Synthesis of peripherally substituted Ti(IV) phthalocyanines bearing bulky catecholate axial ligands

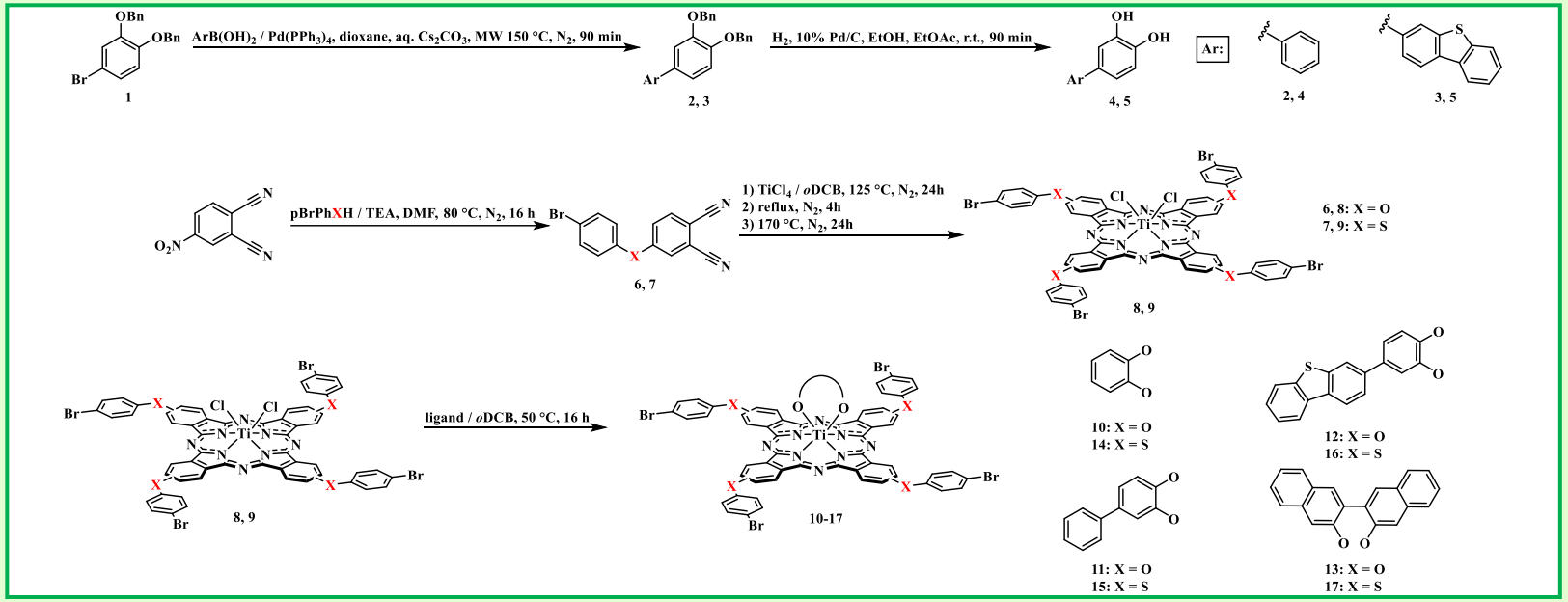
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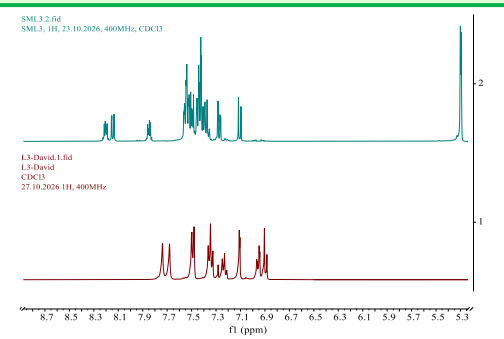
Abstract
In this work, peripherally substituted $TiCl_2$-phthalocyanines were synthesized with 4-bromothiophenolate and 4-bromophenolate moieties, and then catecholate substituents were introduced in the axial position. The catecholate substituents were synthesized via microwave-assisted Suzuki coupling between benzylated catecholate bromides and the corresponding boronic acids or boronic acid esters, followed by reductive debenzylation. The catechol derivatives were then reacted with the peripherally substituted $TiCl_2$-phthalocyanines, yielding the corresponding axially functionalized Ti(IV) phthalocyanines. We found that the Suzuki couplings, required shorter reaction times and achieved higher conversions under microwave conditions compared to conventional conditions. Furthermore, catecholate derivatives showed higher reactivity than racemic BINOL ligands, requiring milder reaction conditions and providing better conversions.

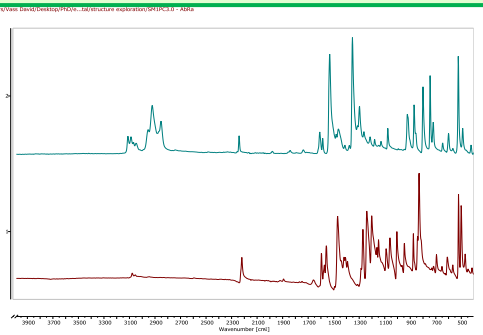
Apparatus
The UV-vis spectra were recorded on a Perkin Elmer Lambda 35 spectrometer. The FTIR spectra were recorded on a Brucker Advance II machine with ATR module. The HRMS spectra were recorded on a rapifleX MALDI-TOF/TOF spectrometer. The NMR spectra were recorded on a Brucker Advance 400 MHz and 600 MHz machine.

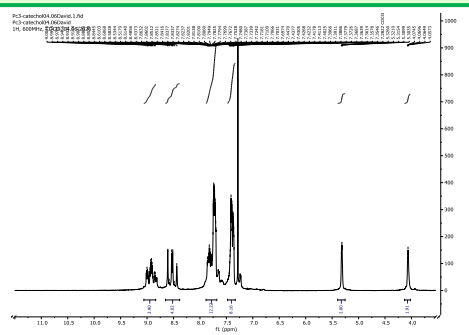
Conclusions
Microwave-assisted Suzuki cross-coupling is a highly effective method for synthesizing benzylated catecholate derivatives, offering a rapid, green procedure that achieves complete conversion and high yields. Furthermore, substituting the axial chlorine ligands on the titanium(IV) centre with catechol derivatives provides a robust and straightforward approach to optimizing the aggregation behaviour of titanium(IV) phthalocyanines.

Acknowledgements
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Fig. 1: Debenzylation of compound **3** (400 MHz, $CDCl_3$)


Fig. 2: Syntesis of coumpound **6** (FTIR-ATR)


Fig. 3: ^{1}H NMR spectrum of **10** ($CDCl_3$, 600 MHz)

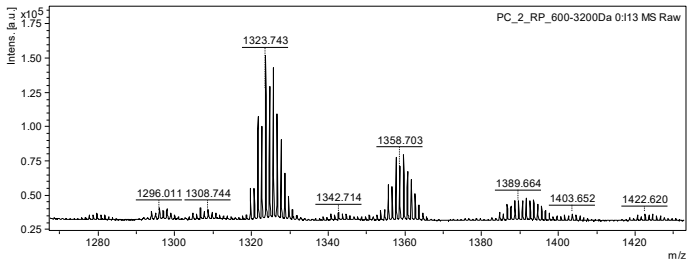


Fig. 4: MALDI-MS spectrum of compound **9**

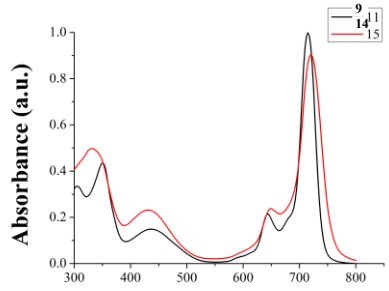


Fig. 5: Stacked UV-vis spectra of compounds **9** and **14** ($CHCl_3$, r.t., 10^{-6} M)