Synthesis of 1,1′-binaphthyls by *photo-dehydro*-Diels–Alder reactions†

Pablo Wessig* and Gunnar Müller

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1,1′-Binaphthyls are prepared by a conceptually novel approach based on the *photo-dehydro*-Diels–Alder reaction.

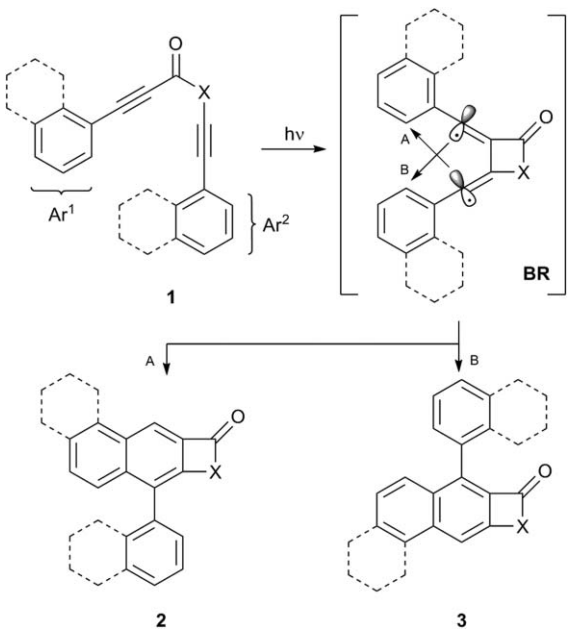
Biaryls play an important role in numerous areas of chemistry. The biaryl structure is wide-spread across many classes of natural products, and many of them have interesting biological activities.[1] Furthermore, compounds with biaryl moieties have found broad application as catalysts in asymmetric synthesis. This is based on the often hindered rotation around the aryl–aryl single bond and the atropisomerism resulting from this. 1,1′-Binaphthyls, especially, have gained great importance as chiral ligands or auxiliaries.[2] 1,1′-Binaphthyl-2,2′-diol (BINOL)[3] and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP)[4] should be mentioned as particularly prominent examples.

Most of the methods for the preparation of biaryls published to date rely on a coupling reaction between two already existing and appropriately-substituted arenes.[5] Besides the classical methods,[6] above all, transition metal-catalyzed coupling reactions of aryl halides, and cross-coupling reactions of arylmetallic reagents and aryl halides have resulted in immense progress being made in biaryl synthesis.[5] Despite this success, a strong motivation to develop new alternative routes to biaryls still persists. Compared to the established procedures, there are hardly any methods in which one of the two arene skeletons is completely newly constructed during the course of the synthesis. Herein, we wish to report a novel approach for constructing the 1,1′-binaphthyl skeleton.

Recently, we reported a photochemically initiated *dehydro*-Diels–Alder reaction (PDDA) between a 3-aryl-ynone moiety and an arylacetylene, which are regularly (but not necessarily) connected by a linker X. The general structure of such reactants is represented by framework **1** (Scheme 1).[7] Spectroscopic investigations and quantum chemical calculations of the mechanism of the PDDA reaction revealed that it proceeds from the triplet state of the ketone **1**, which undergoes a ring closure to biradical **BR**. **BR** may be regarded as the key intermediate of the PDDA reaction. One of the radical centers of **BR** attacks the *ortho*-position of the opposite aryl ring, and in this sense, two alternative reaction paths are possible. If the lower radical center approaches the upper aryl ring Ar^1 (path A), biaryls **2** result; whereas an attack of the upper radical center on the lower aryl ring Ar^2 (path B) leads to products **3**. We found that the site selectivity of these alternative processes may be influenced by either the electronic effect of substituents on the aryl residues or by the blocking of *ortho*-positions by appropriately chosen groups. As depicted in Scheme 1, 1,1′-binaphthyls should be accessible if one of the aryl residues is a 1-naphthyl group. While, recently, we have demonstrated, in principal, the feasibility of this approach with one example,[7a] some drawbacks to the hitherto investigated systems also became clear. Until now, we assumed that the chromophoric group must be an ynone, that is a sp^3 carbon atom must be adjacent to the carbonyl carbon atom, based on our experience of the Norrish–Yang reaction. On the other hand, these ketones required relatively laborious syntheses. Furthermore, linkers bearing a keto group cannot easily be cleaved after ring closure, which is disadvantageous with regard to further synthetic modifications of the biaryls prepared by PDDA reactions. Owing to these reasons, we decided to investigate whether ester groups could be used as linkers instead of ketones. After PDDA reactions, esters can easily be saponified, giving hydroxy-carboxylic acids that are well suited to further structural modification.

Another problem arose with the methyl groups previously used to block the *ortho*-positions. We found that they only partly suppressed attack at this position and tended to migrate[7a] or to be captured by the solvent.[7b] Therefore, expecting a lower migration tendency, in this work we used methoxy groups.

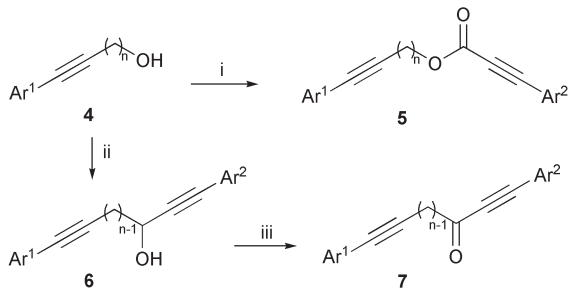
The synthetic route to 1,1′-binaphthyls commences with ω-arylalkynols **4**, which are readily available by the Sonogashira coupling[8] of different iodoarenes with alkynols of different chain length.† Esterification of alcohols **4** with different arylpropiolic



Scheme 1 *Photo-dehydro*-Diels–Alder reaction.

Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, D-12489 Berlin, Germany. E-mail: pablo.wessig@chemie.hu-berlin.de; Fax: +49 30 20937450; Tel: +49 30 20937455

† Electronic supplementary information (ESI) available: Formulae, syntheses and characterisation details of all the compounds prepared. See DOI: 10.1039/b609374d



Scheme 2 Synthesis of esters **5** and ketones **7**. (i) Method A: DCC, DMAP, Ar^2–CC–COOH; method B: 1. $COCl_2$, 2. Ar^2–CC–Li. (ii) 1. DMP, 2. Ar^2–CC–Li. (iii) DMP (DMP = Dess–Martin periodinane).

Table 1 Yields of compounds **5**

Compound	Ar^1	Ar^2	*n*	Method	Yield (%)
5a	Nap	Ph	1	A	96
5b	2-MeO-Nap	Ph	1	A	40
5c	Ph	2-MeO-Nap	1	A	99
5d	Nap	Ph	2	A	88
5e	Ph	Nap	2	B	46
5f	2-MeO-Nap	Ph	2	A	91
5g	Ph	2-MeO-Nap	2	B	54
5h	Ph	Ph	1	A	90
5i	Ph	Ph	2	A	88

[a] Nap = 1-naphthyl.

Table 2 Yields of compounds **6** and **7**

Entry	Ar^1	Ar^2	*n*	Yield of **6** (%)	Yield of **7** (%)
a	Ph	2-MeO-Nap	3	68	52
b	Nap	Ph	4	51	61

[a] Nap = 1-naphthyl.

acids, using DCC/DMAP (method A) or conversion of **4** into the corresponding chloroformates with phosgene and reaction with lithium arylacetylides (method B), afforded esters **5** in moderate to excellent yields. For comparison, we prepared ketones **7** by oxidation of alcohols **4** to their corresponding aldehydes using Dess–Martin periodinane, reaction with lithium arylacetylides and renewed oxidation of the thus obtained secondary alcohols **6** (Scheme 2). The yields of compounds **5–7** are summarized in Table 1 and Table 2.

Irradiations of esters **5** under the previously employed conditions were initially disappointing. The compounds showed very low photochemical reactivity in various solvents and unselective decomposition upon prolonged irradiation times. To rule out whether the longest absorption maximum was shifted below 300 nm, which is the shortest wavelength let through by the irradiation equipment, we measured the UV-vis spectra of esters **5a,b,e,g** and, for comparison, esters **5h** and **5i**, bearing only phenyl groups. The UV-vis spectra of these six compounds are shown in Fig. 1 and Fig. 2. The spectra of the parent compounds **5h** and **5i** reveal a weak absorption band above 300 nm ($\log_{10} \varepsilon \sim 2$), which may be attributed to a n–π* transition. The replacement of one phenyl group by a 1-naphthyl group (**5a** and **5e**) increases the molar extinction coefficient by two orders of magnitude. Presumably, the long-wavelength transition now has more π–π* rather than n–π* character. The red-shift of the absorption

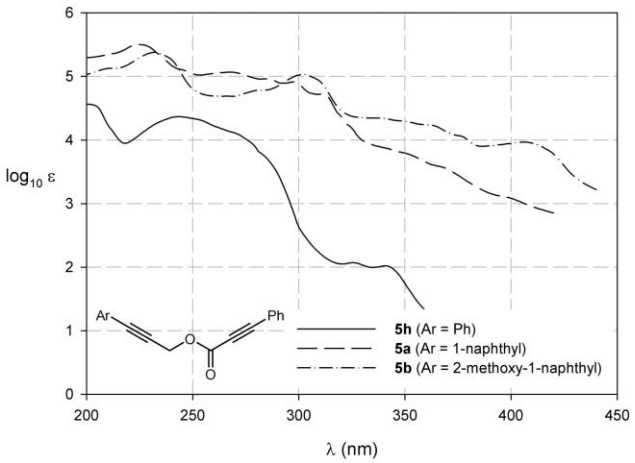


Fig. 1 UV-vis spectra of esters **5a,b,h**.

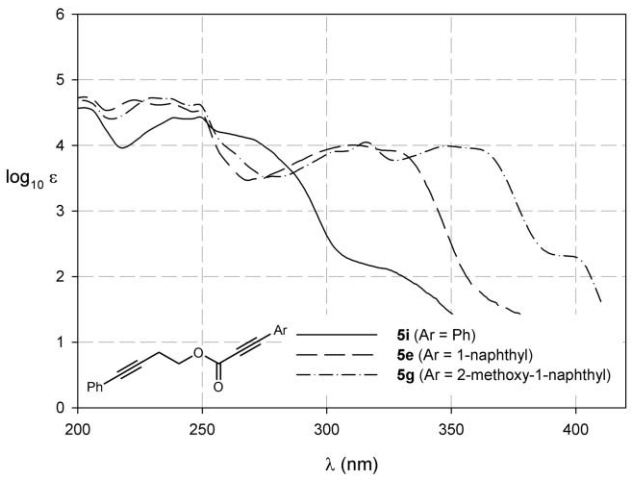
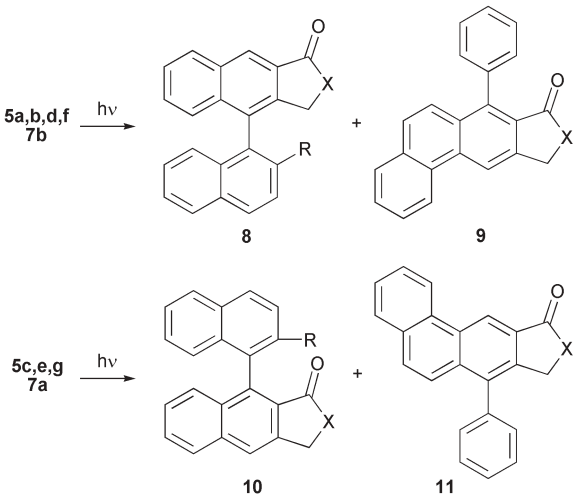


Fig. 2 UV-vis spectra of esters **5e,g,i**.

maxima and their intensity are further increased by the introduction of the methoxy group at the 2-position of the naphthyl moiety. Especially conspicuous is the broad absorption band at 370 nm in the UV-vis spectrum of **5g**, suggesting a charge transfer (CT) transition. As shown below, the latter situation seems to be disadvantageous for the PDDA reaction.

We hypothesized that the possible switch in character of the long-wavelength transition (π–π* instead of n–π*) should result in a lower efficiency of the intersystem crossing (ISC) to the triplet state, and we suspected this to be the reason for the low photochemical reactivity of esters **5**. To prove this hypothesis, we irradiated esters **5**, using acetone as a triplet sensitizer,[9] and observed, to our delight, a dramatically increased reactivity. In the absence of the blocking methoxy group (**5a,d,e**) we always obtained, expectedly, two products, namely the 1,1′-binaphthyls **8** or **10**, as well as phenanthrene derivatives **9** or **11** (Scheme 3, Table 3).

The effect of introducing a methoxy group, remarkably, depends on whether the alcohol side (**5b** and **5f**) or the carboxylic acid side (**5c** and **5g**) of the ester is affected. In the case of compounds **5b** and **5f**, the formation of phenanthrenes is completely suppressed, and the appropriate 1,1′-binaphthyls **8b**



Scheme 3 Photochemical behavior of esters **5** and ketones **7**.

Table 3 Irradiation conditions and product yields of compounds **8–11**

Reactant	Solvent[a]	X	R	Products[b]
5a	A	O	H	**8a** (38%), **9a** (41%)
5b	A	O	OMe	**8b** (46%)
5c	A	O	OMe	**10a** (36%)
5d	A	OCH_2	H	**8c** (41%), **9b** (30%)
5e	A	OCH_2	H	**10b** (36%), **11a** (23%)
5f	A	OCH_2	OMe	**8d** (38%)
5g	A	OCH_2	OMe	**10c** (28%)
7a	M	CH_2	OMe	**10d** (18%)
7b	M	CH_2CH_2	H	**8d** (13%), **9c** (17%)

[a] A = acetone, M = methanol. [b] Irradiation conditions. Starting concentration: 0.01 M, light source: high-pressure mercury arc lamp (150 W, Heraeus), irradiation time: 15–20 h (TLC monitoring).

(46%) and **8d** (38%) were obtained in satisfactory yields. In contrast, compounds **5c** and **5g**, bearing a 3-(2-methoxy-naphth-1-yl)-propiolic ester moiety, showed low reactivity and afforded PDDA products, at best, in marginal yields. As mentioned above, this finding may be caused by the CT character of the long-wavelength transition of these compounds. The irradiation results of ketones **7a** and **7b** confirm that turning to esters was a good decision.

In summary, we report a conceptually novel synthetic route to 1,1′-binaphthyls by the irradiation of propargyl and homopropargyl esters of 3-arylpropiolic acids. Investigations towards the atropselective synthesis of binaphthyls are currently under way.

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