We have introduced the concept of the so-called swivel type cruciforms as a highly flexible tool to tune the molecular properties from amorphous to highly crystalline features. Simple alkoxy substituted binaphthyl building blocks have been introduced randomly into poly(9,9-dioctylfluorene) (PFO) thereby suppressing the formation of side-chain crystallization. On the other hand the all aryl pentathiophene based cruciform exhibited strong π–π interaction between the arms and gave one of the highest values reported to date for wet processed organic field effect transistors (OFETs) utilising oligothiophenes.

Keywords: field effect transistor (FET); lasing; morphology; oligothiophene; polyfluorene (PF)

1. Introduction

Research into the design, understanding and application of organic semiconductors (OSCs) has intensified in the last decade. OSCs are expected to be viable components in a diverse range of optoelectronic devices including organic field effect transistors (OFETs),[1] organic light emitting diodes (OLEDs),[2] lasers[3] and photovoltaic cells.[4] It has recently become clear that the subject of nanoscopic and macroscopic order in π-conjugated systems is extremely important, as it is the solid-state morphology that determines the efficiency of electronic or optoelectronic devices.[5] Recent findings have shown that it is frequently advantageous to apply amorphous materials e.g. for OLED applications, as aggregates tend to promote non-radiative recombination processes.[6] Conversely, efficient intermolecular interaction can greatly enhance the charge carrier mobility. Accordingly, polymers and oligomers that encourage substantial intermolecular π-π overlap are often excellent charge transporting components for organic field-effect transistors (OFETs).[7] Therefore, the ability to control the spatial orientation and packing of both oligomers and polymers when they assemble in the solid state is a worthwhile, although non-trivial endeavour.

In this paper we describe our developments in manipulating the morphology of polymeric and oligomeric OSCs by utilising swivel-cruciform type building blocks based on binaphthyl and biphenyl cores as depicted in Figure 1. The main difference between these cross-like structures and other reported cruciform type molecules[8] is that in the swivel version there is, at least in principle, free rotation between the arms in addition to within the arms. Our initial motivation was to utilize these swivel-cruciform cores to generate non-planar, non-interacting oligomers and polymers. We expected that by disrupting the capacity of a material to planarize we could enhance the likelihood of glass formation.[6]

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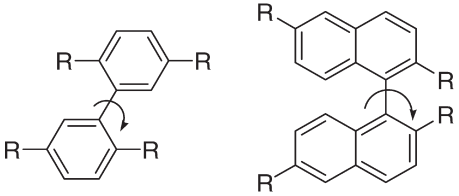


Figure 1.
Structure of swivel – cruciform building blocks.

However, it quickly became clear that by manipulating the pendant groups on these swivel-cruciforms it was possible in some cases in fact to introduce a high degree of order biased by intramolecular π–π interactions, while in other instances the formation of unwanted aggregates could be avoided.

2. Results and Discussion

Polyfluorenes are a perfect example to illustrate the sensitive interplay between molecular and supramolecular structure.[9] Particular interest has been devoted to the packing behaviour of the polymer chains in solid-state films of poly(9,9-dioctylfluorene) (PFO). It has emerged, that aside from a glassy phase (α-phase) in PFO films an aggregated or β-phase occurs, which is characterized by high intra-chain order with a fixed rotational angle of 180° between adjacent monomer units.[10] The tell tale signature of the β-phase can be garnered from photoluminescence (PL) experiments and is indicated by a red-shifted and more structured emission with respect to that of the glassy state or solution PL characteristics. Even low fractions of the β-phase dominate the PL behaviour of the polymer. A rather more drastic consequence of such agglomerated species in PFO films is a decrease in the PL quantum efficiency, which is attributed to the formation of stable quenching polarons.[11] It is expected to be particularly detrimental in applications such as for organic lasers. Therefore, the elimination of the β-phase seemed a worthwhile endeavour for improving the performance of organic thin-film lasers based on PFO.

Based on the perception that interchain interactions should be suppressed by introducing non-planar units into PFO we decided to prepare random copolymers incorporating binaphthyl moieties into the polymer backbone.[12] The dihedral angle between the two adjacent naphthalene rings can range from 60–120° depending on the substitution pattern.[13] Furthermore, the pseudo–orthogonal nature of the binaphthyl unit should simultaneously facilitate the formation of a glassy amorphous state.[14] PFO and the random copolymers incorporating the binaphthyl units were prepared via Nickel-mediated Yamamoto coupling reactions (Figure 2) by simply varying the relative ratios of the comonomers as given in Table 1. The actual amount incorporated was determined by comparing the relative intensities of the $O\text{–}CH_2$ proton signal at about $\delta = 3.9$ ppm resulting from the binaphthyl side-chain to the sum of the aryl proton signals.

The thermal properties were investigated by differential scanning calorimetry (DSC) in the range 0–300 °C with a heating and cooling rate of 10 °C min^{-1}. The incorporation of the binaphthyl unit has a dramatic effect on the thermal properties of the copolymers even at low binaphthyl concentrations. The sample with 4% binaphthyl exhibits both a clear T_g at 78 °C and a T_{LC} at 147 °C. However, unlike PFO itself, no melting peak was found. For the two copolymers with 9.4 and 12.1% binaphthyl content only T_g at 82 °C and 83 °C respectively were observed. The fact that the copolymers with the higher concentration of the binaphthyl unit form stable amorphous glasses with little discernable tendency to crystallise was already encouraging.

However, as stated above the true test to identify the influence of incorporating the binaphthyl spacer is to examine the optical properties of the copolymers in thin film and therefore low temperature ($T = 30$ K) PL measurements were performed. Figure 3 clearly shows that the film formed from

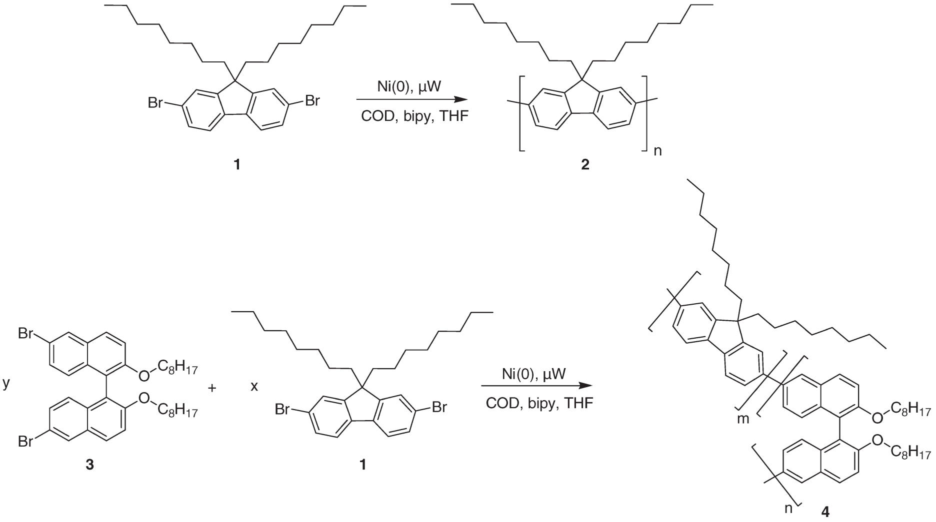


Figure 2.
Synthesis of PFO and the random copolymers incorporating binaphthyl spacers.

Table 1.
Feed ratios for the preparation of the random copolymers **4** and their molecular weight.

Name	X (mmol)	y (mmol)	y/(x + y) (%)	n/(m + n) (%)	Mn	PD
PFO (2)	2.01	0			190,000	2.4
BNPFO[a]-5% (4a)	2.01	0.11	5.19	4.24	90,000	2.1
BNPFO[a]-10% (4b)	2.01	0.22	9.87	9.44	160,000	2.2
BNPFO[a]-15% (4c)	2.01	0.30	12.99	12.05	128,000	1.6

[a] BNPFO: binaphtyl-(9,9-dioctylfluorene)-copolymers

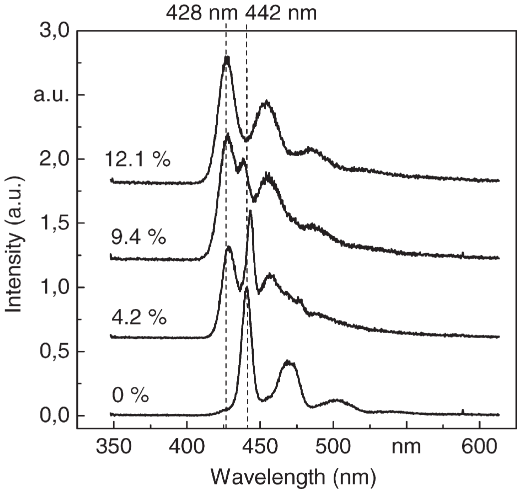


Figure 3.
Low temperature (T = 30 K) photoluminescence spectra of polymers **2** and **4a–4c** in thin films.

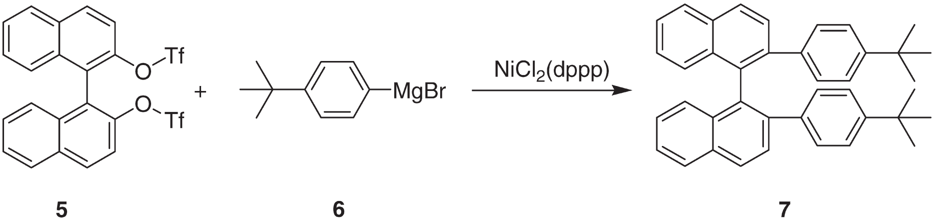


Figure 4.
Synthesis of the binaphthyl based swivel cruciform **7**.

PFO is dominated by the strong PL features originating from ß-phase, with the main transition at $\lambda = 442$ nm. With increasing binaphthyl concentration, the PL contribution from the ß-phase becomes weaker and is totally absent at a concentration of 12.1% with the PL emission now resembling that of the isolated polymer chain in solution.

The implications of the suppression of the ß-phase on the lasing threshold of laser devices utilising these polymers was investigated. Distributed feedback lasers (DFB) based on the respective polymers, as active gain media have been prepared on SiO_2/Si substrates.[12] A minimum threshold for second order DFB lasers based on unmodified PFO is found to be 11.7 μJ/cm^2 ($\lambda = 452$ nm). Towards higher binaphthyl concentrations in the copolymer the laser threshold decreases steadily to 3 μJ/cm^2 for the PFO derivative with 12.1% binaphthyl concentration. Hence, by incorporating the non-planar binaphthyl unit randomly into the PFO backbone we could suppress interchain interaction and concomitantly augment the effectiveness of the lasing process by lowering the energy threshold at which lasing takes place.

While working on a related series of molecules we prepared the binaphthyl derivative **7** by the synthetic route depicted in Figure 4. In our hands the yield was particularly poor but nevertheless, a full characterization, of **7** was achieved. The crystal structure of **7** has been elucidated from single crystals obtained from THF[15] and reveals that the molecule adopts a folded helical conformation in the solid-state that is characterized by an almost parallel orientation and a partial overlap of the 4-tert-butylphenyl rings (Figure 5). Offset parallel geometries are believed to be favourable for π-π interactions.[16] However, it should be noted that a purely geometrical analysis of these distances is only an indirect measure of electronic interactions.[17]

Significantly though, the question as to whether intramolecular π–π stacking rather than crystal packing biases some of these ortho-quater-aryls towards foldamer formation has not been unequivocally communicated. However, in the case where signal assignment is possible, a ^{1}H NMR study may be useful in identifying the driving forces, which induce torsionally flexible molecules to adopt a folded structure. Figure 6 shows the aromatic region of the proton NMR spectrum of **7**. The most notable feature is the high-field position of two directly coupled doublets at $\delta = 6.18$ and 6.77 ppm associated with the protons of the pendant 4-tert-butylphenyl units. This

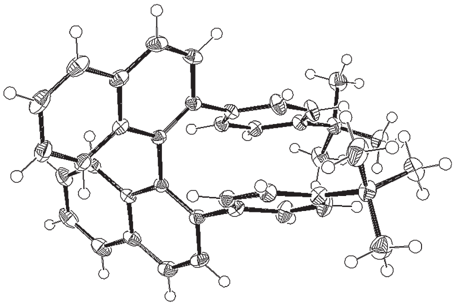


Figure 5.
Two different views of the X-ray structure of compound **7**.

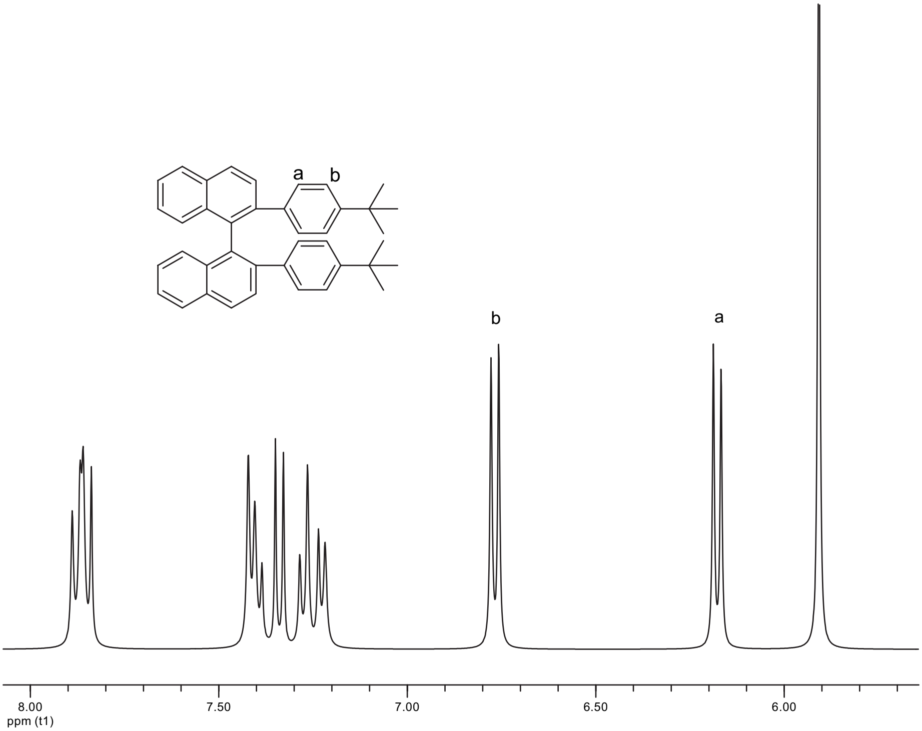


Figure 6.
^{1}H NMR spectrum of **7**.

kind of shielding effect has been observed in conformationally rigid carbohelicenes and is due to the increased overlap of the aromatic rings.[18] In view of this we propose that the pendant phenyl rings of **7** adopt a folded conformation also in solution and most probably originates from the strong σ-π attraction between the protons of one tert-butyl-phenyl unit and its homologous neighbour. This implies that the driving forces that predispose the conformational dynamics of the molecule to favour a folded helical type conformation in the solid-state result from π-related intramolecular interactions.

To date the number of publications, which include crystallographic data of related ortho-oligoaryls that adopt such

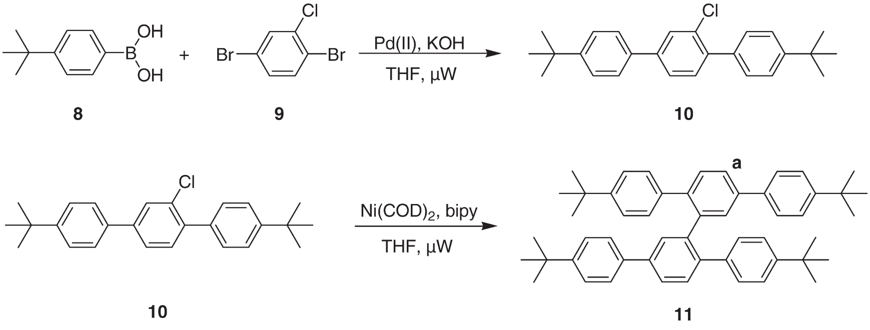


Figure 7.
Synthetic approach towards compound **11**.

helical or folded pattern solid-state patterns are still relatively meager.[19] Therefore we synthesised the "true" cruciform type terphenyl dimer 2,5,2′,5′-tetra(4-tert-butylphenyl)1,1′-biphenyl (**11**) via the strategy depicted in Figure 7.[20]**11** was obtained via a Nickel – mediated microwave – assisted Yamamoto type coupling of **10** in reasonable yields using THF as the solvent at temperatures of about 130 °C.[21]

The X-ray investigation of **11** revealed that it too adopts a folded solid-state structure due to strong intramolecular π–π interactions (Figure 8). Analysis of the ^{1}H-^{1}H COSY, ^{1}H-^{1}H COSYLR and the ROESY spectra of **11** allow an unambiguous assignment of all the protons in the molecule. Figure 10 shows the aromatic region of the proton NMR spectrum of the terphenyl dimer 2,5,2′,5′-tetra(4-tert-butylphenyl)1,1'-biphenyl. The most notable feature is again the high-field position of two directly coupled doublets. They are found at $\delta = 6.34$ and 6.87 ppm and represent the four protons of the 4-tert-butylphenyl units. The spatial proximity between the upfield doublet at $\delta = 6.51$ ppm and the proton signal Ha at $\delta = 7.21$ ppm (Figure 7) from the central tetra-substituted biphenyl unit is manifested by the strong coupling between the signals in the 2D ROESY spectrum.

The strong π–π interaction between the arms of the swivel-cruciform **11** led us to investigate if such a molecular design might be advantageous for solution phase fabrication of ordered thin film OFETs. Hence we synthesised the related all thiophene αα′-dihexylpentathiophene based swivel-cruciform dimer **DHPT-SC** via a palladium assisted Suzuki coupling (Figure 9).[22] Interestingly, this molecular shape seemed to enhance the solubility, which allowed for a detailed characterisation of **DHPT-SC** by NMR spectroscopy and also portended well for the task of preparing ordered thin films from solution. Differential scanning calorimetry (DSC) measurements of **DHPT-SC** showed only one distinct transition at 196 °C (Figure 12). During cooling the isotropic-crystalline transition was observed at 178 °C. Such thermal behaviour indicates the propensity of the molecule to form a reproducible crystalline phase.

Figure 10 shows the scattering pattern from a thin film cast from a chloroform solution and was annealed at 120 °C for 5 minutes followed by slow cooling (1.3 K/min). Interestingly, the appearance of clearly resolved (001) and (002) Bragg peaks indicates that **DHPT-SC** forms a well-ordered layered structure in the solid state as typically observed for (α,(ω-dihexyloligothiophenes.[23] Kiessig thickness fringes are clearly visible up to the first diffraction peak (001) indicating that **DHPT-SC** forms smooth layers of a thickness of 52 nm.

OFETs based on **DHPT-SC** exhibited negative amplification, which is typical of p-type semiconductors with well defined linear and saturation regions. No hysteresis was observed in the measurements, which indicates very good current modulation and

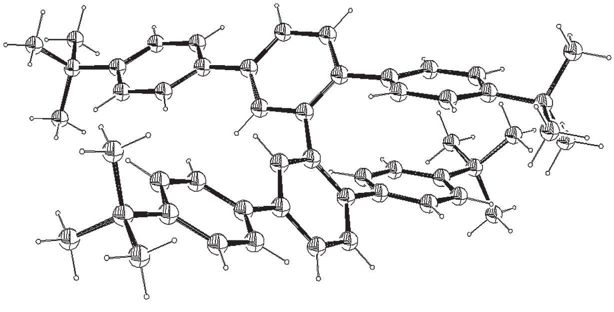
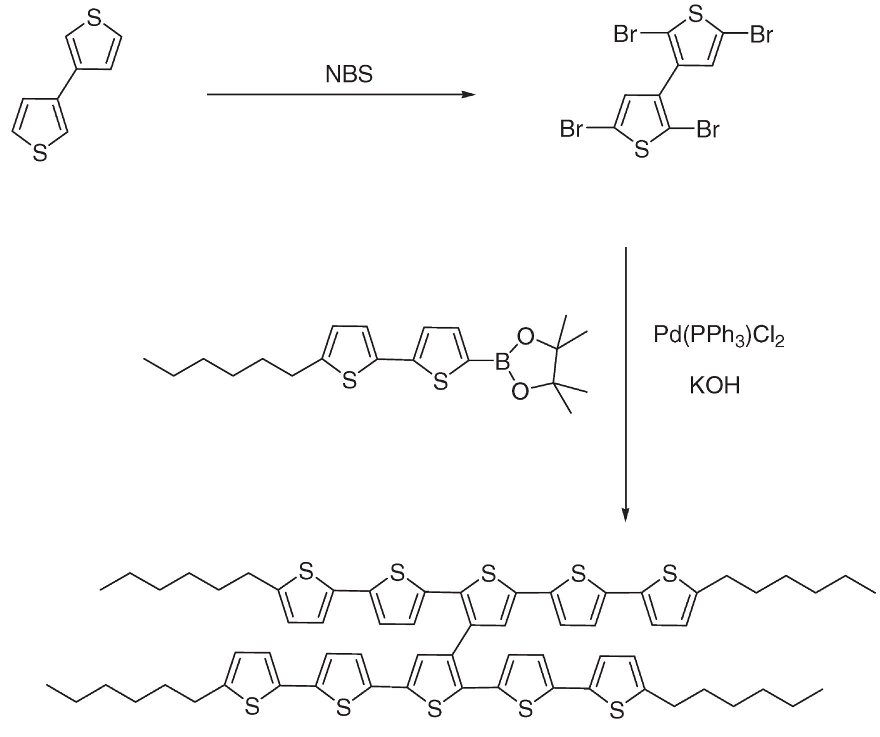


Figure 8.
Single crystal structure of 2,5,2′,5′-tetra(4-tert-butylphenyl)1,1′-biphenyl (**11**).



(**DHPT-SC**)

Figure 9.
Synthetic strategy for the preparation of **DHPT-SC**.

stability during operation. For non-annealed **DHPT-SC**, we obtained a field-effect mobility (μFET) of 9.6×10^{-3} cm^2/Vs and a current on/off ratio of 6×10^4 at VDS = −80 V The device made from the annealed sample gave a slight improvement in charge carrier mobility (μFET of 0.012 cm^2/Vs) with an increased on/off ratio (>105) and is one of the highest values reported to date for wet processed OFETs utilising oligothiophenes.[24]

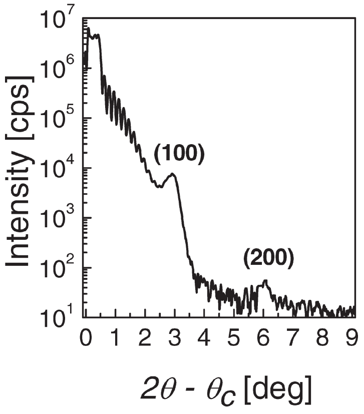


Figure 10.
X-ray reflectivity scan of thin films of **DHPT-SC**.

3. Conclusion

We have demonstrated that the choice of pendant group allows the modulation of the solid-state order of "flexible" cruciform type monomers. Hence, depending on whether a particular application requires an amorphous or crystalline material it may be possible to force a particular morphology by incorporating one or other of these building blocks.

Simple binaphthyl building blocks have been applied in order to suppress the formation of the β-phase in PFO films. The mirroring of the optical properties of the copolymers with those of PFO in solution and the improved threshold characteristics for a second order distributed feedback (DFB) laser reflected the beneficial effect. By replacing the alkoxy groups of the binaphthyl unit with phenyl groups we were able to introduce strong intramolecular order to the structure in the solid-state. Examination of the ^{1}H NMR data of both **7** and the related swivel cruciform **11** confirms the presence of strong π–π related interactions within these molecules both in solution and in the solid state.

A novel pentathiophene based swivel-cruciform DHPT-SC was prepared in order to examine the whether such a motif could assist in increasing the charge carrier mobilities of oligomers spin cast from solution. The material exhibits increased solubility and this allows for the fluidic preparation of homogeneous microcrystalline films. OFETs based on DHPT-SC exhibited high field-effect mobility up to 0.012 cm^2/Vs.

4. Experimental

All reactions were carried out under an argon atmosphere. The solvents were used as commercial p.a. quality. ^{1}H- and ^{13}C-NMR data were obtained on a Bruker ARX 400 spectrometer. The UV–Vis and fluorescence spectra were recorded on a Jasco V-550 spectrophotometer and a Varian-Cary Eclipse spectrometer respectively. Low-resolution mass spectrometry was obtained on a Varian MAT 311A operating at 70 eV (Electron Impact, EI) and reported as m/z and percentage relative intensity.

Synthesis of 2,2′-Bis(4-tert-butylphenyl)-1,1′-binaphthyl (7)

A dried 10 mL reaction vial containing LiCl (150 mg, 3.54 mmol) under argon was charged with 4-tert-butylphenyl-magnesium bromide (4 mmol, 2 mL of a 2M solution), and stirred at −15 °C for 30 min in THF (5 mL). This solution was added slowly to a stirred mixture of 1,1′-binaphthyl-2,2′-bistriflate (500 mg, 0.9 mmol) and $NiCl_2$(dppp) (50 mg, 0.09 mmol) in THF (5 mL) at −15 °C. After 1 h the reaction was allowed to warm up to room temperature and stirred for 12 h at ambient temperature. After quenching with 2N HCl the mixture was poured into water and then extracted with dichloromethane. The organic phase was subsequently washed with water and brine, dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The residue was purified by thin layer chromatography on silica gel with hexanes/ethyl acetate (97:3) as eluent to give **7** in 10% yield. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 °C): $\delta = 7.88$ (d, 2H, J = 8.2 Hz), 7.85 (d, 2H, J = 8.5 Hz), 7.40 (m, 2H), 7.34 (d, 2H, J = 8.5 Hz), 7.29 – 7.20 (m, 4H), 6.77 (d, 4H, J = 8.3 Hz), 6.18 (d, 4H, J = 8.3 Hz), 1.15 (s, 18H) ppm. ^{13}C NMR (100 MHz, $C_2D_2Cl_4$, 80 °C): $\delta = 139.4$, 138.2, 134.8, 134.2, 132.4, 129.1, 128.9, 128.7, 128.2, 127.7, 126.6, 125.6, 124.6, 124.1, 34.4, 31.5, 31.4 ppm. LR-MS (EI, 70eV): m/z = 57 (98.21), 519 [M$^+$] (100.0).

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