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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.
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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),

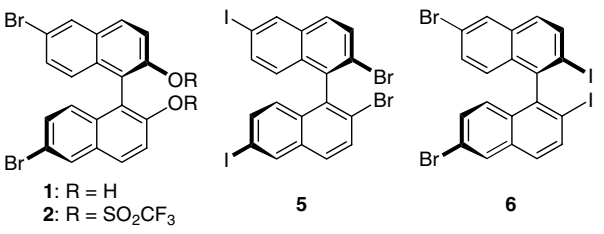

Figure 1. Potential key precursors for the synthesis of 2,2′- and 6,6′-alkynylated 1,1′-binaphthyls.

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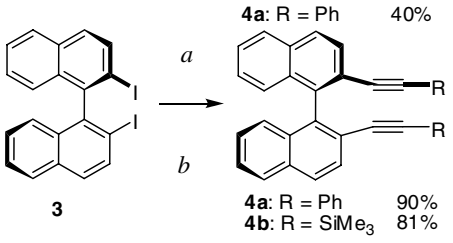
only the synthesis of dibromo diol **1**, potentially convertible to dibromo ditriflate **2**, was described in the literature.[12] However, based on our experience of the introduction of carbon groups to positions 2 and 2′, the reactivity of 1,1′-binaphthyl-2,2′-diyl ditriflate is not sufficient and 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.

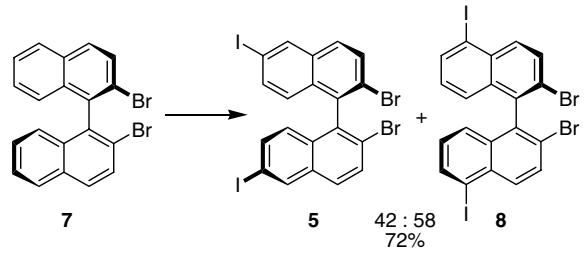
Taking into account the steric hindrance at positions 2 and 2′ and the generally higher reactivity of aryl iodides compared to aryl bromides in cross-coupling reactions, diiodo dibromide **5** should be a more suitable precursor compared to **6**. We expected it to afford higher chemo/regioselectivity 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.

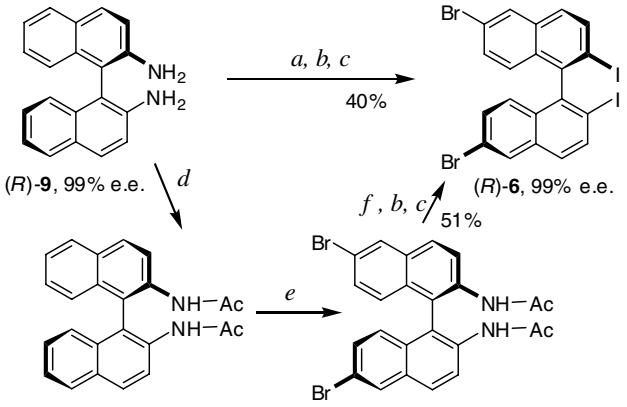
We found that Negishi alkynylation of dibromo diiodide **6** with zinc trimethylsilylacetylide did not proceed with sufficient chemoselectivity, affording a complex mixture of alkynylation products **10**–**13** (Scheme 4). Although this alkynylation takes place initially at the C–I bond (at position 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



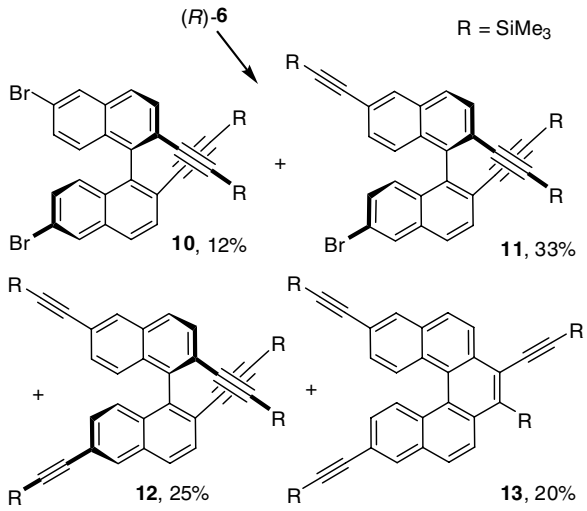
Scheme 1. Dialkynylation of diiodide (*R*)-**3**. Reagents and conditions: (a) phenylethynyl copper (5.0 equiv), pyridine, 115 °C, 20 h; (b) RC≡CZnCl (6.0 equiv), $Pd(PPh_3)_4$ (0.05 equiv), THF, MW at 120 °C, 3 min.



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.

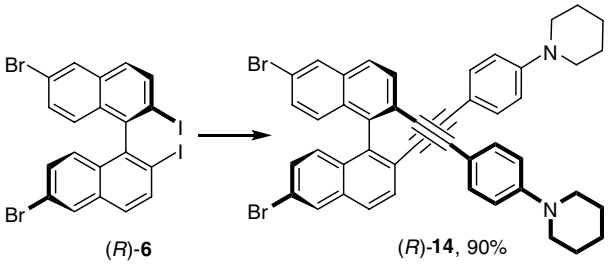
achieve acceptable conversion of the starting dibromo diiodide **6**.

We also investigated the uncatalyzed Stephens–Castro alkynylation, although it did not allow the preparation of the 2,2′-diethynyl derivative, since the corresponding trimethylsilylethynyl copper was not sufficiently thermally stable.[19] Therefore, we used directly an acetylide functionalized with an electron donor group. In this case, the reaction proceeded with high selectivity to form product **14** in high yield (Scheme 5).

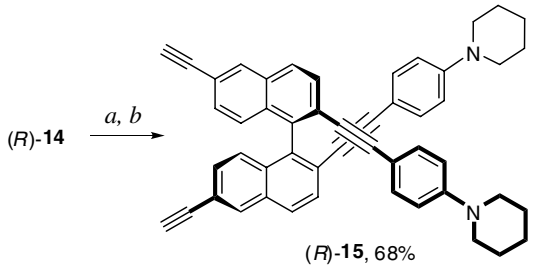
We performed alkynylation of **14** at positions 6 and 6′ with trimethylsilylacetylene under Sonogashira reaction conditions, followed by basic deprotection of the trimethylsilyl group, which afforded intermediate **15** (Scheme 6).

Synthesis of the target bis-NLO-phore **16**[20] and multi-NLO-phore **17**[21] was accomplished in good yields by Sonogashira reaction of **15** with the corresponding nitrophenyl halides (Scheme 7). GPC analysis of multi-NLO-phore **17** shows moderate molecular weight (M_w 9700, M_n 4400 and PDI 2.23), similar to those observed in other Sonogashira polymerizations of binaphthyl oligomers.[22]

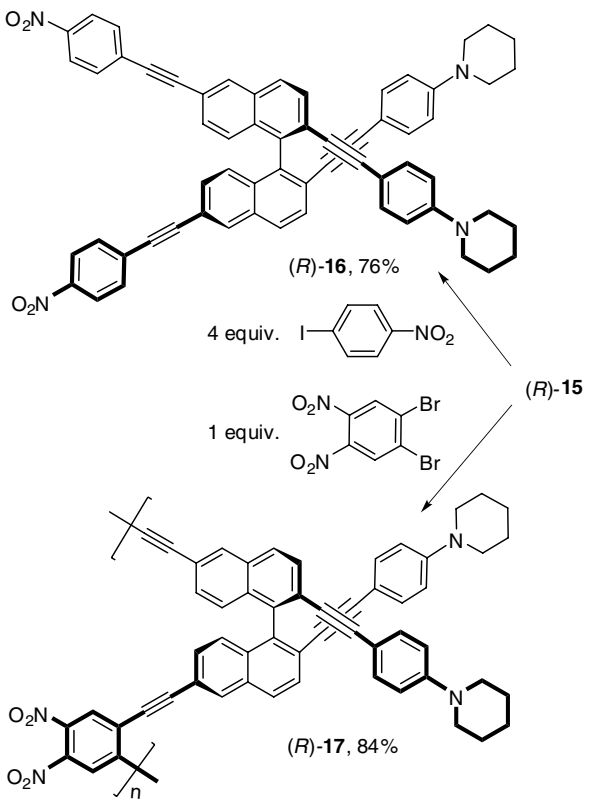
Preliminary information on the extent of conjugation in push–pull molecules can be obtained by the observation of solvatochromic properties by electron spectroscopy.[23] Such derivatives exhibit a slight hypsochromic shift of the charge transfer band absorption maximum (band corresponding to photo-induced charge transfer) and a bathochromic shift of the emission maximum (with excitation at the wavelength of the charge transfer band maximum) upon increasing solvent polarity. This effect is related to the different orientation of dipoles in the ground and excited states (an inevitable prerequisite for NLO properties) and the excitation state life-time versus solvent ability to contribute to dipole stabilization by solvation.



Scheme 5. Stephens–Castro alkynylation of dibromo diiodide (*R*)-**6**. Reagents and conditions: 4-piperidinophenylethynyl copper (6.0 equiv), pyridine, 150 °C, 24 h.



Scheme 6. Sonogashira 6,6′-dialkynylation of **15**. Reagents and conditions: (a) $Me_3SiC{\equiv}CH$ (4.0 equiv), $Pd(PPh_3)_4$ (0.1 equiv), CuI (0.1 equiv), Et_3N, 90 °C, 7 h; (b) K_2CO_3 (6.0 equiv), THF–MeOH (1:1), reflux, 2 h.



Scheme 7. Sonogashira arylation of **15**. Reagents and conditions: $Pd(PPh_3)_4$ (0.1 equiv), CuI (0.1 equiv), Et_3N–THF (1:1), 75 °C, 2 h.

Many nitrophenyl derivatives do not exhibit intensive emission due to effective self-quenching or other effective nonradiative relaxation of the excited state. This was also the case for bis-NLO-phore **16**. However, multi-NLO-phore **17** exhibited low intensive emission with a significant bathochromic shift upon increasing the solvent polarity by excitation at the wavelength of the CT band maximum (388–391 nm) (Table 1, Fig. 2).

In conclusion, we have developed an effective synthetic approach to 1,1′-binaphthyls bearing different alkynyl groups at positions 2,2′, and 6,6′ via dibromo diiodide **6**. The crucial step was accomplished by selective 2,2′-dialkynylation of **6** using a Stephens–Castro thermal reaction. The multi-NLO-phore (*R*)-**17** exhibits extended conjugation between positions 2 and 6, and 2′ and 6′, as proved by a study of its solvatochromic properties. The first hyperpolarizability value of (*R*)-**17** is under determination.

Table 1. Absorption and emission maxima of (*R*)-**16** and (*R*)-**17** measured in solvents of different polarity

Solvent	(*R*)-**16**	(*R*)-**17**	
	Absorption λ_{max} (nm)	Absorption λ_{max} (nm)	Emission[a] λ_{max} (nm)
Benzene	397	391	462
Chloroform	392	388	484
Acetonitrile	390	388	519[b]

[a] Excitation at the wavelength of the CT band maximum.
[b] Mixture of acetonitrile–chloroform (1:1) due to the low solubility of (*R*)-**17** in acetonitrile.

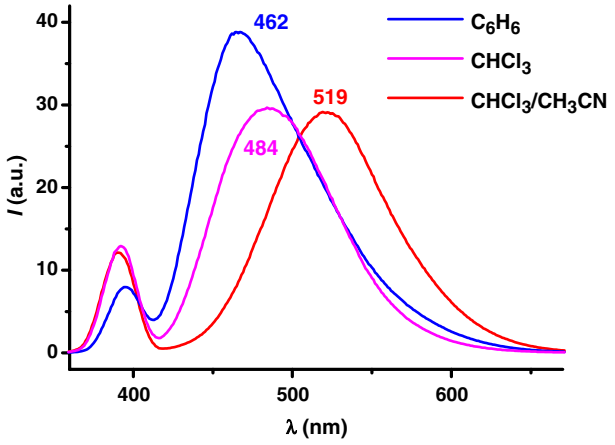


Figure 2. Emission spectra of (*R*)-**17** in various solvents at $c = 1 \times 10^{-5}$ M.

Acknowledgement

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.10.044.

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18. Compound **6**: White crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.09 (d, 2H, $^{4}J = 1.9$ Hz, C_{Ar}-H), 8.07 (d, 2H, $^{3}J = 8.8$ Hz, C_{Ar}-H), 7.63 (d, 2H, $^{3}J = 8.8$ Hz, C_{Ar}-H), 7.36 (dd, 2H, $^{3}J = 8.8$ Hz, $^{4}J = 1.9$ Hz, C_{Ar}-H), 6.90 (d, 2H, $^{3}J = 9.1$ Hz, C_{Ar}-H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 144.3, 136.9, 134.0, 131.2, 130.8, 130.3, 128.8, 127.9, 120.9, 99.9. (*R*)-**6**: Mp 207–209 °C, 99% ee (HPLC, Chiralcel Daicel OD-H). $[\alpha]_D^{19}$ -71 ± 3 (*c* 0.81, $CHCl_3$). (*RS*)-**6**: Mp 290–291 °C. GC–MS-FAB for $C_{20}H_{10}Br_2I_2$: [M+4] 666 (17), [M+2] 664 (34), [M] 662 (17), 412 (25), 410 (50), 408 (26), 250 (100), 125 (54).
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20. (*R*)-**16**: Orange solid, mp 201–203 °C. $[\alpha]_D^{20}$ $+33 \pm 2$ (*c* 2.7, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.24 (m, 4H, C_{Ar}-H), 8.19 (d, 2H, $^{4}J = 1.6$ Hz, C_{Ar}-H), 7.95 (d, 2H, $^{3}J = 8.8$ Hz, C_{Ar}-H), 7.79 (d, 2H, $^{3}J = 8.5$ Hz, C_{Ar}-H), 7.69 (4H, C_{Ar}-H), 7.41 (dd, 2H, $^{3}J = 8.8$ Hz, $^{4}J = 1.6$ Hz, C_{Ar}-H), 7.33 (d, 2H, $^{3}J = 8.5$ Hz, C_{Ar}-H), 6.66 (4H, C_{Ar}-H), 6.63 (4H, C_{Ar}-H), 3.10 (m, 8H, N-CH_2), 1.57 (m, 12H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 151.3, 147.5, 147.0, 139.0, 132.5, 132.4, 132.1, 130.2, 129.3, 128.9, 128.0, 127.8, 126.7, 124.1, 123.7, 119.5, 114.9, 111.9, 96.1, 95.2, 88.4, 87.6, 49.4, 25.4, 24.3. IR (cm^{-1}): 2204, 1517, 1343. HRMS-ESI for $C_{62}H_{46}N_4NaO_4$: calcd 933.3416; found, 933.3505.
21. (*R*)-**17**: $[\alpha]_D^{20}$ $+170 \pm 5$ (*c* 3, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.40 (br, C_{Ar}-H), 8.15 (br, C_{Ar}-H), 7.92–7.65 (br, C_{Ar}-H), 7.42–7.19 (br, C_{Ar}-H), 6.63 (br, C_{Ar}-H), 3.12 (br, N–CH_2), 1.58 (br, CH_2). UV ($CDCl_3$, nm): 272, 299, 388. IR (cm^{-1}): 2200, 1517, 1378.
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