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Synthesis and solvent sorption characteristics of new types of tartaric acid, lactic acid and TADDOL derived receptor compounds

Diana Eißmann, Felix Katzsch, Edwin Weber *

Institut für Organische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Straße 29, D-09599 Freiberg, Sachsen, Germany

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ABSTRACT

Based on a modular design strategy, three new types of tartaric acid, lactic acid and TADDOL derived compounds featuring a linear shaped central backbone and terminally attached functional units corresponding to the above substance classes have been developed. This has led to the synthesis of the compounds **1a**–**6a** (tartaric acid derivatives), **7a**–**11a** (lactic acid derivatives) and **1c**–**6c** (TADDOL derivatives). Preparation of the tartaric acid derivatives involved Pd-catalysed cross-coupling reactions followed by transacetalisation and hydrolysis of the corresponding esters in the final step of the synthetic routes. The derivatives of lactic acid have been prepared on a similar reaction sequence but with the use of lactic esters. The TADDOL derivatives were obtained by Grignard reaction between phenylmagnesium bromide and tartaric esters. Optical rotation data are specified for each compound including intermediates. Organic vapour sorption behaviour of selected compounds coated as solid films on the quartz crystal of a QCM device has been studied. Significant differences in the affinities towards organic solvent vapours are observed. They both depend on structural properties of the respective receptor solvent molecules and solvent polarity as well, showing developmental possibility in the application of vapour sensing.

1. Introduction

Solid materials capable of selectively absorbing organic and inorganic vapours thus providing an opportunity for chemical sensoring, filtering, separation, compound storage or topochemical catalysis are currently a field of high interest.[1,2] The so-called metal-organic frameworks (MOFs), being organic–inorganic hybrid compounds derived from metal coordination to particular ligand type linker molecules, are perhaps the most prominent exponents of this substance class at present.[3] A further family of compounds gaining interest are distinguished by vapour absorption and are completely organic solid materials featuring a framework of organic molecules linked via covalent bonds (COFs) or non-covalent supramolecular interactions.[4] Polymeric frameworks of the covalent type often use boronic ester, Schiff's base, or acetylenic bond formation, while the supramolecularly generated vapour absorbing materials are mostly based on a hydrogen bonded framework structure.[5] For the purposes of the hydrogen bond stabilized networks (HBNs), oligofunctional carboxylic acids as the constituent molecules play a major role such as trimesic acid and analogues[6] or a related group of spacer type bisisophthalic acids.[7] All such compounds in the solid state feature more or less a largely rigid, porous framework structure, classing them as organic zeolites.[8]

Organic zeolites forming sorptive host-guest inclusion compound are also known,[9] aside from more flexible structures, the lattices of which are prone to open in contact with a guest vapour. Respective host structures are often related to clathrate forming compounds, i.e., they possess a bulky molecular constitution, mostly endowed with polar functions (carboxyl or hydroxyl groups), being difficult to access.[10] Thus, unlike the hydrogen bond stabilised networks with the molecules showing outward functional groups, the molecular structures of this specific clathrate host feature *endo*-oriented functional groups; being in a rather difficult situation of forming a stable crystal lattice that promotes the uptake of solvent as a correction.[11] Prototype compounds having this attribute, which can be used for sensor application, involve particular dihydroxy substituted biphenyls[12,13] and roof-shaped molecules,[14] bulkily modified structures of lactic acid,[15,16] or specific derivatives of tartaric acid,[17,18] the latter being called TADDOLs.[19]

Here we report on a series of new tartaric acids (**1a**–**6a**) and lactic acid derived compounds (**7a**–**11a**) including, aside from specific TADDOLs (**3c**–**6c**), a particular new type of bis-TADDOLs (**1c**, **2c**). This shows the remarkable property of vapour sorption

* Corresponding author. E-mail address: edwin.weber@chemie.tu-freiberg.de (E. Weber).

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as solid materials as well as the prospective linker molecules for coordinative framework construction.[2,3] We describe preparation of these compounds and demonstrate their behaviour as sorptive materials towards a variety of organic solvent vapours based on investigation by quartz micro balance with regards to a potential sensor aspect.

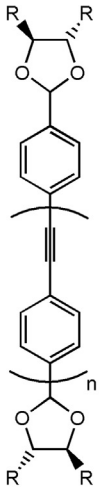
2. Results and discussion

2.1. Design and synthesis of compounds

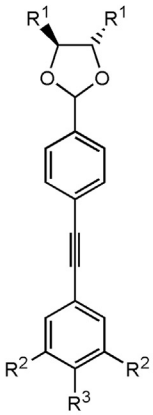
In order to obtain solid materials featuring the desired property of vapour sorption based on tartaric acid, lactic acid and TADDOLs, host compounds that will make use of the solvent inclusion principle in virtue of their bulky constitution paired with the capability of hydrogen bond formation as well as the terminal attachment of the characteristic groups to shape a defined backbone unit should be a promising working plan.[20] This has led to the design of molecules as specified with **1a**–**11a** and **1c**–**6c** in Figs. 1 and 2, of which **1a**–**6a** refer to the compounds derived from tartaric acid, **7a**–**11a** from lactic acid, and **1c**–**6c** being typical of a TADDOL structure.[19] Aside from the characteristic polar terminal groups, rigid spacer units of linear shape are involved in structural formation. These consist of *p*-phenylene and ethynylene moieties, as pointed out in Figs. 1 and 2.

The new tartaric acid derivatives **1a**–**6a** (Fig. 1) were obtained by basic (LiOH) hydrolysis of the corresponding esters **1b**–**6b** in yields ranging between 66 and 87 percent. The respective tartaric ester derivatives **1b**–**6b** were prepared from *L*(+)-diethyl tartrate and corresponding arylaldehyde diethylacetals [**12a** (**1b**), **12b** (**2b**), **13a** (**3b**), **13b** (**4b**), **14a** (**5b**), **14c** (**6b**)] (Fig. 3), following a trans-acetalisation.[21] The respective diethylacetals **12b**, **13a** and **13b** were synthesized via Pd-catalysed cross-coupling reaction[22] between 4-ethynylbenzaldehyde diethylacetal (**14b**) and 4-bromobenzal dehyde diethylacetal, dimethyl 5-iodoisophthalate or ethyl 4-bromobenzoate, respectively. The diethylacetals **14a**[23] and **14b**[24] were prepared according to the literature procedures while **12a** is a purchasable compound. The diethylacetal **14c** was obtained via reaction between **14b** and methyl chloroformiate in the presence of *n*-BuLi.[25]

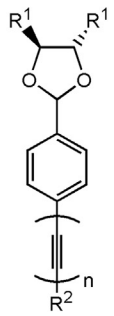
The new lactic acid derivatives **7a**–**11a** (Fig. 2) were prepared from the corresponding ester hydrolysis (LiOH) of **7b**–**11b**, similar to the tartaric acid derivatives. The esters **7b** and **11b** result from substitution reactions between *L*(+)-ethyl lactate and 1,4-



1a n = 0, R = COOH
1b n = 0, R = COOEt
1c n = 0, R = CPh_2OH
2a n = 1, R = COOH
2b n = 1, R = COOEt
2c n = 1, R = CPh_2OH



3a R^1 = COOH, R^2 = COOH, R^3 = H
3b R^1 = COOEt, R^2 = COOMe, R^3 = H
3c R^1 = CPh_2OH, R^2 = CPh_2OH, R^3 = H
4a R^1 = COOH, R^2 = H, R^3 = COOH
4b R^1 = COOEt, R^2 = H, R^3 = COOEt
4c R^1 = CPh_2OH, R^2 = H, R^3 = CPh_2OH



5a n = 0, R^1 = COOH, R^2 = COOH
5b n = 0, R^1 = COOEt, R^2 = COOEt
5c n = 0, R^1 = CPh_2OH, R^2 = CPh_2OH
6a n = 1, R^1 = COOH, R^2 = COOH
6b n = 1, R^1 = COOEt, R^2 = COOMe
6c n = 1, R^1 = CPh_2OH, R^2 = CPh_2OH

Fig. 1. Chemical structures of tartaric acid derivatives **1a**–**6a** including ester intermediates **1b**–**6b** and corresponding TADDOLs **1c**–**6c**, studied in this paper.

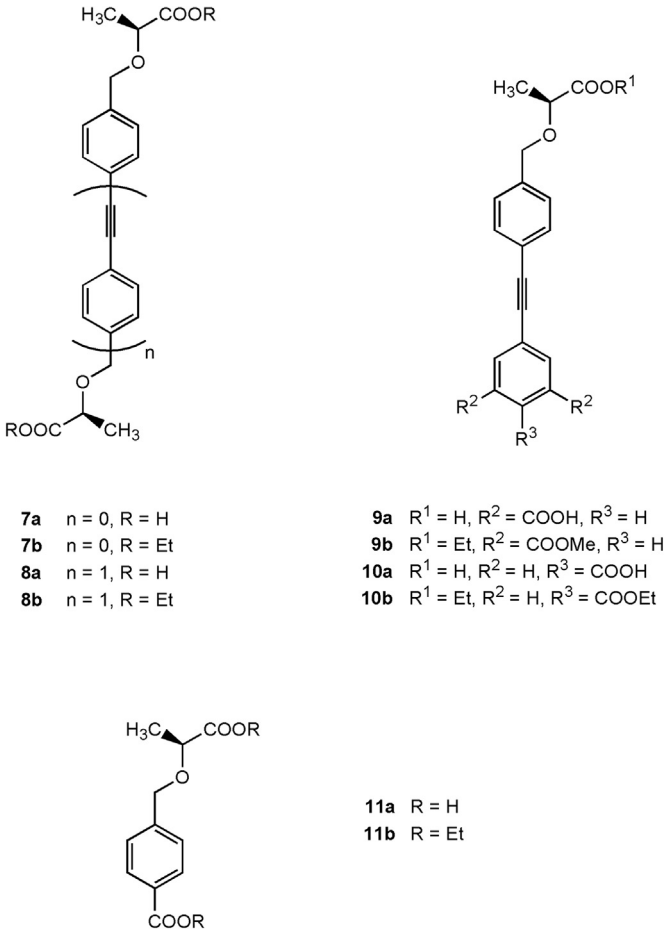


Fig. 2. Chemical structures of lactic acid derivatives **7a**–**11a** including ester intermediates **7b**–**11b**, studied in this paper.

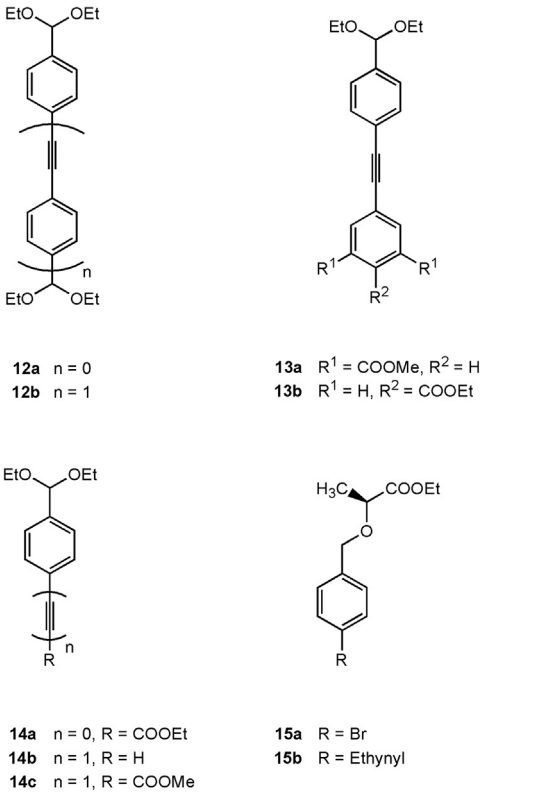


Fig. 3. Chemical structures of acetals and lactate intermediates involved in the syntheses of the target compounds.

bis(bromomethyl) benzene or ethyl 4-(bromomethyl)benzoate; the esters **8b**–**10b** from Pd-catalysed cross coupling reaction[22] between **15b** and **15a**, dimethyl 5-iodoisophthalate or ethyl 4-bromobenzoate, respectively. The lactic ester intermediate **15a** (Fig. 3) was prepared from the substitution reaction of 4-bromobenzyl bromide with *L*(+)-ethyl lactate under basic conditions (NaH), while the ester **15b** (Fig. 3) via Pd-catalysed cross-coupling between **15a** and trimethylsilylacetylene followed by fluoride assisted deprotection of the TMS-protected intermediate compound.

The TADDOLs **1c**–**6c** (Fig. 1) were synthesized in moderate to high yields using common Grignard reactions[26] between phenylmagnesium bromide and corresponding tartaric esters **1b**–**6b**.

All new synthesised compounds are proven in their structures by NMR and IR spectroscopic as well as elemental analytic data. Noteworthy remarks about this are given in the following: Regarding the ^{1}H NMR data of the tartaric acid **1a**–**6a** and ester derivatives **1b**–**6b**, the methine protons located at the asymmetric carbon atoms are split into doublets. Moreover, in the case of these esters, the ethyl groups occur as separate triplets and quartets attributed to the chirality of the compounds. For a similar reason, in the ^{1}H NMR spectra of the lactic acid **7a**–**11a** and ester derivatives **7b**–**11b**, the benzylic methylene protons are represented by two doublets and in the case of the lactic esters, the ethyl groups are split into a triplet and a symmetric multiplet resulting from a $CH^{A}H^{B}$ spin system. Also the acetals **12**–**14** (**a**–**c**) show this splitting of the ethyl groups due to the diastereotopic property of the methylene protons. In the ^{13}C NMR of the tartaric acid and ester derivatives, the methine carbons of the asymmetric centres, the respective carboxylic carbons, and also the carbons of the ethyl groups of the esters appear as two different signals.

A rather complex behaviour regarding the resonances of the aromatic protons is observed for the TADDOLs **1c**–**6c** showing such multiplets in the ^{1}H and a large number of signals in the ^{13}C NMR spectra being difficult to assign. This, however, is in line with a previous finding obtained for closely related TADDOLs[27] providing evidence that a seven-membered ring is formed by an intramolecular hydrogen bond between the two neighbouring OH groups leading to a complex stereochemical environment. The IR spectra of **3c** and **4c** show some unexpected behaviour in that absorption of the ethyne bond cannot be observed, though the molecules are unsymmetrical, with reference to the substitution of the ethynylene unit.

Another point perhaps calling for an explanation is the isolation of the TADDOLs **1c**–**6c** co-crystallized as solvates with acetone. However, TADDOLs and related derivatives are well-known for their specific behaviour to form highly stable and stoichiometric crystalline inclusion compounds with organic solvents[17–19] this being the case also with the aforementioned TADDOLs. A similar argumentation holds for the hydrates of the tartaric acid derivatives **1a**–**6a** considering the distinct enclathration property found for other rigid framework substituted carboxylic acids.[28,29]

2.2. Organic vapour sorption

In demonstration of the expected absorption/desorption behaviour of the newly developed solid compounds towards organic vapour molecules, a quartz crystal microbalance (QCM)[30] as the gravimetric device was used. Here, the corresponding gas-sensing process is shown via the incorporation of the analyte into the chemical layer deposited on the quartz crystal, leading to a mass

increase. As a result, the resonance frequency of the quartz crystal is shifted. The theoretical correlation is given by the Sauerbrey's equation:[31]

$$\Delta f = C\Delta m,$$

where Δf stands for the frequency shift and C for a calibration constant (including the resonance frequency of the non-loaded quartz, the frequency constant of the quartz, its density, and the electrode surface).

In practice, this measurement involves controlled dipping of the gold plated quartz into a 0.01N solution of the respective compound dissolved in ethanol and subsequent evaporation of the solvent to form the receptor layer. Compounds that have been investigated in this respect include the tartaric acids **1a**–**6a**, lactic acid derivatives **7a**–**11a** as well as the TADDOLs **1c**–**6c**. The organic vapours that have been selected for the sorption study are *n*-hexane, tetrahydrofuran (THF), dichloromethane (DCM), acetone and ethanol, these being exemplary solvents of low and high polarity as well as of aprotic and protic nature. Taking into account the molar masses of both the solvent and the absorbent, a factor x' can be deduced indicating the number of solvent molecules being absorbed per molecule of the receptor:

$$x' = \frac{\Delta n(\text{solvent})}{\Delta n(\text{receptor})}.$$

This means an absorption ratio of 100% equals an inclusion stoichiometry of 1:1. The results for the ratio of absorption (x' in mol%) obtained for the different receptor molecules are illustrated in Figs. 4–6.

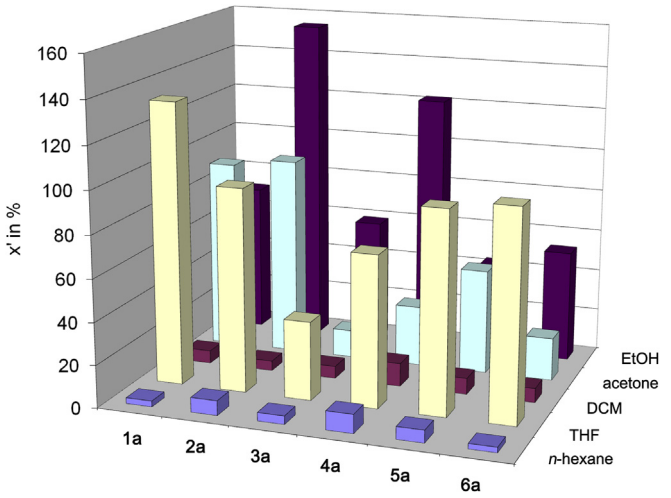


Fig. 4. Comparison of the ratios of absorption involving solid tartaric acid derivatives **1a**–**6a** as QCM coating materials for vapours of various solvents.

With reference to the tartaric acid derivatives **1a**–**6a** (Fig. 4), it is shown that all these compounds absorb *n*-hexane and dichloromethane (DCM) in only small amounts, while THF, acetone and ethanol are absorbed much more efficiently. This can easily be explained by the fact that the molecular structures of the latter solvents behave as efficient hydrogen bond acceptors and form strong hydrogen bonds with the carboxylic acid groups of the receptor molecules. Derivatives **2a**–**4a**, containing a diphenylethyne spacer unit, favour ethanol while compounds **1a**, **5a** and **6a**, featuring a benzene spacer, are most efficient in the absorption of THF. Aside from this structural relation, the presence of an ethynylene unit in the spacer moiety is also important in other respects of the absorption property. This is shown with the different receptor

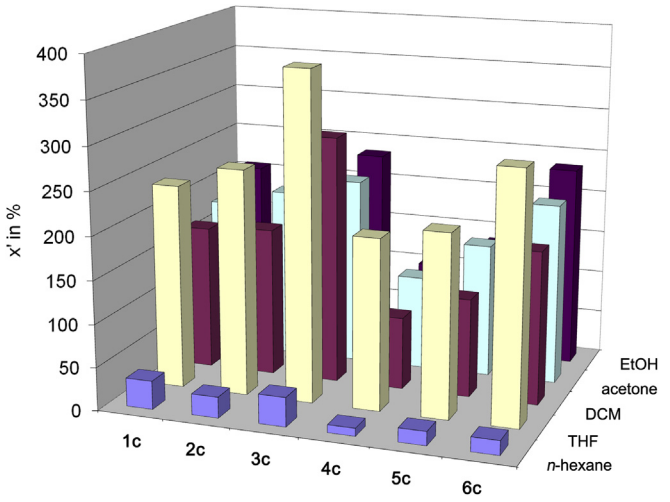


Fig. 5. Comparison of the ratios of absorption involving solid TADDOL derivatives **1c**–**6c** as QCM coating materials for vapours of various solvents.

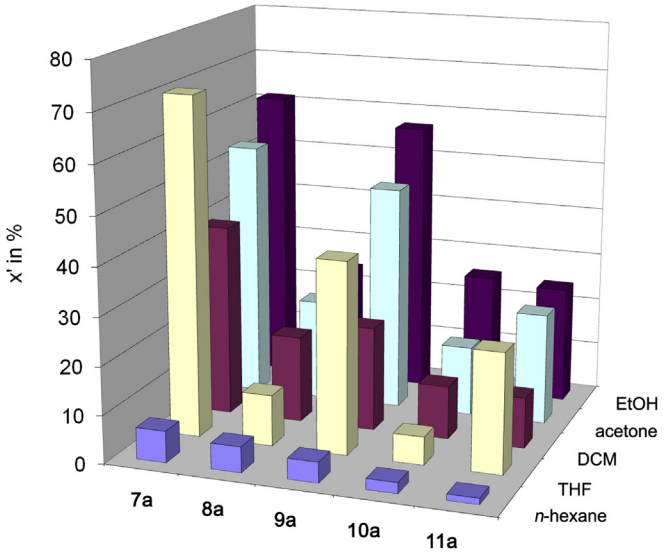


Fig. 6. Comparison of the ratios of absorption involving solid lactic acid derivatives **7a**–**11a** as QCM coating materials for vapours of various solvents.

behaviour of **2a**–**4a** and **6a**, having ethynylene units, as opposed to **1a** and **5a** lacking this particular type of bond. Whereas the ethynylene containing receptor compounds absorb ethanol in higher amounts than acetone, it is the reverse for the receptors free of ethynylene. Moreover, a comparison indicates that in the series of tartaric acid derived receptors, the compounds with a symmetric structure (**1a** and **2a**), tend to show the highest absorption ratios.

Conversion of the tartaric acid functionality of **1a**–**6a** to TADDOL units such as in **1c**–**6c** has a decisive effect on the absorption property of the substance. That is, compared to the acid analogues **1a**–**6a**, the TADDOLs **1c**–**6c** are much more effective and demonstrate distinctly higher ratios of the absorbed vapours, particularly in the case of THF, which is taken up by **3c** in a nearly 1:4 inclusion stoichiometry (Fig. 5). On the other hand, relative to the rest of the solvents, the apolar *n*-hexane is much less preferred by the TADDOLS, as was the case for the tartaric acid derivatives. The polar solvent vapours dichloromethane, acetone and ethanol are roughly equally absorbed in generally moderate amounts, with some variation in the ratio of solvent uptake depending on the respective TADDOL.

Among the molecular solids of the series studied, the lactic acid derivatives **7a**–**11a** are generally the least effective of all in vapour uptake (Fig. 6). Nevertheless, there are preferences for such derivatives. As before, absorption of the apolar *n*-hexane is of no significance, while the more polar solvents ranging from THF to ethanol provide higher degrees of absorption. In more detail, the bis-lactic acid derivative **7a** has high affinity for THF, acetone and EtOH. The tricarboxylic acid derivative **9a** behaves similarly, although in this range of solvents **9a** is slightly less efficient for THF. Forming a sharp contrast to **7a**, the ethynylene spacered analogue **8a** is distinctly inferior in the sorption of the same solvent vapours. Moreover, **10a** features the basic structural framework as contained in **9a** bearing only one acid group in *p*-position, which shows, however, distinct inferiority in solvent sorption to **9a**.

For the potential use of a solid compound as sensor material, not only the quantity of solvent absorption in general but also the relative amounts of absorbed vapours, i.e., the degree of selectivity is of great importance. Considering the data in this respect, there is no compound indicating a respective preference to only one of the examined solvent vapours. However, as derivable from Fig. 4, the tartaric acid receptors could perhaps be used for detection of THF in the presence of *n*-hexane or dichloromethane, just as in selected compounds of this substance class for the detection of acetone or ethanol when *n*-hexane or dichloromethane are present. Nevertheless, as long as the results of the corresponding solvent competition experiments are not in hand, conclusions in this connection invariably suffer to a rather great extent due to uncertainty.

Another precondition for the application of a solid receptor compound in vapour sensing is the reversibility of the absorption and desorption process. In order to allow a short measuring time, this process should be completed as fast as possible. Data of an exemplary study involving the tartaric acid derivative **1a** as the receptor compound and *n*-hexane, dichloromethane, ethanol and acetone as the solvent vapours in this sequence is illustrated in Fig. 7. The diagram shows that at the beginning of the respective analyte gas flow, a very strong decrease of the resonance frequency occurs, which can be explained by overloading due to the high concentration of the saturated gas atmosphere at the beginning of the influx of air. In the respective sensor experiment, all the solvents studied are desorbed by the outflow of synthetic air, which requires a longer time before the initial frequency value is reached. The better the analyte is absorbed, the longer the time is for complete desorption of the solvent from the receptor layer. For comparison, frequency changes of an untreated reference quartz are also given in Fig. 7 ascertaining the effectiveness of the receptor coating without doubt.

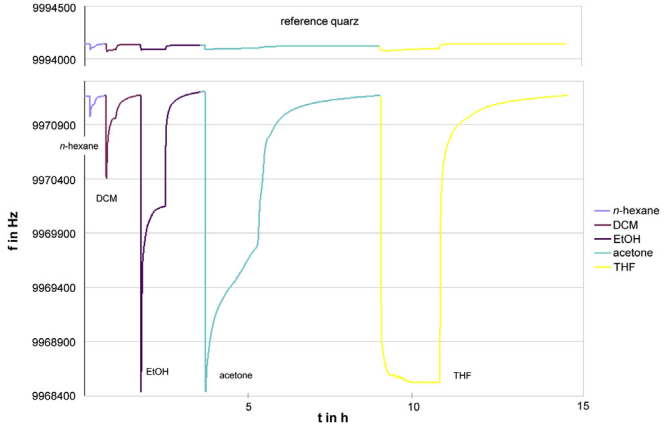


Fig. 7. Absorption and desorption vs time of solid tartaric acid derivative **1a** as QCM coating material for various solvent vapours by response monitoring of frequency change. Sequence of the solvent vapours used in the experiment refers to their rates of absorption.

Owing to the chirality of the receptor molecules being ensured by the presence of the enantiomerical pure tartaric and lactic acid derived building units, enantioselective vapour sorption could have been expected.[15,16] However, corresponding QCM experiments using solvent vapours as racemates or separate enantiomers were found to show only unsatisfactory results.

3. Conclusions

Sequences of reaction steps involving transacetalisation, Pd-catalysed cross-coupling, hydrolysis and Grignard reactions are demonstrated to be successful in the synthesis of new types of tartaric acid, lactic acid and TADDOL derived receptors yielding the compounds in high quantity and purity. As solid coatings of a quartz crystal microbalance (QCM), the compounds prove effective in the sorption of organic solvent vapours leading, however, to different results, depending both on the structural properties of receptor, solvent molecules as well as on solvent polarity. On the part of receptors, a general conclusion with reference to the efficiency of solvent absorption is roughly as follows: TADDOLS>tartaric acid derivatives>lactic acid derivatives. Regarding the variety of solvent vapours, this basically becomes noticeable in the fact that *n*-hexane and dichloromethane are absorbed in only small amounts as compared with THF, acetone and ethanol being in conformity in polarity and hydrogen bonding lines of reasoning. More profound conclusions regarding the sorption behaviour of the different receptors based on the structural interdependence of receptors and analytes are difficult to substantiate. However, deduced from an exemplary study showing reversibility of the absorption/desorption processes, we conclude that the present series of compounds easily provide for the formation of solid receptor layers, which are potentially useful in practical vapour sensing by instrumental means of QCM measurement. In addition to the examples given in this paper, this is an indication to the number of other common solvent vapours but in a qualified sense of enantiospecification. Nevertheless, the present compounds, due to their functional behaviour and chirality, also appear promising as spacer units in the design of the metal coordinated framework structures[2,3] that may meet the requirements of enantioselection in this field of application.

4. Experimental

4.1. General

Melting points were measured on a BÜCHI Melting Point B-450 (BÜCHI Labortechnik AG, Flawil, Switzerland). ^{1}H NMR and ^{13}C NMR spectra (ppm) were recorded on a Bruker DPX 400 (400.1 and 100.6 MHz, respectively) and a Bruker Avance III 500 (500.1 and 125.8 MHz, respectively) using TMS as reference. IR spectra were obtained from a Nicolet FT-IR 510 spectrometer as liquid films in a NaCl cell or in KBr pellets. Optical rotation measurements were performed on a Perkin-Elmer 241 polarimeter at 20 °C and with λ=589.3 nm (Na_D line). The $[\alpha]_D^{20}$ values are given in [deg ml dm^{-1} g^{-1}].

Starting compounds including bromobenzene, 1,4-bis(bromomethyl)benzene, 4-bromobenzaldehyde diethylacetal, 4-bromobenzoic acid, *L*(+)-diethyl tartrate, dimethyl 5-amino isophthalate, ethyl 4-(bromomethyl)benzoate, *L*(+)-ethyl lactate, 4-formylbenzoic acid, terephthalaldehyde bis(diethylacetal) (**12a**) and other reagents were purchased from commercial sources. Dimethyl 5-iodoisophthalate[32] and ethyl 4-bromobenzoate[33] were prepared as described in the literature. Solvents were purified and dried using standard laboratory procedures.

4.2. Synthesis of acetals and lactate intermediates

*4.2.1. 4,4′-Ethynylenedibenzaldehyde bis(diethylacetal) (**12b**).* 4-Bromobenzaldehyde diethylacetal and 4-ethynylbenzaldehyd diethylacetal (**14b**) were reacted using cross-coupling conditions and working up as described in the literature[34] to yield the compound (35%, white solid, mp 72–74 °C) showing the reported analytical data.[34]

*4.2.2. 4-[3,5-Di(methoxycarbonyl)phenylethynyl]benzaldehyde diethylacetal (**13a**).* Dimethyl 5-iodoisophthalate (16.00 g, 50 mmol) and 4-ethynylbenzaldehyde diethylacetal (**14b**) (11.20 g, 55 mmol) were dissolved in degassed triethylamine (250 ml). To the solution, the catalyst [composed of $Pd(PPh_3)_2Cl_2$ (364 mg, 0.5 mmol), CuI (188 mg, 1.0 mmol), PPh_3 (392 mg, 1.5 mmol)] was added and the mixture was stirred under argon at 110 °C until completion of the reaction (DC-analysis). The suspension was diluted with diethyl ether and washed with aqueous NH_4Cl and NaCl solutions. After drying over Na_2SO_4, the solvent was removed under reduced pressure to yield 12.80 g (65%) of a yellow oil after column chromatography (SiO_2, EtOAc/*n*-hexane 1:6, R_f=0.40). MS (GC–MS): *m/z*=396 $[M]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.25 (t, 6H, CH_3, $^3J_{HH}$=7.10); 3.50–3.65 (m, sym., 4H, CH^AH^B); 3.96 (s, 6H, OCH_3); 5.52 (s, 1H, C*H*, acetal); 7.49 (d, 2H, aryl-*H*; $^3J_{HH}$=8.25); 7.55 (d, 2H, aryl-H, $^3J_{HH}$=8.25) 8.36 (s, 2H, aryl-*H*); 8.60 (s, 1H, aryl-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=15.09 (*C*H_3), 52.40 (O*C*H_3); 60.92 (*C*H_2); 87.41, 91.05 (*C*≡*C*); 100.83 (*C*H); 122.23, 124.24, 126.72, 129.90, 130.83, 131.48, 136.35, 139.77 (aryl-*C*); 165.44 (*C*OOMe). IR (NaCl cell): 2217 (C≡C); 1733 (C=O); 1611, 1596, 1505 (C=C, Ar); 1193, 1156, 1059 (acetal). Elemental analysis calculated for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 69.57; H, 6.25.

*4.2.3. 4-[4-(Ethoxycarbonyl)phenylethynyl]benzaldehyde diethylacetal (**13b**).* Ethyl 4-bromobenzoate (11.44 g, 50 mmol) and 4-ethynylbenzaldehyde diethylacetal (**14b**) (11.20 g, 55 mmol) were reacted using the cross-coupling conditions described for the synthesis of (**13a**). Column chromatography (SiO_2, EtOAc/*n*-hexane 1:4, R_f=0.65) yielded 45% of a light yellow solid. mp 37–39 °C. MS (GC–MS): *m/z*=352 $[M]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.23 (t, 6H, CH_3, $^3J_{HH}$=7.10); 1.40 (t, 3H, CH_3, $^3J_{HH}$=7.15); 3.51–3.65 (m, sym., 4H, CH^AH^B); 4.38 (q, 2H, CH_2, $^3J_{HH}$=7.15); 5.52 (s, 1H, C*H*, acetal); 7.48 (d, 2H, aryl-*H*, $^3J_{HH}$=8.25); 7.55 (d, 2H, aryl-*H*, $^3J_{HH}$=8.25); 7.58 (d, 2H, aryl-*H*, $^3J_{HH}$=8.30); 8.03 (d, 2H, aryl-*H*, $^3J_{HH}$=8.30); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=14.31, 15.17 (*C*H_3); 60.91, 61.13 (*C*H_2); 88.84, 92.11 (*C*≡*C*); 100.95 (*C*H); 122.58, 126.73, 127.81, 129.40, 129.81, 131.45, 131.56, 139.71 (aryl-*C*); 166.06 (*C*OOEt). IR (cm^{-1}, KBr): 2214 (C≡C); 1717 (C=O); 1606, 1562, 1515 (C=C, Ar); 1173, 1128, 1059 (acetal). Elemental analysis calculated for $C_{22}H_{24}O_4$: C, 62.04; H, 10.41. Found: C, 61.93; H, 10.18.

*4.2.4. 4-(Ethoxycarbonyl)benzaldehyde diethylacetal (**14a**).* 4-Formylbenzoic acid was reacted with thionyl chloride and triethyl orthoformiate in ethanol according to the literature procedure.[23,34] to yield the compound (90%, yellow liquid) showing analytical data, which correspond to the literature specifications.[23]

*4.2.5. 4-Ethynylbenzaldehyde diethylacetal (**14b**).* 4-Bromobenzaldehyde diethylacetal and MEBINOL were reacted using the cross-coupling conditions and deprotection procedure as described in the literature[24,34] to yield the compound (95%, brownish-red liquid) showing the reported analytical data.[34]

*4.2.6. 4-[2-(Methoxycarbonyl)ethynyl]benzaldehyde diethylacetal (**14c**).* To a stirred solution of 4-ethynylbenzaldehyde diethylacetal (**14b**) (10.21 g, 50 mmol) in THF (150 ml) was added dropwise *n*-BuLi (34.4 ml, 55 mmol, 1.6M in *n*-hexane) at −60 °C under argon. Stirring was continued at the same temperature for 30 min. This mixture was then added to −60 °C cooled methyl chloroformiate (5.67 g, 60 mmol). After warming up to room temperature, the mixture was quenched with water. The aqueous layer was extracted with diethyl ether. The combined organic phases were washed with aqueous Na_2CO_3 and NaCl solutions, then dried (Na_2SO_4) and evaporated under reduced pressure to give a brown oil. Column chromatography (SiO_2, EtOAc/*n*-hexane 1:10, R_f=0.35) yielded 10.75 g (82%) of a yellow oil. MS (GC–MS): *m/z*=262 $[M]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.24 (t, 6H, CH_3, $^3J_{HH}$=7.05); 3.50–3.62 (m, sym., 4H, OCH^AH^B); 3.84 (s, 3H, OCH_3); 5.51 (s, 1H, C*H*, acetal); 7.49 (d, 2H, aryl-H, $^3J_{HH}$=8.25); 7.58 (d, 2H, aryl-*H*, $^3J_{HH}$=8.25); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=15.10 (*C*H_3); 52.72 (O*C*H_3), 61.05 (*C*H_2); 80.41, 86.30 (*C*≡*C*); 100.64 (*C*H, acetal); 119.29, 126.91, 132.83, 141.86 (aryl-*C*); 154.38 (*C*OOMe). IR (NaCl cell): 2224 (C≡C); 1714 (C=O); 1606, 1565 (C=C, Ar); 1169, 1116, 1052 (acetal). Elemental analysis calculated for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.66; H, 6.82.

*4.2.7. Ethyl O-[(4-bromophenyl)methyl]-(S)-lactate (**15a**).* To a cooled (0 °C) suspension of sodium hydride (5.00 g, 125 mmol, 60% suspended in oil) in dichloromethane (60 ml) was added dropwise *L*(+)-ethyl lactate (5.95 g, 50 mmol) dissolved in dichloromethane (25 ml). After having stirred for 30 min, a solution of 4-bromobenzyl bromide in dichloromethane (60 ml) was added dropwise and the mixture was stirred for 5 h at room temperature. Water was added and the mixture was extracted with dichloromethane. The combined organic phases were dried (Na_2SO_4) and evaporated under reduced pressure to yield 7.86 g (55%) of a light-yellow liquid after column chromatography (SiO_2, Et_2O/*n*-hexane 1:9, R_f=0.39). $[\alpha]_D^{20}$=−50.6 (*c*=0.57, $CHCl_3$). MS (GC–MS): *m/z*=286 $[M]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.29 (t, 3H, CH_2CH_3, $^3J_{HH}$=7.15); 1.43 (d, 3H, $CHCH_3$, $^3J_{HH}$=6.85); 4.03 (q, 1H, C*H*, $^3J_{HH}$=6.85); 4.18–4.24 (m, sym., 2H, C$H^AH^BCH_3$); 4.40 (d, 1H, aryl-CH_2, $^2J_{HH}$=11.75); 4.63 (d, 1H, aryl-CH_2, $^2J_{HH}$=11.75); 7.24 (d, 2H, aryl-*H*, $^3J_{HH}$=8.45); 7.46 (d, 2H, aryl-*H*, $^3J_{HH}$=8.45); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=14.13 (CH_2CH_3); 18.55 ($CHCH_3$); 60.77 (CH_2CH_3); 71.06 (aryl-*C*H_2); 74.14 (*C*H); 121.56, 129.42, 131.38, 136.62 (aryl-*C*); 172.89 (*C*OOEt). IR (NaCl cell): 1746 (C=O); 1591 (C=C, Ar); 1071 (C–O); 1027 (C–Br). Elemental analysis calculated for $C_{12}H_{15}O_3Br$: C, 50.19; H, 5.27. Found: C, 50.21; H, 5.33.

*4.2.8. Ethyl O-[(4-ethynylphenyl)methyl]-(S)-lactate (**15b**).* Aryl bromide **15a** (14.36 g, 50 mmol), trimethylsilylacetylene (6.18 g, 63 mmol), $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.5 mmol), CuI (0.19 g, 1.0 mmol) and PPh_3 (0.39 g, 1.5 mmol) in triethylamine (150 ml) were reacted for 5 h at 70 °C using the procedure described for **13a** to yield 13.80 g (91%) of the TMS-protected intermediate compound as a yellow-orange liquid. R_f=0.46 (Et_2O/*n*-hexane 1:6). MS (GC–MS): *m/z*=304 $[M]^+$. For deprotection, to this intermediate compound (12.00 g, 40 mmol) dissolved in THF (65 ml) was added a solution of tetrabutylammonium fluoride (1.17 g, 3.5 mmol) in THF (6.5 ml). The mixture was stirred for 2 h at room temperature and the solvent evaporated to yield 8.17 g (88%) of a yellow liquid after column chromatography (SiO_2, Et_2O/*n*-hexane 1:6, R_f=0.28). $[\alpha]_D^{20}$=−48.6 (*c*=0.23, $CHCl_3$). MS (GC–MS): *m/z*=232 $[M]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.29 (t, 3H, CH_2CH_3, $^3J_{HH}$=7.15); 1.43 (d, 3H, $CHCH_3$, $^3J_{HH}$=6.85); 3.08 (s, 1H, ≡C*H*); 4.03 (q, 1H, C*H*, $^3J_{HH}$=6.85); 4.18–4.24 (m, sym., 2H, C$H^AH^BCH_3$); 4.43 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.00); 4.68 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.00); 7.32 (d, 2H, aryl-*H*; $^3J_{HH}$=8.20); 7.47 (d, 2H, aryl-*H*, $^3J_{HH}$=8.20); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=14.10 (CH_2CH_3); 18.52 ($CHCH_3$); 60.75 (CH_2CH_3); 71.32 (aryl-CH_2); 74.16 (*C*H); 77.18, 83.36 (*C*≡*C*); 121.38, 127.54, 132.02, 138.39 (aryl-*C*); 172.91 (*C*OOEt). IR (NaCl cell): 2108 (C≡C);

1749 (C=O); 1511 (C=C, Ar); 1068 (C–O). Elemental analysis calculated for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.11; H, 6.83.

4.3. Tartaric ester derivatives 1b–6b (general procedure)

To a solution of the corresponding diethyl acetal and *L*(+)-diethyl tartrate in toluene (p.a.), a catalytic amount of pyridinium tosylate was added. In order to remove the by-product ethanol from the mixture, the solvent was distilled off during the reaction. The residue was diluted with diethyl ether and washed with borax and water to remove unreacted *L*(+)-diethyl tartrate. The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. Specific details for each compound including procedure of purification are given below.

*4.3.1. Tetraethyl 2,2′-(benzene-1,4-diyl)bis[(4R,5R)-1,3-dioxolane-4,5-dicarboxylate] (**1b**).* 1,4-Bis(diethoxymethyl)benzene (**12a**) (7.06 g, 25 mmol), *L*(+)-diethyl tartrate (11.31 g, 55 mmol), pyridinium tosylate (0.50 g, 2 mmol) in toluene (300 ml) were used. The crude product was crystallized from toluene to yield 9.18 g (72%) of a white solid. mp. 68–70 °C (lit.[35] mp 69–71 °C). $[\alpha]_D^{20}$=−16.5 (*c*=0.51, $CHCl_3$) [lit.[35] $[\alpha]_D^{20}$=−34.0 (*c*=1.0, MeOH)].^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.30 (t, 6H, C*H*$_3$, $^3J_{HH}$=7.10); 1.35 (t, 6H, C*H*$_3$, $^3J_{HH}$=7.10); 4.26 (q, 4H, C*H*$_2$, $^3J_{HH}$=7.15); 4.32 (q, 4H, C*H*$_2$, $^3J_{HH}$=7.15); 4.84 (d, 2H, C*H*, $^3J_{HH}$=4.05); 4.95 (d, 2H, C*H*, $^3J_{HH}$=4.05); 6.18 (s, 2H, C*H*, acetal); 7.62 (s, 4H, aryl-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=14.03, 14.12 (*C*H$_3$); 62.02, 62.04 (*C*H$_2$); 77.38, 77.59 (*C*H); 106.24 (*C*H, acetal); 127.16, 137.27 (aryl-*C*); 168.94, 169.55 (*C*OOEt). IR (cm^{-1}, KBr): 1752 (C=O); 1619 (C=C, Ar); 1217, 1103, 1071 (acetal). Elemental analysis calculated for $C_{24}H_{30}O_{12}$: C, 56.47; H, 5.92. Found. C, 56.21; H, 6.08.

*4.3.2. Tetraethyl 2,2′-(ethynylene-dibenzene-4,1-diyl)bis[(4R,5R)-1,3-dioxolane-4,5-dicarboxylate] (**2b**).* Bis[4-(diethoxymethyl)phenyl]-acetylene (**12b**) (9.56 g, 25 mmol), *L*(+)-diethyl tartrate (11.31 g, 55 mmol), pyridinium tosylate (0.50 g, 2 mmol) in toluene (500 ml) were used to yield 6.10 g (42%) of a white solid after column chromatography (SiO_2, EtOAc/*n*-hexane 1:2, R_f=0.31). mp. 74–77 °C (lit.[34] mp 74–77 °C). $[\alpha]_D^{20}$=+19.0 (*c*=0.61, $CHCl_3$) [lit.[34] $[\alpha]_D^{20}$=+19.0 (*c*=0.01 mol/l, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.31 (t, 6H, C*H*$_3$, $^3J_{HH}$=7.15); 1.36 (t, 6H, C*H*$_3$, $^3J_{HH}$=7.15); 4.28 (q, 4H, C*H*$_2$, $^3J_{HH}$=7.15); 4.33 (q, 4H, C*H*$_2$, $^3J_{HH}$=7.15); 4.83 (d, 2H, C*H*, $^3J_{HH}$=4.00); 4.95 (d, 2H, C*H*, $^3J_{HH}$=4.00); 6.17 (s, 2H, C*H*, acetal); 7.54–7.59 (m, 8H, aryl-*H*, AA′BB′system); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.08, 14.16 (*C*H$_3$); 62.09, 62.14 (*C*H$_2$); 77.42, 77.69 (*C*H); 89.84 (*C*≡*C*); 106.25 (*C*H, acetal); 124.69, 127.23, 131.64, 135.71 (aryl-*C*); 168.82, 169.25 (*C*OOEt). IR (cm^{-1}, KBr): 1742 (C=O); 1613, 1562, 1521 (C=C, Ar); 1220, 1195, 1100 (acetal). Elemental analysis calculated for $C_{32}H_{34}O_{12}$: C, 62.94; H, 5.61. Found: C, 62.80; H, 5.70.

*4.3.3. Diethyl 2-{4-[3,5-(dimethoxycarbonyl)phenylethynyl]phenyl}-(4R,5R)-1,3-dioxolane-4,5-dicarboxylate (**3b**).* Dimethyl 5-[4-(diethoxymethyl)phenylethynyl]-1,3-benzene dicarboxylate (**13a**) (9.90 g, 25 mmol), *L*(+)-diethyl tartrate (5.66 g, 27.5 mmol), pyridinium tosylate (0.25 g, 1 mmol) in toluene (300 ml) were used to yield 9.82 g (62%) of a yellow oil after column chromatography (SiO_2, EtOAc/*n*-hexane 1:3, R_f=0.27), which crystallized to give a white solid. mp. 66–68 °C. $[\alpha]_D^{20}$=+14.1 (c=0.51, $CHCl_3$). MS (ESI): *m/z*=533.0 $[M+Na]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.31 (t, 3H, C*H*$_3$, $^3J_{HH}$=7.15); 1.36 (t, 3H, C*H*$_3$, $^3J_{HH}$=7.15); 3.95 (s, 6H, OC*H*$_3$); 4.28 (q, 2H, C*H*$_2$, $^3J_{HH}$=7.15); 4.33 (q, 2H, C*H*$_2$, $^3J_{HH}$=7.15); 4.85 (d, 1H, C*H*, $^3J_{HH}$=3.95); 4.97 (d, 1H, C*H*, $^3J_{HH}$=3.95); 6.18 (s, 1H, C*H*, acetal); 7.58 (d, 2H, aryl-*H*, $^3J_{HH}$=8.45); 7.61 (d, 2H, aryl-*H*, $^3J_{HH}$=8.45); 8.35 (s, 2H, aryl-*H*); 8.61 (s, 1H, aryl-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=13.93, 14.01 (*C*H$_3$), 52.37 (O*C*H$_3$); 61.95, 61.96 (*C*H$_2$); 77.22, 77.56 (*C*H); 87.98, 90.67 (*C*≡*C*); 105.98 (*C*H, acetal); 123.89, 123.99, 127.21, 129.99, 130.82, 131.57, 136.06, 136.33 (aryl-*C*); 165.34 (*C*OOMe); 168.84, 169.32 (*C*OOEt). IR (cm^{-1}, KBr): 2217 (C≡C); 1742 (C=O); 1616, 1591, 1515 (C=C, Ar); 1217, 1198, 1106 (acetal). Elemental analysis calculated for $C_{27}H_{26}O_{10}$: C, 63.53; H, 5.13. Found: C, 63.37; H, 5.24.

*4.3.4. Diethyl 2-{4-[4-(ethoxycarbonyl)phenylethynyl]phenyl}-(4R,5R)-1,3-dioxolane-4,5-dicarboxylate (**4b**).* Ethyl 4-[4-(diethoxymethyl)-phenylethynyl]benzoate (**13b**) (8.80 g, 25 mmol), *L*(+)-diethyl tartrate (5.66 g, 27.5 mmol), pyridinium tosylate (0.25 g, 1 mmol) in toluene (250 ml) were used to yield 3.85 g (33%) of a pale yellow solid after column chromatography (SiO_2, EtOAc/*n*-hexane 1:4, R_f=0.35). mp. 70–73 °C. $[\alpha]_D^{20}$=+19.3 (*c*=0.46, $CHCl_3$). MS (ESI): *m/z*=489.0 $[M+Na]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.34 (t, 3H, C*H*$_3$, $^3J_{HH}$=7.15); 1.39 (t, 3H, C*H*$_3$, $^3J_{HH}$=7.15); 1.43 (t, 3H, C*H*$_3$, $^3J_{HH}$=7.15); 4.31 (q, 2H, C*H*$_2$, $^3J_{HH}$=7.15); 4.37 (q, 2H, C*H*$_2$, $^3J_{HH}$=7.15); 4.42 (q, 2H, C*H*$_2$, $^3J_{HH}$=7.15); 4.87 (d, 1H, C*H*, $^3J_{HH}$=4.00); 4.98 (d, 1H, C*H*, $^3J_{HH}$=4.00); 6.20 (s, 1H, C*H*, acetal); 7.61–7.63 (m, 6H, aryl-*H*); 8.05 (d, 2H, aryl-*H*, $^3J_{HH}$=8.10); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=14.07, 14.15, 14.30 (*C*H$_3$); 61.12, 62.09, 62.10 (*C*H$_2$); 77.41, 77.70 (*C*H); 89.47, 91.79 (*C*≡*C*); 106.17 (*C*H, acetal); 124.33, 127.28, 127.64, 129.47, 130.02, 131.51, 131.70, 136.05 (aryl-*C*); 166.02, 168.95, 169.48 (*C*OOEt). IR (cm^{-1}, KBr): 2214 (C≡C); 1761 (C=O); 1606, 1562; 1521 (C=C, Ar); 1220, 1116, 1100 (acetal). Elemental analysis calculated for $C_{26}H_{26}O_8$: C, 66.94; H, 5.62. Found: C, 67.19; H, 5.77.

*4.3.5. Diethyl 2-[4-(ethoxycarbonyl)phenyl]-(4R,5R)-1,3-dioxolane-4,5-dicarboxylate (**5b**).* Ethyl 4-(diethoxymethyl)benzoate (**14a**) (6.30 g, 25 mmol), *L*(+)-diethyl tartrate (5.66 g, 27.5 mmol), pyridinium tosylate (0.25 g, 1 mmol) in toluene (225 ml) were used to yield 6.49 g (71%) of a yellow oil after column chromatography (SiO_2, EtOAc/*n*-hexane 1:4, R_f=0.36). $[\alpha]_D^{20}$=−10.1 (*c*=0.36, $CHCl_3$). MS (GC–MS): *m/z*=365 $[M-H]^+$.^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.30 (t, 3H, C*H*$_3$, $^3J_{HH}$=7.15); 1.36 (t, 3H, C*H*$_3$, $^3J_{HH}$=7.15); 1.40 (t, 3H, C*H*$_3$, $^3J_{HH}$=7.15); 4.26 (q, 2H, C*H*$_2$, $^3J_{HH}$=7.15); 4.33 (q, 2H, C*H*$_2$, $^3J_{HH}$=7.15); 4.38 (q, 2H, C*H*$_2$, $^3J_{HH}$=7.15); 4.85 (d, 1H, C*H*, $^3J_{HH}$=3.90); 4.97 (d, 1H, C*H*, $^3J_{HH}$=3.90); 6.21 (s, 1H, C*H*, acetal); 7.67 (d, 2H, aryl-*H*, $^3J_{HH}$=8.20); 8.07 (d, 2H, aryl-*H*, $^3J_{HH}$=8.20); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=13.96, 14.06, 14.19 (*C*H$_3$); 60.99, 62.00, 62.04 (*C*H$_2$); 77.34, 77.63 (*C*H); 105.83 (*C*H, acetal); 127.03, 129.47, 131.69, 140.14 (aryl-*C*); 166.05, 168.80, 169.32 (*C*OOEt). IR (NaCl cell): 1756 (C=O); 1617, 1580, 1513 (C=C, Ar); 1214, 1174, 1103 (acetal). Elemental analysis calculated for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05. Found: C, 59.00; H, 5.96.

*4.3.6. Diethyl 2-{4-[2-(methoxycarbonyl)ethynyl]phenyl}-(4R,5R)-1,3-dioxolane-4,5-dicarboxylate (**6b**).* Methyl 3-[4-(diethoxymethyl)-phenyl]propynoate (**14c**) (6.55 g, 25 mmol), *L*(+)-diethyl tartrate (5.66 g, 27.5 mmol), pyridinium tosylate (0.25 g, 1 mmol) in toluene (350 ml) were used to yield 5.83 g (62%) of a yellow oil after column chromatography (SiO_2, EtOAc/*n*-hexane 1:3, R_f=0.38). $[\alpha]_D^{20}$=+5.3 (*c*=0.37, $CHCl_3$). MS (GC–MS): *m/z*=375 $[M-H]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.29 (t, 3H, C*H*$_3$, $^3J_{HH}$=7.20); 1.35 (t, 3H, C*H*$_3$, $^3J_{HH}$=7.20); 3.84 (s, 3H, C*H*$_3$); 4.26 (q, 2H, C*H*$_2$, $^3J_{HH}$=7.15); 4.33 (q, 2H, C*H*$_2$, $^3J_{HH}$=7.15); 4.84 (d, 1H, C*H*, $^3J_{HH}$=3.90); 4.95 (d, 1H, C*H*, $^3J_{HH}$=3.90); 6.17 (s, 1H, C*H*, acetal); 7.52 (d, 2H, aryl-*H*, $^3J_{HH}$=8.20); 7.56 (d, 2H, aryl-*H*, $^3J_{HH}$=8.20); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=13.94, 14.03 (*C*H$_3$); 52.72 (*C*H$_3$); 62.02, 62.04 (*C*H$_2$); 77.25, 77.63 (*C*H); 80.77, 85.67 (*C*≡*C*); 105.67 (*C*H, acetal); 120.85, 127.31, 132.83, 138.12 (aryl-*C*); 154.17 (*C*OOMe); 168.79, 169.22 (*C*OOEt). IR (NaCl cell): 2230 (C≡C); 1761 (C=O); 1615, 1571, 1515 (C=C, Ar); 1209, 1171, 1103 (acetal). Elemental analysis calculated for $C_{19}H_{20}O_8$: C, 60.63; H, 5.36. Found: C, 60.34; H, 5.56.

4.4. Tartaric acid derivatives 1a–6a (general procedure)

A solution of the corresponding ester and LiOH in THF and water was stirred at room temperature for 5 h. The reaction mixture was

diluted with water, acidified with 1M HCl and repeatedly extracted with diethyl ether. After washing the combined organic extracts with water and drying it over Na_2SO_4, the solvent was removed under reduced pressure. The obtained crude product was purified by stirring it in cold dichloromethane. Specific details for each compound are given below.

*4.4.1. 2,2′-(Benzene-1,4-diyl)bis[(4R,5R)-1,3-dioxolane-4,5-dicarboxylic acid] (**1a**).* Tetraester **1b** (2.55 g, 5.0 mmol) and LiOH (1.0 g, 41.8 mmol) in THF (125 ml) and water (7.5+35 ml) were used to yield 1.47 g (74%) of a white solid. mp. 108–110 °C (dec). $[\alpha]_D^{20}$=−30.1 (*c*=0.40, EtOH). MS (ESI): *m/z*=397.04 $[M-H]^-$. ^{1}H NMR (DMSO-d_6, 500 MHz): *δ*=4.78 (d, 2H, C*H*, $^3J_{HH}$=3.85); 4.94 (d, 2H, C*H*, $^3J_{HH}$=3.85); 6.04 (s, 2H, C*H*, acetal); 7.63 (s, 4H, aryl-*H*); 13.40 (br, s, 4H, COO*H*); ^{13}C NMR (DMSO-d_6, 125 MHz): *δ*=76.82, 77.33 (*C*H), 104.92 (*C*H, acetal); 127.35, 137.78 (aryl-*C*); 170.72, 171.19 (*C*OOH); IR (cm^{-1}, KBr): 3212 (OH); 1755 (C=O); 1596 (C=C, Ar); 1192, 1122, 1100 (acetal). Elemental analysis calculated for $C_{16}H_{14}O_{12}\cdot 2H_2O$: C, 44.25; H, 4.18. Found: C, 44.29; 4.29.

*4.4.2. 2,2′-(Ethynylene-dibenzene-4,1-diyl)bis[(4R,5R)-1,3-dioxolane-4,5-dicarboxylic acid] (**2a**).* Tetraester **2b** (3.05 g, 5.0 mmol) and LiOH (1.0 g, 41.8 mmol) in THF (110 ml) and water (11+33 ml) were used to yield 1.72 g (69%) of a white solid. mp. 183–186 °C (dec). $[\alpha]_D^{20}$=+11.8 (*c*=0.50, EtOH). MS (MALDI/CCA): *m/z*=685.4 $[M+CCA]^+$. ^{1}H NMR (DMSO-d_6, 500 MHz): *δ*=4.80 (d, 2H, C*H*, $^3J_{HH}$=3.90); 4.85 (d, 2H, C*H*, $^3J_{HH}$=3.85); 6.05 (s, 2H, C*H*, acetal); 7.64 (s, 8H, aryl-*H*); 13.46 (br, s, 4H, COO*H*); ^{13}C NMR (DMSO-d_6, 125 MHz): *δ*=76.80, 77.33 (*C*H); 89.80 (*C*≡*C*); 104.73 (*C*H, acetal); 123.55, 127.84, 131.49, 136.76 (aryl-*C*); 170.69, 171.13 (*C*OOH). IR (cm^{-1}, KBr): 3177 (OH); 1749 (C=O); 1600, 1559, 1521 (C=C, Ar); 1217, 1122, 1103 (acetal). Elemental analysis calculated for $C_{24}H_{18}O_{12}\cdot 2H_2O$: C, 53.94; H, 4.15. Found: C, 54.09; H, 4.32.

*4.4.3. 2-[4-(3,5-Dicarboxyphenylethynyl)phenyl]-(4R,5R)-1,3-dioxolane-4,5-dicarboxylic acid (**3a**).* Tetraester **3b** (2.67 g, 5.0 mmol) and LiOH (1.0 g, 41.8 mmol) in THF (125 ml) and water (12+35 ml) were used to yield 1.85 g (87%) of a white solid. mp. 225–230 °C (dec). $[\alpha]_D^{20}$=+15.5 (*c*=0.42, EtOH). MS (ESI): *m/z*=425.05 $[M-H]^-$. ^{1}H NMR (DMSO-d_6, 500 MHz): *δ*=4.81 (d, 1H, C*H*, $^3J_{HH}$=3.85); 4.97 (d, 1H, C*H*, $^3J_{HH}$=3.85); 6.05 (s, 1H, C*H*, acetal); 7.66 (d, 2H, aryl-*H*; $^3J_{HH}$=8.20); 7.71 (d, 2H, aryl-*H*; $^3J_{HH}$=8.20); 8.28 (s, 2H, aryl-*H*); 8.47 (s, 1H, aryl-*H*); 13.48 (br, s, 4H, COO*H*); ^{13}C NMR (DMSO-d_6, 125 MHz): *δ*=76.84, 77.38 (*C*H); 88.25, 90.64 (*C*≡*C*); 104.73 (*C*H, acetal); 123.15, 123.28, 127.84, 129.97, 131.71, 132.17, 135.73, 137.13 (aryl-*C*); 165.92 (Ar*C*OOH); 170.70, 171.12 (CH*C*OOH). IR (cm^{-1}, KBr): 3082 (OH); 2214 (C≡C); 1720 (C=O); 1600, 1515 (C=C, Ar); 1119; 1100 (acetal). Elemental analysis calculated for $C_{21}H_{14}O_{10}\cdot 2H_2O$: C, 56.76; H, 3.63: Found. C, 56.79; H, 3.91.

*4.4.4. 2-[4-(4-Carboxyphenylethynyl)phenyl]-(4R,5R)-1,3-dioxolane-4,5-dicarboxylic acid (**4a**).* Triester **4b** (2.33 g, 5.0 mmol) and LiOH (0.75 g, 31.3 mmol) in THF (115 ml) and water (11+34 ml) were used to yield 1.51 g (79%) of a white solid. mp.>300 °C (dec). $[\alpha]_D^{20}$=+9.4 (*c*=0.38, EtOH). MS (ESI): *m/z*=381.06 $[M-H]^-$. ^{1}H NMR (DMSO-d_6, 500 MHz): *δ*=4.79 (d, 1H, C*H*, $^3J_{HH}$=3.80); 4.95 (d, 1H, C*H*, $^3J_{HH}$=3.80); 6.05 (s, 1H, C*H*, acetal); 7.66 (s, 4H, aryl-*H*); 7.69 (d, 2H, aryl-*H*, $^3J_{HH}$=8.20); 7.98 (d, 2H, aryl-*H*, $^3J_{HH}$=8.20); 13.35 (br, s, 3H, COO*H*); ^{13}C NMR (DMSO-d_6, 125 MHz): *δ*=76.81, 77.34 (*C*H); 89.43, 91.63 (*C*≡*C*); 104.69 (*C*H, acetal); 123.25, 126.48, 127.89, 129.69, 130.80, 131.61, 131.73, 137.07 (aryl-*C*); 166.78 (Ar*C*OOH), 170.71, 171.13 (CH*C*OOH). IR (cm^{-1}, KBr): 3072 (OH); 2214 (C≡C); 1733 (C=O); 1609, 1562, 1518 (C=C, Ar); 1220, 1125, 1103 (acetal). Elemental analysis calculated for $C_{20}H_{14}O_8\cdot 2H_2O$: C, 57.42; H, 4.34. Found: C, 57.65; H, 4.17.

*4.4.5. 2-(4-Carboxyphenyl)-(4R,5R)-1,3-dioxolane-4,5-dicarboxylic acid (**5a**).* Triester **5b** (1.83 g, 5.0 mmol) and LiOH (0.75 g, 31.3 mmol) in THF (95 ml) and water (9+28 ml) were used to yield 0.93 g (66%) of a white solid. mp. 203–206 °C (dec). $[\alpha]_D^{20}$=−20.6 (*c*=0.28, EtOH). MS (ESI): *m/z*=281.03 $[M-H]^-$. ^{1}H NMR (DMSO-d_6, 500 MHz): *δ*=4.79 (d, 1H, C*H*, $^3J_{HH}$=3.90); 4.94 (d, 1H, C*H*, $^3J_{HH}$=3.90); 6.08 (s, 1H, C*H*, acetal); 7.69 (d, 2H, aryl-*H*, $^3J_{HH}$=8.15); 7.99 (d, 2H, aryl-*H*, $^3J_{HH}$=8.15); 13.63 (br, s, 3H, COO*H*); ^{13}C NMR (DMSO-d_6, 125 MHz): *δ*=76.86, 77.28 (*C*H); 104.47 (*C*H, acetal); 127.51, 129.34, 132.07, 140.70 (aryl-*C*); 167.02 (Ar*C*OOH); 170.54, 171.04 (CH*C*OOH). IR (cm^{-1}, KBr): 3120 (OH); 1755 (C=O); 1619, 1581, 1515 (C=C, Ar); 1223, 1100 (acetal). Elemental analysis calculated for $C_{12}H_{10}O_8\cdot H_2O$: C, 48.01; H, 4.03. Found: C, 48.21; H, 4.14.

*4.4.6. 2-[4-(2-Carboxyethynyl)phenyl]-(4R,5R)-1,3-dioxolane-4,5-dicarboxylic acid (**6a**).* Triester **6b** (1.88 g, 5.0 mmol) and LiOH (0.75 g, 31.3 mmol) in THF (50 ml) and water (10+30 ml) were used to yield 1.18 g (77%) of a white solid. mp. 153–155 °C (dec). $[\alpha]_D^{20}$=−2.9 (*c*=0.30, EtOH). MS (ESI): *m/z*=305.03 $[M-H]^-$. ^{1}H NMR ($CDCl_3$, 500 MHz): *δ*=4.80 (d, 1H, C*H*, $^3J_{HH}$=3.80); 4.96 (d, 1H, C*H*, $^3J_{HH}$=3.80); 6.07 (s, 1H, C*H*, acetal); 7.66–7.71 (m, 4H, aryl-*H*, AA′BB′-system); 13.48 (br, s, 3H, COO*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): *δ*=76.85, 77.45 (*C*H); 82.36, 83.96 (*C*≡*C*); 104.50 (*C*H, acetal); 120.42, 128.00, 132.69, 138.79 (aryl-*C*); 154.29 (≡C*C*OOH); 170.70, 171.07 (CH*C*OOH). IR (cm^{-1}, KBr): 3110 (OH); 2214 (C≡C); 1730 (C=O); 1625, 1508 (C=C, Ar); 1212, 1116, 1100 (acetal). Elemental analysis calculated for $C_{14}H_{10}O_8\cdot H_2O$: C, 51.86; H, 3.73. Found: C, 51.80; H, 3.88.

4.5. Lactic ester derivatives 7b and 11b

A general procedure as described for the synthesis of **15a** applies.

*4.5.1. Diethyl O,O′-[(benzene-1,4-diyl)dimethylene]di-(S)-lactate (**7b**).* 1, 4-Bis(bromomethyl)benzene (6.58 g, 25 mmol) in dichloromethane (25 ml), *L*(+)-ethyl lactate (5.91 g, 50 mmol) in dichloromethane (25 ml) and sodium hydride (5.00 g, 125 mmol, 60% suspended in oil) in dichloromethane (60 ml) were used to yield 1.59 g (19%) of a colourless liquid after column chromatography (SiO_2, EtOAc/*n*-hexane 1:6, R_f=0.21). $[\alpha]_D^{20}$=−74.7 (*c*=0.67, $CHCl_3$). MS (GC–MS): *m/z*=338 $[M]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): *δ*=1.29 (t, 6H, CH_2CH_3, $^3J_{HH}$=7.15); 1.43 (d, 6H, $CHCH_3$, $^3J_{HH}$=6.85); 4.04 (q, 2H, C*H*, $^3J_{HH}$=6.85); 4.20–4.23 (m, sym., 4H, $CH^AH^BCH_3$), 4.44 (d, 2H, aryl-CH_2, $^2J_{HH}$=11.70); 4.69 (d, 2H, aryl-CH_2, $^2J_{HH}$=11.70); 7.34 (s, 4H, aryl-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): *δ*=14.08 (CH_2CH_3); 18.52 ($CHCH_3$); 60.68 (CH_2CH_3); 71.50 (aryl-CH_2); 73.78 (*C*H); 127.91, 137.09 (aryl-*C*); 173.08 (*C*OOEt). IR (NaCl cell): 1749 (C=O); 1518 (C=C, Ar); 1068 (C–O). Elemental analysis calculated for $C_{18}H_{26}O_6$: C, 63.89; H, 7.74. Found: C, 63.67; H, 7.48.

*4.5.2. Ethyl O-[4-(ethoxycarbonyl)phenylmethyl]-(S)-lactate (**11b**).* Ethyl 4-(bromomethyl)benzoate (6.05 g, 25 mmol) in dichloromethane (20 ml), *L*(+)-ethyl lactate (2.94 g, 25 mmol) in dichloromethane (20 ml) and sodium hydride (1.55 g, 65 mmol, 60% suspended in oil) in dichloromethane (30 ml) were used to yield 2.52 g (36%) of a colourless oil after column chromatography (SiO_2, EtOAc/*n*-hexane 1:2, R_f=0.36). $[\alpha]_D^{20}$−49.6 (*c*=0.56, $CHCl_3$). MS (GC–MS): *m/z*=338 $[M]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): *δ*=1.29 (t, 3H, CH_2CH_3, $^3J_{HH}$=7.10); 1.39 (t, 3H, CH_2CH_3, $^3J_{HH}$=7.10); 1.46 (d, 3H, $CHCH_3$, $^3J_{HH}$=6.85); 4.05 (q, 1H, C*H*, $^3J_{HH}$=6.85); 4.20–4.24 (m, sym., 2H, $CH^AH^BCH_3$); 4.37 (q, 2H, CH_2CH_3, $^3J_{HH}$=7.10) 4.51 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.00); 4.75 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.00); 7.42–7.45 (m, 2H,

aryl-*H*); 8.00–8.05 (m, 2H, aryl-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=14.07, 14.15 (CH_2CH_3); 18.48 ($CHCH_3$); 60.76 (CH_2CH_3); 71.17 (aryl-CH_2); 74.30 (*C*H); 127.22, 129.51, 129.72, 142.70 (aryl-*C*); 166.25, 172.83 (*C*OOEt). IR (NaCl cell): 1746 (C=O); 1580 (C=C, Ar); 1073 (C–O). Elemental analysis calculated for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 63.94; H, 7.03.

4.6. Lactic ester derivatives 8b–10b

A general procedure following the synthesis of compound **13a** is used.

*4.6.1. Diethyl O,O′-[ethynylene-bis(benzene-4,1-diyl-methylene)]di-(S)-lactate (**8b**).* Ethyl *O*-[(4-bromophenyl)methyl]-(*S*)-lactate (**15a**) (7.15 g, 25 mmol), Ethyl *O*-[(4-ethynylphenyl)methyl]-(*S*)-lactate (**15b**) (5.80 g, 25 mmol), $Pd(PPh_3)_2Cl_2$ (182 mg, 0.25 mmol), CuI (94 mg, 0.50 mmol), PPh_3 (196 mg, 0.75 mmol) in triethylamine (110 ml) were reacted at 90 °C for 3 h to yield 5.92 g (54%) of a yellow liquid after column chromatography (SiO_2, EtOAc/*n*-hexane 1:4, R_f=0.39). $[\alpha]_D^{20}$=−64.3 (*c*=0.44, $CHCl_3$). MS (GC–MS): *m/z*=438 $[M]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.30 (t, 6H, CH_2CH_3, $^3J_{HH}$=7.15); 1.45 (d, 6H, $CHCH_3$, $^3J_{HH}$=6.85); 4.05 (q, 2H, C*H*, $^3J_{HH}$=6.85); 4.19–4.26 (m, sym., 4H, $CH^AH^BCH_3$); 4.46 (d, 2H, aryl-CH_2, $^2J_{HH}$=11.95); 4.70 (d, 2H, aryl-CH_2, $^2J_{HH}$=11.95); 7.37 (d, 4H, aryl-*H*, $^3J_{HH}$=8.20); 7.51 (d, 4H, aryl-*H*, $^3J_{HH}$=8.20); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=14.19 (CH_2CH_3); 18.62 ($CHCH_3$); 60.84 (CH_2CH_3); 71.52 (aryl-CH_2); 74.20 (*C*H); 89.28 (*C*≡*C*); 122.62, 127.72, 131.59, 137.84 (aryl-*C*); 173.06 (*C*OOEt). IR (NaCl cell): 1746 (C=O); 1613, 1564, 1517 (C=C, Ar); (C–O) 1068. Elemental analysis calculated for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90. Found: C, 70.93; H, 6.79.

*4.6.2. Ethyl O-{4-[3,5-di(methoxycarbonyl)phenylethynyl]phenylmethyl}-(S)-lactate (**9b**).* Dimethyl 5-iodoisophthalate (8.00 g, 25 mmol), ethyl *O*-[(4-ethynylphenyl)methyl]-(*S*)-lactate (**15b**) (5.80 g, 25 mmol), $Pd(PPh_3)_2Cl_2$ (182 mg, 0.25 mmol), CuI (94 mg, 0.50 mmol) and PPh_3 (196 mg, 0.75 mmol) in triethylamine (75 ml) were reacted at 90 °C for 10 h to yield 6.08 g (64%) of a yellow liquid after column chromatography (SiO_2, EtOAc/*n*-hexane 1:4, R_f=0.35). $[\alpha]_D^{20}$=+14.1 (*c*=0.42, $CHCl_3$). MS (GC–MS): *m/z*=424 $[M]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.29 (t, 3H, CH_2CH_3, $^3J_{HH}$=7.15); 1.44 (d, 3H, $CHCH_3$, $^3J_{HH}$=7.15); 3.96 (s, 6H, OCH_3); 4.04 (q, 1H, C*H*, $^3J_{HH}$=6.85); 4.21–4.25 (m, sym., 2H, $CH^AH^BCH_3$); 4.41 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.00); 4.64 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.00); 7.38 (d, 2H, aryl-*H*, $^3J_{HH}$=8.50); 7.53 (d, 2H, aryl-*H*, $^3J_{HH}$=8.50); 8.36 (s, 2H, aryl-*H*); 8.62 (s, 1H, aryl-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=14.21 (CH_2CH_3); 18.66 ($CHCH_3$); 52.50 (OCH_3); 60.90 (CH_2CH_3); 71.49 (aryl-CH_2); 74.32 (*C*H); 87.38, 91.13 (*C*≡*C*); 121.84, 124.36, 127.79, 129.99, 130.92, 131.77, 136.46, 138.55 (aryl-*C*); 165.59 (*C*OOMe), 173.07 (*C*OOEt). IR (NaCl cell): 2216 (C≡C); 1733 (C=O); 1593, 1509 (C=C, Ar); 1067 (C–O). Elemental analysis calculated for $C_{24}H_{24}O_7$: C, 67.91; H, 5.70. Found: C, 67.63; H, 5.84.

*4.6.3. Ethyl O-{4-[4-(ethoxycarbonyl)phenylethynyl]phenylmethyl}-(S)-lactate (**10b**).* Ethyl 4-bromobenzoate (5.72 g, 25 mmol), ethyl *O*-[(4-ethynylphenyl)methyl]-(*S*)-lactate (**15b**) (5.80 g, 25 mmol), $Pd(PPh_3)_2Cl_2$ (182 mg, 0.25 mmol), CuI (94 mg, 0.50 mmol) and PPh_3 (196 mg, 0.75 mmol) in triethylamine (75 ml) were reacted at 90 °C for 10 h to yield 3.04 g (32%) of a yellow liquid after column chromatography (SiO_2, EtOAc/*n*-hexane 1:6, R_f=0.30). $[\alpha]_D^{20}$=27.4 (*c*=0.38, $CHCl_3$). MS (GC–MS): *m/z*=380 $[M]^+$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.30 (t, 3H, CH_2CH_3, $^3J_{HH}$=7.15); 1.43 (t, 3H, CH_2CH_3, $^3J_{HH}$=7.15); 1.46 (d, 3H, $CHCH_3$, $^3J_{HH}$=6.85); 4.06 (q, 1H, C*H*, $^3J_{HH}$=6.85); 4.21–4.26 (m, sym., 2H, $CH^AH^BCH_3$); 4.47 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.00); 4.70 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.00); 7.37 (d, 2H, aryl-*H*, $^3J_{HH}$=8.15); 7.53 (d, 2H, aryl-*H*, $^3J_{HH}$=8.15); 7.58 (d, 2H, aryl-*H*, $^3J_{HH}$=8.40); 8.02 (d, 2H, aryl-*H*, $^3J_{HH}$=8.40); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=14.16, 14.24 (CH_2CH_3); 18.61 ($CHCH_3$); 60.84 (CH_2CH_3); 71.44 (aryl-CH_2); 74.25 (*C*H); 88.68, 92.08 (*C*≡*C*); 122.03, 127.72, 127.76, 129.39, 129.74, 131.42, 131.70, 138.39 (aryl-*C*); 165.96, 173.00 (*C*OOEt). IR (NaCl cell): 2223 (C≡C); 1749 (C=O); 1607, 1560, 1520 (C=C, Ar); 1071 (C–O). Elemental analysis calculated for $C_{23}H_{24}O_5$: C, 72.61; H, 6.36. Found: C, 72.28; H, 6.57.

4.7. Lactic acid derivatives 7a–11a

The general procedure as described for the tartaric acid derivatives **1a**–**6a** via hydrolysis of the corresponding esters applies.

*4.7.1. O,O′-(Benzene-1,4-diyl-dimethylene)di-(S)-lactic acid (**7a**).* Di ester **7b** (1.69 g, 5.0 mmol) and LiOH (0.5 g, 20.9 mmol) in THF (150 ml) and water (15+50 ml) were used to yield 1.37 g (97%) of a white solid. mp. 98–102 °C. $[\alpha]_D^{20}$=−74.75 (*c*=0.28, EtOH). MS (ESI): *m/z*=280.6 $[M-H]^-$. ^{1}H NMR (DMSO-d_6, 500 MHz): δ=1.48 (d, 6H, CH_3, $^3J_{HH}$=6.90); 4.10 (q, 2H, C*H*, $^3J_{HH}$=6.90); 4.51(d, 2H, CH_2, $^2J_{HH}$=11.70); 4.70 (d, 2H, CH_2, $^2J_{HH}$=11.70); 7.36 (s, 4H, aryl-*H*); 10.27 (br, s, 2H, COO*H*); ^{13}C NMR (DMSO-d_6, 125 MHz): δ=18.35 (CH_3); 71.73 (CH_2); 73.42 (*C*H); 128.14, 136.93 (aryl-*C*); 178.60 (*C*OOH). IR (cm^{-1}, KBr): 3129 (OH); 1720 (C=O); 1515 (C=C, Ar); 1074 (C–O). Elemental analysis calculated for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.33; H, 6.60.

*4.7.2. O,O′-[Ethynylene-bis(benzene-4,1-diyl-methylene)]di-(S)-lactic acid (**8a**).* Diester **8b** (2.19 g, 5.0 mmol) and LiOH (0.5 g, 20.9 mmol) in THF (200 ml) and water (20+65 ml) were used to yield 1.51 g (79%) of a white solid. mp. 182–186 °C. $[\alpha]_D^{20}$=−59.05 (*c*=0.38, EtOH). MS (ESI): *m/z*=381.0 $[M-H]^-$. ^{1}H NMR (DMSO-d_6, 500 MHz): δ=1.34 (d, 6H, CH_3, $^3J_{HH}$=6.85); 4.03 (q, 2H, C*H*, $^3J_{HH}$=6.85); 4.46 (d, 2H, CH_2, $^2J_{HH}$=12.25); 4.62 (d, 2H, CH_2, $^2J_{HH}$=12.25); 7.39 (d, 4H, aryl-*H*, $^3J_{HH}$=8.15); 7.54 (d, 4H, aryl-*H*, $^3J_{HH}$=8.15); 12.75 (br, s, 2H, COO*H*); ^{13}C NMR (DMSO-d_6, 125 MHz): δ=18.52 (CH_3); 70.37 (CH_2); 73.76 (*C*H); 89.28 (*C*≡*C*); 121.33, 127.75, 131.33, 139.09 (aryl-*C*); 174.19 (*C*OOH). IR (cm^{-1}, KBr): 3072 (OH); 1711 (C=O); 1609, 1562, 1518 (C=C, Ar); 1065 (C–O). Elemental analysis calculated for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80. Found: C, 68.84; H, 5.73.

*4.7.3. O-[4-(3,5-Dicarboxyphenylethynyl)phenylmethyl]-(S)-lactic acid (**9a**).* Triester **9b** (2.12 g, 5.0 mmol) and LiOH (0.75 g, 31.3 mmol) in THF (200 ml) and water (20+65 ml) were used to yield 1.23 g (67%) of a white solid. mp. 212–215 °C. $[\alpha]_D^{20}$=+15.48 (*c*=0.37, EtOH). MS (ESI): *m/z*=367.0 $[M-H]^-$. ^{1}H NMR (DMSO-d_6, 500 MHz): δ=1.37 (d, 3H, $CHCH_3$, $^3J_{HH}$=6.85); 4.05 (q, 1H, C*H*, $^3J_{HH}$=6.85); 4.49 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.30); 4.65 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.30); 7.44 (d, 2H, aryl-*H*, $^3J_{HH}$=8.15); 7.63 (d, 2H, aryl-*H*, $^3J_{HH}$=8.15); 8.26 (d, 2H, aryl-*H*, $^4J_{HH}$=1.45); 8.45 (t, 1H, aryl-*H*, $^4J_{HH}$=1.30); 12.84 (br, s, 3H, COO*H*); ^{13}C NMR (DMSO-d_6, 125 MHz): δ=18.55 (CH_3); 70.42 (CH_2); 73.82 (*C*H); 87.46, 91.03 (*C*≡*C*); 120.77, 123.47, 127.78, 129.80, 131.66, 132.11, 135.64, 139.66 (aryl-*C*); 165.98 (Ar*C*OOH), 174.26 (*C*OOH). IR (cm^{-1}, KBr): 3075 (OH); 2214 (C≡C); 1708 (C=O); 1597, 1511 (C=C, Ar); 1071 (C–O). Elemental analysis calculated for $C_{20}H_{16}O_7$: C, 65.22; H, 4.38. Found: C, 65.03; H, 4.47.

*4.7.4. O-[4-(4-Carboxyphenylethynyl)phenylmethyl]-(S)-lactic acid (**10a**).* Diester **10b** (1.90 g, 5.0 mmol) and LiOH (0.5 g, 20.9 mmol) in THF (200 ml) and water (20+55 ml) were used to yield 1.10 g (68%) of a white solid. mp. 224–227 °C. $[\alpha]_D^{20}$=−27.1 (*c*=0.32, EtOH). MS (ESI): *m/z*=323.2 $[M-H]^-$. ^{1}H NMR (DMSO-d_6, 500 MHz): δ=1.35 (d, 3H, CH_3, $^3J_{HH}$=6.85); 4.05 (q, 1H, C*H*, $^3J_{HH}$=6.85); 4.48 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.35); 4.64 (d, 1H, aryl-CH_2, $^2J_{HH}$=12.35); 7.42 (d, 2H, aryl-*H*, $^3J_{HH}$=8.15); 7.59 (d, 2H, aryl-*H*, $^3J_{HH}$=8.15); 7.68 (d, 2H, aryl-*H*, $^3J_{HH}$=8.35); 7.98 (d, 2H, aryl-*H*, $^3J_{HH}$=8.35); 12.96 (br, s, 2H,

COO*H*); ^{13}C NMR (DMSO-d_6, 125 MHz): δ=18.54 (*C*H$_3$); 70.35 (*C*H$_2$); 73.81 (*C*H); 88.63, 92.03 (*C*≡*C*); 120.82, 126.67, 127.79, 129.65, 130.72, 131.55, 131.59, 139.66 (aryl-*C*); 166.80 (Ar*C*OOH), 174.21 (*C*OOH). IR (cm^{-1}, KBr): 3072 (OH); 2217 (C≡C); 1711 (C=O); 1606, 1559, 1518 (C=C, Ar); 1062 (C–O). Elemental analysis calculated for $C_{19}H_{16}O_5$: C, 70.36; H, 4.97: Found: C, 70.09; H, 4.83.

*4.7.5. O-(4-Carboxyphenylmethyl)-(S)-lactic acid (**11a**).* Diester **11b** (1.40 g, 5.0 mmol) and LiOH (0.5 g, 20.9 mmol) in THF (150 ml) and water (15+45 ml) were used to yield 0.95 g (85%) of a white solid. mp. 139–142 °C. $[\alpha]_D^{20}$=−54.5 (*c*=0.22, EtOH). MS (ESI): *m/z*=223.0 [M−H]$^-$. ^{1}H NMR (DMSO-d_6, 500 MHz): δ=1.35 (d, 3H, C*H*$_3$, $^3J_{HH}$=6.85); 4.04 (q, 1H, C*H*, $^3J_{HH}$=6.85); 4.51 (d, 1H, C*H*$_2$, $^2J_{HH}$=12.60); 4.68 (d, 1H, C*H*$_2$, $^2J_{HH}$=12.60); 7.47 (d, 2H, aryl-*H*, $^3J_{HH}$=8.10); 7.93 (d, 2H, aryl-*H*, $^3J_{HH}$=8.10); 12.90 (br, s, 2H, COO*H*); ^{13}C NMR (DMSO-d_6, 125 MHz): δ=18.53 (*C*H$_3$); 70.29 (*C*H$_2$); 73.85 (*C*H); 127.30, 129.38, 129.91, 143.42 (aryl-*C*); 167.26 (Ar*C*OOH), 174.17 (*C*OOH). IR (cm^{-1}, KBr): 3079 (OH); 1685 (C=O); 1613, 1575, 1511 (C=C, Ar); 1065 (C–O). Elemental analysis calculated for $C_{11}H_{12}O_5$: C, 58.93; H, 5.39. Found: C, 59.40; H, 5.52.

4.8. TADDOLs 1c–6c (general procedure)

To a solution of phenylmagnesium bromide (prepared from magnesium and bromobenzene in dry THF following the usual procedure)[26] was slowly added the corresponding ester dissolved in dry THF. The mixture was heated under reflux for 6 h, then quenched with ice and diluted with diethyl ether. The organic layer was separated and washed with aqueous NH_4Cl solution. The aqueous layer was extracted several times with diethyl ether. The combined organic phases were washed with water, dried (Na_2SO_4) and evaporated. Specific details for each compound including procedure of purification are given below.

*4.8.1. (4R,4′R,5R,5′R)-α,α,α′,α′,α″,α″,α‴,α‴-Octaphenyl-2,2′-(benzene-1,4-diyl)bis(1,3-dioxolane-4,5-dimethanol) (**1c**).* Tetraester **1b** (1.27 g, 2.5 mmol), Mg (0.73 g, 30.0 mmol) and bromobenzene (4.71 g, 30.0 mmol) in THF (50 ml) were used to yield 1.57 g (66%) of a white solid after crystallization from acetone. mp. 282–283 °C. $[\alpha]_D^{20}$=+48.4 (*c*=0.95, $CHCl_3$). MS (ESI): *m/z*=949.3 [M−H]$^-$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.36 (s, 2H, O*H*); 3.36 (s, 2H, O*H*); 5.08 (d, 2H, C*H*, $^3J_{HH}$=5.00); 5.25 (d, 2H, C*H*, $^3J_{HH}$=5.00); 5.10 (s, 2H, C*H*, acetal); 7.07–7.35 (m, 44H, aryl-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=78.37, 78.53 (*C*–OH); 80.76, 81.60 (*C*H), 104.46 (*C*H, acetal); 126.65, 126.82, 126.99, 127.15, 127.21, 127.33, 127.45, 127.65, 127.82, 128.11, 128.19, 138.10, 142.92, 144.06, 144.18, 146.03 (aryl-*C*). IR (cm^{-1}, KBr): 3370 (OH); 1597, 1496 (C=C, Ar); 1169, 1119, 1100 (acetal). Elemental analysis calculated for $C_{64}H_{54}O_8$· acetone: C, 79.74; H, 5.99. Found: C, 79.65; 6.09.

*4.8.2. (4R,4′R,5R,5′R)-α,α,α′,α′,α″,α″,α‴,α‴-Octaphenyl-2,2′-(ethynylene-dibenzene-4,1-diyl)bis(1,3-dioxolane-4,5-dimethanol) (**2c**).* Tetraester **2b** (1.52 g, 2.5 mmol), Mg (0.73 g, 30.0 mmol) and bromobenzene (4.71 g, 30.0 mmol) in THF (25 ml) were used to yield 2.57 g (98%) of a white solid after crystallization of the oily crude product from acetone/ethanol. mp. 203–206 °C. $[\alpha]_D^{20}$=+136.3 (*c*=1.05, $CHCl_3$). MS (ESI): *m/z*=1049.3 [M−H]$^-$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.44 (s, 2H, O*H*); 3.33 (s, 2H, O*H*); 5.12 (d, 2H, C*H*, $^3J_{HH}$=5.00); 5.29 (d, 2H, C*H*, $^3J_{HH}$=5.00); 5.18 (s, 2H, C*H*, acetal); 7.10–7.50 (m, 48H, aryl-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=78.42, 78.63 (*C*–OH); 80.89, 81.60 (*C*H); 89.59 (*C*≡*C*); 104.50 (*C*H, acetal); 124.07, 126.74, 126.86, 127.02, 127.22, 127.27, 127.38, 127.52, 127,68, 127.88, 128.13, 128.15, 128.24, 131.43, 137.03, 142.99, 143.99, 144.28, 145.95 (aryl-*C*). IR (cm^{-1}, KBr): 3560 (OH); 1597, 1518, 1496 (C=C, Ar); 1173, 1119, 1087 (acetal). Elemental analysis calculated for $C_{72}H_{58}O_8$·acetone: C, 81.20; H, 5.82. Found: C, 80.91; H, 5.98.

*4.8.3. (4R,5R)-α,α,α′,α′-Tetraphenyl-2-{[3,5-bis(diphenylhydroxymethyl)phenyl]ethynylbenzene-4-yl}-1,3-dioxolane-4,5-dimethanol (**3c**).* Tetraester **3b** (1.28 g, 2.5 mmol), Mg (0.73 g, 30.0 mmol) and bromobenzene (4.71 g, 30.0 mmol) in THF (25 ml) were used to yield 2.15 g (88%) of a white solid after column chromatography (SiO_2, EtOAc/*n*-hexane 1:3, R_f=0.29) of the oily crude product and subsequent treatment by stirring with *n*-hexane. mp. 124–127 °C. $[\alpha]_D^{20}$=+69.7 (*c*=0.98, $CHCl_3$). MS (ESI): *m/z*=978.5 [M]$^-$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.31 (s, 1H, O*H*); 3.25 (s, 1H, O*H*); 2.79 (s, 2H, O*H*); 5.12 (d, 1H, C*H*, $^3J_{HH}$=5.00); 5.29 (d, 1H, C*H*, $^3J_{HH}$=5.00); 5.15 (s, 1H, C*H*, acetal); 7.06–7.48 (m, 47H, aryl-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=78.43, 78.62 (*C*–OH); 80.86, 81.56 (*C*H); 81.77 (*C*–OH); 89.00, 90.16 (*C*≡*C*); 104.51 (*C*H, acetal); 126.70, 126.86, 127.02, 127.28, 127.35, 127.39, 127.53, 127.70, 127.79, 127.87, 127.90, 127.98, 128.12, 128.16, 128.24, 129.64, 131.39, 136.91, 142.97, 144.01, 144.26, 145.96, 146.30, 146.71 (aryl-*C*). IR (cm^{-1}, KBr): 3560 (OH); 1594, 1492 (C=C, Ar); 1163, 1116, 1084 (acetal). Elemental analysis calculated for $C_{69}H_{54}O_6$·acetone: C, 83.37; H, 5.83. Found: C, 83.22; H, 6.09.

*4.8.4. (4R,5R)-α,α,α′,α′-Tetraphenyl-2-{[4-diphenylhydroxymethyl)phenyl]ethynylbenzene-4-yl}-1,3-dioxolane-4,5-dimethanol (**4c**).* Triester **4b** (1.14 g, 2.5 mmol), Mg (0.55 g, 22.2 mmol) and bromobenzene (3.53 g, 22.2 mmol) in THF (25 ml) were used to yield 0.89 g (45%) of a white solid after column chromatography (SiO_2, EtOAc/*n*-hexane 1:3, R_f=0.43) of the oily crude product and subsequent treatment by stirring with *n*-hexane. mp. 95–97 °C. $[\alpha]_D^{20}$=+83.1 (*c*=0.79, $CHCl_3$). MS (ESI): *m/z*=795.5 [M−H]$^-$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.80 (s, 1H, O*H*); 3.19 (s, 1H, O*H*); 3.50 (s, 1H, O*H*); 5.14 (d, 1H, C*H*, $^3J_{HH}$=4.95); 5.31 (d, 1H, C*H*, $^3J_{HH}$=4.95); 5.19 (s, 1H, C*H*, acetal); 7.10–7.58 (m, 38H, aryl-*H*); ($CDCl_3$+D_2O, 500 MHz): δ=2.80, 3.19 and 3.50 signals disappear; ^{13}C NMR ($CDCl_3$, 125 MHz): δ=78.34, 78.58 (*C*–OH); 80.86, 81.60 (*C*H); 81.81 (*C*–OH); 89.21, 89.73 (*C*≡*C*); 104.45 (*C*H, acetal); 126.75, 126.88, 127.03, 127.24, 127.34, 127.36, 127.48, 127.63, 127.84, 127.91, 127.97, 128.11, 128.13, 128.20, 128.69, 129.49, 131.12, 131.38, 136.89, 143.00, 144.33, 145.95, 146.45, 147.05 (aryl-*C*). IR (cm^{-1}, KBr): 3563 (OH); 1600, 1521, 1499 (C=C, Ar); 1179, 1112, 1090 (acetal). Elemental analysis calculated for $C_{56}H_{44}O_5$·acetone: C, 82.88; H, 5.89. Found: C, 82.51; H, 5.97.

*4.8.5. (4R,5R)-α,α,α′,α′-Tetraphenyl-2-[4-(diphenylhydroxymethyl)-phenyl]-1,3-dioxolane-4,5-dimethanol (**5c**).* Triester **5b** (0.91 g, 2.5 mmol), Mg (0.55 g, 22.2 mmol) and bromobenzene (3.53 g, 22.2 mmol) in THF (25 ml) were used to yield 0.99 g (57%) of a white solid after column chromatography (SiO_2, EtOAc/*n*-hexane 1:4, R_f=0.32) of the oily crude product and subsequent treatment by stirring with *n*-hexane. mp. 93–96 °C. $[\alpha]_D^{20}$=+38.6 (*c*=0.69, $CHCl_3$). MS(ESI): *m/z*=696.6 [M]$^-$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.59 (s, 1H, O*H*); 2.78 (s, 1H, O*H*); 3.38 (s, 1H, O*H*); 5.11 (d, 1H, C*H*, $^3J_{HH}$=5.05); 5.30 (d, 1H, C*H*, $^3J_{HH}$=5.05); 5.12 (s, 1H, C*H*, acetal); 7.11–7.53 (m, 34H, aryl-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=78.46, 78.52 (*C*–OH); 80.72, 81.45 (*C*H); 81.81 (*C*–OH); 104.68 (*C*H, acetal); 127.30, 127.85, 127.87, 127.89, 127.93, 128.17, 135.78, 141.62, 143.02, 144.22, 145.88, 146.13, 146.59, 148.04 (aryl-*C*). IR (cm^{-1}, KBr): 3557 (OH); 1597, 1496 (C=C, Ar); 1182, 1125, 1087 (acetal). Elemental analysis calculated for $C_{48}H_{40}O_5$·2 acetone: C, 79.78; H, 6.45. Found: C, 79.82; H, 6.28.

*4.8.6. (4R,5R)-α,α,α′,α′-Tetraphenyl-2-{4-[2-(diphenylhydroxymethyl)ethynyl]phenyl}-1,3-dioxolane-4,5-dimethanol (**6c**).* Triester **6b** (0.94 g, 2.5 mmol), Mg (0.55 g, 22.2 mmol) and bromobenzene (3.53 g, 22.2 mmol) in THF (25 ml) were used to yield 1.47 g (82%) of a white solid after column chromatography (SiO_2, EtOAc/*n*-

hexane 1:3, R_f=0.43) of the oily crude product and subsequent treatment by stirring with *n*-hexane. mp. 80–83 °C. $[\alpha]_D^{20}$=+41.3 (*c*=0.72, $CHCl_3$). MS (ESI): *m*/*z*=720.4 $[M-H]^-$. ^1H NMR ($CDCl_3$, 500 MHz): δ=3.24 (s, 1H, O*H*); 3.65 (s, 1H, O*H*); 3.82 (s, 1H, O*H*); 5.09 (d, 1H, C*H*, $^3J_{HH}$=5.20); 5.23 (d, 1H, C*H*, $^3J_{HH}$=5.20); 5.16 (s, 1H, C*H*, acetal); 7.04–7.63 (m, 34H, aryl-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=74.49, 78.17, 78.49 (*C*–OH); 80.80, 81.57 (*C*H); 86.49, 92.49 (*C*≡*C*); 104.21 (*C*H, acetal); 125.92, 126.72, 126.89, 127.46, 127.49, 127.94, 127.99, 128.09, 131.40, 137.17, 142.97, 143.51, 143.97, 144.44, 144.98, 145.85 (aryl-*C*). IR (cm^{-1}, KBr): 3554 (OH); 2227 (C≡C); 1603, 1492 (C=C, Ar); 1179; 1116; 1087 (acetal). Elemental analysis calculated for $C_{50}H_{40}O_5$·acetone: C, 81.72; H, 5.95. Found: C, 81.98; H, 6.18.

4.9. Vapour sorption experiments

For the sorption experiments, a quartz crystal microbalance consisting of two electronic quartzes (10 MHz) with gold electrodes (FOQ Piezo Technik, Germany) was used. The reference quartz is uncoated while the other quartz is coated with the solid receptor compound (**1a**–**6a**, **1c**–**6c** and **7a**–**11a**, respectively). The measurements were carried out at constant temperature (25 °C) and with a constant flow of synthetic air (10 L/h). A multichannel frequency counter (HKR sensor systems Munich, Germany) with a resolution of 1 Hz was used to measure the resonance frequencies of the quartzes, which can be read by a computer using a serial interface. The coating of the quartz was realized by dipping in a 0.01M solution of the respective receptor compound in $CHCl_3$. The change of the frequency is proportional to the increase of the quartz mass induced by the sorption of the added solvent vapour. This relation results from the Sauerbrey equation.[31] In consideration of the molar mass of the used solvents, the percentage of the adsorbed solvent can be obtained:

$$x' = \frac{\Delta n(s)}{\Delta n(r)} = x\frac{M(s)}{M(r)} \qquad \frac{\Delta f(s)}{\Delta f(r)} = \frac{\Delta m(s)}{\Delta m(r)} = x = \frac{\Delta n(s)}{\Delta n(r)}\frac{M(s)}{M(r)}$$

$\Delta f(s)$…frequency shift solvent; $\Delta f(r)$…frequency shift receptor; $\Delta m(s)$…mass of solvent absorbed; $\Delta m(r)$…mass of receptor layer; $M(s)$…molar mass solvent; $M(r)$…molar mass receptor.

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