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Supporting information

Opposite enantioselectivities displayed by supramolecular helical catalysts with non-enantiomeric "sergeants"

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Supplementary Chart S1, Tables S1-S2, and Figures S1-S4

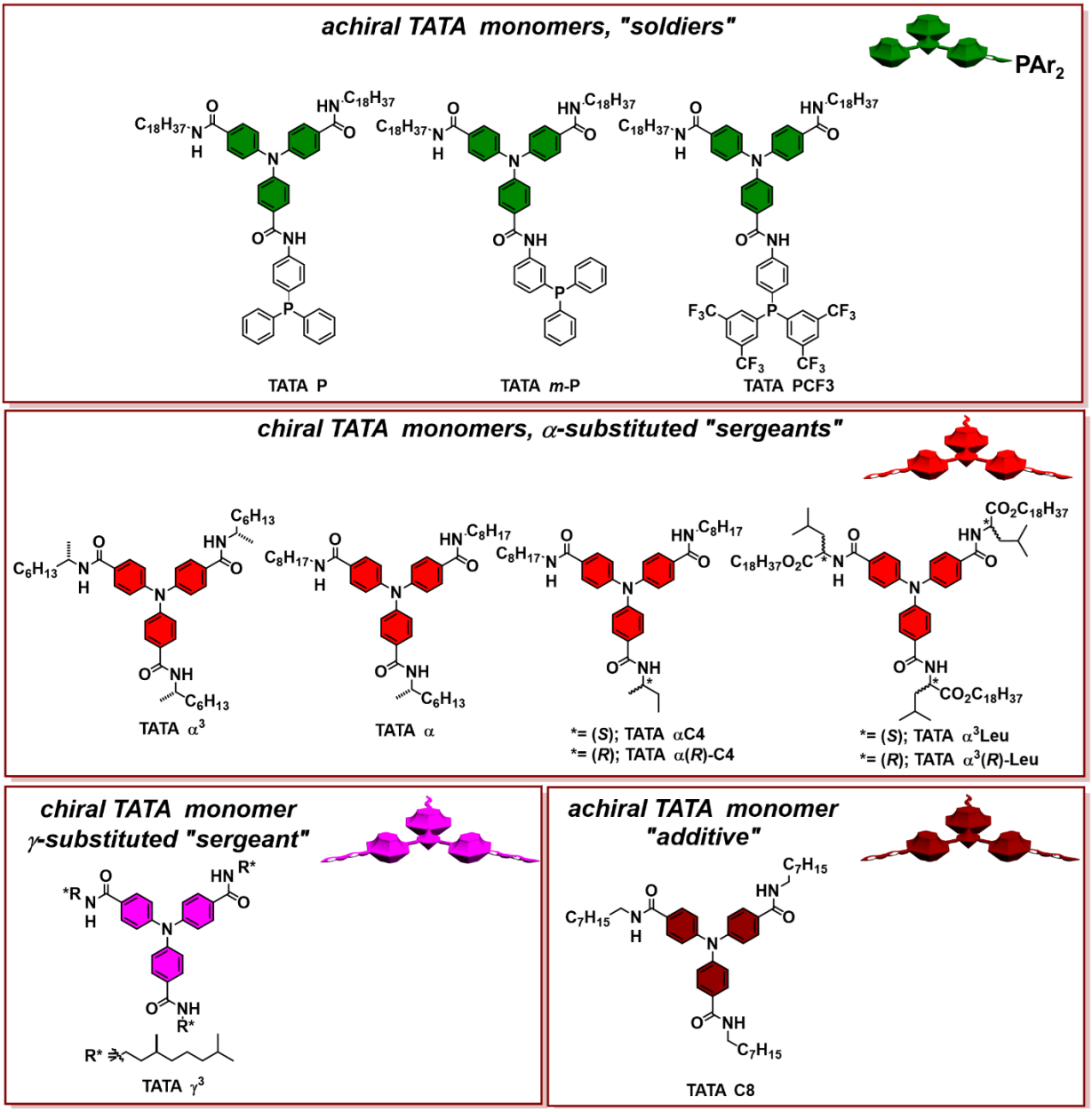


Chart S1. Chemical structures of TATA monomers used in this study.

TATA	MCH	Dec	Tol	DCM	$CHCl_3$	Et_2O	THF	Acet.	EtOAc	CH_3CN	EtOH	MeOH	DMF	DMSO
TATA P	S	S	S	S	S	I	S	I	S	P	S	I	S	I
TATA *m*-P	S	S	S	S	S	I	S	I	S	P	S	I	S	I
TATA PCF3	S	S	S	S	S	I	S	I	S	P	S	I	S	I
TATA α^3	I	I	I	S	S	I	S	I	PS	I	S	S	S	S
TATA α	P	P	G	S	S	P	S	S	PS	I	S	S	S	S
TATA αC4	P	P	G	S	S	P	S	S	S	I	S	S	S	S
TATA α^3 Leu	S	S	S	S	S	S	S	S	S	S	P	I	S	I
TATA γ^3	G	G	S	S	S	P	S	S	S	I	P	S	S	S
TATA C8	P	P	G	S	S	I	S	S	S	P	S	S	S	S

Table S1. Solubility tests for all TATA monomers reported in this manuscript (1 mM, 293 K). MCH= methylcyclohexane. Dec= decalin. Acet= acetone. Tol= toluene. The mixtures are heated up to the boiling point of the solvent and cooled down to 293 K; those which did not dissolve (after several heating cycles) are denoted as insoluble (I), those which precipitated as P, those which remained soluble or partly soluble as S and PS, respectively, and those which yielded a gel as G.

Above: pictures of the gel and the solution formed by **TATA αC4** and **TATA γ^3**, respectively, in toluene (2.9 mM). The gel of **TATA αC4** remains stable for several weeks while the solution of **TATA γ^3** yields a precipitate upon standing for a few days.

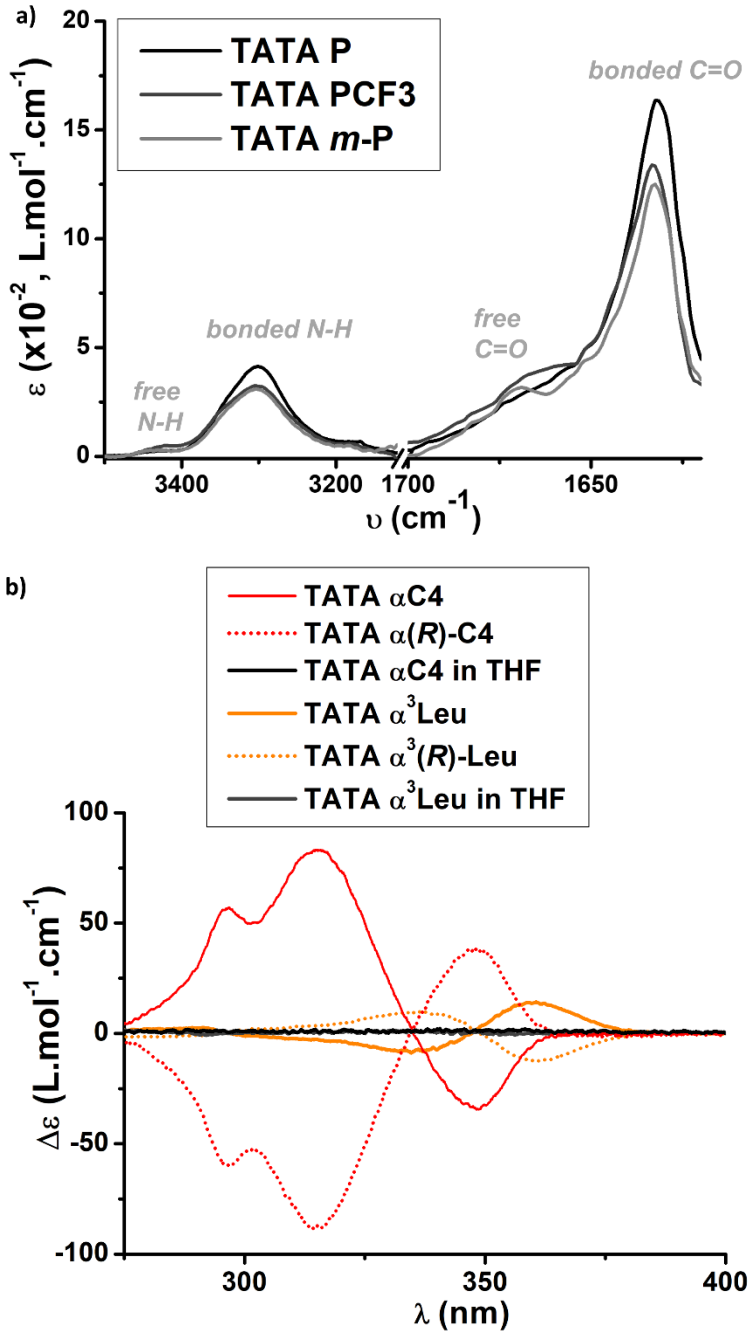


Figure S1. Characterization of the homoassemblies in toluene. a) FT-IR analyses of the TATA "soldiers" in toluene (2.9 mM) at 293 K. Zoom on the amide N─H and C=O bands. b) CD analyses of the "sergeant" enantiomers for **TATA αC4** (2.9 mM) and **TATA α^{3}Leu** (5.8 mM) in toluene and of **TATA αC4** and **TATA α^{3}Leu** in THF at 293 K.

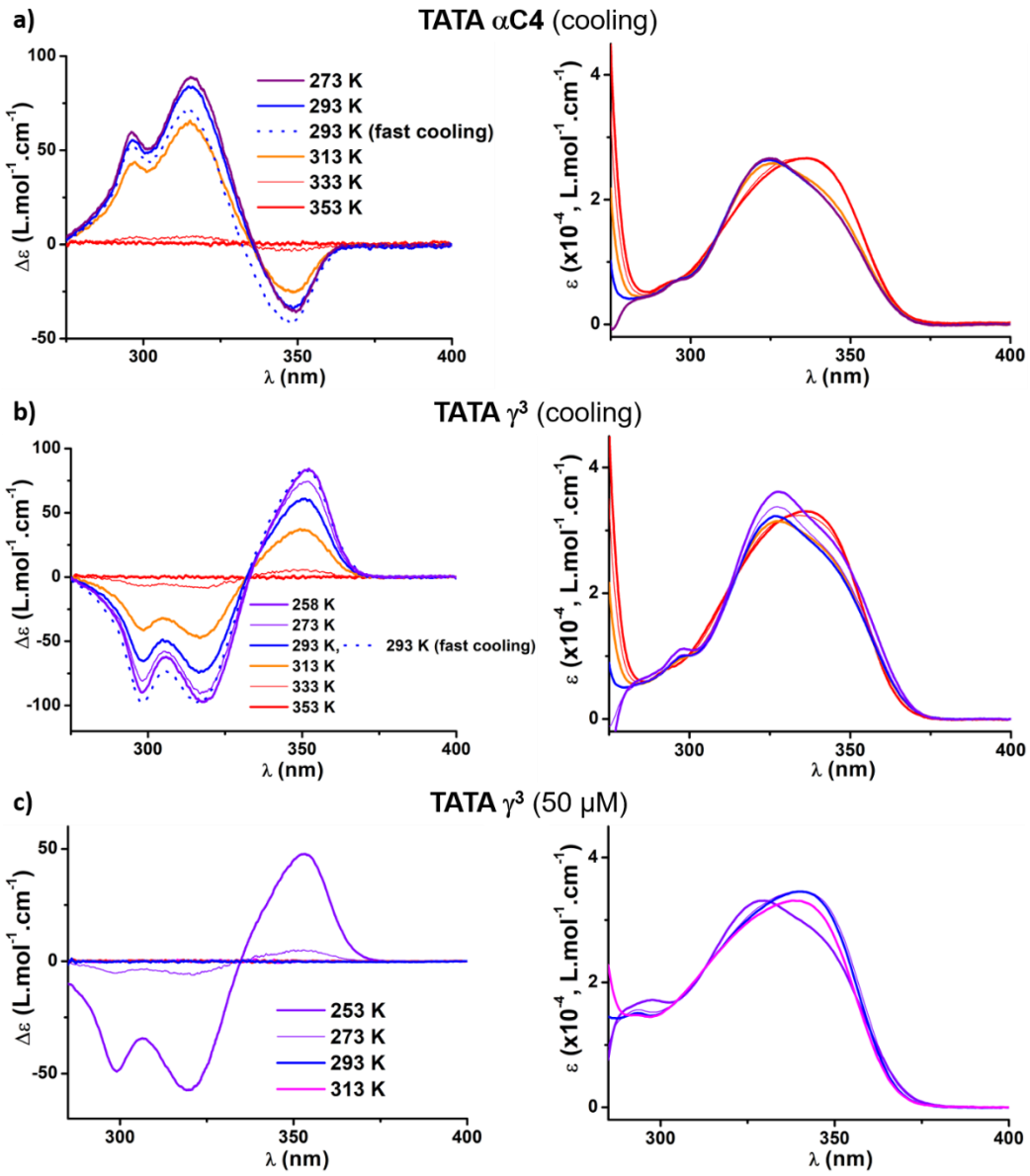
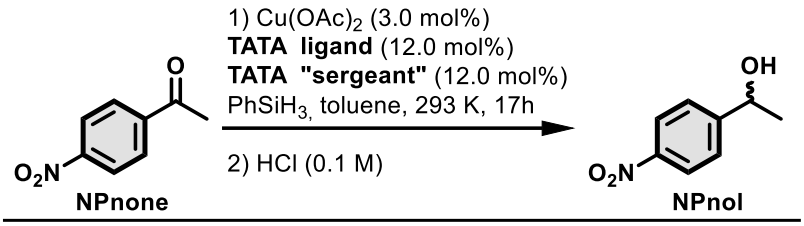


Figure S2. Stability of the helical stacks of TATA αC4 and TATA γ^3 in toluene. a) Variable-temperature CD (left) and UV-Vis (right) analyses of a solution of **TATA αC4** in toluene (2.9 mM, from 353 K to 273 K, 1 K/min except for "fast cooling": 10 K/min). b) Variable-temperature CD (left) and UV-Vis (right) analyses of a solution of **TATA γ^3** in toluene (2.9 mM, from 353 K to 258 K, 1 K/min except for "fast cooling": 10 K/min). c) Variable-temperature CD (top) and UV-Vis (below) analyses of a solution of **TATA γ^3** in toluene (50 µM, from 313 K to 253 K, 1 K/min).

I*nterpretation of Figure S2*: The helical stacks of both **TATA αC4** and **TATA γ^3** are (almost) fully disassembled at 333 K indicating that both assemblies have similar thermodynamic stabilities. Likewise, no inversion of their handedness is observed upon different cooling rates or under more diluted conditions; thus, indicating that supramolecular helices with their preferred handedness, left-handed and right-handed for **TATA αC4** and **TATA γ^3** respectively,[1] are formed under thermodynamic control in toluene.



entry	TATA ligand	TATA « sergeant »	α/γ	conversion	ee±2 (%)
1	**TATA P**	**TATA α³Leu**	α	99%	-1
2[(a)]	**TATA P**	**TATA α³Leu**	α	99%	-1
3	**TATA P**	**TATA αC4**	α	97%	-9
4[(b)]	**TATA P**	**TATA αC4**	α	99%	0
5	**TATA P**	**TATA α**	α	98%	-7
6	**TATA P**	**TATA α³**	α	99%	-7
7	**TATA P**	**TATA γ³**	γ	99%	+1
8	**TATA *m*-P**	**TATA αC4**	α	99%	-1

Table S2. Copper-catalyzed hydrosilylation of 4-nitroacetophenone by means of "sergeants-and-soldiers"-type mixtures composed of **TATA P** or **TATA *m*-P** as TATA ligand and one chiral TATA monomer. For the results obtained with **TATA PCF3** as TATA ligand, see Table 1. Conditions (except otherwise stated): TATA ligand (5.8 mM), TATA "sergeant" (5.8 mM), toluene, 293 K. Ee are indicated as positive and negative when **(*S*)-NPnol** (2nd GC peak) and **(*R*)-NPnol** (1st GC peak) are the major enantiomers, respectively. (a) Reaction conducted with 23.2 mM of **TATA P** and 23.2 mM of **TATA α³Leu**. (b) Reaction conducted in THF instead of toluene.

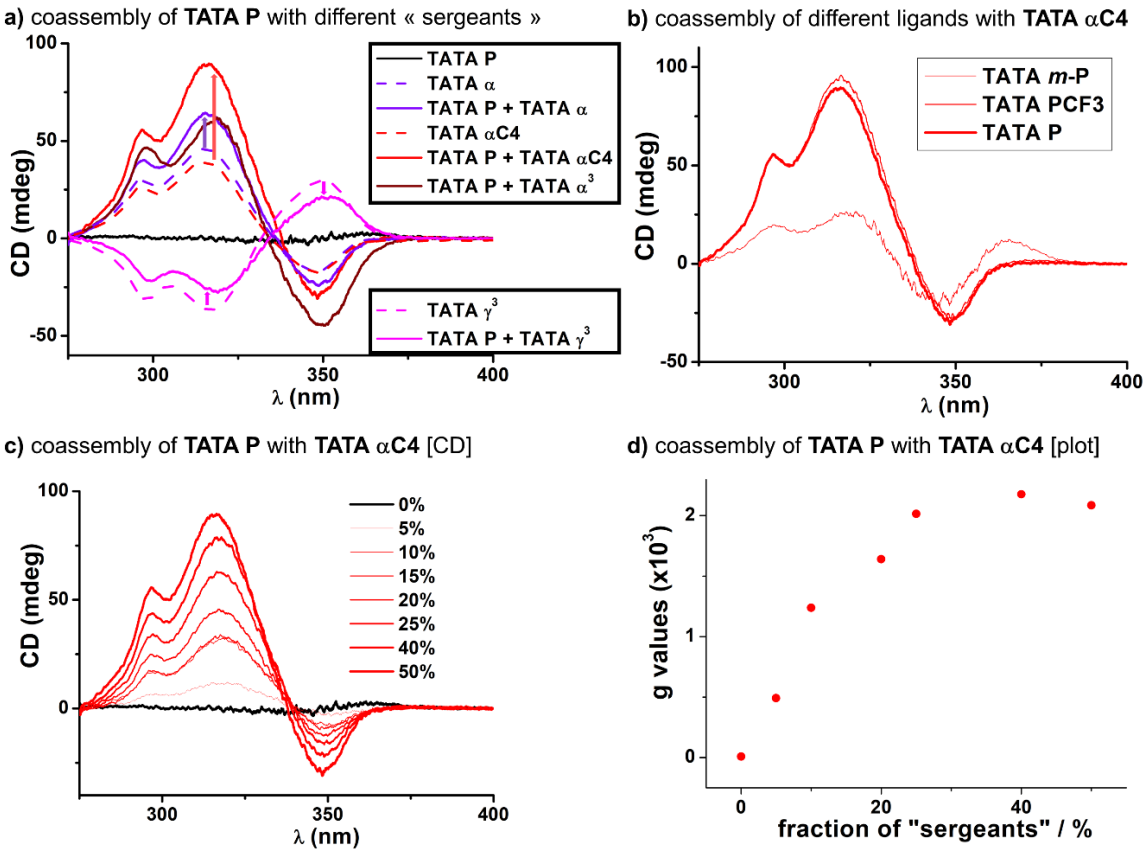


Figure S3. Characterization of the coassemblies in toluene at 293 K. a) CD analyses of the coassemblies formed by mixing **TATA P** (2.9 mM, coordinated to $Cu(OAc)_2$, **TATA P**/$Cu(OAc)_2$= 4) and the different "sergeants" (2.9 mM) in toluene. Comparison with the CD spectra of the "sergeants" alone (2.9 mM). b) CD analyses of the coassemblies formed by mixing the different TATA ligands (2.9 mM, coordinated to $Cu(OAc)_2$, **TATA P**/$Cu(OAc)_2$= 4) and **TATA αC4** (2.9 mM) in toluene. c) CD analyses of the coassemblies formed by mixing **TATA P** (2.9 mM, coordinated to $Cu(OAc)_2$, **TATA P**/$Cu(OAc)_2$= 4) and different amount of **TATA αC4** in toluene. The indicated values correspond to the fraction of **TATA αC4** in the mixtures (fs= **[TATA αC4]/([TATA P] + [TATA αC4]**)). d) Plot of the Kuhn anisotropy factor (g) as a function of the fraction **TATA αC4** for the coassemblies between **TATA P** and **TATA αC4**. The Kuhn anisotropy factor is determined as $g=\theta^{317}/(32982\times Abs^{317})$ where θ^{317} and Abs^{317} are the ellipticity and UV/Vis absorbance measured at λ=317 nm, respectively. For additional characterization of the coassemblies with **TATA PCF3** as ligand see Figures 2-3 and S4.

I*nterpretation*: The higher intensity of CD signals observed for TATA mixtures relatively to the "sergeant" alone (see the corresponding arrows in in Figure S3a) suggests that coassembly occurs between **TATA P** and α-substituted TATA "sergeants" (**TATA α**, **TATA αC4** and **TATA α^3**) through the sergeants-and-soldiers (S&S) effect. This is further evidenced with the S&S experiment performed in Figure S3cd for which 25% of **TATA αC4** is enough to afford homochiral copolymers. **TATA αC4** also forms stable ordered coassembles with **TATA PCF3** but not with **TATA *m*-P** (Figure S3b) probably because of unfavorable geometry of the TATA ligand. Likewise, the CD intensity of the mixture between **TATA P** and **TATA γ^3** is lower than that of **TATA γ^3** alone (see the magenta arrows in Figure S3a) indicating that stable ordered coassembly does not form with this "sergeant" under these conditions.

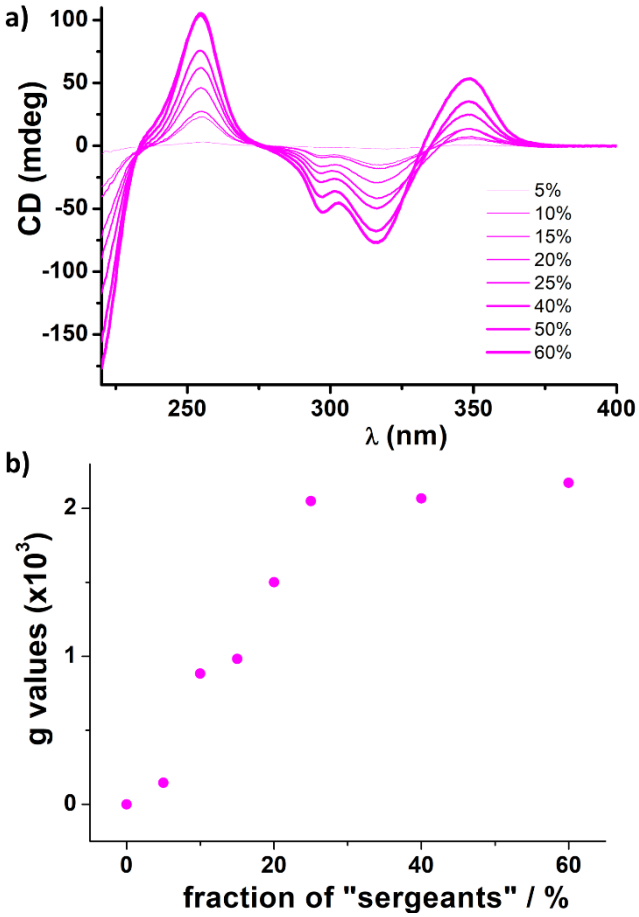


Figure S4. Characterization of the coassemblies between TATA PCF3 and **TATA γ^3** in **MCH at 293 K.** a) CD analyses of the coassemblies formed by mixing **TATA PCF3** (2.9 mM) and different amount of **TATA γ^3** in MCH. b) Plot of the Kuhn anisotropy factor (g at 317 nm) as a function of the fraction **TATA γ^3** for the coassemblies between **TATA PCF3** and **TATA γ^3**.

I*nterpretation*: The nonlinear evolution of the g values as a function of the fraction of "sergeants" in the mixture confirms that **TATA PCF3** and **TATA γ^3** coassembles together in MCH. The plateau of g values reached for 25% of **TATA γ^3** in the mixture is consistent with the trend observed between **TATA P** and **TATA αC4** in toluene, i.e. the extent of the S&S effect is similar for both coassemblies (Figure S3d). Based on these data, it can be anticipated that engaging a fraction of "sergeant" inferior to 25% in the catalytic system would lead to a decrease of enantioselectivity (i.e. below 13% ee for this couple in MCH, see Table 1).

General methods

Synthetic procedures: TATA γ^3 was obtained similarly to the protocol reported in the literature[2] reacting of 4,4',4''-tris-[*p*-carboxylic acid]-triarylamine[3] with oxalyl chloride followed by reaction of the in situ generated tris-acyl chloride with (*S*)-3,7-dimethyloctan-1-amine.[4] The preparation of **TATA P**, **TATA PCF3**, **TATA αC4**, **TATA α(*R*)-C4** and **TATA C8** was reported previously[5] whilst that of the new TATA monomers **TATA α**, **TATA α^3**, **TATA α^3Leu**, **TATA α^3(*R*)-Leu** and **TATA *m*-P** is reported below. Triethylamine, 4-nitroacetophenone, $Cu(OAc)_2$, DMAP, oxalyl chloride, (*R*)/(*S*)-Leucine, octadecan-1-ol, and methylcyclohexane (MCH) were acquired from Sigma Aldrich. EDC•HCl was purchased from ABCR. Phenylsilane was ordered from Apollo Scientific. (*S*)-2-aminooctane was ordered from Alfa Aesar. *Para*-toluene sulfonic acid monohydrate (PTSA•H_2O), was ordered from TCI chemicals. All commercial compounds were used as received except otherwise stated. Dry THF, dry DCM, and dry toluene were obtained from an SPS solvent purification system (IT-Inc). Triethylamine was dried by distillation over CaH_2 and stored in the dark. All inert atmosphere reactions were carried out under an argon atmosphere with standard Schlenk-line techniques. Purification by "flash" chromatography was performed by adsorbing the samples on silica; the adsorbed samples were introduced in the solid loader and purified by means of Reveleris X2 purification system (Buchi®) using pre-packed silica cartridges Ecoflex® (irregular 50 µm silica). NMR spectra were recorded on a Bruker Avance 300 or on a Bruker Avance 400 spectrometer and calibrated to the residual solvent peak: $CDCl_3$ (^{1}H: 7.26 ppm; ^{13}C: 77.16 ppm), DMSO-d_6 (^{1}H: 2.50 ppm) and THF-d_8 (^{1}H: 3.58 ppm; ^{13}C: 67.57 ppm). Peaks are reported with their corresponding multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, qnt: quintet, septet, dt: doublet of triplets), and integration, and respective *J* coupling constants are given in Hertz. Exact mass measurements (HRMS) were obtained on TQ R30-10 HRMS spectrometer by ESI^+ or APCI ionization, and are reported in m/z for the major signal. Solid-state FT-IR analyses were performed by drop casting a solution of the compounds onto KBr cells and by analyzing the resulting films by transmission.

Circular Dichroism (CD) analyses: Circular dichroism (CD) measurements were performed on a Jasco J-1500 spectrometer equipped with a Peltier thermostated cell holder and a Xe arc lamp. CD analyses at room temperature (Figures 1b, 1c, 2, 3, S1b, S3 and S4): Analyses were performed at 293 K with the following parameters: 50 $nm.min^{-1}$ sweep rate, 0.05 nm data pitch, 2.0 nm bandwidth, and between 400 and 275 nm (toluene) or between 400 and 225 nm (MCH). The solutions were placed into a cylindrical spectrosil quartz cell of 0.05 mm (for 2.9 mM solution) or 10 mm (for 50 µM solution) pathlength (Starna® 31/Q/0.05). Solvent (toluene or MCH) and cell contributions at the same temperature were subtracted from the obtained signals. Variable-temperature CD analyses (Figure S2): "*Slow" cooling*: solutions were heated to 353 K and cooled to 273 K, 253 K or 258 K at a rate of 1 K/min and full CD spectra were recorded every 10 K. "*Fast" cooling*: solutions were heated to 353 K and cooled to 293 K at a rate of 10 K/min and full CD spectrum were recorded at 293 K only. All solutions were pre-heated before measurements. For all samples, the LD contribution was negligible ($\Delta LD < 0.005$ dOD) and the shape of the CD

signal was independent of the orientation of the quartz cells. For homoassemblies, the CD intensity is reported as the molar extinction coefficient, calculated as $\Delta\varepsilon = \theta/(32982 \times [TATA] \times l)$, with θ= ellipticity (in mdeg), [TATA]= concentration in TATA monomer (in $mol.L^{-1}$), and l= cell pathlength (in cm).

UV-Vis analyses: UV-Vis absorption spectra were extracted from CD on each of the above samples and obtained after correction of the absorption of air, solvent, and cell.

Fourier-Transform Infrared (FT-IR) analyses: FT-IR measurements were performed on a Nicolet iS10 spectrometer. Spectra of solutions in toluene were measured in a 0.05 cm or 0.1 cm pathlength CaF_2 cell at room temperature and were corrected for air, solvent and cell absorption. Spectra were normalized according to the extinction coefficient ε, with $\varepsilon = Abs/([TATA] \times l)$ with [TATA]= concentration in TATA monomer (in $mol.L^{-1}$), and l= cell pathlength (in cm).

Chiral HPLC analyses: The optical purity of **TATA α^3Leu** and **TATA α^3(*R*)-Leu** was determined by analytical HPLC (Chiralpak IE, heptane/ethanol (80/20) as mobile phase, 1 mL/min). See Figure S5.

Preparation of the solutions for FT-IR and CD analyses and catalytic experiments: see below

Solutions for FT-IR and CD analyses

All solutions were briefly heated after stirring to ensure homogenization and all solutions were gently heated prior to analyses.

Procedure for homoassemblies (Figures 1, S1-S2): The solid corresponding to the desired TATA monomer was dissolved in toluene or MCH and the solution was stirred for 30 minutes at 293 K.

Procedure for TATA coassemblies (Figure 2): The solids corresponding to the desired TATA ligand (2.9 μmol) and TATA "sergeant" (2.9 μmol) were dissolved in toluene or MCH **(**1.0 mL) and the solution was stirred for 30 minutes at 293 K.

Procedure for TATA coassemblies embedding a TATA ligand coordinated to copper (Figure S3) and "sergeants-and-soldiers"-type experiments (Figure S3): A given amount of a stock solution prepared by mixing a TATA ligand (either **TATA P, TATA *m*-P** or **TATA PCF3)** and $Cu(OAc)_2$ in a 1:4 ratio was divided in order to get $Cu(OAc)_2$ (0.13 mg, 0.725 μmol) and TATA ligand (2.9 μmol) in dry THF (500 μL) in each vial. The mixture was stirred for 30 minutes, then the solvent was removed and the tubes were kept under vacuum (10^{-3} mbar) for 1 hour. The solid corresponding to the desired amount of TATA "sergeant" was then added to the vial as well as toluene (1.0 mL) and the solution was stirred for 30 minutes at 293 K.

Procedure for TATA coassemblies embedding TATA C8 (Figure 2): The solids corresponding to **TATA PCF3** (2.0 mg, 1.45 μmol), **TATA C8** (1.0 mg, 1.45 μmol) and **TATA αC4** or **TATA γ^3** (2.9 μmol) were dissolved in toluene or MCH (1.0 mL) and the solution was stirred for 30 minutes at 293 K.

Procedure for TATA coassemblies and "sergeants-and-soldiers"-type experiments with TATA γ^3 (Figure S4): The solids corresponding to **TATA PCF3** (4.1 mg, 2.9 μmol) and the desired amount of **TATA γ^3** (took up from a 2.9 mM solution of in MCH**)** were mixed and the total volume of MCH was set to 1.0 mL. The solution was stirred for 30 minutes at 293 K.

Catalytic experiments

General procedure: Catalytic experiments with TATA mixtures were performed similarly to our previous studies with BTA mixtures.[6] A pre-catalytic mixture composed of the ligand and the copper salt was prepared as follows: oven-dried test tubes were loaded with a stock solution prepared by mixing one of the TATA ligand and $Cu(OAc)_2$, divided in order to get the desired amount of TATA ligand (3.48 μmol, 12.0 mol%) and $Cu(OAc)_2$ (0.16 mg, 0.87 μmol, 1.5 mol%) in dry THF (500 μL) in each tube. The solvent was removed under vacuum and the tubes were kept under vacuum (10^{-3} mbar) for 1 hour. Solids corresponding to the desired amount of the TATA "sergeant" (3.48 μmol, 12.0 mol%, fs = 50%) and 4-nitroacetophenone (4.8 mg, 29.0 μmol, 100 mol%) were added to the tubes as well as the solvent (toluene or MCH, 600 μL) and the solutions were mixed for 30 minutes. The mixtures were then briefly heated to the solvent boiling point. After cooling to room temperature, the stirring bar was introduced and the mixtures were stirred for 15 minutes. Phenylsilane (8 μL, 58 μmol, 200 mol%) was then added and the reaction mixtures were stirred vigorously for 17 h at 293 K. Please note that in the case of **TATA α^3Leu**, the quantities of **TATA P**, $Cu(OAc)_2$ and **TATA α^3Leu** were increased four times in order to get a concentration of **TATA P** of 23.2 mM in toluene (instead of 5.8 mM for conventional catalytic experiments). Typical work-up: Aqueous solution of HCl (10 wt%, 1000 μL) was added and the mixtures were stirred for 30 min (until the solution became transparent). Then, the products were extracted with diethyl ether (500 μL) and ethyl acetate (500 μL) and the organic phase was passed through a small silica plug. The solid was washed with ethyl acetate. The solvents were evaporated and the crude material was analyzed by NMR and by chiral GC. Conversion and enantiomeric excess (*ee*) were determined by chiral GC analysis. *Ee* values are indicated as positive and negative when (*S*)-4-nitroacetophenol and (*R*)-4-nitroacetophenol are the major enantiomers, respectively. Chiral GC analyses:[7] The optical purity was determined by GC analysis: Chiral Cyclosil-B column, 30 m × 250 μm x 0.25 μm, inlet pressure= 12.6 psi. Injection temperature= 250°C; detector temperature= 300°C; column temperature= 135°C. Retention times: 18 min (4-nitroacetophenone), 49 min ((*R*)-4-nitroacetophenol), 51 min ((*S*)-4-nitroacetophenol). Variation in the retention times were noted which were due to the alteration of the chiral stationary column over the years (Figures S8-S9, S11). Better GC separation was obtained with a new stationary column (Figures S7, S10).

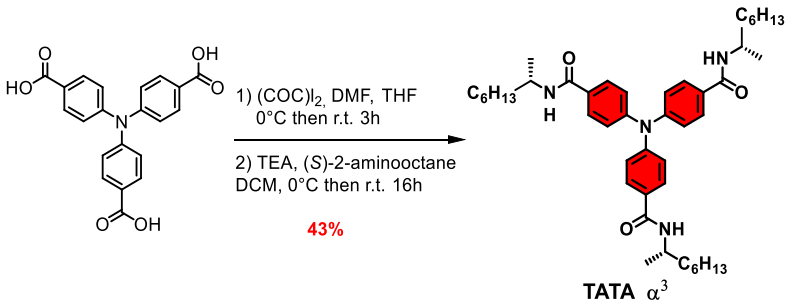
Catalytic tests with the additive TATA C8: Oven-dried test tubes were loaded with a stock solution prepared by mixing **TATA PCF3** and $Cu(OAc)_2$, divided in order to get the desired amount of **TATA PCF3** (2.5 mg, 1.74 μmol, 6.0 mol%) and $Cu(OAc)_2$ (0.08 mg, 0.44 μmol, 1.5 mol%) in dry THF (500 μL) in each tube. The solvent was removed under vacuum and the tubes were kept under vacuum (10^{-3} mbar) for 1 hour. Solids corresponding either to **TATA αC4** or **TATA γ^3** (3.5 μmol, 12.0 mol%, fs = 50%), **TATA C8** (1.2 mg, 1.74 μmol, 6.0 mol%), and 4-nitroacetophenone (2.9 mg, 14.5 μmol, 100 mol%) were added to the tubes as well as toluene (600 μL) and the solutions were mixed for 30 minutes. The mixtures were then briefly heated to the solvent boiling point. After cooling to room temperature, the stirring bar was introduced and the mixtures were stirred for 15 minutes. Phenylsilane (4 μL, 29 μmol, 200 mol%) was then added

and the reaction mixtures were stirred vigorously for 17 h at room temperature. Work-up was performed as above.

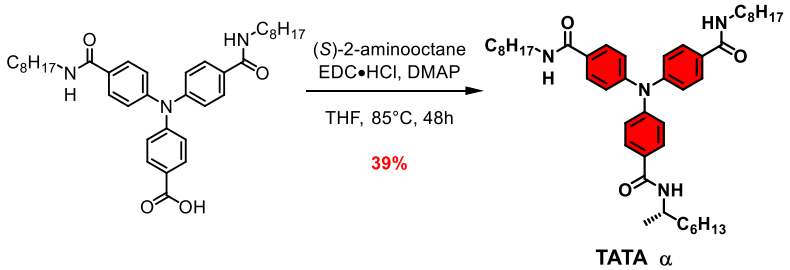
Representative chiral GC analyses are given in Figures S6-S12.

Synthetic procedures

Synthesis of the "sergeants"



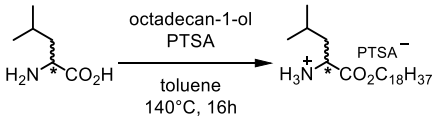
TATA α³: In an oven-dried Schlenk flask under argon atmosphere, 4,4',4''-tris-[*p*-carboxylic acid]-triarylamine[3] (0.55 g, 1.33 mmol, 1.0 equiv.) was dissolved in THF (22 mL). A few droplets of DMF was added and the mixture was cooled to 0°C with an ice-bath. Oxalyl chloride (0.41 mL, 4.77 mmol, 3.6 equiv.) was added dropwise and the stirred mixture was allowed to reach room temperature. After 3 h, the solvent and the excess of oxalyl chloride were evaporated. The acyl chloride intermediate was dissolved in DCM (44 mL), cooled to 0°C with an ice-bath, and (*S*)-2-aminooctane (0.74 mL, 4.37 mmol, 3.3 equiv.) was added. Triethylamine (1.30 mL, 9.28 mmol, 7 equiv.) was added dropwise. The reaction mixture was allowed to reach room temperature and stirred for additional 16 h. 20 mL of brine was added and the reaction mixture was extracted with DCM (3 x 40 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, then filtered through a plug of silica and evaporated. The crude material was purified by "flash" column chromatography (SiO_2, DCM/EtOAc, 80/20) yielding **TATA α³** (0.40 g, 43%) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 7.66 (apparent d, *J*= 8.7 Hz, 6H, CH_{arom}), 7.06 (apparent d, *J*= 8.7 Hz, 6H, CH_{arom}), 5.94 (d, *J*= 8.5 Hz, 3H, NH), 4.17 (septet, *J*= 6.8 Hz, 3H, NHC*H*), 1.60-1.46 (m, 6H, NHCHCH_2), 1.44-1.25 (m, 24H, CH_2), 1.22 (d, *J*= 6.5 Hz, 9H, CHCH_3), 0.87 (t, *J*= 6.8 Hz, 9H, CH_2CH_3) ; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm)= 166.16, 149.33, 130.22, 128.50, 123.96, 45.95, 37.23, 31.91, 29.34, 26.24, 22.74, 21.22, 14.21 ; HMRS (ESI): *m/z* calculated for $C_{45}H_{66}N_4O_3H$ $[M+H]^+$: 711.5208, found: 711.5210 (0.3 ppm) ; FT-IR: υ (cm^{-1})= 3293, 3043, 2956, 2926, 2855, 1629, 1601, 1537, 1499, 1453, 1377, 1352, 1315, 1280, 1181.



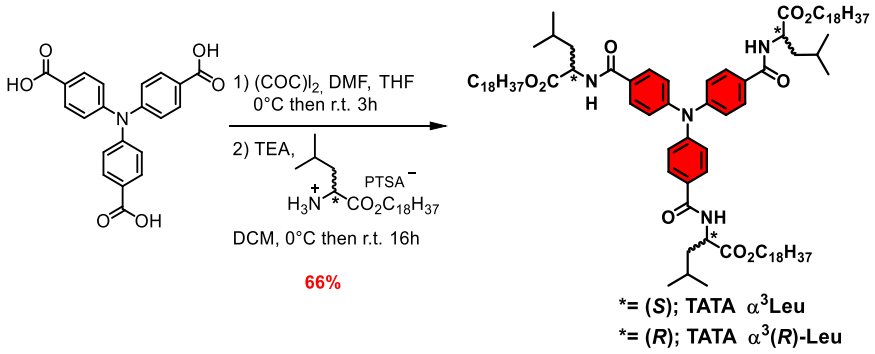
TATA α: In an oven-dried 100 mL Schlenk flask under argon atmosphere, 4,4'-bis-[*p*-octylamide]-4''-[*p*-carboxylic acid]-triarylamine[5] (500 mg, 0.83 mmol, 1.0 equiv.), EDC•HCl

(271 mg, 1.42 mmol, 1.7 equiv.) and DMAP (173 mg, 1.42 mmol, 1.7 equiv.) were solubilized in THF (20 mL). Then *(S)*-2-aminooctane (91 µL, 1.25 mmol, 1.5 equiv.) was added and the reaction mixture was stirred to 85 °C for 48 hours. The reaction mixture was cooled down to room temperature and the solvent was removed under vacuum. The crude material was purified by "flash" column chromatography (SiO_2, DCM/EtOAc, 70/30) yielding pure **TATA α** (230 mg, 39%) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 7.63 (apparent d, *J*= 8.7 Hz, 6H, CH_{arom}), 6.96 (apparent d, *J*= 8.7 Hz, 6H, CH_{arom}), 6.67 (t, *J*= 5.7 Hz, 2H, NH), 6.33 (d, *J*= 8.5 Hz, 1H, NH), 4.15 (septet, *J*= 6.5 Hz, 1H, CH), 3.41 (q, *J*= 6.7 Hz, 4H, NH*CH*$_2$), 1.63-1.43 (m, 6H, NHCH$_2$*CH*$_2$+ CHC*H*$_2$), 1.39-1.18 (m, 31H, 14×CH$_2$+ CHC*H*$_3$), 0.85 (t, *J*= 6.9 Hz, 6H, CH_3), 0.84 (t, *J*= 6.9 Hz, 3H, CH_3) ; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm)= 166.92, 166.25, 149.18, 149.15, 130.16, 129.96, 128.64, 128.61, 123.84, 123.76, 45.94, 40.29, 37.10, 31.90, 31.88, 29.81, 29.43, 29.34, 27.17, 26.28, 22.73, 22.70, 21.11, 14.19, 14.17 ; HMRS (ESI): *m/z* calculated for $C_{45}H_{66}N_4O_3Na$ $[M+Na]^+$: 733.5027, found: 733.5002 (3.4 ppm).

TATA α^{3}Leu and TATA α^3(*R*)-Leu:

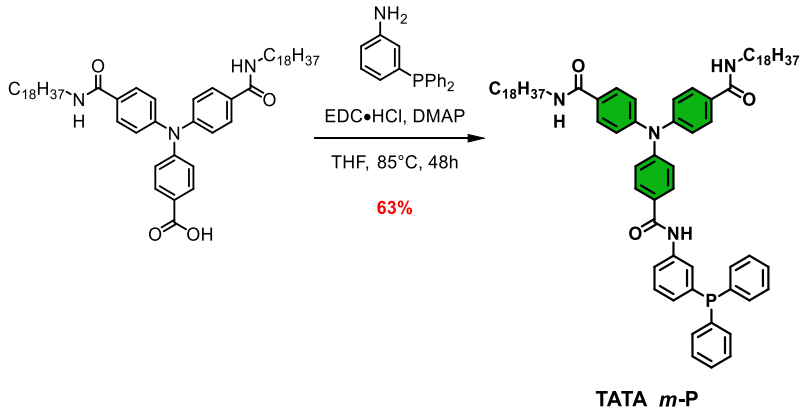


Step 1: In a Dean-Stark apparatus-mounted two-neck flask, *(S)*-Leucine (1.97 g, 15.0 mmol, 1.0 equiv.) was suspended in toluene (150 mL), and PTSA•H_2O (3.42 g, 18.0 mmol, 1.2 equiv.) was added at room temperature. Octadecan-1-ol (4.46 g, 16.5 mmol, 1.1 equiv.) was then added, and the resulting mixture was stirred at reflux temperature overnight. After cooling the reaction mixture to room temperature, the crude reaction mixture was evaporated under reduced pressure and the residue was recrystallized from Et_2O. The resulting precipitate was filtered under vacuum and rinsed with cold Et_2O to remove residual reactants. The colourless solid was then dried under vacuum affording the pure ammonium tosylate (7.01 g, 84%). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm)= 8.29 (br s, 3H, NH_3), 7.48 (apparent d, *J*= 8.1 Hz, 2H, CH_{arom}), 7.11 (apparent d, *J*= 7.8 Hz, 2H, CH_{arom}), 4.18-4.14 (m, 2H, CO_2CH_2), 4.01-3.96 (m, 1H, NH_3CH), 2.29 (s, 3H, $C_{arom}CH_3$), 1.81-1.50 (m, 5H, $CO_2CH_2CH_2$ + $CHCH_2CH$ + $(CH_3)_2CH$), 1.28-1.20 (m, 30H, CH_2), 0.91-0.87 (m, 9H, $CH(CH_3)_2$ + CH_2CH_3).



Step 2: In an oven-dried Schlenk flask under argon atmosphere, 4,4',4''-tris-[*p*-carboxylic acid]-triarylamine[3] (0.50 g, 1.33 mmol, 1 equiv.) was dissolved in THF (22 mL) and cooled to 0 °C with an ice-bath. A few droplets of DMF was then added. Oxalyl chloride (0.41 mL, 4.77 mmol, 3.6 equiv.) was added dropwise and the stirred mixture was allowed to reach room temperature. After 3 h, the solvent and the excess of oxalyl chloride were evaporated and a solution of the (*S*) ammonium tosylate salt (2.43 g, 4.37 mmol, 3.3 equiv.) in DCM (44 mL) was added. After cooling down the mixture at 0 °C, triethylamine (1.30 mL, 9.28 mmol, 7 equiv.) was added, the reaction mixture was warmed to room temperature and stirred overnight. 50 mL of brine was then added and the reaction mixture was extracted with DCM (3 x 100 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, then filtered through a plug of silica and evaporated. The crude product was purified by "flash" column chromatography (SiO_2, DCM/EtOAc, 80/20). The obtained solid was further recrystallized from ethanol to afford **TATA α³Leu** (1.28 g, 66%) as a colourless solid. ^{1}H NMR (400 MHz, THF-d_8): δ (ppm)= 7.83 (apparent d, *J*= 8.7 Hz, 6H, CH_{arom}), 7.70 (d, *J*= 8.5 Hz, 3H, NH), 7.11 (apparent d, *J*= 8.6 Hz, 6H, CH_{arom}), 4.77 (q, *J*= 7.9 Hz, 3H, NH*CH*), 4.09 (t, *J*= 6.7 Hz, 6H, CO_2CH_2), 1.81-1.59 (m, 15H, $CO_2CH_2CH_2$ + $CHCH_2CH$ + $(CH_3)_2CH$), 1.51-1.18 (m, 90H, CH_2), 0.97 (d, *J*= 6.3 Hz, 9H, $(CH_3)_2CH$), 0.96 (d, *J*= 6.3 Hz, 9H, $(CH_3)_2CH$), 0.87 (t, *J*= 6.8 Hz, 9H, CH_2CH_3) ; ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ (ppm)= 173.82, 166.61, 150.55, 130.83, 129.93, 124.55, 65.59, 52.00, 42.06, 33.03, 30.81 (multiple CH_2), 30.76, 30.73, 30.68, 30.46, 30.38, 29.77, 26.98, 23.72, 23.65, 22.16, 14.61 ; HMRS (APCI): *m/z* calculated for $C_{93}H_{156}N_4O_9H$ $[M+H]^+$: 1474.1945, found: 1474.1958 (0.9 ppm) ; FT-IR: υ (cm^{-1})= 3354, 3264, 3057, 2956, 2924, 2853, 1744, 1661, 1636, 1599, 1541, 1500, 1468, 1440, 1387, 1367, 1319, 1273, 1225, 1186, 1163, 1136. **TATA α³(*R*)-Leu** was synthesized following the same procedure using (*R*)-leucine; analytical data are identical to **TATA α³Leu**. Optical purity: Enantiomeric excess > 99%, diastereomeric ratio= 5.2 and 3.9 for **TATA α³Leu** and **TATA α³(*R*)-Leu**, respectively (determined by chiral HPLC, see Figure S5). The origin of the partial epimerization observed for **TATA α³Leu** and **TATA α³(*R*)-Leu** is unknown.

Synthesis of TATA *m*-P



TATA *m*-P

TATA *m*-P: In an oven-dried 100 mL Schlenk flask under argon atmosphere, 4,4'-bis-[*p*-octadecylamide]-4''-[*p*-carboxylic acid]-triarylamine[5] (500 mg, 0.57 mmol, 1.0 equiv.), EDC•HCl (196 mg, 1.02 mmol, 1.8 equiv.) and DMAP (125 mg, 1.02 mmol, 1.8 equiv.) were solubilized in THF (17 mL). Then, a solution of 3-(bis(phenylphosphino))aniline[8] (189 mg, 0.68 mmol, 1.2 equiv.) in THF (3 mL) was added and the reaction mixture was heated to 85 °C for 36 hours. The reaction mixture was cooled down to room temperature and the solvent was removed under vacuum. The crude material was purified by "flash" column chromatography (SiO_2, DCM/EtOAc, 80/20) yielding **TATA *m*-P** (0.406 g, 63%) as a pale-yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 8.21 (s, 1H, NH), 7.90 (dd, *J*= 8.1, 3.0 Hz, 1H, CH_{linker}) 7.70 (apparent d, *J*= 8.7 Hz, 2H, CH_{arom}), 7.64 (apparent d, *J*= 8.7 Hz, 4H, CH_{linker}), 7.39 (dt, *J*= 8.4, 1.8 Hz, 1H, CH_{linker}), 7.34-7.28 (m, 11H, PPh_2 + CH_{linker}), 7.05-7.00 (m, 7H, CH_{arom} + CH_{linker}), 6.28 (t, *J*= 5.7 Hz, 2H, NH), 3.41 (q, *J*= 6.8 Hz, 4H, NHCH_2), 1.59 (qnt, *J*= 7.1 Hz, 4H, $NHCH_2CH_2$), 1.37-1.25 (m, 60H, CH_2), 0.88 (t, *J*= 6.8 Hz, 6H, CH_3) ; ^{13}C{^{1}H} (101 MHz, $CDCl_3$): δ (ppm)= 166.88, 165.28, 149.73, 149.15, 138.47 (m), 136.97 (d, *J*= 11.0 Hz), 133.90 (d, *J*= 19.6 Hz), 130.25, 129.70, 129.39 (d, *J*= 6.6 Hz), 128.96, 128.91, 128.72, 128.65, 128.61, 125.21 (d, *J*= 22.8 Hz), 124.12, 123.61, 121.12, 40.34, 32.06, 29.84 (multiple CH_2), 29.80, 29.79, 29.77, 29.73, 29.50, 27.19, 22.83, 14.26 ; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ (ppm)= ─5.02 ; HMRS (APCI): *m/z* calculated for $C_{75}H_{103}N_4O_3PH$ $[M+H]^+$: 1139.7841, found: 1139.7848 (0.7 ppm) ; FT-IR: υ (cm^{-1}) = 3301, 3188, 3070, 3054, 2922, 2852, 1633, 1599, 1539, 1500, 1480, 1468, 1435, 1411, 1392, 1377, 1311, 1282, 1235, 1184.

Optical purity of TATA α^3Leu (Figure S5)

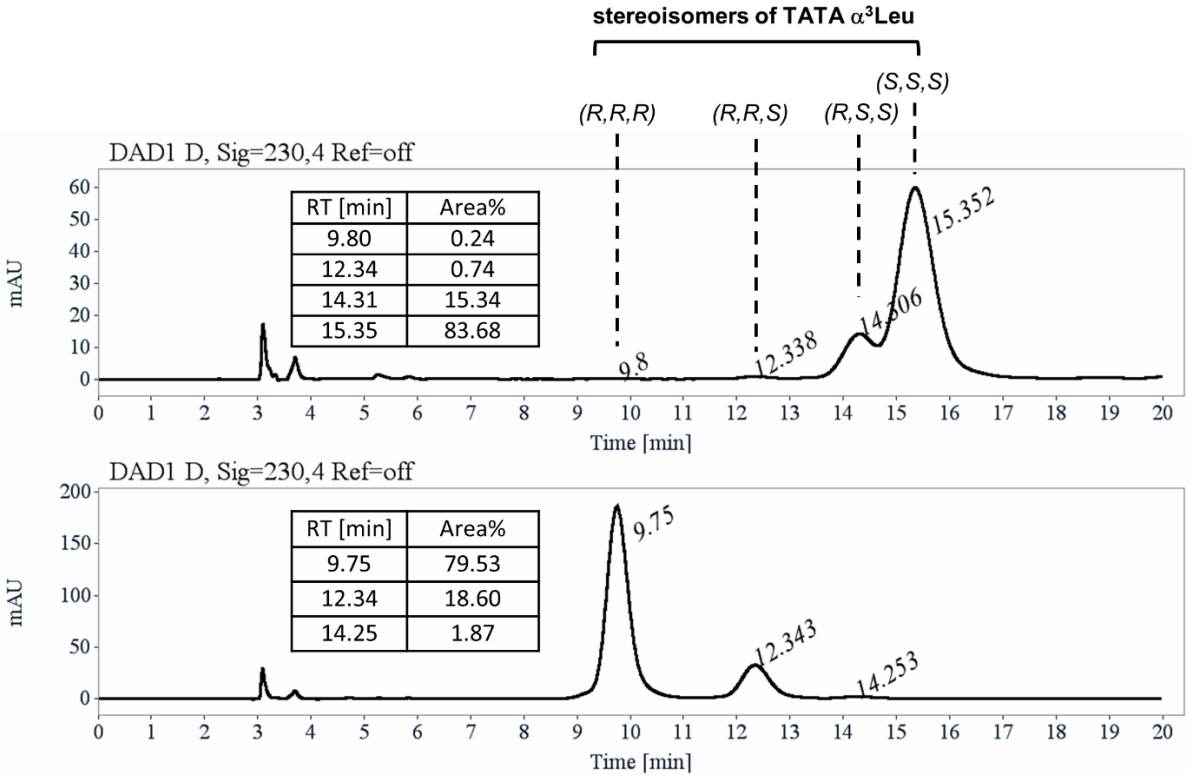
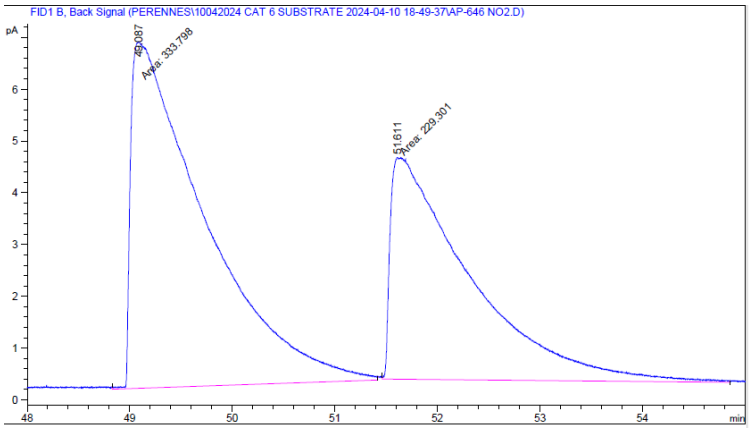


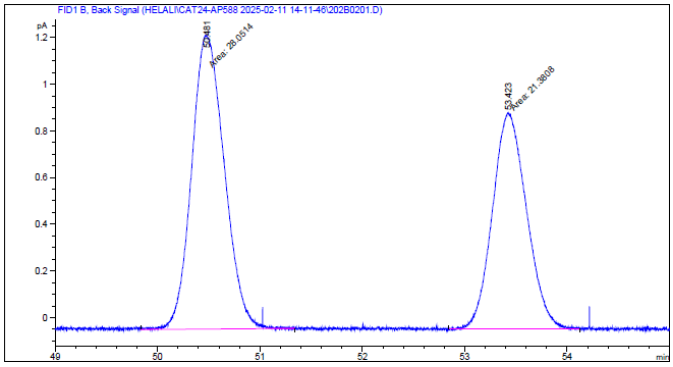
Figure S5. Chiral HPLC analyses of **BTA α^3Leu** (top) and **BTA α^3(*R*)-Leu**. Results: **BTA α^3Leu**: > 99% ee, diastereomeric ratio= 5.2. **BTA α^3(*R*)-Leu**: > 99% ee, diastereomeric ratio= 3.9.

Selected chiral GC traces (Figures S6-S12)



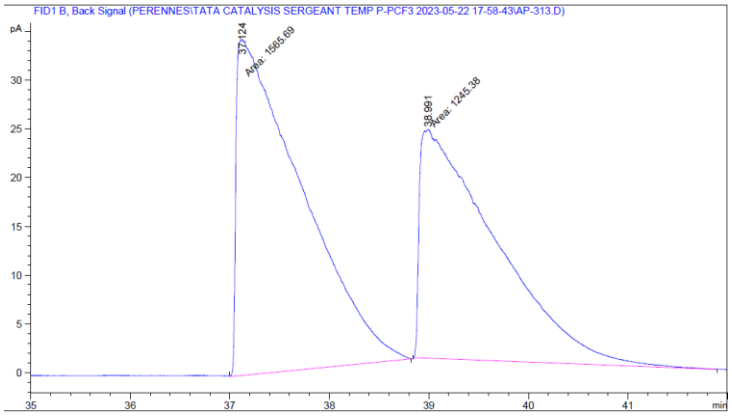
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	49.087	MM	0.8315	333.79816	6.69048	59.27876
2	51.611	MM	0.8926	229.30092	4.28158	40.72124

Figure S6. Chiral GC analysis of Table 1, entry 1. Composition: **TATA PCF3**/[Cu]= 4, **TATA αC4** (fs= 50%), toluene. ─19% *ee*.



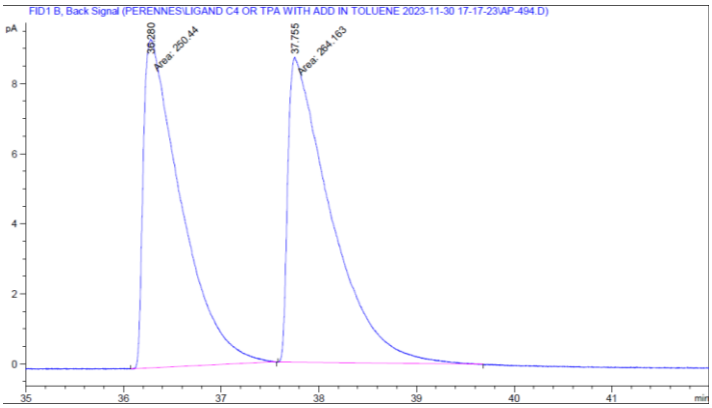
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	50.481	MM	0.3710	28.05144	1.26029	56.74725
2	53.423	MM	0.3849	21.38081	9.25808e-1	43.25275

Figure S7. Chiral GC analysis of Table 1, entry 2. Composition: **TATA PCF3**/[Cu]= 4, **TATA αC4** (fs= 50%), **TATA C8**, toluene. ─13% *ee*.



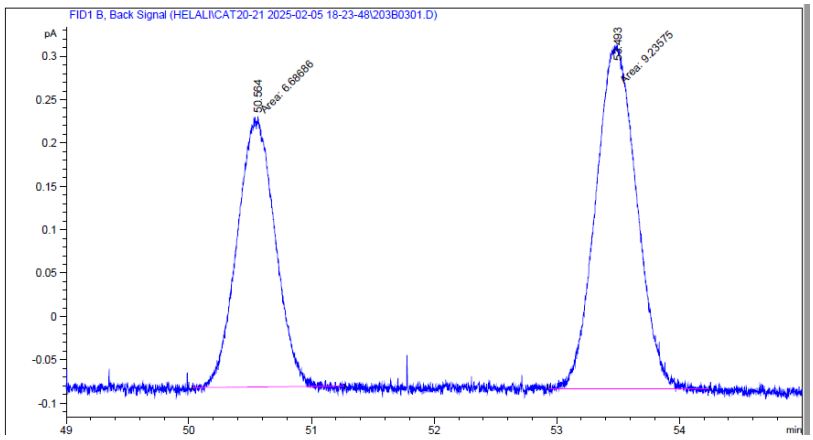
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	37.124	MM	0.7572	1565.68616	34.46139	55.69718
2	38.991	MM	0.8856	1245.38293	23.43893	44.30282

Figure S8. Chiral GC analysis of Table 1, entry 4. Composition: **TATA PCF3**/[Cu]= 4, **TATA** α^3 (fs= 50%), toluene. ─11% *ee*.



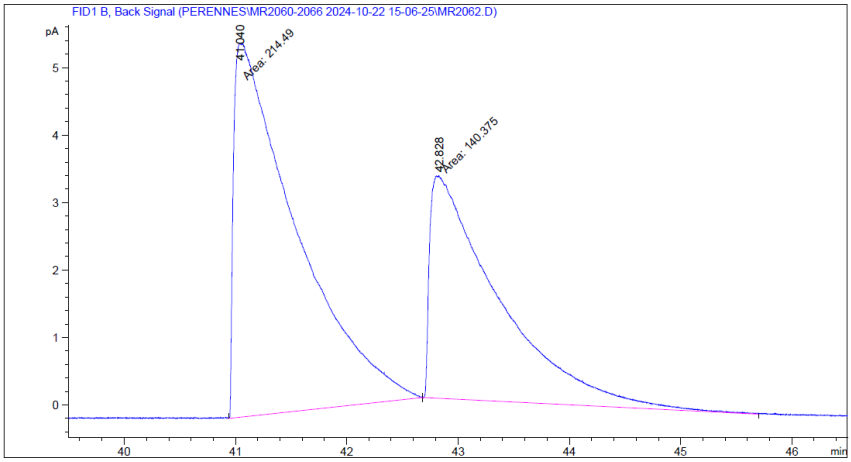
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	36.280	MM	0.4453	250.44049	9.37384	48.66672
2	37.755	MM	0.5062	264.16266	8.69675	51.33328

Figure S9. Chiral GC analysis of Table 1, entry 5. Composition: **TATA PCF3**/[Cu]= 4, **TATA** γ^3 (fs= 50%), toluene. +3% ee.



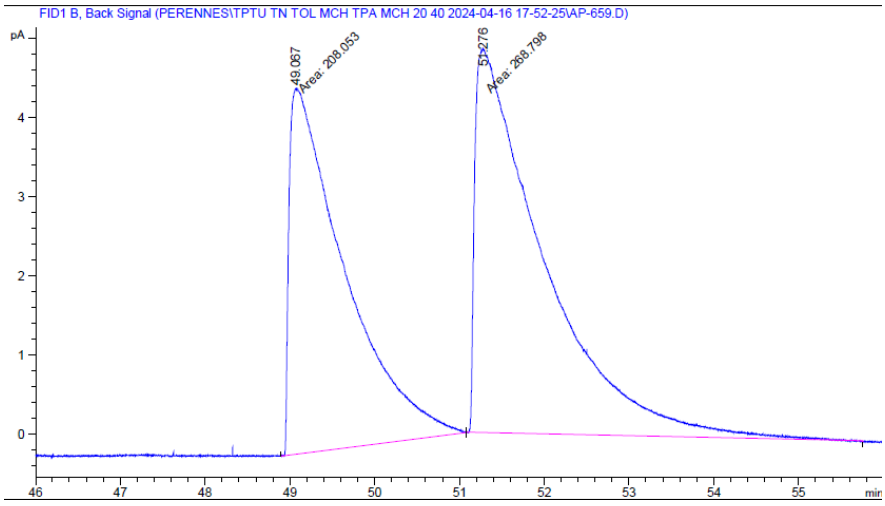
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	50.564	MM	0.3564	6.68686	3.12694e-1	41.99599
2	53.493	MM	0.3895	9.23575	3.95230e-1	58.00401

Figure S10. Chiral GC analysis of Table 1, entry 6. Composition: **TATA PCF3**/[Cu]= 4, **TATA γ^3** (fs= 50%), **TATA C8**, toluene. +16% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	41.040	MM	0.6451	214.49023	5.54180	60.44273
2	42.828	MM	0.7076	140.37500	3.30629	39.55727

Figure S11. Chiral GC analysis of Table 1, entry 7. Composition: **TATA PCF3**/[Cu]= 4, **TATA αC4** (fs= 50%), MCH. ─21% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	49.067	MM	0.7519	208.05334	4.61198	43.63062
2	51.276	MM	0.9257	268.79831	4.83950	56.36938

Figure S12. Chiral GC analysis of Table 1, entry 8. Composition: **TATA PCF3**/[Cu]= 4, **TATA** γ^3 (fs= 50%), MCH. +13% *ee*.

NMR spectra (Figures S13-S21)

Figure S13. ^{1}H NMR ($CDCl_3$) of **TATA α³**.

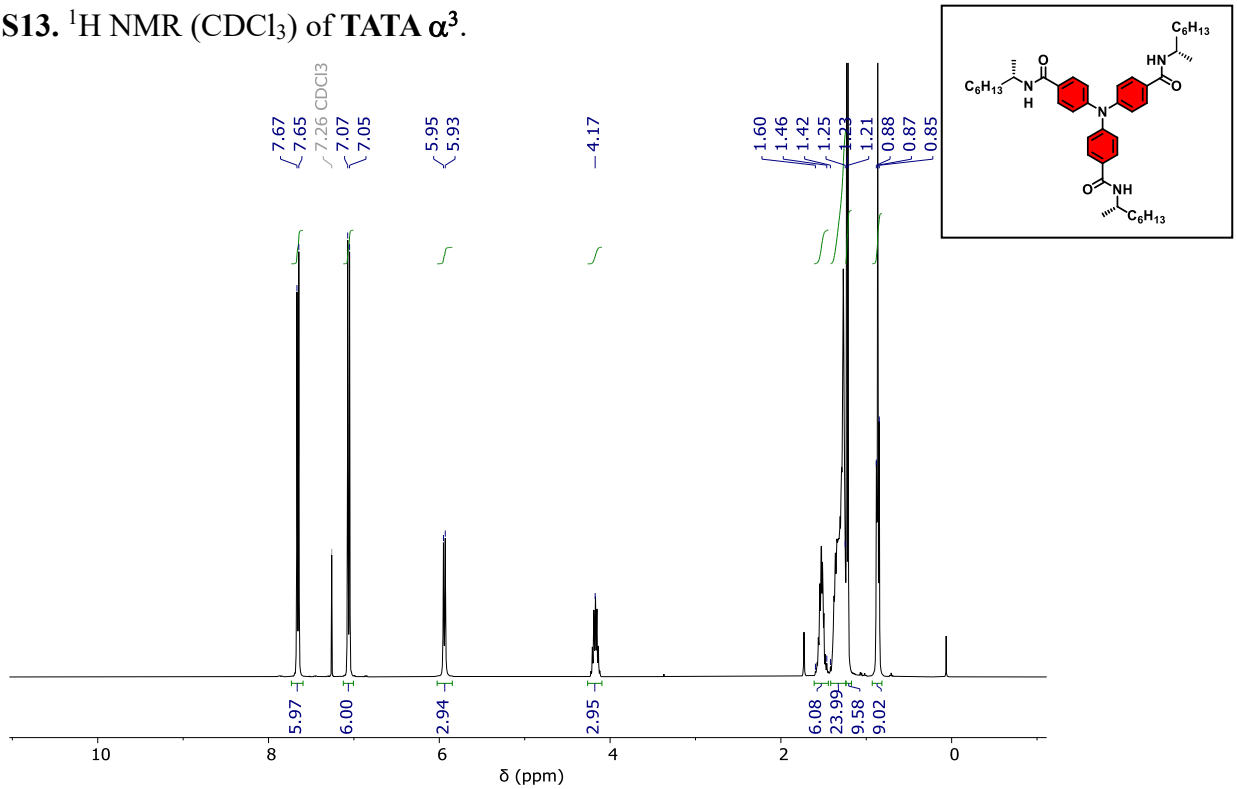


Figure S14. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of **TATA α³**.

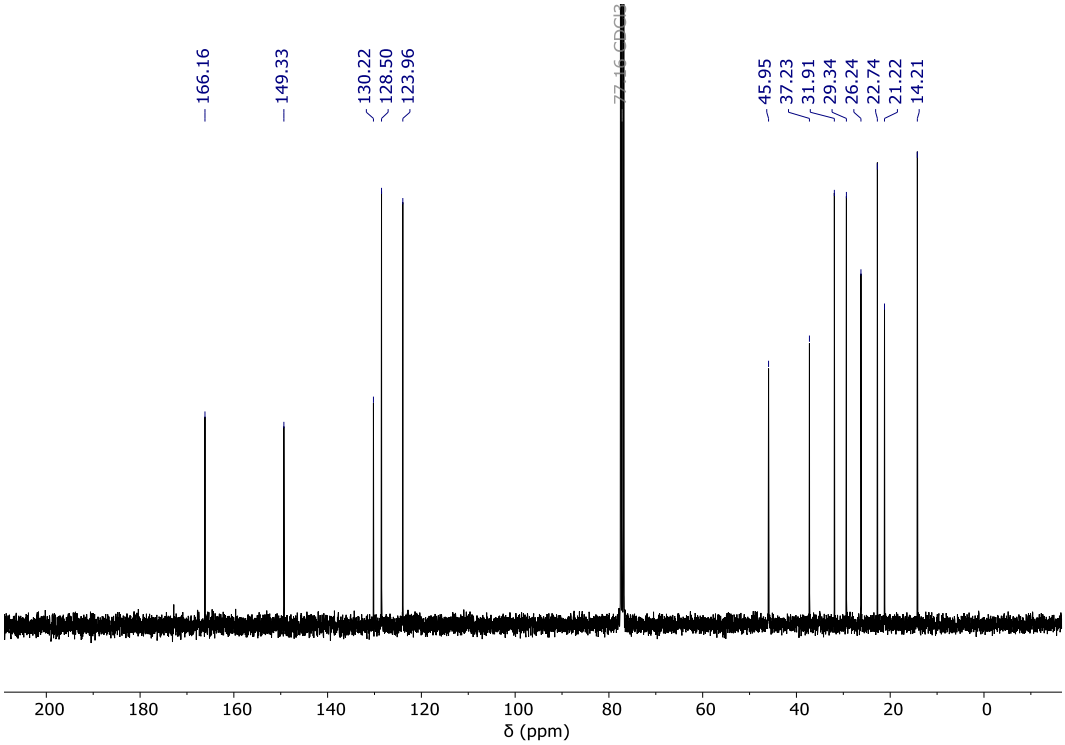


Figure S15. ^{1}H NMR ($CDCl_3$) of **TATA α**.

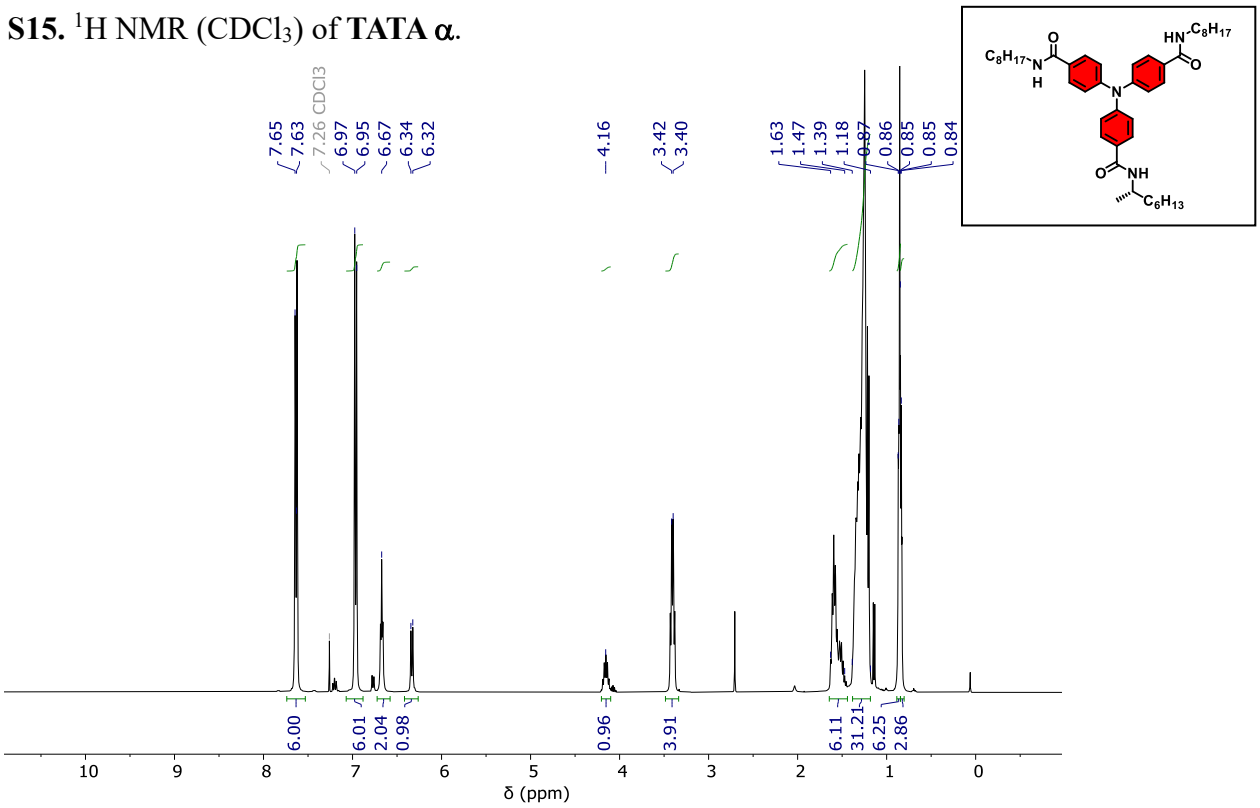


Figure S16. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of **TATA α**.

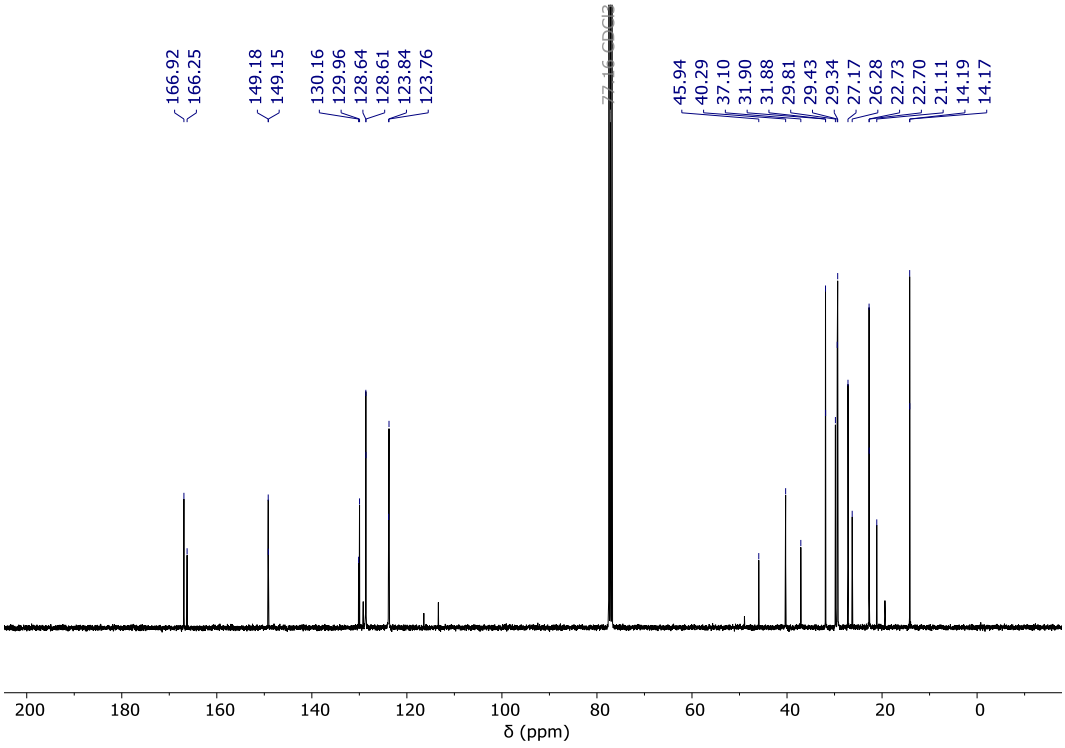


Figure S17. ^{1}H NMR (THF-d_8) of **TATA α^3Leu**.

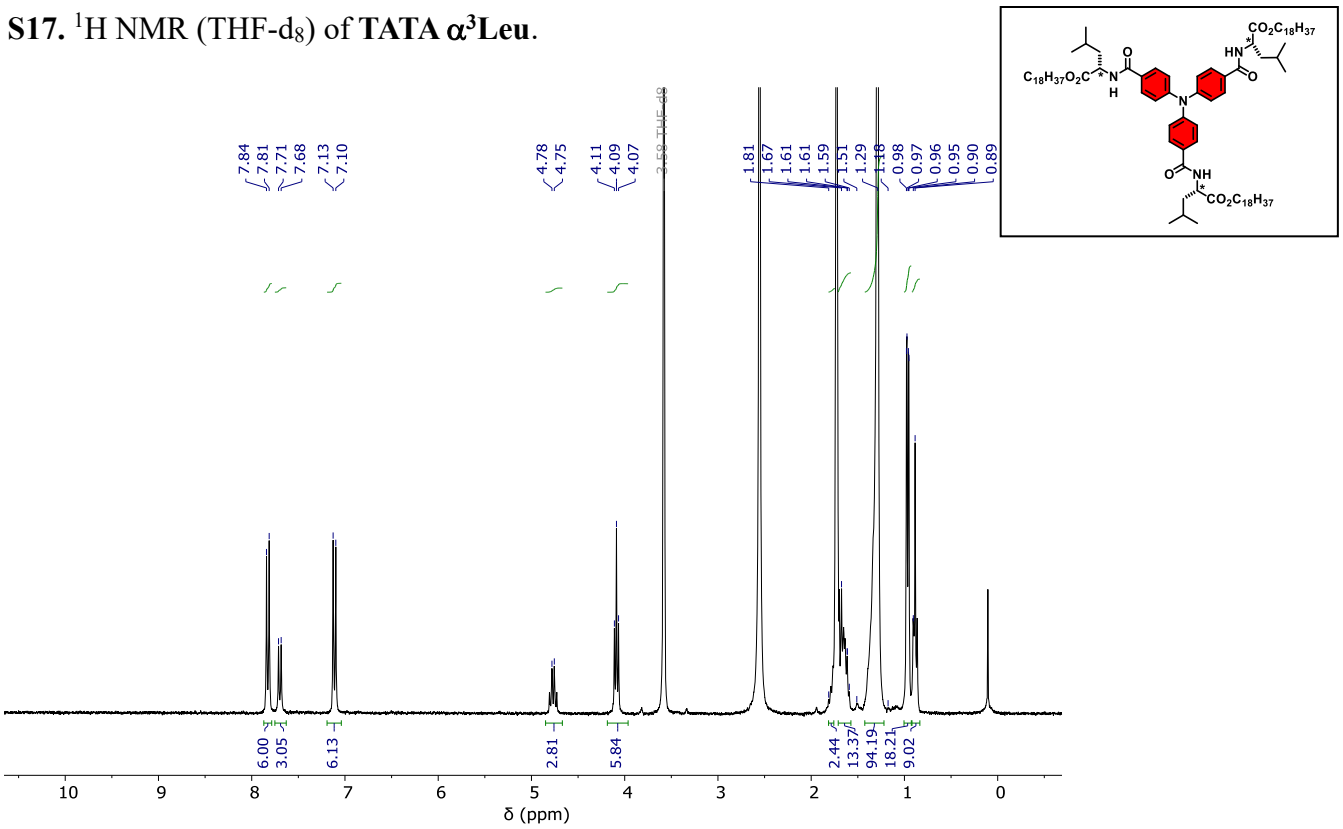


Figure S18. ^{13}C{^{1}H} NMR (THF-d_8) of **TATA α^3Leu**.

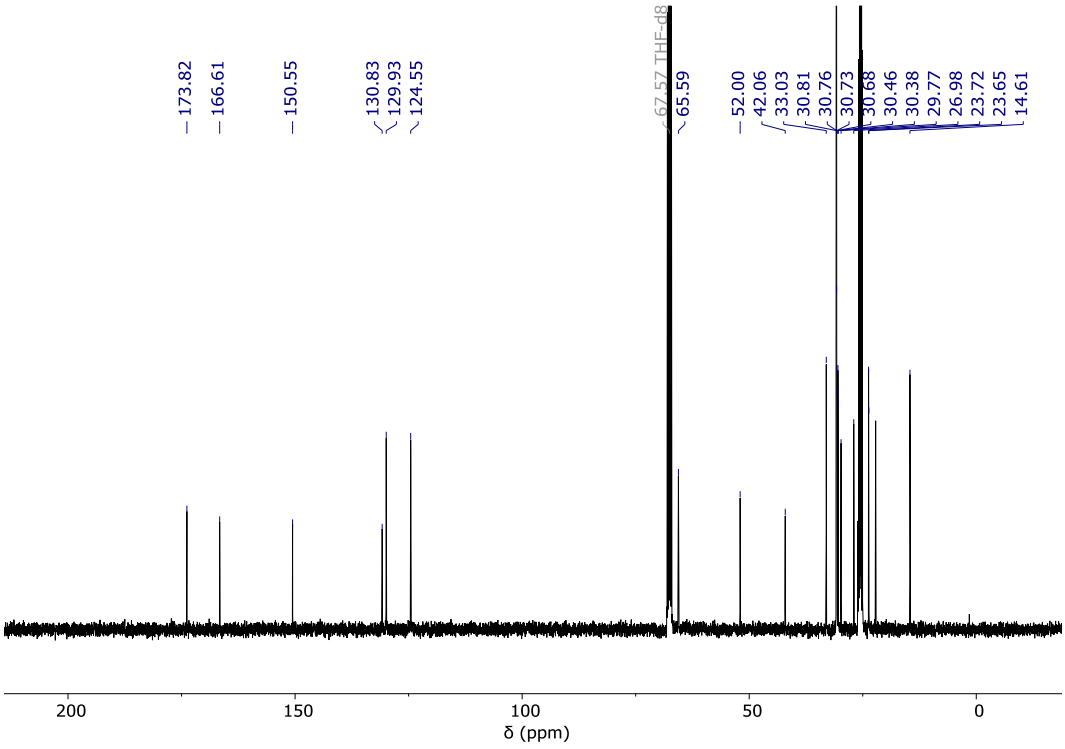


Figure S19. ^{1}H NMR ($CDCl_3$) of **TATA *m*-P**.

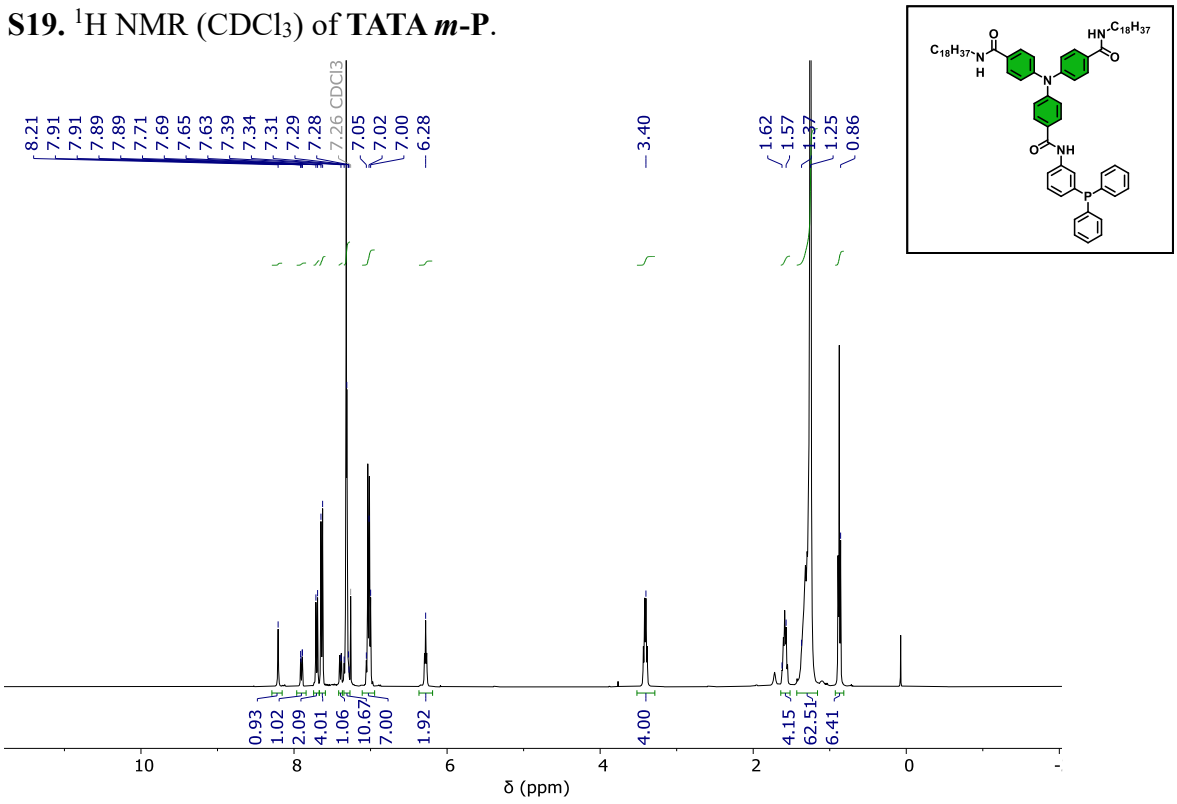


Figure S20. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of **TATA *m*-P**.

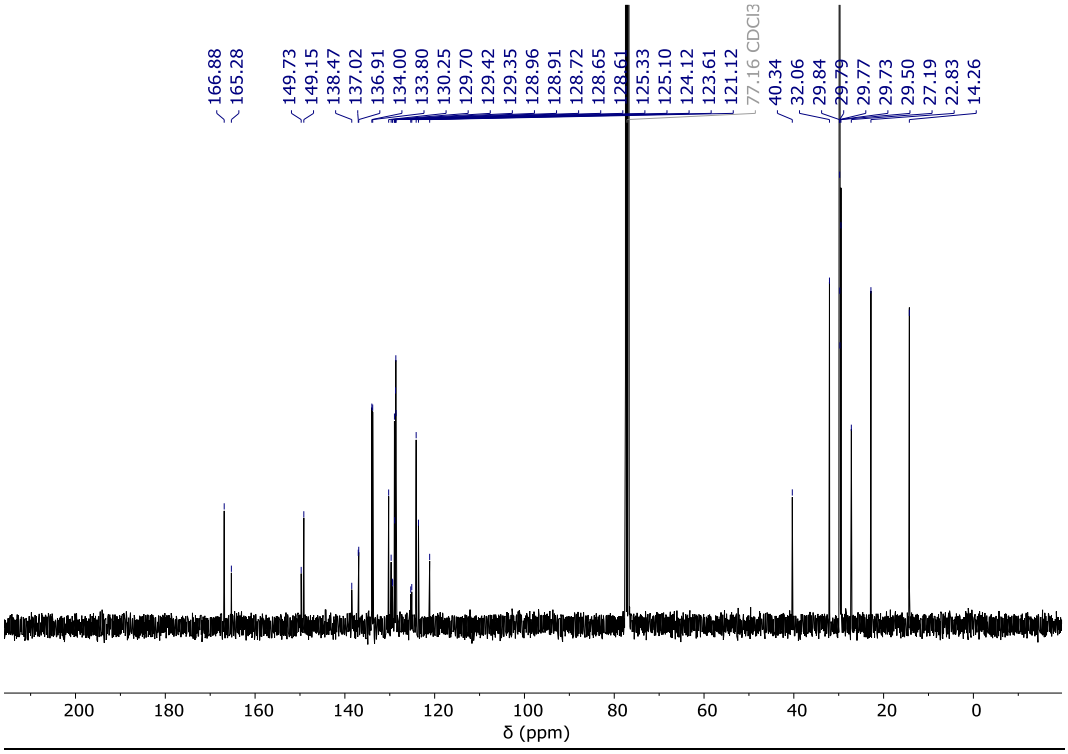
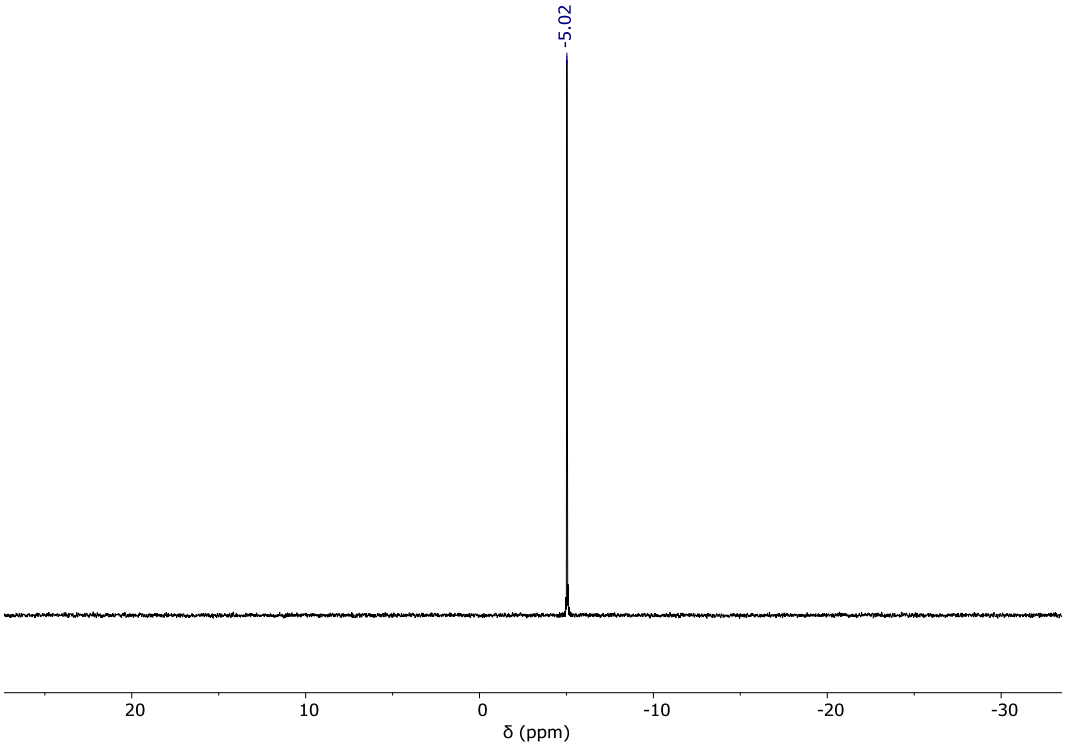


Figure S21. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of **TATA *m*-P**.



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