Supporting Information

On-surface homocoupling reactivity of a chiral bifunctional bromoindanone molecule on Cu(111)

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Chemical synthesis of (*R*)-6-bromo-3-phenyl-2,3-dihydro-1*H*-inden-1-one (BrPhINDO)

Indane nucleus is complex to derivate. To solve this problem, several solutions have been proposed in the literature, mostly involving diverse pre-functionalizations of the substrate, followed by an intramolecular cyclization, providing the indane core.[1,2] The nature of these reactions is diverse but, in our case, this classical strategy was abandoned (Fig S1a). Indeed, the ring closure occurred only on the previously introduced phenyl group due to the presence of the bromine on the cycle (Fig S1b). Based on the work of Zheng et al.,[3] we first performed an oxidation of 6-bromo-2,3-dihydro-1*H*-inden-1-one by mean of a radical bromination followed by an elimination reaction. This intermediate, i.e. 6-bromo-1*H*-inden-1-one, could be obtained in 45% yield (see details in Fig. S1c). Compared to the original procedure, 6-bromo-1*H*-inden-1-one was prepared with one major change, i.e. the solvent used for the reaction. Indeed, CCl_4 was substituted by 1,2-dichloroethane due to its lower toxicity and its easier availability. Afterwards, the phenyl group was introduced through a 1,4-addition with a cuprate, formed with PhLi, providing BrPhINDO with 78% yield. In addition, it is the first example of such reaction performed on the inden-1-one core, allowing to obtain our final product in only two steps. Finally, a semi-preparative chiral HPLC separation was performed to obtain enantiomerically pure BrPhINDO, where both enantiomers were used during the study.

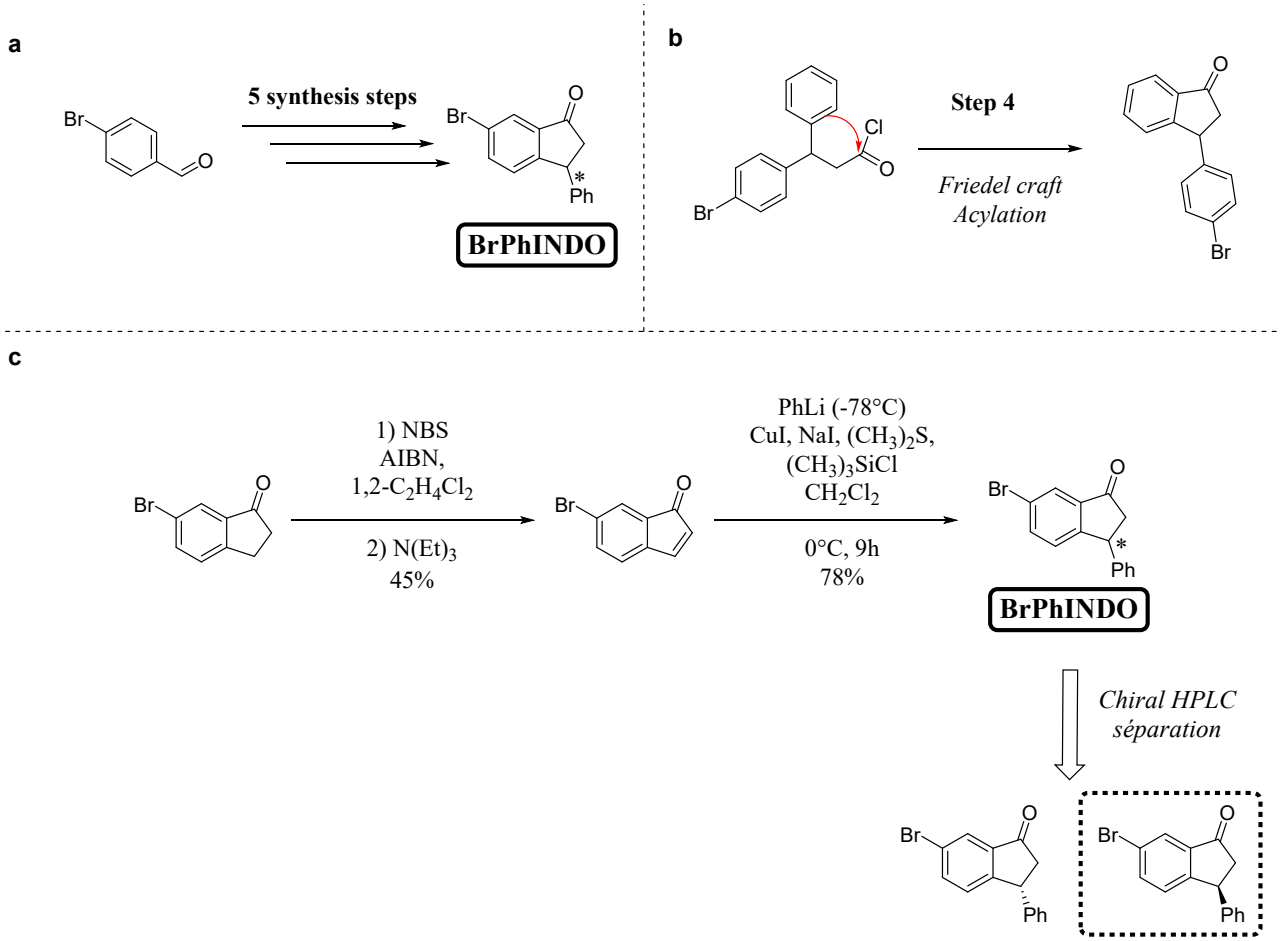

Figure S1: Synthesis strategies to obtain BrPhINDO, details for (a,b) in refs[4,5].

References

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(3) Zheng, S.; Tan, H.; Zhang, X.; Yu, C.; Shen, Z. Synthesis of benzo[c]fluorenone through a one-pot cascade reaction using inden-1-one derivatives. *Tetrahedron Lett.* **2014,** *55*, 975-978.

(4) Knudsen, M. M.; Kalashnyk, N.; Masini, F.; Cramer, J. R.; Laegsgaard, E.; Besenbacher, F.; Linderoth, T. R.; Gothelf, K. V. Controlling Chiral Organization of Molecular Rods on Au(111) by Molecular Design. *J. Am. Chem. Soc.* **2011,** *133*, 4896-4905.

(5) Parveen, N.; Sekar, G. Palladium Nanoparticles-Catalyzed Synthesis of Indanone Derivatives via Intramolecular Reductive Heck Reaction. *Adv. Synth. Catal.* **2019,** *361*, 4581-4595.

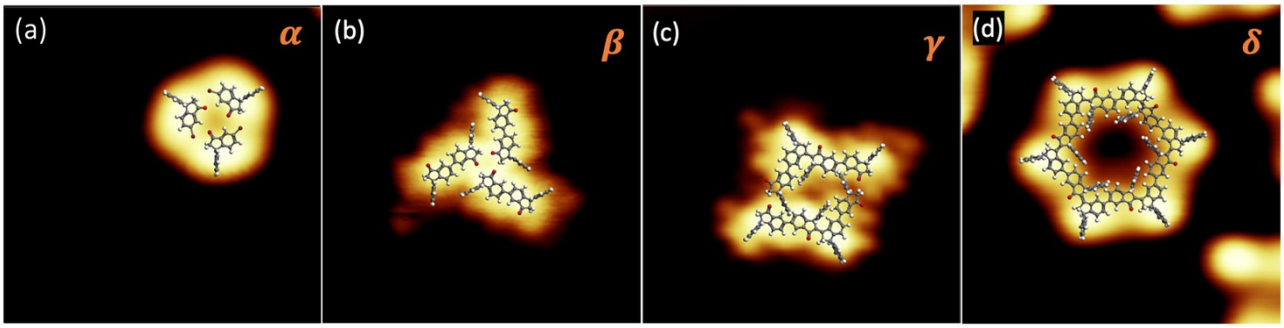

Figure S2: STM images with superimposed models of the different structures observed on Cu(111).

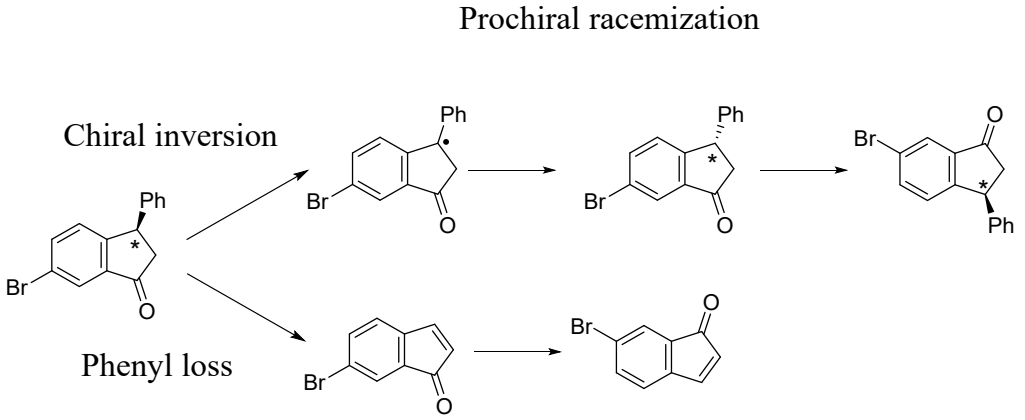

Figure S3: Prochiral racemization of the structures observed due to chiral inversion of the asymmetric carbon or phenyl loss. Prochirality is defined as the loss of symmetry induced by the planar adsorption, i.e. on which side the molecule is lying on the surface; the schematics represents here the top view of the adsorbed systems.

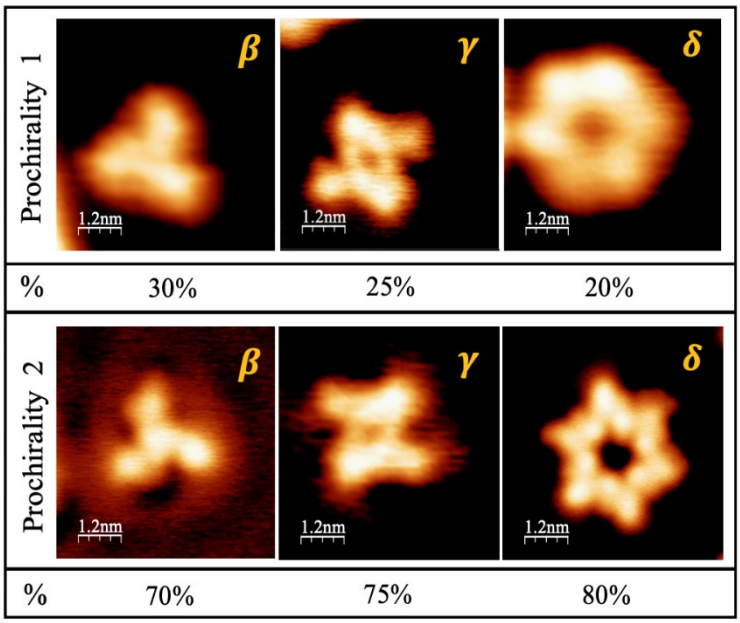

Figure S4: Different structures observed by STM for *S*-BrPhINDO on Cu(111). As expected, the prochirality abundance is inverted with respect to the *R*-BrPhINDO precursor.

	R-BrPhINDO			*S*-BrPhINDO		
	β	γ	δ	β	γ	δ
% of prochirality 1	70	75	85	30	25	20
% of prochirality 2	30	25	15	70	75	80

Table S1: Summary of the relative abundance of the two prochiralities of the β, γ and δ-structures obtained after deposition of the molecules *R*-BrPhINDO and *S*-BrPhINDO on Cu(111).