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# Supporting Information

# Synthesis of Axially Chiral 4,4'-Bipyridines and their Remarkably Selective Self-Assembly into Chiral Metallo-Supramolecular Squares

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- Synthesis of **1** to **9**
- Results of the chiral separation of **3**, **5**, and **6**
- CD spectra of axially chiral compounds **3**, **5**, and **6**
- Racemization of **3** and **5** as followed by CD spectroscopy
- NMR spectra of **1** and **3** – **6**
- Remarks on the symmetry considerations discussed in the main text

**Synthesis of 1 to 9:**

**3,3',5,5'-Tetramethyl-4,4'bipyridine 1:**

In 500 ml of dry diethylether, lutidine (3,5-dimethyl pyridine, 23.7 ml, 0.94 g/ml, 107.2 g/mol, 208.0 mmol), chlorotrimethylsilane (1 eq., 208.0 mmol, 108.6 g/mol, 22.6 g, 0.86 g/ml, 26.3 ml) and sodium powder (1.05 eq., 218.4 mmol, 23.0 g/mol, 5.0 g) are added at 0 °C. The suspension is stirred over night and dried roughly. The residue is extracted with hot toluene. The toluene is removed and the residue is dried roughly, again. An acetone-water-mixture and solid potassium permanganate is added under stirring until the characteristic colour remains. Stirring is continued for further 30 minutes, the solid is filtered off, washed with a warm acetone-water-mixture and the acetone is removed from the filtrate. The aqueous phase is extracted with chloroform. After drying over sodium sulfate and removing of the solvent, the crude product is purified by flash chromatography ($R_f$ = 0.57 (ethylacetate:methanol = 5:1). Yield: 10.1 g (47.8 mmol, 23 %) $^1$H-NMR (400 MHz, $CDCl_3$) s = 8.40 (s, 4H, H-2, H-6, H-2' and H-6'), 1.90 (s, 12H, $H_{CH3}$); $^{13}$C-NMR (100 MHz, $CDCl_3$) s = 149.0, 145.0, 129.6, 16.3; HIRES-MS (EI): exp. 212.1318 Da, calc. for $C_{14}H_{16}N_2$ 212.1313 Da (2.4 ppm); mp: 126°C.

**N,N'-Didodecyl-5,5'-dimethyl-4,4'-bipyridine-3,3'-dicarboxamide 3:**

1) 3,3',5,5'-Tetramethyl-4,4'-bipyridine **1** (1.00 g, 212.3 g/mol, 4.71 mmol) and potassium permanganate (4 eq., 18.8 mmol, 158.0 g/mol, 2.98 g) are stirred in 100 ml of water at 100 °C for twelve hours. The precipitate is filtered of and washed rigorously with water. The aqueous phase is neutralized with HCl, water is removed in vacuo and the residue is dried. The obtained mixture of acids is not separated.

2) The residue is suspended in thionyl chloride (25 ml) and stirred at 78 °C for eight hours. All volatile compounds are removed in vacuo. Again, the obtained mixture of acid chlorides is not separated.

3) The residue, dodecylamine (2 eq. 9.42 mmol, 185.3 g/mol, 1.75 g) and triethylamine (5 ml, excess) are suspended in 15 ml of dry dimethylsulfoxide and stirred for two days. All volatile compounds are removed in vacuo and the crude product is purified by column chromatography ($R_f$ = 0.22 (ethylacetate:methanol = 15:1).Yield: 457 mg, 0.75 mmol, 16% among other byproducts and over three

steps. $^{1}$H-NMR (400 MHz, [$D_6$]-acetone) s = 8.60 (s, 2H, H-2 and H-2' or H-6 and H-6'), 8.53 (s, 2H, H-2 and H-2' or H-6 and H-6'), 7.63 (t, $^{3}J_{HH}$ = 5.7 Hz, 2H, $H_{amide}$), 3.21 (m, 2H, $H_{NH-\underline{CH2}-C11H23}$, 3.10 (m, 2H, $H_{NH-\underline{CH2}-C11H23}$), 1.90 (s, 6H, $H_{CH3}$), 1.23 (br, 40H, $H_{CH2-\underline{(CH2)10}-CH3}$), 0.856 (t, $^{3}J_{HH}$ = 6.8 Hz, 6H, $H_{(CH2)11-\underline{CH3}}$); $^{13}$C-NMR (75 MHz, [$D_6$]-acetone) s = 167.5, 152.5, 145.8, 142.5, 131.6, 130.4, 40.0, 32.0, 29.8, 29.7, 29.7, 29.7, 29.6, 29.5, 29.3, 26.9, 22.8, 16.8, 14.2; HIRES-MS (ESI, acetone): exp. 607.4892 Da, calc. for $M+H^+$ $C_{38}H_{63}N_4O_2$ 607.4946 Da (-8.9 ppm).

**2,2'-(5,5'-Dimethyl-4,4'-bipyridine-3,3'-diyl)diacetic acid 4:**

Under argon, 2,2,6,6-tetramethyl-piperidine (0.8 ml, 0.83 g/ml, 664 mg, 141.25 g/mol, 4.70 mmol) in 10 ml tetrahydrofuran are cooled down to -78°C. *t*-Butyllithium (1 eq., 4.70 mmol, 2.5mol $l^{-1}$ solution in pentane, 1.9 ml) is added. The mixture is stirred for 30 minutes at this temperature, allowed to warm to 0°C, and cooled to -78°C again. 3,3',5,5'-Tetramethyl-4,4'bipyridine **1** (250 mg, 212.3 g/mol, 1.17 mmol, 0.25 eq.) in 5 ml tetrahydrofuran is added and the resulting mixture is stirred for 3 hours at 0°C. At this temperature, gaseous carbon dioxide is introduced until the mixture is colourless. Water (10 ml) is added, the aqueous phase is extracted with dichloromethane and neutralized with hydrochloric acid. All volatile compounds are removed in vacuo. Yield after column chromatography $R_f$ = 0.14 (dichloromethane:methanol = 2:1): (157 mg, 0.52 mmol, 45 %). $^{1}$H-NMR (400 MHz, $D_2O$) s = 8.43 (b, 4H, H-2, H-2', H-6, and H-6'), 3.26 (d, $^{2}J_{HH}$ =15 Hz, 2H, $H_{CH2}$), 3.02 (d, $^{2}J_{HH}$ =15 Hz, 2H, $H_{CH2}$), 1.94 (s, 6H, $H_{CH3}$); $^{13}$C-NMR (100 MHz, $D_2O$) s = 179.8, 149.6, 149.2, 148.6, 135.5, 133.9, 41.6, 18.3; HIRES-MS (ESI, acetone): exp. 299.1005 Da, calc. for $M-H^+$ $C_{16}H_{15}N_2O_4^-$ 299.1037 Da (-10.7 ppm).

**2,2'-(5,5'-Dimethyl-4,4'-bipyridine-3,3'-diyl)bis(dodecylacet-amide) 5:**

Under argon, 2,2'-(5,5'-dimethyl-4,4'-bipyridine-3,3'-diyl)diacetic acid **4** (102 mg, 300.3 g/mol, 0.34 mmol) benzotriazole-1-yl-oxy-tris-pyrrolidino-phosphonium hexafluoro-phosphate (PYBOP) (2 eq., 0.68 mmol, 520.4 g/mol, 356 mg), dodecylamine (2 eq., 0.68 mmol, 185.3 g/mol, 126 mg) and 0.7 ml of ethyldiisopropylamine (12 eq., 4.08 mmol, 129.2 g/mol, 527 mg, 0.76 g/ml) are suspended in 15 ml of dry dimethylsulfoxide and stirred for two days. All volatile compounds are removed in vacuo and the crude product is purified by column chromatography ($R_f$= 0.24 (ethylacetate:methanol = 15:1):Yield: 71 mg, 0.11 mmol, 33%. $^{1}$H-NMR (400 MHz, [$D_6$]-acetone) s = 8.49 (s, 2H, H-2 and H-2'or H-6 and H-6'), 8.41 (s, 2H, H-2 and H-2'or H-6 and H-6'), 7.30 (br, 2H, $H_{amide}$), 3.24 (d, $^{2}J_{HH}$ = 15 Hz, 2 H, $H_{CH2}$), 3.15 (d, $^{2}J_{HH}$ = 15 Hz, 2H, $H_{CH2}$), 3.07 (m, 4H, $H_{\underline{CH2}-(CH2)10-CH3}$), 1.90 (s, $H_{CH3}$, 6H), 1.28 (m, 40H, $H_{CH2-\underline{(CH2)10}-CH3}$), 0.88 (t, $^{3}J_{HH}$ = 7 Hz, 6H, $H_{CH2-(CH2)10-\underline{CH3}}$); $^{13}$C-NMR (75 MHz, [$D_6$]-acetone) s = 170.1, 150.1, 150.0, 144.9, 131.2, 130.0, 40.1, 39.9, 38.3, 32.7, 30.6, 30.4, 30.4, 30.3, 30.2, 27.7, 23.3, 16.7, 14.4; HIRES-MS (ESI, acetone): exp. 635.5207 Da, calc. for $M+H^+$ $C_{40}H_{67}N_4O_2$ 635.5259 Da (-8.2 ppm).

**2,2'-(5,5'-Dimethyl-4,4'-bipyridine-3,3'-diyl)bis(decylacetamide) 6:**

Under argon, 2,2'-(5,5'-dimethyl-4,4'-bipyridine-3,3'-diyl)diacetic acid **4** (102 mg, 300.3 g/mol, 0.34 mmol) benzotriazole-1-yl-oxy-tris-pyrrolidino-phosphonium hexafluoro-phosphate (PYBOP) (2 eq., 0.68 mmol, 520.4 g/mol, 356 mg), decylamine (2 eq., 0.68 mmol, 157.3 g/mol, 107 mg) and 0.7 ml of ethyldiisopropylamine (12 eq., 4.08 mmol, 129.2 g/mol, 527 mg, 0.76 g/ml) are suspended in 15 ml of dry dimethylsulfoxide and stirred for two days. All volatile compounds are removed in vacuo and the crude product is purified by column chromatography ($R_f$= 0.24 (ethylacetate:methanol = 15:1):Yield: 84 mg, 0.14 mmol, 43%. $^1$H-NMR (400 MHz, [$D_6$]-acetone) s = 8.50 (s, 2H, H-2 and H-2'or H-6 and H-6'), 8.41 (s, 2H, H-2 and H-2'or H-6 and H-6'), 7.31 (b, 2H, $H_{amide}$), 3.24 (d, $^2J_{HH}$ = 15 Hz, 2 H, $H_{CH2}$), 3.15 (d, $^2J_{HH}$ = 15 Hz, 2H, $H_{CH2}$), 3.07 (m, 4H, $H_{\underline{CH2}\text{-}C9H19}$), 1.90 (s, 6H, $H_{CH3}$), 1.28 (m, 32H, $H_{CH2\text{-}\underline{(CH2)8}\text{-}CH3}$, 0.88 (t, $^3J_{HH}$ = 7 Hz, 6H, $H_{CH2\text{-}(CH2)8\text{-}\underline{CH3}}$); $^{13}$C-NMR (75 MHz, [$D_6$]-acetone) s = 170.2, 150.2, 150.2, 145.0, 131.3, 130.0, 40.1, 38.4, 32.7, 30.3, 27.7, 23.4, 16.8, 14.4, three signals overlap with acetone signals; HIRES-MS (ESI, acetone): exp. 579.4587 Da, calc. for $M+H^+$ $C_{36}H_{59}N_4O_2$ 579.4633 Da (-7.9 ppm).

**Squares:**

Equimolar amounts of organic ligand (in case of **8a,b** and **9a,b** only one enantiomer of axially chiral dissymmetrical ligand) and metal precursor complexes (dpppM$(OTf)_2$ with M = Pd **a** or Pt **b**) are mixed in acetone (MS, $4\cdot10^{-4}$ M) or [$D_6$]-acetone (NMR, $9\cdot10^{-3}$ M) and stirred for 24 hours before measurement, to avoid kinetically controlled product formation. For CD-spectroscopy the acetone is removed in vacuo, and the resulting residues are dissolved in methanol. Note, that $^{195}$Pt (natural abundance 34%) is the only NMR active Pt-isotope. Thus, phosphorous atoms in **7b** – **9b** are split in one singlet ($^{190}$Pt -$^{194}$Pt and $^{196}$Pt - $^{198}$Pt, 66%) and one dublett ($^{195}$Pt, 34%) at the same chemical shift.

A characterization of the squares by $^{13}$C NMR could not be carried out due to the small amounts of enantiopure ligands obtained from the HPLC separation. Racemic mixtures of the ligands cannot be used instead, because they unavoidably form mixed assemblies with new signals not present in the NMR spectra of the assemblies obtained from enantiopure ligands.

**$[dpppPd1(OTf)_2]_4$ 7a:**

$^1$H-NMR (400 MHz, [$D_6$]-acetone) s = 8.83 (s, 8H, $H_{Py\_out}$), 8.43 (s, 8H, $H_{Py\_in}$), 7.60 (m, 80H, $H_{dppp}$), 3.33 (br, 16H, $H_{dppp}$), 2.41 (br, 8H, $H_{dppp}$), 1.49 (s, 24H, $H_{CH3\_out}$), 1.22 (s, 24H, $H_{CH3\_in}$); $^{31}$P-NMR (162 MHz, [$D_6$]-acetone) s = 9.65 (s, 8P); MS (ESI, acetone): *m/z* = 1223.2 Da M-3OTf$^{3+}$.

**$[dpppPt1(OTf)_2]_4$ 7b:**

$^{1}$H-NMR (400 MHz, [$D_6$]-DMSO) s = 8.46 (s, 8H, $H_{Py\_out}$), 8.36 (s, 8H, $H_{Py\_in}$), 7.48 (m, 80H, $H_{dppp}$), 2.81 (br, 16H, $H_{dppp}$), 1.97 (br, 8H, $H_{dppp}$), 1.42 (s, 24H, $H_{CH3\_out}$), 0.95 (s, 24H, $H_{CH3\_in}$);$^{31}$P-NMR (162 MHz, [$D_6$]-DMSO) s = -12.26 (s), $^{1}J_{195Pt,P}$= 3050 Hz; MS (ESI, acetone): *m/z* = 1341.3 Da M-3OTf$^{3+}$.

**[dpppPd3(OTf)$_2$]$_4$ 8a:**

$^{1}$H-NMR (400 MHz, [$D_6$]-acetone) s = 8.00 (m, 104H, $H_{py}$, $H_{amide}$ and $H_{dppp}$), 3.20 (m, 32H, $H_{NH\text{-}\underline{CH2}\text{-}C11H23}$ and $H_{dppp}$), 1.20 (m, 216H, $H_{CH3}$, $H_{NH\text{-}CH2\text{-}\underline{C11H23}}$ and $H_{dppp}$); $^{31}$P-NMR (162 MHz, [D6]-acetone) s = 10.61 (d, $^{2}J_{PP}$= 33.6 Hz, 2P), 10.17 (d, $^{2}J_{PP}$= 32.0 Hz, 2P), 8.73 (d, $^{2}J_{PP}$= 31.3 Hz, 2P), 8.02 (d, $^{2}J_{PP}$= 33.6 Hz, 2P); MS (ESI, acetone): *m/z* = 2699.0 Da M-2OTf$^{2+}$.

**[dpppPt3(OTf)$_2$]$_4$ 8b:**

$^{1}$H-NMR (400 MHz, [$D_6$]-acetone) s = 8.00 (m, 104H, $H_{py}$, $H_{amide}$ and $H_{dppp}$), 3.20 (m, 32H, $H_{NH\text{-}\underline{CH2}\text{-}C11H23}$ and $H_{dppp}$), 1.20 (m, 216H, $H_{CH3}$, $H_{NH\text{-}CH2\text{-}\underline{C11H23}}$ and $H_{dppp}$); $^{31}$P-NMR (162 MHz, [$D_6$]-acetone) s = -12.26 (d, $^{2}J_{PP}$= 31.3 Hz, 4P), -14.01 (d, $^{2}J_{PP}$= 30.5 Hz, 2P), -14.87 (d, $^{2}J_{PP}$= 31.3 Hz, 2P), $^{1}J_{195Pt,P}$ ca. 3050 Hz, in all three cases; MS (ESI, acetone): *m/z* = 2876.2 Da M-2OTf$^{2+}$.

**[dpppPd5(OTf)$_2$]$_4$ 9a:**

$^{1}$H-NMR (400 MHz, [$D_7$]-DMF) s = 8.62 (br, 8H, H-2 and H-2'or H-6 and H-6'), 8.33 (br, 8H, H-2 and H-2'or H-6 and H-6'), 7.78 (br, 32H, $H_{dppp}$), 7.49 (br, 16H, $H_{dppp}$), 7.41 (br, 32H, $H_{dppp}$), 3.18 (br, 48 H, $H_{CH2}$ , $H_{NH\text{-}\underline{CH2}\text{-}C11H23}$ and $H_{dppp}$), 2.19 (br, 8H, $H_{dppp}$), 1.56 (br, 24H; $H_{CH3}$), 1.14 (br, 160H, $H_{CH2\text{-}\underline{(CH2)10}\text{-}CH3}$), 0.76 (t, $^{3}J_{HH}$ = 7 Hz, 24H, $H_{(CH2)10\text{-}\underline{CH3}}$); $^{31}$P-NMR (162 MHz, [$D_7$]-DMF) s = 16.81 (br, 4P), 10.05 (br, 4P); MS (ESI, acetone): *m/z* = 1787.1 Da M-3OTf$^{3+}$.

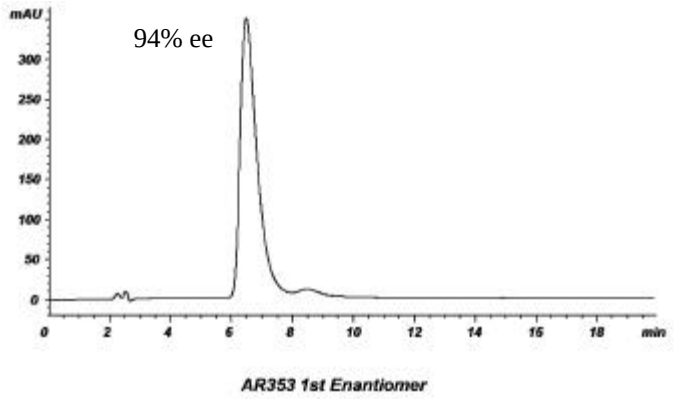
**[dpppPt5(OTf)$_2$]$_4$ 9b:**

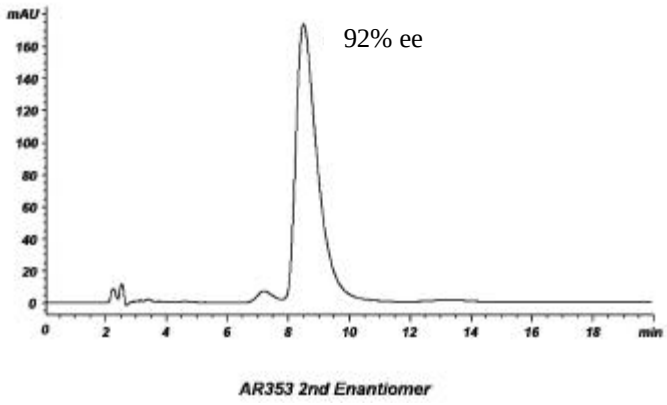
$^{1}$H-NMR (400 MHz, [$D_7$]-DMF) s = 8.60 (br, 16H, H-2, H-2', H-6 and H-6'), 7.51 (br, 80H, $H_{dppp}$), 3.10 (br, 48 H, $H_{CH2}$ , $H_{NH\text{-}\underline{CH2}\text{-}C11H23}$ and $H_{dppp}$), 2.12 (br, 8H, $H_{dppp}$), 1.29 (br, 24H; $H_{CH3}$), 1.13 (br, 160H, $H_{CH2\text{-}\underline{(CH2)10}\text{-}CH3}$), 0.76 (br, 24H, $H_{(CH2)10\text{-}\underline{CH3}}$); $^{31}$P-NMR (162 MHz, [$D_7$]-DMF) s = -9.36 (br, 2P), 11.70 (br, 6P), $^{1}J_{195Pt,P}$ ca. 3100 Hz, in both cases; MS (ESI, acetone): *m/z* = 1905.4 Da M-3OTf$^{3+}$.

**Separation of Enantiomers**

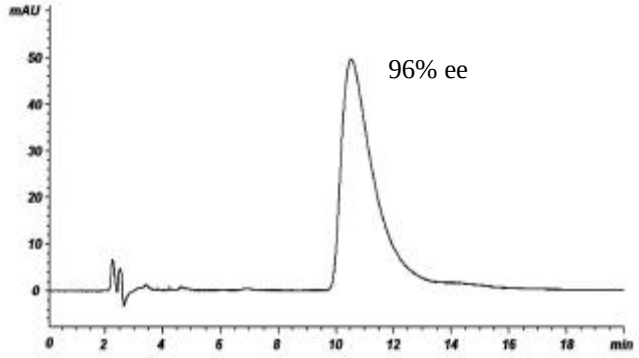
The semi-preparative enantiomer separations of the 4,4'-bipyridine derivatives **3**, **5** and **6** were carried out with an Agilent 1100 Series HPLC system (Waldbronn, Germany), consisting of a quaternary gradient pump, a solvent degasser, a multiple wavelength UV-detector, an autosampler, and a column thermostat. Fraction collection was achieved via time-controlled by an Agilent 1200 Series 12 position/13 port-selection valve integrate downstream at the UV detector unit. System operation and data processing were performed using HP ChemStation software, installed on a personal computer. The enantiomer separations were carried out with a analytical column (250 x 4.6 mm I.D.), packed with a chiral stationary phase based on tris-(3,5-dimethylphenyl)cellulose, covalently immobilized to macroporous 10 µm spherical silica gel (cf. ref. 13 in main text). The employed mobile phase was a mixture of n-heptane/2-propanol (15:1, v/v). The flow rate was 1 mL/min, and the column temperature was kept at 25±1°C. Peaks were monitored by UV detection at multiple wavelengths (230, 254, 270, 360 nm). Samples were injected as filtered solutions in chloroform (50 mg/ml), and injection volumes were typically 30 to 80 µL, corresponding to a specific sample load of 1.5 to 4.0 mg racemic 4,4'-bipyridine derivative per run. Due to the extreme peak tailing of the analytes, even at low sample loads, "safe" fraction collection was firstly programmed to collect the front region of the first eluting enantiomer, to pool the middle section to a mixed fraction, and collect the rear section of the second eluting enantiomer. To improve yields, the mixed fractions were reprocessed after evaporation of the solvents. The first and third fractions were evaporated under reduced pressure at a bath temperature < 40°C to avoid thermally-induced racemization. The respective enantiomerically enriched bi-pyridines were obtained as colourless solids, generally with ee>92%. The chromatograms of the isolated enantiomerically enriched **3**, **5** and **6** are shown below.

**Enantiomer separation of 3:**

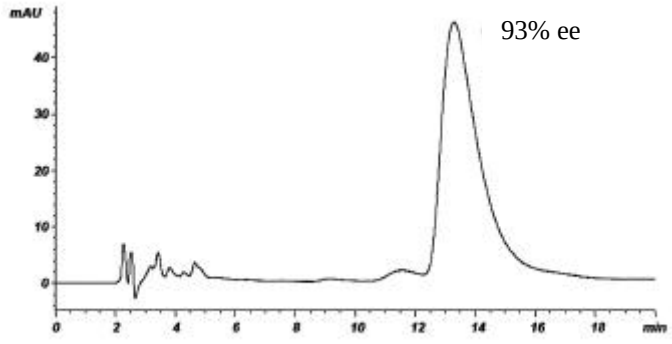


**Enantiomer separation of 5:**

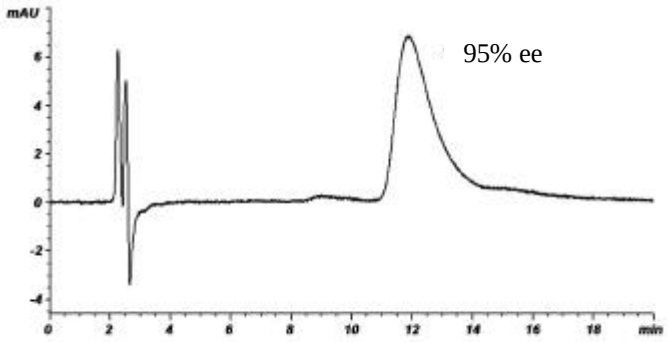



AR358 1st Enantiomer

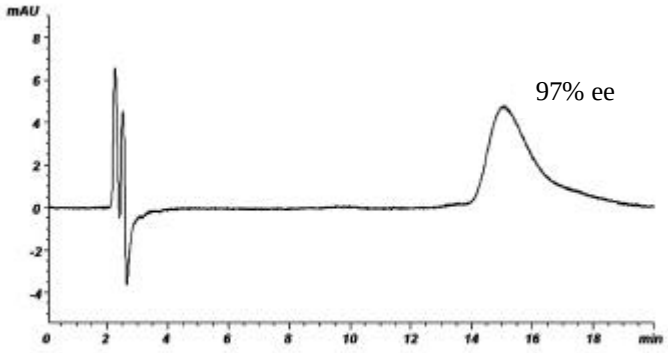



AR358 2nd Enantiomer

**Enantiomer separation of 6:**




AR362 1st Enantiomer




AR362 2nd Enantiomer

**CD spectra of 3, 5, and 6:**

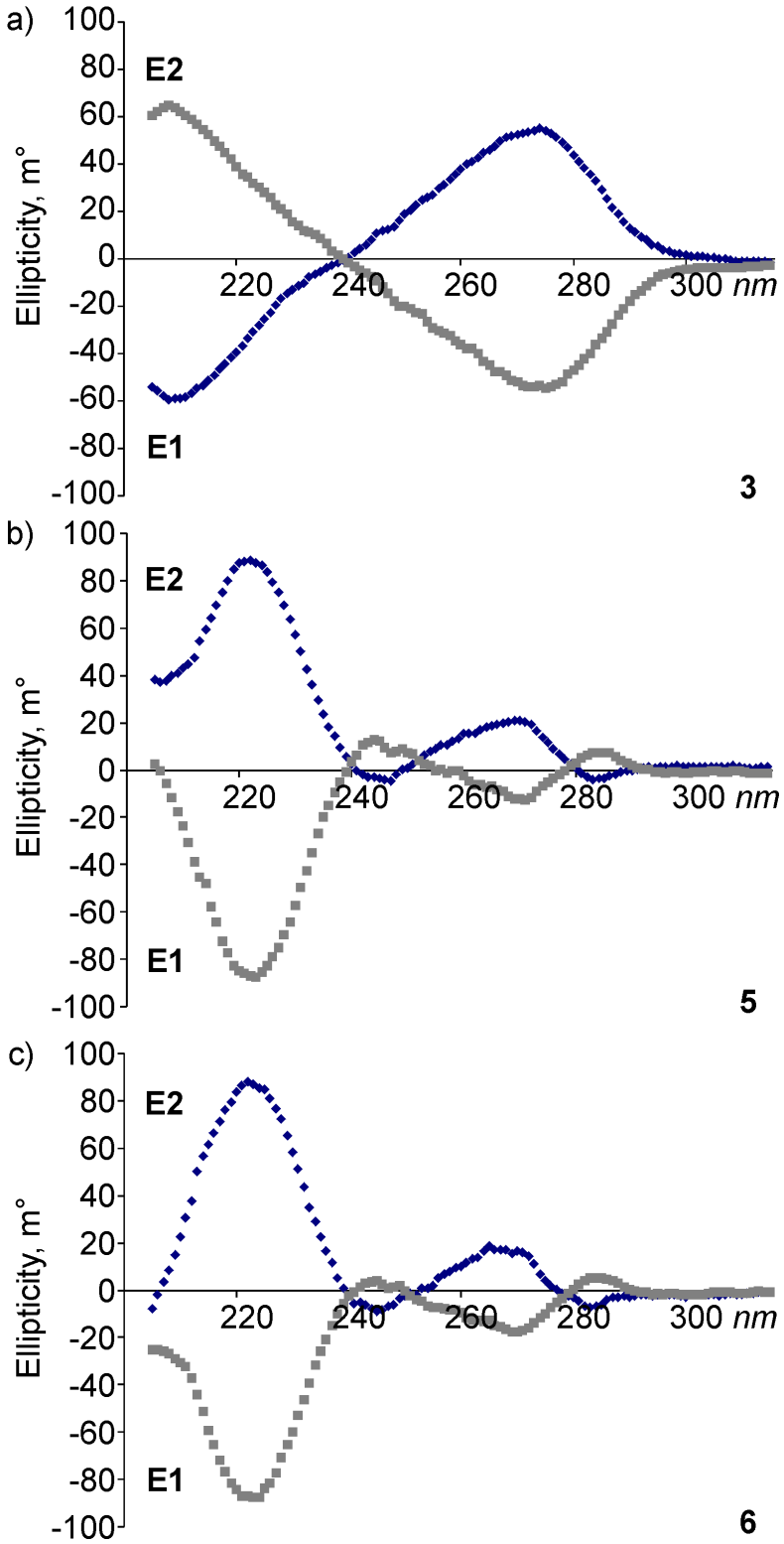



***Figure S1:*** CD-Spectra a) **3** $6 \cdot 10^{-5}$ M, MeOH, 1 mm b) **5** and c) **6** $4 \cdot 10^{-5}$ M, MeOH, 10 mm

**Racemization of 3 and 5 as followed by CD-Spectroscopy:**

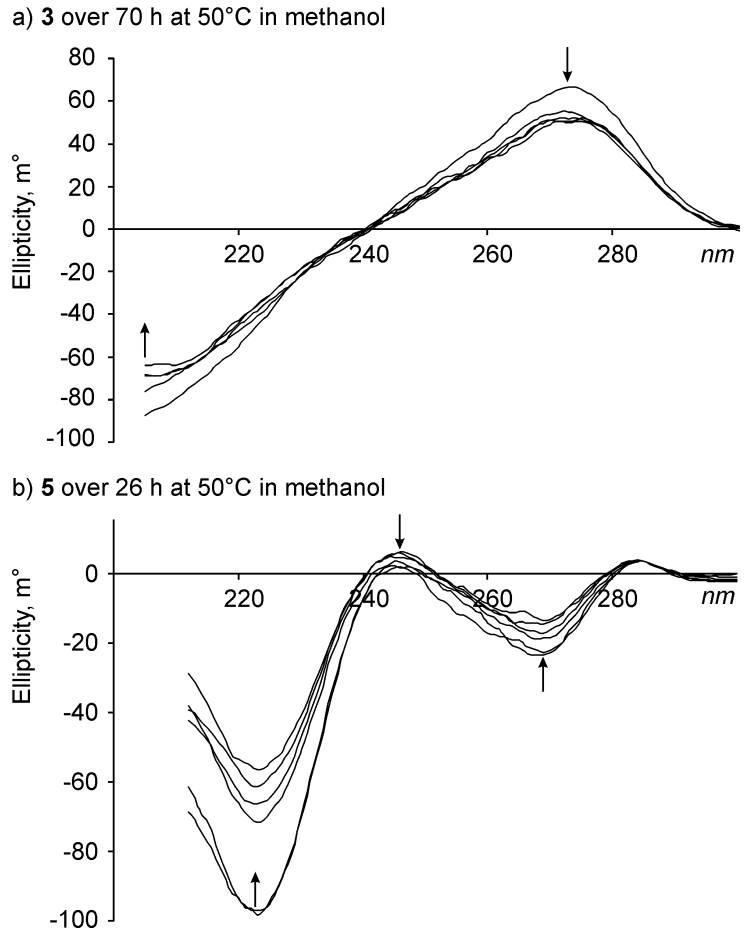
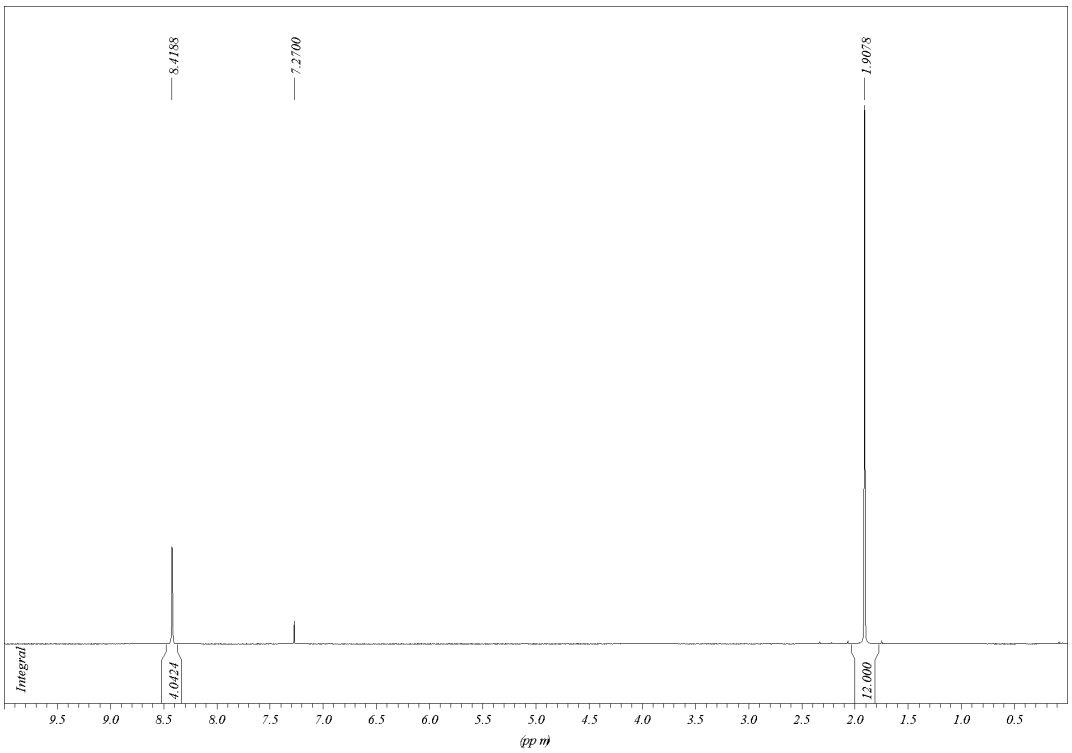
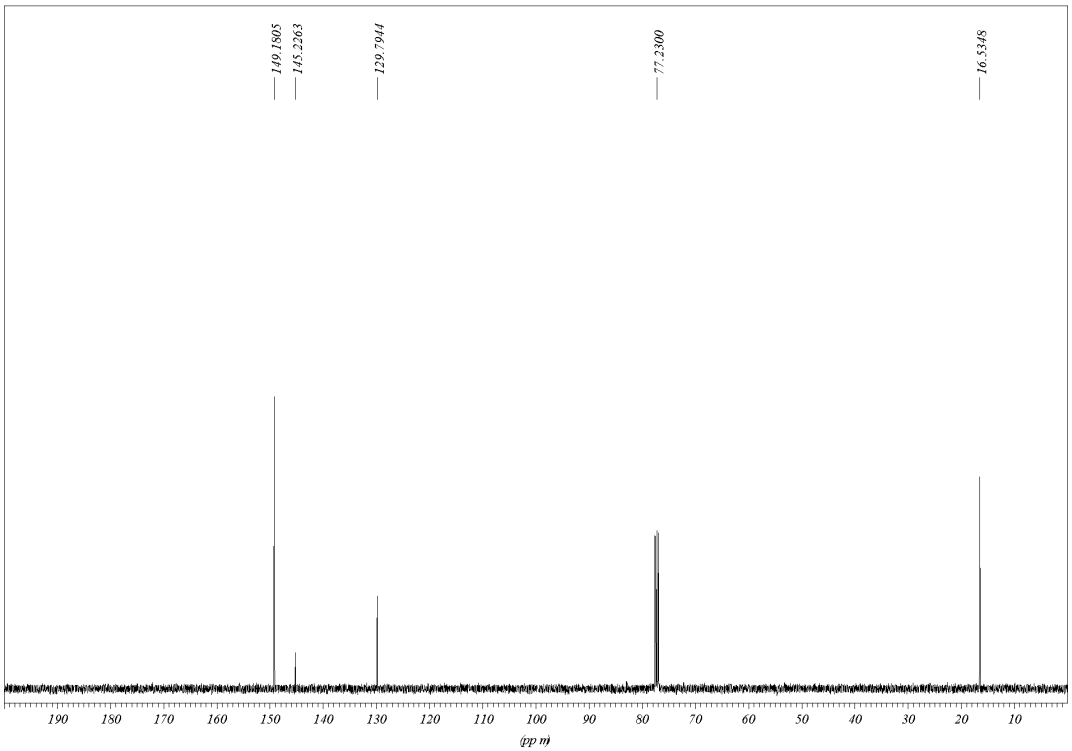


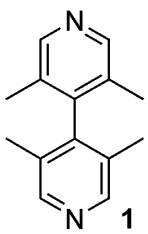

***Figure S2:*** Racemization of **3** and **5** in methanol at 50°C over 70 h and 26 h, respectively, as followed by CD-spectroscopy.

**NMR Spectra of 1 and 3 - 6:**

**1** $CDCl_3$, RT, $^1H$ NMR (400 MHz) and $^{13}C$ NMR (100 MHz)

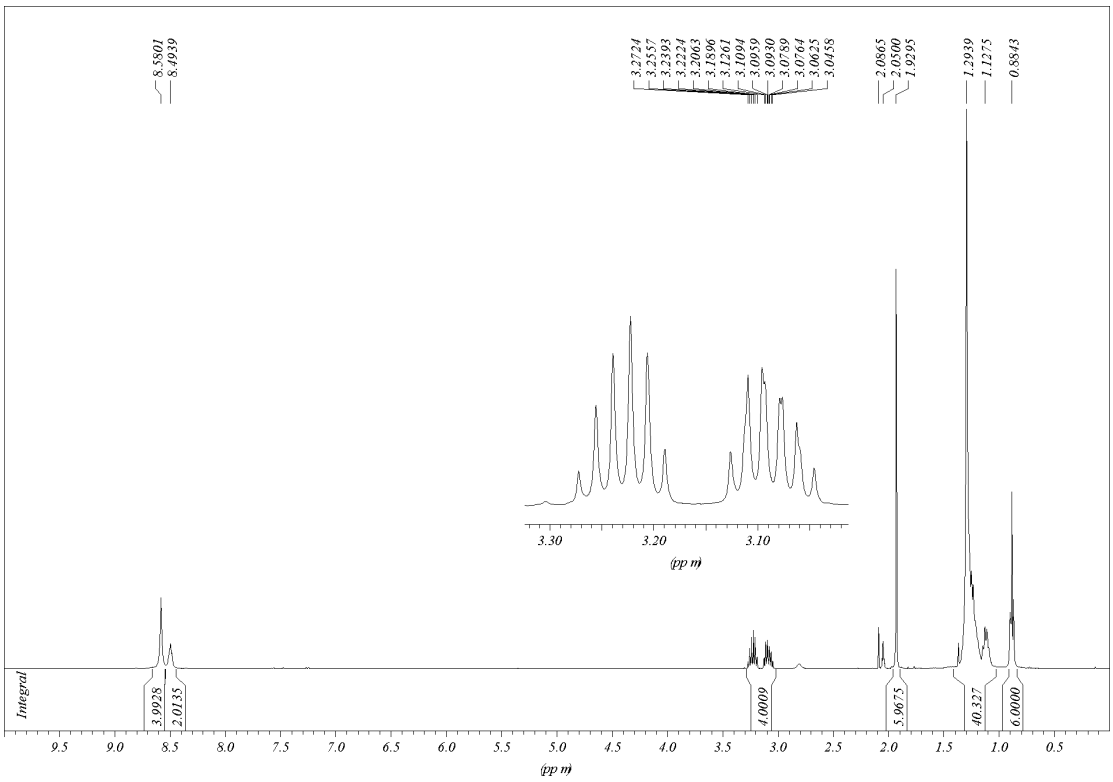


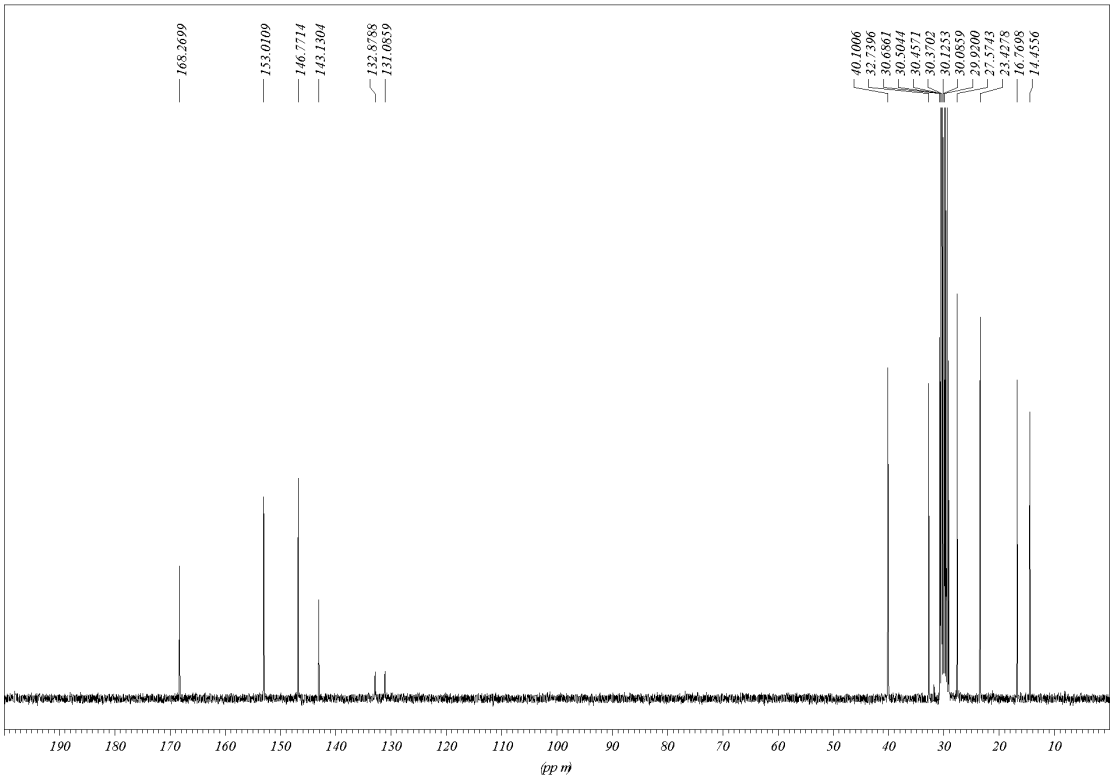



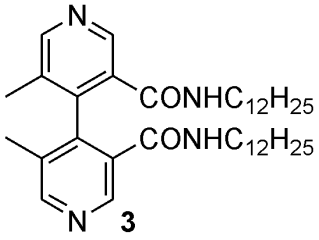




**1**

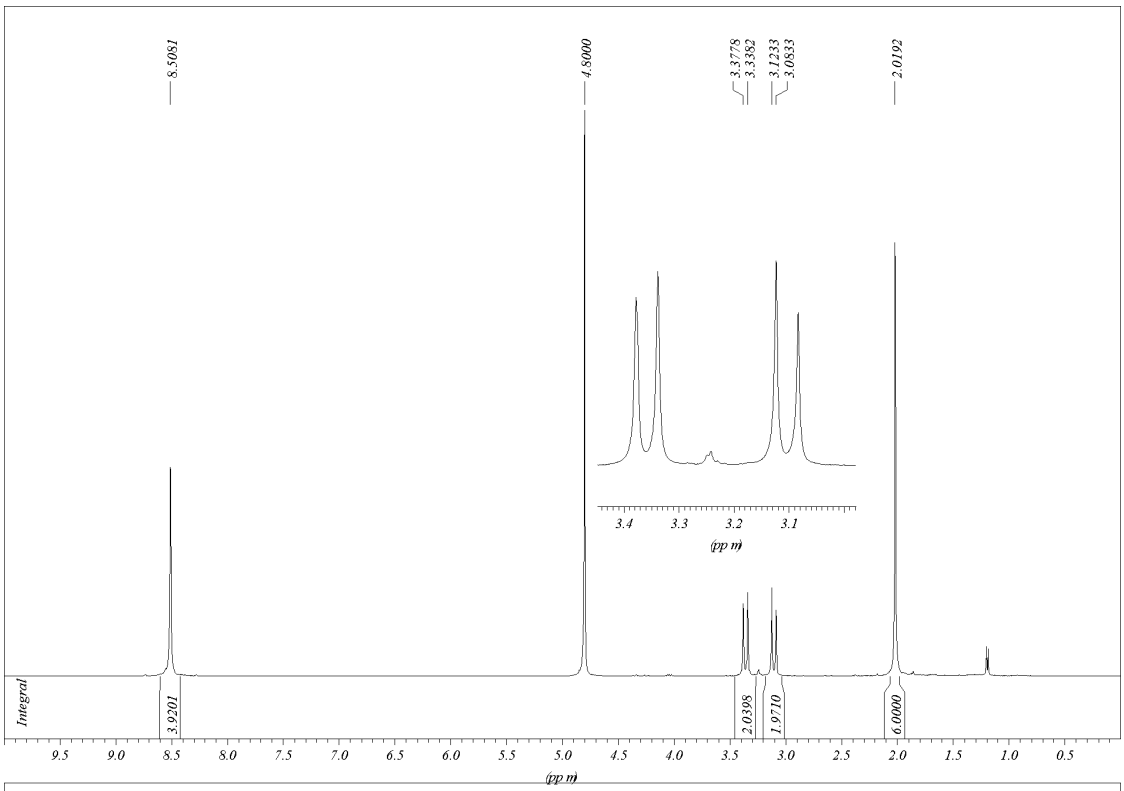
**3** first enatiomer, [$D_6$]-acetone, RT, $^{1}H$ NMR (400 MHz) and $^{13}C$ NMR (75 MHz)

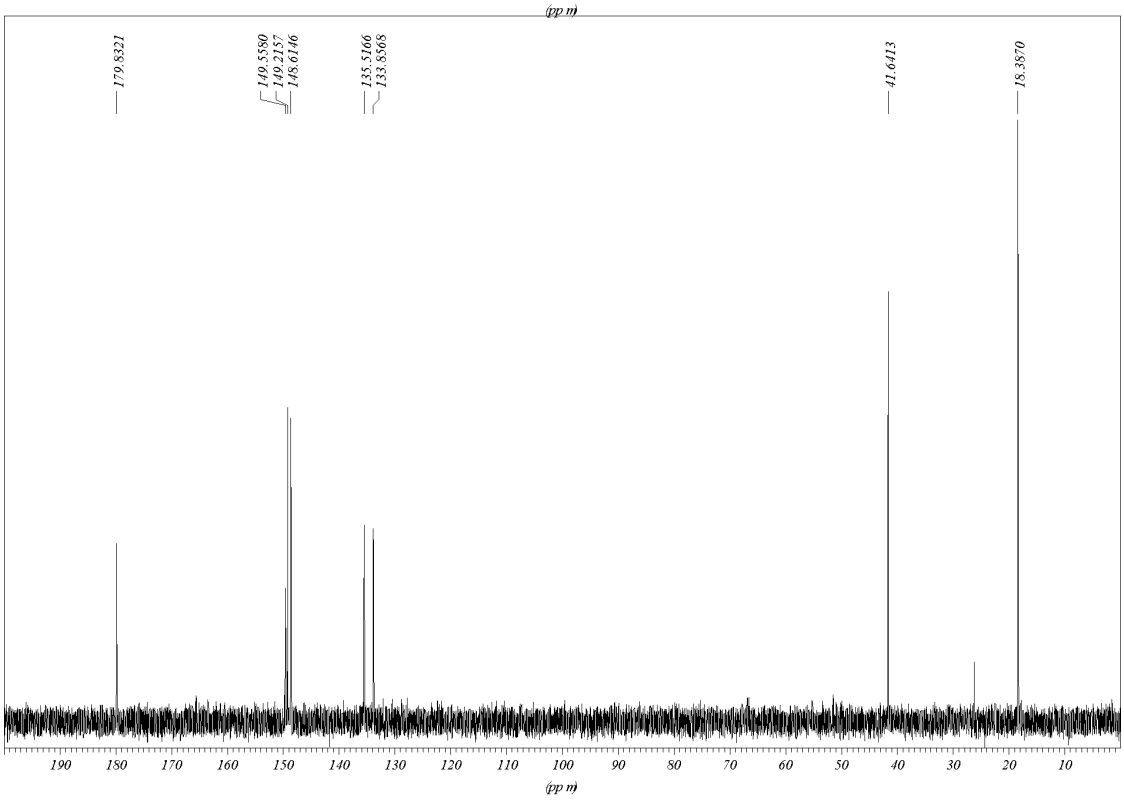


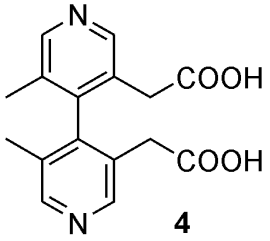



***Rac*-4**, $D_2O$, RT, $^1H$ NMR (400 MHz) and $^{13}C$ NMR (100 MHz)

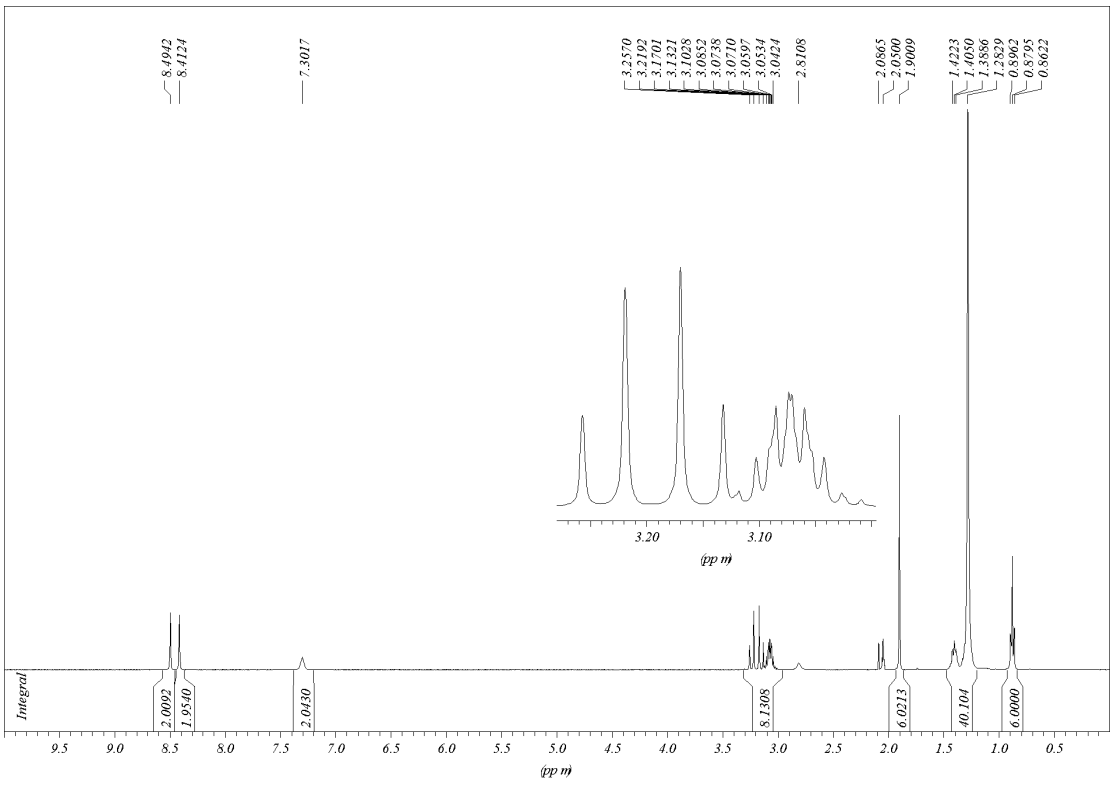


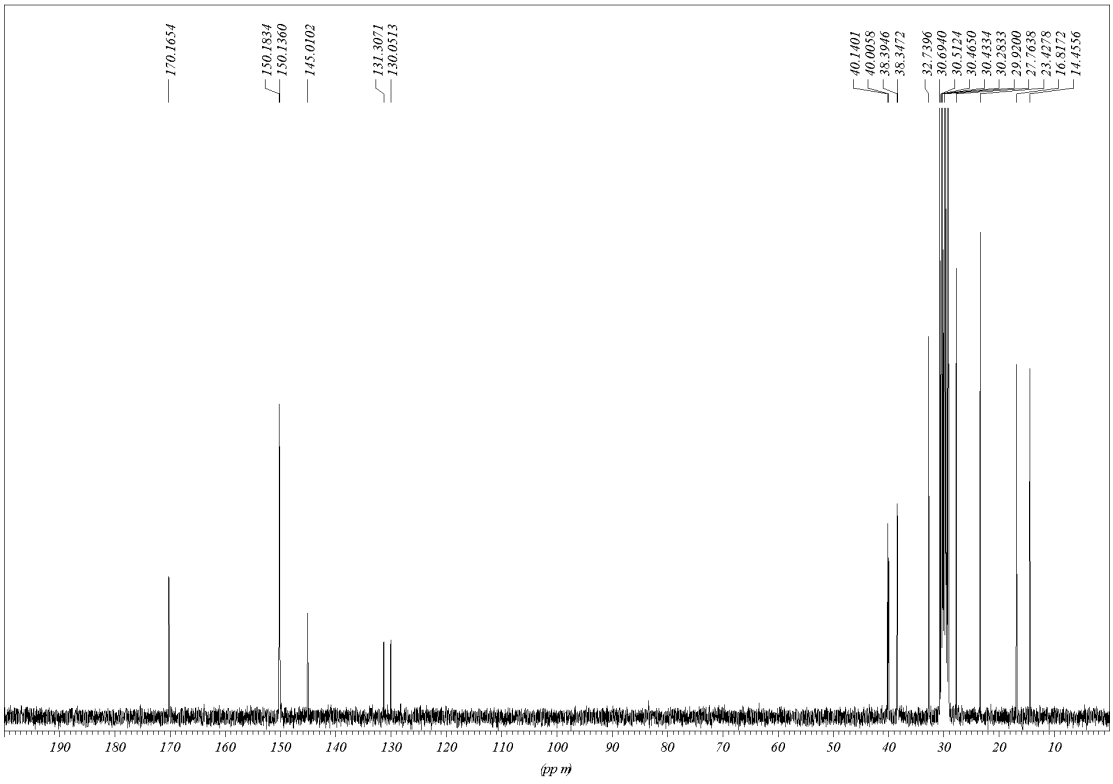



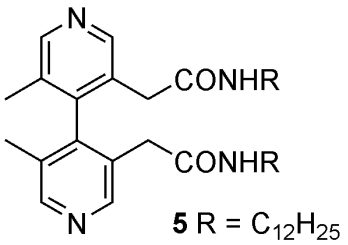




**4**

**5** first enatiomer, [$D_6$]-acetone, RT, $^{1}$H NMR (400 MHz) and $^{13}$C NMR (75 MHz)

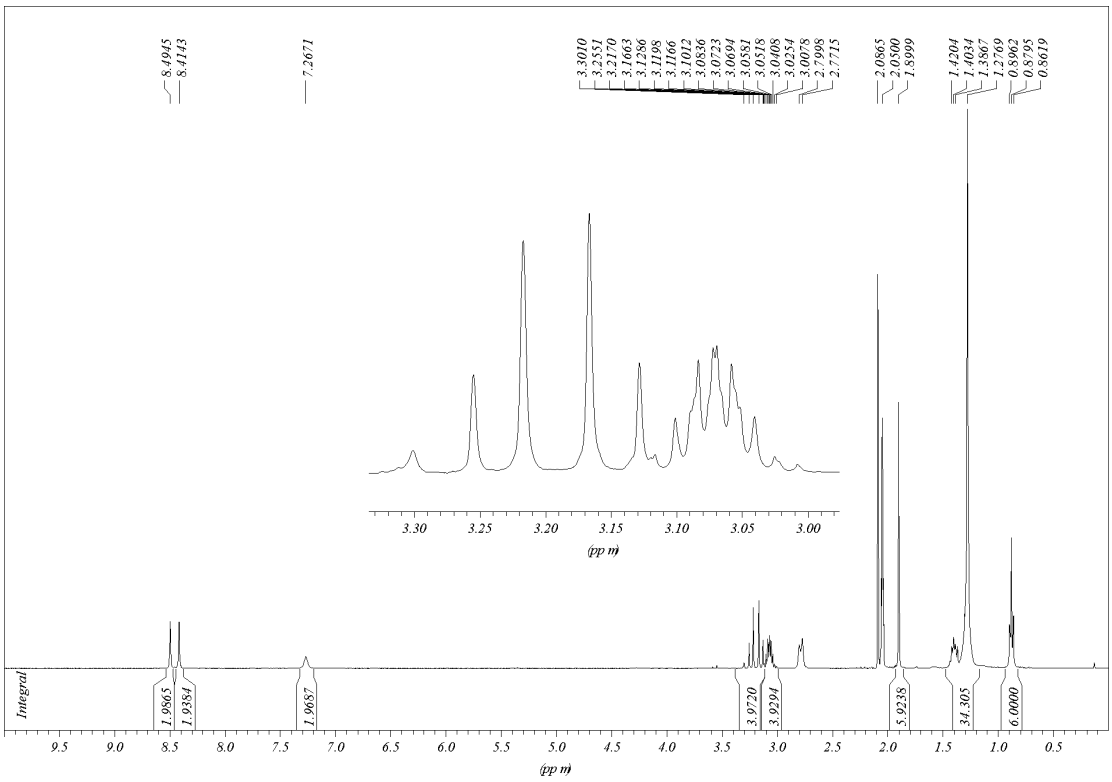


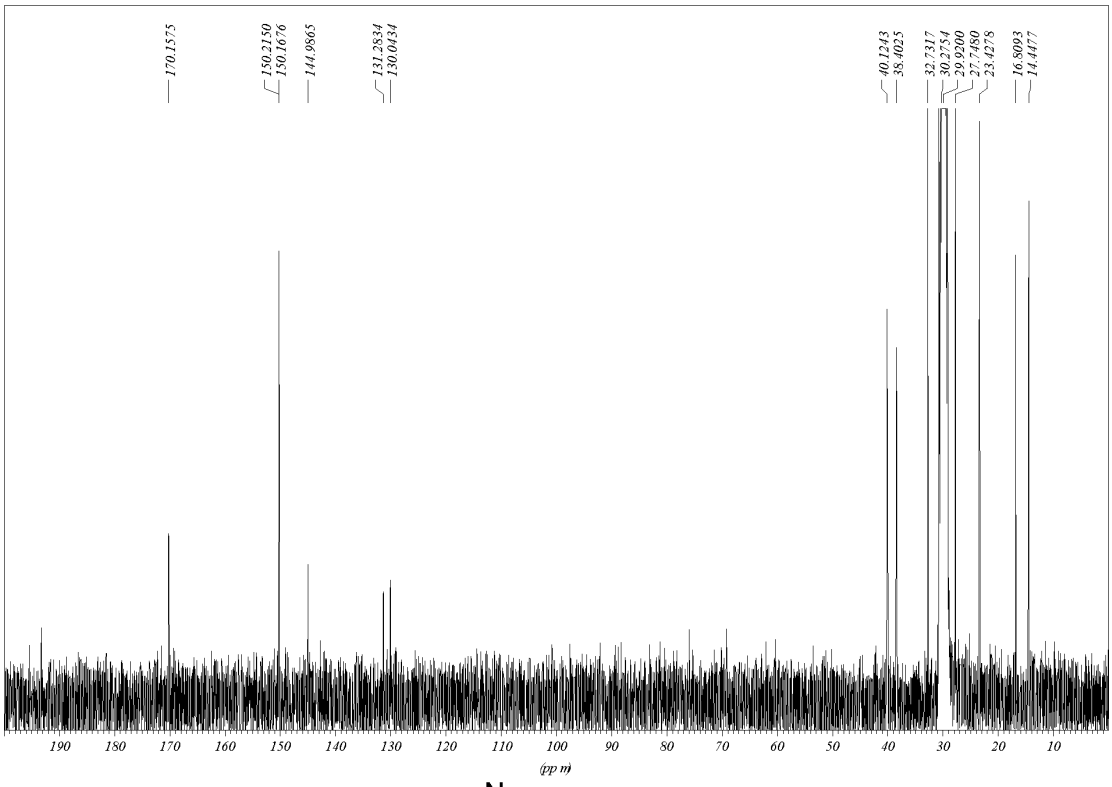



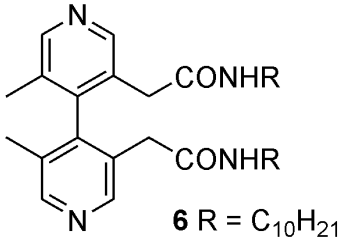




**5** R = $C_{12}H_{25}$

**6** first enatiomer, [$D_6$]-acetone, RT, $^{1}$H NMR (400 MHz) and $^{13}$C NMR (75 MHz)




**6** R = $C_{10}H_{21}$

**Remarks on the symmetry analysis**

The most favorable orientation of the pyridine ligands is that perpendicular to the plane through the four metal centers. Ideally, such a situation can be reached for planar ligands such as dipyridylethylene or azopyridine (see Figure S3 and, for example, Ref. 6a cited in the main text). Molecular modeling clearly suggests that stacking interactions can be formed between each pyridine and one phenyl group from the dppp ligands.

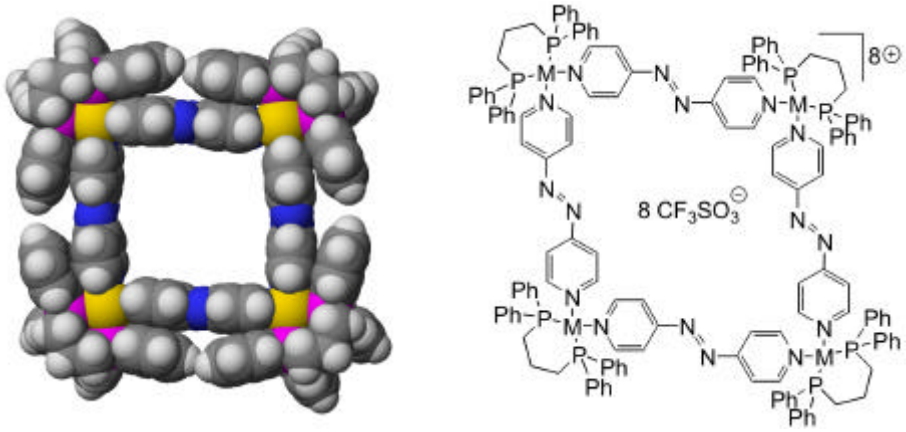



***Figure S3:*** *Molecular modeling of a square formed from azopyridine and (dppp)Pt($CF_3SO_3$)$_2$. Clearly visible is the orientation of the pyridines perpendicular to the plane through the four metal corners and the capability of the pyridines to stack with dppp phenyl groups (optimized with the MM2 force field implemented in CACHE 5.0 (Fujitsu, Krakow, Poland)).*

4,4'-Bipyridine already is not completely planar due to the interactions of *ortho*-hydrogen atoms next to the aryl-aryl bond. However, the torsional angle along the aryl-aryl bond is small enough to be close to the optimum geometry for stacking with the phenyls. Substitution at the 3,3'- and 5,5'-positions will increase this angle. According to molecular modeling, it almost reaches 90$^o$ here. The only reasonable arrangement of the pyridine rings which is in agreement with the neighboring phenyl rings and offers a compromise at the metal centers with respect to the pyridine *ortho*-hydrogens is an arrangement, in which both pyridines are tilted with respect to the M-M-M-M plane by ca. 45$^o$. Such an arrangement is only possible, when the two pyridine rings are not tilted towards each other due to steric congestion from the *ortho*-hydrogens next to the pyridine nitrogens (Figure S4).

For achiral **7a,b**, two different orientations of each bipyridine are thus possible by rotating the ligand by 90$^o$. This leads to the symmetry analysis provided in Scheme 3 in the main text. The axially chiral bipyridine ligands in **8a,b** and **9a,b** have a lower symmetry than those incorporated in **7a,b**. Meaningful conformations can thus be generated as shown in Scheme 4 in the main text. Interconversion between

these conformations are slow, a) because the substituents in 3,3'- and 5,5'-positions collide with the dppp phenyl groups during this rotation (Figure S5), b) because energetically unfavorable conformers are generated, if only one ligand rotates, and c) because the conformer exchange process might thus involve concerted movements of more than one bipyridine ligand.

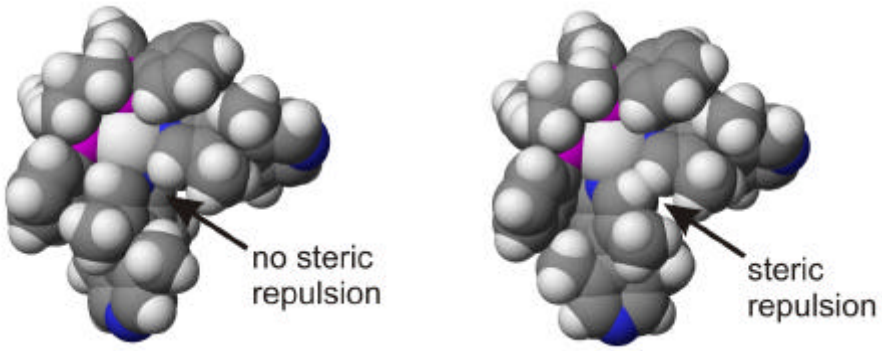



***Figure S4:*** *Molecular modeling of one corner. The left structure is geometry optimized with the MM2 force field implemented in CACHE 5.0 (Fujitsu, Krakow, Poland). The right structure is merely an illustrating snapshot from a non-optimized geometry showing the steric repulsion between pyridine ortho-hydrogen atoms.*

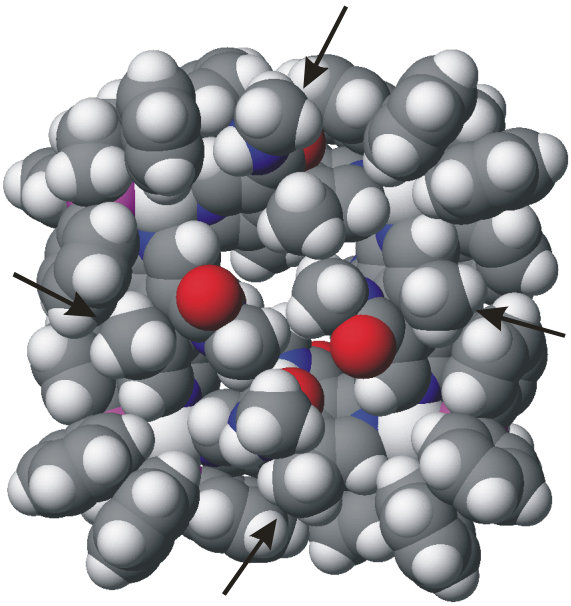


***Figure S5:*** *Molecular modeling of conformer* ***II*** *of* ***8b*** *(dodecyl side chains truncated to methyl groups). It can be seen that dppp phenyl rings adjust themselves to the tilted pyridines as much as possible. However, substituents on the pyridine rings clearly disturb this interaction (arrows).*