

Guidelines for Authors –Experimental data - EJOC:

In the Experimental Section, quantities of reactants, solvents etc. should be included in parentheses [e.g. A solution of triphenylphosphane (500 mg, 1.91 mmol) in dichloromethane (15 mL) was added to...].

All new compounds must be fully characterized (e.g., NMR spectroscopy, IR spectroscopy, mass spectrometry, elemental analysis, specific rotation, etc.) and their purity verified. The ^1H and ^{13}C NMR spectra of all key intermediates and all final products should be included in the Supporting Information. In addition, data for all new compounds should include either elemental analysis (to an accuracy within $\pm 0.4\%$ of the calculated values) or high-resolution mass spectrometry (HRMS) data. For compounds where elemental analysis data is not provided, the HRMS data should be accompanied by NMR spectra with sufficiently low signal-to-noise ratios so that all peaks can be adequately resolved. Note that elemental analysis data **MUST** be provided for papers detailing the isolation and structure elucidation of natural products.

NMR spectroscopic data should be quoted as in the following example: ^1H NMR (300 MHz, C_6D_6 , 25°C): $\delta = 1.3$ (s, 18 H, SiMe_3), 0.9 (d, $^3J_{\text{H,H}} = 5.7$ Hz, 2 H, 2-H) ppm. For each chemical shift, additional information should be given in the order: multiplicity, coupling constant, number of protons, assignment.

Corrected/uncorrected melting points: According to the [IUPAC Gold Book](#), "The term originally signified that a correction was made (not made) for the emergent stem of the thermometer. In current usage it often means that the accuracy of the thermometer was (was not) verified. This current usage is inappropriate and should be abandoned."

Microwave Experiments: The manufacturer and model number of the microwave reactor should be clearly specified. Experiments performed in microwave reactors must report the temperature (or range) achieved during the procedure; wattage rating alone is not sufficient. Because of security reasons and because of vague reaction conditions as a result of varying device properties, even in cases of the same make, EurJOC does not consider manuscripts for publication that are based on chemical reactions performed in domestic microwave ovens

Synthesis of the new unsymmetrical molecular tweezer **3** (octyl tweezer)

Recently, the first unsymmetrical derivative of a lysine-binding molecular tweezer was prepared in our laboratory. It contained on one side of the aromatic cavity a phosphate dianion, whereas the other side was equipped with an octyl ether.

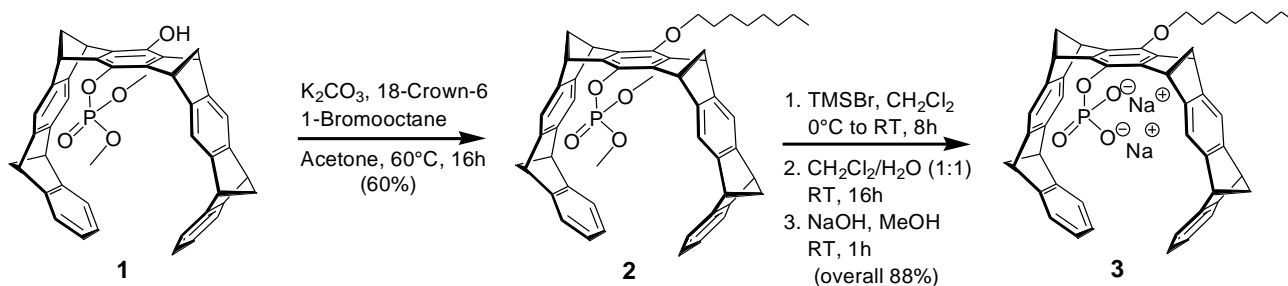


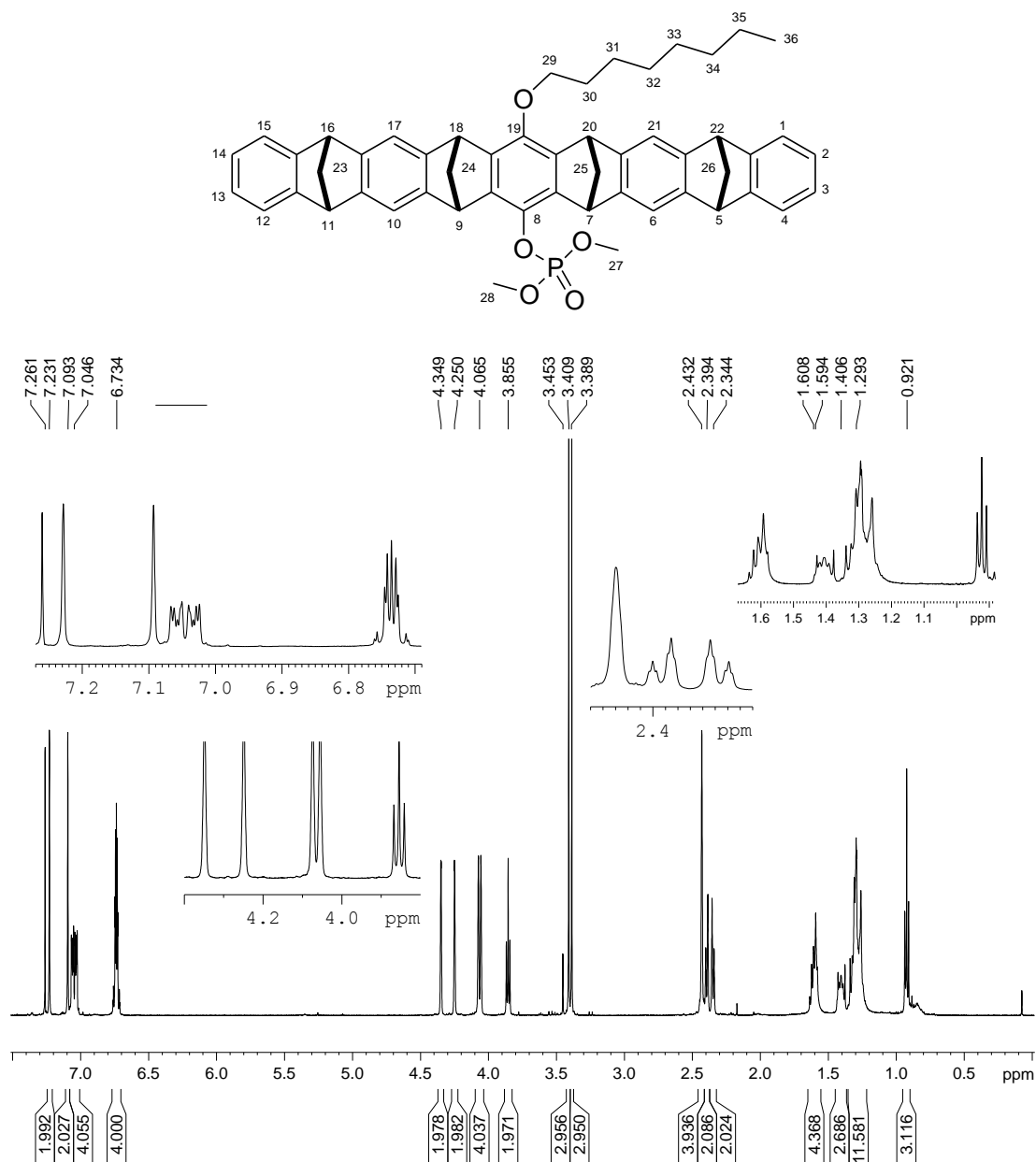
Figure 1. Introduction of an ether moiety via alkylation of **1a** to afford unsymmetrical tweezer **3**.

This alkyl ether was made via nucleophilic displacement on the respective alkyl halide (Williamson synthesis). Herein, the mono(dimethylphosphate) tweezer **1** was deprotonated to generate the nucleophilic phenoxide anion, which reacted with 1-bromooctane under phase transfer catalysis with the aid of 18-crown-6. Treatment of the fully protected intermediate **2** with trimethylsilyl bromide selectively cleaved both methyl esters on phosphorus; subsequent titration with 2 equivalents of NaOH furnished the pure tweezer phosphate as the disodium salt (**3**).

Octyl-dimethoxyphosphoryl-tweezer 2. To a suspension of 22 g (0.0326 mol) tweezer **1** and 5.0 g (0.0326 mol) K_2CO_3 in dry acetone, 9 ml (0.0489 mmol) 1-bromooctane were added. Subsequently, a catalytic amount of 18-crown-6 was also added and the reaction mixture was stirred at 60 °C for 24 h. The mixture was then cooled to room temperature and transferred into a separating funnel. After the addition of saturated aqueous $NaHCO_3$, the aqueous solution was extracted three times with dichloromethane. The combined organic layers were washed once with sat. aq. NH_4Cl and once with 1M aqueous NaCl. The organic phase was dried over Na_2SO_4 , filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography eluting with ethyl acetate/cyclohexane (1:3). (Compound **2** was finally crystallized from methanol to obtain crystals for X-ray structure analysis.)

Yield: 15.0 g (60%)

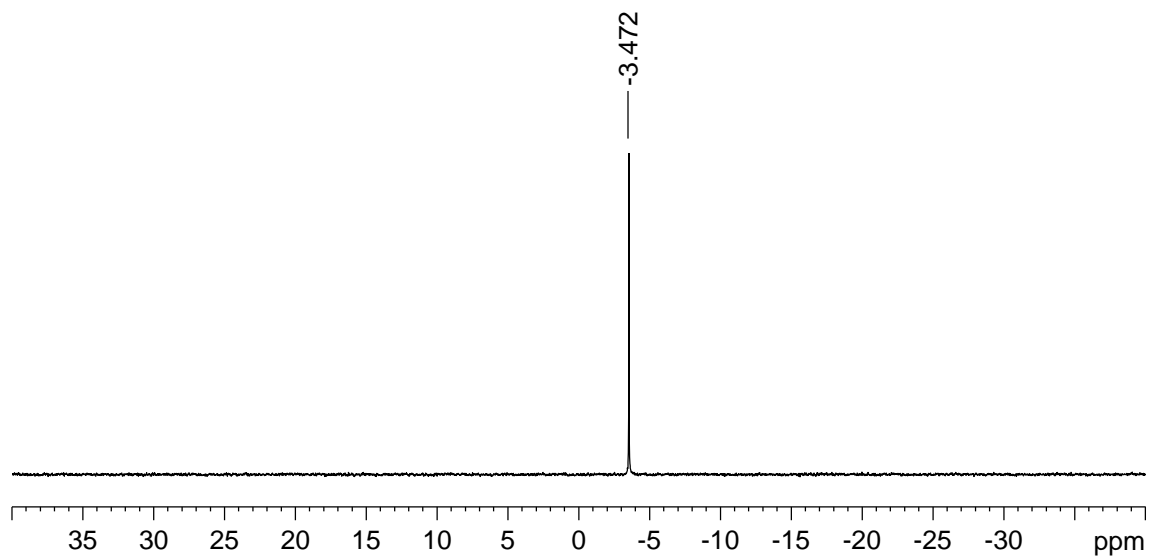
Melting Point: 188 °C



$^1\text{H-NMR}$ spectrum (CDCl_3)

$^1\text{H-NMR}$ (500MHz, CDCl_3): δ [ppm] = 0.92 (t, $^3J_{\text{H,H}} = 7$ Hz, 3H, H-36), 1.29 (m, 8H, H-32, H-33, H-34, H-35), 1.40 (m, 2H, H-31), 1.59 (m, 2H, H-30), 2.35 (d, $^3J_{\text{H,H}} = 6$ Hz, 2H, H-24a, H-25a), 2.39 (d, $^3J_{\text{H,H}} = 6$ Hz, 2H, H-24i, H-25i), 2.43 (s, 4H, H-23, H-26), 3.39 (d, $^3J_{\text{P,H}} = 11$ Hz, 6H, H-27, H-28), 3.85 (t, $^3J_{\text{H,H}} = 7$ Hz, 2H, H-29), 4.05 (s, 4H, H-5, H-11), 4.07 (s, 4H, H-16, H-22), 4.25 (s, 2H, H-18, H-20), 4.35 (s, 2H, H-7, H-9), 6.73 (m, 4H, H-2, H-3, H-13, H-14), 7.05 (dm, 4H, H-1, H-15, H-4, H-12), 7.09 (s, 2H, H-17, H-21), 7.23 (s, 2H, H-6, H-10).

¹³C-NMR (125.7MHz, CDCl₃): δ [ppm] = 14.3 (C-36), 22.9 (C-35), 26.2 (C-34), 29.5 (C-32, C-33), 30.4 (C-31), 31.9 (C-30), 48.6, 51.4 (C-7, C-9, C-18, C-20, C-5, C-11, C-16, C-22), 68.8, 69.7 (C-23, C-26, C-24, C-25), 74.1 (C-29), 116.1, 117.2 (C-17, C-21, C-6, C-10), 121.2, 121.6 (C-1, C-15, C-4, C-12), 124.7 (C-2, C-3, C13, C-14), 134.9, 140.8, 141.2, 145.8 (C-5a, C-16a, C-21a, C-10a, C-7a, C-8a, C-18a, C-19a), 147.1, 147.7 (C-6a, C-9a, C-17a, C-20a, C-8, C-9), 150.6 (C-4a, C-11a, C-15a, C-22a).



³¹P-NMR spectrum (CDCl₃)

³¹P-NMR (202 MHz, CDCl₃): δ [ppm] = -3.47.

HRMS (ESI pos., MeOH): m/z [M+Na]⁺ : C₅₂H₅₁O₅PNa cal. 809.3366, obs. 809.3442.

Octyl-dimethoxyphosphoryl-tweezer 2. To a suspension of 22 g (0.0326 mol) tweezer **1** and 5.0 g (0.0326 mol) K_2CO_3 in dry acetone, 9 ml (0.0489 mmol) 1-bromooctane were added. Subsequently, a catalytic amount of 18-crown-6 was also added and the reaction mixture was stirred at 60 °C for 24 h. The mixture was then cooled to room temperature and transferred into a separating funnel. After the addition of saturated aqueous $NaHCO_3$, the aqueous solution was extracted three times with dichloromethane. The combined organic layers were washed once with sat. aq. NH_4Cl and once with 1M aqueous $NaCl$. The organic phase was dried over Na_2SO_4 , filtered and the solvent was removed under reduced pressure. the crude product was purified by column chromatography eluting with ethyl acetate/cyclohexane (1:3). (Compound **2** was finally crystallized from methanol to obtain crystals for X-ray structure analysis.) **Yield:** 15 g, 60%; **Melting Point:** 188 °C.

1H -NMR (500MHz, $CDCl_3$): δ [ppm] = 0.92 (t, $^3J_{H,H} = 7$ Hz, 3H), 1.29 (m, 8H), 1.40 (m, 2H), 1.59 (m, 2H), 2.35 (d, $^3J_{H,H} = 6$ Hz, 2H), 2.39 (d, $^3J_{H,H} = 6$ Hz, 2H), 2.43 (s, 4H), 3.39 (d, $^3J_{P,H} = 11$ Hz, 6H), 3.85 (t, $^3J_{H,H} = 7$ Hz, 2H), 4.05 (s, 4H), 4.07 (s, 4H), 4.25 (s, 2 H), 4.35 (s, 2H), 6.73 (m, 4H), 7.05 (m, 4H), 7.09 (s, 2H), 7.23 (s, 2H). **^{13}C -NMR** (125.7 MHz, $CDCl_3$): δ [ppm] = 14.3, 22.9, 26.2, 29.5, 30.4, 31.9, 48.6, 51.4, 68.8, 69.7, 74.1, 116.1, 117.2, 121.2, 121.6, 124.7, 134.9, 140.8, 141.2, 145.8, 147.1, 147.7, 150.6. **^{31}P -NMR** (202 MHz, $CDCl_3$): δ [ppm] = -3.47. **HRMS** (ESI pos., MeOH): m/z $[M+Na]^+$: cal. 809.3366, obs. 809.3442.