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Potential 1,1′-binaphthyl NLO-phores with extended conjugation between positions 2 and 6, and 2′ and 6′

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Abstract—A synthetic approach is reported which allows independent introduction of alkynyl groups to positions 2,2′ and then to 6,6′ of binaphthyls. The approach is based on the high selectivity of the Stephens–Castro alkynylation of 6,6′-dibromo-2,2′-diiodo-1,1′-binaphthyl. The tetraalkynylated derivatives exhibit extended conjugation between groups at positions 2 and 6, and 2′ and 6′, achieved by overcoming steric hindrance at positions 2 and 2′ by using alkynyl spacers.

C_2-Symmetric 1,1′-binaphthyls represent one of the most important groups of non-natural chiral-pool compounds.[1] During the last decade, they have been investigated for the design and preparation of NLO materials, motivated by their easy synthetic accessibility in enantiopure form (axial chirality), configurational stability (especially of 2,2′-substituted derivatives) and extended conjugation between positions 2 and 6, and 2′ and 6′, respectively. Derivatives, bearing acceptor groups at positions 6 and 6′ and donor groups at positions 2 and 2′, exhibited remarkably high values of the first hyperpolarizability β,[2–8] measured by EFISH[9] or HRS[10] techniques. However, antiparallel orientation of dipoles in the crystal lattice results in low second harmonic generation efficiency,[2] measured by the Kurtz–Perry powder test.[11] It was shown that this drawback can be overcome by the preorganization of dipoles by their fixation to either helical multipolar polymers,[3] or branched[4] or supramolecular polymers.[5]

Comparison of 2,2′- and 6,6′-substituted 1,1′-binaphthyl bis-NLO-phores to analogous monomeric 2 and 6-substituted naphthalenes shows that in the case of simple 2,2′-dialkoxy derivatives, the first hyperpolarizabilities correspond to the vector sum of the two naphthalene units of the molecule with no significant interaction between the dipoles.[6] However, bridged 2,2′-oligomethylenedioxy derivatives[6,7] and more donating 2,2′-bis(alkylamino) derivatives[3] exhibit lowered second harmonic generation efficiency due to the sterically induced twist of the donor groups resulting in ineffective overlap of the donor atom lone electron pairs with the π-systems of the naphthalene moieties. To obtain binaphthyl derivatives with a potentially more efficient NLO response, we aimed to synthesize derivatives where groups at positions 2 and 2′ are attached to the binaphthyl via sterically non-demanding conductive spacers, in particular ethynediyl units. Donor groups attached via such spacers at positions 2 and 2′ are expected to adopt optimal geometry to overlap orbitals with the binaphthyl-containing π-system.

For the synthesis of such target 2,2′- and 6,6′-alkynylated binaphthyls we needed to develop a synthetic method for independent introduction of alkynyl groups to positions 2,2′ and 6,6′. Among potential precursors (Fig. 1),

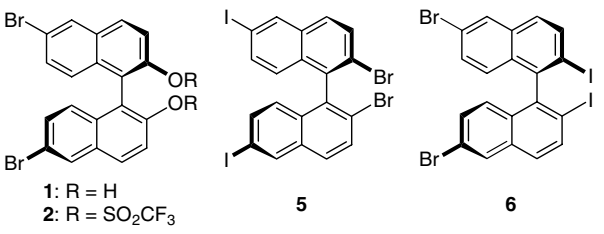

Figure 1. Potential key precursors for the synthesis of 2,2′- and 6,6′-alkynylated 1,1′-binaphthyls.

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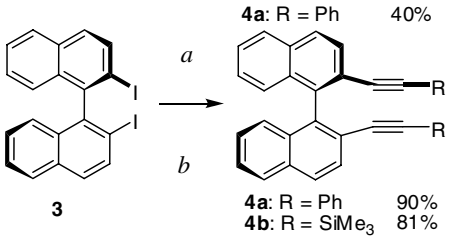
only the synthesis of dibromo diol **1**, potentially convertible to dibromo ditriflate **2**, was described in the literature.[12] However, based on our experience of the introduction of carbon groups to positions 2 and 2′, the reactivity of 1,1′-binaphthyl-2,2′-diyl ditriflate is not sufficient and only methylation could be performed effectively.[13–15] On the other hand, Sonogashira alkynylation of the more reactive diiodide **3** results in the formation of helicene products.[16] We showed that 2,2′-dialkynylation of diiodide **3** can be accomplished stereoconservatively (Scheme 1) either via thermal Stephens–Castro reaction with copper phenylacetylide[14] (40% yield) or by palladium catalyzed Negishi alkynylation of 2,2′-diiodide (*R*)-**3** (up to 90% yield).[14,15] Synthesis of 2,2′-dialkynylated derivatives **4** was also reported from 1,1′-binaphthyl-2,2′-dicarbaldehyde,[17] but the preparation of the latter from accessible starting materials requires several steps. Therefore, the preparation of diiodo dibromide **5** or dibromo diiodide **6**, as candidates for precursors, is necessary.

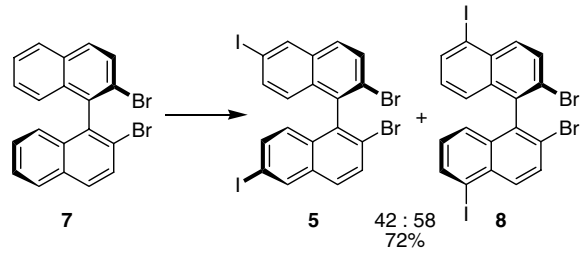
Taking into account the steric hindrance at positions 2 and 2′ and the generally higher reactivity of aryl iodides compared to aryl bromides in cross-coupling reactions, diiodo dibromide **5** should be a more suitable precursor compared to **6**. We expected it to afford higher chemo/regioselectivity in different alkynylations at positions 2,2′ and 6,6′, due to a match of steric and electronic effects. However, we failed to find an effective method for its synthesis, since the iodination of dibromide **7** did not proceed regioselectively: 5,5′-diiodo dibromide **8** was formed besides the target 6,6′-diiodo dibromide **5** (Scheme 2). Moreover, compounds **5** and **8** were difficult to separate.

We succeeded in the synthesis of dibromo diiodide **6** by direct bromination of diamine **9** using tetrabutylammonium tribromide, followed by transformation of the amino groups into iodine substituents (Scheme 3).[18] Protection of the amino groups of diamine **9** by acetylation was necessary for direct bromination with bromine (Scheme 3), otherwise oxidation products of diamine **9** predominated in the reaction mixture. The enantiomeric purity of dibromo diiodide **6** was proved by enantioselective HPLC using a Chiralcel Daicel OD-H column.

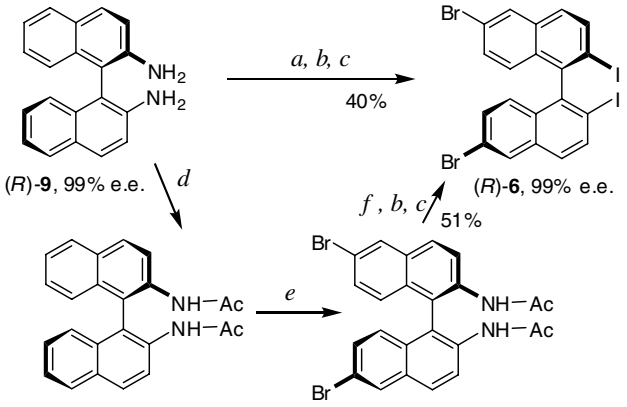
We found that Negishi alkynylation of dibromo diiodide **6** with zinc trimethylsilylacetylide did not proceed with sufficient chemoselectivity, affording a complex mixture of alkynylation products **10**–**13** (Scheme 4). Although this alkynylation takes place initially at the C–I bond (at position 2, then at 2′) and only then at the C–Br bond (at positions 6 and 6′), at least 6 equiv of organozinc reagent were required to initiate the reaction and to



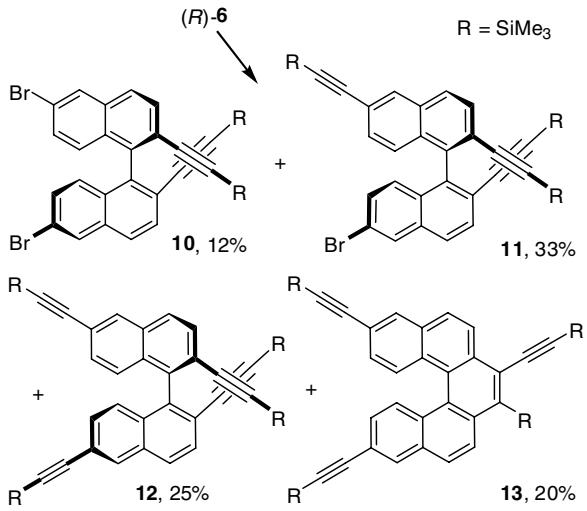
Scheme 1. Dialkynylation of diiodide (*R*)-**3**. Reagents and conditions: (a) phenylethynyl copper (5.0 equiv), pyridine, 115 °C, 20 h; (b) RC≡CZnCl (6.0 equiv), $Pd(PPh_3)_4$ (0.05 equiv), THF, MW at 120 °C, 3 min.



Scheme 2. Iodination of dibromide (*R*)-**7**. Reagents and conditions: I_2 (3.0 equiv), AgOTf (6.0 equiv), CH_2Cl_2, rt, 48 h.



Scheme 3. Synthesis of dibromo diiodide (*R*)-**6**. Reagents and conditions: (a) NBu_4Br_3 (2.7 equiv), CH_2Cl_2, rt, 2 h; (b) $NaNO_2$ (3.3 equiv), CF_3CO_2H, 0–5 °C, 30 min; (c) KI (25 equiv), 0 °C, 2 h; (d) Ac_2O (4.4 equiv), pyridine, 70 °C, 2.5 h; (e) Br_2 (5.0 equiv), DMF, 90 °C, 11 h; (f) KOH (40 equiv), EtOH–H_2O (2:1), reflux, 2 h.



Scheme 4. Negishi alkynylation of dibromo diiodide (*R*)-**6**. Reagents and conditions: $Me_3SiC{\equiv}CZnCl$ (6.0 equiv), $Pd(PPh_3)_4$ (0.05 equiv), THF, reflux, 2 h.