

Synthesis and application of azolium ionic liquid tagged TADDOL catalysts

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Dedicated to Prof. Dr. Rainer Beckert on the occasion of his 60th birthday

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Abstract

Ionic liquid (IL) tagged organocatalysts based on TADDOL ($\alpha, \alpha, \alpha', \alpha'$ -tetraaryl-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol) comprising various aryl substituents tethered with triazolium and imidazolium based ionic liquids are synthesised in good yields. Investigation of these IL-tagged catalysts on hydrogen-bonding catalyzed hetero-Diels-Alder (HDA) reactions between activated dienes (such as Rawal's diene and Brassard's diene) and benzaldehyde indicated their potential and limitations for applications in organocatalysis.

Introduction

Seebach et al. introduced TADDOLs ($\alpha, \alpha, \alpha', \alpha'$ -tetraaryl-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol) **1** (Figure 1) as bidentate alkoxide ligands and chiral auxiliaries in 1983.¹ Since then, TADDOLs have been successfully utilized as chiral scaffolds in organic synthesis.² Various methodologies have been implemented for the immobilization of TADDOL catalysts with the aim of improving their recyclability and reuse as well as their efficiency and stability mainly as ligands for metal catalysis.³⁻⁵ TADDOL catalysts immobilized on solid supports can exhibit drawbacks such as low catalyst loading, mass transfer dependent diffusion, low mechanical strength, diminished selectivity and loss of catalytic activity during immobilization. There has been much effort to circumvent these drawbacks, which are often considered inherent to the immobilization of catalysts with solid supports.

Ionic liquids (IL) have shown interesting ability as phase tags for organocatalysts.⁶⁻¹⁵ Ionic liquid tagged catalysts can be tuned to attain a required physical property, such as solubility, or compatibility with the reaction medium and thermal stability.¹⁶ In this way improved recovery

and recycling and sometimes even better catalytic activity can be attained.^{17-19,14} Accordingly, we envisaged that a properly functionalized ionic liquid tag can render TADDOLs novel properties and improve their usefulness as organocatalysts. Immobilizing TADDOL catalysts with ionic liquids has the potential to render the TADDOLs tuneable solubility for working under homogeneous conditions, without diminishing their catalytic activity or their amount of catalyst loading, unlike TADDOLs immobilized on solid supports. There have not been reports about investigations of the advantages of ionic liquid tags in immobilizing TADDOL catalysts. Here we report the results of our investigations on the use of 1,2,3-triazolium salts and imidazolium salts as suitable ionic liquid tags for TADDOLs (Figure 1, formula 2).

While imidazolium salts have been fully established as ionic liquids, 1,2,3-triazolium salts were unknown in this areas until recently. We and later on others have developed 1,2,3-triazolium salts as versatile IL structures which have found various application as ILs in organocatalysis.^{20-22,13,9} They are easily accessible by Cu-catalyzed cycloaddition of azides and terminal alkynes (Meldal-Sharpleess click reaction)²³ followed by N-alkylation of the resulting 1,2,3-triazole.^{20,24} Since functionality can be introduced virtually by all substituents found in the reactants this synthesis renders very versatile. In addition, the counterion can be easily changed for further tuning of the ionic liquid properties.

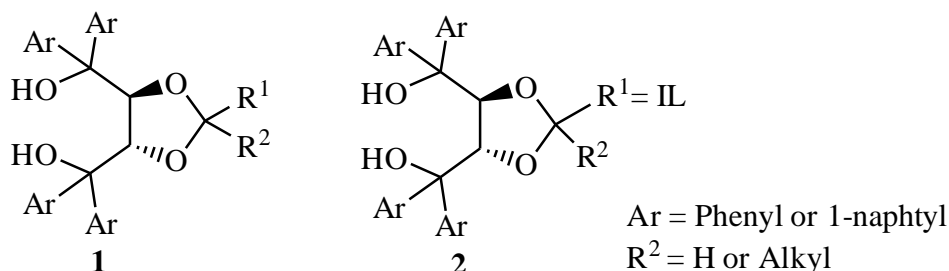
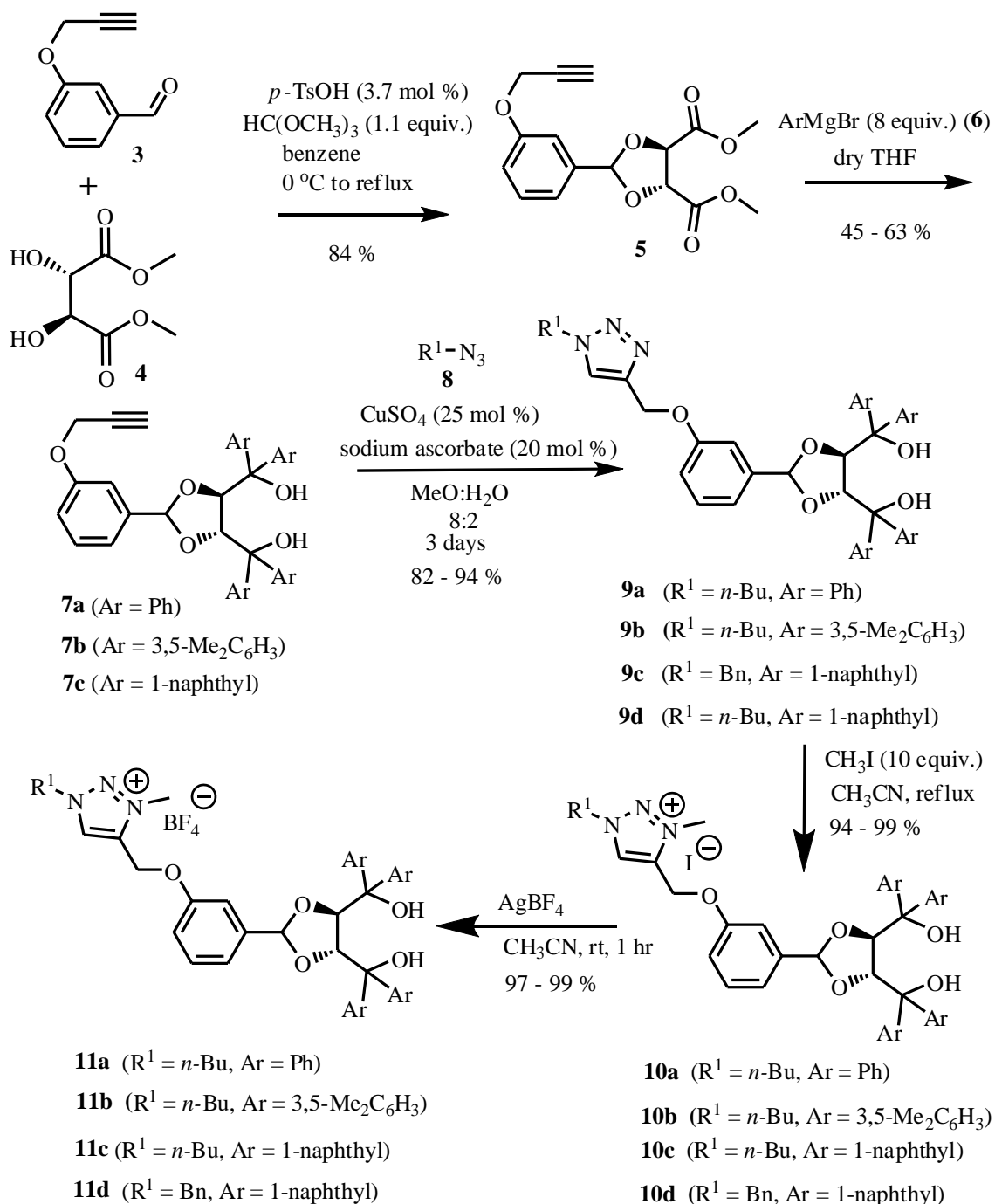


Figure 1. Structure of TADDOL catalysts and envisaged IL-tagging (IL = 1,2,3-triazolium or imidazolium).

Result and Discussion

TADDOLs are often synthesized starting from dialkyl tartrate and a ketone or an aldehyde forming a 1,4-dioxolane with two ester functions, which are eventually transformed into diarylcarbinols by reaction with Grignard reagents.² In principle, ionic liquid tags could be tethered either to the aryl groups of the carbinol substructures or to the substituents in position 2 of the dioxolane ring.²⁵ We chose the latter possibility for its straightforwardness. In order to have much structural flexibility we established the TADDOL moiety at an early stage and various IL-tags were linked at a later stage by means of a propargyl group enabling Cu-catalyzed Meldal-Sharpleess click reaction. Thus propargylated 3-hydroxybenzaldehyde **3**^{26,27} was

condensed with dimethyl *L*-(+)-tartate **4** in the presence of trimethyl orthoformate and catalytic amounts of *p*-toluene sulfonic acid to furnish the intended dioxolane ring system **5** in good yield. Consecutively Grignard reaction (8 equivalents of Grignard reagent **6**) was employed to introduce the necessary aromatic sub-units into the 3-propargyloxyisomer **5** smoothly to furnish the envisaged tetraaryl substituted products **7** (Scheme 1).



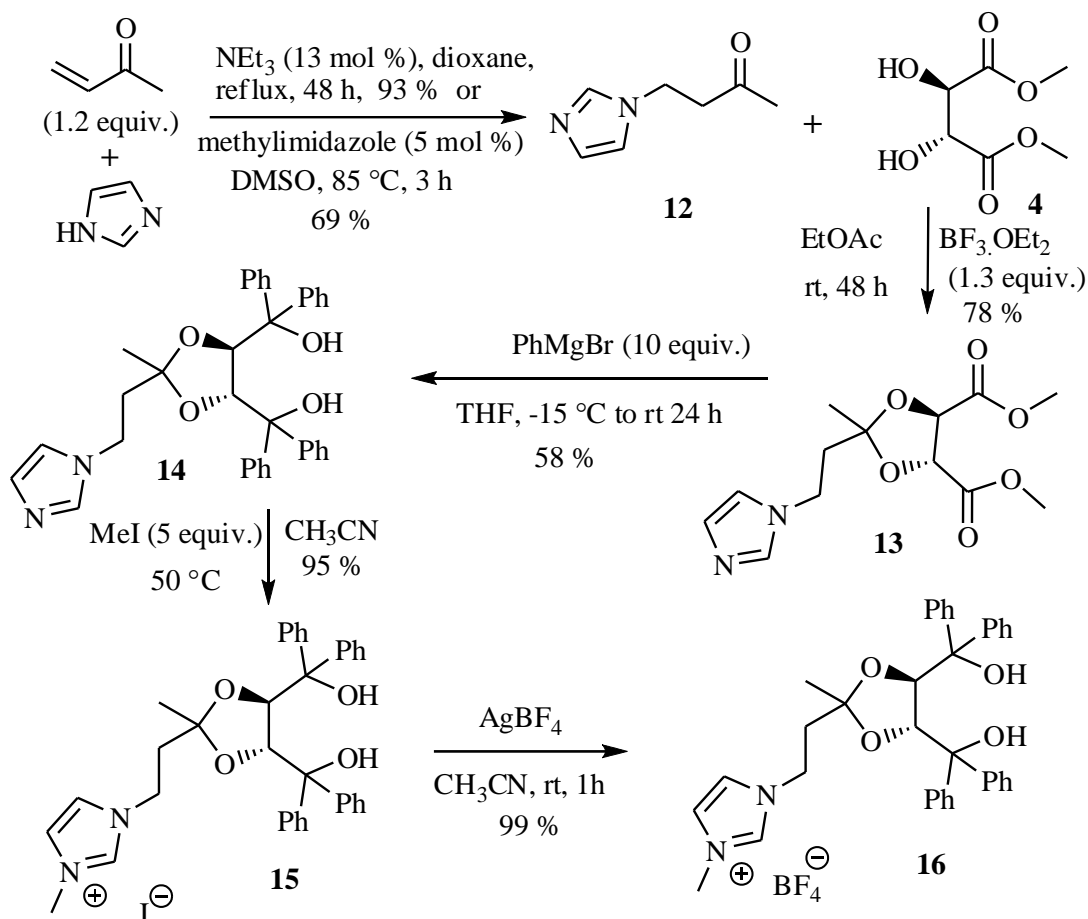
Scheme 1. Synthesis of 1,2,3-triazolium ionic liquid tagged TADDOL catalysts **10** and **11**.

The isomeric product of **5** which was obtained from 4-hydroxybenzaldehyde was found to be unstable and difficult to handle at the later stages of the synthesis. It furnished uncomfortably low yields in the consecutive steps. Seemingly, the electron donating property of the propargyloxy group at position 4 increased the ability to stabilize positive charges at the benzyldiene position and thus renders the dioxolane ring more sensitive to ring opening under the influence of acids or Lewis acids, a phenomenon which was reported in the literature.²⁸

Now the floor was laid for Cu (I)-catalyzed click reaction with azides. We chose butyl or benzyl azide **8** and used the well-established click reaction method utilizing Cu(II)-sulphate (25 mol%) in the presence of Na-ascorbate (20 mol%) in DMF:methanol (1:1) mixture. The 1,2,3-triazoles **9** were obtained in excellent yields. The transformation into the corresponding 1,2,3-triazolium iodides **10** was achieved in high yields by a straight forward alkylation using excess of methyl iodide (10 equivalents) in acetonitrile. Reactions attempted with other methylating agents such as methyl triflate (MeOTf) at room temperature and at -25 °C furnished very low yields. Nevertheless, exchange of iodide by other anions was possible by salt metathesis, such as with silver tetrafluoroborate leading to 1,2,3-triazolium tetrafluoroborates **11** in quantitative yields.

In order to attain imidazolium-tagged TADDOL catalysts we started with 4-(imidazole-1-yl)-butanone **12**, which was reported as the Michael addition product of imidazole to methyl vinyl ketone in the presence of catalytic amounts of N-methylimidazole in DMSO (Scheme 2).²⁹ Unlike in the reported procedures we used triethylamine base. The consecutive use of trimethyl orthoformate procedure previously applied for the synthesis of the analogous 1,3-dioxolane **6** did not provide the desired product for ketone **12**. This is presumably due to the low reactivity of the aliphatic ketone **12** as compared to the aldehyde **6** under this reaction condition. The 1,3-dioxolane **13** was prepared in good yield by reaction of **12** with dimethyl tartrate in the presence of the Lewis acid boron trifluoride etherate in ethyl acetate. The subsequent Grignard reaction with phenyl magnesium bromide (10 fold excess) provided the carbinol **14** in 58 % yield. N-Methylation with methyl iodide (5 equivalents) to imidazolium salt **15** and further salt metathesis to the tetrafluoroborate **16** with silver tetrafluoroborate took place in excellent yields.

With these IL-tagged TADDOLs in hand we approached their application as IL-tagged organocatalysts. We report here our first attempts to use them in hetero-Diels –Alder reactions (HDA reaction) as potential recyclable catalysts. The IL-tagged TADDOL catalysts (**10**, **11**, **15** and **16**) were first investigated in the hydrogen-bonding promoted HDA reaction of Brassard's diene **17** with benzaldehyde (Table 1). Initially, the reaction was carried out at room temperature using 2.5 - 5.0 molar equivalent of freshly distilled benzaldehyde in the presence of 20 mol % of catalyst. The catalysts constitute ionic liquid subunits, which have limited solubility in non-polar solvents. However, they are completely soluble in excess of benzaldehyde, which serves as a solvent for the neat reactions. Under these conditions the intended cycloadducts **18** were obtained, however, as racemates with low to moderate yields (Table 1). The same reaction was reported by K. Ding et al,³⁰ for non-supported naphthyl TADDOLs affording 67 % yield and 83 % ee. A cycloaddition product was not reported when the TADDOL catalyst was missing.



Scheme 2. Synthesis of imidazolium ionic liquid tagged TADDOL catalysts **15** and **16**.

In our cases the best yield (58 %) was obtained with the naphthyl TADDOL **11c** at room temperature. As shown with the catalyst **11d** (entries 8-10, Table 1) lowering the reaction temperature resulted in diminished yields. This effect can also be attributed to the fact that the viscosity of the mixture increased which hampers miscibility of the reaction solution and causes crystallization of the catalyst. In order to alleviate this problem, additional solvents such as toluene, dichloromethane and carbon tetrachloride were used. Non-polar solvents such as toluene often being considered to increase selectivity,³¹ furnished only trace amounts of the product in our case (not shown). This can be ascribed to the low solubility of the IL-tagged catalysts in non-polar solvents. The more polar solvent dichloromethane and carbon tetrachloride did not improve the yield or enantioselectivity (entries 11, 12, Table 1).

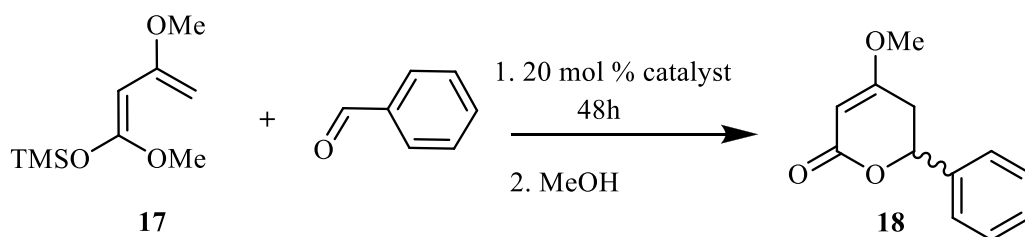


Table 1. Selected examples of HDA reaction between Brassard's diene **17** and benzaldehyde

Entry	Catalyst	Solvent	T °C	% Yield ^a
1	10a	-	24	49
2	10b	-	24	52
3	11c	-	24	58
4	10d	-	0	32
5	11a	-	-24	11
6	11b	-	24	47
7	11c	-	0	36
8	11d	-	24	22
9	11d	-	-24	12
10	11d	-	-78	-
11	11d	CH ₂ Cl ₂	-24	10
12	11d	CCl ₄	-24	14

^a isolated yields.

The 1,2,3-triazolium and imidazolium tagged organocatalysts were further tested in HDA reaction of Rawal's diene **19** with benzaldehyde (Table 2). The reactions were carried out with 5-10 molar equivalent of benzaldehyde in the presence of 20 mol % of catalyst. At 0 °C and in the case of **10d**, **11b** and **13** even at -24 °C the intended cycloaddition adducts **20** were obtained in a non-enantioselective fashion in low yields. It turned out that phenyl substituted triazolium-tagged TADDOLs are less effective than 1-naphthyl-substituted TADDOLs (Table 2, compare entries 1, 2 and 3 or entries 3 and 5). Catalysts **11b** and **15** even failed to give a product at -24 °C (entries 5 and 12). A more systematic variation of conditions was performed with catalyst **11d**. Here, low enantioselectivities (maximum 26 % ee) were observed when the catalyst **11d** (20 mol%) was used in the reactions conducted at -24 and -78 °C (entries 7 – 8). Lowering the catalyst loading to 10 mol% resulted in a decrease in yield while the enantioselectivity was not affected (Table 2, entries 7 and 9) Since unlike Brassard's diene Rawal's diene is reactive enough to undergo HDA reaction with benzaldehyde without the aid of any catalysts at room temperature the uncatalyzed cycloaddition is likely to run as background reaction thus giving low enantioselectivities or even racemic products.³²⁻³⁴

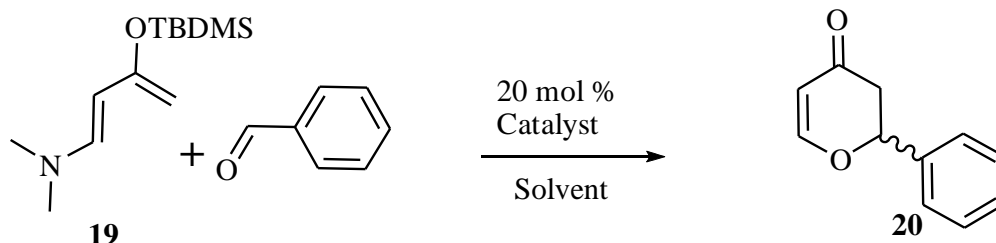


Table 2. Applications of 1,2,3-triazolium and imidazolium IL-tagged TADDOL catalysts in the HDA reaction between Rawal's diene **19** and benzaldehyde

Entry	Catalyst	Solvent	T °C	% Yield ^a	% ee
1	10b	-	0	26	-
2	10c	-	0	37	-
3	10d	-	-24	11	-
4	11a	-	0	17	-
5	11b	-	-24	-	-
6	11d	-	0	34	-
7	11d	-	-24	41	12
8	11d	-	-78	32	26
9	11d^b	-	-24	19	12
10	11d	CH ₂ Cl ₂	-24	16	-
11	11d	CCl ₄	-24	14	-
12	15	-	-24	-	-
13	16	-	-24	17	-

^a isolated yields. ^b 10 mol % catalyst.

The fact that 1-naphthyl-substituted TADDOLs perform better than phenyl-substituted ones in terms of enantioselectivity was well documented in the literature for untagged TADDOL catalysts.³⁰ This improved efficiency is attributed to the better steric shielding ability of the naphthyl group and the stronger π - π donor-acceptor interaction (π -stacking) between the naphthyl substituents and the aldehyde.

When the IL-tagged TADDOLs were applied to the cycloaddition with Rawal's diene an increase in the viscosity of the reaction medium and crystallization of the catalyst was observed with decreasing temperature as in the case of Brassard's diene (*v.s.*). To circumvent this obstacle small amounts of toluene were added. However, this did not improve the solubility of the catalyst at lower temperatures. . When CH₂Cl₂ (entry 10, Table 2) and CCl₄ (entry 11, Table 2) were used as solvents no enantioselectivities were observed and the yields were lower. Attempts to improve the selectivity by increasing the amount of IL-tagged organocatalyst at various temperatures had shown incomplete dissolution of the catalyst in the reaction mixture. Consequently, the investigations were made at a catalyst concentration of 20 % or less.

Conclusions

In summary, ionic liquid tagged TADDOLs are reported for the first time. 1,2,3-Triazolium or imidazolium units were used as ionic liquid tags. The former were obtained via Meldal-Sharpless “click”-reaction of propargyloxy-substituted TADDOLs and N-methylation of the resulting 1,2,3-triazoles eventually followed by salt metathesis with silver tetrafluoroborate. The imidazolium moiety was introduced by the Michael-addition of imidazole to methyl vinyl ketone and building up the dioxolane ring with dimethyl tartrate followed by Grignard reaction and N-methylation. Both synthetic routes are straight forward and allow the preparation of the IL-tagged TADDOLs in good yields. The IL-tagged TADDOLs were applied to hetero-Diels Alder reactions between Brassard’s diene or Rawals’ diene and benzaldehyde. In the former case only racemic cycloaddition products were obtained while in latter case modest enantioselectivities were observed.

Experimental Section

General. ^1H -NMR and ^{13}C -NMR solution spectra were recorded at 300 MHz and 75 MHz, respectively; with a Bruker AC 300 in CDCl_3 as the solvent in 5 mm NMR tubes with TMS as internal standard. The assignment of ^{13}C signals is based on APT measurements. HRMS was obtained with a Waters UPLC, LCT Premier XE instrument. Determination of enantioselectivities was achieved using chiral columns (Daicel Chemical Industries LTD), mobile phase: *n*-hexane : *i*-propanol (98:20 - 80:20), flow rate: 0.5-1.0 mL / min. The optical rotations were measured on a Perkin Elmer-241 polarimeter. The measurements were made at a wavelength of 589 nm using 100 x 3.5 mm cuvette.

3-Propargyloxybenzaldehyde (3). A solution of 3-hydroxybenzaldehyde (3.66 g, 30 mmol) in DMF (50 mL) was placed in a two necked flask fitted with an efficient reflux condenser. Na_2CO_3 (12.45 g, 90 mmol) was added. The reaction mixture was heated to 55 – 60 °C for half an hour and was cooled to room temperature. Then propargyl bromide 80% in toluene (4.05 mL, 36 mmol) was added. The reaction mixture was stirred at the same temperature while its progress was being followed by TLC. After completion (about 4 h) the mixture was poured into ice water (100 mL) with stirring. The resulting solution was extracted with Et_2O (100 mL) three times. The combined organic extracts were washed with additional cold water (100 mL) two times and dried with MgSO_4 . The organic solvent was removed under reduced pressure to furnish the title product as a yellowish liquid. Yield 92%. ^1H NMR (300 MHz CDCl_3): δ ppm = 10.0 (s, 1H), 7.68 - 7.37 (m, 3 H), 7.32 - 7.16 (m, 1 H), 4.74 (d, J = 2.41, 2 H), 2.57 (t, J = 2.39, 2.39 Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm = 191.8 (Ph- $\text{C}=\text{O}$), 158.0 ($\text{C}_{\text{ph}}-\text{O}$), 137.7 ($\text{C}_{\text{ph}}-\text{CHO}$),

130.1 - 113.5 ($\underline{\text{C}}_{\text{H}_{\text{ph}}}$), 77.9 ($\text{CH}_2\text{-}\underline{\text{C}}\equiv\text{CH}$), 76.2 ($\text{CH}_2\text{-}\underline{\text{C}}\equiv\text{CH}$), 55.9 ($\underline{\text{C}}\text{H}_2\text{-}\underline{\text{C}}\equiv\text{CH}$). HRMS (ESI): Found: m/z 159.0480. Calculated for $\text{C}_{10}\text{H}_7\text{O}_2$ (M-H^+): 159.0446.

(4*R*,5*R*)-2-(3-(Prop-2-ynyloxy)phenyl)-1,3-dioxolane-4,5-dicarboxylate dimethyl ester (5). A solution of 3-propargyloxybenzaldehyde **3** (4.3 g, 26.9 mmol) in dry benzene (30 mL) at 0 °C was kept in a distillation set up under a steady flow of argon. (**Caution:** benzene is a carcinogenic substance). *p*-TsOH catalyst (172 mg, 1 mmol) was added followed by trimethyl orthoformate (TMOF) (4 mL, 30 mmol). The mixture was stirred at the same temperature for half an hour and *L*(+)-dimethyl tartrate **4** (5.3 g, 30 mmol) was added. Then, it was heated gently to 60 °C, at which point an azeotropic distillate started. N.B. The temperature of the heating oil bath was kept between 75 – 85 °C until the benzene/methanol azeotrope boiling at about 57 °C has ceased to distil off. The heating was continued until the temperature of the distillate increases to 80 °C. After the completion of the reaction was confirmed by TLC the remaining benzene was distilled off under reduced pressure within a well ventilated fume hood. The resulting oil was diluted with CH_2Cl_2 , neutralized by Et_3N and washed with distilled water (100 mL) and brine (100 mL) to furnish the title product (**6**) as a pale yellow oil. Yield 84%. ^1H NMR (300 MHz CDCl_3): δ = 7.37 - 7.28 (m, 1 H), 7.23 – 7.18 (m, 2 H), 7.03 – 6.99 (m, 1 H), 6.12 (m, 1 H), 4.98 (d, J = 3.96 Hz, 1 H), 4.70 (d, J = 2.40 Hz, 1 H), 4.66 (m, 2 H), 3.86 (s, 3H), 3.81 (s, 3H), 2.54 (t, J = 2.40, 2.40 Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 169.9, 169.4 ($\text{O}=\underline{\text{C}}\text{-O-CH}_3$), 157.6 ($\underline{\text{C}}_{\text{ph}}\text{-O}$), 136.9 ($\underline{\text{C}}_{\text{ph}}\text{-CH-O}$), 129.5 - 113.2 ($\underline{\text{C}}_{\text{H}_{\text{ph}}}$), 106.3 ($\text{C}_{\text{ph}}\text{-}\underline{\text{C}}\text{H-O}_2$), 78.4 ($\text{CH}_2\text{-}\underline{\text{C}}\equiv\text{CH}$), 77.4 ($\text{CH}_2\text{-}\underline{\text{C}}\equiv\text{CH}$), 77.1 ($\text{O-}\underline{\text{C}}\text{H-CH-O}$), 76.7 ($\text{O-CH-}\underline{\text{C}}\text{H-O}$), 55.8 ($\underline{\text{C}}\text{H}_2\text{-}\underline{\text{C}}\equiv\text{CH}$), 52.9 ($\text{O}=\text{C-O-}\underline{\text{C}}\text{H}_3$). HRMS (ESI): Found: m/z 319.0819. Calculated for $\text{C}_{16}\text{H}_{15}\text{O}_7$ (M-H^+): 319.0818. $[\alpha]_D^{28} = -19.4$ ($c = 1$, CHCl_3).

((4*R*,5*R*)-2-(3-(Prop-2-ynyloxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol) (7a). Grignard reagent was prepared from magnesium turnings (2.0 g, 83 mmol) in dry THF (80 mL) with a slow addition of bromobenzene (12.56 g, 80 mmol) in a three neck round-bottom flask fitted with a efficient condenser which has been oven dried and flushed with argon. The reaction mixture was set to reflux by itself with a controlled addition of the bromobenzene. After the complete consumption of the Mg tunings refluxing was continued for additional one hour using a water-bath. After this time the mixture was allowed to cool to room temperature and was further cooled to -15 °C. To it was added 2-(3-(prop-2-ynyloxy)phenyl)-1,3-dioxolane-4,5-dicarboxylate dimethyl ester **6** (3.2 g, 10 mmol) in dry THF (30 mL) while keeping the temperature below -10 °C. After complete addition of **6** the reaction flask was allowed to warm to room temperature and was left to stir overnight. The resulting solution was diluted by Et_2O (200 mL) and quenched by concentrated NH_4Cl 100 mL at 0 °C. The ether phase was separated and dried with MgSO_4 , the solvent was removed under vacuum to give a yellow solid, which was purified by silica gel column chromatography using cyclohexane: ethyl acetate (7.5:2.5) to furnish pure product as yellowish oil. Yield 63%. ^1H NMR (300 MHz CDCl_3) δ = 7.54 – 6.88 (m, 24 H), 5.47(s, 1 H), 5.30 (s, 1 H), 5.27 (s, 1 H), 4.64 (dd, J = 8.57, 2.42 Hz, 2 H), 2.52 (t, J = 2.40, 2.40 Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ = 157.8 ($\underline{\text{C}}_{\text{ph}}\text{-O}$), 166.9 ($\underline{\text{C}}_{\text{ph}}\text{-C-OH}$), 136.9 ($\underline{\text{C}}_{\text{ph}}\text{-CH-O}$), 129.5 - 113.2 ($\underline{\text{C}}_{\text{H}_{\text{ph}}}$), 106.3 ($\text{C}_{\text{ph}}\text{-}\underline{\text{C}}\text{H-O}_2$), 79.9 ($\text{CH}_2\text{-}\underline{\text{C}}\equiv\text{CH}$), 79.4 ($\text{CH}_2\text{-}\underline{\text{C}}\equiv\text{CH}$), 78.1 ($\text{O-}\underline{\text{C}}\text{H-CH-O}$),

77.7 (O-CH-CH-O), 56.8 (CH₂-C≡CH). HRMS (ESI): Found: *m/z* 567.2074. Calculated for C₃₈H₃₁O₅ (M-H⁺): 567.2071.

((4*R*,5*R*)-2-(3-(Prop-2-ynyloxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(bis(3,5-dimethylphenyl)methanol) (7b). By analogous procedure as **7a** from 3,5-dimethyl-bromobenzene (11.1 g, 80 mmol) and **6** (3.2 g, 10 mmol). Yield 69%. ¹H NMR (300 MHz CDCl₃): δ = 7.42 - 6.58 (m, 16 H), 5.53 (s, 1 H), 5.36 (s, 1 H), 5.22 (s, 1 H), 4.64 (dd, *J* = 8.57, 2.42 Hz, 2 H), 2.53 - 2.19 (m, 24 H), 1.96 - 1.85 (m, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = 160.0 (C_{ph}-O), 155.9 - 113.9 (C_{ph} and CH_{ph}), 104.9 (C_{ph}-CH-O₂), 81.6 (CH₂-C≡CH), 81.0 (CH₂-C≡CH), 79.1 (O-CH-CH-O), 78.6 (O-CH-CH-O), 60.7 (CH₂-C≡CH), 52.9 (O=C-O-CH₃), 21.7 - 19.5 (Ph-CH₃). HRMS (ESI): Found: *m/z* 679.3419. Calculated for C₄₆H₄₇O₅ (M-H⁺): 679.3423.

((4*R*,5*R*)-2-(3-(Prop-2-ynyloxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(dinaphthalen-1-ylmethanol) (7c). By analogous procedure as **7a** and **7b** from 1-naphthylbromide (10.49 g, 50 mmol) and **6** (3.2 g, 10 mmol). Yield 81 %. ¹H NMR (300 MHz CDCl₃): δ = 8.67 - 6.89 (m, 32 H), 5.54 (s, 1 H), 5.35 (s, 1H), 5.22 (s, 1 H), 4.63 (dd, *J* = 8.61, 2.40 Hz, 2 H), 1.94 - 1.86 (m, 1 H). ¹³C NMR (75 MHz, CDCl₃) δ = 159.9 - 118.0 (C_{ph} and CH_{ph}), 104.9 (C_{ph}-CH-O₂), 83.2(O-CH-CH-O), 82.9 (O-CH-CH-O), 80.0 (Ph-C-OH), 79.8(Ph-C-OH), 79.1 (CH₂-C≡CH), 78.6 (CH₂-C≡CH), 56.9 (CH₂-C≡CH). HRMS (ESI): Found: *m/z* 767.2784. Calculated for C₅₄H₃₉O₅ (M-H⁺): 767.2797.

((4*R*,5*R*)-2-(3-((1-Butyl-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol) (9a). (4*R*,5*R*)-2-(3-(Prop-2-ynyloxy)phenyl)-1,3-dioxolane-4,5-diyl) bis(diphenylmethanol) **7a** (1 g, 1.76 mmol) was dissolved in DMF : MeOH, 1:1 (20 mL). Butyl azide (174 mg, 1.76 mmol) and CuSO₄ (71 mg, 0.44 mmol) was added followed by sodium ascorbate (70 mg, 0.35 mmol) with vigorous stirring. The mixture was left to stir for three days. The resulting solution was diluted with CH₂Cl₂ (200 mL) and was washed several times with ice cold water. The organic phase was separated and dried with MgSO₄ and the solvent was removed under vacuum to give a yellow solid, which was purified by column chromatography using cyclohexane: ethyl acetate (7.5 : 2.5) to furnish the title product **9a**. Yield 82%. ¹H NMR (300 MHz CDCl₃): δ = 7.73 - 7.13 (m, 22 H), 7.03 - 6.76 (m, 3 H), 5.37 (d, *J* = 4.97 Hz, 1 H), 5.24 (s, 1 H), 5.20 (d, *J* = 4.96 Hz, 1 H), 5.09 (d, *J* = 2.69 Hz, 2 H), 4.33 (t, *J* = 7.23, 7.23 Hz, 2 H), 1.96 - 1.82 (m, 2 H), 1.38 (dd, *J* = 14.77, 7.33 Hz, 2 H), 0.99 (t, *J* = 7.38, 7.38 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃) δ = 158.1 (O-C_{ph}), 146.0 - 113.0 (N-CH=C, CH_{ph} and C_{ph}), 104.6 (C-CH₂-CH-O₂), 81.6 (O-CH-CH-O), 80.9 (O-CH-CH-O), 78.6 ((Ph)₂-C-OH), 78.5 ((Ph)₂-C-OH), 61.9 (C-CH₂-O), 50.1 (CH₂-CH₂-N), 32.2 (CH₂-CH₂-CH₂), 19.7 (CH₂-CH₂-CH₃), 13.5 (CH₂-CH₂-CH₃). HRMS (ESI): Found: *m/z* 666.2969. Calculated for C₄₂H₄₀N₃O₅ (M-H⁺): 666.2968. [α]_D²⁹ = + 38.8° (*c* = 1, CCl₃).

((4*R*,5*R*)-2-(3-((1-Butyl-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(di(3,5-dimethylphenyl)methanol) (9b). By analogous procedure as **9a** from (4*R*,5*R*)-2-(3-(prop-2-ynyloxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(bis(3,5-dimethylphenyl)methanol) **7b**, (4.5 g, 6.6 mmol) and butyl azide (680 mg, 6.9 mmol). Yield 94%. M.p. 81 – 84 °C. ¹H NMR (300 MHz CDCl₃): δ = 7.33 - 6.71 (m, 17 H), 5.45 (d, *J* = 3.91 Hz, 1 H), 5.38 (s, 1 H), 5.24 (d, *J*

= 4.58 Hz, 1 H), 5.23 (m, 2 H), 4.34 (t, $J = 7.23, 7.23$ Hz, 2 H), 2.46 - 2.25 (m, 24 H), 1.96-1.82 (m, 2 H), 1.56 (dd, $J = 14.77, 7.33$ Hz, 2 H), 0.99 (t, $J = 7.38, 7.38$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 159.8$ (O- C_{ph}), 155.7 - 113.7 (N- $\text{CH}=\text{C}$, $\text{CH}=\text{C}-\text{CH}_2$, CH_{ph} and C_{ph}), 104.6 (C- $\text{CH}_2-\text{CH}-\text{O}$), 81.4 (O- $\text{CH}-\text{CH}-\text{O}$), 80.7 (O- $\text{CH}-\text{CH}-\text{O}$), 78.9 ((Ph) $_2$ - $\text{C}-\text{OH}$), 78.3 ((Ph) $_2$ - $\text{C}-\text{OH}$), 60.5 (C- CH_2-O), 52.6 ($\text{CH}_2-\text{CH}_2-\text{N}$), 26.8 ($\text{CH}_2-\text{CH}_2-\text{CH}_2$), 21.5 - 20.8 (Ph- CH_3), 19.3 ($\text{CH}_2-\text{CH}_2-\text{CH}_3$), 14.0 ($\text{CH}_2-\text{CH}_2-\text{CH}_3$). HRMS (ESI): Found: m/z 778.4222. Calculated for $\text{C}_{50}\text{H}_{56}\text{N}_3\text{O}_5$ (M- H^+): 778.4220.

((4*R*,5*R*)-2-(3-((1-Butyl-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-1,3-dioxolane-4,5-

diyl)bis(dinaphthalen-1-ylmethanol) (9c). By analogous procedure as **9a** from ((4*R*,5*R*)-2-(3-(prop-2-ynyloxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(dinaphthalen-1-ylmethanol) **7c** (1.53 g, 2 mmol) and butyl azide (200 mg, 2 mmol) was obtained the title product as colour less oil. Yield 92%. ^1H NMR (300 MHz CDCl_3): δ ppm = 8.73 - 7.27 (m, 33 H), 5.57 (s, 1 H), 5.34 (d, $J = 4.01$ Hz, 1 H), 5.30 (d, $J = 4.24$ Hz, 1 H), 5.14 (d, $J = 4.48$ Hz, 2 H), 4.35 (t, $J = 7.29, 7.29$ Hz, 2 H), 1.93 - 1.87 (m, 2 H), 1.44 - 1.28 (m, 2 H), 0.95 (t, $J = 7.33, 7.33$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm = 156.5 (O- C_{ph}), 148.3 - 114.1 (N- $\text{CH}=\text{C}$, $\text{CH}=\text{C}-\text{CH}_2$, CH_{ph} and C_{ph}), 106.2 (O- $\text{CH}-\text{O}$), 82.4 (O- $\text{CH}-\text{CH}-\text{O}$), 81.8 (O- $\text{CH}-\text{CH}-\text{O}$), 80.1 ((Ph) $_2$ - $\text{C}-\text{OH}$), 79.3 ((Ph) $_2$ - $\text{C}-\text{OH}$), 62.5 (C- CH_2-O), 53.7 ($\text{CH}_2-\text{CH}_2-\text{N}$), 31.1 ($\text{CH}_2-\text{CH}_2-\text{CH}_2$), 19.8 ($\text{CH}_2-\text{CH}_2-\text{CH}_3$), 13.4 ($\text{CH}_2-\text{CH}_2-\text{CH}_3$). HRMS (ESI): Found: m/z 868.3762. Calculated for $\text{C}_{58}\text{H}_{50}\text{N}_3\text{O}_5$ (M+ H^+): 868.3760.

((4*R*,5*R*)-2-(3-((1-Benzyl-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-1,3-dioxolane-4,5-

diyl)bis(dinaphthalen-1-ylmethanol) (9d). By analogous procedure as **9a** from ((4*R*,5*R*)-2-(3-(prop-2-ynyloxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(dinaphthalen-1-ylmethanol) **7c** (1.53 g, 2 mmol) and benzyl azide (266 mg, 2 mmol) was obtained the title product as colour less oil. Yield 98%. ^1H NMR (300 MHz CDCl_3): δ ppm = 8.69 - 7.07 (m, 38 H), 5.56 (s, 1 H), 5.43 (s, 2 H), 5.37 (d, $J = 4.01$ Hz, 1 H), 5.31 (d, $J = 4.24$ Hz, 1 H), 5.14 (d, $J = 4.48$ Hz, 2 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 156.5$ (O- C_{ph}), 148.5 - 111.3 (N- $\text{CH}=\text{C}$, $\text{CH}=\text{C}-\text{CH}_2$, CH_{ph} and C_{ph}), 106.5 (O- $\text{CH}-\text{O}$), 81.5 (O- $\text{CH}-\text{CH}-\text{O}$), 81.2 (O- $\text{CH}-\text{CH}-\text{O}$), 79.5 ((Ph) $_2$ - $\text{C}-\text{OH}$), 78.7 ((Ph) $_2$ - $\text{C}-\text{OH}$), 61.8 (C- CH_2-O), 53.6 (Ph- CH_2-N). HRMS (ESI): Found: m/z 902.3585. Calculated for $\text{C}_{61}\text{H}_{48}\text{N}_3\text{O}_5$ (M+ H^+): 902.3594.

((4*R*,5*R*)-4-((3-(4,5-Bis(hydroxydiphenylmethyl)-1,3-dioxolan-2-yl)phenoxy)methyl)-1-

butyl-3-methyl-1*H*-1,2,3-triazol-3-ium iodide (10a). ((4*R*,5*R*)-2-(3-((1-butyl-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol) **9a**, (1 g, 1.5 mmol) was dissolved in CH_3CN (2 mL) in a two neck sealed flask fitted with efficient reflux condenser and a balloon, to it was injected methyl iodide (0.94 mL, 15 mmol). The reaction mixture was heated at 55 °C overnight. Volatiles were removed from the resulting liquid to furnish yellow solid product. Yield 98%. M.p. 115 - 117 °C. ^1H NMR (300 MHz CDCl_3): δ ppm = 7.53 - 7.05 (m, 22 H), 7.01 - 6.89 (m, 2H), 6.82 (d, $J = 7.69$ Hz, 1 H), 5.40 (d, $J = 4.97$ Hz, 1 H), 5.32 (d, $J = 4.57$ Hz, 1 H), 5.19 (d, $J = 4.72$ Hz, 1 H), 5.09 (d, $J = 2.69$ Hz, 2 H), 4.46 (t, $J = 7.32, 7.32$ Hz, 2 H), 4.20 (s, N- CH_3 , 3 H), 1.93 - 1.78 (m, $\text{CH}_2-\text{CH}_2-\text{CH}_2$, 2 H), 1.37-1.21 (m, $\text{CH}_2-\text{CH}_2-\text{CH}_3$, 2 H), 0.89 (t, $J = 7.34, 7.34$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm = 156.5 (O- C_{ph}), 145.4 -

113.8 (N-CH=C, CH_{ph}, C_{ph} and CH=C-CH₂), 104.5 (Ph-CH-O₂), 81.5 (O-CH-CH-O), 80.9 (O-CH-CH-O), 79.1((Ph)₂-C-OH), 78.7 ((Ph)₂-C-OH), 58.7 (C-CH₂-O), 54.0(CH₂-CH₂-N), 39.7 (N-CH₃), 31.1 (CH₂-CH₂-CH₂), 19.3 (CH₂-CH₂-CH₃), 13.4 (CH₂-CH₂-CH₃). HRMS (ESI), Found: *m/z* 682.3276. Calculated for C₄₃H₄₄N₃O₅ (M⁺): 682.3275. $[\alpha]_D^{28} = +48.7^\circ$ (*c* = 1, CCl₃).

((4*R*,5*R*)-4-((3-(4,5-Bis(bis(3,5-dimethylphenyl)(hydroxy)methyl)-1,3-dioxolan-2-yl)phenoxy)methyl)-1-butyl-3-methyl-1*H*-1,2,3-triazol-3-ium iodide (10b). By analogues procedure as **10a** from ((4*R*,5*R*)-2-(3-((1-butyl-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(bis(3,5-dimethylphenyl)methanol) **9b** (1.3 g, 1,66 mmol) and methyl iodide (1.0 mL, 16 mmol). Yield 99%. M.p. 130 – 135 °C. ¹H NMR (300 MHz CDCl₃) δ ppm = 7.43 - 6.67 (m, 17 H), 5.71 (s, 1 H), 5.34 (d, *J* = 4.01 Hz, 1 H), 5.20 (d, *J* = 4.24 Hz, 1 H), 5.14 (d, *J* = 4.48 Hz, 2 H), 4.55 (t, *J* = 7.29, 7.29 Hz, 2 H), 4.22 (s, 3 H), 2.36 - 2.15 (m, 24 H), 1.90 - 1.73 (m, 2 H), 1.44 - 1.28 (m, 2 H), 0.95 (t, *J* = 7.33, 7.33 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃) δppm 156.5 (O-C_{ph}), 145.5 - 113.4 (N-CH=C, CH=C-CH₂, CH_{ph} and C_{ph}), 104.6 (O-CH-O), 81.5 (O-CH-CH-O), 81.2 (O-CH-CH-O), 79.5 ((Ph)₂-C-OH), 78.7 ((Ph)₂-C-OH), 61.8 (C-CH₂-O), 53.6 (CH₂-CH₂-N), 39.7 (N-CH₃), 31.2 (CH₂-CH₂-CH₂), 21.6 (8C, Ph-CH₃), 19.4 (CH₂-CH₂-CH₃), 13.5 (CH₂-CH₂-CH₃). HRMS (ESI): Found: *m/z* 794.4527. Calculated for C₅₁H₆₀N₃O₅ (M⁺): 794.4527, $[\alpha]_D^{28} = +60.5^\circ$ (*c* = 1, CHCl₃).

(4*R*,5*R*)-4-((3-(4,5-Bis(hydroxydinaphthalen-1-ylmethyl)-1,3-dioxolan-2-yl)phenoxy)-methyl)-1-butyl-3-methyl-1*H*-1,2,3-triazol-3-ium iodide (10c). By analogous procedure as **10a** from ((4*R*,5*R*)-2-(3-((1-butyl-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(dinaphthalen-1-ylmethanol) **9d** (1.3 g, 1,5 mmol) and methyl iodide (1.0 mL, 16 mmol). Yield 94%. M.p. 177 - 181 °C. ¹H NMR (300 MHz CDCl₃) δ ppm = 8.95 - 6.49 (m, 33 H), 6.05 (m, 1 H), 5.95 (m, 1 H), 5.73 (s, 1 H), 4.93 (s, 2 H), 4.42 (s, 3H), 4.32 (t, *J* = 7.05, 7.05 Hz, 2 H), 1.87 - 1.73 (m, 2 H), 1.30 (dd, *J* = 14.76, 7.32 Hz, 2 H), 0.88 (t, *J* = 7.36, 7.36 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): δppm = 158.4 (O-CH_{ph}), 143.2 - 116.2 (N-CH=C, CH=C-CH₂, CH_{ph} and C_{ph}), 113.7 (C-CH₂-CH-O), 105.2 (O-CH-O), 82.9 (O-CH-CH-O), 82.3 (O-CH-CH-O), 79.6 (C_{ph}-C-OH), 62.1(C-CH₂-O), 49.7 (CH₂-CH₂-N), 37.8 (N-CH₃), 32.0 (CH₂-CH₂-CH₂), 19.5 (CH₂-CH₂-CH₃), 13.5 (CH₂-CH₂-CH₃). HRMS (ESI): Found: *m/z* 882.3898. Calculated for C₅₉H₅₂N₃O₅ (M⁺): 882.3901. $[\alpha]_D^{28} = +98.7$ (*c* = 1, CHCl₃).

(4*R*,5*R*)-1-benzyl-4-((3-(4,5-bis(hydroxydinaphthalen-1-ylmethyl)-1,3-dioxolan-2-yl)phenoxy)methyl)-3-methyl-1*H*-1,2,3-triazol-3-ium iodide (10d). By analogous procedure as **10a** from (((4*R*,5*R*)-2-(3-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-1,3-dioxolane-4,5-diyl)bis(dinaphthalen-1-ylmethanol) **9c** (901 mg, 1 mmol) and methyl iodide (0.62 mL, 10 mmol) was obtained a yellow solid product. Yield 98%. ¹H NMR (300 MHz CDCl₃): δ ppm = 8.74 - 7.17 (m, 38 H), 5.59 (s, 1 H), 5.54 (m, 2 H), 5.36 (d, *J* = 4.01 Hz, 1H), 5.33 (d, *J* = 4.24 Hz, 1H), 5.14 (d, *J* = 4.48 Hz, 2 H), 3.96 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ ppm = 156.5 (O-C_{ph}), 148.5 - 111.3 (N-CH=C, CH=C-CH₂, CH_{ph} and C_{ph}), 106.5 (O-CH-O), 81.5 (O-CH-CH-O), 81.2 (O-CH-CH-O), 79.5 ((Ph)₂-C-OH), 78.7 ((Ph)₂-C-OH), 61.8 (C-CH₂-O), 53.6 (Ph-CH₂-N), 37.6 (N-CH₃). HRMS (ESI): Found: *m/z* 916.3742. Calculated for C₆₂H₅₀N₃O₅ (M⁺): 916.3745.

(4*R*,5*R*)-4-((3-(4,5-bis(hydroxydiphenylmethyl)-1,3-dioxolan-2-yl)phenoxy)methyl)-1-butyl-3-methyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate (11a). ((4*R*,5*R*)-4-((3-(4,5-bis(hydroxydiphenylmethyl)-1,3-dioxolan-2-yl)phenoxy)methyl)-1-butyl-3-methyl-1*H*-1,2,3-triazol-3-ium iodide **10a** (809 mg, 1 mmol) was dissolved in CH₃CN (2 mL). To it was added AgBF₄ (195 mg, 1.0 mmol). The mixture was stirred at room temperature for 1 hour. The AgI precipitate was filtered and volatiles were removed from the resulting liquid to furnish as a yellowish viscous liquid product. Yield 98%. ¹H NMR (300 MHz CDCl₃): δ ppm = 7.65 - 7.11 (m, 22 H), 7.01 - 6.89 (m, 2 H), 6.87 (d, *J* = 7.70 Hz, 1 H), 5.40 (d, *J* = 4.95 Hz, 1 H), 5.35 (d, *J* = 4.70 Hz, 1 H), 5.19 (d, *J* = 4.70 Hz, 1 H), 5.09 (d, *J* = 2.69 Hz, 2 H), 4.46 (t, *J* = 7.33, 7.33 Hz, 2 H), 4.20 (s, 3 H), 1.93 - 1.78 (m, 2 H), 1.35 - 1.24 (m, 2 H), 0.88 (t, *J* = 7.34, 7.34 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ ppm = 156.5 (O-C_{ph}), 145.4 - 113.8 (N-CH=C, CH=C-CH₂, CH_{ph} and C_{ph}), 104.5 (C-CH₂-CH-O₂), 81.5 (O-CH-CH-O), 80.7 (O-CH-CH-O), 79.0((Ph)₂-C-OH), 78.7 ((Ph)₂-C-OH), 58.6 (C-CH₂-O), 54.3(CH₂-CH₂-N), 38.9 (N-CH₃), 31.3 (CH₂-CH₂-CH₂), 19.3 (CH₂-CH₂-CH₃), 13.4 (CH₂-CH₂-CH₃).

((4*R*,5*R*)-4-((3-(4,5-Bis(bis(3,5-dimethylphenyl)(hydroxy)methyl)-1,3-dioxolan-2-yl)phenoxy)methyl)-1-butyl-3-methyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate (11b). (4*R*,5*R*)-4-((3-(4,5-bis(bis(3,5-dimethylphenyl)(hydroxy)methyl)-1,3-dioxolan-2-yl)phenoxy)methyl)-1-butyl-3-methyl-1*H*-1,2,3-triazol-3-ium iodide **10b** (922 mg, 1 mmol) was dissolved in CH₃CN (2 mL) and to it was added AgBF₄ (195 mg, 1.0 mmol). The reaction mixture was stirred at room temperature for 1 hour. The AgI precipitate was filtered and volatiles were removed from the resulting liquid to furnish the product as a brownish viscous liquid. Yield 99%. ¹H NMR (300 MHz CDCl₃): δ ppm = 7.43 - 6.67 (m, 17 H), 5.71 (s, 1 H), 5.34 (d, *J* = 4.01 Hz, 1 H), 5.20 (d, *J* = 4.24 Hz, 1 H), 5.14 (d, *J* = 4.48 Hz, 2 H), 4.55 (t, *J* = 7.29, 7.29 Hz, 2 H), 4.22 (s, 3 H), 2.36 - 2.15 (m, 24 H), 1.90 - 1.73 (m, 2 H), 1.44 - 1.28 (m, 2 H), 0.95 (t, *J* = 7.33, 7.33 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ ppm = 156.3 (O-C_{ph}), 144.7 - 111.1 (N-CH=C, CH=C-CH₂, CH_{ph} and C_{ph}), 104.6 (O-CH-O), 82.0 (O-CH-CH-O), 81.8(O-CH-CH-O), 80.0((Ph)₂-C-OH), 78.7 ((Ph)₂-C-OH), 61.8 (C-CH₂-O), 53.6 (CH₂-CH₂-N), 39.7 (N-CH₃), 31.2 (CH₂-CH₂-CH₂), 21.6 (Ph-CH₃), 19.4 (CH₂-CH₂-CH₃), 13.5 (CH₂-CH₂-CH₃).

(4*R*,5*R*)-4-((3-(4,5-Bis(hydroxydinaphthalen-1-ylmethyl)-1,3-dioxolan-2-yl)phenoxy)-methyl)-1-butyl-3-methyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate (11c). (4*R*,5*R*)-4-((3-(4,5-bis(hydroxydinaphthalen-1-ylmethyl)-1,3-dioxolan-2-yl)phenoxy)methyl)-1-butyl-3-methyl-1*H*-1,2,3-triazol-3-ium iodide **10c** (1.1 g, 1 mmol) was dissolved in CH₃CN (2 mL) to it was added AgBF₄ (195 mg, 1.0 mmol). The mixture was stirred at room temperature for 1 hour. The AgI precipitate was filtered and volatiles were removed from the resulting liquid to furnish yellowish viscous liquid product. Yield 99%. ¹H NMR (300 MHz CDCl₃): δ ppm = 8.95 - 6.49 (m, 33 H), 6.05 (m, 1 H), 5.95 (m, 1 H), 5.74 (s, 1 H), 4.94 (s, 2 H), 4.41 (s, 3 H), 4.33 (t, *J* = 7.05, 7.05 Hz, 2 H), 1.90 - 1.71 (m, 2 H), 1.30 (dd, *J* = 14.77, 7.33 Hz, 2 H), 0.89 (t, *J* = 7.38, 7.38 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ ppm = 159.2 (O-CH_{ph}), 144.6 - 117.4 (N-CH=C, CH_{ph} and C_{ph}), 113.7 (C-CH₂-CH-O), 106.4 (O-CH-O), 82.9 (O-CH-CH-O), 82.3 (O-CH-CH-O), 79.6 (C_{ph}-C-

OH), 62.1 (C-CH₂-O), 49.9 (CH₂-CH₂-N), 38.5 (N-CH₃), 32.1 (CH₂-CH₂-CH₂), 20.2 (CH₂-CH₂-CH₃), 14.1 (CH₂-CH₂-CH₃).

(4*R*,5*R*)-1-Benzyl-4-((3-(4,5-bis(hydroxydinaphthalen-1-ylmethyl)-1,3-dioxolan-2-yl)phenoxy)methyl)-3-methyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate (11d). (4*R*,5*R*)-1-Benzyl-4-((3-(4,5-bis(hydroxydinaphthalen-1-ylmethyl)-1,3-dioxolan-2-yl)phenoxy)methyl)-3-methyl-1*H*-1,2,3-triazol-3-ium iodide **10d** (1.0 g, 1 mmol) was dissolved in CH₃CN (2 mL) and to it was added AgBF₄ (195 mg, 1.0 mmol). The mixture was stirred at room temperature for 1 hour. The AgI precipitate was filtered and volatiles were removed from the resulting liquid to furnish the product as a pale yellow viscous liquid. Yield 97%. ¹H NMR (300 MHz CDCl₃): δ ppm = 8.70 - 7.15 (m, 38 H), 5.61 (s, 1 H), 5.53 (s, 2 H), 5.35 (d, *J* = 4.01 Hz, 1 H), 5.36 (d, *J* = 4.23 Hz, 1 H), 5.13 (d, *J* = 4.46 Hz, 2 H), 4.0 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ ppm = 156.4 (O-C_{ph}), 147.9 - 111.1 (N-CH=C, CH=C-CH₂, CH_{ph} and C_{ph}), 106.3 (O-CH-O), 81.0 (O-CH-CH-O), 79.8 (O-CH-CH-O), 79.5 ((Ph)₂-C-OH), 78.6 ((Ph)₂-C-OH), 61.7 (C-CH₂-O), 53.5 (Ph-CH₂-N), 37.5 (N-CH₃).

4-(Imidazol-1-yl)butan-2-one (12).²⁹ To a stirred solution of imidazole (1.36 g, 20.0 mmol) in dry DMSO (20 mL) was added catalytic amount methylimidazole (82 mg, 1.0 mmol) and the mixture was cooled to 0 °C. To it was added methyl vinyl ketone (1.68 g, 24.0 mmol) and was allowed to warm to room temperature and heated up to 85 °C. When TLC indicated the complete consumption of the starting materials (about three hours) the reaction was made to cool to room temperature. It was diluted with distilled water (50 mL) and was extracted with ethyl acetate (50 mL) three times. The organic layer was separated and washed with additional water (50 mL). The organic phase was then dried with anhydrous sodium sulphate and volatiles were removed under reduced pressure to furnish the desired product as clear yellow oil. Yield 69 %. ¹H NMR (300 MHz CDCl₃): δ ppm = 7.40 (s, 1 H), 6.92 (s, 1 H), 6.87 (s, 1 H), 4.22 - 4.05 (m, 2 H), 2.84 (m, 2 H), 2.06 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ ppm = 205.1 (CH₃-C=O), 137.2 (N=CH-N), 128.9 (N-CH=CH-N), 119.7 (N-CH=CH-N), 44.3 (N-CH₂-CH₂), 40.8 (C-CH₂-CH₂), 30.1 (O-C-CH₃).

4-(Imidazol-1-yl)butan-2-one (improved route) (12). To a stirred solution of methyl-vinyl-ketone (1.40 g, 20.0 mmol) and imidazole (1.36 g, 20.0 mmol) in dry dioxane (20 mL) was added triethylamine (0.55 mL, 4.0 mmol). The reaction mixture refluxed overnight. Volatiles were removed under reduced pressure from the resulting solution. The resulting yellowish oil was subjected to column chromatographic purification with methanol/chloroform gradient 1:19 to furnish **12** in 93% yield.

((4*R*,5*R*)-2-(2-(1*H*-Imidazol-1-yl)ethyl)-2-methyl-1,3-dioxolane-4,5-dicarboxylate dimethyl ester (13). *L*-(+)-dimethyl tartrate **4** (1.8 g, 10.1 mmol) and 4-(imidazol-1-yl)butan-2-one **12** (920 mg, 6.75 mmol) were dissolved in ethyl acetate (25 mL). The reaction flask was placed in an ice bath to keep the temperature below 20 °C during the reaction. To the mixture was added BF₃:OEt₂ (3.6 mL, 13.5 mmol) dropwise. The reaction mixture was left to stir overnight. The resulting solution was poured into saturated sodium bicarbonate solution (50 mL) and was extracted with EtOAc (50 mL) three times. The organic layers were combined and washed with

distilled water (50 mL) three times and dried over magnesium sulphate. Removal of volatiles under vacuum furnished the desired product as viscous liquid. Yield 78%. ^1H NMR (300 MHz CDCl_3): δ ppm = 7.43 (s, 1 H), 6.98 (m, 2 H), 4.83 (d, $J = 5.74$ Hz, 1 H), 4.66 (d, $J = 5.74$ Hz, 1 H), 4.19-3.98 (m, 2 H), 3.78 (s, 6 H), 2.24 - 2.17 (m, 2 H), 1.40 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm = 169.8 ($\text{O}=\underline{\text{C}}-\text{OCH}_3$), 169.4 ($\text{O}=\underline{\text{C}}-\text{OCH}_3$), 137.4 ($\text{N}=\underline{\text{C}}\text{H}-\text{N}$), 123.6 ($\text{N}-\underline{\text{C}}\text{H}=\underline{\text{C}}\text{H}-\text{N}$), 121.8 ($\text{N}-\underline{\text{C}}\text{H}=\underline{\text{C}}\text{H}-\text{N}$), 113.3 ($\text{O}-\underline{\text{C}}-\text{CH}_3$), 81.4 ($\text{O}-\underline{\text{C}}\text{H}-\text{CH}$), 79.8 ($\text{CH}-\underline{\text{C}}\text{H}-\text{O}$), 53.7 ($\text{C}-\text{O}-\underline{\text{C}}\text{H}_3$), 52.1 ($\text{C}-\text{O}-\underline{\text{C}}\text{H}_3$), 44.7 ($\text{N}-\underline{\text{C}}\text{H}_2-\text{CH}_2$), 42.0 ($\text{C}-\underline{\text{C}}\text{H}_2-\text{CH}_2$), 24.6 ($\text{O}_2-\text{C}-\underline{\text{C}}\text{H}_3$). $[\alpha]_D^{28} = -14.5^\circ$ ($c = 1$, CHCl_3).

((4*R*,5*R*)-2-(2-(1*H*-Imidazol-1-yl)ethyl)-2-methyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol) (14). A reaction flask fitted with an efficient condenser was dried with hot air-gun and flushed with argon 3 times. Grignard reagent was prepared from magnesium turnings (243 mg, 10 mmol) in dry THF (15 mL) with a slow addition of bromobenzene (1.9 g, 12 mmol). Initially the reaction mixture was set to reflux by itself with a controlled addition of the bromobenzene. After the complete consumption of the Mg turnings refluxing was continued for 1 h using a water-bath. 2-(2-(1*H*-imidazol-1-yl)ethyl)-2-methyl-1,3-dioxolane-4,5-dicarboxylate dimethyl ester **13** (298 mg, 1 mmol) in dry THF (2 mL) was slowly added to the Grignard reagent at room temperature. The reaction mixture was left to stir overnight. The resulting solution was diluted with Et_2O (20 mL) and quenched by 1N aq HCl (50 mL) at 0 °C. The ether phase was separated and dried with MgSO_4 and the solvent was removed under vacuum to give the title product as yellowish solid. Yield 58%. M.p. 103 - 105 °C. ^1H NMR (300 MHz CDCl_3): δ ppm = 8.58 (s, 1 H), 7.43 - 7.22 (m, 20 H), 7.11 (m, 1 H), 6.65 (m, 1 H), 4.74 (d, $J = 7.95$ Hz, 1 H), 4.56 (d, $J = 7.98$ Hz, 1 H), 3.76 (m, 1 H), 3.59 (m, 1 H), 1.93 (m, 1 H), 1.82 (m, 1 H), 0.90 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm = 146.0 - 142.1 ($\text{HO}-\text{C}-\underline{\text{C}}_{\text{ph}}$), 134.6 ($\text{N}=\underline{\text{C}}\text{H}-\text{N}$), 129.2 - 125.8 ($\underline{\text{C}}\text{H}_{\text{ph}}$ and $\text{N}-\underline{\text{C}}\text{H}-\underline{\text{C}}\text{H}-\text{N}$), 108.6 ($\text{O}-\underline{\text{C}}-\text{CH}_3$), 81.7 ($\text{O}-\underline{\text{C}}\text{H}-\text{CH}$), 79.9 ($\text{CH}-\underline{\text{C}}\text{H}-\text{O}$), 78.1 ($(\text{Ph})_2-\underline{\text{C}}-\text{OH}$), 78.1 ($(\text{Ph})_2-\underline{\text{C}}-\text{OH}$), 44.1 ($\text{N}-\underline{\text{C}}\text{H}_2-\text{CH}_2$), 39.8 ($\text{C}-\underline{\text{C}}\text{H}_2-\text{CH}_2$), 25.6 ($\text{O}_2-\text{C}-\underline{\text{C}}\text{H}_3$). $[\alpha]_D^{28} = -23.1^\circ$ ($c = 1$, CHCl_3), HRMS (ESI): Found: m/z 545.2446. calculated for $\text{C}_{35}\text{H}_{33}\text{N}_2\text{O}_4$ ($\text{M}-\text{H}^+$): 545.2440.

(4*R*,5*R*)-1-(2-(4,5-Bis(hydroxydiphenylmethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)-3-methyl-1*H*-imidazol-3-ium iodide (15). A stirred solution of TADDOL **14** (5.43 g, 10.0 mmol) was dissolved in acetonitrile (100 mL) in a sealed two necked flask fitted with an efficient reflux condenser and an argon filled balloon. Methyl iodide (7 g, 50 mmol) was injected dropwise. The reaction mixture was refluxed overnight. From the resulting yellowish solution, volatiles were removed with a rotary evaporator under a well-ventilated hood to give the title product as a brown thick liquid. Yield 95%. ^1H NMR (300 MHz CDCl_3): δ ppm = 8.91 (s, 1 H), 7.43 - 7.12 (m, 20 H), 6.92 - 6.84 (m, 2 H), 4.67 (d, $J = 7.85$ Hz, 1 H), 4.48 (d, $J = 7.85$ Hz, 1 H), 3.76 (s, 3 H), 3.72 - 3.53 (m, 2 H), 2.16 - 1.98 (m, 1 H), 1.92 - 1.75 (m, 1 H), 0.87 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm = 145.6 - 141.9 ($\text{HO}-\text{C}-\underline{\text{C}}_{\text{ph}}$), 135.8 ($\text{N}=\underline{\text{C}}\text{H}-\text{N}$), 129.0-127.4 ($\underline{\text{C}}\text{H}_{\text{ph}}$), 123.8 and 122.1 ($\text{N}-\underline{\text{C}}\text{H}=\underline{\text{C}}\text{H}-\text{N}$), 108.7 ($\text{O}-\underline{\text{C}}-\text{CH}_3$), 81.7 ($\text{O}-\underline{\text{C}}\text{H}-\text{CH}$), 80.0 ($\text{CH}-\underline{\text{C}}\text{H}-\text{O}$), 78.2 ($(\text{Ph})_2-\underline{\text{C}}-\text{OH}$), 78.1 ($(\text{Ph})_2-\underline{\text{C}}-\text{OH}$), 45.0 ($\text{N}-\underline{\text{C}}\text{H}_2-\text{CH}_2$), 39.5 ($\text{C}-\underline{\text{C}}\text{H}_2-\text{CH}_2$), 37.1 ($\text{N}-\underline{\text{C}}\text{H}_3$), 25.6 ($\text{O}_2-\text{C}-\underline{\text{C}}\text{H}_3$).

$[\alpha]_D^{28} = -15.8$ ($c = 1$, CHCl_3). HRMS (ESI): Found: m/z 561.2748. Calculated for $\text{C}_{21}\text{H}_{26}\text{N}_3\text{O}_3\text{S}$ (M^+): 561.2748.

(4*R*,5*R*)-1-(2-(4,5-Bis(hydroxydiphenylmethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)-3-methyl-1*H*-imidazol-3-ium tetrafluoroborate (16). To a solution of (4*R*,5*R*)-1-(2-(4,5-bis(hydroxydiphenylmethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)-3-methyl-1*H*-imidazol-3-ium iodide **15** (690 mg, 1 mmol) in CH_3CN (2 mL) AgBF_4 (195 mg, 1.0 mmol) was added. The reaction mixture was stirred at room temperature for one hour. The solid precipitate (AgI) was filtered off and volatiles were removed from the filtrate to furnish the title product as a brown viscous liquid. Yield 99%. ^1H NMR (300 MHz CDCl_3): δ ppm = 8.90 (1 H, s, $\text{N}=\underline{\text{C}}\text{H}-\text{N}$), 7.39 - 7.19 (m, 20 H), 6.93 - 6.93 (m, 2 H), 4.77 (d, $J = 7.85$ Hz, 1 H), 4.50 (d, $J = 7.85$ Hz, 1 H), 3.76 (s, 3 H), 3.70 - 3.49 (m, 2 H), 2.16 - 1.98 (m, 1 H), 1.92 - 1.75 (m, 1 H), 0.87 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm = 145.8 - 141.9 ($\text{HO}-\text{C}-\underline{\text{C}}_{\text{ph}}$), 136.1 ($\text{N}=\underline{\text{C}}\text{H}-\text{N}$), 129.0 - 126.9 ($\underline{\text{C}}\text{H}_{\text{ph}}$), 123.8 and 122.1 ($\text{N}-\underline{\text{C}}\text{H}-\underline{\text{C}}\text{H}-\text{N}$), 108.7 ($\text{O}-\underline{\text{C}}-\text{CH}_3$), 81.7 ($\text{O}-\underline{\text{C}}\text{H}-\text{CH}$), 80.0 ($\text{CH}-\underline{\text{C}}\text{H}-\text{O}$), 78.2 ($\text{Ph})_2-\underline{\text{C}}-\text{OH}$), 78.1 ($\text{Ph})_2-\underline{\text{C}}-\text{OH}$), 45.0 ($\text{N}-\underline{\text{C}}\text{H}_2-\text{CH}_2$), 39.5 ($\text{C}-\underline{\text{C}}\text{H}_2-\text{CH}_2$), 37.2 ($\text{N}-\underline{\text{C}}\text{H}_3$), 25.6 ($\text{O}_2-\text{C}-\underline{\text{C}}\text{H}_3$).

4-Methoxy-6-phenyl-5,6-dihydro-2*H*-pyran-2-one (18).³⁰ The TADDOL catalyst **11d** (97 mg, 0.1 mmol) was placed in a small reaction vial. The air was evacuated at 10 mbar and was flushed with argon three times. A freshly distilled benzaldehyde (256 mg, 2.5 mmol) was then injected and the contents were cooled to -24 °C. Brassard's diene **17** (102 mg, 0.5 mmol) was added and the mixture was stirred at -24 °C. At the completion of the reaction MeOH (0.5 mL) was added and stirred for 30 min at the same temperature. Volatiles were solvent was evaporated and the remainder was extracted with Et_2O (3 mL) 3 times. The Et_2O phase was removed to furnish the title product after column chromatography (Cyclohexane: Ethyl acetate, 2 : 1). Yield 49%. ^1H NMR (300 MHz CDCl_3): δ ppm = 7.41 - 7.19 (m, 5 H), 5.47 (m, 1 H), 5.31 (s, 1 H), 3.78 (s, 3 H), 2.85 - 2.88 (m, 1 H), 2.64 - 2.56 (m, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm = 171.3 ($\text{CH}=\underline{\text{C}}-\text{O}$), 167.4 ($\text{O}-\underline{\text{C}}=\text{O}$), 139.6 ($\text{C}_{\text{ph}}-\underline{\text{C}}\text{H}-\text{O}$), 129.9 - 124.4 ($\underline{\text{C}}\text{H}_{\text{ph}}$), 89.4 ($\text{C}=\underline{\text{C}}\text{H}-\text{C}$), 76.9 ($\text{O}-\underline{\text{C}}\text{H}-\text{CH}_2$), 56.8 ($\underline{\text{C}}\text{H}_3-\text{O}$), 35.1 ($\text{C}-\underline{\text{C}}\text{H}_2-\text{CH}$). Enantioselectivity = 12 % (HPLC on a Chiralpak AD column, $\lambda = 215$ nm, Eluent *i*- PrOH -hexane (85:15), flow rate = 1.0 mL min^{-1} ; $t_R = 16.31$ min (minor), 18.06 min (major)).

2-Phenyl-2*H*-pyran-4(3*H*)-one (20).³⁵ Rawal's diene **19** (114 mg, 0.5 mmol) was injected into a solution of catalyst **11d** (97 mg 0.1 mmol) and freshly distilled benzaldehyde (530 mg, 5 mmol) in a sealed reaction flask under argon atmosphere at -78 °C. After 48 hours at the same temperature dry Et_2O (2 mL) was injected to separate the reaction mixture from the IL-tagged catalyst by precipitation, the Et_2O phase was subjected to acetyl chloride 352 μL at -78 °C. The mixture was then stirred for half hour and volatiles were removed. The residue was purified by column chromatography (Cyclohexane : EtOAc , 3:1) to furnish the title product. Yield 32%. ^1H NMR (300 MHz, CDCl_3): δ ppm = 7.67 - 7.43 (m, 5 H), 7.31(s, 1 H), 5.56 (d, $J = 6.02$, 1 H), 5.45 (dd, $J = 14.39$, 3.51 Hz, 1 H), 2.94 - 2.88 (m, 1 H), 2.69 - 2.56 (m, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm = 195.2 ($\text{CH}-\underline{\text{C}}=\text{O}$), 163.4 ($\text{O}-\underline{\text{C}}\text{H}=\text{CH}$), 131.6 - 126.1 ($\underline{\text{C}}\text{H}_{\text{ph}}$, $\underline{\text{C}}_{\text{ph}}$), 107.4 ($\text{C}-\underline{\text{C}}\text{H}=\text{CH}$), 89.4 ($\text{Ph}-\underline{\text{C}}\text{H}-\text{O}$), 43.4 ($\text{C}-\underline{\text{C}}\text{H}_2-\text{CH}$). Enantioselectivity = 26% (HPLC on a

Chiralpak OD column, $\lambda = 215$ nm, Eluent *i*-PrOH–hexane (9:1), flow rate = 0.5 mL min⁻¹; *t*_R = 34.4 min (major), 40.3 min (minor).

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