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Synthesis of Homochiral Tris-indanyl Molecular Rods

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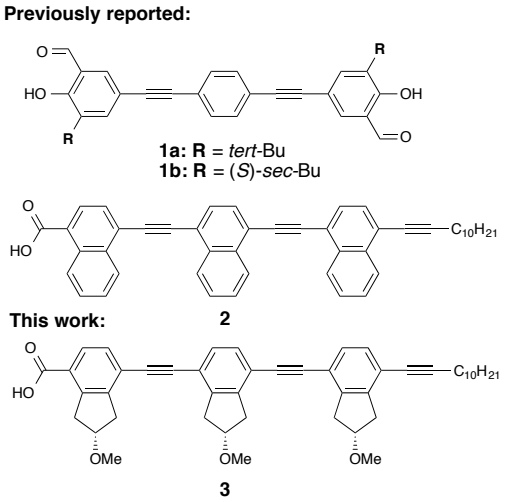
Homochiral tris-indanyl molecular rods designed for supramolecular surface self-assembly were synthesized. The chiral indanol moiety was constructed via a Ti-mediated alkyne trimerization. Further manipulations resulted in a homochiral indanol monomer. This was employed as the precursor for successive Sonogashira and Ohira-Bestman reactions towards the homochiral tris-indanyl molecular rods. The molecular rods will be applied for scanning tunnelling microscopy studies of their surface self-assembly and chirality.

Introduction

In recent years increasing attention has been devoted to the formation and characterization of chiral surface assemblies.[1,2,3,4,5] The formation of homochiral patterns on surfaces has potential applications in the areas of asymmetric, heterogeneous catalysis,[6,7,8] enantioselective separation,[9,10,11] and fundamental studies of chiral molecular recognition.[12] When confined to a surface prochiral molecules will exhibit point- and organizational chirality due to broken symmetry.[13] Despite the formation of local, homochiral assemblies the surface remains globally racemic due to a statistical mixture of surface conformers. Crystallographic and scanning tunneling microscopy (STM) studies have revealed that the chirality of assemblies of prochiral molecules can be steered by doping the surface with homochiral molecules.[14,15,16] As a consequence, this has led to the introduction of the so-called sergeants and soldiers principle[17,18] which describes the relay and amplification of inherent stereochemical information in sergeant molecules through achiral soldier molecules. Several sergeant-type molecular systems takes advantage of the simple coupling of homochiral alkanes to aromatic systems.[19,20,21] We have previously reported on molecular rods (**1)** containing terminal salicylaldehydes. These molecules could switch between conformational states when absorbed on surfaces (Scheme 1). It was observed that the introduction of a homochiral center at the salicylaldehyde, as in **1b**, created a strong bias for a preferred conformation when absorbed at a surface.[22] Additionally, the chiral moiety of **1b** served as sergeants by steering the assembly of co-deposited achiral analogs **1a**



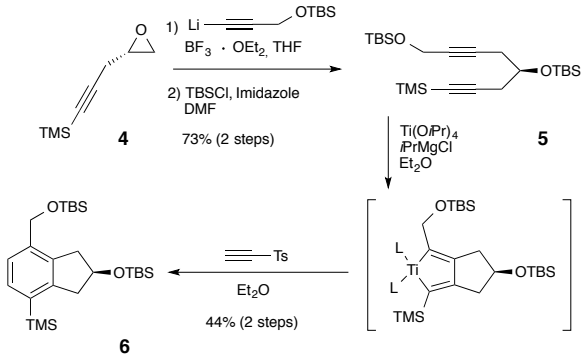
Scheme 1. Structures of previously reported salicylaldehyde **1**,tris-naphthyl molecular rods **2**, and the targeted tris-indanyl derivative **3**.

As a next generation switch molecule for studies of surface chirality we have recently reported on the synthesis and preliminary STM investigations of an achiral trisnaphthyl rod (**2,** Scheme 1).[23] The three naphthylene units in compound **2** have freedom to rotate around the oligo(ethynylene-naphthylene) backbone in the gas/solvated state. However, when compound **2** is absorbed on a surface, with its backbone and naphthyl moieties parallel to the surface plane, each naphthyl moiety can assume one of two discrete orientations pointing either right or left compared to the backbone. As a result, the compound can obtain $2^3 = 8$ different chiral surface conformations and the conformers can be distinguished by UHV-STM.[23] Whereas **2** led to a statistical mixture of surface

conformers, we propose the indane compound **3** as a homochiral analog that may obtain preferred surface conformations and potentially serve as a molecular sergeant for molecules such as **2**. Here we describe the design and synthesis of the chiral analog **3** which consists of three homochiral indan-2-ol moieties connected by ethynylene spokes. The two ends of the molecular rod are functionalized with a carboxylic acid and a dodecynyl moiety, since these end groups have proven to be important for the formation of lamella type nanostructures of rigid molecular rods on the surface. Surface conformers of molecules such as **2** and **3** can be translated into a three-digit binary code. The potential of controlling the conformation, amplifying this information in non-chiral analogues and reading the information by STM may offer the first steps towards processing digital information in molecules through their conformations.

Results and discussion

The key building block in the structure of **3** is the homochiral indan-2-ol moiety. Regioselective synthesis of such highly substituted, asymmetric benzenes has traditionally posed a challenge. As a solution we applied a slightly modified protocol developed by Sato and coworkers providing access to the optically active indan-2-ol motif.[24]

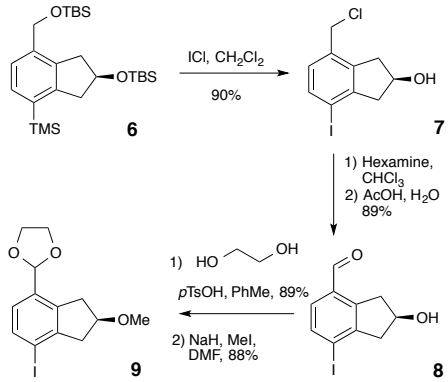


Scheme 2. Preparation of the homochiral indan-2-ol motif.

The epoxide **4** serves as a convenient precursor for the preparation of the optically active indan-2-ol motif and was prepared from commercially available (*S*)-epichlorohydrin.[24] The first step shown in scheme 2 is a ring opening of **4** with lithium TBS-propargylide followed by TBS protection providing the 1,6-dialkyne **5** in 73% yield. Treatment of **5** with an *in situ* generated divalent titanium species and subsequent addition of Ts-acetylene results in the formation of three new carbon-carbon bonds and afforded **6** in 44% yield over two steps. According to Suzuki *et al*. the reaction is a cyclotrimerization and proceeds via a Ti-dialkene species.[25]

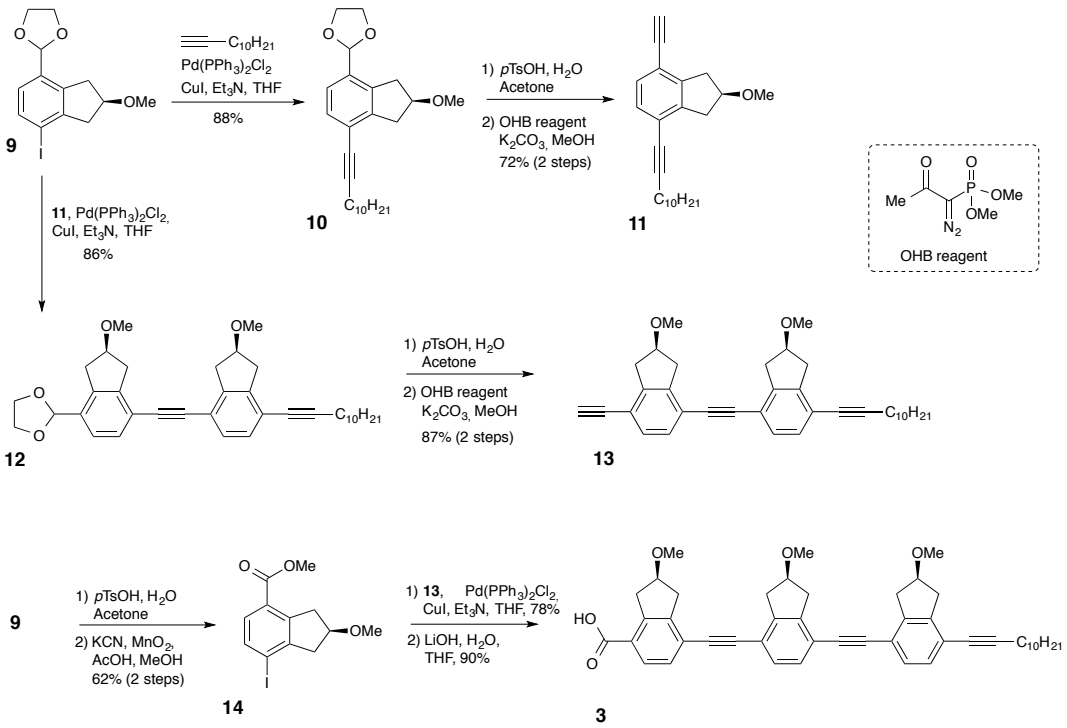
The cyclotrimerization product **6** was treated with ICl in order to selectively iodinate the aromatic system by *ipso*-substitution of the TMS group (Scheme 3). Interestingly, this led to multiple reactions. In addition to the *ipso*-substitution the TBS protection group at the secondary alcohol was removed. Furthermore, the TBS protected benzyl alcohol was cleanly converted to the corresponding benzyl chloride **7**. To the best of our knowledge, the synthesis of benzyl chlorides from silyl protected benzyl alcohols and deprotection of TBS protected aliphatic alcohols by treatment with ICl have not been reported previously. Therefore, we have investigated the deprotection of TBS protected aliphatic alcohols in presence of ICl further. Three TBS protected alcohols of cyclohexanol, 1-decanol and 2-indanol were each treated with an equimolar amount of ICl at 0 °C in CH_2Cl_2 for 4 to 12h. In all three cases the deprotected alcohols were obtained in yields ranging from 63-83% (See supporting information for details). Based on the in four examples shown here the reactivity of ICl towards TBS-alkyl ether deprotection seems to be general.

Although unexpected, the additional conversion of the benzylic OTBS moiety in **6** to the benzyl chloride in **7** was convenient since it allowed for a selective oxidation of the benzyl chloride to the corresponding aldehyde in the presence of the aliphatic alcohol.



Scheme 3. Preparation of a homochiral indan-2-ol monomer.

In a Sommelet reaction compound **7** was, by treatment with hexamethylenetetramine followed by acidic hydrolysis of the resulting ammonium salt, converted to the corresponding benzaldehyde **8** in an good yield of 89%. Benzaldehyde **8** was protected as the 1,3-dioxolane with ethylene glycol in 87% yield followed by methylation of the secondary alcohol with MeI under basic conditions in 88% yield. This provided key building block **9**.



Scheme 4. Coupling of the indanyl moieties to form tris(indanylene ethynylene

The asymmetric building block **9** served as precursor for the iterative approach to constructing the tris(indanylene ethynylene) backbone (Scheme 4). First aryl iodide **9** was alkynylated in a Sonogashira reaction. After acidic deprotection of the acetal the resulting benzaldehyde was converted to the terminal alkyne **11** in an Ohira-Bestman reaction.[26] In the next step **11** was combined with **9** in yet another Sonogashira reaction to give the bis(indanylethynylene) acetal **12**.

This dimer was again deprotected and reacted in an Ohira-Bestman reaction affording terminal alkyne **13**. The methyl ester **14** was prepared from **9** in a satisfactory yield over two steps by deprotecting the acetal followed by a Corey-Gilman-Ganem oxidation of the resulting benzaldehyde. The tris-indanyl rod was finally constructed by coupling of methyl ester **14** with **13** in 78% yield followed by basic hydrolysis of the ester to furnish the target compound **3** in 90% yield. After hydrolysis of the ester group, in the last step of the synthesis, compound **3** precipitates as an amorphous yellow powder that is insoluble in most solvents but slightly soluble in warm DMSO. Compound **3** will be used for sublimation into a UHV-STM chamber and subsequent STM studies on a Au substrate and will constitute a separate study.

Conclusion

We have synthesized the homochiral tris(indanylene ethynylene) molecular rod **3** in 21 steps by means of divergent synthesis. The key reaction of the synthesis is the construction of the enantiopure 1,6-dialkyne **5** from a readily available homopropargyl epoxide **4** and the subsequent cyclotrimerization which provides the central indan-2-ol **6**. We discovered a convenient tri-fold action of ICl on the indan-2-ol adduct **6** to give the required indan-2-ol building block **9**. Subsequent iterative Sonogashira coupling reactions and Ohira-Bestman reactions finally led to target compound **3**. Furthermore we investigated the reactivity of ICl towards TBS-alkyl ethers which revealed a general trend. Compound **3** is designed for supramolecular surface assembly studies by UHV-STM. Preliminary studies on a related achiral compound suggest that this compound assemble in lamella type lattice structures and that the three aromatic moieties in the rod type compounds can switch from side to side affecting neighbouring molecules. Thus we will investigate the application of **3** as a sergeant molecule in such assemblies since our hypothesis is that it will adopt a preferred conformation at the surface due to its intrinsic chirality and thus direct the assembly of other non-chiral molecules.

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Experimental section

General methods

Moisture and oxygen sensitive reactions were carried out under argon atmosphere in flame-dried vessels. THF, CH_2Cl_2 and toluene were purchased dry and passed over activated alumina in a M-Braun MB-SPS 800. Et_2O was dried over sodium. DMF and MeOH were purchased dry and stored over mol. sieves. All other solvents used were HPLC grade purity. Reactions were monitored with TLC using Merck ® silica gel 60 F_{254} TLC plates. Bands on TLC plates were visualized under UV-light (254 or 298 nm) by basic $KMnO_4$ developer or *p*-anisaldehyde developer. Dimethyl(1-diazo-2-oxopropyl)phosphonate and *p*-toluenesulfonylacetylene were prepared according to literature procedures.[27,28] Precipitated MnO_2 was prepared according to a literature procedure[29] and activated by storage at 100 °C overnight. All other reagents were used without further purification. NMR experiments were carried out using a Bruker 400 spectrometer. ^{13}C NMR spectrum for compound **3** was recorded on a Bruker 600 spectrometer equipped with a cryo probe using 7000 scans. Chemical shifts (δ) are reported relative to solvent signals. LRMS experiments were carried out using Electrospray (ESI) or atmospheric pressure chemical (APCI) ionization. Preparative column chromatography was carried out using Merck ® silica gel 60 (230-400 mesh). IR measurements were carried out on a Perkin Elmer Spectrum Two FT-IR spectrometer. Optical rotation measurements were carried out in a Perkin-Elmer 241 polarimeter.

(*S*)-(2-(3-Trimethylsilyl)-2-propynyl)oxirane (4) To a stirred solution of trimethylsilylacetylene (21 mL, 148 mmol) in THF (240 mL) cooled to -78 °C was slowly added *n*-BuLi (60 mL, 2.5 M in hexanes, 148 mmol). After 10 min $BF_3{\cdot}OEt_2$ (18.37 mL, 148 mmol) was added. Then after another 10 minutes at -78 °C (*S*)-epichlorohydrin (7.78 mL, 99.2 mmol) was added after which the resulting mixture was stirred for 1 hour at -78 °C and then allowed to warm to 0 °C. The reaction was quenched with sat. aq. NH_4Cl (600 mL), warmed to rt, and extracted with Et_2O (3x100 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude alcohol was dissolved in CH_2Cl_2 (600 mL) where after NaOH (9.52 g, 238 mmol) was added. The resulting suspension was stirred at rt for 2 days and neutralized with sat. aq. NH_4Cl (300 mL). Then, the mixture was transferred to a separation funnel and extracted with Et_2O (3x100 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, eluent: EtOAc/pentane 5:95 v/v). This afforded (*S*)-2(3-trimethylsilyl-2-propynyl)oxirane as a colorless oil (9.68 g, 62.7 mmol, 63% yield). R_f = 0.65 (silica, EtOAc/pentane 5:95 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 3.13-3.07 (m, 1H), 2.81-2.77 (m, 1H), 2.70-2.63 (m, 2H), 2.49 (dd, *J* = 5.2, 17.5 1H), 0.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 100.8, 87.1, 49.7, 46.3, 23.6, 0.0. IR (neat) ν_{max} 2960, 2179 cm^{-1}. HRMS (ES) *m/z* $[M + Na]^+$ calcd for $C_8H_{14}OSiNa$: 177.0712. Found: 177.0715. $[\alpha]_D^{20}$ +22.4 (*c* 0.25, $CHCl_3$)

(*S*)-1,5-bis(*tert*-butyldimethylsilyloxy)-8-trimethylsilylocta-2,7-diyne (5) To a stirred solution of *t*-butyldimethylsilylpropargyl ether (8.39 g, 49.3 mmol) in THF (50 mL) was slowly added *n*-BuLi (2.5 M in hexanes, 19.7 mL, 49.3 mmol) at -78 °C. After 1 hour was added **4** (3.80 g, 24.6 mmol) in THF (25 mL) followed by $BF_3{\cdot}Et_2O$ (6.08 mL, 49.3 mmol). The solution was stirred at -78 °C for 2 hours after which the reaction was warmed to 0 °C and quenched by the addition of sat. aq. NH_4Cl (50 mL). The mixture was extracted with Et_2O (3x50 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude alcohol was dissolved in DMF (50 mL) after which imidazole (3.35 g, 49.3 mmol) and TBSCl (5.57 g, 37 mmol) were added successively at 0 °C. The resulting yellow solution was stirred at rt. overnight at which TLC analysis indicated total conversion. Hereafter, the reaction was quenched by the addition of sat. aq. $NaHCO_3$ (40 mL) at 0 °C. The mixture was extracted with Et_2O (3x40 mL) where after the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified with dry column vacuum chromatography (d= 1.5 cm, silica height = 7 cm) starting w. 100% heptane and increasing the eluent strength with 1% EtOAc per 20 mL fraction. This afforded the title compound as a colorless oil (7.88 g, 17.9 mmol, 73% yield) R_f = 0.5 (silica, EtOAc/pentane 3:97 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 4.34 – 4.24 (m, 2H), 3.97 – 3.87 (m, 1H), 2.61 – 2.34 (m,

4H), 0.91 (s, 9H), 0.88 (s, 9H) 0.14 (s, 9H), 0.12 – 0.08 (m, 12H).[13]C NMR (100 MHz, $CDCl_3$) δ 104.2, 86.4, 82.0, 80.8, 70.3, 52.1, 28.5, 27.6, 26.0, 25.9, 18.5, 18.2, 0.2, -4.4, -4.5, -5.0. IR (neat) ν_{max} 2955, 2929, 2857, 1472 cm^{-1}. HRMS (ES) *m/z* $[M + H]^+$ calcd for $C_{23}H_{47}O_2Si_3$: 439.2884. Found: 439.2883. $[\alpha]_D^{20}$ +2.2 (*c* 1, $CHCl_3$).

(*R*)-*tert*-Butyl((2-((*tert*-butyldimethylsilyl)oxy)-7-(trimethylsilyl)-2,3-dihydro-1H-inden-4-yl)methoxy) dimethylsilane (6) To a solution of **5** (1.05 g, 2.39 mmol) in Et_2O (10 mL) was added Ti(O-*i*-Pr)$_4$ (0.87 mL, 2.87 mmol) where after the mixture was cooled to -78 °C. To the mixture was added *i*-PrMgCl (2 M in Et_2O, 2.99 mL, 5.98 mmol) drop wise via syringe at -78 °C to afford a yellow, homogeneous solution. The mixture was slowly warmed to -60 °C over a time period of 30 minutes. During this period the solution turned deep red to the point that it was no longer transparent. The mixture was stirred for 4 h while maintaining the temperature between -60 and -40 °C after which a solution of *p*-toluenesulfonylacetylene (862 mg, 4.79 mmol) in Et_2O (3 mL) was introduced via syringe. After stirring overnight at rt the reaction was terminated by the addition of water (1.2 mL). Then, after 15 minutes the resulting slurry was filtered through a short pad of Celite using Et_2O as the solvent. The resulting filtrate was then concentrated *in vacuo* and purified by flash column chromatography. (SiO_2, EtOAc/pentane 2:98 v/v). This afforded the product as a slightly yellow oil (485 mg, 1.04 mmol, 44% yield). R_f = 0.6 (silica, EtOAc/pentane 2:98 v/v) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.5, 1H), 7.23 (d, *J* = 7.5, 1H), 4.71 – 4.63 (m, 3H), 3.18 (dd, *J* = 6.8, 15.6, 1H), 3.06 (dd, *J* = 6.8, 15.9, 1H), 2.92 (dd, *J* = 5.7, 15.6, 1H), 2.75 (dd, *J* = 5.6, 15.8, 1H), 0.95 (s, 9H), 0.91 (s, 9H), 0.28 (s, 9H), 0.12 – 0.09 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 138.1, 137.6, 133.8, 132.5, 123.8, 73.8, 63.5, 43.8, 40.1, 26.1, 18.6, 18.4, -0.5, -4.5, -5.1. IR (neat) ν_{max} 2953, 2927, 2853, 1472 cm^{-1}. HRMS (ES) *m/z* $[M + Na]^+$ calcd for $C_{25}H_{48}NaO_2Si_3$: 487.2860. Found: 487.2861. $[\alpha]_D^{20}$ -0.5 (*c* 1, $CHCl_3$).

(*R*)-4-(Chloromethyl)-7-iodo-2,3-dihydro-1H-inden-2-ol (7) To a solution of **6** (485 mg, 1.04 mmol) in CH_2Cl_2 (1 mL) was added a solution of ICl (583 mg, 3.7 mmol) in CH_2Cl_2 (2 mL) at 0 °C after which the mixture was stirred for 2.5 hours at this temperature. The reaction was quenched by the addition of sat. aq. $Na_2S_2O_3$ which resulted in a yellow suspension. Then the mixture was diluted with water and extracted with CH_2Cl_2 (3x30 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, EtOAc/pentane 3:7 v/v). This afforded the title compound as colorless crystals (290 mg, 940 µmol, 90% yield). Mp (uncorr.): 91-95 °C. R_f = 0.3 (silica, EtOAc/pentane 3:7 v/v) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0, 1H), 6.91 (d, *J* = 8.0, 1H), 4.76 – 4.69 (m, 1H), 4.52 (d, *J* = 11.5, 1H), 4.48 (d, *J* = 11.5, 1H) 3.38 (dd, *J* = 6.0, 16.9, 1H), 3.22 (dd, *J* = 6.0, 17.1, 1H), 3.13 (dd, *J* = 2.7, 16.9, 1H), 2.93 (dd, *J* = 2.7, 17.1, 1H), 1.90 (br. s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 146.5, 141.1, 136.7, 133.6, 129.1, 94.5, 70.8, 48.2, 44.0, 42.3. IR (neat) ν_{max} 3306, 2926, 1577 cm^{-1}. HRMS (ES) *m/z* $[M + Na]^+$ calcd for $C_{10}H_{10}ClINaO$: 330.9363. Found: 330.9360. $[\alpha]_D^{20}$ +4.7 (*c* 1, $CHCl_3$)

(*R*)-2-Hydroxy-7-iodo-2,3-dihydro-1H-indene-4-carbaldehyde (8) To a solution of **7** (250 mg, 811 µmol) in $CHCl_3$ (1.5 mL) was added hexamethylenetetramine (341 mg, 2.43 mmol) where after the mixture was stirred at rt for 2 days at which TLC indicated full conversion. The solvent was removed *in vacuo* where after the remaining residue was dissolved in AcOH/water (1:1 v/v, 2 mL). To the solution was added hexamethylenetetramine (450 mg, 3.3 mmol) and the resulting mixture was refluxed for 2 h. The excess acid was slowly quenched with sat. aq. $NaHCO_3$ at 0 °C. The mixture was diluted with water and extracted with CH_2Cl_2 (3x20 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica, EtOAc/pentane 35:65 v/v). This afforded the title compound as colorless crystals (207 mg, 719 µmol, 89% yield). Mp (uncorr.): 111-113 °C. R_f = 0.3 (silica, EtOAc/pentane 35:65 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.82 (d, *J* = 8.1, 1H), 7.36 (d, *J* = 8.0, 1H), 4.84 – 4.77 (m, 1H), 3.62 – 3.56 (m, 2H), 3.22 (dd, *J* = 6.0, 17.2, 1H), 2.97 (dd, *J* = 17.2, 2.3, 1H) (O-H proton is missing probably due to deuterium exchange). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 148.2, 143.0, 137.0, 132.3, 131.2, 102.3, 71.0, 47.5, 43.5. IR (neat) ν_{max} 3412, 2727, 1674, 1564 cm^{-1}. HRMS (ES) *m/z* $[M + Na]^+$ calcd for $C_{10}H_9INaO_2$: 310.9545. Found: 310.9531. $[\alpha]_D^{20}$ -27.2 (*c* 1, $CHCl_3$).

(*R*)-4-(1,3-Dioxolan-2-yl)-7-iodo-2,3-dihydro-1H-inden-2-ol (8a) To a solution of **8** (120 mg, 417 µmol) in toluene (0.7 mL) and $CHCl_3$ (0.3 mL) was added ethylene glycol (1.09 g, 17.50 mmol), anhydrous $MgSO_4$, and $TsOH \cdot H_2O$. The reaction vessel was fitted with a reflux condenser and the resulting suspension was stirred overnight at 90 °C. Hereafter, the suspension was filtered, neutralized with sat. aq. $NaHCO_3$, and diluted with water. The mixture was extracted with CH_2Cl_2 (3x10 mL) after which the combined organic extracts were washed with brine, dried over $MgSO_4$, and

concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica, acetone/pentane 2.5:7.5 v/v). This afforded the title compound as colorless crystals (121 mg, 364 µmol, 87% yield). Mp (uncorr.): 91-95 °C. R_f = 0.3 (silica, acetone/pentane 2.5:7.5 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1, 1H), 7.05 (d, *J* = 8.1, 1H), 5.77 (s, 1H), 4.77 - 4.63 (m, 1H), 4.18 - 3.97 (m, 4H), 3.40 (dd, *J* = 6.1, 17.1, 1H), 3.24 – 3.13 (m, 2H), 2.91 (dd, *J* = 2.8, 17.1, 1H), 1.76 (br d, *J* = 5.2, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 140.4, 136.1, 133.6, 126.5, 102.4, 95.2, 71.0, 65.3, 65.3, 47.8, 42.5. IR (neat) ν_{max} 3490, 2929, 2896, 1674, 1584 cm^{-1}. HRMS (ES) *m/z* [M + H] $^+$ calcd for $C_{12}H_{14}IO_3$: 332.9988. Found: 332. 9982. $[\alpha]_D^{20}$ -1.5 (*c* 0.8, $CHCl_3$)

(*R*)-2-(7-Iodo-2-methoxy-2,3-dihydro-1H-inden-4-yl)-1,3-dioxolane (9) To a solution of **8a** (150 mg, 0.45 mmol) in DMF (3 mL) was added NaH (36 mg, 0.9 mmol from a 60 wt% suspension in mineral oil) at 0 °C after which mixture was stirred for 20 min. Then, CH_3I (141 µL, 2.3 mmol) was added. After stirring overnight at rt the mixture was diluted with water and extracted with EtOAc (3x10 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash chromatography (silica, EtOAc/pentane 3:7 v/v). This afforded the title compound as colorless crystals (138 mg, 0.4 mmol, 88% yield). Mp (uncorr.): 87-91 °C. R_f = 0.3 (silica, EtOAc/pentane 3:7 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1, 1H), 7.03 (d, *J* = 8.1, 1H), 5.79 (s, 1H), 4.27 – 4.20 (m, 1H), 4.14 – 3.98 (m, 4H), 3.42 – 3.35 (m, 4H), 3.22 (dd, *J* = 4.0, 17.0, 1H), 3.13 (dd, *J* = 6.5, 16.9, 1H), 2.97 (dd, *J* = 4.0, 16.9, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 140.4, 136.2, 133.8, 126.4, 102.5, 95.0, 80.0, 65.4, 65.3, 56.7, 44.2, 39.2. IR (neat) ν_{max} 2974, 2910, 2889 cm^{-1}. HRMS (ES) *m/z* [M + H] $^+$ calcd for $C_{13}H_{16}IO_3$: 347.0144. Found: 347. 0143. $[\alpha]_D^{20}$ +6.2 (*c* 1, $CHCl_3$)

(*S*)-2-(7-(Dodec-1-yn-1-yl)-2-methoxy-2,3-dihydro-1H-inden-4-yl)-1,3-dioxolane (10) To a flame-dried flask was added **9** (35 mg, 104 µmol), $Pd(PPh_3)_2Cl_2$ (7.3 mg, 10 µmol), and CuI (2 mg, 10 µmol). The flask was left under vacuum for 30 minutes and evacuated three times with argon. Hereafter, THF (2 mL) was added and the resulting suspension was bubbled with argon. Subsequently, Et_3N (72 µL, 520 µmol) followed by dodecyne (0.11 mL, 0.52 mmol), both degassed with argon, was added and the reaction was left to react overnight at rt. Then, the black suspension was diluted with CH_2Cl_2 and transferred to a separation funnel and extracted with CH_2Cl_2 (3x10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness *in vacuo*. The residue was purified by flash column chromatography (silica, EtOAc/pentane 1:9 v/v). The product was isolated as a yellow oil (35 mg, 88%) R_f = 0.35 (silica, EtOAc/pentane 1:9 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.0, 1H), 7.11 (d, *J* = 8.0, 1H), 5.72 (s, 1H), 4.20 – 4.13 (m, 1H), 4.05 – 3.88 (m, 4H), 3.28 (s, 3H), 3.18 (dd, *J* = 6.7, 16.7, 1H), 3.11 (dd, *J* = 6.7, 16.9, 1H), 3.01 – 2.88 (m, 2H), 2.32 (t, *J* = 7.0, 2H), 1.54 – 1.13 (m, 16H), 0.78 (t, *J* = 6.9, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 139.8, 133.1, 130.0, 124.9, 121.9, 103.0, 94.4, 81.4, 79.1, 65.3, 65.3, 56.6, 38.4, 37.7, 31.8, 29.5, 29.4, 29.2, 29.0, 28.7, 28.7, 22.5, 19.3, 13.9. IR (neat) ν_{max} 2924, 2854 cm^{-1}. HRMS (ES) *m/z* [M + H] $^+$ calcd for $C_{25}H_{37}O_3$: 385.2742. Found: 385.2742. $[\alpha]_D^{20}$ +3.2 (*c* 1, $CHCl_3$)

(*R*)-4-(Dodec-1-yn-1-yl)-7-ethynyl-2-methoxy-2,3-dihydro-1H-indene (11) To a solution of **10** (35 mg, 91 µmol) in acetone (2 mL) was added $TsOH{\cdot}H_2O$ (19 mg, 100 µmol) after which the reaction was left to react overnight at rt. Hereafter, the mixture was transferred to a separation funnel and extracted with CH_2Cl_2 (3x10mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness. The crude aldehyde (100% conversion by ^{1}H NMR) was then dissolved in dry MeOH (3 mL). Hereafter, oven-dried K_2CO_3 (28 mg, 0.20 mmol) followed by dimethyl(1-diazo-2-oxopropyl)phosphonate (175 mg, 0.91 mmol) was added. After reacting overnight the mixture was transferred to a separation funnel and extracted with CH_2Cl_2 (3x10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The remaining residue was purified by flash column chromatography (silica, EtOAc/pentane 1:9 v/v). The product was isolated as a white film (22.1 mg, 72% over two steps) R_f = 0.3 (silica, EtOAc/pentane 1:9 v/v).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.9, 1H), 7.14 (d, *J* = 7.9, 1H), 4.30 – 4.20 (m, 1H), 3.39 (s, 3H), 3.30 – 3.18 (m, 3H), 3.13 – 3.01 (m, 2H), 2.43 (t, *J* = 7.0, 2H), 1.68 – 1.19 (m, 16H), 0.87 (t, *J* = 7.0, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 143.9, 130.6, 130.0, 121.8, 118.1, 95.8, 82.2, 81.0, 80.8, 78.9, 56.6, 39.2, 39.0, 31.8, 29.5, 29.4, 29.2, 29.0, 28.7, 28.6, 22.5, 19.4, 13.9. IR (neat) ν_{max} 3298, 2924, 2854 cm^{-1}. HRMS (ES) *m/z* [M + H] $^+$ calcd for $C_{24}H_{33}O$: 337.5231. Found: 337.5230. $[\alpha]_D^{20}$ -1.2 (*c* 1, $CHCl_3$).

2-((*S*)-7-(((*S*)-7-(Dodec-1-yn-1-yl)-2-methoxy-2,3-dihydro-1H-inden-4-yl)ethynyl)-2-methoxy-2,3-dihydro-1H-inden-4-yl)-1,3-dioxolane (12) To a suspension of $Pd(PPh_3)_2Cl_2$ (4 mg, 5 µmol) and CuI (1 mg, 4.5 µmol) in THF (1 mL) was added **9** (23 mg, 66.4 µmol) after which the mixture was degassed with argon for 30 minutes. To the mixture was added Et_3N (43 µL, 333 µmol) and **11** (22 mg 66.4 µmol) which afforded a dark suspension. After stirring overnight at

40 °C the mixture was filtered through a plug of Celite with Et_2O and concentrated *in vacuo*. The crude product was purified with flash column chromatography (silica, EtOAc/pentane 14:86 v/v). This afforded the title product as a colorless oil (32 mg, 30 µmol, 86% yield) R_f = 0.2 (silica, EtOAc/pentane 14:86 v/v).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.9, 1H), 7.31 (d, *J* = 8.0, 1H), 7.24 (d, *J* = 7.9, 1H), 7.18 (d, *J* = 7.9, 1H), 5.85 (s, 1H), 4.36 - 4.24 (m, 2H), 4.18 – 4.01 (m, 4H), 3.40 (s, 3H), 3.40 (s, 3H), 3.37 – 3.22 (m, 4H), 3.19 – 3.04 (m, 4H), 2.44 (t, *J* = 7.0, 2H), 1.68 – 1.57 (m, 2H), 1.53 – 1.40 (m, 2H), 1.39 – 1.22 (m, 12H), 0.88 (t, *J* = 6.9, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.5, 143.3, 139.8, 133.8, 129.8, 129.7, 129.6, 124.8, 121.0, 120.8, 119.1, 102.7, 95.6, 91.9, 91.5, 81.3, 80.8, 79.1, 77.4, 65.5, 65.4, 56.8, 39.5, 39.4, 38.8, 38.0, 32.1, 29.8, 29.7, 29.5, 29.3, 29.0, 28.9, 22.8, 19.8, 14.3. IR (neat) ν_{max} 2922, 2853 cm^{-1}. HRMS (ES) *m/z* [M + H]$^+$ calcd for $C_{37}H_{47}O_4$: 555.3474. Found: 555.3498. $[\alpha]_D^{20}$ +1.6 (*c* 1, $CHCl_3$)

(*S*)-4-(Dodec-1-yn-1-yl)-7-(((*R*)-7-ethynyl-2-methoxy-2,3-dihydro-1H-inden-4-yl)ethynyl)-2-methoxy-2,3-dihydro-1H-indene (13) To a solution of **12** (16 mg, 30 µmol) in acetone (0.5 mL) was added $TsOH{\cdot}H_2O$ (6 mg, 30 µmol) after which the mixture was stirred for 2 hours. The mixture was neutralized with sat. aq. $NaHCO_3$, diluted with water and extracted with CH_2Cl_2 (3x10 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude aldehyde was dissolved in CH_2Cl_2 (0.4 mL) and MeOH (0.6 mL). To the solution was added dry K_2CO_3 (8.3 mg, 60 µmol) and dimethyl(1-diazo-2-oxopropyl)phosphonate (7 mg, 36 µmol). After stirring overnight at rt the mixture was diluted with water and extracted with CH_2Cl_2 (3x10 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica, EtOAc/pentane 12:88 v/v). This afforded the title compound as a yellow oil (13 mg, 26 µmol, 87% yield) R_f = 0.2 (silica, EtOAc/pentane 12:88 v/v).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 3H),7.18 (d, *J* = 7.9, 1H), 4.34 - 4.25 (m, 2H), 3.42 – 3.38 (m, 6H), 3.35 - 3.22 (m, 5H), 3.19 - 3.05 (m, 4H), 2.44 (t, *J* = 7.1, 2H), 1.50 - 1.39 (m, 2H), 1.36 – 1.23 (m, 14H), 0.87 (t, *J* = 7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.6, 143.5, 143.3, 130.4, 129.8, 129.7, 129.6, 121.2, 120.6, 118.9, 118.7, 95.7, 92.7, 91.6, 82.1, 81.6, 80.8, 80.7, 79.1, 56.8, 39.6, 39.6, 39.4, 39.3, 32.1, 29.9, 29.8, 29.7, 29.5, 29.3, 29.0, 28.9, 22.8, 19.8, 14.3. IR (neat) ν_{max} 2922, 2853 cm^{-1}. HRMS (ES) *m/z* [M + H]$^+$ calcd for $C_{36}H_{43}O_2$: 507.3263. Found: 507.3266. $[\alpha]_D^{20}$ -0.7 (*c* 1, $CHCl_3$)

(*R*)-Methyl 7-iodo-2-methoxy-2,3-dihydro-1H-indene-4-carboxylate (14) To a solution of **9** (33 mg, 95 µmol) in acetone (0.8 mL) was added $TsOH{\cdot}H_2O$ (18 mg, 95 µmol) and the mixture was stirred for 3 h after which TLC analysis indicated total conversion. The mixture was neutralized with sat. aq. $NaHCO_3$, diluted with water, and extracted with CH_2Cl_2 (3x10 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude aldehyde was dissolved in CH_2Cl_2 (0.7 mL) and MeOH (0.8 mL). To the solution were added KCN (30 mg, 0.46 mmol) and AcOH (16 µL, 0.3 mmol). The homogeneous mixture was added precipitated, activated MnO_2 (161 mg, 1.85 mmol). After being stirred vigorously overnight at 40 °C the dark suspension was filtered through Celite with CH_2Cl_2 and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica, EtOAc/pentane 15:85 v/v). This afforded the title compound as a colorless wax (19 mg, 59 µmol, 62% yield) R_f = 0.3 (silica, EtOAc/pentane 15:85 v/v). ^{1}H NMR (400 MHz, CDCl3) δ 7.65 (d, *J* = 8.3, 1H), 7.53 (d, *J* = 8.3, 1H), 4.26 – 4.18 (m, 1H), 3.88 (s, 3H), 3.58 (d, *J* = 4.7, 2H), 3.38 (s, 3H), 3.14 (dd, *J* = 6.3, 17.1, 1H), 3.02 (dd, *J* = 3.1, 17.1, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 147.5, 144.0, 136.4, 129.9, 126.7, 100.2, 79.5, 56.6, 52.1, 44.6, 42.1. IR (neat) ν_{max} 2947, 2923, 1720, 1572 cm^{-1}. HRMS (ES) *m/z* [M + Na]$^+$ calcd for $C_{12}H_{13}INaO_3$: 354.9807. Found: 354.9802. $[\alpha]_D^{20}$ +4.5 (*c* 1, $CHCl_3$)

(*S*)-Methyl 7-(((*S*)-7-(((*S*)-7-(dodec-1-yn-1-yl)-2-methoxy-2,3-dihydro-1H-inden-4-yl)ethynyl)-2-methoxy-2,3-dihydro-1H-inden-4-yl)ethynyl)-2-methoxy-2,3-dihydro-1H-indene-4-carboxylate (14a) To a suspension of $Pd(PPh_3)_2Cl_2$ (1.5 mg, 2 µmol) and CuI (0.4 mg, 2 µmol) in THF (1 mL) was added **14** (7 mg, 21 µmol) and the mixture was degassed with argon for 30 min. To the mixture was added Et_3N (19 µL, 130 µmol) and **13** (10 mg, 20 µmol) which afforded a dark suspension. After stirring overnight at rt the mixture was filtered through a plug of Celite with Et_2O and concentrated *in vacuo*. The crude product was purified by flash chromatography (silica, EtOAc/pentane 2:8 v/v). This furnished the product as a red gum (11 mg, 15 µmol, 78% yield) R_f = 0.2 (silica, EtOAc/pentane 2:8 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1, 1H), 7.39 (d, *J* = 8.1, 1H), 7.36 - 7.31 (m, 2H), 7.29 - 7.23 (m, 1H), 7.19 (d, *J* = 7.9, 1H), 4.38 - 4.25 (m, 3H), 3.91 (s, 3H), 3.50 (dd, *J* = 4.8, 7.7, 1H), 3.46 - 3.05 (m, 20H), 2.45 (t, *J* = 7.0, 2H), 1.67 – 1.58 (m, 2H), 1.52 – 1.41 (m, 2H), 1.38 – 1.28 (m, 12H), 0.89 (t, *J* = 6.8, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 145.2, 143.8, 143.8, 143.6, 143.5, 143.4, 129.9, 129.8, 129.8, 129.7, 129.6, 128.7, 126.5, 124.3, 121.2, 120.5, 119.5, 118.9, 95.8, 93.6, 92.9, 92.0, 91.8, 80.8, 80.8, 80.7, 79.1, 77.4, 56.8, 56.7, 56.6,

52.1, 40.9, 39.6, 39.5, 39.4, 39.1, 32.1, 29.8, 29.7, 29.5, 29.3, 29.1, 29.0, 22.8, 19.8, 14.3. IR (neat) ν_{max} 2925, 2854, 1719 cm^{-1}. HRMS (ES) *m/z* [M + H] $^{+}$ calcd for $C_{48}H_{55}O_5$: 711.4049. Found: 711.4047. $[\alpha]_D^{20}$ +5.6 (*c* 0.7, $CHCl_3$)

(*S*)-7-(((*S*)-7-(((*S*)-7-(Dodec-1-yn-1-yl)-2-methoxy-2,3-dihydro-1*H*-inden-4-yl)ethynyl)-2-methoxy-2,3-dihydro-1*H*-inden-4-yl)ethynyl)-2-methoxy-2,3-dihydro-1*H*-indene-4-carboxylic acid (3) To a solution of **14a** (7 mg, 11.25 µmol) in water (0.4 mL) and THF (0.4 mL) was added LiOH (11 mg, 0.45 mmol) after which the mixture was stirred overnight at 90 °C in a sealed tube. Then, the mixture was added conc. hydrochloric acid where after a yellow precipitate formed. The suspension was filtered and the remaining solid washed thoroughly with water and CH_2Cl_2. This afforded the title compound as a yellow solid (7 mg, 10 µmol, 90%). Mp (uncorr.): 232 °C (decomp.). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.01 (br. s, 1H), 7.79 (d, *J* = 8.1, 1H), 7.51 – 7.40 (m, 3H), 7.34 (d, *J* = 7.9, 1H), 7.22 (d, *J* = 7.9, 1H), 4.38 – 4.30 (m, 1H), 4.30 – 4.24 (m, 2H), 3.48 – 3.37 (m, 2H), 3.29 – 3.00 (m, 15H), 3.00 – 2.91 (m, 1H), 1.63 – 1.39 (m, 4H), 1.39 – 1.13 (m, 14H), 0.85 (t, *J* = 6.5, 3H) (3 protons from a methoxy group is missing. These are suspected to be under the signal from water). ^{13}C NMR (150 MHz, DMSO-d_6) δ 155.1, 155.0, 154.9, 144.2, 144.0, 143.8, 143.8, 129.8, 129.7, 129.5, 129.1, 128.5, 121.1, 120.9, 120.7, 119.4, 118.1, 116.6, 96.2, 92.6, 91.8, 80.2, 79.9, 79.0, 55.9, 55.9, 55.8, 41.7, 41.6, 41.5, 41.3, 38.6, 31.4, 29.1, 29.0, 28.8, 28.6, 28.3, 28.2, 22.2, 18.9, 14.1. (see supplementary information for note on missing carbons). IR (neat) ν_{max} 3375 (br), 2926, 2192, 1679, 1595, 1417 cm^{-1}. HRMS (ES) *m/z* [M - H] $^{-}$ calcd for $C_{47}H_{51}O_5$: 695.3737. Found: 695.3739. Specific optical rotation were not obtained due to low solubility.

Supporting information

^{1}H NMR, ^{13}C NMR, MS, IR spectra for compounds **3**-**14a**,

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