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Improved synthesis of 2,2′-dimethoxy-1,1′-binaphthyl-3,3′-diacetic acid derivatives

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Abstract—During the past decade, the chemistry of BINAP, BINAM, and BINOL derivatives experienced an important development due to multiple applications in catalysis, metallo-supramolecular chemistry and material science. Consequently, the need to develop functionalized binaphthyl derivatives became crucial. In this context, we were interested in preparing 2,2′-dimethoxy-1,1′-binaphthyl-3,3′-diacetic acid species. The latter were efficiently prepared using a modified Arndt–Eistert reaction that afforded the expected chiral diacid in good yield. Compared to the method we described earlier, this new strategy allows the preparation of the target homologated diacid chloride in a very efficient manner, limiting wastes and tedious column chromatographies.
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In recent years, enantioselective catalysis became an essential tool for organic chemists.[1] In parallel, the development of chiral materials underwent tremendous strides, with for instance applications in the preparation of chromophores exhibiting non-linear properties.[2] Among the large number of chiral ligands available, binaphthyl derivatives undoubtedly stand at the top of the hill. Indeed, they are readily available in both racemic and enantiomerically pure forms, and relatively cheap. In addition, they were shown to be robust toward oxidation, and able to efficiently transfer the chiral information.[3] Taken together, those properties made binaphthyl derivatives very attractive chiral pools. Despite the wide range of applications, the functionalization pathways of the binaphthyl skeleton remain quite limited, and often require modifications of the naphthyl rings before aryl–aryl coupling and subsequent optical resolution.[4] Among the possible modifications of the binaphthyl moiety, many involve functionalizations of the alkoxy groups (route a, Fig. 1), or reactions on the thermodynamically favored 6,6′-positions (route b, Fig. 1).[5]

On the other hand, very few chemical reactions were performed on the less reactive 3,3′-positions. The latter generally require ortho-lithiation using *n*-BuLi and TMEDA and subsequent electrophilic attacks by silylated acetylides, carbon dioxide, or DMF.[6,7] Other electrophiles such as MeI were also used.[5]

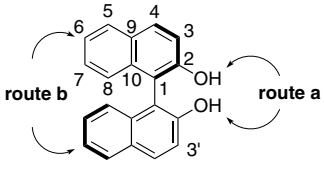

Figure 1.

In the course of our study concerning the enantioselective epoxidation of terminal olefin using binaphthyl strapped porphyrins, we were interested in the preparation of the *homologated* binaphthyl dicarboxylic acid **6** (Scheme 1).[3,8]

We first adopted a long and tedious multistep reaction sequence based on preliminary works reported by Stock and Kellogg.[6] After protection of the alkoxy functions using MeI and *ortho*-lithiation, DMF was added affording the expected dialdehyde (**2**) in 70% yield. Subsequently, the aldehyde functions were reduced with sodium borohydride affording the dialcohol (**3**) quantitatively. The latter was converted to the dibromo derivative (**4**) in 77% yield. At last, **4** was reacted with NaCN and hydrolyzed to the corresponding dicarboxylic acid

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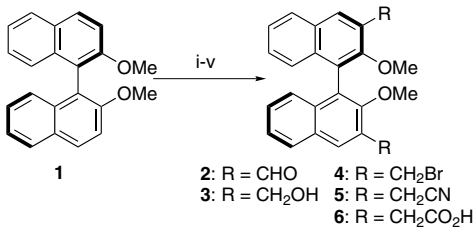


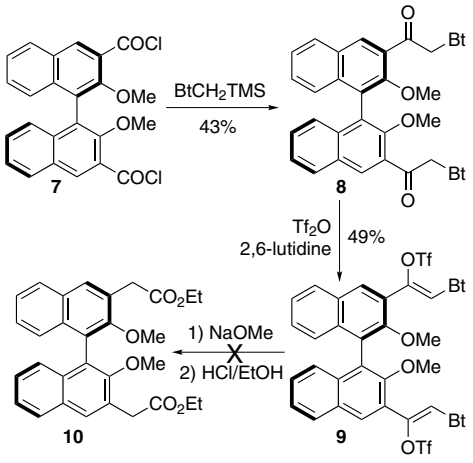
Scheme 1. Reagents and conditions: (i) *n*-BuLi/TMEDA then DMF; (ii) $NaBH_4$; (iii) PBr_3; (iv) NaCN; (v) KOH then HCl.

(**6**) after protonation with HCl. While quite efficient (36% overall yield), this multistep, time consuming synthesis suffered from a recurrent need to purify many intermediates by silica-gel column chromatographies and large amounts of dichloromethane. In order to upscale the synthesis and to make it more environmentally friendly, we decided to develop a more efficient approach toward the homologated diacid **6**.

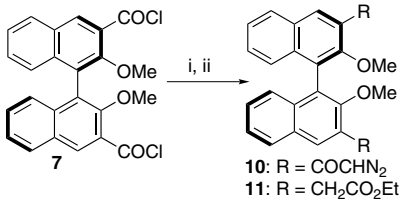
At first, we considered using the benzotriazole-assisted homologation of carboxylic acids recently described by Katritzky et al.[9] Accordingly, condensation of diacyl chloride **7**[10,11] with excess of $BtCH_2TMS$ afforded the expected bis-(*N*-binaphthyl-methyl)benzotriazole **8** in 43% yield. Subsequently, reaction with triflic anhydride in the presence of 2,6-lutidine led to the corresponding bis-enol triflate **9** in 49% yield. Unfortunately, upon addition of $NaOCH_3$ in refluxing acetonitrile and subsequent acidolysis, no homologated diester was isolated (Scheme 2).

As the benzotriazole-assisted homologation of carboxylic acids was proved to be really efficient and quite general earlier, we came to the conclusion that the particular geometry of the binaphthyl structure as well as the crowded character of the 3,3′-positions were responsible for the lack of reactivity. Similar behaviors have already been exemplified in the binaphthyl series.[6] As a consequence, we considered using a different approach, namely the well-known Arndt–Eistert homologation of acyl chlorides.[12] Surprisingly, when **7** was reacted with CH_2N_2 no reproducible results could be obtained. Considering that the random observations could derive from the use of the highly reactive diazomethane, we then considered using the more stable and safer trimethylsilyldiazomethane ($TMSCHN_2$) reagent.[13]

Condensation of 2.5 equiv of $TMSCHN_2$ with **7** in the presence of dry triethylamine readily afforded the expected diazoketone **10** in 62% yield (Scheme 3). It is worth noting that while not absolutely necessary, **10** could be purified over silica-gel and fully characterized by NMR (Fig. 2).[14]



Scheme 2. Homologation according to Katritzky's method.



Scheme 3. Reagents and conditions: (i) $TMSCHN_2$, NEt_3; (ii) $PhCO_2$-Ag, NEt_3, EtOH.

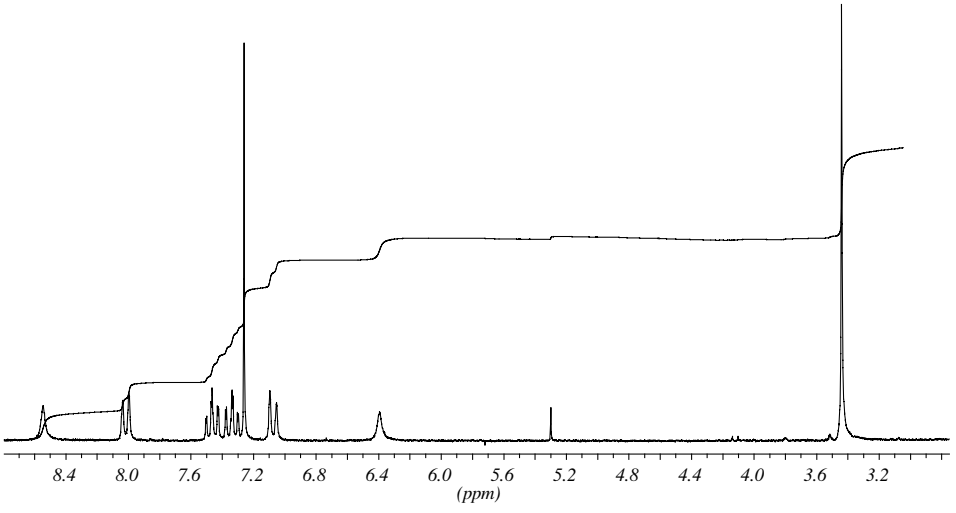


Figure 2. ^1H NMR spectrum of **10**.

Subsequently, **10** was rearranged to the corresponding diester **11** in 78% yield according to a classical Wolff rearrangement in ethanol and in the presence of silver benzoate (Scheme 3).[15] In parallel, we also tested a thermal rearrangement at 180 °C in benzyl alcohol, but the reaction appeared low yielding and the benzyl ester very difficult to purify. For these reasons, we preferred the preparation of the ethyl ester that could be quantitatively saponified to the expected diacid **6**.

In conclusion, we report a new and straightforward synthesis of the 2,2′-dimethoxy-1,1′-binaphthyl-3,3′-diacetic acid **6**. Compared to the time-consuming method reported earlier by our group, this new approach allows the preparation of the 'homologated' diacid in a more efficient way, limiting tedious separations and the amount of waste. Work is currently devoted to evaluating the properties of the chiral diacid, and studying its incorporation in supramolecular assemblies.

Acknowledgements

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8. The terminology 'homologated' adopted here, refers to the classical homologation of acid chloride using the Arndt–Eistert methodology.
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14. While not absolutely necessary, the chromatography allows a much easier purification at the next step.
15. Experimental procedure for the preparation of **10**: At −40 °C, a 50-mL round-bottom flask equipped with a stir bar and an argon inlet was charged with a solution of **7** (2.4 mmol) in dry THF/CH_3CN (5 mL of each). Freshly distilled NEt_3 (0.84 mL, 6 mmol) and $TMSCHN_2$ (3 mL, 6 mmol) were then successively added and the orange solution was allowed to stir for 72 h. Finally, the crude product was diluted with Et_2O (30 mL) and successively washed with a 10% aqueous solution of citric acid and a saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4 and concentrated in vacuo affording an orange crude product. The latter was either purified by a silica-gel column chromatography (eluent: Et_2O/petroleum ether: 6/4) or directly taken in absolute EtOH (40 mL). A solution of $PhCO_2Ag$ (288 mg, 1.25 mmol) in dry triethylamine (6.6 mL, 47.7 mmol) was then added to the alcoholic solution of **10**. The resulting mixture was placed in an ultrasound bath and sonicated for 1 h. After the solvents were removed in vacuo, the crude product was dissolved in ether and successively washed with a 10% aqueous solution of citric acid, saturated $NaHCO_3$ solution and water. The organic layer was dried over Na_2SO_4 and concentrated in vacuum to give an orange oil. The latter was purified by column chromatography (eluent CH_2Cl_2/cyclohexane: 8/2) affording a pale yellow oil (565 mg), corresponding to the expected diester **11**. After two steps, the overall yield averages 49%.^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.92 (s, 2H, H_4), 7.88 (d, J = 8.3 Hz, 2H, H_5), 7.41 (m, 2H, H_7), 7.26 (m, 2H, H_6), 7.23 (m, 2H, H_8), 4.23 (q, J = 7.0 Hz, 4H, CH_2CH_3), 4.02 (d, J = 16.2 Hz, 2H, CH_2CO_2Et), 3.88 (d, J = 16.2 Hz, 2H, CH_2CO_2Et), 3.29 (s, 6H, OCH_3), 1,29 (t, J = 7.0 Hz, 6H, CH_2CH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.1 (CO), 155.5 (C_2), 134.2 (C_9), 130.9 (C_4), 130.7 (C_{10}), 128.6 (C_3), 128.0 (C_5), 126.5 (C_6), 126.0 (C_8), 125.1 (C_7), 124.1 (C_1), 61.1 (CH_2CH_3), 60.8 (OCH_3), 37.3 (CH_2CO_2Et), 14.5 (CH_2CH_3). MS (DCI^+) *m*/*z*: calcd for $C_{30}H_{30}O_6$: 486. Found: 486. Anal. Calcd for $C_{30}H_{30}O_6$: C, 74.06; H, 6.21. Found: C, 74.14; H, 6.73.